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A crystalline monosubstituted carbene

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Supplementary Information For:

A Crystalline Mono-Substituted Carbene

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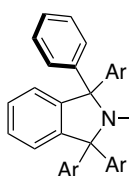
I. Supplementary Methods

General: All reactions were carried out using a standard glovebox or Schlenk techniques under argon. Some of the spectra contain signals from residual solvents, although, as we described in the experimental procedures, most of the compounds were thoroughly dried at least at 120 °C for one night under high vacuum. The difficulty for removing the residual solvent can be attributed to the bulky 3D structure of our systems, resulting in a lot of voids in the crystal lattice. The co-crystallization of solvents is visible from the residual electron density in the crystal voids observed by X-ray crystallography. Due to this contamination, collecting EA data matches chemical formula failed.

Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVA300 (^1H : 300 MHz, ^{19}F : 282 MHz, ^{31}P : 121 MHz, ^{77}Se : 57 MHz), JEOL ECA500 (^1H : 500 MHz, ^{19}F : 471 MHz, ^{31}P : 202 MHz), Varian VX500 equipped with a nitrogen-cooled Cold Probe (^1H : 500 MHz, ^{13}C : 126 MHz), or Bruker AVA800 equipped with a nitrogen-cooled CryoProbe (^1H : 800 MHz, ^{13}C : 201 MHz) spectrometer, at ambient temperature unless otherwise noted. Chemical shift values for protons are referenced to the residual proton resonance of CDCl_3 (δ : 7.26), benzene- d_6 (δ : 7.16), toluene- d_8 (δ : 2.08), or CD_3CN (δ : 1.94), or the proton resonance of *tert*-butyl methyl ether (δ : 3.08 and 1.10, referenced to TMS). Chemical shift values for carbons are referenced to the carbon resonance of CDCl_3 (δ : 77.16), benzene- d_6 (δ : 128.06), CH_3CN (δ : 118.26), 1,2-dichloroethane (δ : 44.45, referenced to TMS), or *tert*-butyl methyl ether (δ : 72.27, 49.14, and 27.19, referenced to TMS). Chemical shifts for other heteroatoms are referenced to CFCl_3 (^{19}F), H_3PO_4 (^{31}P) and Me_2Se (^{77}Se). Coupling constants J are given in Hertz as positive values regardless of their real individual signs. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal. Infrared spectra were recorded in a ThermoScientific Nicolet 6700 FT-IR instrument in a dichloromethane solution, or in a Bruker ALPHA II FTIR Spectrometer in a neat solid state. The intensities of the selected peaks are abbreviated as follows: s = strong, m = medium, w = weak, br = broad. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory on an Agilent 6230 Accurate-Mass TOFMS spectrometer. Single crystal X-ray diffraction data were collected on Bruker Apex diffractometers using Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu- $\text{K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at the UC San Diego Crystallography Facility. Melting points were measured with an electrothermal MEL-TEMP apparatus.

Materials: Solvents were dried over sodium (diethyl ether, tetrahydrofuran, pentane, or toluene), calcium hydride (methyl *tert*-butyl ether, hexanes, heptane, dichloromethane, or chloroform), or P_2O_5 (acetonitrile), distilled under argon, and stored over activated molecular sieves. The following compounds were prepared according to literature procedures: *N*-methylphthalimide,¹ 5'-bromo-1,1':3',1''-terphenyl,² 5'-iodo-3,3'',5,5''-tetrakis(trifluoromethyl)-1,1':3',1''-terphenyl,³ (PhP)₅.⁴ All other starting materials were purchased from commercial sources and used without further purification unless otherwise noted.

N-methyl-1,1,3,3-tetraphenylisoindoline (**1a**)

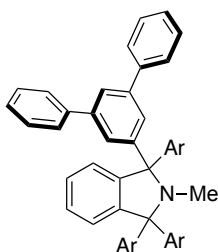


Phenylmagnesium bromide was prepared from bromobenzene (56.7 mL, 540 mmol) and magnesium turnings (19.4 g, 800 mmol) activated by 1,2-dibromoethane in diethyl ether (250 mL) at room temperature. The solution of the Grignard reagent was cannulated into a solution of *N*-methylphthalimide (14.5 g, 90 mmol) in toluene (200 mL) at room temperature. The mixture was heated in an oil bath at 120 °C, and concentrated until the volume was reduced to ca. 200 mL. Then, the Schlenk flask was sealed and stirred at 120 °C for 1 day. After cooling to room temperature, the reaction mixture was quenched by addition of a saturated aqueous NH₄Cl solution, and extracted by using DCM (3 x 300 mL). The combined organic phase was dried over MgSO₄, filtered, evaporated to dryness, and the residue was purified by flash silica-gel column chromatography (hexane/EtOAc = 97/3 to 90/10). The obtained crude **1a** was triturated with hot hexane (ca. 100 mL), the mixture was cooled to room temperature, filtered, and the solid dried in *vacuo* at 120 °C overnight. Compound **1a** was obtained as a colorless solid (21.4 g, 49.0 mmol, 54% yield).

NOTE: Use of THF instead of diethyl ether for the preparation of the Grignard reagent leads to significant decrease of the yield of **1a**.

mp: 184–185 °C; **TLC** (hexane: ethyl acetate, 90:10 v/v): *R_f* = 0.67; **¹H NMR** (800 MHz, CDCl₃) δ 7.29–7.24 (m, 14H), 7.24–7.21 (m, 2H), 7.17–7.13 (m, 8H), 2.46 (s, 3H); **¹³C NMR** (201 MHz, CDCl₃) δ 145.6 (2C, 4°), 144.9 (4C, 4°), 129.4 (8C, 3°), 127.6 (8C, 3°), 127.4 (2C, 3°), 126.7 (4C, 3°), 125.0 (2C, 3°), 79.5 (2C, 4°), 28.9 (1C, N-CH₃); **HRMS** (*m/z*): [M+H]⁺ calcd. for C₃₃H₂₈N, 438.2216; found, 438.2214.

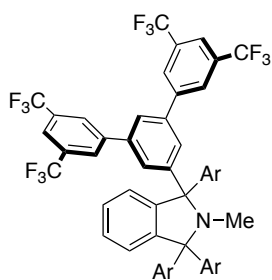
N-methyl-1,1,3,3-tetrakis(1,1':3',1''-terphen-5'-yl)isoindoline (**1b**)



(1,1':3',1''-terphen-5'-yl)magnesium bromide was prepared from 5'-bromo-1,1':3',1''-terphenyl (13.0 g, 42 mmol) and magnesium turnings (6.0 g) activated by 1,2-dibromoethane in diethyl ether (100 mL) at room temperature. The solution of the Grignard reagent was cannulated into a solution of *N*-methylphthalimide (1.13 g, 7.0 mmol) in toluene (50 mL) at room temperature. The mixture was heated in oil bath at 120 °C, and concentrated until the volume was reduced to ca. 50 mL. Then, the Schlenk flask was sealed and stirred at 120 °C for 1 day. After cooling to room temperature, the reaction mixture was quenched by addition of a saturated aqueous NH₄Cl solution, and extracted by using DCM (3 x 50 mL). The combined organic phase was dried over MgSO₄, filtered, evaporated to dryness, and the residue was purified by flash silica-gel column chromatography (hexane/EtOAc = 97/3 to 90/10). The obtained crude **1b** was triturated with hot hexane (ca. 100 mL), cooled to room temperature, filtered, and the solid was dried in *vacuo* at 120 °C overnight. Compound **1b** was obtained as a colorless solid (2.48 g, 2.37 mmol, 34% yield).

mp: 284–286 °C (decomp.); **TLC** (hexane: ethyl acetate, 90:10 v/v): *R_f* = 0.30; **¹H NMR** (800 MHz, CDCl₃) δ 7.68 (s, 4H), 7.48–7.43 (m, 10H), 7.41 (d, *J* = 7.4 Hz, 16H), 7.36–7.24 (m, 24H), 2.90 (s, 3H); **¹³C NMR** (201 MHz, CDCl₃) δ 146.0 (4C, 4°), 145.3 (2C, 4°), 141.3 (8C, 4°), 141.2 (8C, 4°), 128.8 (16C, 3°), 128.0 (2C, 3°), 127.3 (24C, 3°), 127.0 (8C, 3°), 125.1 (2C, 3°), 125.0 (4C, 3°), 80.3 (2C, 4°), 29.3 (1C, N-CH₃); **HRMS** (*m/z*): [M+H]⁺ calcd. for C₈₁H₅₈N, 1046.4720; found, 1046.4711.

***N*-methyl-1,1,3,3-tetrakis(3,3'',5,5''-tetra(trifluoromethyl)-1,1':3',1''-terphen-5'-yl)isoindoline (1c)**



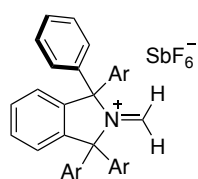
(3,3'',5,5''-tetra(trifluoromethyl)-1,1':3',1''-terphen-5'-yl)magnesium iodide was prepared from 5'-iodo-3,3'',5,5''-tetra(trifluoromethyl)-1,1':3',1''-terphenyl (3.49 g, 6.0 mmol) and magnesium turnings (1.0 g) activated by 1,2-dibromoethane in diethyl ether (20 mL) at room temperature. The suspension of the Grignard reagent was cannulated into a solution of *N*-methylphthalimide (161 mg, 1.0 mmol) in toluene (10 mL) at room temperature. The mixture was heated in oil bath at 120 °C,

and concentrated until the volume was reduced to ca. 10 mL. Then the Schlenk flask was sealed and stirred at 120 °C for 1 day. After cooling to room temperature, the mixture was quenched by a saturated aqueous NH₄Cl solution and extracted with DCM (3 x 50 mL). The combined organic phase was dried over MgSO₄, filtered through a pad of Celite, evaporated to dryness, and the residue was purified by flash silica-gel column chromatography (hexane/EtOAc = 97/3 to 90/10). All fractions containing **1c** were combined and evaporated to dryness. The obtained crude **1c** was washed with hexane and benzene repeatedly, and then dried *in vacuo* at 120 °C overnight, to afford **1c** as a colorless solid (783 mg, 0.37 mmol, 37% yield).

NOTE: Compound **1c** could be synthesized in multi-gram scale in a single batch from 5.0 mmol of *N*-methylphthalimide and 30 mmol of 5'-iodo-3,3'',5,5''-tetra(trifluoromethyl)-1,1':3',1''-terphenyl, yet with lower yield of 22%.

mp: 253–255 °C; **TLC** (hexane: ethyl acetate, 90:10 v/v): *R_f* = 0.72; **¹H NMR** (800 MHz, CDCl₃) δ 7.81 (s, 8H), 7.72 (s, 16H), 7.68 (s, 4H), 7.50 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.45–7.42 (m, 10H), 2.93 (s, 3H); **¹³C NMR** (201 MHz, CDCl₃) δ 146.3 (4C, 4°), 143.8 (2C, 4°), 141.8 (8C, 4°), 139.8 (8C, 4°), 132.5 (q, ²*J*_{C-F} = 33.5 Hz, 16C, 4°), 129.6 (2C, 3°), 127.9 (8C, 3°), 127.0 (br s, 16C, 3°), 125.7 (4C, 3°), 124.9 (2C, 3°), 123.1 (q, ¹*J*_{C-F} = 272.9 Hz, 16C, 4°), 122.0 (br s, 8C, 3°), 80.6 (2C, 4°), 29.0 (1C, N-CH₃); **¹⁹F NMR** (282 MHz, CDCl₃) δ –63.1; **HRMS** (*m/z*): [*M*+H]⁺ calcd. for C₉₇H₄₄F₄₈N, 2134.2702; found, 2134.2616.

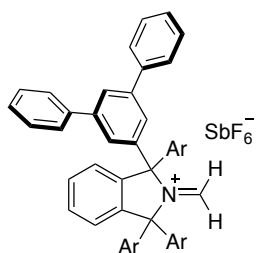
***N*-methylene-1,1,3,3-tetraphenylisoindolinium hexafluoroantimonate (2a)**



A mixture of **1a** (875 mg, 2.0 mmol) and NO·SbF₆ (585 mg, 2.2 mmol) in DCM (10 mL) was stirred at room temperature for 3 hours. The resulting solution was filtered through a cannula equipped with a glass filter, and evaporated to dryness. Then, the obtained solid was thoroughly dried *in vacuo* at 140 °C overnight. After cooling to room temperature, the solid residue was washed with ether (3 x 10 mL), and dried *in vacuo* at 140 °C overnight, to afford **2a** as an off-white solid (924 mg, 1.37 mmol, 69% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.44 (s, 2H), 7.63 (dd, *J* = 5.8, 3.2 Hz, 2H), 7.43–7.26 (m, 12H), 7.22 (dd, *J* = 5.8, 3.2 Hz, 2H), 7.08–6.94 (m, 8H); **¹³C NMR** (126 MHz, CDCl₃) δ 166.8 (1C, N=CH₂), 139.6 (2C, 4°), 136.4 (4C, 4°), 130.9 (2C, 3°), 130.3 (4C, 3°), 129.6 (8C, 3°), 128.7 (8C, 3°), 126.3 (2C, 3°), 89.4 (2C, 4°); **¹⁹F NMR** (471 MHz, CDCl₃) δ –122.9 (br m); **HRMS** (*m/z*): [*M*]⁺ calcd. for C₃₃H₂₆N, 436.2060; found, 436.2058.

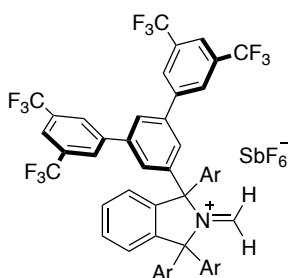
***N*-methylene-1,1,3,3-tetrakis(1,1':3',1''-terphen-5'-yl)isoindolinium hexafluoroantimonate (2b)**



A mixture of **1b** (523 mg, 0.50 mmol) and NO·SbF₆ (159 mg, 0.60 mmol) in DCM (10 mL) was stirred at room temperature for 3 hours. The resulting solution was filtered through a cannula equipped with a glass filter, and evaporated to dryness. Then, the obtained solid was thoroughly dried *in vacuo* at 140 °C overnight. After cooling to room temperature, the solid residue was washed with toluene (3 x 5 mL), and dried *in vacuo* at 140 °C overnight, to afford **2b** as an off-white solid (352 mg, 275 mmol, 55% yield).

¹H NMR (300 MHz, CDCl₃) δ 9.10 (s, 2H), 7.75–7.67 (m, 6H), 7.47 (dd, *J* = 5.8, 3.2 Hz, 2H), 7.39 – 7.21 (m, 48H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.0 (1C, N=CH₂), 143.7 (8C, 4°), 139.8 (2C, 4°), 139.5 (8C, 4°), 138.0 (4C, 4°), 131.4 (2C, 3°), 129.1 (16C, 3°), 128.6 (4C, 3°), 128.3 (8C, 3°), 127.4 (16C, 3°), 126.3 (2C, 3°), 126.1 (8C, 3°), 90.0 (2C, 4°); **¹⁹F NMR** (471 MHz, CDCl₃) δ –121.7 (br m); **HRMS** (*m/z*): [*M*]⁺ calcd. for C₈₁H₅₈N, 1044.4564; found, 1044.4556.

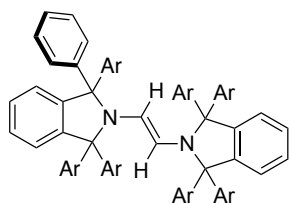
***N*-methylene-1,1,3,3-tetrakis(3,3'',5,5''-tetra(trifluoromethyl)-1,1':3',1''-terphen-5'-yl)isoindolinium hexafluoroantimonate (2c)**



A mixture of **1c** (1.07 g, 0.50 mmol) and NO·SbF₆ (160 mg, 0.60 mmol) in acetonitrile (15 mL) was stirred at room temperature for 3 hours. The resulting solution was filtered through a cannula equipped with a glass filter, and evaporated to dryness. Then, the obtained solid was thoroughly dried *in vacuo* at 140 °C overnight. After cooling to room temperature, the solid residue was washed with a minimum amount of DCM, and dried *in vacuo* at 140 °C overnight, to afford **2c** as an orange solid (1.15 g, 0.49 mmol, 98% yield). Recrystallization from hot 1,1,2,2-tetrachloroethane solution afforded single crystals suitable for X-ray crystallographic analysis.

¹H NMR (300 MHz, CDCl₃) δ 9.42 (s, 2H), 7.94 (dd, *J* = 5.9, 3.1 Hz, 2H), 7.73 (s, 8H), 7.67 (s, 4H), 7.66–7.58 (s, 16H), 7.53 (dd, *J* = 5.9, 3.1 Hz, 2H), 7.43–7.31 (s, 8H); **¹³C NMR** (201 MHz, CH₃CN) δ 172.3 (1C, N=CH₂), 141.8 (8C, 4°), 140.9 (8C, 4°), 140.0 (4C, 4°), 139.4 (2C, 4°), 132.7 (2C, 3°), 132.4 (q, ²*J*_{C-F} = 33.4 Hz, 16C, 4°), 129.5 (4C, 3°), 129.2 (8C, 3°), 128.7 (16C, 3°), 127.4 (2C, 3°), 124.2 (q, ¹*J*_{C-F} = 272.4 Hz, 16C, 4°), 122.9 (8C, 3°), 89.6 (2C, 4°); **¹⁹F NMR** (471 MHz, CDCl₃) δ –63.2, –119.8 (br); **HRMS** (*m/z*): [*M*]⁺ calcd. for C₉₇H₄₂F₄₈N, 2132.2545; found, 2132.2557.

(*E*)-1,2-bis(1,1,3,3-tetraphenylisoindolin-2-yl)ethylene (**4a**)

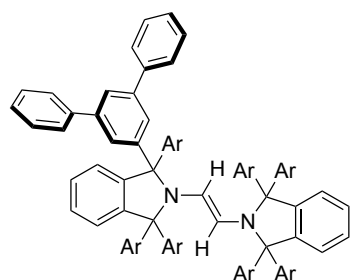


In a 15-mL scintillation vial, a mixture of **2a** (33.6 mg, 50 μ mol) and KHMDS (12.0 mg, 60 μ mol) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. Then, precooled *tert*-butyl methyl ether (2.0 mL) was added, and the mixture was stirred with cooling for 10 minutes. ^1H NMR monitoring of the pale red solution using C_6D_6 as an internal locking solvent revealed immediate formation of **4a**. After further stirring at room temperature for 3 hours, the pale red solution was passed through a glass filter, and evaporated to dryness. The obtained solid was dissolved into benzene, passed through a plug of Florisil, dried in *vacuo* at 120 $^\circ\text{C}$ overnight, to afford **4a** as a colorless powder (22.0 mg, 25 μ mol, quantitative yield).

NOTE: Compound **4a** is sensitive to oxygen.

^1H NMR (300 MHz, C_6D_6) δ 7.11–6.98 (m, 12H), 6.97–6.85 (m, 36H), 5.61 (s, 2H, $\text{NCH}=\text{CHN}$); ^{13}C NMR (126 MHz, C_6D_6) δ 145.9 (4C, 4 $^\circ$), 145.0 (8C, 4 $^\circ$), 130.3 (16C, 3 $^\circ$), 127.7 (4C, 3 $^\circ$), 127.6 (16C, 3 $^\circ$), 126.7 (4C, 3 $^\circ$), 126.6 (4C, 3 $^\circ$), 124.7 (2C, 3 $^\circ$), 124.6 (2C, 3 $^\circ$), 114.6 (2C, $\text{NCH}=\text{CHN}$), 80.3 (4C, 4 $^\circ$); **HRMS** (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{66}\text{H}_{51}\text{N}_2$, 871.4047; found, 871.4028.

(*E*)-1,2-bis(1,1,3,3-tetrakis(1,1':3',1''-terphen-5'-yl)isoindolin-2-yl)ethylene (**4b**)

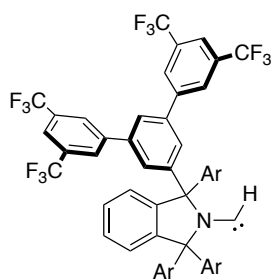


In a 15-mL scintillation vial, a mixture of **2b** (64.1 mg, 50 μ mol) and KHMDS (12.0 mg, 60 μ mol) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. Then, precooled toluene- d_8 (2.0 mL) was added, and the mixture was stirred with cooling for 10 minutes. ^1H NMR monitoring of the blue-green suspension suggested the existence of free carbene **3b** at low temperature but also concomitant formation of dimer **4b** (See Supplementary Figure 19). After further stirring at room temperature for 3 hours, the bright yellow solution was passed through a glass filter, and evaporated to dryness. The obtained solid was dissolved into THF, passed through a plug of Florisil, dried in *vacuo* at 120 $^\circ\text{C}$ overnight, to afford **4b** as a yellow powder (50.2 mg, 48 μ mol, 96% yield). Recrystallization from toluene/hexane (bi-layering) at room temperature afforded single crystals suitable for X-ray crystallographic analysis.

NOTE: Compound **4b** is sensitive to oxygen. The highly broad nature of the NMR spectra of **4a** can be attributed to slow rotation of hindered terphenyl substituents (See also the X-ray structure in Supplementary Figure 59).

^1H NMR (300 MHz, C_6D_6) δ 8.61–6.47 (m, 112H), 6.04 (br s, 2H, $\text{NCH}=\text{CHN}$); ^{13}C NMR (126 MHz, 1,2-dichloroethane) δ 146.8 (4 $^\circ$), 141.0 (4 $^\circ$), 139.7 (4 $^\circ$), 138.4 (4 $^\circ$), 130.7 (3 $^\circ$), 128.8 (3 $^\circ$), 127.2 (3 $^\circ$), 124.5 (3 $^\circ$), (Note: The signals in the aromatic region could not be fully counted, due to the highly broad spectrum) 111.5 ($\text{NCH}=\text{CHN}$), 82.8 (4 $^\circ$); **HRMS** (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{162}\text{H}_{115}\text{N}_2$, 2087.9055; found, 2087.9098.

***N*-methylidene-1,1,3,3-tetrakis(3,3'',5,5''-tetra(trifluoromethyl)-1,1':3,1''-terphen-5'-yl)isoindoline (3c)**

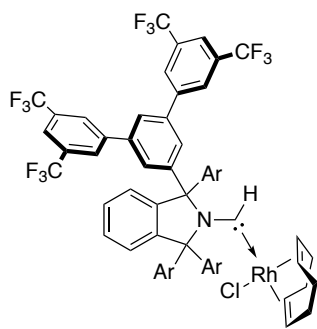


In a 15-mL scintillation vial, a mixture of **2c** (94.7 mg, 40 μ mol) and KHMDS (10.0 mg, 50 μ mol) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. Then, precooled *tert*-butyl methyl ether (2.0 mL) was added, and the mixture was stirred with cooling for 10 minutes. The yellow solution was quickly passed through a glass filter and layered by cold heptane (ca. 15 mL). The bi-layered solution was stored at -40 $^{\circ}$ C overnight, to afford **3c** as yellowish crystals (47.2 mg, 22 μ mol, 55% yield).

Note: Compound **3c** gradually decomposes in solution at room temperature or even at -40 $^{\circ}$ C. The lifetime of **3c** was found highly dependent to the solvent used (*tert*-butyl methyl ether > diethyl ether >> THF). While the decomposition pathways are unclear due to the formation of multiple decomposed products, the formation of the carbene dimer has never been detected by NMR and MALDI-TOF-MS analyses.

1 H NMR (300 MHz, MTBE + C_6D_6) δ 13.81 (s, 1H), 8.01–7.45 (m, 40H); **13 C NMR** (201 MHz, MTBE) δ 320.0 ($^1J_{C-H}$ = 95.3 Hz, 3 $^{\circ}$), 147.2 (4 $^{\circ}$), 145.1 (4 $^{\circ}$), 143.1 (4 $^{\circ}$), 142.9 (4 $^{\circ}$), 142.5 (4 $^{\circ}$), 140.8 (4 $^{\circ}$), 140.2 (4 $^{\circ}$), 139.8 (4 $^{\circ}$), 133.1 (br m, $^2J_{C-F}$ could not be determined, 4 $^{\circ}$), 130.8 (3 $^{\circ}$), 129.3 (3 $^{\circ}$), 128.5 (3 $^{\circ}$), 127.8 (3 $^{\circ}$), 126.9 (3 $^{\circ}$), 123.8 (br q, $^1J_{C-F}$ = 272 Hz, 4 $^{\circ}$), 122.4 (3 $^{\circ}$), 122.3 (3 $^{\circ}$), 122.1 (3 $^{\circ}$) (Note: The signals in the aromatic region could not be fully counted, due to the broad and complex spectrum), 89.1 (4 $^{\circ}$), 86.3 (4 $^{\circ}$); **19 F NMR** (282 MHz, MTBE + C_6D_6) δ -63.1, -63.2; **IR** (ATR, neat): 2981.8 (w), 1621.0 (w), 1593.0 (w), 1460.7 (w), 1388.6 (w), 1366.2 (s), 1275.0 (s), 1232.3 (s), 1171.0 (w), 1124.7 (s), 987.2 (w), 896.4 (m), 882.3 (m), 844.6 (m), 757.2 (w), 704.8 (m), 682.0 (m), 668.0 (m), and 638.7 (m) cm^{-1} .

(3c)Rh(cod)Cl



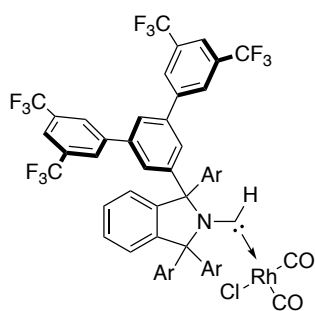
In a 15-mL scintillation vial, a mixture of **2c** (47.3 mg, 20 μ mol), [RhCl(cod)]₂ (4.9 mg, 10 μ mol), and KHMDS (6.0 mg, 30 μ mol) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. Then, precooled THF (2.0 mL) was added, and the mixture was stirred with cooling for 30 minutes. Then the cooling bath was removed, and the mixture was further stirred at room temperature overnight. The resulting mixture was passed through a glass filter, evaporated to dryness, recrystallized from chloroform/hexane (vapor diffusion)

at room temperature, to afford the titled compound as orange crystals suitable for X-ray crystallographic analysis. The obtained crystals were grounded and dried in *vacuo* at room temperature overnight to afford the titled compound as an orange powder (20.5 mg, 8.6 μ mol, 43% yield, ignoring contamination with hexanes). Attempts to remove co-crystallized hexanes such as by drying at higher temperature (e.g. 100 $^{\circ}$ C) and azeotropic distillation using chloroform or pentane resulted in partial decomposition of the product. Due to the difficulty in removal of hexanes, 1 H and 13 C NMR signals are tentatively assigned. Since the chemical identity was evidenced by HRMS and X-ray crystallographic analyses, the titled compound was used for next step without further purification.

NOTE: The titled compound is mildly sensitive to water, decomposing to formamide.

¹H NMR (300 MHz, CDCl₃) δ 13.61 (d, ²J_{Rh-H} = 3.3 Hz, 1H), 7.90–7.35 (m, 43H), 7.07 (d, *J* = 7.7 Hz, 1H), 3.14 (br, 2H), 1.59 (br, 4H), 1.27 (br, 2H); **¹³C NMR** (126 MHz, CDCl₃) δ 257.3 (3°), 143.9 (4°), 143.1 (4°), 141.8 (4°), 140.8 (4°), 139.7 (4°), 132.6 (br m, ²J_{C-F} could not be determined, 4°), 131.0 (3°), 130.8 (3°), 130.1 (3°), 128.8 (3°), 127.9 (3°), 127.2 (3°), 126.3 (3°), 125.9 (3°), 125.5 (3°), 123.0 (br q, ²J_{C-F} = 273 Hz, 4°), 122.5 (3°), 122.0 (3°) (Note: The signals in the aromatic region could not be fully counted, due to the broad and complex spectrum), 105.3 (3°), 100.2 (3°), 89.3 (4°), 85.0 (4°), 70.8 (3°), 67.2 (3°), 32.3 (2°), 27.8 (2°); **¹⁹F NMR** (282 MHz, CDCl₃) δ −63.0 (br), −63.2; **HRMS** (*m/z*): [M+TFA-H][−] calcd. for C₁₀₅H₅₃ClF₄₈NRh·CF₃CO₂, 2490.2011; found, 2490.2014.

***Cis*-(3c)Rh(CO)₂Cl (5)**



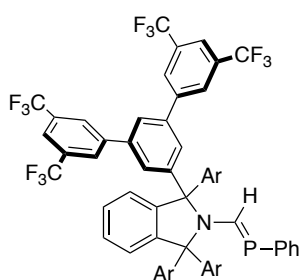
To a solution of (3c)Rh(cod)Cl (15.0 mg, 6.7 μmol) in CDCl₃ (1.5 mL) in a 5-mm NMR tube was bubbled carbon monoxide for 5 minutes at room temperature. Immediate color change from orange to pale yellow was observed, and clean formation of **5** was confirmed by ¹H NMR monitoring. After evaporation, compound **5** was obtained as a yellow powder (12.1 mg, 5.2 μmol, 78% yield, ignoring contamination with hexanes). Recrystallization from chloroform/hexane (vapor diffusion) under CO atmosphere at room temperature

afforded single crystals suitable for X-ray crystallographic analysis.

NOTE: Compound **5** is mildly sensitive to water, decomposing to formamide.

¹H NMR (300 MHz, CDCl₃) δ 12.33 (d, ²J_{Rh-H} = 2.5 Hz, 1H), 8.00–7.61 (m, 39H), 7.16 (d, *J* = 7.5 Hz, 1H); **¹³C NMR** (126 MHz, CH₃CN) δ 242.4 (d, ¹J_{Rh-Carbene} = 38.4 Hz, 3°), 184.7 (d, ¹J_{Rh-CO} = 53.0 Hz, 4°), 181.5 (d, ¹J_{Rh-CO} = 77.4 Hz, 4°), 141.8 (4°), 141.6 (4°), 141.1 (4°), 140.8 (4°), 140.5 (4°), 139.8 (4°), 132.7 (q, ²J_{C-F} = 31.2 Hz, 4°), 132.4 (q, ²J_{C-F} = 31.2 Hz, 4°), 131.5 (3°), 130.6 (3°), 129.0 (3°), 127.7 (3°), 127.5 (3°), 127.4 (3°), 127.0 (3°), 126.1 (3°), 122.9 (br q, ²J_{C-F} = 273 Hz, 4°), 122.5 (3°), 122.1 (3°), (Note: The signals in the aromatic region could not be fully counted, due to the broad and complex spectrum) 90.5 (4°), 86.4 (4°); **¹⁹F NMR** (282 MHz, CDCl₃) δ −63.2; **IR** (DCM solution): 2086.4 and 2006.2 cm^{−1}. **HRMS** (*m/z*): [M−CO−Cl]⁺ calcd. for C₉₈H₄₁F₄₈NORh, 2262.1471; found, 2262.1535 (Note: Due to the labile nature of CO, only the mono carbonyl complex was detected.).

***N*-((phenylphosphaneylidene)methyl)-1,1,3,3-tetrakis(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)isoindoline (3c-PPh adduct 6)**



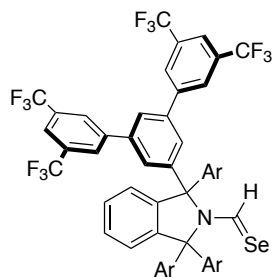
In a 15-mL scintillation vial, a mixture of **2c** (47.3 mg, 20 μ mol) and KHMDS (6.0 mg, 30 μ mol) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. Then, precooled THF (2.0 mL) was added, and the mixture was stirred with cooling for 10 minutes. The mixture was transferred into another 15-mL scintillation vial containing (PhP)₅ (1.1 mg, 2.0 μ mol), and the mixture was stirred with cooling for another 30 minutes. Then, the cooling bath was removed

and the mixture was stirred at room temperature overnight. The crude mixture was analyzed by ¹H, ¹³C, and ³¹P NMR, which showed the presence of **6**, formamide, (PhP)₅ and other unidentified products. Compound **6** could not be separated from the other products and therefore was not isolated. The characteristic NMR signals listed below are correlated in ¹H, ¹³C HSQC and ¹H, ³¹P HMBC analyses, and in good agreement with those of related compounds such as Me₂NCH=PPh.⁵

NOTE: Compound **6** is highly sensitive to water and oxygen.

¹H NMR (300 MHz, THF + C₆D₆) δ 9.41 (d, ²J_{P-H} = 16.2 Hz, NCH=PPh); **¹³C NMR** (126 MHz, THF + C₆D₆) δ 178.4 (d, ¹J_{C-P} = 50.9 Hz, NCH=PPh); **³¹P NMR** (121 MHz, THF + C₆D₆) δ 107.2; **³¹P NMR** (121 MHz, CDCl₃) δ 110.9; **HRMS** (m/z): [M+Na-2H]⁻ calcd. for C₁₀₃H₄₄F₄₈NP·Na, 2260.2348; found, 2260.2353.

1,1,3,3-tetrakis(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)isoindoline-2-carboselenaldehyde (3c-Se adduct 7)



In a 15-mL scintillation vial, a mixture of **2c** (47.3 mg, 20 μ mol), elemental selenium (5.0 mg, 63 μ mol), and KHMDS (6.0 mg, 30 μ mol) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. Then, precooled THF (2.0 mL) was added, and the mixture was stirred with cooling for 30 minutes. The cooling bath was removed, and the mixture was stirred at room temperature overnight. The resulting mixture was passed through a glass filter, and the filtrate was evaporated to

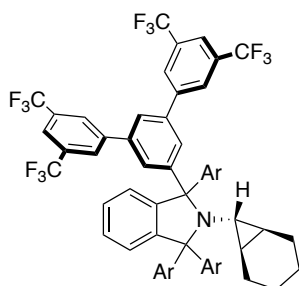
dryness. The solid residue was recrystallized from chloroform/hexane (vapor diffusion) at room temperature, giving **7** as orange crystals suitable for X-ray crystallographic analysis. The crystals were grounded and dried *in vacuo* at 120 °C overnight, to afford **7** as an orange powder (28.7 mg, 13 μ mol, 65% yield).

NOTE: Compound **7** is mildly sensitive to water, decomposing to formamide.

¹H NMR (300 MHz, CDCl₃) δ 11.99 (s, 1H, NCHSe), 7.84–7.78 (m, 10H), 7.73 (m, 4H), 7.69 (br s, 16H), 7.63–7.58 (m, 5H), 7.51 (m, 4H), 7.38 (d, *J* = 7.0 Hz, 1H); **¹³C NMR** (126 MHz, CDCl₃) δ 192.4 (1C, NCHSe), 144.5 (2C, 4°), 143.3 (1C, 4°), 141.5 (4C, 4°), 140.8 (4C, 4°), 140.6 (4C, 4°), 140.0 (1C, 4°), 139.3 (2C, 4°), 139.0 (4C, 4°), 132.6 (q, *J* = 33.6 Hz, 8C, 4°), 132.3 (q, *J* = 33.6 Hz, 8C, 4°), 131.3 (1C, 3°), 130.9 (1C, 3°), 129.3 (4C, 3°), 127.6 (4C, 3°), 126.8 (20C, 3°), 125.7 (1C, 3°), 124.9 (1C, 3°), 122.9 (q, *J* = 275.6 Hz, 8C, 4°), 122.8 (q, *J* = 275.6 Hz, 8C, 4°), 122.3 (4C, 3°), 121.9 (4C, 3°), 86.7 (1C, 4°), 83.3 (1C, 4°); **¹⁹F NMR** (282 MHz, CDCl₃) δ -63.1, -63.2; **⁷⁷Se NMR** (57 MHz, CDCl₃) δ 978.7 (Note: While acetone-*d*₆ is a standard solvent for ⁷⁷Se NMR study, Ulrich and coworkers reported that ⁷⁷Se NMR signals observed in CDCl₃ are in good agreement with those observed in acetone-*d*₆.⁶); **HRMS** (m/z): [M+TFA-H]⁻ calcd. for

C₉₇H₄₁F₄₈NSe·CF₃CO₂, 2324.1514; found, 2324.1493.

***N*-(bicyclo[4.1.0]heptan-7-yl)-1,1,3,3-tetrakis(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)isoindoline (3c–cyclohexene adduct 8)**

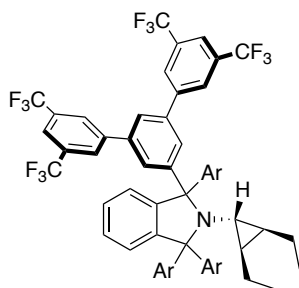


In a 15-mL scintillation vial, a mixture of **2c** (47.3 mg, 20 μmol) and cyclohexene (100 mg, 1.2 mmol, distilled from calcium hydride and stored over 3 Å molecular sieves) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. Then, a precooled solution of KHMDS (6.0 mg, 30 μmol) in MTBE (2.0 mL) was added, and the mixture was stirred with cooling for 30 minutes. Then, the resulting mixture was passed through a glass filter, evaporated to dryness, recrystallized from chloroform/hexane (vapor diffusion) at room temperature, to

afford **8** as colorless crystals suitable for X-ray crystallographic analysis. The crystals were grounded and dried in *vacuo* at 120 °C overnight to afford **8** as a colorless powder (40.7 mg, 18 μmol, 92% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.81 (s, 8H), 7.73 (s, 16H), 7.70 (s, 4H), 7.61 (s, 8H), 7.43–7.36 (m, 2H), 7.25–7.20 (m, 2H), 2.31 (NCH, br s, 1H), 1.50–0.69 (m, 10H); ¹³C NMR (201 MHz, CDCl₃) δ 147.1 (4C, 4°), 144.3 (2C, 4°), 141.7 (8C, 4°), 139.2 (8C, 4°), 132.5 (q, ²J_{C-F} = 33.7 Hz, 16C, 4°), 129.4 (2C, 3°), 128.8 (8C, 3°), 126.8 (16C, 3°), 125.4 (4C, 3°), 124.8 (2C, 3°), 123.1 (q, ¹J_{C-F} = 273 Hz, 16C, 4°), 122.0 (8C, 3°), 81.7 (2C, 4°), 40.1 (1C, NCHR₂), 23.4 (2C, 2°), 21.3 (2C, 2°), 19.5 (2C, 3°); ¹⁹F NMR (282 MHz, CDCl₃) δ –63.1; HRMS (m/z): [M+TFA–H][–] calcd. for C₁₀₃H₅₁F₄₈N·CF₃CO₂, 2326.3111; found, 2326.3102.

***N*-((1*r*,2*R*,3*S*)-2,3-diethylcyclopropyl)-1,1,3,3-tetrakis(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)isoindoline (3c–*cis*-3-hexene adduct 9)**



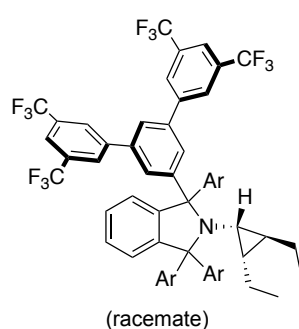
In a 15-mL scintillation vial, a mixture of **2c** (47.2 mg, 20 μmol) and *cis*-3-hexene (100 mg, 1.2 mmol, distilled from calcium hydride and stored over 3 Å molecular sieves) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. A precooled solution of KHMDS (6.0 mg, 30 μmol) in MTBE (2.0 mL) was added, and the mixture was stirred with cooling for 30 minutes. ¹³C NMR analysis of the crude mixture suggested the formation of a single major product (judging

from quaternary carbon signals alpha to the nitrogen atom. See Supplementary Figure 43.). Then, the resulting mixture was passed through a glass filter, and evaporated to dryness. The solid residue was analyzed by quantitative ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard, and the NMR yield of **9** was determined to be 88% (See Supplementary Figure 44.). The absence of the *trans*-isomer **10** was confirmed by ¹⁹F NMR analysis of the same mixture (See Supplementary Figure 45.), which supports that **3c** reacts as a singlet species in a concerted manner.

