

## Supporting Information

# Synthetic Protocol for Diarylethenes through Suzuki–Miyaura Coupling

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### Table of Contents

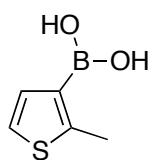
Instrumentation and Materials .....	S2
General Procedures and Compound Data .....	S2
Spectral Data for the New Compounds .....	S9

## Experimental Section

### Instrumental and Materials

$^1\text{H}$  NMR (300 MHz)  $^{13}\text{C}$  NMR (126 MHz) and  $^{19}\text{F}$  NMR (282 MHz) spectra were taken on Varian Mercury and INOVA spectrometer, and chemical shifts were reported as the delta scale in ppm relative to  $\text{CHCl}_3$  and DMSO as internal reference for  $^1\text{H}$  NMR ( $\delta = 7.260$  ppm for  $\text{CHCl}_3$ , 2.500 ppm for DMSO) and  $^{13}\text{C}$  NMR ( $\delta = 77.0$  ppm for  $\text{CHCl}_3$ ) and hexafluorobenzene as external reference for  $^{19}\text{F}$  NMR ( $\delta = -162.9$  ppm). UV/vis absorption and steady-state fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and a Shimadzu RF-5300PC spectrometer, respectively. High resolution ESI-TOF mass spectra were taken on a Bruker microTOF. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-200). X-ray data were taken on a Bruker SMART APEX X-Ray diffractometer equipped with a large area CCD detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 3-Thienylboronic acid (**1a**)<sup>1</sup>, 2,5-dimethyl-3-thienylboronic acid (**1e**)<sup>2</sup>, and 2,5-dimethyl-3-thienylboronic acid pinacol ester (**1f**)<sup>3</sup> were synthesized according to the reported literatures.

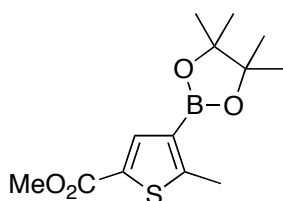
#### 2-methyl-3-thienylboronic acid (**1b**).<sup>4</sup>



A solution of 3-bromo-2-methylthiophene (5.19 g, 29.3 mmol) and triisopropylborate (13.5 mL, 58.5 mmol) in dry THF (110 mL) in three-necked round bottomed flask with a dropping funnel, a three-way stopcock and a rubber septum was cooled to  $-78\text{ }^\circ\text{C}$  under nitrogen atmosphere. *n*-Butyllithium (36.6 mL, 58.5 mmol, 1.6 M in hexane) was added dropwise over 20 min via the dropping funnel. After the addition was completed, the mixture was gradually warmed to  $-20\text{ }^\circ\text{C}$  with stirring for additional 1 h. The reaction mixture was

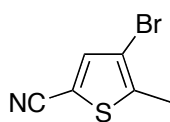
warmed to r.t., and then the reaction was quenched with 1*N* aqueous HCl. The resulting solution was extracted with ethyl acetate twice, washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then evaporated. Recrystallization with acetonitrile afforded 2-methyl-3-thienylboronic acid (2.70 g, 65%) as white microcrystals. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.23 (d, *J* = 5.0 Hz, 1H), 7.14 (d, *J* = 5.0 Hz, 1H) and 2.59 (s, 3H) ppm; <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ = 148.5, 133.5, 132.8, 121.3, and 15.5 ppm; HR-MS (ESI-MS): *m/z* = 140.0221, calcd for (C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>BS)<sup>−</sup> = 140.0223 ([*M* − *H*]<sup>−</sup>).

### 5-(methoxycarbonyl)-2-methyl-3-thienylboronic acid pinacol ester (1g).<sup>5</sup>



A Schlenk tube containing 3-bromo-2-methoxycarbonyl-5-methylthiophene (1.59 g, 6.76 mmol), bis(pinacolate)diboron (2.57 g, 10.1 mmol), X-Phos (32.2 mg, 67.6 μmol), Pd<sub>2</sub>dba<sub>3</sub>•CHCl<sub>3</sub> (34.9 mg, 33.8 μmol) and KOAc (1.32 mmol) was flushed with nitrogen, and then the mixture was dissolved in dry dioxane (6 mL). The reaction mixture was refluxed for 24 h. The resulting solution was filtered through short pad of Celite, and then the filtrate was concentrated in vacuo. Purification by silica-gel column chromatography with ethyl acetate/hexane afforded the product (687 mg, 2.43 mmol) in 36% yield.

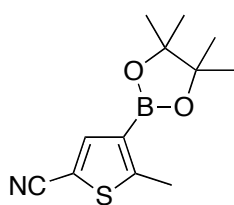
### 3-bromo-4-cyano-1-methylthiophene. (5)



To a solution of 3-bromo-5-formyl-2-methylthiophene (328 mg, 1.60 mmol) in pyridine (10 mL) was added NH<sub>2</sub>OH•HCl (133 mg, 1.92 mmol). The reaction mixture was then stirred at room temperature for 1 h. Acetic anhydride (227 μL, 2.40 mmol) was then added and the resulting solution was refluxed for 2 h. The reaction was quenched with water, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, and then the residue was

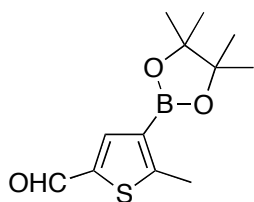
separated by column chromatography on silica-gel (ethyl acetate/hexane) to provide the product (1.35 g, 6.68 mmol) in 84% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.44 (s, 1H), and 2.46 (s, 3H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 143.1, 140.0, 113.7, 110.7, 107.7, and 15.6 ppm; HR-MS (ESI-MS):  $m/z$  = 223.9150, calcd for  $(\text{C}_6\text{H}_4\text{NSBr})^+ = 223.9140$  ( $[M + \text{Na}]^+$ ).

