

Supplementary Information

Sila-spirocyclization Involving Unstrained C(*sp*³)–Si Bond Cleavage

Yufeng Shi,¹ Xiaonan Shi,¹ Jinyu Zhang,¹ Ying Qin,¹ Bo Li,^{2*} and Dongbing Zhao^{1*}

¹State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

²Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91106 (USA)

* Correspondence: bli3@caltech.edu (B. L.) & dongbing.chem@nankai.edu.cn (D. Z.)

Table of Content

1. Supplementary Notes	2
2. Supplementary Methods	3
Synthesis of Starting Materials	3
Characterization of Products 1	7
Pd-Catalyzed Spirocyclization Reaction of 1.....	27
Condition Screening.....	27
General procedure	28
Characterization of Products 2	28
Removal of the Protecting Group (-Ts) in Spirosilacycle 2dd	55
General Procedure.....	55
Characterization of Product 5.....	56
3. Supplementary Discussion	56
Experimental Mechanistic Study	56
Computational Studies	59
Quantum Mechanical Studies	59
Energies and Coordinates of Calculated Structures	60
4. Supplementary Figures	62
NMR Spectra	62
5. Supplementary References.....	163

1. Supplementary Notes

Unless otherwise noted, all reactions were set up on a Schlenk vacuum line or in a glovebox using oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars under a N₂ atmosphere with dry solvents. Et₂O and toluene were distilled with Na before using. Other dry solvents or commercially available chemicals were obtained from Adamas-beta, Alfa Aesar, J&K, Sigma-Aldrich, Energy Chemical, Bide Pharmatech, Sinocompound, TCI, Sinocompound and used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on SANPONT SGF254 glass plates. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 365 nm) and/or iodine. Column chromatography was performed using GENERAL-REAGENT silica gel (200-300 mesh).

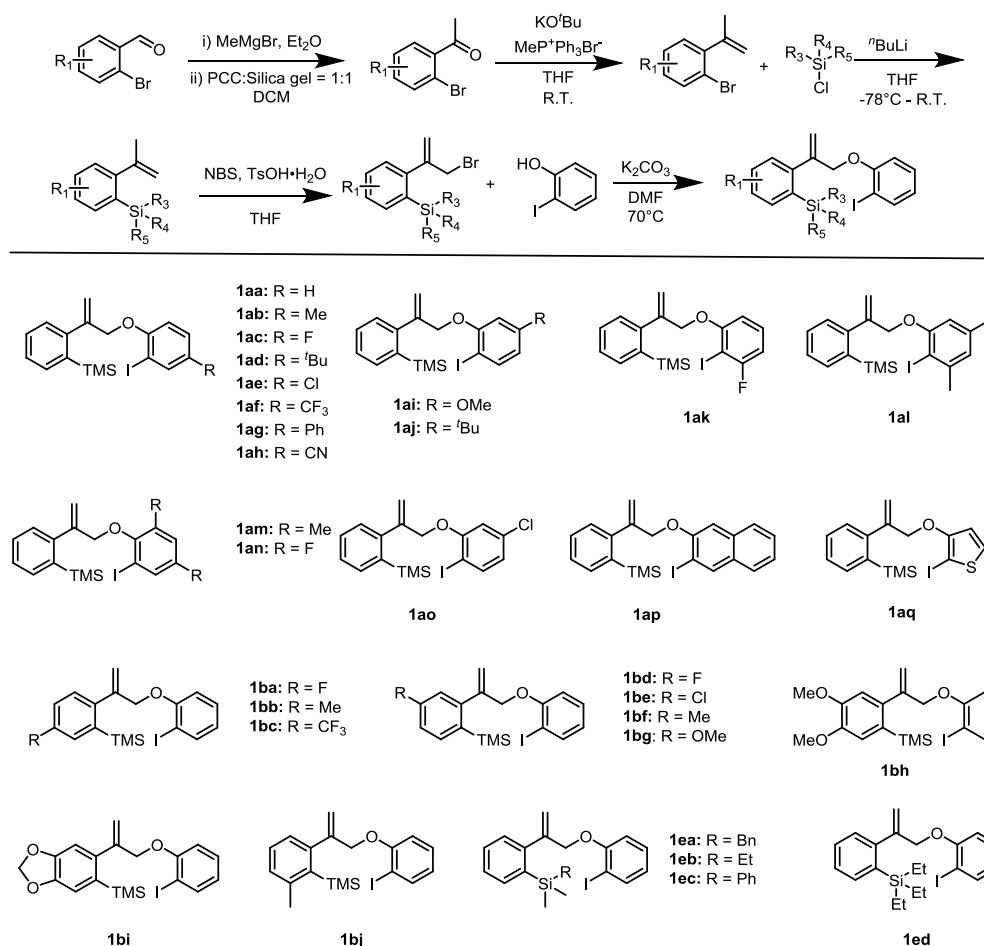
Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV 400 spectrometer at 400 MHz for ¹H NMR, 100 MHz for ¹³C NMR, 376 MHz for ¹⁹F NMR using CDCl₃ as solvent. ¹H and ¹³C NMR are reported (ppm) relative to the CDCl₃ peak ($\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm). All coupling constants (*J* values) were reported in Hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), triplet of doublets (td) and multiplet (m).

GC-MS analysis were performed on a GC-MS with an EI mode (Thermo Scientific Trace 300/GC-System and ISQ/QD). High-resolution mass spectra (HRMS) were performed on a Q Exactive GC-Orbitrap MS (EI). The residues of the catalytic reactions were purified on C18(ODS) column (5 μ m, 21.2x250 mm) with CH₃CN by preparative RP-HPLC with an Bonna-Agela CHEETAH HP series.

2. Supplementary Methods

Synthesis of Starting Materials

Procedure A:



Step I: 1-(2-Bromophenyl) ethan-1-one derivatives were prepared following a previously reported procedure^[1]. To a solution of 2-bromobenzaldehyde derivatives (commercially available chemicals; 20 mmol) in THF (20 mL) was added MeMgBr (commercially available chemicals; 24 mmol) dropwise at 0 °C under N₂, and stirred at the same temperature. Upon completion, the reaction was quenched with saturated NH₄Cl solution and extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated to deliver the corresponding secondary benzylic alcohols, which were directly used for the next

without further purification. To a solution of 1-(2-bromophenyl) ethan-1-ol derivatives (15 mmol) in DCM was added a mixture of PCC (45.0 mmol) and silica gel [PCC/silica gel = 1/1 (w/w)]. The resulted reaction mixture was stirred at room temperature. Upon completion, the reaction mixture was then filtered through a pad of silica gel with EtOAc as eluent. The resulting solution was concentrated, and the residue was purified by silica gel chromatography column to yield the desired 1-(2-bromophenyl) ethan-1-one derivatives.

Step II: Following a modified literature procedure^[2], to the mixture of methyl triphenylphosphonium bromide (40 mmol, 2 equiv.) and *t*BuOK (50.0 mmol, 2.5 equiv.) was added anhydrous THF (50.0 mL) and stirred at rt. for 20 min. under argon, then the solution of ketone (20 mmol, 1.0 equiv.) in THF (50.0 mL) was added slowly, the resulting solution was allowed to stir at rt. overnight. To the mixture was added sat. NH₄Cl, then THF was removed and the mixture was extracted with EtOAc (3 x 30 mL), the combined EtOAc solution was washed with brine, dried over anhydrous Na₂SO₄. After removing the solvent, the residue was purified by flash chromatography on silica gel to yield 1-bromo-2-(prop-1-en-2-yl) benzene derivatives.

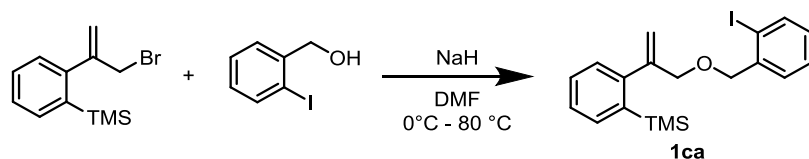
Step III: Following a modified literature procedure^[3], a solution of *n*BuLi in hexane (11 mmol, 1.1 equiv., 2.5 M in hexane) was added dropwise to a solution of 1-bromo-2-(prop-1-en-2-yl) benzene derivatives (10 mmol, 1.0 equiv.) in anhydrous THF (20 mL) at -78 °C. After the reaction mixture was stirred at this temperature for 0.5 hour, chlorosilane (12 mmol, 1.2 equiv.) was added via a syringe. Then, the mixture was warmed to room temperature. The solvent was removed in vacuo, and evaporated under reduced pressure to give trimethyl(2-(prop-1-en-2-yl) phenyl) silane derivatives, which was used for the next step without purification.

Step IV: Following a modified literature procedure^[2], in an oven dried flask trimethyl (2-(prop-1-en-2-yl) phenyl) silane derivatives (8 mmol, 1.0 equiv.) was dissolved in anhydrous THF (3.0 mL/mmol). To the resulting solution *N*-Bromosuccinimide (NBS, 8.4mmol, 1.05 equiv.) and TsOH (0.8 mmol, 0.1 equiv.) was added and the solution was

refluxed at 80 °C for 4 h. Reaction mixture was cooled to rt and the reaction mixture was taken in petroleum ether (15 mL/mmol), washed with H₂O (15 mL × 3). Organic phase was dried over anh. Na₂SO₄, concentrated under reduced pressure to afford the corresponding compounds.

Step V: Following a modified literature procedure ^[4], to a solution of 2-iodophenol (5 mmol, 1.0 equiv.) and K₂CO₃ (7.5 mmol, 1.5 equiv.) in DMF (10 mL) was added allyl halide (6 mmol, 1.2 equiv). The reaction mixture was allowed to warm at 70 °C and stirred overnight. The reaction was quenched with water (10 mL), and extracted with ethyl acetate (3 × 10 mL), wash with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the products **1**.

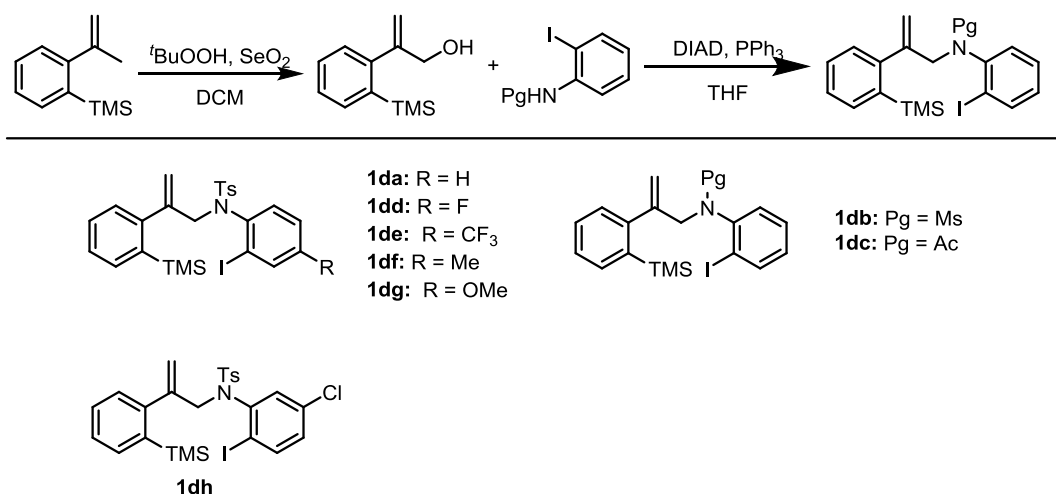
Procedure B:



(2-(3-Bromoprop-1-en-2-yl) phenyl) trimethylsilane was prepared following **Procedure A**.

Following a modified literature procedure ^[5], to a suspension of NaH (60% in oil, 6 mmol, 1.2 equiv.) in DMF (10 mL) were added (2-iodophenyl) methanol (5 mmol, 1.0 equiv.) in DMF (5 mL) at 0 °C under Ar atmosphere. When the evolution of H₂ has ceased, (2-(3-bromoprop-1-en-2-yl) phenyl) trimethylsilane (5.5 mmol, 1.0 equiv.) was added. The reaction mixture was heated to 80 °C overnight. The reaction mixture was quenched with water and extracted with Et₂O. The organic phase was dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography (PE: EA = 40:1) to afford compound **1ca**.

Procedure C:



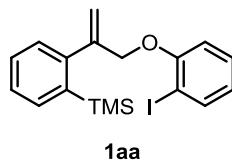
Trimethyl(2-(prop-1-en-2-yl) phenyl) silane was prepared following **Procedure A**.

Step I: Following a modified literature procedure^[6], to a stirred suspension of SeO_2 (15 mmol, 1.5 equiv.) in CH_2Cl_2 (10 mL) at R.T. was added a solution of tert-butyl hydroperoxide (70% in water, 15 mmol, 1.5 equiv.). After 10 min a solution of trimethyl(2-(prop-1-en-2-yl) phenyl) silane (10.0 mmol, 1.0 equiv.) in CH_2Cl_2 (5 mL) was added and the mixture stirred at ambient temperature for 4 h. Saturated aqueous NaHCO_3 (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were washed with water and brine, dried (MgSO_4) and evaporated. Flash chromatography (PE: EA = 5:1) afforded 2-(2-(trimethylsilyl) phenyl) prop-2-en-1-ol as a clear colorless oil (yield = 50%).

Step II: Following a modified literature procedure^[7], to a flame-dried flask were added PPh_3 (15 mmol, 1.5 equiv.), aryl iodide (10.05 mmol, 1.05 equiv.), allylic alcohol (10 mmol, 1.0 equiv.) and anhydrous THF (40 mL) sequentially under Ar atmosphere at room temperature. A solution of DIAD (15 mmol, 1.5 equiv.) in 10 mL of anhydrous THF was added dropwise via addition funnel at 0 °C. The resulting mixture was allowed to warm to room temperature naturally with stirring. After the reaction was complete as monitored by TLC, the reaction mixture was concentrated on a rotary evaporator and the residue was purified by chromatography on silica gel to afford the desired product

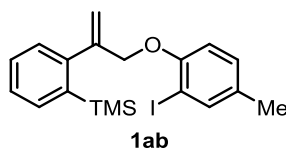
Characterization of Products 1

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1aa)



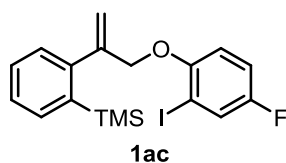
Following the **procedure A**, **1aa** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 50% yield (2 g, 5 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.80 (m, 1H), 7.58 (m, 1H), 7.39 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 6.79 (m, 1H), 6.72 (m, 1H), 5.88 (q, $J = 1.8$ Hz, 1H), 5.24 (d, $J = 1.8$ Hz, 1H), 4.67 (d, $J = 1.8$ Hz, 2H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.13, 145.02, 144.66, 138.65, 137.73, 134.17, 128.52, 127.73, 125.98, 121.82, 115.19, 111.24, 85.67, 70.92, 52.55, -0.00. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{21}\text{IOSi}$ $[\text{M}]^+$: 408.04. Found: 408.15.

(2-(3-(2-Iodo-4-methylphenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ab)



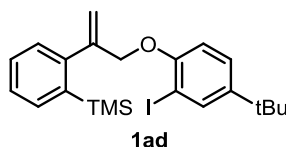
Following the **procedure A**, **1ab** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 57% yield (2.4 g, 5.7 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.63 (m, 1H), 7.61 – 7.56 (m, 1H), 7.41 – 7.28 (m, 2H), 7.27 – 7.23 (m, 1H), 7.07 (m, 1H), 6.68 (m, 1H), 5.86 (d, $J = 1.8$ Hz, 1H), 5.22 (q, $J = 1.8$ Hz, 1H), 4.63 (t, $J = 1.8$ Hz, 2H), 2.26 (s, 3H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 154.18, 145.16, 144.84, 139.03, 137.82, 134.22, 131.42, 129.00, 127.77, 127.70, 125.99, 115.08, 111.05, 85.49, 71.09, 19.16, -0.00. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{23}\text{IOSi}$ $[\text{M}]^+$: 422.06. Found: 422.15.

(2-(3-(4-Fluoro-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ac)



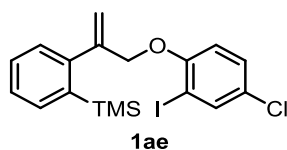
Following the **procedure A**, **1ac** was obtained as a white solid ($R_f = 0.25$, petroleum ether) in 42% yield (1.8 g, 4.2 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.64 (m, 1H), 7.56 (m, 1H), 7.40 – 7.36 (m, 2H), 7.30 – 7.28 (m, 1H), 7.09 – 6.98 (m, 1H), 6.76 (m, 1H), 5.89 (p, $J = 1.5$ Hz, 1H), 5.28 (t, $J = 1.5$ Hz, 1H), 4.67 (t, $J = 1.5$ Hz, 2H), 0.35 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.00 (d, $J = 243.7$ Hz), 152.92 (d, $J = 2.4$ Hz), 144.92, 144.63, 137.76, 134.23, 127.71, 126.04, 125.48, 125.23, 115.27, 114.68 (d, $J = 22.8$ Hz), 111.39 (d, $J = 8.1$ Hz), 85.08 (d, $J = 8.7$ Hz), 71.73, -0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -121.76. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{FIO}_2\text{Si}$ $[\text{M}]^+$: 426.03. Found: 426.13.

(2-(3-(4-(tert-Butyl)-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ad)



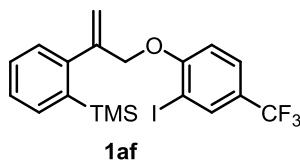
Following the **procedure A**, **1ad** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 44% yield (2.0 g, 4.4 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.79 (m, 1H), 7.59 (m, 1H), 7.42 – 7.22 (m, 4H), 6.72 (m, 1H), 5.86 (s, 1H), 5.22 (s, 1H), 4.65 (m, 2H), 1.28 (s, 9H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 154.01, 145.17, 144.90, 144.84, 137.80, 135.77, 134.19, 127.75, 127.67, 125.96, 125.37, 115.08, 110.71, 85.57, 71.03, 33.18, 30.55, 0.00. **MS (EI)** calcd. for $\text{C}_{22}\text{H}_{29}\text{IOSi}$ $[\text{M}]^+$: 464.10. Found: 464.25.

(2-(3-(4-Chloro-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ae)



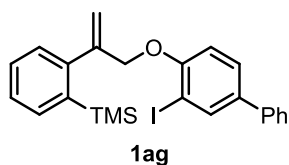
Following the **procedure A**, **1ae** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 40% yield (1.77 g, 4.0 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.77 (m, 1H), 7.59 (m, 1H), 7.40 – 7.28 (m, 2H), 7.27 – 7.22 (m, 2H), 6.70 (m, 1H), 5.83 (q, $J = 1.8$ Hz, 1H), 5.24 (d, $J = 1.8$ Hz, 1H), 4.64 (d, $J = 1.8$ Hz, 2H), 0.29 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 155.19, 144.86, 144.45, 137.88, 137.83, 134.29, 134.29, 128.33, 127.76, 126.12, 125.80, 115.43, 111.72, 85.84, 71.43, 0.00. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{ClIOSi}$ $[\text{M}]^+$: 442.00. Found: 441.95

(2-(3-(2-Iodo-4-(trifluoromethyl)phenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1af)



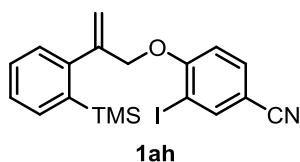
Following the **procedure A**, **1af** was obtained as a yellow liquid ($R_f = 0.3$, petroleum ether) in 46% yield (2.2 g, 4.6 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 8.05 (m, 1H), 7.58 (m, 2H), 7.35 (m, 2H), 7.25 – 7.16 (m, 1H), 6.83 (m, 1H), 5.85 (q, $J = 1.8$ Hz, 1H), 5.27 (d, $J = 1.8$ Hz, 1H), 4.72 (t, $J = 1.8$ Hz, 2H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 158.73, 144.66, 144.13, 137.85, 135.86 (q, $J = 3.7$ Hz), 134.35, 127.81, 127.78, 126.22, 126.09 (q, $J = 3.7$ Hz), 123.76 (q, $J = 30.4$ Hz), 122.42 (q, $J = 269.3$ Hz), 115.66, 110.54, 85.31, 71.30, -0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -61.62. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{20}\text{F}_3\text{IOSi}$ $[\text{M}]^+$: 476.03. Found: 476.35.

(2-(3-((3-Iodo-[1,1'-biphenyl]-4-yl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane
(1ag)



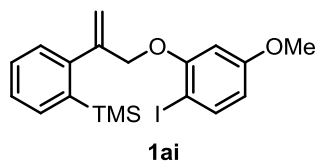
Following the **procedure B**, **1ag** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 42% yield (2.0 g, 4.2 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 8.06 (m, 1H), 7.65 – 7.59 (m, 1H), 7.53 (m, 3H), 7.43 (s, 2H), 7.40 – 7.27 (m, 4H), 6.87 (m, 1H), 5.91 (q, $J = 1.8$ Hz, 1H), 5.27 (q, $J = 1.8$ Hz, 1H), 4.73 (t, $J = 1.8$ Hz, 2H), 0.33 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 155.60, 144.96, 144.59, 138.34, 137.74, 137.15, 135.05, 134.19, 127.91, 127.72, 127.69, 127.12, 126.27, 126.01, 125.82, 115.23, 111.20, 86.09, 71.07, 0.00. **MS (EI)** calcd. for $\text{C}_{24}\text{H}_{25}\text{IOSi}$ $[\text{M}]^+$: 484.07. Found: 483.87.

3-Iodo-4-((2-(2-(trimethylsilyl)phenyl)allyl)oxy)benzonitrile (1ah)



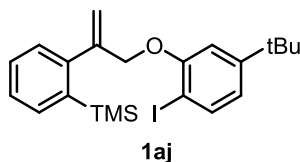
Following the **procedure A**, **1ah** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 52% yield (2.3 g, 5.2 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 8.08 (m, 1H), 7.61 (m, 2H), 7.35 (m, 2H), 7.24 (m, 1H), 6.82 (m, 1H), 5.82 (q, $J = 1.7$ Hz, 1H), 5.28 (q, $J = 1.7$ Hz, 1H), 4.73 (d, $J = 1.7$ Hz, 2H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 159.65, 144.41, 143.78, 142.07, 137.84, 134.39, 133.14, 127.84, 127.76, 126.29, 116.68, 115.94, 110.94, 105.33, 85.64, 71.43, 0.00. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{20}\text{INOSi}$ $[\text{M}]^+$: 433.04. Found: 433.03.

1-(2-(1-(4-Ethylphenyl)vinyl)phenyl)-1-methylsiletane (1ai)



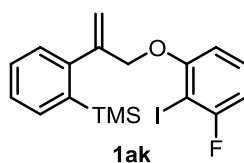
Following the **procedure A**, **1ai** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 42% yield (1.8 g, 4.2 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 (m, 1H), 7.62 – 7.56 (m, 1H), 7.34 (m, 2H), 7.27 (m, 1H), 6.40 (s, 1H), 6.34 (m, 1H), 5.87 (d, $J = 1.8$ Hz, 1H), 5.24 (d, $J = 1.8$ Hz, 1H), 4.64 (t, $J = 1.8$ Hz, 2H), 3.77 (s, 3H), 0.30 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.44, 156.99, 145.07, 144.60, 138.39, 137.86, 134.25, 127.82, 127.73, 126.05, 115.31, 106.70, 99.35, 74.41, 70.96, 54.68, 0.00. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{23}\text{IO}_2\text{Si}$ $[\text{M}]^+$: 438.05. Found: 438.10.

(2-(3-(5-(tert-Butyl)-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1aj)



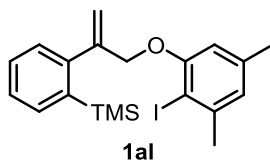
Following the **procedure A**, **1aj** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 56% yield (2.6 g, 5.6 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (m, 1H), 7.61 (m, 1H), 7.42 – 7.29 (m, 2H), 7.27 (m, 1H), 6.82 (m, 1H), 6.78 (m, 1H), 5.91 (d, $J = 1.9$ Hz, 1H), 5.24 (d, $J = 1.9$ Hz, 1H), 4.69 (t, $J = 1.9$ Hz, 2H), 1.29 (s, 9H), 0.32 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.94, 152.53, 145.20, 144.82, 137.93, 137.89, 134.23, 127.82, 127.73, 126.02, 119.24, 109.09, 115.06, 81.96, 70.86, 34.03, 30.39, 0.00. **MS (EI)** calcd. for $\text{C}_{22}\text{H}_{29}\text{IOSi}$ $[\text{M}]^+$: 464.10. Found: 464.19.

(2-(3-(3-Fluoro-2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ak)



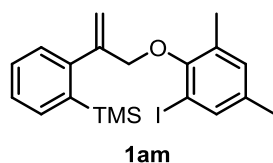
Following the **procedure A**, **1ak** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 46% yield (2.0 g, 4.6mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.60 (m, 2H), 7.34 (m, 2H), 7.19 (m, 1H), 6.73 (m, 1H), 6.59 (m, 1H), 5.59 (q, $J = 1.7$ Hz, 1H), 5.19 (q, $J = 1.7$ Hz, 1H), 4.63 (t, $J = 1.7$ Hz, 2H), 0.29 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 163.01 (d, $J = 247.1$ Hz), 157.17, 144.74, 144.19, 138.76 (d, $J = 9.9$ Hz), 137.81, 134.29, 127.77, 126.13, 115.56, 108.71 (d, $J = 21.8$ Hz), 100.03, 99.77, 78.46, 71.20, -0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -92.06. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{FIOSi}$ $[\text{M}]^+$: 426.03. Found: 426.25.

(2-(3-(2-Iodo-3,5-dimethylphenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1al)



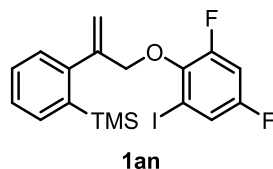
Following the **procedure A**, **1al** was obtained as a colorless liquid ($R_f = 0.3$, petroleum ether) in 55% yield (2.4 g, 5.5 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.60 (m, 1H), 7.39 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 6.74 (d, $J = 1.8$ Hz, 1H), 6.43 (d, $J = 1.8$ Hz, 1H), 5.94 (t, $J = 1.8$ Hz, 1H), 5.24 (q, $J = 1.8$ Hz, 1H), 4.65 (t, $J = 1.8$ Hz, 2H), 2.45 (s, 3H), 2.27 (s, 3H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.06, 145.23, 144.87, 142.15, 137.95, 137.83, 134.20, 127.75, 127.68, 125.96, 122.68, 115.01, 109.40, 88.58, 71.06, 27.68, 20.36, 0.00. **MS (EI)** calcd. for $\text{C}_{20}\text{H}_{25}\text{IOSi}$ $[\text{M}]^+$: 436.07. Found: 436.00.

(2-(3-(2-Iodo-4,6-dimethylphenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1am)



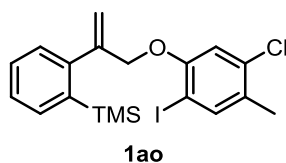
Following the **procedure A**, **1am** was obtained as a pale yellow liquid ($R_f = 0.6$, petroleum ether) in 49% yield (2.2 g, 4.9mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 – 7.56 (m, 1H), 7.49 – 7.42 (m, 1H), 7.37 – 7.26 (m, 2H), 7.27 – 7.21 (m, 1H), 6.99 – 6.91 (m, 1H), 5.84 (d, $J = 1.8$ Hz, 1H), 5.22 (q, $J = 1.8$ Hz, 1H), 4.49 (t, $J = 1.8$ Hz, 2H), 2.26 (s, 3H), 2.23 (s, 3H), 0.33 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.37, 145.41, 145.24, 137.36, 136.29, 134.55, 133.84, 131.17, 130.69, 127.49, 127.24, 125.50, 114.50, 90.57, 73.73, 19.06, 15.84, 0.00. **MS (EI)** calcd. for $\text{C}_{20}\text{H}_{25}\text{IOSi}$ $[\text{M}]^+$: 436.07 Found: 436.09.

(2-(3-(2,4-Difluoro-6-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1an)



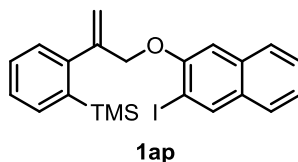
Following the **procedure A**, **1an** was obtained as a colorless oil ($R_f = 0.4$, petroleum ether) in 57% yield (2.5 g, 5.7 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60 – 7.55 (m, 1H), 7.34 – 7.27 (m, 3H), 7.23 (m, 1H), 6.88 (m, 1H), 5.84 (q, $J = 1.8$ Hz, 1H), 5.23 (q, $J = 1.8$ Hz, 1H), 4.68 (q, $J = 1.8$ Hz, 2H), 0.32 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.41 (dd, $J = 249.3, 11.7$ Hz), 153.16 (dd, $J = 254.3, 12.7$ Hz), 145.11, 144.90, 141.57 (dd, $J = 12.8, 4.2$ Hz), 137.65, 134.07, 127.65, 127.49, 125.80, 120.20 (dd, $J = 24.6, 3.8$ Hz), 115.11, 104.70 (dd, $J = 26.7, 23.4$ Hz), 90.26 (dd, $J = 10.2, 2.6$ Hz), 75.29, 0.00. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -115.36, -122.12. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{19}\text{F}_2\text{IOSi}$ $[\text{M}]^+$: 444.02. Found: 444.09.

**(2-(3-(5-Chloro-2-iodo-4-methylphenoxy)prop-1-en-2-yl)phenyl)trimethylsilane
(1ao)**



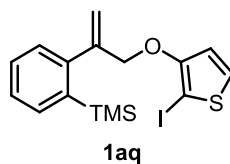
Following the **procedure A**, **1ao** was obtained as a yellow liquid ($R_f = 0.3$, petroleum ether) in 50% yield (2.3 g, 5.0 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.65 (m, 1H), 7.62 – 7.52 (m, 1H), 7.34 (m, 2H), 7.26 – 7.22 (m, 1H), 6.78 (s, 1H), 5.83 (d, $J = 1.8$ Hz, 1H), 5.24 (d, $J = 1.8$ Hz, 1H), 4.62 (t, $J = 1.8$ Hz, 2H), 2.27 (s, 3H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 154.94, 144.84, 144.43, 139.74, 137.80, 134.26, 133.97, 129.40, 127.74, 126.08, 115.31, 112.20, 107.85, 82.85, 71.33, 17.93, 0.00. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{22}\text{ClIOSi}$ $[\text{M}]^+$: 456.02. Found: 456.13

(2-(3-((3-Iodonaphthalen-2-yl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ap)



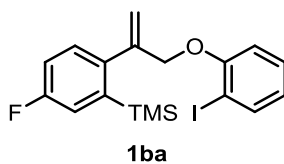
Following the **procedure A**, **1ap** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 38% yield (1.7 g, 3.8 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 8.38 (s, 1H), 7.73 – 7.63 (m, 3H), 7.49 – 7.43 (m, 1H), 7.43 – 7.33 (m, 4H), 7.08 (s, 1H), 6.01 (q, $J = 1.8$ Hz, 1H), 5.32 (q, $J = 1.8$ Hz, 1H), 4.82 (t, $J = 1.8$ Hz, 2H), 0.36 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 153.08, 145.08, 144.59, 138.40, 137.84, 134.24, 133.25, 129.53, 127.81, 127.73, 126.06, 126.03, 125.76, 125.71, 123.50, 115.21, 105.73, 87.59, 70.97, 0.00. **MS (EI)** calcd. for $\text{C}_{22}\text{H}_{23}\text{IOSiL}$ $[\text{M}]^+$: 458.06. Found: 458.03.

(2-(3-((2-Iodothiophen-3-yl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane (1aq)



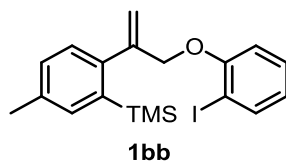
Following the **procedure A**, **1aq** was obtained as a colorless oil ($R_f = 0.5$, petroleum ether) in 39% yield (1.6 g, 3.9 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.65 – 7.56 (m, 1H), 7.43 (m, 1H), 7.39 – 7.28 (m, 2H), 7.24 (m, 1H), 6.68 (m, 1H), 5.74 (q, $J = 1.8$ Hz, 1H), 5.22 (q, $J = 1.8$ Hz, 1H), 4.71 (t, $J = 1.8$ Hz, 2H), 0.33 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 157.72, 145.13, 144.93, 137.66, 134.15, 129.05, 127.63, 127.61, 125.91, 115.77, 115.00, 73.71, 54.11, 0.00. **MS (EI)** calcd. for $\text{C}_{16}\text{H}_{19}\text{IOSSi}$ $[\text{M}]^+$: 414.00. Found: 414.15.

(5-Fluoro-2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ba)



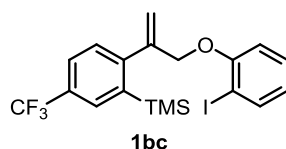
Following the **procedure A**, **1ba** was obtained as a blue liquid ($R_f = 0.3$, petroleum ether) in 24% yield (1.0 g, 2.4 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.80 (m, 1H), 7.33 – 7.27 (m, 1H), 7.23 (m, 2H), 7.03 (m, 1H), 6.79 (m, 1H), 6.73 (m, 1H), 5.87 (d, $J = 1.8$ Hz, 1H), 5.23 (q, $J = 1.8$ Hz, 1H), 4.63 (t, $J = 1.8$ Hz, 2H), 0.30 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 161.18 (d, $J = 248.5$ Hz), 156.37, 144.12, 141.26 (d, $J = 3.4$ Hz), 141.01 (d, $J = 3.3$ Hz), 138.98, 129.93 (d, $J = 7.5$ Hz), 128.80, 122.18, 120.64 (d, $J = 18.6$ Hz), 116.34, 114.68 (d, $J = 20.9$ Hz), 111.53, 85.89, 71.29, -0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -115.62. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{FIOSSi}$ $[\text{M}]^+$: 426.03. Found: 425.88.

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-5-methylphenyl)trimethylsilane (1bb)



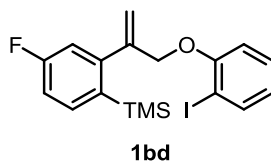
Following the **procedure A**, **1bb** was obtained as a pale yellow solid ($R_f = 0.4$, petroleum ether) in 48% yield (2.0 g, 4.8 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (m, 1H), 7.42 (s, 1H), 7.30 (m, 1H), 7.22 – 7.15 (m, 2H), 6.81 (m, 1H), 6.74 (m, 1H), 5.89 (t, $J = 1.7$ Hz, 1H), 5.24 (q, $J = 1.7$ Hz, 1H), 4.68 (m, 2H), 2.39 (s, 3H), 0.32 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.20, 144.55, 142.16, 138.68, 137.61, 135.40, 134.88, 128.54, 128.44, 127.76, 121.80, 115.11, 111.26, 85.66, 71.00, 20.44, 0.00. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{23}\text{IOSi}$ $[\text{M}]^+$: 422.06. Found: 422.22.

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-5-(trifluoromethyl)phenyl)trimethylsilane (1bc)



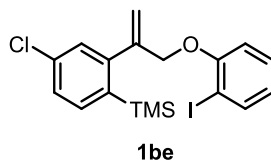
Following the **procedure A**, **1bc** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 33% yield (1.6 g, 3.3 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 – 7.78 (m, 2H), 7.59 (m, 1H), 7.40 (m, 1H), 7.29 (m, 1H), 6.79 (m, 1H), 6.77 – 6.71 (m, 1H), 5.92 (q, $J = 1.8$ Hz, 1H), 5.27 (q, $J = 1.8$ Hz, 1H), 4.79 – 4.50 (q, $J = 1.8$ Hz, 2H), 0.33 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.61, 160.52, 141.57, 137.61, 129.97 (q, $J = 31.8$ Hz), 129.22 (q, $J = 3.6$ Hz), 128.09 (q, $J = 3.5$ Hz), 126.63, 124.05, 122.55 (q, $J = 271$ Hz), 122.29, 110.68, 87.45, 78.00, 58.43, 29.24, -0.77. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -62.49. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{20}\text{F}_3\text{IOSi}$ $[\text{M}]^+$: 476.03. Found: 476.22.

(4-Fluoro-2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1bd)



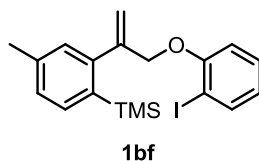
Following the **procedure A**, **1bd** was obtained as a colorless oil ($R_f = 0.5$, petroleum ether) in 42% yield (1.8 g, 4.2 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (m, 1H), 7.61 – 7.51 (m, 1H), 7.38 – 7.27 (m, 1H), 7.08 – 6.98 (m, 2H), 6.81 (m, 1H), 6.74 (m, 1H), 5.89 (q, $J = 1.7$ Hz, 1H), 5.28 (q, $J = 1.7$ Hz, 1H), 4.66 (t, $J = 1.7$ Hz, 2H), 0.30 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.57 (d, $J = 249.3$ Hz), 156.06, 147.38 (d, $J = 7.0$ Hz), 143.67, 138.73, 136.10, 133.28, 133.25, 128.57, 121.97, 115.02, (d, $J = 19.9$ Hz), 113.00 (d, $J = 19.0$ Hz), 111.21, 85.61, 70.75, 0.02. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -112.96. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{FIOSi}$ $[\text{M}]^+$: 426.03. Found: 426.34.

(4-Chloro-2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)trimethylsilane (1be)



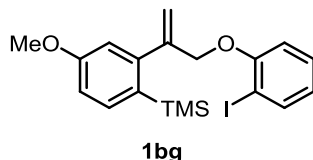
Following the **procedure A**, **1be** was obtained as a colorless liquid ($R_f = 0.3$, petroleum ether) in 43% yield (1.9 g, 4.3 mmol). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (m, 1H), 7.51 (m, 1H), 7.35 – 7.26 (m, 3H), 6.81 (m, 1H), 6.75 (m, 1H), 5.96 – 5.74 (m, 1H), 5.39 – 5.14 (m, 1H), 4.70 – 4.60 (m, 2H), 0.30 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.15, 146.79, 143.72, 138.84, 136.20, 135.61, 133.94, 128.65, 128.05, 126.19, 122.07, 116.49, 111.32, 85.71, 70.91, 0.00. **MS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{ClIOSi}$ $[\text{M}]^+$: 442.00. Found: 441.97.

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-4-methylphenyl)trimethylsilane (1bf)



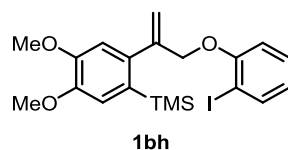
Following the **procedure A**, **1bf** was obtained as a yellow oil (R_f = 0.5, petroleum ether) in 40% yield (1.7 g, 4.0 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.81 (m, 1H), 7.49 (m, 1H), 7.32 – 7.26 (m, 1H), 7.15 (m, 1H), 7.12 (m, 1H), 6.81 (m, 1H), 6.74 (m, 1H), 5.86 (q, J = 1.8 Hz, 1H), 5.24 (q, J = 1.8 Hz, 1H), 4.67 (t, J = 1.8 Hz, 2H), 2.37 (s, 3H), 0.29 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.23, 145.13, 144.71, 138.70, 137.59, 134.30, 134.12, 128.66, 128.54, 126.86, 121.81, 115.19, 111.26, 85.64, 71.03, 20.35, 0.00. **MS (EI)** calcd. For $\text{C}_{19}\text{H}_{23}\text{IOSi}$ $[\text{M}]^+$: 422.06. Found: 422.32

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-4-methoxyphenyl)trimethylsilane (1bg)



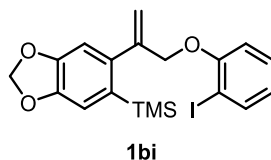
Following the **procedure A**, **1bg** was obtained as a yellow oil (R_f = 0.3, petroleum ether) in 52% yield (2.3 g, 5.2 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.81 (m, 1H), 7.51 (d, J = 8.3 Hz, 1H), 7.28 (m, 1H), 6.88 (dd, J = 8.3, 2.4 Hz, 1H), 6.84 – 6.76 (m, 2H), 6.73 (d, J = 2.4 Hz, 1H), 5.87 (q, J = 1.8 Hz, 1H), 5.26 (q, J = 1.8 Hz, 1H), 4.67 (t, J = 1.8 Hz, 2H), 3.83 (s, 3H), 0.27 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 158.89, 156.13, 146.71, 144.42, 138.63, 135.61, 128.61, 128.48, 121.79, 115.25, 113.65, 111.55, 111.21, 85.58, 70.87, 54.24, -0.00. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{23}\text{IO}_2\text{Si}$ $[\text{M}]^+$: 438.05. Found: 437.95.

(2-(3-(2-iodophenoxy)prop-1-en-2-yl)-4,5-dimethoxyphenyl)trimethylsilane (1bh)



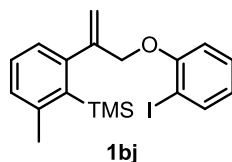
Following the **procedure A**, **1bh** was obtained as a yellow oil (R_f = 0.4, petroleum ether) in 45% yield (2.1 g, 4.5 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.80 (m, 1H), 7.29 (m, 1H), 7.04 (s, 1H), 6.84 – 6.79 (m, 2H), 6.77 – 6.67 (m, 1H), 5.87 (t, J = 1.7 Hz, 1H), 5.27 (d, J = 1.7 Hz, 1H), 4.66 (t, J = 1.7 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 0.29 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.10, 148.13, 146.64, 144.32, 138.61, 138.52, 128.73, 128.48, 121.77, 116.40, 115.87, 111.35, 111.17, 85.56, 71.10, 54.97, 54.93, -0.00. **MS (EI)** calcd. for $\text{C}_{20}\text{H}_{25}\text{IO}_3\text{Si}$ $[\text{M}]^+$: 468.06. Found: 468.00.

(6-(3-(2-Iodophenoxy)prop-1-en-2-yl)benzo[d][1,3]dioxol-5-yl)trimethylsilane (1bi)



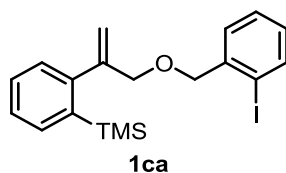
Following the **procedure A**, **1bi** was obtained as a colorless oil (R_f = 0.4, petroleum ether) in 54% yield (2.3 g, 5.5 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.81 (m, 1H), 7.33 – 7.26 (m, 1H), 7.04 (s, 1H), 6.85 – 6.77 (m, 2H), 6.74 (m, 1H), 5.96 (s, 2H), 5.85 (t, J = 1.8 Hz, 1H), 5.24 (t, J = 1.8 Hz, 1H), 4.63 (d, J = 1.8 Hz, 2H), 0.28 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.00, 146.84, 145.68, 143.98, 139.33, 138.56, 130.49, 128.42, 121.73, 115.78, 113.01, 111.07, 108.71, 99.92, 85.49, 70.88, 0.00. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{21}\text{IO}_3\text{Si}$ $[\text{M}]^+$: 452.03. Found: 451.88.

(2-(3-(2-Iodophenoxy)prop-1-en-2-yl)-6-methylphenyl)trimethylsilane (1bj)



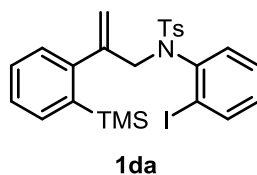
Following the **procedure A**, **1bj** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 37% yield (1.6 g, 3.7 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.80 (m, 1H), 7.39 (s, 1H), 7.32 – 7.27 (m, 1H), 7.17 (s, 2H), 6.79 (m, 1H), 6.73 (m, 1H), 5.86 (d, $J = 1.8$ Hz, 1H), 5.22 (d, $J = 1.8$ Hz, 1H), 4.65 (t, $J = 1.8$ Hz, 2H), 2.37 (s, 3H), 0.29 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.22, 144.55, 142.18, 138.69, 137.63, 135.41, 134.89, 128.55, 128.45, 127.76, 121.81, 115.11, 111.28, 85.67, 71.02, 20.43, -0.02. **MS (EI)** calcd. for $\text{C}_{19}\text{H}_{23}\text{IOSi}$ $[\text{M}]^+$: 422.06. Found: 422.00.

(2-(3-((2-Iodobenzyl)oxy)prop-1-en-2-yl)phenyl)trimethylsilane (1ca)



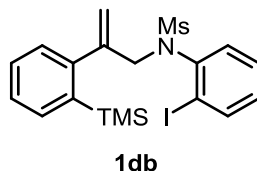
Following the **procedure B**, **1ca** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 44% yield (1.9 g, 4.4 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.60 (m, 1H), 7.34 (m, 1H), 7.28 (m, 1H), 7.19 – 7.00 (m, 3H), 6.95 (m, 1H), 6.77 (m, 1H), 5.36 (p, $J = 1.7$ Hz, 1H), 4.90 (p, $J = 1.7$ Hz, 1H), 4.40 (d, $J = 1.7$ Hz, 2H), 4.03 (q, $J = 1.7$ Hz, 2H), 0.06 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 146.73, 145.85, 139.58, 138.16, 137.39, 134.02, 128.18, 127.65, 127.53, 127.49, 127.29, 125.62, 113.86, 96.55, 75.57, 73.12, 0.00. **MS (EI)** calcd. For $\text{C}_{19}\text{H}_{23}\text{IOSi}$ $[\text{M}]^+$: 422.06. Found: 422.26.

***N*-(2-iodophenyl)-4-methyl-*N*-(2-(2(trimethylsilyl) phenyl) allyl) benzene sulfonamide (1da)**



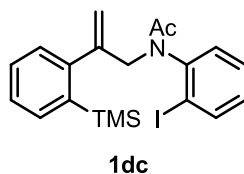
Following the **procedure C**, **1da** was obtained as a yellow solid ($R_f = 0.4$, petroleum ether/ethyl acetate = 20:1) in 46% yield (2.4 g, 4.6 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.84 (m, 1H), 7.58 – 7.53 (m, 2H), 7.50 – 7.45 (m, 1H), 7.28 (m, 2H), 7.23 (m, 4H), 7.08 – 6.88 (m, 2H), 5.66 (q, $J = 1.5$ Hz, 1H), 5.12 (q, $J = 1.5$ Hz, 1H), 4.68 (dt, $J = 17.5, 1.5$ Hz, 1H), 4.35 (dt, $J = 17.5, 1.5$ Hz, 1H), 2.42 (s, 3H), 0.09 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 146.22, 145.33, 142.99, 140.88, 140.14, 137.40, 136.06, 134.29, 132.22, 129.03, 128.81, 128.04, 127.91, 127.44, 125.93, 116.71, 99.94, 57.13, 20.93, - 0.00. **MS (EI)** calcd. For $\text{C}_{25}\text{H}_{28}\text{INO}_2\text{SSi}$ $[\text{M}]^+$: 561.07. Found: 560.95.

***N*-(2-iodophenyl)-*N*-(2-(2-(trimethylsilyl)phenyl)allyl)methanesulfonamide (1db)**



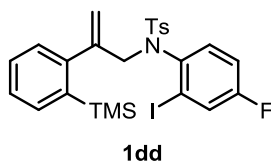
Following the **procedure C**, **1db** was obtained as a yellow solid ($R_f = 0.4$, petroleum ether/ethyl acetate = 20:1r) in 46% yield (1.6 g, 4.6 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.93 (m, 1H), 7.50 (m, 1H), 7.46 (m, 1H), 7.36 (m, 1H), 7.33 – 7.19 (m, 2H), 7.13 – 7.01 (m, 2H), 5.66 (q, $J = 1.7$ Hz, 1H), 5.17 (q, $J = 1.3$ Hz, 1H), 4.83 (dt, $J = 17.7, 1.7$ Hz, 1H), 4.30 (dt, $J = 17.7, 1.3$ Hz, 1H), 3.02 (s, 3H), 0.10 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 146.11, 145.79, 140.53, 140.19, 137.56, 134.47, 133.24, 129.43, 128.43, 128.25, 128.00, 126.12, 116.46, 98.95, 57.28, 40.83, 0.00. **MS (EI)** calcd. For $\text{C}_{19}\text{H}_{24}\text{INO}_2\text{SSi}$ $[\text{M}]^+$: 485.03. Found: 485.01.

***N*-(2-iodophenyl)-*N*-(2-(2-(trimethylsilyl)phenyl)allyl)acetamide (**1dc**)**



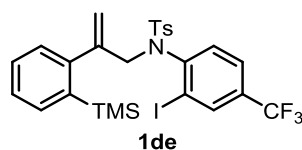
Following the **procedure C**, **1dc** was obtained as a yellow solid ($R_f = 0.4$, petroleum ether/ethyl acetate = 20:1 in 37% yield (1.7 g, 3.7 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.94 (m, 1H), 7.52 (m, 1H), 7.34 (m, 1H), 7.31 – 7.23 (m, 2H), 7.14 (m, 1H), 7.10 – 7.03 (m, 2H), 5.41 (q, $J = 1.7$ Hz, 1H), 5.24 (dt, $J = 16.9, 1.7$ Hz, 1H), 5.13 (q, $J = 1.4$ Hz, 1H), 3.58 (dt, $J = 16.9, 1.4$ Hz, 1H), 1.85 (s, 3H), 0.17 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 169.62, 146.49, 145.04, 144.92, 139.64, 137.38, 134.18, 129.64, 129.09, 128.57, 127.87, 127.76, 125.77, 114.34, 99.32, 54.78, 22.06, -0.00. **MS (EI)** calcd. For $\text{C}_{20}\text{H}_{24}\text{INO}_2\text{Si}$ $[\text{M}]^+$: 449.07. Found: 449.02.

***N*-(4-fluoro-2-iodophenyl)-4-methyl-*N*-(2-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (**1dd**)**



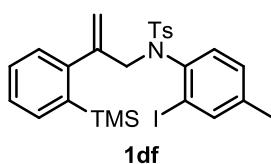
Following the **procedure C**, **1dd** was obtained as a yellow solid ($R_f = 0.4$, petroleum ether/ethyl acetate = 20:1) in 41% yield (2.4 g, 4.1 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.55 (m, 3H), 7.52 – 7.45 (m, 1H), 7.26 – 7.21 (m, 4H), 7.14 (m, 1H), 6.99 (m, 2H), 5.62 (q, $J = 1.5$ Hz, 1H), 5.13 (d, $J = 1.5$ Hz, 1H), 4.68 (dt, $J = 17.3, 1.5$ Hz, 1H), 4.32 (dt, $J = 17.3, 1.5$ Hz, 1H), 2.42 (s, 3H), 0.11 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 160.44 (d, $J = 254.1$ Hz), 146.09, 145.32, 143.14, 137.40, 137.25 (d, $J = 3.5$ Hz), 135.93, 134.36, 133.00 (d, $J = 9.0$ Hz), 128.88, 128.00 (d, $J = 13.7$ Hz), 127.44, 126.93, 126.68, 125.99, 116.82, 114.90 (d, $J = 22.0$ Hz), 99.86 (d, $J = 8.5$ Hz), 57.29, 20.92, 0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -111.42. **MS (EI)** calcd. For $\text{C}_{25}\text{H}_{27}\text{FINO}_2\text{SSi}$ $[\text{M}]^+$: 579.06. Found: 578.92.

***N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methyl-*N*-(2-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (1de)**



Following the **procedure C**, **1de** was obtained as a yellow solid ($R_f = 0.4$, petroleum ether/ethyl acetate = 20:1) in 43% yield (1.8 g, 4.3 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 8.07 (m, 1H), 7.57 (s, 1H), 7.55 (s, 1H), 7.54 – 7.50 (m, 1H), 7.48 (m, 1H), 7.25 (m, 5H), 6.92 (m, 1H), 5.61 (m, 1H), 5.17 – 5.10 (m, 1H), 4.67 (d, $J = 17.2$ Hz, 1H), 4.40 (d, $J = 17.2$ Hz, 1H), 2.43 (s, 3H), 0.09 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 145.81, 145.11, 144.50, 143.46, 137.42, 137.06 (q, $J = 3.7$ Hz), 135.78, 134.45, 132.31, 130.73 (q, $J = 33.2$ Hz), 129.06, 128.08, 127.98, 127.42, 126.12, 124.85 (q, $J = 3.7$ Hz), 121.89 (q, $J = 273.1$ Hz), 117.12, 99.90, 56.99, 20.96, 0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -61.58. **MS (EI)** calcd. For $\text{C}_{26}\text{H}_{27}\text{F}_3\text{INO}_2\text{SSi}$ $[\text{M}]^+$: 629.05. Found: 629.00.

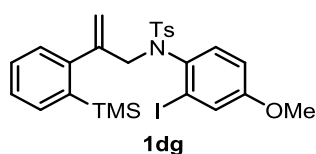
***N*-(2-iodo-4-methylphenyl)-4-methyl-*N*-(2-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (1df)**



Following the **procedure C**, **1df** was obtained as a yellow solid ($R_f = 0.4$, petroleum ether/ethyl acetate = 20:1) in 39% yield (2.2 g, 3.9 mmol). **^1H NMR (400 MHz, CDCl_3)** δ 7.67 (m, 1H), 7.56 (m, 2H), 7.51 – 7.45 (m, 1H), 7.26 – 7.22 (m, 3H), 7.22 – 7.20 (m, 1H), 7.09 (m, 2H), 6.99 – 6.94 (m, 1H), 5.65 (q, $J = 1.4$ Hz, 1H), 5.11 (d, $J = 1.4$ Hz, 1H), 4.65 (dt, $J = 17.3$ Hz, 1.4 Hz, 1H), 4.33 (dt, $J = 17.3$, 1.4 Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 0.11 (s, 9H). **^{13}C NMR (101 MHz, CDCl_3)** δ 146.32, 145.29, 142.84, 140.50, 139.35, 138.14, 137.43, 136.14, 134.26, 131.63, 128.75, 128.69,

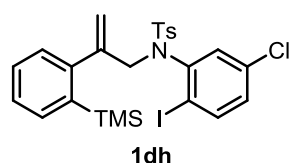
128.01, 127.86, 127.44, 125.87, 116.64, 99.64, 57.11, 20.91, 19.82, 0.00. **MS (EI)** calcd. For C₂₆H₃₀INO₂SSi [M]⁺: 575.08. Found: 575.02

***N*-(2-iodo-4-methoxyphenyl)-4-methyl-*N*-(2-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (1dg)**



Following the **procedure C**, **1dg** was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 34% yield (2.0 g, 3.4 mmol). **¹H NMR (400 MHz, CDCl₃)** δ 7.56 (m, 1H), 7.54 (m, 1H), 7.51 – 7.44 (m, 1H), 7.34 (m, 1H), 7.23 (m, 4H), 7.10 (m, 1H), 7.01 – 6.94 (m, 1H), 6.81 (m, 1H), 5.64 (d, J = 1.4 Hz, 1H), 5.12 (q, J = 1.4 Hz, 1H), 4.66 (dt, J = 17.4, 1.4 Hz, 1H), 4.31 (dt, J = 17.4, 1.4 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H), 0.12 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 158.49, 146.35, 145.39, 142.81, 137.42, 136.13, 134.26, 133.51, 132.39, 128.75, 128.02, 127.86, 127.44, 125.86, 124.80, 116.62, 113.54, 100.23, 57.31, 54.98, 20.90, 0.00. **MS (EI)** calcd. For C₂₆H₃₀INO₃SSi [M]⁺: 591.08. Found: 591.03.

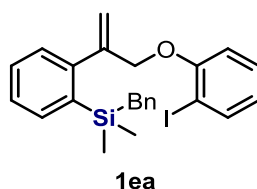
***N*-(5-chloro-2-iodophenyl)-4-methyl-*N*-(2-(2-(trimethylsilyl)phenyl)allyl)benzenesulfonamide (1dh)**



Following the **procedure C**, **1dh** was obtained as a yellow solid (R_f = 0.4, petroleum ether/ethyl acetate = 20:1) in 42% yield (2.5 g, 4.2 mmol). **¹H NMR (400 MHz, CDCl₃)** δ 7.73 (m, 1H), 7.57 (m, 2H), 7.48 (m, 1H), 7.25 (m, 4H), 7.03 (m, 1H), 6.99 (m, 1H), 6.94 – 6.90 (m, 1H), 5.60 (s, 1H), 5.14 (s, 1H), 4.64 (d, J = 17.1 Hz, 1H), 4.33 (d, J = 17.1 Hz, 1H), 2.43 (s, 3H), 0.10 (s, 9H). **¹³C NMR (101 MHz, CDCl₃)** δ 145.81, 145.13, 143.30, 142.20, 140.50, 137.33, 135.76, 134.36, 133.63, 132.30,

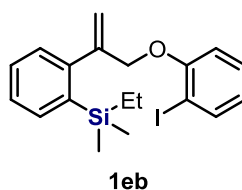
129.25, 128.91, 128.09, 127.93, 127.43, 126.11, 117.10, 97.36, 57.10, 20.94, 0.00. **MS (EI)** calcd. For $C_{25}H_{27}ClINO_2SSi$ $[M]^+$: 595.03. Found: 594.99.

Benzyl(2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)dimethylsilane (1ea)



Following the **procedure A**, **1ea** was obtained as a yellow oil (R_f = 0.3, petroleum ether) in 49% yield (2.4 g, 4.9 mmol). **1H NMR (400 MHz, $CDCl_3$)** δ 7.79 (m, 1H), 7.55 (m, 1H), 7.42 – 7.22 (m, 4H), 7.16 (m, 2H), 7.09 – 7.02 (m, 1H), 6.97 – 6.88 (m, 2H), 6.73 (m, 2H), 5.89 (q, J = 1.8 Hz, 1H), 5.20 (q, J = 1.8 Hz, 1H), 4.60 (t, J = 1.8 Hz, 2H), 2.36 (s, 2H), 0.25 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.38, 147.46, 147.01, 141.20, 140.94, 138.30, 136.85, 130.79, 130.21, 130.16, 129.80, 129.50, 128.23, 125.51, 124.15, 117.62, 113.61, 87.94, 73.24, 28.54, 0.00. **MS (EI)** calcd. for $C_{24}H_{25}IOSi$ $[M]^+$: 484.07. Found: 484.06.

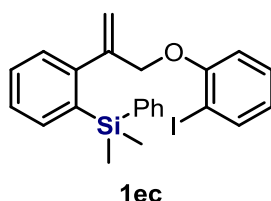
Ethyl(2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)dimethylsilane (1eb)



Following the **procedure A**, **1eb** was obtained as a yellow solid (R_f = 0.3, petroleum ether) in 37% yield (1.6 g, 3.7 mmol). **1H NMR (400 MHz, $CDCl_3$)** δ 7.88 (m, 1H), 7.74 – 7.60 (m, 1H), 7.42 (m, 2H), 7.39 – 7.31 (m, 2H), 6.88 (m, 1H), 6.80 (m, 1H), 5.98 (d, J = 1.8 Hz, 1H), 5.33 (d, J = 1.8 Hz, 1H), 4.76 (t, J = 1.8 Hz, 2H), 1.11 – 0.95 (m, 3H), 0.95 – 0.76 (m, 2H), 0.39 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.56, 147.59, 147.09, 141.07, 139.09, 136.91, 130.93, 130.23, 130.04, 128.31, 124.23,

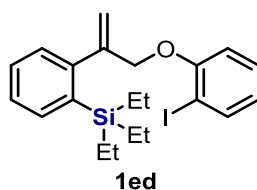
117.48, 113.67, 88.11, 73.34, 10.19, 9.25, 0.00. **MS (EI)** calcd. for C₁₉H₂₃IOSi [M]⁺: 422.06. Found: 422.04.

1-(4,5-Dimethoxy-2-(1-(4-methoxyphenyl)vinyl)phenyl)-1-methylsiletane (1ec)



Following the **procedure A**, **1ec** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 46% yield (2.2 g, 4.6 mmol). **¹H NMR (400 MHz, CDCl₃)** δ 7.76 (m, 1H), 7.66 – 7.59 (m, 1H), 7.49 – 7.43 (m, 2H), 7.41 – 7.29 (m, 2H), 7.28 – 7.11 (m, 5H), 6.68 (m, 1H), 6.37 (m, 1H), 5.75 (d, $J = 1.8$ Hz, 1H), 5.09 (q, $J = 1.8$ Hz, 1H), 4.10 (t, $J = 1.8$ Hz, 2H), 0.59 (s, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 157.45, 147.08, 145.92, 139.91, 139.70, 137.33, 136.34, 134.78, 133.59, 129.80, 129.59, 129.40, 128.27, 127.39, 123.01, 117.28, 112.62, 86.96, 71.77, 0.00. **MS (EI)** calcd. for C₂₃H₂₃IOSi [M]⁺: 470.06. Found: 470.04.

Triethyl(2-(3-(2-iodophenoxy)prop-1-en-2-yl)phenyl)silane (1ed)



Following the **procedure A**, **1ed** was obtained as a colorless oil ($R_f = 0.3$, petroleum ether) in 40% yield (1.8 g, 4.0 mmol). **¹H NMR (400 MHz, CDCl₃)** δ 7.73 (m, 1H), 7.47 (m, 1H), 7.33 – 7.12 (m, 4H), 6.73 (m, 1H), 6.66 (m, 1H), 5.77 (q, $J = 1.8$ Hz, 1H), 5.12 (q, $J = 1.8$ Hz, 1H), 4.59 (t, $J = 1.8$ Hz, 2H), 0.91 – 0.80 (m, 9H), 0.81 – 0.71 (m, 6H). **¹³C NMR (101 MHz, CDCl₃)** δ 157.13, 146.49, 145.62, 139.59, 136.12, 135.34, 129.45, 128.92, 128.42, 126.64, 122.75, 115.69, 112.24, 86.62, 71.82, 7.66, 4.42. **MS (EI)** calcd. for C₂₁H₂₇IOSi [M]⁺: 450.09. Found: 450.04.

Pd-Catalyzed Spirocyclization Reaction of 1

Condition Screening

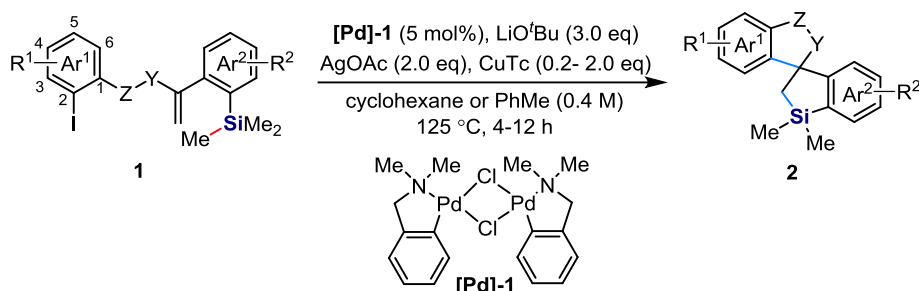
Supplementary Table S1. Optimization of reaction conditions ^a

Reaction scheme: 1aa $\xrightarrow[\text{Base, Additive, Solvent, 125 } ^\circ\text{C, 12 h}]{[\text{Pd}]\text{-cat. (5 \%), Ligand (10 \%)}$ 2aa + 3aa

Entry	[Pd] Source	Ligand	Base	Additive (X eq.)	Solvent	2aa[%] ^[b]	3aa[%] ^[b]
1	[Pd(allyl)Cl] ₂	P ^t Bu ₃	LiO ^t Bu	p-NO ₂ PhCHO (1)	PhMe	10	28
2	[Pd(allyl)Cl] ₂	P ^t Bu ₃	LiO ^t Bu	KBr (2)	PhMe	34	20
3	[Pd(allyl)Cl] ₂	P ^t Bu ₃	LiO ^t Bu	AgBr (2)	PhMe	45	Trace
4	[Pd(allyl)Cl] ₂	P ^t Bu ₃	LiO ^t Bu	NaBr (2)	PhMe	20	25
5	Pd(P ^t Bu) ₃	-	LiO ^t Bu	AgBr (2)	PhMe	Trace	40
6	Pd(dppf)Cl ₂	-	LiO ^t Bu	AgBr (2)	PhMe	47	34
7	[Pd]-1	-	LiO ^t Bu	AgBr (2)	PhMe	38	Trace
8	[Pd]-1	-	LiO ^t Bu	Ag ₃ PO ₄ (2)	PhMe	57	12
9	[Pd]-1	-	LiO ^t Bu	Ag ₂ CO ₃ (2)	PhMe	20	Trace
10	[Pd]-1	-	LiO ^t Bu	AgOAc (2)	PhMe	67	28
11	[Pd]-1	-	LiO ^t Bu	TcCu (1)	PhMe	40	N.D.
12	[Pd]-1	-	LiO ^t Bu	-	PhMe	20	10
13	[Pd]-1	-	LiO ^t Bu	AgOAc(2)+TcCu (1)	PhMe	72	Trace
14	[Pd]-1	-	LiO ^t Bu	AgOAc(2)+TcCu (1)	Dioxane	40	Trace
15	[Pd]-1	-	LiO ^t Bu	AgOAc(2)+TcCu (1)	PhCl	65	Trace
16	[Pd]-1	-	LiO ^t Bu	AgOAc(2)+TcCu (1)	DCE	68	Trace
17	[Pd]-1	-	LiO ^t Bu	AgOAc(2)+TcCu (1)	Cy	72 ^c	Trace
18	[Pd]-1	-	LiO ^t Bu	AgOAc(2)+TcCu (0.5)	Cy	84 ^c	Trace
19	[Pd]-1	-	LiO^tBu	AgOAc(2)+TcCu (0.2)	Cy	90^c	Trace
20	[Pd]-1	-	LiO ^t Bu	AgOAc(2)+TcCu (0.5)	PhMe	85 ^c	10
21	[Pd]-1	-	NaO ^t Bu	AgOAc(2)+TcCu (0.2)	Cy	N.R.	-
22	[Pd]-1	-	KO ^t Bu	AgOAc(2)+TcCu (0.2)	Cy	N.R.	-

^a Reactions were carried out by using **[Pd]-1** catalyst (5 mol%), ligand (10 mol%), base (0.6 mmol, 3.0 equiv.), **1aa** (0.2 mmol) in solvent (0.4 M) for 12 h at 125 °C under an N₂ atmosphere. ^b Yield was determined by NMR analysis of the mixture. ^c Isolated Yield. N.D.: No Detected. N.R.: No Reaction.

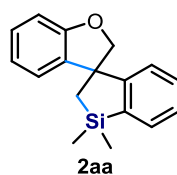
General procedure



In a nitrogen-filled glovebox, an oven-dried 15 mL screw capped sealed tube was charged with a magnetic stir bar, **1** (0.20 mmol), **[Pd]-1** (5 mmol%), AgOAc (2 equiv), LiO^tBu (3 equiv), additive and cyclohexane or PhMe (0.5 mL). The tube was sealed, then removed from the glovebox, and the formed mixture was stirred at 125 °C under N₂ for 12 h. After being cooled to room temperature, Saturated aqueous NH₄Cl (5 mL) was added and the mixture was extracted with EA (3 × 5 mL). The combined organic phases were washed with water and brine, dried (MgSO₄) and evaporated. The crude product was purified by preparative RP-HPLC on reversed phase column (C18(ODS)) (eluent: CH₃CN) to afford the corresponding product.

Characterization of Products 2

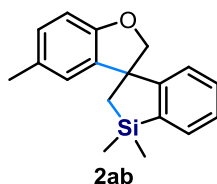
1',1'-Dimethyl-1',2'-dihydro-2*H*-spiro[benzofuran-3,3'-benzo[*b*]silole] (**2aa**)



Following the general procedure, the reaction was carried out with **1aa** (81.6 mg, 0.2 mmol), **[Pd]-1** (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg,

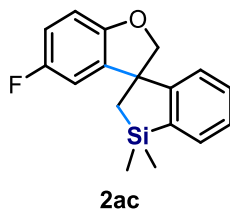
0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (47.9 mg, 0.180 mmol, 90% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.56 (m, 1H), 7.38 – 7.27 (m, 2H), 7.17 (m, 1H), 7.08 – 7.04 (m, 1H), 6.98 – 6.75 (m, 3H), 4.43 (m, 1H), 4.40 (m, 1H), 1.53 (d, J = 15.2 Hz, 1H), 1.35 (d, J = 15.2 Hz, 1H), 0.43 (s, 3H), 0.36 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 160.40, 156.56, 140.40, 138.25, 132.24, 130.98, 128.68, 127.48, 126.18, 123.99, 121.88, 110.26, 87.70, 58.25, 29.33, -0.00, -0.80. **HRMS (EI)** calcd. for $\text{C}_{17}\text{H}_{18}\text{OSi}$ $[\text{M}]^+$: 266.1127. Found: 266.1129.

1',1',5-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ab)



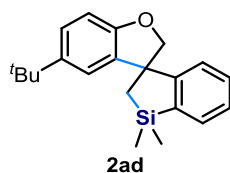
Following the general procedure, the reaction was carried out with **1ab** (84.4mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (47 mg, 0.166 mmol, 83% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.56 (m, 1H), 7.38 – 7.27 (m, 2H), 7.07 (m, 1H), 6.97 (m, 1H), 6.79 (m, 1H), 6.71 – 6.66 (m, 1H), 4.42 (d, J = 8.4 Hz, 1H), 4.38 (d, J = 8.4 Hz, 1H), 2.25 (s, 3H), 1.52 (d, J = 15.1 Hz, 1H), 1.34 (d, J = 15.1 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 158.32, 156.57, 140.42, 138.17, 132.20, 131.19, 130.92, 129.09, 127.43, 126.22, 124.44, 109.75, 87.74, 58.31, 29.16, 21.49, -0.81, -0.88. **HRMS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{OSi}$ $[\text{M}]^+$: 280.1283. Found: 280.1277.

5-Fluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ac)



Following the general procedure, the reaction was carried out with **1ac** (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (46 mg, 0.160 mmol, 80% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.64 – 7.53 (m, 1H), 7.38 – 7.27 (m, 2H), 7.08 (m, 1H), 6.89 – 6.77 (m, 2H), 6.63 (m, 1H), 4.45 (d, J = 8.5 Hz, 1H), 4.41 (d, J = 8.5 Hz, 1H), 1.55 (d, J = 15.2 Hz, 1H), 1.30 (d, J = 15.2 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 158.70 (d, J = 237.6 Hz), 156.30, 155.69, 140.45, 139.67 (d, J = 7.5 Hz), 132.35, 131.07, 127.72, 126.08, 114.90 (d, J = 24.3 Hz), 111.01 (d, J = 24.5 Hz), 110.47 (d, J = 8.6 Hz), 88.17, 58.60, 29.09, -0.00, -0.81. **¹⁹F NMR (376 MHz, CDCl₃)** δ -123.14. **HRMS (EI)** calcd. for C₁₇H₁₇FOSi [M]⁺: 284.1033. Found: 284.1028.

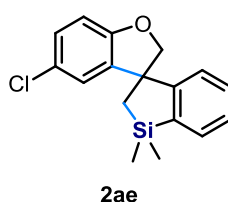
5-(tert-Butyl)-1,1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]silole] (2ad)



Following the general procedure, the reaction was carried out with **1ad** (92.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (61.2 mg, 0.190 mmol, 95% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.62 – 7.54 (m, 1H), 7.37 – 7.26 (m, 2H), 7.20 (m, 1H), 7.07 (m, 1H), 6.97 (m, 1H), 6.82 (m,

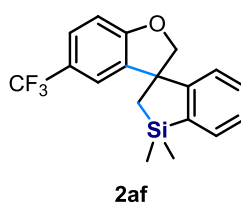
1H), 4.41 (d, $J = 8.3$ Hz, 1H), 4.36 (d, $J = 8.3$ Hz, 1H), 1.53 (d, $J = 15.1$ Hz, 1H), 1.35 (d, $J = 15.1$ Hz, 1H), 1.25 (s, 9H), 0.45 (s, 3H), 0.37 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 158.23, 156.64, 145.00, 140.44, 137.49, 132.23, 130.93, 127.38, 126.13, 125.47, 120.80, 109.28, 87.71, 58.51, 35.08, 32.35, 29.23, 0.00, -0.86. **HRMS (EI)** calcd. for $\text{C}_{21}\text{H}_{26}\text{OSi}$ $[\text{M}]^+$: 322.1753. Found: 322.1750.

5-Chloro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ae)



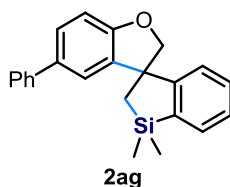
Following the general procedure, the reaction was carried out with **1ae** (88.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (44 mg, 0.146 mmol, 73% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.60 – 7.54 (m, 1H), 7.34 (m, 1H), 7.30 (m, 1H), 7.11 (m, 1H), 7.05 (m, 1H), 6.87 (m, 1H), 6.81 (m, 1H), 4.45 (d, $J = 8.5$ Hz, 1H), 4.41 (d, $J = 8.5$ Hz, 1H), 1.54 (d, $J = 15.1$ Hz, 1H), 1.30 (d, $J = 15.1$ Hz, 1H), 0.44 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 159.10, 155.65, 140.49, 140.23, 132.38, 131.14, 128.62, 127.78, 126.53, 126.14, 124.23, 111.31, 88.21, 58.43, 29.36, 0.00, -0.82. **HRMS (EI)** calcd. for $\text{C}_{17}\text{H}_{17}\text{ClOSi}$ $[\text{M}]^+$: 300.0737. Found: 300.0729.

1',1'-Dimethyl-5-(trifluoromethyl)-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2af)



Following the general procedure, the reaction was carried out with **1af** (95.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (32 mg, 0.096 mmol, 48% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.2. **¹H NMR (400 MHz, CDCl₃)** δ 7.61 – 7.54 (m, 1H), 7.48 – 7.42 (m, 1H), 7.39 – 7.28 (m, 2H), 7.18 (m, 1H), 7.01 (m, 1H), 6.95 (m, 1H), 4.51 (d, *J* = 8.5 Hz, 1H), 4.46 (d, *J* = 8.5 Hz, 1H), 1.56 (d, *J* = 15.1 Hz, 1H), 1.32 (d, *J* = 15.1 Hz, 1H), 0.45 (s, 3H), 0.37 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 163.05, 155.50, 140.54, 139.07, 132.47, 131.23, 127.87, 126.71 (q, *J* = 3.8 Hz), 125.17 (q, *J* = 272.7 Hz), 126.04, 124.36 (q, *J* = 32.3 Hz), 121.49 (q, *J* = 3.5 Hz), 110.38, 88.41, 57.95, 29.76, 0.00, -0.91. **¹⁹F NMR (376 MHz, CDCl₃)** δ -60.92. **HRMS (EI)** calcd. for C₁₈H₁₇F₃OSi [M]⁺: 334.1001. Found: 334.1028.

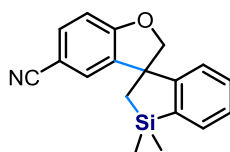
1',1'-Dimethyl-5-phenyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ag)



Following the general procedure, the reaction was carried out with **1ag** (95.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (50.6 mg, 0.148 mmol, 74% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.63 – 7.56 (m, 1H), 7.52 – 7.45 (m, 2H), 7.43 (m, 1H), 7.39 – 7.23 (m, 5H), 7.17 (m, 1H), 7.15 – 7.10 (m, 1H), 6.97 (m, 1H), 4.49 (d, *J* = 8.5 Hz, 1H), 4.45 (d, *J* = 8.5 Hz, 1H), 1.58 (d, *J* = 15.2 Hz, 1H), 1.40 (d, *J* = 15.2 Hz, 1H), 0.46 (s, 3H), 0.38 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.55, 155.67, 141.23, 139.94, 138.32, 134.83, 131.69,

130.43, 128.64, 127.13, 126.96, 126.75, 126.53, 125.64, 122.18, 109.80, 87.45, 57.74, 28.91, -0.57, -1.40. **HRMS (EI)** calcd. for $C_{23}H_{22}OSi$ $[M]^+$: 342.1440. Found: 342.1470.

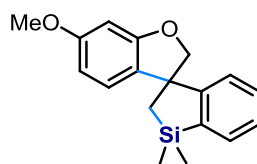
6-Methoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ah)



2ah

Following the general procedure, the reaction was carried out with **1ah** (86.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35 mg, 0.120 mmol, 60% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.2. **1H NMR (400 MHz, $CDCl_3$)** δ 7.58 (m, 1H), 7.49 (m, 1H), 7.38 – 7.28 (m, 2H), 7.20 (m, 1H), 6.98 (m, 1H), 6.94 (m, 1H), 4.54 (d, J = 8.8 Hz, 1H), 4.49 (d, J = 8.8 Hz, 1H), 1.55 (d, J = 15.1 Hz, 1H), 1.29 (d, J = 15.1 Hz, 1H), 0.46 (s, 3H), 0.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.45, 152.55, 138.00, 137.60, 131.59, 130.07, 128.82, 125.89, 125.56, 123.41, 117.62, 108.83, 102.63, 86.14, 55.29, 27.43, -2.51, -3.34. **HRMS (EI)** calcd. for $C_{18}H_{17}NOSi$ $[M]^+$: 291.1079. Found: 291.1059.

6-Methoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ai)

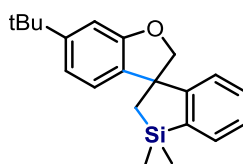


2ai

Following the general procedure, the reaction was carried out with **1ai** (87.6mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg,

0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (40 mg, 0.136 mmol, 68% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.57 (m, 1H), 7.38– 7.26 (m, 2H), 7.08 (m, 1H), 6.83 (m, 1H), 6.51 (s, 1H), 6.46 (m, 1H), 4.47 (d, J = 8.5 Hz, 1H), 4.43 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H), 1.53 (d, J = 15.1, 1H), 1.34 (d, J = 15.1, 1H), 0.44 (s, 3H), 0.37 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 161.70, 160.98, 156.86, 140.31, 132.25, 130.98, 130.46, 127.44, 126.10, 124.12, 107.54, 96.72, 88.50, 57.73, 56.17, 29.43, -0.00, -0.80. **HRMS (EI)** calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Si}$ $[\text{M}]^+$: 296.1233. Found: 296.1225.

