

Supplementary Information

Amide Synthesis via Molecular Shuffling of Carboxylic Acids

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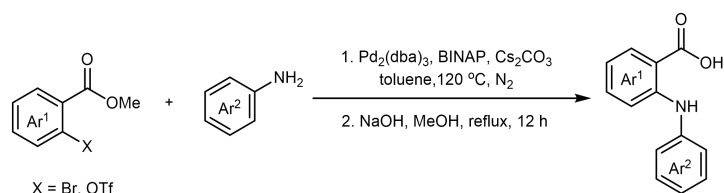
1. General information

The reactions were carried out in 25 mL Schlenk tubes under N₂ atmosphere. All heating and stirring were conducted on the IKA (Model: RCT B S025). Reagents were used as received unless otherwise noted, and solvents were purified according to standard operating procedures. Column chromatography was performed using Silica Gel 60 (300–400 mesh). The reactions were monitored by GC and GC-MS. GC-MS results were recorded on GC-MS QP2010, and GC analysis was performed on GC 2010 plus. The ¹H, ¹³C and ¹⁹F NMR spectra were recorded on a Bruker ADVANCE III spectrometer at 400 MHz, 100 MHz, and 376 MHz, respectively, and chemical shifts were reported in parts per million (ppm) with deuterated chloroform as solvent. The atmospheric pressure chemical ionization (APCI) and electron ionization methods were used for the HRMS measurement, and the mass analyzer type was TOF for APCI and EI. All solvents and reagents were purchased from Energy Chemical, Alfa Aesar, and Aladdin.

2. Experimental procedure

2.1 Preparation of the starting materials

General procedure A for the preparation of carboxylic acids 2a–20a, 22a–38a and 40a:

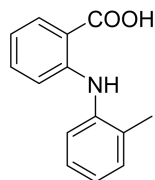


1. To a solution of bromide (or triflate) (10 mmol) in toluene (0.1 M) was added amine (1.2 equiv), Cs₂CO₃ (2 equiv), BINAP (7.5 mol%), and Pd₂(dba)₃ (5 mol%) at room temperature. The reaction mixture was stirred at 120 °C for 24 h. After the reaction was complete, the mixture was cooled to room temperature, diluted with EtOAc, washed with 2 M aq HCl (× 3) and brine, and dried over sodium sulfate. The solution was concentrated, loaded onto silica gel, and purified by silica gel chromatography.

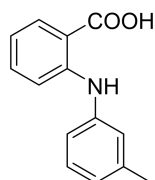
To a solution of the methyl ester (1 equiv) in MeOH (0.2 M) was added NaOH (2 equiv per ester group) in water (0.2 M) at room temperature. The reaction mixture was stirred under reflux for

12 h. Once the reaction appeared complete by TLC analysis, MeOH was evaporated from the reaction mixture, the resultant solution was cooled to 0 °C and acidified to pH 2 with 2 M aq HCl. The resultant precipitated product was collected by vacuum filtration and washed with water.¹

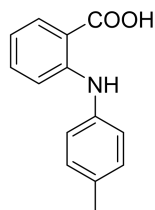
Analytical data of substrates:



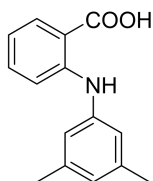
2-(*o*-tolylamino)benzoic acid 2a: White solid (1.52 g, 67% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.53 (s, 1H), 7.91 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.23 (td, *J* = 7.6, 1.7 Hz, 1H), 7.08 (td, *J* = 7.4, 1.3 Hz, 1H), 6.89 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.74 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 2.22 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₂ [M+H]⁺ : 228.1025, found: 228.0955.



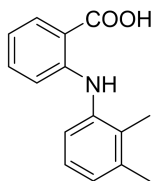
2-(*m*-tolylamino)benzoic acid 3a: White solid (1.81 g, 80% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.63 (s, 1H), 7.92 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.40 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.06 (d, *J* = 6.6 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 2.31 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₂ [M+H]⁺ : 228.1025, found: 228.0997.



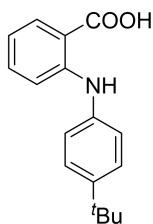
2-(*p*-tolylamino)benzoic acid 4a: White solid (2 g, 88% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.60 (s, 1H), 7.92 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.35 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.12 – 7.18 (m, 5H), 6.74 (t, *J* = 7.0 Hz, 1H), 2.28 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₂ [M+H]⁺ : 228.1025, found: 228.0994.



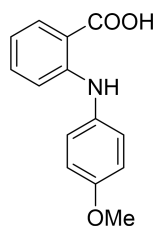
2-((3,5-dimethylphenyl)amino)benzoic acid 5a: White solid (2.1 g, 89% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.59 (s, 1H), 7.91 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.40 (ddd, *J* = 8.8, 7.1, 1.7 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.87 (s, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 6.73 (s, 1H), 2.27 (s, 6H). **HRMS** (ESI): calcd for C₁₅H₁₅NO₂ [M+H]⁺ : 242.1181, found: 242.1154.



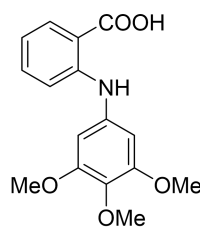
2-((2,3-dimethylphenyl)amino)benzoic acid 6a: White solid (1.7 g, 69% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.48 (s, 1H), 7.90 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.31 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.03 (dd, *J* = 5.8, 3.1 Hz, 1H), 6.76 – 6.67 (m, 2H), 2.29 (s, 3H), 2.11 (s, 3H). **HRMS** (ESI): calcd for C₁₅H₁₅NO₂ [M+H]⁺ : 242.1181, found: 242.1158.



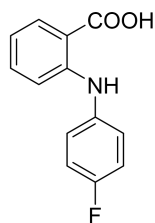
2-((4-(tert-butyl)phenyl)amino)benzoic acid 7a: White solid (2.4 g, 90% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.64 (s, 1H), 7.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.22 – 7.13 (m, 3H), 6.75 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 1.28 (s, 9H). **HRMS** (ESI): calcd for C₁₇H₁₉NO₂ [M+H]⁺ : 270.1494, found: 270.1469.



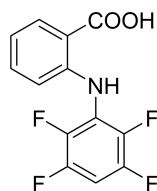
2-((4-methoxyphenyl)amino)benzoic acid 8a: White solid (2.1 g, 86% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.45 (s, 1H), 7.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.34 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.03 – 6.96 (m, 2H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.70 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 3.78 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₃ [M+H]⁺ : 244.0974, found: 244.0933.



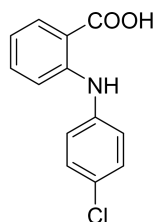
2-((3,4,5-trimethoxyphenyl)amino)benzoic acid 9a: White solid (2.4 g, 80% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 2:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.53 (s, 1H), 7.90 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.40 (ddd, *J* = 8.7, 7.0, 1.7 Hz, 1H), 7.24 (dd, *J* = 8.6, 1.1 Hz, 1H), 6.77 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 6.57 (s, 2H), 3.78 (s, 6H), 3.67 (s, 3H). **HRMS** (ESI): calcd for C₁₆H₁₇NO₅ [M+H]⁺ : 304.1185, found: 304.1153.



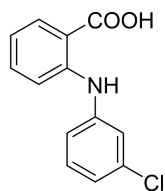
2-((4-fluorophenyl)amino)benzoic acid 10a: White solid (1.9 g, 83% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.60 (s, 1H), 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.34 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.26 (ddt, *J* = 8.4, 5.8, 2.8 Hz, 2H), 7.20 – 7.12 (m, 2H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.75 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H). **HRMS** (ESI): calcd for C₁₃H₁₀FO₂ [M+H]⁺ : 232.0774, found: 232.0735.



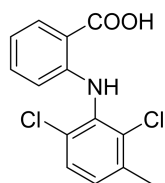
2-((2,3,5,6-tetrafluorophenyl)amino)benzoic acid 11a: White solid (2.3 g, 81% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.53 (s, 1H), 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.75 (d, *J* = 10.7 Hz, 1H), 7.40 – 7.45 (m, 1H), 6.89 (td, *J* = 7.6, 2.4 Hz, 1H), 6.70 (dt, *J* = 8.8, 3.0 Hz, 1H). **HRMS** (ESI): calcd for C₁₃H₇F₄NO₂ [M+H]⁺ : 286.0491, found: 286.0498.



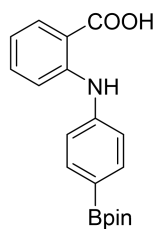
2-((4-chlorophenyl)amino)benzoic acid 12a: White solid (2.1 g, 84% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.69 (s, 1H), 7.95 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.39 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 – 7.19 (m, 3H), 6.86 – 6.77 (m, 1H). **HRMS** (ESI): calcd for C₁₃H₁₀ClNO₂ [M+H]⁺ : 248.0478, found: 248.0460.



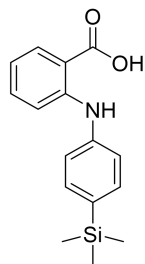
2-((3-chlorophenyl)amino)benzoic acid 13a: White solid (1.9 g, 77% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.67 (s, 1H), 7.95 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.44 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.20 (dd, *J* = 8.0, 2.2 Hz, 1H), 7.06 (dd, *J* = 7.9, 2.1 Hz, 1H), 6.91 – 6.82 (m, 1H). **HRMS** (ESI): calcd for C₁₃H₁₀ClNO₂ [M+H]⁺ : 248.0478, found: 248.0450.



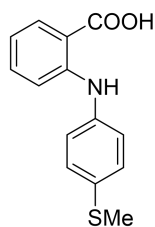
2-((2,6-dichloro-3-methylphenyl)amino)benzoic acid 14a: White solid (1.8 g, 60% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.54 (s, 1H), 7.93 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.28 (m, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 8.2 Hz, 1H), 2.37 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₁Cl₂NO₂ [M+H]⁺ : 296.0245, found: 296.0222.



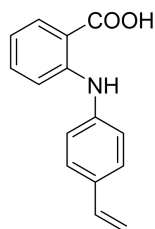
2-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzoic acid 15a: White solid (3 g, 89% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, CDCl₃): δ 9.45 (s, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 6.84 (ddd, *J* = 8.1, 5.0, 3.2 Hz, 1H), 1.40 (s, 12H). **HRMS** (ESI): calcd for C₁₉H₂₂BNO₄ [M+H]⁺ : 340.1724, found: 340.1727.



2-((4-(trimethylsilyl)phenyl)amino)benzoic acid 16a: White solid (2.2 g, 76% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆) δ 9.69 (s, 1H), 7.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.41 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.32 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.82 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 1H), 0.25 (s, 9H). **HRMS** (ESI): calcd for C₁₆H₁₉NO₂Si [M+H]⁺ : 286.1263, found: 286.1266.

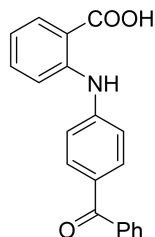


2-((4-(methylthio)phenyl)amino)benzoic acid 17a: Yellow solid (2.3 g, 88% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): 9.62 (s, 1H), 7.93 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.38 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.20 (m, 2H), 7.18 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.78 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 2.47 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₂S [M+H]⁺ : 260.0745, found: 260.0748.

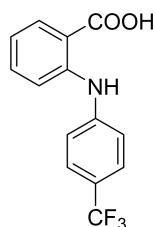


2-((4-vinylphenyl)amino)benzoic acid 18a: White solid (2 g, 82% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.70 (s, 1H), 7.97 – 7.90 (m, 1H), 7.51 – 7.36 (m, 3H),

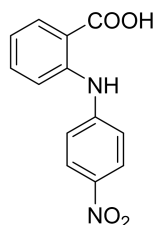
7.30 (d, $J = 8.4$ Hz, 1H), 7.24 (d, $J = 8.2$ Hz, 2H), 6.83 (t, $J = 7.7$ Hz, 1H), 6.72 (dd, $J = 17.7$, 10.9 Hz, 1H), 5.76 (d, $J = 17.6$ Hz, 1H), 5.19 (d, $J = 10.9$ Hz, 1H). **HRMS** (ESI): calcd for $C_{15}H_{13}NO_2$ $[M+H]^+$: 240.1025, found: 240.1001.



2-((4-benzoylphenyl)amino)benzoic acid 19a: White solid (2.6 g, 82% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **1H NMR** (400 MHz, DMSO- d_6): δ 9.90 (s, 1H), 7.98 (dd, $J = 8.0$, 1.5 Hz, 1H), 7.78 – 7.70 (m, 4H), 7.67 – 7.61 (m, 1H), 7.59 – 7.51 (m, 4H), 7.38 – 7.30 (m, 2H), 6.99 (ddd, $J = 8.2$, 6.4, 1.9 Hz, 1H). **HRMS** (ESI): calcd for $C_{20}H_{15}NO_3$ $[M+H]^+$: 318.1130, found: 318.1099.

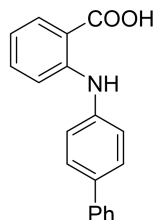


2-((4-(trifluoromethyl)phenyl)amino)benzoic acid 20a: Light yellow solid (2.4 g, 84% yield). The product was purified by silica gel column chromatography, using petroleum ether /EtOAc = 5:1 (v/v) as an eluent. **1H NMR** (400 MHz, DMSO- d_6): δ 9.78 (s, 1H), 7.97 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.56 – 7.47 (m, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 6.97 (ddd, $J = 8.2$, 6.8, 1.5 Hz, 1H). **HRMS** (ESI): calcd for $C_{14}H_{10}F_3NO_2$ $[M+H]^+$: 282.0742, found: 282.0739.

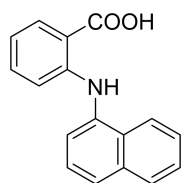


2-((4-nitrophenyl)amino)benzoic acid 22a: Yellow solid (2.3 g, 88% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an

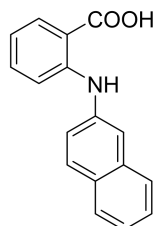
eluent. **¹H NMR** (400 MHz, CDCl₃): δ 9.74 (s, 1H), 8.24 (d, *J* = 9.0 Hz, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 3.8 Hz, 2H), 7.32 (d, *J* = 9.1 Hz, 2H), 7.04 (dt, *J* = 8.1, 4.2 Hz, 1H). **HRMS** (ESI): calcd for C₁₃H₁₀N₂O₄ [M+H]⁺ : 259.0719, found: 259.0706.



2-([1,1'-biphenyl]-4-ylamino)benzoic acid 23a: White solid (2 g, 69% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.49 (s, 1H), 7.84 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.32 (m, 8H), 7.24 (td, *J* = 7.4, 1.3 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 6.77 – 6.69 (m, 1H). **HRMS** (ESI): calcd for C₁₉H₁₅NO₂ [M+H]⁺ : 290.1181, found: 290.1175.

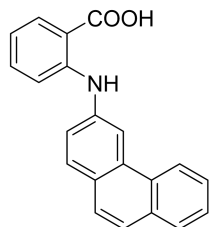


2-(naphthalen-1-ylamino)benzoic acid 24a: White solid (1.8 g, 69% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, CDCl₃): δ 9.65 (s, 1H), 8.11 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.97 – 7.90 (m, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.59 – 7.49 (m, 4H), 7.35 – 7.25 (m, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H). **HRMS** (ESI): calcd for C₁₇H₁₃NO₂ [M+H]⁺ : 264.1025, found: 264.1017.

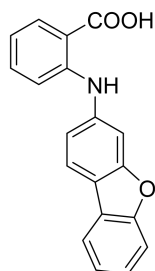


2-(naphthalen-2-ylamino)benzoic acid 25a: White solid (1.9 g, 72% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an

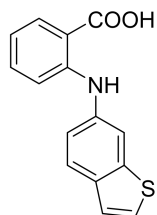
eluent. **¹H NMR** (400 MHz, CDCl₃): δ 9.54 (s, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.86 (t, *J* = 9.3 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.73 (s, 1H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.47 – 7.35 (m, 4H), 6.83 (t, *J* = 7.3 Hz, 1H). **HRMS** (ESI): calcd for C₁₇H₁₃NO₂ [M+H]⁺ : 264.1025, found: 264.1015.



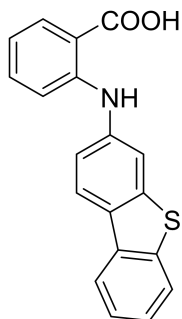
2-(phenanthren-3-ylamino)benzoic acid 26a: White solid (2.4 g, 78% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.81 (s, 1H), 7.97 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 3H), 7.49 – 7.44 (m, 3H), 7.38 (d, *J* = 8.5 Hz, 3H), 6.94 (ddd, *J* = 8.2, 6.7, 1.7 Hz, 2H). **HRMS** (ESI): calcd for C₂₁H₁₅NO₂ [M+H]⁺ : 314.1181, found: 314.1175.



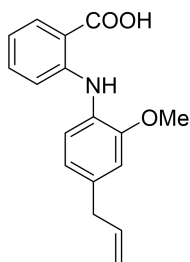
2-(dibenzo[b,d]furan-3-ylamino)benzoic acid 27a: White solid (2.4 g, 80% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.91 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.99 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.36 (td, *J* = 7.5, 1.0 Hz, 1H), 7.26 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.85 (ddd, *J* = 8.1, 6.4, 1.8 Hz, 1H). **HRMS** (ESI): calcd for C₁₉H₁₃NO₃ [M+H]⁺ : 304.0974, found: 304.0958.



2-(benzo[*b*]thiophen-6-ylamino)benzoic acid 28a: White solid (2.2 g, 82% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.77 (s, 1H), 7.96 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.77 (d, *J* = 2.1 Hz, 1H), 7.75 (d, *J* = 5.4 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.27 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.22 (d, *J* = 7.3 Hz, 1H), 6.78 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H). **HRMS** (ESI): calcd for C₁₅H₁₁NO₂S [M+H]⁺ : 270.0589, found: 270.0577.

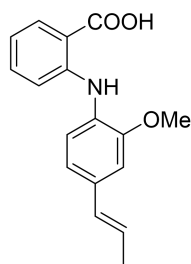


2-(dibenzo[*b,d*]thiophen-3-ylamino)benzoic acid 29a: White solid (2.7 g, 86% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.84 (s, 1H), 8.36 (dd, *J* = 7.1, 1.9 Hz, 1H), 8.27 (d, *J* = 2.2 Hz, 1H), 8.01 (t, *J* = 7.3 Hz, 2H), 7.97 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.51 (td, *J* = 7.3, 1.6 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.44 – 7.38 (m, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 6.81 (t, *J* = 7.5 Hz, 1H). **HRMS** (ESI): calcd for C₁₉H₁₃NO₂S [M+H]⁺ : 320.0745, found: 320.0732.

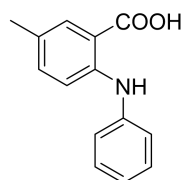


2-((4-allyl-2-methoxyphenyl)amino)benzoic acid 30a: White solid (2.4 g, 85% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.36 (s, 1H), 8.09 (dq, *J* = 5.9, 2.0 Hz, 1H), 7.46 – 7.34 (m, 2H), 7.33 – 7.24 (m, 2H), 7.02 – 6.90 (m, 1H), 6.82 – 6.73 (m, 1H), 6.57 – 6.38 (m, 1H), 6.22 (dq, *J* = 15.7, 6.5 Hz, 1H), 5.80 (dq, *J* = 11.6, 7.2 Hz, 1H), 3.92 (s, 3H), 1.99 (dd, *J*

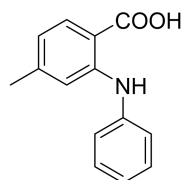
= 7.2, 1.8 Hz, 1H), 1.93 (dd, J = 6.6, 1.7 Hz, 1H). **HRMS** (ESI): calcd for $C_{17}H_{17}NO_3$ $[M+H]^+$: 284.1287, found: 284.1265.



(E)-2-((2-methoxy-4-(prop-1-en-1-yl)phenyl)amino)benzoic acid 31a: White solid (2.2 g, 79% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **1H NMR** (400 MHz, DMSO- d_6): δ 9.67 (s, 1H), 7.94 (dd, J = 7.9, 1.7 Hz, 1H), 7.39 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.23 (dd, J = 8.6, 1.1 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 6.92 (dd, J = 8.2, 1.8 Hz, 1H), 6.77 (ddd, J = 8.1, 7.1, 1.1 Hz, 1H), 6.38 (dd, J = 15.8, 1.7 Hz, 1H), 6.24 (dq, J = 15.8, 6.4 Hz, 1H), 3.86 (s, 3H), 1.85 (dd, J = 6.5, 1.6 Hz, 3H). **HRMS** (ESI): calcd for $C_{17}H_{17}NO_3$ $[M+H]^+$: 284.1287, found: 284.1226.

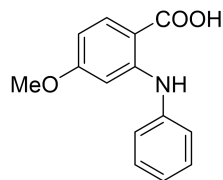


5-methyl-2-(phenylamino)benzoic acid 32a: White solid (2 g, 88% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **1H NMR** (400 MHz, DMSO- d_6): δ 9.49 (s, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.34 (dd, J = 8.5, 7.3 Hz, 2H), 7.27 – 7.16 (m, 4H), 7.08 – 6.99 (m, 1H), 2.24 (s, 3H). **HRMS** (ESI): calcd for $C_{14}H_{13}NO_2$ $[M+H]^+$: 228.1025, found: 228.0992.

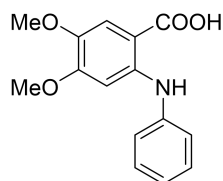


4-methyl-2-(phenylamino)benzoic acid 33a: White solid (2 g, 88% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an

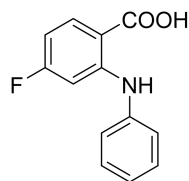
eluent. **¹H NMR** (400 MHz, CDCl₃): δ 9.33 (s, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.07 (s, 1H), 6.62 (d, *J* = 8.2 Hz, 1H), 2.30 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₂ [M+H]⁺ : 228.1025, found: 228.0997.



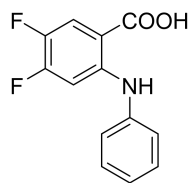
4-methoxy-2-(phenylamino)benzoic acid 34a: White solid (2.1 g, 85% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.84 (s, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.14 – 7.07 (m, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 6.40 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.74 (s, 3H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₃ [M+H]⁺ : 244.0974, found: 244.0928.



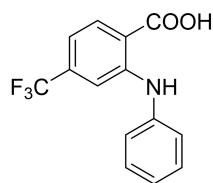
4,5-dimethoxy-2-(phenylamino)benzoic acid 35a: White solid (2.2 g, 81% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.60 (s, 1H), 7.39 (s, 1H), 7.38 – 7.33 (m, 2H), 7.30 – 7.23 (m, 2H), 7.03 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.85 (s, 1H), 3.74 (s, 3H), 3.73 (s, 3H). **HRMS** (ESI): calcd for C₁₅H₁₅NO₄ [M+H]⁺ : 274.1079, found: 274.1055.



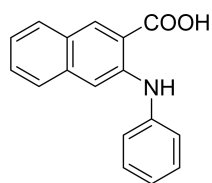
4-fluoro-2-(phenylamino)benzoic acid 36a: White solid (2 g, 88% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, CDCl₃): δ 9.50 (s, 1H), 8.08 (dd, *J* = 8.9, 6.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 5.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.85 (dd, *J* = 12.1, 2.2 Hz, 1H), 6.56 – 6.43 (m, 1H). **HRMS** (ESI): calcd for C₁₃H₁₀FO₂ [M+H]⁺ : 232.0774, found: 232.0755.



4,5-difluoro-2-(phenylamino)benzoic acid 37a: Yellow solid (2.2 g, 88% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.67 (s, 1H), 7.85 (dd, *J* = 11.5, 9.3 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.19 – 7.13 (m, 1H), 7.07 (dd, *J* = 13.5, 7.0 Hz, 1H). **HRMS** (ESI): calcd for C₁₃H₉F₂NO₂ [M+H]⁺ : 250.0680, found: 250.0655.

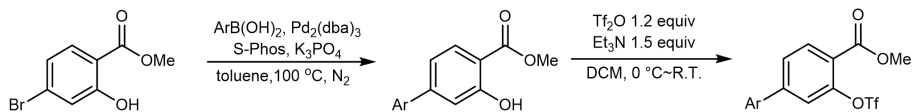


2-(phenylamino)-4-(trifluoromethyl)benzoic acid 38a: White solid (2.3 g, 82% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.78 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.35 – 7.28 (m, 3H), 7.19 (dq, *J* = 11.4, 7.6, 5.7 Hz, 1H), 7.05 (q, *J* = 7.1, 6.5 Hz, 1H). **HRMS** (ESI): calcd for C₁₄H₁₀F₃NO₂ [M+H]⁺ : 282.0742, found: 282.0739.



3-(phenylamino)-2-naphthoic acid 40a: White solid (2.3 g, 89% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.47 (s, 1H), 8.64 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.61 (s, 1H), 7.48 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1H), 7.43 – 7.34 (m, 4H), 7.29 (ddd, *J* = 8.1, 6.7, 1.1 Hz, 1H), 7.08 (tt, *J* = 7.0, 1.5 Hz, 1H). **HRMS** (ESI): calcd for C₁₇H₁₃NO₂ [M+H]⁺ : 264.1025, found: 264.1009.

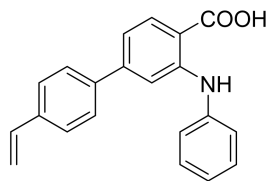
General procedure B for the preparation of triflates:



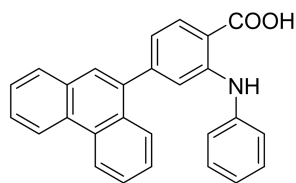
1. In a dry Schlenk tube purged with N₂, methyl bromosalicylate (230 mg, 1 mmol, 1 equiv), ArB(OH)₂ (2 mmol, 2 equiv), Pd₂(dba)₃ (45.8 mg, 0.05 mmol, 0.05 equiv), S-Phos (41 mg, 0.1 mmol, 0.1 equiv) and K₃PO₄ (530.7 mg, 2.5 mmol, 2.5 equiv) were added in toluene (5 mL). The reaction mixture was heated at 100 °C for 24 h. Then the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc (10 : 1) as the eluent to give the desired products **39a**, **41a–45a** as precursors for the next step.

2. General procedure for the preparation of substrate triflate according to Ganem's procedure: To a solution of phenols (10 mmol) in DCM (50 mL) and Et₃N (2.1 mL, 1.5 equiv) was slowly added trifluoromethanesulfonic anhydride (2 mL, 1.2 equiv) at 0 °C. Then the reaction mixture was warmed up to room temperature and stirred overnight. The reaction mixture was transferred to a 100 mL separatory funnel and extracted with DCM (25 mL × 3). The organic phase was collected and washed with brine, dried over Na₂SO₄, and concentrated. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/EtOAc.²

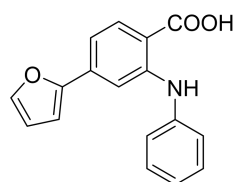
Analytical data of substrates:



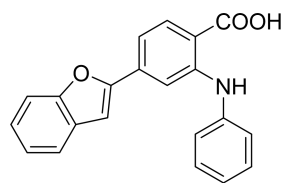
3-(phenylamino)-4'-vinyl-[1,1'-biphenyl]-4-carboxylic acid 39a: White solid (2.2 g, 69% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.79 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 1H), 7.59 – 7.53 (m, 4H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.34 (d, *J* = 7.1 Hz, 2H), 7.16 – 7.03 (m, 2H), 6.77 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.88 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.31 (d, *J* = 10.9 Hz, 1H). HRMS (ESI): calcd for C₂₁H₁₇NO₂ [M+H]⁺ : 316.1338, found: 316.1335.



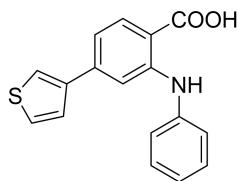
4-(phenanthren-9-yl)-2-(phenylamino)benzoic acid 41a: White solid (2.6 g, 66% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.83 (s, 1H), 8.90 (d, *J* = 8.2 Hz, 1H), 8.83 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 6.3 Hz, 1H), 7.91 (d, *J* = 6.9 Hz, 1H), 7.80 (s, 1H), 7.74 – 7.68 (m, 2H), 7.67 – 7.61 (m, 2H), 7.37 – 7.23 (m, 5H), 7.05 – 6.93 (m, 2H). **HRMS** (ESI): calcd for C₂₇H₁₉NO₂ [M+H]⁺ : 390.1494, found: 390.1492.



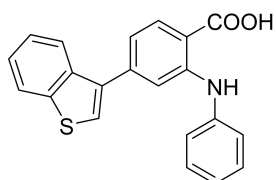
4-(furan-2-yl)-2-(phenylamino)benzoic acid 42a: White solid (2 g, 71% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.76 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 1.7 Hz, 1H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.42 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.35 – 7.27 (m, 2H), 7.18 – 7.09 (m, 2H), 7.01 (d, *J* = 3.4 Hz, 1H), 6.61 (dd, *J* = 3.4, 1.8 Hz, 1H). **HRMS** (ESI): calcd for C₁₇H₁₃NO₃ [M+H]⁺ : 280.0974, found: 280.0939.



4-(benzofuran-2-yl)-2-(phenylamino)benzoic acid 43a: White solid (1.7 g, 74% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 8.07 (dd, *J* = 8.5, 3.6 Hz, 1H), 7.73 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.32 – 7.35 (m, 4H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 7.3 Hz, 1H). **HRMS** (ESI): calcd for C₂₁H₁₅NO₃ [M+H]⁺ : 330.1130, found: 330.1116.

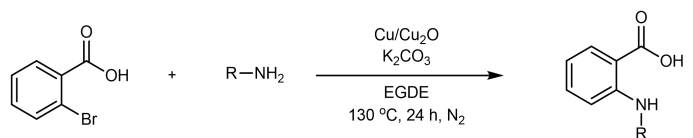


2-(phenylamino)-4-(thiophen-3-yl)benzoic acid 44a: White solid (2.3 g, 77% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.77 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.85 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.61 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.35 – 7.30 (m, 2H), 7.13 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H). **HRMS** (ESI): calcd for C₁₇H₁₃NO₂S [M+H]⁺ : 296.0745, found: 296.0717.



4-(benzo[b]thiophen-3-yl)-2-(phenylamino)benzoic acid 45a: White solid (2.7 g, 79% yield). The product was purified by silica gel column chromatography, using petroleum ether /EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 9.79 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 7.1 Hz, 1H), 7.88 (d, *J* = 7.0 Hz, 2H), 7.47 – 7.33 (m, 7H), 7.16 – 7.06 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 1H). **HRMS** (ESI): calcd for C₂₁H₁₅NO₂S [M+H]⁺ : 346.0902, found: 346.0906.

General procedure C for the preparation of carboxylic acids 46a–48a:

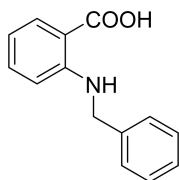


R = Bn, cyclohexyl, octyl

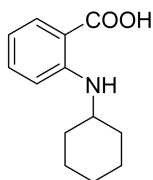
A mixture of 2-bromobenzoic acid (10 mmol), alkylamine (2 equiv, 20 mmol), K₂CO₃ (1 equiv, 10 mmol), Cu powder (10 mol%, 1 mmol), Cu₂O (5 mol%, 0.5 mmol) and ethylene glycol diethyl ether (5 mL) was heated to 130 °C for 24 h under nitrogen. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The residue was poured into H₂O (30 mL), treated with charcoal and the mixture was filtered through celite. The filtrate was then acidified with dilute HCl to pH 5, which was dissolved in aq Na₂CO₃ (5%, 100 mL)

and the solution was filtered through celite and subjected to precipitation as described above. Flash chromatography (petroleum ether/EtOAc = 5:1) afforded the desired N-alkyl anthranilic acids.³

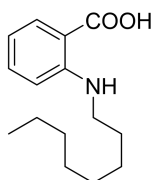
Analytical data of substrates:



2-(benzylamino)benzoic acid 46a: White solid (1.2 g, 55% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 7.82 (dd, J = 8.0, 1.7 Hz, 1H), 7.36 (d, J = 4.4 Hz, 4H), 7.34 – 7.25 (m, 2H), 6.68 (d, J = 8.4 Hz, 1H), 6.58 (t, J = 7.5 Hz, 1H), 4.48 (s, 2H). **HRMS** (ESI): calcd for C₁₄H₁₃NO₂ [M+H]⁺ : 228.1025, found: 228.0990.



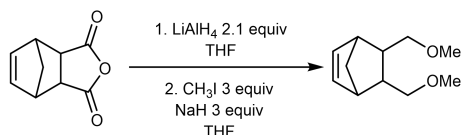
2-(cyclohexylamino)benzoic acid 47a: White solid (1.5 g, 70% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H NMR** (400 MHz, DMSO-*d*₆): δ 7.80 (dd, J = 8.0, 1.7 Hz, 1H), 7.33 (ddd, J = 8.6, 6.9, 1.8 Hz, 1H), 6.74 (d, J = 8.5 Hz, 1H), 6.52 (t, J = 7.3 Hz, 1H), 3.42 (dt, J = 9.7, 5.5 Hz, 1H), 1.96 – 1.89 (m, 2H), 1.70 – 1.65 (m, 2H), 1.59 – 1.54 (m, 1H), 1.44 – 1.34 (m, 2H), 1.30 – 1.19 (m, 3H). **HRMS** (ESI): calcd for C₁₃H₁₇NO₂ [M+H]⁺ : 220.1338, found: 220.1314.



2-(octylamino)benzoic acid 48a: White solid (1.6 g, 66% yield). The product was purified by silica gel column chromatography, using petroleum ether/EtOAc = 5:1 (v/v) as an eluent. **¹H**

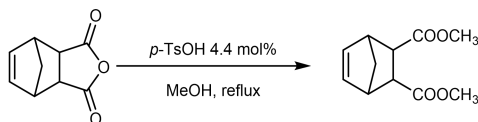
NMR (400 MHz, DMSO-*d*₆): δ 7.79 (dd, J = 8.0, 1.7 Hz, 1H), 7.40 – 7.31 (m, 1H), 6.71 (d, J = 8.5 Hz, 1H), 6.55 (t, J = 7.5 Hz, 1H), 3.15 (t, J = 6.9 Hz, 2H), 1.59 (p, J = 7.0 Hz, 2H), 1.39 – 1.20 (m, 10H), 0.91 – 0.83 (m, 3H). **HRMS** (ESI): calcd for C₁₅H₂₃NO₂ [M+H]⁺ : 250.1807, found: 250.1782.

General procedure for the preparation of NBEs:

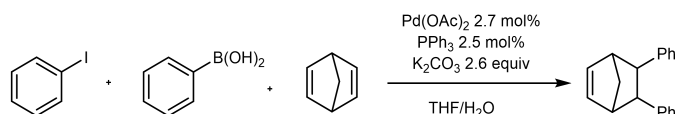


Procedure D: 1. A flame-dried flask was charged with LiAlH₄ (10.5 mmol, 2.1 equiv) and cooled to 0 °C. THF (10 mL, 0.5 M) was added dropwise and the suspension was stirred at 0 °C for 5 min. The nadic anhydride (5 mmol, 1 equiv) was added portion-wise over 10 min and the reaction mixture was allowed to warm to room temperature and was stirred for an additional 15 h. The crude mixture was cooled to 0 °C and 1 mL of deionized H₂O was added dropwise, followed by 1 mL of 15% NaOH and then 2 mL of deionized H₂O. The mixture was filtered and concentrated to yield a white solid. The crude diol was used without any further purification.⁴

2. A flame-dried flask was charged with NaH (3 equiv) and the mineral oil was removed by washing three times with hexanes. The flask was cooled to 0 °C and THF (10 mL) was added slowly. In a separate flask the crude diol (1 equiv) was diluted in THF (2 mL) and cannulated over the suspension at 0 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. The reaction was cooled to 0 °C and MeI (3 equiv) was added dropwise. The reaction was warmed to room temperature and stirred for 18 h. The reaction mixture was cooled to 0 °C and quenched with MeOH (until reaction mixture turned transparent) after which the volatiles were evaporated. The crude mixture was diluted with H₂O and extracted three times with Et₂O. The combined organic layers were washed once with H₂O, brine, dried over Na₂SO₄, filtered and concentrated.⁵ The resulting crude residue was purified by flash column chromatography over silica gel eluting with petroleum ether to afford the desired product as a colorless oil (0.5 g, 60% yield). **¹H NMR** (400 MHz, DMSO-*d*₆): δ 6.12 (t, J = 1.9 Hz, 2H), 3.20 (s, 6H), 3.14 – 3.10 (m, 2H), 2.91 (t, J = 9.1 Hz, 2H), 2.83 – 2.85 (m, 2H), 2.40 – 2.32 (m, 2H), 1.39 – 1.34 (m, 1H), 1.30 – 1.26 (m, 1H).

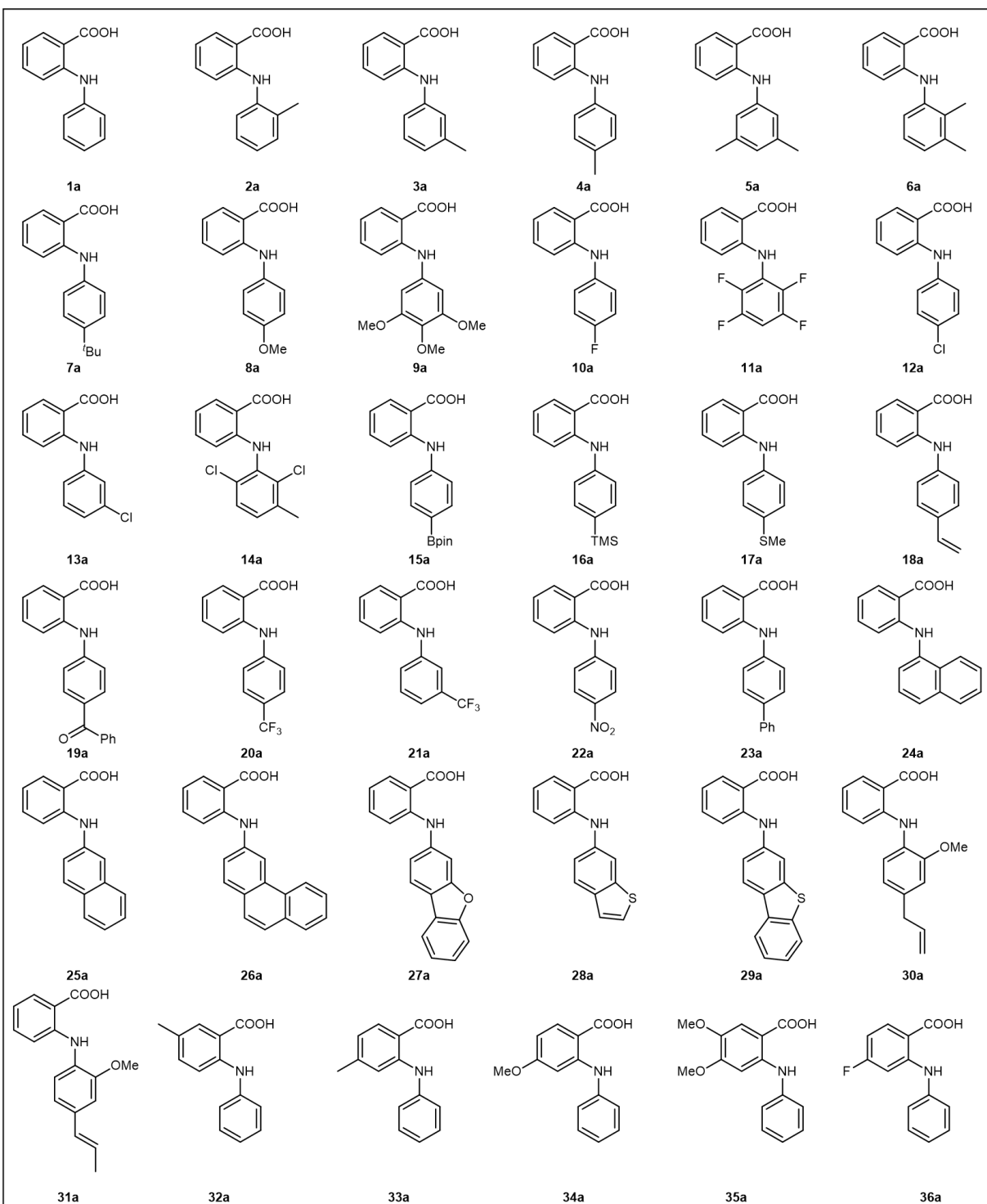


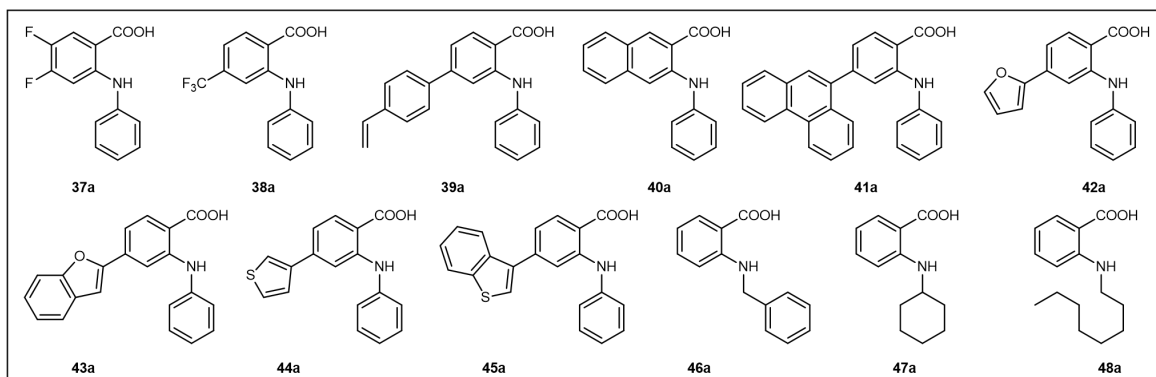
Procedure E: Nadic anhydride (5 mmol) and *p*-TsOH (4.4 mol%) were dissolved in 20 mL of methanol in a 100 mL flask. The mixture was kept refluxing for approximately 12 hours. After methanol was removed by evaporation, the mixture was then distilled under reduced pressure and purified by flash column chromatography over silica gel eluting with petroleum ether /EtOAc = 5:1 (v/v) to afford the desired product as a colorless oil (0.9 g, 88% yield).⁶ **¹H NMR** (400 MHz, DMSO-*d*₆): δ 6.14 (t, *J* = 1.9 Hz, 2H), 3.50 (s, 6H), 3.37 (t, *J* = 1.6 Hz, 2H), 3.06 – 3.08 (m, 2H), 1.38 (dt, *J* = 8.4, 1.6 Hz, 1H), 1.30 (dt, *J* = 8.4, 1.9 Hz, 1H).



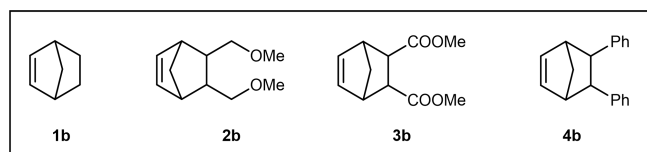
Procedure F: A 25 mL Schlenk flask was charged with iodobenzene (2.5 mmol, 1 equiv), phenylboronic acid (2.75 mmol, 1.1 equiv), 2,5-norbornadiene (2.75 mmol, 1.1 equiv), triphenylphosphine (16 mg, 0.062 mmol, 2.5 mol%), K₂CO₃ (0.912 g, 6.6 mmol, 2.6 equiv), THF (5 mL), water (5 mL), and a stirbar. The mixture was then degassed via three freeze-pump-thaw cycles, and Pd(OAc)₂ (6 mg, 2.7 mol% in 250 μL of degassed THF) was added via syringe under a nitrogen backflow. The reaction was degassed once more and heated at 60 °C overnight. The two phases were separated, and the aqueous phase was extracted with 2 × 15 mL of CH₂Cl₂. The organic layers were combined, extracted with 5% NaCl (1 × 25 mL) to remove colored palladium impurities, and dried over Na₂SO₄. Afterward, the solvent was removed with a rotary evaporator. The resulting crude residue was purified by flash column chromatography over silica gel eluting with petroleum ether to afford the desired product as a white solid (0.4 g, 65% yield).⁷ **¹H NMR** (400 MHz, DMSO-*d*₆): δ 6.99 (dd, *J* = 8.1, 6.7 Hz, 4H), 6.95 – 6.85 (m, 6H), 6.48 (t, *J* = 1.8 Hz, 2H), 3.17 (d, *J* = 1.7 Hz, 2H), 3.04 (t, *J* = 1.9 Hz, 2H), 2.32 – 2.25 (m, 1H), 1.72 (dt, *J* = 8.7, 1.8 Hz, 1H).

Starting materials of carboxylic acids

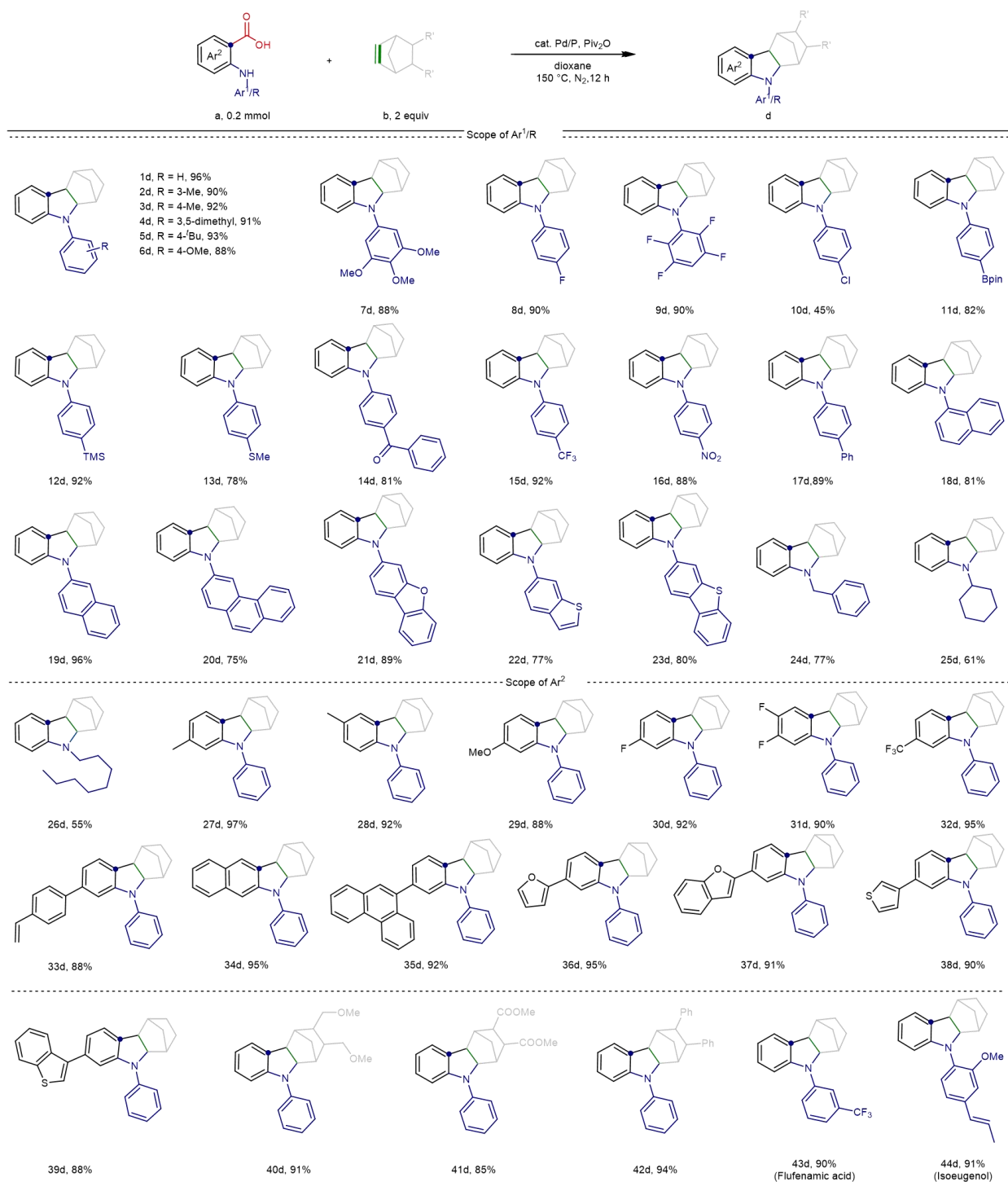




Starting materials of NBEs

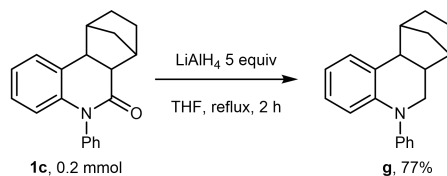


2.2 Substrate scope of decarbonylative amination

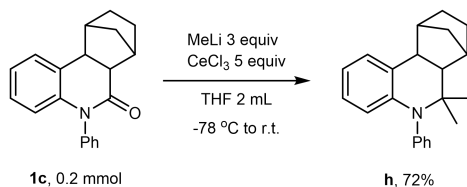


Supplementary figure S1: Reaction conditions: benzoic acid **a** (0.2 mmol), alkene **b** (2 equiv), Pd(OAc)₂ (5 mol%), cataCXium A (20 mol%), Piv₂O (1.5 equiv), 1,4-dioxane (8 mL), 150 °C, N₂, 12 h. Isolated yields.

2.3 Synthetic applications

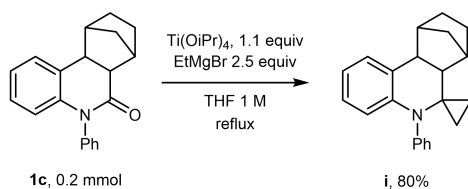


To a solution of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**1c**) (56 mg, 0.2 mmol) in dry THF (8 mL) was added LiAlH_4 (41 mg, 1.1 mmol, 5 equiv) in two portions at 0 °C. The resulting solution was warmed to room temperature and then heated to reflux. Upon completion, the resulting solution was cooled down to 0 °C and slowly quenched with a saturated aqueous solution of NH_4Cl and stirred for 1 hour. The resulting aqueous phase was extracted with EtOAc (3×20 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography over silica gel eluting with petroleum ether to afford the desired product as a colorless oil (42.4 mg, 77% yield).⁸ **^1H NMR** (400 MHz, CDCl_3): δ 7.35 (td, $J = 7.4$, 1.8 Hz, 2H), 7.29 (d, $J = 9.0$ Hz, 1H), 7.22 – 7.14 (m, 2H), 7.08 – 6.96 (m, 2H), 6.94 – 6.86 (m, 2H), 3.64 (dd, $J = 11.8$, 5.6 Hz, 1H), 3.41 (dd, $J = 11.8$, 5.6 Hz, 1H), 2.85 (d, $J = 9.0$ Hz, 1H), 2.51 (d, $J = 4.2$ Hz, 1H), 2.29 (dt, $J = 10.0$, 5.6 Hz, 1H), 2.10 (d, $J = 3.1$ Hz, 1H), 1.82 – 1.76 (m, 1H), 1.72 (ddd, $J = 15.8$, 8.2, 4.2 Hz, 1H), 1.59 (tt, $J = 11.4$, 4.0 Hz, 1H), 1.53 – 1.45 (m, 1H), 1.42 – 1.35 (m, 1H), 1.08 (d, $J = 9.9$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 147.7, 146.2, 131.5, 129.6, 129.2, 125.8, 121.9, 121.7, 120.3, 116.7, 51.9, 45.8, 45.4, 44.9, 42.5, 34.4, 30.3, 29.3.

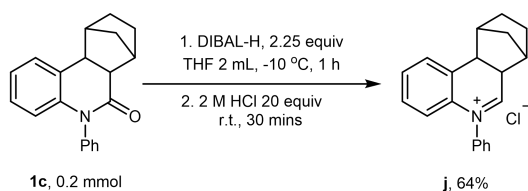


A solution of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**1c**) (0.2 mmol, 1 equiv) and CeCl_3 (5 equiv) in THF (2 mL) was stirred at -78 °C for 1 h. A solution of a 1.3 M solution of MeLi in diethyl ether (3 equiv) was added dropwise, keeping the internal temperature below -78 °C. After warming to room temperature over 4 hours, the reaction mixture was quenched with 1 M HCl aqueous solution, and diluted with DCM. The organic layer was

washed with water and brine, sequentially. After that, the organic layer was dried over Na₂SO₄, and filtered. The resulting crude residue was purified by flash column chromatography over silica gel eluting with petroleum ether to afford the desired product as a colorless oil (43.7 mg, 72% yield).⁹ **¹H NMR** (400 MHz, CDCl₃): δ 7.56 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 1H), 3.16 (d, *J* = 9.4 Hz, 1H), 2.50 (s, 1H), 2.25 – 2.17 (m, 2H), 2.10 – 2.03 (m, 1H), 1.67 (d, *J* = 5.6 Hz, 2H), 1.40 (d, *J* = 10.0 Hz, 2H), 1.35–1.37 (m, 1H), 1.30 (s, 3H), 0.94 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 144.5, 142.3, 136.3, 129.2, 128.5, 126.3, 122.1, 120.0, 119.6, 117.1, 74.5, 60.2, 47.1, 44.2, 40.4, 37.7, 33.8, 31.5, 30.9, 25.7.



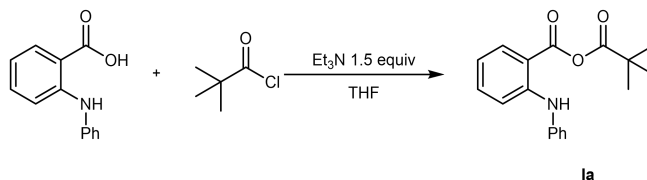
To a solution of EtMgBr (3 M in Et₂O, 2.5 equiv) in THF was added Ti(O^{*i*}Pr)₄ (1.1 equiv) at -78 °C and stirred for 5–10 min. A solution of **1c** (0.2 mmol, 1 equiv) in THF (1 M lactam) was added dropwise at the same temperature, the mixture was allowed to warm up to room temperature within 1–2 h and was subsequently heated to reflux (70 °C) for 24 h. Upon warming to room temperature, the reaction mixture was quenched with 10% aq. NaOH (0.5 M) and diluted with Et₂O. Anhydrous Na₂SO₄ and NaOH pellets were added and the mixture was stirred at rt until the colour changed to white/yellow and a fine precipitate was formed. The suspension was filtered, the precipitate was washed with Et₂O and the combined filtrates were washed with brine, dried over Na₂SO₄ and the solvent was removed under reduced pressure. The resulting crude residue was purified by flash column chromatography over silica gel eluting with petroleum ether to afford the desired product as a colorless oil (48.2 mg, 80% yield).¹⁰ **¹H NMR** (400 MHz, CDCl₃): δ 7.46 – 7.40 (m, 1H), 7.29 – 7.20 (m, 2H), 7.19 – 7.12 (m, 4H), 7.02 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.91 (t, *J* = 7.2 Hz, 1H), 2.79 (d, *J* = 8.8 Hz, 1H), 2.63 (d, *J* = 4.4 Hz, 1H), 2.42 (d, *J* = 8.8 Hz, 1H), 1.86 – 1.81 (m, 1H), 1.76 – 1.66 (m, 1H), 1.55 (tt, *J* = 12.2, 4.2 Hz, 1H), 1.47 (d, *J* = 9.8 Hz, 1H), 1.40 – 1.33 (m, 1H), 1.31 – 1.25 (m, 1H), 1.12 (ddd, *J* = 10.6, 6.2, 4.8 Hz, 1H), 1.06 (d, *J* = 9.8 Hz, 1H), 0.93 – 0.87 (m, 1H), 0.75 – 0.64 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 147.1, 146.8, 136.5, 128.9, 128.5, 125.4, 124.0, 119.9, 117.4, 48.5, 45.9, 41.7, 40.5, 39.2, 34.8, 30.6, 28.5, 14.4, 12.3.



To a solution of **1c** (0.2 mmol) in dry THF (2 mL) was slowly added a solution of diisobutylaluminium hydride (DIBAL-H, 1.5 M in methylbenzene, 0.3 mL) at -10 °C under N₂. The mixture was stirred at -10 °C for 1 h and then warmed to room temperature. Saturated MgSO₄ was added dropwise until a colorless precipitate was formed, and the mixture was stirred vigorously for an additional 30 min. The mixture was diluted with diethyl ether and filtered through Celite. Removal of solvents gave crude residue. Then the residue was poured into 2 M HCl (2 mL). The acidic solution was stirred for an additional 30 min, and then evaporated to give crude product which was further purified by silica gel column chromatography (DCM/MeOH = 10:1) to afford the product **j** in 64% yield (39.6 mg).¹¹ **¹H NMR** (400 MHz, CDCl₃) δ 7.43 (t, *J* = 7.8 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.27 – 7.18 (m, 1H), 7.00 (dd, *J* = 5.9, 3.3 Hz, 2H), 6.83 – 6.70 (m, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 3.04 (d, *J* = 3.7 Hz, 1H), 2.98 (d, *J* = 3.6 Hz, 1H), 2.92 (s, 1H), 1.89 – 1.79 (m, 2H), 1.63 – 1.58 (m, 1H), 1.56 – 1.45 (m, 2H), 1.37 (dt, *J* = 9.1, 2.0 Hz, 1H), 1.30 (d, *J* = 3.3 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 144.6, 143.3, 129.7, 126.1, 125.5, 125.2, 124.9, 124.6, 121.4, 120.0, 114.4, 44.6, 41.4, 40.6, 38.2, 29.9, 27.9.

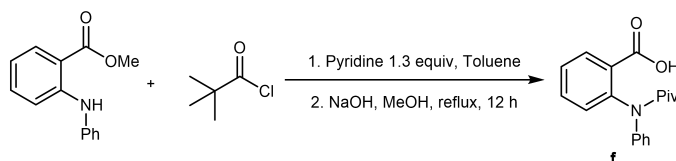
2.4 Control experiments

Synthesis of mixed anhydride **1a**



To an oven-dried round bottom flask equipped with a stirring bar containing a solution of pivaloyl chloride (1.5 equiv) in anhydrous THF (2 mL) was added dropwise triethylamine (1.5 equiv) in THF (4 mL) at -15 °C. Subsequently, N-phenylanthranilic acid (2 mmol, 1 equiv) in THF (2 mL) was added dropwise into the solution at -15 °C. The reaction mixture was stirred at -15 °C overnight and poured into ice-cold saturated aqueous NaHCO₃ solution. The aqueous solution was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give mixed anhydride **1a** as yellow oil (0.5 g, 85% yield).¹² **¹H NMR** (400 MHz, CDCl₃): δ 9.46 (s, 1H), 7.87 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.76 (ddd, *J* = 8.0, 6.9, 0.9 Hz, 1H), 1.42 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 174.0, 164.9, 149.9, 139.8, 135.9, 132.1, 129.5, 124.6, 123.5, 117.0, 113.9, 110.0, 40.3, 26.7. **HRMS** (ESI): calcd for C₁₈H₁₉NO₃ [M+H]⁺ : 298.1443, found: 298.1451.

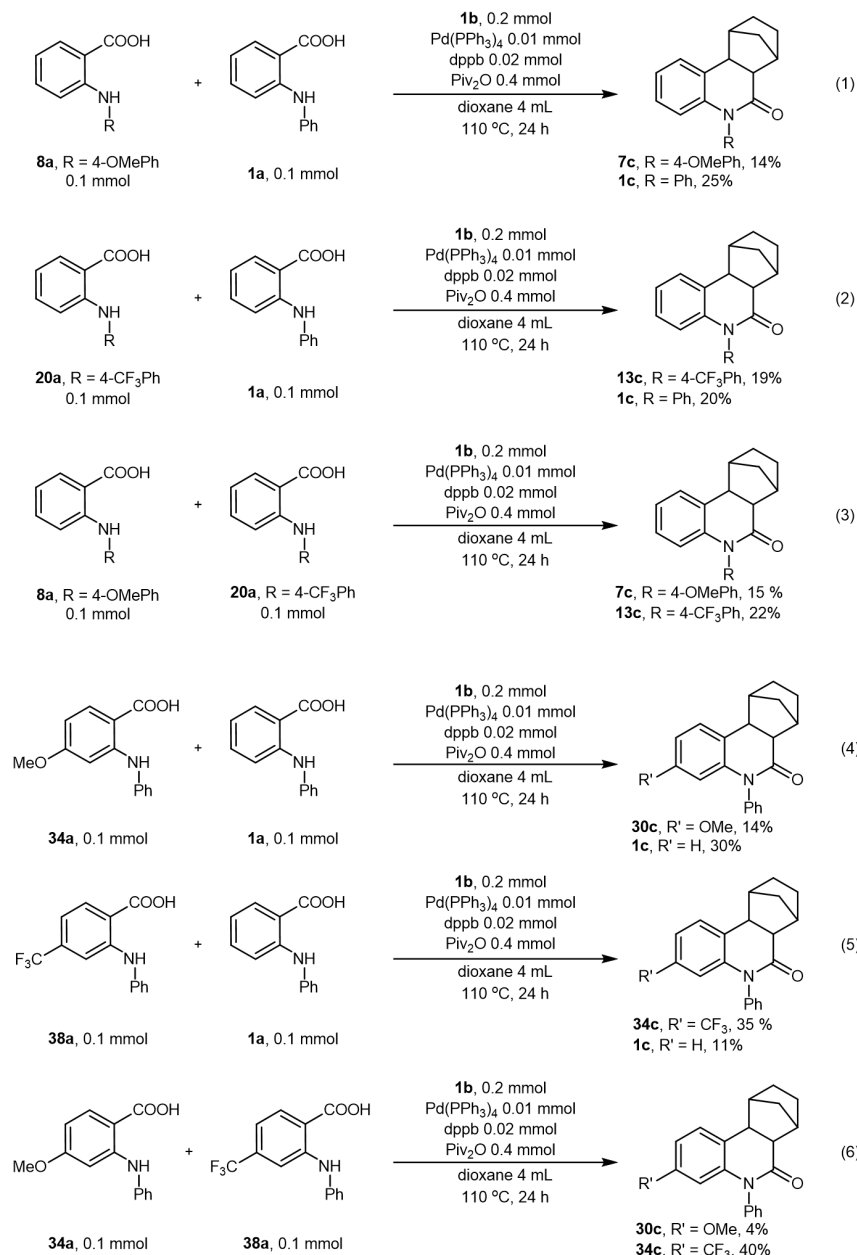
Synthesis of 2-(N-phenylpivalamido)benzoic acid **f**



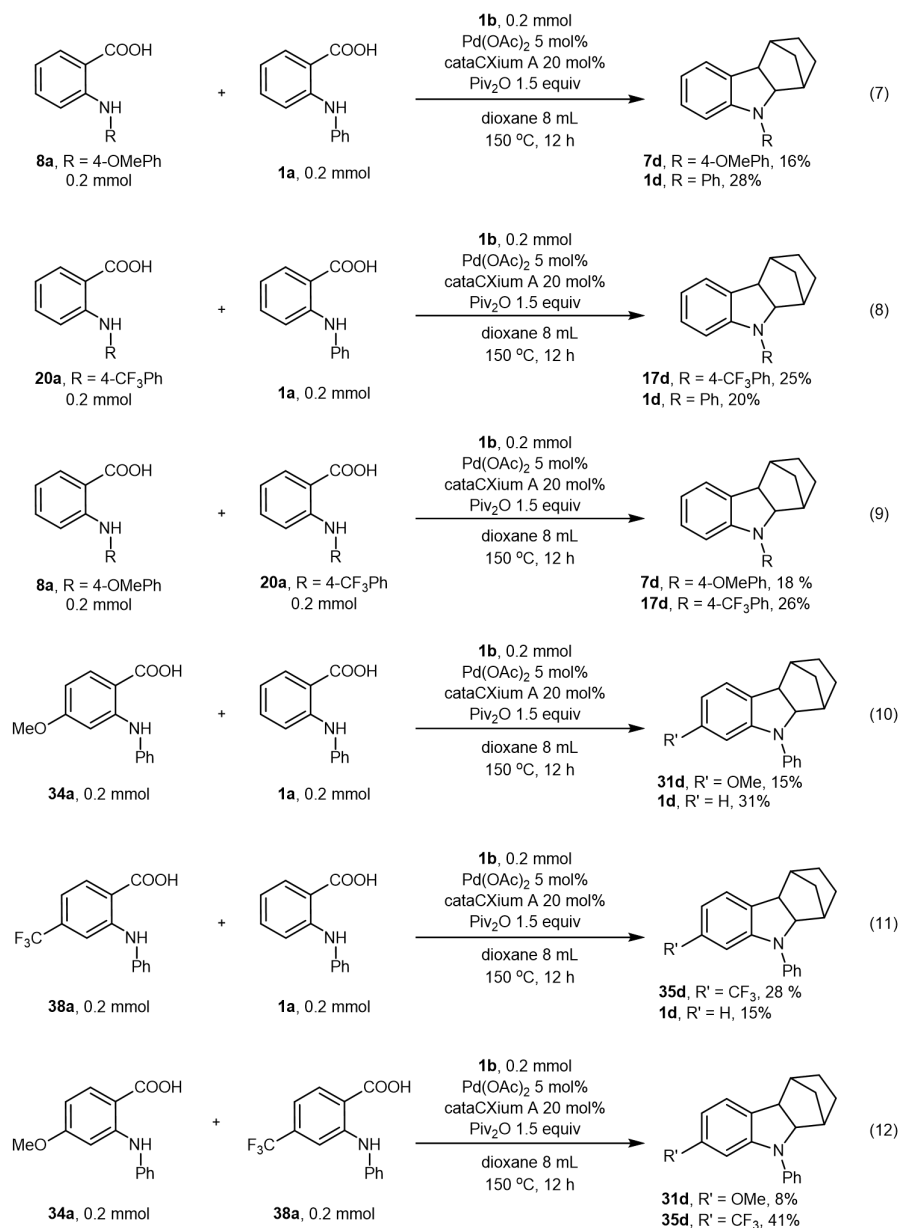
Pivaloyl chloride (735 μL, 6 mmol) was added to a solution of amine (5 mmol) and pyridine (604 μL, 7.5 mmol) in toluene (25 mL) at room temperature, and the resulting mixture was refluxed for 72 h. Then, the mixture was cooled to room temperature, diluted with DCM (75 mL) and washed with water (4 × 150 mL). The combined aqueous phases were washed with DCM (1 × 80 mL) and then the combined organic phases were dried over Na₂SO₄, filtered and concentrated under vacuum, the resulting crude residue was purified by flash column chromatography over silica gel eluting with petroleum ether /EtOAc = 2:1 (v/v) to afford the

desired product as a white solid (1.1 g, 75% yield). **¹H NMR** (400 MHz, DMSO-*d*₆): δ 7.83 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.50 – 7.54 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.36 (m, 2H), 7.26 (d, *J* = 7.9 Hz, 1H), 1.05 (s, 9H); **¹³C NMR** (100 MHz, DMSO-*d*₆): δ 177.6, 167.7, 144.7, 144.5, 133.0, 131.0, 130.4, 130.2, 129.8, 129.5, 127.9, 127.2, 41.2, 29.5. **HRMS** (ESI): calcd for C₁₈H₁₉NO₃ [M+H]⁺ : 298.1443, found: 298.1449.

2.5 Intermolecular competition experiments

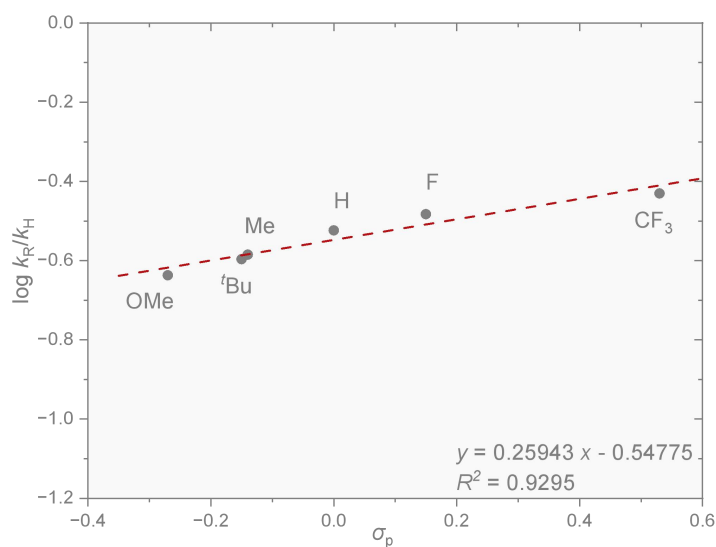
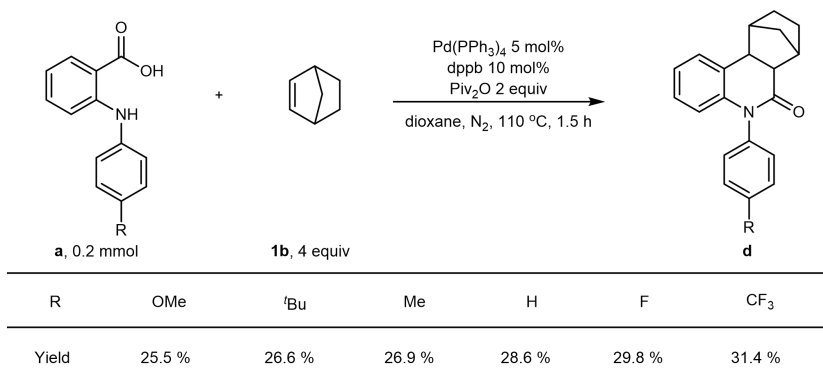


Experimental procedure taking eq 1 as an example: An oven-dried 25 mL Schlenk tube was charged with 2-((4-methoxyphenyl)amino)benzoic acid **8a** (0.2 mmol, 1 equiv), 2-(phenylamino)benzoic acid **1a** (0.2 mmol, 1 equiv), NBE **1b** (0.2 mmol, 1 equiv), Pd(PPh₃)₄ (5 mol%) and dppb (10 mol%). Subsequently, Piv₂O (2 equiv), and 1,4-dioxane (4 mL) were added under N₂. The reaction mixture was allowed to react at 110 °C for 24 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard.

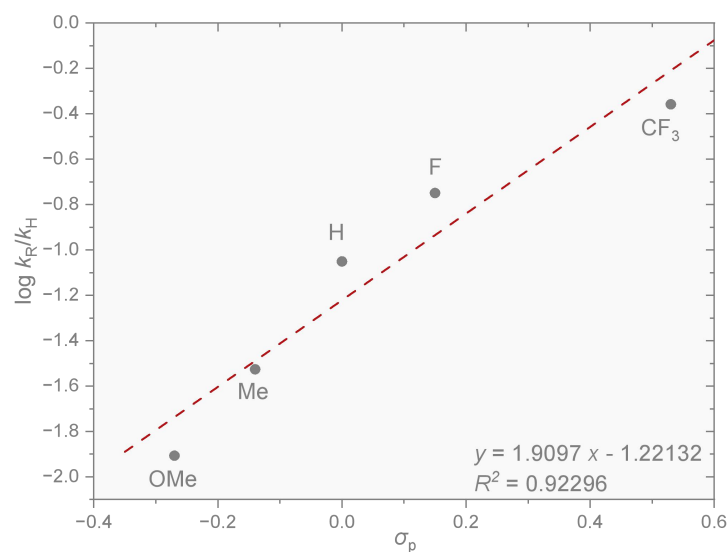
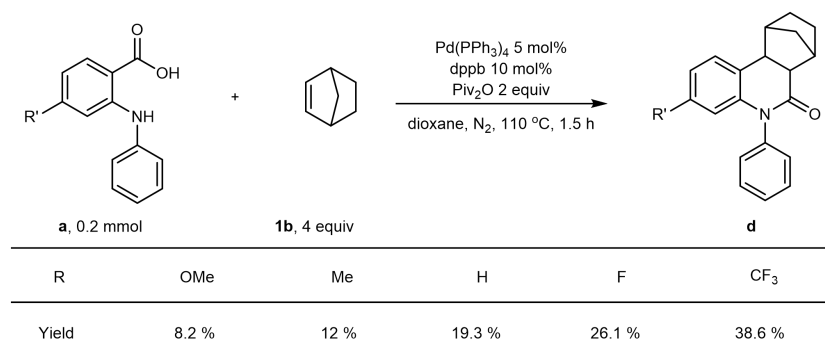


Experimental procedure taking eq 7 as an example: An oven-dried 25 mL Schlenk tube was charged with 2-((4-methoxyphenyl)amino)benzoic acid **8a** (0.2 mmol, 1 equiv), 2-(phenylamino)benzoic acid **1a** (0.2 mmol, 1 equiv), NBE **1b** (0.2 mmol, 1 equiv), Pd(OAc)₂ (5 mol%) and cataCXium A (20 mol%). Subsequently, Piv₂O (1.5 equiv), and 1,4-dioxane (8 mL) were added under N₂. The reaction mixture was allowed to react at 150 °C for 12 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard.

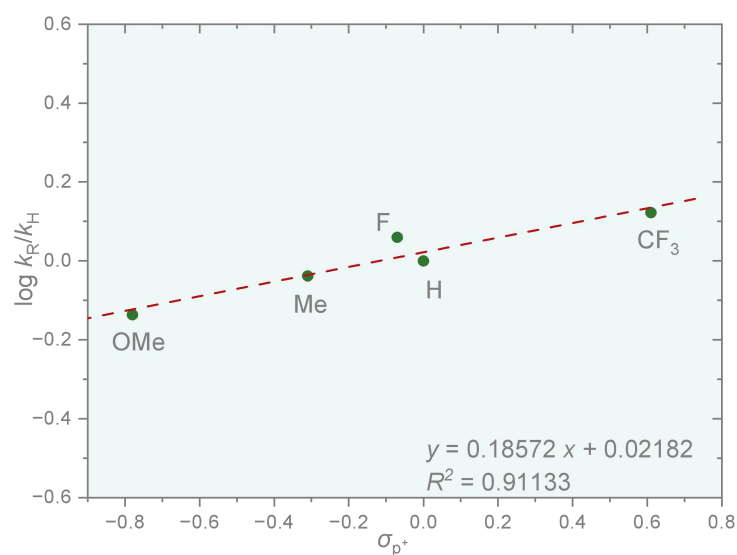
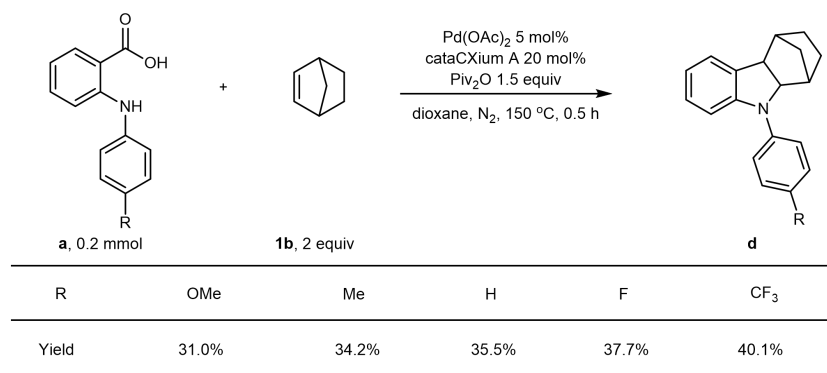
2.6 Substituent effect of substrates



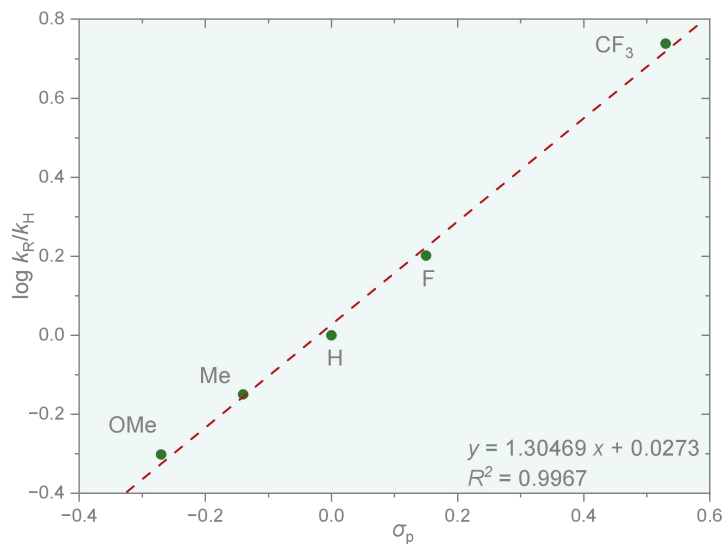
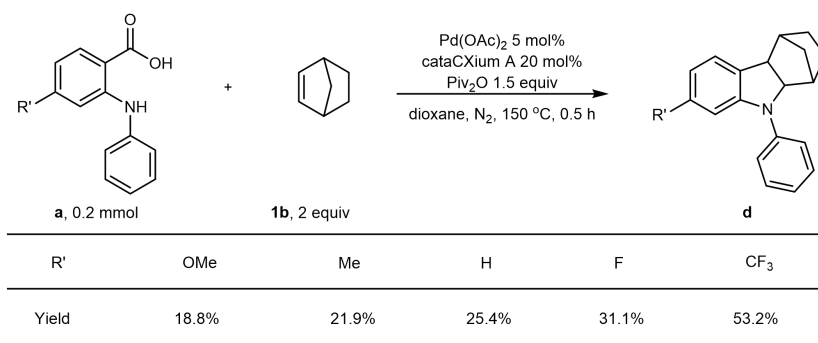
A typical experimental procedure of CO reinsertion process: An oven-dried 25 mL Schlenk tube was charged with substituted 2-(phenylamino)benzoic acid **a** (0.2 mmol), NBE **1b** (4 equiv), $\text{Pd(PPh}_3)_4$ (5 mol%) and dppb (10 mol%). Subsequently, Piv_2O (2 equiv) and 1,4-dioxane (4 mL) were added under N_2 . The reaction mixture was allowed to react at 110 °C for 1.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.



A typical experimental procedure of CO reinsertion process: An oven-dried 25 mL Schlenk tube was charged with substituted 2-(phenylamino)benzoic acid **a** (0.2 mmol), NBE **1b** (4 equiv), Pd(PPh₃)₄ (5 mol%) and dppb (10 mol%). Subsequently, Piv₂O (2 equiv) and 1,4-dioxane (4 mL) were added under N₂. The reaction mixture was allowed to react at 110 °C for 1.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.



A typical experimental procedure of decarbonylative process: An oven dried 25 mL Schlenk tube was charged with substituted 2-(phenylamino)benzoic acid **a** (0.2 mmol), NBE **1b** (2 equiv), Pd(OAc)₂ (5 mol%) and cataCXium A (20 mol%). Subsequently, Piv₂O (1.5 equiv) and 1,4-dioxane (8 mL) were added under N₂. The reaction mixture was allowed to react at 150 °C for 0.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.

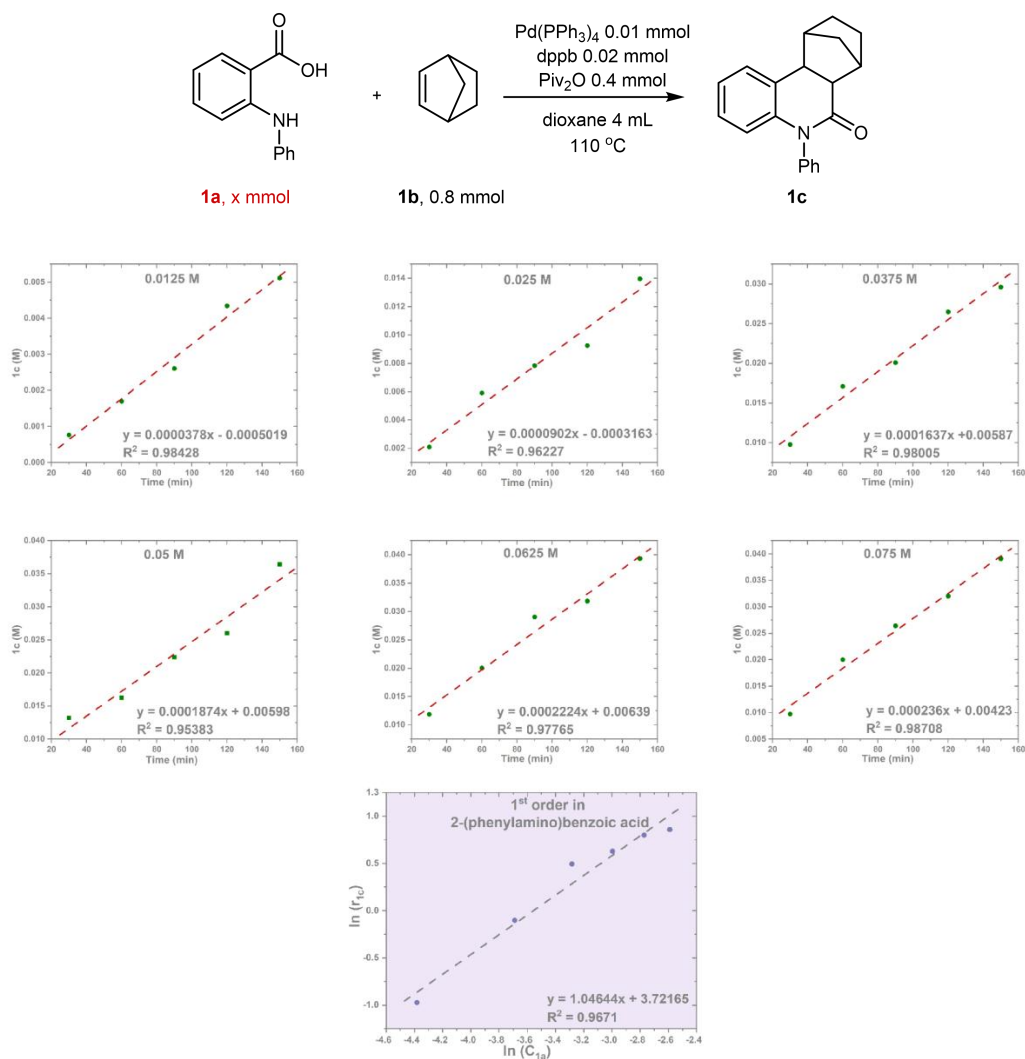


A typical experimental procedure of decarbonylative process: An oven dried 25 mL Schlenk tube was charged with substituted 2-(phenylamino)benzoic acid **a** (0.2 mmol), NBE **1b** (2 equiv), Pd(OAc)₂ (5 mol%) and cataCXium A (20 mol%). Subsequently, Piv₂O (1.5 equiv) and 1,4-dioxane (8 mL) were added under N₂. The reaction mixture was allowed to react at 150 °C for 0.5 h. The reaction mixture was cooled down to room temperature, and yields were determined by GC using tridecane as an internal standard.

2.7 Reaction progress kinetic analysis

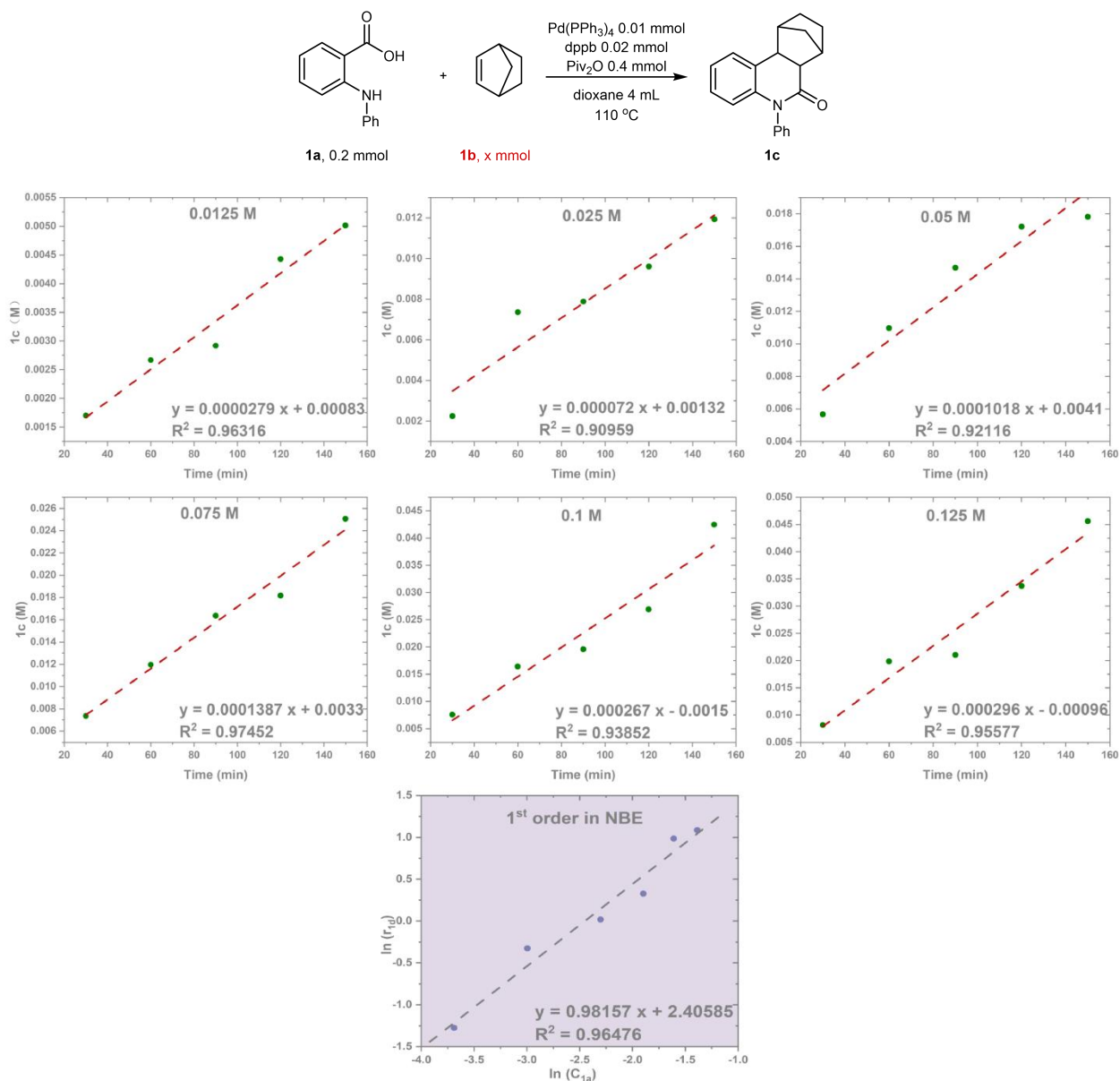
To provide further information about the reaction mechanism, kinetic experiments were performed to establish the rate laws of the cyclization using the reaction of **1a** and **1b** as a model reaction. All the kinetic data were taken at the time points in the early stage of reaction. With the help of GC tracking on product formation, we evaluated the dependence of the average rate after the initiation period on the **1a**, **1b**, Pd catalyst and **1c** or **1d** concentrations in each case. (Note: Every indicated times represent one independent experiment).

The rate on the concentration of **1a** in CO reinsertion process



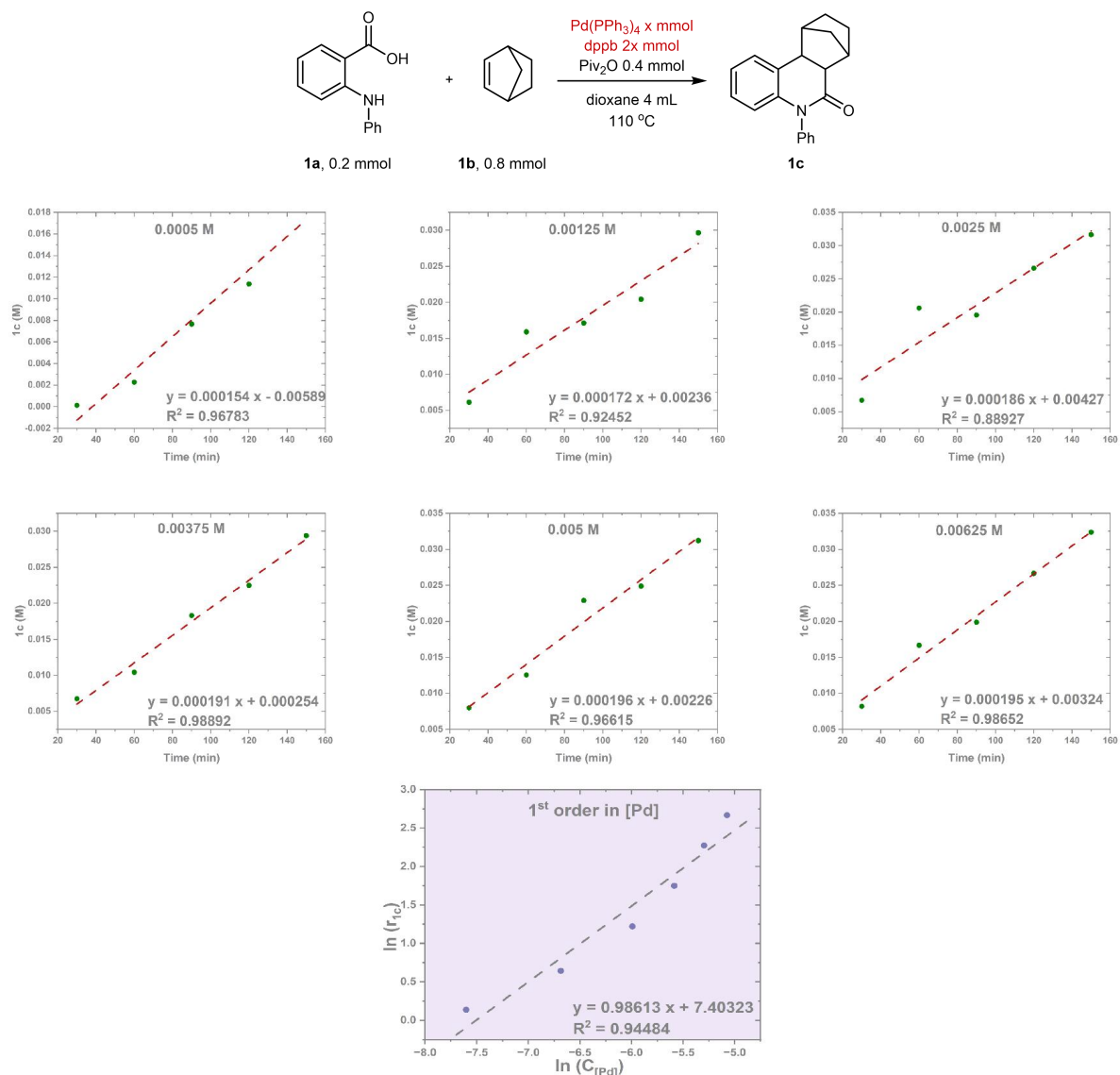
Supplementary figure S2. Plot of the rise of product and the rate on the concentration of **1a** from the reaction of **1b** (0.8 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.01 mmol), dppb (0.02 mmol), Piv_2O (0.4 mmol) with 0.05 mmol, 0.1 mmol, 0.15 mmol, 0.2 mmol, 0.25 mmol, 0.3 mmol of **1a**.

The rate on the concentration of **1b** in CO reinsertion process



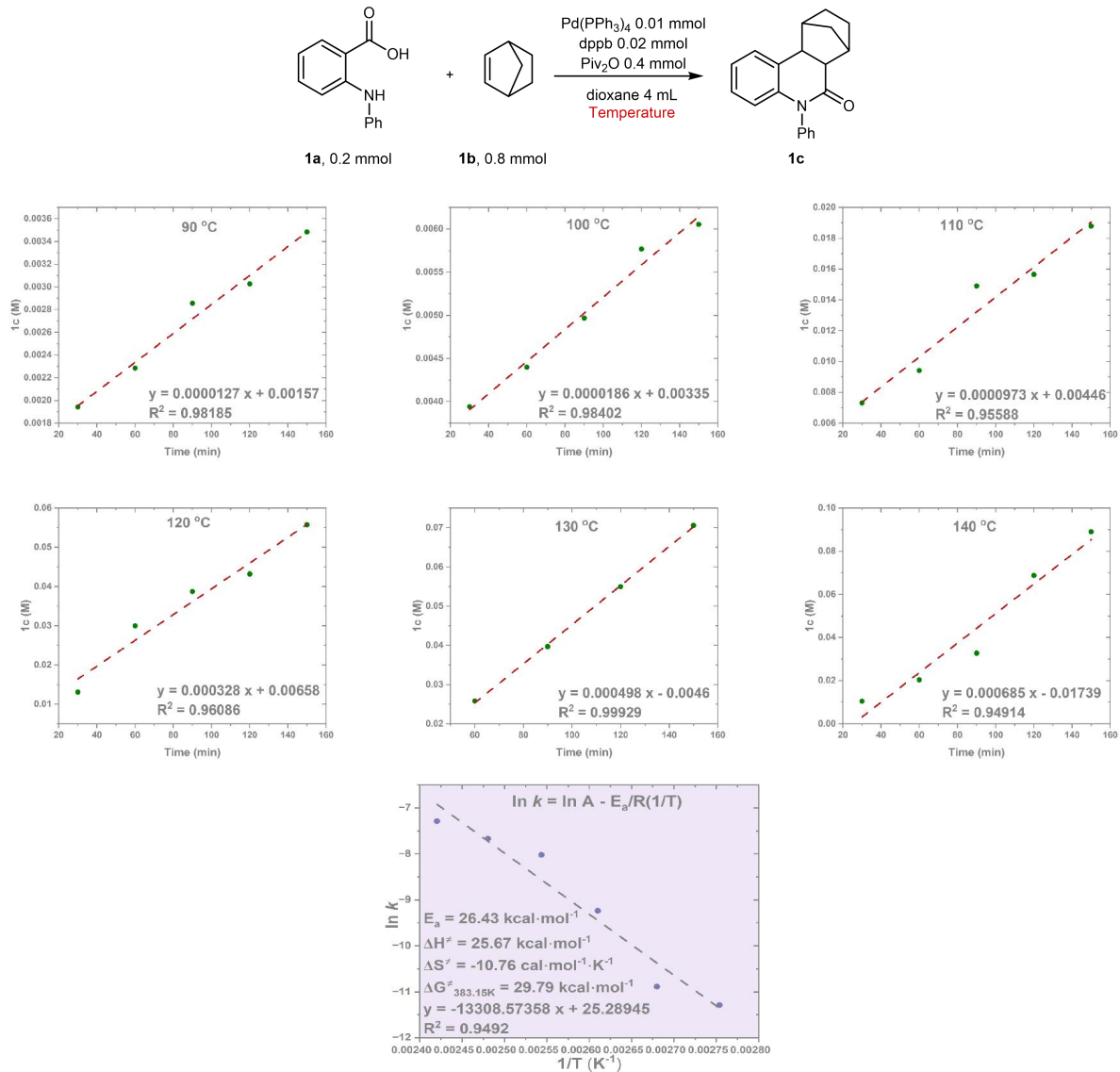
Supplementary figure S3. Plot of the rise of product and the rate on the concentration of **1b** from the reaction of **1a** (0.2 mmol), $\text{Pd(PPh}_3)_4$ (0.01 mmol), dppb (0.02 mmol), Piv_2O (0.4 mmol) with 0.1 mmol, 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, 1 mmol of **1b**.

The rate on the concentration of $\text{Pd}(\text{PPh}_3)_4$ in CO reinsertion process



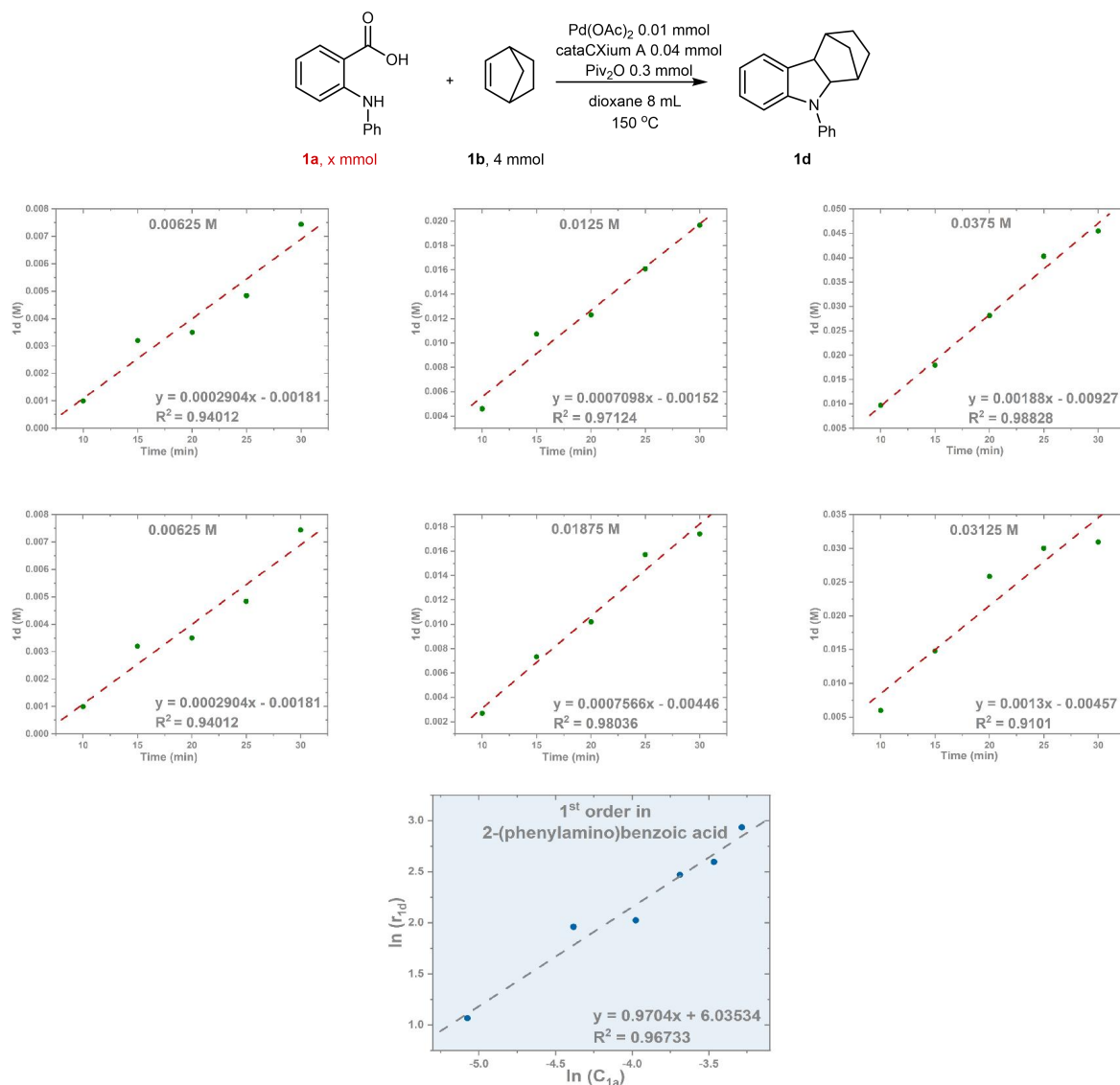
Supplementary figure S4. Plot of the rise of product and the rate on the concentration of $[\text{Pd}]$ from the reaction of **1a** (0.2 mmol), **1b** (0.8 mmol), Piv_2O (0.4 mmol) with 0.002 mmol, 0.005 mmol, 0.01 mmol, 0.015 mmol, 0.02 mmol, 0.025 mmol of $[\text{Pd}]$.

Arrhenius plot: plot of $\ln k$ vs $1/T$



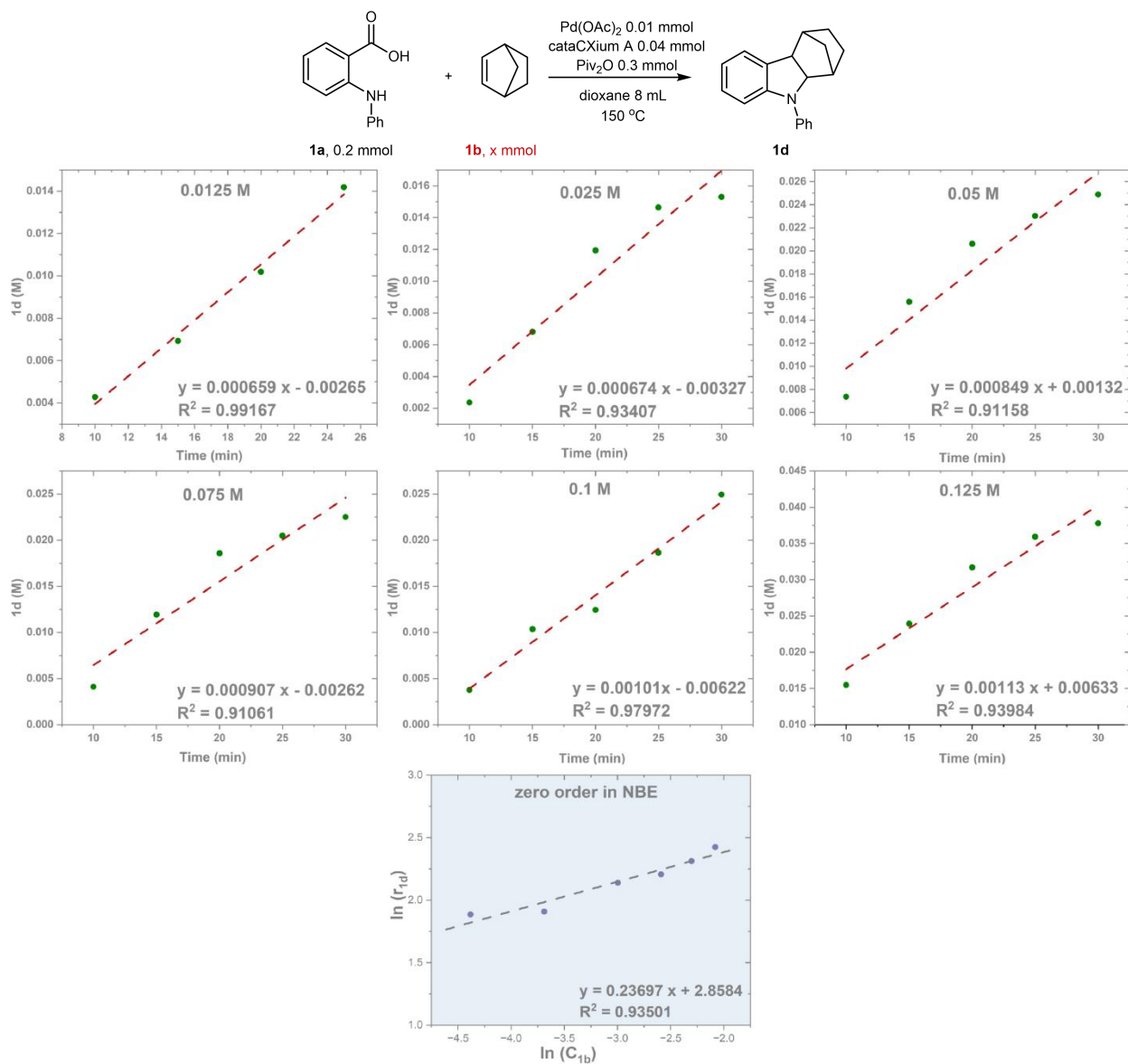
Supplementary figure S5. Comparison of the temperature dependence of the rate constant for the **1a** and **1b**; an Arrhenius plot of $\ln k$ vs. $1/T$ for the reaction of **1a** and **1b**.

The rate on the concentration of **1a** in decarbonylative process



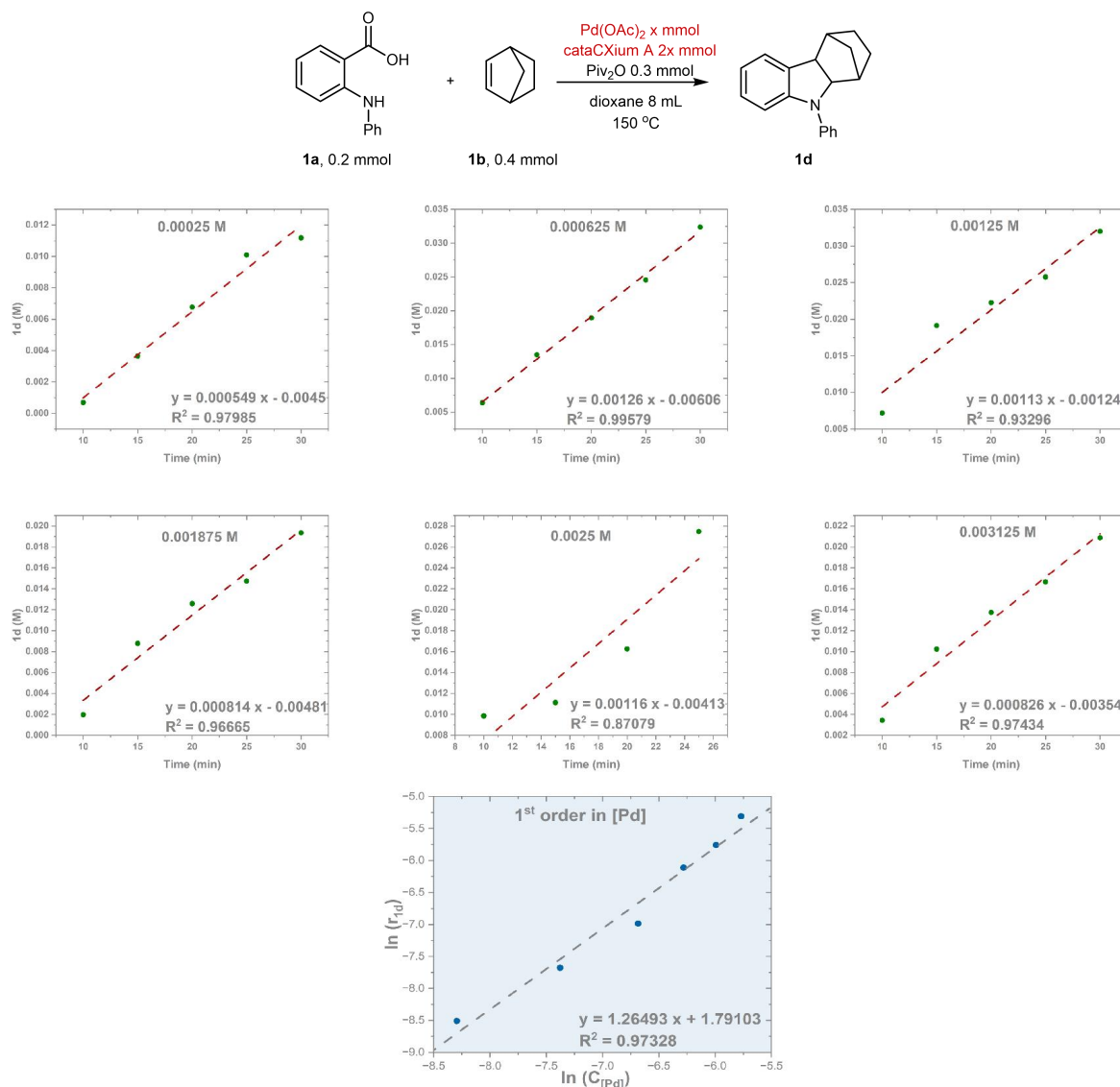
Supplementary figure S6. Plot of the rise of product and the rate on the concentration of **1a** from the reaction of **1b** (0.4 mmol), Pd(OAc)₂ (0.01 mmol), cataCXium A (0.04 mmol), Piv₂O (0.3 mmol) with 0.05 mmol, 0.1 mmol, 0.15 mmol, 0.2 mmol, 0.25 mmol, 0.3 mmol of **1a**.

The rate on the concentration of **1b** in decarbonylative process



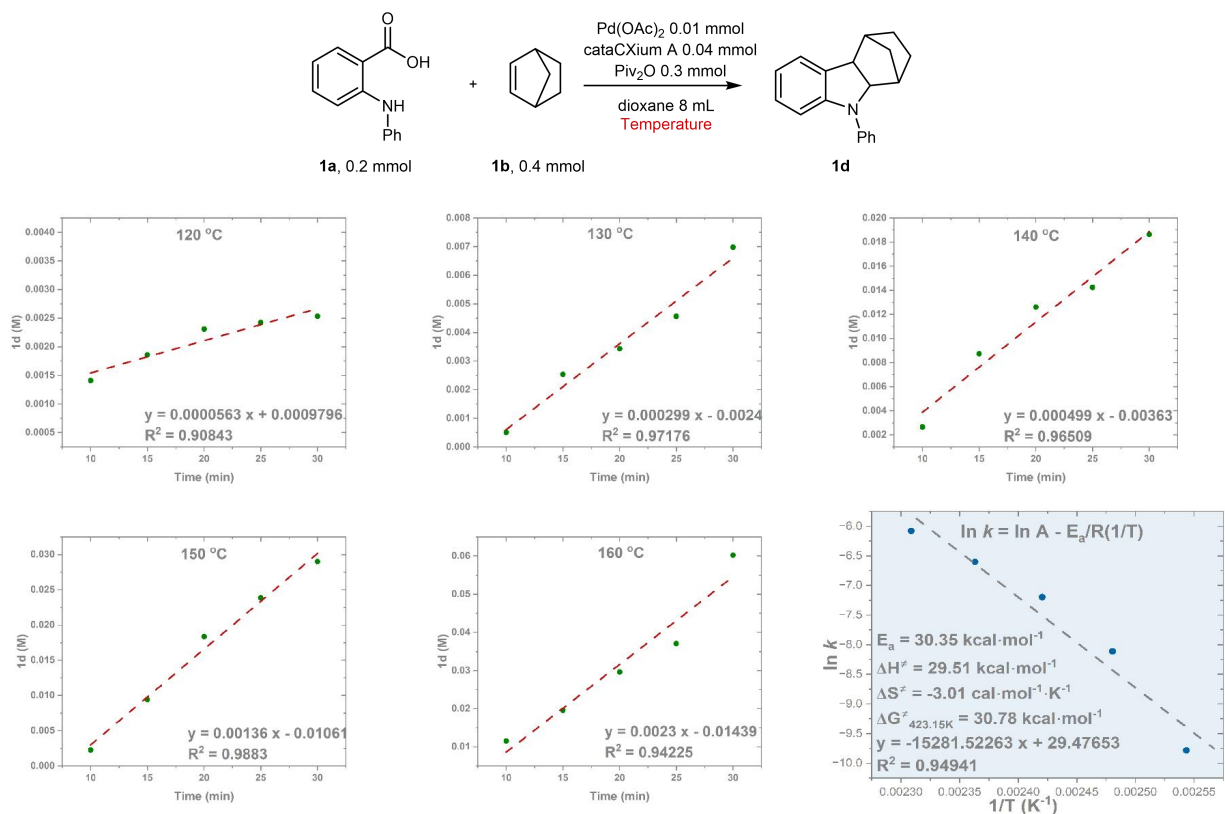
Supplementary figure S7. Plot of the rise of product and the rate on the concentration of **1b** from the reaction of **1a** (0.2 mmol), Pd(OAc)₂ (0.01 mmol), cataCXium A (0.04 mmol), Piv₂O (0.3 mmol) with 0.1 mmol, 0.2 mmol, 0.4 mmol, 0.6 mmol, 0.8 mmol, 1 mmol of **1b**.

The rate on the concentration of Pd(OAc)₂ in decarbonylative process



Supplementary figure S8. Plot of the rise of product and the rate on the concentration of [Pd] from the reaction of **1a** (0.2 mmol), **1b** (0.4 mmol), Piv₂O (0.3 mmol) with 0.002 mmol, 0.005 mmol, 0.01 mmol, 0.015 mmol, 0.02 mmol, 0.025 mmol of [Pd].

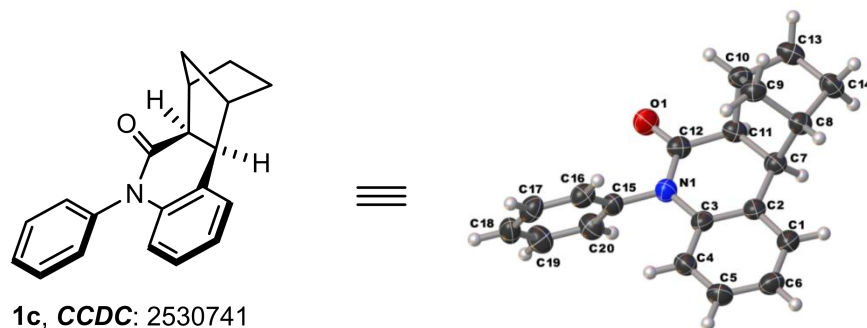
Arrhenius plot: plot of $\ln k$ vs $1/T$



Supplementary figure S9. Comparison of the temperature dependence of the rate constant for the **1a** and **1b**; an Arrhenius plot of $\ln k$ vs. $1/T$ for the reaction of **1a** and **1b**.

3. X-ray crystallographic data

X-ray data for compound **1c**, CCDC: 2530741



Crystals of **1c** suitable for X-ray crystallography were grown from a PE (petroleum ether)/DCM (dichloromethane) mixed solvent. A suitable crystal was selected and mounted on a Bruker D8 Venture diffractometer. The crystal was kept at 170.00 K during data collection using microfocus sealed tube Cu-K α radiation. Using Olex2, the structure was solved with the SHELXT structure solution program via intrinsic phasing and refined with the SHELXL refinement package by Least Squares minimization.

Supplementary table 1. Crystal data and structure refinement for **1c**

Empirical formula	C ₂₀ H ₁₉ NO
Formula weight	289.36
Temperature/K	170.00
Crystal system	triclinic
Space group	P-1
a/Å	5.6313(3)
b/Å	15.2569(7)
c/Å	17.8807(9)
α /°	83.315(3)
β /°	84.908(3)
γ /°	79.596(3)
Volume/Å ³	1497.10(13)
Z	4
ρ_{calc} /cm ³	1.284
μ /mm ⁻¹	0.611
F(000)	616.0
Crystal size/mm ³	0.15 × 0.02 × 0.01

Continued supplementary table 1. Crystal data and structure refinement for **1c**

Radiation	CuK α (λ = 1.54178)
2 θ range for data collection/ $^{\circ}$	4.988 to 136.718
Index ranges	$-6 \leq h \leq 6$, $-18 \leq k \leq 17$, $-21 \leq l \leq 21$
Reflections collected	12819
Independent reflections	5386 [$R_{\text{int}} = 0.0363$, $R_{\text{sigma}} = 0.0393$]
Data/restraints/parameters	5386/0/397
Goodness-of-fit on F^2	1.046
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0432$, $wR_2 = 0.1123$
Final R indexes [all data]	$R_1 = 0.0544$, $wR_2 = 0.1184$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.36/-0.21

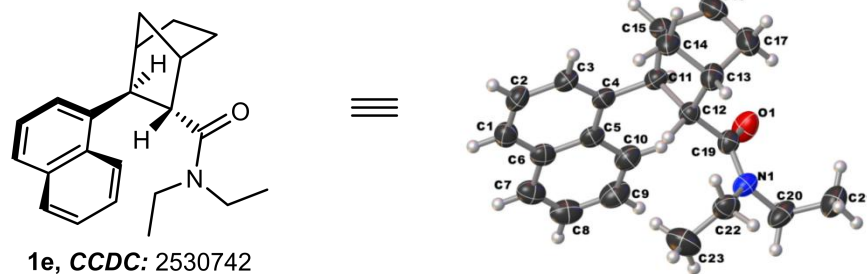
Supplementary table 2. Bond distance data of compound **1c**

Bond		Length($\text{\AA}$)	Bond		Length($\text{\AA}$)
O1	C12	1.2200(19)	C4	C5	1.384(2)
O2	C29	1.2185(19)	C1	C6	1.387(2)
N2	C24	1.4288(18)	C17	C16	1.390(2)
N2	C35	1.4425(18)	C17	C18	1.383(2)
N2	C29	1.3769(19)	C15	C16	1.388(2)
N1	C3	1.4277(19)	C15	C20	1.381(2)
N1	C15	1.4463(19)	C22	C21	1.384(2)
N1	C12	1.379(2)	C31	C30	1.529(2)
C24	C23	1.394(2)	C5	C6	1.383(2)
C24	C25	1.395(2)	C10	C9	1.534(2)
C23	C27	1.5092(19)	C10	C11	1.546(2)
C23	C22	1.398(2)	C10	C13	1.529(2)
C3	C2	1.398(2)	C12	C11	1.513(2)
C3	C4	1.403(2)	C7	C8	1.548(2)
C27	C28	1.556(2)	C7	C11	1.554(2)
C27	C32	1.552(2)	C30	C34	1.534(2)
C28	C29	1.513(2)	C9	C8	1.534(2)
C28	C30	1.550(2)	C8	C14	1.540(2)
C35	C36	1.382(2)	C26	C21	1.384(2)
C35	C40	1.383(2)	C18	C19	1.381(2)
C2	C1	1.397(2)	C34	C33	1.544(2)
C2	C7	1.517(2)	C20	C19	1.382(2)
C25	C26	1.385(2)	C13	C14	1.537(2)
C36	C37	1.386(2)	C40	C39	1.393(2)
C32	C31	1.527(2)	C37	C38	1.383(2)
C32	C33	1.534(2)	C38	C39	1.378(2)

Supplementary table 3. Bond angle data of compound **1c**

Angle			Degree(°)	Angle			Degree(°)
C24	N2	C35	119.18(12)	C20	C15	N1	118.93(14)
C29	N2	C24	124.06(12)	C20	C15	C16	120.55(14)
C29	N2	C35	116.57(12)	C21	C22	C23	121.92(14)
C3	N1	C15	119.39(12)	C32	C31	C30	94.33(12)
C12	N1	C3	124.08(13)	C6	C5	C4	120.33(14)
C12	N1	C15	116.52(12)	C9	C10	C11	101.36(12)
C23	C24	N2	120.52(13)	C13	C10	C9	101.39(13)
C23	C24	C25	119.94(13)	C13	C10	C11	109.04(13)
C25	C24	N2	119.54(13)	C15	C16	C17	118.98(15)
C24	C23	C27	122.82(13)	O1	C12	N1	121.00(14)
C24	C23	C22	118.27(13)	O1	C12	C11	119.32(14)
C22	C23	C27	118.86(13)	N1	C12	C11	119.67(13)
C2	C3	N1	120.49(13)	C2	C7	C8	112.16(12)
C2	C3	C4	119.68(14)	C2	C7	C11	114.82(12)
C4	C3	N1	119.83(13)	C8	C7	C11	102.49(11)
C23	C27	C28	114.53(12)	C5	C6	C1	118.81(14)
C23	C27	C32	111.46(12)	C31	C30	C28	101.39(12)
C32	C27	C28	102.70(11)	C31	C30	C34	102.04(12)
C29	C28	C27	118.62(12)	C34	C30	C28	108.18(13)
C29	C28	C30	107.95(13)	C10	C9	C8	94.11(12)
C30	C28	C27	102.82(12)	C9	C8	C7	101.38(12)
C36	C35	N2	119.07(13)	C9	C8	C14	101.79(12)
C36	C35	C40	120.91(14)	C14	C8	C7	108.40(12)
C40	C35	N2	120.02(14)	C21	C26	C25	120.13(14)
C3	C2	C7	122.56(13)	C26	C21	C22	119.09(14)
C1	C2	C3	118.09(14)	C10	C11	C7	103.35(12)
C1	C2	C7	119.34(13)	C12	C11	C10	108.97(12)
C26	C25	C24	120.62(14)	C12	C11	C7	118.37(12)
C35	C36	C37	119.23(15)	C19	C18	C17	119.89(15)
C31	C32	C27	101.41(11)	C30	C34	C33	103.26(12)
C31	C32	C33	102.11(12)	C15	C20	C19	119.94(15)
C33	C32	C27	108.44(12)	C32	C33	C34	103.02(12)
C5	C4	C3	120.69(14)	C10	C13	C14	103.43(12)
O2	C29	N2	120.67(14)	C35	C40	C39	119.23(16)
O2	C29	C28	119.94(13)	C38	C37	C36	120.45(16)
N2	C29	C28	119.33(13)	C13	C14	C8	103.26(12)
C6	C1	C2	122.39(15)	C18	C19	C20	120.13(15)
C18	C17	C16	120.50(15)	C39	C38	C37	119.98(15)
C16	C15	N1	120.51(14)	C38	C39	C40	120.18(16)

X-ray data for compound **1e**, CCDC: 2530742



Crystals of **1e** suitable for X-ray crystallography were grown from a PE (petroleum ether)/DCM (dichloromethane) mixed solvent. A suitable crystal was selected and mounted on a Bruker D8 Venture diffractometer. The crystal was kept at 170.00 K during data collection using microfocus sealed tube Cu-K α radiation. Using Olex2, the structure was solved with the SHELXT structure solution program via intrinsic phasing and refined with the SHELXL refinement package by Least Squares minimization.

Supplementary table 4. Crystal data and structure refinement for **1e**

Empirical formula	C ₂₂ H ₂₇ NO
Formula weight	321.44
Temperature/K	170.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	10.1423(2)
b/Å	11.6243(3)
c/Å	15.3584(4)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1810.71(8)
Z	4
ρ_{calc} /cm ³	1.179
μ /mm ⁻¹	0.546
F(000)	696.0
Crystal size/mm ³	0.21 × 0.17 × 0.15
Radiation	CuK α (λ = 1.54178)
2 θ range for data collection/°	9.542 to 136.806
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 18
Reflections collected	16764

Continued supplementary table 4. Crystal data and structure refinement for **1e**

Independent reflections	3288 [$R_{\text{int}} = 0.0252$, $R_{\text{sigma}} = 0.0220$]
Data/restraints/parameters	3288/0/219
Goodness-of-fit on F^2	1.068
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0287$, $wR_2 = 0.0734$
Final R indexes [all data]	$R_1 = 0.0289$, $wR_2 = 0.0736$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.12/-0.13
Flack parameter	0.08(5)

Supplementary table 5. Bond distance data of compound **1e**

Bond			Length($\text{\AA}$)	Bond			Length($\text{\AA}$)
O1	C19		1.2295(18)	C1	C6		1.417(2)
N1	C19		1.354(2)	C6	C7		1.415(2)
N1	C20		1.465(2)	C11	C15		1.543(2)
N1	C22		1.466(2)	C10	C9		1.373(2)
C19	C12		1.5223(19)	C7	C8		1.363(3)
C4	C3		1.379(2)	C14	C13		1.536(2)
C4	C5		1.435(2)	C14	C15		1.536(3)
C4	C11		1.516(2)	C8	C9		1.400(3)
C3	C2		1.410(2)	C13	C17		1.527(3)
C5	C6		1.427(2)	C20	C21		1.504(3)
C5	C10		1.423(2)	C15	C16		1.542(2)
C12	C11		1.574(2)	C22	C23		1.518(3)
C12	C13		1.551(2)	C17	C16		1.554(3)
C2	C1		1.360(2)				

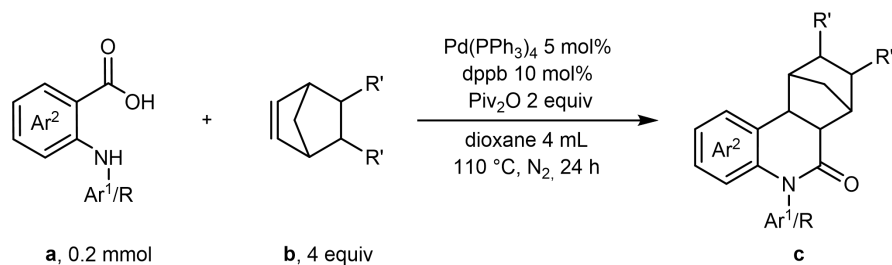
Supplementary table 6. Bond angle data of compound **1e**

Angle				Degree($^\circ$)				Angle				Degree($^\circ$)			
C19	N1	C20		119.28(13)	C7	C6	C1	120.46(15)							
C19	N1	C22		124.88(13)	C4	C11	C12	112.29(12)							
C20	N1	C22		115.60(13)	C4	C11	C15	115.86(12)							
O1	C19	N1		120.80(13)	C15	C11	C12	102.11(12)							
O1	C19	C12		121.58(14)	C9	C10	C5	120.65(16)							
N1	C19	C12		117.61(13)	C8	C7	C6	121.07(16)							
C3	C4	C5		117.97(14)	C13	C14	C15	94.33(13)							
C3	C4	C11		121.71(13)	C7	C8	C9	119.54(16)							
C5	C4	C11		120.32(13)	C14	C13	C12	100.99(12)							
C4	C3	C2		122.33(14)	C17	C13	C12	110.21(14)							
C6	C5	C4		119.46(13)	C17	C13	C14	101.16(14)							
C10	C5	C4		123.03(14)	N1	C20	C21	113.02(14)							

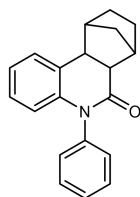
Continued supplementary table 6. Bond angle data of compound **1e**

C10	C5	C6	117.50(14)	C14	C15	C11	103.15(12)
C19	C12	C11	114.66(12)	C14	C15	C16	101.27(15)
C19	C12	C13	112.80(12)	C16	C15	C11	107.19(14)
C13	C12	C11	103.16(12)	N1	C22	C23	112.55(16)
C1	C2	C3	120.37(14)	C10	C9	C8	121.41(16)
C2	C1	C6	120.14(14)	C13	C17	C16	103.17(14)
C1	C6	C5	119.72(14)	C15	C16	C17	103.14(15)
C7	C6	C5	119.82(14)				

4. Characterization data for products

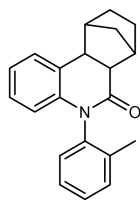


An oven dried 25 mL Schlenk tube was charged with 2-aminobenzoic acid **a** (0.2 mmol, 1 equiv), NBE **b** (0.8 mmol, 4 equiv) Pd(PPh₃)₄ (5 mol%), and dppb (10 mol%). Subsequently, Piv₂O (0.4 mmol, 2 equiv), and 1,4-dioxane (4 mL) were added under N₂. The reaction mixture was heated at 110 °C for 24 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to give a desired product compound **1c–50c**.



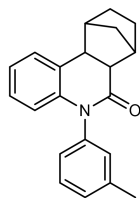
5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**1c**)

The representative general procedure mentioned above was followed. The desired product **1c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a white solid in 93% yield (53.8 mg). mp: 240–244 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.57 (t, *J* = 7.8 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.0 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 2H), 7.00 (dtd, *J* = 17.0, 7.2, 1.2 Hz, 2H), 6.16 (d, *J* = 7.8 Hz, 1H), 3.26 (d, *J* = 10.0 Hz, 1H), 2.98 (d, *J* = 9.8 Hz, 2H), 2.56 (d, *J* = 2.4 Hz, 1H), 1.83 – 1.70 (m, 2H), 1.63 (t, *J* = 8.2 Hz, 3H), 1.30 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 170.0, 139.8, 138.6, 130.1, 129.7, 128.3, 126.8, 125.0, 122.9, 116.1, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3. HRMS (ESI): calcd for C₂₀H₁₉NO [M+H]⁺ : 290.1539, found: 290.1546.



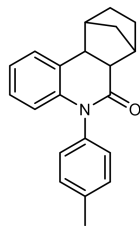
5-(*o*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**2c**)

The representative general procedure mentioned above was followed. The desired product **2c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.53) as a white solid in 82% yield (49.7 mg). mp: 241–244 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42 – 7.35 (m, 3H), 7.28 (d, J = 7.0 Hz, 1H), 7.10 (dd, J = 5.6, 3.2 Hz, 1H), 7.00 (dt, J = 19.8, 7.2 Hz, 2H), 6.06 (d, J = 7.8 Hz, 1H), 3.35 – 3.22 (m, 1H), 3.12 – 2.89 (m, 2H), 2.57 (s, 1H), 2.13 (d, J = 26.0 Hz, 3H), 1.81 – 1.70 (m, 2H), 1.68 – 1.61 (m, 3H), 1.33 – 1.27 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.3, 138.9, 137.3, 136.5, 131.5, 129.8, 129.3, 128.6, 127.8, 127.1, 125.1, 123.0, 115.4, 49.3, 48.6, 45.2, 34.8, 29.7, 29.4, 28.9, 17.7. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$: 304.1696, found: 304.1692.



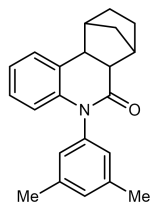
5-(*m*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**3c**)

The representative general procedure mentioned above was followed. The desired product **3c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a white solid in 79% yield (47.9 mg). mp: 239–241 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.40 (t, J = 7.8 Hz, 1H), 7.26 – 7.18 (m, 2H), 6.96 (qd, J = 8.0, 7.6, 1.6 Hz, 4H), 6.13 (dd, J = 7.8, 1.4 Hz, 1H), 3.20 (d, J = 10.0 Hz, 1H), 2.93 (dd, J = 6.4, 2.6 Hz, 2H), 2.53 – 2.48 (m, 1H), 2.39 (s, 3H), 1.78 – 1.66 (m, 2H), 1.58 (t, J = 8.2 Hz, 3H), 1.24 (d, J = 10.4 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.9, 139.8, 138.4, 129.9, 129.6, 129.1, 126.8, 125.0, 122.9, 116.2, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.2, 21.4. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$: 304.1696, found: 304.1691.



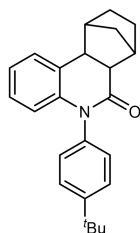
5-(*p*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**4c**)

The representative general procedure mentioned above was followed. The desired product **4c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.50) as a white solid in 84% yield (50.9 mg). mp: 239–241 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 6.95 (pd, *J* = 7.2, 1.4 Hz, 2H), 6.19 – 6.12 (m, 1H), 3.20 (d, *J* = 10.0 Hz, 1H), 2.97 – 2.89 (m, 2H), 2.50 (d, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 1.77 – 1.66 (m, 2H), 1.62 – 1.55 (m, 3H), 1.24 (d, *J* = 10.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 170.0, 139.9, 138.1, 135.8, 130.7, 129.6, 126.8, 125.0, 122.8, 116.2, 49.4, 48.6, 45.2, 45.2, 34.7, 29.4, 29.2, 21.3. HRMS (ESI): calcd for C₂₁H₂₁NO [M+H]⁺ : 304.1696, found: 304.1699.



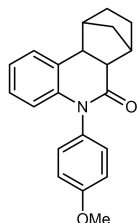
5-(3,5-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**5c**)

The representative general procedure mentioned above was followed. The desired product **5c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.55) as a white solid in 84% yield (53.2 mg). mp: 241–244 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.23 – 7.19 (m, 1H), 7.05 (s, 1H), 6.99 – 6.91 (m, 2H), 6.78 (d, *J* = 4.4 Hz, 2H), 6.14 (dd, *J* = 7.8, 1.8 Hz, 1H), 3.20 (d, *J* = 10.0 Hz, 1H), 2.92 (d, *J* = 9.8 Hz, 2H), 2.49 (d, *J* = 2.4 Hz, 1H), 2.35 (s, 6H), 1.78 – 1.64 (m, 2H), 1.58 (t, *J* = 8.2 Hz, 3H), 1.27 – 1.22 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 169.9, 139.9, 139.8, 139.7, 138.3, 130.1, 129.6, 126.8, 126.7, 126.4, 124.9, 122.8, 116.3, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3, 21.3. HRMS (ESI): calcd for C₂₂H₂₃NO [M+H]⁺ : 318.1852, found: 318.1850.



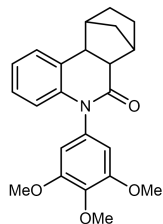
5-(4-(*tert*-butyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**6c**)

The representative general procedure mentioned above was followed. The desired product **6c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.53) as a white solid in 90% yield (62.1 mg). mp: 240–242 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.57 (d, J = 8.8 Hz, 2H), 7.26 (dd, J = 6.8, 1.8 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.05 – 6.96 (m, 2H), 6.20 (dd, J = 7.8, 1.8 Hz, 1H), 3.25 (d, J = 10.0 Hz, 1H), 3.01 – 2.94 (m, 2H), 2.55 (d, J = 2.6 Hz, 1H), 1.83 – 1.71 (m, 2H), 1.64 (dd, J = 14.8, 5.0 Hz, 3H), 1.42 (s, 9H), 1.32 – 1.27 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.0, 151.1, 139.9, 135.7, 129.6, 127.0, 126.8, 125.0, 122.8, 116.2, 49.4, 48.7, 45.2, 45.2, 34.7, 34.6, 31.4, 29.4, 29.3. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{NO}$ $[\text{M}+\text{H}]^+$: 346.2165, found: 346.2161.



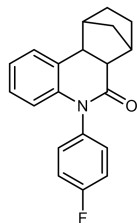
5-(4-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**7c**)

The representative general procedure mentioned above was followed. The desired product **7c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.48) as a white solid in 80% yield (51.0 mg). mp: 233–238 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.27 (dd, J = 6.8, 2.0 Hz, 1H), 7.09 (t, J = 11.4 Hz, 4H), 7.05 – 6.97 (m, 2H), 6.23 (dd, J = 7.6, 1.6 Hz, 1H), 3.91 (s, 3H), 3.25 (d, J = 10.0 Hz, 1H), 2.97 (d, J = 9.6 Hz, 2H), 2.55 (d, J = 2.4 Hz, 1H), 1.78 (ddd, J = 13.0, 8.4, 3.8 Hz, 2H), 1.66 (s, 1H), 1.64 – 1.61 (m, 2H), 1.29 (d, J = 12.0 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.2, 159.2, 140.1, 131.1, 130.3, 129.9, 129.7, 126.8, 125.1, 122.9, 116.2, 115.4, 55.5, 49.4, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 320.1645, found: 320.1644.



5-(3,4,5-trimethoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**8c**)

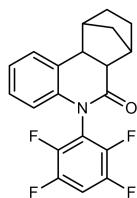
The representative general procedure mentioned above was followed. The desired product **8c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.45) as a white solid in 82% yield (62.2 mg). mp: 228–230 °C; **¹H NMR** (400 MHz, $CDCl_3$): δ 7.18 – 7.14 (m, 1H), 6.97 – 6.89 (m, 2H), 6.30 (d, J = 13.2 Hz, 2H), 6.16 – 6.11 (m, 1H), 3.83 (s, 3H), 3.76 (d, J = 9.4 Hz, 6H), 3.14 (d, J = 9.8 Hz, 1H), 2.86 (d, J = 10.2 Hz, 2H), 2.45 (d, J = 2.8 Hz, 1H), 1.74 – 1.57 (m, 2H), 1.51 (d, J = 8.8 Hz, 3H), 1.19 (d, J = 7.8 Hz, 1H); **¹³C NMR** (100 MHz, $CDCl_3$): δ 169.8, 154.4, 154.3, 139.7, 137.6, 134.1, 129.6, 126.9, 124.9, 123.0, 116.2, 106.2, 105.7, 60.9, 56.1, 49.3, 48.7, 45.2, 45.1, 34.8, 29.4, 29.3. **HRMS** (ESI): calcd for $C_{23}H_{25}NO_4$ $[M+H]^+$: 380.1856, found: 380.1852.



5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**9c**)

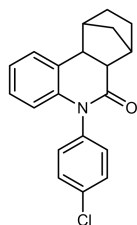
The representative general procedure mentioned above was followed. The desired product **9c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.57) as a white solid in 85% yield (52.2 mg). mp: 175–177 °C; **¹H NMR** (400 MHz, $CDCl_3$): δ 7.29 – 7.22 (m, 2H), 7.22 – 7.16 (m, 2H), 7.02 (pd, J = 7.2, 1.4 Hz, 2H), 6.18 – 6.14 (m, 1H), 3.26 (d, J = 10.0 Hz, 1H), 2.97 (d, J = 9.8 Hz, 2H), 2.55 (d, J = 2.2 Hz, 1H), 1.84 – 1.67 (m, 2H), 1.63 (t, J = 8.8 Hz, 3H), 1.29 (d, J = 10.2 Hz, 1H); **¹³C NMR** (100 MHz, $CDCl_3$): δ 169.9, 161.4 (d, J = 243.4 Hz), 141.2 (d, J = 9.6 Hz), 138.1, 130.9, 130.9, 130.3, 129.1 (d, J = 37.4 Hz), 128.7, 120.6 (d, J = 3.2 Hz), 109.6, 109.4, 103.7, 103.4, 49.3, 48.6, 45.2, 44.7, 34.7,

29.4, 29.1; **¹⁹F NMR** (376 MHz, CDCl₃): δ -113.17. **HRMS** (ESI): calcd for C₂₀H₁₈FNO [M+H]⁺ : 308.1445, found: 308.1449.



5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**10c**)

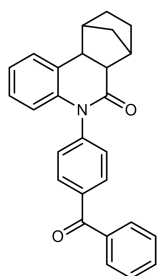
The representative general procedure mentioned above was followed. The desired product **10c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a white solid in 82% yield (59.2 mg). mp: 120–122 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.32 (dd, *J* = 10.0, 4.0 Hz, 1H), 7.29 – 7.21 (m, 1H), 7.14 – 7.06 (m, 2H), 6.24 (d, *J* = 8.0 Hz, 1H), 3.29 (d, *J* = 9.8 Hz, 1H), 3.02 (d, *J* = 9.8 Hz, 1H), 2.95 (d, *J* = 2.8 Hz, 1H), 2.56 (s, 1H), 1.84 – 1.71 (m, 2H), 1.68 – 1.59 (m, 3H), 1.30 (d, *J* = 10.4 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 169.4, 147.8 – 147.5 (m), 145.7 – 144.7 (m), 143.3 – 141.7 (m), 137.1, 130.3, 127.5, 125.2, 124.0, 117.9 (t, *J* = 15.5 Hz), 114.1, 106.7 (t, *J* = 22.6 Hz), 49.3, 48.6, 45.4, 45.2, 34.6, 29.3, 29.2; **¹⁹F NMR** (376 MHz, CDCl₃): δ -137.82 (ddd, *J* = 21.2, 17.6, 10.4 Hz, 2F), -143.94 – -144.18 (m, 1F), -145.00 – -145.24 (m, 1F). **HRMS** (ESI): calcd for C₂₀H₁₅F₄NO [M+H]⁺ : 362.1163, found: 362.1160.



5-(4-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**11c**)

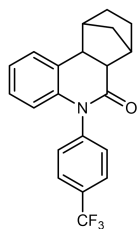
The representative general procedure mentioned above was followed. The desired product **11c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a white solid in 89% yield (57.5 mg). mp: 229–231 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.23 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.03

– 6.93 (m, 2H), 6.12 (dd, $J = 7.8, 1.4$ Hz, 1H), 3.21 (d, $J = 10.0$ Hz, 1H), 2.92 (d, $J = 9.8$ Hz, 2H), 2.51 (d, $J = 2.6$ Hz, 1H), 1.77 – 1.64 (m, 2H), 1.62 – 1.52 (m, 3H), 1.24 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 139.5, 137.1, 134.2, 130.3, 129.8, 126.9, 125.1, 123.2, 115.9, 49.3, 48.7, 45.2, 34.7, 29.4, 29.2. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{18}\text{ClNO}$ $[\text{M}+\text{H}]^+$: 324.1150, found: 324.1154.



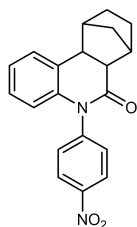
5-(4-benzoylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**12c**)

The representative general procedure mentioned above was followed. The desired product **12c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.45$) as a white solid in 71% yield (55.8 mg). mp: 240–244 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.97 (d, $J = 8.6$ Hz, 2H), 7.91 – 7.84 (m, 2H), 7.66 – 7.57 (m, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 7.29 – 7.22 (m, 1H), 7.01 (td, $J = 7.4, 1.4$ Hz, 1H), 6.96 (td, $J = 7.6, 1.6$ Hz, 1H), 6.13 (dd, $J = 8.0, 1.2$ Hz, 1H), 3.24 (d, $J = 9.8$ Hz, 1H), 2.96 (d, $J = 9.8$ Hz, 2H), 2.53 (d, $J = 2.8$ Hz, 1H), 1.82 – 1.65 (m, 2H), 1.64 – 1.53 (m, 3H), 1.27 (dt, $J = 10.2, 1.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 195.9, 169.9, 142.4, 139.2, 137.4, 137.3, 132.7, 131.8, 130.1, 129.9, 129.5, 128.4, 126.9, 125.0, 123.3, 115.9, 49.3, 48.7, 45.2, 34.8, 29.4, 29.2. HRMS (ESI): calcd for $\text{C}_{27}\text{H}_{23}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 394.1802, found: 394.1806.



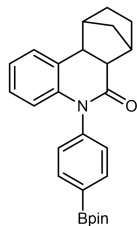
5-(4-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**13c**)

The representative general procedure mentioned above was followed. The desired product **13c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a white solid in 76% yield (54.3 mg). mp: 188–190 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.83 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 6.0 Hz, 1H), 7.05 (td, J = 7.4, 1.2 Hz, 1H), 7.00 (td, J = 7.8, 7.4, 1.4 Hz, 1H), 6.12–6.08 (m, 1H), 3.27 (d, J = 9.8 Hz, 1H), 3.00–2.94 (m, 2H), 2.56 (s, 1H), 1.83 – 1.70 (m, 2H), 1.63 (t, J = 8.4 Hz, 3H), 1.30 (d, J = 9.8 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.9, 141.9, 139.2, 130.5 (d, J = 32.8 Hz), 129.9, 127.2 (q, J = 3.7 Hz), 126.9, 125.1, 123.9 (q, J = 270.8 Hz), 123.3, 115.8, 49.3, 48.6, 45.2, 34.8, 29.4, 29.2; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): δ -62.55. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{18}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 358.1413, found: 358.1418.



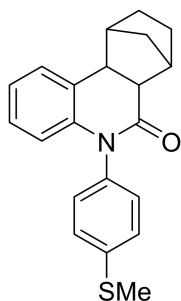
5-(4-nitrophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**14c**)

The representative general procedure mentioned above was followed. The desired product **14c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a white solid in 82% yield (54.8 mg). mp: 235–236 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.44 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.08 (t, J = 7.4 Hz, 1H), 7.02 (t, J = 7.8 Hz, 1H), 6.10 (d, J = 8.0 Hz, 1H), 3.29 (d, J = 9.8 Hz, 1H), 3.02–2.94 (m, 2H), 2.58 (s, 1H), 1.84 – 1.72 (m, 2H), 1.63 (dd, J = 12.0, 6.8 Hz, 3H), 1.32 (d, J = 10.2 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.9, 147.5, 144.7, 138.8, 130.7, 130.1, 127.1, 125.4, 125.1, 123.6, 115.6, 49.3, 48.7, 45.2, 45.2, 34.8, 29.4, 29.1. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 335.1390, found: 335.1392.



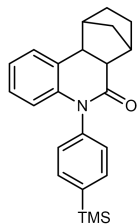
5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**15c**)

The representative general procedure mentioned above was followed. The desired product **15c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.47) as a white solid in 64% yield (53.1 mg). mp: 220–223 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.33 (m, 1H), 7.17 – 7.08 (m, 3H), 6.95 – 6.81 (m, 2H), 6.05 – 6.01 (m, 1H), 3.14 (d, *J* = 9.7 Hz, 1H), 2.86 (dd, *J* = 9.8, 3.1 Hz, 2H), 2.43 (d, *J* = 3.4 Hz, 1H), 1.73 – 1.55 (m, 2H), 1.56 – 1.46 (m, 3H), 1.29 (s, 8H), 1.22 (dd, *J* = 27.9, 2.1 Hz, 4H), 1.15 (d, *J* = 5.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 169.8, 141.3, 139.7, 136.6, 129.7, 126.8, 124.9, 122.9, 116.1, 84.0, 49.3, 48.7, 45.2, 45.2, 34.7, 29.4, 29.2, 24.9, 24.8. HRMS (ESI): calcd for C₂₆H₃₀BNO₃ [M+H]⁺ : 416.2392, found: 416.2393.



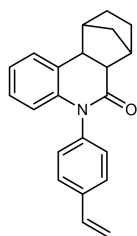
5-(4-(methylthio)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**16c**)

The representative general procedure mentioned above was followed. The desired product **16c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.52) as a white solid in 88% yield (59.0 mg). mp: 207–210 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.00 (pd, *J* = 7.4, 1.6 Hz, 2H), 6.20 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.24 (d, *J* = 10.0 Hz, 1H), 2.96 (d, *J* = 9.6 Hz, 2H), 2.56 (s, 3H), 2.55 – 2.52 (m, 1H), 1.78 – 1.68 (m, 2H), 1.60 (d, *J* = 8.6 Hz, 3H), 1.30 – 1.25 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 170.1, 139.7, 138.9, 135.3, 129.7, 127.8, 126.8, 125.0, 122.9, 116.1, 49.3, 48.7, 45.2, 34.7, 29.4, 29.2, 15.7. HRMS (ESI): calcd for C₂₁H₂₁NOS [M+H]⁺ : 336.1417, found: 336.1412.



5-(4-(trimethylsilyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**17c**)

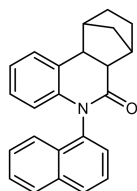
The representative general procedure mentioned above was followed. The desired product **17c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a white solid in 75% yield (54.2 mg). mp: 203–205 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.66 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 6.9 Hz, 1H), 7.15 (d, J = 7.2 Hz, 2H), 7.01 – 6.89 (m, 2H), 6.14 (d, J = 7.8 Hz, 1H), 3.21 (d, J = 10.0 Hz, 1H), 2.93 (d, J = 9.9 Hz, 2H), 2.50 (s, 1H), 1.77 – 1.64 (m, 2H), 1.59 (t, J = 10.4 Hz, 3H), 1.26 – 1.18 (m, 1H), 0.31 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.3, 142.1, 141.1, 140.3, 136.4, 130.9, 128.1, 126.3, 124.2, 117.5, 50.7, 49.9, 46.5, 46.5, 36.0, 30.7, 30.6, 0.3. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{27}\text{NOSi}$ $[\text{M}+\text{H}]^+$: 362.1935, found: 362.1932.



5-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**18c**)

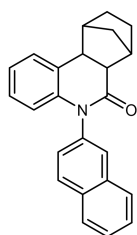
The representative general procedure mentioned above was followed. The desired product **18c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.58) as a white solid in 83% yield (52.3 mg). mp: 221–223 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.48 (d, J = 8.4 Hz, 2H), 7.18 – 7.13 (m, 1H), 7.06 (d, J = 7.8 Hz, 2H), 6.95 – 6.82 (m, 2H), 6.69 (dd, J = 17.6, 10.8 Hz, 1H), 6.13 – 6.06 (m, 1H), 5.72 (d, J = 17.6 Hz, 1H), 5.24 (d, J = 10.8 Hz, 1H), 3.13 (d, J = 10.0 Hz, 1H), 2.89 – 2.82 (m, 2H), 2.46 – 2.40 (m, 1H), 1.70 – 1.58 (m, 2H), 1.50 (t, J = 8.0 Hz, 3H), 1.17 (d, J = 10.6 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.9,

139.7, 137.9, 137.6, 136.1, 129.7, 127.8, 126.8, 125.0, 122.9, 116.1, 114.9, 49.3, 48.7, 45.2, 45.1, 34.7, 29.4, 29.2. **HRMS** (ESI): calcd for C₂₂H₂₁NO [M+H]⁺ : 316.1696, found: 316.1693.



5-(naphthalen-1-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**19c**)

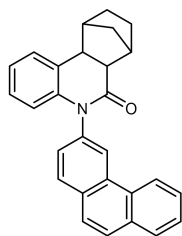
The representative general procedure mentioned above was followed. The desired product **19c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.56) as a white solid in 65% yield (44.1 mg). mp: 245–249 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.61 – 7.55 (m, 1H), 7.50 (q, *J* = 6.0, 5.0 Hz, 1H), 7.43 (dd, *J* = 15.0, 8.0 Hz, 1H), 7.35 (t, *J* = 6.4 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 5.90 (d, *J* = 8.4 Hz, 1H), 3.34 (d, *J* = 10.0 Hz, 1H), 3.06 (d, *J* = 13.6 Hz, 1H), 3.01 (d, *J* = 8.7 Hz, 1H), 2.60 (d, *J* = 23.9 Hz, 1H), 1.83 – 1.70 (m, 3H), 1.63 (d, *J* = 7.6 Hz, 2H), 1.26 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.1, 139.6, 135.4, 135.1, 134.8, 130.3, 129.7, 129.0, 128.6, 127.4, 127.0, 126.5, 126.2, 124.9, 123.0, 122.3, 116.3, 49.5, 48.7, 45.3, 35.4, 34.9, 29.7, 29.4. **HRMS** (ESI): calcd for C₂₄H₂₁NO [M+H]⁺ : 340.1696, found: 340.1697.



5-(naphthalen-2-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**20c**)

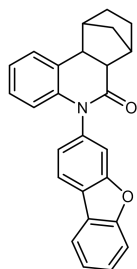
The representative general procedure mentioned above was followed. The desired product **20c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a white solid in 82% yield (55.6 mg). mp: 233–236 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.62 (s, 1H), 7.45 (pd, *J* = 6.8, 3.4 Hz, 2H), 7.18 (d, *J* = 6.2 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 6.82 (t, *J* = 7.2

Hz, 1H), 6.06 (d, $J = 8.2$ Hz, 1H), 3.18 (d, $J = 10.0$ Hz, 1H), 2.90 (d, $J = 10.0$ Hz, 2H), 2.46 (s, 1H), 1.71 – 1.59 (m, 2H), 1.58 – 1.48 (m, 3H), 1.18 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.1, 139.8, 136.1, 134.1, 132.9, 130.2, 129.7, 128.1, 127.9, 126.9, 126.7, 126.5, 125.1, 123.0, 116.3, 49.4, 48.8, 45.3, 34.8, 29.5, 29.3. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$: 340.1696, found: 340.1694.



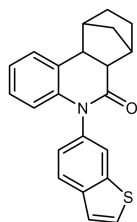
5-(phenanthren-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**21c**)

The representative general procedure mentioned above was followed. The desired product **21c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.54$) as a white solid in 74% yield (57.6 mg). mp: 240–242 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.88 (d, $J = 8.8$ Hz, 1H), 8.74 (d, $J = 8.2$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.79 – 7.70 (m, 3H), 7.67 (t, $J = 7.2$ Hz, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 7.4$ Hz, 1H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.94 (t, $J = 7.4$ Hz, 1H), 6.19 (d, $J = 8.2$ Hz, 1H), 3.31 (d, $J = 10.0$ Hz, 1H), 3.04 (d, $J = 10.4$ Hz, 2H), 2.59 (s, 1H), 1.82 – 1.72 (m, 2H), 1.68 – 1.62 (m, 3H), 1.31 (d, $J = 11.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.2, 139.9, 133.2, 132.3, 130.1, 130.0, 129.7, 128.7, 127.7, 126.9, 126.9, 126.8, 126.6, 125.1, 124.9, 123.0, 122.9, 116.3, 49.4, 48.8, 45.3, 34.8, 29.5, 29.3. **HRMS** (ESI): calcd for $\text{C}_{28}\text{H}_{23}\text{NO}$ $[\text{M}+\text{H}]^+$: 390.1852, found: 390.1852.



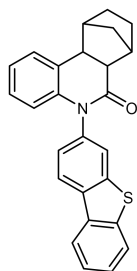
5-(dibenzo[*b,d*]furan-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**22c**)

The representative general procedure mentioned above was followed. The desired product **22c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a white solid in 85% yield (64.5 mg). mp: 216–217 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.08 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.4 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.42 (d, J = 5.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.25 (d, J = 6.4 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 6.99 (td, J = 7.4, 1.2 Hz, 1H), 6.92 (td, J = 8.0, 1.4 Hz, 1H), 6.15 (dd, J = 8.2, 0.8 Hz, 1H), 3.24 (d, J = 10.0 Hz, 1H), 2.98 (d, J = 9.8 Hz, 2H), 2.53 (d, J = 2.4 Hz, 1H), 1.82 – 1.67 (m, 2H), 1.68 – 1.55 (m, 3H), 1.28 (d, J = 10.0 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.2, 156.9, 139.9, 137.4, 129.7, 127.6, 126.9, 125.0, 124.5, 123.7, 123.1, 123.0, 121.8, 120.8, 116.2, 111.9, 49.4, 48.8, 45.3, 34.8, 29.5, 29.3. **HRMS** (ESI): calcd for $\text{C}_{26}\text{H}_{21}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 380.1645, found: 380.1645.



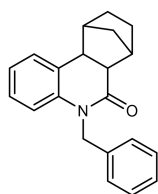
5-(benzo[*b*]thiophen-6-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**23c**)

The representative general procedure mentioned above was followed. The desired product **23c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.54) as a white solid in 76% yield (52.4 mg). mp: 228–232 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.05 (d, J = 8.4 Hz, 1H), 7.69 (s, 1H), 7.55 (d, J = 5.4 Hz, 1H), 7.38 (d, J = 5.4 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H), 6.95 (t, J = 7.8 Hz, 1H), 6.18 (d, J = 8.2 Hz, 1H), 3.28 (d, J = 9.8 Hz, 1H), 3.01 (d, J = 10.4 Hz, 2H), 2.57 (s, 1H), 1.78 (m, 2H), 1.70 – 1.59 (m, 3H), 1.31 (d, J = 11.0 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.3, 141.0, 140.0, 139.6, 135.1, 129.7, 127.8, 126.8, 125.3, 125.0, 124.9, 124.4, 124.1, 123.9, 122.9, 116.3, 49.4, 48.7, 45.3, 34.8, 29.4, 29.2. **HRMS** (ESI): calcd for $\text{C}_{22}\text{H}_{19}\text{NOS}$ $[\text{M}+\text{H}]^+$: 346.1260, found: 346.1261.



5-(dibenzo[*b,d*]thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**24c**)

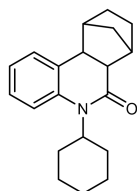
The representative general procedure mentioned above was followed. The desired product **24c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.52) as a white solid in 82% yield (64.8 mg). mp: 230–232 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.74 (s, 1H), 7.64 (t, *J* = 8.8 Hz, 3H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 6.84 (s, 1H), 3.42 (d, *J* = 9.9 Hz, 1H), 3.04 (d, *J* = 9.9 Hz, 1H), 3.01 (s, 1H), 2.64 (s, 1H), 1.83 – 1.74 (m, 2H), 1.70 – 1.64 (m, 3H), 1.31 (d, *J* = 10.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 169.9, 139.9, 138.6, 137.9, 135.1, 134.4, 133.8, 130.3, 128.6, 126.8, 125.5, 124.2, 123.5, 122.9, 121.4, 108.4, 49.9, 48.6, 45.5, 45.3, 34.8, 29.4, 29.3. HRMS (ESI): calcd for C₂₆H₂₁NOS [M+H]⁺ : 396.1417, found: 396.1411.



5-benzyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**25c**)

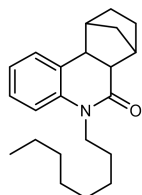
The representative general procedure mentioned above was followed. The desired product **25c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.50) as a white solid in 76% yield (46.1 mg). mp: 233–235 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.22 (td, *J* = 6.8, 2.2 Hz, 2H), 7.19 – 7.08 (m, 4H), 6.98 – 6.84 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.32 (s, 1H), 4.93 (s, 1H), 3.09 (d, *J* = 10.0 Hz, 1H), 2.94 – 2.81 (m, 2H), 2.38 (s, 1H), 1.70 – 1.55 (m, 2H), 1.49 (tt, *J* = 11.4, 5.4 Hz, 2H), 1.43 – 1.35 (m, 1H), 1.20 – 1.10 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 170.1, 137.7, 136.9, 129.8, 128.8, 127.2, 127.0, 126.3,

125.8, 122.9, 115.2, 49.3, 48.3, 45.6, 45.3, 45.0, 34.7, 29.6, 29.1. **HRMS** (ESI): calcd for $C_{21}H_{21}NO$ $[M+H]^+$: 304.1696, found: 304.1692.



5-cyclohexyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**26c**)

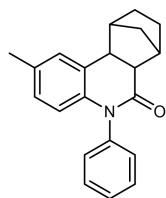
The representative general procedure mentioned above was followed. The desired product **26c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.50) as a white solid in 70% yield (41.3 mg). mp: 210–212 °C; **1H NMR** (400 MHz, $CDCl_3$): δ 7.18 – 7.11 (m, 2H), 7.03 (d, J = 8.6 Hz, 1H), 6.97 (td, J = 7.4, 1.2 Hz, 1H), 4.07 (s, 1H), 2.98 (d, J = 9.8 Hz, 1H), 2.77 (d, J = 4.0 Hz, 1H), 2.71 (d, J = 9.8 Hz, 1H), 2.52 (qd, J = 12.2, 3.4 Hz, 1H), 2.45 – 2.34 (m, 2H), 1.92 – 1.81 (m, 2H), 1.77 – 1.62 (m, 4H), 1.52 – 1.44 (m, 3H), 1.40 – 1.23 (m, 4H), 1.12 (dt, J = 10.0, 1.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 139.2, 130.2, 126.9, 126.8, 122.3, 114.6, 57.3, 49.7, 49.0, 45.5, 45.4, 34.3, 29.4, 29.3, 29.2, 29.0, 26.8, 26.5, 25.5. **HRMS** (ESI): calcd for $C_{20}H_{25}NO$ $[M+H]^+$: 296.2009, found: 296.2012.



5-octyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**27c**)

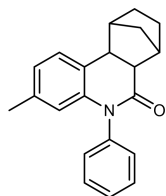
The representative general procedure mentioned above was followed. The desired product **27c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a white solid in 62% yield (40.3 mg). mp: 232–235 °C; **1H NMR** (400 MHz, $CDCl_3$): δ 7.21 (t, J = 7.8 Hz, 2H), 7.03 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 8.2 Hz, 1H), 4.07 – 3.95 (m, 1H), 3.92 – 3.80 (m, 1H), 3.11 (d, J = 10.0 Hz, 1H), 2.87 (d, J = 3.2 Hz, 1H), 2.80 (d, J = 10.0 Hz, 1H), 2.43 (s, 1H), 1.76 – 1.58 (m, 5H), 1.56 (dd, J = 6.4, 3.2 Hz, 1H), 1.40 – 1.27 (m, 11H), 1.16 (d, J = 10.2 Hz, 1H), 0.91 (t, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.5, 137.6, 130.1, 127.2, 125.9, 122.5, 114.1, 49.3, 48.2, 45.1, 44.9, 41.6, 34.4, 31.8, 29.4, 29.4, 29.3,

29.2, 27.0, 26.9, 22.6, 14.1. **HRMS** (ESI): calcd for C₂₂H₃₁NO [M+H]⁺ : 326.2478, found: 326.2478.



2-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**28c**)

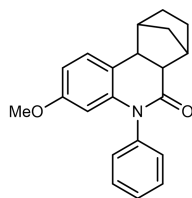
The representative general procedure mentioned above was followed. The desired product **28c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a white solid in 95% yield (57.6 mg). mp: 224–228 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.51 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.04 (s, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 3.17 (d, *J* = 10.0 Hz, 1H), 2.91 (d, *J* = 9.8 Hz, 2H), 2.51 (s, 1H), 2.26 (s, 3H), 1.78 – 1.66 (m, 2H), 1.58 (t, *J* = 8.6 Hz, 3H), 1.24 (d, *J* = 10.6 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 169.8, 138.7, 137.5, 132.4, 130.2, 130.0, 128.2, 127.4, 124.8, 116.0, 49.3, 48.7, 45.2, 45.2, 34.7, 29.4, 29.3, 20.5. **HRMS** (ESI): calcd for C₂₁H₂₁NO [M+H]⁺ : 304.1696, found: 304.1692.



3-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**29c**)

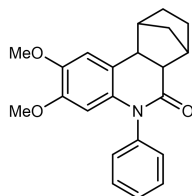
The representative general procedure mentioned above was followed. The desired product **29c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.50) as a white solid in 82% yield (49.7 mg). mp: 224–228 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.52 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 7.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 5.91 (s, 1H), 3.17 (d, *J* = 10.0 Hz, 1H), 2.91 (d, *J* = 8.2 Hz, 2H), 2.47 (s, 1H), 2.10 (s, 3H), 1.74 – 1.65 (m, 2H), 1.57 (t, *J* = 9.6 Hz, 3H), 1.23 (d, *J* = 10.0 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.2, 139.6, 138.6, 136.7, 130.1, 129.6, 128.3, 123.8,

122.1, 116.6, 49.3, 48.7, 45.2, 44.9, 34.7, 29.5, 29.2, 21.3. **HRMS** (ESI): calcd for C₂₁H₂₁NO [M+H]⁺ : 304.1696, found: 304.1694



3-methoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**30c**)

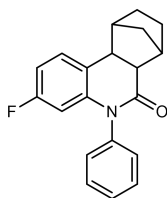
The representative general procedure mentioned above was followed. The desired product **30c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.45) as a white solid in 85% yield (54.2 mg). mp: 234–236 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.55 – 7.46 (m, 2H), 7.46 – 7.37 (m, 1H), 7.20 – 7.09 (m, 3H), 6.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.68 (d, *J* = 2.4 Hz, 1H), 3.59 (s, 3H), 3.15 (d, *J* = 10.0 Hz, 1H), 2.94 – 2.87 (m, 2H), 2.45 (d, *J* = 2.8 Hz, 1H), 1.74 – 1.64 (m, 2H), 1.63 – 1.50 (m, 3H), 1.29 – 1.23 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.2, 158.3, 140.8, 138.5, 130.5, 130.0, 129.4, 129.0, 128.4, 117.4, 107.6, 102.9, 55.1, 49.2, 48.6, 45.1, 44.5, 34.6, 29.5, 29.0. **HRMS** (ESI): calcd for C₂₁H₂₁NO₂ [M+H]⁺ : 320.1645, found: 320.1642.



2,3-dimethoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**31c**)

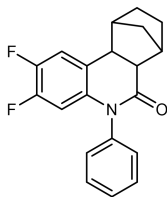
The representative general procedure mentioned above was followed. The desired product **31c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.42) as a white solid in 73% yield (51.0 mg). mp: 221–224 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 6.64 (s, 1H), 5.59 (s, 1H), 3.79 (s, 3H), 3.41 (s, 3H), 3.07 (d, *J* = 10.0 Hz, 1H), 2.84 (d, *J* = 9.8 Hz, 2H), 2.42 (s, 1H), 1.64 (d, *J* = 10.8 Hz, 2H), 1.51 (dd, *J* = 15.4, 8.4 Hz, 3H), 1.18 (d, *J* = 7.0 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 169.7, 147.5, 144.8, 138.6, 133.3, 130.0, 128.3, 116.4, 112.5,

101.13, 56.4, 55.7, 48.9, 48.6, 45.2, 45.1, 34.6, 29.4, 29.1. **HRMS** (ESI): calcd for C₂₂H₂₃NO₃ [M+H]⁺ : 350.1751, found: 350.1750.



3-fluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**32c**)

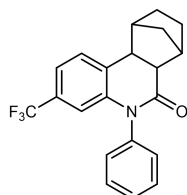
The representative general procedure mentioned above was followed. The desired product **32c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a white solid in 85% yield (52.2 mg). mp: 177–179 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.54 (dd, *J* = 11.4, 4.4 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.17 (dd, *J* = 7.8, 6.6 Hz, 3H), 6.67 (td, *J* = 8.2, 2.4 Hz, 1H), 5.84 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.18 (d, *J* = 10.0 Hz, 1H), 2.92 (d, *J* = 9.8 Hz, 2H), 2.46 (d, *J* = 2.6 Hz, 1H), 1.77 – 1.64 (m, 2H), 1.60 – 1.51 (m, 3H), 1.28 – 1.23 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 169.9, 162.5, 160.1, 141.2 (d, *J* = 9.7 Hz), 130.9 (d, *J* = 9.3 Hz), 130.2, 129.1 (d, *J* = 38.4 Hz), 128.6, 120.6 (d, *J* = 3.2 Hz), 109.6, 109.4, 103.7, 103.4, 49.3, 48.5, 45.2, 44.7, 34.7, 29.4, 29.1; **¹⁹F NMR** (376 MHz, CDCl₃): δ -114.32. **HRMS** (ESI): calcd for C₂₀H₁₈FNO [M+H]⁺ : 308.1445, found: 308.1451.



2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**33c**)

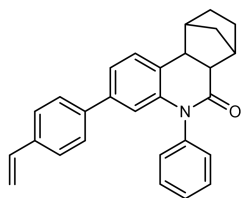
The representative general procedure mentioned above was followed. The desired product **33c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a white solid in 92% yield (59.8 mg). mp: 129–133 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.62 – 7.53 (m, 2H), 7.53 – 7.45 (m, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 7.05 (dd, *J* = 10.2, 8.8 Hz, 1H), 5.97 (dd, *J* = 12.4, 7.2 Hz, 1H), 3.17 (d, *J* = 10.0 Hz, 1H), 2.94 (d, *J* = 9.4 Hz, 2H), 2.49 (s, 1H), 1.82 – 1.67 (m, 2H), 1.63 – 1.54 (m, 3H), 1.35 – 1.27 (m, 1H); **¹³C NMR** (100 MHz,

CDCl₃): δ 169.4, 149.6 (d, J = 13.4 Hz), 147.1 (dd, J = 13.1, 6.0 Hz), 144.7 (d, J = 12.9 Hz), 138.1, 136.4 (d, J = 5.3 Hz), 130.4, 128.8, 121.1 (t, J = 4.3 Hz), 117.8, 117.7, 105.6, 105.4, 49.3, 48.3, 45.2, 44.8, 34.7, 29.3, 28.9; **¹⁹F NMR** (376 MHz, CDCl₃): δ -138.52 (ddd, J = 21.6, 11.9, 8.9 Hz), -143.53 – -150.55 (m). **HRMS** (ESI): calcd for C₂₀H₁₇F₂NO [M+H]⁺ :326.1351, found: 326.1352.



5-phenyl-3-(trifluoromethyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**34c**)

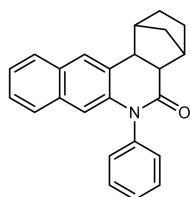
The representative general procedure mentioned above was followed. The desired product **34c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.53) as a white solid in 89% yield (63.5 mg). mp: 178–181 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.51 – 7.45 (m, 2H), 7.43 – 7.36 (m, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.09 (d, J = 7.4 Hz, 2H), 6.27 (s, 1H), 3.17 (d, J = 9.8 Hz, 1H), 2.92 – 2.84 (m, 2H), 2.44 (d, J = 2.6 Hz, 1H), 1.74 – 1.59 (m, 2H), 1.55 – 1.47 (m, 3H), 1.20 (d, J = 15.2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 169.6, 140.4, 137.8, 130.4, 130.3, 129.3 (q, J = 128.6 Hz), 128.8, 125.0, 122.3, 119.4 (q, J = 3.8 Hz), 112.7 (q, J = 4.1 Hz), 49.5, 48.5, 45.2, 45.2; **¹⁹F NMR** (376 MHz, CDCl₃): δ -62.82. **HRMS** (ESI): calcd for C₂₁H₁₈F₃NO [M+H]⁺ : 358.1413, found: 358.1412.



5-phenyl-3-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**35c**)

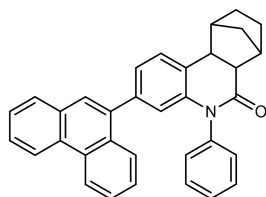
The representative general procedure mentioned above was followed. The desired product **35c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc

(5:1, $R_f = 0.55$) as a white solid in 81% yield (63.3 mg). mp: 230–232 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.58 (t, $J = 7.8$ Hz, 2H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.41 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 1H), 7.32 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 6.73 (dd, $J = 17.6, 10.8$ Hz, 1H), 6.39 (d, $J = 1.2$ Hz, 1H), 5.77 (d, $J = 17.6$ Hz, 1H), 5.28 (d, $J = 10.8$ Hz, 1H), 3.29 (d, $J = 9.8$ Hz, 1H), 3.01 (d, $J = 9.8$ Hz, 2H), 2.59 (s, 1H), 1.84 – 1.75 (m, 2H), 1.66 (dd, $J = 18.8, 8.6$ Hz, 3H), 1.32 (d, $J = 10.6$ Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.1, 140.3, 139.9, 139.5, 138.5, 136.7, 136.2, 130.2, 128.5, 126.9, 126.6, 124.2, 121.5, 114.6, 114.1, 49.4, 48.7, 45.2, 45.0, 34.8, 29.4, 29.3. **HRMS** (ESI): calcd for C₂₈H₂₅NO [M+H]⁺ : 392.2009, found: 392.2006.



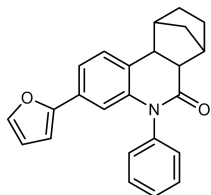
6-phenyl-2,3,4,4a,6,12b-hexahydro-1,4-methanobenzo[b]phenanthridin-5(1H)-one (**36c**)

The representative general procedure mentioned above was followed. The desired product **36c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.52$) as a white solid in 92% yield (62.4 mg). mp: 240–242 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.80 – 7.71 (m, 2H), 7.63 (t, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.49 – 7.45 (m, 1H), 7.39 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 6.50 (s, 1H), 3.47 (d, $J = 9.8$ Hz, 1H), 3.07 – 2.98 (m, 2H), 2.65 (s, 1H), 1.85 – 1.75 (m, 2H), 1.73 – 1.61 (m, 3H), 1.30 (d, $J = 8.4$ Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.1, 138.9, 138.8, 132.4, 130.2, 129.9, 128.8, 128.5, 127.2, 126.9, 126.2, 126.1, 124.8, 112.3, 50.3, 48.6, 45.4, 45.3, 34.7, 29.5, 29.3. **HRMS** (ESI): calcd for C₂₄H₂₁NO [M+H]⁺ : 340.1696, found: 340.1691.



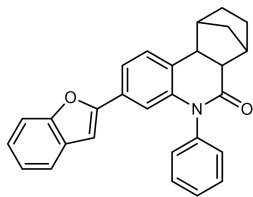
3-(phenanthren-9-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**37c**)

The representative general procedure mentioned above was followed. The desired product **37c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a white solid in 80% yield (74.4 mg). mp: 241–243 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.73 (dd, J = 21.8, 8.2 Hz, 2H), 7.92 – 7.83 (m, 2H), 7.74 – 7.58 (m, 3H), 7.58 – 7.53 (m, 2H), 7.49 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.23 (dd, J = 7.6, 1.4 Hz, 1H), 6.40 (d, J = 1.4 Hz, 1H), 3.37 (d, J = 10.0 Hz, 1H), 3.07 (d, J = 9.8 Hz, 2H), 2.68 (s, 1H), 1.90 – 1.73 (m, 3H), 1.72 – 1.62 (m, 2H), 1.39 (d, J = 10.4 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.1, 139.9, 139.5, 138.5, 138.0, 131.4, 130.8, 130.6, 130.1, 129.9, 129.6, 128.6, 128.4, 127.3, 126.9, 126.7, 126.7, 126.5, 126.4, 124.8, 124.2, 122.9, 122.5, 117.7, 49.4, 48.8, 45.2, 45.2, 34.9, 29.5, 29.3. **HRMS** (ESI): calcd for $\text{C}_{34}\text{H}_{27}\text{NO}$ $[\text{M}+\text{H}]^+$: 466.2165, found: 466.2162.



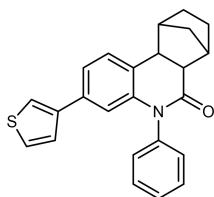
3-(furan-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**38c**)

The representative general procedure mentioned above was followed. The desired product **38c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.50) as a white solid in 81% yield (57.5 mg). mp: 212–215 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.60 (dd, J = 11.6, 4.4 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.36 (t, J = 1.2 Hz, 1H), 7.33 (dd, J = 7.8, 1.6 Hz, 1H), 7.27 (dt, J = 9.8, 5.0 Hz, 3H), 6.46 (d, J = 1.6 Hz, 1H), 6.39 (d, J = 1.2 Hz, 2H), 3.25 (d, J = 9.8 Hz, 1H), 2.99 (d, J = 9.8 Hz, 2H), 2.55 (d, J = 2.6 Hz, 1H), 1.82 – 1.69 (m, 2H), 1.66 – 1.58 (m, 3H), 1.30 (dd, J = 6.4, 4.0 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.1, 153.3, 142.1, 140.2, 138.4, 130.2, 130.1, 129.7, 128.5, 124.2, 118.6, 111.5, 111.4, 105.1, 49.3, 48.7, 45.2, 45.1, 34.7, 29.5, 29.2. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 356.1645, found: 356.1649.



3-(benzofuran-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**39c**)

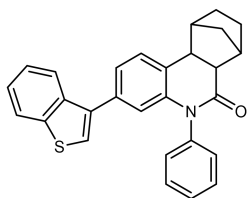
The representative general procedure mentioned above was followed. The desired product **39c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a white solid in 86% yield (69.7 mg). mp: 210–213 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (t, J = 7.6 Hz, 2H), 7.59 – 7.51 (m, 3H), 7.47 – 7.43 (m, 1H), 7.35 (d, J = 8.0 Hz, 1H), 7.32 – 7.24 (m, 3H), 7.21 (td, J = 7.4, 1.2 Hz, 1H), 6.72 (s, 1H), 6.63 (d, J = 1.6 Hz, 1H), 3.28 (d, J = 9.8 Hz, 1H), 3.01 (d, J = 10.0 Hz, 2H), 2.59 (d, J = 2.4 Hz, 1H), 1.86 – 1.72 (m, 2H), 1.68 – 1.62 (m, 3H), 1.32 (d, J = 12.0 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.9, 155.3, 154.7, 140.3, 138.3, 130.3, 129.2, 129.0, 128.6, 125.6, 124.3, 122.9, 120.8, 119.6, 112.4, 111.2, 101.4, 49.4, 48.7, 45.2, 34.8, 29.4, 29.3. **HRMS** (ESI): calcd for $\text{C}_{28}\text{H}_{23}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 406.1802, found: 406.1809.



5-phenyl-3-(thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**40c**)

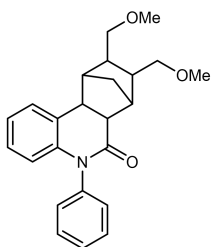
The representative general procedure mentioned above was followed. The desired product **40c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.48) as a white solid in 79% yield (58.6 mg). mp: 218–224 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.59 (t, J = 7.8 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.28 – 7.23 (m, 2H), 7.19 (dd, J = 2.8, 1.2 Hz, 1H), 7.10 (dd, J = 5.0, 1.2 Hz, 1H), 6.38 (d, J = 1.2 Hz, 1H), 3.27 (d, J = 9.8 Hz, 1H), 3.00 (d, J = 9.8 Hz, 2H), 2.57 (s, 1H), 1.84 – 1.71 (m, 2H), 1.70 – 1.59 (m, 3H), 1.31 (d, J = 10.2 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 170.1, 141.7, 140.3, 138.4,

134.6, 130.2, 128.5, 126.2, 126.1, 123.9, 121.1, 120.3, 114.1, 49.3, 48.7, 45.2, 45.0, 34.8, 29.5, 29.2. **HRMS** (ESI): calcd for C₂₄H₂₁NOS [M+H]⁺ : 372.1417, found: 372.1419.



3-(benzo[*b*]thiophen-3-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**41c**)

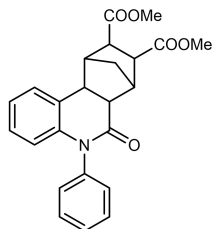
The representative general procedure mentioned above was followed. The desired product **41c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.45) as a white solid in 88% yield (74.1 mg). mp: 239–240 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.88 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.71 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.30 – 7.25 (m, 4H), 6.42 (d, *J* = 1.2 Hz, 1H), 3.33 (d, *J* = 10.0 Hz, 1H), 3.04 (d, *J* = 9.8 Hz, 2H), 2.63 (s, 1H), 1.89 – 1.71 (m, 3H), 1.69 – 1.57 (m, 2H), 1.35 (d, *J* = 10.2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.0, 140.6, 140.2, 138.5, 137.5, 137.3, 134.6, 130.1, 128.5, 124.4, 124.4, 124.3, 123.4, 123.1, 122.9, 122.7, 116.3, 49.3, 48.7, 45.2, 45.2, 34.9, 29.5, 29.3. **HRMS** (ESI): calcd for C₂₈H₂₃NOS [M+H]⁺ : 422.1573, found: 422.1577.



8,9-bis(methoxymethyl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**42c**)

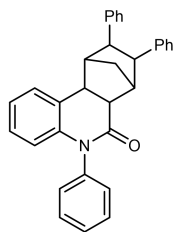
The representative general procedure mentioned above was followed. The desired product **42c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.50) as a white solid in 80% yield (60.3 mg). mp: 238–245 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.52 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.20 – 7.14 (m, 3H), 7.03 – 6.90 (m,

2H), 6.18 – 6.10 (m, 1H), 3.72 (dd, $J = 9.6, 5.4$ Hz, 1H), 3.62 (t, $J = 9.4$ Hz, 1H), 3.51 (d, $J = 6.4$ Hz, 2H), 3.46 (s, 3H), 3.36 (s, 3H), 3.10 (d, $J = 10.0$ Hz, 1H), 2.96 (s, 1H), 2.60 (s, 1H), 2.47 – 2.34 (m, 2H), 1.71 (d, $J = 10.4$ Hz, 1H), 1.41 (d, $J = 10.4$ Hz, 1H), 1.26 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 169.9, 140.1, 138.5, 130.0, 129.6, 128.3, 126.7, 124.9, 123.0, 116.1, 71.1, 70.1, 59.1, 58.9, 52.3, 48.4, 42.4, 40.2, 40.0, 37.0, 35.8. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 378.2064, found: 378.2066.



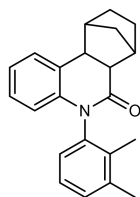
dimethyl 6-oxo-5-phenyl-5,6,6a,7,8,9,10,10a-octahydro-7,10-methanophenanthridine-8,9-dicarboxylate (**43c**)

The representative general procedure mentioned above was followed. The desired product **43c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.52$) as a white solid in 70% yield (56.7 mg). mp: 241–244 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.50 (q, $J = 7.3$ Hz, 3H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.16 (s, 2H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.95 (t, $J = 7.7$ Hz, 1H), 6.13 (d, $J = 8.2$ Hz, 1H), 4.08 (d, $J = 10.1$ Hz, 1H), 3.72 (d, $J = 9.5$ Hz, 6H), 3.37 (dd, $J = 11.8, 4.7$ Hz, 1H), 3.30 (d, $J = 4.1$ Hz, 1H), 3.25 (d, $J = 10.1$ Hz, 1H), 2.96 (dd, $J = 11.8, 3.2$ Hz, 1H), 2.74 (s, 1H), 1.79 (d, $J = 10.6$ Hz, 1H), 1.46 (d, $J = 10.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.8, 172.4, 169.4, 139.5, 138.4, 130.1, 130.0, 129.5, 128.4, 127.0, 124.4, 123.3, 116.2, 52.1, 51.7, 51.1, 48.0, 47.5, 45.6, 44.1, 37.9, 36.5. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 406.1649, found: 406.1641.



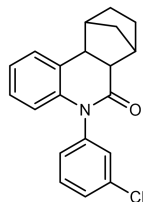
5,8,9-triphenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**44c**)

The representative general procedure mentioned above was followed. The desired product **44c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.53) as a white solid in 91% yield (80.3 mg). mp: 239–241 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.61 (t, J = 7.4 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.31 – 7.27 (m, 2H), 7.11 – 7.00 (m, 7H), 6.96 (q, J = 7.0 Hz, 5H), 6.24 (dt, J = 7.8, 2.8 Hz, 1H), 3.75 (s, 2H), 3.63 (d, J = 10.0 Hz, 1H), 3.40 (s, 1H), 3.33 (d, J = 10.0 Hz, 1H), 2.95 (s, 1H), 2.37 (d, J = 11.0 Hz, 1H), 2.02 (d, J = 11.0 Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.4, 141.8, 141.5, 139.9, 138.5, 130.2, 129.9, 128.7, 128.6, 128.5, 127.6, 127.5, 127.2, 125.5, 125.4, 124.3, 123.2, 116.3, 54.8, 54.3, 54.1, 50.3, 49.5, 46.5, 34.1. **HRMS** (ESI): calcd for $\text{C}_{32}\text{H}_{27}\text{NO}$ $[\text{M}+\text{H}]^+$: 442.2165, found: 442.2166.



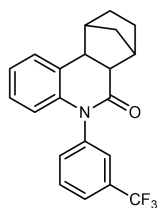
5-(2,3-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**45c**)

The representative general procedure mentioned above was followed. The desired product **45c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a white solid in 92% yield (58.4 mg). mp: 218–223 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.25 – 7.20 (m, 3H), 7.01 – 6.88 (m, 3H), 6.02 (dd, J = 7.8, 1.4 Hz, 1H), 3.28 – 3.18 (m, 1H), 2.99 – 2.91 (m, 2H), 2.52 (t, J = 5.4 Hz, 1H), 2.35 (s, 3H), 1.98 (d, J = 28.8 Hz, 3H), 1.79 – 1.67 (m, 2H), 1.64 – 1.55 (m, 3H), 1.29 – 1.23 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.3, 139.1, 138.6, 137.3, 135.3, 130.1, 129.7, 127.0, 126.2, 124.9, 122.9, 115.7, 49.4, 48.5, 45.2, 45.2, 34.7, 29.3, 29.3, 20.5, 13.9. **HRMS** (ESI): calcd for $\text{C}_{22}\text{H}_{23}\text{NO}$ $[\text{M}+\text{H}]^+$: 318.1852, found: 318.1851.



