

## SUPPORTING INFORMATION

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### Supporting Information

#### **Hybrid materials comprising ferrocene and diamminoborane moieties: linear concatenation versus macrocyclization**

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### Table of Contents

|                                |           |
|--------------------------------|-----------|
| <b>1. Experimental Section</b> | <b>3</b>  |
| General procedures             | 3         |
| Syntheses                      | 4         |
| NMR spectra                    | 7         |
| High resolution mass spectra   | 30        |
| GPC traces                     | 37        |
| Electrochemical studies        | 37        |
| X-ray crystallography          | 41        |
| Author Contribution            | 43        |
| <br>                           |           |
| <b>2. References</b>           | <b>44</b> |

## 1. Experimental Procedures

**General procedures.** All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in a MBraun glove box. Solvents (toluene, dichloromethane, *n*-pentane and *n*-hexane) were dried and degassed by means of an Innovative Technology solvent purification system (SPS).

Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over CaH<sub>2</sub> (CDCl<sub>3</sub>) or Na (C<sub>6</sub>D<sub>6</sub>) and freshly distilled prior to use. 1,1'-[*N,N'*-bis(trimethylsilyl)diamino]ferrocene (**1**)<sup>[1]</sup>, *N*-ferrocenyl-*N*-trimethylsilylamine (**6**)<sup>[2]</sup> and dibromo(phenyl)borane<sup>[3]</sup>, MesLi<sup>[4]</sup>, MesBCl<sub>2</sub><sup>[5]</sup>, TipBCl<sub>2</sub><sup>[6]</sup>, TipBBr<sub>2</sub><sup>[7]</sup>, *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine<sup>[8]</sup> and *N*-(trimethylsilyl)-aniline<sup>[9]</sup> were prepared according to procedures described in the literature.

Unless otherwise stated, NMR spectra were recorded at 25 °C on a Bruker Avance III HD spectrometer operating at 300 MHz, on a Bruker Avance Neo I 500 spectrometer operating at 500 MHz or on a Bruker Avance Neo I 600 spectrometer operating at 600 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (<sup>1</sup>H) or the deuterated solvent itself (<sup>13</sup>C) and reported relative to external SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C) or BF<sub>3</sub>·OEt<sub>2</sub> (<sup>11</sup>B) standards.

Mass spectra were obtained with the use of a Thermo Scientific Exactive Plus Orbitrap MS system employing liquid injection field desorption ionization (LIFDI) and showed excellent congruence with the calculated isotopic distribution patterns.

Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-K $\alpha$  radiation. The crystals were cooled using an Oxford Cryostreams low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)<sup>[10]</sup> and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F<sup>2</sup> of all data, using SHELXL<sup>[11]</sup> software and the SHELXLE graphical user interface.<sup>[12]</sup>

Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Tetra-*n*-butylammonium hexafluorophosphate ([*n*-Bu<sub>4</sub>N][PF<sub>6</sub>]) was employed as the supporting electrolyte. Compensation for resistive losses (iR drop) was employed for all measurements. Cyclic voltammetry scans were conducted with a scan rate of 250 mV/s. The scans were referenced after the addition of a small amount of decamethylferrocene (bis(pentamethylcyclopentadienyl)iron(II)) as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple.

GPC chromatograms were recorded on an Agilent 1260 Infinity II Series, equipped with two PSS SDV 3  $\mu$ m 1000Å (300x8 mm) columns and one PSS SDV 3  $\mu$ m 1000Å (300x8 mm) column, at 25 °C with a flow rate of 1 mL min<sup>-1</sup> and calibrated against polystyrene standards. The samples were diluted in THF and toluene as internal standard. Detection was carried out via UV signal ( $\lambda$  = 254 nm). Evaluation of the chromatograms was performed using WinGPC software.

## SUPPORTING INFORMATION

### Syntheses

**Synthesis of dibromo-(2,4,6-trimethylphenyl)borane (MesBBr<sub>2</sub>).** To a suspension of mesyllithium (2.52 g, 20.0 mmol, 1 equiv.) in *n*-hexane (200 mL) was added a solution of BBr<sub>3</sub> (1M in *n*-hexane, 50 mmol, 2.5 equiv.) at -78°C. The mixture was warmed to room temperature overnight. The formed salt was removed by filtration with *n*-pentane (3 x 15 mL) and the solvent was removed *in vacuo*. After distillation, a colorless liquid was obtained (2.88 g, 10.0 mmol, 50 % yield). The obtained data correspond well with the published data.<sup>[13]</sup>

**General procedure for the synthesis of [3]ferrocenophanes 2<sup>Ar</sup> (Ar = Ph, Mes, Tip).** To a stirred solution of 1,1'-[*N,N'*-bis(trimethylsilyl)amino]ferrocene (**1**) (0.20 mmol) in DCM (5 mL) was added a solution of ArBBr<sub>2</sub> (0.20 mmol) in DCM (5 mL) at ambient temperature. The reaction mixture was stirred overnight, then all volatiles were removed *in vacuo*.

**Compound 2<sup>Ph</sup>:** Light brown solid. Yield 47.4 mg (0.157 mmol, 77%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.61 (m, 2H, *H*-Ph), 7.39 (m, 3H, *H*-Ph), 4.24 (s, 4H, *H*-Cp), 4.07 (s, 4H, *H*-Cp), 4.04 (br s, 2H, *NH*) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>): δ = 33.0 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 131.8 (s, C-Ph), 129.3 (s, C-Ph), 128.2 (s, C-Ph), 97.5 (s, Cp-C<sub>ipso</sub>-NH), 70.3 (s, C-Cp), 68.1 (s, C-Cp) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>16</sub>H<sub>15</sub>BF<sub>2</sub>FeN<sub>2</sub>: 302.0672; found 302.0665.

**Compound 2<sup>Mes</sup>:** Brown solid. Yield 43.0 mg (0.099 mmol, 50%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 6.85 (s, 2H, *H*-Ar<sub>Mes</sub>), 4.22 (t, 4H, *H*-Cp), 4.08 (t, 4H, *H*-Cp), 3.68 (br s, 2H, *NH*), 2.42 (s, 6H, *o*-CH<sub>3</sub>-Ar<sub>Mes</sub>); 2.29 (s, 3H, *p*-CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>): δ = 33.6 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>): δ = 140.3 (s, C-Ar<sub>Mes</sub>), 137.4 (s, C-Ar<sub>Mes</sub>), 127.1 (s, *m*-C-Ar<sub>Mes</sub>), 97.1 (s, C<sub>ipso</sub>-NH), 70.2 (s, C-Cp), 68.0 (s, C-Cp), 22.1 (s, *o*-CH<sub>3</sub>-Ar<sub>Mes</sub>), 21.3 (s, *p*-CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>19</sub>H<sub>21</sub>BF<sub>2</sub>FeN<sub>2</sub>: 344.1142; found 344.1134.

**Compound 2<sup>Tip</sup>:** Brown solid. Yield 53.7 mg (0.125 mmol, 63%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.01 (s, 2H, *H*-Ar<sub>Tip</sub>), 4.23 (t, 4H, *H*-Cp), 4.08 (t, 4H, *H*-Cp), 3.73 (br s, 2H, *NH*), 3.22 (sept, 2H, *p*-CH-(CH<sub>3</sub>)<sub>2</sub>) 2.90 (sept, 1H, *o*-CH-(CH<sub>3</sub>)<sub>2</sub>), 1.30 (m, 18H, CH-(CH<sub>3</sub>)<sub>2</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ = 33.8 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>): δ = 151.3 (s, *o*-C-Ar<sub>Tip</sub>), 148.7 (s, *p*-C-Ar<sub>Tip</sub>), 120.2 (s, *m*-C-Ar<sub>Tip</sub>), 97.2 (s, C<sub>ipso</sub>-NH), 70.2 (s, C-Cp), 68.0 (s, C-Cp), 34.5 (s, *p*-CH-(CH<sub>3</sub>)<sub>2</sub>), 34.2 (s, *o*-CH-(CH<sub>3</sub>)<sub>2</sub>), 25.1 (s, *o*-CH-(CH<sub>3</sub>)<sub>2</sub>), 24.2 (s, *p*-CH-(CH<sub>3</sub>)<sub>2</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>25</sub>H<sub>33</sub>BF<sub>2</sub>FeN<sub>2</sub>: 428.2081; found 428.2072.

**Synthesis of 3<sup>Mes</sup>.** To a stirred solution of MesBCl<sub>2</sub> (181.7 mg, 0.9 mmol) in DCM (2 mL) was added a solution of 1,1'-[*N,N'*-bis(trimethylsilyl)amino]ferrocene (**1**) (102.3 mg, 0.28 mmol) in 6 mL DCM at -78°C. The reaction mixture was stirred overnight. The solvent was exchanged to *n*-pentane (10 mL), a suspension was formed and a solid precipitated. Off-white solid. Isomeric mixture, only main isomer characterized. Yield 130.3 mg (0.24 mmol, 85%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 6.84-6.79 (s, 4H, *H*-Ar<sub>Mes</sub>), 5.97-5.64 (s, 2H, *NH*), 4.57-3.83 (br m, 8H, *H*-Cp), 2.33-2.23 (m, 18H, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>): δ = 38.7 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>): δ = 138.8 (s, C-Ar<sub>Mes</sub>), 138.5 (s, C-Ar<sub>Mes</sub>), 127.6 (s, *m*-C-Ar<sub>Mes</sub>), 66.6 (s, C-Cp), 62.1 (s, C-Cp), 22.2 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>), 21.8 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>), 21.4 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>28</sub>H<sub>32</sub>B<sub>2</sub>N<sub>2</sub>FeCl<sub>2</sub>: 544.1473; found 544.1474.

**Synthesis of 3<sup>Tip</sup>.** To a stirred solution of TipBCl<sub>2</sub> (36.3 mg, 1.28 mmol) in 4 mL DCM was added a solution of 1,1'-[*N,N'*-bis(trimethylsilyl)amino]ferrocene (**1**) (148.9 mg, 0.41 mmol) in 4 mL DCM at -78°C. The reaction mixture was stirred overnight. The solvent was exchanged to *n*-pentane (6 mL), a suspension was formed and a solid precipitated. The supernatant liquid was removed by filtration and the product was dried *in vacuo*. Off-white solid. Yield 218.7 mg (0.31 mmol, 75%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 6.99 (d, 2H, *H*-Ar<sub>Tip</sub>), 6.95 (d, 2H, *H*-Ar<sub>Tip</sub>), 6.03-5.75 (s, 2H, *NH*), 4.51-4.48 (m, 2H, *H*-Cp), 4.05 (t, 1H, *H*-Cp), 3.98 (t, 1H, *H*-Cp), 3.80-3.77 (m, 3H, *H*-Cp), 3.72 (t, 1H, *H*-Cp<sub>s</sub>), 2.99-2.74 (m, 6H, CH-(CH<sub>3</sub>)<sub>2</sub>), 1.30-1.22 (m, 30H, CH-(CH<sub>3</sub>)<sub>2</sub>), 1.16-1.12 (m, 6H, CH-(CH<sub>3</sub>)<sub>2</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CDCl<sub>3</sub>): δ = 38.7 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (76 MHz, CDCl<sub>3</sub>): δ = 150.3 (s, 2C, C-Ar<sub>Tip</sub>), 150.1 (s, C-Ar<sub>Tip</sub>), 149.7 (s, 2C, C-Ar<sub>Tip</sub>), 120.6 (s, *m*-C-Ar<sub>Tip</sub>), 66.6 (s, C-Cp), 66.4 (s, C-Cp), 66.3 (s, C-Cp), 66.1 (s, C-Cp), 64.1 (s, C-Cp), 63.9 (s, C-Cp), 62.5 (s, C-Cp), 62.4 (s, C-Cp), 35.0 (s, 2C, CH-(CH<sub>3</sub>)<sub>2</sub>), 34.8 (s, 2C, CH-(CH<sub>3</sub>)<sub>2</sub>), 34.6 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 34.5 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 25.2 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 24.8 (s, 2C, CH-(CH<sub>3</sub>)<sub>2</sub>), 24.7 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 24.2 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 24.0 (s, CH-(CH<sub>3</sub>)<sub>2</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>40</sub>H<sub>56</sub>B<sub>2</sub>Cl<sub>2</sub>FeN<sub>2</sub>: 712.3351; found 712.3336.

**Formation of 4<sup>Mes</sup> and 5<sup>Mes</sup>.** To a stirred solution of 3<sup>Mes</sup> (54.9 mg, 0.10 mmol) in 3 mL DCM was added dropwise a cooled (-78°C) solution of 1,1'-[*N,N'*-bis(trimethylsilyl)amino]ferrocene (**1**) (36.3 mg, 0.10 mmol) in 20 mL at -78°C. The reaction mixture was stirred overnight. The solvent was exchanged to *n*-pentane (20 mL), a suspension was formed and a solid precipitated. The supernatant liquid was removed by filtration and the product was dried *in vacuo*. **The product contains a mixture of different ferrocenophane**

## SUPPORTING INFORMATION

**compounds (see HRMS measurement), which could not be separated from each other.** Overall yield 38.8 mg (0.056 mmol, 56%) of a brown solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.85 (s, 4H,  $H\text{-Ar}_{\text{Mes}}$ ), 6.08 (s, 2H,  $NH$ ), 4.20 (s, 2H,  $NH$ ), 4.00 (t, 4H,  $H\text{-Cp}$ ), 3.86 (t, 4H,  $H\text{-Cp}$ ), 3.82 (t, 4H,  $H\text{-Cp}$ ), 3.54 (t, 4H,  $H\text{-Cp}$ ), 2.36-2.32 (s, 18H,  $\text{CH}_3\text{-Ar}_{\text{Mes}}$ ) ppm;  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 29.8 ppm. HRMS (LIFDI)  $m/z$  calcd. for  $\text{C}_{38}\text{H}_{42}\text{B}_2\text{Fe}_2\text{N}_4$ : 688.2289; found 688.2272 (other masses included  $5^{\text{Mes}}$ ; calcd. for  $\text{C}_{57}\text{H}_{63}\text{B}_3\text{Fe}_3\text{N}_6$ : 1032.3436; found: 1032.3411 ([3.3.3]ferrocenophane); calcd. for  $\text{C}_{76}\text{H}_{84}\text{B}_4\text{Fe}_4\text{N}_8$ : 1376.4583; found: 1376.4554 ([3.3.3.3]ferrocenophane).

**Synthesis of [3.3]ferrocenophane  $4^{\text{Tip}}$ .** To a stirred solution of  $3^{\text{Tip}}$  (79.1 mg, 0.11 mmol) in 3 mL DCM was added dropwise a cooled ( $-78^\circ\text{C}$ ) solution of 1,1'-[ $N,N'$ -bis(trimethylsilyl)amino]ferrocene (**1**) (39.9 mg, 0.11 mmol) in 20 mL DCM at  $-78^\circ\text{C}$ . The reaction mixture was stirred overnight. The solvent was exchanged to *n*-pentane (20 mL), a suspension was formed and a solid precipitated. The supernatant liquid was removed by filtration and the product was dried *in vacuo*. Off-white solid. Yield 22.2 mg (0.026 mmol, 24%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.00 (s, 4H,  $H\text{-Ar}_{\text{Tip}}$ ), 6.06 (s, 2H,  $NH$ ), 4.27 (s, 2H,  $NH$ ), 3.96 (t, 4H,  $H\text{-Cp}$ ), 3.83 + 3.81 (2x t, 8H,  $H\text{-Cp}$ ), 3.51 (t, 4H,  $H\text{-Cp}$ ), 3.04 (sept, 4H,  $\text{CH}(\text{CH}_3)_2$ ), 2.92 (sept, 2H,  $\text{CH}(\text{CH}_3)_2$ ), 1.31-1.23 (m, 36H,  $\text{CH}(\text{CH}_3)_2$ ) ppm;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 32.0 ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.6 (s,  $\text{C-Ar}_{\text{Tip}}$ ), 149.2 (s,  $\text{C-Ar}_{\text{Tip}}$ ), 120.3 (s,  $m\text{-C-Ar}_{\text{Tip}}$ ), 105.7 (s,  $\text{C}_{\text{ipso-NH}}$ ), 101.9 (s,  $\text{C}_{\text{ipso-NH}}$ ), 63.9 (s,  $\text{C-Cp}$ ), 63.4 (s,  $\text{C-Cp}$ ), 61.0 (s,  $\text{C-Cp}$ ), 60.8 (s,  $\text{C-Cp}$ ), 34.6 (s,  $\text{CH}(\text{CH}_3)_2$ ), 34.5 (s,  $\text{CH}(\text{CH}_3)_2$ ), 25.5 (s,  $\text{CH}(\text{CH}_3)_2$ ), 24.3 (s,  $\text{CH}(\text{CH}_3)_2$ ), 24.2 (s,  $\text{CH}(\text{CH}_3)_2$ ) ppm. HRMS (LIFDI)  $m/z$  calcd. for  $\text{C}_{50}\text{H}_{66}\text{B}_2\text{Fe}_2\text{N}_4$ : 856.4167; found 856.4149.