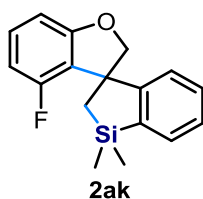
6-(tert-Butyl)-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2aj)



2aj

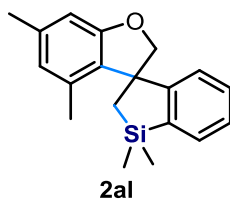
Following the general procedure, the reaction was carried out with **1aj** (92.8mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (51.5 mg, 0.160 mmol, 80% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.57 (m, 1H), 7.40 – 7.26 (m, 2H), 7.10 (m, 1H), 7.01 – 6.90 (m, 2H), 6.86 (m, 1H), 4.45 (d, J = 8.4 Hz, 1H), 4.41 (d, J = 8.4 Hz, 1H), 1.53 (d, J = 15.0, 1H), 1.38 (d, J = 15.0, 1H), 1.34 (s, 9H), 0.44 (s, 3H), 0.37 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 161.30, 157.58, 153.30, 141.15, 135.88, 132.99, 131.70, 128.19, 126.99, 123.93, 119.72, 108.27, 88.70, 58.85, 36.26, 32.95, 30.03, 0.81, -0.00. **HRMS (EI)** calcd. for $\text{C}_{21}\text{H}_{26}\text{OSi}$ $[\text{M}]^+$: 322.1753. Found: 322.1740.

4-Fluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ak)



Following the general procedure, the reaction was carried out with **1ak** (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.2 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid; (40.5 mg, 0.142 mmol, 71% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.56 (m, 1H), 7.32 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 6.83 (m, 1H), 6.68 – 6.50 (m, 2H), 4.48 (d, J = 8.5 Hz, 1H), 4.44 (d, J = 8.5 Hz, 1H), 1.52 (d, J = 15.1 Hz, 1H), 1.30 (d, J = 15.1 Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 163.73 (d, J = 243.3 Hz), 161.52 (d, J = 12.9 Hz), 156.28, 140.41, 134.99 (d, J = 2.7 Hz), 132.36, 131.08, 127.64, 126.06, 124.35 (d, J = 10.2 Hz), 108.51 (d, J = 22.8 Hz), 98.67 (d, J = 26.6 Hz), 88.82, 57.70, 29.57, -0.00, -0.80. **¹⁹F NMR (376 MHz, CDCl₃)** δ -114.37. **HRMS (EI)** calcd. for C₁₇H₁₇FOSi [M]⁺: 284.1033. Found: 284.1030.

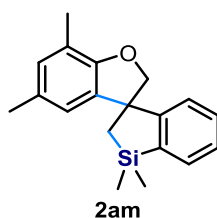
1',1',4,6-Tetramethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2al)



Following the general procedure, the reaction was carried out with **1al** (87.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 4 h. The title compound was obtained as a white solid (43 mg, 0.146 mmol, 73% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.58

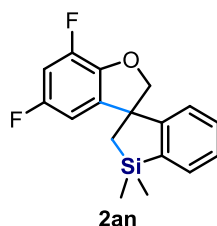
– 7.53 (m, 1H), 7.37 – 7.28 (m, 2H), 7.12 (m, 1H), 6.57 (s, 1H), 6.49 (s, 1H), 4.36 (d, $J = 8.4$ Hz, 1H), 4.26 (d, $J = 8.4$ Hz, 1H), 2.31 (s, 3H), 1.74 (s, 3H), 1.51 (d, $J = 15.2$ Hz, 1H), 1.27 (d, $J = 15.2$ Hz, 1H), 0.39 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 160.71, 155.65, 140.18, 138.79, 133.99, 132.01, 131.70, 130.65, 126.98, 125.93, 124.52, 108.33, 87.96, 58.11, 26.70, 21.74, 18.26, 0.00, -1.23. **HRMS (EI)** calcd. For $\text{C}_{19}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$: 294.1440. Found: 294.1443.

**1',1',5,7-Tetramethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole]
(2am)**



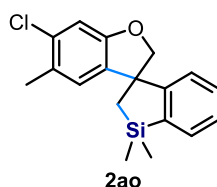
Following the general procedure, the reaction was carried out with **1am** (87.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (40.5 mg, 0.138 mmol, 69% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.61 – 7.49 (m, 1H), 7.40 – 7.22 (m, 2H), 7.08 (m, 1H), 6.81 (s, 1H), 6.56 (s, 1H), 4.42 (d, $J = 8.4$ Hz, 1H), 4.36 (d, $J = 8.4$ Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 1.51 (d, $J = 15.1$ Hz, 1H), 1.31 (d, $J = 15.1$ Hz, 1H), 0.42 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 157.47, 141.24, 138.29, 134.38, 132.94, 131.86, 131.66, 131.31, 128.16, 127.06, 122.47, 120.59, 88.30, 59.43, 29.96, 22.22, 16.56, 0.81, -0.00. **HRMS (EI)** calcd. For $\text{C}_{19}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$: 294.1440. Found: 294.1429.

5,7-Difluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]-silole] (2an)



Following the general procedure, the reaction was carried out with **1an** (87.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35.0 mg, 0.116 mmol, 58% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.2. **¹H NMR (400 MHz, CDCl₃)** δ 7.61 – 7.55 (m, 1H), 7.33 (m, 2H), 7.07 (m, 1H), 6.72 (m, 1H), 6.44 (m, 1H), 4.53 (d, *J* = 8.6 Hz, 1H), 4.48 (d, *J* = 8.6 Hz, 1H), 1.57 (d, *J* = 15.1 Hz, 1H), 1.29 (d, *J* = 15.1 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 158.60 (dd, *J* = 241.1, 8.8 Hz), 148.00 (dd, *J* = 249.2, 12.6 Hz), 144.06 (dd, *J* = 10.7, 2.7 Hz), 143.05 (dd, *J* = 8.7, 3.6 Hz), 141.33, 133.28, 133.26, 132.02, 128.78, 126.86, 107.22 (dd, *J* = 24.3, 3.8 Hz), 104.79 (dd, *J* = 28.1, 20.9 Hz), 89.78, 59.95, 29.83, 0.79, -0.00. **¹⁹F NMR (376 MHz, CDCl₃)** δ -119.48, -135.12. **HRMS (EI)** calcd. For C₁₇H₁₆F₂OSi [M]⁺: 302.0938. Found: 302.0935.

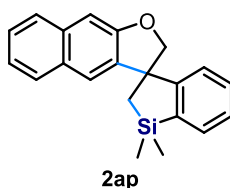
5,7-Difluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]-silole] (2ao)



Following the general procedure, the reaction was carried out with **1ao** (91.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6

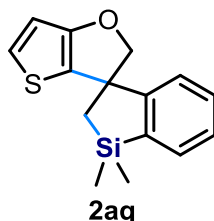
mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (41 mg, 0.130 mmol, 65% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.61 – 7.51 (m, 1H), 7.38 – 7.26 (m, 2H), 7.05 (m, 1H), 6.90 (s, 1H), 6.76 (s, 1H), 4.43 (d, J = 8.5 Hz, 1H), 4.39 (d, J = 8.5 Hz, 1H), 2.25 (s, 3H), 1.52 (d, J = 15.2 Hz, 1H), 1.30 (d, J = 15.2 Hz, 1H), 0.44 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 159.24, 156.05, 140.47, 137.20, 133.66, 132.34, 131.07, 129.06, 127.65, 126.14, 125.65, 111.01, 88.26, 58.04, 29.36, 20.33, 0.01, -0.80. **HRMS (EI)** calcd. For $\text{C}_{18}\text{H}_{19}\text{ClOSi}$ $[\text{M}]^+$: 314.0894. Found: 314.0893.

**1,1-Dimethyl-1,2-dihydro-2'*H*-spiro[benzo[*b*]silole-3,3'-naphtho[2,3-*b*]furan]
(2ap)**



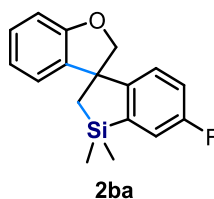
Following the general procedure, the reaction was carried out with **1ap** (91.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (50 mg, 0.158 mmol, 79% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.74 (d, J = 8.2 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.43 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 (m, 1H), 7.21 (s, 1H), 7.13 – 7.05 (m, 1H), 4.51 (d, J = 8.4 Hz, 1H), 4.47 (d, J = 8.4 Hz, 1H), 1.64 (d, J = 15.1 Hz, 1H), 1.42 (d, J = 15.1 Hz, 1H), 0.48 (s, 3H), 0.39 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 160.03, 156.74, 142.20, 141.37, 135.75, 133.05, 131.75, 131.46, 129.19, 128.37, 128.18, 127.13, 127.02, 124.60, 123.45, 105.33, 88.51, 58.67, 30.56, 0.76, 0.00. **HRMS (EI)** calcd. For $\text{C}_{21}\text{H}_{20}\text{OSi}$ $[\text{M}]^+$: 316.1283. Found: 316.1275.

1,1-dimethyl-1,2-dihydro-2'*H*-spiro[benzo[*b*]silole-3,3'-thieno[3,2-*b*]furan] (2aq)



Following the general procedure, the reaction was carried out with **1aq** (82.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (38 mg, 0.140 mmol, 70% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.57 – 7.50 (m, 1H), 7.37 (m, 1H), 7.31 – 7.28 (m, 1H), 7.27 (m, 1H), 7.10 (d, *J* = 5.1 Hz, 1H), 6.63 (d, *J* = 5.1 Hz, 1H), 4.76 (s, 2H), 1.55 (d, *J* = 15.1 Hz, 1H), 1.42 (d, *J* = 15.1 Hz, 1H), 0.41 (s, 3H), 0.34 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 162.54, 156.71, 139.88, 132.52, 131.39, 128.85, 128.08, 127.97, 125.95, 112.59, 94.18, 58.52, 29.03, -0.00, -0.69. **HRMS (EI)** calcd. For C₁₅H₁₆OSSi [M]⁺: 272.0691. Found: 272.0686.

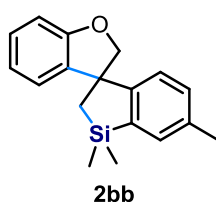
6'-Fluoro-1',1'-dimethyl-1',2'-dihydro-2*H*-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ba)



Following the general procedure, the reaction was carried out with **1ba** (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (49.5 mg, 0.174 mmol, 87% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.22 – 7.13 (m, 2H), 6.99 (m, 2H), 6.93 – 6.86 (m, 3H), 4.43 (d, *J* = 8.5 Hz, 1H), 4.35 (d, *J*

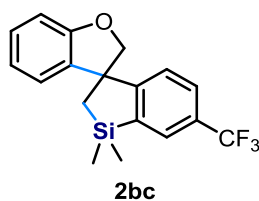
= 8.5 Hz, 1H), 1.55 (d, J = 15.2 Hz, 1H), 1.37 (d, J = 15.2 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 163.78 (d, J = 247.8 Hz), 161.26, 152.90, 144.12 (d, J = 4.9 Hz), 138.96, 129.80, 128.80 (d, J = 7.5 Hz), 124.80, 122.94, 119.10 (d, J = 22.5 Hz), 118.84 (d, J = 18.9 Hz), 111.33, 88.51, 58.60, 30.59, 0.77, 0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -116.92. **HRMS (EI)** calcd. For $\text{C}_{17}\text{H}_{17}\text{FOSi}$ $[\text{M}]^+$: 284.1033. Found: 284.1028.

1',1',6'-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2bb)



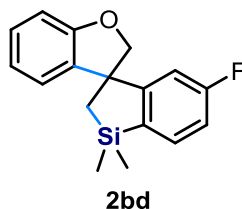
Following the general procedure, the reaction was carried out with **1bb** (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.04 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (51.5 mg, 0.184 mmol, 92% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.39 – 7.34 (m, 1H), 7.16 (m, 2H), 6.99 – 6.80 (m, 4H), 4.43 (d, J = 8.4 Hz, 1H), 4.38 (d, J = 8.4 Hz, 1H), 2.36 (s, 3H), 1.52 (d, J = 15.1 Hz, 1H), 1.33 (d, J = 15.1 Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 160.32, 153.67, 140.49, 138.34, 136.95, 132.66, 131.97, 128.57, 125.96, 123.91, 121.83, 110.19, 87.71, 57.82, 29.50, 21.67, -0.00, -0.81. **HRMS (EI)** calcd. For $\text{C}_{18}\text{H}_{20}\text{OSi}$ $[\text{M}]^+$: 280.1283. Found: 280.1278.

1',1',6'-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2bc)



Following the general procedure, the reaction was carried out with **1bc** (95.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (48 mg, 0.144 mmol, 72% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.91 – 7.72 (m, 1H), 7.54 (m, 1H), 7.20 (m, 1H), 7.14 (m, 1H), 6.97 – 6.86 (m, 3H), 4.45 (d, *J* = 8.6 Hz, 1H), 4.38 (d, *J* = 8.6 Hz, 1H), 1.57 (d, *J* = 15.3 Hz, 1H), 1.41 (d, *J* = 15.3 Hz, 1H), 0.48 (s, 3H), 0.39 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 160.61, 160.52, 141.57, 137.61, 129.97 (q, *J* = 31.7 Hz), 129.27, 129.22 (q, *J* = 3.5 Hz), 128.09 (q, *J* = 3.4 Hz), 126.63, 125.27 (q, *J* = 273.7 Hz), 124.05, 122.29, 110.68, 87.45, 58.43, 29.24, -0.00, -0.77. **¹⁹F NMR (376 MHz, CDCl₃)** δ -62.17. **HRMS (EI)** calcd. For C₁₈H₁₇F₃OSi [M]⁺: 334.1001. Found: 334.0084.

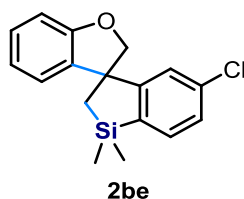
5'-Fluoro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2bd)



Following the general procedure, the reaction was carried out with **1bd** (85.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35 mg, 0.122 mmol, 61% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.50 (m, 1H), 7.22 – 7.15 (m, 1H), 7.02 – 6.88 (m, 4H), 6.72 (m, 1H), 4.44 (d, *J* = 8.5 Hz, 1H), 4.38 (d, *J* = 8.5 Hz, 1H), 1.54 (d, *J* = 15.2 Hz, 1H), 1.39 (d, *J* = 15.2 Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 164.96 (d, *J* = 248.6 Hz), 159.72, 159.02, 136.85, 134.94 (d, *J* = 3.0 Hz), 133.26 (d, *J* = 8.5 Hz), 128.38, 123.32, 121.42, 114.60 (d, *J* = 21.1 Hz), 112.40 (d, *J* = 20.6 Hz), 109.83, 86.72, 57.53, 28.87, -0.55, -

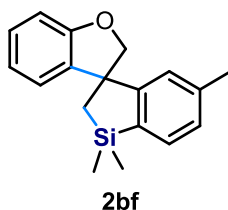
1.32. ^{19}F NMR (376 MHz, CDCl_3) δ -110.72. HRMS (EI) calcd. For $\text{C}_{17}\text{H}_{17}\text{FOSi}$ $[\text{M}]^+$: 284.1033. Found: 284.1025.

5'-Chloro-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2be)



Following the general procedure, the reaction was carried out with **1be** (88.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (52 mg, 0.174 mmol, 87% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. ^1H NMR (400 MHz, CDCl_3) δ 7.47 (m, 1H), 7.26 – 7.23 (m, 1H), 7.20 (m, 1H), 7.02 (m, 1H), 6.91 (m, 3H), 4.43 (d, J = 8.6 Hz, 1H), 4.38 (d, J = 8.6 Hz, 1H), 1.54 (d, J = 15.2 Hz, 1H), 1.37 (d, J = 15.2 Hz, 1H), 0.44 (s, 3H), 0.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.41, 158.77, 138.69, 137.46, 137.40, 133.51, 129.08, 128.02, 126.35, 124.00, 122.15, 110.54, 87.42, 58.26, 29.46, -0.00, -0.77. HRMS (EI) calcd. For $\text{C}_{17}\text{H}_{17}\text{FOSi}$ $[\text{M}]^+$: 300.0737. Found: 300.0733.

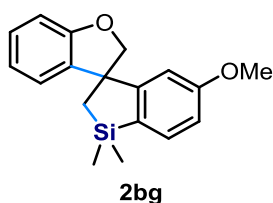
1',1',5'-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2bf)



Following the general procedure, the reaction was carried out with **1bf** (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title

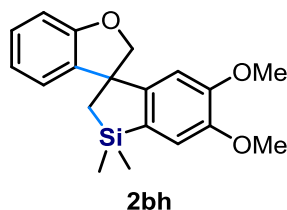
compound was obtained as a white solid (34 mg, 0.122 mmol, 61% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.46 (m, 1H), 7.22 – 7.15 (m, 1H), 7.11 (m, 1H), 6.98 – 6.84 (m, 4H), 4.43 (d, J = 8.5 Hz, 1H), 4.40 (d, J = 8.5 Hz, 1H), 2.27 (s, 3H), 1.52 (d, J = 15.1 Hz, 1H), 1.33 (d, J = 15.1 Hz, 1H), 0.42 (s, 3H), 0.34 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 159.77, 156.28, 140.49, 137.69, 136.36, 131.54, 128.08, 128.00, 126.11, 123.44, 121.26, 109.62, 87.14, 57.52, 29.01, 21.62, -0.50, -1.29. **HRMS (EI)** calcd. For $\text{C}_{18}\text{H}_{20}\text{OSi}$ $[\text{M}]^+$: 280.1283. Found: 280.1277.

5'-Methoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2bg)



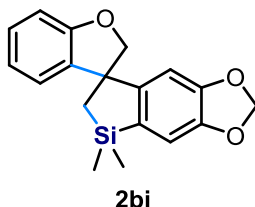
Following the general procedure, the reaction was carried out with **1bg** (87.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35.5 mg, 0.120 mmol, 60% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.47 (m, 1H), 7.21 – 7.13 (m, 1H), 7.01 – 6.76 (m, 4H), 6.57 (m, 1H), 4.44 (d, J = 8.5 Hz, 1H), 4.40 (d, J = 8.5 Hz, 1H), 3.71 (s, 3H), 1.53 (d, J = 15.1 Hz, 1H), 1.34 (d, J = 15.1 Hz, 1H), 0.41 (s, 3H), 0.34 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 162.20, 160.13, 158.57, 137.72, 133.11, 131.20, 128.45, 123.78, 121.66, 114.03, 110.91, 110.01, 87.31, 58.04, 55.51, 29.54, 0.00, -0.81. **HRMS (EI)** calcd. For $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Si}$ $[\text{M}]^+$: 296.1233. Found: 296.1220.

5',6'-Dimethoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2bh)



Following the general procedure, the reaction was carried out with **1bh** (93.6 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (28 mg, 0.086mmol, 43% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.17 (m, 1H), 6.98 – 6.92 (m, 2H), 6.89 (m, 2H), 6.55 (s, 1H), 4.41 (d, J = 8.5 Hz, 1H), 4.39 (d, J = 8.5 Hz, 1H), 3.92 (s, 3H), 3.71 (s, 3H), 1.53 (d, J = 15.1 Hz, 1H), 1.30 (d, J = 15.1 Hz, 1H), 0.42 (s, 3H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 160.75, 152.40, 149.82, 149.72, 138.75, 131.92, 129.12, 124.39, 122.41, 113.58, 110.73, 109.26, 87.97, 58.57, 57.02, 56.87, 30.33, 0.74, 0.00. **HRMS (EI)** calcd. For C₁₉H₂₂O₃Si [M]⁺: 326.1338. Found: 326.1326.

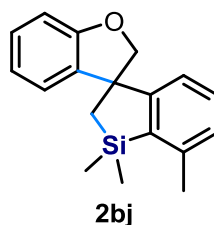
5',6'-Dimethoxy-1',1'-dimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[b]-silole] (2bi)



Following the general procedure, the reaction was carried out with **1bi** (90.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 4 h. The title compound was obtained as a white solid (34.1 mg, 0.11 mmol, 55% yield). R_f

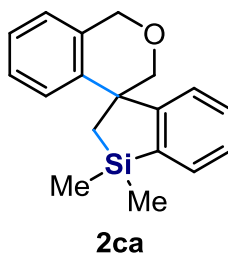
(petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.21 – 7.10 (m, 1H), 6.99 – 6.79 (m, 4H), 6.51 (s, 1H), 5.92 (s, 2H), 4.40 (d, *J* = 8.5 Hz, 1H), 4.36 (d, *J* = 8.5 Hz, 1H), 1.52 (d, *J* = 15.1 Hz, 1H), 1.34 (d, *J* = 15.1 Hz, 1H), 0.40 (s, 3H), 0.32 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 160.09, 150.81, 150.56, 147.77, 137.90, 132.60, 128.55, 123.72, 121.73, 110.15, 110.04, 106.71, 101.50, 87.29, 57.80, 29.57, 0.00, -0.77. **HRMS (EI)** calcd. For C₁₈H₁₈O₃Si [M]⁺: 310.1025. Found: 310.1018.

1',1',7'-Trimethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2bj)



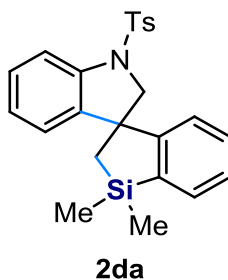
Following the general procedure, the reaction was carried out with **1bj** (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 4 h. The title compound was obtained as a white solid (37.5 mg, 0.134 mmol, 67% yield). *R_f* (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.38 (s, 1H), 7.16 (m, 2H), 7.03 – 6.84 (m, 4H), 4.42 (m, 1H), 4.38 (m, 1H), 2.36 (s, 3H), 1.53 (d, *J* = 15.1 Hz, 1H), 1.33 (d, *J* = 15.1 Hz, 1H), 0.43 (s, 3H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 160.32, 153.67, 140.49, 138.34, 136.96, 132.66, 131.97, 128.57, 125.96, 123.91, 121.83, 110.19, 87.72, 57.82, 29.50, 21.67, -0.00, -0.81. **HRMS (EI)** calcd. For C₁₈H₂₀O₂Si [M]⁺: 280.1283. Found: 280.1277.

1,1-Dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,4'-isochromane] (2ca)



Following the general procedure, the reaction was carried out with **1ca** (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (38.2 mg, 0.2 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (25.2 mg, 0.090 mmol, 45% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.63 – 7.55 (m, 1H), 7.33 – 7.21 (m, 2H), 7.21 – 7.08 (m, 2H), 7.04 – 6.99 (m, 1H), 6.96 – 6.89 (m, 1H), 6.85 (m, 1H), 4.94 (m, 2H), 3.72 (m, 2H), 1.84 (d, J = 15.6 Hz, 1H), 1.16 (d, J = 15.6 Hz, 1H), 0.41 (s, 3H), 0.38 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 157.04, 145.42, 142.16, 134.56, 132.62, 130.50, 129.01, 127.89, 127.72, 127.53, 126.62, 124.48, 78.70, 69.70, 52.33, 29.16, 0.75, 0.00. **HRMS (EI)** calcd. For C₁₈H₂₀OSi [M]⁺: 280.1283. Found: 280.1281.

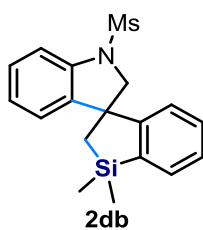
1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline] (2da)



Following the general procedure, the reaction was carried out with **1da** (112.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (38.2 mg, 0.2 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (25.2 mg, 0.090 mmol, 47% yield). R_f

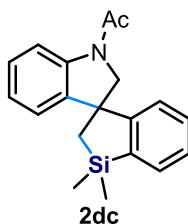
(petroleum ether/ethyl acetate = 10:1) = 0.5. **¹H NMR (400 MHz, CDCl₃)** δ 7.73 (m, 3H), 7.58 – 7.46 (m, 1H), 7.25 – 7.20 (m, 4H), 7.14 (m, 1H), 6.98 (m, 1H), 6.79 (m, 1H), 6.53 (m, 1H), 3.93 (d, *J* = 10.2 Hz, 1H), 3.73 (d, *J* = 10.2 Hz, 1H), 2.40 (s, 3H), 1.27 (d, *J* = 15.2 Hz, 1H), 1.10 (d, *J* = 15.2 Hz, 1H), 0.37 (s, 3H), 0.37 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 157.37, 145.64, 143.20, 142.96, 141.48, 135.48, 133.18, 131.77, 131.21, 129.45, 129.03, 128.47, 126.96, 125.74, 125.39, 115.71, 68.22, 57.10, 31.33, 23.10, 0.94, 0.00. **HRMS (EI)** calcd. For C₂₄H₂₅NO₂Si [M]⁺: 419.1375. Found: 419.1369.

1,1-Dimethyl-1'-(methylsulfonyl)-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline] (2db)



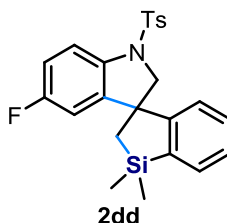
Following the general procedure, the reaction was carried out with **1db** (89.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.7 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (34.3 mg, 0.100 mmol, 50% yield). *R_f* (petroleum ether/ethyl acetate = 10:1) = 0.5. **¹H NMR (400 MHz, CDCl₃)** δ 7.58 (m, 1H), 7.49 (m, 1H), 7.31 (m, 2H), 7.28 – 7.22 (m, 1H), 7.05 (m, 1H), 7.00 – 6.89 (m, 2H), 3.95 (d, *J* = 9.9 Hz, 1H), 3.82 (d, *J* = 9.9 Hz, 1H), 2.94 (s, 3H), 1.58 (d, *J* = 15.1 Hz, 1H), 1.27 (d, *J* = 15.1 Hz, 1H), 0.43 (s, 3H), 0.39 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 156.01, 142.07, 141.92, 140.69, 132.51, 130.99, 128.81, 127.83, 125.98, 124.91, 124.71, 113.70, 67.84, 56.21, 35.13, 30.03, -0.00, -0.86. **HRMS (EI)** calcd. For C₁₈H₂₁NO₂SSi [M]⁺: 343.1062. Found: 343.1055.

1-(1,1-Dimethyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indolin]-1'-yl)ethan-1-one
(2dc)



Following the general procedure, the reaction was carried out with **1dc** (89.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (38.2 mg, 0.2 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (31.3 mg, 0.102 mmol, 51% yield). *R_f* (petroleum ether/ethyl acetate = 10:1) = 0.5. **¹H NMR (400 MHz, CDCl₃)** δ 8.27 (m, 1H), 7.64 – 7.50 (m, 1H), 7.36 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 7.04 (m, 1H), 6.92 (m, 2H), 4.01 (d, *J* = 10.1 Hz, 1H), 3.99 (d, *J* = 10.1 Hz, 1H), 2.18 (s, 3H), 1.48 (d, *J* = 15.2 Hz, 1H), 1.38 (d, *J* = 15.2 Hz, 1H), 0.44 (s, 3H), 0.40 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 170.03, 157.88, 143.73, 142.96, 140.95, 133.22, 131.99, 129.28, 128.52, 126.85, 125.88, 124.63, 118.26, 68.37, 57.14, 31.49, 25.68, 1.00, 0.00. **HRMS (EI)** calcd. For C₁₉H₂₁NOSi [M]⁺: 307.1392. Found: 307.1383.

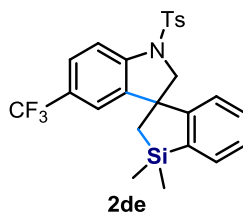
5'-Fluoro-1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline]
(2dd)



Following the general procedure, the reaction was carried out with **1dd** (115.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (50.7 mg, 0.116 mmol, 58% yield).

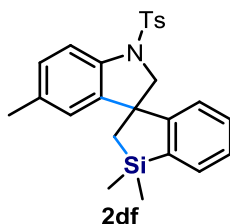
R_f (petroleum ether/ethyl acetate = 10:1) = 0.4. **^1H NMR (400 MHz, CDCl_3)** δ 7.68 (m, 3H), 7.56 – 7.49 (m, 1H), 7.25 (m, 3H), 7.15 (m, 1H), 6.92 (m, 1H), 6.57 – 6.43 (m, 2H), 3.92 (d, J = 10.4 Hz, 1H), 3.73 (d, J = 10.4 Hz, 1H), 2.42 (s, 3H), 1.22 (d, J = 15.1 Hz, 1H), 1.02 (d, J = 15.1 Hz, 1H), 0.36 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 160.78 (d, J = 242.6 Hz), 155.71, 144.93, 144.44 (d, J = 7.5 Hz), 140.60, 138.12, 134.25, 132.38, 130.99, 130.36, 128.15, 127.80, 125.94, 115.98 (d, J = 8.6 Hz), 115.19 (d, J = 23.6 Hz), 111.62 (d, J = 24.0 Hz), 67.61, 56.27, 30.40, 22.21, 0.00, -0.95. **^{19}F NMR (376 MHz, CDCl_3)** δ -118.63. **HRMS (EI)** calcd. For $\text{C}_{24}\text{H}_{24}\text{FNO}_2\text{SSi}$ $[\text{M}]^+$: 437.1281. Found: 437.1273.

5'-Fluoro-1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline] (2de)



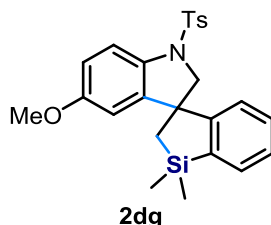
Following the general procedure, the reaction was carried out with **1de** (125.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (14.7 mg, 0.1 mmol) in PhMe (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (39.0 mg, 0.080 mmol, 40% yield). R_f (petroleum ether/ethyl acetate = 10:1) = 0.4. **^1H NMR (400 MHz, CDCl_3)** δ 7.80 (m, 1H), 7.73 (m, 2H), 7.53 (m, 2H), 7.33 – 7.24 (m, 3H), 7.18 (m, 1H), 7.05 (m, 1H), 6.53 (m, 1H), 3.98 (d, J = 10.2, 1H), 3.78 (d, J = 10.2 Hz, 1H), 2.42 (s, 3H), 1.33 (d, J = 15.1, 1H), 1.10 (d, J = 15.1 Hz, 1H), 0.40 (s, 3H), 0.38 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.42, 146.30, 146.00, 143.89, 141.67, 135.35, 133.54, 132.13, 131.54, 129.01, 128.96, 127.90 (q, J = 32.6 Hz), 127.24 (q, J = 3.7 Hz), 126.87, 125.85 (q, J = 273.1 Hz), 122.71 (q, J = 3.3 Hz), 115.41, 68.51, 57.02, 31.59, 23.24, 1.03, 0.00. **^{19}F NMR (376 MHz, CDCl_3)** δ -63.85. **HRMS (EI)** calcd. For $\text{C}_{25}\text{H}_{24}\text{F}_3\text{NO}_2\text{SSi}$ $[\text{M}]^+$: 487.1249. Found: 487.1223.

1,1,5'-Trimethyl-1'-tosyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline] (2df)



Following the general procedure, the reaction was carried out with **1df** (120.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (55.4 mg, 0.128 mmol, 64% yield). R_f (petroleum ether/ethyl acetate = 10:1) = 0.5. **¹H NMR (400 MHz, CDCl₃)** δ 7.70 (m, 2H), 7.61 (m, 1H), 7.51 (m, 1H), 7.21 (m, 3H), 7.14 (m, 1H), 7.03 (m, 1H), 6.59 (s, 1H), 6.52 (m, 1H), 3.89 (d, J = 10.2 Hz, 1H), 3.69 (d, J = 10.2 Hz, 1H), 2.40 (s, 3H), 2.21 (s, 3H), 1.23 (d, J = 15.2 Hz, 1H), 1.07 (d, J = 15.2 Hz, 1H), 0.36 (s, 3H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 157.48, 145.53, 143.26, 141.51, 140.70, 135.48, 135.35, 133.15, 131.74, 131.18, 130.09, 129.08, 128.43, 127.04, 125.89, 115.57, 68.34, 57.11, 31.28, 23.12, 22.51, 0.95, 0.00. **HRMS (EI)** calcd. For C₂₅H₂₇NO₂SSi [M]⁺: 433.1532. Found: 433.1523.

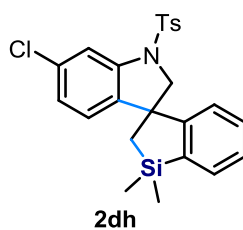
5'-Methoxy-1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline] (2dg)



Following the general procedure, the reaction was carried out with **1dg** (118.2 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (62.9 mg, 0.140 mmol, 70% yield).

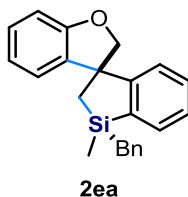
R_f (petroleum ether/ethyl acetate = 10:1) = 0.5. **^1H NMR (400 MHz, CDCl_3)** δ 7.67 (m, 3H), 7.51 (m, 1H), 7.25 – 7.19 (m, 3H), 7.14 (m, 1H), 6.78 (m, 1H), 6.58 – 6.45 (m, 1H), 6.31 (m, 1H), 3.89 (d, J = 10.4 Hz, 1H), 3.70 (d, J = 10.4 Hz, 1H), 3.68 (s, 3H), 2.40 (s, 3H), 1.18 (d, J = 15.1 Hz, 1H), 1.04 (d, J = 15.1 Hz, 1H), 0.36 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 157.76, 156.28, 144.60, 143.83, 140.59, 135.68, 134.33, 132.25, 130.89, 130.24, 128.22, 127.57, 126.08, 115.98, 113.96, 109.92, 67.52, 56.50, 56.22, 30.34, 22.19, 0.00, -0.94. **HRMS (EI)** calcd. For $\text{C}_{25}\text{H}_{27}\text{NO}_3\text{SSi}$ $[\text{M}]^+$: 449.1481. Found: 449.1474.

6'-Chloro-1,1-dimethyl-1'-tosyl-1,2-dihydrospiro[benzo[*b*]silole-3,3'-indoline] (2dh)



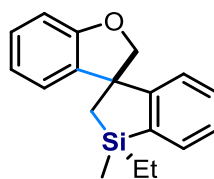
Following the general procedure, the reaction was carried out with **1dh** (119.0 mg, 0.2 mmol), $[\text{Pd}]\text{-I}$ (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (47.1mg, 0.104 mmol, 52% yield). R_f (petroleum ether/ethyl acetate = 10:1) = 0.5. **^1H NMR (400 MHz, CDCl_3)** δ 7.79 – 7.64 (m, 3H), 7.52 (m, 1H), 7.34 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.15 (m, 1H), 6.94 (m, 1H), 6.70 (m, 1H), 6.52 (m, 1H), 3.93 (d, J = 10.2 Hz, 1H), 3.73 (d, J = 10.2 Hz, 1H), 2.42 (s, 3H), 1.26 (d, J = 15.1 Hz, 1H), 1.05 (d, J = 15.1 Hz, 1H), 0.37 (s, 3H), 0.35 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 156.80, 146.03, 144.12, 141.80, 141.51, 135.29, 135.19, 133.32, 131.91, 131.41, 129.01, 128.70, 126.83, 126.25, 125.83, 115.97, 68.56, 56.76, 31.41, 23.17, 0.93, 0.00. **HRMS (EI)** calcd. For $\text{C}_{24}\text{H}_{24}\text{ClNO}_2\text{SSi}$ $[\text{M}]^+$: 453.0986. Found: 453.0979.

1'-Benzyl-1'-methyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ea)



Following the general procedure, the reaction was carried out with **1ea** (96.8 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (26 mg, 0.076 mmol, 38% yield, dr = 1:1). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. For the first diastereoisomer: **¹H NMR (400 MHz, CDCl₃)** δ 7.45 (m, 1H), 7.32 (m, 1H), 7.25 – 7.17 (m, 3H), 7.17 – 7.07 (m, 2H), 7.03 (m, 3H), 6.88 (m, 1H), 6.84 (m, 1H), 6.64 (m, 1H), 4.39 (d, J = 8.7 Hz, 1H), 4.37 (d, J = 8.7 Hz, 1H), 2.52 (d, J = 13.9 Hz, 1H), 2.45 (d, J = 13.9 Hz, 1H), 1.46 (d, J = 15.4 Hz, 1H), 1.36 (d, J = 15.4 Hz, 1H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.63, 156.24, 138.68, 138.05, 137.66, 132.11, 130.62, 128.44, 128.35, 128.06, 126.84, 125.74, 124.53, 123.31, 121.32, 109.58, 87.45, 57.35, 26.63, 25.30, -2.53. For the second diastereoisomer: **¹H NMR (400 MHz, CDCl₃)** δ 7.50 – 7.44 (m, 1H), 7.36 – 7.26 (m, 2H), 7.19 (m, 2H), 7.16 – 7.12 (m, 1H), 7.12 – 7.06 (m, 1H), 6.98 (m, 1H), 6.94 (m, 2H), 6.89 – 6.81 (m, 3H), 3.98 (d, J = 8.7 Hz, 1H), 3.83 (d, J = 8.7 Hz, 1H), 2.45 (d, J = 13.8 Hz, 1H), 2.35 (d, J = 13.8 Hz, 1H), 1.54 (d, J = 15.5 Hz, 1H), 1.26 (d, J = 15.5 Hz, 1H), 0.41 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.70, 156.45, 138.80, 137.81, 137.79, 132.06, 130.63, 128.45, 128.27, 128.08, 126.87, 125.73, 124.64, 123.26, 121.27, 109.56, 86.87, 57.51, 26.48, 25.73, -2.93. **HRMS (EI)** calcd. For C₂₃H₂₂OSi [M]⁺: 342.1440. Found: 342.1435.

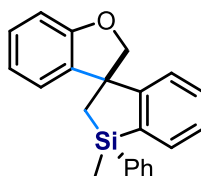
1'-Ethyl-1'-methyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2eb)



2eb

Following the general procedure, the reaction was carried out with **1eb** (84.4 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (38.1 mg, 0.136 mmol, 68% yield, dr = 1:1). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **¹H NMR (400 MHz, CDCl₃)** δ 7.56 (m, 2H), 7.54 – 7.41 (m, 1H), 7.31 (m, 4H), 7.17 (m, 2H), 7.09 – 7.03 (m, 2H), 6.98 – 6.84 (m, 5H), 4.49 – 4.41 (m, 3H), 4.41 – 4.35 (m, 1H), 1.55 (d, J = 15.3 Hz, 1H), 1.48 (d, J = 15.3 Hz, 1H), 1.35 (d, J = 17.0 Hz, 1H), 1.28 (d, J = 17.0 Hz, 1H), 1.14 – 1.01 (m, 6H), 0.99 – 0.87 (m, 4H), 0.41 (s, 3H), 0.35 (s, 3H). **¹³C NMR (101 MHz, CDCl₃)** δ 159.82, 159.72, 156.26, 156.21, 139.77, 139.07, 138.95, 137.80, 131.97, 131.90, 130.38, 130.35, 128.06, 126.79, 126.77, 125.70, 125.67, 123.82, 123.37, 123.32, 121.90, 121.30, 121.28, 119.73, 111.22, 109.63, 87.39, 87.33, 57.59, 27.11, 26.70, 10.29, 7.70, 7.61, 7.57, 7.29, 6.97, 6.79, -2.81, -3.71. **HRMS (EI)** calcd. For C₁₈H₂₀OSi [M]⁺: 280.1283. Found: 280.1275.

1'-Methyl-1'-phenyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ec)

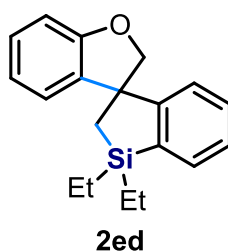


2ec

Following the general procedure, the reaction was carried out with **1ec** (94.0 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h.

The title compound was obtained as a white solid (14.4 mg, 0.044 mmol, 22% yield, dr = 1:1). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.71 – 7.65 (m, 1H), 7.60 (m, 3H), 7.50 (m, 2H), 7.45 – 7.26 (m, 10H), 7.22 – 7.09 (m, 4H), 6.99 (m, 1H), 6.94 – 6.80 (m, 5H), 4.53 (d, J = 8.5 Hz, 1H), 4.49 (d, J = 8.5 Hz, 1H), 4.29 (m, 2H), 1.79 (d, J = 15.3 Hz, 1H), 1.70 (d, J = 15.3 Hz, 1H), 1.63 (d, J = 15.3 Hz, 1H), 1.50 (d, J = 15.3 Hz, 1H), 0.70 (s, 3H), 0.67 (s, 3H). **^{13}C NMR (101 MHz, CDCl_3)** δ 162.29, 162.13, 159.25, 140.17, 139.90, 139.84, 139.51, 138.75, 136.74, 136.56, 134.84, 133.21, 132.19, 132.03, 130.57, 130.50, 129.58, 129.52, 128.20, 128.16, 125.92, 125.75, 123.75, 112.12, 112.09, 89.62, 89.20, 60.25, 59.99, 30.84, 30.71, -0.00, -0.16. **HRMS (EI)** calcd. For $\text{C}_{22}\text{H}_{20}\text{OSi}$ $[\text{M}]^+$: 328.1283. Found: 328.1275.

1',1'-diethyl-1',2'-dihydro-2H-spiro[benzofuran-3,3'-benzo[*b*]silole] (2ed)

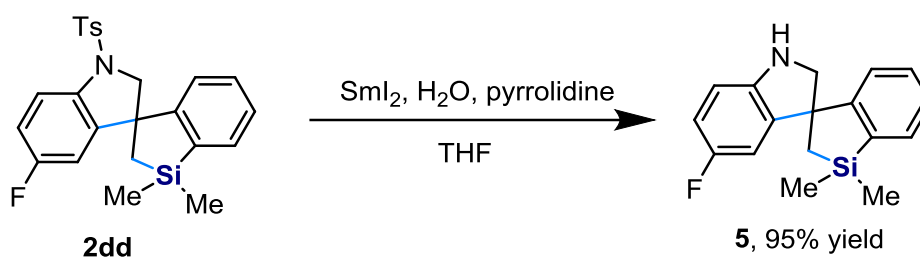


Following the general procedure, the reaction was carried out with **1ed** (90.0 mg, 0.2 mmol), [Pd]-1 (5.5 mg, 0.01 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and TcCu (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for 12 h. The title compound was obtained as a white solid (35.2 mg, 0.120 mmol, 60% yield). R_f (petroleum ether/dichloromethane = 20:1) = 0.3. **^1H NMR (400 MHz, CDCl_3)** δ 7.55 (dd, J = 7.3, 1.6 Hz, 1H), 7.32 (dd, J = 7.3, 1.6 Hz, 1H), 7.28 (m, 1H), 7.17 (m, 1H), 7.05 (m, 1H), 6.94 – 6.82 (m, 3H), 4.43 (d, J = 8.5 Hz, 1H), 4.39 (d, J = 8.5 Hz, 1H), 1.48 (d, J = 15.4 Hz, 1H), 1.31 (d, J = 15.4 Hz, 1H), 1.04 (m, 6H), 0.95 – 0.87 (m, 2H), 0.86 – 0.76 (m, 2H). **^{13}C NMR (101 MHz, CDCl_3)** δ 159.71, 156.55, 138.10, 138.03, 132.20, 130.34, 128.02, 126.66, 125.80, 123.28, 121.30, 109.58, 87.69, 57.54, 24.90,

7.79, 7.63, 5.77, 4.92. **HRMS (EI)** calcd. For $C_{19}H_{22}OSi$ $[M]^+$: 294.1440. Found: 294.1434.

Removal of the Protecting Group (-Ts) in Spirosilacycle **2dd**

General Procedure



The compound **5** was prepared according to the literature with modification.^[8]

Preparation of SmI_2 in THF

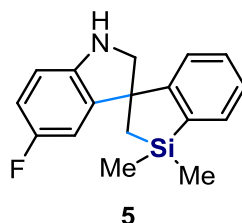
Diiodoethane (13 mmol, 3.65 g) was added to THF (100 ml). To this was added samarium metal (19 mmol, 2.85 g, powder). The mixture was allowed to stir at room temperature under a nitrogen atmosphere for one hour. This yields a deep-blue 0.13 M solution of SmI_2 .

Experiment:

To a solution of SmI_2 (13 mL, 0.13 M, 1 mmol) in THF was added the sulfonamide (0.1 mmol) followed by water (60 μL , 0.3 mmol) and pyrrolidine (173 μL , 2 mmol) under a nitrogen atmosphere. The reaction mixture immediately turned white upon addition of amine. The resulting mixture was diluted with diethyl ether (16 mL) and treated with a solution of potassium sodium tartrate and potassium carbonate (10% w/v each). The aqueous phase was extracted with two portions of diethyl ether. The organic extracts were pooled, dried and evaporated to yield the crude amine. The crude product was purified by preparative RP-HPLC on reversed phase column (C18(ODS)) (eluent: CH_3CN) to afford the corresponding product **5** (27mg, 0.095 mmol, 95% yield).

Characterization of Product 5

5'-Fluoro-1,1-dimethyl-1,2-dihydrospiro[benzo[b]silole-3,3'-indoline]. (5)

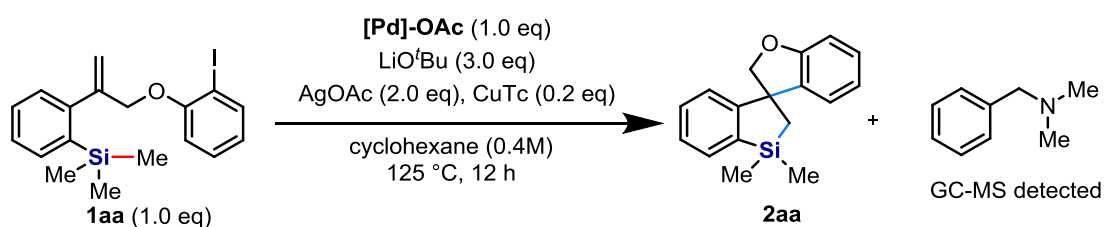


Compound **5** was obtained as colorless oil ($R_f = 0.3$, petroleum ether: ethyl acetate = 5:1) in 95% yield. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 – 7.41 (m, 1H), 7.22 (m, 1H), 7.19 – 7.13 (m, 1H), 7.00 (m, 1H), 6.66 (m, 1H), 6.55 (m, 1H), 6.45 (m, 1H), 3.45 (d, $J = 8.9$ Hz, 1H), 3.39 (d, $J = 8.9$ Hz, 1H), 1.51 (d, $J = 15.1$ Hz, 1H), 1.05 (d, $J = 15.1$ Hz, 1H), 0.30 (s, 3H), 0.25 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.01 (d, $J = 241.0$ Hz), 148.11, 142.64, 141.33, 133.02, 131.43, 128.12, 127.06, 115.01, 114.77, 111.86 (d, $J = 23.5$ Hz), 111.56 (d, $J = 8.3$ Hz), 66.91, 59.36, 29.13, 0.88, 0.01. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -125.05. HRMS (EI) calcd. For $\text{C}_{17}\text{H}_{18}\text{FNSi}$ $[\text{M}]^+$: 283.1193. Found: 283.1188.

3. Supplementary Discussion

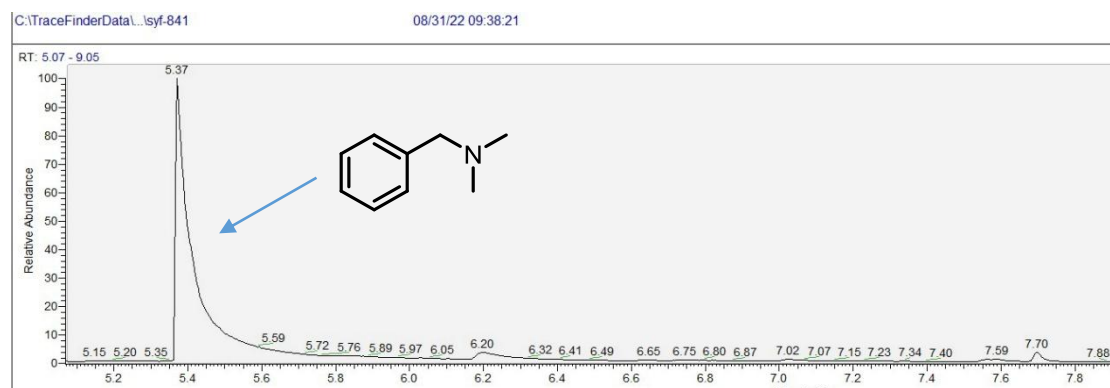
Experimental Mechanistic Study

GC Analyse of the Gas Composition of the Reactions



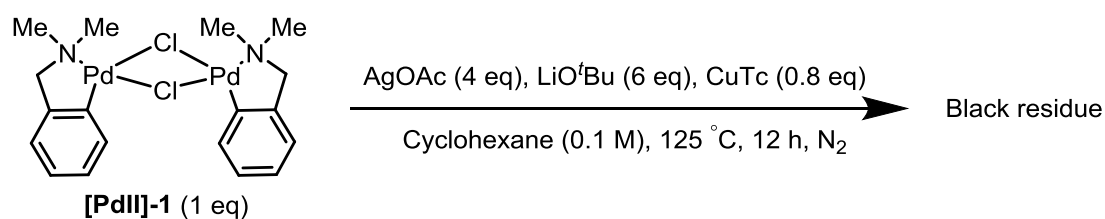
Experiment: Under the protection of nitrogen, the reaction was carried out with **1aa** (81.6 mg, 0.2 mmol), **[Pd]-OAc** (0.2 mmol), AgOAc (66.8 mg, 0.4 mmol), LiO^tBu (48 mg, 0.6 mmol), and CuTc (7.64 mg, 0.04 mmol) in cyclohexane (0.5 mL) at 125 °C for

12 h. Then, the crude product was analyzed by GC-MS.

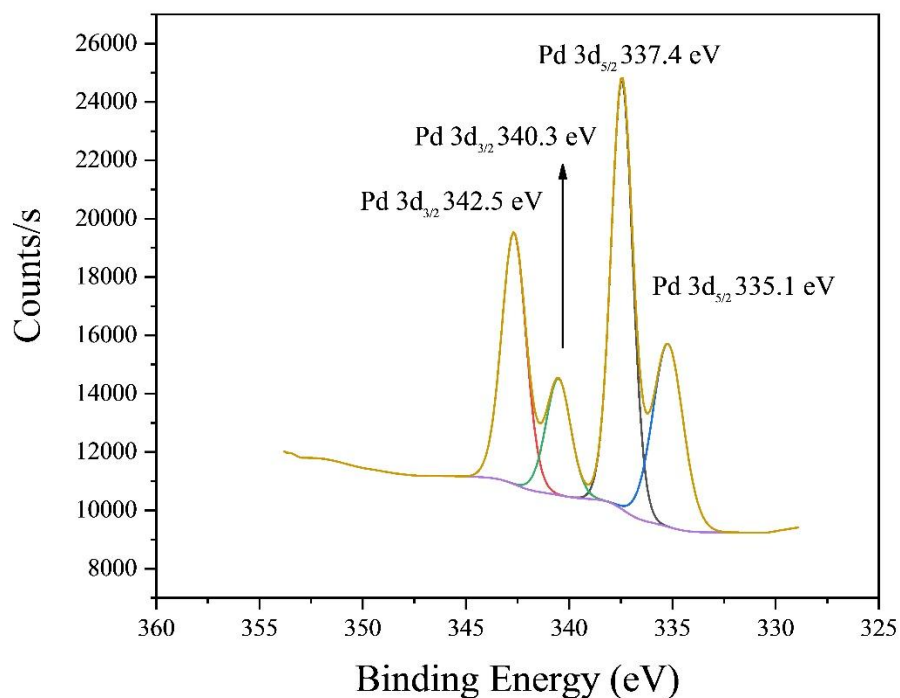


Supplementary Figure 1. GC analyses of the reaction of **1aa** in the presence of stoichiometric amount of [Pd]-OAc complex

X-ray Photoelectron Spectroscopy Analysis of Palladium Catalysts



In a nitrogen-filled glovebox, an oven-dried 15 mL screw capped sealed tube was charged with a magnetic stir bar, [Pd]-1 (55.2 mg, 0.1 mmol, 1.0 equiv), AgOAc (66.8 mg, 0.4 mmol, 4.0 equiv), LiO^tBu (48 mg, 0.6 mmol, 6.0 equiv), additive and cyclohexane (1.0 mL). The tube was sealed, then removed from the glovebox, and the formed mixture was stirred at 125 °C under N₂ for 12 h. After being cooled to room temperature, the organic phases were evaporated and the residues obtained for XPS test.



Supplementary Figure 2. XPS analysis of reaction residue to identify Pd(0) species

To gain information about the oxidation state of the Pd species, analysis of Pd 3d by X-ray photoelectron spectroscopy (XPS) was performed. All measurements were performed on a Thermo Scientific ESCALAB 250Xi spectrometer equipped with a monochromatic Al K α X-ray source. The pressure throughout the analysis chamber was less than 10⁻⁷ mbar. Samples were finely ground in a glovebox and pressed into aluminum foil before being placed on a sample holder and transferred to the XPS instrument in a sealed container to avoid exposure to air during transport. All results were analyzed with use of the Advantage software package. Charge correction was calibrated with C 1s (284.8 eV) as reference.

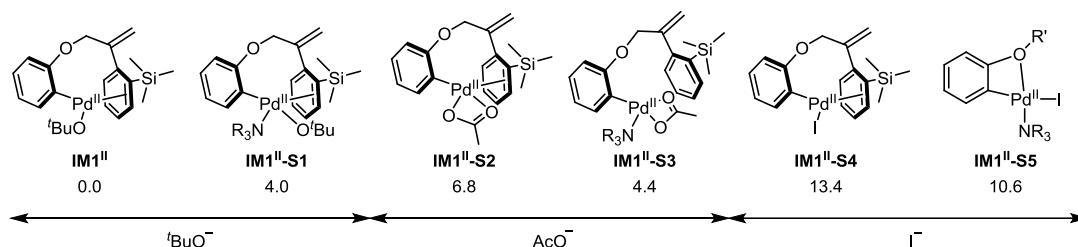
The spectra showed that the electron binding energies of Pd 3d_{3/2} and 3d_{5/2} in black residue were 340.3 eV and 335.1 eV (see Supplementary Figure 2), respectively, which is consistent with the position for metallic Pd.^[10] Further analysis showed that the electron binding energy (342.5 eV and 337.4 eV) were very close to the corresponding electron binding energy in PdO reported in the literature.^[11] In summary, we deduced that the palladium complex for this Pd-catalyzed sila-spirocyclization of **1aa** can produce Pd(0).

Computational Studies

Quantum Mechanical Studies

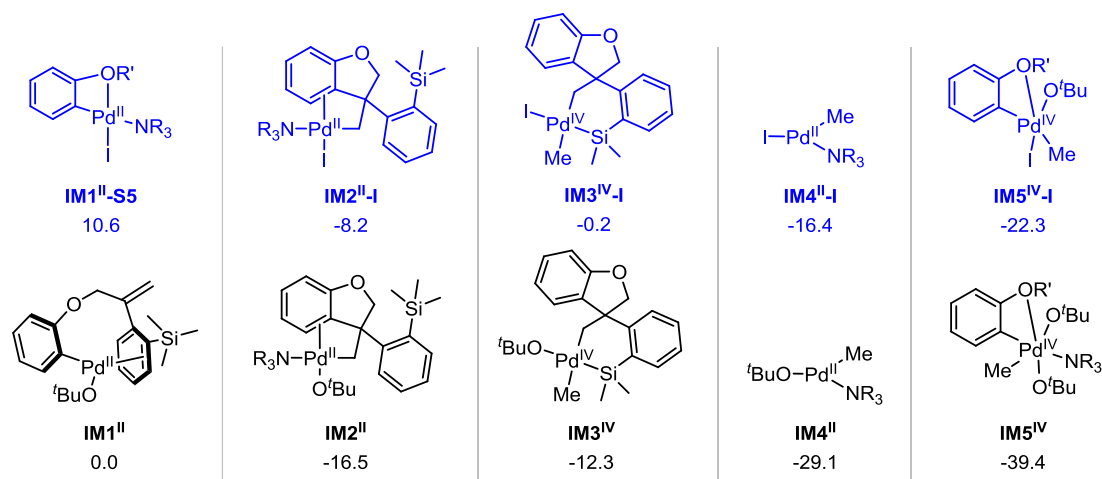
Method. Density functional theory calculations were carried out in Gaussian 16.^[12] Geometry optimization and frequency calculation employed the M06-L functional^[13] and the def2-SV(P) basis set.^[14] Single-point energies were then computed with the PBE0-D3 hybrid functional,^[15] the def2-TZVP basis set,^[14] and the SMD implicit solvation model^[16] for cyclohexane. Free energies were calculated using the GoodVibes code applying quasi-harmonic corrections.^[17] We assumed a concentration of 1 mol/L and a temperature of 398.15 K in all calculations.

Ligand Exchange. Possible ligation modes were evaluated on **IM1^{II}**. Supplementary Figure 3 presents calculated energies of ligand exchanges involving ^tBuO[−], AcO[−] and I[−]. The calculations show that **IM1^{II}** with the ligation of ^tBuO[−] is of the lowest-energy in the scope of our investigation.



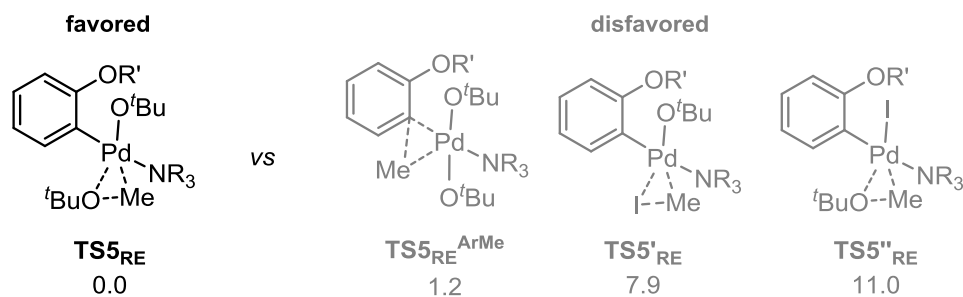
Supplementary Figure 3. Possible coordination modes of **IM1^{II}**. Relative free energies are shown in kcal/mol. Considered ligand exchanges involve AgI/AgOAc, LiO^tBu/LiOAc and NR₃.

To further evaluate the influence of I[−]/^tBuO[−] exchange, Supplementary Figure 4 compares the free-energy profiles with the ligations of these two anions. Our calculations show that the ^tBuO[−]-coordinated species are substantially lower in energy than the I[−]-coordinated counterparts. The result again supports the favorability of the ligand exchange.



Supplementary Figure 4. Effect of I^-/tBuO^- exchange on the free-energy profile (unit: kcal/mol).

Reductive Elimination. In addition, several possibly competing reductive elimination pathways were also considered. The results in Supplementary Figure 5 suggest that the following two pathways are kinetically less likely due to elevated activation barrier: (1) formation of Ar-Me bond from reductive elimination ($\text{TS5}_{\text{RE}}^{\text{ArMe}}$), (2) reductive elimination with I^- substituting one tBuO^- ($\text{TS5}'_{\text{RE}}$ and $\text{TS5}''_{\text{RE}}$).



Supplementary Figure 5. Relative free energies of possible reductive-elimination pathways (unit: kcal/mol).

Energies and Coordinates of Calculated Structures

Supplementary Table 2. Energies, enthalpies, and free energies of all calculated structures.

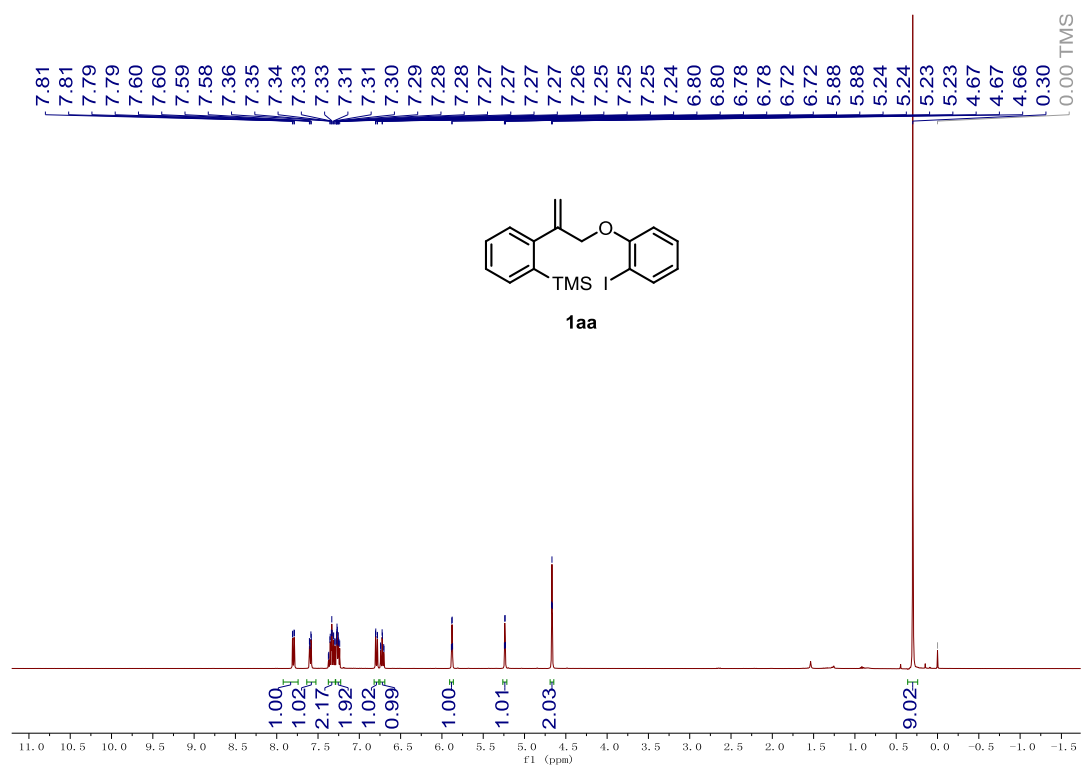
Imaginary frequencies of all transition states

	E (a.u.)	H (a.u.)	G (a.u.)	ν_{imag} (cm^{-1})
1aa	-1360.310142	-1359.938274	-1360.048278	

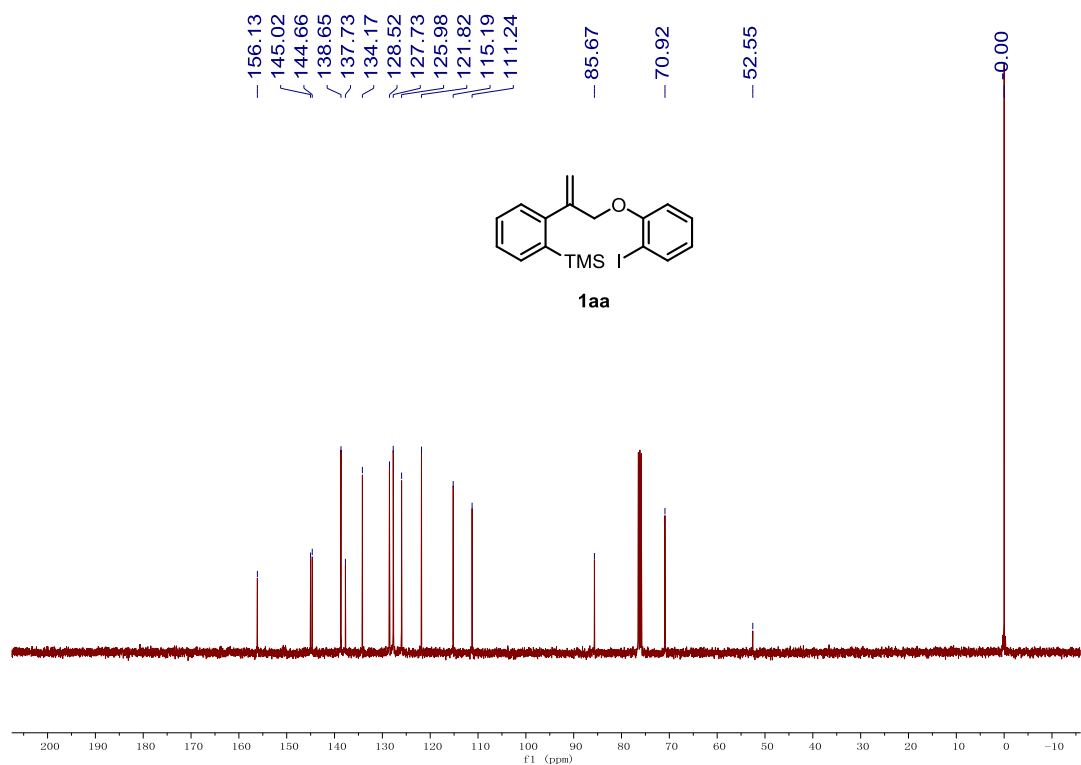
2aa	-1022.742602	-1022.412805	-1022.504362	
AgI	-444.764425	-444.758747	-444.796127	
AgOAc	-375.331716	-375.271678	-375.322048	
LiOAc	-235.915152	-235.854215	-235.899226	
LiO ^t Bu	-240.436963	-240.298866	-240.352587	
MeO ^t Bu	-272.761065	-272.584109	-272.639251	
NR ₃	-174.328517	-174.198890	-174.243829	
IM1^{II}	-1423.387087	-1422.880765	-1423.012122	
IM1^{II}-S1	-1597.738929	-1597.100026	-1597.249585	
IM1^{II}-S2	-1418.853391	-1418.423836	-1418.547932	
IM1^{II}-S3	-1593.212452	-1592.650868	-1592.795610	
IM1^{II}-S4	-1488.269266	-1487.895407	-1488.011492	
IM1^{II}-S5	-1662.626090	-1662.120973	-1662.259735	
IM2^{II}	-1597.771892	-1597.132380	-1597.282322	
IM3^{IV}	-1423.409621	-1422.902375	-1423.031677	
IM4^{II}	-575.018218	-574.710387	-574.797999	
IM5^{IV}	-1870.474403	-1869.660372	-1869.842037	
IM2^{II}-I	-1662.662102	-1662.154915	-1662.289747	
IM3^{IV}-I	-1488.295490	-1487.919887	-1488.033147	
IM4^{II}-I	-639.902817	-639.726959	-639.798496	
IM5^{IV}-I	-1760.991662	-1760.442971	-1760.591549	
TS1_{MI}	-1597.730456	-1597.092329	-1597.239357	-230.48
TS1'_{MI}	-1423.363221	-1422.857303	-1422.984901	-313.26
TS2_{OA}	-1423.393699	-1422.887285	-1423.012112	-90.73
TS3_{RE}	-1423.405440	-1422.899493	-1423.026906	-44.62
TS4_{OA}	-1760.974869	-1760.427900	-1760.575767	-61.82
TS5_{RE}	-1870.435138	-1869.622279	-1869.802512	-387.89
TS5'_{RE}	-1935.323831	-1934.644489	-1934.810646	-223.73
TS5''_{RE}	-1935.319587	-1934.639725	-1934.805603	-374.44
TS5_{RE}^{ArMe}	-1870.434382	-1869.620620	-1869.800535	-363.62
TS6_{RE}	-574.955397	-574.648758	-574.734828	-511.46

4. Supplementary Figures

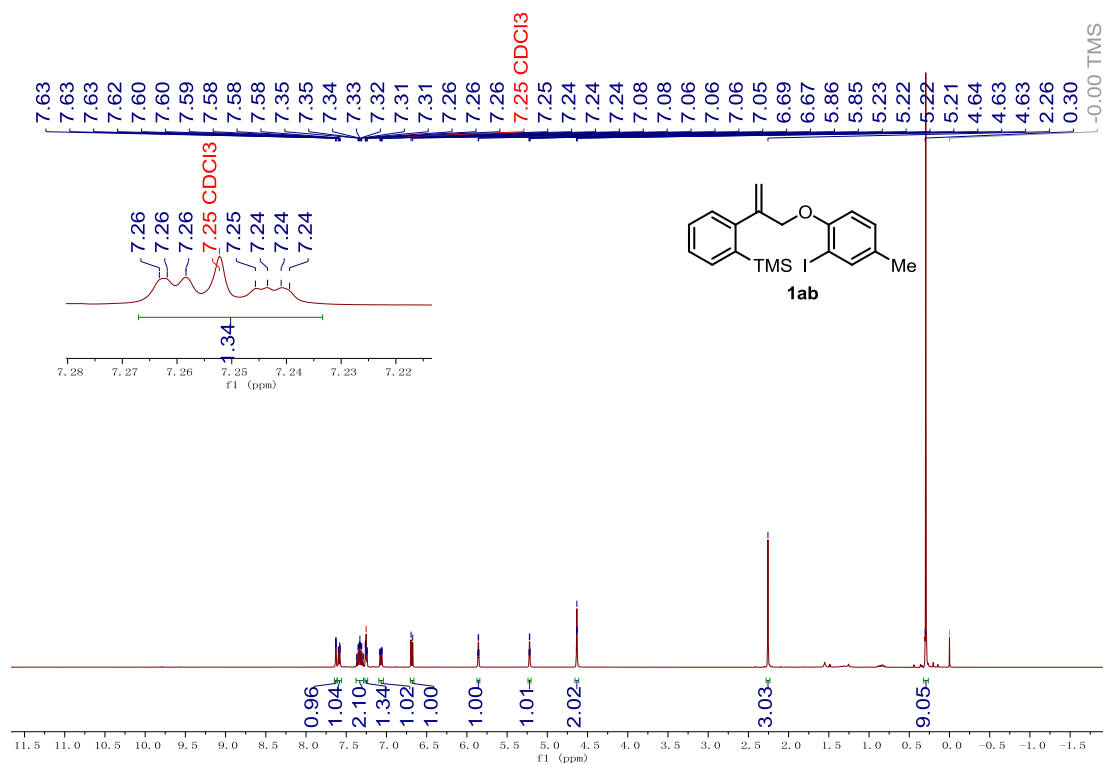
NMR Spectra



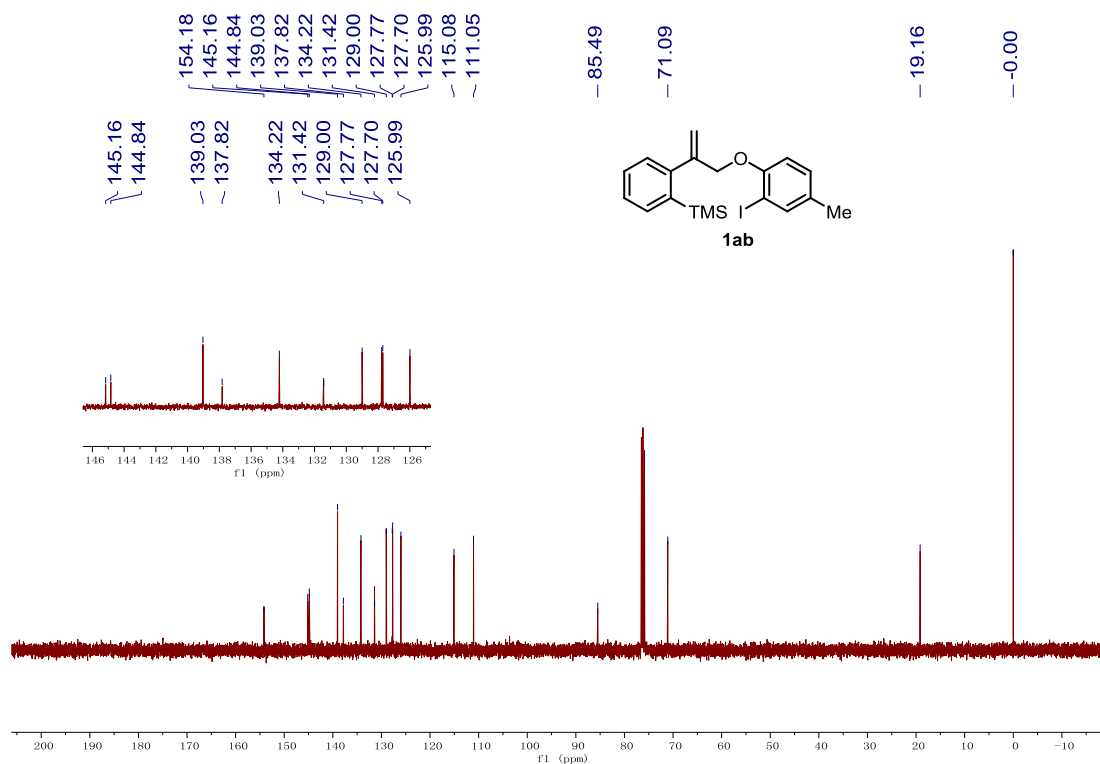
Supplementary Figure 6. ¹H NMR (400 MHz, CDCl₃) spectra of **1aa**



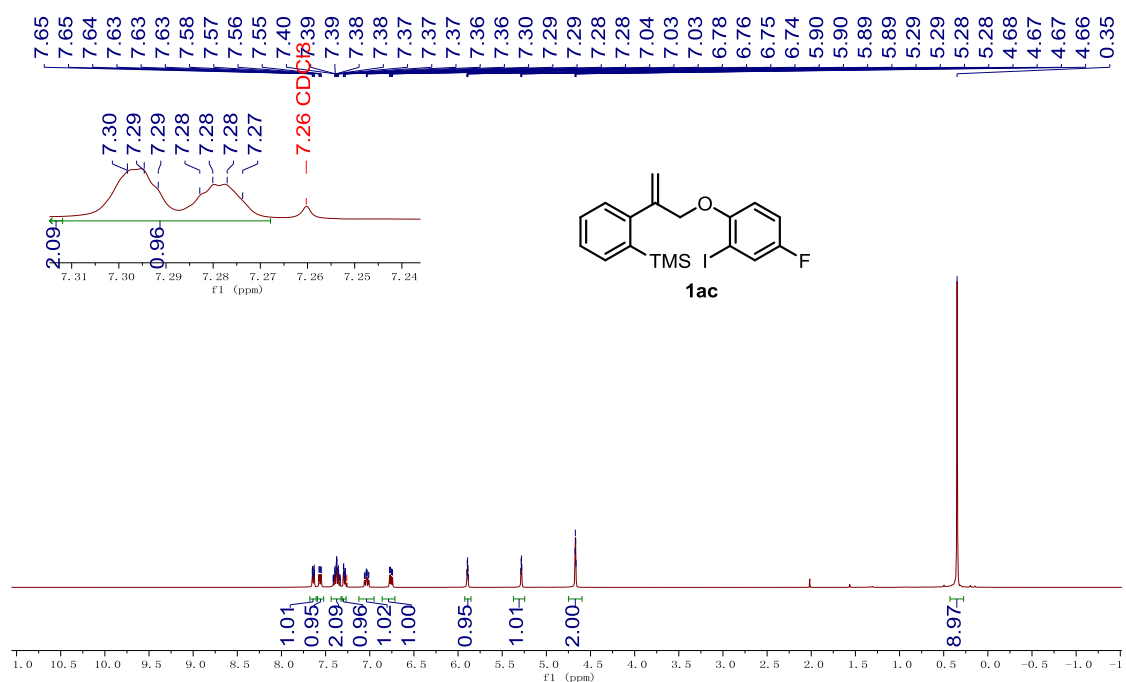
Supplementary Figure 7. ¹³C NMR (101 MHz, CDCl₃) spectra of **1aa**



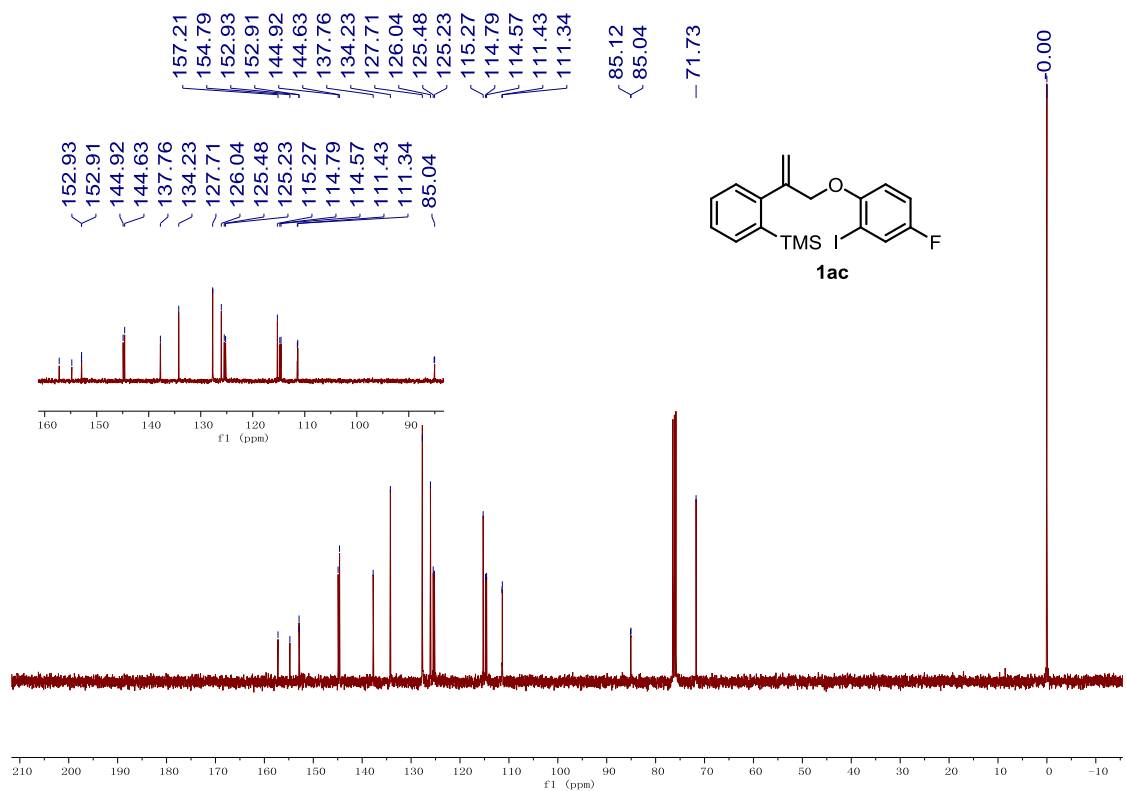
Supplementary Figure 8. ¹H NMR (400 MHz, CDCl₃) spectra of 1ab