The same reaction was repeated, and the obtained solid residue was recrystallized from chloroform/hexane (vapor diffusion) at room temperature, to afford **9** as colorless crystals suitable for X-ray crystallographic analysis. The crystals were grounded and dried in *vacuo* at 120 °C overnight, to afford **9** as a colorless powder (22.5 mg, 10 μmol, 51% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.80 (s, 8H), 7.72 (s, 16H), 7.68 (s, 4H), 7.61 (s, 8H), 7.41 (m, 2H), 7.22 (dd, *J* = 5.8, 3.2 Hz, 2H), 2.10 (NCH, br s, 1H), 1.30–1.18 (CH₂CH₃, m, 2H), 0.90 (CHCH₂CH₃, m, 4H), 0.51 (CH₂CH₃, t, *J* = 7.0 Hz, 6H); **¹³C NMR** (201 MHz, CDCl₃) δ 146.8 (4C, 4°), 144.7 (2C, 4°), 141.7 (8C, 4°), 139.2 (8C, 4°), 132.6 (q, ²*J*_{C-F} = 33.3 Hz, 16C, 4°), 129.4 (2C, 3°), 128.9 (8C, 3°), 126.8 (16C, 3°), 125.4 (4C, 3°), 124.7 (2C, 3°), 123.1 (q, ¹*J*_{C-F} = 273 Hz, 16C, 4°), 122.0 (8C, 3°), 81.4 (2C, 4°), 41.3 (1C, NCHR₂), 27.0 (2C, 3°), 20.6 (2C, 2°), 13.6 (2C, 1°); **¹⁹F NMR** (282 MHz, CDCl₃) δ –63.1; **HRMS** (*m/z*): [M+TFA–H][–] calcd. for C₁₀₃H₅₃F₄₈N·CF₃CO₂, 2328.3267; found, 2328.3235.

***N*-((2*RS*,3*RS*)-2,3-diethylcyclopropyl)-1,1,3,3-tetrakis(3,3'',5,5''-tetrakis(trifluoromethyl)-[1,1':3',1''-terphenyl]-5'-yl)isoindoline (3*c*–*trans*-3-hexene adduct 10)**

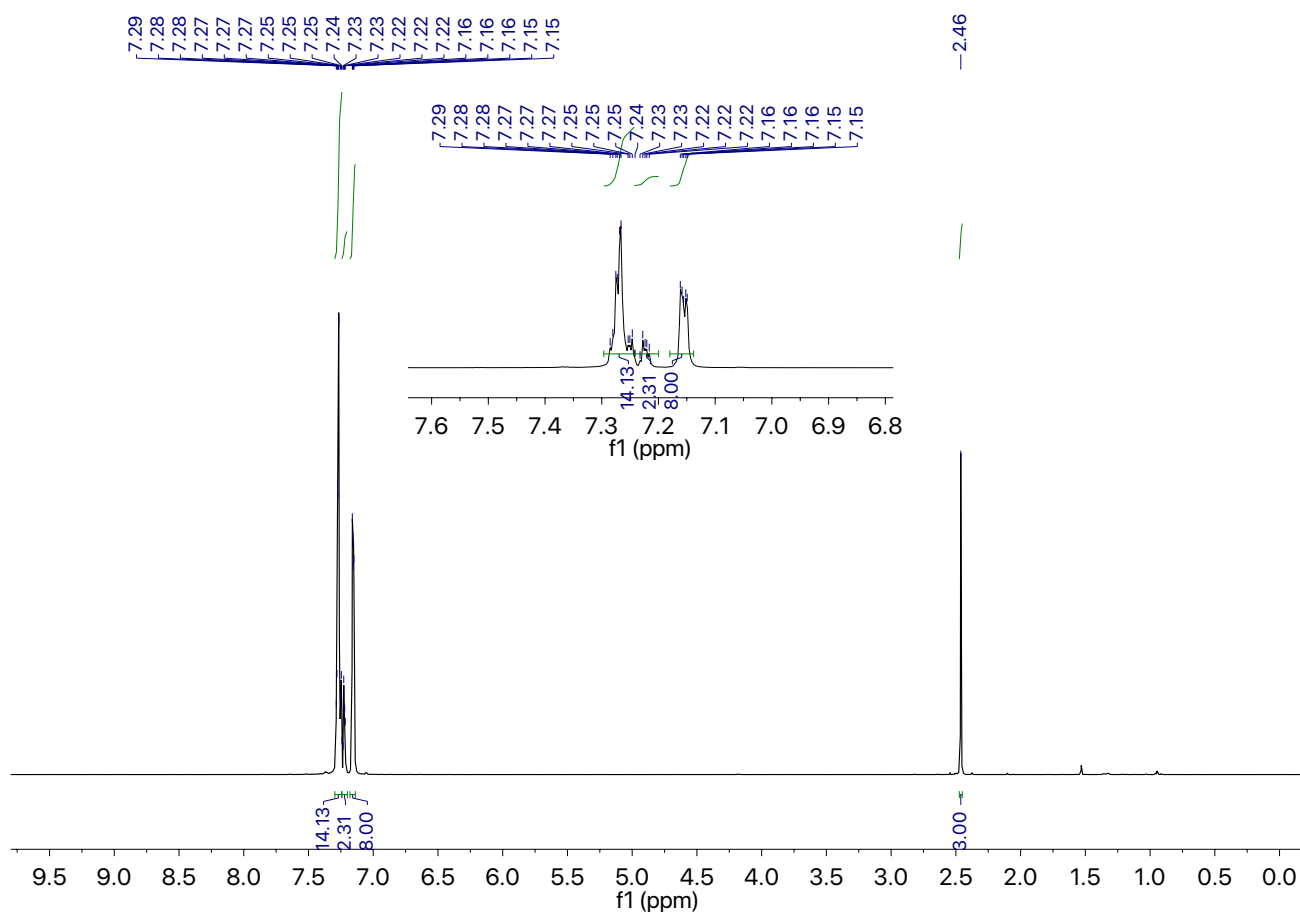


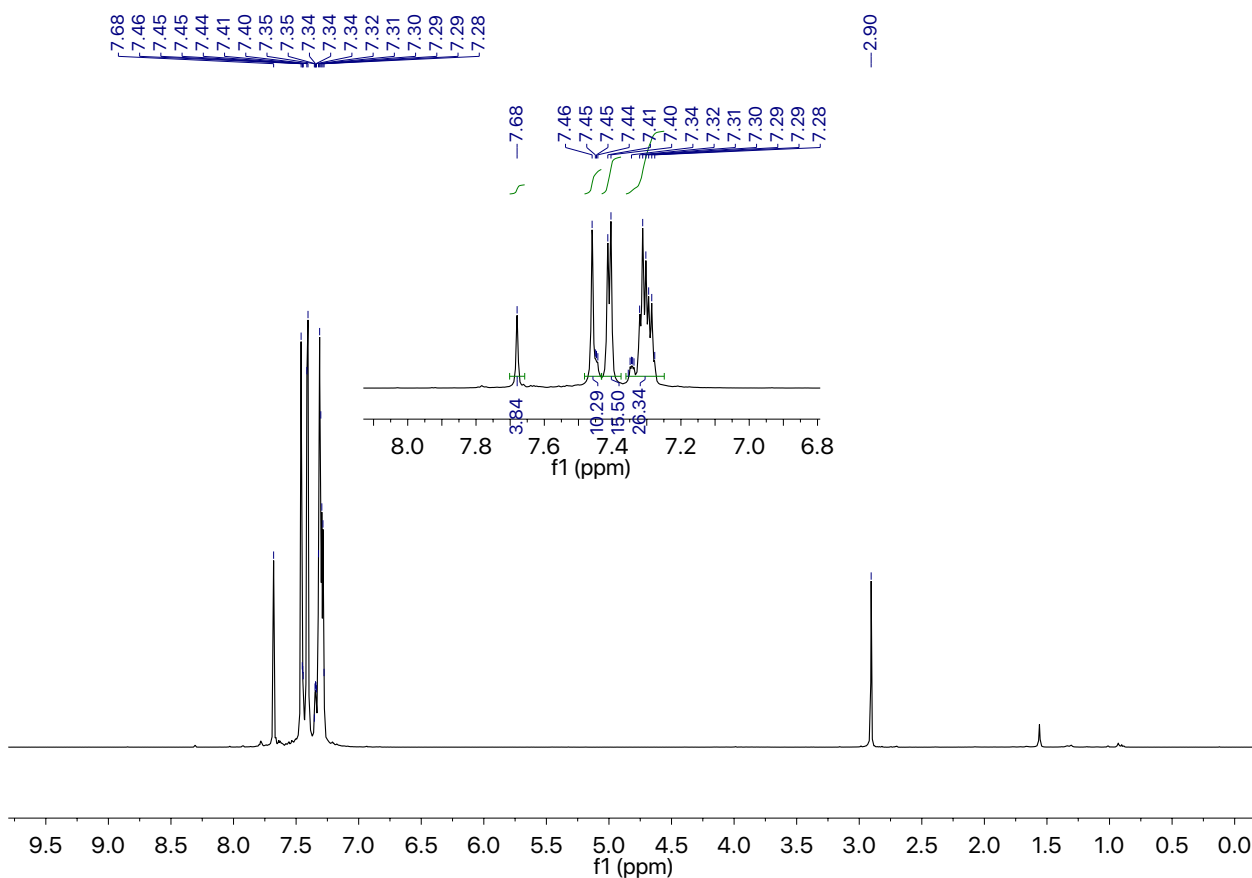
In a 15-mL scintillation vial, a mixture of **2c** (47.4 mg, 20 μmol) and *trans*-3-hexene (100 mg, 1.2 mmol, distilled from calcium hydride and stored over 3 Å molecular sieves) was chilled for 1 hour in a glovebox coldwell cooled with dry ice/acetone bath. A precooled solution of KHMDS (6.0 mg, 30 μmol) in MTBE (2.0 mL) was added, and the mixture was stirred with cooling for 30 minutes. ¹³C NMR analysis of the crude mixture suggested the formation of a single major product and a minor side product (judging from quaternary carbon signals alpha to the nitrogen atom. See Supplementary Figure 48.). Then, the resulting mixture was passed through a glass filter, and evaporated to dryness. The solid residue was analyzed by quantitative ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard, and the NMR yield of **10** was determined to be 72% (See Supplementary Figure 50.). The formation of **10** as a major product was also confirmed by ¹⁹F NMR analysis of the same mixture (See Supplementary Figure 51.).

The same reaction was repeated and the obtained solid residue was recrystallized from chloroform/hexane (vapor diffusion) at room temperature, to afford **10** as pale yellow crystals suitable for X-ray crystallographic analysis. The crystals were grounded and dried in *vacuo* at 120 °C overnight, to afford **10** as a yellowish powder (22.3 mg, 10 μmol, 50% yield).

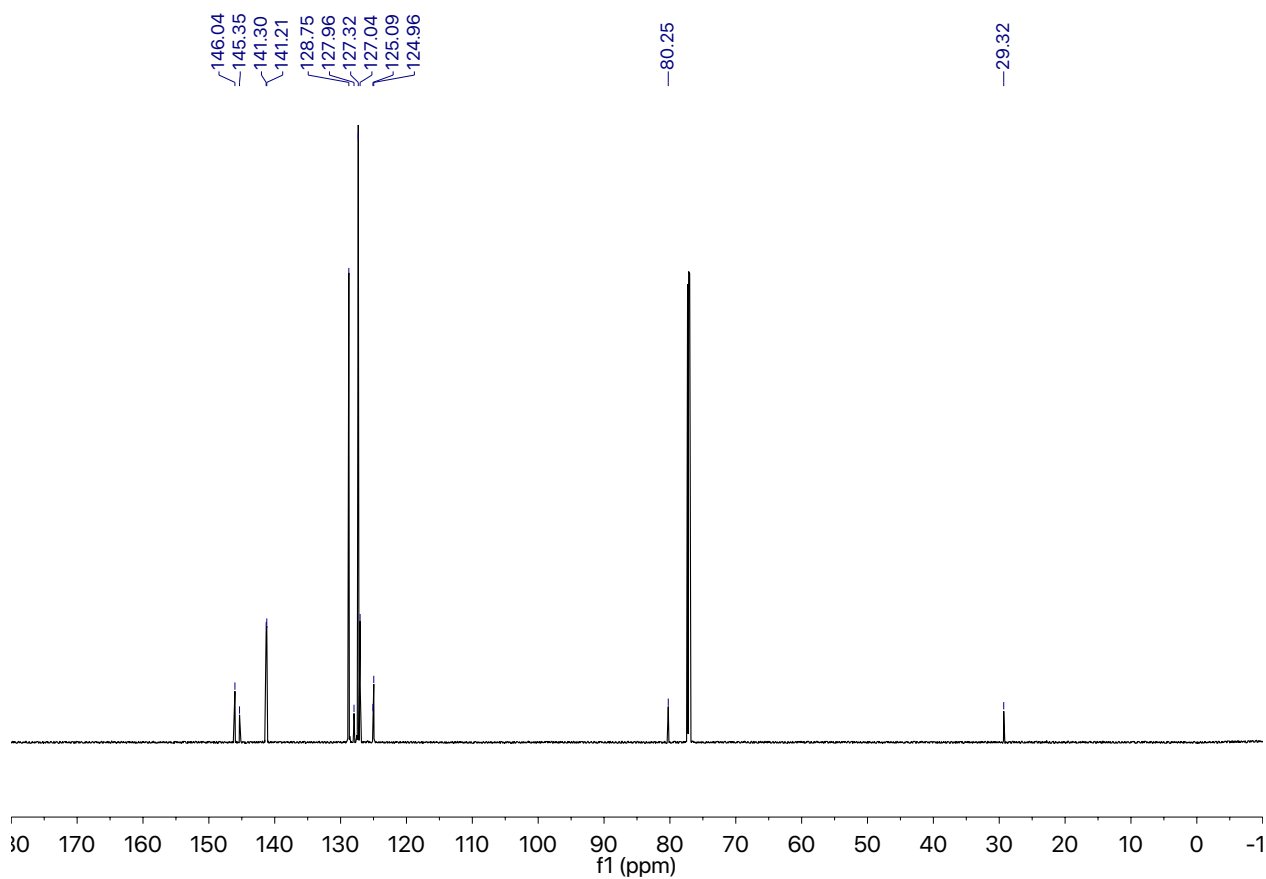
¹H NMR (500 MHz, C₆D₆) δ 7.98 (s, 4H), 7.77 (s, 8H), 7.73 (s, 4H), 7.72 (s, 4H), 7.66 (s, 4H), 7.59 (s, 8H), 7.33 (s, 2H), 7.05 (s, 2H), 6.98 (m, 4H), 2.37 (dd, *J* = 6.3, 4.9 Hz, 1H), 1.48 (m, 1H), 1.18 (m, 3H), 0.99 (t, *J* = 7.2 Hz, 3H), 0.66–0.49 (m, 5H); **¹³C NMR** (126 MHz, CDCl₃) δ 147.2 (2C, 4°), 145.5 (2C, 4°), 144.9 (2C, 4°), 141.9 (4C, 4°), 141.8 (4C, 4°), 139.0 (br, 8C, 4°), 132.6 (q, ²*J*_{C-F} = 33.4 Hz, 8C, 4°), 132.4 (q, ²*J*_{C-F} = 33.4 Hz, 8C, 4°), 129.7 (3°), 129.5 (4C, 3°), 129.4 (4C, 3°), 129.1 (3°), 126.8 (br s, 16C, 3°), 125.8–125.4 (overlapped peaks, 6C, 3°), 123.1 (q, ¹*J*_{C-F} = 274 Hz, 8C, 4°), 123.0 (q, ¹*J*_{C-F} = 274 Hz, 8C, 4°), 122.0 (br s, 8C, 3°), 82.1 (2C, 4°), 46.4 (1C, NCHR₂), 31.3 (1C, 3°), 29.4 (1C, 3°), 27.0 (1C, 2°), 24.0 (1C, 2°), 14.2 (1C, 1°), 12.4 (1C, 1°); **¹⁹F NMR** (471 MHz, CDCl₃) δ –62.97, –63.04; **HRMS** (*m/z*): [M+TFA–H][–] calcd. for C₁₀₃H₅₃F₄₈N·CF₃CO₂, 2328.3267; found, 2328.3274.

II. Supplementary Figures 1-54

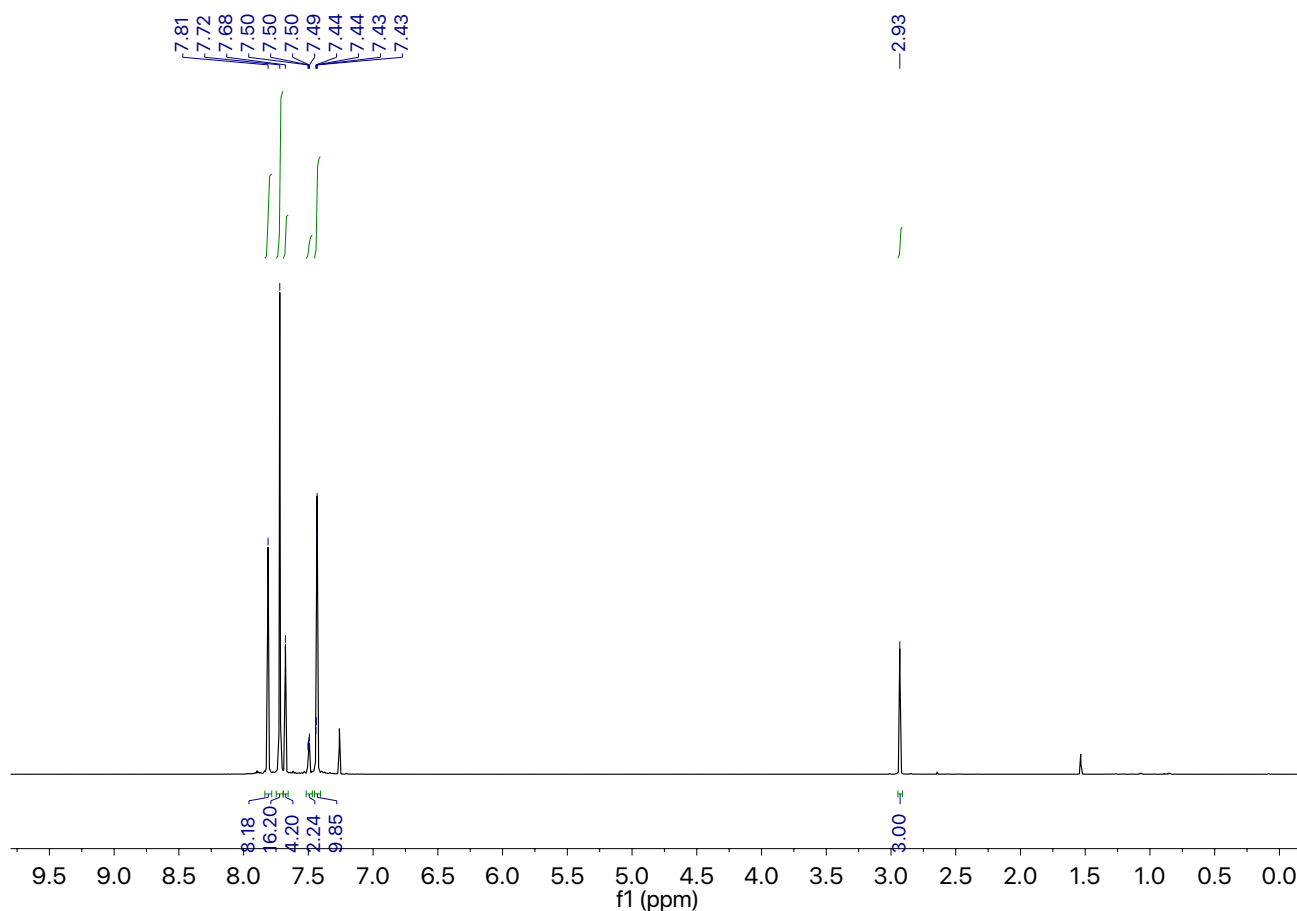




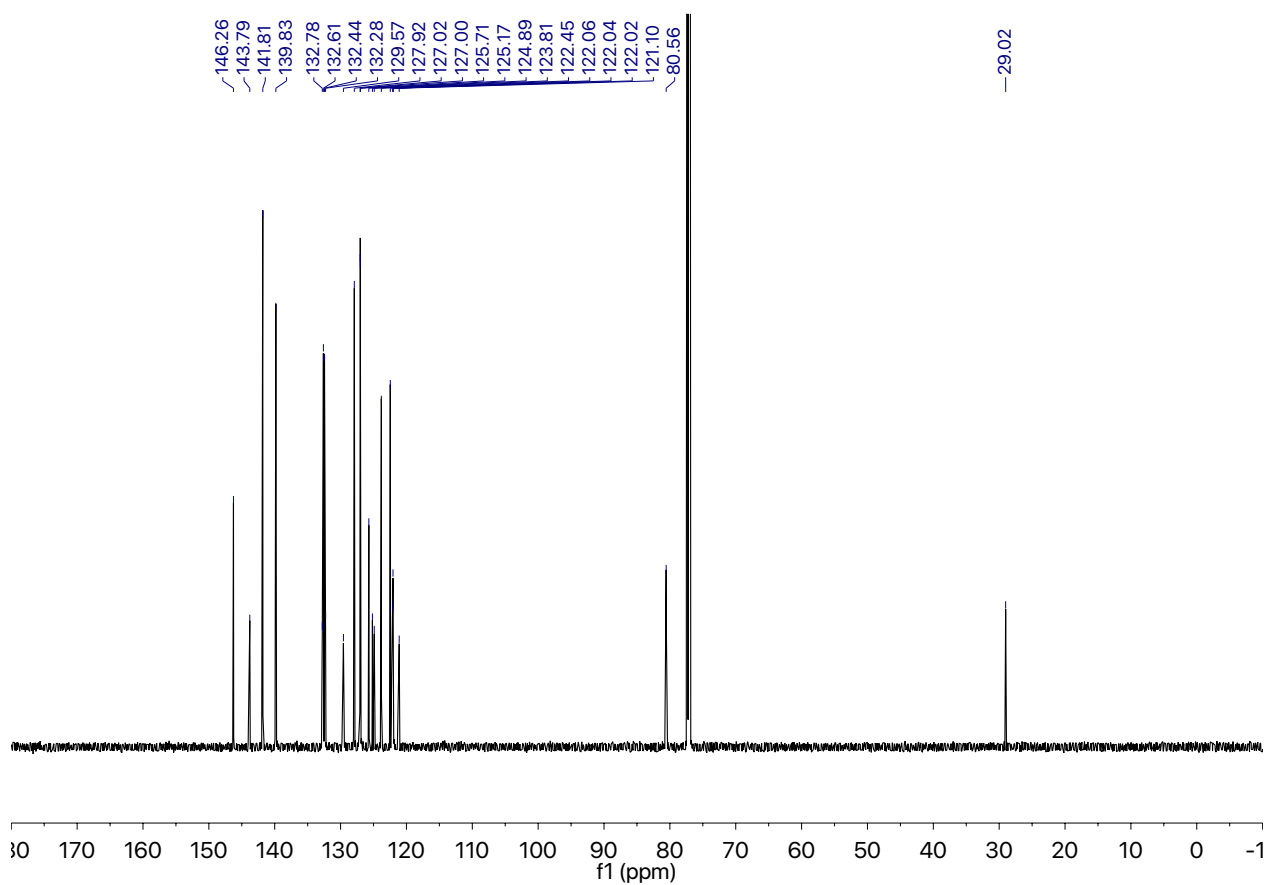
Supplementary Figure 3. ¹H NMR spectrum (800 MHz, CDCl₃) of **1b**.



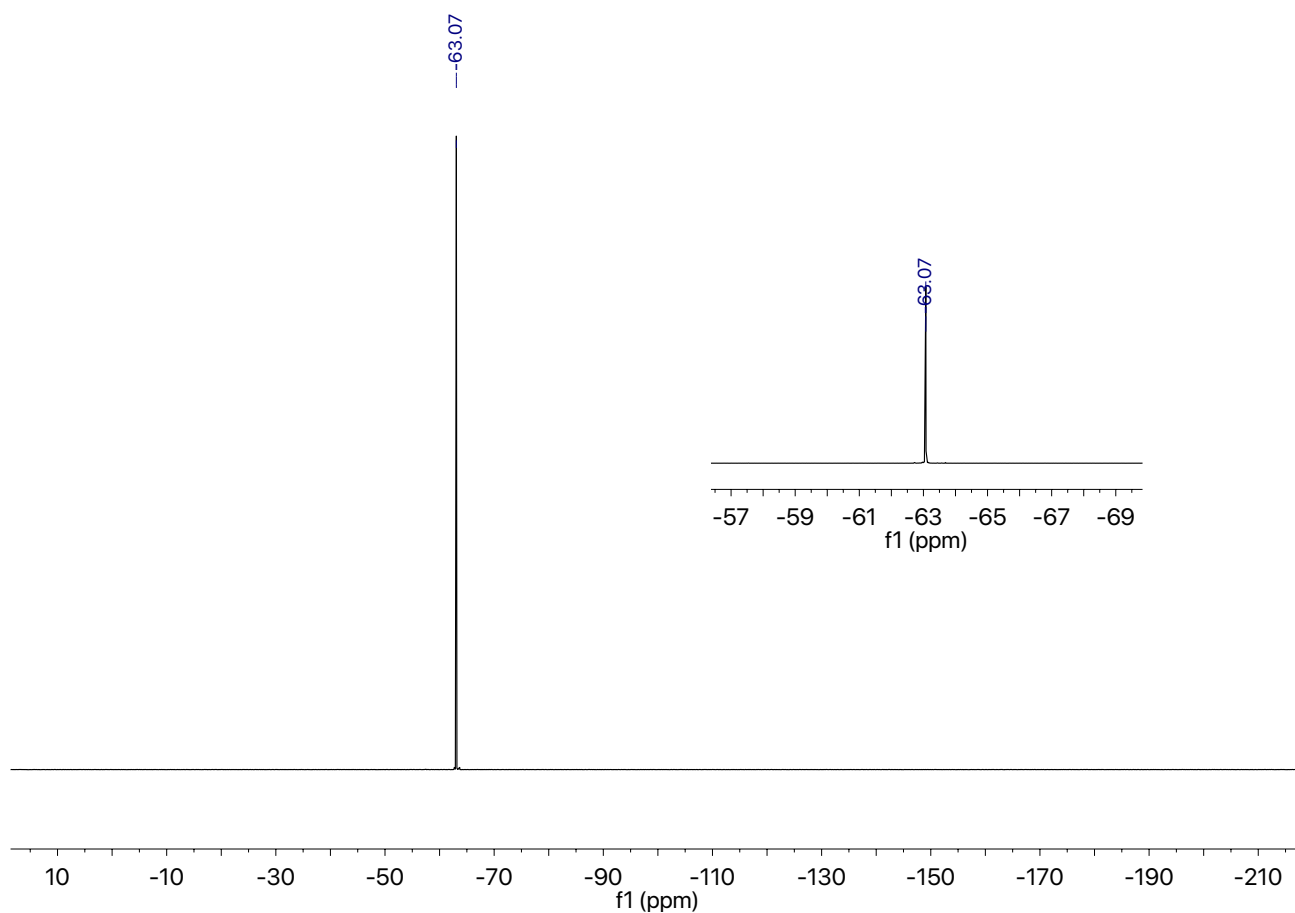
Supplementary Figure 4. ¹³C{¹H} NMR spectrum (201 MHz, CDCl₃) of **1b**.



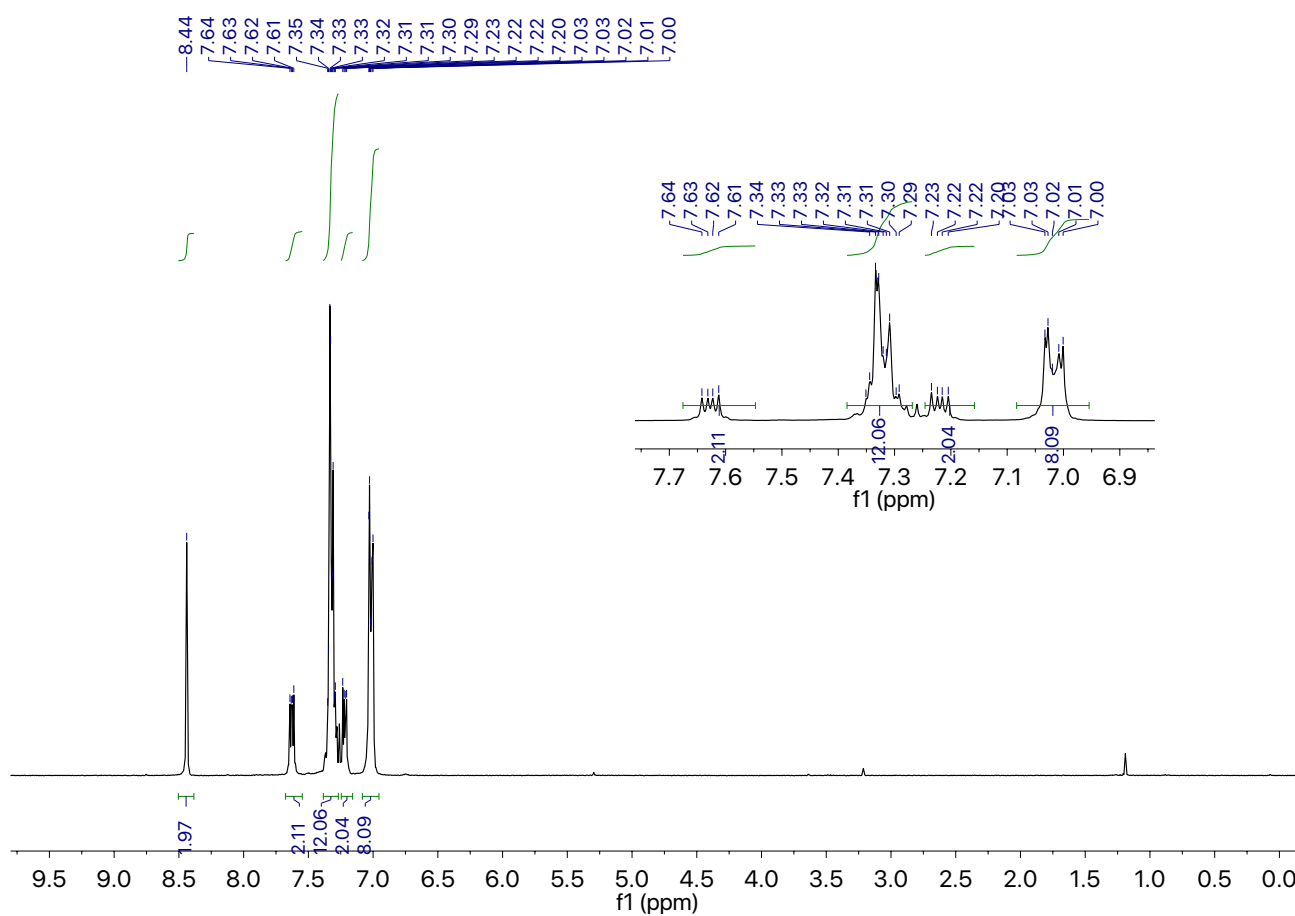
Supplementary Figure 5. ¹H NMR spectrum (800 MHz, CDCl₃) of **1c**.



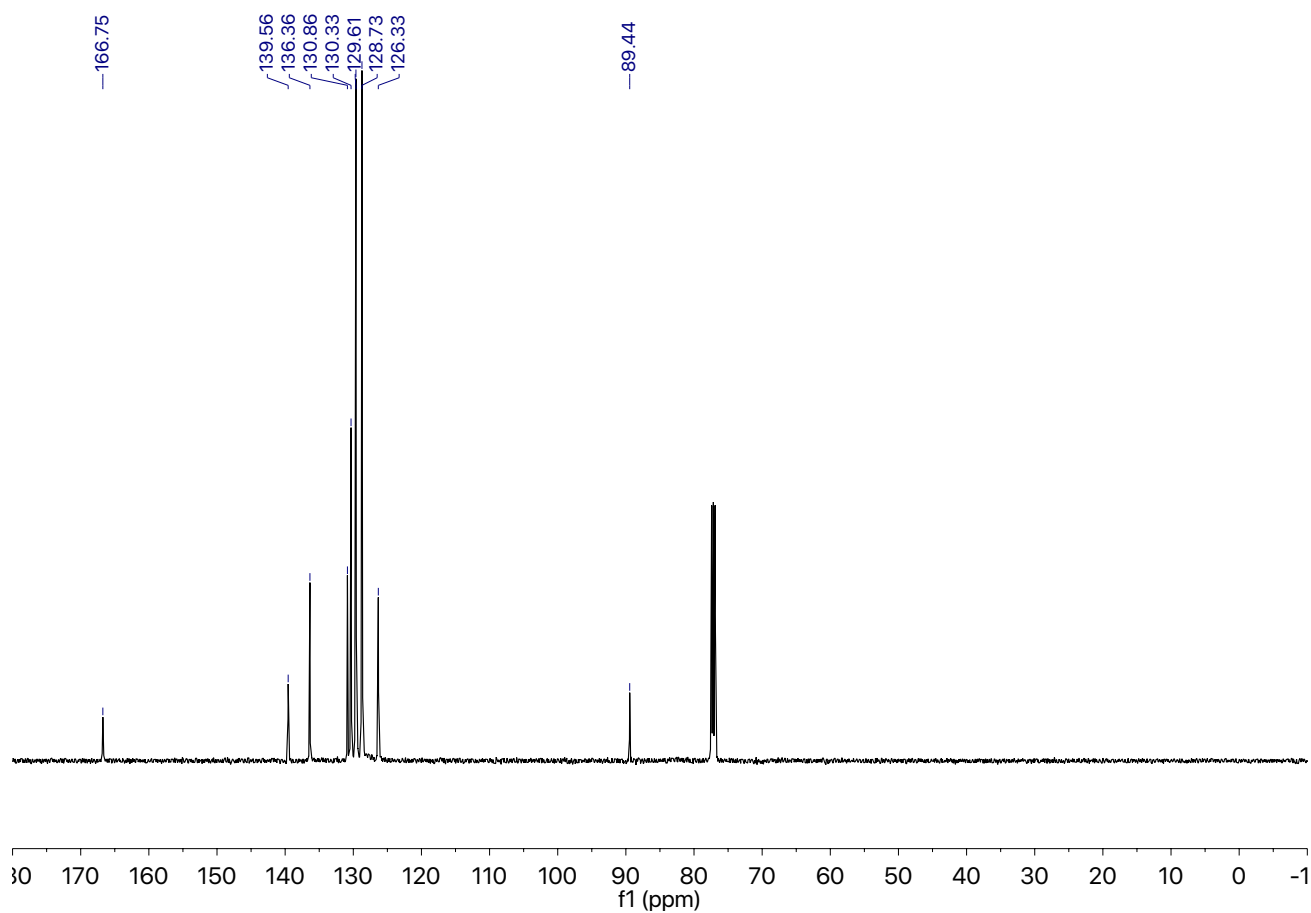
Supplementary Figure 6. ¹³C{¹H} NMR spectrum (201 MHz, CDCl₃) of **1c**.



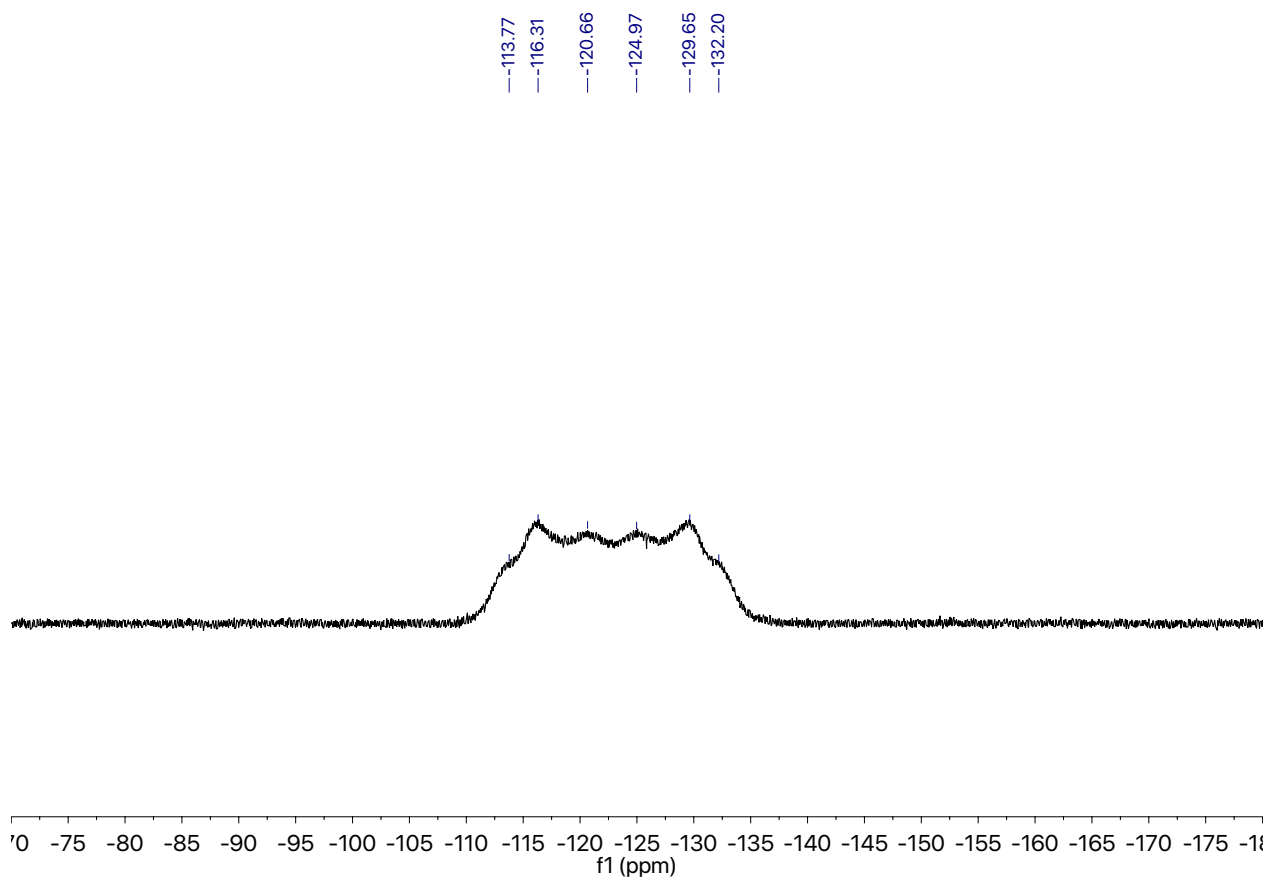
Supplementary Figure 7. ^{19}F NMR spectrum (282 MHz, CDCl_3) of **1c**.



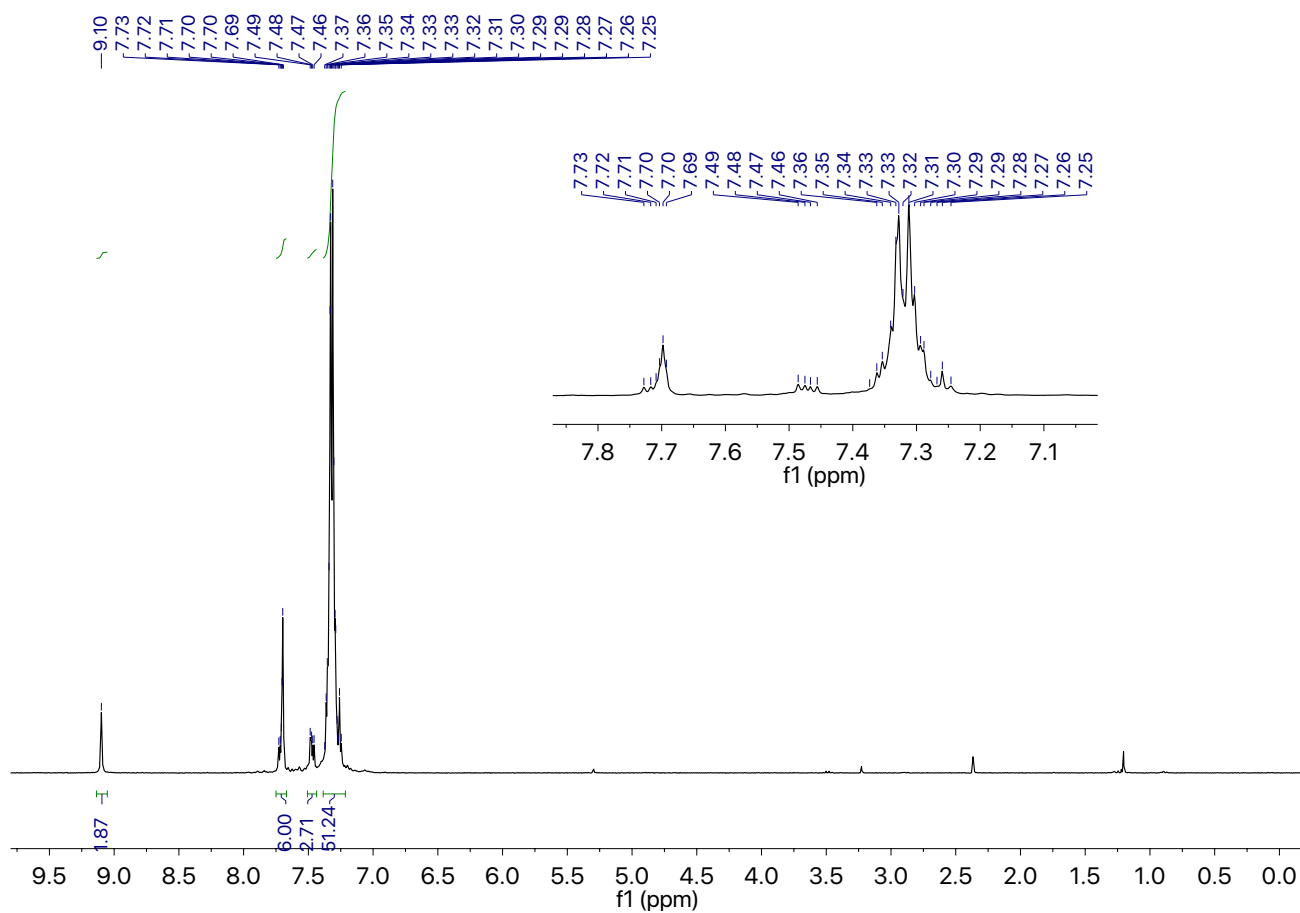
Supplementary Figure 8. ^1H NMR spectrum (300 MHz, CDCl_3) of **2a**.



