Supporting Information

C(sp^2)-H Activation with Pyridine Dicarbene Iron Dialkyl Complexes: Hydrogen Isotope Exchange of Arenes Using Benzene-d_6 as a Deuterium Source

Javier Corpas,[a,b] Peter Viereck[a] and Paul J. Chirik[a]*

[a]Department of Chemistry, Frick Laboratory
Princeton University, Princeton, NJ 08544, USA

[b]Department of Organic Chemistry, Universidad Autónoma de Madrid, c/ Fco. Tomás y Valiente 7, Cantoblanco 28049, Madrid (Spain).

**pchirik@princeton.edu*

Table of Contents

I. General Considerations

IA. Materials.

Compounds **[Fe]-1**, **[Fe]-2**, **[Fe]-3**, **[Fe]-5, and [Fe]-5-N_2** were prepared according to literature procedures.[1] All other substrates were purchased from commercial sources (Millipore Sigma, Alfa Aesar, TCI or Acros Organics) and used as received. Hydrogen gas was purchased from Air Gas and passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to a high vacuum line.

IB. Methods.

All air- and moisture-sensitive manipulations were carried out using a high vacuum Schlenk line (1 mmHg) or in an MBraun inert atmosphere (nitrogen) glovebox. Glassware was stored in a preheated oven prior to use. The solvents used for air- and moisture-sensitive manipulations were dried and deoxygenated using literature procedures.[2] Celite was dried at 180 ºC under high vacuum for 3 days prior to use. Deuterated solvents for NMR spectroscopy analysis of air sensitive iron complexes (benzene-*d*6) were distilled from sodium metal under high vacuum and stored in the glovebox. All liquid substrates used in catalytic labeling reactions were dried by stirring over CaH_2 under static vacuum at 23 ºC for 12 hours and then distilled under high vacuum and stored in the glovebox. Solid substrates were dried under high vacuum for 12 hours at 23 ºC and then stored in the glovebox. Catalytic HIE experiments were carried out in a high vacuum Schlenk line attached to a hydrogen gas tank.

IC. Instrumentation and Software.

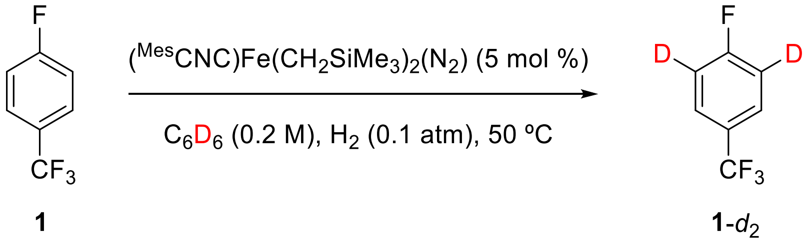
^{1}H NMR spectra were recorded at 23 ºC on a Bruker NanoBay 300 MHz or Avance III 500 MHz spectrometers operating at 300.13 MHz or 500.46 MHz, respectively. Proton-decoupled conventional and quantitative ^{13}C{^{1}H} NMR spectra were recorded at 23 ºC on Bruker NanoBay 300 MHz or Avance III 500 MHz spectrometers operating at 75.48 MHz or 125.85 MHz, respectively. ^{19}F NMR spectra were collected at 23 ºC on a Bruker 300 AVANCE spectrometer operating at 282 MHz. All of the former experiments were performed at the Princeton University Nuclear Magnetic Resonance Facility. All ^{1}H and ^{13}C NMR chemical shifts are reported in part per million (ppm) relative to $SiMe_4$ using the ^{1}H ($CDCl_3$: 7.26 ppm; benzene-*d*6: 7.16 ppm) and $^{13}C\{^{1}H\}$ ($CDCl_3$: 77.16 ppm; benzene-*d*6: 128.06 ppm) chemical shifts of the solvent as a standard. NMR data for diamagnetic compounds are reported as follows: chemical shift (multiplicity, coupling constants in Hz, integration, assignment). NMR data for paramagnetic substances are reported as follows: chemical shift (integration, width at half height in Hz) where s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, and br = broad. NMR spectra were processed using the MestReNova software suite.[3]

High-resolution mass spectra were obtained at Princeton University mass spectrometry facilities using an Agilent 6210 TOF LC/MS. Infrared spectroscopy was conducted on a Thermo-Nicolet iS10 FT-IR spectrometer calibrated with a polystyrene standard.

II. General Catalytic Procedure And Products

In a 20 mL scintillation vial, the arene (0.1 mmol) and pre-catalyst (^{Mes}CNC)Fe(CH$_2$SiMe$_3$)$_2$(N$_2$) **[Fe]-1** (3.5 mg, 0.005 mmol) were dissolved in 0.5 mL of benzene-*d*$_6$ and transferred to a J-Young NMR tube. The tube was sealed and taken outside the glovebox and attached to a high-vacuum line. The solution was then frozen by submersion of the bottom of the tube (only the portion containing the reaction mixture) in liquid nitrogen (-196 °C). After evacuating the headspace, ~0.10 atm of H$_2$ were added as determined by a Hg monometer. The J-Young NMR tube was sealed and the reaction mixture was thawed to 23 °C. The J-Young tube was then mixed by vertical rotation (if possible) at the temperature indicated in each case for the necessary time. At the end of the reaction, the mixture of benzene and deuterated arene were transferred to another J-Young tube via vacuum distillation (23 °C, 10 mtorr) or filtered off using silica gel and eluted with benzene for high boiling compounds. Reaction progress was monitored by decrease of the corresponding ^{1}H NMR signal intensities relative to a natural abundance site, and by ^{19}F NMR where applicable. Deuterium incorporation was determined by a combination of ^{1}H, quantitative ^{13}C{^{1}H}, and ^{19}F NMR spectroscopy.

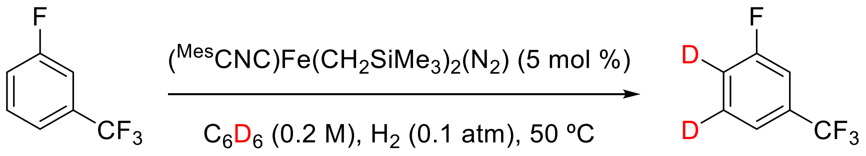
Deuteration of 4-benzotrifluoride (1):



Prepared according to the general procedure. Deuteration of 4-benzotrifluoride **1** was carried out using benzene-*d*$_6$ as the solvent. After 3.5 h at 50 °C, benzene-*d*$_6$ and deuterated 4-benzotriluoride **1**-*d*$_2$ were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-*d*$_6$):** δ 7.04 (d, *J* = 5.0 Hz, 1H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-**

***d_6*):** δ 164.6 (d, *J* = 251.7 Hz), 127.8 – 127.6 (m), 126.6 (q, *J* = 32.9 Hz), 124.5 (d, *J* = 271.6 Hz), 115.7 (td, *J* = 25.3, 22.0 Hz, labeled, > 98 %) ppm.

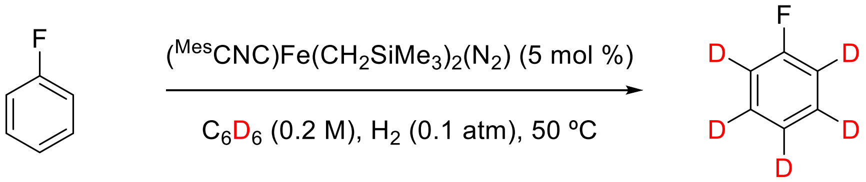
Deuteration of 3-benzotrifluoride (2):



2 **2**-*d_2*

Prepared using the general procedure. Deuteration of 3-benzotrifluoride **2** was carried out using benzene-*d_6* as solvent. After 1.5 h at 50 °C, benzene-*d_6* and deuterated 3-benzotriluoride **2**-*d_2* were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-*d_6*):** δ 6.98 (d, *J* = 8.6 Hz, 1H), 6.92 (s, 1H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-*d_6*):** δ 162.6 (d, *J* = 248.4 Hz), 132.62 (qd, *J* = 33.1, 7.8 Hz), 130.5 (td, *J* = 25.3, 7.9 Hz, labeled, > 98 %), 123.94 (qd, *J* = 272.4, 3.0 Hz), 120.90 (t, *J* = 3.8 Hz), 118.5 (td, *J* = 25.2, 20.8 Hz, labeled, > 98 %), 112.92 (dq, *J* = 24.3, 3.8 Hz) ppm.

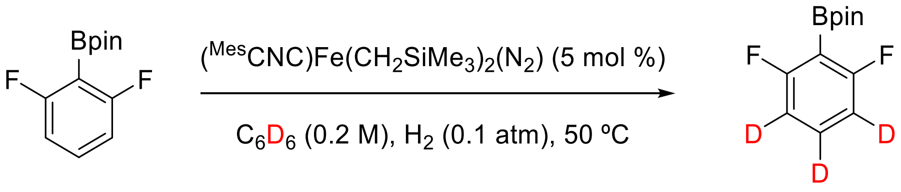
Deuteration of fluorobenzene (3):



3 **3**-*d_5*

Prepared using the general procedure. Deuteration of fluorobenzene **3** was carried out using benzene-*d_6* as the solvent. After 3 h at 50 °C, benzene-*d_6* and deuterated fluorobenzene **3**-*d_5* were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-*d_6*):** δ 7.16 (residual peak of benzene-*d_6*). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-*d_6*):** δ 112.4 (d, *J* = 246 Hz), 78.8 (td, *J* = 24.6, 7.8 Hz, labeled, > 98 %), 72.8 (t, *J* = 24.6 Hz, labeled, > 98 %), 64.1 (td, *J* = 24.9, 21.2 Hz, labeled, > 98 %) ppm.

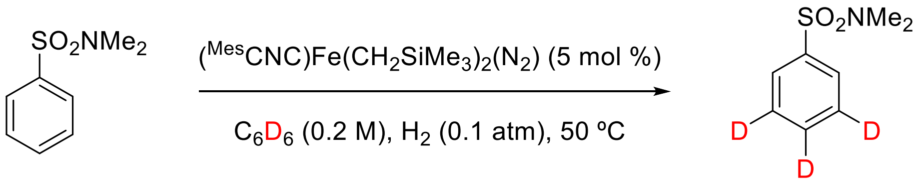
Deuteration of 2-(2,6-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4):



4 **4**-d_3

Prepared using the general procedure. Deuteration of **4** was carried out using benzene-d_6 as the solvent. After 3 hours at 50 °C, benzene-d_6 and **4**-d_3 were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-d_6):** δ 7.22 (t, *J* = 5.8 Hz, 0.03 H), 6.71 (d, *J* = 8.2 Hz, 0.06 H), 1.26 (s, 12H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-d_6):** δ 165.5 (dd, *J* = 250.5, 12.7 Hz), 132.0 – 131.3 (m, labeled, 97 %), 110.1 – 109.4 (m, labeled, 97 %), 83.2 (s), 23.7 (s) ppm.

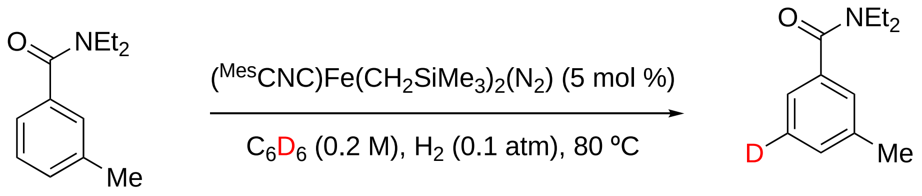
Deuteration of *N,N*-dimethylphenylsulfonamide (5):



5 **5**-d_3

Prepared using the general procedure. Deuteration of *N,N*-dimethylphenylsulfonamide **5** was carried out using benzene-d_6 as the solvent. After 2 hours at 50 °C, **5**-d_3 was collected by filtration through a pad of silica gel prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, Chlorofom-*d*):** δ 7.78 (s, 2H), 2.70 (s, 6H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, Chloroform-*d*):** δ 135.5, 132.4 (t, *J* = 24.7 Hz, labeled, > 98 %), 128.8 (t, *J* = 24.9 Hz, labeled, > 98 %), 127.7, 38.1 ppm.

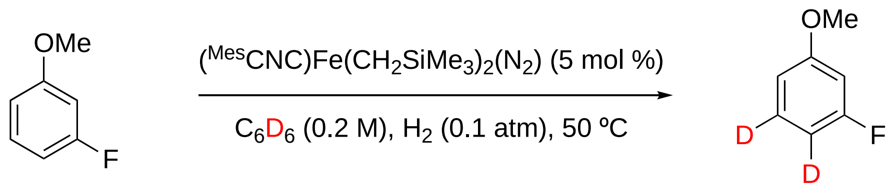
Deuteration of N,N-diethyl-3-methylbenzamide (6):



6 **6-*d*₁**

Prepared using the general procedure. Deuteration of N,N-diethyl-3-methylbenzamide **6** was carried out using benzene-*d*$_6$ as solvent. After 3 h at 80 °C, complete conversion was observed by disappearance of a ^{1}H NMR signal. Observed as a mixture of 2 rotamers. **^{1}H NMR (500 MHz, benzene-*d*$_6$):** δ 7.25 – 7.16 (m, 2H, overlapping), 6.91 (s, J = 7.7 Hz, 1H), [3.33 (s, 2H), 2.90 (s, 2H)], 2.04 (s, 3H), [1.06 (s, 3H), 0.73 (s, 3H)]. **Quantitative ^{13}C{^{1}H} NMR (101 MHz, benzene-*d*$_6$):** δ 170.72, 138.51, 138.07, 129.59, 123.81 (unlabeled 2%), 123.53 (t, *J* = 24.5 Hz, labeled, 98%), 43.04, 39.58, 21.25, 13.68.

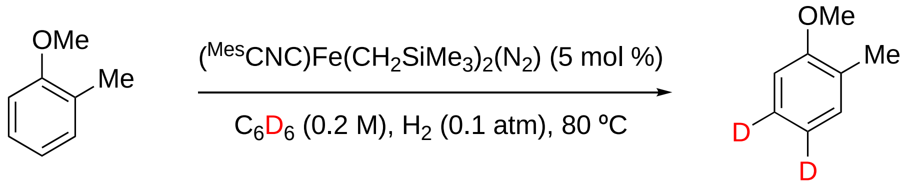
Deuteration of 3-fluoroanisole (7):



7 **7**-*d*₂

Prepared using the general procedure. Deuteration of 3-fluoroanisole **7** was carried out using benzene-*d*$_6$ as solvent. After 4 h at 50 °C, benzene-*d*$_6$ and deuterated 3-fluoroanisole **7**-*d*$_2$ were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-*d*$_6$):** δ 6.52 (dd, *J* = 11.0, 2.5 Hz, 1H), 6.47 (bs, 1H), 3.11 (s, 3H). **Quantitative ^{13}C{^{1}H} NMR (126 MHz, benzene-*d*$_6$):** δ 164.5 (d, *J* = 244.5 Hz), 161.8 (d, *J* = 10.7 Hz), 130.3 (td, *J* = 24.6, 10 Hz, labeled, > 98 %), 110.6, 107.4 (td, *J* = 25.1, 20.9 Hz, labeled, > 98 %), 101.9 (d, *J* = 24.8 Hz), 55.1 ppm.

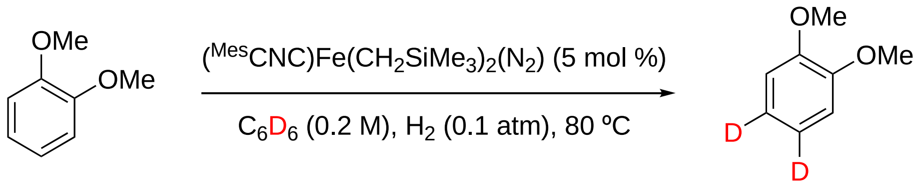
Deuteration of 2-methylanisole (8):



8 **8**-d_2

Prepared using the general procedure. Deuteration of 2-methylanisole **8** was carried out using benzene-d_6 as solvent. After 4 h at 80 °C, benzene-d_6 and deuterated 2-methylanisole **8**-d_2 were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-d_6):** δ 7.06 (s, 1H), 6.54 (s, 1H), 3.33 (s, 3H), 2.29 (s, 3H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-d_6):** δ 158.2, 130.9, 126.8 (t, J = 24.2 Hz, labeled, >98 %), 126.7, 120.3 (t, J = 24.4 Hz, labeled, >98 %), 110.0, 54.7, 16.5 ppm.

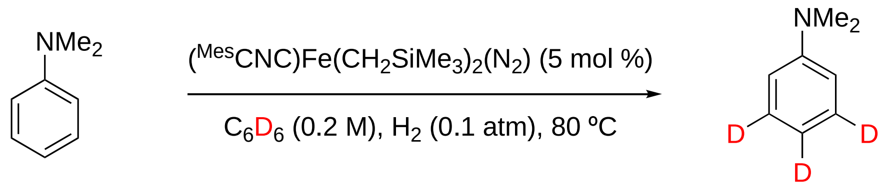
Deuteration of 1,2-dimethoxybenzene (9):



9 **9**-d_2

Prepared using the general procedure. Deuteration of 1,2-dimethoxybenzene **9** was carried out using benzene-d_6 as solvent. After 8 h at 80 °C, benzene-d_6 and deuterated 1,2-dimethoxybenzene **9**-d_2 were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-d_6):** δ 6.64 (s, 1H), 3.40 (s, 3H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-d_6):** δ 150.4, 120.9 (t, J = 24.5 Hz, labeled, >98 %), 112.4, 55.5 ppm.

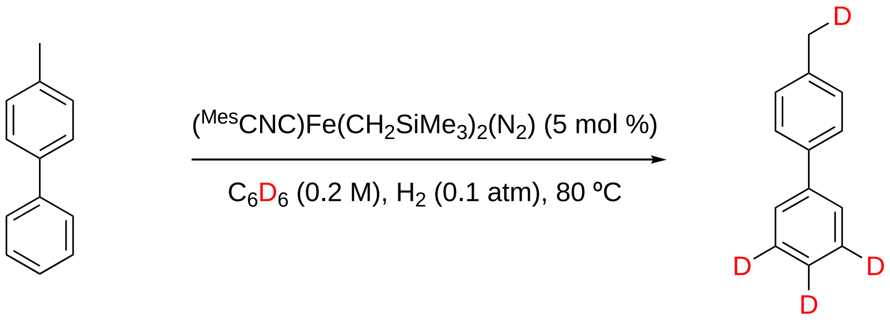
Deuteration of *N,N*-dimethylaniline (10):



10 **10**-*d*$_3$

Prepared using the general procedure. Deuteration of *N,N*-dimethylaniline **10** was carried out using benzene-*d*$_6$ as solvent. After 8 h at 80 °C, benzene-*d*$_6$ and deuterated *N,N*-dimethylaniline **10**-*d*$_3$ were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-*d*$_6$):** δ 7.28 – 7.22 (m, labeled, 0.76 H), 6.80 (bs, labeled, 0.38 H), 6.64 (s, 2 H), 2.51 (s, 6H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-*d*$_6$):** δ 151.2, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0 (2 carbons, labeled, 62 % D), 117.3, 117.2, 117.1, 117.0, 116.9, 116.8, 116.7, 116.6 (labeled, 62 % D), 113.3, 113.2 (1 carbon, no labeled), 40.5 ppm.

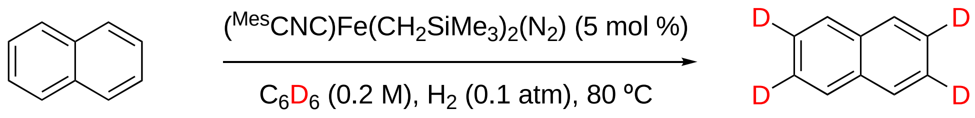
Deuteration of 4-phenyltoluene (11):



11 **11**-*d*$_4$

Prepared using the general procedure. Deuteration of 4-phenyltoluene **11** was carried out using benzene-*d*$_6$ as solvent. After 2 h at 80 °C, the deuterated 4-phenyltoluene **11**-*d*$_4$ was collected by filtration trough a pad of silica gel prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, Chloroform-*d*):** δ 7.62 (s, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.43 (s, labeled, 2.6 H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, ,Chloroform-*d*):** δ 141.2, 138.4, 137.1, 129.5, 128.4 (t, *J* = 24.3 Hz, labeled, > 98 %), 127.1, 126.9, 126.5 (t, *J* = 24.5 Hz, labeled, > 98 %), 21.2, 21.0, 20.9, 20.7 (labeled, 14 % D) ppm.

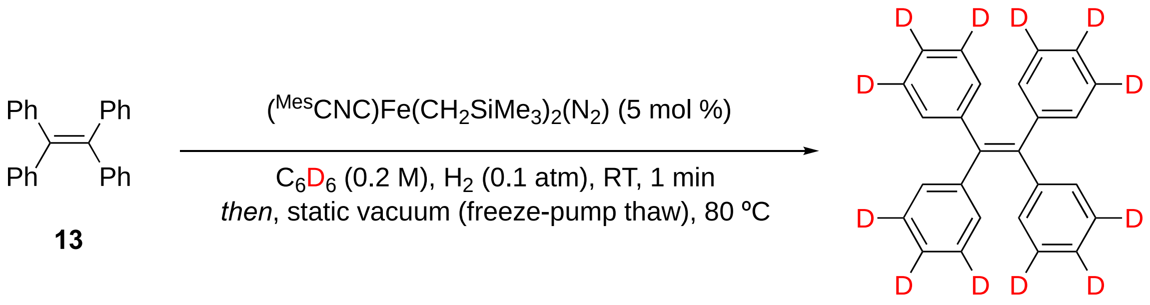
Deuteration of naphthalene (12):



12 **12**-*d*$_4$

Prepared using the general procedure. Deuteration of naphthalene **12** was carried out using benzene-*d*$_6$ as solvent. After 2 h at 80 °C, the deuterated naphthalene **12**-*d*$_4$ was collected by filtration trough a pad of silica gel prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, Chloroform-*d*):** δ 7.87 (s, 4H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, , Chloroform-*d*):** δ 133.6, 127.9, 125.6 (t, *J* = 24.4 Hz, labeled, > 98 % D) ppm.

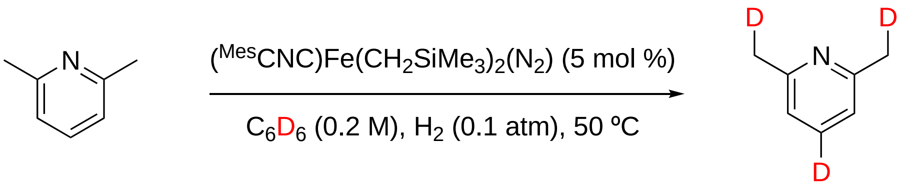
Deuteration of 1,1,2,2-tetraphenylethylene (13):



13 **13**-*d*$_{12}$

Prepared using a modification of the general procedure: in a N_2-filled glovebox, 1,1,2,2-tetraphenylethylene **13** (33.2 mg, 0.1 mmol) and pre-catalyst (^{Mes}CNC)Fe(CH_2SiMe_3)$_2$(N_2) **[Fe]-1** (3.5 mg, 0.005 mmol) were dissolved in 0.5 mL of benzene-*d*$_6$ and were transferred to a J-Young NMR tube. The tube was taken outside the glovebox and connected to a high-vacuum line. After freeze-pump thawing, the N_2 atmosphere was removed and the tube was filled back with H_2 (0.1 atm). Once the frozen solution was melted, the suspension was stirred at room temperature for 1 min, observing that the solution turns from purple to a yellowish-brown color, indicating the formation of the corresponding iron-hydride species. The J-Young NMR tube was connected again to the vacuum line and H_2 was removed via freeze-pump thawing. The solution was warmed up to 80 °C under static vacuum. After 24 h, the deuterated 1,1,2,2-tetraphenylethylene **13**-*d_{12}* was collected by filtration trough a pad of silica gel prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, Chloroform-*d*):** δ 7.13 (bs, labeled, 0.05 H), 7.11 (bs, labeled, 0.1 H), 7.06 (s, 8H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, , Chloroform-*d*):** δ 143.8, 141.1, 131.3, 127.4 (t, *J* = 24.1 Hz, labeled, 95 %), 126.1 (t, *J* = 24.1 Hz, labeled, 95 %) ppm.

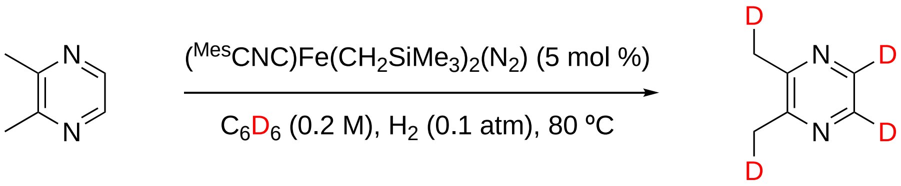
Deuteration of 2,6-lutidine (14):



14 **14**-*d_3*

Prepared using the general procedure. Deuteration of 2,6-lutidine **14** was carried out using benzene-*d_6* as solvent. After 3 h at 50 °C, benzene-*d_6* and deuterated 2,6-lutidine **14**-*d_3* were collected by vacuum transfer prior to ^{1}H-NMR analysis. **^{1}H NMR (500 MHz, benzene-*d_6*):** δ 6.57 (s, 2H), 2.42 (s, labeled, 4 H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-*d_6*):** δ 158.0, 135.8 (t, *J* = 24.4 Hz, labeled, > 98 % D), 119.8, 24.6, 24.5, 24.3, 24.2 (labeled, 33 % D) ppm.

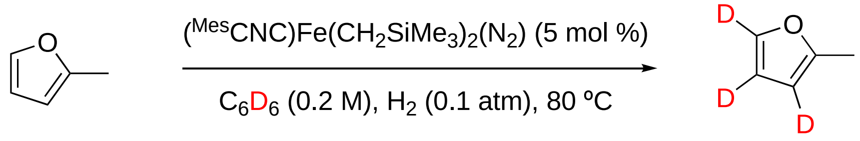
Deuteration of 2,3-dimethylpyrazine (15):



15 **15**-*d_4*

Prepared using the general procedure. Deuteration of 2,3-dimethylpyrazine **15** was carried out using benzene-*d_6* as solvent. After 5 h at 80 °C, benzene-*d_6* and deuterated 2,3-dimethylpyrazine **15**-*d_4* were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-*d_6*):** δ 2.15 (s, labeled, 5.2 H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-*d_6*):** δ 152.7, 141.2 (t, *J* = 27.5 Hz, labeled, > 98 % D), 21.9, 21.8, 21.6, 21.5 (labeled, 14 % D) ppm.

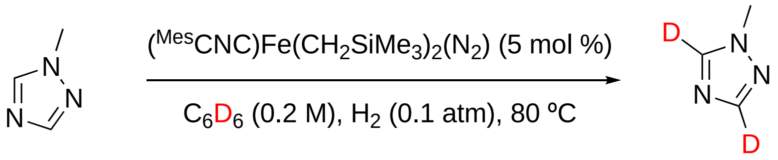
Deuteration of 2-methylfuran (16):



16 **16**-*d*$_3$

Prepared using the general procedure. Deuteration of 2-methylfuran **16** was carried out using benzene-d_6 as solvent. After 3 h at 80 °C, benzene-d_6 and deuterated 2-methylfuran **16**-d_3 were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-d_6):** δ 5.78 (s, labeled, 0.65 H), 2.00 (s, 3H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-d_6):** δ 152.0, 140.8 (t, *J* = 27.2 Hz, labeled, > 98 % D), 110.3 (t, *J* = 26.7 Hz, labeled, > 98 % D), 105.7, 105.5, 105.3 (labeled, 65 % D), 13.3 ppm.

Deuteration of 1-methyl-1*H*-1,2,4-triazole (17):



17 **17**-*d*$_2$

Prepared using the general procedure. Deuteration of 1-methyl-1*H*-1,2,4-triazole **17** was carried out using benzene-d_6 as solvent. After 5 h at 80 °C, benzene-d_6 and deuterated 1-methyl-1*H*-1,2,4-triazole **17**-d_2 were collected by vacuum transfer prior to ^{1}H NMR analysis. **^{1}H NMR (500 MHz, benzene-d_6):** δ 2.82 (s, 3H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz, benzene-d_6):** δ 152.2 (t, *J* = 31.2 Hz, labeled, > 98 %), 143.4 (t, *J* = 31.0 Hz, labeled, > 98 % D), 34.9 ppm.

Unsucessful Substrates:

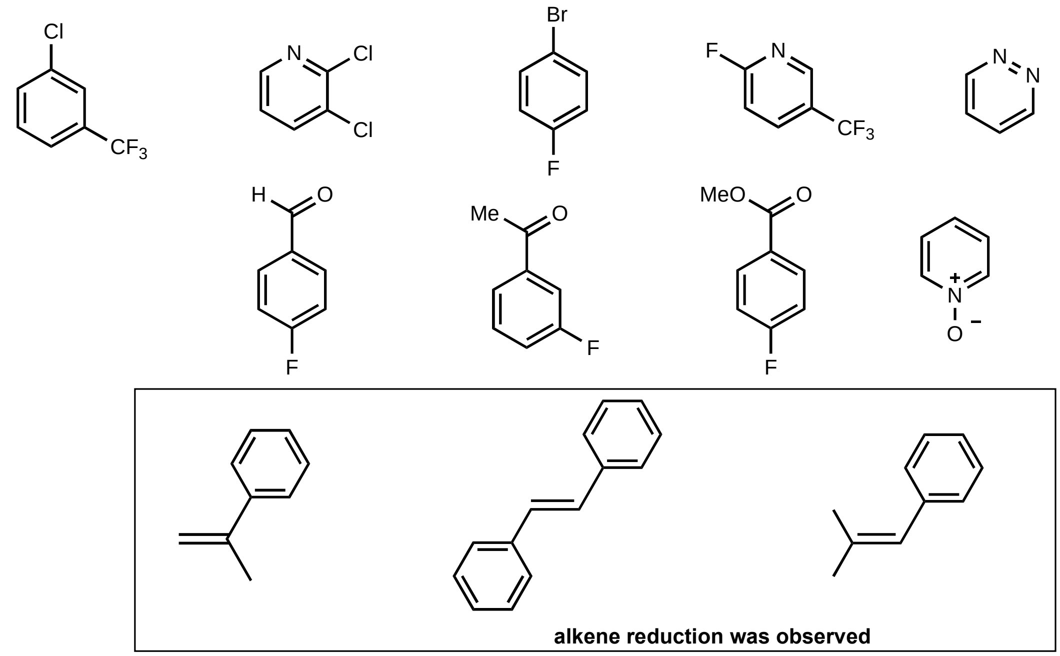
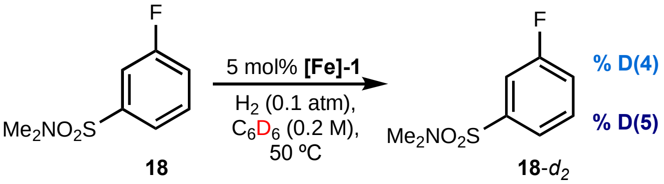


Figure S1. Unsucessful substrates in catalytic HIE reaction using the standard conditions.

III. Selectivity studies

Site selectivity: analysis by ^{2}H NMR



Substrate **18** was subjected under the general conditions for the deuteration of arenes and aliquots were taken from the reaction at different reaction times. The residue was filtered through a pad of silica gel, and the solvent was removed in vacuo to yield the corresponding partially deuterated **18-**d_2, which was further analyzed by ^{2}H NMR spectroscopy in order to obtain the relative 4-position:5-position deuteration during the time-course experiment. The chemical shift for each deuterium atom in this case was obtained by comparison with the *ortho*-to-fluorine **18**-d_1, prepared according to the reported procedure,[4] and using acetone-d_6 as internal standard for calibration. After full conversion, **18**-d_2 was obtained as a white solid. **^{1}H NMR (500 MHz, Chloroform-*d*):** δ 7.54 (s, 1H), 7.45 (dd, *J* = 8.2, 1.5 Hz, 1H), 2.70 (s, 6H). **Quantitative ^{13}C{^{1} H} NMR (126 MHz,Chloroform-*d*):** δ 162.5 (d, *J* = 251.5 Hz), 137.6 (d, *J* = 6.4 Hz), 130.6 (td, *J* = 25.6; 7.8 Hz, labeled, > 98 %), 123.4 (d, *J* = 3.2 Hz), 119.7 (td, *J* = 25.3; 20.9 Hz, labeled, > 98%), 115.0 (d, *J* = 24.0 Hz), 37.9 ppm.

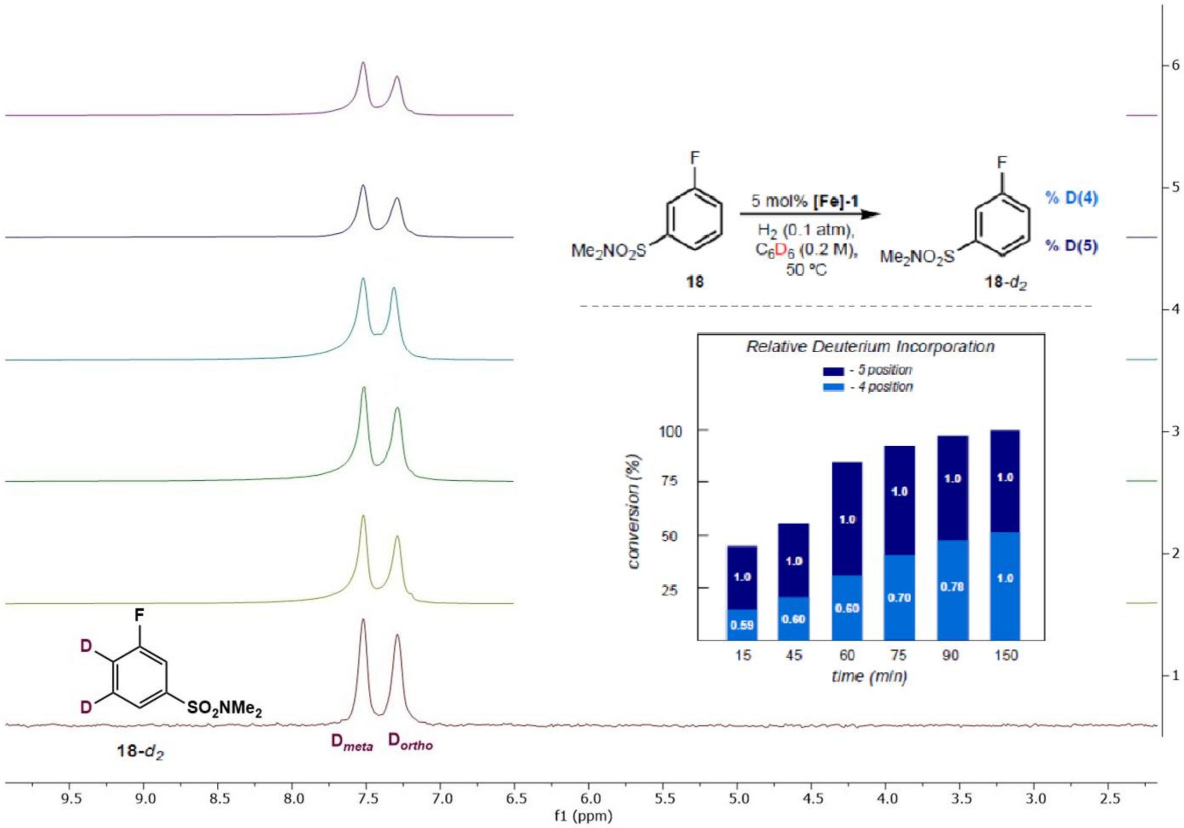


Figure S2. Time-course experiment by ^{2}H NMR spectrum (400 MHz, Chloroform) for the deuteration of **18** at different time intervals: 15 min (first), 45 min (second), 60 min (third), 75 min (fourth), 90 min (fifth), and 150 min (sixth).

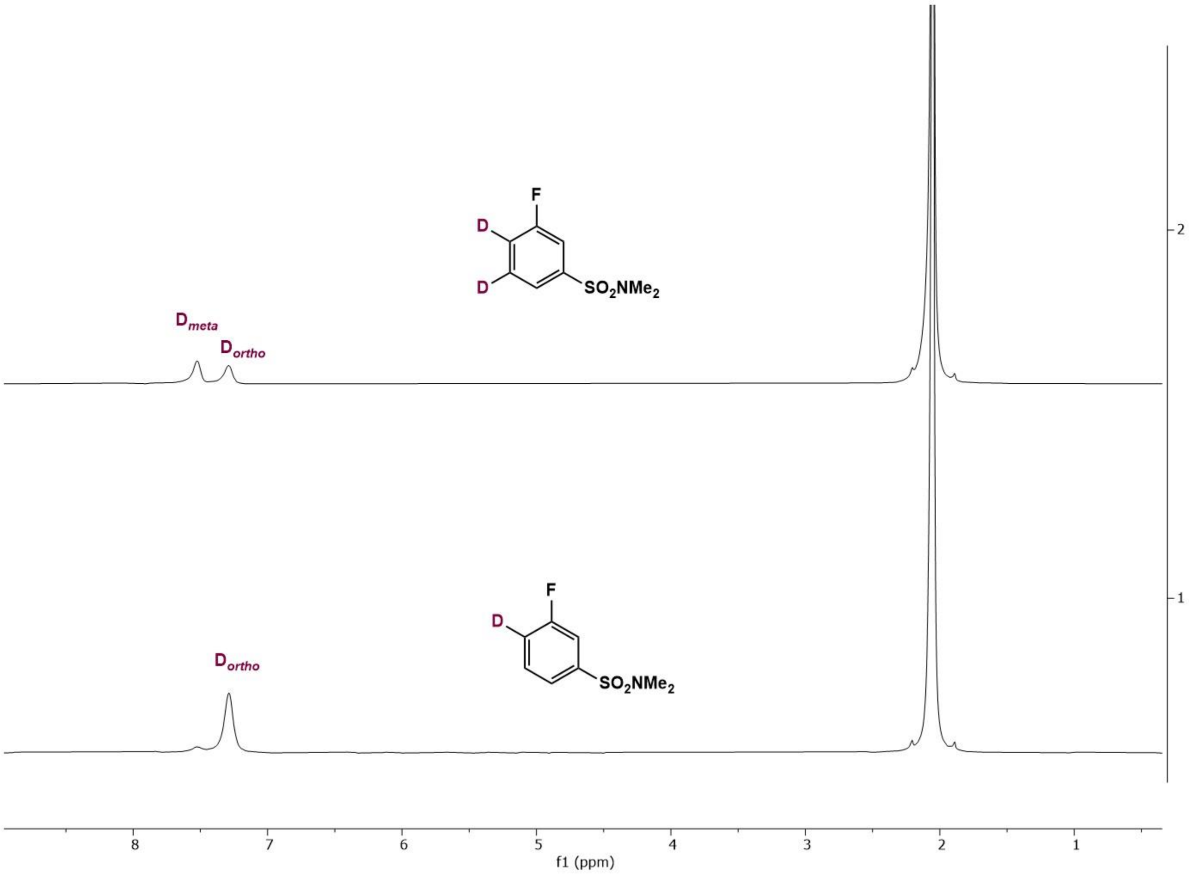


Figure S3. ^{2}H NMR (400 MHz, Chloroform) chemical shift assignment of D$_{ortho}$ and D$_{meta}$ *in* **18**-d_2 by comparison with *ortho*-to-fluorine **18**-d_1 using acetone-d_6 as internal standard.