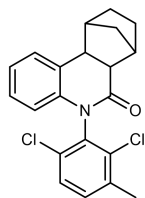
5-(3-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**46c**)

The representative general procedure mentioned above was followed. The desired product **46c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.56) as a white solid in 94% yield (60.7 mg). mp: 211–214 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.55 – 7.50 (m, 1H), 7.48 (dt, J = 8.0, 1.6 Hz, 1H), 7.32 – 7.24 (m, 2H), 7.15 (d, J = 7.4 Hz, 1H), 7.04 (pd, J = 7.4, 1.6 Hz, 2H), 6.17 (dd, J = 7.8, 1.4 Hz, 1H), 3.27 (d, J = 10.0 Hz, 1H), 2.98 (d, J = 9.8 Hz, 2H), 2.57 (d, J = 2.2 Hz, 1H), 1.86 – 1.69 (m, 2H), 1.64 (t, J = 8.8 Hz, 3H), 1.31 (d, J = 10.2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 169.9, 139.8, 139.4, 135.5, 131.0, 129.9, 128.7, 126.9, 125.0, 123.3, 115.9, 49.3, 48.7, 45.2, 34.8, 29.5, 29.2. **HRMS** (ESI): calcd for C₂₀H₁₈ClNO [M+H]⁺ : 324.1150, found: 324.1154.



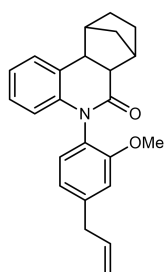
5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**47c**)

The representative general procedure mentioned above was followed. The desired product **47c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.54) as a white solid in 75% yield (53.5 mg). mp: 188–190 °C; **¹H NMR** (400 MHz, CDCl₃): δ 7.72 – 7.64 (m, 2H), 7.47 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.32 – 7.22 (m, 1H), 7.07 – 6.92 (m, 2H), 6.04 (d, J = 8.0 Hz, 1H), 3.23 (d, J = 9.9 Hz, 1H), 3.09 – 2.87 (m, 2H), 2.53 (d, J = 3.6 Hz, 1H), 1.83 – 1.65 (m, 2H), 1.61 – 1.55 (m, 3H), 1.27 (d, J = 10.4 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.1, 139.2 (d, J = 12.6 Hz), 130.7, 129.9, 127.0, 125.3 (d, J = 3.7 Hz), 125.1, 123.6 (q, J = 272.6 Hz), 115.7, 49.3, 48.7, 45.2, 34.8, 29.4, 29.2; **¹⁹F NMR** (376 MHz, CDCl₃): δ -62.48. **HRMS** (ESI): calcd for C₂₁H₁₈F₃NO [M+H]⁺ : 358.1413, found: 358.1417.



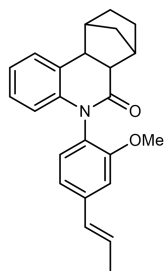
5-(2,6-dichloro-3-methylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**48c**)

The representative general procedure mentioned above was followed. The desired product **48c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a white solid in 83% yield (61.6 mg). mp: 210–213 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.38 (dd, J = 8.4, 1.8 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.00 (dtd, J = 16.8, 7.4, 1.2 Hz, 2H), 5.96 (dd, J = 5.4, 3.8 Hz, 1H), 3.26 (d, J = 10.0 Hz, 1H), 2.97 (d, J = 10.2 Hz, 2H), 2.53 (s, 1H), 2.42 (d, J = 2.8 Hz, 3H), 1.81 – 1.66 (m, 3H), 1.60 – 1.55 (m, 2H), 1.25 (s, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 168.6, 136.9, 135.3, 133.7, 132.2, 131.4, 130.1, 128.1, 127.3, 125.0, 123.4, 114.1, 49.2, 48.5, 45.2, 45.0, 34.9, 29.5, 29.3, 20.5. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{NO}$ $[\text{M}+\text{H}]^+$: 372.0916, found: 372.0914.



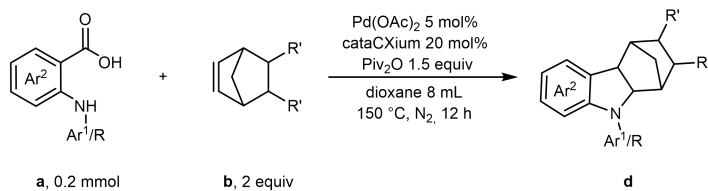
5-(4-allyl-2-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**49c**)

The representative general procedure mentioned above was followed. The desired product **49c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.50) as a white solid in 91% yield (65.3 mg). mp: 221–224 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.21 (d, J = 7.1 Hz, 1H), 7.13 – 6.88 (m, 6H), 6.43 (d, J = 15.7 Hz, 1H), 6.35 – 6.22 (m, 1H), 6.17 (ddd, J = 8.0, 4.0, 1.8 Hz, 1H), 3.73 (s, 3H), 3.19 (dd, J = 10.1, 5.6 Hz, 1H), 2.91 (q, J = 5.7 Hz, 2H), 2.48 (dd, J = 11.4, 3.6 Hz, 1H), 1.91 (dd, J = 6.5, 1.6 Hz, 2H), 1.73 (dddd, J = 27.0, 13.0, 7.9, 3.1 Hz, 3H), 1.56 (dt, J = 7.6, 4.2 Hz, 2H), 1.23 – 1.15 (m, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 169.9, 155.3, 139.8, 139.4, 130.7, 130.2, 129.6, 126.9, 125.2, 119.0, 115.4, 109.7, 55.7, 49.5, 48.8, 45.3, 45.2, 34.3, 29.3, 18.6. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 360.1958, found: 360.1955.

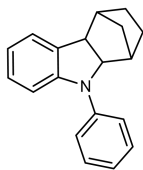


(*E*)-5-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**50c**)

The representative general procedure mentioned above was followed. The desired product **50c** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.51) as a white solid in 89% yield (63.9 mg). mp: 231–233 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.25 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.09 (d, *J* = 1.8 Hz, 1H), 7.07 – 7.03 (m, 2H), 6.99 (td, *J* = 7.3, 1.8 Hz, 2H), 6.48 (dd, *J* = 15.7, 1.8 Hz, 1H), 6.38 – 6.27 (m, 1H), 6.22 (ddd, *J* = 7.8, 3.7, 1.9 Hz, 1H), 3.77 (d, *J* = 1.6 Hz, 3H), 3.24 (dd, *J* = 10.0, 5.4 Hz, 1H), 3.02 – 2.91 (m, 2H), 2.57 – 2.48 (m, 1H), 1.95 (dd, *J* = 6.5, 1.6 Hz, 3H), 1.85 – 1.74 (m, 2H), 1.67 – 1.55 (m, 3H), 1.27 – 1.19 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 169.9, 155.3, 139.9, 139.3, 130.7, 130.2, 129.7, 126.9, 125.1, 119.0, 115.4, 109.7, 55.7, 49.6, 48.7, 45.3, 45.2, 34.3, 29.4, 27.2, 18.6. HRMS (ESI): calcd for C₂₄H₂₅NO₂ [M+H]⁺ : 360.1958, found: 360.1955.

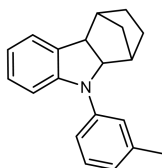


An oven dried 25 mL Schlenk tube was charged with 2-aminobenzoic acid **a** (0.2 mmol, 1 equiv), NBE **b** (0.4 mmol, 2 equiv) Pd(OAc)₂ (5 mol%), and cataCXium A (20 mol%). Subsequently, Piv₂O (0.3 mmol, 1.5 equiv), and 1,4-dioxane (8 mL) were added under N₂. The reaction mixture was heated at 150 °C for 12 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give a desired product compound **1d–44d**.



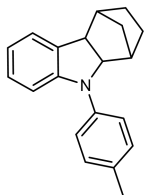
9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**1d**)

The representative general procedure mentioned above was followed. The desired product **1d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R*_f = 0.60) as a colorless oil in 96% yield (49.1 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, *J* = 4.2 Hz, 4H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 2H), 6.78 (t, *J* = 7.2 Hz, 1H), 4.33 (d, *J* = 8.2 Hz, 1H), 3.39 (d, *J* = 8.2 Hz, 1H), 2.58 (d, *J* = 3.0 Hz, 1H), 2.44 (s, 1H), 1.69 – 1.57 (m, 3H), 1.52 – 1.44 (m, 1H), 1.35 (d, *J* = 7.0 Hz, 1H), 1.19 (d, *J* = 10.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 148.8, 143.7, 133.7, 129.2, 127.2, 125.0, 121.5, 119.4, 118.5, 108.2, 71.1, 50.5, 43.5, 41.2, 32.4, 28.6, 25.3. HRMS (ESI): calcd for C₁₉H₁₉N [M+H]⁺ : 262.1590, found: 262.1596.



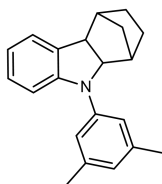
9-(*m*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**2d**)

The representative general procedure mentioned above was followed. The desired product **2d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.52$) as a colorless oil in 90% yield (49.5 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.22 – 7.17 (m, 1H), 7.13 (s, 1H), 7.11 – 7.06 (m, 2H), 7.00 (ddd, $J = 8.0, 7.4, 0.8$ Hz, 1H), 6.92 (d, $J = 7.8$ Hz, 1H), 6.78 (d, $J = 7.4$ Hz, 1H), 6.67 (td, $J = 7.3, 1.0$ Hz, 1H), 4.22 (d, $J = 8.4$ Hz, 1H), 3.28 (d, $J = 8.4$ Hz, 1H), 2.47 (d, $J = 3.4$ Hz, 1H), 2.34 (s, 3H), 1.58 – 1.48 (m, 3H), 1.41 – 1.34 (m, 1H), 1.26 (dd, $J = 4.8, 2.6$ Hz, 1H), 1.13 – 1.06 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 148.9, 143.7, 138.9, 133.6, 128.9, 127.2, 124.9, 122.4, 120.2, 118.3, 116.8, 108.2, 71.1, 50.4, 43.5, 41.1, 32.4, 28.6, 25.3, 21.7. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{N}$ $[\text{M}+\text{H}]^+$: 276.1747, found: 276.1747.



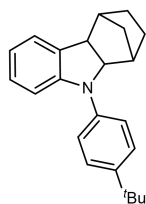
9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3d**)

The representative general procedure mentioned above was followed. The desired product **3d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.55$) as a colorless oil in 92% yield (50.6 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.26 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.91 (d, $J = 7.8$ Hz, 1H), 6.72 (t, $J = 7.4$ Hz, 1H), 4.27 (d, $J = 8.4$ Hz, 1H), 3.35 (d, $J = 8.4$ Hz, 1H), 2.51 (d, $J = 3.4$ Hz, 1H), 2.38 (s, 3H), 1.64 – 1.57 (m, 3H), 1.44 (dd, $J = 12.4, 6.4$ Hz, 1H), 1.32 – 1.28 (m, 2H), 1.20 – 1.13 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 149.3, 141.1, 133.4, 131.3, 129.7, 127.2, 124.9, 120.0, 118.0, 107.7, 71.3, 50.5, 43.5, 41.1, 32.4, 29.8, 28.6, 25.3, 20.8. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{N}$ $[\text{M}+\text{H}]^+$: 276.1747, found: 276.1742.



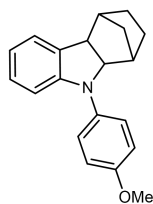
9-(3,5-dimethylphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**4d**)

The representative general procedure mentioned above was followed. The desired product **4d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.53$) as a colorless oil in 91% yield (52.6 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.06 (d, $J = 7.2$ Hz, 1H), 7.02–6.97 (m, 1H), 6.94 – 6.88 (m, 3H), 6.66 (td, $J = 7.4, 0.8$ Hz, 1H), 6.63 (s, 1H), 4.21 (d, $J = 8.4$ Hz, 1H), 3.27 (d, $J = 8.4$ Hz, 1H), 2.51 – 2.44 (m, 1H), 2.33 (d, $J = 3.4$ Hz, 1H), 2.30 (s, 6H), 1.58 – 1.49 (m, 3H), 1.43 – 1.33 (m, 1H), 1.26 (dd, $J = 4.8, 2.6$ Hz, 1H), 1.13 – 1.06 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 149.1, 143.6, 138.7, 133.5, 127.2, 124.9, 123.6, 118.2, 117.5, 108.2, 71.2, 50.4, 43.5, 41.2, 32.4, 28.6, 25.3, 21.6. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{23}\text{N}$ $[\text{M}+\text{H}]^+$: 290.1903, found: 290.1902.



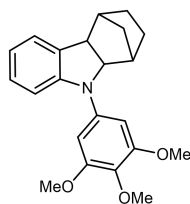
9-(4-(*tert*-butyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**5d**)

The representative general procedure mentioned above was followed. The desired product **5d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.57$) as a colorless oil in 93% yield (59.0 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.40 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 1H), 6.96 (d, $J = 7.8$ Hz, 1H), 6.71 (t, $J = 7.4$ Hz, 1H), 4.28 (d, $J = 8.2$ Hz, 1H), 3.35 (d, $J = 8.2$ Hz, 1H), 2.54 (d, $J = 3.2$ Hz, 1H), 2.39 (s, 1H), 1.63 – 1.55 (m, 3H), 1.37 (s, 9H), 1.32 – 1.29 (m, 2H), 1.15 (d, $J = 10.4$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 149.1, 144.3, 141.0, 133.4, 127.2, 125.9, 124.8, 119.2, 118.1, 107.9, 71.2, 50.4, 43.4, 41.2, 34.3, 32.4, 31.5, 28.6, 25.3. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{27}\text{N}$ $[\text{M}+\text{H}]^+$: 318.2216, found: 318.2216.



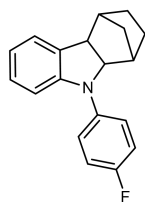
9-(4-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**6d**)

The representative general procedure mentioned above was followed. The desired product **6d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.51$) as a colorless oil in 88% yield (51.2 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.32 – 7.28 (m, 2H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.04 (t, $J = 7.8$ Hz, 1H), 6.98 – 6.93 (m, 2H), 6.74 (d, $J = 7.8$ Hz, 1H), 6.69 (t, $J = 7.4$ Hz, 1H), 4.22 (d, $J = 8.0$ Hz, 1H), 3.87 (s, 3H), 3.36 (d, $J = 8.2$ Hz, 1H), 2.46 (d, $J = 3.8$ Hz, 1H), 2.41 (s, 1H), 1.68 – 1.57 (m, 3H), 1.50 – 1.41 (m, 1H), 1.30 – 1.26 (m, 1H), 1.22 – 1.16 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 155.2, 150.3, 137.0, 132.9, 127.3, 124.8, 122.8, 117.6, 114.6, 106.9, 71.9, 55.6, 50.6, 43.5, 41.2, 32.4, 28.7, 25.2. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$: 292.1696, found: 292.1694.



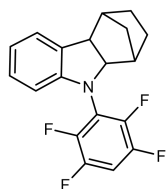
10-(3,4,5-trimethoxyphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**7d**)

The representative general procedure mentioned above was followed. The desired product **7d** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (10:1, $R_f = 0.50$) as a colorless oil in 88% yield (61.8 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.08 (d, $J = 7.2$ Hz, 1H), 7.01 (ddd, $J = 8.0, 7.4, 0.8$ Hz, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 6.67 (td, $J = 7.4, 0.8$ Hz, 1H), 6.53 (s, 2H), 4.17 (d, $J = 8.2$ Hz, 1H), 3.84 (s, 9H), 3.30 (d, $J = 8.4$ Hz, 1H), 2.48 (d, $J = 3.2$ Hz, 1H), 2.35 (s, 1H), 1.62 – 1.49 (m, 3H), 1.46 – 1.35 (m, 1H), 1.26 (s, 1H), 1.17 – 1.11 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 153.6, 149.3, 139.9, 133.4, 127.3, 124.9, 118.2, 107.8, 98.3, 71.8, 61.0, 56.2, 50.5, 43.4, 41.4, 32.5, 28.5, 25.2. **HRMS** (ESI): calcd for $\text{C}_{22}\text{H}_{25}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 352.1907, found: 352.1905.



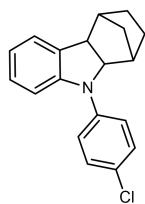
9-(4-fluorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**8d**)

The representative general procedure mentioned above was followed. The desired product **8d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.57$) as a colorless oil in 90% yield (50.2 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.33 – 7.27 (m, 2H), 7.13 (d, $J = 7.2$ Hz, 1H), 7.09 – 7.02 (m, 3H), 6.82 (d, $J = 8.0$ Hz, 1H), 6.72 (t, $J = 7.2$ Hz, 1H), 4.22 (d, $J = 8.4$ Hz, 1H), 3.36 (d, $J = 8.4$ Hz, 1H), 2.46 (d, $J = 3.4$ Hz, 1H), 2.40 (s, 1H), 1.65 – 1.55 (m, 3H), 1.44 (t, $J = 8.4$ Hz, 1H), 1.31 (s, 1H), 1.17 (d, $J = 10.4$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 158.1 (d, $J = 241.2$ Hz), 149.3, 139.9, 133.2, 127.3, 124.9, 121.8 (d, $J = 7.7$ Hz), 118.3, 115.8 (d, $J = 22.3$ Hz), 107.4, 71.7, 50.5, 43.4, 41.2, 32.3, 28.6, 25.2; **^{19}F NMR** (376 MHz, CDCl_3): δ -121.00. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{FN}$ $[\text{M}+\text{H}]^+$: 280.1496, found: 280.1496.



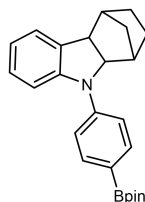
9-(2,3,5,6-tetrafluorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**9d**)

The representative general procedure mentioned above was followed. The desired product **9d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.55$) as a colorless oil in 90% yield (60.1 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.10 (d, $J = 7.4$ Hz, 1H), 7.04 – 6.97 (m, 1H), 6.90 (tt, $J = 9.8, 7.2$ Hz, 1H), 6.73 (td, $J = 7.4, 0.8$ Hz, 1H), 6.26 – 6.19 (m, 1H), 4.36 (d, $J = 8.2$ Hz, 1H), 3.35 (d, $J = 8.2$ Hz, 1H), 2.38 (s, 1H), 2.13 (d, $J = 3.8$ Hz, 1H), 1.65 (d, $J = 10.4$ Hz, 1H), 1.60 – 1.48 (m, 2H), 1.43 – 1.34 (m, 1H), 1.19 (ddd, $J = 11.1, 4.4, 1.7$ Hz, 1H), 1.15 – 1.10 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 148.7, 147.8 (t, $J = 12.2$ Hz), 145.3 (d, $J = 15.9$ Hz), 131.7, 127.4, 124.7, 121.7 (t, $J = 13.2$ Hz), 119.1, 107.1 (t, $J = 8.2$ Hz), 101.6 (t, $J = 23.1$ Hz), 70.7, 51.2, 43.5, 40.9, 32.2, 28.4, 24.9; **^{19}F NMR** (376 MHz, CDCl_3): δ -139.32, -140.97, -145.62. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{15}\text{F}_4\text{N}$ $[\text{M}+\text{H}]^+$: 334.1213, found: 334.1214.



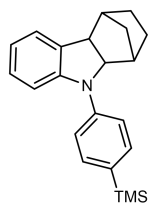
9-(4-chlorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**10d**)

The representative general procedure mentioned above was followed. The desired product **10d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.61$) as a colorless oil in 45% yield (26.6 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.29 – 7.20 (m, 4H), 7.10 (d, $J = 7.2$ Hz, 1H), 7.02 (t, $J = 7.8$ Hz, 1H), 6.90 (d, $J = 8.0$ Hz, 1H), 6.71 (t, $J = 7.4$ Hz, 1H), 4.19 (d, $J = 8.2$ Hz, 1H), 3.30 (d, $J = 8.2$ Hz, 1H), 2.46 (d, $J = 3.3$ Hz, 1H), 2.35 (s, 1H), 1.63 – 1.57 (m, 2H), 1.47 (dt, $J = 10.3, 2.0$ Hz, 1H), 1.42 – 1.37 (m, 1H), 1.27 – 1.24 (m, 1H), 1.11 (dt, $J = 10.2, 1.6$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 148.3, 142.3, 133.6, 129.1, 127.2, 125.9, 125.0, 120.4, 118.9, 108.2, 71.1, 50.4, 43.4, 40.9, 32.3, 28.5, 25.2. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{ClN}$ $[\text{M}+\text{H}]^+$: 296.1201, found: 296.1203.



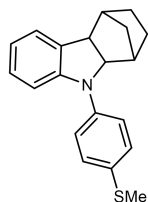
10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**11d**)

The representative general procedure mentioned above was followed. The desired product **11d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.5$) as a colorless oil in 82% yield (63.5 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.81 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.19 – 7.05 (m, 3H), 6.78 (td, $J = 7.0, 1.2$ Hz, 1H), 4.33 (d, $J = 8.2$ Hz, 1H), 3.35 (d, $J = 8.2$ Hz, 1H), 2.58 (s, 1H), 2.40 (s, 1H), 1.63 (dt, $J = 10.8, 5.2$ Hz, 2H), 1.56 – 1.46 (m, 2H), 1.39 (s, 12H), 1.36 – 1.29 (m, 1H), 1.14 (d, $J = 10.2$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 147.8, 146.2, 135.9, 134.0, 127.2, 125.0, 119.2, 117.4, 109.1, 83.5, 70.6, 50.3, 43.4, 40.8, 32.3, 29.7, 28.5, 25.2, 24.8. **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{30}\text{BNO}_2$ $[\text{M}+\text{H}]^+$: 388.2442, found: 388.2444.



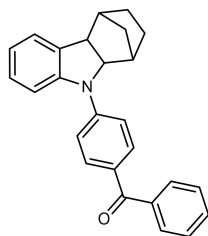
9-(4-(trimethylsilyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**12d**)

The representative general procedure mentioned above was followed. The desired product **12d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.6$) as a colorless oil in 92% yield (61.3 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.55 (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.21 – 7.14 (m, 1H), 7.13 – 7.07 (m, 2H), 6.84 – 6.73 (m, 1H), 4.34 (d, $J = 8.2$ Hz, 1H), 3.38 (d, $J = 8.2$ Hz, 1H), 2.60 (s, 1H), 2.43 (s, 1H), 1.72 – 1.62 (m, 2H), 1.61 – 1.55 (m, 1H), 1.51 – 1.44 (m, 1H), 1.34 (dd, $J = 12.8, 3.8$ Hz, 1H), 1.18 (d, $J = 10.4$ Hz, 1H), 0.35 (s, 9H); **^{13}C NMR** (100 MHz, CDCl_3): δ 148.6, 144.4, 134.5, 134.1, 132.0, 127.4, 125.2, 119.6, 118.9, 118.3, 108.8, 70.9, 50.6, 43.6, 41.3, 32.7, 28.8, 25.5, 1.6. **HRMS** (ESI): calcd for $\text{C}_{22}\text{H}_{27}\text{NSi}$ $[\text{M}+\text{H}]^+$: 334.1986, found: 334.1986.



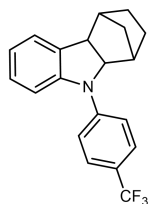
9-(4-(methylthio)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**13d**)

The representative general procedure mentioned above was followed. The desired product **13d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.55$) as a colorless oil in 78% yield (47.9 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.23 – 7.13 (m, 4H), 7.01 (d, $J = 7.2$ Hz, 1H), 6.94 (t, $J = 7.8$ Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 6.62 (t, $J = 7.2$ Hz, 1H), 4.14 (d, $J = 8.2$ Hz, 1H), 3.22 (d, $J = 8.2$ Hz, 1H), 2.40 (s, 3H), 2.27 (s, 1H), 1.59 – 1.52 (m, 1H), 1.50 (tt, $J = 8.8, 4.4$ Hz, 1H), 1.42 (d, $J = 10.3$ Hz, 1H), 1.36 – 1.28 (m, 1H), 1.18 (dd, $J = 5.0, 2.2$ Hz, 1H), 1.03 (dt, $J = 10.6, 1.4$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 148.5, 141.7, 133.6, 129.6, 129.2, 127.3, 124.9, 120.0, 118.6, 108.2, 71.2, 50.4, 43.4, 41.0, 32.3, 28.5, 25.2, 17.6. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{NS}$ $[\text{M}+\text{H}]^+$: 308.1467, found: 308.1466.



(4-(1,2,3,4,4a,9a-hexahydro-9H-1,4-methanocarbazol-9-yl)phenyl)(phenyl)methanone (**14d**)

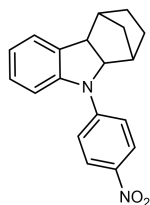
The representative general procedure mentioned above was followed. The desired product **14d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.49$) as a colorless oil in 81% yield (59.1 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.90 (d, $J = 8.8$ Hz, 2H), 7.86 – 7.80 (m, 2H), 7.61 (t, $J = 7.2$ Hz, 1H), 7.52 (t, $J = 7.4$ Hz, 2H), 7.40 (d, $J = 8.8$ Hz, 2H), 7.27 (d, $J = 8.0$ Hz, 1H), 7.20 (d, $J = 7.2$ Hz, 1H), 7.15 (t, $J = 7.6$ Hz, 1H), 6.87 (t, $J = 7.2$ Hz, 1H), 4.33 (d, $J = 8.0$ Hz, 1H), 3.40 (d, $J = 8.0$ Hz, 1H), 2.66 (s, 1H), 2.43 (s, 1H), 1.66 (dq, $J = 12.4, 7.6, 6.2$ Hz, 2H), 1.47 (d, $J = 7.6$ Hz, 2H), 1.39 (d, $J = 5.8$ Hz, 1H), 1.17 (d, $J = 10.4$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 195.1, 147.7, 146.8, 138.7, 134.6, 132.2, 131.6, 129.7, 128.9, 128.2, 127.3, 125.3, 120.5, 116.3, 110.1, 70.6, 50.3, 43.3, 40.9, 32.4, 28.3, 25.3. **HRMS** (ESI): calcd for $\text{C}_{26}\text{H}_{23}\text{NO}$ $[\text{M}+\text{H}]^+$: 366.1852, found: 366.1851.



9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**15d**)

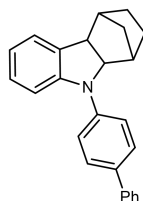
The representative general procedure mentioned above was followed. The desired product **15d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.59$) as a colorless oil in 92% yield (60.6 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.53 (d, $J = 8.8$ Hz, 2H), 7.35 (d, $J = 8.6$ Hz, 2H), 7.16 – 7.11 (m, 1H), 7.11 – 7.04 (m, 2H), 6.81 – 6.75 (m, 1H), 4.24 (d, $J = 8.2$ Hz, 1H), 3.32 (d, $J = 8.2$ Hz, 1H), 2.53 (d, $J = 3.2$ Hz, 1H), 2.37 (s, 1H), 1.65 – 1.54 (m, 2H), 1.46 – 1.38 (m, 2H), 1.28 (dd, $J = 13.6, 2.4$ Hz, 1H), 1.14 – 1.07 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 147.2, 146.6, 134.2, 127.2, 126.3 (q, $J = 3.8$ Hz), 125.2, 124.6 (q, $J = 278.0$), 121.9 (q, $J = 32.7$ Hz), 120.0, 117.4, 109.3, 70.8, 50.3, 43.3, 40.8, 32.3, 28.4, 25.3; **^{19}F**

NMR (376 MHz, CDCl₃): δ -61.51. **HRMS** (ESI): calcd for C₂₀H₁₈F₃N [M+H]⁺ : 330.1464, found: 330.1464.



9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**16d**)

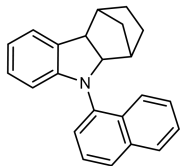
The representative general procedure mentioned above was followed. The desired product **16d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R*_f = 0.61) as a colorless oil in 88% yield (53.9 mg). **¹H NMR** (400 MHz, CDCl₃): δ 8.26 – 8.18 (m, 2H), 7.39 – 7.31 (m, 2H), 7.31 – 7.24 (m, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.13 (m, 1H), 6.94 (td, *J* = 7.4, 0.8 Hz, 1H), 4.28 (d, *J* = 8.0 Hz, 1H), 3.42 (d, *J* = 8.0 Hz, 1H), 2.63 (s, 1H), 2.44 (s, 1H), 1.67 (dq, *J* = 12.0, 7.4, 5.8 Hz, 2H), 1.48 (td, *J* = 9.0, 7.8, 2.2 Hz, 1H), 1.38 (t, *J* = 9.4 Hz, 2H), 1.17 (d, *J* = 10.6 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.2, 145.9, 139.7, 134.9, 127.4, 125.7, 125.5, 121.7, 115.8, 110.8, 70.8, 50.3, 43.2, 40.9, 32.4, 28.2, 25.4. **HRMS** (ESI): calcd for C₁₉H₁₈N₂O₂ [M+H]⁺ : 307.1441, found: 307.1441.



9-([1,1'-biphenyl]-4-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**17d**)

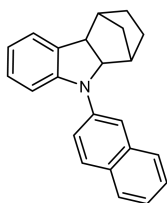
The representative general procedure mentioned above was followed. The desired product **17d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R*_f = 0.62) as a colorless oil in 89% yield (60.0 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.60 – 7.56 (m, 2H), 7.56 – 7.53 (m, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 – 7.26 (m, 1H), 7.12 – 7.08 (m, 1H), 7.07 – 7.01 (m, 2H), 6.71 (ddd, *J* = 7.4, 6.0, 2.4 Hz, 1H), 4.27 (d, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 8.2 Hz, 1H), 2.54 (d, *J* = 2.8 Hz, 1H), 2.36 (s, 1H), 1.64 – 1.55 (m, 2H), 1.52 (dd, *J* = 7.0, 5.0 Hz, 1H), 1.43 – 1.37 (m, 1H), 1.30 – 1.24 (m, 1H), 1.14 – 1.09 (m, 1H); **¹³C NMR** (100

MHz, CDCl₃): δ 148.5, 142.9, 140.9, 133.9, 133.8, 128.8, 127.7, 127.3, 126.7, 126.6, 125.0, 119.2, 118.7, 108.5, 71.0, 50.4, 43.5, 41.1, 32.4, 28.6, 25.3. **HRMS** (ESI): calcd for C₂₅H₂₃N [M+H]⁺ : 338.1903, found: 338.1903.



9-(naphthalen-1-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**18d**)

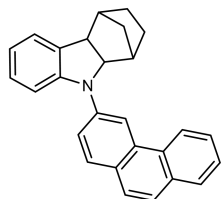
The representative general procedure mentioned above was followed. The desired product **18d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R_f* = 0.60) as a colorless oil in 81% yield (50.4 mg). **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (dd, *J* = 28.6, 9.1 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.54 (dt, *J* = 22.6, 6.9 Hz, 4H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.93 (dt, *J* = 23.6, 7.7 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.03 (dd, *J* = 137.4, 7.9 Hz, 1H), 4.41 (dd, *J* = 44.5, 8.3 Hz, 1H), 3.56 (d, *J* = 8.3 Hz, 1H), 2.53 (d, *J* = 24.9 Hz, 1H), 2.36 – 2.10 (m, 1H), 1.97 (dd, *J* = 73.6, 10.1 Hz, 1H), 1.66 (tt, *J* = 15.8, 11.1, 8.1 Hz, 1H), 1.49 (qd, *J* = 15.3, 13.2, 5.1 Hz, 2H), 1.36 (d, *J* = 10.0 Hz, 1H), 1.24 (t, *J* = 10.8 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 152.9, 141.4, 135.5, 132.4, 131.8, 128.7, 127.5, 126.5, 126.2, 124.7, 123.3, 117.1, 106.8, 74.6, 51.4, 43.7, 41.9, 33.3, 29.1, 25.0. **HRMS** (ESI): calcd for C₂₃H₂₁N [M+H]⁺ : 312.1747, found: 312.1747.



9-(naphthalen-2-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**19d**)

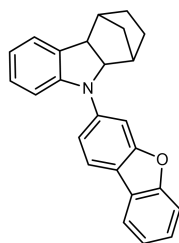
The representative general procedure mentioned above was followed. The desired product **19d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R_f* = 0.62) as a colorless oil in 96% yield (59.7 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.75 (t, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 2.2 Hz, 1H), 7.51 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.41 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.31 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.12 – 7.10 (m, 1H), 7.07 –

7.02 (m, 2H), 6.72 (ddd, $J = 7.3, 5.5, 3.0$ Hz, 1H), 4.36 (d, $J = 8.2$ Hz, 1H), 3.32 (d, $J = 8.2$ Hz, 1H), 2.50 (d, $J = 3.4$ Hz, 1H), 2.36 (s, 1H), 1.60 – 1.51 (m, 3H), 1.45 – 1.35 (m, 1H), 1.32 – 1.22 (m, 1H), 1.10 (dt, $J = 10.3, 1.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.8, 141.3, 134.4, 133.8, 129.4, 128.8, 127.6, 127.3, 126.8, 126.4, 125.1, 123.9, 120.6, 118.8, 115.1, 108.2, 71.2, 50.5, 43.5, 41.2, 32.4, 28.6, 25.3. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{21}\text{N}$ $[\text{M}+\text{H}]^+$: 312.1747, found: 312.1745.



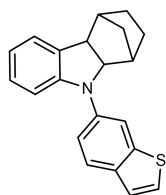
9-(phenanthren-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**20d**)

The representative general procedure mentioned above was followed. The desired product **20d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.65$) as a colorless oil in 75% yield (54.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 8.48 (dd, $J = 8.6, 4.8$ Hz, 2H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.61 (dd, $J = 12.0, 5.6$ Hz, 2H), 7.53 (dt, $J = 14.8, 6.0$ Hz, 3H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.05 (dd, $J = 7.2, 4.8$ Hz, 2H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.66 (t, $J = 7.2$ Hz, 1H), 4.28 (d, $J = 8.2$ Hz, 1H), 3.25 (d, $J = 8.2$ Hz, 1H), 2.47 (s, 1H), 2.29 (s, 1H), 1.51 – 1.45 (m, 3H), 1.32 (t, $J = 8.2$ Hz, 1H), 1.24 – 1.16 (m, 1H), 1.03 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 142.2, 133.9, 133.2, 131.2, 130.5, 128.6, 127.5, 127.3, 126.7, 126.6, 125.6, 125.1, 124.9, 123.7, 122.1, 119.6, 118.9, 116.2, 108.4, 71.1, 50.5, 43.5, 41.2, 32.5, 28.6, 25.4. **HRMS** (ESI): calcd for $\text{C}_{27}\text{H}_{23}\text{N}$ $[\text{M}+\text{H}]^+$: 362.1903, found: 362.1905.



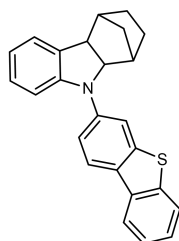
9-(dibenzo[*b,d*]furan-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**21d**)

The representative general procedure mentioned above was followed. The desired product **21d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.51$) as a colorless oil in 89% yield (62.5 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.86 – 7.78 (m, 2H), 7.50 (t, $J = 5.4$ Hz, 2H), 7.35 (td, $J = 7.8, 1.4$ Hz, 1H), 7.32 – 7.26 (m, 2H), 7.08 (dt, $J = 14.6, 7.6$ Hz, 3H), 6.74 (ddd, $J = 8.2, 6.8, 1.8$ Hz, 1H), 4.30 (d, $J = 8.2$ Hz, 1H), 3.32 (d, $J = 8.2$ Hz, 1H), 2.53 (d, $J = 2.8$ Hz, 1H), 2.36 (s, 1H), 1.61 – 1.50 (m, 3H), 1.43 – 1.36 (m, 1H), 1.26 (dd, $J = 12.4, 3.8$ Hz, 1H), 1.14 – 1.07 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 157.4, 156.4, 148.4, 143.5, 133.9, 127.3, 125.9, 125.1, 124.6, 122.8, 120.9, 119.8, 119.1, 117.9, 114.9, 111.4, 108.5, 101.9, 71.5, 50.5, 43.5, 41.1, 32.4, 28.5, 25.3. **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$: 352.1696, found: 352.1694.



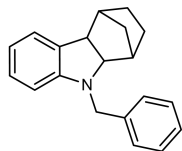
9-(benzo[*b*]thiophen-6-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**22d**)

The representative general procedure mentioned above was followed. The desired product **22d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.50$) as a colorless oil in 77% yield (48.8 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.70 (d, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 2.0$ Hz, 1H), 7.33 (d, $J = 5.4$ Hz, 1H), 7.25 (dd, $J = 8.7, 2.2$ Hz, 1H), 7.17 – 7.13 (m, 1H), 7.01 (d, $J = 7.2$ Hz, 1H), 6.93 (t, $J = 7.6$ Hz, 1H), 6.81 (d, $J = 7.8$ Hz, 1H), 6.60 (t, $J = 7.4$ Hz, 1H), 4.20 (d, $J = 8.2$ Hz, 1H), 3.23 (d, $J = 8.2$ Hz, 1H), 2.38 (d, $J = 3.6$ Hz, 1H), 2.28 (s, 1H), 1.50 – 1.44 (m, 3H), 1.30 (dd, $J = 12.6, 6.4$ Hz, 1H), 1.19 – 1.11 (m, 2H), 1.03 (d, $J = 10.2$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 149.5, 140.8, 140.7, 133.5, 133.4, 127.3, 124.9, 123.6, 122.9, 118.8, 118.3, 114.7, 107.6, 71.8, 50.6, 43.5, 41.1, 32.4, 28.6, 25.3. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{19}\text{NS}$ $[\text{M}+\text{H}]^+$: 318.1311, found: 318.1312.



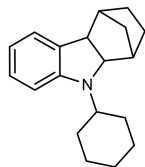
9-(dibenzo[*b,d*]thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**23d**)

The representative general procedure mentioned above was followed. The desired product **23d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R_f* = 0.54) as a colorless oil in 80% yield (58.7 mg). **¹H NMR** (400 MHz, CDCl₃): δ 8.02 – 7.96 (m, 2H), 7.75 – 7.71 (m, 1H), 7.67 (dd, *J* = 8.6, 3.0 Hz, 1H), 7.33 (ddt, *J* = 7.4, 6.0, 3.4 Hz, 3H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.62 (td, *J* = 7.4, 0.8 Hz, 1H), 4.24 (d, *J* = 8.2 Hz, 1H), 3.25 (d, *J* = 8.2 Hz, 1H), 2.40 (d, *J* = 2.8 Hz, 1H), 2.29 (s, 1H), 1.48 (ddd, *J* = 11.4, 10.2, 7.2 Hz, 3H), 1.31 (t, *J* = 8.4 Hz, 1H), 1.16 (dd, *J* = 12.8, 3.8 Hz, 1H), 1.04 (dd, *J* = 10.2, 1.4 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.4, 140.9, 140.4, 136.6, 135.4, 133.5, 132.7, 127.4, 126.8, 125.1, 124.3, 123.4, 123.0, 121.7, 120.7, 118.5, 112.9, 107.6, 71.8, 50.6, 43.5, 41.2, 32.4, 28.6, 25.3. **HRMS** (ESI): calcd for C₂₅H₂₁NS [M+H]⁺ : 368.1467, found: 368.1466.



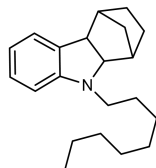
9-benzyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**24d**)

The representative general procedure mentioned above was followed. The desired product **24d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R_f* = 0.59) as a colorless oil in 77% yield (42.3 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.38 – 7.31 (m, 4H), 7.29 (dd, *J* = 5.8, 2.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.58 (td, *J* = 7.4, 0.8 Hz, 1H), 6.24 (d, *J* = 7.8 Hz, 1H), 4.48 – 4.36 (m, 2H), 3.69 (d, *J* = 8.4 Hz, 1H), 3.32 (d, *J* = 8.4 Hz, 1H), 2.36 (d, *J* = 3.0 Hz, 1H), 2.29 (d, *J* = 4.4 Hz, 1H), 1.64 (dd, *J* = 10.0, 1.6 Hz, 1H), 1.56 (ddt, *J* = 14.8, 12.0, 4.0 Hz, 2H), 1.40 – 1.35 (m, 1H), 1.21 – 1.13 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 153.5, 139.5, 131.6, 128.5, 127.7, 127.1, 126.8, 124.3, 116.1, 104.6, 71.9, 51.2, 51.0, 43.3, 41.2, 32.7, 28.8, 25.0. **HRMS** (ESI): calcd for C₂₀H₂₁N [M+H]⁺ : 276.1747, found: 276.1747.



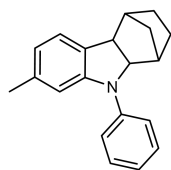
9-cyclohexyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**25d**)

The representative general procedure mentioned above was followed. The desired product **25d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.54$) as a colorless oil in 61% yield (32.6 mg). **^1H NMR** (400 MHz, CDCl_3) δ 7.18 – 7.11 (m, 2H), 7.03 (d, $J = 8.6$ Hz, 1H), 6.97 (td, $J = 7.4, 1.2$ Hz, 1H), 4.12 – 4.05 (m, 1H), 2.98 (d, $J = 9.8$ Hz, 1H), 2.77 (d, $J = 4.0$ Hz, 1H), 2.71 (d, $J = 9.8$ Hz, 1H), 2.52 (qd, $J = 12.2, 3.4$ Hz, 1H), 2.46 – 2.33 (m, 2H), 1.92 – 1.81 (m, 2H), 1.80 – 1.62 (m, 4H), 1.54 – 1.43 (m, 3H), 1.40 – 1.23 (m, 4H), 1.12 (dt, $J = 10.0, 1.4$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 132.5, 127.4, 124.2, 115.9, 106.0, 67.1, 55.9, 51.2, 44.1, 43.3, 32.4, 29.7, 29.4, 28.8, 28.1, 27.2, 26.0, 25.4, 14.2. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{25}\text{N}$ $[\text{M}+\text{H}]^+$: 268.2060, found: 268.2062.



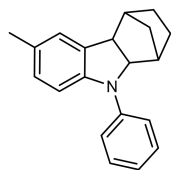
9-octyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**26d**)

The representative general procedure mentioned above was followed. The desired product **26d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.58$) as a colorless oil in 55% yield (32.7 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.04 – 6.94 (m, 2H), 6.51 (t, $J = 6.8$ Hz, 1H), 6.25 (d, $J = 7.4$ Hz, 1H), 3.60 (d, $J = 8.4$ Hz, 1H), 3.24 (d, $J = 8.2$ Hz, 1H), 3.14 (t, $J = 7.4$ Hz, 2H), 2.33 (d, $J = 21.0$ Hz, 2H), 1.63 – 1.55 (m, 6H), 1.38 – 1.30 (m, 10H), 1.23 – 1.12 (m, 2H), 0.92 (t, $J = 6.8$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 153.5, 131.8, 127.6, 124.2, 115.5, 104.4, 71.4, 50.9, 47.2, 43.3, 41.6, 32.5, 31.9, 29.5, 29.3, 28.8, 27.8, 27.3, 25.2, 22.7, 14.1. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{31}\text{N}$ $[\text{M}+\text{H}]^+$: 298.2529, found: 298.2526.



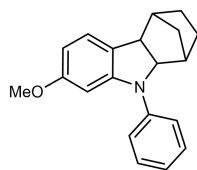
7-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**27d**)

The representative general procedure mentioned above was followed. The desired product **27d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.59$) as a colorless oil in 97% yield (53.4 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.28 – 7.19 (m, 4H), 6.88 (td, $J = 6.2, 3.2$ Hz, 2H), 6.70 (s, 1H), 6.47 – 6.40 (m, 1H), 4.16 (d, $J = 8.2$ Hz, 1H), 3.17 (d, $J = 8.2$ Hz, 1H), 2.38 (d, $J = 3.4$ Hz, 1H), 2.24 (s, 1H), 2.18 (s, 3H), 1.50 – 1.41 (m, 3H), 1.34 – 1.24 (m, 1H), 1.17 – 1.08 (m, 1H), 1.01 (dt, $J = 10.2, 1.4$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 148.9, 143.7, 137.0, 130.8, 129.1, 124.6, 121.4, 119.6, 119.2, 108.9, 71.4, 50.1, 43.4, 41.0, 32.3, 28.5, 25.3, 21.8. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{N}$ $[\text{M}+\text{H}]^+$: 276.1747, found: 276.1746.



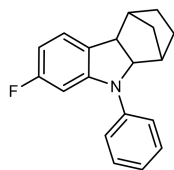
6-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**28d**)

The representative general procedure mentioned above was followed. The desired product **28d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.55$) as a colorless oil in 92% yield (50.6 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.37 – 7.33 (m, 4H), 7.01 – 6.94 (m, 3H), 6.89 (d, $J = 8.0$ Hz, 1H), 4.26 (d, $J = 8.2$ Hz, 1H), 3.33 (d, $J = 8.2$ Hz, 1H), 2.56 (s, 1H), 2.41 – 2.36 (m, 1H), 2.32 (s, 3H), 1.62 (td, $J = 10.8, 10.0, 4.2$ Hz, 2H), 1.55 (d, $J = 10.4$ Hz, 1H), 1.48 – 1.40 (m, 1H), 1.32 (d, $J = 5.4$ Hz, 1H), 1.16 (d, $J = 10.2$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 146.3, 144.2, 133.9, 129.1, 127.9, 127.4, 125.8, 120.8, 118.6, 108.4, 71.3, 50.4, 43.4, 41.2, 32.4, 28.6, 25.3, 20.7. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{N}$ $[\text{M}+\text{H}]^+$: 276.1747, found: 276.1747.



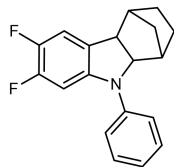
7-methoxy-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**29d**)

The representative general procedure mentioned above was followed. The desired product **29d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.49$) as a colorless oil in 88% yield (51.2 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.25 – 7.20 (m, 4H), 6.89 (ddd, $J = 5.8, 4.0, 2.0$ Hz, 2H), 6.45 (d, $J = 2.4$ Hz, 1H), 6.15 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.19 (d, $J = 8.0$ Hz, 1H), 3.66 (s, 3H), 3.15 (d, $J = 8.2$ Hz, 1H), 2.37 (d, $J = 3.2$ Hz, 1H), 2.22 (s, 1H), 1.51 – 1.42 (m, 3H), 1.34 – 1.24 (m, 1H), 1.22 – 1.11 (m, 1H), 1.07 – 0.96 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 159.7, 150.1, 143.4, 129.2, 126.2, 124.9, 121.7, 119.8, 102.6, 95.4, 71.9, 55.4, 49.7, 43.5, 40.9, 32.3, 28.4, 25.2. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$: 292.1696, found: 292.1696.



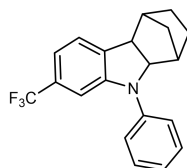
7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**30d**)

The representative general procedure mentioned above was followed. The desired product **30d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.55$) as a colorless oil in 92% yield (51.3 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.36 – 7.30 (m, 2H), 7.27 (dt, $J = 8.4, 1.6$ Hz, 2H), 7.00 (tt, $J = 7.4, 1.2$ Hz, 1H), 6.95 (ddd, $J = 7.8, 5.8, 0.8$ Hz, 1H), 6.58 (dd, $J = 11.0, 2.2$ Hz, 1H), 6.33 (ddd, $J = 9.2, 8.0, 2.4$ Hz, 1H), 4.30 (d, $J = 8.2$ Hz, 1H), 3.23 (d, $J = 8.2$ Hz, 1H), 2.43 (d, $J = 3.4$ Hz, 1H), 2.30 (s, 1H), 1.59 – 1.49 (m, 3H), 1.41 – 1.33 (m, 1H), 1.27 – 1.18 (m, 1H), 1.13 – 1.08 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 163.0 (d, $J = 240.5$ Hz), 150.4 (d, $J = 12.0$ Hz), 142.8, 129.3, 128.9 (d, $J = 2.1$ Hz), 125.0 (d, $J = 10.8$ Hz), 122.3, 120.1, 104.2, 103.9, 95.8, 95.5, 72.0, 49.7, 43.5, 40.9, 32.2, 28.4, 25.1; **^{19}F NMR** (376 MHz, CDCl_3): δ -115.38. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{FN}$ $[\text{M}+\text{H}]^+$: 280.1402, found: 280.1403.



6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**31d**)

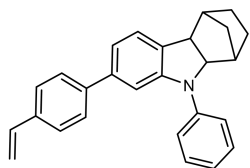
The representative general procedure mentioned above was followed. The desired product **31d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.57$) as a colorless oil in 90% yield (53.4 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.32 (tt, $J = 3.8$, 1.8 Hz, 2H), 7.23 (dd, $J = 8.6$, 1.2 Hz, 2H), 6.99 (dd, $J = 10.4$, 4.2 Hz, 1H), 6.87 – 6.81 (m, 1H), 6.66 (dd, $J = 12.0$, 6.6 Hz, 1H), 4.25 (d, $J = 8.2$ Hz, 1H), 3.23 (d, $J = 8.2$ Hz, 1H), 2.45 (d, $J = 3.6$ Hz, 1H), 2.29 (s, 1H), 1.59 – 1.46 (m, 3H), 1.40 – 1.32 (m, 1H), 1.27 – 1.18 (m, 1H), 1.16 – 1.10 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 149.4 (d, $J = 242.1$), 145.2 (d, $J = 10.4$ Hz), 144.4 (d, $J = 13.6$ Hz), 143.1, 142.1 (d, $J = 13.8$ Hz), 129.3, 128.6 (dd, $J = 5.3$, 2.8 Hz), 122.2, 119.5, 113.4 (d, $J = 1.4$ Hz), 113.3 (d, $J = 1.3$ Hz), 97.2, 96.9, 71.9, 49.9, 43.3, 41.2, 32.3, 28.3, 25.1; **^{19}F NMR** (376 MHz, CDCl_3): δ -139.43 – -139.69 (m), -150.75 – -151.33 (m). **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{17}\text{F}_2\text{N}$ $[\text{M}+\text{H}]^+$: 298.1402, found: 298.1404.



9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**32d**)

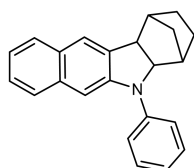
The representative general procedure mentioned above was followed. The desired product **32d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.59$) as a colorless oil in 95% yield (62.5 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.31 – 7.25 (m, 2H), 7.23 – 7.19 (m, 1H), 7.04 (d, $J = 7.6$ Hz, 1H), 7.00 – 6.94 (m, 2H), 6.83 (dd, $J = 7.6$, 0.6 Hz, 1H), 4.24 (d, $J = 8.4$ Hz, 1H), 3.22 (d, $J = 8.2$ Hz, 1H), 2.37 (d, $J = 3.6$ Hz, 1H), 2.28 (s, 1H), 1.52 – 1.41 (m, 3H), 1.35 – 1.29 (m, 1H), 1.17 (dd, $J = 4.8$, 2.8 Hz, 1H), 1.09 – 1.04 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 149.6, 142.6, 137.4, 129.7 (q, $J = 31.1$ Hz), 129.5, 124.8, 124.6 (d, $J = 270.7$ Hz), 122.8, 120.4, 115.2 (q, $J = 4.0$ Hz), 103.6 (q, $J = 3.8$ Hz), 71.5, 50.1, 43.5, 41.0, 32.4,

28.5, 25.1; **¹⁹F NMR** (376 MHz, CDCl₃): δ -62.61 (d, *J* = 29.0 Hz). **HRMS** (ESI): calcd for C₂₀H₁₈F₃N [M+H]⁺ : 330.1464, found: 330.1464.



9-phenyl-7-(4-vinylphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**33d**)

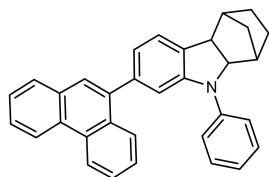
The representative general procedure mentioned above was followed. The desired product **33d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R_f* = 0.63) as a colorless oil in 88% yield (58.1 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.23 – 7.19 (m, 2H), 7.06 (td, *J* = 6.4, 1.2 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.80 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.83 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H), 4.37 (d, *J* = 8.2 Hz, 1H), 3.39 (d, *J* = 8.2 Hz, 1H), 2.56 (s, 1H), 2.45 (s, 1H), 1.65 (dd, *J* = 12.6, 6.6 Hz, 3H), 1.51 – 1.44 (m, 1H), 1.33 (s, 1H), 1.20 (d, *J* = 10.2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 149.5, 143.5, 141.4, 140.3, 136.5, 136.3, 133.1, 129.3, 127.3, 126.5, 125.1, 121.8, 119.9, 117.6, 113.7, 106.6, 71.6, 50.2, 43.5, 41.1, 32.5, 28.6, 25.3. **HRMS** (ESI): calcd for C₂₇H₂₅N [M+H]⁺ : 364.2060, found: 364.2062.



5-phenyl-2,3,4,4a,5,11b-hexahydro-1H-1,4-methanobenzo[*b*]carbazole (**34d**)

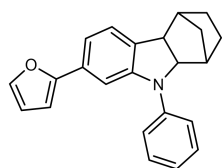
The representative general procedure mentioned above was followed. The desired product **34d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R_f* = 0.59) as a colorless oil in 95% yield (59.1 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.55 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 10.8, 4.0 Hz, 1H), 7.19 (s, 1H), 7.15 – 7.09 (m, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.45 (d, *J* = 7.8 Hz, 1H), 2.53 (d, *J* = 8.6 Hz, 2H), 1.66 (td, *J* = 11.0, 3.8 Hz, 2H), 1.57 (d, *J* = 9.2 Hz, 1H), 1.51 (t, *J* = 8.4 Hz, 1H), 1.34 (s, 2H), 1.18 (dd, *J* = 10.2, 1.2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 147.3, 143.1, 136.9, 134.6, 129.3, 128.8, 127.2, 126.1,

125.7, 123.4, 122.3, 122.2, 120.5, 100.7, 70.9, 49.6, 44.1, 40.7, 32.4, 28.6, 25.2. **HRMS** (ESI): calcd for C₂₃H₂₁N [M+H]⁺ : 312.1747, found: 312.1746.



7-(phenanthren-9-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**35d**)

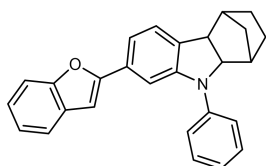
The representative general procedure mentioned above was followed. The desired product **35d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R*_f = 0.58) as a colorless oil in 92% yield (80.4 mg). **¹H NMR** (400 MHz, CDCl₃): δ 8.82 (d, *J* = 8.2 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.4 Hz, 1H), 7.77 (s, 1H), 7.74 – 7.69 (m, 2H), 7.68 – 7.64 (m, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.23 – 7.19 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.95 (dd, *J* = 7.4, 1.2 Hz, 1H), 4.43 (d, *J* = 8.2 Hz, 1H), 3.49 (d, *J* = 8.2 Hz, 1H), 2.64 (d, *J* = 3.2 Hz, 1H), 2.53 (s, 1H), 1.78 – 1.65 (m, 3H), 1.59 – 1.47 (m, 1H), 1.41 – 1.33 (m, 1H), 1.32 – 1.22 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 148.7, 143.5, 139.9, 139.5, 132.9, 131.7, 131.4, 130.6, 129.9, 129.2, 128.6, 127.2, 127.2, 126.8, 126.4, 126.4, 124.6, 122.8, 122.5, 121.6, 120.7, 119.5, 109.9, 71.5, 50.3, 43.5, 41.1, 32.6, 28.6, 25.3. **HRMS** (ESI): calcd for C₃₃H₂₇N [M+H]⁺ : 438.2216, found: 438.2218.



7-(furan-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**36d**)

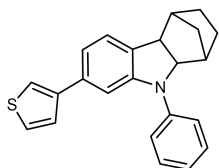
The representative general procedure mentioned above was followed. The desired product **36d** was isolated by column chromatography over silica gel and eluted with petroleum ether (*R*_f = 0.51) as a colorless oil in 95% yield (62.2 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.46 (d, *J* = 1.6 Hz, 1H), 7.41 (d, *J* = 4.2 Hz, 4H), 7.31 – 7.29 (m, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (ddd, *J* = 13.6, 7.0, 2.8 Hz, 2H), 6.59 (d, *J* = 3.2 Hz, 1H), 6.48 (dd, *J* = 3.2, 1.8 Hz, 1H), 4.32 (d, *J* = 8.2

Hz, 1H), 3.35 (d, $J = 8.2$ Hz, 1H), 2.54 (d, $J = 3.4$ Hz, 1H), 2.41 (s, 1H), 1.66 – 1.57 (m, 3H), 1.44 (dd, $J = 12.2, 6.4$ Hz, 1H), 1.33 – 1.29 (m, 1H), 1.20 – 1.15 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.7, 149.2, 143.6, 141.6, 133.2, 130.2, 129.3, 125.0, 121.9, 119.9, 114.7, 111.5, 104.5, 103.5, 71.7, 50.2, 43.4, 41.1, 32.4, 28.5, 25.3. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{21}\text{NO}$ $[\text{M}+\text{H}]^+$: 328.1696, found: 328.1692.



7-(benzofuran-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**37d**)

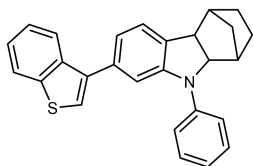
The representative general procedure mentioned above was followed. The desired product **37d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.50$) as a colorless oil in 91% yield (68.6 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, $J = 7.4$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.44 (d, $J = 4.6$ Hz, 5H), 7.34 – 7.23 (m, 3H), 7.20 (d, $J = 7.6$ Hz, 1H), 7.14 – 7.07 (m, 1H), 6.96 (s, 1H), 4.35 (d, $J = 8.2$ Hz, 1H), 3.38 (d, $J = 8.2$ Hz, 1H), 2.55 (s, 1H), 2.44 (s, 1H), 1.72 – 1.56 (m, 3H), 1.46 (t, $J = 8.4$ Hz, 1H), 1.37 – 1.27 (m, 3H), 1.20 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.8, 154.7, 149.4, 143.4, 134.6, 129.7, 129.4, 125.1, 123.9, 122.8, 122.2, 120.7, 120.2, 115.9, 111.1, 104.2, 100.8, 71.7, 50.3, 43.5, 41.1, 32.5, 28.5, 25.3. **HRMS** (ESI): calcd for $\text{C}_{27}\text{H}_{23}\text{NO}$ $[\text{M}+\text{H}]^+$: 378.1852, found: 378.1850.



9-phenyl-7-(thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**38d**)

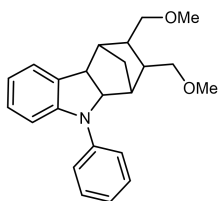
The representative general procedure mentioned above was followed. The desired product **38d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.52$) as a colorless oil in 90% yield (61.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, $J = 2.8$ Hz, 5H), 7.38 (d, $J = 2.2$ Hz, 2H), 7.23 (d, $J = 1.2$ Hz, 1H), 7.17 (d, $J = 7.4$ Hz, 1H), 7.07 (ddd, $J = 8.4, 5.8, 2.4$ Hz, 1H), 7.00 (dd, $J = 7.4, 1.4$ Hz, 1H), 4.35 (d, $J = 8.2$ Hz, 1H), 3.38 (d, $J = 8.2$ Hz, 1H), 2.56 (d, $J = 3.4$ Hz, 1H), 2.44 (s, 1H), 1.68 – 1.57 (m, 3H), 1.47 (t, $J = 8.4$ Hz, 1H),

1.37 – 1.30 (m, 1H), 1.20 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.4, 143.6, 143.1, 135.3, 132.9, 129.3, 126.7, 125.8, 125.1, 121.9, 119.9, 119.9, 117.3, 106.3, 71.7, 50.2, 43.4, 41.1, 32.5, 28.6, 25.3. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{21}\text{NS}$ $[\text{M}+\text{H}]^+$: 344.1467, found: 344.1466.



7-(benzo[*b*]thiophen-3-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**39d**)

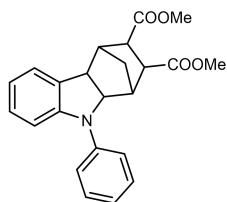
The representative general procedure mentioned above was followed. The desired product **39d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.55$) as a colorless oil in 88% yield (69.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 8.05 – 8.00 (m, 1H), 7.99 – 7.93 (m, 1H), 7.45 – 7.40 (m, 5H), 7.40 – 7.35 (m, 2H), 7.25 (d, $J = 7.4$ Hz, 1H), 7.22 (d, $J = 1.2$ Hz, 1H), 7.04 (tt, $J = 7.2, 1.4$ Hz, 1H), 6.99 (dd, $J = 7.4, 1.4$ Hz, 1H), 4.40 (d, $J = 8.2$ Hz, 1H), 3.43 (d, $J = 8.2$ Hz, 1H), 2.59 (d, $J = 3.4$ Hz, 1H), 2.49 (s, 1H), 1.74 – 1.63 (m, 3H), 1.50 (dd, $J = 11.6, 5.2$ Hz, 1H), 1.35 (s, 1H), 1.24 (d, $J = 10.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.3, 143.5, 140.7, 138.9, 138.2, 135.2, 133.3, 129.3, 125.0, 124.3, 123.3, 122.9, 121.8, 119.8, 119.2, 108.2, 71.5, 50.3, 43.6, 41.1, 32.5, 28.6, 25.3. **HRMS** (ESI): calcd for $\text{C}_{27}\text{H}_{23}\text{NS}$ $[\text{M}+\text{H}]^+$: 394.1624, found: 394.1622.



2,3-bis(methoxymethyl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**40d**)

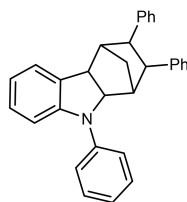
The representative general procedure mentioned above was followed. The desired product **40d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.50$) as a colorless oil in 91% yield (63.5 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.36 (dd, $J = 8.6, 1.2$ Hz, 2H), 7.32 – 7.27 (m, 2H), 7.09 – 7.02 (m, 3H), 6.93 (t, $J = 7.2$ Hz, 1H), 6.74 – 6.69 (m, 1H), 4.45 (d, $J = 8.2$ Hz, 1H), 3.61 – 3.54 (m, 2H), 3.52 (d, $J = 7.2$ Hz, 2H), 3.47 (t, $J = 9.2$ Hz,

1H), 3.41 (s, 3H), 3.38 (s, 3H), 2.69 (s, 1H), 2.43 (s, 1H), 2.41 – 2.32 (m, 2H), 1.58 (d, $J = 10.4$ Hz, 1H), 1.27 – 1.19 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.6, 143.9, 133.8, 129.1, 127.1, 124.8, 120.8, 118.9, 117.8, 109.3, 70.4, 69.9, 65.2, 58.9, 58.8, 46.6, 44.9, 43.5, 40.0, 38.9, 33.5. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{27}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 350.2115, found: 350.2116.



dimethyl 9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole-2,3-dicarboxylate (**41d**)

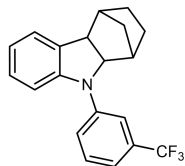
The representative general procedure mentioned above was followed. The desired product **41d** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (10:1, $R_f = 0.50$) as a colorless oil in 85% yield (64.1 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.45 (d, $J = 7.8$ Hz, 2H), 7.37 (t, $J = 7.8$ Hz, 2H), 7.14 (d, $J = 7.2$ Hz, 1H), 7.08 (d, $J = 4.0$ Hz, 2H), 6.99 (t, $J = 7.2$ Hz, 1H), 6.75 (dq, $J = 8.0, 4.2$ Hz, 1H), 4.94 (d, $J = 8.2$ Hz, 1H), 3.89 (d, $J = 8.2$ Hz, 1H), 3.76 (d, $J = 4.6$ Hz, 6H), 3.20 (dd, $J = 11.8, 4.2$ Hz, 1H), 3.08 (dd, $J = 11.8, 4.4$ Hz, 1H), 2.87 (d, $J = 3.8$ Hz, 1H), 2.73 (d, $J = 3.6$ Hz, 1H), 1.76 (d, $J = 10.6$ Hz, 1H), 1.28 (d, $J = 10.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.6, 172.3, 148.7, 143.3, 132.7, 129.2, 127.4, 124.8, 121.3, 118.8, 118.7, 108.7, 65.3, 51.8, 51.6, 46.9, 46.2, 45.1, 44.7, 44.7. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 378.1700, found: 378.1702.



2,3,9-triphenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**42d**)

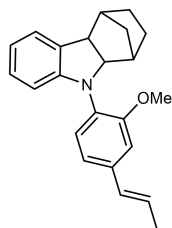
The representative general procedure mentioned above was followed. The desired product **42d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.57$) as a colorless oil in 94% yield (77.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.16 (m, 4H), 7.05 (d, $J = 7.2$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.95 – 6.86 (m, 6H), 6.85 – 6.82 (m, 2H),

6.81 – 6.77 (m, 4H), 6.65 (td, $J = 7.2, 0.8$ Hz, 1H), 4.48 (d, $J = 8.2$ Hz, 1H), 3.57 (d, $J = 8.2$ Hz, 1H), 3.42 (d, $J = 9.6$ Hz, 1H), 3.29 (d, $J = 9.6$ Hz, 1H), 2.77 (s, 1H), 2.69 (s, 1H), 2.11 (d, $J = 11.0$ Hz, 1H), 1.83 (d, $J = 11.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 148.0, 142.3, 140.7, 140.6, 131.4, 128.2, 127.7, 127.6, 126.5, 126.5, 126.4, 124.4, 124.3, 124.1, 120.7, 118.5, 117.7, 107.2, 70.9, 52.4, 50.6, 49.4, 47.6, 46.1, 30.6. HRMS (ESI): calcd for $\text{C}_{31}\text{H}_{27}\text{N}$ $[\text{M}+\text{H}]^+$: 414.2216, found: 414.2216.



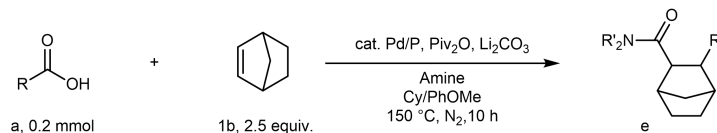
9-(3-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**43d**)

The representative general procedure mentioned above was followed. The desired product **43d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.56$) as a colorless oil in 90% yield (59.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.61 (s, 1H), 7.47 (dt, $J = 15.6, 8.4$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 7.2$ Hz, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 7.05 (d, $J = 7.8$ Hz, 1H), 6.87 – 6.75 (m, 1H), 4.29 (d, $J = 8.2$ Hz, 1H), 3.39 (d, $J = 8.2$ Hz, 1H), 2.55 (d, $J = 2.8$ Hz, 1H), 2.43 (s, 1H), 1.71 – 1.58 (m, 2H), 1.56 – 1.45 (m, 2H), 1.35 – 1.31 (m, 1H), 1.18 (dt, $J = 10.2, 1.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 147.7, 144.2, 133.9, 131.5 (d, $J = 32.0$ Hz), 129.6, 127.3, 125.2, 124.2 (d, $J = 270.9$ Hz), 121.6, 119.6, 117.4 (q, $J = 3.6$ Hz), 114.9 (q, $J = 3.6$ Hz), 108.6, 71.0, 50.4, 43.4, 41.0, 32.4, 28.4, 25.3; ^{19}F NMR (376 MHz, CDCl_3): δ -62.48 (d, $J = 17.1$ Hz). HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{18}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$: 330.1464, found: 330.1464.

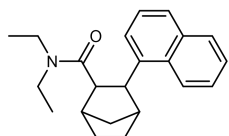


(*E*)-9-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**44d**)

The representative general procedure mentioned above was followed. The desired product **44d** was isolated by column chromatography over silica gel and eluted with petroleum ether ($R_f = 0.55$) as a colorless oil in 91% yield (60.2 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.34 (d, $J = 8.0$ Hz, 1H), 7.09 (d, $J = 7.2$ Hz, 1H), 7.00–6.93 (m, 3H), 6.64 (td, $J = 7.2, 0.8$ Hz, 1H), 6.48–6.37 (m, 2H), 6.25 (dq, $J = 15.6, 6.6$ Hz, 1H), 4.39 (d, $J = 8.2$ Hz, 1H), 3.88 (s, 3H), 3.32 (d, $J = 8.2$ Hz, 1H), 2.37 (d, $J = 3.2$ Hz, 1H), 2.15 (d, $J = 4.4$ Hz, 1H), 1.95 (dd, $J = 6.6, 1.4$ Hz, 3H), 1.67 (d, $J = 10.0$ Hz, 1H), 1.61–1.48 (m, 2H), 1.45–1.36 (m, 1H), 1.25–1.15 (m, 1H), 1.11 (dt, $J = 10.0, 1.2$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 154.9, 151.2, 135.6, 132.4, 130.8, 130.3, 127.1, 125.9, 125.1, 124.5, 118.6, 117.1, 109.8, 106.9, 70.5, 55.6, 50.8, 43.5, 40.6, 32.3, 28.7, 25.2, 18.5. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{25}\text{NO}$ $[\text{M}+\text{H}]^+$: 332.2009, found: 332.2009.

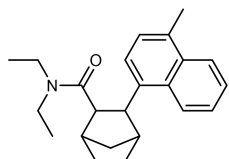


An oven dried 25 mL Schlenk tube was charged with carboxylic acid **a** (0.2 mmol, 1 equiv), NBE **b** (0.5 mmol, 2.5 equiv), Et₃N (0.6 mmol, 3 equiv), Pd₂(dba)₃ (5 mol%), Xphos (10 mol%) (4-F-Ph)₃P (1 mol%) and Li₂CO₃ (1 equiv). Subsequently, Piv₂O (0.3 mmol, 1.5 equiv), and cyclohexane/anisole (1:1, 1 mL) were added under N₂. The reaction mixture was heated at 150 °C for 10 h. After completion of the reaction, the reaction mixture was cooled down to room temperature, and yields were measured by GC using tridecane as an internal standard. The residue was purified by flash column chromatography on silica gel to give a desired product compound **1e–65e**.



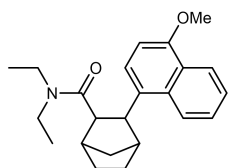
N,N-diethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**1e**)

The representative general procedure mentioned above was followed. The desired product **1e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.43) as a white solid in 85% yield (54.6 mg), mp: 213–217 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.20 – 8.15 (m, 1H), 7.81 – 7.76 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.35 (m, 4H), 4.11 (d, *J* = 4.9 Hz, 1H), 3.56 – 3.23 (m, 3H), 3.10 (dq, *J* = 14.4, 7.1 Hz, 1H), 2.95 – 2.84 (m, 1H), 2.68 (d, *J* = 2.7 Hz, 1H), 2.47 (s, 1H), 1.97 (d, *J* = 9.7 Hz, 1H), 1.81 – 1.66 (m, 3H), 1.51 (dd, *J* = 9.7, 1.5 Hz, 1H), 1.48 – 1.34 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.2, 142.8, 134.0, 132.1, 128.4, 126.2, 125.7, 125.4, 125.1, 125.0, 121.9, 52.5, 45.5, 42.6, 41.9, 41.1, 40.7, 39.5, 29.3, 24.4, 14.7, 13.2. **HRMS** (ESI): calcd for C₂₂H₂₇NO [M+H]⁺ : 322.2165, found: 322.2165.



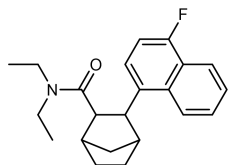
N,N-diethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**2e**)

The representative general procedure mentioned above was followed. The desired product **2e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.49) as a white solid in 81% yield (54.3 mg), mp: 208–211 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.32 – 8.13 (m, 1H), 8.04 – 7.92 (m, 1H), 7.54 – 7.37 (m, 2H), 7.32 (d, J = 7.4 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 4.08 (d, J = 4.9 Hz, 1H), 3.56 – 3.23 (m, 3H), 3.11 (dq, J = 14.3, 7.1 Hz, 1H), 2.90 (t, J = 3.9 Hz, 1H), 2.65 (s, 3H), 2.46 (s, 1H), 1.96 (d, J = 9.7 Hz, 1H), 1.74 (dt, J = 15.5, 7.1, 2.6 Hz, 4H), 1.55 – 1.46 (m, 1H), 1.47 – 1.37 (m, 1H), 1.16 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.3, 141.0, 133.1, 132.2, 132.0, 125.8, 125.6, 125.4, 125.3, 124.4, 121.7, 52.5, 45.4, 42.6, 41.9, 41.1, 40.7, 39.5, 29.3, 24.5, 19.4, 14.7, 13.2. **HRMS** (ESI): calcd for C₂₃H₂₉NO [M+H]⁺ : 336.2322, found: 336.2322.



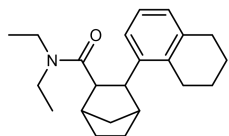
N,N-diethyl-3-(4-methoxynaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**3e**)

The representative general procedure mentioned above was followed. The desired product **3e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, R_f = 0.51) as a white solid in 79% yield (55.5 mg), mp: 199–202 °C. **¹H NMR** (400 MHz, CDCl₃): δ 8.26 – 8.12 (m, 1H), 8.10 – 7.98 (m, 1H), 7.41 – 7.32 (m, 2H), 7.24 (d, J = 8.0 Hz, 1H), 6.66 (d, J = 8.1 Hz, 1H), 3.90 (s, 3H), 3.43 – 3.15 (m, 3H), 3.11 – 2.92 (m, 1H), 2.86 – 2.73 (m, 1H), 2.58 (d, J = 2.9 Hz, 1H), 2.39 (s, 1H), 1.88 (d, J = 9.7 Hz, 1H), 1.76 – 1.60 (m, 4H), 1.43 (dd, J = 9.6, 1.5 Hz, 1H), 1.39 – 1.30 (m, 1H), 1.09 (t, J = 7.2 Hz, 3H), 0.77 (t, J = 7.2 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.4, 153.6, 134.9, 132.9, 126.3, 126.0, 124.9, 124.8, 122.7, 121.7, 102.8, 55.4, 52.6, 45.1, 42.5, 41.9, 41.1, 40.7, 39.5, 29.7, 29.3, 24.5, 14.7, 13.2. **HRMS** (ESI): calcd for C₂₃H₂₉NO₂ [M+H]⁺ : 352.2271, found: 352.2270.



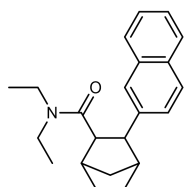
N,N-diethyl-3-(4-fluoronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**4e**)

The representative general procedure mentioned above was followed. The desired product **4e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.41) as a colorless oil in 74% yield (50.2 mg). **¹H NMR** (400 MHz, CDCl₃) δ 8.11 (dq, J = 7.8, 3.4, 2.7 Hz, 1H), 8.06 – 7.96 (m, 1H), 7.47 – 7.34 (m, 2H), 7.26 (dd, J = 8.1, 5.3 Hz, 1H), 6.98 (dd, J = 10.3, 8.1 Hz, 1H), 3.97 (d, J = 5.1 Hz, 1H), 3.28 (s, 2H), 3.05 (s, 1H), 2.76 (ddd, J = 5.5, 4.2, 1.7 Hz, 1H), 2.58 (dt, J = 3.3, 1.5 Hz, 1H), 2.44 – 2.37 (m, 1H), 1.88 (dt, J = 9.7, 1.9 Hz, 1H), 1.72 – 1.63 (m, 2H), 1.66 – 1.58 (m, 1H), 1.45 (dd, J = 9.8, 1.6 Hz, 1H), 1.42 – 1.29 (m, 1H), 1.18 (t, J = 5.7 Hz, 3H), 1.06 (t, J = 6.9 Hz, 3H), 0.81 – 0.78 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.2, 157.3 (d, J = 249.9 Hz), 138.8 (d, J = 4.4 Hz), 133.36 (d, J = 4.1 Hz), 126.7, 125.8, 125.8, 125.2, 125.2, 124.1 (d, J = 15.5 Hz), 121.6, 121.5, 120.8, 120.7, 108.4, 108.2, 52.9, 45.2, 42.6, 41.2, 39.6, 29.7, 29.4, 24.4; **¹⁹F NMR** (376 MHz, CDCl₃): δ -126.81. **HRMS** (ESI): calcd for C₂₂H₂₆FNO [M+H]⁺ : 340.2071, found: 340.2070.



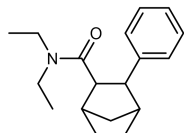
N,N-diethyl-3-(5,6,7,8-tetrahydronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**5e**)

The representative general procedure mentioned above was followed. The desired product **5e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.47) as a colorless oil in 60% yield (39.0 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.10 (d, J = 6.6 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.1 Hz, 1H), 3.58 (d, J = 4.5 Hz, 1H), 3.52 – 3.40 (m, 2H), 3.25 (dq, J = 13.9, 7.1 Hz, 2H), 3.09 – 2.94 (m, 1H), 2.75 (dt, J = 12.7, 5.8 Hz, 3H), 2.64 (dt, J = 17.0, 6.8 Hz, 1H), 2.47 (s, 1H), 2.29 (s, 1H), 1.89 (d, J = 9.8 Hz, 1H), 1.84 – 1.72 (m, 2H), 1.68 – 1.56 (m, 3H), 1.38 (dd, J = 9.7, 1.5 Hz, 2H), 1.25 (s, 2H), 1.10 (td, J = 7.1, 2.3 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.9, 144.6, 137.6, 135.9, 126.9, 124.8, 122.6, 50.9, 45.2, 43.7, 41.8, 40.9, 40.5, 38.8, 30.5, 29.6, 26.7, 24.2, 23.5, 22.7, 14.9, 13.1. **HRMS** (ESI): calcd for C₂₂H₃₁NO [M+H]⁺ : 326.2478, found: 326.2478.



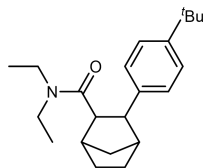
N,N-diethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**6e**)

The representative general procedure mentioned above was followed. The desired product **6e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R*_f = 0.44) as a white solid in 64% yield (41.1 mg), mp: 214–218 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 1H), 7.63 (s, 1H), 7.48 – 7.35 (m, 2H), 7.30 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.70 (d, *J* = 5.4 Hz, 1H), 3.63 (dt, *J* = 14.0, 7.0 Hz, 1H), 3.44 (dq, *J* = 14.4, 7.1 Hz, 1H), 3.22 (dp, *J* = 14.0, 7.1 Hz, 2H), 3.00 – 2.83 (m, 1H), 2.67 (d, *J* = 3.3 Hz, 1H), 2.52 (s, 1H), 1.96 – 1.84 (m, 1H), 1.71 – 1.55 (m, 3H), 1.49 (dd, *J* = 9.7, 1.5 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.8, 144.4, 133.5, 131.8, 127.9, 127.6, 127.4, 126.6, 125.8, 125.0, 123.7, 54.1, 48.9, 41.8, 41.6, 41.3, 40.3, 39.3, 29.8, 29.7, 23.8, 14.9, 13.3. **HRMS** (ESI): calcd for C₂₂H₂₇NO [M+H]⁺ : 322.2165, found: 322.2165.



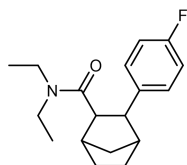
N,N-diethyl-3-phenylbicyclo[2.2.1]heptane-2-carboxamide (**7e**)

The representative general procedure mentioned above was followed. The desired product **7e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R*_f = 0.49) as a white solid in 55% yield (29.9 mg), mp: 222–226 °C. **¹H NMR** (400 MHz, CDCl₃): δ 7.26 (t, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 3.61 (dt, *J* = 13.6, 7.0 Hz, 1H), 3.54 (d, *J* = 5.3 Hz, 1H), 3.44 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.22 (tq, *J* = 13.9, 7.1 Hz, 2H), 2.93 – 2.84 (m, 1H), 2.53 (d, *J* = 3.2 Hz, 1H), 2.48 (s, 1H), 1.82 (d, *J* = 9.7 Hz, 1H), 1.61 (ddd, *J* = 13.5, 6.8, 3.1 Hz, 2H), 1.57 – 1.50 (m, 1H), 1.45 – 1.40 (m, 1H), 1.26 (d, *J* = 4.6 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.8, 146.9, 128.3, 126.7, 125.4, 54.0, 48.8, 42.1, 41.6, 41.2, 40.3, 39.2, 29.8, 27.1, 23.7, 14.9, 13.2. **HRMS** (ESI): calcd for C₁₈H₂₅NO [M+H]⁺ : 272.2009, found: 272.2008.



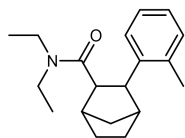
3-(4-(tert-butyl)phenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**8e**)

The representative general procedure mentioned above was followed. The desired product **8e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.49) as a yellow oil in 49% yield (32.1 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.28 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 3.58 (dq, J = 14.0, 7.1 Hz, 1H), 3.51 (d, J = 5.0 Hz, 1H), 3.43 (dq, J = 14.3, 7.1 Hz, 1H), 3.23 (ddq, J = 20.6, 14.0, 7.1 Hz, 2H), 2.97 – 2.87 (m, 1H), 2.51 (d, J = 3.5 Hz, 1H), 2.48 (s, 1H), 1.82 (d, J = 9.7 Hz, 1H), 1.70 (s, 1H), 1.61 – 1.48 (m, 3H), 1.40 (dd, J = 9.7, 1.6 Hz, 1H), 1.29 (s, 6H), 1.25 (s, 3H), 1.12 (q, J = 7.0 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.9, 148.1, 143.8, 126.4, 125.2, 53.7, 48.3, 42.2, 41.5, 41.1, 40.2, 39.1, 34.3, 31.4, 29.7, 23.8, 14.9, 13.3. **HRMS** (ESI): calcd for C₂₂H₃₃NO [M+H]⁺ : 328.2635, found: 328.2635.



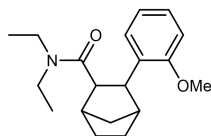
N,N-diethyl-3-(4-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**9e**)

The representative general procedure mentioned above was followed. The desired product **9e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a yellow oil in 50% yield (28.9 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.15 (d, J = 5.6 Hz, 1H), 7.13 (d, J = 5.5 Hz, 1H), 6.94 (t, J = 8.7 Hz, 2H), 3.61 (dq, J = 14.0, 7.1 Hz, 1H), 3.50 (d, J = 5.3 Hz, 1H), 3.44 (dq, J = 14.4, 7.1 Hz, 1H), 3.21 (ddt, J = 25.3, 14.0, 7.1 Hz, 2H), 2.81 (t, J = 3.9 Hz, 1H), 2.48 (d, J = 3.9 Hz, 2H), 1.79 (d, J = 9.7 Hz, 1H), 1.67 (s, 2H), 1.59 – 1.50 (m, 2H), 1.47 – 1.41 (m, 1H), 1.13 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.6, 160.9 (d, J = 243.4 Hz), 142.6, 127.9 (d, J = 7.7 Hz), 114.9 (d, J = 20.9 Hz), 54.5, 48.1, 42.2, 41.5, 41.2, 40.3, 39.2, 29.8, 23.6, 14.9, 13.3; **¹⁹F NMR** (376 MHz, CDCl₃): δ -118.28. **HRMS** (ESI): calcd for C₁₈H₂₄FNO [M+H]⁺ : 290.1915, found: 290.1915.



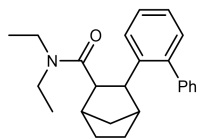
N,N-diethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**10e**)

The representative general procedure mentioned above was followed. The desired product **10e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R*_f = 0.44) as a yellow oil in 51% yield (28.5 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.29 – 7.24 (m, 1H), 7.19 – 7.10 (m, 2H), 7.10 – 7.03 (m, 1H), 3.60 (d, *J* = 4.8 Hz, 1H), 3.48 (tq, *J* = 14.5, 7.1 Hz, 2H), 3.29 – 3.17 (m, 2H), 3.06 – 2.95 (m, 1H), 2.48 (s, 1H), 2.36 (s, 1H), 2.29 (s, 3H), 1.89 (d, *J* = 9.7 Hz, 1H), 1.73 (s, 1H), 1.68 – 1.55 (m, 3H), 1.47 – 1.36 (m, 1H), 1.10 (td, *J* = 7.1, 4.6 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.8, 144.6, 136.9, 130.4, 125.5, 125.4, 125.0, 51.1, 45.8, 43.3, 41.6, 40.9, 40.3, 38.9, 29.5, 24.1, 20.3, 14.8, 13.1. **HRMS** (ESI): calcd for C₁₉H₂₇NO [M+H]⁺ : 286.2171, found: 286.2169.



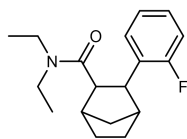
N,N-diethyl-3-(2-methoxyphenyl)bicyclo[2.2.1]heptane-2-carboxamide (**11e**)

The representative general procedure mentioned above was followed. The desired product **11e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, *R*_f = 0.49) as a yellow oil in 51% yield (30.7 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.25 (d, *J* = 7.6 Hz, 1H), 7.19 – 7.12 (m, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 3.70 (s, 3H), 3.57 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.50 (d, *J* = 4.5 Hz, 1H), 3.42 (dq, *J* = 14.4, 7.1 Hz, 1H), 3.27 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.15 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.72 (t, *J* = 3.8 Hz, 1H), 2.61 (s, 1H), 2.39 (s, 1H), 1.76 (d, *J* = 9.5 Hz, 1H), 1.70 – 1.59 (m, 3H), 1.44 – 1.38 (m, 1H), 1.33 (dq, *J* = 9.1, 4.5, 3.9 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.5, 157.4, 134.9, 126.4, 125.5, 119.8, 109.9, 54.7, 52.0, 44.3, 41.6, 41.0, 40.4, 40.2, 39.0, 28.7, 24.7, 14.7, 13.5. **HRMS** (ESI): calcd for C₁₉H₂₇NO₂ [M+H]⁺ : 302.2115, found: 302.2115.



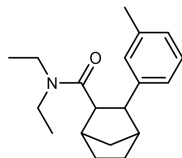
3-([1,1'-biphenyl]-2-yl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**12e**)

The representative general procedure mentioned above was followed. The desired product **12e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.52) as a yellow oil in 49% yield (34.2 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.39 (q, *J* = 8.4, 7.7 Hz, 3H), 7.34 – 7.28 (m, 4H), 7.20 (qd, *J* = 7.5, 1.6 Hz, 2H), 3.71 (d, *J* = 5.4 Hz, 1H), 3.46 (tq, *J* = 14.4, 7.1 Hz, 2H), 3.21 (dq, *J* = 14.4, 7.1 Hz, 1H), 3.14 – 3.08 (m, 1H), 2.92 (dq, *J* = 14.0, 7.1 Hz, 1H), 2.43 (s, 1H), 2.17 (d, *J* = 2.9 Hz, 1H), 1.86 (d, *J* = 9.8 Hz, 1H), 1.72 (s, 1H), 1.37 (ddt, *J* = 11.2, 8.6, 4.1 Hz, 2H), 1.31 – 1.23 (m, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.9, 143.7, 142.9, 141.9, 130.4, 129.4, 127.8, 127.0, 126.6, 125.4, 125.3, 50.7, 45.2, 44.9, 41.4, 41.0, 40.0, 38.2, 29.3, 23.5, 14.7, 13.2. **HRMS** (ESI): calcd for C₂₄H₂₉NO [M+H]⁺ : 348.2322, found: 348.2322.



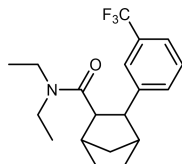
N,N-diethyl-3-(2-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**13e**)

The representative general procedure mentioned above was followed. The desired product **13e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.55) as a yellow oil in 46% yield (26.6 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.32 – 7.23 (m, 1H), 7.13 (tdd, *J* = 7.2, 5.2, 1.7 Hz, 1H), 7.06 (td, *J* = 7.5, 1.3 Hz, 1H), 6.97 (ddd, *J* = 10.5, 8.0, 1.3 Hz, 1H), 3.66 (d, *J* = 5.0 Hz, 1H), 3.58 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.45 (dq, *J* = 14.4, 7.1 Hz, 1H), 3.22 (tq, *J* = 14.4, 7.1 Hz, 2H), 2.88 (t, *J* = 4.0 Hz, 1H), 2.58 (s, 1H), 2.47 (s, 1H), 1.86 (s, 1H), 1.75 (d, *J* = 9.7 Hz, 1H), 1.71 – 1.62 (m, 2H), 1.50 – 1.32 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.5, 161.2 (d, *J* = 245.9 Hz), 133.4 (d, *J* = 15.0 Hz), 127.0, 126.8, 123.6 (d, *J* = 3.5 Hz), 115.3 (d, *J* = 22.4 Hz), 51.9, 43.2, 41.7, 41.1, 41.0, 40.4, 39.0, 29.0, 24.2, 14.7, 13.3; **¹⁹F NMR** (376 MHz, CDCl₃): δ -113.33. **HRMS** (ESI): calcd for C₁₈H₂₄FNO [M+H]⁺ : 290.1915, found: 290.1915.



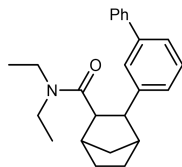
N,N-diethyl-3-(*m*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**14e**)

The representative general procedure mentioned above was followed. The desired product **14e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.50) as a yellow oil in 50% yield (28.5 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.24 (td, *J* = 7.9, 6.1 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.93 (dt, *J* = 10.6, 2.2 Hz, 1H), 6.86 (td, *J* = 8.4, 2.5 Hz, 1H), 3.64 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.57 (d, *J* = 5.5 Hz, 1H), 3.47 (dq, *J* = 14.3, 7.4 Hz, 1H), 3.32 – 3.18 (m, 2H), 2.86 (ddd, *J* = 5.7, 3.9, 1.8 Hz, 1H), 2.67 – 2.48 (m, 2H), 1.71 – 1.62 (m, 2H), 1.56 (ddd, *J* = 9.3, 5.5, 2.3 Hz, 2H), 1.37 – 1.27 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.10 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.5, 164.2, 149.7, 129.7, 122.5, 113.5, 112.3, 54.2, 48.6, 42.0, 41.6, 41.2, 40.3, 39.3, 29.8, 23.6, 14.9, 13.3, 1.0. **HRMS** (ESI): calcd for C₁₉H₂₇NO [M+H]⁺ : 286.2165, found: 286.2165.



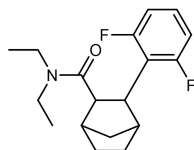
N,N-diethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**15e**)

The representative general procedure mentioned above was followed. The desired product **15e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.50) as a yellow oil in 50% yield (31.2 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.43 (s, 1H), 7.42 – 7.30 (m, 3H), 3.61 (q, *J* = 7.2, 6.8 Hz, 2H), 3.45 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.23 (ddt, *J* = 13.6, 9.4, 7.0 Hz, 2H), 2.91 – 2.79 (m, 1H), 2.56 (d, *J* = 3.7 Hz, 1H), 2.52 (s, 1H), 1.78 (d, *J* = 9.8 Hz, 1H), 1.71 – 1.51 (m, 3H), 1.49 – 1.44 (m, 1H), 1.44 – 1.37 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.3, 147.7, 130.5 (d, *J* = 31.9 Hz), 130.2, 128.7, 124.2 (d, *J* = 272.3 Hz), 123.2 (d, *J* = 3.7 Hz), 122.3 (d, *J* = 3.8 Hz), 54.1, 48.6, 41.8, 41.5, 41.2, 40.4, 39.2, 29.7, 23.5, 14.7, 13.1; **¹⁹F NMR** (376 MHz, CDCl₃): δ -62.52. **HRMS** (ESI): calcd for C₁₉H₂₄F₃NO [M+H]⁺ : 340.1883, found: 340.1883.



3-([1,1'-biphenyl]-3-yl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**16e**)

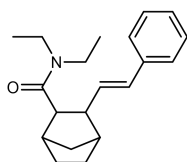
The representative general procedure mentioned above was followed. The desired product **16e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.44) as a yellow oil in 49% yield (34.0 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.56 (d, J = 7.4 Hz, 2H), 7.47 – 7.39 (m, 3H), 7.39 – 7.30 (m, 3H), 7.18 (d, J = 7.4 Hz, 1H), 3.59 (dd, J = 14.9, 6.0 Hz, 2H), 3.44 (dq, J = 14.2, 7.1 Hz, 1H), 3.23 (ddt, J = 18.2, 14.0, 7.1 Hz, 2H), 3.02 – 2.89 (m, 1H), 2.58 (d, J = 2.6 Hz, 1H), 2.50 (s, 1H), 1.86 (d, J = 9.7 Hz, 1H), 1.72 – 1.52 (m, 3H), 1.43 (ddd, J = 13.1, 7.3, 2.0 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.8, 147.4, 141.5, 141.3, 128.8, 128.7, 127.2, 127.1, 125.8, 125.6, 124.5, 54.0, 49.0, 42.3, 41.6, 41.3, 40.4, 39.4, 29.8, 27.1, 23.8, 14.9, 13.3. **HRMS** (ESI): calcd for C₂₄H₂₉NO [M+H]⁺ : 348.2322, found: 348.2322.



3-(2,6-difluorophenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**17e**)

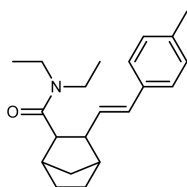
The representative general procedure mentioned above was followed. The desired product **17e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.49) as a yellow oil in 46% yield (28.3 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.08 (tq, J = 10.5, 5.3, 4.2 Hz, 1H), 6.80 (dq, J = 8.7, 4.6 Hz, 2H), 3.82 (s, 1H), 3.60 (dq, J = 14.1, 7.1 Hz, 1H), 3.48 (dq, J = 14.3, 7.1 Hz, 1H), 3.32 (t, J = 4.6 Hz, 1H), 3.19 (ddq, J = 20.7, 13.9, 7.1 Hz, 2H), 2.50 (s, 2H), 1.99 (d, J = 9.8 Hz, 1H), 1.68 – 1.52 (m, 3H), 1.43 (d, J = 9.7 Hz, 2H), 1.10 (q, J = 7.3 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.5, 161.5 (d, J = 245.5 Hz), 161.4 (d, J = 245.4 Hz), 127.1 (t, J = 11.0 Hz), 120.9 (t, J = 16.7 Hz), 111.6 (d, J = 13.1 Hz), 111.68 (d, J = 27.6 Hz), 50.5, 43.2, 41.6, 41.4, 40.8, 39.8, 39.7, 30.1, 23.7, 14.7, 13.2; **¹⁹F NMR** (376 MHz,

CDCl_3): δ -110.36 (d, J = 7.7 Hz). **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{23}\text{F}_2\text{NO}$ $[\text{M}+\text{H}]^+$: 308.1820, found: 308.1820.



(*E*)-*N,N*-diethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**18e**)

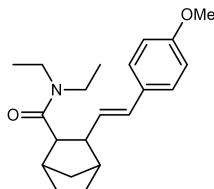
The representative general procedure mentioned above was followed. The desired product **18e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a yellow oil in 82% yield (48.7 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.34 – 7.25 (m, 4H), 7.22 – 7.13 (m, 1H), 6.36 (d, J = 15.8 Hz, 1H), 6.12 (dd, J = 15.8, 8.1 Hz, 1H), 3.61 (dq, J = 14.0, 7.1 Hz, 1H), 3.47 (dq, J = 14.3, 7.1 Hz, 1H), 3.27 (dq, J = 14.3, 7.1 Hz, 1H), 3.16 (dq, J = 14.0, 7.1 Hz, 1H), 3.08 – 3.01 (m, 1H), 2.68 (td, J = 4.5, 1.7 Hz, 1H), 2.44 (s, 1H), 2.22 (d, J = 3.6 Hz, 1H), 1.71 (d, J = 9.7 Hz, 1H), 1.64 – 1.43 (m, 3H), 1.41 – 1.32 (m, 2H), 1.15 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 171.6, 137.7, 134.8, 128.3, 128.2, 126.7, 125.9, 51.8, 47.3, 43.0, 41.4, 40.8, 40.0, 38.6, 28.8, 23.8, 14.8, 13.2. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{27}\text{NO}$ $[\text{M}+\text{H}]^+$: 298.2165, found: 298.2165.



(*E*)-*N,N*-diethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**19e**)

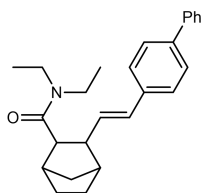
The representative general procedure mentioned above was followed. The desired product **19e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a yellow oil in 79% yield (49.2 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.21 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.32 (d, J = 15.8 Hz, 1H), 6.06 (dd, J = 15.8, 8.1 Hz, 1H), 3.61 (dq, J = 14.0, 7.0 Hz, 1H), 3.47 (dq, J = 14.3, 7.1 Hz, 1H), 3.26 (dq, J = 14.3, 7.1 Hz, 1H), 3.15 (dq, J = 14.0, 7.0 Hz, 1H), 3.05 – 2.99 (m, 1H), 2.67 (td, J = 4.5, 1.6 Hz, 1H), 2.43 (s, 1H), 2.31 (s, 3H), 2.21 (d, J = 3.5 Hz, 1H), 1.70 (d, J = 9.7 Hz, 1H), 1.59 – 1.47 (m, 2H), 1.41 –

1.33 (m, 1H), 1.26 (s, 2H), 1.13 (dt, $J = 14.5, 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 136.4, 135.0, 133.9, 129.0, 128.0, 125.8, 51.9, 47.4, 43.0, 41.4, 40.8, 40.0, 38.6, 29.6, 28.8, 23.8, 21.0, 14.8, 13.2. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{29}\text{NO}$ $[\text{M}+\text{H}]^+$: 312.2322, found: 312.2322.



(*E*)-*N,N*-diethyl-3-(4-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**20e**)

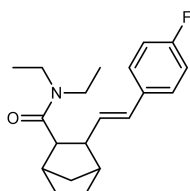
The representative general procedure mentioned above was followed. The desired product **20e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.40$) as a yellow oil in 77% yield (50.4 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, $J = 8.9$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 2H), 6.30 (d, $J = 15.8$ Hz, 1H), 5.97 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.79 (s, 3H), 3.61 (dq, $J = 14.0, 7.1$ Hz, 1H), 3.47 (dq, $J = 14.5, 7.1$ Hz, 1H), 3.27 (dq, $J = 14.2, 7.0$ Hz, 1H), 3.15 (dq, $J = 14.0, 7.1$ Hz, 1H), 3.06 – 2.97 (m, 1H), 2.66 (td, $J = 4.5, 1.6$ Hz, 1H), 2.43 (s, 1H), 2.20 (d, $J = 3.6$ Hz, 1H), 1.70 (dt, $J = 9.8, 1.9$ Hz, 1H), 1.54 (ddd, $J = 15.5, 8.1, 3.6$ Hz, 2H), 1.38 – 1.32 (m, 2H), 1.26 (d, $J = 4.6$ Hz, 1H), 1.15 (t, $J = 7.1$ Hz, 3H), 1.11 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 158.6, 132.8, 130.6, 127.6, 126.9, 113.8, 55.2, 52.0, 47.4, 43.1, 41.4, 40.8, 40.0, 38.6, 28.8, 23.8, 14.8, 13.2. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{29}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 328.2271, found: 328.2271.



(*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**21e**)

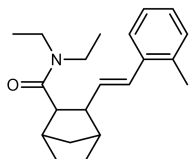
The representative general procedure mentioned above was followed. The desired product **21e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.47$) as a yellow oil in 70% yield (52.3 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.54 – 7.49 (m, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 7.38 – 7.31 (m, 4H), 7.25 (ddd, $J = 7.4, 5.5, 1.1$ Hz, 1H), 6.33 (d, $J = 15.8$ Hz, 1H), 6.09 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.63 – 3.35 (m, 2H), 3.30 – 3.08 (m,

2H), 3.02 – 2.95 (m, 1H), 2.62 (td, $J = 4.5, 1.6$ Hz, 1H), 2.38 (s, 1H), 2.17 (d, $J = 3.7$ Hz, 1H), 1.65 (d, $J = 9.8$ Hz, 2H), 1.56 – 1.40 (m, 3H), 1.34 – 1.29 (m, 1H), 1.07 (dt, $J = 14.1, 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 140.8, 139.5, 136.8, 135.1, 128.7, 127.7, 127.1, 126.8, 126.3, 51.9, 47.5, 43.0, 40.9, 38.6, 28.8, 23.8, 14.8, 13.2. HRMS (ESI): calcd for $\text{C}_{26}\text{H}_{31}\text{NO}$ $[\text{M}+\text{H}]^+$: 374.2478, found: 374.2478.



(*E*)-*N,N*-diethyl-3-(4-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**22e**)

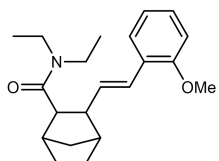
The representative general procedure mentioned above was followed. The desired product **22e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.52$) as a yellow oil in 65% yield (41.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.30 (dd, $J = 8.4, 5.7$ Hz, 2H), 6.98 (t, $J = 8.7$ Hz, 2H), 6.34 (d, $J = 15.8$ Hz, 1H), 6.05 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.63 (dq, $J = 14.1, 7.1$ Hz, 1H), 3.50 (dq, $J = 14.3, 7.1$ Hz, 1H), 3.30 (dq, $J = 14.4, 7.1$ Hz, 1H), 3.18 (dq, $J = 14.0, 7.0$ Hz, 1H), 3.10 – 3.02 (m, 1H), 2.69 (t, $J = 3.6$ Hz, 1H), 2.47 (s, 1H), 2.23 (d, $J = 3.5$ Hz, 1H), 1.72 (d, $J = 9.7$ Hz, 1H), 1.57 – 1.52 (m, 1H), 1.39 (dd, $J = 12.2, 4.9$ Hz, 2H), 1.33 – 1.25 (m, 2H), 1.18 (t, $J = 7.2$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.6, 161.8 (d, $J = 245.5$ Hz), 134.6, 133.9 (d, $J = 3.2$ Hz), 127.3 (d, $J = 7.8$ Hz), 127.1, 115.2 (d, $J = 21.5$ Hz), 52.0, 47.4, 43.1, 41.5, 40.9, 40.1, 38.6, 29.7, 28.9, 23.8, 14.8, 13.2; ^{19}F NMR (376 MHz, CDCl_3): δ -115.80. HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{26}\text{FNO}$ $[\text{M}+\text{H}]^+$: 316.2071, found: 316.2071.



(*E*)-*N,N*-diethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**23e**)

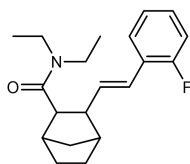
The representative general procedure mentioned above was followed. The desired product **23e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc

(5:1, R_f = 0.56) as a yellow oil in 67% yield (41.7 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.42 (d, J = 6.4 Hz, 1H), 7.22 – 7.10 (m, 3H), 6.59 (d, J = 15.7 Hz, 1H), 6.04 (dd, J = 15.7, 8.1 Hz, 1H), 3.65 (dq, J = 14.0, 7.1 Hz, 1H), 3.54 (dq, J = 14.4, 7.1 Hz, 1H), 3.31 (dq, J = 14.6, 7.2 Hz, 1H), 3.21 (dt, J = 14.0, 7.0 Hz, 1H), 3.14 – 3.07 (m, 1H), 2.74 (td, J = 4.5, 1.6 Hz, 1H), 2.49 (s, 1H), 2.35 (s, 3H), 2.28 (d, J = 3.7 Hz, 1H), 1.76 (d, J = 9.8 Hz, 1H), 1.60 (dt, J = 9.5, 4.3 Hz, 1H), 1.48 – 1.38 (m, 2H), 1.30 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.7, 136.9, 136.5, 135.1, 130.1, 126.8, 126.0, 125.9, 125.3, 51.9, 47.7, 43.3, 41.6, 41.0, 40.2, 38.6, 29.7, 28.9, 23.9, 19.9, 14.9, 13.3. **HRMS** (ESI): calcd for C₂₁H₂₉NO [M+H]⁺ : 312.2322, found: 312.2322.



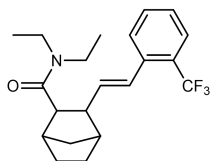
(*E*)-*N,N*-diethyl-3-(2-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**24e**)

The representative general procedure mentioned above was followed. The desired product **24e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, R_f = 0.46) as a yellow oil in 65% yield (42.5 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.43 (dd, J = 7.6, 1.5 Hz, 1H), 7.26 – 7.15 (m, 1H), 6.92 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.73 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 7.7 Hz, 1H), 3.85 (s, 3H), 3.66 (dq, J = 14.1, 7.1 Hz, 1H), 3.54 (dq, J = 14.4, 7.1 Hz, 1H), 3.30 (dq, J = 14.2, 7.0 Hz, 1H), 3.19 (dq, J = 14.0, 7.1 Hz, 1H), 3.11 – 3.03 (m, 1H), 2.76 (td, J = 4.5, 1.5 Hz, 1H), 2.48 (s, 1H), 2.28 (d, J = 3.1 Hz, 1H), 1.60 (ddd, J = 12.9, 10.5, 6.6 Hz, 2H), 1.55 – 1.47 (m, 1H), 1.42 – 1.36 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.8, 156.4, 135.6, 127.8, 126.9, 126.2, 122.8, 120.5, 110.8, 55.4, 51.7, 47.7, 43.2, 41.5, 41.0, 40.1, 38.6, 28.9, 23.9, 14.8, 13.3. **HRMS** (ESI): calcd for C₂₁H₂₉NO₂ [M+H]⁺ : 328.2271, found: 328.2271.



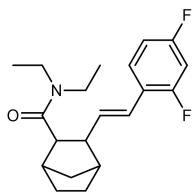
(*E*)-*N,N*-diethyl-3-(2-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**25e**)

The representative general procedure mentioned above was followed. The desired product **25e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a yellow oil in 59% yield (37.2 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.39 (td, J = 7.7, 1.6 Hz, 1H), 7.14 (dtd, J = 9.5, 5.2, 1.7 Hz, 1H), 7.10 – 6.93 (m, 2H), 6.49 (d, J = 16.1 Hz, 1H), 6.22 (dd, J = 16.1, 7.8 Hz, 1H), 3.63 (dq, J = 14.1, 7.1 Hz, 1H), 3.49 (dq, J = 14.3, 7.1 Hz, 1H), 3.27 (dq, J = 14.3, 7.1 Hz, 1H), 3.15 (dq, J = 14.0, 7.1 Hz, 1H), 3.09 – 3.01 (m, 1H), 2.71 (td, J = 4.6, 1.6 Hz, 1H), 2.45 (s, 1H), 2.25 (d, J = 3.7 Hz, 1H), 1.70 (d, J = 9.8 Hz, 1H), 1.43 – 1.32 (m, 2H), 1.25 (s, 4H), 1.17 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.6, 160.0 (d, J = 248.4 Hz), 137.8, 137.7, 127.9 (d, J = 8.2 Hz), 127.2, 127.1, 125.5, 125.4, 123.9 (d, J = 3.5 Hz), 120.7, 115.6 (d, J = 22.1 Hz), 51.6, 47.7, 43.0, 41.5, 40.9, 40.1, 38.6, 29.7, 28.9, 23.9, 14.8, 13.2; **¹⁹F NMR** (376 MHz, CDCl₃): δ -118.40. **HRMS** (ESI): calcd for C₂₀H₂₆FNO [M+H]⁺ : 316.2071, found: 316.2071.



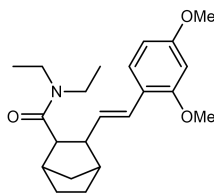
(*E*)-*N,N*-diethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**26e**)

The representative general procedure mentioned above was followed. The desired product **26e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.58) as a yellow oil in 55% yield (40.2 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.61 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.35 – 7.26 (m, 1H), 6.72 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 15.8, 7.0 Hz, 1H), 3.68 – 3.58 (m, 1H), 3.58 – 3.48 (m, 1H), 3.30 (dt, J = 14.7, 7.2 Hz, 1H), 3.22 (dt, J = 14.0, 7.0 Hz, 1H), 3.15 – 3.08 (m, 1H), 2.77 (td, J = 4.7, 1.6 Hz, 1H), 2.49 (s, 1H), 2.31 (d, J = 3.6 Hz, 1H), 1.74 (s, 1H), 1.69 (d, J = 9.8 Hz, 1H), 1.61 – 1.48 (m, 2H), 1.43 – 1.36 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.5, 139.5, 137.2, 131.7, 127.2, 127.0 (d, J = 29.7 Hz), 125.6 (d, J = 5.7 Hz), 125.3 (d, J = 250.3 Hz), 123.0, 51.2, 47.2, 42.7, 41.6, 41.0, 40.2, 38.5, 28.8, 23.9, 14.7, 13.2; **¹⁹F NMR** (376 MHz, CDCl₃): δ -59.63. **HRMS** (ESI): calcd for C₂₁H₂₆F₃NO [M+H]⁺ : 366.2039, found: 366.2039.



(*E*)-3-(2,4-difluorostyryl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**27e**)

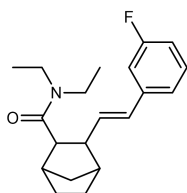
The representative general procedure mentioned above was followed. The desired product **27e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, *R_f* = 0.44) as a yellow oil in 52% yield (34.7 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.34 (td, *J* = 8.6, 6.5 Hz, 1H), 6.84 – 6.68 (m, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 7.8 Hz, 1H), 3.62 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.56 – 3.42 (m, 1H), 3.28 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.15 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.09 – 3.01 (m, 1H), 2.69 (td, *J* = 4.5, 1.7 Hz, 1H), 2.46 (s, 1H), 2.23 (d, *J* = 3.8 Hz, 1H), 1.73 – 1.62 (m, 1H), 1.58 (ddd, *J* = 11.5, 7.4, 4.2 Hz, 1H), 1.54 – 1.41 (m, 2H), 1.40 – 1.33 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.5, 161.7 (d, *J* = 246.7 Hz), 161.6 (d, *J* = 246.7 Hz), 161.2, 161.1, 137.3, 127.9 (d, *J* = 5.7 Hz), 127.8 (d, *J* = 5.7 Hz), 121.9 (d, *J* = 3.8 Hz), 121.8 (d, *J* = 4.3 Hz), 119.9, 104.1, 103.8, 103.6, 51.7, 47.7, 43.0, 41.5, 40.9, 40.1, 38.6, 28.9, 23.8, 14.8, 13.2; **¹⁹F NMR** (376 MHz, CDCl₃): δ -112.57, -114.32. **HRMS** (ESI): calcd for C₂₀H₂₅F₂NO [M+H]⁺ : 334.1977, found: 334.1977.



(*E*)-3-(2,4-dimethoxystyryl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**28e**)

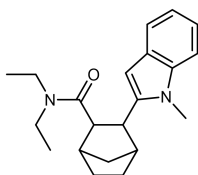
The representative general procedure mentioned above was followed. The desired product **28e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, *R_f* = 0.46) as a yellow oil in 56% yield (40.0 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.39 – 7.24 (m, 1H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.49 – 6.37 (m, 2H), 6.01 (dd, *J* = 16.0, 7.8 Hz, 1H), 3.79 (s, 6H), 3.61 (dq, *J* = 14.1, 7.1 Hz, 1H), 3.49 (dq, *J* = 14.5, 7.2 Hz, 1H), 3.26 (dq, *J* = 14.3, 7.1 Hz, 1H), 3.15 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.04 – 2.96 (m, 1H), 2.71 (td, *J* = 4.5, 1.6 Hz, 1H),

2.43 (s, 1H), 2.22 (d, $J = 3.2$ Hz, 1H), 1.70 (d, $J = 9.7$ Hz, 1H), 1.53 (td, $J = 6.0, 2.9$ Hz, 1H), 1.40 – 1.29 (m, 2H), 1.25 (s, 2H), 1.17 (t, $J = 7.1$ Hz, 3H), 1.11 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.3, 159.8, 157.2, 133.5, 127.0, 122.4, 119.9, 104.6, 98.4, 55.4, 51.8, 47.7, 43.3, 41.5, 40.9, 40.1, 38.6, 29.7, 29.2, 23.9, 14.8, 13.2. **HRMS** (ESI): calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 358.2377, found: 358.2377.



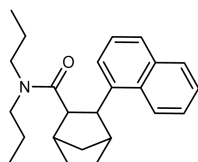
(*E*)-*N,N*-diethyl-3-(3-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**29e**)

The representative general procedure mentioned above was followed. The desired product **29e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.52$) as a yellow oil in 57% yield (35.9 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.29 – 7.18 (m, 1H), 7.07 (d, $J = 7.9$ Hz, 1H), 7.02 (d, $J = 10.0$ Hz, 1H), 6.87 (td, $J = 8.4, 2.6$ Hz, 1H), 6.33 (d, $J = 15.8$ Hz, 1H), 6.12 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.62 (dq, $J = 14.1, 7.0$ Hz, 1H), 3.48 (dq, $J = 14.6, 7.3$ Hz, 1H), 3.27 (dq, $J = 14.4, 7.1$ Hz, 1H), 3.15 (dq, $J = 14.1, 7.1$ Hz, 1H), 3.05 (dd, $J = 8.1, 5.0$ Hz, 1H), 2.66 (t, $J = 4.7$ Hz, 1H), 2.46 (d, $J = 4.3$ Hz, 1H), 2.22 (d, $J = 4.2$ Hz, 1H), 1.78 (s, 1H), 1.70 (d, $J = 9.9$ Hz, 1H), 1.57 (dddd, $J = 19.5, 15.1, 9.9, 5.3$ Hz, 2H), 1.42 – 1.32 (m, 2H), 1.14 (dt, $J = 16.8, 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.5, 163.1 (d, $J = 244.3$ Hz), 140.2, 140.1, 136.3, 129.8 (d, $J = 8.3$ Hz), 127.3 (d, $J = 2.2$ Hz), 121.9, 113.6 (d, $J = 21.3$ Hz), 112.3, 112.1, 51.9, 47.3, 43.0, 41.5, 40.9, 40.1, 38.6, 28.9, 23.8, 14.9, 13.2; ^{19}F NMR (376 MHz, CDCl_3): δ -113.91. **HRMS** (ESI): calcd for $\text{C}_{20}\text{H}_{26}\text{FNO}$ $[\text{M}+\text{H}]^+$: 316.2071, found: 316.2071.



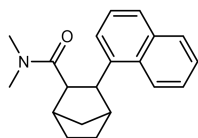
N,N-diethyl-3-(1-methyl-1H-indol-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**30e**)

The representative general procedure mentioned above was followed. The desired product **30e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, R_f = 0.42) as a colorless oil in 53% yield (34.4 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.52 (d, J = 7.7 Hz, 1H), 7.24 (dd, J = 7.0, 1.1 Hz, 1H), 7.14 (td, J = 8.2, 7.6, 1.2 Hz, 1H), 7.09 – 7.01 (m, 1H), 6.23 (s, 1H), 3.65 (s, 3H), 3.51 (tq, J = 14.2, 7.1 Hz, 2H), 3.26 (dp, J = 20.5, 7.1 Hz, 2H), 3.09 – 3.02 (m, 1H), 2.50 (d, J = 21.1 Hz, 1H), 1.95 (d, J = 9.8 Hz, 1H), 1.71 – 1.61 (m, 1H), 1.59 – 1.38 (m, 2H), 1.25 (s, 2H), 1.18 – 1.14 (m, 3H), 1.12 (t, J = 6.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.4, 145.9, 137.5, 127.6, 120.6, 119.7, 119.2, 108.8, 97.0, 51.6, 43.0, 41.9, 41.7, 40.8, 40.4, 38.9, 29.8, 29.0, 23.9, 14.9, 13.2. **HRMS** (ESI): calcd for C₂₁H₂₈N₂O [M+H]⁺ : 325.2274, found: 325.2274.



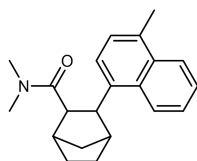
3-(naphthalen-1-yl)-*N,N*-dipropylbicyclo[2.2.1]heptane-2-carboxamide (**31e**)

The representative general procedure mentioned above was followed. The desired product **31e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a colorless oil in 65% yield (45.5 mg). **¹H NMR** (400 MHz, CDCl₃): δ 8.23 (dt, J = 6.4, 3.4 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.47 (dd, J = 6.3, 3.5 Hz, 4H), 4.17 (d, J = 5.0 Hz, 1H), 3.49 (ddd, J = 13.3, 9.5, 5.9 Hz, 1H), 3.37 – 3.16 (m, 2H), 3.10 – 3.02 (m, 1H), 3.02 – 2.95 (m, 1H), 2.71 (d, J = 3.4 Hz, 1H), 2.53 (s, 1H), 2.03 (d, J = 9.7 Hz, 1H), 1.84 – 1.75 (m, 2H), 1.70 (s, 2H), 1.56 (dd, J = 9.6, 1.5 Hz, 1H), 1.53 – 1.43 (m, 1H), 1.36 (dddd, J = 12.3, 9.9, 8.0, 2.3 Hz, 1H), 1.32 – 1.21 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.69 (t, J = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.6, 142.8, 134.0, 132.2, 129.0, 128.4, 126.3, 125.8, 125.4, 125.1, 125.0, 122.0, 52.5, 49.4, 48.1, 45.4, 42.8, 41.1, 39.6, 29.4, 24.5, 22.4, 21.0, 11.5, 11.0. **HRMS** (ESI): calcd for C₂₄H₃₃NO [M+H]⁺ : 350.2478, found: 350.2478.



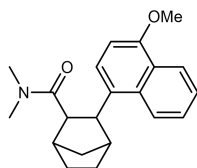
N,N-dimethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**32e**)

The representative general procedure mentioned above was followed. The desired product **32e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a colorless oil in 70% yield (41.0 mg). **¹H NMR** (400 MHz, CDCl₃): δ 8.23 (d, J = 8.2 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.52 – 7.36 (m, 4H), 4.15 (d, J = 5.0 Hz, 1H), 3.11 – 3.04 (m, 1H), 2.98 (s, 3H), 2.95 (s, 3H), 2.61 (d, J = 3.6 Hz, 1H), 2.56 (s, 1H), 2.01 – 1.92 (m, 1H), 1.74 (dt, J = 11.8, 4.4 Hz, 2H), 1.51 (dd, J = 9.8, 1.5 Hz, 1H), 1.25 (s, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 173.0, 142.6, 134.0, 132.3, 128.4, 126.4, 125.8, 125.5, 125.1, 124.9, 122.1, 52.2, 45.0, 43.3, 40.2, 39.4, 37.2, 36.0, 29.7, 29.6, 24.4. **HRMS** (ESI): calcd for C₂₀H₂₃NO [M+H]⁺ : 294.1852, found: 294.1852.



N,N-dimethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**33e**)

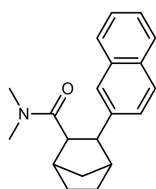
The representative general procedure mentioned above was followed. The desired product **33e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.51) as a colorless oil in 64% yield (39.3 mg). **¹H NMR** (400 MHz, CDCl₃): δ 8.29 (dt, J = 7.3, 2.7 Hz, 1H), 8.06 – 7.99 (m, 1H), 7.59 – 7.49 (m, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.30 (s, 1H), 4.16 (d, J = 5.1 Hz, 1H), 3.15 – 3.07 (m, 1H), 3.03 (s, 3H), 2.99 (s, 3H), 2.70 (s, 3H), 2.64 (d, J = 3.8 Hz, 1H), 2.60 (s, 1H), 2.01 (d, J = 9.7 Hz, 1H), 1.86 – 1.61 (m, 4H), 1.54 (dd, J = 9.7, 1.5 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 173.2, 140.8, 133.1, 132.3, 132.2, 125.9, 125.5, 125.4, 125.3, 124.5, 121.8, 52.3, 45.0, 43.3, 40.2, 39.4, 37.2, 36.0, 29.5, 24.4, 19.4. **HRMS** (ESI): calcd for C₂₁H₂₅NO [M+H]⁺ : 308.2009, found: 308.2009.



3-(4-methoxynaphthalen-1-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**34e**)

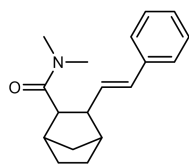
The representative general procedure mentioned above was followed. The desired product **34e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc

(2:1, R_f = 0.51) as a colorless oil in 65% yield (42.0 mg). **¹H NMR** (400 MHz, $CDCl_3$): δ 8.33 – 8.26 (m, 1H), 8.19 (d, J = 7.9 Hz, 1H), 7.50 (dddd, J = 18.5, 8.0, 6.8, 1.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 5.33 (s, 1H), 4.07 (d, J = 5.1 Hz, 1H), 4.01 (s, 3H), 3.10 – 3.04 (m, 1H), 3.01 (s, 3H), 2.97 (s, 3H), 2.61 (d, J = 3.5 Hz, 1H), 2.58 (s, 1H), 1.99 (d, J = 9.7 Hz, 1H), 1.76 (dt, J = 11.5, 4.2 Hz, 2H), 1.71 – 1.65 (m, 1H), 1.53 (dd, J = 9.7, 1.5 Hz, 1H); **¹³C NMR** (100 MHz, $CDCl_3$): δ 173.2, 153.8, 134.6, 133.0, 126.3, 126.0, 124.8, 124.7, 122.1, 121.8, 102.8, 55.4, 52.4, 44.6, 43.2, 40.2, 39.4, 37.2, 36.0, 29.5, 24.4. **HRMS** (ESI): calcd for $C_{21}H_{25}NO_2$ $[M+H]^+$: 324.1958, found: 324.1958.



N,N-dimethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**35e**)

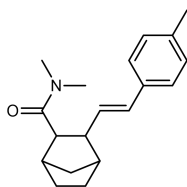
The representative general procedure mentioned above was followed. The desired product **35e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, R_f = 0.51) as a colorless oil in 65% yield (42.0 mg). **¹H NMR** (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.5 Hz, 1H), 7.67 (s, 1H), 7.54 – 7.41 (m, 2H), 7.37 (dd, J = 8.5, 1.7 Hz, 1H), 3.74 (d, J = 5.5 Hz, 1H), 3.07 (s, 3H), 3.04 (s, 3H), 2.69 (d, J = 3.6 Hz, 1H), 2.63 (s, 1H), 1.98 (d, J = 9.8 Hz, 1H), 1.69 (dq, J = 12.0, 7.1, 5.8 Hz, 3H), 1.60 – 1.52 (m, 1H), 1.29 (s, 2H); **¹³C NMR** (100 MHz, $CDCl_3$): δ 172.7, 144.3, 133.5, 131.8, 128.0, 127.6, 127.5, 126.5, 125.9, 125.1, 124.0, 54.5, 48.8, 42.2, 40.4, 39.4, 37.2, 36.0, 30.0, 29.7, 23.8. **HRMS** (ESI): calcd for $C_{20}H_{23}NO$ $[M+H]^+$: 294.1852, found: 294.1852.



(*E*)-*N,N*-dimethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**36e**)

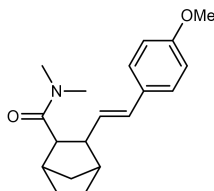
The representative general procedure mentioned above was followed. The desired product **36e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc

(5:1, R_f = 0.53) as a colorless oil in 65% yield (35.0 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 15.8, 8.3 Hz, 1H), 3.09 (s, 3H), 3.00 (s, 3H), 2.82 – 2.73 (m, 1H), 2.54 (s, 1H), 2.26 (d, J = 3.9 Hz, 1H), 1.76 (dt, J = 9.8, 1.6 Hz, 1H), 1.57 (dddd, J = 19.3, 13.5, 9.3, 4.0 Hz, 2H), 1.48 – 1.25 (m, 4H); **^{13}C NMR** (100 MHz, CDCl_3): δ 172.6, 137.7, 134.8, 128.4, 128.3, 126.8, 126.0, 52.2, 47.4, 43.0, 40.1, 38.6, 37.2, 35.8, 29.0, 23.9. **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{23}\text{NO}$ $[\text{M}+\text{H}]^+$: 270.1852, found: 270.1852.



(*E*)-*N,N*-dimethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**37e**)

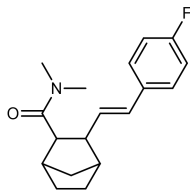
The representative general procedure mentioned above was followed. The desired product **37e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.52) as a colorless oil in 56% yield (31.7 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.25 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 6.36 (d, J = 15.8 Hz, 1H), 6.08 (dd, J = 15.8, 8.3 Hz, 1H), 3.08 (s, 3H), 2.99 (s, 3H), 2.79 – 2.72 (m, 1H), 2.53 (s, 1H), 2.34 (s, 3H), 2.24 (d, J = 3.9 Hz, 1H), 1.79 – 1.70 (m, 1H), 1.56 (tdd, J = 15.4, 11.6, 6.1 Hz, 2H), 1.47 – 1.34 (m, 3H), 1.38 – 1.23 (m, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 172.7, 136.5, 134.9, 133.8, 129.1, 128.1, 125.8, 52.3, 47.4, 43.1, 40.1, 38.6, 37.2, 29.0, 23.9, 21.1. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{25}\text{NO}$ $[\text{M}+\text{H}]^+$: 284.2009, found: 284.2009.



(*E*)-3-(4-methoxystyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**38e**)

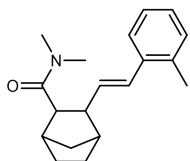
The representative general procedure mentioned above was followed. The desired product **38e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, R_f = 0.57) as a colorless oil in 56% yield (33.5 mg). **^1H NMR** (400 MHz, CDCl_3): δ 7.28

(dd, $J = 8.5, 1.8$ Hz, 2H), 6.91 – 6.80 (m, 2H), 6.33 (d, $J = 15.8$ Hz, 1H), 5.99 (dd, $J = 15.8, 8.3$ Hz, 1H), 3.81 (s, 3H), 3.08 (s, 3H), 2.99 (s, 3H), 2.78 – 2.66 (m, 1H), 2.52 (s, 1H), 2.23 (d, $J = 4.4$ Hz, 1H), 1.78 – 1.69 (m, 1H), 1.55 (dddd, $J = 19.1, 13.5, 9.2, 4.0$ Hz, 2H), 1.40 (dd, $J = 6.3, 1.6$ Hz, 3H), 1.28 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.7, 158.6, 132.7, 130.5, 127.7, 127.0, 113.9, 55.3, 52.4, 47.4, 43.1, 40.0, 38.6, 37.2, 35.8, 29.0, 23.9. HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 300.1958, found: 300.1958.



(*E*)-3-(4-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**39e**)

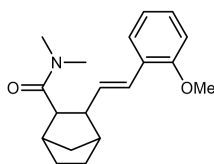
The representative general procedure mentioned above was followed. The desired product **39e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.51$) as a colorless oil in 50% yield (28.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.30 (dt, $J = 8.7, 2.4$ Hz, 2H), 7.04 – 6.94 (m, 2H), 6.35 (d, $J = 15.8$ Hz, 1H), 6.04 (dd, $J = 15.8, 8.4$ Hz, 1H), 3.09 (s, 3H), 2.99 (s, 3H), 2.75 (t, $J = 4.0$ Hz, 1H), 2.54 (s, 1H), 2.23 (d, $J = 3.9$ Hz, 1H), 1.78 – 1.70 (m, 2H), 1.66 – 1.47 (m, 2H), 1.47 – 1.22 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.9 (d, $J = 245.7$ Hz), 134.5, 133.9, 127.3 (d, $J = 7.8$ Hz), 127.2, 115.3 (d, $J = 21.5$ Hz), 52.3, 47.3, 43.0, 40.1, 38.6, 37.2, 35.8, 29.0, 23.9; ^{19}F NMR (376 MHz, CDCl_3): δ -115.73. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{22}\text{FNO}$ $[\text{M}+\text{H}]^+$: 288.1758, found: 288.1758.



(*E*)-*N,N*-dimethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**40e**)

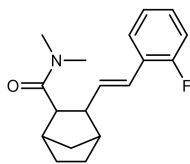
The representative general procedure mentioned above was followed. The desired product **40e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.54$) as a colorless oil in 58% yield (32.5 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, $J = 6.2$ Hz, 1H), 7.21 – 7.09 (m, 3H), 6.59 (d, $J = 15.6$ Hz, 1H), 6.02 (dd, $J = 15.7, 8.3$ Hz, 1H),

3.10 (s, 3H), 3.01 (s, 3H), 2.82 – 2.75 (m, 1H), 2.55 (s, 1H), 2.35 (s, 3H), 2.27 (d, $J = 3.1$ Hz, 1H), 1.77 (d, $J = 9.8$ Hz, 1H), 1.67 – 1.51 (m, 2H), 1.48 – 1.26 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.7, 136.8, 136.3, 135.2, 130.2, 126.8, 126.0, 125.9, 125.2, 52.2, 47.6, 43.3, 40.1, 38.6, 37.2, 35.9, 28.9, 24.0, 19.9. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{25}\text{NO}$ $[\text{M}+\text{H}]^+$: 284.2009, found: 284.2009.



(E)-3-(2-methoxystyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**41e**)

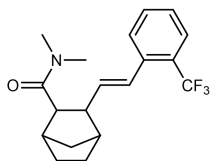
The representative general procedure mentioned above was followed. The desired product **41e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.49$) as a colorless oil in 61% yield (36.5 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.42 (dd, $J = 7.6, 1.5$ Hz, 1H), 7.24 – 7.16 (m, 1H), 6.92 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 6.73 (d, $J = 15.9$ Hz, 1H), 6.15 (dd, $J = 16.0, 8.2$ Hz, 1H), 3.86 (s, 3H), 3.10 (s, 3H), 3.00 (s, 3H), 2.87 – 2.76 (m, 1H), 2.54 (s, 1H), 2.28 (d, $J = 3.7$ Hz, 1H), 1.77 (d, $J = 9.7$ Hz, 1H), 1.56 (dtd, $J = 20.8, 11.7, 10.4, 5.1$ Hz, 2H), 1.49 – 1.36 (m, 3H), 1.34 – 1.26 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.8, 156.4, 135.4, 127.8, 126.7, 126.2, 122.9, 120.5, 110.8, 55.4, 52.1, 47.7, 43.2, 40.1, 38.6, 37.2, 35.8, 28.9, 24.0. **HRMS** (ESI): calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 300.1958, found: 300.1958.



(E)-3-(2-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**42e**)

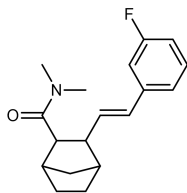
The representative general procedure mentioned above was followed. The desired product **42e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.49$) as a colorless oil in 57% yield (32.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.40 (td, $J = 7.7, 1.6$ Hz, 1H), 7.15 (dtd, $J = 9.5, 5.1, 1.7$ Hz, 1H), 7.08 – 7.03 (m, 1H), 7.04 – 6.98 (m, 1H), 6.51 (d, $J = 16.1$ Hz, 1H), 6.22 (dd, $J = 16.0, 8.1$ Hz, 1H), 3.08 (s, 3H), 2.98 (s, 3H), 2.80 –

2.74 (m, 1H), 2.53 (s, 1H), 2.26 (d, $J = 3.9$ Hz, 1H), 1.73 (d, $J = 9.8$ Hz, 1H), 1.55 (ddp, $J = 24.0$, 11.9, 6.1, 5.6 Hz, 2H), 1.44 – 1.37 (m, 3H), 1.34 – 1.22 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.5, 160.1 (d, $J = 248.5$ Hz), 137.7, 128.0 (d, $J = 8.3$ Hz), 127.2, 125.5, 125.4, 123.9 (d, $J = 3.4$ Hz), 120.9, 115.7 (d, $J = 22.3$ Hz), 52.0, 47.8, 43.0, 40.2, 38.6, 37.3, 35.9, 28.9, 24.0; ^{19}F NMR (376 MHz, CDCl_3): δ -118.29. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{22}\text{FNO}$ $[\text{M}+\text{H}]^+$: 288.1758, found: 288.1758.



(*E*)-*N,N*-dimethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**43e**)

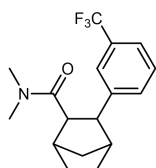
The representative general procedure mentioned above was followed. The desired product **43e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.43$) as a colorless oil in 53% yield (35.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.59 (dd, $J = 15.3$, 7.8 Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.34 – 7.26 (m, 1H), 6.73 (d, $J = 15.7$ Hz, 1H), 6.13 (dd, $J = 15.7$, 7.2 Hz, 1H), 3.10 (s, 3H), 3.00 (s, 3H), 2.85 – 2.77 (m, 1H), 2.55 (s, 1H), 2.31 (d, $J = 3.8$ Hz, 1H), 1.71 (d, $J = 9.8$ Hz, 1H), 1.58 (dddd, $J = 20.0$, 14.9, 11.8, 6.3 Hz, 2H), 1.46 – 1.36 (m, 3H), 1.30 (dd, $J = 15.6$, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.5, 139.4, 137.1, 131.7, 126.8 (d, $J = 61.9$ Hz), 125.6 (d, $J = 5.7$ Hz), 124.1, 121.6 (d, $J = 283.4$ Hz), 51.6, 47.1, 42.7, 40.2, 38.5, 37.2, 35.9, 28.9, 23.9; ^{19}F NMR (376 MHz, CDCl_3): δ -59.58. HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{22}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 338.1726, found: 338.1726.



(*E*)-3-(3-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**44e**)

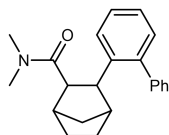
The representative general procedure mentioned above was followed. The desired product **44e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.47$) as a colorless oil in 49% yield (38.1 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.25

(td, $J = 7.9, 6.2$ Hz, 1H), 7.09 (d, $J = 7.8$ Hz, 1H), 7.07 – 7.02 (m, 1H), 6.89 (td, $J = 8.2, 2.2$ Hz, 1H), 6.36 (d, $J = 15.8$ Hz, 1H), 6.14 (dd, $J = 15.8, 8.3$ Hz, 1H), 3.09 (s, 3H), 2.99 (s, 3H), 2.75 (t, $J = 4.0$ Hz, 1H), 2.54 (s, 1H), 2.24 (d, $J = 3.9$ Hz, 1H), 1.73 (d, $J = 9.8$ Hz, 1H), 1.66 – 1.47 (m, 2H), 1.45 – 1.37 (m, 3H), 1.34 – 1.24 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.5, 163.1 (d, $J = 244.7$ Hz), 140.2, 136.2, 129.8 (d, $J = 8.4$ Hz), 127.4, 121.9 (d, $J = 2.4$ Hz), 113.7, 113.5, 112.4, 112.2, 52.2, 47.3, 42.9, 40.1, 38.6, 37.2, 35.8, 29.0, 23.9; ^{19}F NMR (376 MHz, CDCl_3): δ -113.87. **HRMS** (ESI): calcd for $\text{C}_{18}\text{H}_{22}\text{FNO}$ $[\text{M}+\text{H}]^+$: 288.1758, found: 288.1758.



N,N-dimethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**45e**)

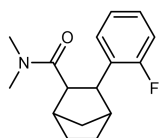
The representative general procedure mentioned above was followed. The desired product **45e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.49$) as a colorless oil in 45% yield (28.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.48 (s, 1H), 7.42 (q, $J = 7.1$ Hz, 3H), 3.64 (d, $J = 5.5$ Hz, 1H), 3.07 (s, 3H), 3.02 (s, 3H), 2.95 (t, $J = 4.7$ Hz, 1H), 2.62 (s, 1H), 2.55 (d, $J = 3.4$ Hz, 1H), 1.85 (d, $J = 9.9$ Hz, 1H), 1.75 – 1.55 (m, 2H), 1.55 – 1.39 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.2, 147.7, 130.69, 130.61 (d, $J = 31.7$ Hz), 128.8, 124.32 (d, $J = 272.5$ Hz), 122.5 (d, $J = 3.8$ Hz), 54.6, 48.6, 42.3, 40.4, 39.4, 37.2, 36.0, 29.9, 23.7; ^{19}F NMR (376 MHz, CDCl_3): δ -62.43. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{20}\text{F}_3\text{NO}$ $[\text{M}+\text{H}]^+$: 312.1570, found: 312.1570.



3-([1,1'-biphenyl]-2-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**46e**)

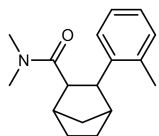
The representative general procedure mentioned above was followed. The desired product **46e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.55$) as a colorless oil in 47% yield (30.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.41 (t, $J = 7.5$ Hz, 3H), 7.37 – 7.29 (m, 4H), 7.23 (td, $J = 7.3, 1.2$ Hz, 1H), 7.19 (dd, $J = 7.5, 1.7$ Hz,

1H), 3.70 (d, $J = 5.2$ Hz, 1H), 3.23 – 3.06 (m, 1H), 2.96 (s, 3H), 2.77 (s, 3H), 2.47 (s, 1H), 2.31 (d, $J = 3.9$ Hz, 1H), 1.87 (d, $J = 9.8$ Hz, 1H), 1.44 (ddd, $J = 11.2, 9.4, 4.6$ Hz, 1H), 1.35 – 1.29 (m, 3H), 1.27 (d, $J = 6.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.9, 143.8, 142.9, 142.0, 130.6, 129.4, 127.9, 127.1, 126.7, 125.6, 125.4, 51.5, 45.3, 44.2, 40.2, 38.4, 37.1, 35.7, 29.1, 24.1. **HRMS** (ESI): calcd for $\text{C}_{22}\text{H}_{25}\text{NO}$ $[\text{M}+\text{H}]^+$: 320.2009, found: 320.2009.



3-(2-fluorophenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**47e**)

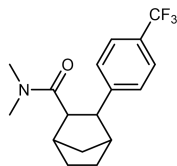
The representative general procedure mentioned above was followed. The desired product **47e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.56$) as a colorless oil in 44% yield (23.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.39 (ddd, $J = 3.8, 2.5, 1.8$ Hz, 1H), 7.20 (td, $J = 7.5, 1.1$ Hz, 1H), 7.08 – 7.05 (m, 1H), 6.97 (ddd, $J = 10.7, 8.0, 1.4$ Hz, 1H), 3.68 (d, $J = 5.2$ Hz, 1H), 3.14 (s, 3H), 3.04 (s, 3H), 2.99 (s, 2H), 2.94 (d, $J = 1.6$ Hz, 2H), 2.54 (dd, $J = 3.8, 2.3$ Hz, 1H), 1.77 (dt, $J = 9.8, 1.9$ Hz, 1H), 1.67 (s, 1H), 1.48 – 1.40 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 172.5, 133.3, 133.1, 131.1 (d, $J = 8.1$ Hz), 129.0, 125.9 (d, $J = 253.1$ Hz), 123.6 (d, $J = 3.5$ Hz), 115.7 (d, $J = 21.6$ Hz), 115.4 (d, $J = 22.5$ Hz), 52.0, 43.0, 41.5, 40.2, 38.9, 37.2, 35.9, 34.9, 29.2, 24.2; ^{19}F NMR (376 MHz, CDCl_3): δ -113.93. **HRMS** (ESI): calcd for $\text{C}_{16}\text{H}_{20}\text{FNO}$ $[\text{M}+\text{H}]^+$: 262.1602, found: 262.1602.



N,N-dimethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**48e**)

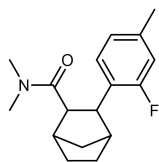
The representative general procedure mentioned above was followed. The desired product **48e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.53$) as a colorless oil in 49% yield (25.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.22 – 7.16 (m, 1H), 7.08 (dd, $J = 11.1, 7.1$ Hz, 2H), 7.03 – 6.98 (m, 1H), 3.54 (d, $J = 5.4$ Hz, 1H), 3.02 (t, $J = 5.0$ Hz, 1H), 2.98 (s, 3H), 2.88 (s, 3H), 2.48 (d, $J = 4.5$ Hz, 1H), 2.26 (s, 1H), 2.23 (s, 3H), 1.83 (d, $J = 9.9$ Hz, 1H), 1.70 (d, $J = 4.4$ Hz, 1H), 1.62 – 1.50 (m, 2H), 1.38 – 1.31 (m, 2H); ^{13}C

NMR (100 MHz, CDCl₃): δ 172.9, 144.6, 137.1, 130.5, 125.6, 125.2, 51.4, 45.6, 43.6, 40.1, 38.9, 37.3, 35.9, 29.8, 24.2, 20.5. **HRMS** (ESI): calcd for C₁₇H₂₃NO [M+H]⁺ : 258.1852, found: 258.1852.



N,N-dimethyl-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**49e**)

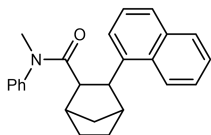
The representative general procedure mentioned above was followed. The desired product **49e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, R_f = 0.55) as a colorless oil in 46% yield (28.6 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 3.54 (d, *J* = 5.7 Hz, 1H), 2.96 (s, 3H), 2.92 (s, 3H), 2.82 (t, *J* = 4.9 Hz, 1H), 2.51 (s, 1H), 2.47 (d, *J* = 4.1 Hz, 1H), 1.74 (d, *J* = 9.9 Hz, 1H), 1.64 (s, 1H), 1.61 – 1.54 (m, 1H), 1.49 (dd, *J* = 12.2, 6.2 Hz, 1H), 1.45 – 1.40 (m, 1H), 1.38 (d, *J* = 6.1 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.3, 150.9, 127.9 (d, *J* = 32.6 Hz), 127.1, 125.5 (d, *J* = 35.1 Hz), 125.3, 125.3, 124.1 (d, *J* = 225.5 Hz), 54.8, 48.5, 41.9, 40.4, 39.4, 37.2, 36.0, 29.9, 23.7; **¹⁹F NMR** (376 MHz, CDCl₃): δ -62.30. **HRMS** (ESI): calcd for C₁₇H₂₀F₃NO [M+H]⁺ : 312.1570, found: 312.1570.



3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**50e**)

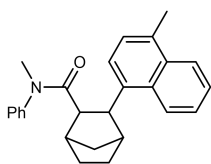
The representative general procedure mentioned above was followed. The desired product **50e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, R_f = 0.55) as a colorless oil in 43% yield (23.7 mg). **¹H NMR** (400 MHz, CDCl₃): δ 7.17 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 11.5 Hz, 1H), 3.67 (d, *J* = 5.0 Hz, 1H), 3.07 (s, 3H), 3.03 (s, 3H), 2.56 (s, 2H), 2.33 (s, 3H), 1.84 – 1.76 (m, 1H), 1.67 (ddd, *J* = 9.1, 6.5, 4.5 Hz, 2H), 1.60 – 1.52 (m, 1H), 1.49 – 1.42 (m, 1H), 1.30 (s, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.7, 161.0 (d, *J* = 245.5 Hz), 145.9, 137.4, 130.1 (d, *J* = 15.1 Hz), 126.8, 124.2 (d, *J*

= 2.8 Hz), 120.3, 116.1 (d, $J = 22.3$ Hz), 52.2, 42.8, 41.6, 40.3, 38.9, 37.2, 35.9, 29.2, 24.2, 20.8; **^{19}F NMR** (376 MHz, CDCl_3): δ -114.97. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{22}\text{FNO}$ $[\text{M}+\text{H}]^+$: 276.1758, found: 276.1758.



N-methyl-3-(naphthalen-1-yl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**51e**)

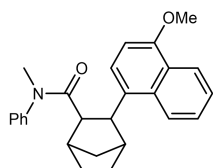
The representative general procedure mentioned above was followed. The desired product **51e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.45$) as a colorless oil in 67% yield (47.6 mg). **^1H NMR** (400 MHz, CDCl_3) δ 8.24 (d, $J = 8.5$ Hz, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.63 – 7.55 (m, 1H), 7.55 – 7.49 (m, 1H), 7.45 (dd, $J = 4.9, 1.7$ Hz, 1H), 7.35 (d, $J = 7.4$ Hz, 1H), 7.28 – 7.25 (m, 3H), 7.14 – 7.08 (m, 1H), 6.89 (s, 1H), 4.06 (d, $J = 5.3$ Hz, 1H), 3.30 (s, 3H), 2.88 (d, $J = 4.2$ Hz, 1H), 2.52 (d, $J = 3.1$ Hz, 1H), 2.22 (s, 1H), 1.95 (d, $J = 9.7$ Hz, 1H), 1.87 (dt, $J = 11.7, 5.9$ Hz, 1H), 1.75 (tt, $J = 12.0, 4.2$ Hz, 1H), 1.58 (d, $J = 9.6$ Hz, 1H), 1.46 (t, $J = 11.9$ Hz, 1H), 1.30 (s, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 173.6, 144.1, 143.4, 141.9, 134.1, 132.3, 129.6, 129.0, 128.6, 128.4, 127.7, 126.3, 125.7, 125.5, 125.1, 124.9, 121.8, 51.6, 46.1, 43.5, 41.4, 39.3, 38.0, 29.7, 24.1. **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{25}\text{NO}$ $[\text{M}+\text{H}]^+$: 356.2009, found: 356.2009.



N-methyl-3-(4-methylnaphthalen-1-yl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**52e**)

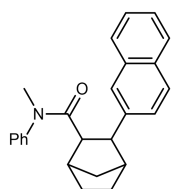
The representative general procedure mentioned above was followed. The desired product **52e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.48$) as a colorless oil in 59% yield (43.6 mg). **^1H NMR** (400 MHz, CDCl_3): δ 8.26 – 8.17 (m, 1H), 7.99 (dd, $J = 7.1, 2.4$ Hz, 1H), 7.53 (ddt, $J = 10.1, 6.7, 3.4$ Hz, 2H), 7.31 – 7.22 (m, 3H), 7.15 (d, $J = 7.3$ Hz, 1H), 6.94 (d, $J = 7.3$ Hz, 1H), 6.88 (s, 2H), 4.00 (d, $J = 5.2$ Hz, 1H), 3.26 (s, 3H), 2.86 (t, $J = 4.2$ Hz, 1H), 2.64 (s, 3H), 2.45 (d, $J = 3.3$ Hz, 1H), 2.17 (s, 1H), 1.97 –

1.78 (m, 2H), 1.70 (ddt, $J = 11.9, 8.0, 4.1$ Hz, 1H), 1.51 (d, $J = 9.6$ Hz, 1H), 1.45 – 1.37 (m, 1H), 1.25 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.6, 144.1, 140.0, 133.1, 132.3, 132.1, 129.6, 129.2, 128.8, 127.7, 125.8, 125.3, 124.6, 121.5, 51.4, 45.9, 43.6, 41.4, 39.2, 38.0, 29.7, 29.6, 27.1, 24.2. **HRMS** (ESI): calcd for $\text{C}_{26}\text{H}_{27}\text{NO}$ $[\text{M}+\text{H}]^+$: 370.2165, found: 370.2165.



3-(4-methoxynaphthalen-1-yl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**53e**)

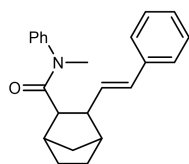
The representative general procedure mentioned above was followed. The desired product **53e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.43$) as a colorless oil in 58% yield (44.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 8.32 – 8.25 (m, 1H), 8.13 (d, $J = 8.5$ Hz, 1H), 7.60 – 7.52 (m, 1H), 7.52 – 7.44 (m, 1H), 7.24 (dd, $J = 5.6, 2.3$ Hz, 3H), 6.95 (d, $J = 8.0$ Hz, 1H), 6.89 – 6.80 (m, 2H), 6.64 (d, $J = 8.0$ Hz, 1H), 3.95 (s, 3H), 3.92 (d, $J = 5.3$ Hz, 1H), 3.26 (s, 3H), 2.80 (t, $J = 4.1$ Hz, 1H), 2.45 (d, $J = 3.4$ Hz, 1H), 2.16 (s, 1H), 2.00 – 1.85 (m, 1H), 1.84 – 1.76 (m, 1H), 1.69 (tt, $J = 12.1, 4.1$ Hz, 1H), 1.51 (d, $J = 9.4$ Hz, 1H), 1.44 – 1.36 (m, 1H), 1.26 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.7, 153.7, 144.2, 133.9, 133.1, 129.6, 127.8, 126.3, 126.1, 124.6, 122.3, 121.6, 102.8, 55.4, 51.7, 45.7, 43.4, 41.4, 39.3, 38.1, 29.6, 27.1, 24.2. **HRMS** (ESI): calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 386.2115, found: 386.2115.



N-methyl-3-(naphthalen-2-yl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**54e**)

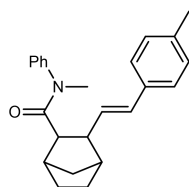
The representative general procedure mentioned above was followed. The desired product **54e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.55$) as a colorless oil in 51% yield (36.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, $J = 7.7$ Hz, 1H), 7.73 (t, $J = 7.7$ Hz, 2H), 7.43 (q, $J = 7.1$ Hz, 3H), 7.33 (p, $J = 6.8$ Hz, 3H), 7.26

(d, $J = 1.5$ Hz, 1H), 7.10 (d, $J = 7.3$ Hz, 1H), 3.58 (d, $J = 5.7$ Hz, 1H), 3.30 (s, 3H), 2.91 (t, $J = 4.9$ Hz, 1H), 2.51 (s, 1H), 2.11 (d, $J = 4.8$ Hz, 1H), 1.64 (d, $J = 7.8$ Hz, 4H), 1.50 (d, $J = 9.9$ Hz, 1H), 1.26 (d, $J = 4.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.3, 144.1, 143.7, 133.4, 131.81, 129.7, 127.9, 127.8, 127.6, 127.5, 126.8, 125.9, 125.1, 123.8, 53.3, 49.7, 42.8, 41.4, 39.1, 38.1, 29.9, 23.7. **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{25}\text{NO}$ $[\text{M}+\text{H}]^+$: 356.2009, found: 356.2009.



(E)-N-methyl-N-phenyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (55e)

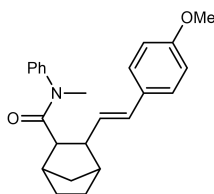
The representative general procedure mentioned above was followed. The desired product **55e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.52$) as a colorless oil in 61% yield (40.4 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.37 (dt, $J = 17.5, 7.0$ Hz, 4H), 7.29 – 7.26 (m, 3H), 7.18 (t, $J = 7.0$ Hz, 3H), 6.29 (d, $J = 15.8$ Hz, 1H), 5.96 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.26 (s, 3H), 3.01 – 2.89 (m, 1H), 2.54 (s, 1H), 2.11 (s, 1H), 2.02 (s, 1H), 1.61 (dd, $J = 14.6, 4.8$ Hz, 1H), 1.57 – 1.47 (m, 2H), 1.32 (dd, $J = 15.2, 7.5$ Hz, 2H), 1.15 (d, $J = 9.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.1, 144.2, 137.8, 134.6, 129.7, 128.5, 128.3, 127.9, 126.9, 126.0, 51.9, 49.3, 43.3, 40.7, 38.6, 38.1, 28.9, 23.8. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{25}\text{NO}$ $[\text{M}+\text{H}]^+$: 332.2009, found: 332.2009.



(E)-N-methyl-3-(4-methylstyryl)-N-phenylbicyclo[2.2.1]heptane-2-carboxamide (56e)

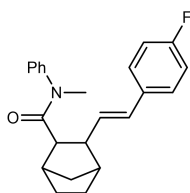
The representative general procedure mentioned above was followed. The desired product **56e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.57$) as a colorless oil in 59% yield (40.7 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.39 (dd, $J = 8.0, 6.6$ Hz, 2H), 7.35 – 7.29 (m, 1H), 7.17 (t, $J = 8.0$ Hz, 4H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.25 (d, $J = 15.8$ Hz, 1H), 5.90 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.26 (s, 3H), 2.99 – 2.85 (m, 1H), 2.52

(s, 1H), 2.32 (s, 3H), 2.10 (s, 1H), 2.01 (s, 1H), 1.71 – 1.57 (m, 1H), 1.55 – 1.47 (m, 2H), 1.32 (t, $J = 9.6$ Hz, 2H), 1.15 (d, $J = 9.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.2, 144.2, 136.6, 135.0, 133.6, 129.7, 129.2, 128.1, 127.9, 127.8, 125.9, 52.0, 48.2, 43.3, 41.1, 38.6, 38.1, 29.0, 23.8, 21.2. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{NO}$ $[\text{M}+\text{H}]^+$: 346.2165, found: 346.2165.



(E)-3-(4-methoxystyryl)-N-methyl-N-phenylbicyclo[2.2.1]heptane-2-carboxamide (57e)

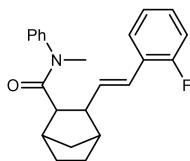
The representative general procedure mentioned above was followed. The desired product **57e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.53$) as a colorless oil in 57% yield (41.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.39 (dd, $J = 8.0, 6.6$ Hz, 2H), 7.34 (d, $J = 7.4$ Hz, 1H), 7.22 (d, $J = 8.6$ Hz, 2H), 7.17 (d, $J = 7.2$ Hz, 2H), 6.88 – 6.73 (m, 2H), 6.23 (d, $J = 15.8$ Hz, 1H), 5.82 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.80 (s, 3H), 3.26 (s, 3H), 2.88 (d, $J = 6.2$ Hz, 1H), 2.52 (s, 1H), 2.09 (s, 1H), 2.01 (s, 1H), 1.55 – 1.47 (m, 2H), 1.31 (dd, $J = 17.5, 6.9$ Hz, 3H), 1.14 (d, $J = 9.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.2, 158.7, 144.2, 132.5, 130.6, 129.6, 127.9, 127.8, 127.6, 127.1, 113.9, 55.3, 52.1, 48.2, 43.4, 41.1, 38.6, 38.0, 29.0, 23.8. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 362.2115, found: 362.2115.



(E)-3-(4-fluorostyryl)-N-methyl-N-phenylbicyclo[2.2.1]heptane-2-carboxamide (58e)

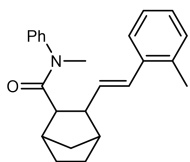
The representative general procedure mentioned above was followed. The desired product **58e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.53$) as a colorless oil in 53% yield (37.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.37 (dq, $J = 14.9, 7.6$ Hz, 4H), 7.24 (dd, $J = 8.8, 5.9$ Hz, 2H), 7.17 (d, $J = 7.5$ Hz, 2H), 6.97 (t, $J = 8.5$ Hz, 2H), 6.25 (d, $J = 16.0$ Hz, 1H), 5.87 (dd, $J = 15.8, 8.2$ Hz, 1H), 3.27 (s, 3H), 3.03 – 2.85

(m, 1H), 2.52 (d, $J = 4.3$ Hz, 1H), 2.09 (d, $J = 3.4$ Hz, 1H), 2.02 (d, $J = 4.5$ Hz, 1H), 1.76 (s, 1H), 1.59 (d, $J = 9.9$ Hz, 1H), 1.58 – 1.49 (m, 2H), 1.33 (d, $J = 10.0$ Hz, 1H), 1.15 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.1, 161.9 (d, $J = 245.7$ Hz), 144.1, 134.3, 133.9, 129.7, 127.9 (d, $J = 4.1$ Hz), 127.4, 127.4, 127.2, 115.3 (d, $J = 21.3$ Hz), 52.0, 48.1, 43.3, 41.1, 38.6, 38.1, 29.0, 23.8; ^{19}F NMR (376 MHz, CDCl_3): δ -115.70. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{24}\text{FNO}$ $[\text{M}+\text{H}]^+$: 350.1915, found: 350.1915.



(*E*)-3-(2-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**59e**)

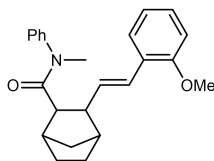
The representative general procedure mentioned above was followed. The desired product **59e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.56$) as a colorless oil in 49% yield (34.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.41 (t, $J = 7.4$ Hz, 2H), 7.35 (q, $J = 6.3$ Hz, 2H), 7.19 (d, $J = 7.4$ Hz, 2H), 7.14 (ddd, $J = 9.6, 4.6, 1.9$ Hz, 1H), 7.06 (d, $J = 7.5$ Hz, 1H), 7.03 – 6.93 (m, 1H), 6.42 (d, $J = 16.0$ Hz, 1H), 6.07 (dd, $J = 16.0, 7.6$ Hz, 1H), 3.27 (s, 3H), 2.93 (d, $J = 5.6$ Hz, 1H), 2.57 (s, 1H), 2.13 (s, 1H), 2.03 (s, 1H), 1.71 (s, 1H), 1.68 – 1.53 (m, 1H), 1.52 (s, 2H), 1.32 (d, $J = 10.1$ Hz, 1H), 1.15 (d, $J = 9.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.0, 160.0 (d, $J = 248.4$ Hz), 144.2, 137.3, 129.7, 128.0, 127.9, 127.9, 127.0 (d, $J = 4.0$ Hz), 125.6, 125.4, 123.9 (d, $J = 3.6$ Hz), 120.7, 115.6 (d, $J = 22.1$ Hz), 51.6, 48.4, 43.3, 41.1, 38.6, 38.0, 29.0, 23.8; ^{19}F NMR (376 MHz, CDCl_3): δ -118.49. HRMS (ESI): calcd for $\text{C}_{23}\text{H}_{24}\text{FNO}$ $[\text{M}+\text{H}]^+$: 350.1915, found: 350.1913.



(*E*)-*N*-methyl-3-(2-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**60e**)

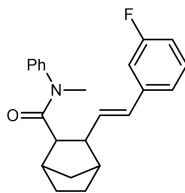
The representative general procedure mentioned above was followed. The desired product **60e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.51$) as a colorless oil in 51% yield (35.2 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.40 (t,

$J = 7.3$ Hz, 2H), 7.36 – 7.28 (m, 2H), 7.20 – 7.15 (m, 2H), 7.14 – 7.08 (m, 3H), 6.47 (d, $J = 15.7$ Hz, 1H), 5.84 (dd, $J = 15.7, 8.0$ Hz, 1H), 3.27 (s, 3H), 2.97 – 2.90 (m, 1H), 2.56 (s, 1H), 2.30 (s, 3H), 2.12 (s, 1H), 2.04 (s, 1H), 1.64 (d, $J = 7.8$ Hz, 1H), 1.59 – 1.51 (m, 2H), 1.23 (s, 3H), 1.16 (d, $J = 9.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.2, 144.2, 136.9, 136.1, 135.1, 130.2, 129.7, 127.7, 126.8, 125.9, 125.4, 51.9, 48.3, 43.3, 41.2, 38.6, 38.1, 28.9, 27.0, 23.8, 19.9. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{NO}$ $[\text{M}+\text{H}]^+$: 346.2165, found: 346.2165.



(E)-3-(2-methoxystyryl)-N-methyl-N-phenylbicyclo[2.2.1]heptane-2-carboxamide (61e)

The representative general procedure mentioned above was followed. The desired product **61e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (2:1, $R_f = 0.51$) as a colorless oil in 49% yield (35.4 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.39 (t, $J = 7.3$ Hz, 2H), 7.34 (d, $J = 7.3$ Hz, 2H), 7.19 (dd, $J = 6.1, 3.2$ Hz, 3H), 6.88 (t, $J = 7.5$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.63 (d, $J = 16.0$ Hz, 1H), 5.96 (dd, $J = 15.9, 7.8$ Hz, 1H), 3.83 (s, 3H), 3.27 (s, 3H), 2.99 – 2.83 (m, 1H), 2.57 (s, 1H), 2.13 (s, 1H), 2.02 (s, 1H), 1.79 – 1.59 (m, 1H), 1.58 – 1.50 (m, 2H), 1.42 – 1.25 (m, 2H), 1.20 – 1.09 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.3, 156.4, 144.3, 135.2, 129.6, 127.9, 126.9, 126.2, 122.7, 120.5, 110.8, 55.4, 51.8, 48.5, 43.4, 41.2, 38.6, 38.0, 29.5, 29.0, 27.1, 23.8. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 362.2115, found: 362.2115.

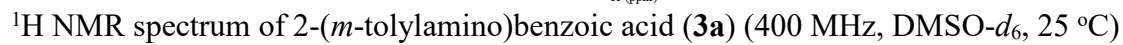


(E)-3-(3-fluorostyryl)-N-methyl-N-phenylbicyclo[2.2.1]heptane-2-carboxamide (62e)

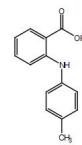
The representative general procedure mentioned above was followed. The desired product **62e** was isolated by column chromatography over silica gel and eluted with petroleum ether/EtOAc (5:1, $R_f = 0.52$) as a colorless oil in 46% yield (33.0 mg). ^1H NMR (400 MHz, CDCl_3): δ 7.41 (t,

$J = 7.3$ Hz, 2H), 7.35 (t, $J = 7.4$ Hz, 1H), 7.30 – 7.21 (m, 1H), 7.18 (t, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.99 (d, $J = 10.2$ Hz, 1H), 6.87 (td, $J = 8.5, 2.6$ Hz, 1H), 6.25 (d, $J = 15.7$ Hz, 1H), 5.97 (dd, $J = 15.8, 8.1$ Hz, 1H), 3.27 (s, 3H), 2.97 – 2.89 (m, 1H), 2.52 (t, $J = 4.5$ Hz, 1H), 2.10 (d, $J = 3.5$ Hz, 1H), 2.02 (d, $J = 4.5$ Hz, 1H), 1.59 (d, $J = 9.2$ Hz, 1H), 1.53 (q, $J = 6.5, 5.1$ Hz, 2H), 1.38 – 1.28 (m, 2H), 1.16 (d, $J = 9.9$ Hz, 1H); **^{13}C NMR** (100 MHz, CDCl_3): δ 172.9, 163.1 (d, $J = 244.8$ Hz), 144.1, 140.2, 135.9, 129.9 (d, $J = 8.6$ Hz), 129.7, 127.9, 127.3, 121.9 (d, $J = 2.8$ Hz), 113.6 (d, $J = 21.7$ Hz), 112.4, 112.2, 51.9, 48.1, 43.2, 41.1, 38.6, 38.1, 29.0, 23.8; **^{19}F NMR** (376 MHz, CDCl_3): δ -113.84. **HRMS** (ESI): calcd for $\text{C}_{23}\text{H}_{24}\text{FNO}$ $[\text{M}+\text{H}]^+$: 350.1915, found: 350.1915.

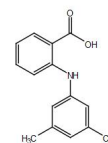
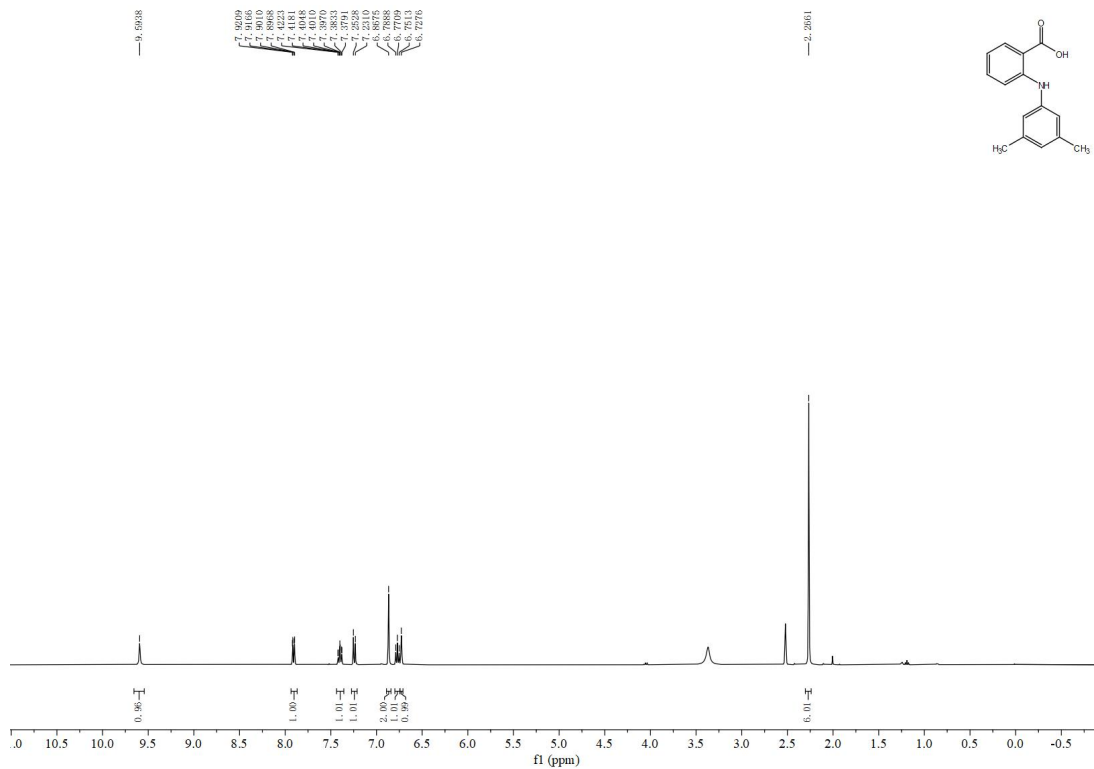
¹H NMR spectrum of 2-(*o*-tolylamino)benzoic acid (**2a**) (400 MHz, DMSO-*d*₆, 25 °C)



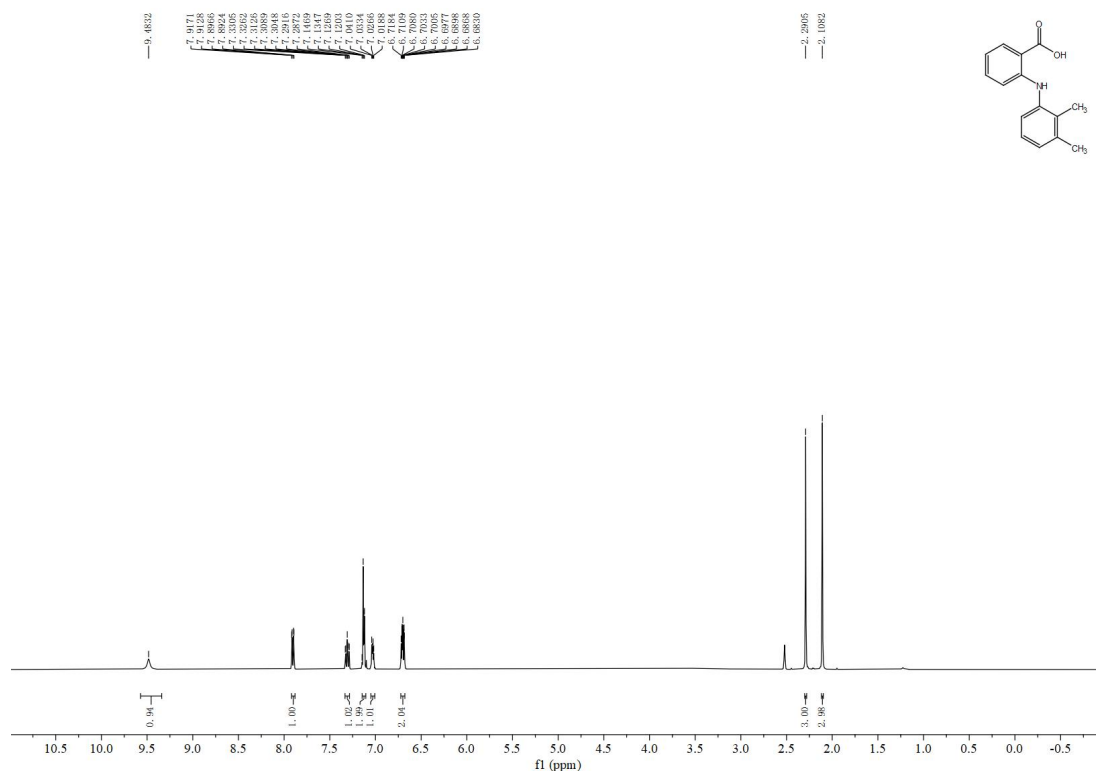
—9. 5024



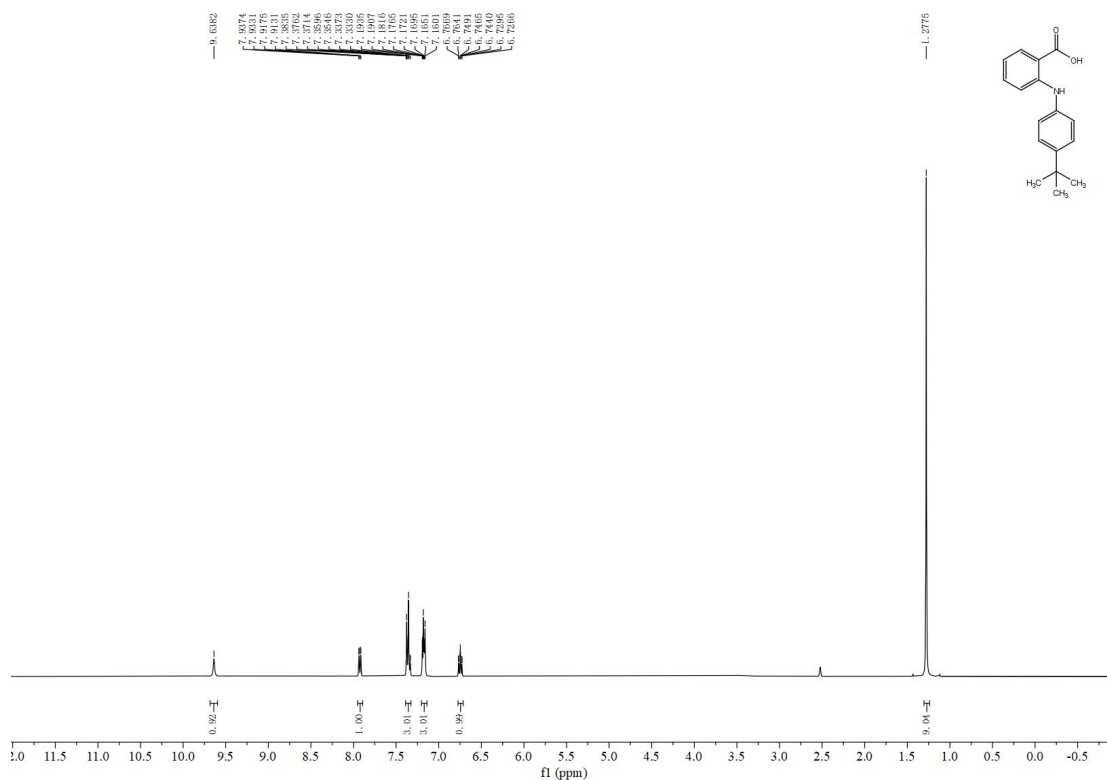
9. 5938



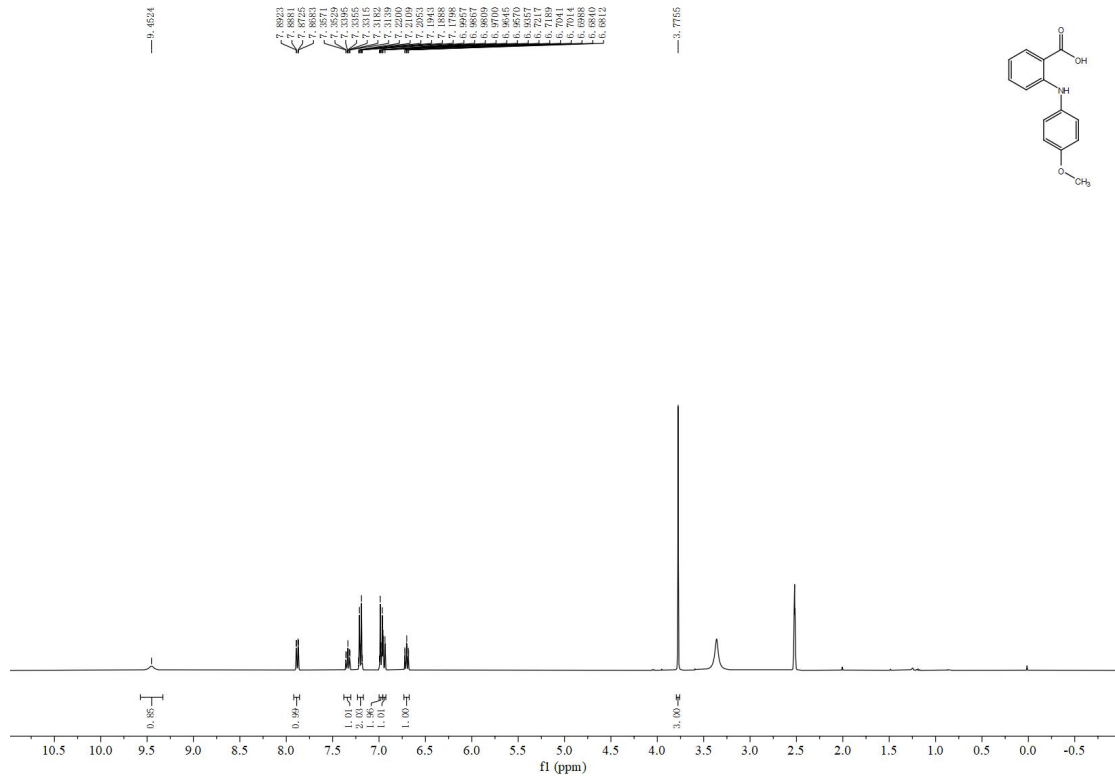
^1H NMR spectrum of 2-((2,3-dimethylphenyl)amino)benzoic acid (**6a**) (400 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$)



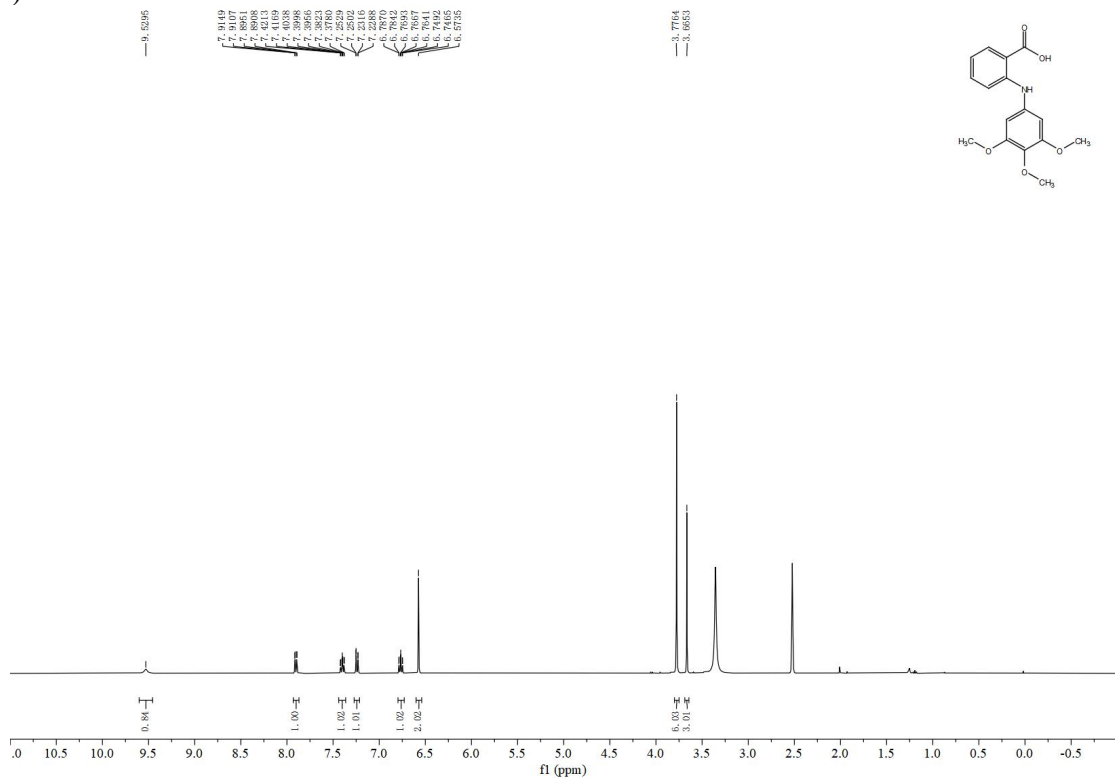
^1H NMR spectrum of 2-((4-(tert-butyl)phenyl)amino)benzoic acid (**7a**) (400 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$)



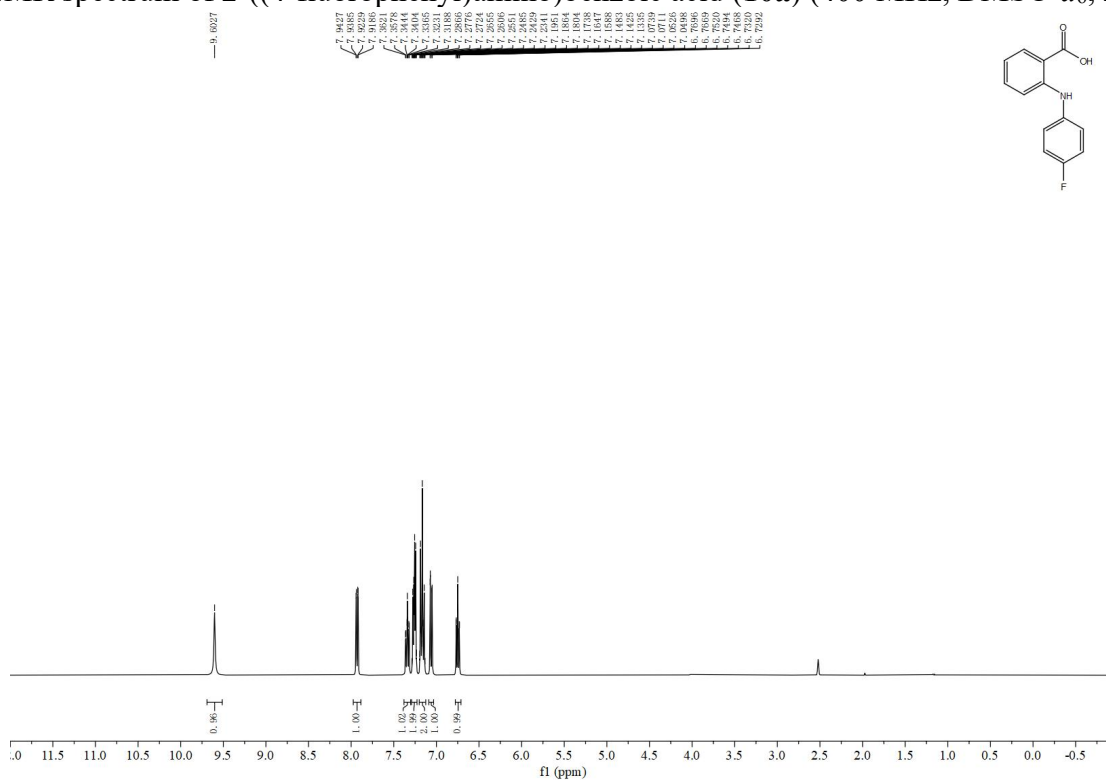
¹H NMR spectrum of 2-((4-methoxyphenyl)amino)benzoic acid (**8a**) (400 MHz, DMSO-*d*₆, 25 °C)



¹H NMR spectrum of 2-((3,4,5-trimethoxyphenyl)amino)benzoic acid (**9a**) (400 MHz, DMSO-*d*₆, 25 °C)



^1H NMR spectrum of 2-((4-fluorophenyl)amino)benzoic acid (**10a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)

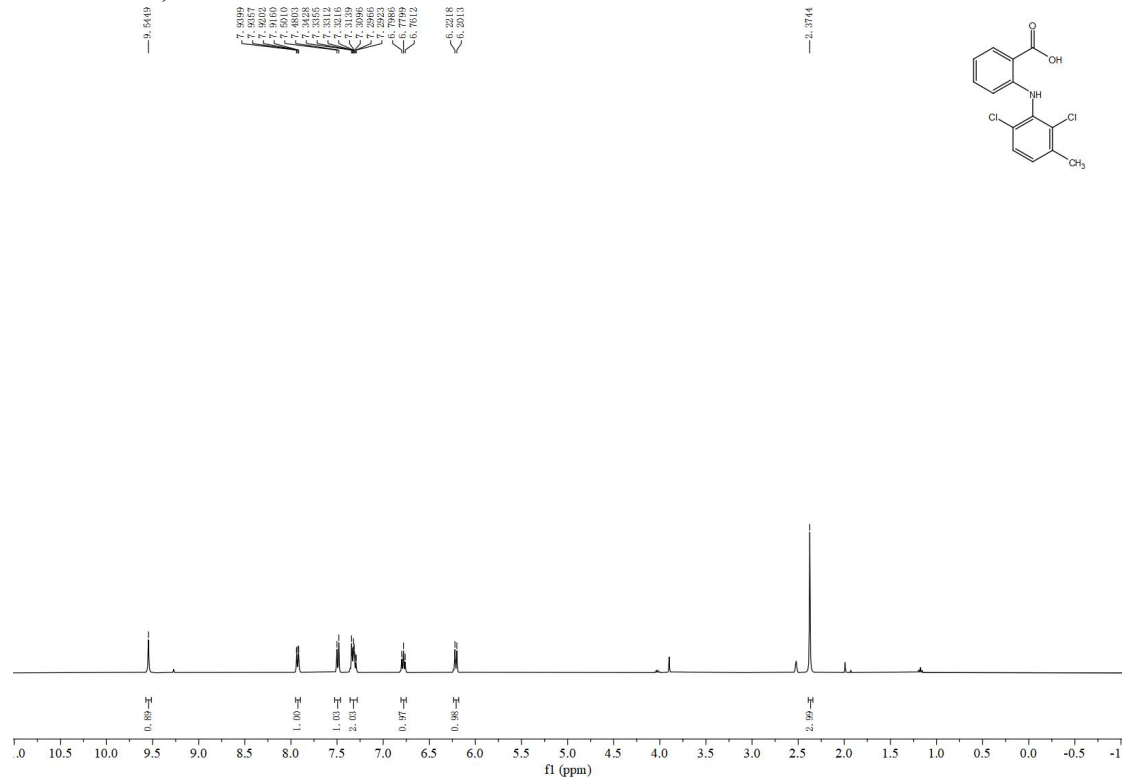


Chemical structure of 2-(4-chlorophenyl)benzamide (12a): NC(=O)c1ccccc1-c2ccc(Cl)cc2

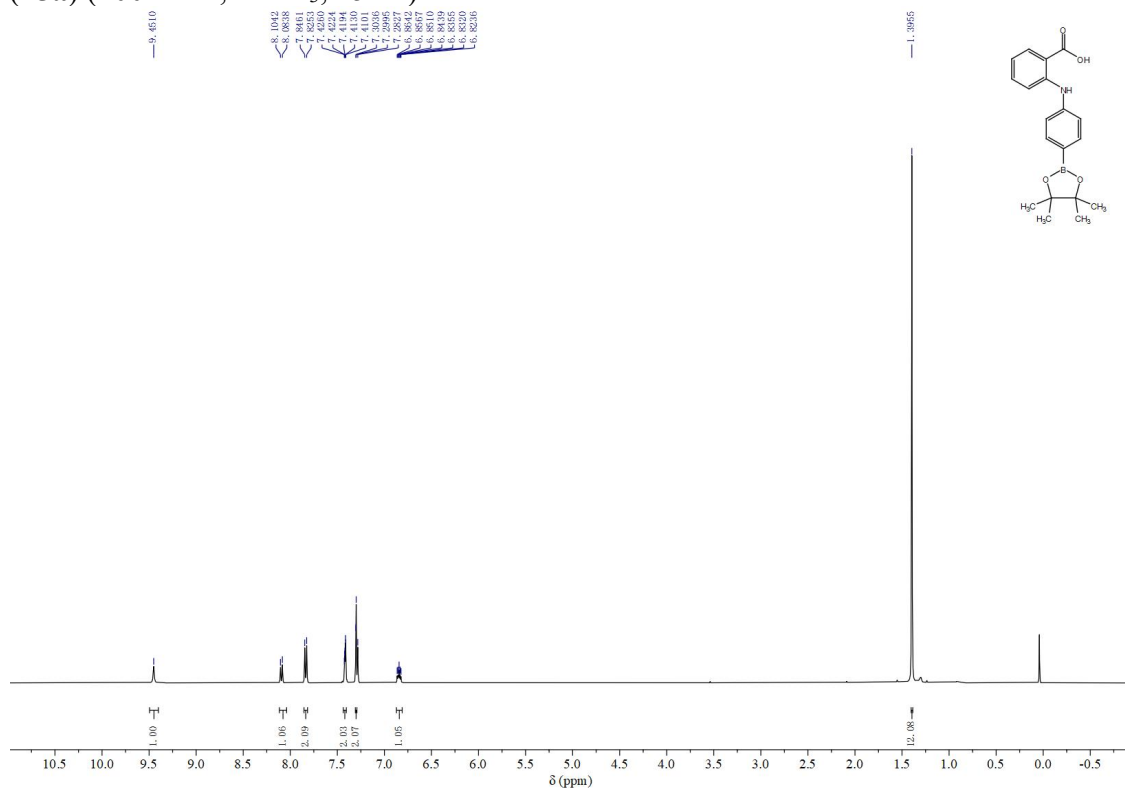
¹H NMR spectrum (DMSO-d₆) of 2-(4-chlorophenyl)benzamide (12a). The spectrum shows peaks at 9.861, 7.958, 7.940, 7.922, 7.909, 7.886, 7.872, 7.857, 7.851, 7.251, 7.211, 7.139, and 7.062 ppm. Integration values are 1.00, 2.00, 2.00, and 2.01.