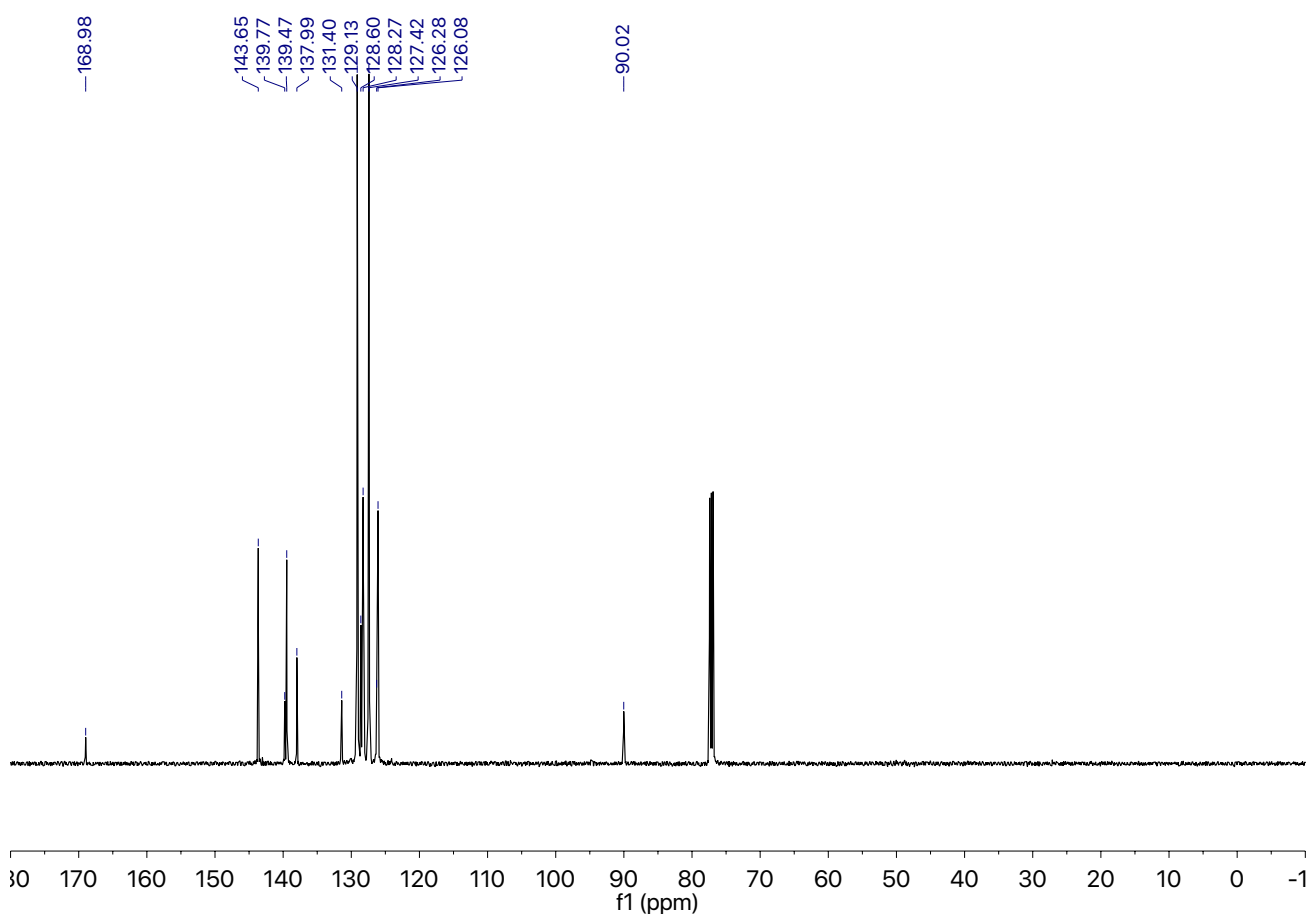
Supplementary Figure 9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **2a**.



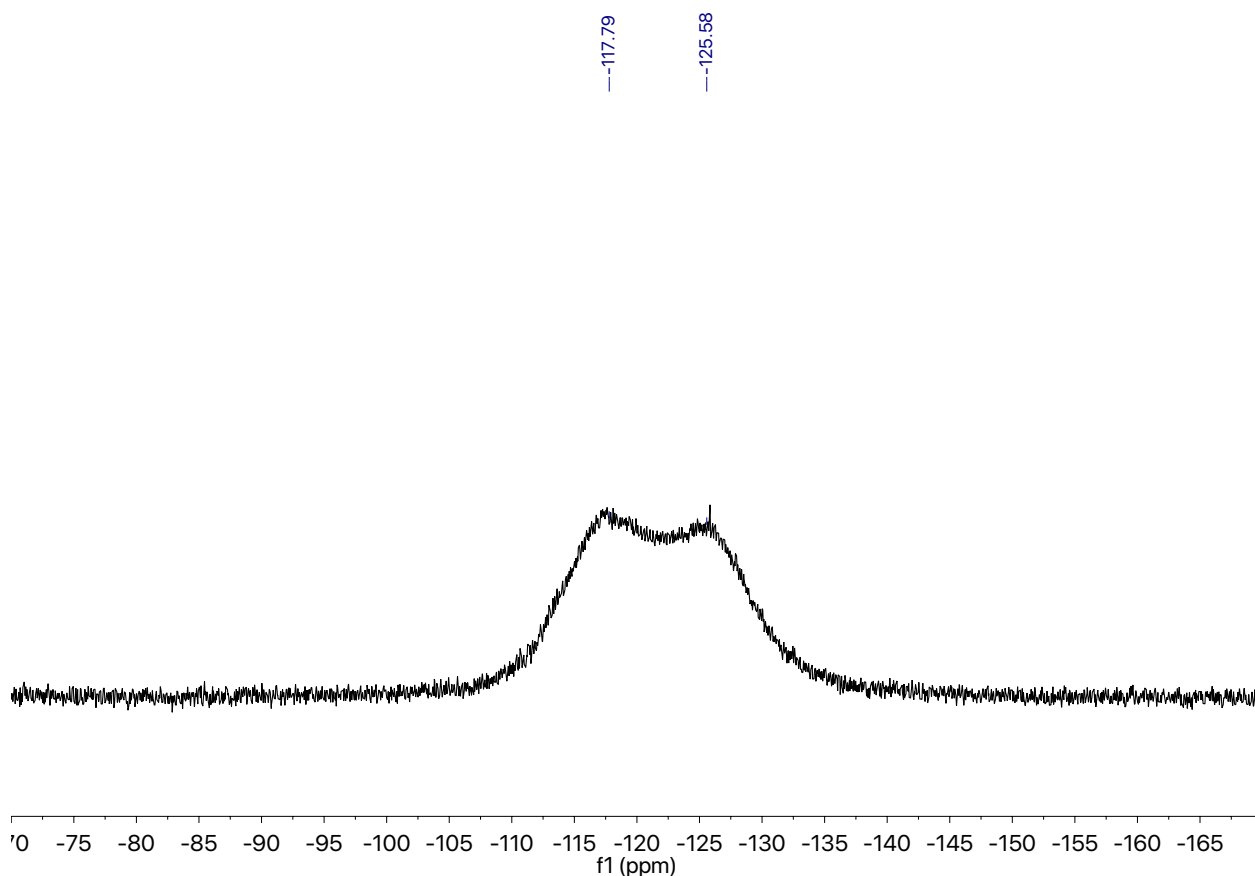
Supplementary Figure 10. ^{19}F NMR spectrum (471 MHz, CDCl_3) of **2a**.



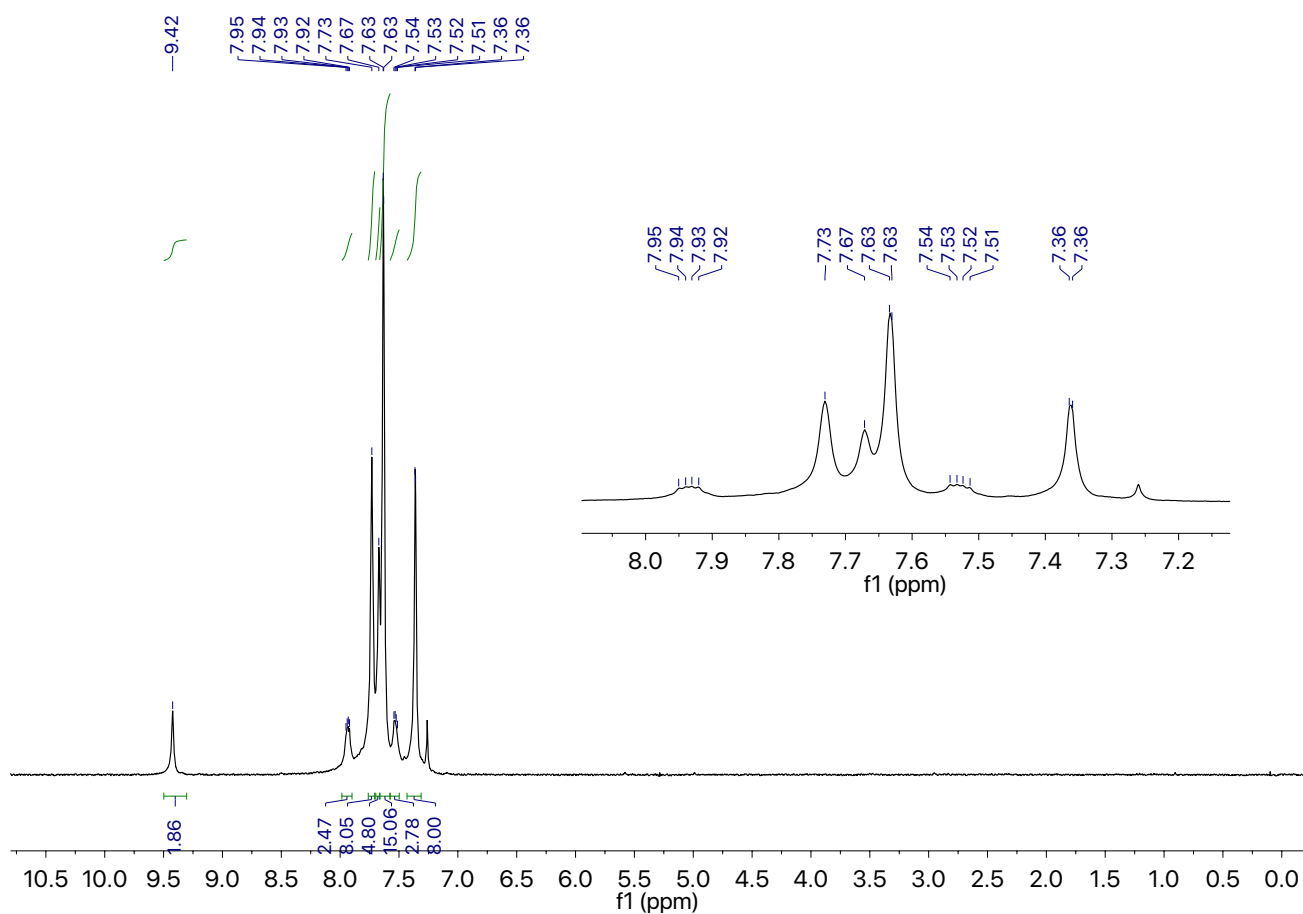
Supplementary Figure 11. ¹H NMR spectrum (300 MHz, CDCl₃) of **2b**.



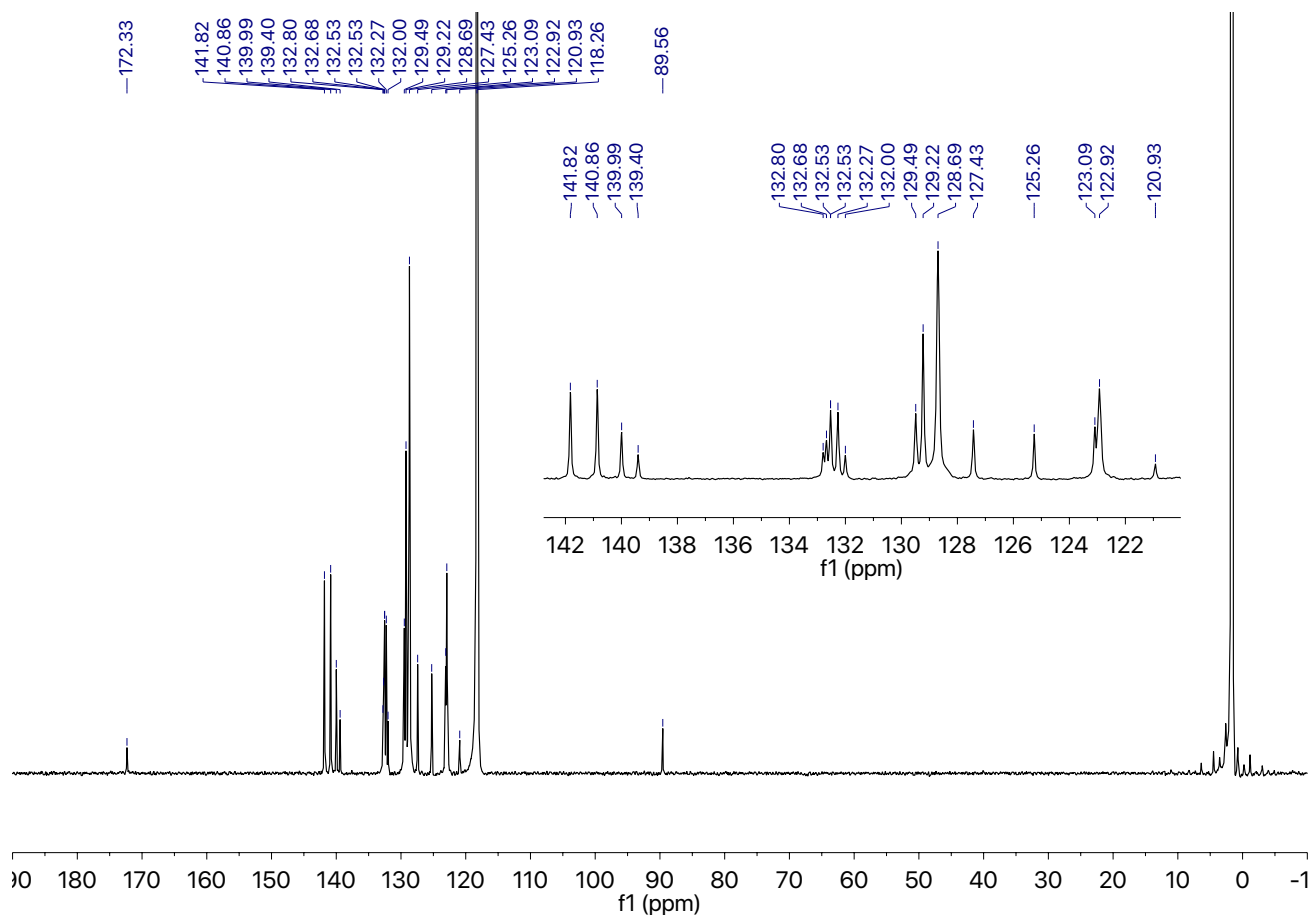
Supplementary Figure 12. ¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of **2b**.



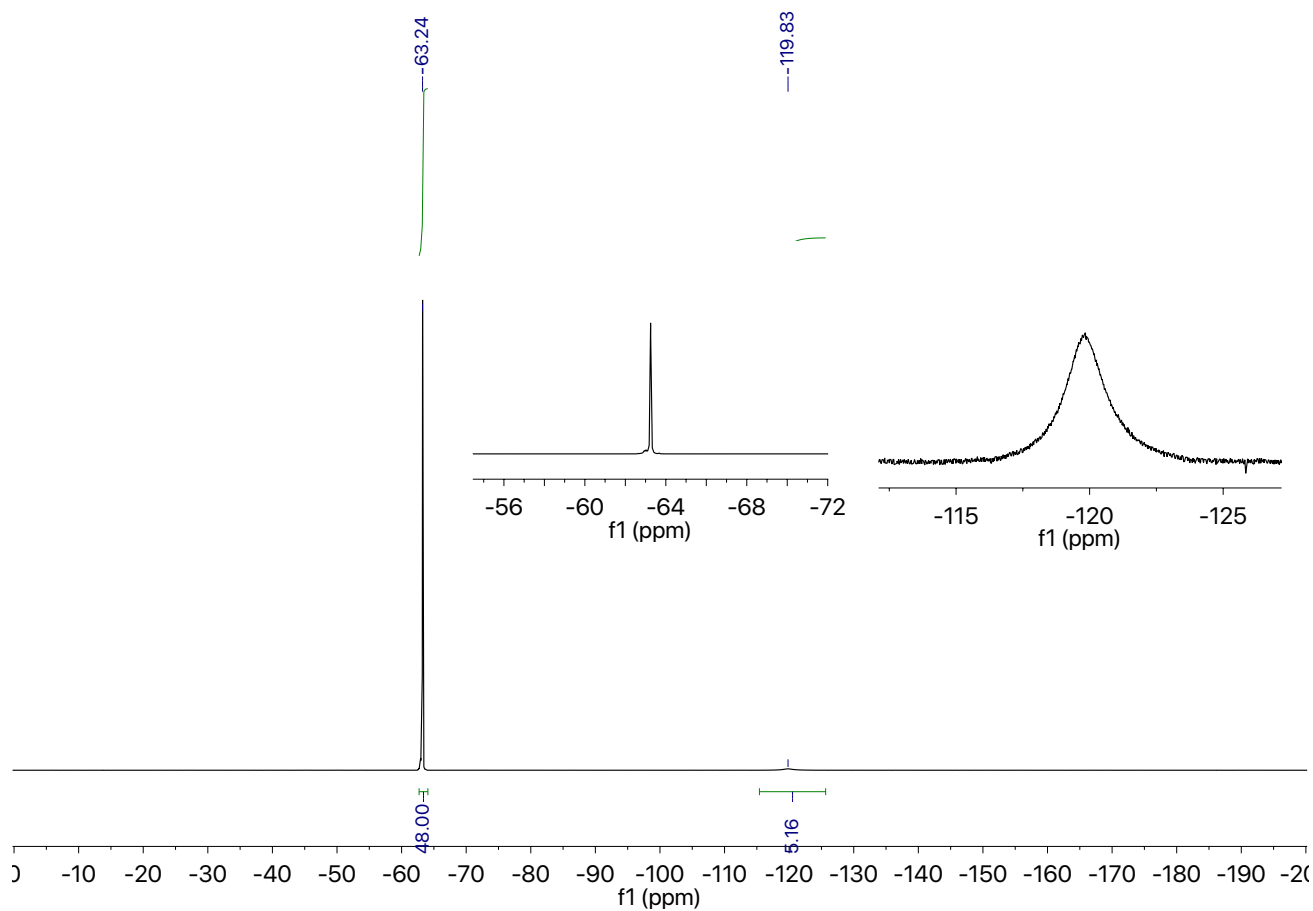
Supplementary Figure 13. ^{19}F NMR spectrum (471 MHz, CDCl_3) of **2b**.



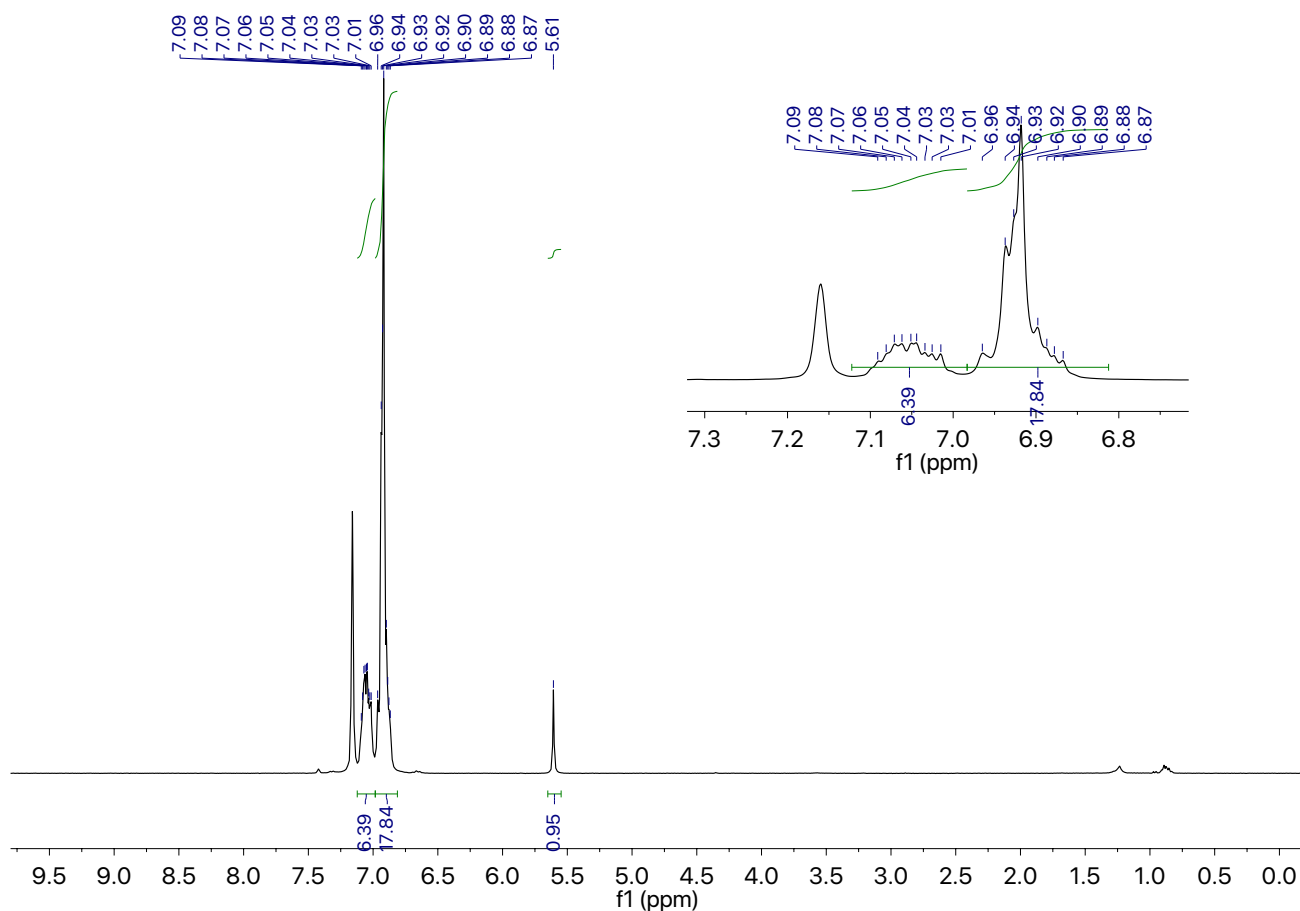
Supplementary Figure 14. ^1H NMR spectrum (300 MHz, CDCl_3) of **2c**.



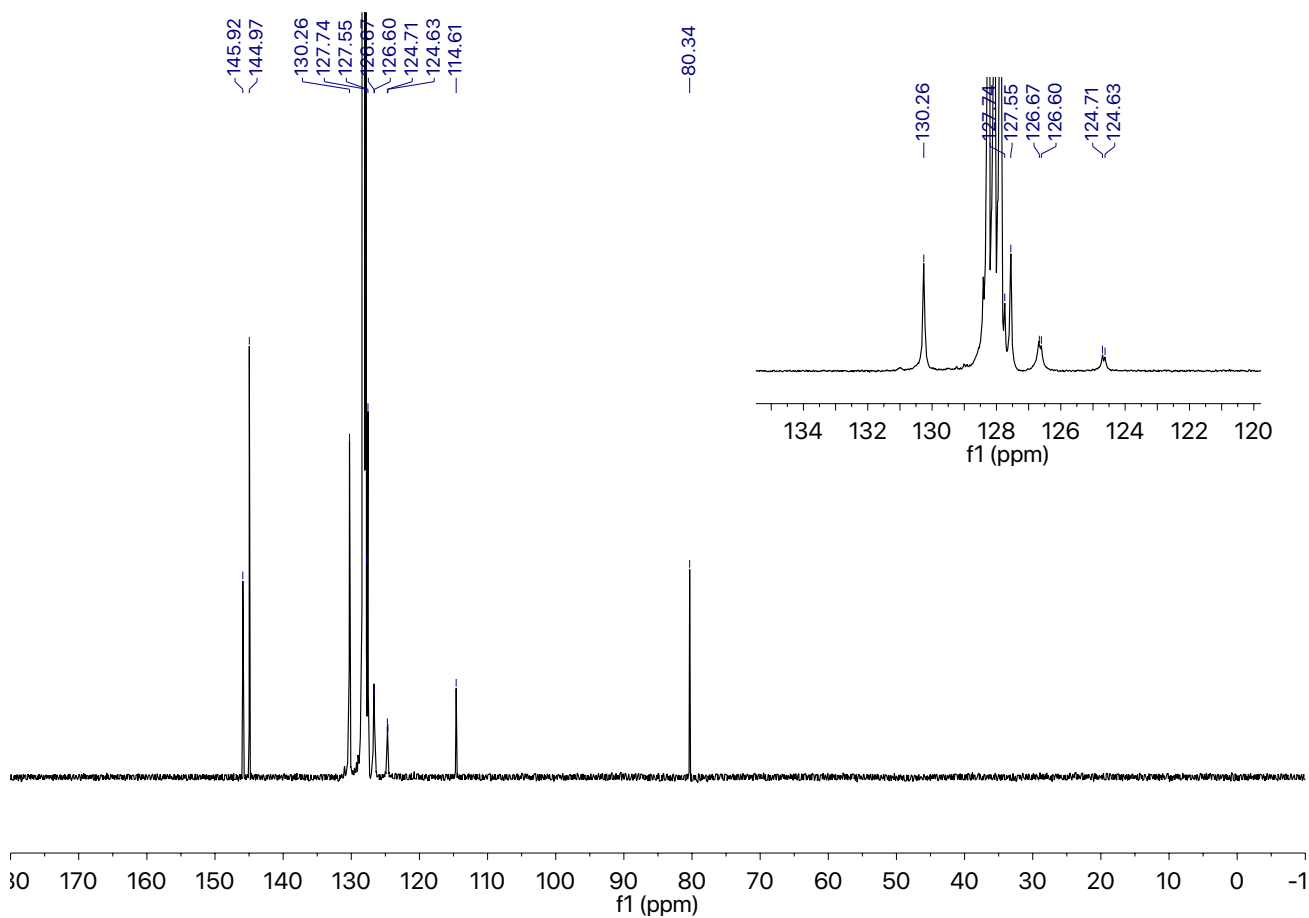
Supplementary Figure 15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (201 MHz, CH_3CN) of **2c**



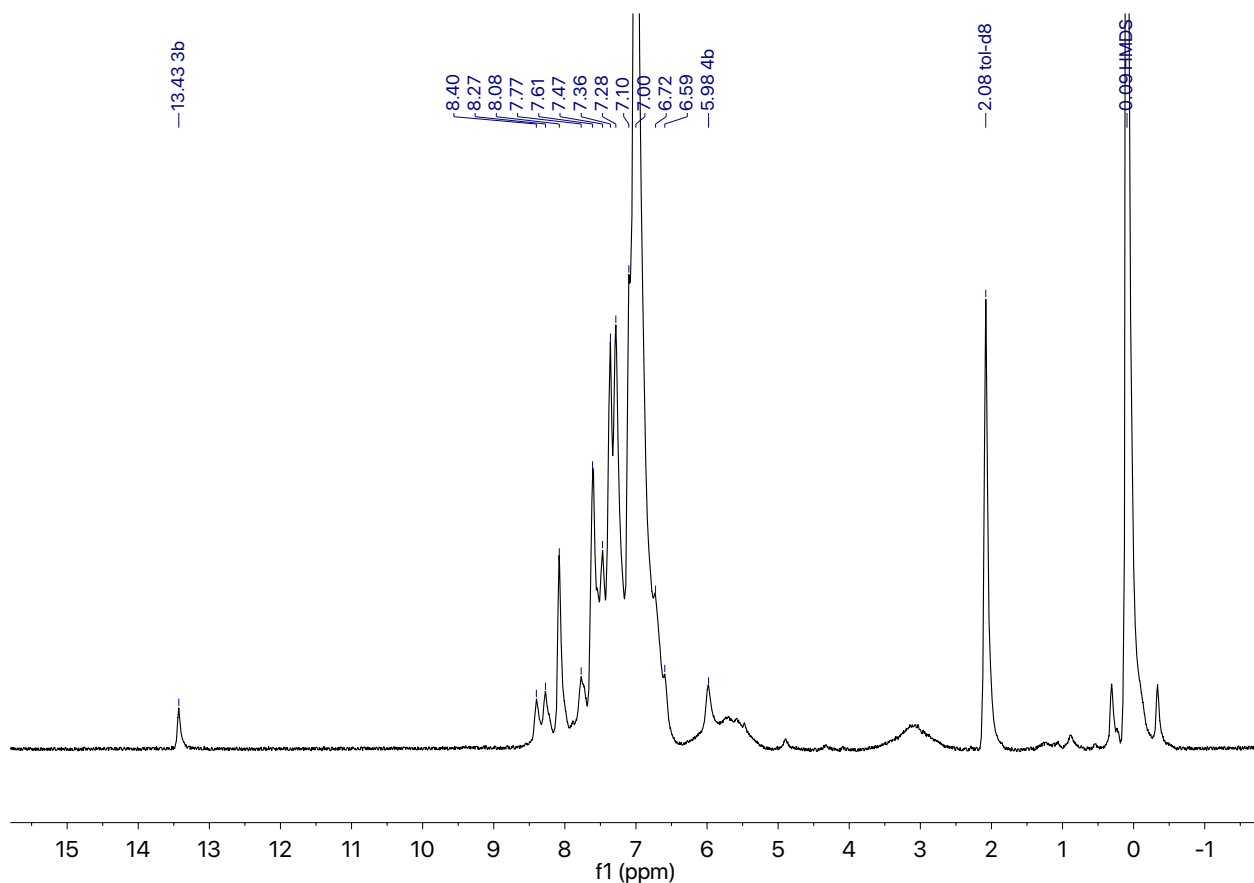
Supplementary Figure 16. ^{19}F NMR spectrum (471 MHz, CDCl_3) of **2c**.



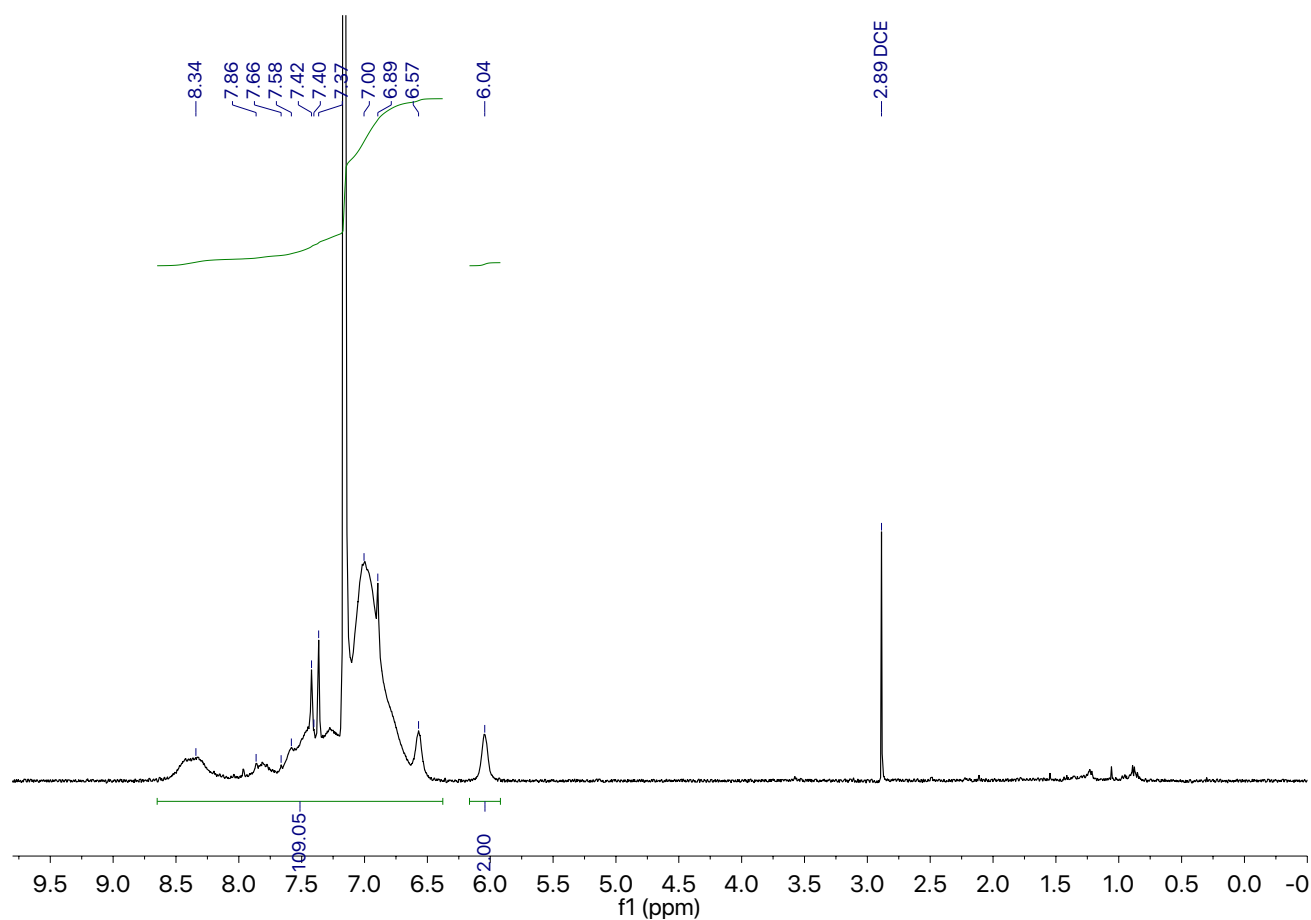
Supplementary Figure 17. ¹H NMR spectrum (300 MHz, C₆D₆) of **4a**.



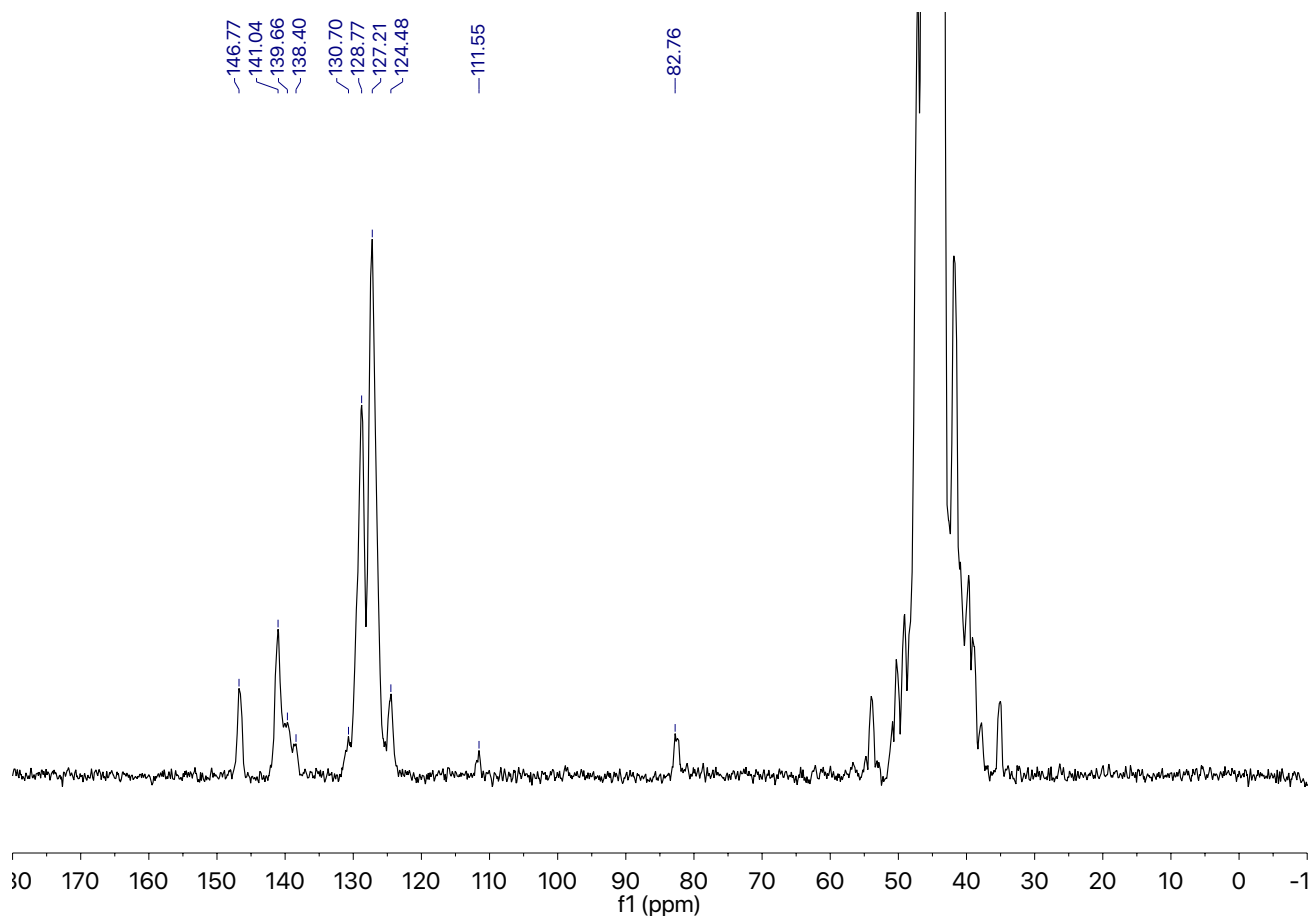
Supplementary Figure 18. ¹³C{¹H} NMR spectrum (126 MHz, C₆D₆) of **4a**.