**General Procedure for the Synthesis of  $7^{\text{Ar}}$  ( $\text{Ar} = \text{Mes}, \text{Tip}$ ).** To a stirred solution of **6** (0.25 mmol) in DCM (1 mL) was added a solution of  $\text{ArBBr}_2$  (0.125 mmol) in 2 mL DCM at  $-78^\circ\text{C}$ . The reaction mixture was warmed to room temperature and stirred overnight. The solvent was exchanged to *n*-pentane (3 mL), a suspension was formed and a solid precipitated.

**Compound  $7^{\text{Mes}}$ :** Off-white solid. Yield 55.5 mg (0.1 mmol, 79%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 6.86 (s, 2H,  $H\text{-Ar}_{\text{Mes}}$ ), 5.56 (s, 1H,  $NH$ ), 4.26 (s, 5H,  $H\text{-Cp}_{\text{unsubstit.}}$ ), 4.21 (t, 2H,  $H\text{-Cp}_{\text{substit.}}$ ), 4.11 (s, 5H,  $H\text{-Cp}_{\text{unsubstit.}}$ ), 4.05 (t, 2H,  $H\text{-Cp}_{\text{substit.}}$ ), 4.04 (s, 1H,  $NH$ ), 3.72 (s, 2H,  $H\text{-Cp}_{\text{substit.}}$ ), 3.68 (s, 2H,  $H\text{-Cp}_{\text{substit.}}$ ), 2.31 (s, 3H,  $p\text{-CH}_3\text{-Ar}_{\text{Mes}}$ ), 2.31 (s, 6H,  $o\text{-CH}_3\text{-Ar}_{\text{Mes}}$ ) ppm;  $^{11}\text{B}\{^1\text{H}\}$  NMR (190 MHz,  $\text{CDCl}_3$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 29.8 ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 139.8 (s,  $o\text{-C-Ar}_{\text{Mes}}$ ), 137.7 (s,  $p\text{-C-Ar}_{\text{Mes}}$ ), 136.4 (br s,  $\text{C}_{\text{ipso-B-Ar}_{\text{Mes}}}$ ), 127.0 (s,  $m\text{-C-Ar}_{\text{Mes}}$ ), 103.5 (s,  $\text{C}_{\text{ipso-NH}}$ ), 100.7 (s,  $\text{C}_{\text{ipso-NH}}$ ), 69.0 (s,  $\text{C-Cp}_{\text{unsubstit.}}$ ), 68.9 (s,  $\text{C-Cp}_{\text{unsubstit.}}$ ), 64.4 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 63.3 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 61.5 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 58.7 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 22.0 (s,  $p\text{-CH}_3\text{-Ar}_{\text{Mes}}$ ), 21.4 (s,  $o\text{-CH}_3\text{-Ar}_{\text{Mes}}$ ) ppm. HRMS (LIFDI)  $m/z$  calcd. for  $\text{C}_{29}\text{H}_{31}\text{BFe}_2\text{N}_2$ : calcd. 530.1274; found 530.1266.

**Compound  $7^{\text{Tip}}$ :** Dark brown solid. Yield 100.0 mg (16.3 mmol, 65%)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 6.96 (s, 2H,  $H\text{-Ar}_{\text{Tip}}$ ), 5.39 (br s, 1H,  $NH$ ), 4.24 (s, 5H,  $H\text{-Cp}_{\text{unsubstit.}}$ ), 4.18 (s, 2H,  $H\text{-Cp}_{\text{substit.}}$ ), 4.13 (s, 1H,  $NH$ ; 5H,  $H\text{-Cp}_{\text{unsubstit.}}$ ), 4.04 (s, 2H,  $H\text{-Cp}_{\text{substit.}}$ ), 3.70 (s, 4H,  $H\text{-Cp}_{\text{substit.}}$ ), 2.89 (sept, 3H,  $\text{CH}(\text{CH}_3)_2$ ), 1.24-1.13 (m, 18H,  $\text{CH}(\text{CH}_3)_2$ ) ppm;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 30.7 ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ,  $-30^\circ\text{C}$ ):  $\delta$  = 150.5 (s,  $p\text{-C-Ar}_{\text{Tip}}$ ), 148.8 (s,  $o\text{-C-Ar}_{\text{Tip}}$ ), 120.2 (s,  $m\text{-C-Ar}_{\text{Tip}}$ ), 100.6 (s,  $\text{C}_{\text{ipso-NH}}$ ), 69.0 (s,  $\text{C-Cp}_{\text{unsubstit.}}$ ), 64.4 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 61.6 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 34.3 (s,  $p\text{-CH}(\text{CH}_3)_2$ ), 34.1 (s,  $o\text{-CH}(\text{CH}_3)_2$ ), 25.6 (s,  $o\text{-CH}(\text{CH}_3)_2$ ), 24.2 (s,  $p\text{-CH}(\text{CH}_3)_2$ ), 24.0 (s,  $o\text{-CH}(\text{CH}_3)_2$ ) ppm. HRMS (LIFDI)  $m/z$  calcd. for  $\text{C}_{35}\text{H}_{43}\text{Fe}_2\text{BN}_2$ : calcd. 614.2213; found 614.2203.

**General Procedure for the Synthesis of  $8^{\text{Ar}}$  ( $\text{Ar} = \text{Mes}, \text{Tip}$ ).** To a stirred solution of  $\text{ArBCl}_2$  (0.5 mmol) in DCM (1.5 mL) was added a solution of **6** (0.5 mmol) in 3.5 mL DCM at ambient temperature. The reaction mixture was stirred overnight. The solvent was exchanged to *n*-pentane (4 mL), a suspension was formed and a solid precipitated.

**Compound  $8^{\text{Mes}}$ :** Off-white solid. Isomeric mixture, only main isomer characterized. Yield 147.6 mg (0.4 mmol, 80%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.83 (s, 2H,  $H\text{-Ar}_{\text{Mes}}$ ), 6.03 (s, 1H,  $NH$ ), 4.11 (s, 5H,  $H\text{-Cp}_{\text{unsubstit.}}$ ), 3.82-3.78 (m, 4H,  $H\text{-Cp}_{\text{substit.}}$ ), 2.36 (s, 3H,  $\text{CH}_3\text{-Ar}_{\text{Mes}}$ ), 2.27 (s, 6H,  $\text{CH}_3\text{-Ar}_{\text{Mes}}$ ) ppm;  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 38.8 ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 139.1 (s,  $\text{C-Ar}_{\text{Mes}}$ ), 138.6 (s,  $\text{C-Ar}_{\text{Mes}}$ ), 127.5 (s,  $m\text{-C-Ar}_{\text{Mes}}$ ), 98.8 (s,  $\text{C}_{\text{ipso-NH}}$ ), 69.3 (s,  $\text{C-Cp}_{\text{unsubstit.}}$ ), 64.6 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 60.9 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 21.7 (s,  $\text{CH}_3\text{-Ar}_{\text{Mes}}$ ), 21.4 (s,  $\text{CH}_3\text{-Ar}_{\text{Mes}}$ ) ppm.

**Compound  $8^{\text{Tip}}$ :** Off-white solid. Yield 167.7 mg (0.37 mmol, 74%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 6.95 (s, 2H,  $H\text{-Ar}_{\text{Tip}}$ ), 6.01 (s, 1H,  $NH$ ), 4.12 (s, 5H,  $H\text{-Cp}_{\text{unsubstit.}}$ ), 3.81-3.77 (m, 4H,  $H\text{-Cp}_{\text{substit.}}$ ), 2.92-2.75 (m, 3H,  $\text{CH}(\text{CH}_3)_2$ ), 1.25 (d, 12 H,  $\text{CH}(\text{CH}_3)_2$ ), 1.15 (d, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm;  $^{11}\text{B}\{^1\text{H}\}$  NMR (96 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 39.2 ppm;  $^{13}\text{C}\{^1\text{H}\}$  NMR (76 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.0 (s,  $\text{C-Ar}_{\text{Tip}}$ ), 149.7 (s,  $\text{C-Ar}_{\text{Tip}}$ ), 120.5 (s,  $m\text{-C-Ar}_{\text{Tip}}$ ), 99.0 (s,  $\text{C}_{\text{ipso-NH}}$ ), 69.2 (s,  $\text{C-Cp}_{\text{unsubstit.}}$ ), 64.6 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 61.6 (s,  $\text{C-Cp}_{\text{substit.}}$ ), 35.0 (s,  $\text{CH}(\text{CH}_3)_2$ ), 34.5 (s,  $\text{CH}(\text{CH}_3)_2$ ), 25.2 (s,  $\text{CH}(\text{CH}_3)_2$ ), 24.2 (s,  $\text{CH}(\text{CH}_3)_2$ ), 24.0 (s,  $\text{CH}(\text{CH}_3)_2$ ) ppm.

**Synthesis of 9<sup>Mes</sup>.** To a stirred solution of **8<sup>Mes</sup>** (77.0 mg, 0.21 mmol) in 3 mL DCM was added a solution of 1,1'-[*N,N'*-bis(trimethylsilyl)di-amino]ferrocene (**1**) (38.0 mg, 0.105 mmol) in 5 mL DCM at ambient temperature. The reaction mixture was stirred overnight, and all volatiles were removed *in vacuo*. The crude product was redissolved in *n*-pentane (8 mL) and the supernatant liquid was removed by filtration and the solvent (filtrate) was removed *in vacuo*. Orange solid. Yield 56.8 mg (0.065 mmol, 62%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, -40°C): δ = 6.90 (s, 1H, *H*-Ar<sub>Mes</sub>), 6.86 (s, 3H, *H*-Ar<sub>Mes</sub>), 5.59-5.48 (s, 2H, *NH*), 4.26-4.25 (m, 1H, *H*-Cp<sub>unsubstit.</sub>), 4.24 (s, 3H, *H*-Cp<sub>unsubstit.</sub>), 4.22 (s, 1H, *H*-Cp<sub>unsubstit.</sub>), 4.19 (t, 1H, *H*-Cp<sub>substit.</sub>), 4.18 (t, 1H, *H*-Cp<sub>substit.</sub>), 4.15 (t, 1H, *H*-Cp<sub>substit.</sub>), 4.12 (t, 1H, *H*-Cp<sub>substit.</sub>), 4.11-4.10 (s, 3H, *H*-Cp<sub>unsubstit.</sub>), 4.08-4.07 (m, 1H, *H*-Cp<sub>unsubstit.</sub>), 4.07 (s, 2H, *NH*), 4.03-4.00 (m, 5H, *H*-Cp<sub>substit.</sub>), 3.84 (t, 1H, *H*-Cp<sub>substit.</sub>), 3.77 (t, 1H, *H*-Cp<sub>substit.</sub>), 3.72 (t, 1H, *H*-Cp<sub>substit.</sub>), 3.69 (t, 1H, *H*-Cp<sub>substit.</sub>), 3.67-3.62 (m, 3H, *H*-Cp<sub>substit.</sub>), 3.57 (t, 1H, *H*-Cp<sub>substit.</sub>), 2.34-2.28 (m, 16H, CH<sub>3</sub>-Ar<sub>Mes</sub>), 2.24 (s, 2H, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, -40°C): δ = 30.3 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 139.8 (s, C-Ar<sub>Mes</sub>), 137.7 (s, C-Ar<sub>Mes</sub>), 127.2 (s, CH<sub>meta</sub>-Ar<sub>Mes</sub>), 69.1 (s, C-Cp<sub>unsubstit.</sub>), 69.0 (s, C-Cp<sub>unsubstit.</sub>), 66.3 (s, C-Cp<sub>substit.</sub>), 65.3 (s, C-Cp<sub>substit.</sub>), 65.2 (s, C-Cp<sub>substit.</sub>), 65.1 (s, C-Cp<sub>substit.</sub>), 64.6 (s, C-Cp<sub>substit.</sub>), 63.4 (s, C-Cp<sub>substit.</sub>), 63.1 (s, C-Cp<sub>substit.</sub>), 61.9 (s, C-Cp<sub>substit.</sub>), 60.1 (s, C-Cp<sub>substit.</sub>), 59.3 (s, C-Cp<sub>substit.</sub>), 59.1 (s, C-Cp<sub>substit.</sub>), 22.8 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>), 22.1 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>), 21.4 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>48</sub>H<sub>52</sub>B<sub>2</sub>Fe<sub>3</sub>N<sub>4</sub>: 874.2421; found 874.2398.

**Synthesis of 9<sup>TIP</sup>.** To a stirred solution of **8<sup>TIP</sup>** (74.4 mg, 0.165 mmol) in 3 mL DCM was added a solution of 1,1'-[*N,N'*-bis(trimethylsilyl)di-amino]ferrocene (**1**) (29.7 mg, 82.5 μmol) in 5 mL DCM at ambient temperature. The reaction mixture was stirred overnight, and all volatiles were removed *in vacuo*. The crude product was redissolved in *n*-pentane (4 mL) and the supernatant liquid was removed by filtration and the solvent (filtrate) was removed *in vacuo*. Orange solid. Yield 31.7 mg (0.03 mmol, 36%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, -40°C): δ = 7.02-6.94 (s, 4H, *H*-Ar<sub>TIP</sub>), 5.43-5.30 (s, 2H, *NH*), 4.24 (s, 1H, *H*-Cp<sub>unsubstit.</sub>), 4.23 (s, 3H, *H*-Cp<sub>unsubstit.</sub>), 4.21 (t, 1H, *H*-Cp<sub>substit.</sub>), 4.19-4.18 (m, 3H, *H*-Cp<sub>unsubstit.</sub>, *H*-Cp<sub>substit.</sub>), 4.15 (t, 2H, *H*-Cp<sub>substit.</sub>), 4.12-4.11 (m, 4H, *H*-Cp<sub>unsubstit.</sub>, *NH*), 4.07 (s, 3H, *H*-Cp<sub>unsubstit.</sub>), 4.02-3.98 (m, 3H, *H*-Cp<sub>substit.</sub>), 3.74-3.73 (m, 2H, *H*-Cp<sub>substit.</sub>), 3.69 (t, 1H, *H*-Cp<sub>substit.</sub>), 3.66-3.63 (m, 3H, *H*-Cp<sub>substit.</sub>), 3.60 (t, 1H, *H*-Cp<sub>substit.</sub>), 3.56 (t, 1H, *H*-Cp<sub>substit.</sub>), 2.93-2.83 (sept, 6H, CH-(CH<sub>3</sub>)<sub>2</sub>), 1.29-1.06 (m, 36H, CH-(CH<sub>3</sub>)<sub>2</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, -40°C): δ = 29.7 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 150.8 (s, C-Ar<sub>TIP</sub>), 120.2 (s, *m*-C-Ar<sub>TIP</sub>), 69.1 (s, C-Cp<sub>unsubstit.</sub>), 68.8 (s, C-Cp<sub>unsubstit.</sub>), 66.5 (s, C-Cp<sub>substit.</sub>), 65.4 (s, C-Cp<sub>substit.</sub>), 63.5 (s, C-Cp<sub>substit.</sub>), 63.4 (s, C-Cp<sub>substit.</sub>), 62.0 (s, C-Cp<sub>substit.</sub>), 61.8 (s, C-Cp<sub>substit.</sub>), 60.8 (s, C-Cp<sub>substit.</sub>), 60.2 (s, C-Cp<sub>substit.</sub>), 60.1 (s, C-Cp<sub>substit.</sub>), 34.5 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 34.2 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 25.7 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 24.3 (s, CH-(CH<sub>3</sub>)<sub>2</sub>), 24.1 (s, CH-(CH<sub>3</sub>)<sub>2</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>60</sub>H<sub>76</sub>B<sub>2</sub>Fe<sub>3</sub>N<sub>4</sub>: 1042.4299; found 1042.4273.