[illegible]

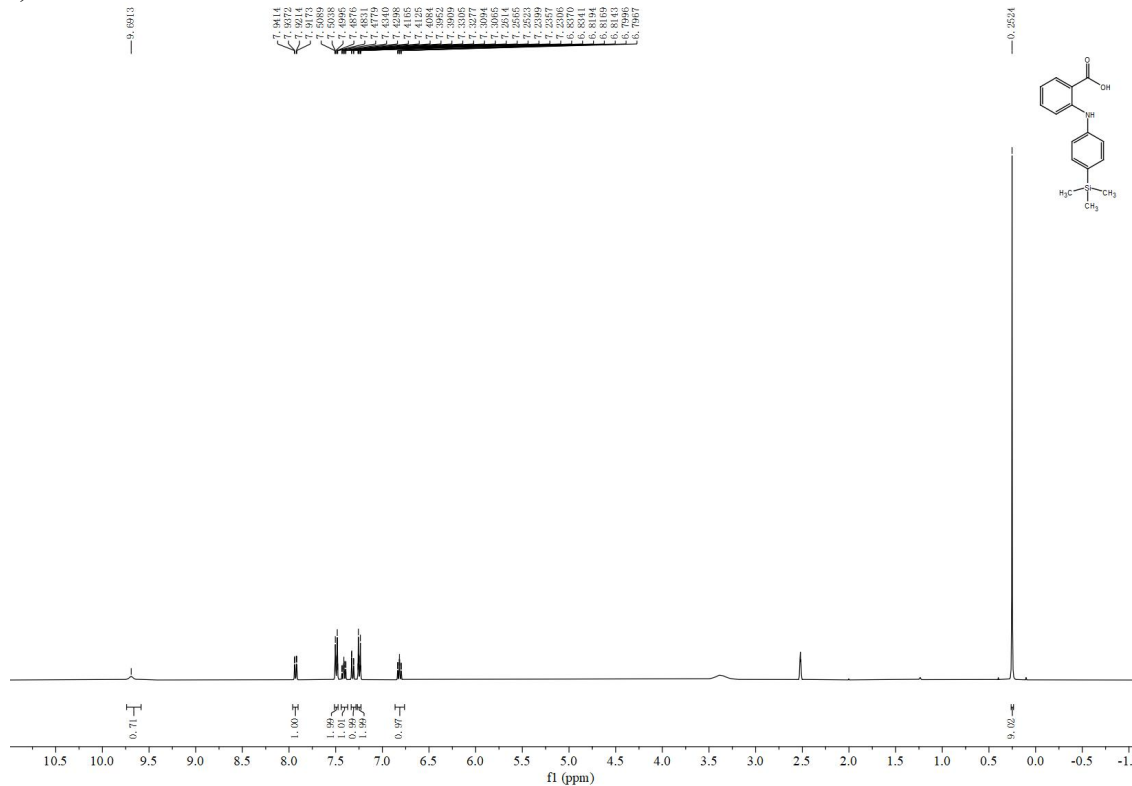
¹H NMR spectrum of 2-((2,6-dichloro-3-methylphenyl)amino)benzoic acid (**14a**) (400 MHz, DMSO-*d*₆, 25 °C)



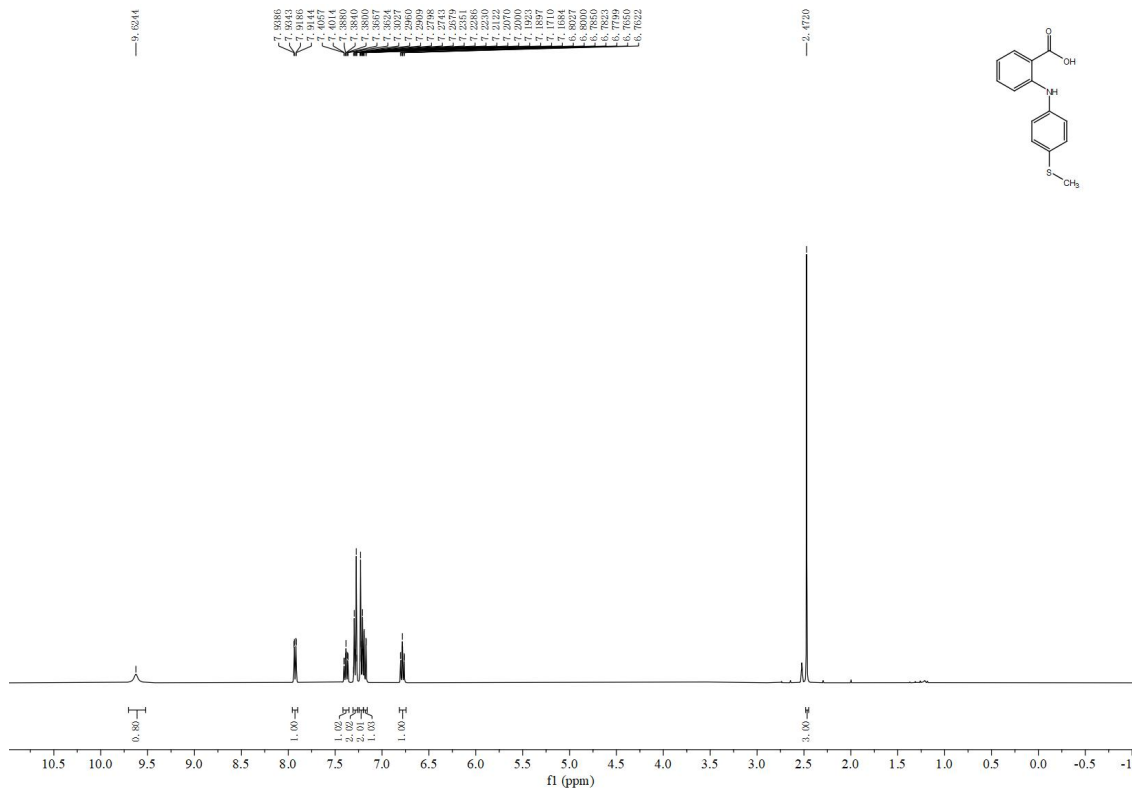
¹H NMR spectrum of 2-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amino)benzoic acid (**15a**) (400 MHz, CDCl₃, 25 °C)



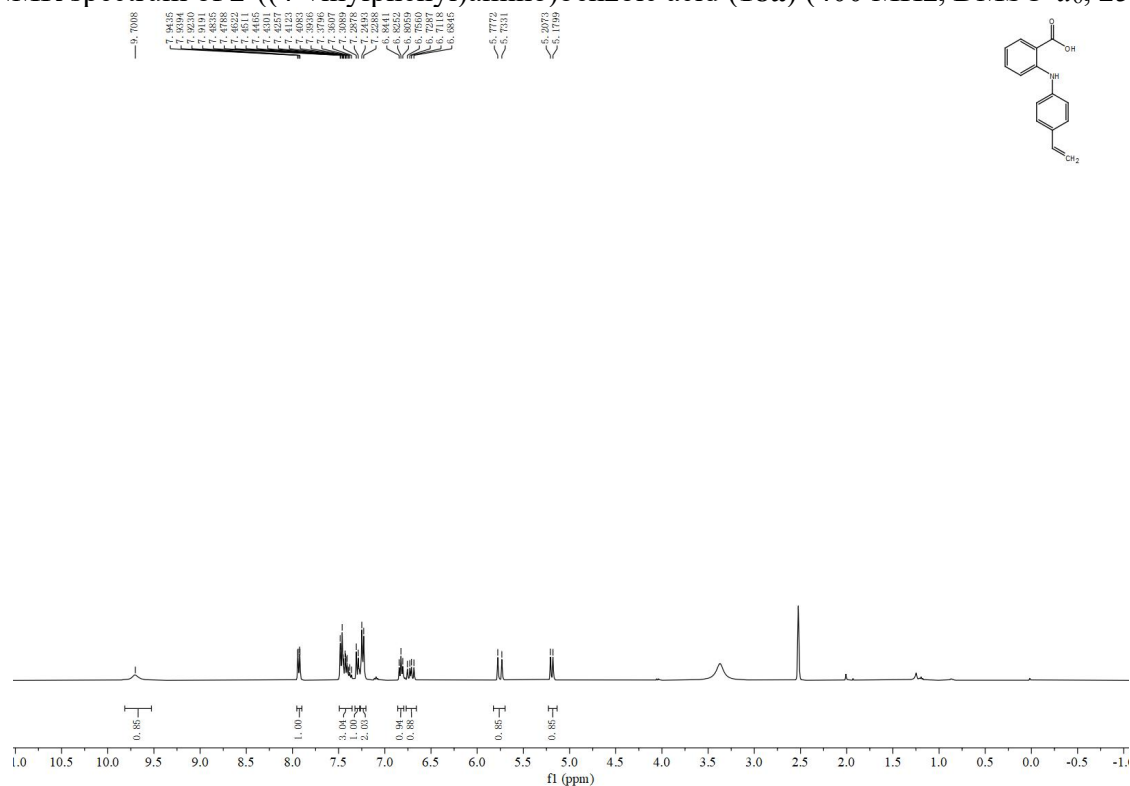
¹H NMR spectrum of 2-((4-(trimethylsilyl)phenyl)amino)benzoic acid (**16a**) (400 MHz, CDCl₃, 25 °C)



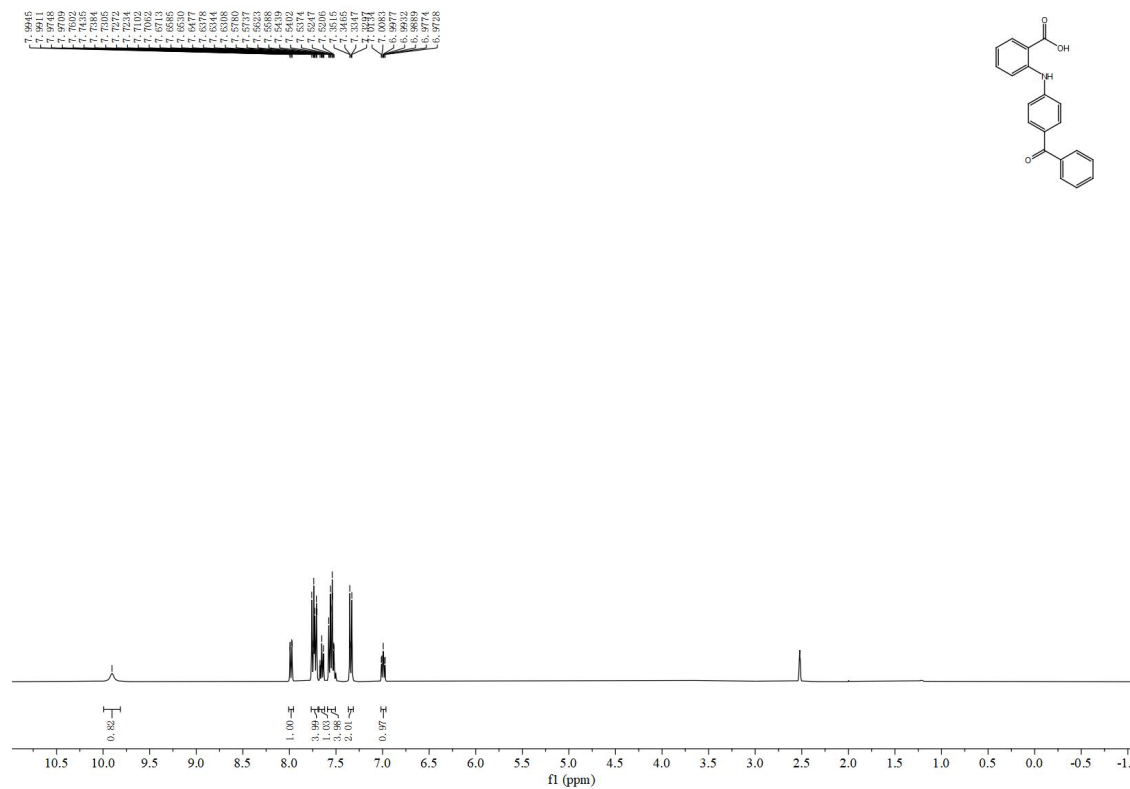
¹H NMR spectrum of 2-((4-(methylthio)phenyl)amino)benzoic acid (**17a**) (400 MHz, CDCl₃, 25 °C)



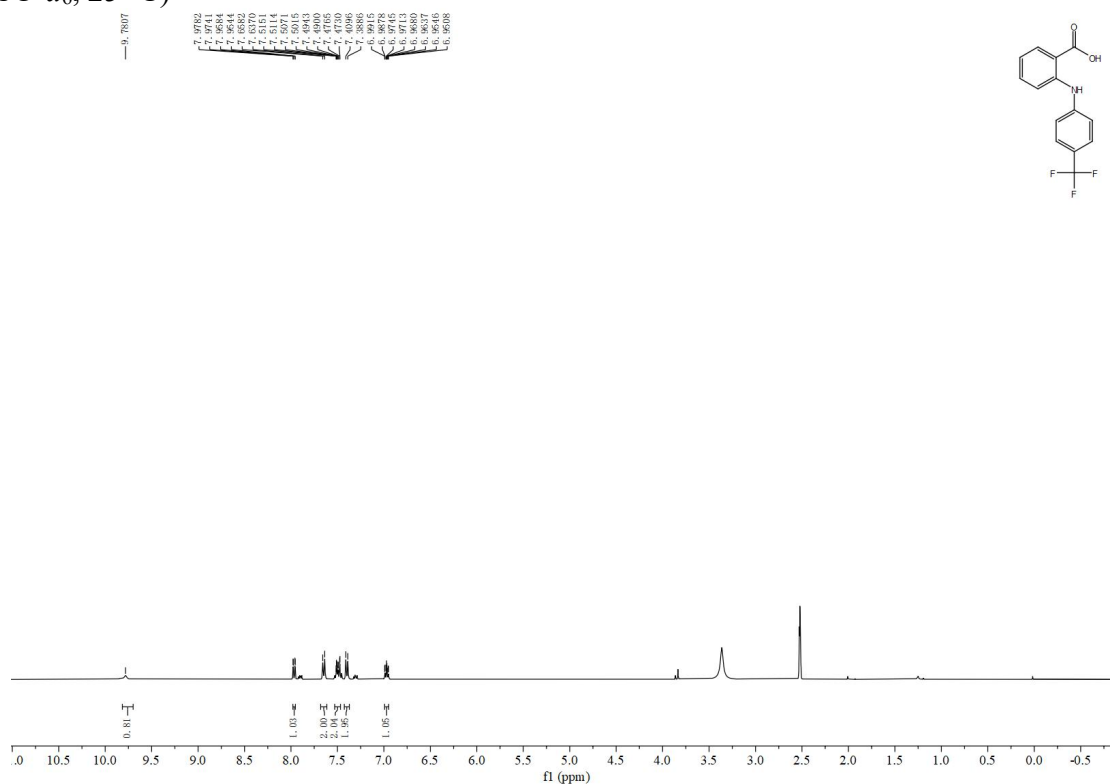
^1H NMR spectrum of 2-((4-vinylphenyl)amino)benzoic acid (**18a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)



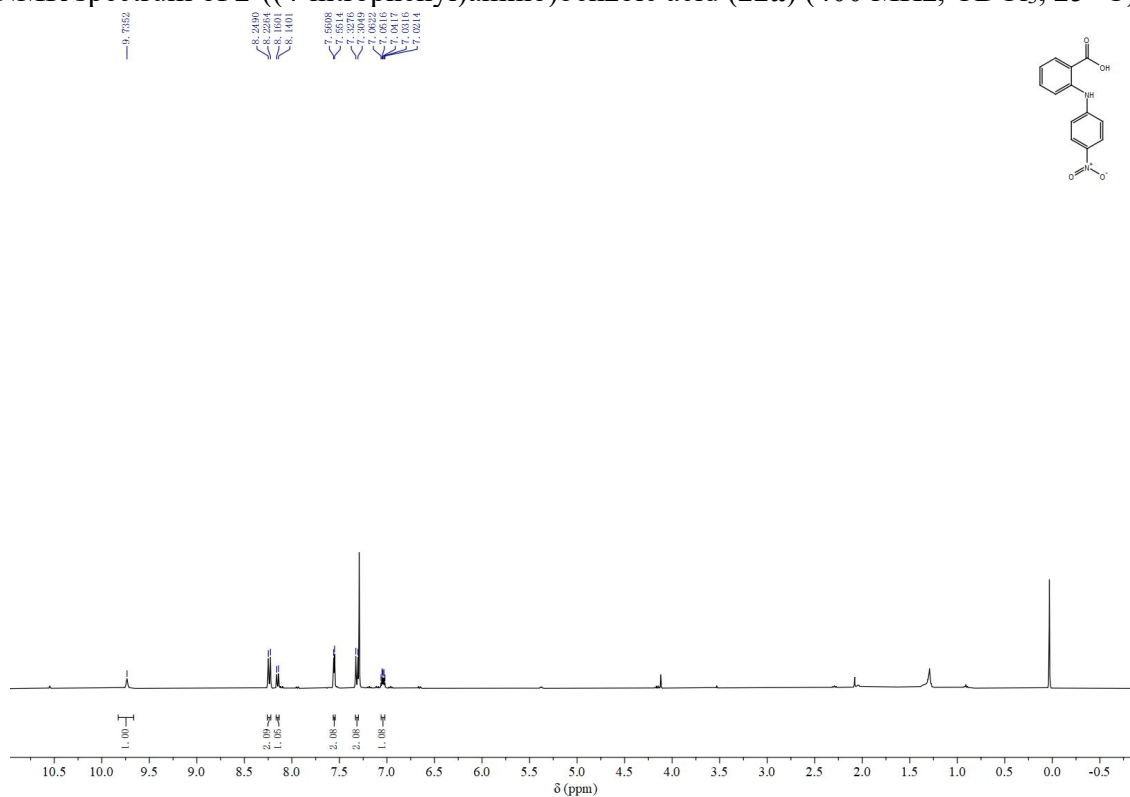
^1H NMR spectrum of 2-((4-benzoylphenyl)amino)benzoic acid (**19a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)



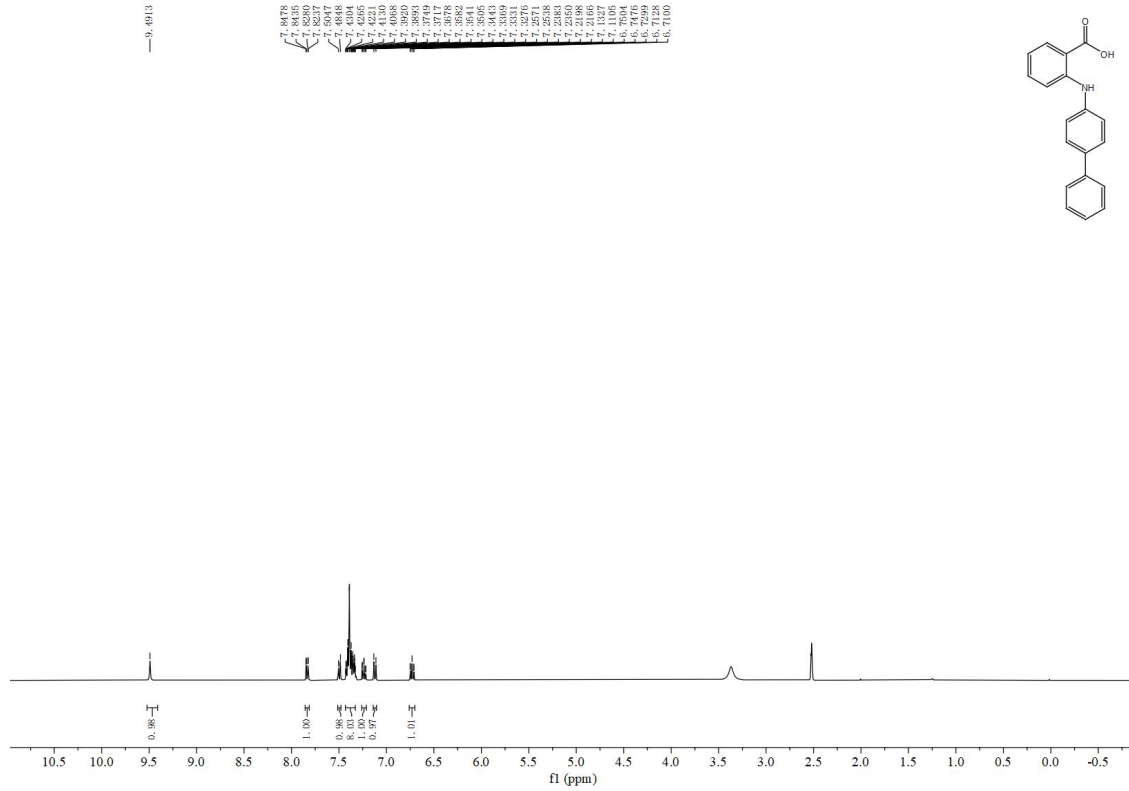
^1H NMR spectrum of 2-((4-(trifluoromethyl)phenyl)amino)benzoic acid (**20a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)



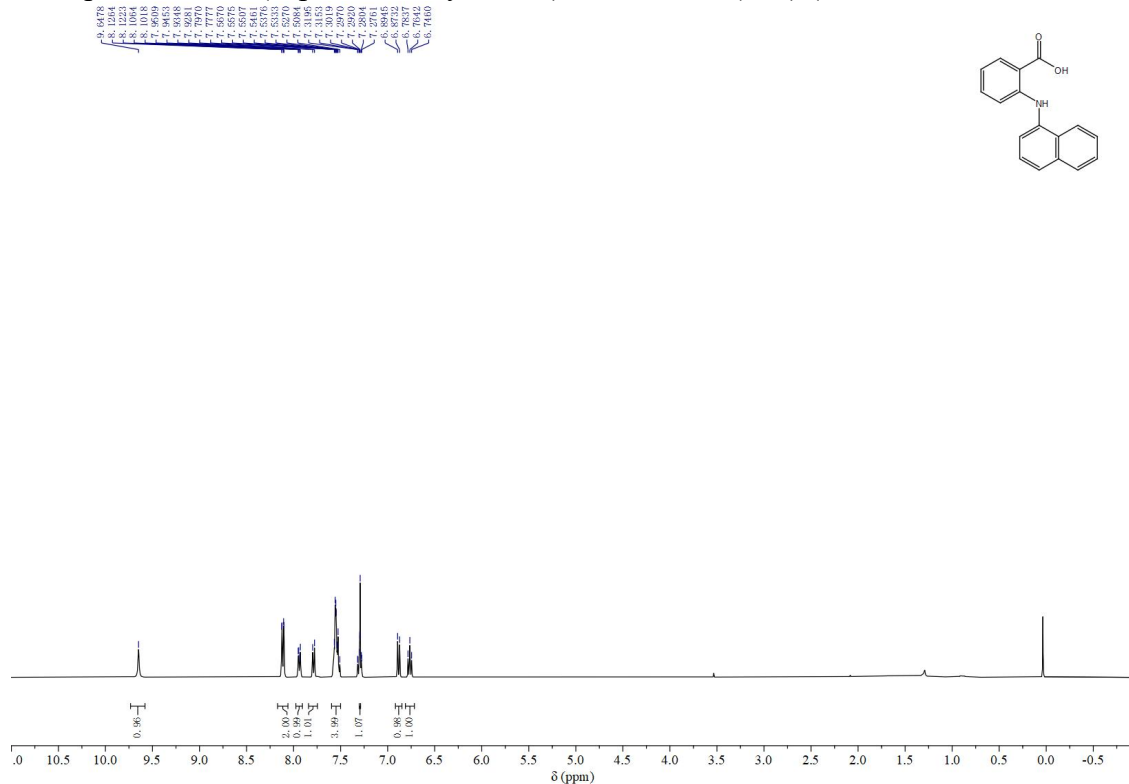
^1H NMR spectrum of 2-((4-nitrophenyl)amino)benzoic acid (**22a**) (400 MHz, CDCl_3 , 25 °C)



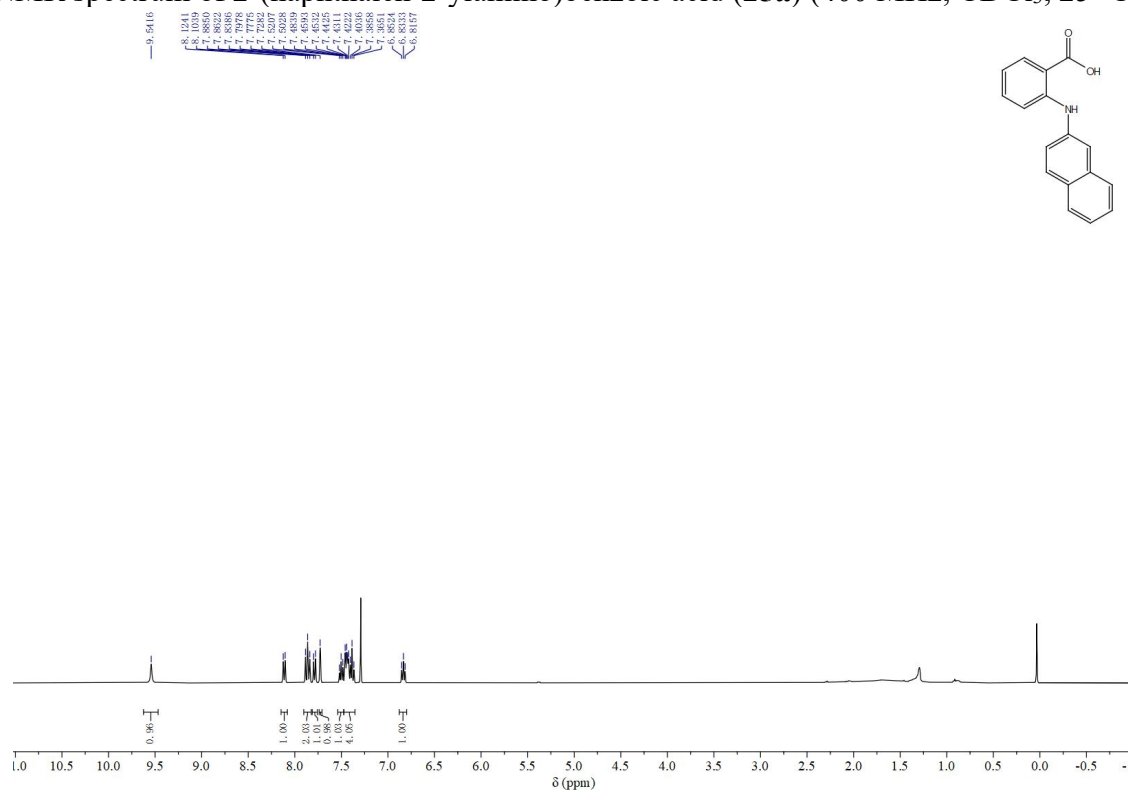
¹H NMR spectrum of 2-([1,1'-biphenyl]-4-ylamino)benzoic acid (**23a**) (400 MHz, DMSO-*d*₆, 25 °C)



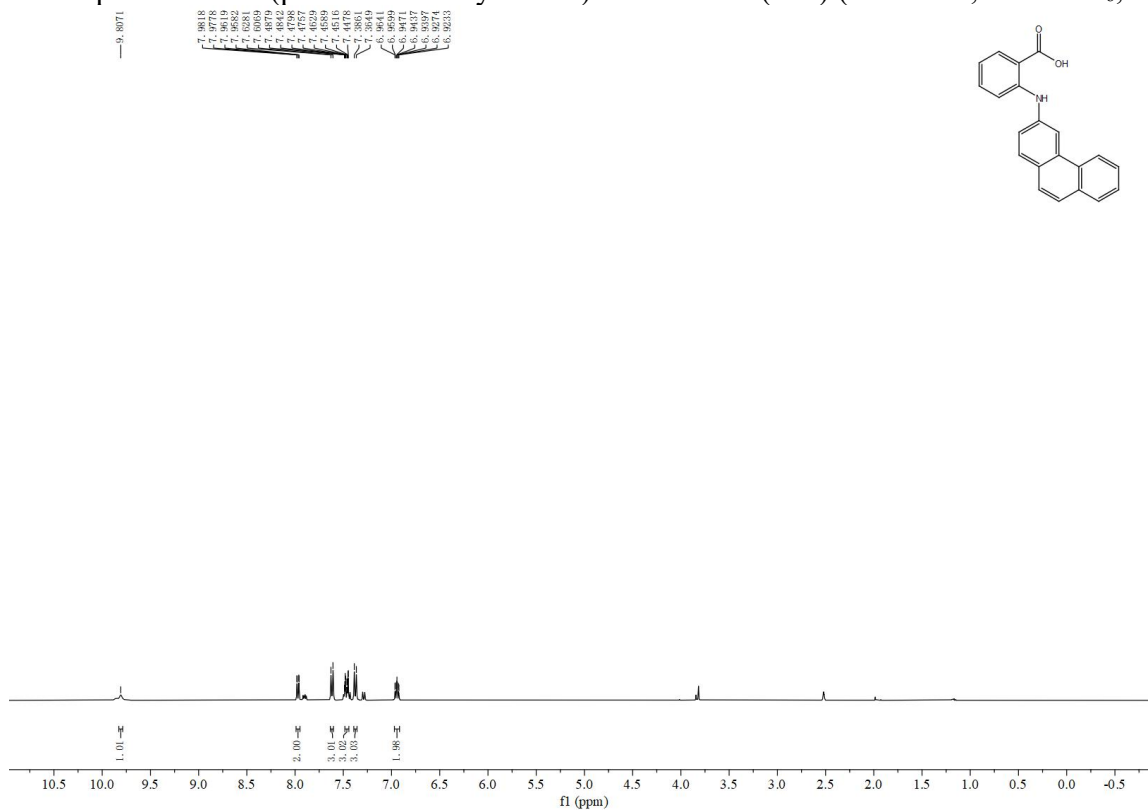
¹H NMR spectrum of 2-(naphthalen-1-ylamino)benzoic acid (**24a**) (400 MHz, CDCl₃, 25 °C)



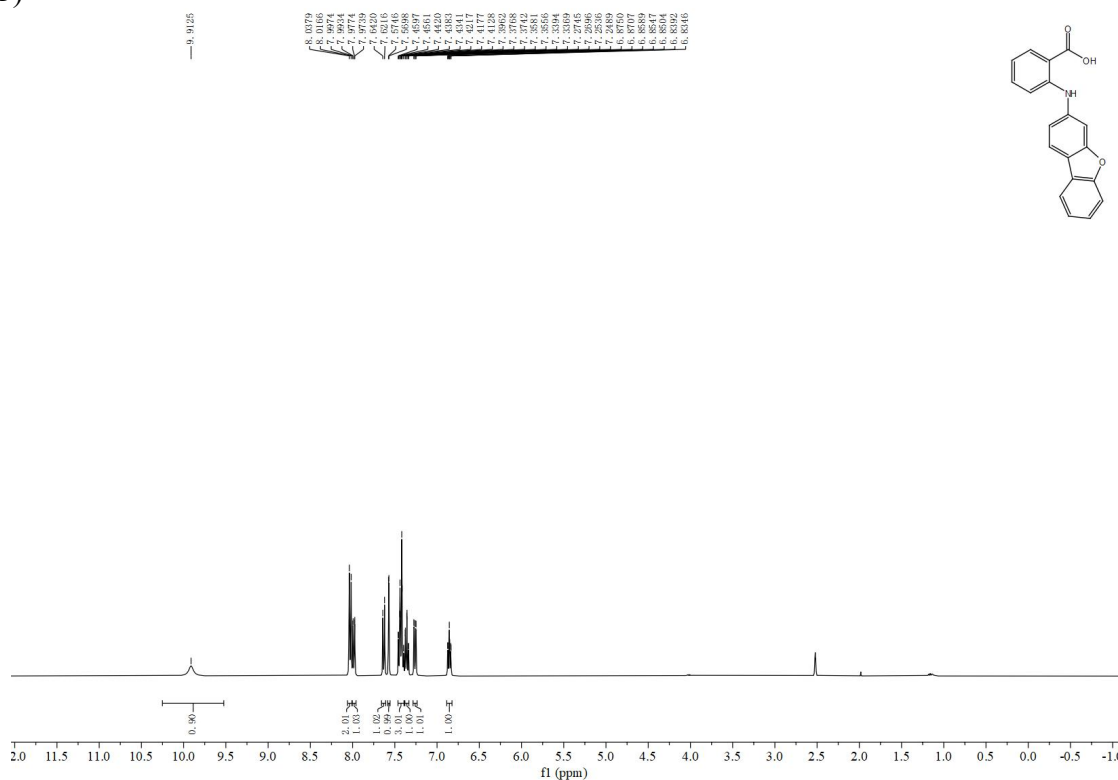
^1H NMR spectrum of 2-(naphthalen-2-ylamino)benzoic acid (**25a**) (400 MHz, CDCl_3 , 25 °C)



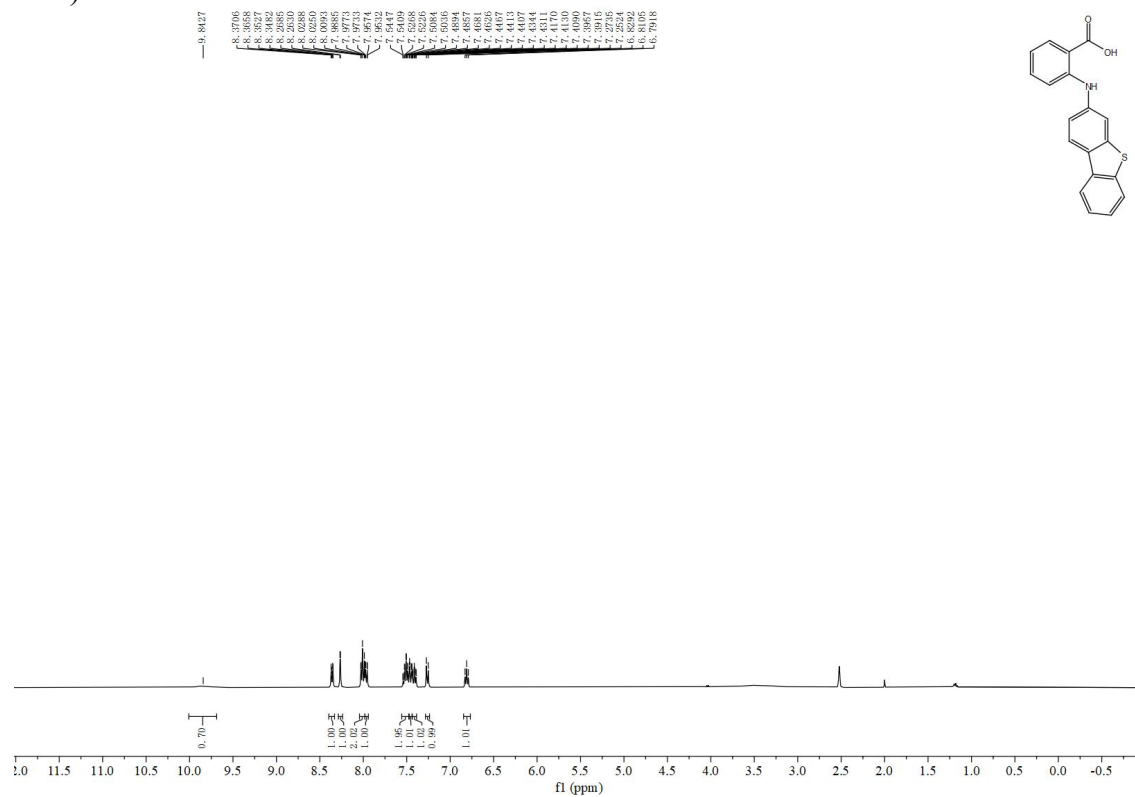
^1H NMR spectrum of 2-(phenanthren-3-ylamino)benzoic acid (**26a**) (400 MHz, $\text{DMSO}-d_6$, 25 °C)



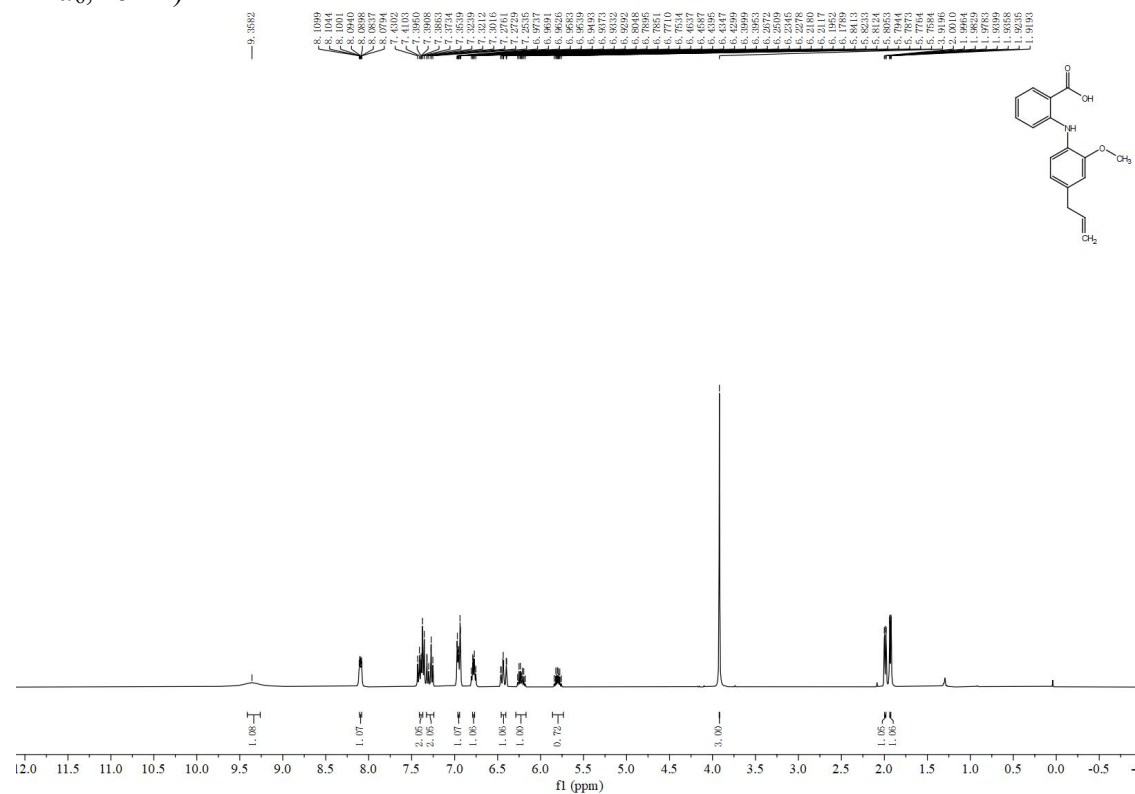
^1H NMR spectrum of 2-(dibenzo[b,d]furan-3-ylamino)benzoic acid (**27a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)



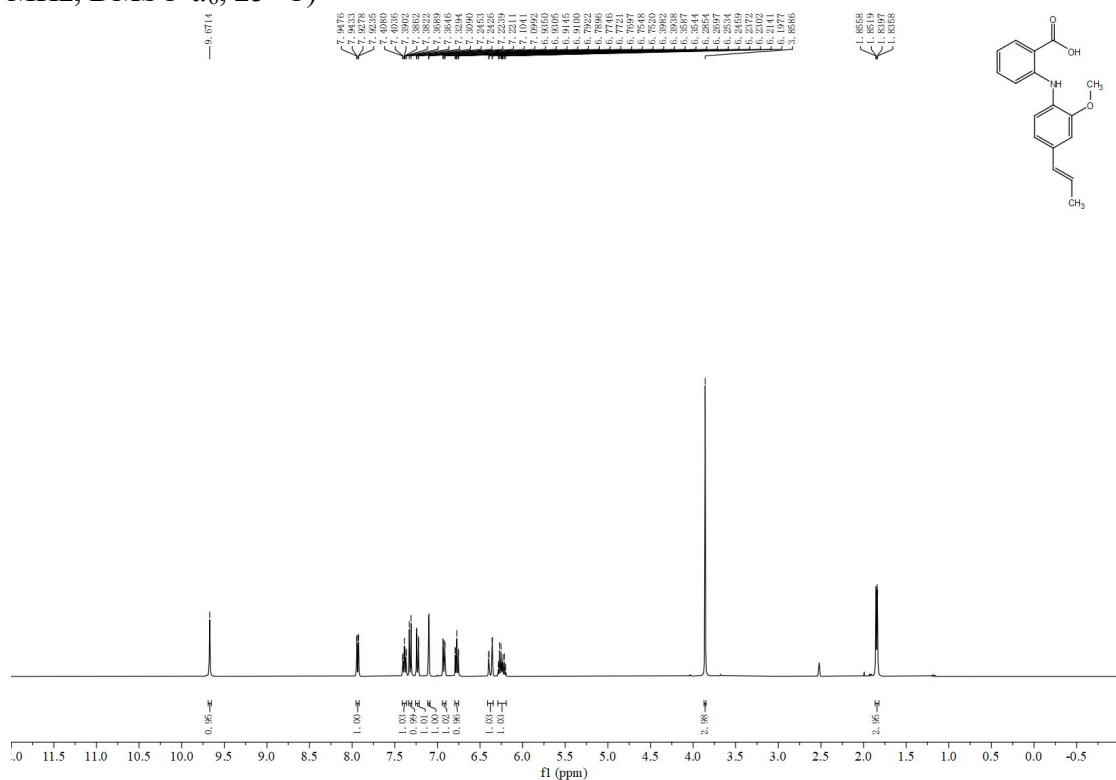
^1H NMR spectrum of 2-(dibenzo[*b,d*]thiophen-3-ylamino)benzoic acid (**29a**) (400 MHz, DMSO-*d*₆, 25 °C)



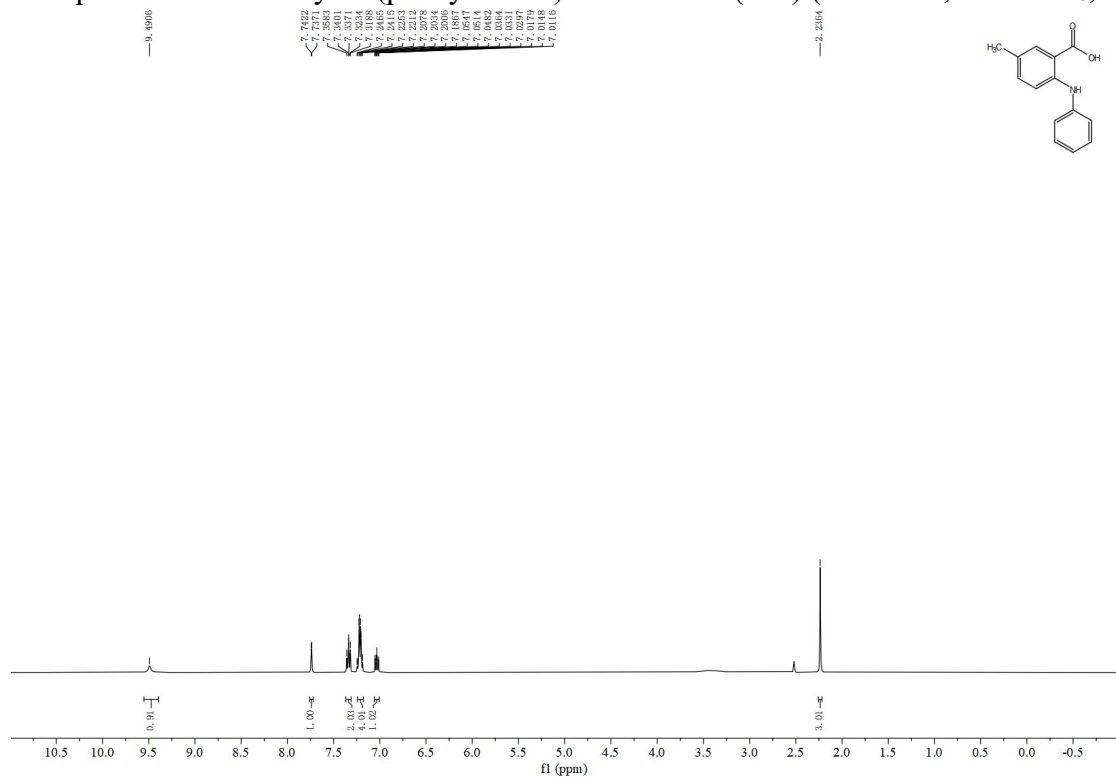
^1H NMR spectrum of 2-((4-allyl-2-methoxyphenyl)amino)benzoic acid (**30a**) (400 MHz, DMSO-*d*₆, 25 °C)



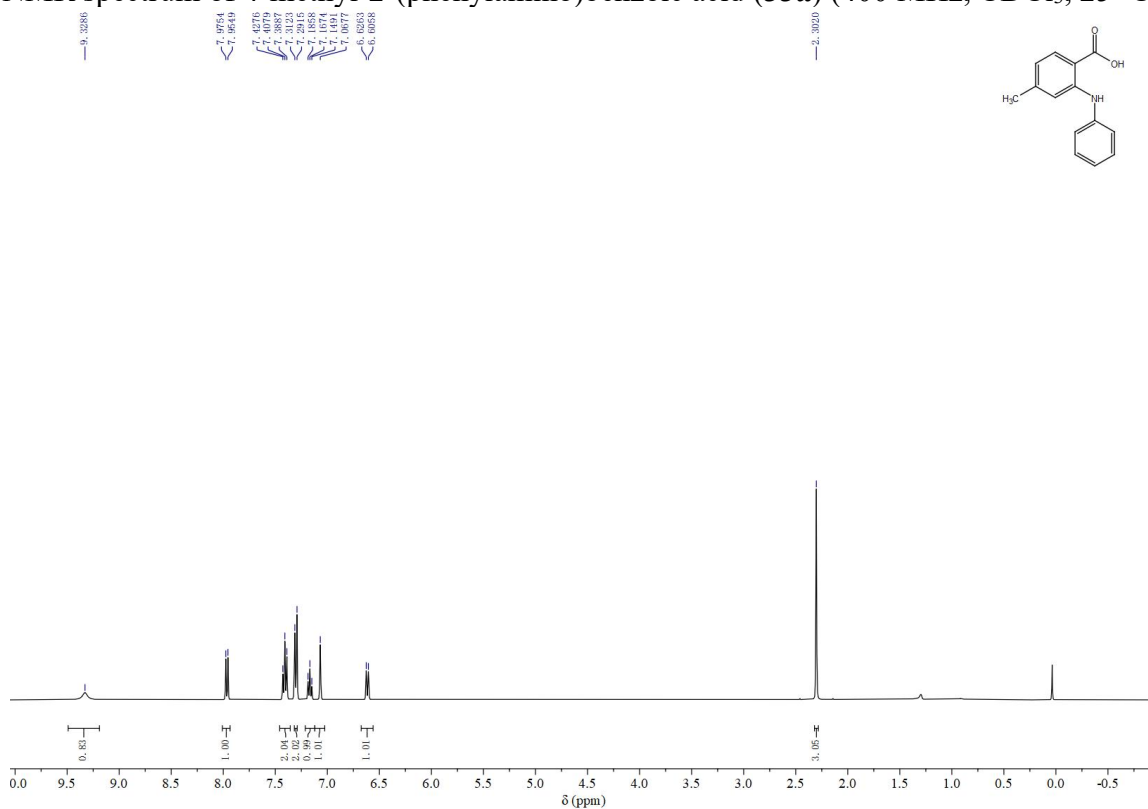
¹H NMR spectrum of (*E*)-2-((2-methoxy-4-(prop-1-en-1-yl)phenyl)amino)benzoic acid (**31a**) (400 MHz, DMSO-*d*₆, 25 °C)



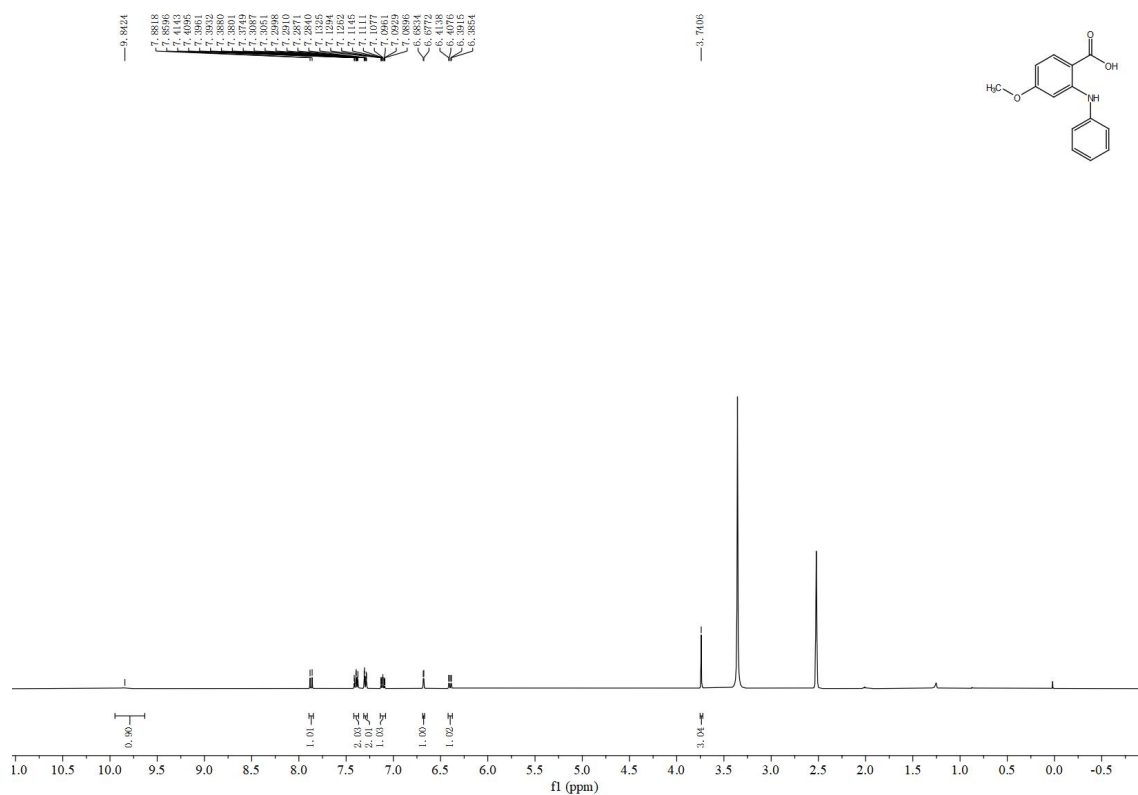
¹H NMR spectrum of 5-methyl-2-(phenylamino)benzoic acid (**32a**) (400 MHz, DMSO-*d*₆, 25 °C)



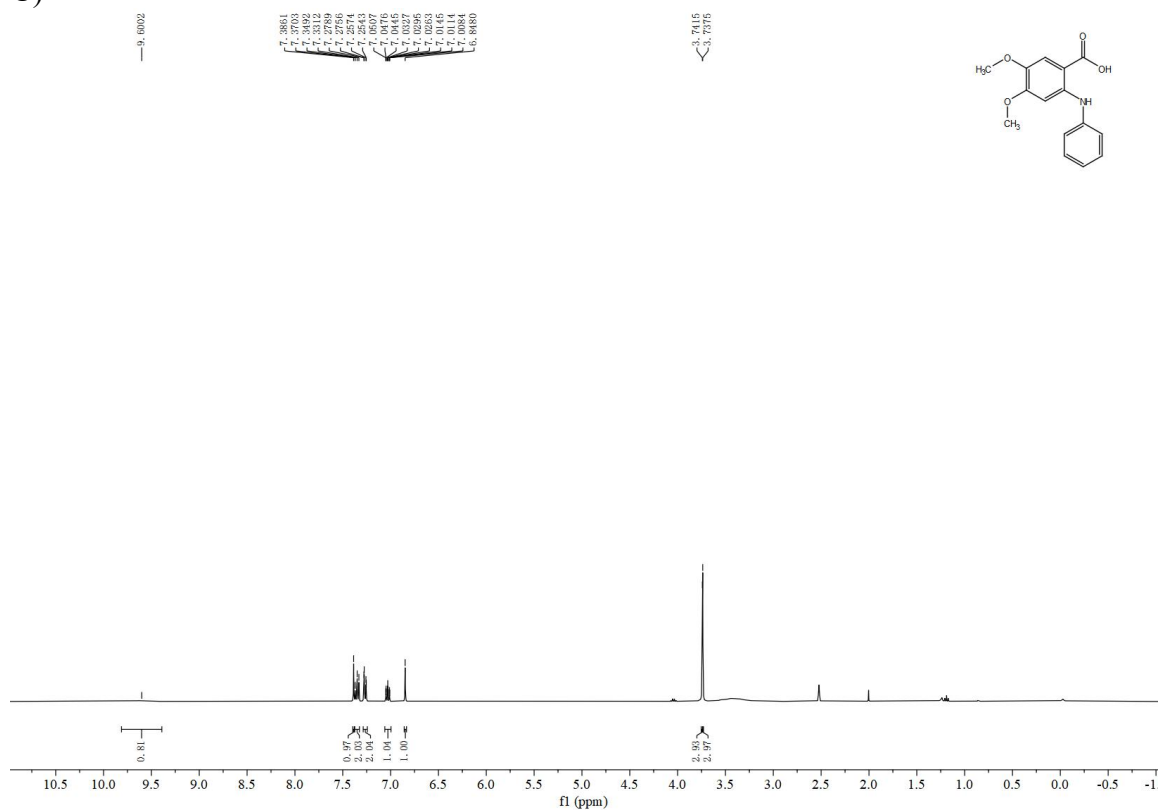
¹H NMR spectrum of 4-methyl-2-(phenylamino)benzoic acid (**33a**) (400 MHz, CDCl₃, 25 °C)



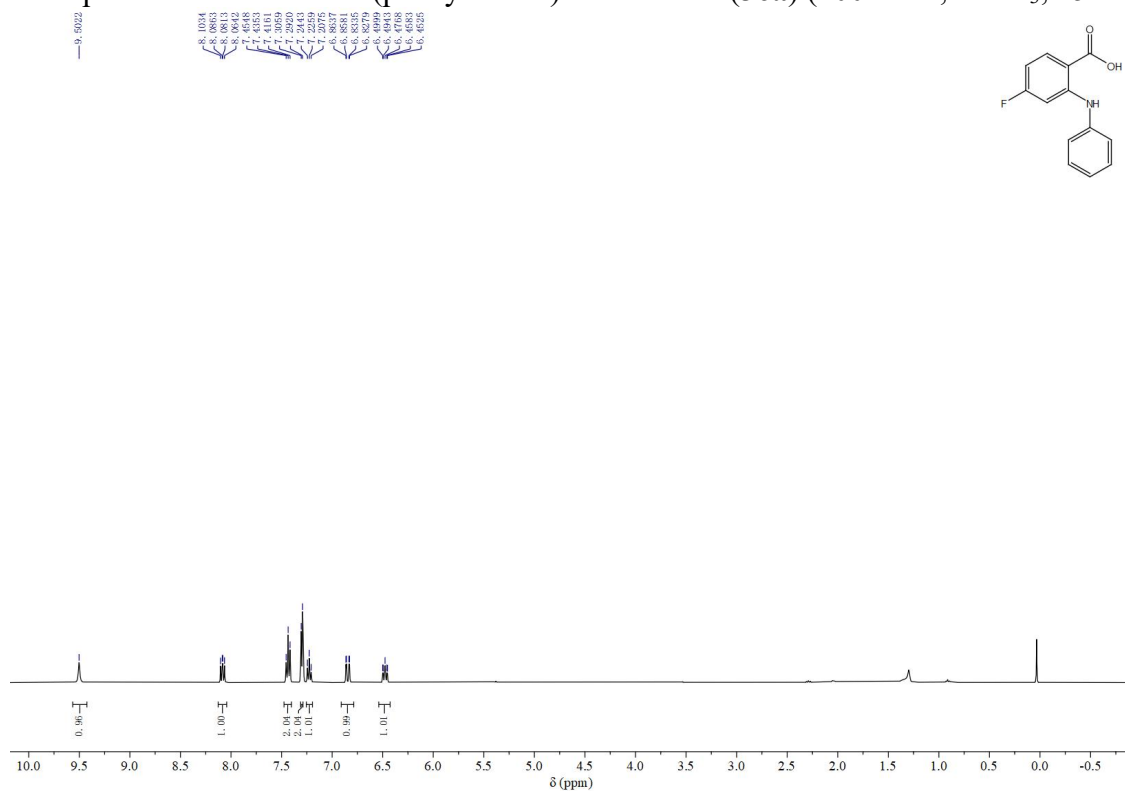
¹H NMR spectrum of 4-methoxy-2-(phenylamino)benzoic acid (**34a**) (400 MHz, DMSO-*d*₆, 25 °C)



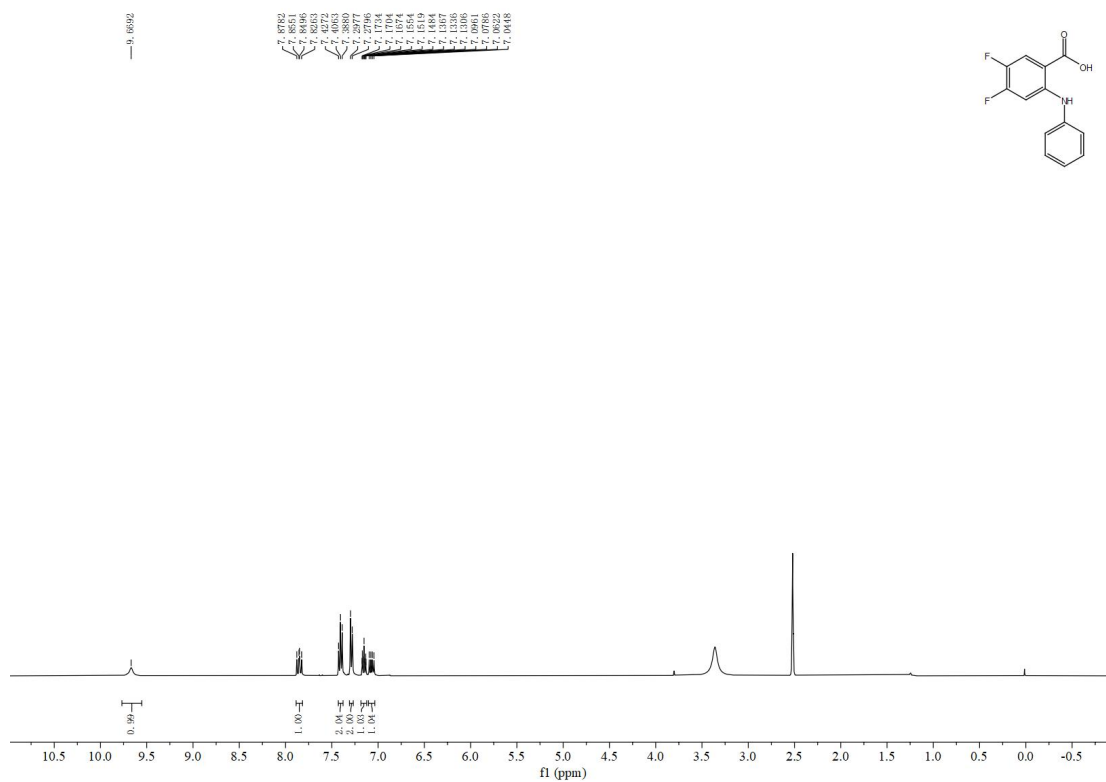
^1H NMR spectrum of 4,5-dimethoxy-2-(phenylamino)benzoic acid (**35a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)



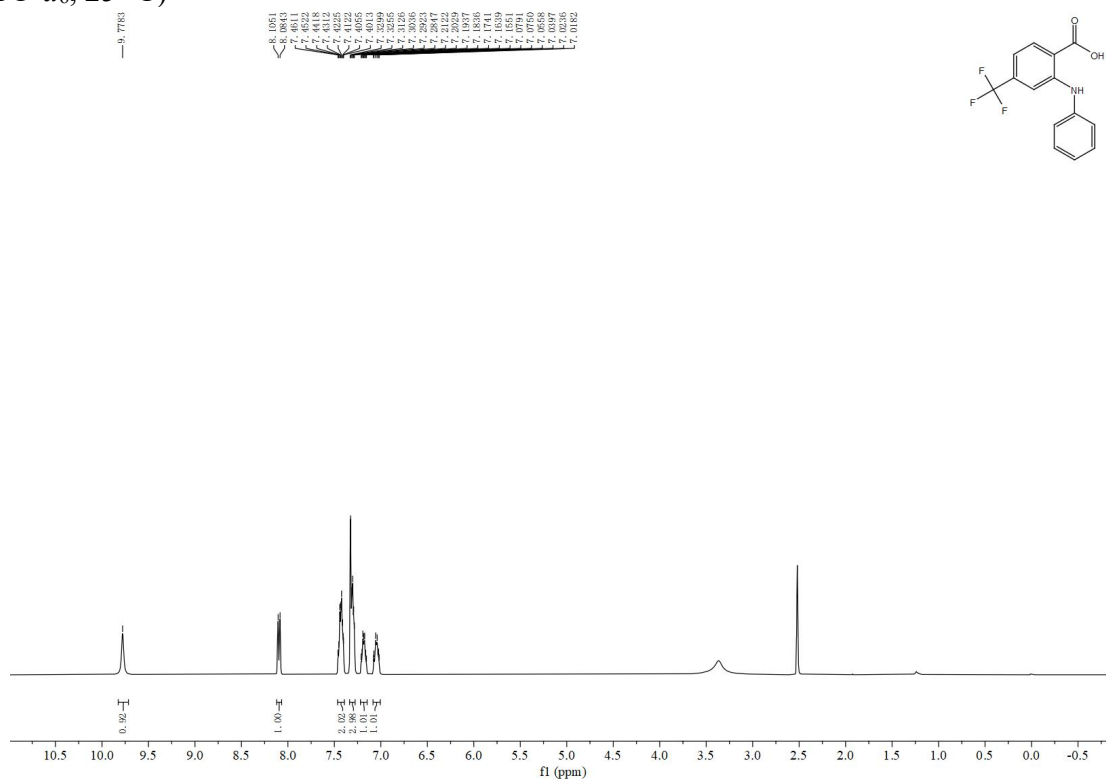
^1H NMR spectrum of 4-fluoro-2-(phenylamino)benzoic acid (**36a**) (400 MHz, CDCl_3 , 25 °C)



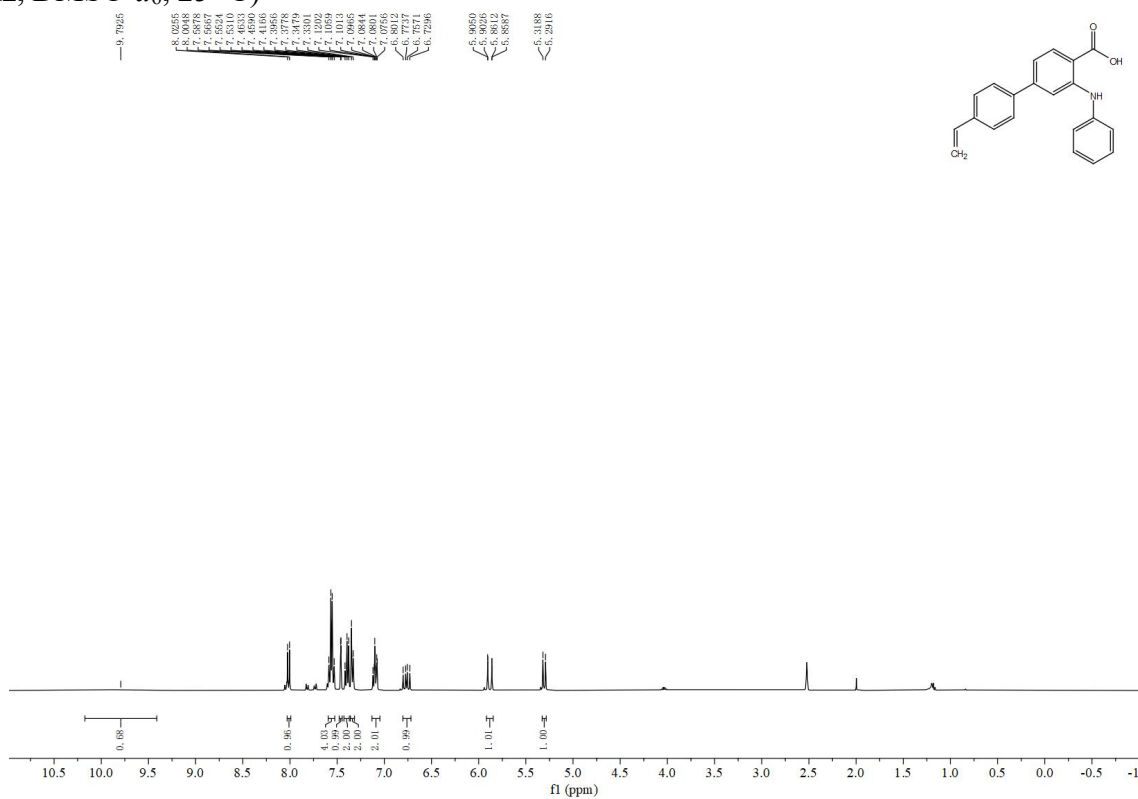
^1H NMR spectrum of 4,5-difluoro-2-(phenylamino)benzoic acid (**37a**) (400 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$)



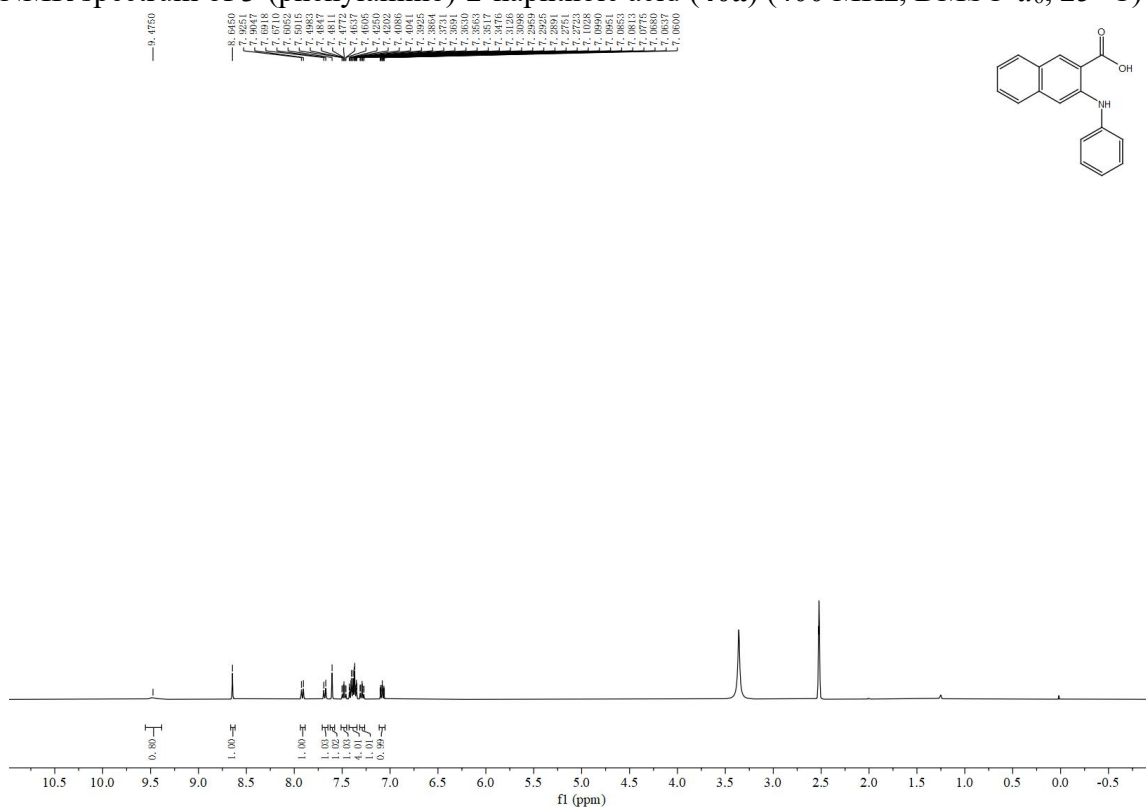
^1H NMR spectrum of 2-(phenylamino)-4-(trifluoromethyl)benzoic acid (**38a**) (400 MHz, $\text{DMSO-}d_6$, 25 $^\circ\text{C}$)



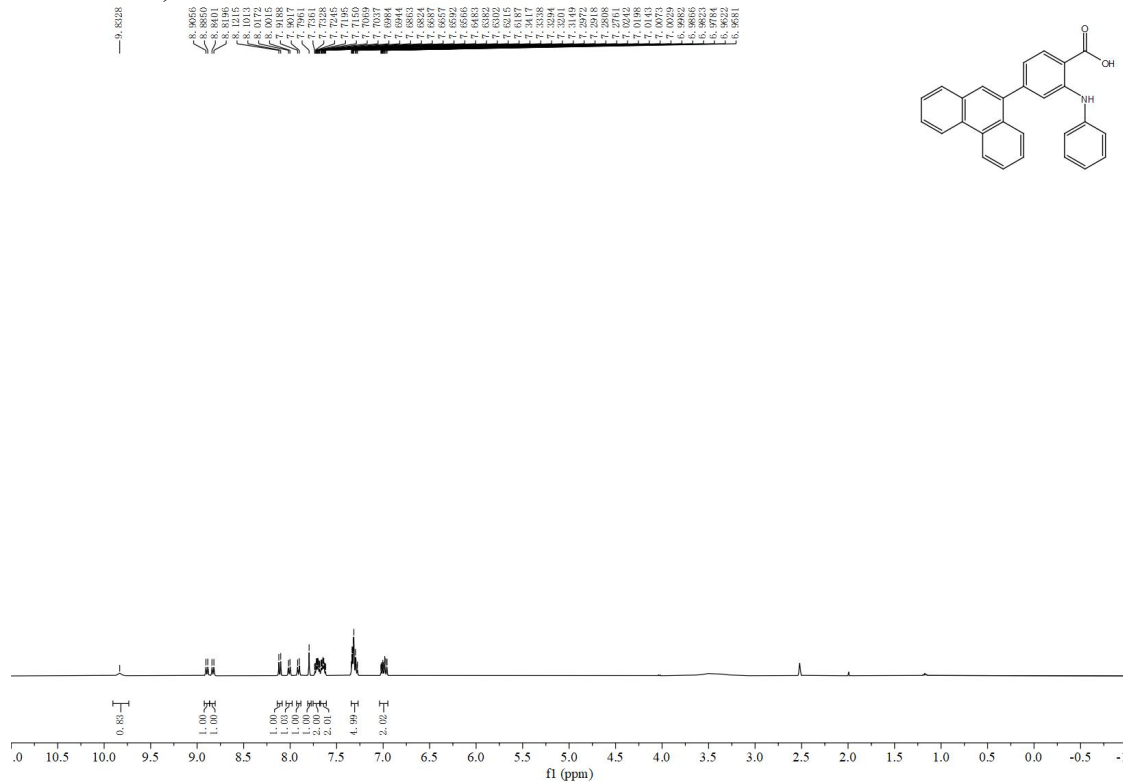
^1H NMR spectrum of 3-(phenylamino)-4'-vinyl-[1,1'-biphenyl]-4-carboxylic acid (**39a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)



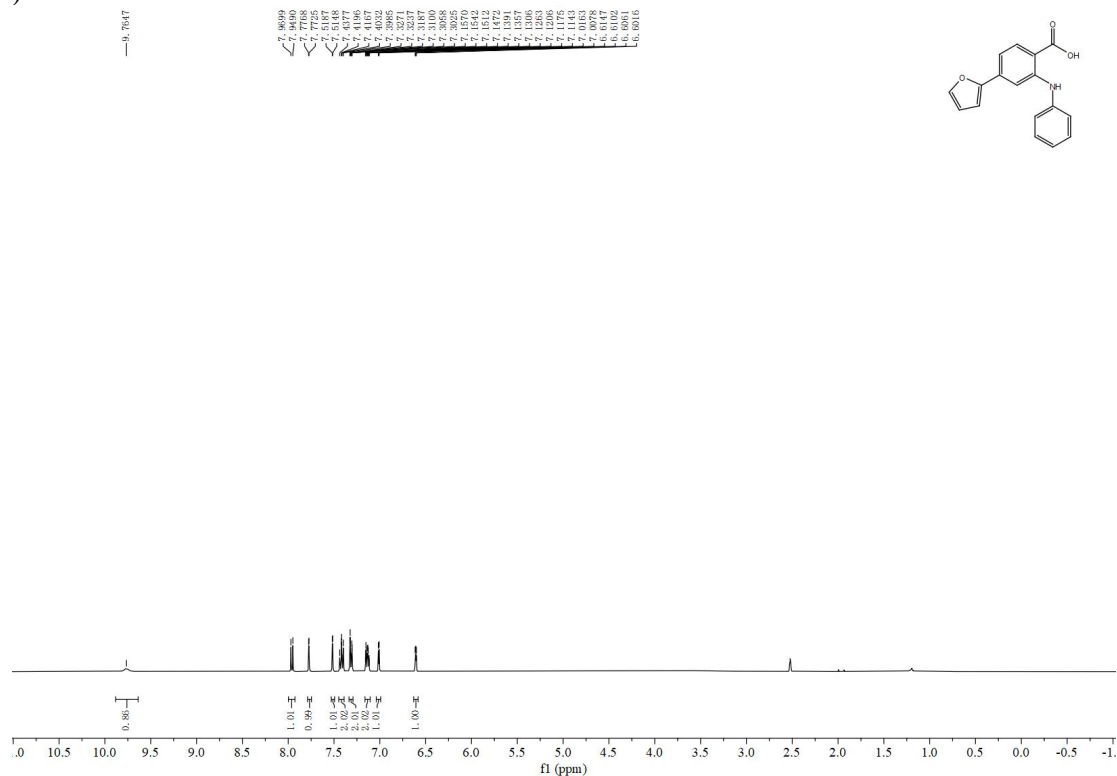
^1H NMR spectrum of 3-(phenylamino)-2-naphthoic acid (**40a**) (400 MHz, $\text{DMSO-}d_6$, 25 °C)



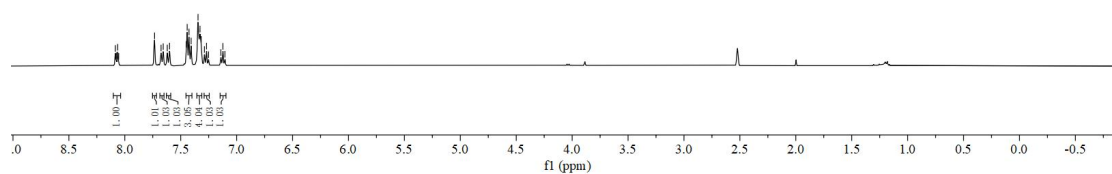
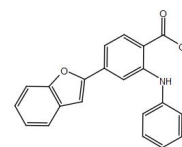
¹H NMR spectrum of 4-(phenanthren-9-yl)-2-(phenylamino)benzoic acid (**41a**) (400 MHz, DMSO-*d*₆, 25 °C)



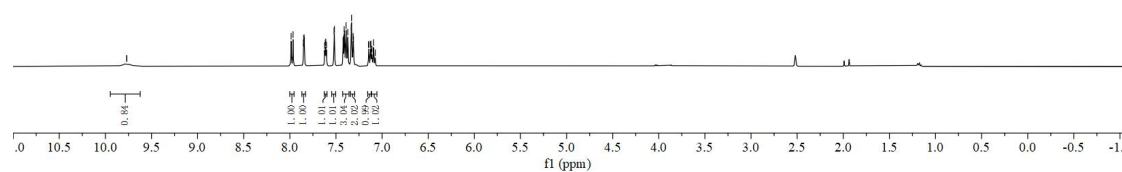
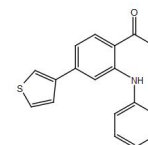
¹H NMR spectrum of 4-(furan-2-yl)-2-(phenylamino)benzoic acid (**42a**) (400 MHz, DMSO-*d*₆, 25 °C)



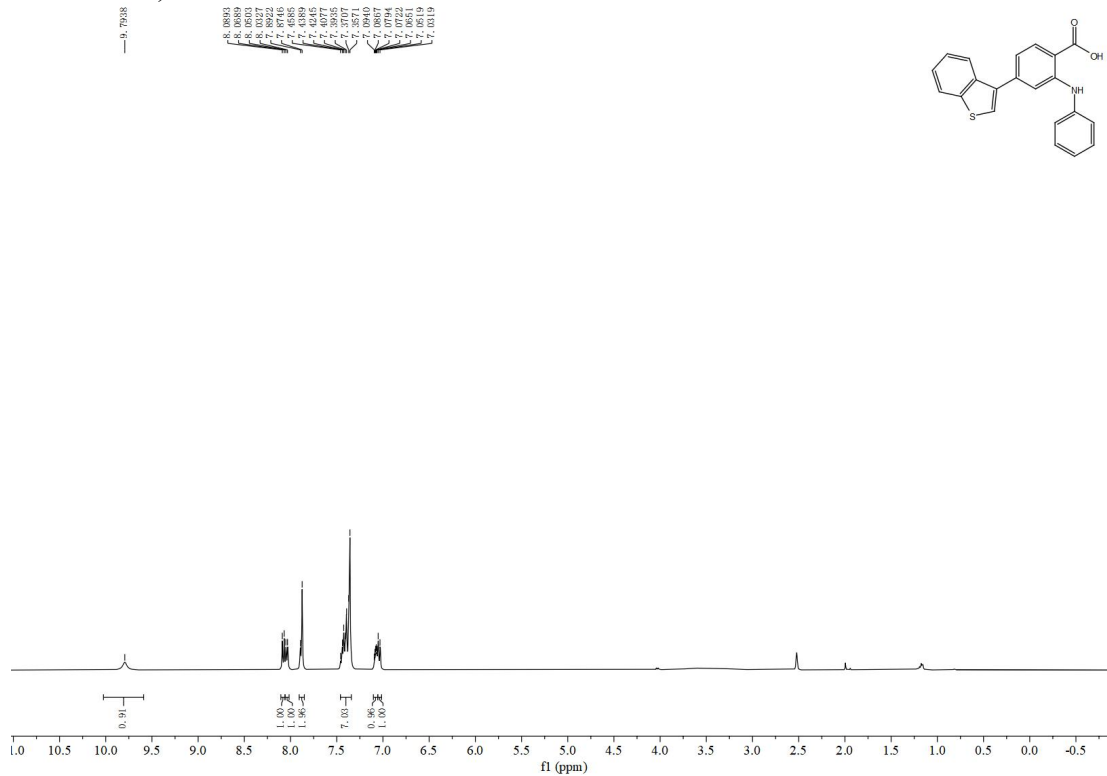
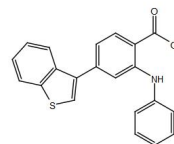
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7. 6569
7. 6205
7. 6002
7. 4502
7. 4425
7. 4261
7. 4071
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7. 3278
7. 3172
7. 2881
7. 2594
7. 2510
7. 1412
7. 1230
7. 1048



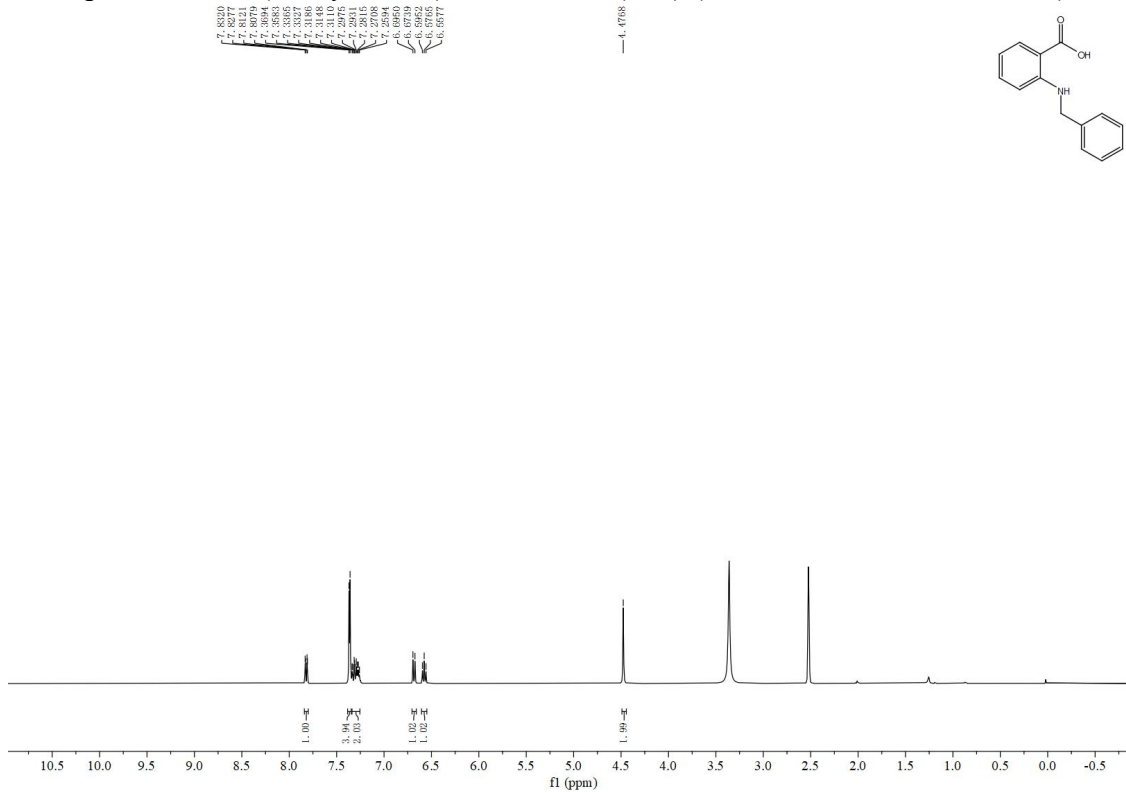
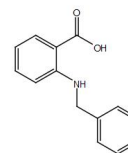
9. 7682
9. 7681



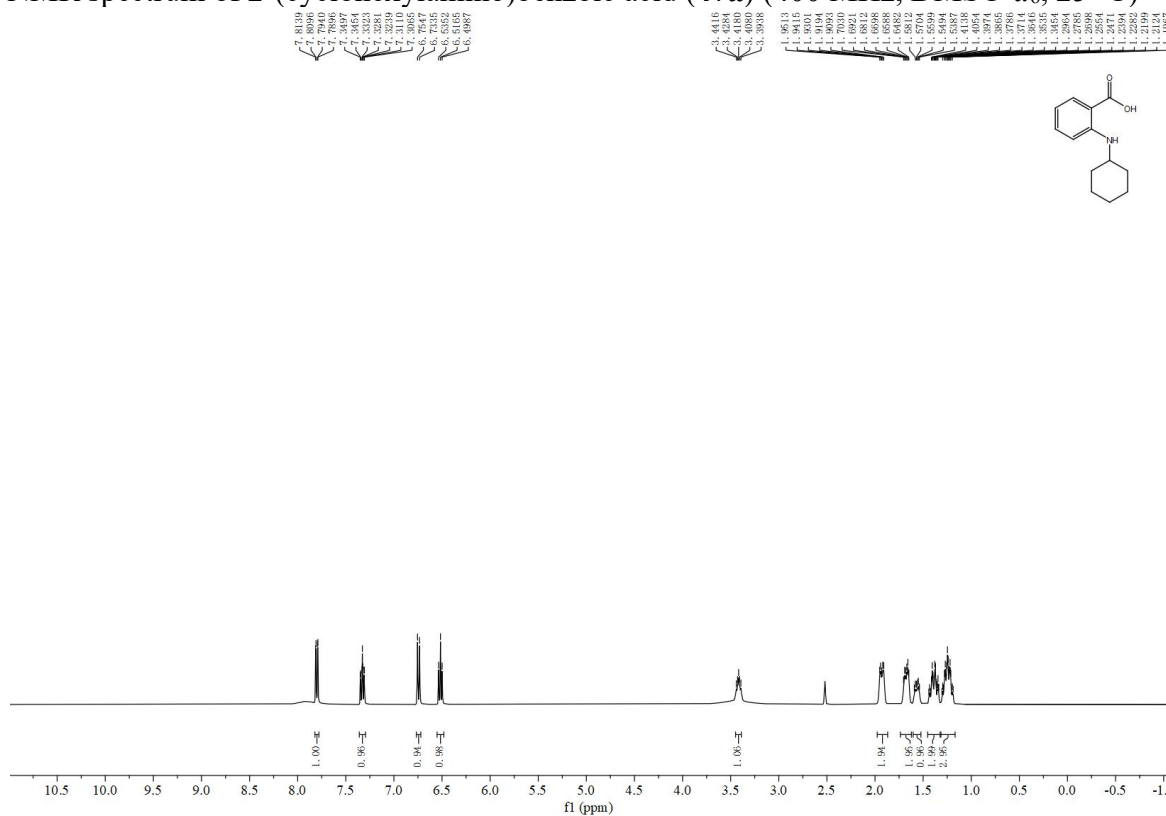
—9. 7538



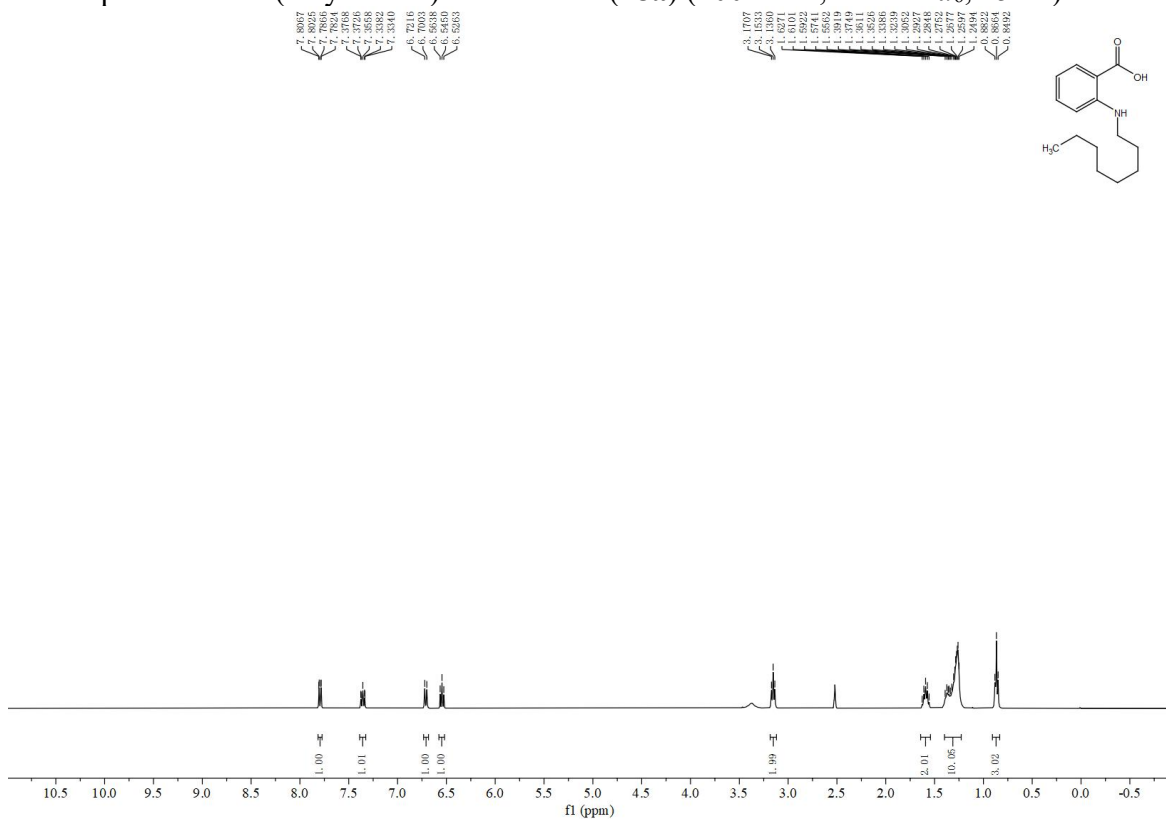
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7.3583
7.3365
7.3327
7.3186
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6.5765
6.5577



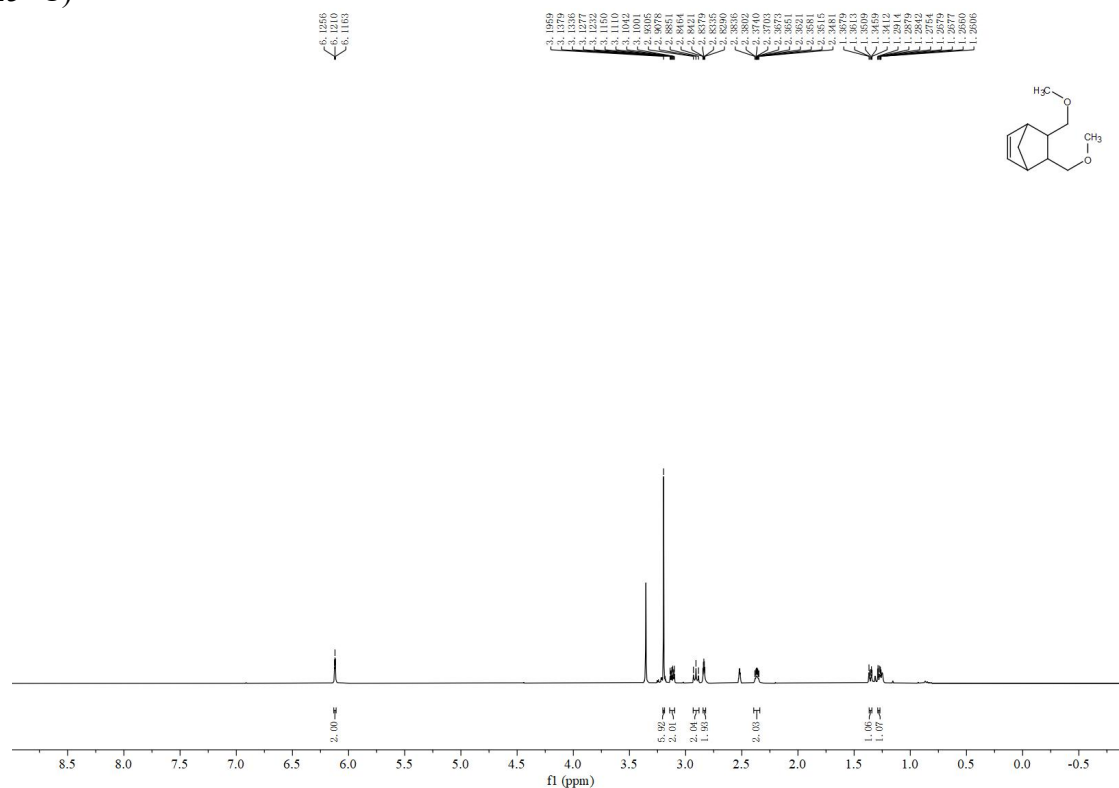
^1H NMR spectrum of 2-(cyclohexylamino)benzoic acid (**47a**) (400 MHz, DMSO- d_6 , 25 °C)



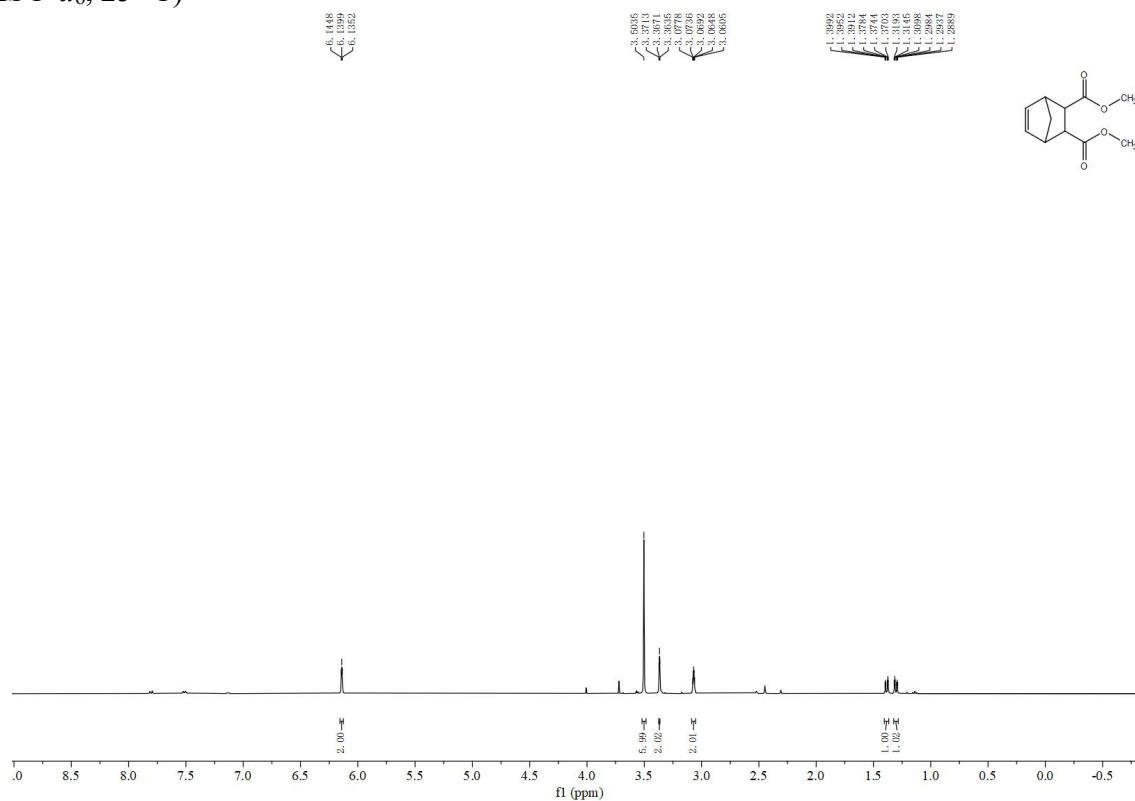
^1H NMR spectrum of 2-(octylamino)benzoic acid (**48a**) (400 MHz, DMSO- d_6 , 25 °C)



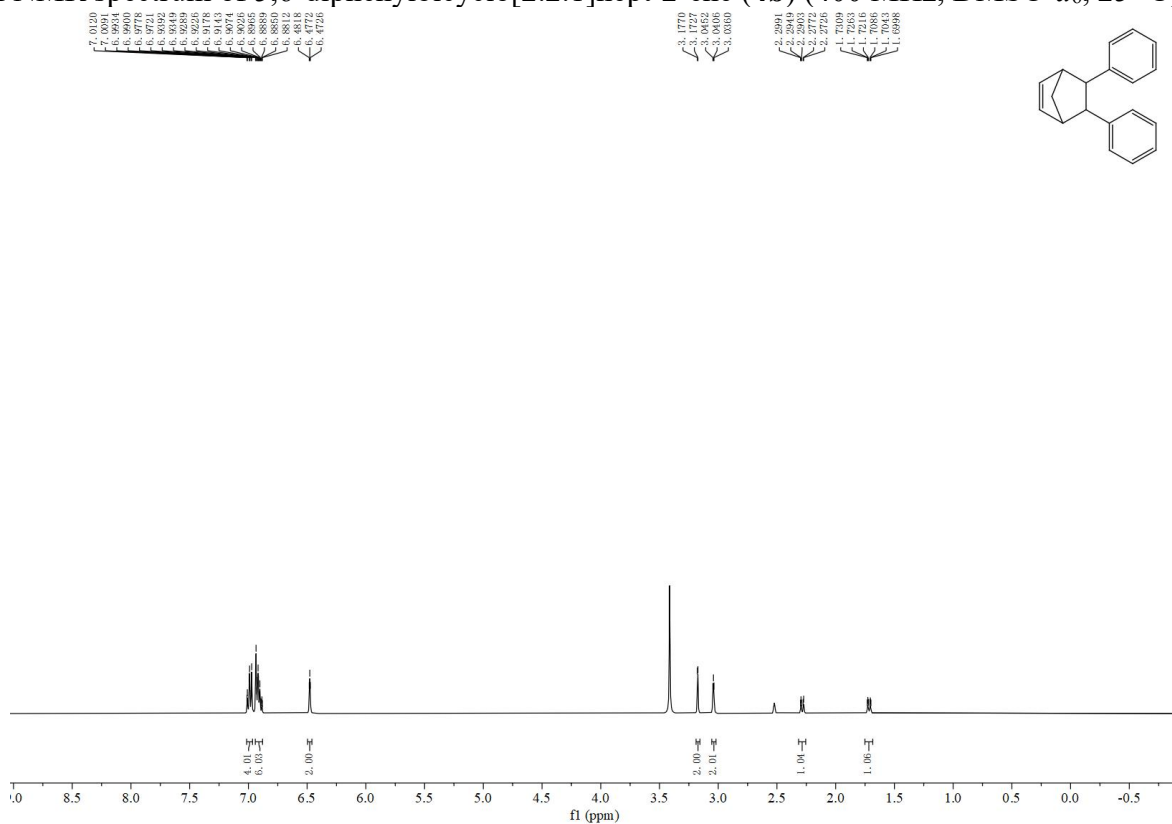
¹H NMR spectrum of 5,6-bis(methoxymethyl)bicyclo[2.2.1]hept-2-ene (**2b**) (400 MHz, DMSO-*d*₆, 25 °C)



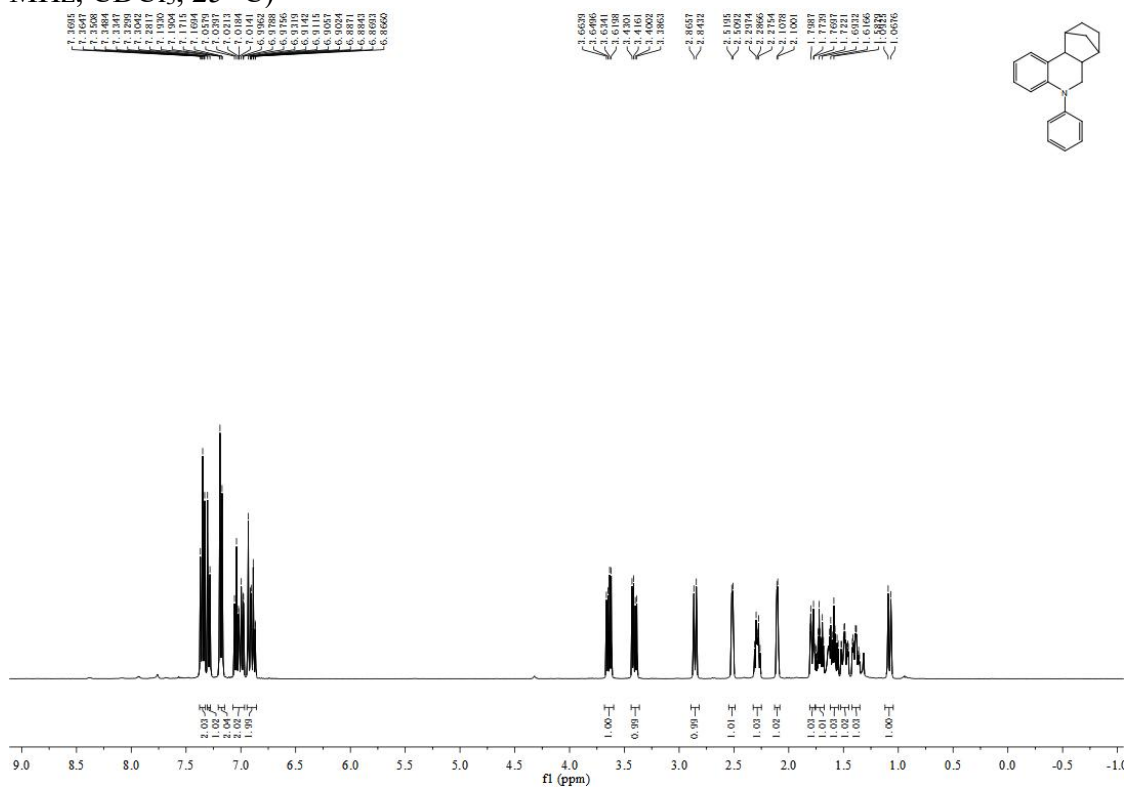
¹H NMR spectrum of dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (**3b**) (400 MHz, DMSO-*d*₆, 25 °C)



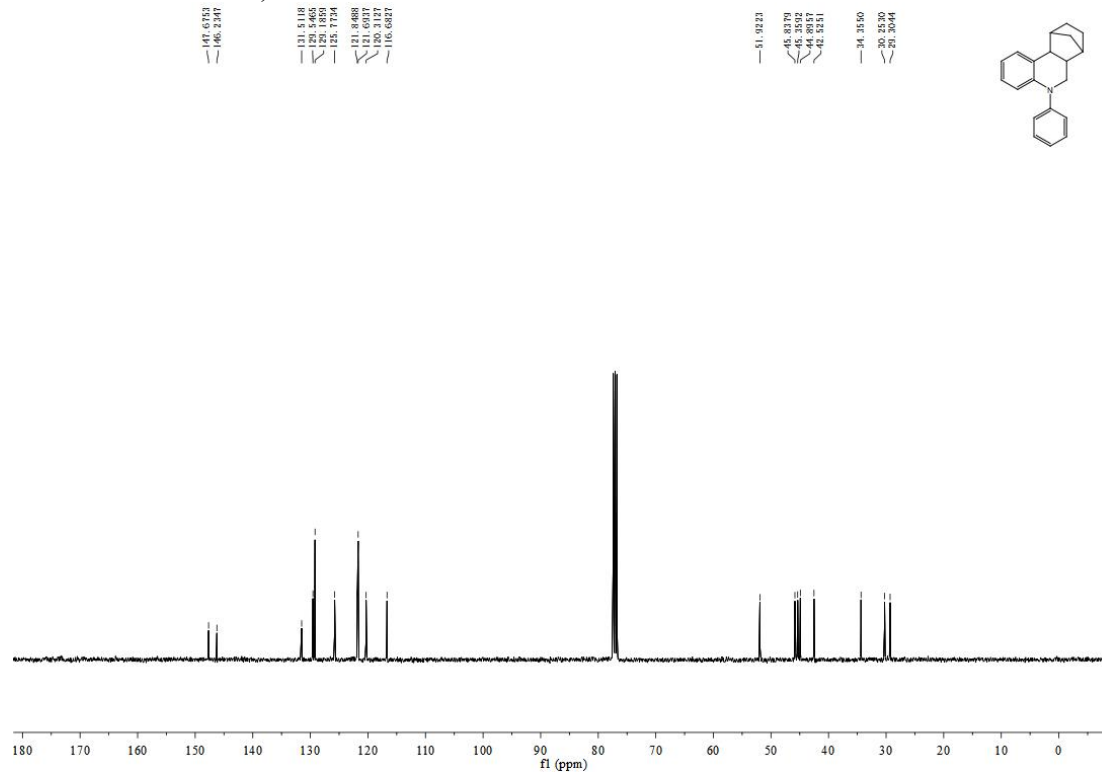
^1H NMR spectrum of 5,6-diphenylbicyclo[2.2.1]hept-2-ene (**4b**) (400 MHz, $\text{DMSO}-d_6$, 25 °C)



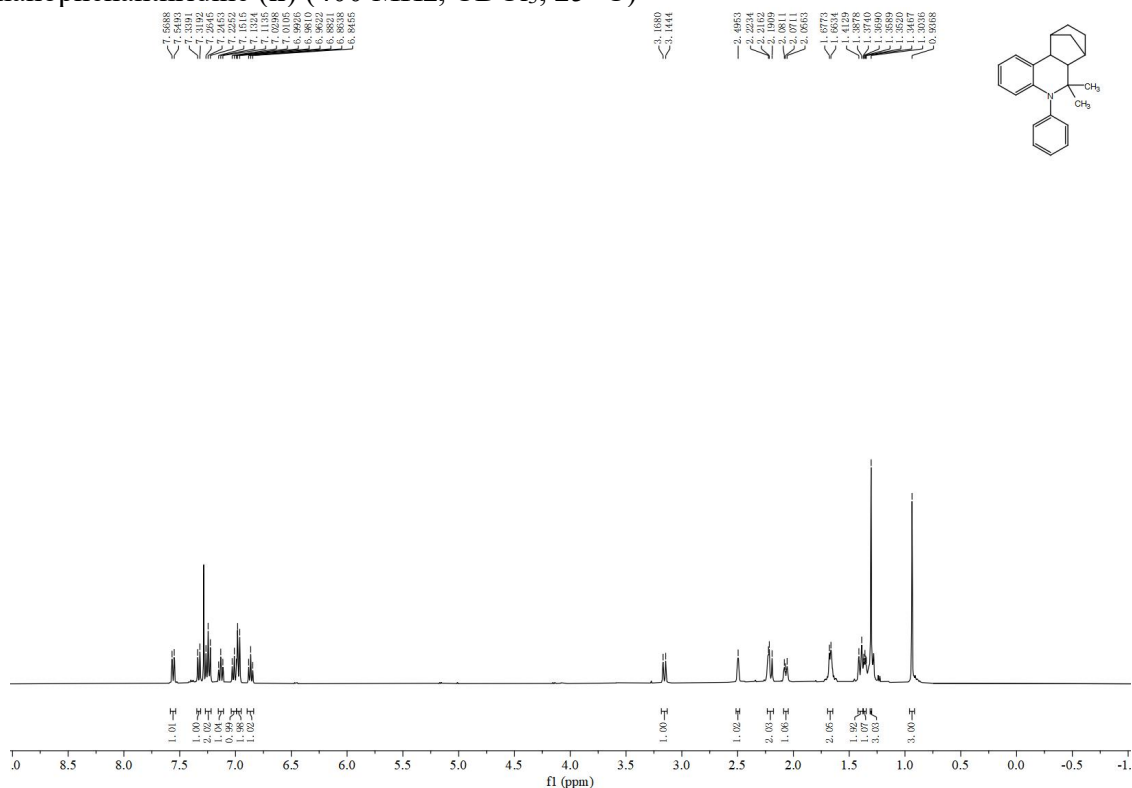
^1H NMR spectrum of 5-phenyl-5,6,6a,7,8,9,10,10a-octahydro-7,10-methanophenanthridine (**g**) (400 MHz, CDCl_3 , 25 °C)



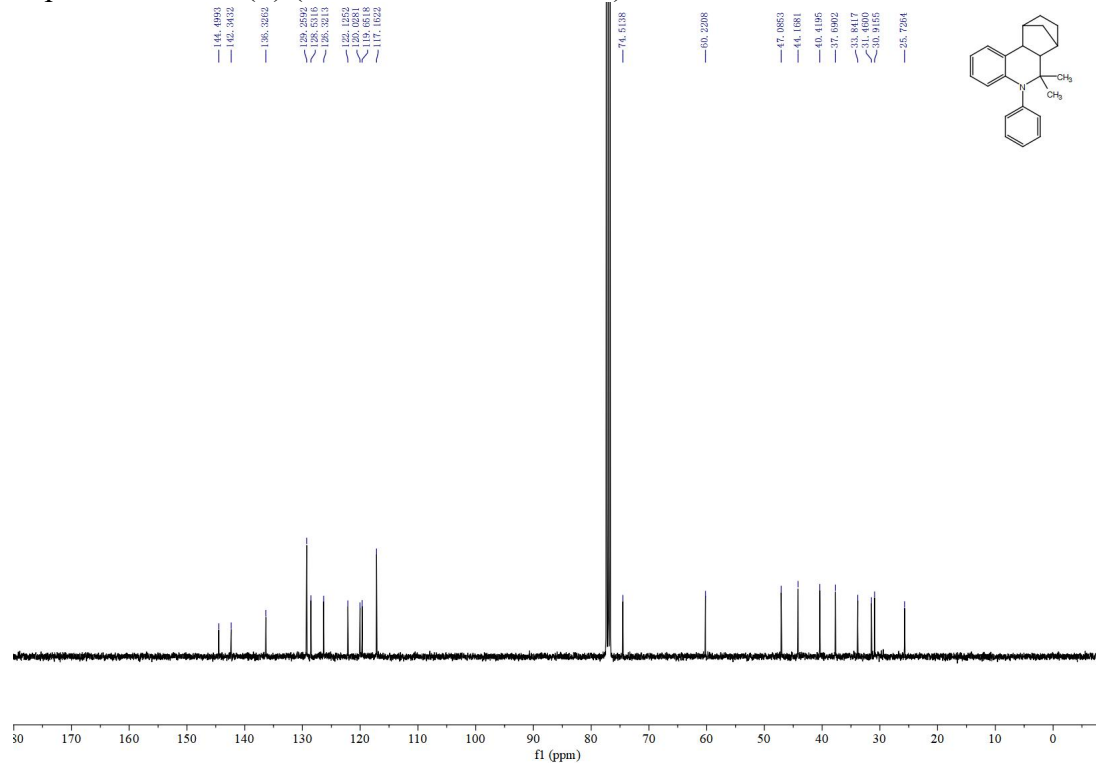
^{13}C NMR spectrum of 5-phenyl-5,6,6a,7,8,9,10,10a-octahydro-7,10-methanophenanthridine (**g**) (100 MHz, CDCl_3 , 25 °C)



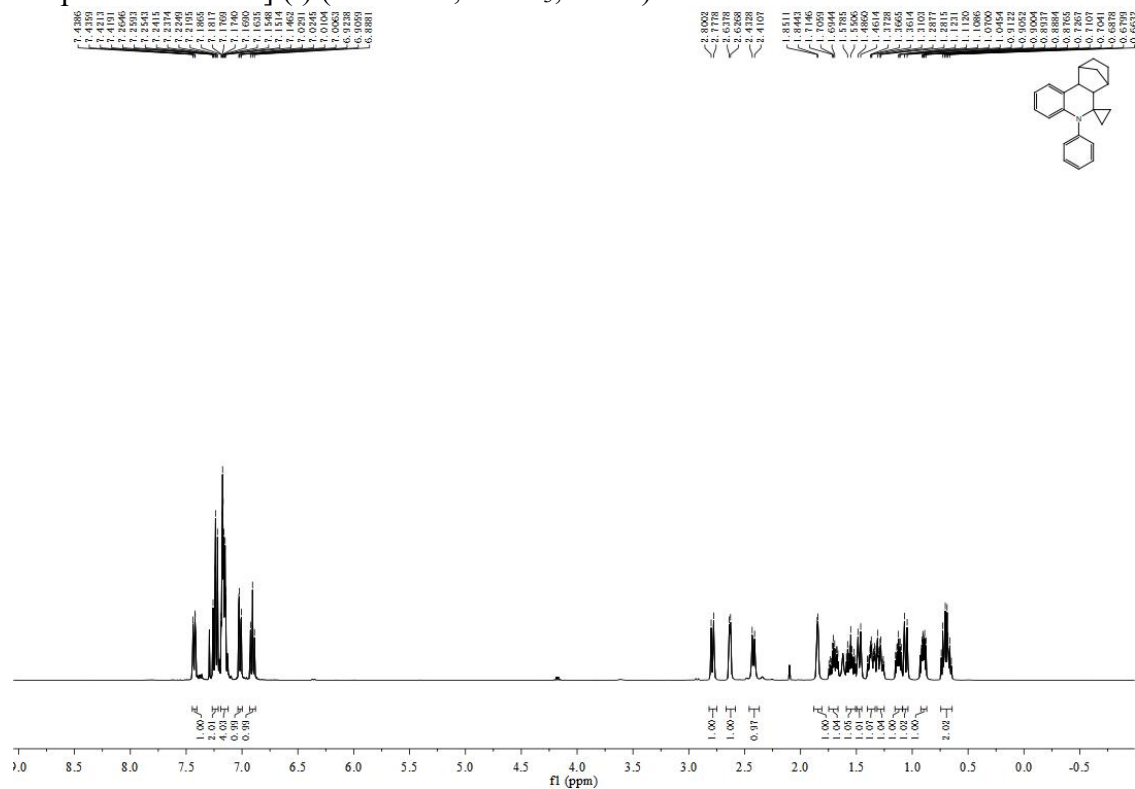
^1H NMR spectrum of 6,6-dimethyl-5-phenyl-5,6,6a,7,8,9,10,10a-octahydro-7,10-methanophenanthridine (**h**) (400 MHz, CDCl_3 , 25 °C)

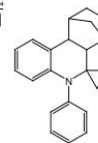
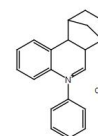
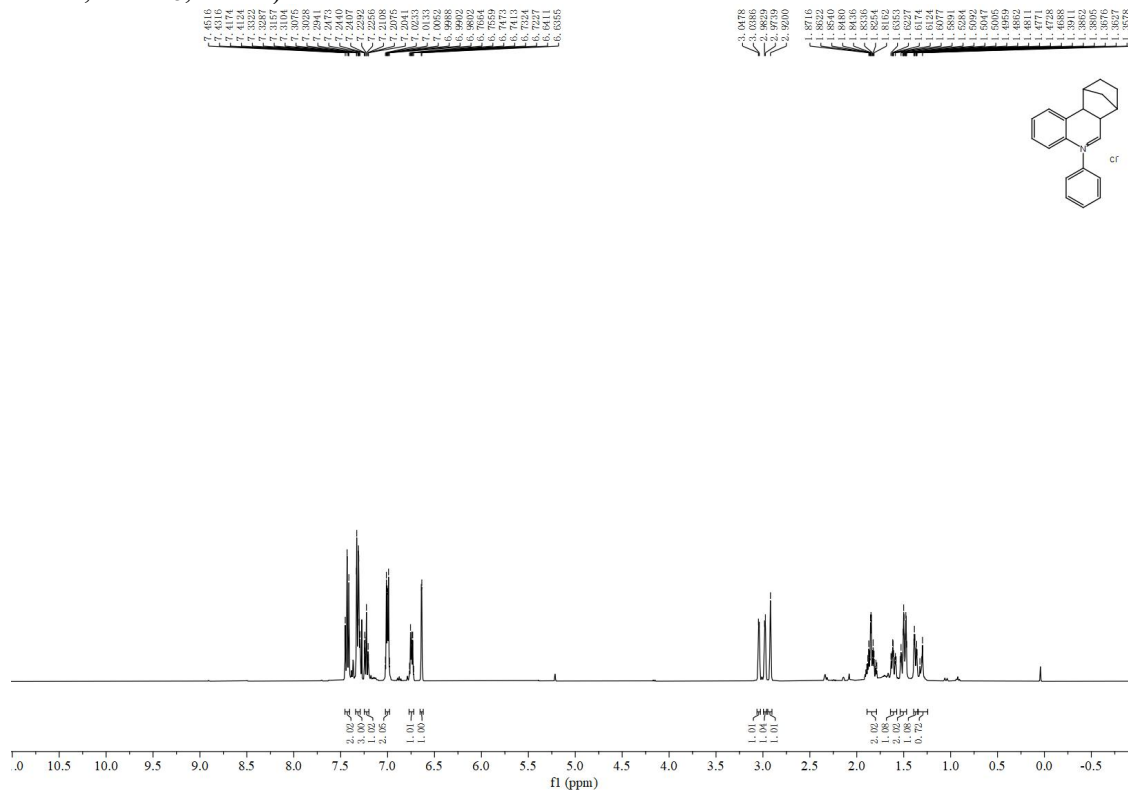


¹³C NMR spectrum of 6,6-dimethyl-5-phenyl-5,6,6a,7,8,9,10,10a-octahydro-7,10-methanophenanthridine (**h**) (100 MHz, CDCl₃, 25 °C)

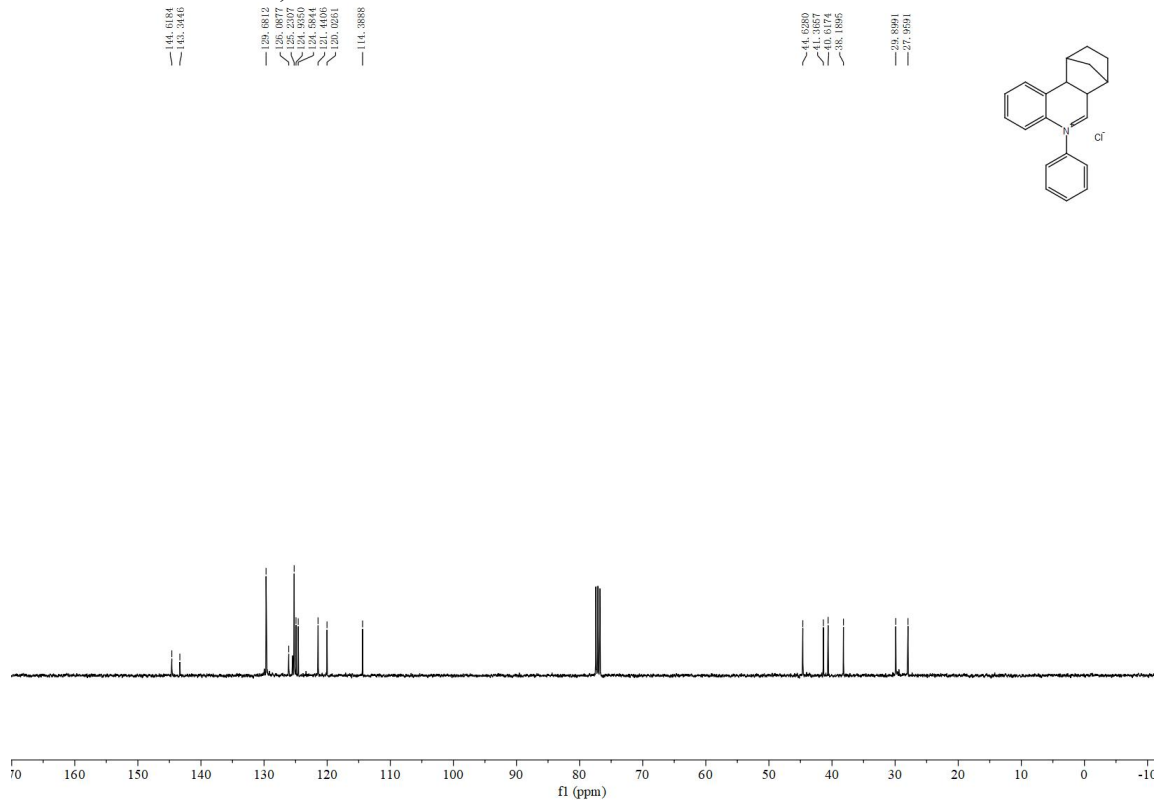


¹H NMR spectrum of 5'-phenyl-6a',7',8',9',10',10a'-hexahydro-5'H-spiro[cyclopropane-1,6'-[7,10]methanophenanthrid-in-ine] (**i**) (400 MHz, CDCl₃, 25 °C)

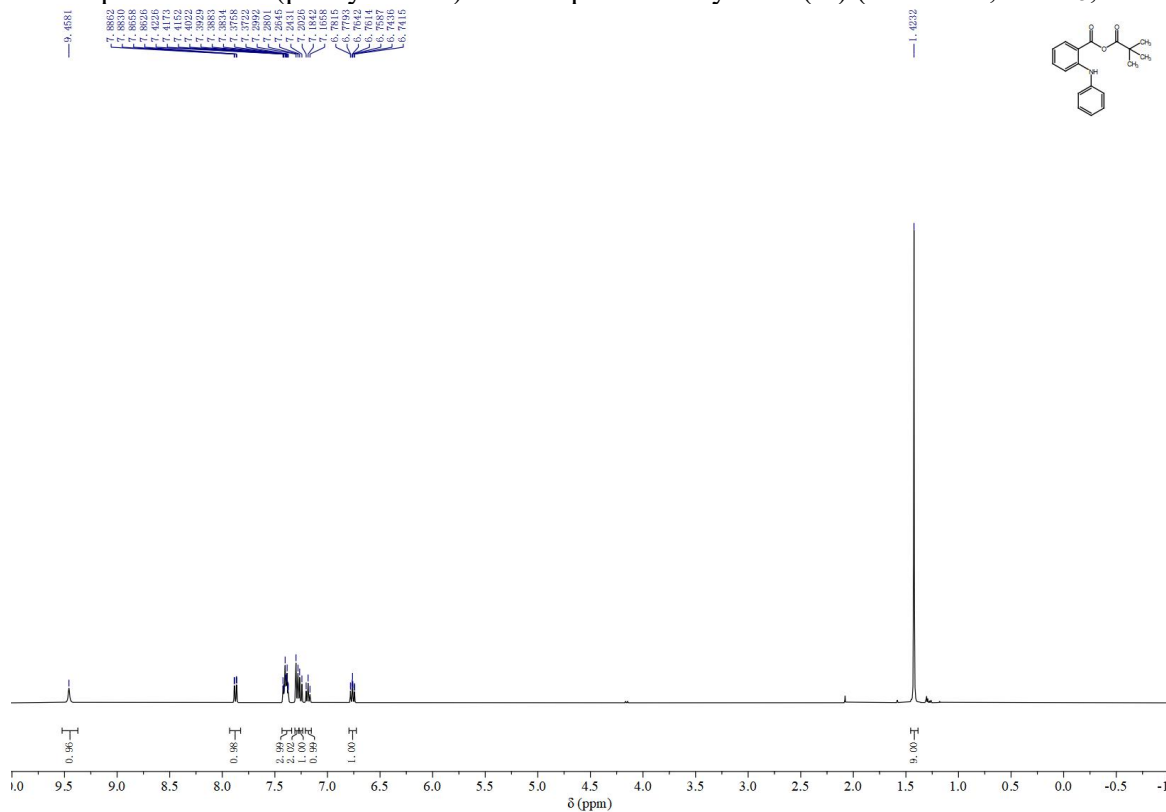


[illegible][illegible]

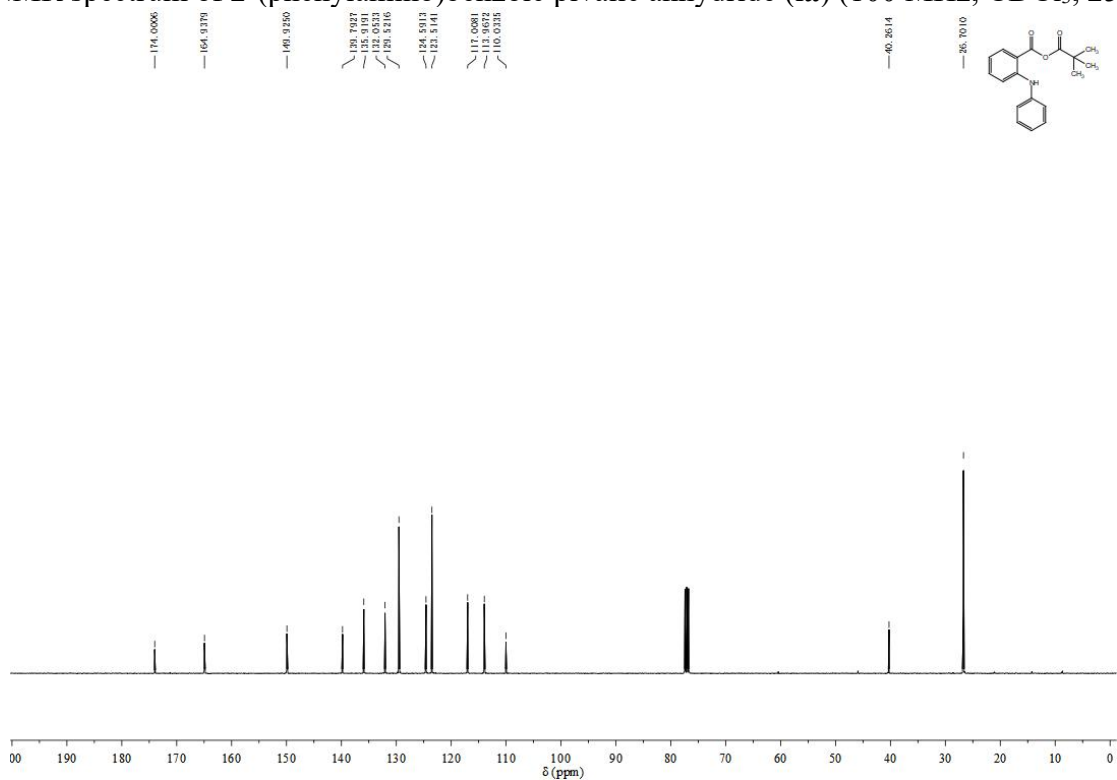
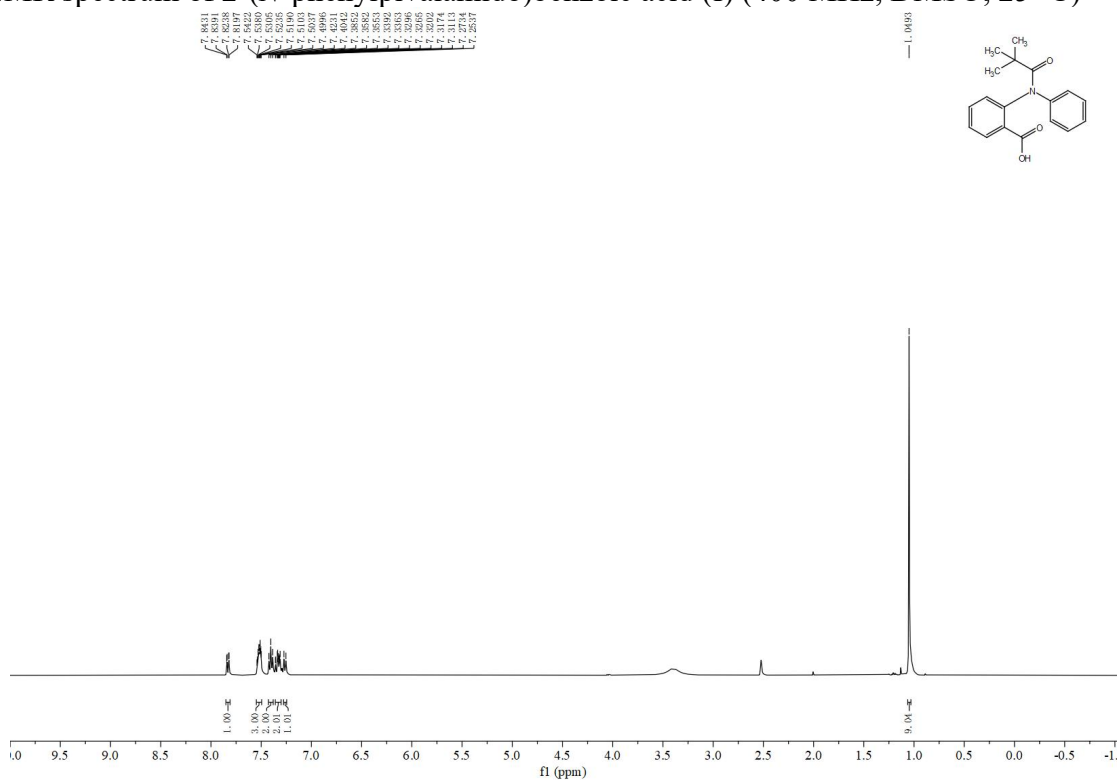
¹³C NMR spectrum of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-5-ium (j) (100 MHz, CDCl₃, 25 °C)



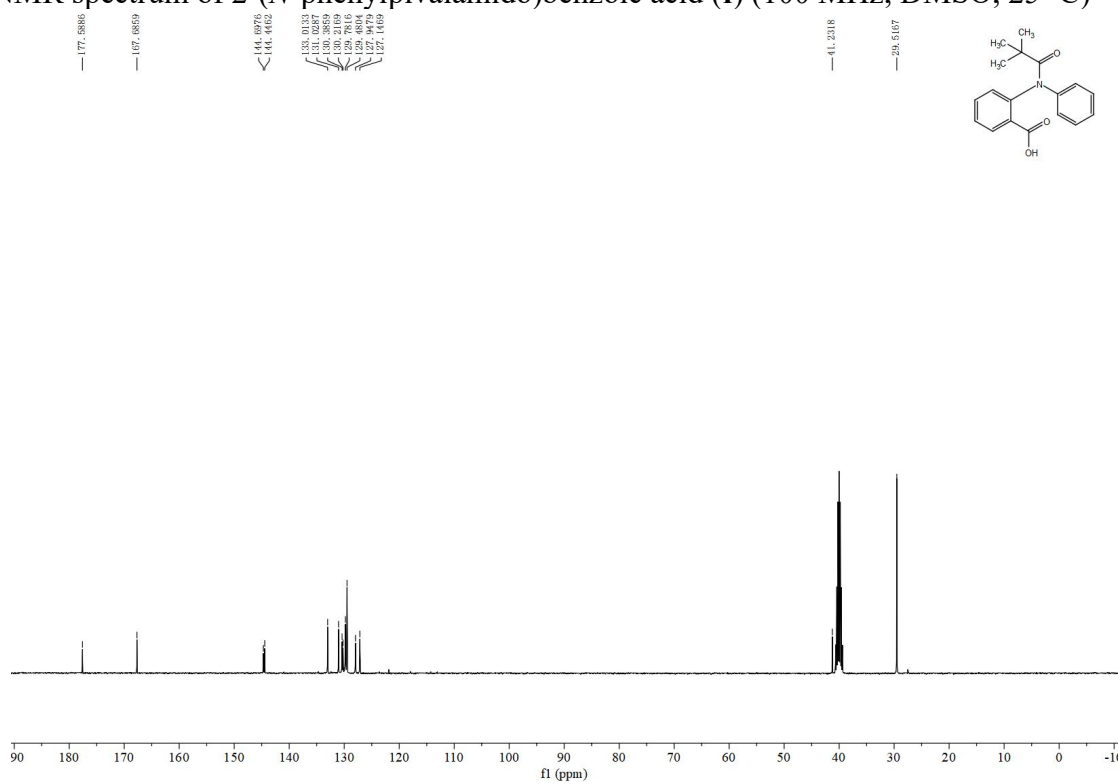
¹H NMR spectrum of 2-(phenylamino)benzoic pivalic anhydride (**1a**) (400 MHz, CDCl₃, 25 °C)



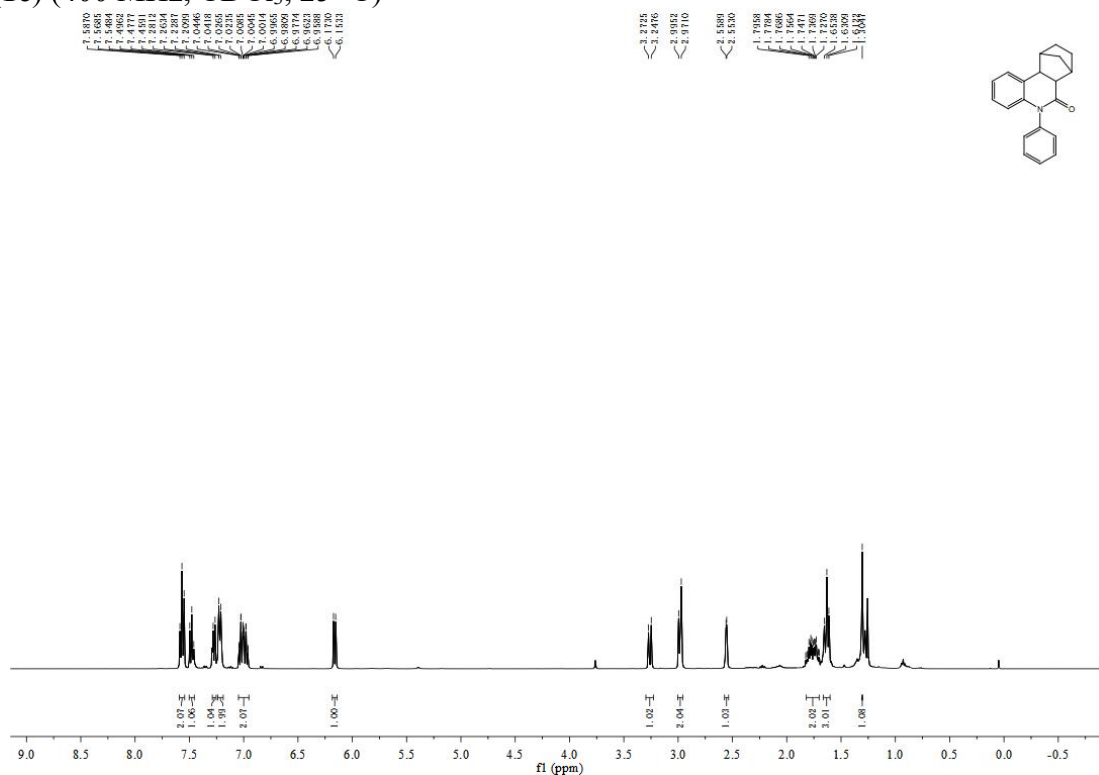
¹³C NMR spectrum of 2-(phenylamino)benzoic pivalic anhydride (**1a**) (100 MHz, CDCl₃, 25 °C)

¹H NMR spectrum of 2-(*N*-phenylpivalamido)benzoic acid (**f**) (400 MHz, DMSO, 25 °C)

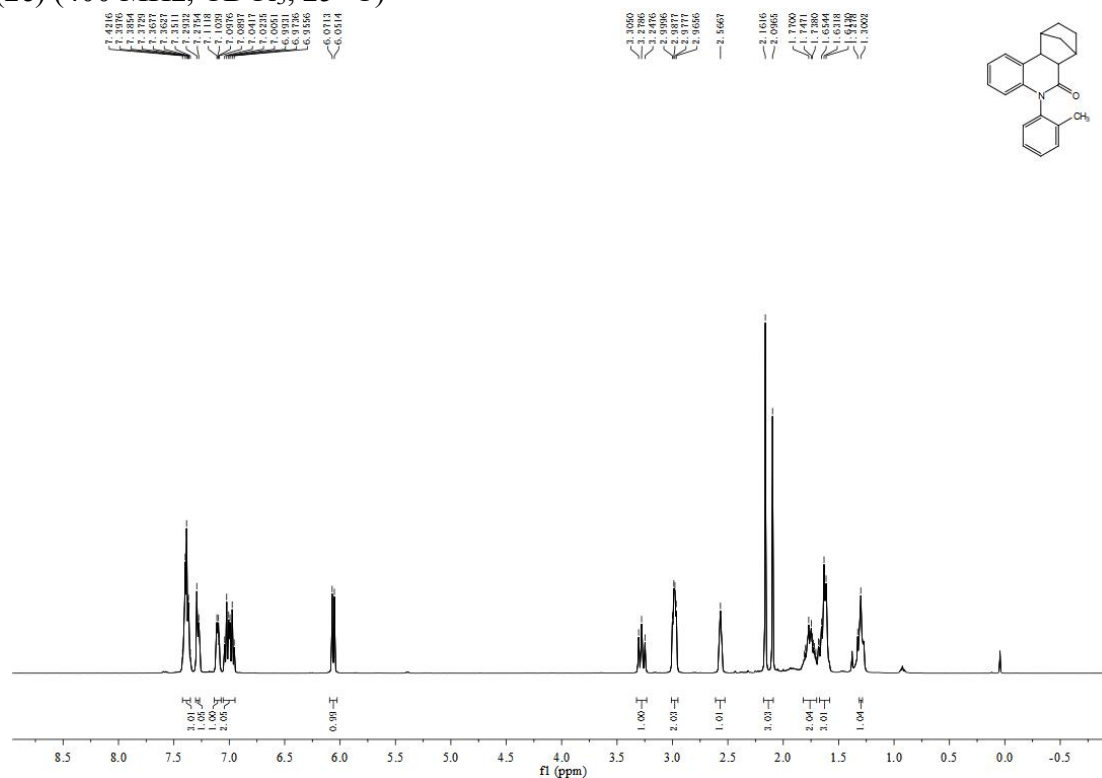
^{13}C NMR spectrum of 2-(*N*-phenylpivalamido)benzoic acid (**f**) (100 MHz, DMSO, 25 °C)



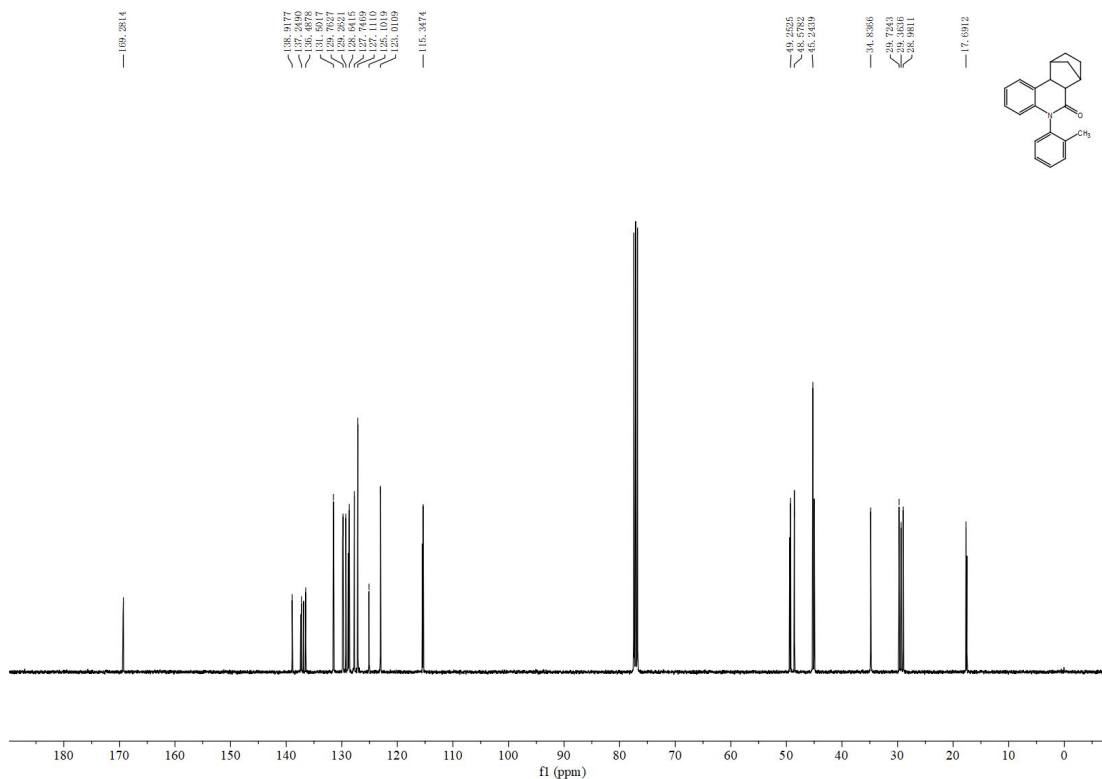
^1H NMR spectrum of 5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**1c**) (400 MHz, CDCl_3 , 25 °C)



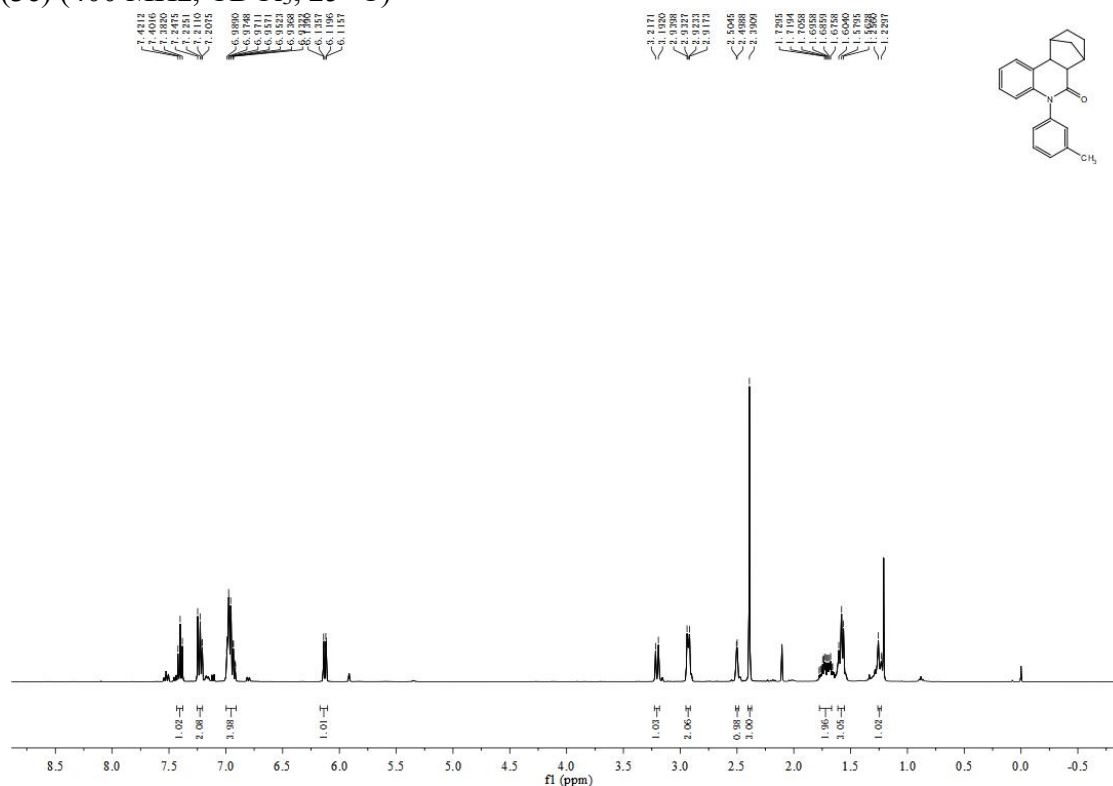
^1H NMR spectrum of 5-(*o*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**2c**) (400 MHz, CDCl_3 , 25 °C)



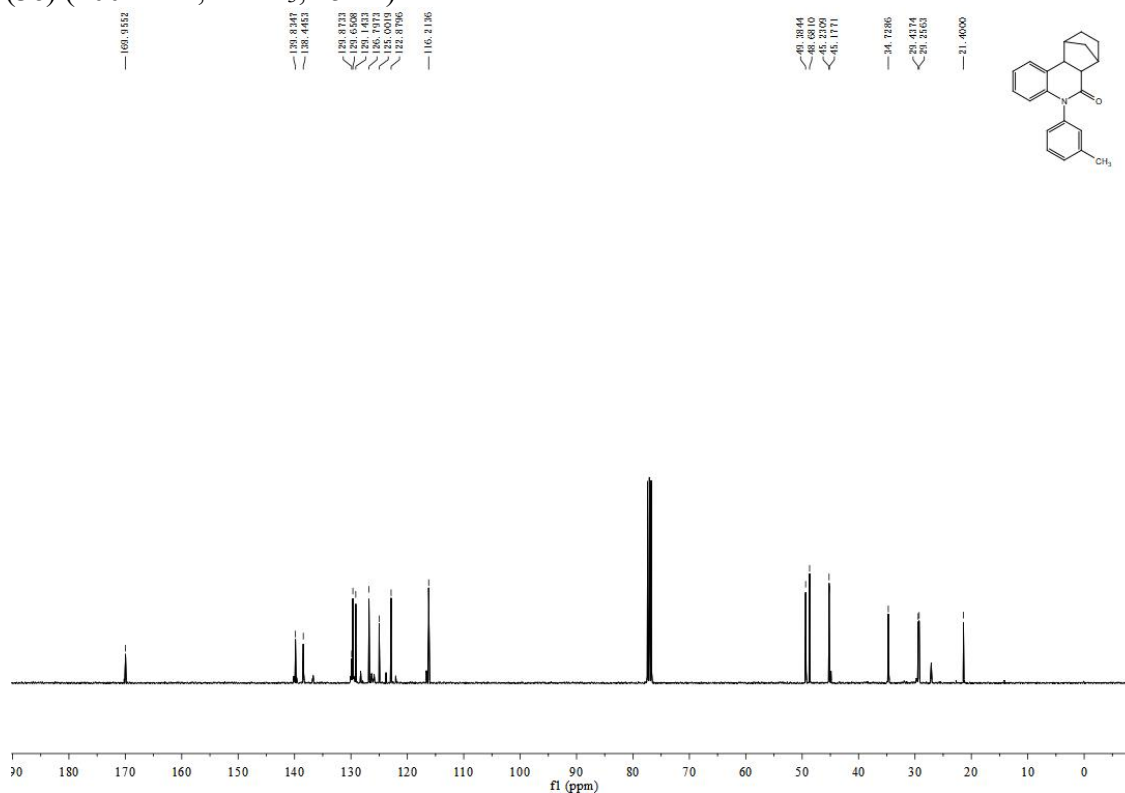
^{13}C NMR spectrum of 5-(*o*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(*5H*)-one (**2c**) (100 MHz, CDCl_3 , 25 °C)



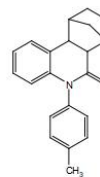
^1H NMR spectrum of 5-(*m*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**3c**) (400 MHz, CDCl_3 , 25 °C)



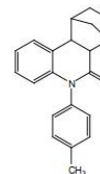
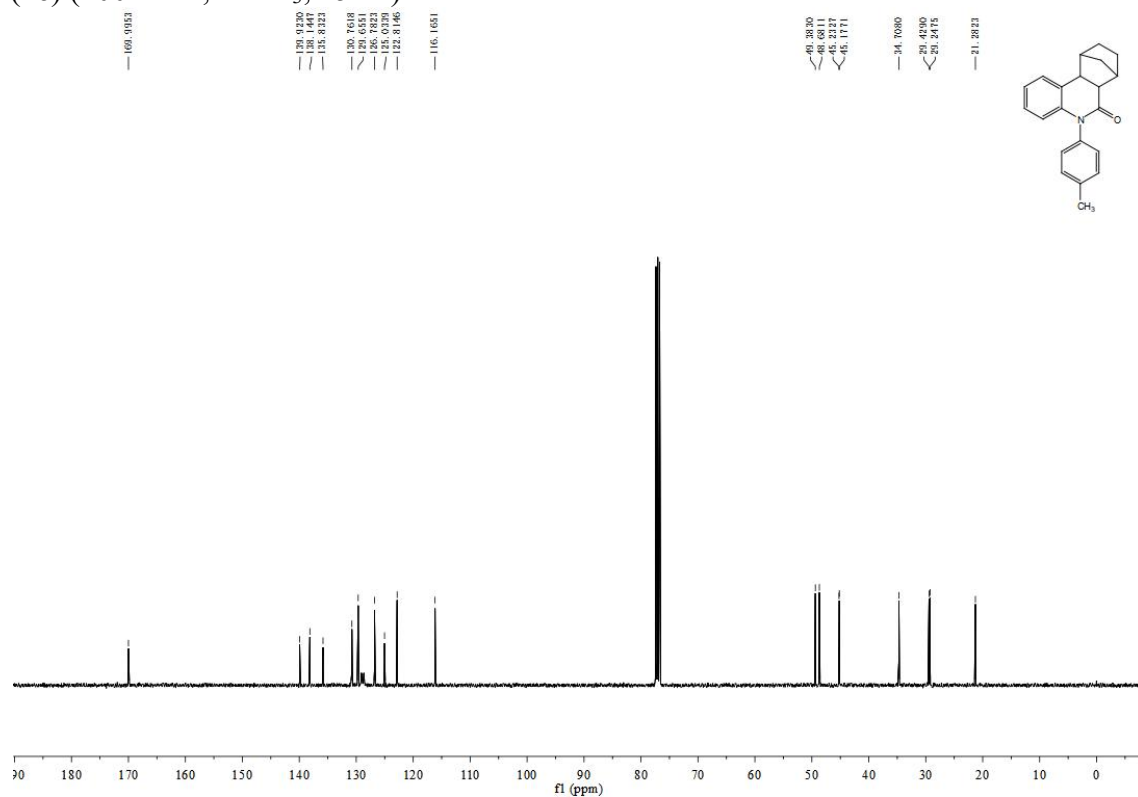
^{13}C NMR spectrum of 5-(*m*-tolyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**3c**) (100 MHz, CDCl_3 , 25 °C)



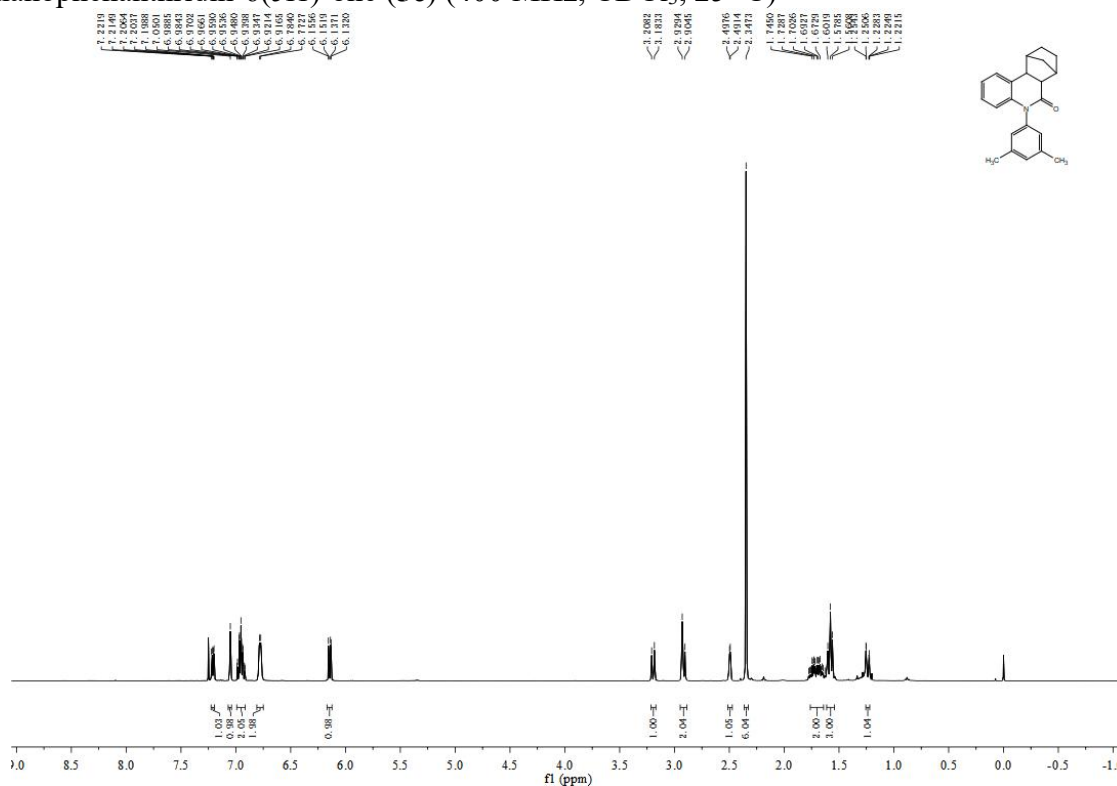
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7. 3 080
7. 2 234
7. 2 251
7. 2 078
7. 0 570
7. 0 350
6. 9 920
6. 9 889
6. 9 741
6. 9 706
6. 9 566
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6. 9 182
6. 9 140
6. 1 681
6. 1 488
6. 1 450



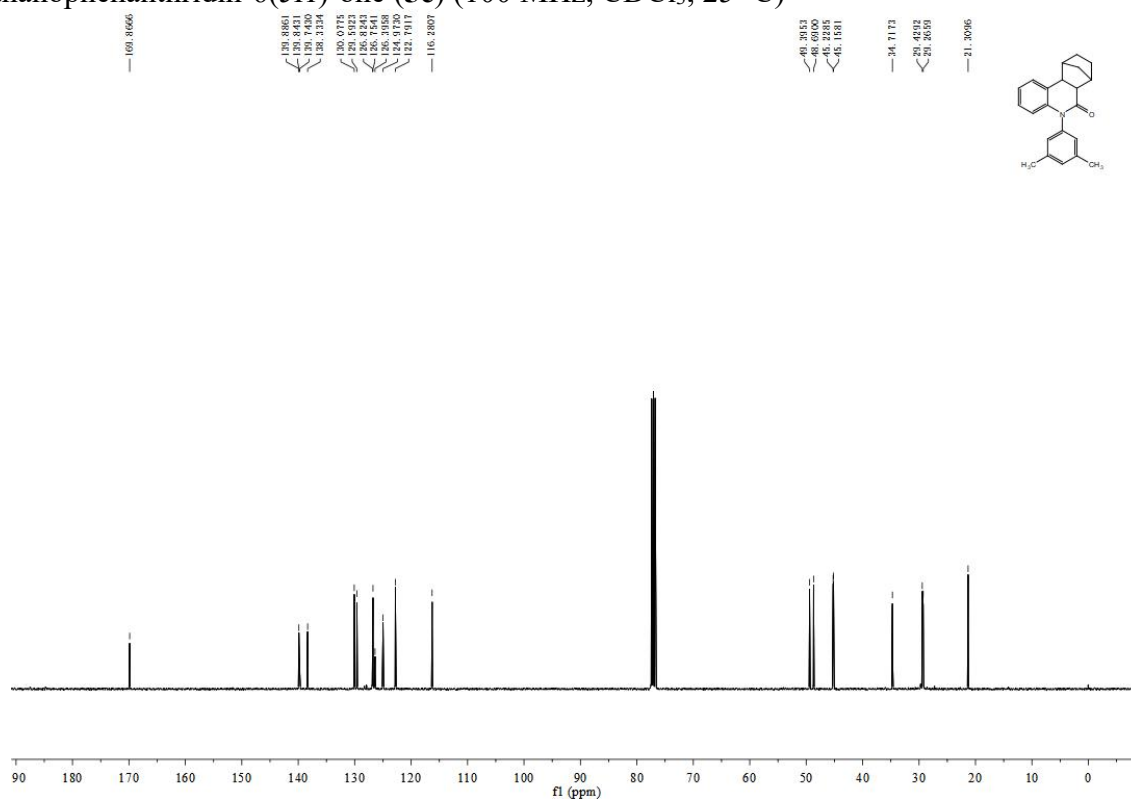
—	169.9953
—	139.9230
—	138.1447
—	135.8323
—	130.7618
—	129.6551
—	126.7823
—	125.0339
—	122.8146



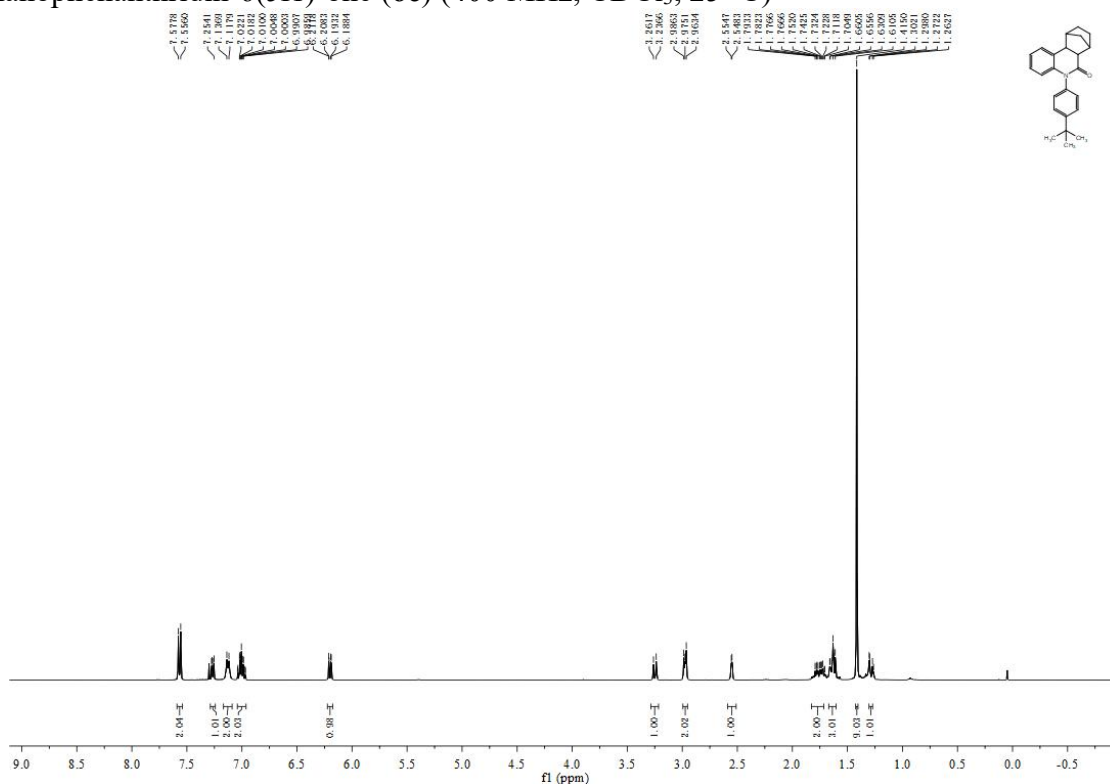
^1H NMR spectrum of 5-(3,5-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**5c**) (400 MHz, CDCl_3 , 25 °C)



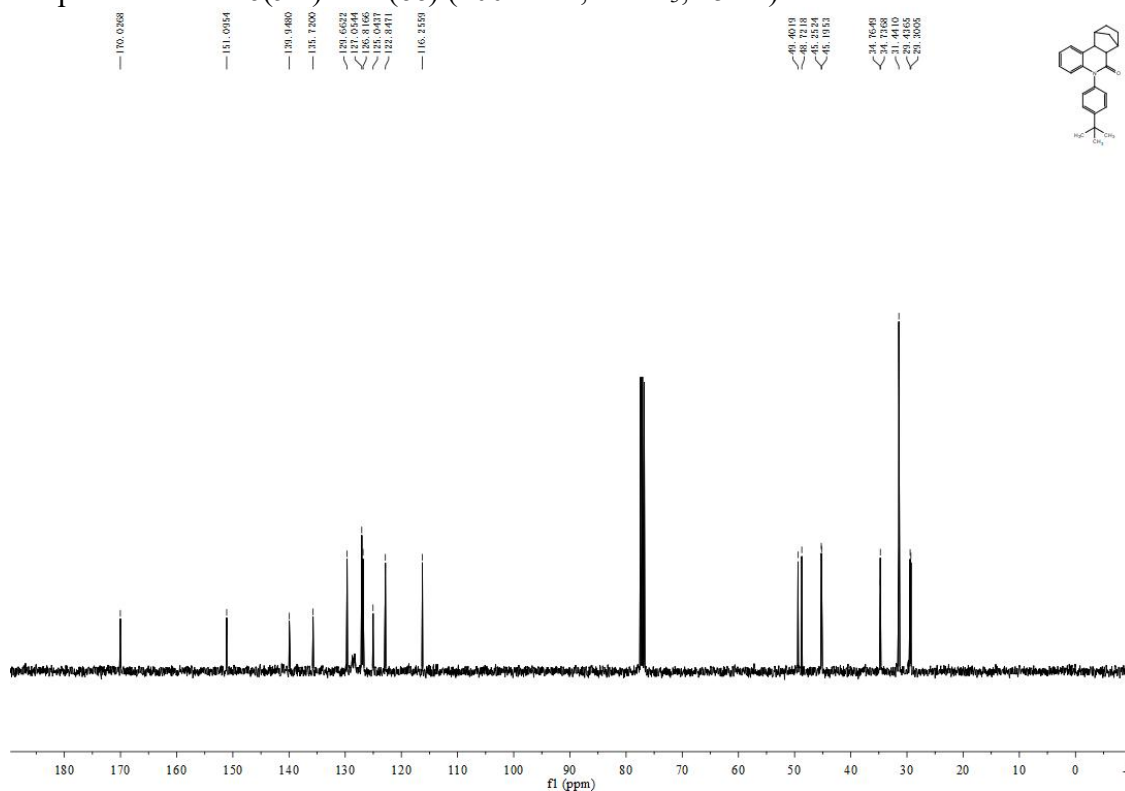
^{13}C NMR spectrum of 5-(3,5-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**5c**) (100 MHz, CDCl_3 , 25 °C)



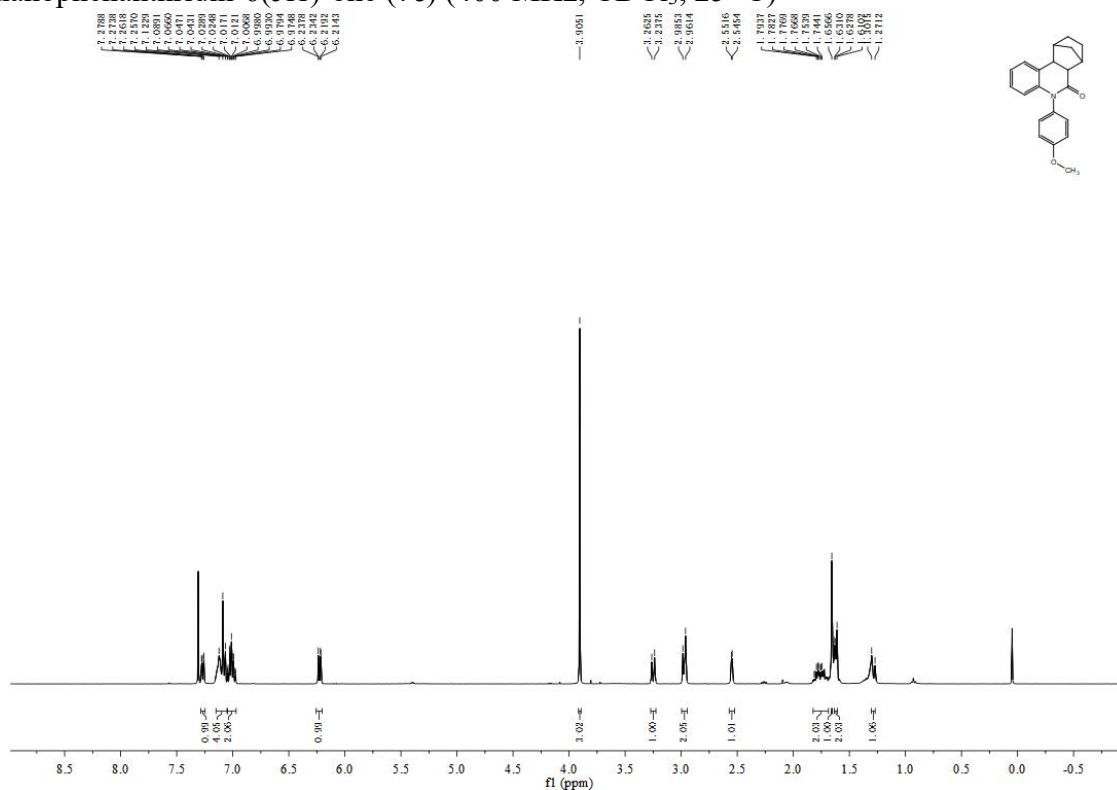
^1H NMR spectrum of 5-(4-(*tert*-butyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**6c**) (400 MHz, CDCl_3 , 25 °C)



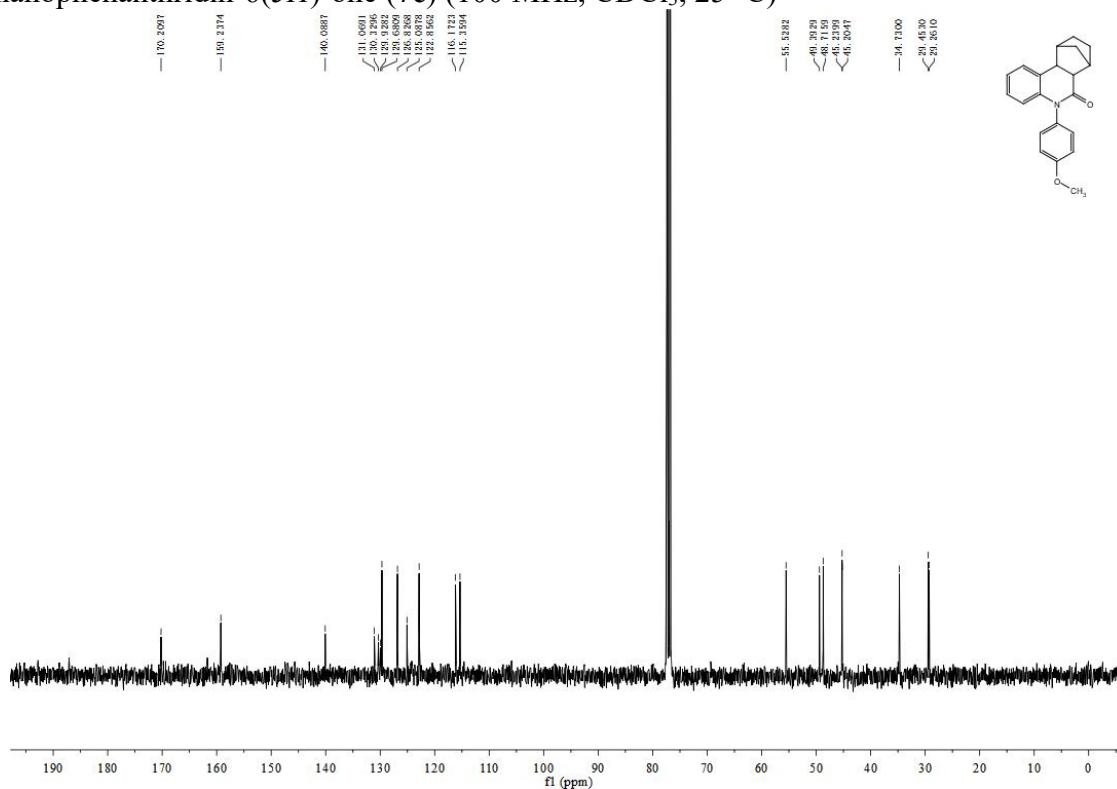
^{13}C NMR spectrum of 5-(4-(*tert*-butyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**6c**) (100 MHz, CDCl_3 , 25 °C)



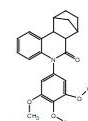
^1H NMR spectrum of 5-(4-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**7c**) (400 MHz, CDCl_3 , 25 °C)



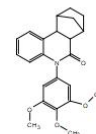
^{13}C NMR spectrum of 5-(4-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**7c**) (100 MHz, CDCl_3 , 25 °C)



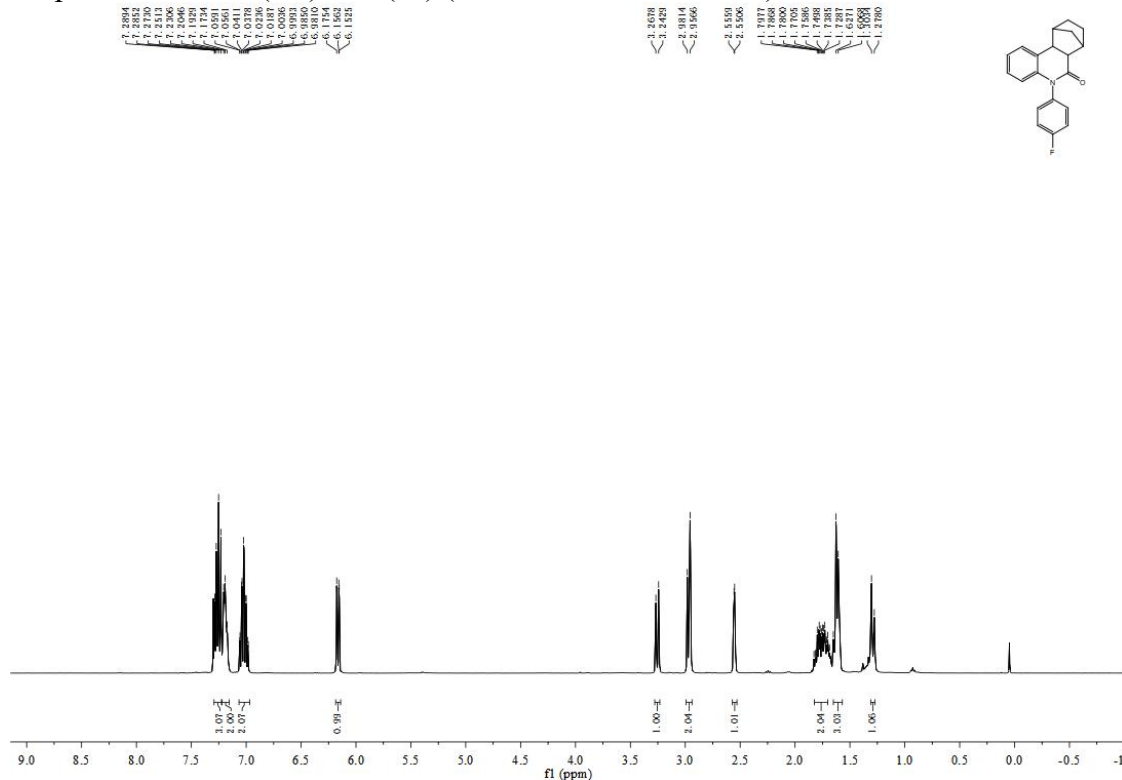
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6, 9268			
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6, 9163			
6, 9141			
6, 9018			
6, 8954			
6, 8912			
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6, 8812			
6, 8740			
6, 8614			
6, 8431			
6, 8301			
6, 8233			
6, 8144			
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	3, 7671	3, 1252	2, 4418
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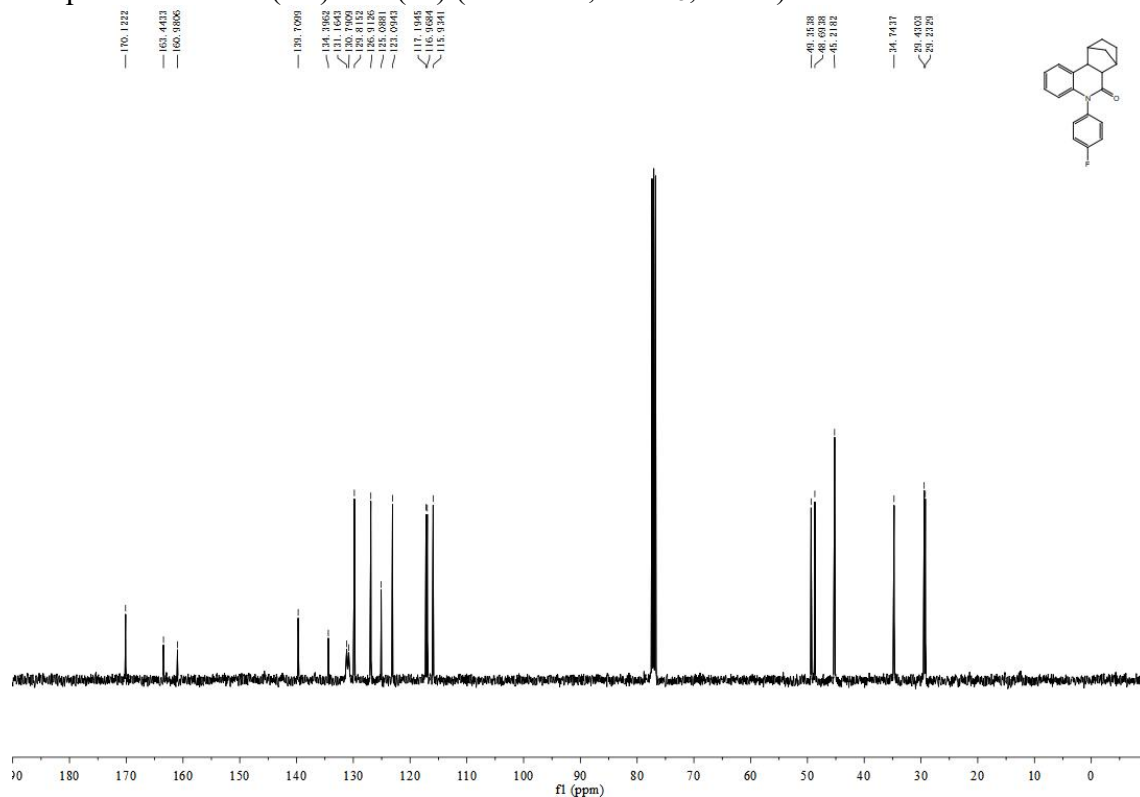
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— 154. 3137
— 137. 6482
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— 129. 6904
— 129. 6646
— 126. 9608
— 124. 1339
— 121. 0869
— 116. 2058
— 106. 1919
— 105. 7076
— 60. 9011
— 56. 1187
— 49. 3121
— 48. 1658
— 45. 1651
— 43. 0994
— 34. 8611
— 29. 3820
— 29. 2643



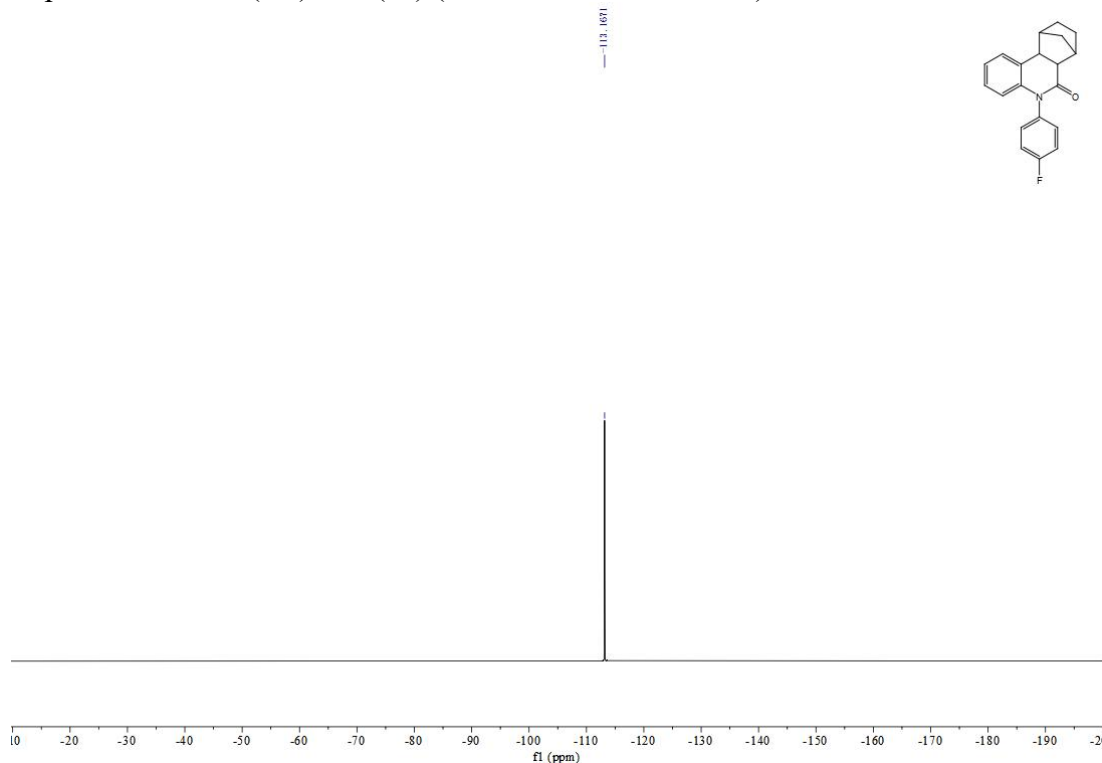
^1H NMR spectrum of 5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**9c**) (400 MHz, CDCl_3 , 25 °C)



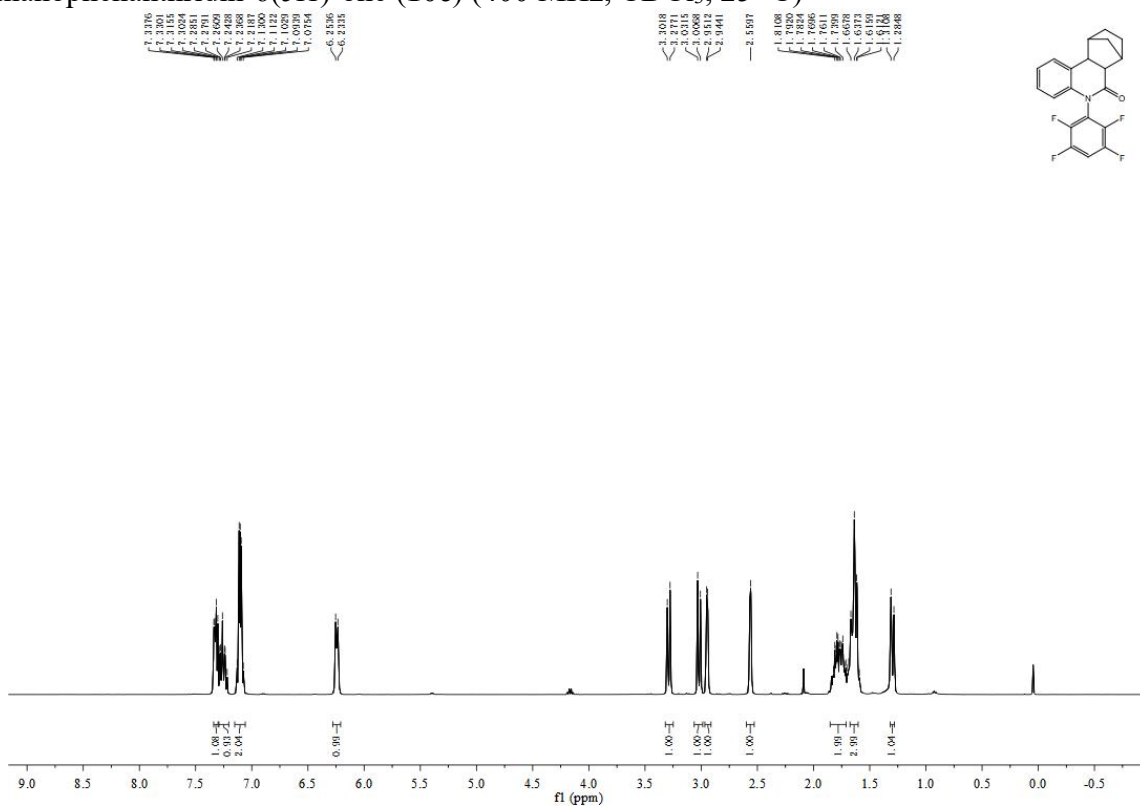
^{13}C NMR spectrum of 5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**9c**) (100 MHz, CDCl_3 , 25 °C)