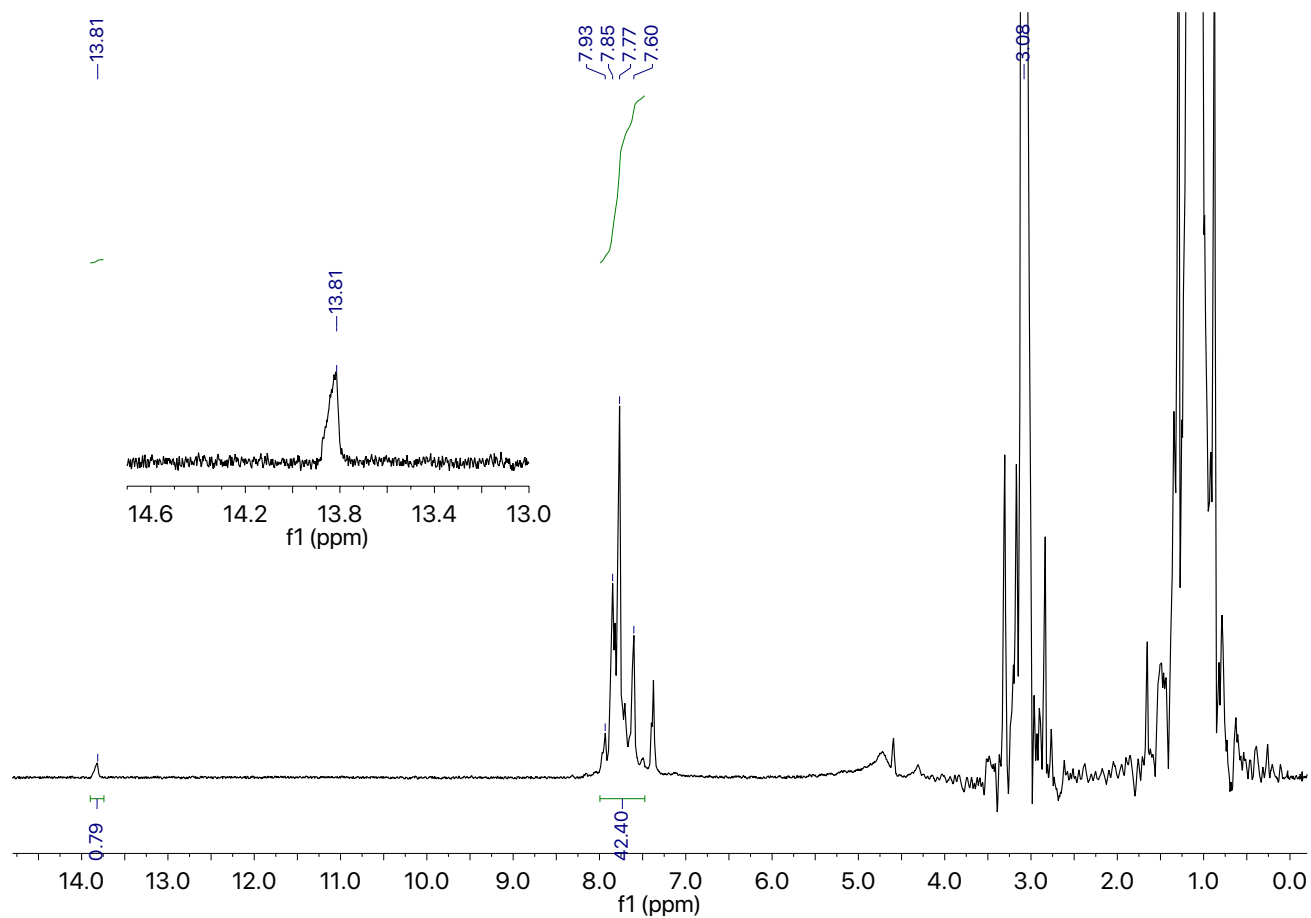
Supplementary Figure 19. ^1H NMR spectrum (300 MHz, toluene- d_8) of crude mixture containing **3b** and **4b**.



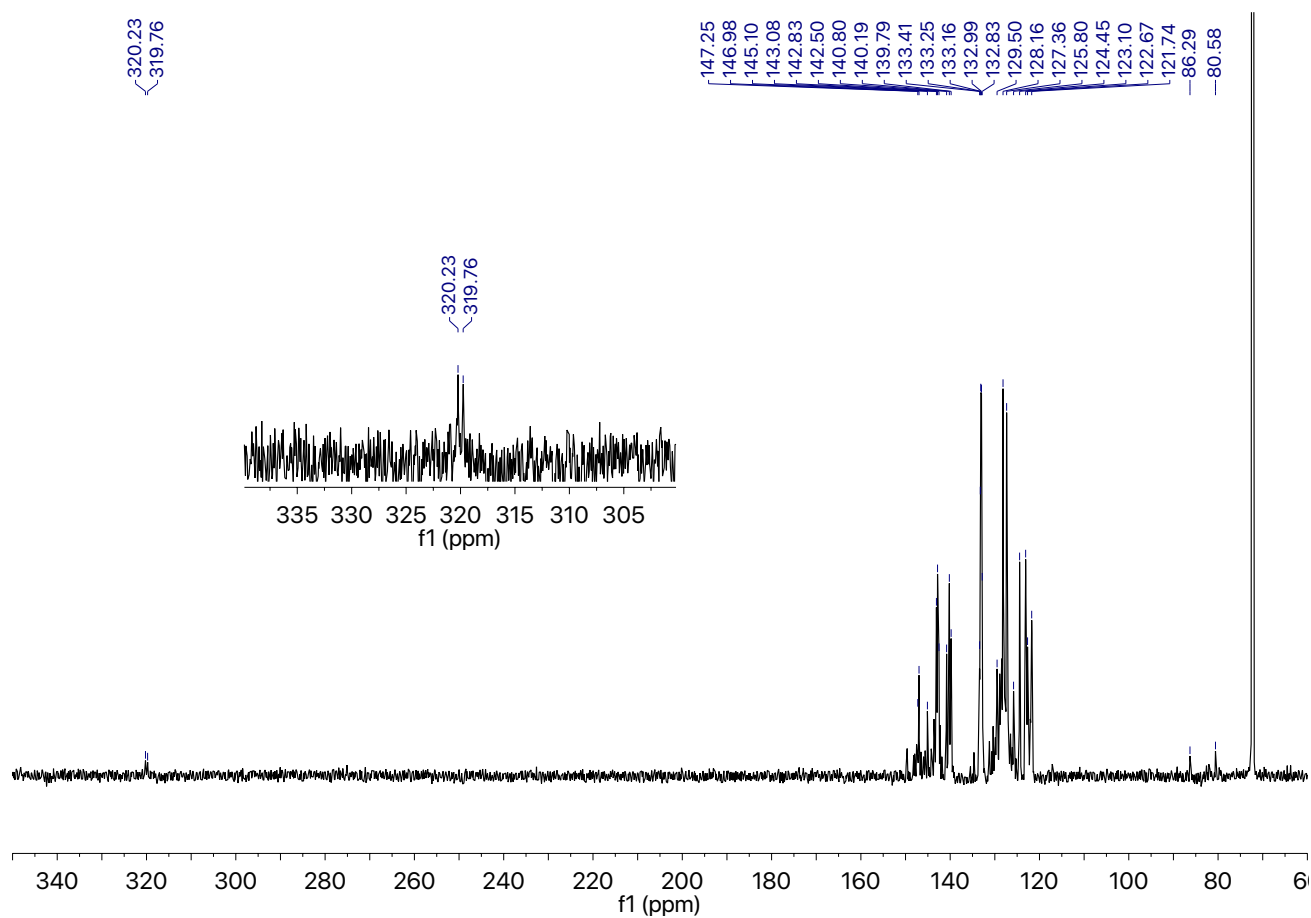
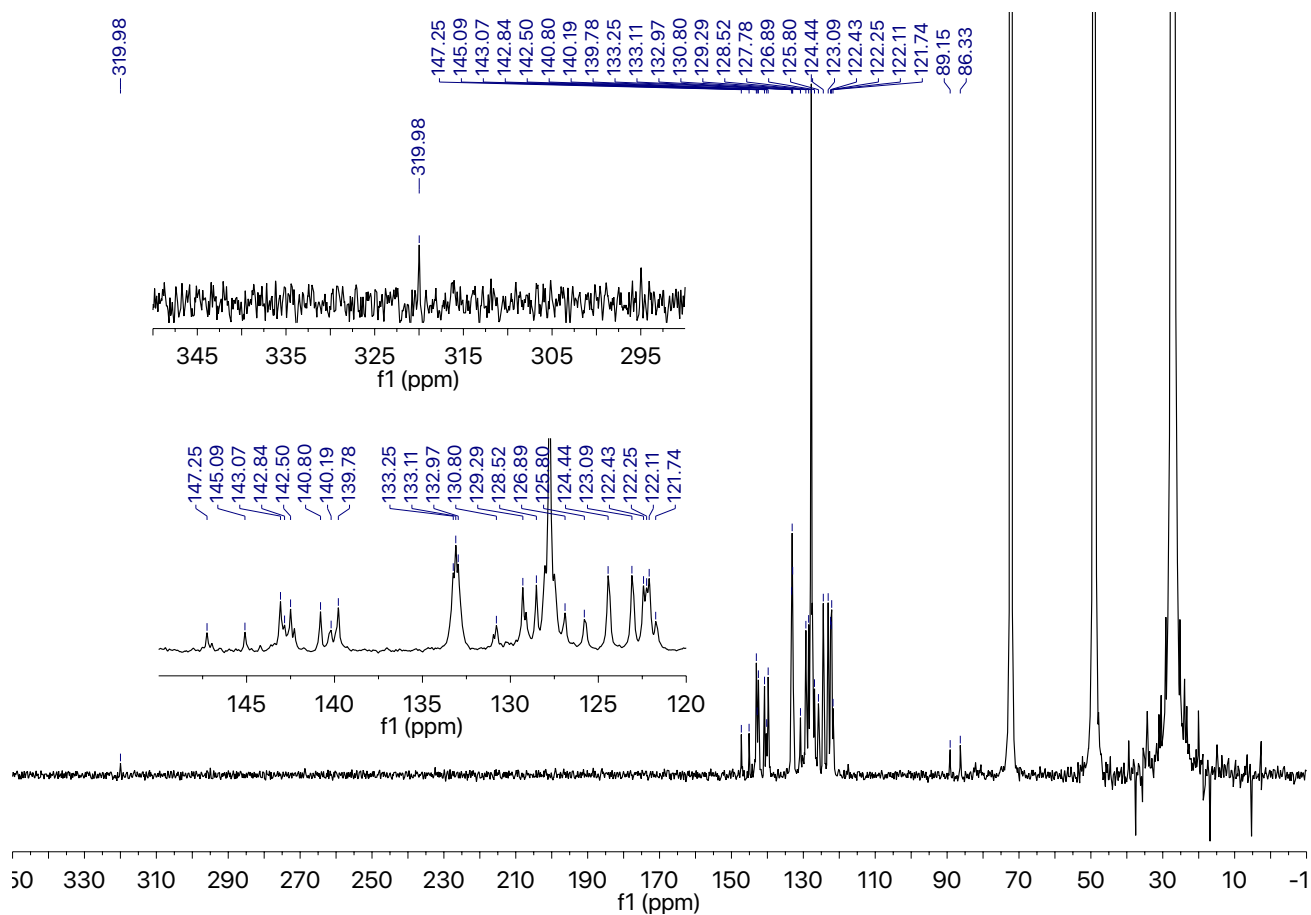
Supplementary Figure 20. ^1H NMR spectrum (300 MHz, C_6D_6) of **4b**.

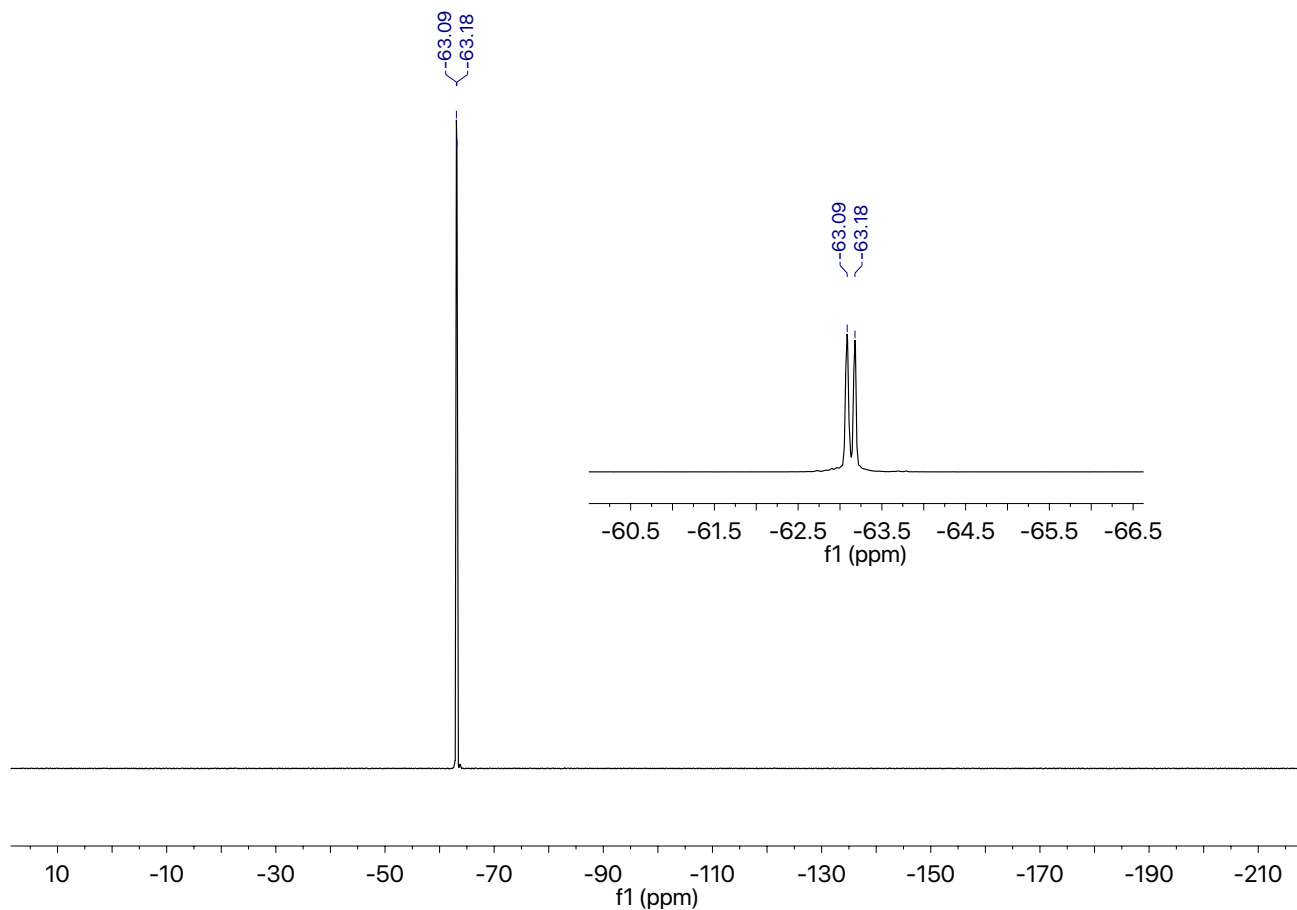


Supplementary Figure 21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, 1,2-dichloroethane) of **4b**.

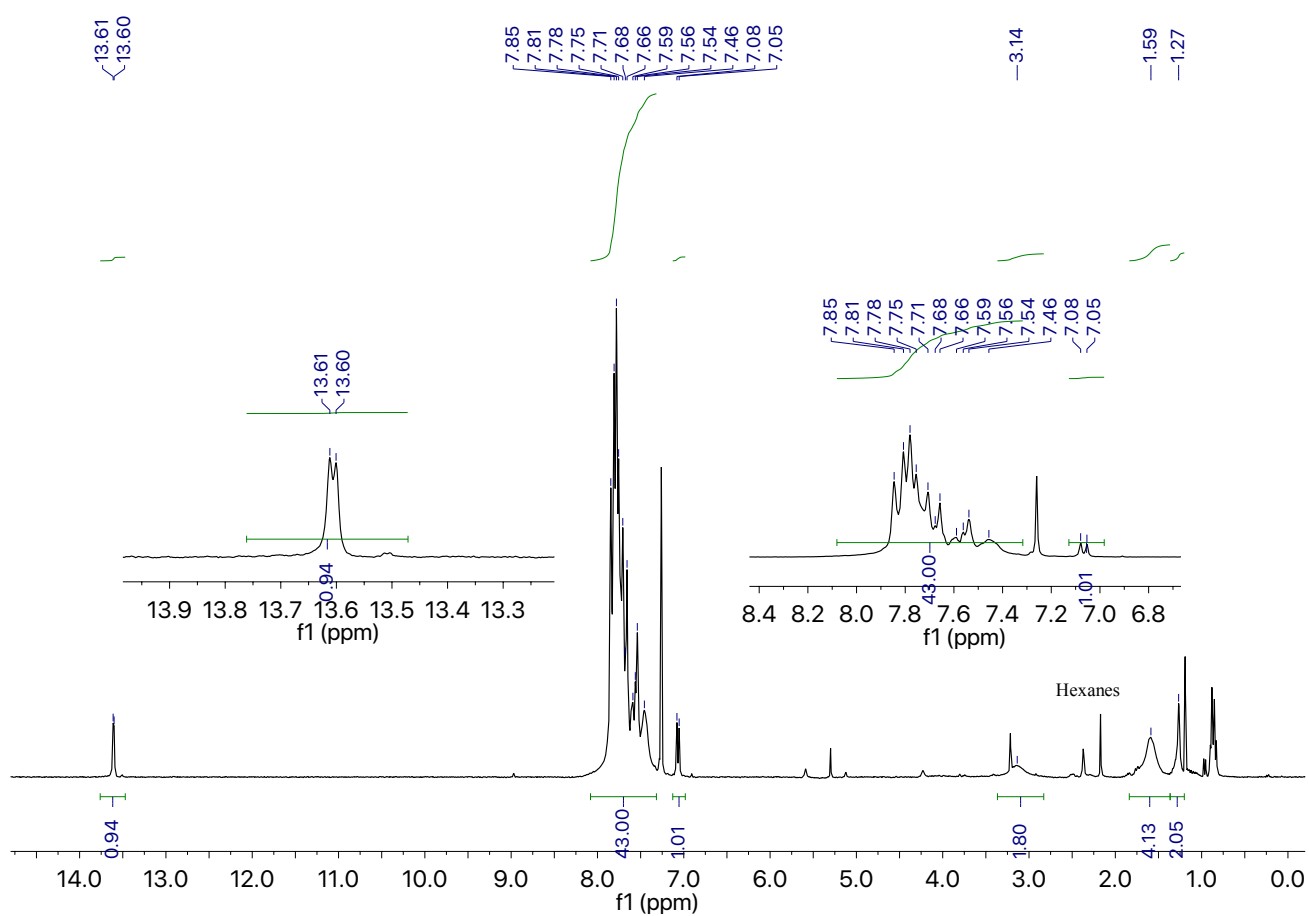


Supplementary Figure 22. ^1H NMR spectrum (300 MHz, MTBE + C_6D_6) of **3c**.

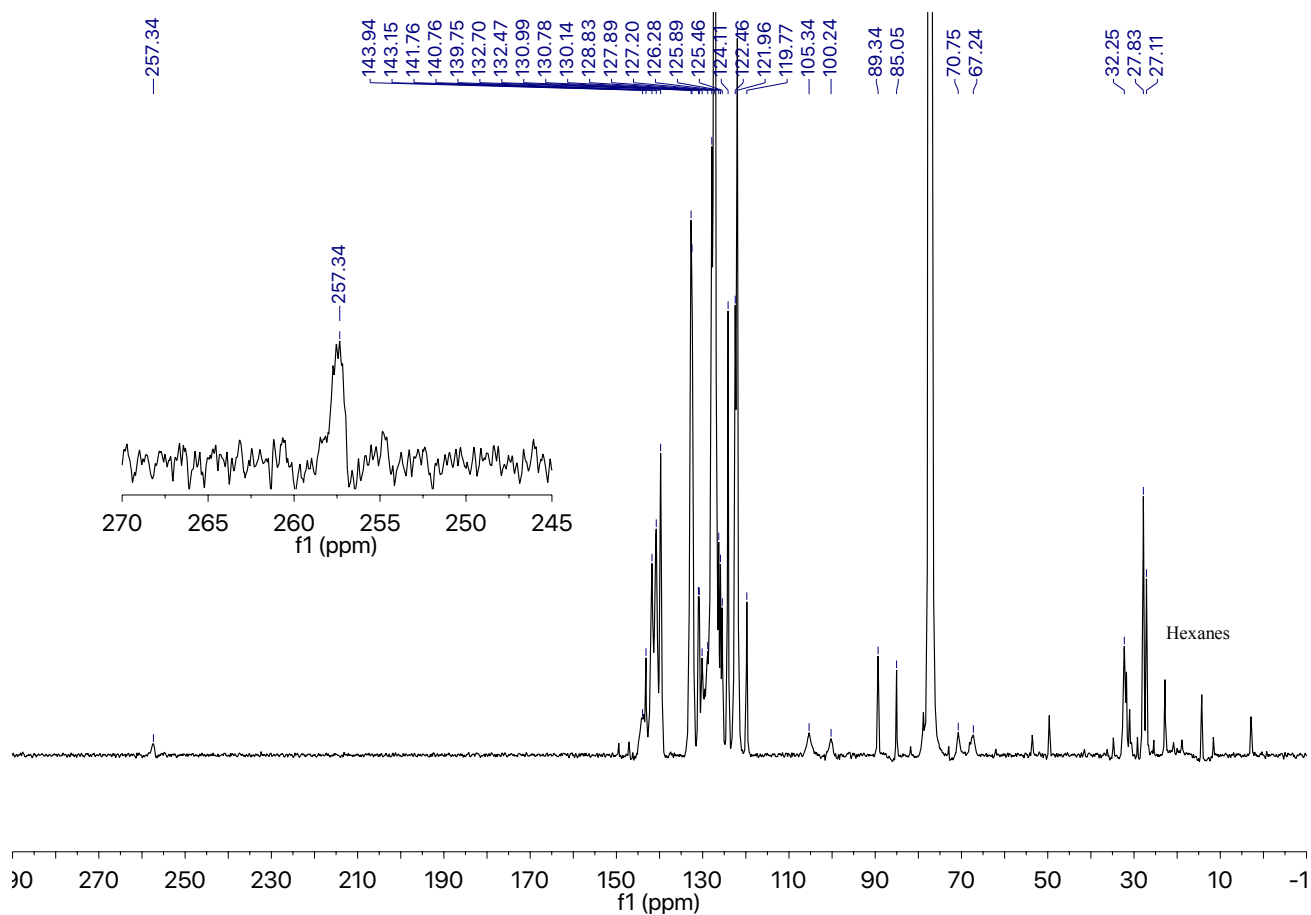




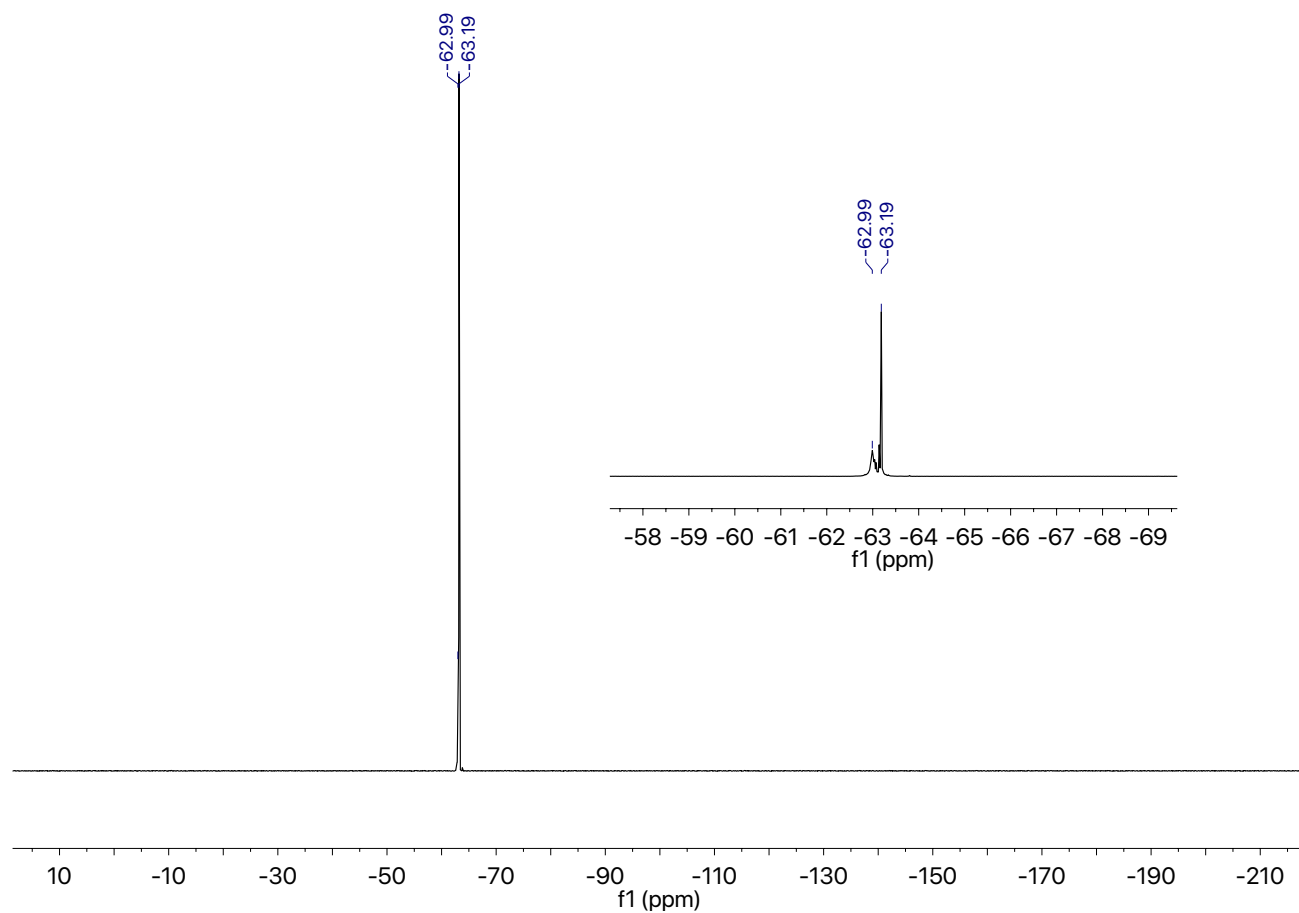
Supplementary Figure 25. ^{19}F NMR spectrum (282 MHz, MTBE + C_6D_6) of **3c**.



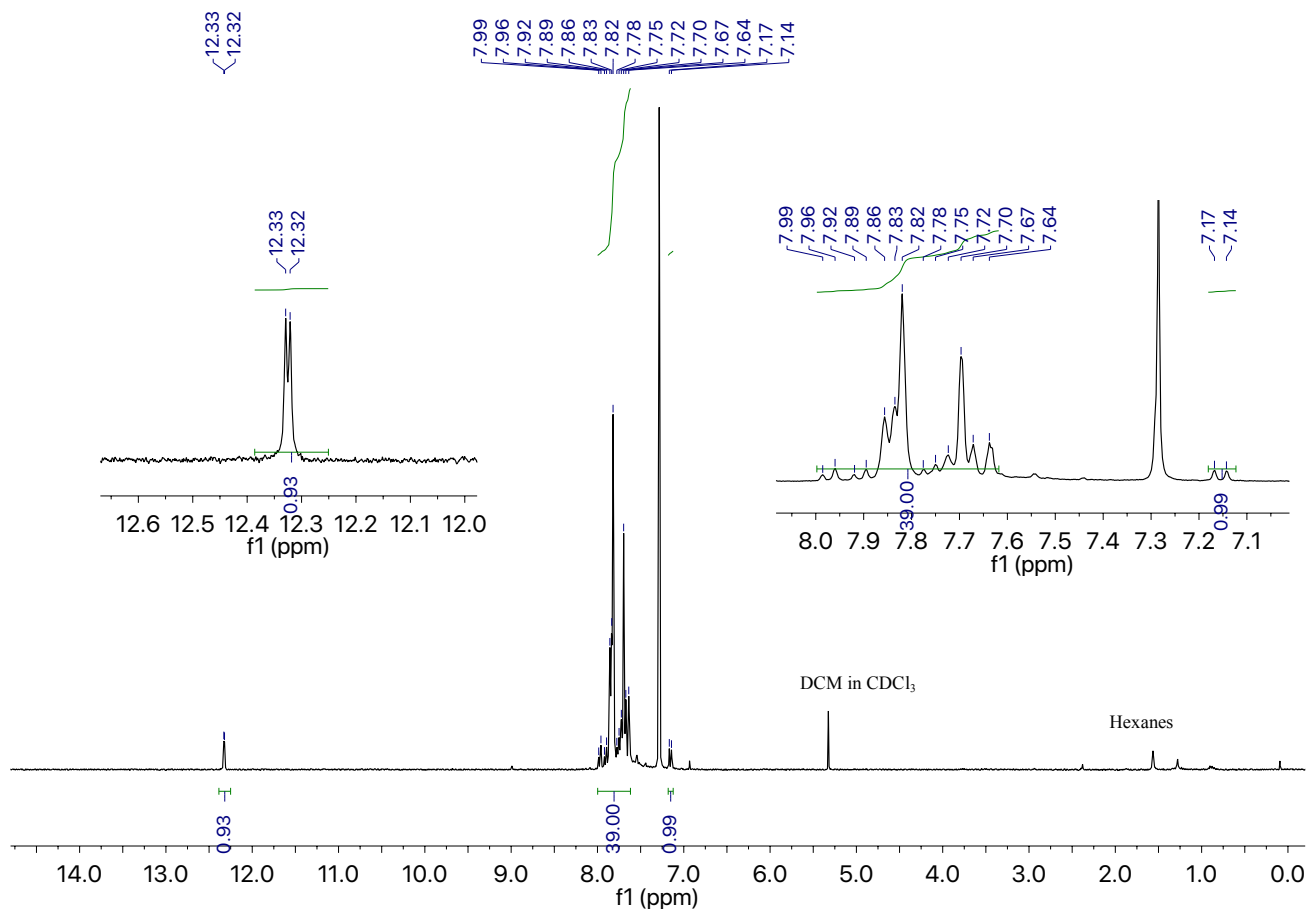
Supplementary Figure 26. ^1H NMR spectrum (300 MHz, CDCl_3) of **(3c)Rh(cod)Cl**.



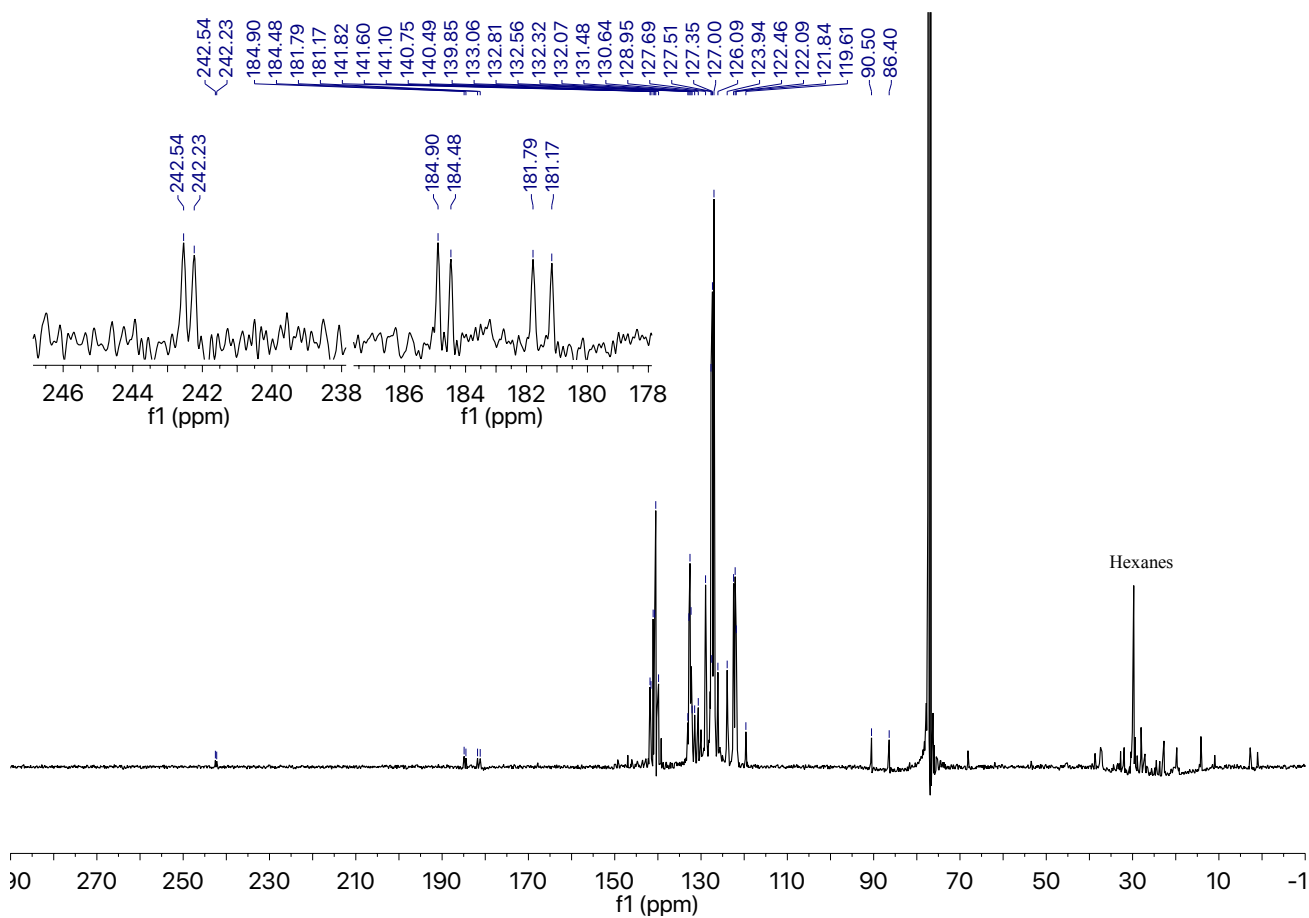
Supplementary Figure 27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **(3c)Rh(cod)Cl**.



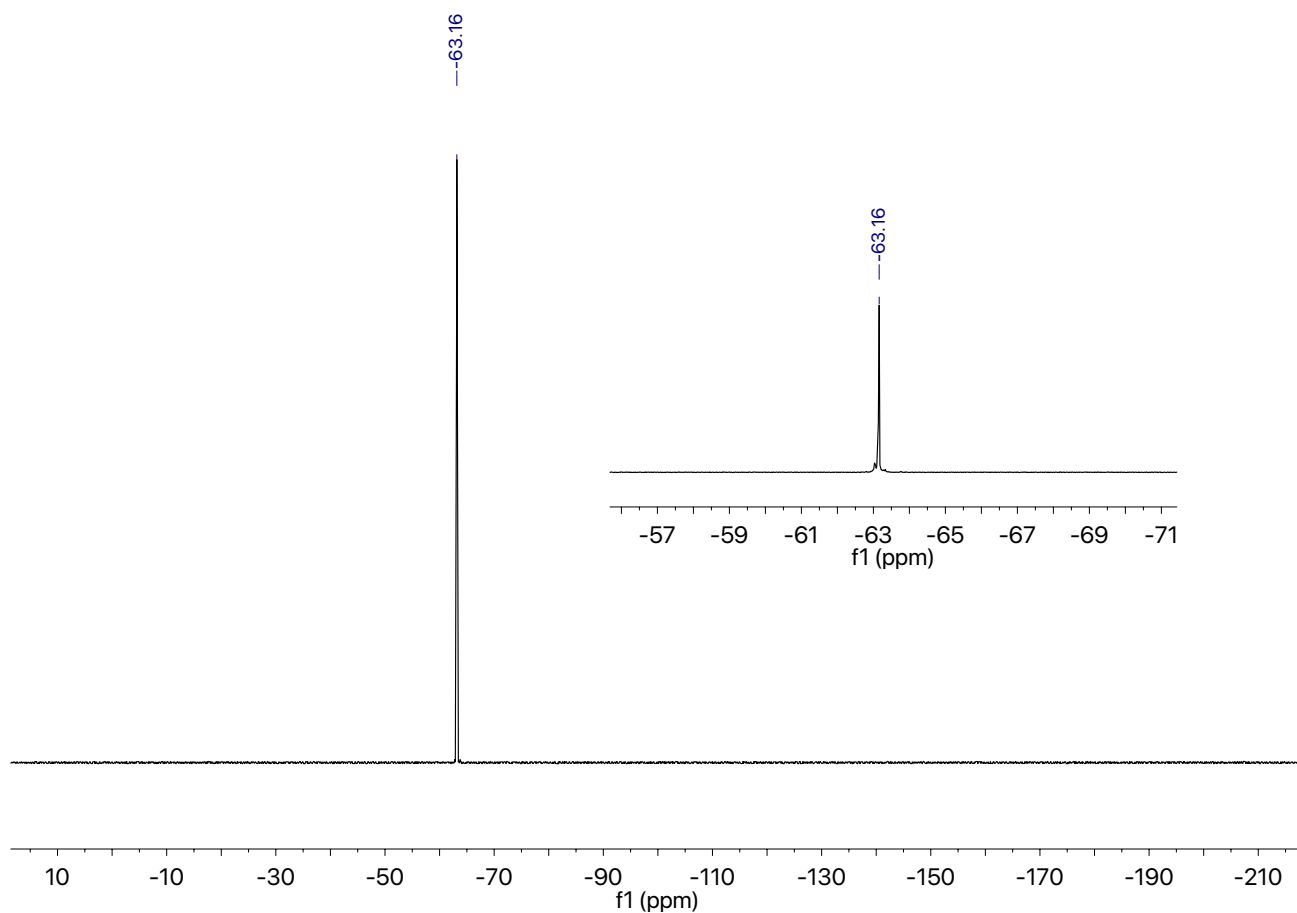
Supplementary Figure 28. ^{19}F NMR spectrum (282 MHz, CDCl_3) of **(3c)Rh(cod)Cl**.



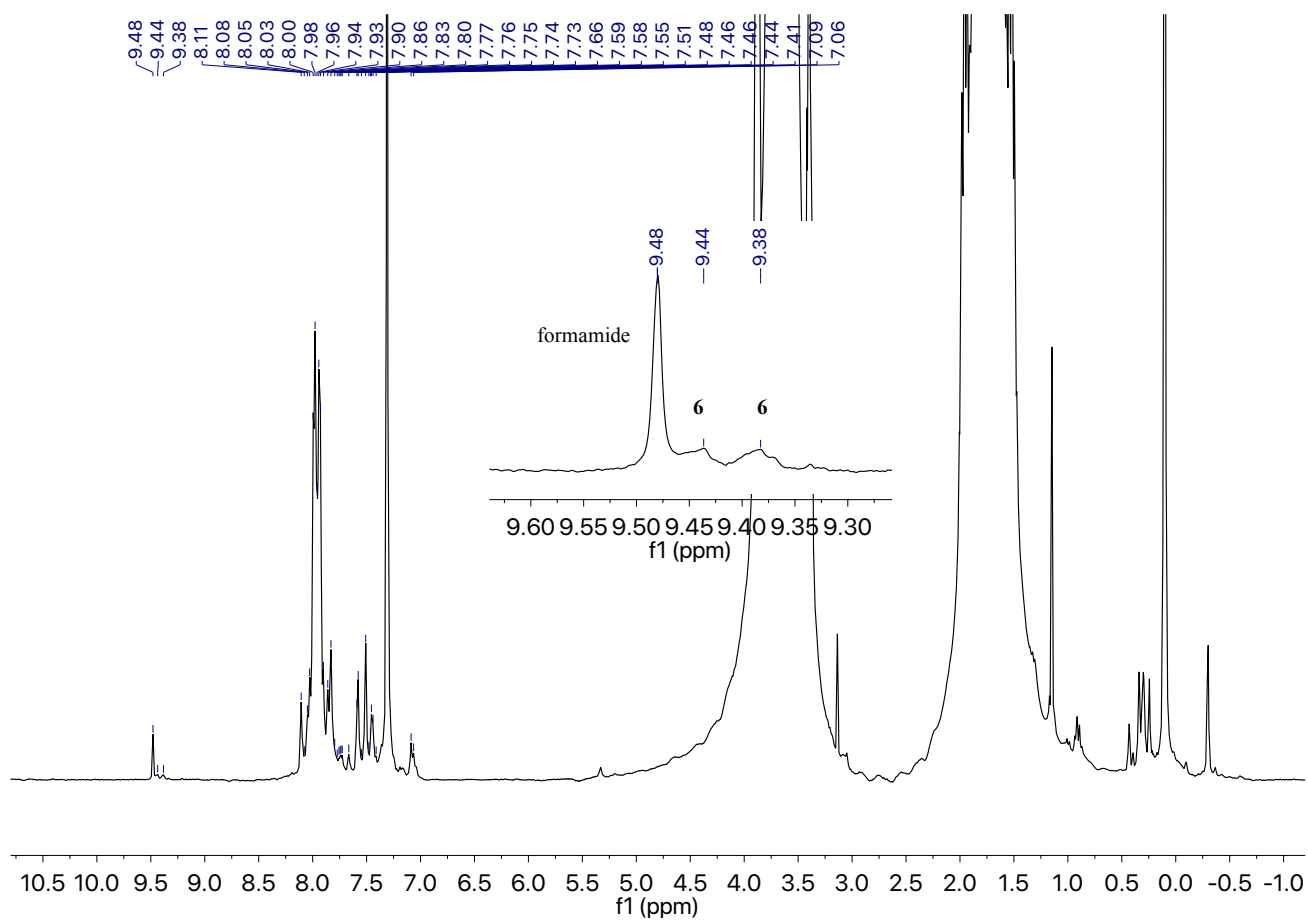
Supplementary Figure 29. ^1H NMR spectrum (300 MHz, CDCl_3) of **5**.