**Polycondensation to give 10.** To a stirred solution of **3<sup>Mes</sup>** (45.0 mg, 0.083 mmol) in 2 mL DCM was added a solution of *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine (20.9 mg, 0.083 mmol) in 2 mL DCM at ambient temperature. The reaction was stirred overnight. (*p*-Bu)<sub>6</sub>H<sub>4</sub>NHSiMe<sub>3</sub> (23.6 mg, 0.1 mmol) was added and stirred for 2h. Subsequently, the mixture was precipitated into cooled *n*-pentane (-78°C). The supernatant liquid was removed by filtration and the product was dried *in vacuo*. Brown solid. Yield 31.0 mg (0.053, 64%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 6.86-6.24 (m, 4H, *H*-Ar<sub>Mes</sub>, 4H, *H*-Ar<sub>Ph</sub>, 2H, *NH*), 4.22-3.60 (m, 8H, *H*-Cp<sub>substit.</sub>, 2H, *NH*) 2.29-2.21 (m, 18H, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (161 MHz, CDCl<sub>3</sub>): δ = 31.1 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>): δ = 142.6 (s, C-Ar<sub>Ph</sub>), 139.8 (s, C-Ar<sub>Mes</sub>), 137.6 (s, C-Ar<sub>Mes</sub>), 128.1 (s, C-Ar<sub>Ph</sub>), 127.3 (s, CH<sub>meta</sub>-Ar<sub>Mes</sub>), 126.2 (s, C-Ar<sub>Ph</sub>), 119.1 (s, C-Ar<sub>Ph</sub>), 115.2 (s, C-Ar<sub>Ph</sub>), 66.1 (s, C-Cp), 63.3 (s, C-Cp), 31.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.8 (s, CH<sub>3</sub>-*t*Bu), 22.0 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>), 21.4 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for [C<sub>34</sub>H<sub>38</sub>B<sub>2</sub>FeN<sub>4</sub>]<sub>n</sub>: n=2 (1160.5259), n=3 (1740.7960), n=4 (2321.0592); found n=2 (1160.5242), n=3 (1740.7896), n=4 (2321.0622).

**Synthesis of 11.** To a stirred solution of **8<sup>Mes</sup>** (56.3 mg, 0.154 mmol) in 2 mL DCM was added *N*-(trimethylsilyl)-aniline (26.6 mg, 0.16 mmol). The reaction mixture was stirred overnight, and all volatiles were removed *in vacuo*. Dark-brown oil. Yield: 64.4 mg (0.152 mmol, 99%) <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.04 (t, 2H, *H*-Ar<sub>Ph</sub>), 6.83 (s, 2H, *H*-Ar<sub>Mes</sub>), 6.80-6.76 (m, 1H, *H*-Ar<sub>Ph</sub>), 6.61 (d, 2H, *H*-Ar<sub>Ph</sub>), 6.24 (s, 1H, *NH*), 4.26, 4.23 (2x s, 7H, *H*-Cp<sub>substit.</sub>, *H*-Cp<sub>unsubstit.</sub>), 4.16 (s, 1H, *NH*), 4.03 (s, 2H, *H*-Cp<sub>substit.</sub>), 2.31, 2.28 (2x s, 9H, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm; <sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, CDCl<sub>3</sub>): δ = 30.9 ppm; <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CDCl<sub>3</sub>): δ = 139.8 (s, C-Ar<sub>Mes</sub>), 137.8 (s, C-Ar<sub>Mes</sub>), 129.1 (s, C-Ar<sub>Ph</sub>), 127.4 (s, CH<sub>meta</sub>-Ar<sub>Mes</sub>), 120.5 (s, C-Ar<sub>Ph</sub>), 118.2 (s, C-Ar<sub>Ph</sub>), 100.5 (s, C<sub>ipso</sub>-NH), 69.1 (s, C-Cp<sub>unsubstit.</sub>), 64.6 (s, C-Cp<sub>substit.</sub>), 62.1 (s, C-Cp<sub>substit.</sub>), 22.0 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>), 21.4 (s, CH<sub>3</sub>-Ar<sub>Mes</sub>) ppm. HRMS (LIFDI) *m/z* calcd. for C<sub>25</sub>H<sub>27</sub>BFeN<sub>2</sub>: 422.1611; found 422.1604.

# SUPPORTING INFORMATION

## NMR spectra

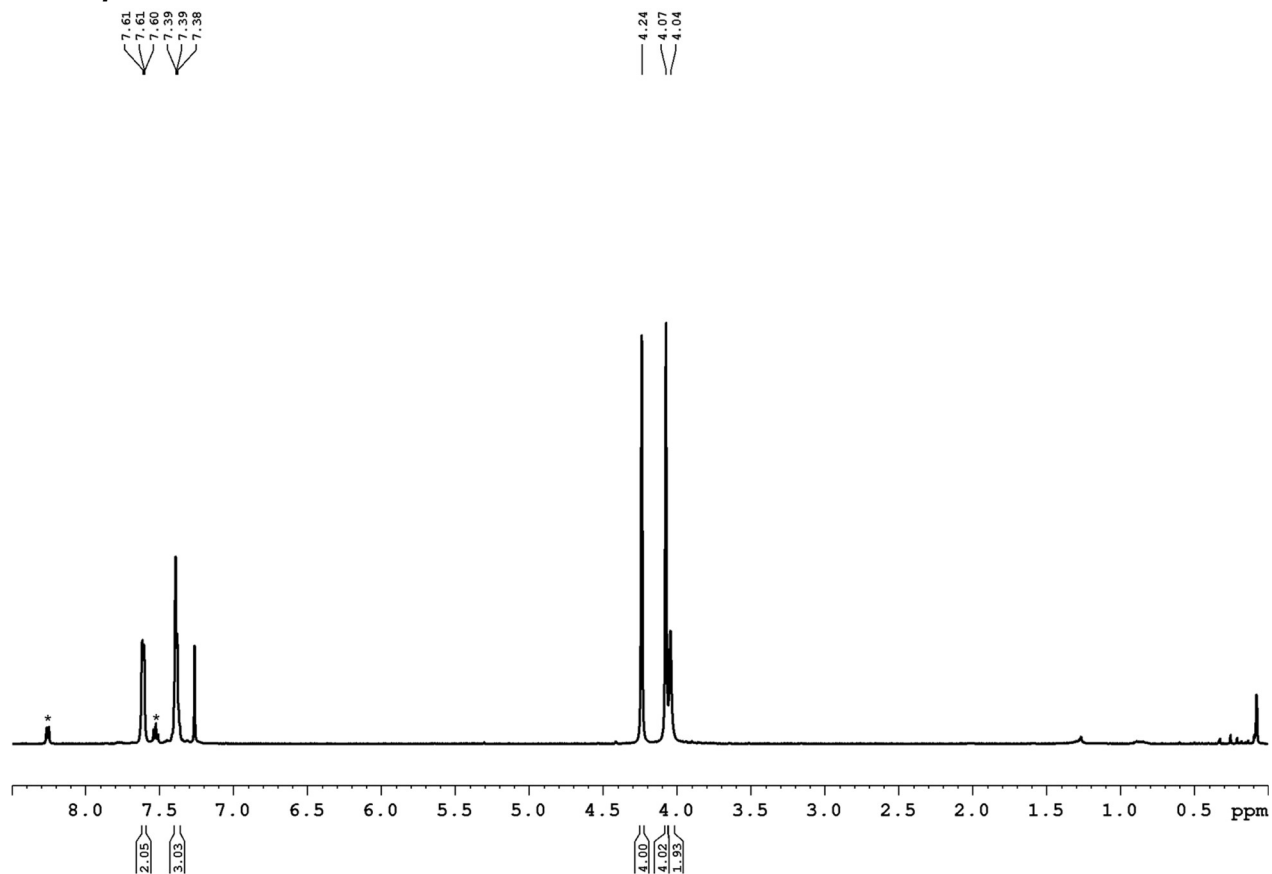


Figure S1.  $^1\text{H}$  NMR spectrum of  $2^{\text{Ph}}$  (500 MHz, in  $\text{CDCl}_3$ ); \* = impurity ( $\text{PhBBr}_2$ ).

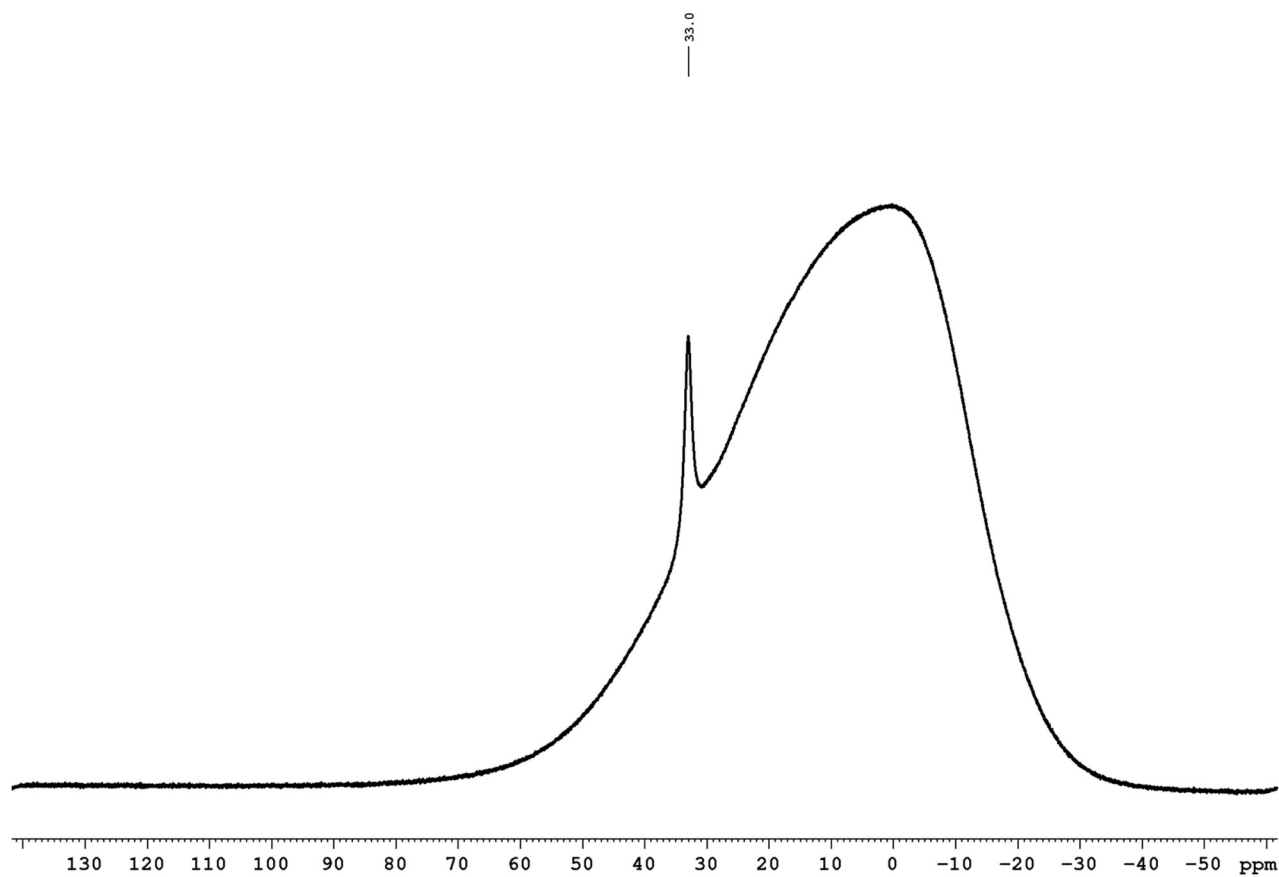


Figure S2.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $2^{\text{Ph}}$  (160 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

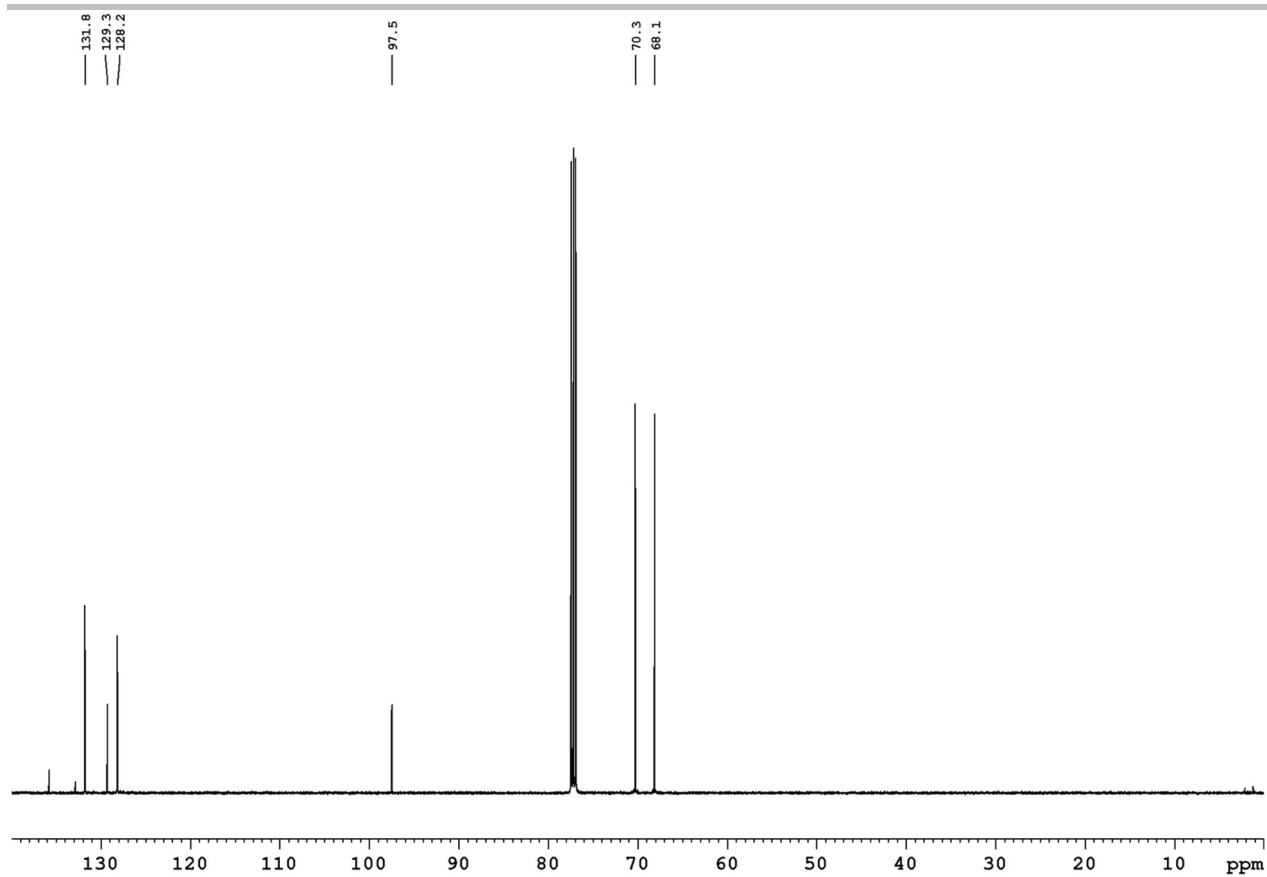


Figure S3.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2<sup>Ph</sup>** (125 MHz, in  $\text{CDCl}_3$ ).

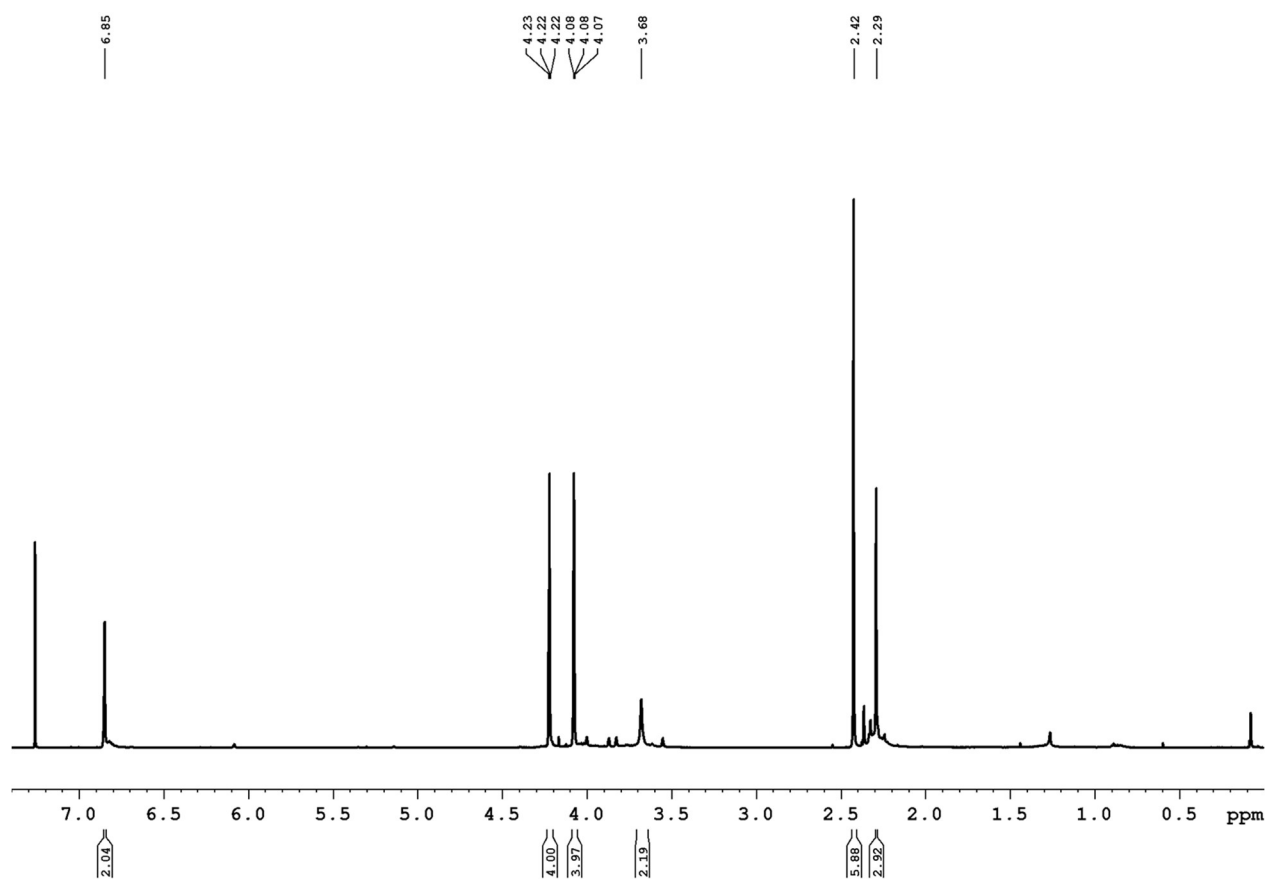


Figure S4.  $^1\text{H}$  NMR spectrum of **2<sup>Mes</sup>** (500 MHz, in  $\text{CDCl}_3$ ).