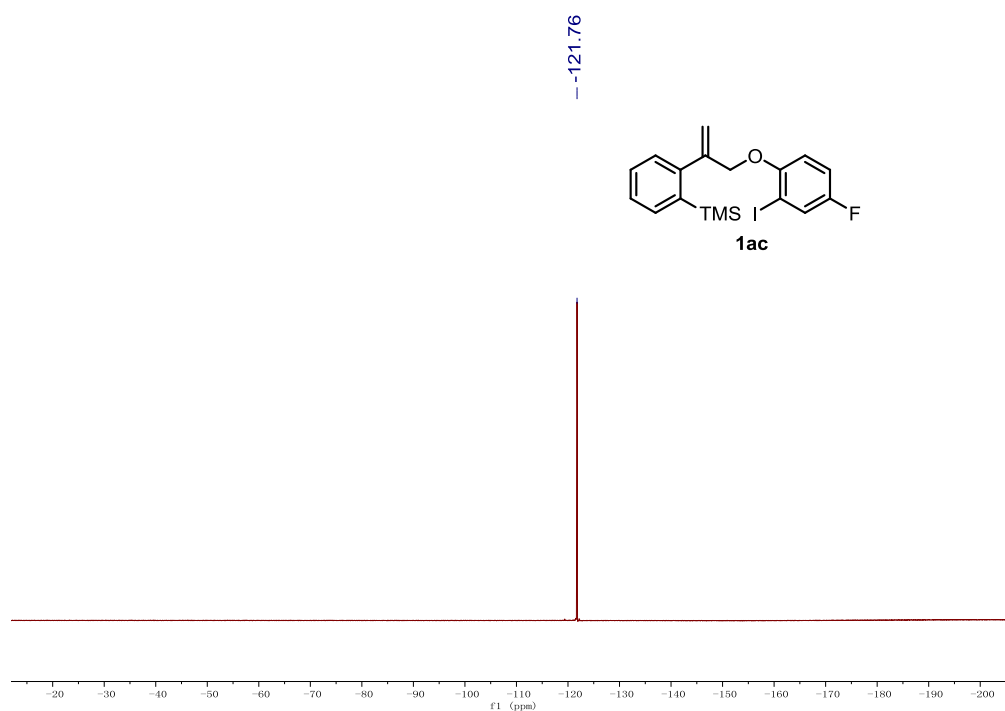
Supplementary Figure 9. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ab



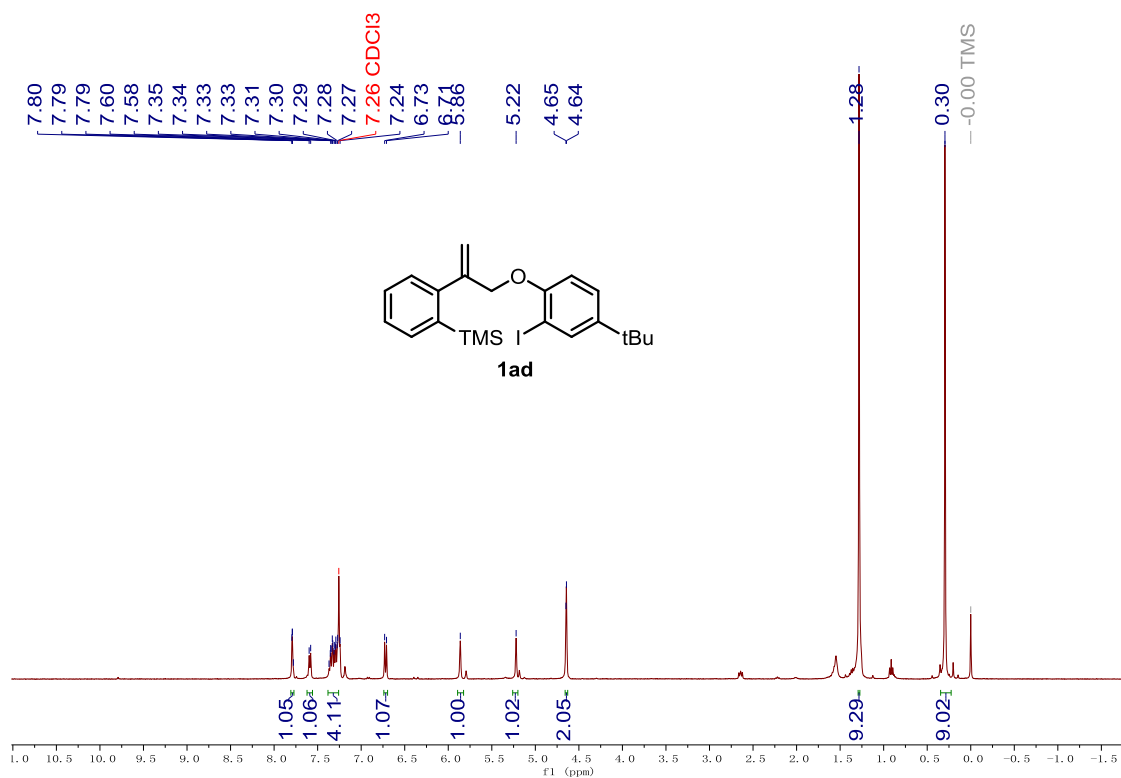
Supplementary Figure 10. ¹H NMR (400 MHz, CDCl₃) spectra of 1ac



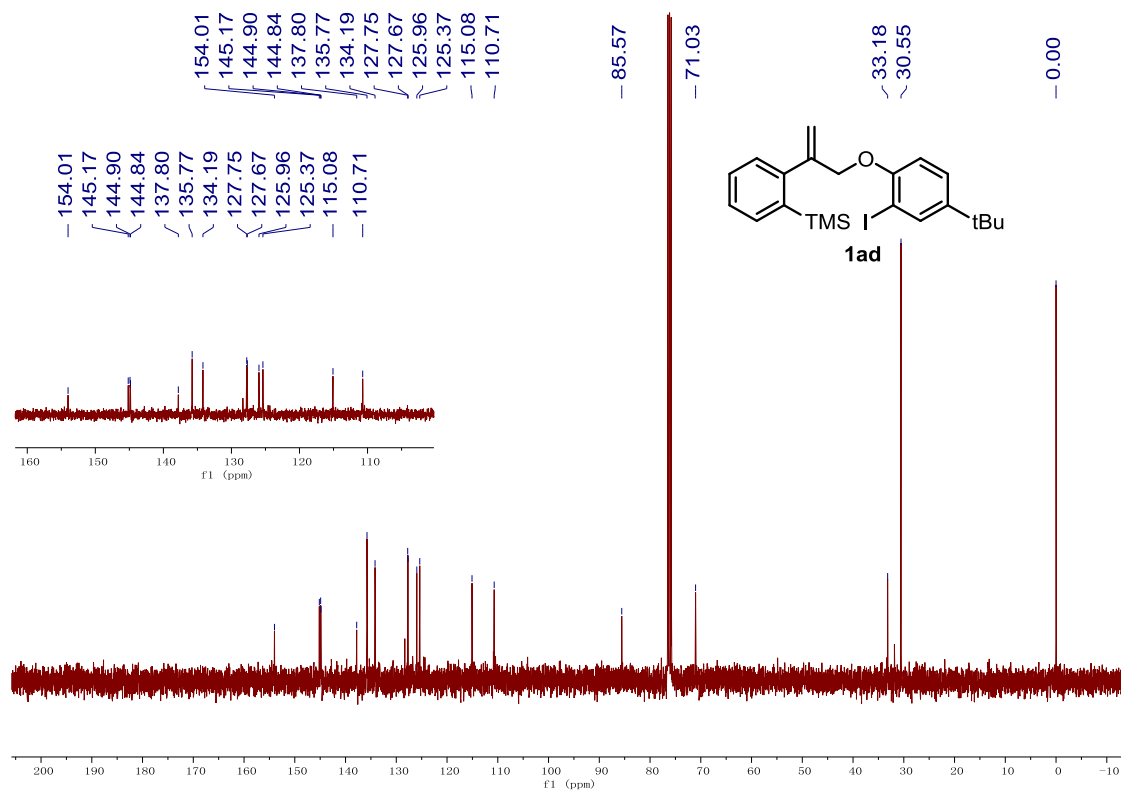
Supplementary Figure 11. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ac



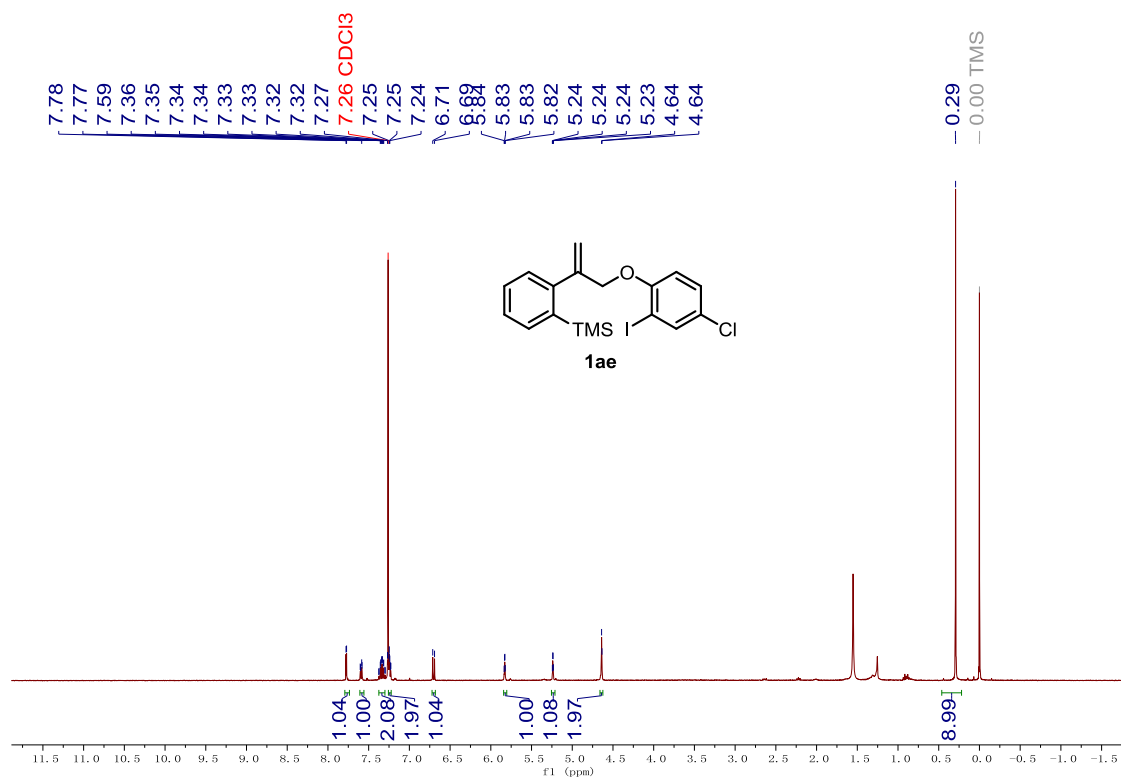
Supplementary Figure 12. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1ac**



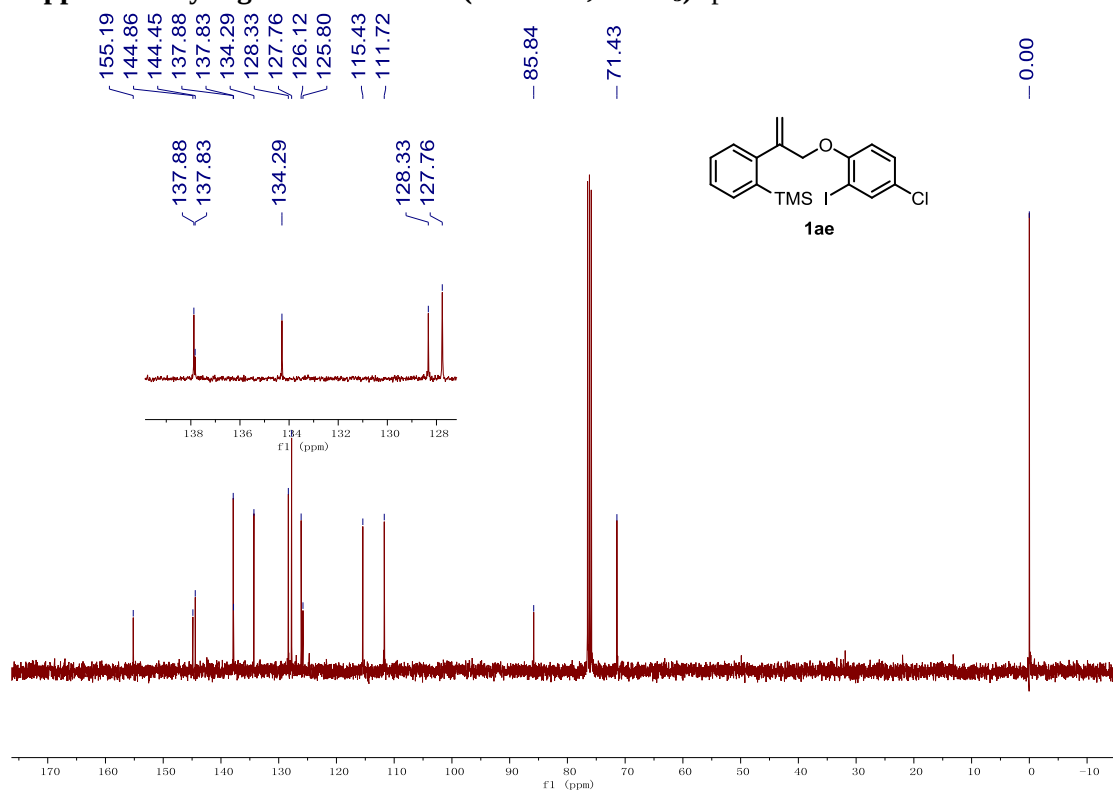
Supplementary Figure 13. ¹H NMR (400 MHz, CDCl₃) spectra of **1ad**



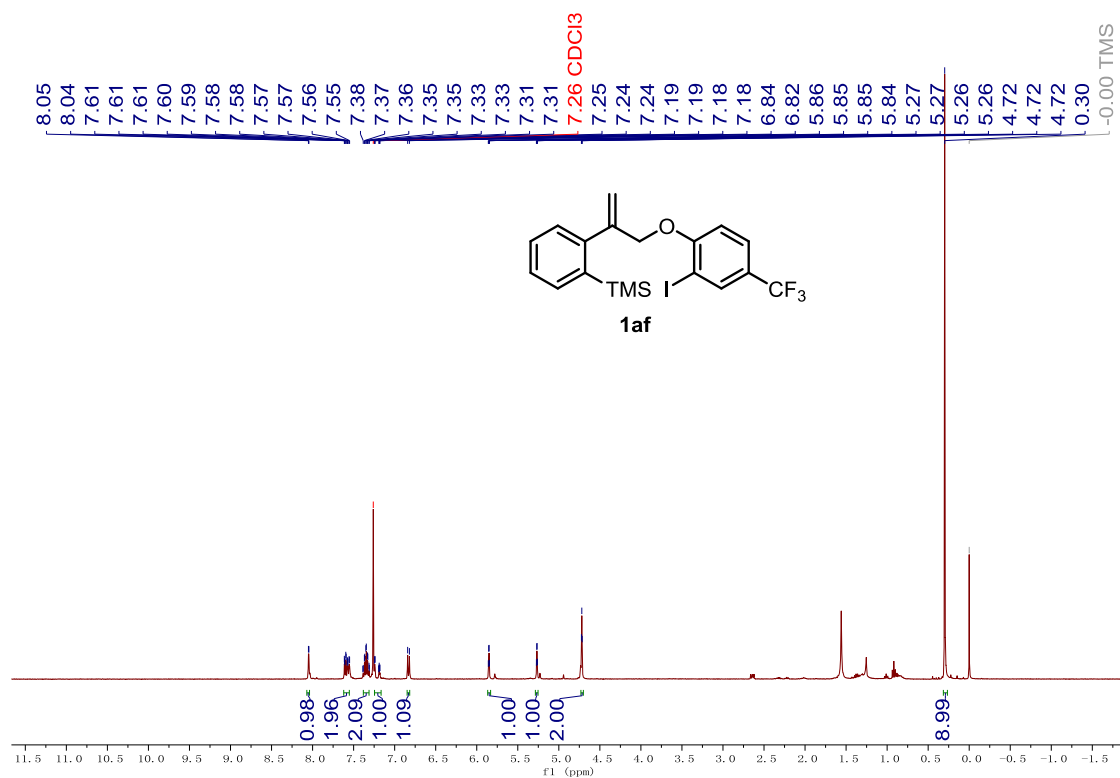
Supplementary Figure 14. ¹³C NMR (101 MHz, CDCl₃) spectra of **1ad**



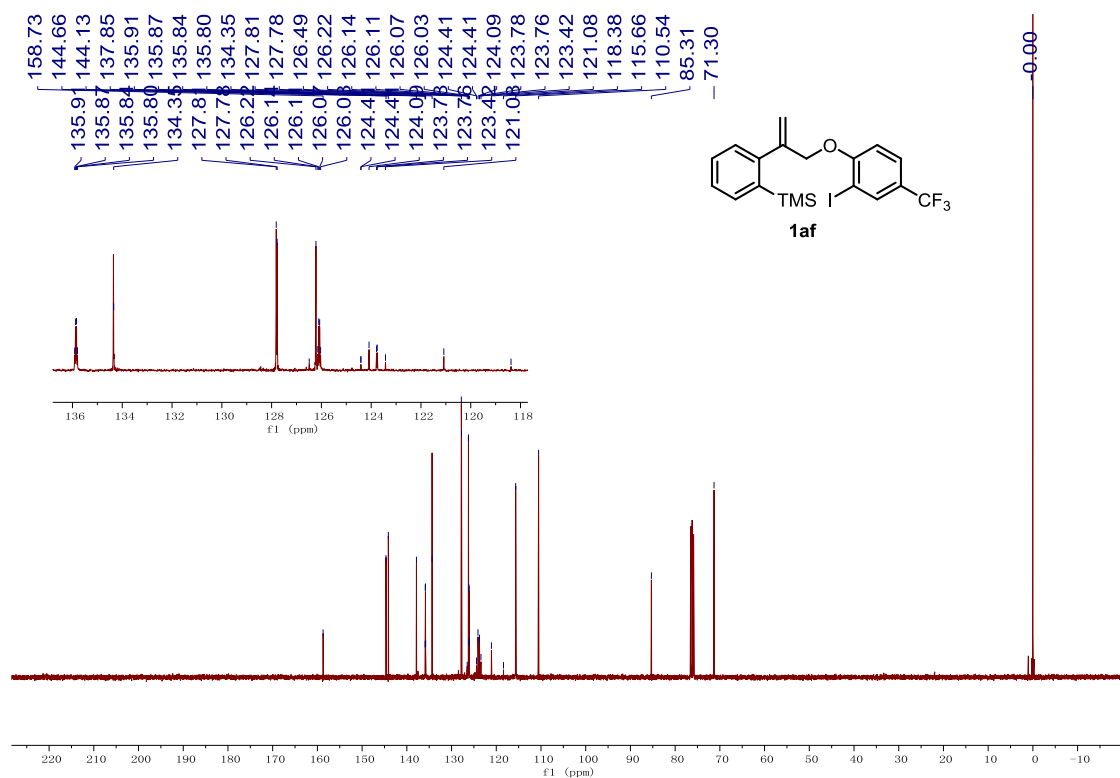
Supplementary Figure 15. ¹H NMR (400 MHz, CDCl₃) spectra of 1ae



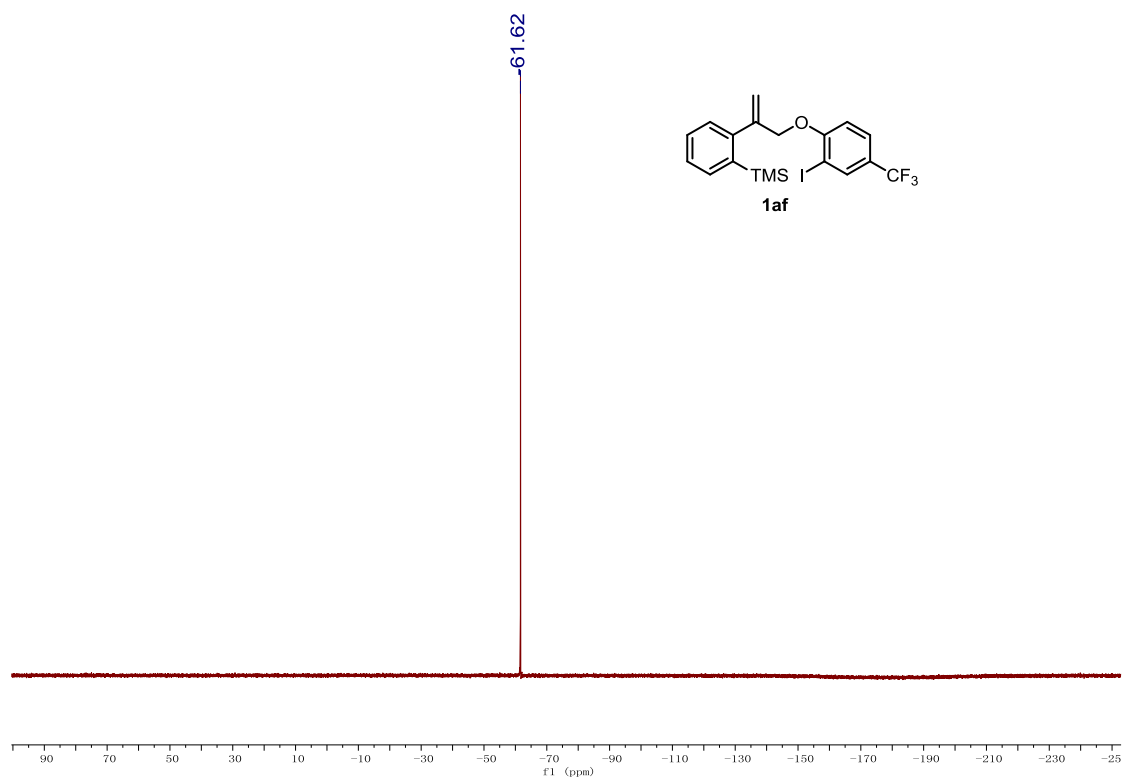
Supplementary Figure 16. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ae



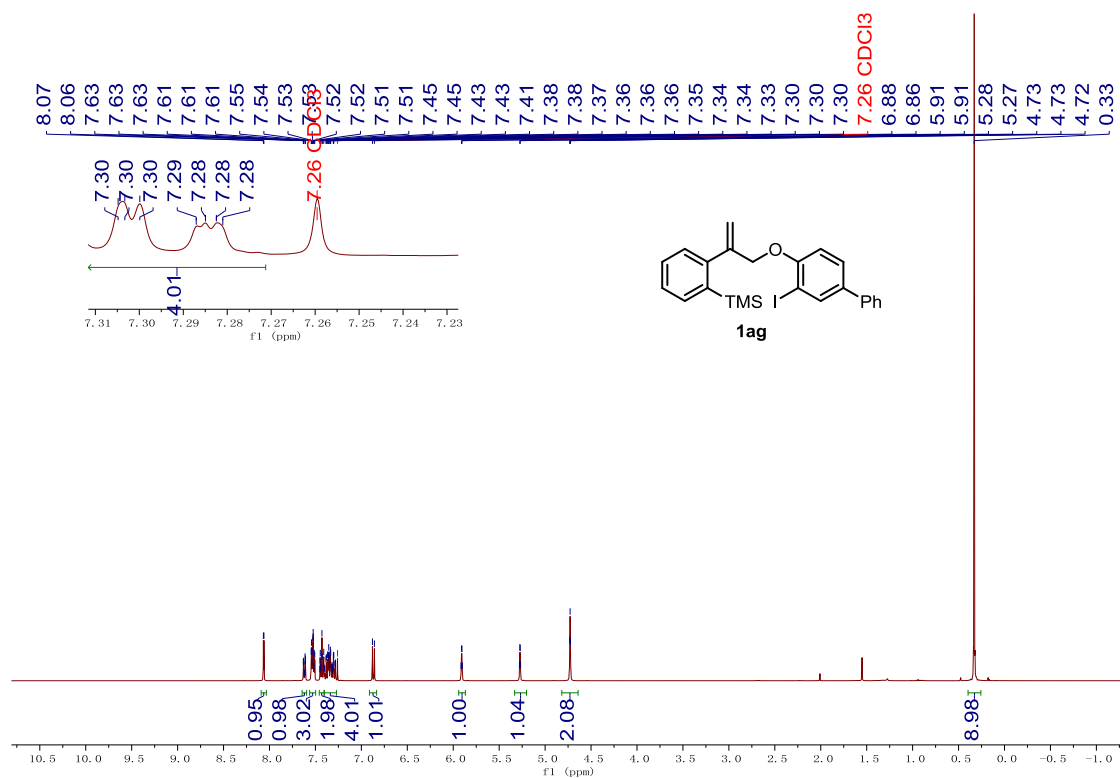
Supplementary Figure 17. ¹H NMR (400 MHz, CDCl₃) spectra of 1af



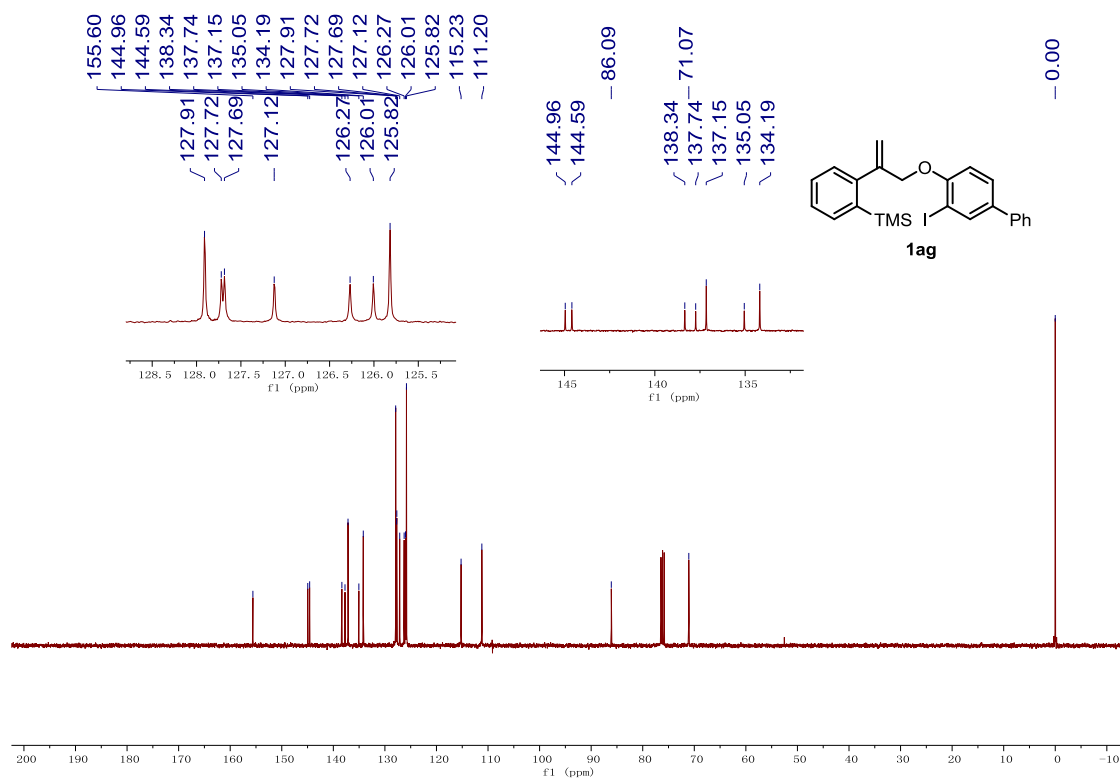
Supplementary Figure 18. ¹³C NMR (101 MHz, CDCl₃) spectra of 1af



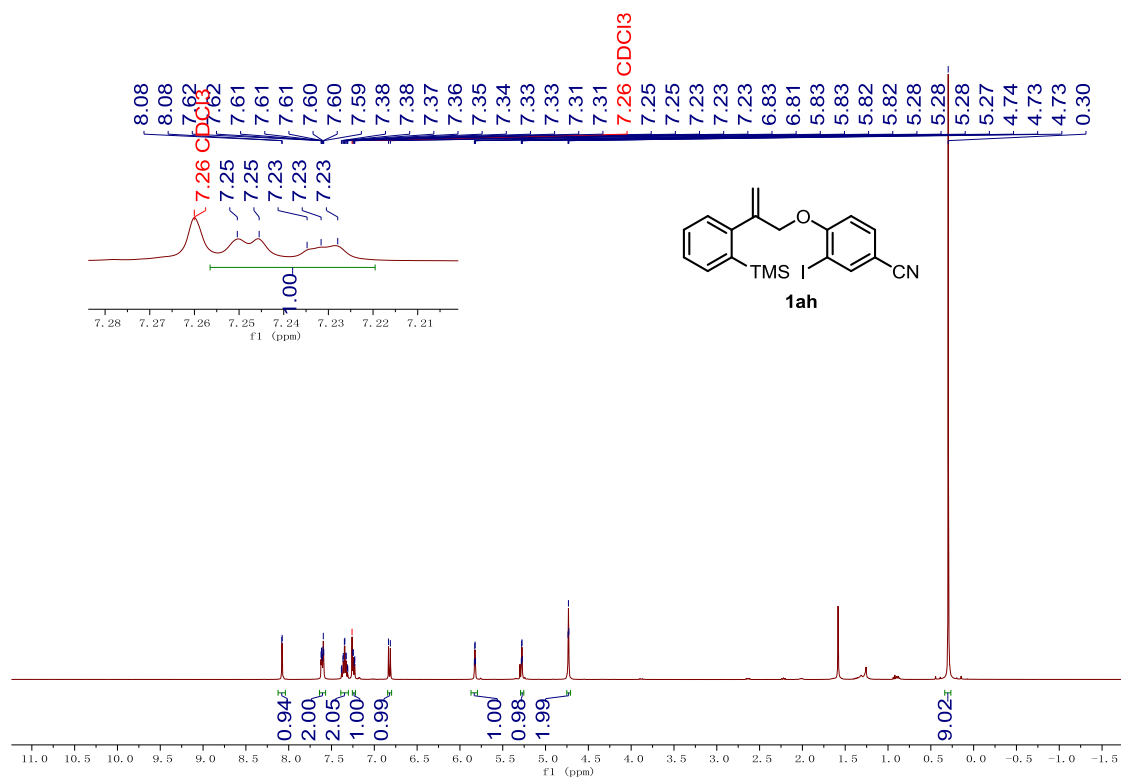
Supplementary Figure 19. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1af**



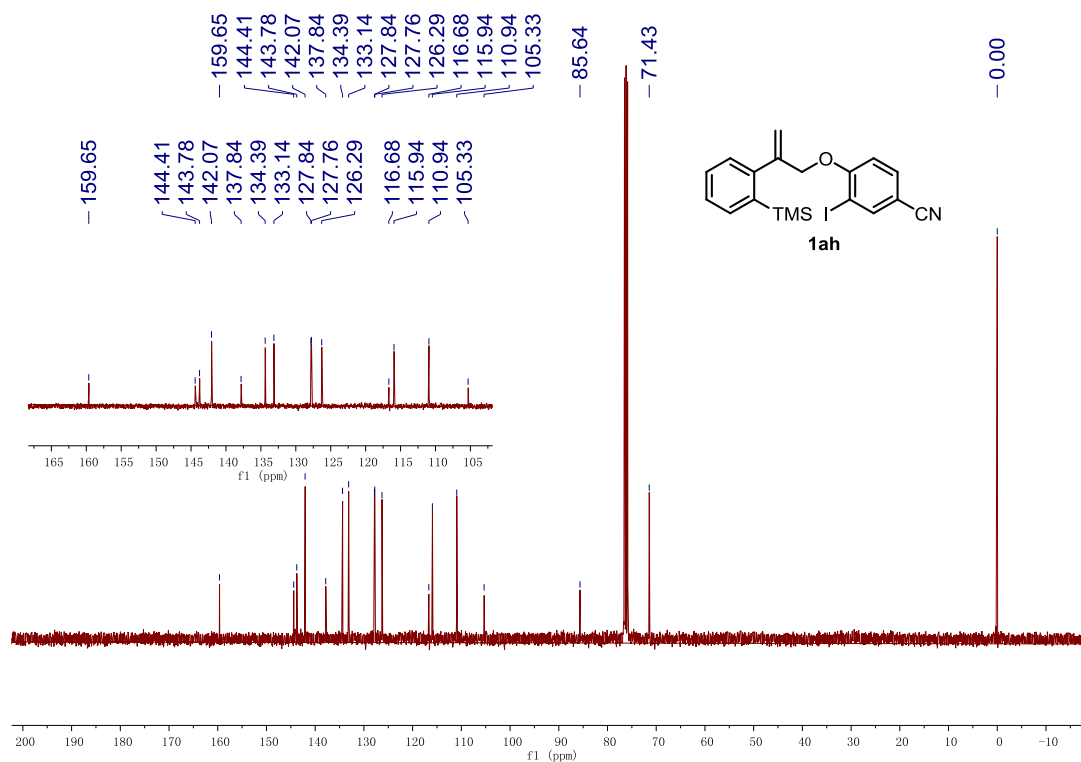
Supplementary Figure 20. ¹H NMR (400 MHz, CDCl₃) spectra of 1ag



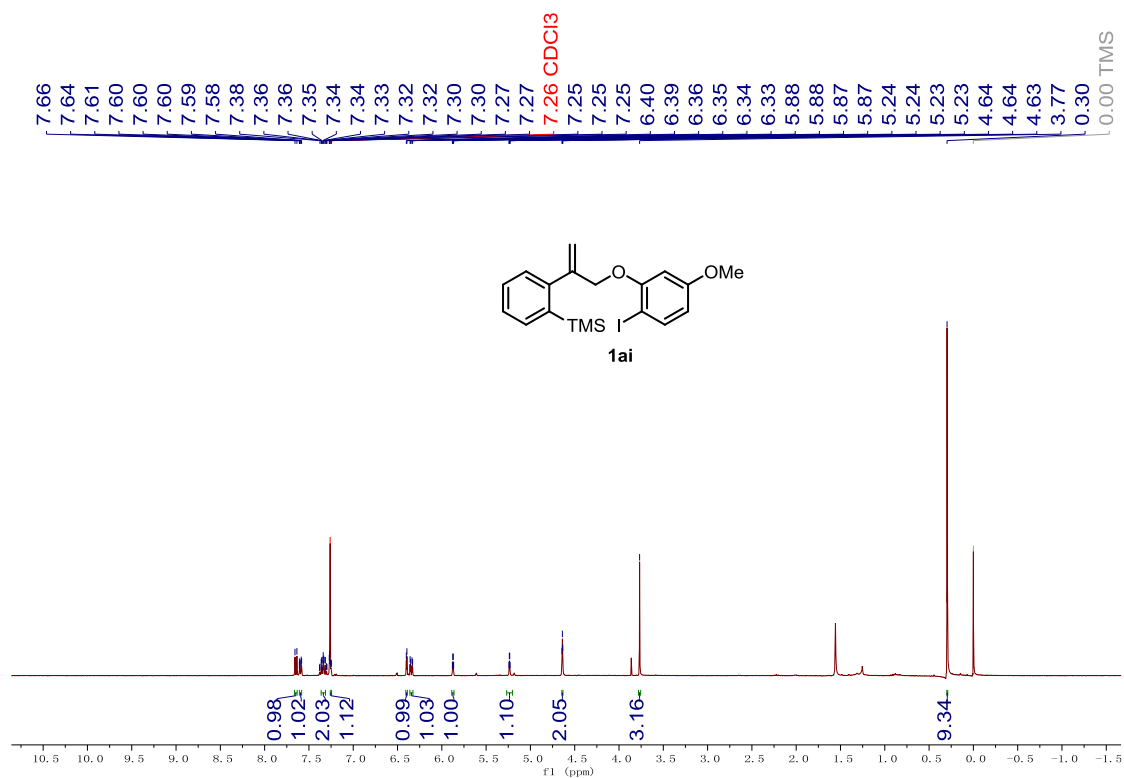
Supplementary Figure 21. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ag



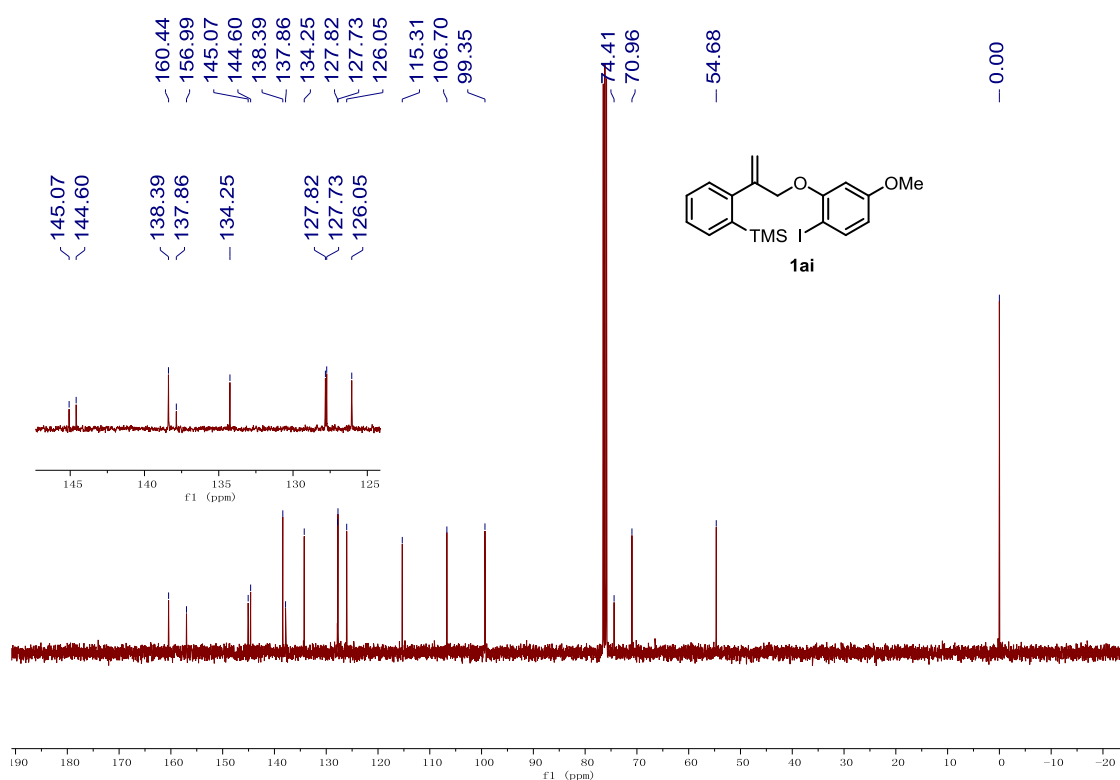
Supplementary Figure 22. ¹H NMR (400 MHz, CDCl₃) spectra of 1ah



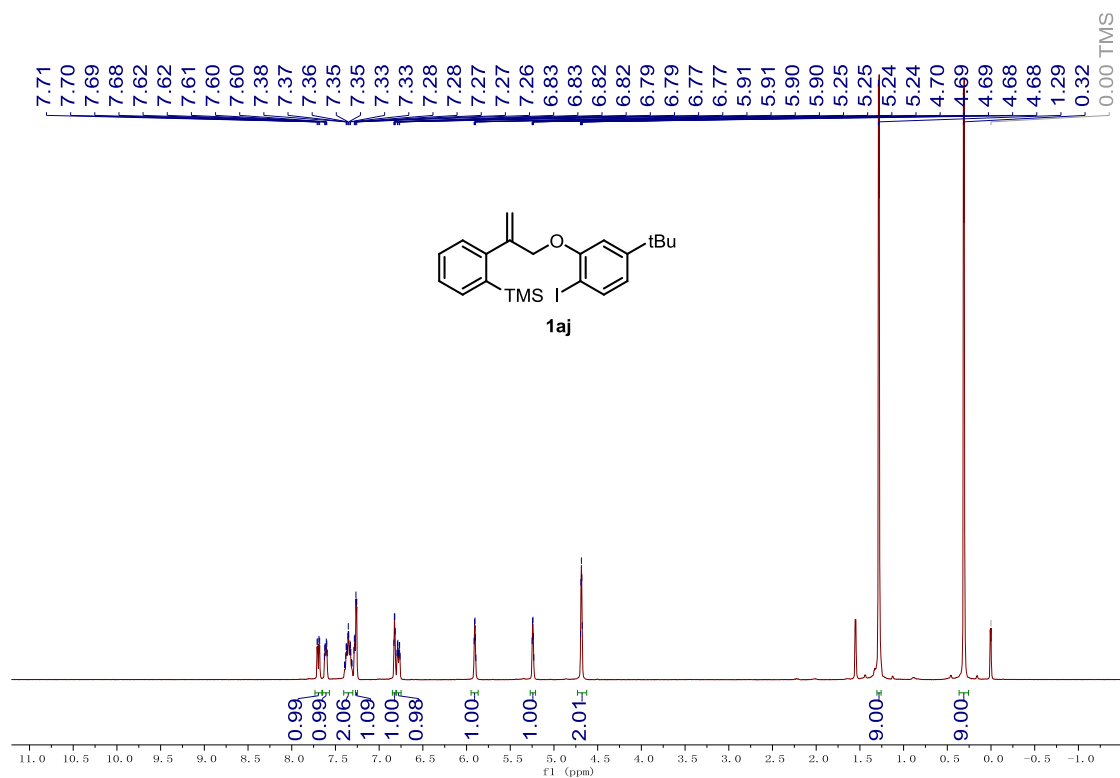
Supplementary Figure 23. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ah



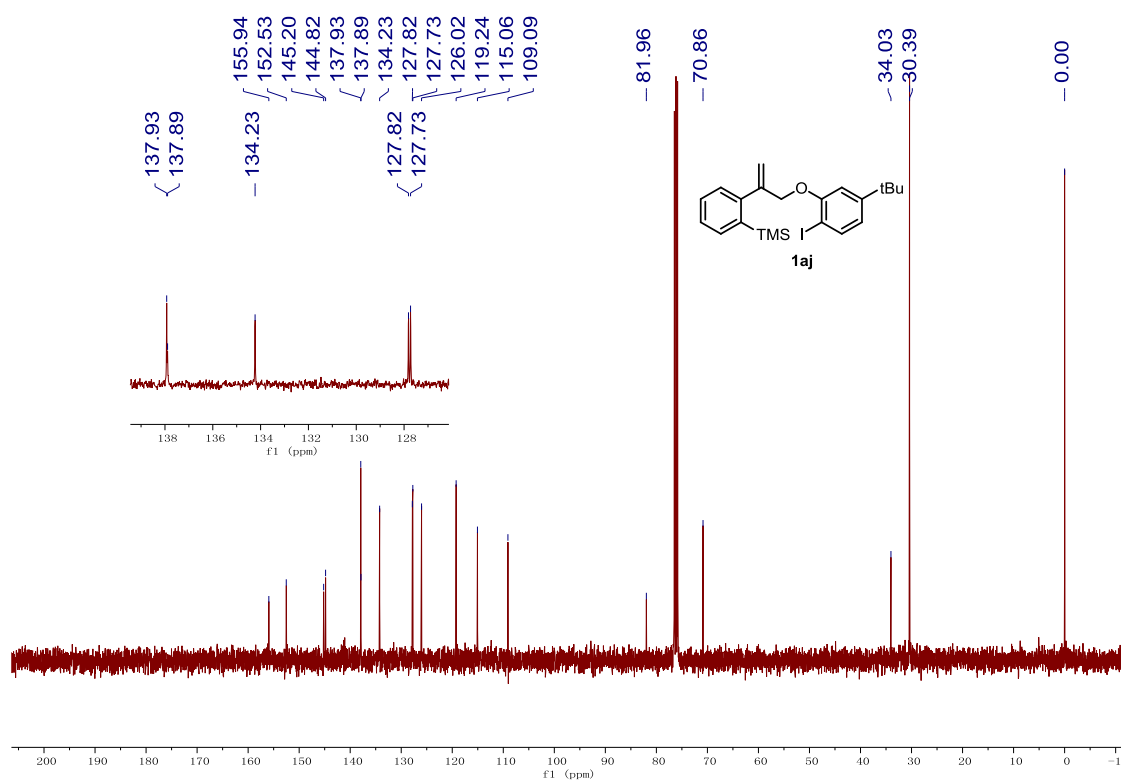
Supplementary Figure 24. ¹H NMR (400 MHz, CDCl₃) spectra of **1ai**



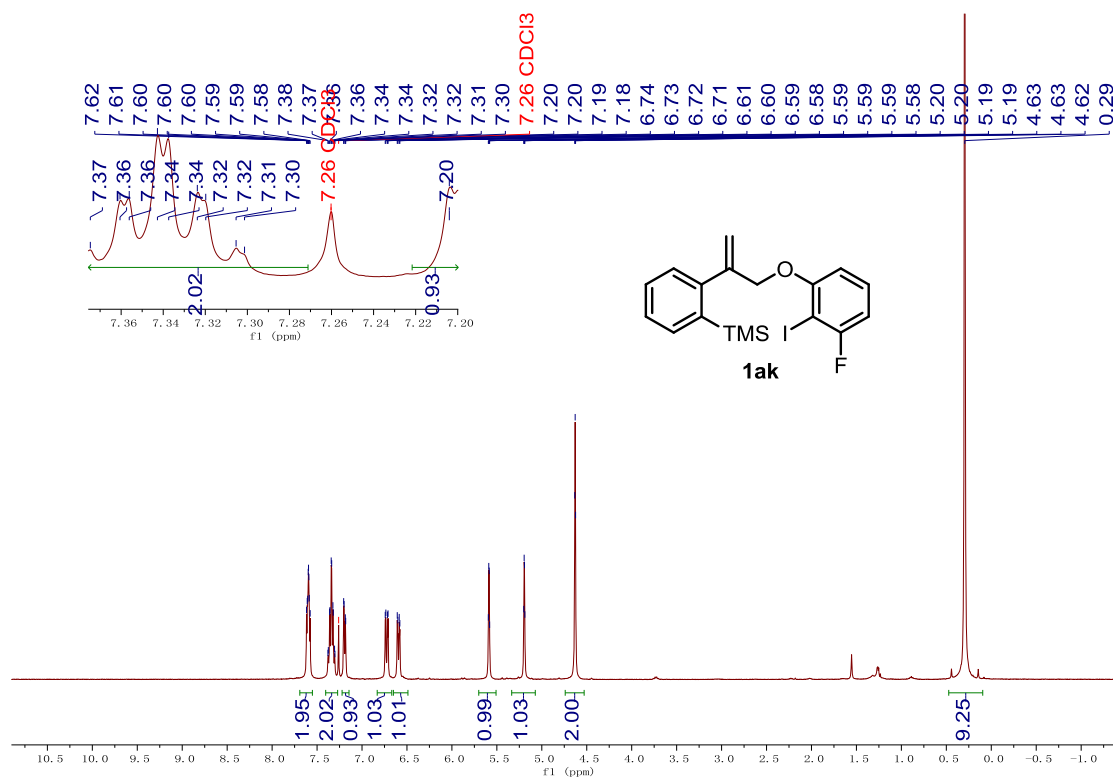
Supplementary Figure 25. ¹³C NMR (101 MHz, CDCl₃) spectra of **1ai**



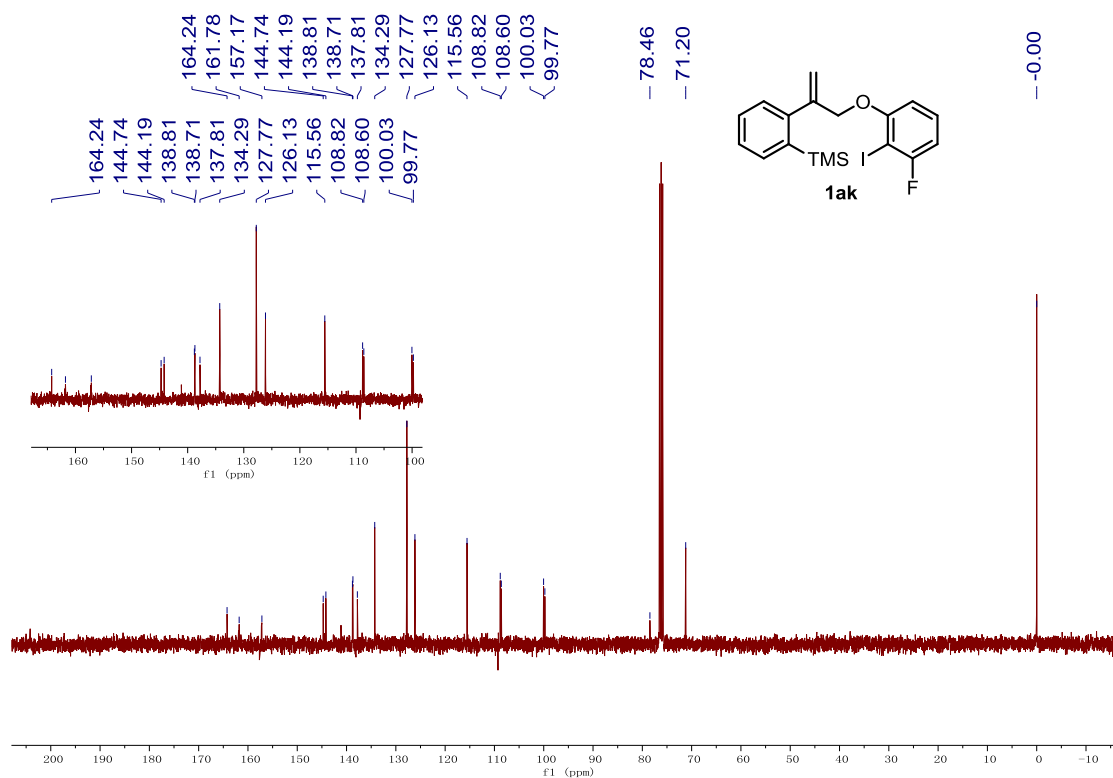
Supplementary Figure 26. ¹H NMR (400 MHz, CDCl₃) spectra of **1aj**



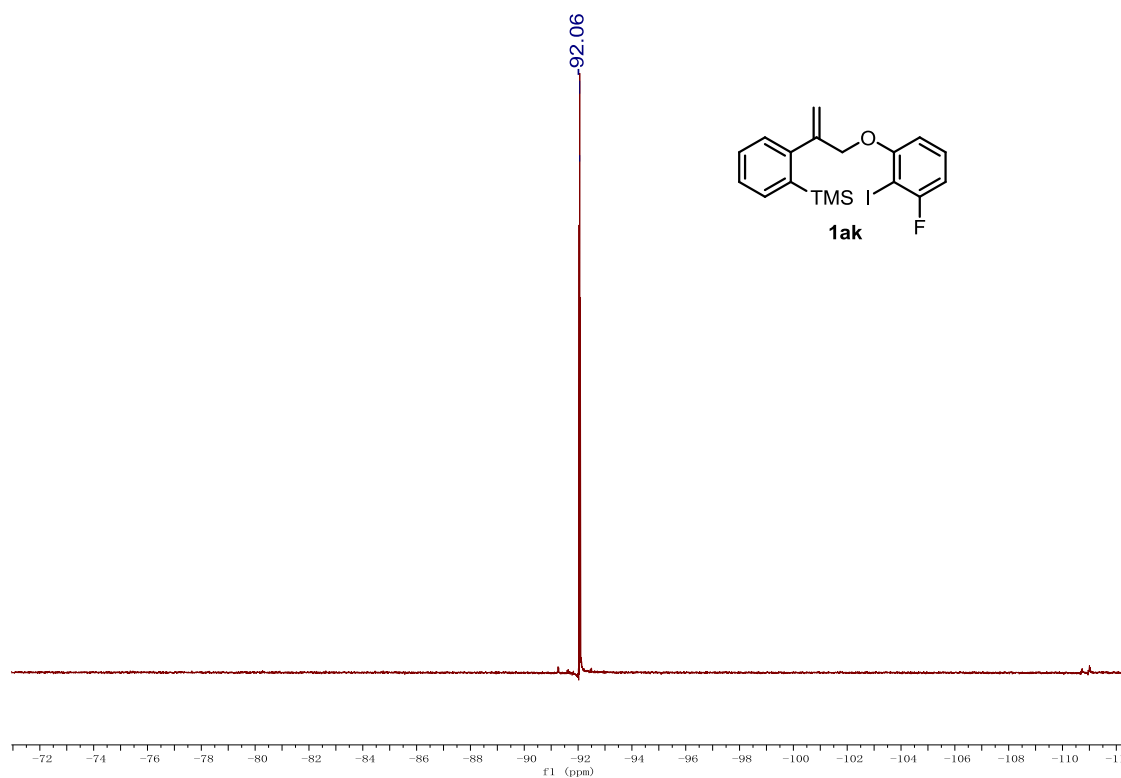
Supplementary Figure 27. ¹³C NMR (101 MHz, CDCl₃) spectra of **1aj**



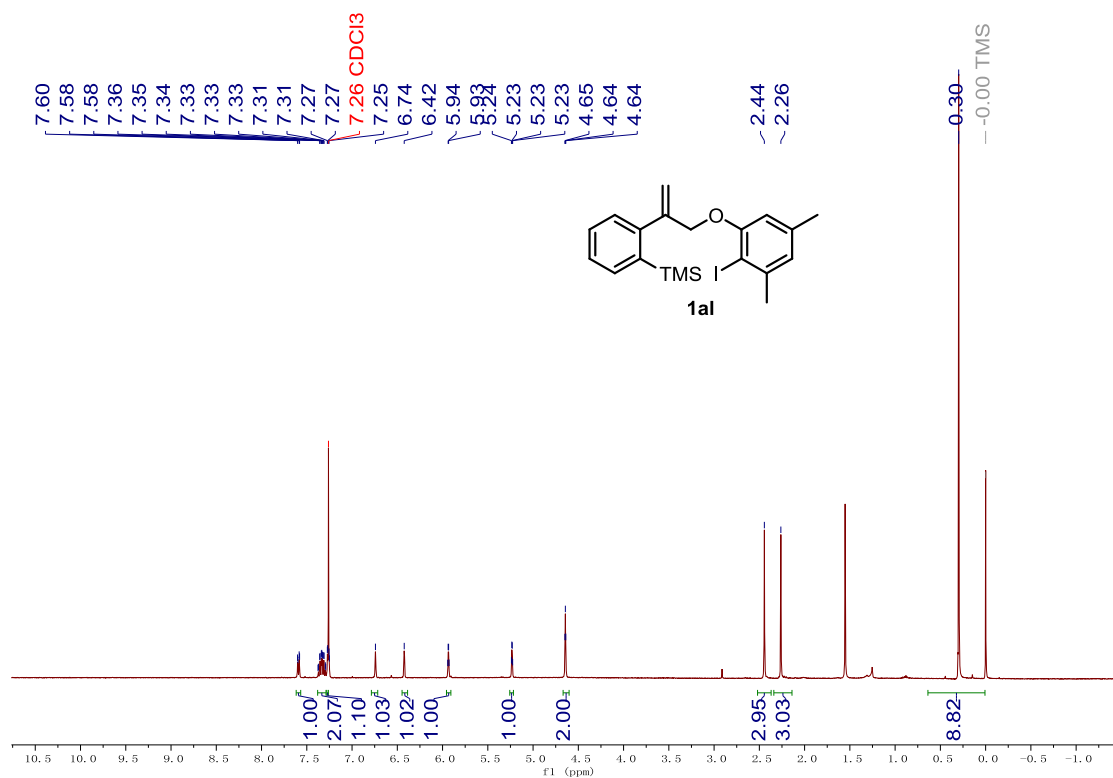
Supplementary Figure 28. ¹H NMR (400 MHz, CDCl₃) spectra of 1ak



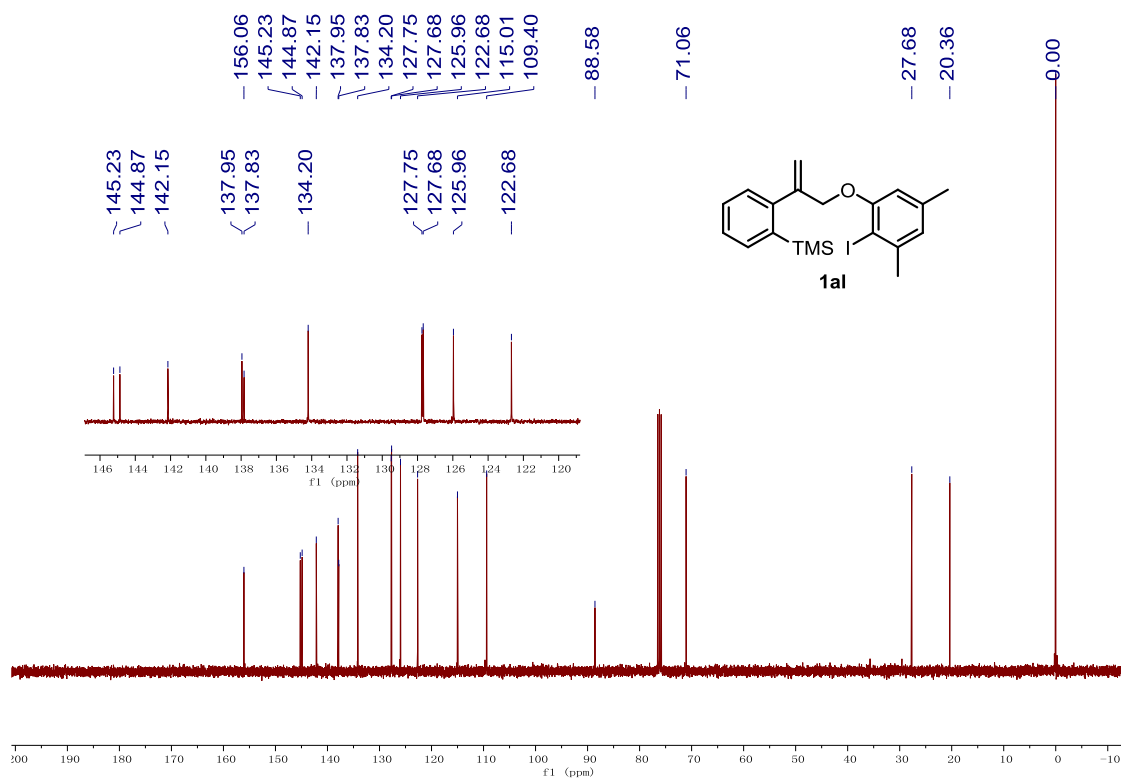
Supplementary Figure 29. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ak



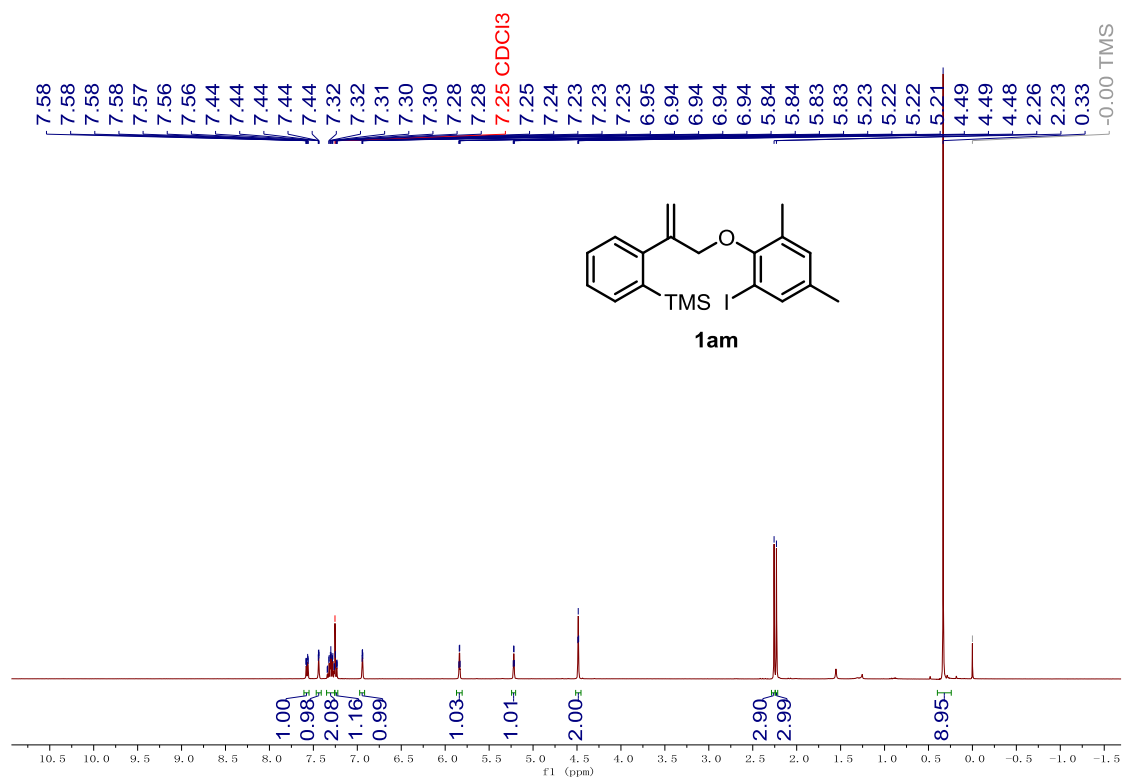
Supplementary Figure 30. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1ak**



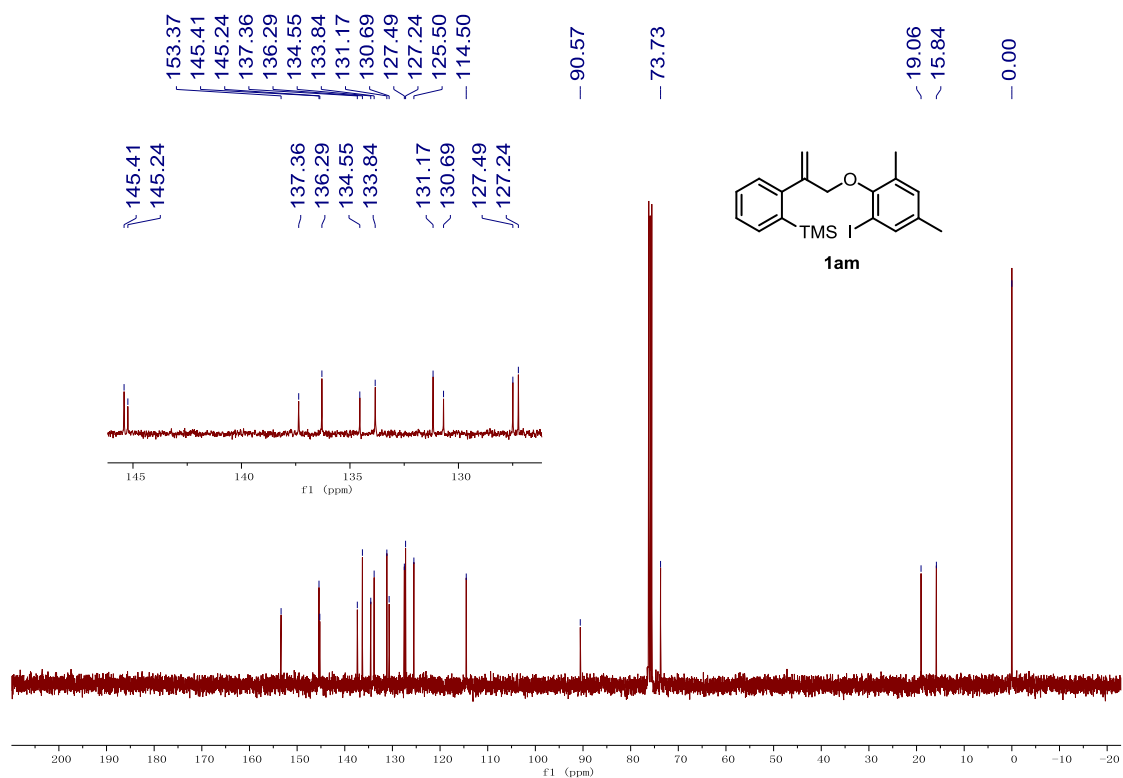
Supplementary Figure 31. ¹H NMR (400 MHz, CDCl₃) spectra of 1al



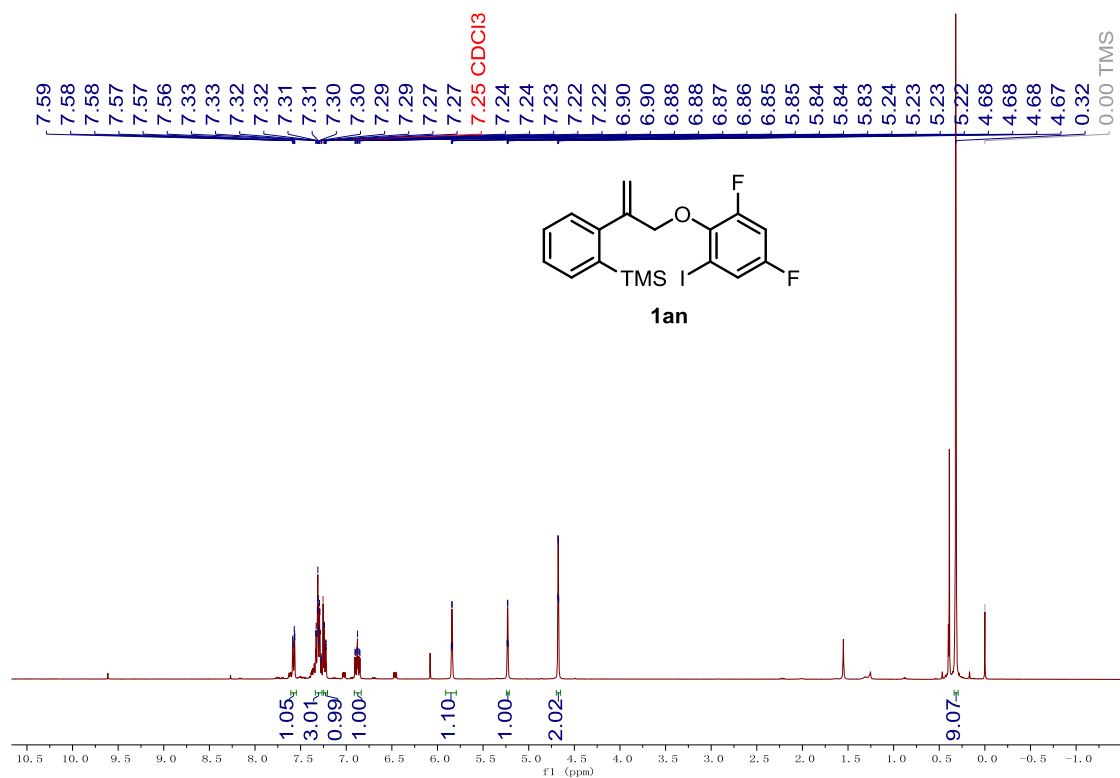
Supplementary Figure 32. ¹³C NMR (101 MHz, CDCl₃) spectra of 1al



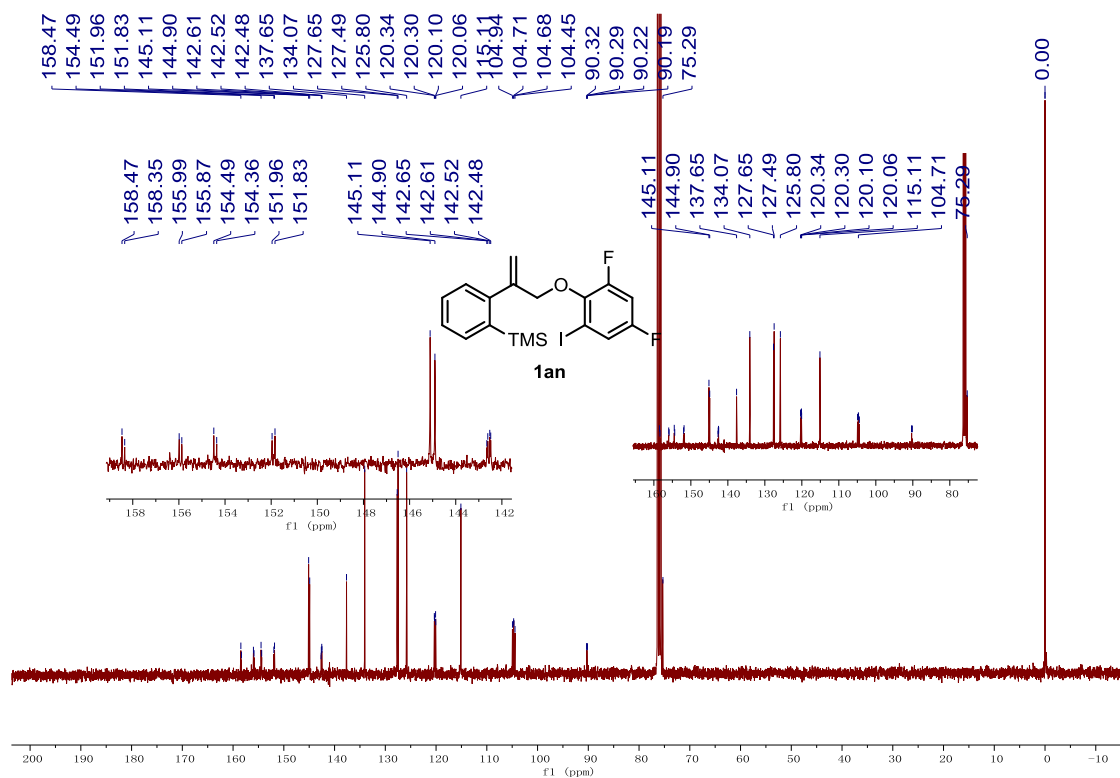
Supplementary Figure 33. ¹H NMR (400 MHz, CDCl₃) spectra of **1am**



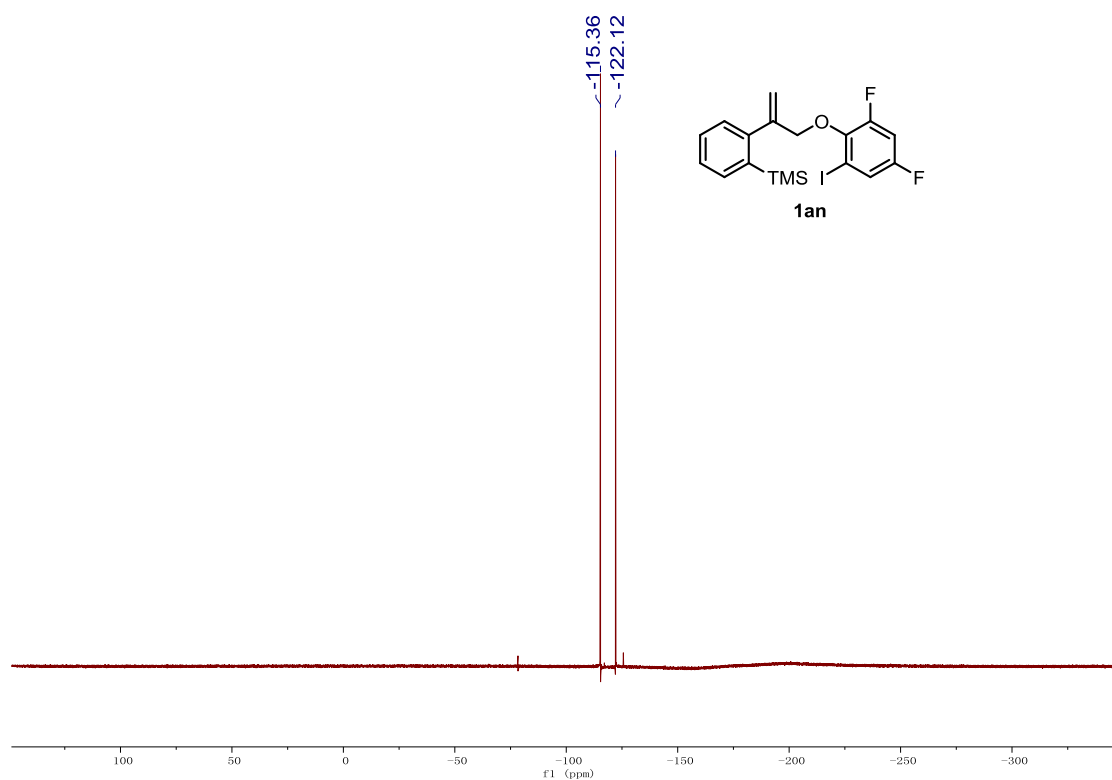
Supplementary Figure 34. ¹³C NMR (101 MHz, CDCl₃) spectra of **1am**



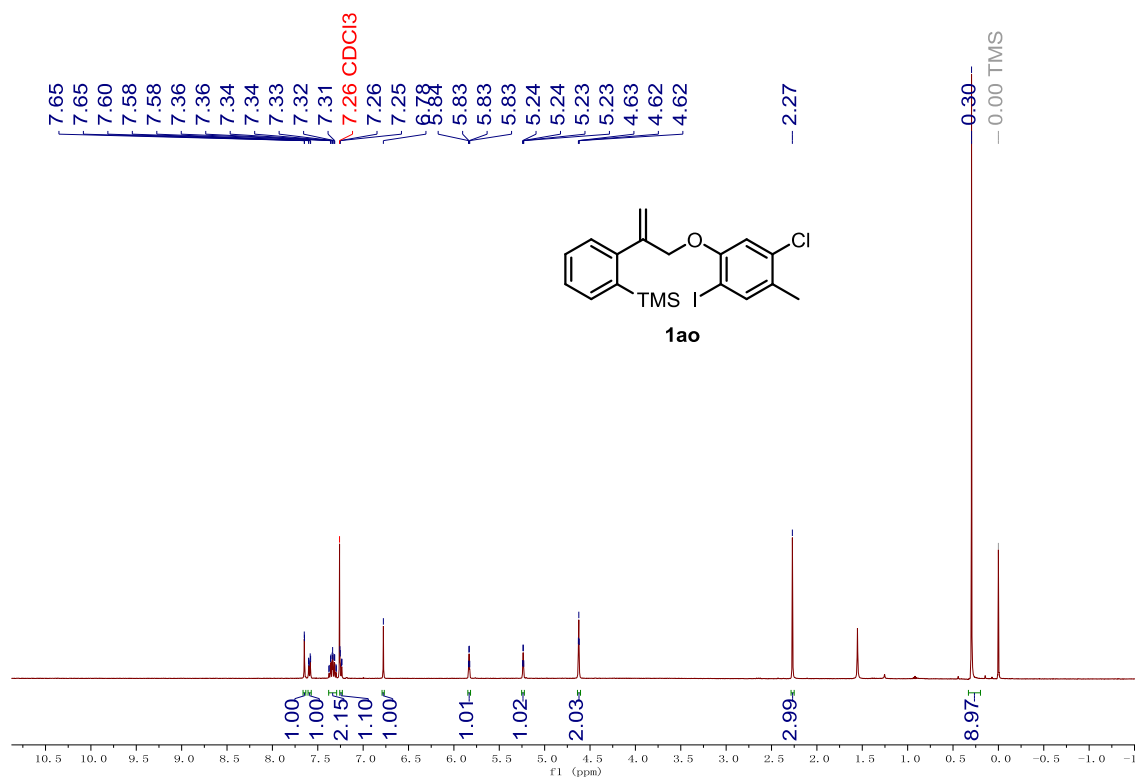
Supplementary Figure 35. ¹H NMR (400 MHz, CDCl₃) spectra of 1an



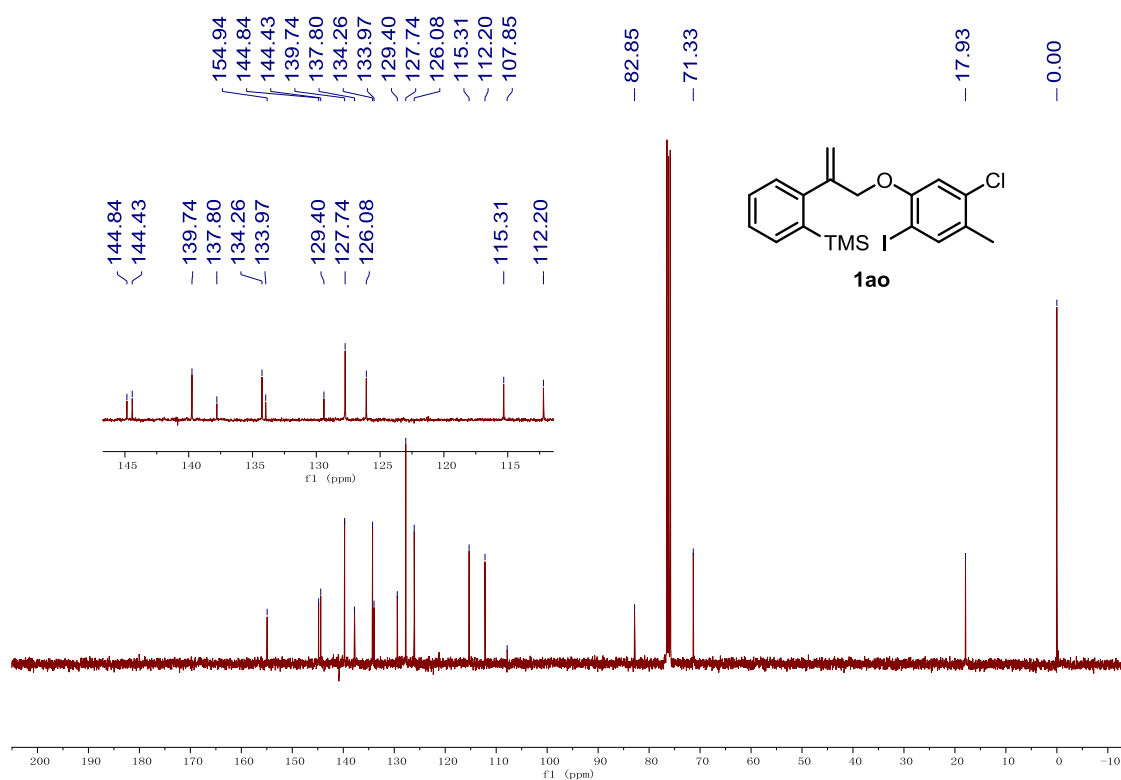
Supplementary Figure 36. ¹³C NMR (101 MHz, CDCl₃) spectra of 1an