**(4-cyano-1-methylthienyl)-3-boronic acid pinacol ester (1h).**



A Schlenk tube containing 3-bromo-2-cyano-5-methylthiophene **5** (590 mg, 2.92 mmol), bis(pinacolate)diboron (889 mg, 3.50 mmol), bis(diphenylphosphino)ferrocene (16.2 mg, 29.2  $\mu\text{mol}$ ),  $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$  (15.1 mg, 14.6  $\mu\text{mol}$ ) and KOAc (5.84 mmol) was flushed with nitrogen, and then the mixture was dissolved in dry dioxane (3 mL). The reaction mixture was refluxed for 24 h. The resulting solution was filtered through short pad of Celite, and then the filtrate was concentrated in vacuo. Purification by silica-gel column chromatography with ethyl acetate/hexane afforded the product (465 mg, 1.87 mmol) in 64% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.74 (s, 1H), 2.70 (s, 3H), and 1.32 (s, 12H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 159.6, 144.4, 114.5, 106.1, 83.9, 24.8, 16.0 ppm; HR-MS (ESI-MS):  $m/z$  = 271.0923, calcd for  $(\text{C}_{12}\text{H}_{16}\text{NO}_2\text{BS})^+ = 271.0923$  ( $[M + \text{Na}]^+$ ).

**(5-formyl-2-methylthienyl)-3-boronic acid pinacol ester (1i)**

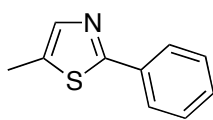


A Schlenk tube containing 3-bromo-2-formyl-5-methylthiophene (900 mg, 4.39 mmol), bis(pinacolate)diboron (1.34 g, 5.27 mmol),  $\text{PdCl}_2\text{dppf}$  (160 mg, 0.24 mmol), and KOAc (862 mg, 8.78 mmol) was flushed with nitrogen, and then the mixture was dissolved in dry dioxane (4 mL). The reaction mixture was refluxed for 48 h. The resulting solution was filtered through short pad of Celite, then the filtrate was concentrated in



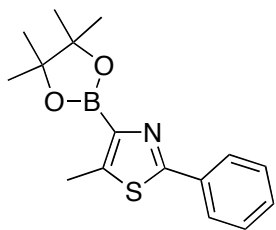
vacuo. Purification by silica-gel column chromatography with ethyl acetate/hexane furnished the product (378 mg, 1.50 mmol) in 34% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  9.80 (s, 1H), 7.91 (s, 1H), 2.74 (s, 3H), and 1.30 (s, 12H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 182.9, 163.2, 153.6, 144.4, 83.8, 24.9, 16.9 ppm; HR-MS (ESI-MS):  $m/z$  = 274.0925, calcd for  $(\text{C}_{12}\text{H}_{17}\text{O}_3\text{BS})^+ = 274.0920$  ( $[M + \text{Na}]^+$ ).

### 5-methyl-2-phenylthiazole.<sup>6</sup>



A Schlenk tube containing 2-bromo-5-methylthiazole (2.14 g, 12.0 mmol) and phenylboronic acid (1.83 g, 15.0 mmol) was flushed with nitrogen gas, and then degassed dioxane (12 mL) was added. To the solution were added a degassed aqueous solution of  $\text{K}_2\text{CO}_3$  (5.48 g, 45.0 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.693 g, 0.600 mmol). After refluxing for 36 h, the resulting solution was filtered through a short pad of Celite, and the filtrate was then evaporated. Column chromatography on silica-gel with ethyl acetate/hexane (1/10, v/v) afforded the product (1.13 g, 6.45 mmol, 54%) as pale yellow liquid.

### 5-methyl-2-phenyl-3-thiazolyl-tetramethyl-1,3-dioxaborolane (1k).<sup>6</sup>



A two-necked flask containing **1** (0.740 g, 4.22 mmol) was flushed with nitrogen and dry THF (25 mL) was added. The mixture was cooled to  $-78\text{ }^\circ\text{C}$ .  $t\text{BuLi}$  (1.6 M in pentane, 3.16 mL) was added dropwise, and the mixture was then stirred for 30 min. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.12 mL, 5.49 mmol) was added and the mixture was allowed to warm up to room temperature over a period of 1 h. After an addition of methanol, the mixture was extracted with ethyl acetate, and the combined organic layers were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and then evaporated. The residue was filtered through a short pad of

silica with ethyl acetate to afford the product (408 mg, 1.34 mmol) in 32 % yield.

**General Procedure for Suzuki–Miyaura cross coupling reaction of 1,2-dichlorohexafluorocyclopentene with arylboronic acids (Method A).**

A Schlenk tube containing arylboronic acid (1.50 mmol, 3 equiv), Pd<sub>2</sub>dba<sub>3</sub>•CHCl<sub>3</sub> (2.56 mg, 2.50 μmol, 1 mol% Pd), X-Phos (4.77 mg, 10 μmol, 2 mol%) and K<sub>3</sub>PO<sub>4</sub> (319 mg, 1.50 mmol, 3 equiv) was flushed with nitrogen by three times. Then 1,2-dichlorohexafluorocyclopentene (75.0 μL, 0.50 mmol) and deoxygenated dry dioxane (1.5 mL) were added. The resulting suspension was refluxed for 16 h. After the reaction was completed, the mixture was filtered through a short pad of Celite with hexane and the filtrate was evaporated to dryness. Purification by column chromatography on silica-gel with hexane as an eluent afforded the corresponding diarylethenes in high yields. 1,2-Bis(3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2a**)<sup>7</sup>, 1,2-bis(2'-dimethyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2b**)<sup>8</sup>, 1,2-bis(3'-phenyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2c**)<sup>9</sup>, 1,2-bis(3'-furanyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2d**)<sup>7</sup> and 1,2-bis(2',5'-dimethyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2e**)<sup>10</sup> were characterized by their high resolution mass spectra and <sup>1</sup>H and <sup>13</sup>C NMR spectra, showing essentially the same spectra as those reported in literatures.