# SUPPORTING INFORMATION

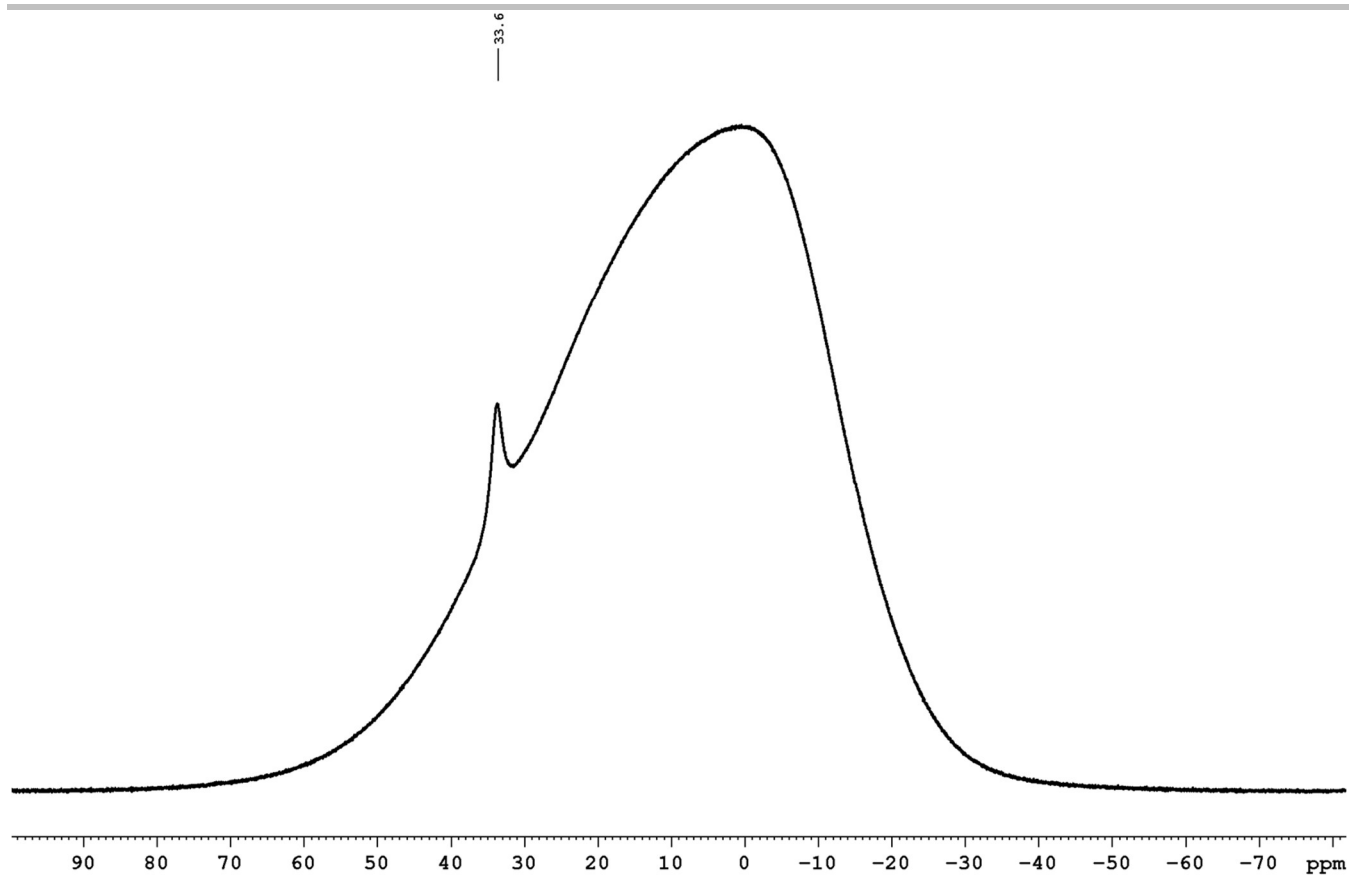


Figure S5.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $2^{\text{Mes}}$  (160 MHz, in  $\text{CDCl}_3$ ).

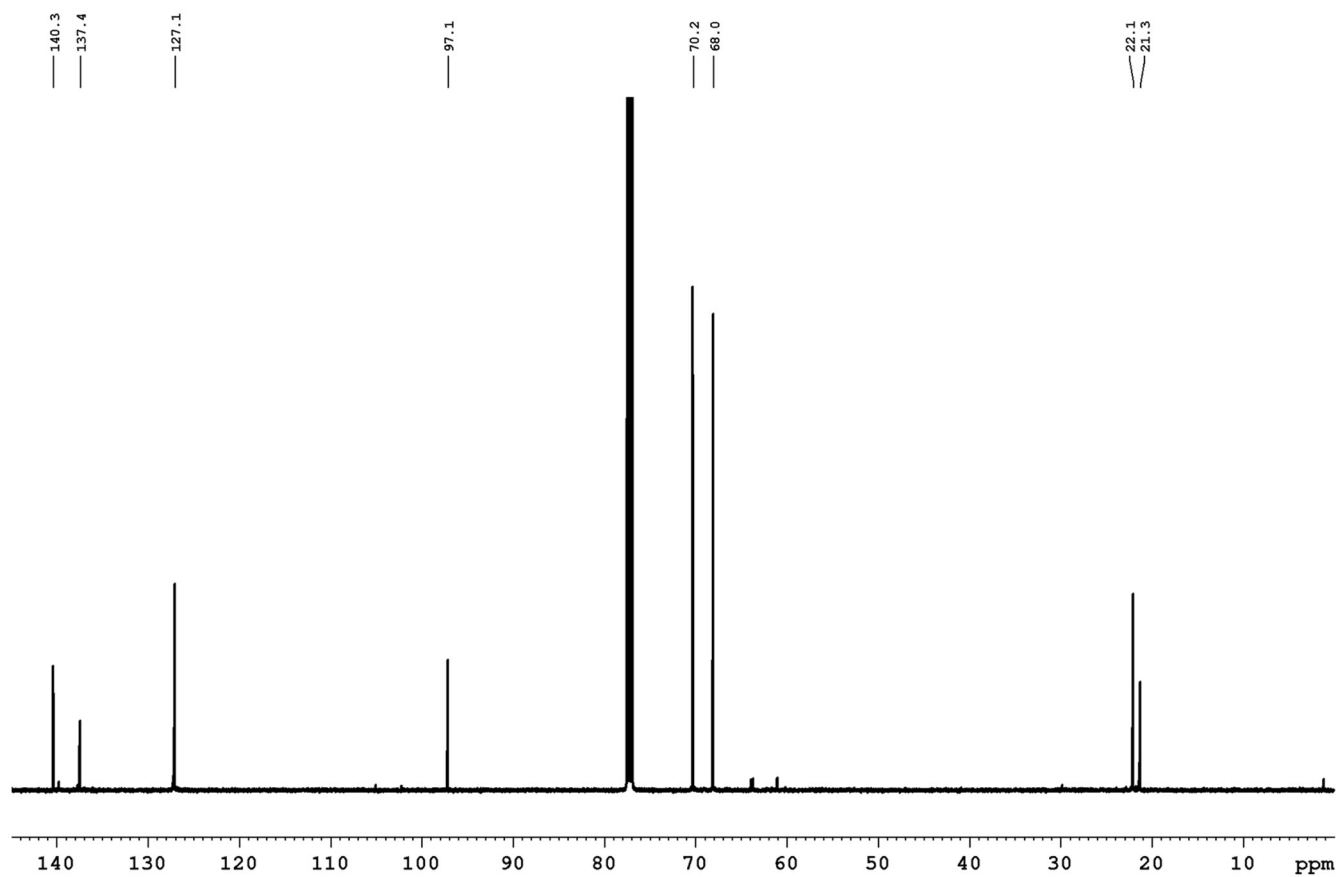


Figure S6.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $2^{\text{Mes}}$  (125 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

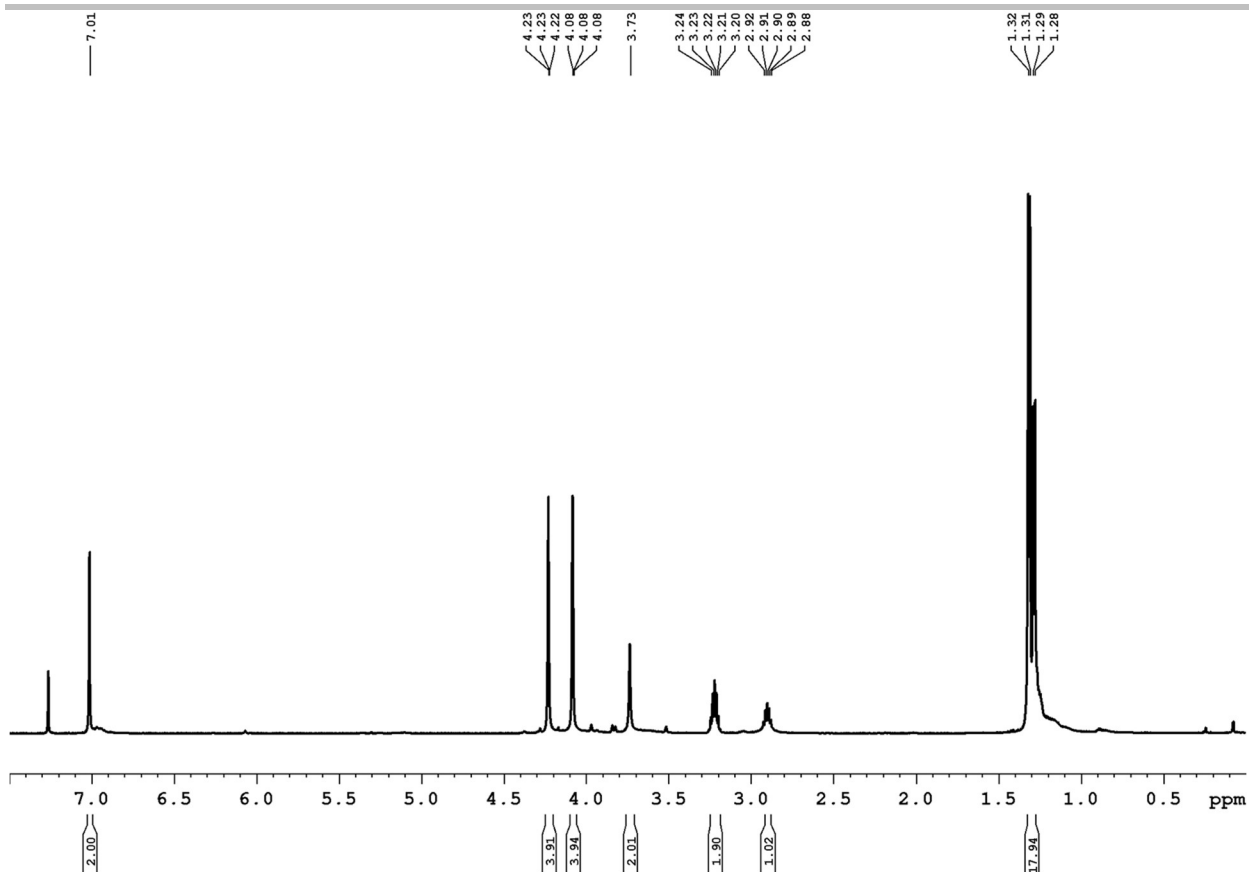


Figure S7.  $^1\text{H}$  NMR spectrum of  $2^{\text{TIP}}$  (600 MHz, in  $\text{CDCl}_3$ ).

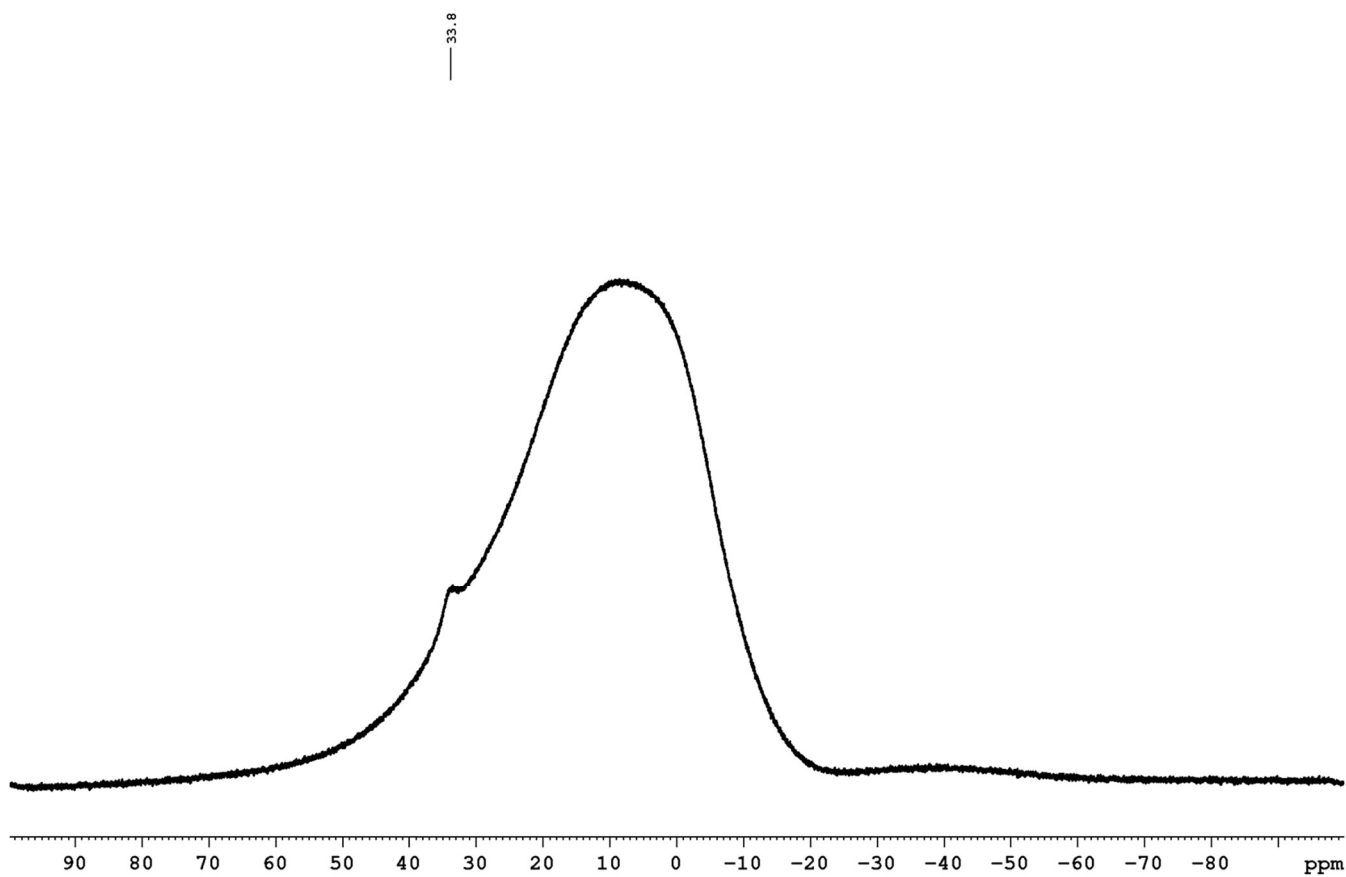


Figure S8.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $2^{\text{TIP}}$  (193 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