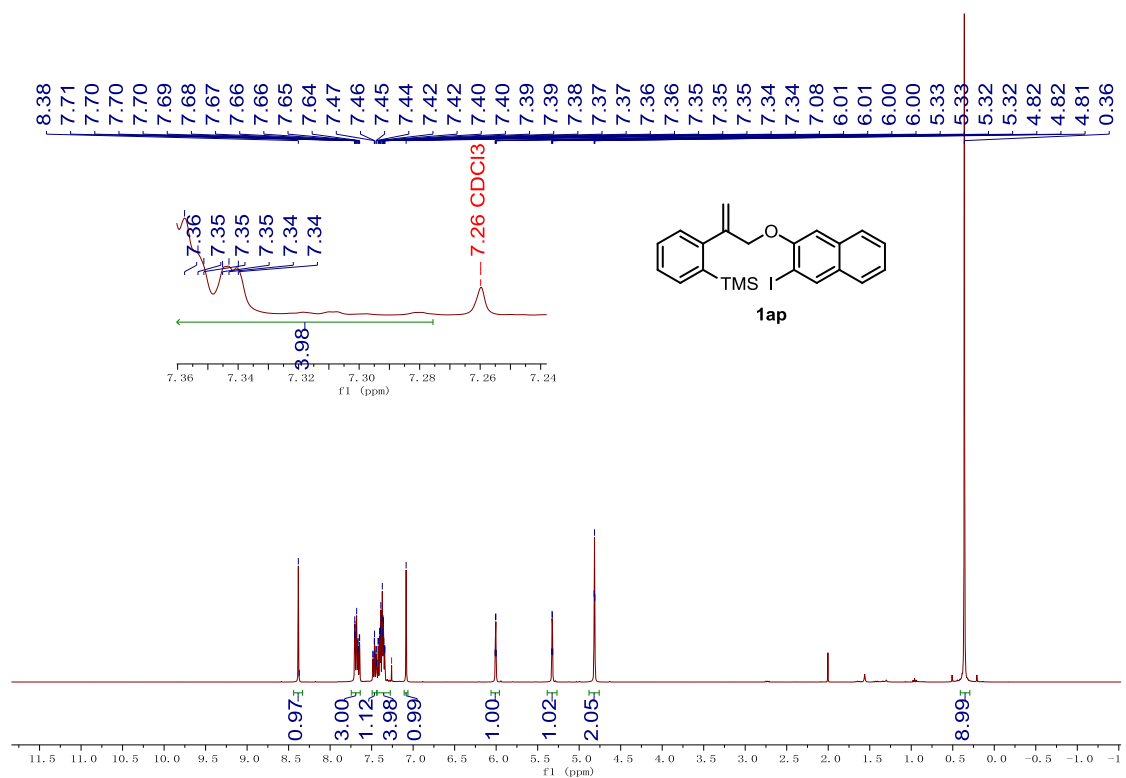
Supplementary Figure 37. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1an**



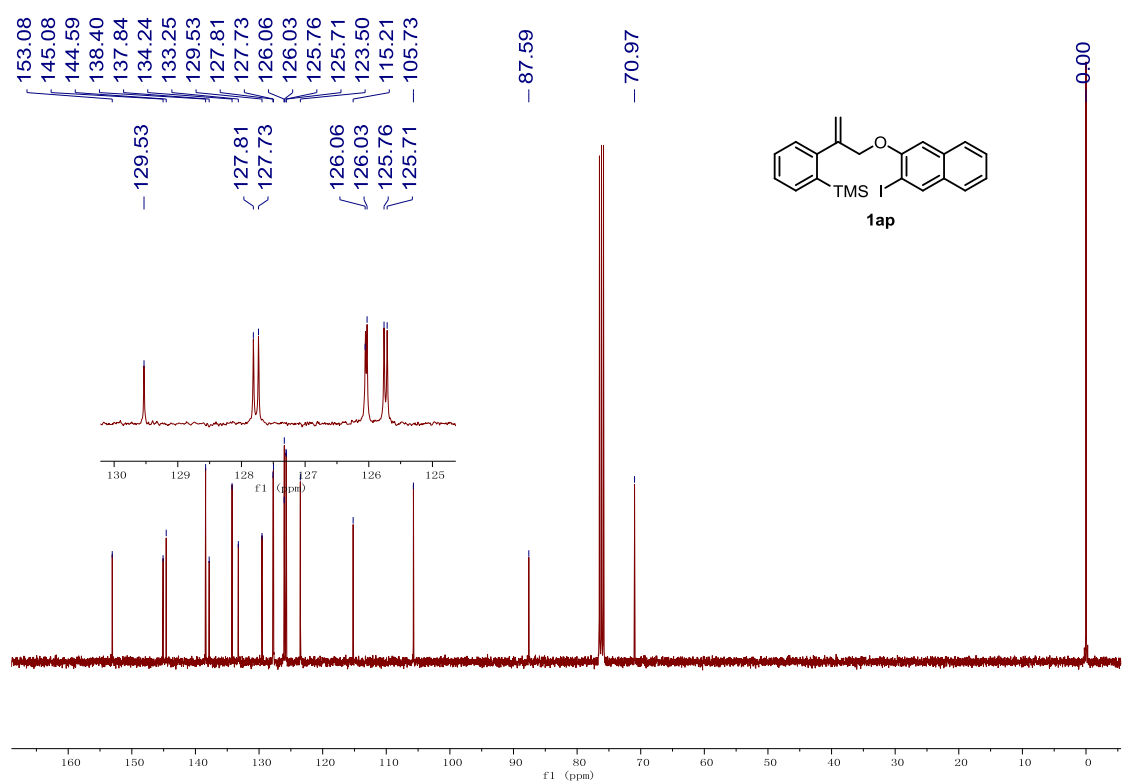
Supplementary Figure 38. ¹H NMR (400 MHz, CDCl₃) spectra of 1ao



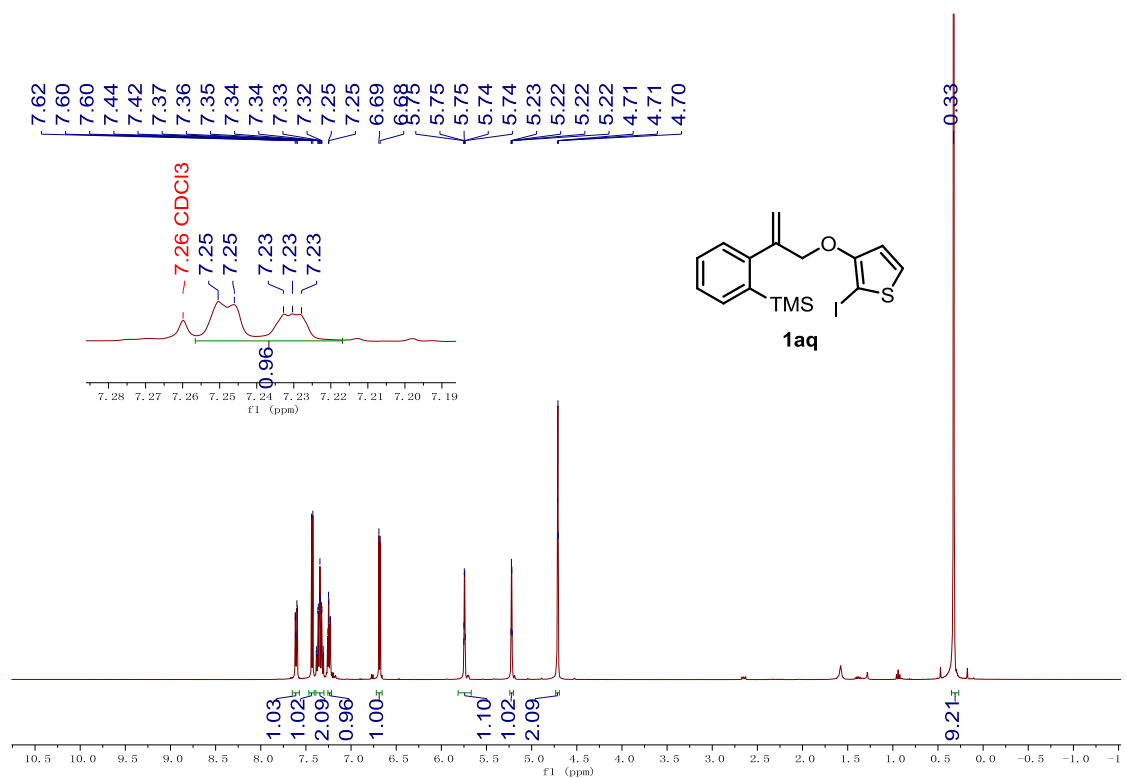
Supplementary Figure 39. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ao



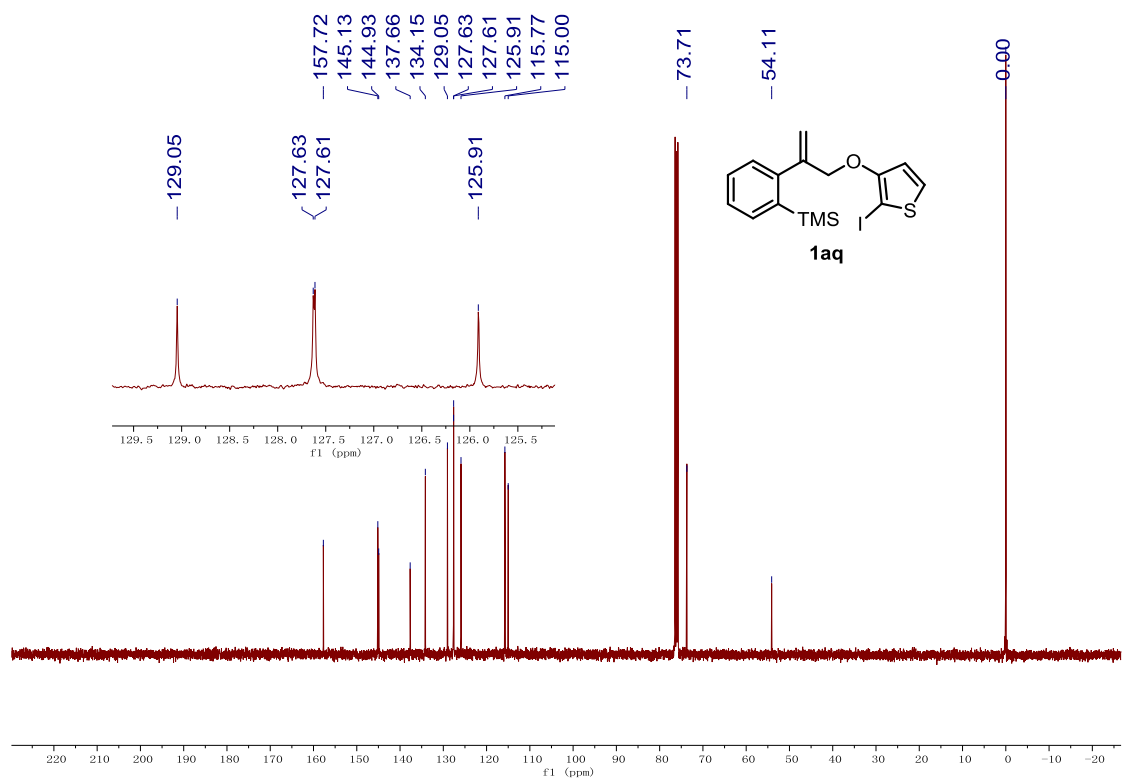
Supplementary Figure 40. ¹H NMR (400 MHz, CDCl₃) spectra of **1ap**



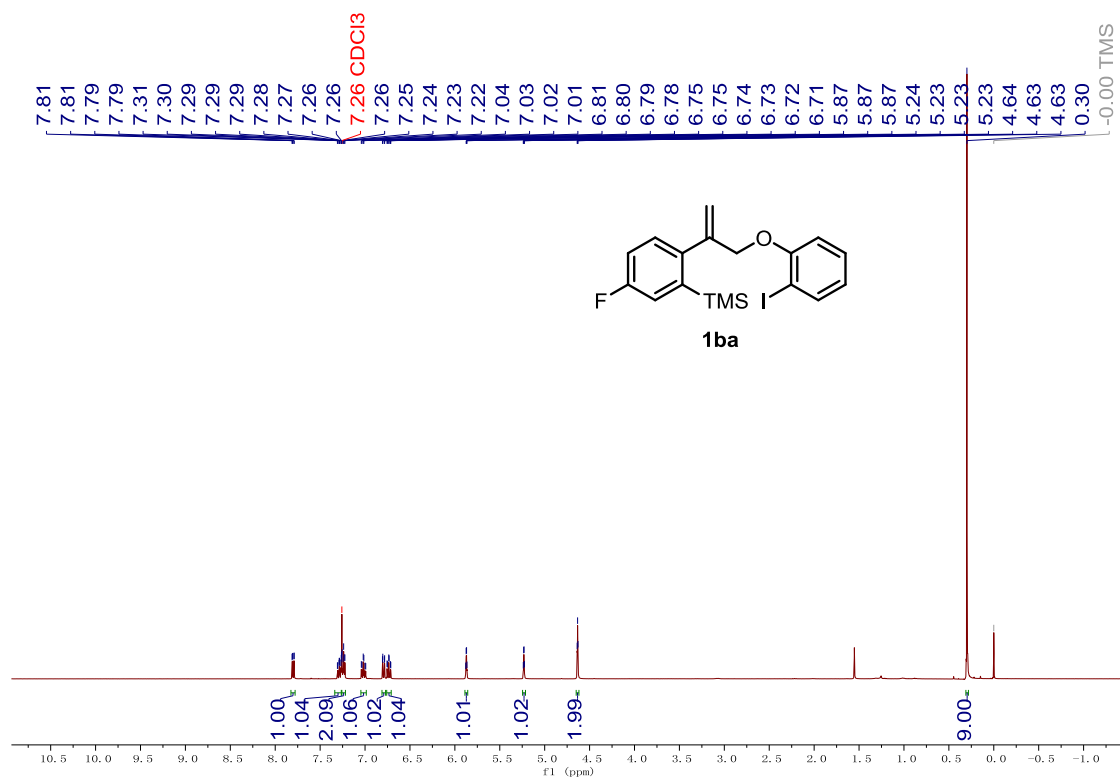
Supplementary Figure 41. ¹³C NMR (101 MHz, CDCl₃) spectra of **1ap**



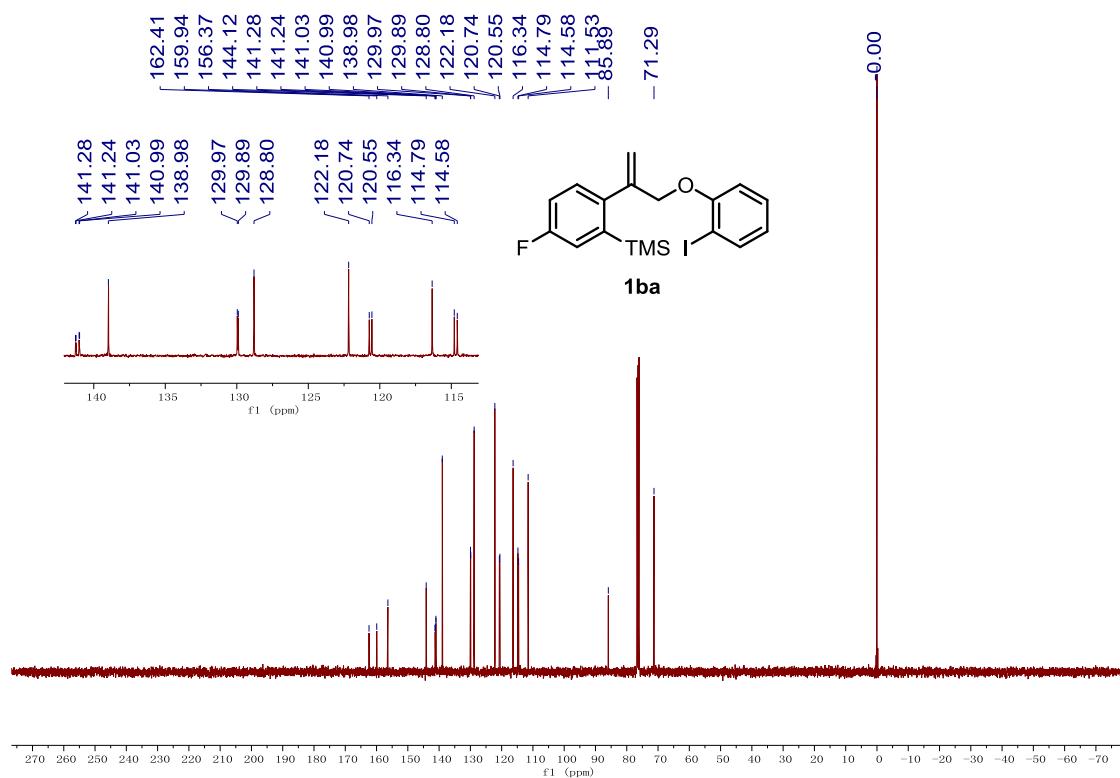
Supplementary Figure 42. ¹H NMR (400 MHz, CDCl₃) spectra of 1aq



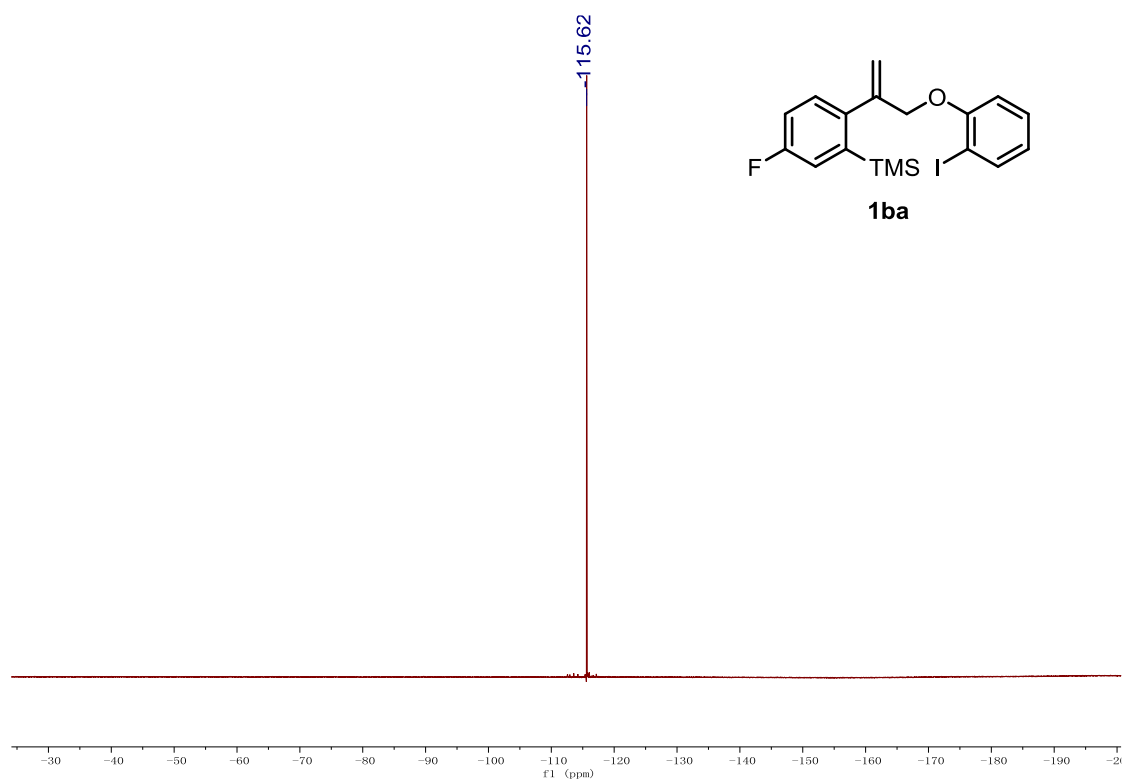
Supplementary Figure 43. ¹³C NMR (101 MHz, CDCl₃) spectra of 1aq



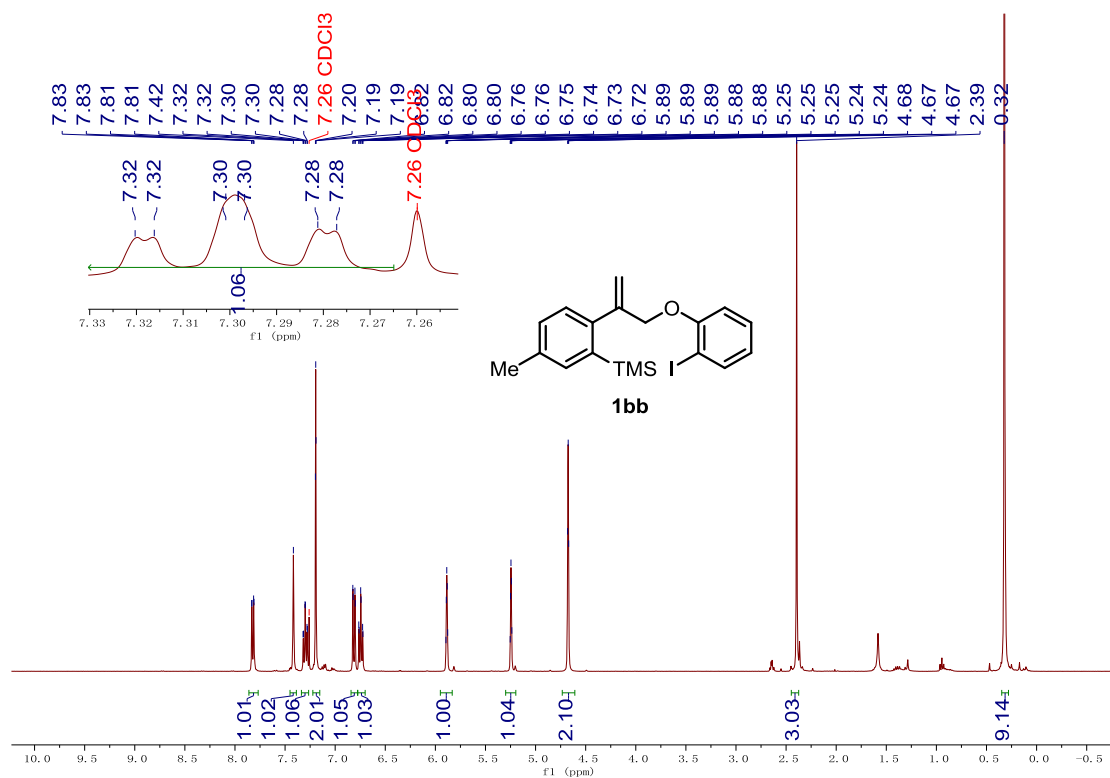
Supplementary Figure 44. ¹H NMR (400 MHz, CDCl₃) spectra of **1ba**



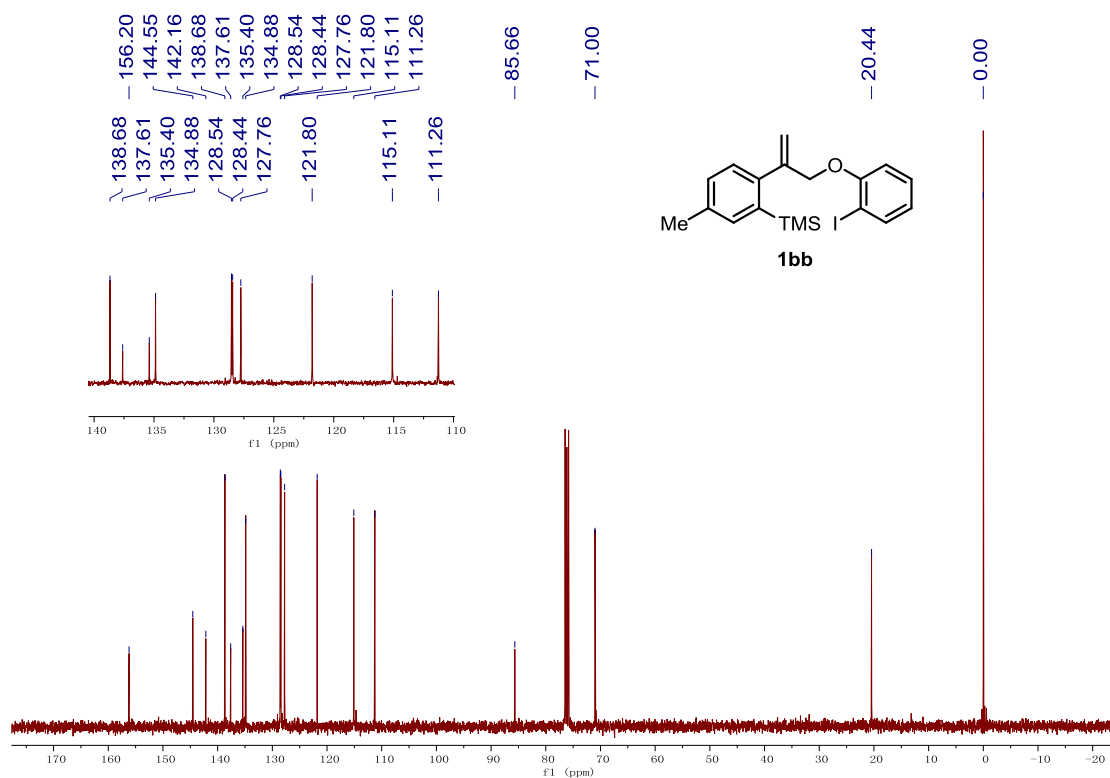
Supplementary Figure 45. ¹³C NMR (101 MHz, CDCl₃) spectra of **1ba**



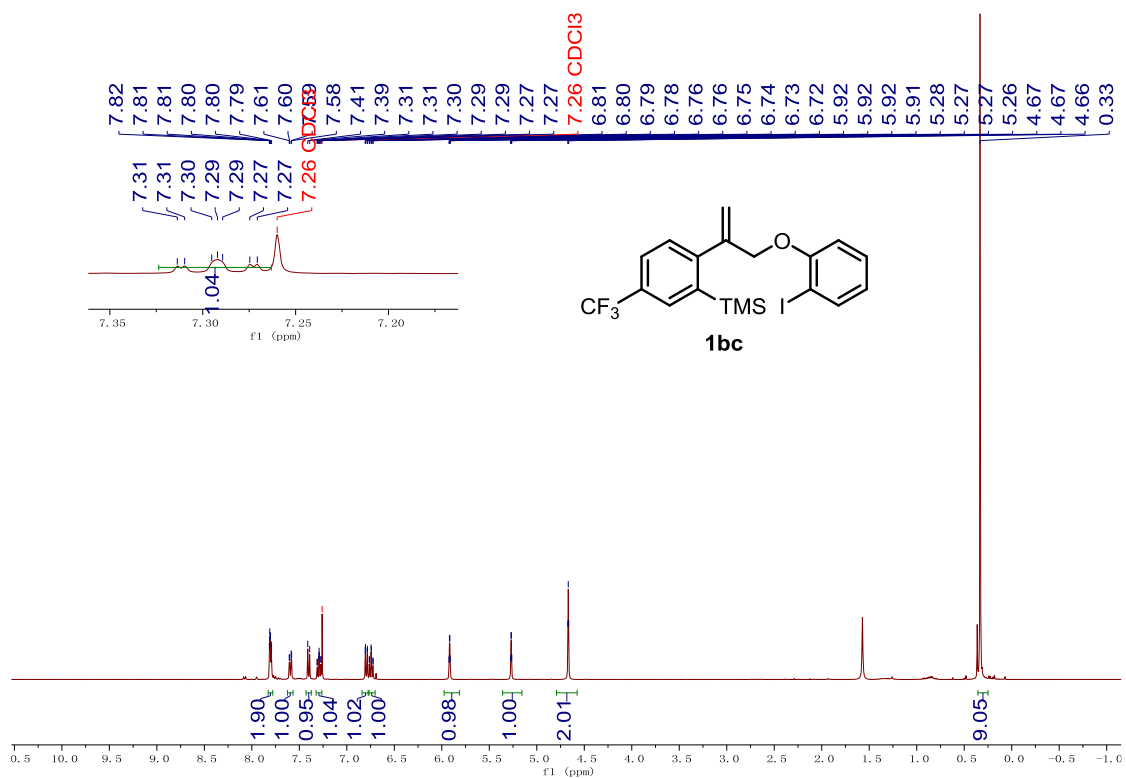
Supplementary Figure 46. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1ba**



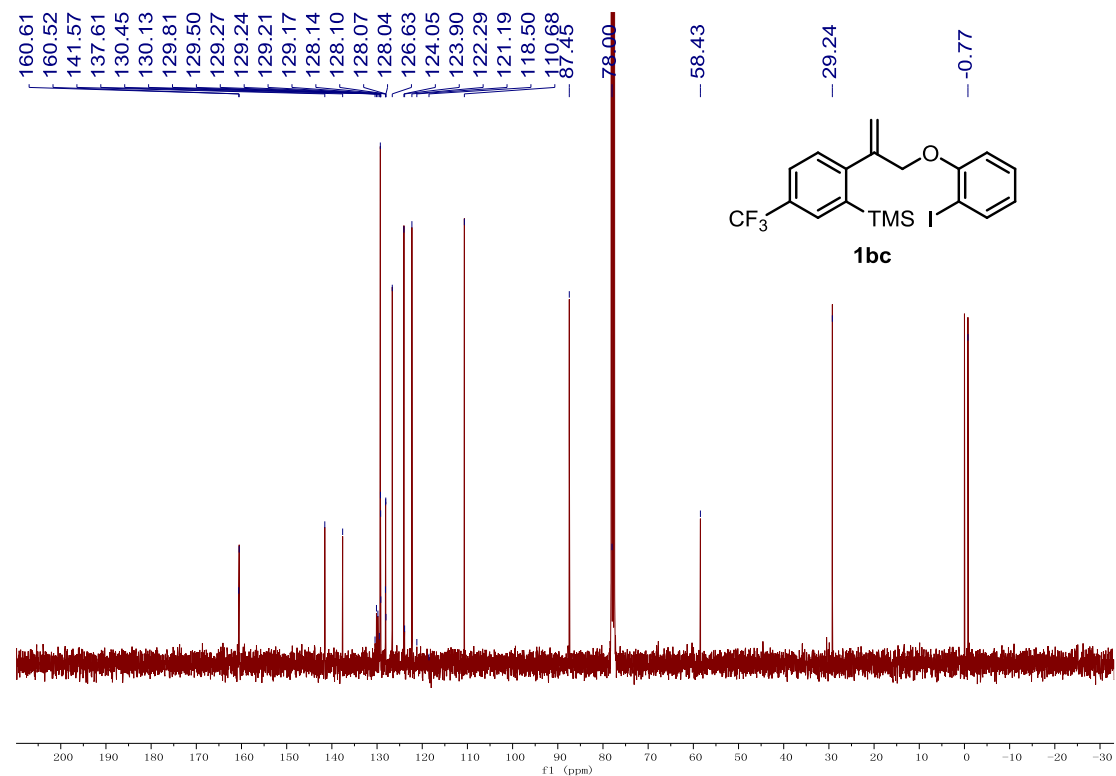
Supplementary Figure 47. ¹H NMR (400 MHz, CDCl₃) spectra of **1bb**



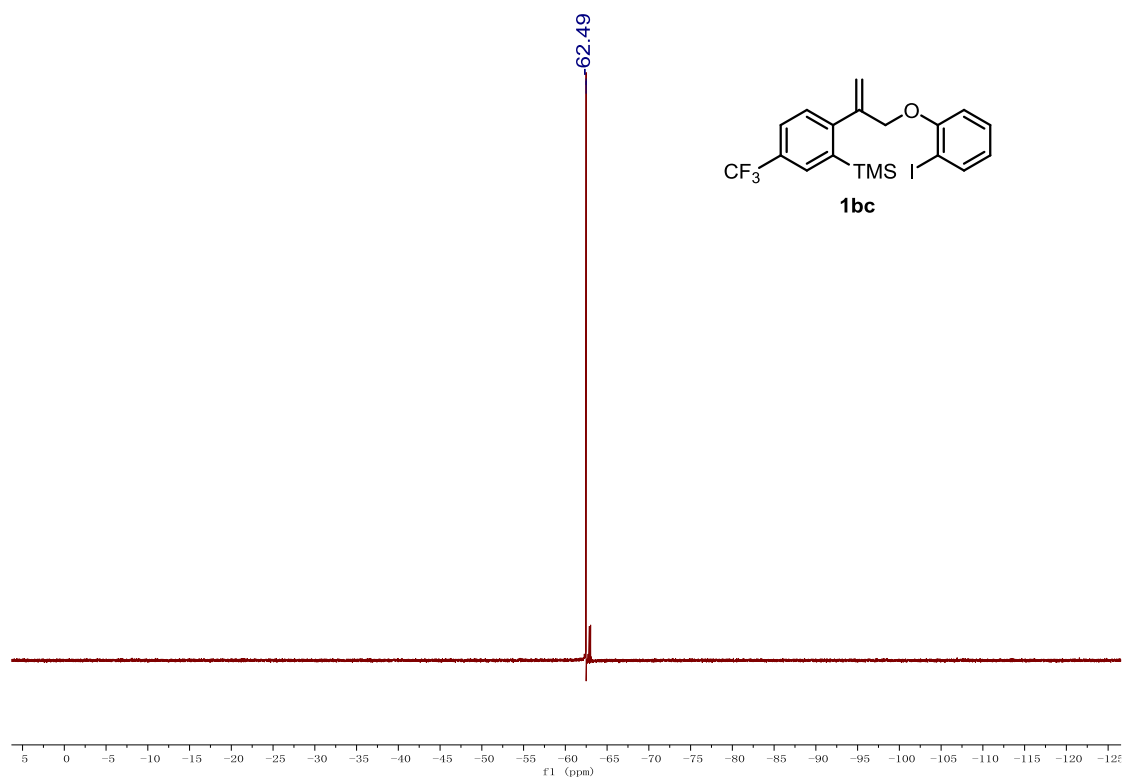
Supplementary Figure 48. ¹³C NMR (101 MHz, CDCl₃) spectra of **1bb**



Supplementary Figure 49. ¹H NMR (400 MHz, CDCl₃) spectra of **1bc**

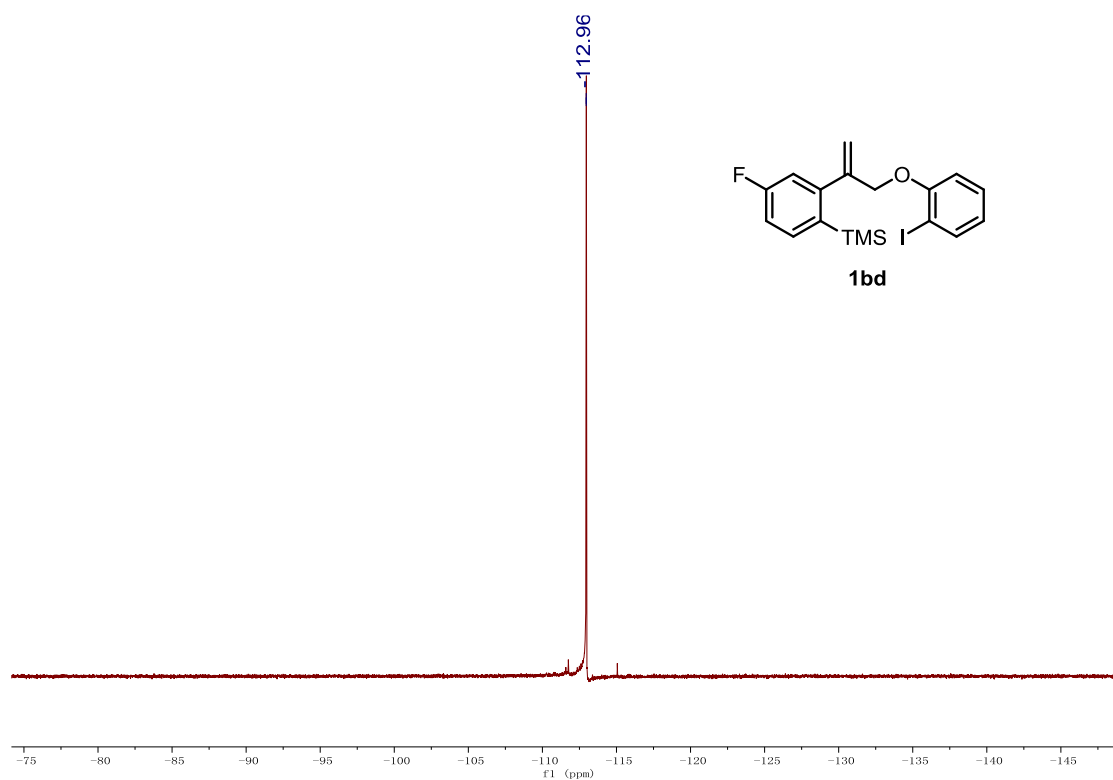


Supplementary Figure 50. ¹³C NMR (101 MHz, CDCl₃) spectra of **1bc**

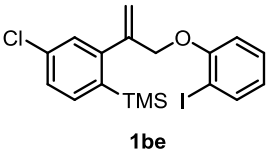


Supplementary Figure 51. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1bc**





Supplementary Figure 54. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1bd**



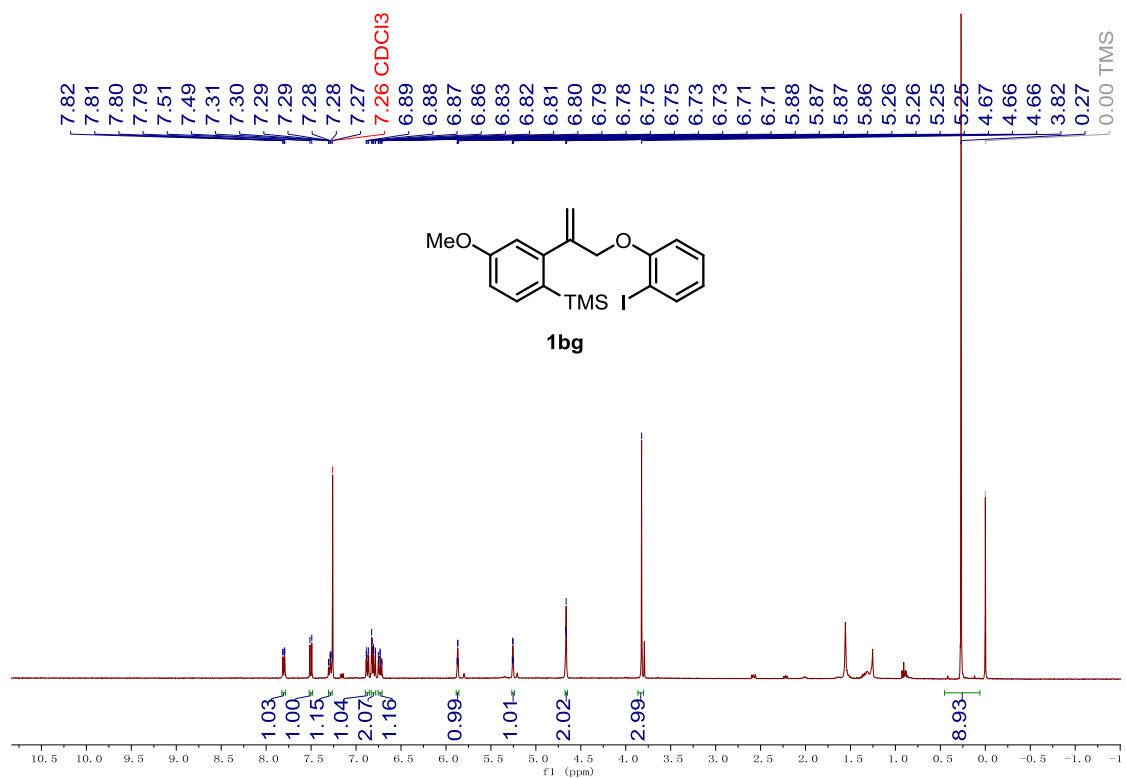
Chemical structure of **1be**: CC(C)(C)C(=C)c1cc(Cl)ccc1COc2ccccc2I

¹³C NMR spectrum (CDCl₃) of **1be**. The spectrum shows peaks corresponding to the structure, with the TMS group labeled 'TMS' and the compound labeled '1be'.

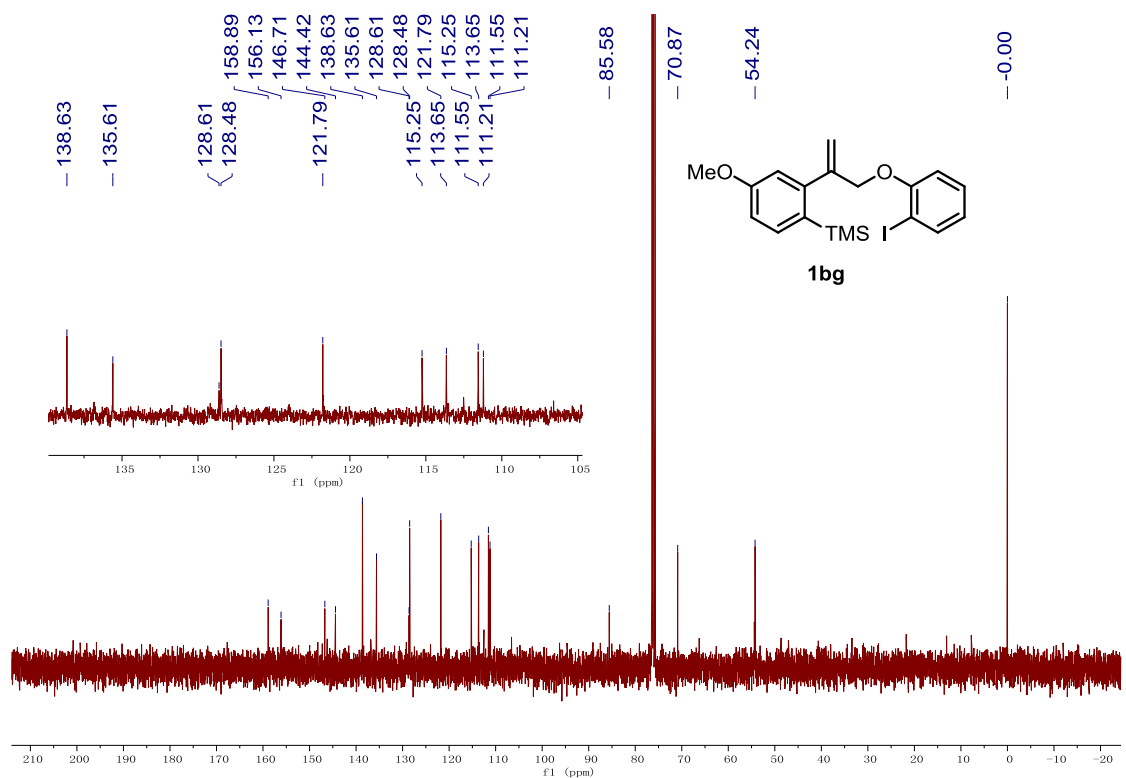
Chemical shift values (ppm):

- 146.79, 143.72, 138.84, 136.20, 135.61, 133.94
- 128.65, 128.05, 126.19, 122.07
- 116.49, 111.32
- 70.91, 85.71
- 0.00 (TMS)

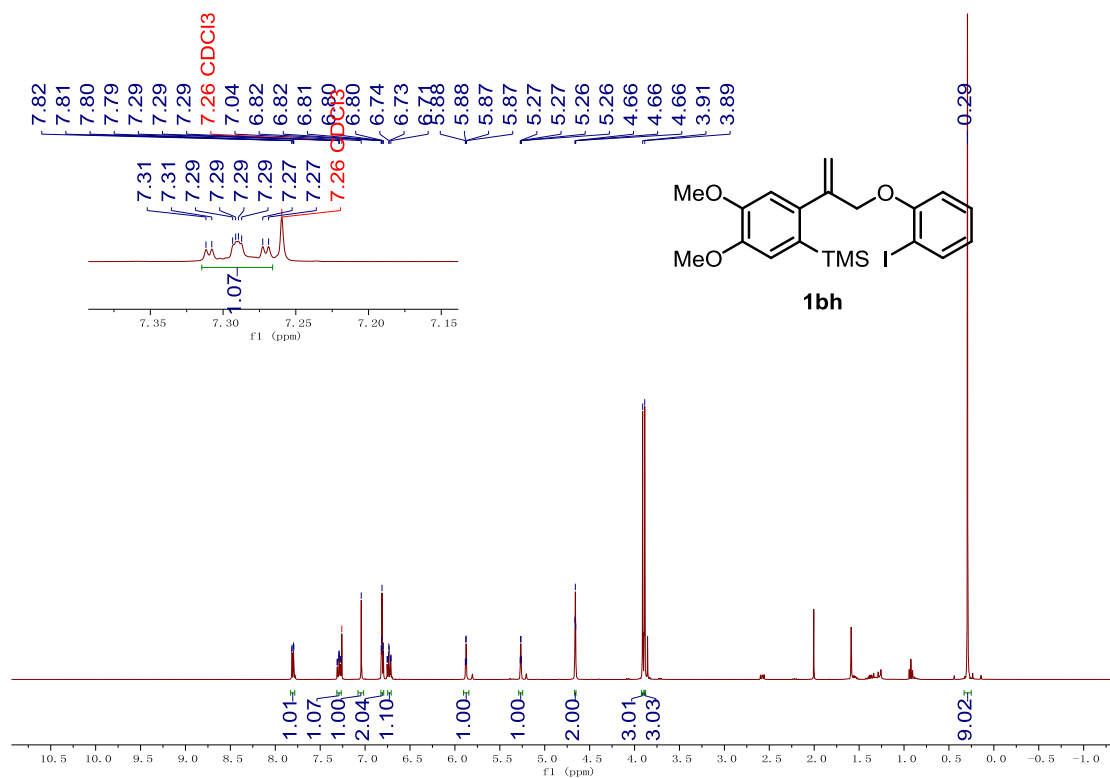
s90



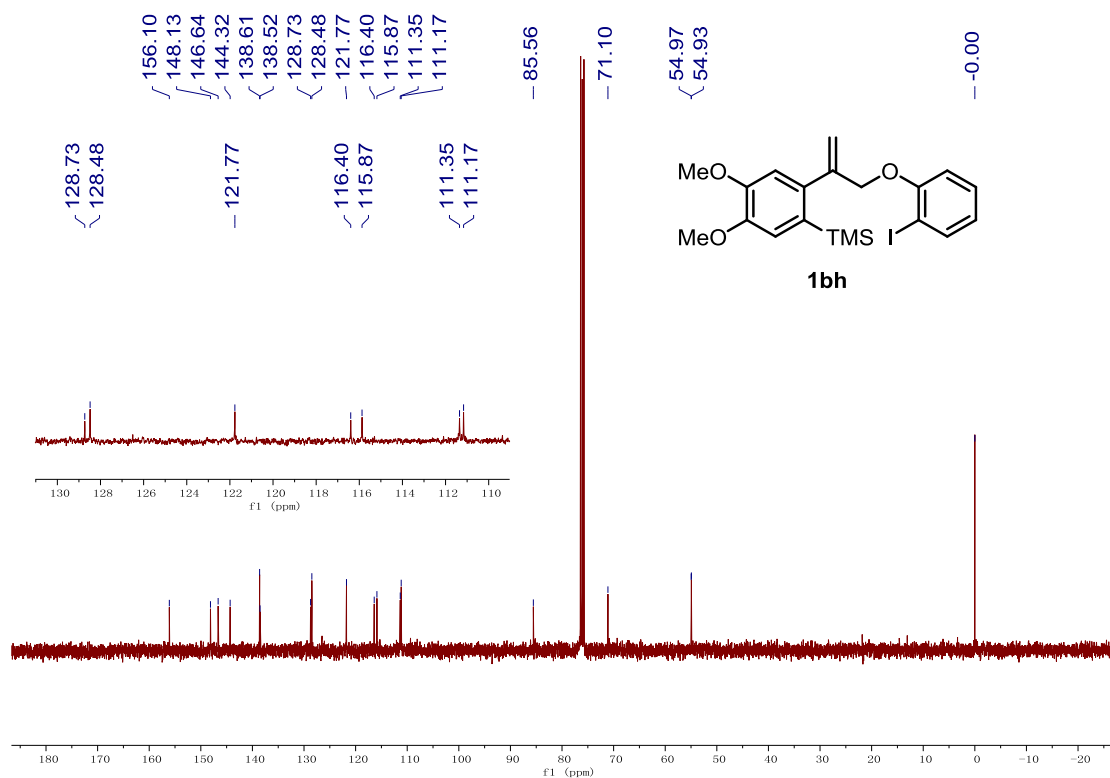
Supplementary Figure 59. ¹H NMR (400 MHz, CDCl₃) spectra of **1bg**



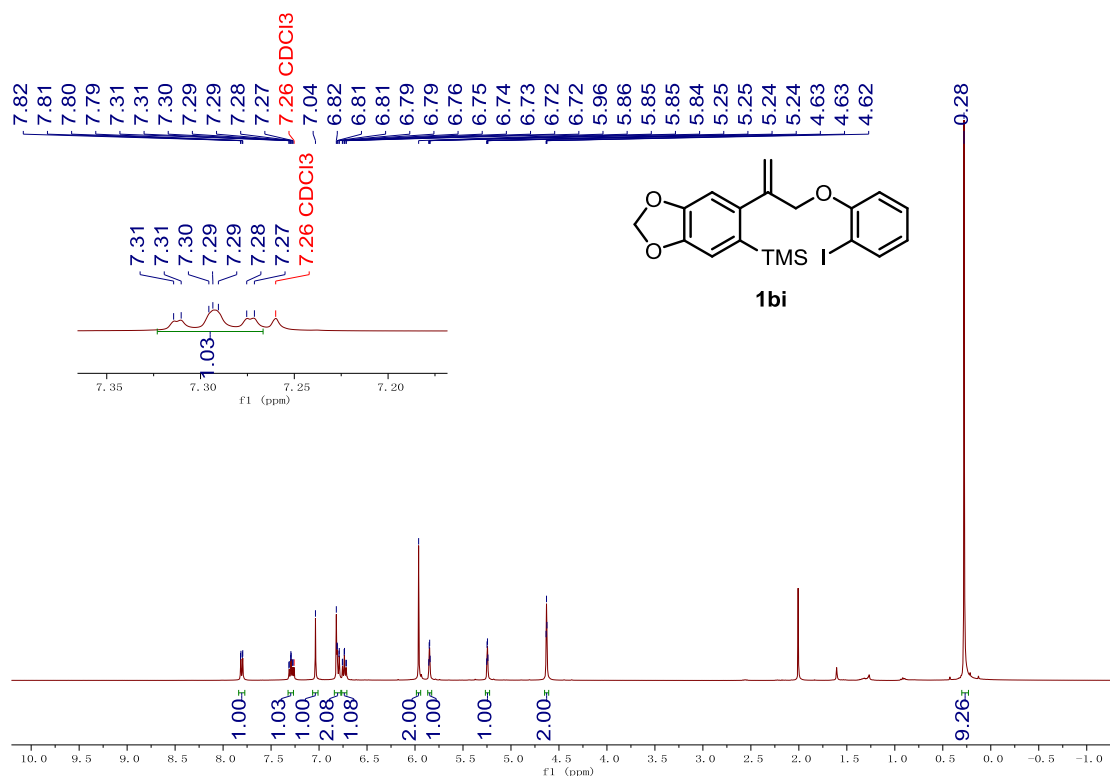
Supplementary Figure 60. ¹³C NMR (101 MHz, CDCl₃) spectra of **1bg**



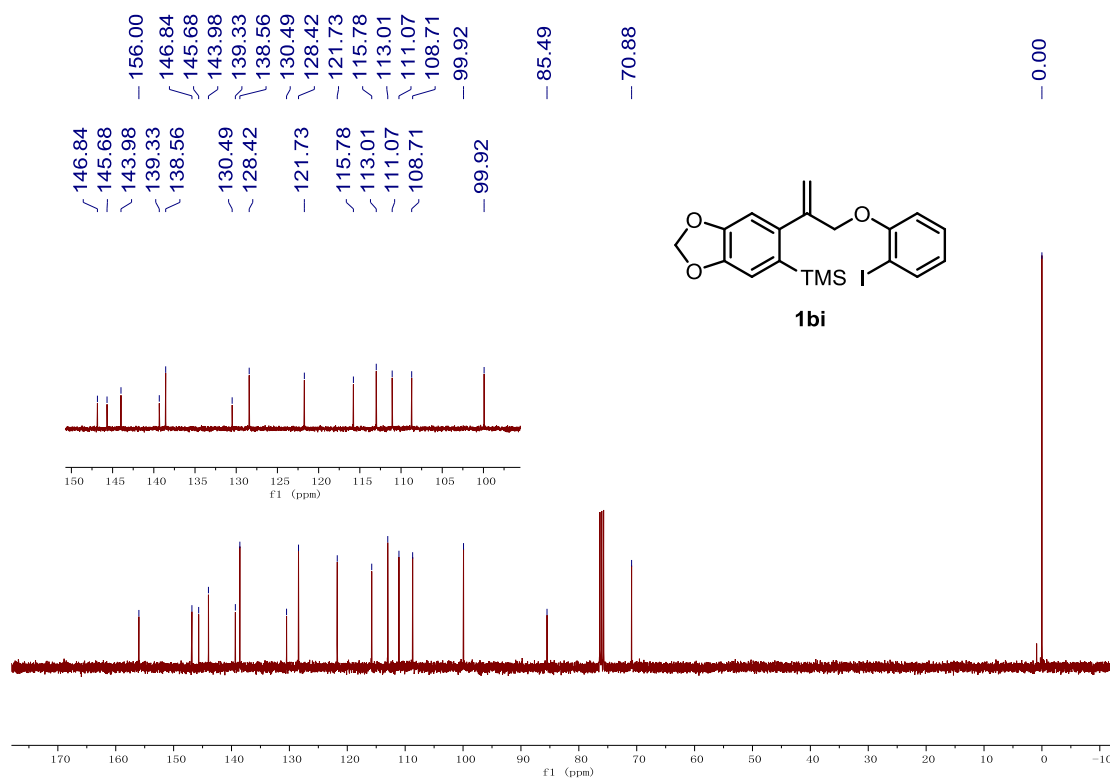
Supplementary Figure 61. ¹H NMR (400 MHz, CDCl₃) spectra of 1bh



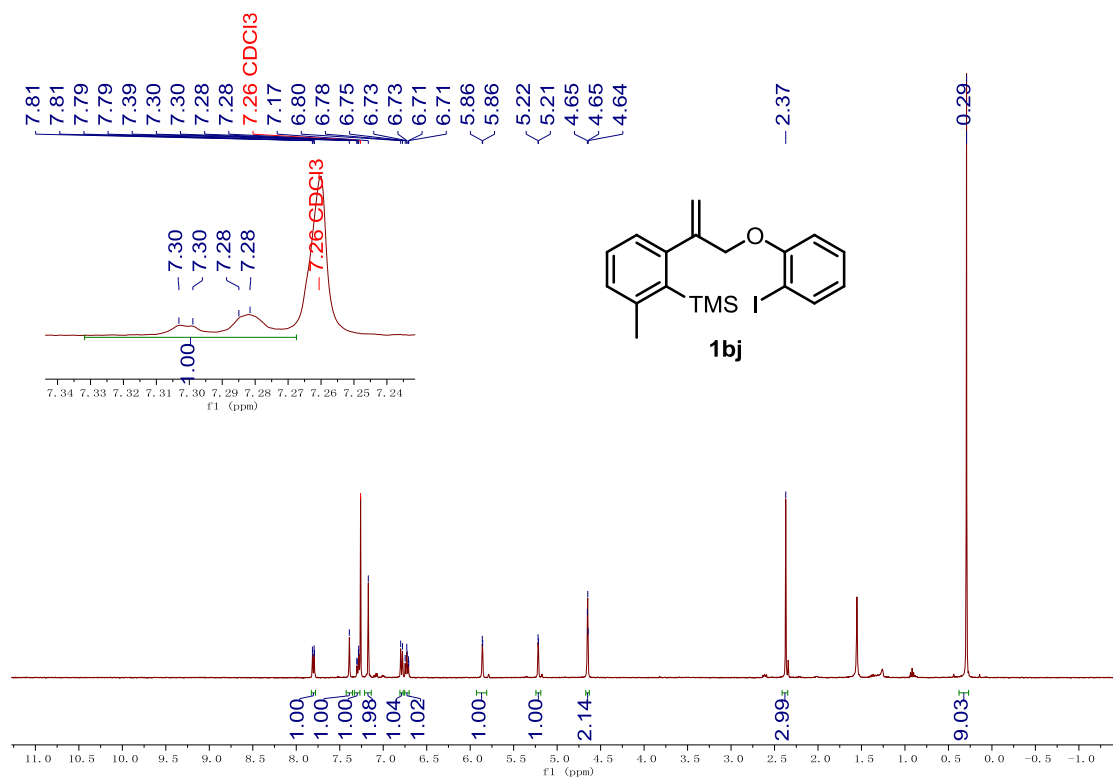
Supplementary Figure 62. ¹³C NMR (101 MHz, CDCl₃) spectra of 1bh



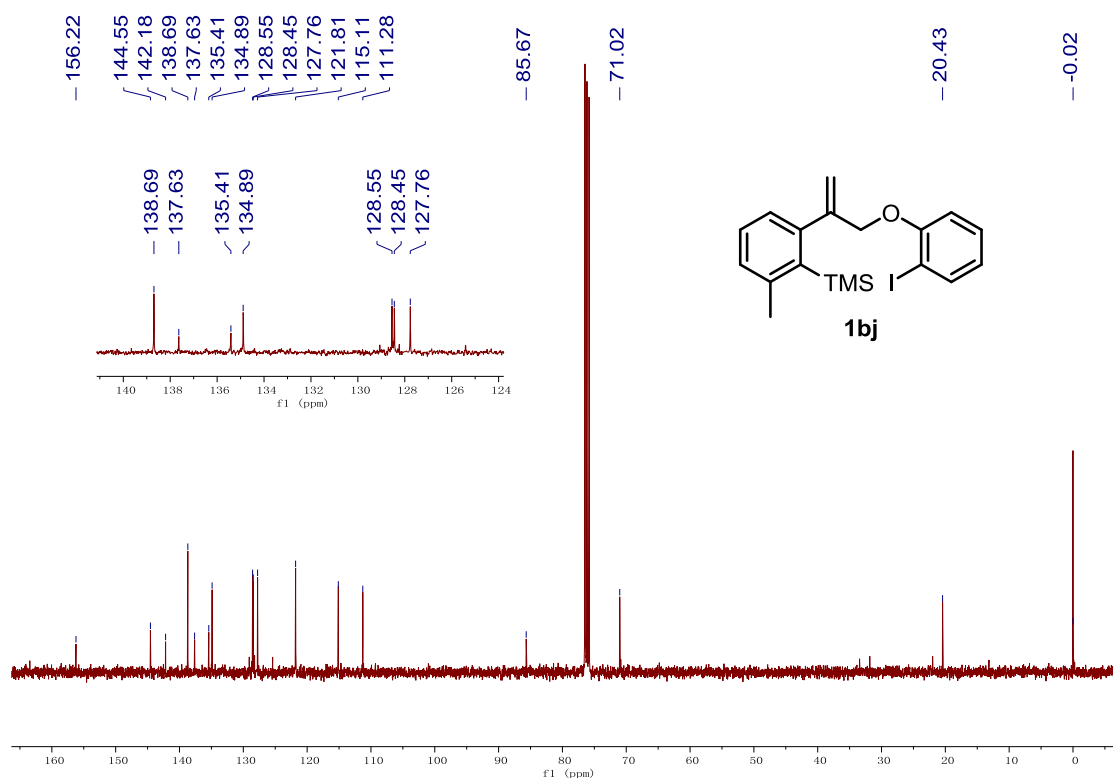
Supplementary Figure 63. ¹H NMR (400 MHz, CDCl₃) spectra of 1bi



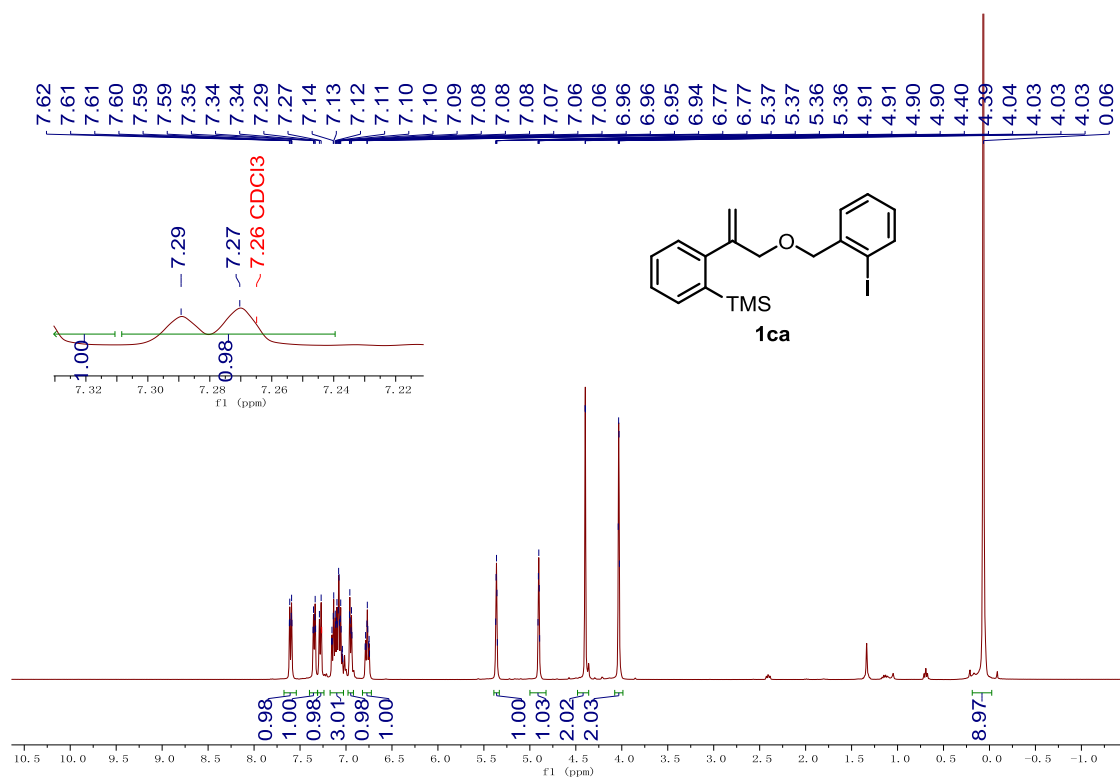
Supplementary Figure 64. ¹³C NMR (101 MHz, CDCl₃) spectra of 1bi



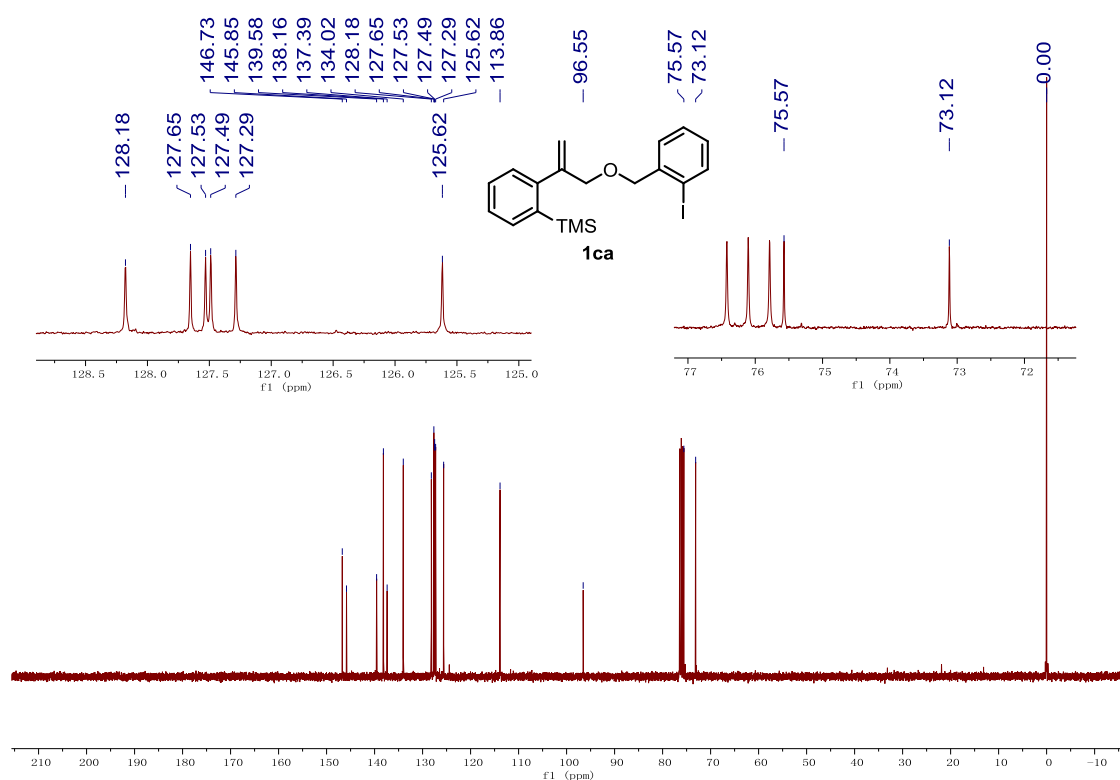
Supplementary Figure 65. ¹H NMR (400 MHz, CDCl₃) spectra of **1bj**



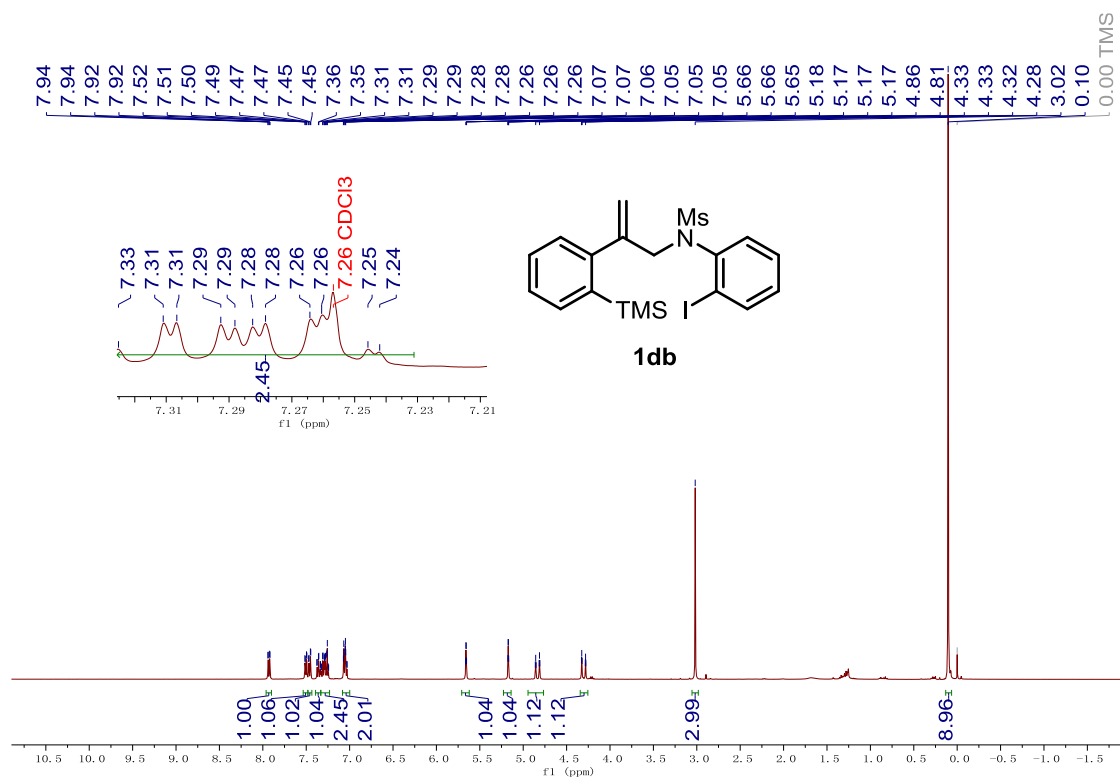
Supplementary Figure 66. ¹³C NMR (101 MHz, CDCl₃) spectra of **1bj**



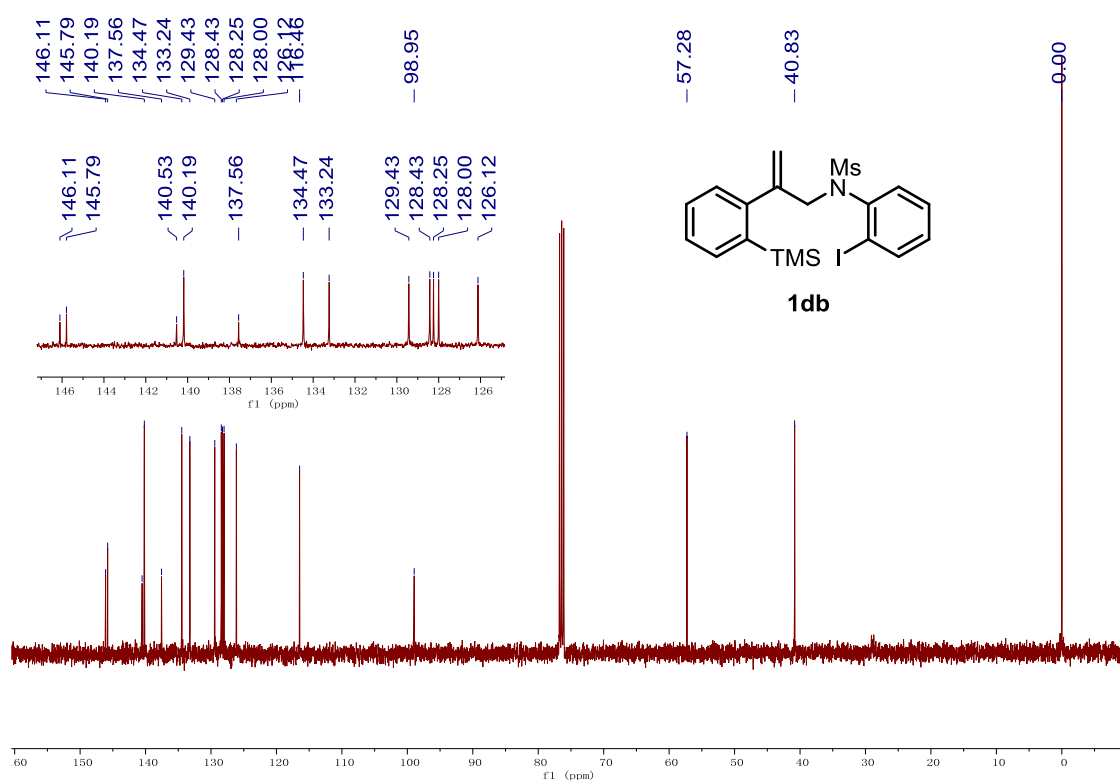
Supplementary Figure 67. ¹H NMR (400 MHz, CDCl₃) spectra of **1ca**



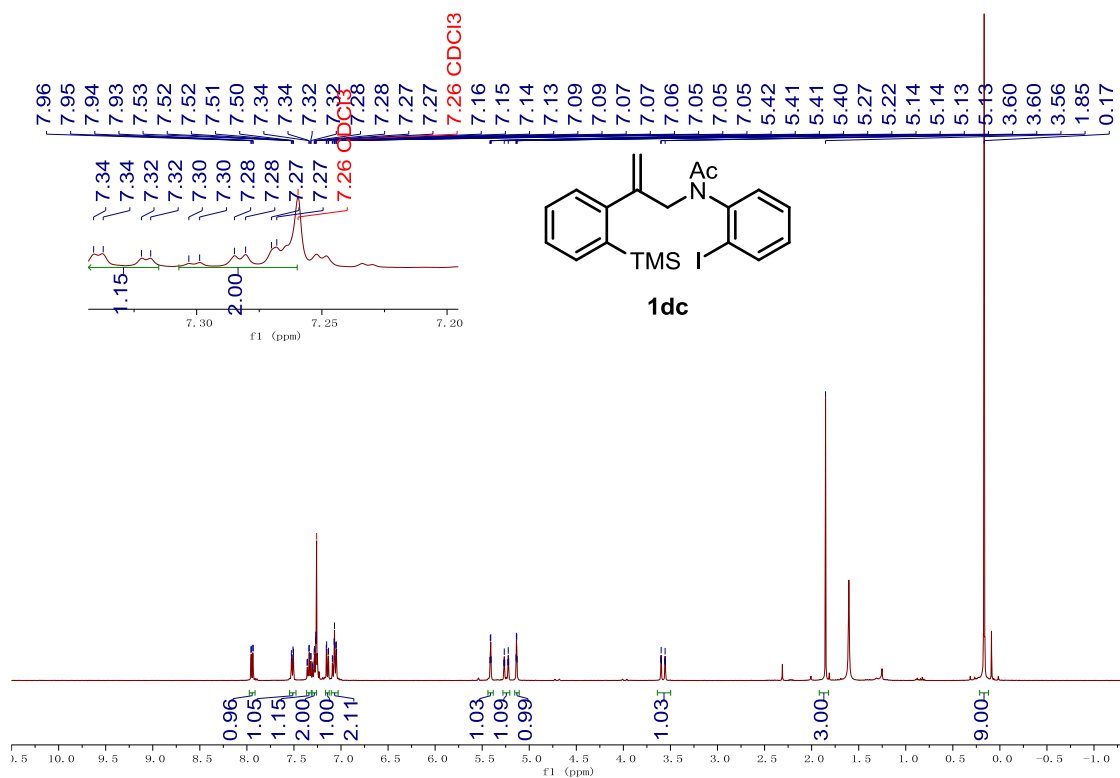
Supplementary Figure 68. ¹³C NMR (101 MHz, CDCl₃) spectra of **1ca**



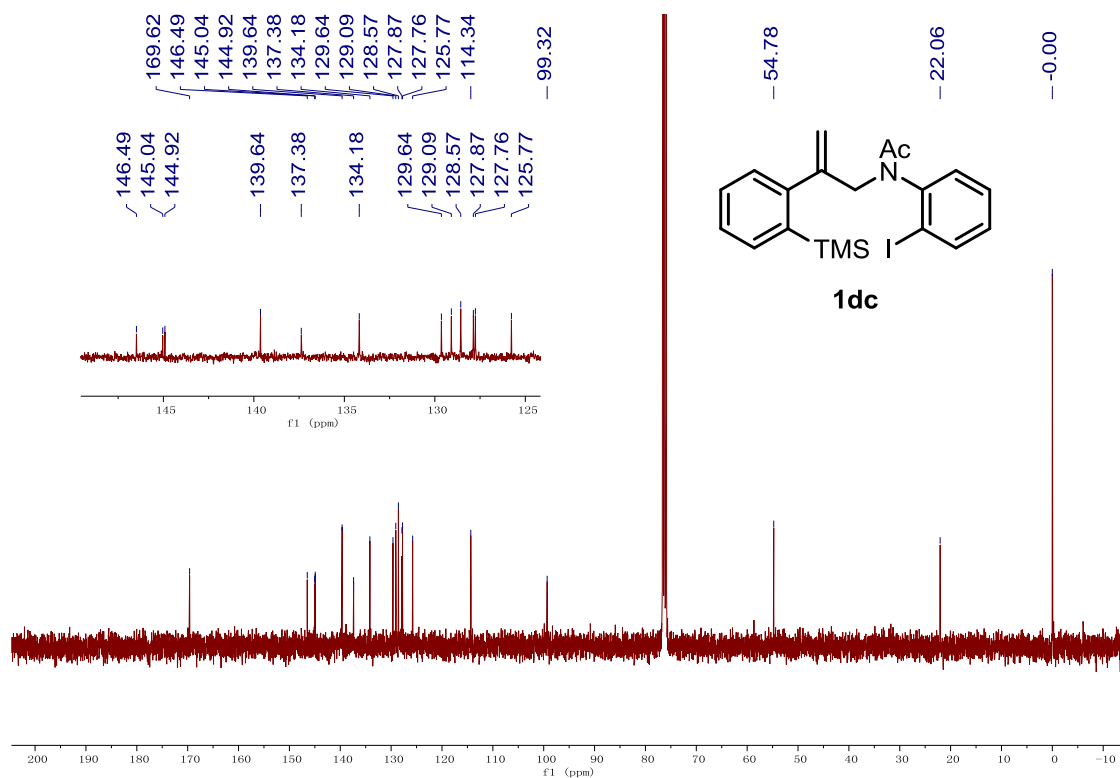
Supplementary Figure 71. ¹H NMR (400 MHz, CDCl₃) spectra of **1db**



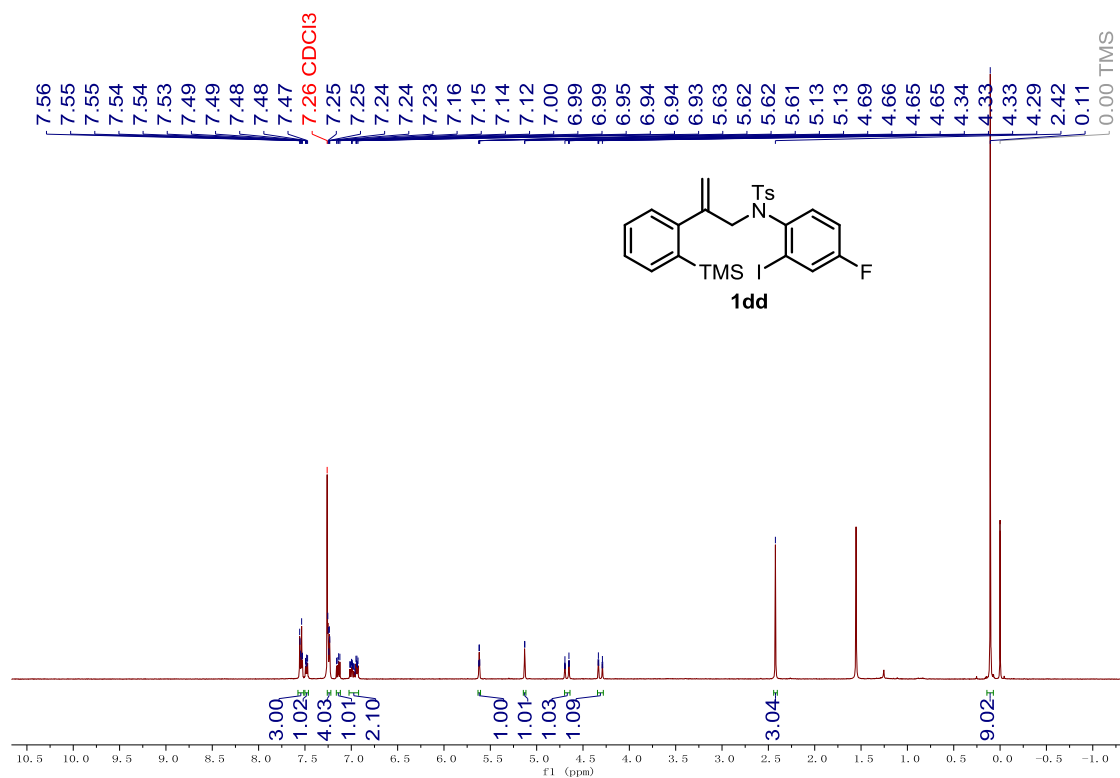
Supplementary Figure 72. ¹³C NMR (101 MHz, CDCl₃) spectra of **1db**