**General Procedure for Suzuki–Miyaura cross coupling reaction of 1,2-dichlorohexafluorocyclopentene with arylboronic acids (Method B).**

A Schlenk tube containing arylboronic acid (1.50 mmol), Pd<sub>2</sub>dba<sub>3</sub>•CHCl<sub>3</sub> (2.56 mg, 2.50 μmol, 1 mol% Pd), PCy<sub>3</sub> (2.80 mg, 0.010 mmol) and CsF ( mg, 4.50 mmol) was flushed with nitrogen by three times. Then 1,2-dichlorocyclopentene (75.0 μL, 0.50 mmol) followed by the deoxygenated toluene/H<sub>2</sub>O (10/1, v/v) (1.5 mL) was added. The resulting suspension was refluxed for 16 h. After the reaction was

completed, the mixture was filtered through a short pad of Celite with hexane and the filtrate was evaporated to dryness. Purification by column chromatography on silica-gel with hexane as an eluent afforded the corresponding diarylethenes in high yields. 1,2-Bis(5'-cyano-2'-methyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2h**)<sup>11</sup> 1,2-bis(5'-formyl-2'-methyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2i**)<sup>12</sup> and 1,2-bis(5-methyl-2-phenyl-3-thiazolyl)-3,3,4,4,5,5-hexafluorocyclopentene (**2j**)<sup>6</sup> were characterized by their high-resolution mass and <sup>1</sup>H and <sup>13</sup>C NMR spectra, showing essentially the same spectra as those reported in literatures.

**1,2-Bis(5'-methoxycarbonyl-2'-methyl-3'-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (2g)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.76 (s, 2H, thienyl-β), 3.89 (s, 6H, CO<sub>2</sub>CH<sub>3</sub>) and 1.94 (s, 6H, CH<sub>3</sub>) ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -111.6 (t, *J* = 5.36 Hz, 4F), -133.1 (t, *J* = 5.36 Hz, 2F). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 161.4, 148.4, 132.7, 131.6, 125.1, 52.2, 14.6 ppm; HR-MS (ESI-MS): *m/z* = 507.0131, calcd for (C<sub>19</sub>H<sub>14</sub>F<sub>6</sub>S<sub>2</sub>O<sub>4</sub>)<sup>+</sup> = 507.0130 ([*M* + *Na*]<sup>+</sup>).

**1,2-Bis(tris(3,5-di-tert-butylphenyl)porphyrinato Ni(II)-2'-yl)-3,3,4,4,5,5-hexafluorocyclopentene (4a).**

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.64 (s, 2H, *meso*), 9.31 (s, 2H, pyrrole-β), 8.62 (d, *J* = 5.1 Hz, 2H, pyrrole-β), 8.53 – 8.48 (m, 10H, pyrrole-β), 7.74 (s, 2H, Ar-H), 7.68 (s, 4H, Ar-H), 7.60 (s, 2H, Ar-H), 7.57 (m, 6H, Ar-H), 1.43 (s, 36H, *t*Bu), 1.35 (s, 36H, CH<sub>3</sub>), 1.32 (s, 36H, CH<sub>3</sub>) ppm; <sup>19</sup>F NMR (CDCl<sub>3</sub>): δ -131.6 (t, *J* = 5.4 Hz, 2F), -110.4 (t, *J* = 5.4 Hz, 4F) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 149.0, 148.8, 148.7, 143.4, 143.2, 143.0, 142.6, 142.3, 140.6, 139.6, 139.4, 138.9, 134.3, 132.6, 132.5, 132.5, 132.3, 132.3, 132.1, 129.7, 129.1, 128.6, 128.4, 121.2, 121.0, 120.9, 120.7, 120.4, 119.3, 102.6, 34.9, 34.8, 34.8, 31.6, 31.6, 31.5 ppm.; UV/vis (ε [cm<sup>-1</sup> M<sup>-1</sup>]) λ = 409 (250000), 532 (25000) and 574 (15000) nm.; HR-MS

(ESI-MS):  $m/z = 2055.9813$ , calcd for  $(C_{129}H_{142}F_6N_8Ni_2)^+ = 2055.9861 ([M + Na]^+)$ . Crystal data: Single crystals were grown from EtOAc/CH<sub>3</sub>CN solution.  $C_{95}H_{16}F_{30}N_8O$ ,  $M_w = 1855.16$ , Triclinic, space group  $P-1$  (No. 2),  $a = 17.203(5) \text{ \AA}$ ,  $b = 17.778(5) \text{ \AA}$ ,  $c = 24.873(5) \text{ \AA}$ ,  $\alpha = 88.392(5)^\circ$ ,  $\beta = 70.931(5)^\circ$ ,  $\gamma = 768.140(5)^\circ$ ,  $V = 6635(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calc}} = 1.155 \text{ g/cm}^3$ ,  $T = 153 \text{ K}$ , 37160 measured reflections, 17491 unique reflections,  $R_1 = 0.0909$  ( $I > 2.0\sigma(I)$ ),  $wR_2 = 0.2749$  (all data)  $GOF = 1.043$  ( $I > 2.0\sigma(I)$ ). Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-xxxxxxx. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**1,2-Bis(5',10',15'-trihexylporphyrinato-2'-yl)-3,3,4,4,5,5-hexafluorocyclopentene (4b).**

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.65 (s, 2H, *meso*), 9.16 (s, 2H, pyrrole- $\beta$ ), 9.07 (d,  $J = 5.1 \text{ Hz}$ , 2H, pyrrole- $\beta$ ), 9.05 (d,  $J = 4.8 \text{ Hz}$ , 2H, pyrrole- $\beta$ ), 9.00 (d, 2H,  $J = 5.1 \text{ Hz}$ , pyrrole- $\beta$ ), 8.93 (d,  $J = 4.8 \text{ Hz}$ , 2H, pyrrole- $\beta$ ), 8.37 (d,  $J = 5.1 \text{ Hz}$ , 2H, pyrrole- $\beta$ ), 7.98 (d,  $J = 4.8 \text{ Hz}$ , 2H, pyrrole- $\beta$ ), 4.34 (t,  $J = 7.4 \text{ Hz}$ , 4H), 4.22 (t,  $J = 7.7 \text{ Hz}$ , 4H), 3.92 (t,  $J = 7.4 \text{ Hz}$ , 4H), 2.08-1.93 (m, 12H), 1.47-1.23 (m, 24H), 0.82 (m, 18H) ppm.; The <sup>13</sup>C NMR spectrum could not be obtained due to the low solubility of compound **4b**. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta$  -131.2 (t,  $J' = 5.4 \text{ Hz}$ , 4F), -109.3 (t,  $J = 5.4 \text{ Hz}$ , 2F) ppm; UV/vis ( $\epsilon$  [cm<sup>-1</sup> M<sup>-1</sup>])  $\lambda$  = 410 (190000), 541 (19000) and 585 (12000) nm; HR-MS (ESI-MS):  $m/z = 1409.6214$ , calcd for  $(C_{81}H_{94}F_6N_8Ni_2)^+ = 1409.6285 ([M + H]^+)$ .