IV. Preparation of $(4\text{-NMe}_2{}^{\text{Mes}}\text{CNC})\text{Fe}(\text{CH}_2\text{SiMe}_3)_2(\text{N}_2)$ ([Fe]-4)

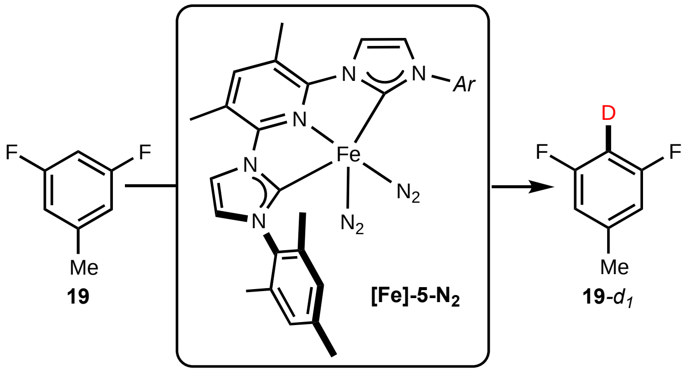
Prepared according to an analogous procedure.[1c]

4-NMe$_2$^{Mes}CNC(HBr)$_2$. To a glass ampule was added 4-(dimethylamino)-2,6-dibromopyridine (560 mg, 2 mmol, 1 equiv.) and ^{Mes}Imidazole (1118 mg, 6 mmol, 3 equiv.). The ampule was evacuated, flame sealed, and heated to 200 °C for 1 week. The ampule was allowed to cool to room temperature, broken open, and the contents of the ampule dissolved in DCM. Et$_2$O was added, resulting in the formation of an off white precipitate, which was filtered and washed with Et$_2$O, to yield 830 mg (64 % yield) of (4-NMe$_2$^{Mes}CNC)(HBr)$_2$ as an off-white solid. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.69 (t, J = 1.7 Hz, 2H), 9.72 (t, J = 2.0 Hz, 2H), 7.71 (s, 2H), 7.29 (s, 2H), 7.01 (s, 4H), 3.34 (s, 6H), 2.32 (s, 6H), 2.17 (s, 12H). **^{13}C NMR (126 MHz, Chloroform-*d*):** δ 159.24, 146.27, 141.32, 137.31, 134.07, 130.69, 129.89, 124.00, 97.88, 41.78, 21.17, 17.97. **HRMS** (ESI+): m/2z calculated for $C_{31}H_{36}N_6^{2+}$ ([M]2+) 246.1496, found m/2z 246.1497.

4-NMe$_2$^{Mes}CNC. In a N$_2$-filled glovebox a 20 mL scintillation vial was charged with 4-NMe$_2$-^{Mes}CNC(HBr)$_2$. (400 mg, 0.61 mmol, 1.0 equiv) and THF (ca. 10 mL) and the resulting suspension was cooled in the cold well (–196 °C) for 20 min. A 20 mL scintillation vial was charged with KHMDS (258 mg, 1.29 mmol, 2.1 equiv) and THF (ca. 5 mL) and the resulting suspension was cooled in the freezer (–35 °C) for 20 min. The cold solution of KHMDS in THF was added to the cold suspension of 4-NMe$_2$^{Mes}CNC(HBr)$_2$ and the resulting mixture was allowed to warm to RT while being stirred for 1 h. All volatiles were removed *in vacuo* and the residue was triturated in pentane (ca. 10 mL). All volatiles were removed *in vacuo* and the residue was taken up in toluene (ca. 10 mL). The mixture was filtered through celite (eluent: toluene) and all volatiles were removed from the filtrate *in vacuo* to yield 190 mg (82% yield) of 4-NMe$_2$-^{Mes}CNC as an off-white solid. **^{1}H NMR (400 MHz, Benzene-*d$_6$*)** δ 8.37 (d, J = 1.7 Hz, 2H), 8.08 (s, 2H), 6.81 (s, 4H), 6.53 (d, J = 1.7 Hz, 2H), 2.30 (s, 7H), 2.15 (s, 18H). **^{13}C NMR (101 MHz, Benzene-*d$_6$*)** δ 217.86, 157.75, 153.29, 138.88, 137.11, 135.11, 128.79, 120.62, 116.75, 94.26, 38.50, 20.67, 17.75.

(4-NMe$_2$^{Mes}CNC)Fe(CH$_2$SiMe$_3$)$_2$(N$_2$). Freshly prepared (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$[1c] (162 mg, 0.42 mmol, 1.2 equiv.) was dissolved in pentane (ca. 4 mL) and placed in in the freezer (–35 °C) for 20 min. A 20 mL scintillation vial was charged with 4-NMe$_2$-^{Mes}CNC (172 mg, 0.351 mmol, 1.0 equiv) and cold pentane (ca. 10 mL, –35 °C). The cold solution containing (py)$_2$Fe(CH$_2$SiMe$_3$)$_2$ was added to the cold suspension of 4-NMe$_2$-^{Mes}CNC and the resulting mixture was allowed to warm to RT while being stirred for 1 h during which time a microcrystalline solid precipitated from the reaction mixture. The resulting violet suspension was concentrated to ca. 2 mL and filtered. The solid was washed with cold pentane (3 x 3 mL) and dried under vacuum to yield 202 mg (76% yield) of (4-NMe$_2$-^{Mes}CNC)Fe(CH$_2$SiMe$_3$)$_2$(N$_2$) as a violet-brown solid. **Anal. Cald.** For: $C_{39}H_{56}FeN_8Si_2$: C, 62.54; H, 7.54; N, 14.96. Found: C, 62.19; H, 7.57, N, 14.50. **IR (Benzene-*d$_6$*):** ν_{NN} = 2113 cm^{-1}. **^{1}H NMR (400 MHz, Benzene-*d$_6$*)** δ 7.20 (s, 2H, 3,5-Py-*H*), 6.74 (s, 4H, Ar-*H*), 6.36 (s, 2H, Im-Ar*H*), 6.26 (s, 2H, Im-Ar*H*), 2.45 (s, 6H, Ar-4-C*H*$_3$), 2.36 (s, 12H, Ar-2,6-C*H*$_3$), 2.04 (s, 6H, N(C*H*$_3$)$_2$), -0.30 (s, 18H, (CH$_2$Si(C*H*$_3$)$_3$)$_2$), -0.97 (s, 4H, (C*H*$_2$SiMe$_3$)$_2$). **^{13}C NMR (101 MHz, Benzene-*d$_6$*)** δ 153.10 (2-pyr *C*), 152.91 (4-pyr *C*), 137.69 (1-Mes *C*), 136.80 (2/4-Mes *C*), 136.20 (2/4-Mes *C*), 129.10 (4/5-imidazolylidene *C*), 124.33 (4/5-imidazolylidene *C*), 112.83 (3-Mes *C*), 85.47 (3-pyr *C*), 39.42 (-N(*C*H$_3$)$_2$), 20.64 (4-Mes –(*C*H$_3$)), 19.02 (2,6-Mes –(*C*H$_3$)), 2.76 (CH$_2$Si(*C*H$_3$)$_3$). (-*C*H$_2$Si(CH$_3$)$_3$ and 2-imidazolylidene C not located).

V. Time Course of H/D Exchange



5 mol% [Fe], C_6D_6 (0.2 M), 23 ºC
H_2 (0.1 atm) v. Static Vacuum

Reactions conducted using a modified procedure for the catalytic deuteration of arenes. From a single stock solution of **19** (0.2 mmol, 26 mg), **[Fe]-5-N_2** (0.01 mmol, 6 mg) in benzene-d_6 was added to two separate J-Young tubes. In one J-Young tube, the atmosphere was exchanged for H_2 (0.1 atm) as per the general procedure for the catalytic deuteration of arenes. The other J-Young tube was attached to a high vacuum line, the contents of the vessel frozen with liquid N_2, and the atmosphere of the tube evacuated. The J-Young tube was sealed, allowed to thaw, frozen again with liquid N_2 and evacuated. This was repeated one more time for a total of 3 evacuations. Both tubes were allowed to warm to room temperature (23 °C), and reaction progress analyzed by ^{19}F NMR spectroscopy for the allocated time.

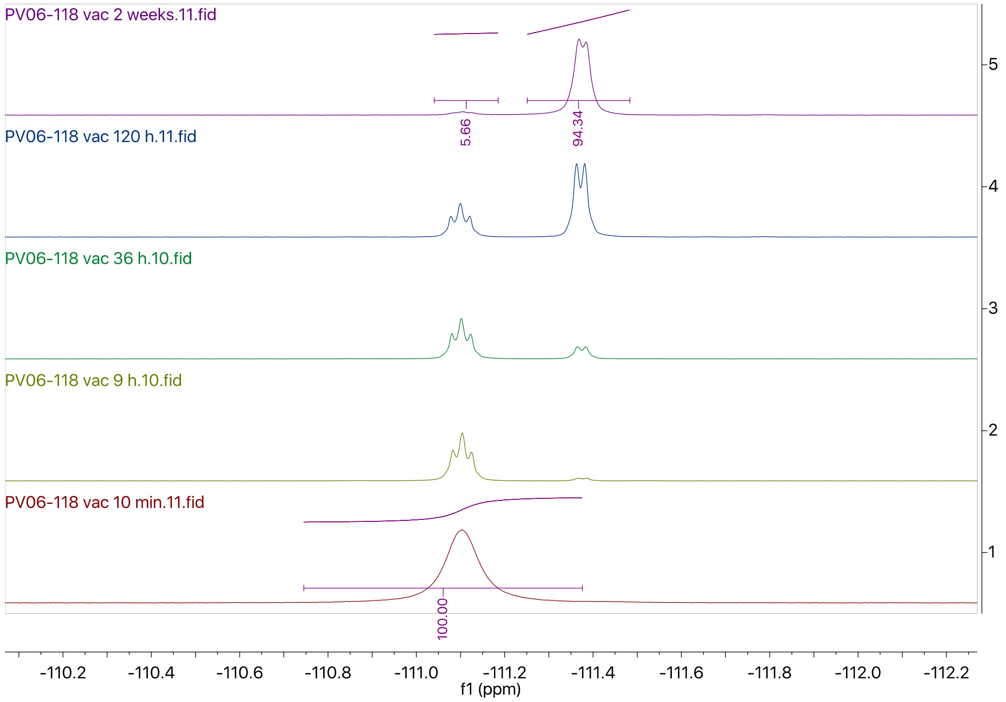


Figure S4. Selected timepoints of **[Fe]-5-N_2** and **19** under static vacuum.

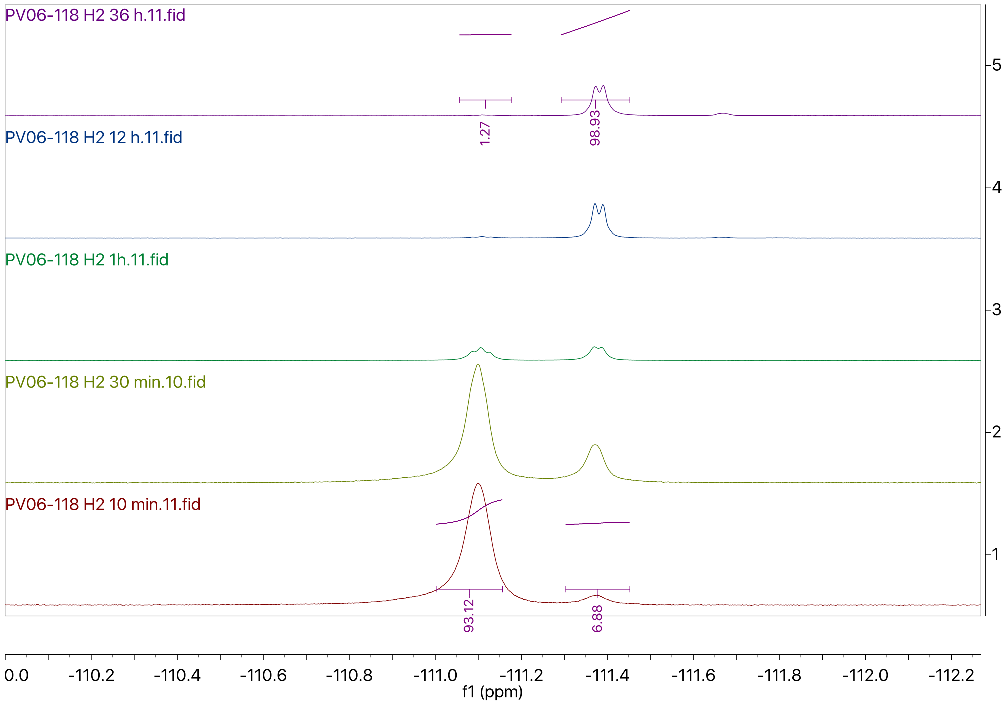


Figure S5. Selected timepoints of **[Fe]-5-N_2** and **19** under H_2 (0.1 atm).

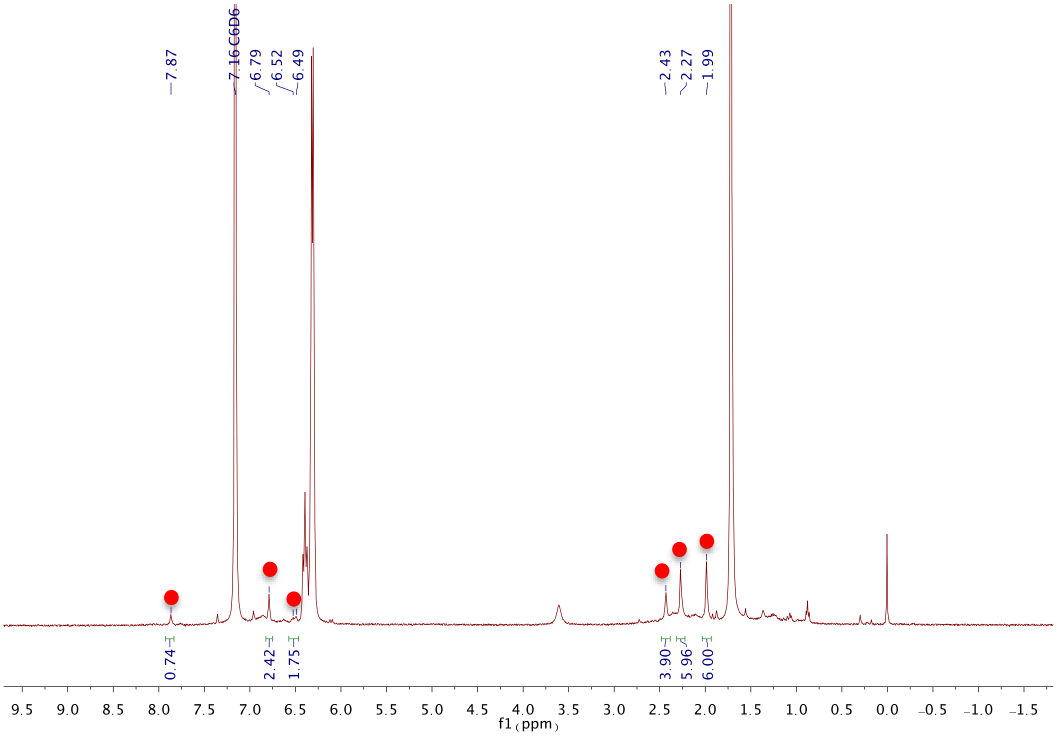


Figure S6. ^{1}H NMR Spectrum of the reaction mixture after 96 h. (3,5-Me_2-^{Mes}CNC)Fe(N_2)$_2$^{1c} labeled with red circle.

VI. Spectroscopic Data

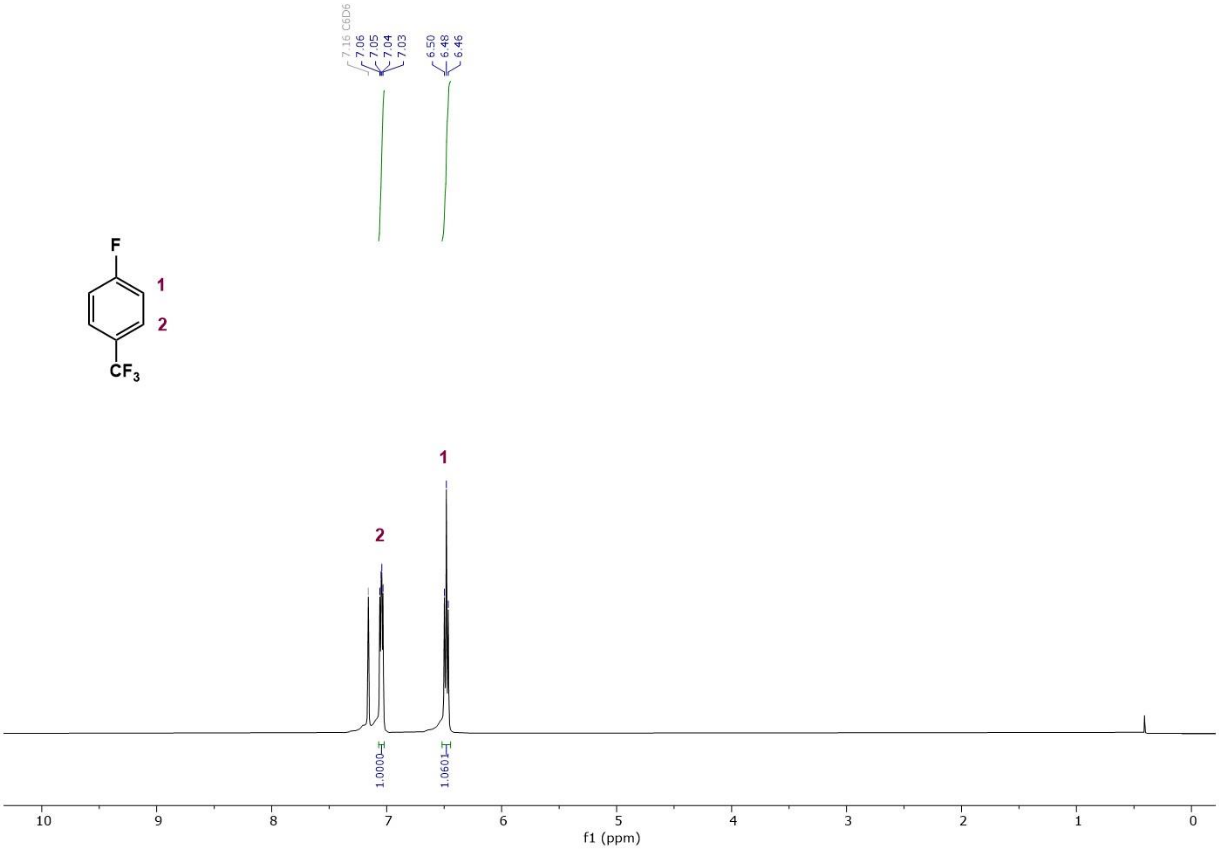


Figure S7. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **1**.

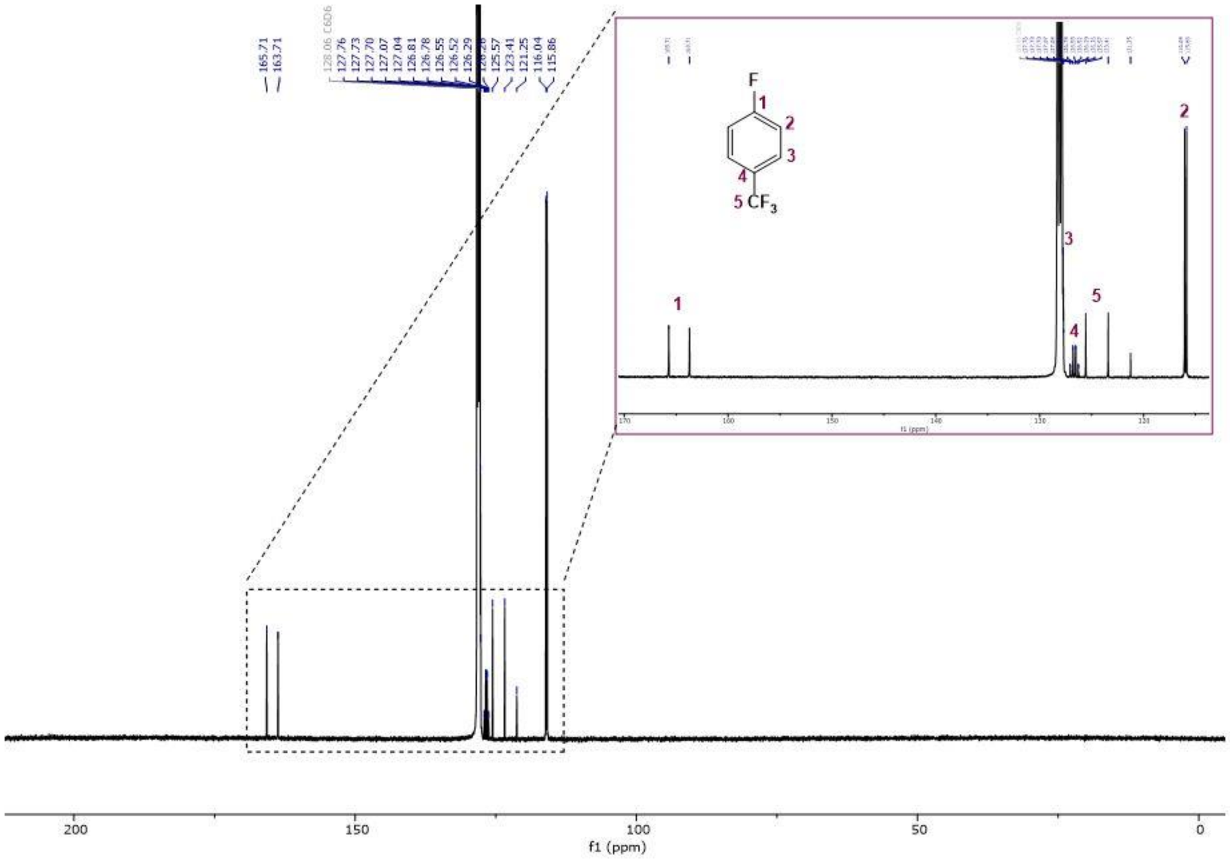


Figure S8. ^{13}C{^{1}H} NMR spectrum (126 MHz, benzene-d_6) of natural abundance **1**.

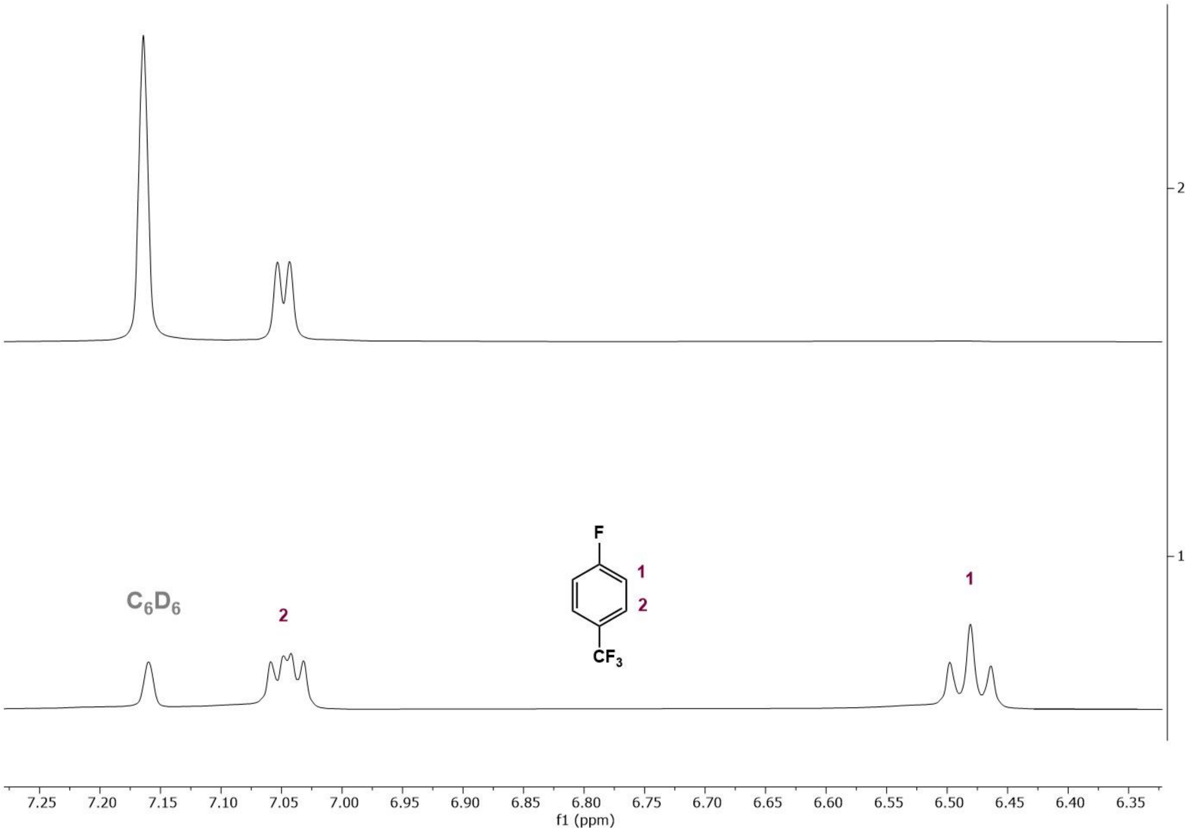


Figure S9. Stacked ^{1}H NMR spectra of **1**: labeled, **1**-*d*$_2$ (top) and natural abundance **1** (bottom).

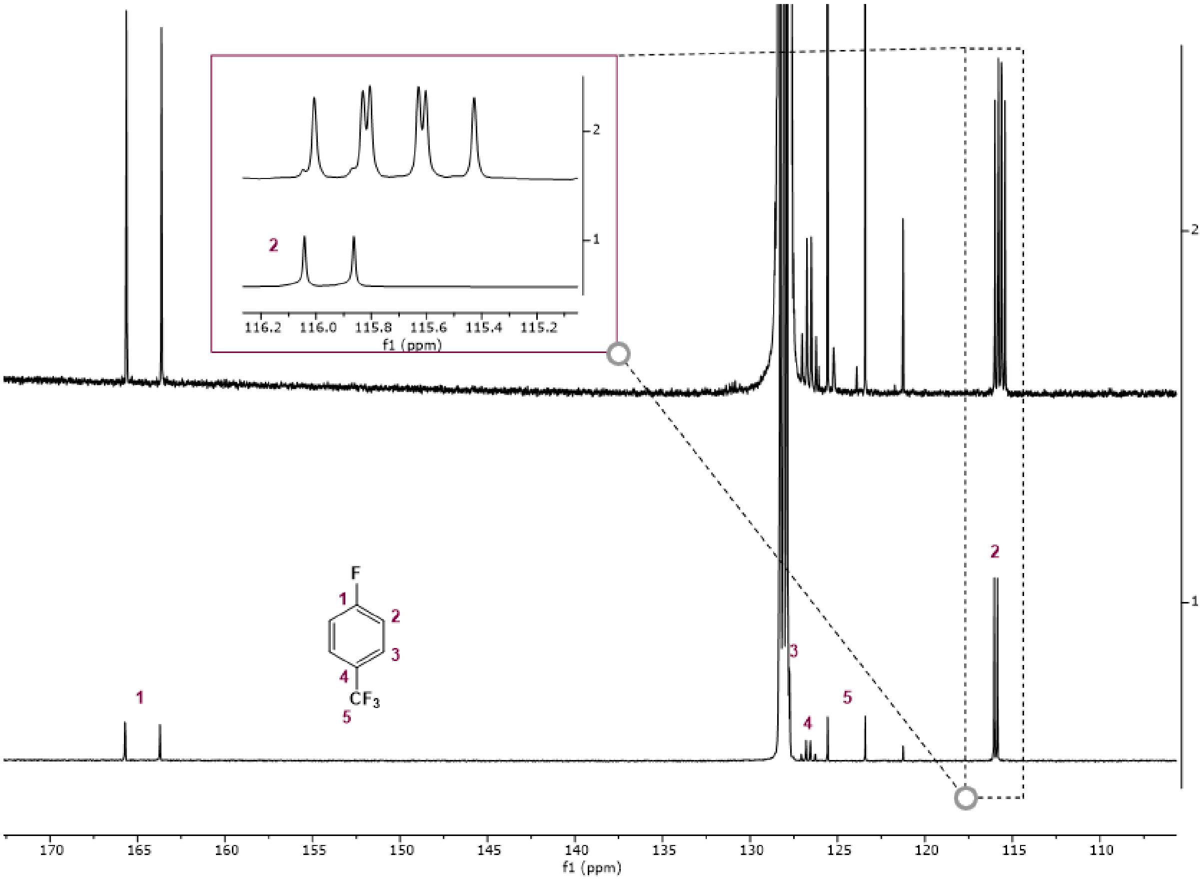


Figure S10. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **1**: labeled, **1**-*d_2* (top) and natural abundance **1** (bottom).

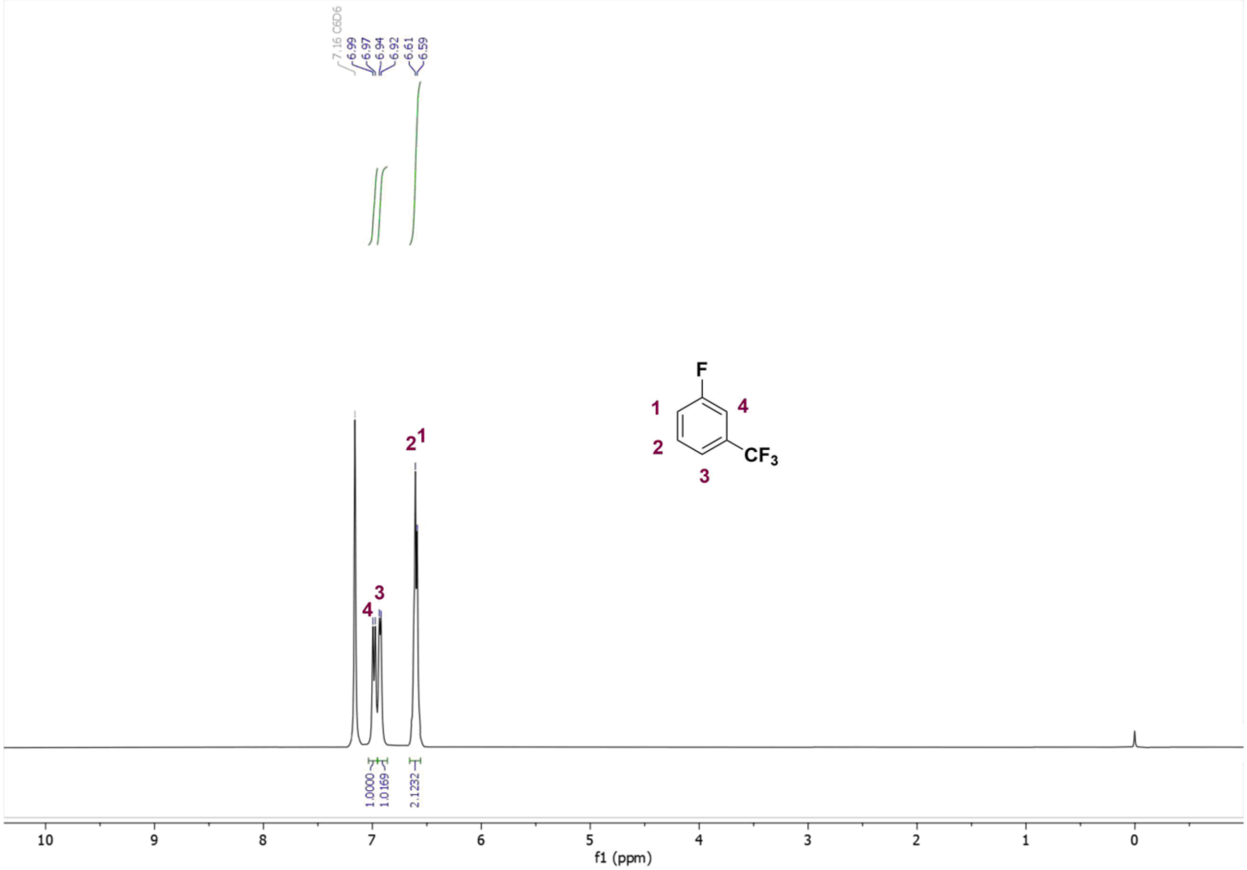


Figure S11. ^{1}H NMR spectrum (500 MHz, benzene-*d₆*) of natural abundance **2**.

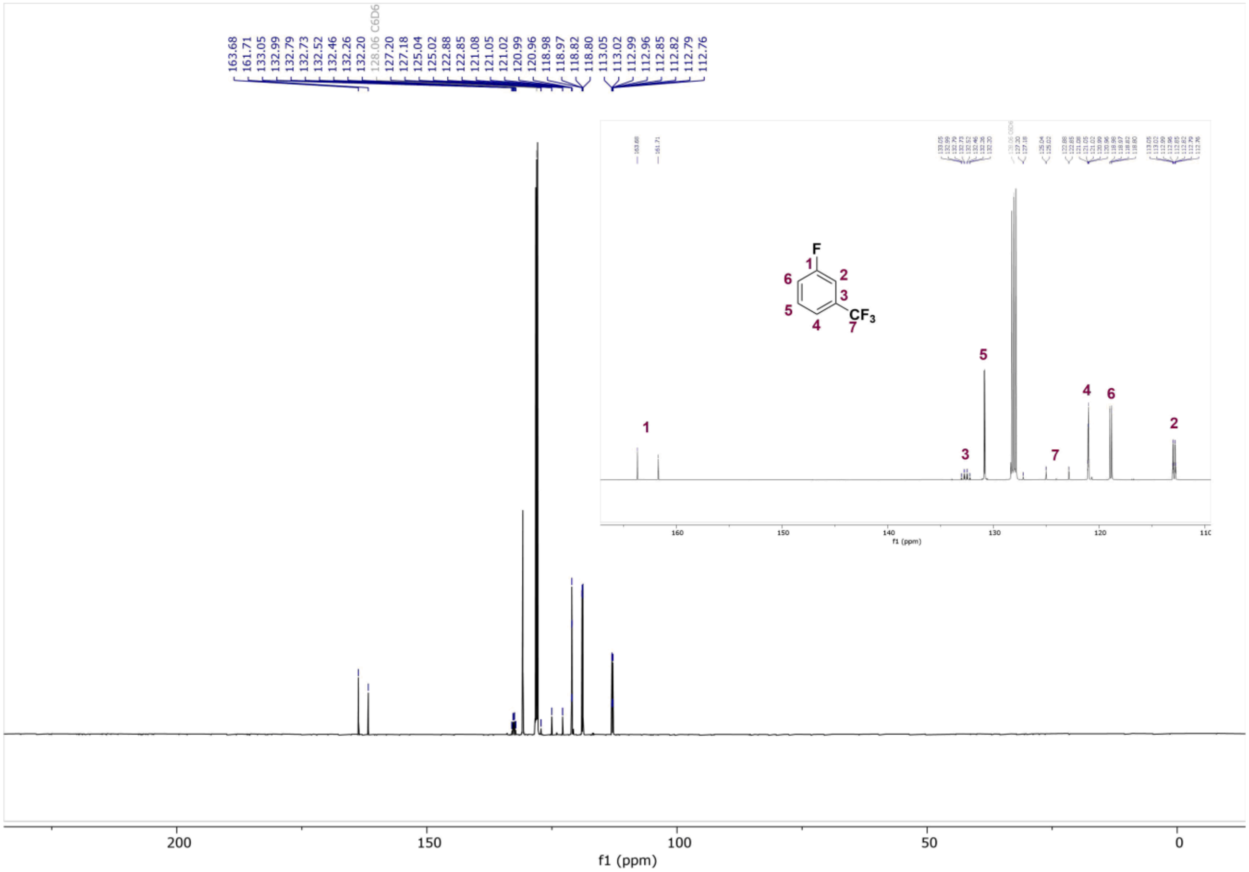


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, benzene-d_6) of natural abundance **2**.

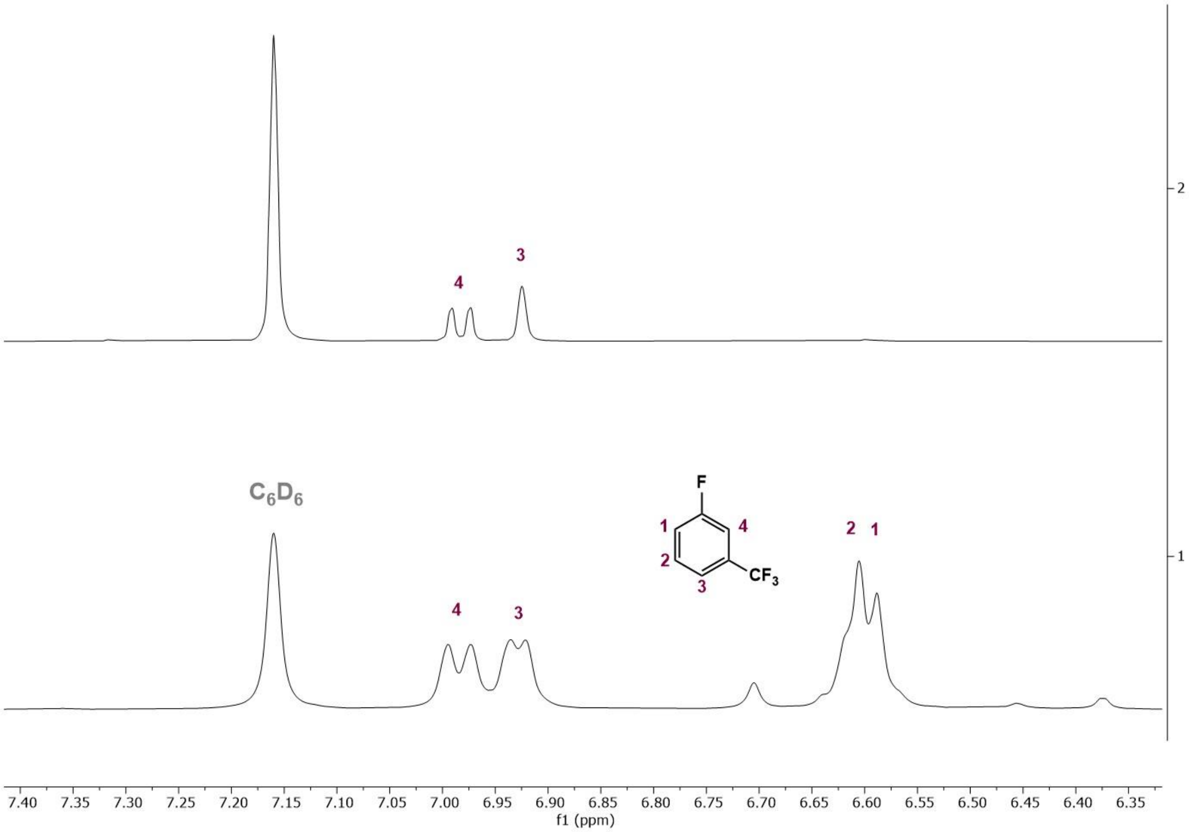


Figure S13. Stacked ^{1}H NMR spectra of **2**: labeled, **2**-*d*$_2$ (top) and natural abundance **2** (bottom).