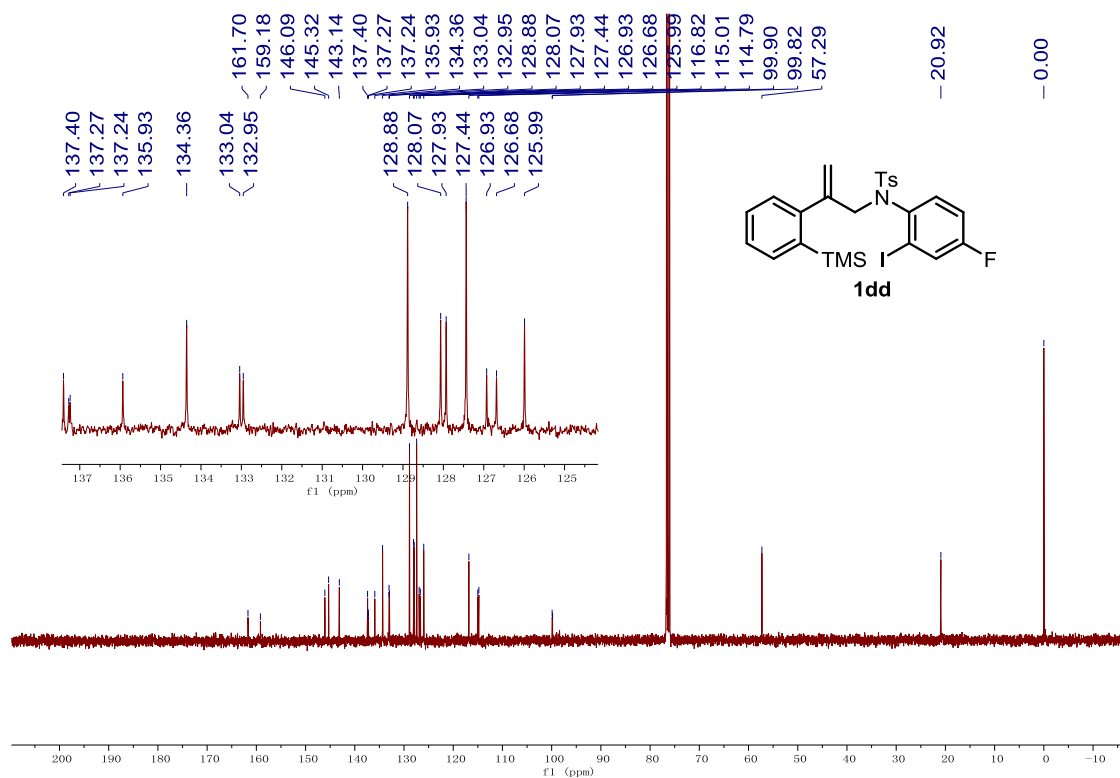
Supplementary Figure 73. ¹H NMR (400 MHz, CDCl₃) spectra of 1dc



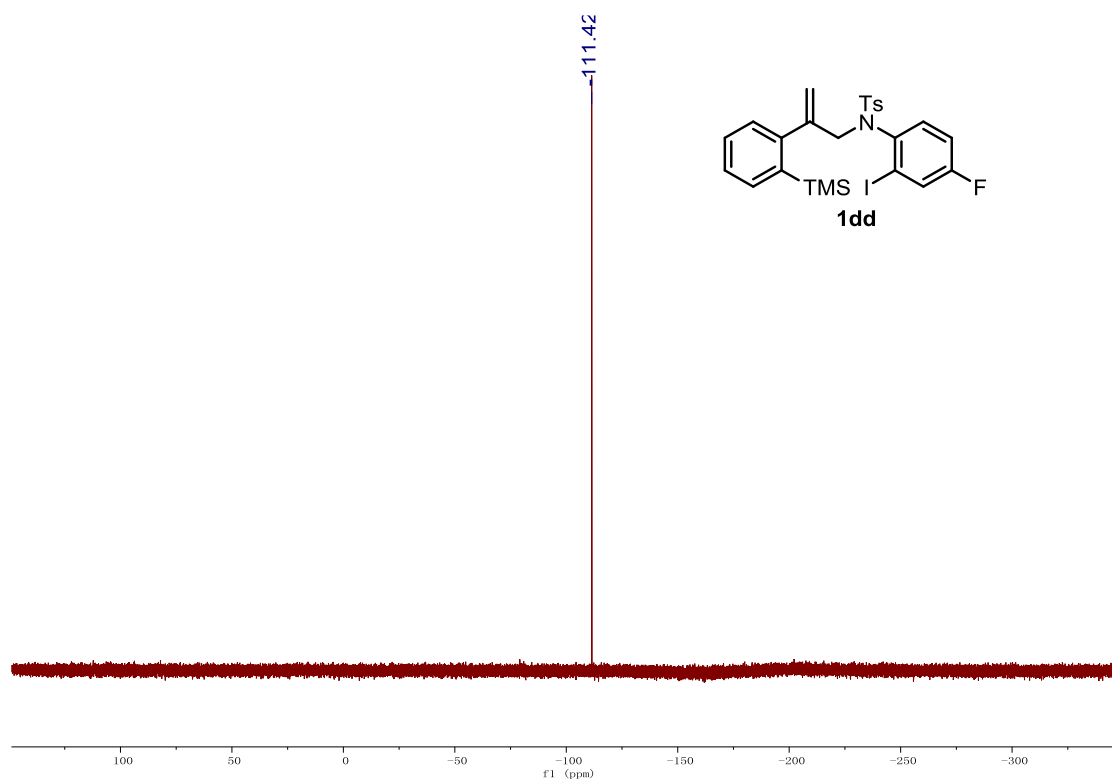
Supplementary Figure 74. ¹³C NMR (101 MHz, CDCl₃) spectra of 1dc



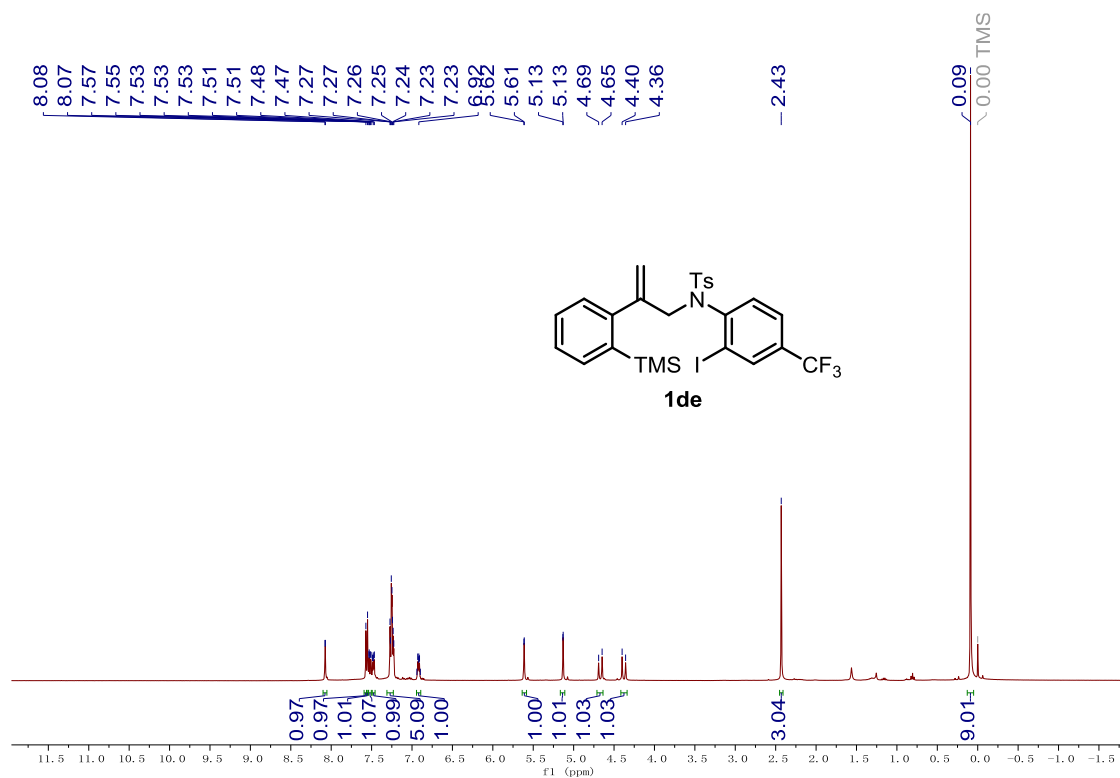
Supplementary Figure 75. ¹H NMR (400 MHz, CDCl₃) spectra of 1dd



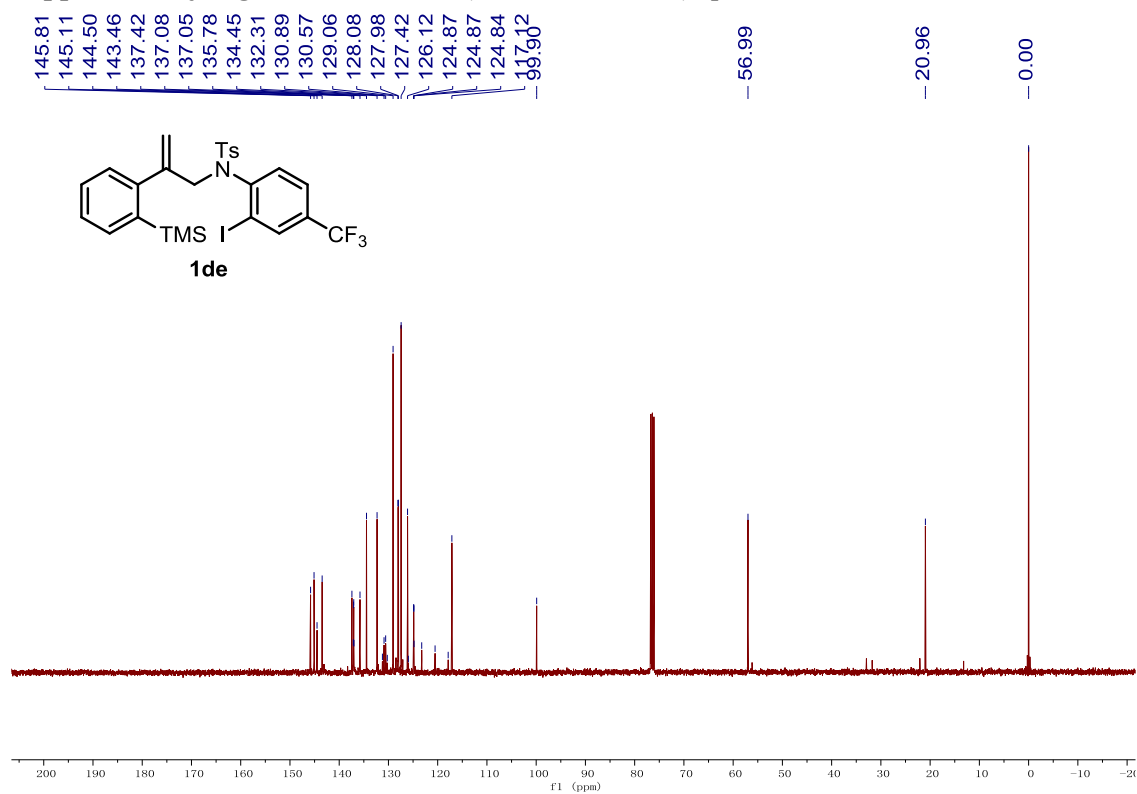
Supplementary Figure 76. ¹³C NMR (101 MHz, CDCl₃) spectra of 1dd



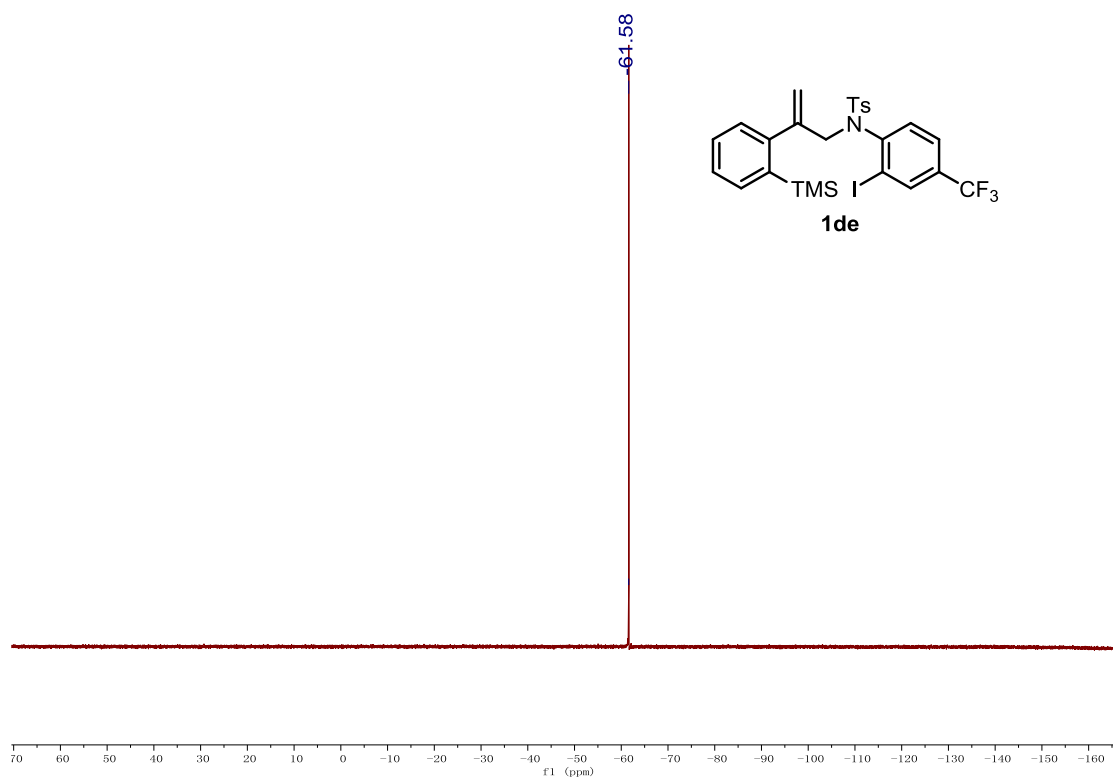
Supplementary Figure 77. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1dd**



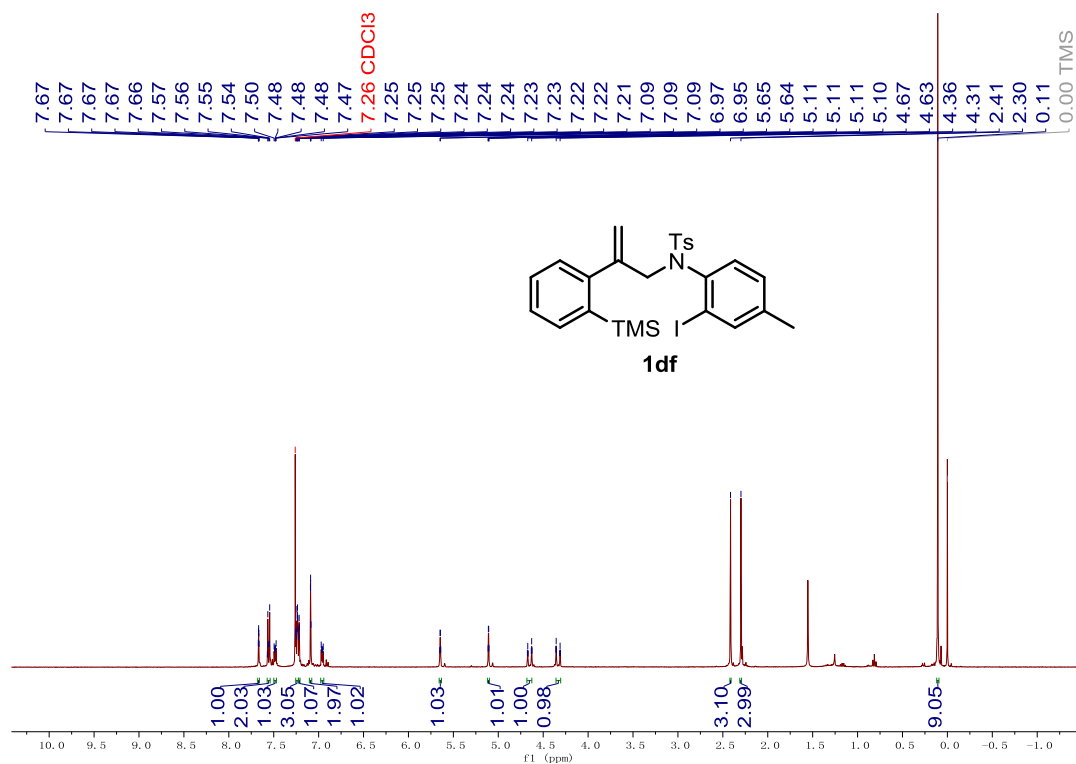
Supplementary Figure 78. ¹H NMR (400 MHz, CDCl₃) spectra of **1de**



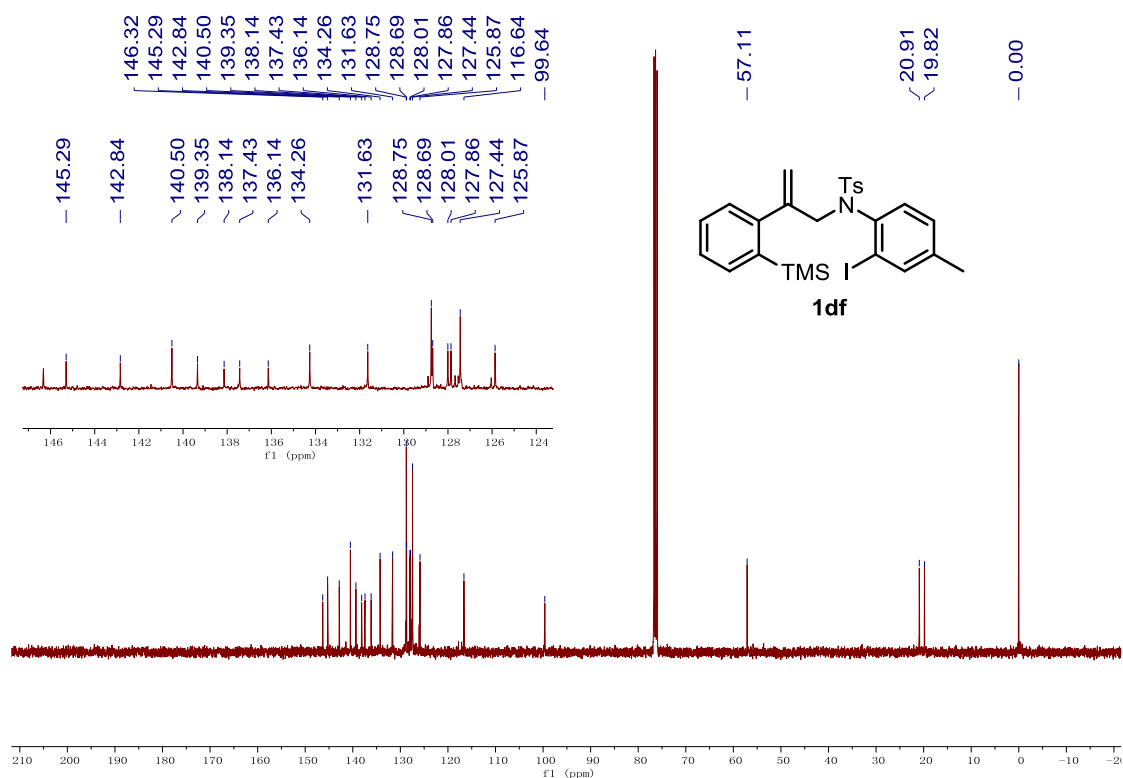
Supplementary Figure 79. ¹³C NMR (101 MHz, CDCl₃) spectra of **1de**



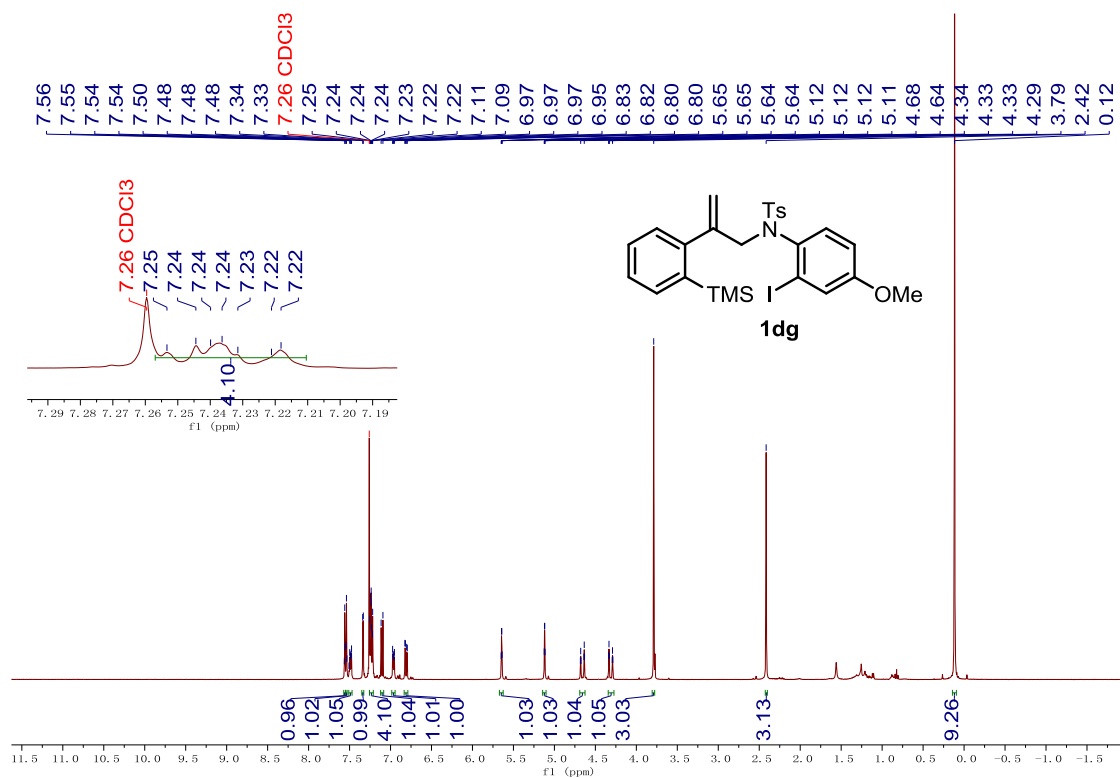
Supplementary Figure 80. ^{19}F NMR (376 MHz, CDCl_3) spectra of **1de**



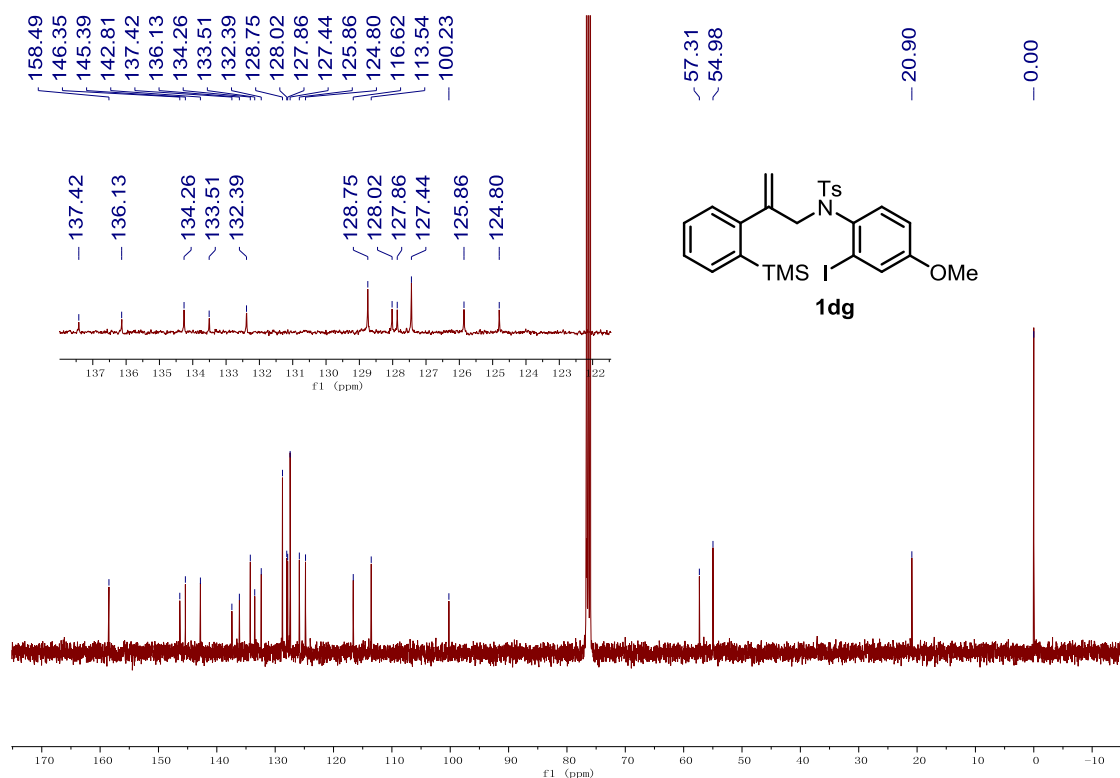
Supplementary Figure 81. ¹H NMR (400 MHz, CDCl₃) spectra of **1df**



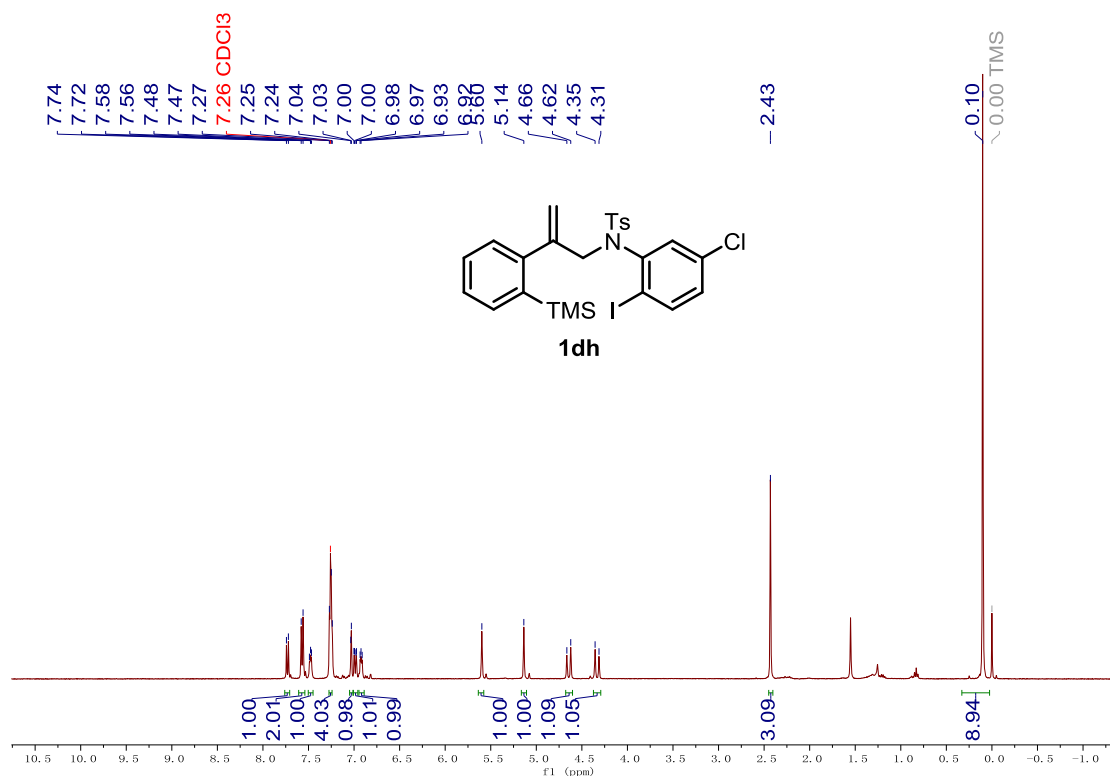
Supplementary Figure 82. ¹³C NMR (101 MHz, CDCl₃) spectra of **1df**



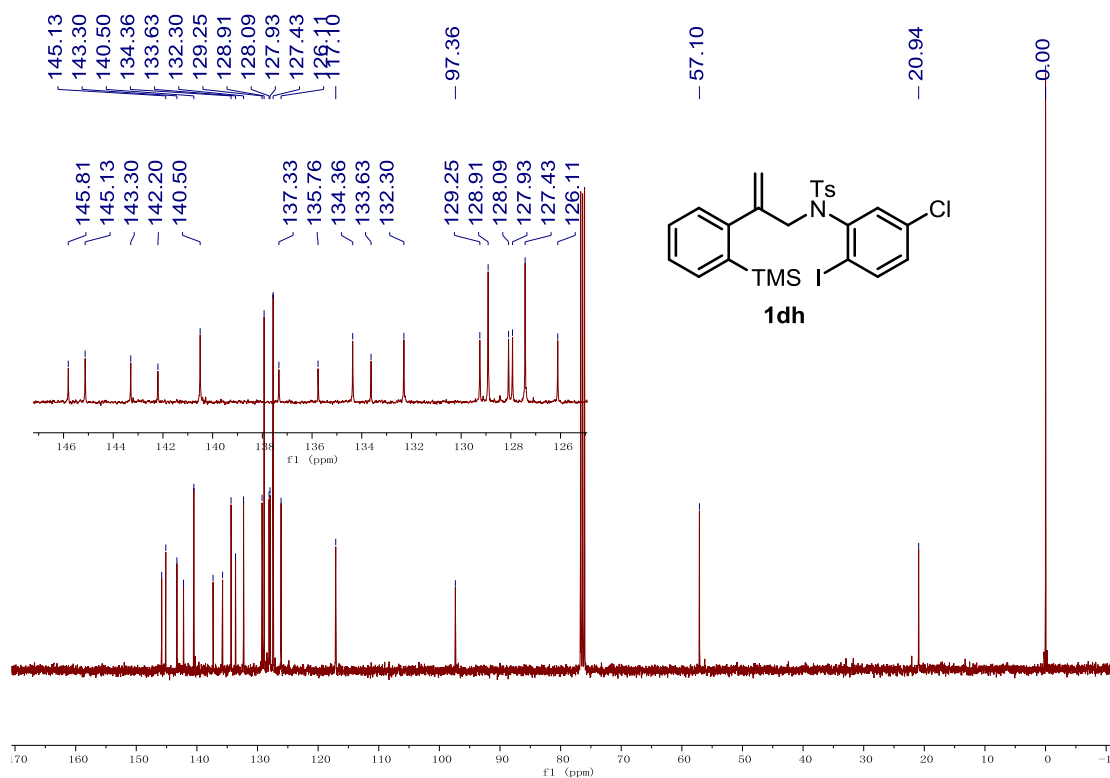
Supplementary Figure 83. ¹H NMR (400 MHz, CDCl₃) spectra of 1dg



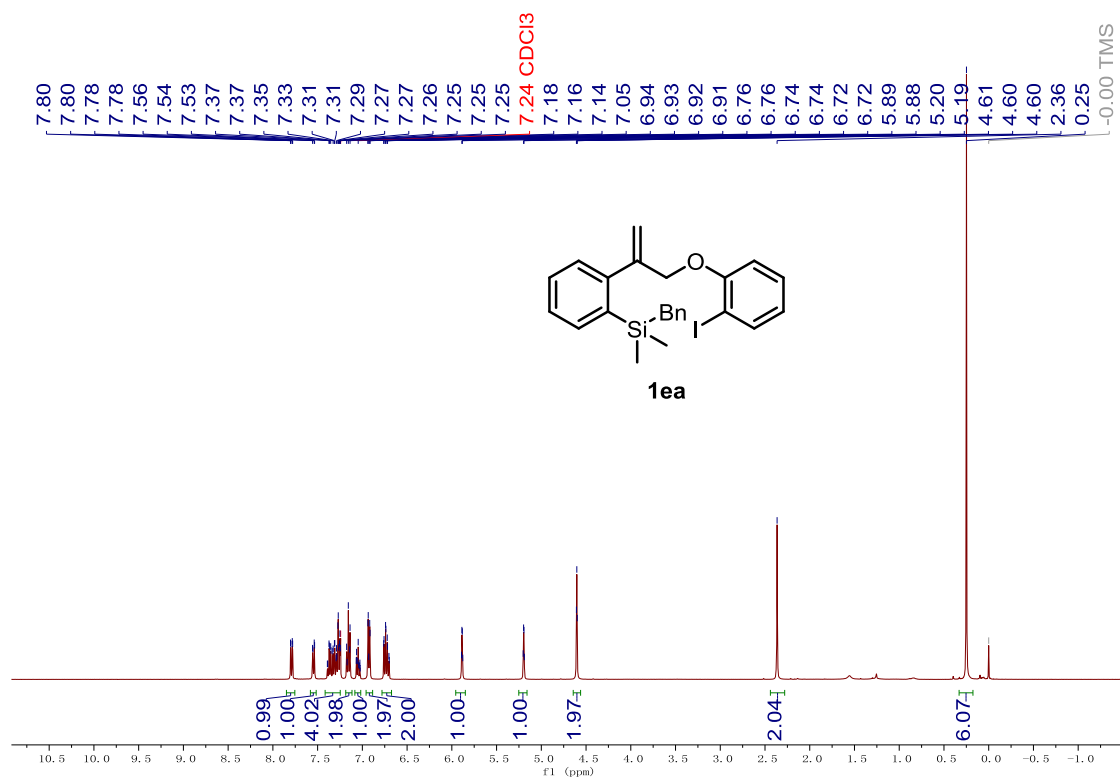
Supplementary Figure 84. ¹³C NMR (101 MHz, CDCl₃) spectra of 1dg



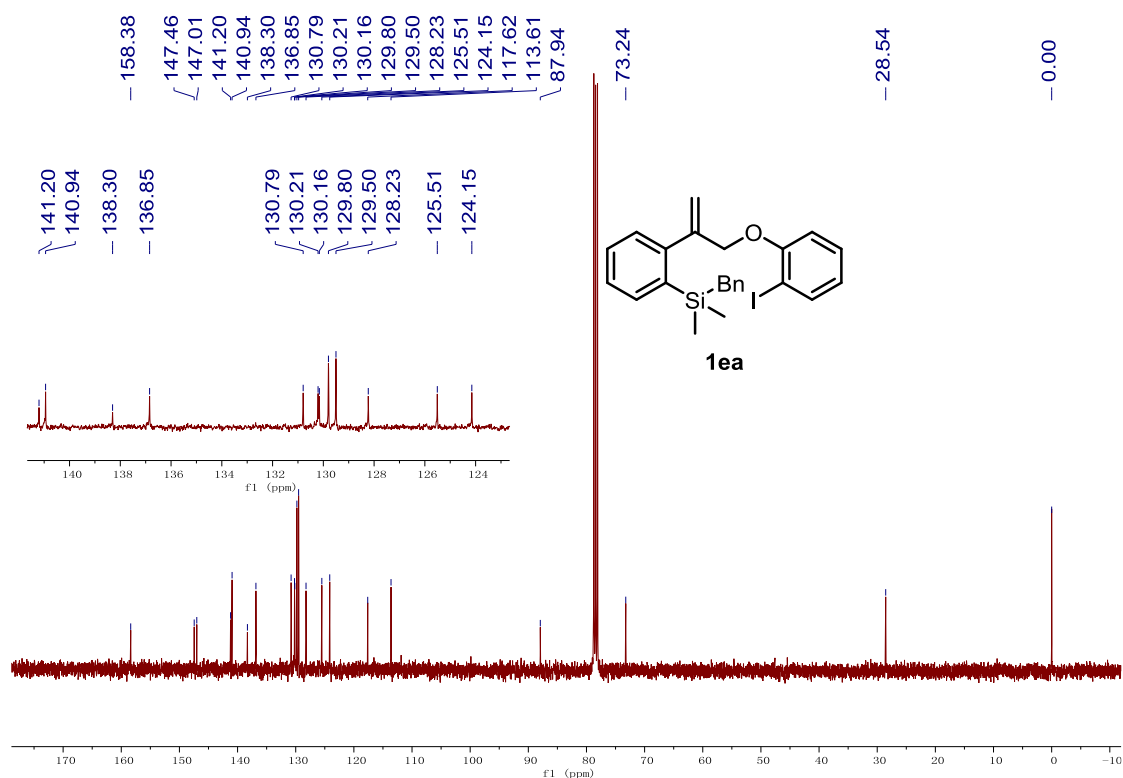
Supplementary Figure 85. ¹H NMR (400 MHz, CDCl₃) spectra of 1dh



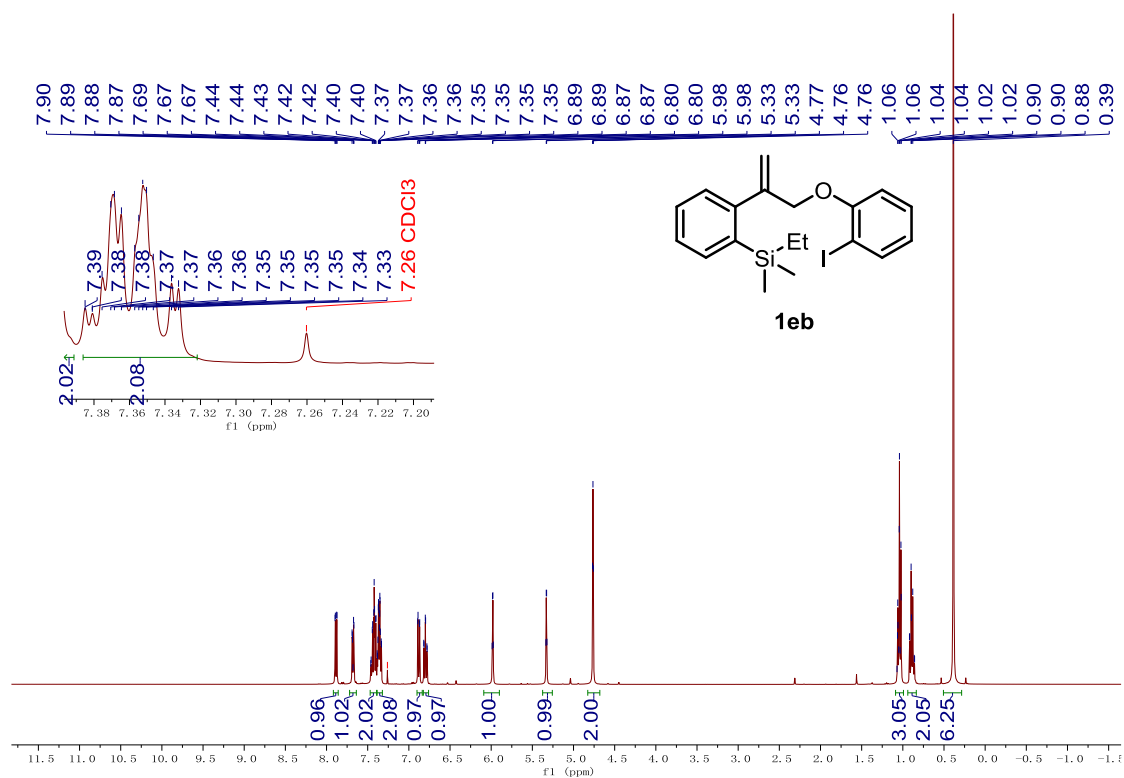
Supplementary Figure 86. ¹³C NMR (101 MHz, CDCl₃) spectra of 1dh



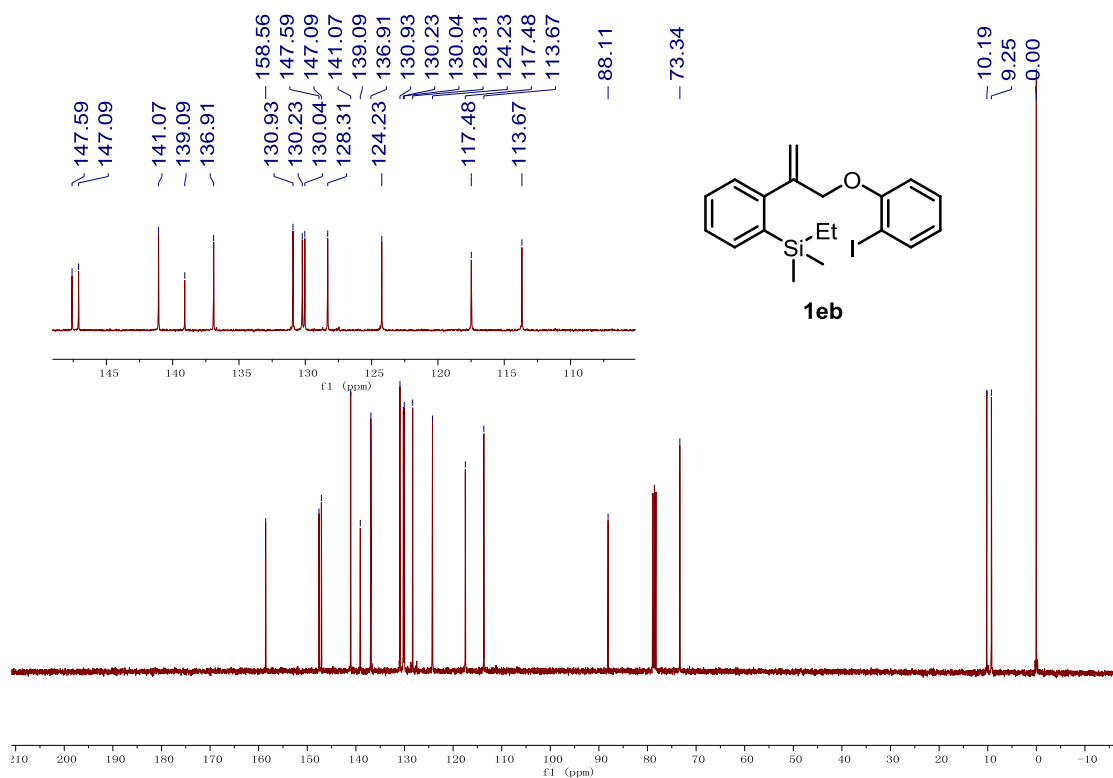
Supplementary Figure 87. ¹H NMR (400 MHz, CDCl₃) spectra of **1ea**



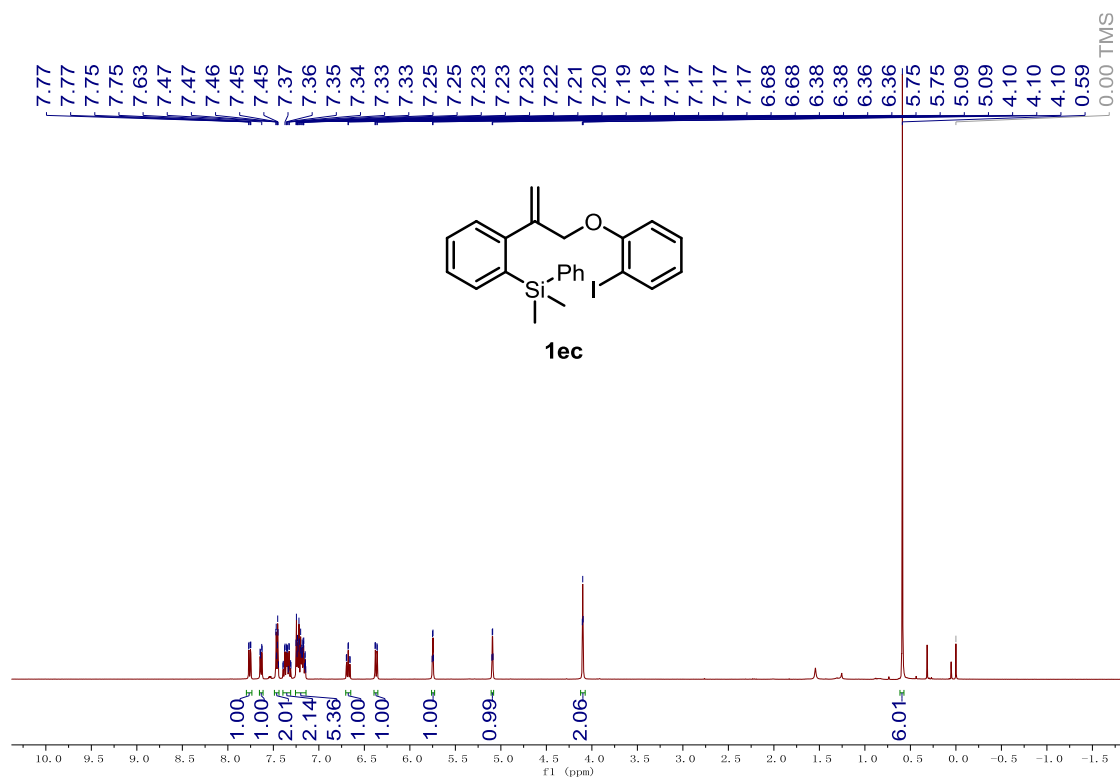
Supplementary Figure 88. ¹³C NMR (101 MHz, CDCl₃) spectra of **1ea**



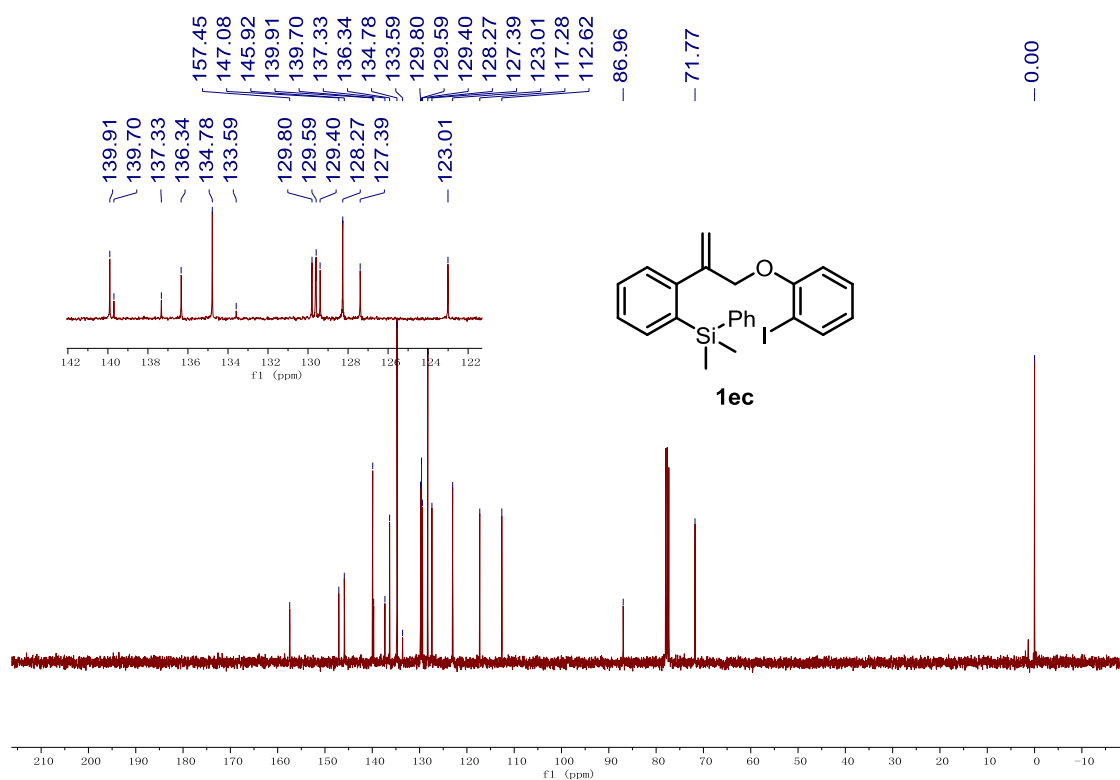
Supplementary Figure 89. ¹H NMR (400 MHz, CDCl₃) spectra of 1eb



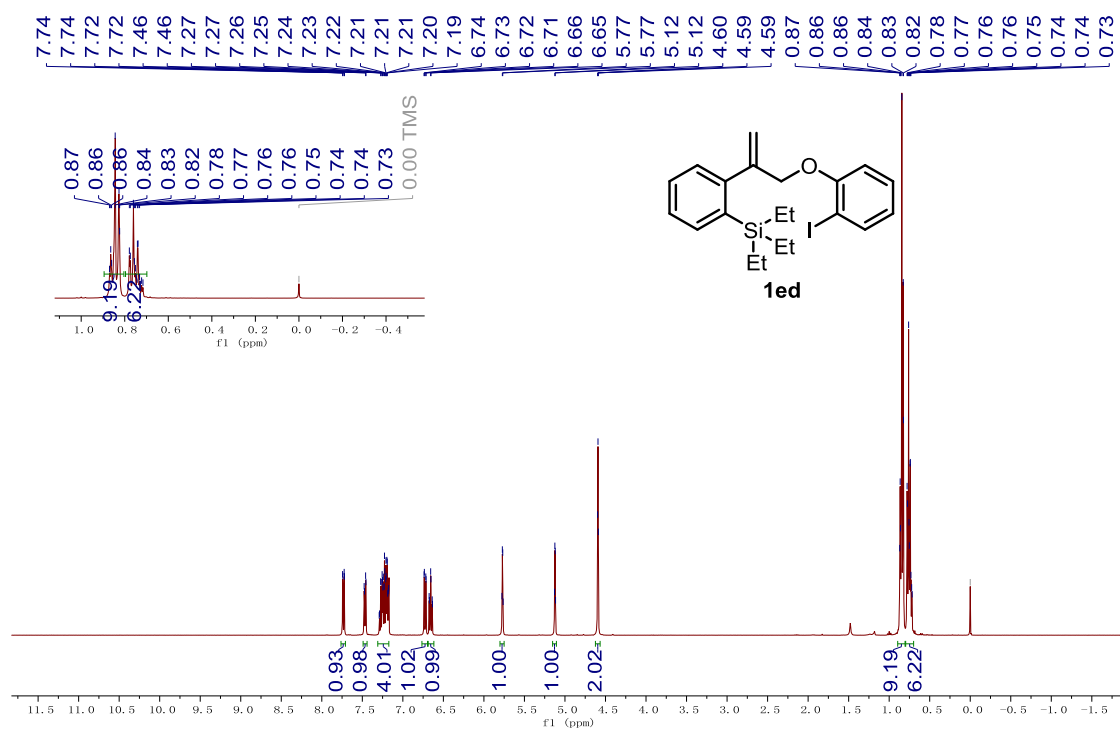
Supplementary Figure 90. ¹³C NMR (101 MHz, CDCl₃) spectra of 1eb



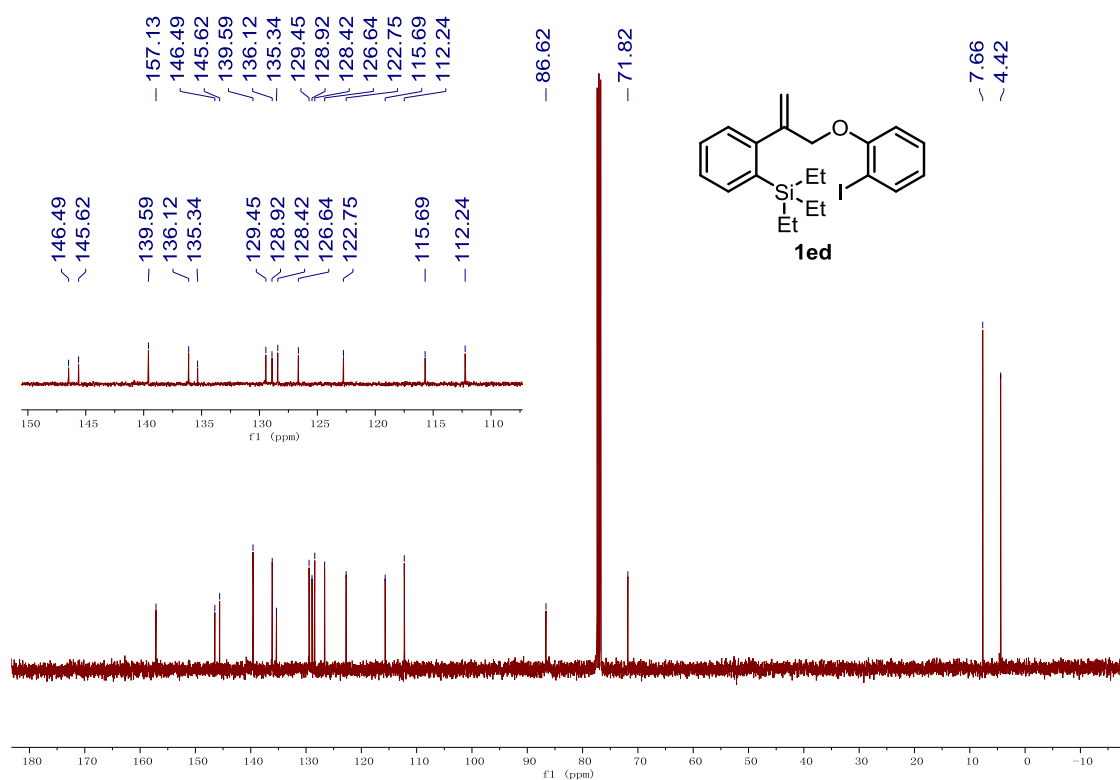
Supplementary Figure 91. ¹H NMR (400 MHz, CDCl₃) spectra of **1ec**



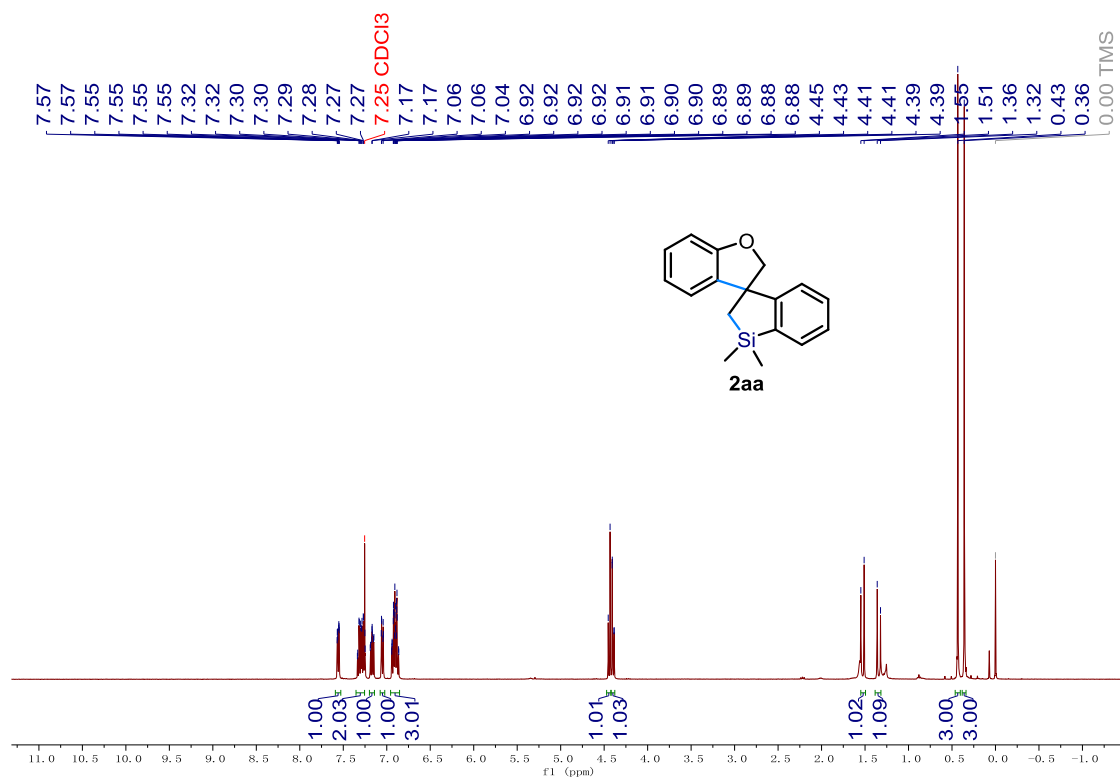
Supplementary Figure 92. ¹³C NMR (101 MHz, CDCl₃) spectra of **1ec**



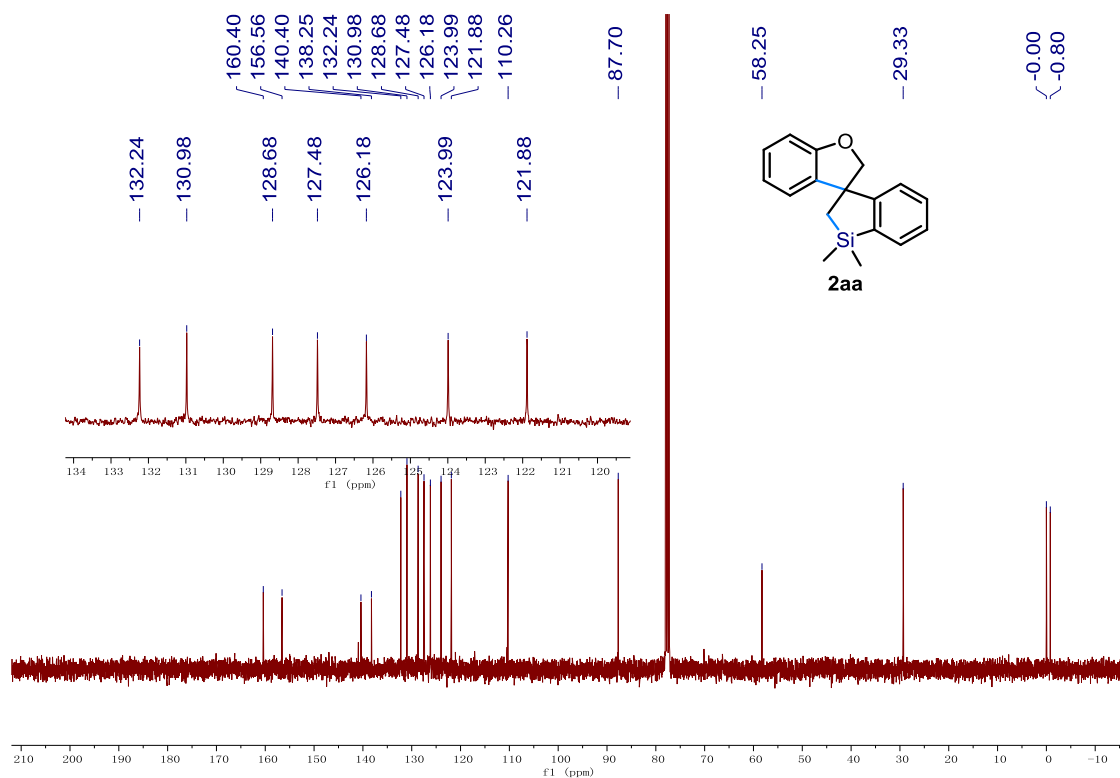
Supplementary Figure 93. ¹H NMR (400 MHz, CDCl₃) spectra of 1ed



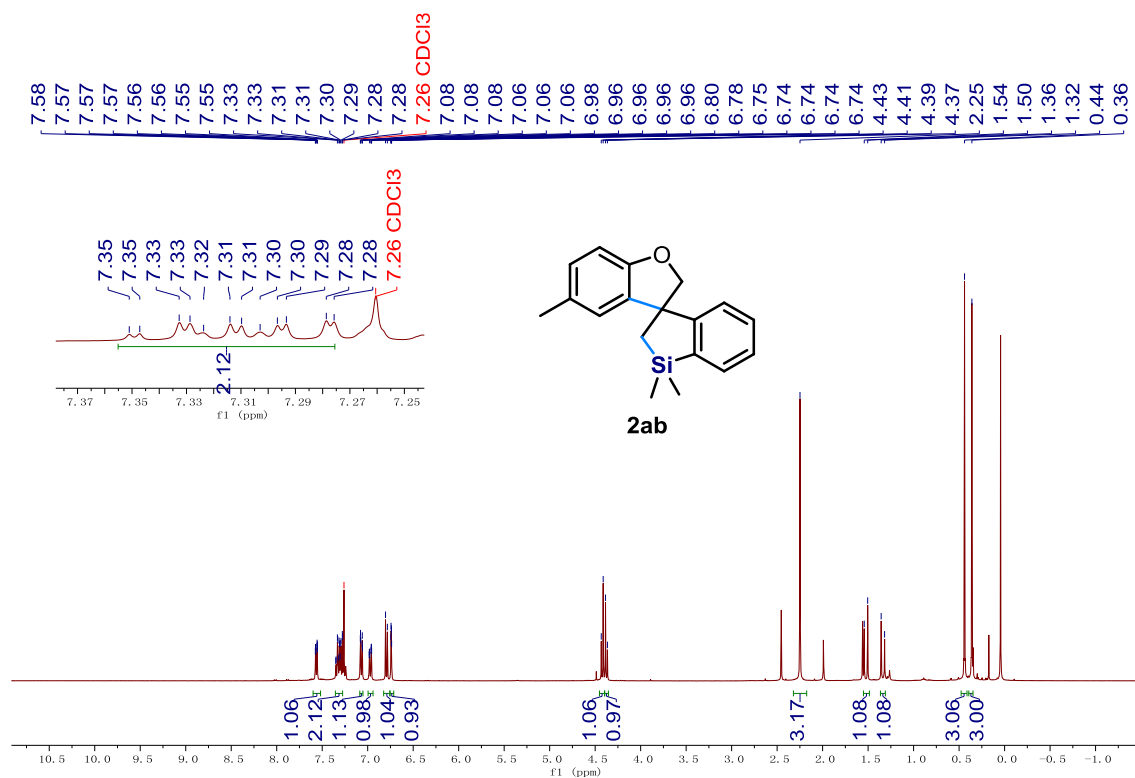
Supplementary Figure 94. ¹³C NMR (101 MHz, CDCl₃) spectra of 1ed



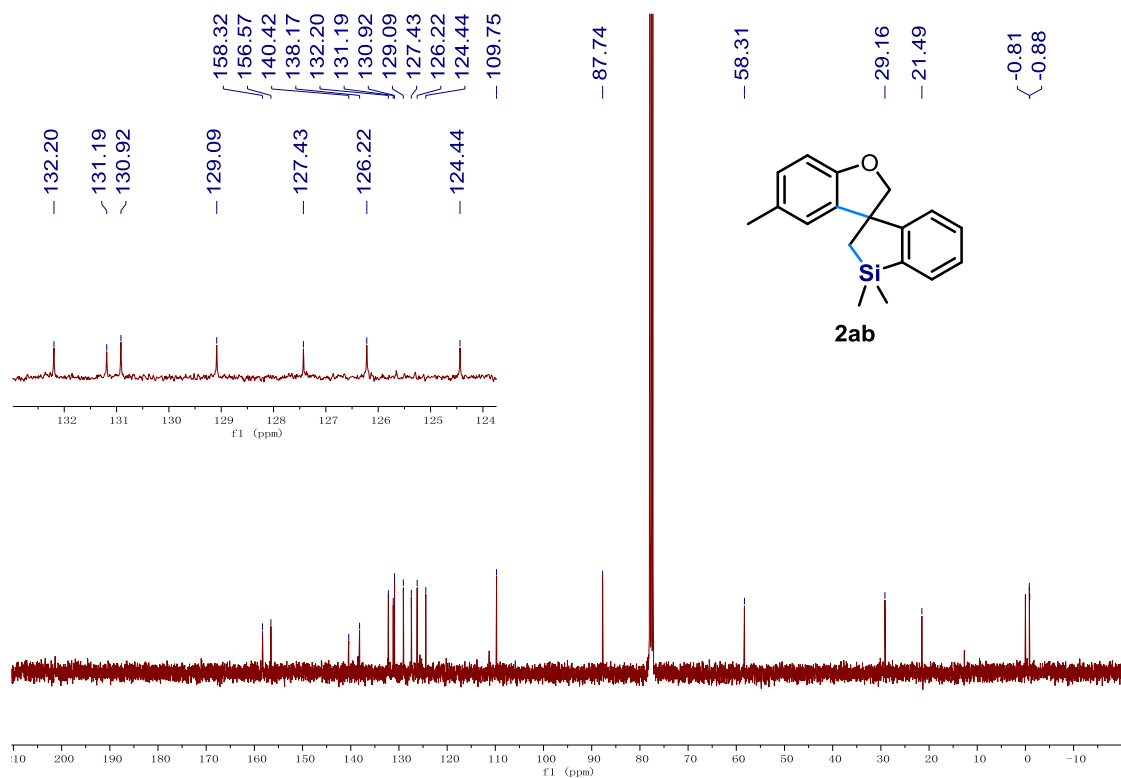
Supplementary Figure 95. ¹H NMR (400 MHz, CDCl₃) spectra of 2aa



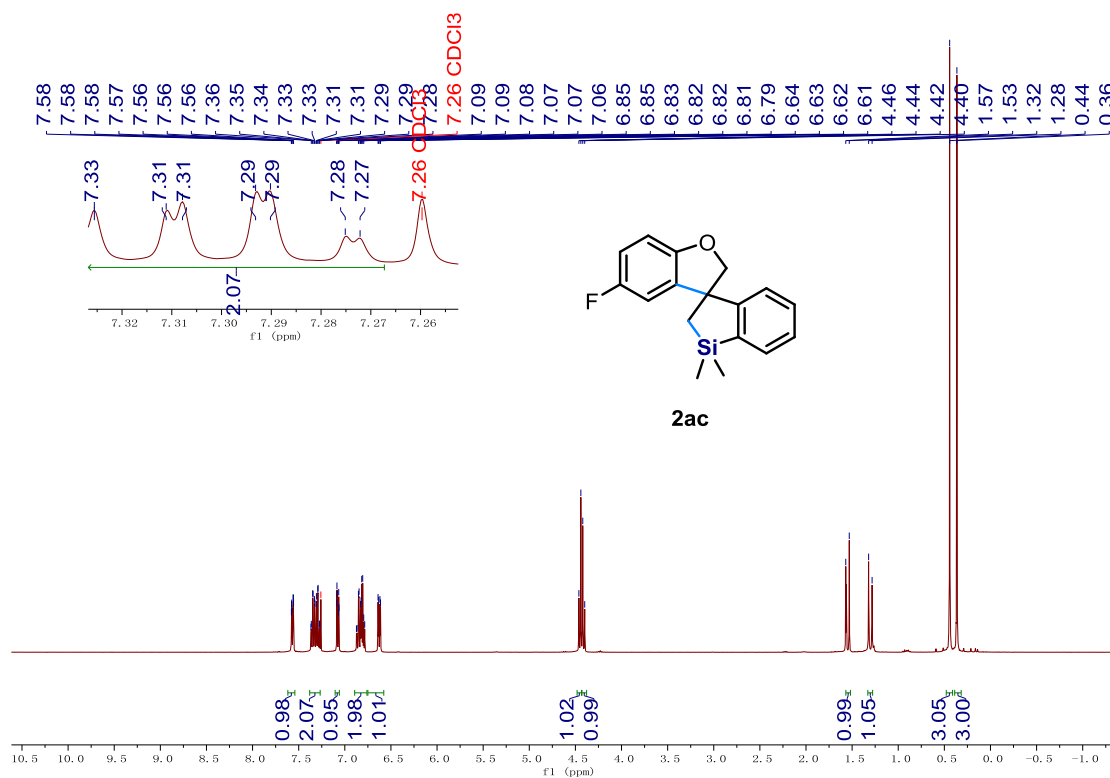
Supplementary Figure 96. ¹³C NMR (101 MHz, CDCl₃) spectra of 2aa



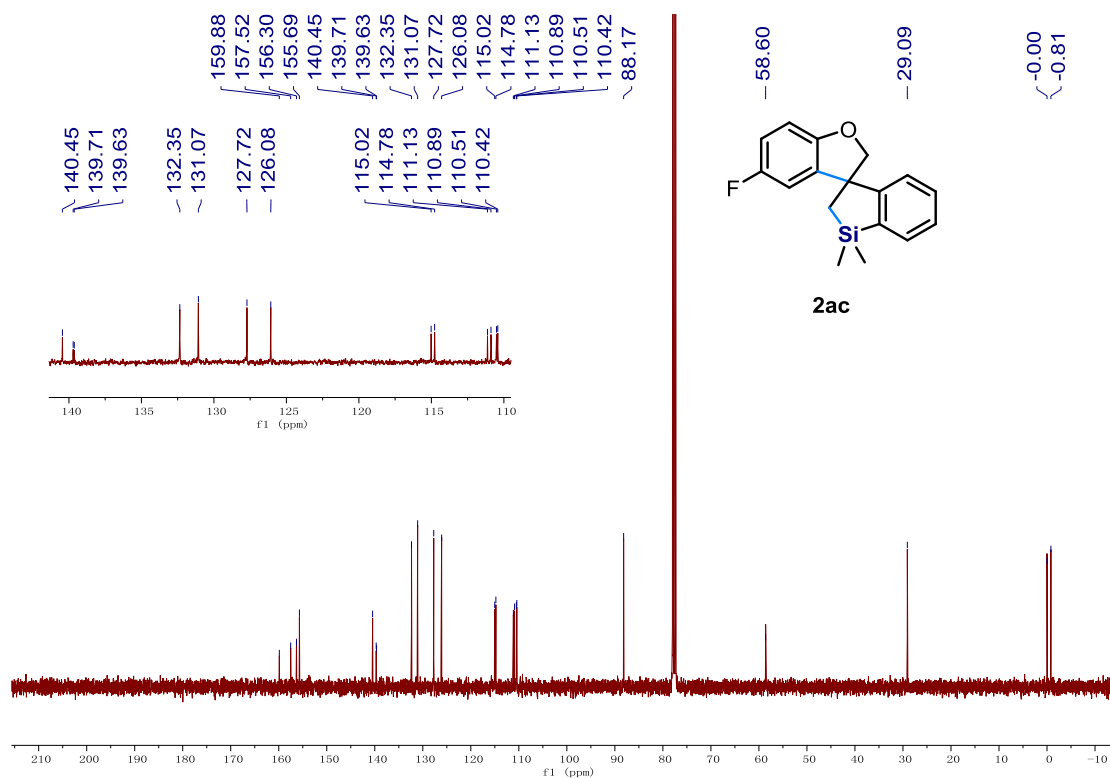
Supplementary Figure 97. ¹H NMR (400 MHz, CDCl₃) spectra of 2ab



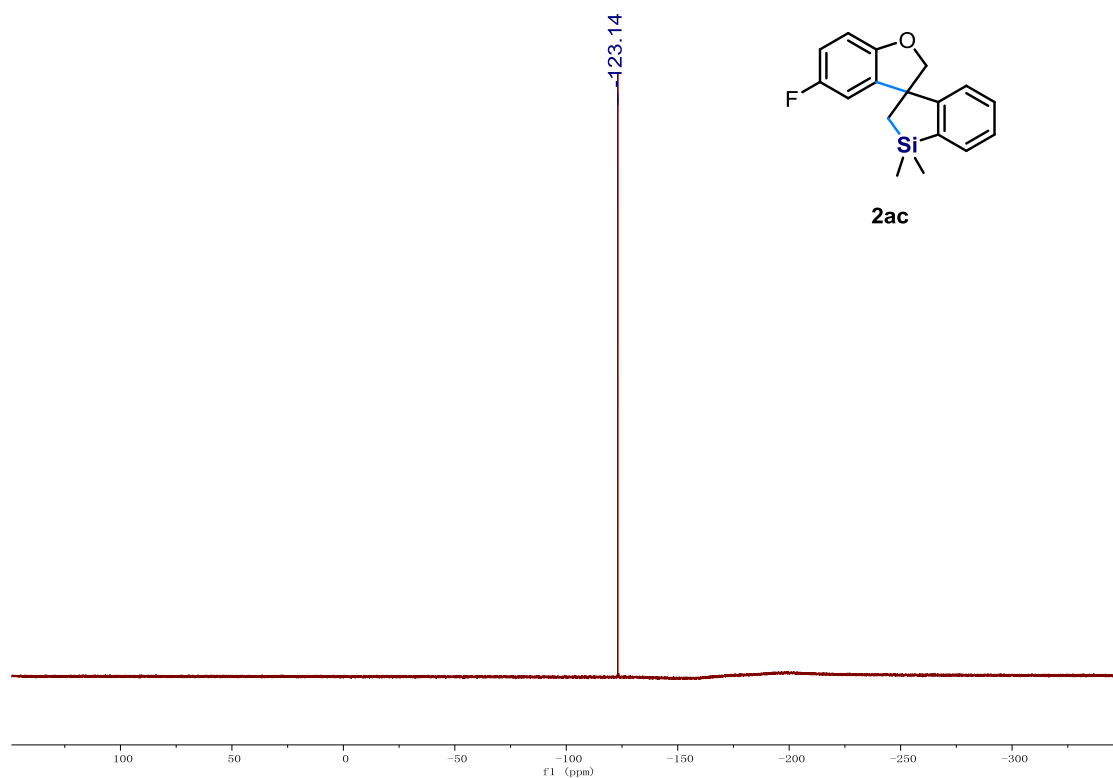
Supplementary Figure 98. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ab



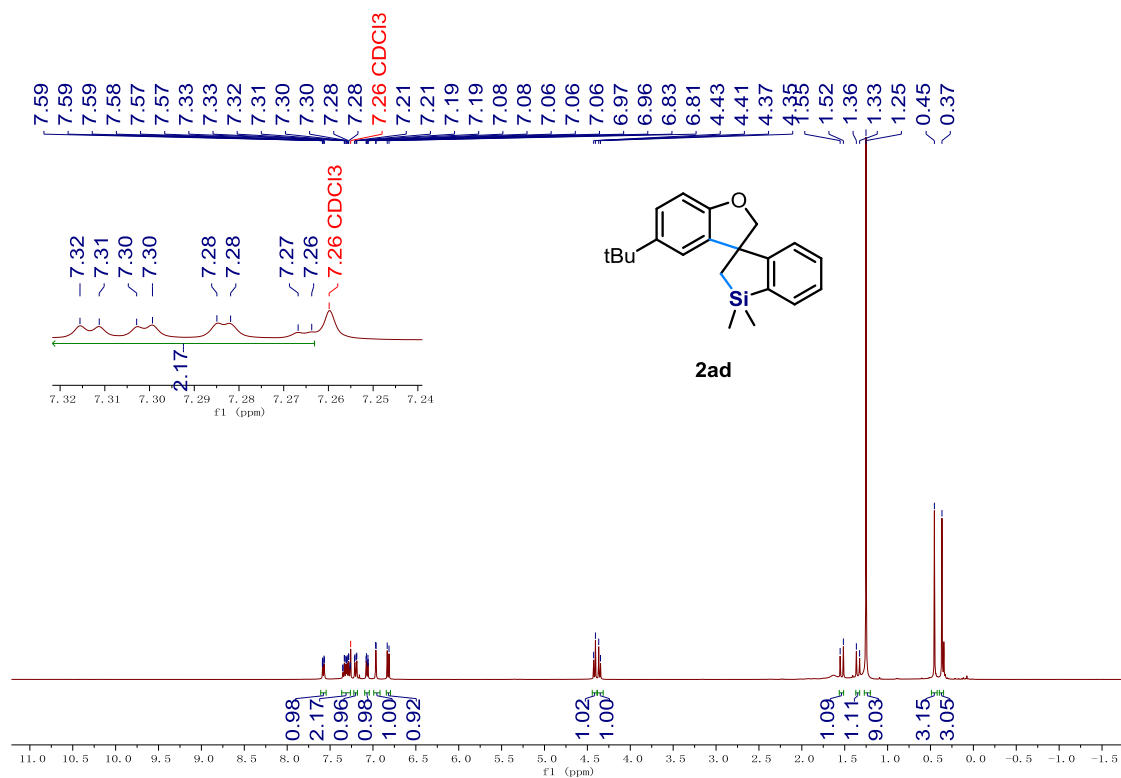
Supplementary Figure 99. ¹H NMR (400 MHz, CDCl₃) spectra of 2ac



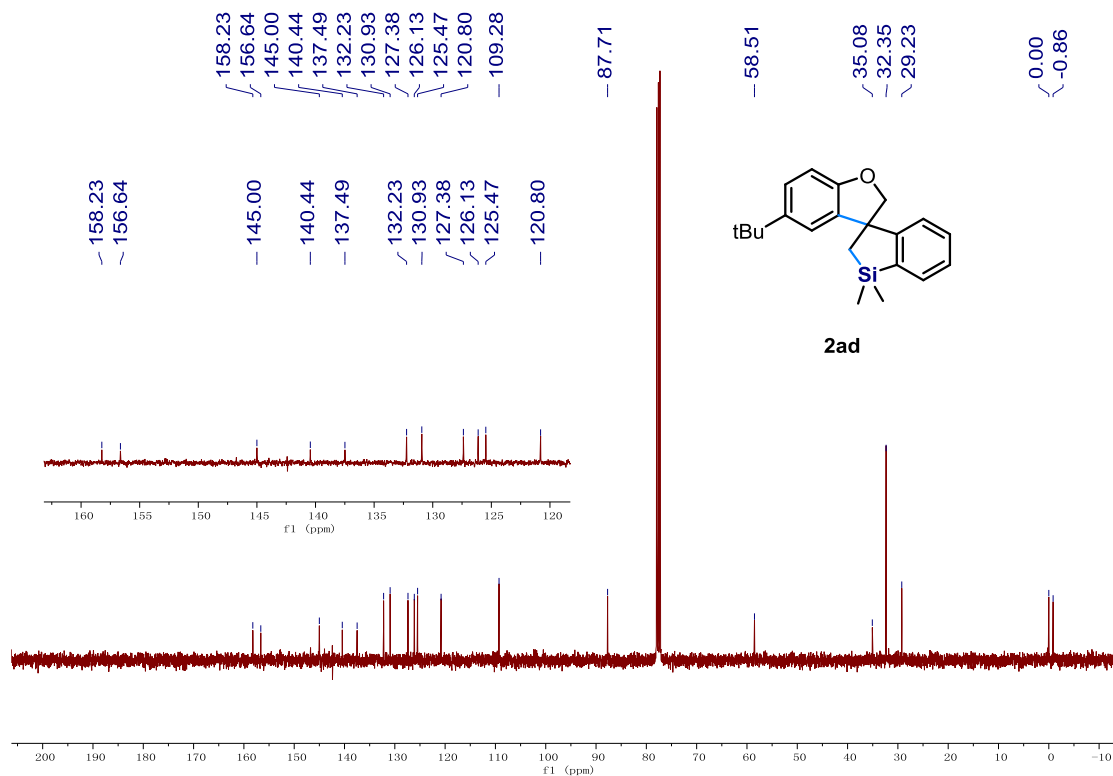
Supplementary Figure 100. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ac