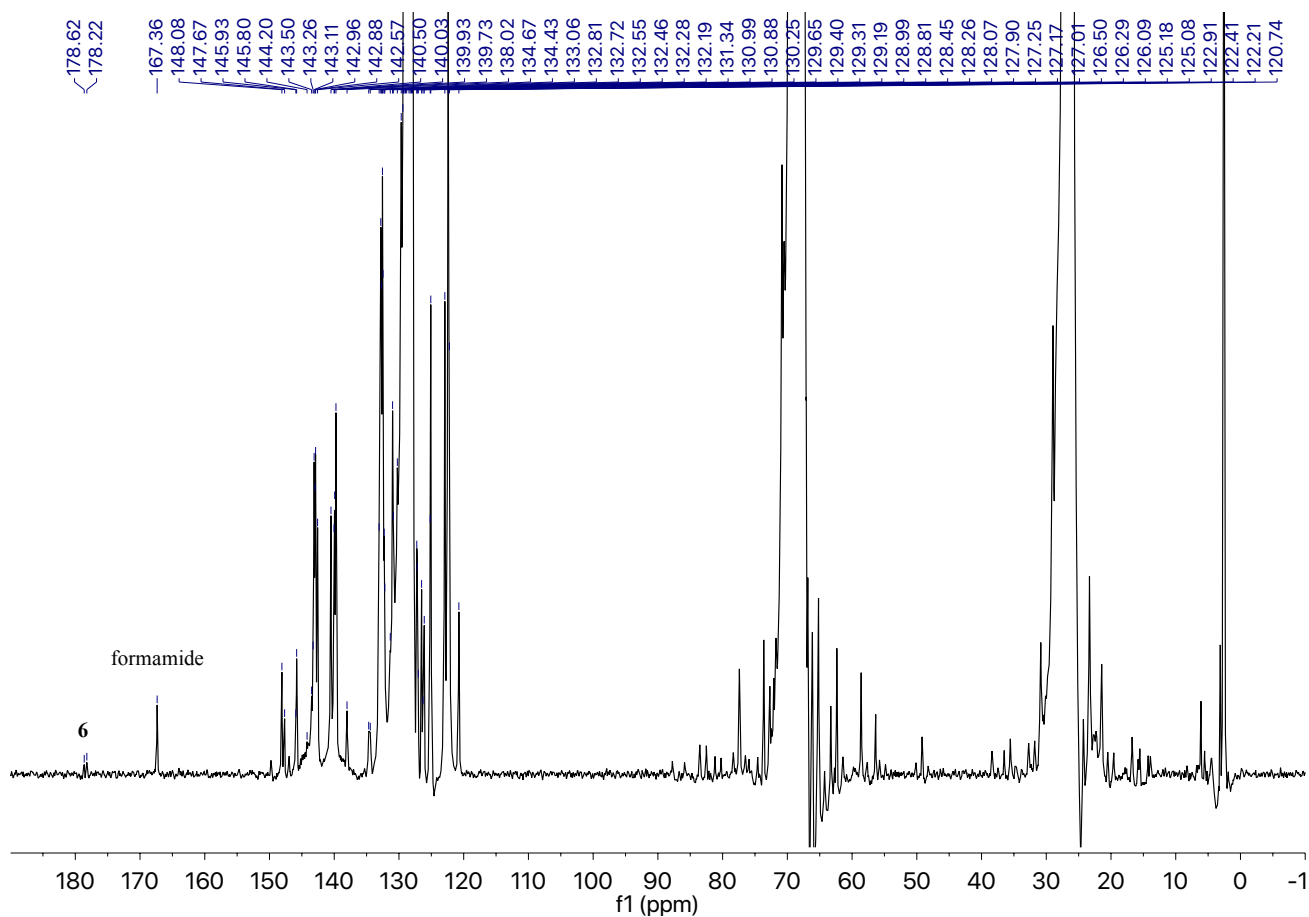
Supplementary Figure 30. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **5**.



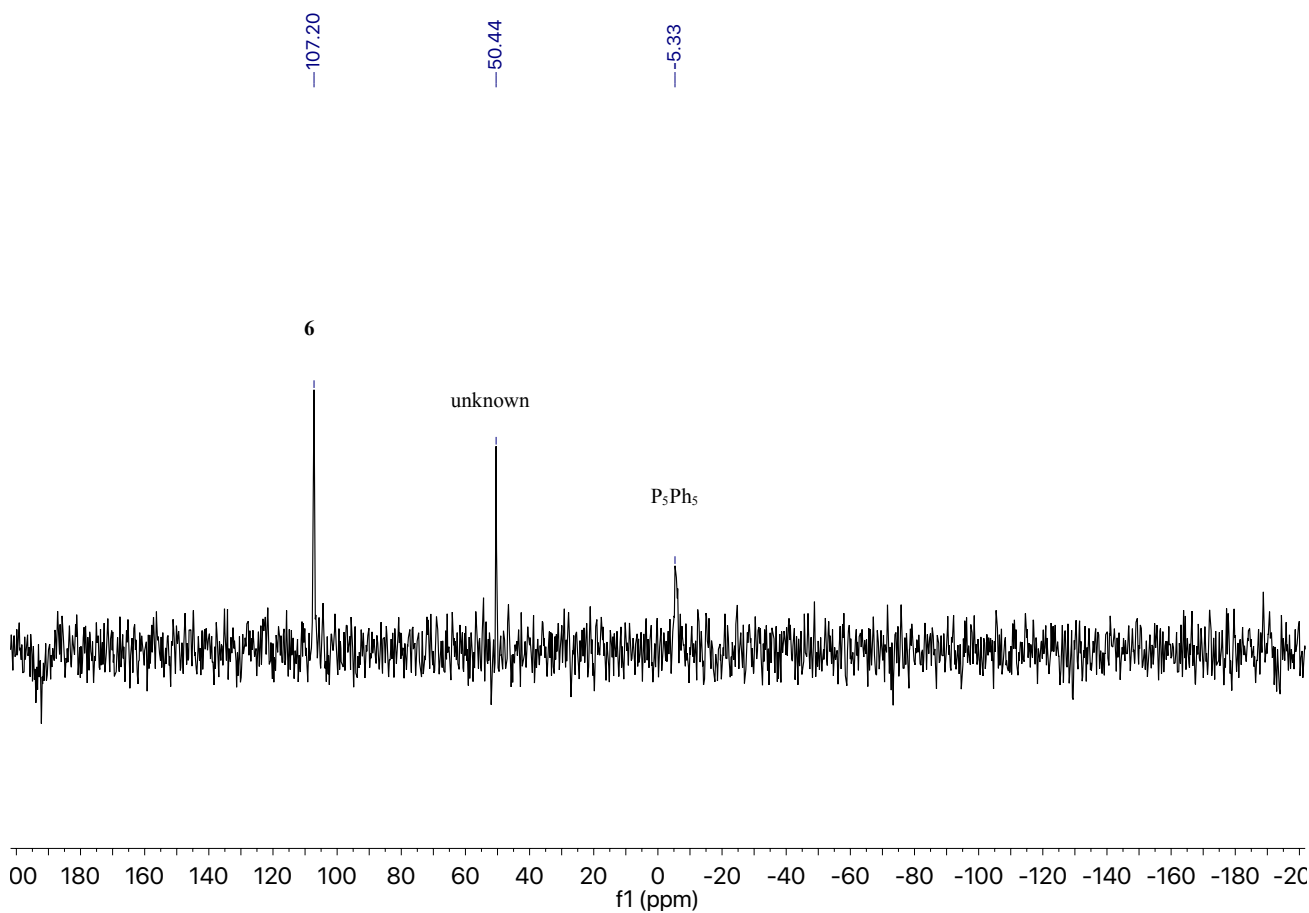
Supplementary Figure 31. ^{19}F NMR spectrum (282 MHz, CDCl_3) of **5**.



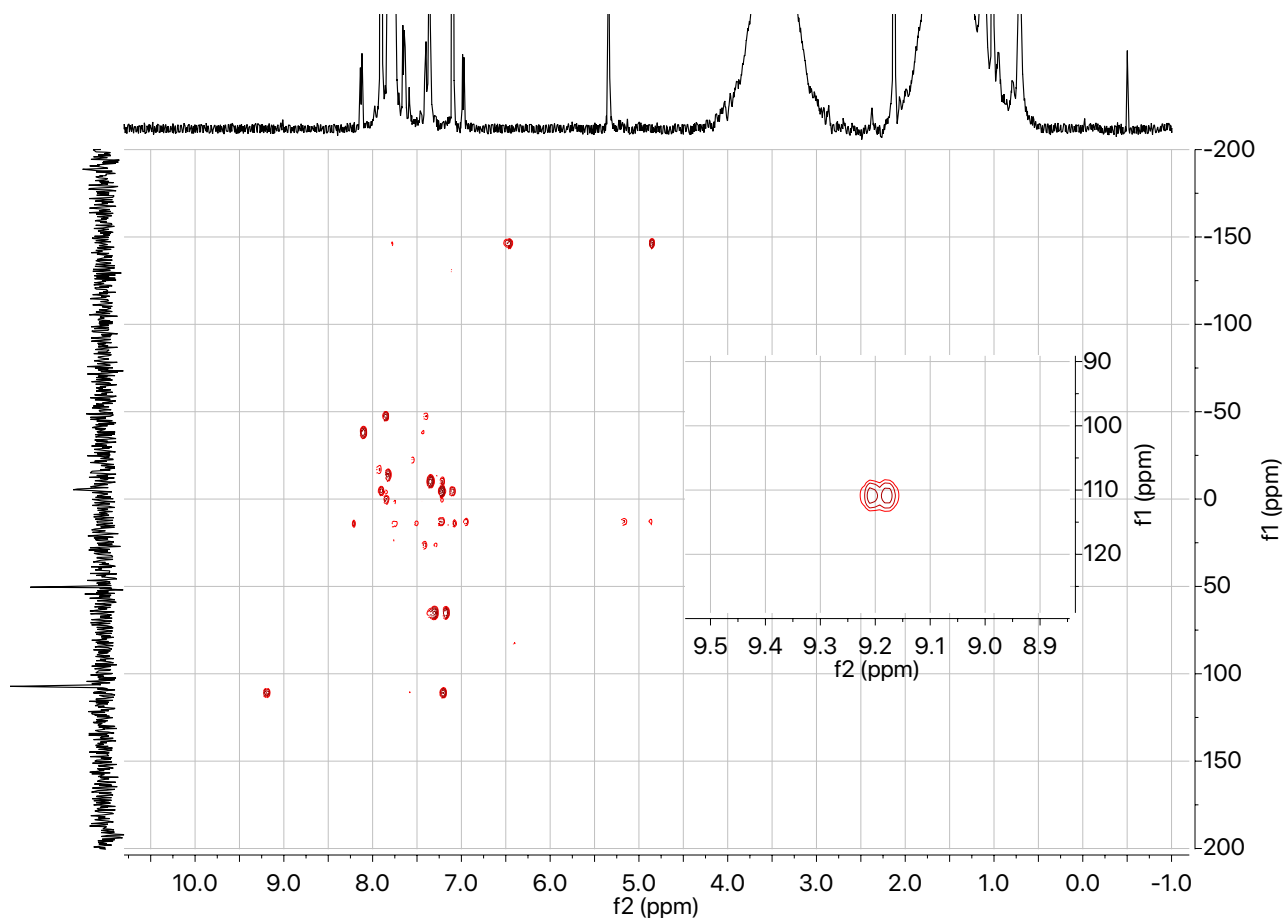
Supplementary Figure 32. ^1H NMR spectrum (300 MHz, $\text{THF} + \text{C}_6\text{D}_6$) of crude mixture containing **6**.



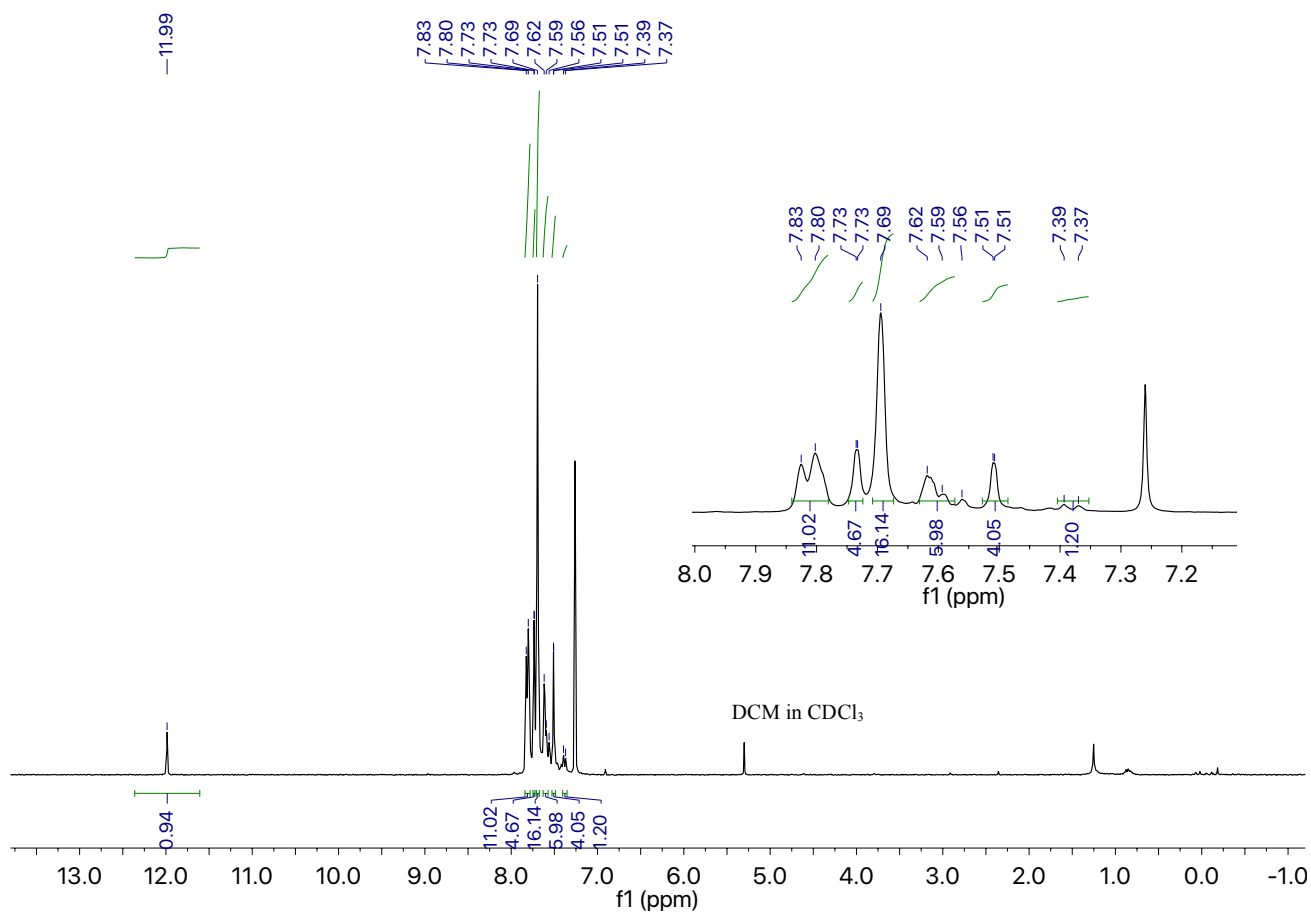
Supplementary Figure 33. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, THF + C_6D_6) of crude mixture containing **6**.



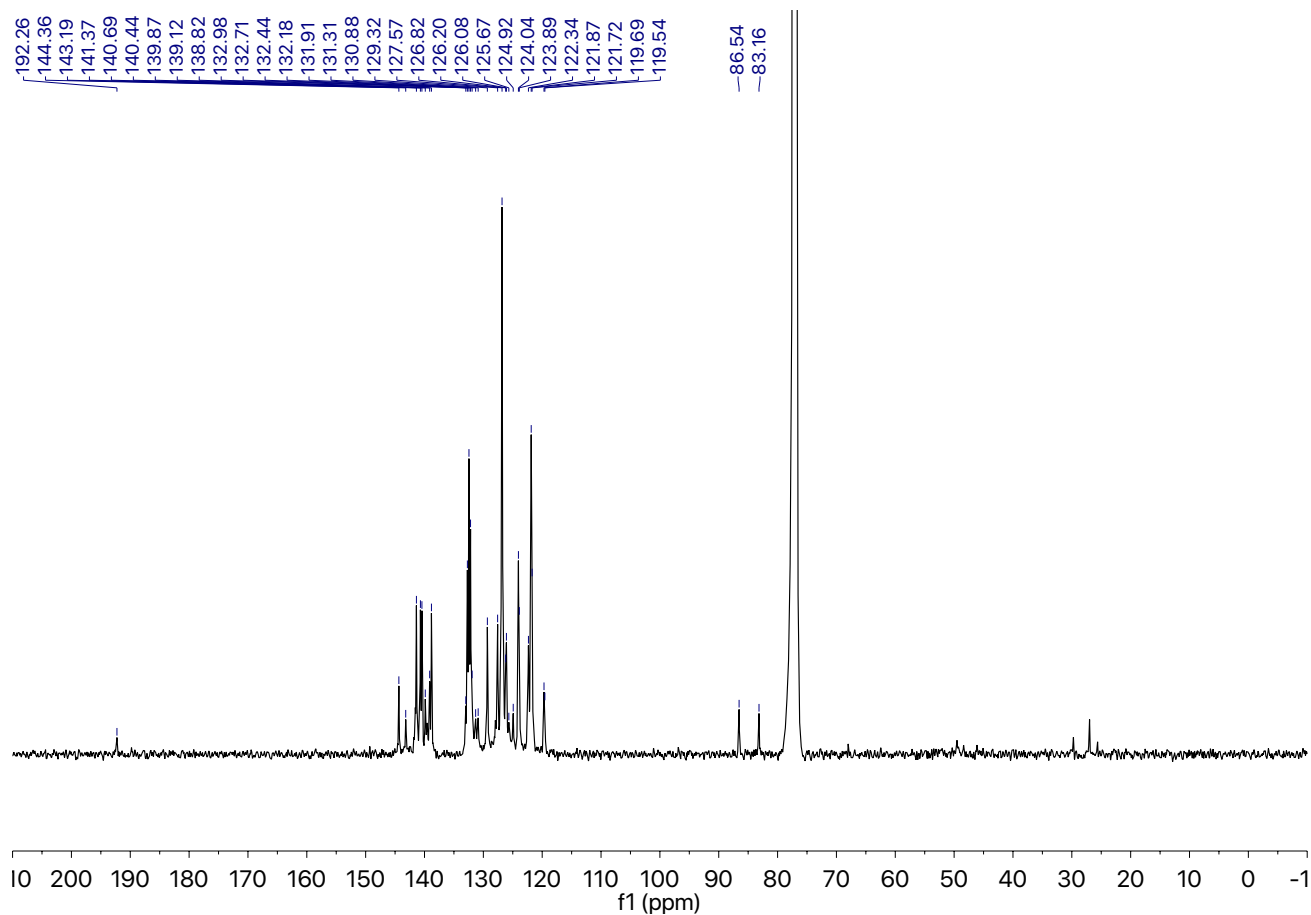
Supplementary Figure 34. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (121 MHz, THF + C_6D_6) of crude mixture containing **6**.



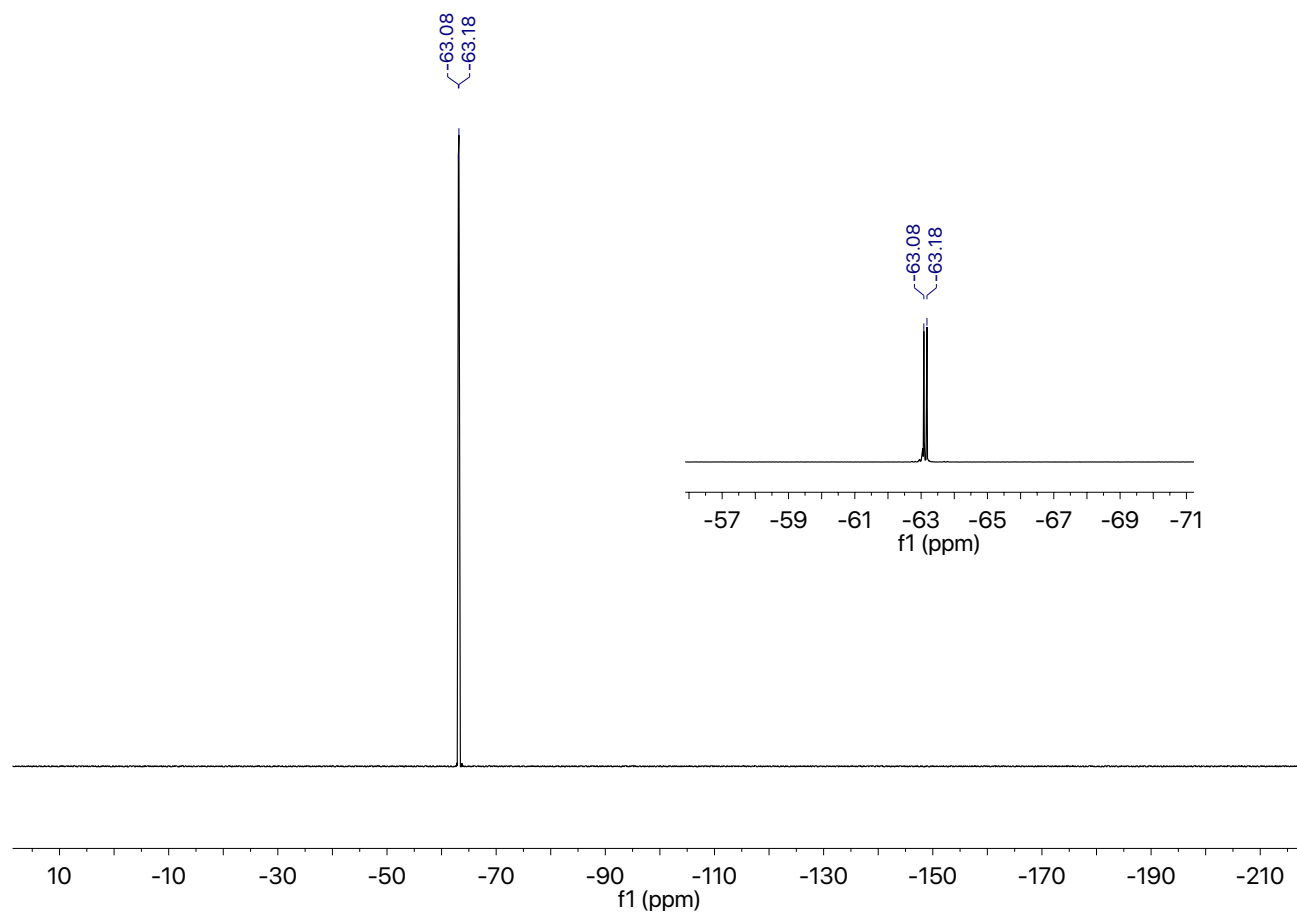
Supplementary Figure 35. ^1H , ^{31}P HMBC NMR spectrum (CDCl_3) of crude mixture containing **6**.



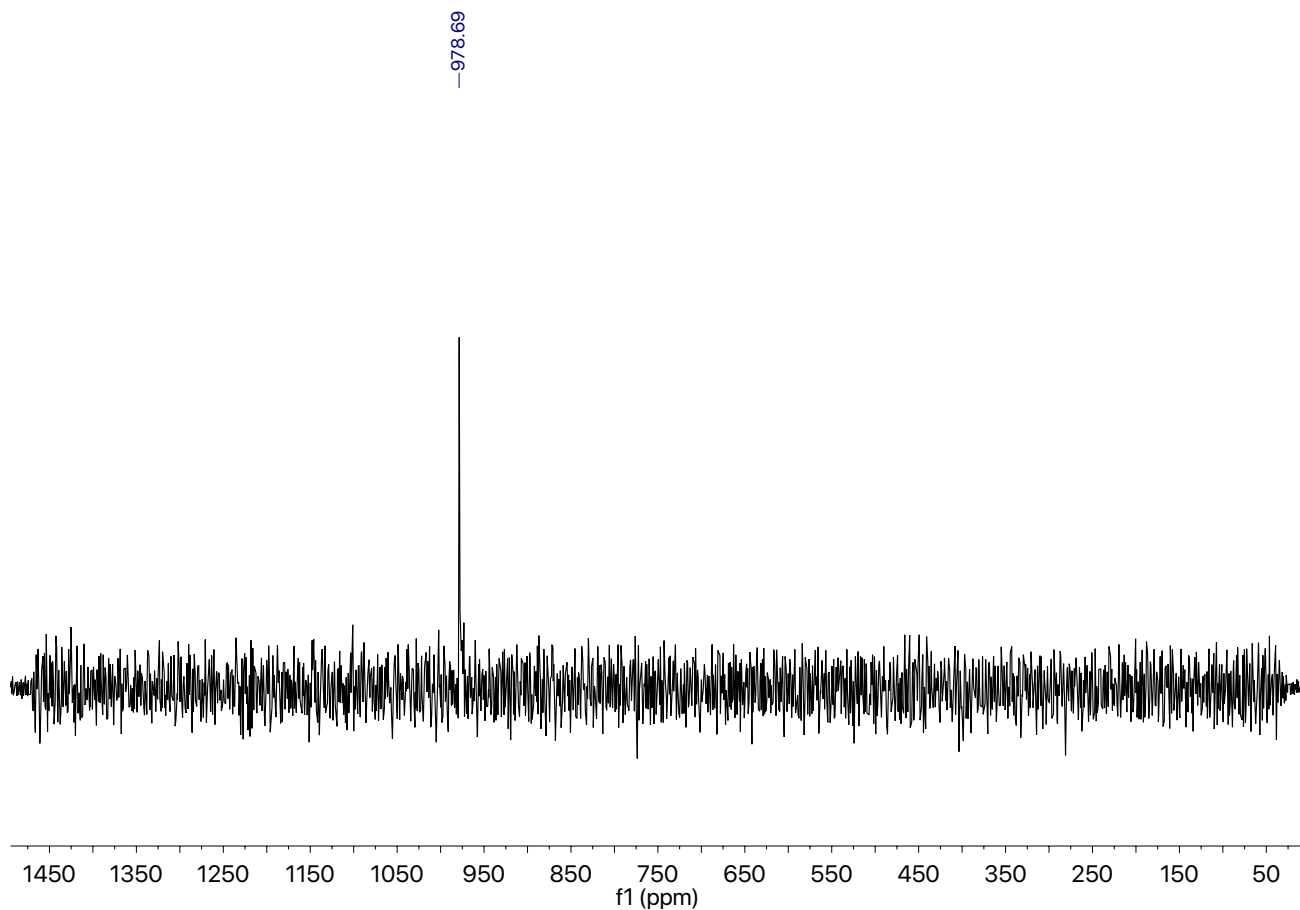
Supplementary Figure 36. ^1H NMR spectrum (300 MHz, CDCl_3) of **7**.



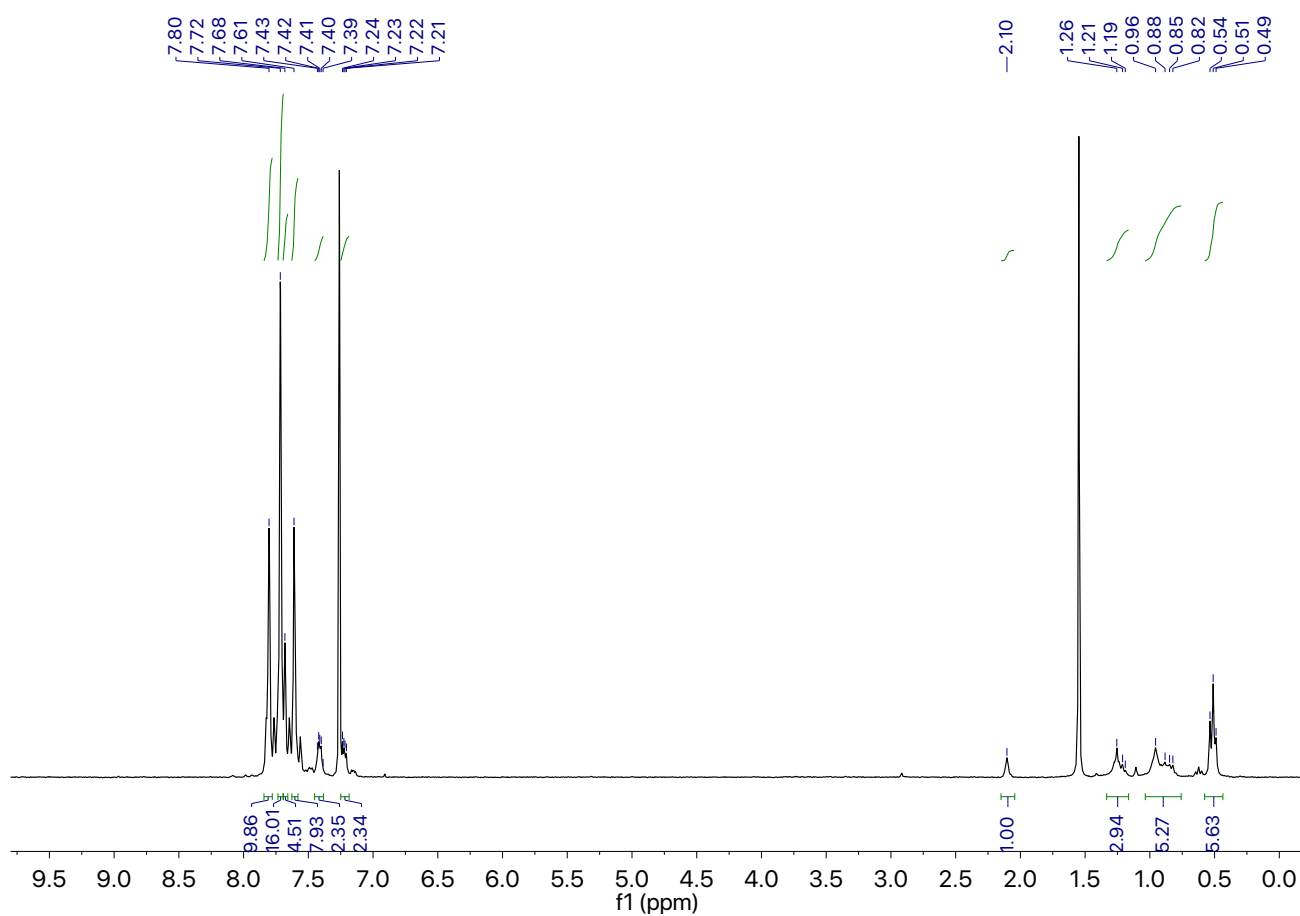
Supplementary Figure 37. ¹³C{¹H} NMR spectrum (126 MHz, CDCl₃) of 7.



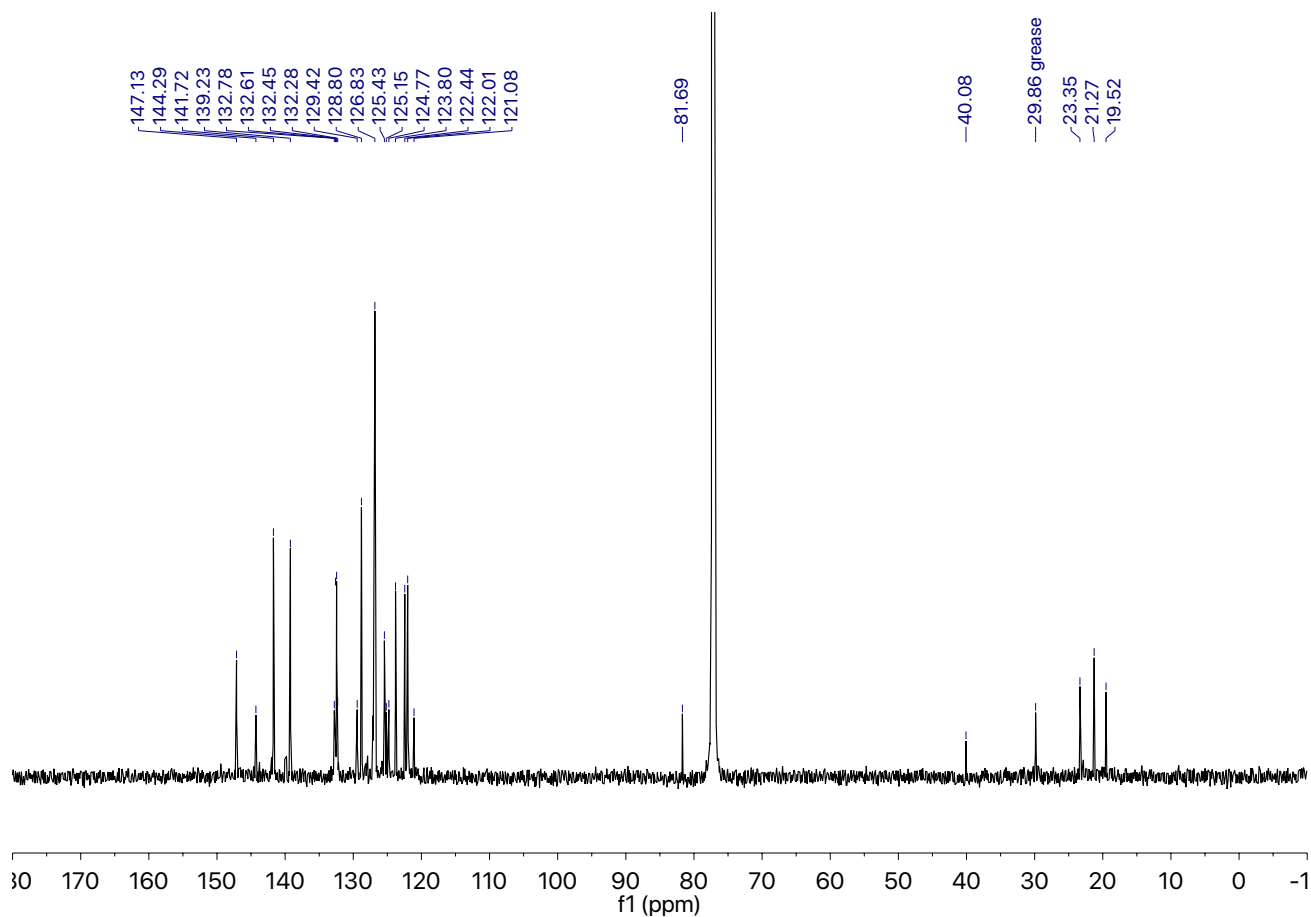
Supplementary Figure 38. ¹⁹F NMR spectrum (282 MHz, CDCl₃) of 7.



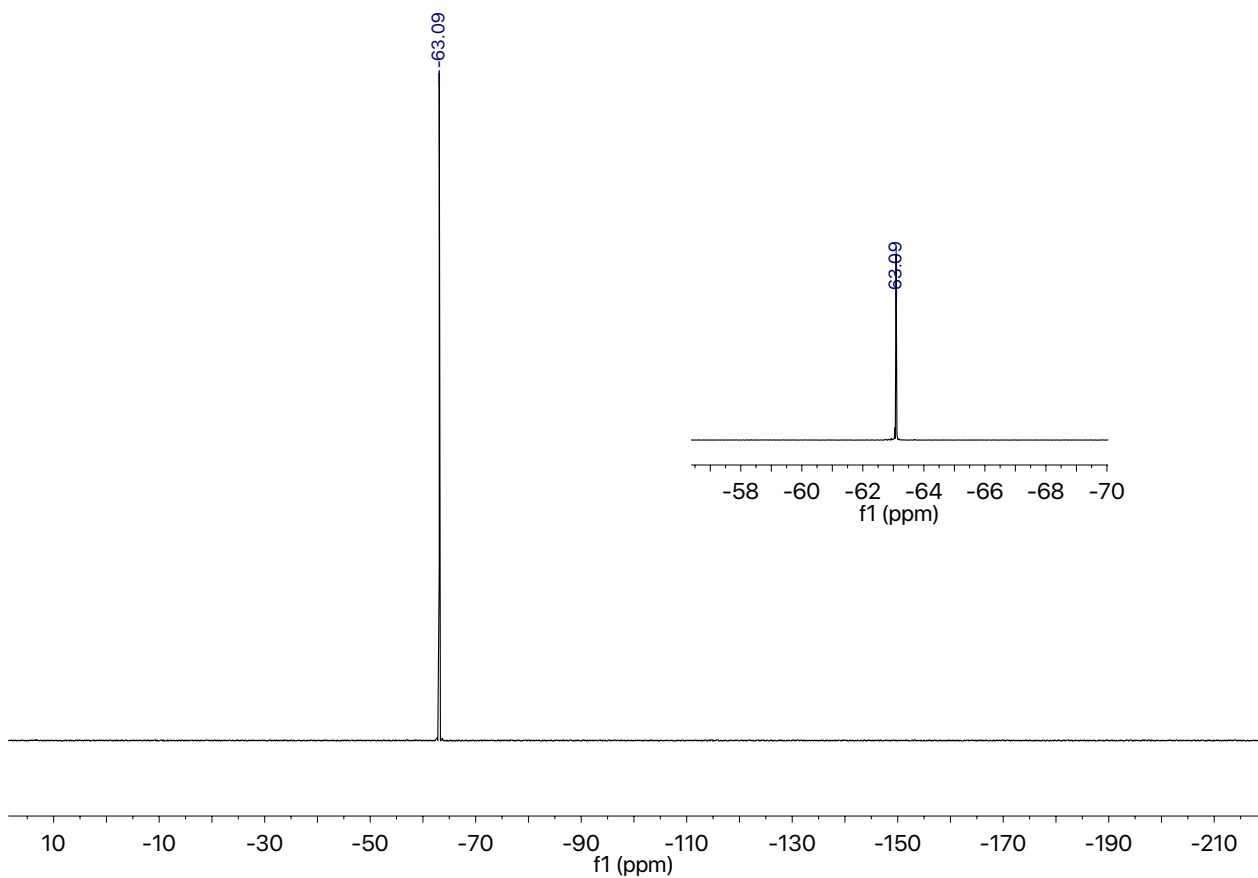
Supplementary Figure 39. ^{77}Se NMR spectrum (282 MHz, CDCl_3) of **7**.