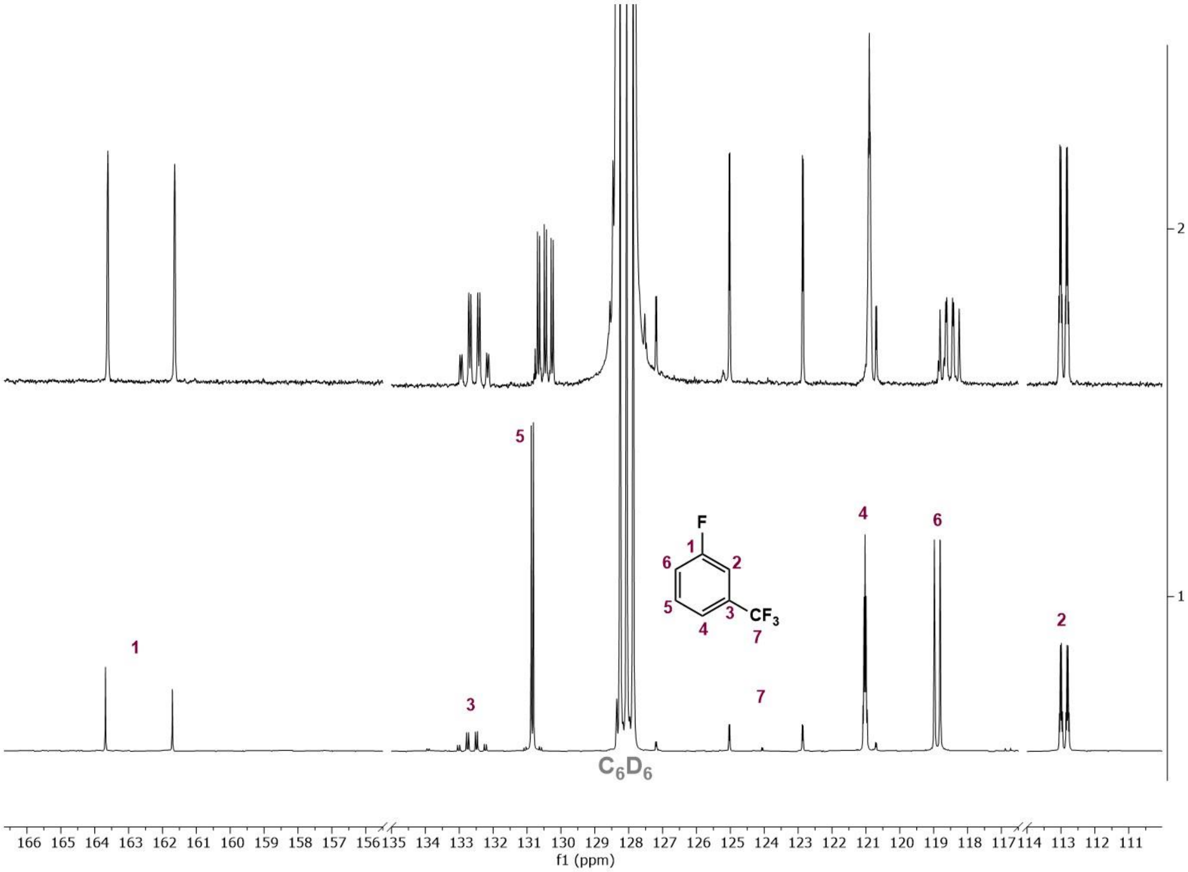


Figure S14. Stacked $^{13}C\{^1H\}$ NMR spectra of **2**: labeled, **2**-*d*$_2$ (top) and natural abundance **2** (bottom).

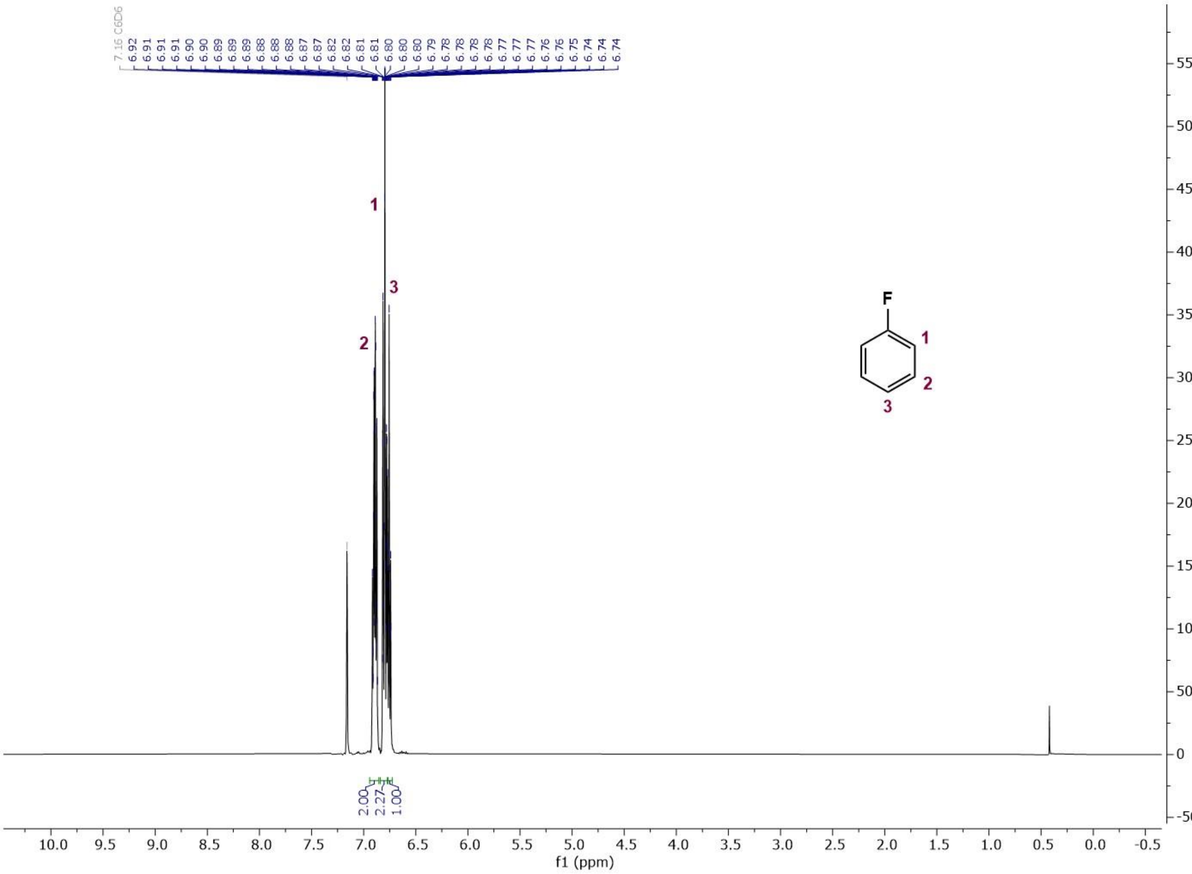


Figure S15. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **3**.

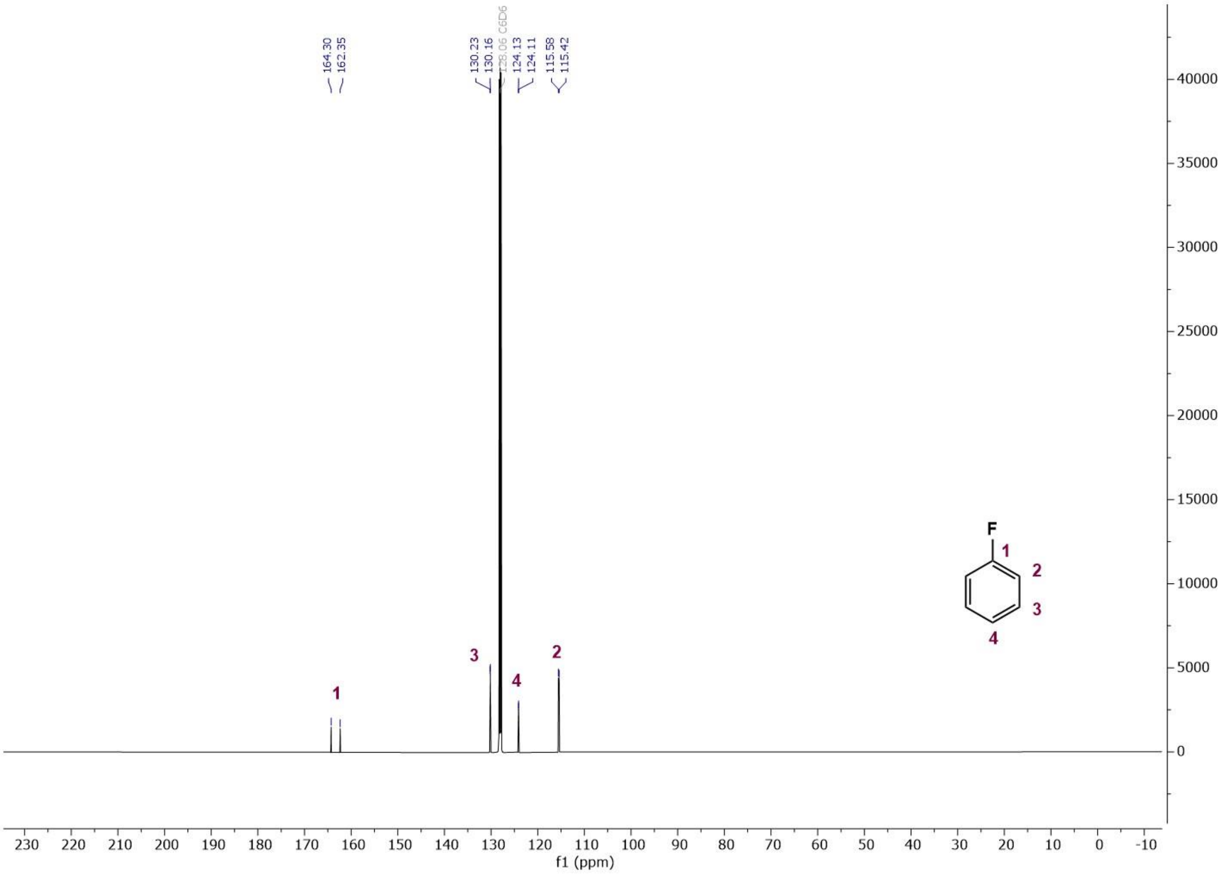


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, benzene-*d*$_6$) of natural abundance **3**.

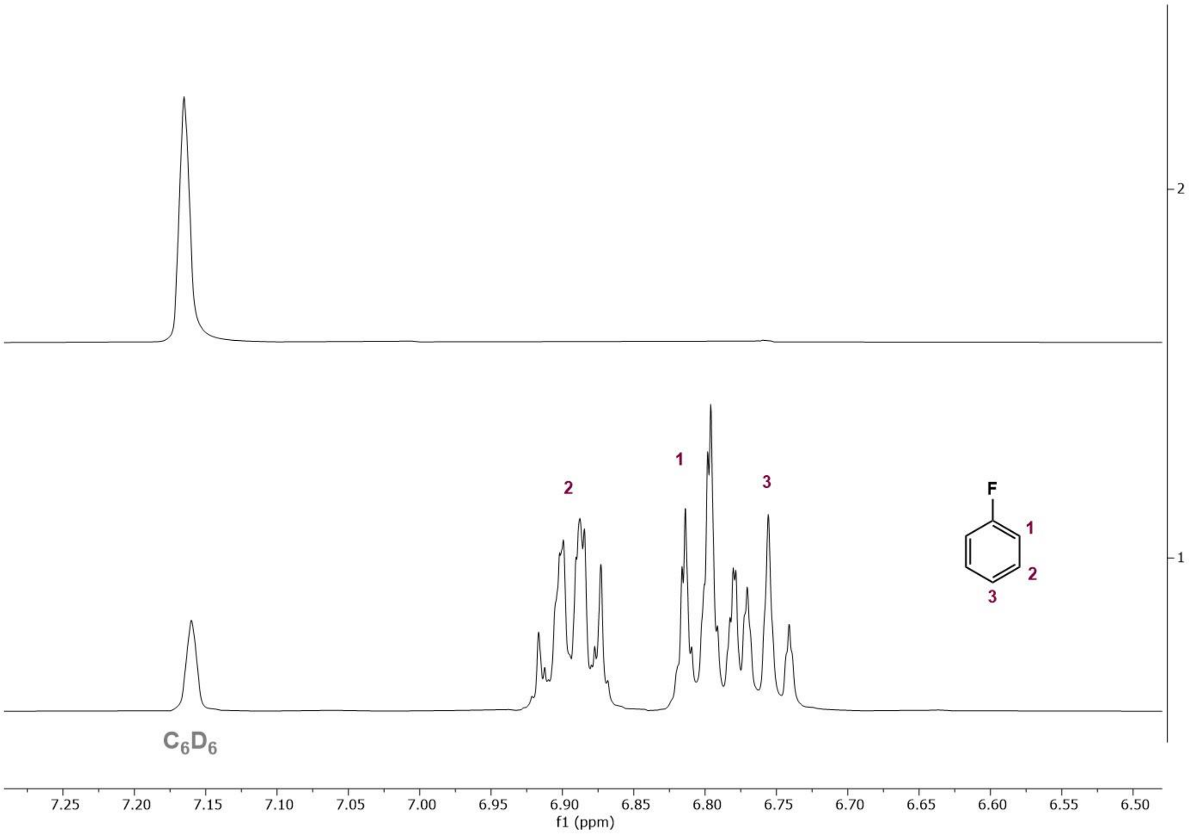


Figure S17. Stacked ^{1}H NMR spectra of **3**: labeled, **3**-d_5 (top) and natural abundance **3** (bottom).

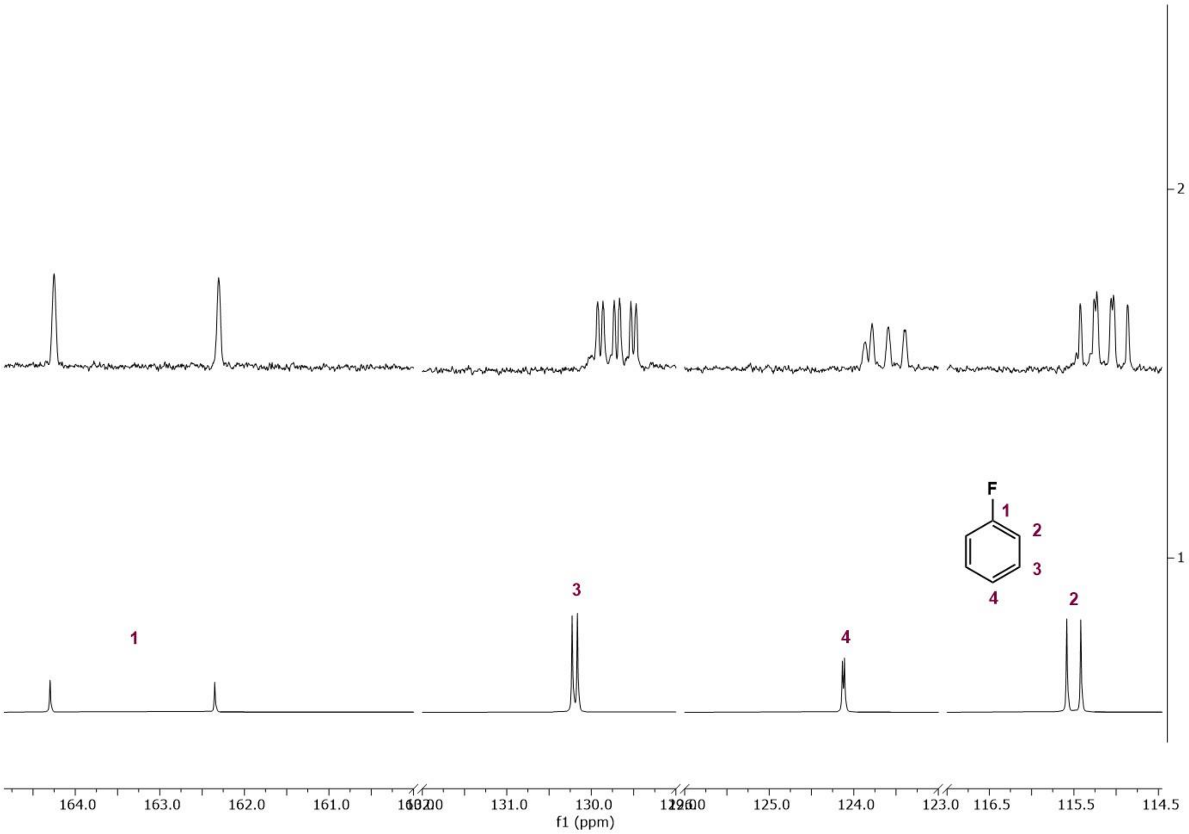


Figure S18. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **3**: labeled, **3**-d_5 (top) and natural abundance **3** (bottom).

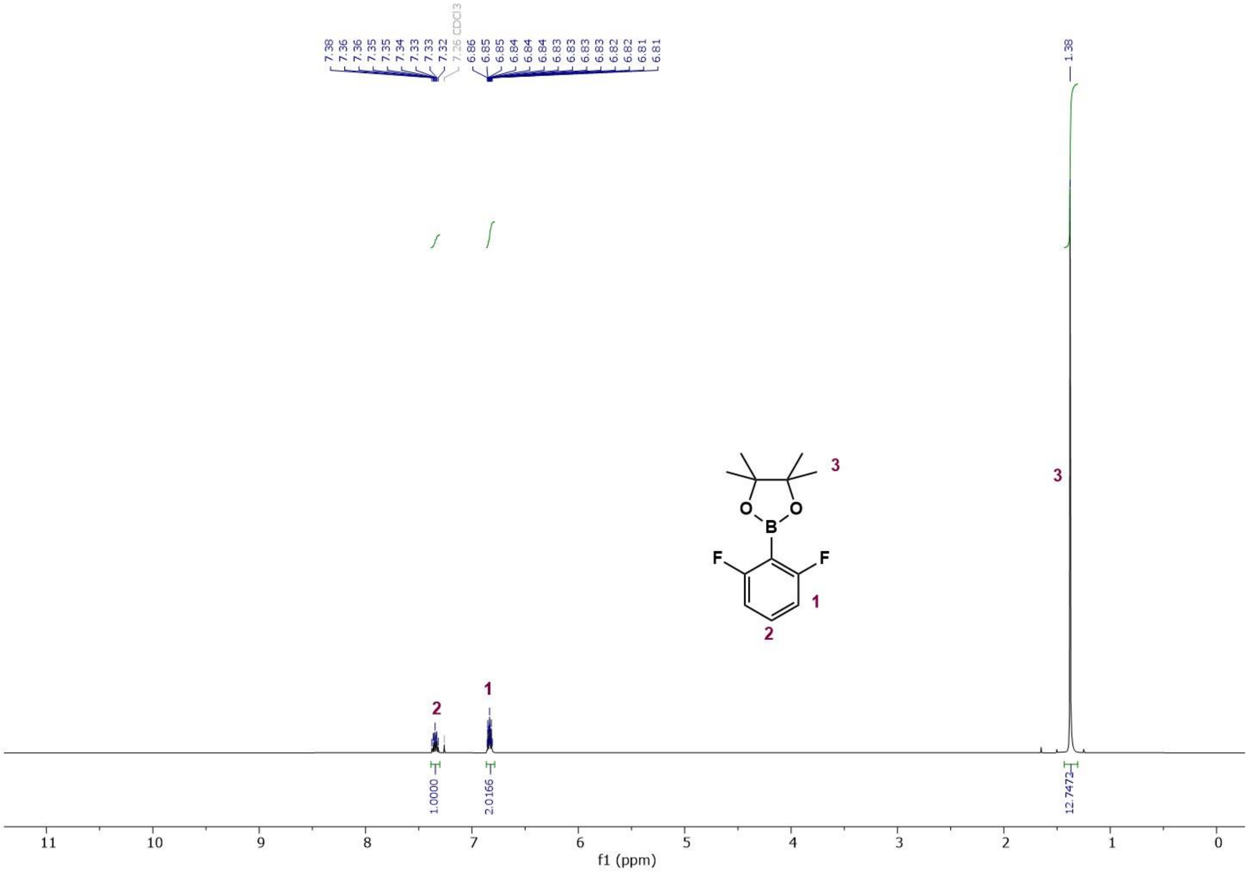


Figure S19. ^{1}H NMR spectrum (500 MHz, benzene-*d*$_6$) of natural abundance **4**.

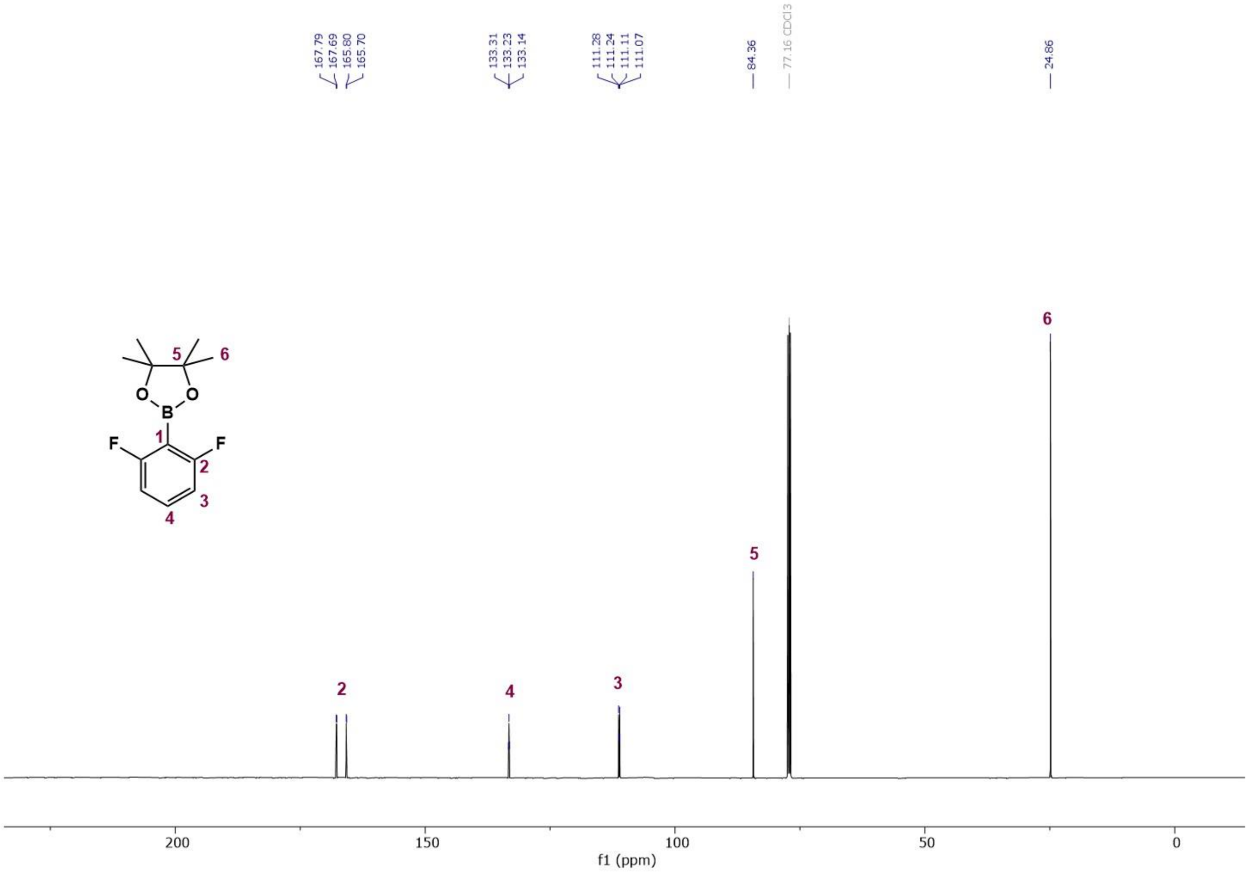


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, benzene-*d*$_6$) of natural abundance **4**.

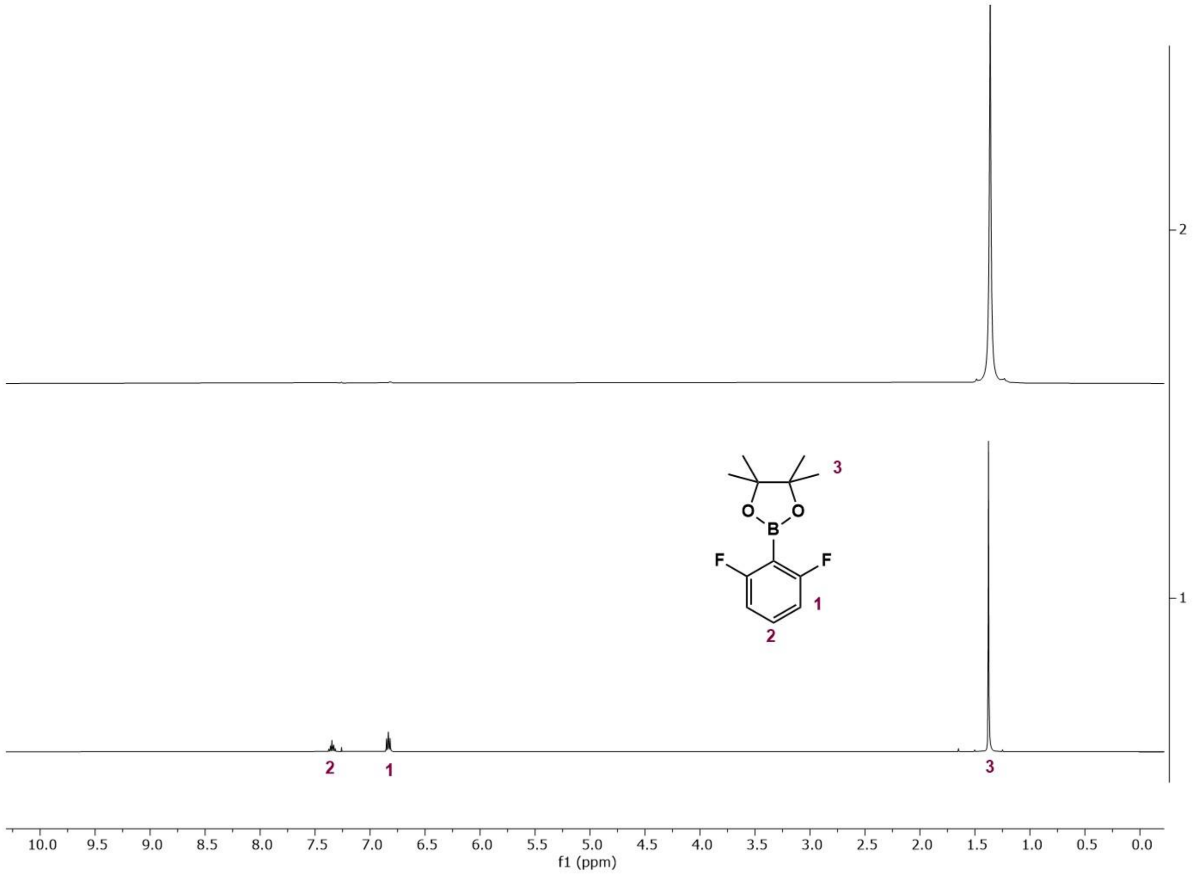


Figure S21. Stacked ^1H NMR spectra of **4**: labeled, **4**-d_3 (top) and natural abundance **4** (bottom).

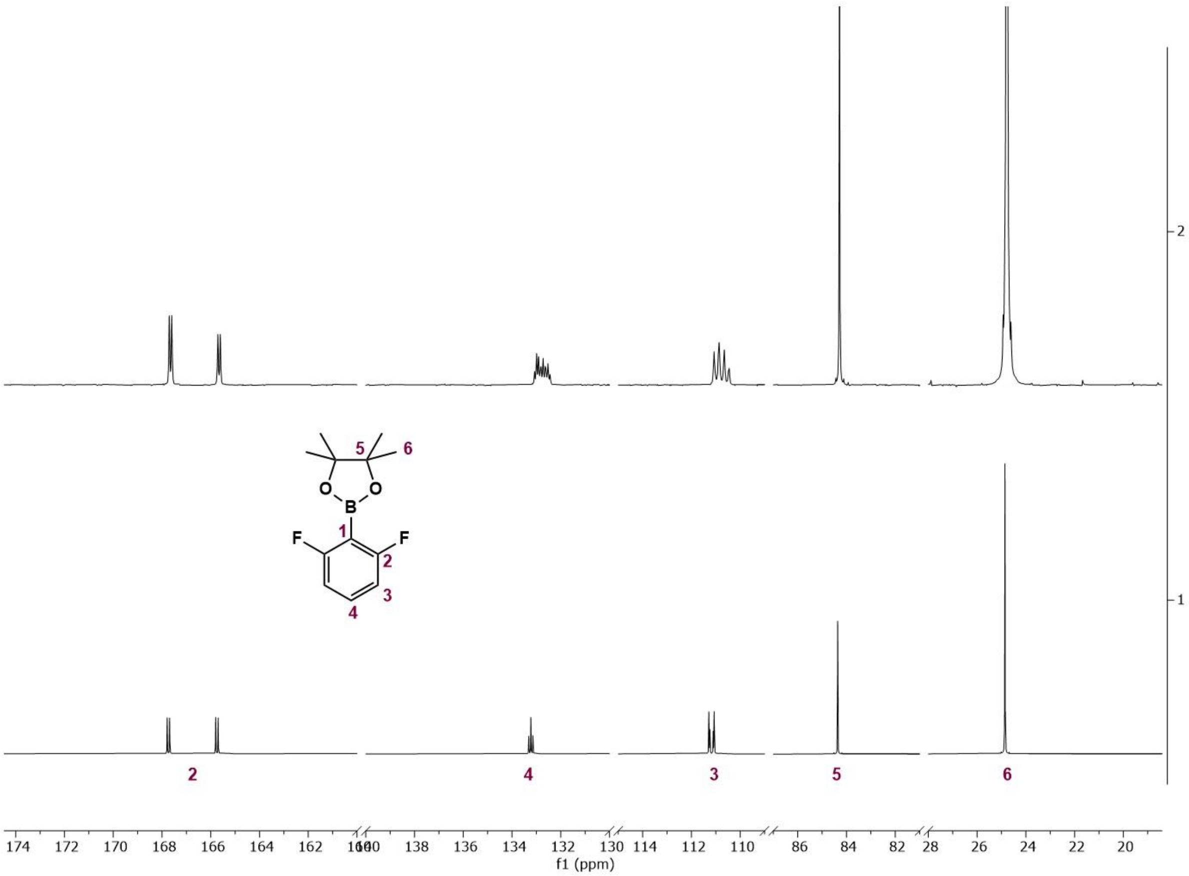


Figure S22. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **4**: labeled, **4**-*d*$_3$ (top) and natural abundance **4** (bottom).

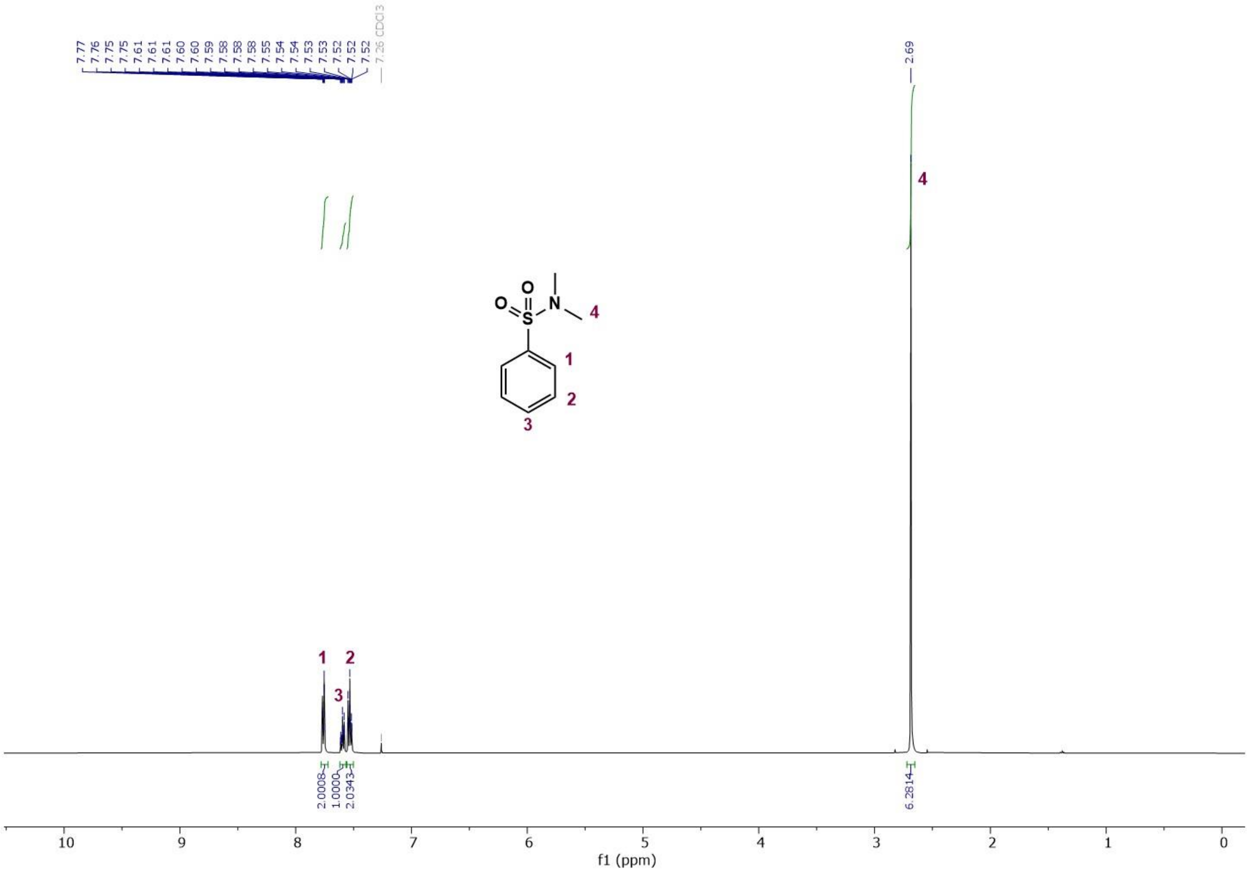


Figure S23. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **5**.

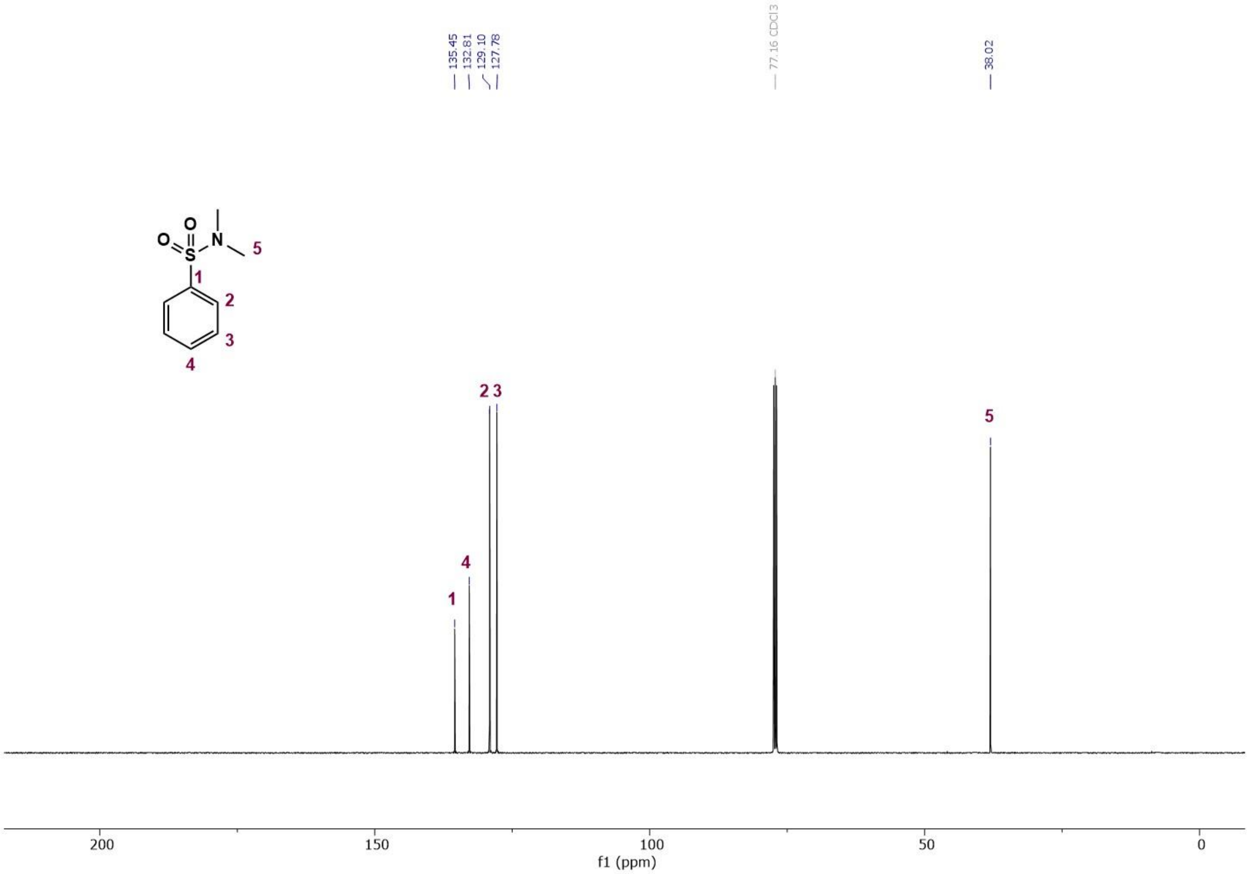


Figure S24. ^{13}C NMR spectrum (126 MHz, chloroform-*d*) of **5**.