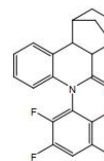
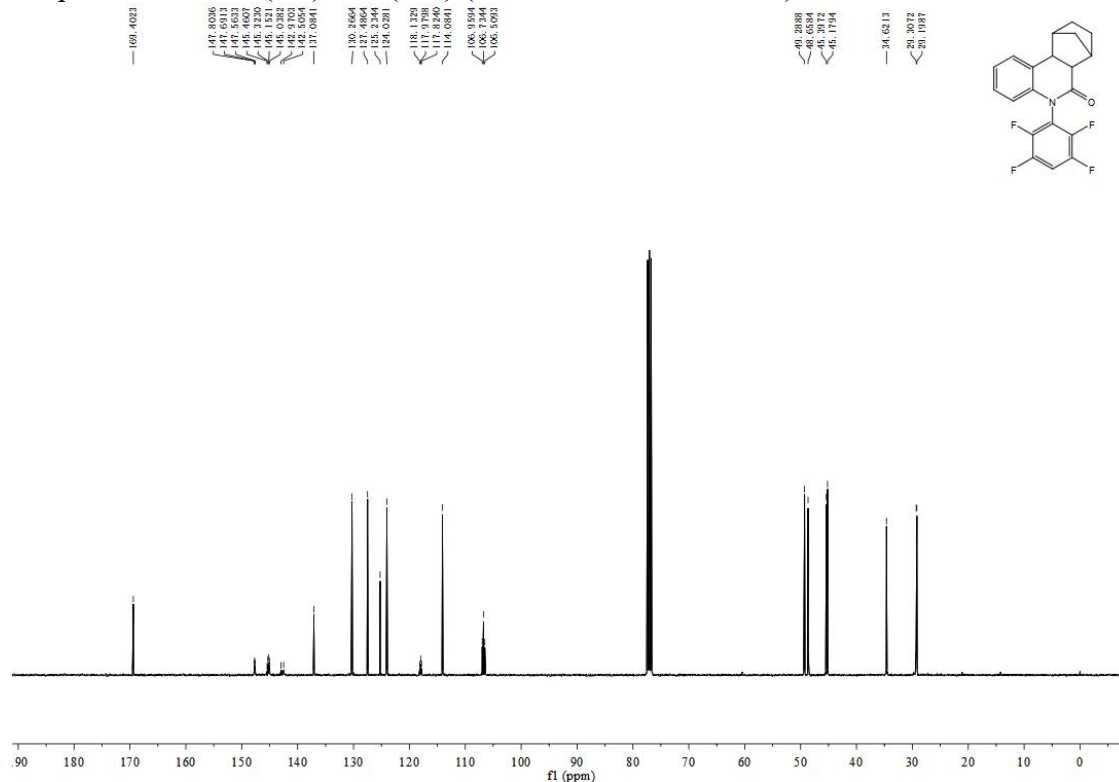
^{19}F NMR spectrum of 5-(4-fluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**9c**) (376 MHz, CDCl_3 , 25 °C)



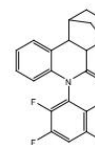
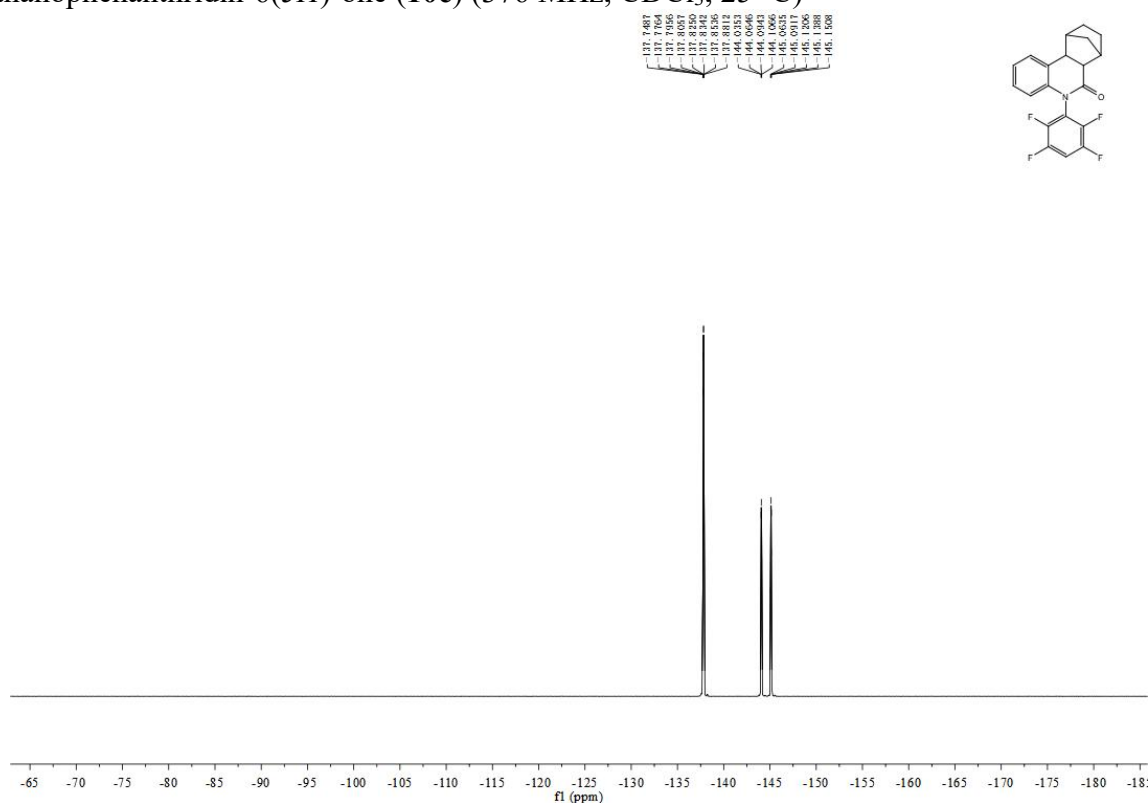
^1H NMR spectrum of 5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**10c**) (400 MHz, CDCl_3 , 25 °C)



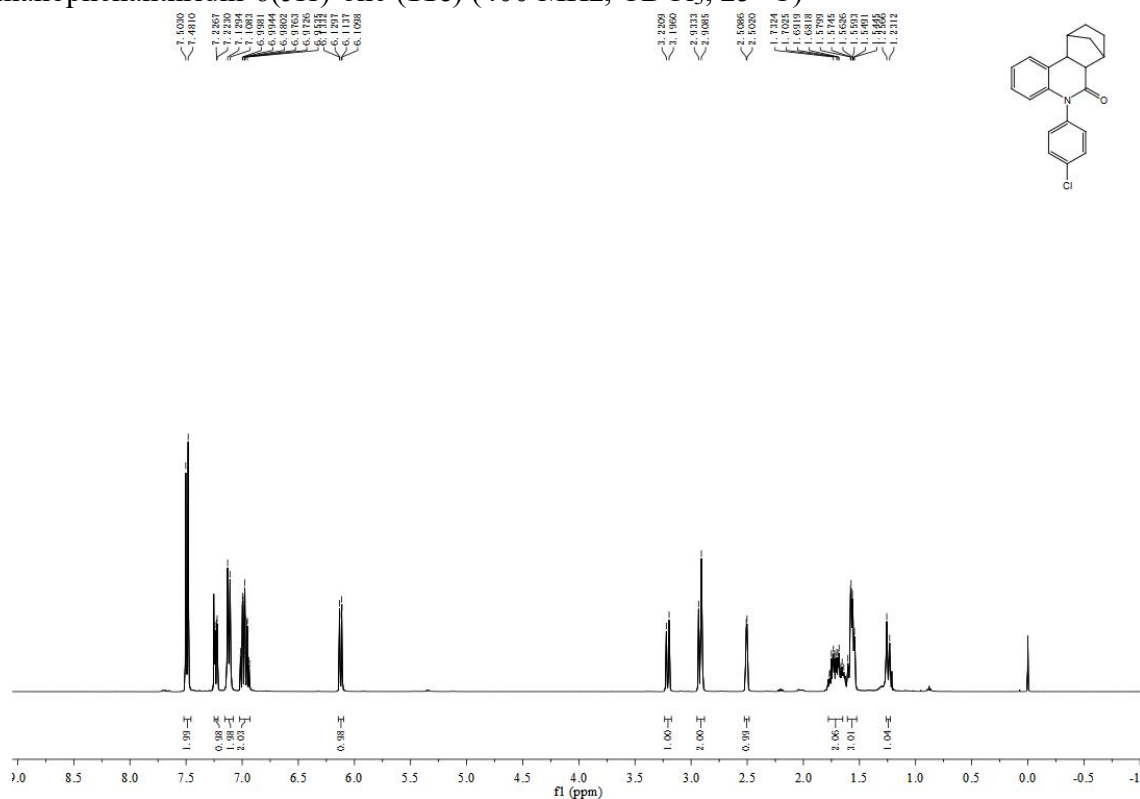
^{13}C NMR spectrum of 5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**10c**) (100 MHz, CDCl_3 , 25 °C)



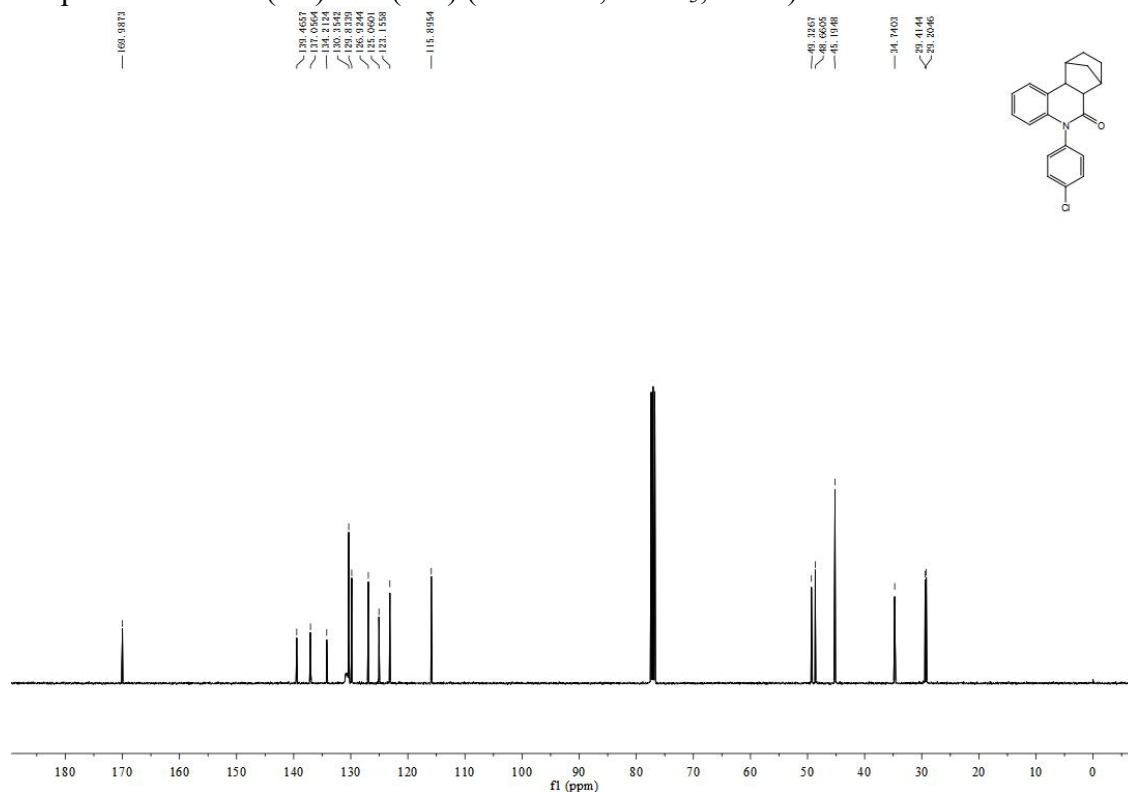
^{19}F NMR spectrum of 5-(2,3,5,6-tetrafluorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**10c**) (376 MHz, CDCl_3 , 25 °C)



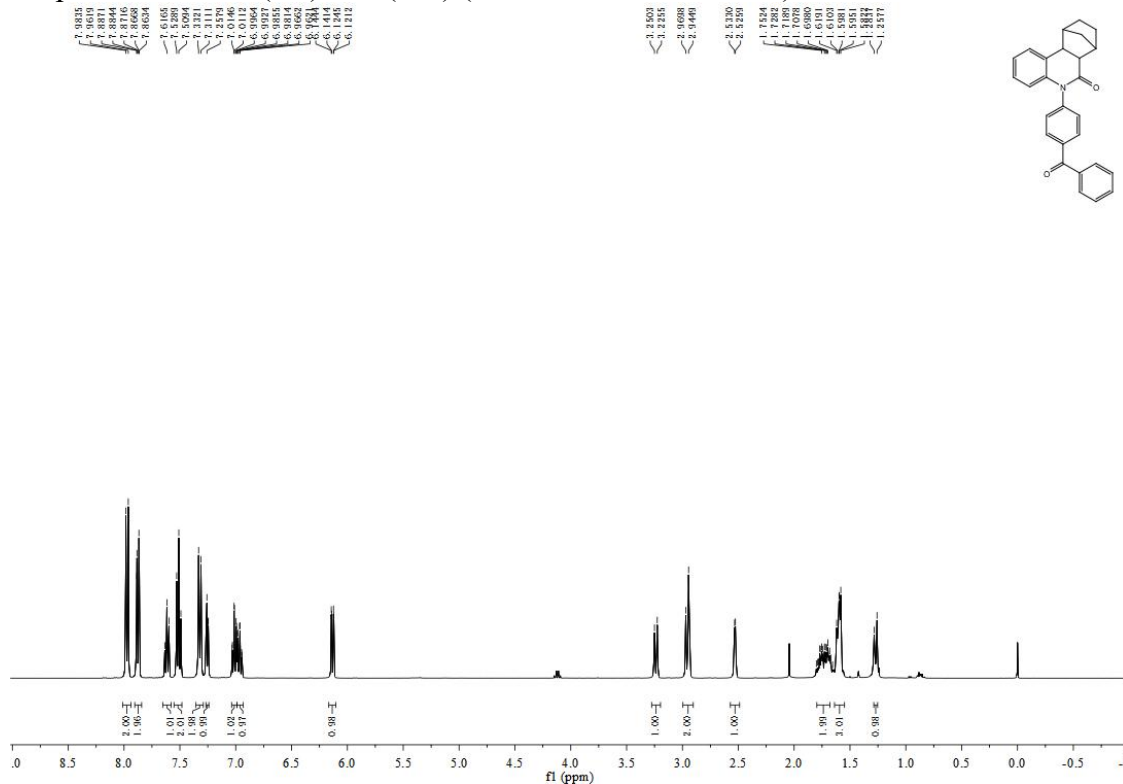
^1H NMR spectrum of 5-(4-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**11c**) (400 MHz, CDCl_3 , 25 °C)



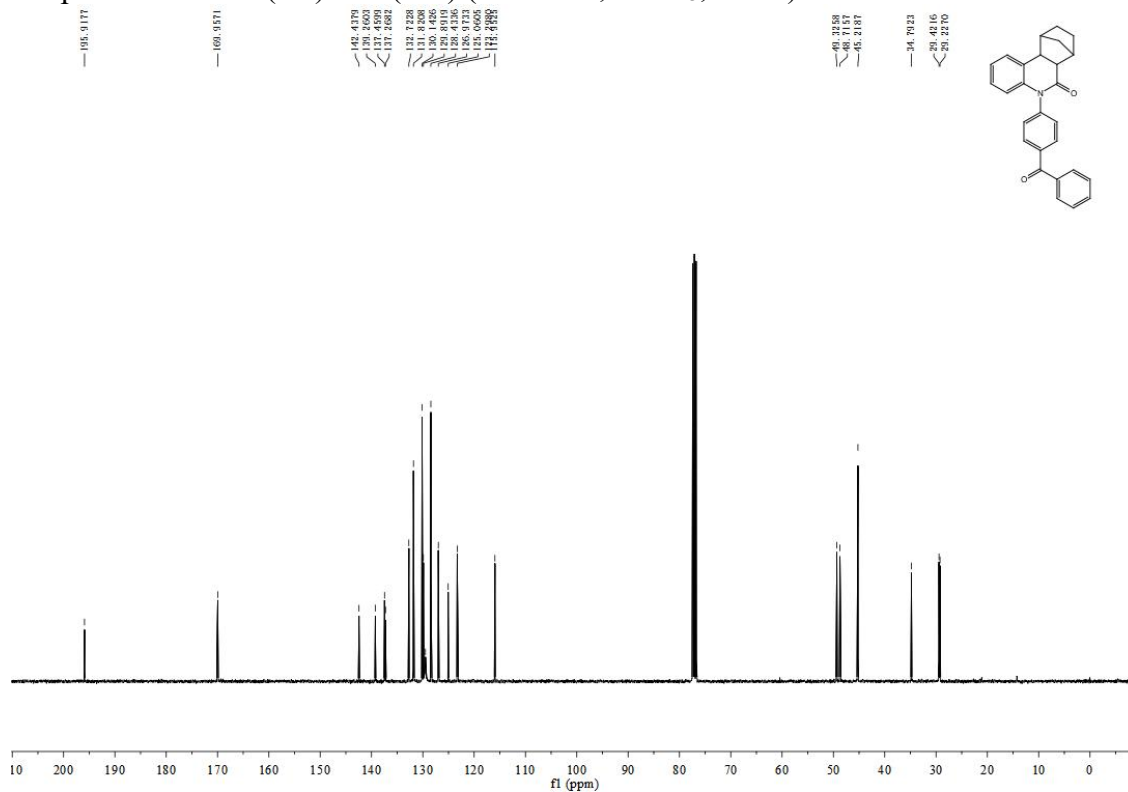
^{13}C NMR spectrum of 5-(4-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**11c**) (100 MHz, CDCl_3 , 25 °C)



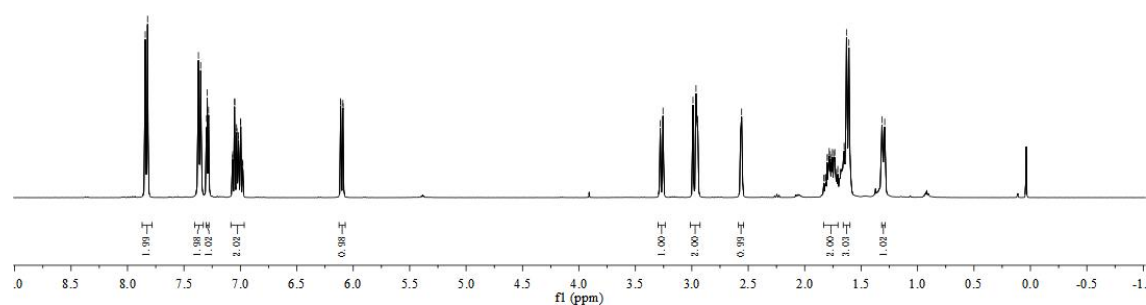
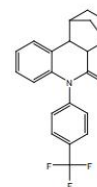
^1H NMR spectrum of 5-(4-benzoylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**12c**) (400 MHz, CDCl_3 , 25 °C)



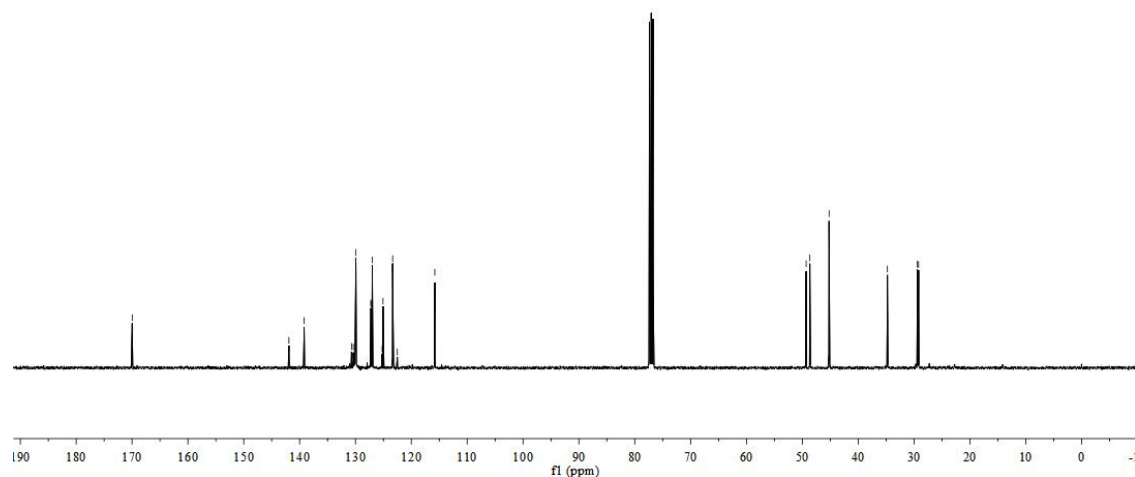
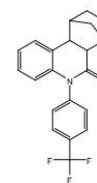
^{13}C NMR spectrum of 5-(4-benzoylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**12c**) (100 MHz, CDCl_3 , 25 °C)



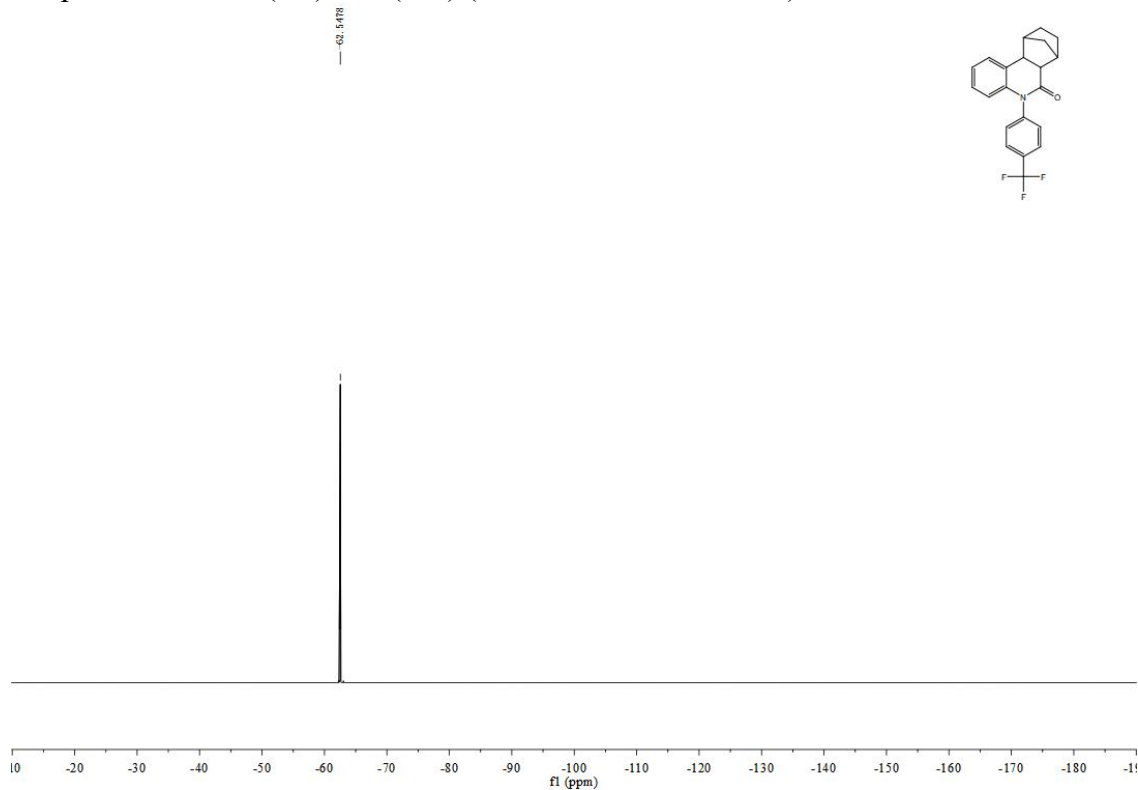
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7.2817
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7.0203
7.0199
7.0161
6.9989
6.9967
6.9938
6.9918
6.9893
2.2801
2.2553
2.9899
2.9630
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1.6508
1.6298
1.6045
1.5913



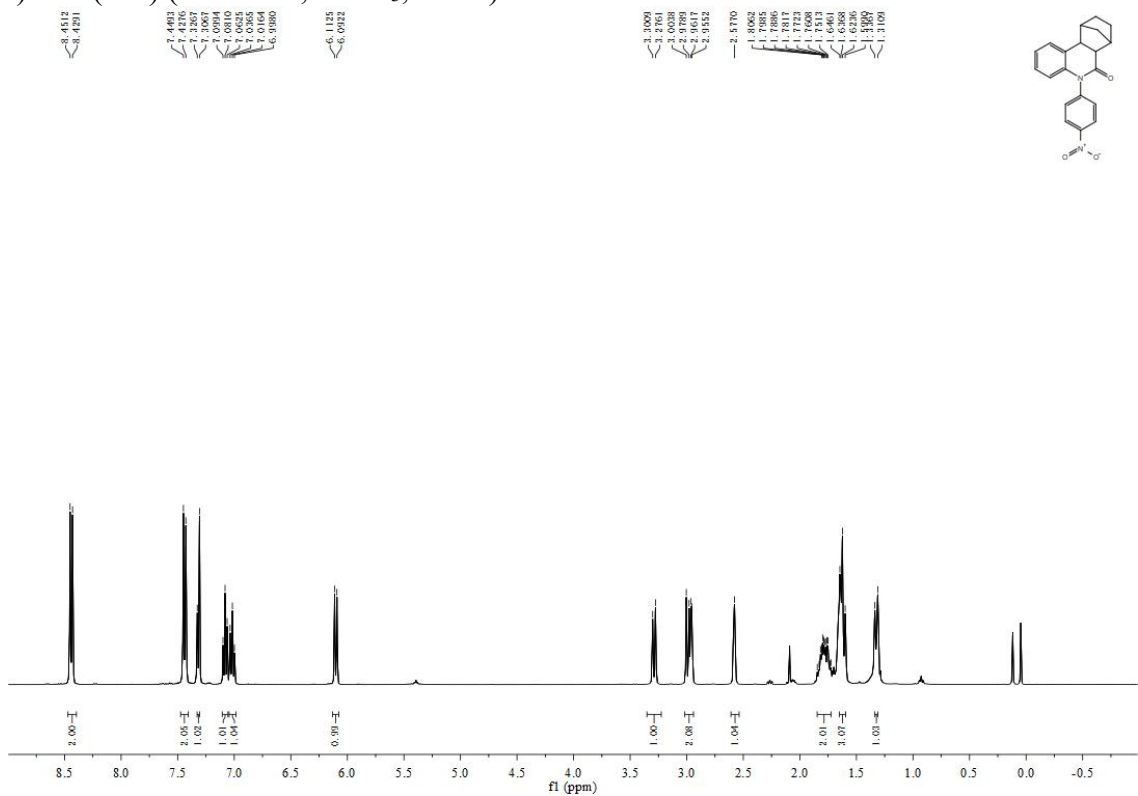
— 169. 9665
— 139. 1835
— 141. 9178
— 130. 7129
— 130. 3870
— 129. 9280
— 127. 2492
— 127. 2130
— 125. 9189
— 125. 0676
— 123. 3410
— 122. 5118
— 115. 7910
— 93. 2118
— 48. 6538
— 45. 2053
— 34. 7664
— 29. 4002
— 29. 1908



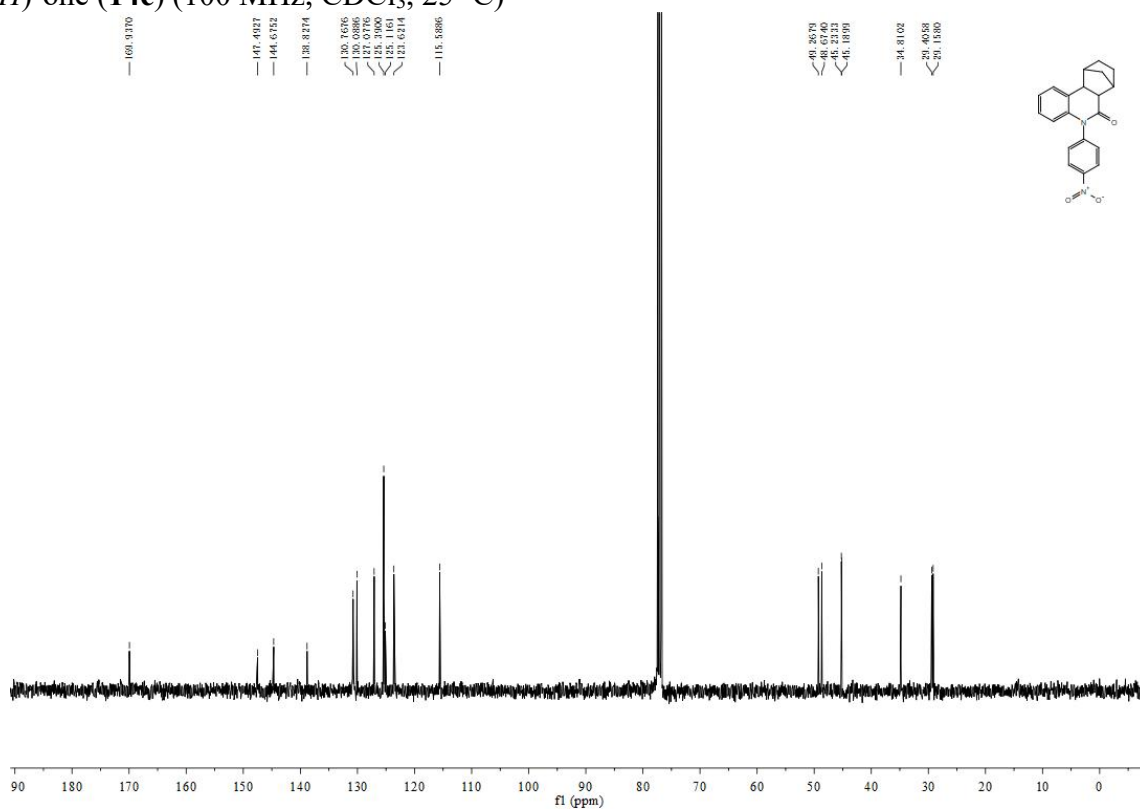
^{19}F NMR spectrum of 5-(4-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**13c**) (376 MHz, CDCl_3 , 25 °C)



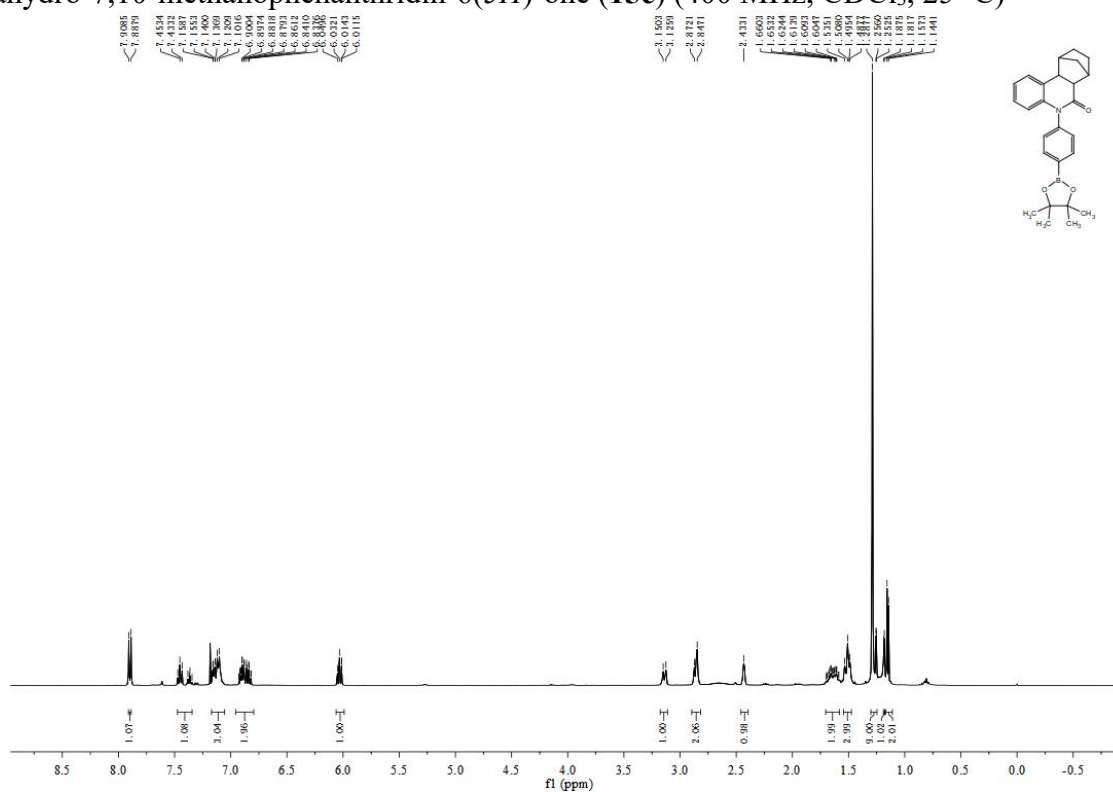
^1H NMR spectrum of 5-(4-nitrophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**14c**) (400 MHz, CDCl_3 , 25 °C)



¹³C NMR spectrum of 5-(4-nitrophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**14c**) (100 MHz, CDCl₃, 25 °C)



¹H NMR spectrum of 5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**15c**) (400 MHz, CDCl₃, 25 °C)



Chemical structure of compound 10 is shown in the top right corner. The structure is a complex molecule featuring a central benzene ring substituted with a carbonyl group, a cyclohexyl group, and a 1,3-dioxolane ring. The 1,3-dioxolane ring is substituted with two methyl groups and a phenyl group.

13C NMR spectrum (f1 (ppm)) showing peaks at the following chemical shifts (ppm):

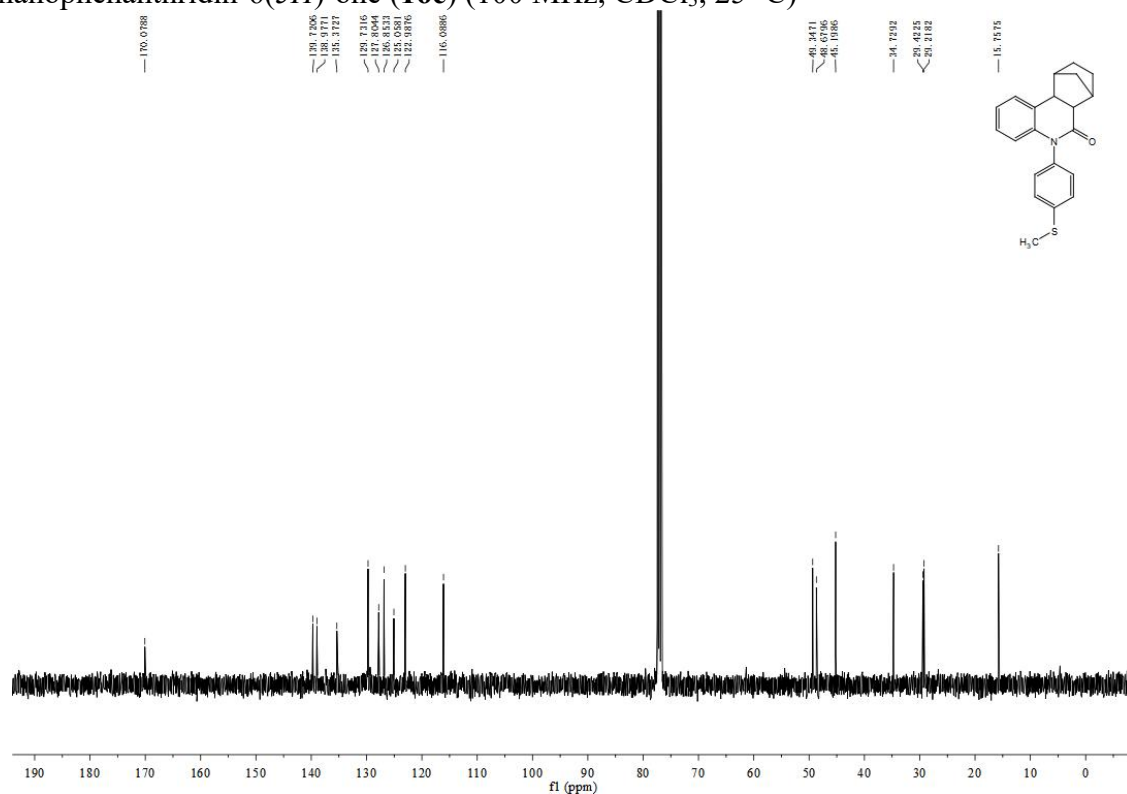
- 169.797
- 141.288
- 139.648
- 136.559
- 129.675
- 126.809
- 124.979
- 122.929
- 116.137
- 84.019
- 49.347
- 48.668
- 45.241
- 45.153
- 34.742
- 29.436
- 29.225
- 24.908
- 24.884

Chemical structure of compound 10: COC(=O)C12CC3CC4C(C1)C(C2)C(C3)C4

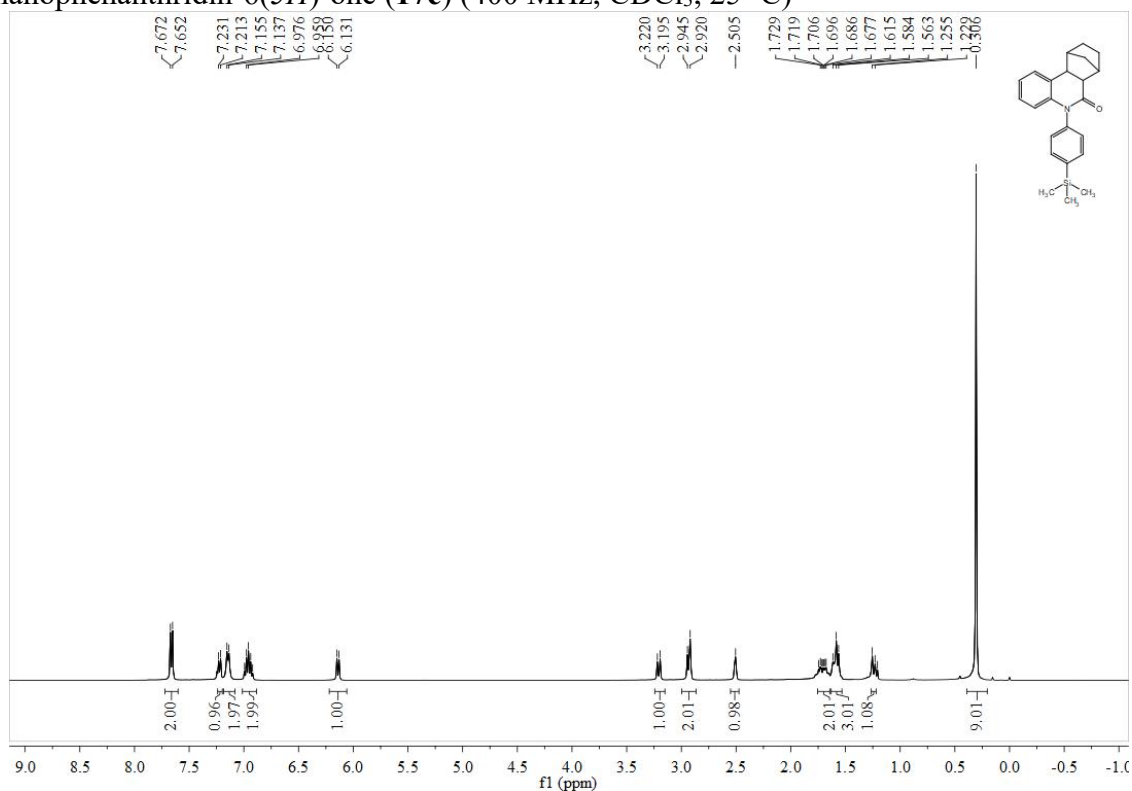
¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm (f1), ranging from 9.0 to -0.5. The spectrum shows several multiplets in the aromatic region (6.0-7.5 ppm), a singlet for the methoxy group at 3.8 ppm, a large solvent peak at 7.26 ppm, and aliphatic signals between 1.0 and 2.5 ppm. Integration values are provided below the baseline.

Chemical Shift (ppm)	Integration
7.4258	0.91
7.4041	0.91
7.3824	0.91
7.3606	0.91
7.3487	0.91
7.3269	0.91
7.3051	0.91
7.2834	0.91
7.2616	0.91
7.2398	0.91
7.2180	0.91
7.1962	0.91
7.1744	0.91
7.1526	0.91
7.1308	0.91
7.1090	0.91
7.0872	0.91
7.0654	0.91
7.0436	0.91
7.0218	0.91
7.0000	0.91
6.9782	0.91
6.9564	0.91
6.9346	0.91
6.9128	0.91
6.8910	0.91
6.8692	0.91
6.8474	0.91
6.8256	0.91
6.8038	0.91
6.7820	0.91
6.7602	0.91
6.7384	0.91
6.7166	0.91
6.6948	0.91
6.6730	0.91
6.6512	0.91
6.6294	0.91
6.6076	0.91
6.5858	0.91
6.5640	0.91
6.5422	0.91
6.5204	0.91
6.4986	0.91
6.4768	0.91
6.4550	0.91
6.4332	0.91
6.4114	0.91
6.3896	0.91
6.3678	0.91
6.3460	0.91
6.3242	0.91
6.3024	0.91
6.2806	0.91
6.2588	0.91
6.2370	0.91
6.2152	0.91
6.1934	0.91
6.1716	0.91
6.1498	0.91
6.1280	0.91
6.1062	0.91
6.0844	0.91
6.0626	0.91
6.0408	0.91
6.0190	0.91
5.9972	0.91
5.9754	0.91
5.9536	0.91
5.9318	0.91
5.9100	0.91
5.8882	0.91
5.8664	0.91
5.8446	0.91
5.8228	0.91
5.8010	0.91
5.7792	0.91
5.7574	0.91
5.7356	0.91
5.7138	0.91
5.6920	0.91
5.6702	0.91
5.6484	0.91
5.6266	0.91
5.6048	0.91
5.5830	0.91
5.5612	0.91
5.5394	0.91
5.5176	0.91
5.4958	0.91
5.4740	0.91
5.4522	0.91
5.4304	0.91
5.4086	0.91
5.3868	0.91
5.3650	0.91
5.3432	0.91
5.3214	0.91
5.2996	0.91
5.2778	0.91
5.2560	0.91
5.2342	0.91
5.2124	0.91
5.1906	0.91
5.1688	0.91
5.1470	0.91
5.1252	0.91
5.1034	0.91
5.0816	0.91
5.0598	0.91
5.0380	0.91
5.0162	0.91
4.9944	0.91
4.9726	0.91
4.9508	0.91
4.9290	0.91
4.9072	0.91
4.8854	0.91
4.8636	0.91
4.8418	0.91
4.8200	0.91
4.7982	0.91
4.7764	0.91
4.7546	0.91
4.7328	0.91
4.7110	0.91
4.6892	0.91
4.6674	0.91
4.6456	0.91
4.6238	0.91

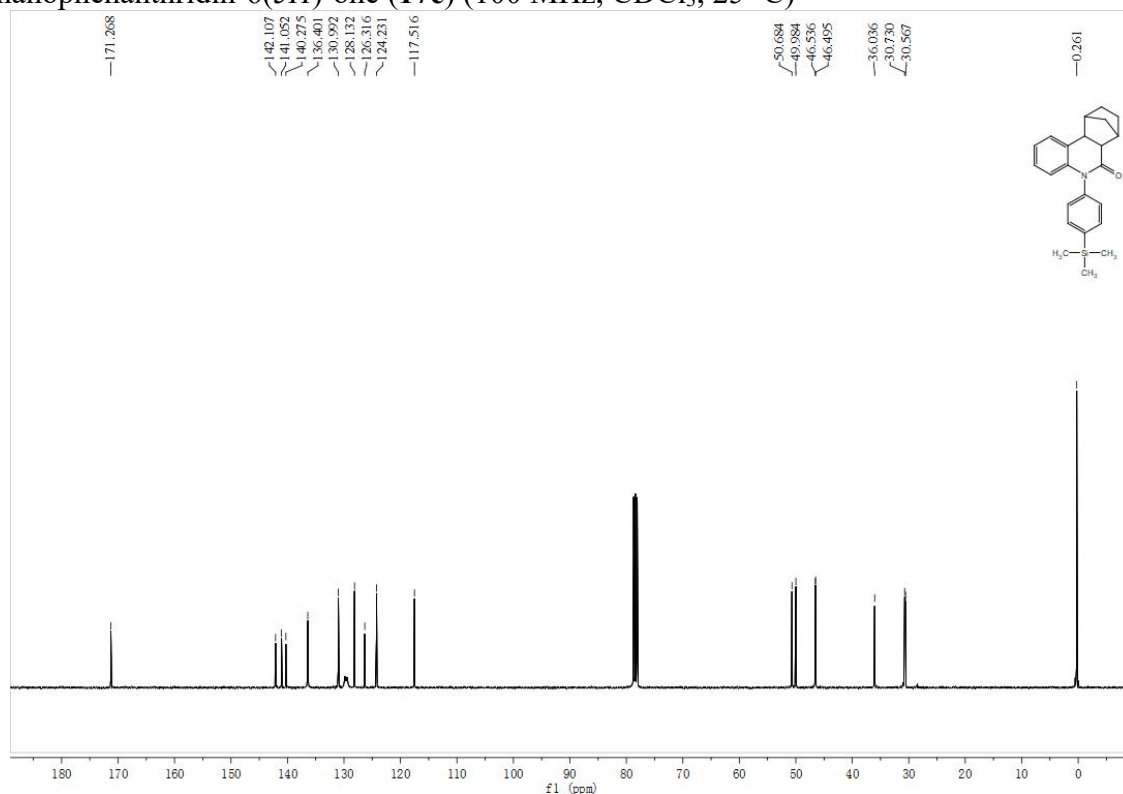
^{13}C NMR spectrum of 5-(4-(methylthio)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**16c**) (100 MHz, CDCl_3 , 25 °C)



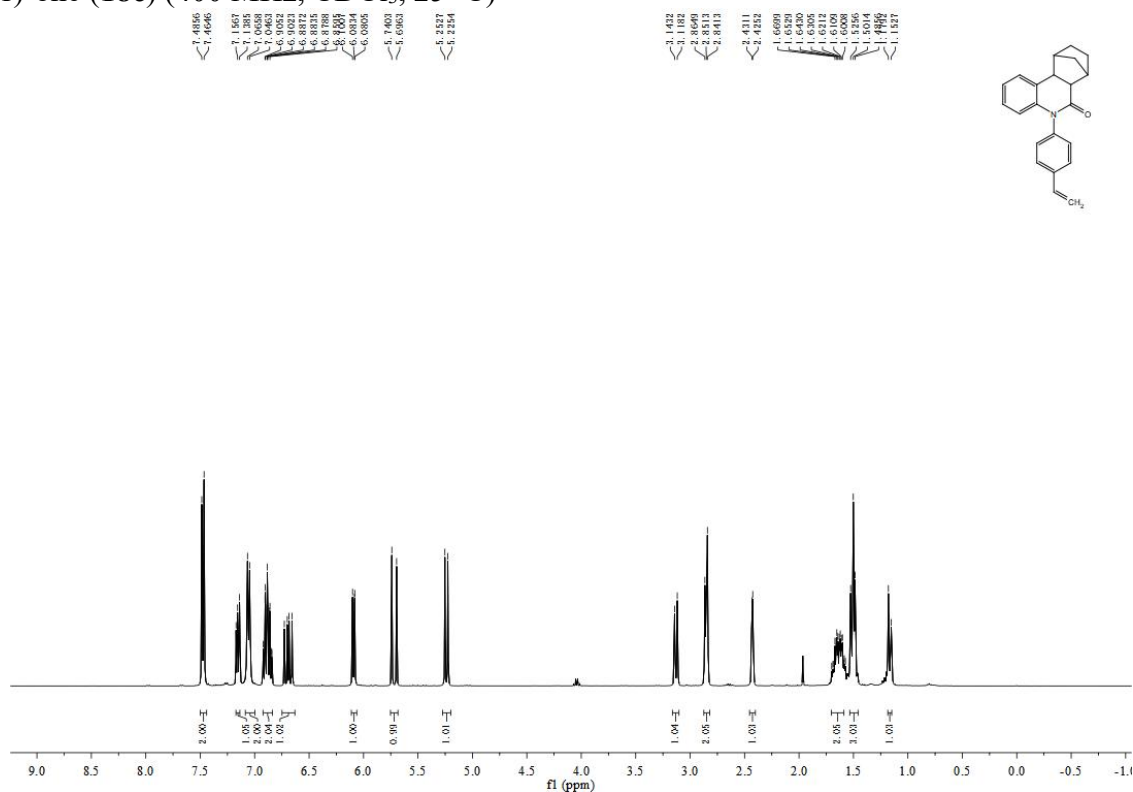
^1H NMR spectrum of 5-(4-(trimethylsilyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**17c**) (400 MHz, CDCl_3 , 25 °C)



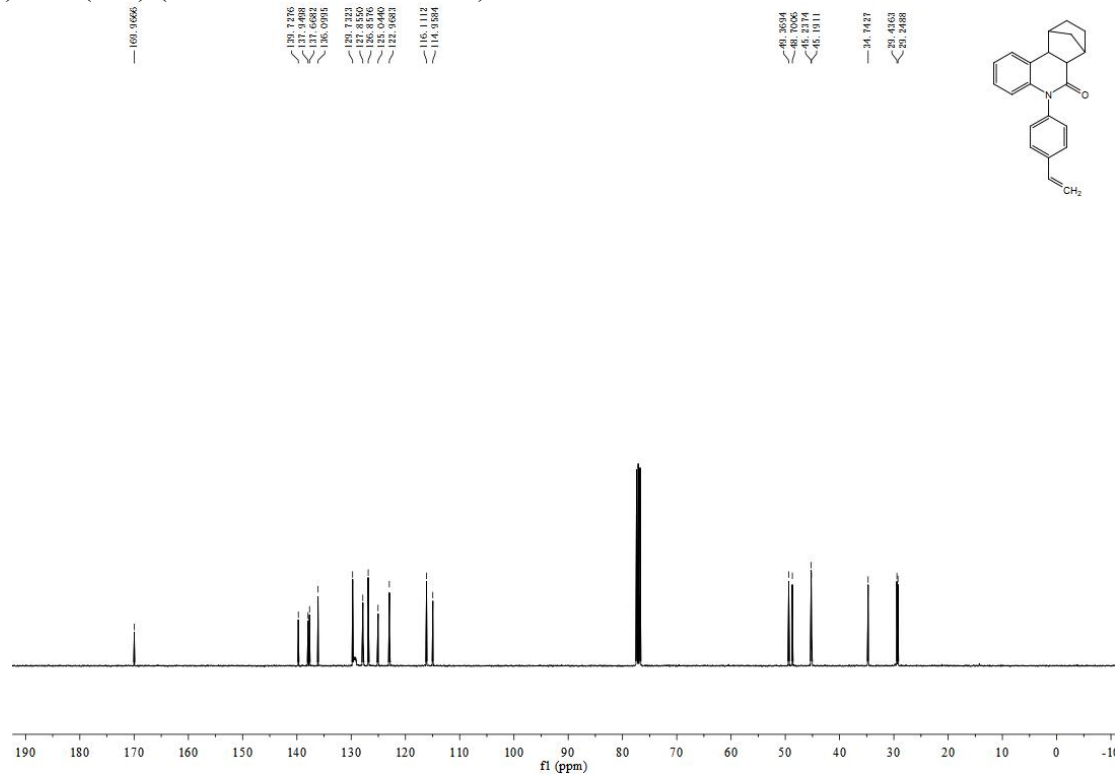
^{13}C NMR spectrum of 5-(4-(trimethylsilyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**17c**) (100 MHz, CDCl_3 , 25 °C)



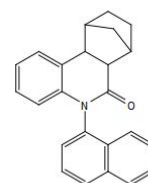
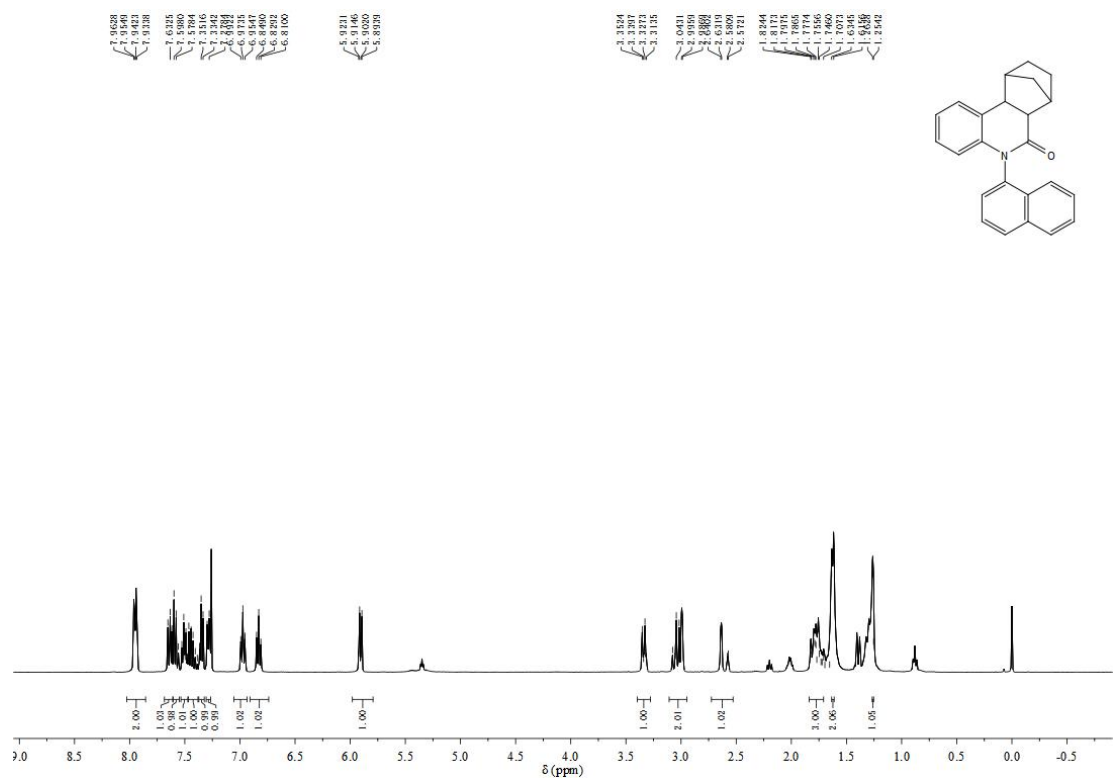
^1H NMR spectrum of 5-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**18c**) (400 MHz, CDCl_3 , 25 °C)



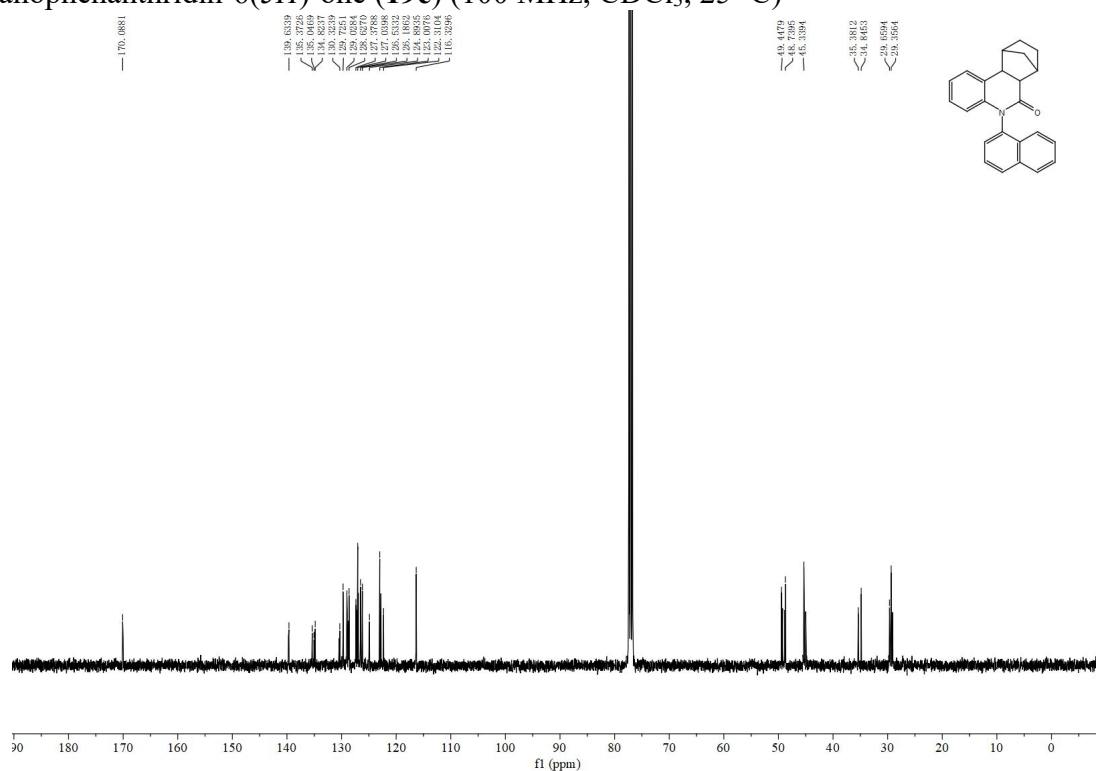
^{13}C NMR spectrum of 5-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**18c**) (100 MHz, CDCl_3 , 25 °C)



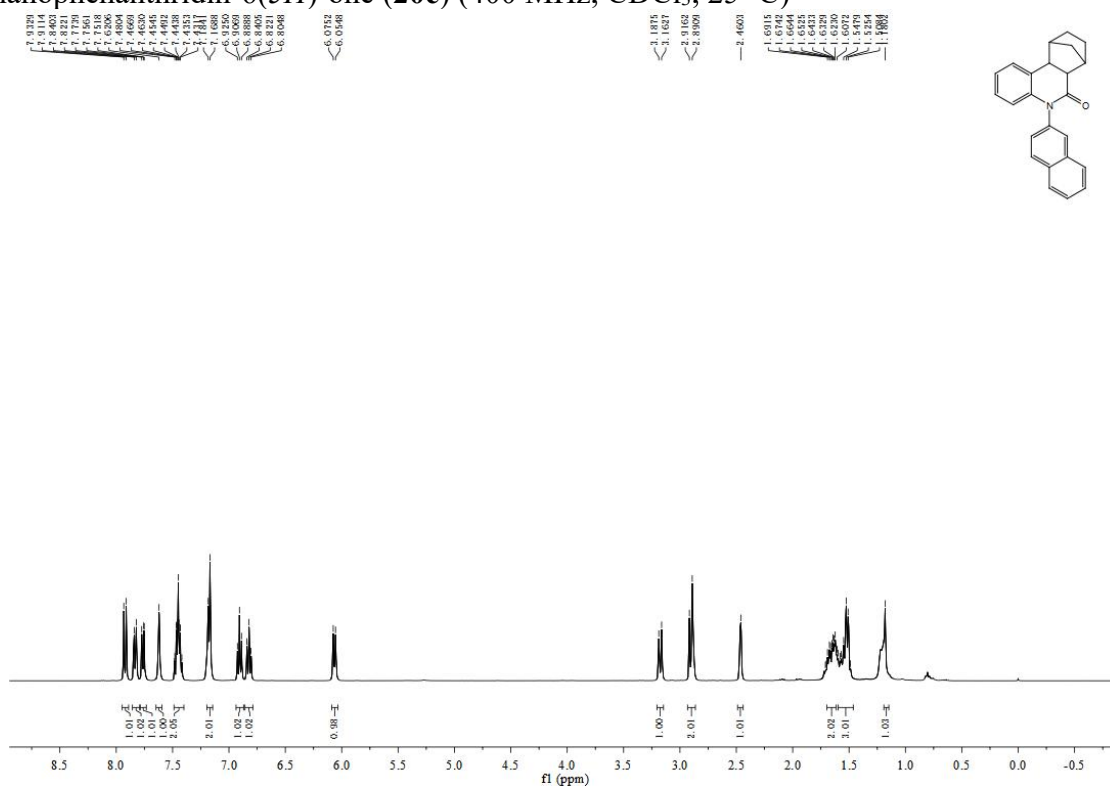
^1H NMR spectrum of 5-(naphthalen-1-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**19c**) (400 MHz, CDCl_3 , 25 °C)



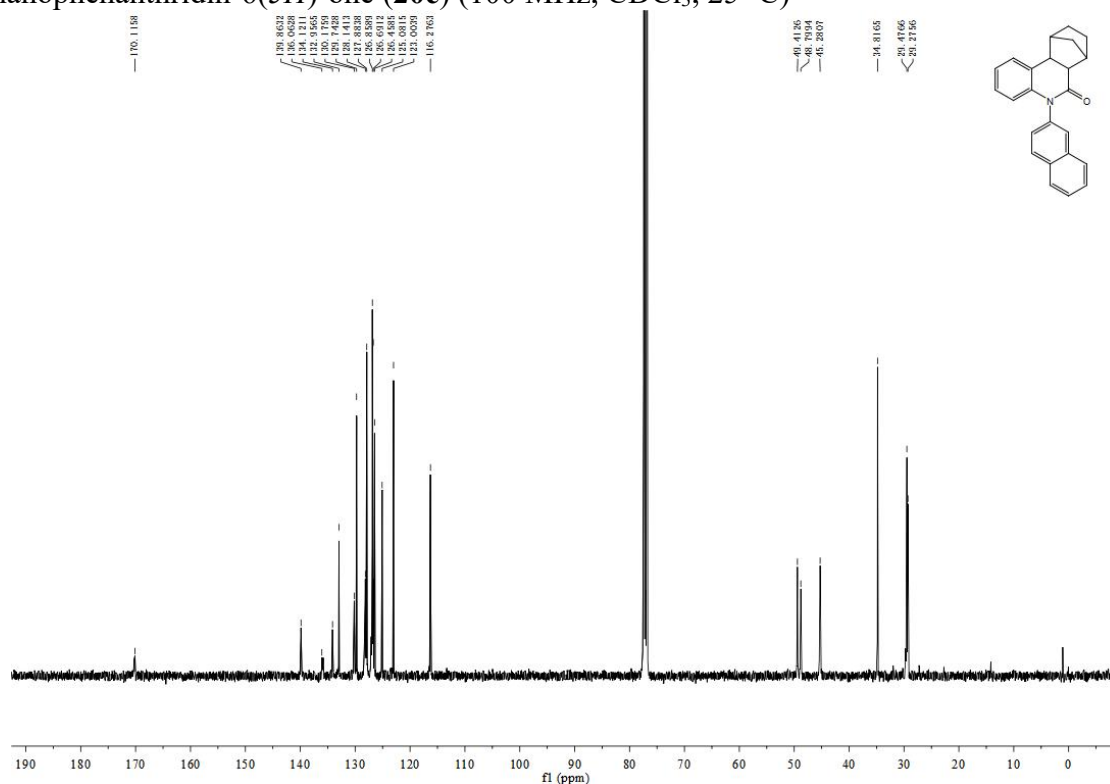
^{13}C NMR spectrum of 5-(naphthalen-1-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**19c**) (100 MHz, CDCl_3 , 25 °C)



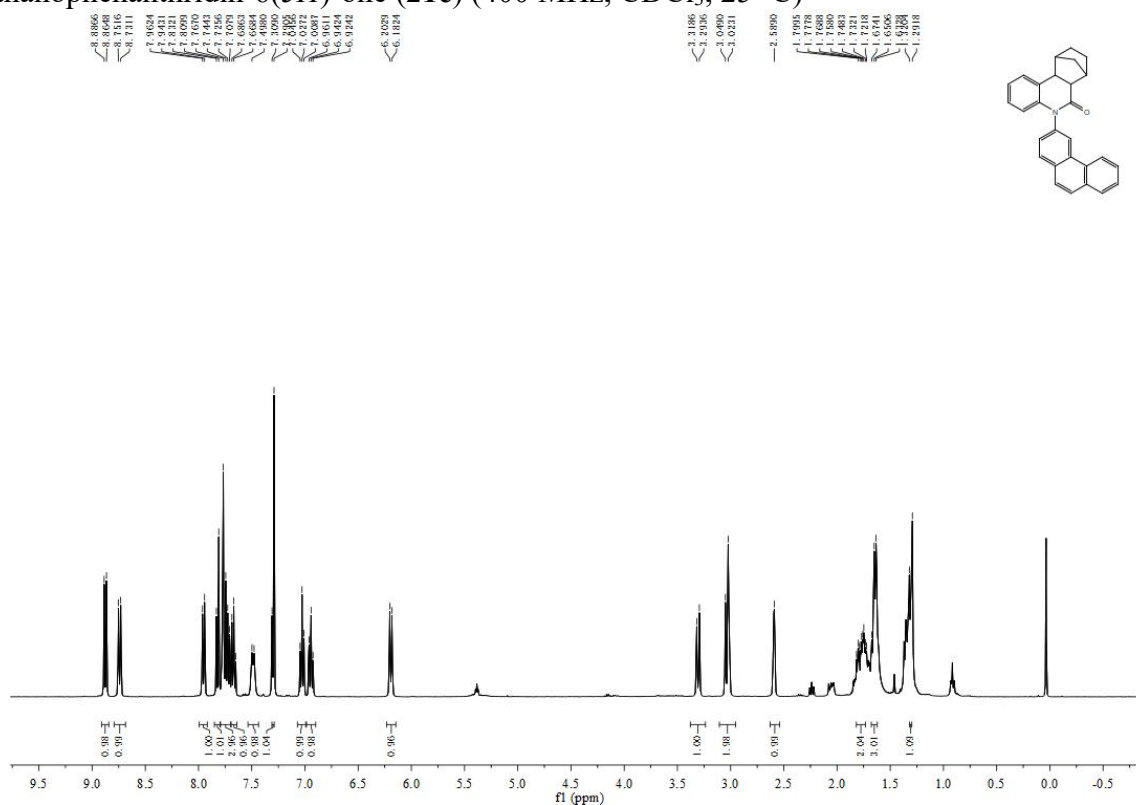
^1H NMR spectrum of 5-(naphthalen-2-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**20c**) (400 MHz, CDCl_3 , 25 °C)



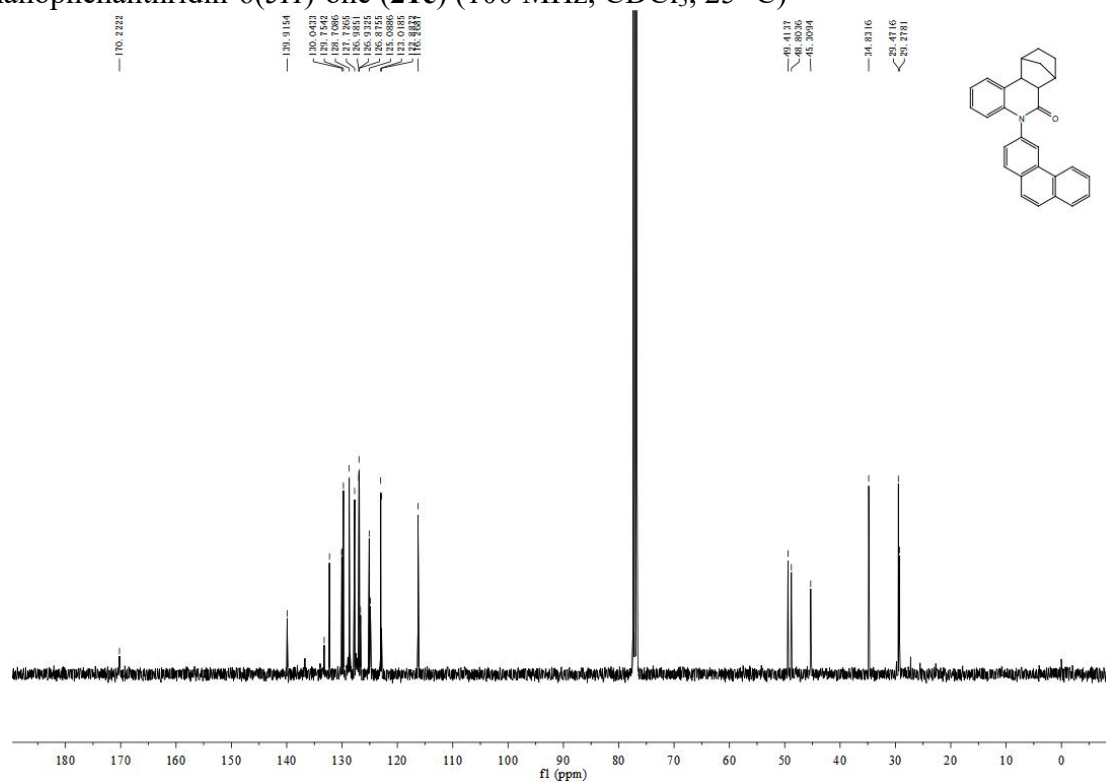
^{13}C NMR spectrum of 5-(naphthalen-2-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**20c**) (100 MHz, CDCl_3 , 25 °C)



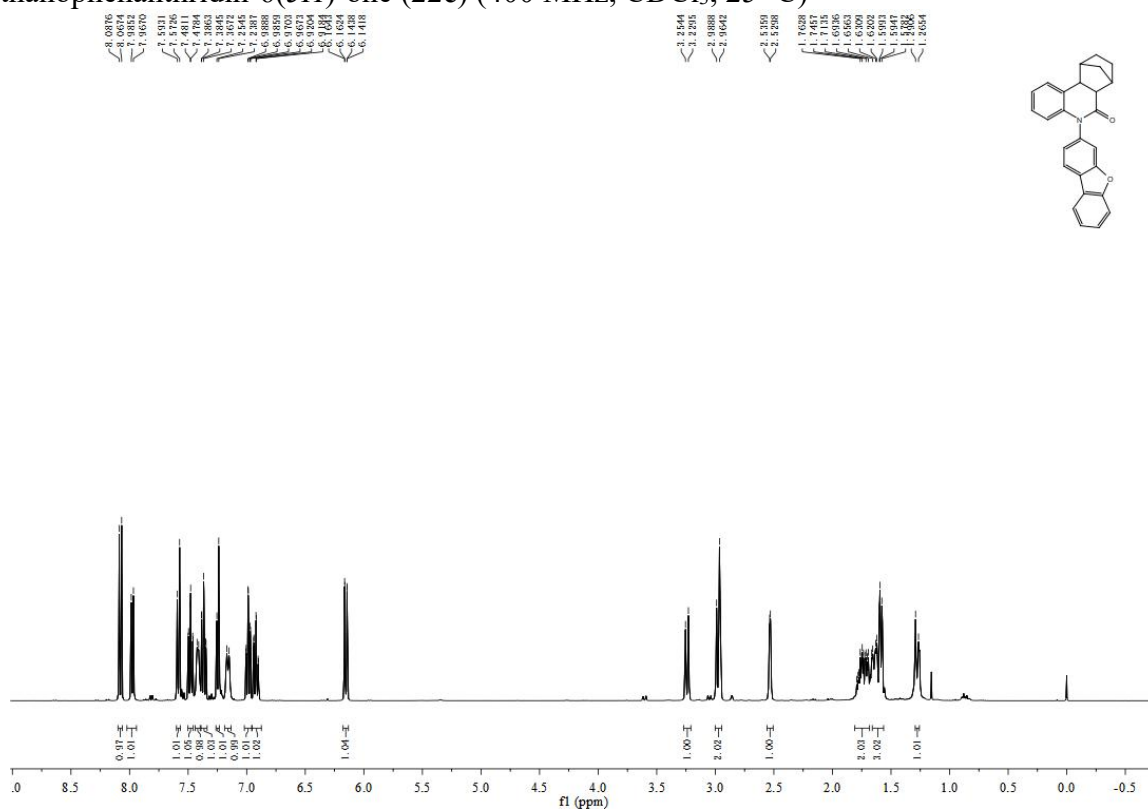
^1H NMR spectrum of 5-(phenanthren-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**21c**) (400 MHz, CDCl_3 , 25 °C)



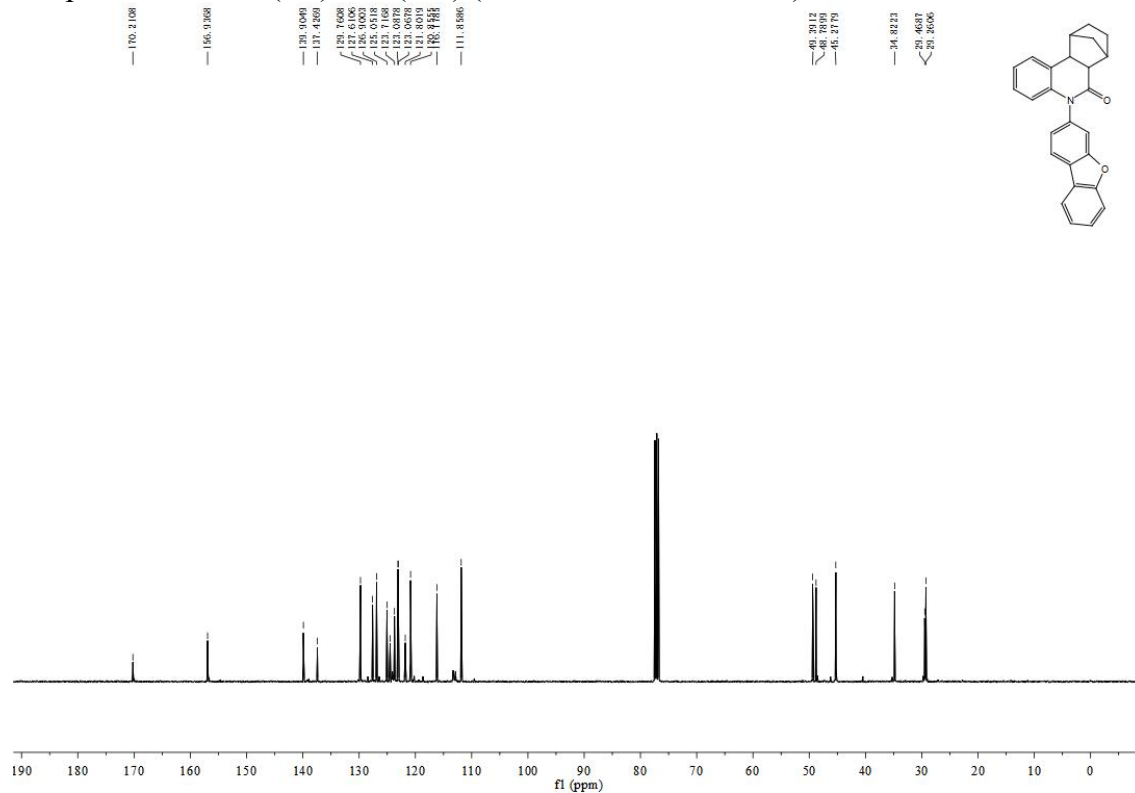
^{13}C NMR spectrum of 5-(phenanthren-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**21c**) (100 MHz, CDCl_3 , 25 °C)



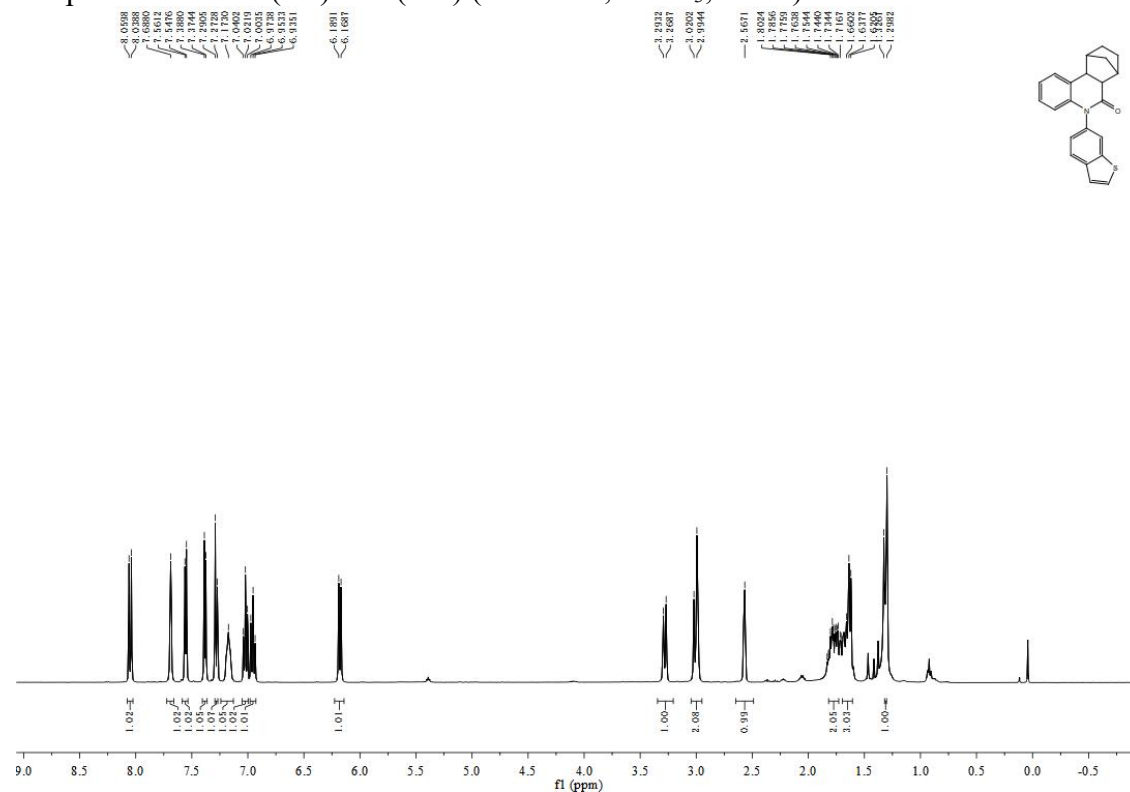
^1H NMR spectrum of 5-(dibenzo[*b,d*]furan-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**22c**) (400 MHz, CDCl_3 , 25 °C)



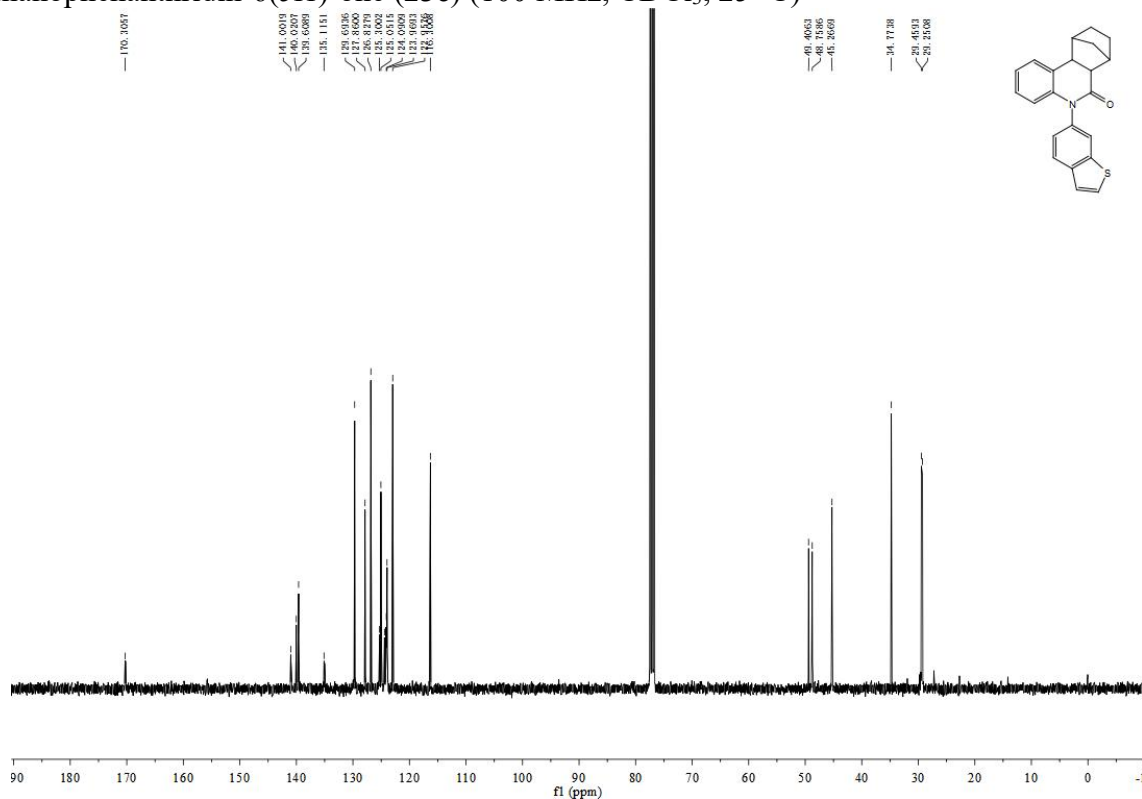
^{13}C NMR spectrum of 5-(dibenzo[*b,d*]furan-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**22c**) (100 MHz, CDCl_3 , 25 °C)



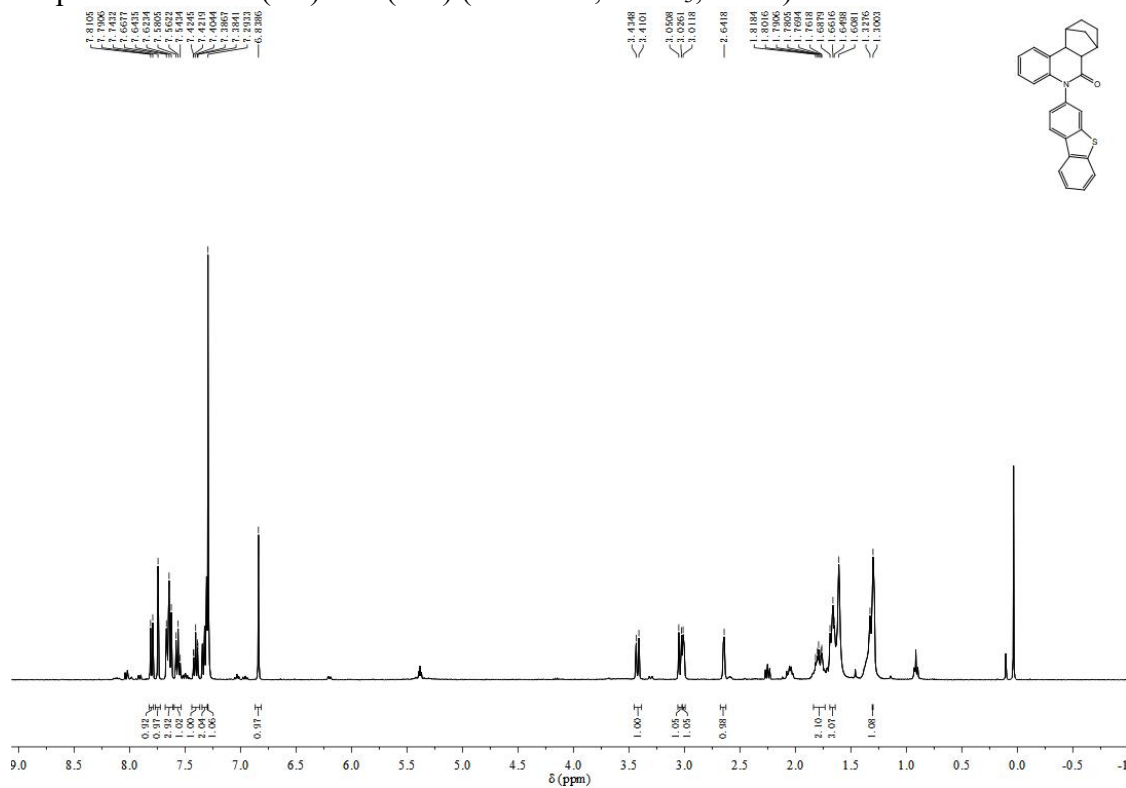
^1H NMR spectrum of 5-(benzo[*b*]thiophen-6-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**23c**) (400 MHz, CDCl_3 , 25 °C)



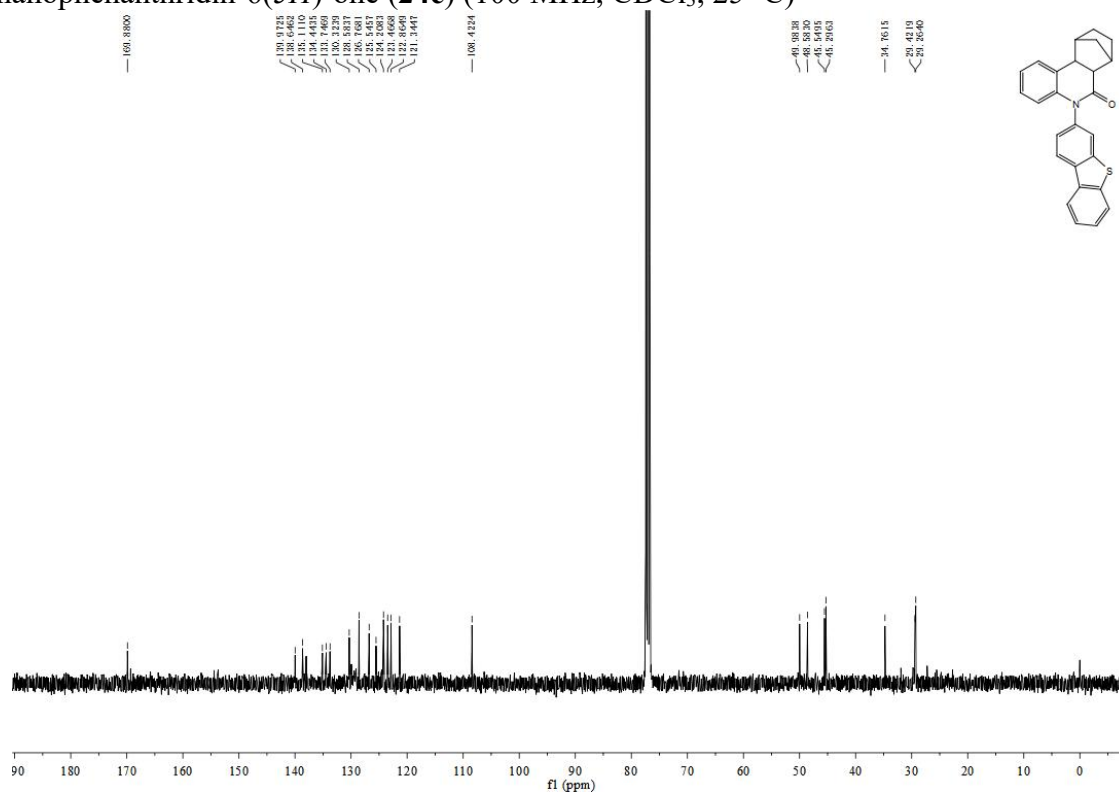
¹³C NMR spectrum of 5-(benzo[*b*]thiophen-6-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**23c**) (100 MHz, CDCl₃, 25 °C)



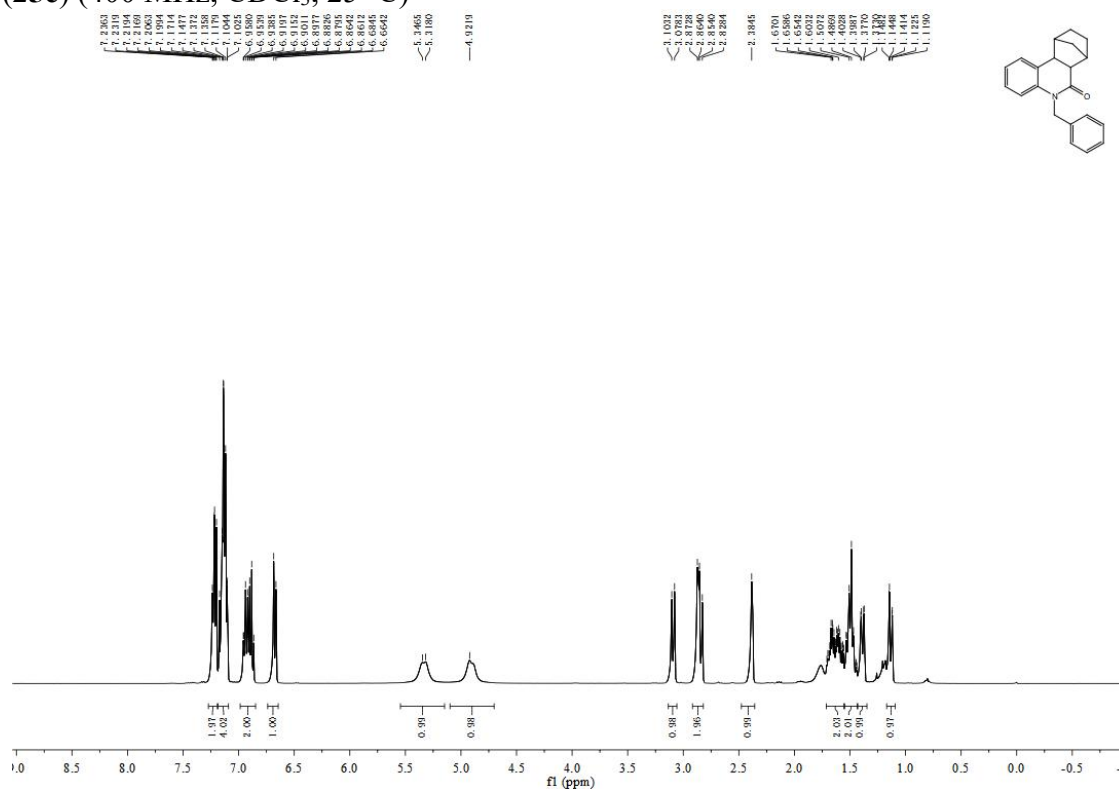
¹H NMR spectrum of 5-(dibenzo[*b,d*]thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**24c**) (400 MHz, CDCl₃, 25 °C)



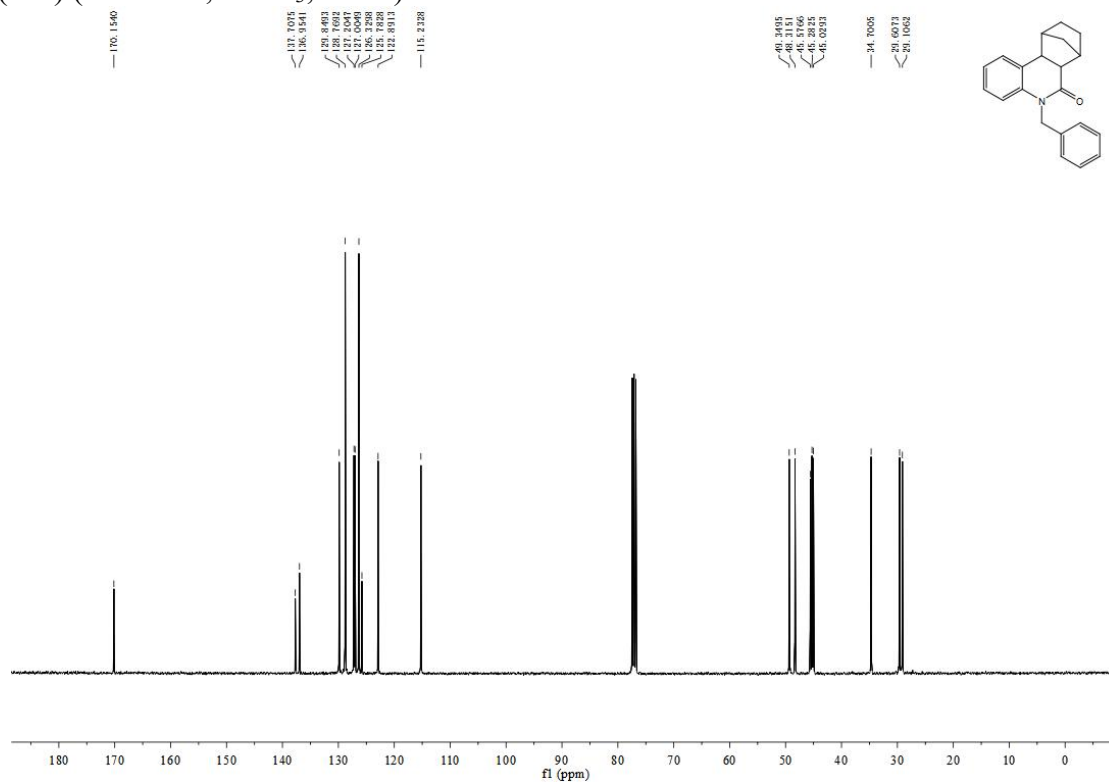
^{13}C NMR spectrum of 5-(dibenzo[*b,d*]thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**24c**) (100 MHz, CDCl_3 , 25 °C)



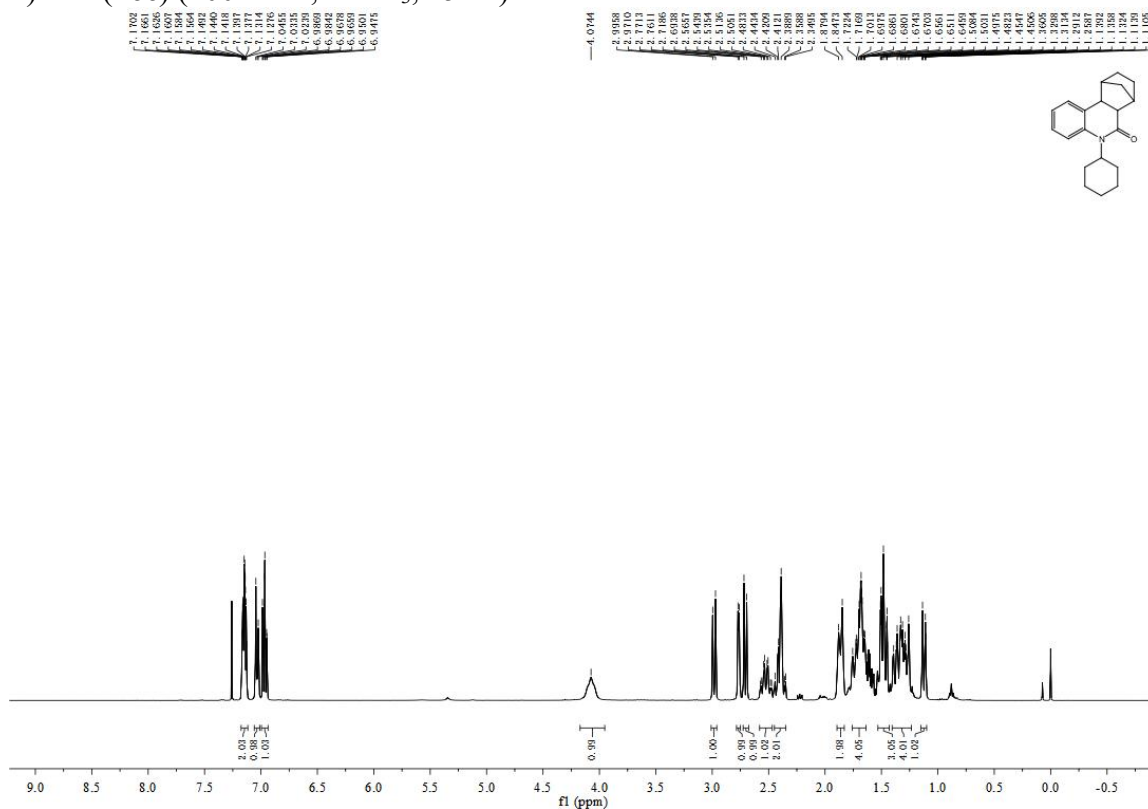
^1H NMR spectrum of 5-benzyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**25c**) (400 MHz, CDCl_3 , 25 °C)



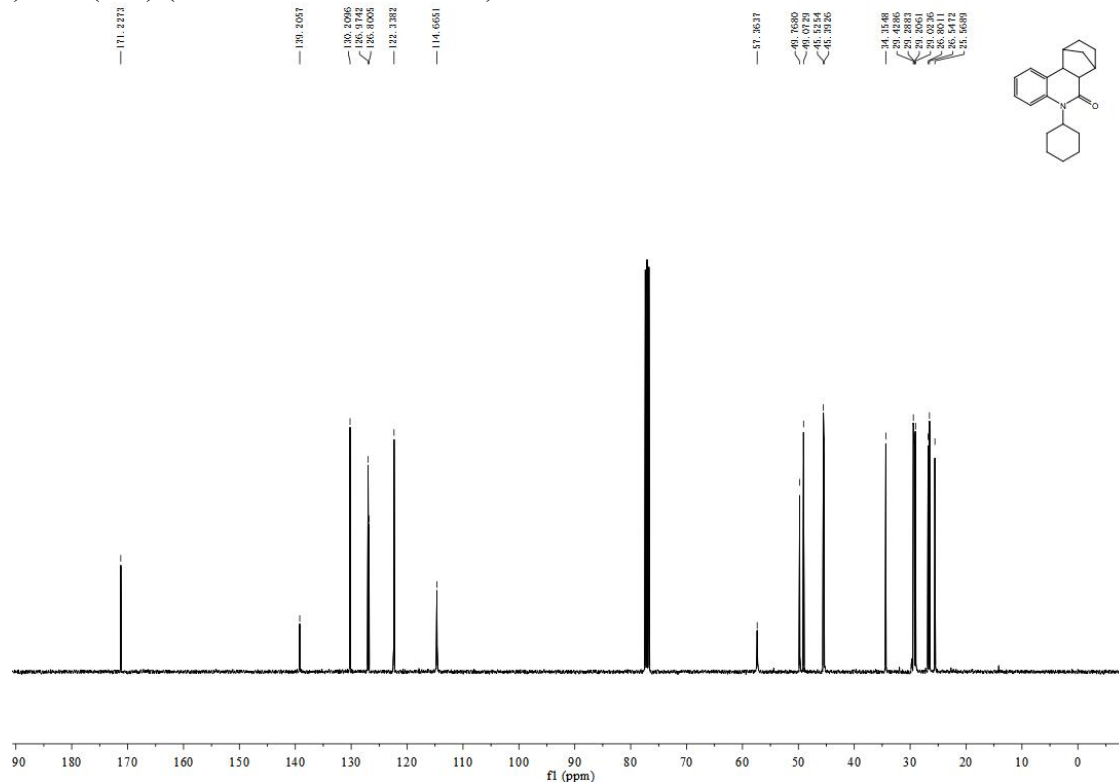
^{13}C NMR spectrum of 5-benzyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**25c**) (100 MHz, CDCl_3 , 25 °C)



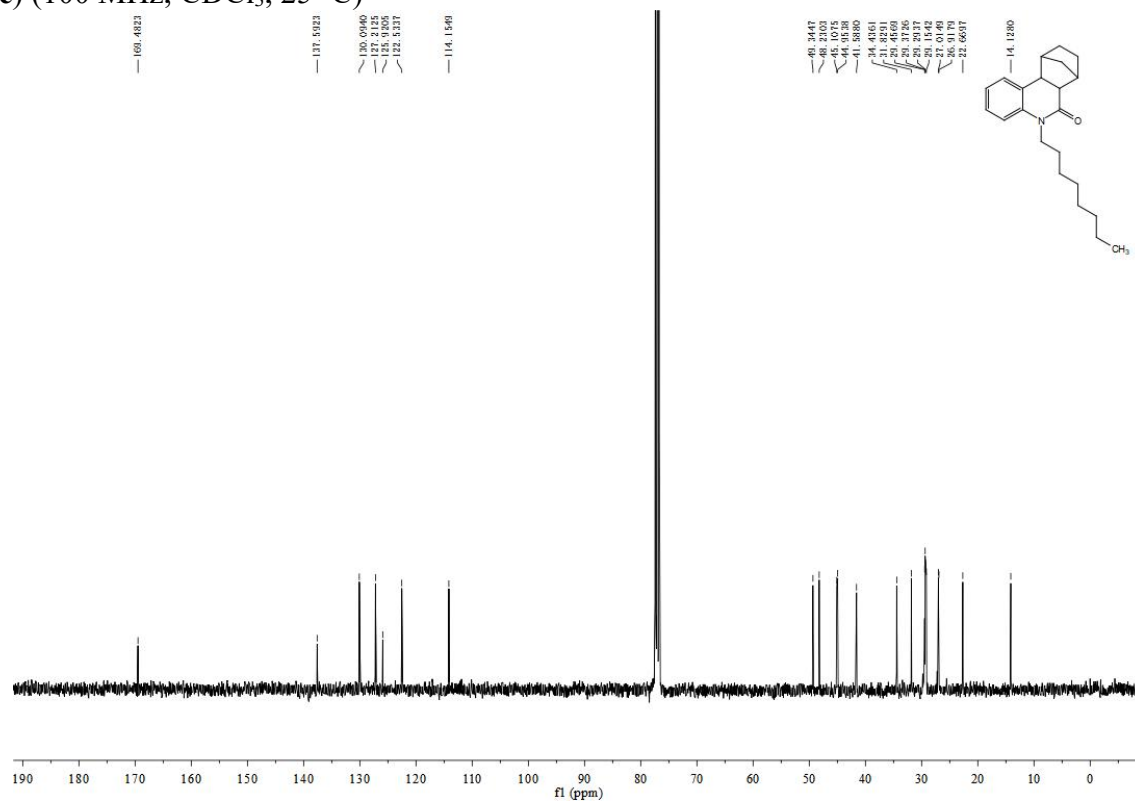
^1H NMR spectrum of 5-cyclohexyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**26c**) (400 MHz, CDCl_3 , 25 °C)



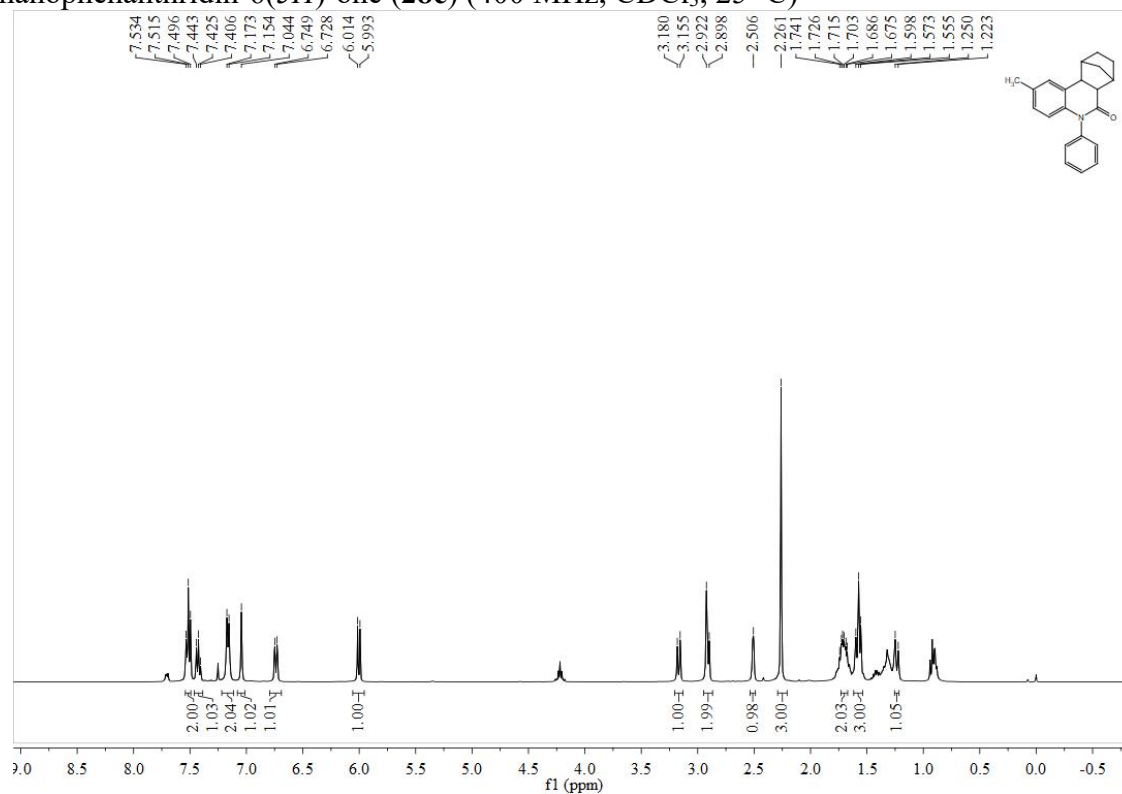
^{13}C NMR spectrum of 5-cyclohexyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**26c**) (100 MHz, CDCl_3 , 25 °C)



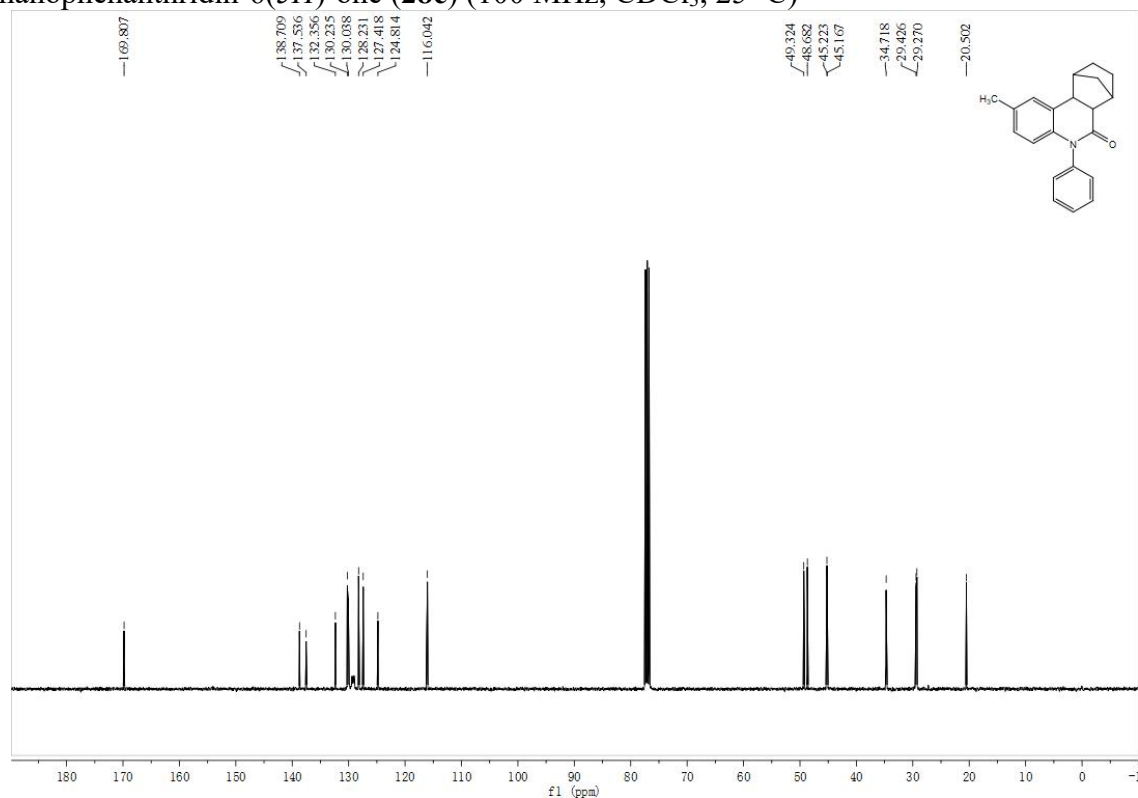
^{13}C NMR spectrum of 5-octyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**27c**) (100 MHz, CDCl_3 , 25 °C)



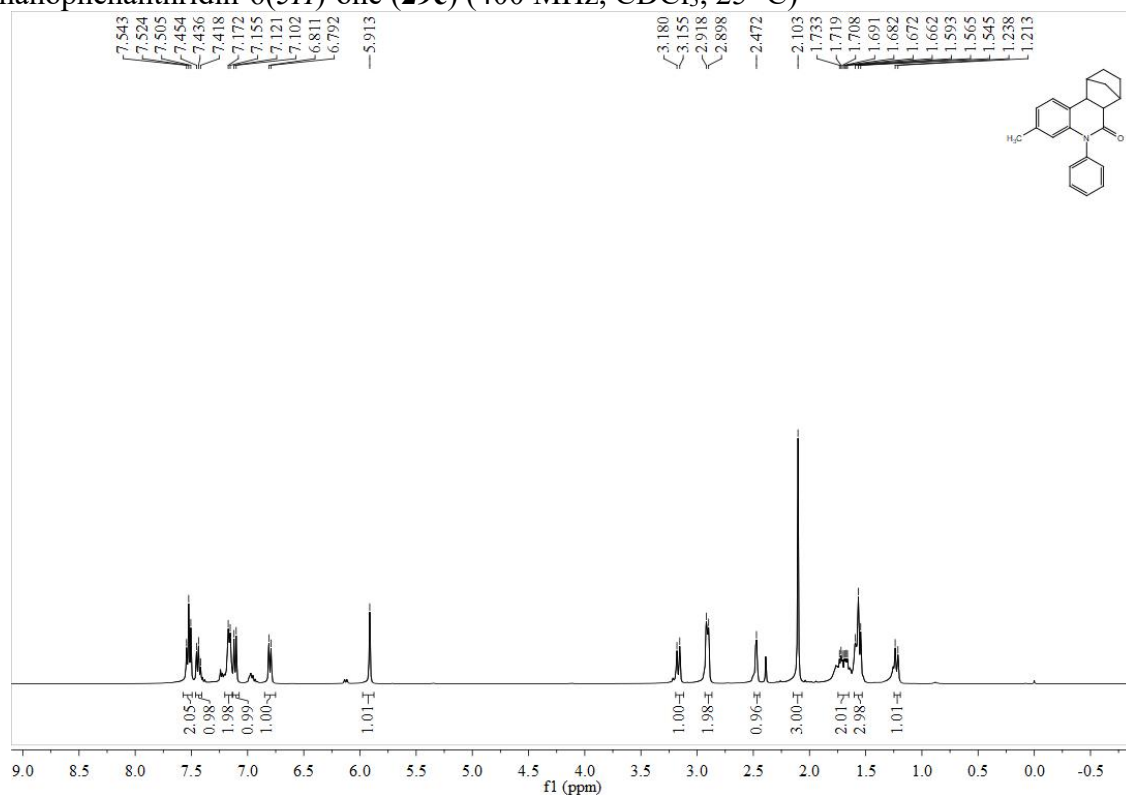
^1H NMR spectrum of 2-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**28c**) (400 MHz, CDCl_3 , 25 °C)



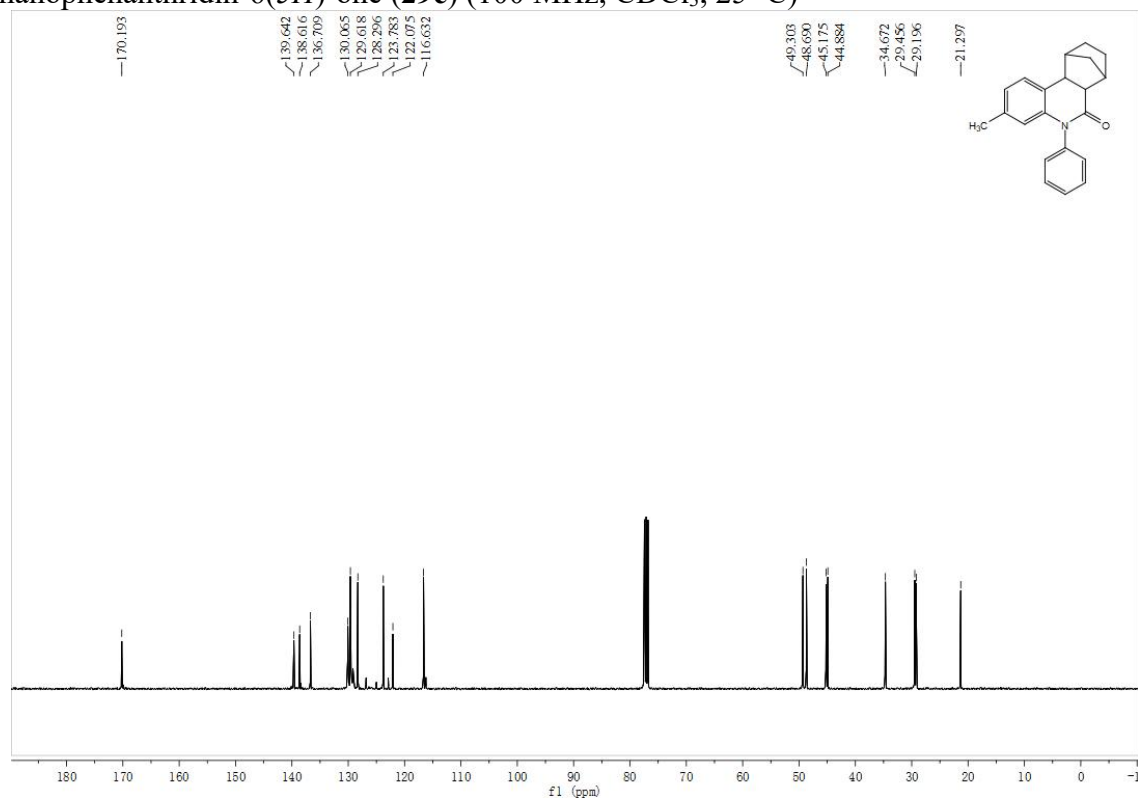
^{13}C NMR spectrum of 2-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**28c**) (100 MHz, CDCl_3 , 25 °C)



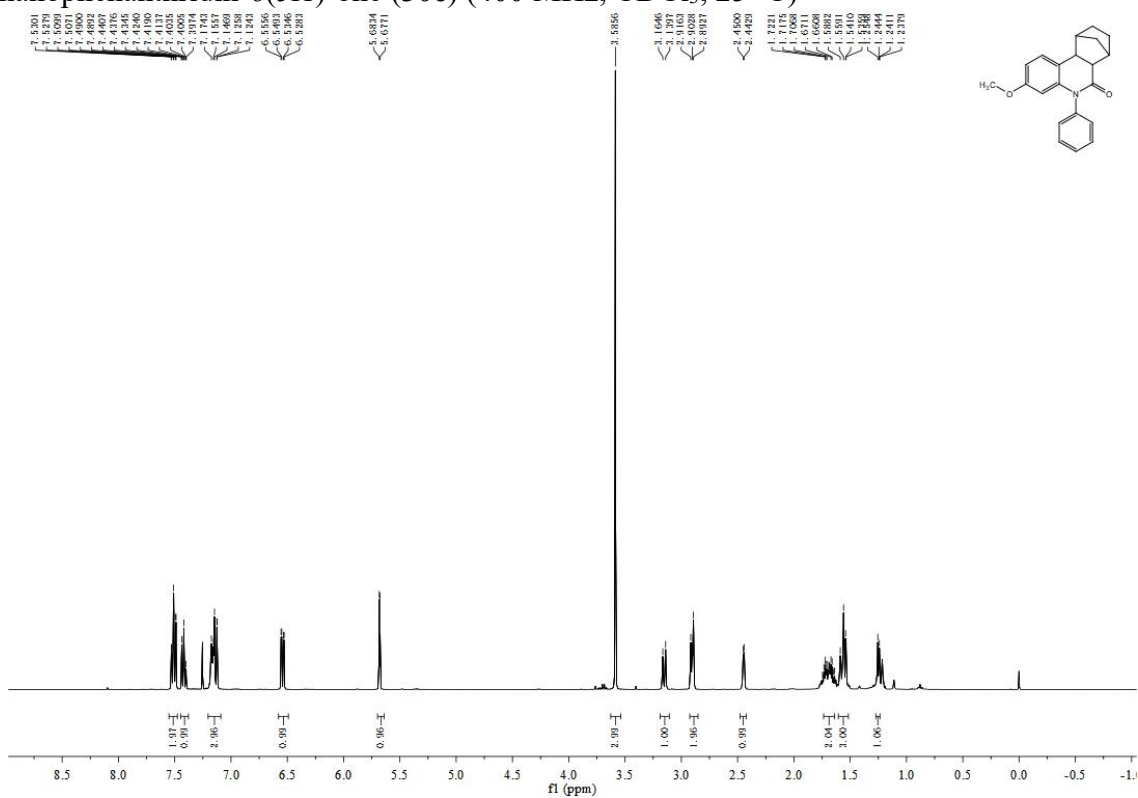
^1H NMR spectrum of 3-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**29c**) (400 MHz, CDCl_3 , 25 °C)



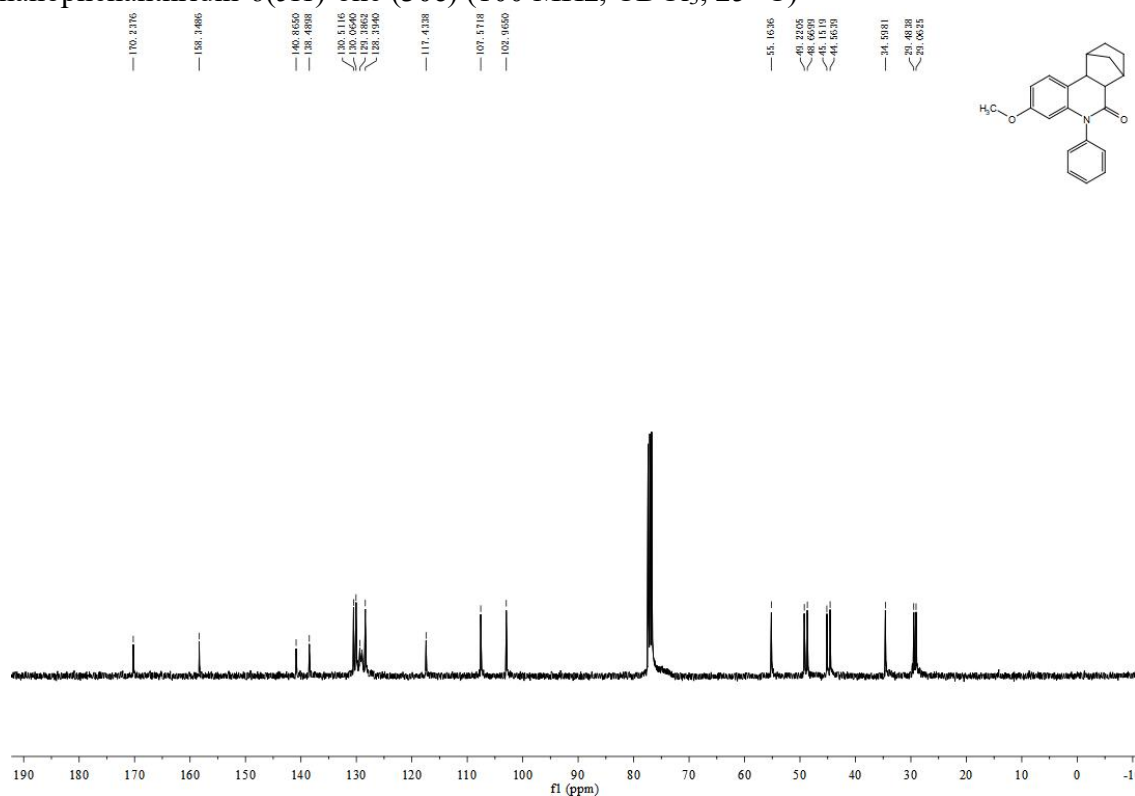
^{13}C NMR spectrum of 3-methyl-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**29c**) (100 MHz, CDCl_3 , 25 °C)



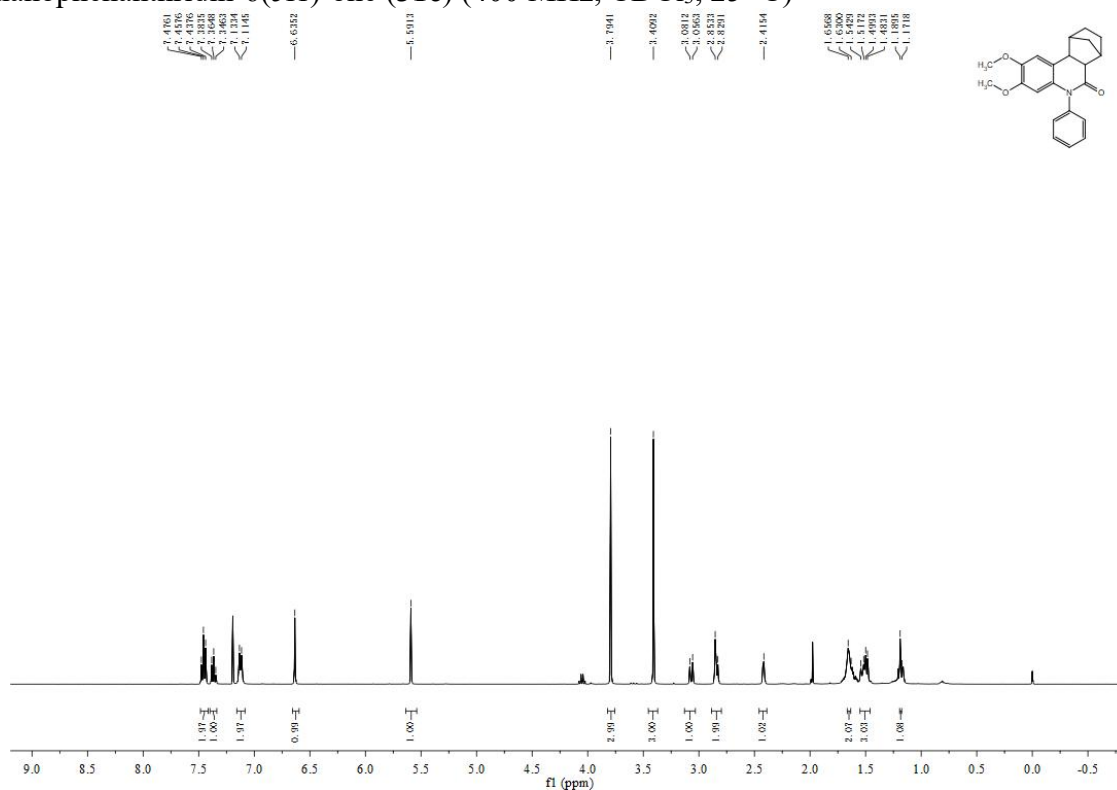
^1H NMR spectrum of 3-methoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5H)-one (**30c**) (400 MHz, CDCl_3 , 25 °C)



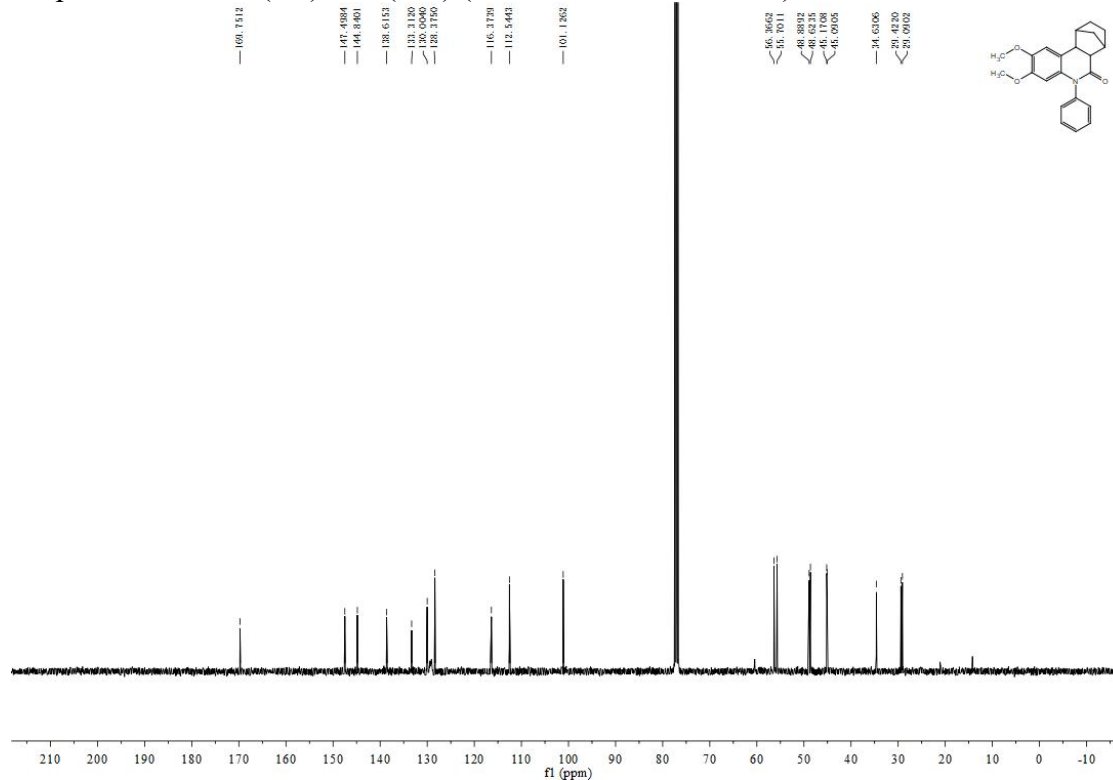
^{13}C NMR spectrum of 3-methoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**30c**) (100 MHz, CDCl_3 , 25 °C)



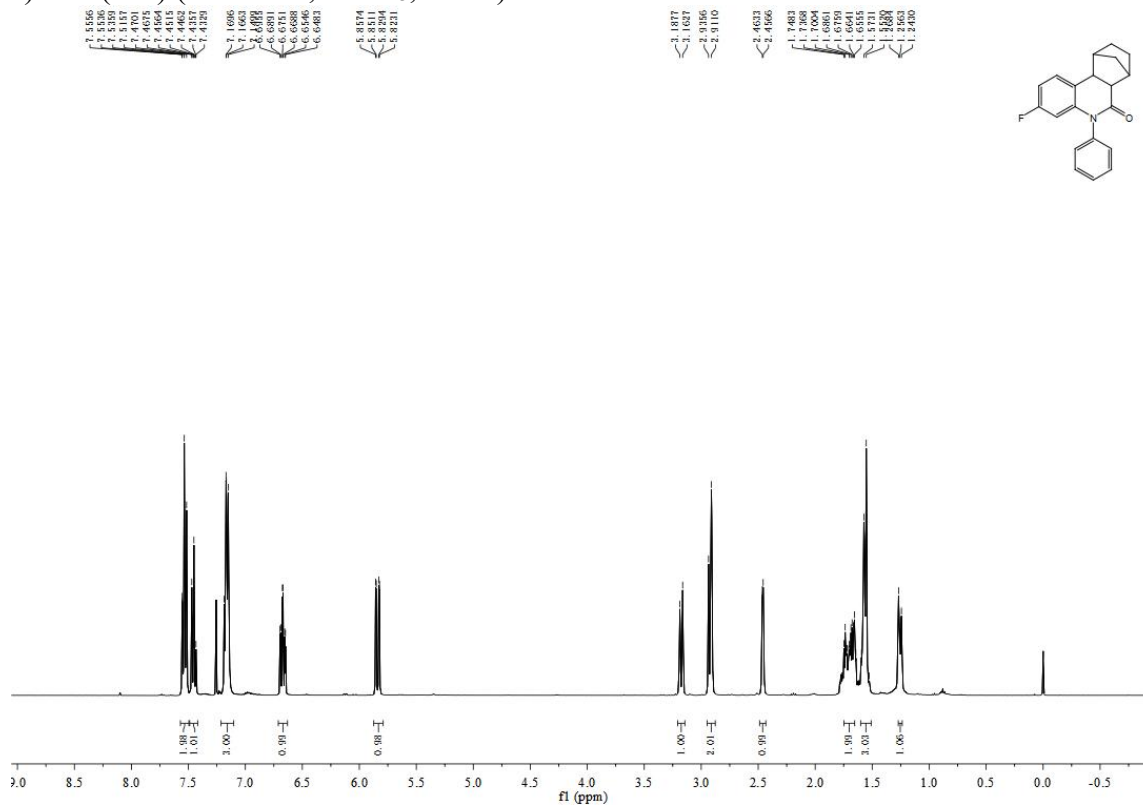
^1H NMR spectrum of 2,3-dimethoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**31c**) (400 MHz, CDCl_3 , 25 °C)



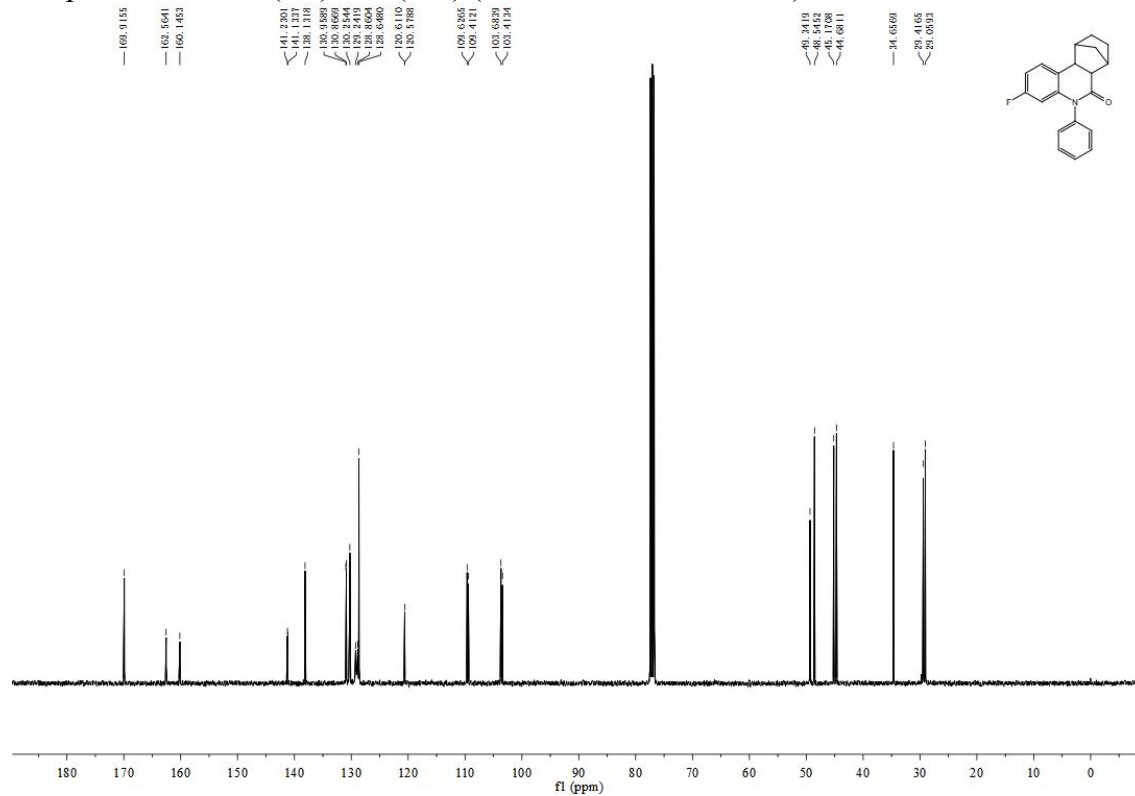
^{13}C NMR spectrum of 2,3-dimethoxy-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**31c**) (100 MHz, CDCl_3 , 25 °C)



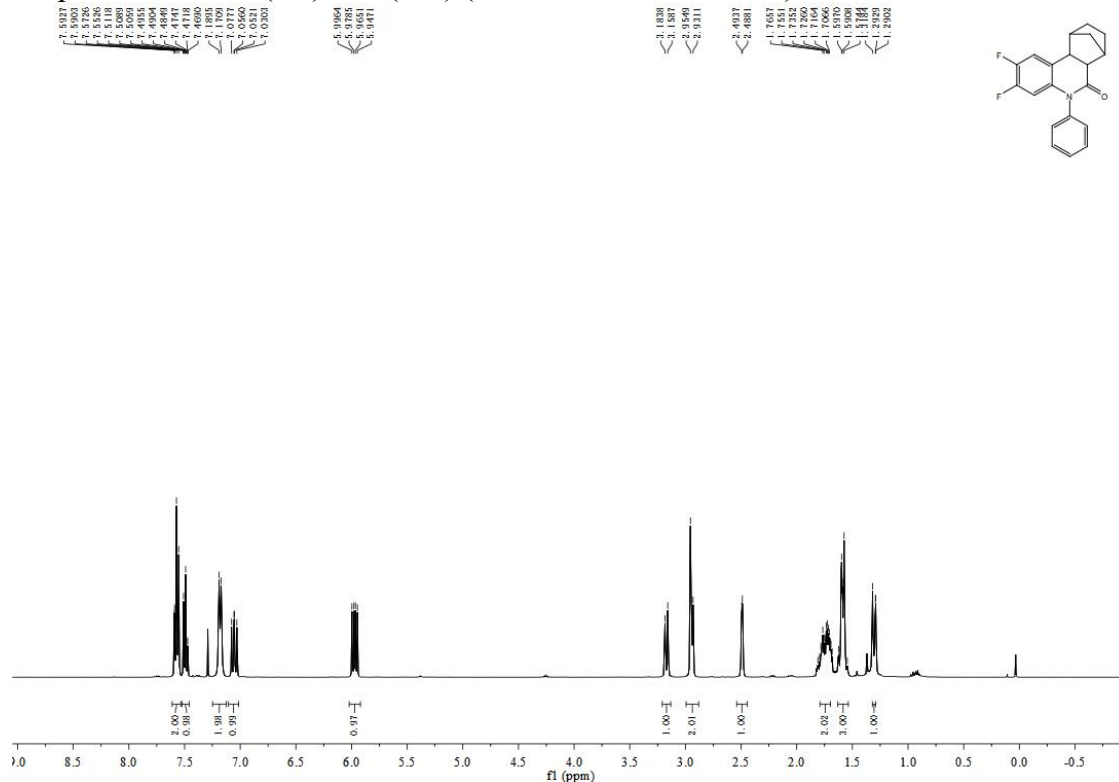
^1H NMR spectrum of 3-fluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**32c**) (400 MHz, CDCl_3 , 25 °C)



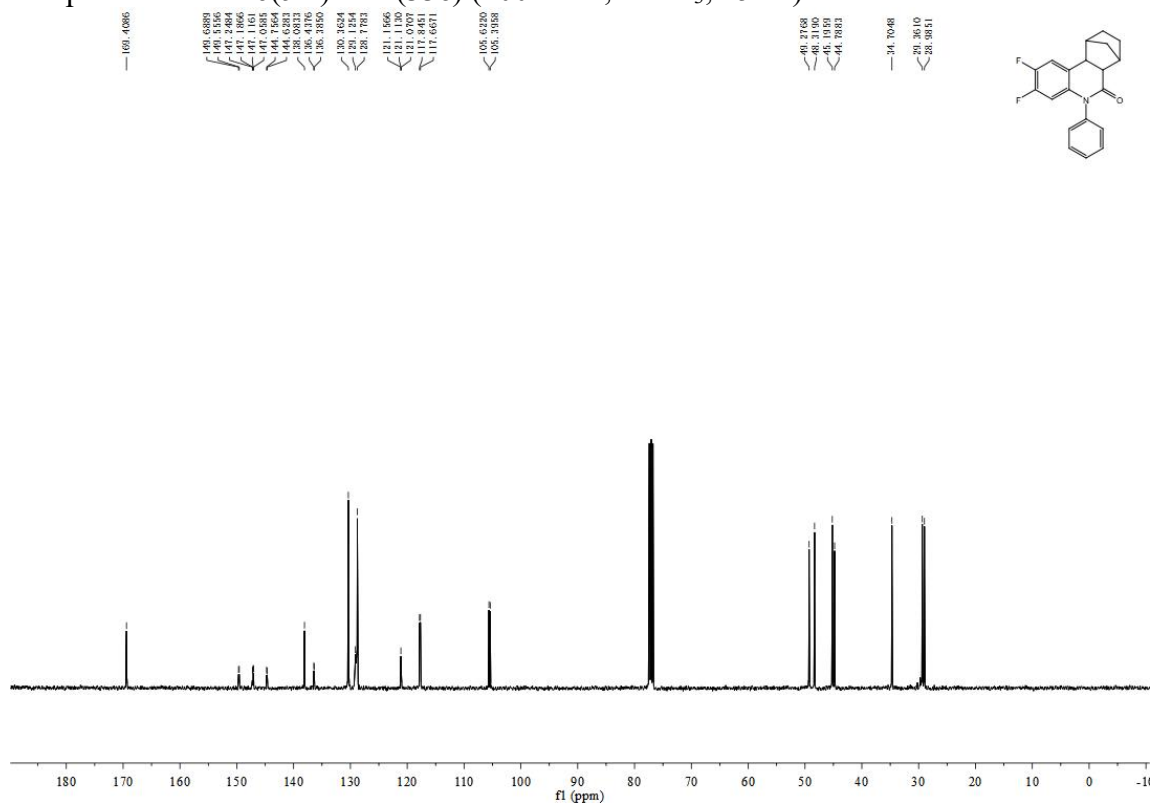
^{13}C NMR spectrum of 3-fluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**32c**) (100 MHz, CDCl_3 , 25 °C)



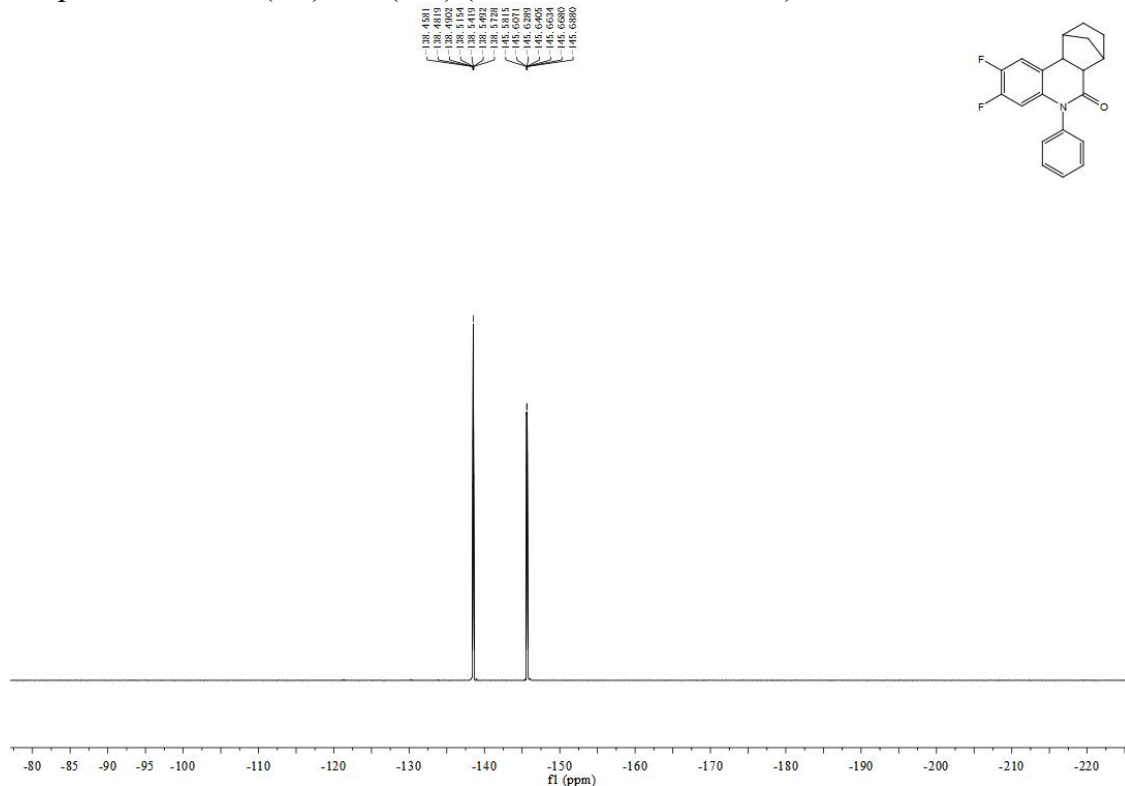
^1H NMR spectrum of 2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**33c**) (400 MHz, CDCl_3 , 25 °C)



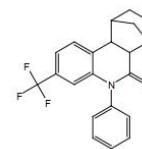
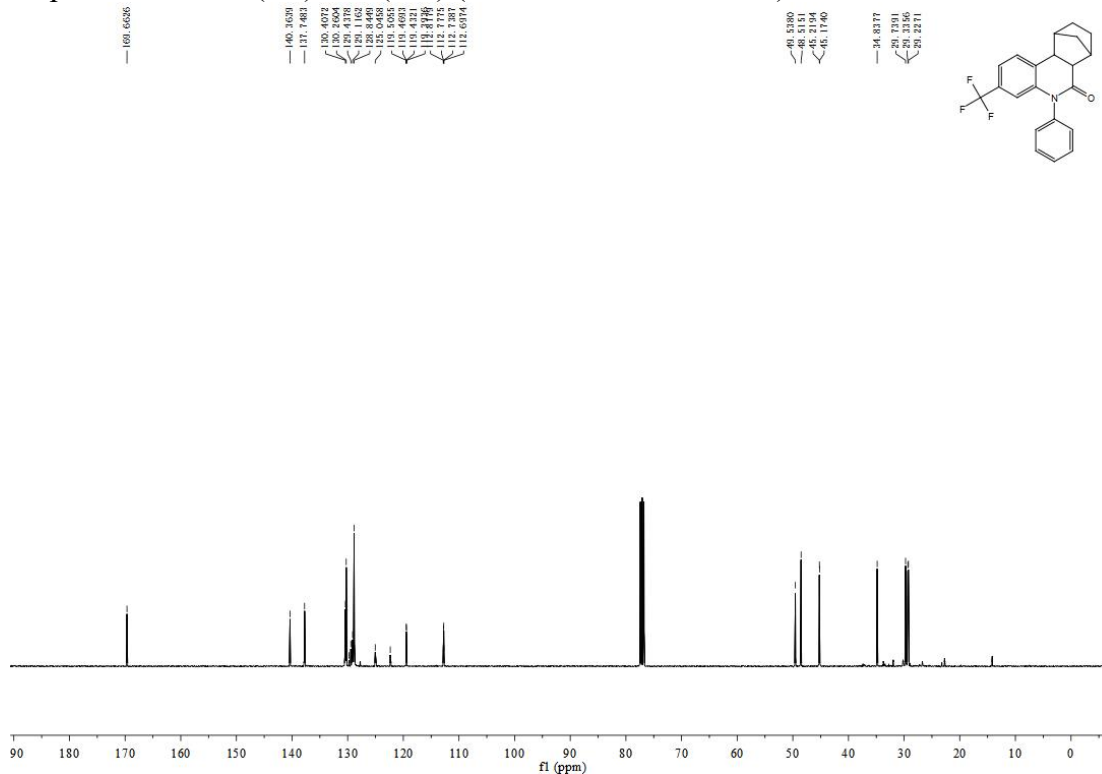
^{13}C NMR spectrum of 2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**33c**) (100 MHz, CDCl_3 , 25 °C)



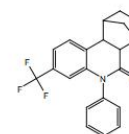
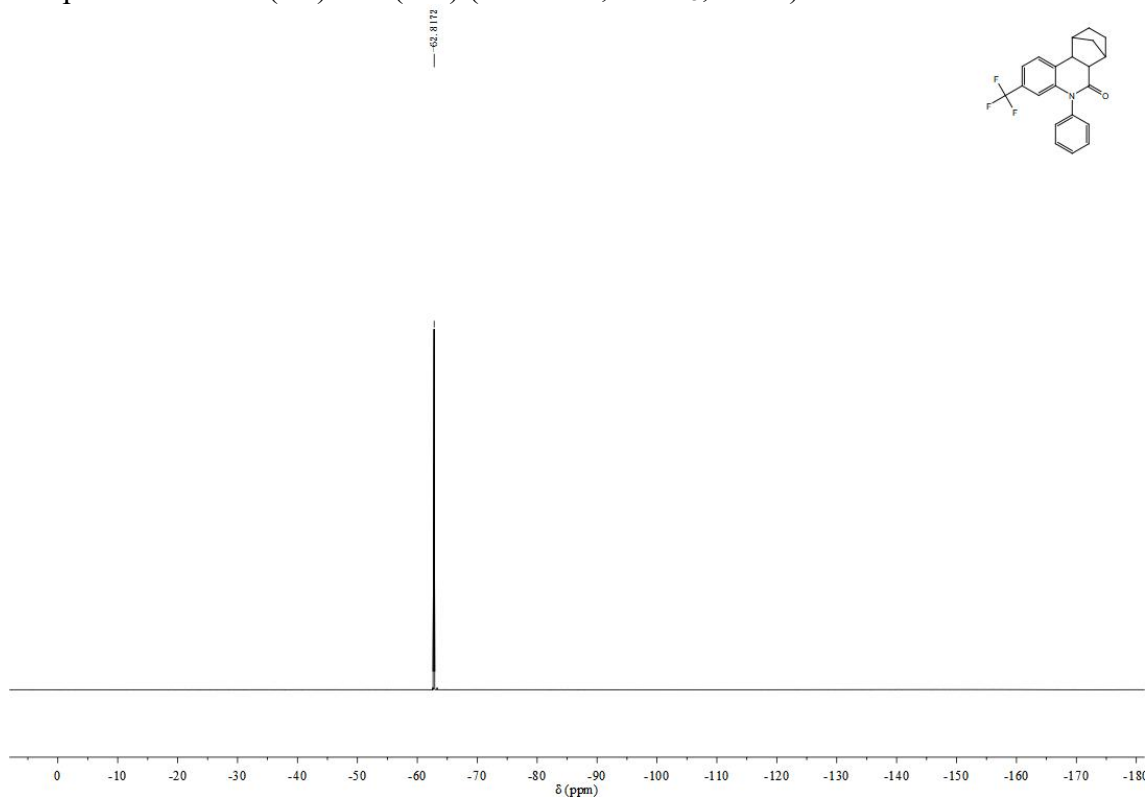
^{19}F NMR spectrum of 2,3-difluoro-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**33c**) (376 MHz, CDCl_3 , 25 °C)



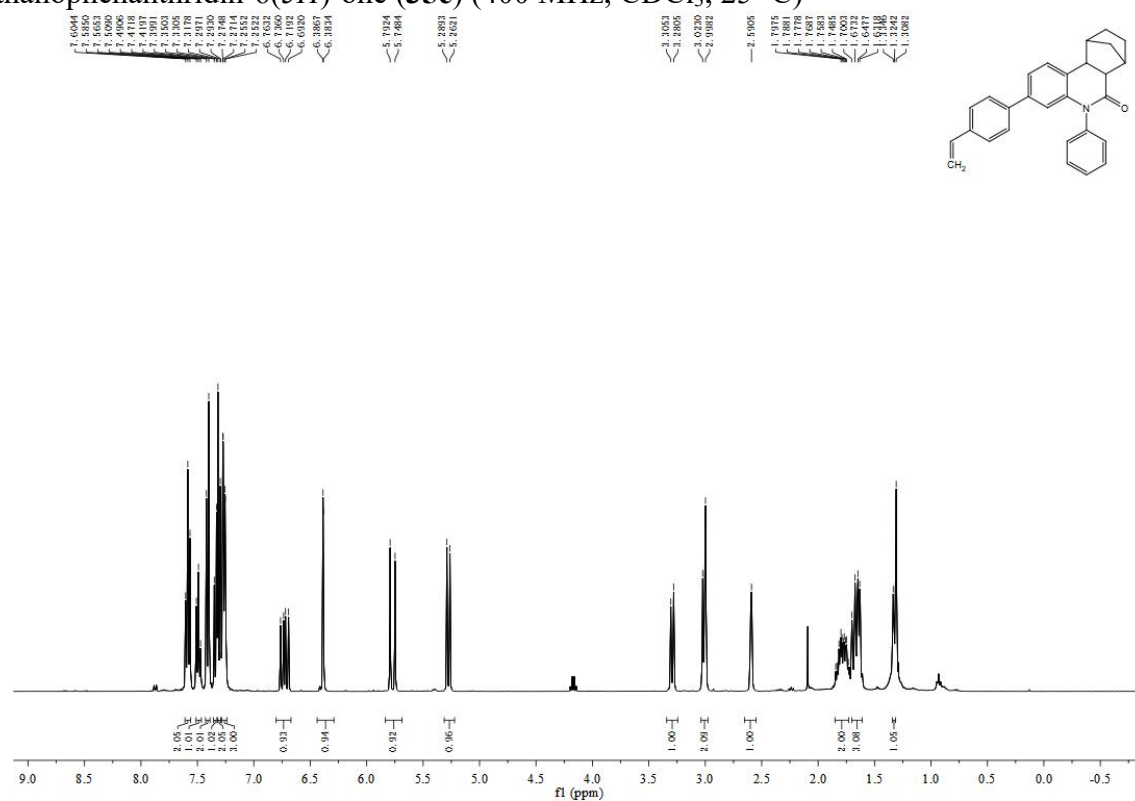
^{13}C NMR spectrum of 5-phenyl-3-(trifluoromethyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**34c**) (100 MHz, CDCl_3 , 25 °C)



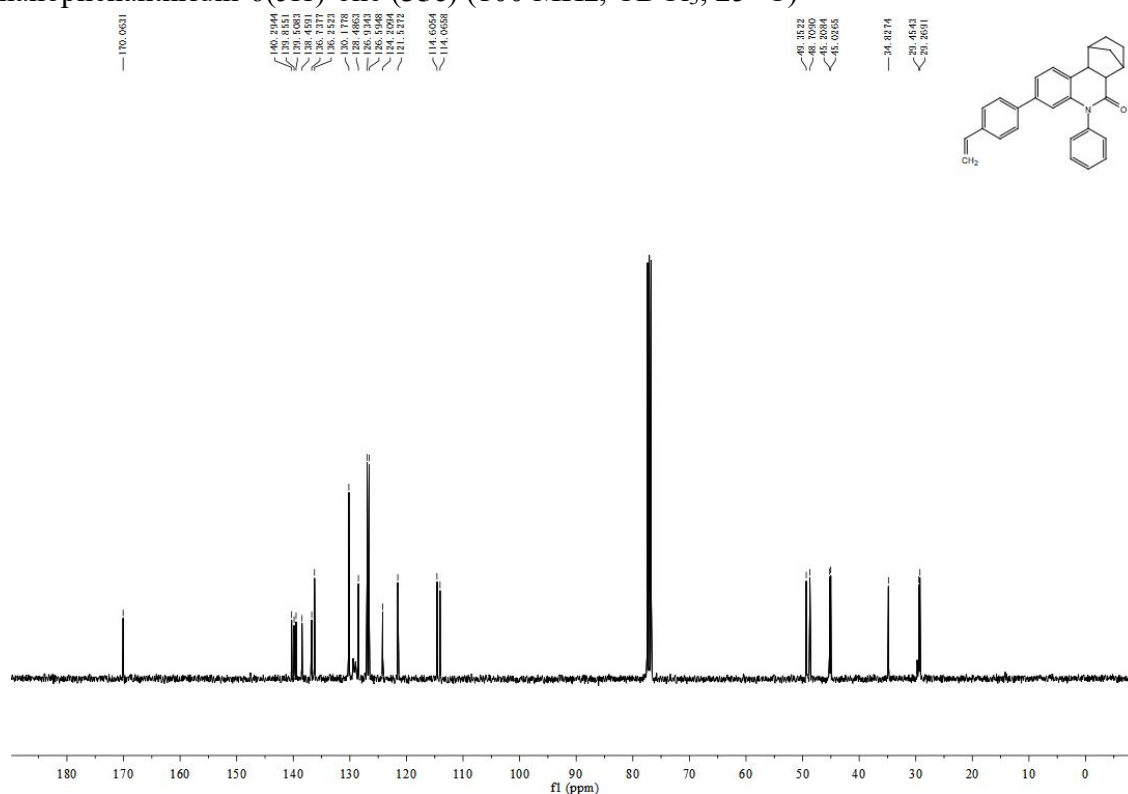
^{19}F NMR spectrum of 5-phenyl-3-(trifluoromethyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**34c**) (376 MHz, CDCl_3 , 25 °C)



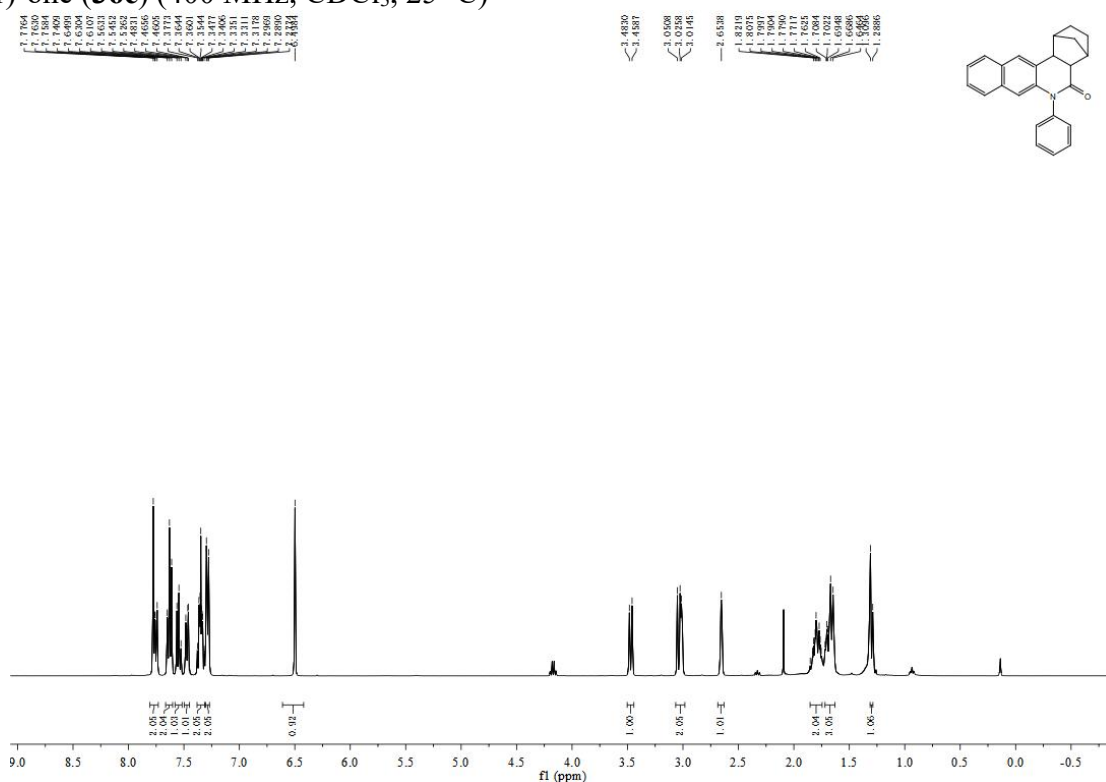
^1H NMR spectrum of 5-phenyl-3-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**35c**) (400 MHz, CDCl_3 , 25 °C)



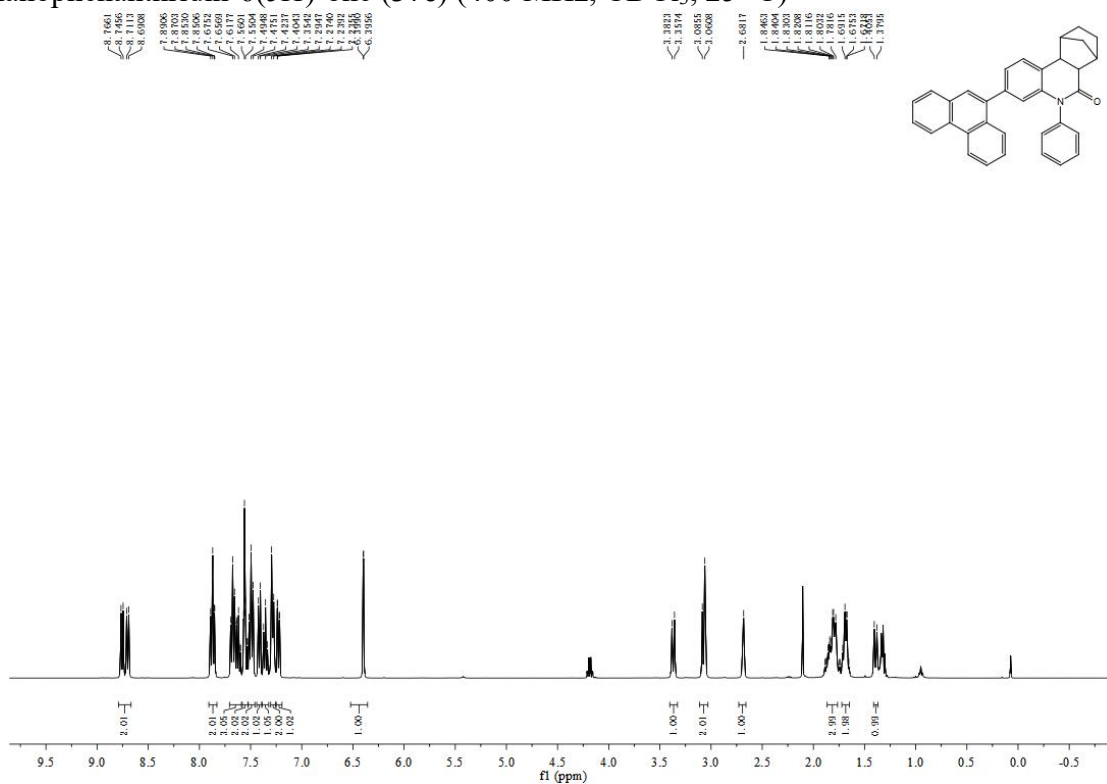
^{13}C NMR spectrum of 5-phenyl-3-(4-vinylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**35c**) (100 MHz, CDCl_3 , 25 °C)



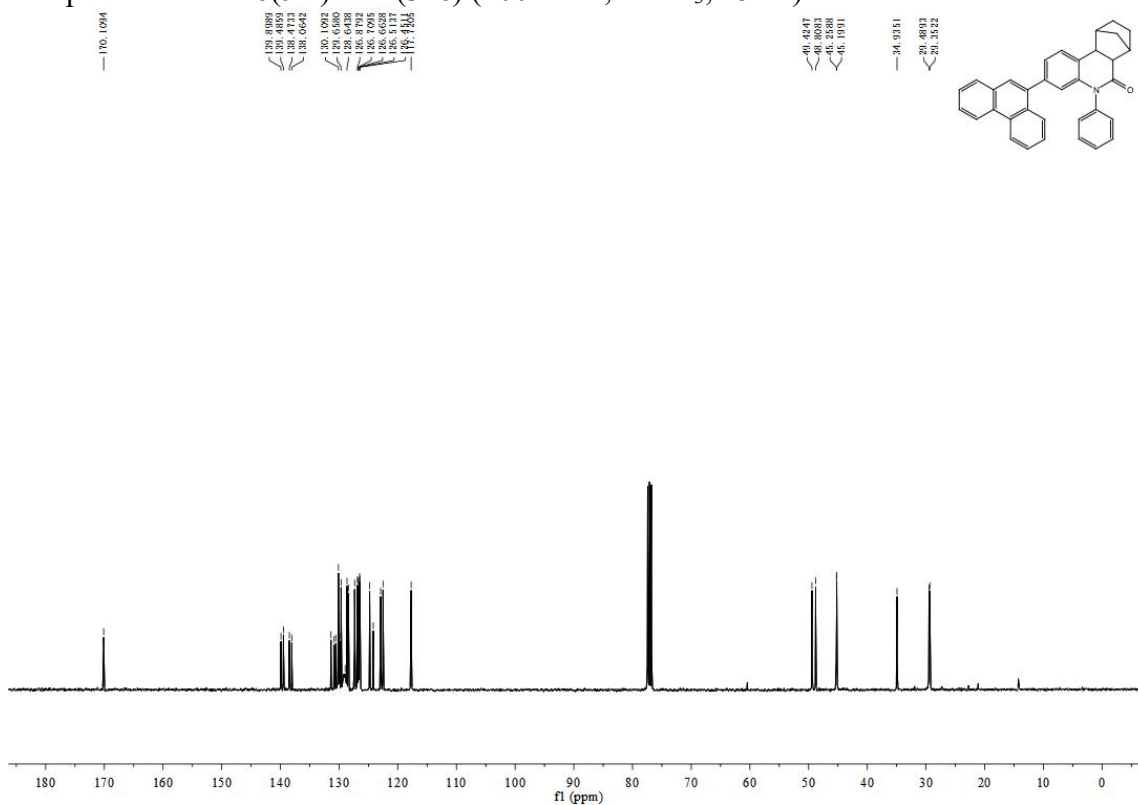
^1H NMR spectrum of 6-phenyl-2,3,4,4a,6,12b-hexahydro-1,4-methanobenzo[b]phenanthridin-5(1*H*)-one (**36c**) (400 MHz, CDCl_3 , 25 °C)



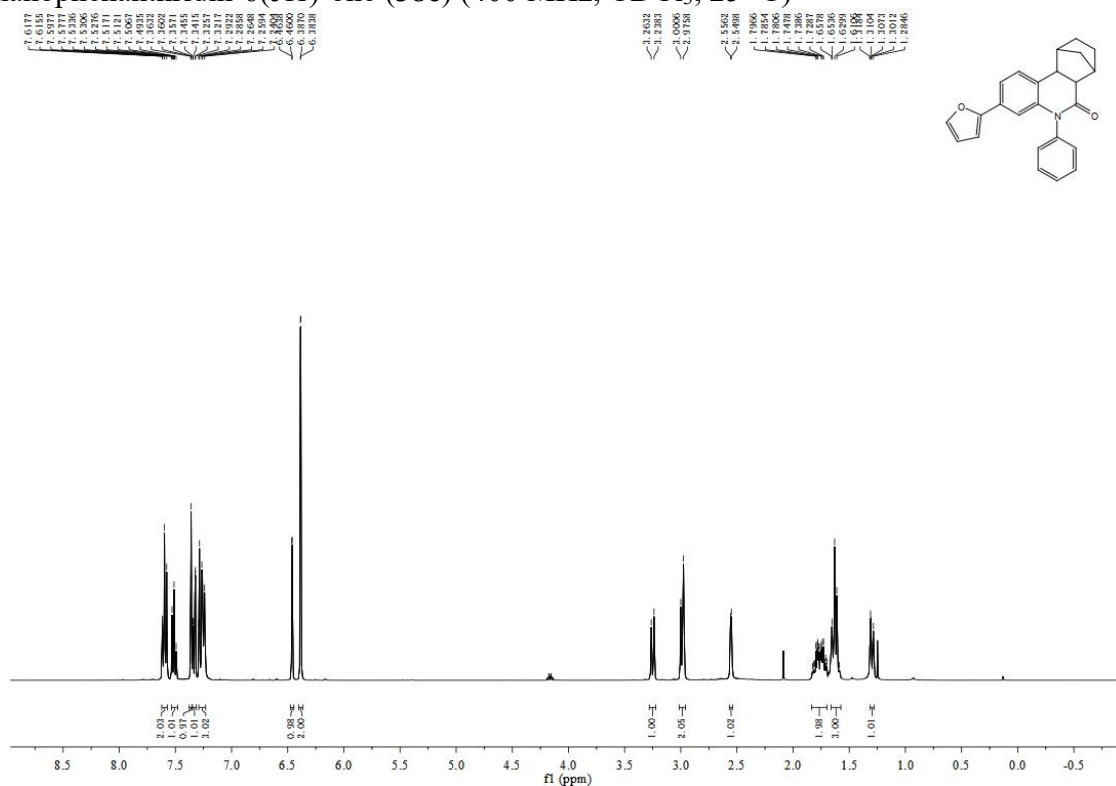
^1H NMR spectrum of 3-(phenanthren-9-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**37c**) (400 MHz, CDCl_3 , 25 °C)



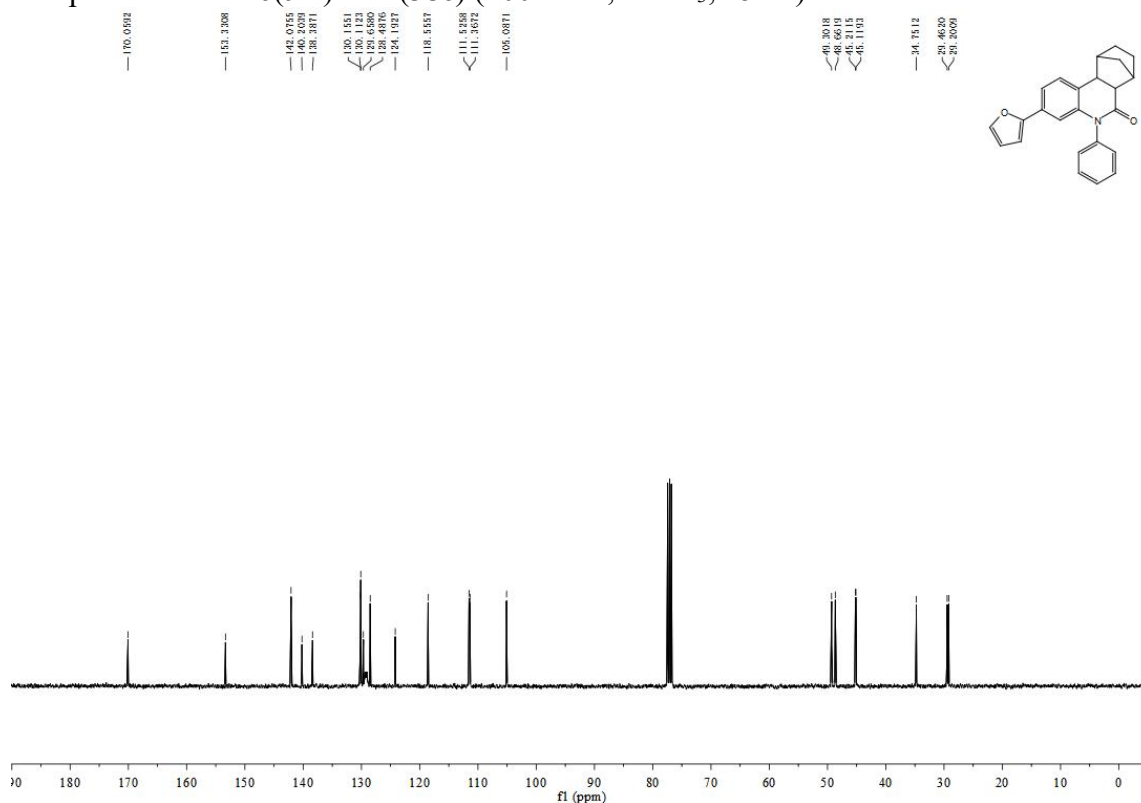
^{13}C NMR spectrum of 3-(phenanthren-9-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**37c**) (100 MHz, CDCl_3 , 25 °C)



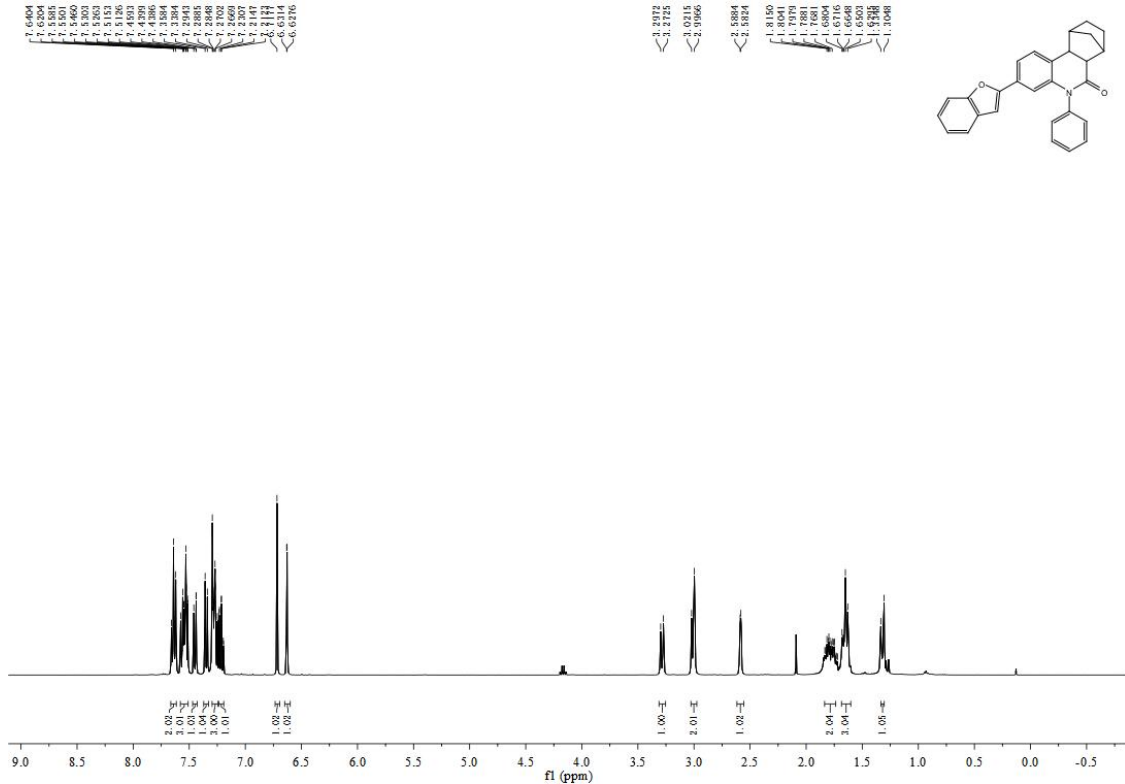
^1H NMR spectrum of 3-(furan-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**38c**) (400 MHz, CDCl_3 , 25 °C)



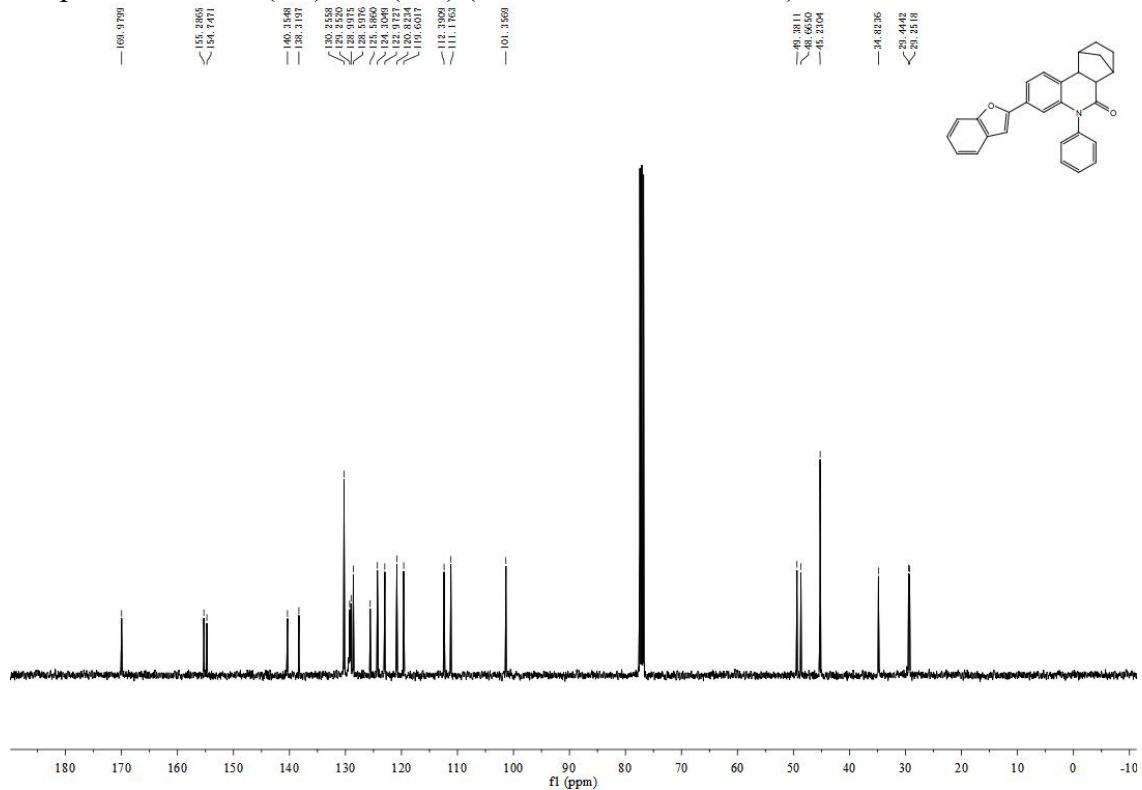
^{13}C NMR spectrum of 3-(furan-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**38c**) (100 MHz, CDCl_3 , 25 °C)



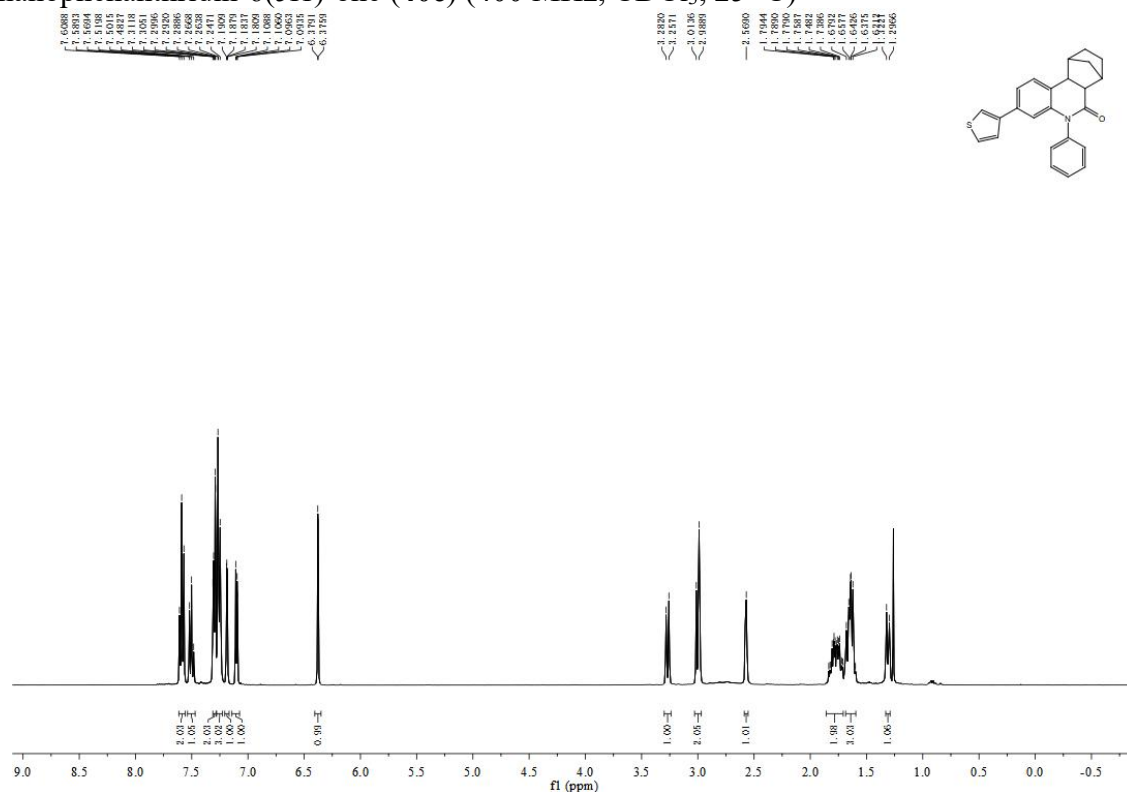
¹H NMR spectrum of 3-(benzofuran-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**39c**) (400 MHz, CDCl₃, 25 °C)



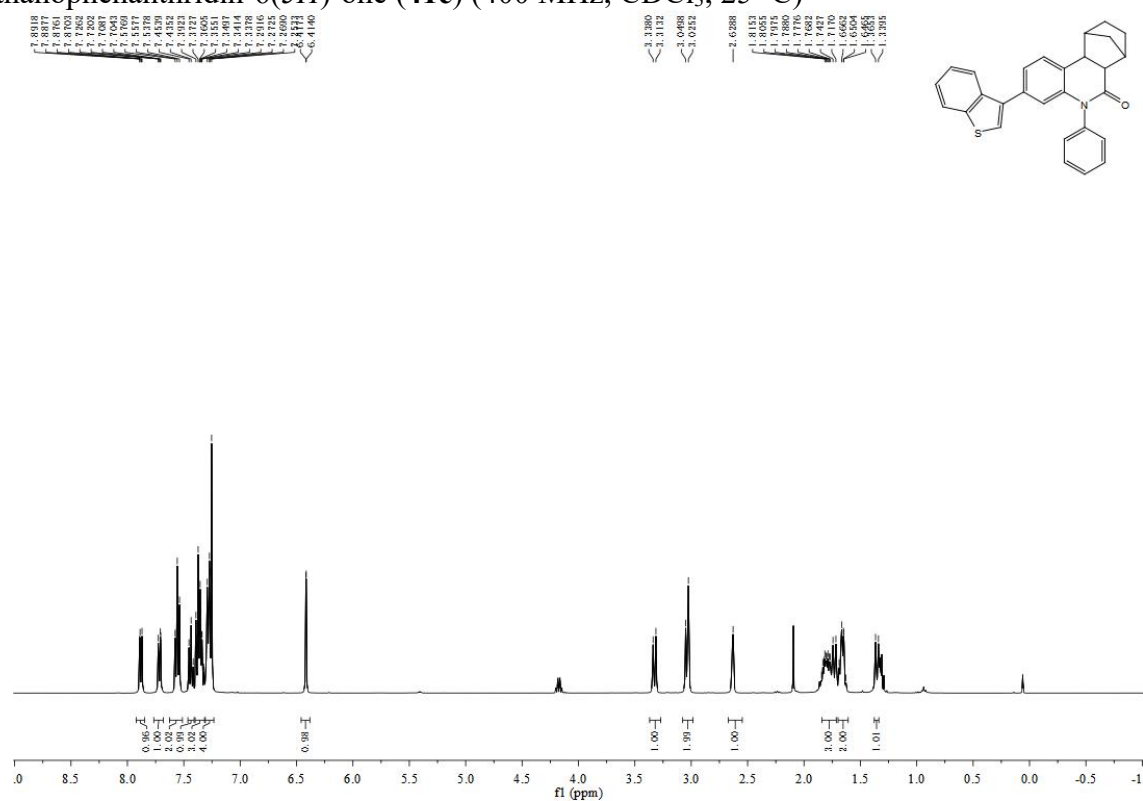
¹³C NMR spectrum of 3-(benzofuran-2-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**39c**) (100 MHz, CDCl₃, 25 °C)



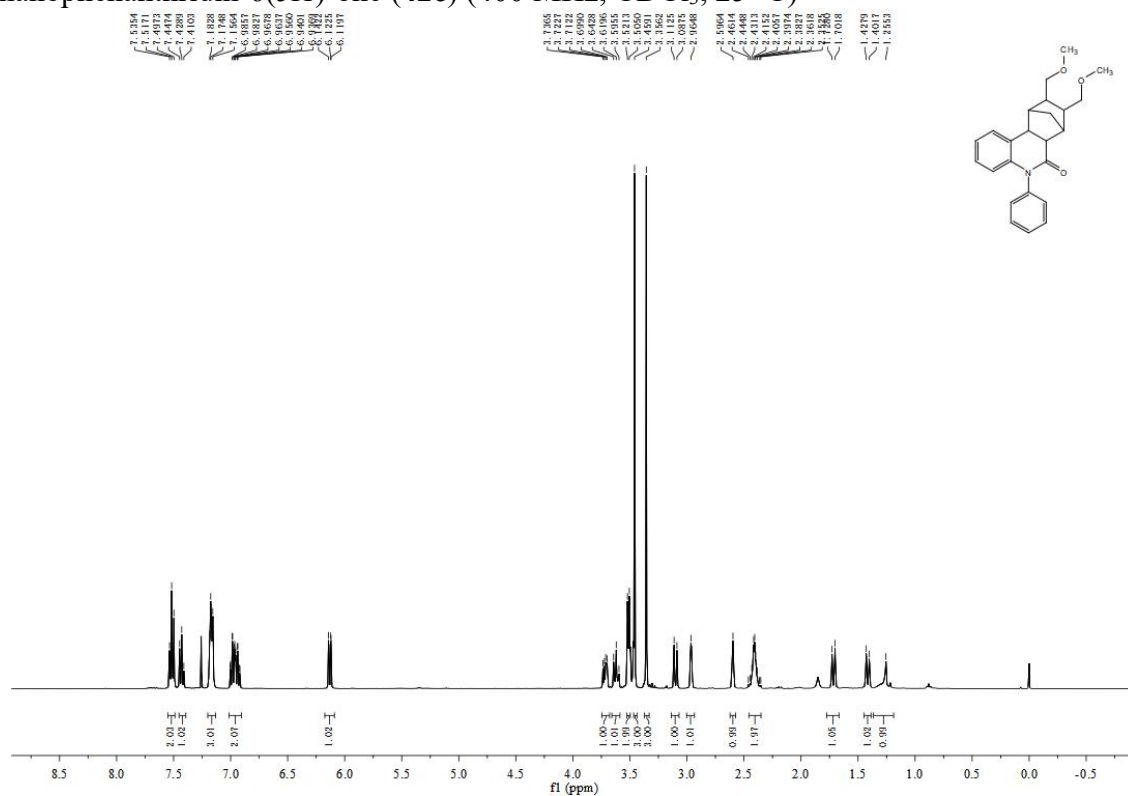
^1H NMR spectrum of 5-phenyl-3-(thiophen-3-yl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**40c**) (400 MHz, CDCl_3 , 25 °C)