**Spectral data for new compounds.**

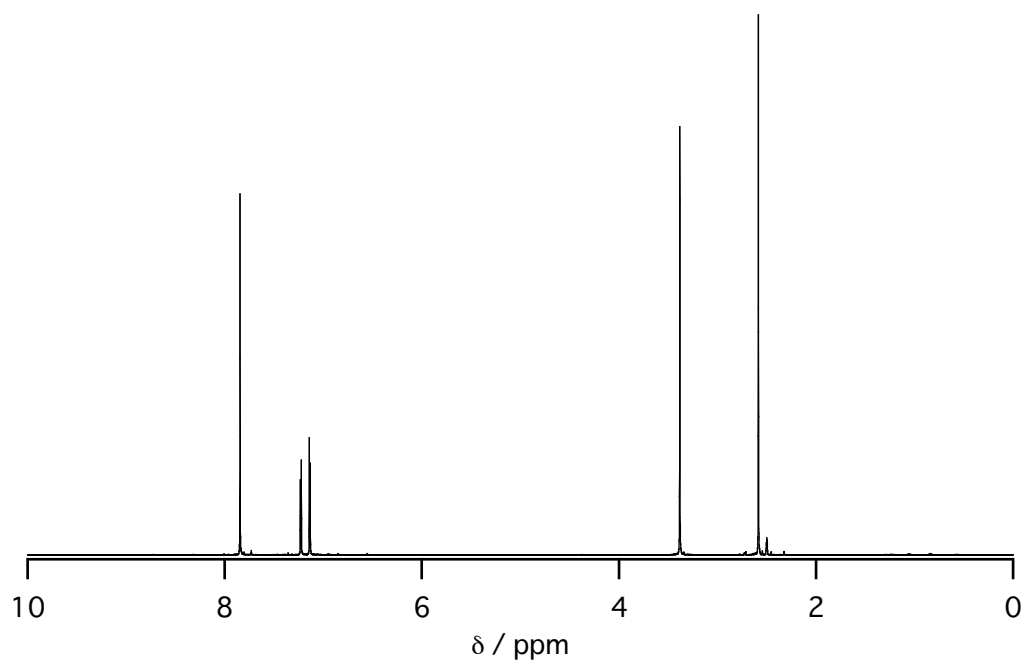


Figure S1.  $^1\text{H}$  NMR spectrum of **1b** in  $\text{DMSO}-d_6$ .

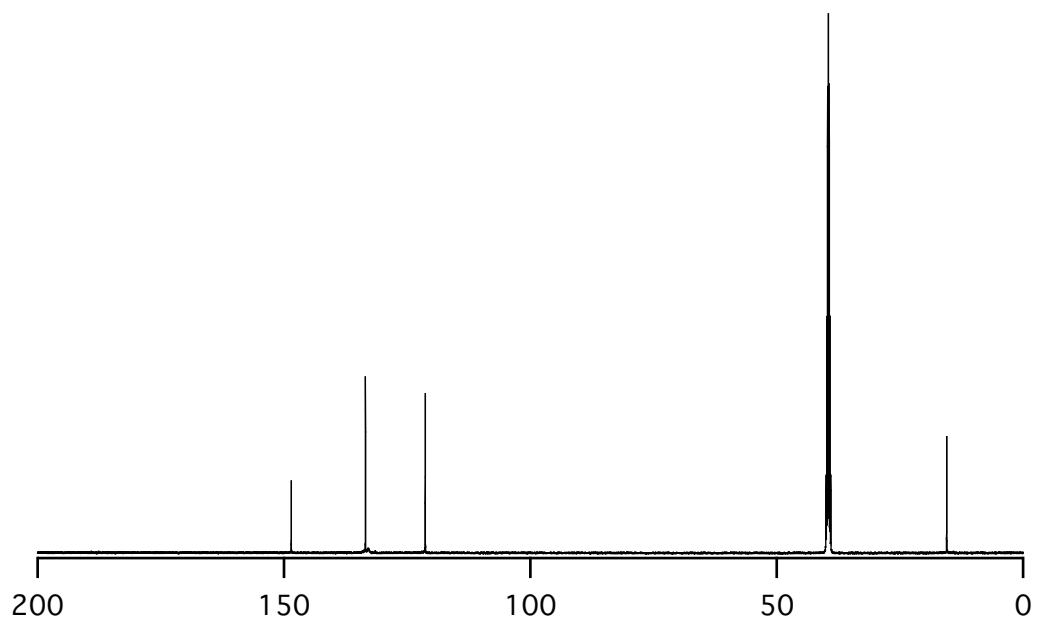


Figure S2.  $^{13}\text{C}$  NMR spectrum of **1b** in  $\text{DMSO}-d_6$ .