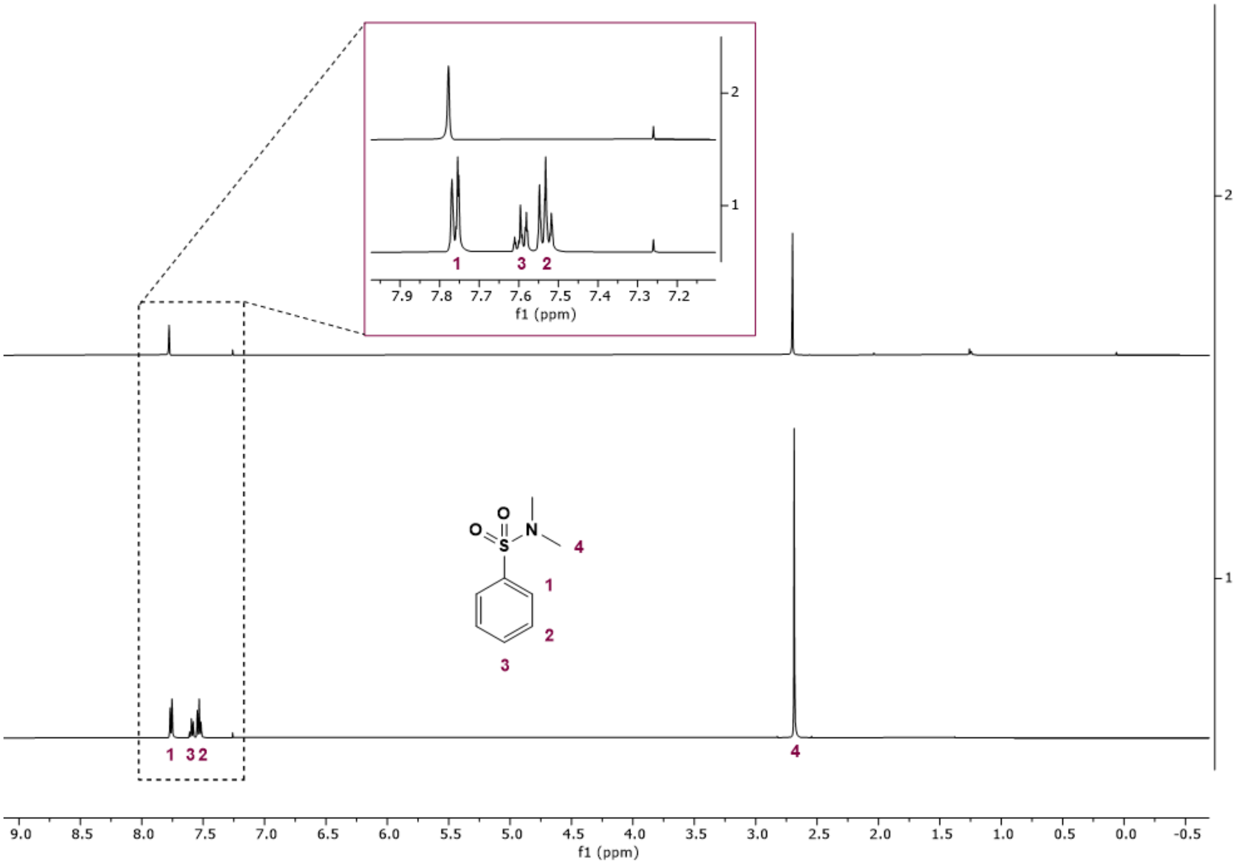


Figure S25. Stacked ^{1}H NMR spectra of **5**: labeled, **5**-d_3 (top) and natural abundance **5** (bottom).

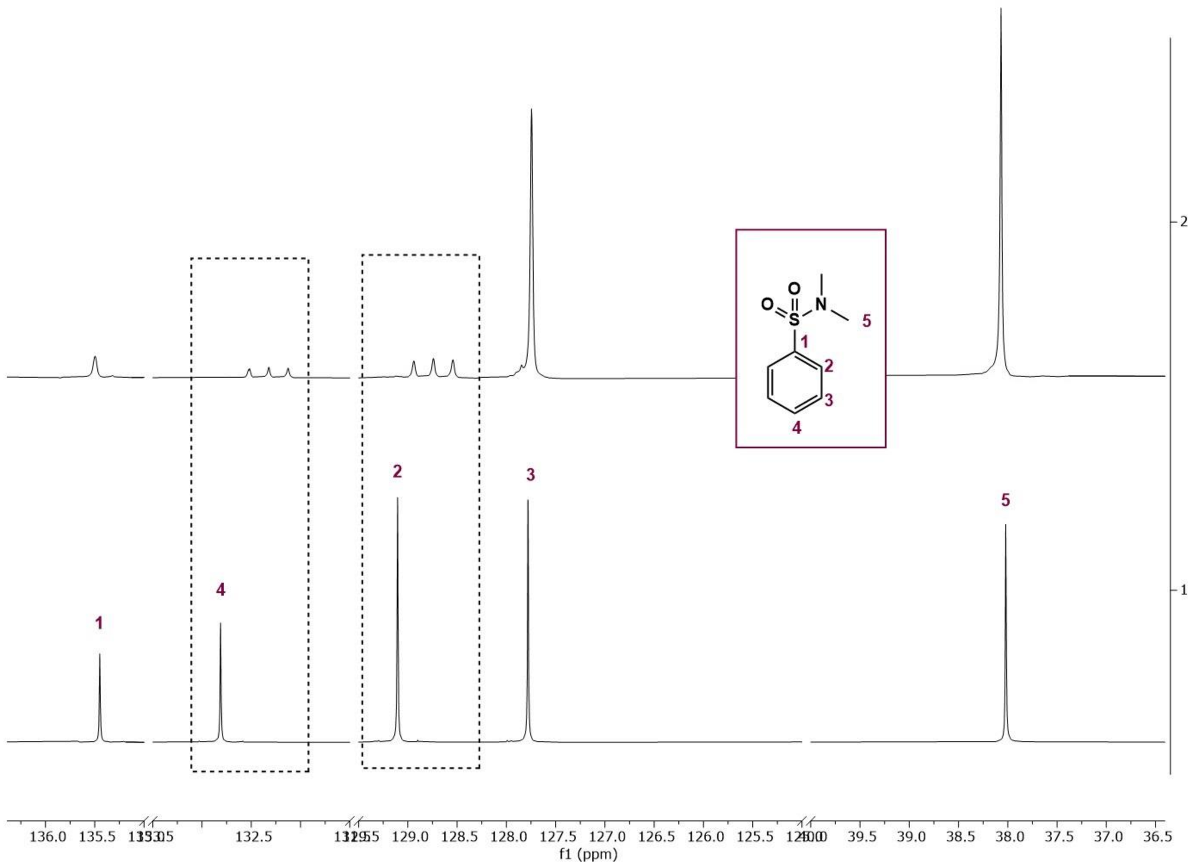


Figure S26. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **5**: labeled, **5**-d_3 (top) and natural abundance **5** (bottom).

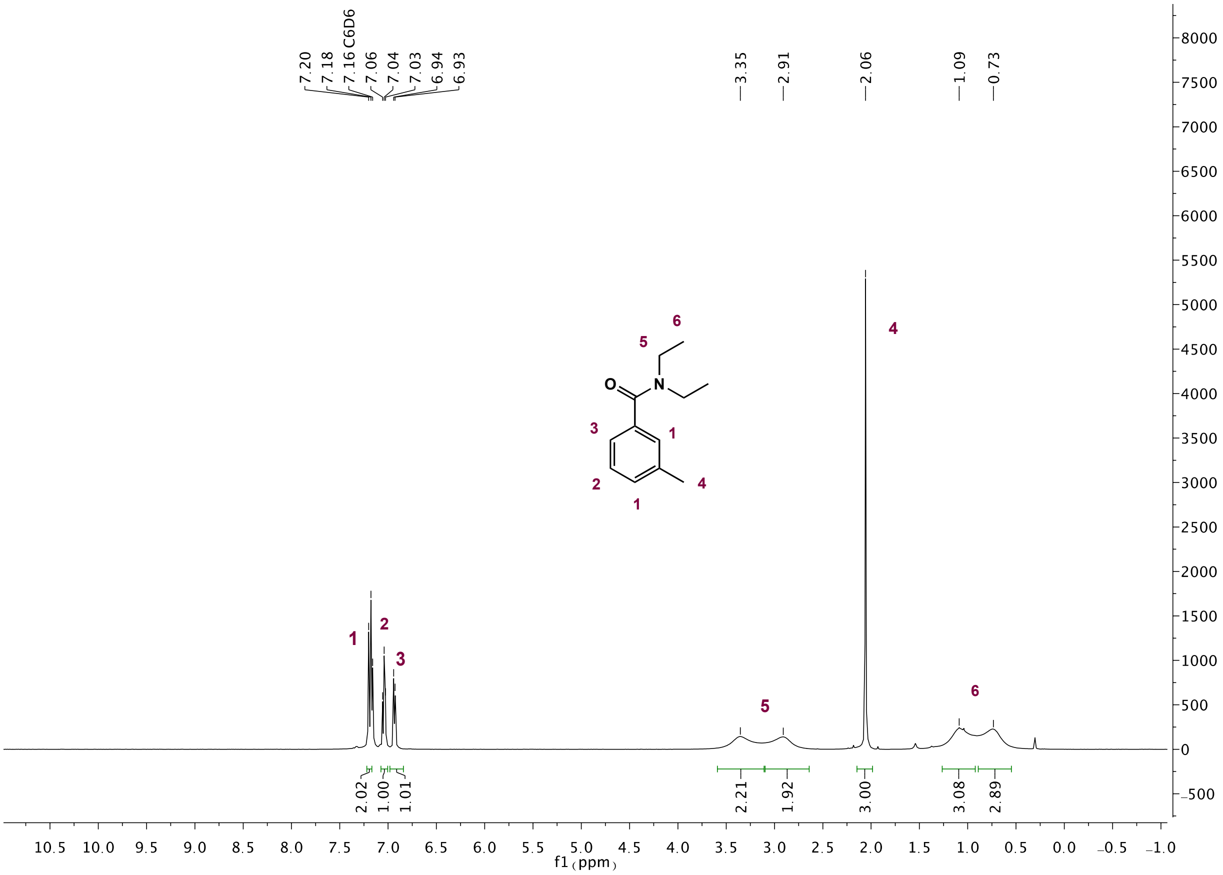


Figure S27. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **6**.

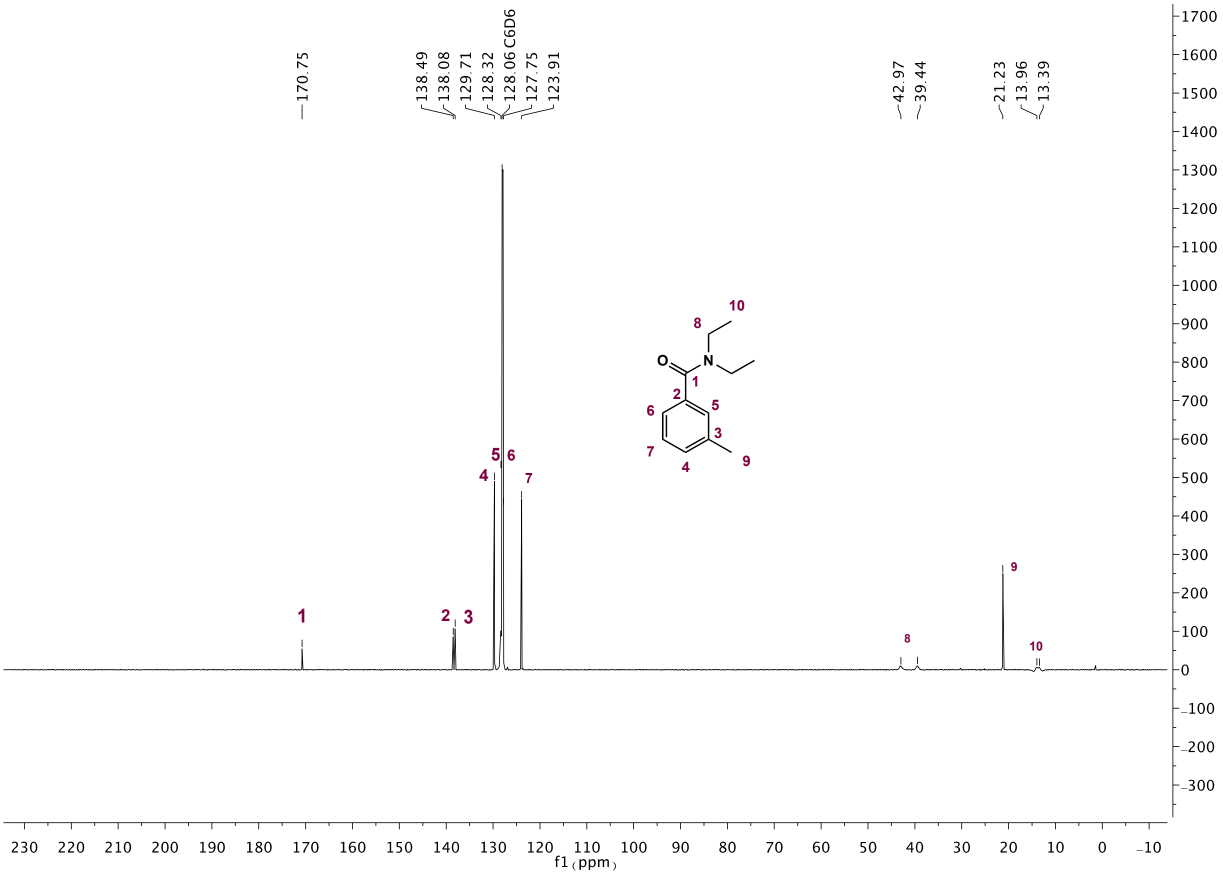


Figure S28. $^{13}C\{^1H\}$ NMR spectrum (126 MHz, benzene-d$_6$) of natural abundance **6.**

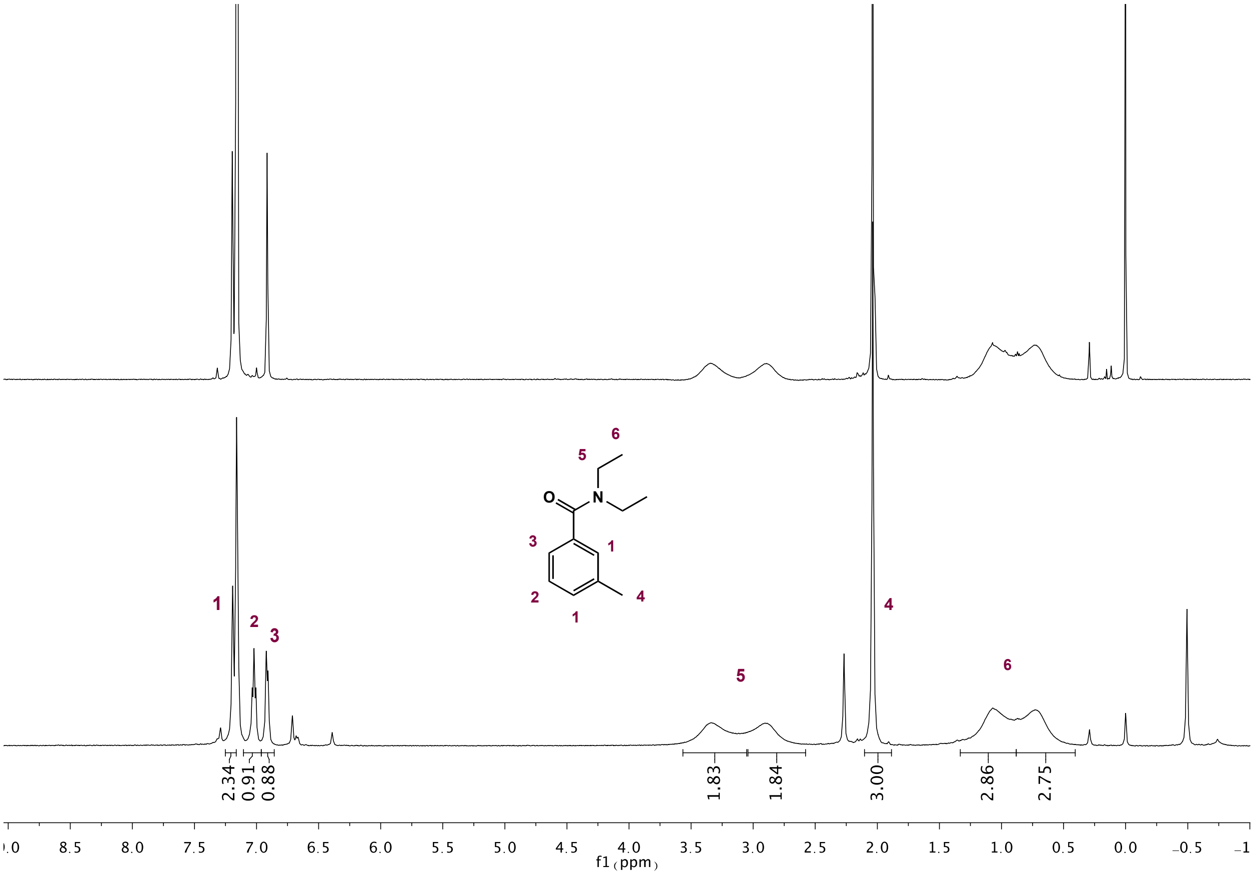


Figure S29. Stacked ^{1}H NMR spectra (400 MHz, benzene-d_6) of **6**: labeled, **6**-d_1 (top) and natural abundance **5** (bottom).

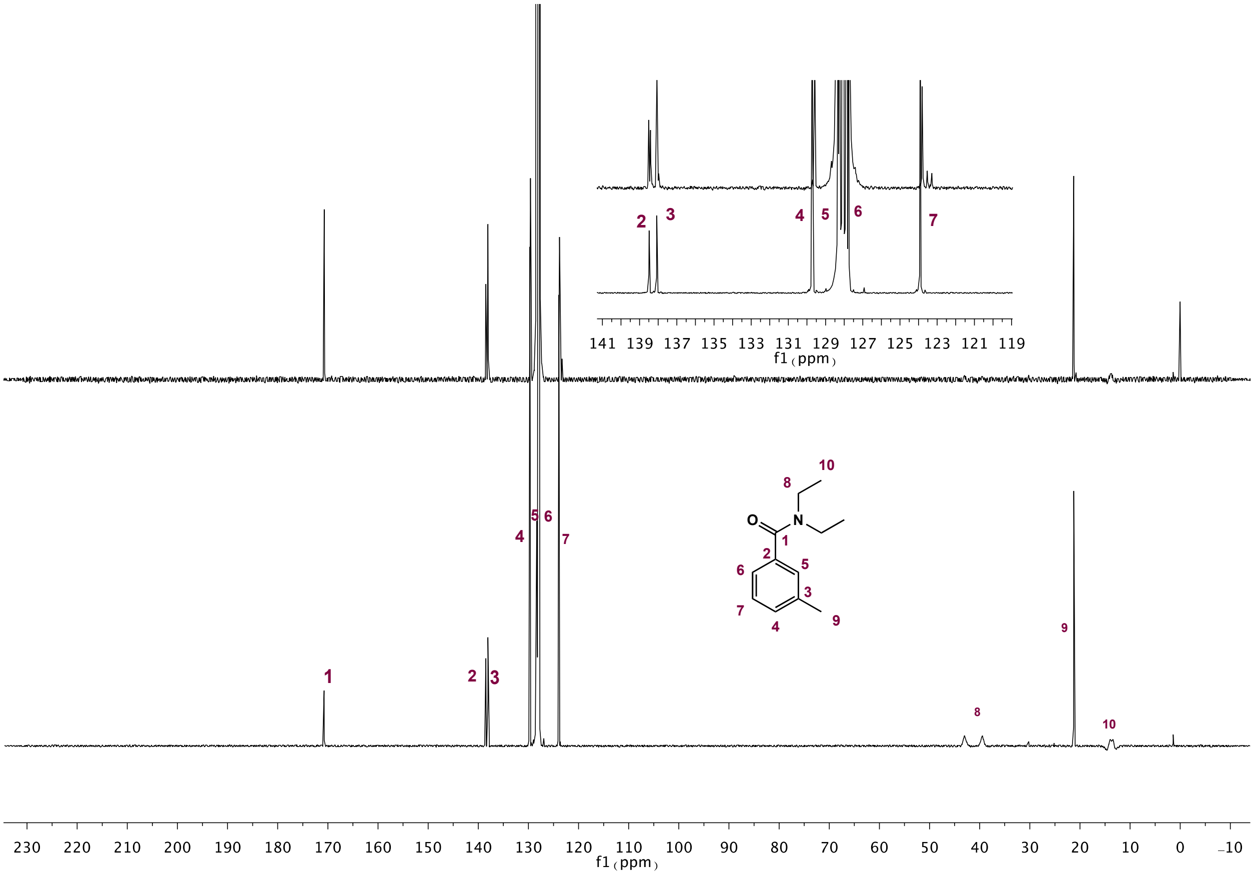


Figure S30. Stacked ^{13}C NMR spectra (126 MHz, benzene-d_6) of **6**: labeled, **6**-d_1 (top) and natural abundance **6** (bottom).

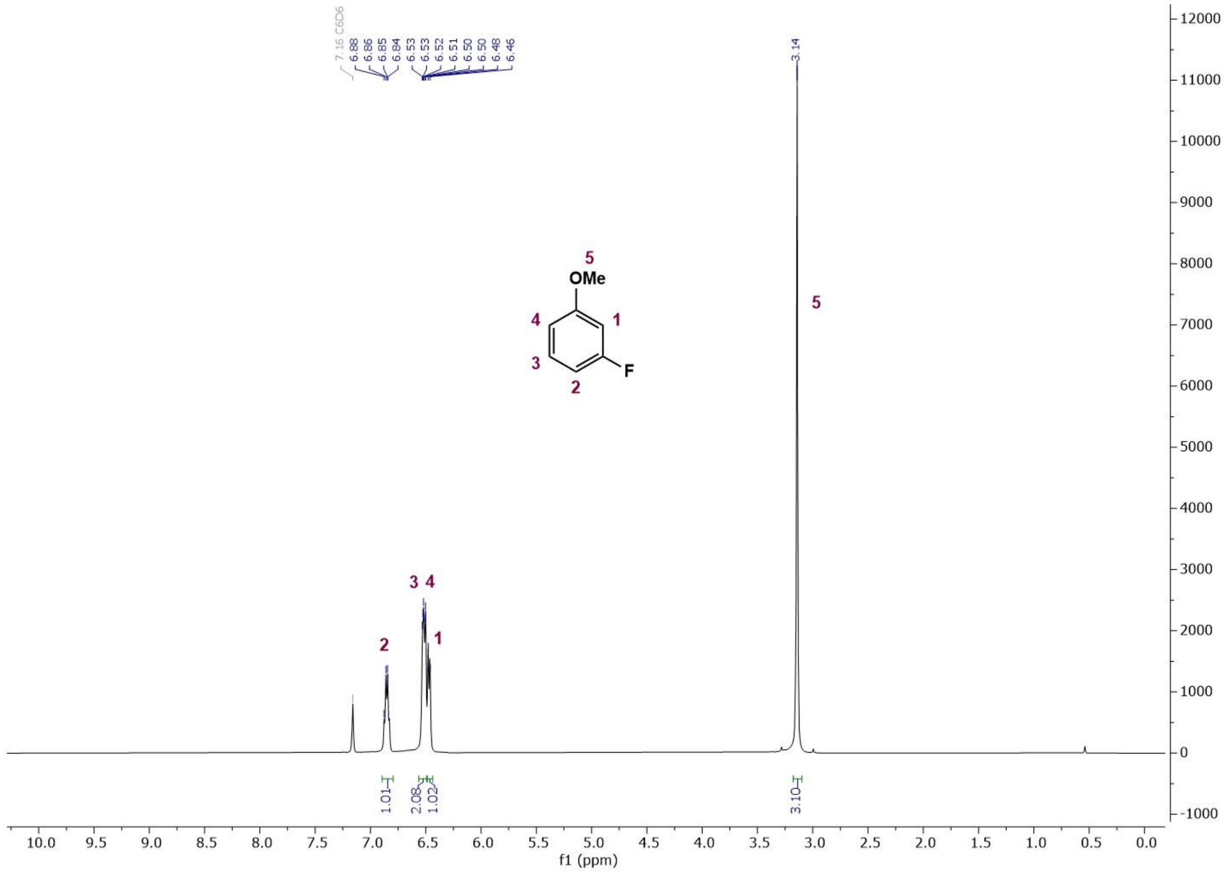


Figure S31. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **7**.

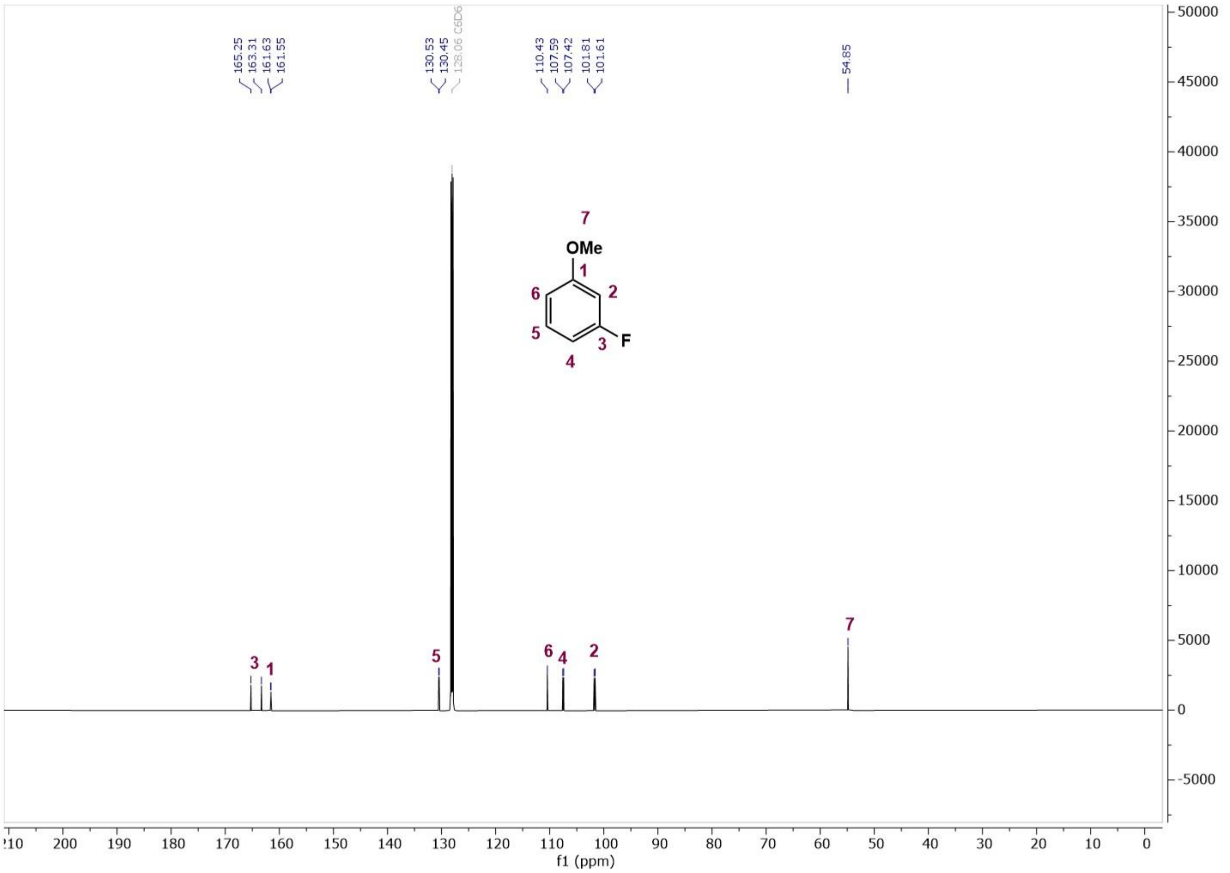


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, benzene-d_6) of natural abundance **7**.

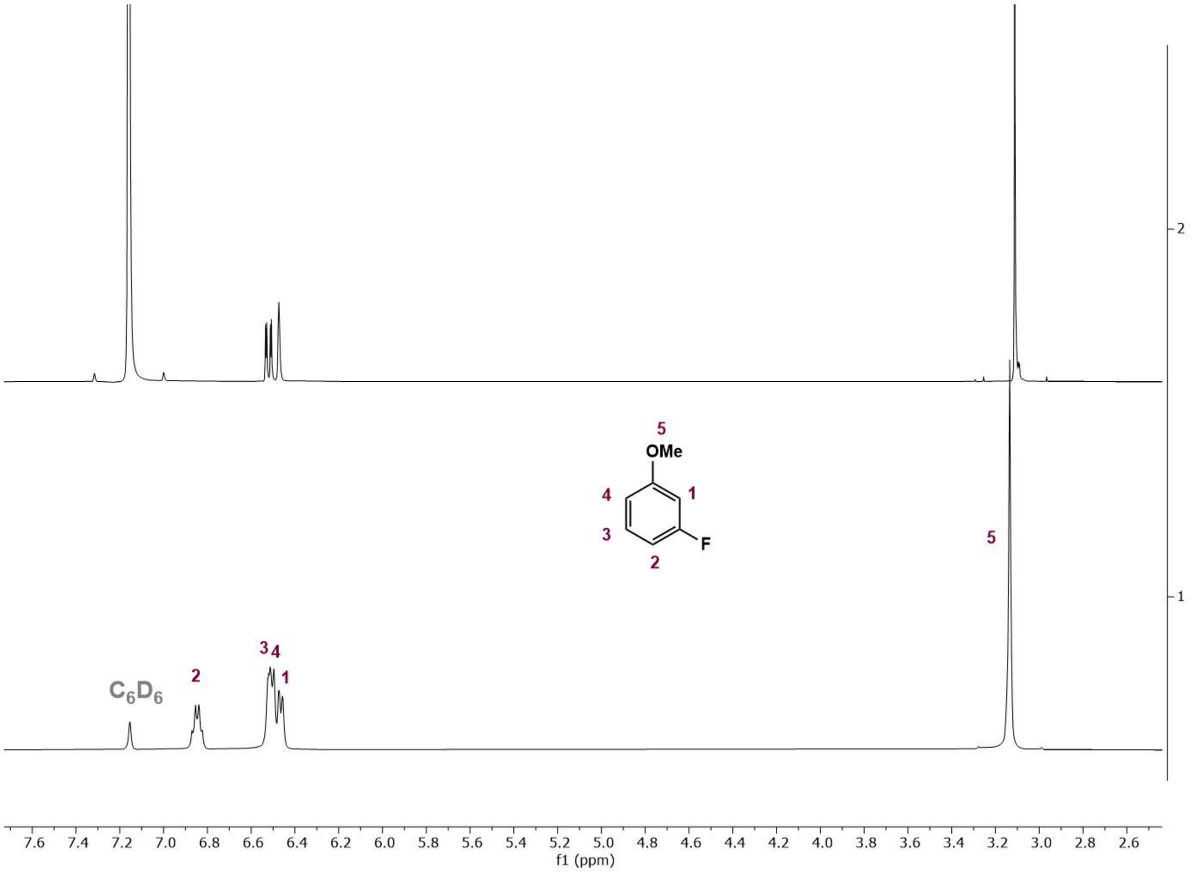


Figure S33. Stacked ^{1}H NMR spectra of **7**: labeled, **7**-*d*$_2$ (top) and natural abundance **7** (bottom).

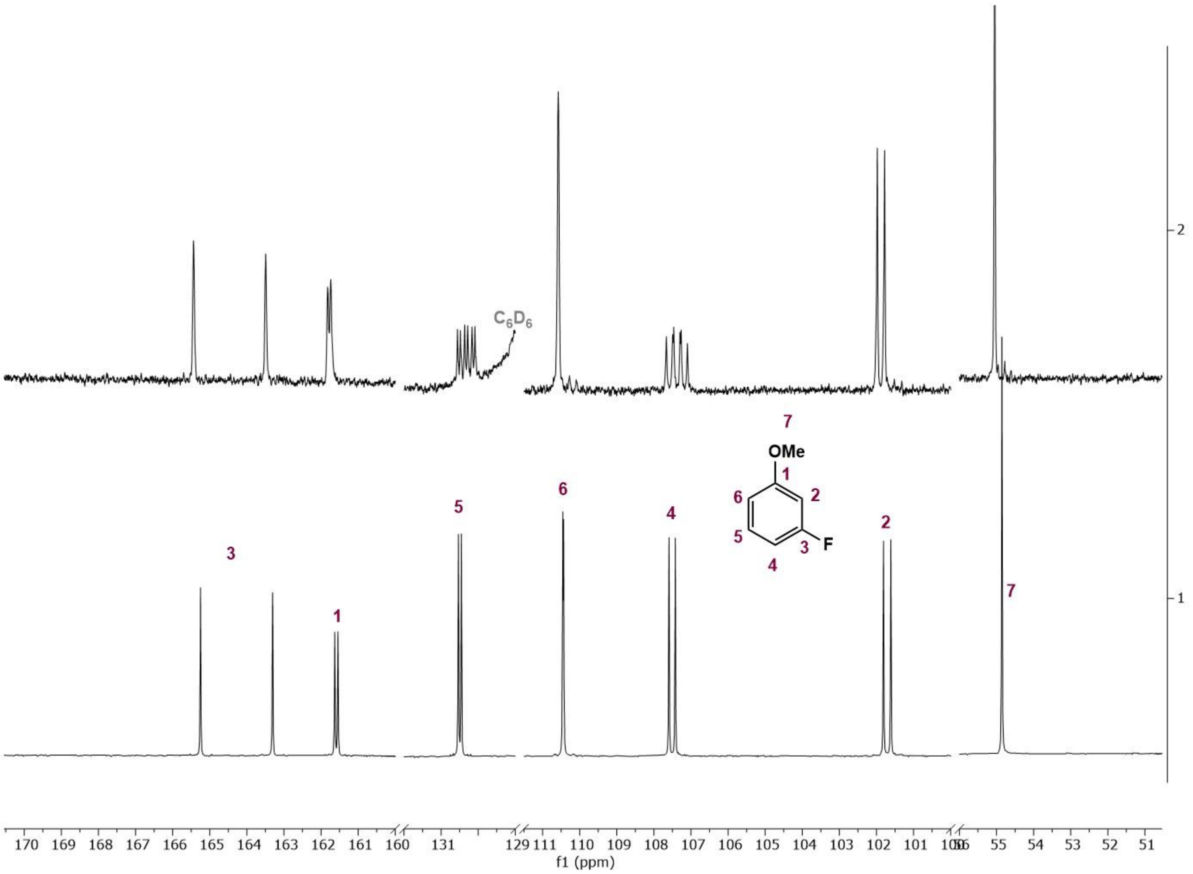


Figure S34. Stacked $^{13}C\{^1H\}$ NMR spectra of **7**: labeled, **7**-*d*2 (top) and natural abundance **7** (bottom).

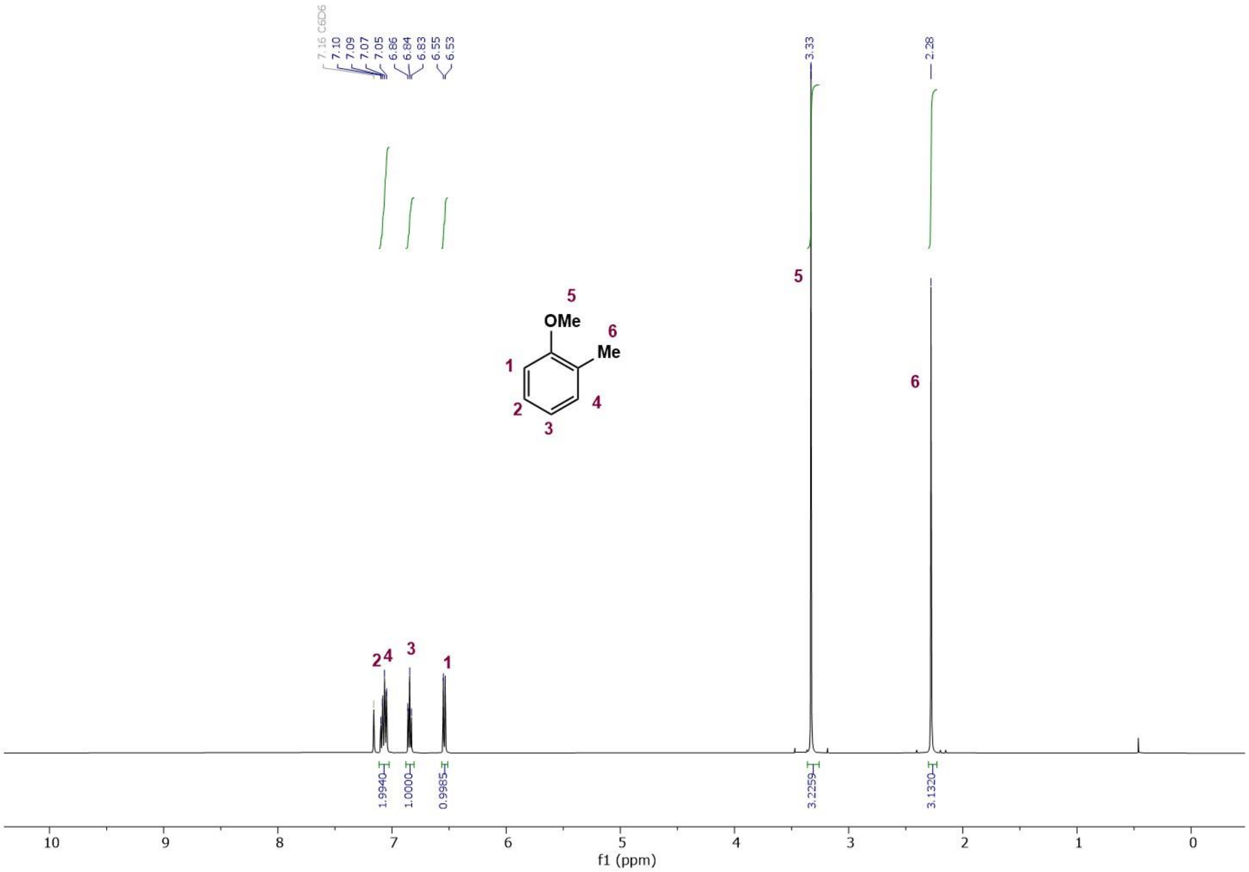


Figure S35. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **8**.