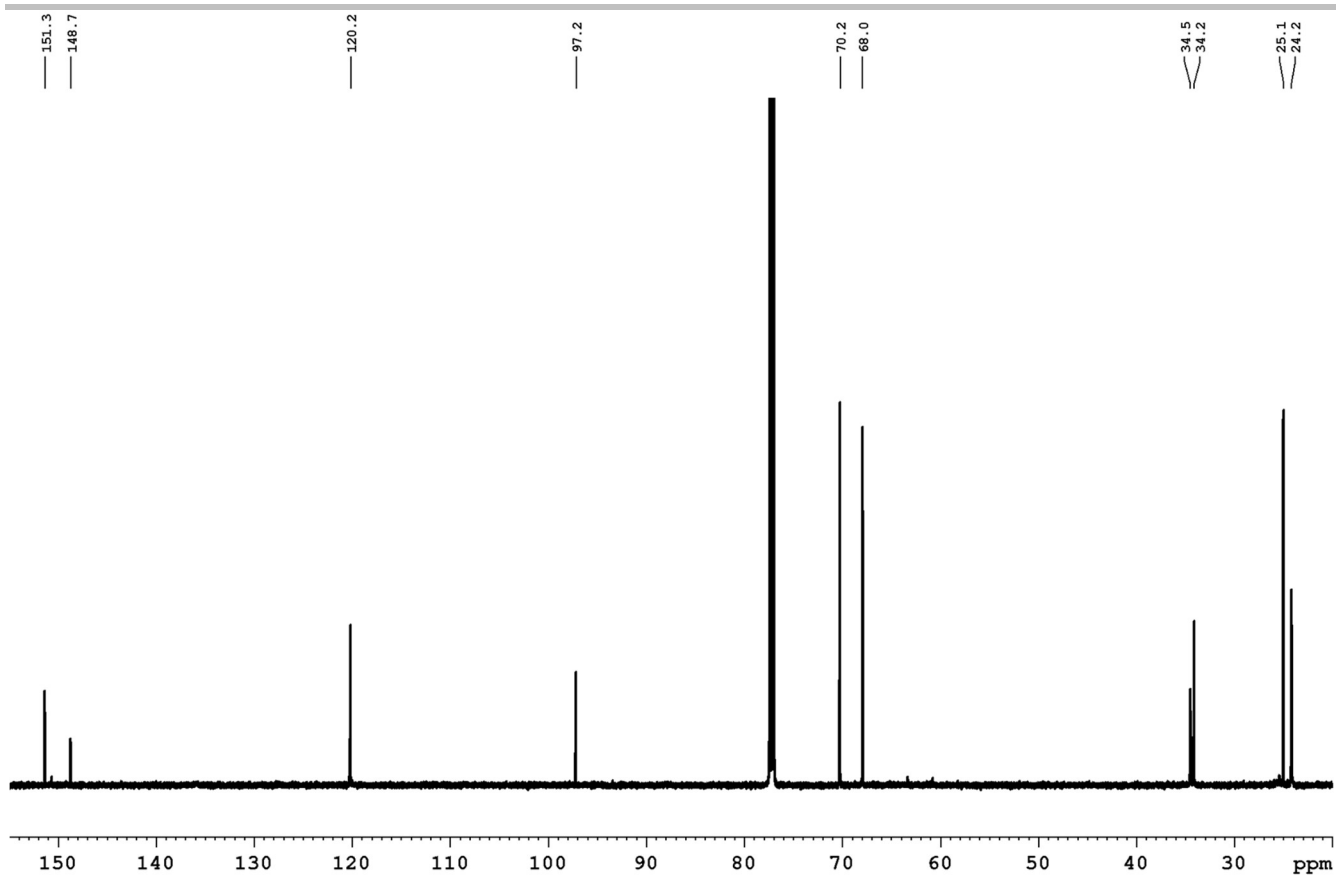


Figure S9.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $2^{\text{TIP}}$  (151 MHz, in  $\text{CDCl}_3$ ).

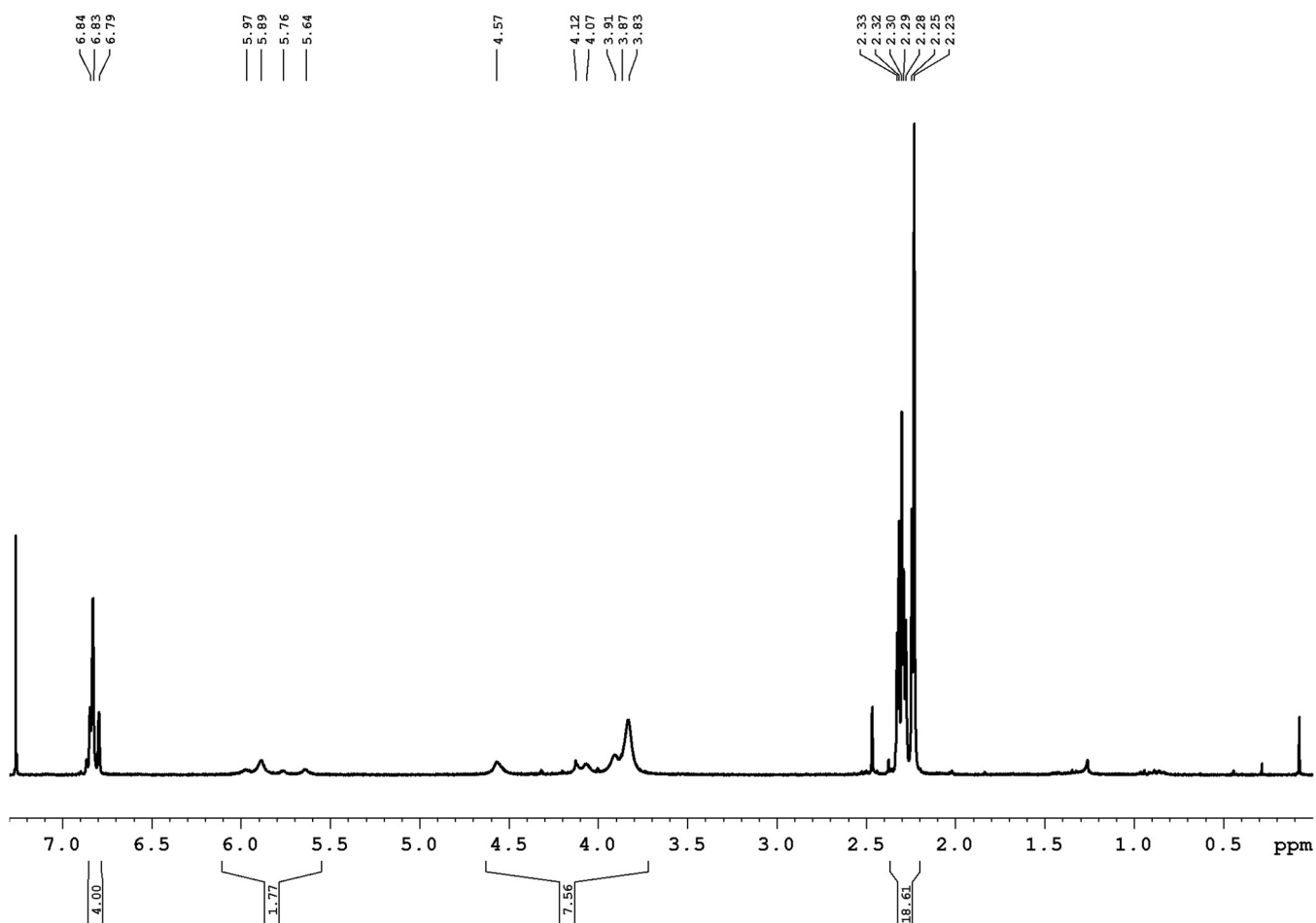


Figure S10.  $^1\text{H}$  NMR spectrum of  $3^{\text{Mes}}$  (300 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

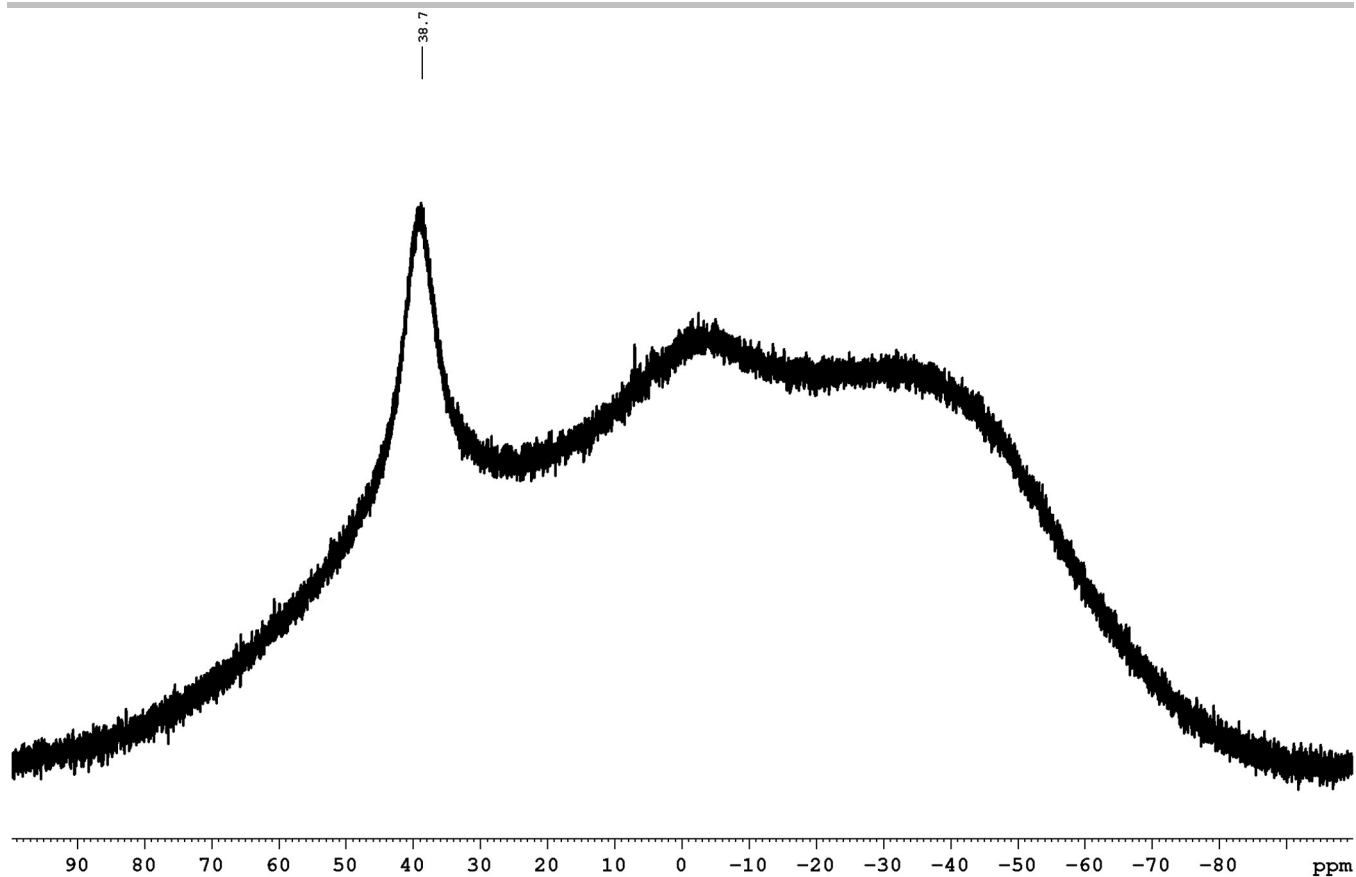


Figure S11.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $3^{\text{Mes}}$  (96 MHz, in  $\text{CDCl}_3$ ).

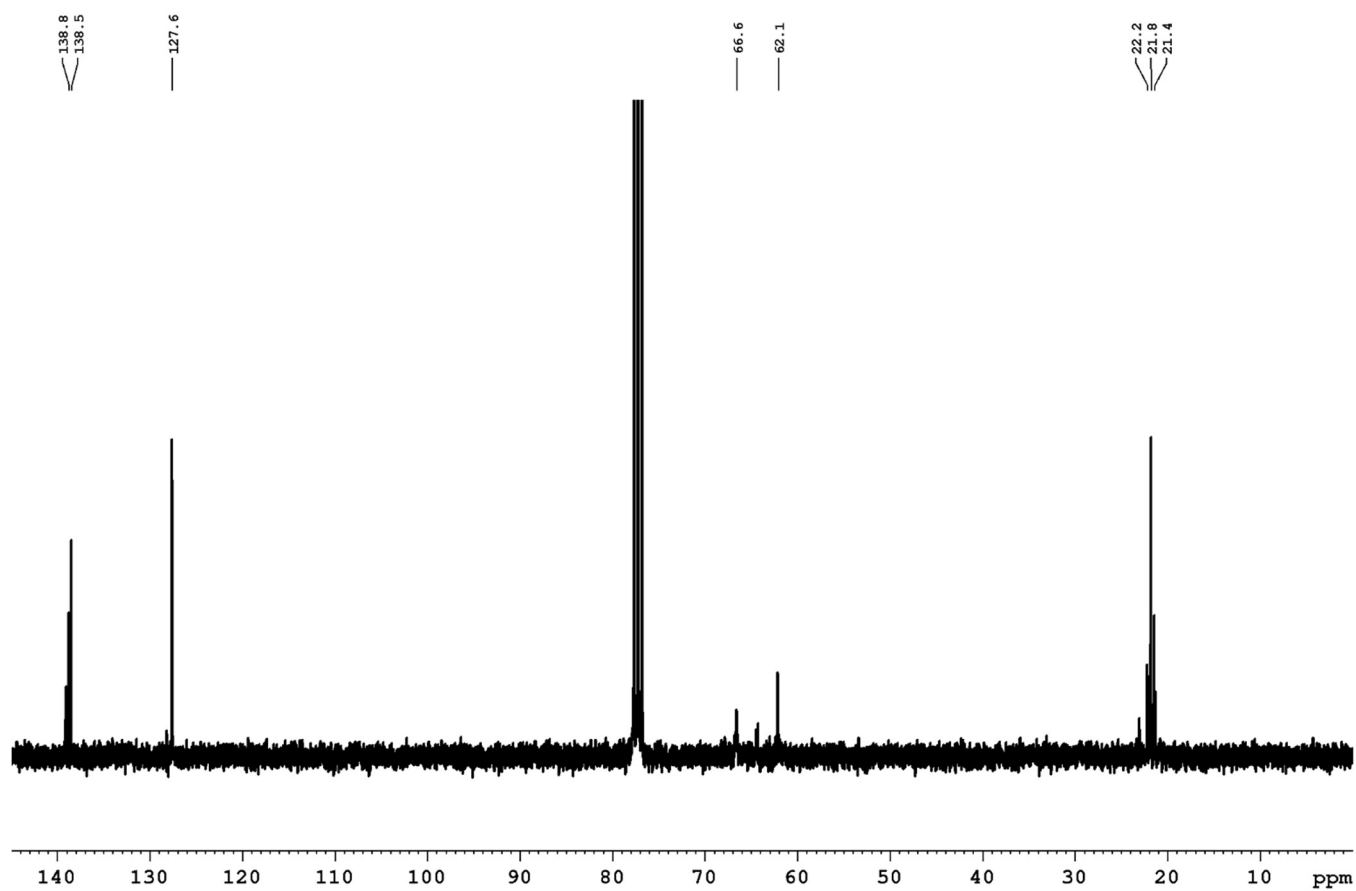


Figure S12.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $3^{\text{Mes}}$  (76 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