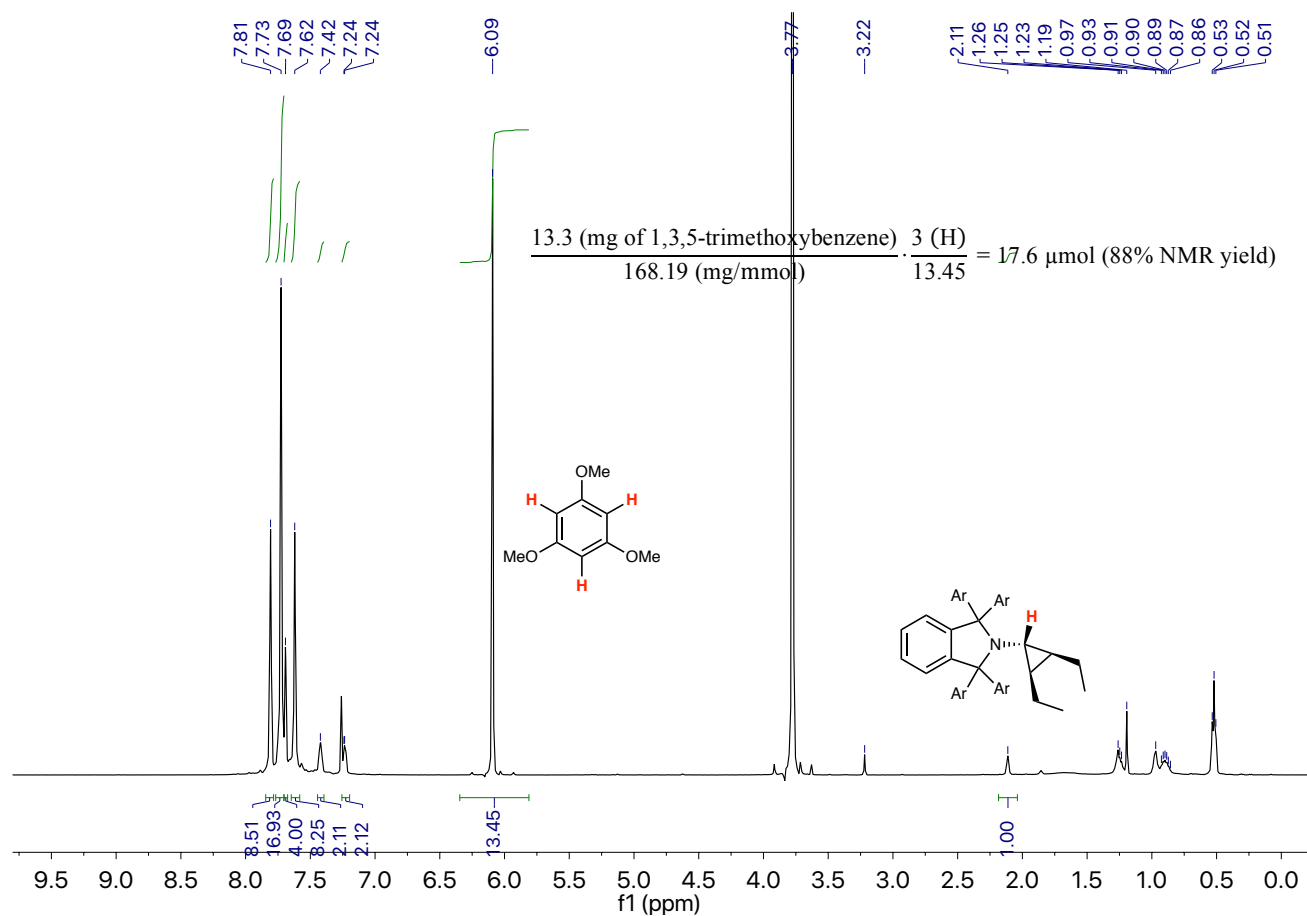
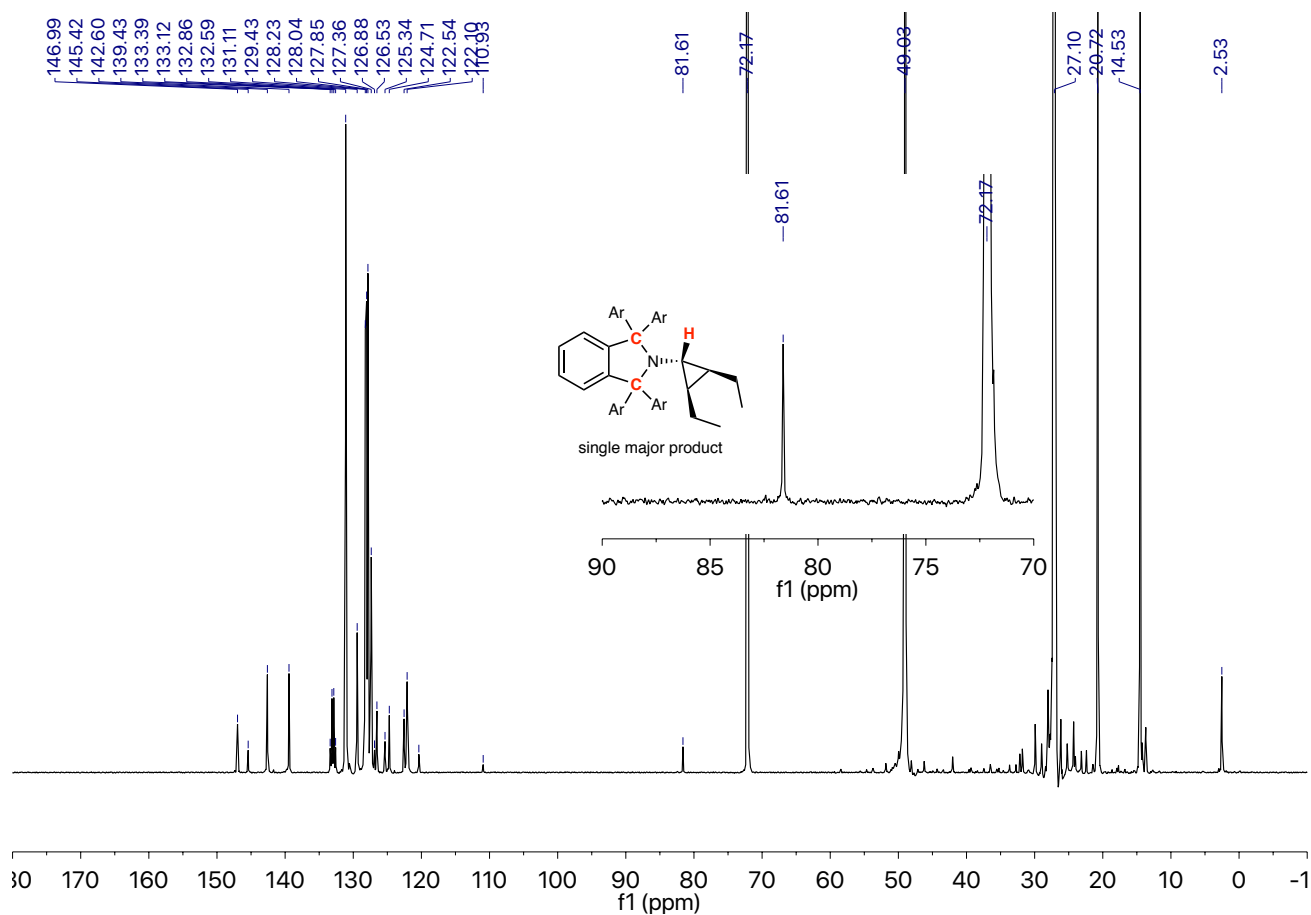
Supplementary Figure 40. ^1H NMR spectrum (300 MHz, CDCl_3) of **8**.

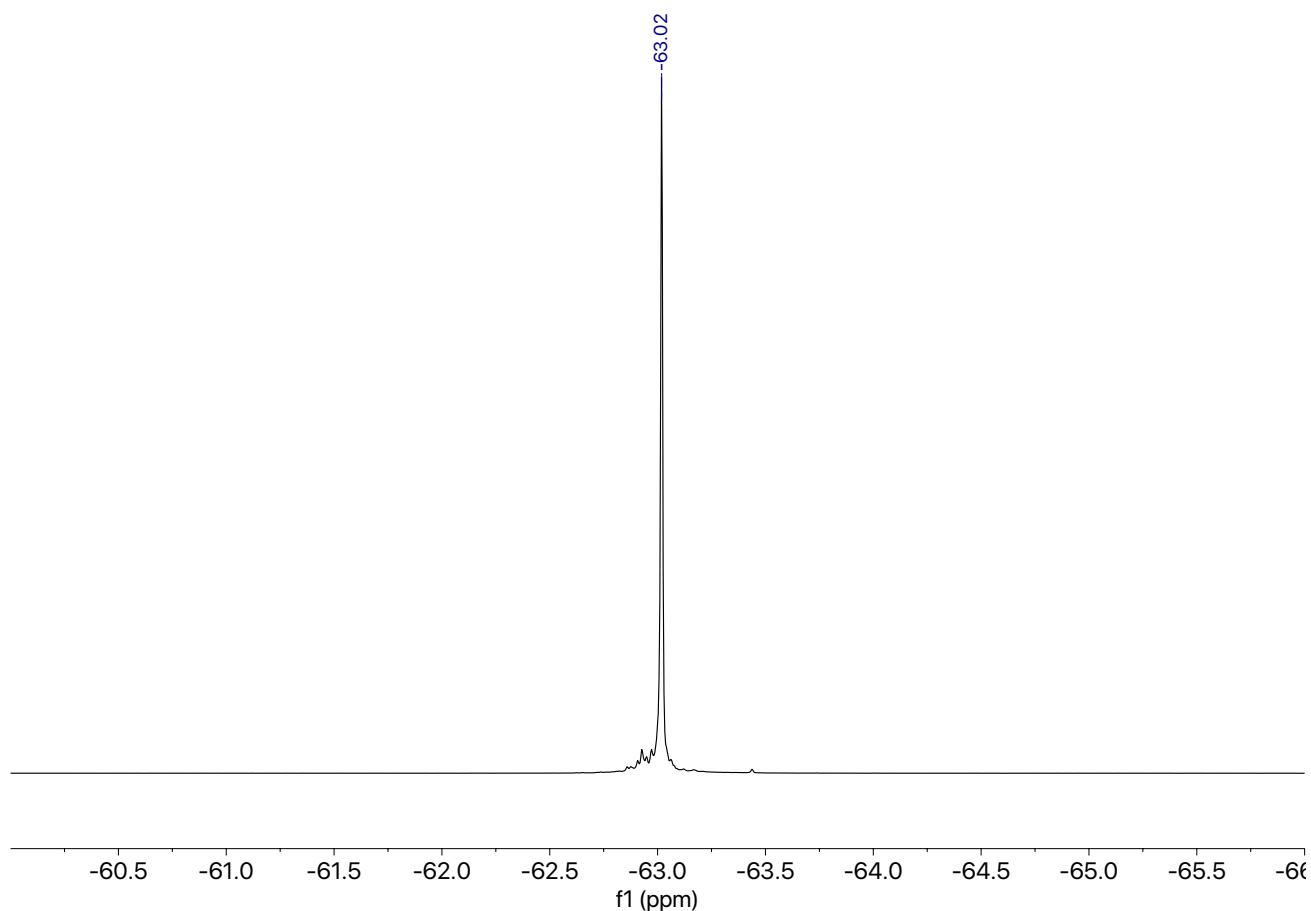


Supplementary Figure 41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (201 MHz, CDCl_3) of **8**.

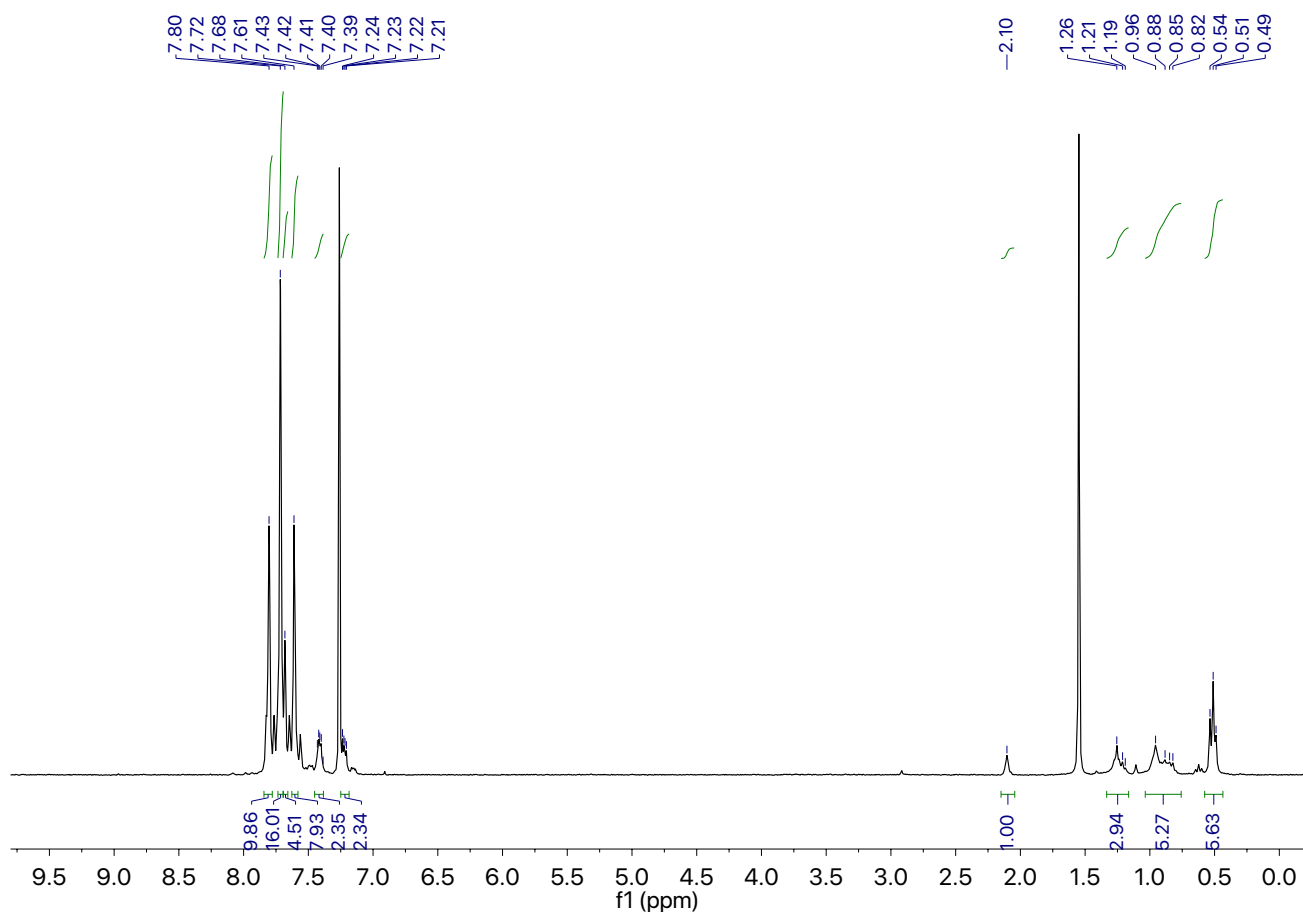


Supplementary Figure 42. ^{19}F NMR spectrum (282 MHz, CDCl_3) of **8**.

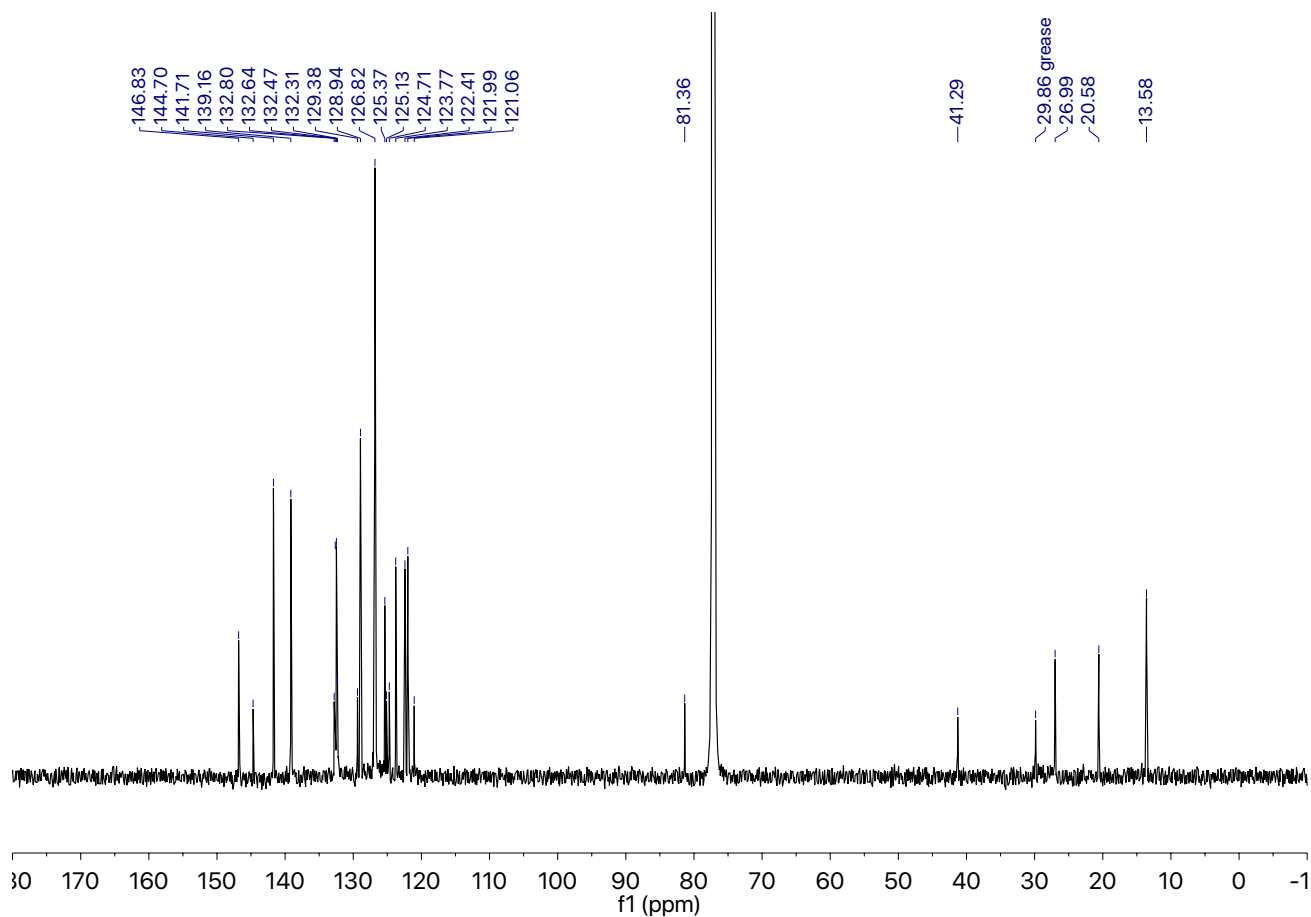




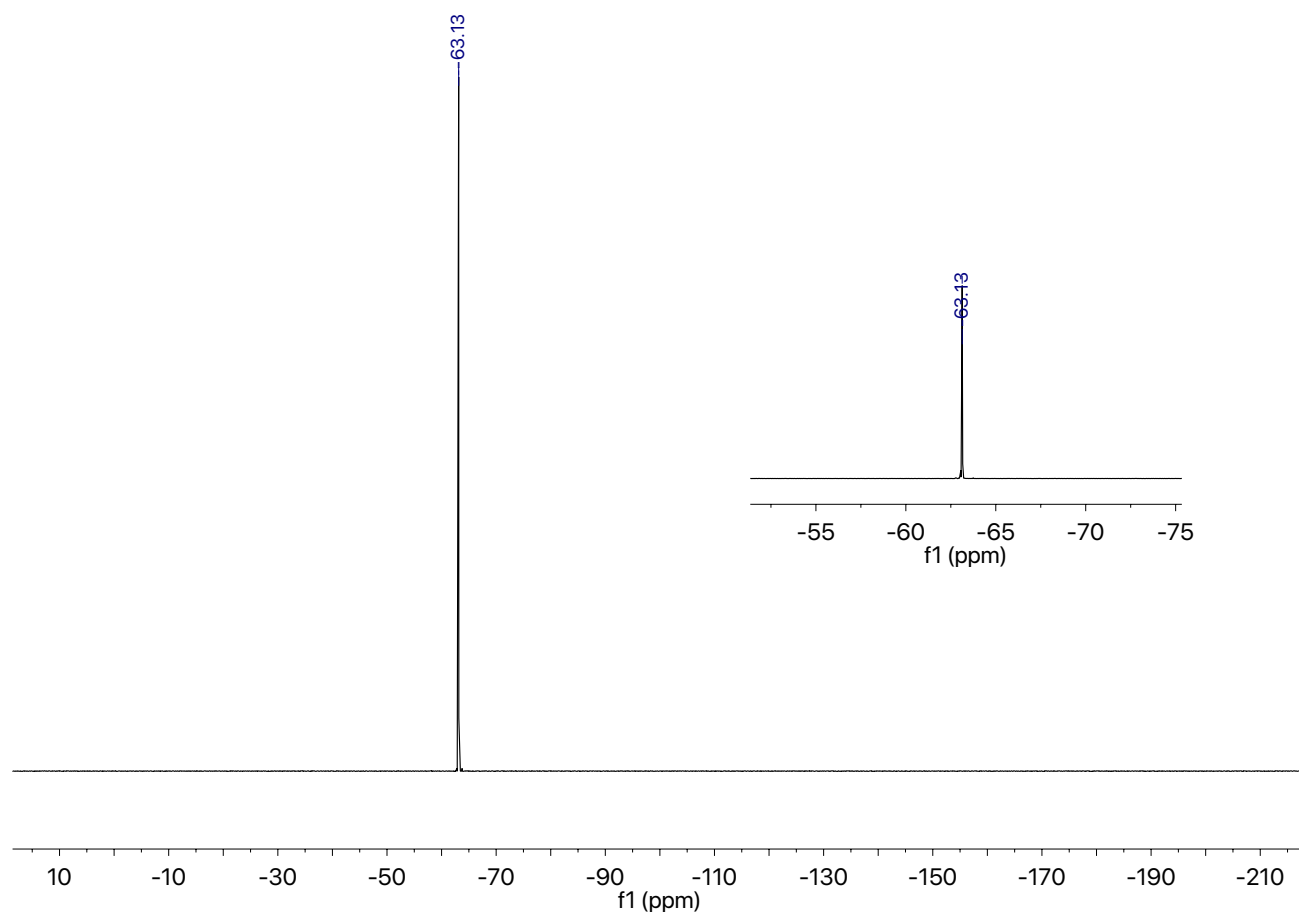
Supplementary Figure 45. ^{19}F NMR spectrum (471 MHz, CDCl_3) of crude mixture containing **9** and 1,3,5-trimethoxybenzene.



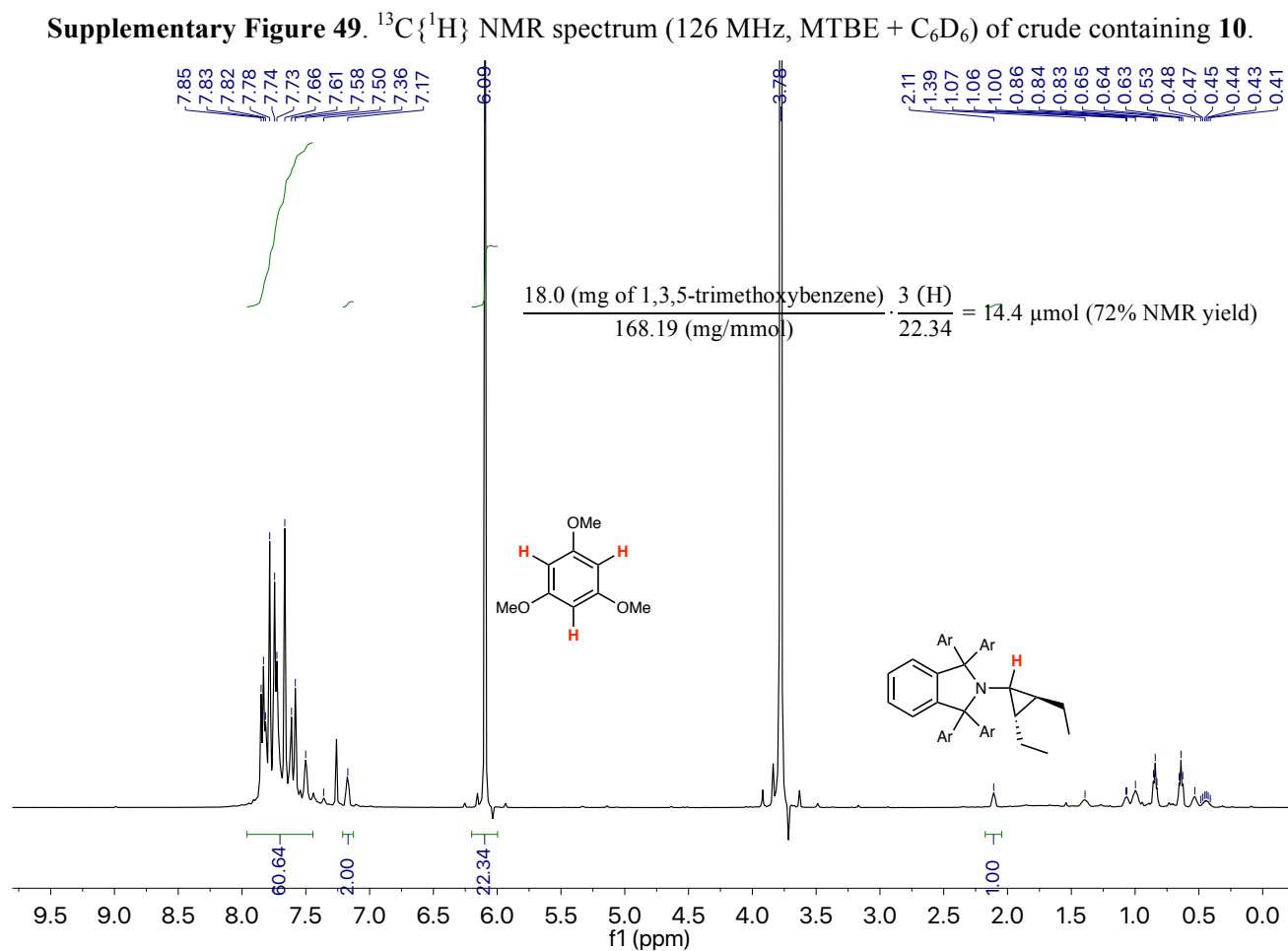
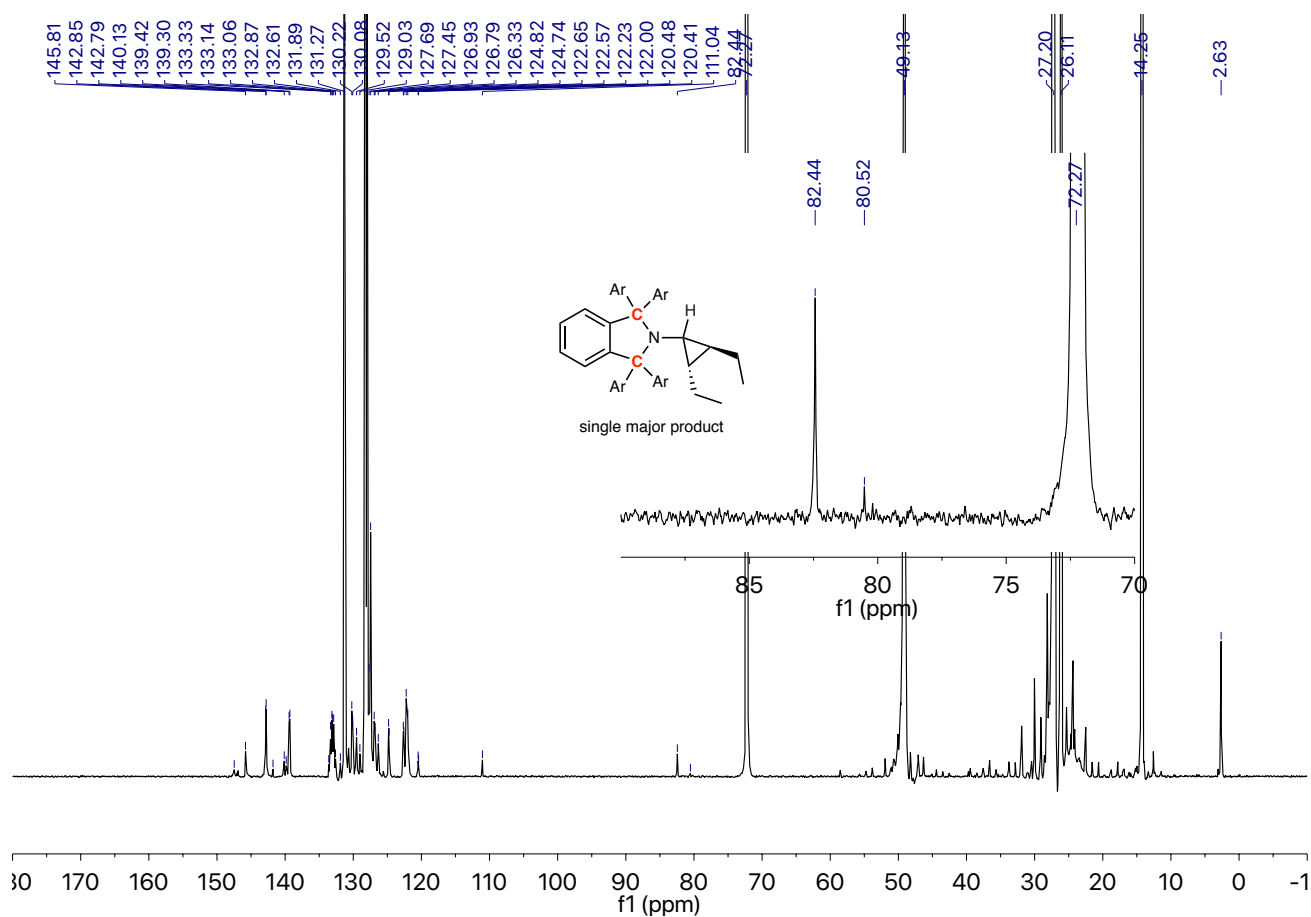
Supplementary Figure 46. ^1H NMR spectrum (300 MHz, CDCl_3) of **9**.

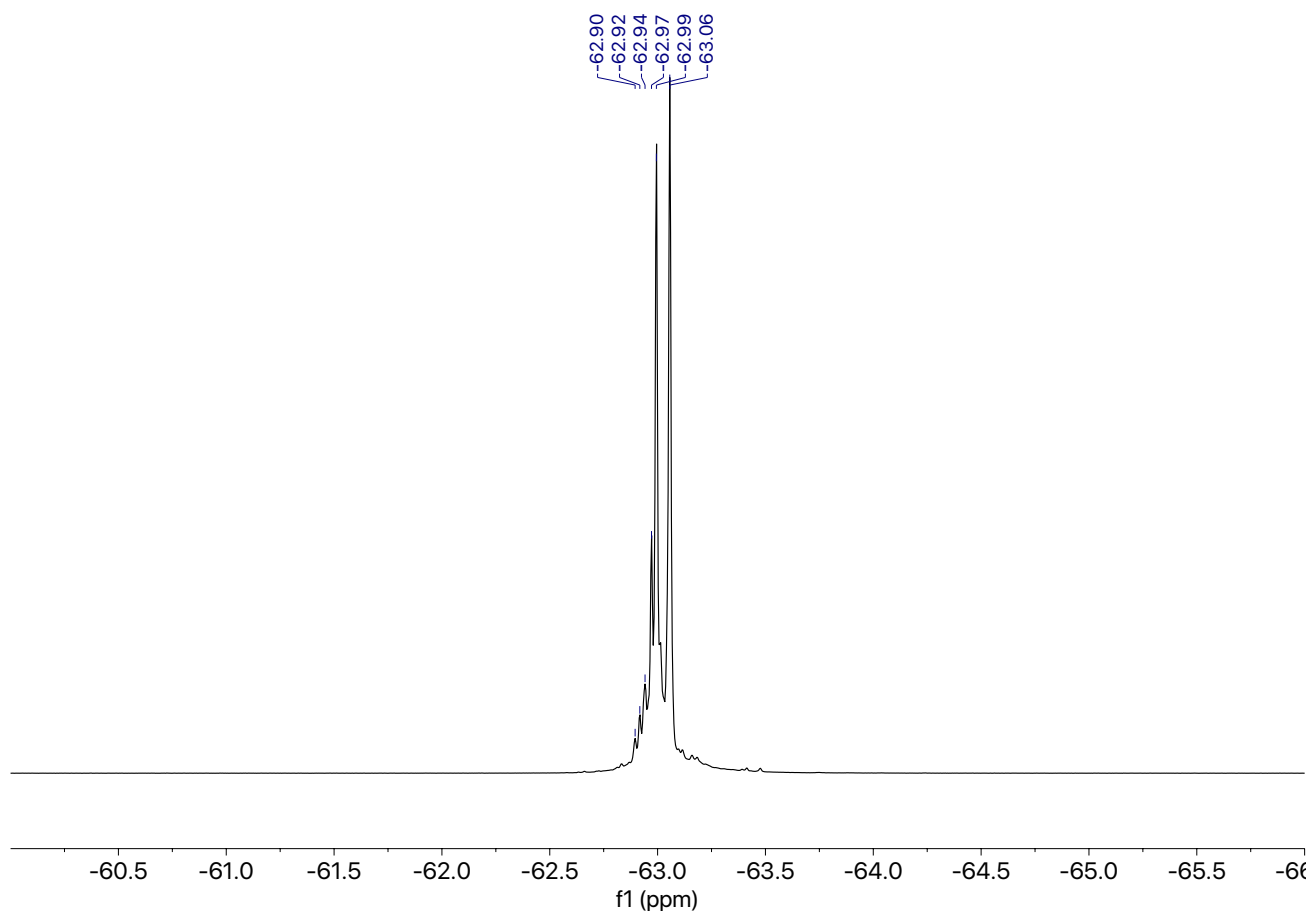


Supplementary Figure 47. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (201 MHz, CDCl_3) of **9**.

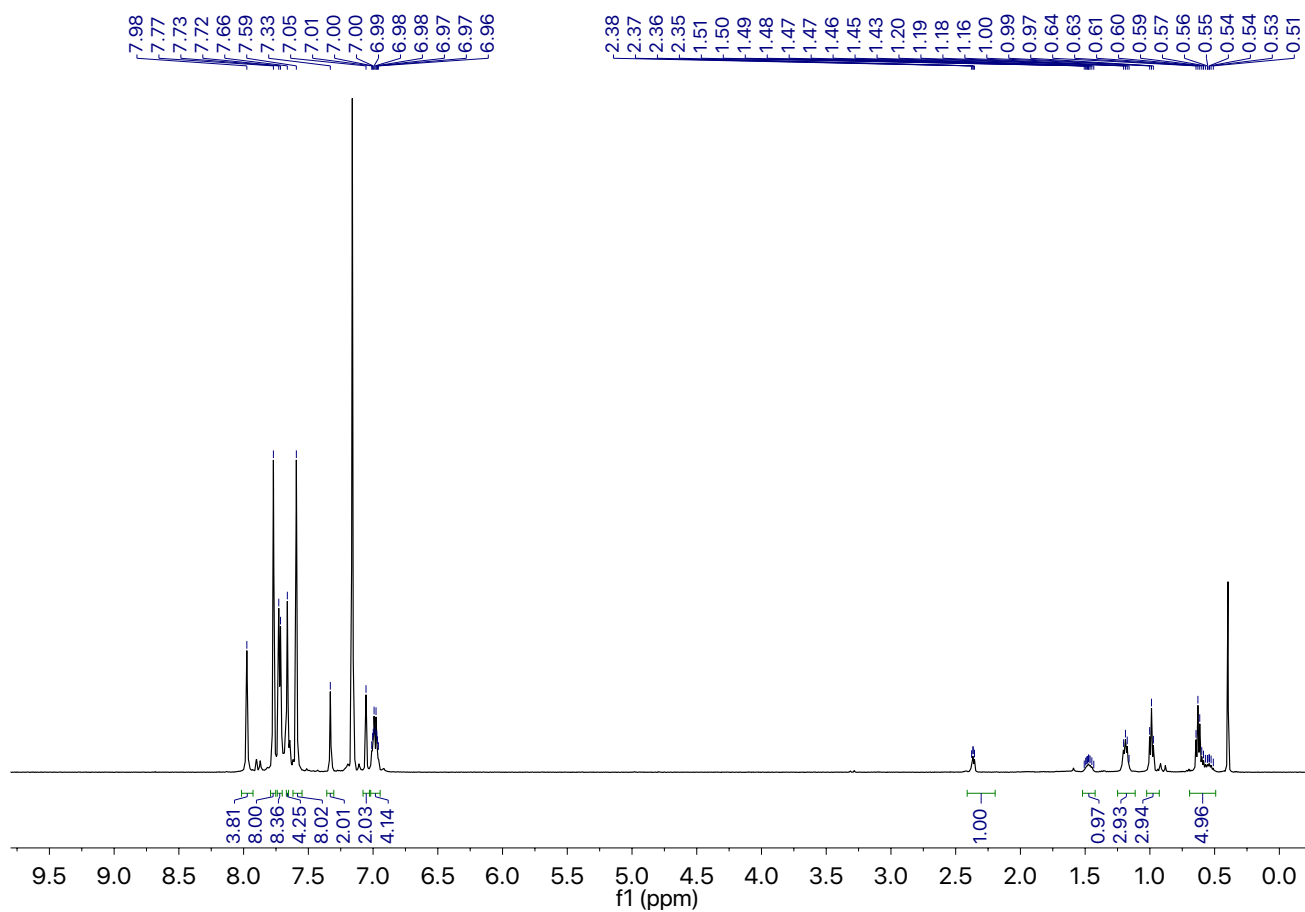


Supplementary Figure 48. ^{19}F NMR spectrum (282 MHz, CDCl_3) of **9**.