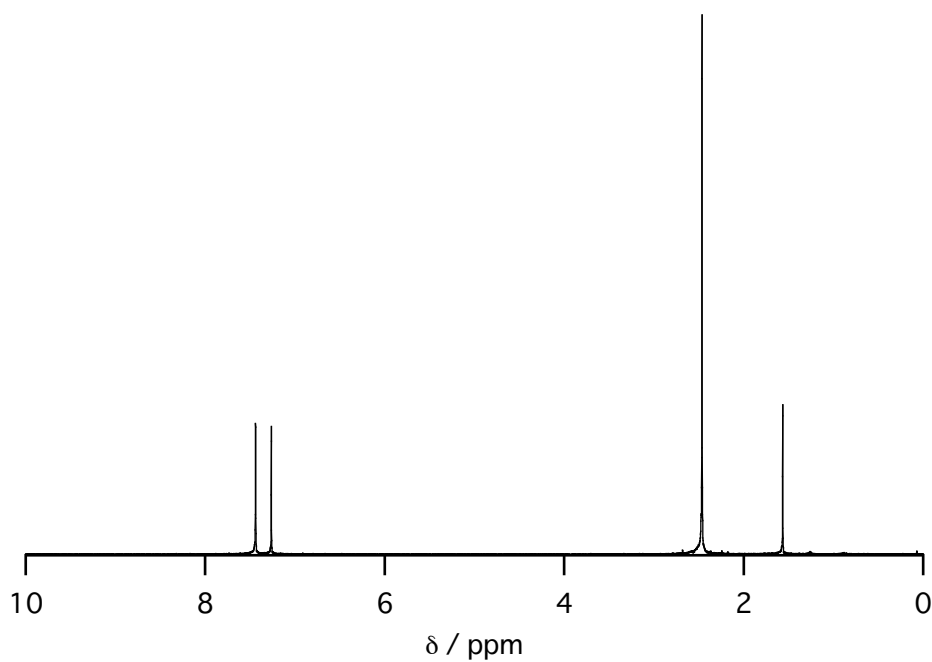


Figure S3. <sup>1</sup>H NMR spectrum of **5** in CDCl<sub>3</sub>.

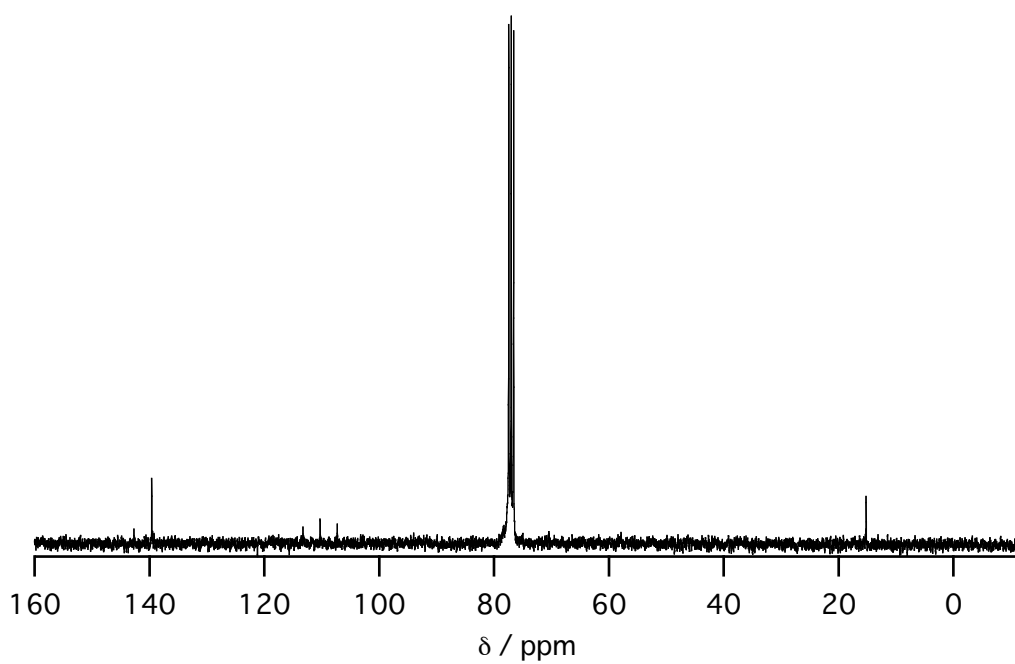


Figure S4. <sup>13</sup>C NMR spectrum of **5** in CDCl<sub>3</sub>.

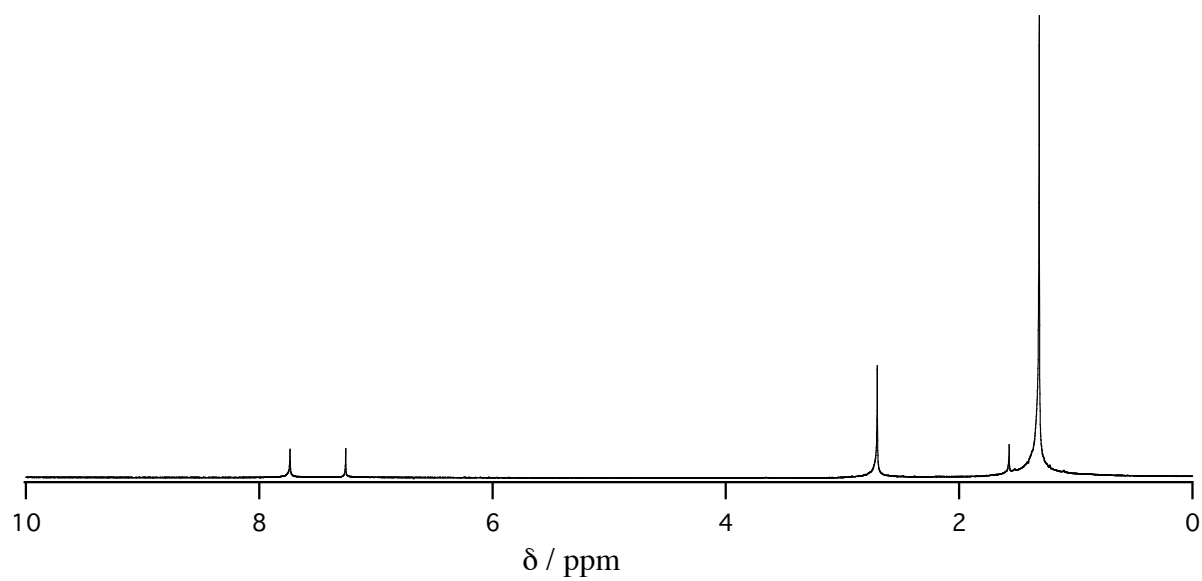


Figure S5. <sup>1</sup>H NMR spectrum of **1h** in CDCl<sub>3</sub>.