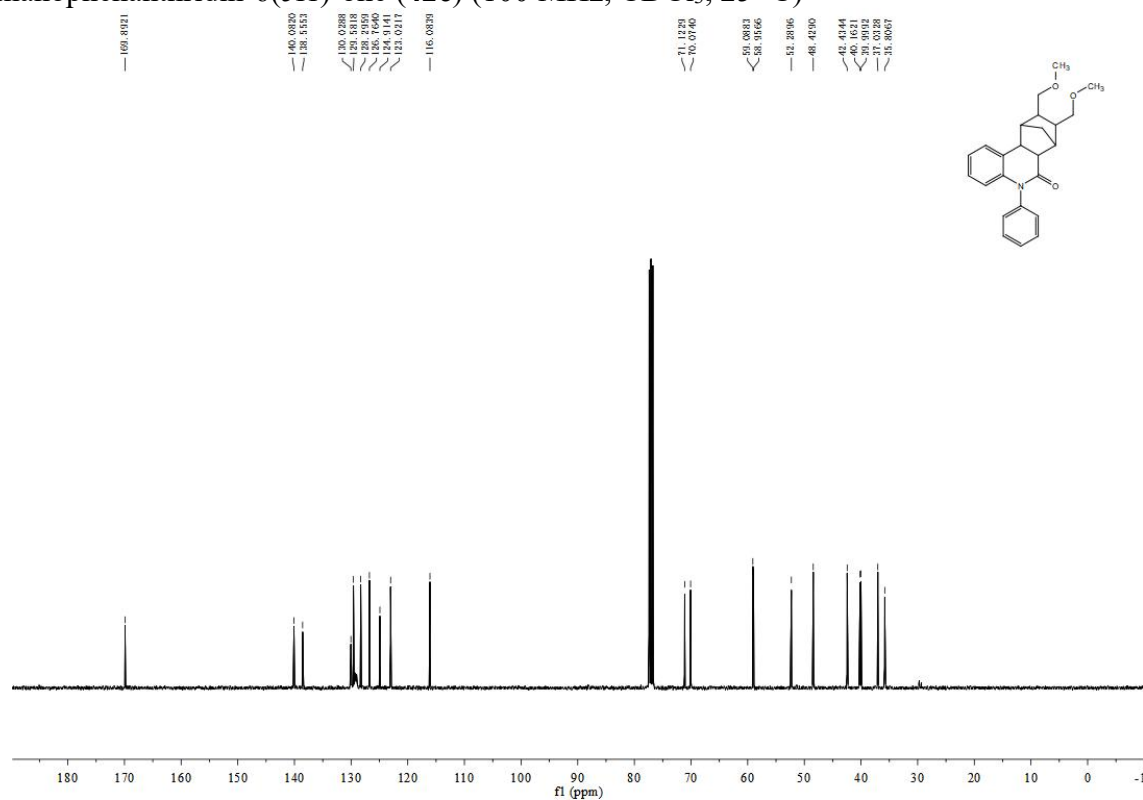
^1H NMR spectrum of 3-(benzo[*b*]thiophen-3-yl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**41c**) (400 MHz, CDCl_3 , 25 °C)



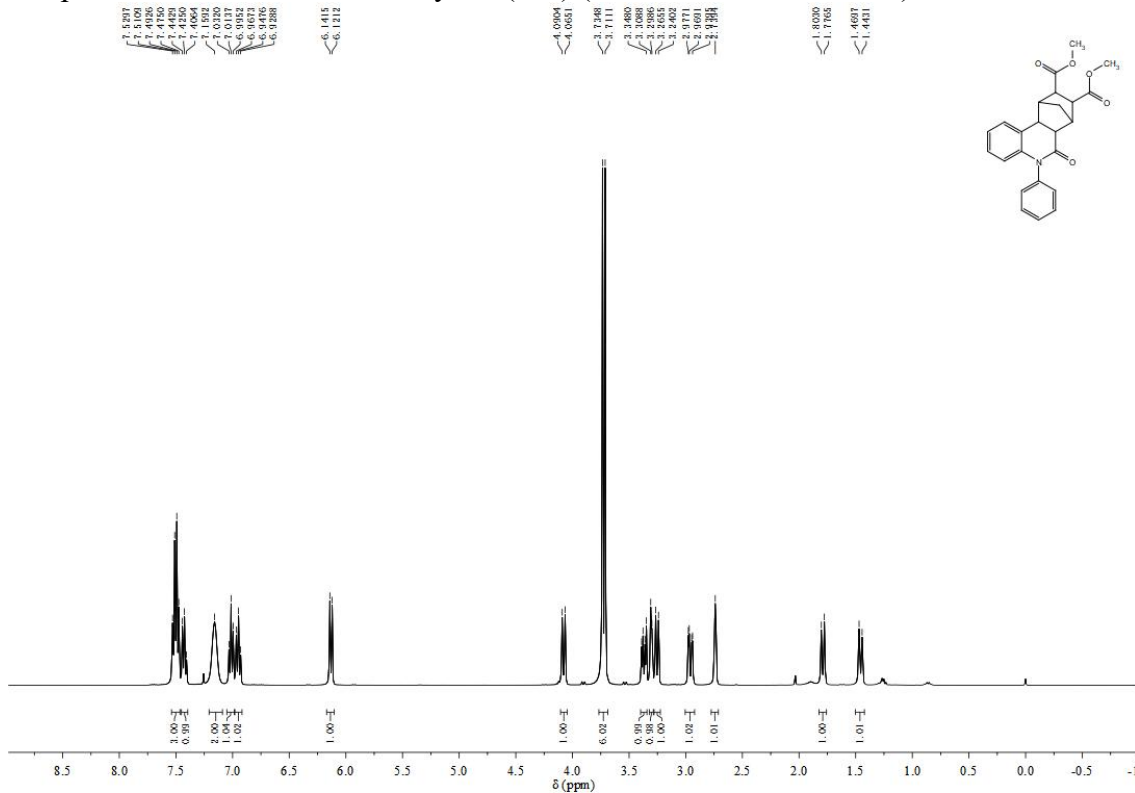
^1H NMR spectrum of 8,9-bis(methoxymethyl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**42c**) (400 MHz, CDCl_3 , 25 °C)



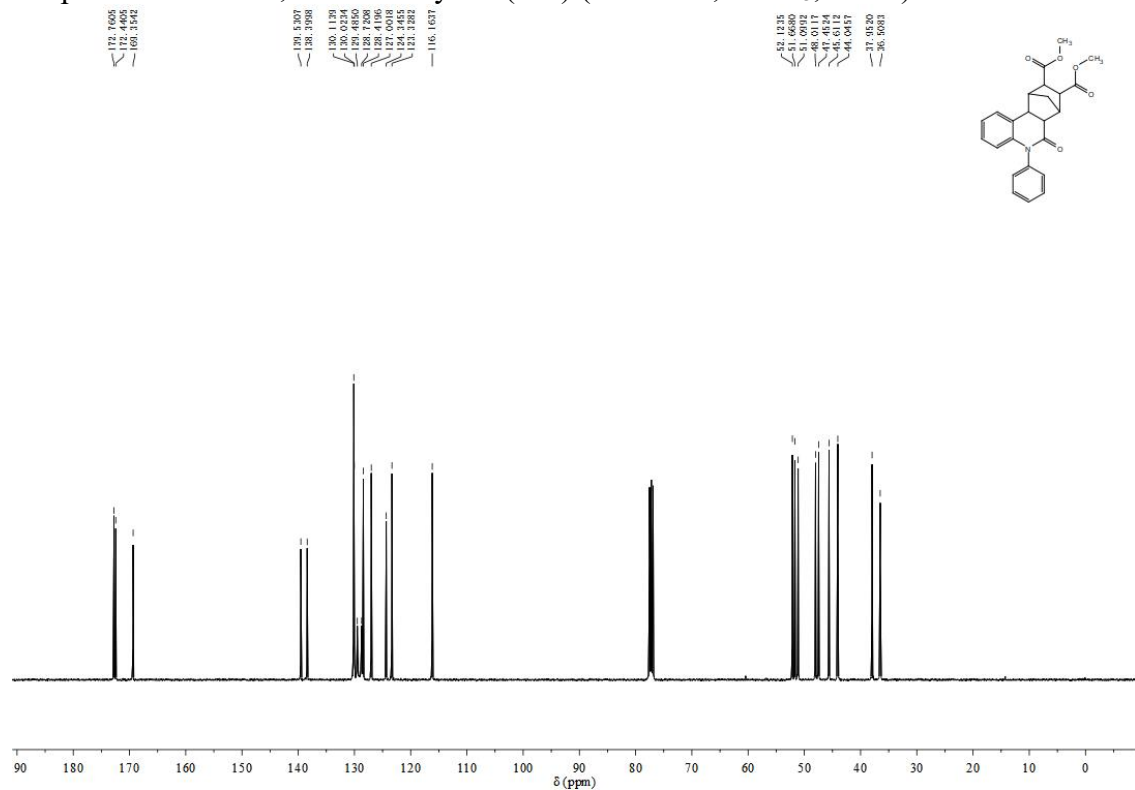
^{13}C NMR spectrum of 8,9-bis(methoxymethyl)-5-phenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**42c**) (100 MHz, CDCl_3 , 25 °C)



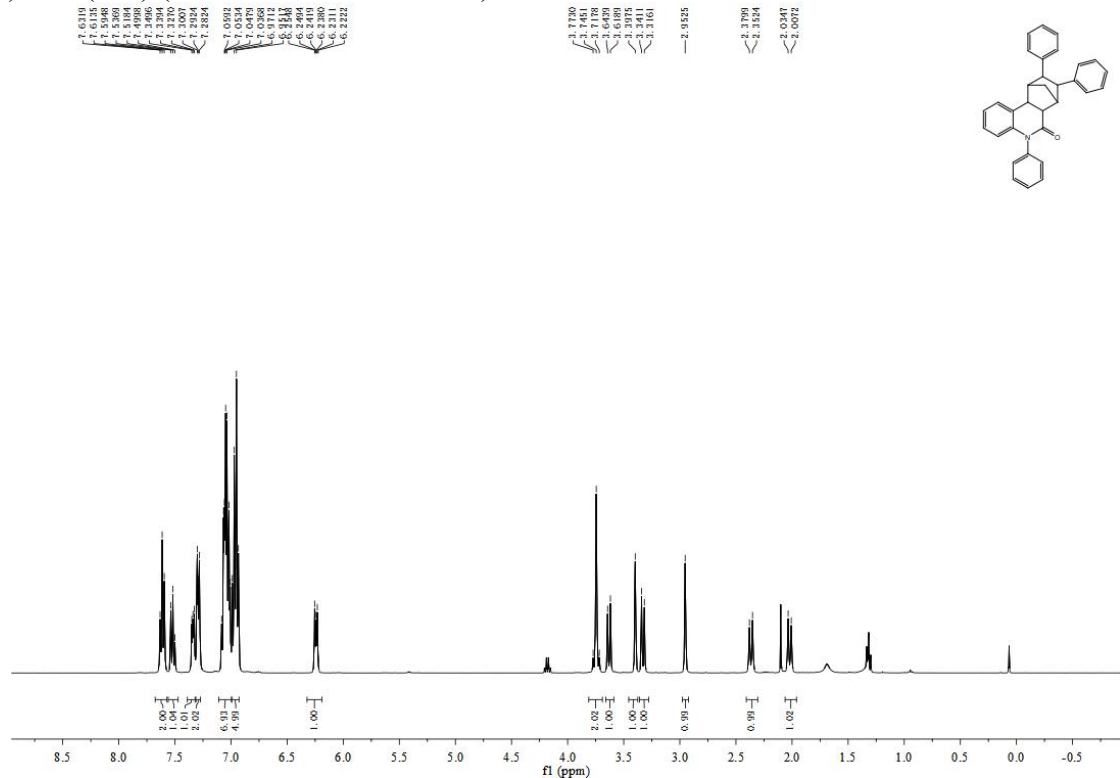
^1H NMR spectrum of dimethyl 6-oxo-5-phenyl-5, 6, 6a, 7, 8, 9, 10, 10a-octahydro-7, 10-methanophenanthridine-8, 9-dicarboxylate (**43c**) (400 MHz, CDCl_3 , 25 °C)



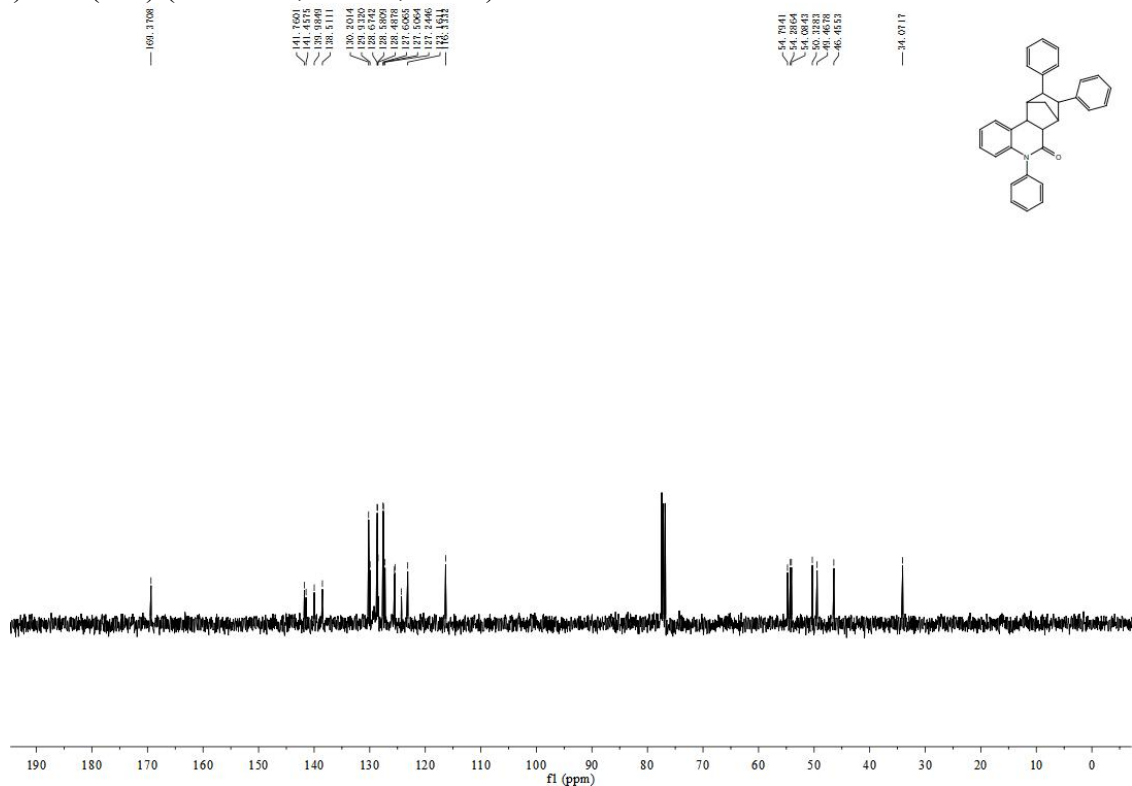
^{13}C NMR spectrum of dimethyl 6-oxo-5-phenyl-5, 6, 6a, 7, 8, 9, 10, 10a-octahydro-7, 10-methanophenanthridine-8, 9-dicarboxylate (**43c**) (100 MHz, CDCl_3 , 25 °C)



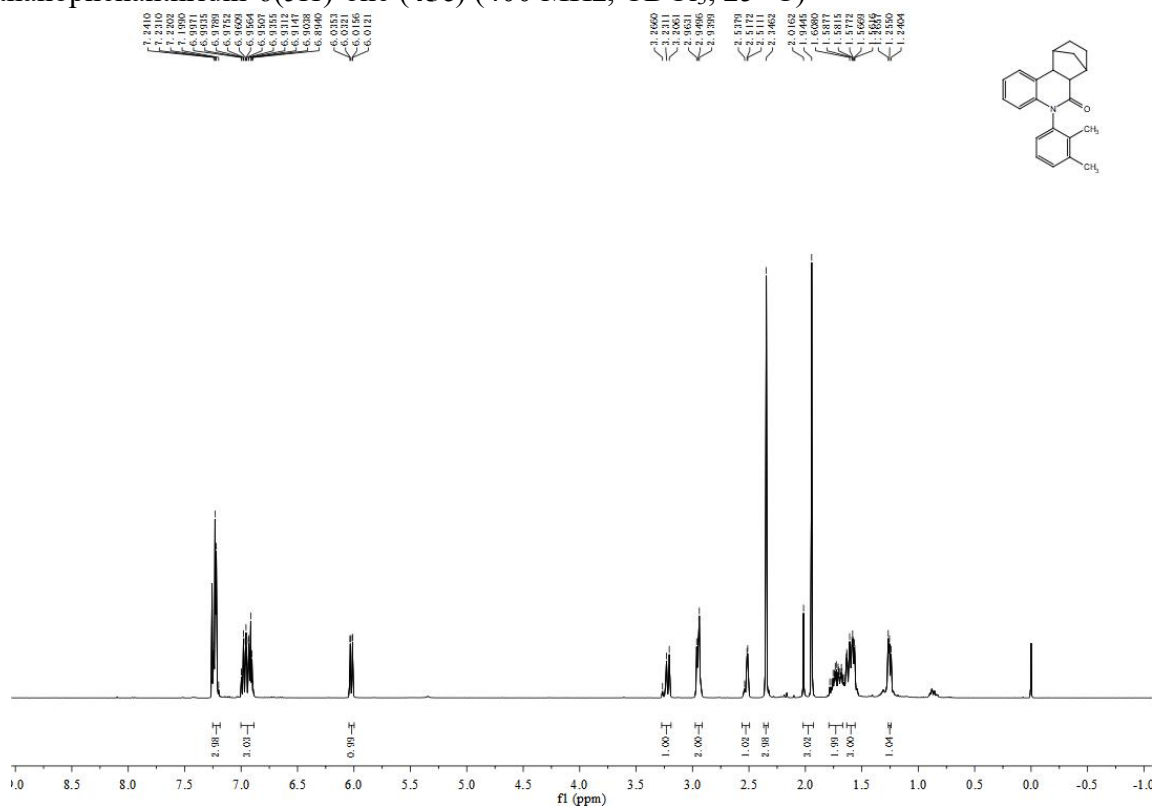
¹H NMR spectrum of 5,8,9-triphenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**44c**) (400 MHz, CDCl₃, 25 °C)



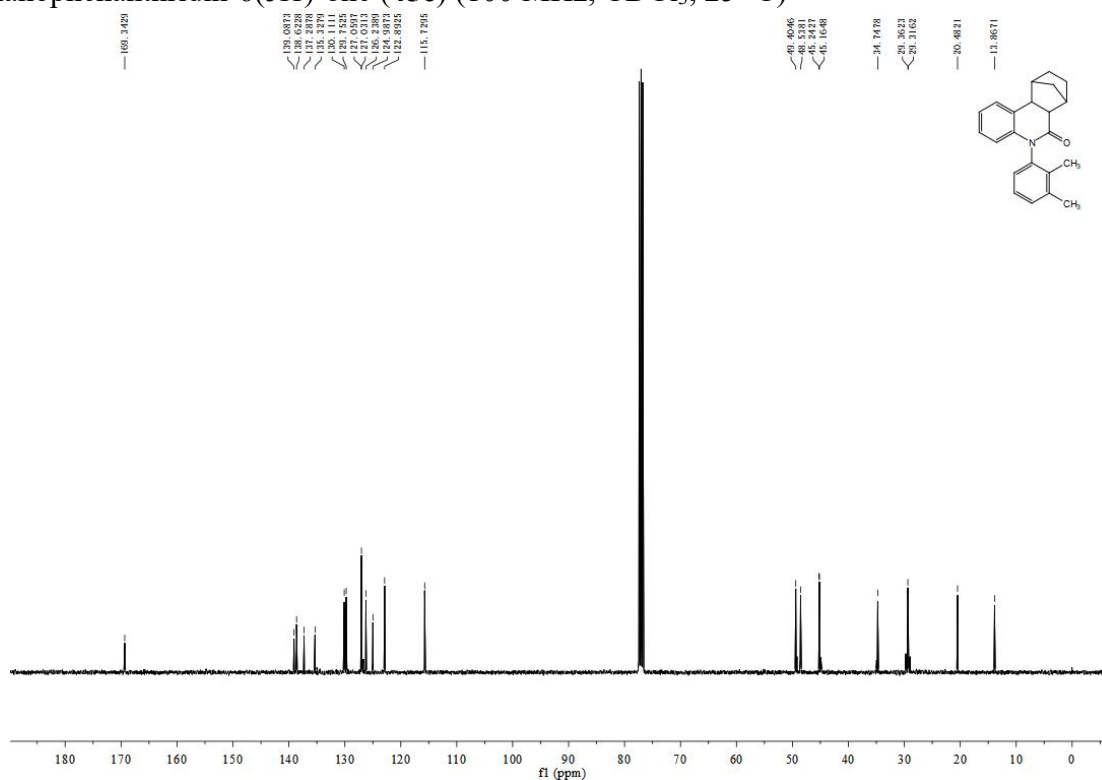
¹³C NMR spectrum of 5,8,9-triphenyl-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**44c**) (100 MHz, CDCl₃, 25 °C)



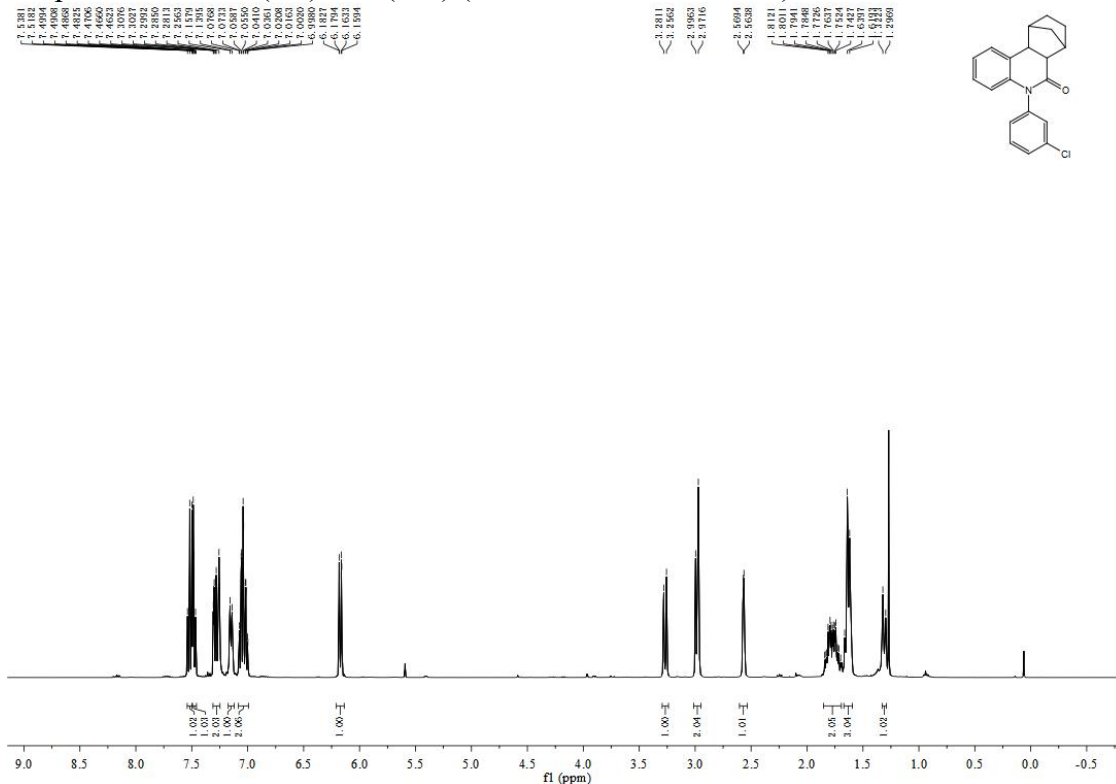
^1H NMR spectrum of 5-(2,3-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**45c**) (400 MHz, CDCl_3 , 25 °C)



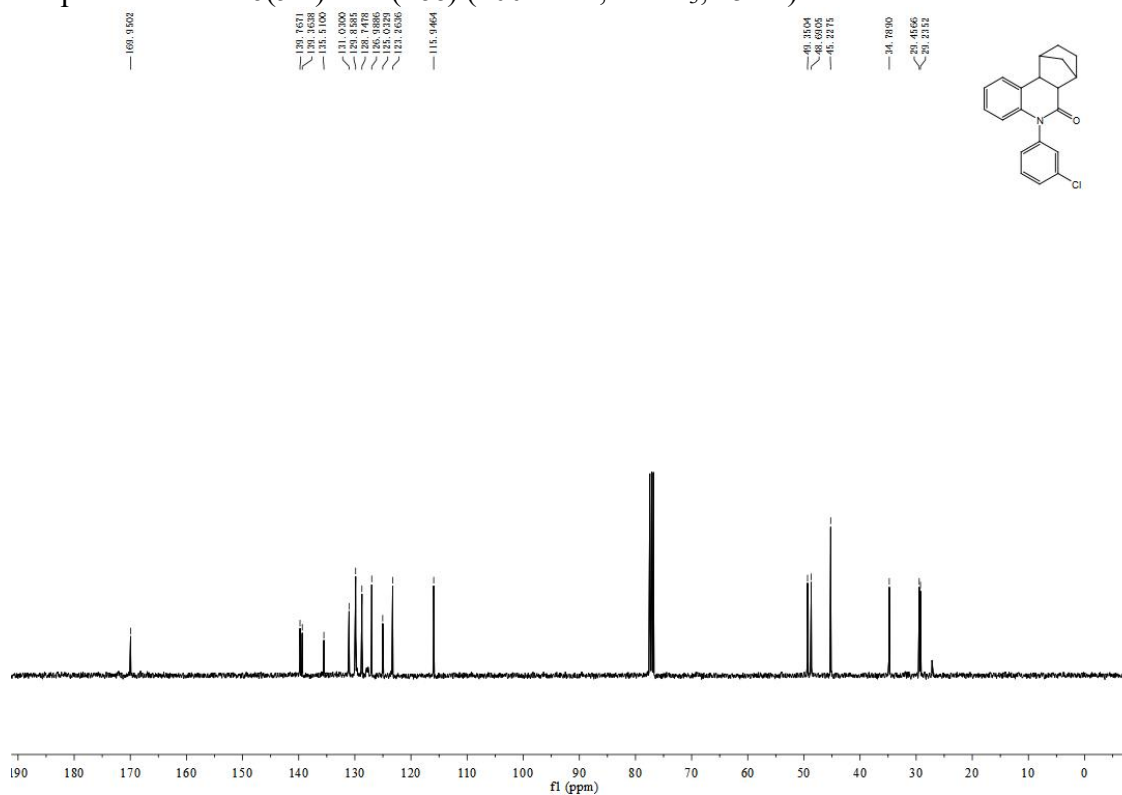
^{13}C NMR spectrum of 5-(2,3-dimethylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**45c**) (100 MHz, CDCl_3 , 25 °C)



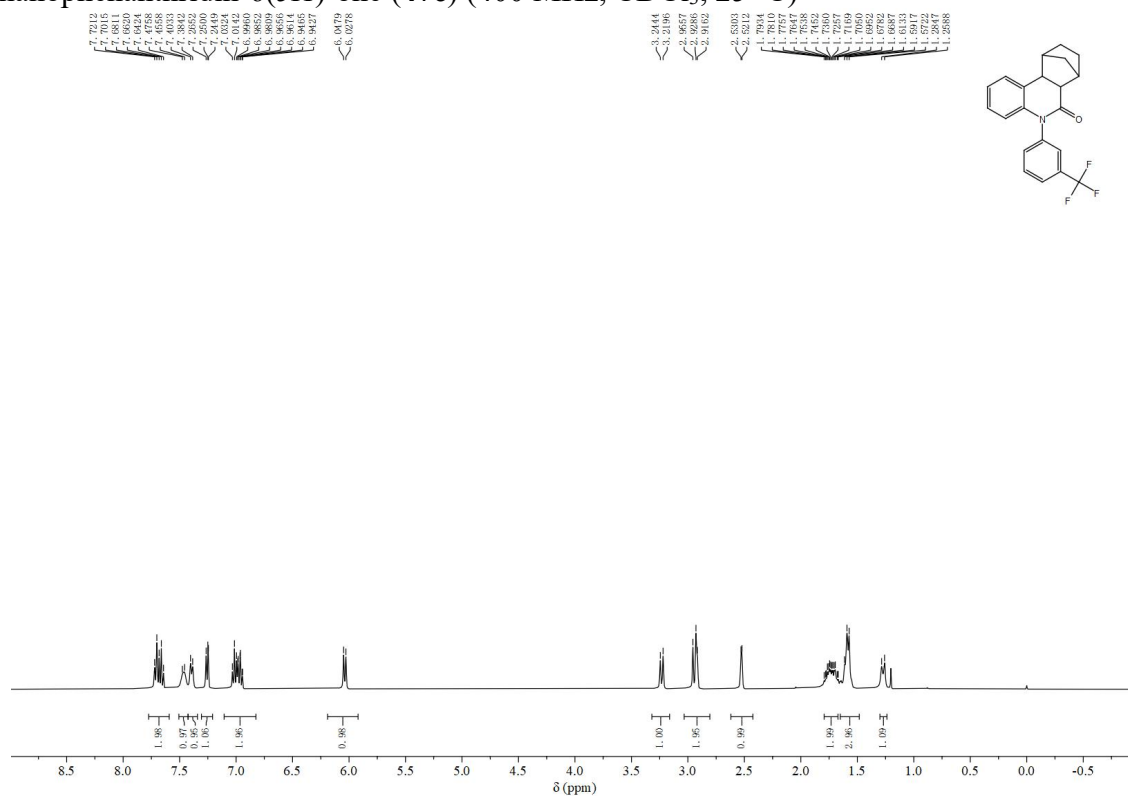
¹H NMR spectrum of 5-(3-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**46c**) (400 MHz, CDCl₃, 25 °C)



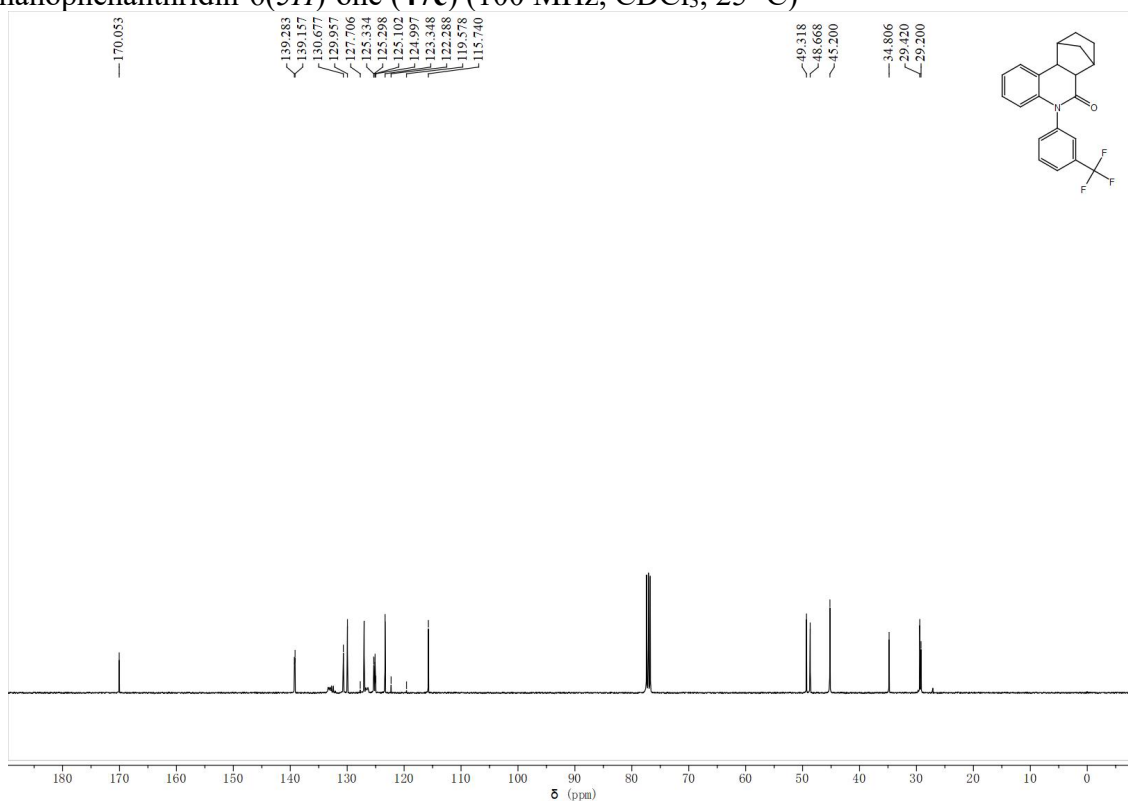
¹³C NMR spectrum of 5-(3-chlorophenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**46c**) (100 MHz, CDCl₃, 25 °C)



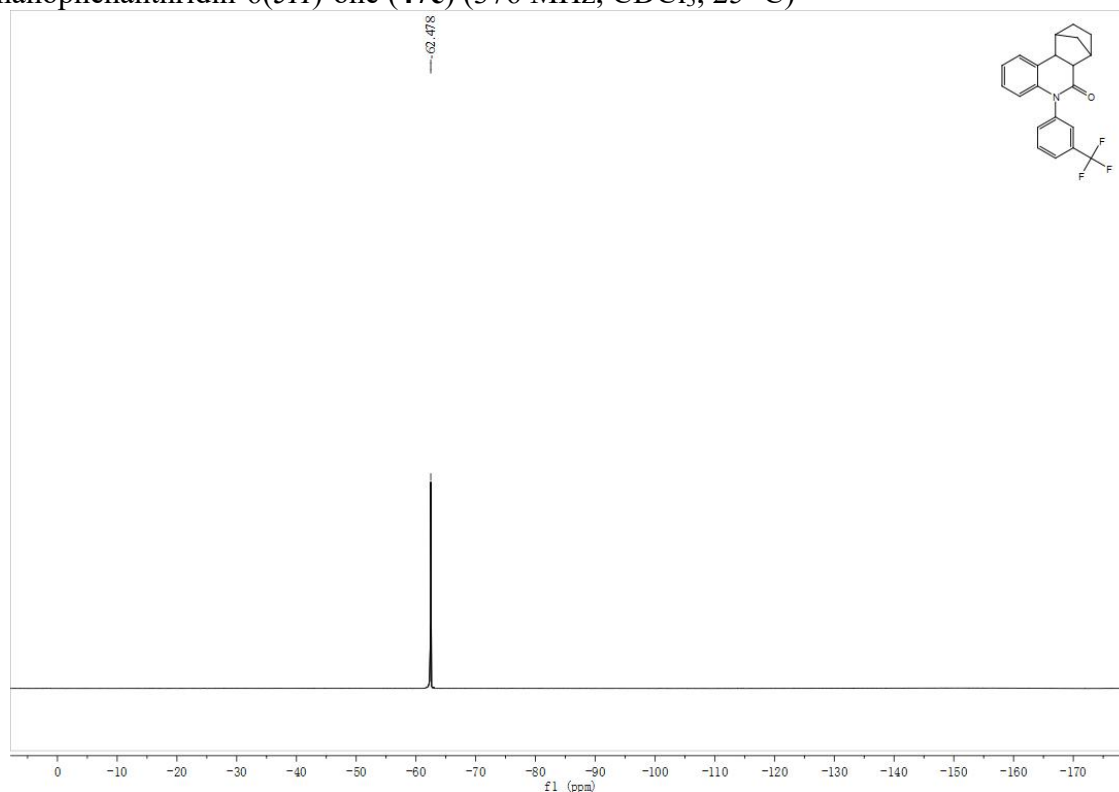
^1H NMR spectrum of 5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**47c**) (400 MHz, CDCl_3 , 25 °C)



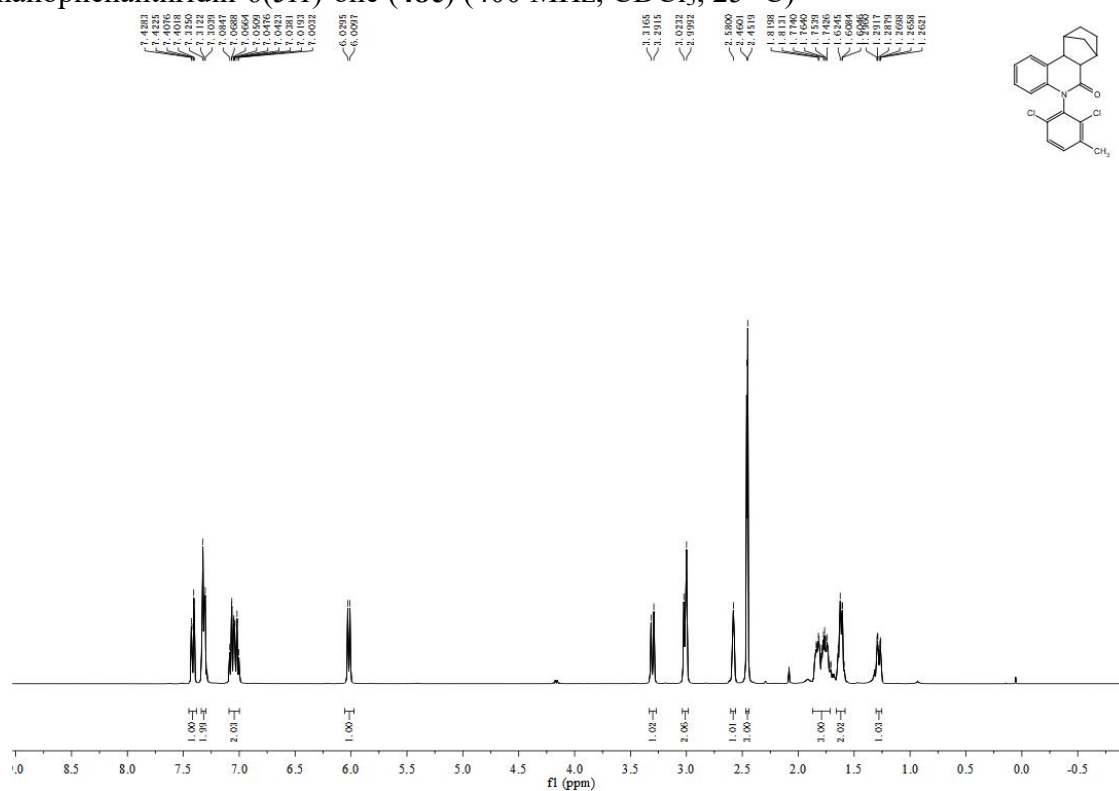
^{13}C NMR spectrum of 5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**47c**) (100 MHz, CDCl_3 , 25 °C)



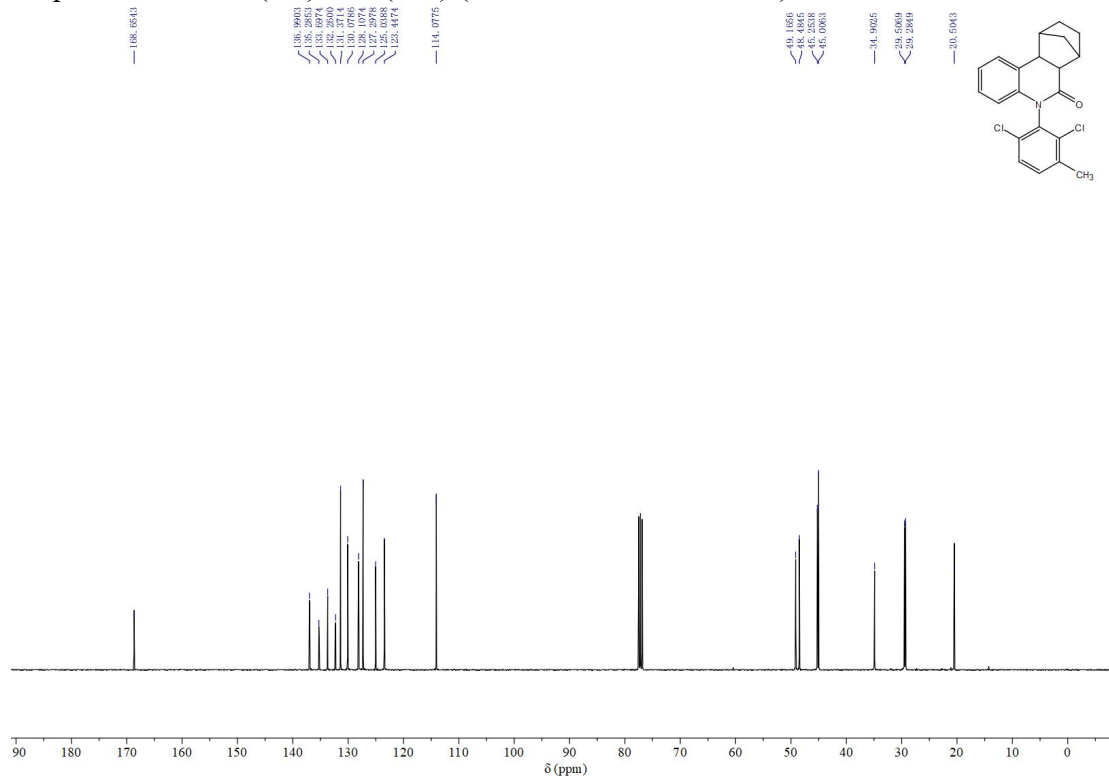
^{19}F NMR spectrum of 5-(3-(trifluoromethyl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**47c**) (376 MHz, CDCl_3 , 25 °C)



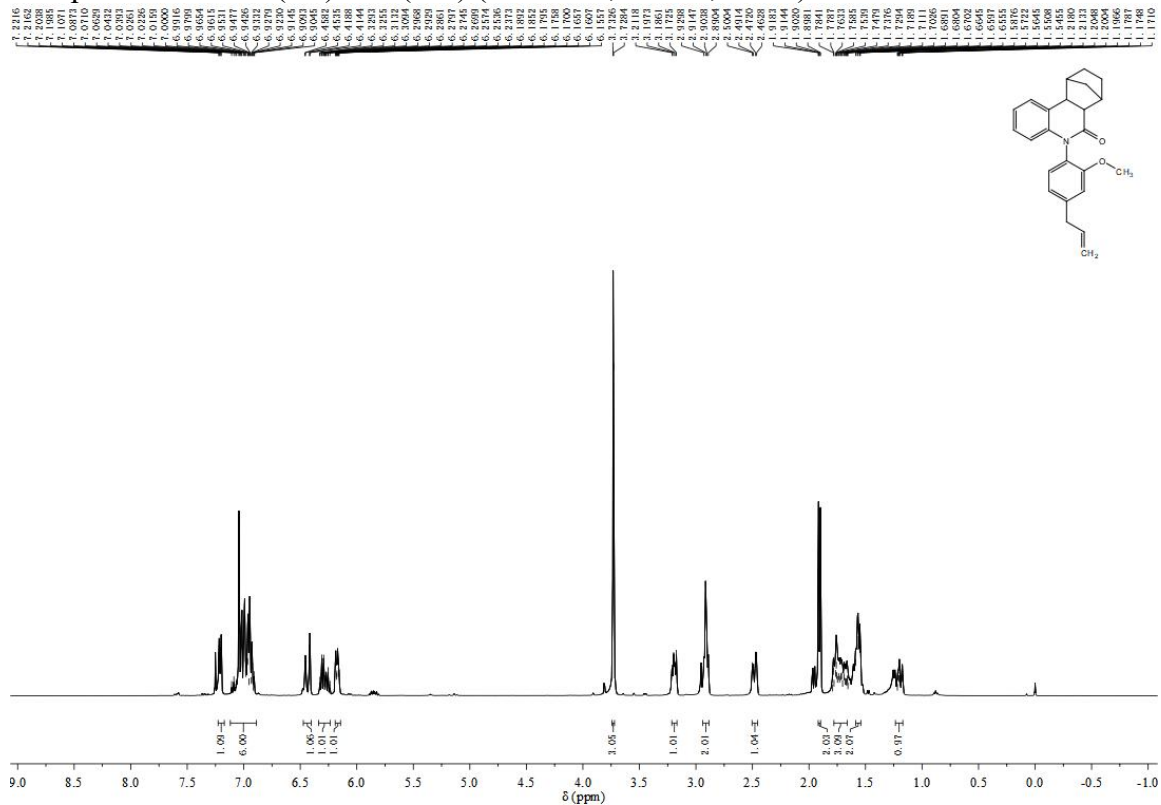
^1H NMR spectrum of 5-(2,6-dichloro-3-methylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**48c**) (400 MHz, CDCl_3 , 25 °C)



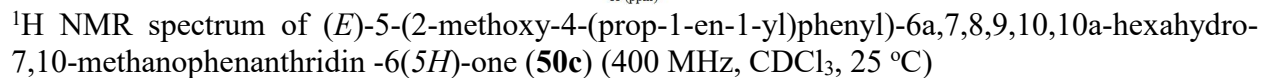
^{13}C NMR spectrum of 5-(2,6-dichloro-3-methylphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**48c**) (100 MHz, CDCl_3 , 25 °C)



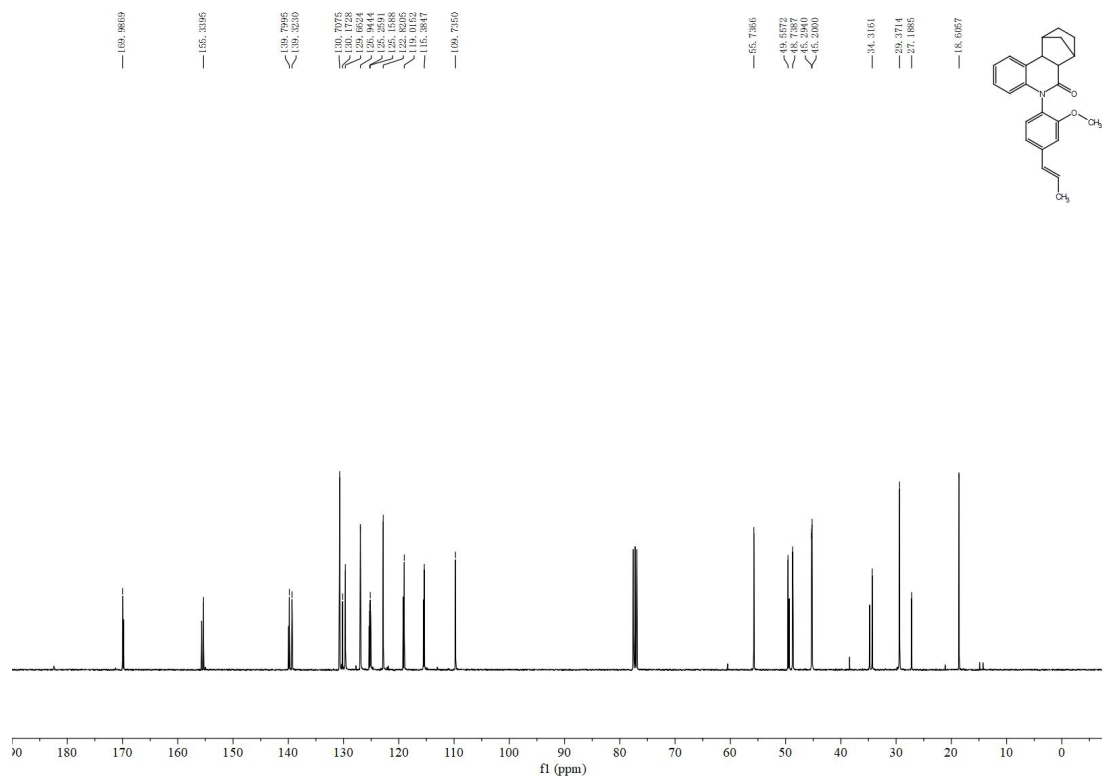
^1H NMR spectrum of 5-(4-allyl-2-methoxyphenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**49c**) (400 MHz, CDCl_3 , 25 °C)



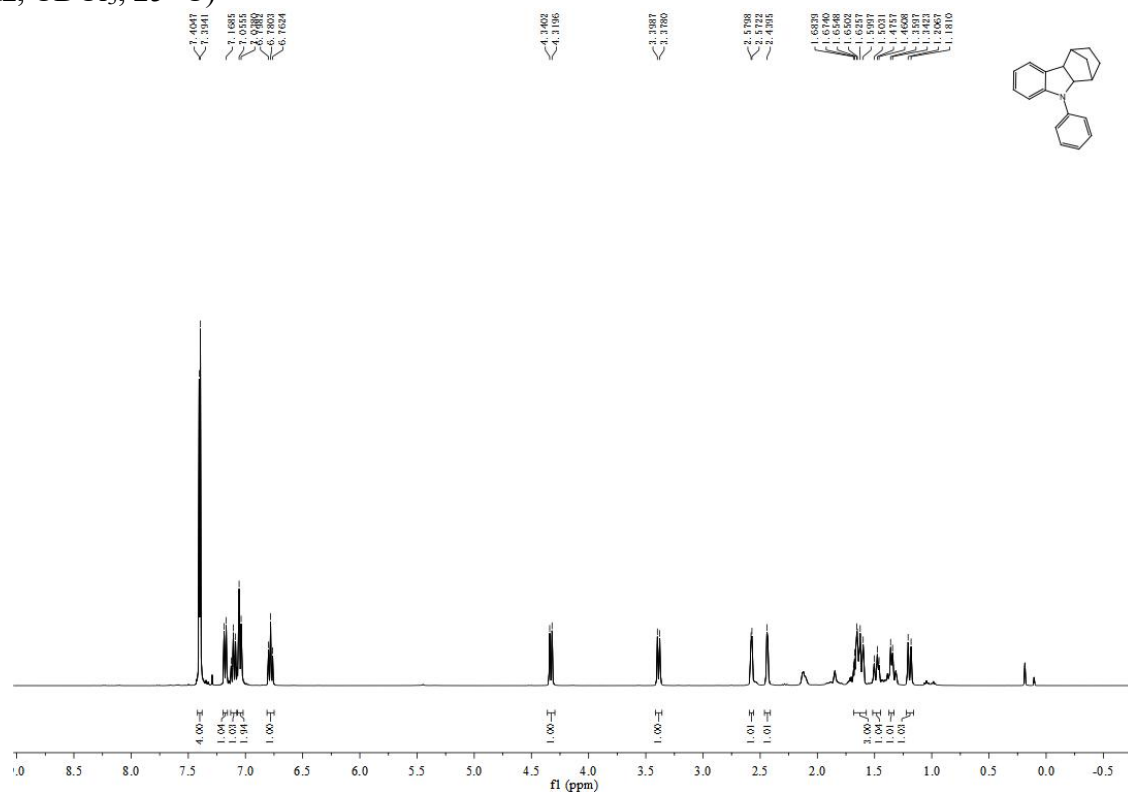
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— 22, 7416
— 19, 0077
— 15, 3516
— 109, 7095
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— 29, 3417
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[illegible]

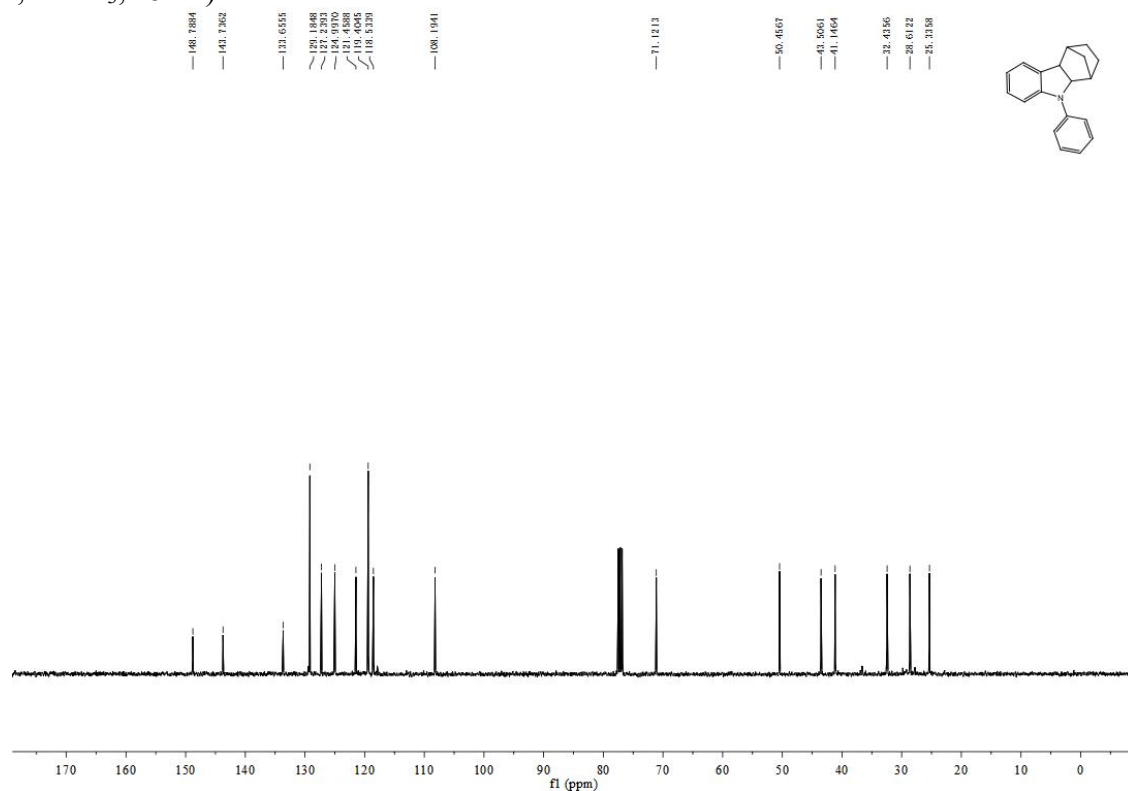
^{13}C NMR spectrum of (*E*)-5-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-6a,7,8,9,10,10a-hexahydro-7,10-methanophenanthridin-6(5*H*)-one (**50c**) (100 MHz, CDCl_3 , 25 °C)



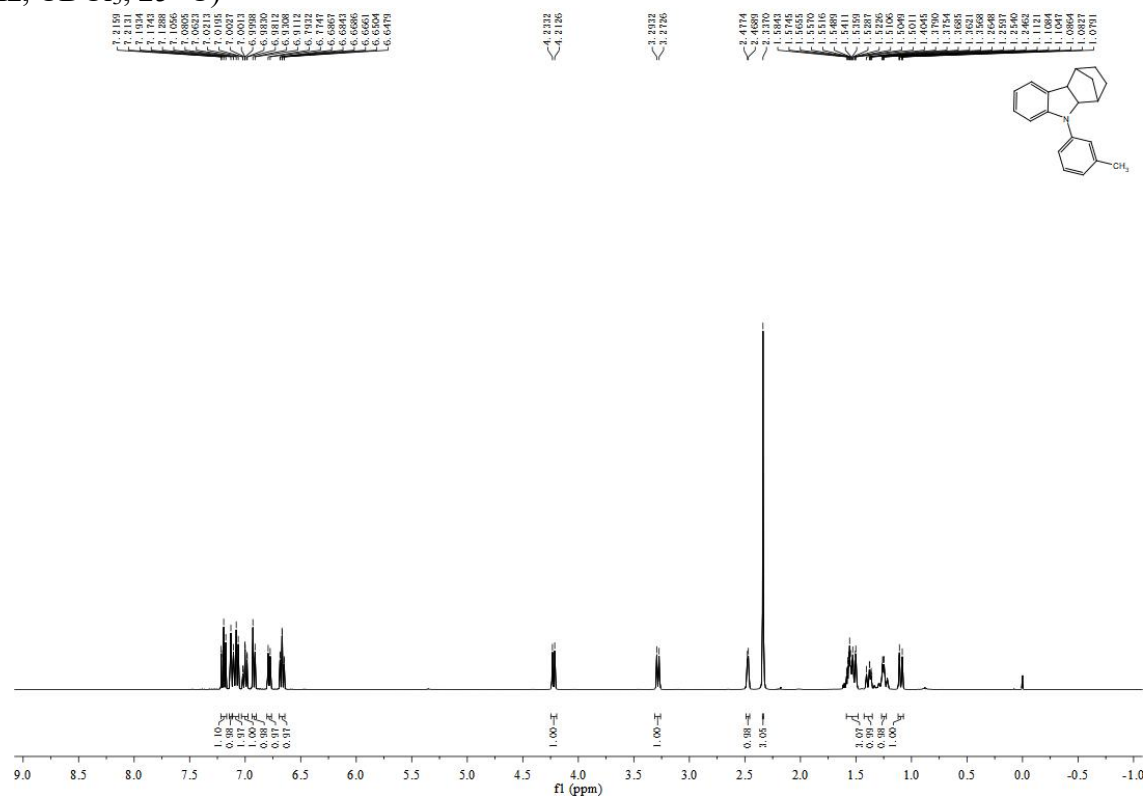
¹H NMR spectrum of 9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**1d**) (400 MHz, CDCl₃, 25 °C)



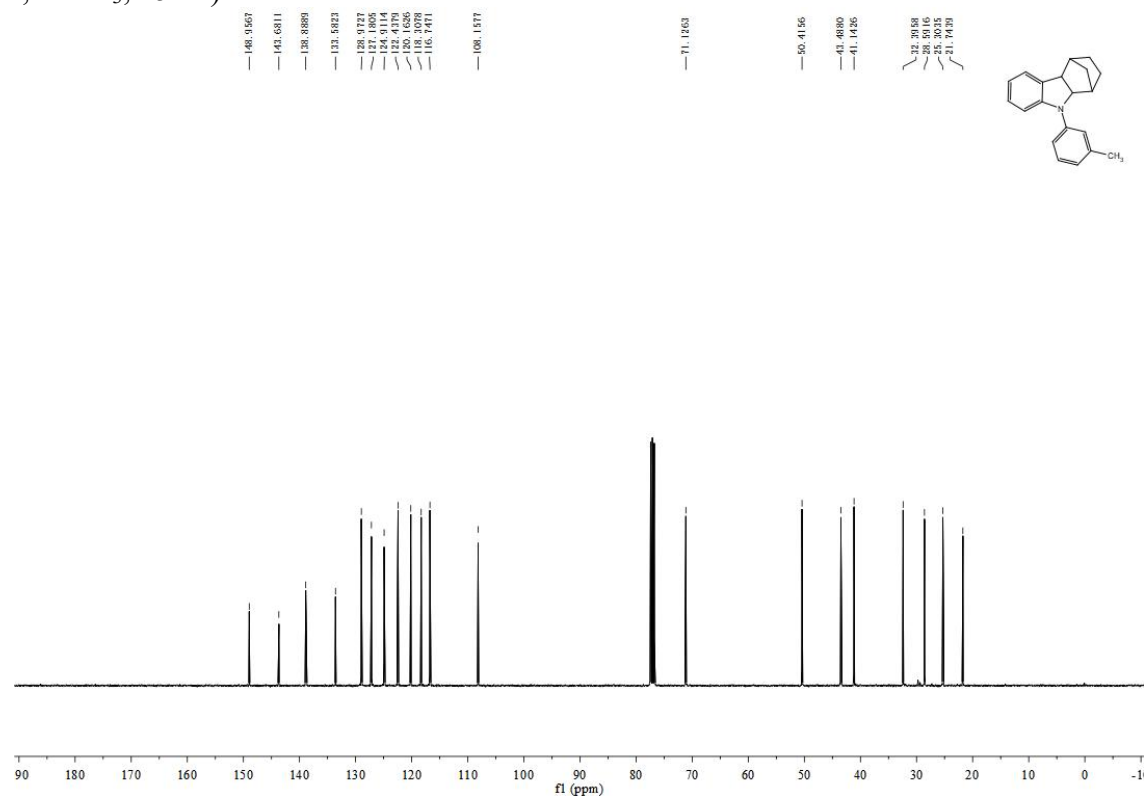
¹³C NMR spectrum of 9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**1d**) (100 MHz, CDCl₃, 25 °C)



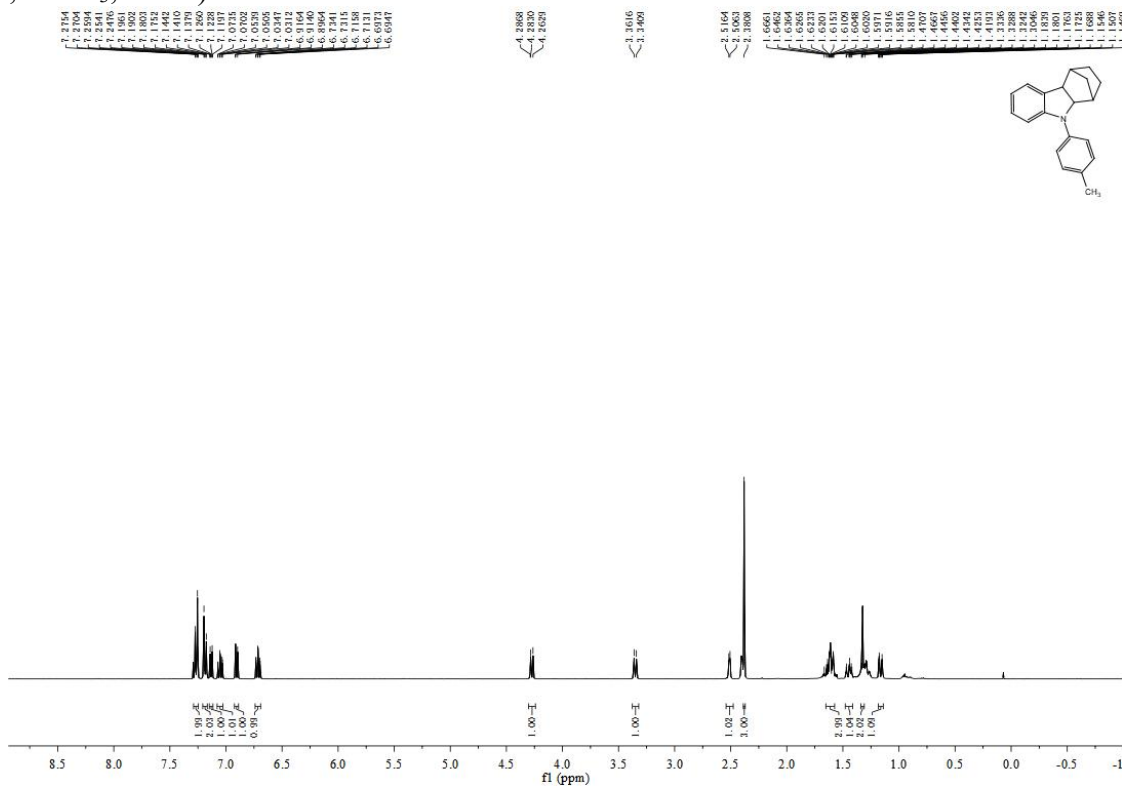
^1H NMR spectrum of 9-(*m*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**2d**) (400 MHz, CDCl_3 , 25 °C)



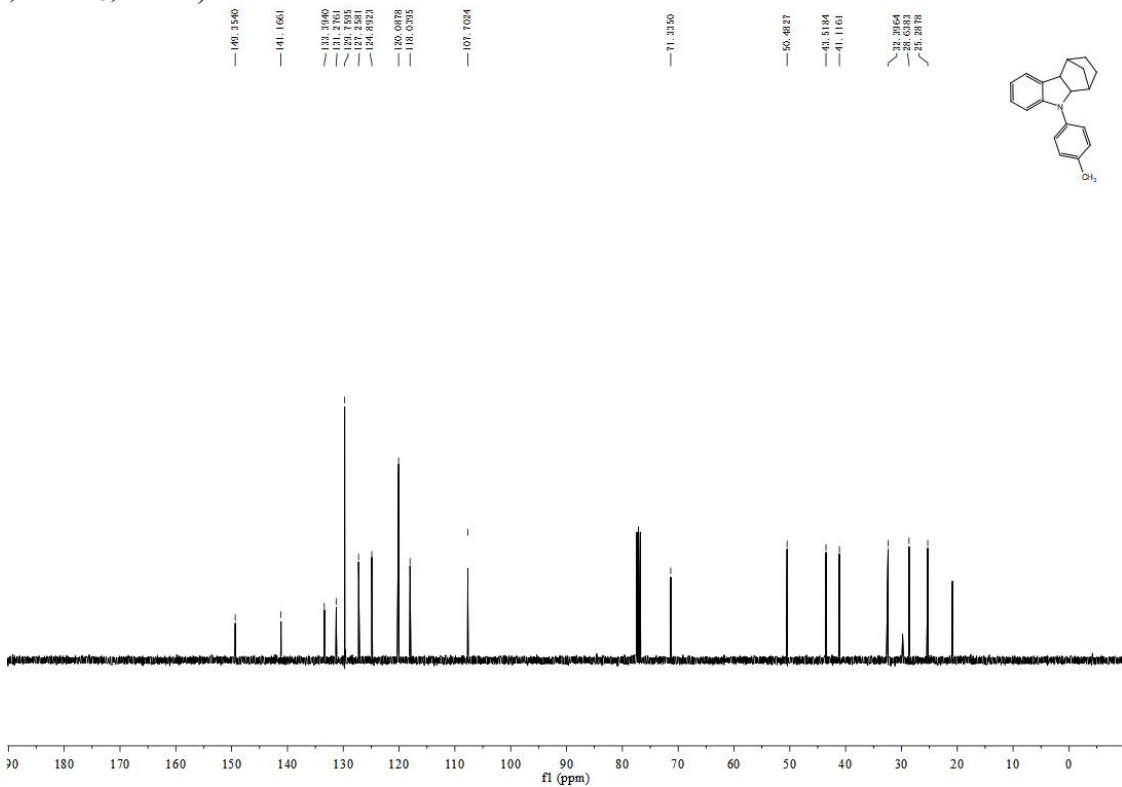
^{13}C NMR spectrum of 9-(*m*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**2d**) (100 MHz, CDCl_3 , 25 °C)



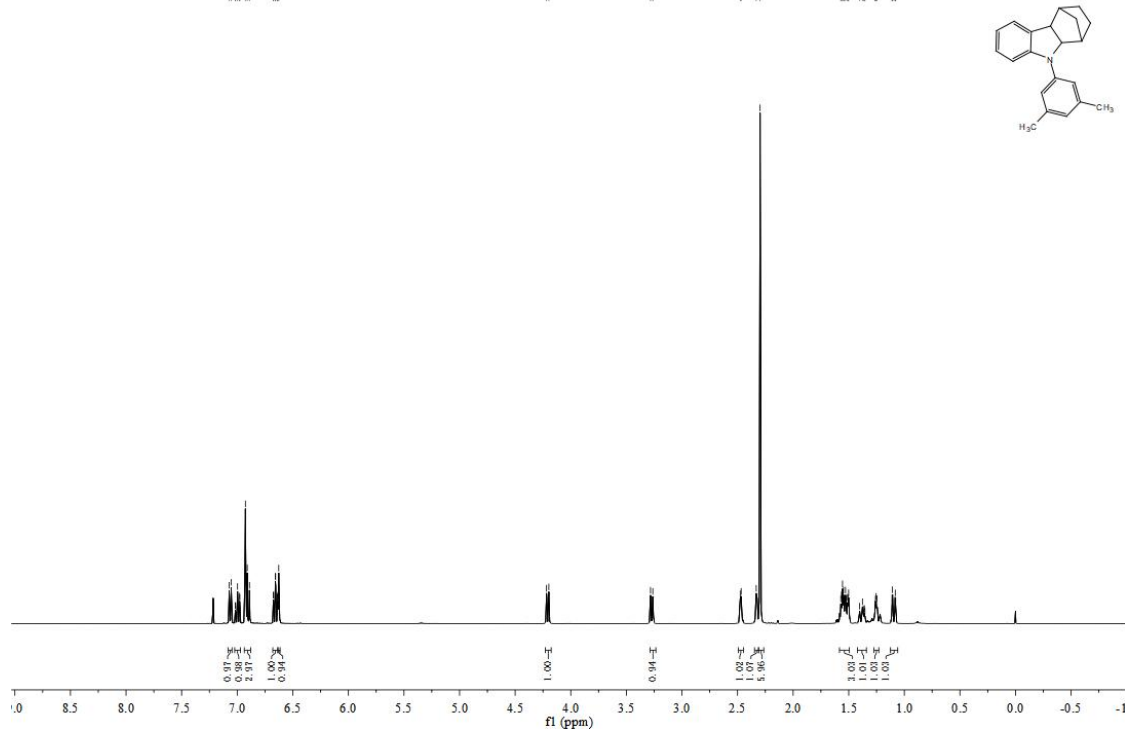
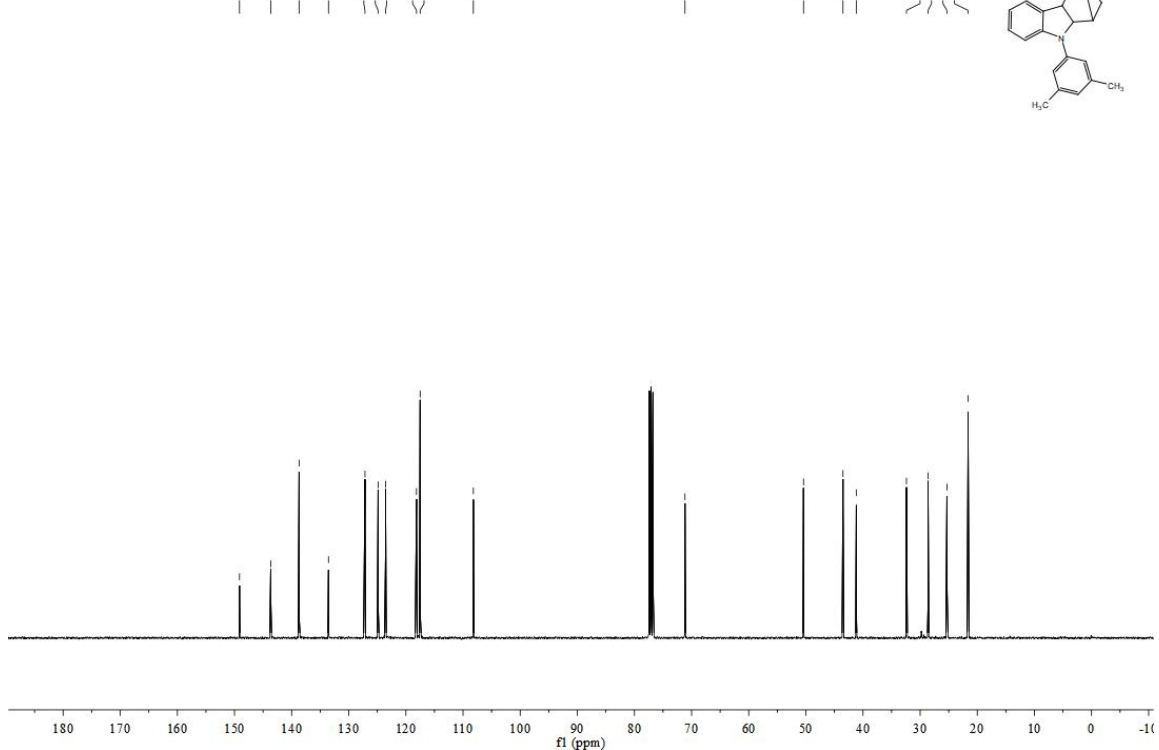
¹H NMR spectrum of 9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3d**) (400 MHz, CDCl₃, 25 °C)



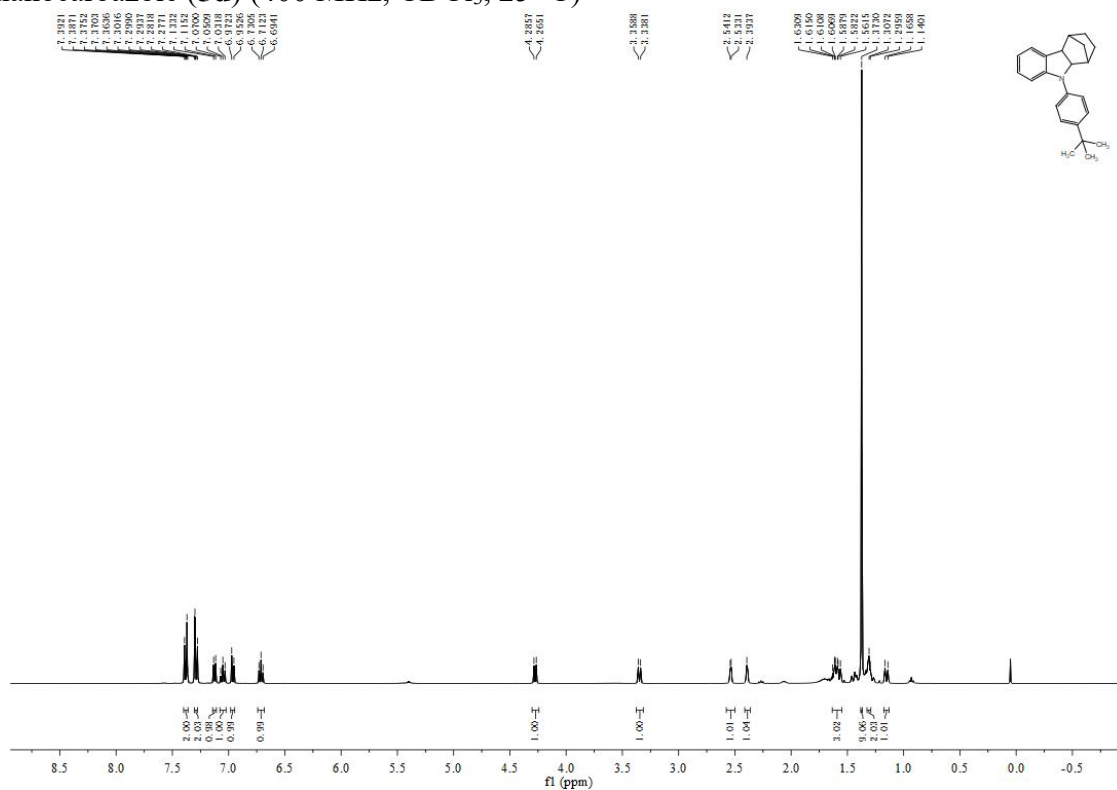
¹³C NMR spectrum of 9-(*p*-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3d**) (100 MHz, CDCl₃, 25 °C)



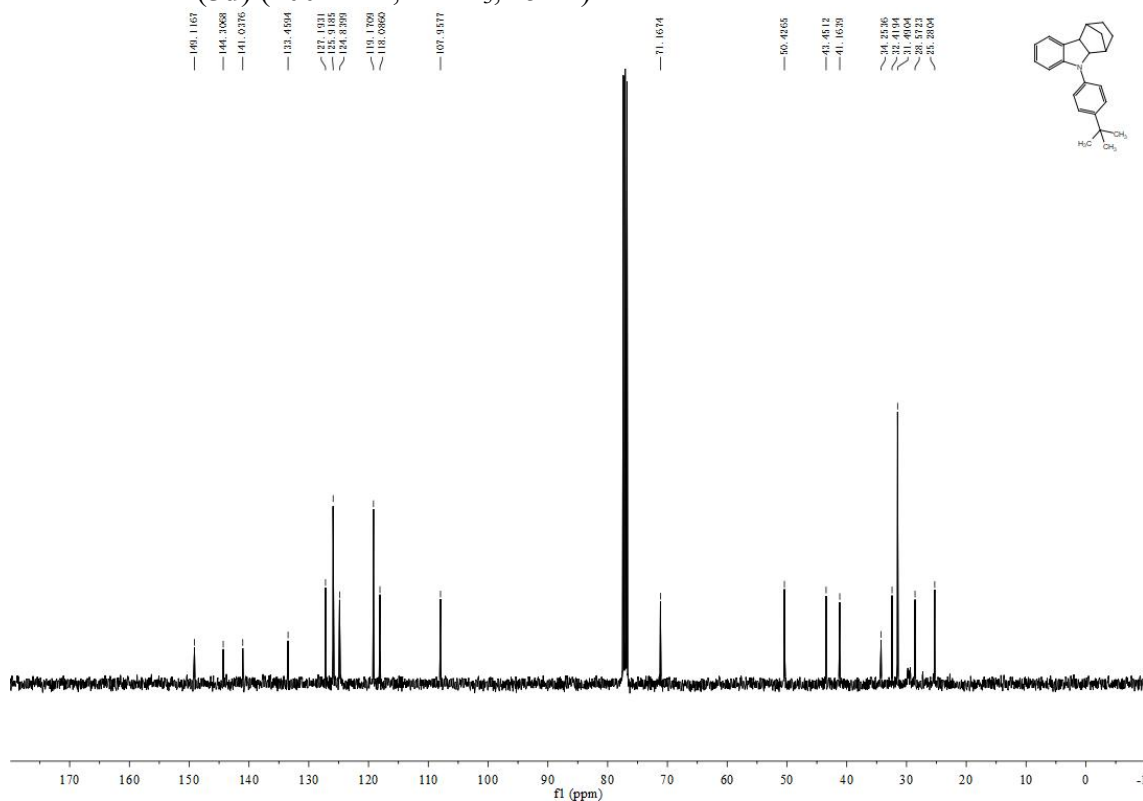
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[illegible]

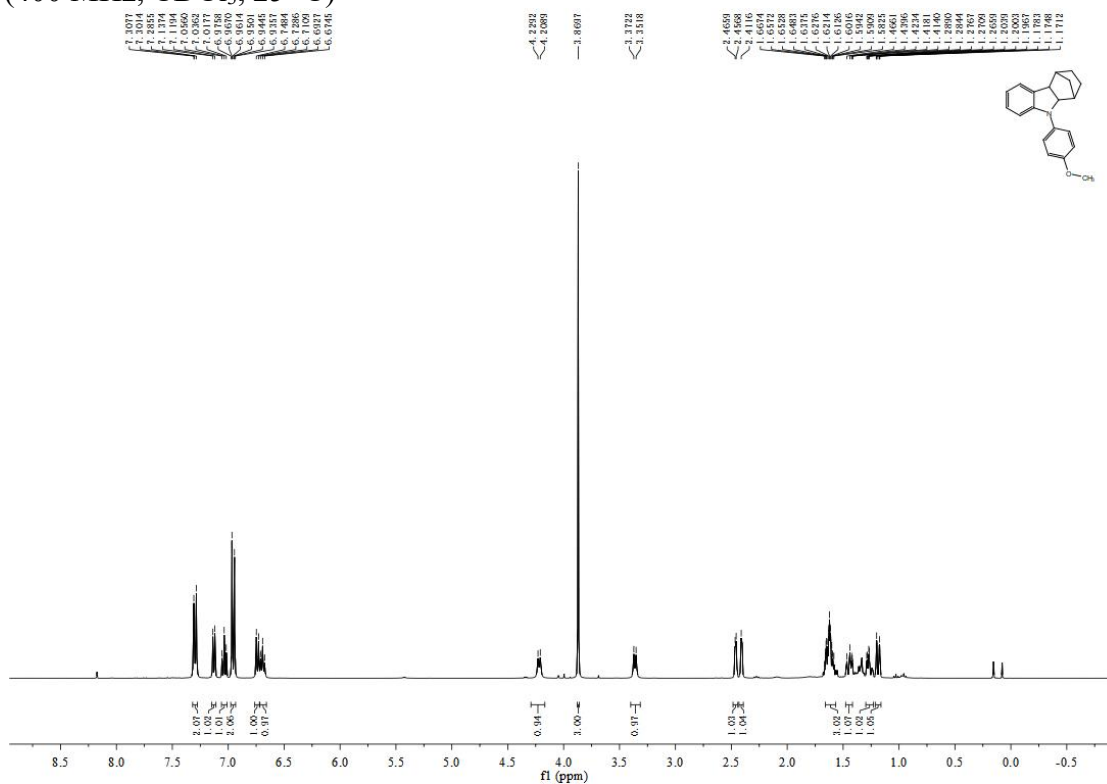
^1H NMR spectrum of 9-(4-(*tert*-butyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**5d**) (400 MHz, CDCl_3 , 25 °C)



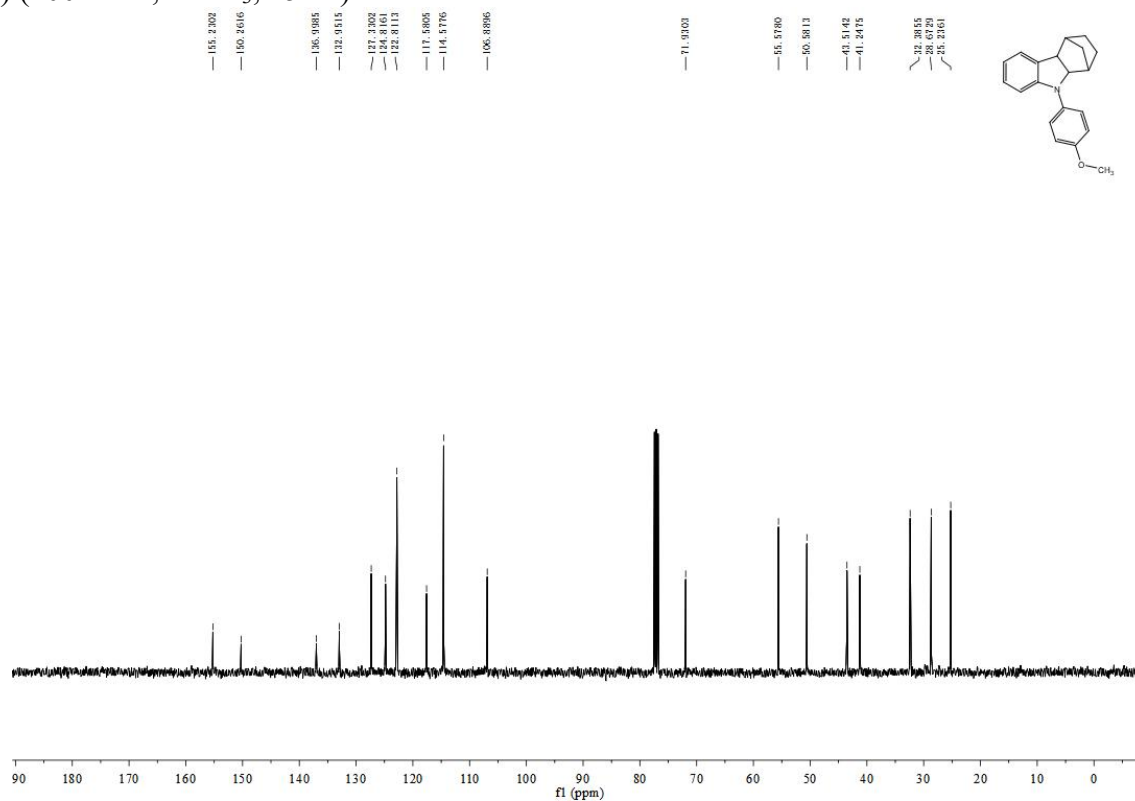
^{13}C NMR spectrum of 9-(4-(*tert*-butyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**5d**) (100 MHz, CDCl_3 , 25 °C)



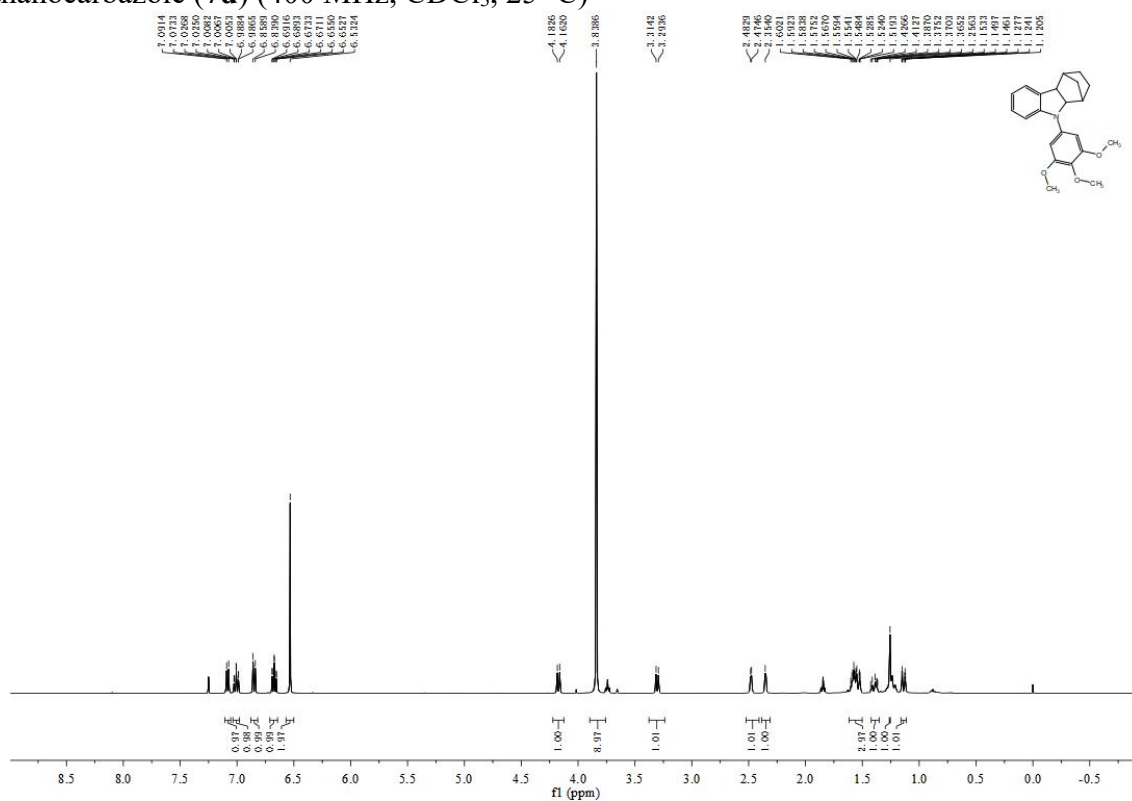
¹H NMR spectrum of 9-(4-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**6d**) (400 MHz, CDCl₃, 25 °C)



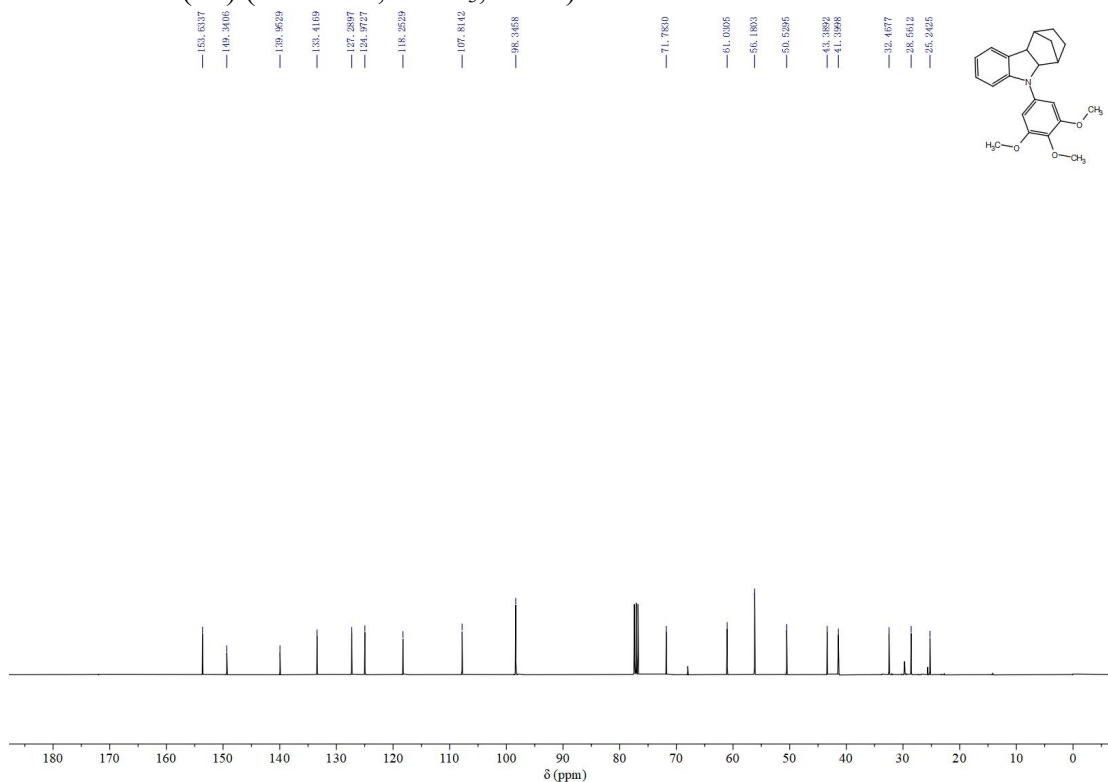
¹³C NMR spectrum of 9-(4-methoxyphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**6d**) (100 MHz, CDCl₃, 25 °C)



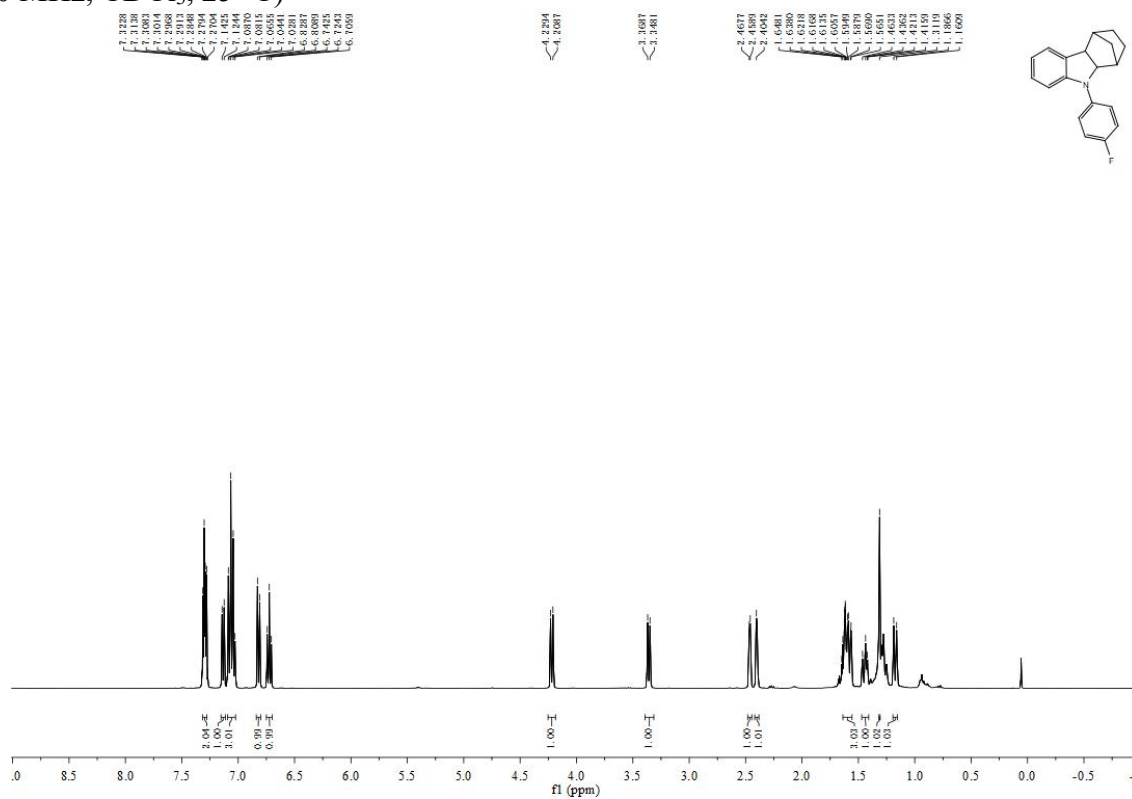
^1H NMR spectrum of 10-(3,4,5-trimethoxyphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**7d**) (400 MHz, CDCl_3 , 25 °C)



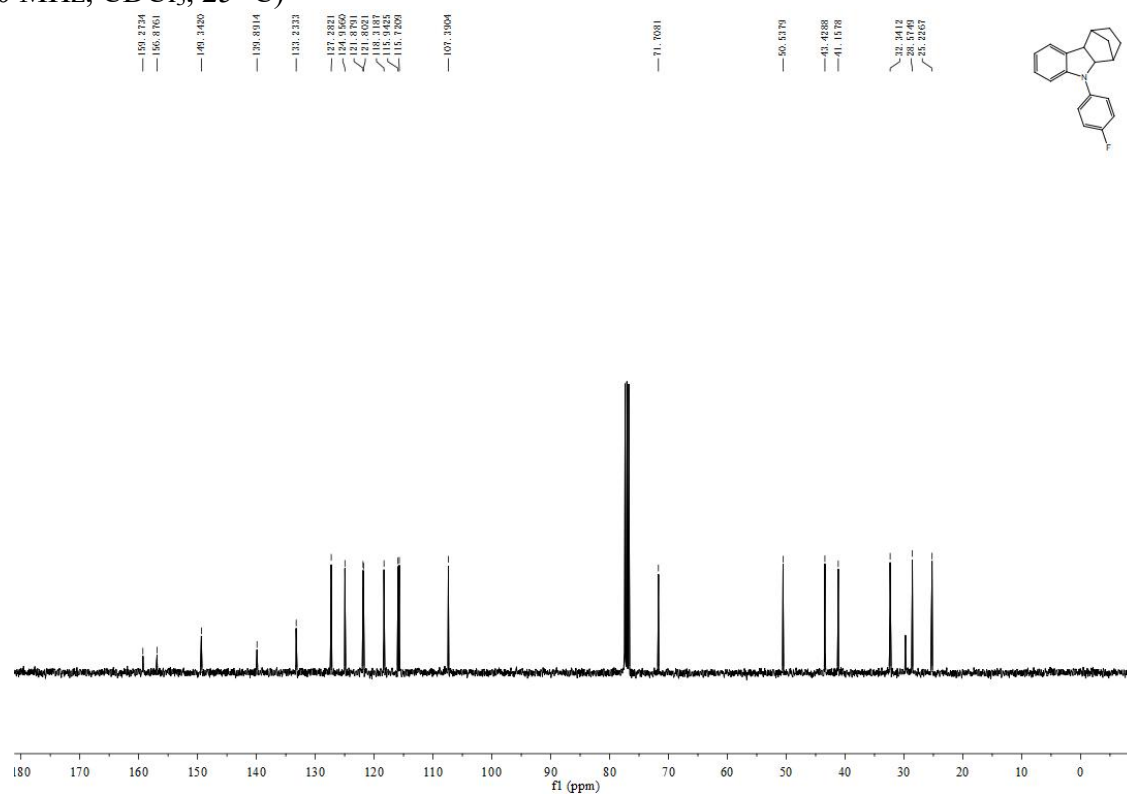
^{13}C NMR spectrum of 10-(3,4,5-trimethoxyphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**7d**) (100 MHz, CDCl_3 , 25 °C)

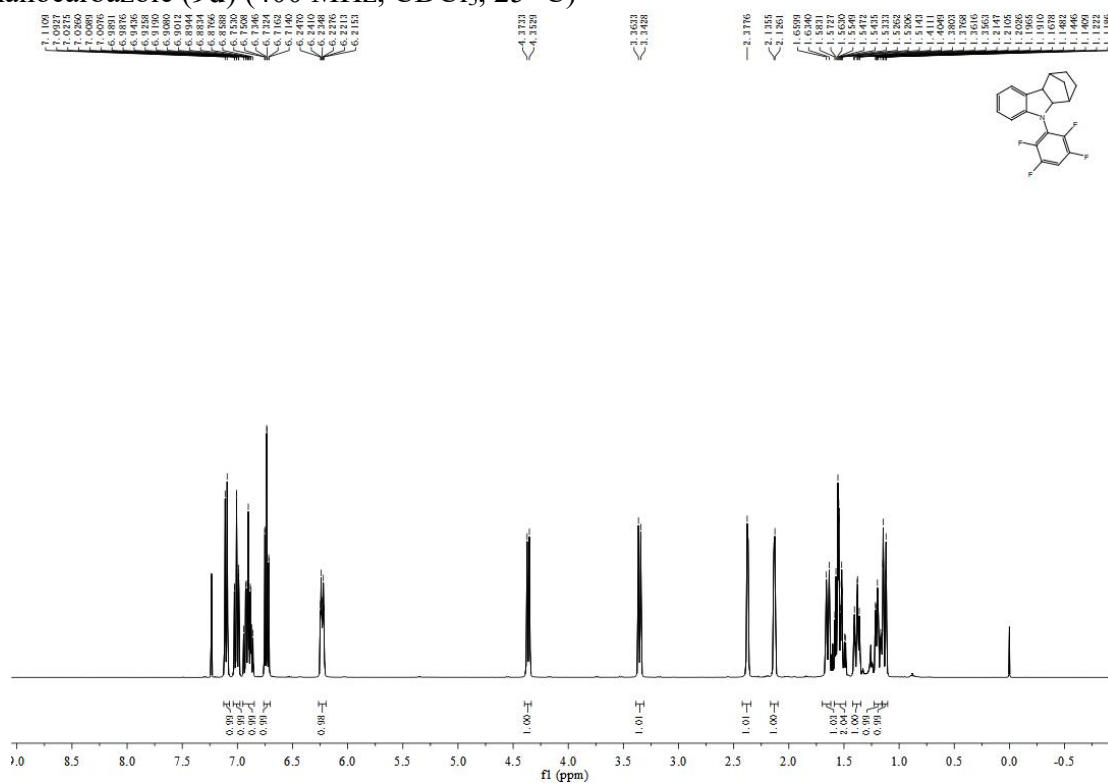
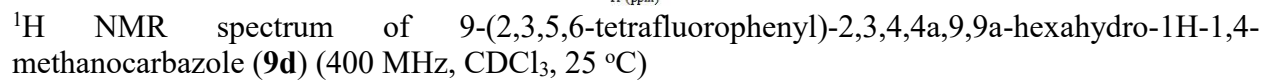


^1H NMR spectrum of 9-(4-fluorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**8d**) (400 MHz, CDCl_3 , 25 °C)

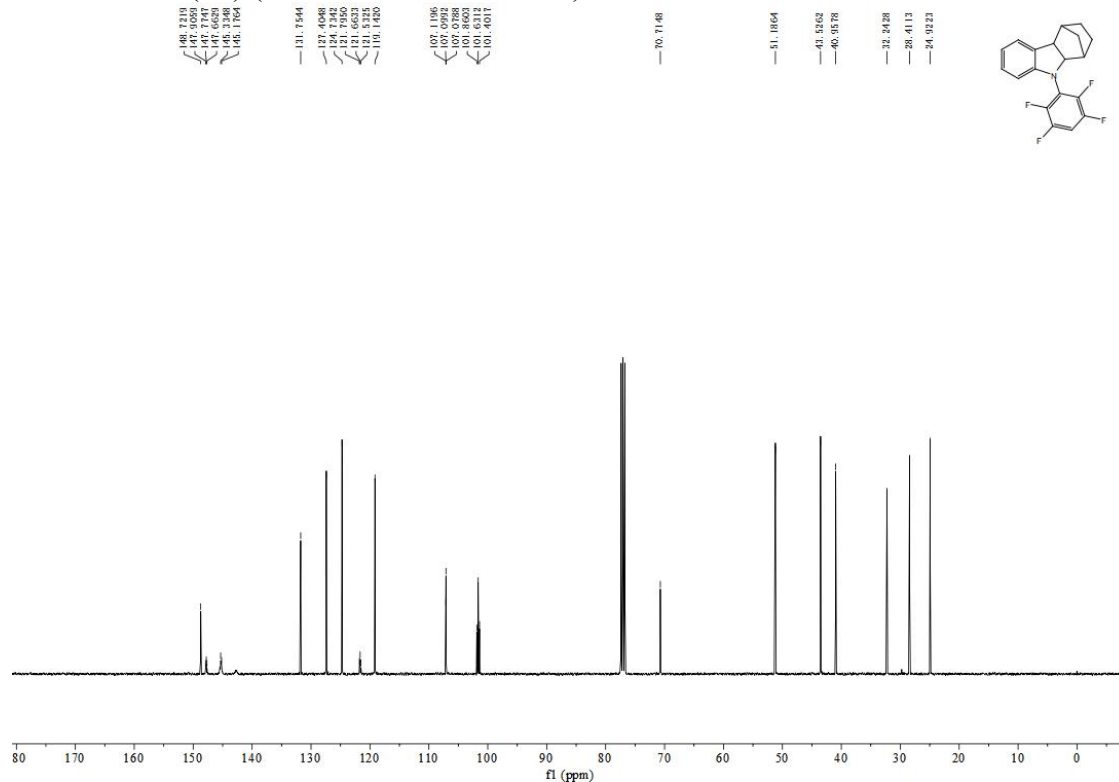


^{13}C NMR spectrum of 9-(4-fluorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**8d**) (100 MHz, CDCl_3 , 25 °C)

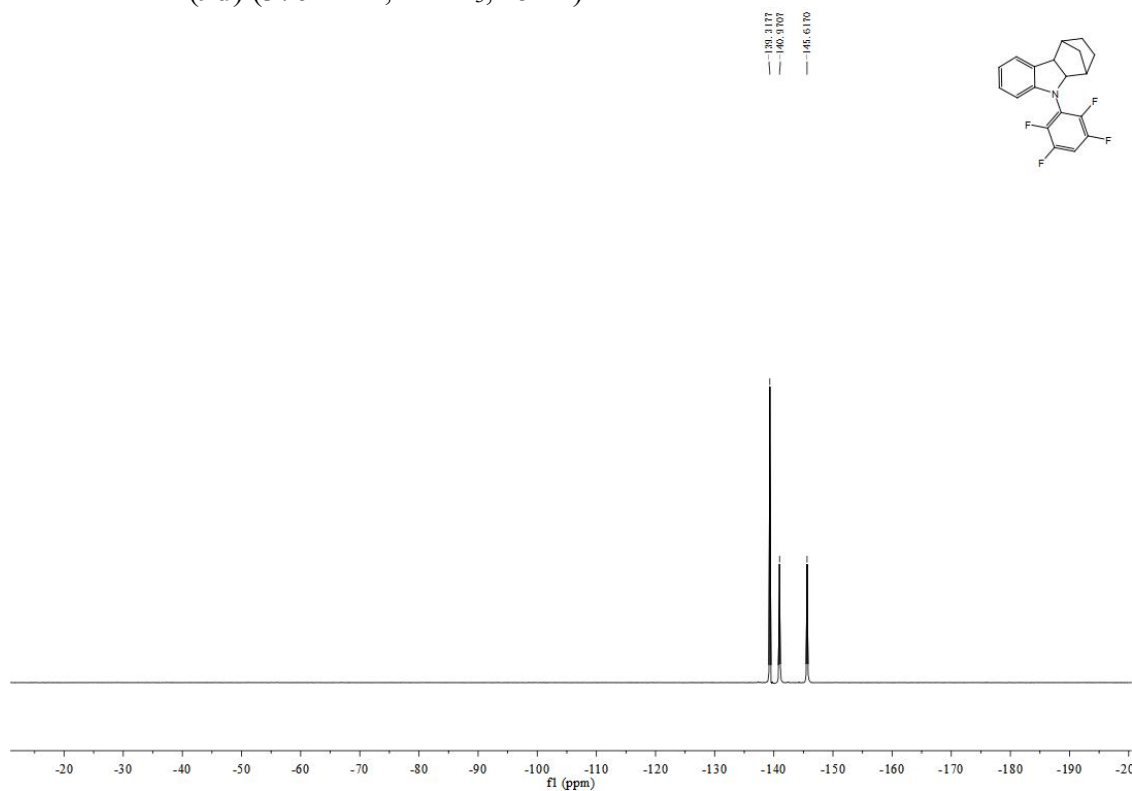


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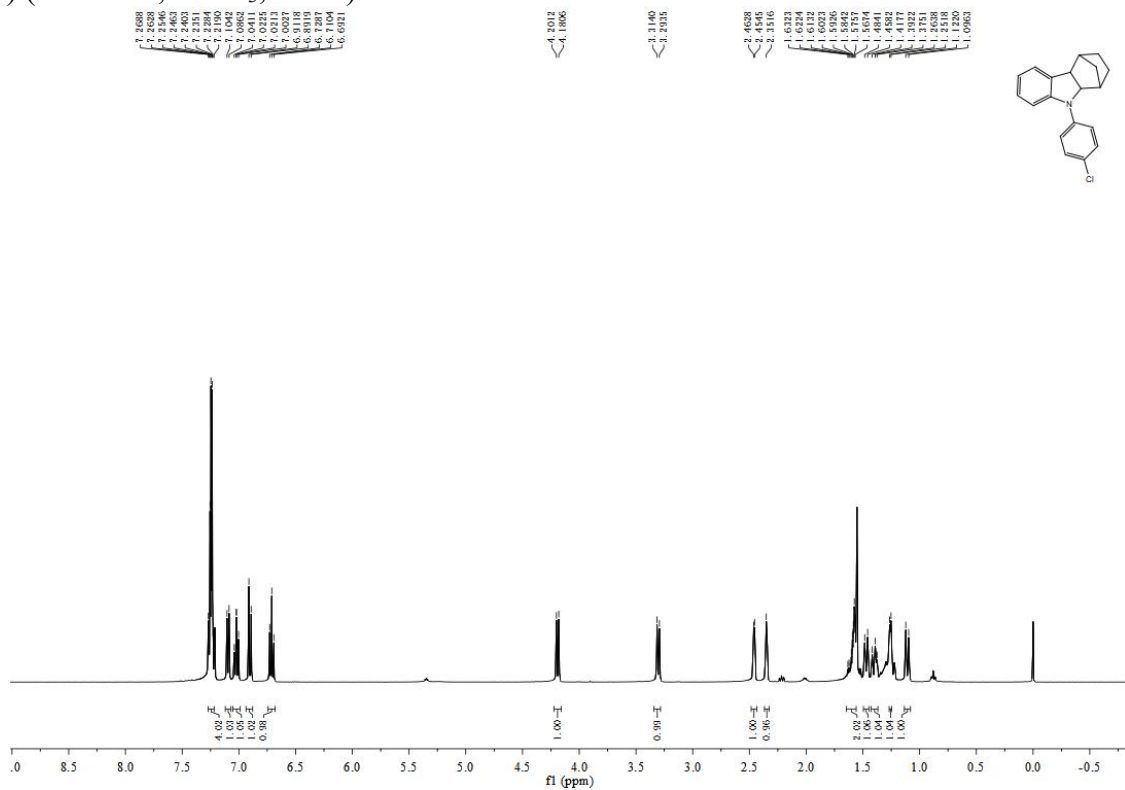
^{13}C NMR spectrum of 9-(2,3,5,6-tetrafluorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**9d**) (100 MHz, CDCl_3 , 25 °C)



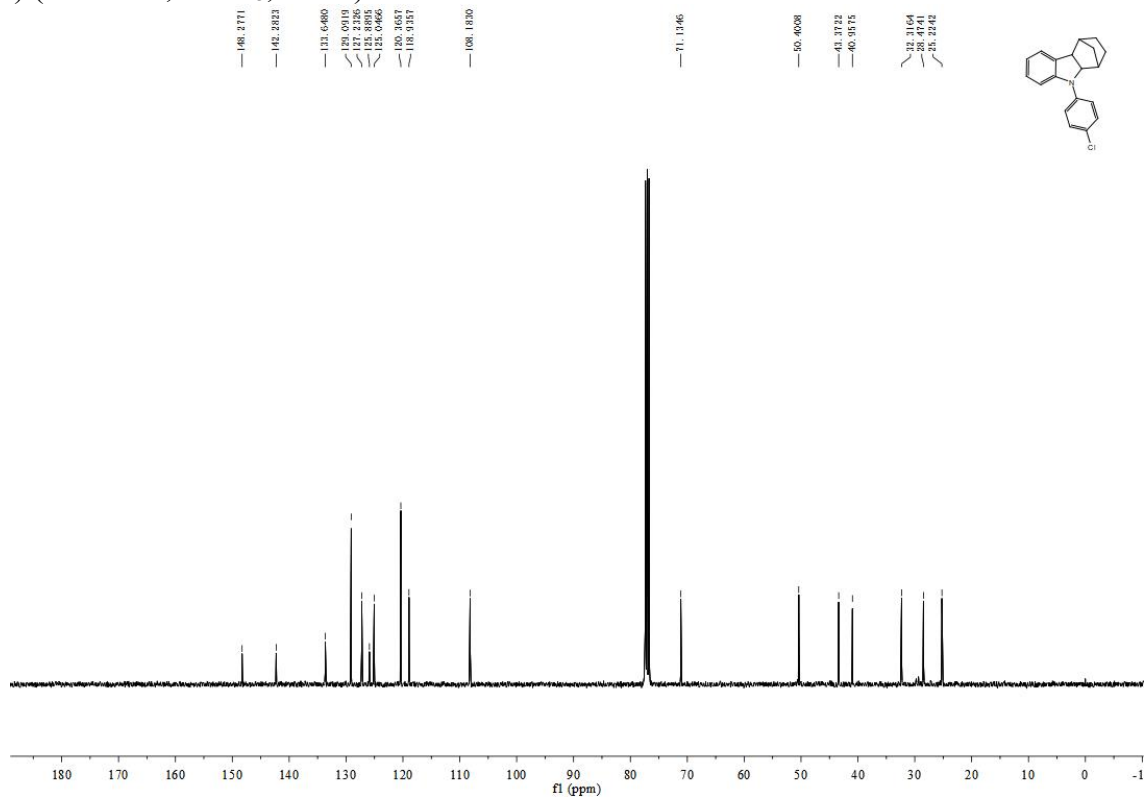
^{19}F NMR spectrum of 9-(2,3,5,6-tetrafluorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**9d**) (376 MHz, CDCl_3 , 25 °C)



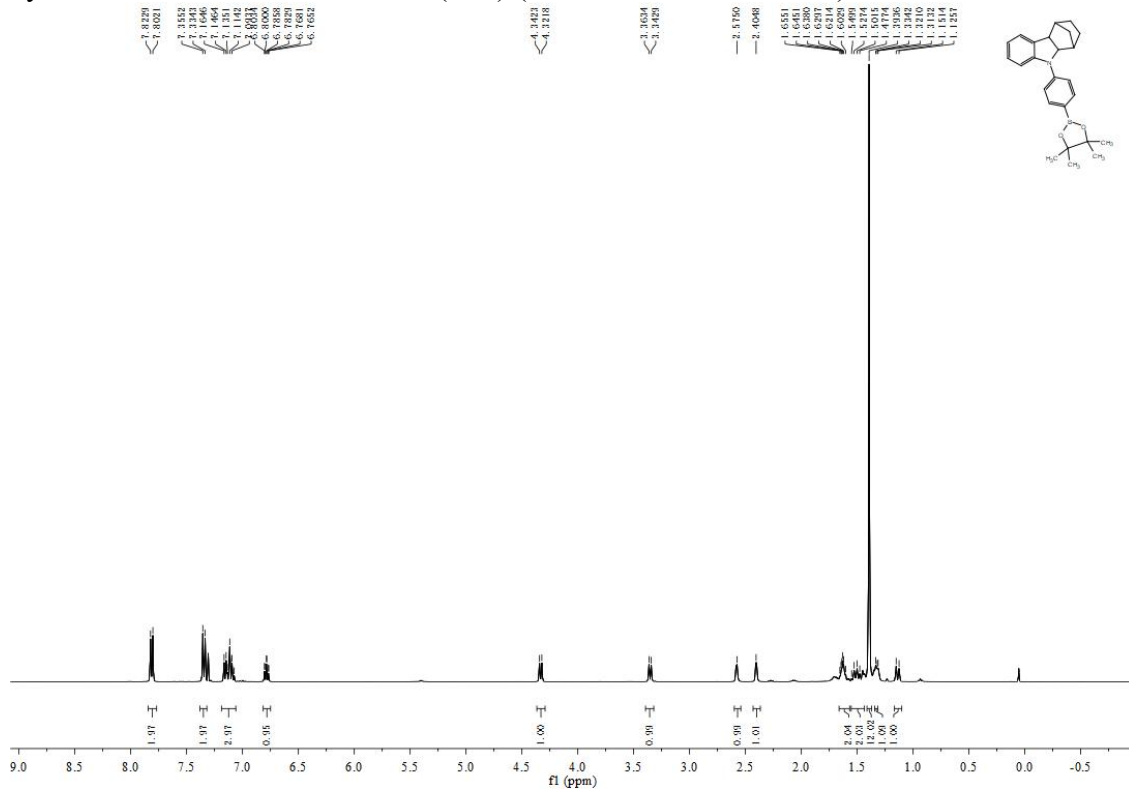
¹H NMR spectrum of 9-(4-chlorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**10d**) (400 MHz, CDCl₃, 25 °C)



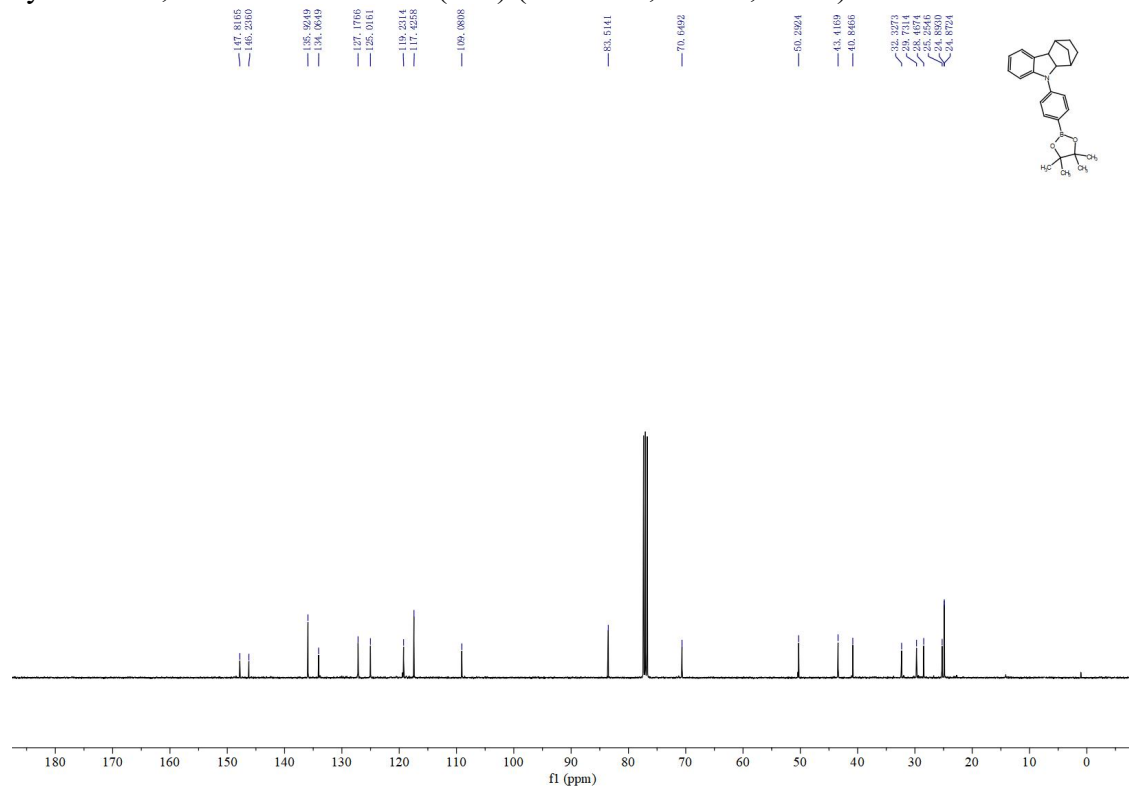
¹³C NMR spectrum of 9-(4-chlorophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**10d**) (100 MHz, CDCl₃, 25 °C)



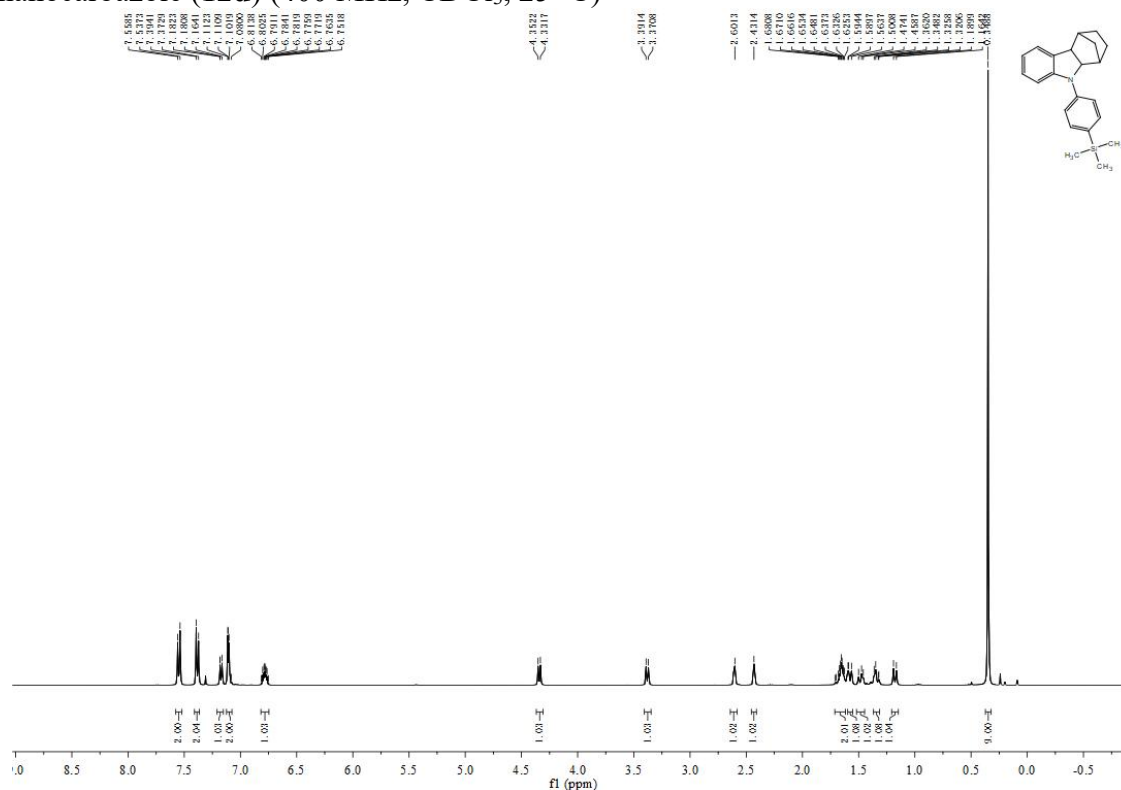
¹H NMR spectrum of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**11d**) (400 MHz, CDCl₃, 25 °C)



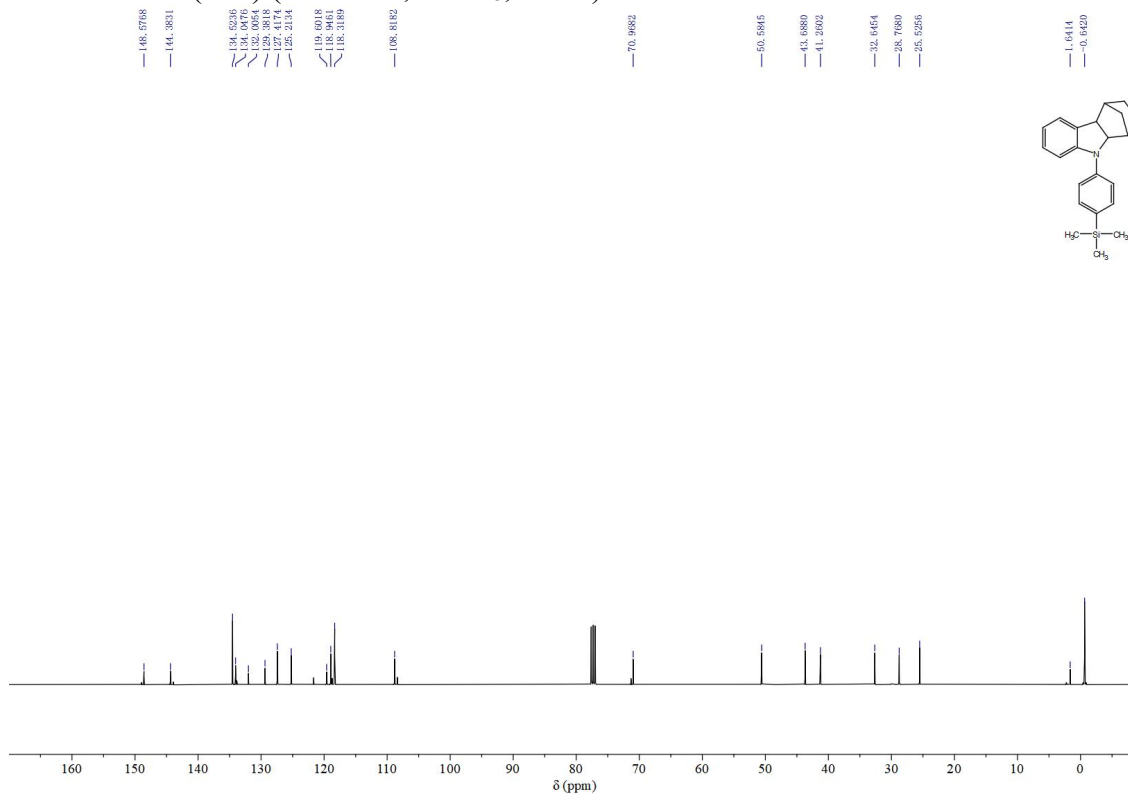
¹³C NMR spectrum of 10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**11d**) (100 MHz, CDCl₃, 25 °C)



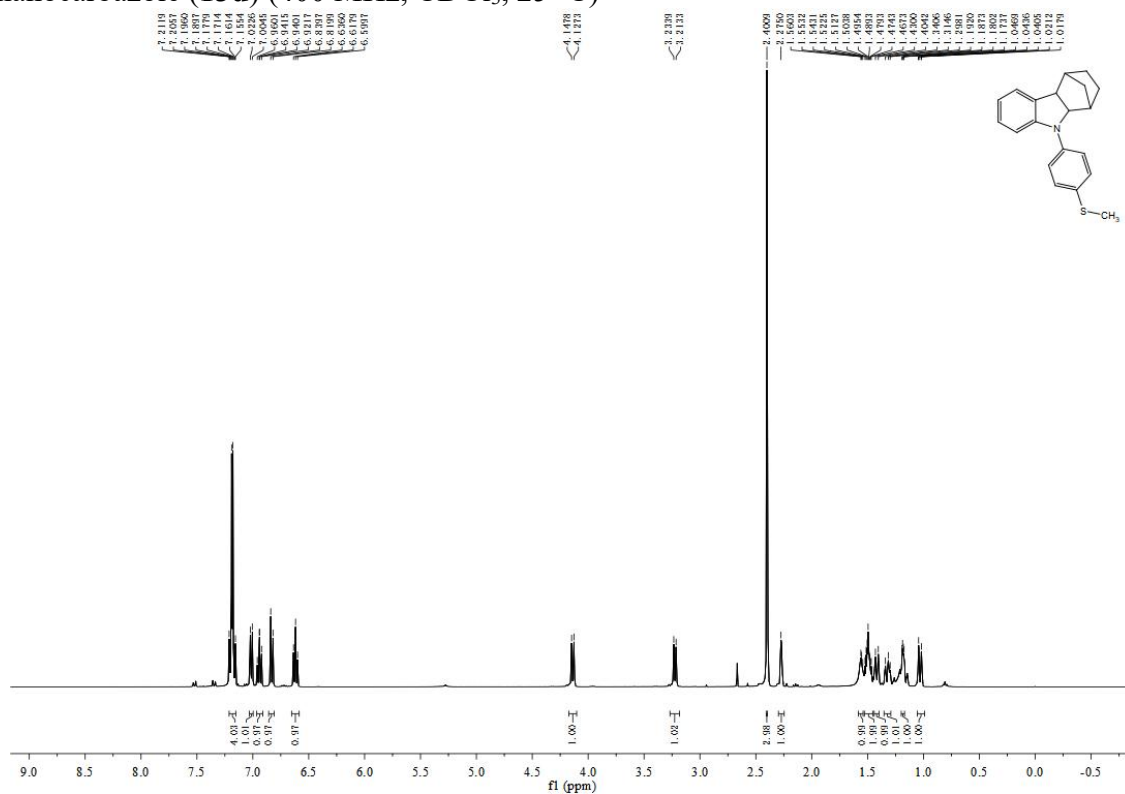
^1H NMR spectrum of 9-(4-(trimethylsilyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**12d**) (400 MHz, CDCl_3 , 25 °C)



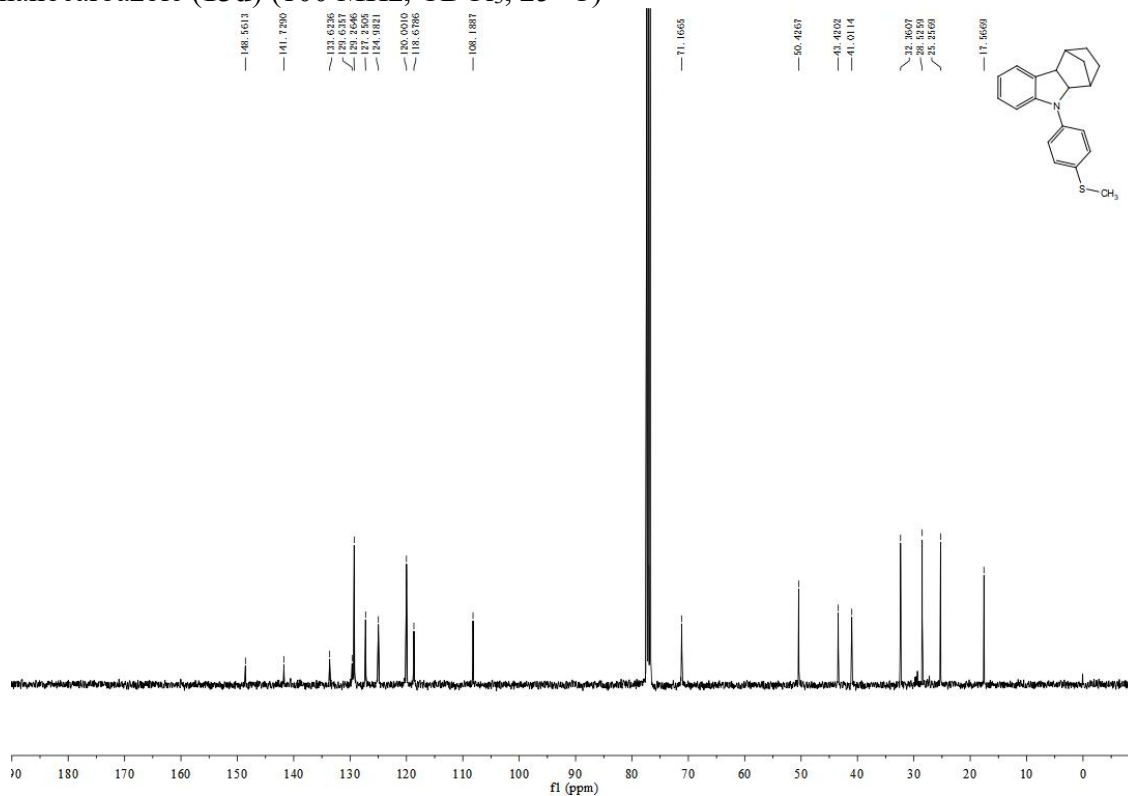
^{13}C NMR spectrum of 9-(4-(trimethylsilyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**12d**) (100 MHz, CDCl_3 , 25 °C)



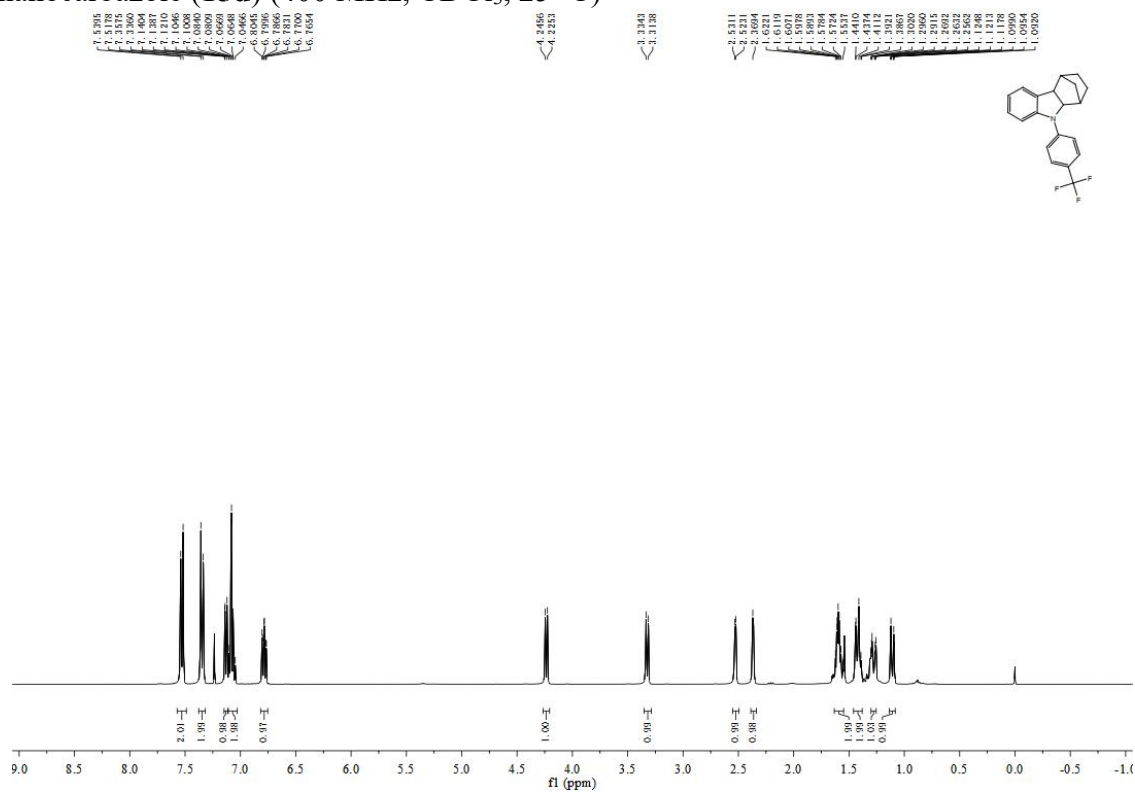
^1H NMR spectrum of 9-(4-(methylthio)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**13d**) (400 MHz, CDCl_3 , 25 °C)



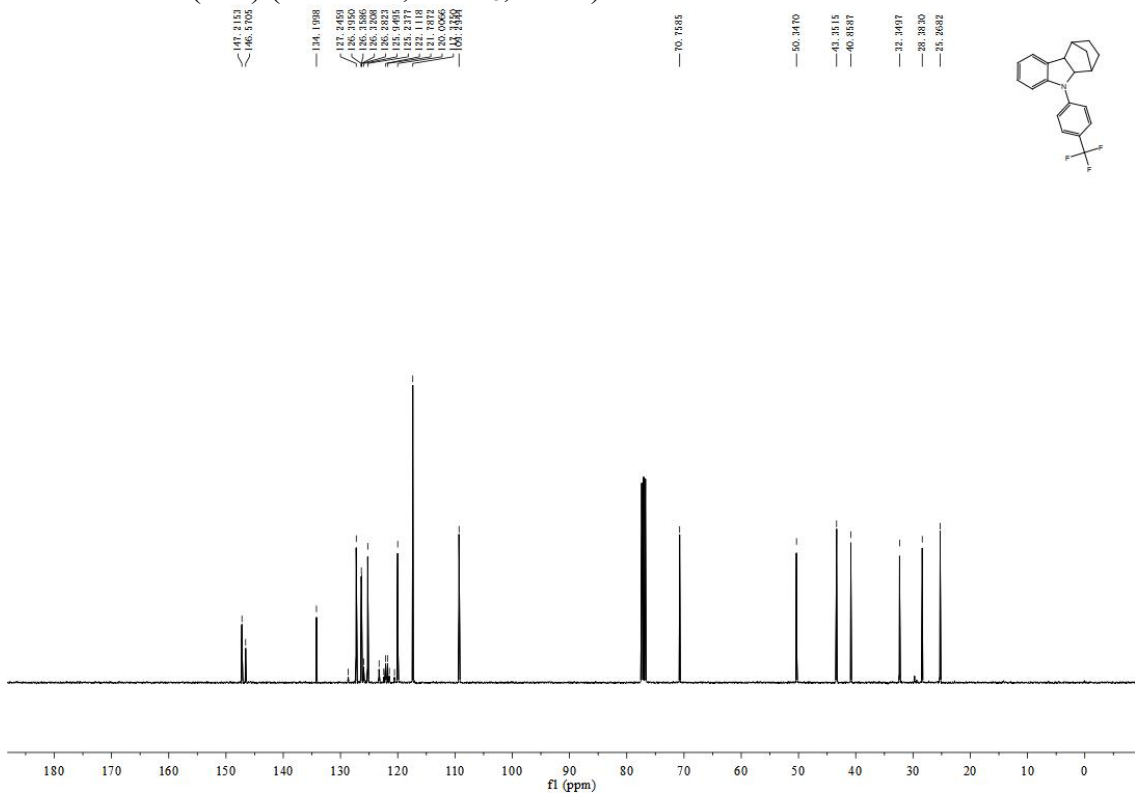
^{13}C NMR spectrum of 9-(4-(methylthio)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**13d**) (100 MHz, CDCl_3 , 25 °C)



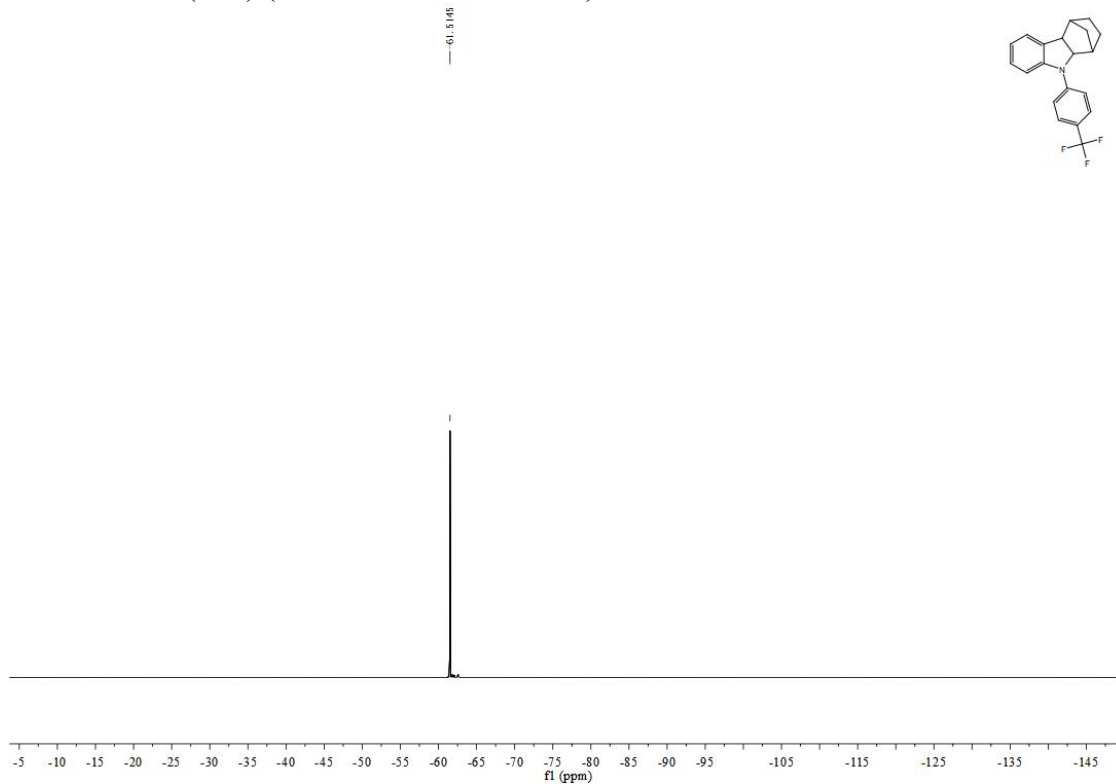
¹H NMR spectrum of 9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**15d**) (400 MHz, CDCl₃, 25 °C)



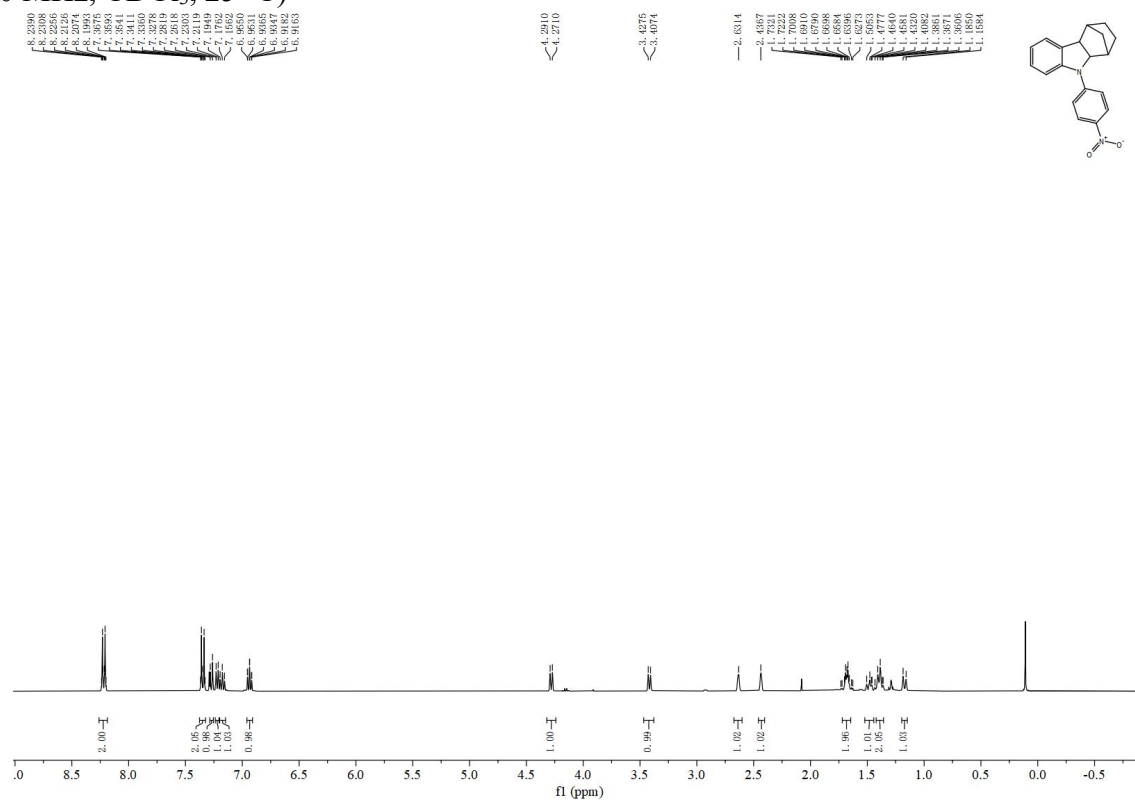
¹³C NMR spectrum of 9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**15d**) (100 MHz, CDCl₃, 25 °C)



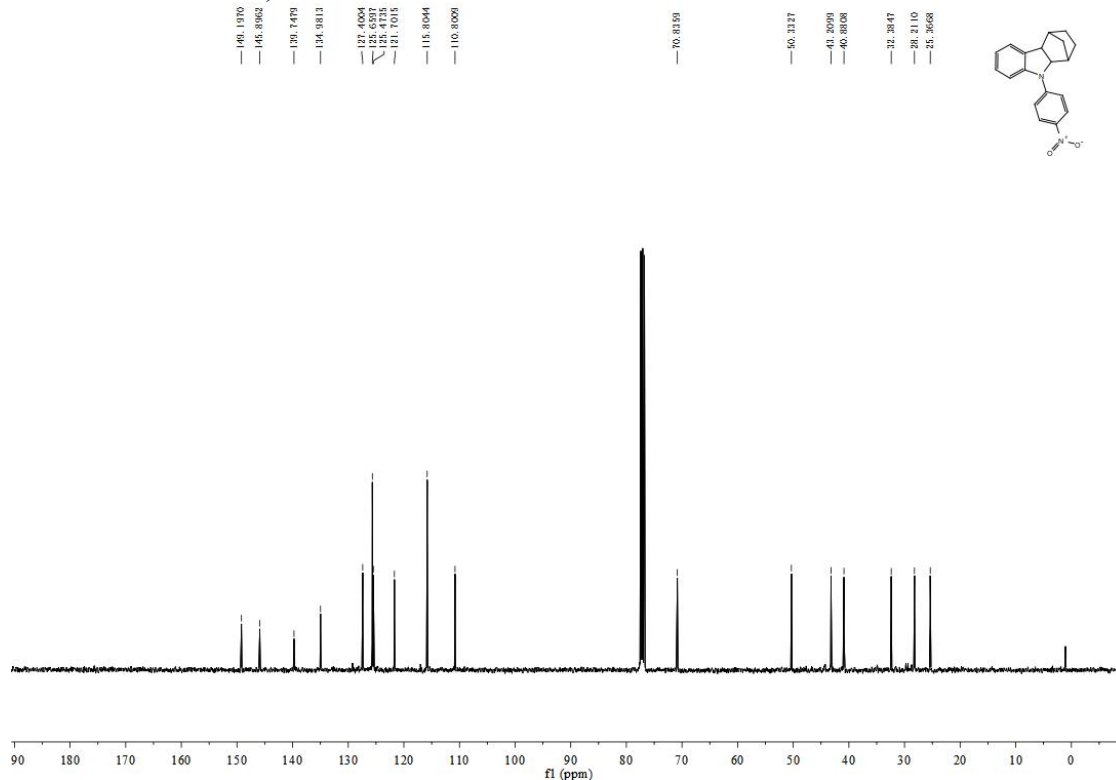
^{19}F NMR spectrum of 9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**15d**) (376 MHz, CDCl_3 , 25 °C)



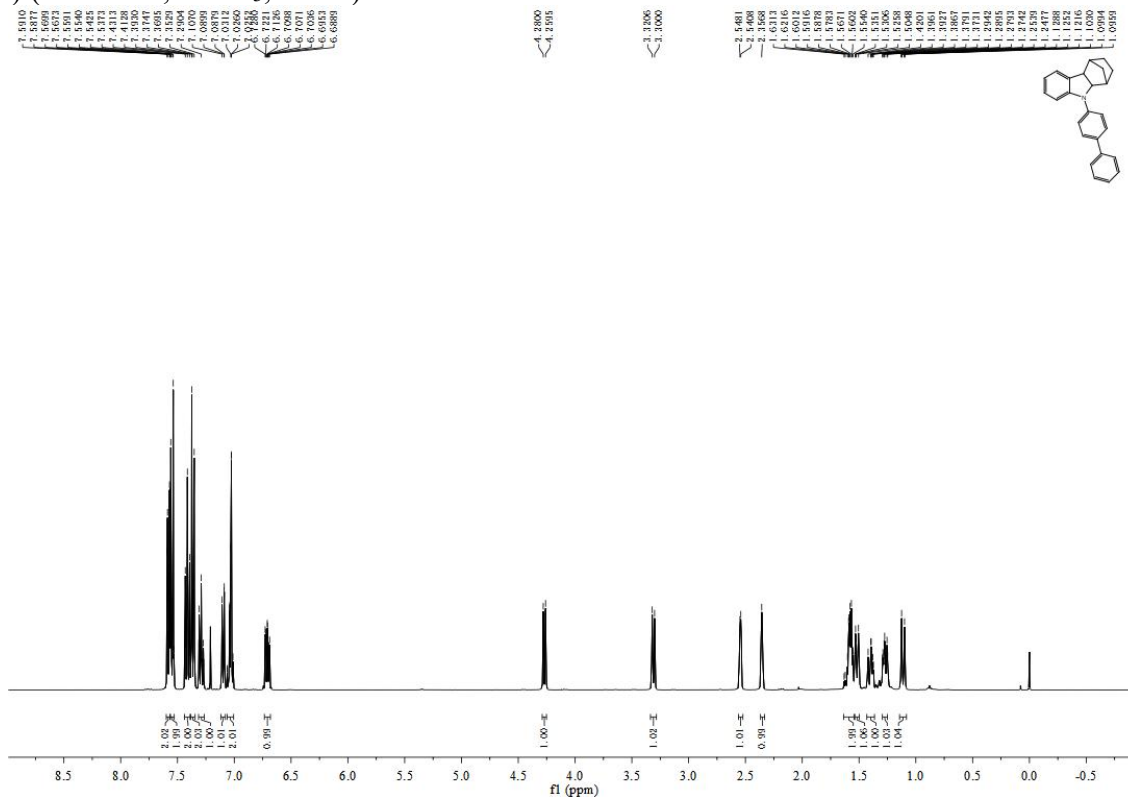
^1H NMR spectrum of 9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**16d**) (400 MHz, CDCl_3 , 25 °C)



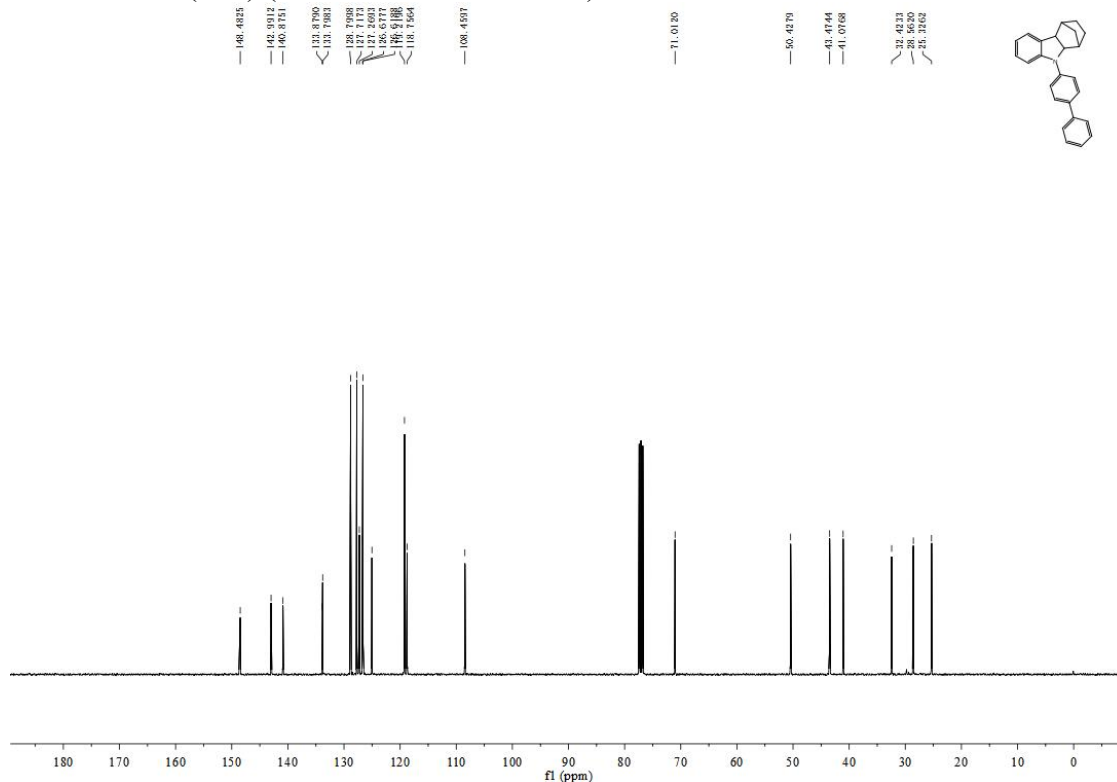
^{13}C NMR spectrum of 9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**16d**) (100 MHz, CDCl_3 , 25 °C)



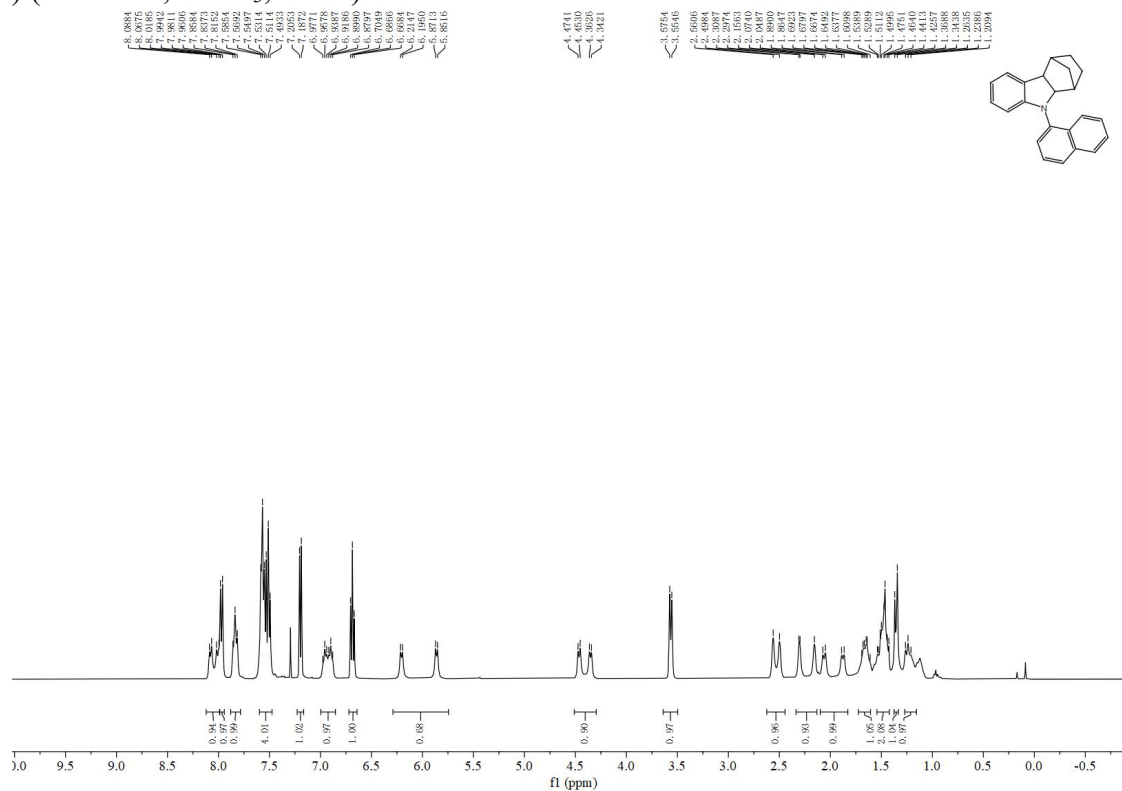
^1H NMR spectrum of 9-([1,1'-biphenyl]-4-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**17d**) (400 MHz, CDCl_3 , 25 °C)



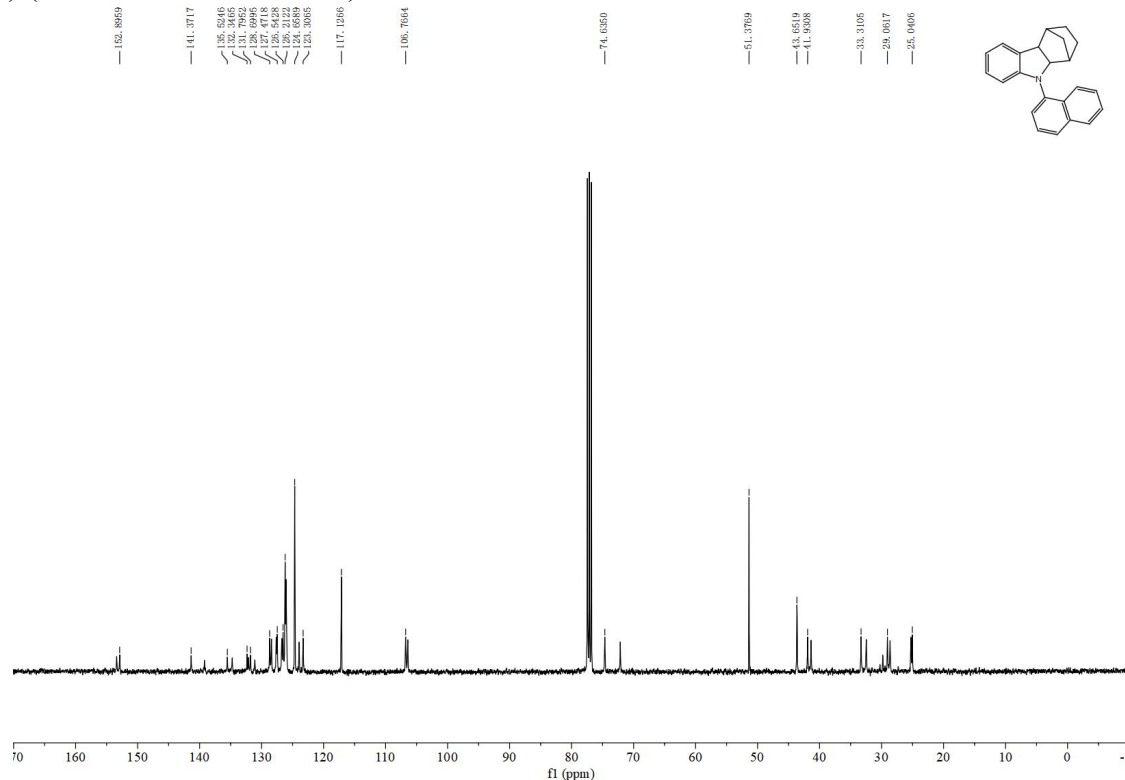
^{13}C NMR spectrum of 9-([1,1'-biphenyl]-4-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**17d**) (100 MHz, CDCl_3 , 25 °C)



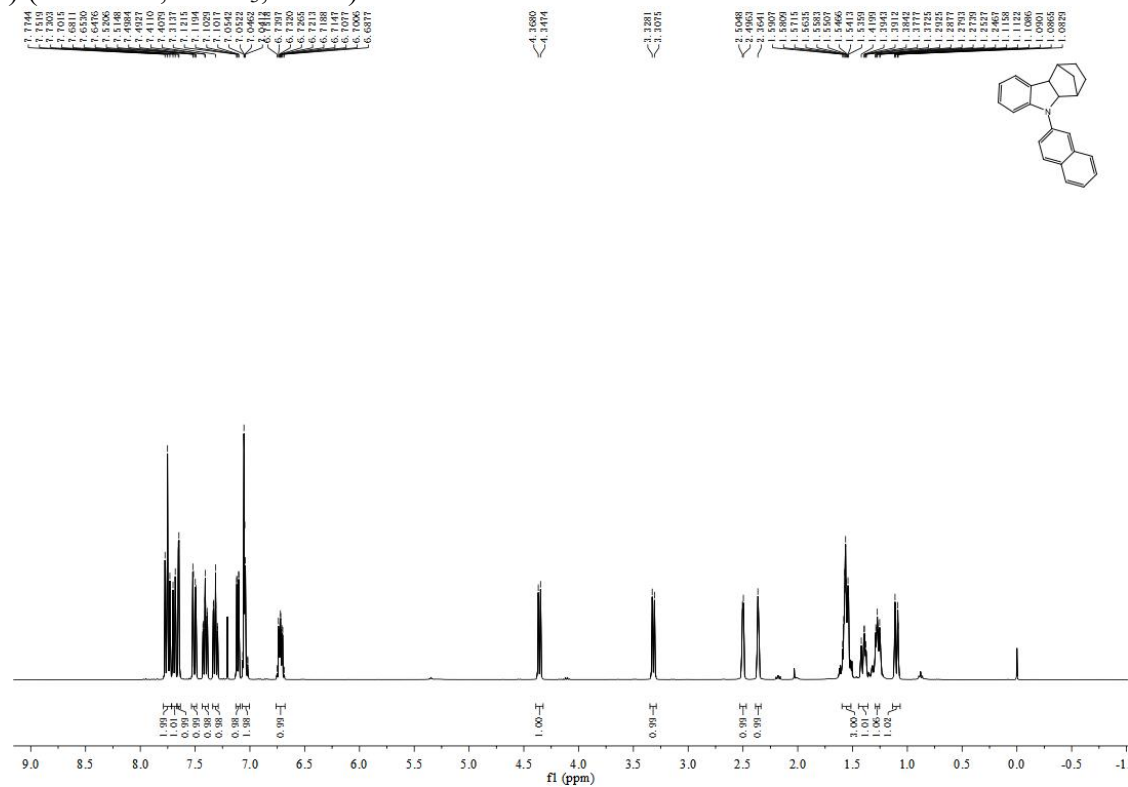
^1H NMR spectrum of 9-(naphthalen-1-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**18d**) (400 MHz, CDCl_3 , 25 °C)



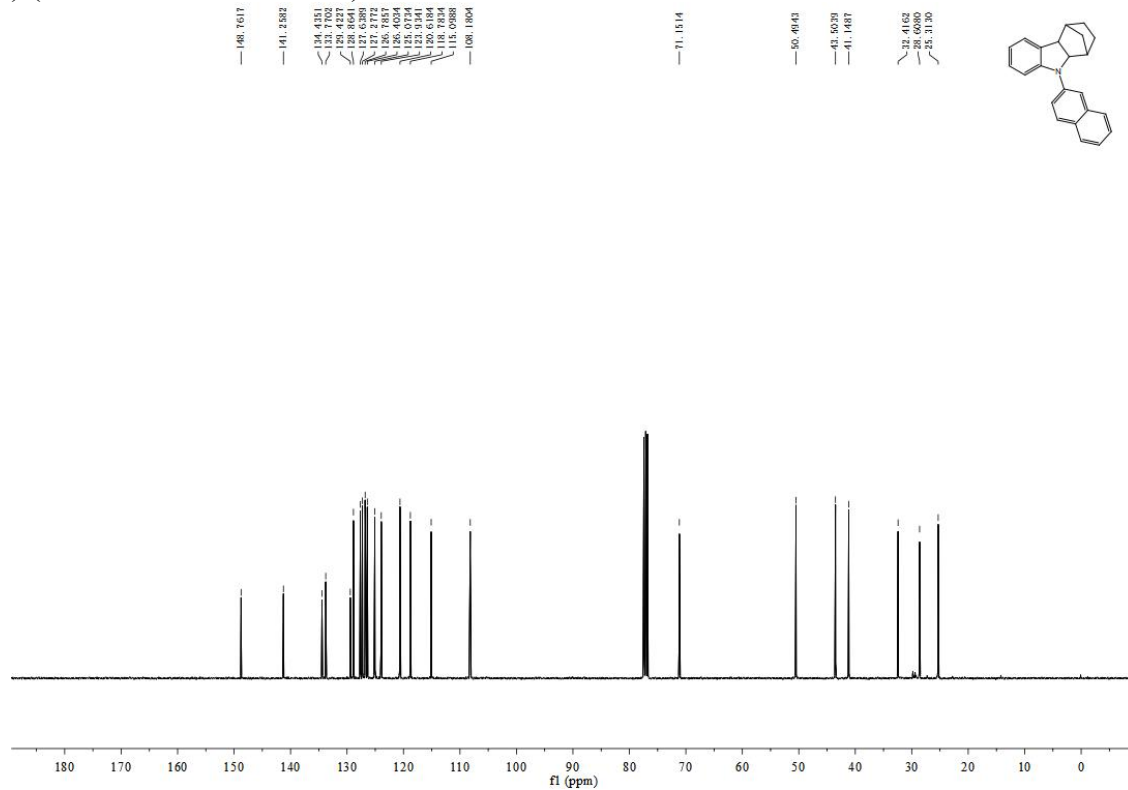
^{13}C NMR spectrum of 9-(naphthalen-1-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**18d**) (100 MHz, CDCl_3 , 25 °C)



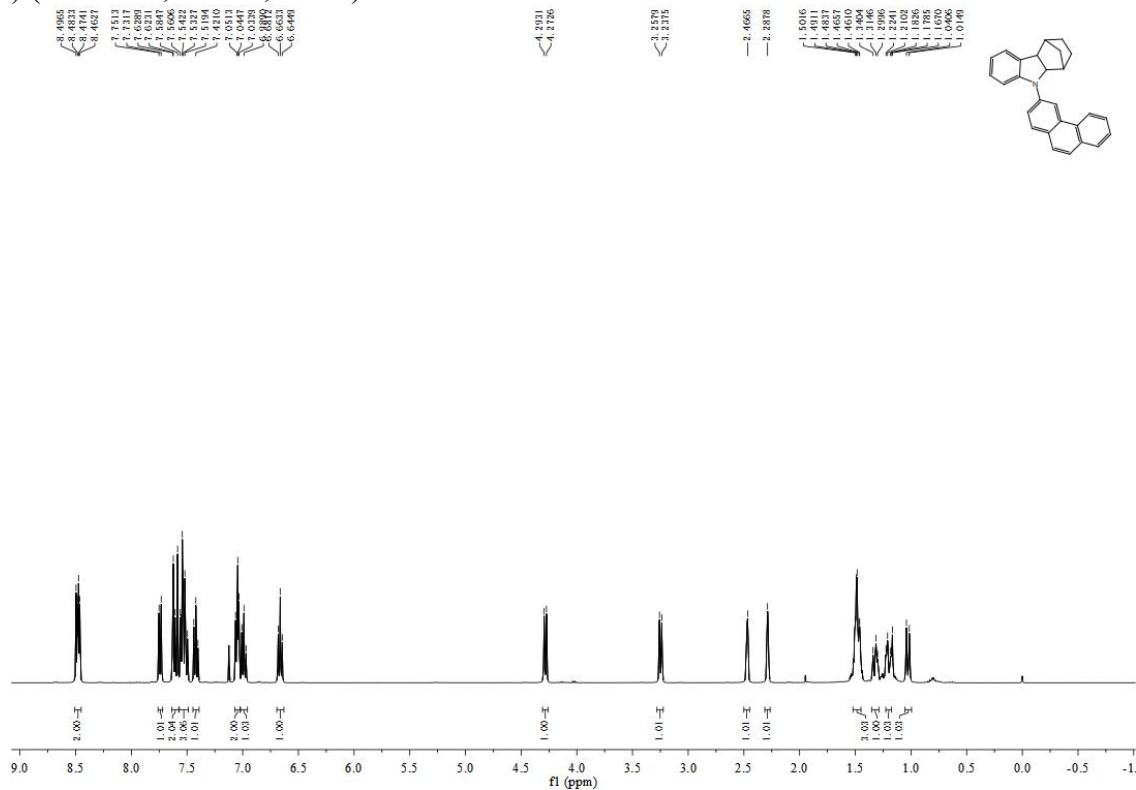
^1H NMR spectrum of 9-(naphthalen-2-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**19d**) (400 MHz, CDCl_3 , 25 °C)



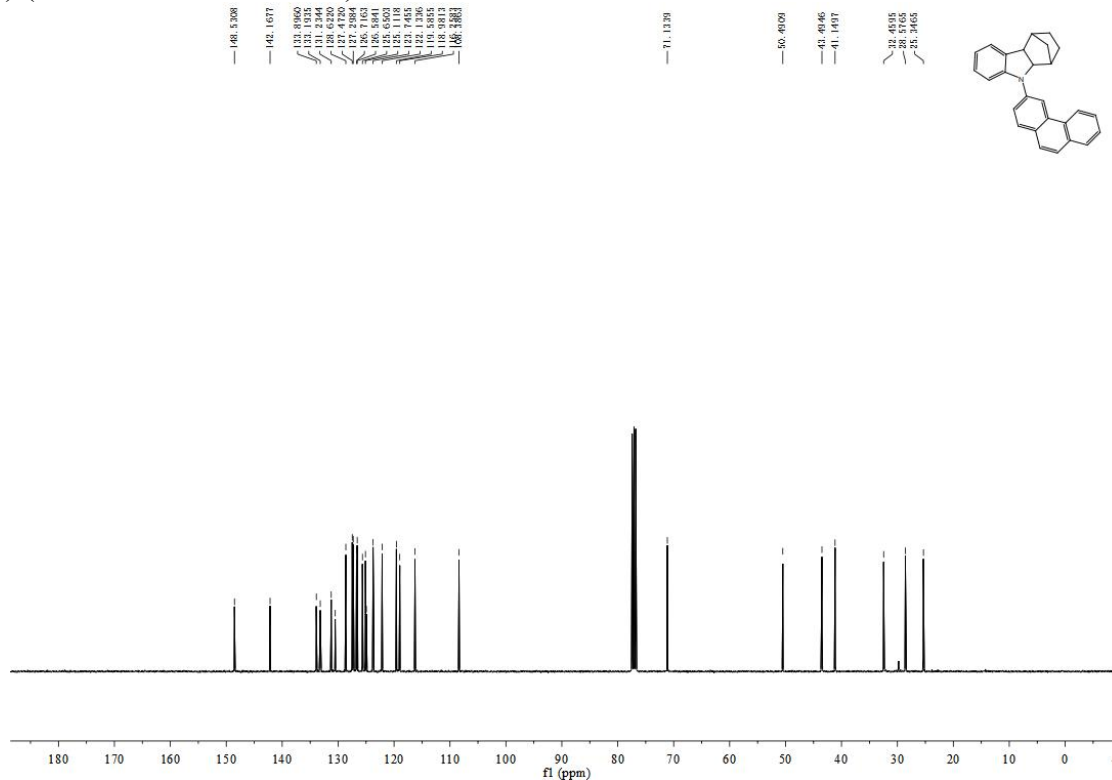
^{13}C NMR spectrum of 9-(naphthalen-2-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**19d**) (100 MHz, CDCl_3 , 25 °C)



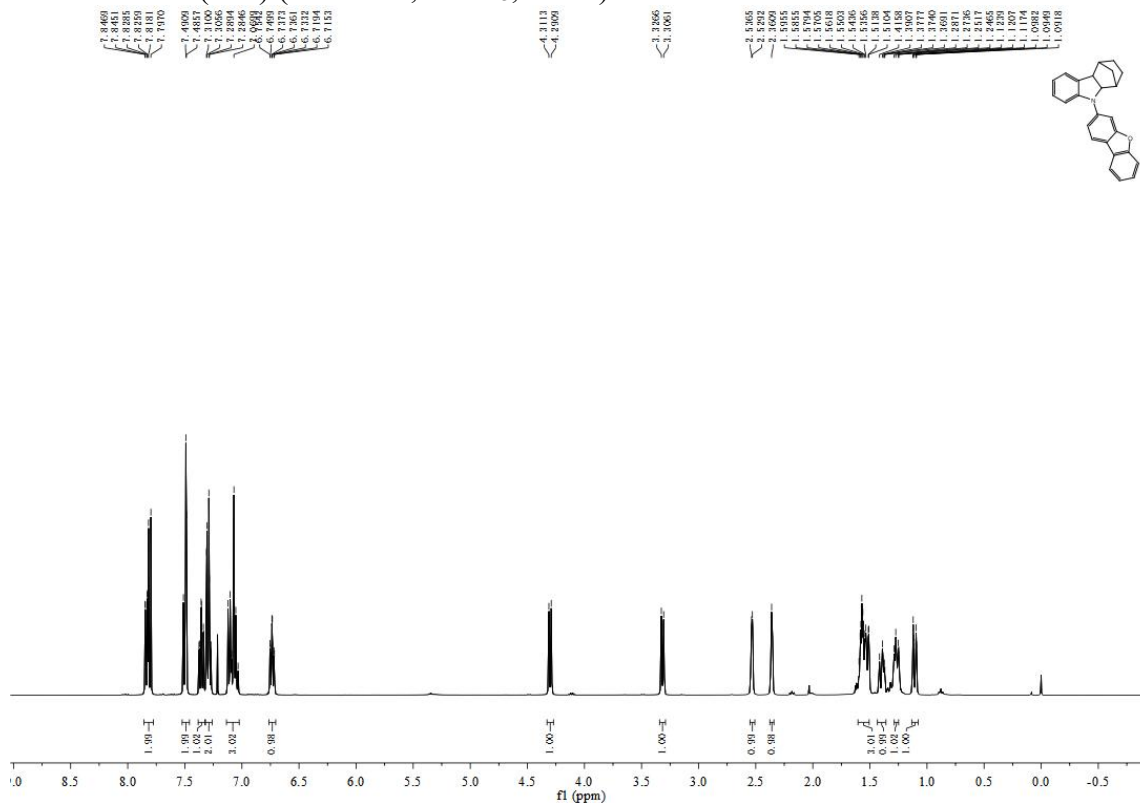
^1H NMR spectrum of 9-(phenanthren-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**20d**) (400 MHz, CDCl_3 , 25 °C)



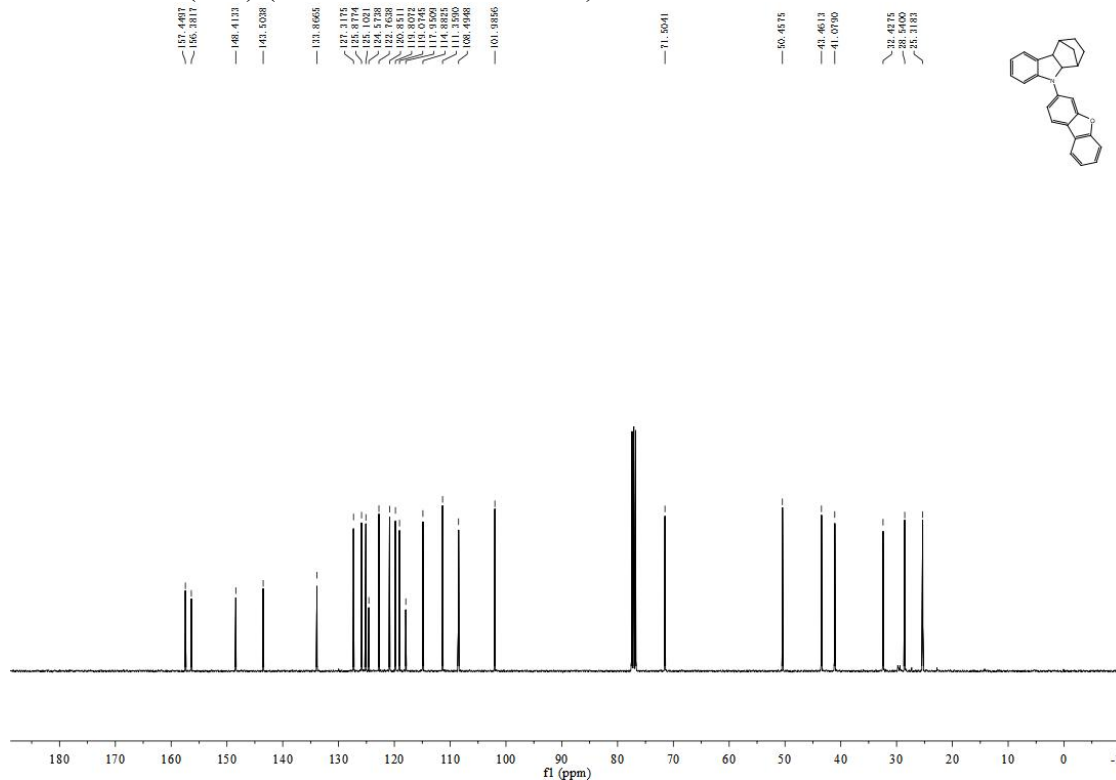
^{13}C NMR spectrum of 9-(phenanthren-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**20d**) (100 MHz, CDCl_3 , 25 °C)



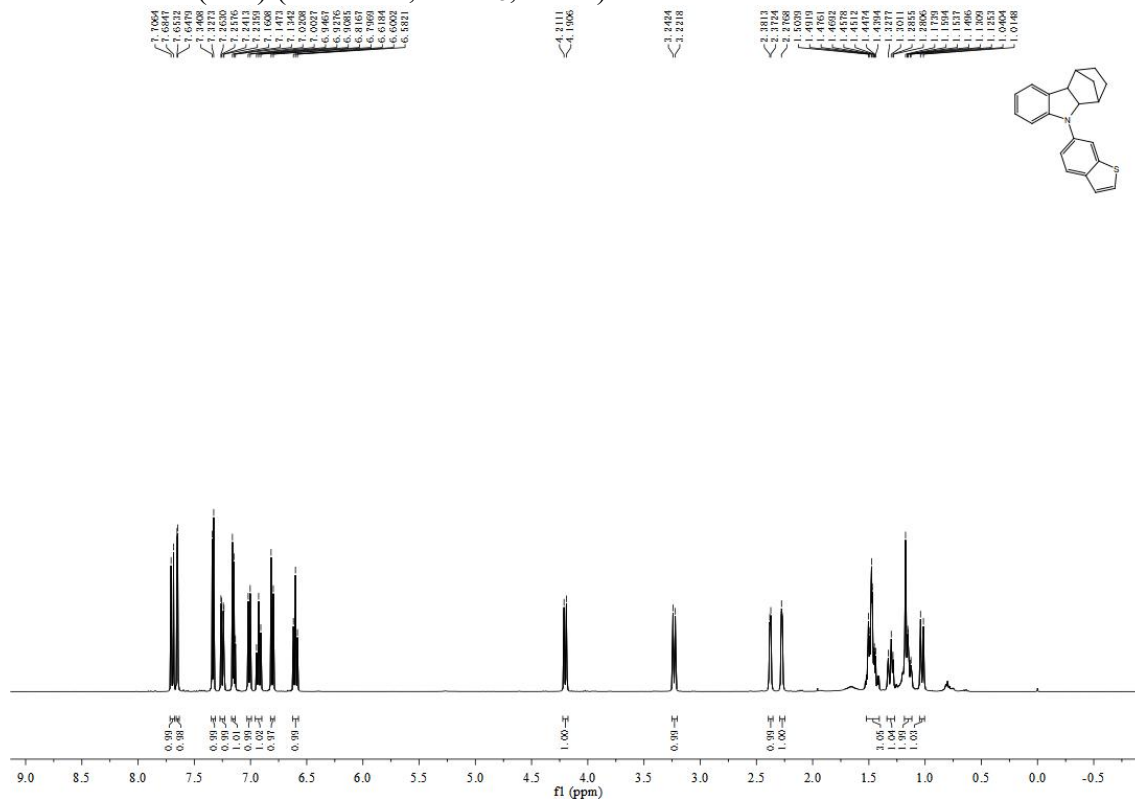
^1H NMR spectrum of 9-(dibenzo[*b,d*]furan-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**21d**) (400 MHz, CDCl_3 , 25 °C)



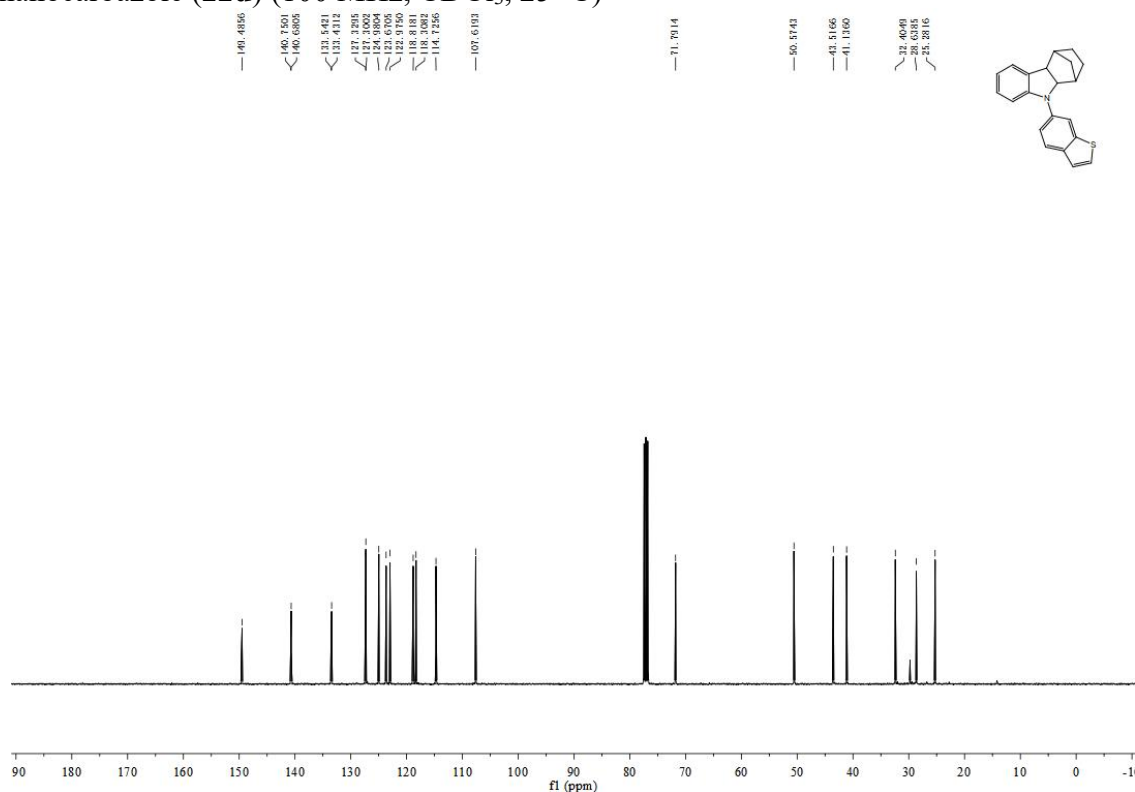
^{13}C NMR spectrum of 9-(dibenzo[*b,d*]furan-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**21d**) (100 MHz, CDCl_3 , 25 °C)



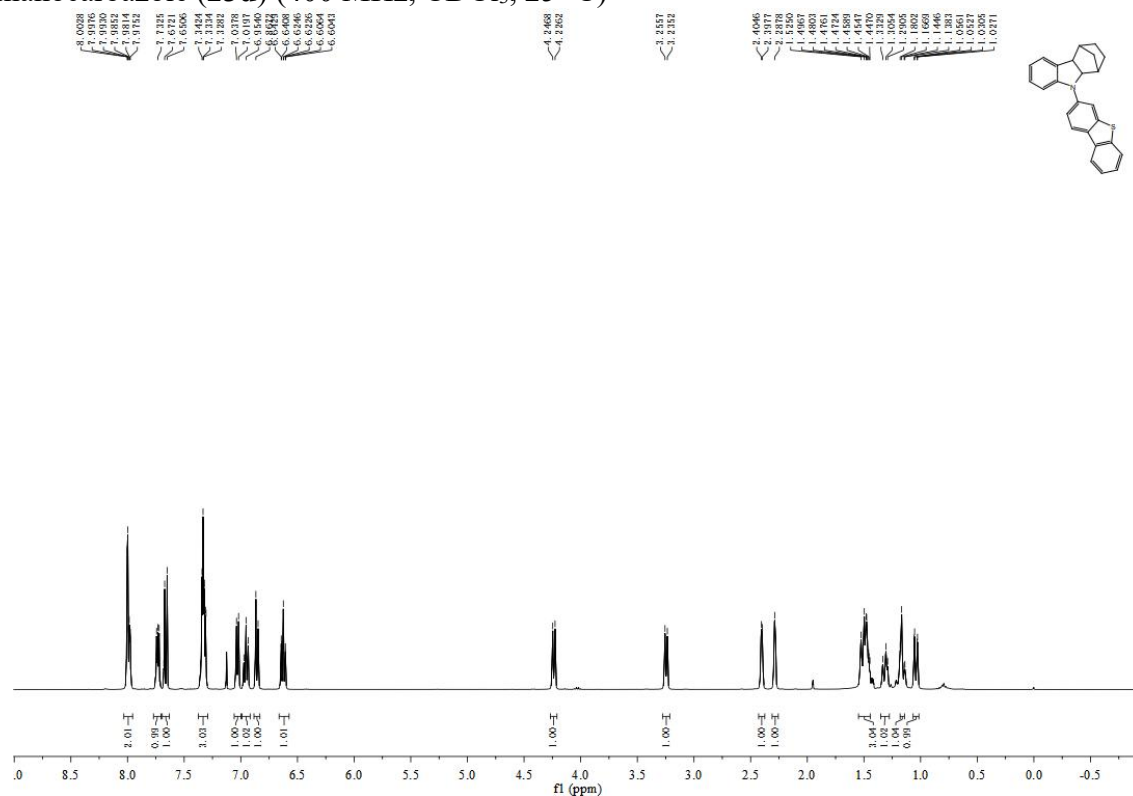
^1H NMR spectrum of 9-(benzo[*b*]thiophen-6-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**22d**) (400 MHz, CDCl_3 , 25 °C)