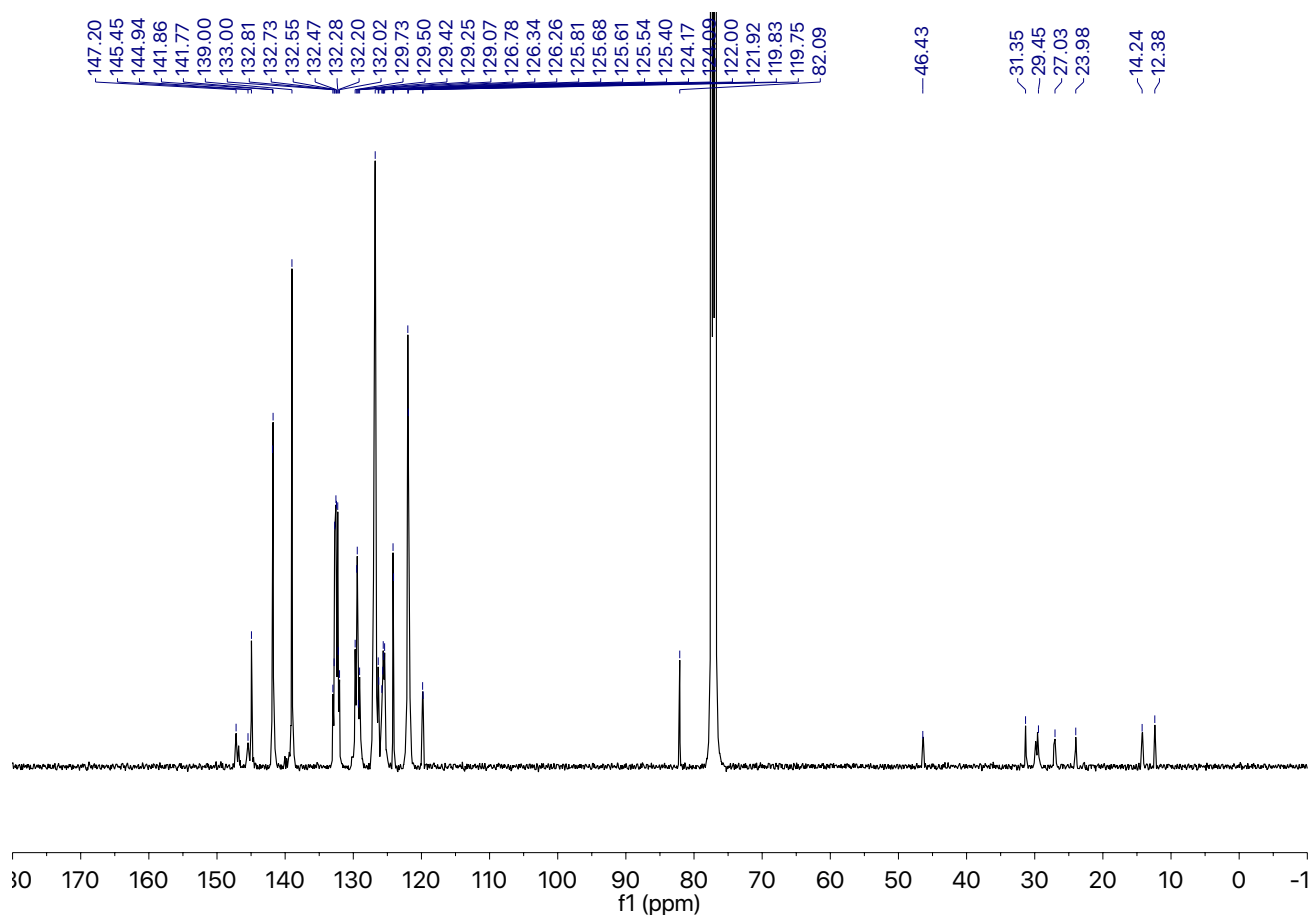




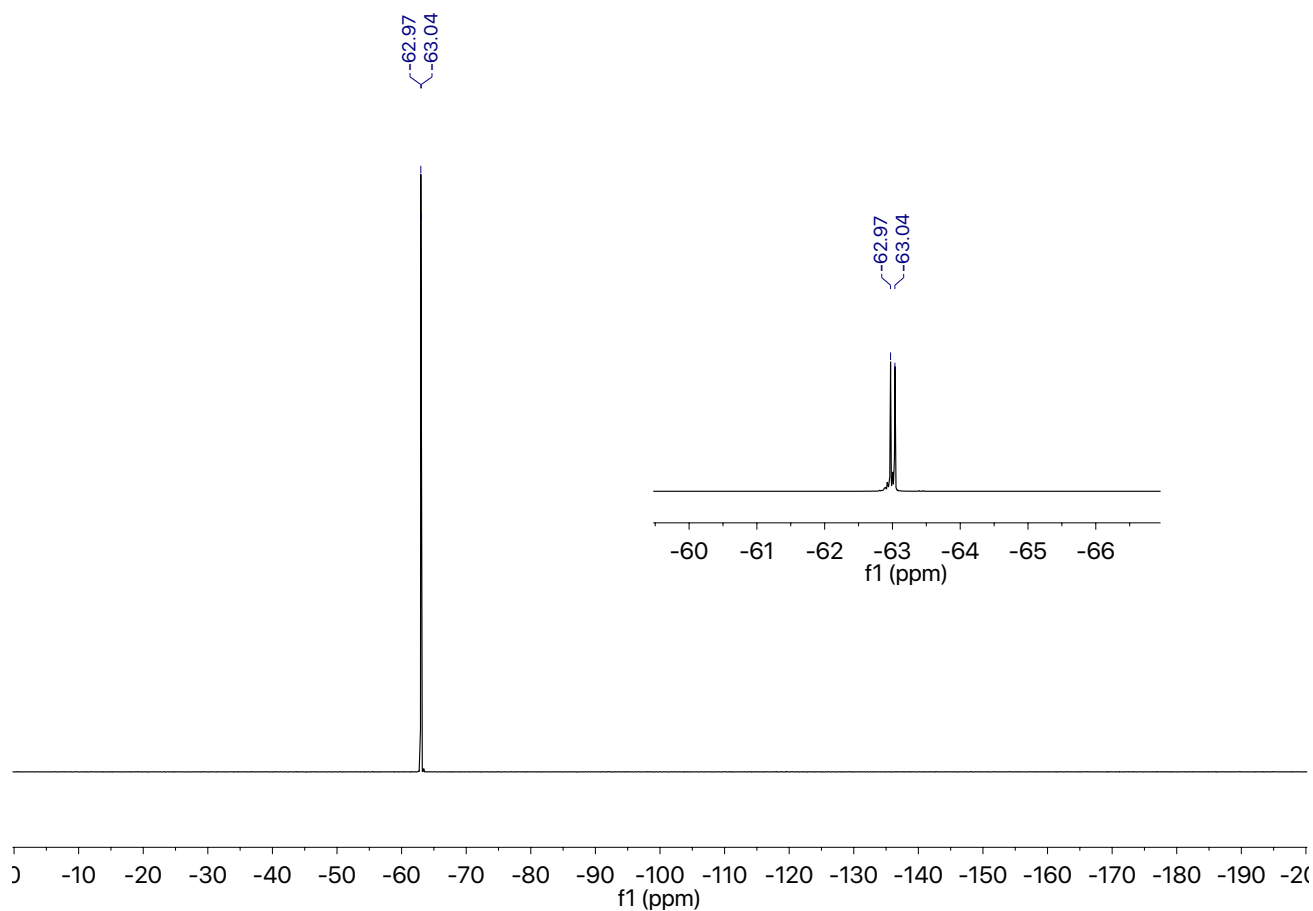
Supplementary Figure 51. ¹⁹F NMR spectrum (471 MHz, CDCl₃) of crude mixture containing **10** and 1,3,5-trimethoxybenzene.



Supplementary Figure 52. ¹H NMR spectrum (500 MHz, C₆D₆) of **10**.



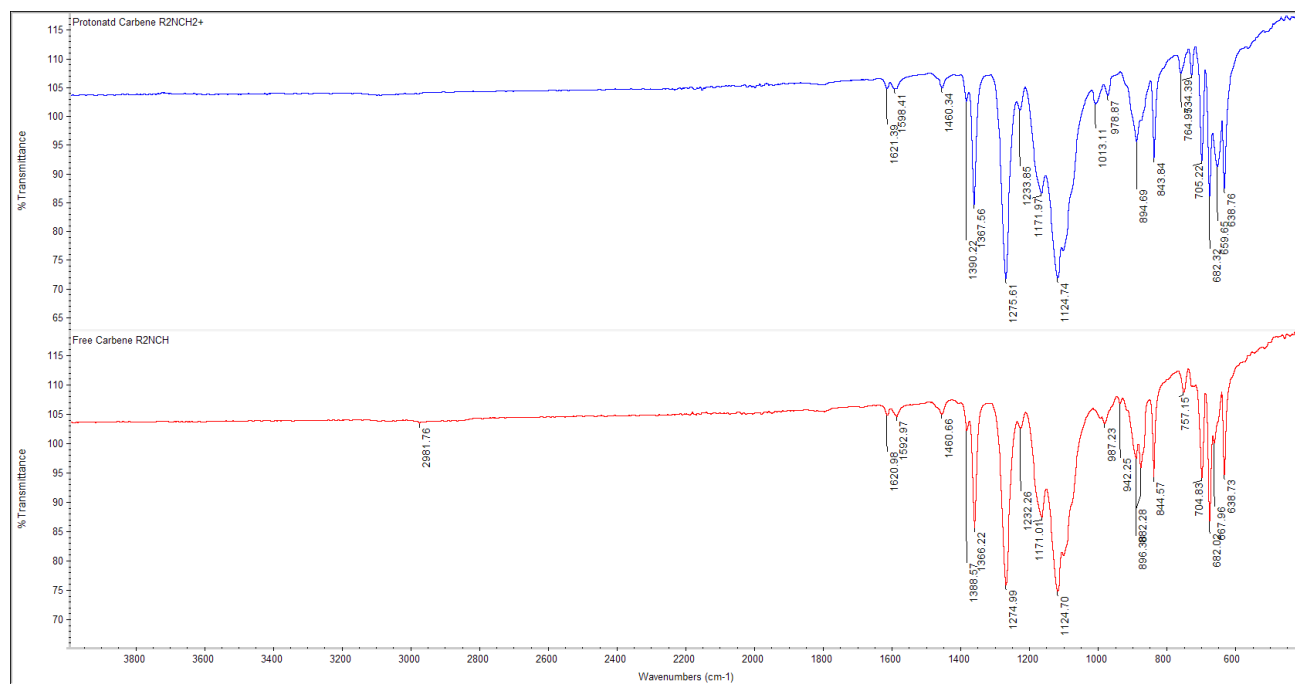
Supplementary Figure 53. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, CDCl_3) of **10**.



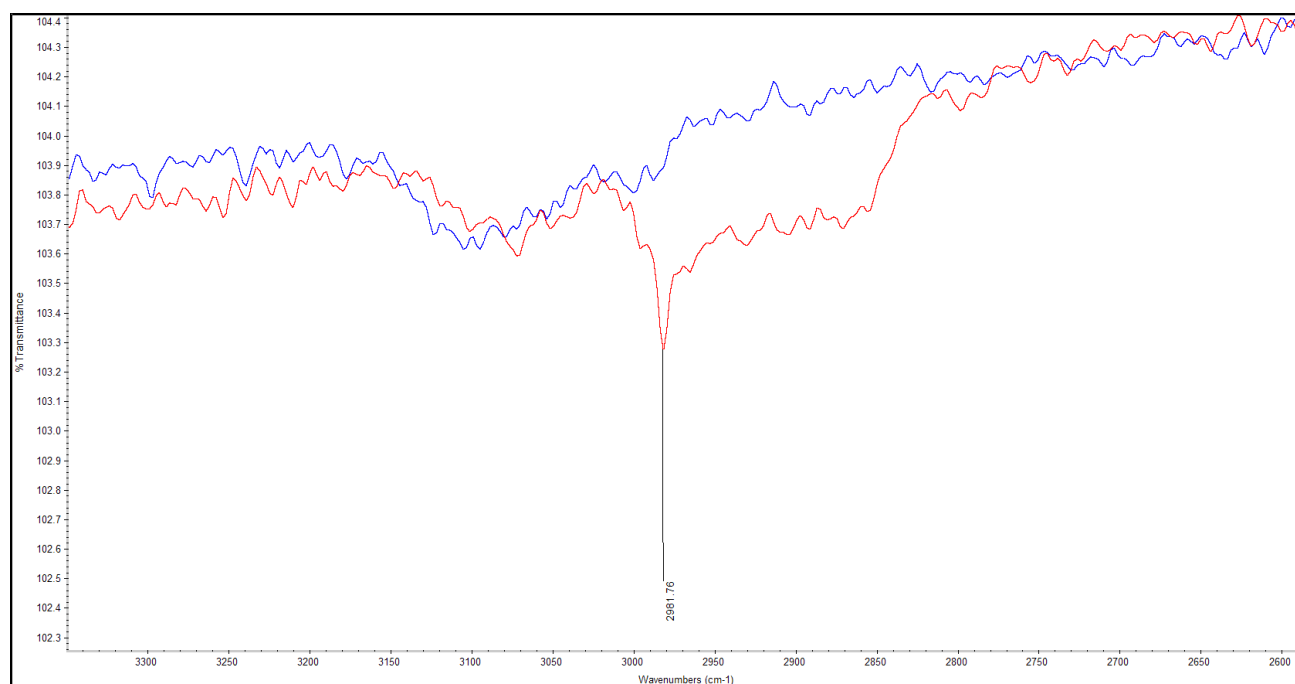
Supplementary Figure 54. ^{19}F NMR spectrum (471 MHz, CDCl_3) of **10**.

III. Supplementary Figures 55-56

In the IR spectrum of **3c**, a weak but sharp signal at 2981.8 cm^{-1} was newly appeared and assigned to the C-H stretching of the (carbene carbon)-hydrogen. This assignment is in accordance with the DFT estimations (B3LYP/6-31G* and B3LYP/def2-TZVPP), which predicted the signal at 2912.2 cm^{-1} and 2931.7 cm^{-1} , respectively. It should be noted that the C-H stretching of the parent aminomethylene (H-C-NH₂) was observed at 2812.5 and 2809.1 cm^{-1} in argon matrix at 12 K .⁷



Supplementary Figure 55. ATR-FTIR Spectra of **2c** (top, blue) and **3c** (bottom, red).



Supplementary Figure 56. Expanded and superimposed ATR-FTIR Spectra of **2c** (blue) and **3c** (red).

IV. Supplementary Tables 1-9

General: All the crystallographic analyses were performed at least twice and represent the best achievable data given the reactivity of the materials and the stability of these crystals. To prevent desolvation and/or decomposition the crystals were plated in Trilene oil, which was pre-dried at 200 °C under vacuum for 48h. In all cases, the Trilene oil was saturated with the crystallization solvents mixture before plating. In the case of carbene **3c**, the plate containing saturated Trilene oil was pre-cooled at -40 °C before plating the crystals. It was further maintained below -40 °C during the selection and mounting process using under a constant flow of liquid nitrogen vapors to prevent the otherwise extremely rapid decomposition/desolvation of the crystals.

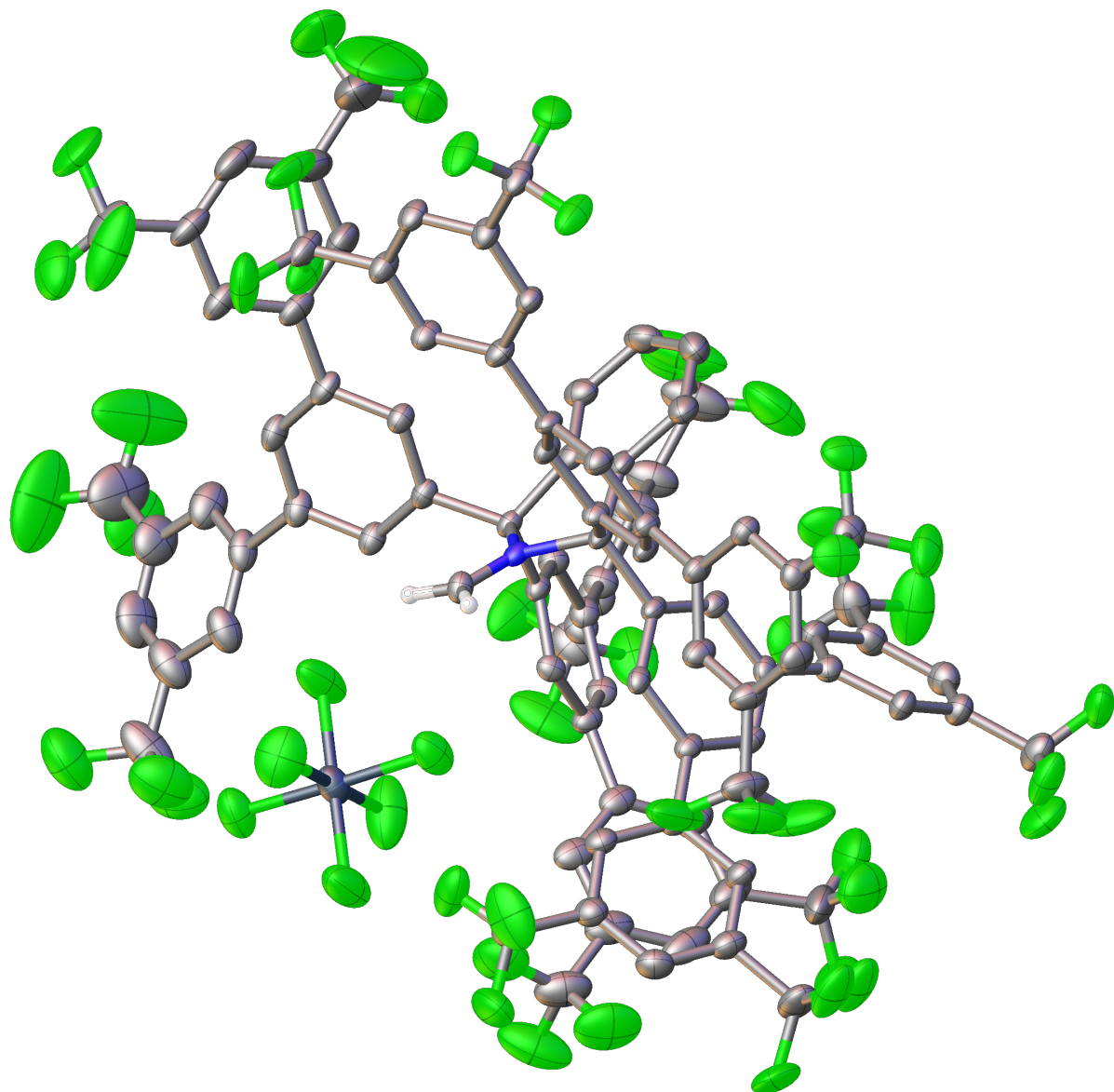
Supplementary Table 1

Crystal data and structure refinement for **Compound 2c - CCDC 1814366**

Identification code	gb_rj_rn_12222017b_0m_a_sq_sq
Empirical formula	C ₉₇ H ₄₂ F ₅₄ NSb
Formula weight	2369.06
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	16.2032(5)
b/Å	17.9406(6)
c/Å	20.9575(7)
α/°	106.368(2)
β/°	97.648(2)
γ/°	112.273(2)
Volume/Å ³	5208.0(3)
Z	2
ρ _{calc} /g/cm ³	1.511
μ/mm ⁻¹	3.391
F(000)	2336.0
Crystal size/mm ³	0.23 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.71 to 136.868
Index ranges	-19 ≤ h ≤ 18, -21 ≤ k ≤ 21, -25 ≤ l ≤ 25
Reflections collected	65889
Independent reflections	18954 [R _{int} = 0.0702, R _{sigma} = 0.0619]
Data/restraints/parameters	18954/345/1493
Goodness-of-fit on F ²	1.040
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0794, wR ₂ = 0.2153
Final R indexes [all data]	R ₁ = 0.0918, wR ₂ = 0.2302
Largest diff. peak/hole / e Å ⁻³	2.01/-1.10

IUCr's Checkcif provided two level B errors

```
# start Validation Reply Form
_vrf_PLAT434_gb_rj_rn_12222017b_0m_a_sq_sq
PROBLEM: Short Inter HL..HL Contact F10 ..F23A      2.41 Ang.
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
_vrf_PLAT434_gb_rj_rn_12222017b_0m_a_sq_sq
PROBLEM: Short Inter HL..HL Contact F30 ..F48      2.48 Ang.
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
# end Validation Reply Form
```



Solid state structure of **2c**. Ellipsoids represent 50% probability. Hydrogen atoms except on methylene moiety have been omitted for clarity.

Supplementary Table 2

Crystal data and structure refinement for **Carbene 3c** - CCDC 1814371

Identification code	test3_a_sq
Empirical formula	C ₉₇ H ₄₁ F ₄₈ N
Formula weight	2132.31
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2/c
a/Å	23.874(3)
b/Å	36.280(4)
c/Å	16.899(2)
$\alpha/^\circ$	90
$\beta/^\circ$	121.222(4)
$\gamma/^\circ$	90
Volume/Å ³	12517(3)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.131
μ/mm^{-1}	0.116
F(000)	4248.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	2.288 to 44.092
Index ranges	-25 ≤ h ≤ 25, -38 ≤ k ≤ 27, -17 ≤ l ≤ 17
Reflections collected	21662
Independent reflections	7469 [R_{int} = 0.0596, R_{sigma} = 0.0818]
Data/restraints/parameters	7469/178/745
Goodness-of-fit on F ²	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0757, wR_2 = 0.2193
Final R indexes [all data]	R_1 = 0.1252, wR_2 = 0.2528
Largest diff. peak/hole / e Å ⁻³	0.36/-0.29

IUCr's Checkcif provided one level A error and two level B errors

start Validation Reply Form;

_vrf_THETM01_test3_a_sq;

PROBLEM: The value of sine(theta_max)/wavelength is less than 0.550

RESPONSE: Data were collected on high brilliance rotating anode. Poorly diffracting crystals. Despite numerous attempts no diffraction was observed beyond 0.95 resolutions

;

_vrf_PLAT230_test3_a_sq;

PROBLEM: Hirshfeld Test Diff for C6 --C7 . 9.4 s.u.

RESPONSE: Thermal motion of the atoms

;

_vrf_PLAT411_test3_a_sq;

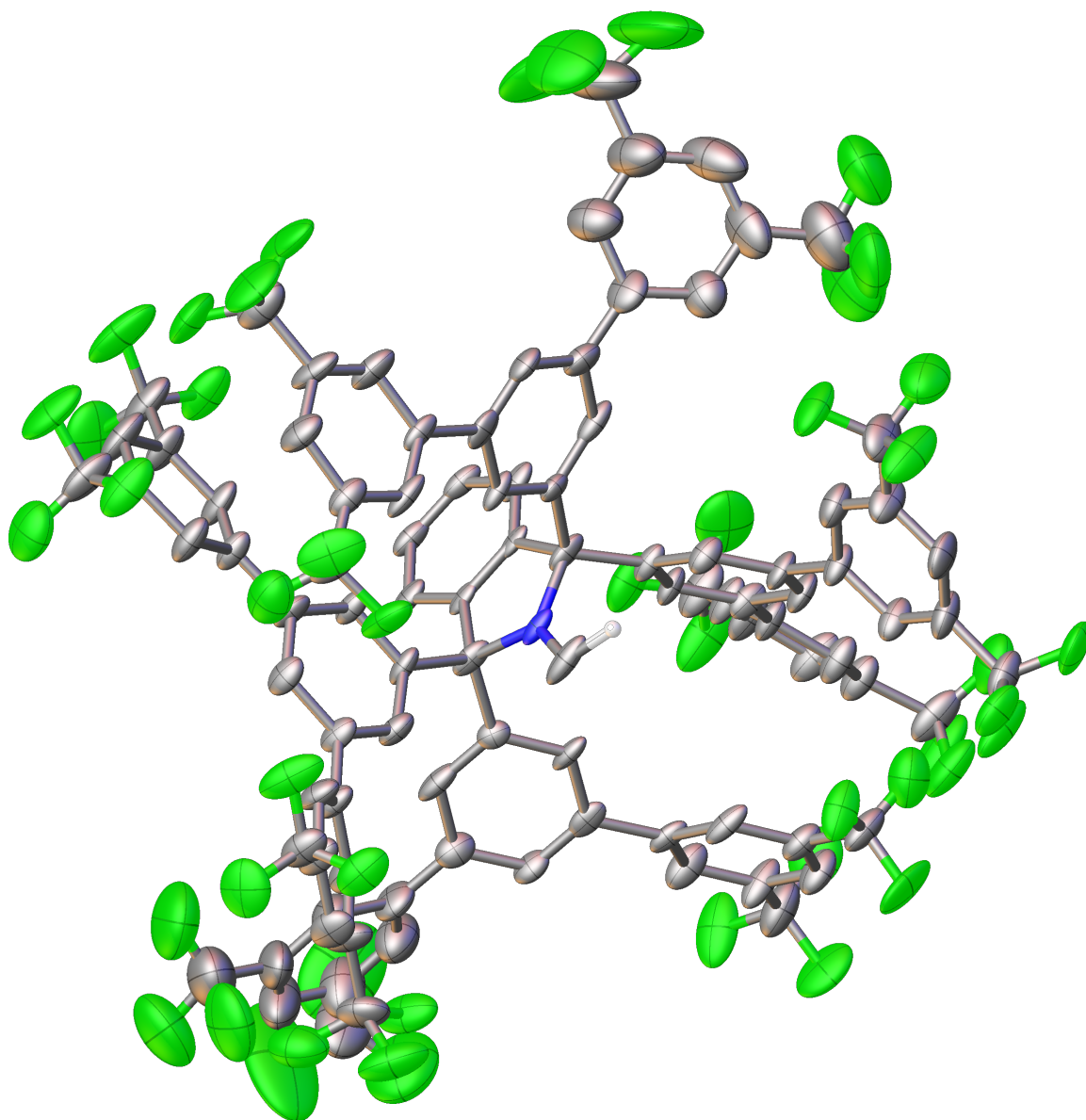
PROBLEM: Short Inter H...H Contact H1 ..H37 . 1.86 Ang.

RESPONSE: The location of H1 was determined according to residual density around the C1 carbon atom.

However due to the thermal motion of C1 and the quality of the data, it could not reliably be refined and was fixed with the FIX xyz command.

;

end Validation Reply Form



Solid state structure of **3c**. Ellipsoids represent 50% probability. Hydrogen atoms except on carbene carbon have been omitted for clarity.

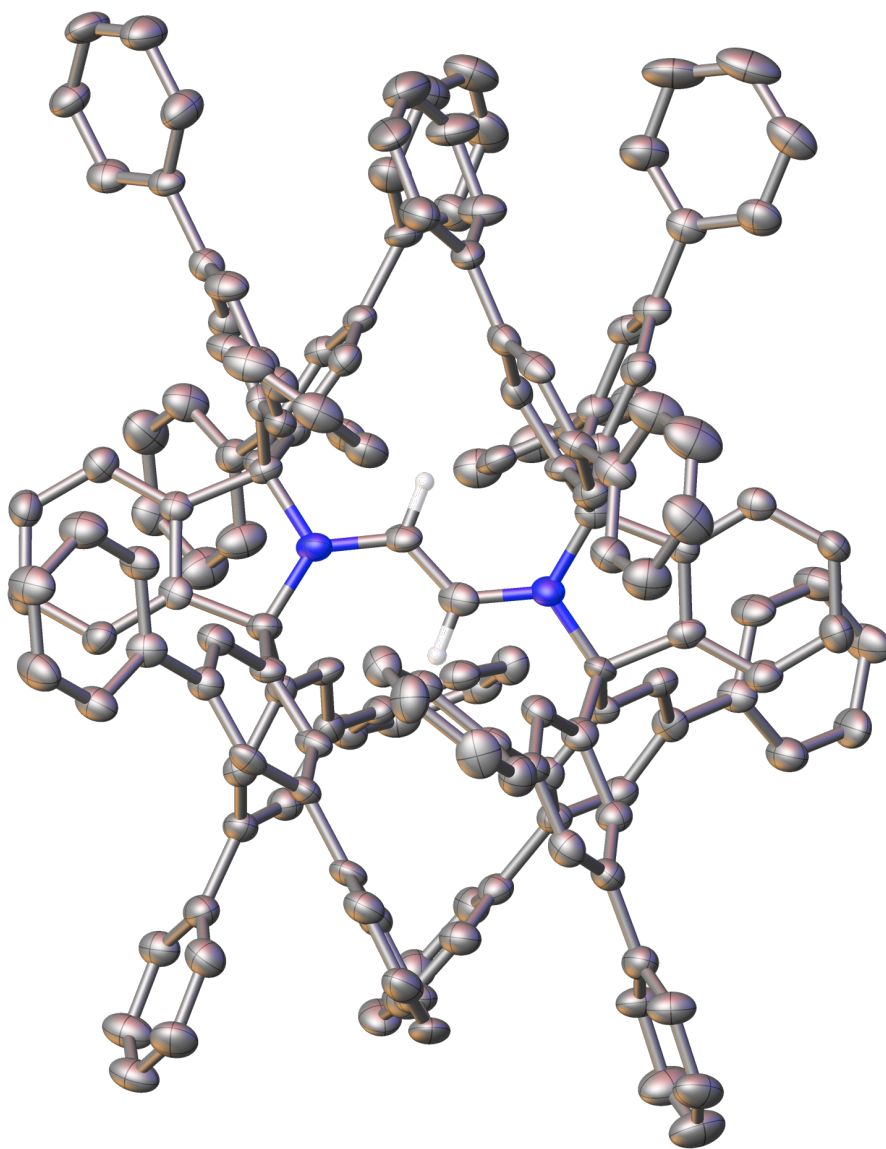
Supplementary Table 3

Crystal data and structure refinement for **4b** - CCDC 1814370

Identification code	gb_rj_rn_3_0m_sq_sq
Empirical formula	C ₁₆₂ H ₁₁₄ N ₂
Formula weight	2088.55
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	17.7766(9)
b/Å	35.1897(16)
c/Å	23.8464(14)
α /°	90
β /°	103.983(4)
γ /°	90
Volume/Å ³	14475.2(13)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	0.958
μ/mm^{-1}	0.414
F(000)	4400.0
Crystal size/mm ³	0.3 × 0.1 × 0.1
Radiation	CuK α (λ = 1.54178)
2 θ range for data collection/°	4.57 to 112.512
Index ranges	-19 ≤ h ≤ 16, -33 ≤ k ≤ 37, -25 ≤ l ≤ 23
Reflections collected	56452
Independent reflections	18864 [R _{int} = 0.1471, R _{sigma} = 0.1678]
Data/restraints/parameters	18864/0/1477
Goodness-of-fit on F ²	0.930
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0740, wR ₂ = 0.1632
Final R indexes [all data]	R ₁ = 0.1600, wR ₂ = 0.2007
Largest diff. peak/hole / e Å ⁻³	0.24/-0.24

IUCr's Checkcif provided one level A error

```
# start Validation Reply Form;
_vrf_THETM01_gb_rj_rn_3_0m_sq_sq
;
PROBLEM: The value of sine(theta_max)/wavelength is less than 0.550
RESPONSE: Data were collected on high brilliance rotating anode. Poorly diffracting crystals. Despite numerous
attempts no diffraction was observed beyond 0.93 resolutions
;
# end Validation Reply Form
```



Solid state structure of **4b**. Ellipsoids represent 50% probability. Hydrogen atoms except on alkenyl moiety and solvent molecules (toluene) have been omitted for clarity.

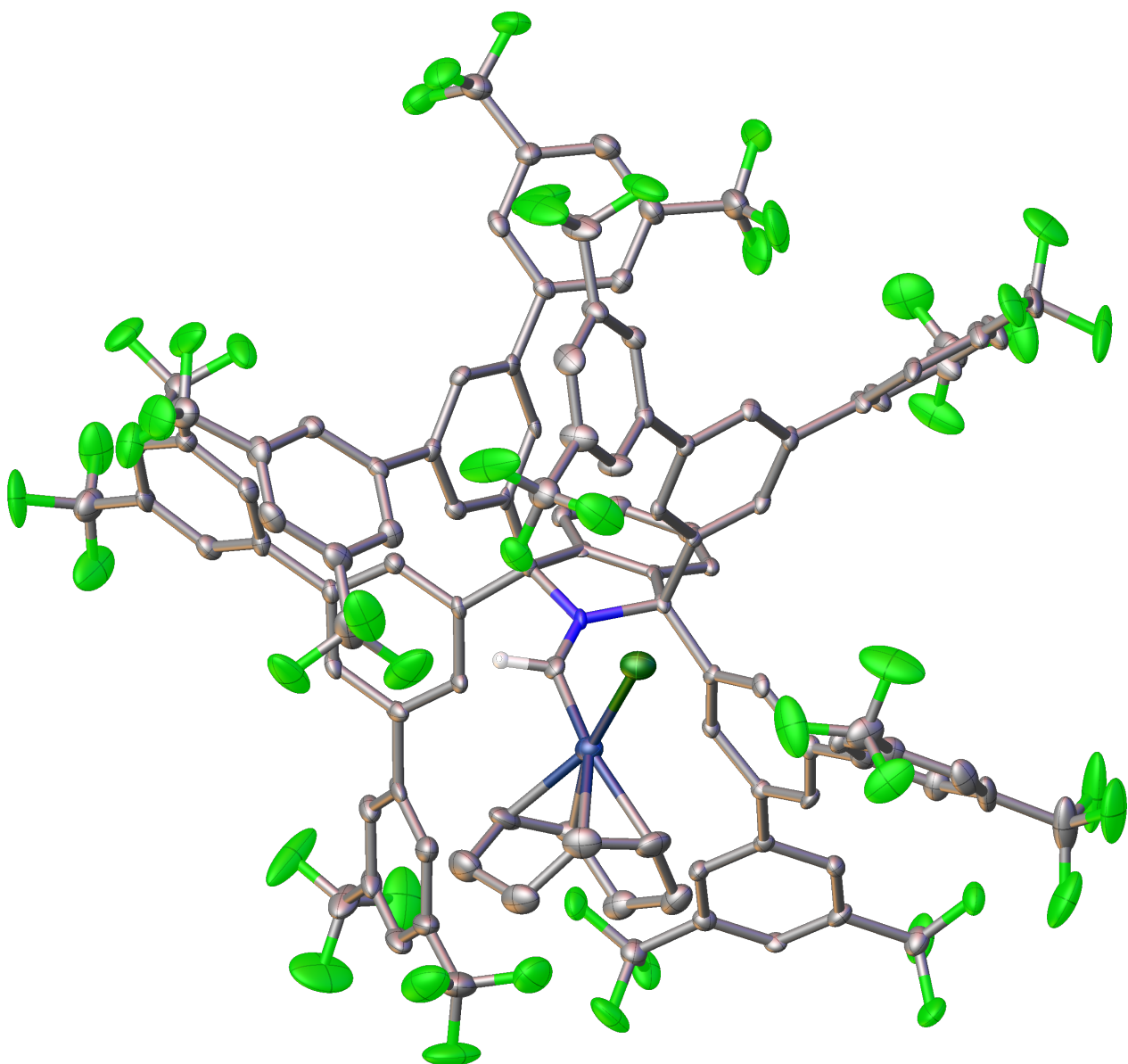
Supplementary Table 4

Crystal data and structure refinement for **(3c)Rh(cod)Cl** - CCDC 1814368

Identification code	GB_RJ_RN_Rh_10182017_0m
Empirical formula	C ₁₀₅ H ₅₃ ClF ₄₈ NRh
Formula weight	2378.84
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	18.6162(11)
b/Å	23.3966(13)
c/Å	23.6243(12)
$\alpha/^\circ$	90
$\beta/^\circ$	106.741(3)
$\gamma/^\circ$	90
Volume/Å ³	9853.6(10)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.604
μ/mm^{-1}	0.341
F(000)	4736.0
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	2.504 to 50.806
Index ranges	-22 ≤ h ≤ 22, -24 ≤ k ≤ 28, -28 ≤ l ≤ 28
Reflections collected	71203
Independent reflections	18051 [R_{int} = 0.0685, R_{sigma} = 0.0801]
Data/restraints/parameters	18051/277/1513
Goodness-of-fit on F ²	1.030
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0661, wR_2 = 0.1734
Final R indexes [all data]	R_1 = 0.1137, wR_2 = 0.2026
Largest diff. peak/hole / e Å ⁻³	1.22/-1.32

IUCr's Checkcif provided two level B error

```
# start Validation Reply Form
_vrf_PLAT213_gb_rj_rn_rh_10182017_0m_a_sq;
PROBLEM: Atom F4 has ADP max/min Ratio
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
_vrf_PLAT213_gb_rj_rn_rh_10182017_0m_a_sq;
PROBLEM: Atom F40 has ADP max/min Ratio
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
# end Validation Reply Form
```



Solid state structure of **(3c)**Rh(cod)Cl. Ellipsoids represent 50% probability. Hydrogen atoms except on carbene carbon have been omitted for clarity.

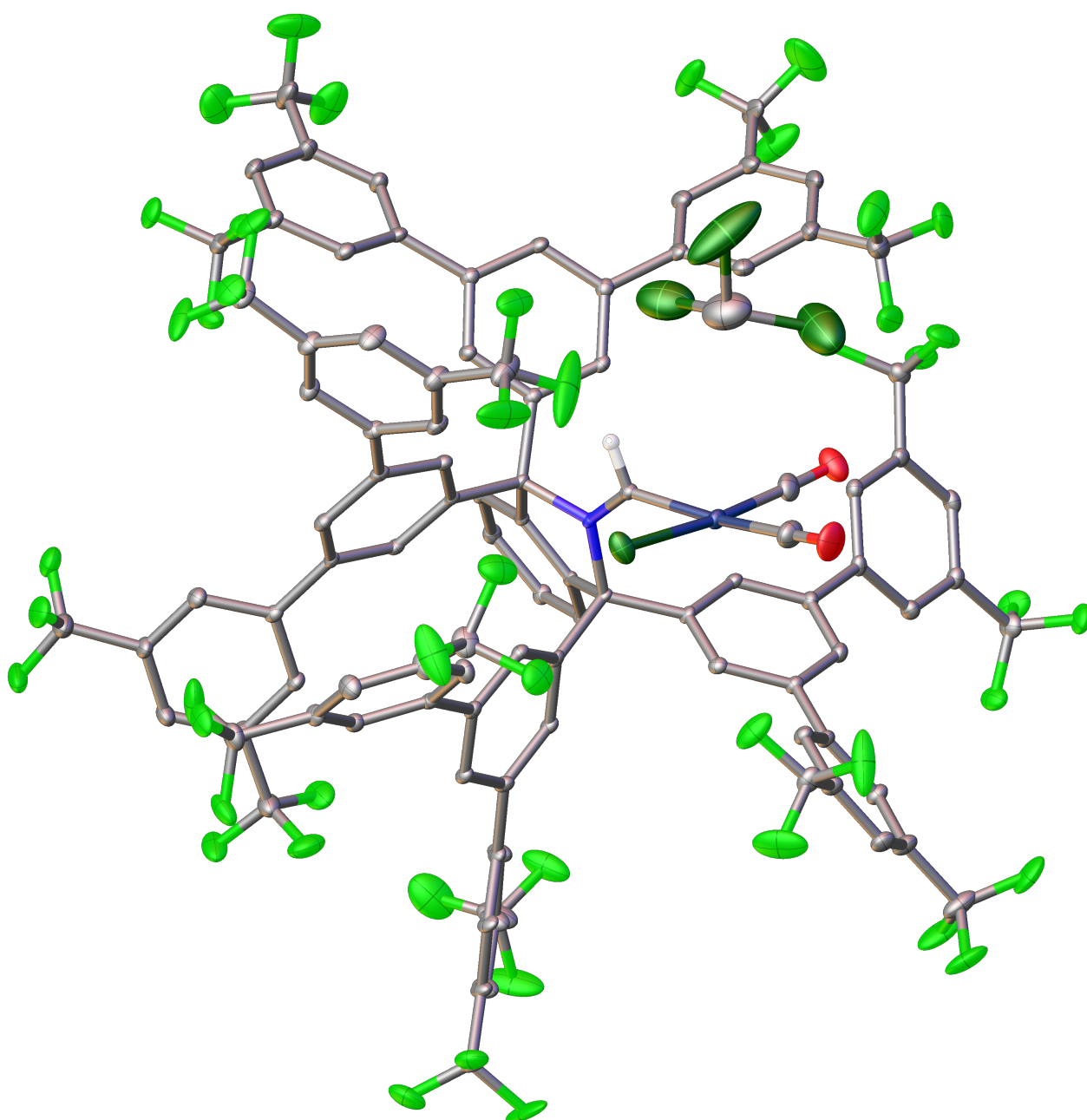
Supplementary Table 5

Crystal data and structure refinement for Compound 5 - CCDC 1835936

Identification code	GB_RN_01042018_Prelim_a_sq
Empirical formula	C ₁₀₀ H ₄₂ Cl ₄ F ₄₈ NO ₂ Rh
Formula weight	2446.05
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	18.5567(16)
b/Å	23.353(2)
c/Å	23.8508(18)
$\alpha/^\circ$	90
$\beta/^\circ$	105.989(2)
$\gamma/^\circ$	90
Volume/Å ³	9936.0(14)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.635
μ/mm^{-1}	0.420
F(000)	4840.0
Crystal size/mm ³	0.6 × 0.23 × 0.05
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	2.49 to 51.144
Index ranges	-22 ≤ h ≤ 22, -27 ≤ k ≤ 28, -28 ≤ l ≤ 28
Reflections collected	266174
Independent reflections	18396 [R_{int} = 0.0884, R_{sigma} = 0.0355]
Data/restraints/parameters	18396/117/1459
Goodness-of-fit on F ²	1.041
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0712, wR_2 = 0.1899
Final R indexes [all data]	R_1 = 0.0913, wR_2 = 0.2121
Largest diff. peak/hole / e Å ⁻³	1.88/-1.68

IUCr's Checkcif provided four level B error

```
# start Validation Reply Form
_vrf_PLAT213_prelim_a_sq;
PROBLEM: Atom F27 has ADP max/min Ratio ..... 4.6 prolat
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
_vrf_PLAT220_prelim_a_sq;
PROBLEM: Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 6.8 Ratio
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
_vrf_PLAT230_prelim_a_sq;
PROBLEM: Hirshfeld Test Diff for Cl4 --C04F . 7.1 s.u.
RESPONSE: Thermal motion of the atoms. Disordered CHCl3 molecule
;
_vrf_PLAT241_prelim_a_sq;
PROBLEM: High 'MainMol' Ueq as Compared to Neighbors of Cl2 Check
RESPONSE: Problem originates from a disordered CHCl3 molecule.
;
_vrf_PLAT242_prelim_a_sq;
PROBLEM: Low 'MainMol' Ueq as Compared to Neighbors of C04F Check
RESPONSE: Problem originates from a disordered CHCl3 molecule.
;
# end Validation Reply Form
```



Solid state structure of **5**. Ellipsoids represent 50% probability. Hydrogen atoms except on carbene carbon have been omitted for clarity.