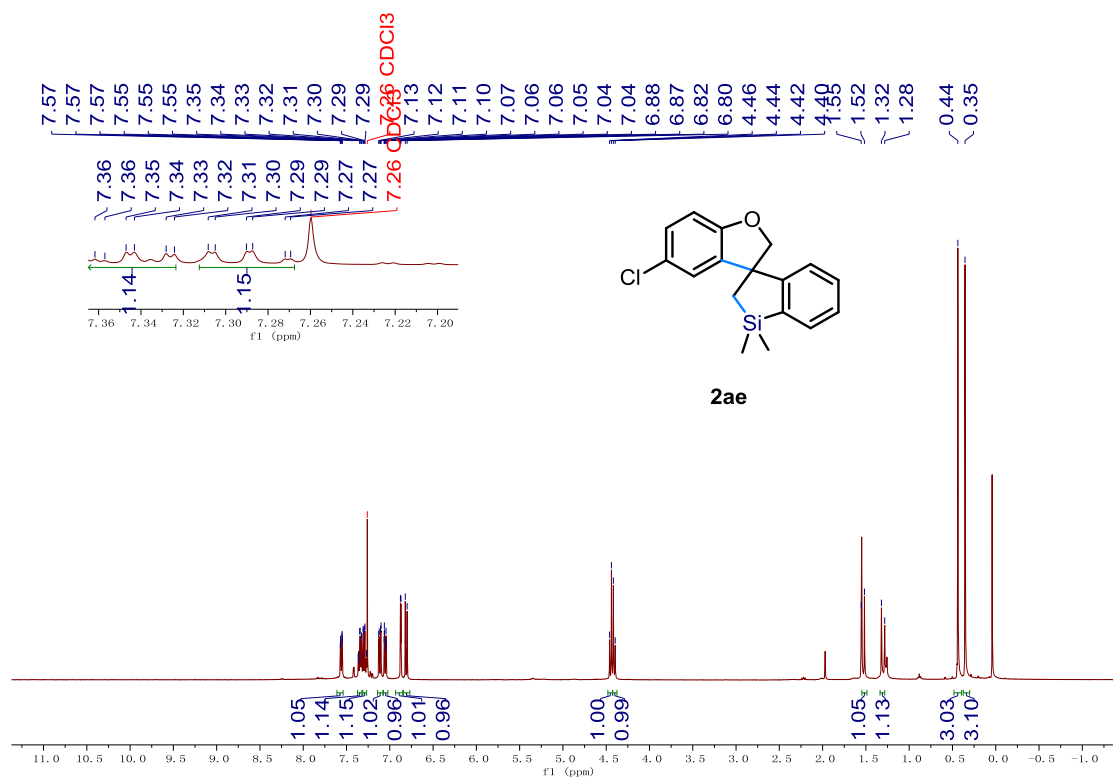
Supplementary Figure 101. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2ac**



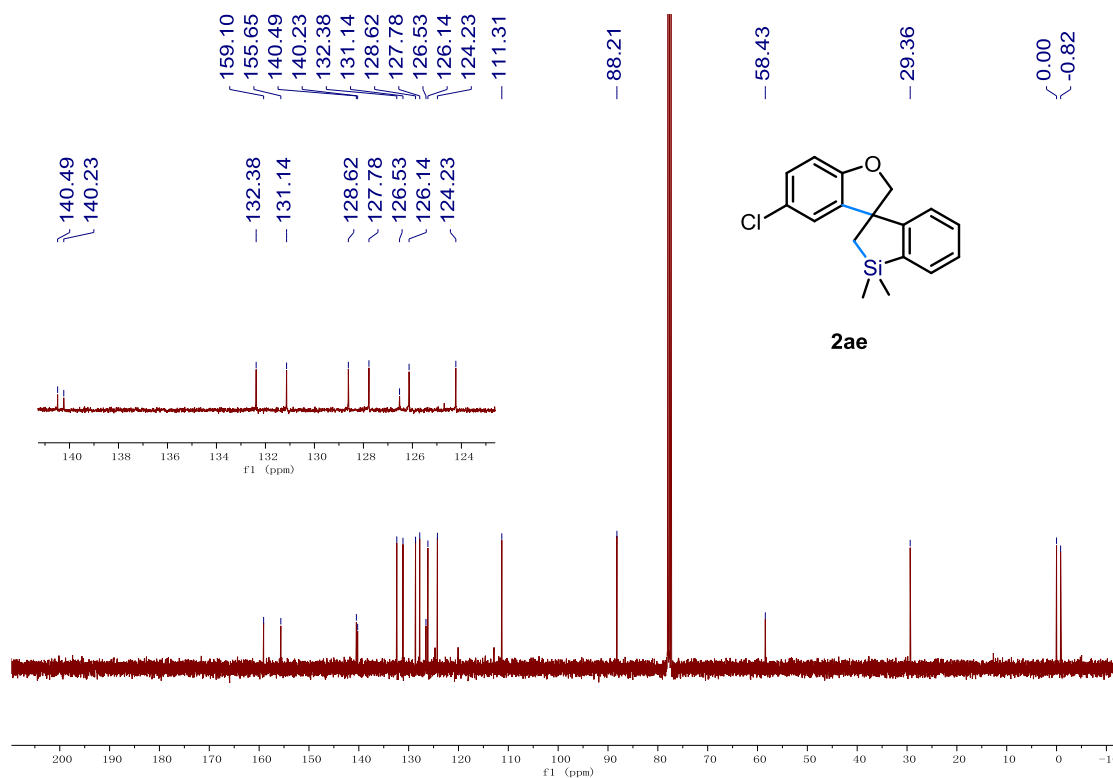
Supplementary Figure 102. ¹H NMR (400 MHz, CDCl₃) spectra of 2ad



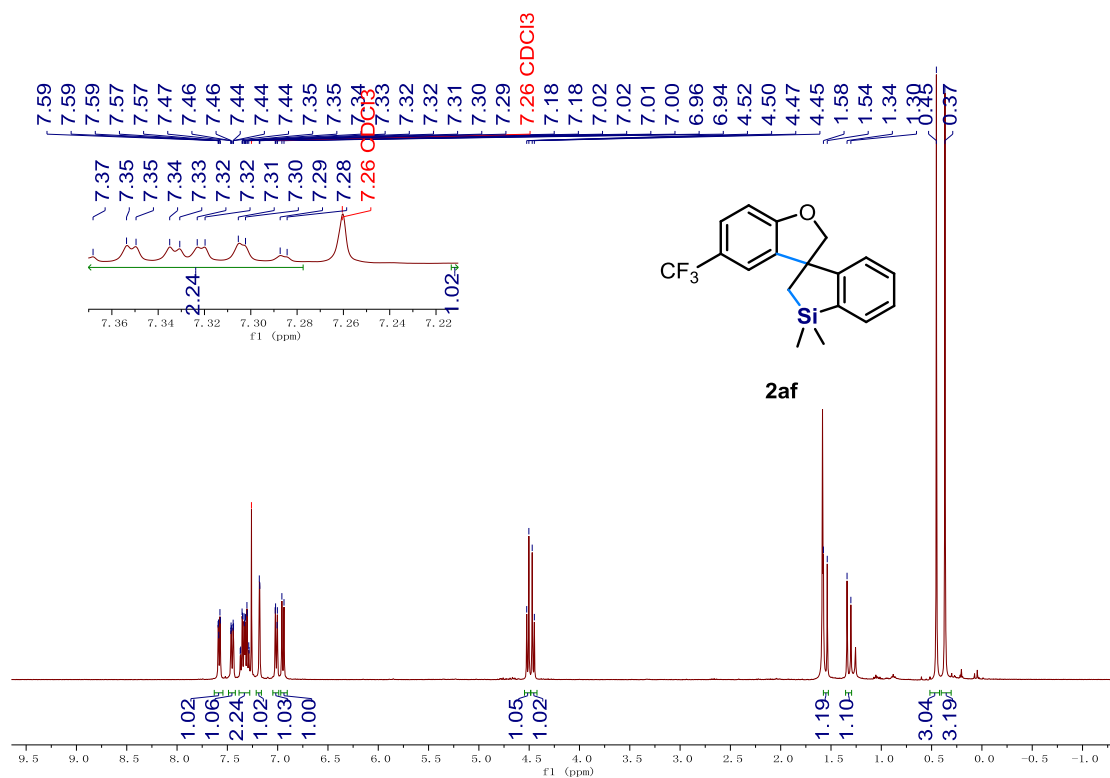
Supplementary Figure 103. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ad



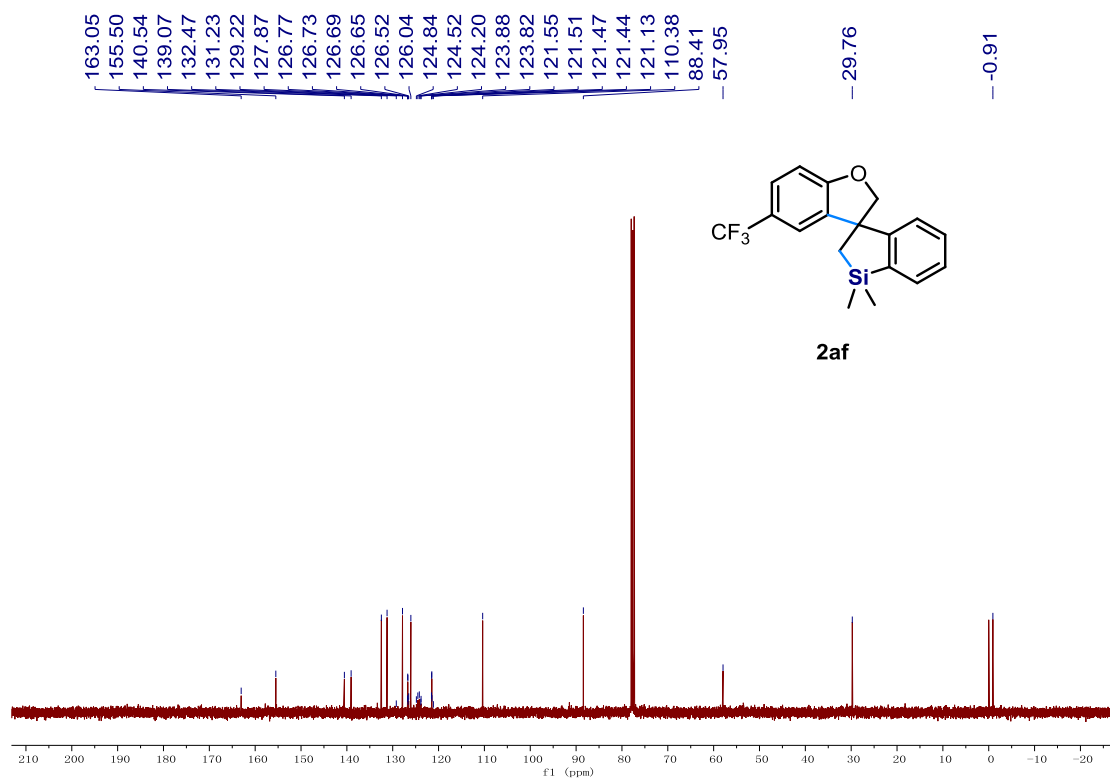
Supplementary Figure 104. ¹H NMR (400 MHz, CDCl₃) spectra of 2ae



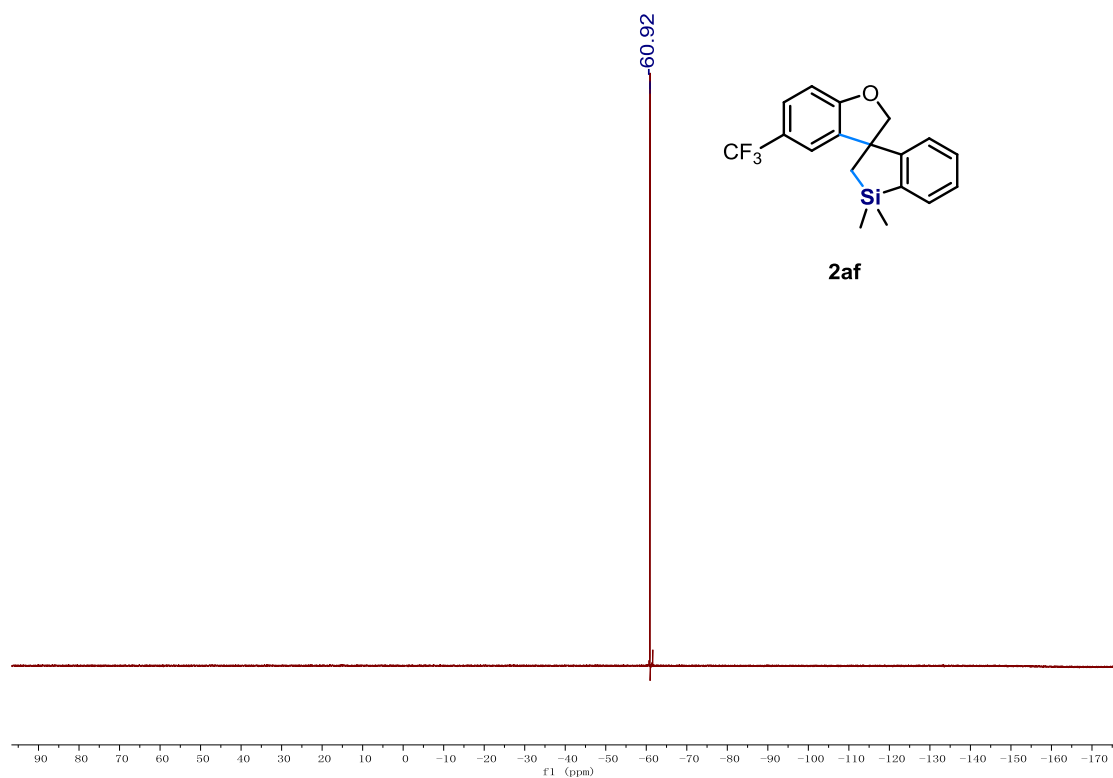
Supplementary Figure 105. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ae



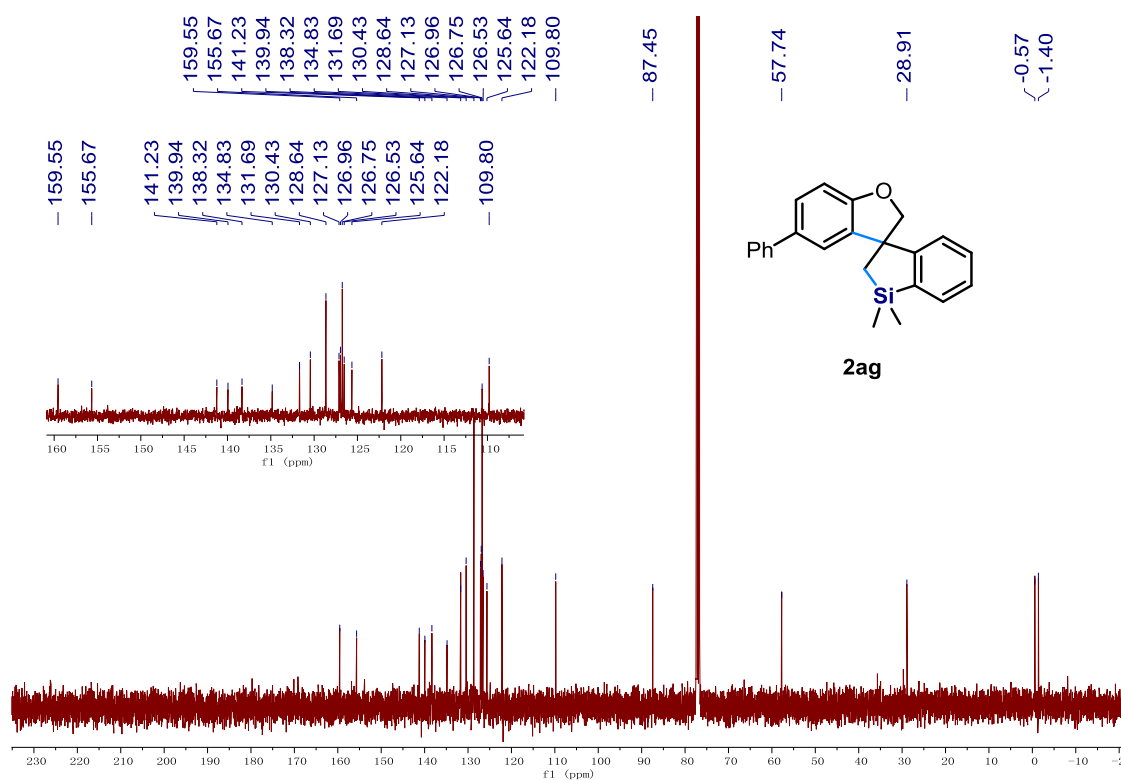
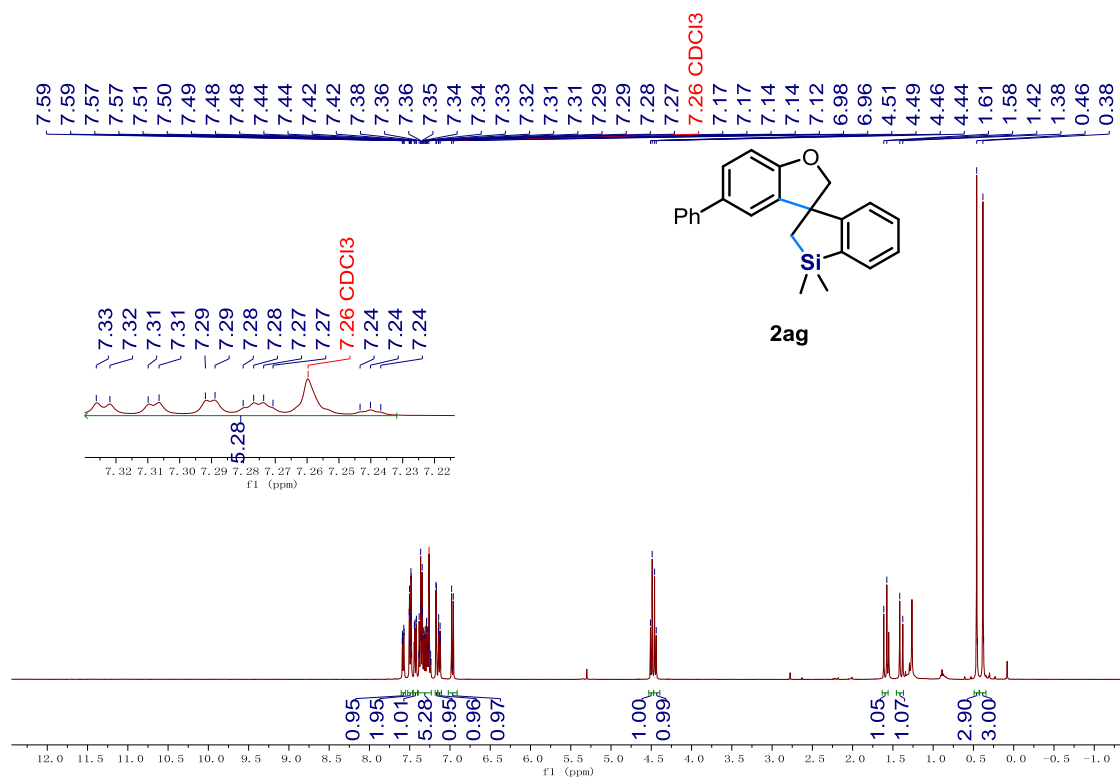
Supplementary Figure 106. ¹H NMR (400 MHz, CDCl₃) spectra of 2af

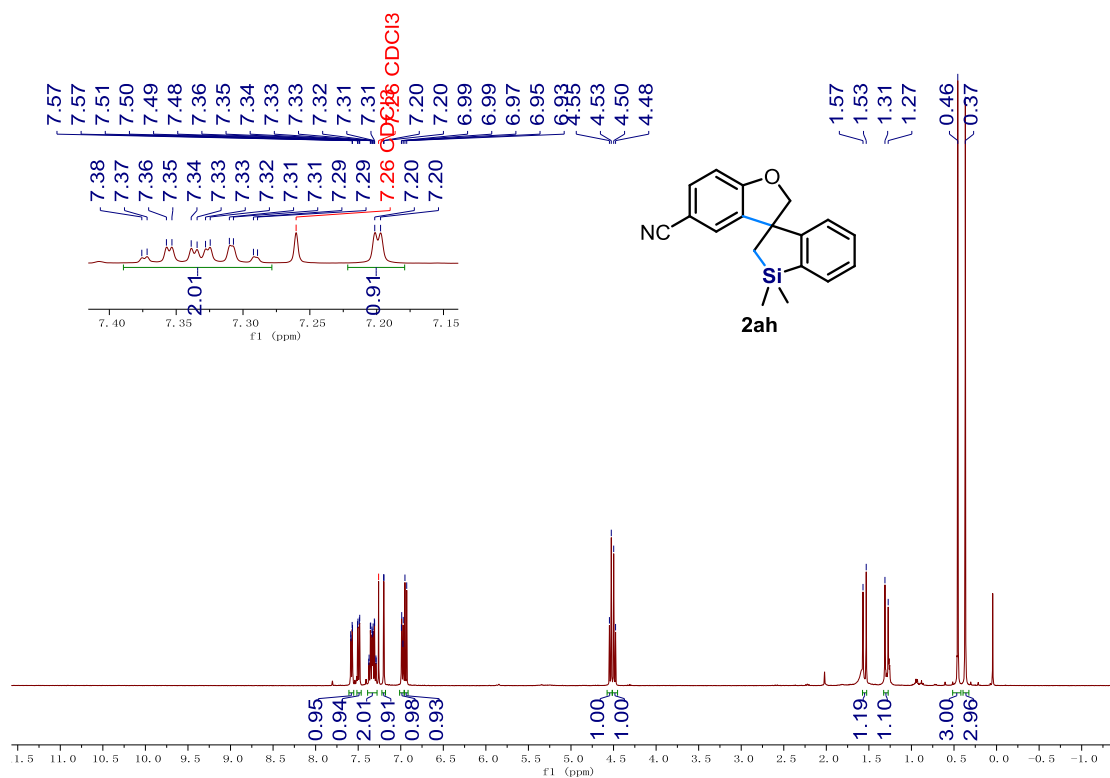


Supplementary Figure 107. ¹³C NMR (101 MHz, CDCl₃) spectra of 2af

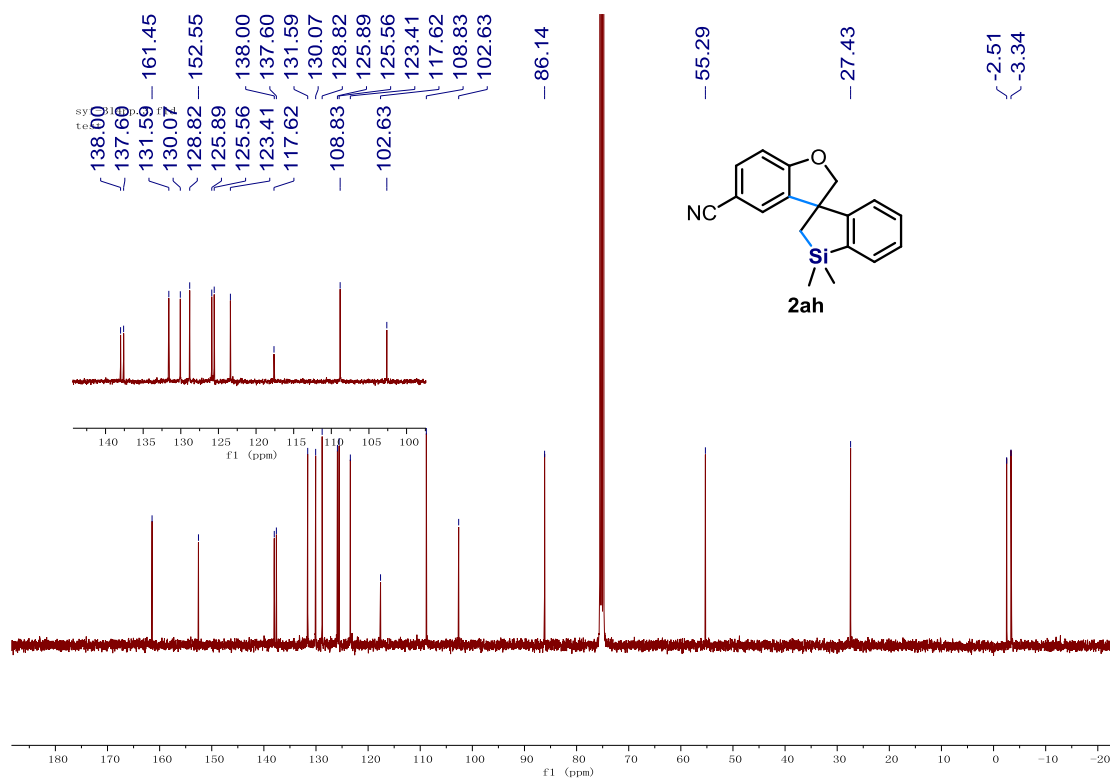


Supplementary Figure 108. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2af**

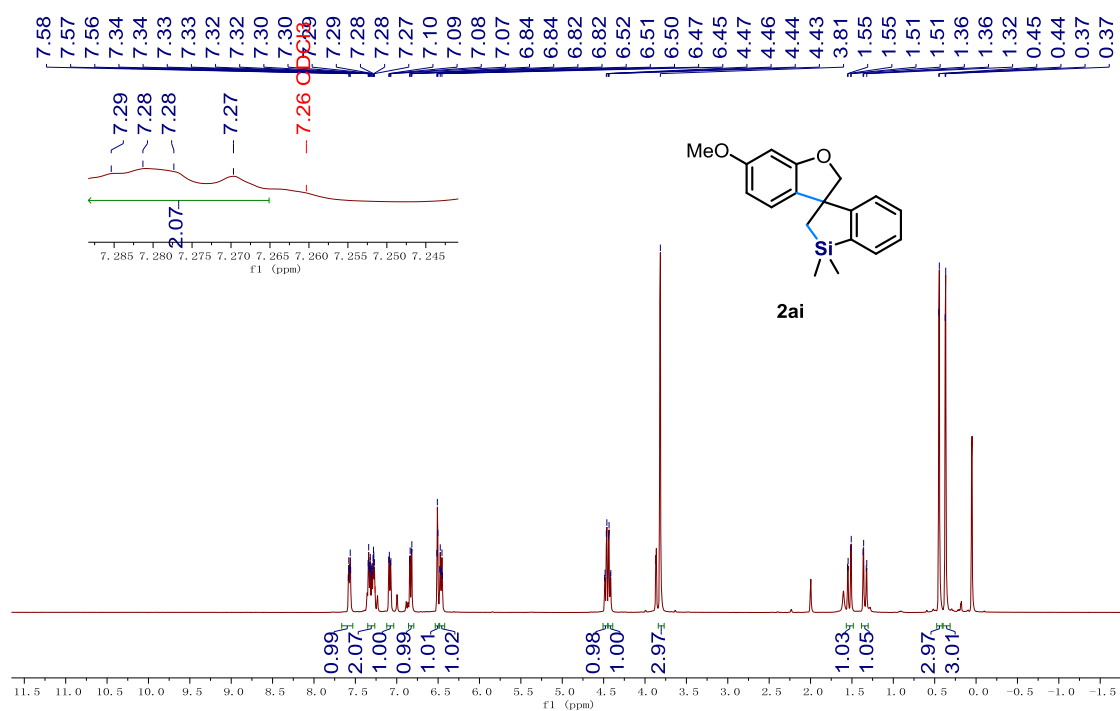




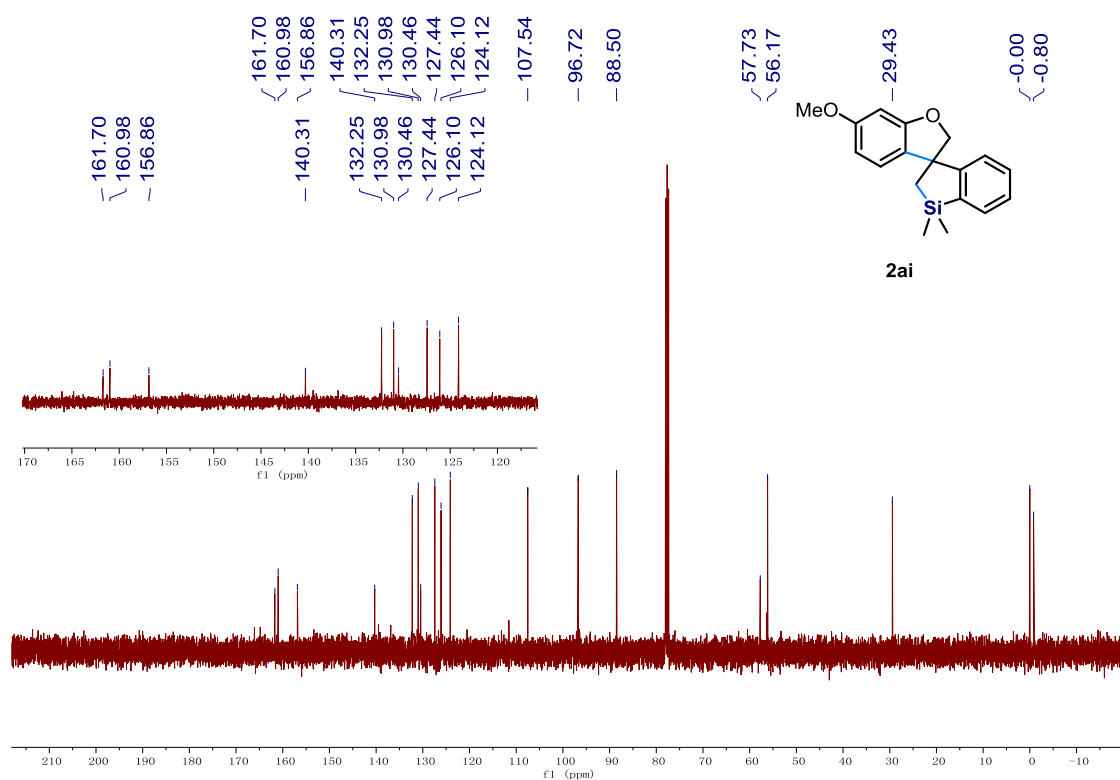
Supplementary Figure 111. ¹H NMR (400 MHz, CDCl₃) spectra of 2ah



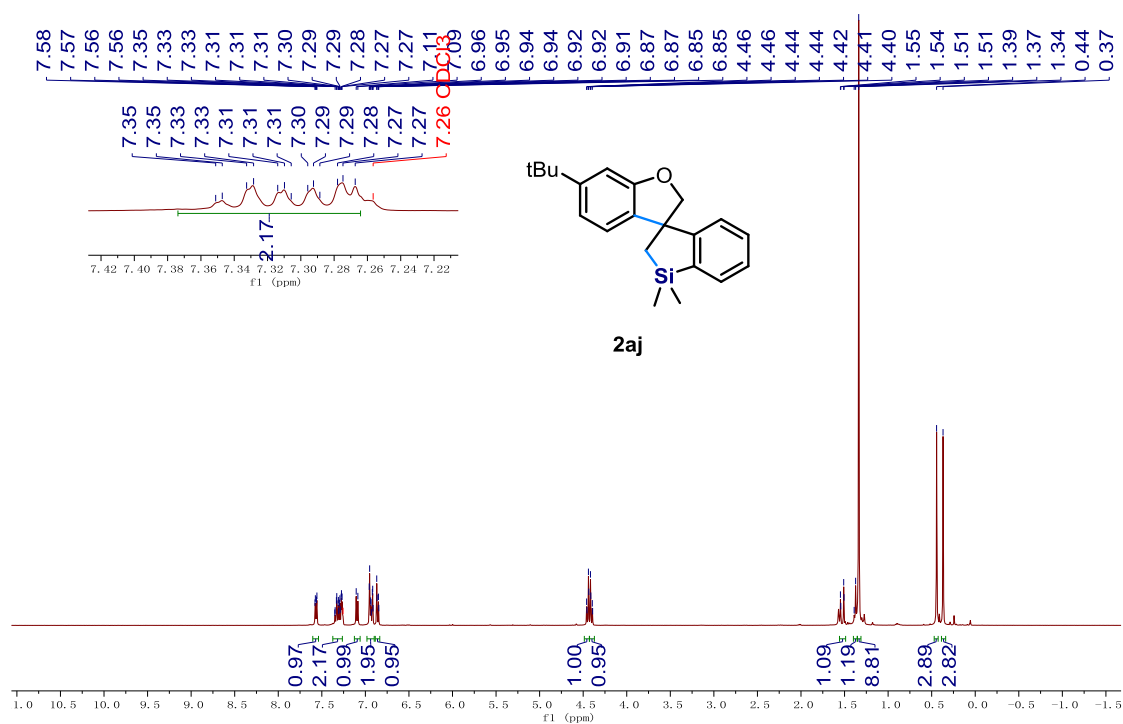
Supplementary Figure 112. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ah



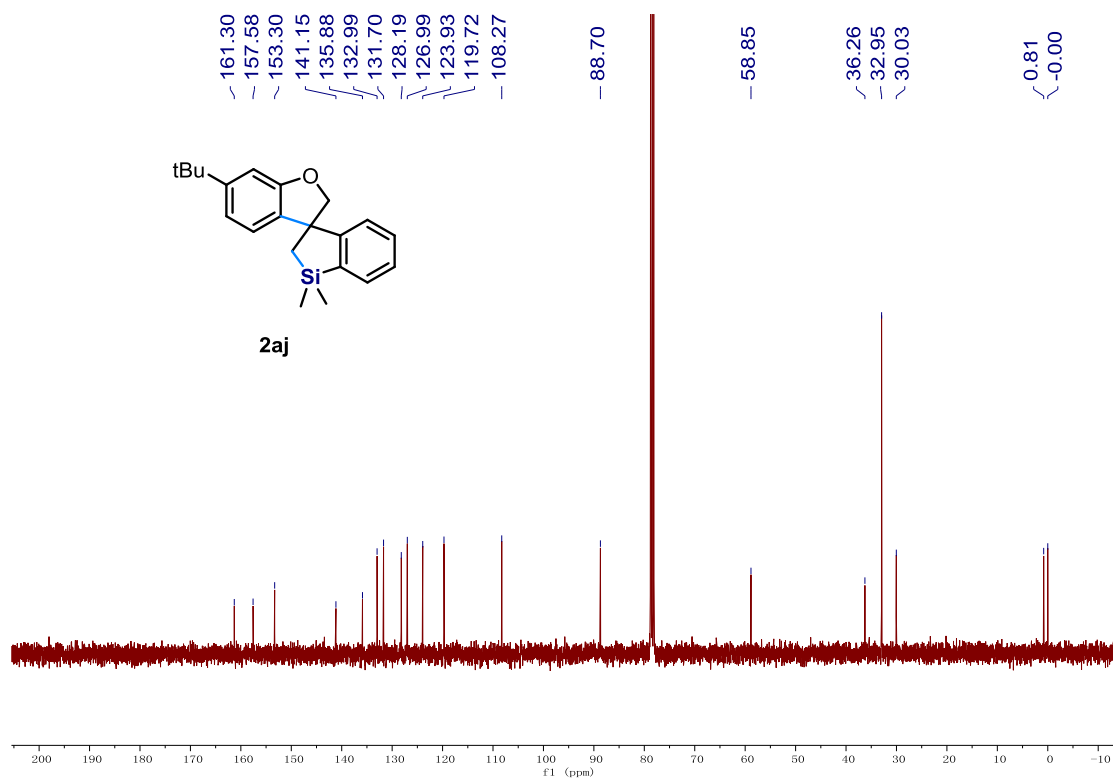
Supplementary Figure 113. ¹H NMR (400 MHz, CDCl₃) spectra of 2ai



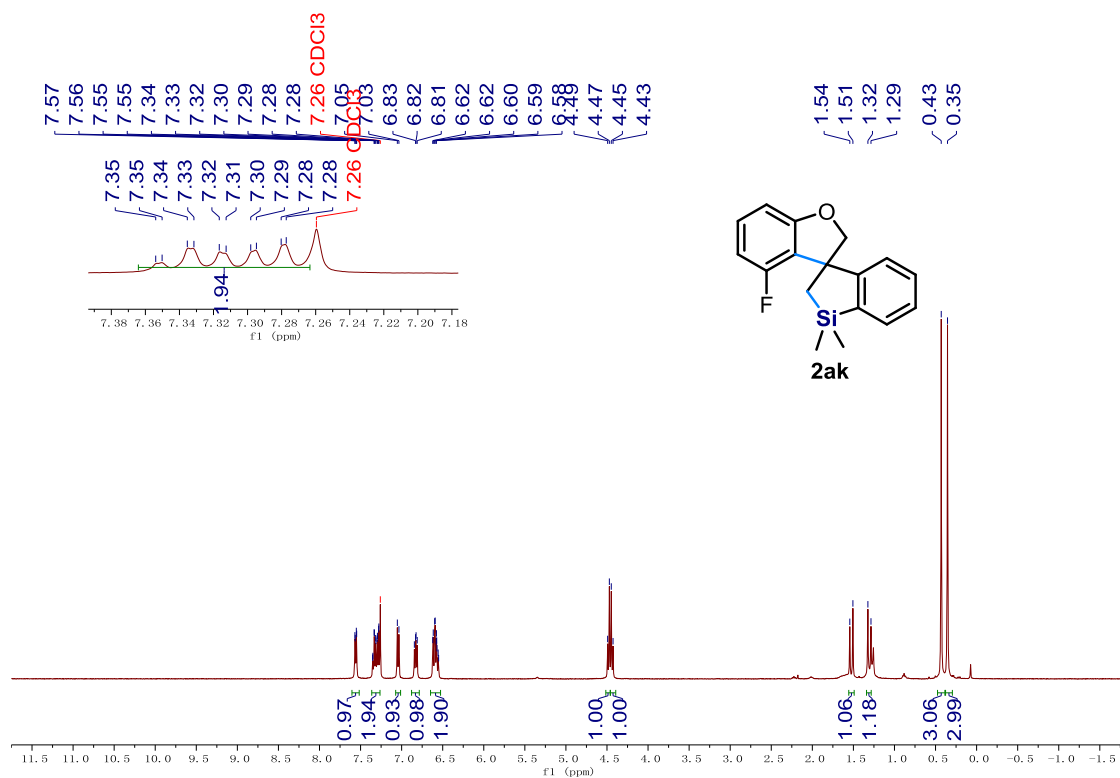
Supplementary Figure 114. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ai



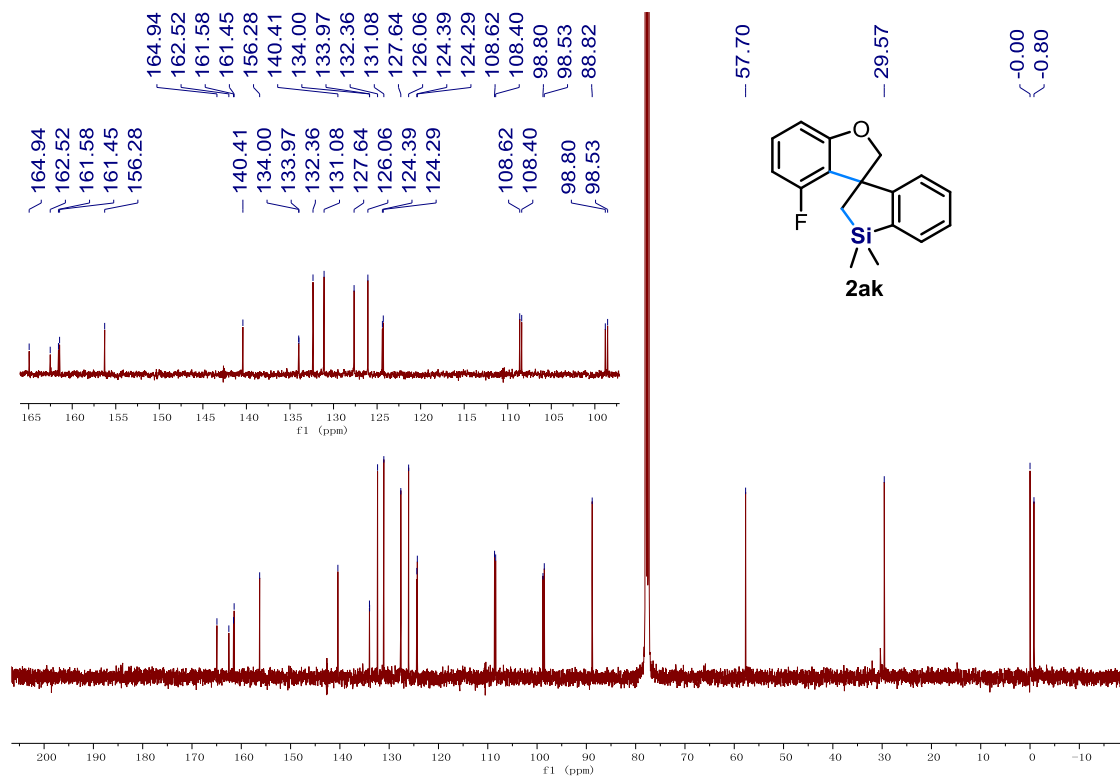
Supplementary Figure 115. ¹H NMR (400 MHz, CDCl₃) spectra of **2aj**



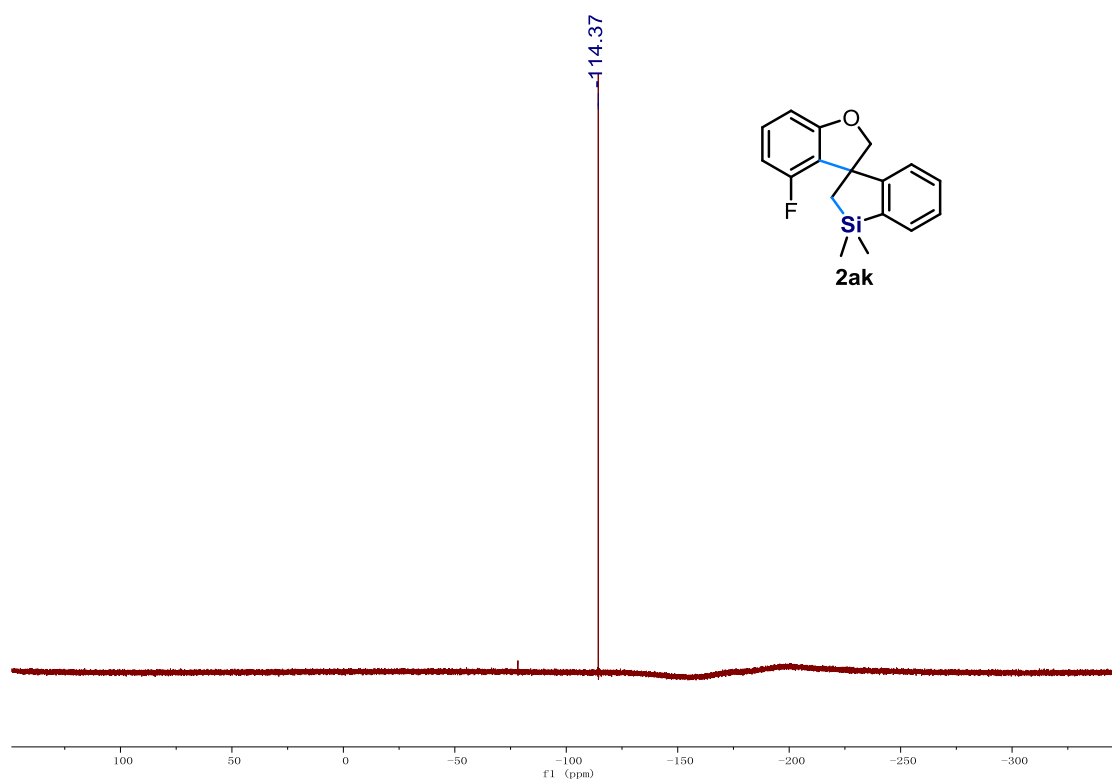
Supplementary Figure 116. ¹³C NMR (101 MHz, CDCl₃) spectra of **2aj**



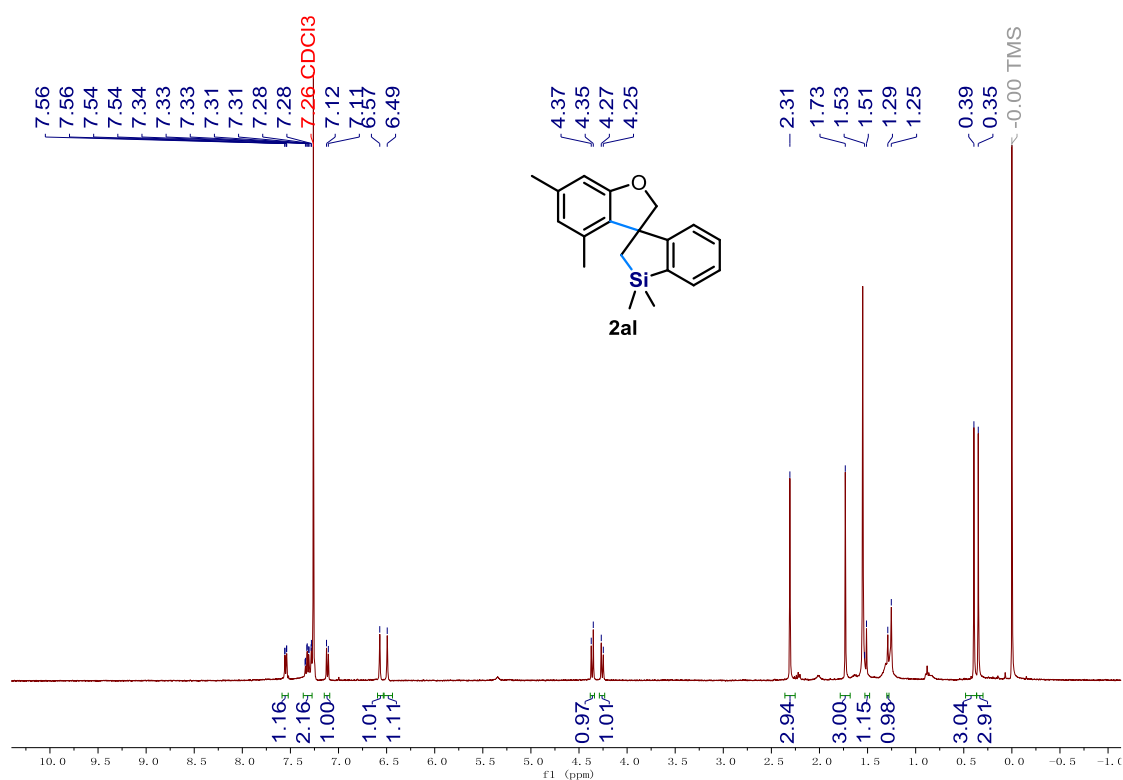
Supplementary Figure 117. ¹H NMR (400 MHz, CDCl₃) spectra of 2ak



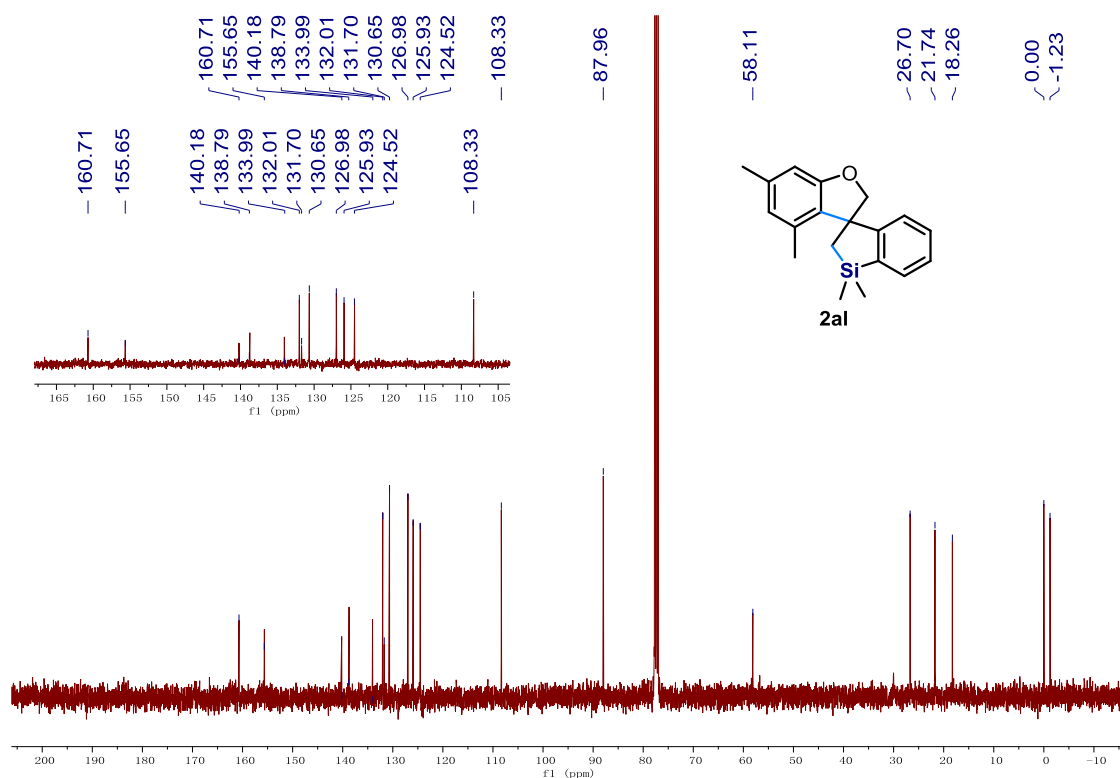
Supplementary Figure 118. ¹³C NMR (101 MHz, CDCl₃) spectra of 2aj



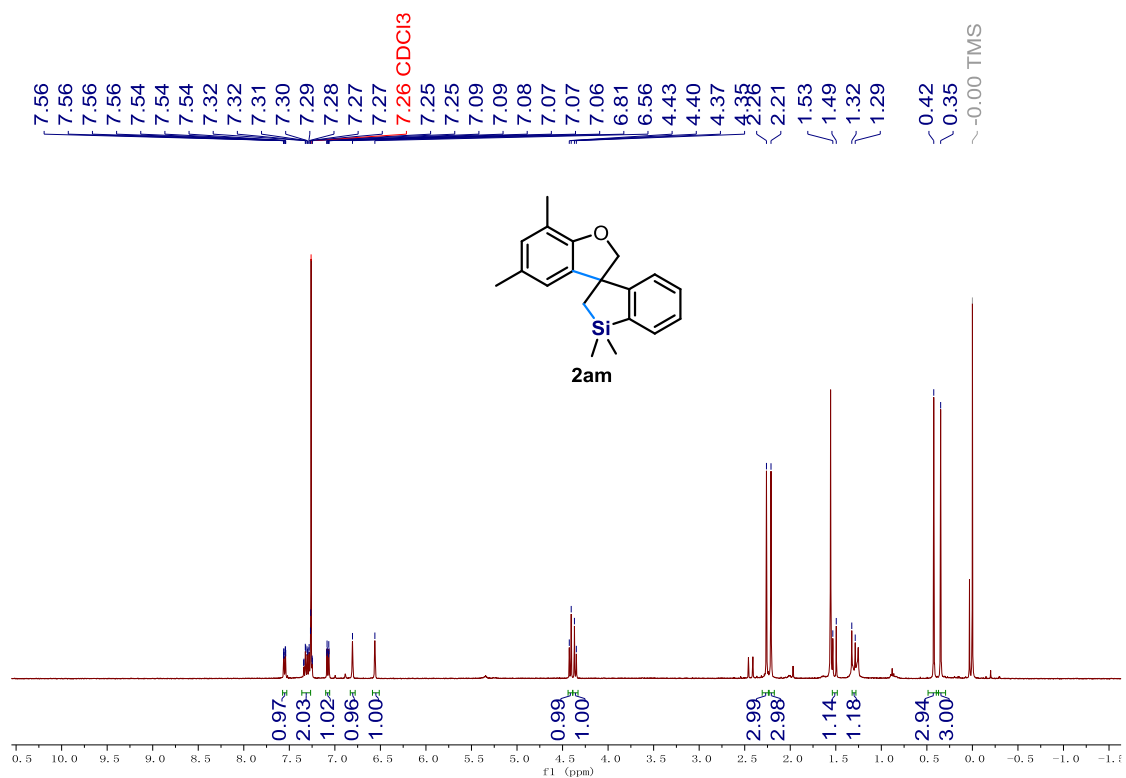
Supplementary Figure 119. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2ak**



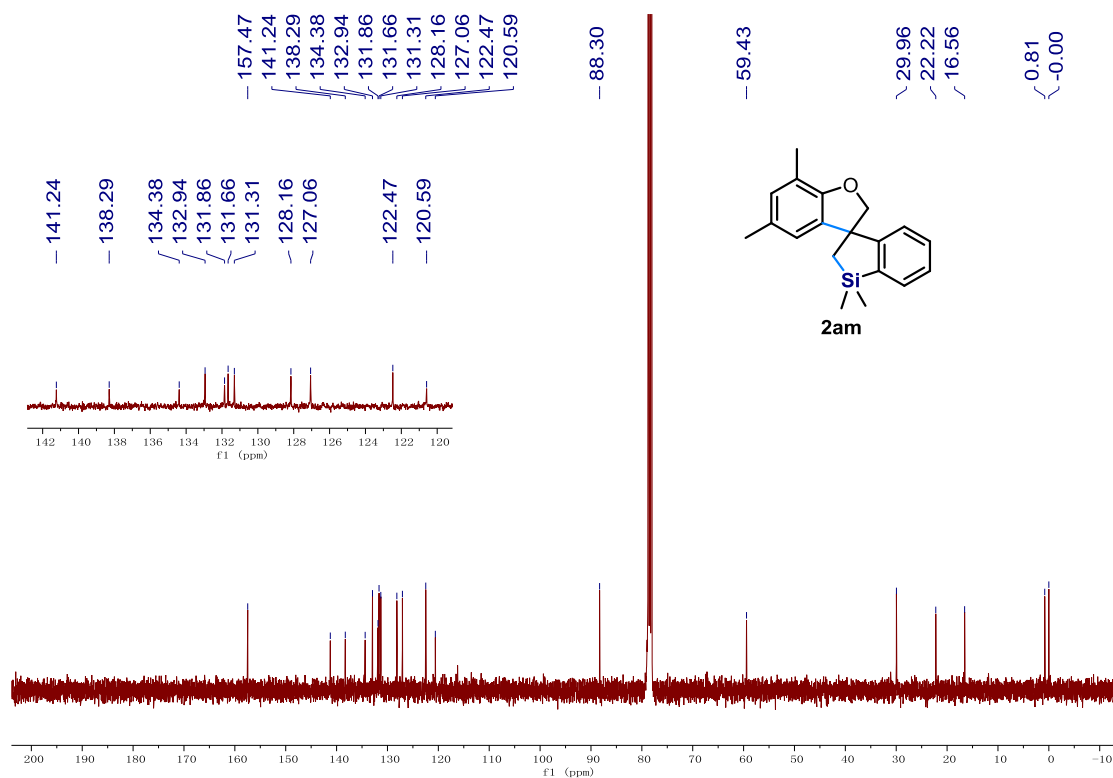
Supplementary Figure 120. ¹H NMR (400 MHz, CDCl₃) spectra of 2al



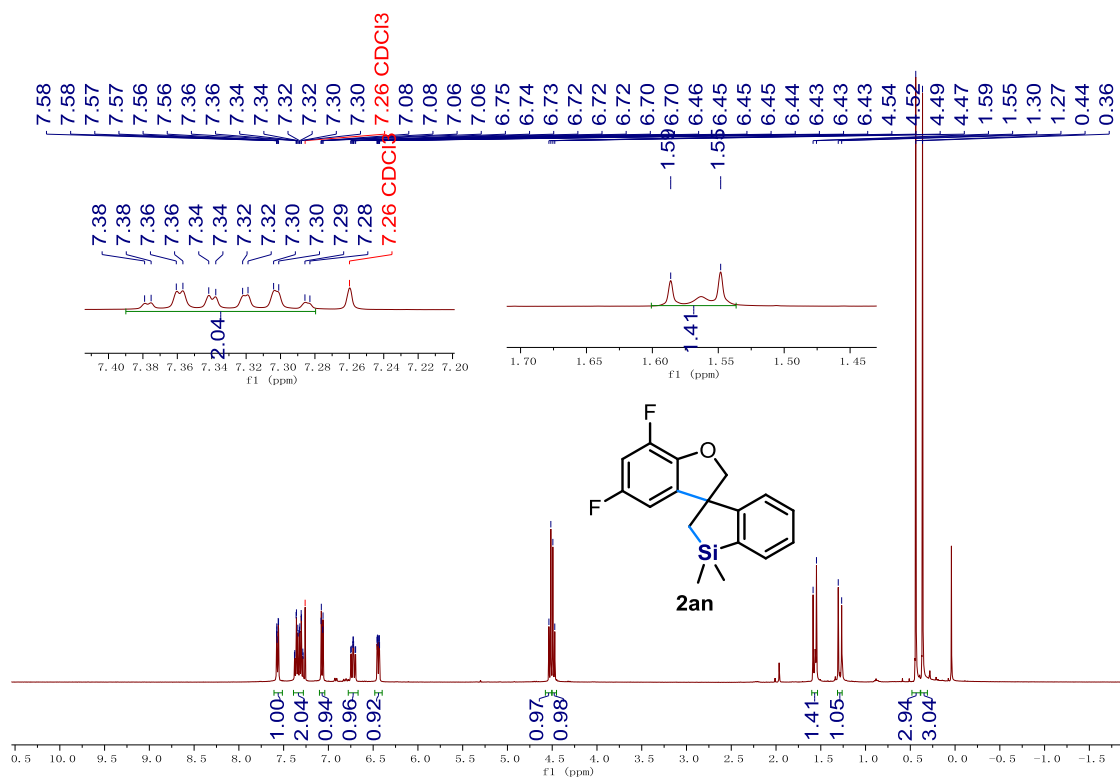
Supplementary Figure 121. ¹³C NMR (101 MHz, CDCl₃) spectra of 2al



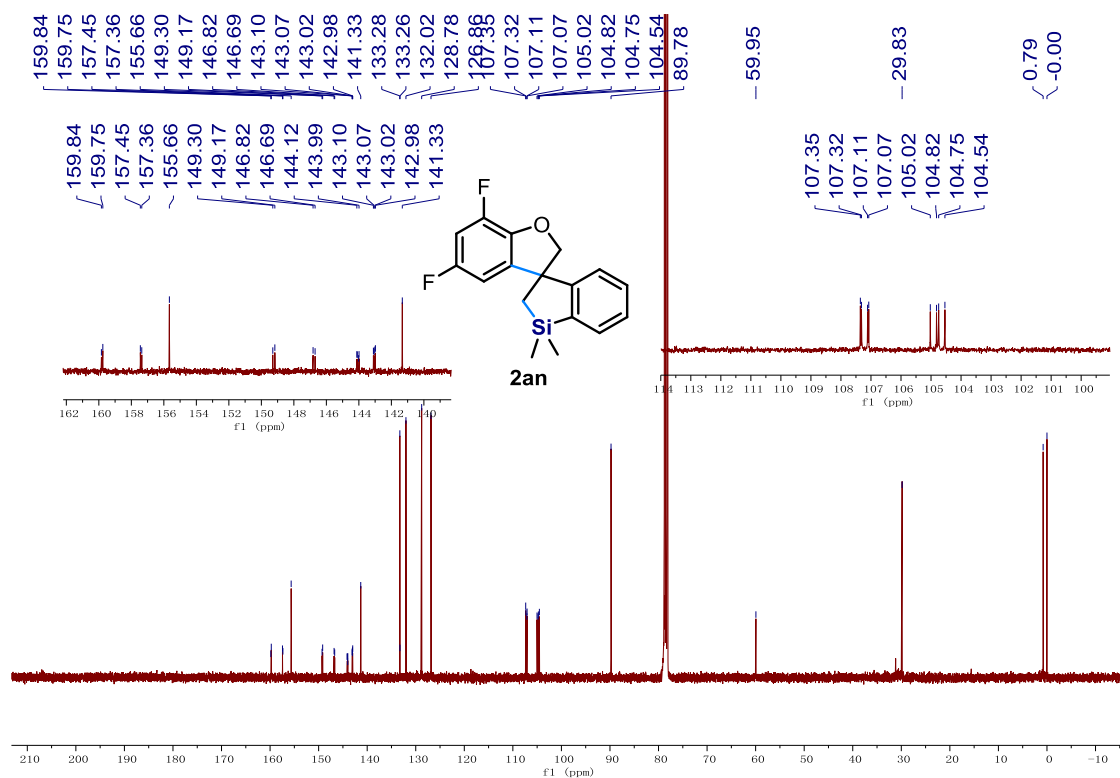
Supplementary Figure 122. ¹H NMR (400 MHz, CDCl₃) spectra of 2am



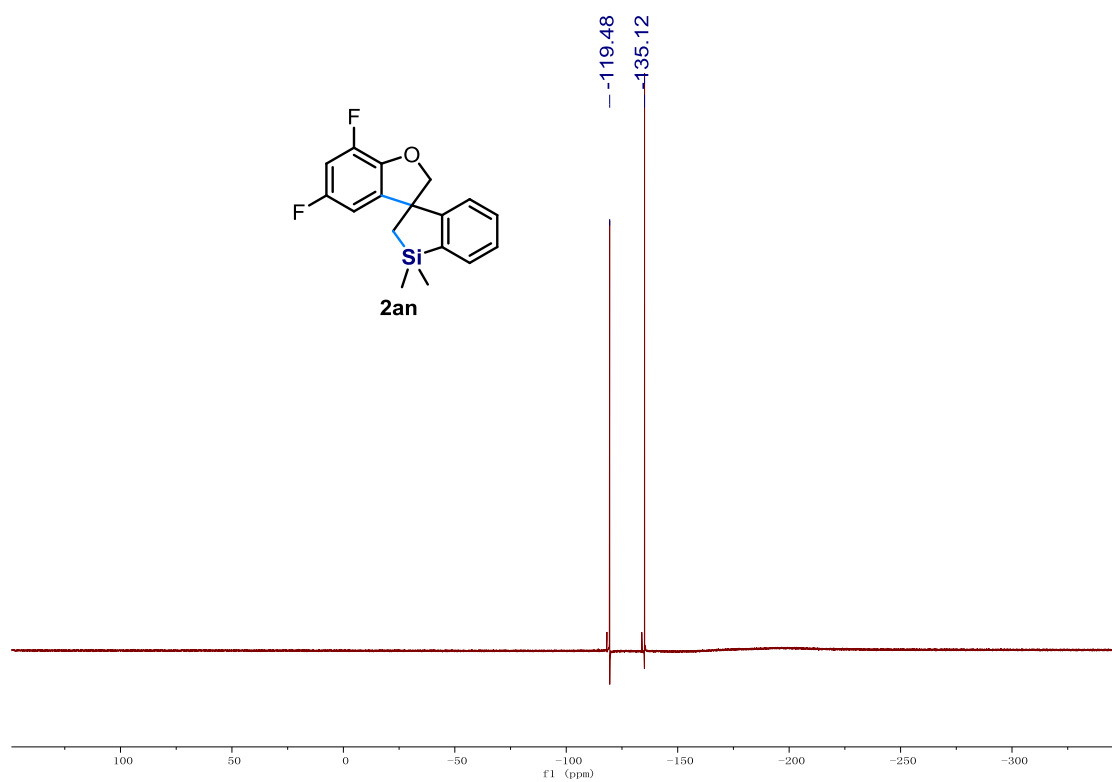
Supplementary Figure 123. ¹³C NMR (101 MHz, CDCl₃) spectra of 2am



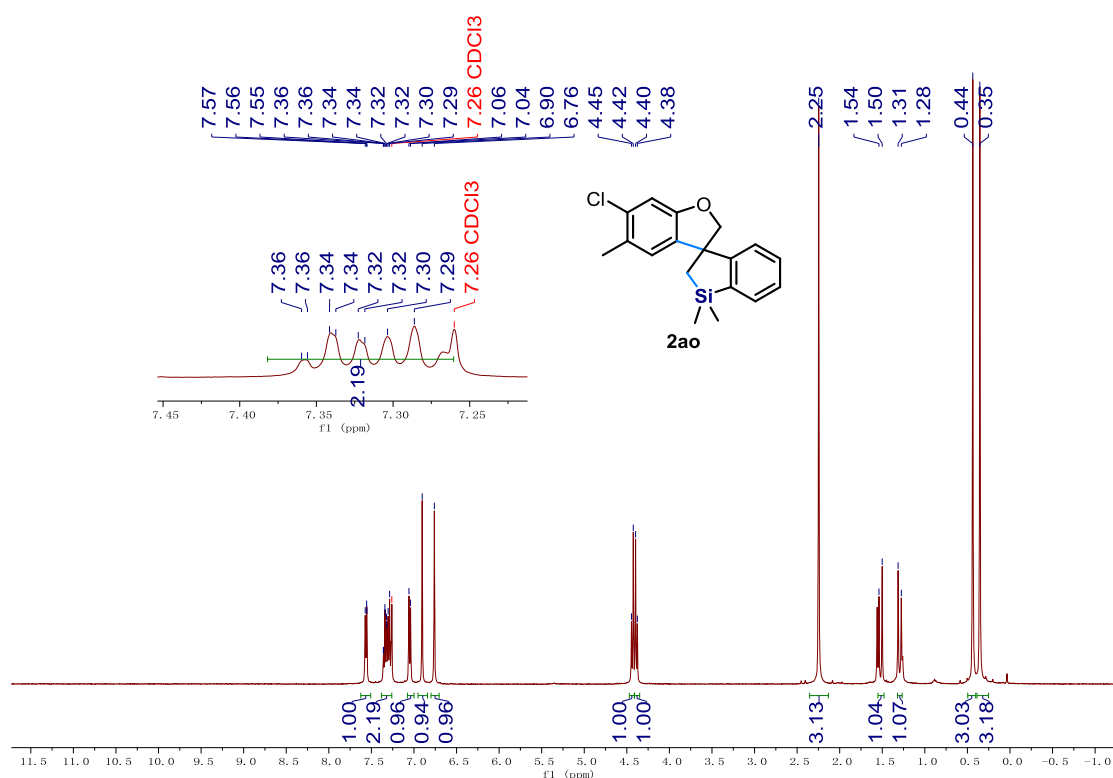
Supplementary Figure 124. ¹H NMR (400 MHz, CDCl₃) spectra of 2an



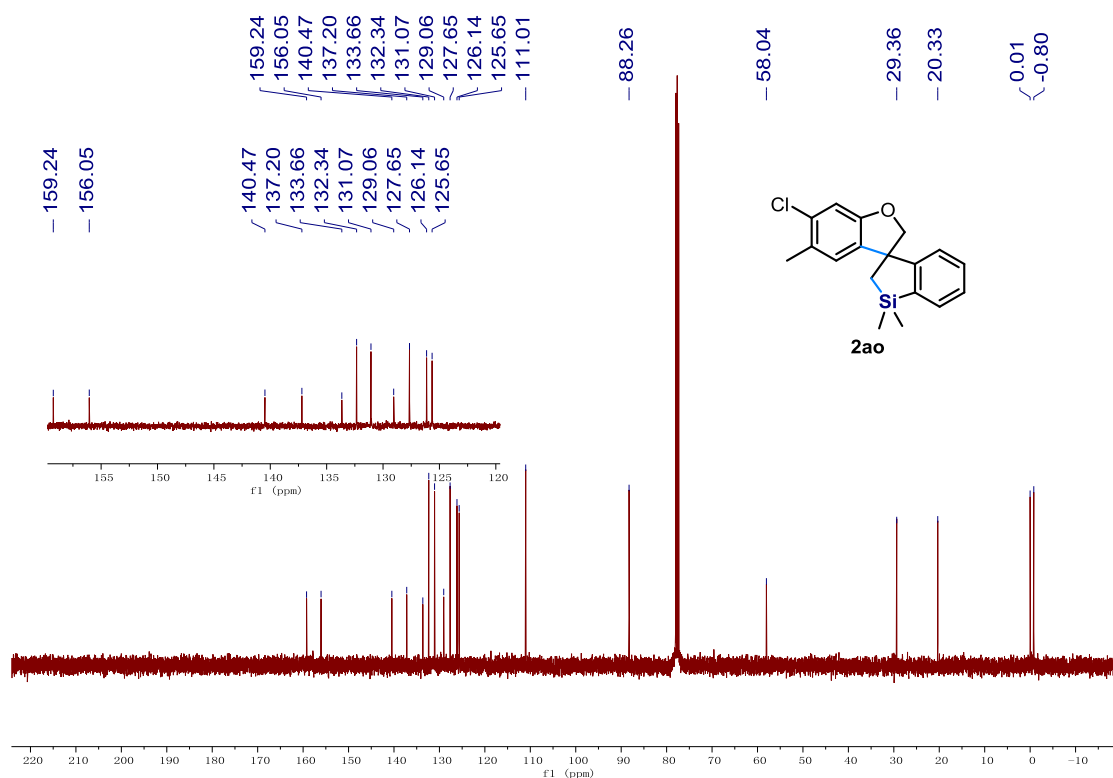
Supplementary Figure 125. ¹³C NMR (101 MHz, CDCl₃) spectra of 2an



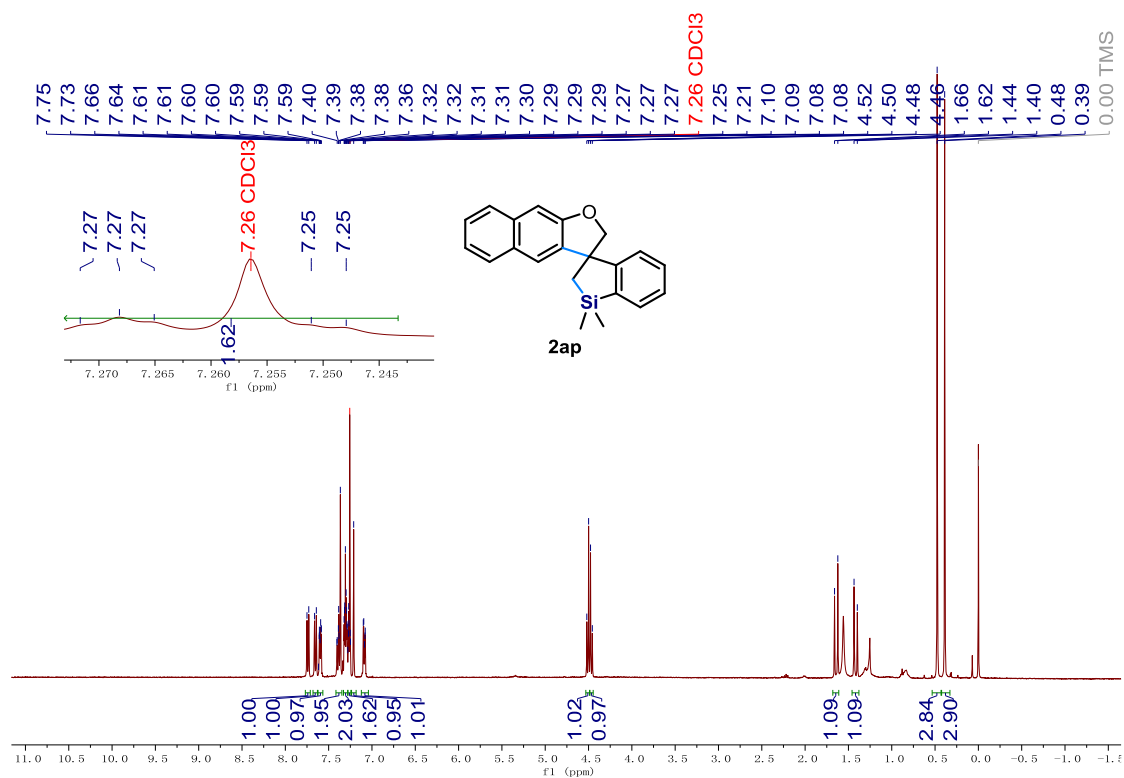
Supplementary Figure 126. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2an**



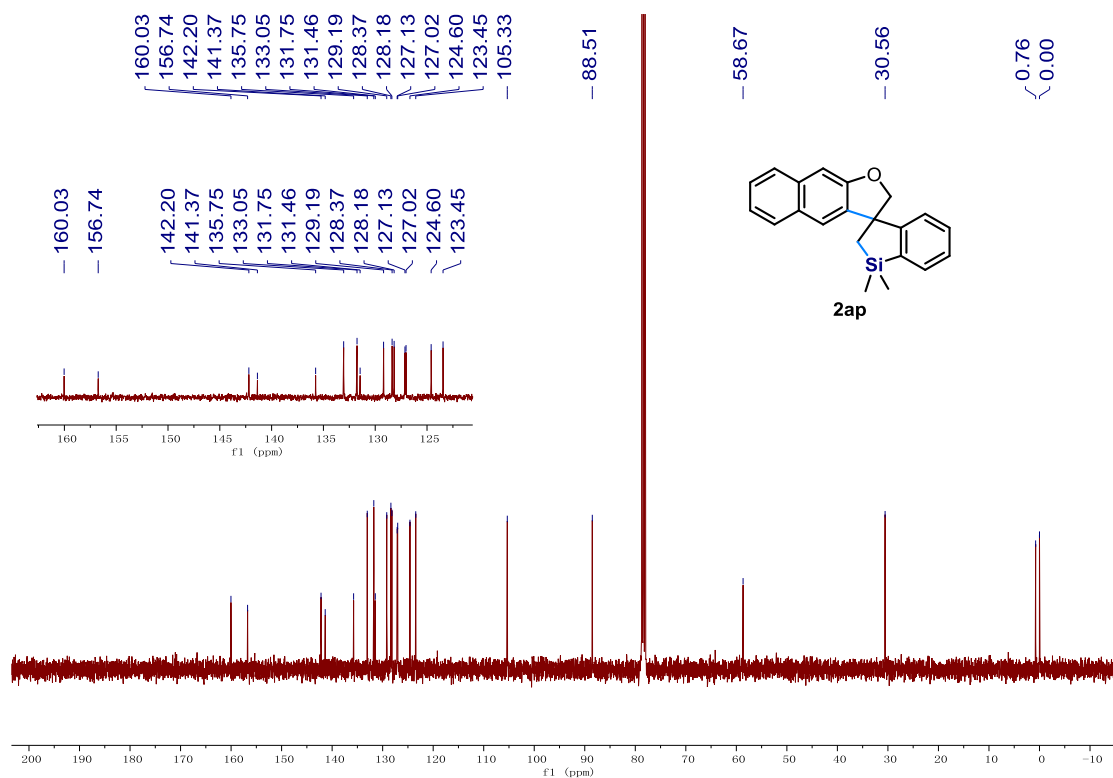
Supplementary Figure 127. ¹H NMR (400 MHz, CDCl₃) spectra of 2ao



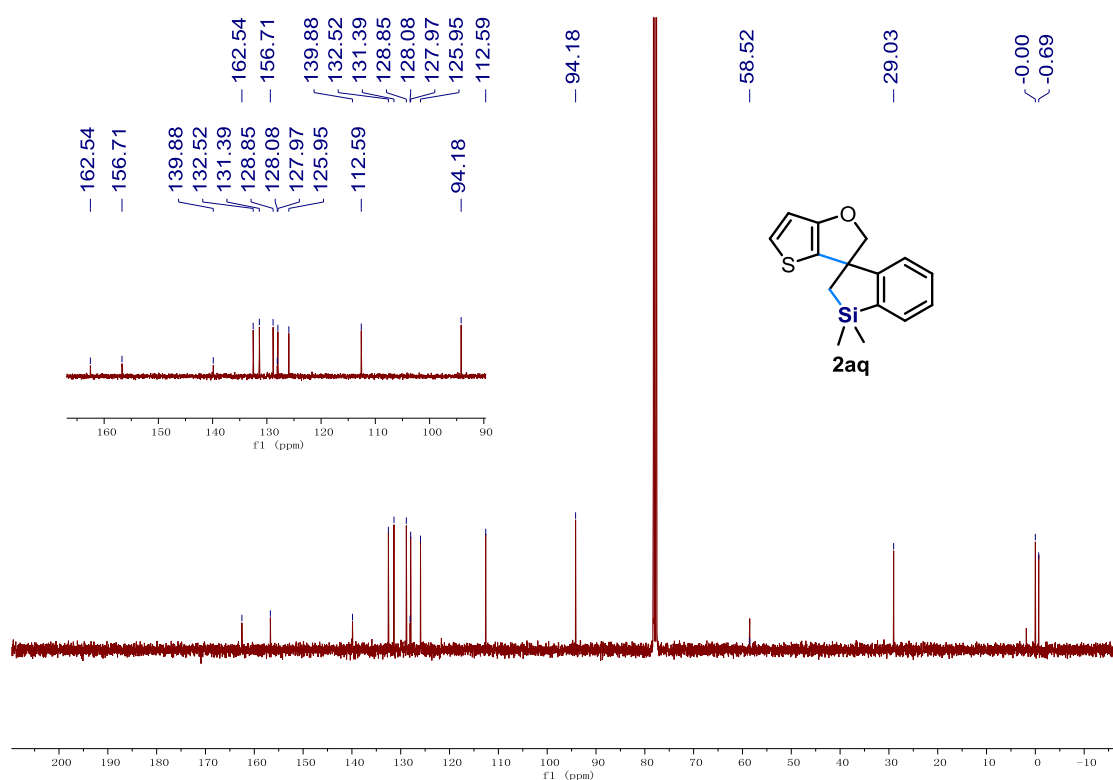
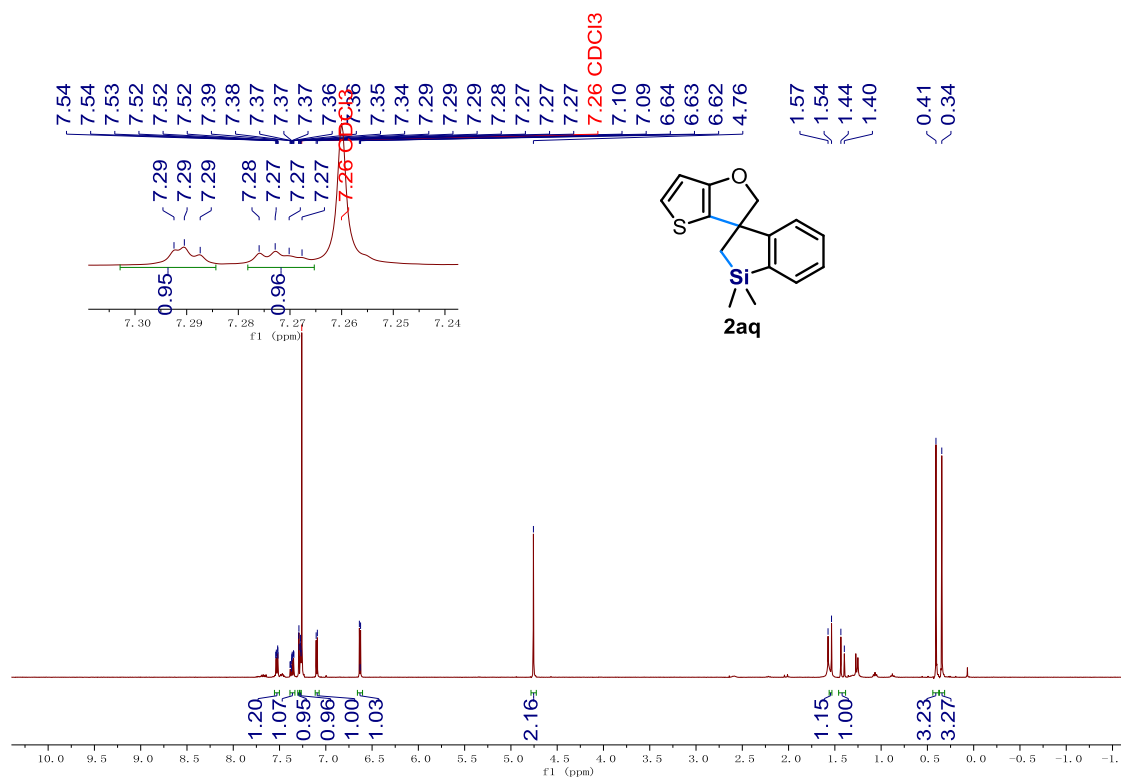
Supplementary Figure 128. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ao