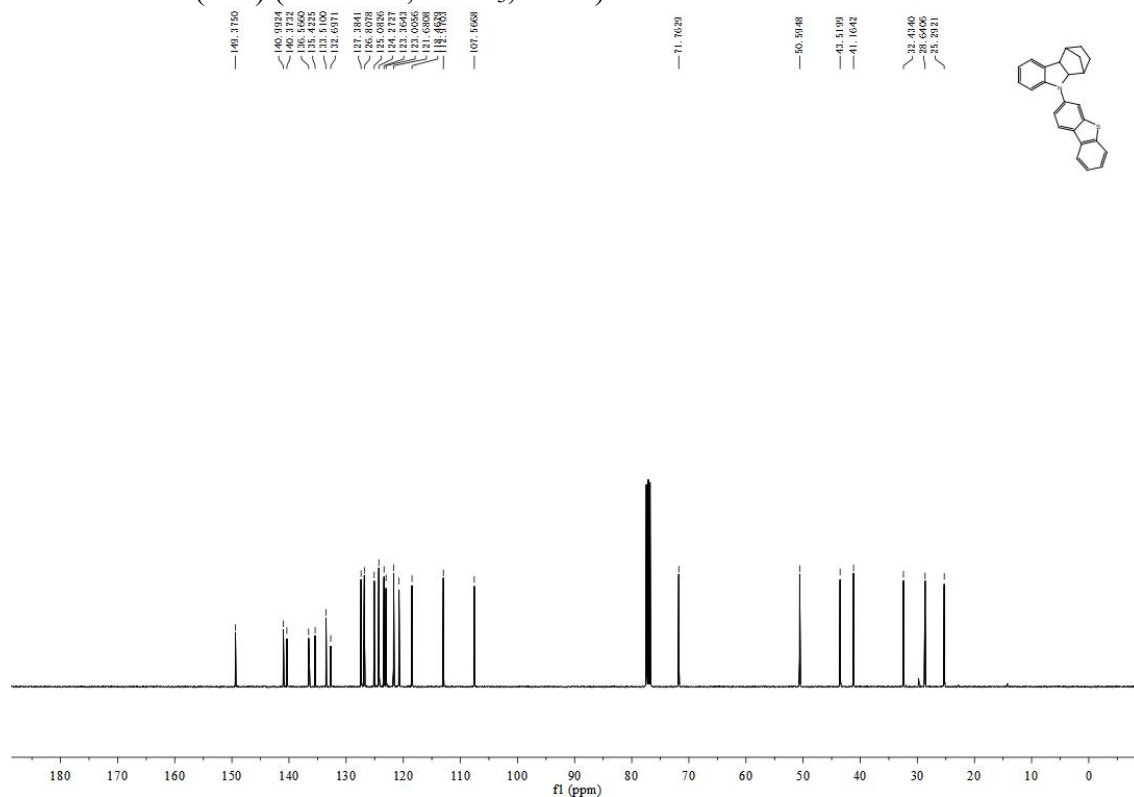
¹³C NMR spectrum of 9-(benzo[*b*]thiophen-6-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**22d**) (100 MHz, CDCl₃, 25 °C)



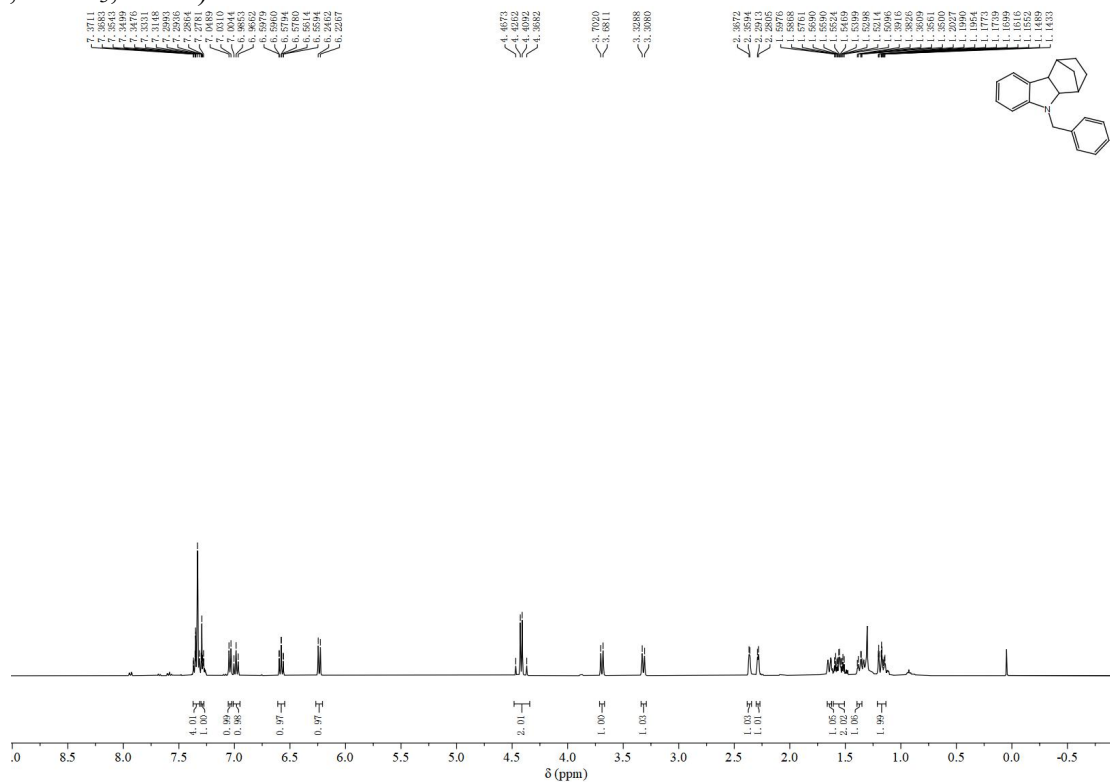
¹H NMR spectrum of 9-(dibenzo[*b,d*]thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**23d**) (400 MHz, CDCl₃, 25 °C)



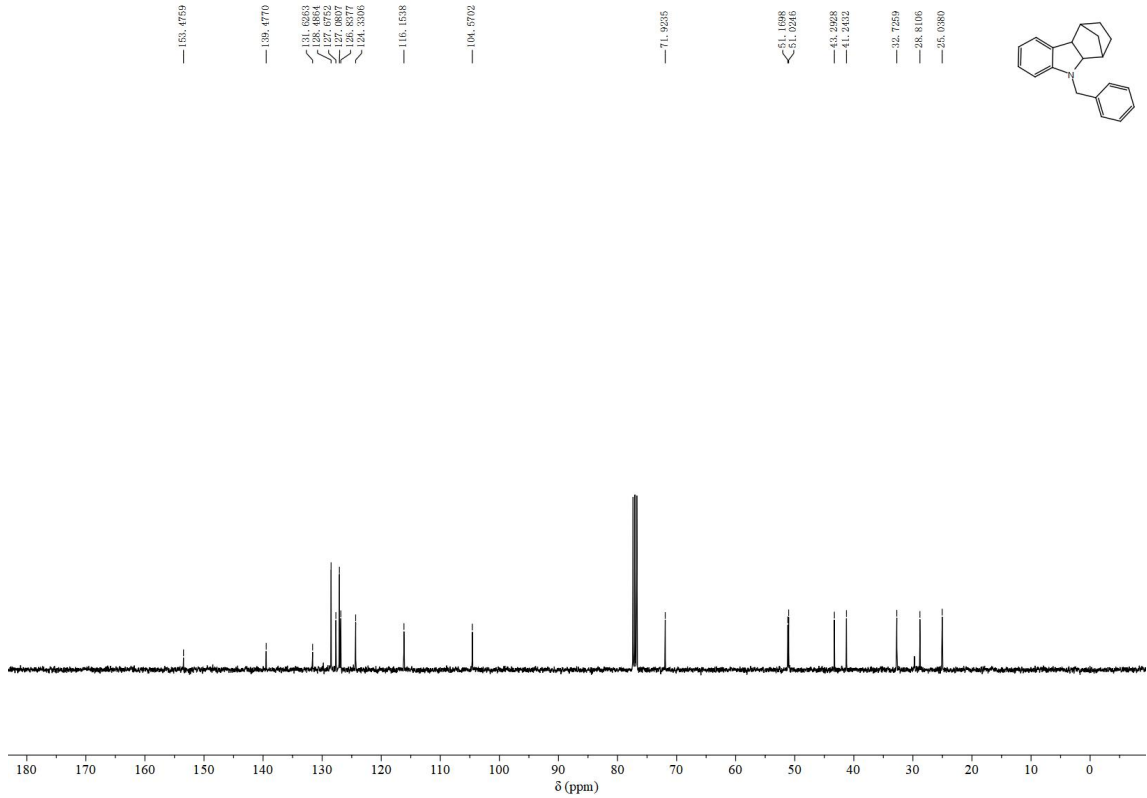
¹³C NMR spectrum of 9-(dibenzo[*b,d*]thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**23d**) (100 MHz, CDCl₃, 25 °C)



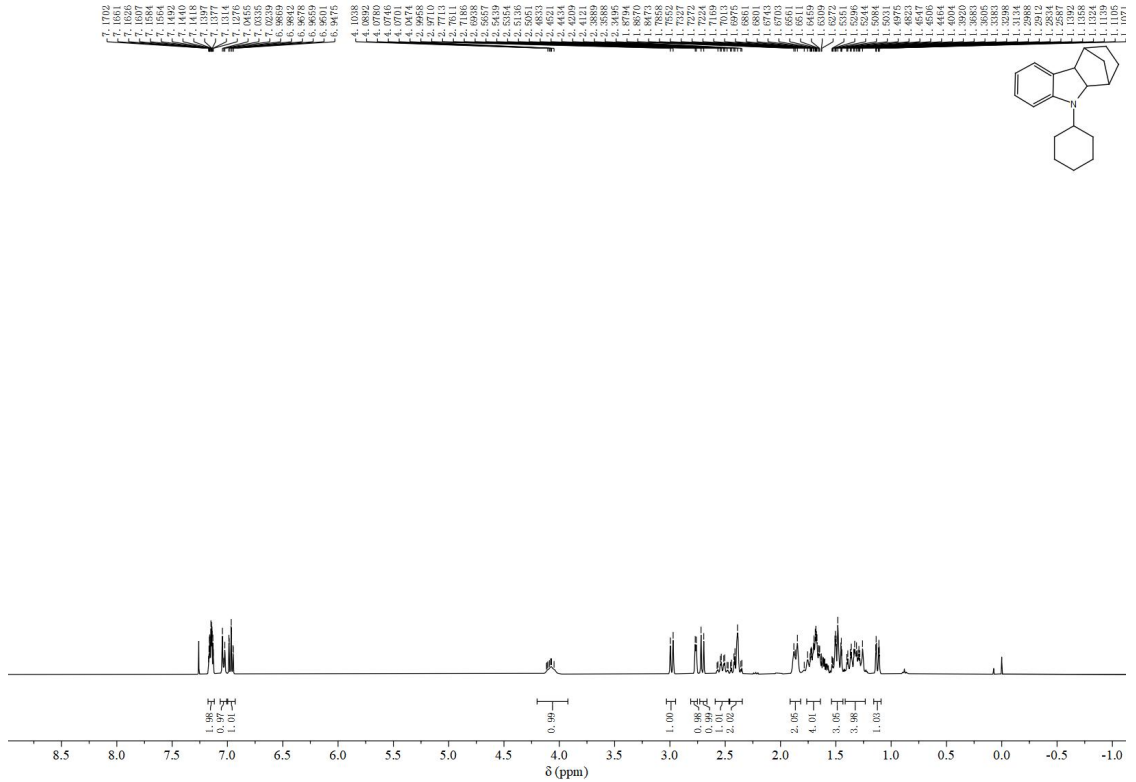
¹H NMR spectrum of 9-benzyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**24d**) (400 MHz, CDCl₃, 25 °C)



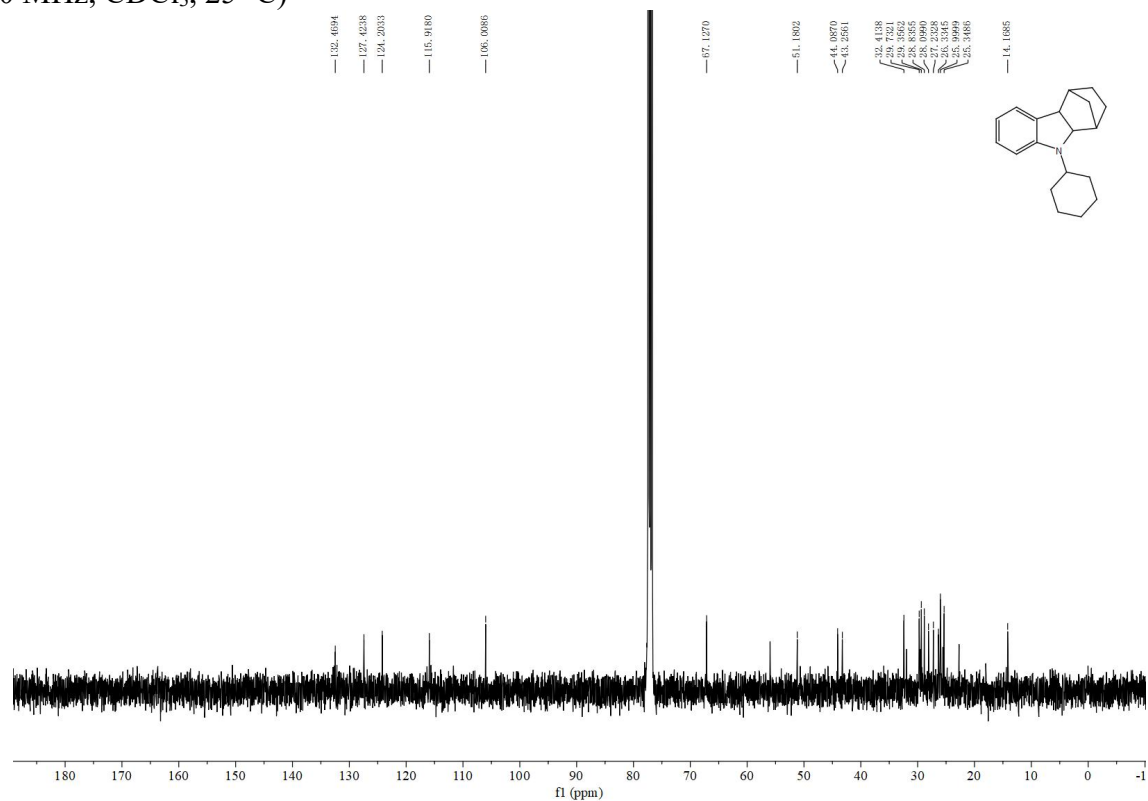
¹³C NMR spectrum of 9-benzyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**24d**) (100 MHz, CDCl₃, 25 °C)



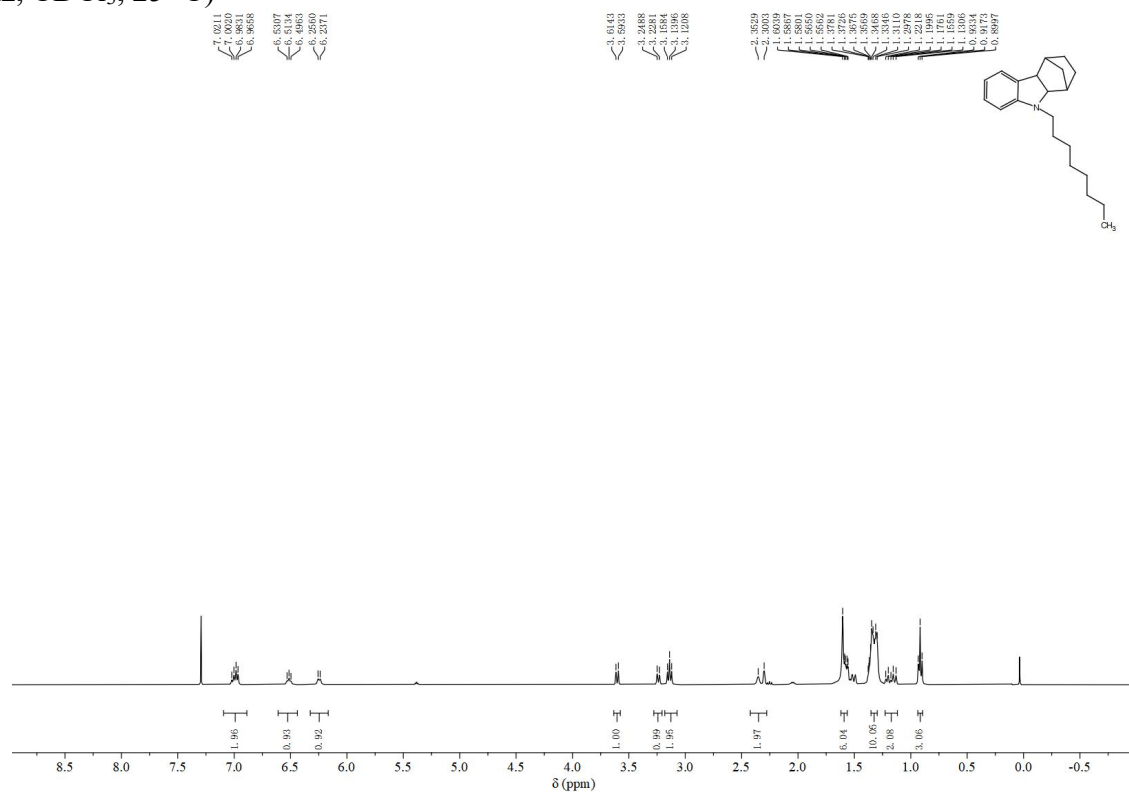
¹H NMR spectrum of 9-cyclohexyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**25d**) (400 MHz, CDCl₃, 25 °C)



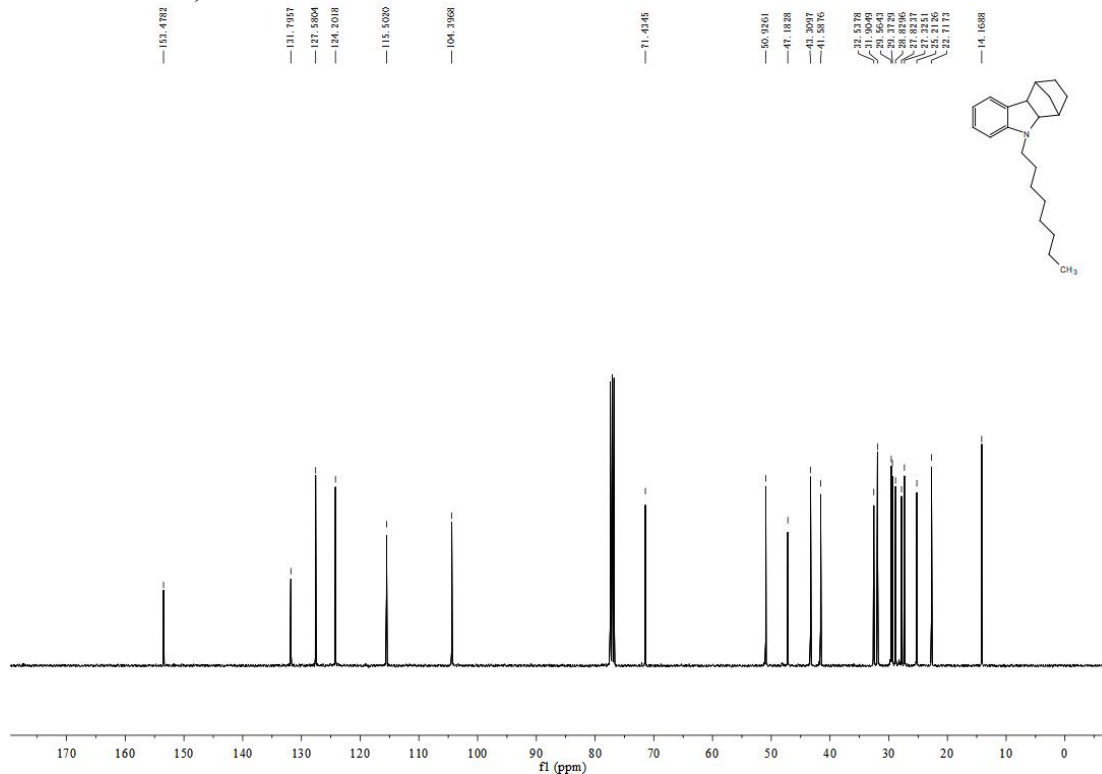
^{13}C NMR spectrum of 9-cyclohexyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**25d**) (100 MHz, CDCl_3 , 25 °C)



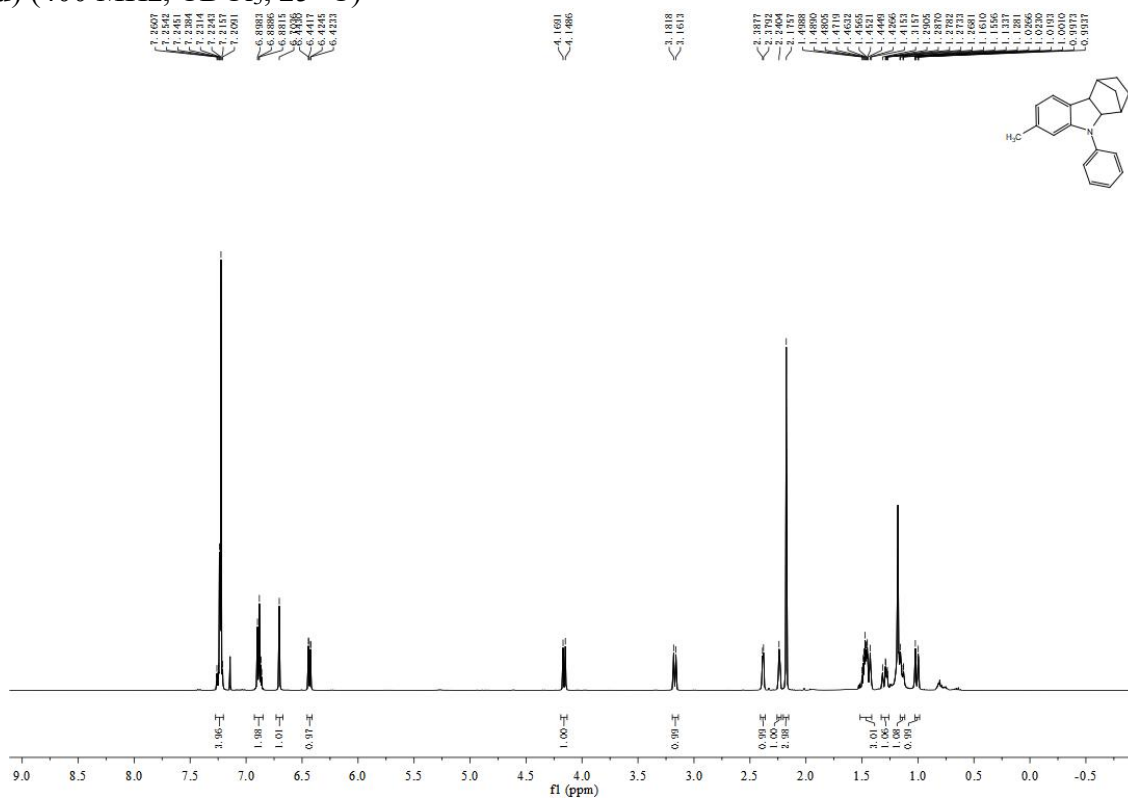
^1H NMR spectrum of 9-octyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**26d**) (400 MHz, CDCl_3 , 25 °C)



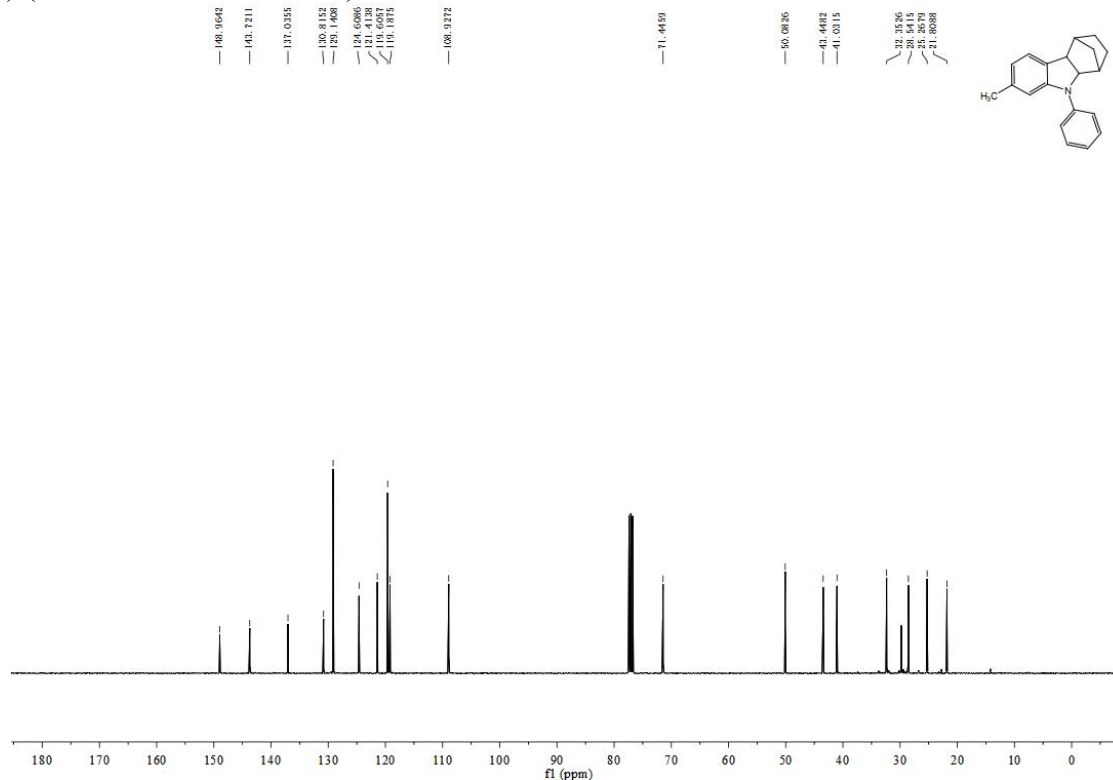
^{13}C NMR spectrum of 9-octyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**26d**) (100 MHz, CDCl_3 , 25 °C)



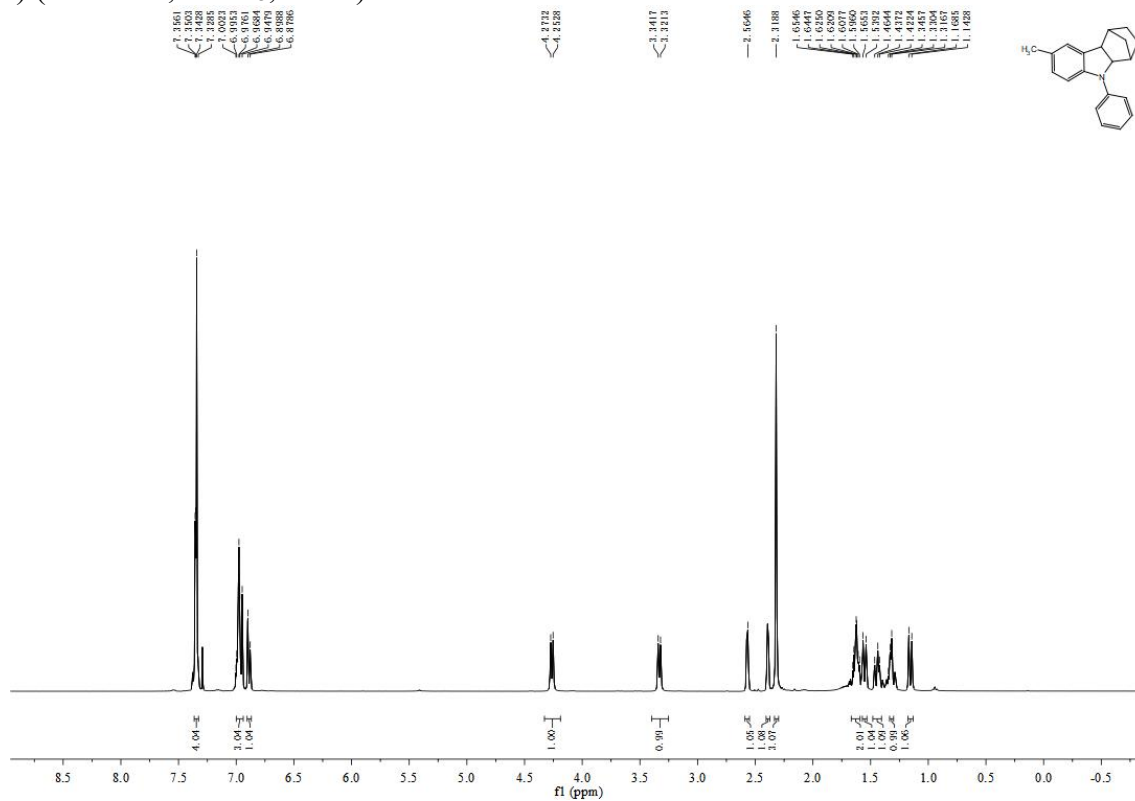
^1H NMR spectrum of 7-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**27d**) (400 MHz, CDCl_3 , 25 °C)



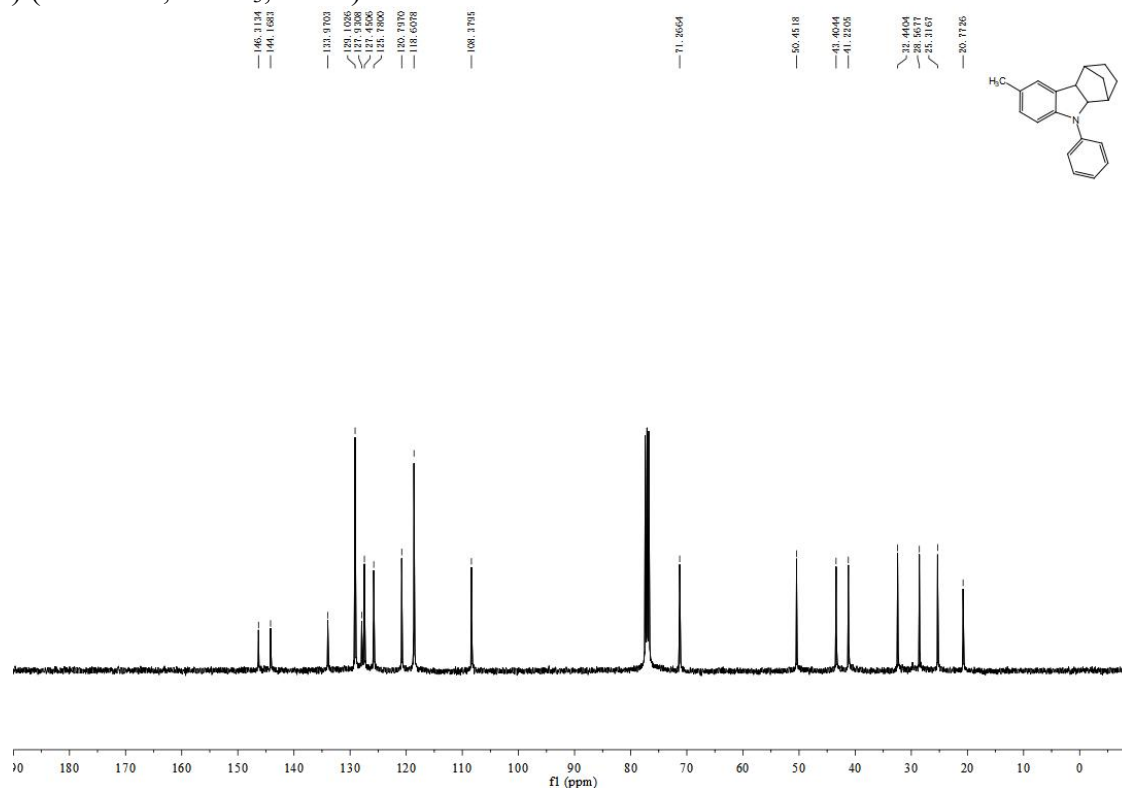
^{13}C NMR spectrum of 7-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**27d**) (100 MHz, CDCl_3 , 25 °C)



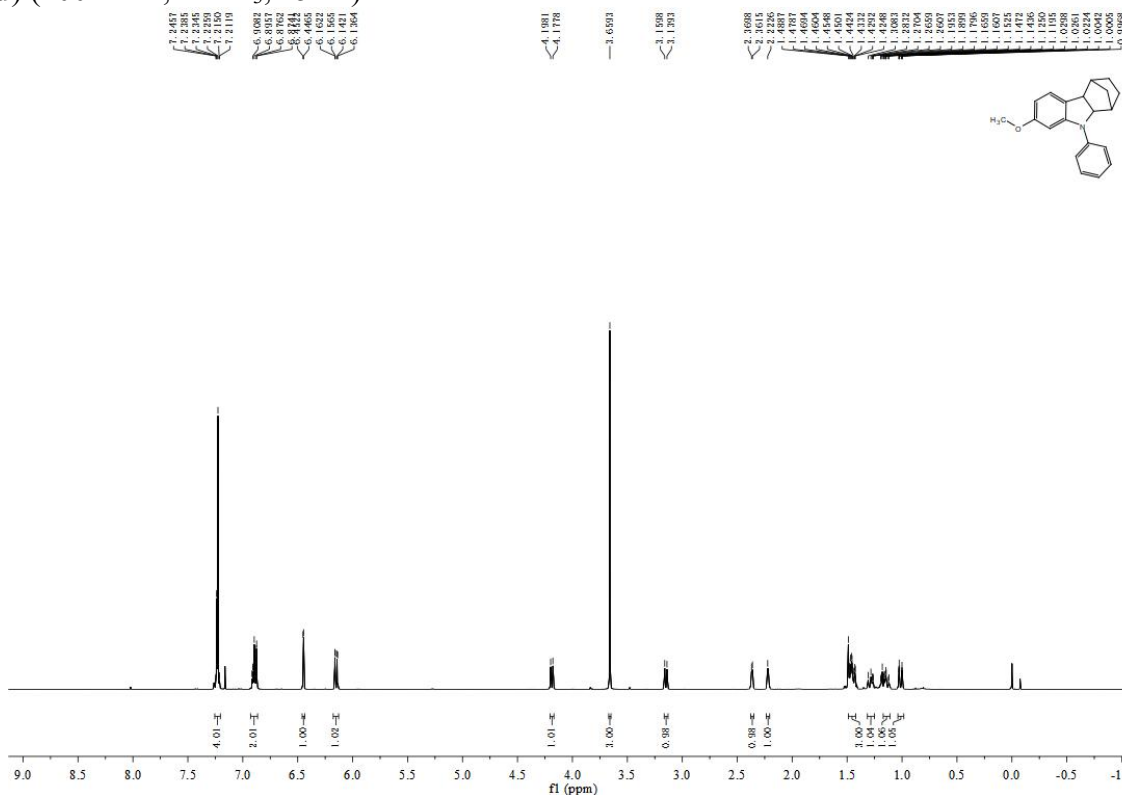
^1H NMR spectrum of 6-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**28d**) (400 MHz, CDCl_3 , 25 °C)



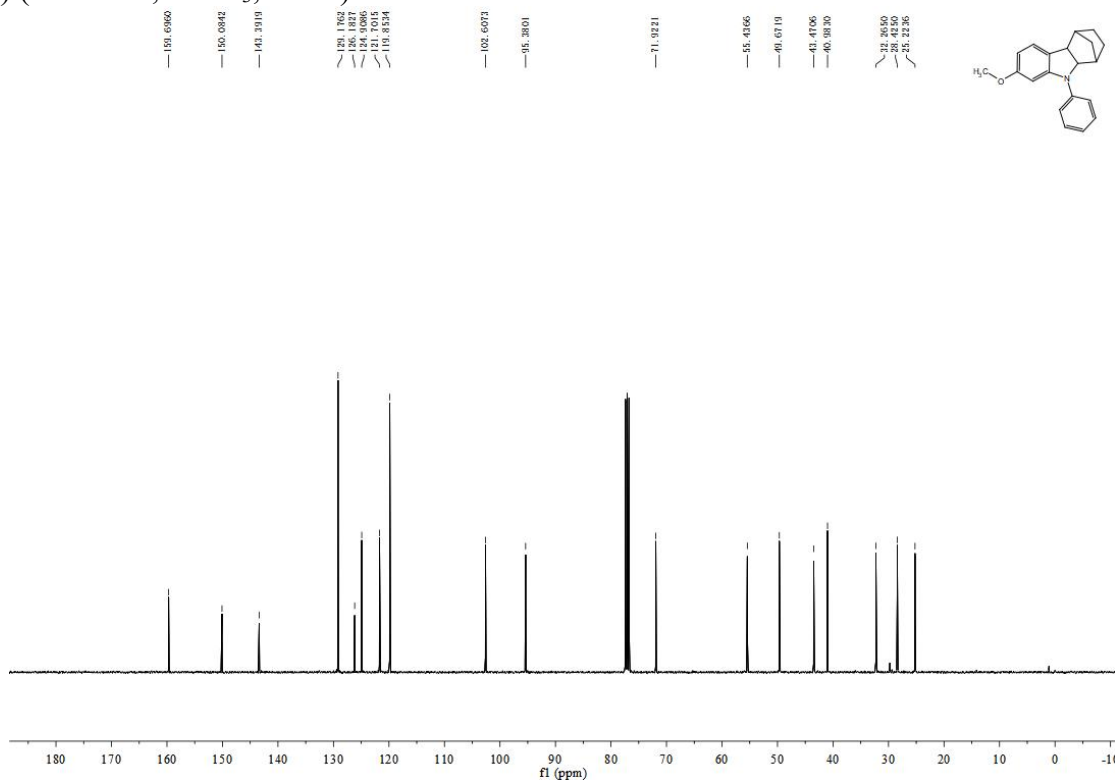
^{13}C NMR spectrum of 6-methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**28d**) (100 MHz, CDCl_3 , 25 °C)



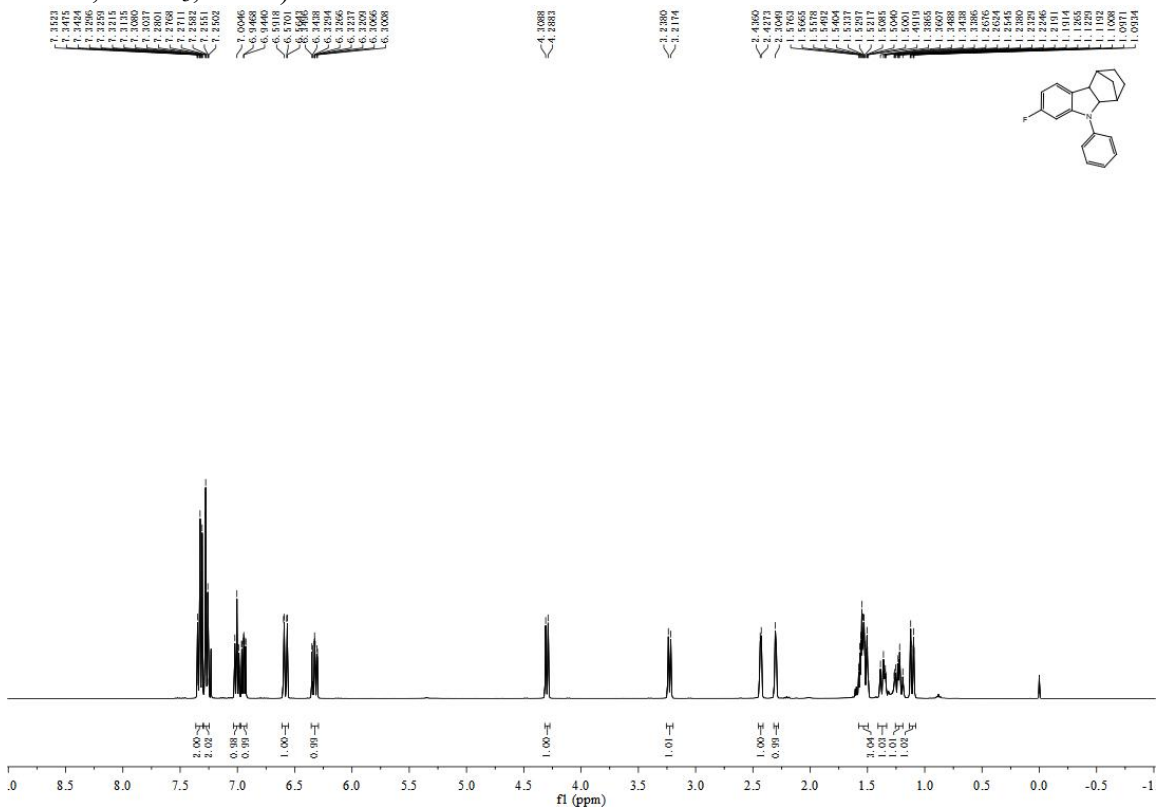
^1H NMR spectrum of 7-methoxy-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**29d**) (400 MHz, CDCl_3 , 25 °C)



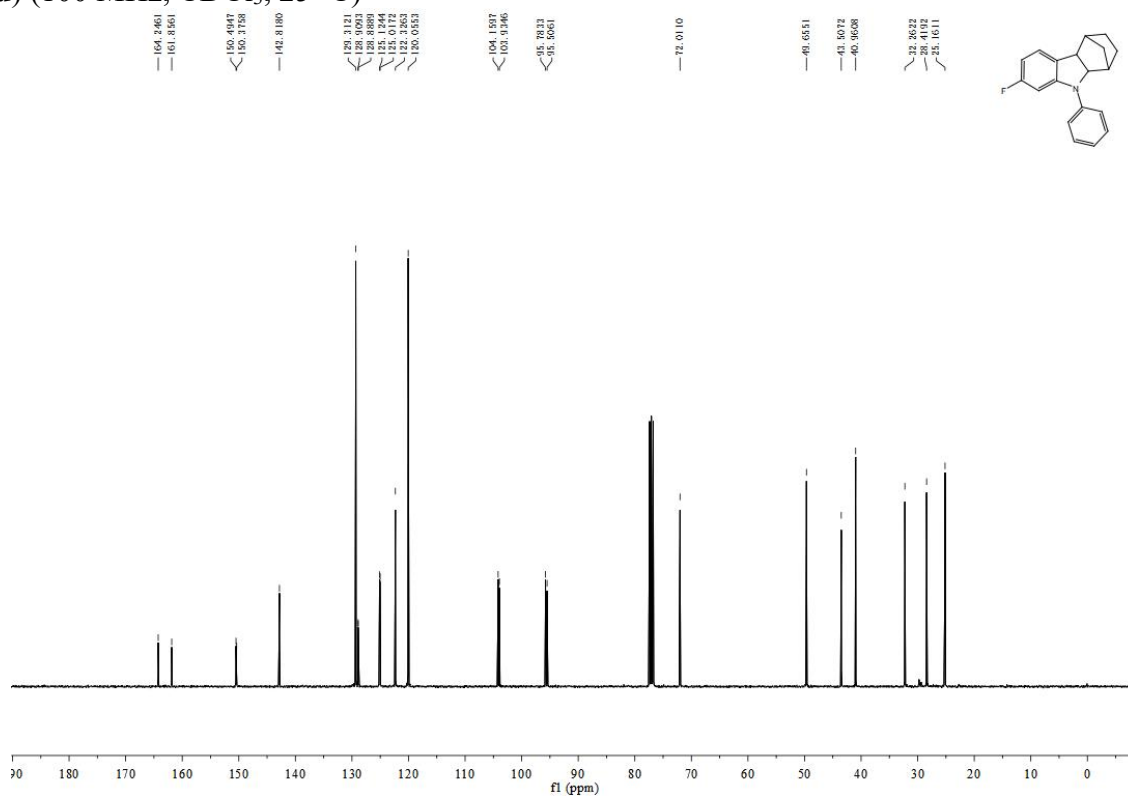
¹³C NMR spectrum of 7-methoxy-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**29d**) (100 MHz, CDCl₃, 25 °C)



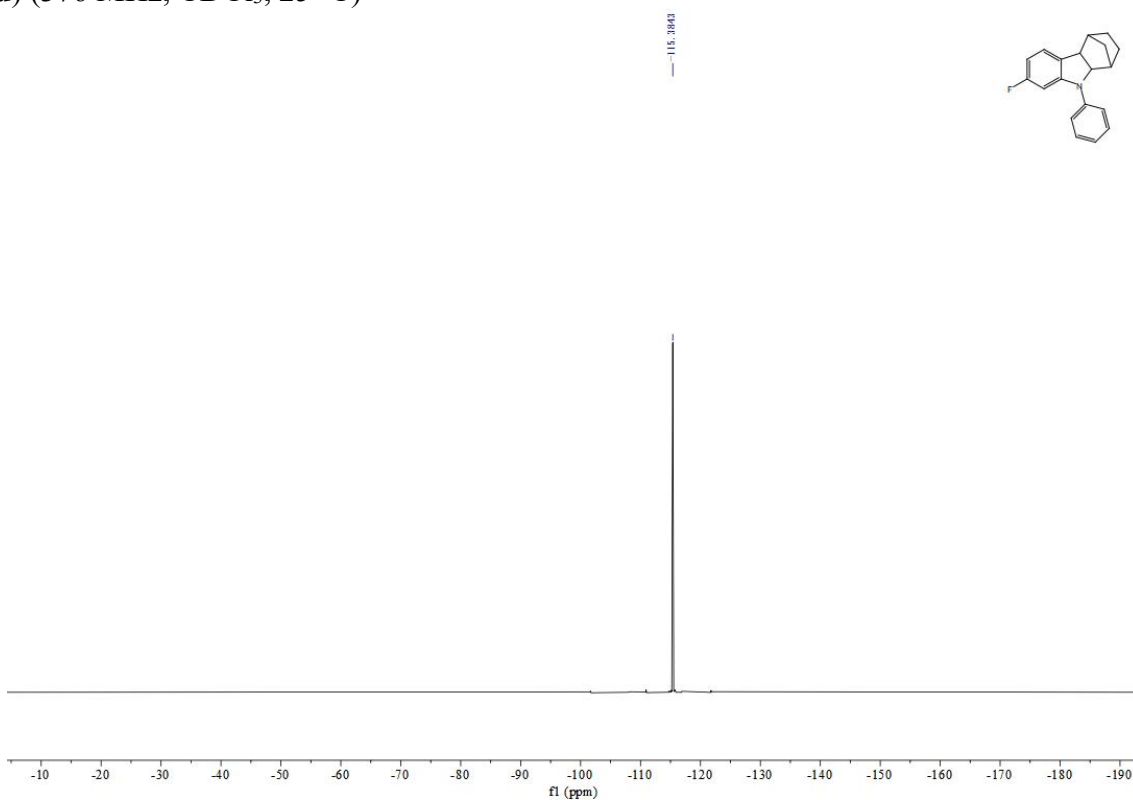
¹H NMR spectrum of 7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**30d**) (400 MHz, CDCl₃, 25 °C)



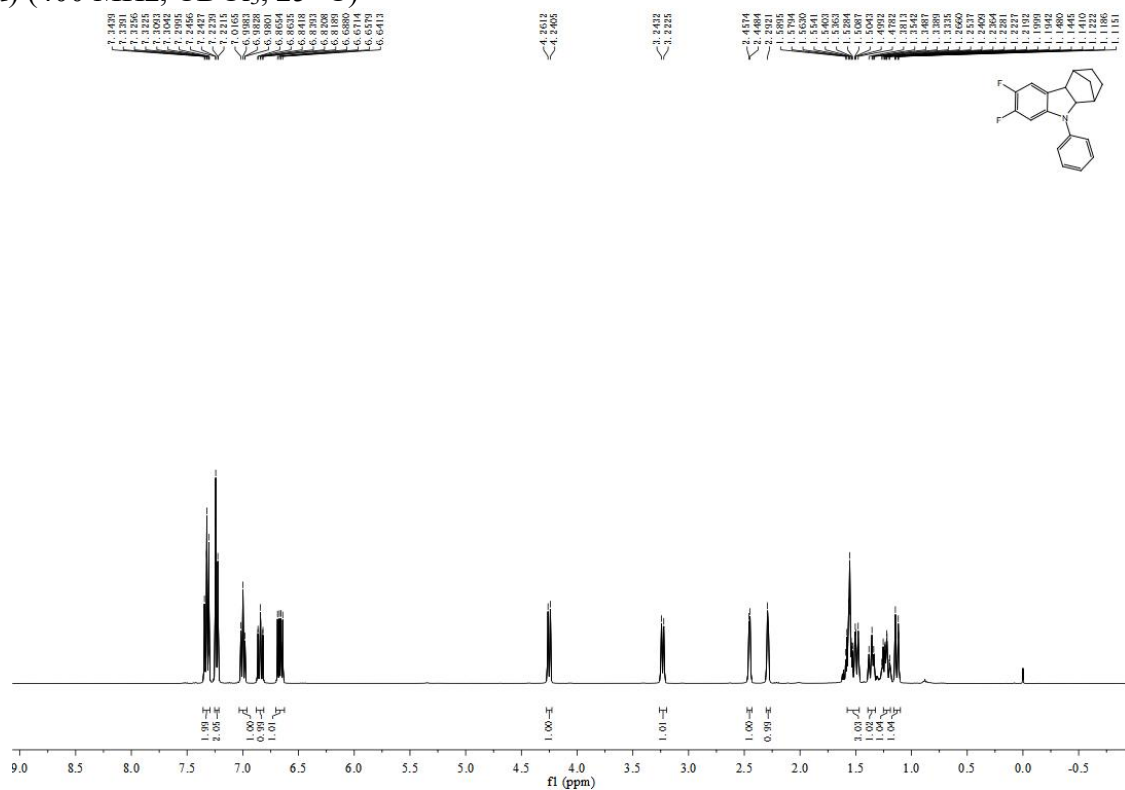
^{13}C NMR spectrum of 7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**30d**) (100 MHz, CDCl_3 , 25 °C)



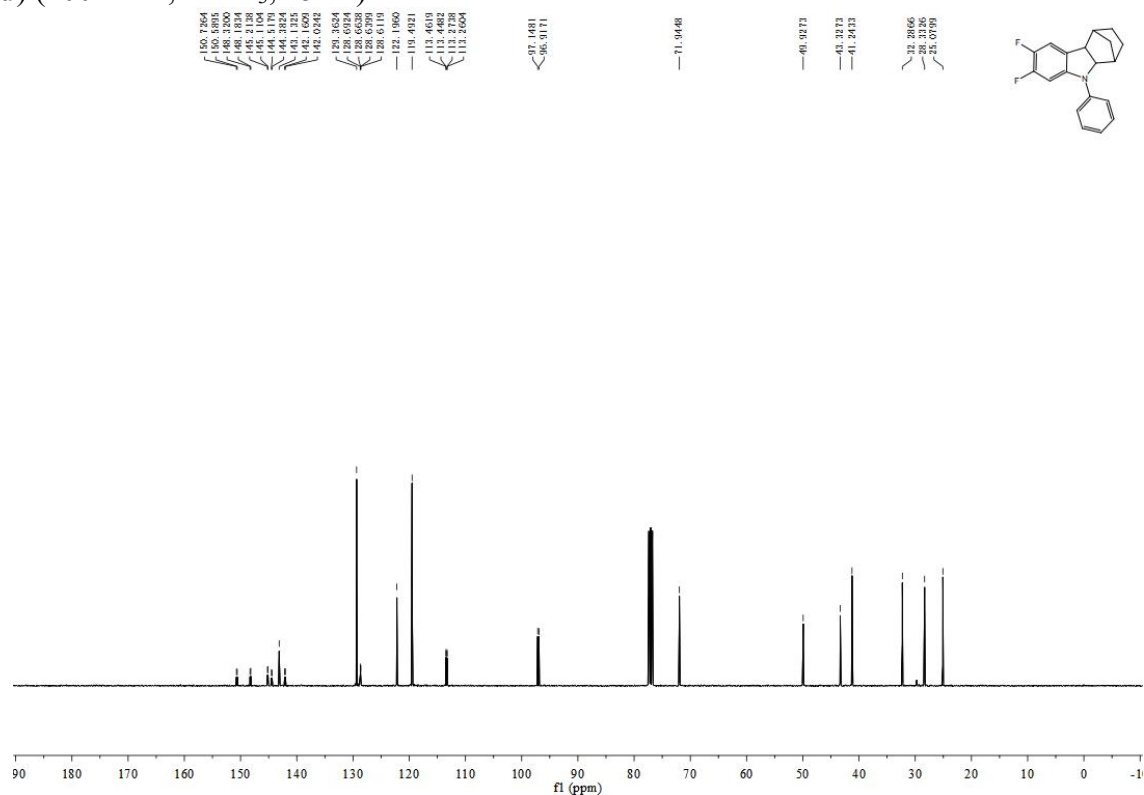
^{19}F NMR spectrum of 7-fluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**30d**) (376 MHz, CDCl_3 , 25 °C)



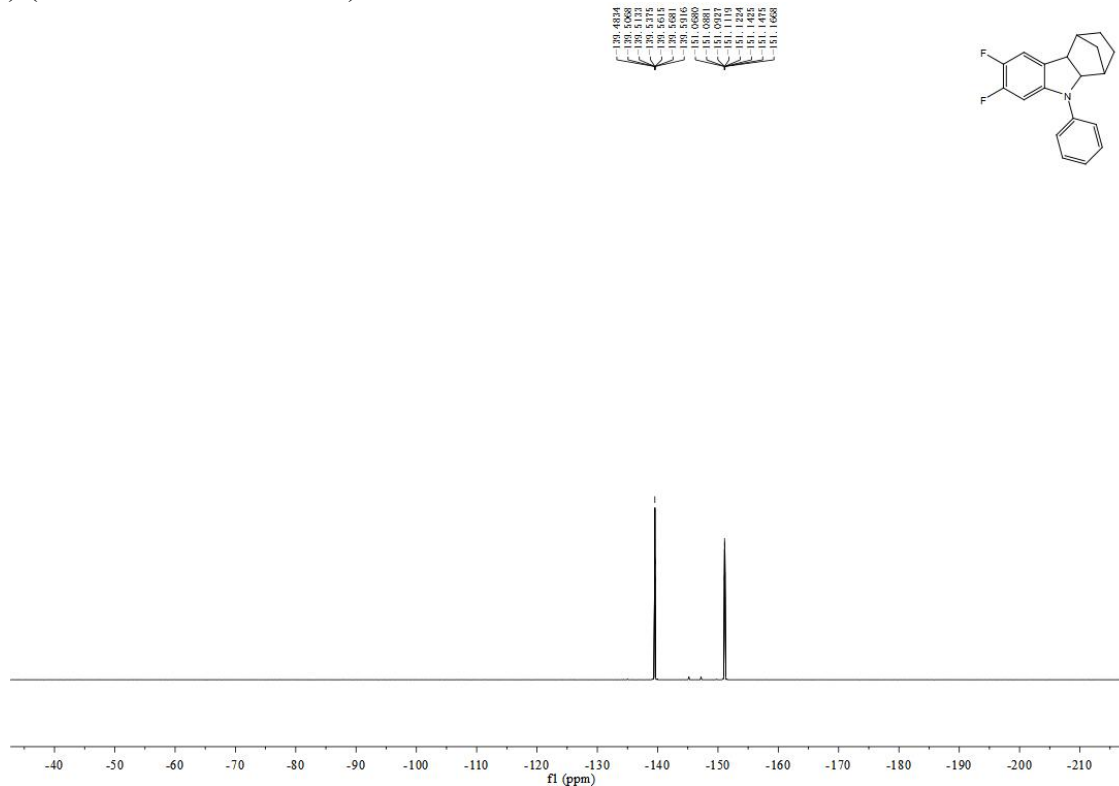
¹H NMR spectrum of 6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**31d**) (400 MHz, CDCl₃, 25 °C)



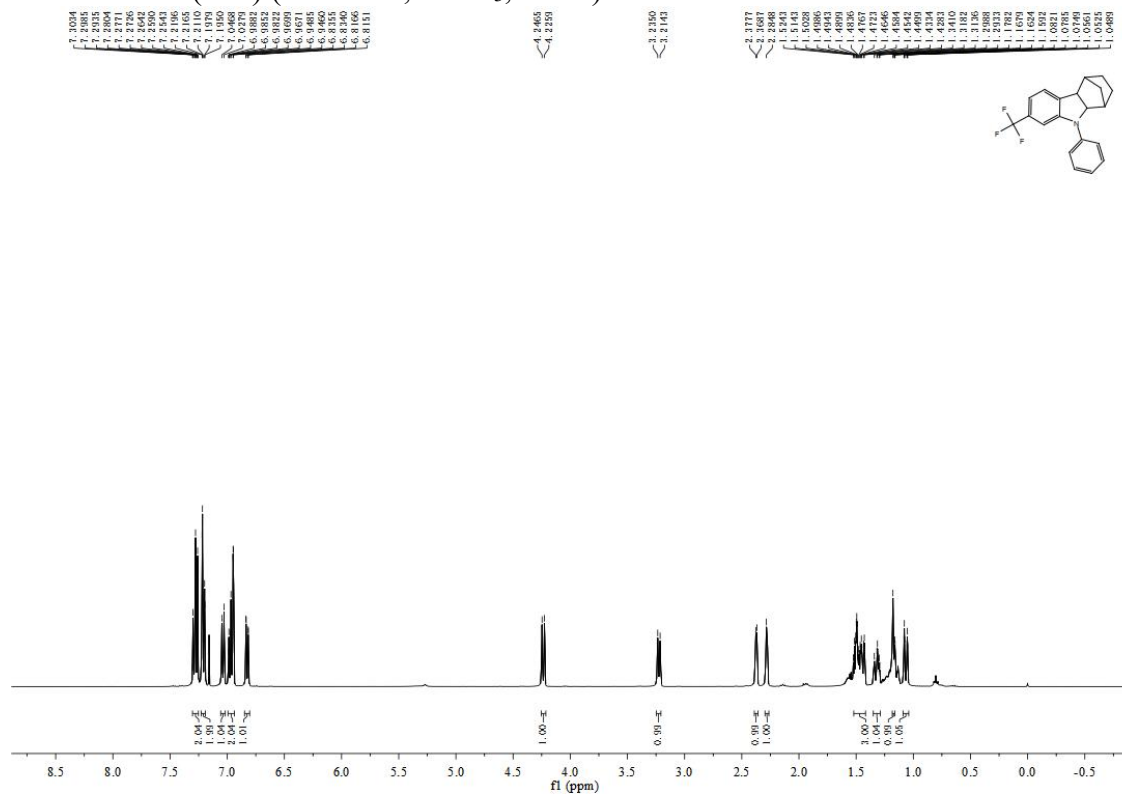
¹³C NMR spectrum of 6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**31d**) (100 MHz, CDCl₃, 25 °C)



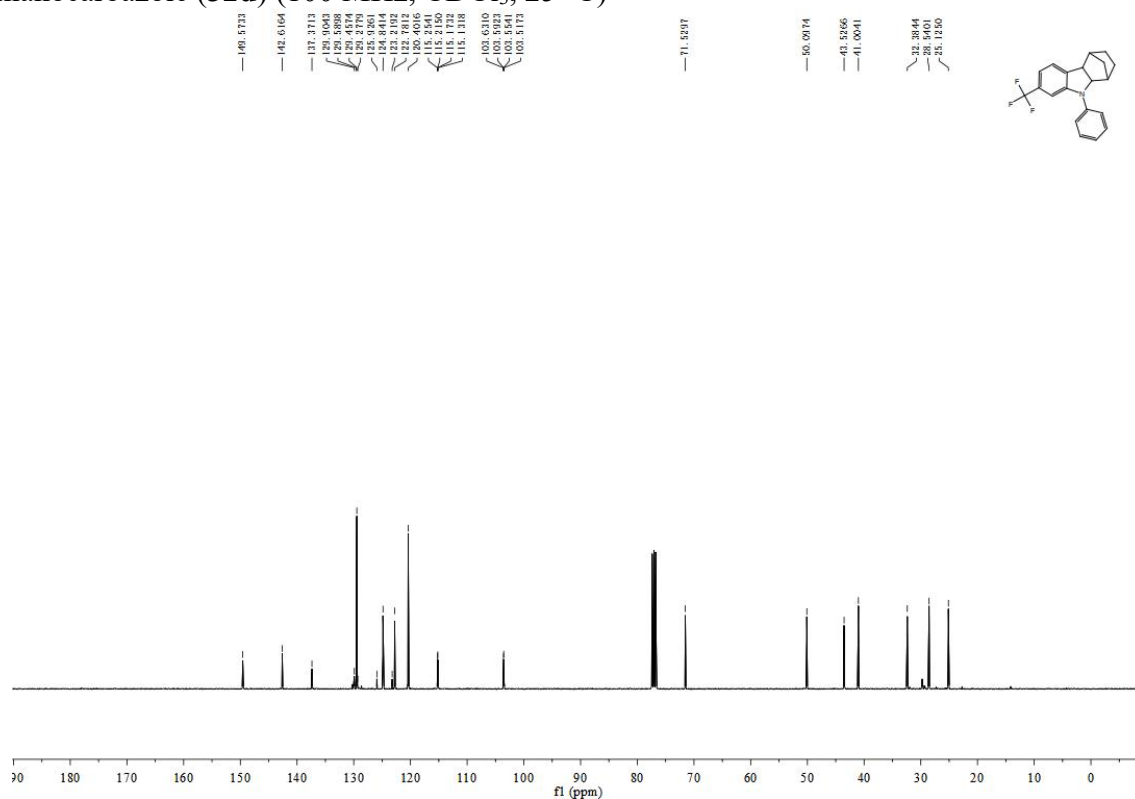
^{19}F NMR spectrum of 6,7-difluoro-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**31d**) (376 MHz, CDCl_3 , 25 °C)



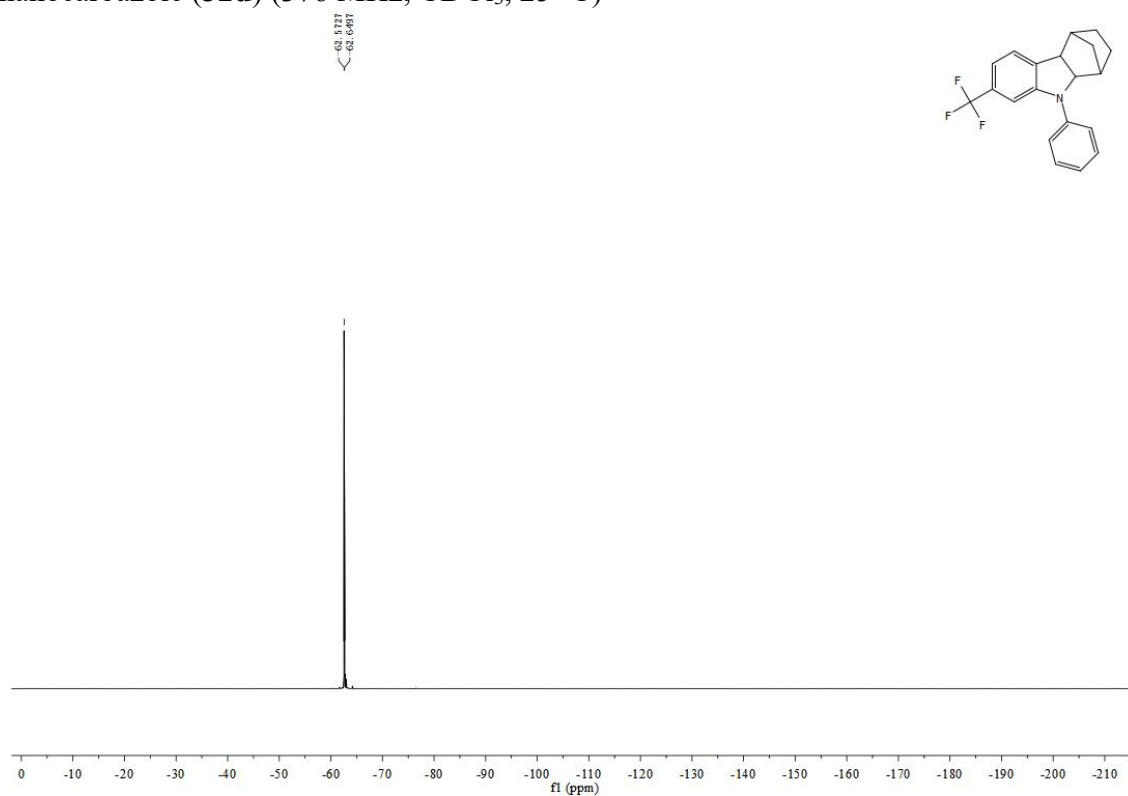
^1H NMR spectrum of 9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**32d**) (400 MHz, CDCl_3 , 25 °C)



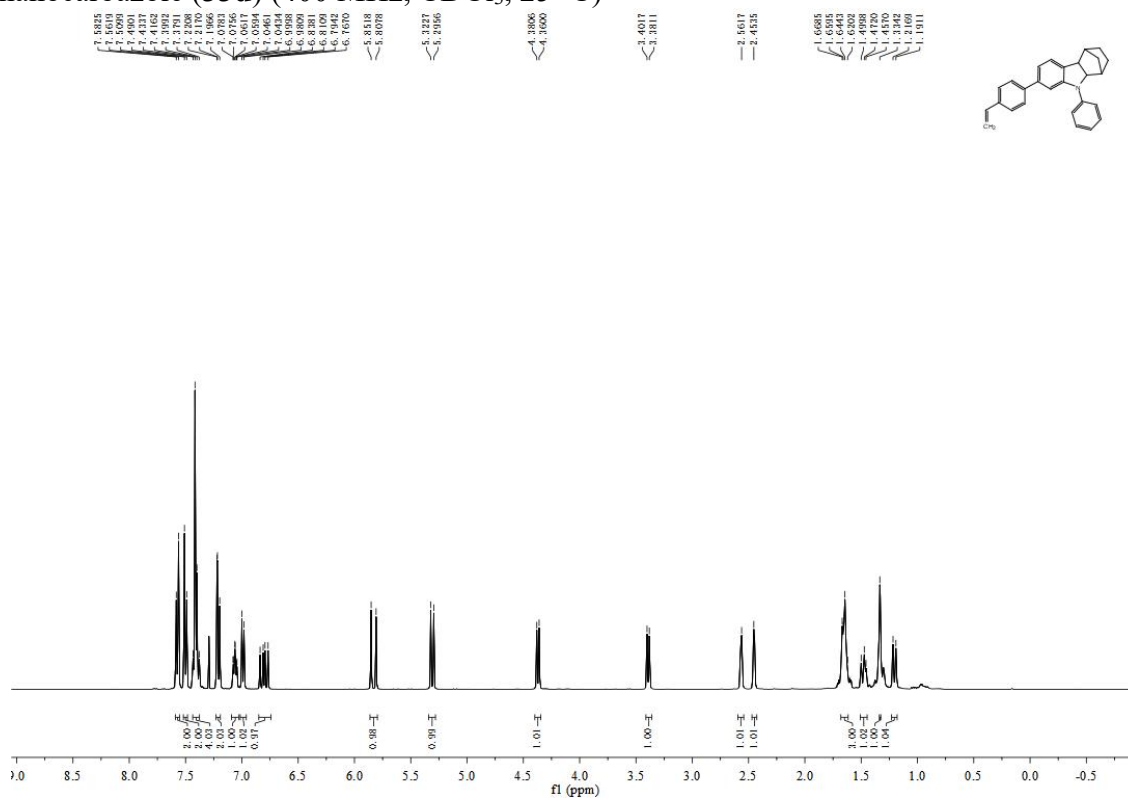
^{13}C NMR spectrum of 9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**32d**) (100 MHz, CDCl_3 , 25 °C)



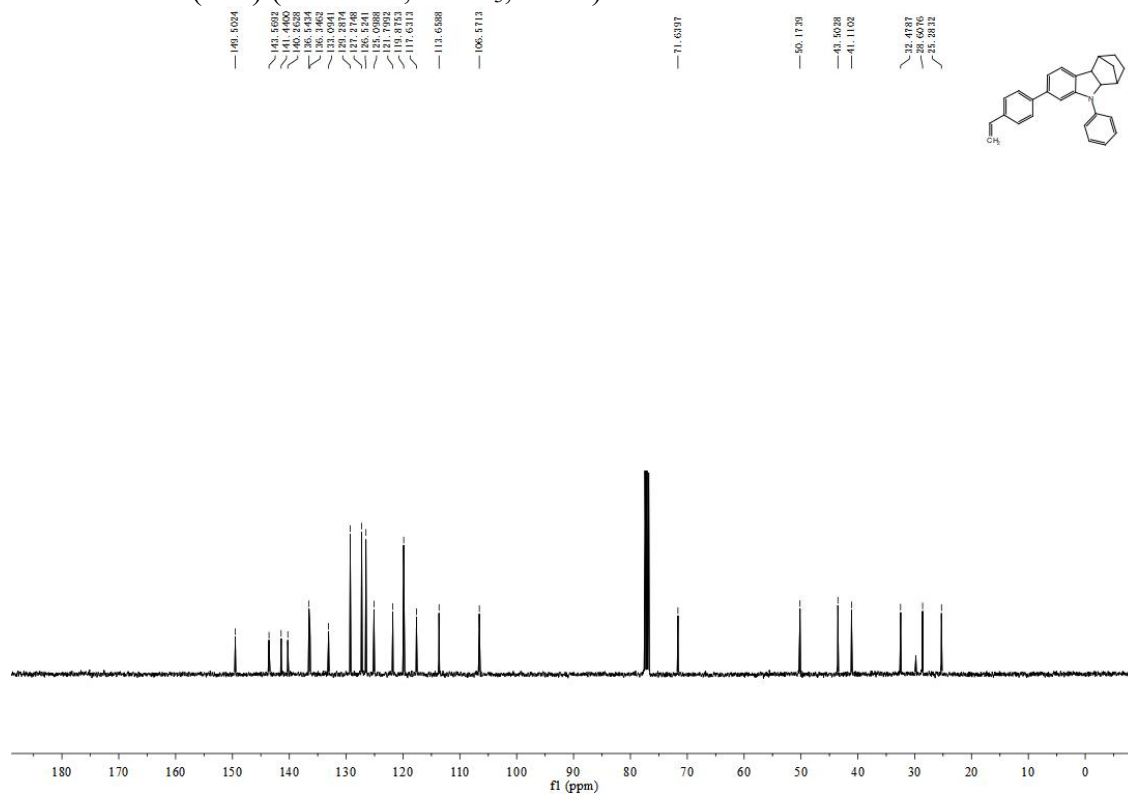
^{19}F NMR spectrum of 9-phenyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**32d**) (376 MHz, CDCl_3 , 25 °C)



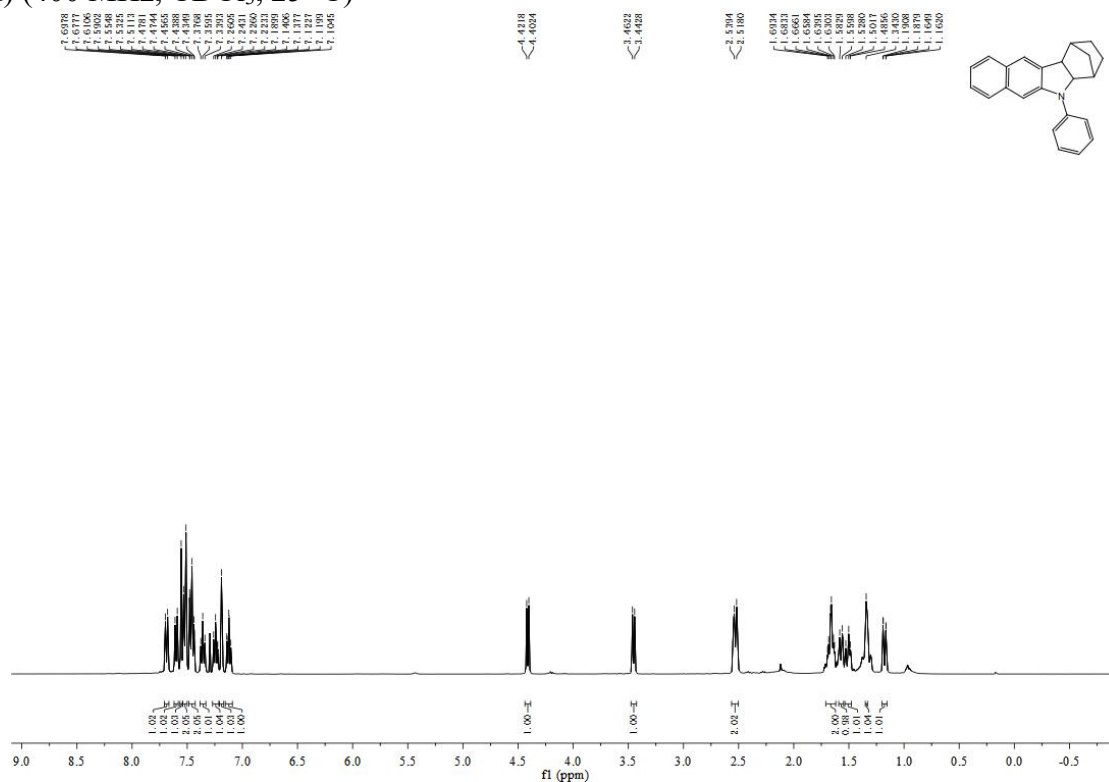
^1H NMR spectrum of 9-phenyl-7-(4-vinylphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**33d**) (400 MHz, CDCl_3 , 25 °C)



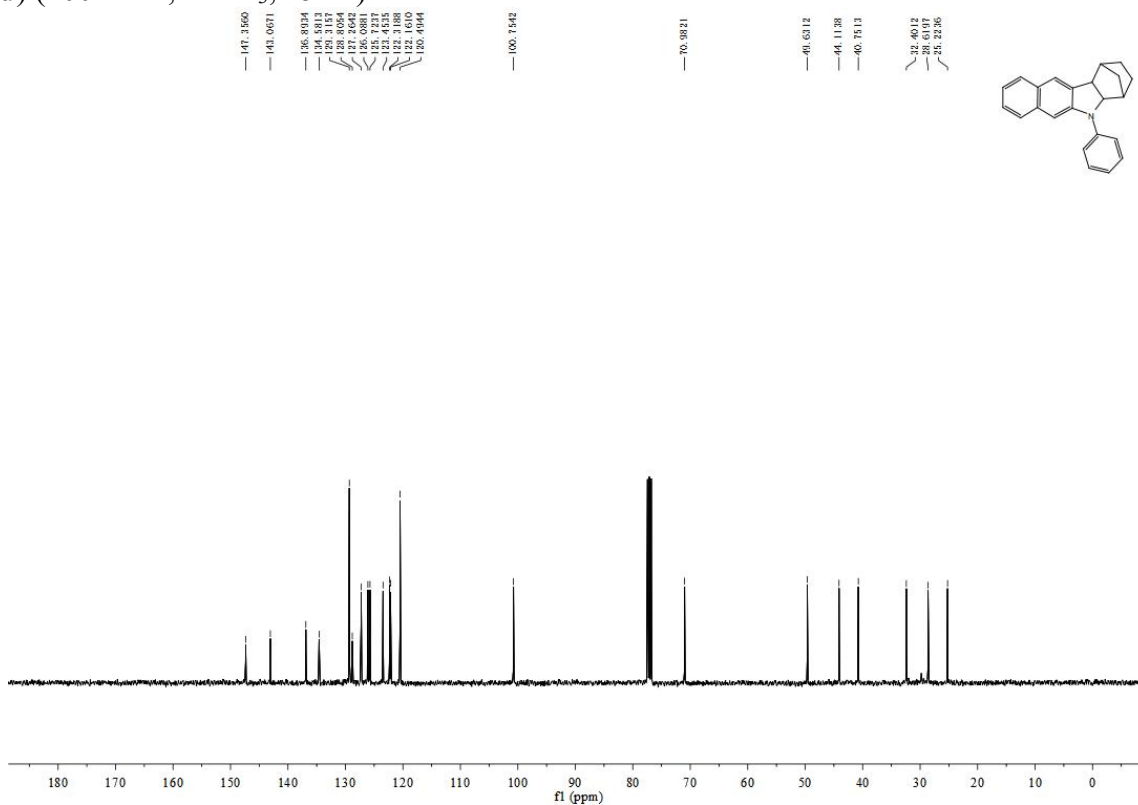
^{13}C NMR spectrum of 9-phenyl-7-(4-vinylphenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**33d**) (100 MHz, CDCl_3 , 25 °C)



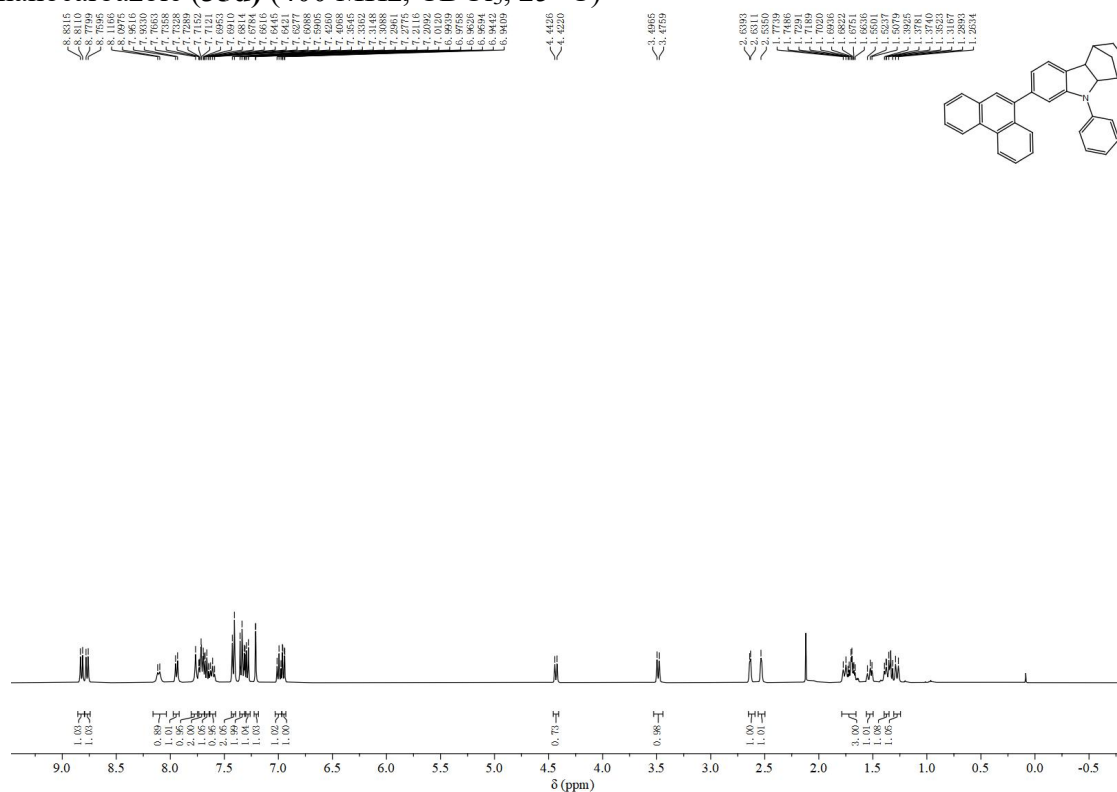
¹H NMR spectrum of 5-phenyl-2,3,4,4a,5,11b-hexahydro-1H-1,4-methanobenzo[*b*]carbazole (**34d**) (400 MHz, CDCl₃, 25 °C)



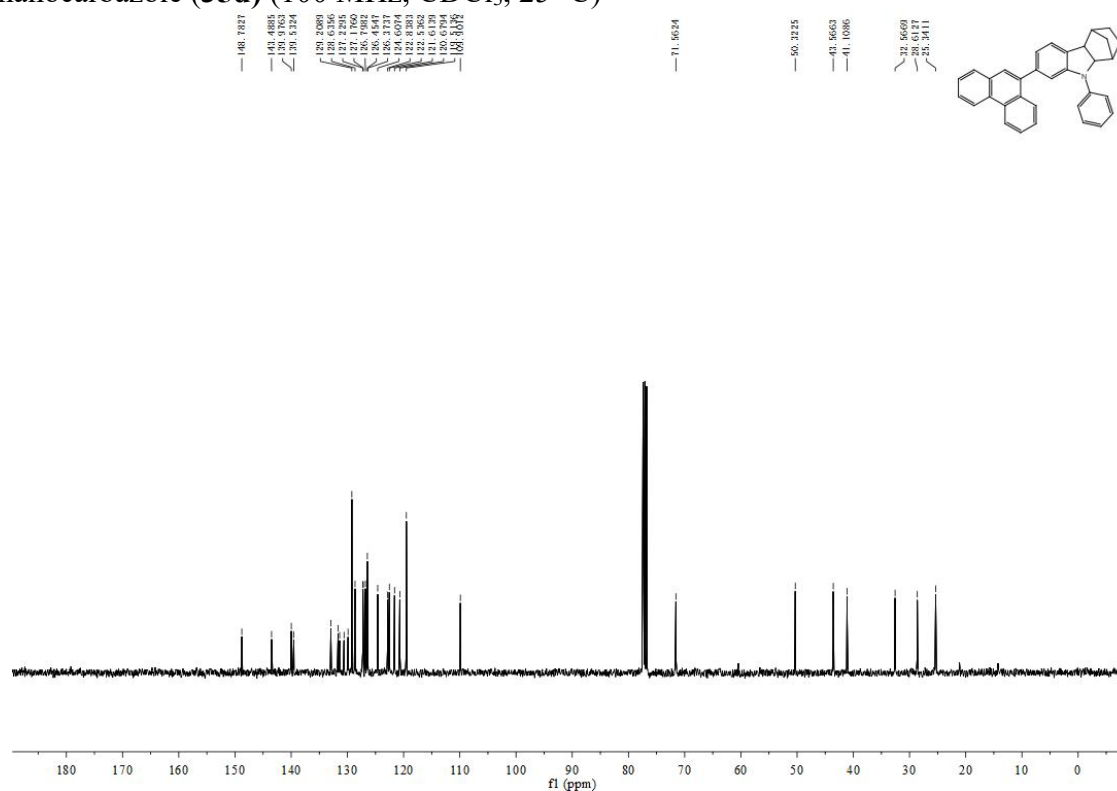
¹³C NMR spectrum of 5-phenyl-2,3,4,4a,5,11b-hexahydro-1H-1,4-methanobenzo[*b*]carbazole (**34d**) (100 MHz, CDCl₃, 25 °C)



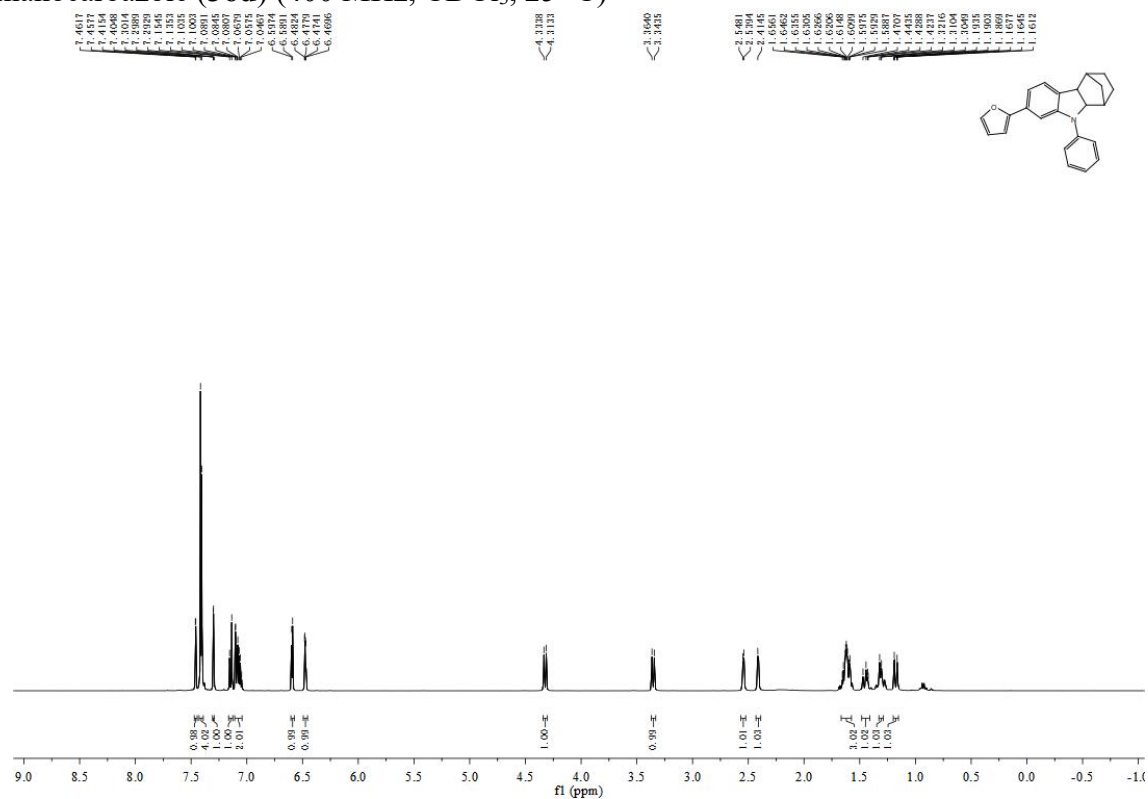
^1H NMR spectrum of 7-(phenanthren-9-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**35d**) (400 MHz, CDCl_3 , 25 °C)



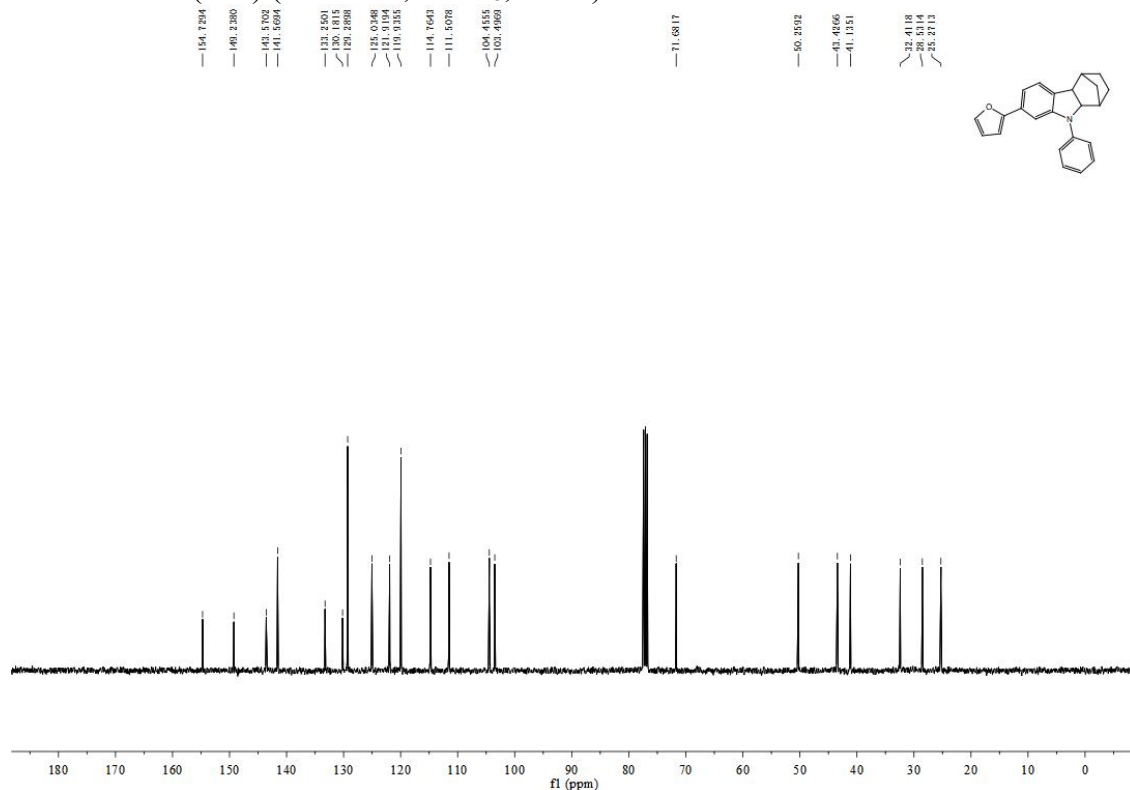
^{13}C NMR spectrum of 7-(phenanthren-9-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**35d**) (100 MHz, CDCl_3 , 25 °C)



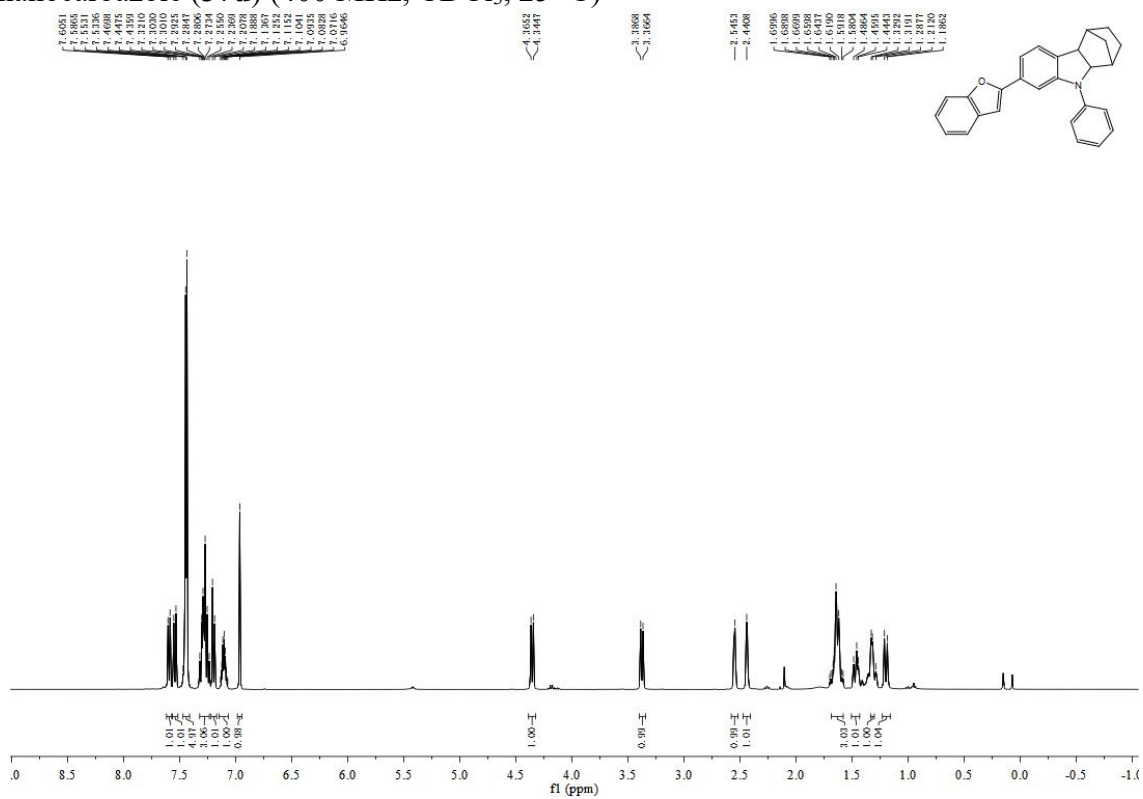
^1H NMR spectrum of 7-(furan-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**36d**) (400 MHz, CDCl_3 , 25 °C)



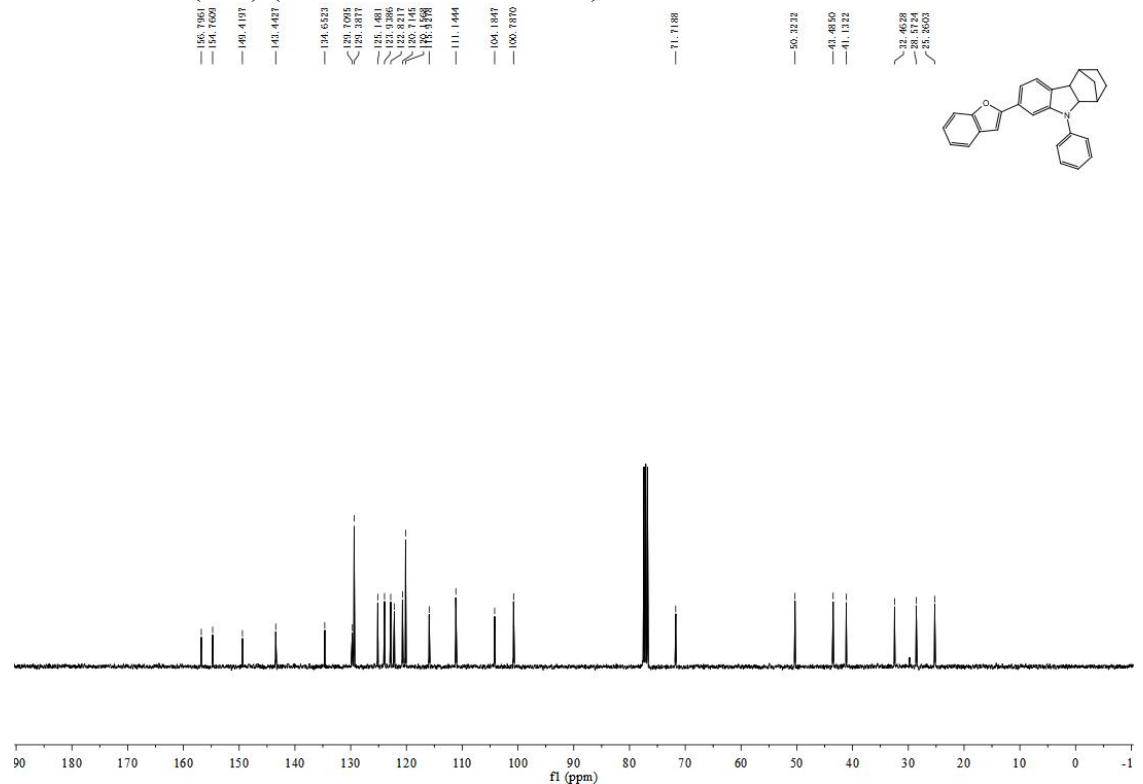
^{13}C NMR spectrum of 7-(furan-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**36d**) (100 MHz, CDCl_3 , 25 °C)



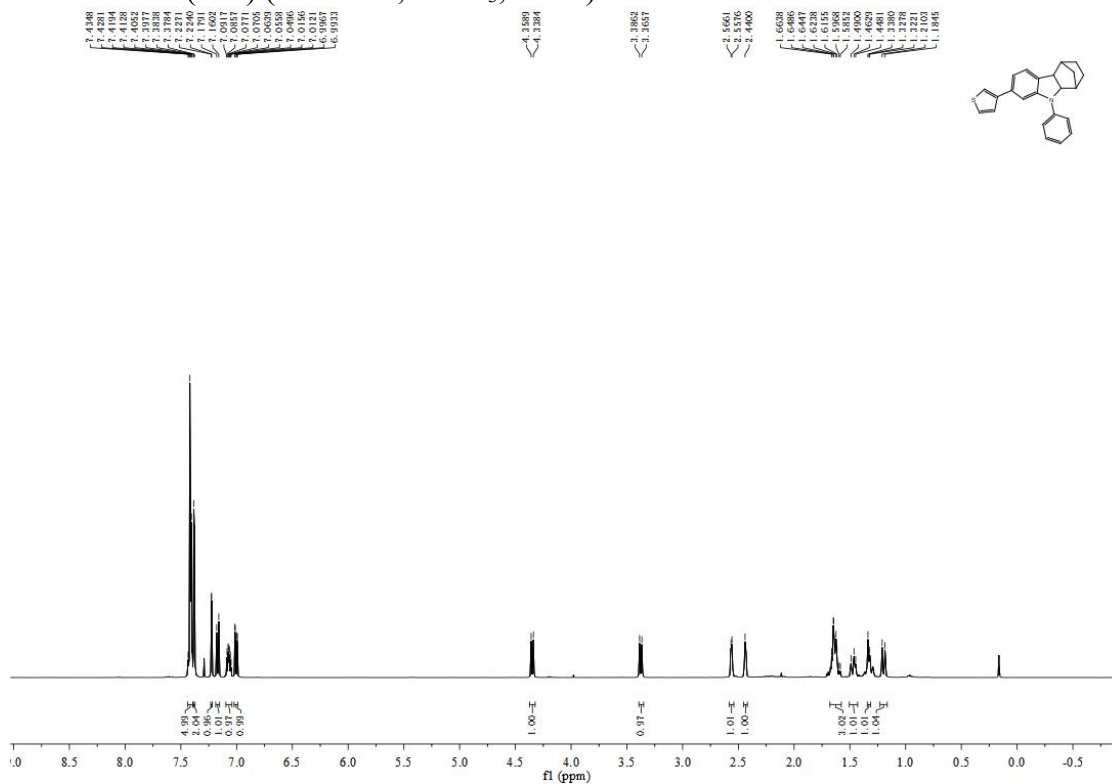
¹H NMR spectrum of 7-(benzofuran-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**37d**) (400 MHz, CDCl₃, 25 °C)



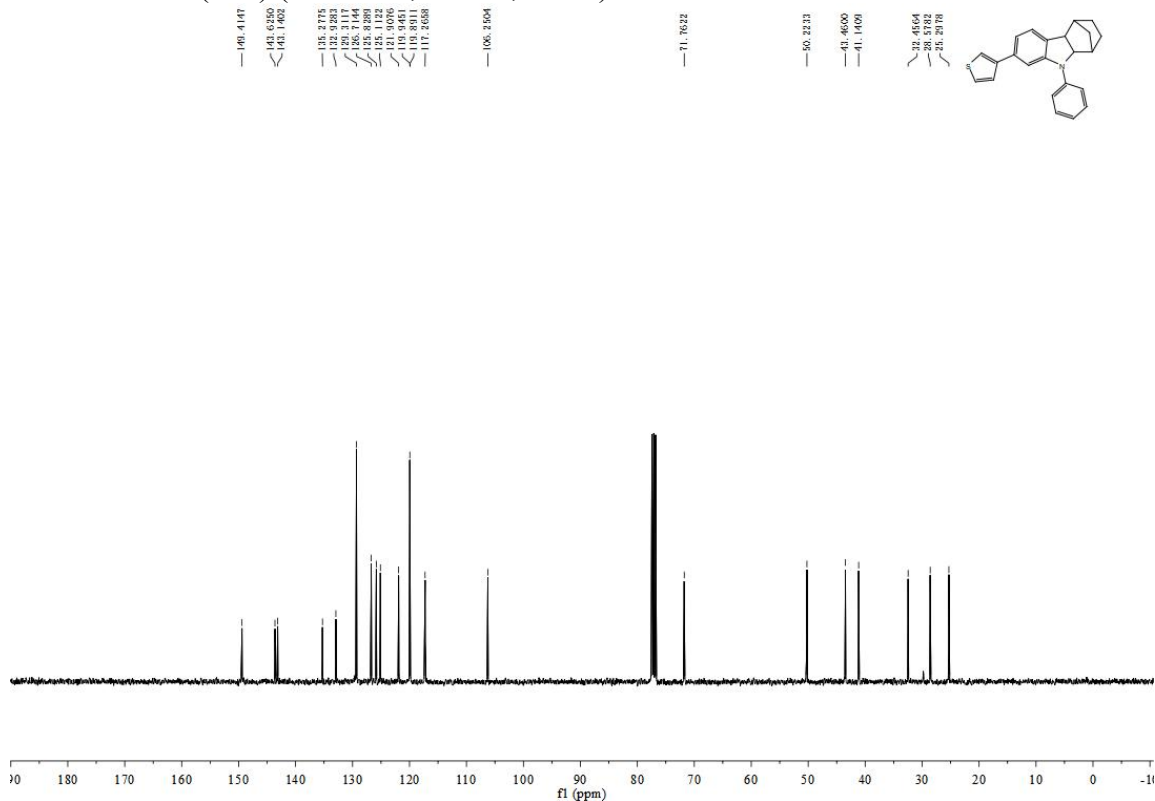
¹³C NMR spectrum of 7-(benzofuran-2-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**37d**) (100 MHz, CDCl₃, 25 °C)



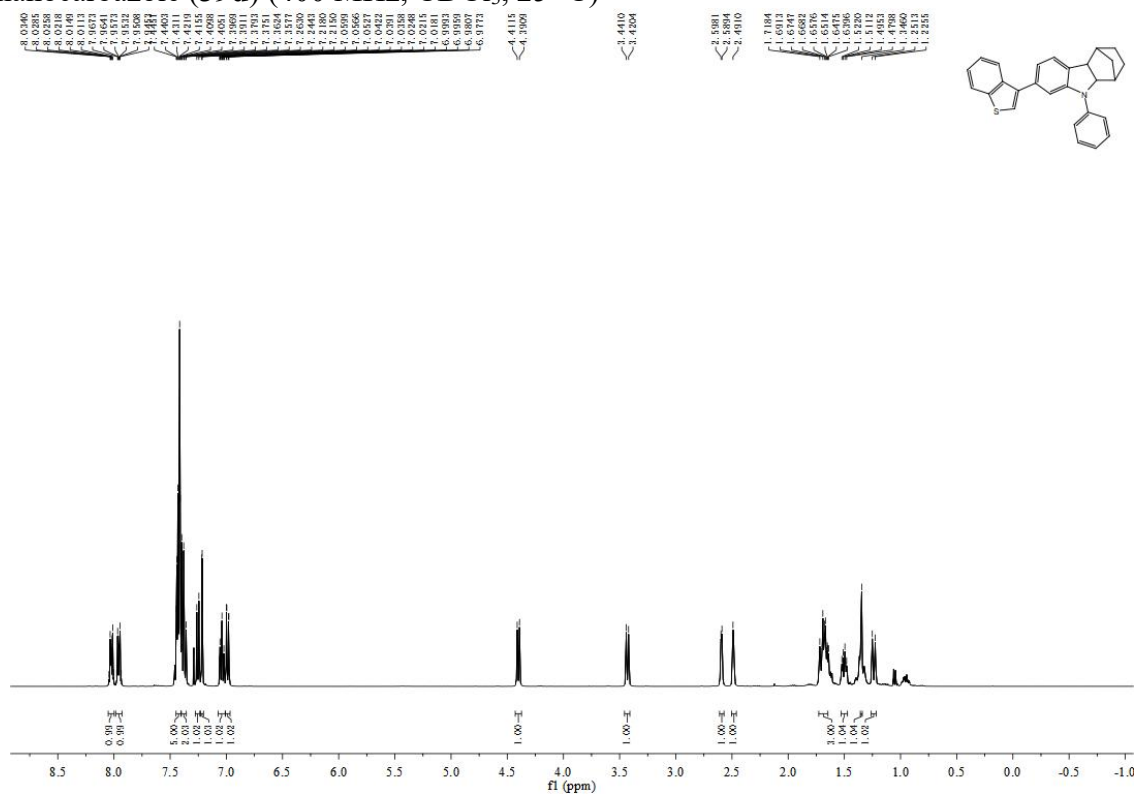
¹H NMR spectrum of 9-phenyl-7-(thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**38d**) (400 MHz, CDCl₃, 25 °C)



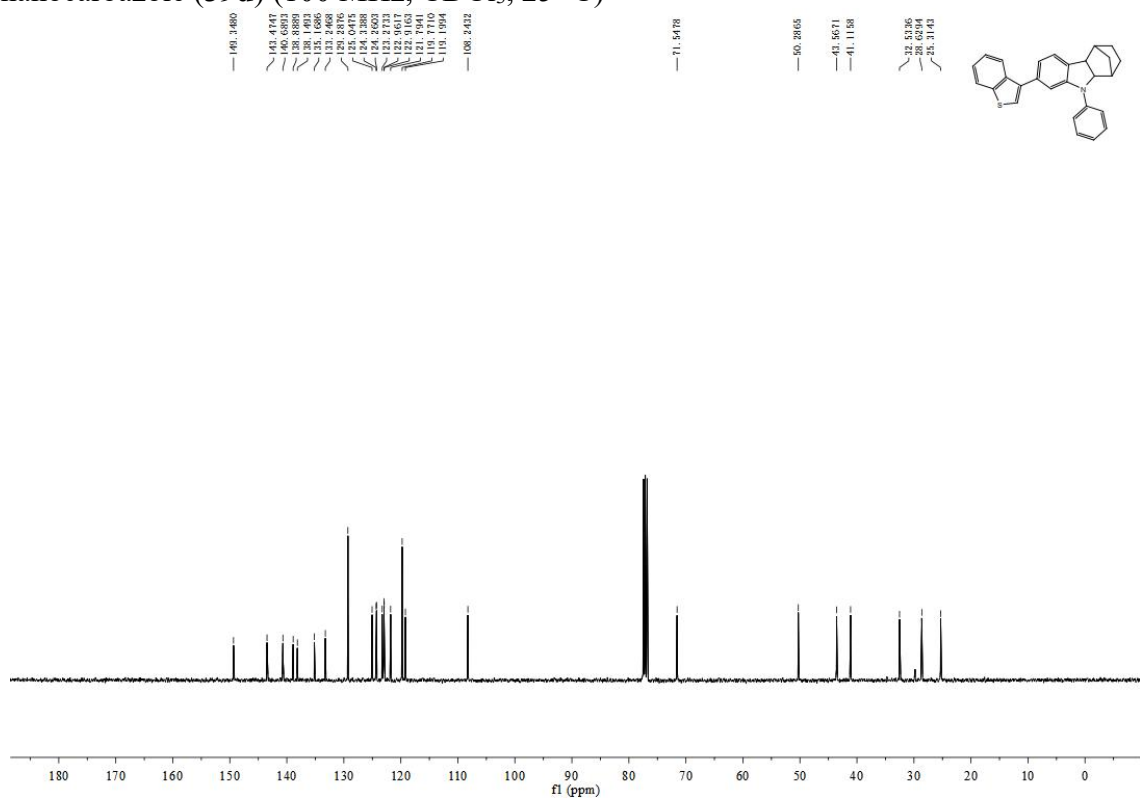
¹³C NMR spectrum of 9-phenyl-7-(thiophen-3-yl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**38d**) (100 MHz, CDCl₃, 25 °C)



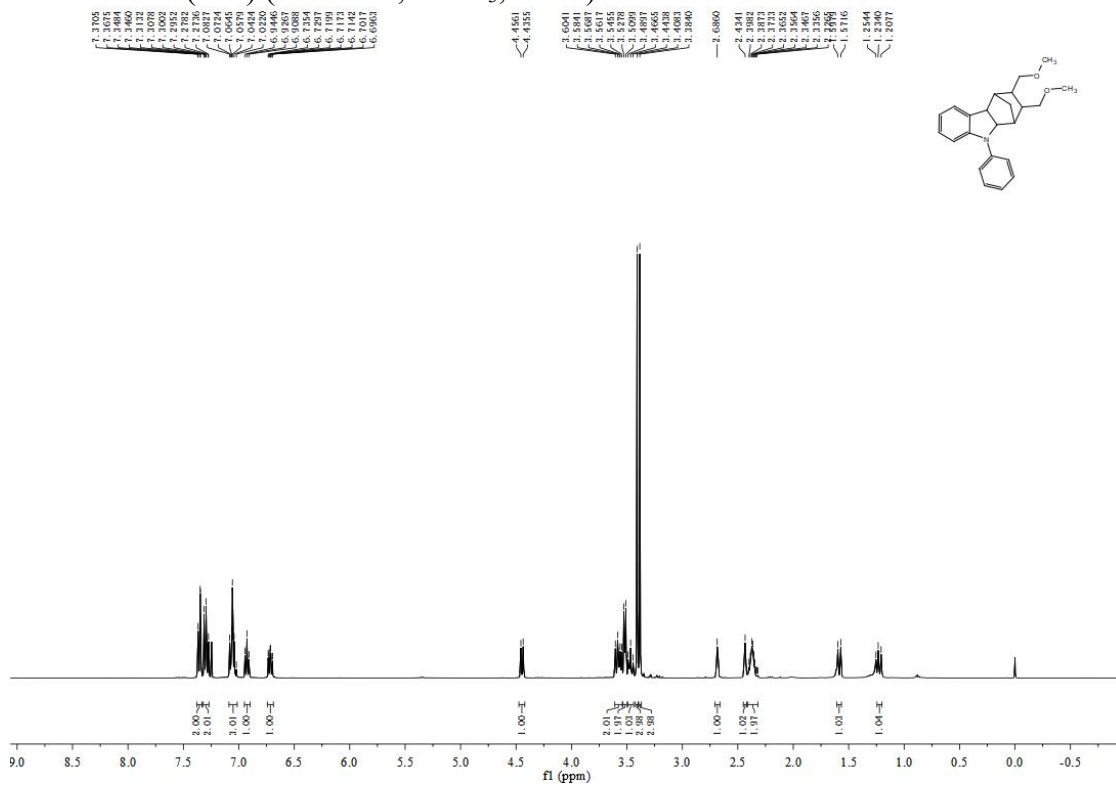
¹H NMR spectrum of 7-(benzo[*b*]thiophen-3-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**39d**) (400 MHz, CDCl₃, 25 °C)



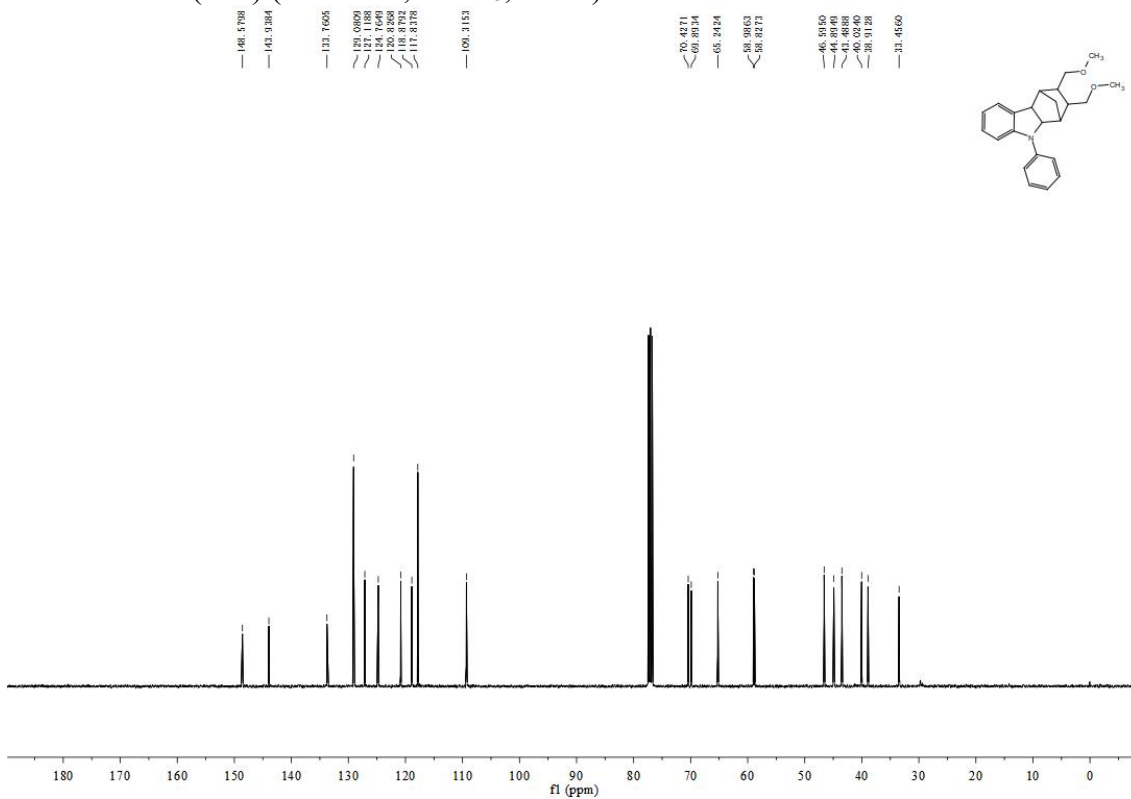
¹³C NMR spectrum of 7-(benzo[*b*]thiophen-3-yl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**39d**) (100 MHz, CDCl₃, 25 °C)



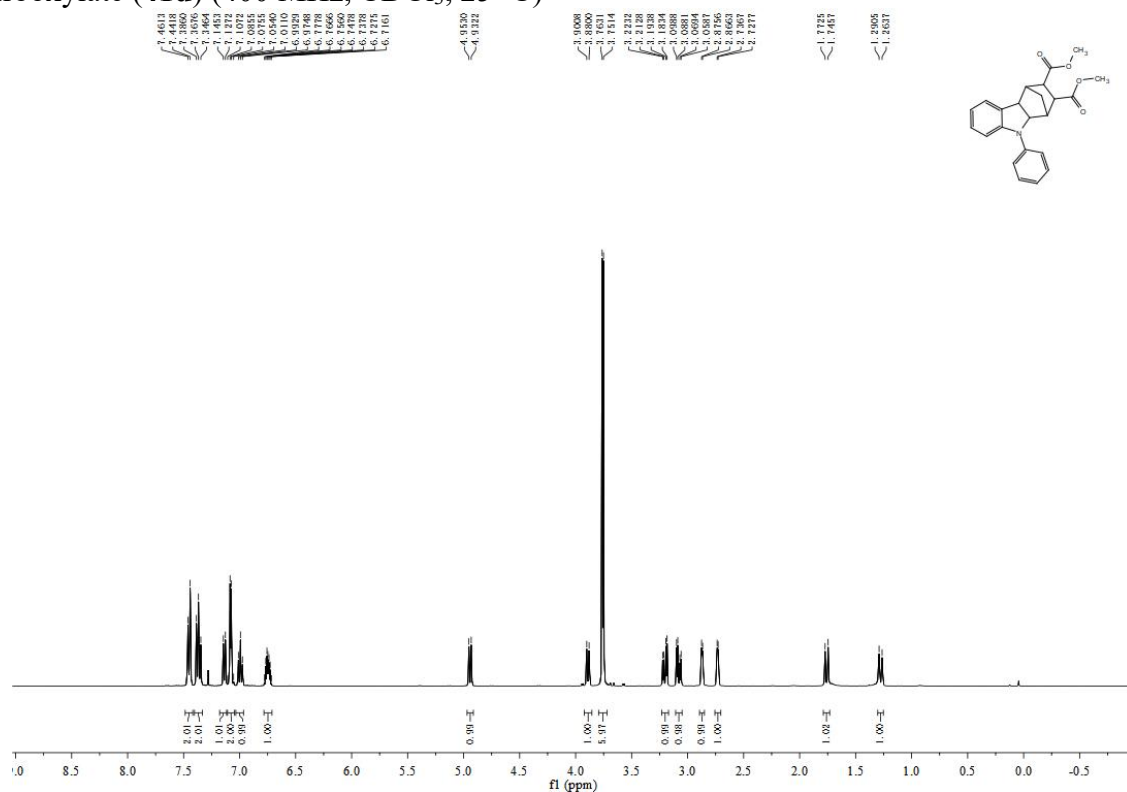
¹H NMR spectrum of 2,3-bis(methoxymethyl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**40d**) (400 MHz, CDCl₃, 25 °C)



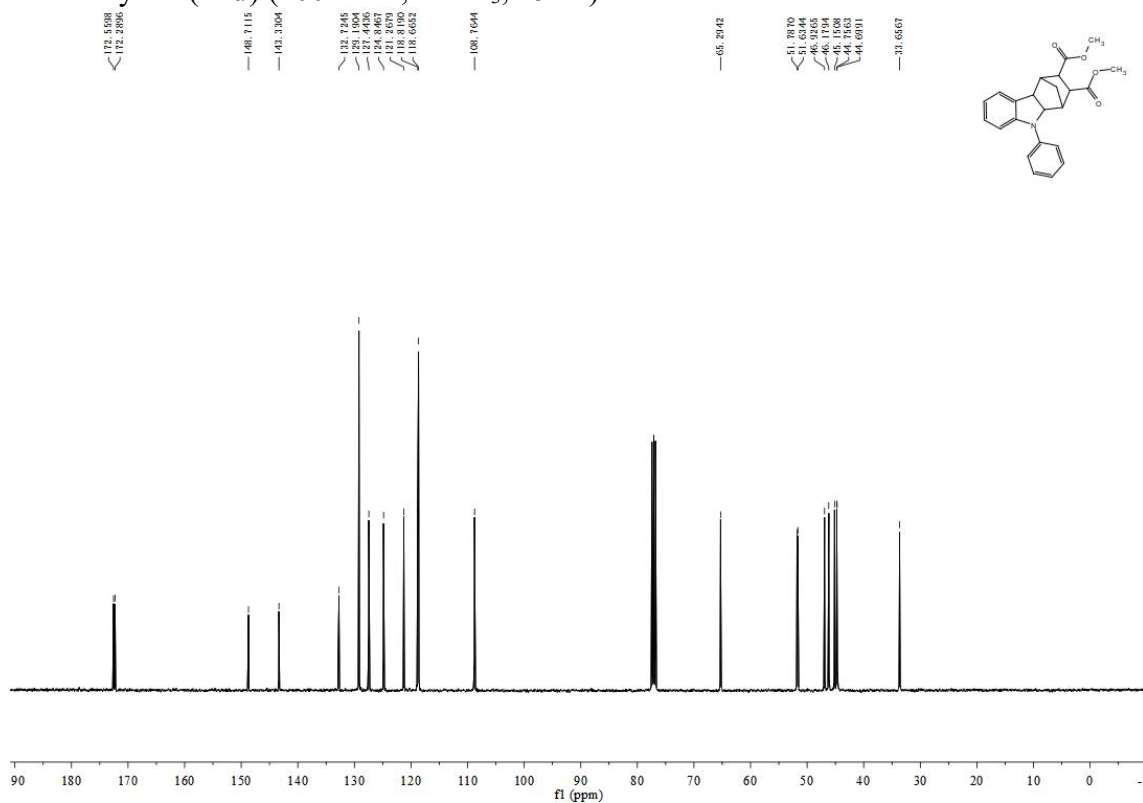
¹³C NMR spectrum of 2,3-bis(methoxymethyl)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**40d**) (100 MHz, CDCl₃, 25 °C)



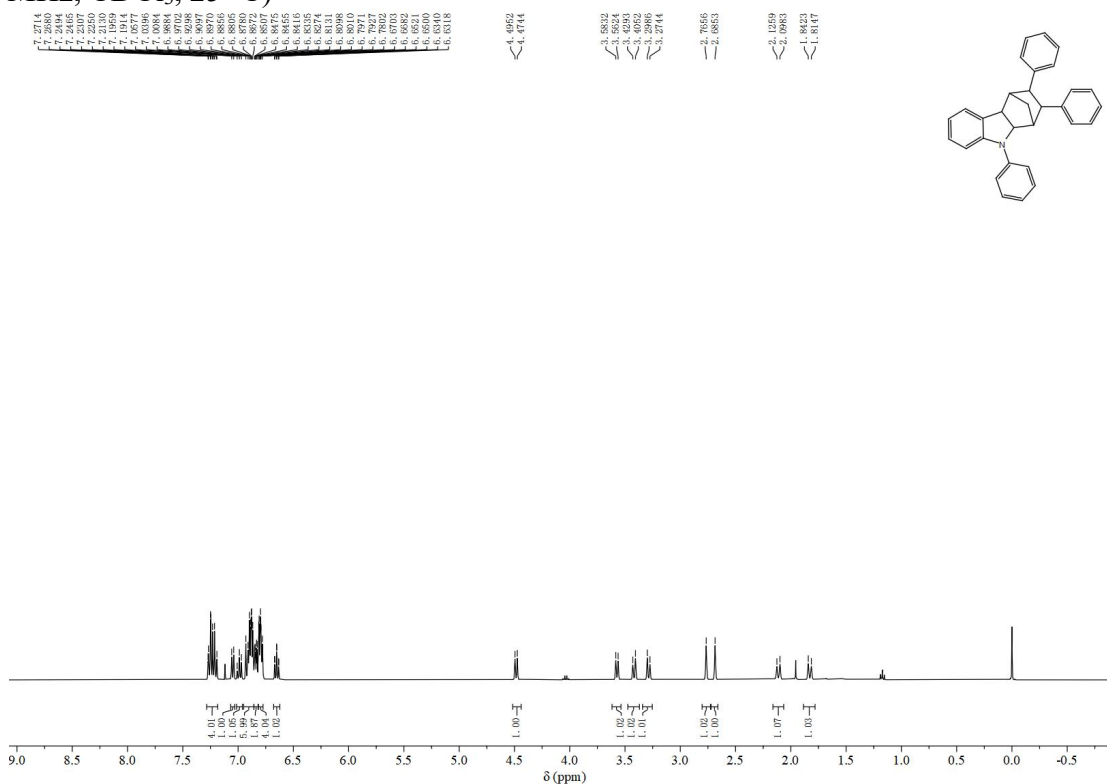
¹H NMR spectrum of dimethyl 9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole-2,3-dicarboxylate (**41d**) (400 MHz, CDCl₃, 25 °C)



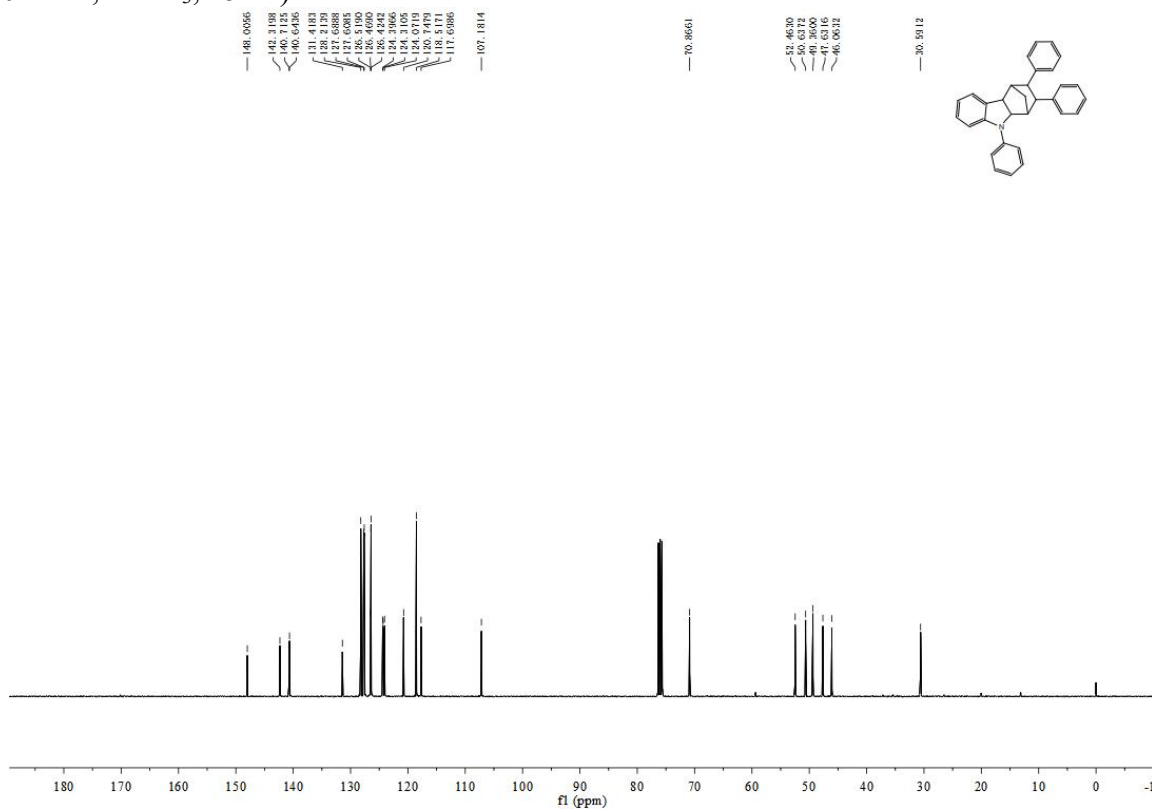
¹³C NMR spectrum of dimethyl 9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole-2,3-dicarboxylate (**41d**) (100 MHz, CDCl₃, 25 °C)



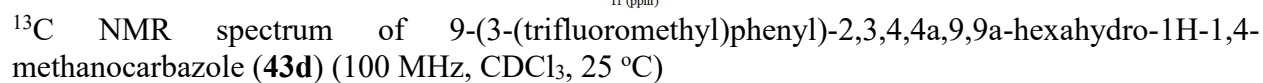
^1H NMR spectrum of 2,3,9-triphenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**42d**) (400 MHz, CDCl_3 , 25 °C)



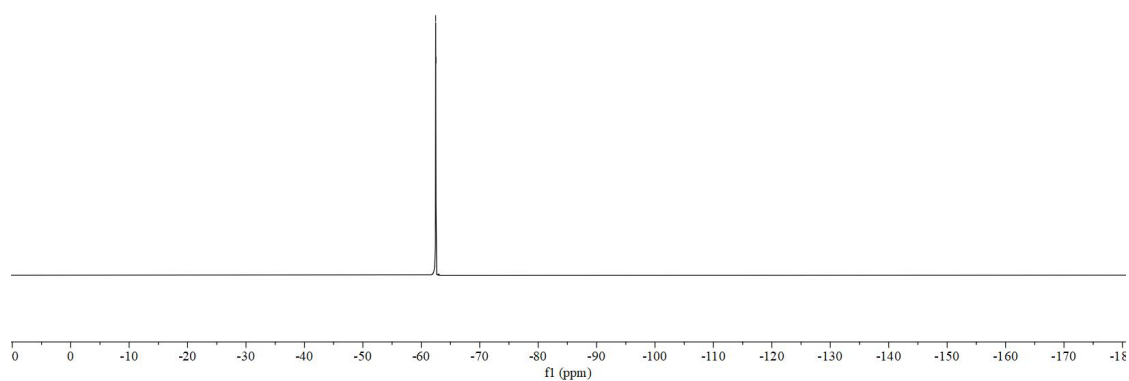
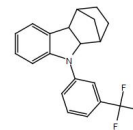
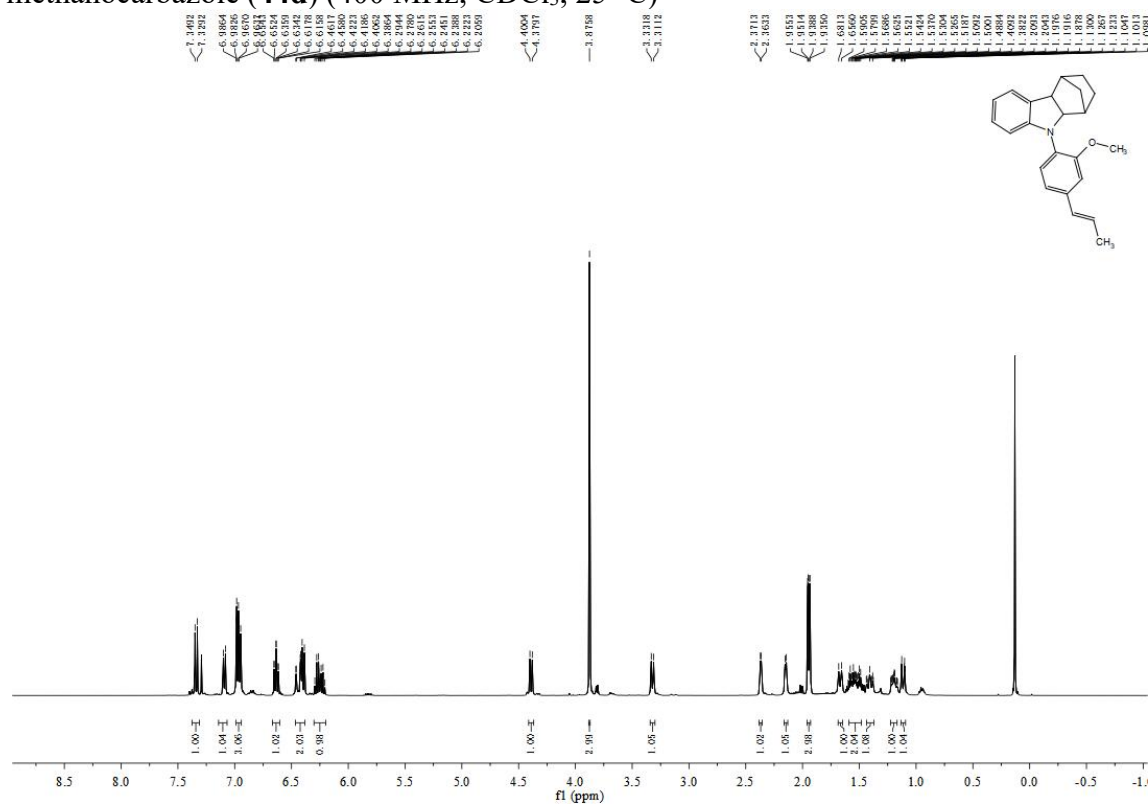
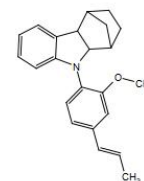
^{13}C NMR spectrum of 2,3,9-triphenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**42d**) (100 MHz, CDCl_3 , 25 °C)



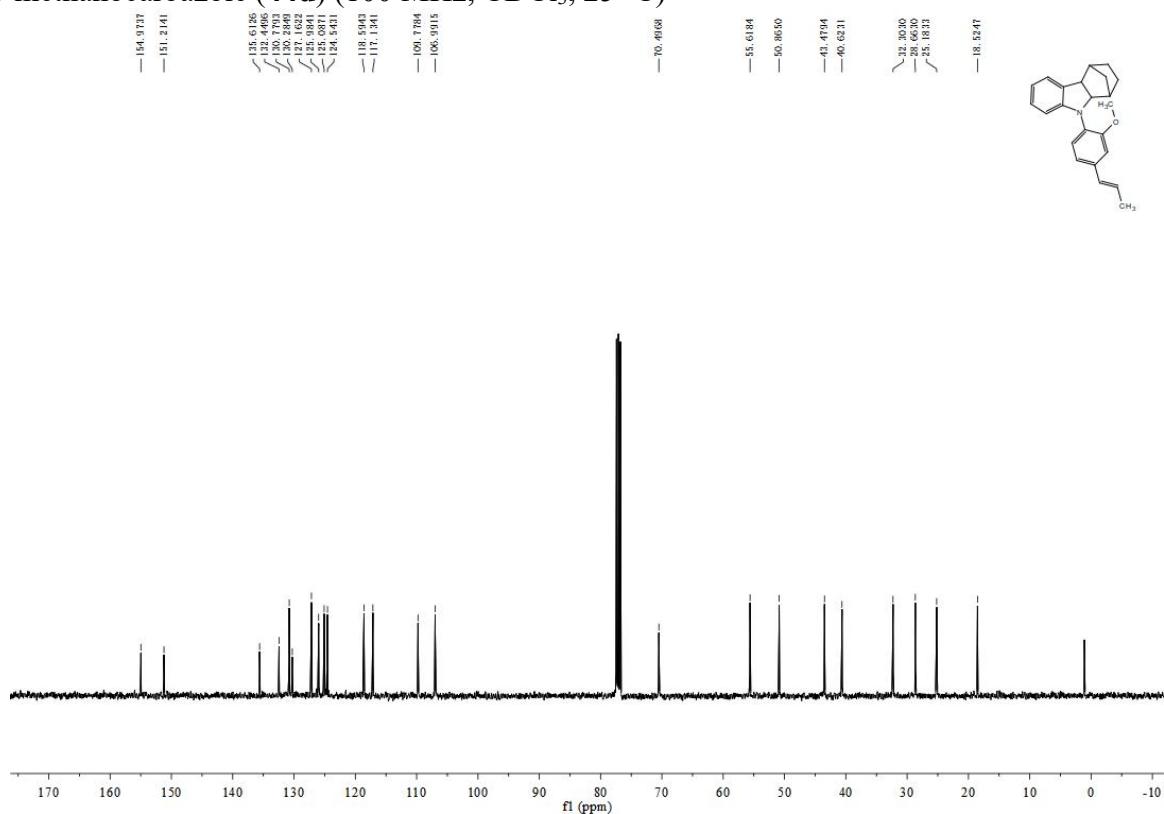

-7.5462
-7.5452
-7.4988
-7.4176
-7.3990
-7.3801
-7.1811
-7.1517
-7.1197
-7.1187
-7.0823
-7.0440
-7.0054
-6.7817
-6.7809
-6.7454



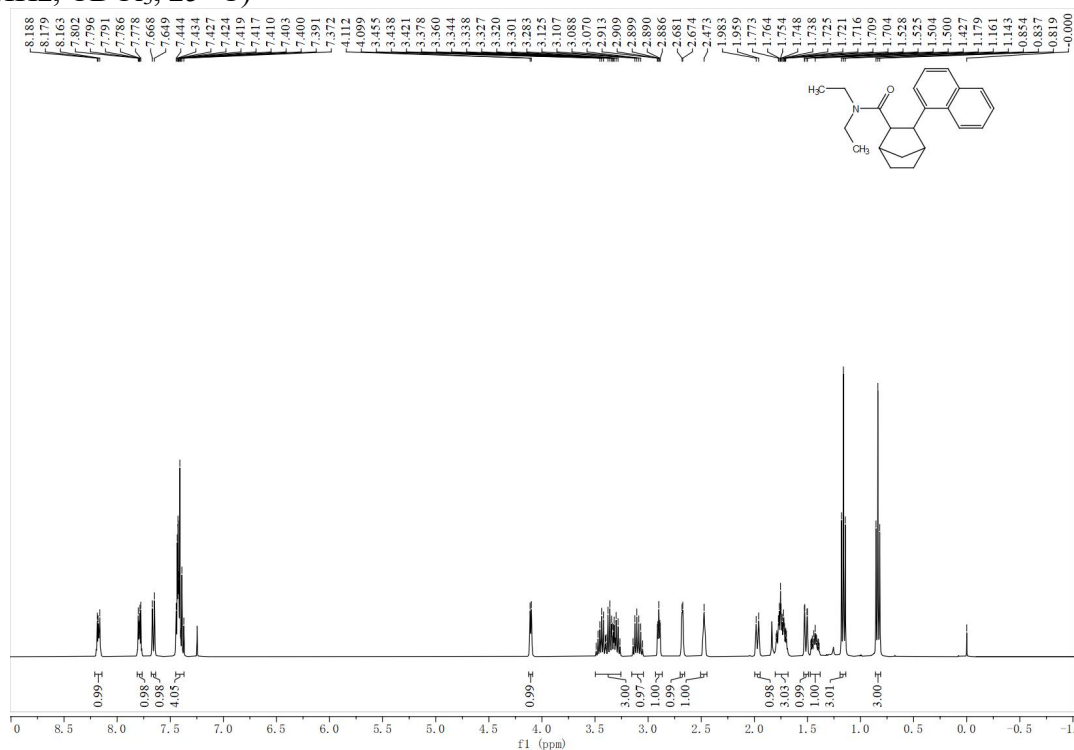
Y-62, 4603
Y-62, 5057


$$\begin{array}{r} 7.3492 \\ - 7.3292 \\ \hline \end{array}$$


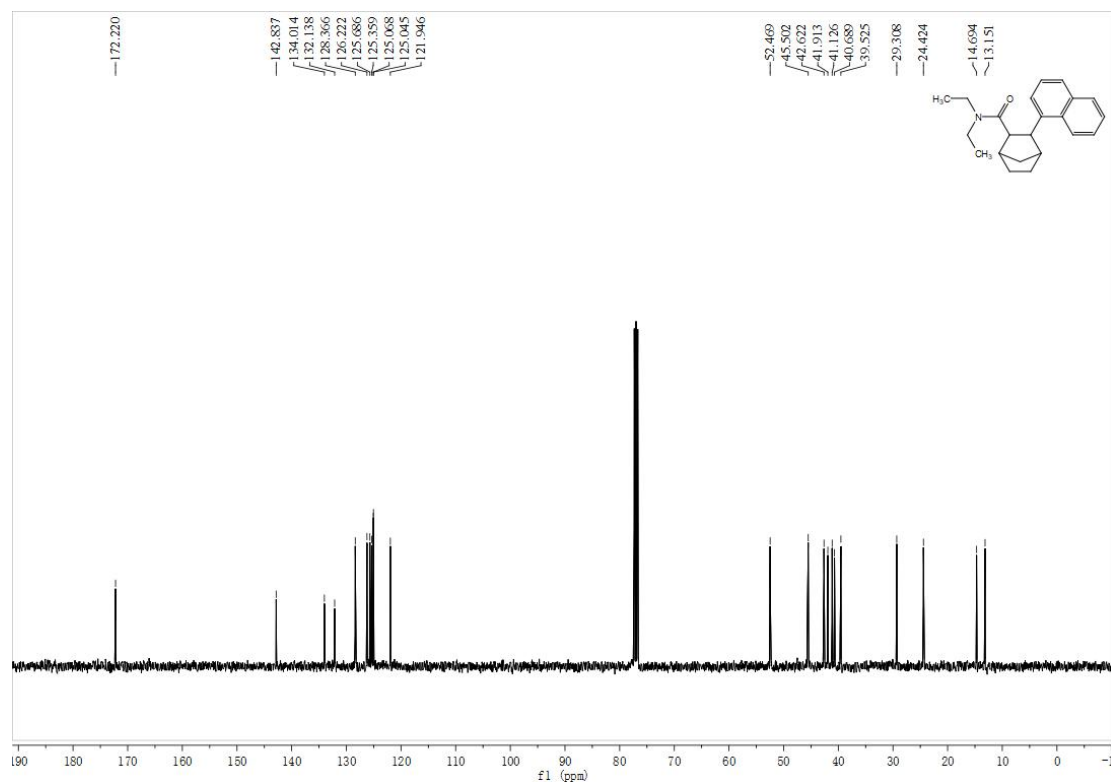
^{13}C NMR spectrum of (*E*)-9-(2-methoxy-4-(prop-1-en-1-yl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**44d**) (100 MHz, CDCl_3 , 25 °C)



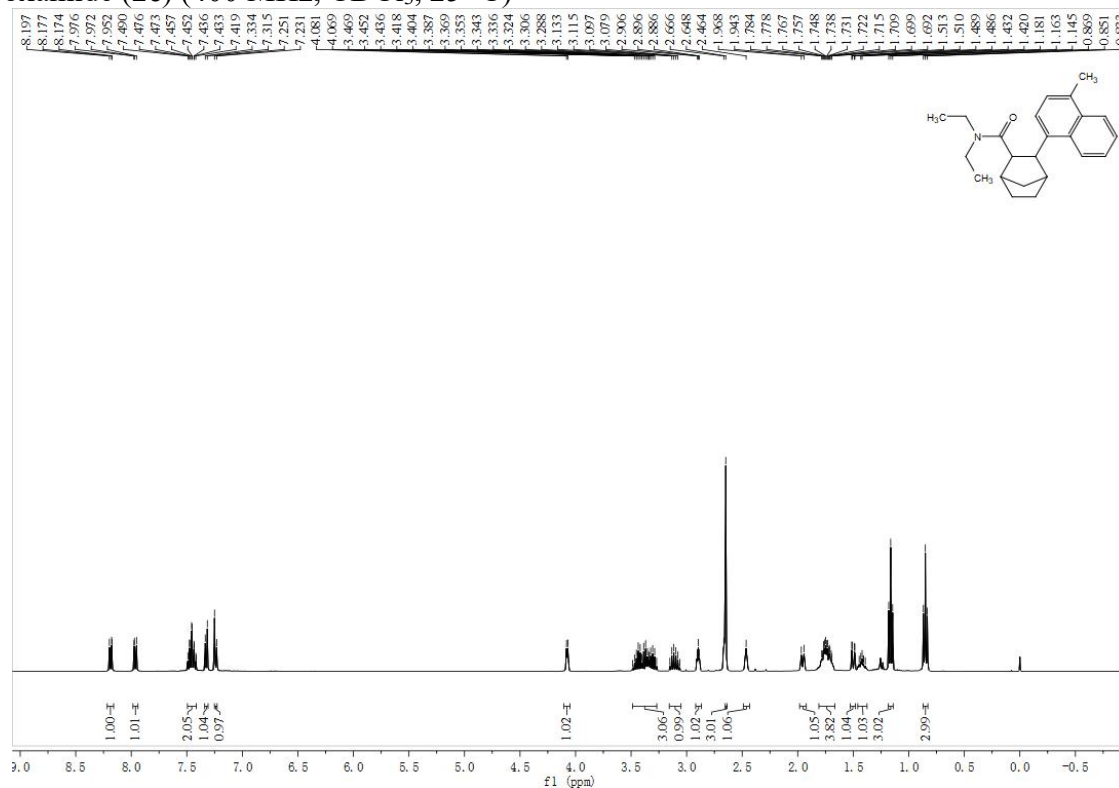
^1H NMR spectrum of *N,N*-diethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**1e**) (400 MHz, CDCl_3 , 25 °C)



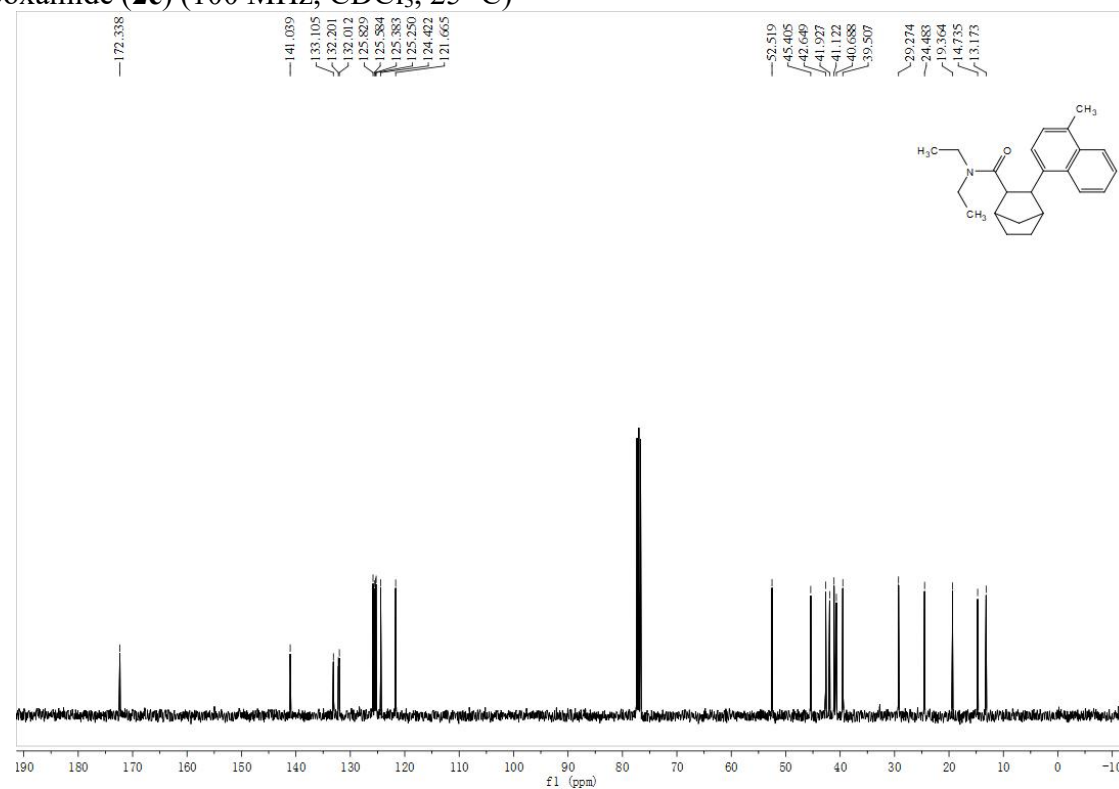
^{13}C NMR spectrum of *N,N*-diethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**1e**) (100 MHz, CDCl_3 , 25 °C)



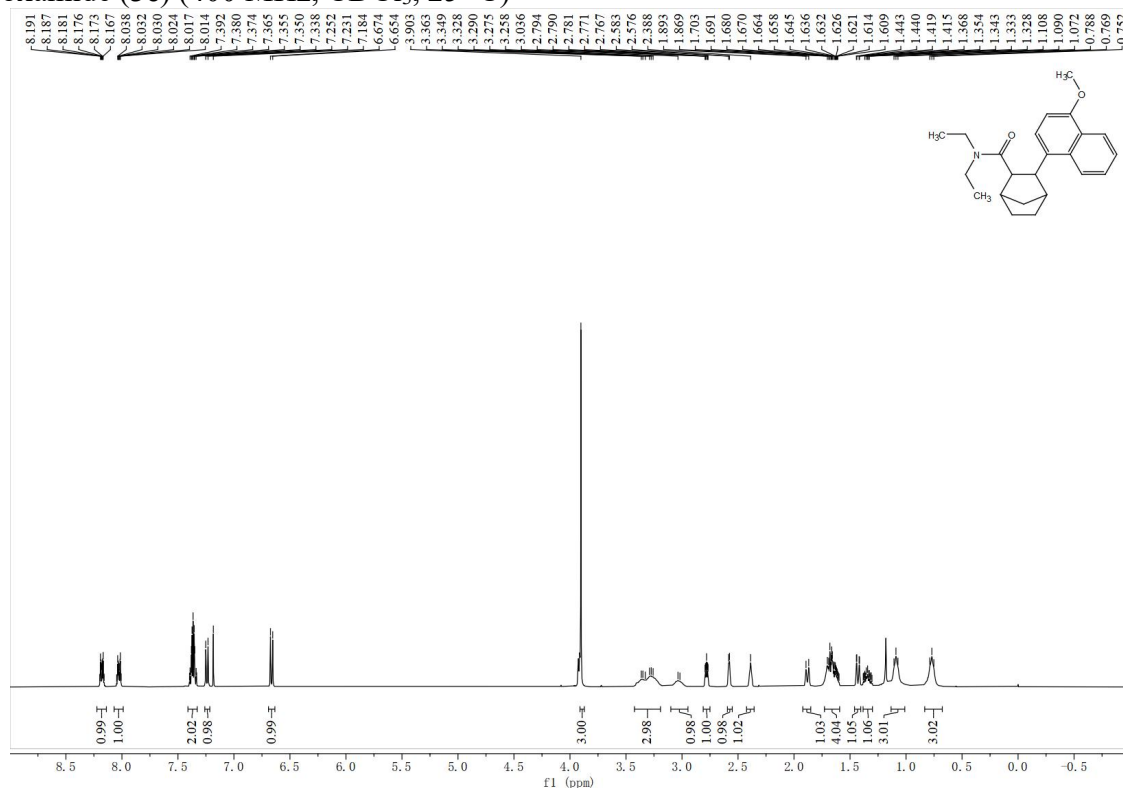
^1H NMR spectrum of *N,N*-diethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**2e**) (400 MHz, CDCl_3 , 25 °C)



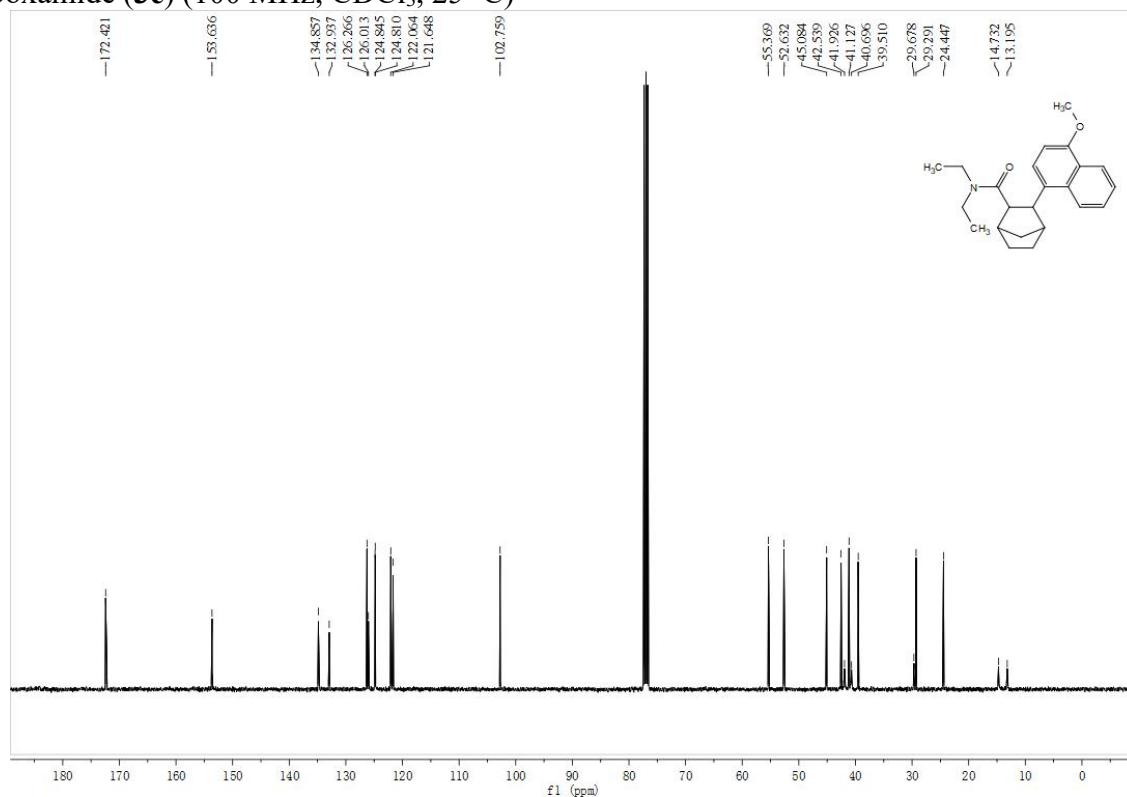
^{13}C NMR spectrum of *N,N*-diethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**2e**) (100 MHz, CDCl_3 , 25 °C)



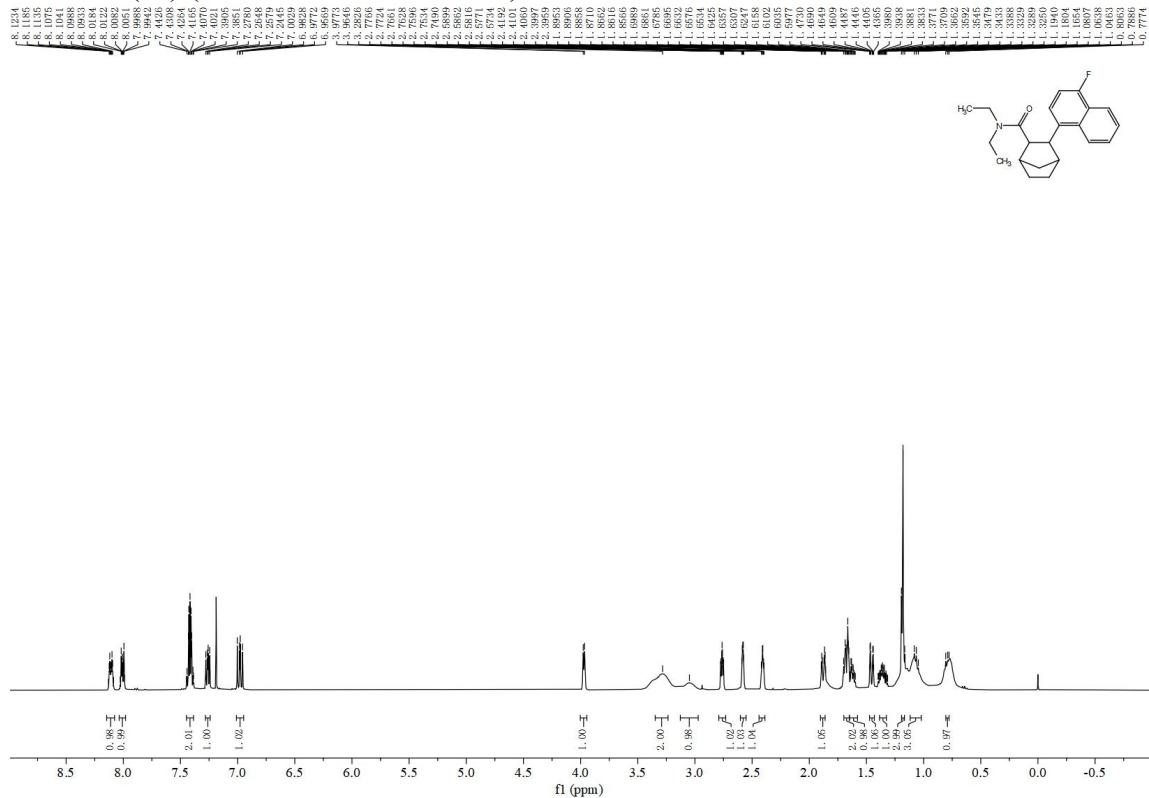
¹H NMR spectrum of *N,N*-diethyl-3-(4-methoxynaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**3e**) (400 MHz, CDCl₃, 25 °C)



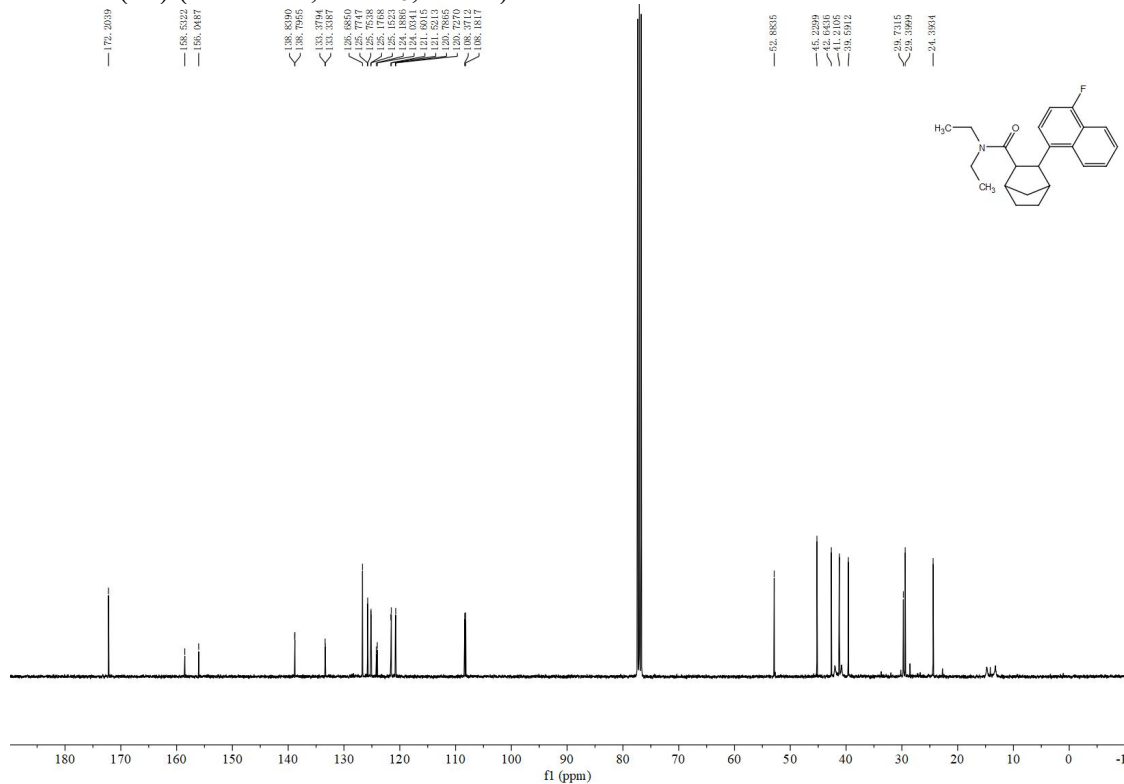
¹³C NMR spectrum of *N,N*-diethyl-3-(4-methoxynaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**3e**) (100 MHz, CDCl₃, 25 °C)



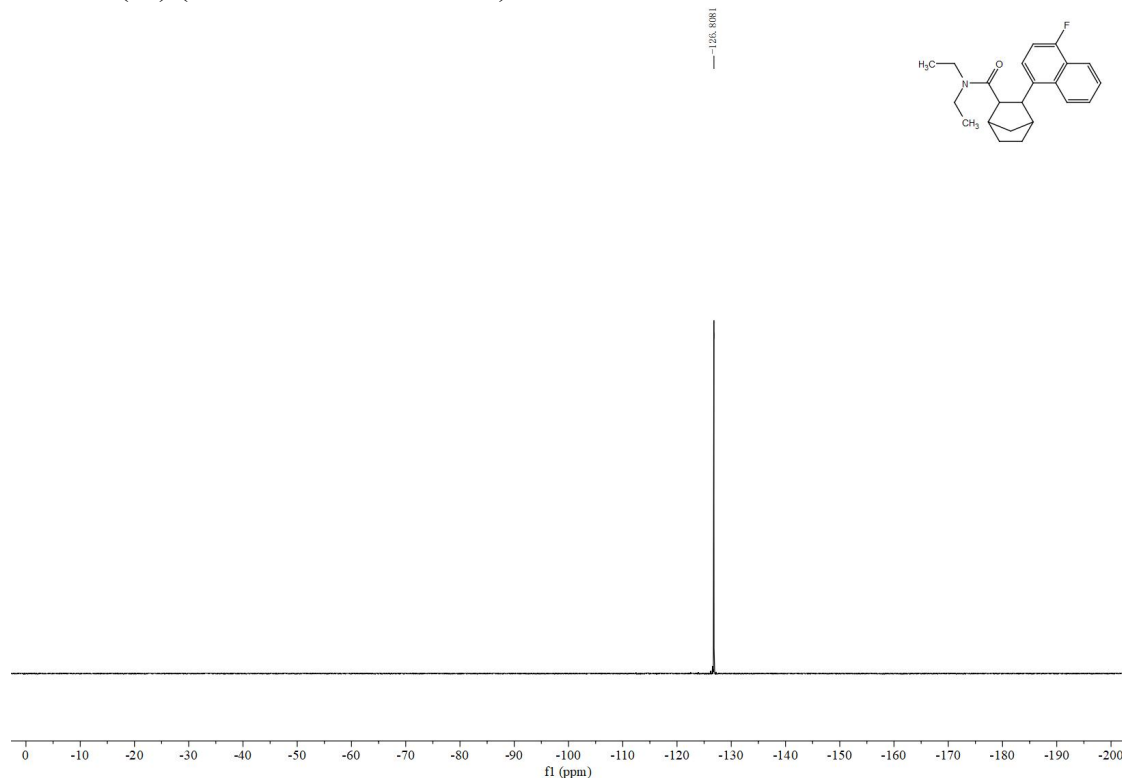
^1H NMR spectrum of *N,N*-diethyl-3-(4-fluoronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**4e**) (400 MHz, CDCl_3 , 25 °C)



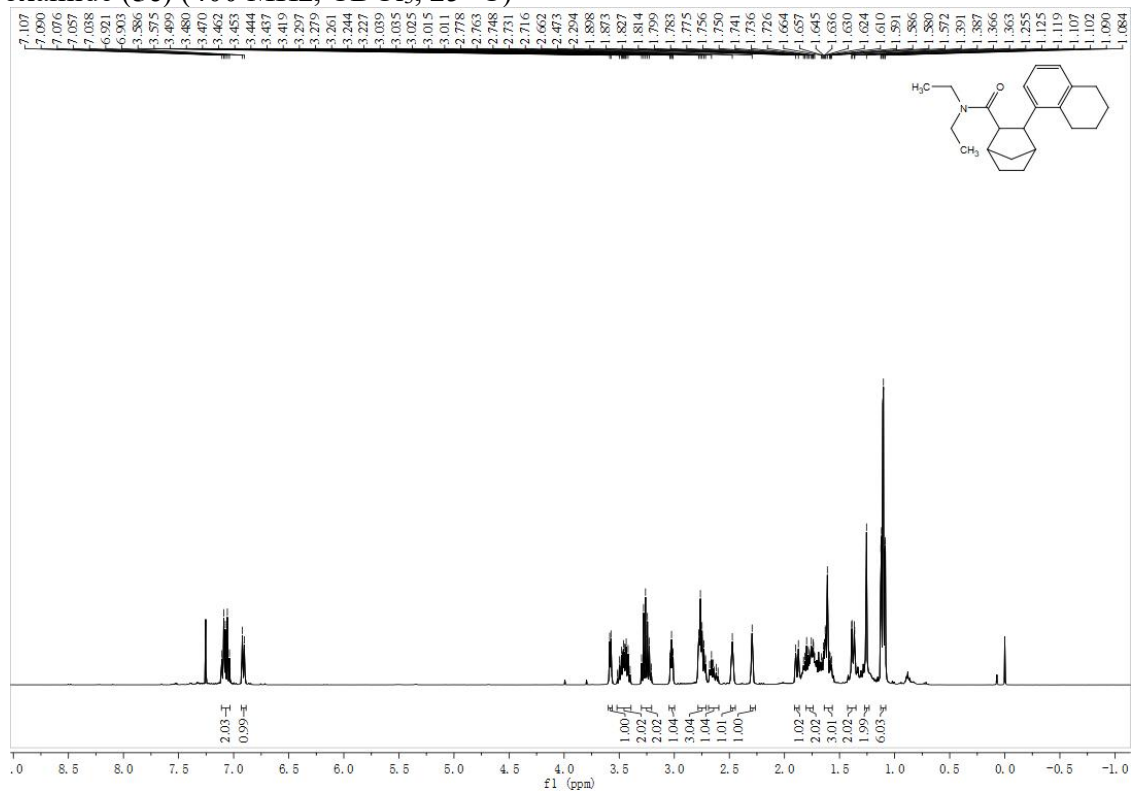
^{13}C NMR spectrum of *N,N*-diethyl-3-(4-fluoronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**4e**) (100 MHz, CDCl_3 , 25 °C)



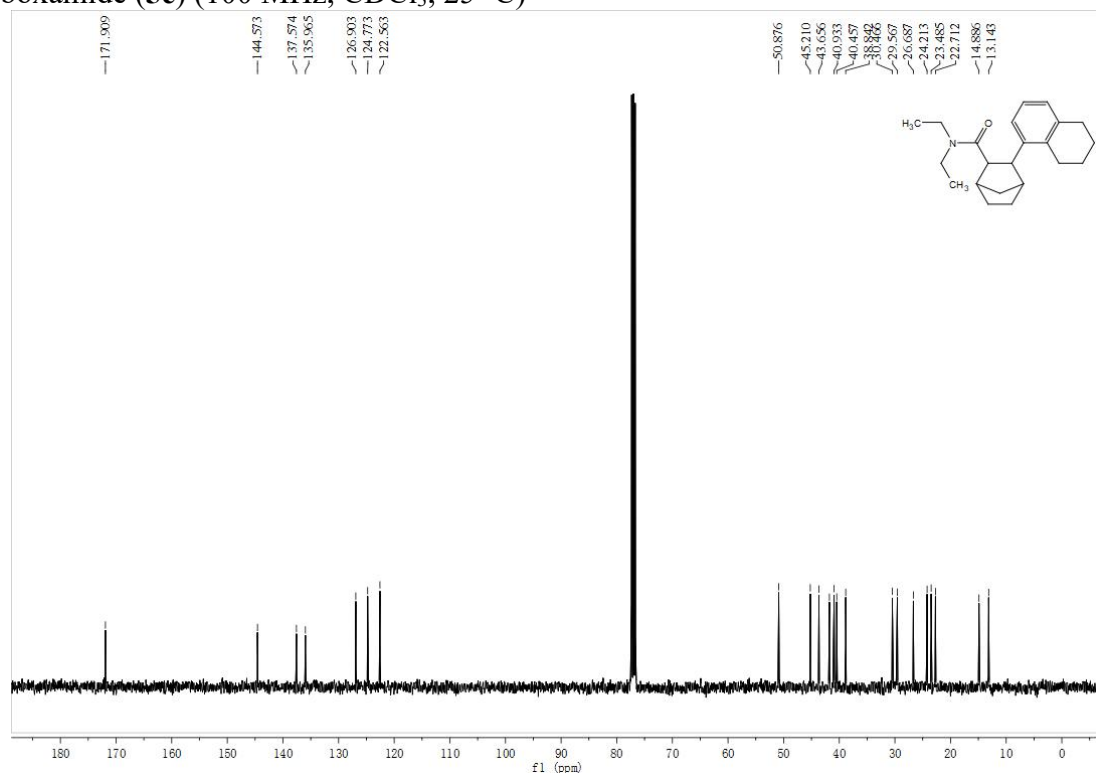
^{19}F NMR spectrum of *N,N*-diethyl-3-(4-fluoronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**4e**) (376 MHz, CDCl_3 , 25 °C)



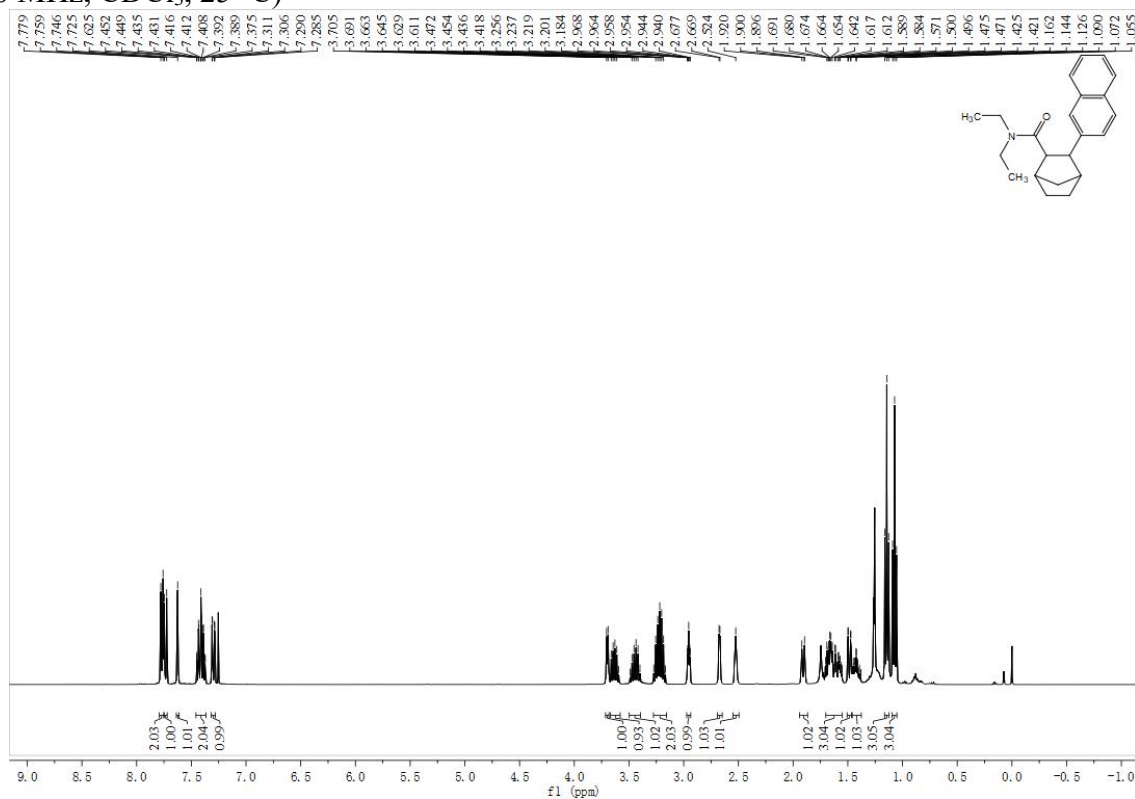
^1H NMR spectrum of *N,N*-diethyl-3-(5,6,7,8-tetrahydronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**5e**) (400 MHz, CDCl_3 , 25 °C)



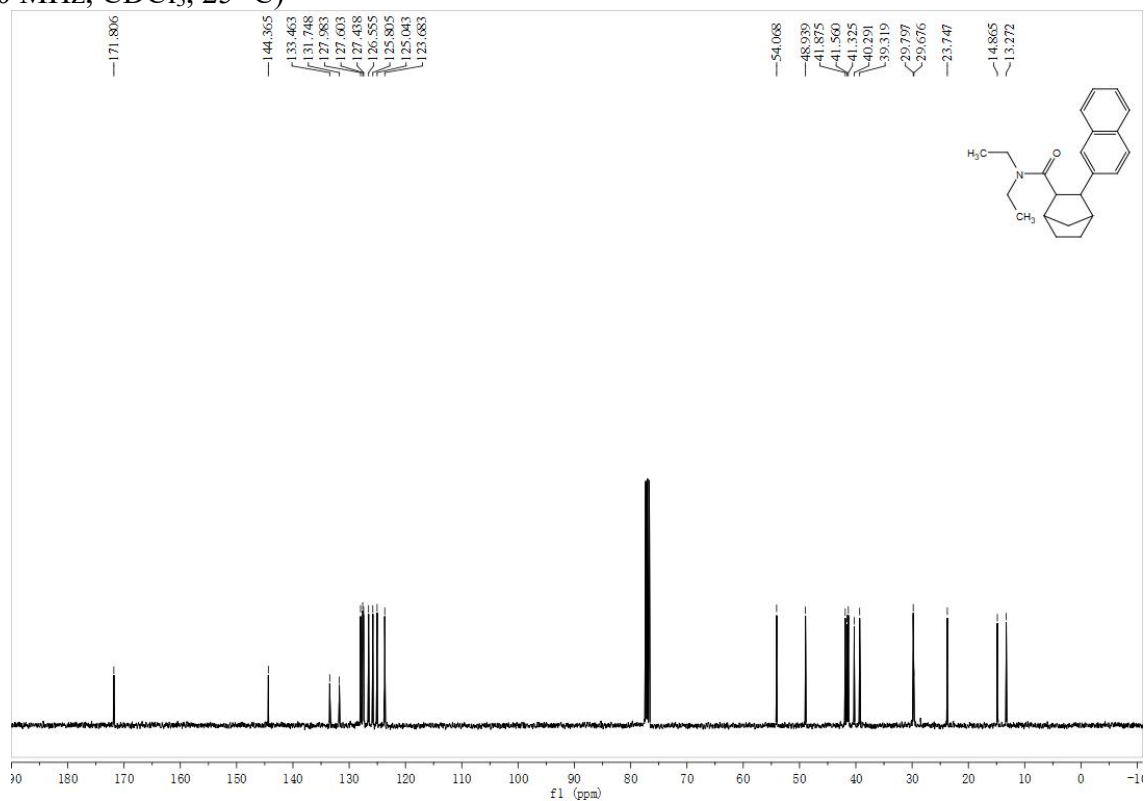
^{13}C NMR spectrum of *N,N*-diethyl-3-(5,6,7,8-tetrahydronaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**5e**) (100 MHz, CDCl_3 , 25 °C)



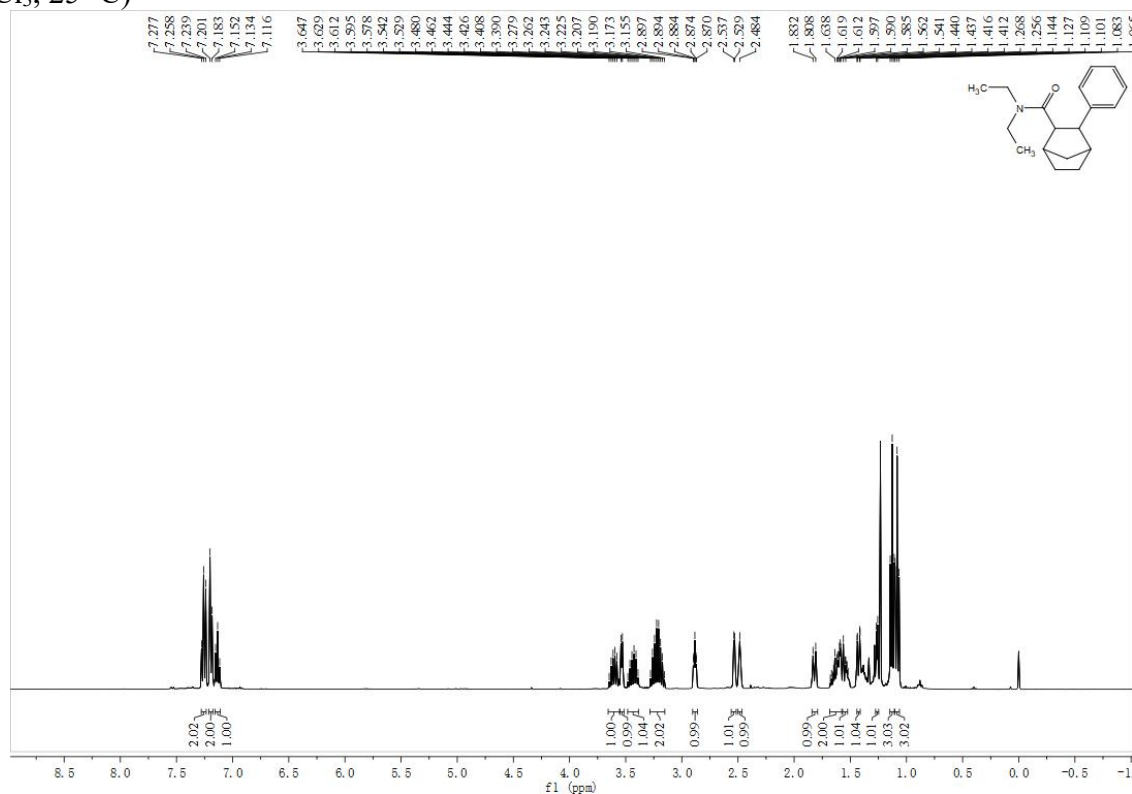
^1H NMR spectrum of *N,N*-diethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**6e**) (400 MHz, CDCl_3 , 25 °C)



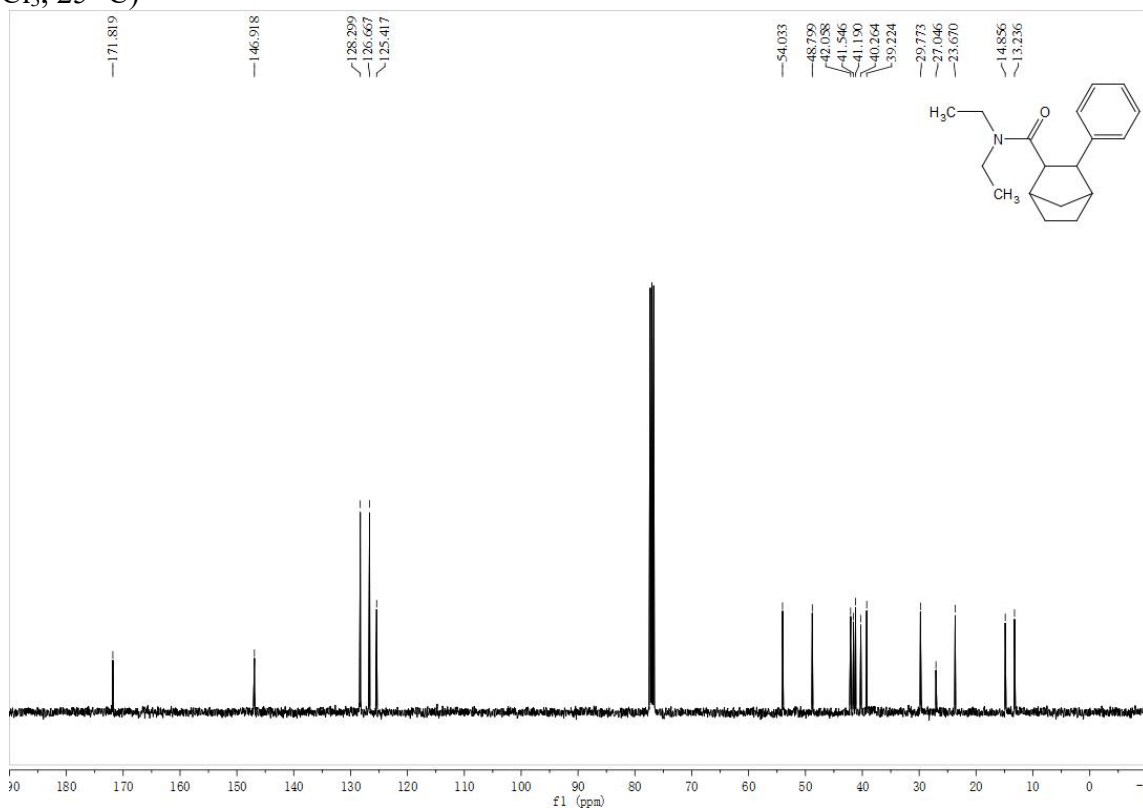
^{13}C NMR spectrum of *N,N*-diethyl-3-(naphthalen-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**6e**) (100 MHz, CDCl_3 , 25 °C)



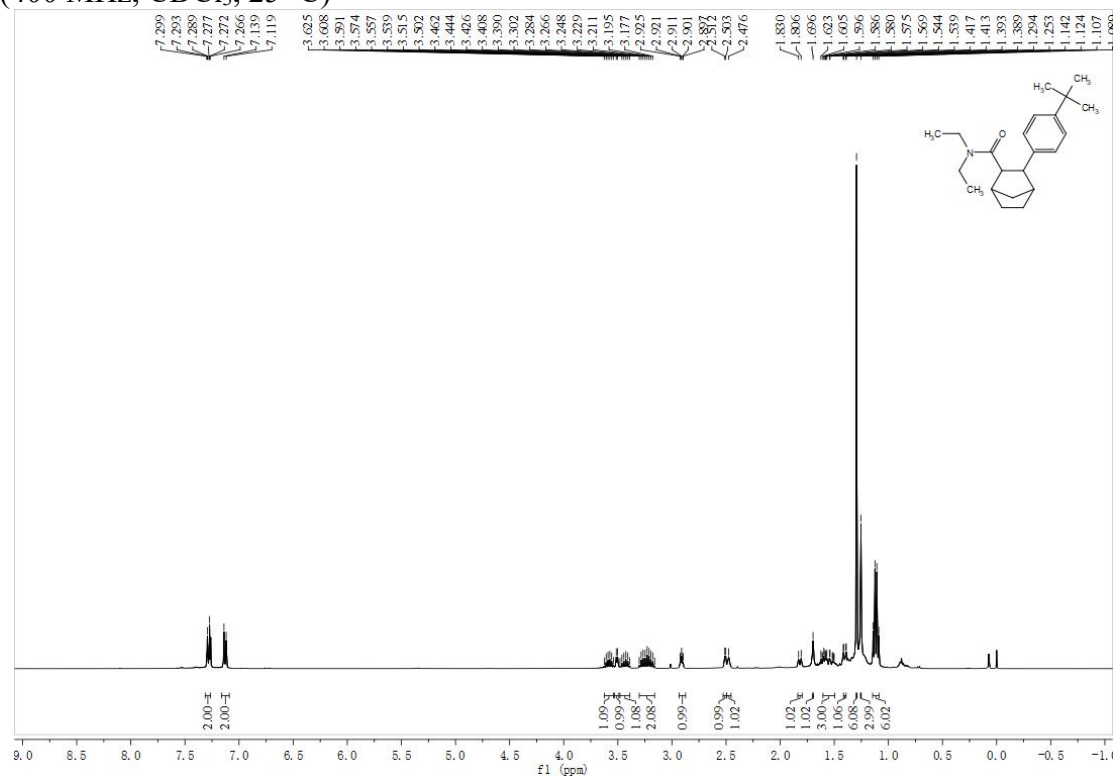
^1H NMR spectrum of *N,N*-diethyl-3-phenylbicyclo[2.2.1]heptane-2-carboxamide (**7e**) (400 MHz, CDCl_3 , 25 °C)



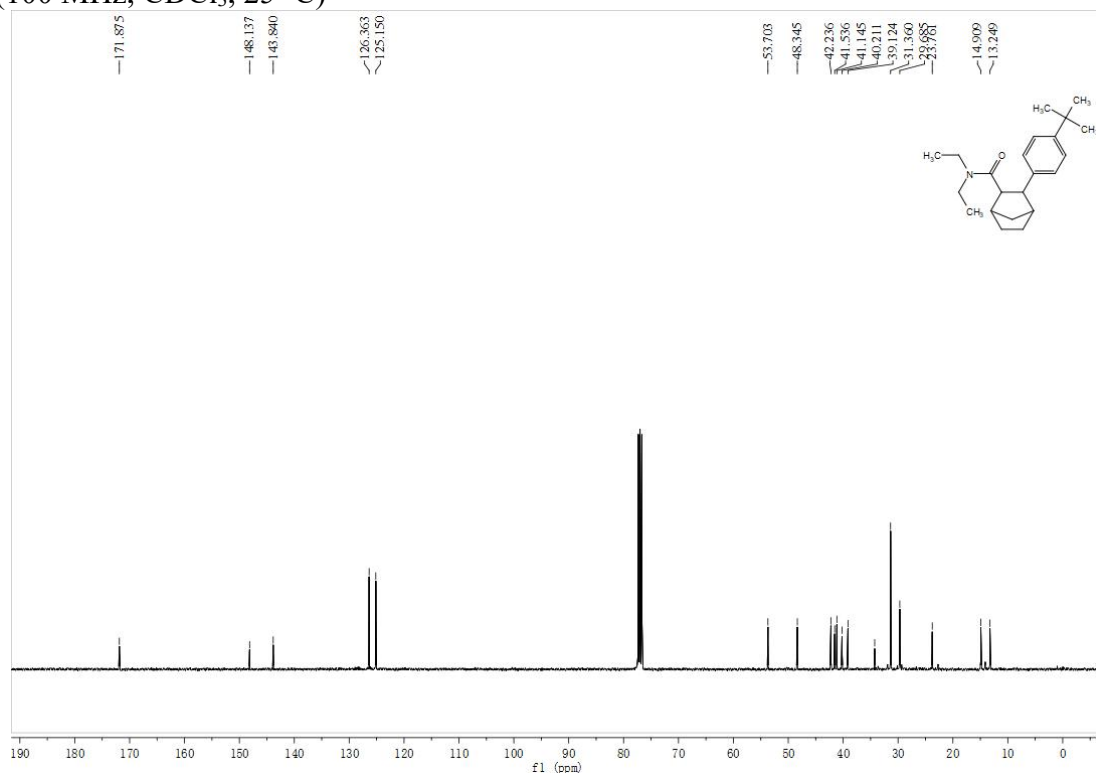
^{13}C NMR spectrum of *N,N*-diethyl-3-phenylbicyclo[2.2.1]heptane-2-carboxamide (**7e**) (100 MHz, CDCl_3 , 25 °C)