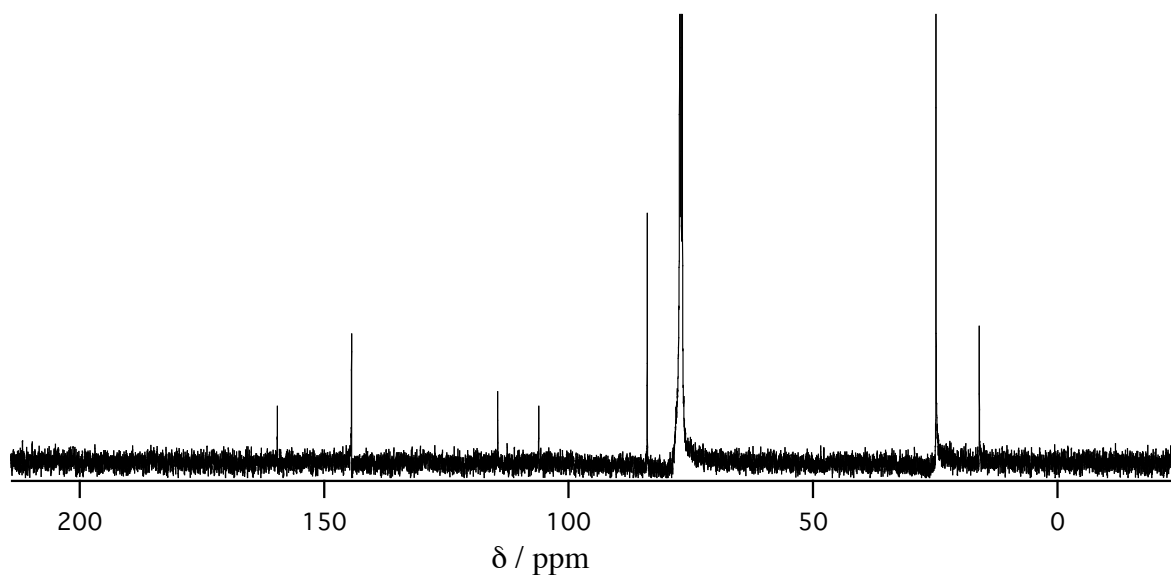


Figure S6. <sup>13</sup>C NMR spectrum of **1h** in CDCl<sub>3</sub>.

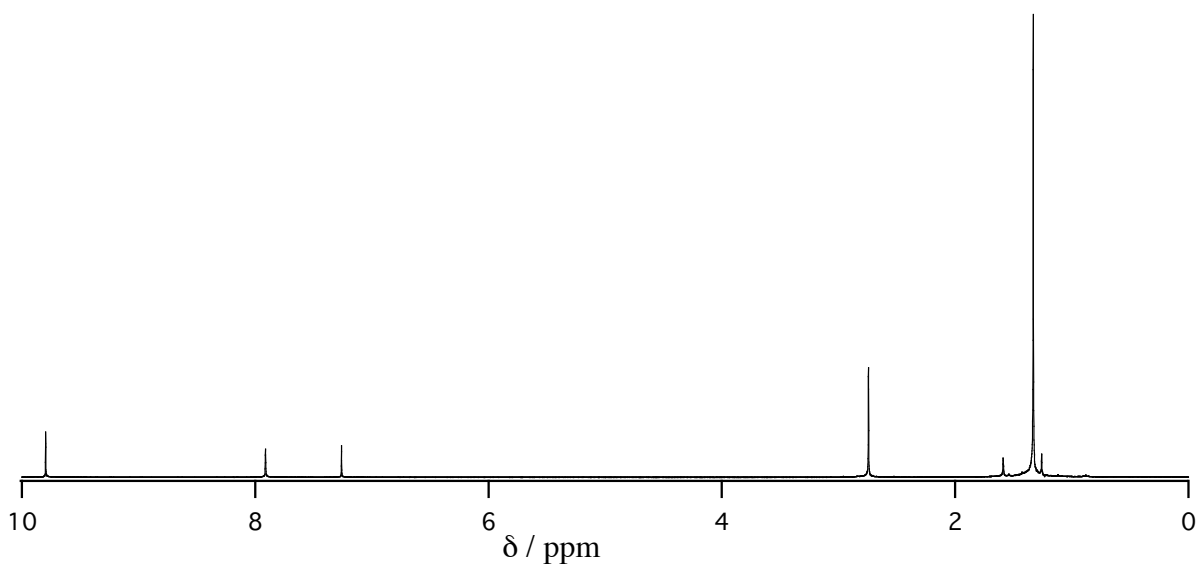


Figure S7.  $^1\text{H}$  NMR spectrum of **1i** in  $\text{CDCl}_3$ .

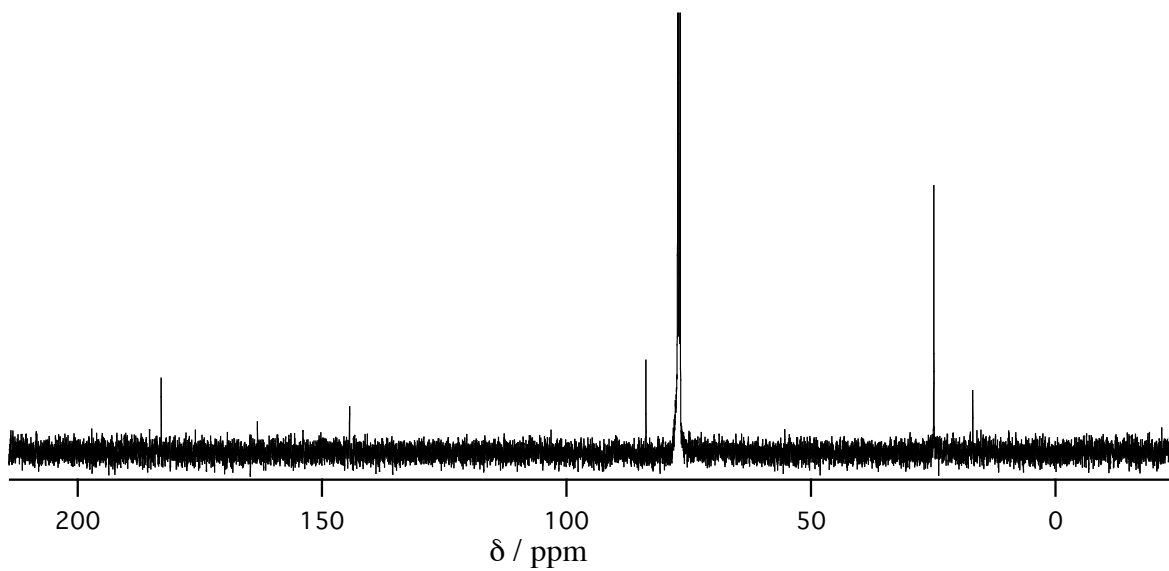


Figure S8.  $^{13}\text{C}$  NMR spectrum of **1i** in  $\text{CDCl}_3$ .