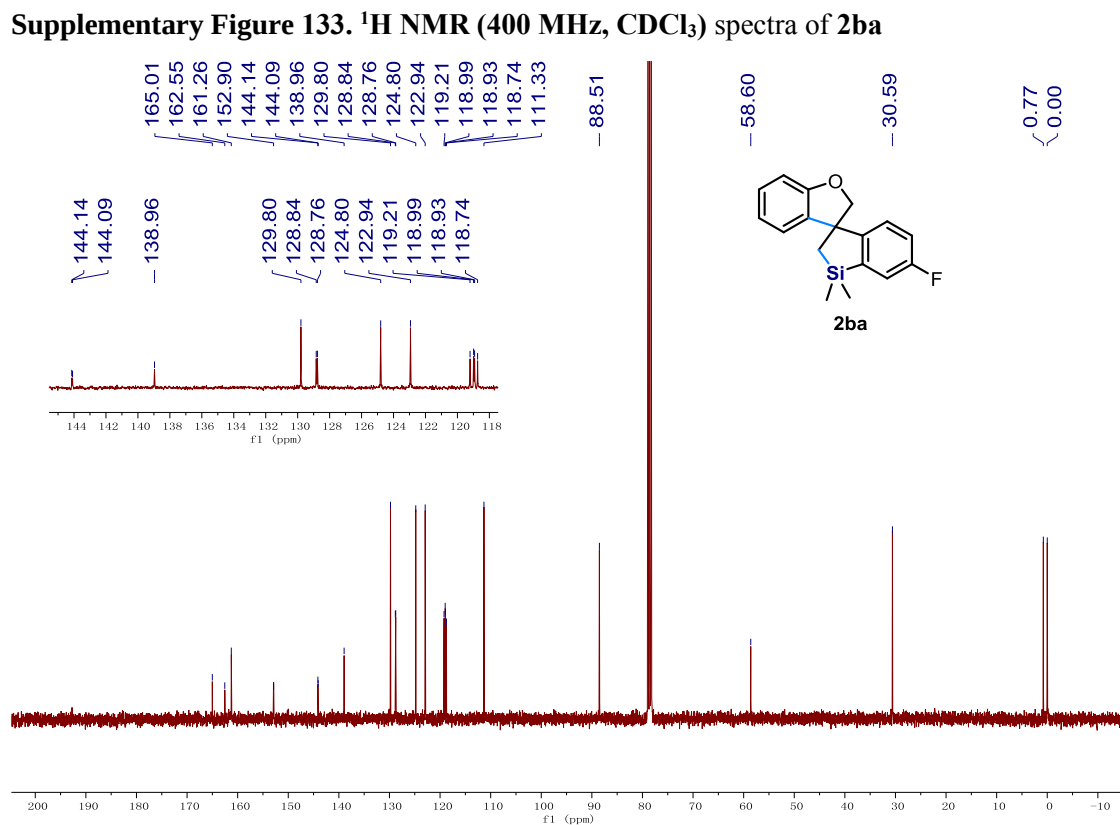
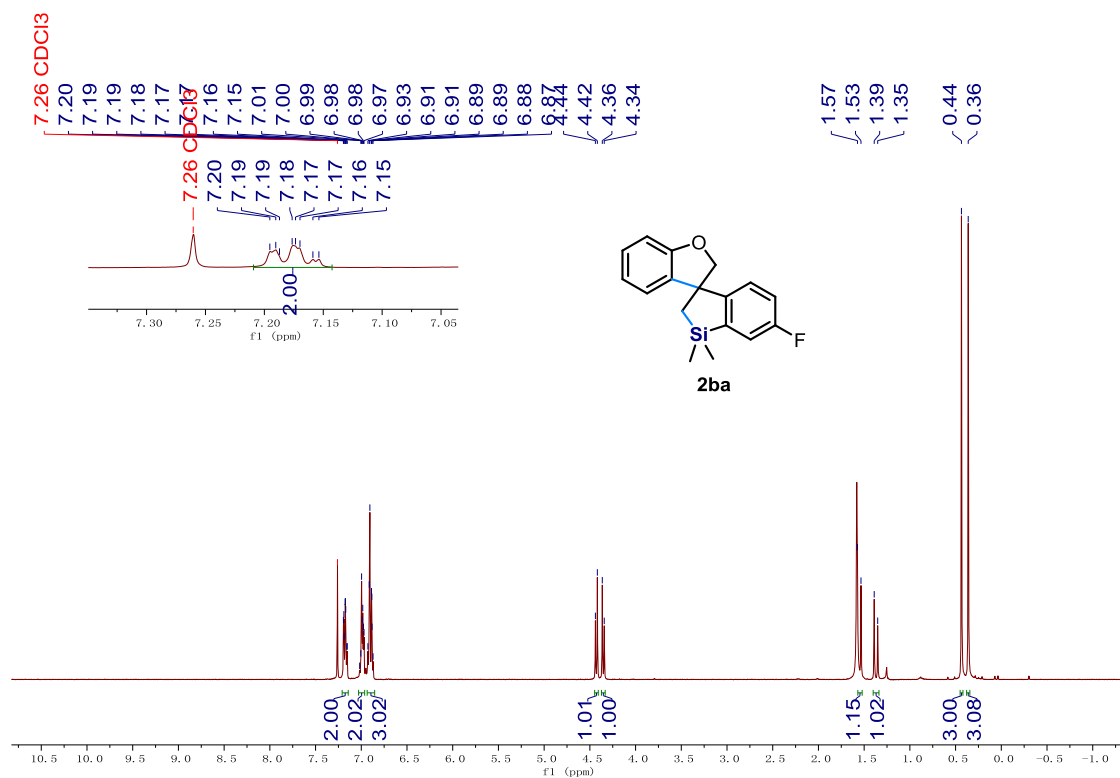


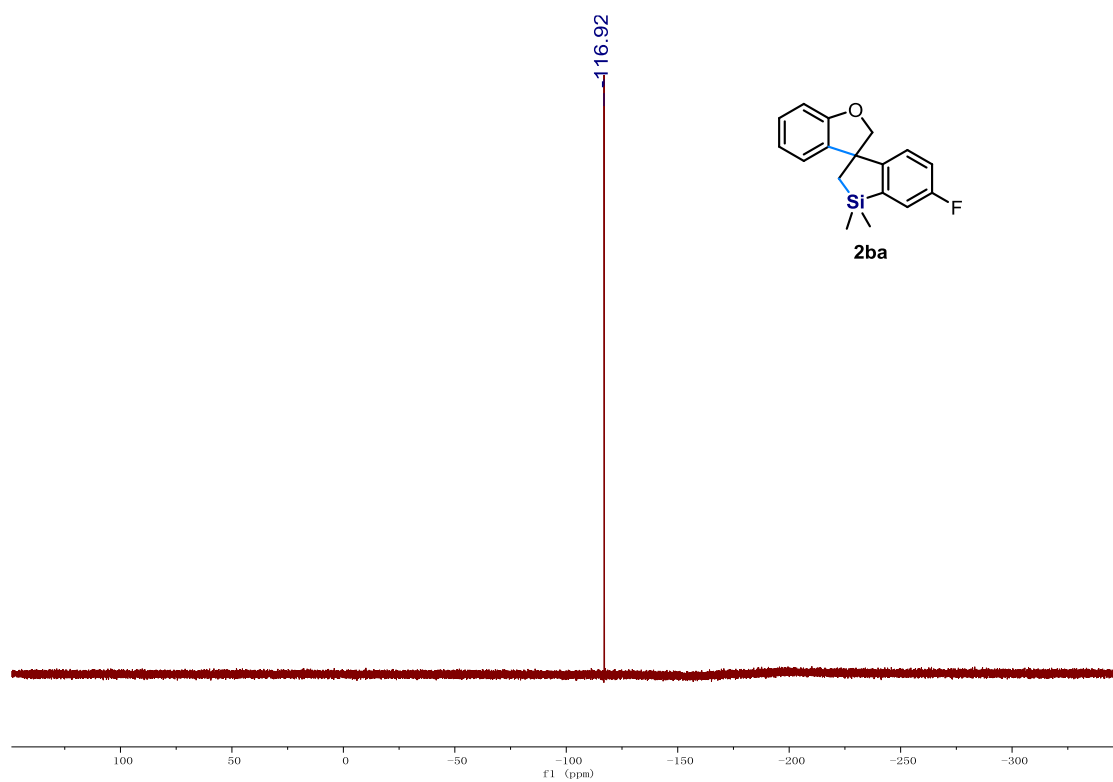
Supplementary Figure 129. ^1H NMR (400 MHz, CDCl_3) spectra of 2ap



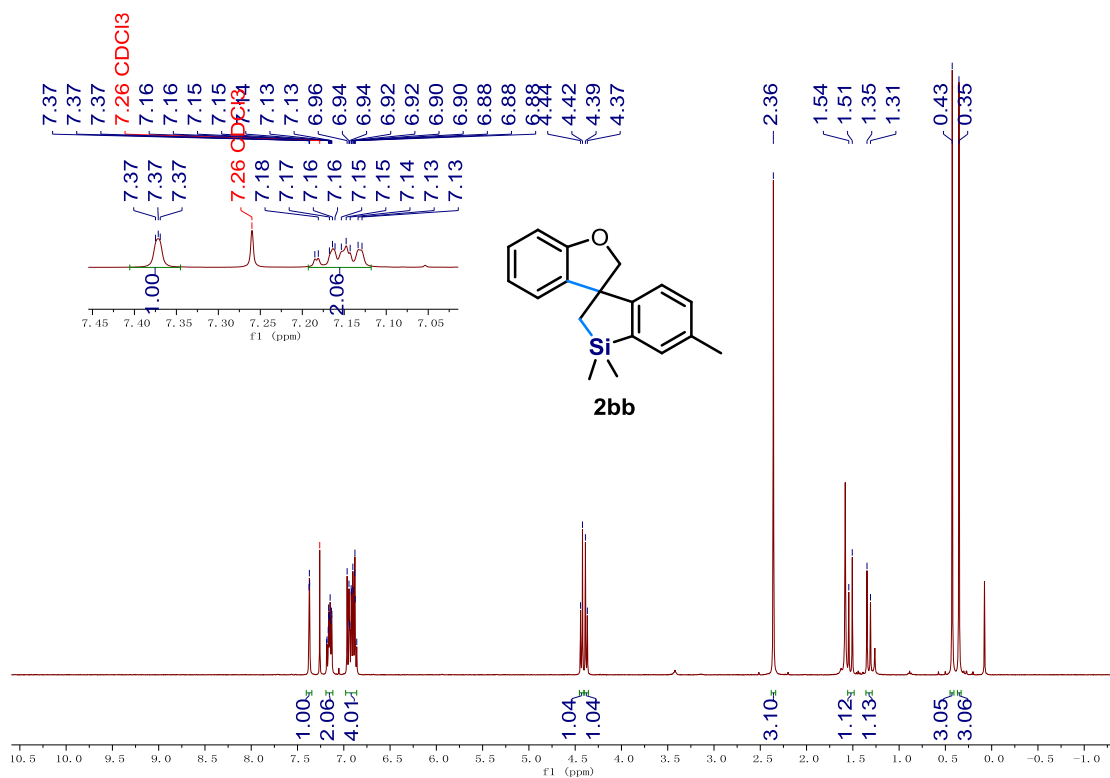
Supplementary Figure 130. ^{13}C NMR (101 MHz, CDCl_3) spectra of 2ap



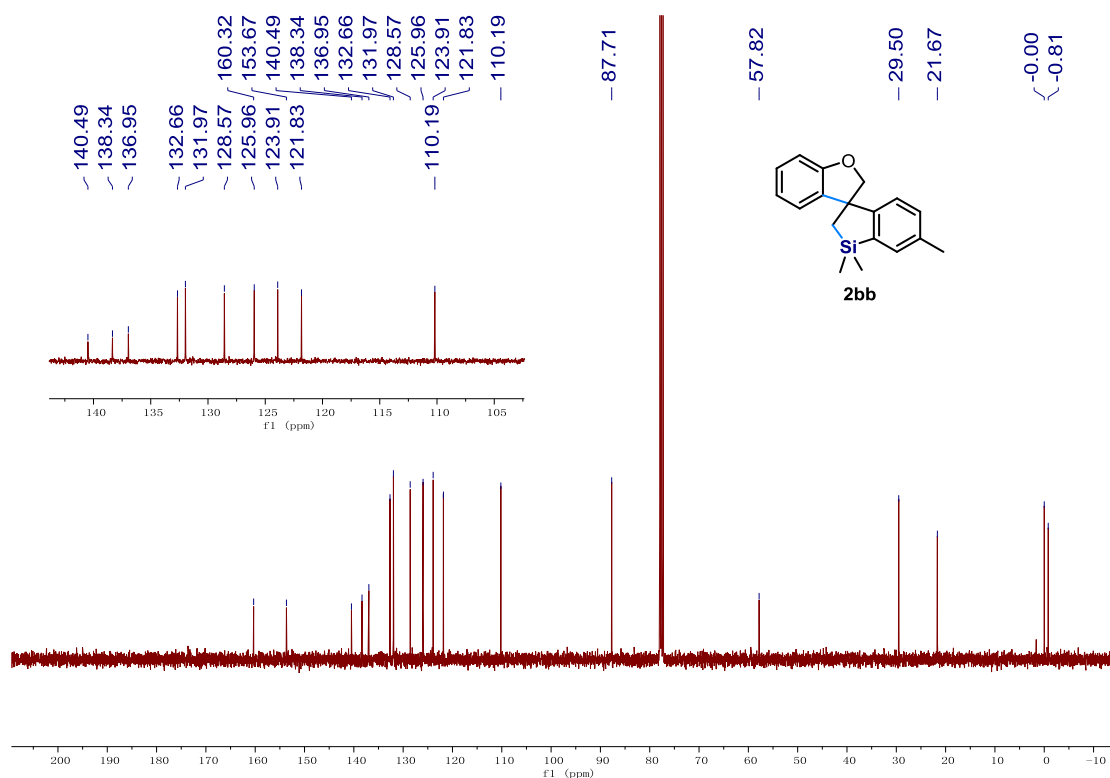




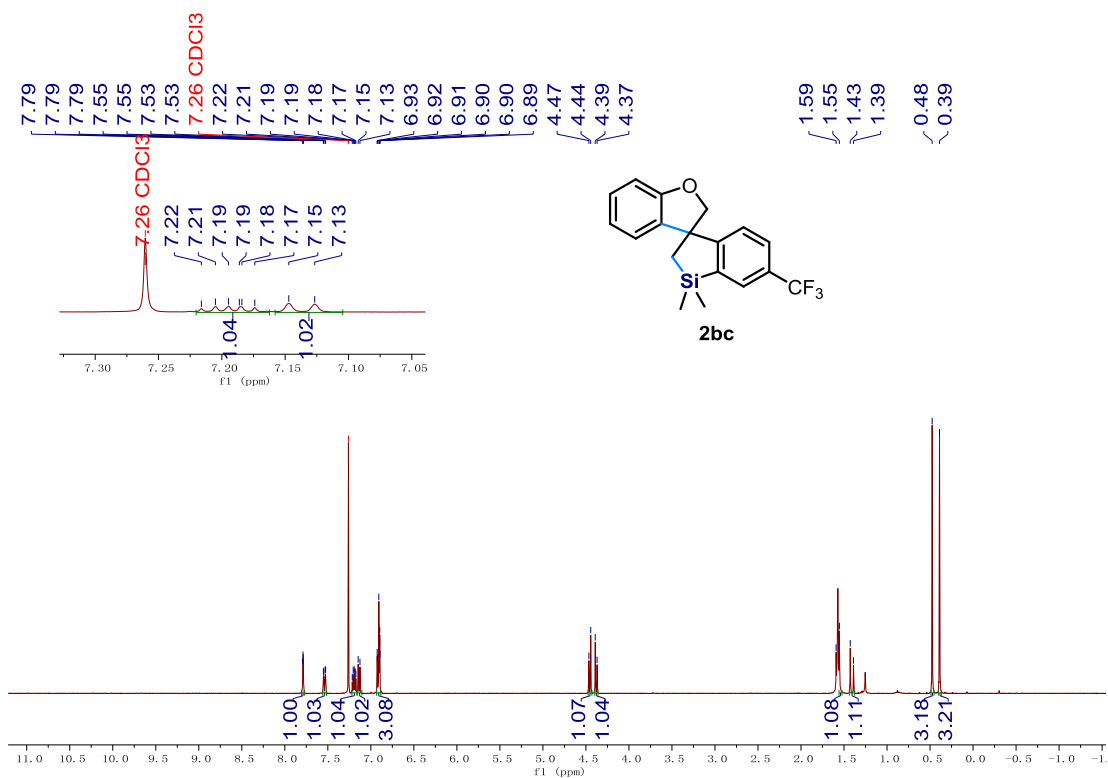
Supplementary Figure 135. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2ba**



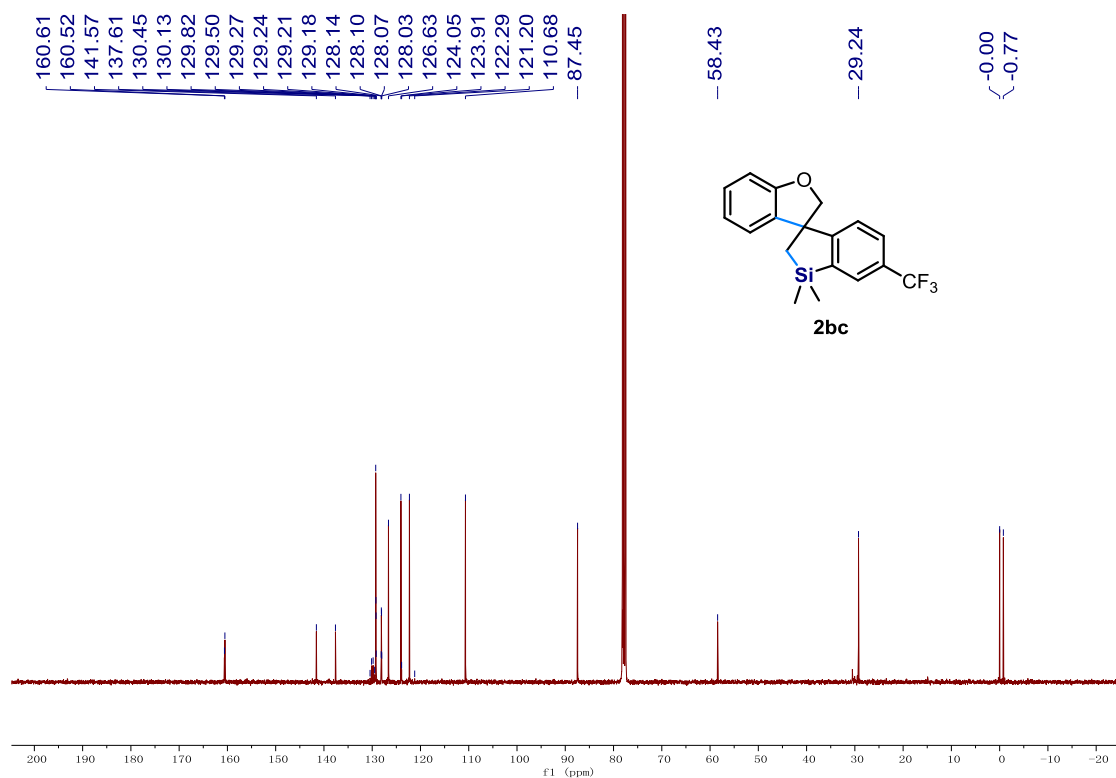
Supplementary Figure 136. ¹H NMR (400 MHz, CDCl₃) spectra of 2bb



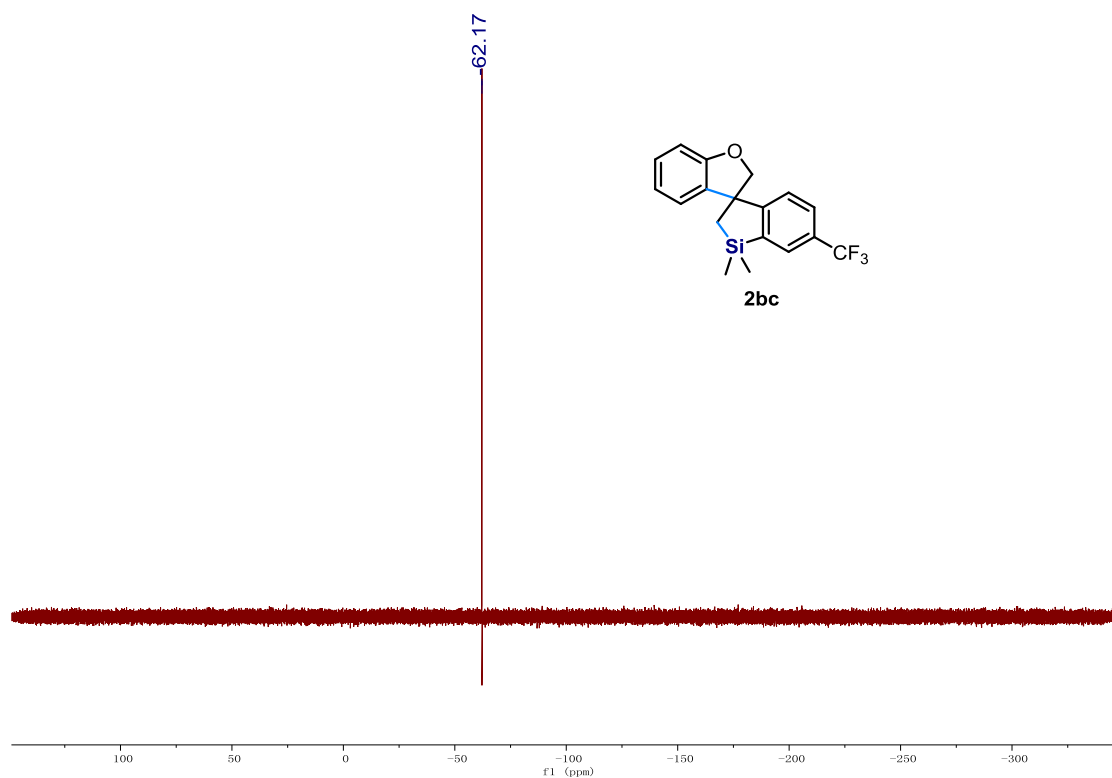
Supplementary Figure 137. ¹³C NMR (101 MHz, CDCl₃) spectra of 2bb



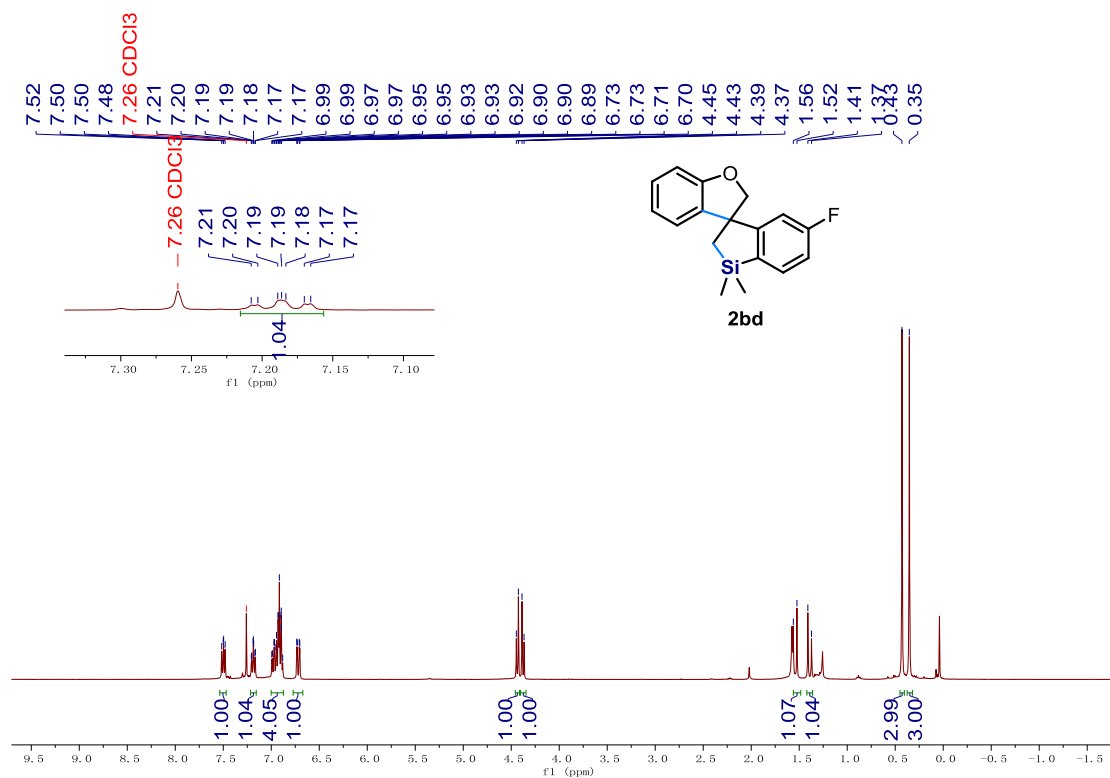
Supplementary Figure 138. ¹H NMR (400 MHz, CDCl₃) spectra of 2bc



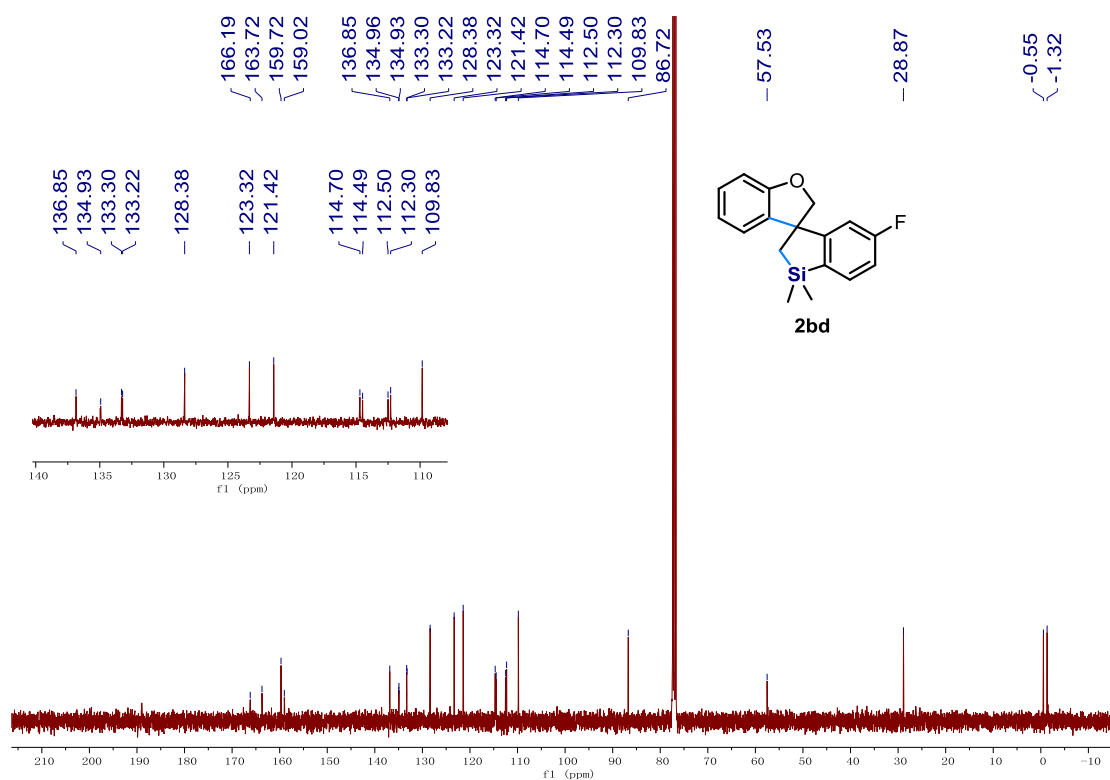
Supplementary Figure 139. ¹³C NMR (101 MHz, CDCl₃) spectra of 2bc



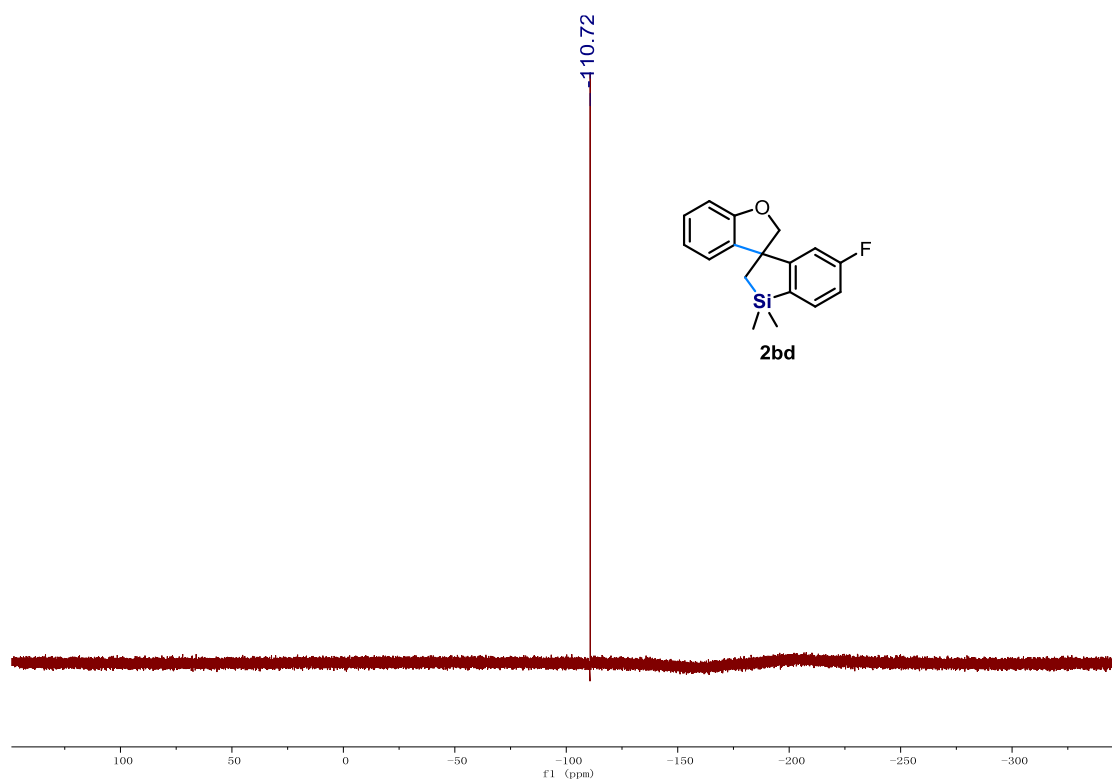
Supplementary Figure 140. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2bc**



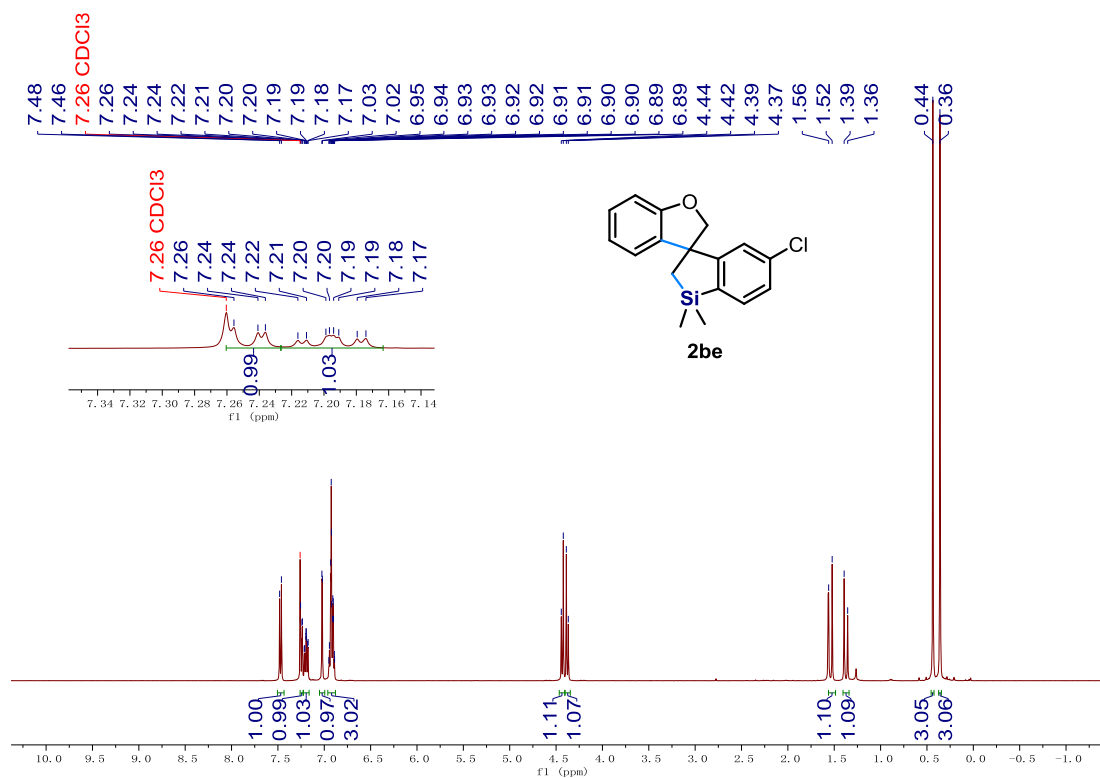
Supplementary Figure 141. ¹H NMR (400 MHz, CDCl₃) spectra of 2bd



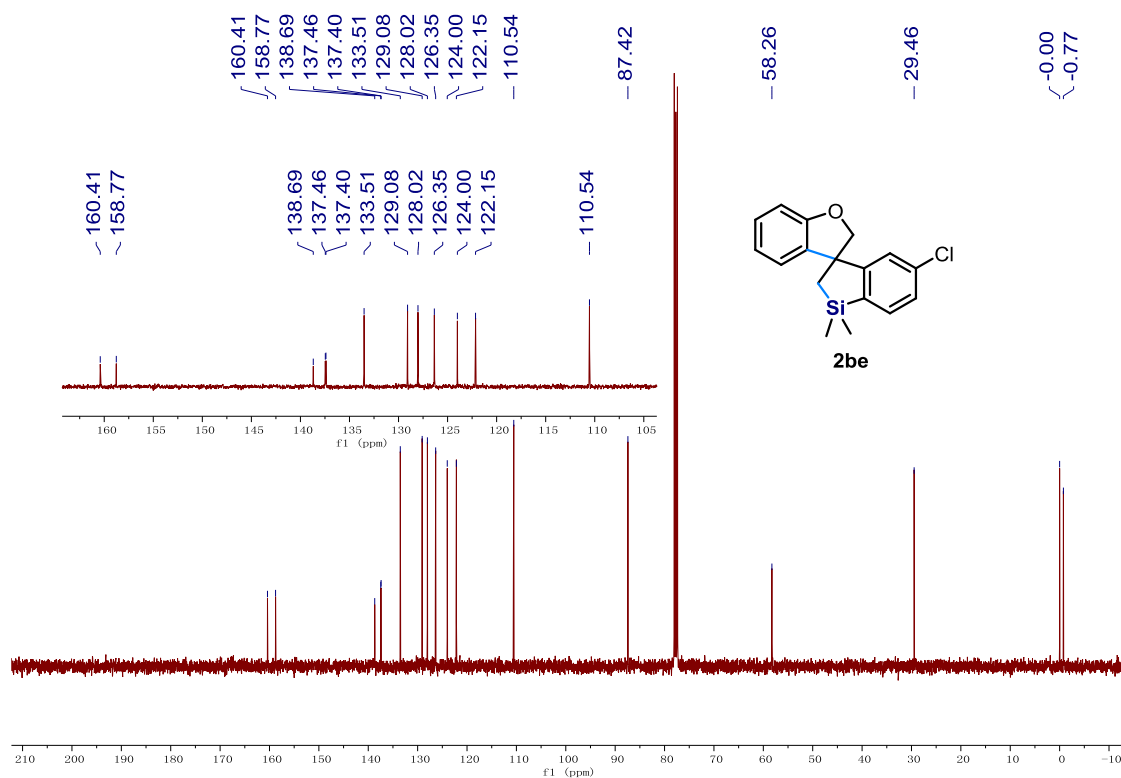
Supplementary Figure 142. ¹³C NMR (101 MHz, CDCl₃) spectra of 2bd



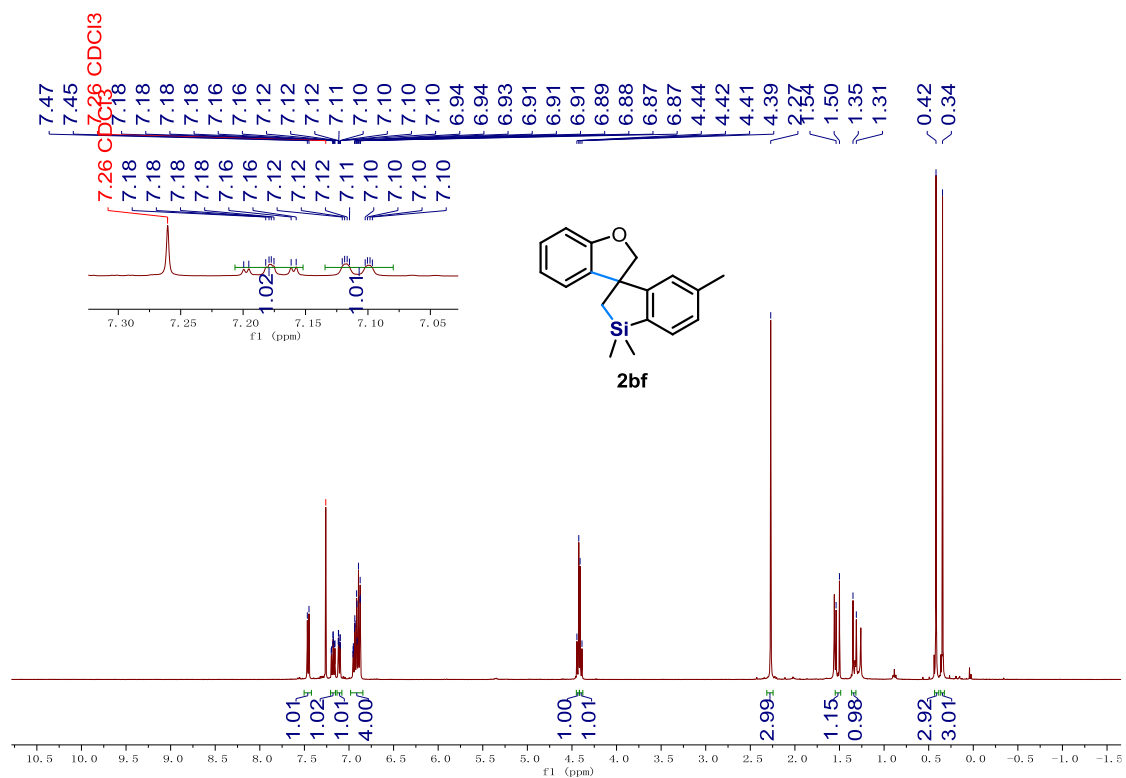
Supplementary Figure 143. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2bd**



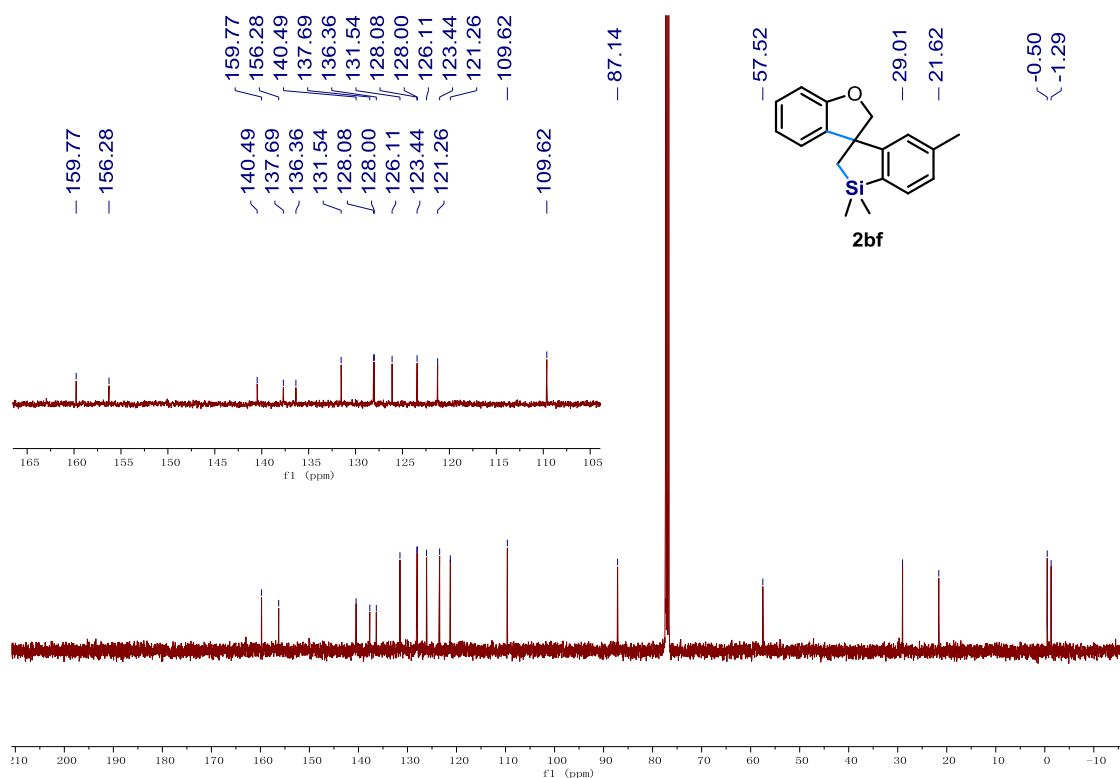
Supplementary Figure 144. ¹H NMR (400 MHz, CDCl₃) spectra of 2be



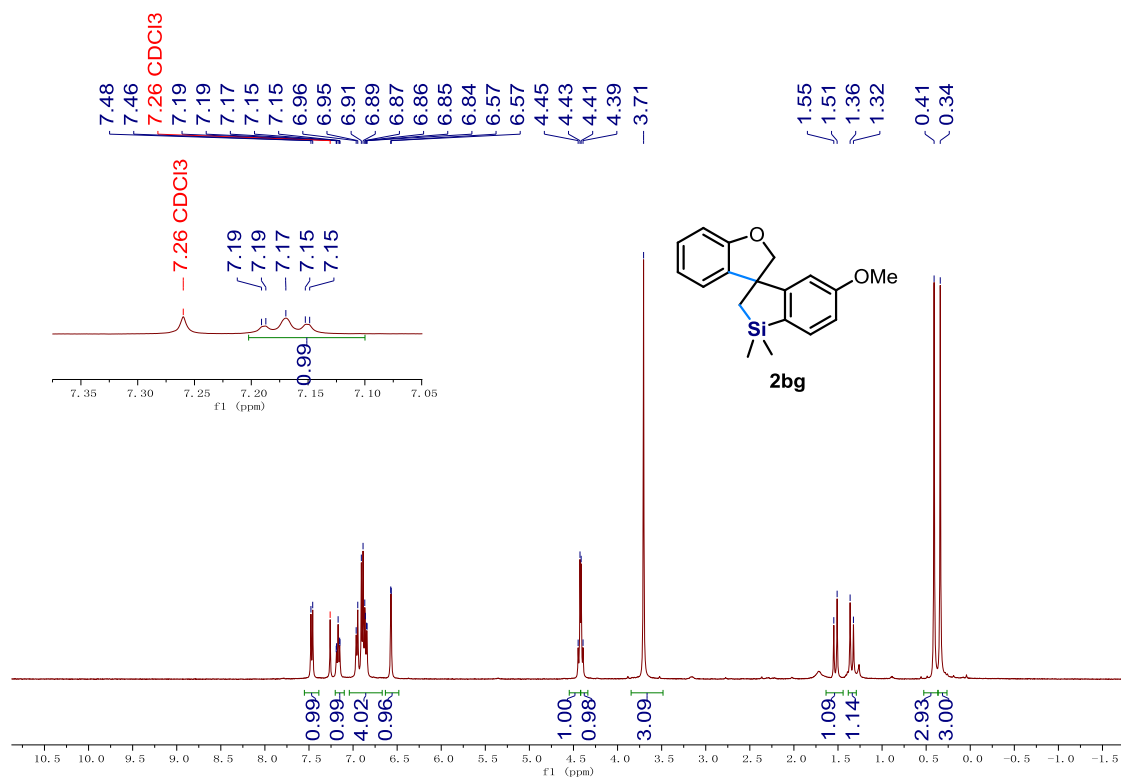
Supplementary Figure 145. ¹³C NMR (101 MHz, CDCl₃) spectra of 2be



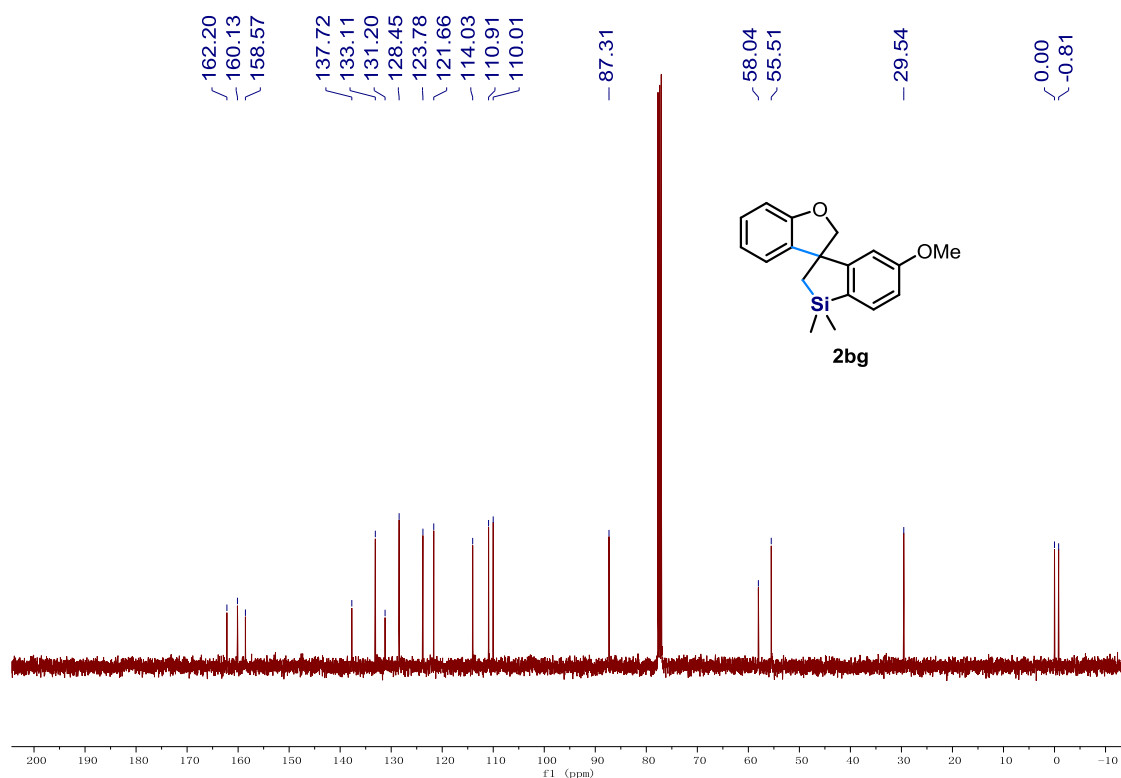
Supplementary Figure 146. ¹H NMR (400 MHz, CDCl₃) spectra of 2bf



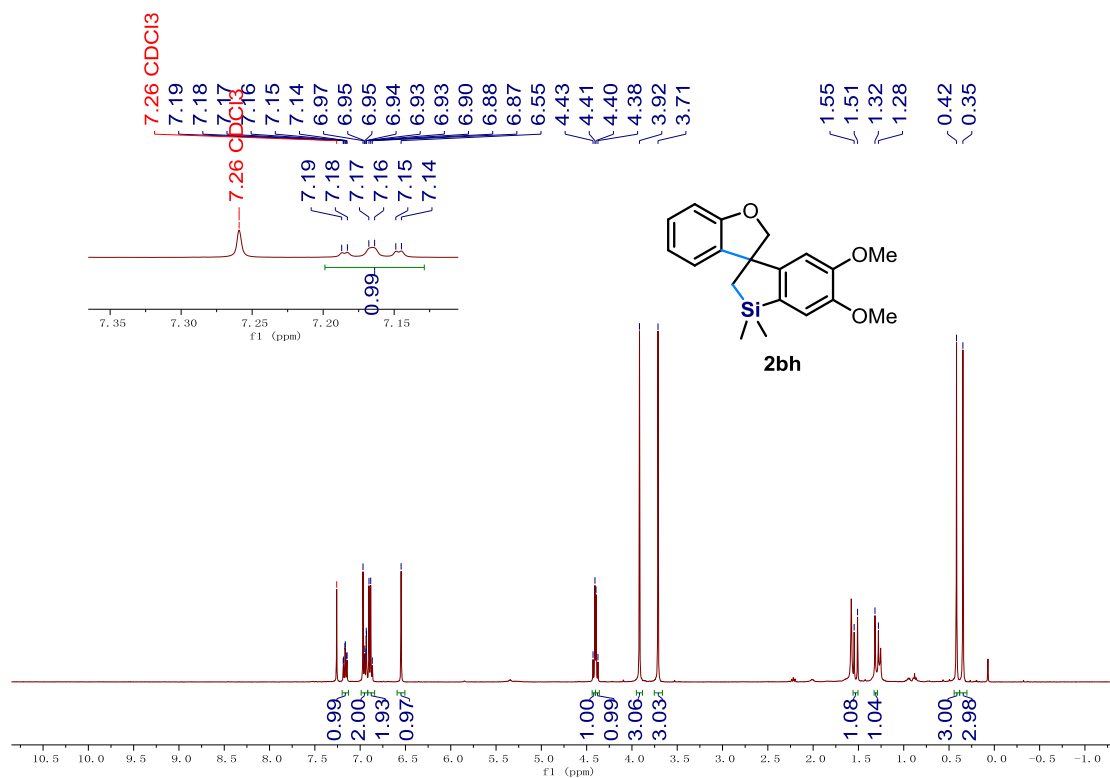
Supplementary Figure 147. ¹³C NMR (101 MHz, CDCl₃) spectra of 2bf



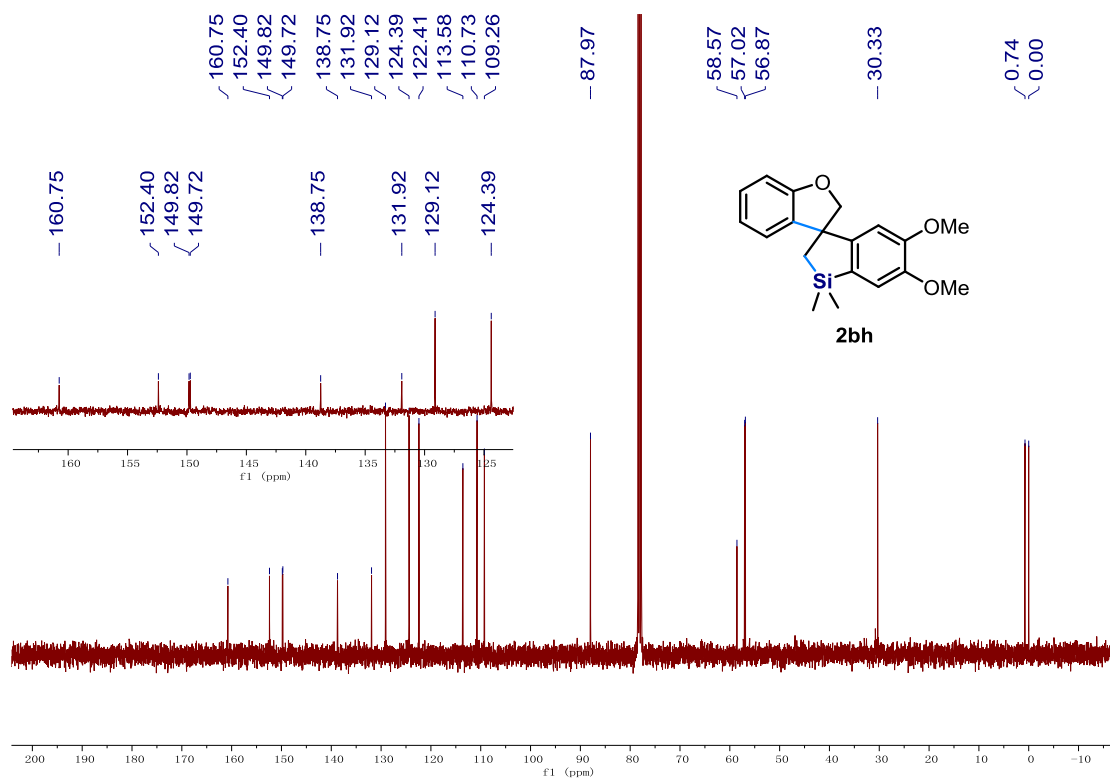
Supplementary Figure 148. ¹H NMR (400 MHz, CDCl₃) spectra of **2bg**



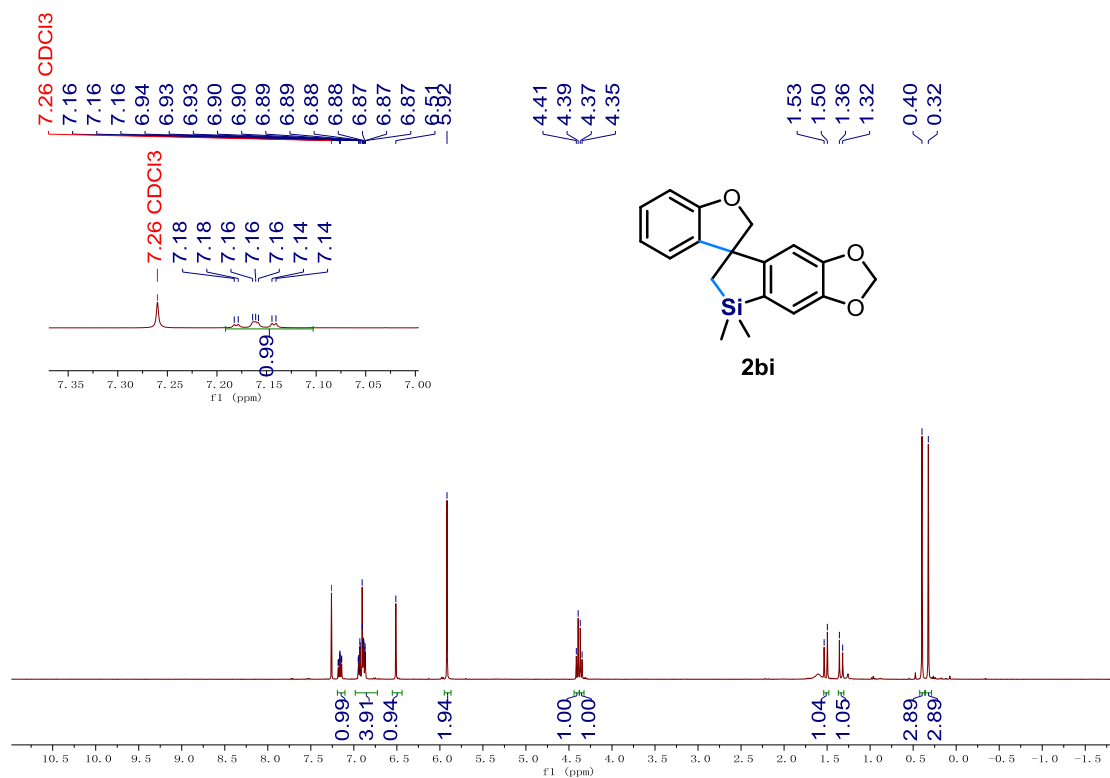
Supplementary Figure 149. ¹³C NMR (101 MHz, CDCl₃) spectra of **2bg**



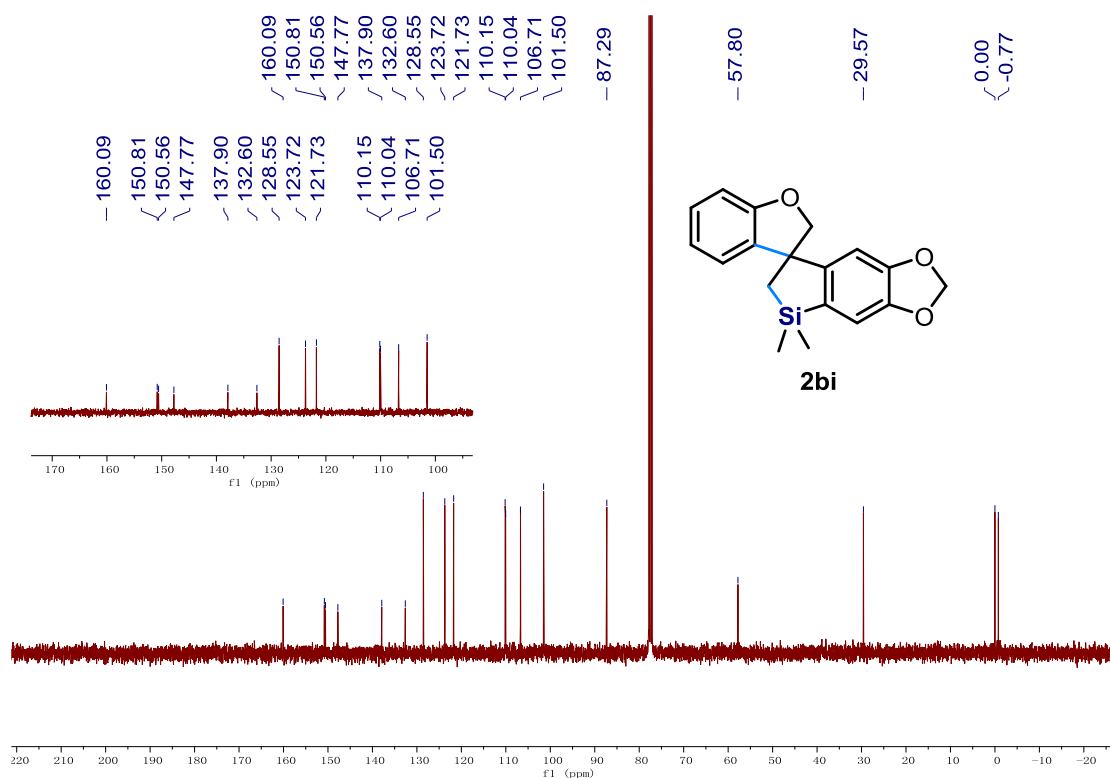
Supplementary Figure 150. ¹H NMR (400 MHz, CDCl₃) spectra of 2bh



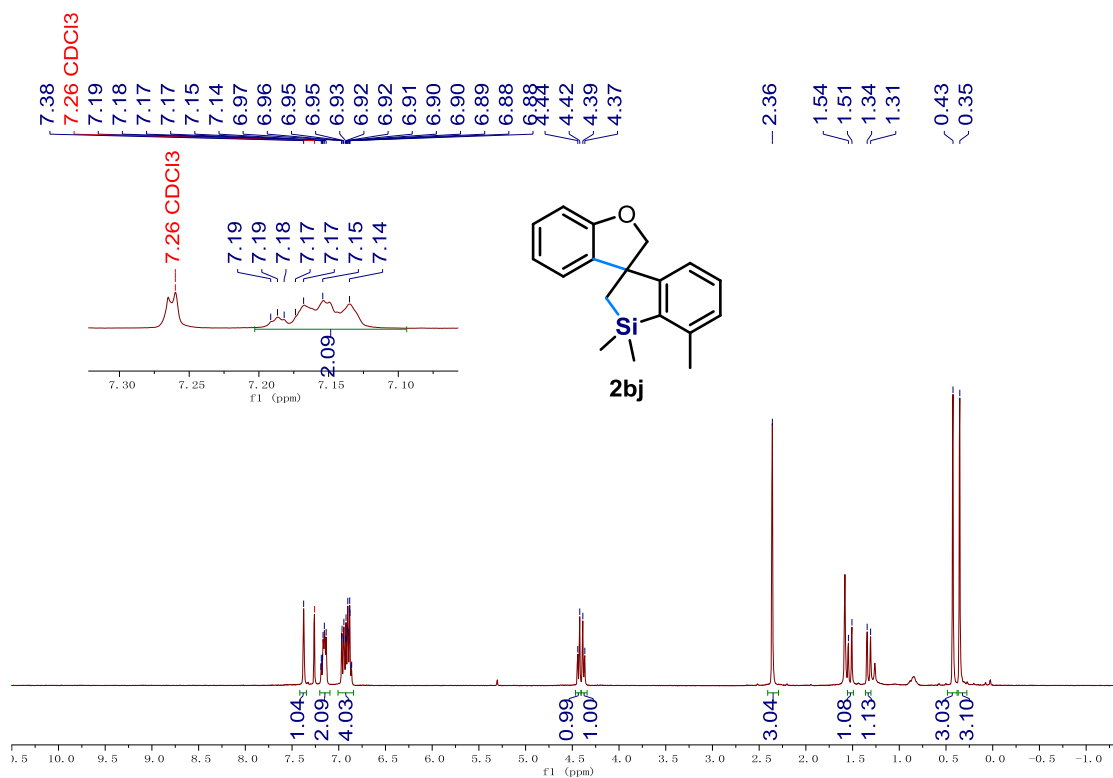
Supplementary Figure 151. ¹³C NMR (101 MHz, CDCl₃) spectra of 2bh



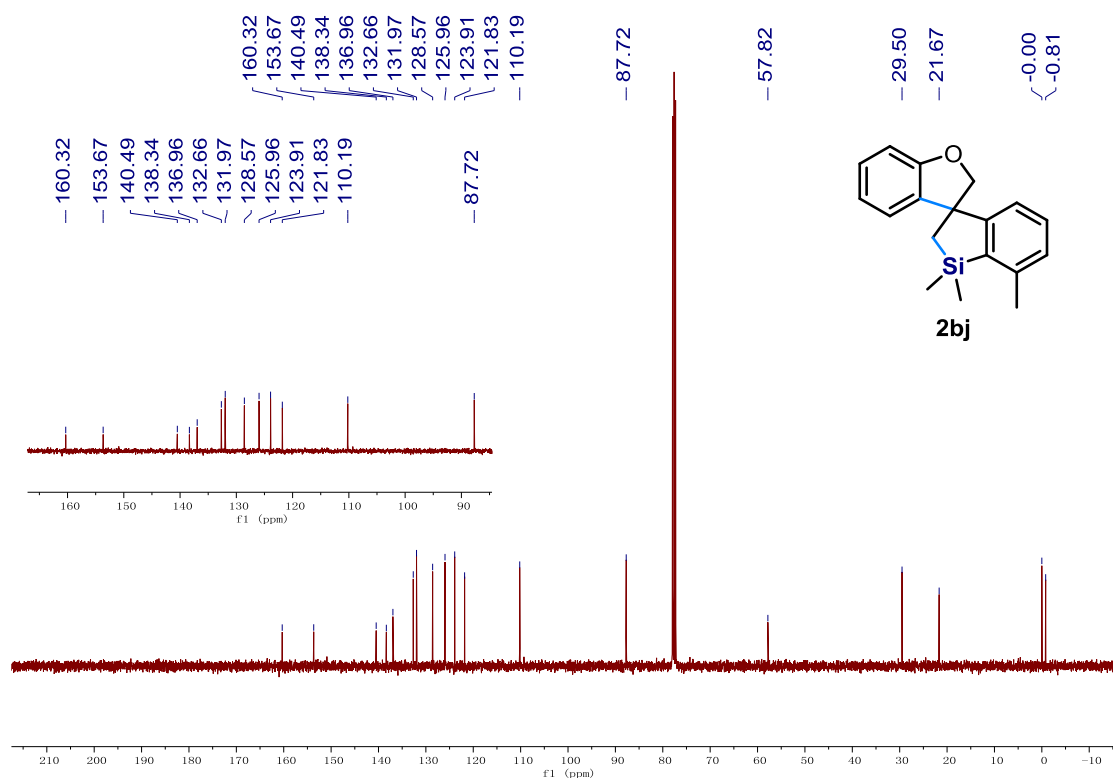
Supplementary Figure 152. ¹H NMR (400 MHz, CDCl₃) spectra of 2bi



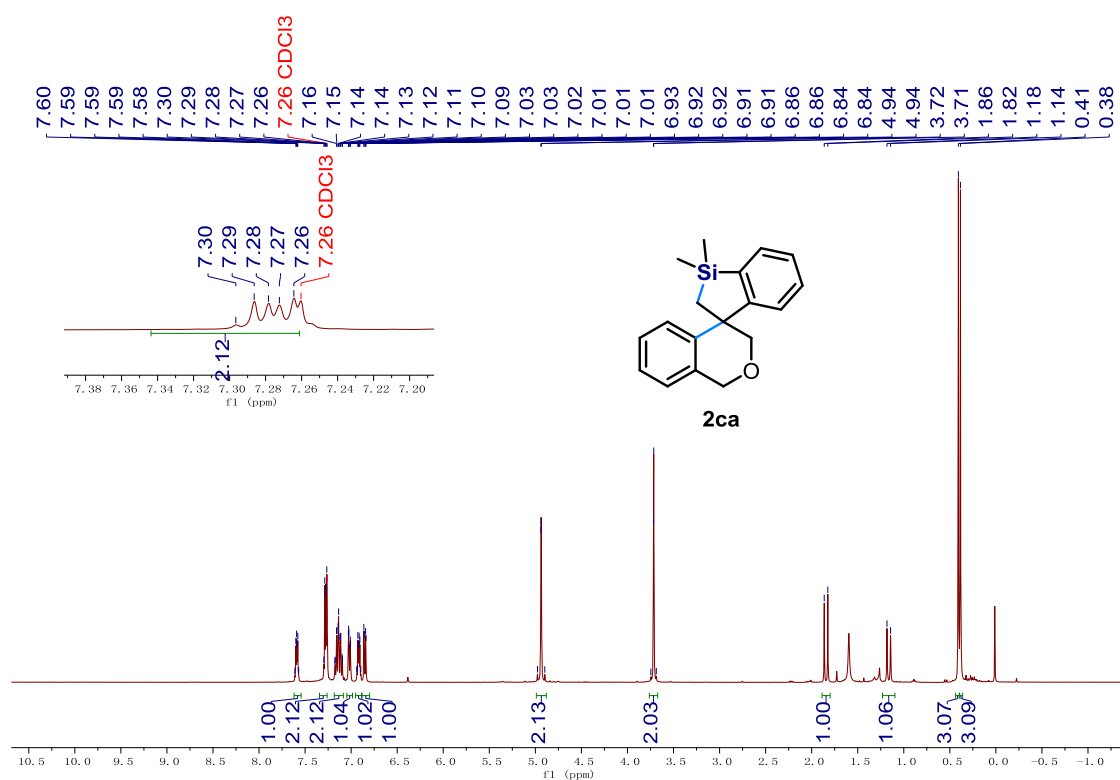
Supplementary Figure 153. ¹³C NMR (101 MHz, CDCl₃) spectra of 2bi



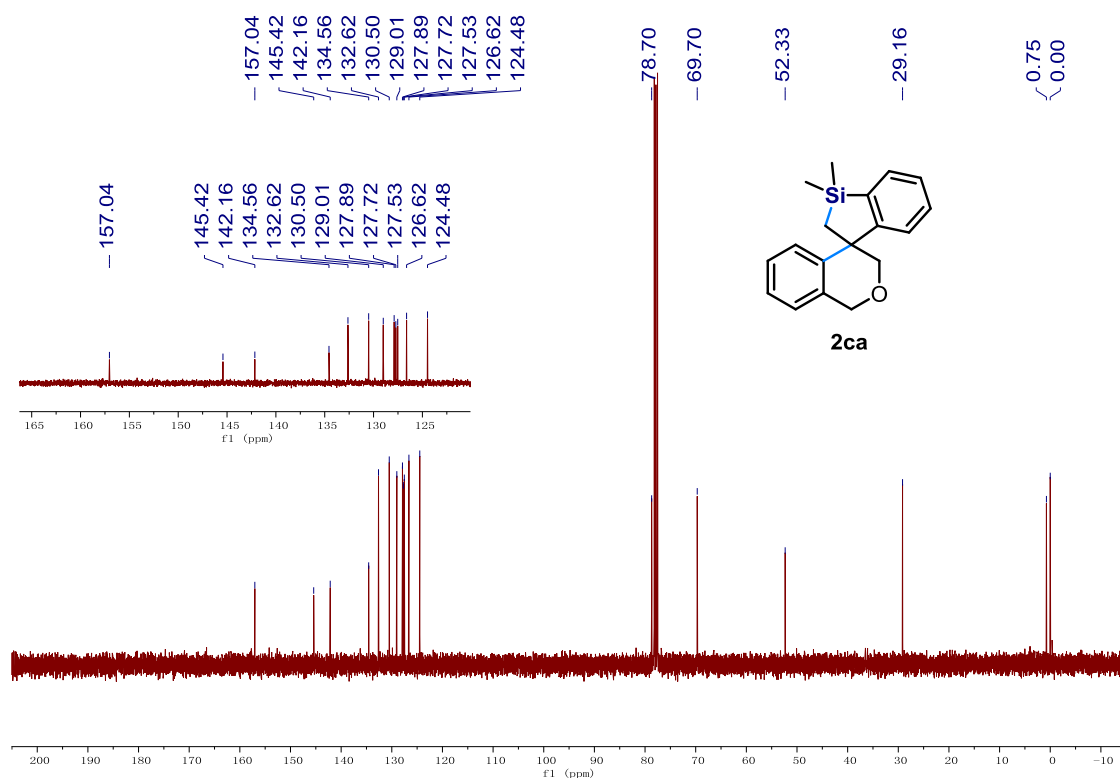
Supplementary Figure 154. ¹H NMR (400 MHz, CDCl₃) spectra of 2bj



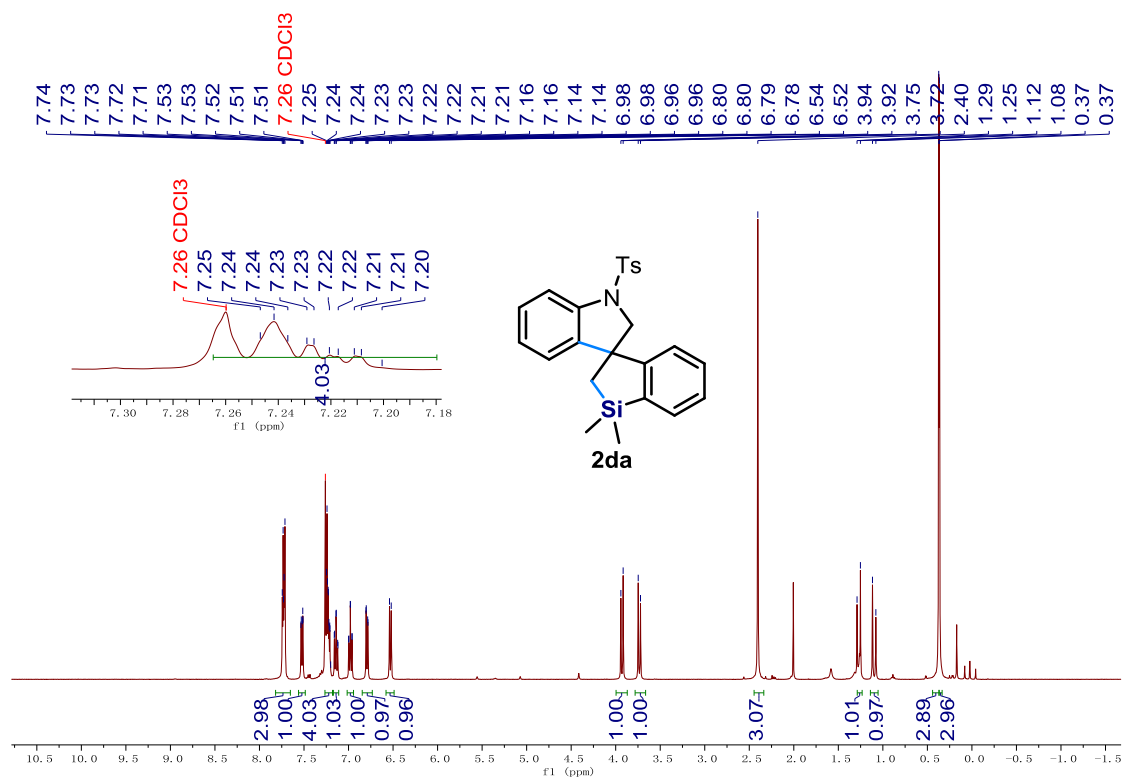
Supplementary Figure 155. ¹³C NMR (101 MHz, CDCl₃) spectra of 2bj



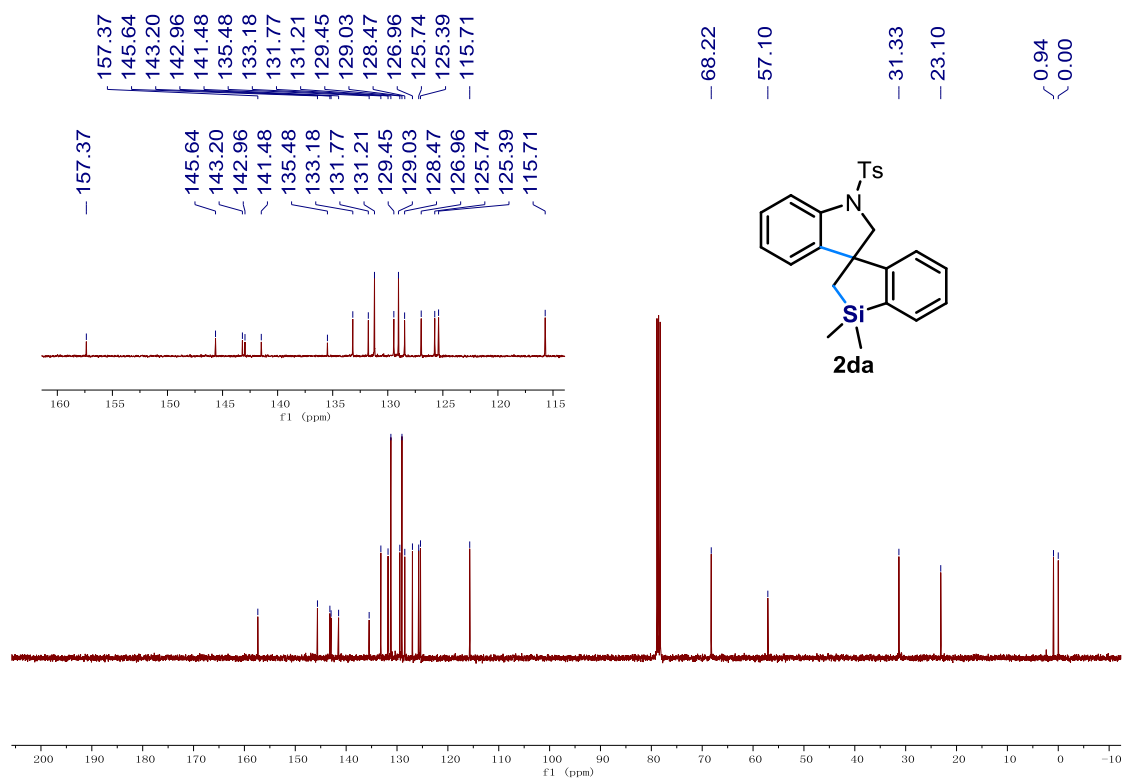
Supplementary Figure 156. ¹H NMR (400 MHz, CDCl₃) spectra of 2ca