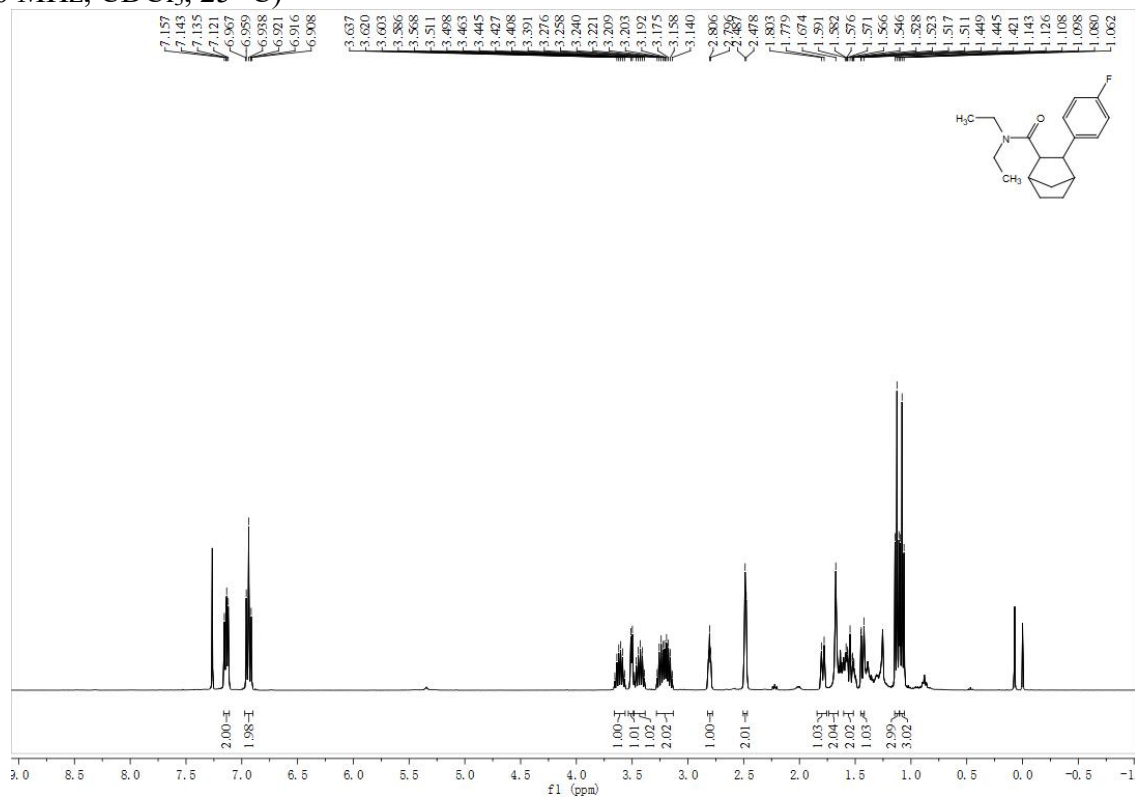
^1H NMR spectrum of 3-(4-(*tert*-butyl)phenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**8e**) (400 MHz, CDCl_3 , 25 °C)



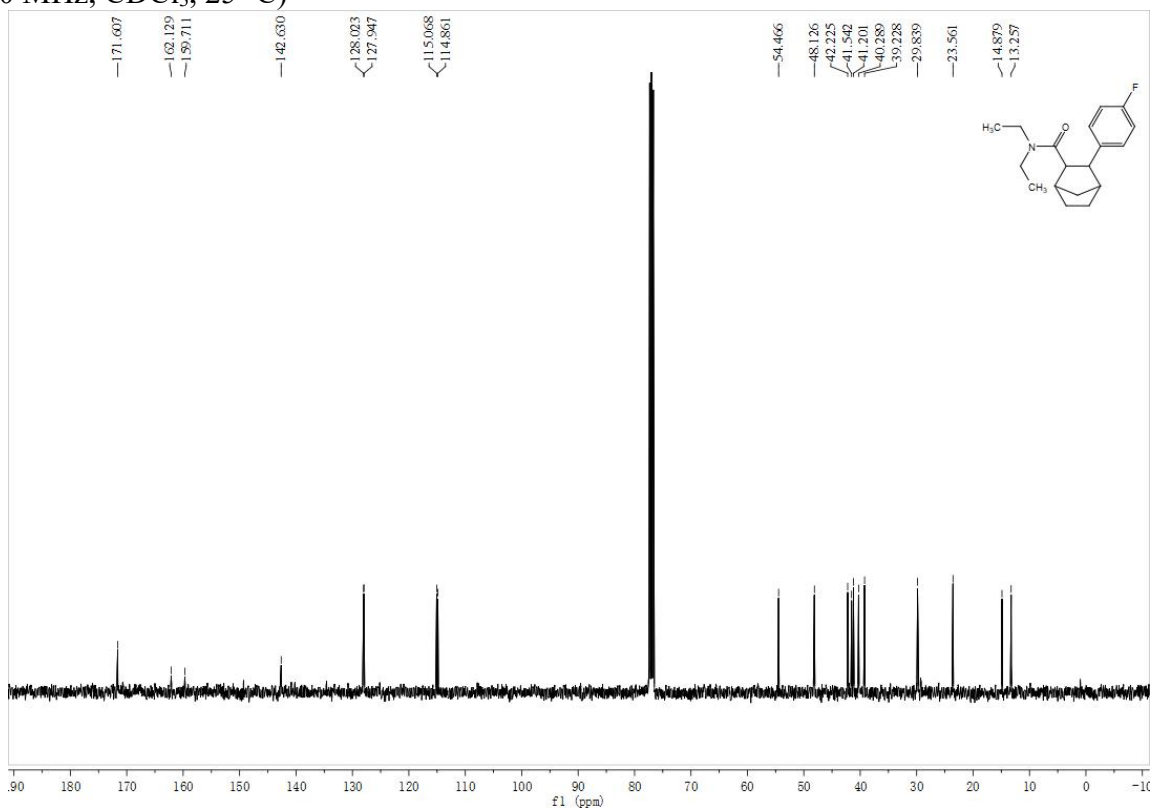
^{13}C NMR spectrum of 3-(4-(*tert*-butyl)phenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**8e**) (100 MHz, CDCl_3 , 25 °C)



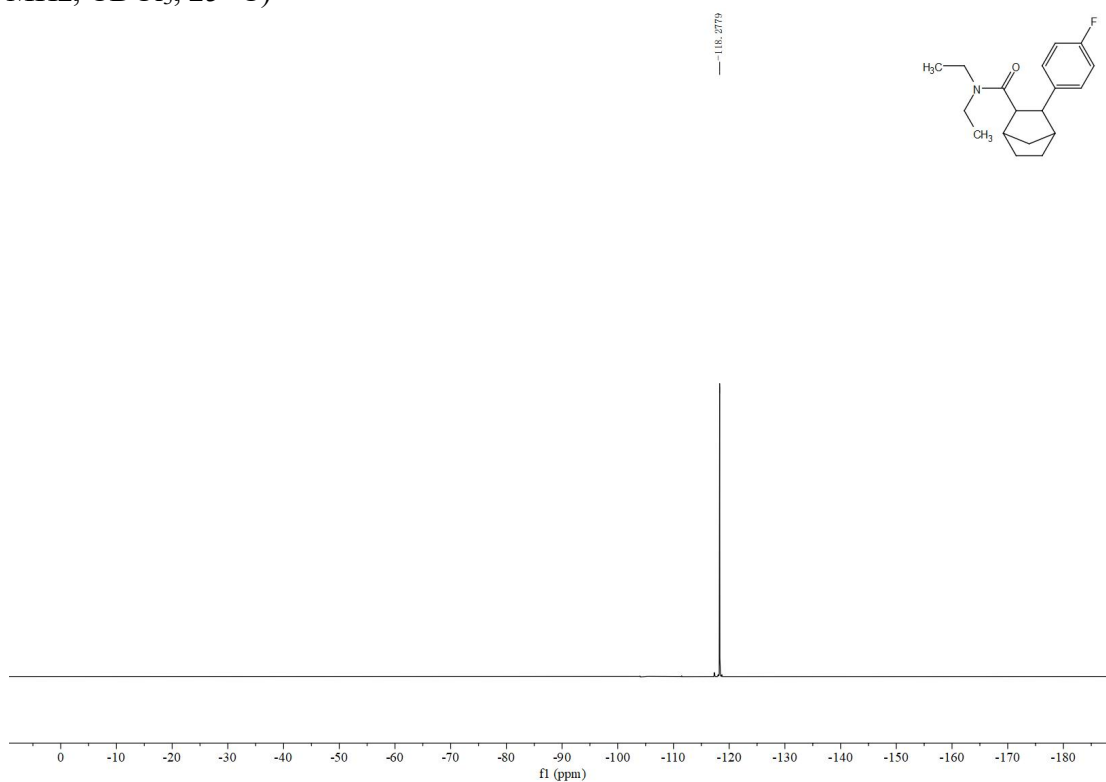
^1H NMR spectrum of *N,N*-diethyl-3-(4-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**9e**) (400 MHz, CDCl_3 , 25 °C)



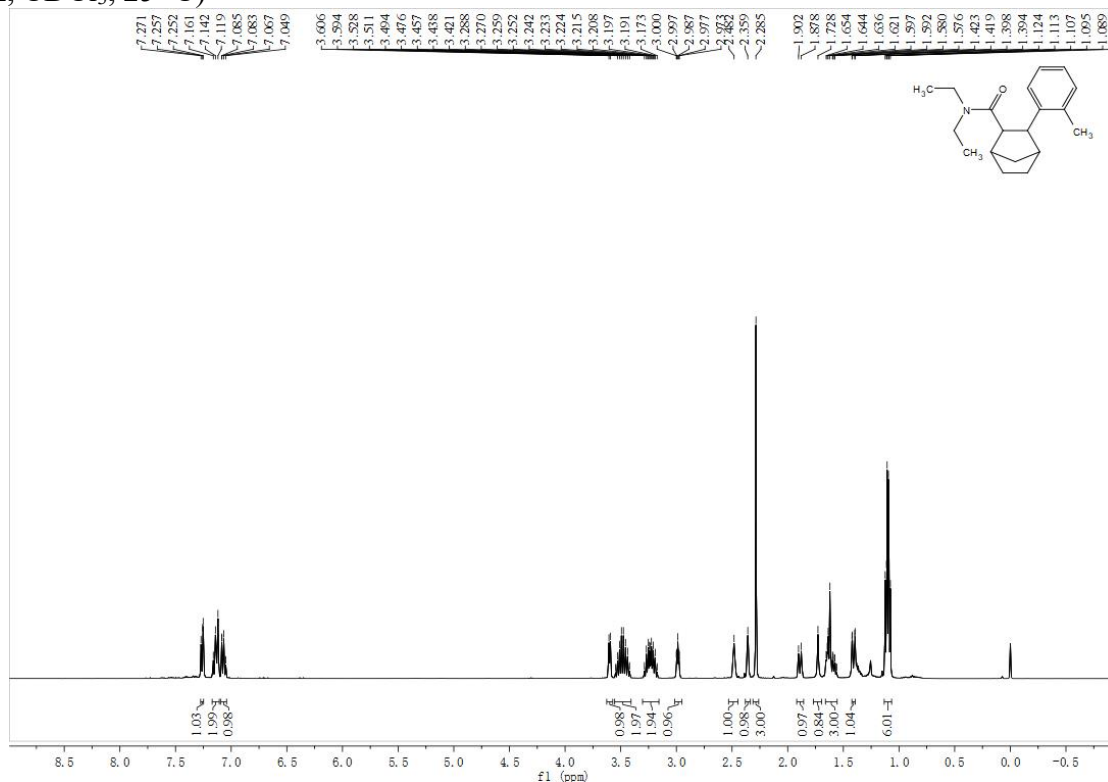
^{13}C NMR spectrum of *N,N*-diethyl-3-(4-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**9e**) (100 MHz, CDCl_3 , 25 °C)



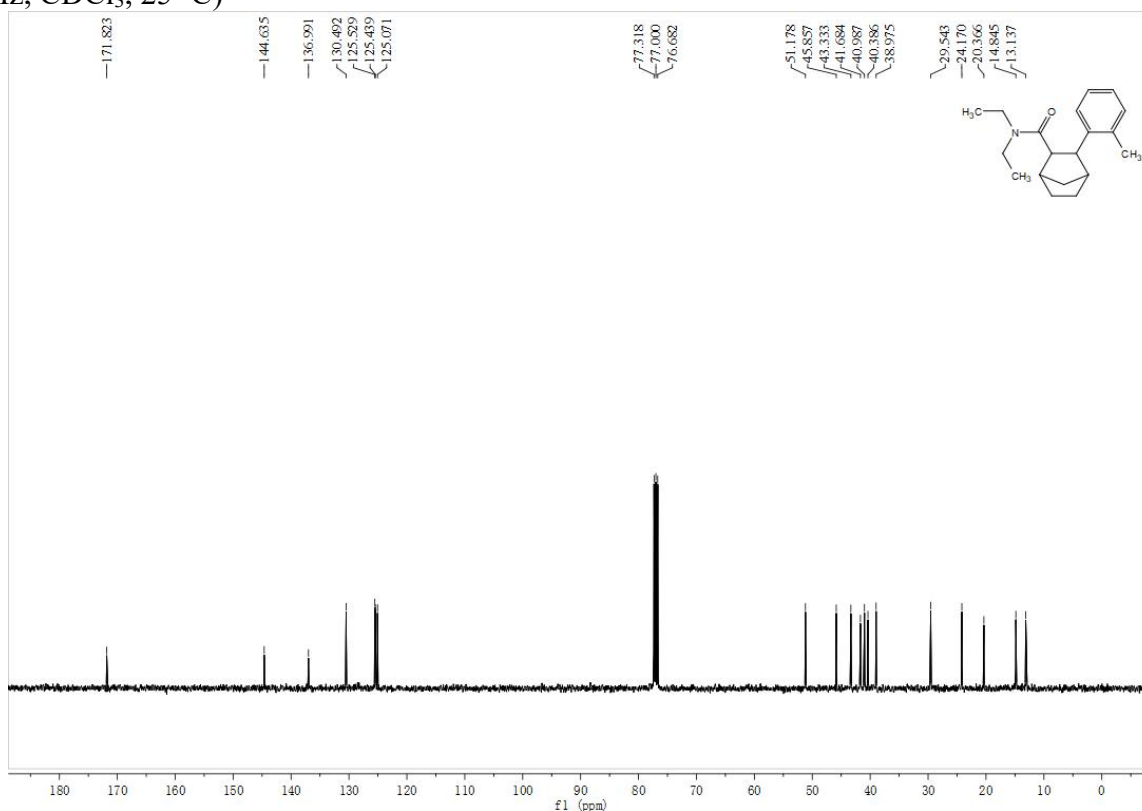
^{19}F NMR spectrum of *N,N*-diethyl-3-(4-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**9e**) (376 MHz, CDCl_3 , 25 °C)



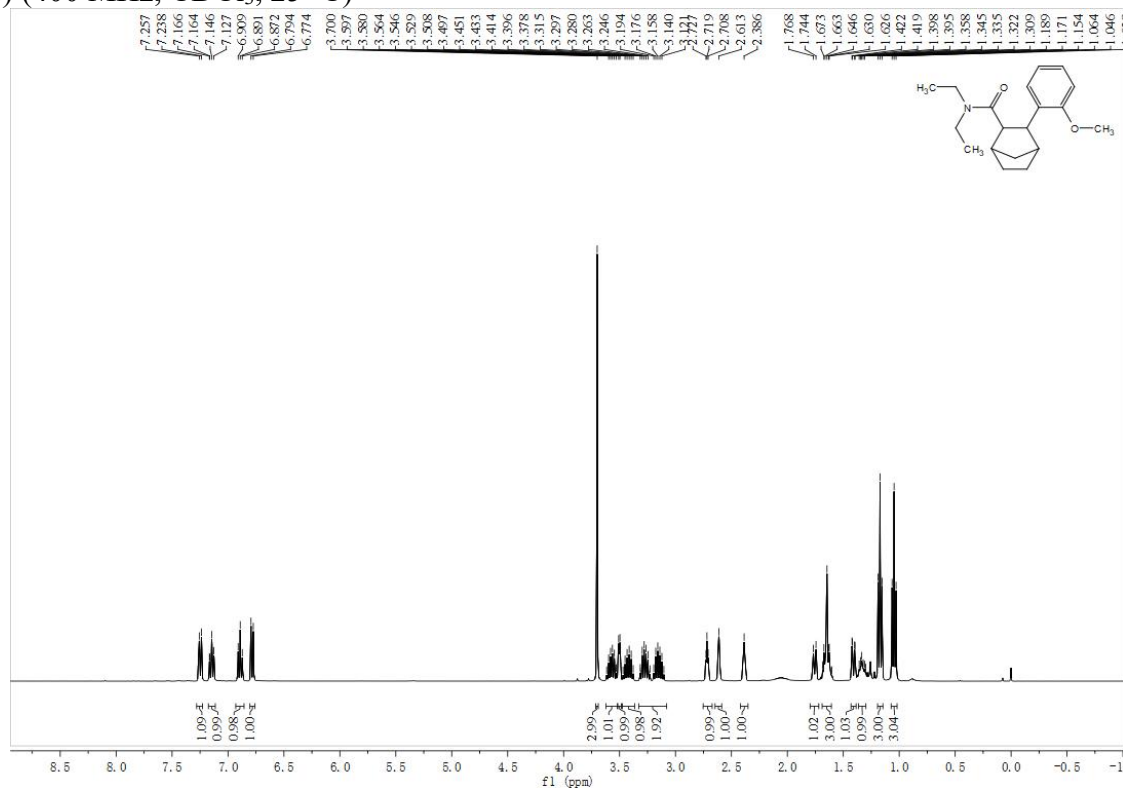
^1H NMR spectrum of *N,N*-diethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**10e**) (400 MHz, CDCl_3 , 25 °C)



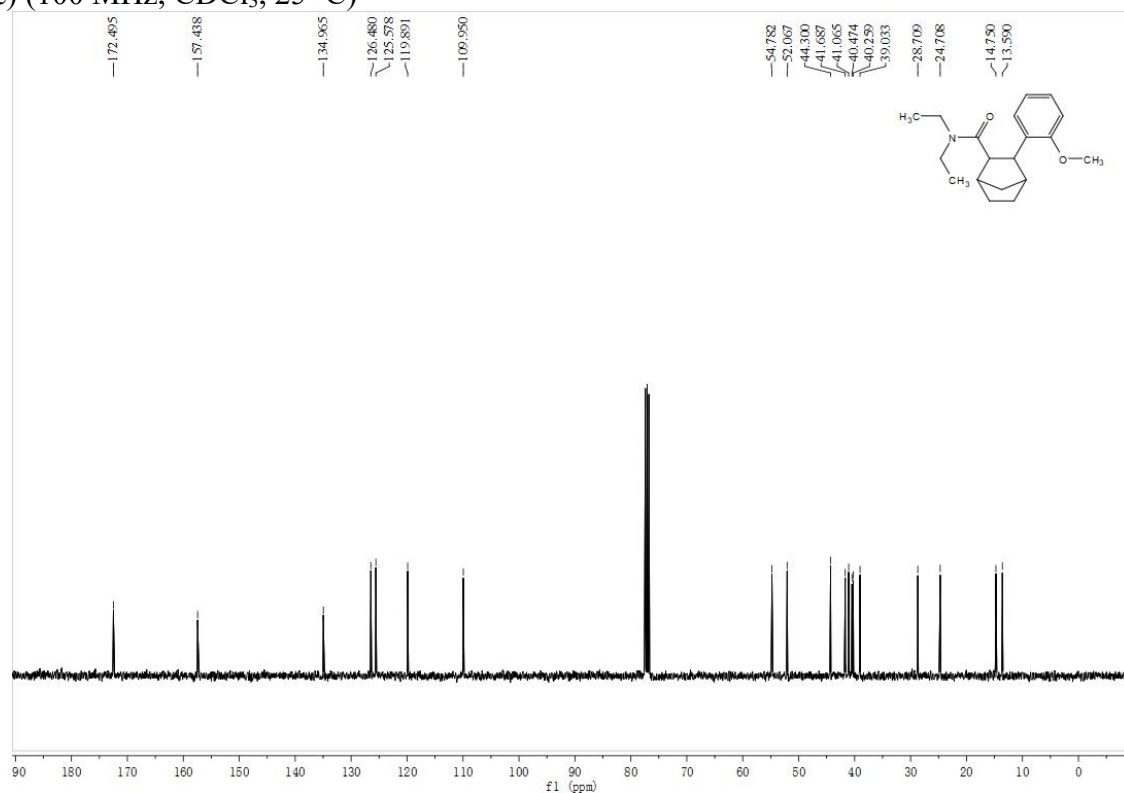
^{13}C NMR spectrum of *N,N*-diethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**10e**) (100 MHz, CDCl_3 , 25 °C)



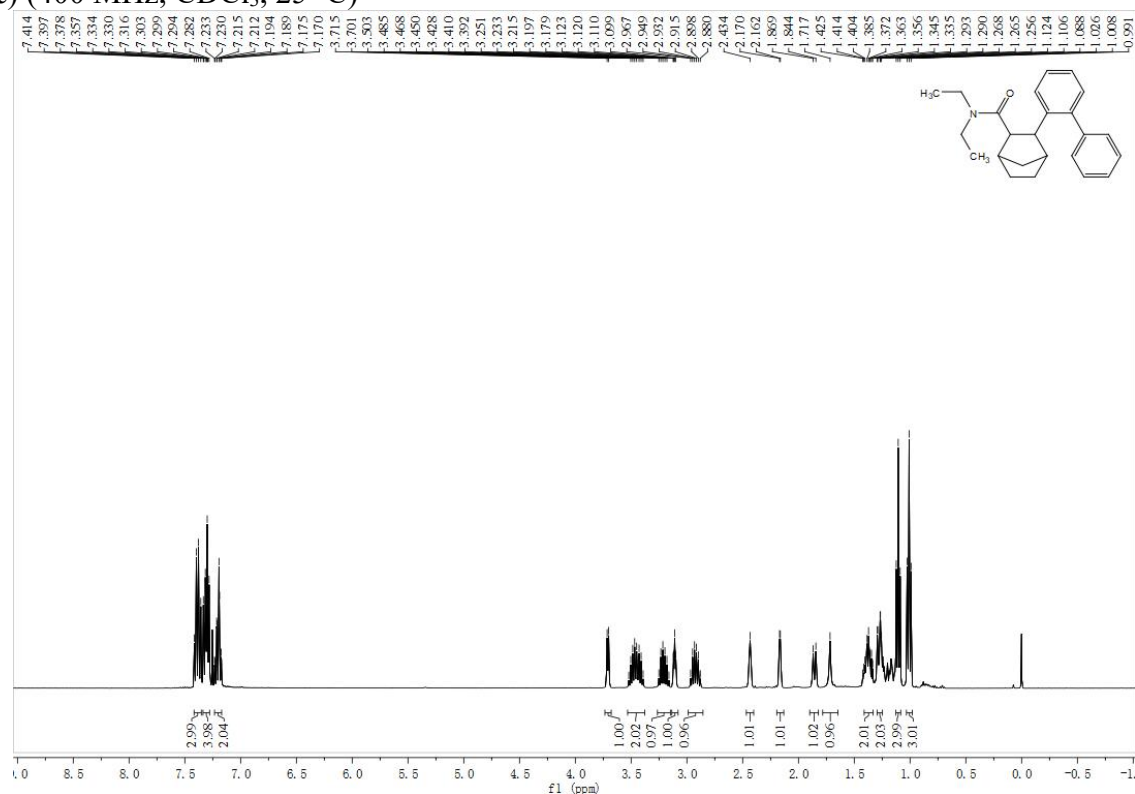
^1H NMR spectrum of *N,N*-diethyl-3-(2-methoxyphenyl)bicyclo[2.2.1]heptane-2-carboxamide (**11e**) (400 MHz, CDCl_3 , 25 °C)



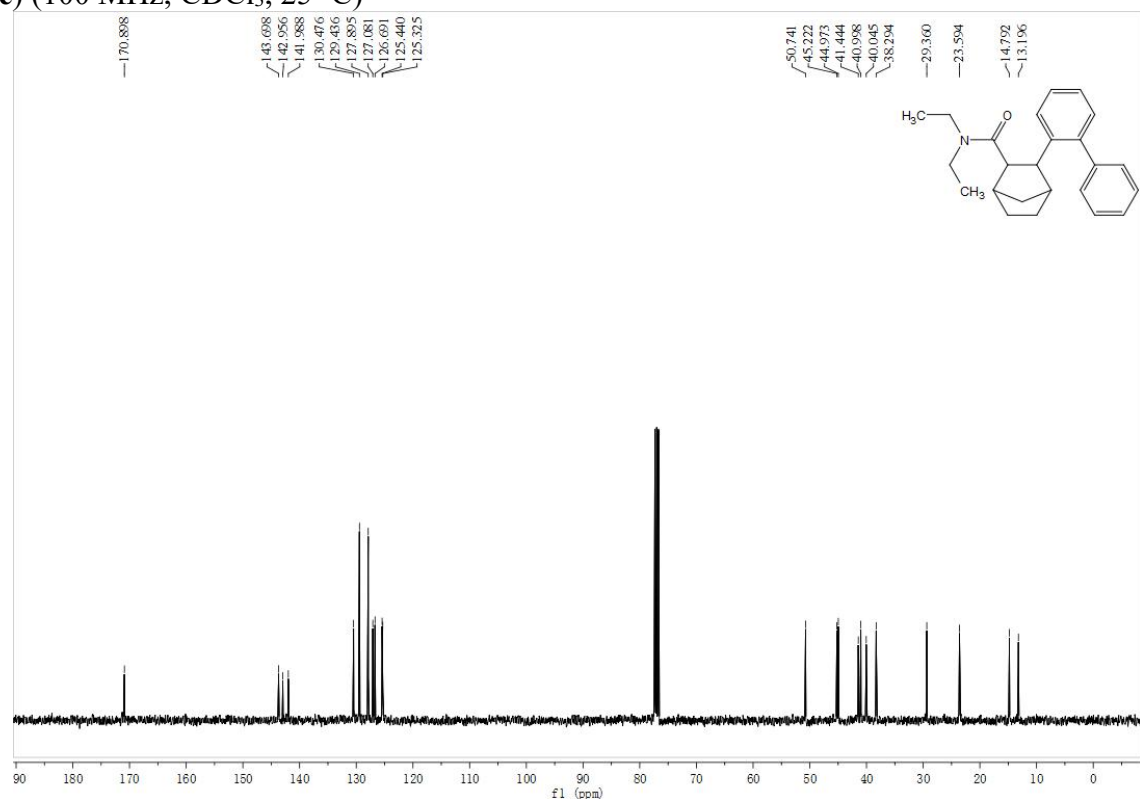
^{13}C NMR spectrum of *N,N*-diethyl-3-(2-methoxyphenyl)bicyclo[2.2.1]heptane-2-carboxamide (**11e**) (100 MHz, CDCl_3 , 25 °C)



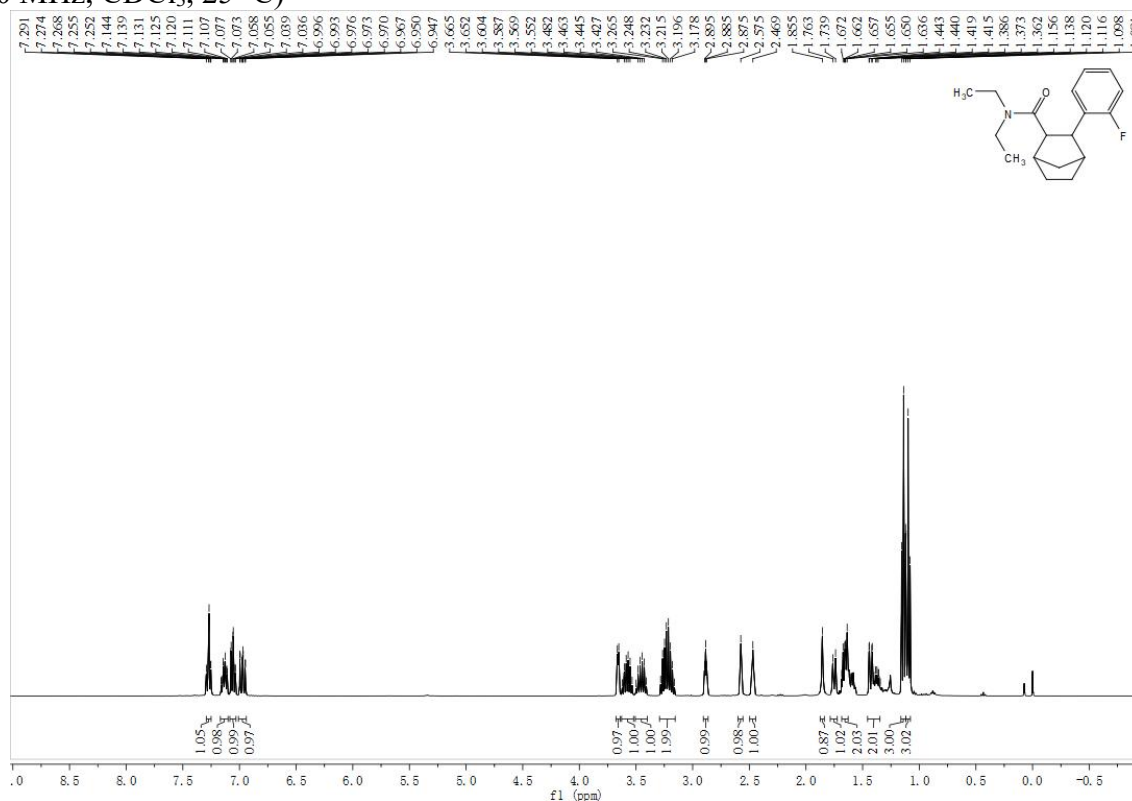
^1H NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-N,N-diethylbicyclo[2.2.1]heptane-2-carboxamide (**12e**) (400 MHz, CDCl_3 , 25 °C)



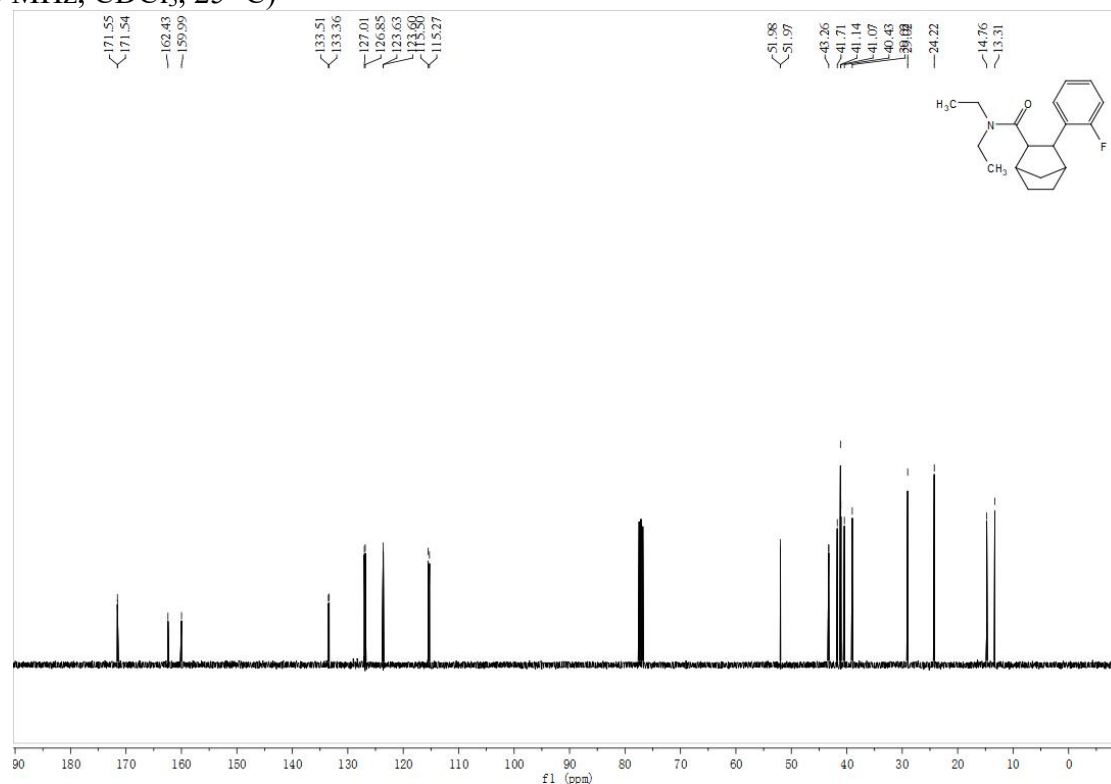
^{13}C NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-N,N-diethylbicyclo[2.2.1]heptane-2-carboxamide (**12e**) (100 MHz, CDCl_3 , 25 °C)



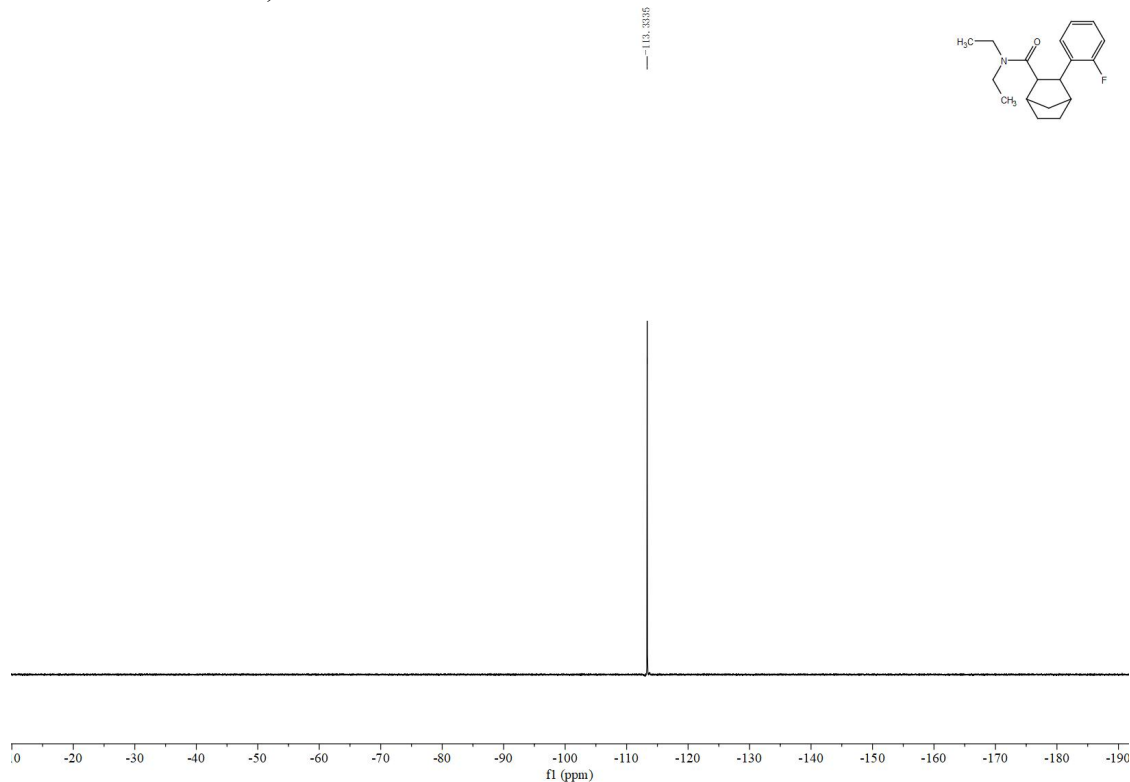
^1H NMR spectrum of *N,N*-diethyl-3-(2-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**13e**) (400 MHz, CDCl_3 , 25 °C)



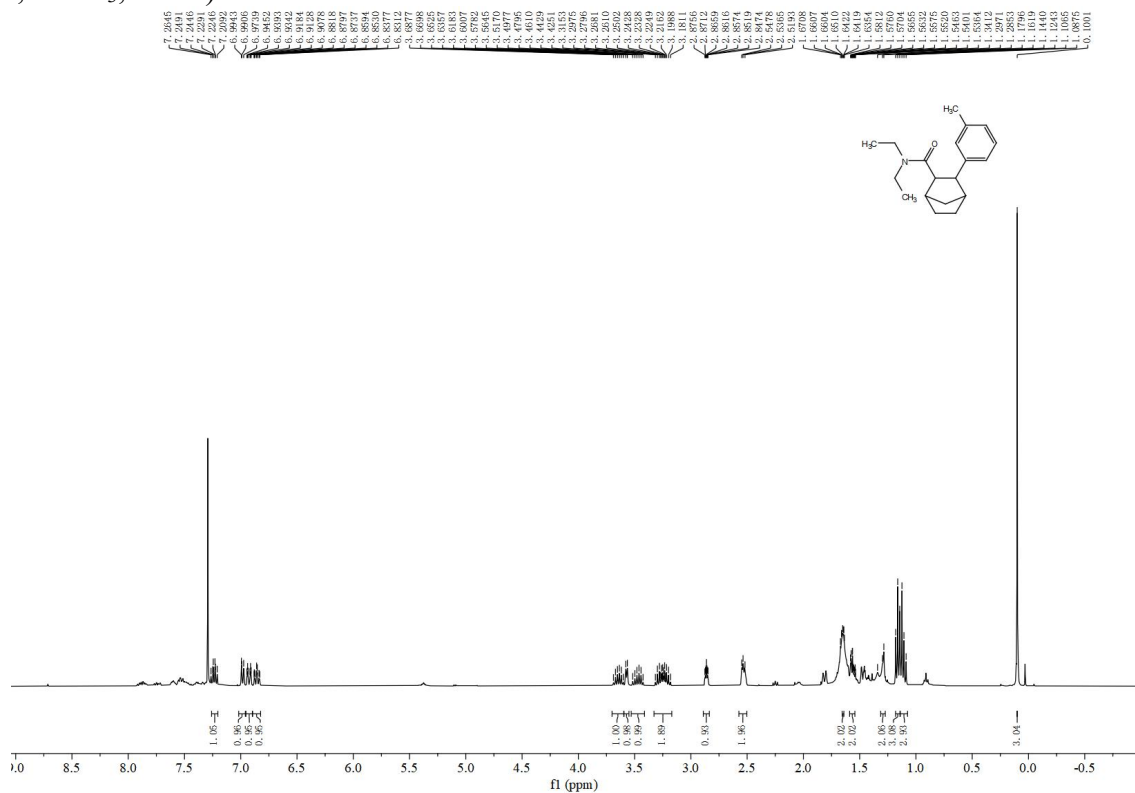
^{13}C NMR spectrum of *N,N*-diethyl-3-(2-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**13e**) (100 MHz, CDCl_3 , 25 °C)



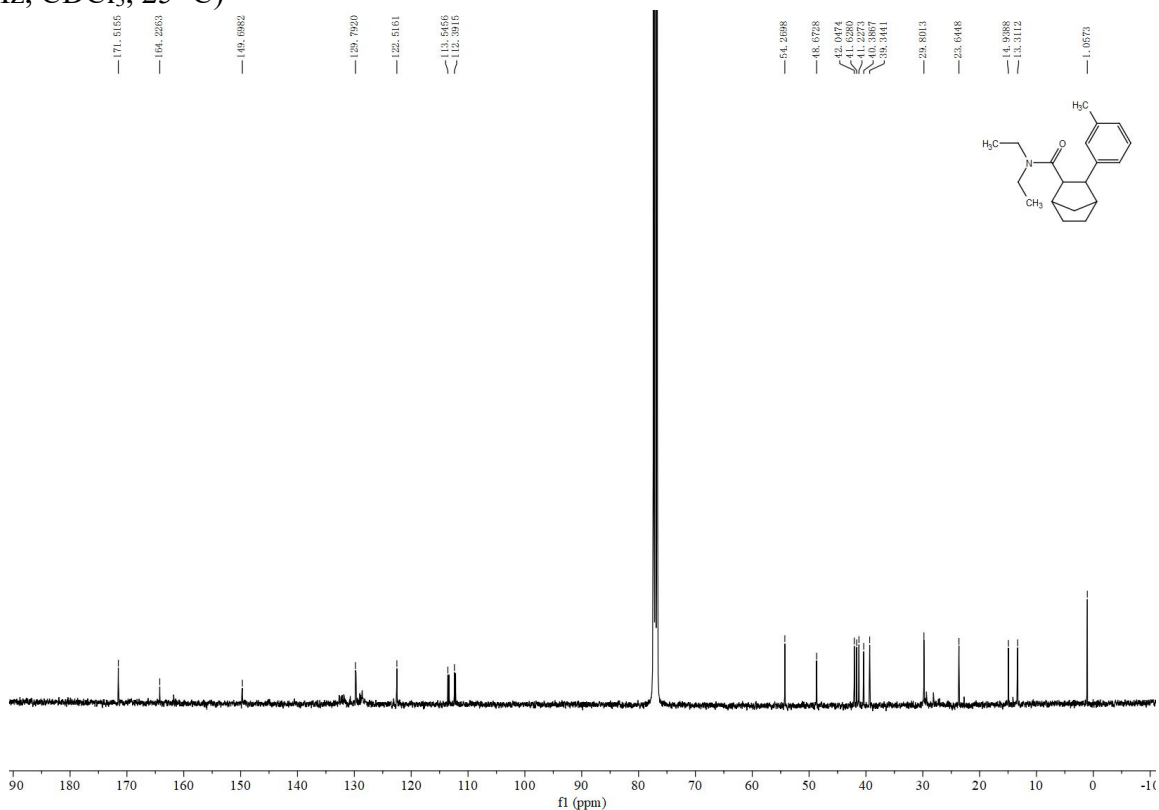
^{19}F NMR spectrum of *N,N*-diethyl-3-(2-fluorophenyl)bicyclo[2.2.1]heptane-2-carboxamide (**13e**) (376 MHz, CDCl_3 , 25 °C)



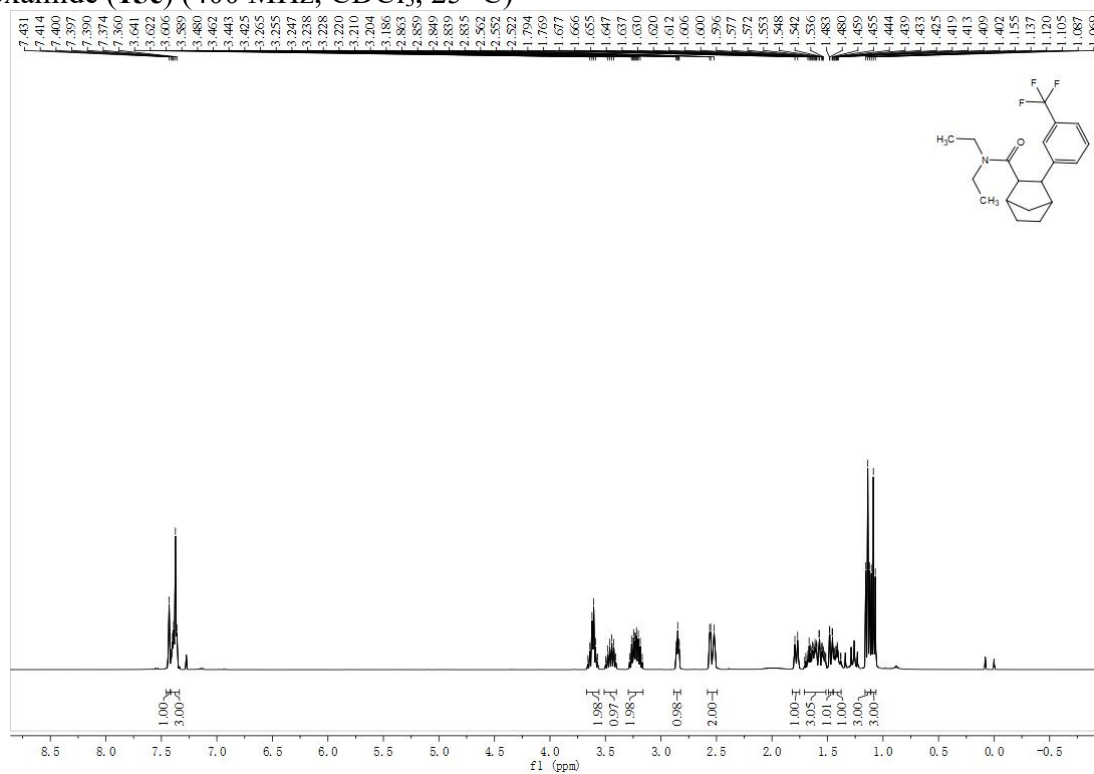
^1H NMR spectrum of *N,N*-diethyl-3-(*m*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**14e**) (400 MHz, CDCl_3 , 25 °C)



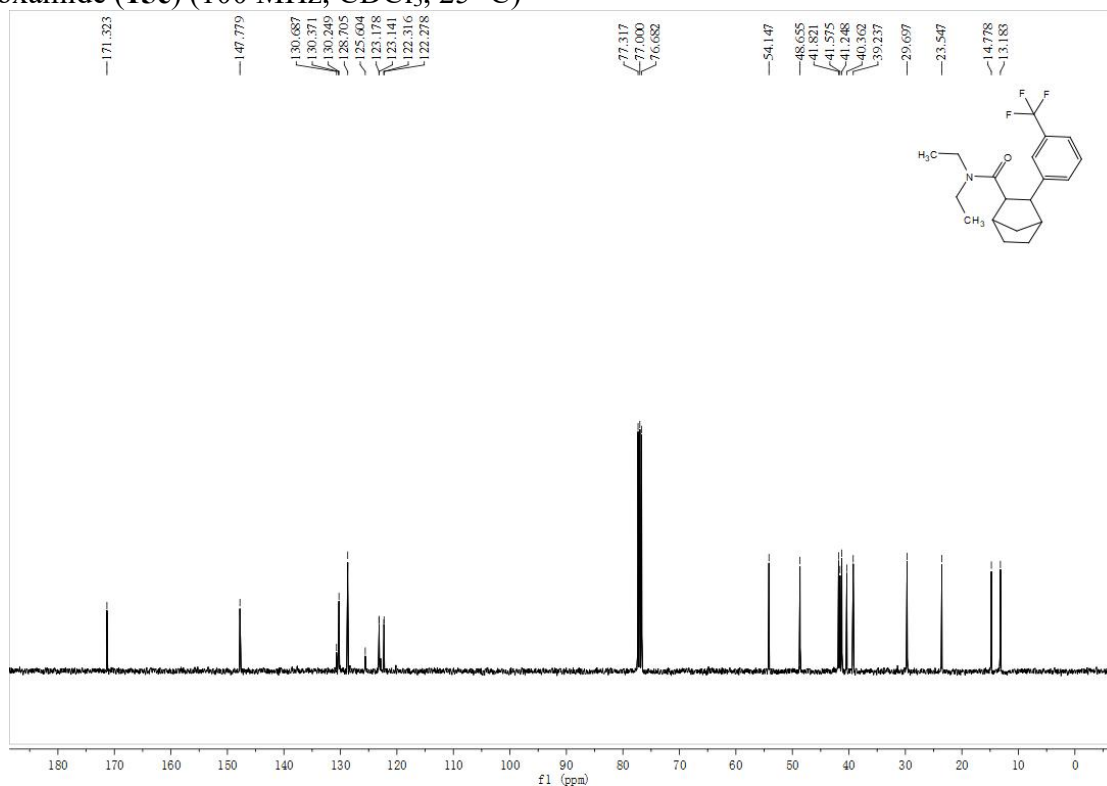
¹³C NMR spectrum of *N,N*-diethyl-3-(*m*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**14e**) (100 MHz, CDCl₃, 25 °C)



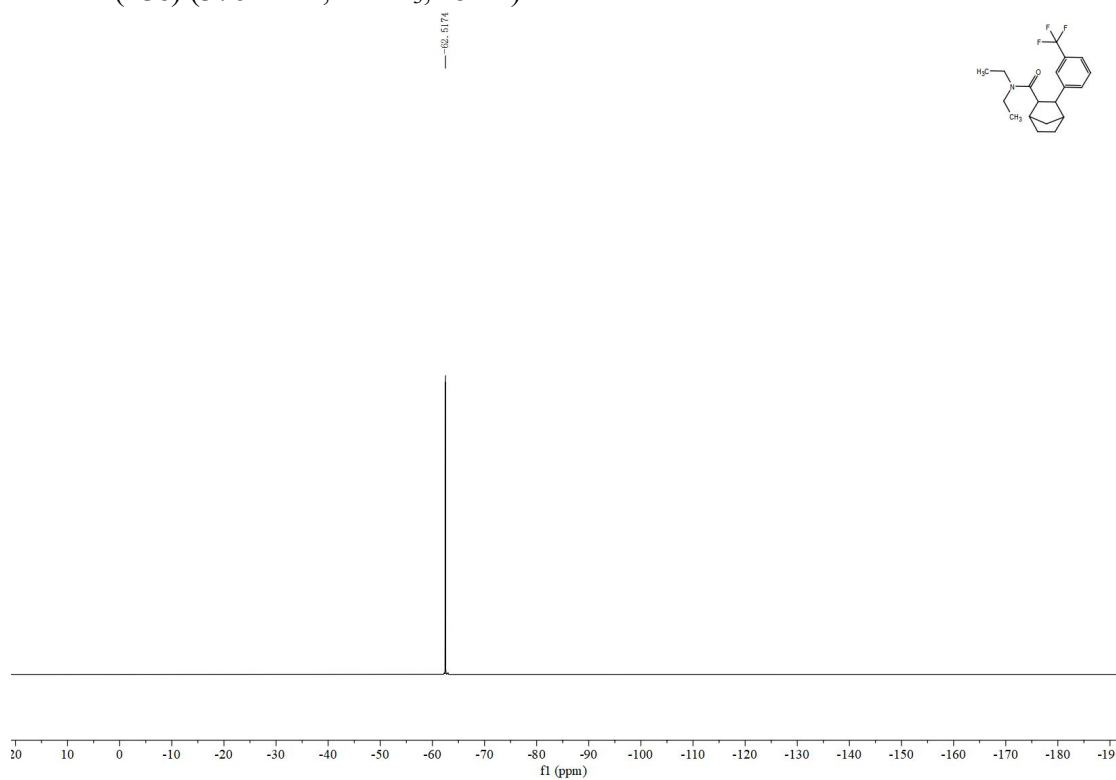
¹H NMR spectrum of *N,N*-diethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**15e**) (400 MHz, CDCl₃, 25 °C)



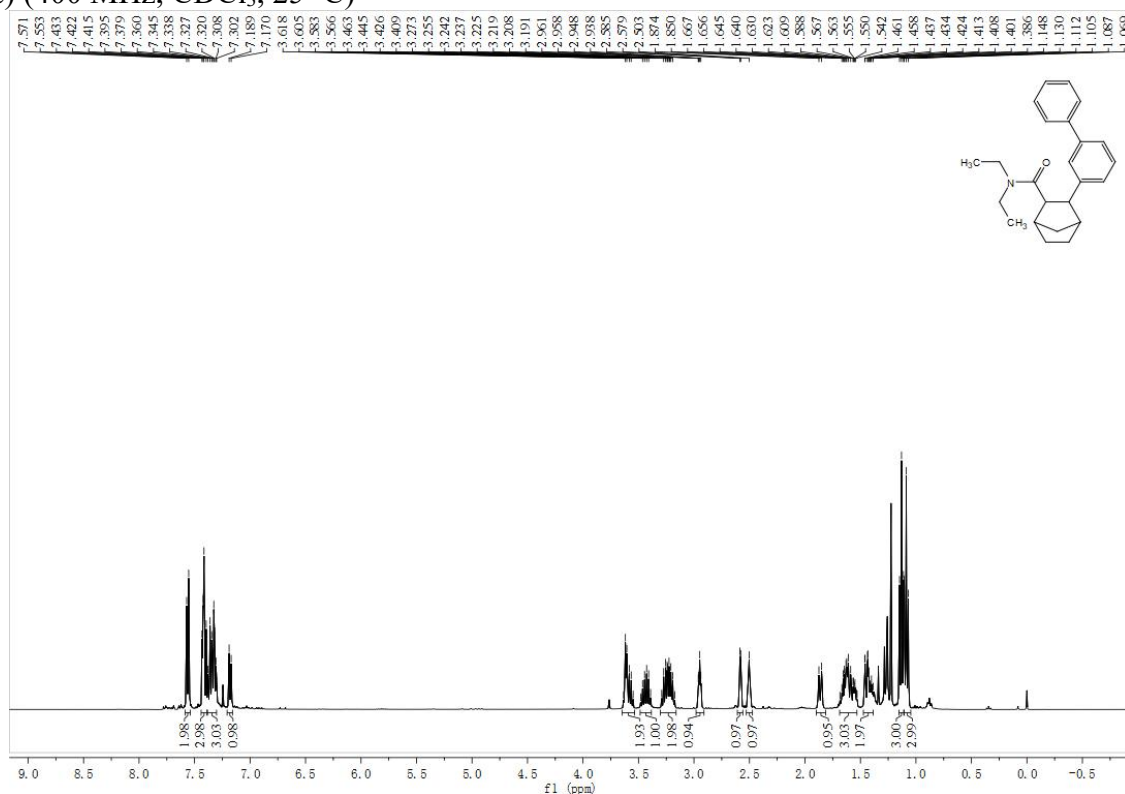
^{13}C NMR spectrum of *N,N*-diethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**15e**) (100 MHz, CDCl_3 , 25 °C)



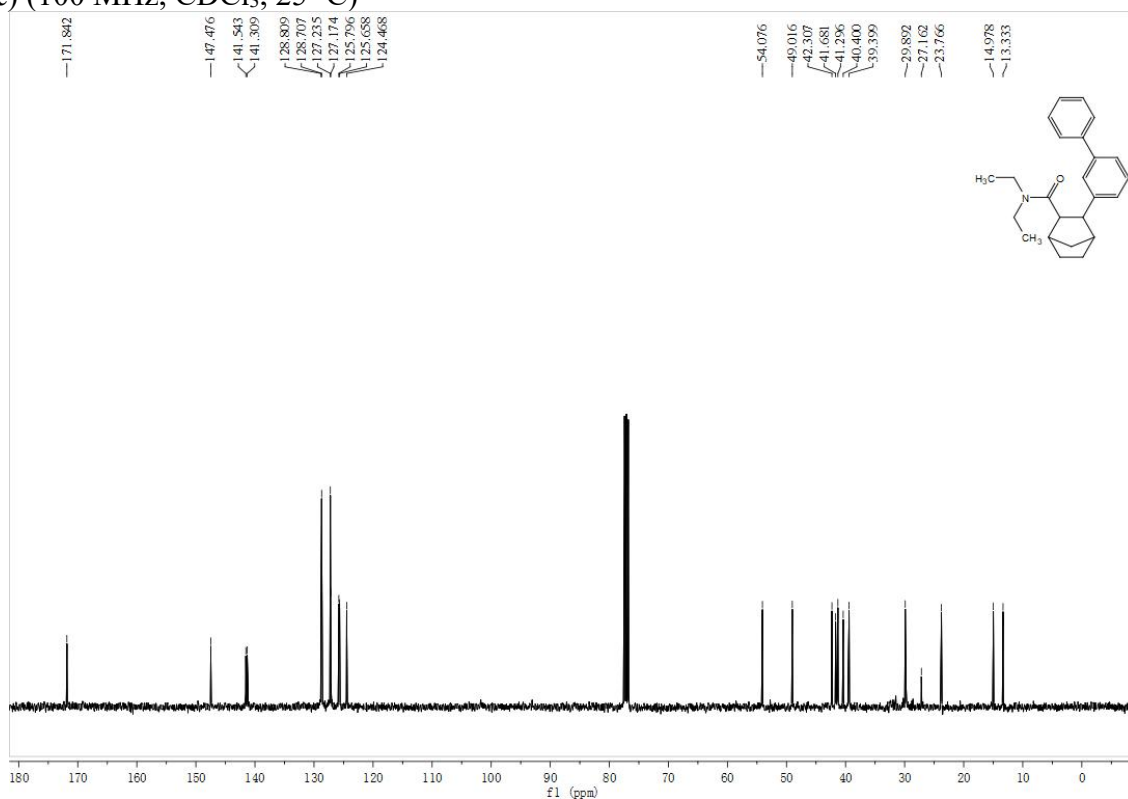
^{19}F NMR spectrum of *N,N*-diethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**15e**) (376 MHz, CDCl_3 , 25 °C)



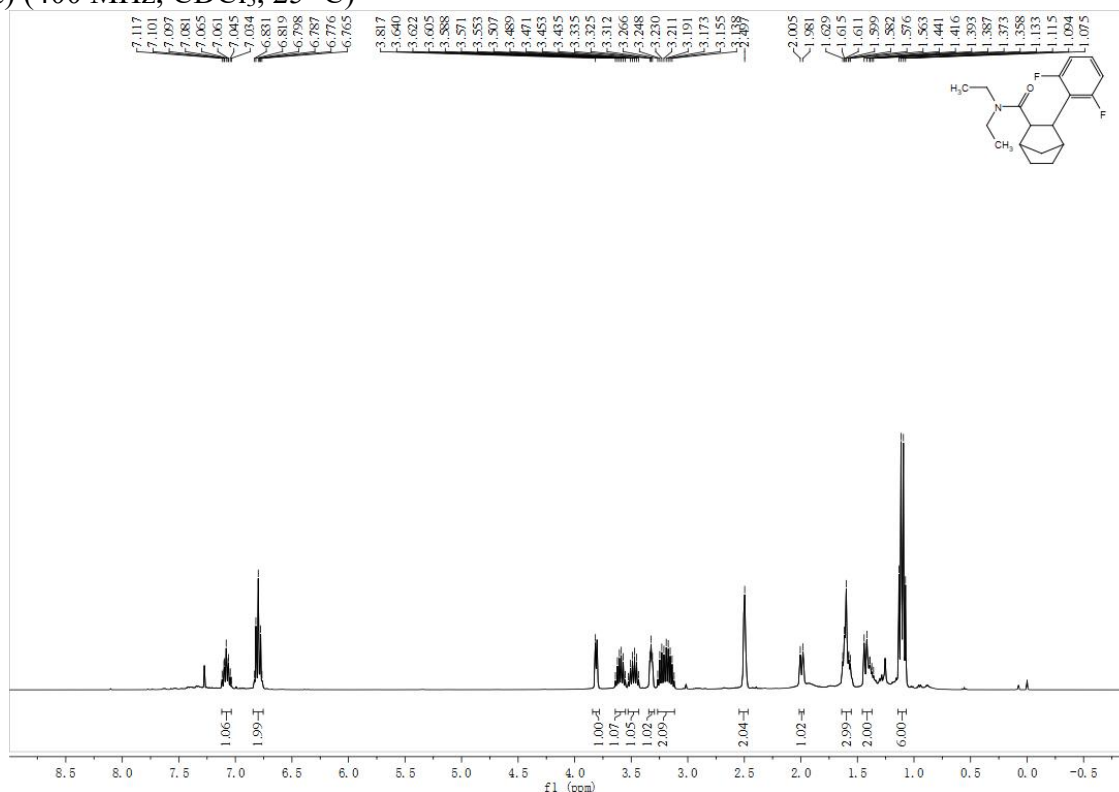
^1H NMR spectrum of 3-([1,1'-biphenyl]-3-yl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**16e**) (400 MHz, CDCl_3 , 25 °C)



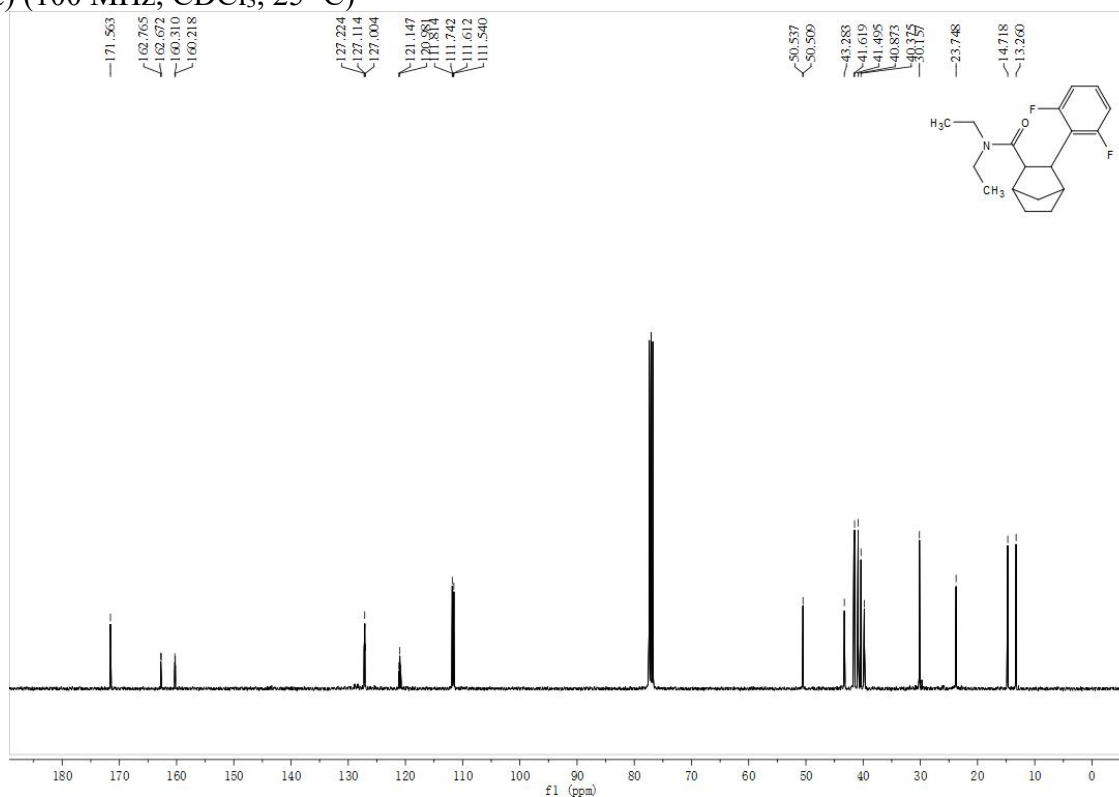
^{13}C NMR spectrum of 3-([1,1'-biphenyl]-3-yl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**16e**) (100 MHz, CDCl_3 , 25 °C)



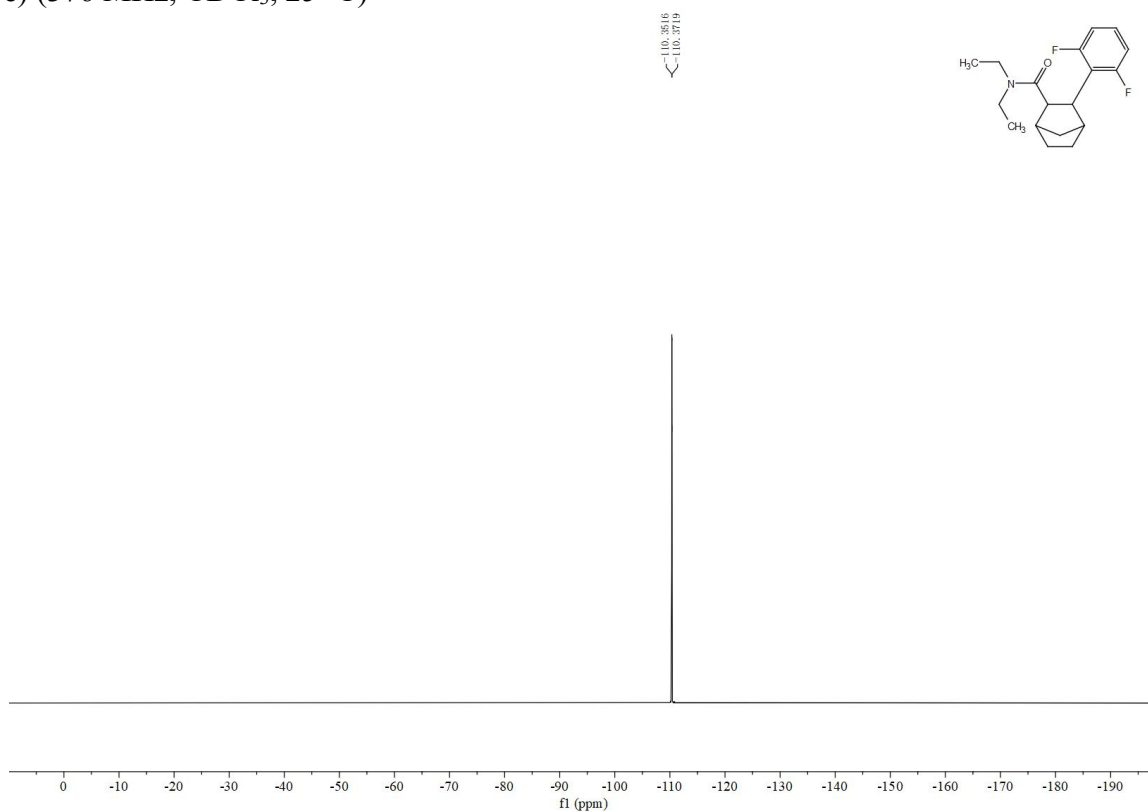
^1H NMR spectrum of 3-(2,6-difluorophenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**17e**) (400 MHz, CDCl_3 , 25 °C)



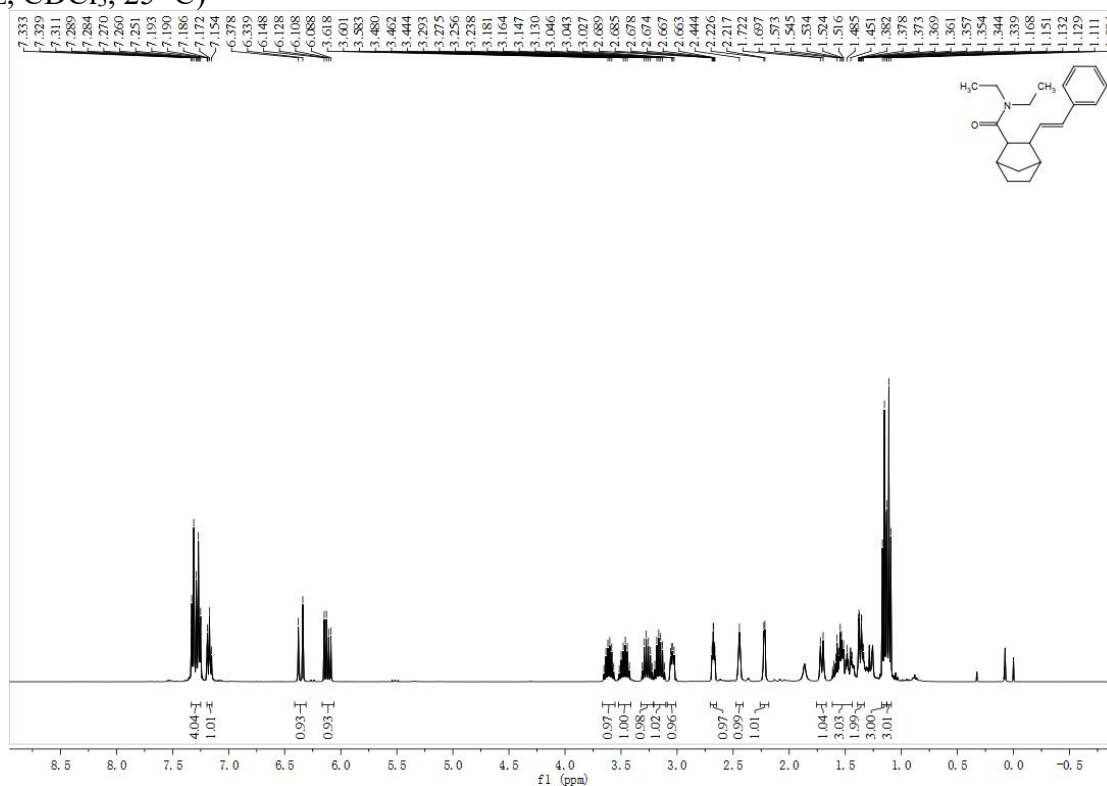
^{13}C NMR spectrum of 3-(2,6-difluorophenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**17e**) (100 MHz, CDCl_3 , 25 °C)



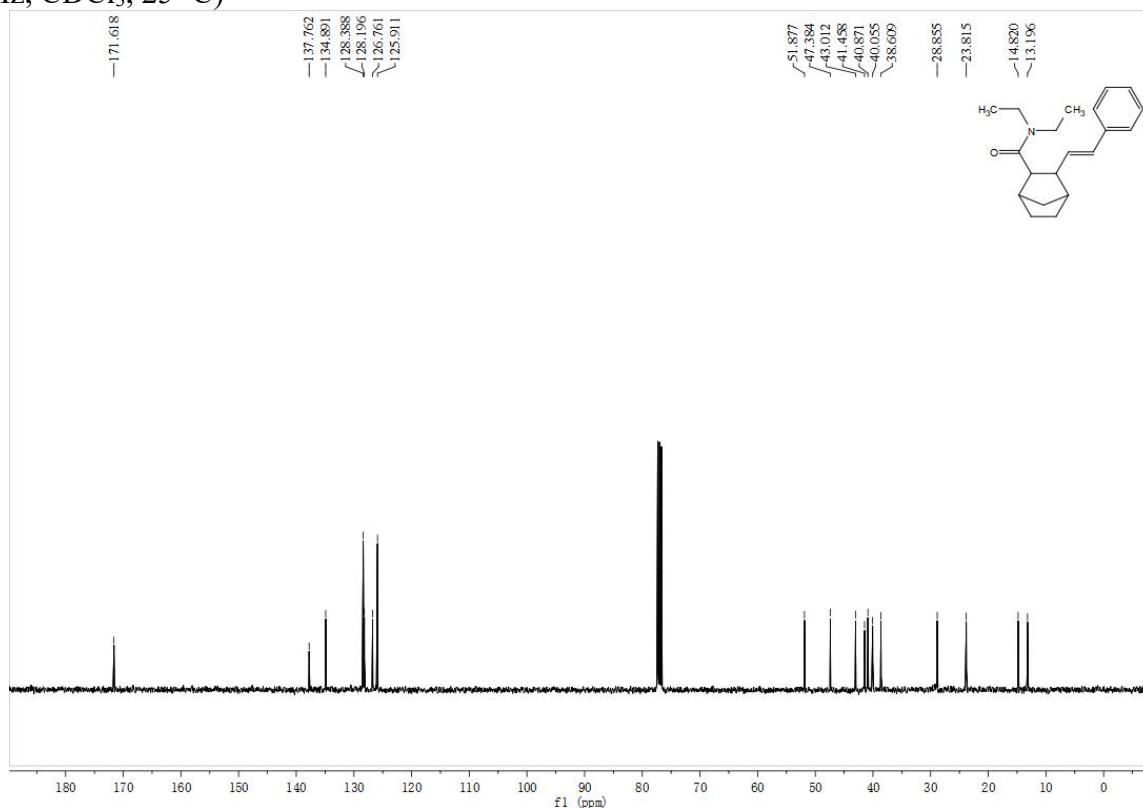
^{19}F NMR spectrum of 3-(2,6-difluorophenyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**17e**) (376 MHz, CDCl_3 , 25 °C)



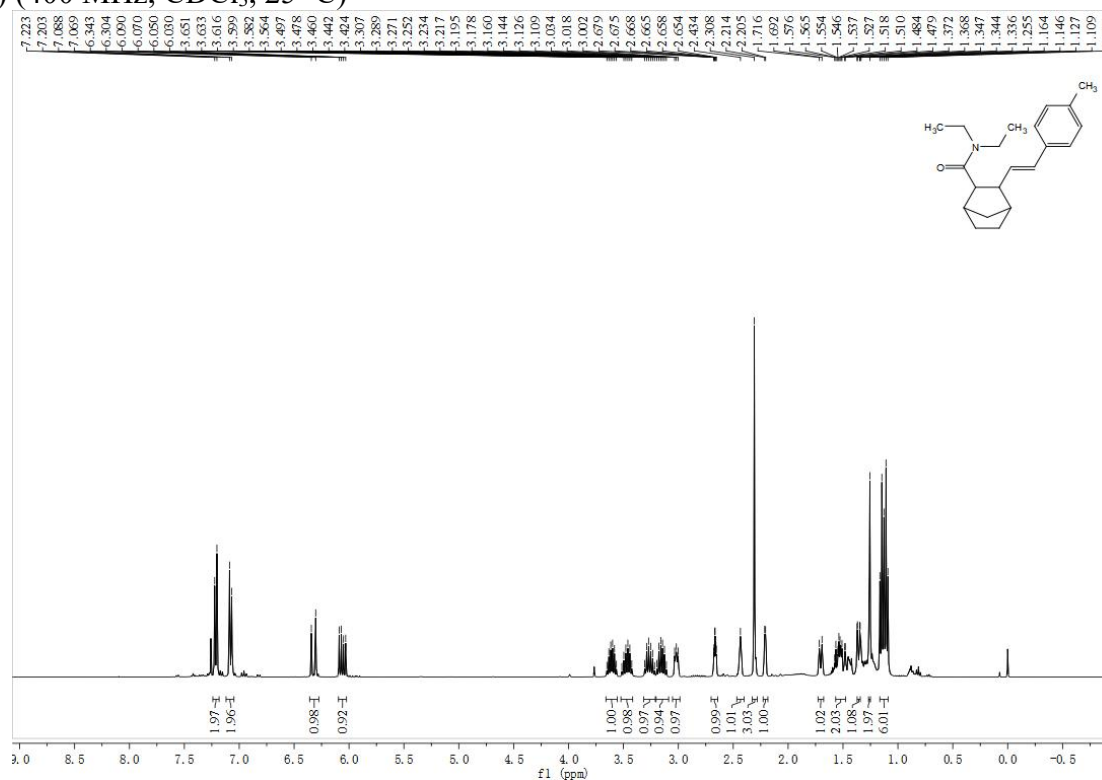
^1H NMR spectrum of (*E*)-*N,N*-diethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**18e**) (400 MHz, CDCl_3 , 25 °C)



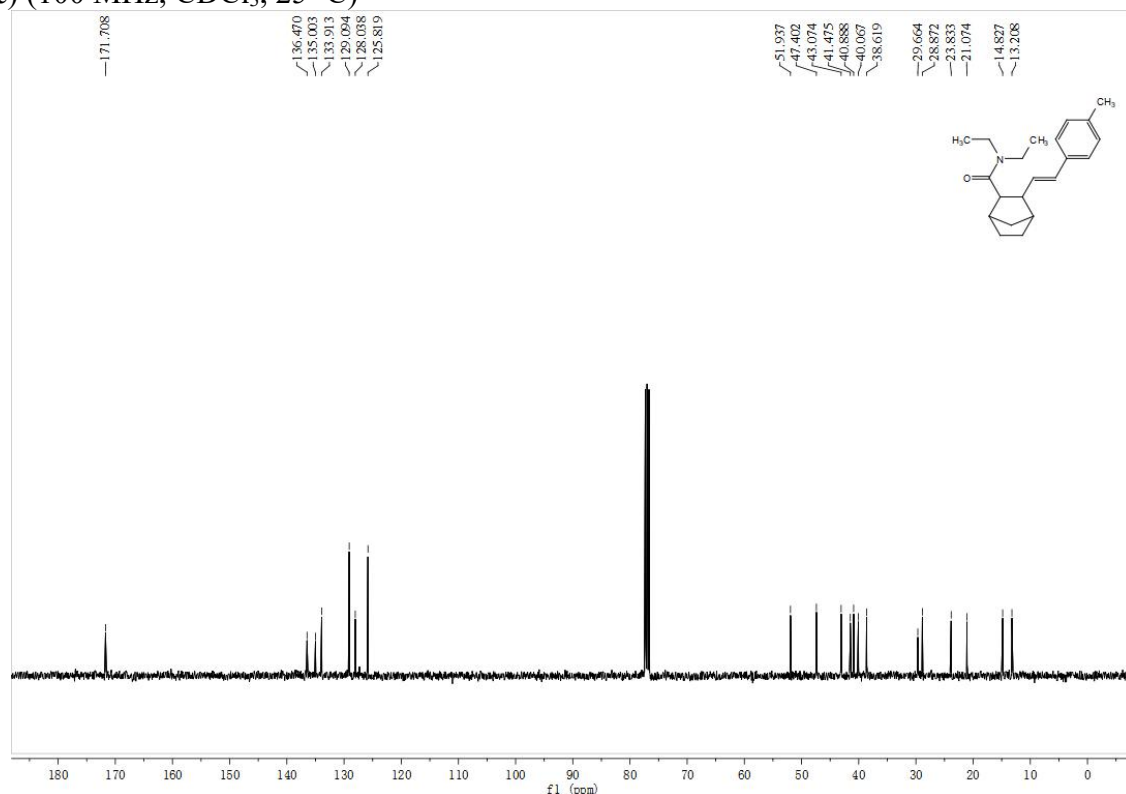
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**18e**) (100 MHz, CDCl_3 , 25 °C)



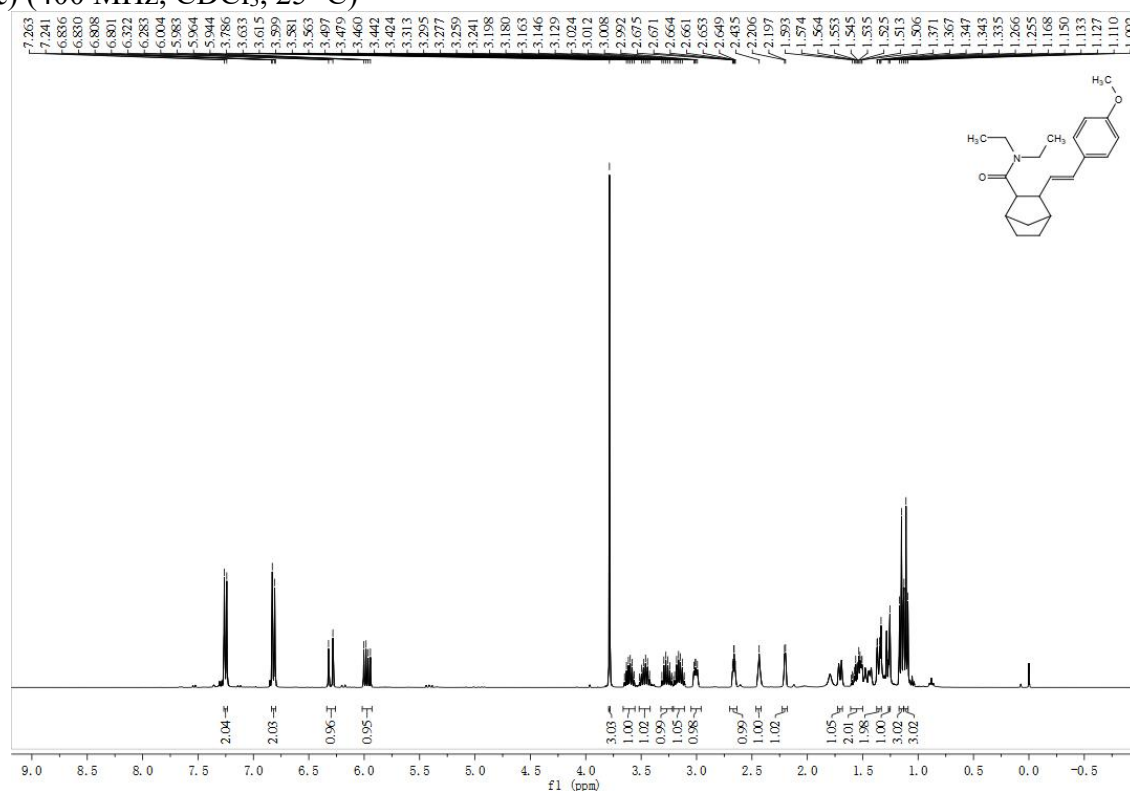
^1H NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**19e**) (400 MHz, CDCl_3 , 25 °C)



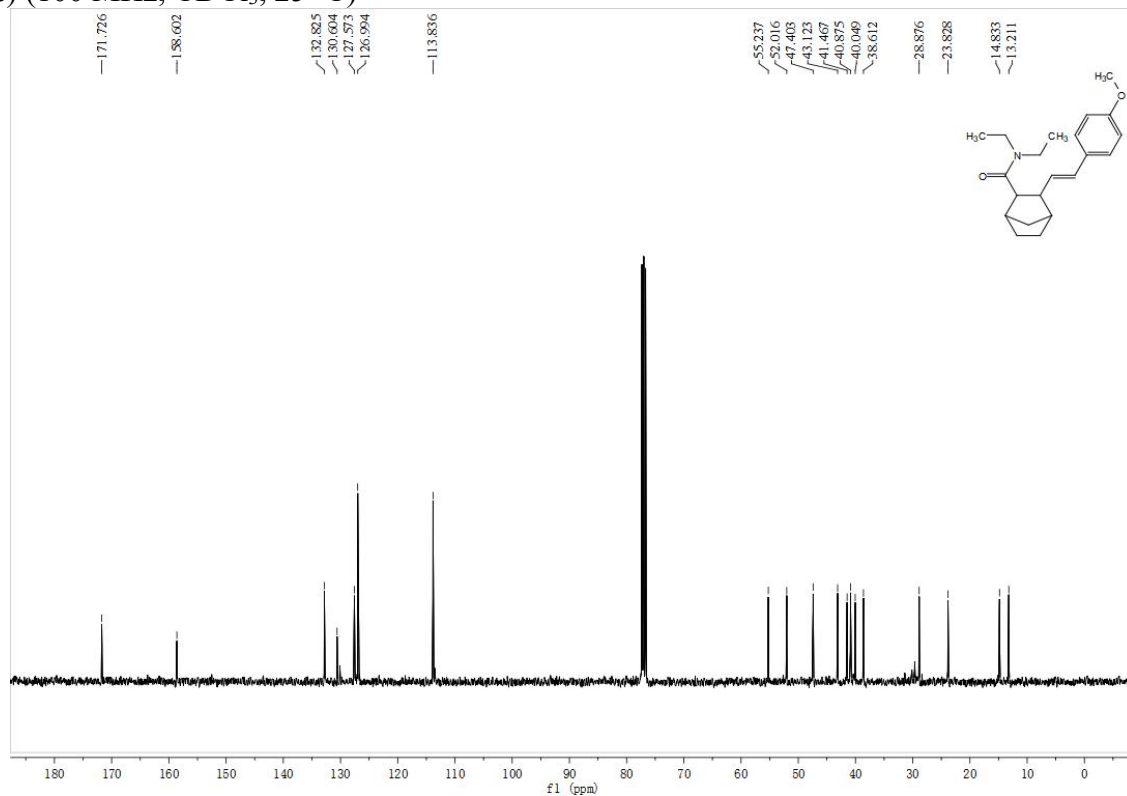
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**19e**) (100 MHz, CDCl_3 , 25 °C)



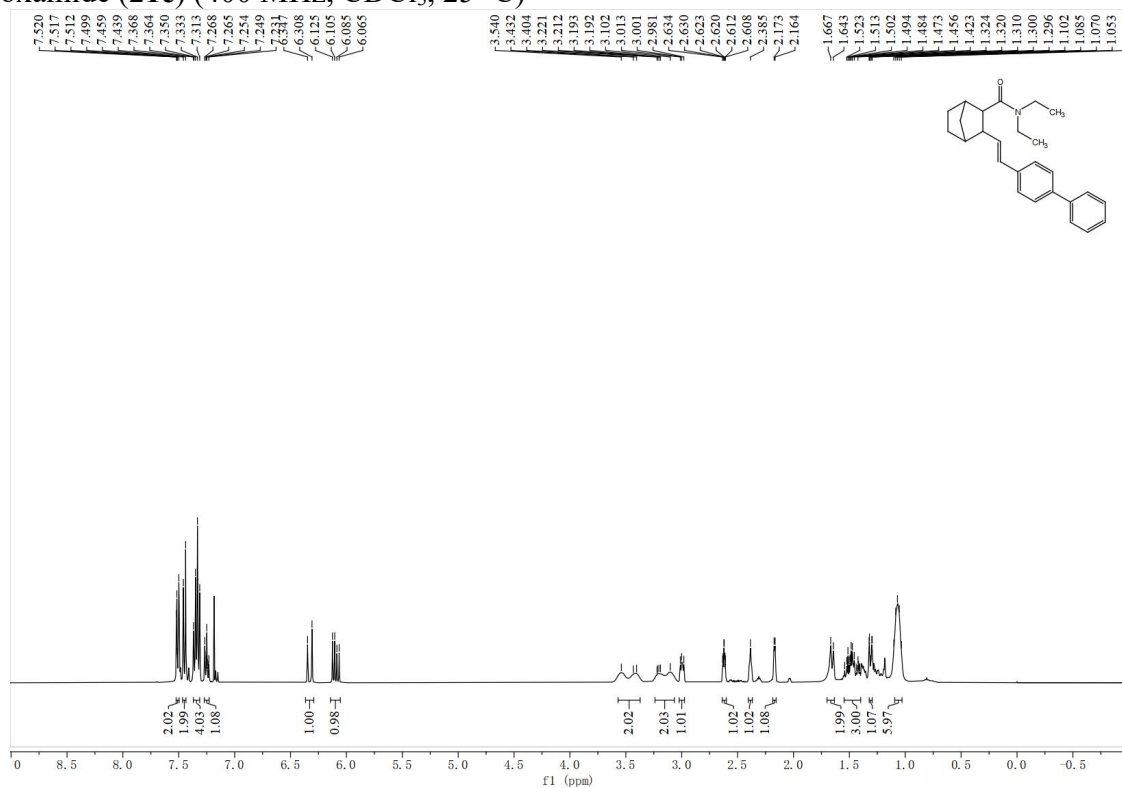
^1H NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**20e**) (400 MHz, CDCl_3 , 25 °C)



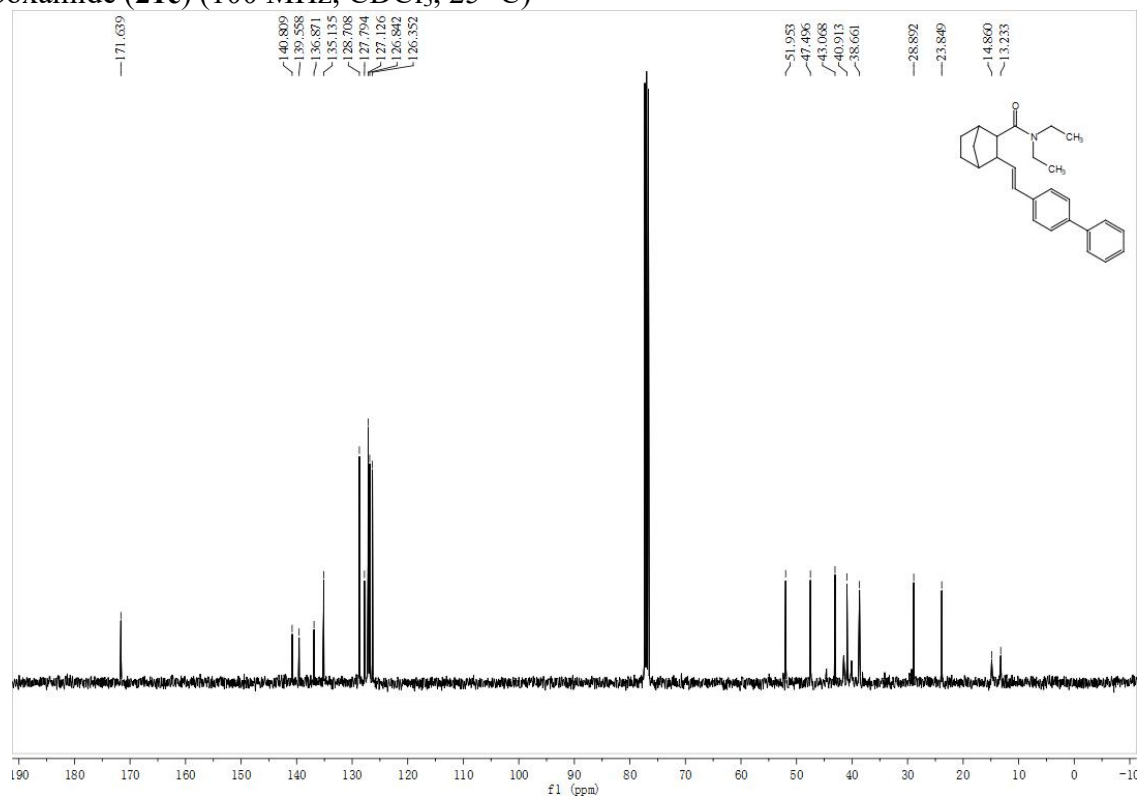
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**20e**) (100 MHz, CDCl_3 , 25 °C)



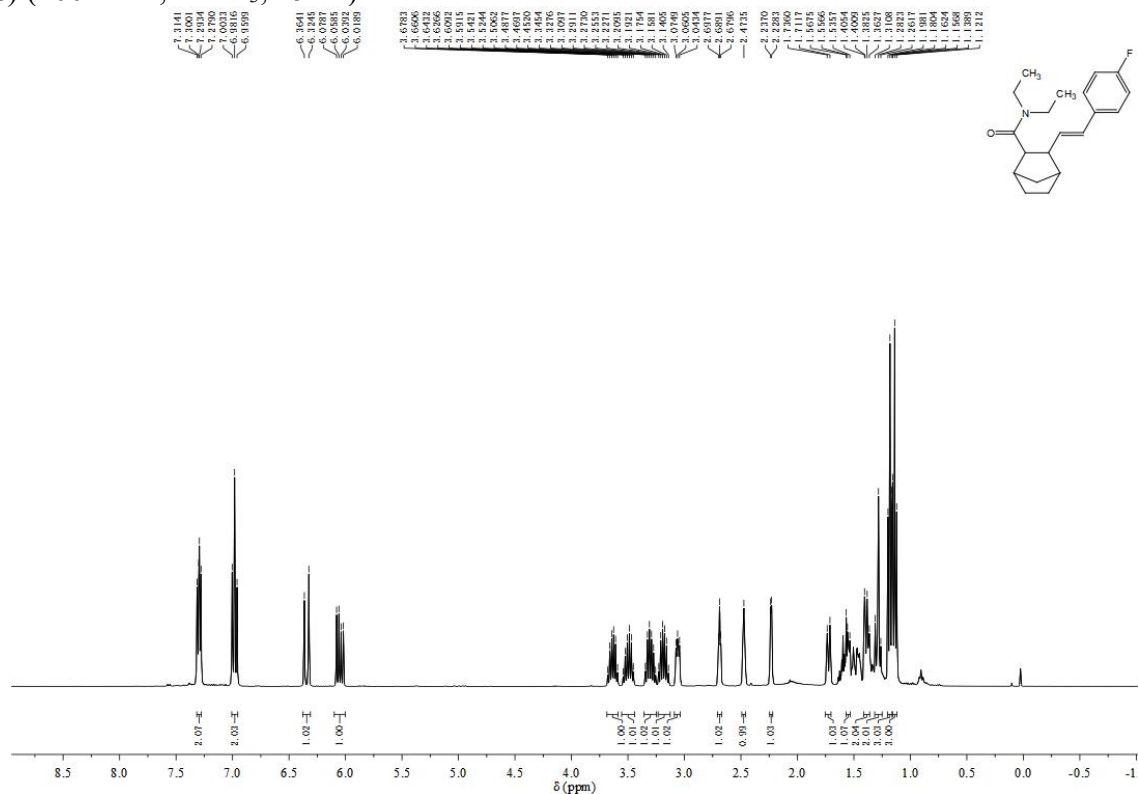
^1H NMR spectrum of (*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**21e**) (400 MHz, CDCl_3 , 25 °C)



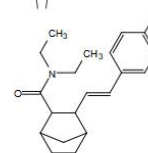
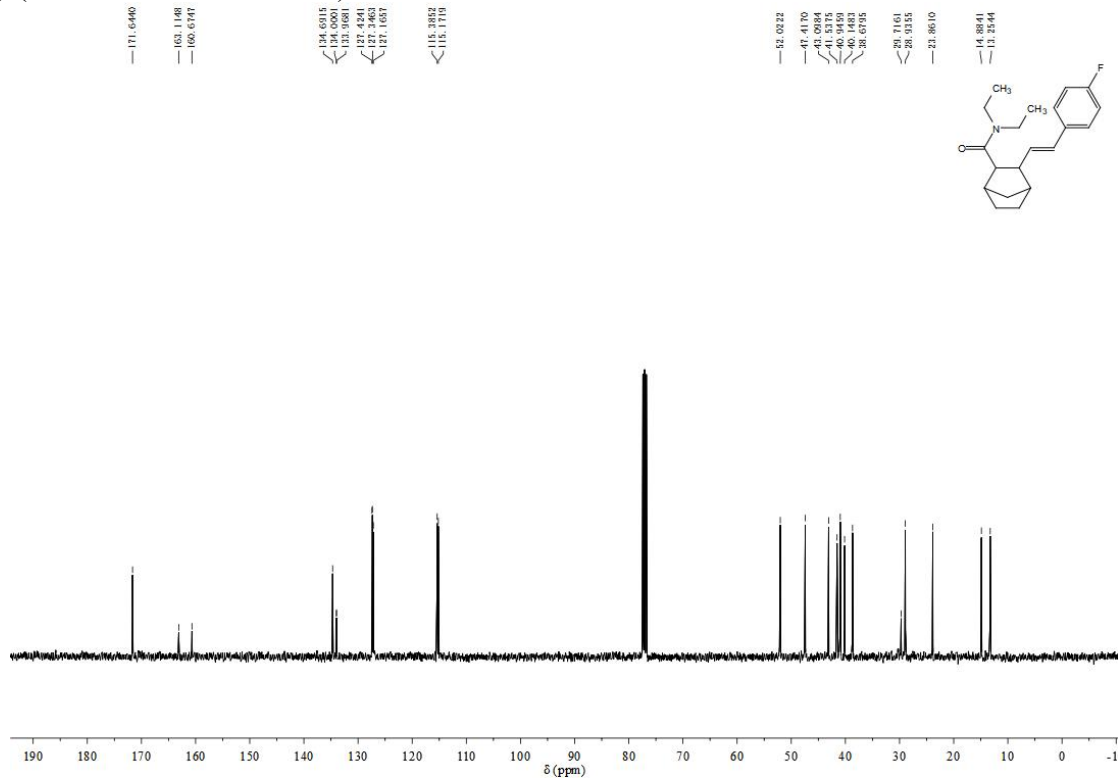
¹³C NMR spectrum of (*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**21e**) (100 MHz, CDCl₃, 25 °C)



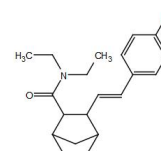
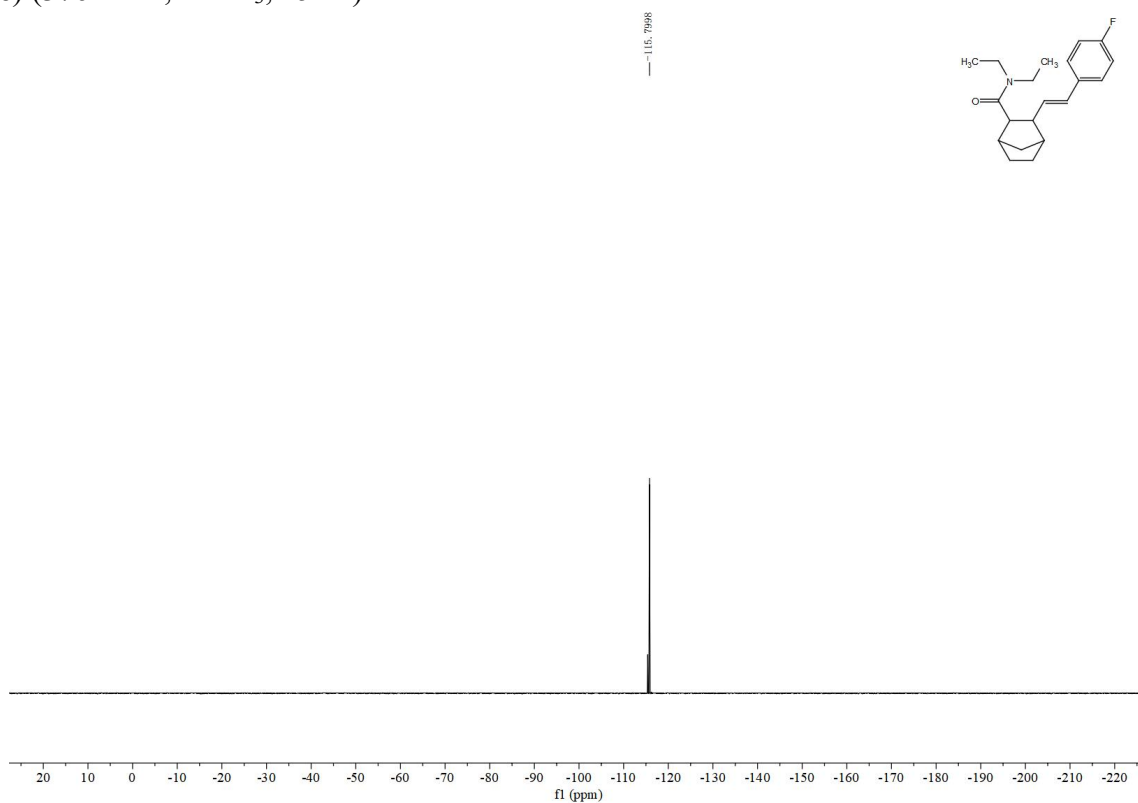
¹H NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**22e**) (400 MHz, CDCl₃, 25 °C)



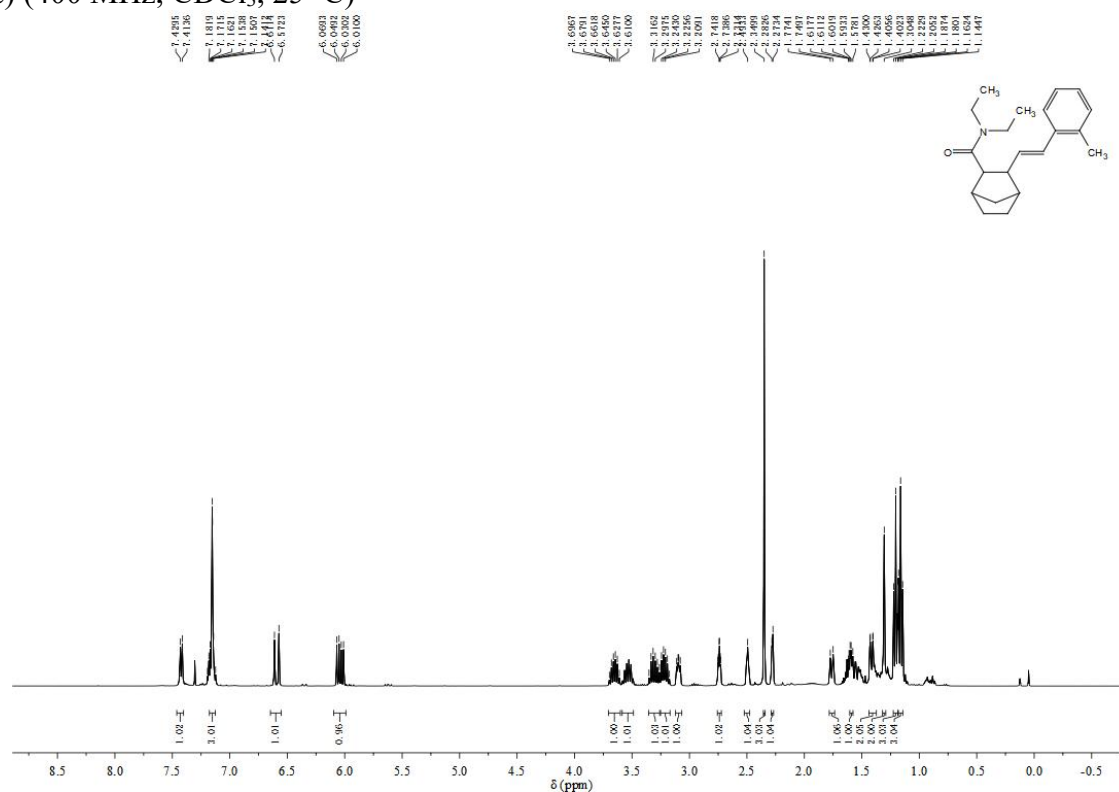
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**22e**) (100 MHz, CDCl_3 , 25 °C)



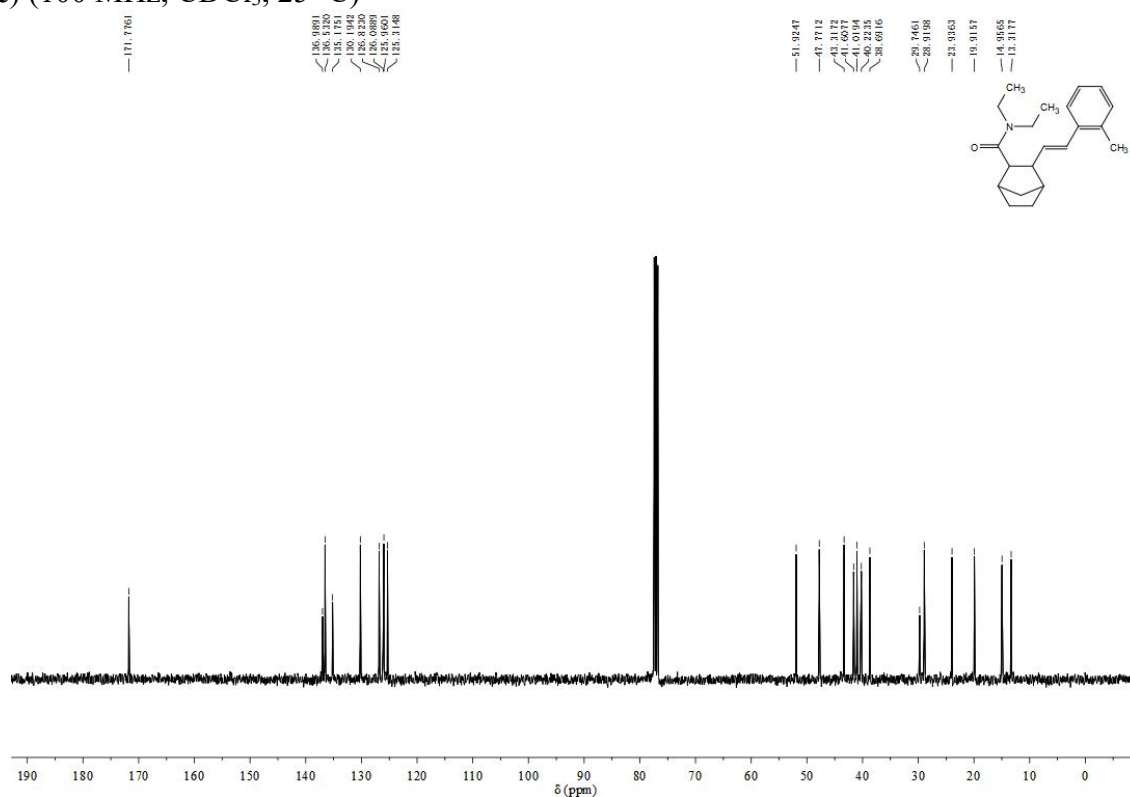
^{19}F NMR spectrum of (*E*)-*N,N*-diethyl-3-(4-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**22e**) (376 MHz, CDCl_3 , 25 °C)



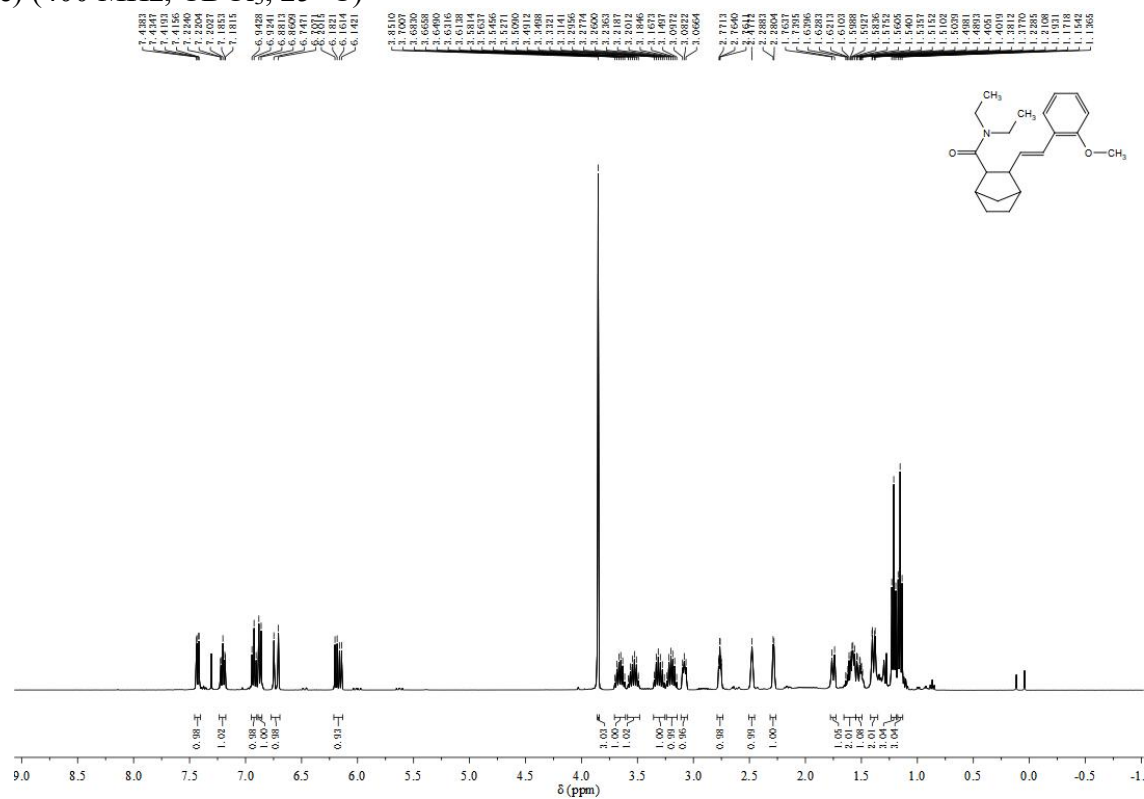
^1H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**23e**) (400 MHz, CDCl_3 , 25 °C)



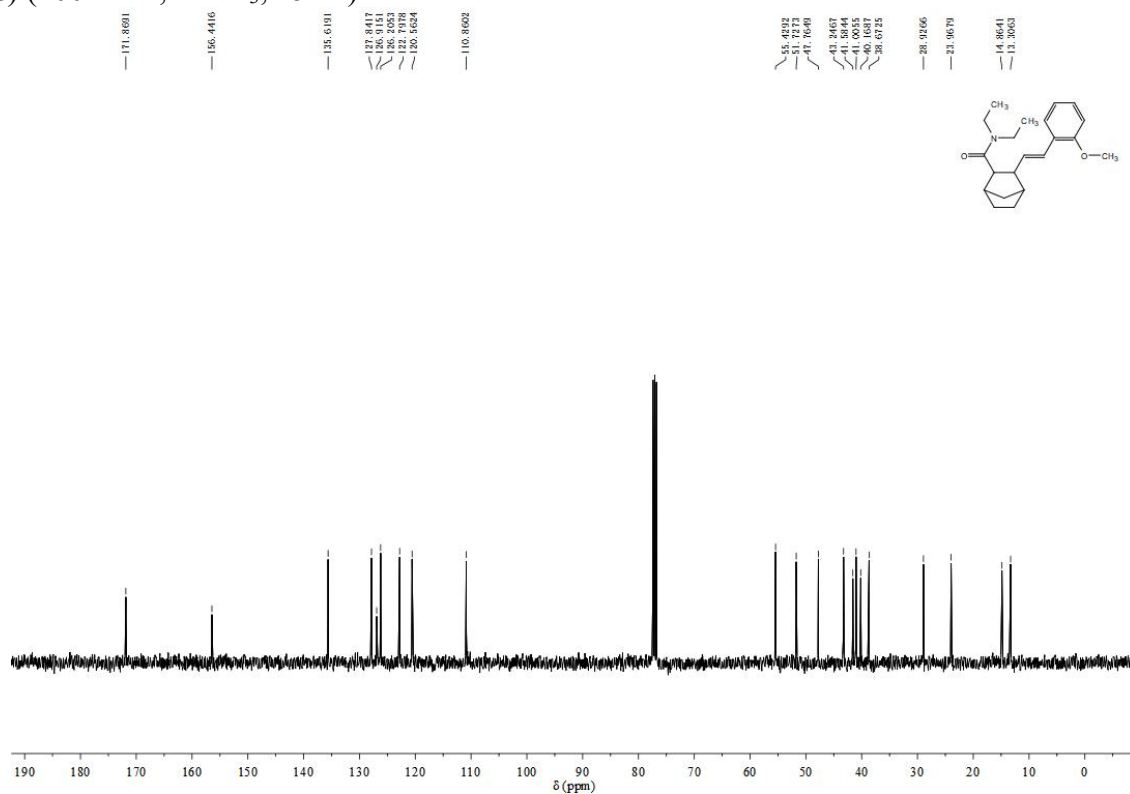
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**23e**) (100 MHz, CDCl_3 , 25 °C)



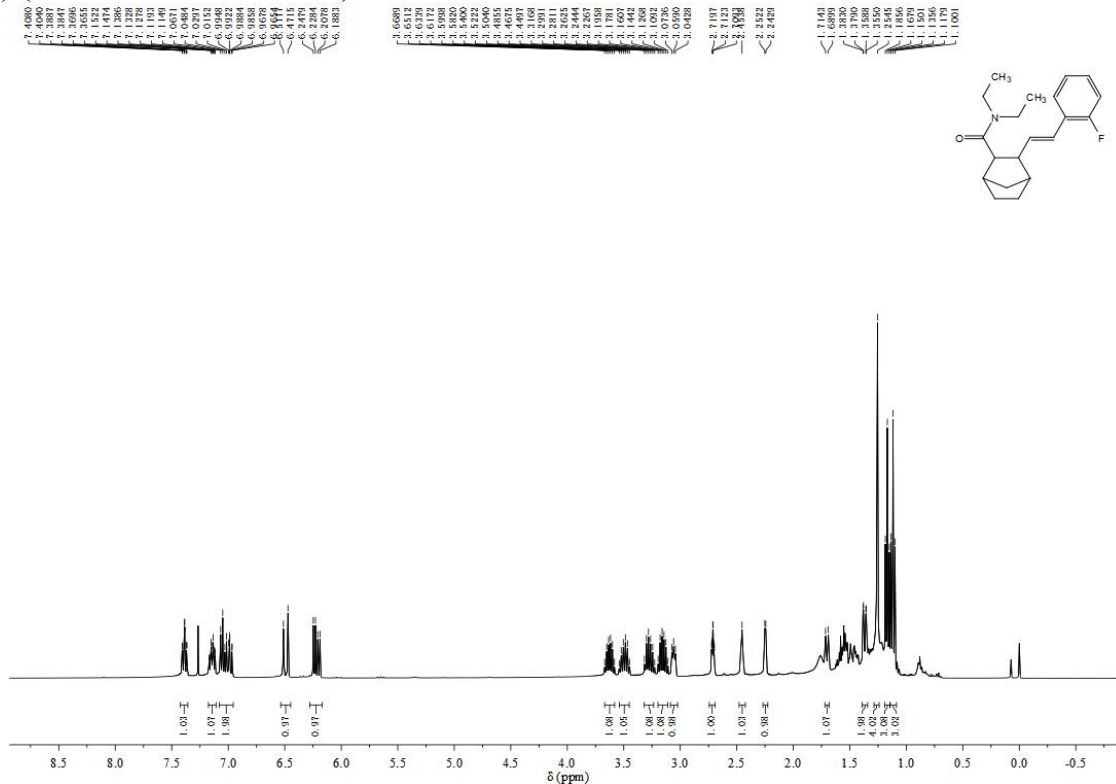
^1H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**24e**) (400 MHz, CDCl_3 , 25 °C)



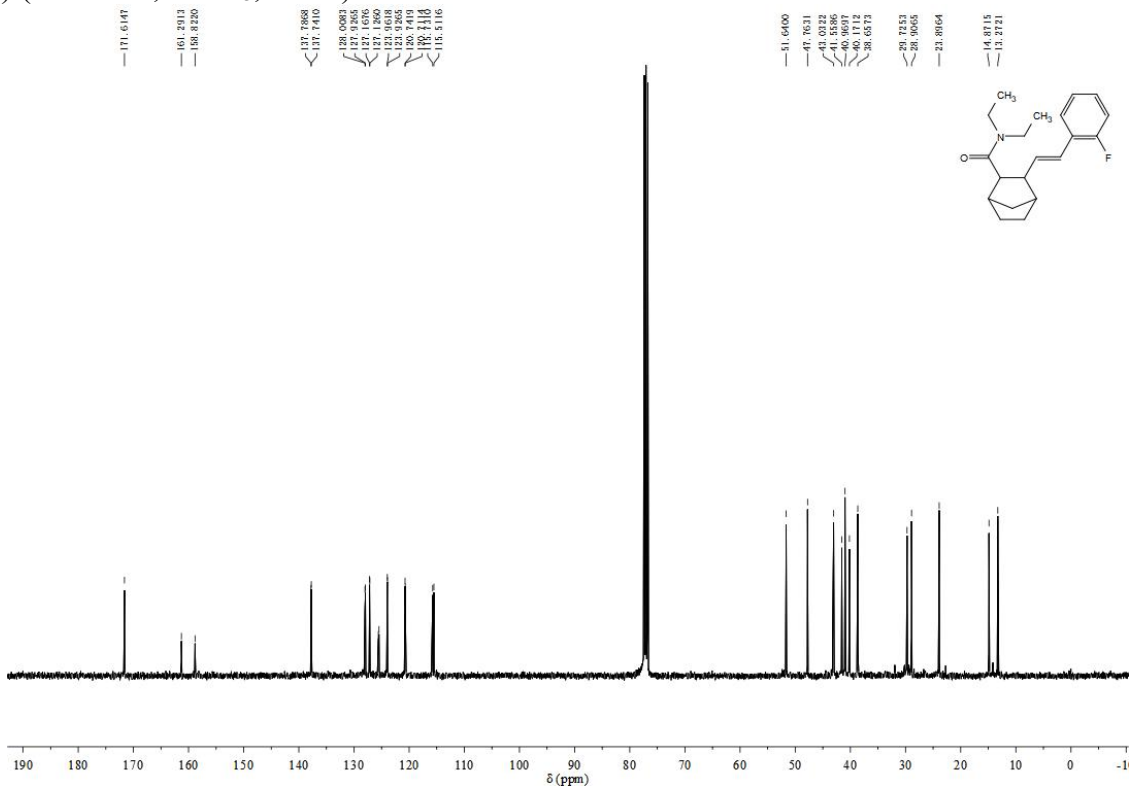
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-methoxystyryl)bicyclo[2.2.1]heptane-2-carboxamide (**24e**) (100 MHz, CDCl_3 , 25 °C)



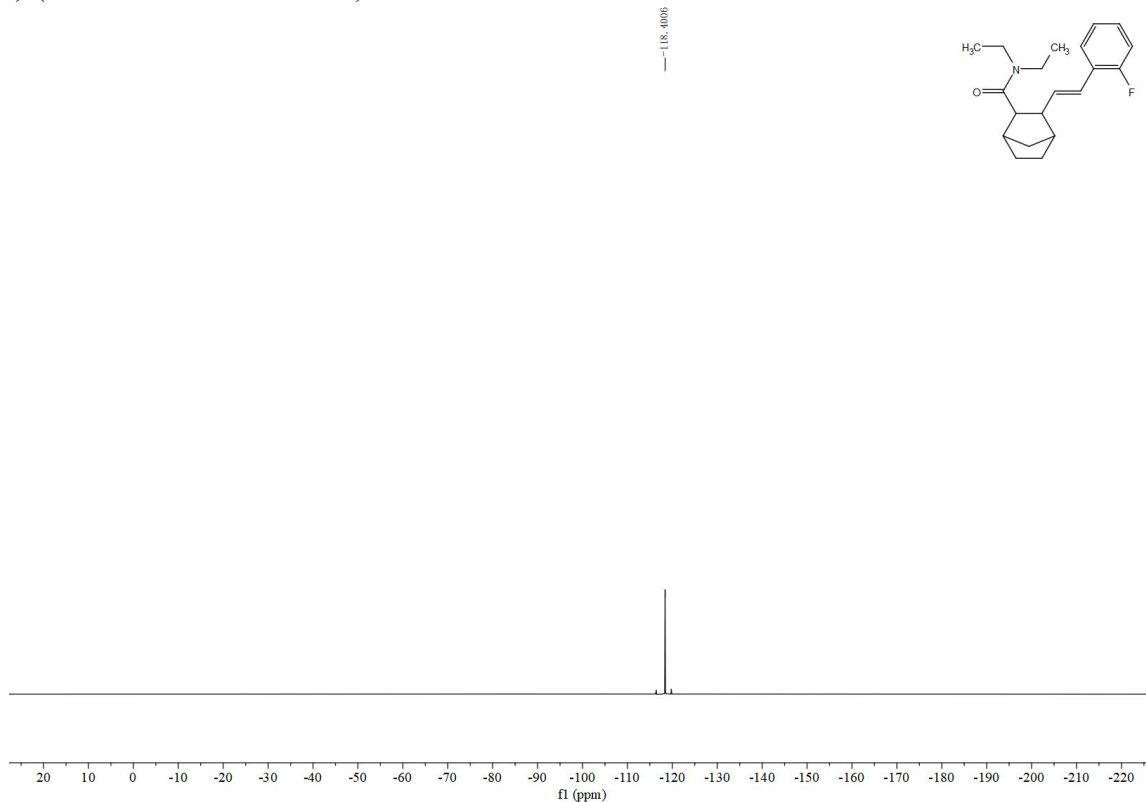
¹H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**25e**) (400 MHz, CDCl₃, 25 °C)



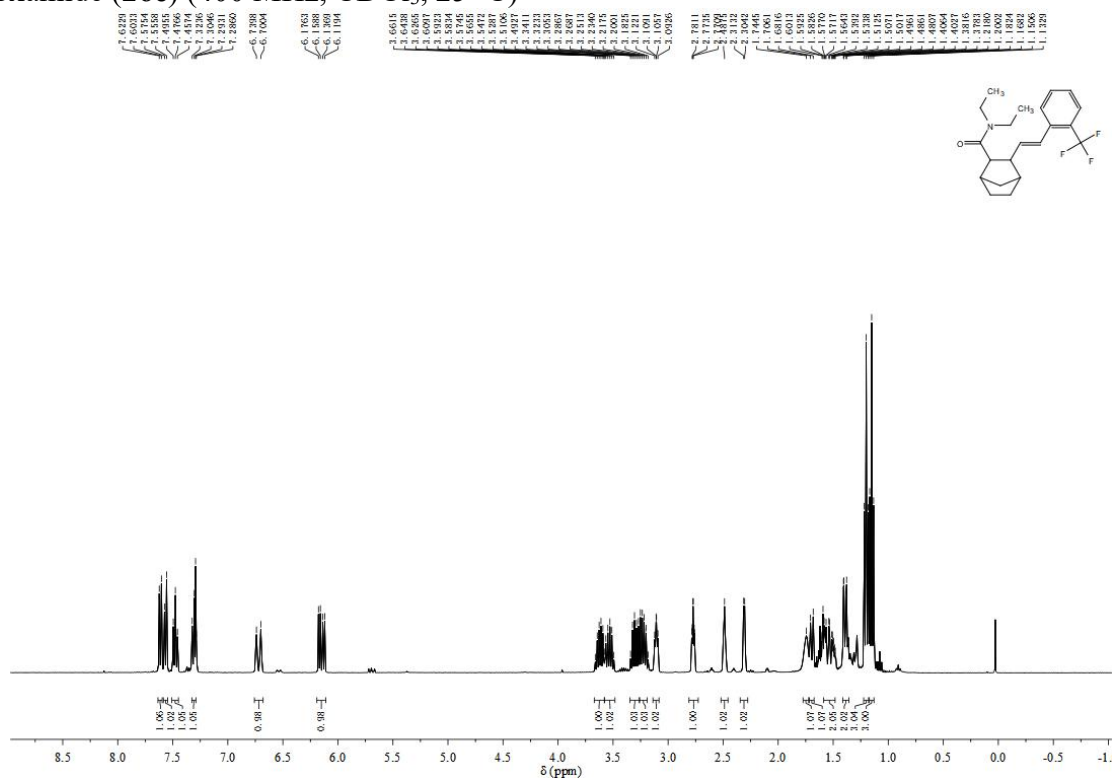
¹³C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**25e**) (100 MHz, CDCl₃, 25 °C)



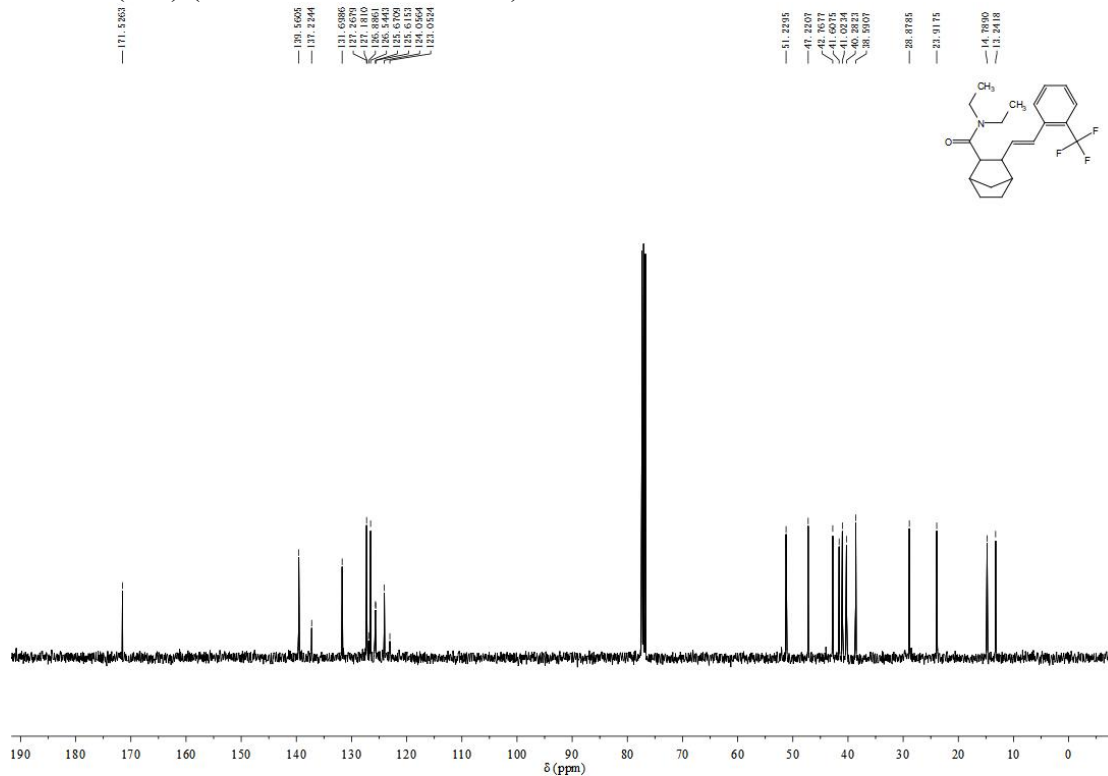
^{19}F NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**25e**) (376 MHz, CDCl_3 , 25 °C)



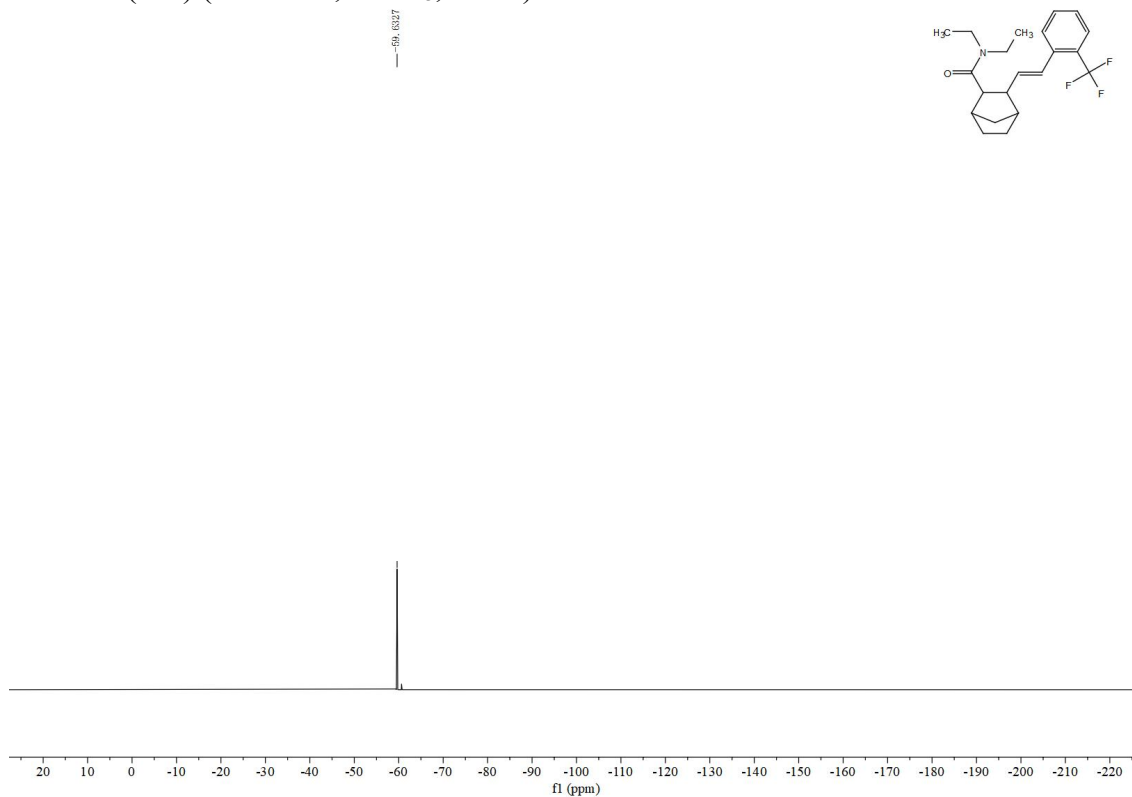
^1H NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**26e**) (400 MHz, CDCl_3 , 25 °C)



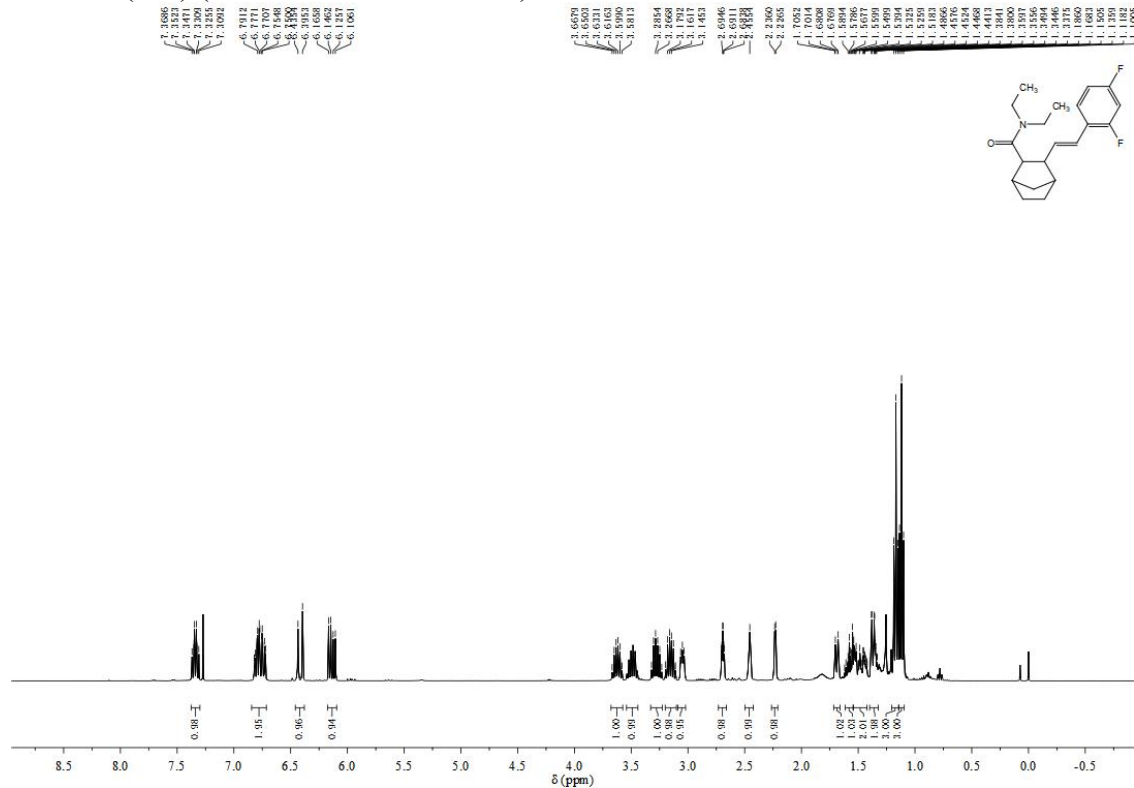
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**26e**) (100 MHz, CDCl_3 , 25 °C)



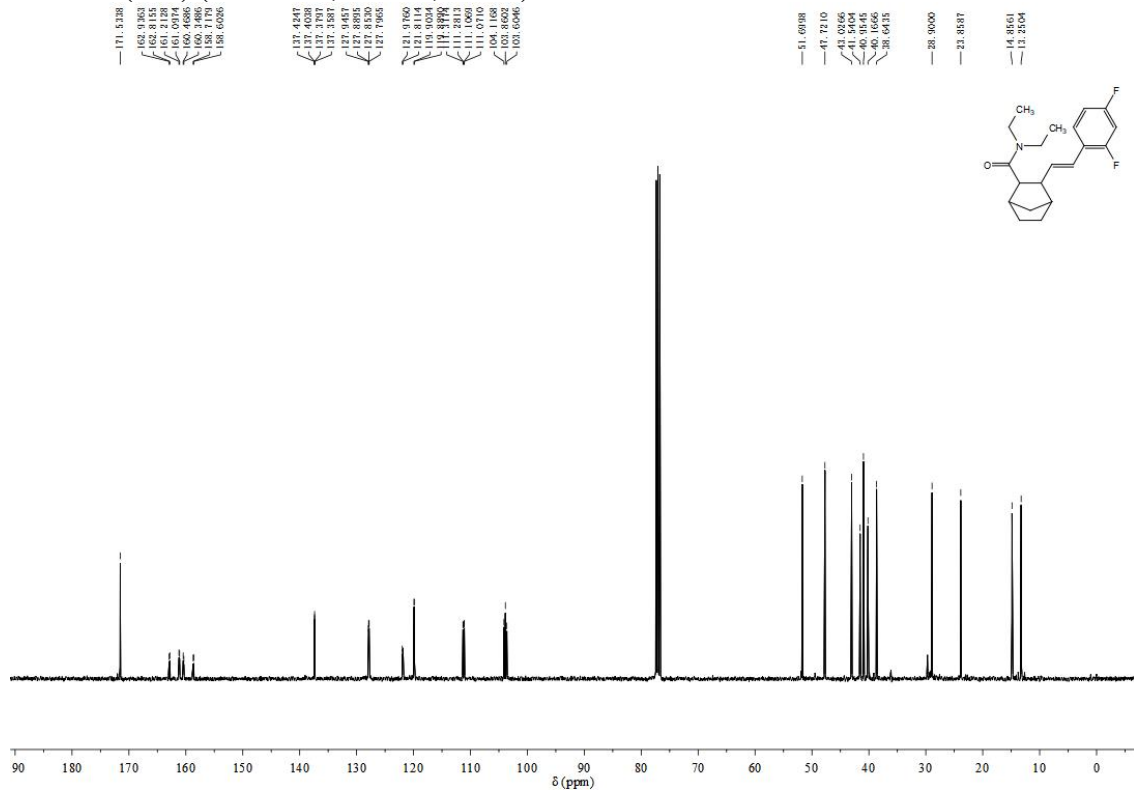
^{19}F NMR spectrum of (*E*)-*N,N*-diethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**26e**) (376 MHz, CDCl_3 , 25 °C)



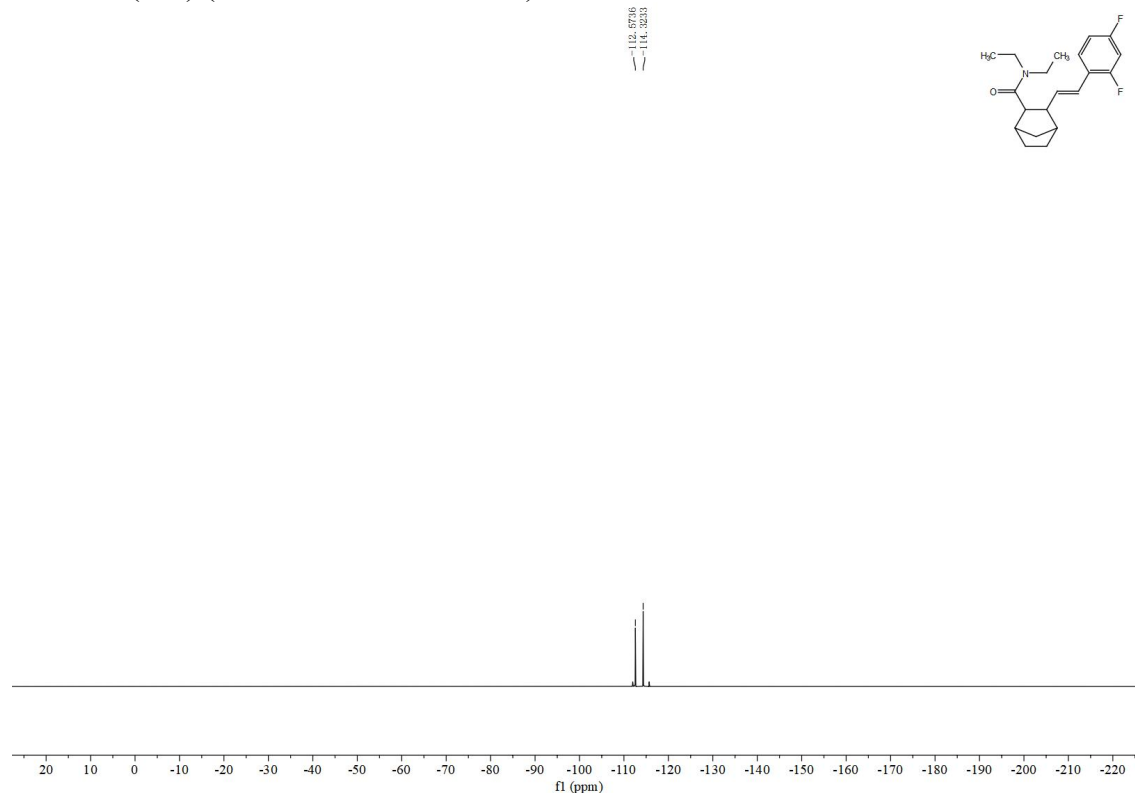
¹H NMR spectrum of (*E*)-3-(2,4-difluorostyryl)-*N,N*-diethylbicyclo [2.2.1] heptane-2-carboxamide (**27e**) (400 MHz, CDCl₃, 25 °C)



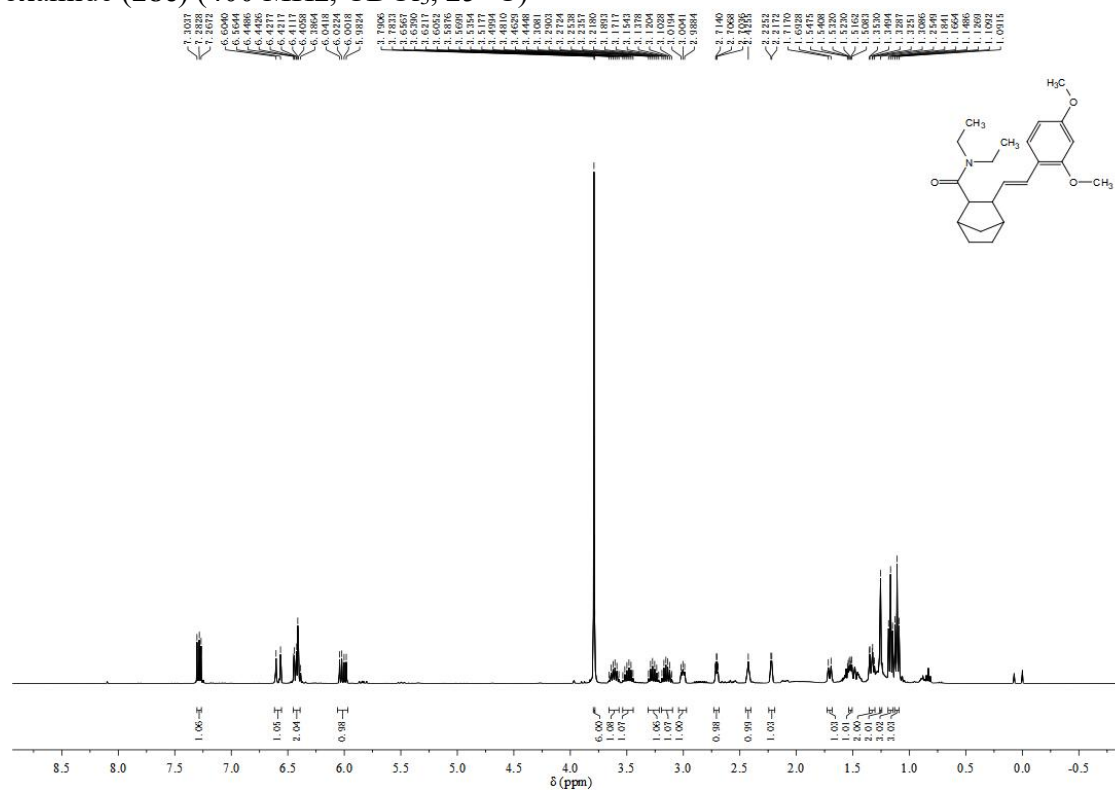
¹³C NMR spectrum of (*E*)-3-(2,4-difluorostyryl)-*N,N*-diethylbicyclo [2.2.1] heptane-2-carboxamide (**27e**) (100 MHz, CDCl₃, 25 °C)



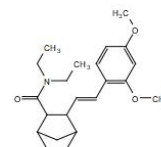
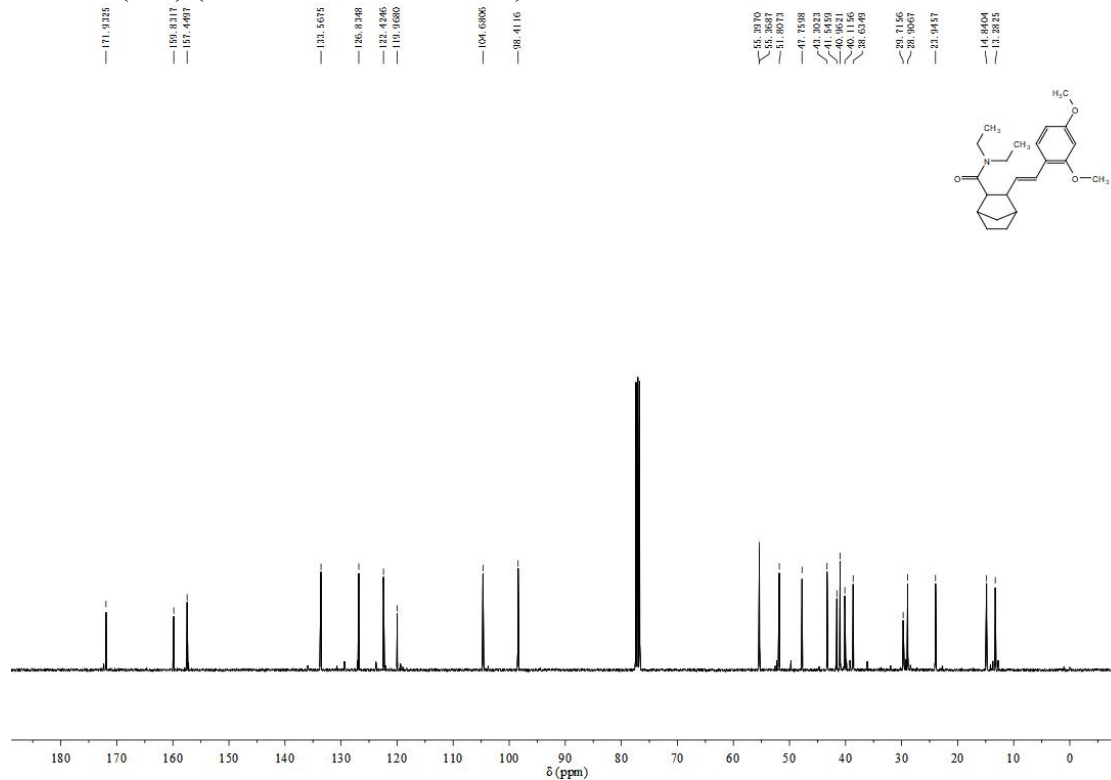
¹⁹F NMR spectrum of (*E*)-3-(2,4-difluorostyryl)-*N,N*-diethylbicyclo [2.2.1] heptane-2-carboxamide (**27e**) (376 MHz, CDCl₃, 25 °C)



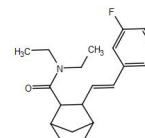
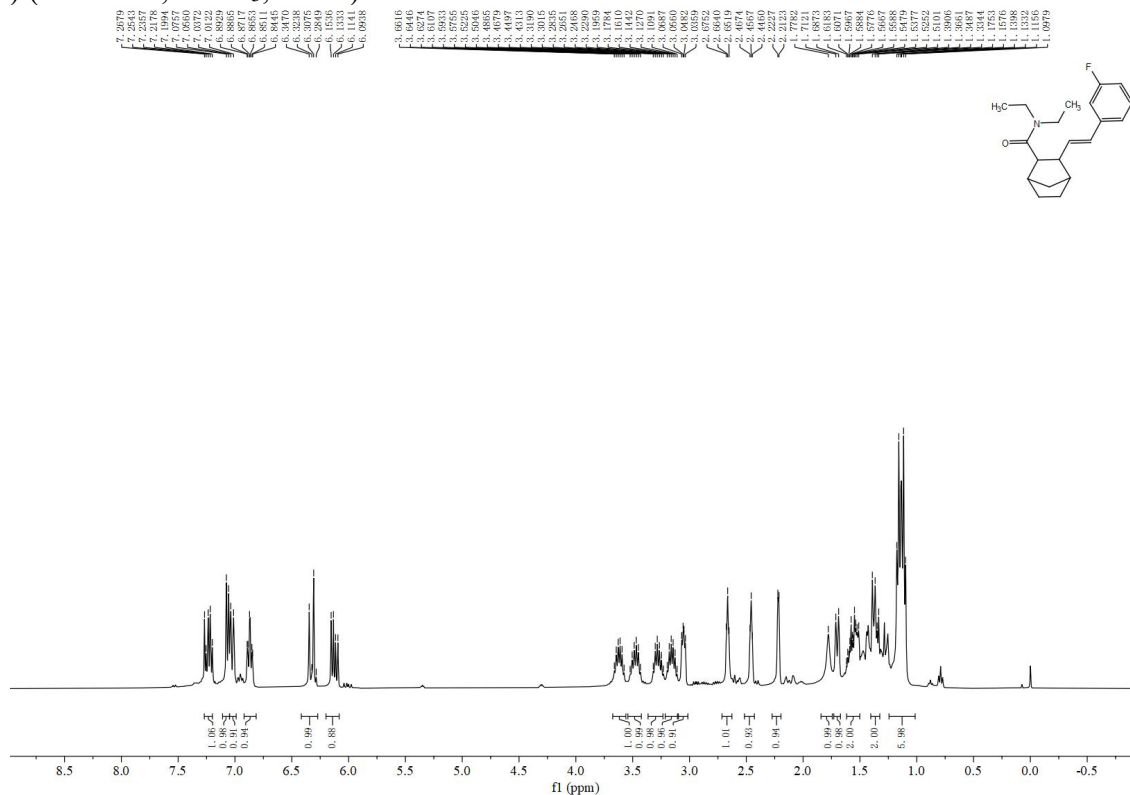
¹H NMR spectrum of (*E*)-3-(2,4-dimethoxystyryl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**28e**) (400 MHz, CDCl₃, 25 °C)



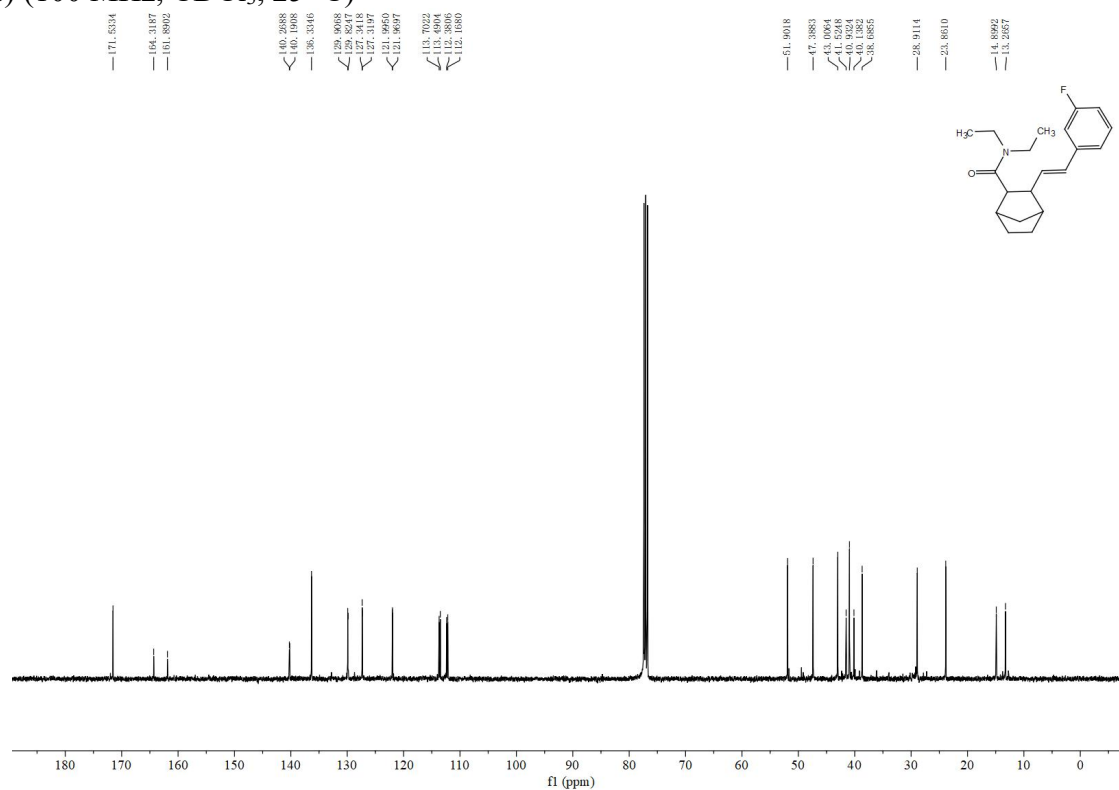
^{13}C NMR spectrum of (*E*)-3-(2,4-dimethoxystyryl)-*N,N*-diethylbicyclo[2.2.1]heptane-2-carboxamide (**28e**) (100 MHz, CDCl_3 , 25 °C)



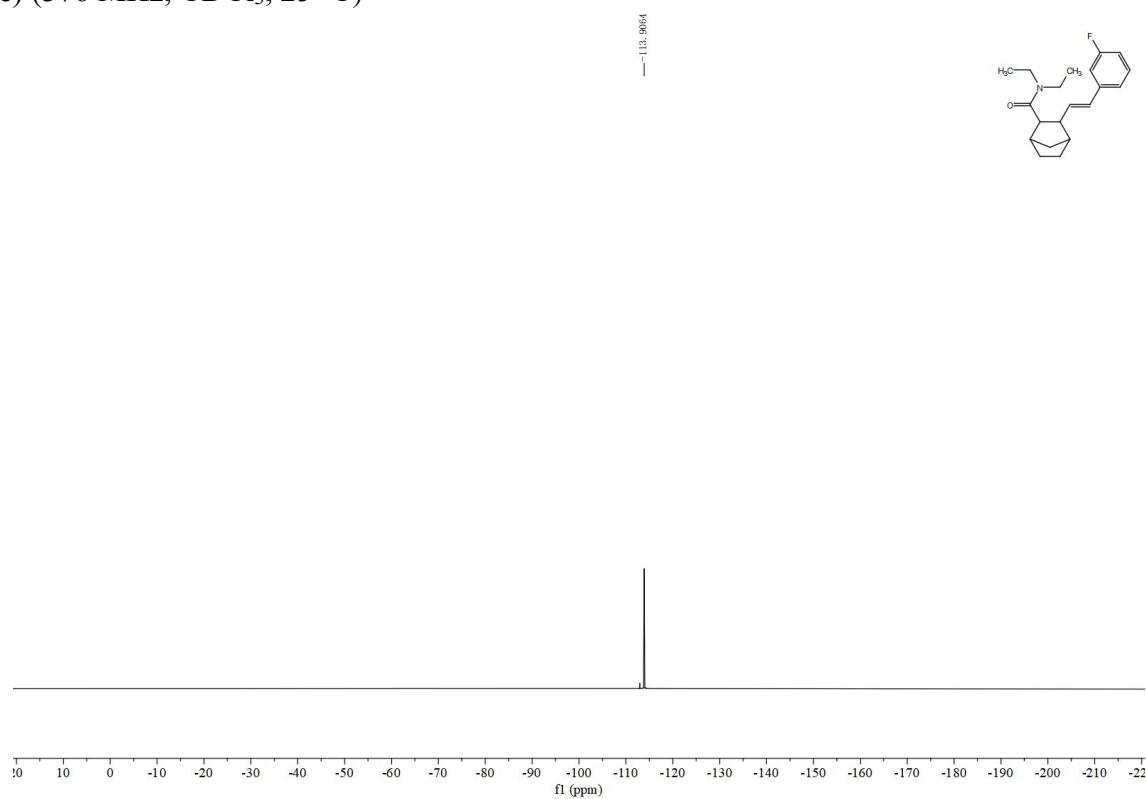
^1H NMR spectrum of (*E*)-*N,N*-diethyl-3-(3-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**29e**) (400 MHz, CDCl_3 , 25 °C)



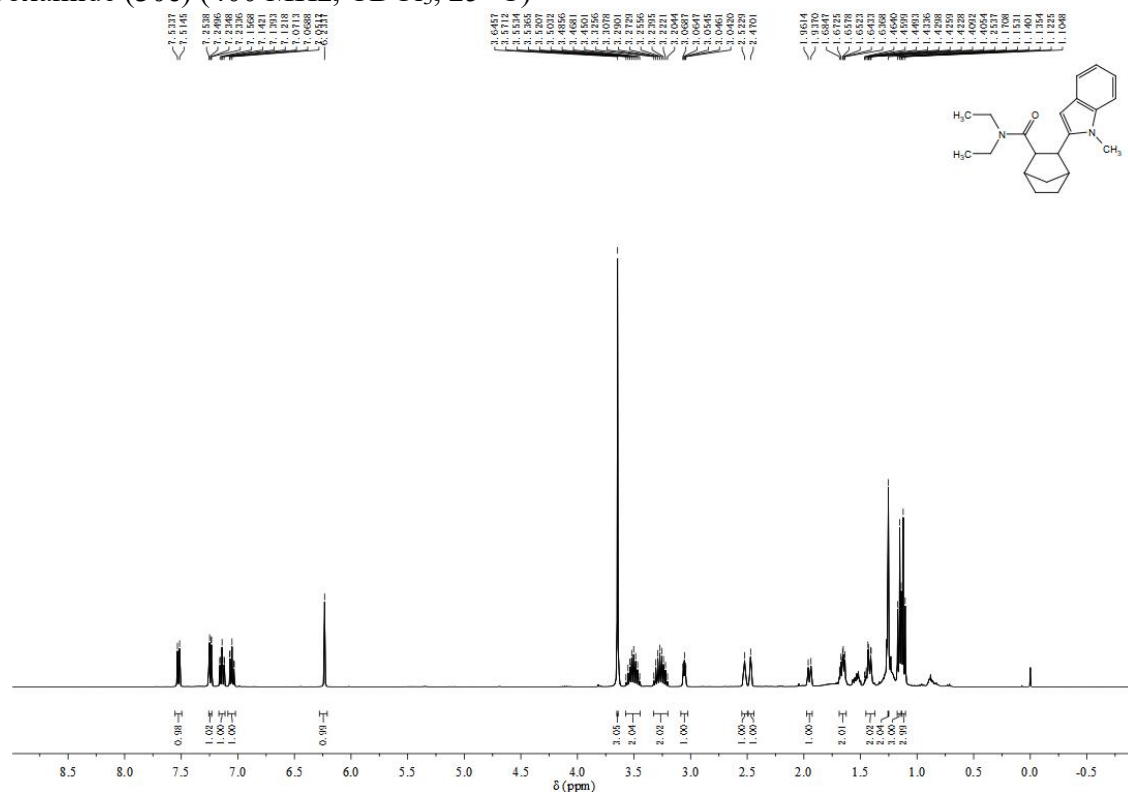
^{13}C NMR spectrum of (*E*)-*N,N*-diethyl-3-(3-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**29e**) (100 MHz, CDCl_3 , 25 °C)



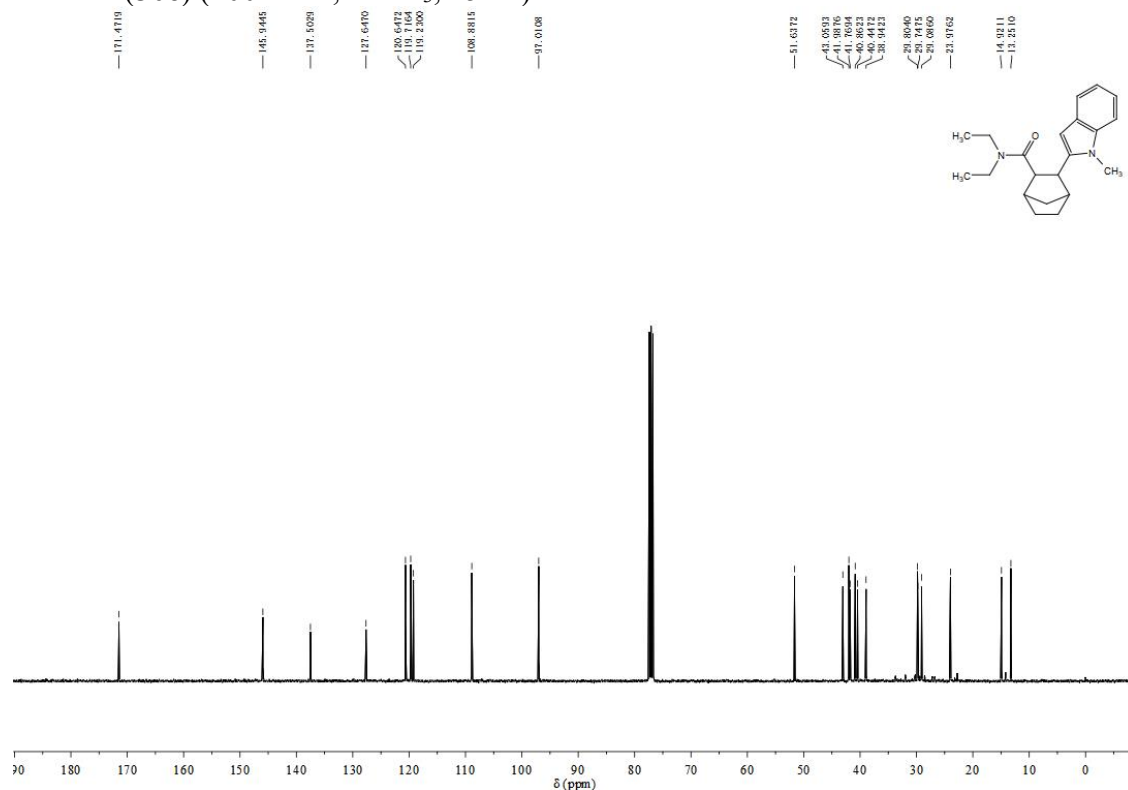
^{19}F NMR spectrum of (*E*)-*N,N*-diethyl-3-(3-fluorostyryl)bicyclo[2.2.1]heptane-2-carboxamide (**29e**) (376 MHz, CDCl_3 , 25 °C)



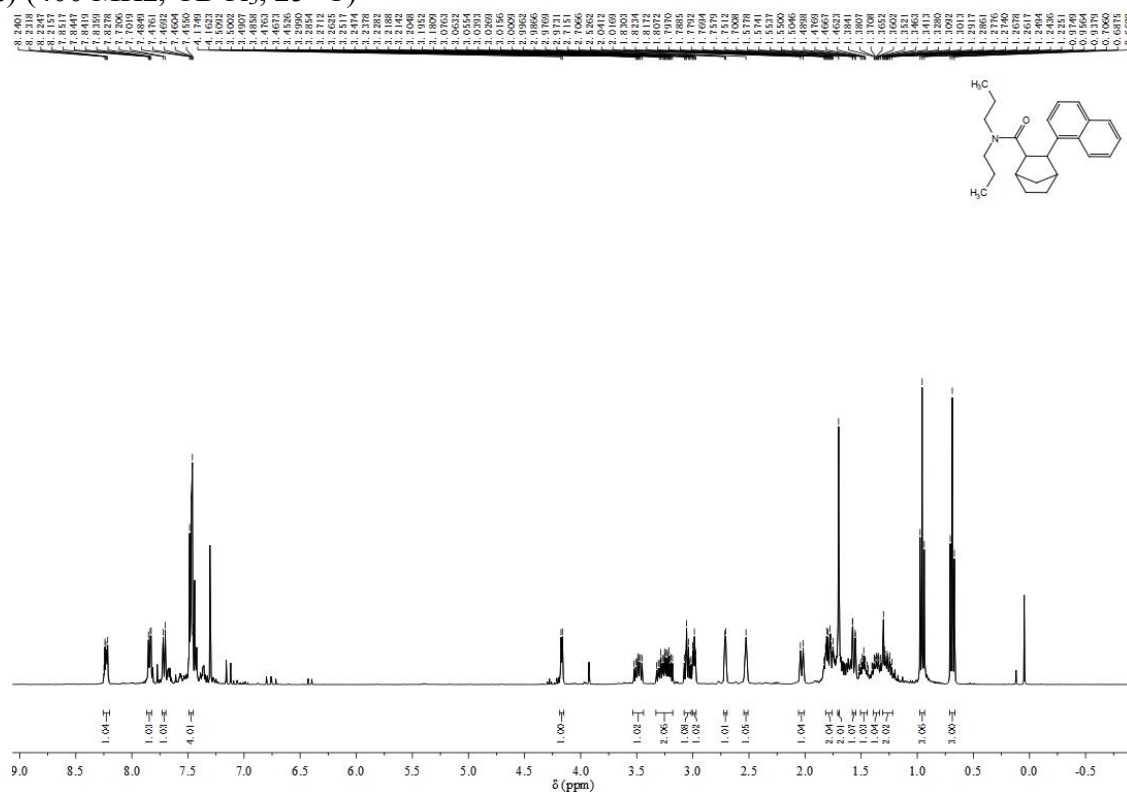
^1H NMR spectrum of *N,N*-diethyl-3-(1-methyl-1*H*-indol-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**30e**) (400 MHz, CDCl_3 , 25 °C)



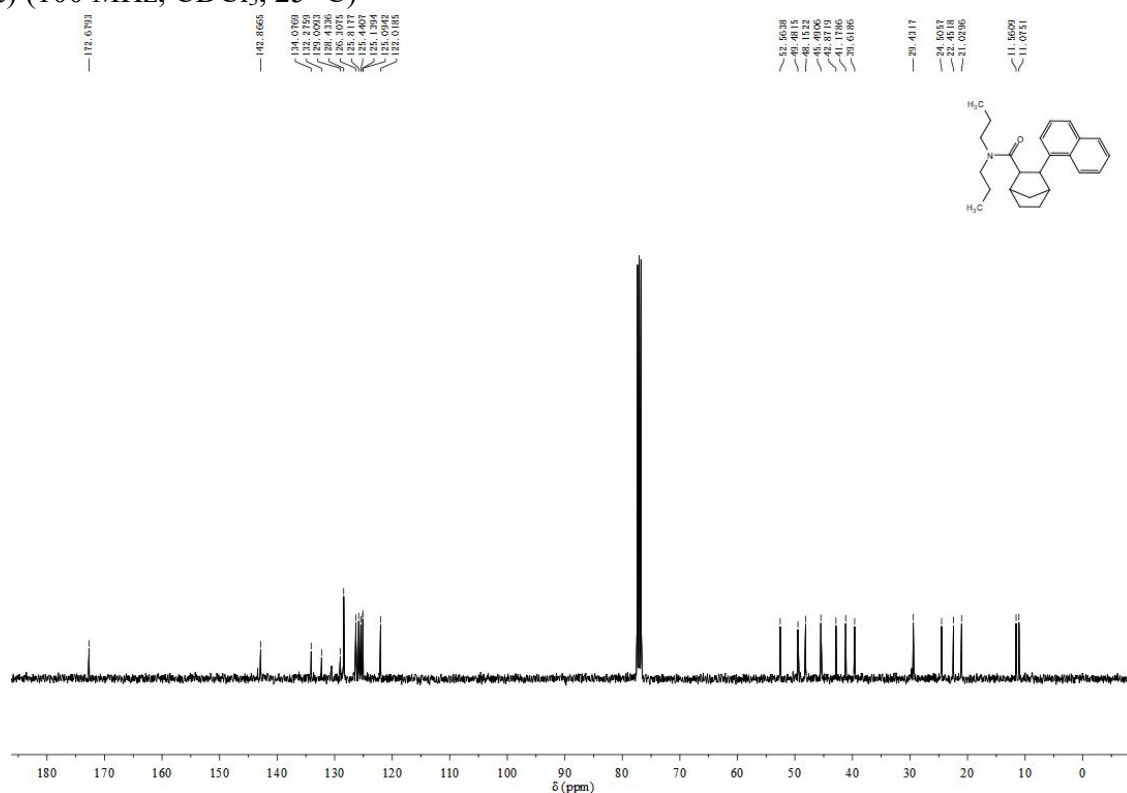
^{13}C NMR spectrum of *N,N*-diethyl-3-(1-methyl-1*H*-indol-2-yl)bicyclo[2.2.1]heptane-2-carboxamide (**30e**) (100 MHz, CDCl_3 , 25 °C)



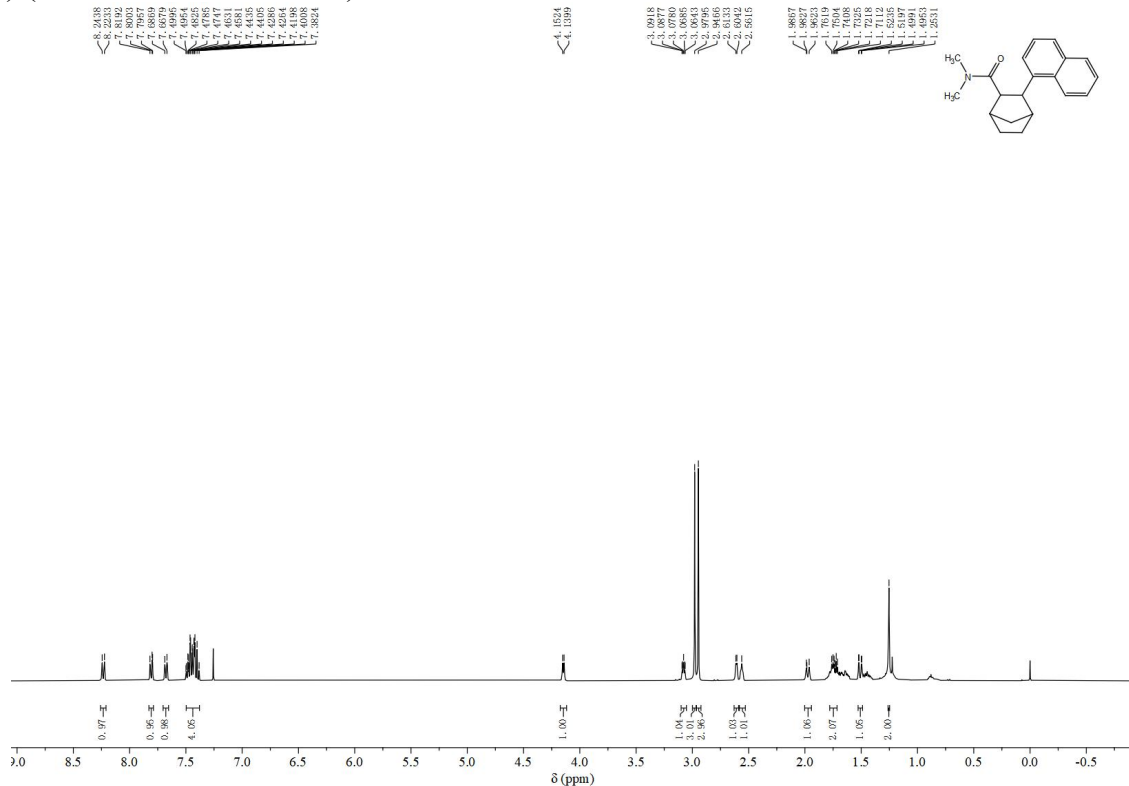
^1H NMR spectrum of 3-(naphthalen-1-yl)-*N,N*-dipropylbicyclo[2.2.1]heptane-2-carboxamide (**31e**) (400 MHz, CDCl_3 , 25 °C)



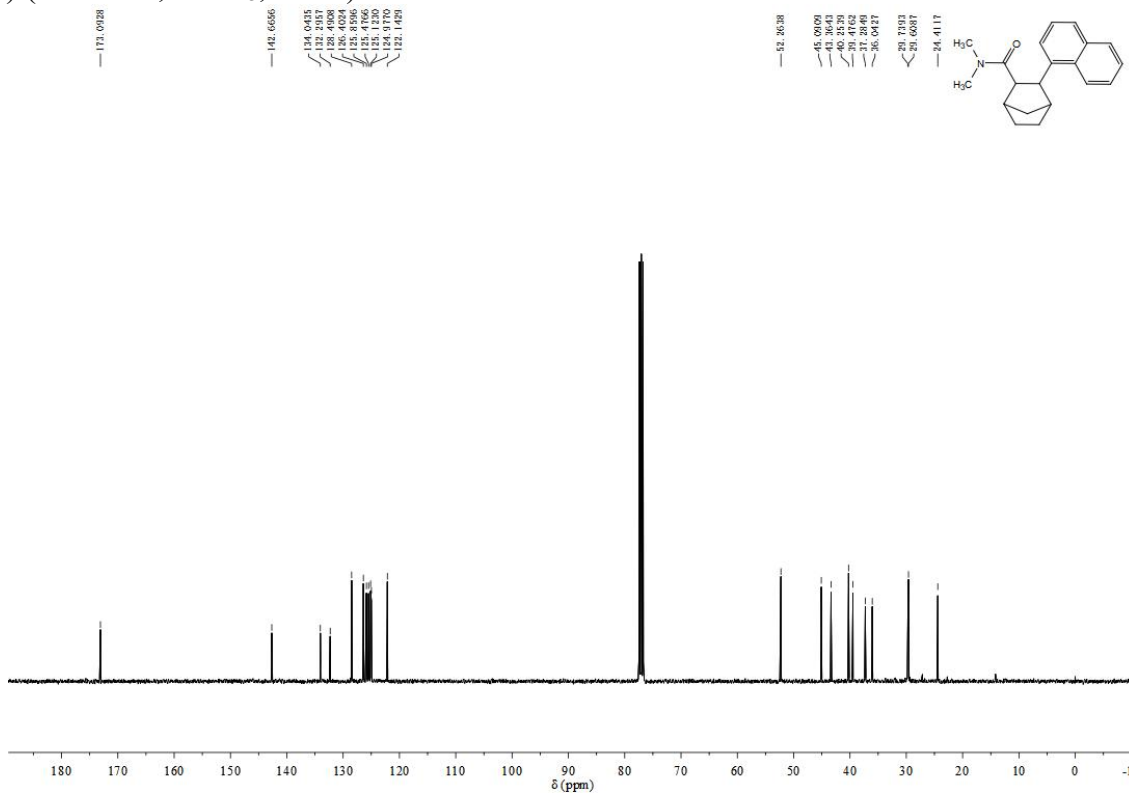
^{13}C NMR spectrum of 3-(naphthalen-1-yl)-*N,N*-dipropylbicyclo[2.2.1]heptane-2-carboxamide (**31e**) (100 MHz, CDCl_3 , 25 °C)



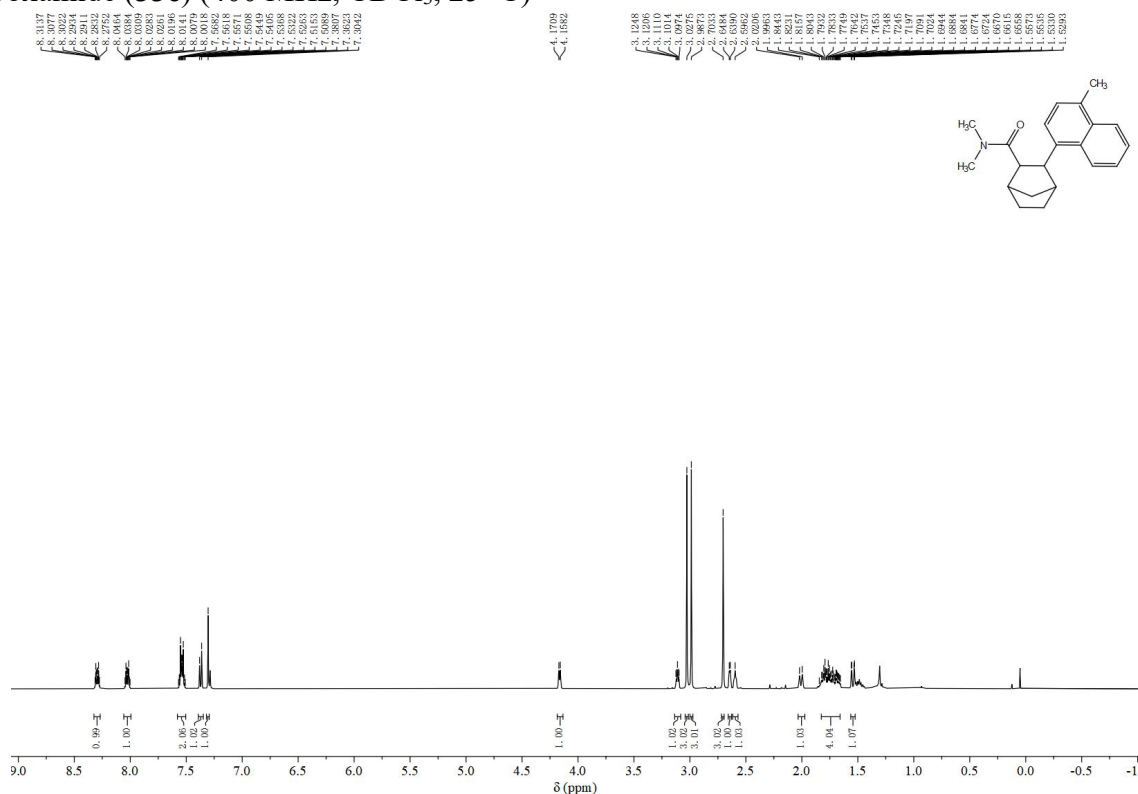
¹H NMR spectrum of *N,N*-dimethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**32e**) (400 MHz, CDCl₃, 25 °C)



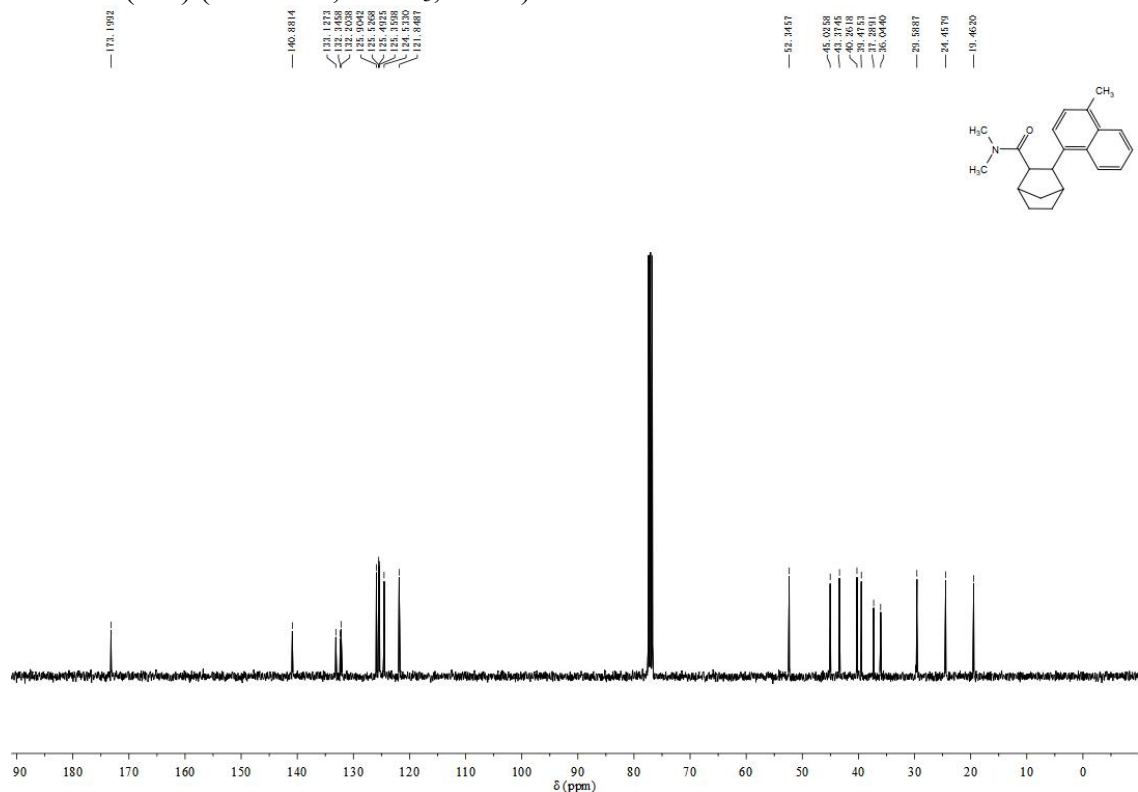
¹³C NMR spectrum of *N,N*-dimethyl-3-(naphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**32e**) (100 MHz, CDCl₃, 25 °C)



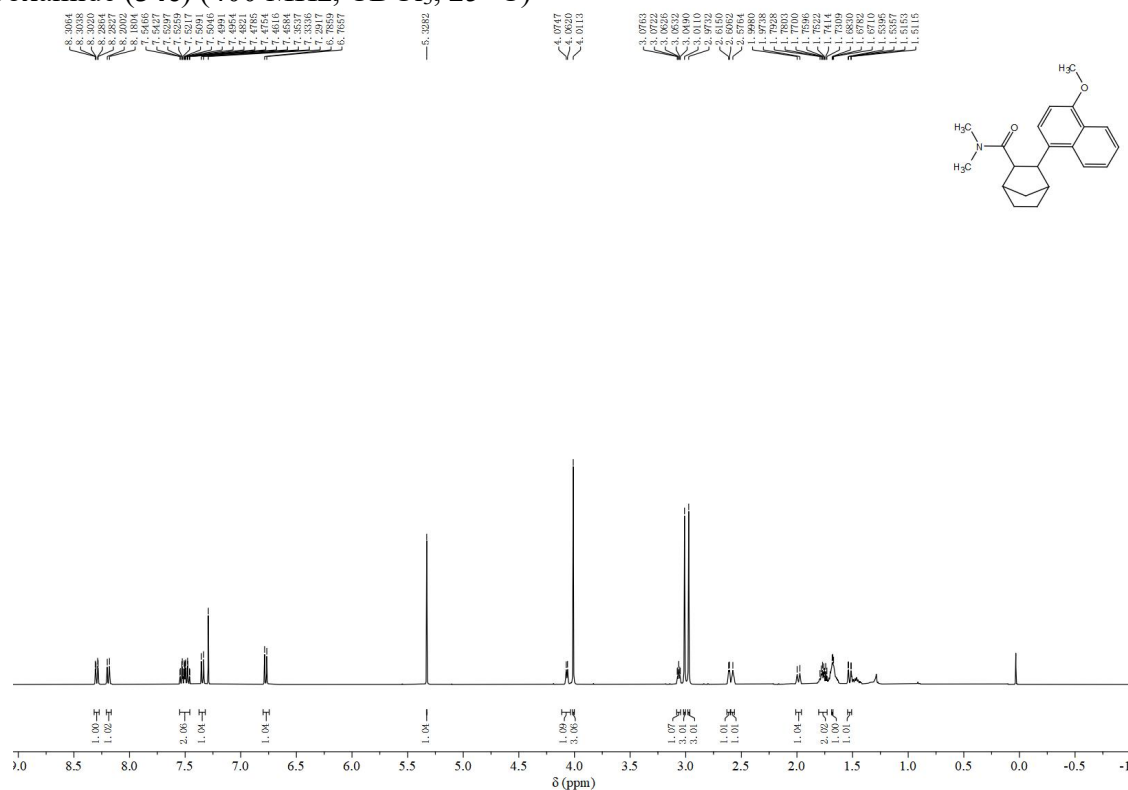
^1H NMR spectrum of *N,N*-dimethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**33e**) (400 MHz, CDCl_3 , 25 °C)



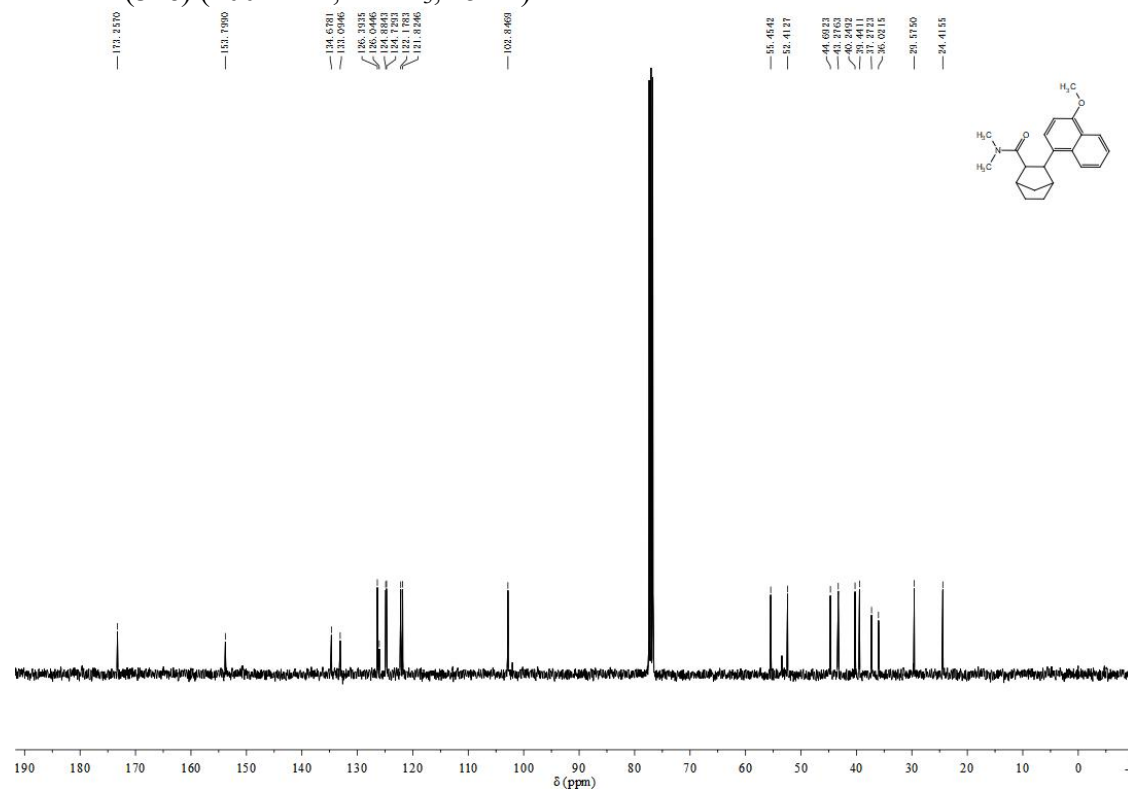
^{13}C NMR spectrum of *N,N*-dimethyl-3-(4-methylnaphthalen-1-yl)bicyclo[2.2.1]heptane-2-carboxamide (**33e**) (100 MHz, CDCl_3 , 25 °C)