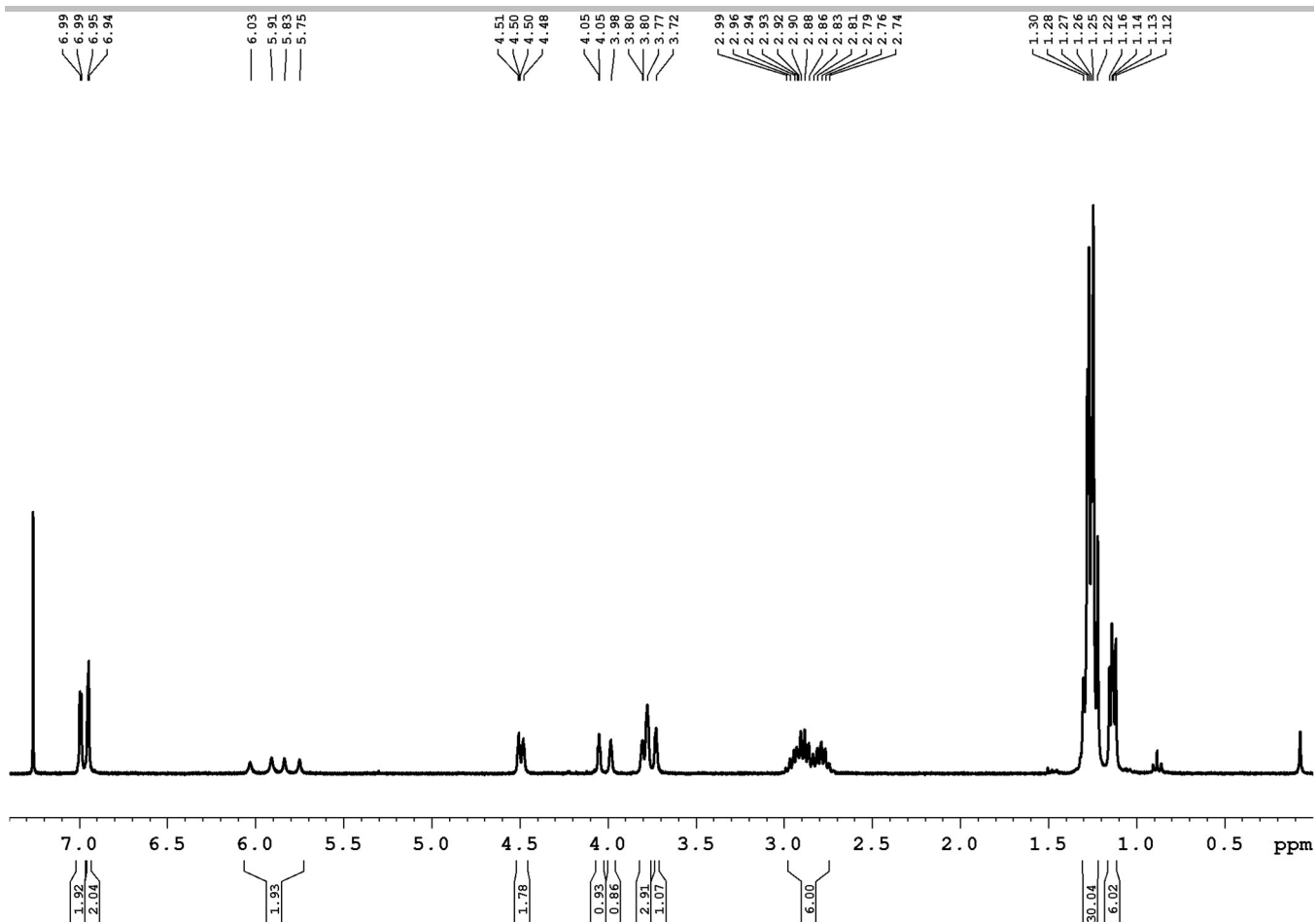


Figure S13.  $^1\text{H}$  NMR spectrum of  $3^{\text{TP}}$  (300 MHz, in  $\text{CDCl}_3$ ).

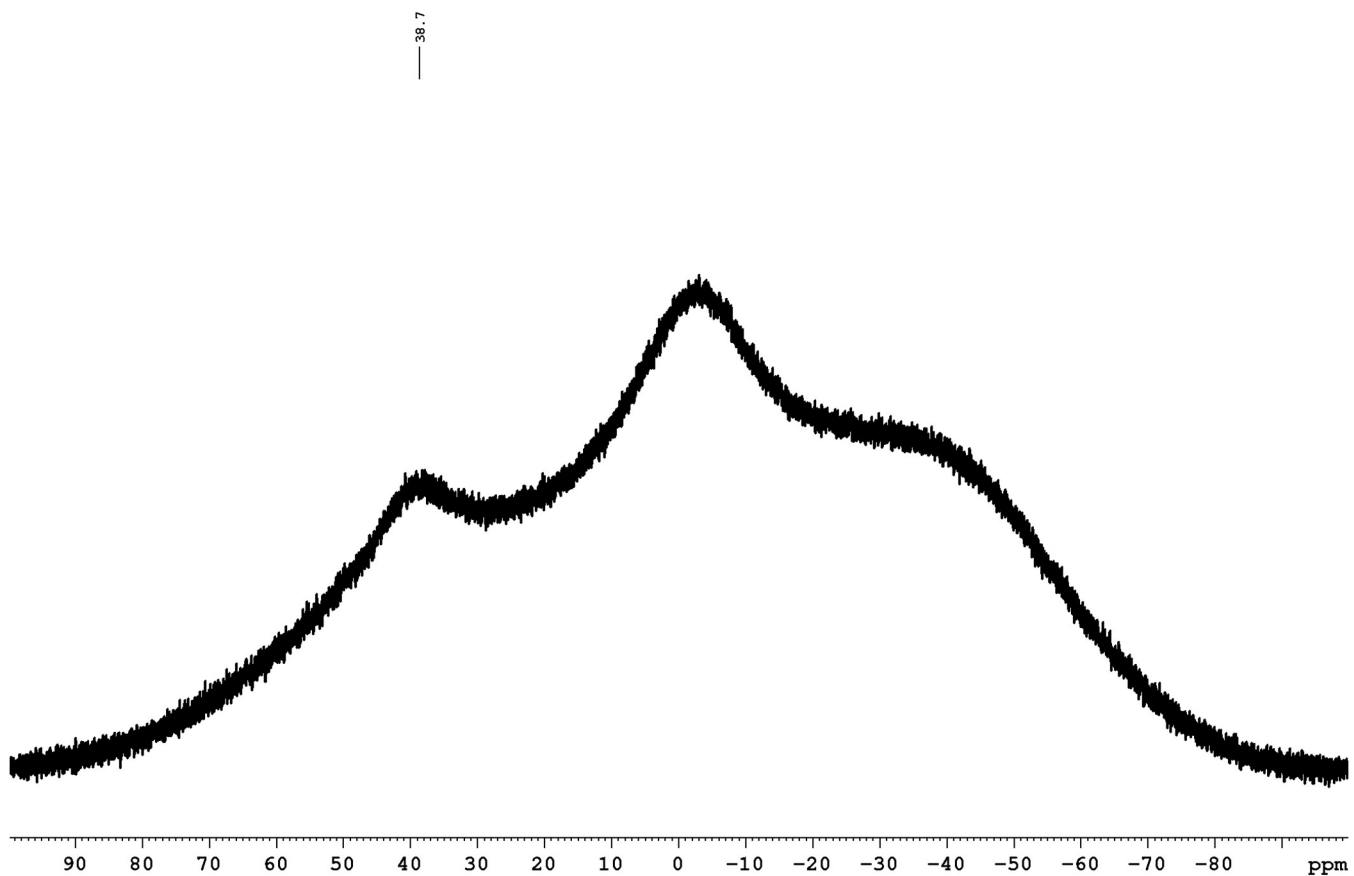


Figure S14.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $3^{\text{TP}}$  (96 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

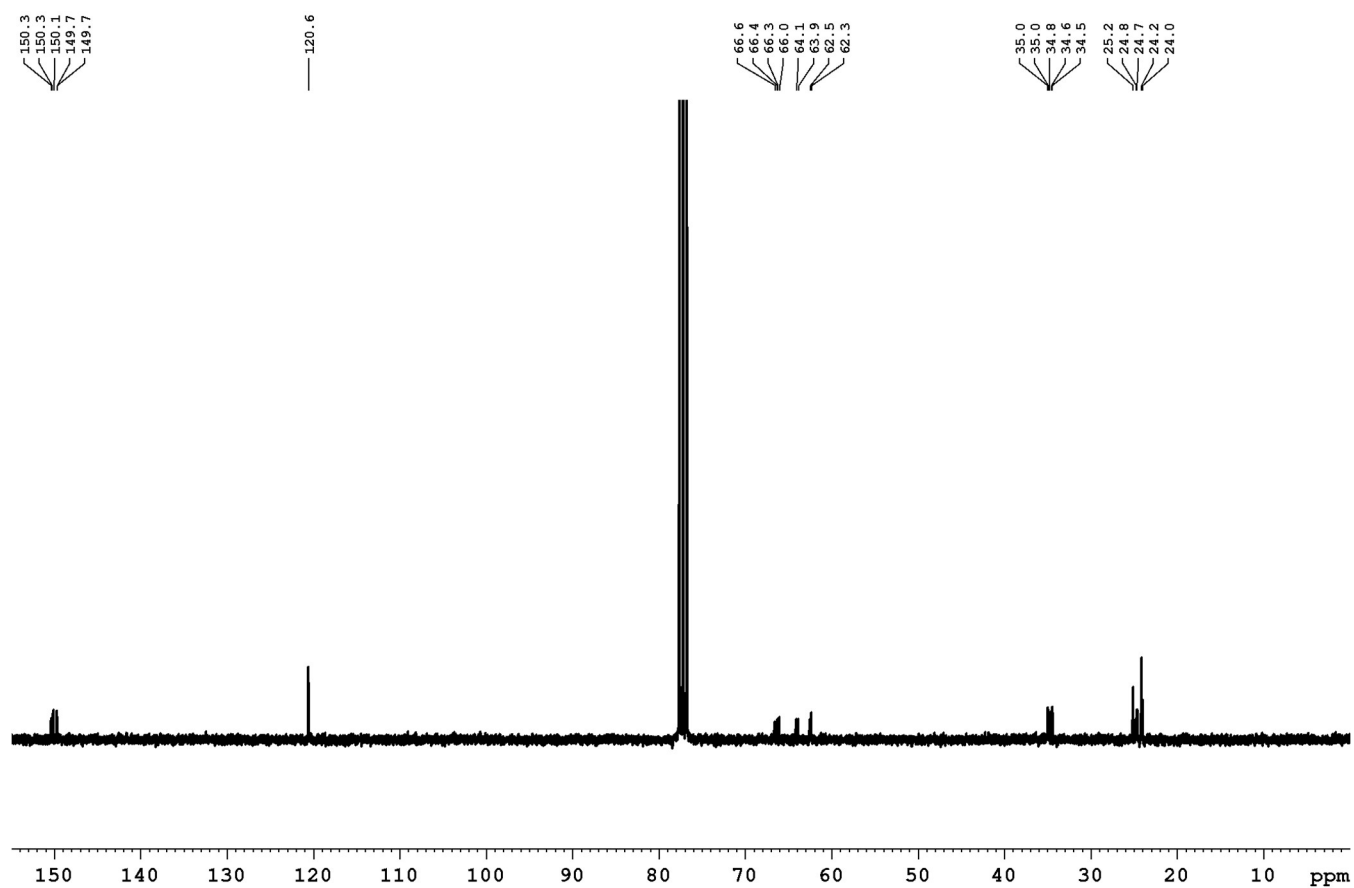


Figure S15.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $3^{\text{TPp}}$  (76 MHz, in  $\text{CDCl}_3$ ).

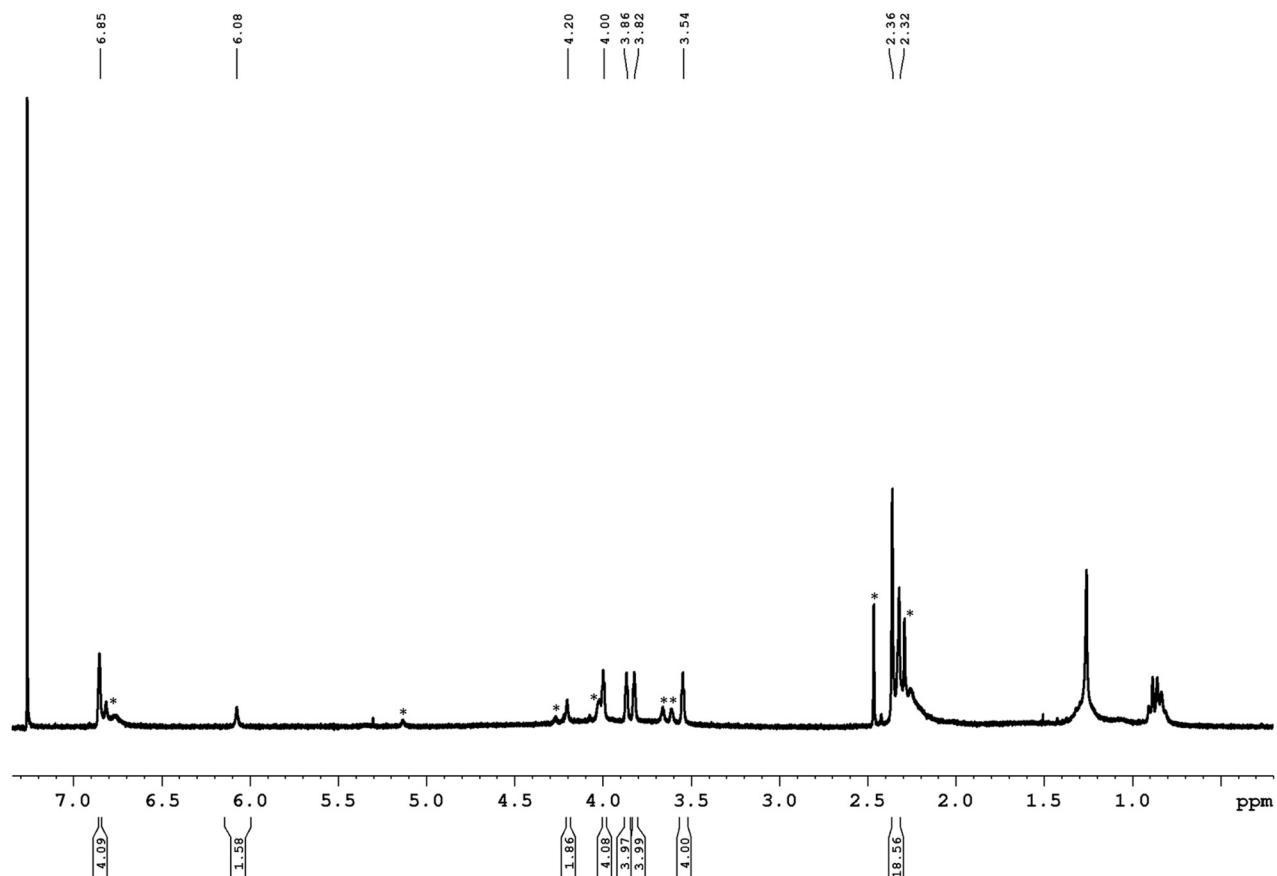


Figure S16.  $^1\text{H}$  NMR spectrum of  $4^{\text{Mes}}$  (300 MHz, in  $\text{CDCl}_3$ ); \* = other ferrocenophane species.