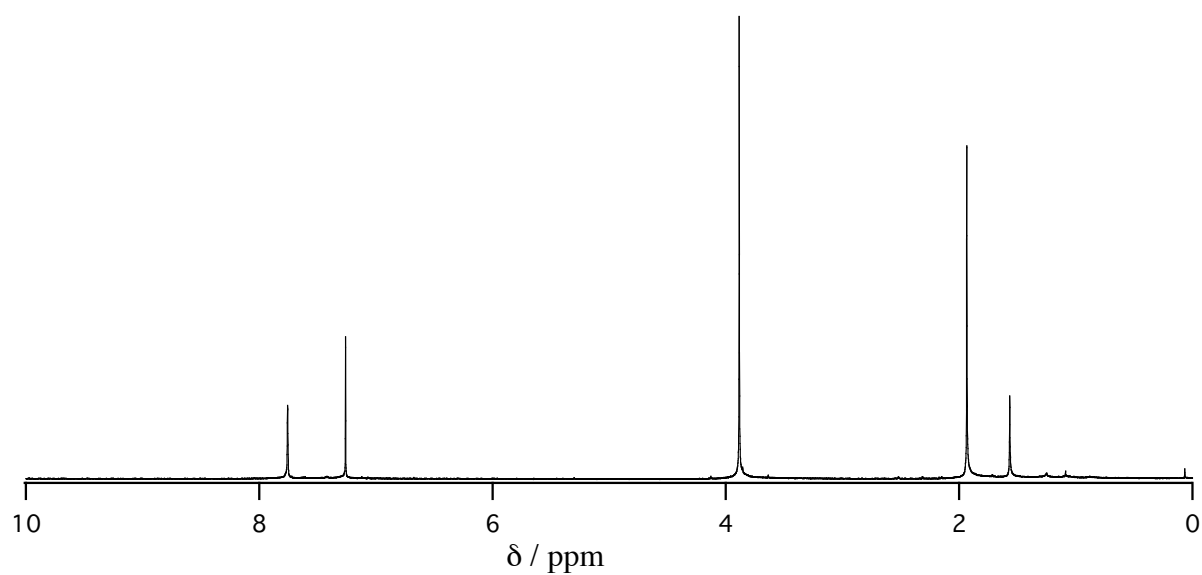


Figure S9.  $^1\text{H}$  NMR spectrum of **2g** in  $\text{CDCl}_3$ .

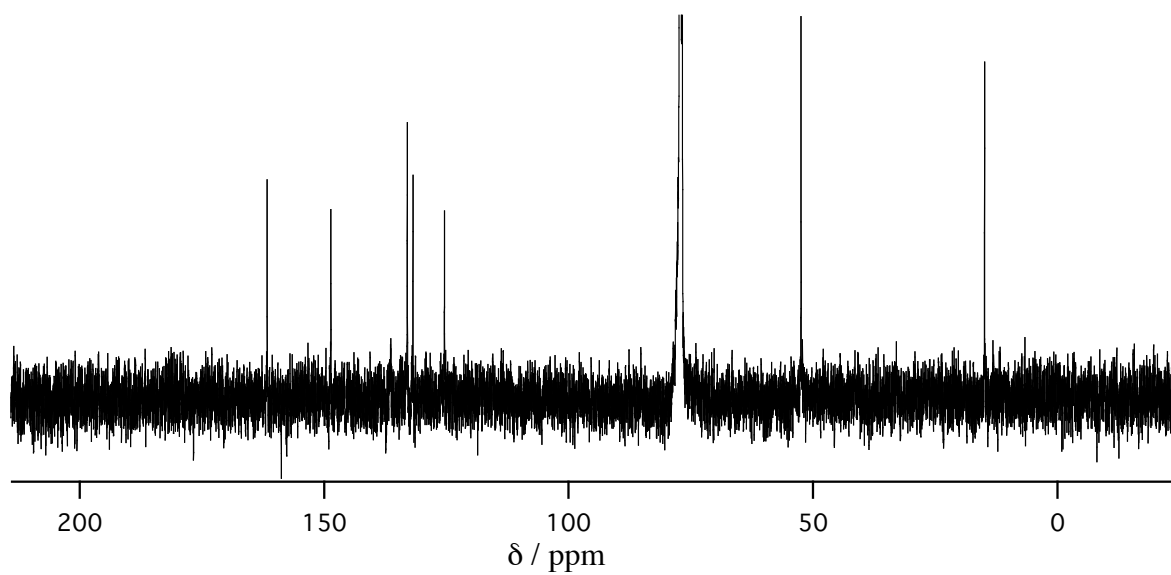


Figure S10.  $^{13}\text{C}$  NMR spectrum of **2g** in  $\text{CDCl}_3$ .