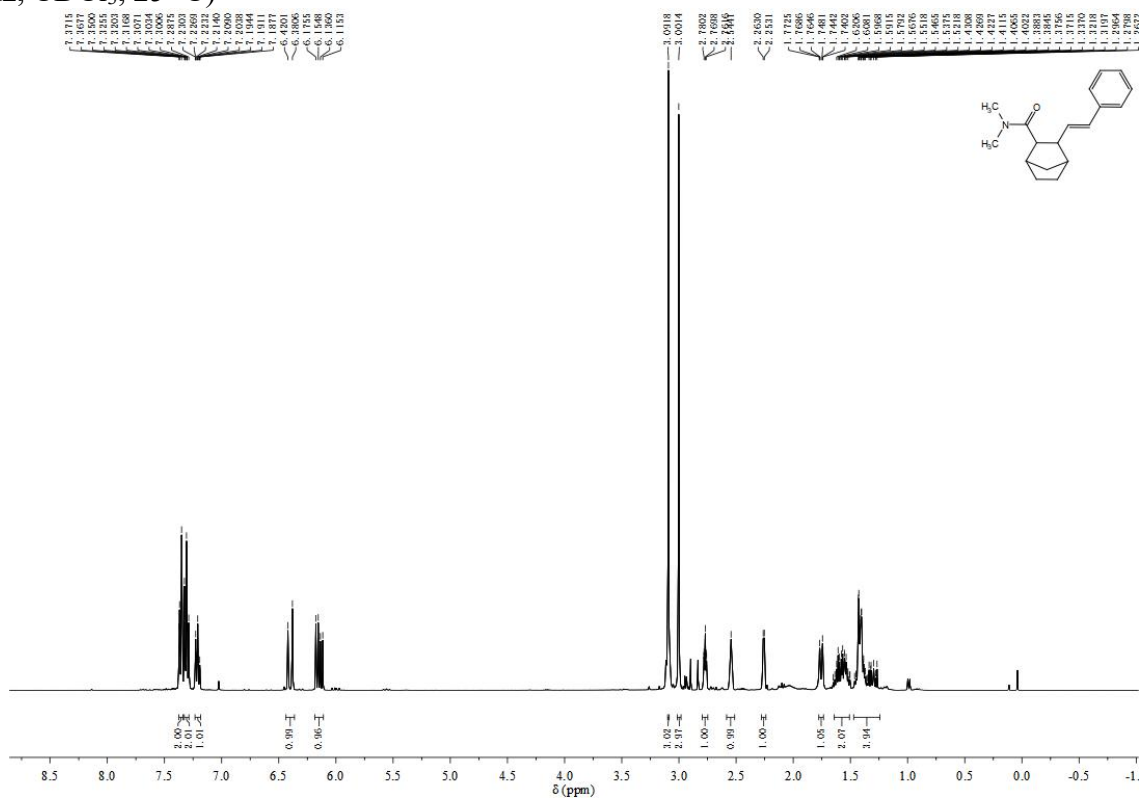
^1H NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**34e**) (400 MHz, CDCl_3 , 25 °C)



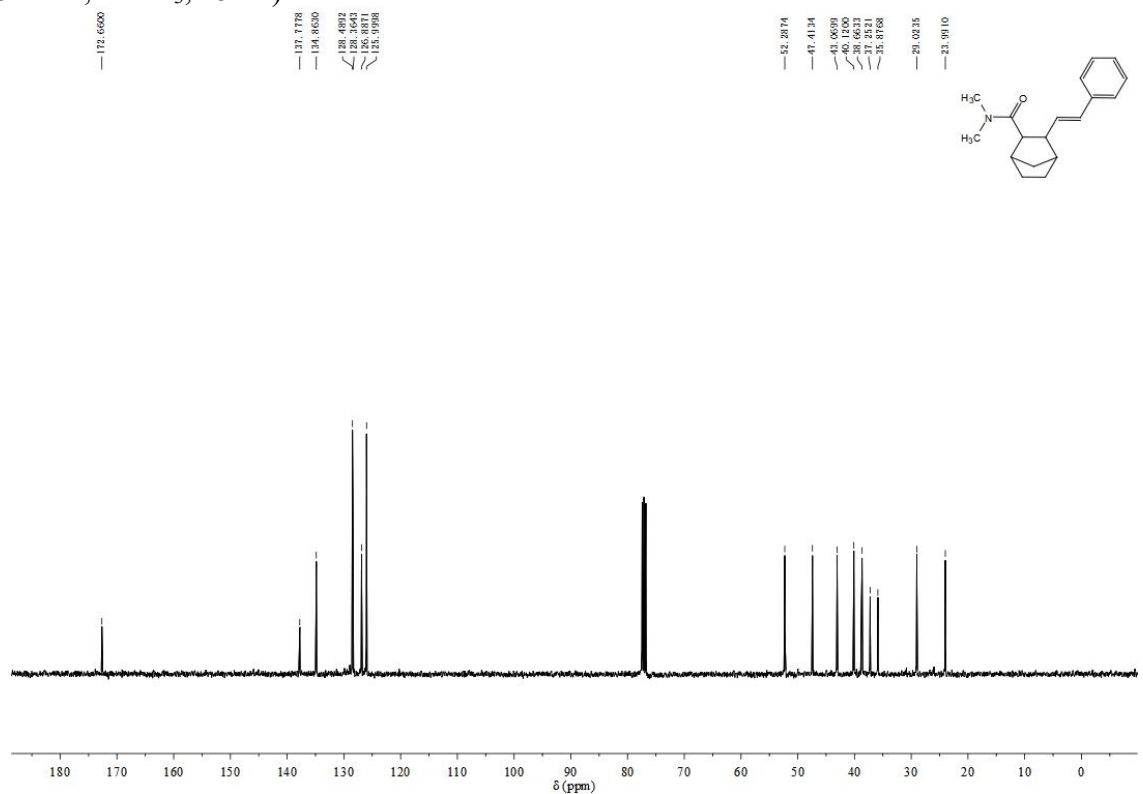
^{13}C NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**34e**) (100 MHz, CDCl_3 , 25 °C)



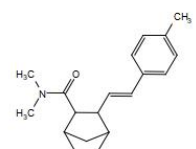
¹H NMR spectrum of (*E*)-*N,N*-dimethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**36e**) (400 MHz, CDCl₃, 25 °C)



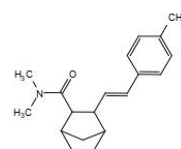
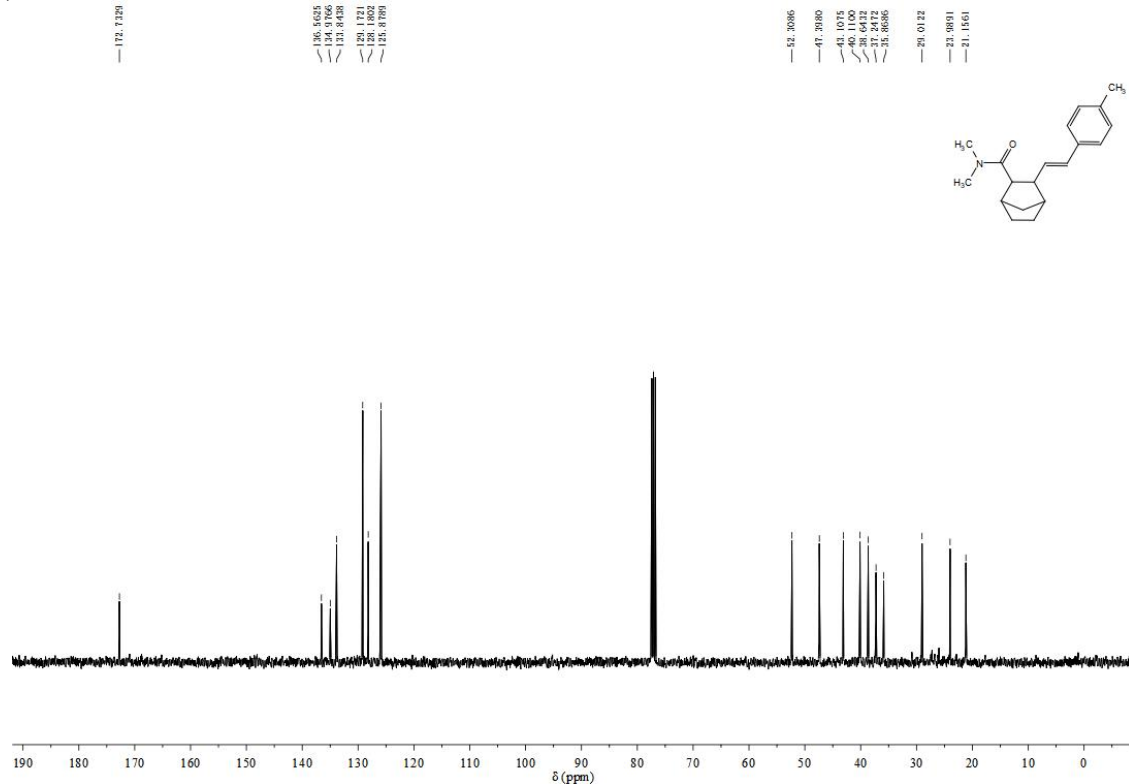
¹³C NMR spectrum of (*E*)-*N,N*-dimethyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**36e**) (100 MHz, CDCl₃, 25 °C)



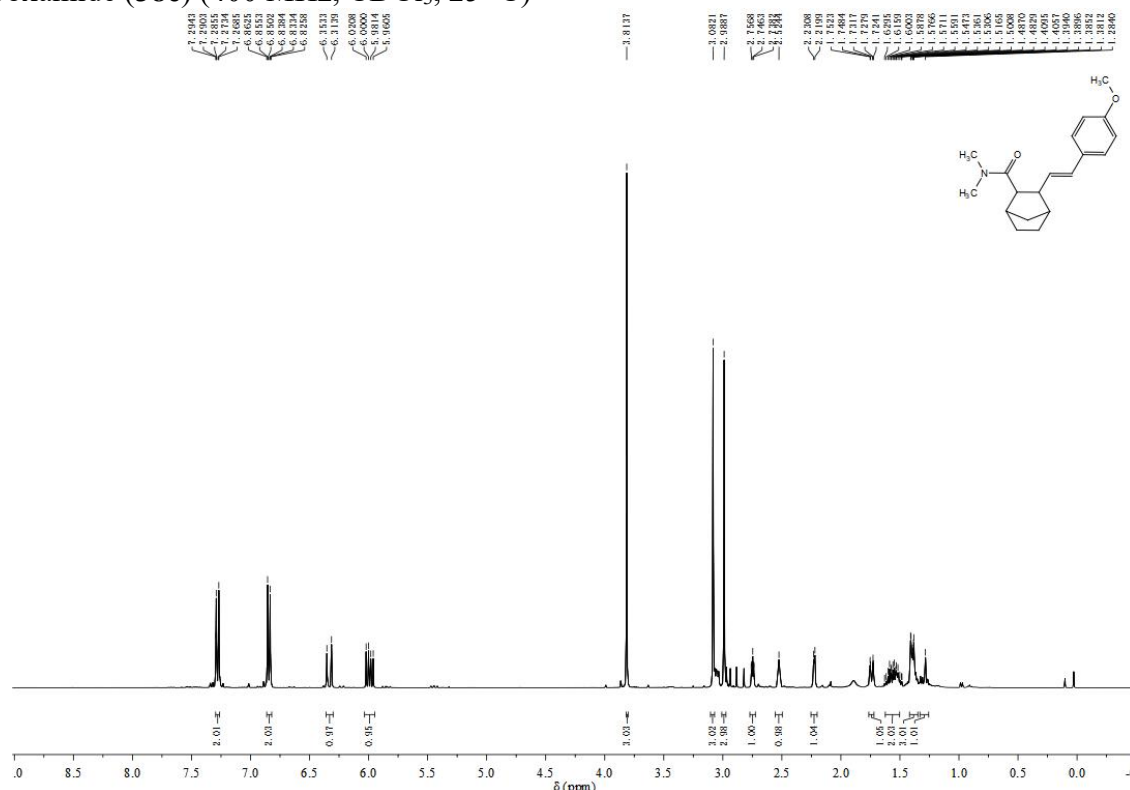
7.2555	6.7888	3.0840
7.2554	6.7887	2.9931
7.2554	6.7887	2.7663
7.2554	6.7887	2.5600
7.2554	6.7887	2.3807
7.2554	6.7887	2.2347
7.2554	6.7887	2.1142
7.2554	6.7887	1.9931
7.2554	6.7887	1.8720
7.2554	6.7887	1.7509
7.2554	6.7887	1.6298
7.2554	6.7887	1.5087
7.2554	6.7887	1.3876
7.2554	6.7887	1.2665
7.2554	6.7887	1.1454
7.2554	6.7887	1.0243
7.2554	6.7887	0.9032
7.2554	6.7887	0.7821
7.2554	6.7887	0.6610
7.2554	6.7887	0.5399
7.2554	6.7887	0.4188
7.2554	6.7887	0.2977
7.2554	6.7887	0.1766
7.2554	6.7887	0.0555



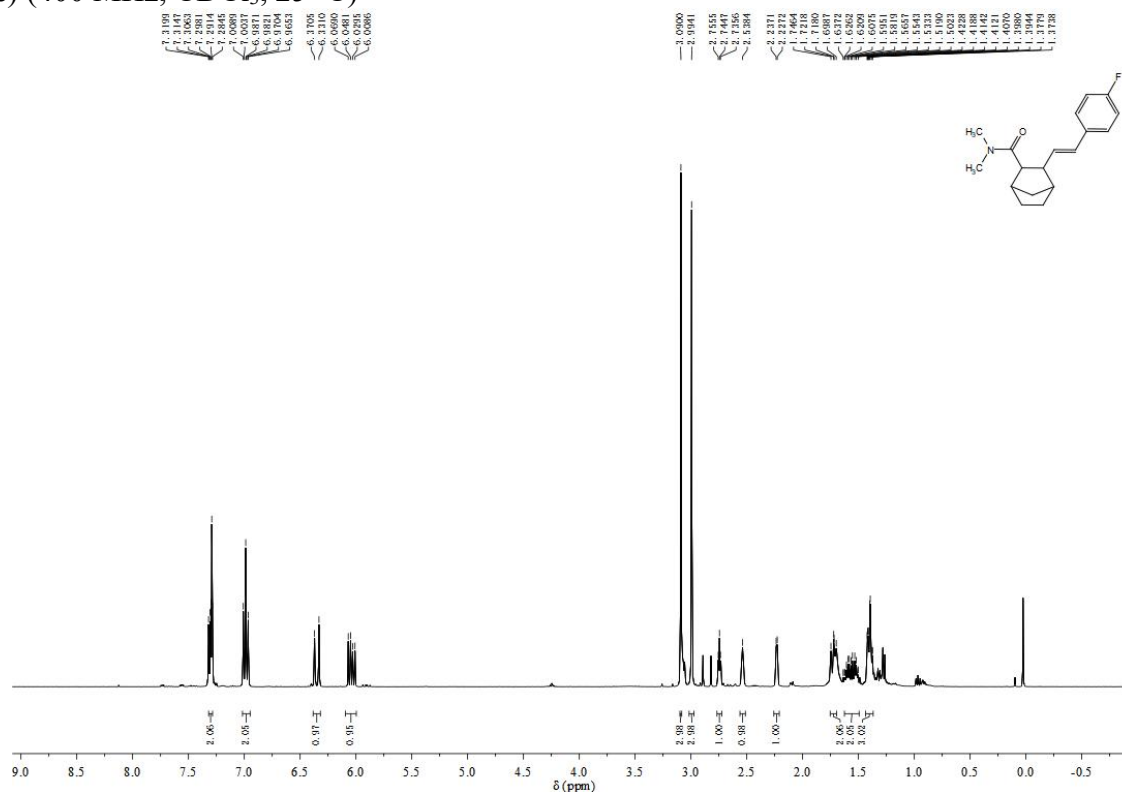
-172	7329
-136	5625
-138	1731
-133	4458
-130	1731
-128	1862
-125	8789
-52	3086
-47	3780
-43	1075
-40	1100
-37	2472
-35	8686
-29	0122
-21	9891
-21	1561



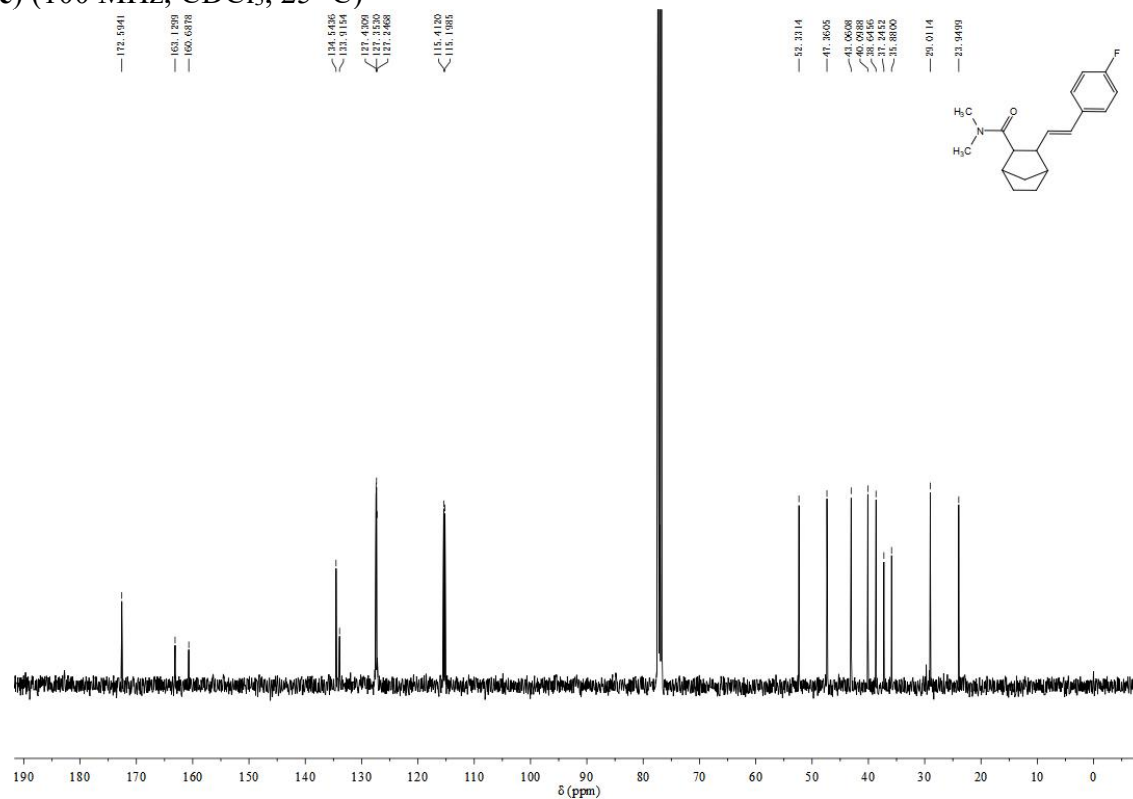
^1H NMR spectrum of (*E*)-3-(4-methoxystyryl)-*N,N*-dimethylbicyclo [2.2.1] heptane-2-carboxamide (**38e**) (400 MHz, CDCl_3 , 25 °C)



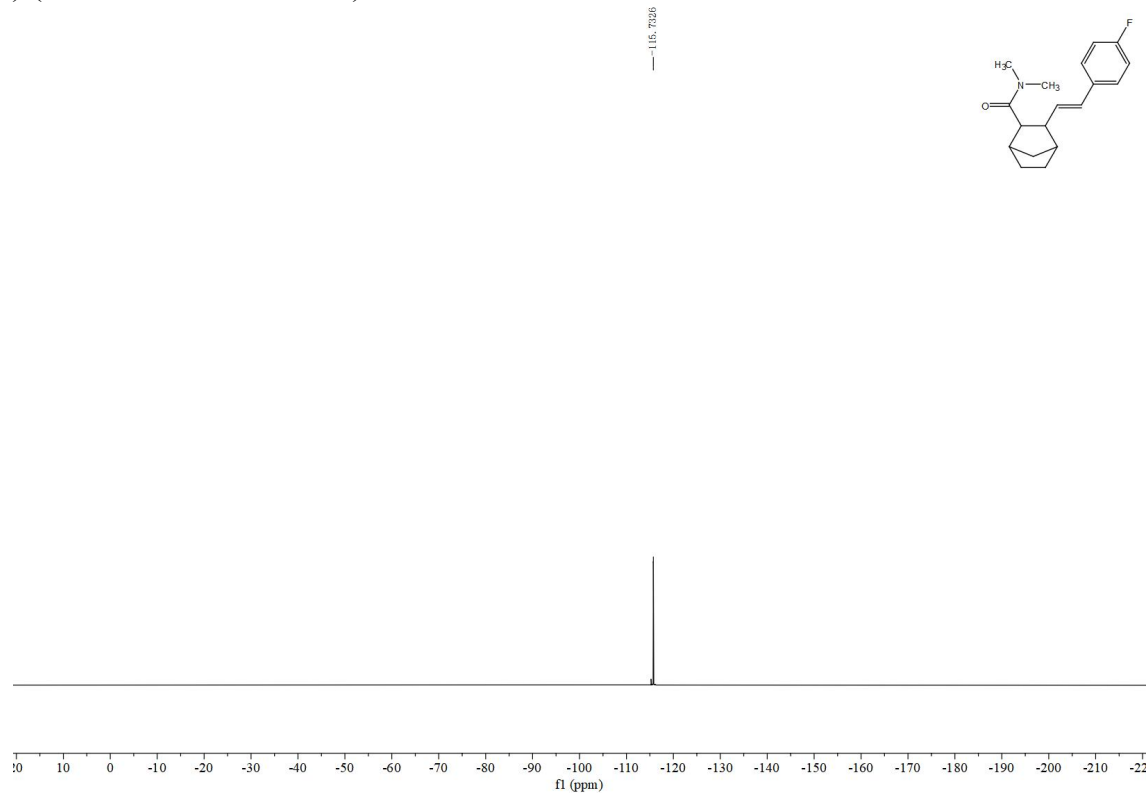
^1H NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**39e**) (400 MHz, CDCl_3 , 25 °C)



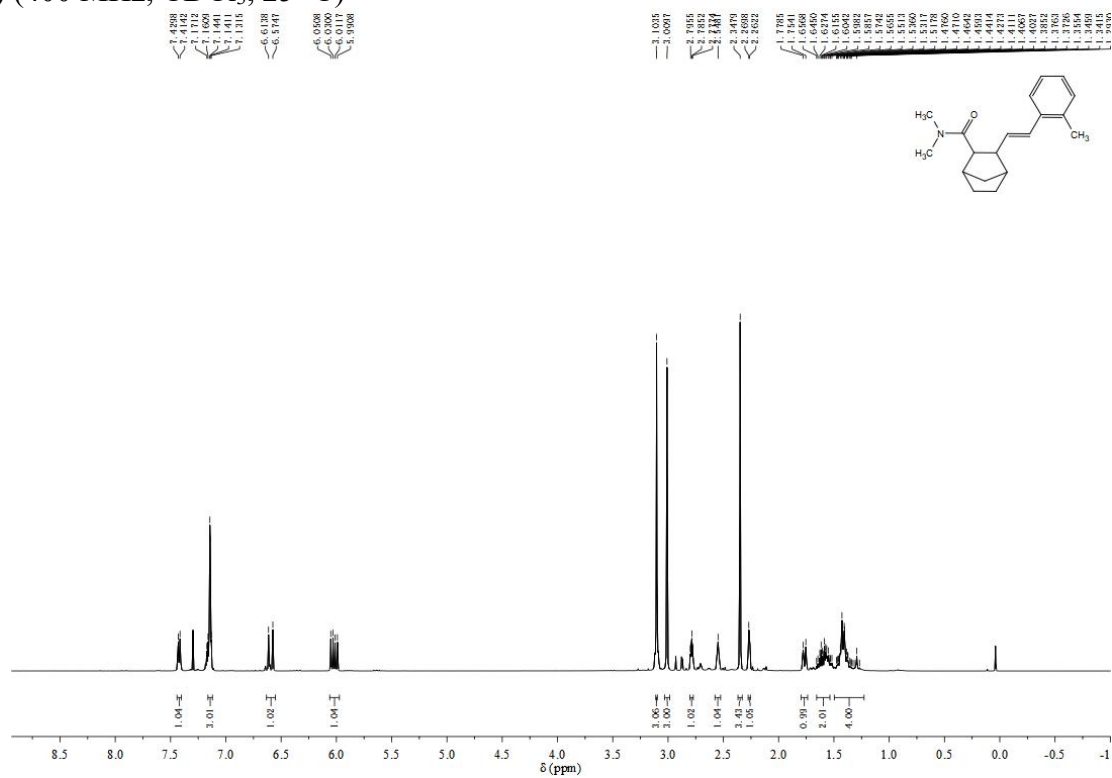
^{13}C NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**39e**) (100 MHz, CDCl_3 , 25 °C)



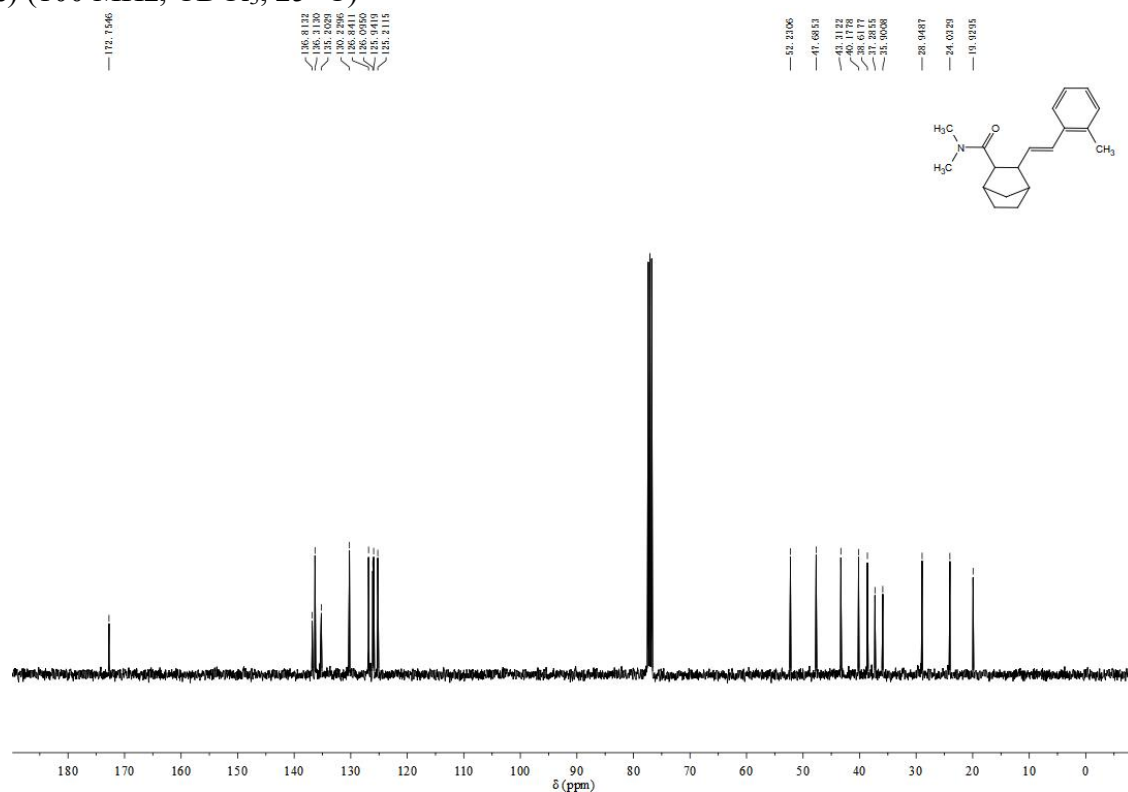
^{19}F NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**39e**) (376 MHz, CDCl_3 , 25 °C)



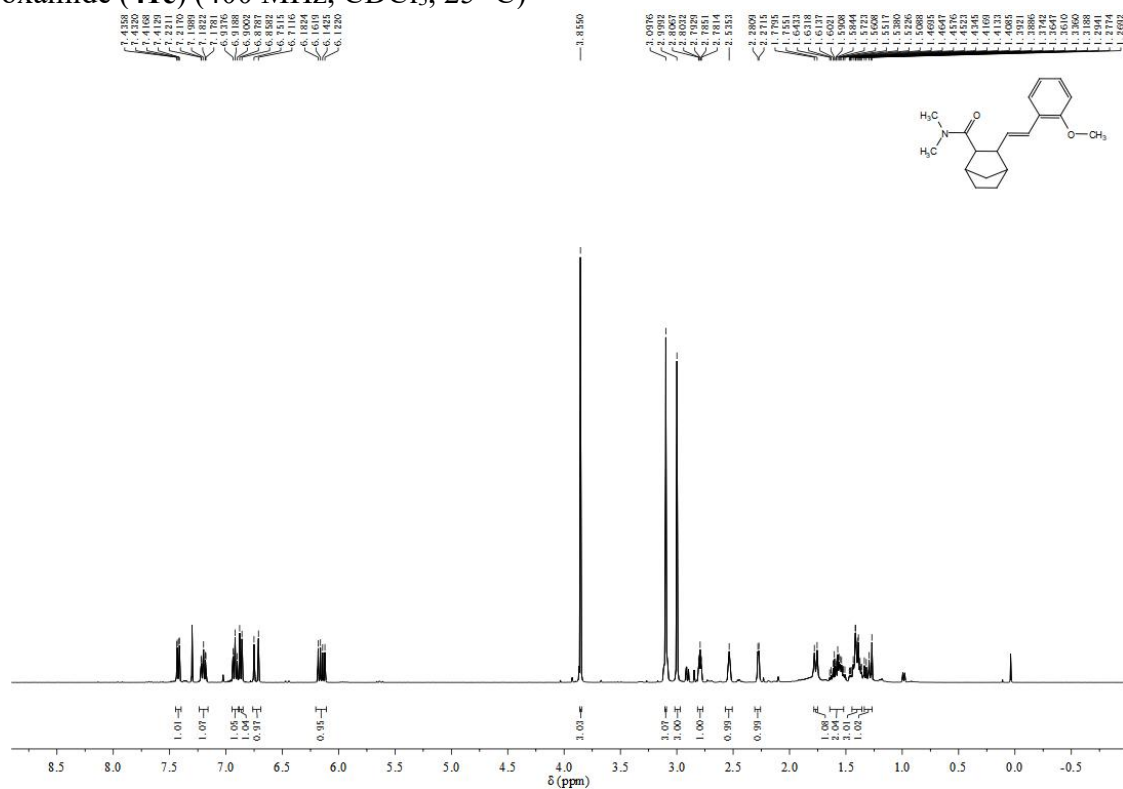
^1H NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**40e**) (400 MHz, CDCl_3 , 25 °C)



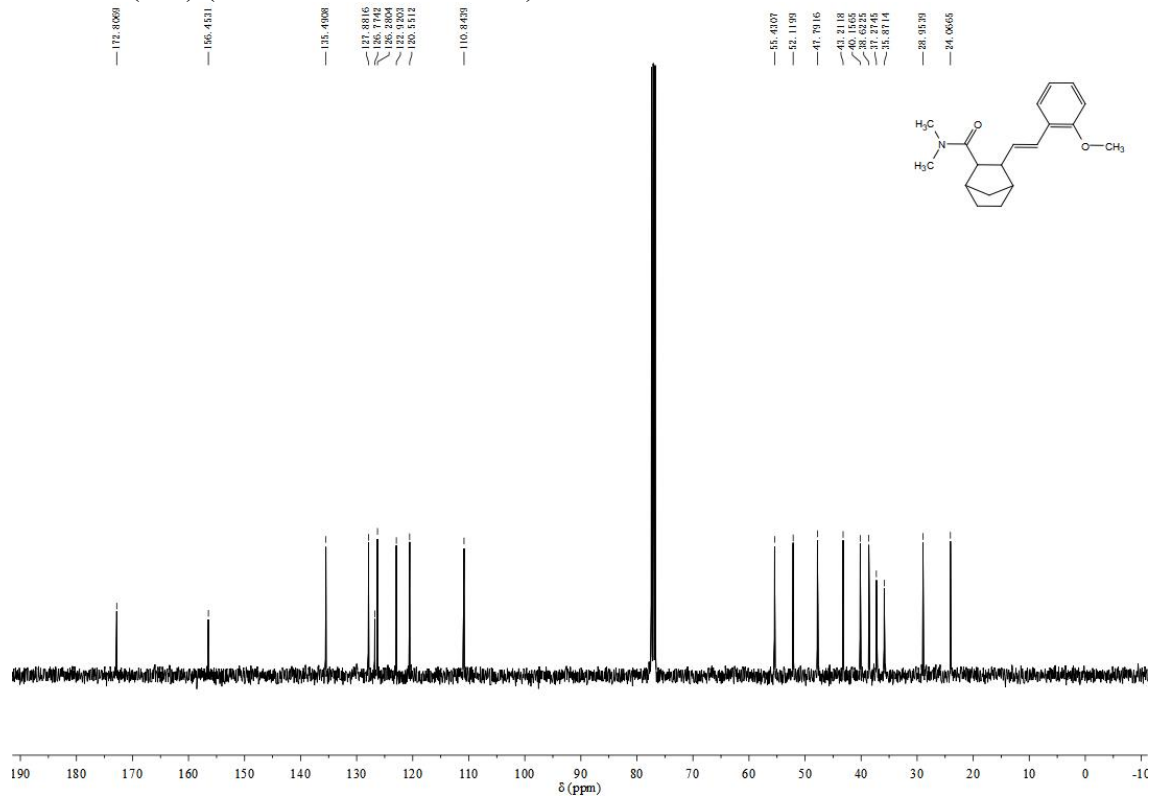
^{13}C NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-methylstyryl)bicyclo[2.2.1]heptane-2-carboxamide (**40e**) (100 MHz, CDCl_3 , 25 °C)



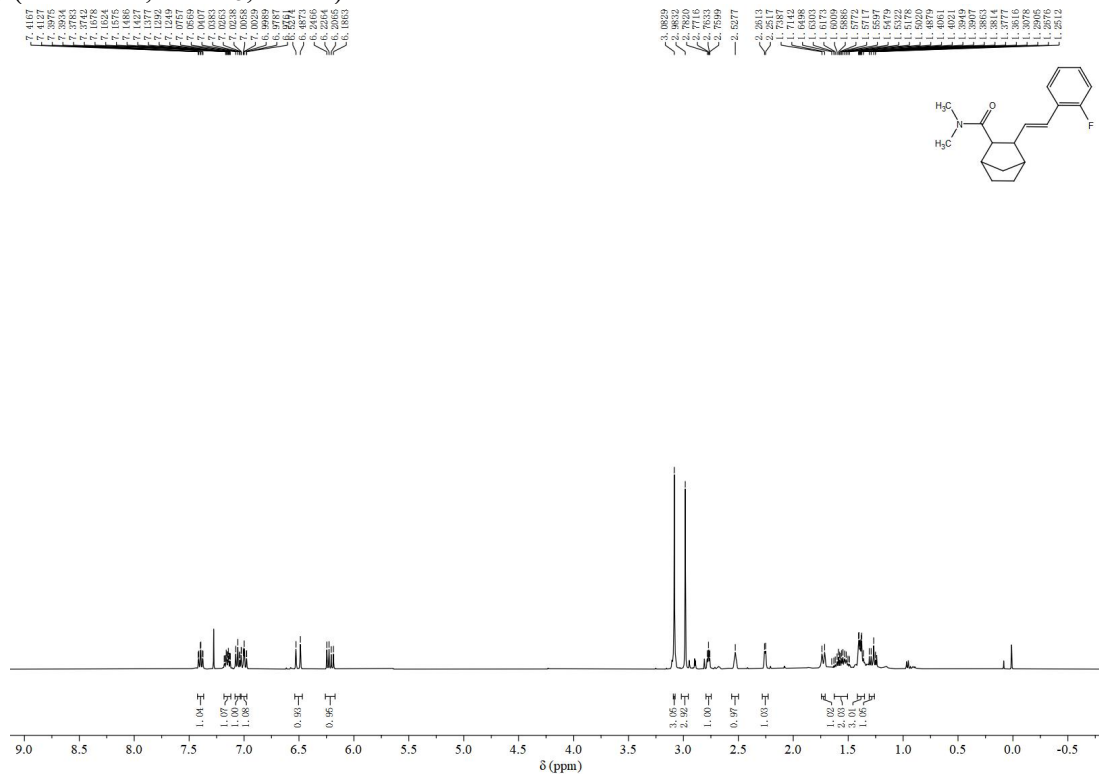
^1H NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**41e**) (400 MHz, CDCl_3 , 25 °C)



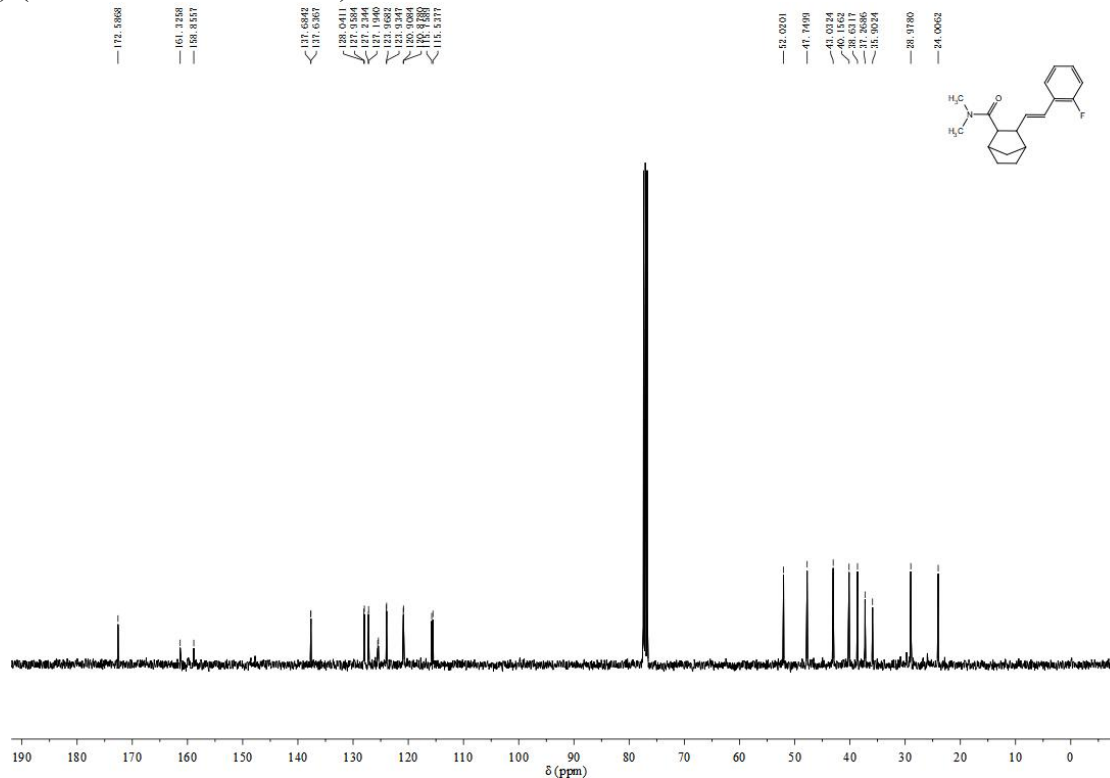
^{13}C NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N,N*-dimethylbicyclo [2.2.1] heptane-2-carboxamide (**41e**) (100 MHz, CDCl_3 , 25 °C)



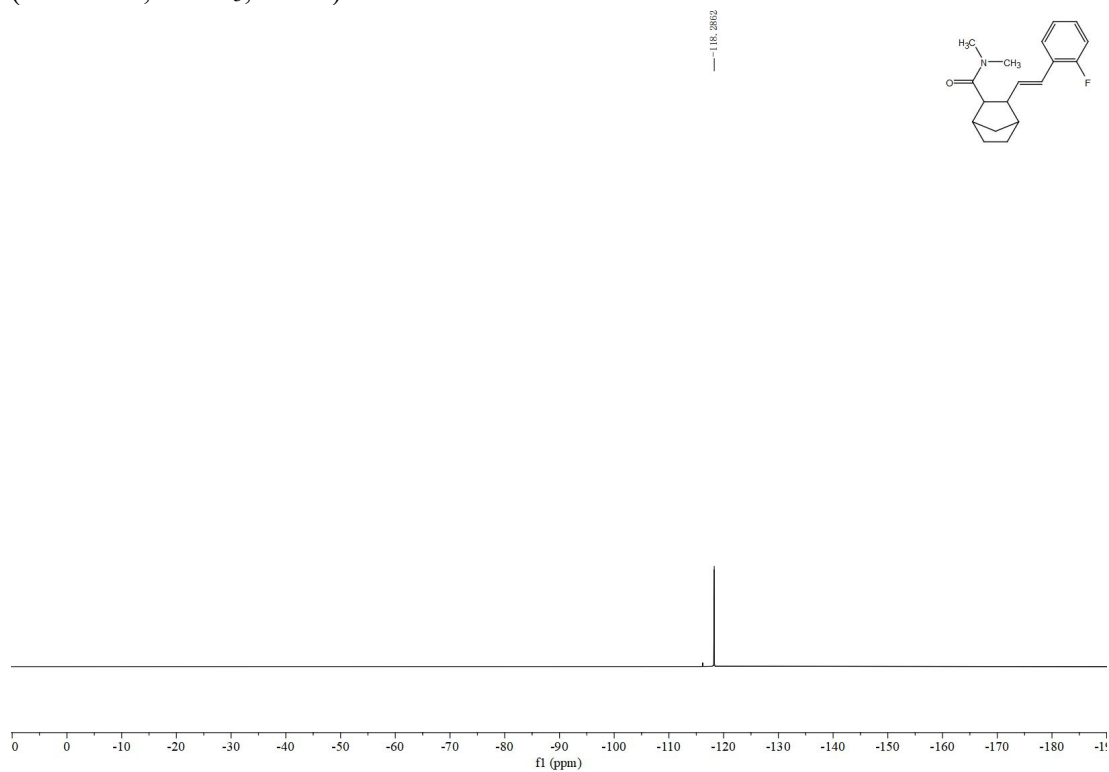
^1H NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**42e**) (400 MHz, CDCl_3 , 25 °C)



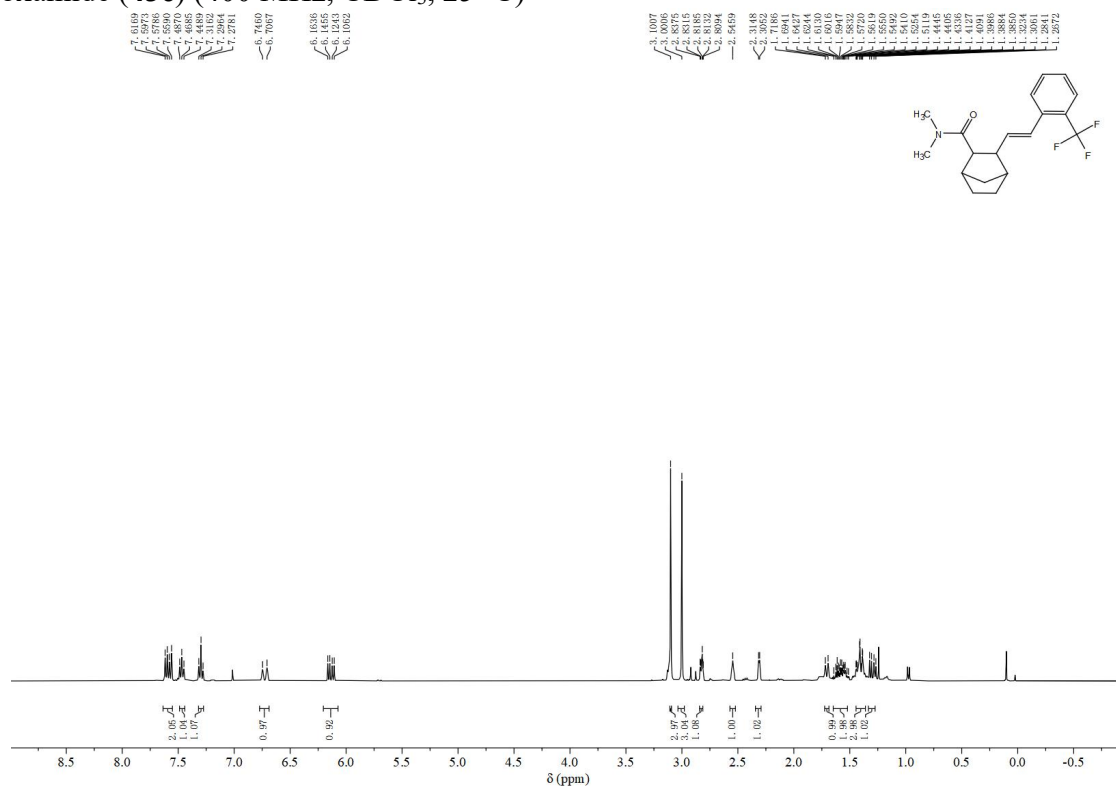
^{13}C NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**42e**) (100 MHz, CDCl_3 , 25 °C)



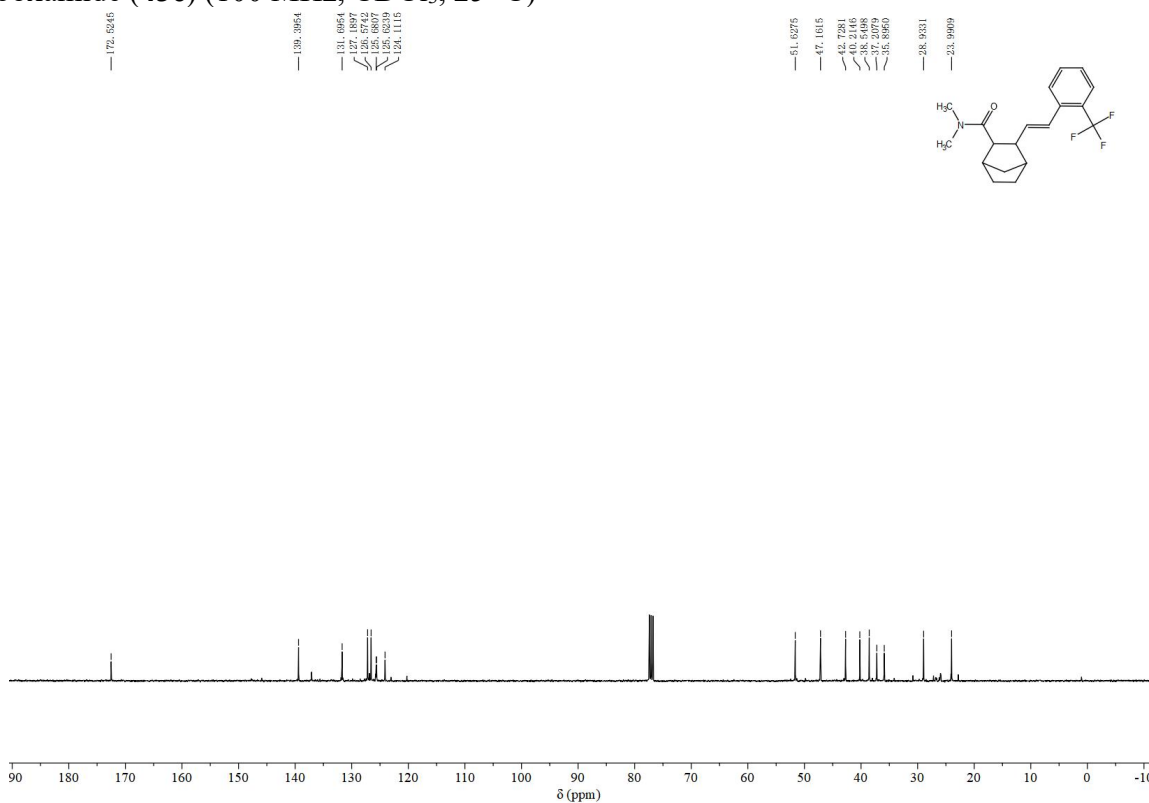
^{19}F NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**42e**) (376 MHz, CDCl_3 , 25 °C)



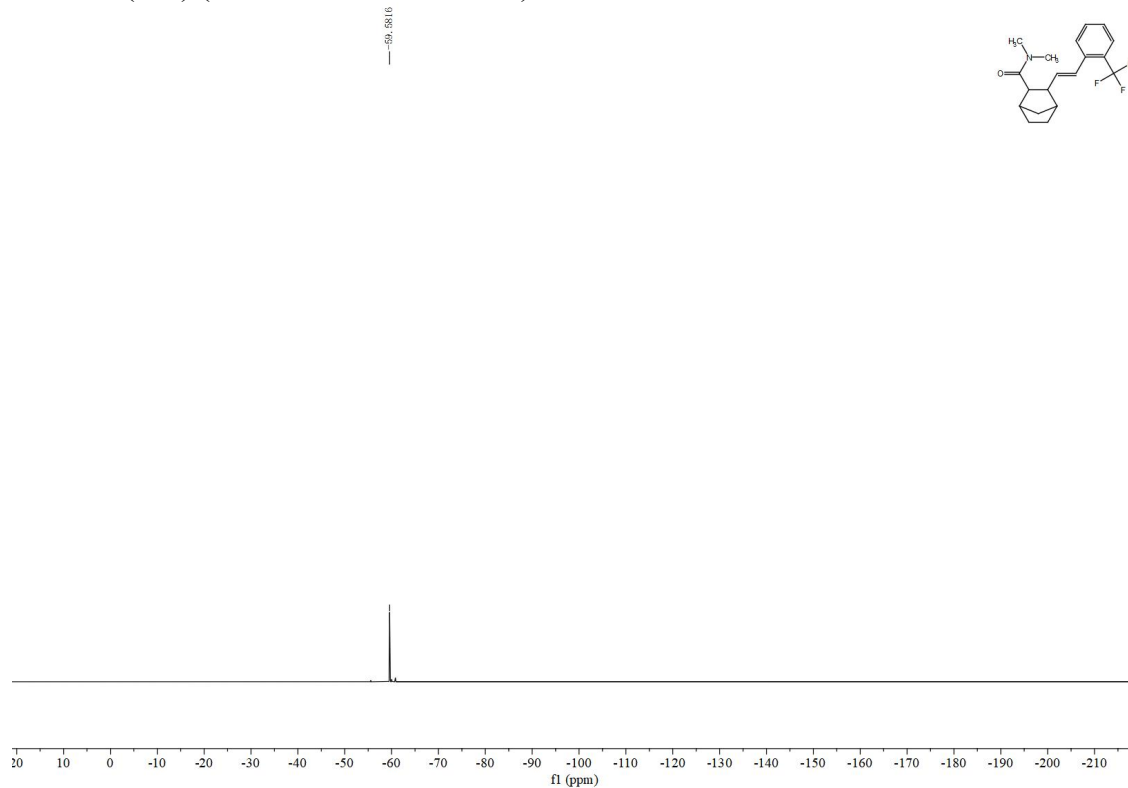
^1H NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**43e**) (400 MHz, CDCl_3 , 25 °C)



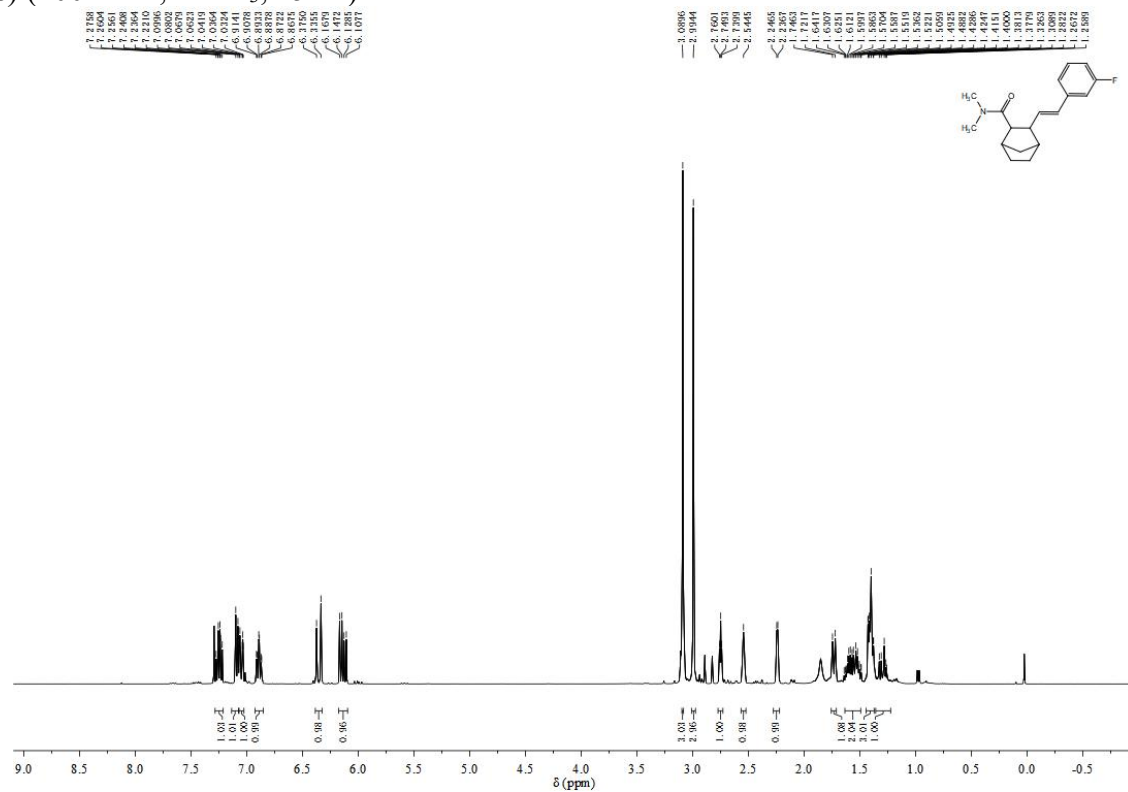
^{13}C NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**43e**) (100 MHz, CDCl_3 , 25 °C)



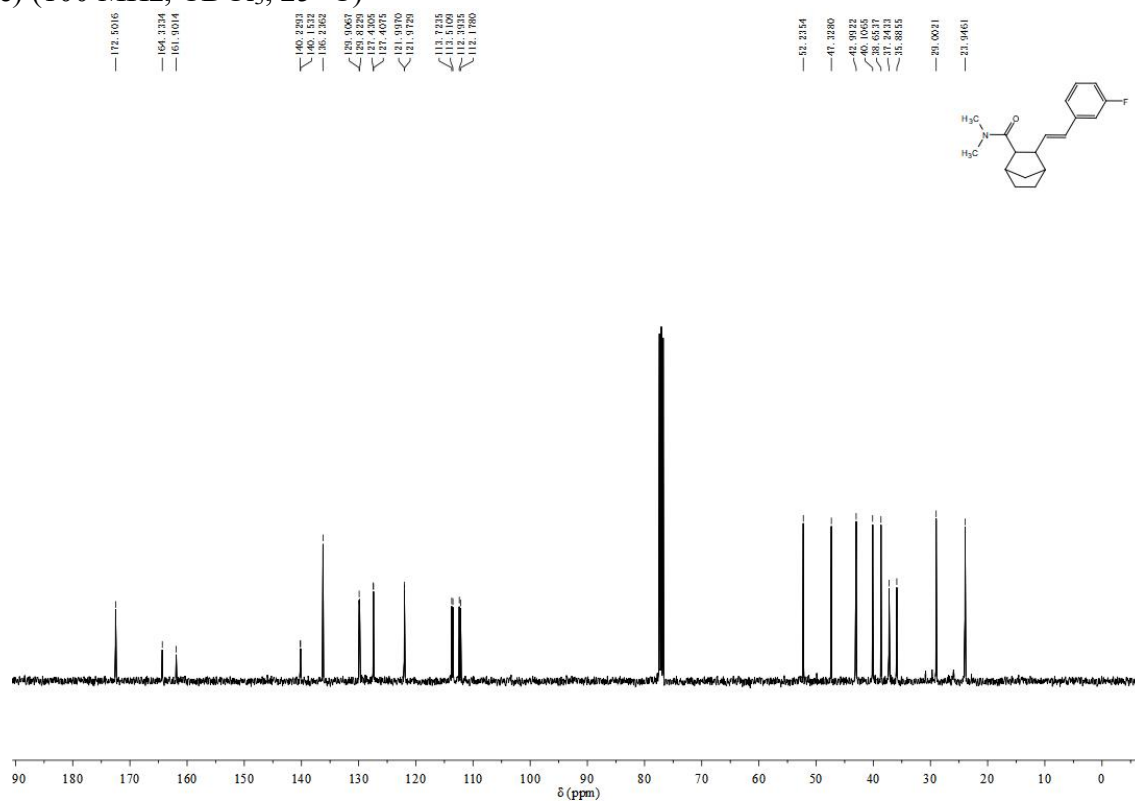
^{19}F NMR spectrum of (*E*)-*N,N*-dimethyl-3-(2-(trifluoromethyl)styryl)bicyclo[2.2.1]heptane-2-carboxamide (**43e**) (376 MHz, CDCl_3 , 25 °C)



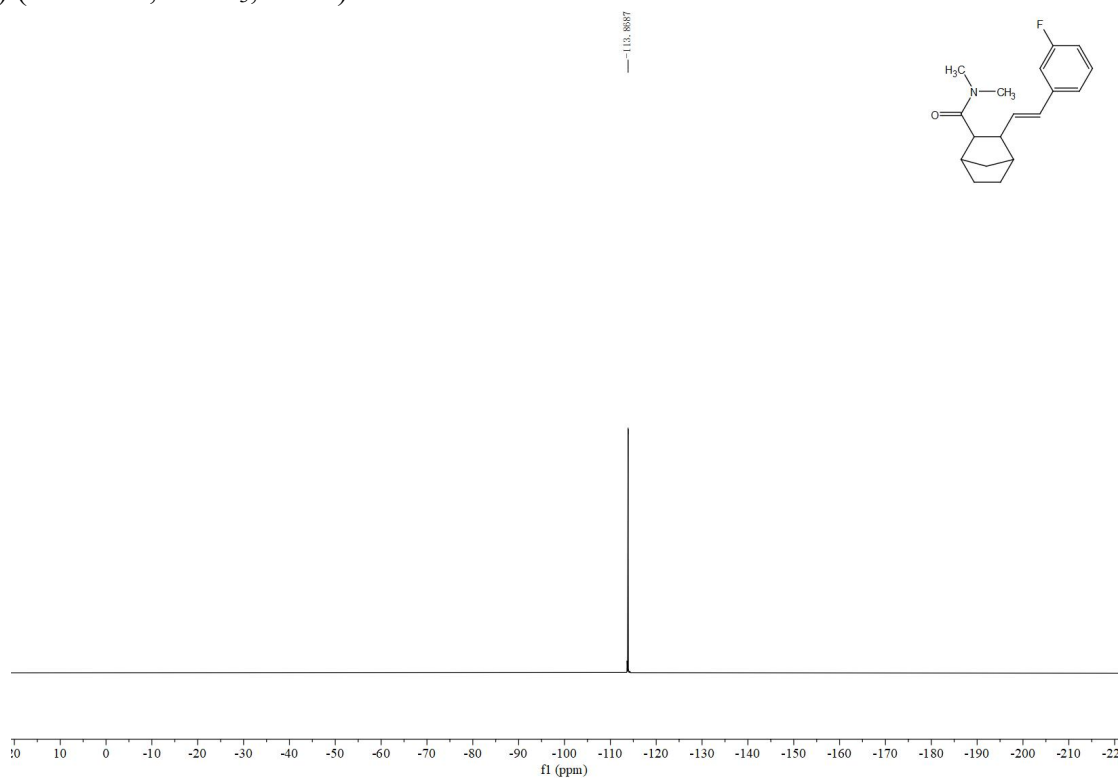
^1H NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**44e**) (400 MHz, CDCl_3 , 25 °C)



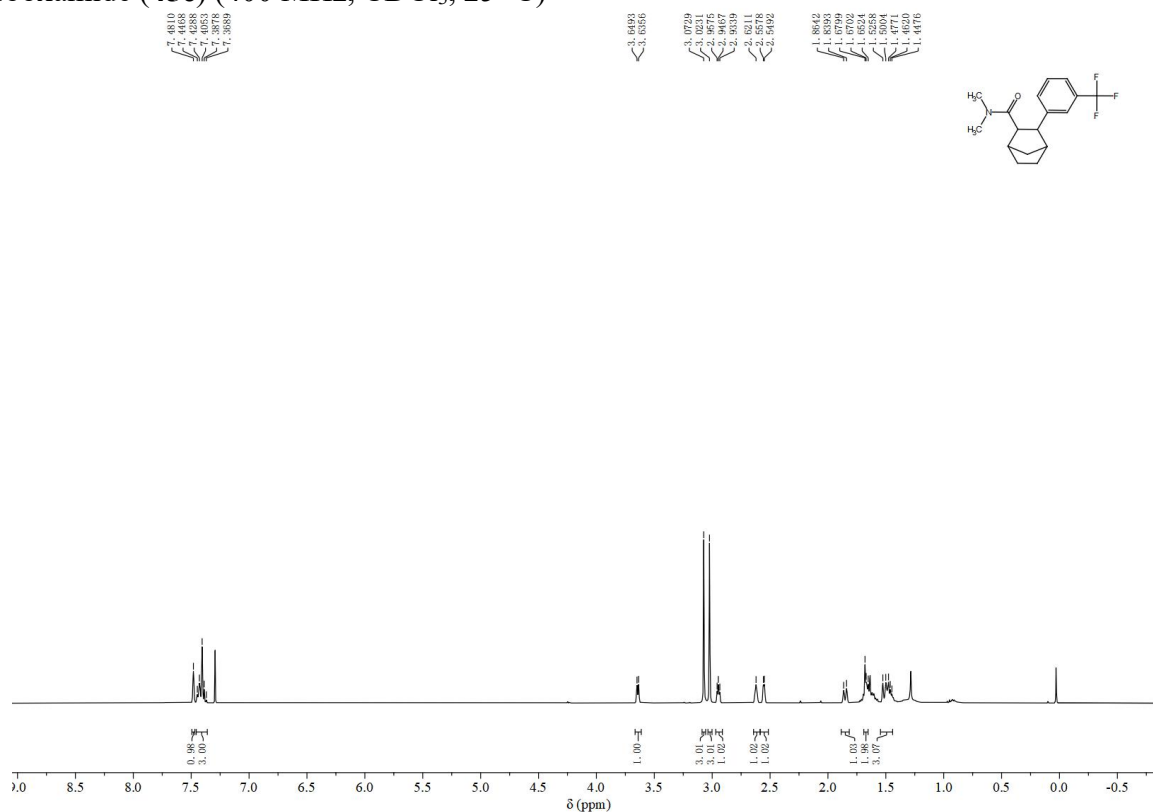
^{13}C NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**44e**) (100 MHz, CDCl_3 , 25 °C)



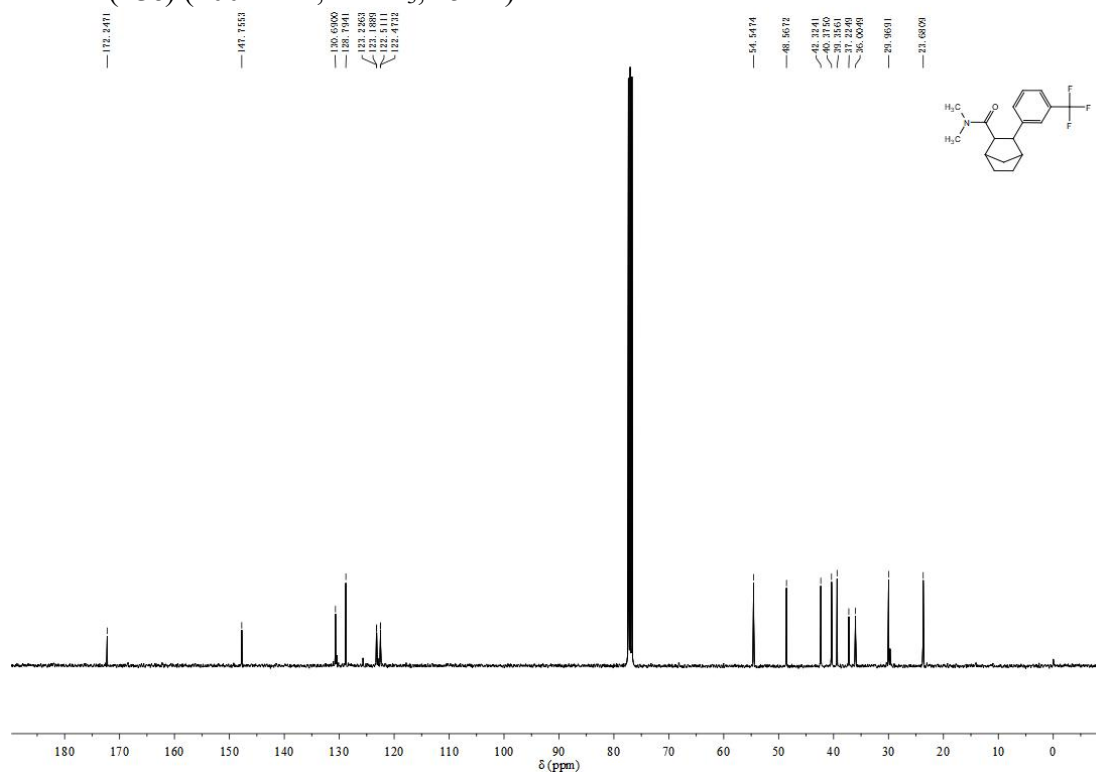
^{19}F NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**44e**) (376 MHz, CDCl_3 , 25 °C)



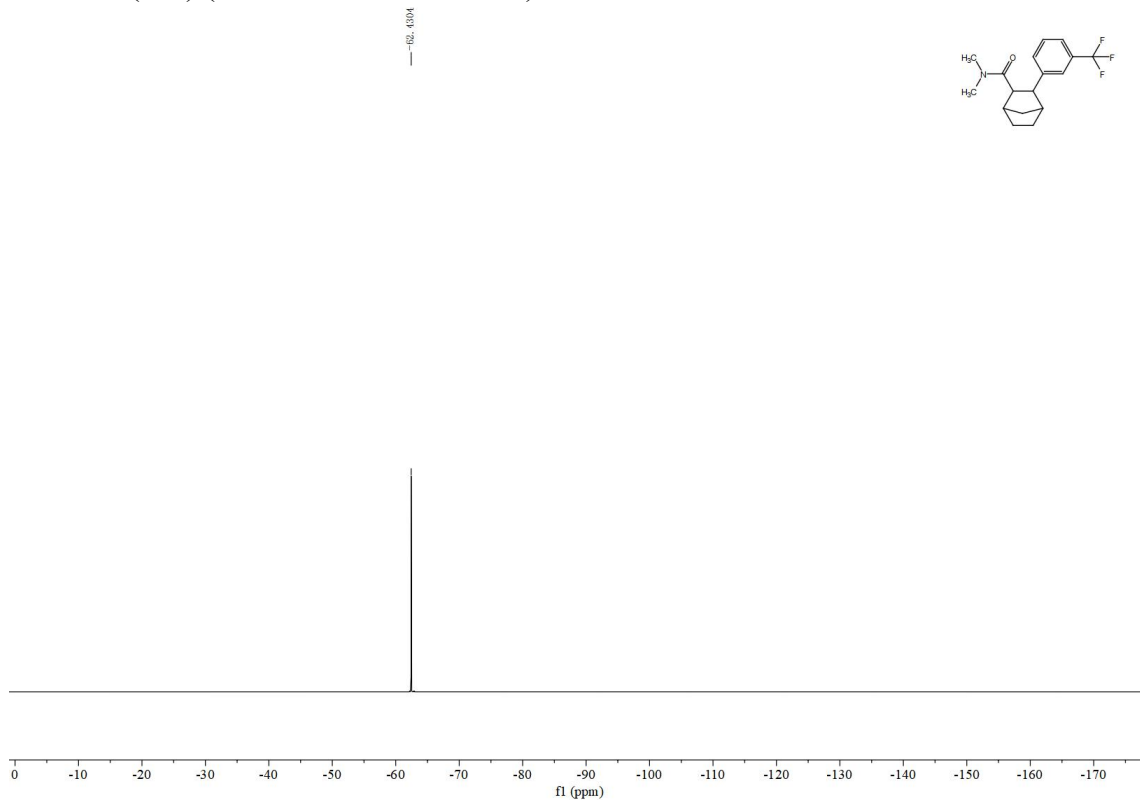
^1H NMR spectrum of *N,N*-dimethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**45e**) (400 MHz, CDCl_3 , 25 °C)



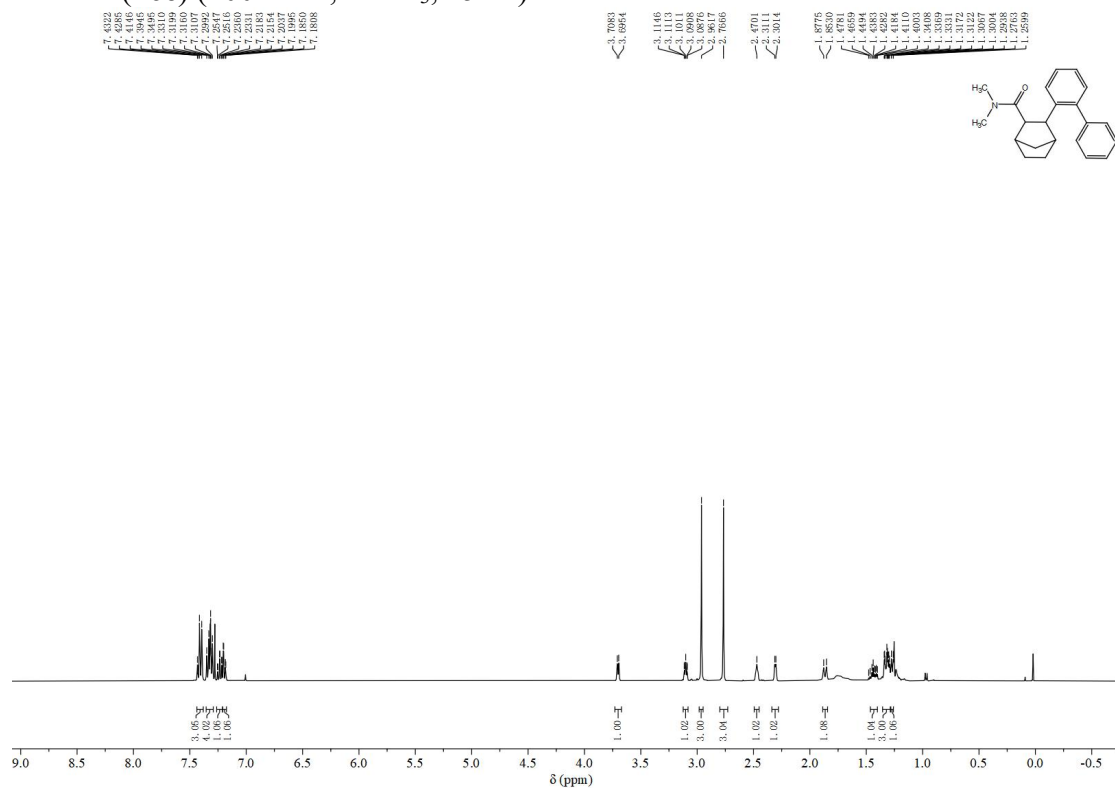
^{13}C NMR spectrum of *N,N*-dimethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**45e**) (100 MHz, CDCl_3 , 25 °C)



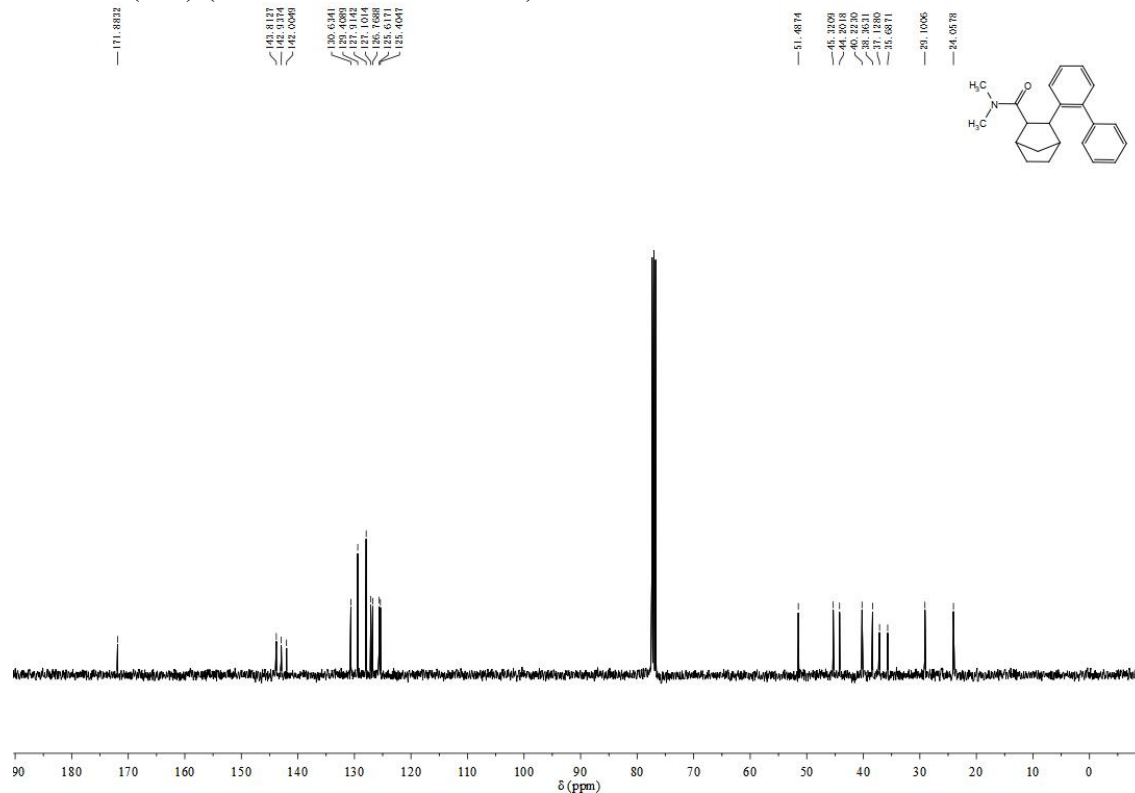
^{19}F NMR spectrum of *N,N*-dimethyl-3-(3-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**45e**) (376 MHz, CDCl_3 , 25 °C)



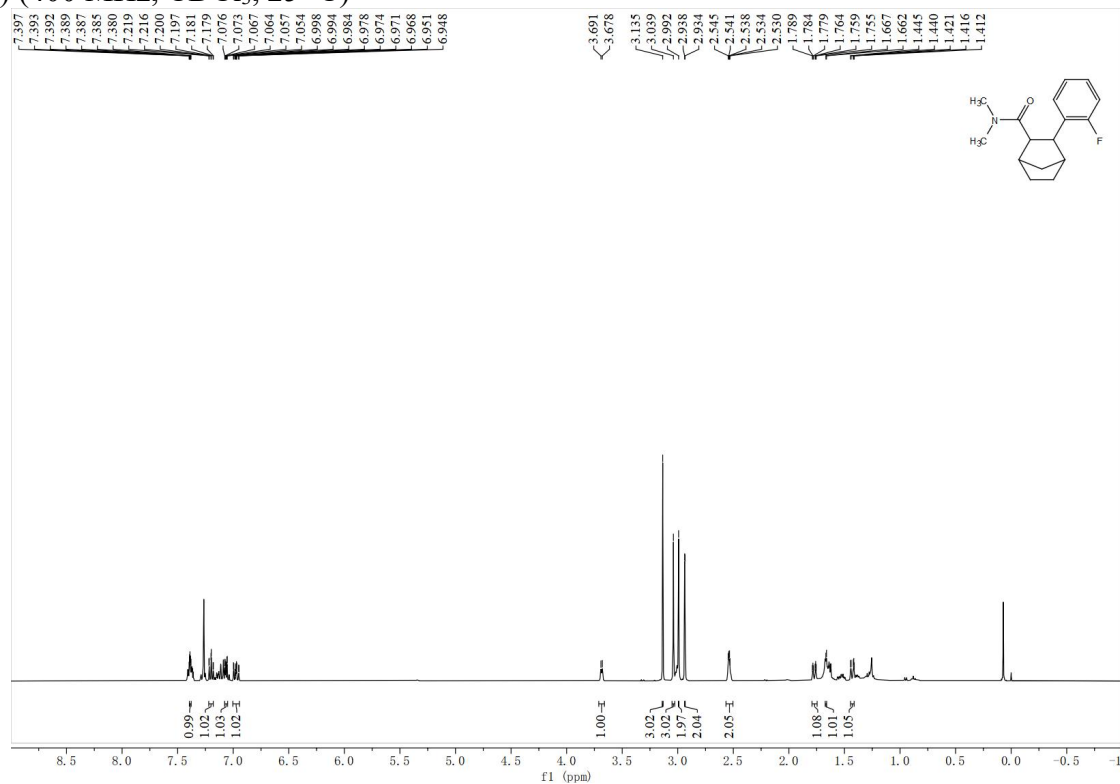
^1H NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**46e**) (400 MHz, CDCl_3 , 25 °C)



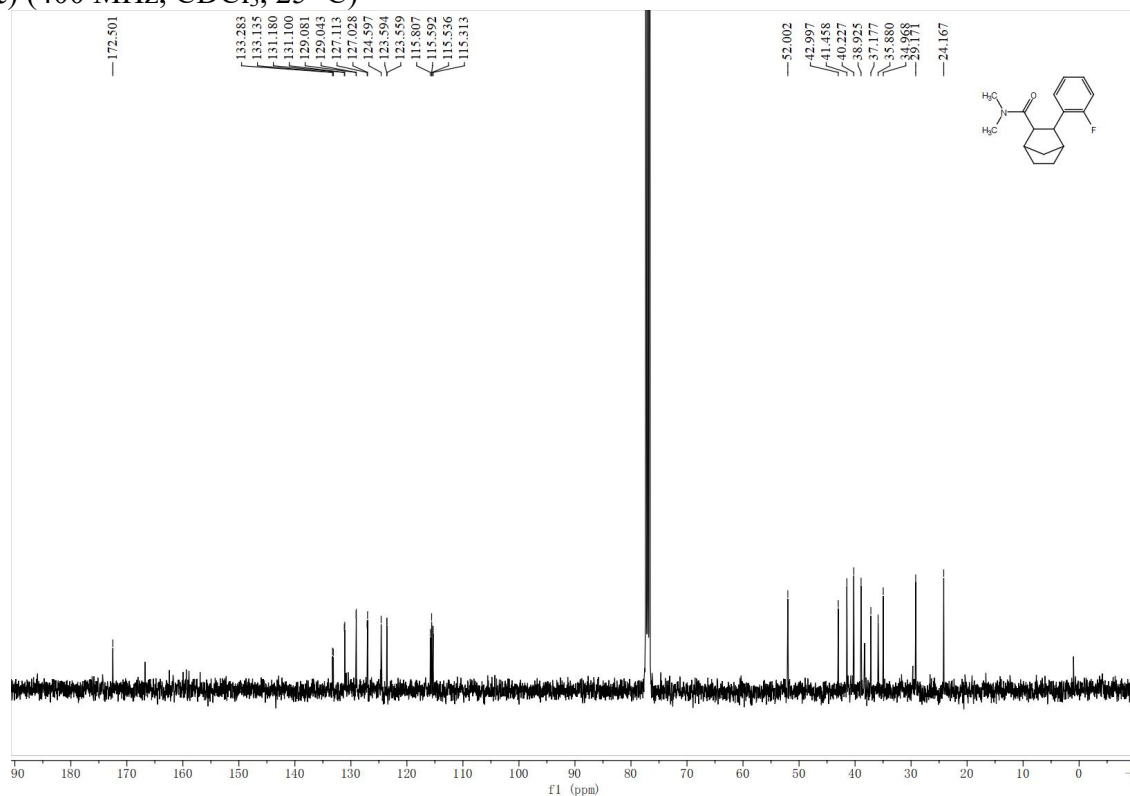
^{13}C NMR spectrum of 3-([1,1'-biphenyl]-2-yl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**46e**) (100 MHz, CDCl_3 , 25 °C)



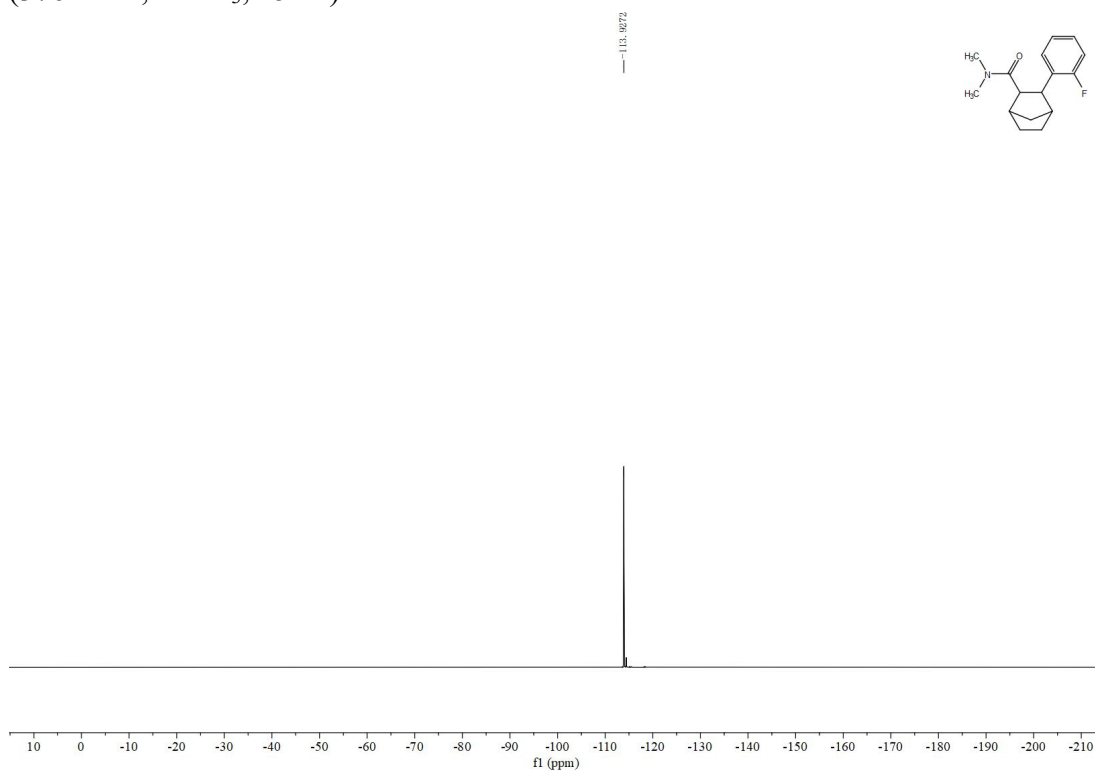
^1H NMR spectrum of 3-(2-fluorophenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**47e**) (400 MHz, CDCl_3 , 25 °C)



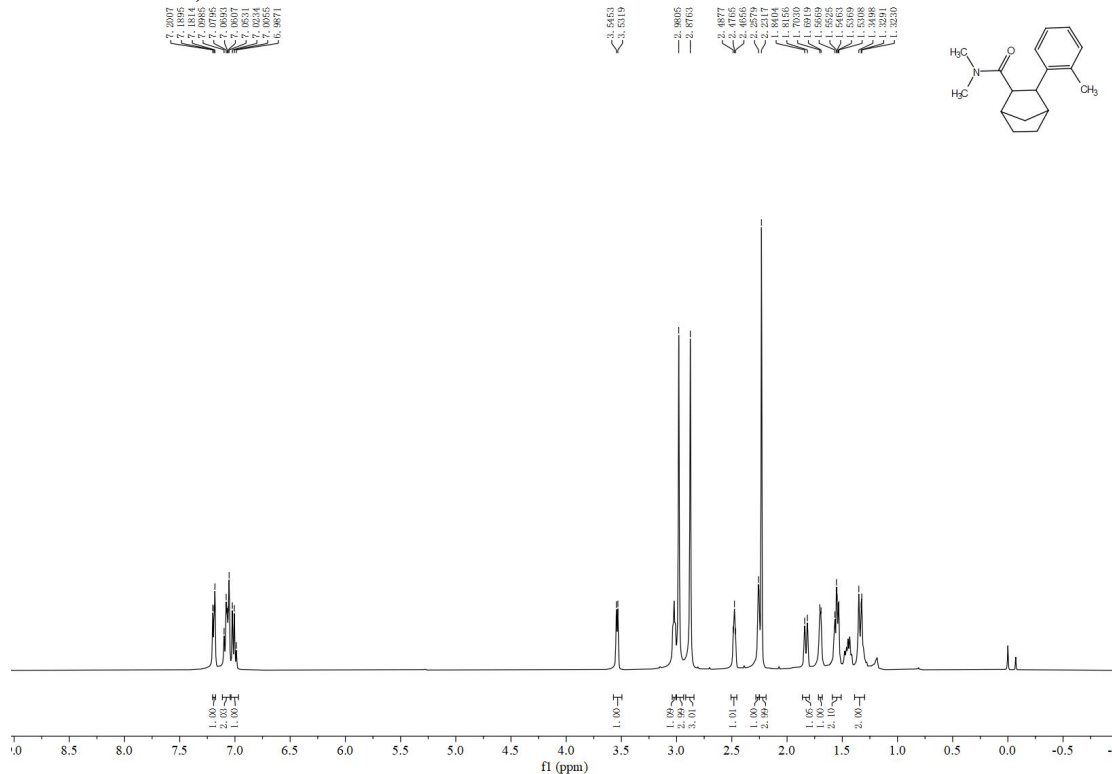
^{13}C NMR spectrum of 3-(2-fluorophenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**47e**) (400 MHz, CDCl_3 , 25 °C)



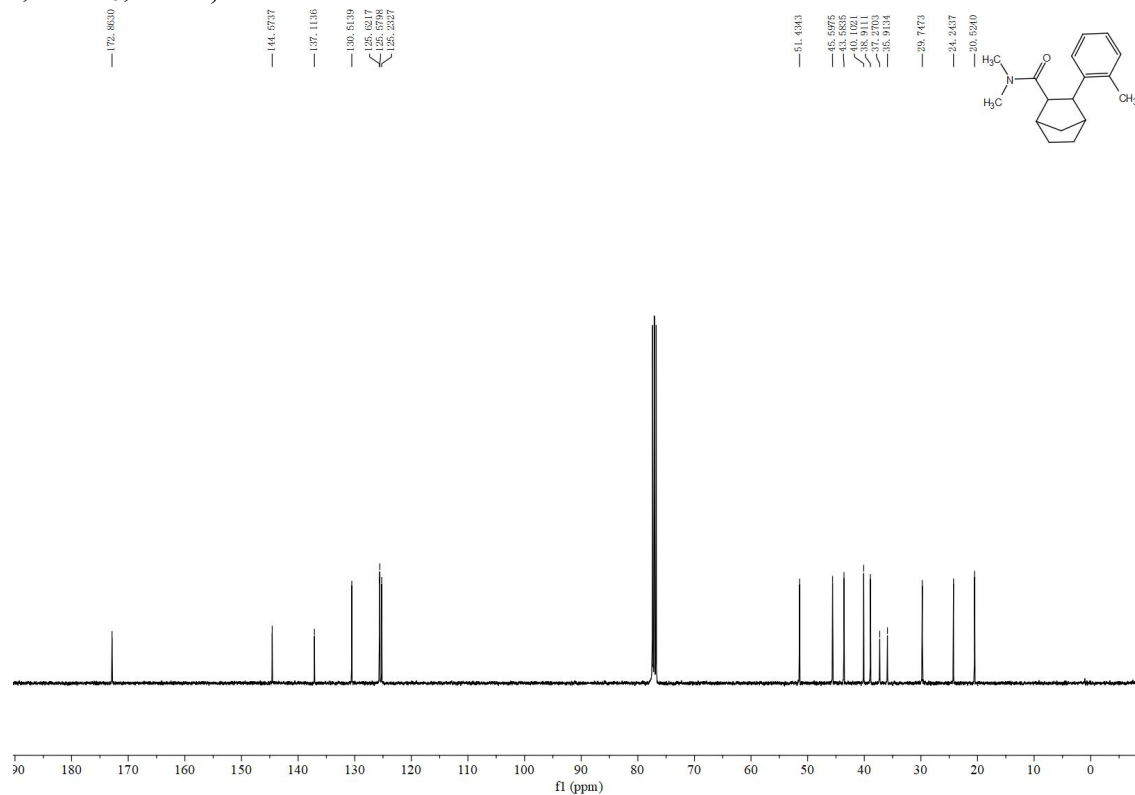
^{19}F NMR spectrum of 3-(2-fluorophenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**47e**) (376 MHz, CDCl_3 , 25 °C)

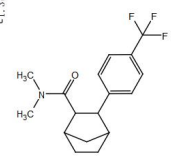


^1H NMR spectrum of *N,N*-dimethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**48e**) (400 MHz, CDCl_3 , 25 °C)

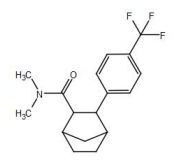


^{13}C NMR spectrum of *N,N*-dimethyl-3-(*o*-tolyl)bicyclo[2.2.1]heptane-2-carboxamide (**48e**) (100 MHz, CDCl_3 , 25 °C)

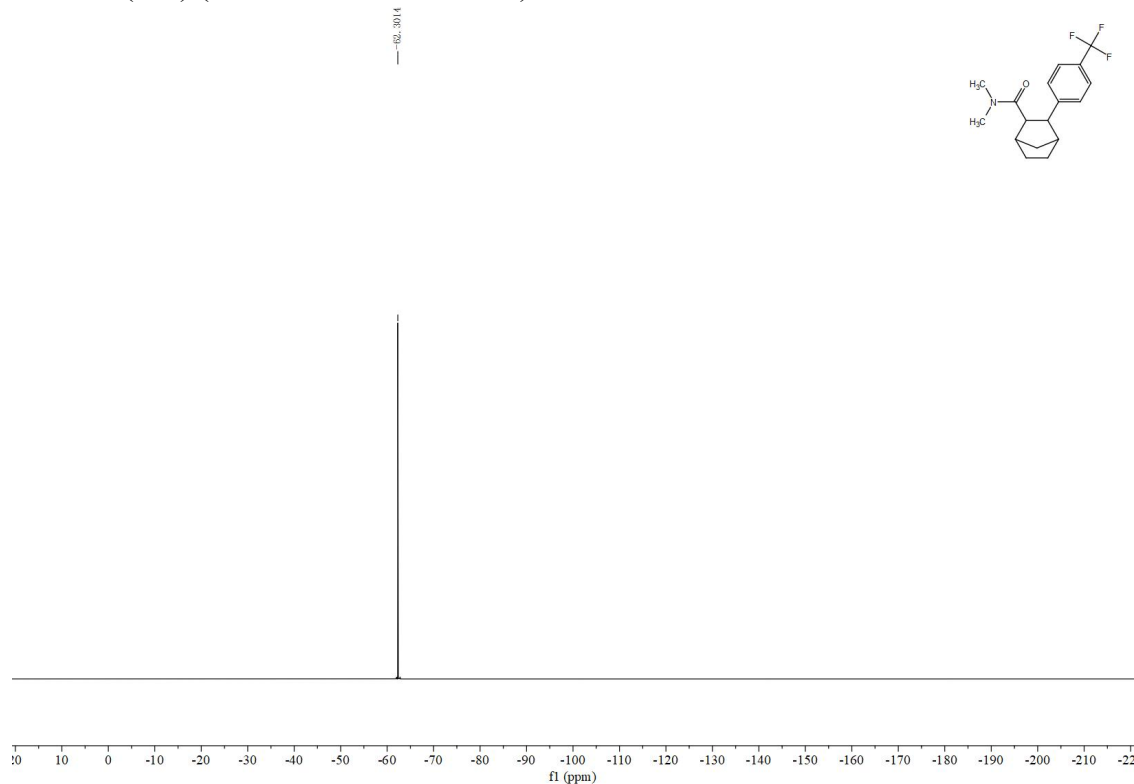


$$\begin{array}{r} 7.4445 \\ 7.4246 \\ 7.2503 \\ 7.2304 \end{array}$$


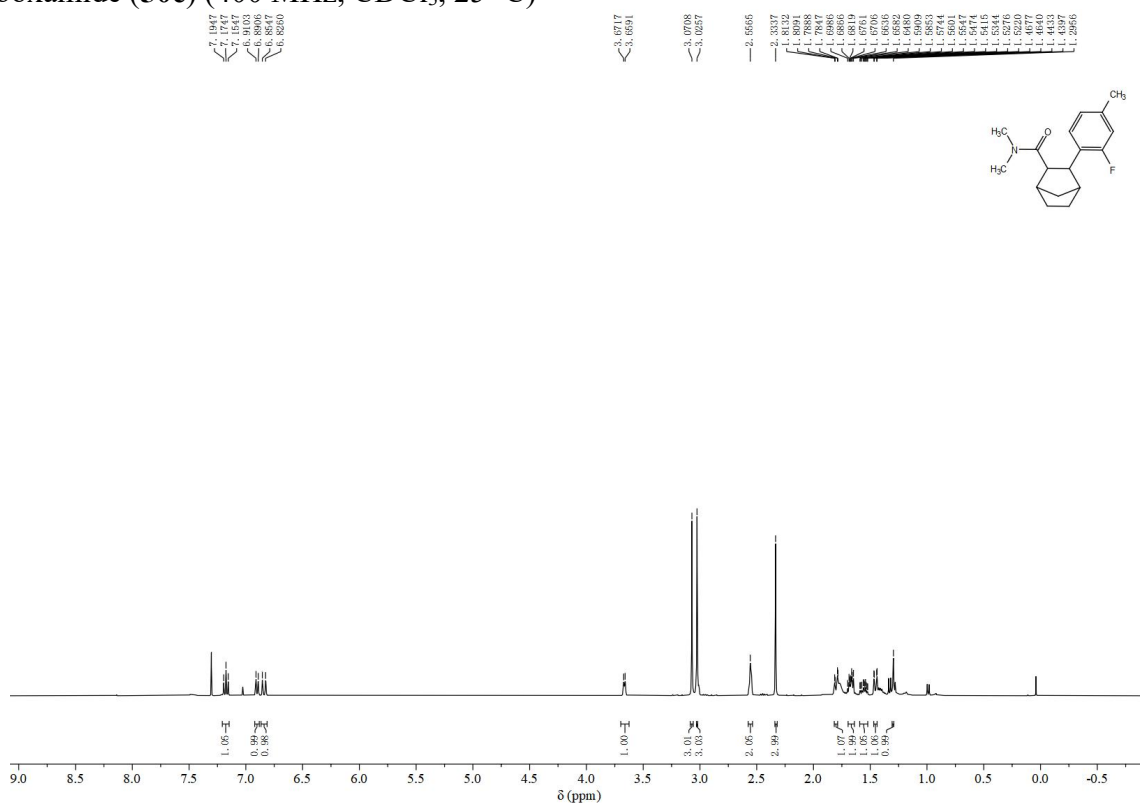
—172. 2623



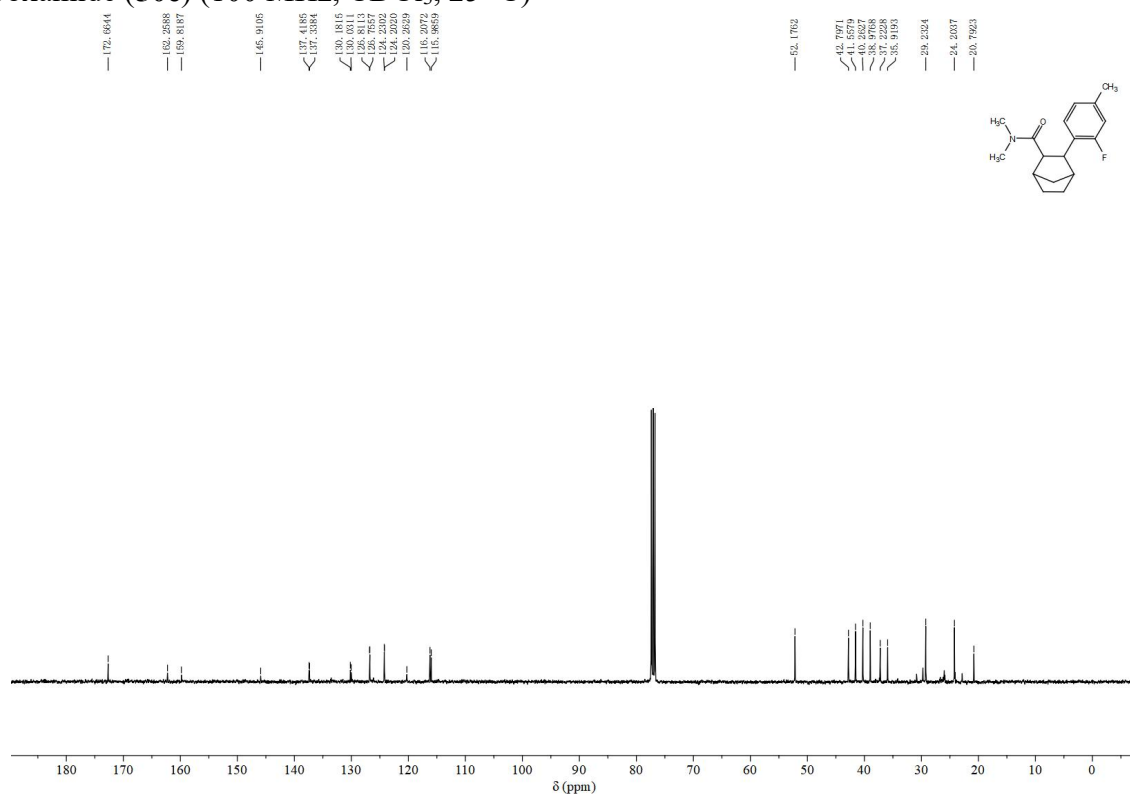
^{19}F NMR spectrum of *N,N*-dimethyl-3-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]heptane-2-carboxamide (**49e**) (376 MHz, CDCl_3 , 25 °C)



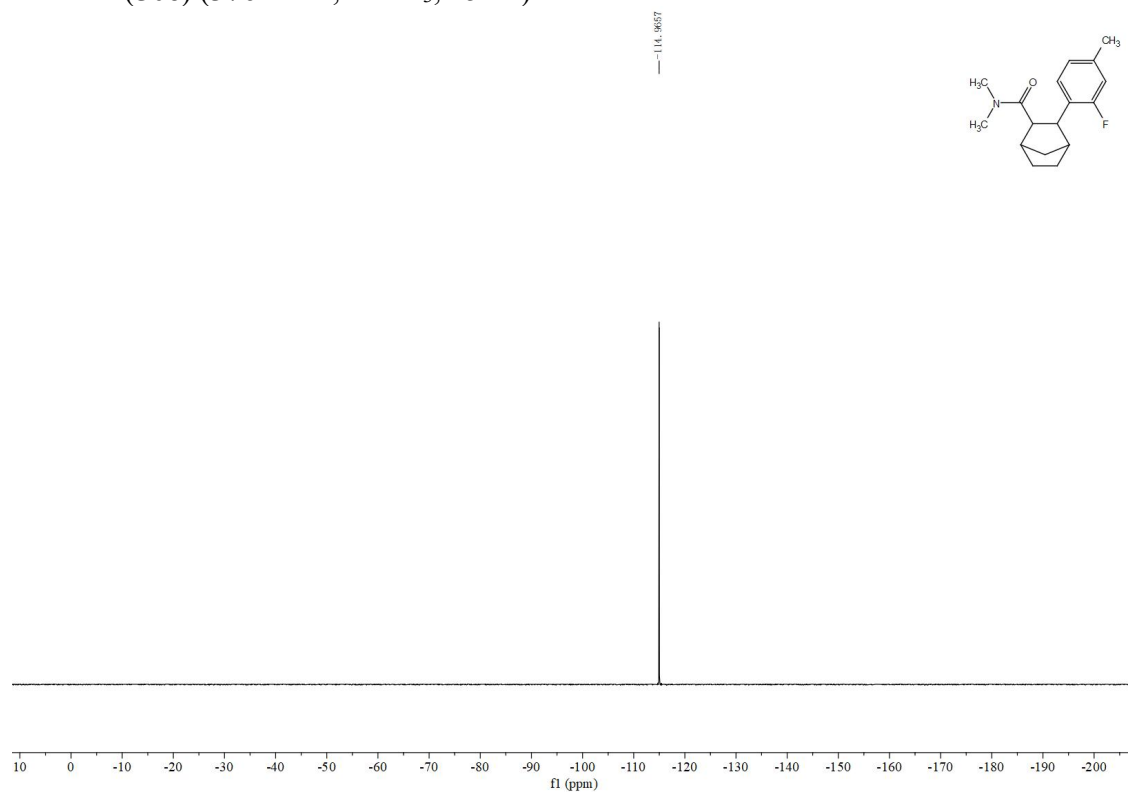
^1H NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**50e**) (400 MHz, CDCl_3 , 25 °C)



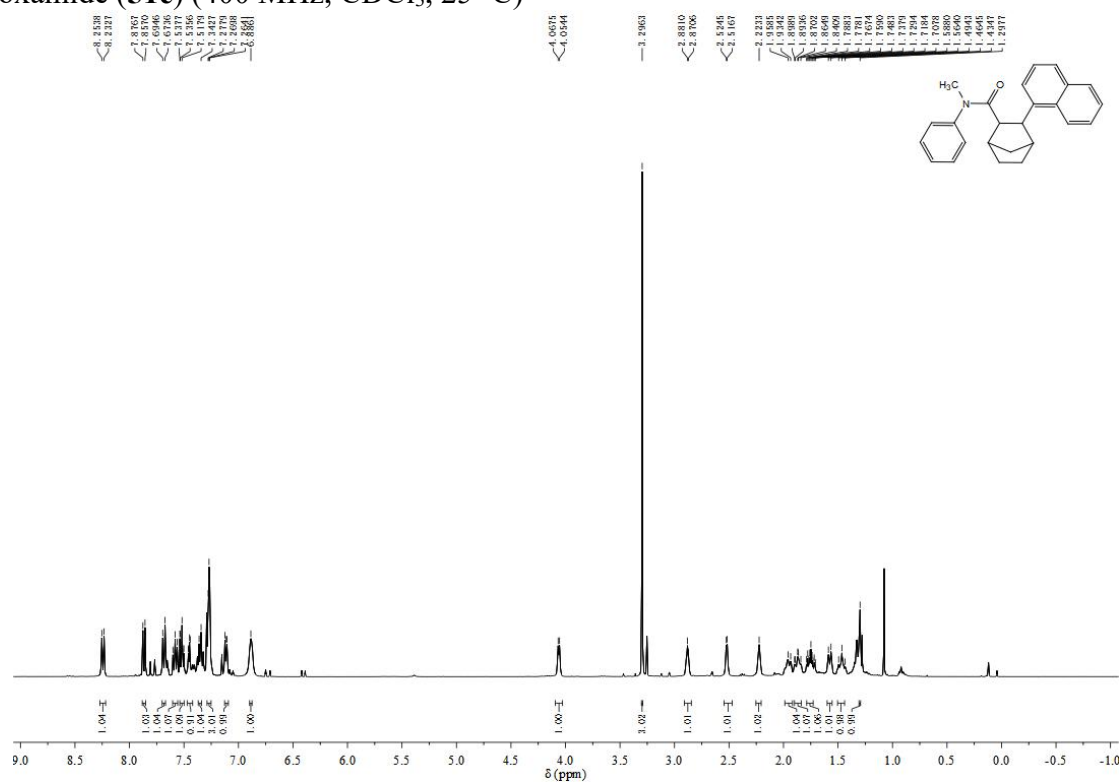
^{13}C NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**50e**) (100 MHz, CDCl_3 , 25 °C)



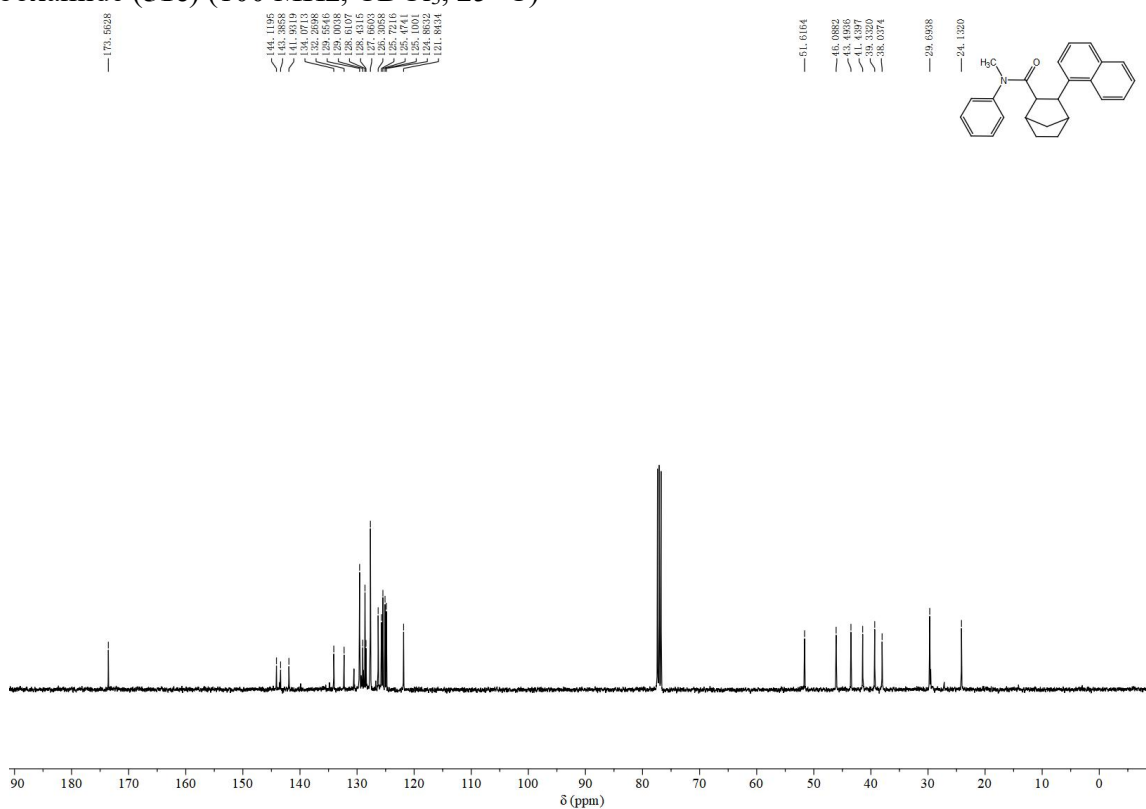
^{19}F NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**50e**) (376 MHz, CDCl_3 , 25 °C)

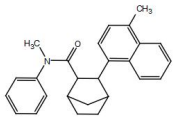
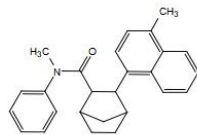
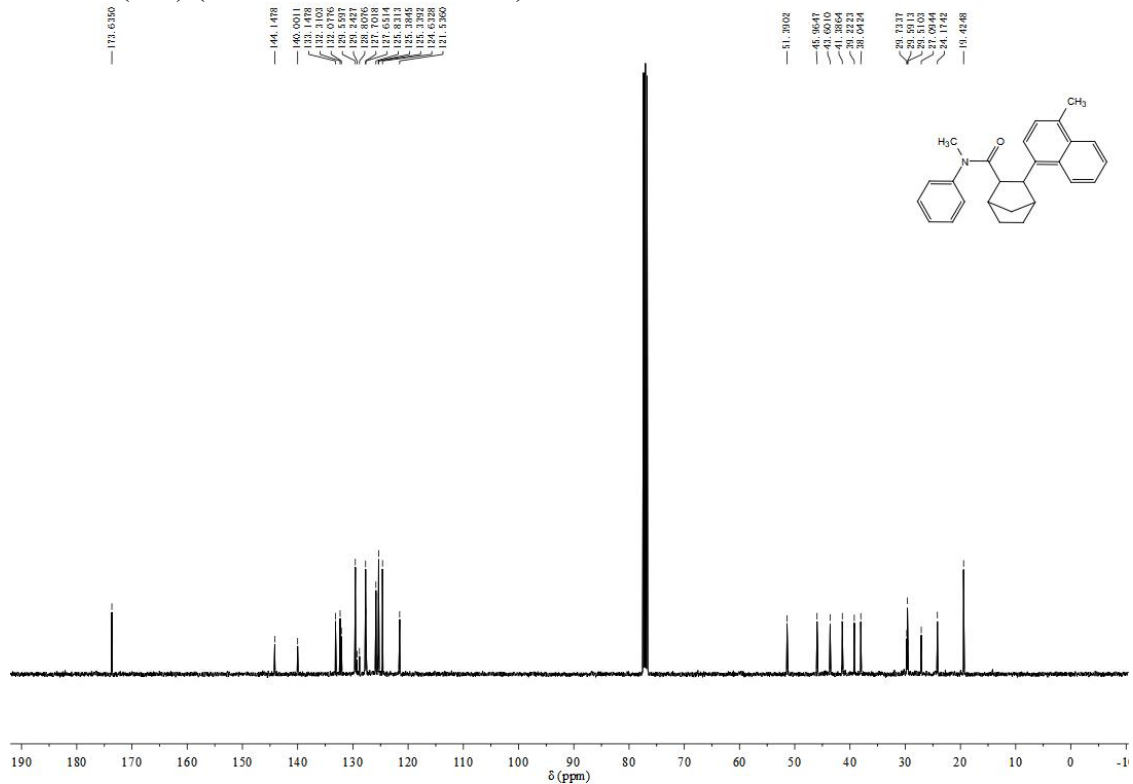


¹H NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**51e**) (400 MHz, CDCl₃, 25 °C)

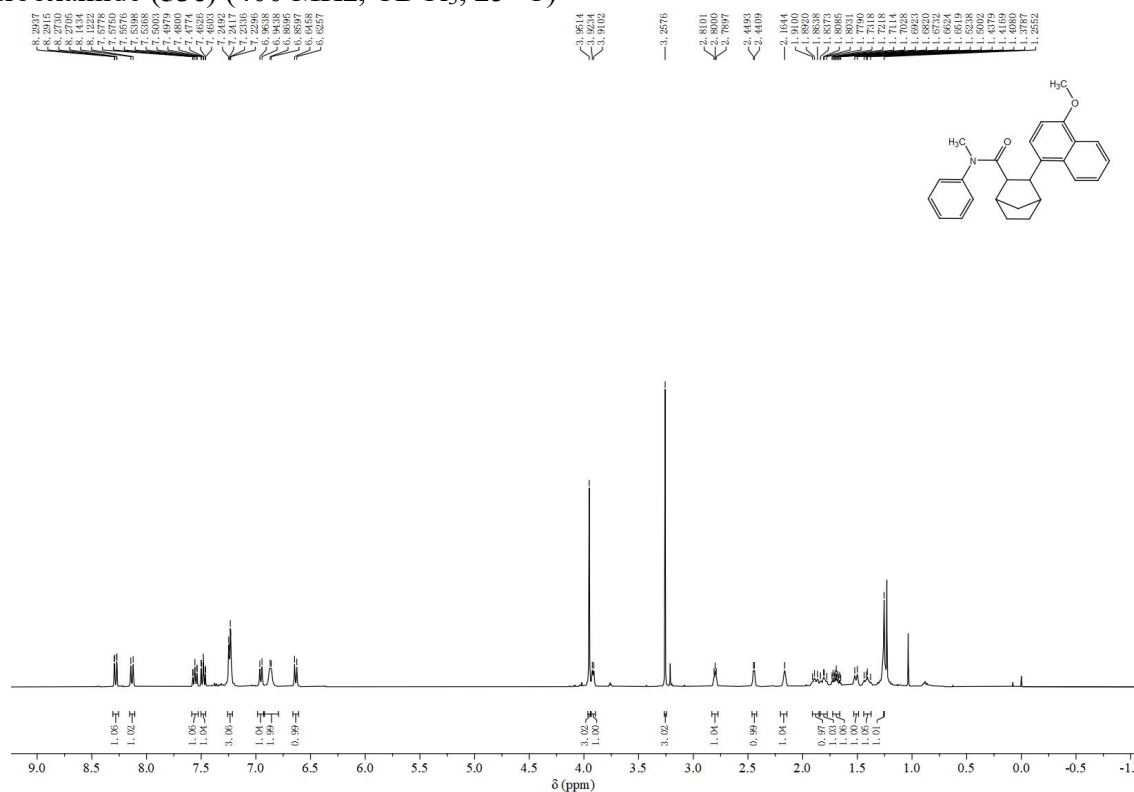


¹³C NMR spectrum of 3-(2-fluoro-4-methylphenyl)-*N,N*-dimethylbicyclo[2.2.1]heptane-2-carboxamide (**51e**) (100 MHz, CDCl₃, 25 °C)

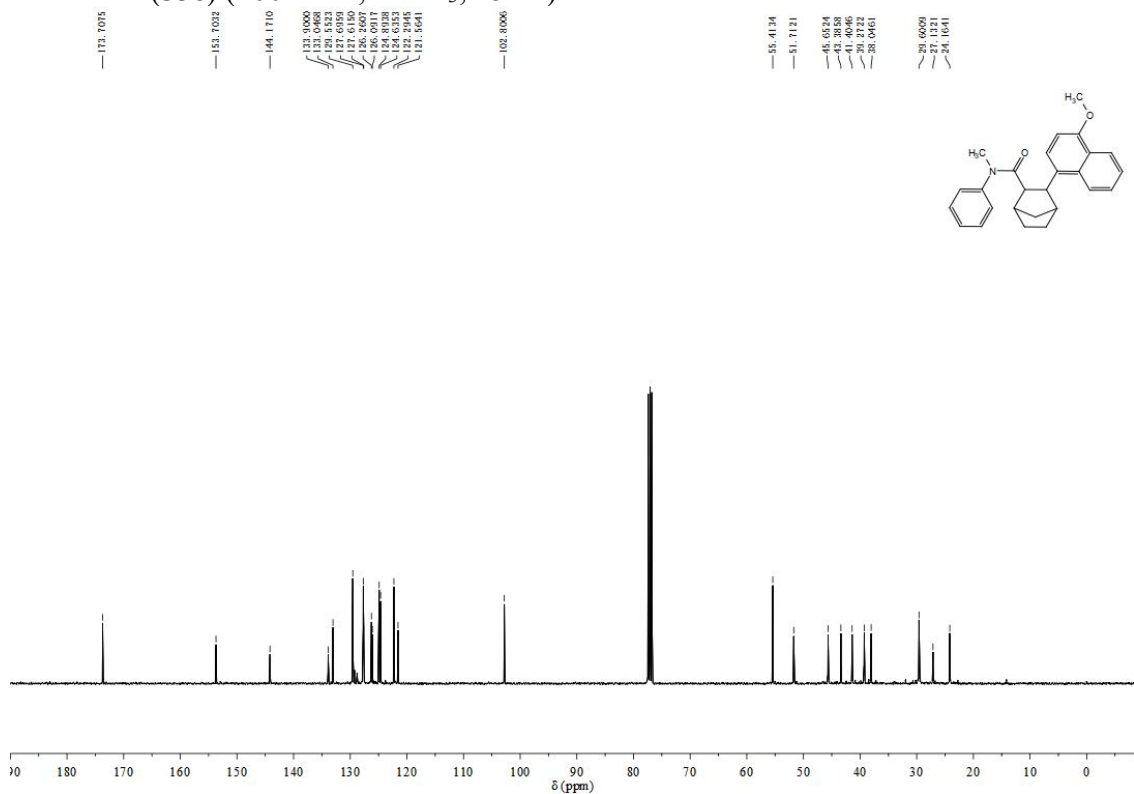


[illegible][illegible]

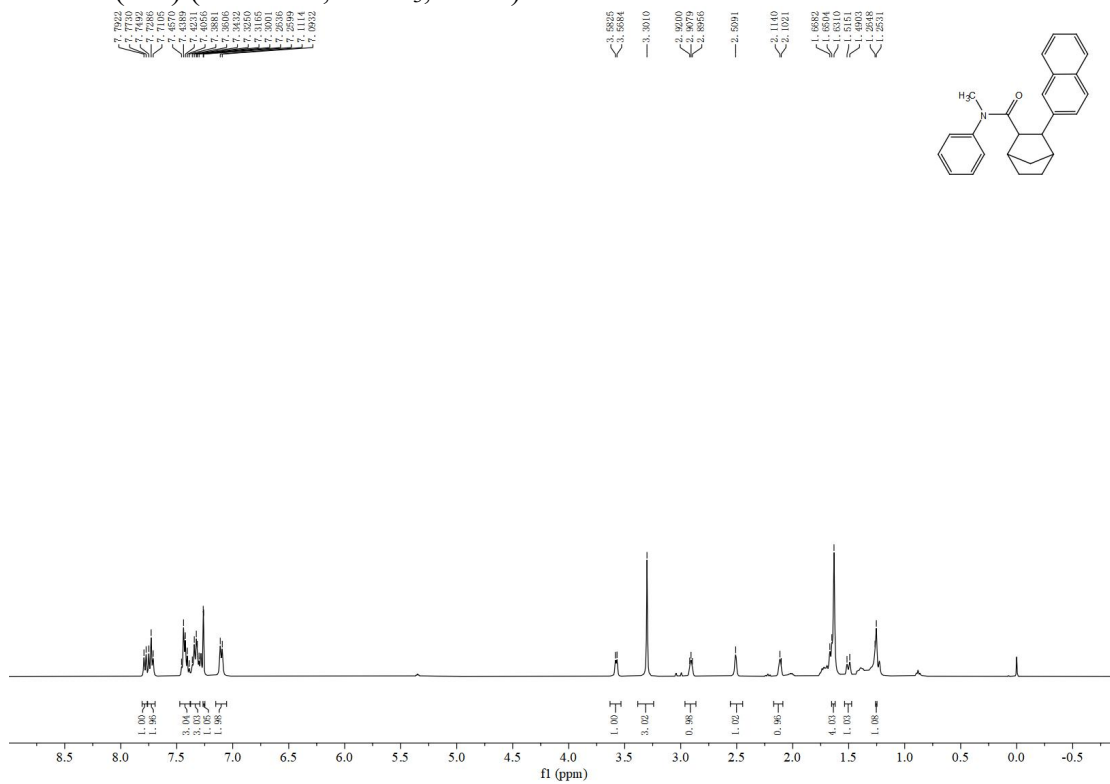
^1H NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**53e**) (400 MHz, CDCl_3 , 25 °C)



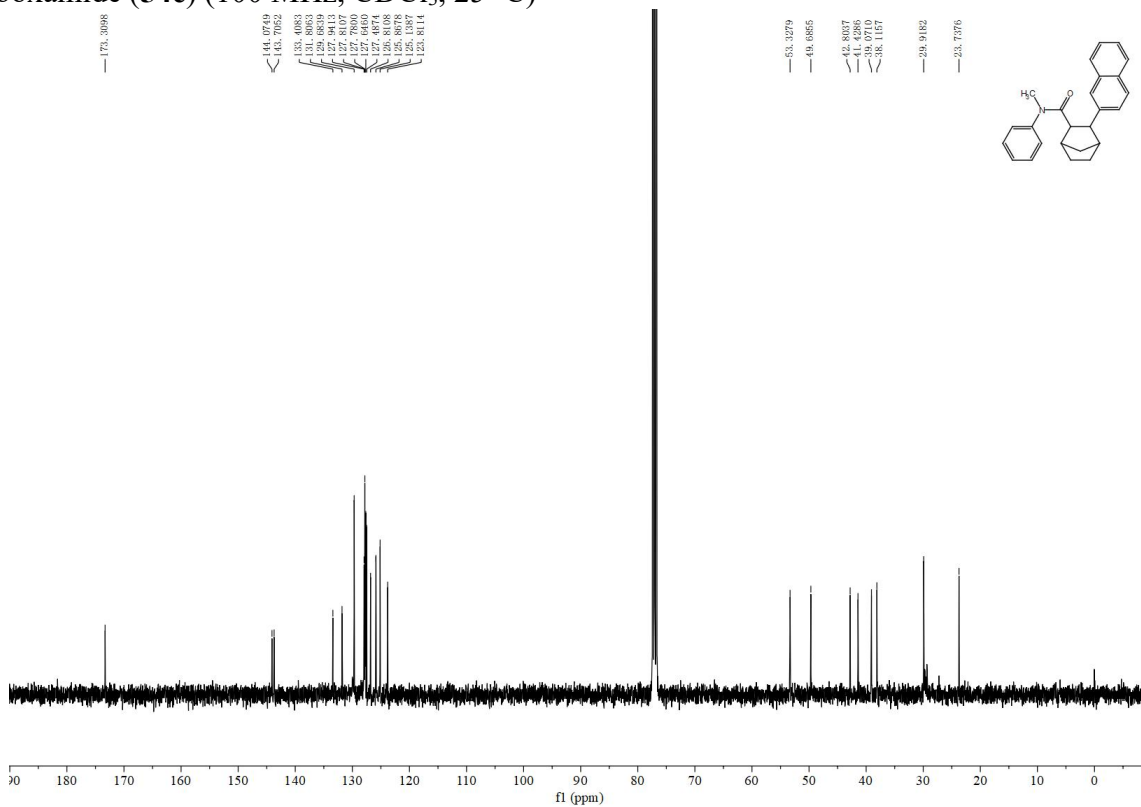
^{13}C NMR spectrum of 3-(4-methoxynaphthalen-1-yl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**53e**) (100 MHz, CDCl_3 , 25 °C)



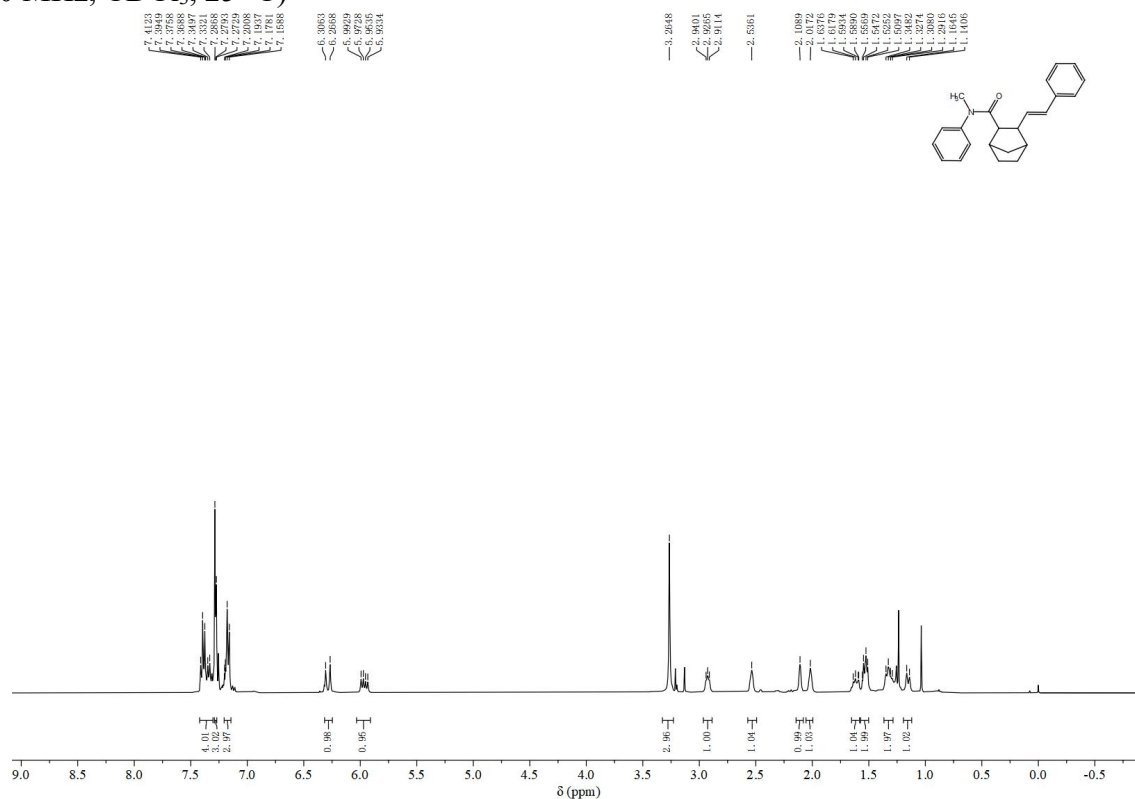
¹H NMR spectrum of *N*-methyl-3-(naphthalen-2-yl)-*N*-phenylbicyclo [2.2.1] heptane-2-carboxamide (**54e**) (400 MHz, CDCl₃, 25 °C)



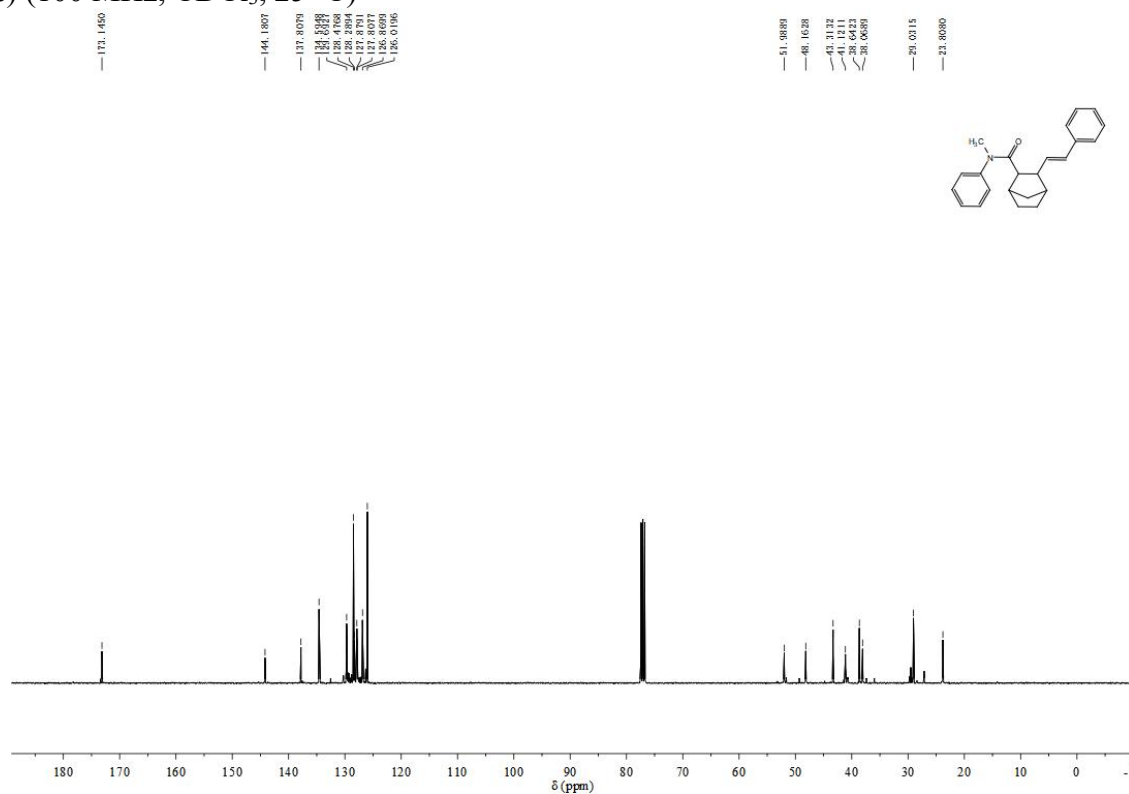
¹³C NMR spectrum of *N*-methyl-3-(naphthalen-2-yl)-*N*-phenylbicyclo [2.2.1] heptane-2-carboxamide (**54e**) (100 MHz, CDCl₃, 25 °C)



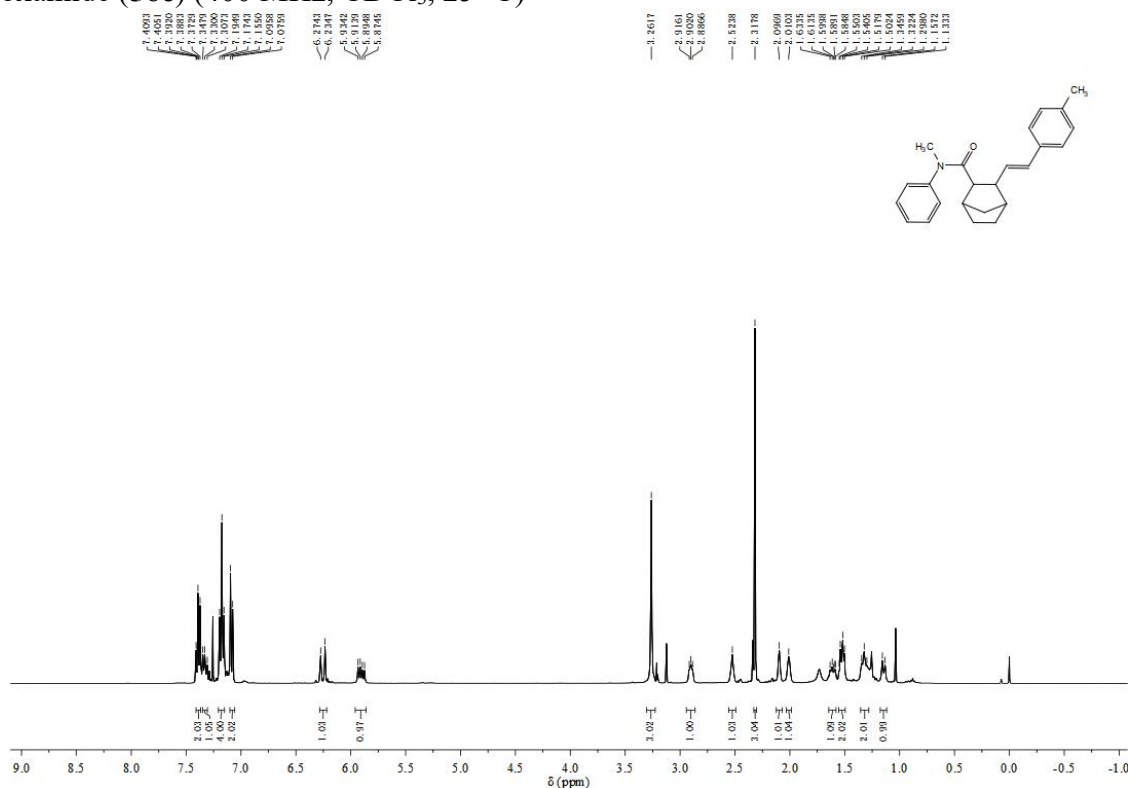
¹H NMR spectrum of (*E*)-*N*-methyl-*N*-phenyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**55e**) (400 MHz, CDCl₃, 25 °C)



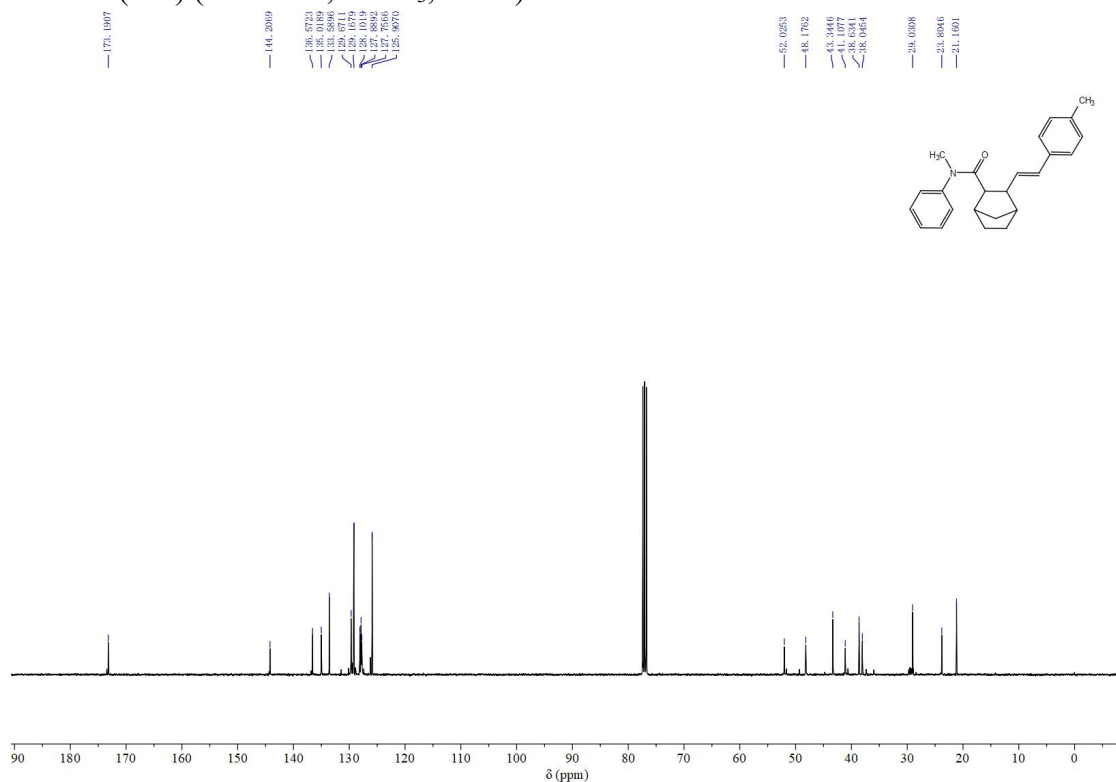
¹³C NMR spectrum of (*E*)-*N*-methyl-*N*-phenyl-3-styrylbicyclo[2.2.1]heptane-2-carboxamide (**55e**) (100 MHz, CDCl₃, 25 °C)



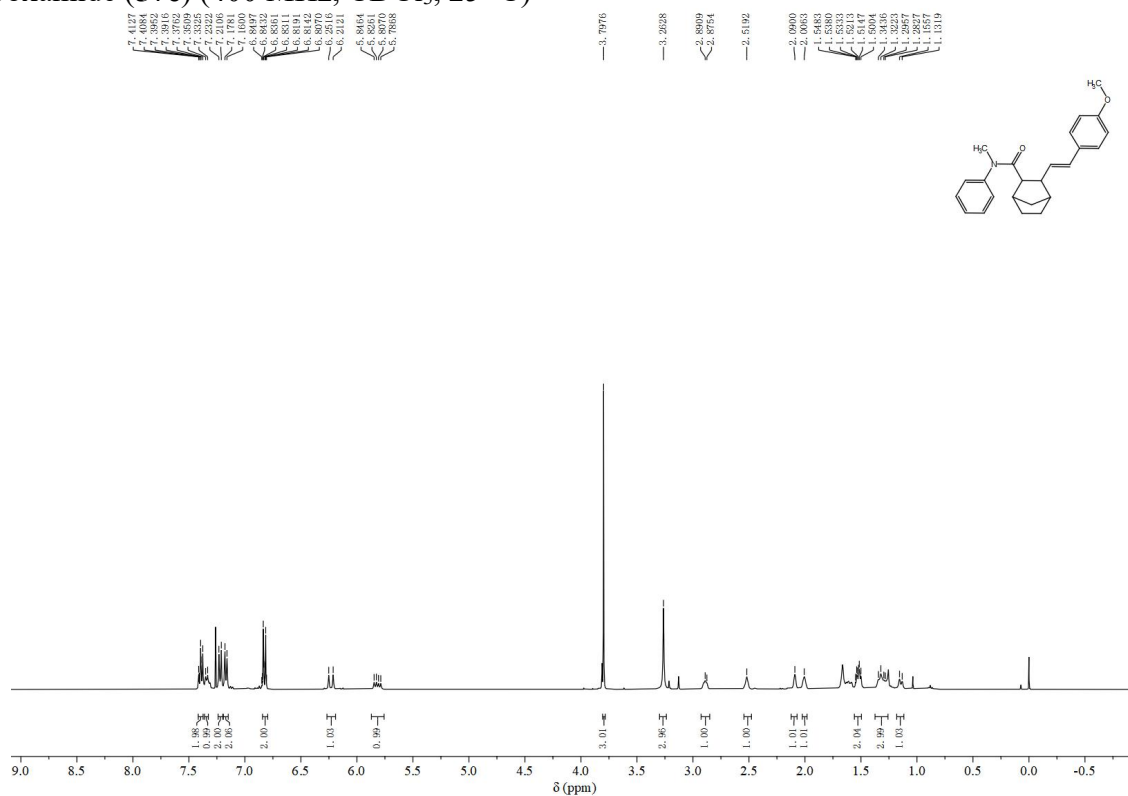
^1H NMR spectrum of (*E*)-*N*-methyl-3-(4-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**56e**) (400 MHz, CDCl_3 , 25 °C)



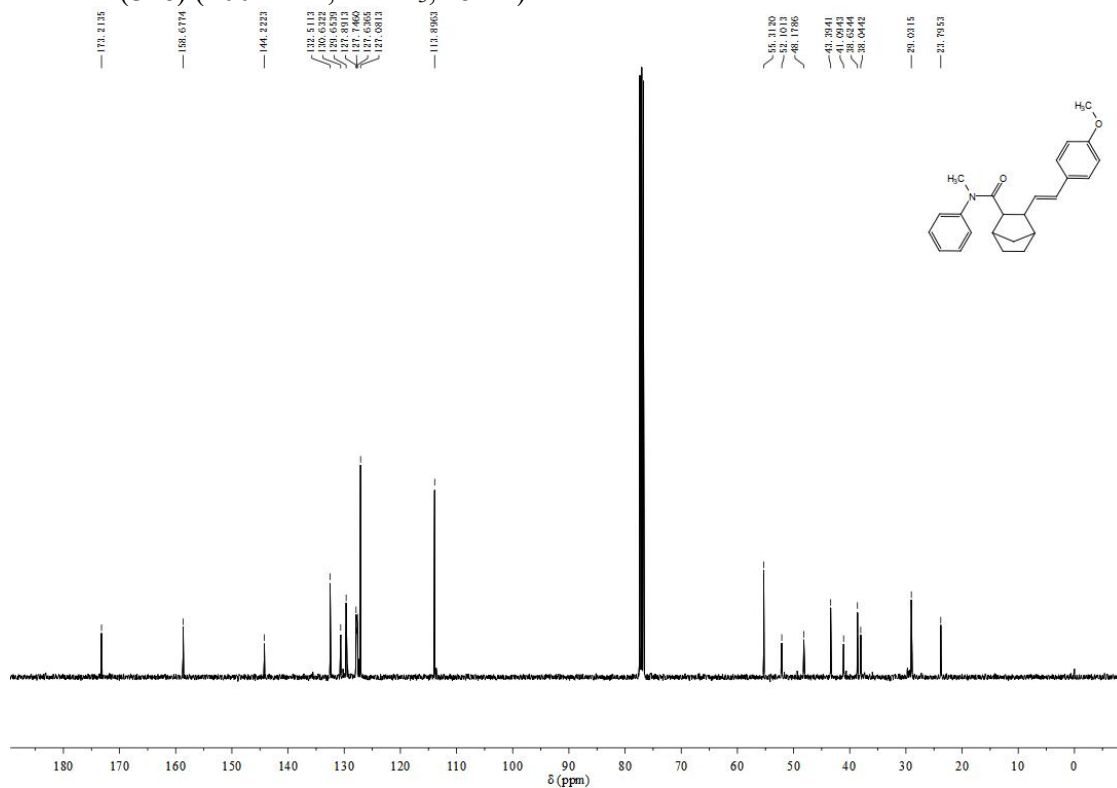
^{13}C NMR spectrum of (*E*)-*N*-methyl-3-(4-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**56e**) (100 MHz, CDCl_3 , 25 °C)



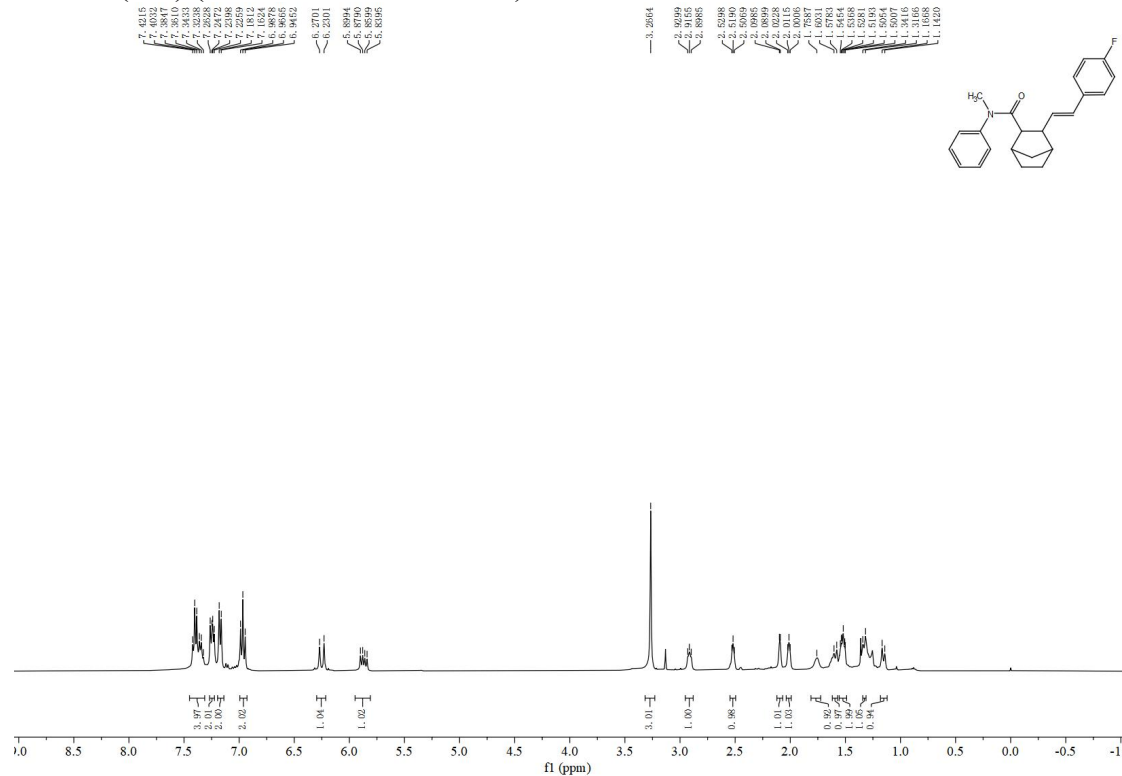
^1H NMR spectrum of (*E*)-3-(4-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**57e**) (400 MHz, CDCl_3 , 25 °C)



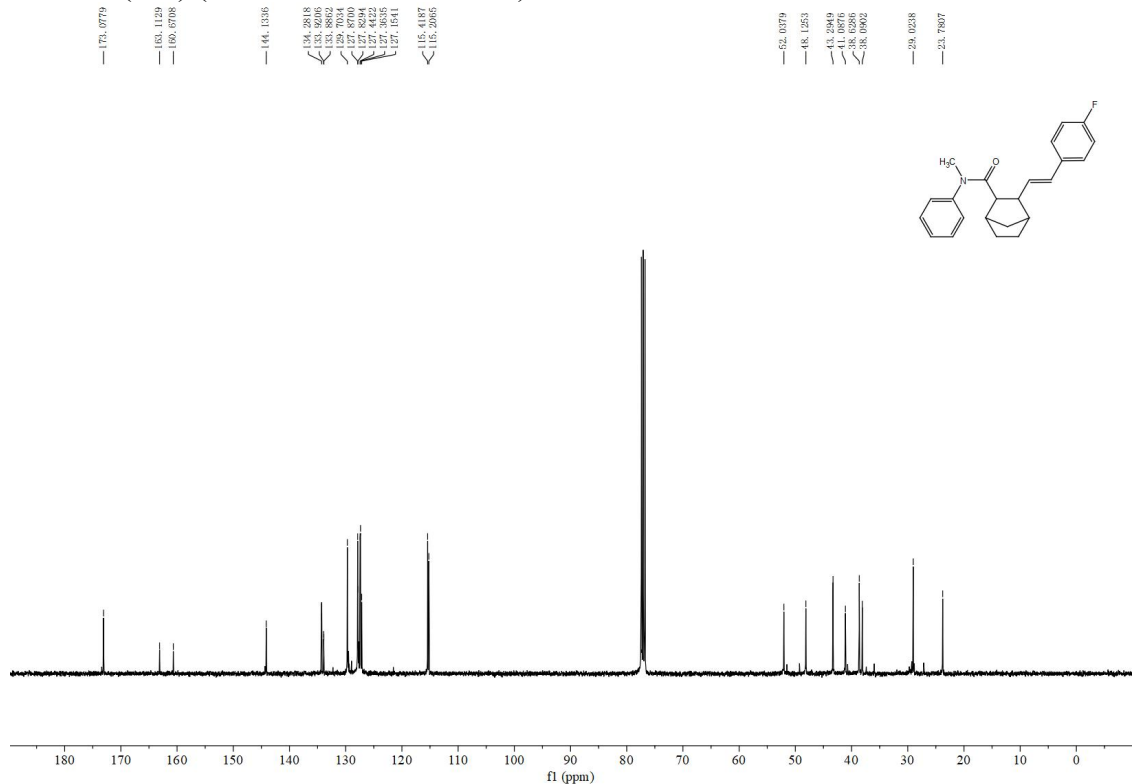
^{13}C NMR spectrum of (*E*)-3-(4-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**57e**) (100 MHz, CDCl_3 , 25 °C)



¹H NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**58e**) (400 MHz, CDCl₃, 25 °C)



¹³C NMR spectrum of (*E*)-3-(4-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**58e**) (100 MHz, CDCl₃, 25 °C)



Chemical structure of the compound is shown above the spectrum. The structure is a bicyclic compound with a carbonyl group, a phenyl ring, and a fluorophenyl group.

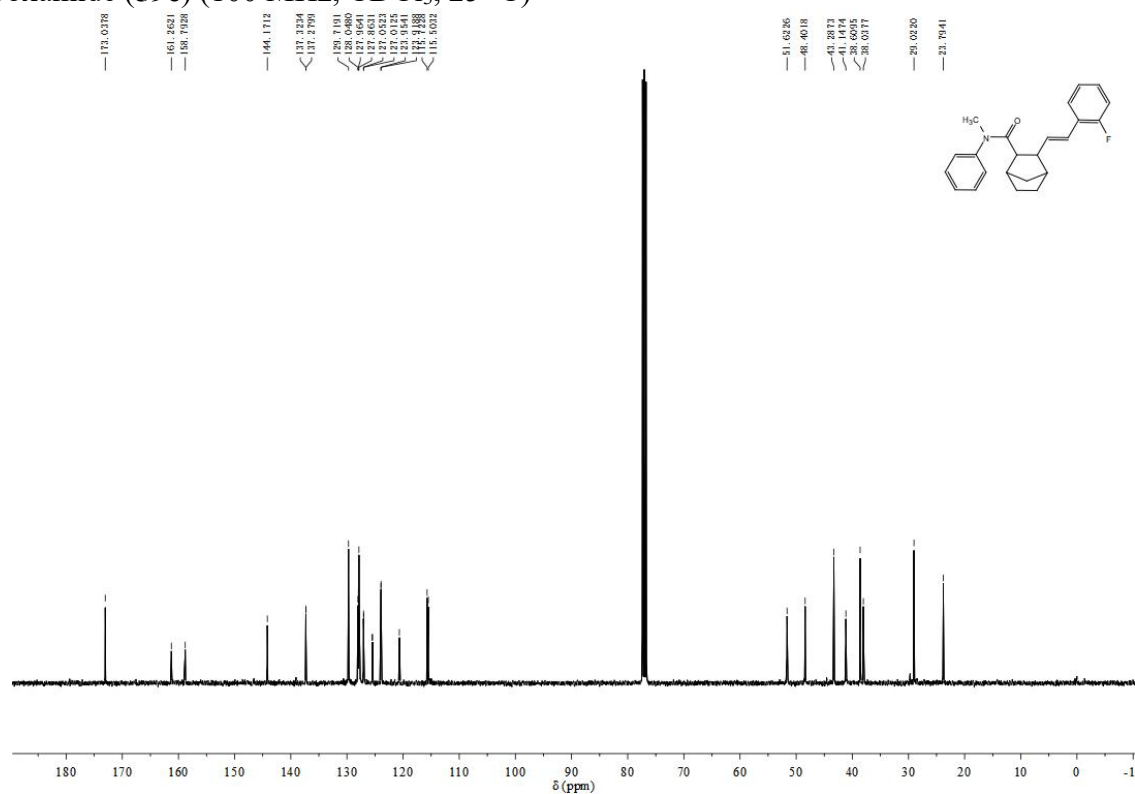
The spectrum shows a single sharp peak at $\delta = 115.6990$ ppm, which is labeled as CDCl_3 . The x-axis is labeled δ (ppm) and ranges from -22 to 10.

Chemical structure of compound 10: CC12CCCC1(C2)C(=O)N(c3ccccc3)/C=C/c4cc(F)ccc4

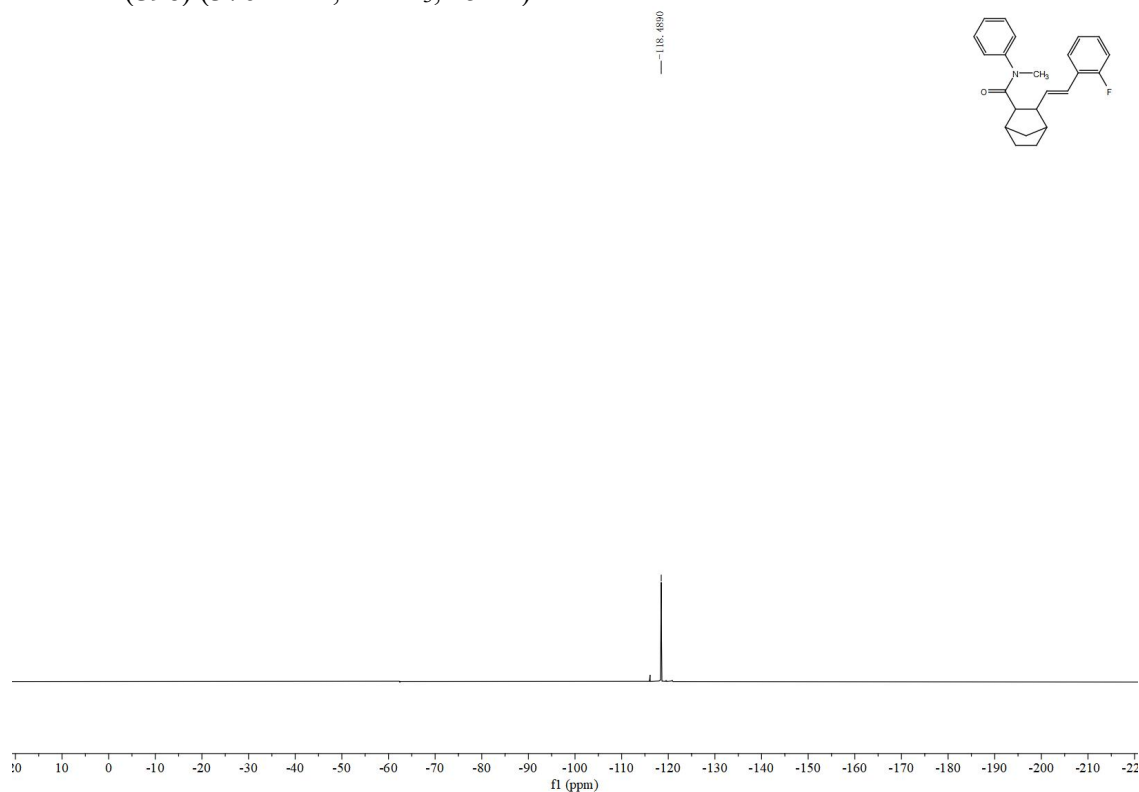
¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift δ (ppm) from 0.0 to 8.0. The spectrum shows several multiplets in the aromatic region (7.0-7.5 ppm), a doublet at 6.2 ppm, a singlet at 3.2 ppm, and several multiplets in the aliphatic region (1.0-2.5 ppm). Integration values are provided below the peaks.

Chemical shift data (ppm): 7.452, 7.451, 7.450, 7.394, 7.393, 7.392, 7.391, 7.390, 7.389, 7.388, 7.387, 7.386, 7.385, 7.384, 7.383, 7.382, 7.381, 7.380, 7.379, 7.378, 7.377, 7.376, 7.375, 7.374, 7.373, 7.372, 7.371, 7.370, 7.369, 7.368, 7.367, 7.366, 7.365, 7.364, 7.363, 7.362, 7.361, 7.360, 7.359, 7.358, 7.357, 7.356, 7.355, 7.354, 7.353, 7.352, 7.351, 7.350, 7.349, 7.348, 7.347, 7.346, 7.345, 7.344, 7.343, 7.342, 7.341, 7.340, 7.339, 7.338, 7.337, 7.336, 7.335, 7.334, 7.333, 7.332, 7.331, 7.330, 7.329, 7.328, 7.327, 7.326, 7.325, 7.324, 7.323, 7.322, 7.321, 7.320, 7.319, 7.318, 7.317, 7.316, 7.315, 7.314, 7.313, 7.312, 7.311, 7.310, 7.309, 7.308, 7.307, 7.306, 7.305, 7.304, 7.303, 7.302, 7.301, 7.300, 7.299, 7.298, 7.297, 7.296, 7.295, 7.294, 7.293, 7.292, 7.291, 7.290, 7.289, 7.288, 7.287, 7.286, 7.285, 7.284, 7.283, 7.282, 7.281, 7.280, 7.279, 7.278, 7.277, 7.276, 7.275, 7.274, 7.273, 7.272, 7.271, 7.270, 7.269, 7.268, 7.267, 7.266, 7.265, 7.264, 7.263, 7.262, 7.261, 7.260, 7.259, 7.258, 7.257, 7.256, 7.255, 7.254, 7.253, 7.252, 7.251, 7.250, 7.249, 7.248, 7.247, 7.246, 7.245, 7.244, 7.243, 7.242, 7.241, 7.240, 7.239, 7.238, 7.237, 7.236, 7.235, 7.234, 7.233, 7.232, 7.231, 7.230, 7.229, 7.228, 7.227, 7.226, 7.225, 7.224, 7.223, 7.222, 7.221, 7.220, 7.219, 7.218, 7.217, 7.216, 7.215, 7.214, 7.213, 7.212, 7.211, 7.210, 7.209, 7.208, 7.207, 7.206, 7.205, 7.204, 7.203, 7.202, 7.201, 7.200, 7.199, 7.198, 7.197, 7.196, 7.195, 7.194, 7.193, 7.192, 7.191, 7.190, 7.189, 7.188, 7.187, 7.186, 7.185, 7.184, 7.183, 7.182, 7.181, 7.180, 7.179, 7.178, 7.177, 7.176, 7.175, 7.174, 7.173, 7.172, 7.171, 7.170, 7.169, 7.168, 7.167, 7.166, 7.165, 7.164, 7.163, 7.162, 7.161, 7.160, 7.159, 7.158, 7.157, 7.156, 7.155, 7.154, 7.153, 7.152, 7.151, 7.150, 7.149, 7.148, 7.147, 7.146, 7.145, 7.144, 7.143, 7.142, 7.141, 7.140, 7.139, 7.138, 7.137, 7.136, 7.135, 7.134, 7.133, 7.132, 7.131, 7.130, 7.129, 7.128, 7.127, 7.126, 7.125, 7.124, 7.123, 7.122, 7.121, 7.120, 7.119, 7.118, 7.117, 7.116, 7.115, 7.114, 7.113, 7.112, 7.111, 7.110, 7.109, 7.108, 7.107, 7.106, 7.105, 7.104, 7.103, 7.102, 7.101, 7.100, 7.099, 7.098, 7.097, 7.096, 7.095, 7.094, 7.093, 7.092, 7.091, 7.090, 7.089, 7.088, 7.087, 7.086, 7.085, 7.084, 7.083, 7.082, 7.081, 7.080, 7.079, 7.078, 7.077, 7.076, 7.075, 7.074, 7.073, 7.072, 7.071, 7.070, 7.069, 7.068, 7.067, 7.066, 7.065, 7.064, 7.063, 7.062, 7.061, 7.060, 7.059, 7.058, 7.057, 7.056, 7.055, 7.054, 7.053, 7.052, 7.051, 7.050, 7.049, 7.048, 7.047, 7.046, 7.045, 7.044, 7.043, 7.042, 7.041, 7.040, 7.039, 7.038, 7.037, 7.036, 7.035, 7.034, 7.033, 7.032, 7.031, 7.030, 7.029, 7.028, 7.027, 7.026, 7.025, 7.024, 7.023, 7.022, 7.021, 7.020, 7.019, 7.018, 7.017, 7.016, 7.015, 7.014, 7.013, 7.012, 7.011, 7.010, 7.009, 7.008, 7.007, 7.006, 7.005, 7.004, 7.003, 7.002, 7.001, 7.000, 6.999, 6.998, 6.997, 6.996, 6.995, 6.994, 6.993, 6.992, 6.991, 6.990, 6.989, 6.988, 6.987, 6.986, 6.985, 6.984, 6.983, 6.982, 6.981, 6.980, 6.979, 6.978, 6.977, 6.976, 6.975, 6.974, 6.973, 6.972, 6.971, 6.970, 6.969, 6.968, 6.967, 6.966, 6.965, 6.964, 6.963, 6.962, 6.961, 6.960, 6.959, 6.958, 6.957, 6.956, 6.955, 6.954, 6.953, 6.952, 6.951, 6.950, 6.949, 6.948, 6.947, 6.946, 6.945, 6.944, 6.943, 6.942, 6.941, 6.940, 6.939, 6.938, 6.937, 6.936, 6.935, 6.934, 6.933, 6.932, 6.931, 6.930, 6.929, 6.928, 6.927, 6.926, 6.925, 6.924, 6.923, 6.922, 6.921, 6.920, 6.919, 6.918, 6.917, 6.916, 6.915, 6.914, 6.913, 6.912, 6.911, 6.910, 6.909, 6.908, 6.907, 6.906, 6.905, 6.904, 6.903, 6.902, 6.901, 6.900, 6.899, 6.898, 6.897, 6.896, 6.895, 6.894, 6.893, 6.892, 6.891, 6.890, 6.889, 6.888, 6.887, 6.886, 6.885, 6.884, 6.883, 6.882, 6.881, 6.880, 6.879, 6.878, 6.877, 6.876, 6.875, 6.874, 6.873, 6.872, 6.871, 6.870, 6.869, 6.868, 6.867, 6.866, 6.865, 6.864, 6.863, 6.862, 6.861, 6.860, 6.859, 6.858, 6.857, 6.856, 6.85

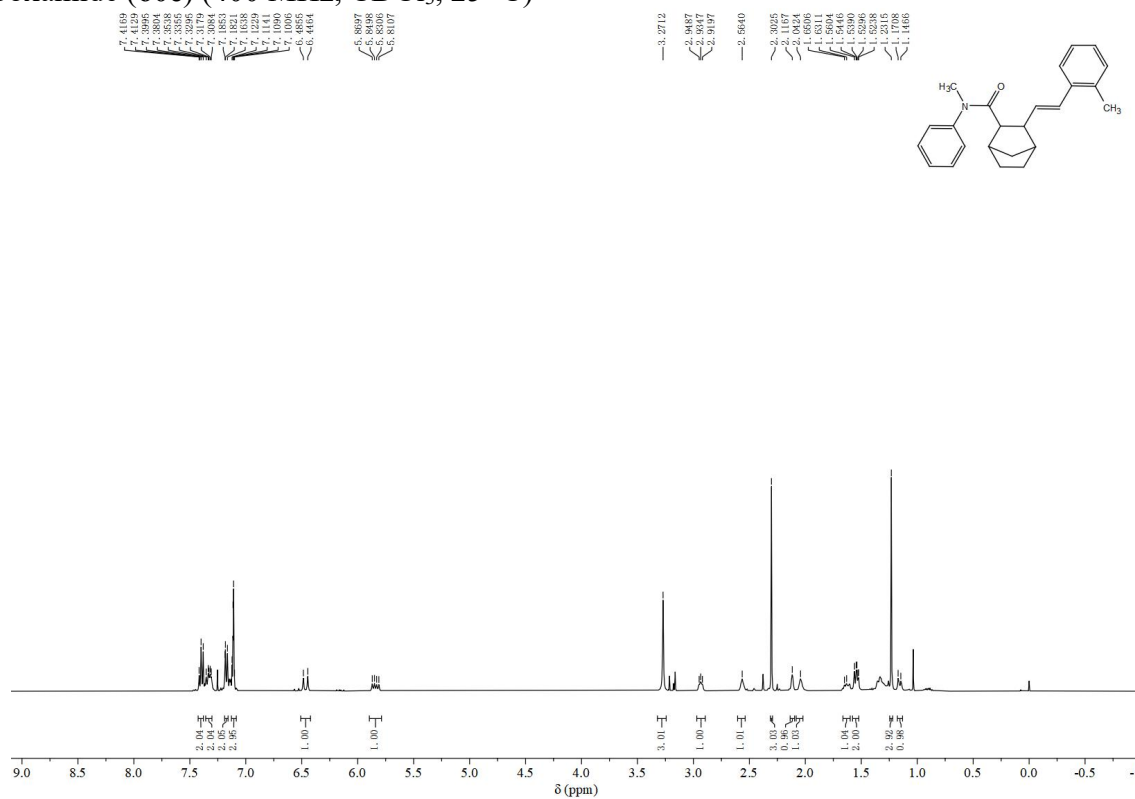
^{13}C NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**59e**) (100 MHz, CDCl_3 , 25 °C)



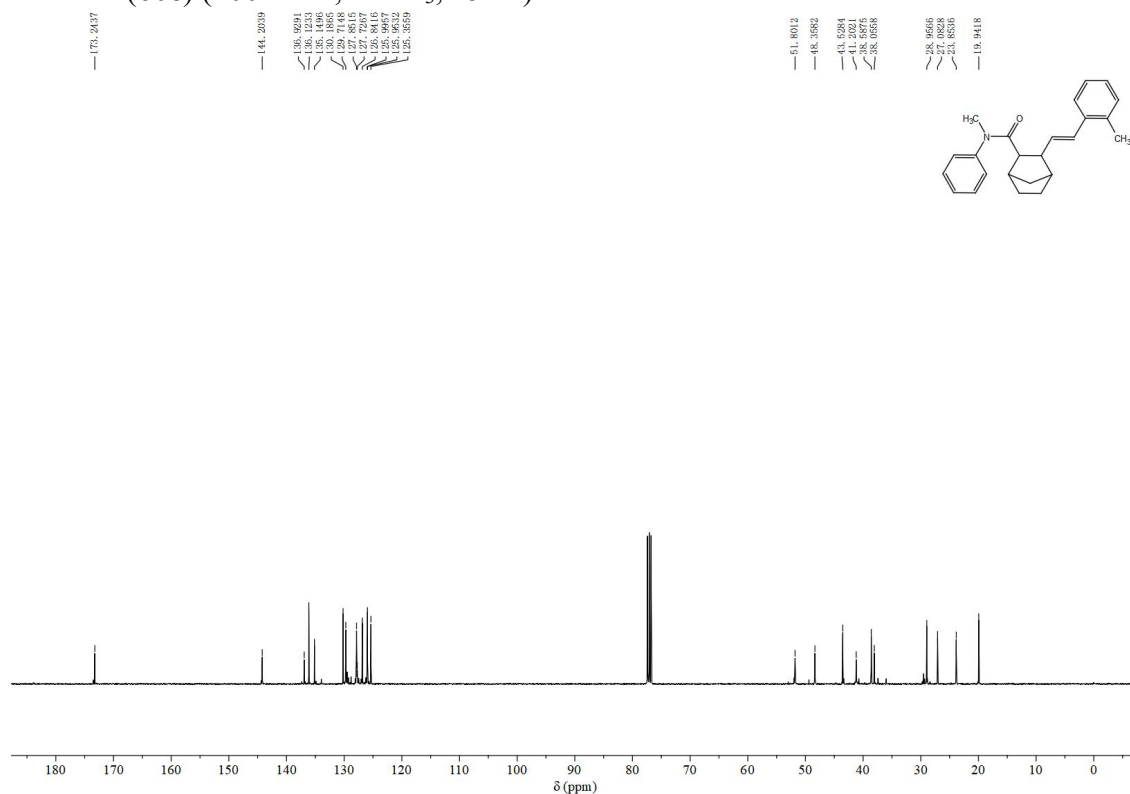
^{19}F NMR spectrum of (*E*)-3-(2-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**59e**) (376 MHz, CDCl_3 , 25 °C)



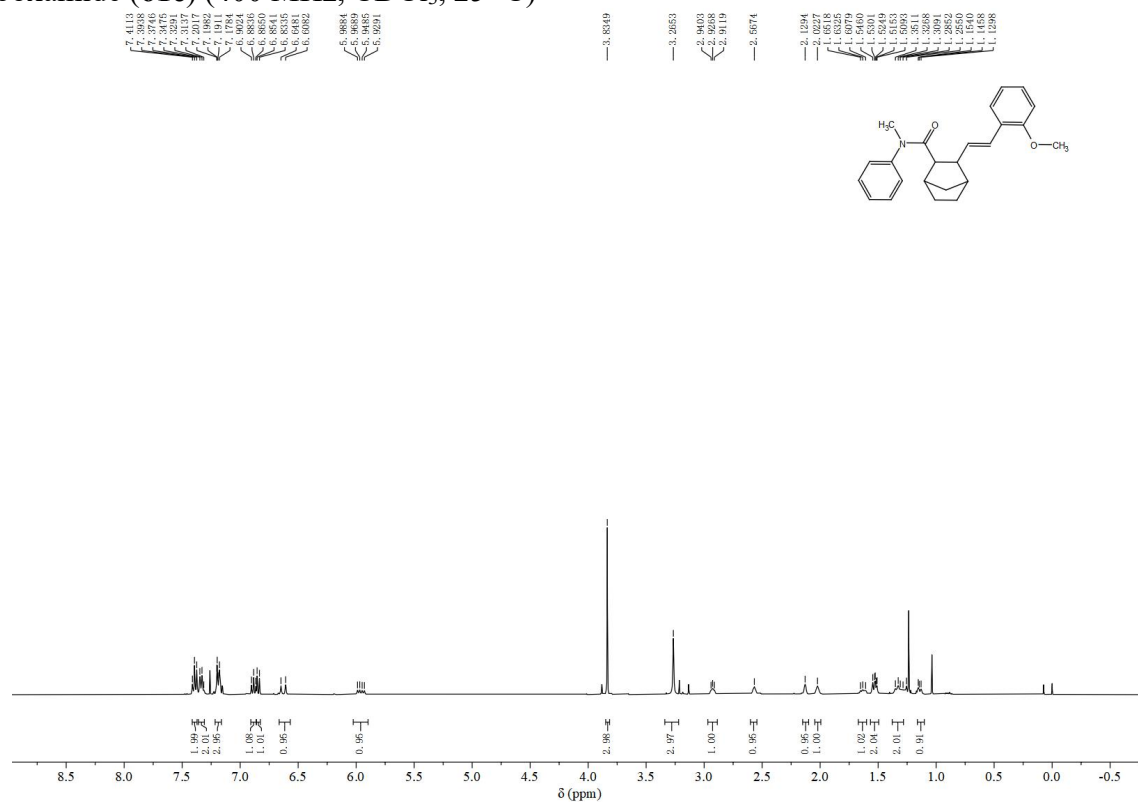
^1H NMR spectrum of (*E*)-*N*-methyl-3-(2-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**60e**) (400 MHz, CDCl_3 , 25 °C)



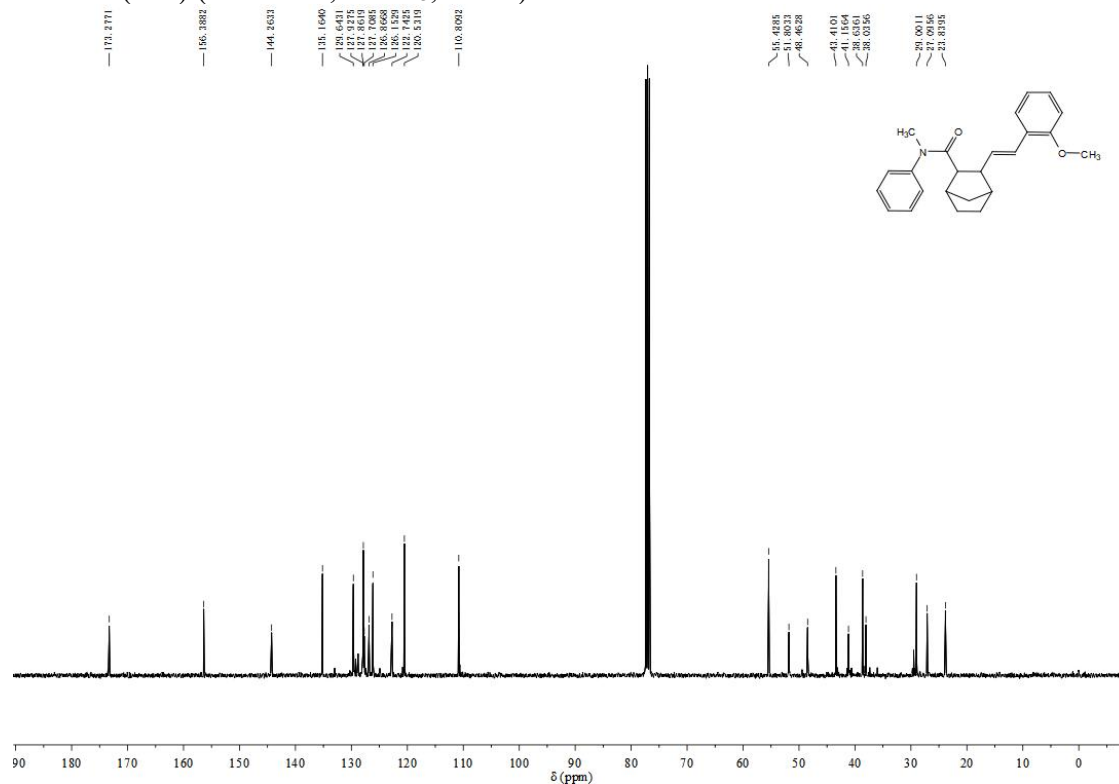
^{13}C NMR spectrum of (*E*)-*N*-methyl-3-(2-methylstyryl)-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**60e**) (100 MHz, CDCl_3 , 25 °C)



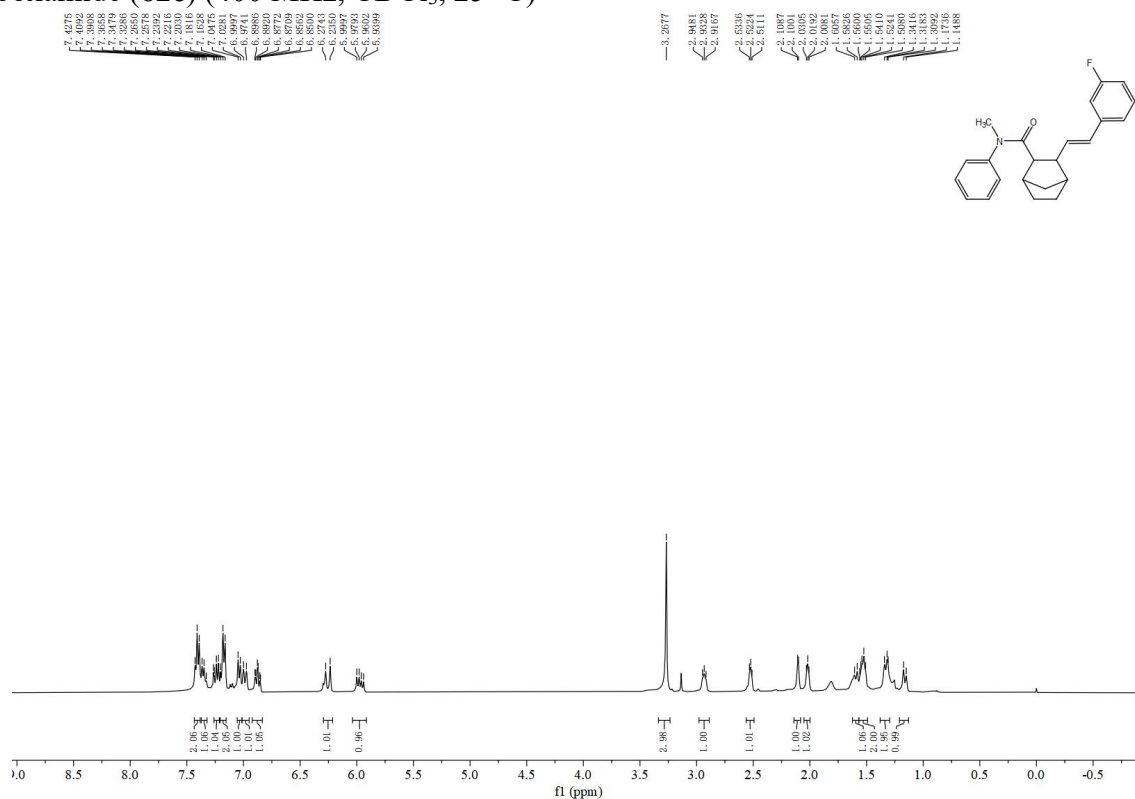
^1H NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**61e**) (400 MHz, CDCl_3 , 25 °C)



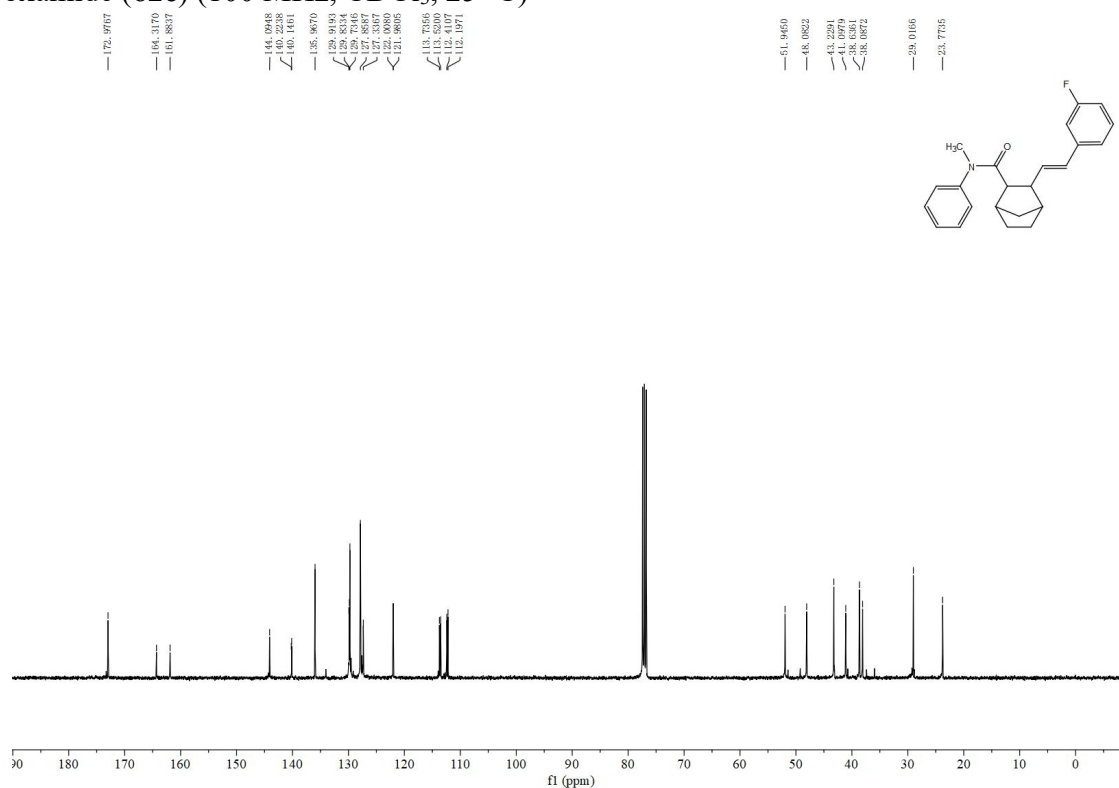
^{13}C NMR spectrum of (*E*)-3-(2-methoxystyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**61e**) (100 MHz, CDCl_3 , 25 °C)



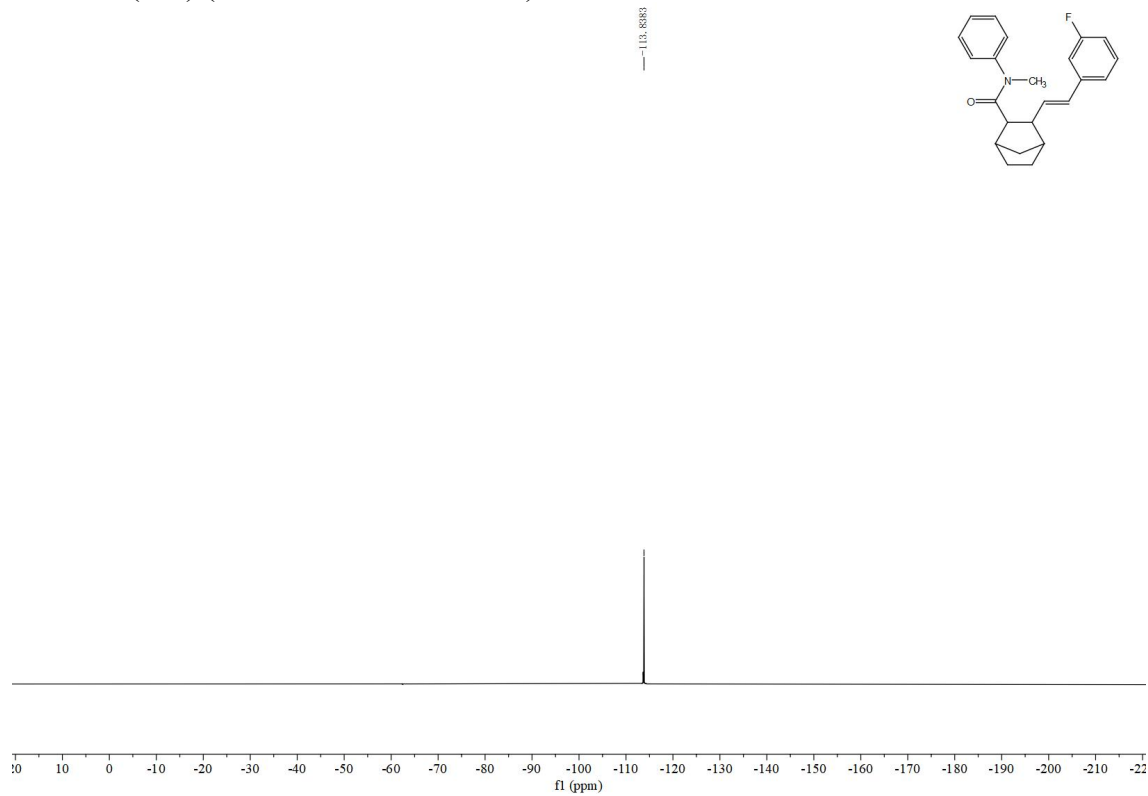
^1H NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**62e**) (400 MHz, CDCl_3 , 25 °C)



^{13}C NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**62e**) (100 MHz, CDCl_3 , 25 °C)



^{19}F NMR spectrum of (*E*)-3-(3-fluorostyryl)-*N*-methyl-*N*-phenylbicyclo[2.2.1]heptane-2-carboxamide (**62e**) (376 MHz, CDCl_3 , 25 °C)



6. Supplementary references

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