Supplementary Table 6

Crystal data and structure refinement for Compound 7 - CCDC 1814367

Identification code	GB_RJ_RNSe2_0m
Empirical formula	C ₉₇ H ₄₁ F ₄₈ NSe
Formula weight	2211.27
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	15.7628(4)
b/Å	17.8043(4)
c/Å	18.6294(4)
$\alpha/^\circ$	91.0630(10)
$\beta/^\circ$	95.7110(10)
$\gamma/^\circ$	97.3210(10)
Volume/Å ³	5157.3(2)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.424
μ/mm^{-1}	1.680
F(000)	2192.0
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	CuK α (λ = 1.54178)
2 θ range for data collection/ $^\circ$	4.77 to 118.068
Index ranges	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	73458
Independent reflections	14651 [R_{int} = 0.1033, R_{sigma} = 0.0632]
Data/restraints/parameters	14651/192/1452
Goodness-of-fit on F ²	1.194
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0949, wR_2 = 0.2550
Final R indexes [all data]	R_1 = 0.1365, wR_2 = 0.2882
Largest diff. peak/hole / e Å ⁻³	1.33/-0.84

IUCr's Checkcif provided one level B error

start Validation Reply Form;

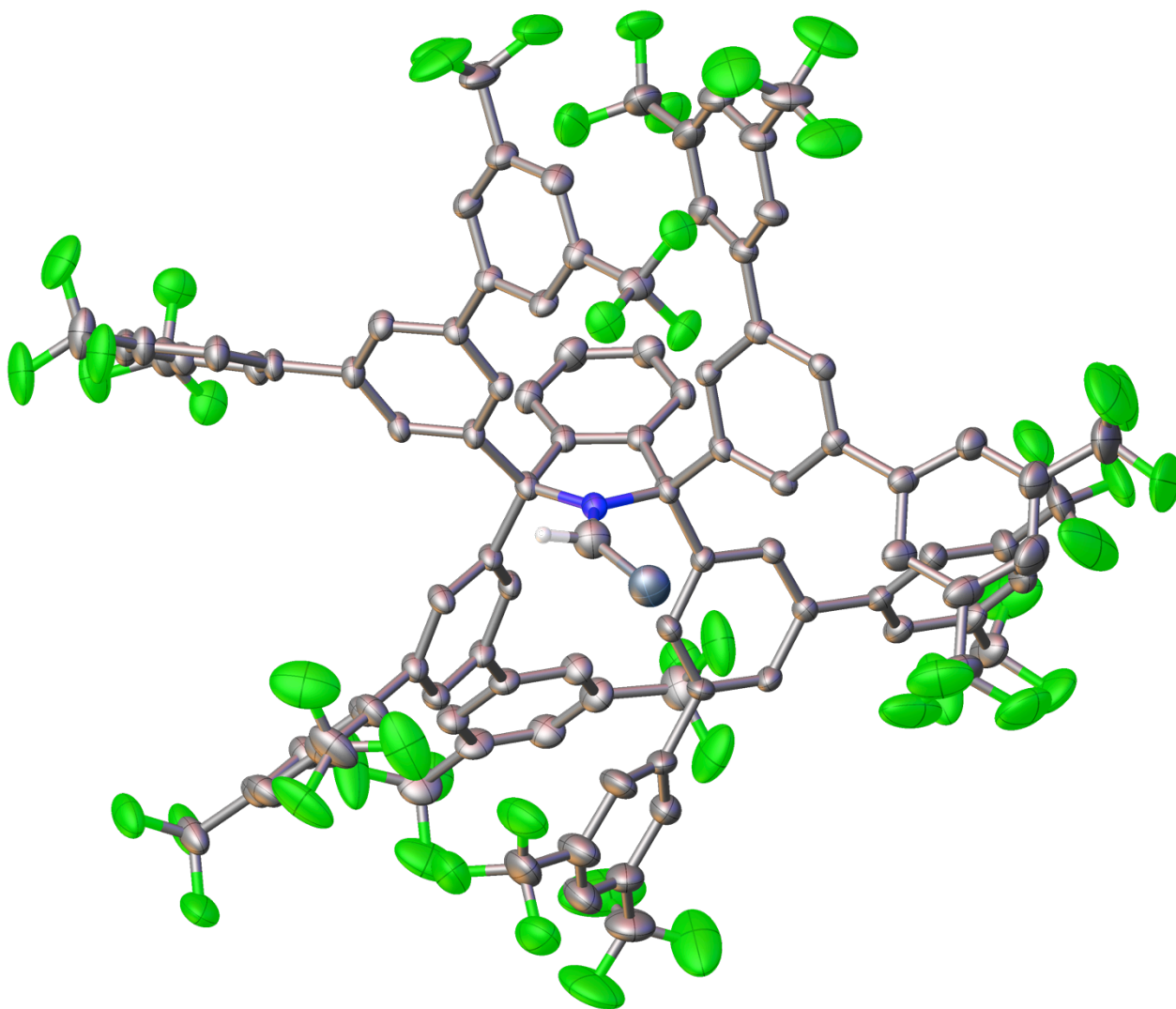
_vrf_THETM01__gb_rj_rnse2_0m_a_sq;

PROBLEM: The value of sine(theta_max)/wavelength is less than 0.575

RESPONSE: Data were collected on high brilliance rotating anode. Poorly diffracting crystals. Despite numerous attempts no diffraction was observed beyond 0.90 resolutions

;

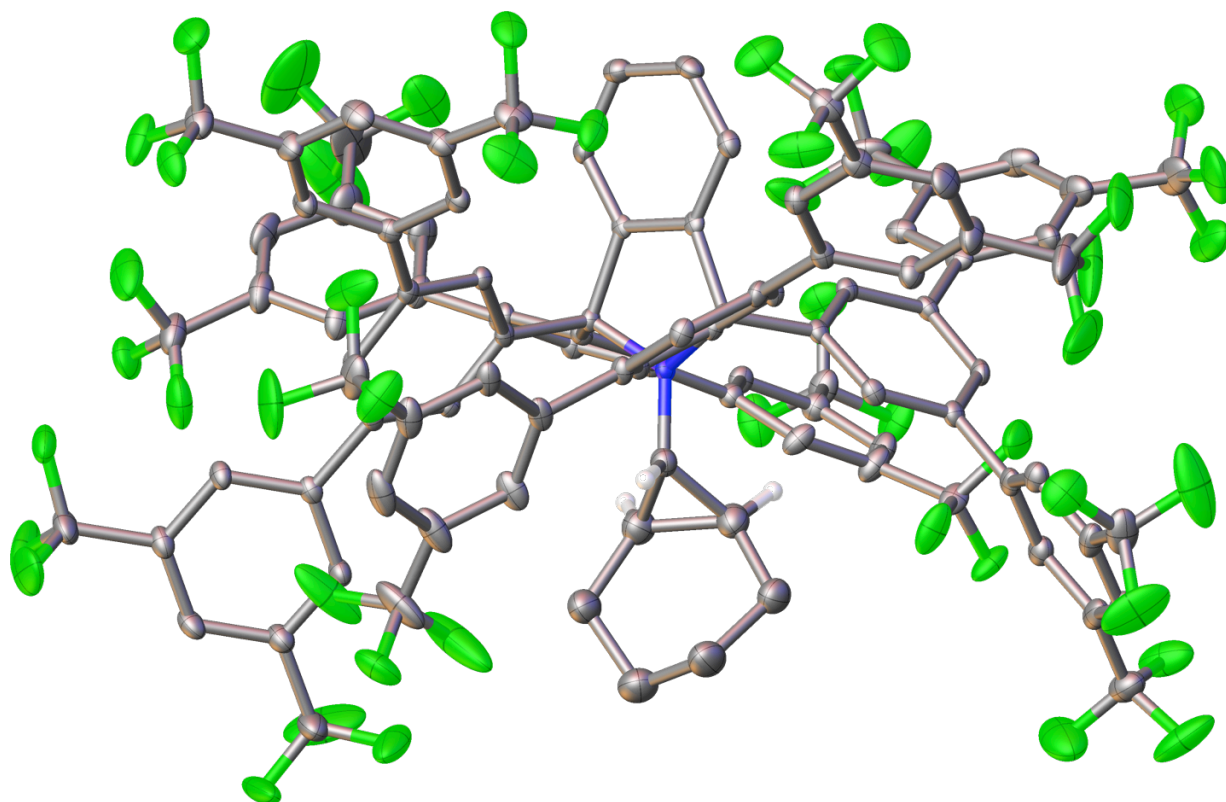
end Validation Reply Form



Solid state structure of **7**. Ellipsoids represent 50% probability. Hydrogen atoms except on selenoformamide have been omitted for clarity.

Supplementary Table 7**Crystal data and structure refinement for Compound 8 - CCDC 1814369**

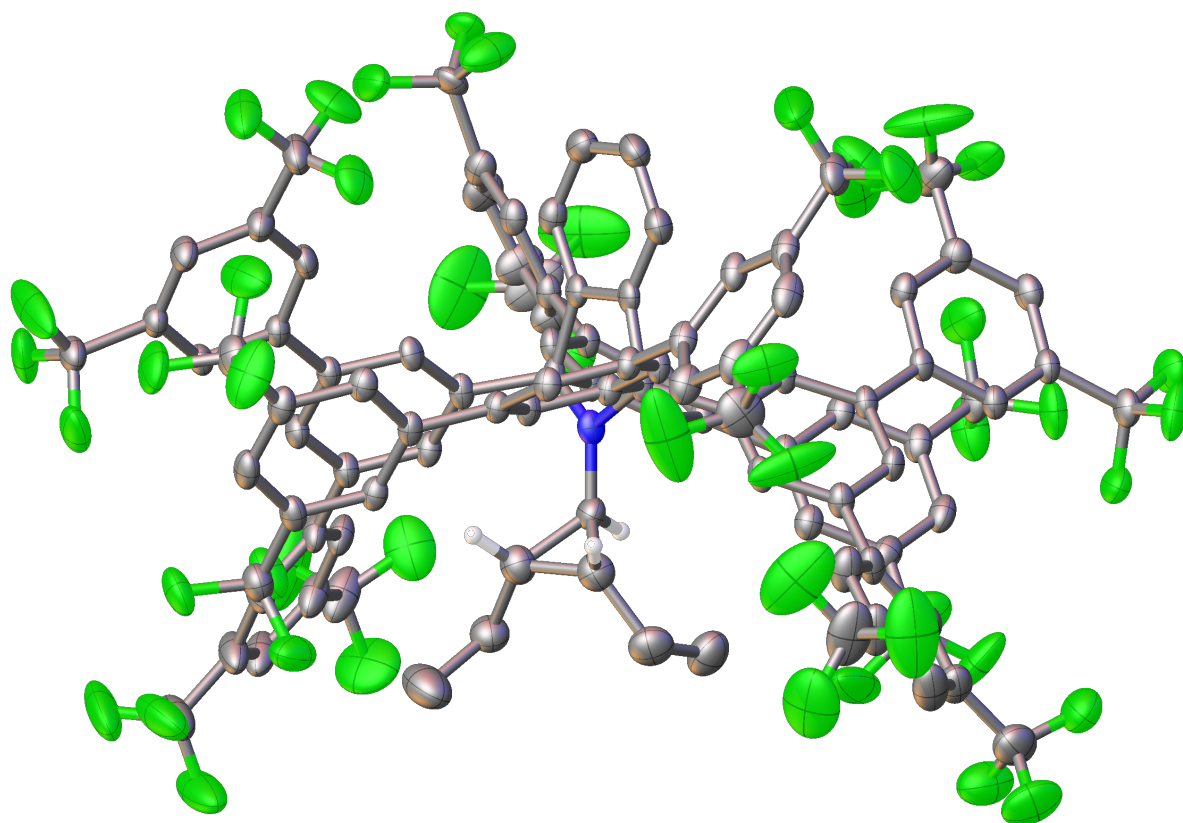
Identification code	GB_RJ_RN_113017
Empirical formula	C ₁₀₃ H ₅₁ F ₄₈ N
Formula weight	2214.45
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	15.6809(6)
b/Å	17.3369(8)
c/Å	19.2948(8)
$\alpha/^\circ$	85.082(2)
$\beta/^\circ$	78.7610(10)
$\gamma/^\circ$	81.200(2)
Volume/Å ³	5075.8(4)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.449
μ/mm^{-1}	0.146
F(000)	2216.0
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	2.38 to 50.904
Index ranges	-16 ≤ h ≤ 18, -20 ≤ k ≤ 20, -23 ≤ l ≤ 23
Reflections collected	86301
Independent reflections	18677 [R_{int} = 0.0355, R_{sigma} = 0.0348]
Data/restraints/parameters	18677/297/1562
Goodness-of-fit on F ²	1.023
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0615, wR_2 = 0.1385
Final R indexes [all data]	R_1 = 0.0840, wR_2 = 0.1506
Largest diff. peak/hole / e Å ⁻³	0.68/-0.67



Solid state structure of **8**. Ellipsoids represent 50% probability. Hydrogen atoms except on cyclopropane moiety have been omitted for clarity.

Supplementary Table 8**Crystal data and structure refinement for Compound 9 - CCDC 1814372**

Identification code	GB_RJ_RN_112917_0m
Empirical formula	C ₁₀₃ H ₅₃ F ₄₈ N
Formula weight	2216.46
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	16.0386(8)
b/Å	18.5013(12)
c/Å	18.5527(12)
$\alpha/^\circ$	107.434(2)
$\beta/^\circ$	114.354(2)
$\gamma/^\circ$	90.861(2)
Volume/Å ³	4723.7(5)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.558
μ/mm^{-1}	0.157
F(000)	2220.0
Crystal size/mm ³	0.2 × 0.2 × 0.1
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/ $^\circ$	3.366 to 50.812
Index ranges	-19 ≤ h ≤ 19, -22 ≤ k ≤ 22, -22 ≤ l ≤ 22
Reflections collected	74556
Independent reflections	17345 [R_{int} = 0.0327, R_{sigma} = 0.0311]
Data/restraints/parameters	17345/204/1481
Goodness-of-fit on F ²	1.017
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0629, wR_2 = 0.1588
Final R indexes [all data]	R_1 = 0.0901, wR_2 = 0.1788
Largest diff. peak/hole / e Å ⁻³	0.71/-0.54



Solid state structure of **9**. Ellipsoids represent 50% probability. Hydrogen atoms except on cyclopropane moiety have been omitted for clarity.

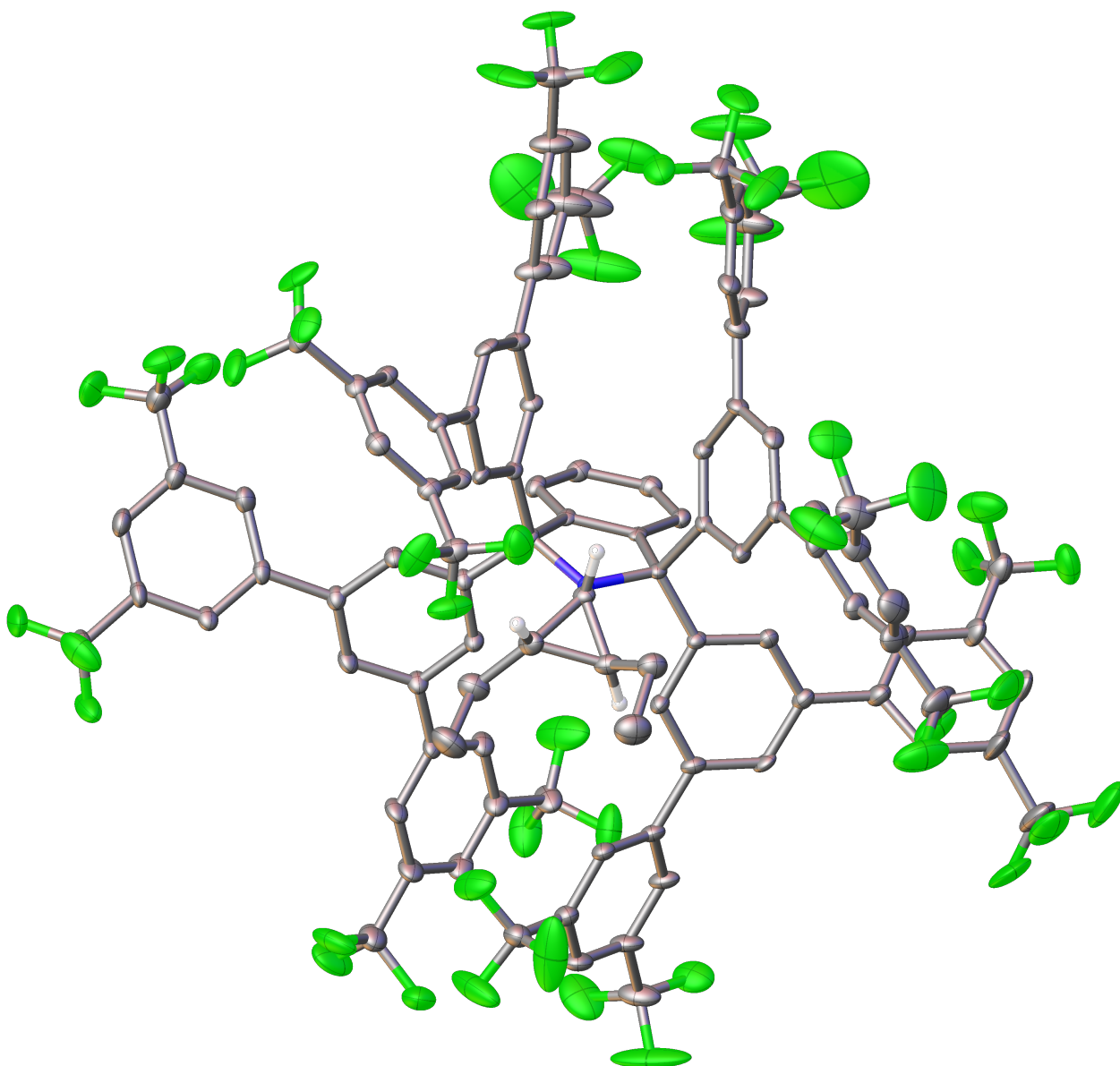
Supplementary Table 9

Crystal data and structure refinement for Compound 10 - CCDC 1835937

Identification code	GB_RJ_RN_20180329_0m_a_sq_sq
Empirical formula	C ₁₀₃ H ₅₃ F ₄₈ N
Formula weight	2216.46
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	14.9856(9)
b/Å	15.4379(9)
c/Å	27.5452(16)
α/°	104.1490(10)
β/°	92.4820(10)
γ/°	117.0170(10)
Volume/Å ³	5416.3(6)
Z	2
ρ _{calc} /g/cm ³	1.359
μ/mm ⁻¹	0.137
F(000)	2220.0
Crystal size/mm ³	0.25 × 0.032 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.028 to 49.65
Index ranges	-17 ≤ h ≤ 16, -16 ≤ k ≤ 18, -32 ≤ l ≤ 32
Reflections collected	81825
Independent reflections	18596 [R _{int} = 0.0436, R _{sigma} = 0.0445]
Data/restraints/parameters	18596/347/1530
Goodness-of-fit on F ²	1.015
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0882, wR ₂ = 0.2312
Final R indexes [all data]	R ₁ = 0.1247, wR ₂ = 0.2601
Largest diff. peak/hole / e Å ⁻³	1.05/-0.76

IUCr's Checkcif provided four level B error

```
# start Validation Reply Form
_vrf_PLAT097_gb_rj_rn_20180329_0m_a_sq_sq;
PROBLEM: Large Reported Max. (Positive) Residual Density      1.05 eA-3
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
_vrf_PLAT213_gb_rj_rn_20180329_0m_a_sq_sq;
PROBLEM: Atom F17A      has ADP max/min Ratio .....      4.2 prolat
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.;
_vrf_PLAT220_gb_rj_rn_20180329_0m_a_sq_sq
;
PROBLEM: Non-Solvent Resd 1 C  Ueq(max)/Ueq(min) Range      7.7 Ratio
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
_vrf_PLAT241_gb_rj_rn_20180329_0m_a_sq_sq;
PROBLEM: High 'MainMol' Ueq as Compared to Neighbors of      F16 Check
RESPONSE: Problem originates from multiple highly disordered CF3 fragments.
;
# end Validation Reply Form
```



Solid state structure of **10**. Ellipsoids represent 50% probability. Hydrogen atoms except on cyclopropane moiety have been omitted for clarity.

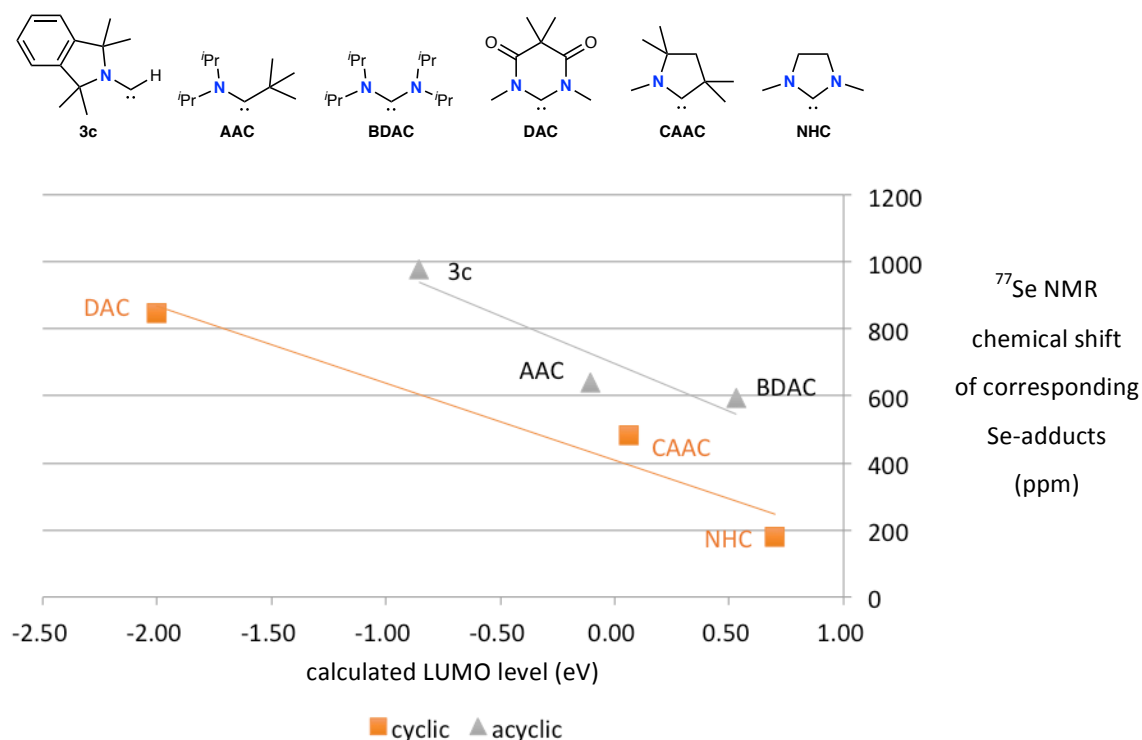
V. Supplementary Data and Figure 57

All calculations were performed with the Gaussian09 program package.⁸ The theoretical approach is based on the framework of density functional theory (DFT).

All calculations were performed with the B3LYP functional^{9–11} using Pople's 6-31G*¹² or Ahlrich's def2-TZVPP basis set.^{13,14} Ground states were fully optimized without constraints at the corresponding level of theory and uniquely characterized by occurrence of no imaginary frequencies and verified by the corresponding frequency calculation. NMR shielding tensors were computed with the Gauge-Independent Atomic Orbital (GIAO) method implemented in Gaussian09 program packages.^{15–19} Gibbs free reaction energies and enthalpies were calculated for standard conditions ($p = 1$ atm, $T = 298$ K) and are unscaled.

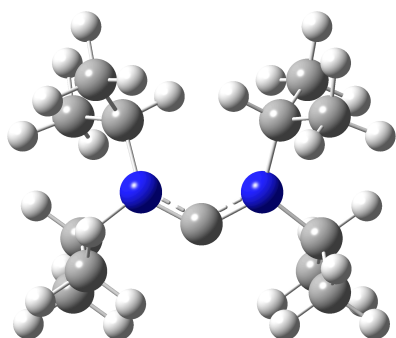
Correlation between the calculated LUMO and the experimentally determined π -accepting ability

In Supplementary Figure 57, the calculated LUMO energy (B3LYP/def2-TZVPP) and the experimentally determined π -accepting ability (^{77}Se NMR chemical shifts of the corresponding Se-adducts) of cyclic and acyclic carbenes are plotted. A linear correlation is observed if acyclic carbenes (**3c**, **AAC**, and **BDAC**) and cyclic carbenes (**DAC**, **CAAC**, and **NHC**) are treated as separated groups. This trend suggests that the direct comparison between an acyclic and a cyclic carbene based on their LUMO levels could be erroneous. It is illustrated when comparing BDAC and NHC; while the calculated LUMO of **BDAC** (+0.53 eV) and **NHC** (+0.70 eV) are quite close, their ^{77}Se NMR chemical shifts of the corresponding Se-adducts are significantly different (+593 and +181 ppm, respectively).



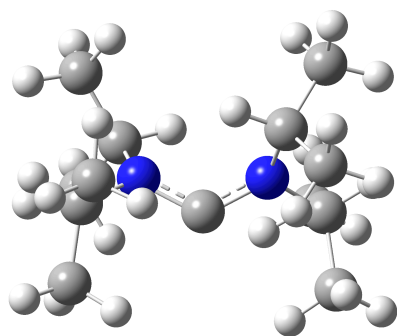
Supplementary Figure 57. Correlation between the calculated LUMO levels (B3LYP/def2-TZVPP) and the experimentally determined π -accepting ability (^{77}Se NMR chemical shifts of the Se-adducts) of cyclic and acyclic carbenes.

bis(diisopropylamino)carbene (singlet state)



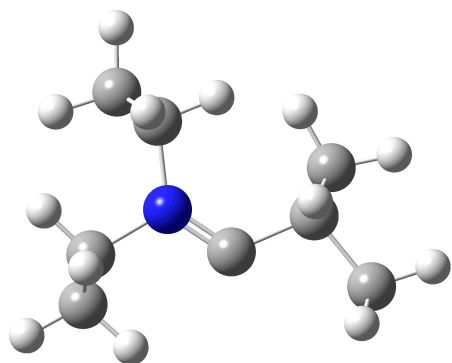
C	0.000001	-0.688635	-0.000026
N	1.185838	-0.062514	-0.039758
C	2.347524	-0.966445	-0.290435
H	3.233670	-0.332029	-0.282763
C	2.260366	-1.604866	-1.676206
H	3.152383	-2.202198	-1.876565
H	1.384673	-2.249724	-1.735074
H	2.176838	-0.844070	-2.453836
C	2.510173	-2.022311	0.802636
H	3.386654	-2.641246	0.601347
H	2.636292	-1.563706	1.783638
H	1.627021	-2.657615	0.833590
C	1.542310	1.342078	0.311269
H	0.627967	1.808247	0.657156
C	2.071854	2.133834	-0.887753
H	3.011415	1.717587	-1.254841
H	1.360734	2.123937	-1.714318
H	2.259687	3.173341	-0.610360
C	2.505925	1.419210	1.503846
H	2.625564	2.462446	1.801899
H	2.113091	0.867427	2.357281
H	3.498067	1.032374	1.273240
N	-1.185842	-0.062525	0.039729
C	-2.347516	-0.966462	0.290436
H	-3.233657	-0.332038	0.282881
C	-2.510266	-2.022254	-0.802693
H	-1.627118	-2.657559	-0.833766
H	-3.386731	-2.641198	-0.601371
H	-2.636466	-1.563582	-1.783653
C	-2.260252	-1.604978	1.676156
H	-2.176652	-0.844236	2.453831
H	-3.152261	-2.202312	1.876548
H	-1.384563	-2.249852	1.734910
C	-1.542317	1.342085	-0.311221
H	-0.627966	1.808283	-0.657047
C	-2.505887	1.419296	-1.503830
H	-2.625500	2.462551	-1.801828
H	-2.113027	0.867558	-2.357282
H	-3.498043	1.032461	-1.273286
C	-2.071912	2.133758	0.887834
H	-3.011484	1.717478	1.254857
H	-1.360824	2.123809	1.714427
H	-2.259742	3.173282	0.610505

bis(diisopropylamino)carbene (triplet state)



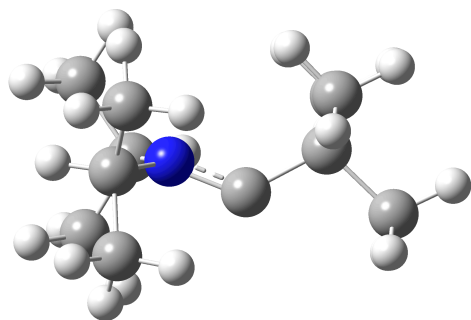
C	-0.000001	0.000004	0.597827
N	1.216406	-0.079545	-0.041587
C	2.237944	-0.977524	0.527773
H	3.168067	-0.750495	0.005123
C	1.889709	-2.440807	0.245252
H	2.661069	-3.103429	0.641695
H	0.942423	-2.702017	0.718881
H	1.799698	-2.620860	-0.826257
C	2.475884	-0.751431	2.026764
H	3.282226	-1.395492	2.383161
H	2.747718	0.282424	2.235640
H	1.572887	-0.982905	2.591809
C	1.665910	1.088723	-0.839949
H	0.736751	1.578201	-1.132834
C	2.378394	0.655502	-2.123101
H	3.339752	0.179803	-1.921848
H	1.764710	-0.044434	-2.690234
H	2.574027	1.526150	-2.751814
C	2.496312	2.098820	-0.041179
H	2.684941	2.993066	-0.638918
H	1.967847	2.399718	0.863419
H	3.465463	1.686895	0.246512
N	-1.216409	0.079545	-0.041588
C	-2.237947	0.977530	0.527765
H	-3.168073	0.750491	0.005125
C	-2.475875	0.751458	2.026761
H	-1.572874	0.982943	2.591796
H	-3.282217	1.395521	2.383155
H	-2.747703	-0.282395	2.235654
C	-1.889716	2.440809	0.245221
H	-1.799713	2.620846	-0.826290
H	-2.661073	3.103436	0.641661
H	-0.942426	2.702027	0.718840
C	-1.665911	-1.088733	-0.839936
H	-0.736751	-1.578220	-1.132801
C	-2.496327	-2.098814	-0.041159
H	-2.684946	-2.993074	-0.638881
H	-1.967878	-2.399692	0.863456
H	-3.465484	-1.686883	0.246506
C	-2.378376	-0.655534	-2.123106
H	-3.339739	-0.179835	-1.921876
H	-1.764685	0.044394	-2.690240
H	-2.573996	-1.526193	-2.751808

(diisopropylamino)(*tert*-butyl)carbene (singlet state)



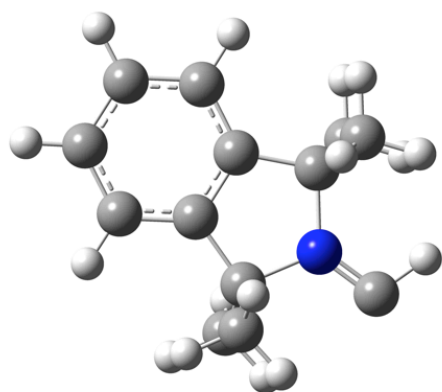
C	0.549683	-0.811066	0.000001
C	1.953456	-0.201468	-0.000004
C	2.243971	0.615910	1.278726
H	3.312235	0.833359	1.344482
H	1.715304	1.566774	1.320588
H	1.971630	0.042199	2.166806
C	2.243887	0.616439	-1.278407
H	1.971428	0.043127	-2.166710
H	1.715288	1.567355	-1.319809
H	3.312159	0.833847	-1.344169
C	2.927734	-1.399768	-0.000284
H	3.967896	-1.062483	-0.000256
H	2.762061	-2.024214	0.877582
H	2.761997	-2.023858	-0.878393
N	-0.533858	-0.093923	0.000028
C	-1.835199	-0.860350	-0.000007
H	-2.630632	-0.116491	-0.000027
C	-1.965756	-1.703291	1.264178
H	-2.920547	-2.231754	1.265018
H	-1.155391	-2.429398	1.303996
H	-1.918623	-1.084863	2.161503
C	-1.965687	-1.703275	-1.264210
H	-2.920473	-2.231746	-1.265106
H	-1.918515	-1.084829	-2.161522
H	-1.155313	-2.429372	-1.303999
C	-0.702231	1.400950	-0.000001
H	0.300928	1.804179	-0.000004
C	-1.394466	1.896120	1.271339
H	-2.429736	1.561092	1.339701
H	-0.866420	1.555551	2.161661
H	-1.403749	2.987515	1.280127
C	-1.394484	1.896059	-1.271352
H	-1.403808	2.987454	-1.280181
H	-0.866431	1.555475	-2.161664
H	-2.429742	1.560990	-1.339698

(diisopropylamino)(*tert*-butyl)carbene (triplet state)



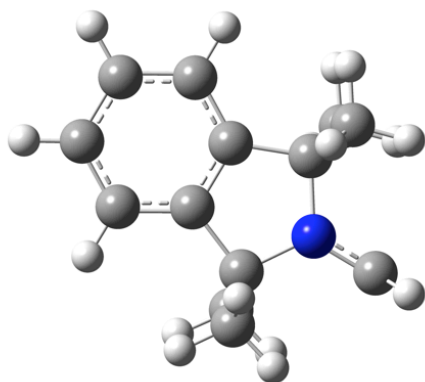
C	0.625255	-0.009736	-0.631247
C	2.020251	0.171414	-0.081980
C	2.390223	-0.948032	0.914736
H	2.331445	-1.928645	0.440846
H	3.412606	-0.810177	1.276101
H	1.725139	-0.942700	1.778068
C	2.142381	1.531461	0.641946
H	1.934767	2.359255	-0.037509
H	1.451686	1.593465	1.484076
H	3.155673	1.661742	1.030082
C	3.007081	0.138687	-1.260756
H	4.031630	0.278271	-0.908953
H	2.952986	-0.816113	-1.785226
H	2.779164	0.926632	-1.979345
N	-0.584875	0.028819	0.001756
C	-1.420876	-1.198113	0.069488
H	-2.434031	-0.854581	0.278824
C	-0.998887	-2.104305	1.227089
H	-1.694043	-2.940783	1.322157
H	-0.003449	-2.514494	1.060634
H	-0.989784	-1.557320	2.169738
C	-1.455891	-1.971527	-1.252738
H	-2.139645	-2.818402	-1.171810
H	-1.787825	-1.339383	-2.075185
H	-0.465802	-2.352178	-1.503360
C	-1.306698	1.331097	-0.008201
H	-0.518233	2.076680	-0.100295
C	-2.030789	1.583648	1.315515
H	-2.863655	0.895339	1.467748
H	-1.347418	1.482296	2.158479
H	-2.440399	2.595172	1.326657
C	-2.235976	1.500234	-1.214844
H	-2.653895	2.508552	-1.228218
H	-1.686733	1.346470	-2.143418
H	-3.072493	0.800204	-1.186432

mono-substituted carbene (singlet state)



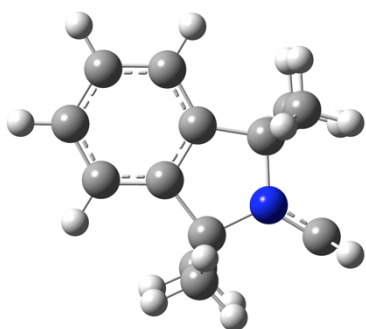
C	-2.87901000	0.12731000	0.00019100
N	-1.59213200	0.03006000	-0.00011000
C	-0.72050300	1.27345400	0.00000100
C	0.66920700	0.69033500	-0.00000900
C	0.65256800	-0.69804000	-0.00004400
C	-0.75240400	-1.24505200	-0.00007800
C	1.87754500	1.37773900	0.00001500
C	3.06851300	0.66010400	0.00000700
C	3.05110000	-0.73302300	-0.00002500
C	1.84140400	-1.41860300	-0.00005100
H	-3.30667300	-0.89078000	0.00042100
H	1.89776400	2.46011800	0.00003800
H	4.01386700	1.18638800	0.00002500
H	3.98247400	-1.28361600	-0.00003300
H	1.83323300	-2.50137600	-0.00008100
C	-1.01193200	2.09649800	-1.25826700
H	-0.80243200	1.52136700	-2.16028100
H	-2.06195600	2.38507800	-1.26397600
H	-0.39304400	2.99435100	-1.27339900
C	-1.01198400	2.09627000	1.25841700
H	-2.06200600	2.38486900	1.26412500
H	-0.80253900	1.52096700	2.16033400
H	-0.39308900	2.99411500	1.27375600
C	-1.05648900	-2.06053500	1.26061600
H	-0.84225800	-1.48513700	2.16041900
H	-2.10539100	-2.35802600	1.27886300
H	-0.44774100	-2.96516300	1.27944300
C	-1.05639300	-2.06061300	-1.26074200
H	-0.44763600	-2.96523700	-1.27946400
H	-2.10528500	-2.35812700	-1.27906100
H	-0.84209600	-1.48526900	-2.16056400

mono-substituted carbene (triplet state)



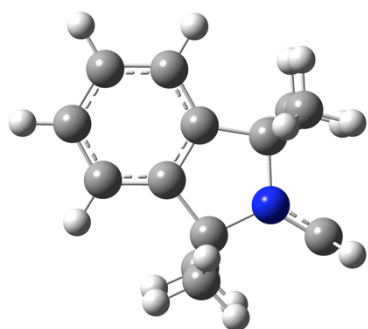
C	-2.89536700	-0.00000100	-0.04379800
N	-1.55028100	-0.00000100	-0.10825800
C	-0.74006500	1.25118700	0.00830700
C	0.66457300	0.69439500	-0.01254300
C	0.66457300	-0.69439500	-0.01254300
C	-0.74006400	-1.25118800	0.00830700
C	1.86164900	1.39928300	-0.01992000
C	3.06236600	0.69641300	-0.02913900
C	3.06236700	-0.69641100	-0.02914000
C	1.86165000	-1.39928200	-0.01992000
H	-3.57376600	0.00000700	-0.90139000
H	1.86838300	2.48198200	-0.01998300
H	4.00098900	1.23463300	-0.03737100
H	4.00099000	-1.23463000	-0.03737100
H	1.86838500	-2.48198100	-0.01998300
C	-1.02797100	2.17098700	-1.18640700
H	-0.80337400	1.66774500	-2.12621500
H	-2.07848100	2.46372700	-1.19061100
H	-0.42447100	3.07752200	-1.12658300
C	-1.04020900	1.98836800	1.32515300
H	-2.08751500	2.28834400	1.35587000
H	-0.83991400	1.34884600	2.18386400
H	-0.41873400	2.88084700	1.40932500
C	-1.04020700	-1.98836800	1.32515300
H	-0.83991500	-1.34884700	2.18386400
H	-2.08751300	-2.28834700	1.35586800
H	-0.41873200	-2.88084700	1.40932600
C	-1.02796900	-2.17098800	-1.18640700
H	-0.42447000	-3.07752300	-1.12658300
H	-2.07848000	-2.46372600	-1.19061200
H	-0.80337100	-1.66774500	-2.12621500

di(amido)carbene (singlet state)



N	1.150650	1.087786	-0.006053
N	-1.150630	1.087797	-0.006099
O	2.355196	-0.822795	-0.273049
O	-2.355233	-0.822769	-0.272860
C	1.274566	-0.305894	-0.113065
C	0.000018	1.802510	0.038558
C	-1.274584	-0.305869	-0.112978
C	-0.000006	-1.119982	0.052030
C	-0.000046	-2.304643	-0.925305
H	-0.000041	-1.961615	-1.960107
H	-0.889710	-2.908469	-0.765889
H	0.889590	-2.908516	-0.765904
C	0.000031	-1.641825	1.516778
H	0.000047	-0.824716	2.239188
H	0.888615	-2.249532	1.679222
H	-0.888550	-2.249524	1.679255
C	2.412074	1.843544	-0.020387
H	3.061543	1.502395	0.783690
H	2.931921	1.693666	-0.965050
H	2.156259	2.888471	0.109497
C	-2.412039	1.843589	-0.020507
H	-2.931734	1.693888	-0.965285
H	-3.061643	1.502313	0.783401
H	-2.156214	2.888489	0.109577

di(amido)carbene (triplet state)



N	1.195456	1.044682	0.041565
N	-1.195334	1.044771	0.041451
O	2.299098	-0.843198	-0.596338
O	-2.299144	-0.843012	-0.596385
C	1.275526	-0.326009	-0.188208
C	0.000076	1.606722	0.368375
C	-1.275525	-0.325873	-0.188272
C	-0.000039	-1.112928	0.152694
C	-0.000094	-2.444373	-0.598828
H	-0.000010	-2.288148	-1.676578
H	-0.889609	-3.013761	-0.339822
H	0.889307	-3.013898	-0.339712
C	-0.000143	-1.363516	1.684889
H	-0.000108	-0.431428	2.250357
H	0.885084	-1.935919	1.961012
H	-0.885486	-1.935792	1.960897
C	2.377226	1.892066	-0.111966
H	3.242445	1.241554	-0.189764
H	2.297801	2.500471	-1.013240
H	2.473325	2.543899	0.754930
C	-2.377061	1.892241	-0.111939
H	-2.298099	2.500039	-1.013667
H	-3.242451	1.241844	-0.188787
H	-2.472472	2.544669	0.754581

VI. Supplementary References

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