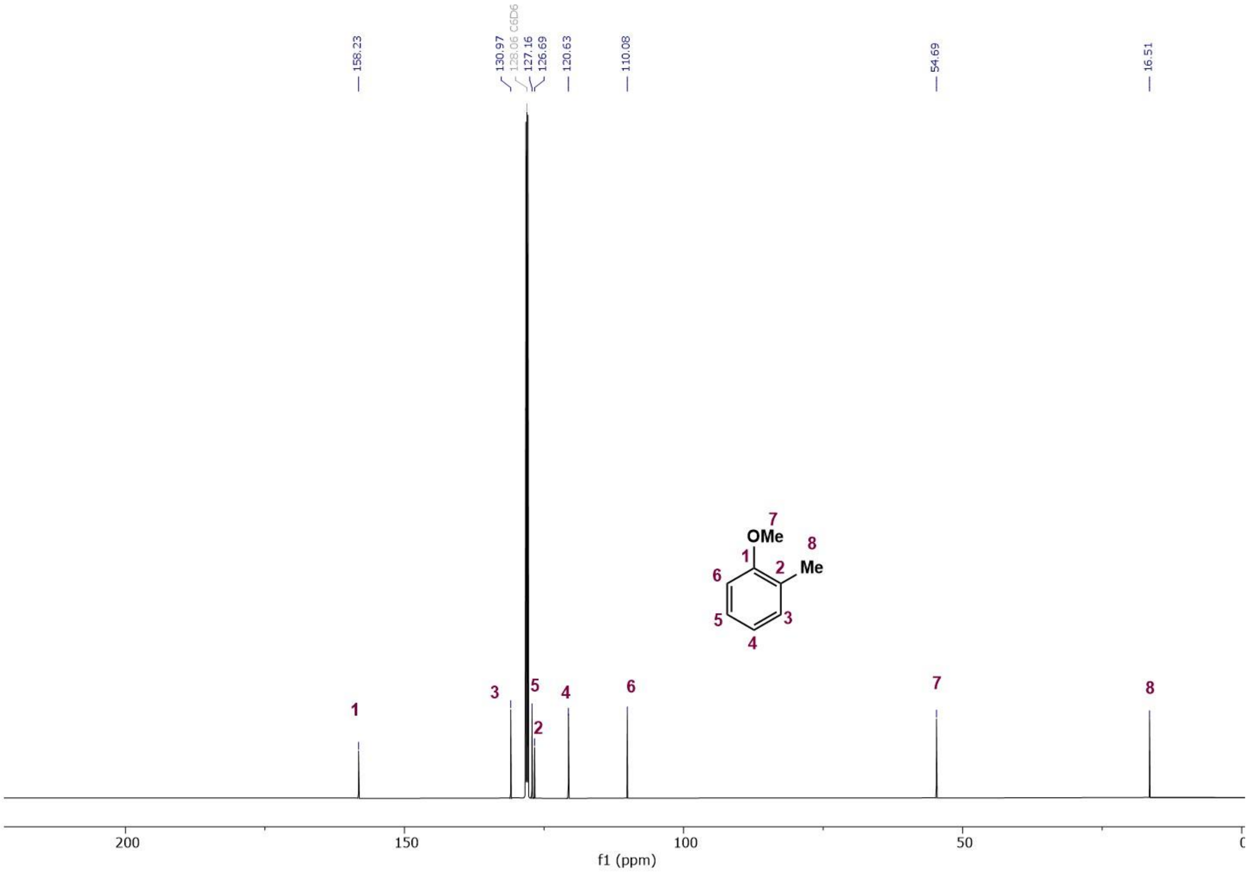


Figure S36. $^{13}C\{^1H\}$ NMR spectrum (126 MHz, benzene-d_6) of natural abundance **8**.

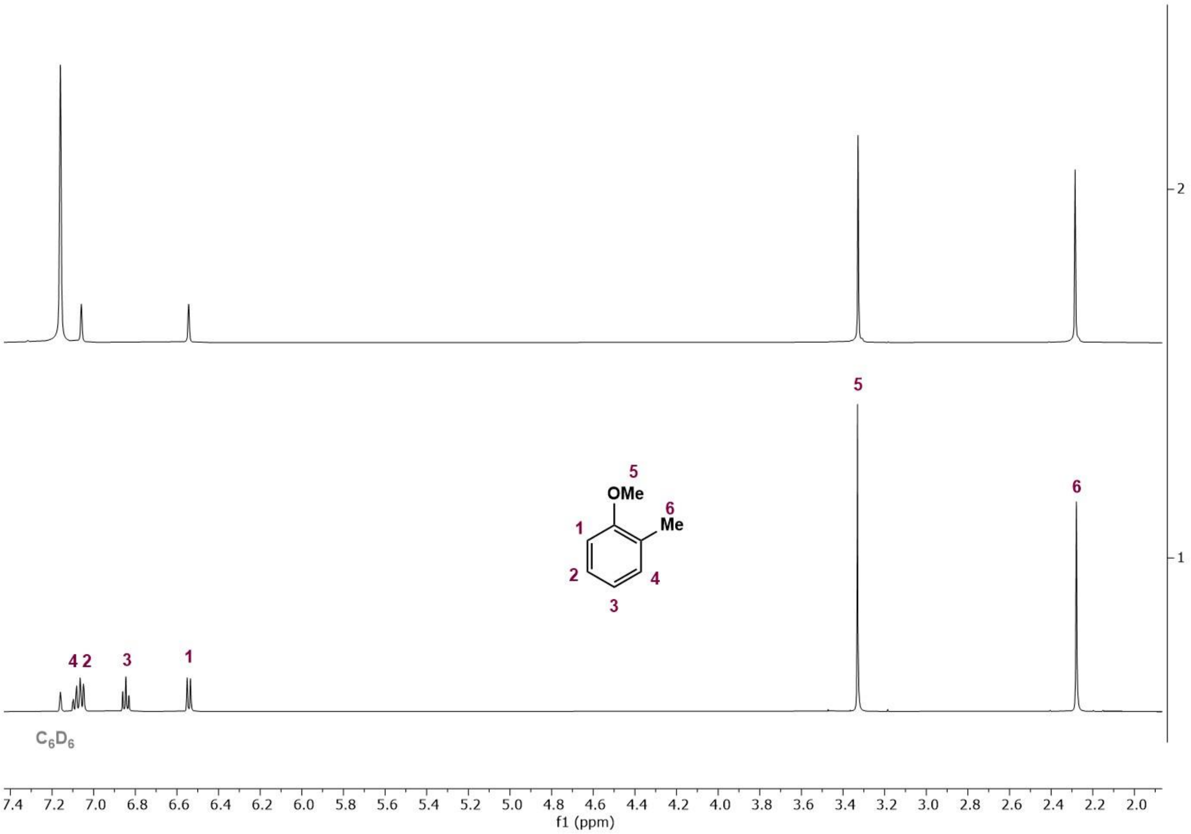


Figure S37. Stacked ^{1}H NMR spectra of **8**: labeled, **8**-d_2 (top) and natural abundance **8** (bottom).

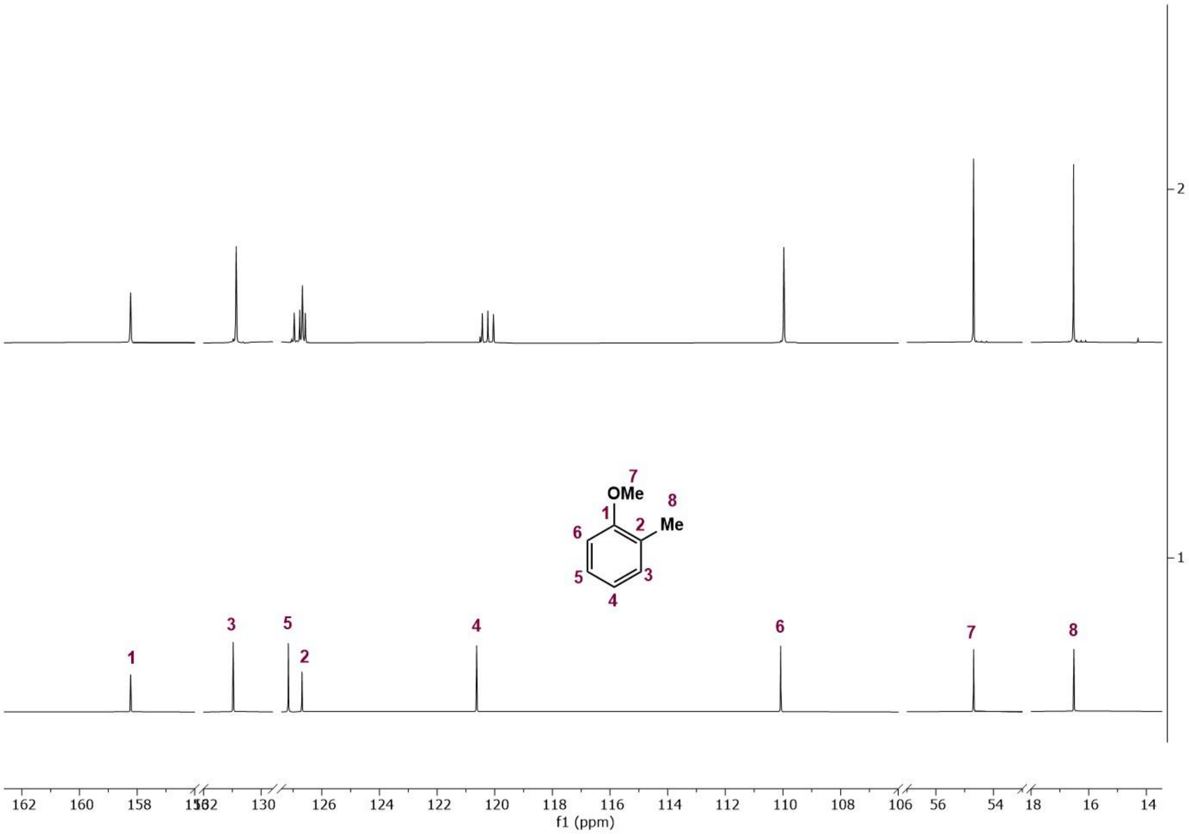


Figure S38. Stacked $^{13}C\{^1H\}$ NMR spectra of **8**: labeled, **8**-*d*$_2$ (top) and natural abundance **8** (bottom).

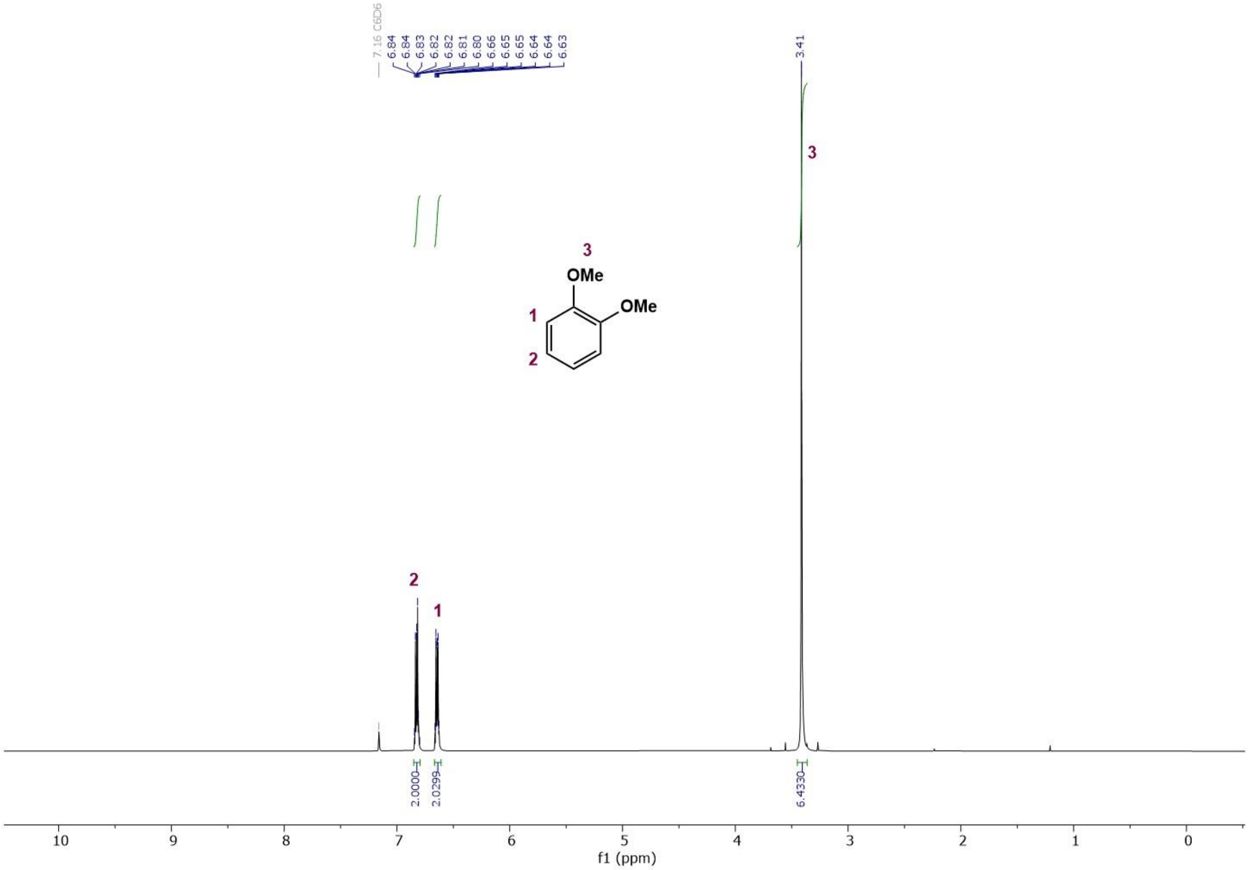


Figure S39. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **9**.

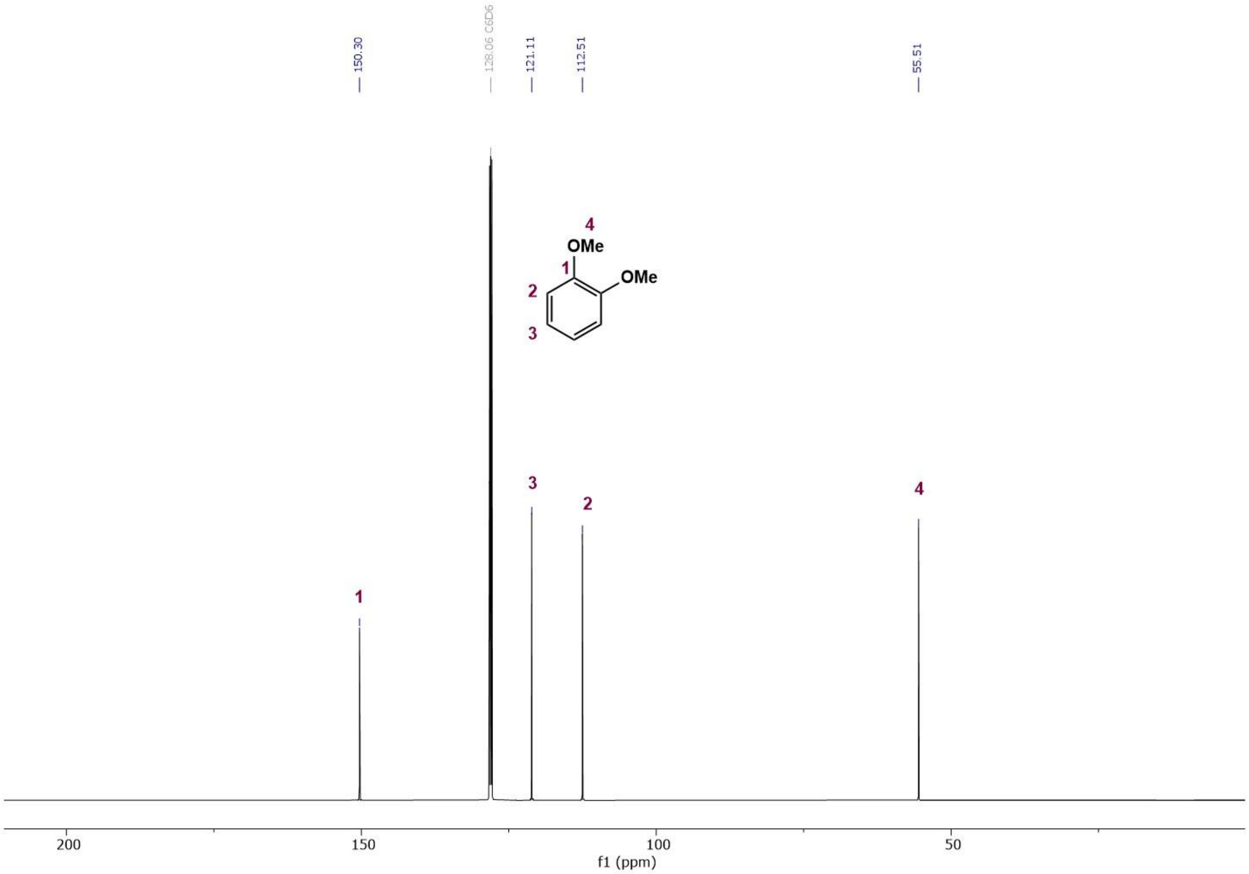


Figure S40. $^{13}C\{^1H\}$ NMR spectrum (126 MHz, benzene-d_6) of natural abundance **9**.

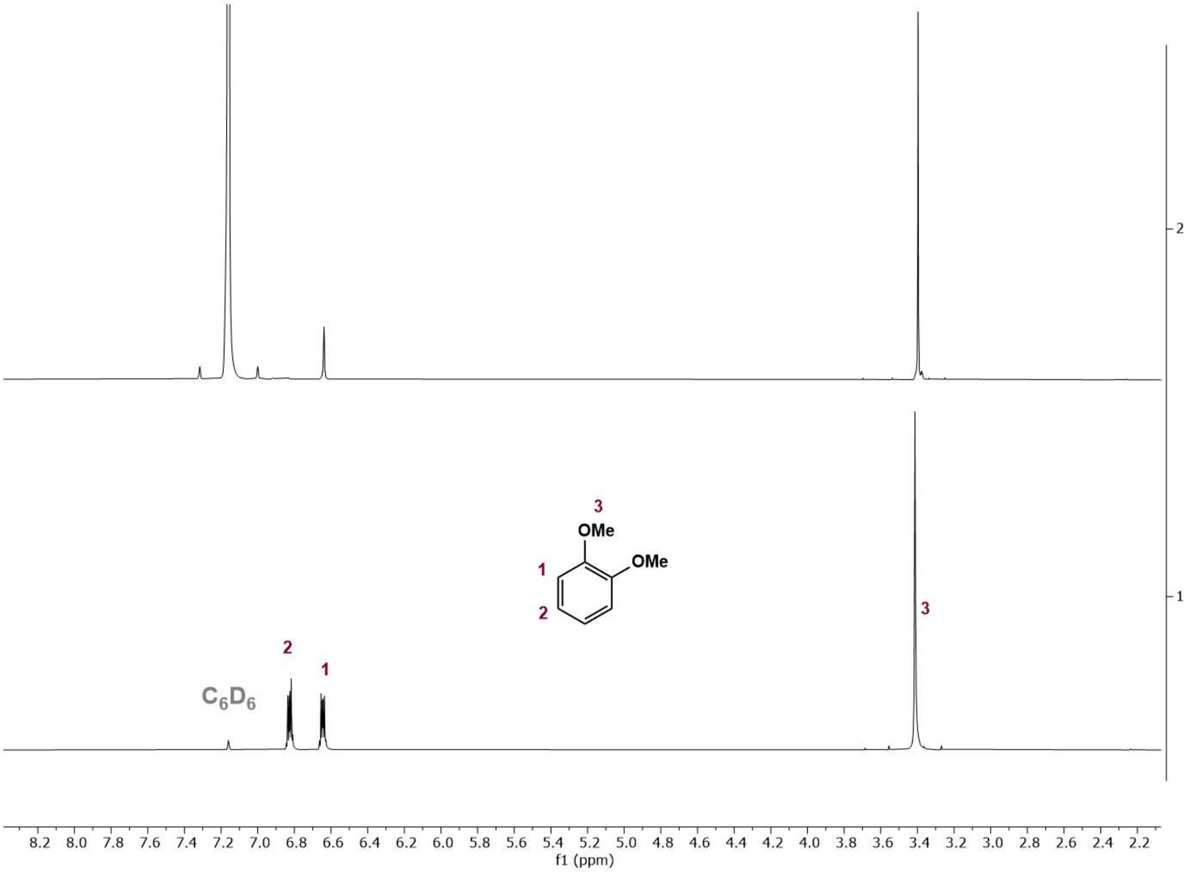


Figure S41. Stacked $^{13}C\{^1H\}$ NMR spectra of **9**: labeled, **9**-*d*$_2$ (top) and natural abundance **9** (bottom).

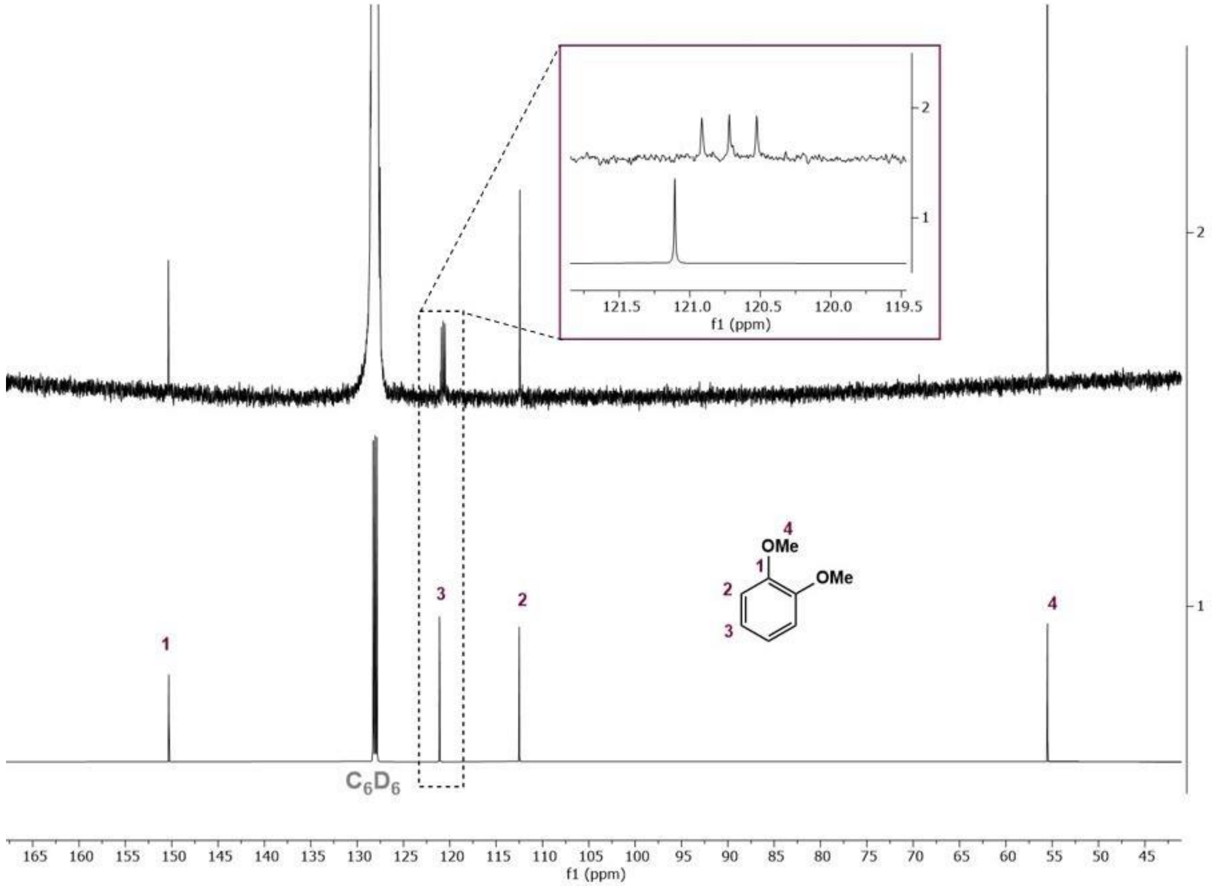


Figure S42. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **9**: labeled, **9**-*d_2* (top) and natural abundance **9** (bottom).

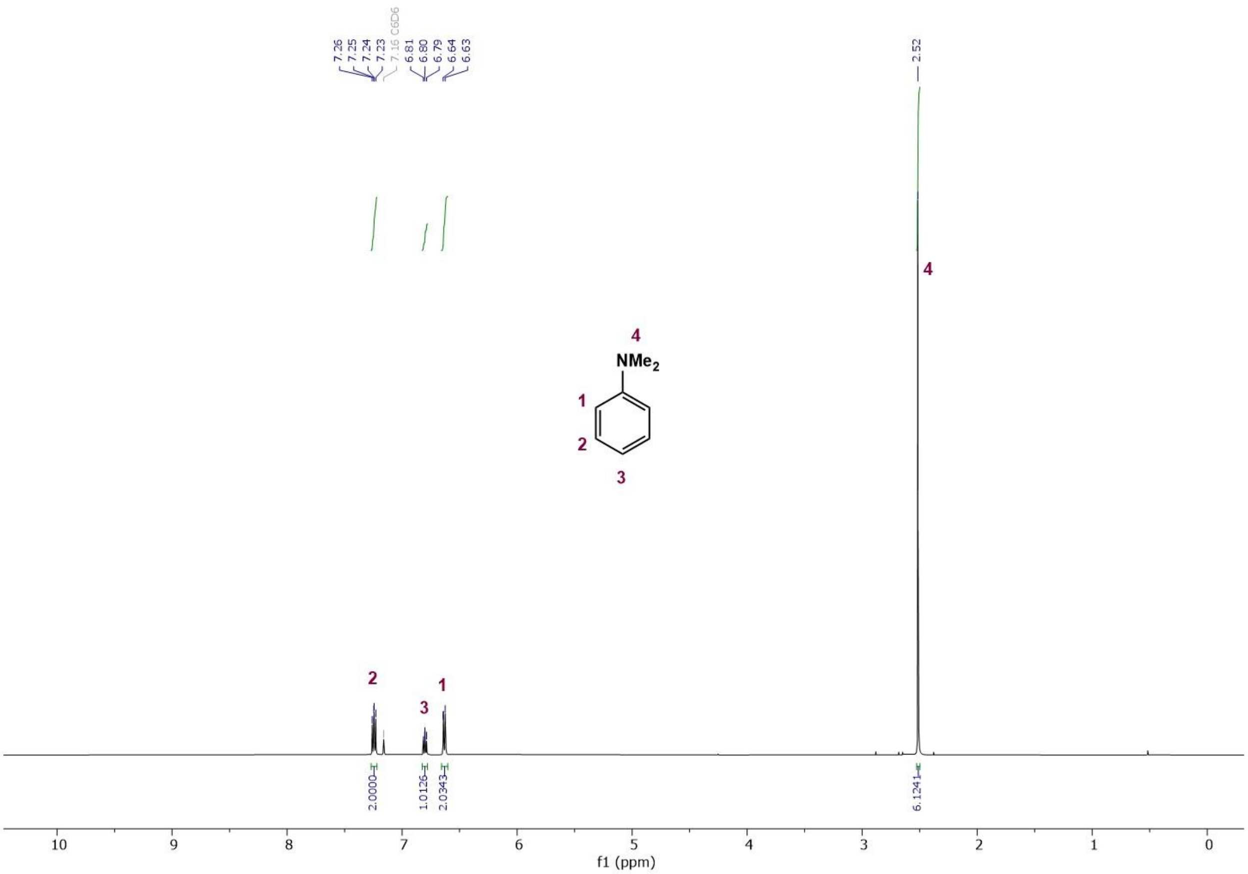


Figure S43. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **10**.

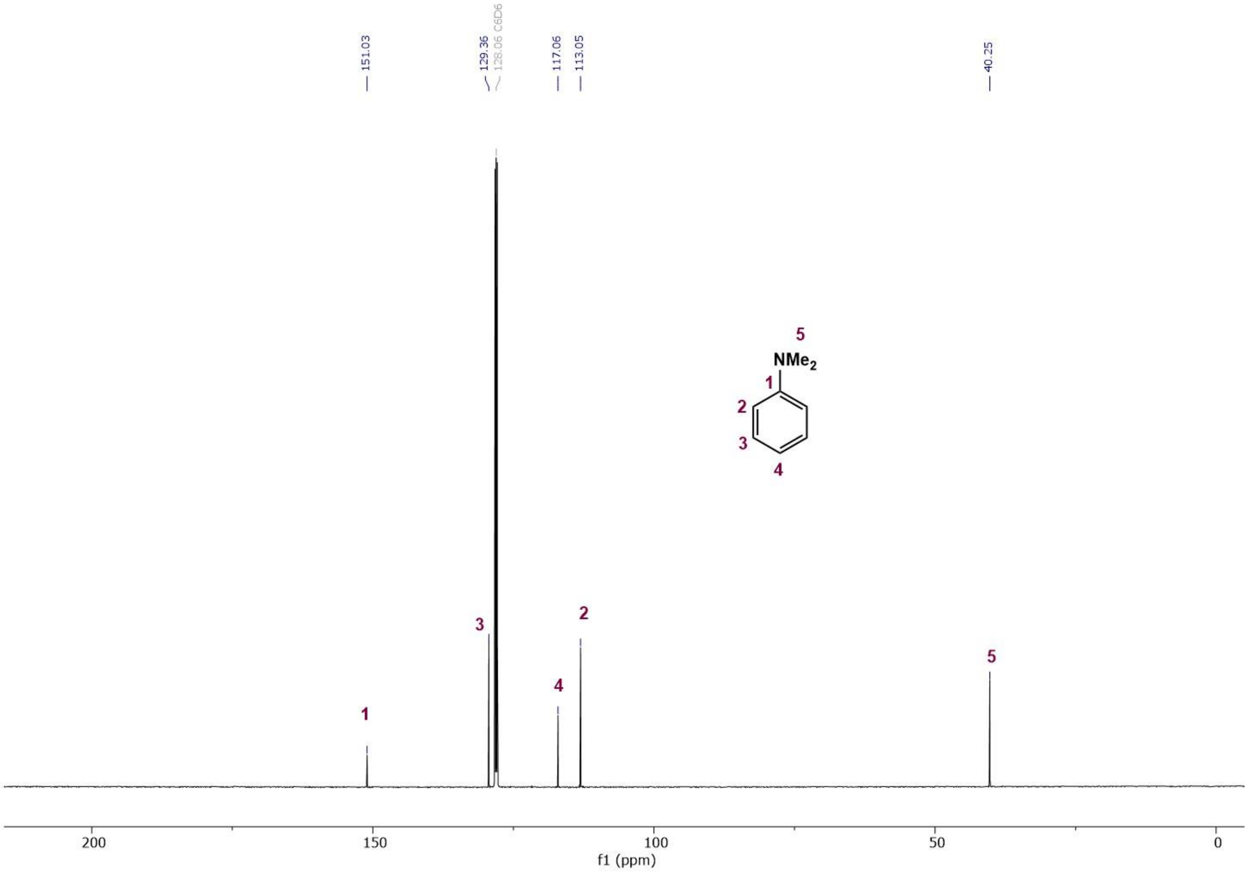


Figure S44. $^{13}C\{^1H\}$ NMR spectrum (126 MHz, benzene-d_6) of natural abundance **10**.

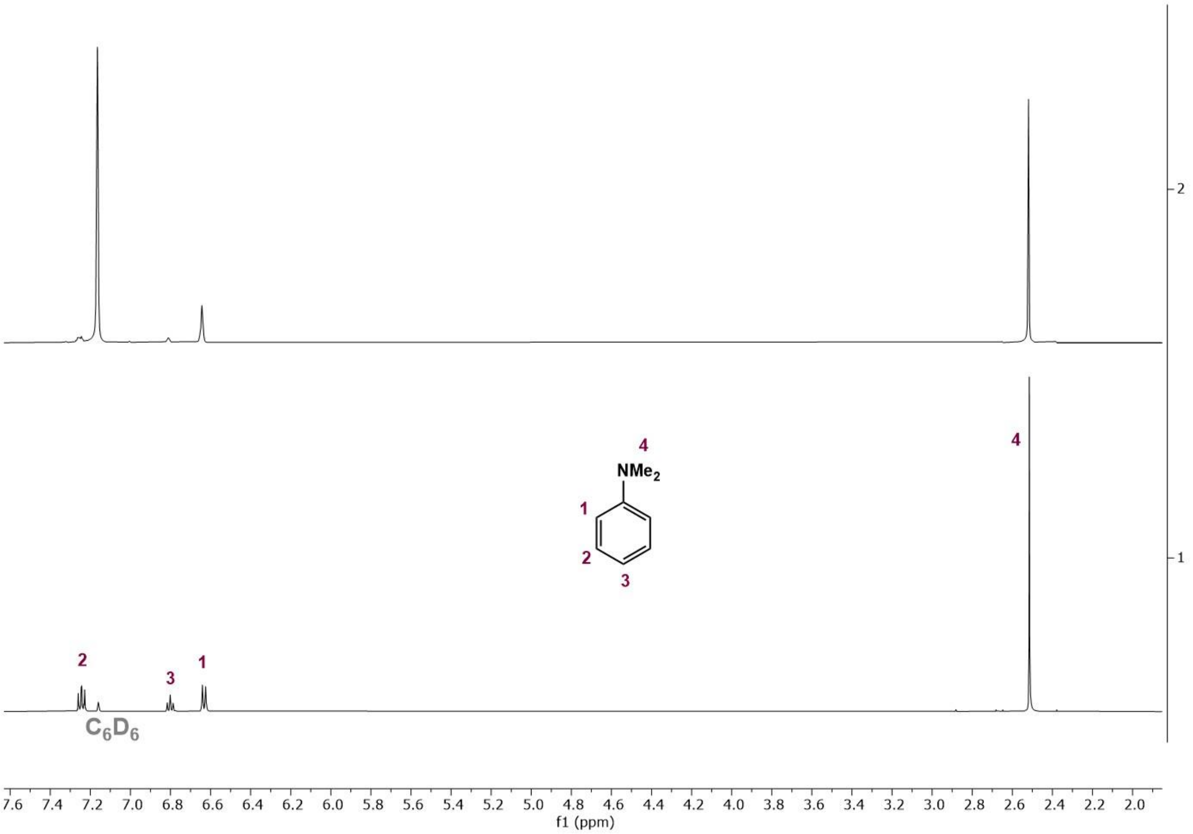


Figure S45. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **10**: labeled, **10**-*d*$_2$ (top) and natural abundance **10** (bottom).

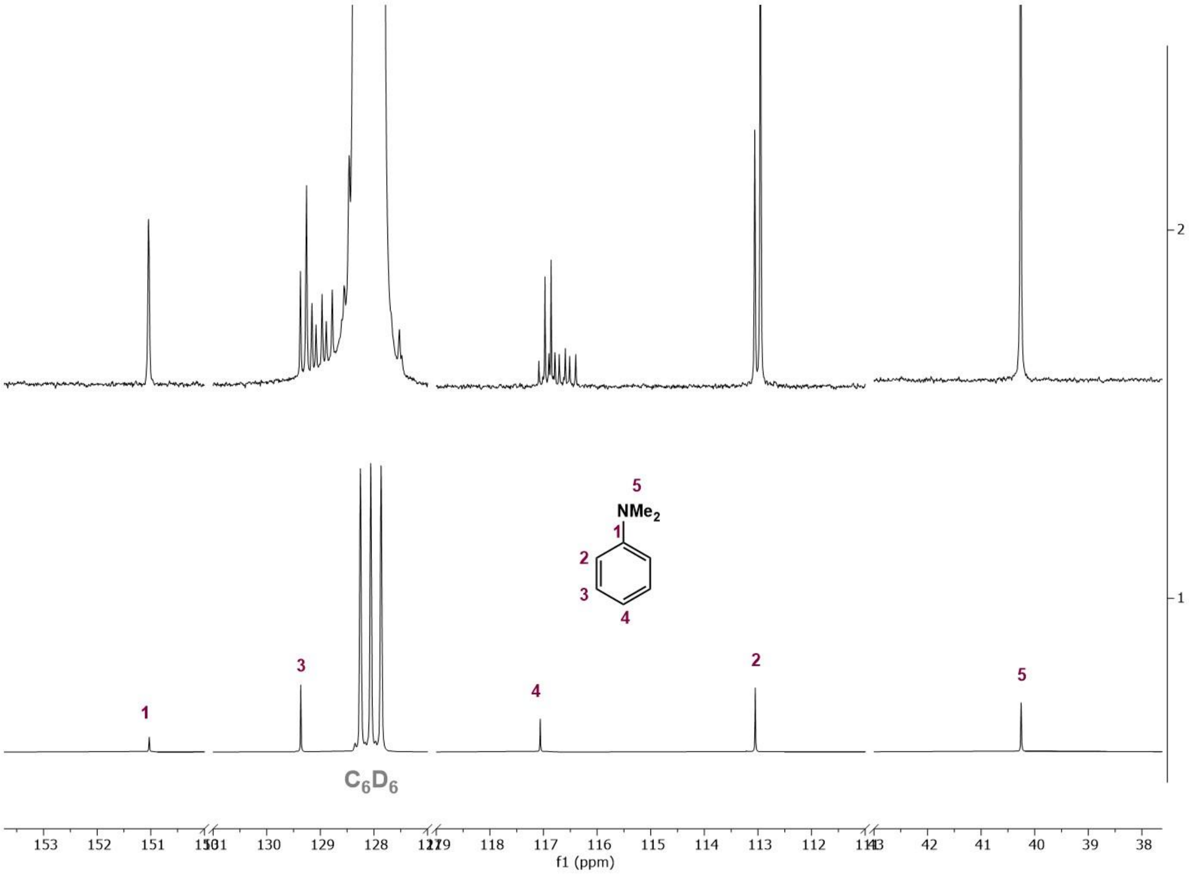


Figure S46. Stacked $^{13}C\{^1H\}$ NMR spectra of **10**: labeled, **10**-*d*$_2$ (top) and natural abundance **10** (bottom).