# SUPPORTING INFORMATION

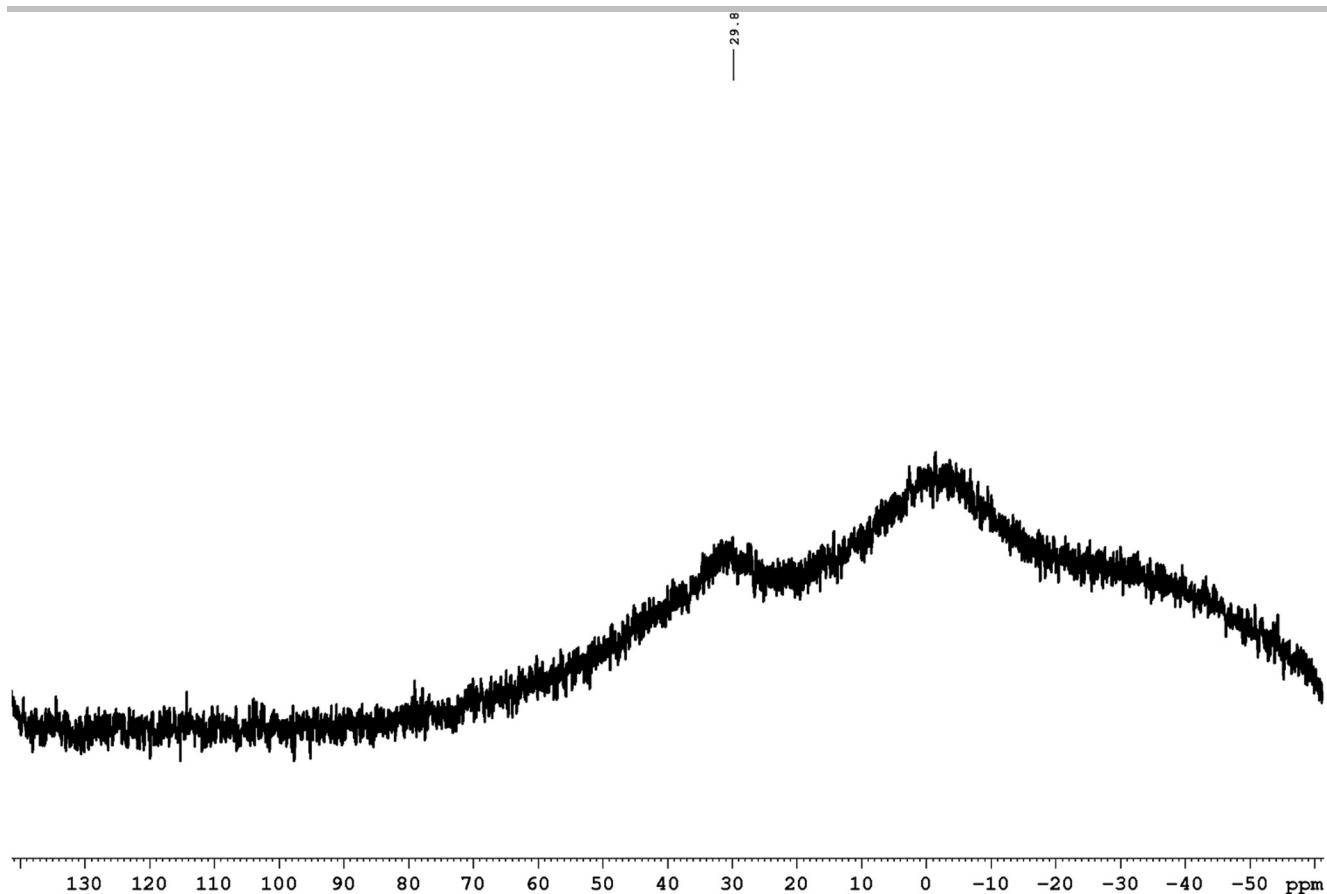


Figure S17.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $4^{\text{Mes}}$  (96 MHz, in  $\text{CDCl}_3$ ).

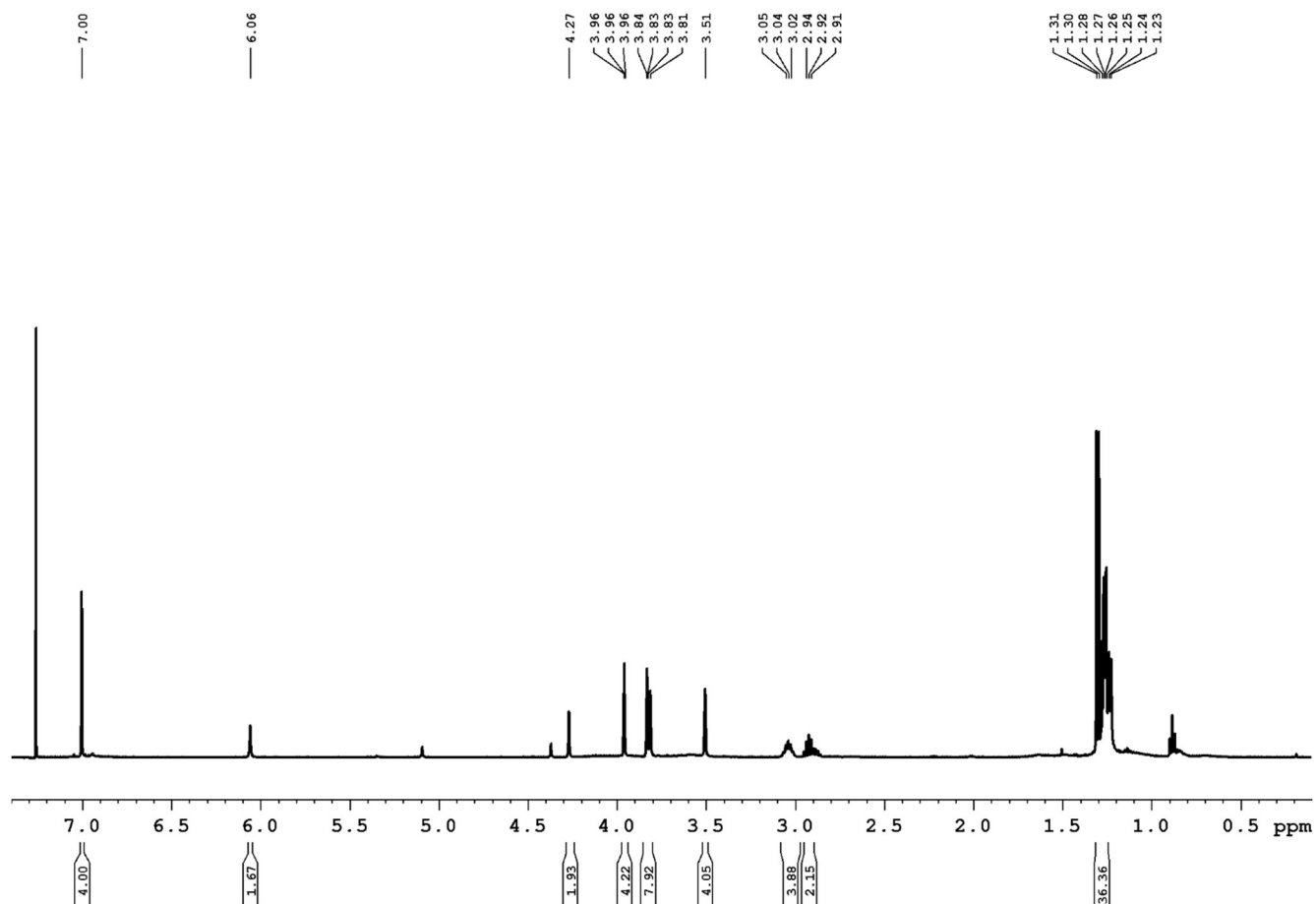


Figure S18.  $^1\text{H}$  NMR spectrum of  $4^{\text{TP}}$  (600 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

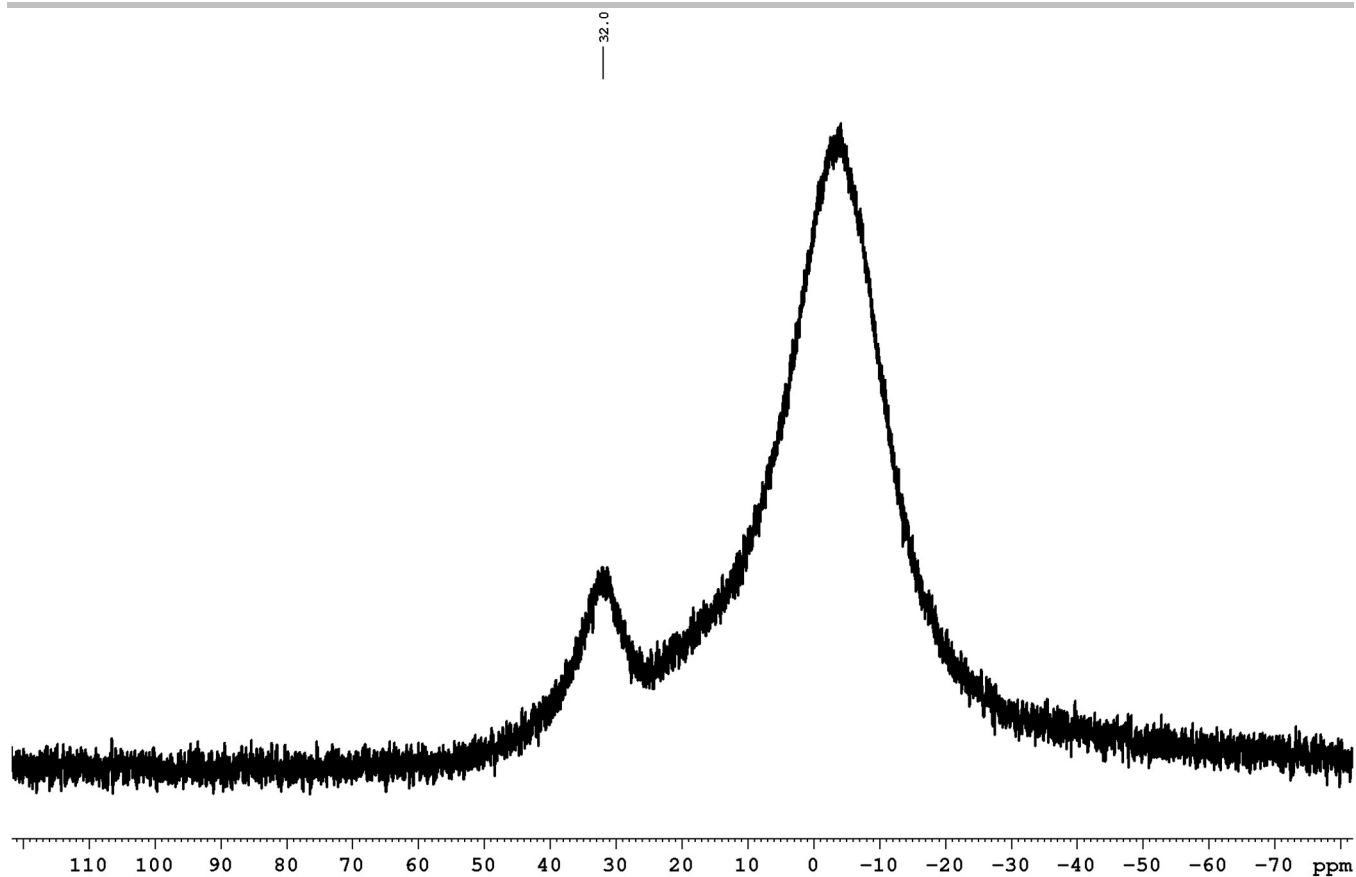


Figure S19.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $4^{\text{TIP}}$  (160 MHz, in  $\text{CDCl}_3$ ).

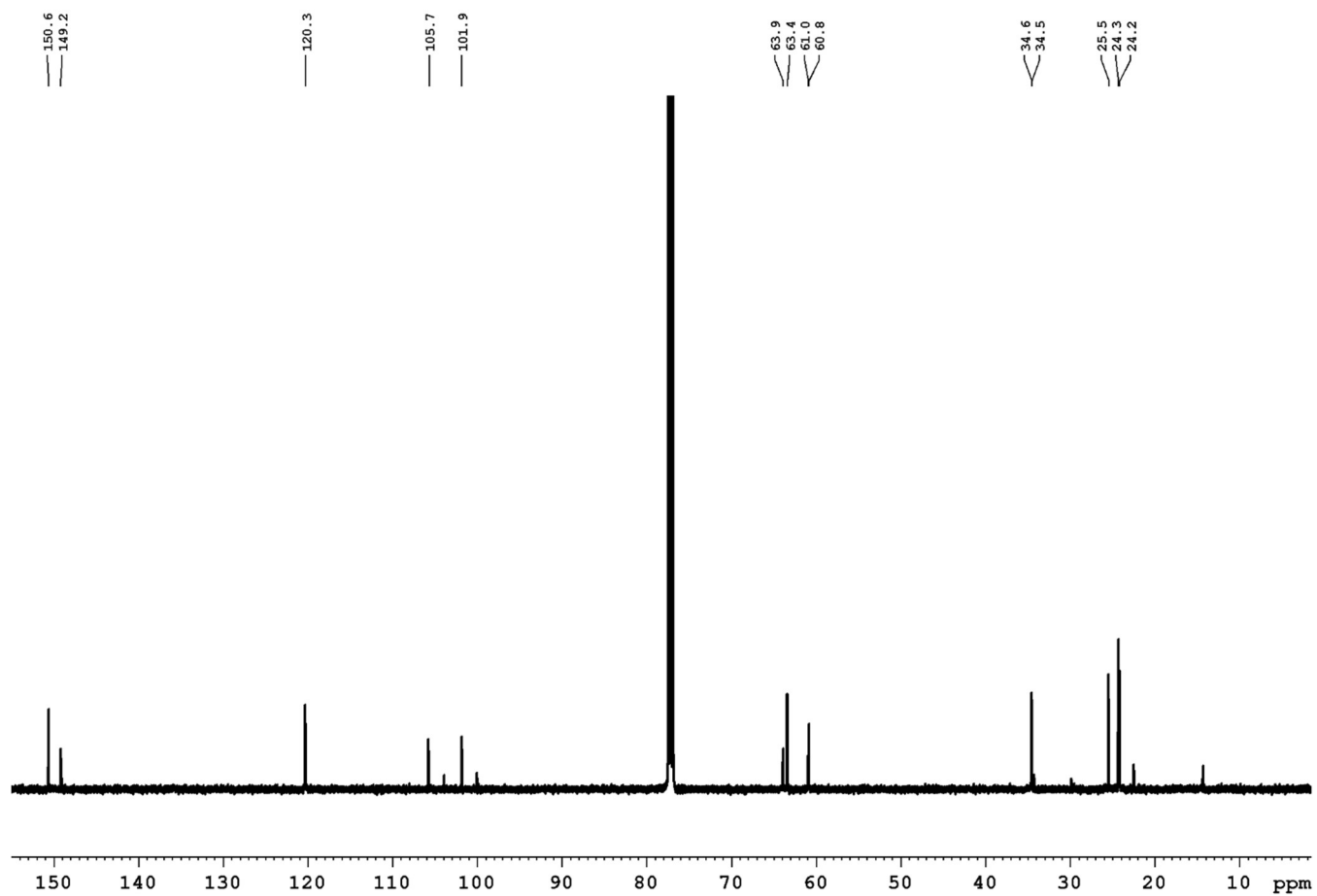


Figure S20.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $4^{\text{TIP}}$  (125 MHz, in  $\text{CDCl}_3$ ).



# SUPPORTING INFORMATION

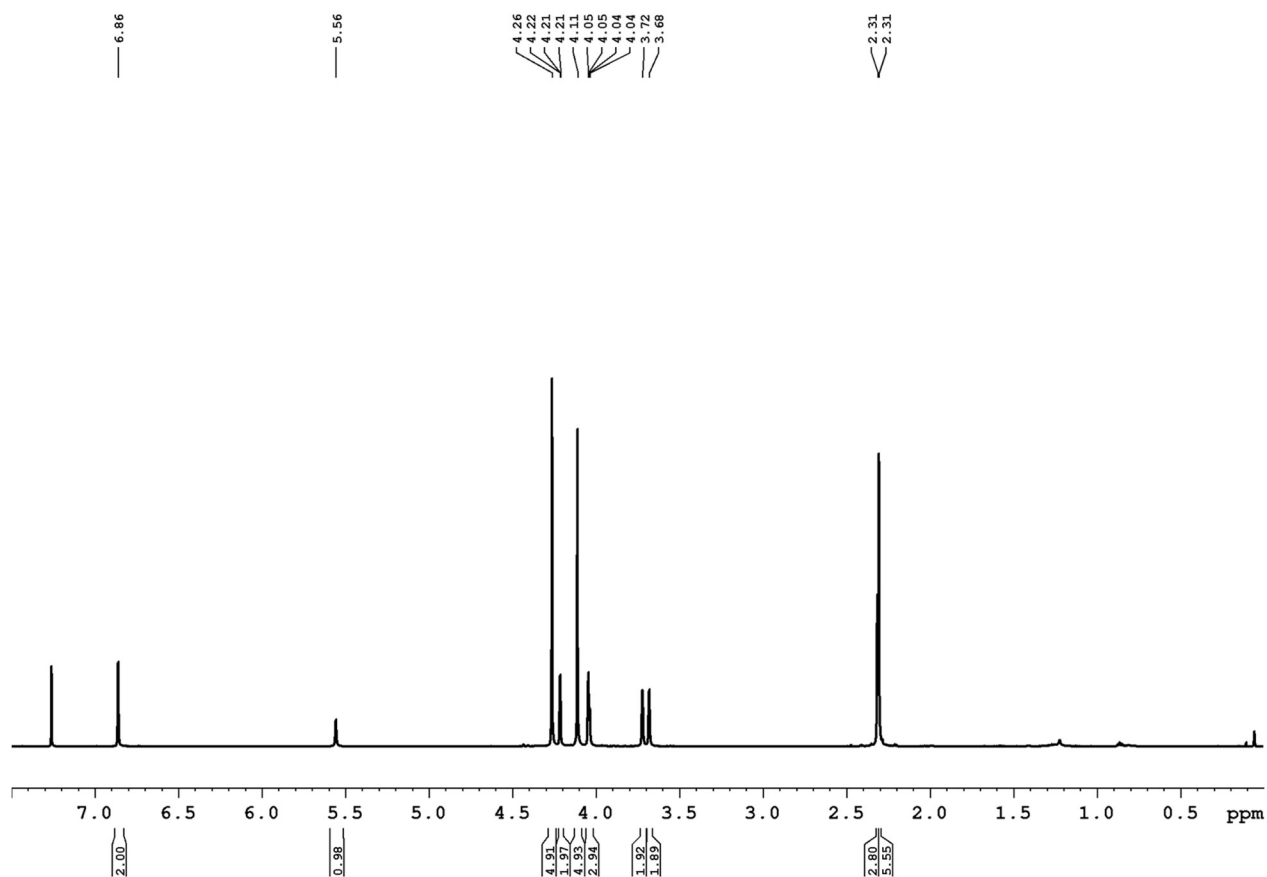


Figure S21.  $^1\text{H}$  NMR spectrum of  $7^{\text{Mes}}$  (600 MHz, in  $\text{CDCl}_3$ , at  $-30^\circ\text{C}$ ).