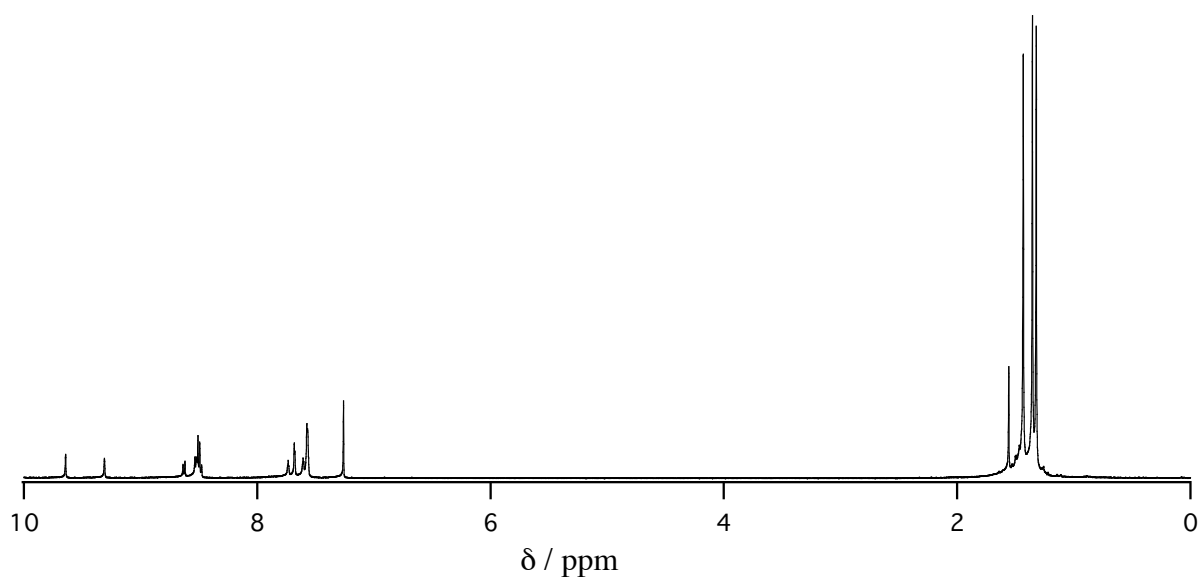


Figure S11.  $^1\text{H}$  NMR spectrum of **4a** in  $\text{CDCl}_3$ .

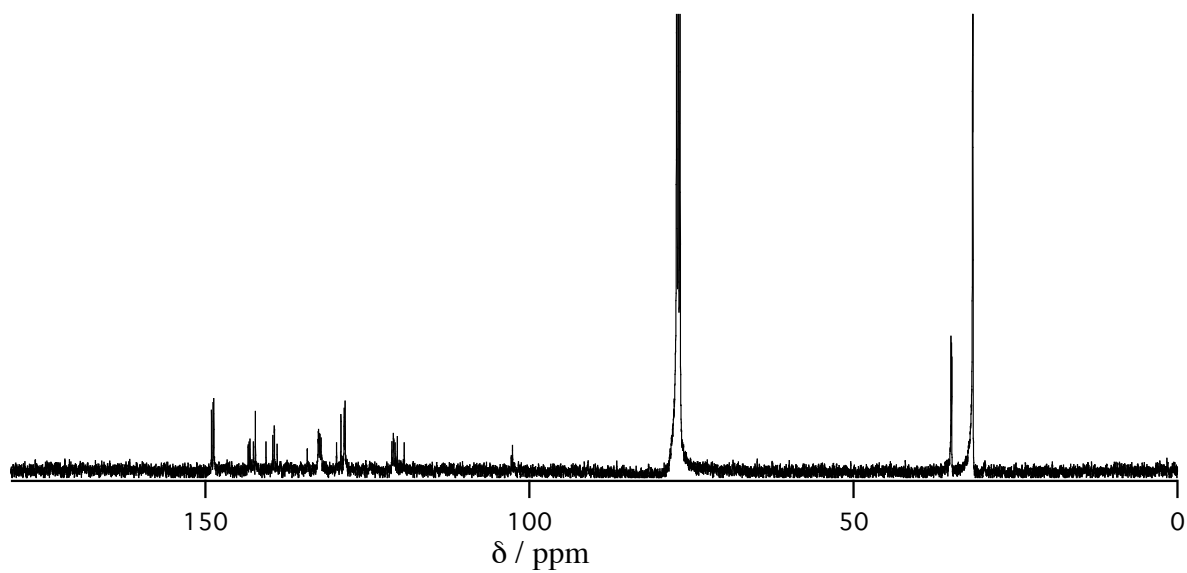


Figure S12.  $^{13}\text{C}$  NMR spectrum of **4a** in  $\text{CDCl}_3$ .

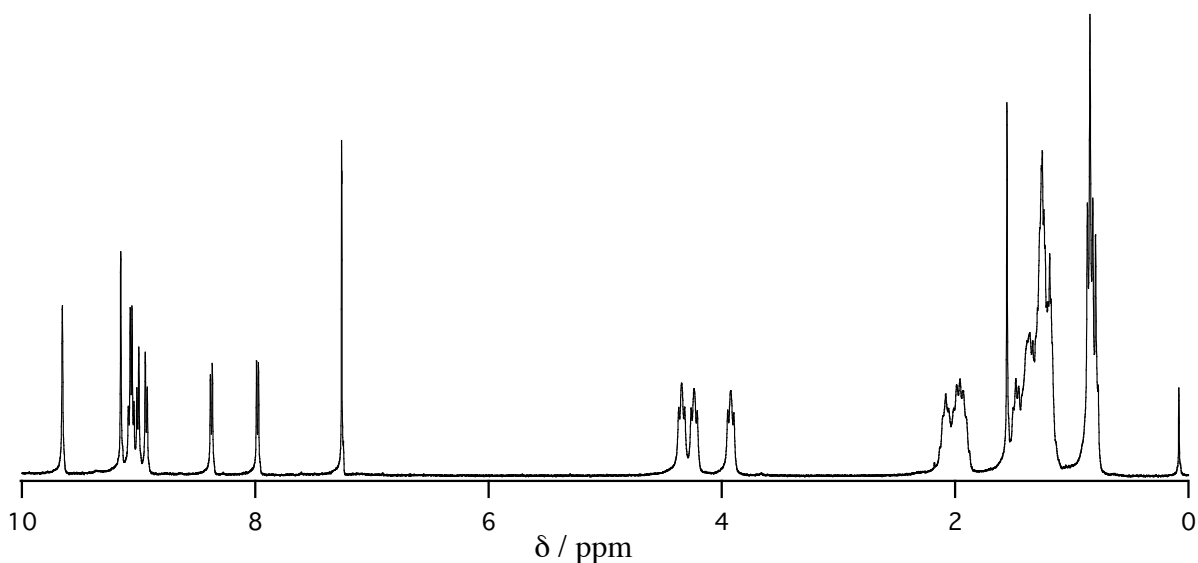


Figure S13.  $^1\text{H}$  NMR spectrum of **4b** in  $\text{CDCl}_3$ .

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