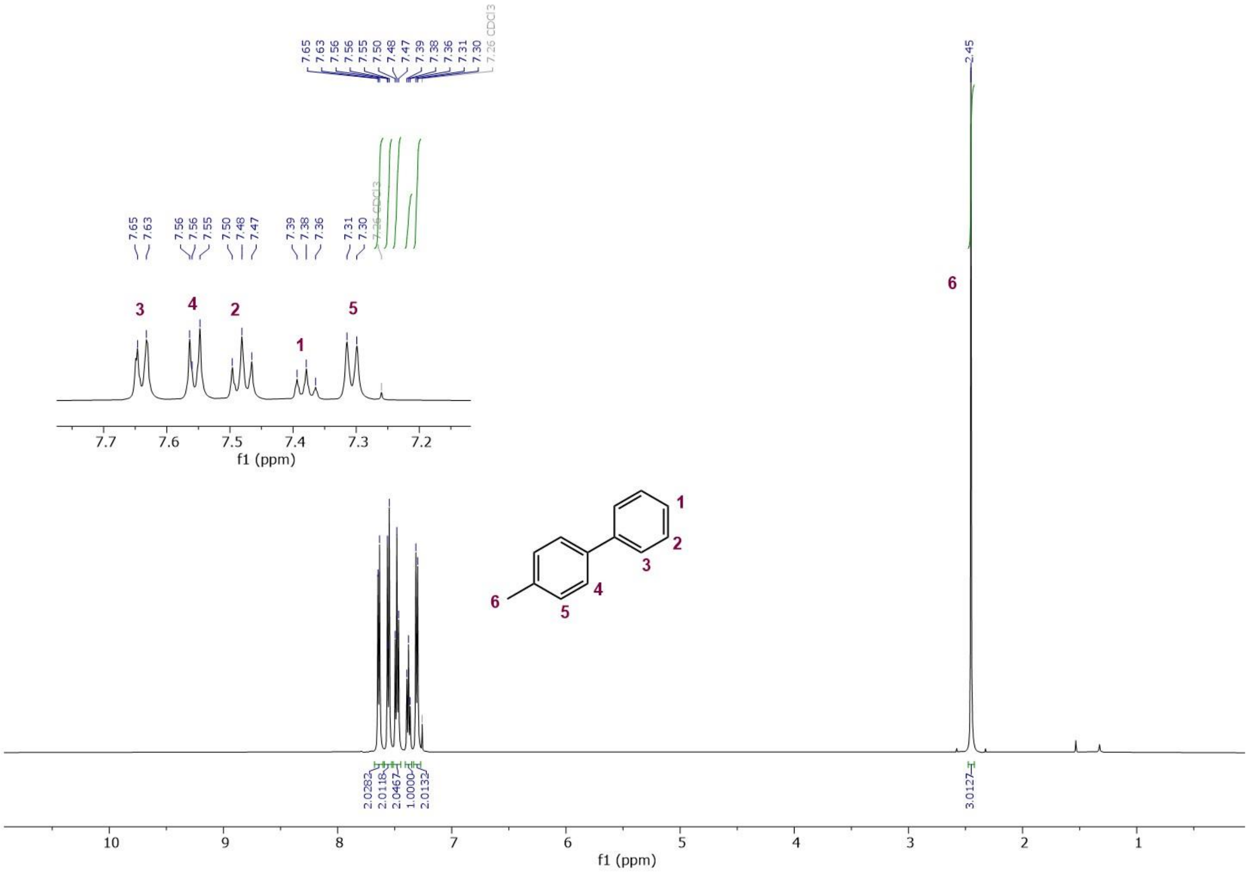


Figure S47. ^{1}H NMR spectrum (500 MHz, chloroform-*d*) of natural abundance **11**.

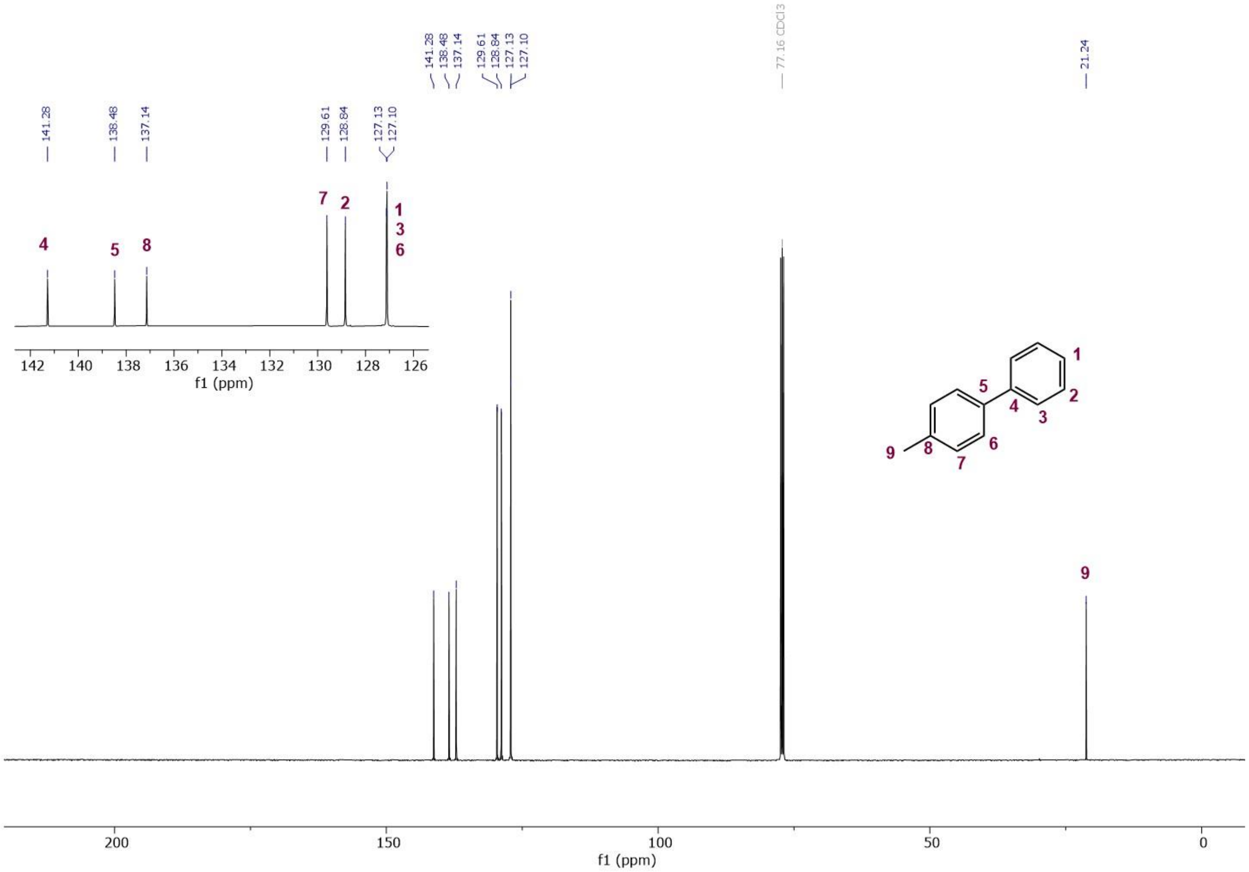


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, chloroform-*d*) of natural abundance **11**.

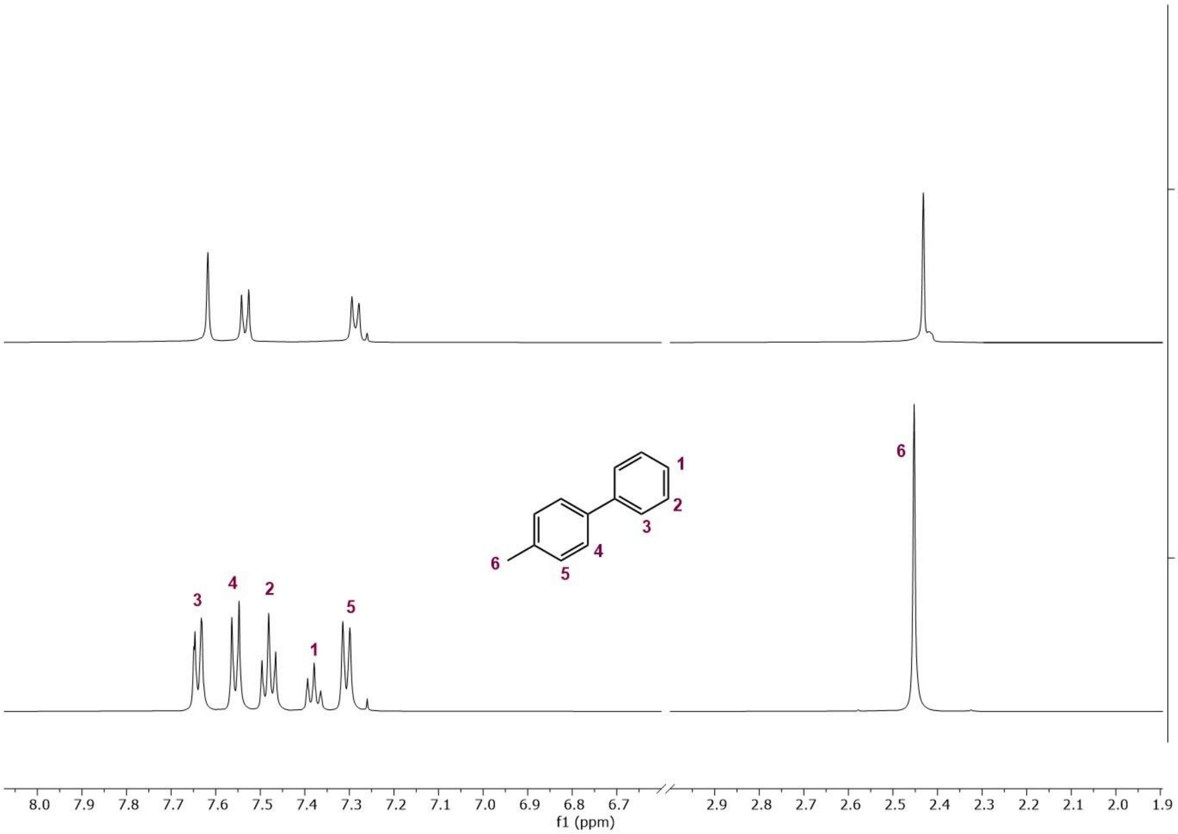


Figure S49. Stacked ^{1}H NMR spectra of **11**: labeled, **11**-*d*$_4$ (top) and natural abundance **11** (bottom).

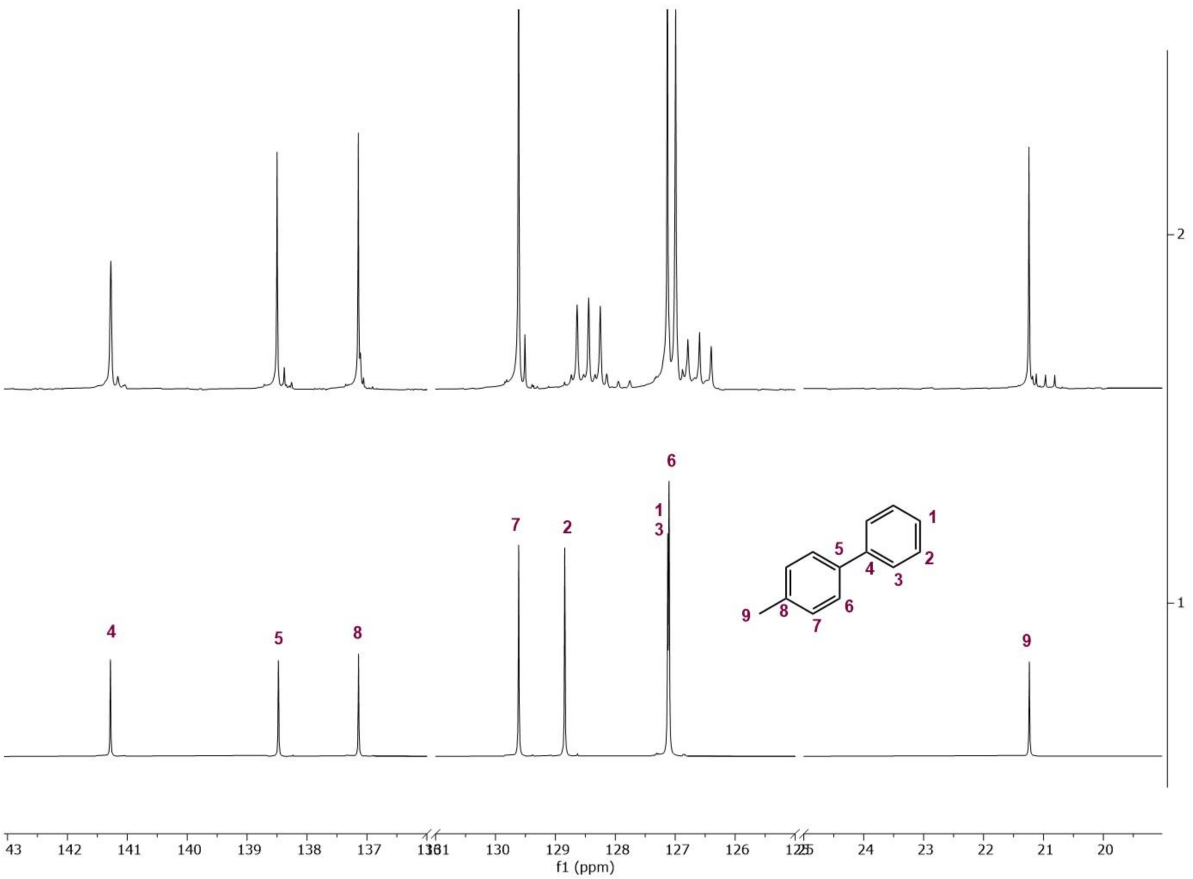


Figure S50. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **11**: labeled, **11**-*d₄* (top) and natural abundance **11** (bottom).

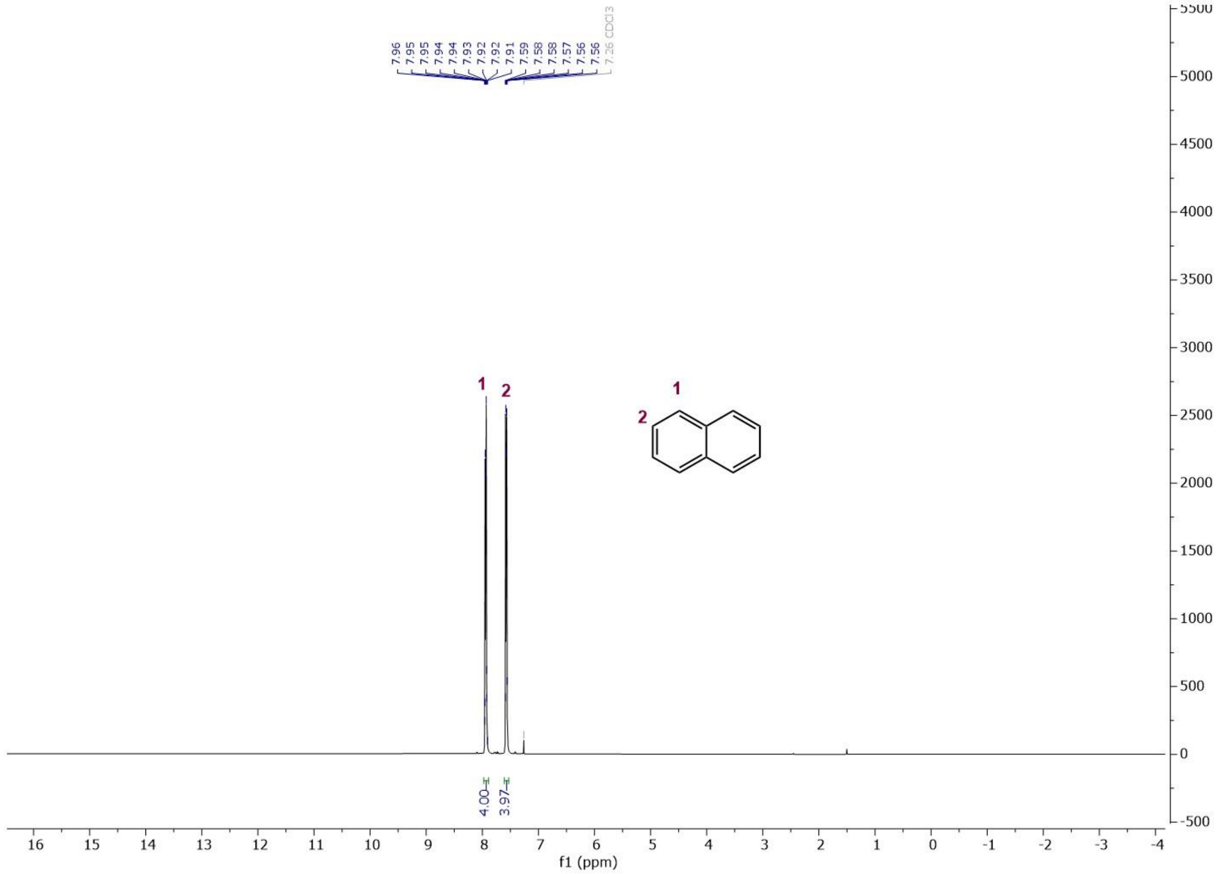


Figure S51. ^{1}H NMR spectrum (500 MHz, chloroform-*d*) of natural abundance **12**.

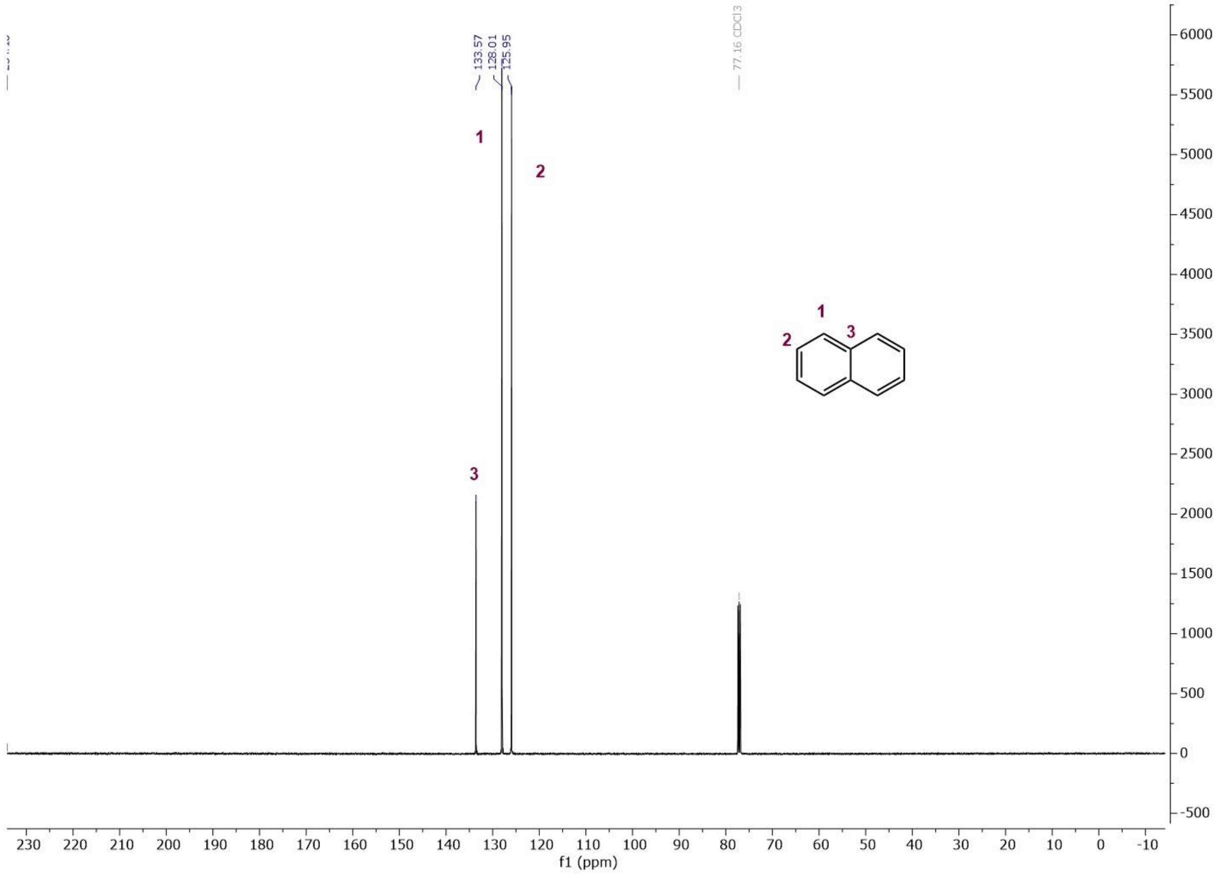


Figure S52. $^{13}C\{^1H\}$ NMR spectrum (126 MHz, chloroform-*d*) of natural abundance **12**.

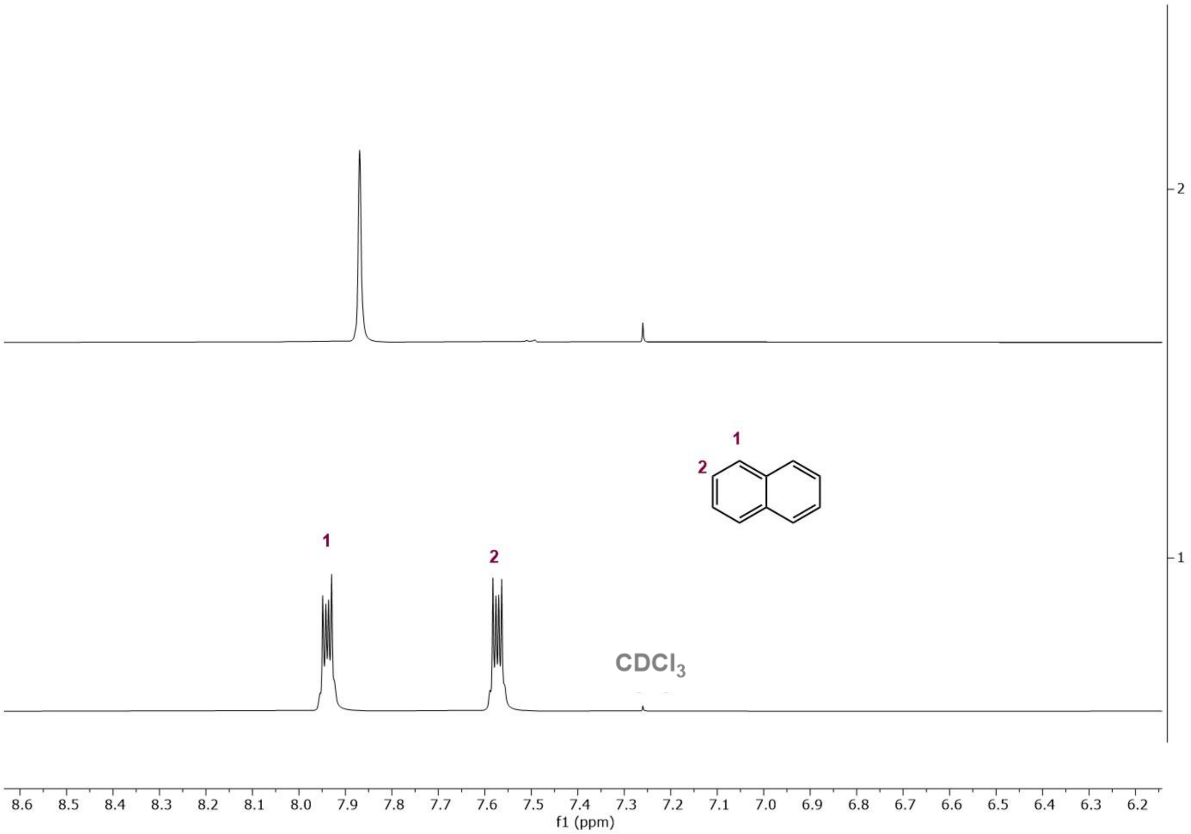


Figure S53. Stacked ^{1}H NMR spectra of **12**: labeled, **12**-*d*$_4$ (top) and natural abundance **12** (bottom).

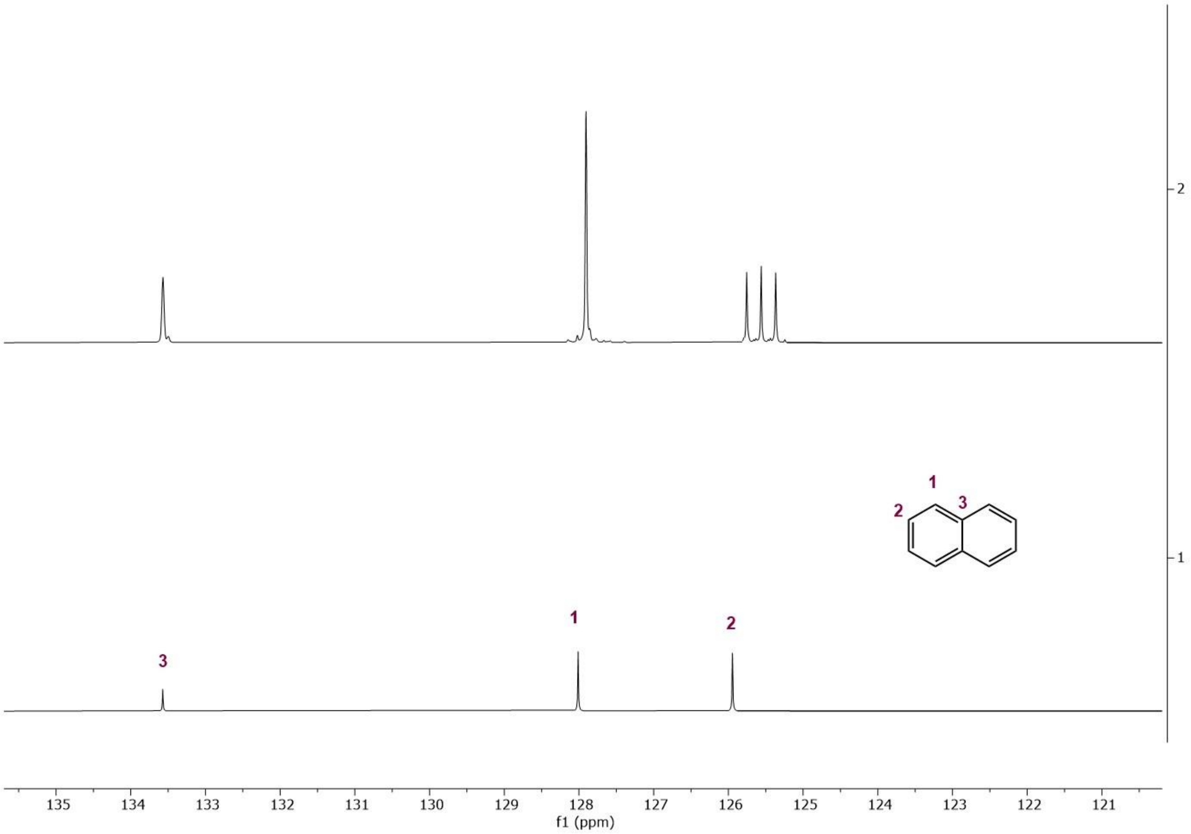


Figure S54. Stacked $^{13}C\{^1H\}$ NMR spectra of **12**: labeled, **12**-*d₄* (top) and natural abundance **12** (bottom).

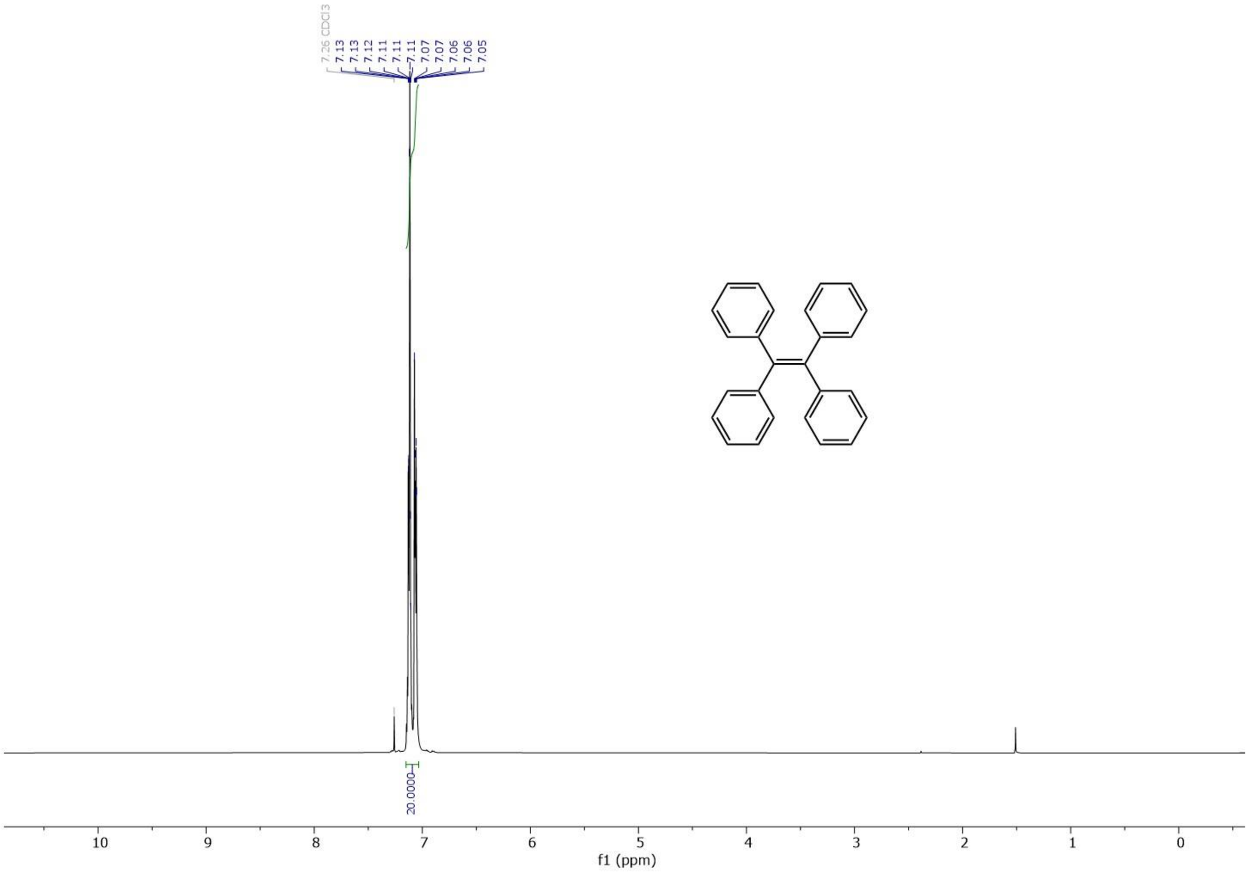


Figure S55. ^{1}H NMR spectrum (500 MHz, chloroform-*d*) of natural abundance **13**.

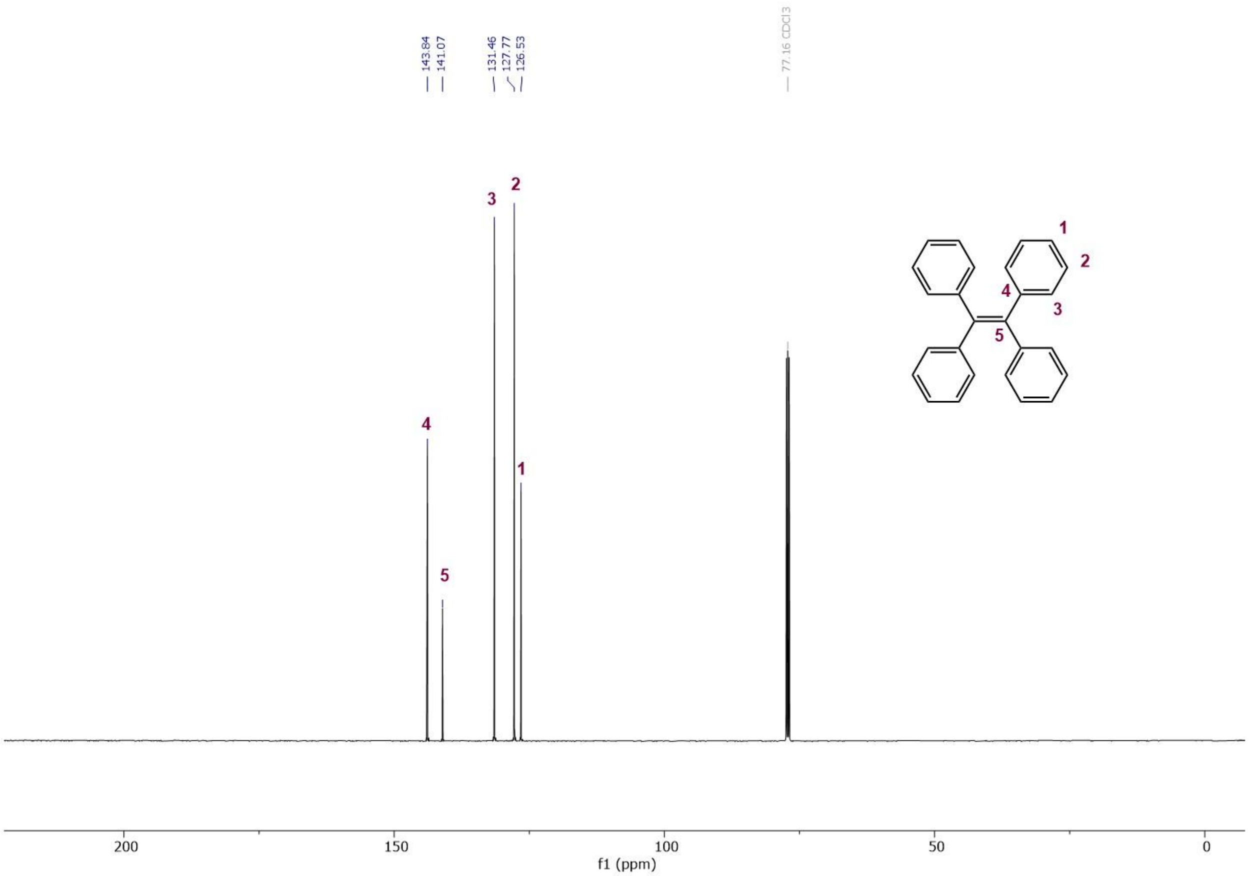


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, chloroform-*d*) of natural abundance **13**.

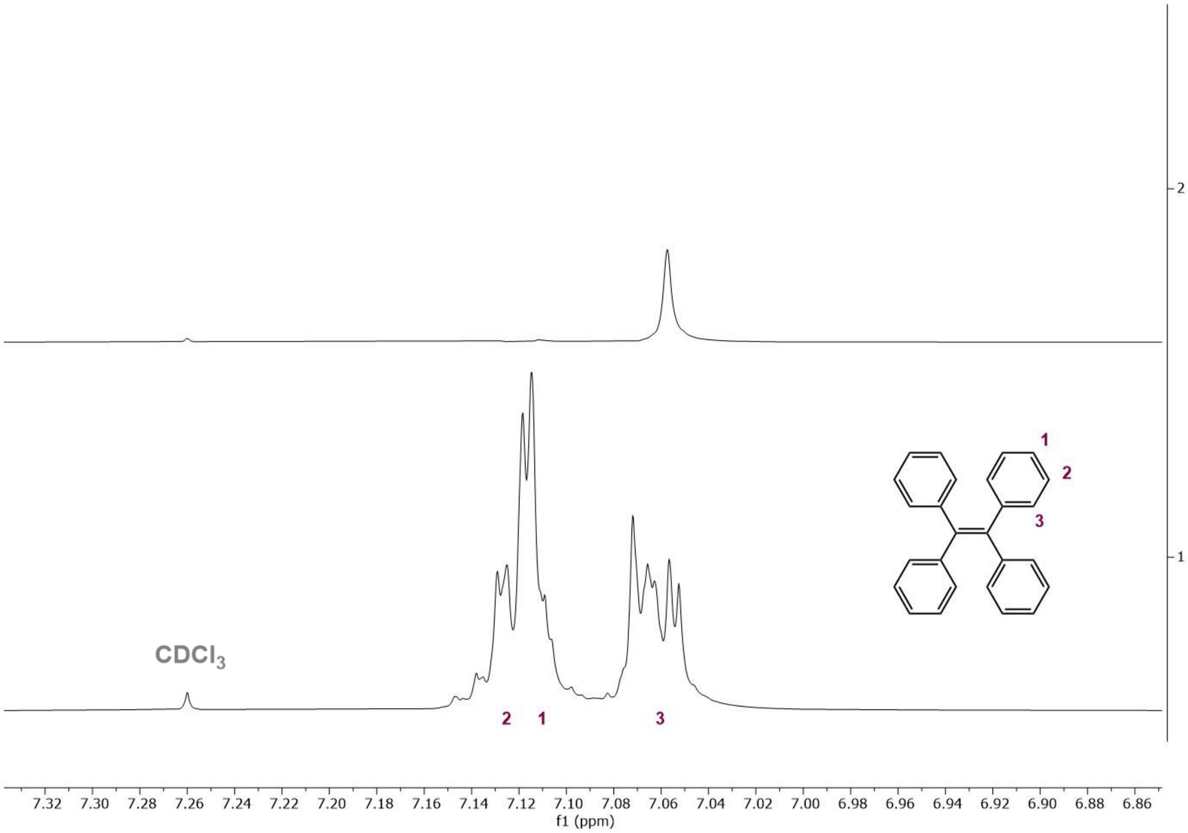


Figure S57. Stacked ^{1}H NMR spectra of **13**: labeled, **13**-*d*$_{12}$ (top) and natural abundance **13** (bottom).

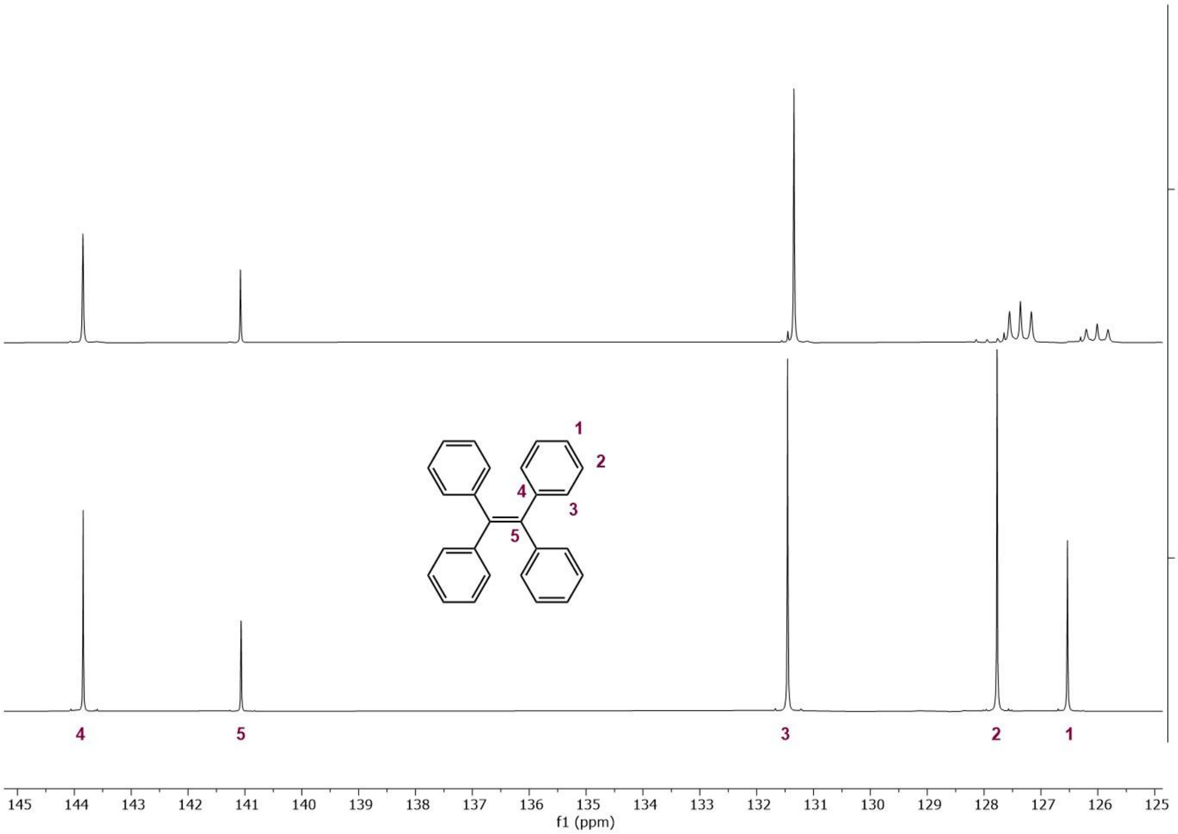


Figure S58. Stacked $^{13}C\{^1H\}$ NMR spectra of **13**: labeled, **13**-*d12* (top) and natural abundance **13** (bottom).