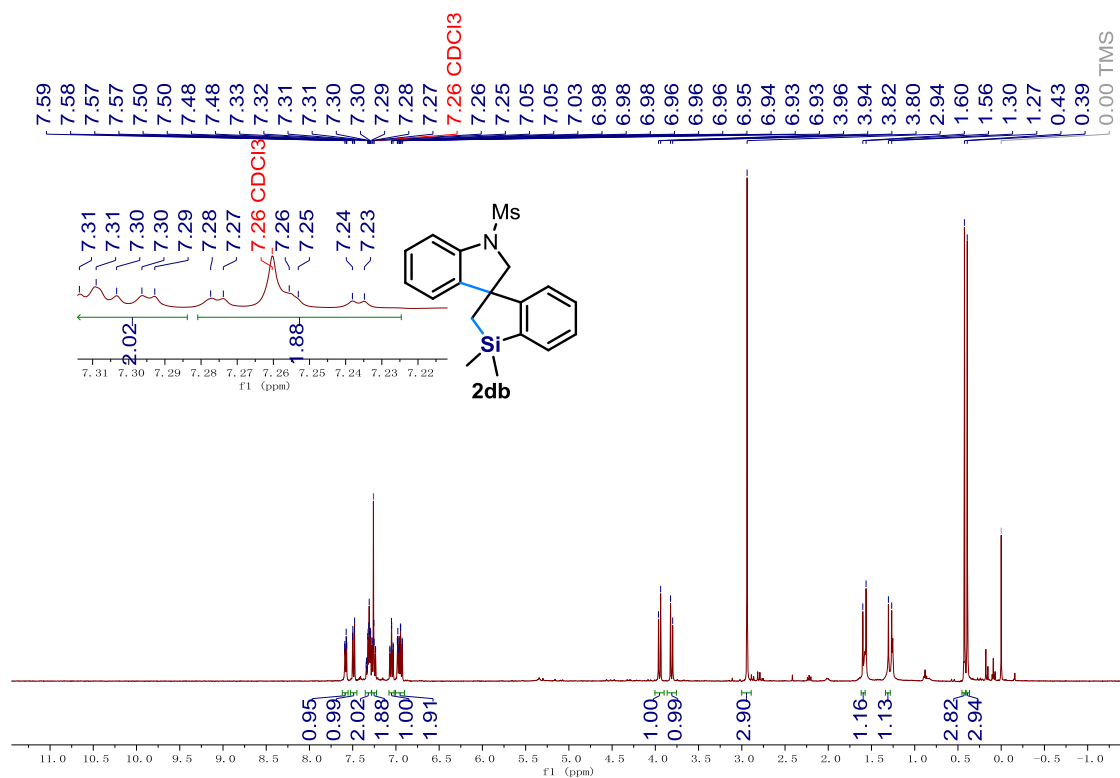
Supplementary Figure 157. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ca



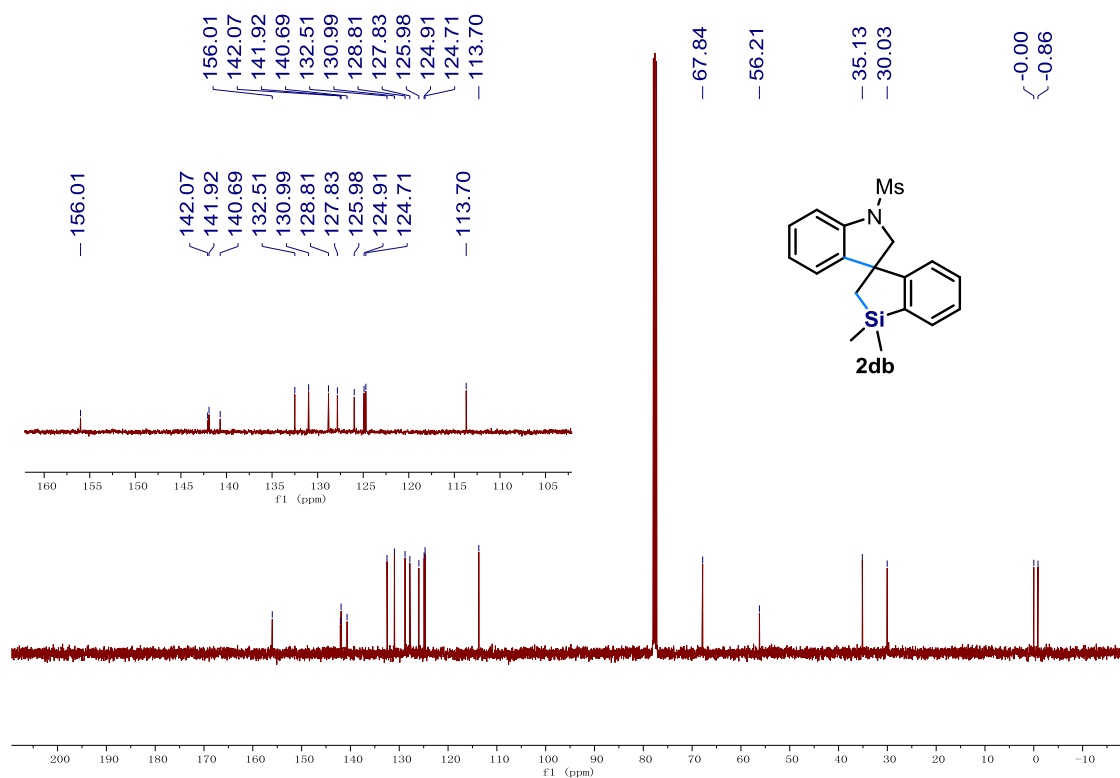
Supplementary Figure 158. ¹H NMR (400 MHz, CDCl₃) spectra of 2da



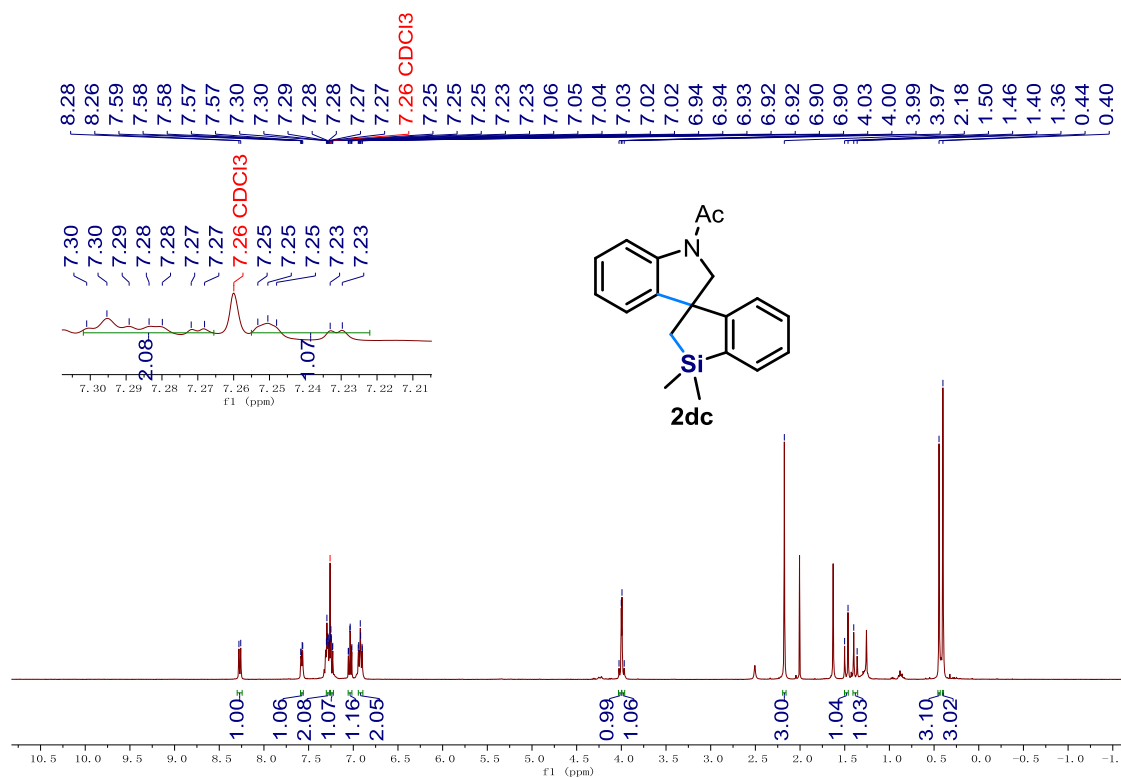
Supplementary Figure 159. ¹³C NMR (101 MHz, CDCl₃) spectra of 2da



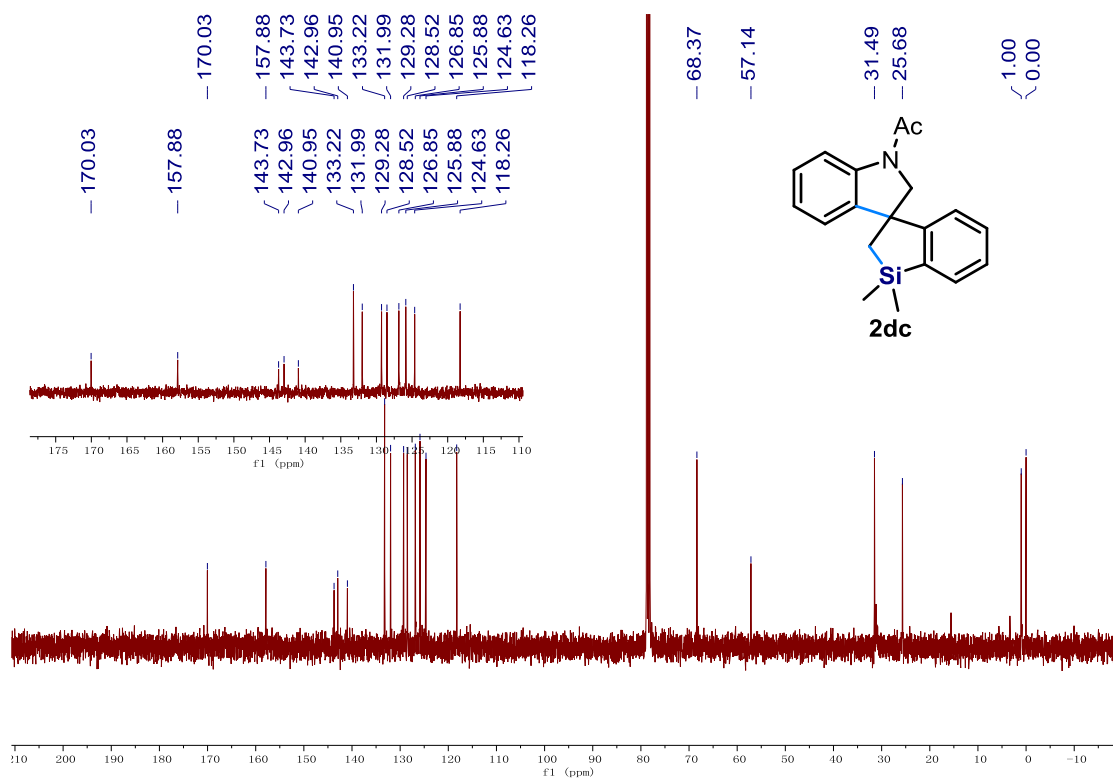
Supplementary Figure 160. ¹H NMR (400 MHz, CDCl₃) spectra of 2db



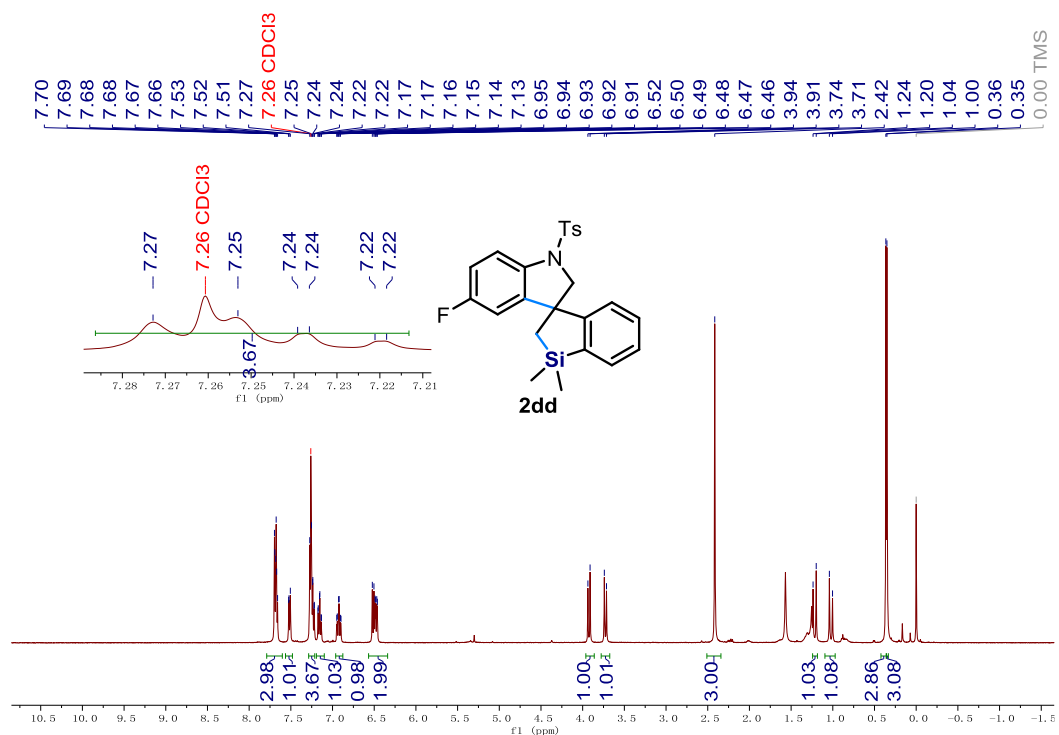
Supplementary Figure 161. ¹³C NMR (101 MHz, CDCl₃) spectra of 2db



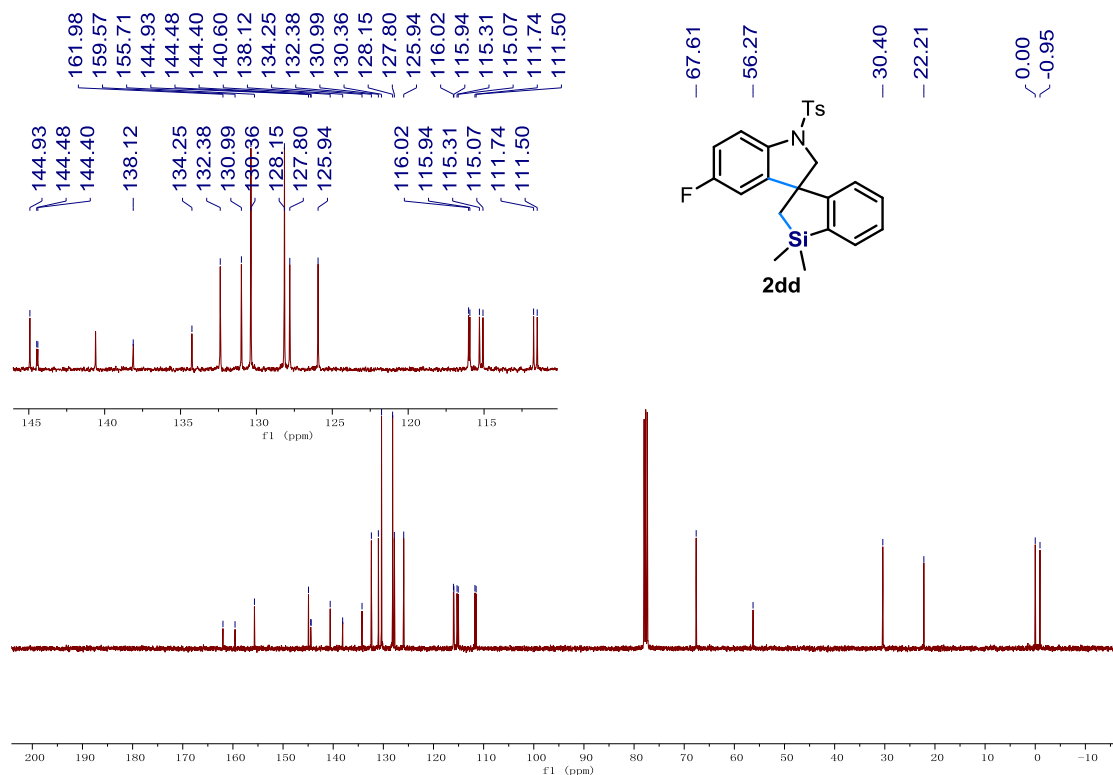
Supplementary Figure 162. ¹H NMR (400 MHz, CDCl₃) spectra of 2dc



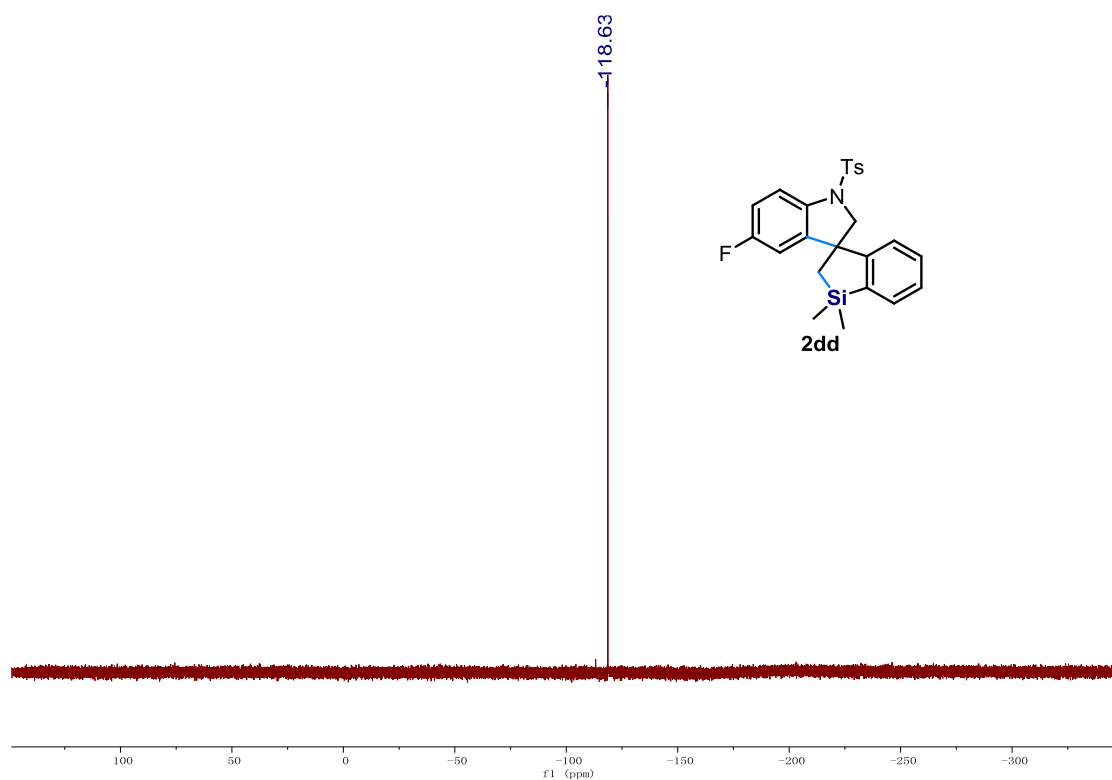
Supplementary Figure 163. ¹³C NMR (101 MHz, CDCl₃) spectra of 2dc



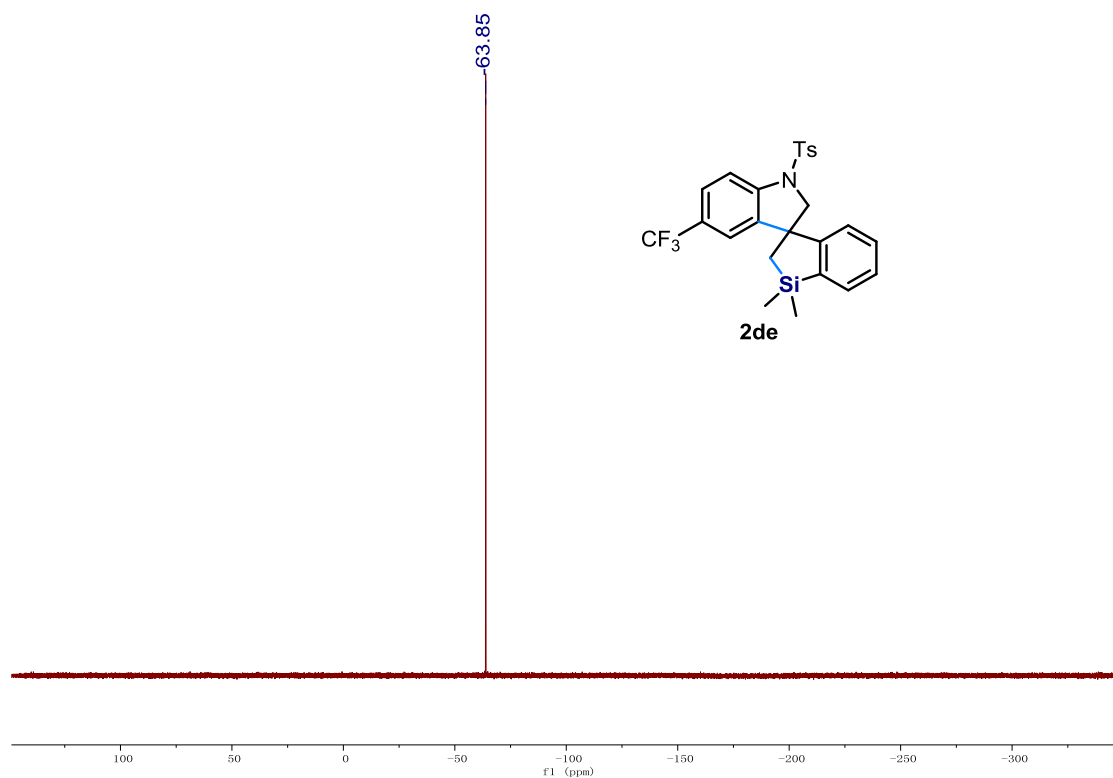
Supplementary Figure 164. ¹H NMR (400 MHz, CDCl₃) spectra of 2dd



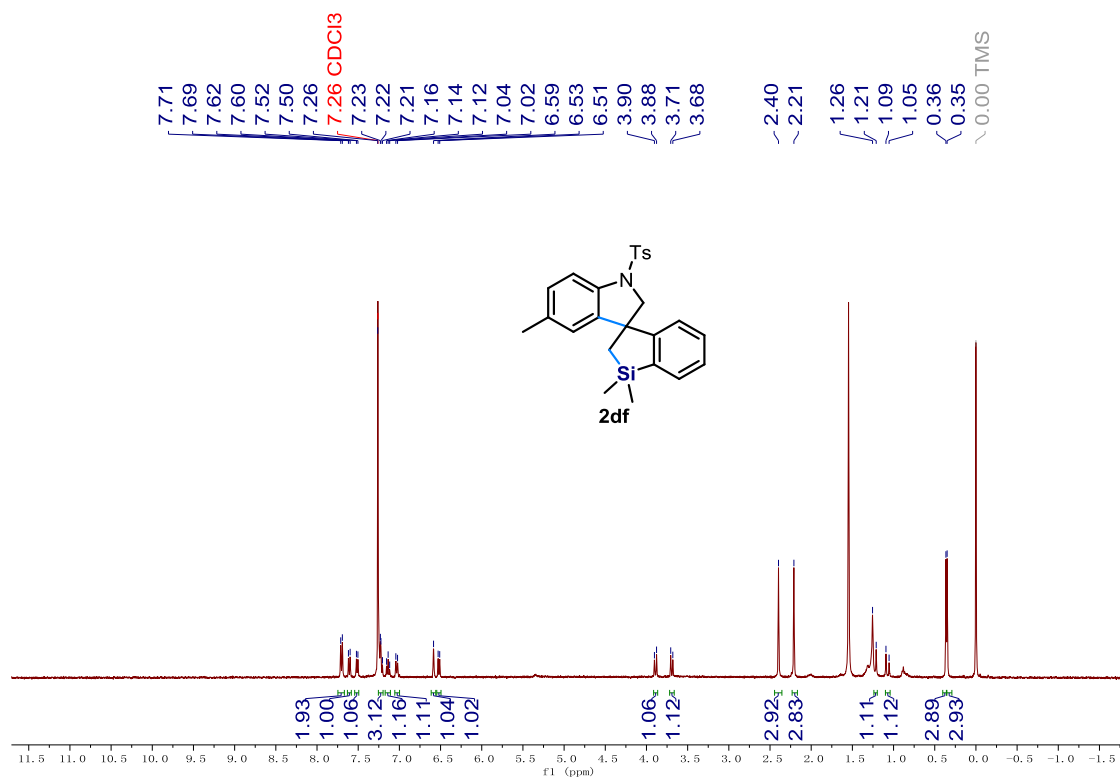
Supplementary Figure 165. ¹³C NMR (101 MHz, CDCl₃) spectra of 2dd



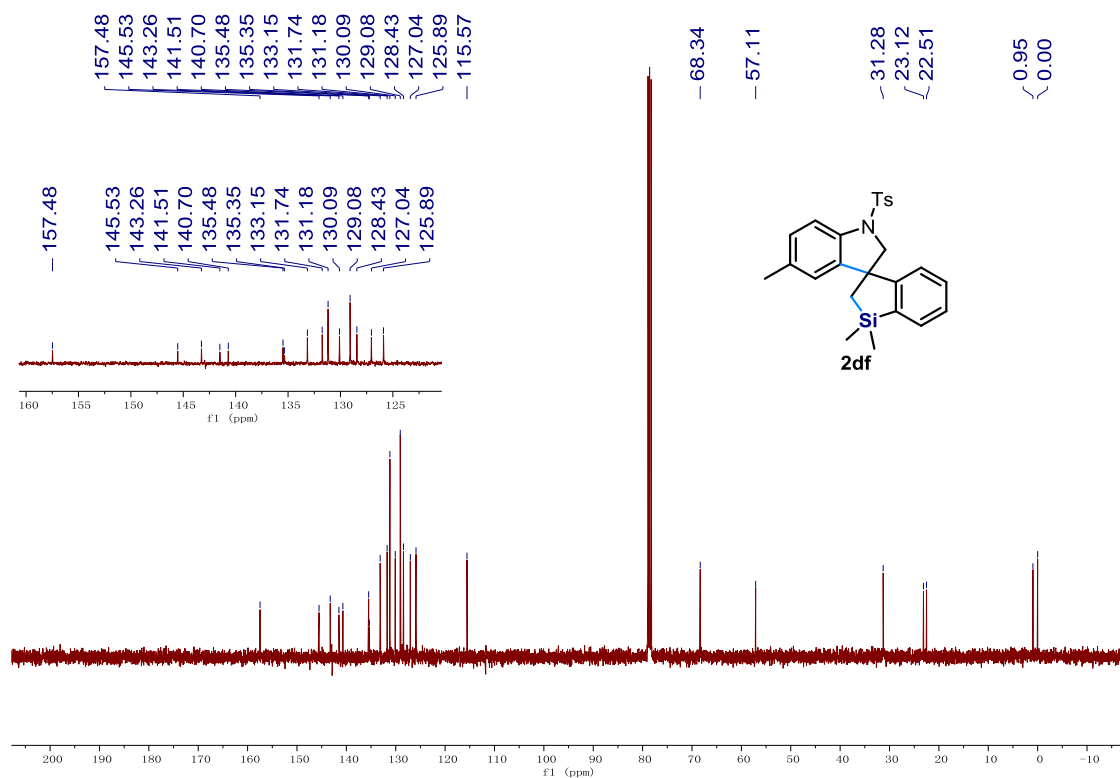
Supplementary Figure 166. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2dd**



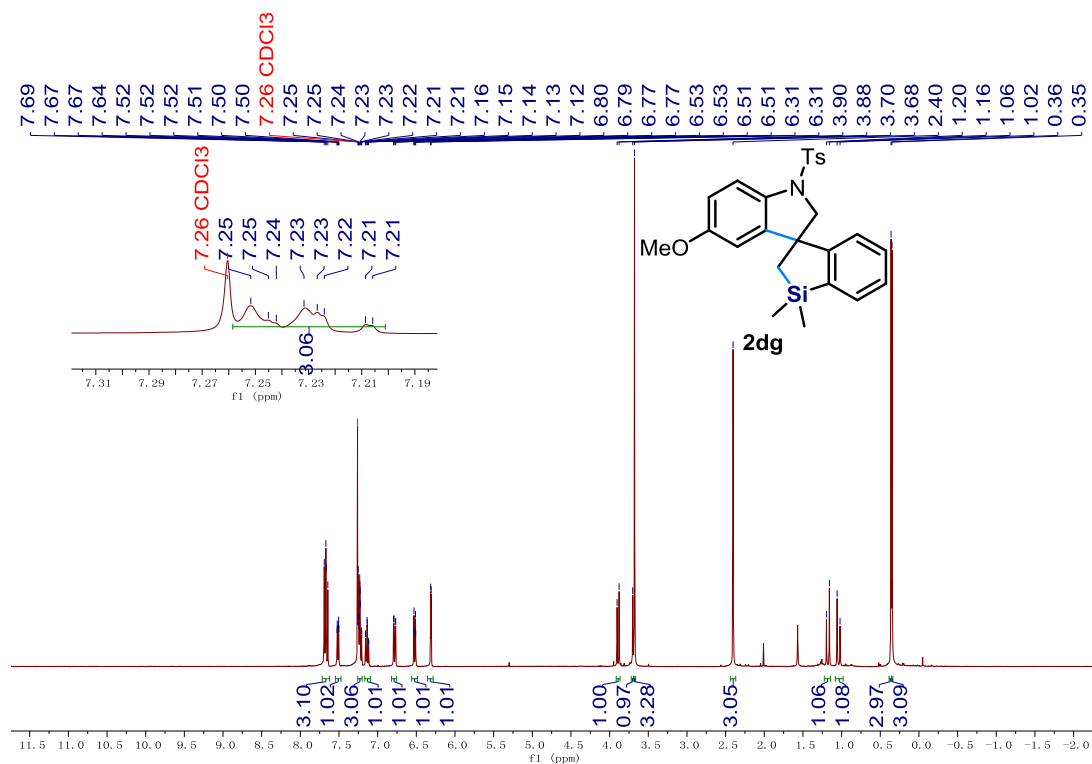
Supplementary Figure 169. ^{19}F NMR (376 MHz, CDCl_3) spectra of **2de**



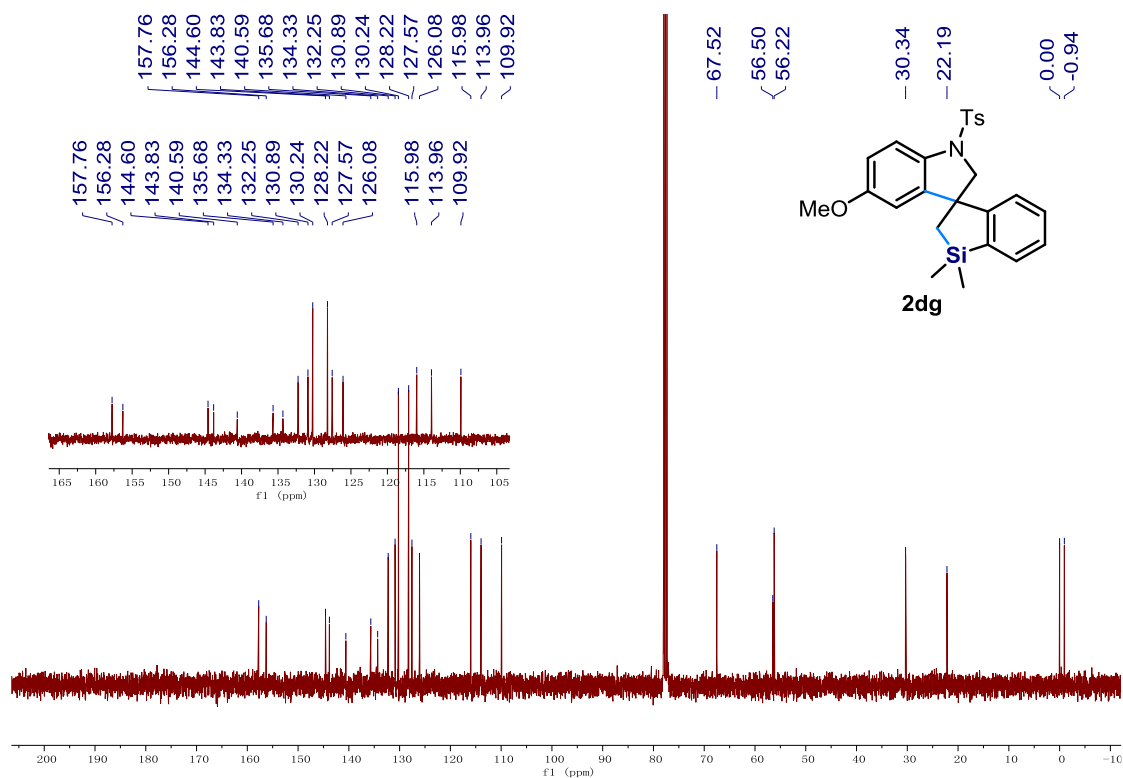
Supplementary Figure 170. ¹H NMR (400 MHz, CDCl₃) spectra of **2df**



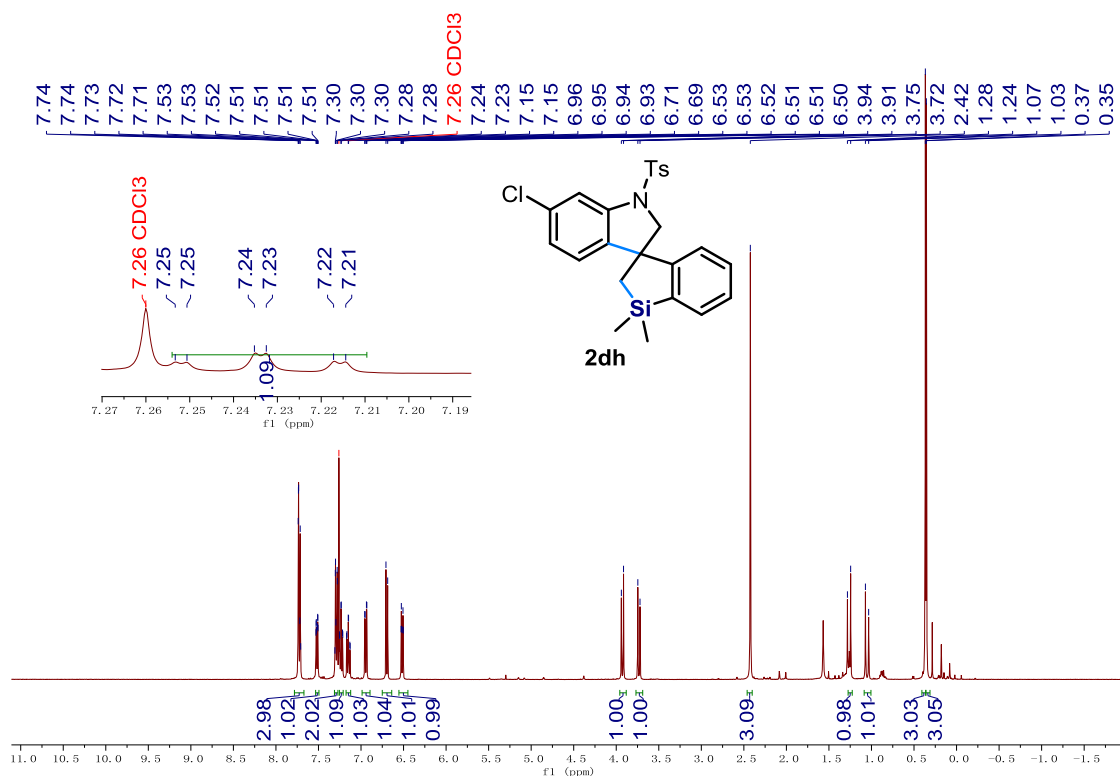
Supplementary Figure 171. ¹³C NMR (101 MHz, CDCl₃) spectra of **2df**



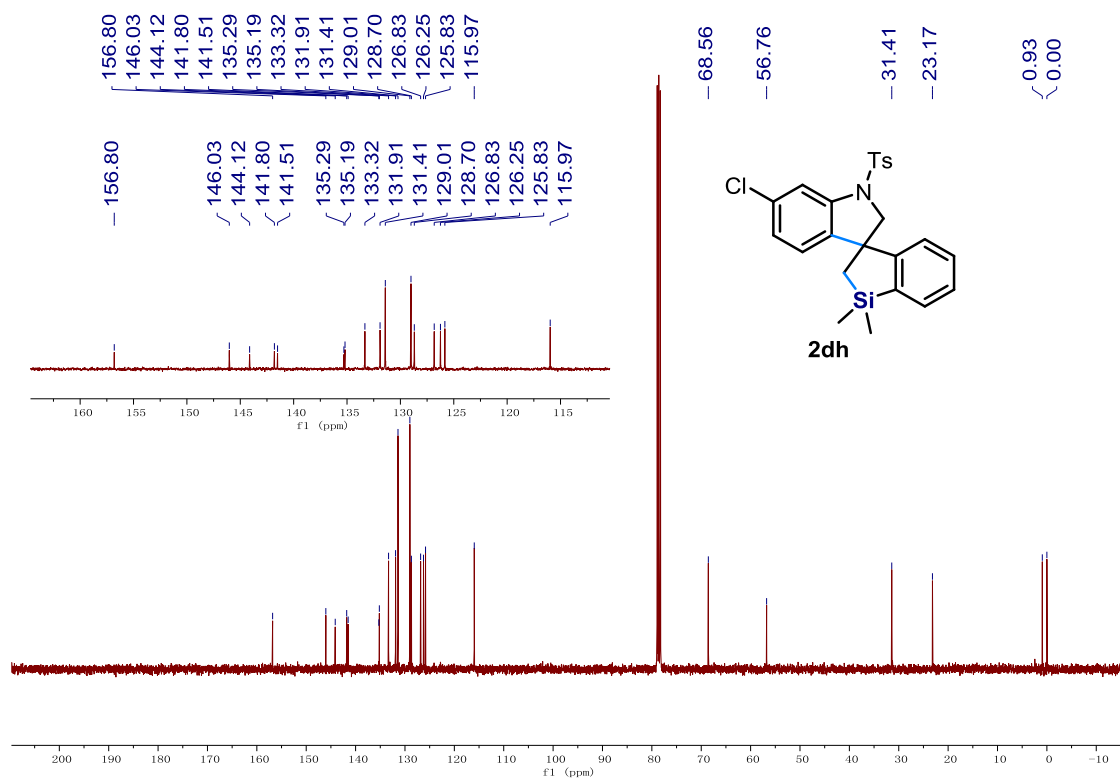
Supplementary Figure 172. ¹H NMR (400 MHz, CDCl₃) spectra of 2dg



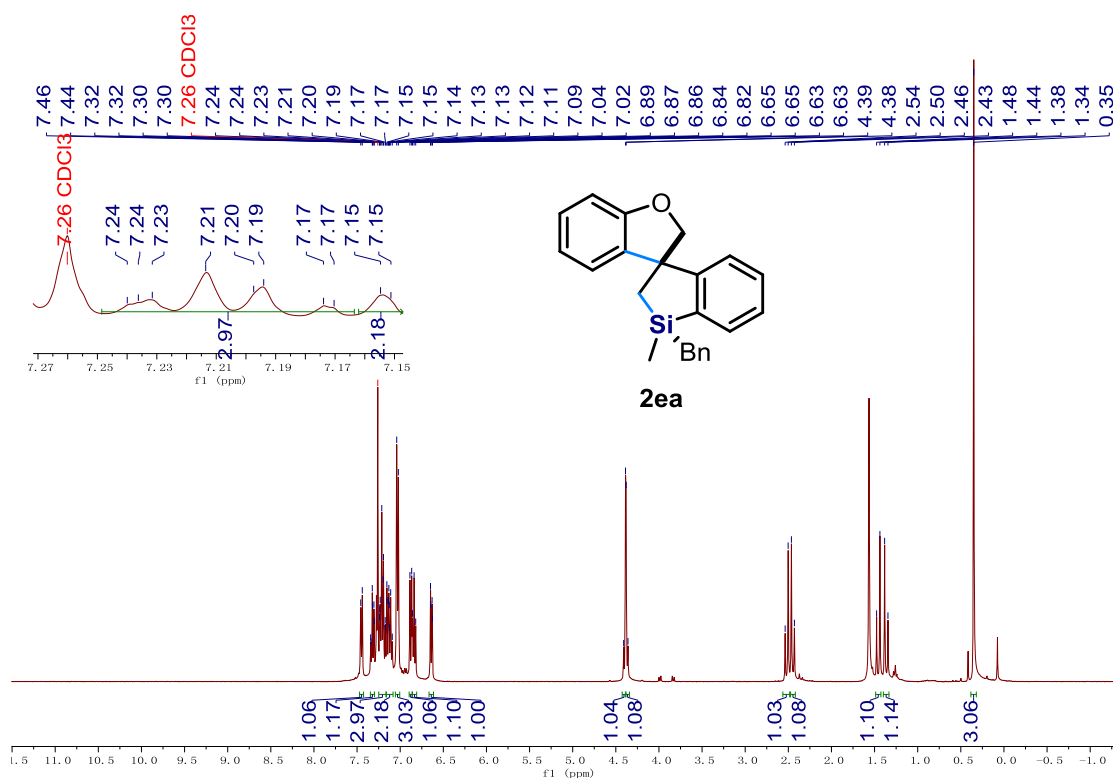
Supplementary Figure 173. ¹³C NMR (101 MHz, CDCl₃) spectra of 2dg



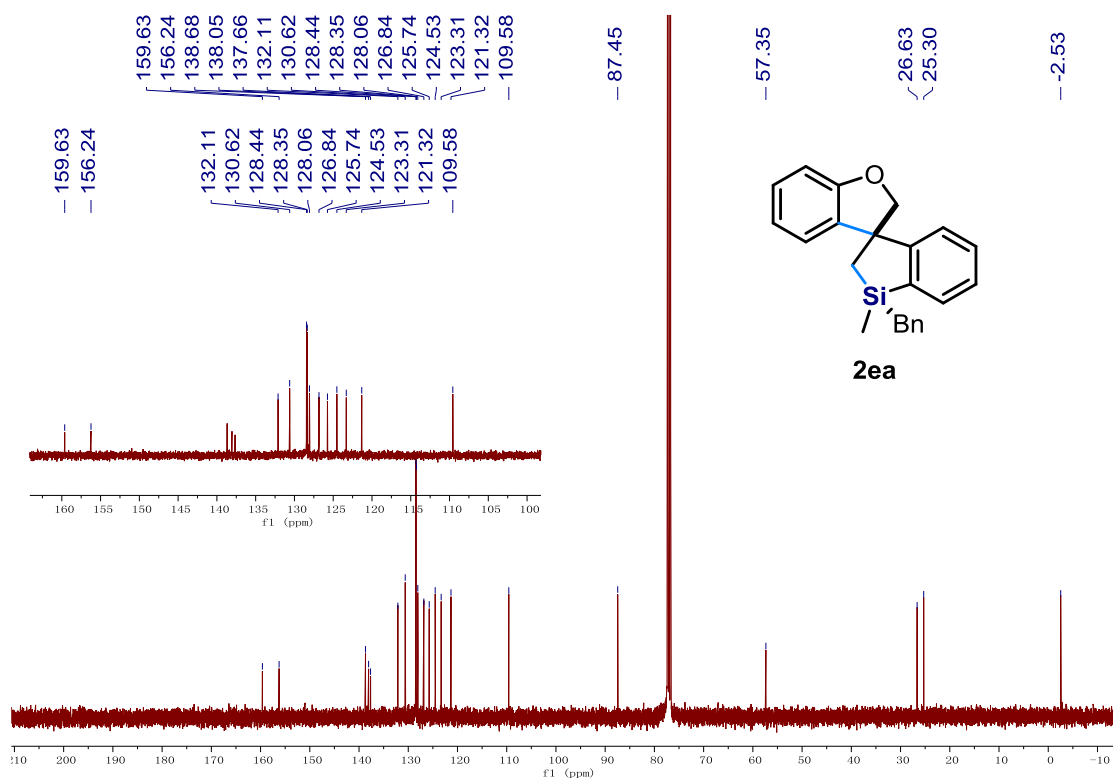
Supplementary Figure 174. ¹H NMR (400 MHz, CDCl₃) spectra of 2dh



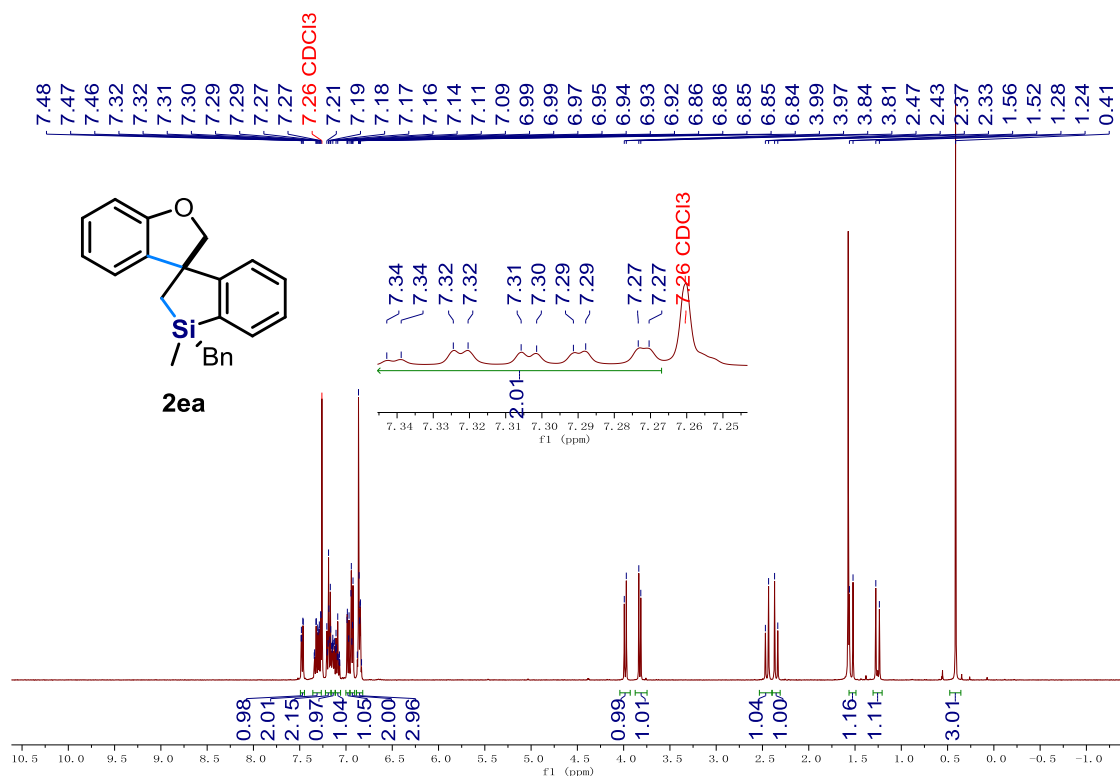
Supplementary Figure 175. ¹³C NMR (101 MHz, CDCl₃) spectra of 2dh



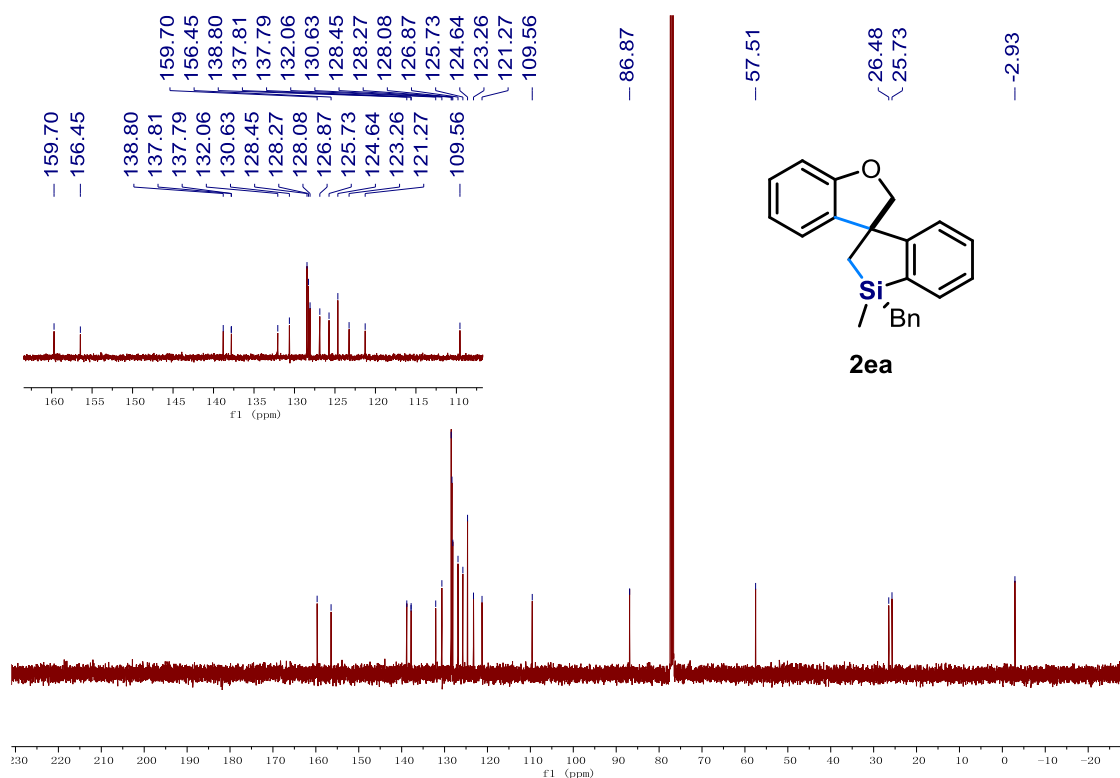
Supplementary Figure 178. ¹H NMR (400 MHz, CDCl₃) spectra of the first diastereoisomer 2ea



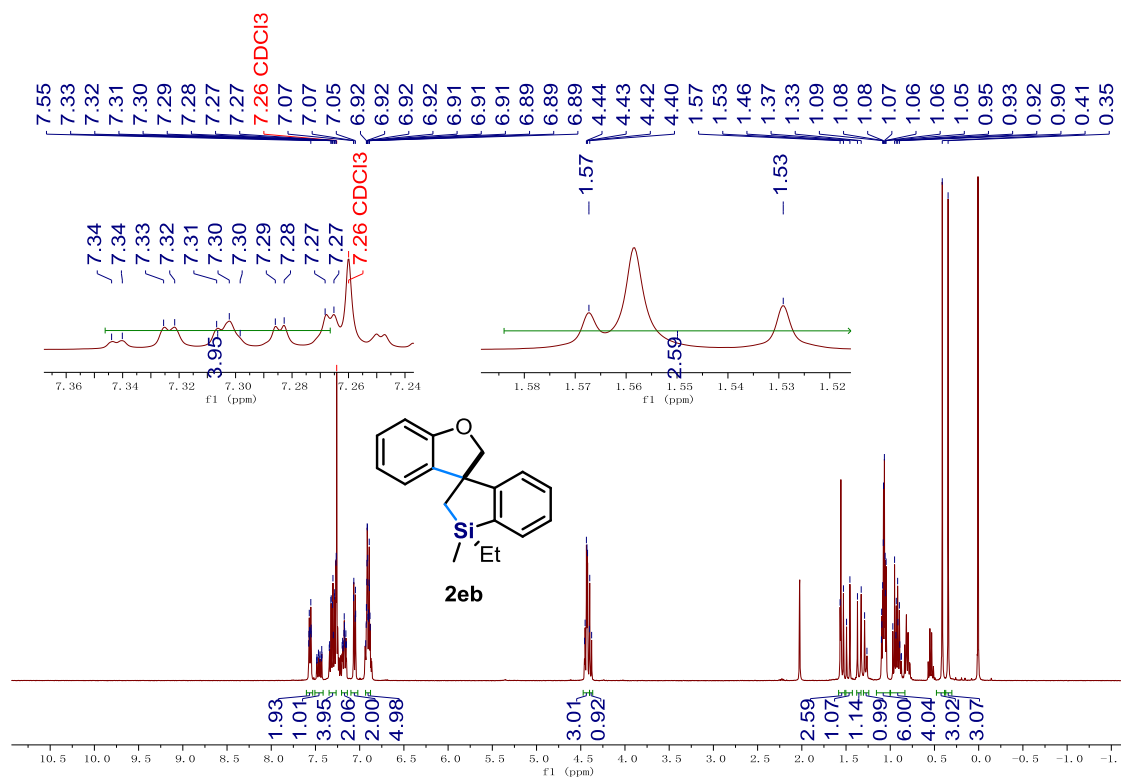
Supplementary Figure 177. ¹³C NMR (101 MHz, CDCl₃) spectra of the first diastereoisomer 2ea



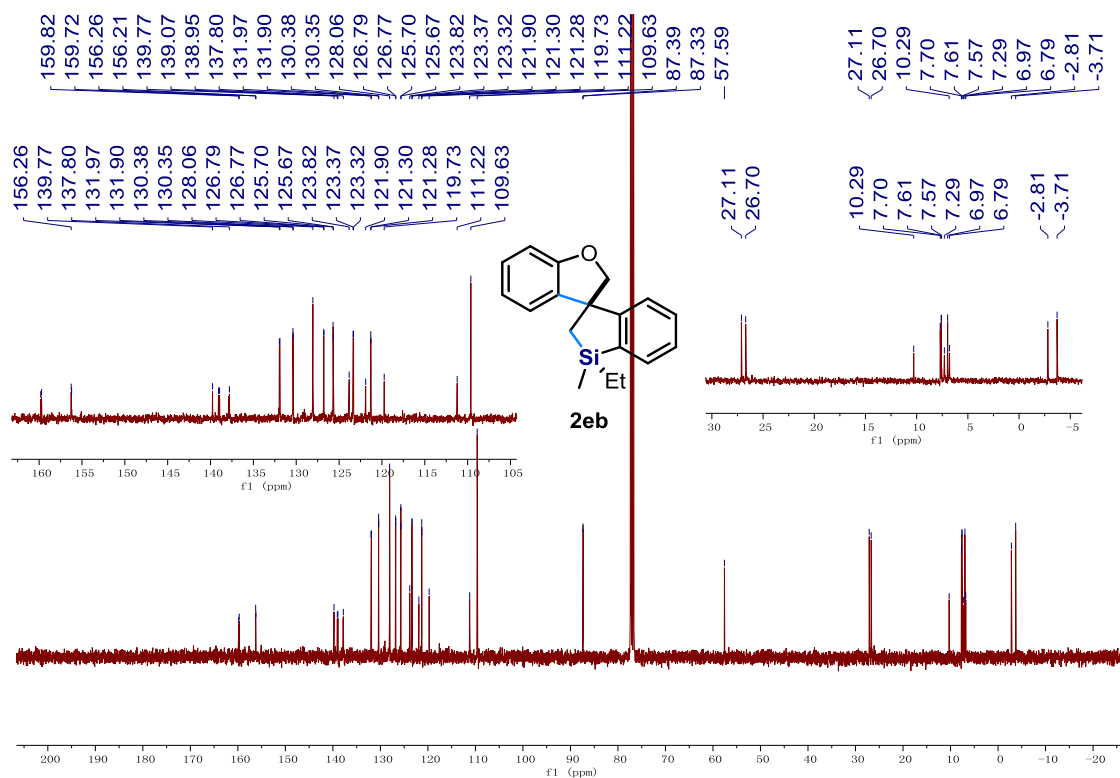
Supplementary Figure 178. ¹H NMR (400 MHz, CDCl₃) spectra of the second diastereoisomer **2ea**



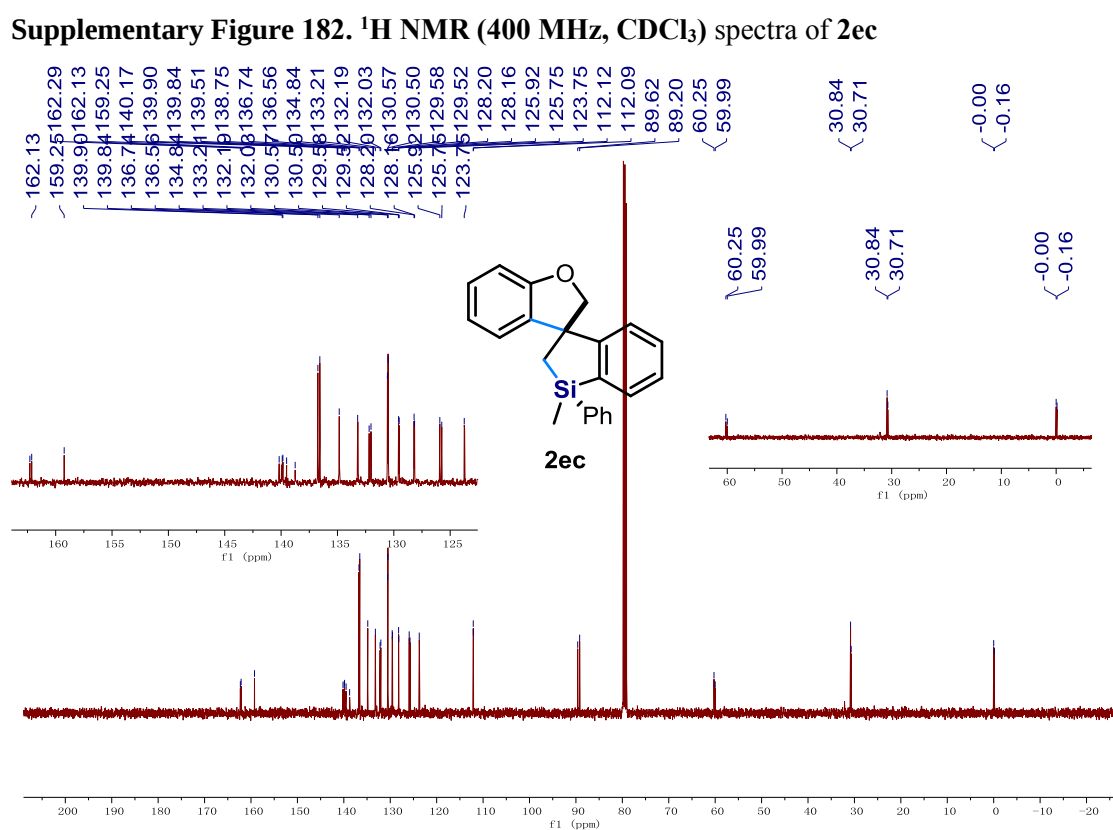
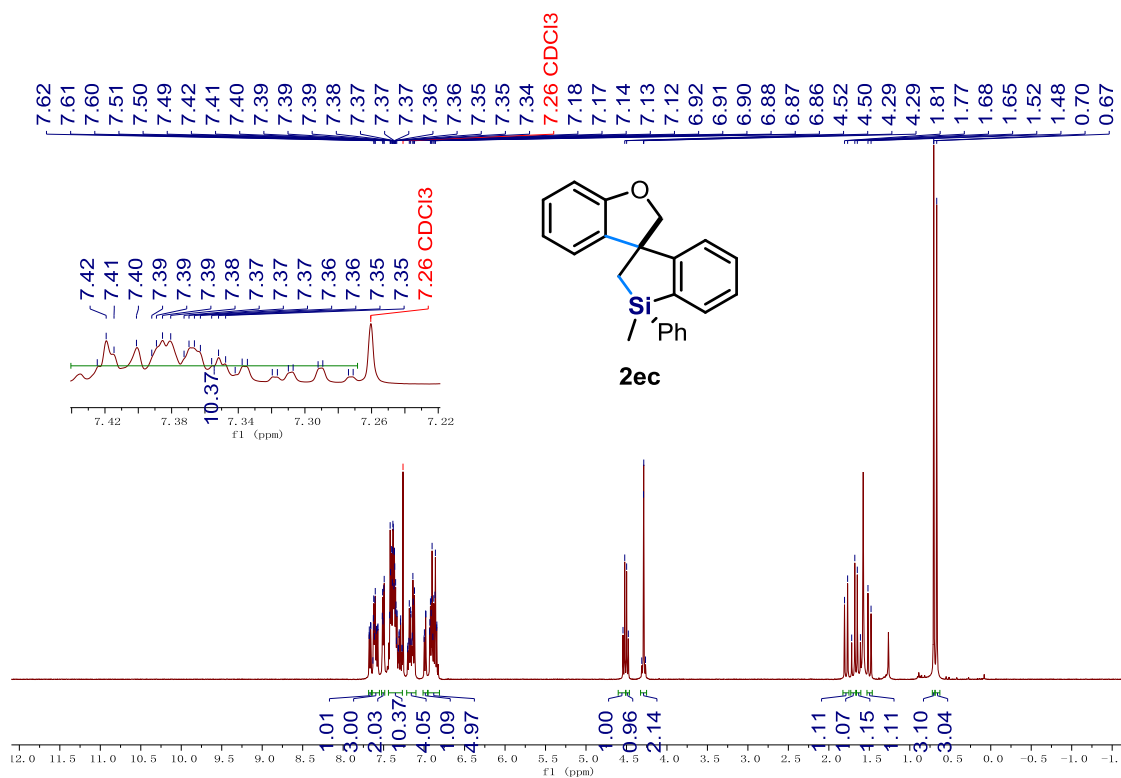
Supplementary Figure 179. ¹³C NMR (101 MHz, CDCl₃) spectra of the second diastereoisomer **2ea**

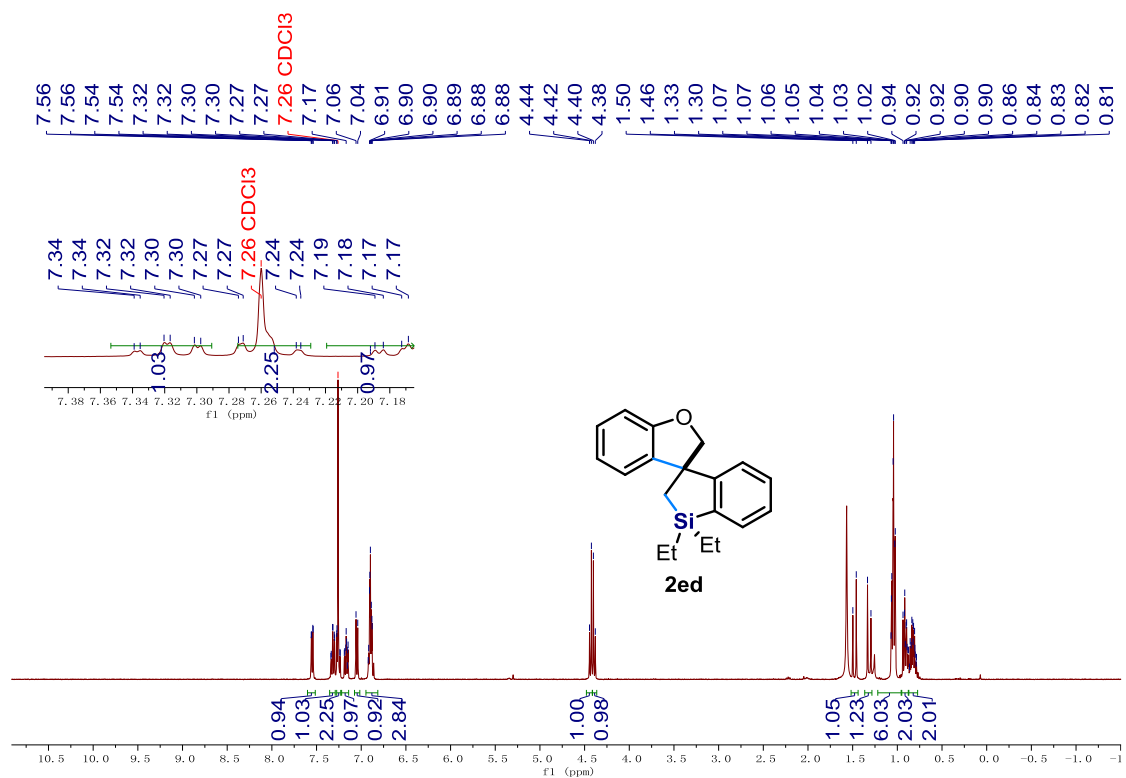


Supplementary Figure 180. ¹H NMR (400 MHz, CDCl₃) spectra of 2eb

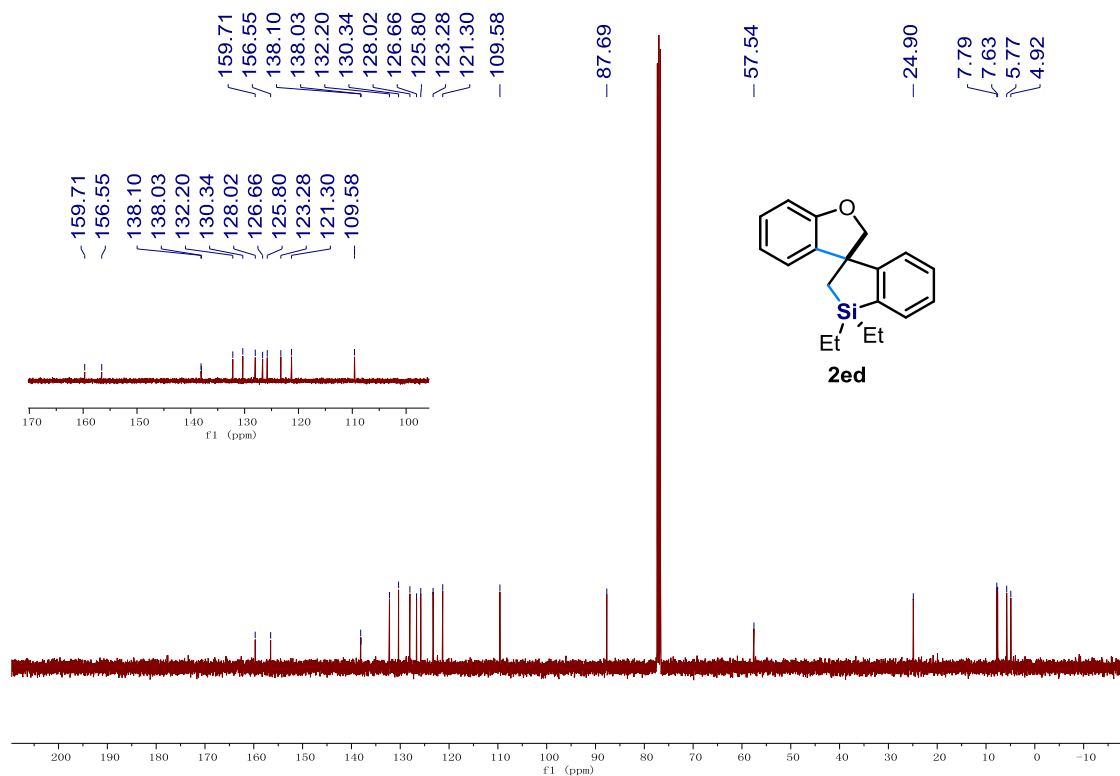


Supplementary Figure 181. ¹³C NMR (101 MHz, CDCl₃) spectra of 2eb

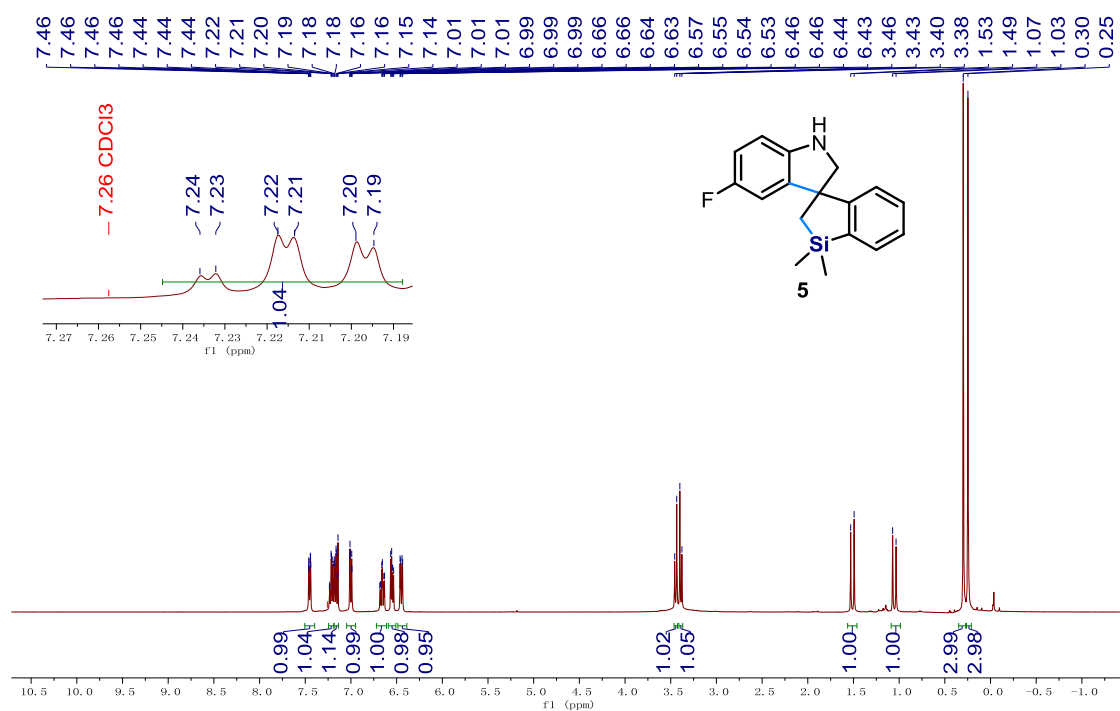




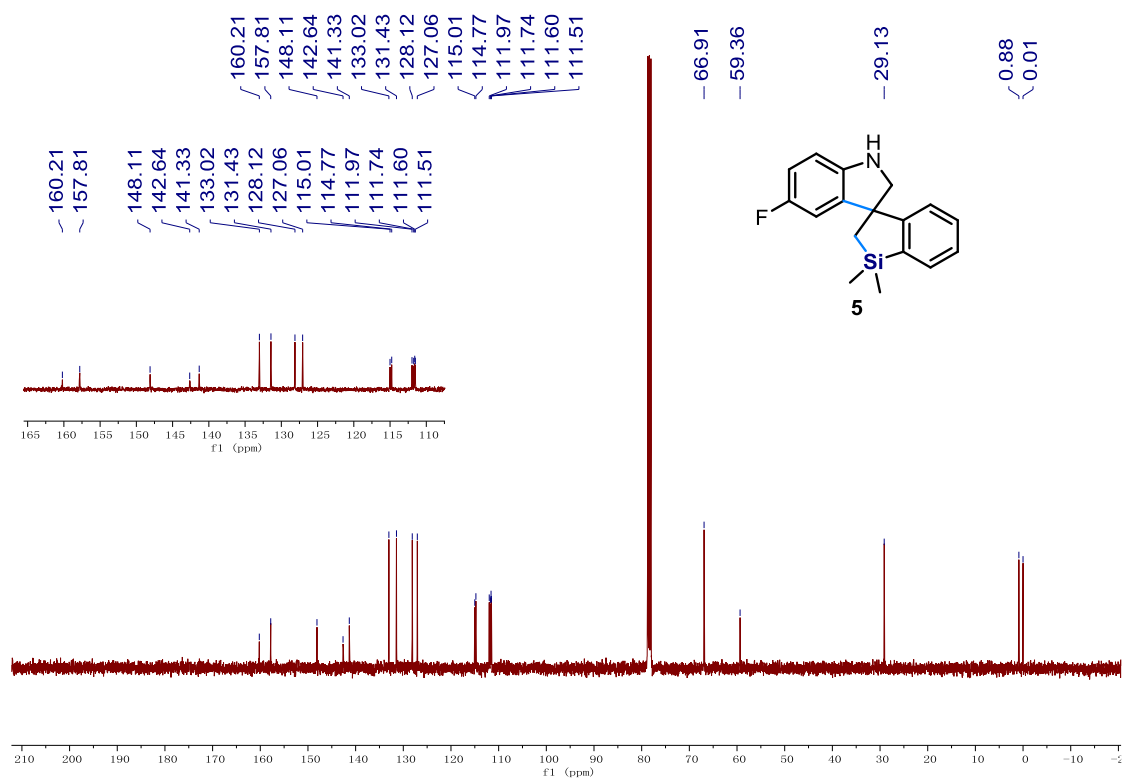
Supplementary Figure 184. ¹H NMR (400 MHz, CDCl₃) spectra of 2ed



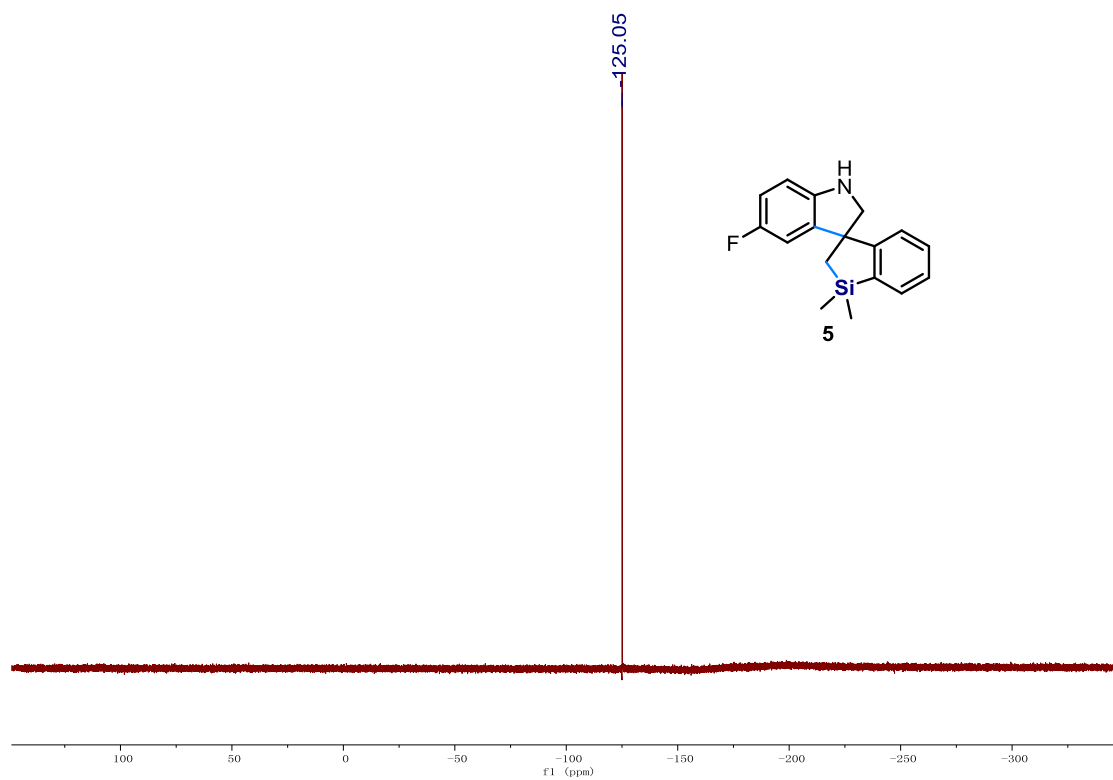
Supplementary Figure 185. ¹³C NMR (101 MHz, CDCl₃) spectra of 2ed



Supplementary Figure 186. ^1H NMR (400 MHz, CDCl_3) spectra of **5**



Supplementary Figure 187. ^{13}C NMR (101 MHz, CDCl_3) spectra of **5**



Supplementary Figure 188. ^{19}F NMR (376 MHz, CDCl_3) spectra of **5**

5. Supplementary References

1. X. Chang, P.-L. Ma, H.-C. Chen, C.-Y. Li, and P. Wang, *Angew. Chem. Int. Ed.* **2020**, *59*, 8937–8940.
2. C. B. Tripathi and S. Mukherjee, *Angew. Chem. Int. Ed.* **2013**, *125*, 8608–8611.
3. J.-L. Han, Y. Qin, C.-W. Ju, and D. Zhao, *Angew. Chem. Int. Ed.* **2020**, *59*, 6555–6560.
4. S. G. Newman and M. Lautens, *J. Am. Chem. Soc.* **2011**, *133*, 1778–1780.
5. Y.-Q. Zhang, X.-Q. Zhu, Y. Xu, H.-Z. Bu, J.-L. Wang, T.-Y. Zhai, J.-M. Zhou, and L.-W. Ye, *Green Chem.* **2019**, *21*, 3023–3028.
6. Y. Zhao, X. Xing, S. Zhang and D. Z. Wan, *Org. Biomol. Chem.* **2014**, *12*, 4314–4317.
7. J. Ye, Z. Shi, T. Sperger, Y. Yasukawa, C. Kingston, F. Schoenebeck, M. Lautens, *Nat. Chem.* **2017**, *9*, 361–368.
8. T. Ankner, G. Hilmersson, *Org. Lett.* **2009**, *11*, 3, 503–506.
9. Y. Liang, S. Zhang, and Z. Xi, *J. Am. Chem. Soc.* **2011**, *133*, 9204–9207.
10. C. J. Jenks, S.-L. Chang, J. W. Andereg, P. A. Thiel, and D. W. Lynch, *J. Phys. Rev. B* **1996**, *54*, 6301–6306.
11. M. C. Militello and S. J. Simko, Palladium Oxide (PdO) by XPS. *Surface Science Spectra* **1994**, *3*, 395–401.
12. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams - Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Jr. Throssell, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision A.03; Gaussian, Inc.: Wallingford, CT, **2016**.
13. Y. Zhao & D. G. Truhlar, *J. Chem. Phys.* **2006**, *125*, 194101.
14. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
15. a) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158–6170; b) S. Grimme, S.

- Ehrlich, L. Georigk, *J. Comput. Chem.* **2011**, 32, 1456-1465.
16. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, 113, 6378–6396.
17. a) G. Luchini, J. V. Alegre-Requena, I. Funes-Ardoiz, R. S. Paton, *F1000Research* **2006**, 9, 291-305; b) S. Grimme, *Chem. Eur. J.* **2012**, 18, 9955-9964; c) Y. Li, J. Gomes, S. M. Sharada, A. T. Bell, M. Head-Gordon, *J. Phys. Chem. C* **2015**, 119, 1840–1850.