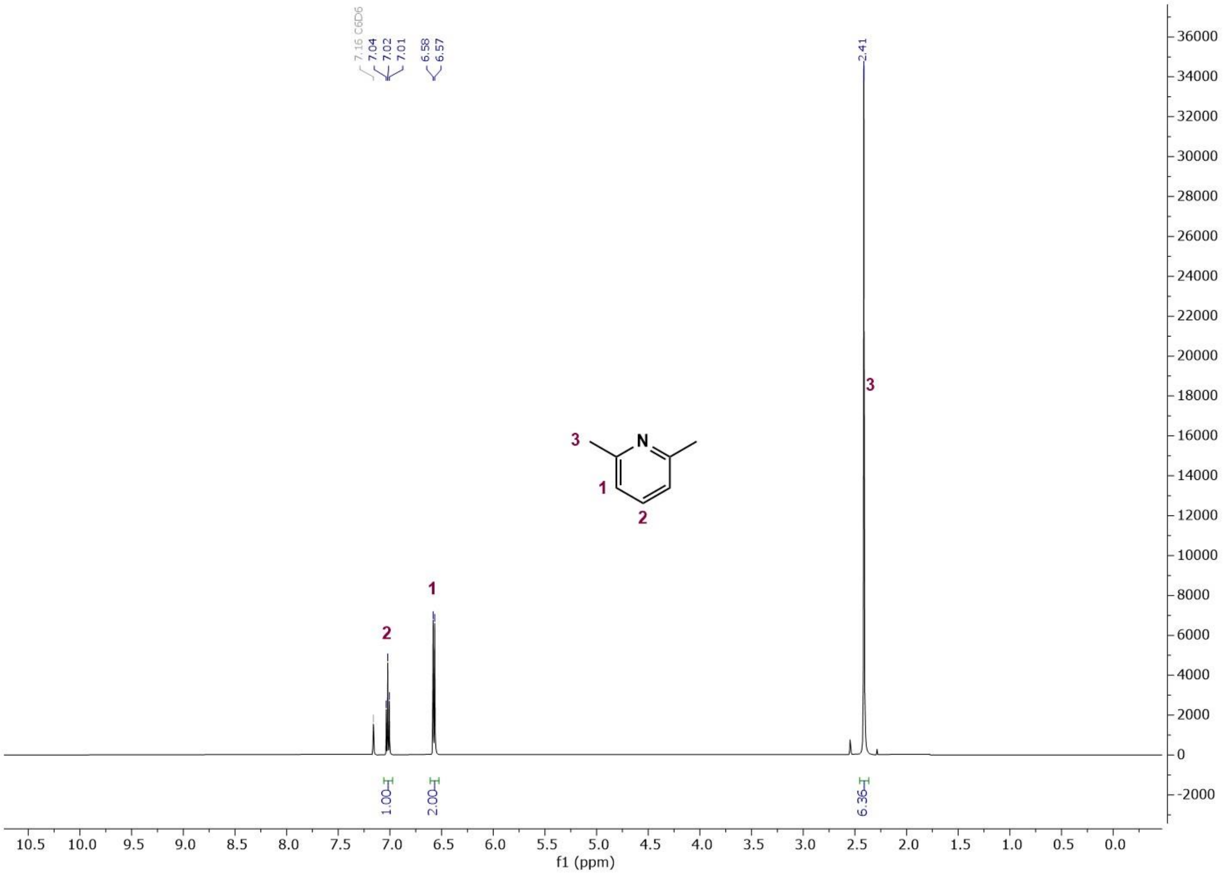


Figure S59. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **14**.

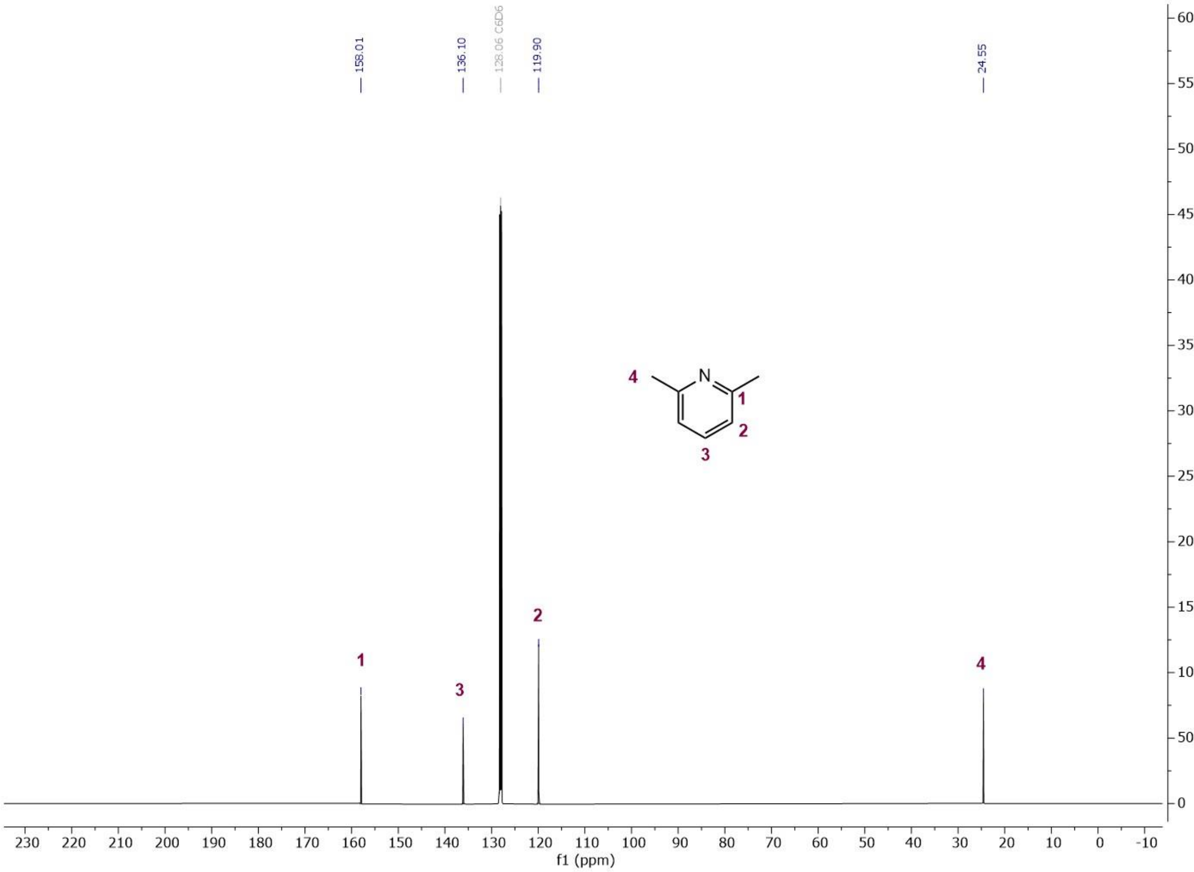


Figure S60. $^{13}C\{^1H\}$ NMR spectrum (126 MHz, benzene-*d*$_6$) of natural abundance **14**.

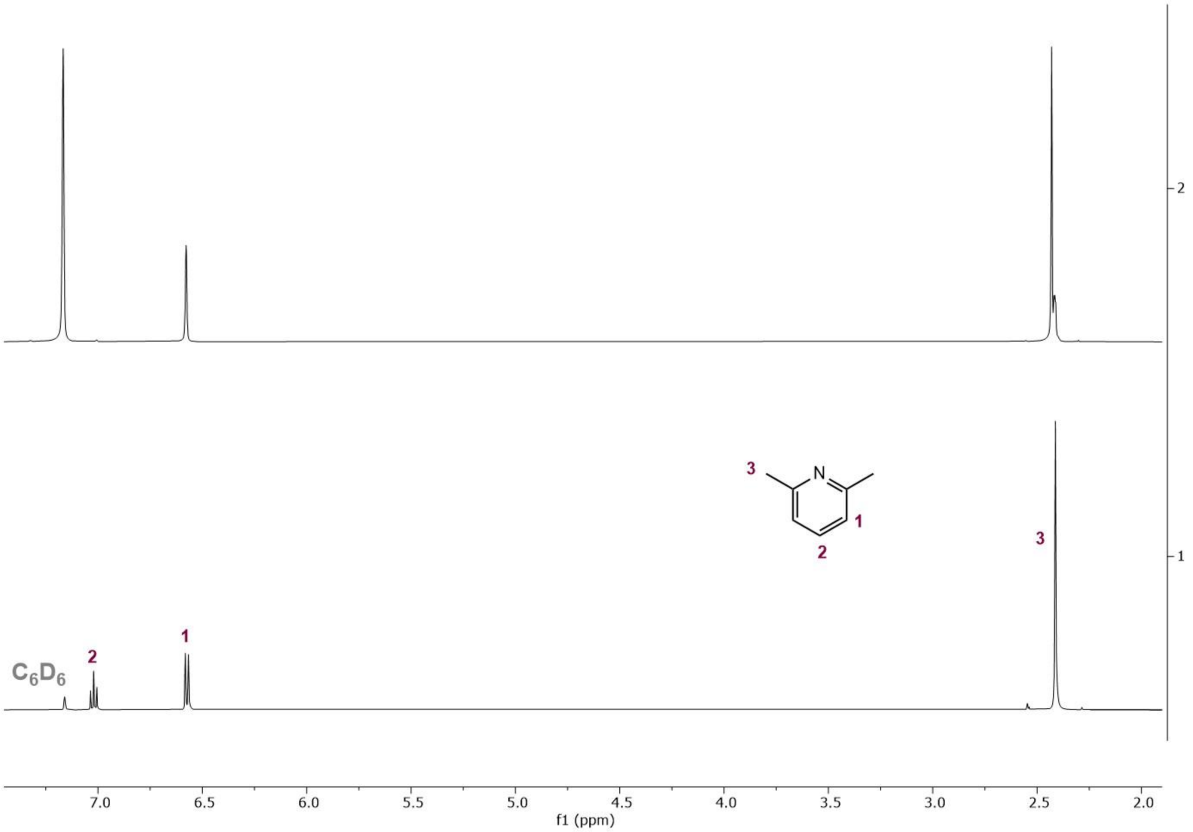


Figure S61. Stacked ^{1}H NMR spectra of **14**: labeled, **14**-d_3 (top) and natural abundance **14** (bottom).

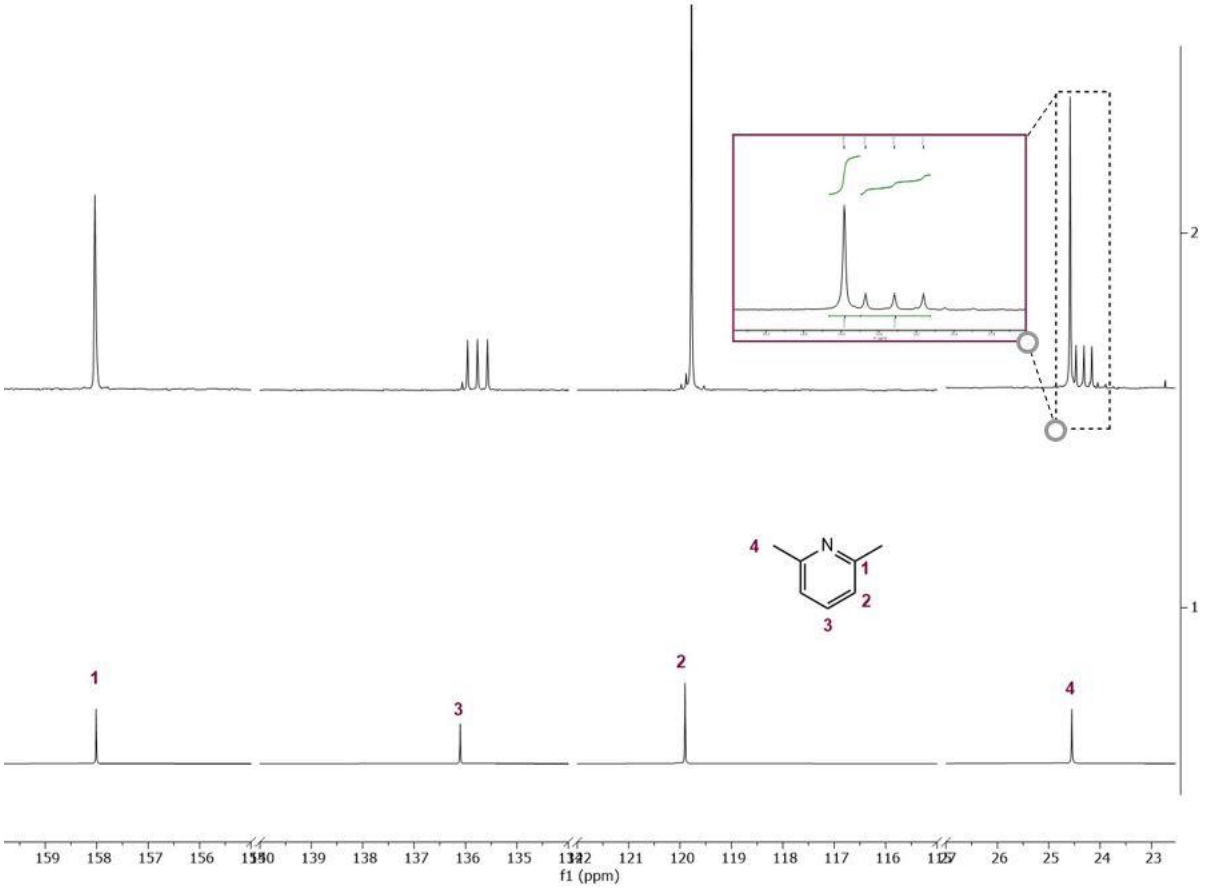


Figure S62. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **14**: labeled, **14**-d_3 (top) and natural abundance **14** (bottom).

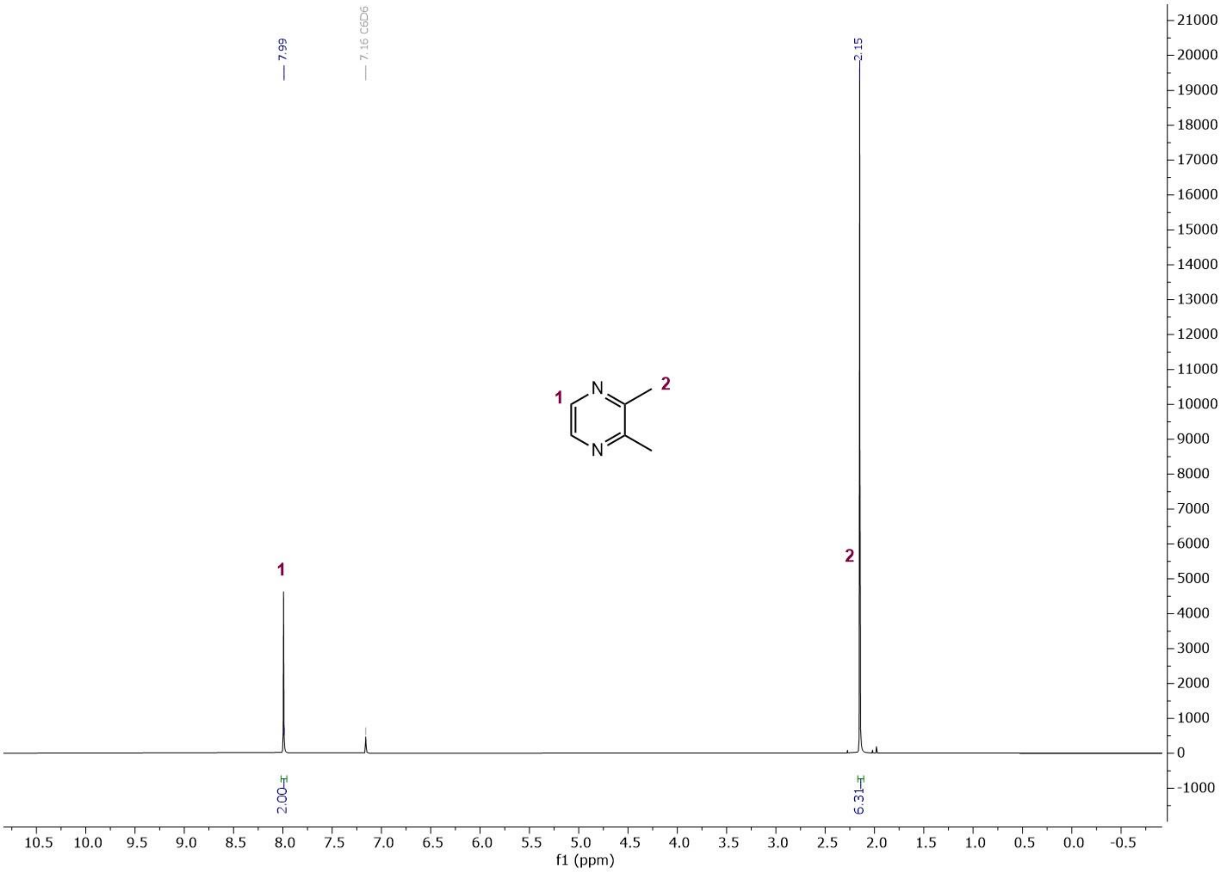


Figure S63. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **15**.

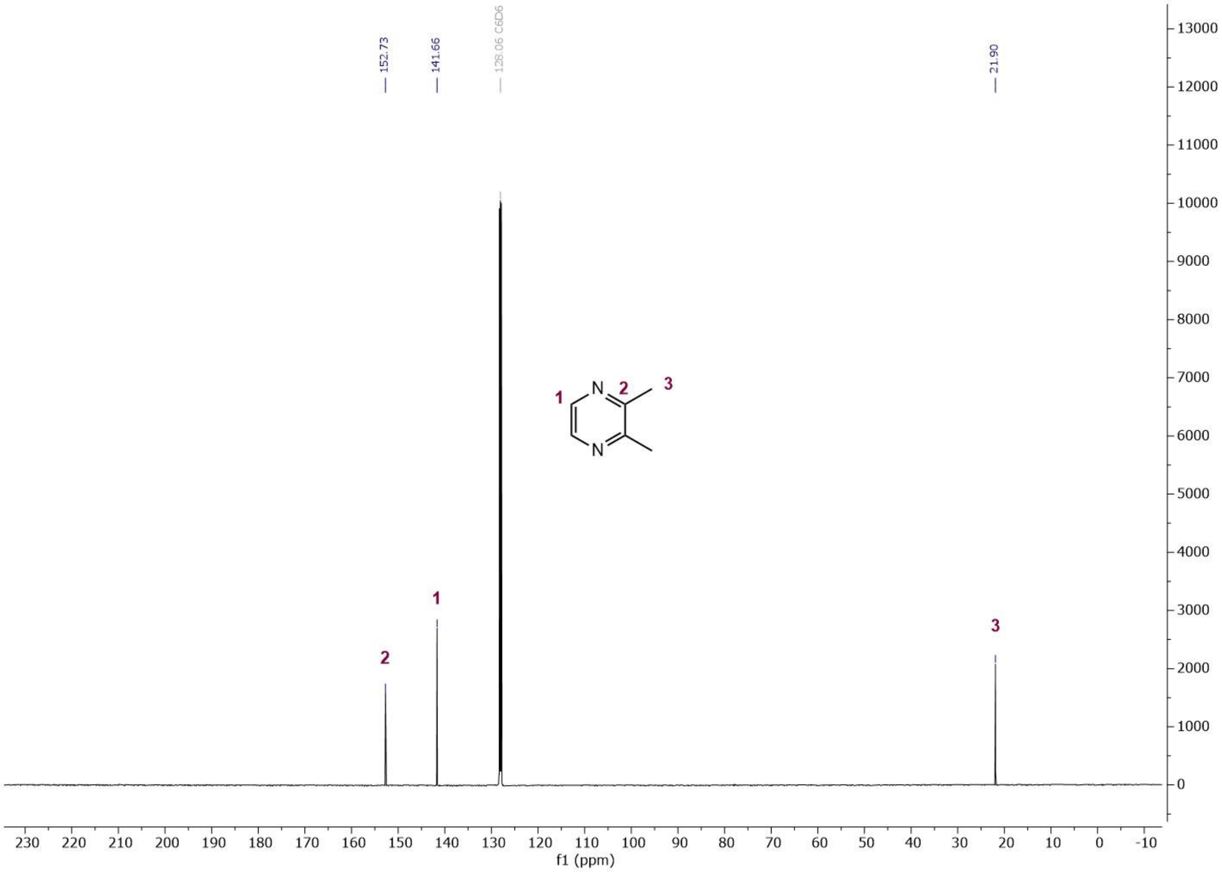


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum (500 MHz, benzene-d_6) of natural abundance **15**.

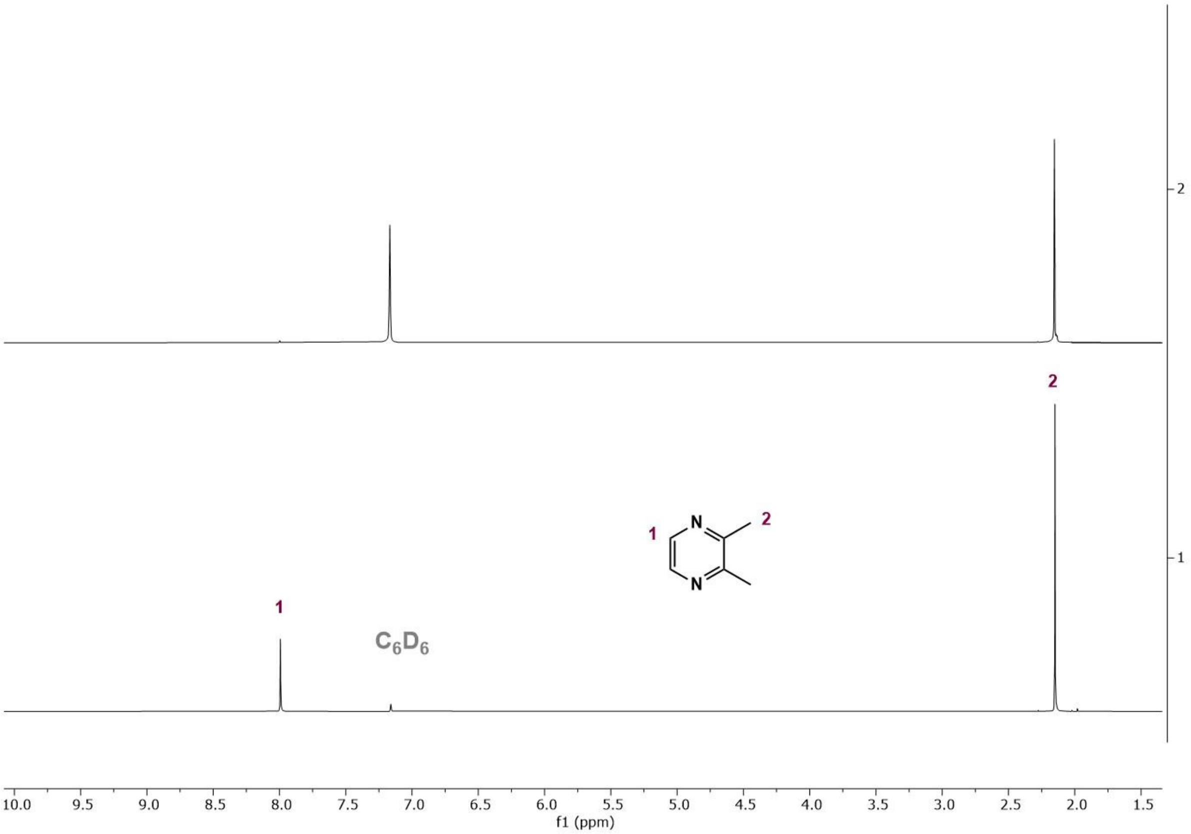


Figure S65. Stacked ^{1}H NMR spectra of **15**: labeled, **15**-*d₄* (top) and natural abundance **15** (bottom).

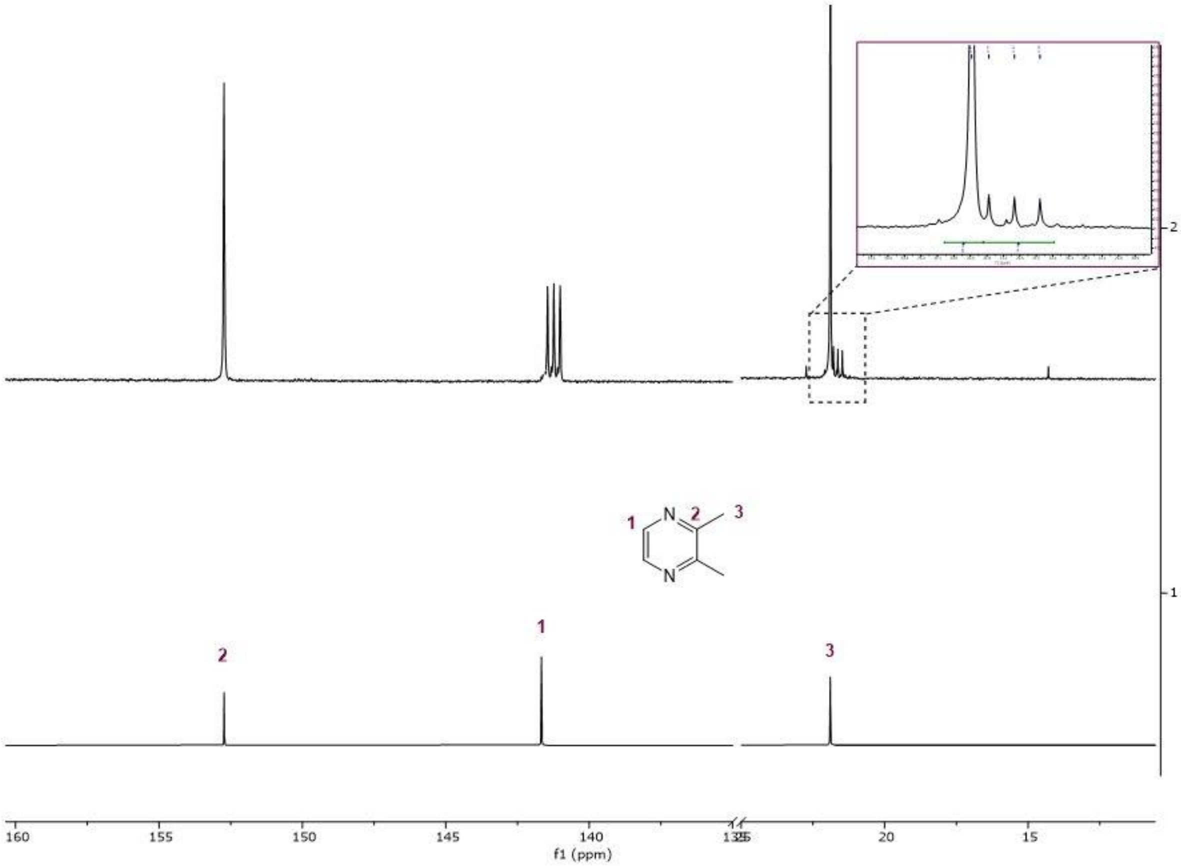


Figure S66. Stacked $^{13}C\{^1H\}$ NMR spectra of **15**: labeled, **15**-*d₄* (top) and natural abundance **15** (bottom).

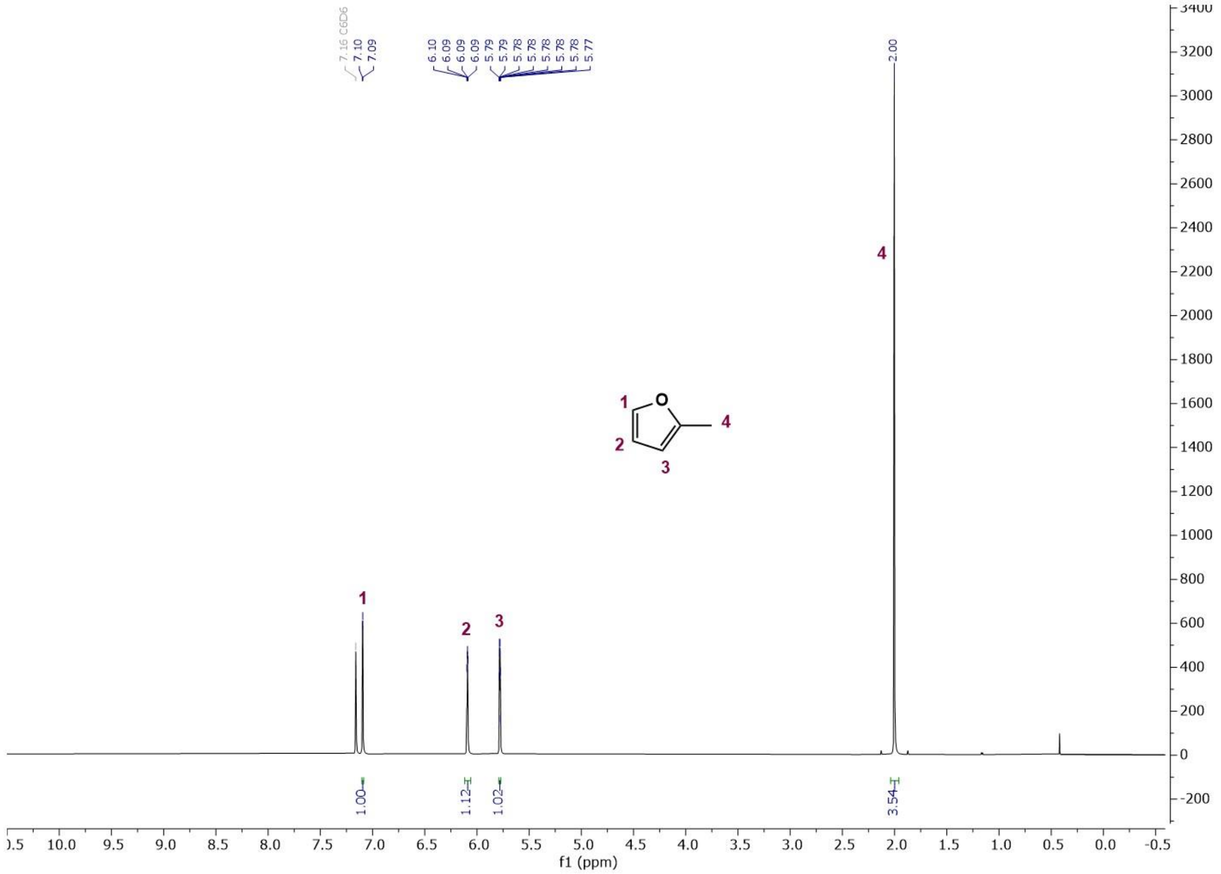


Figure S67. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **16**.

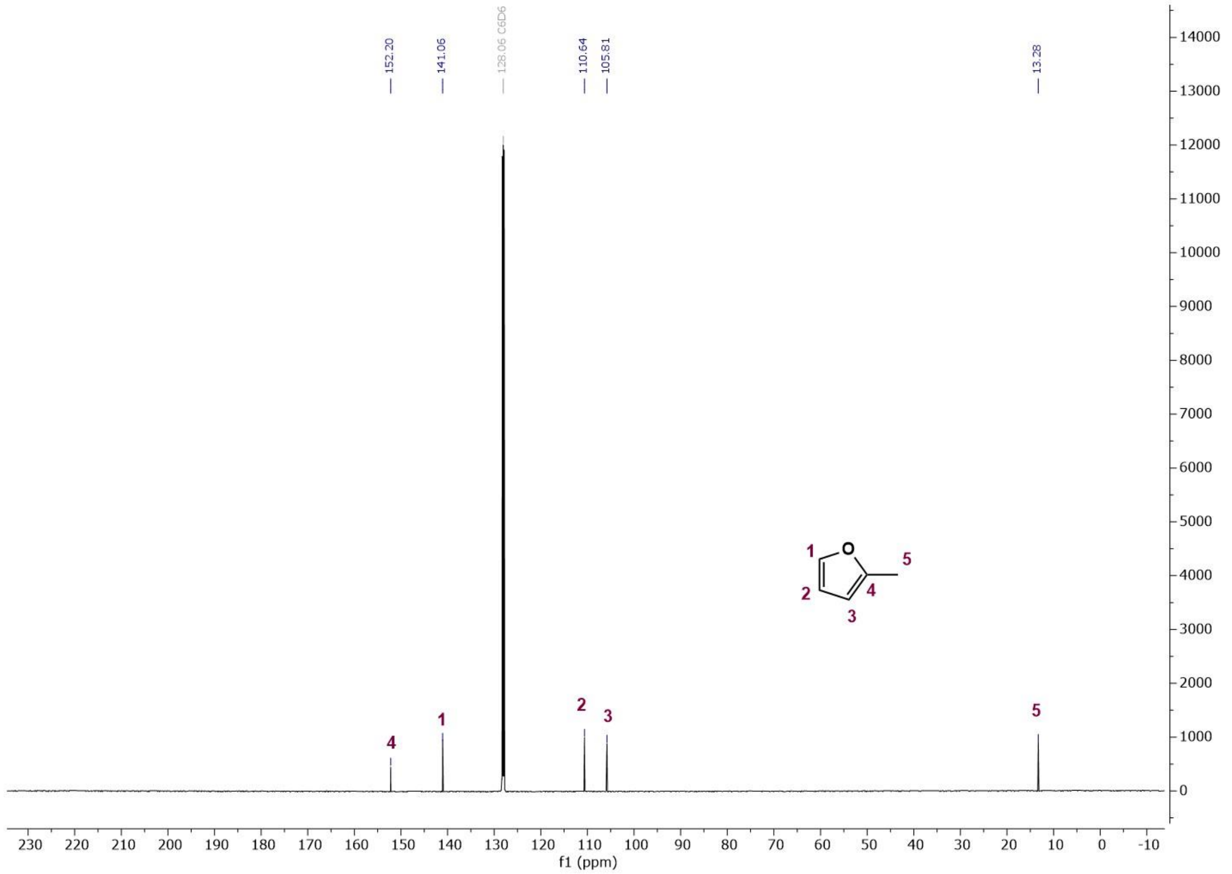


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, benzene-d_6) of natural abundance **16**.

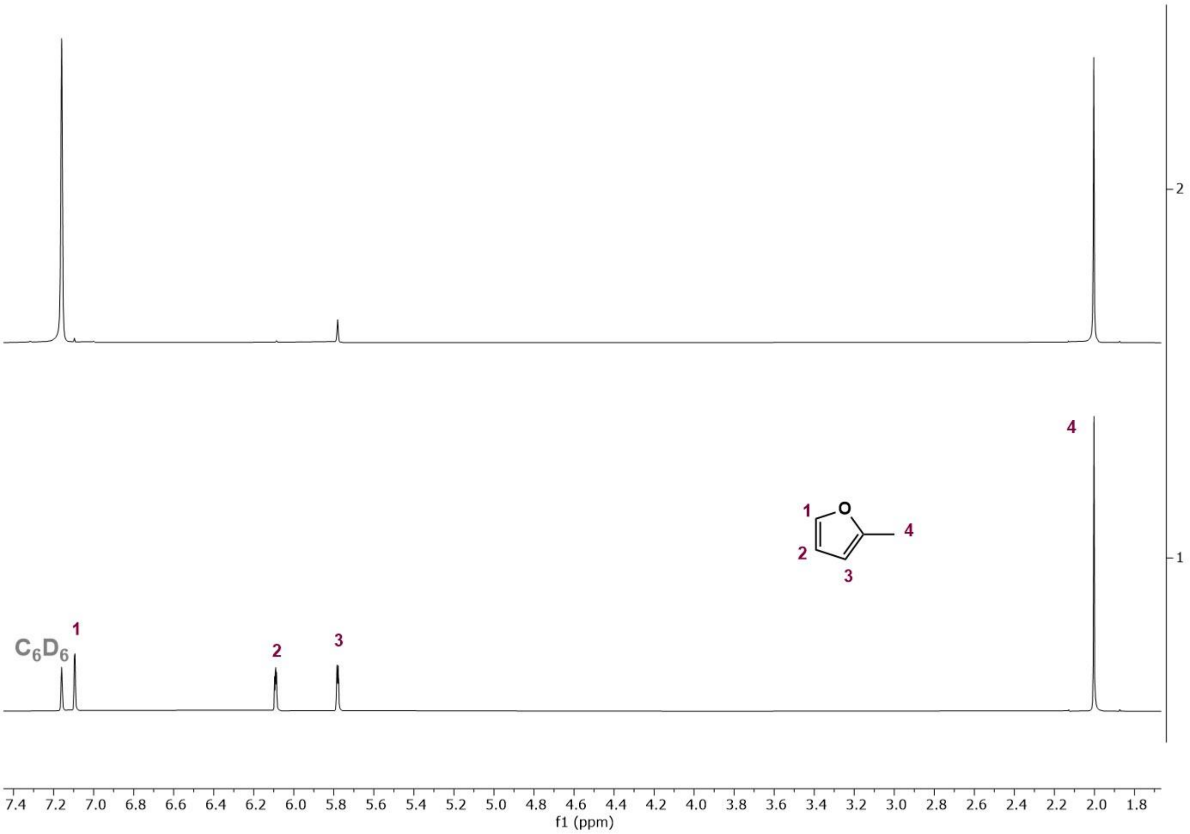


Figure S69. Stacked ^{1}H NMR spectra of **16**: labeled, **16**-d_3 (top) and natural abundance **16** (bottom).

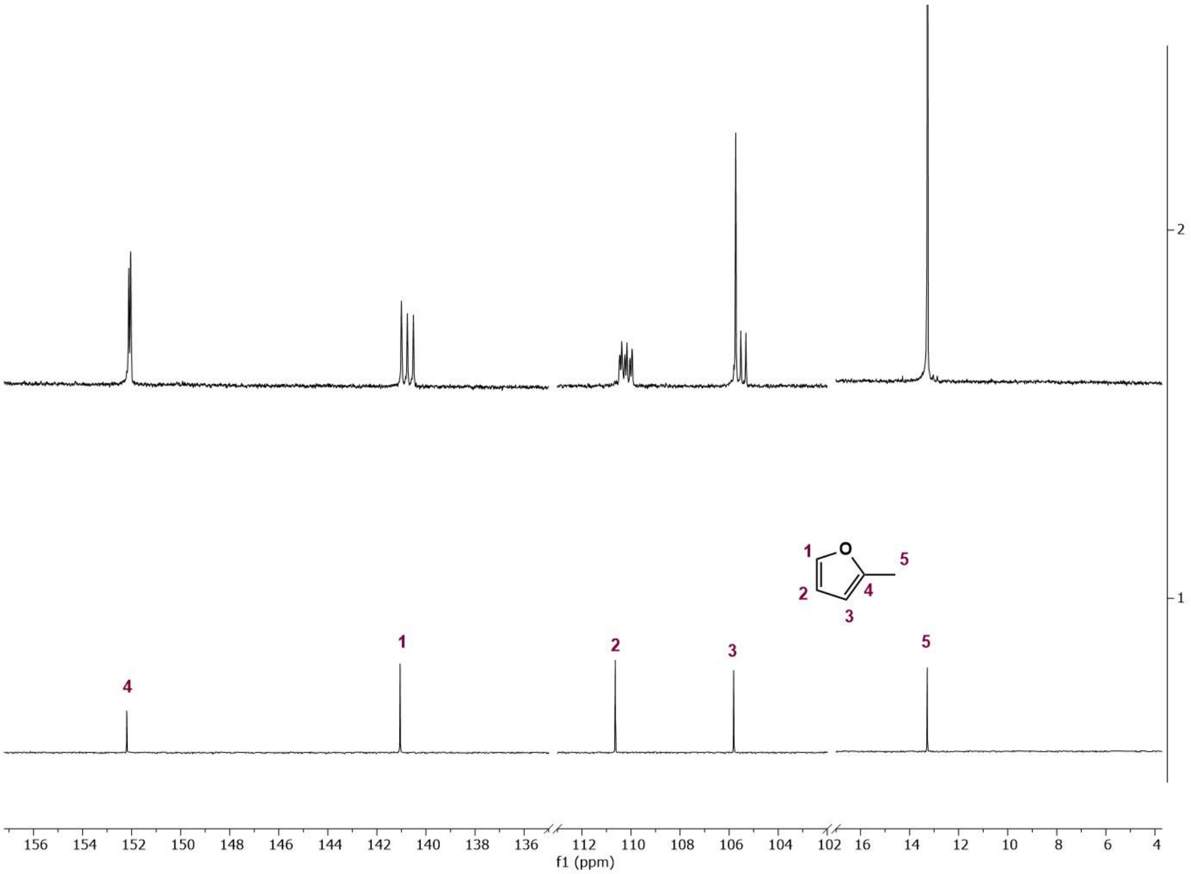


Figure S70. Stacked $^{13}C\{^{1}H\}$ NMR spectra of **16**: labeled, **16**-d_3 (top) and natural abundance **16** (bottom).

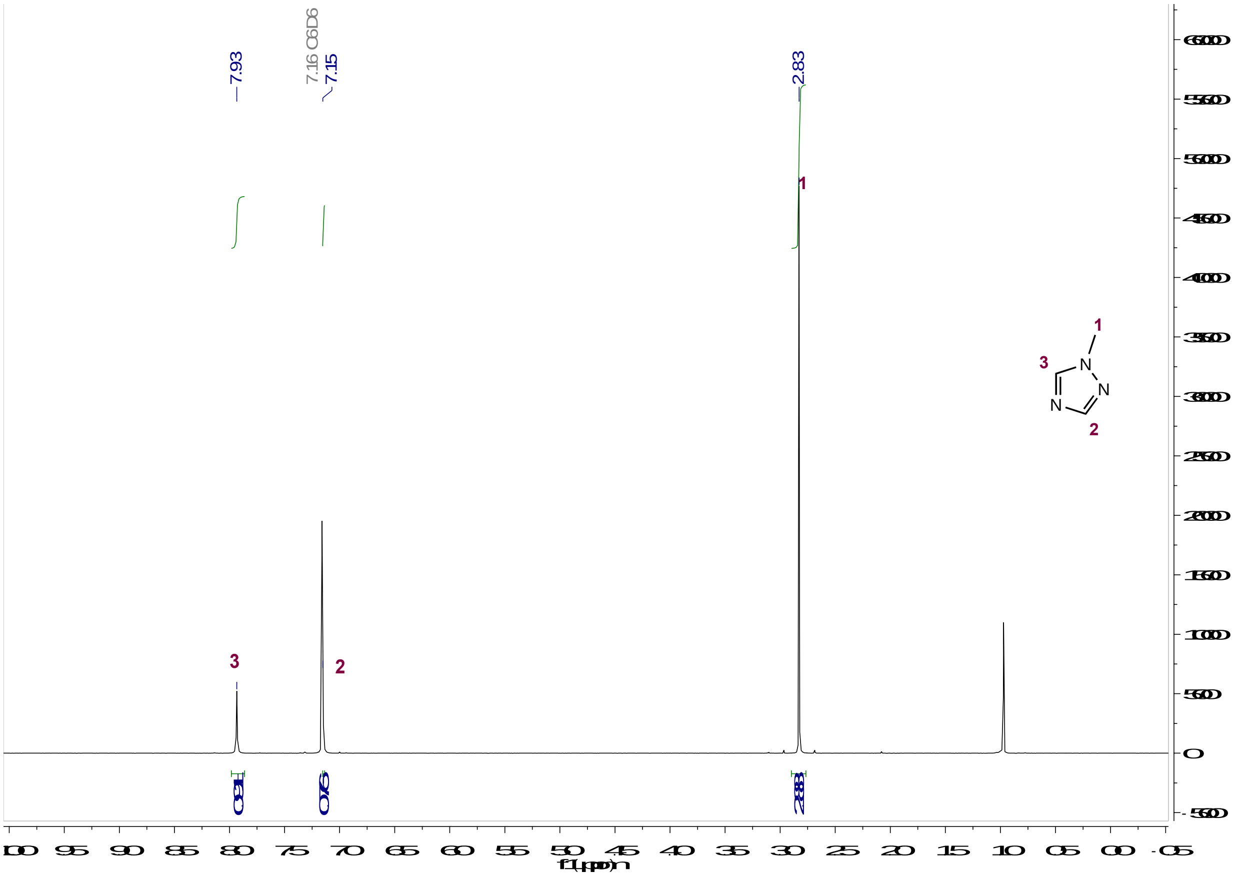


Figure S71. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of natural abundance **17**.

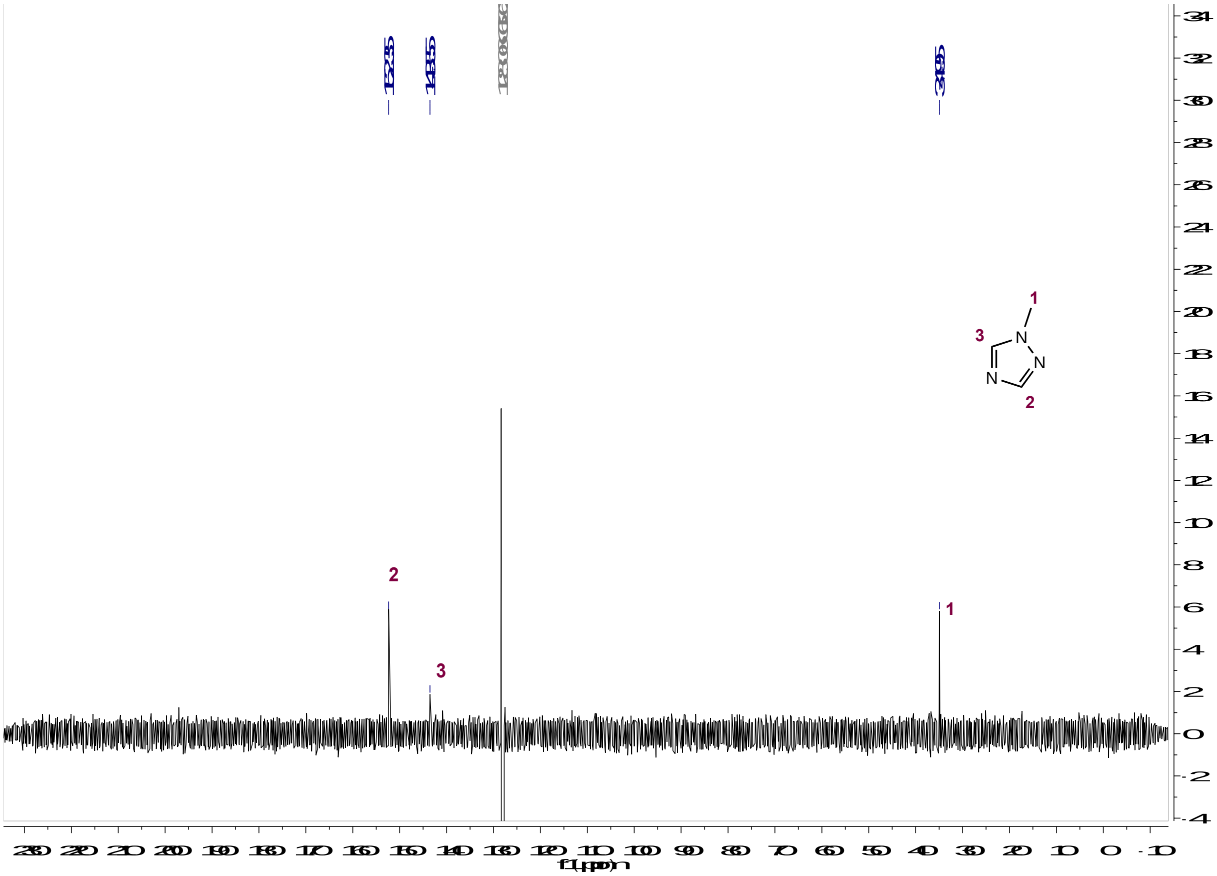


Figure S72. ^{13}C (APT) NMR spectrum (126 MHz, benzene-d_6) of natural abundance **17**.

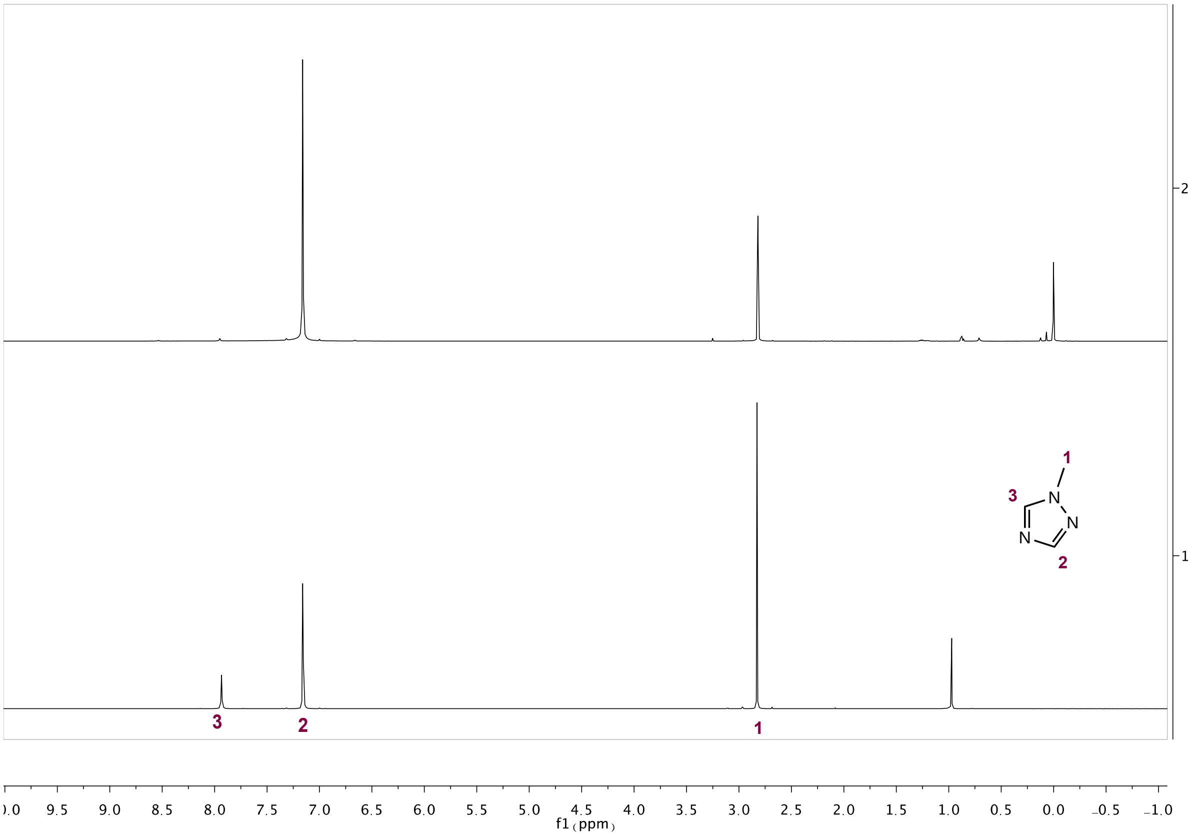


Figure S73. Stacked ^{1}H NMR spectra of **17**: labeled, **17**-d_2 (top) and natural abundance **17** (bottom).

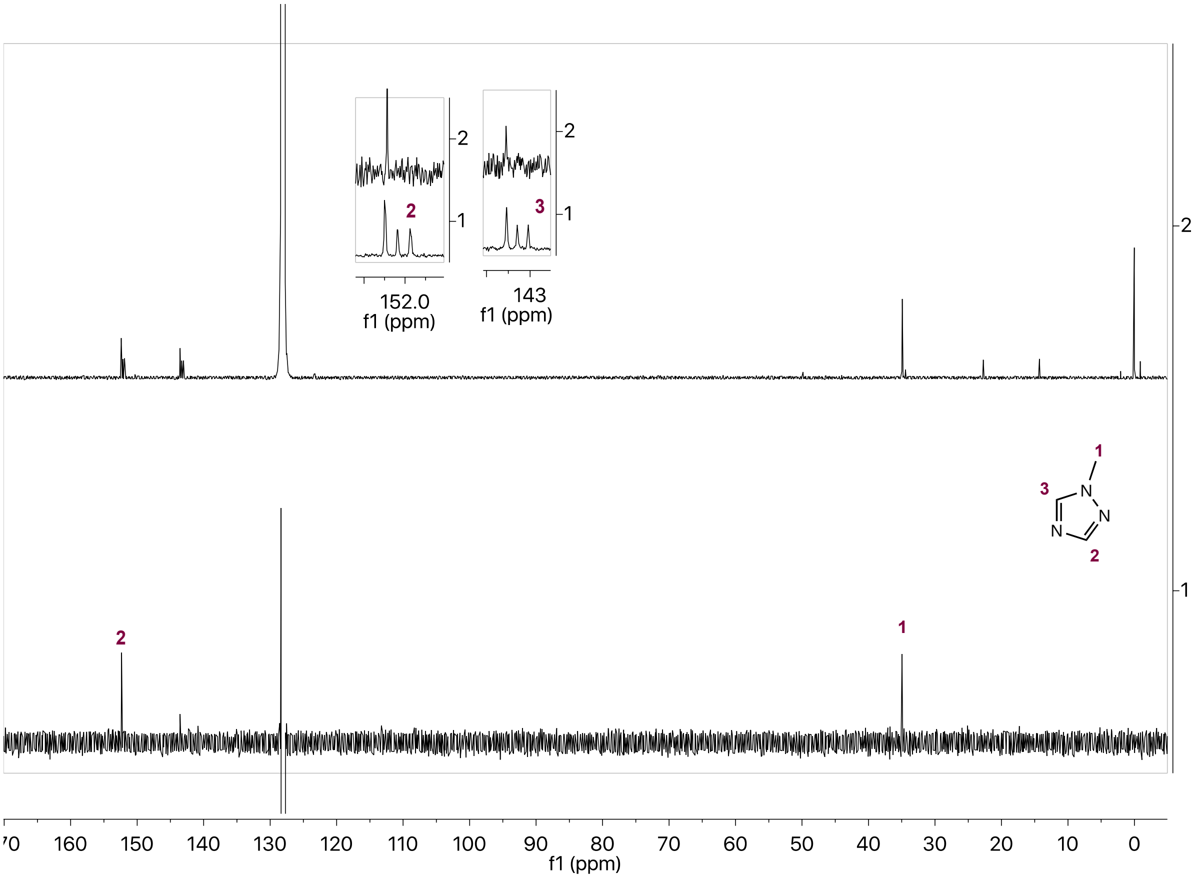


Figure S74. Stacked ^{13}C NMR spectra of **17**: labeled, **17**-d_2 (top) and natural abundance **17** (bottom).

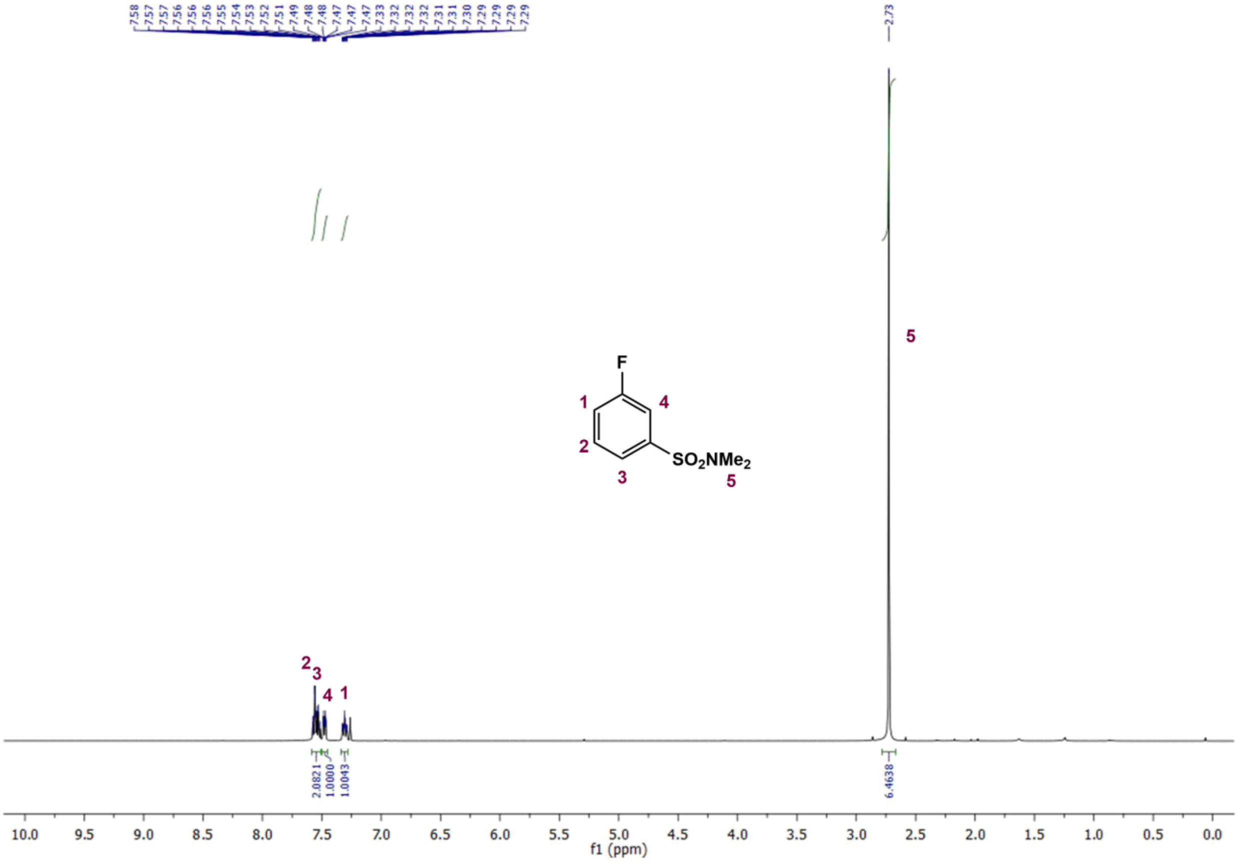


Figure S75. ^{1}H NMR spectrum (500 MHz, chloroform-*d*) of natural abundance **18**.

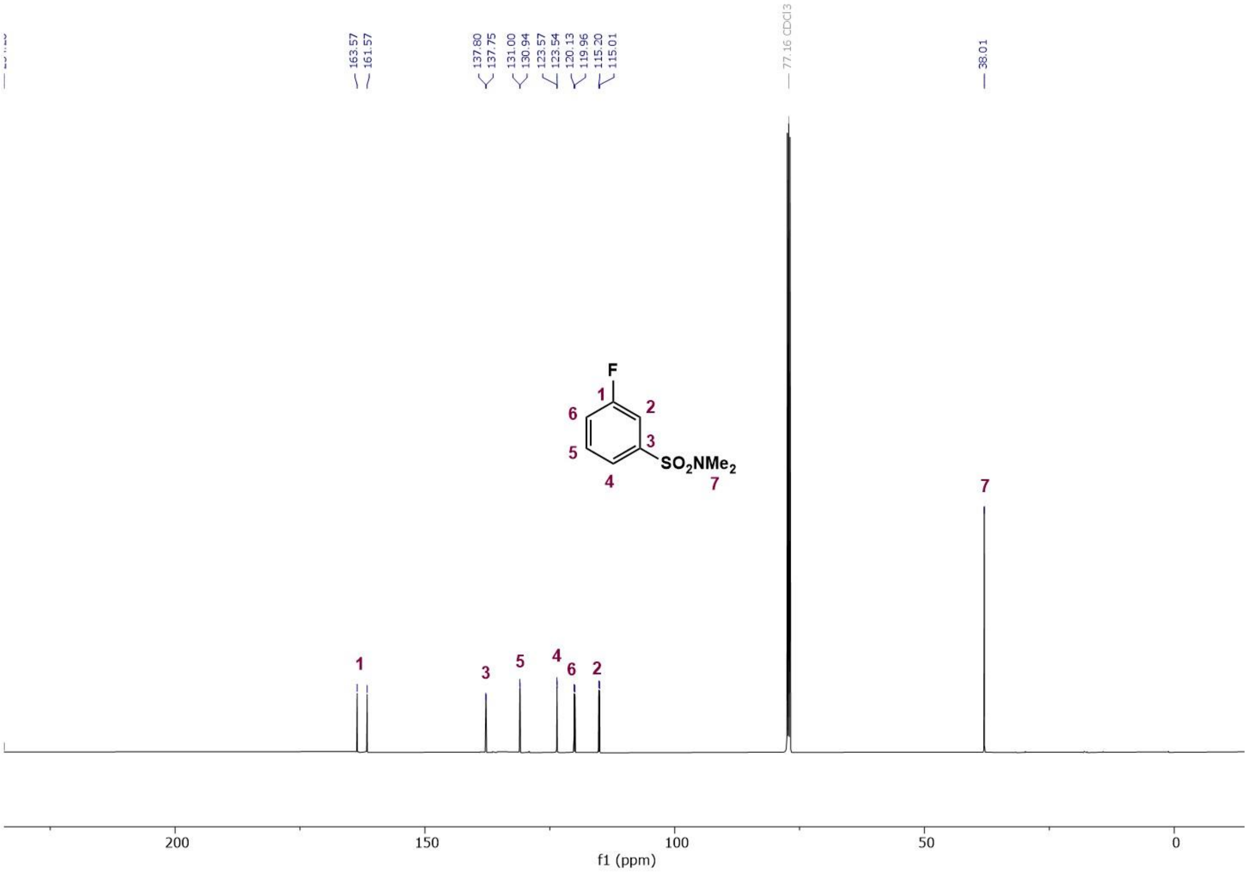


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, chloroform-*d*) of natural abundance **18**.

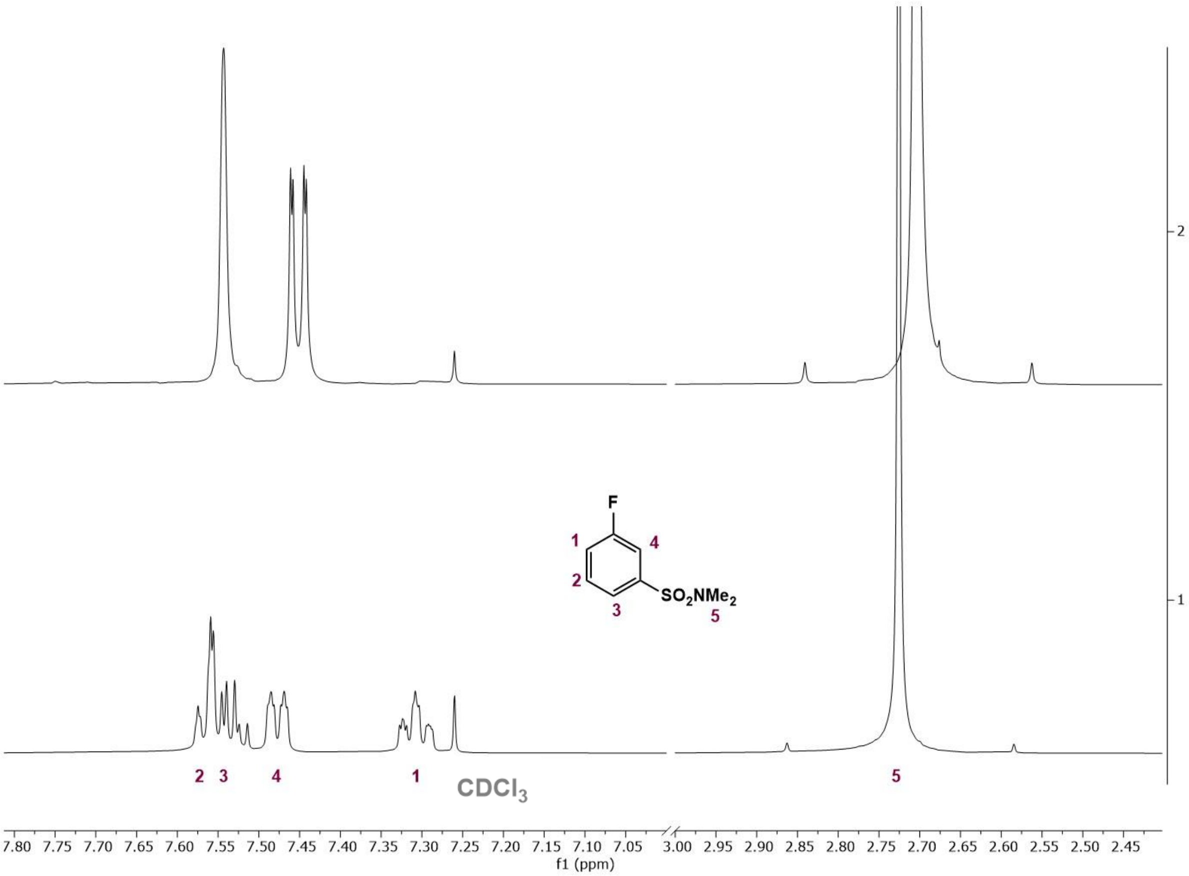


Figure S77. Stacked ^{1}H NMR spectra of **18**: labeled, **18**-*d*$_2$ (top) and natural abundance **18** (bottom).

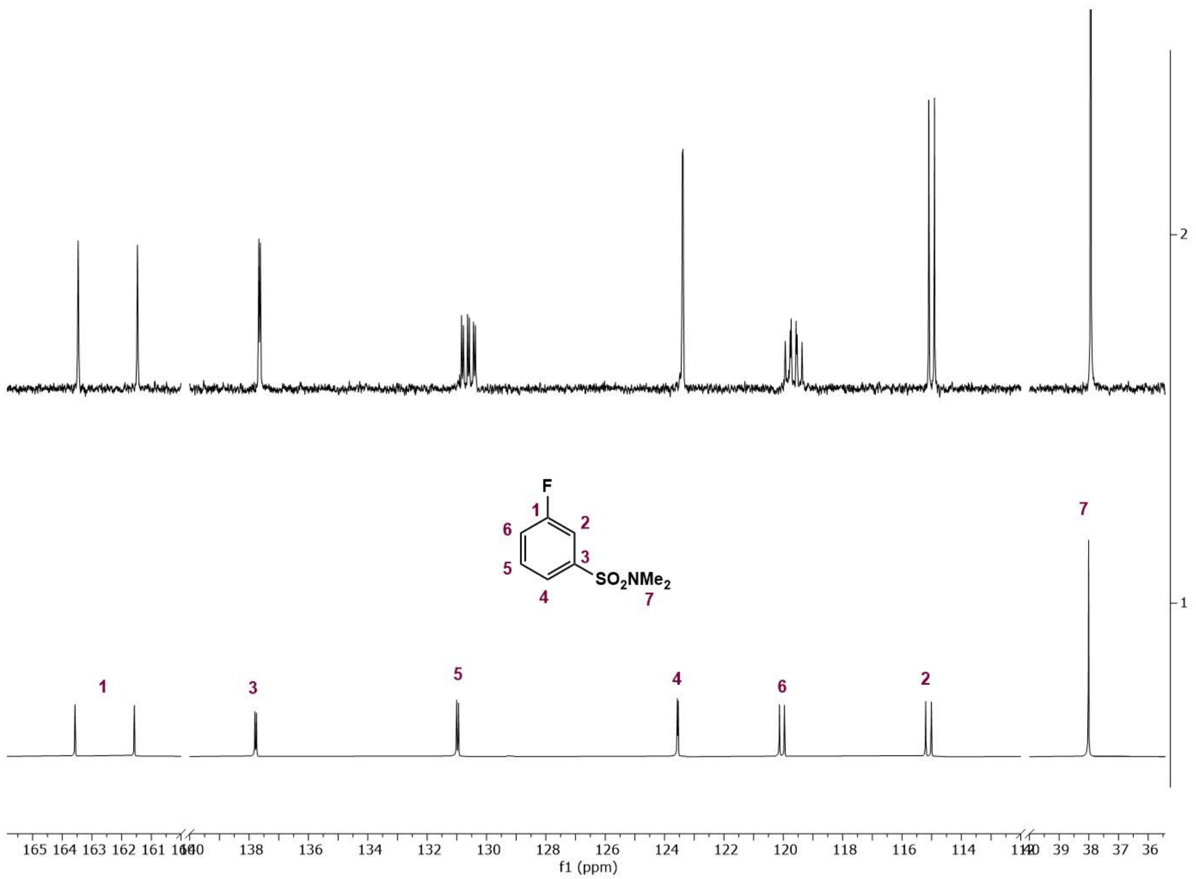


Figure S78. Stacked $^{13}C\{^1H\}$ NMR spectra of **18**: labeled, **18**-*d*$_2$ (top) and natural abundance **18** (bottom).

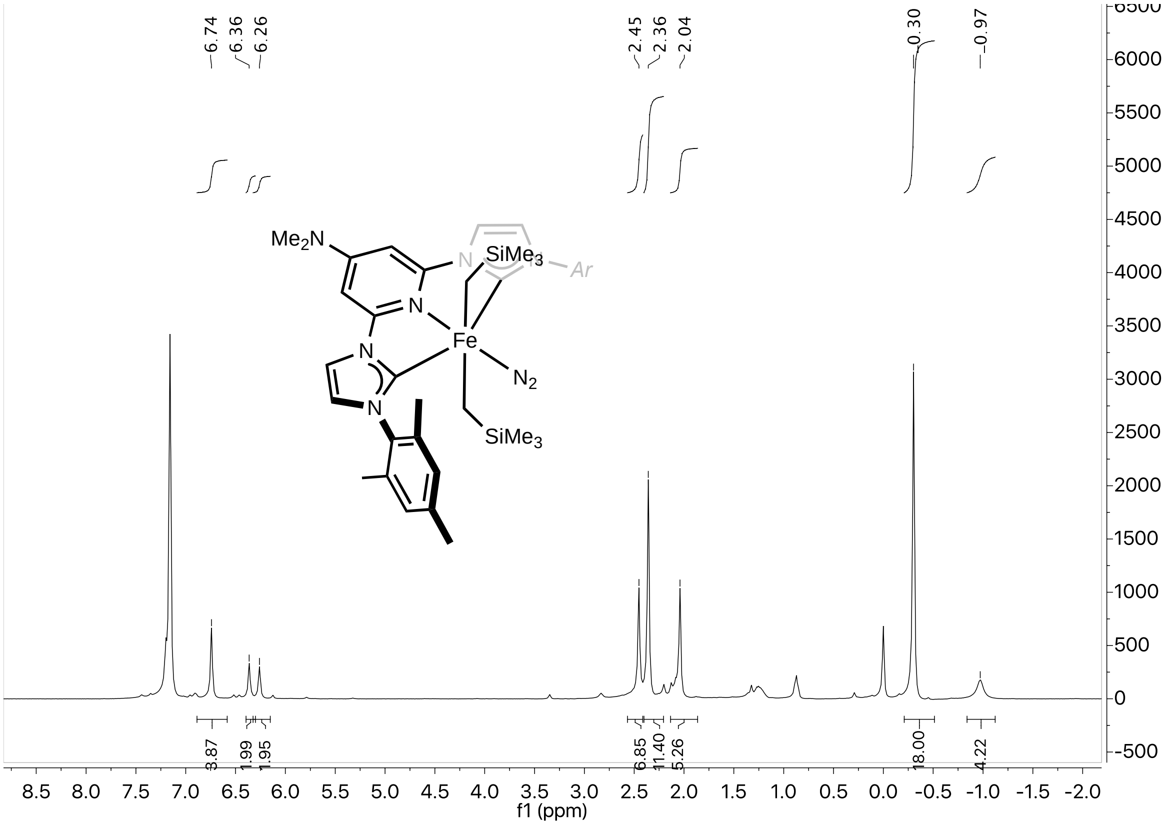


Figure S79. ^{1}H NMR spectrum (400 MHz, benzene-d_6) of **[Fe]-4**.

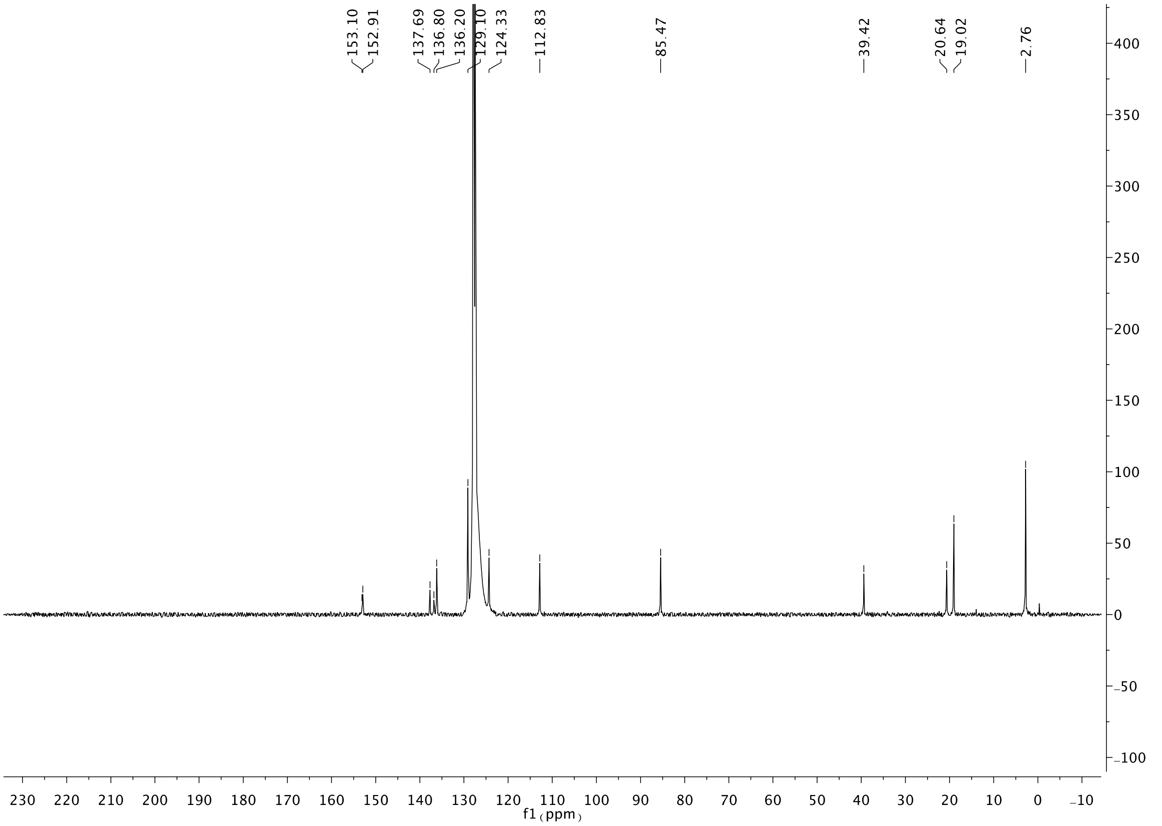


Figure S80. ^{13}C NMR spectrum (400 MHz, benzene-d_6) of **[Fe]-4**.

References

1 (a) Yu, R. P.; Hesk, D.; Rivera, N.; Pelczer, I.; Chirik, P. J. Iron-catalysed tritiation of pharmaceuticals. *Nature* **2016**, *529*, 195-199. (b) Yu, R. P.; Darmon, J. M.; Semproni, S. P.; Turner, Z. R.; Chirik, P. J. Synthesis of Iron Hydride Complexes Relevant to Hydrogen Isotope Exchange in Pharmaceuticals. *Organometallics* **2017**, *36*, 4341-4343. (c) Rummelt, S. M.; Darmon, J. M.; Yu, R. P.; Viereck, P.; Pabst, T. P.; Turner, Z. R.; Margulieux, G. W.; Gu, S.; Chirik, P. J. Synthesis, Structure, and Hydrogenolysis of Pyridine Dicarbene Iron Dialkyl Complexes. *Organometallics* **2019**, *38*, 3159-3168.

2 Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics* **1996**, *15*, 1518–1520.

3 MestReNova Version 12.0.1-20560 c 2018 Mestrelab Research S.L.

4 Pabst, T. P.; Obligacion, J. V.; Rochette, E.; Pappas, I. Chirik, P. J. Cobalt-catalyzed borylation of fluorinated arenes: Thermodynamic control of C(sp^2)–H oxidative addition results in *ortho* to fluorine selectivity. *J. Am. Chem. Soc.* **2019***, 141*, 15378-15389.