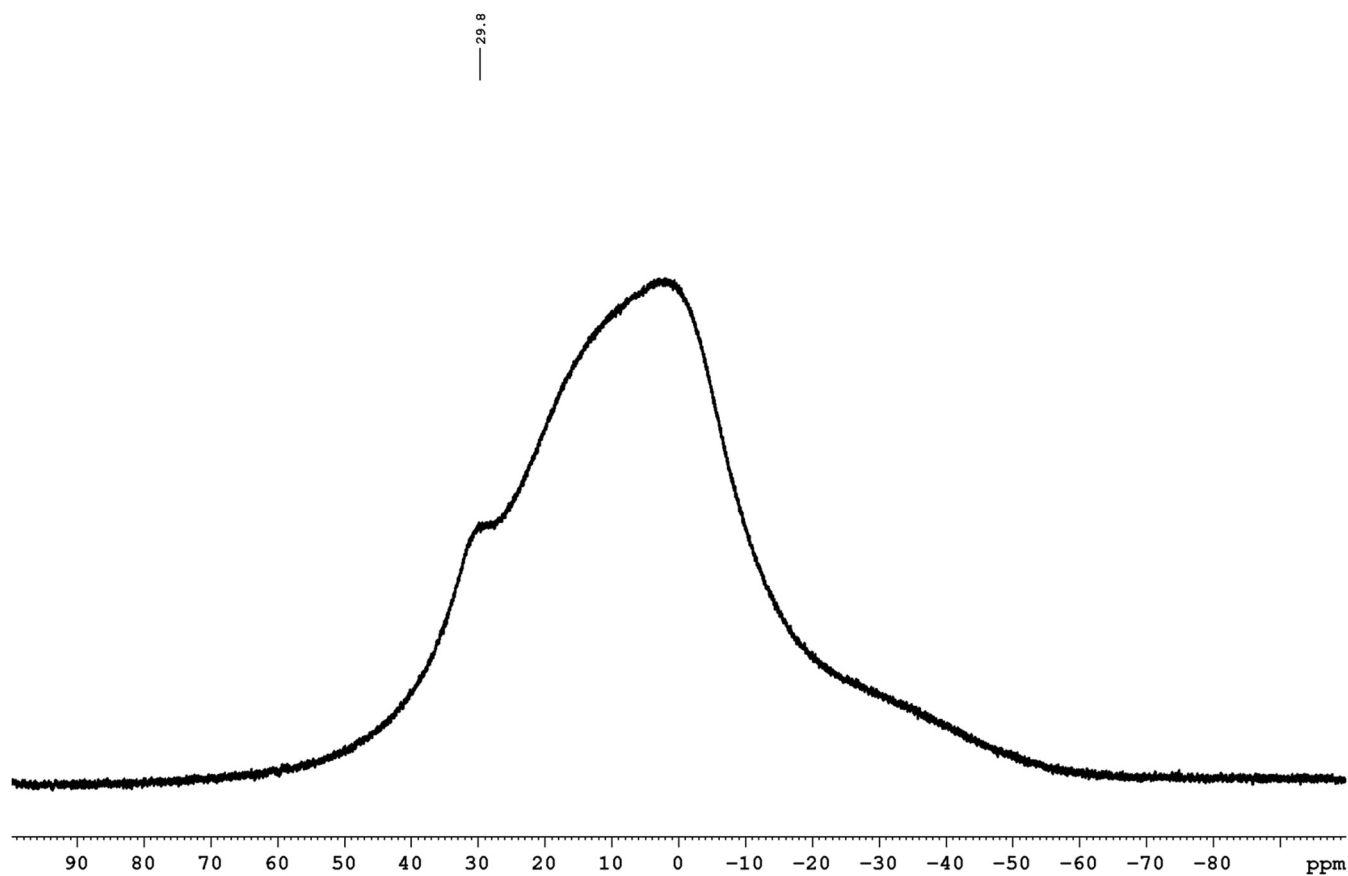


Figure S22.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $7^{\text{Mes}}$  (190 MHz, in  $\text{CDCl}_3$ , at  $-30^\circ\text{C}$ ).

# SUPPORTING INFORMATION

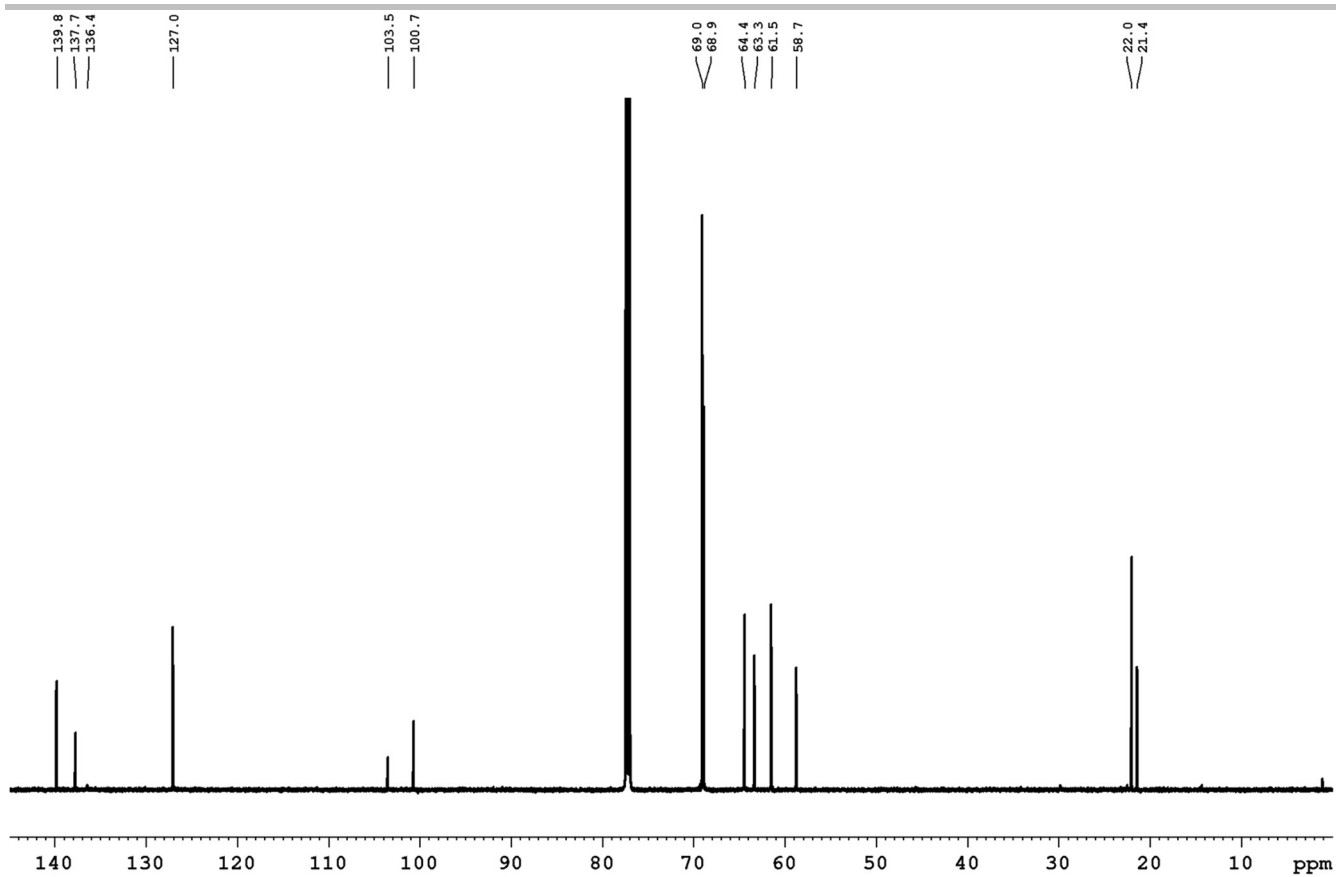


Figure S23.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $7^{\text{Mes}}$  (150 MHz, in  $\text{CDCl}_3$ , at  $-30^\circ\text{C}$ ).

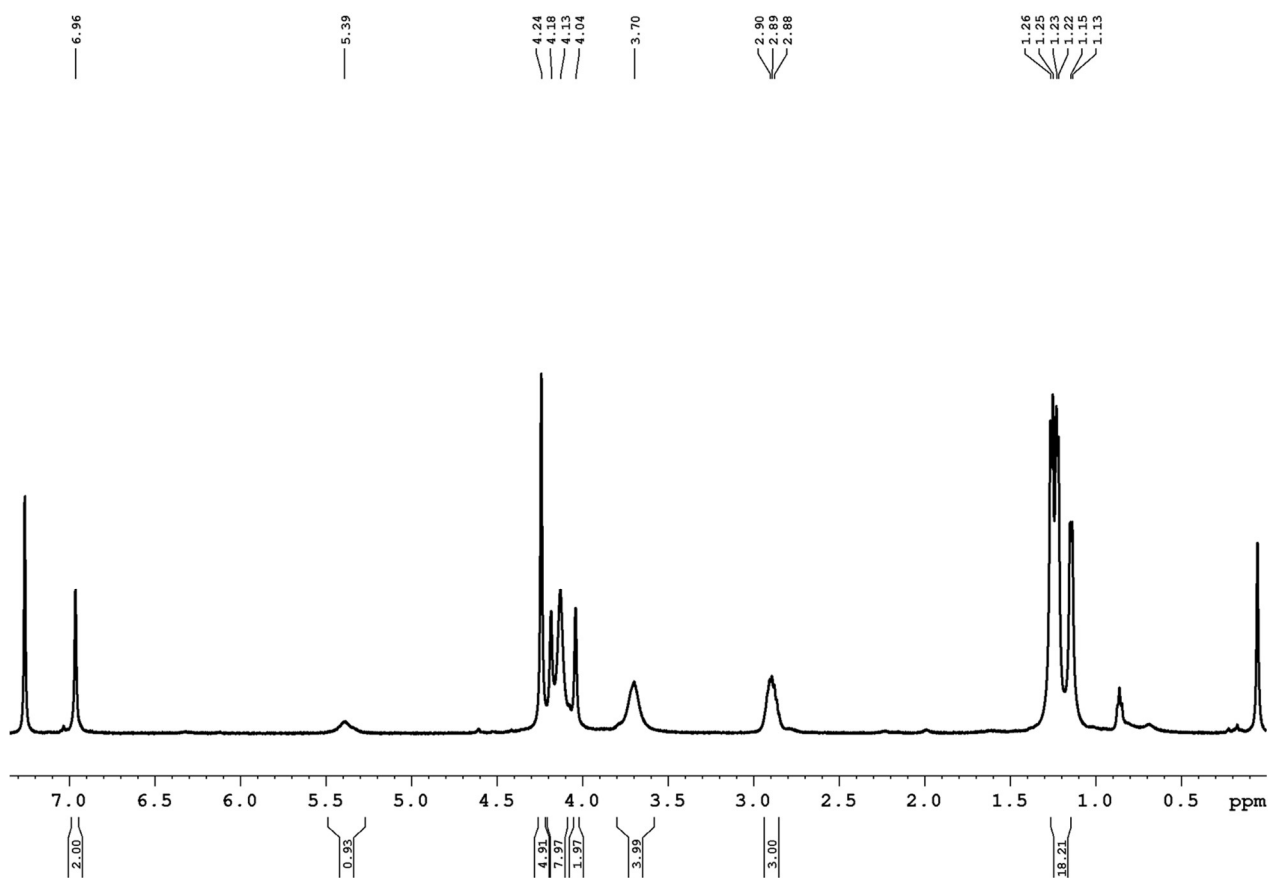


Figure S24.  $^1\text{H}$  NMR spectrum of  $7^{\text{TIP}}$  (500 MHz, in  $\text{CDCl}_3$ , at  $-30^\circ\text{C}$ ).

# SUPPORTING INFORMATION

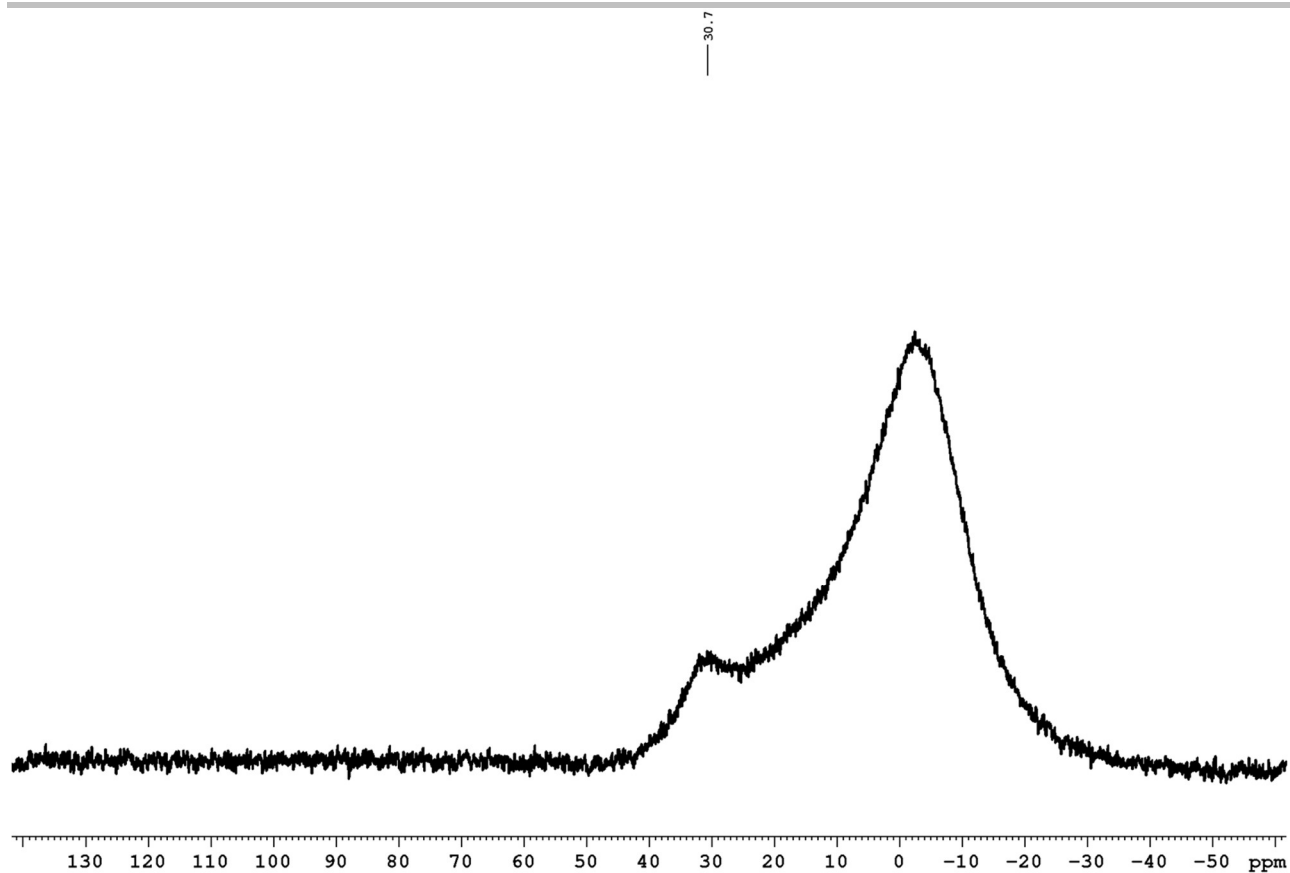


Figure S25.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $7^{\text{Tp}}$  (160 MHz, in  $\text{CDCl}_3$ , at  $-30^\circ\text{C}$ ).

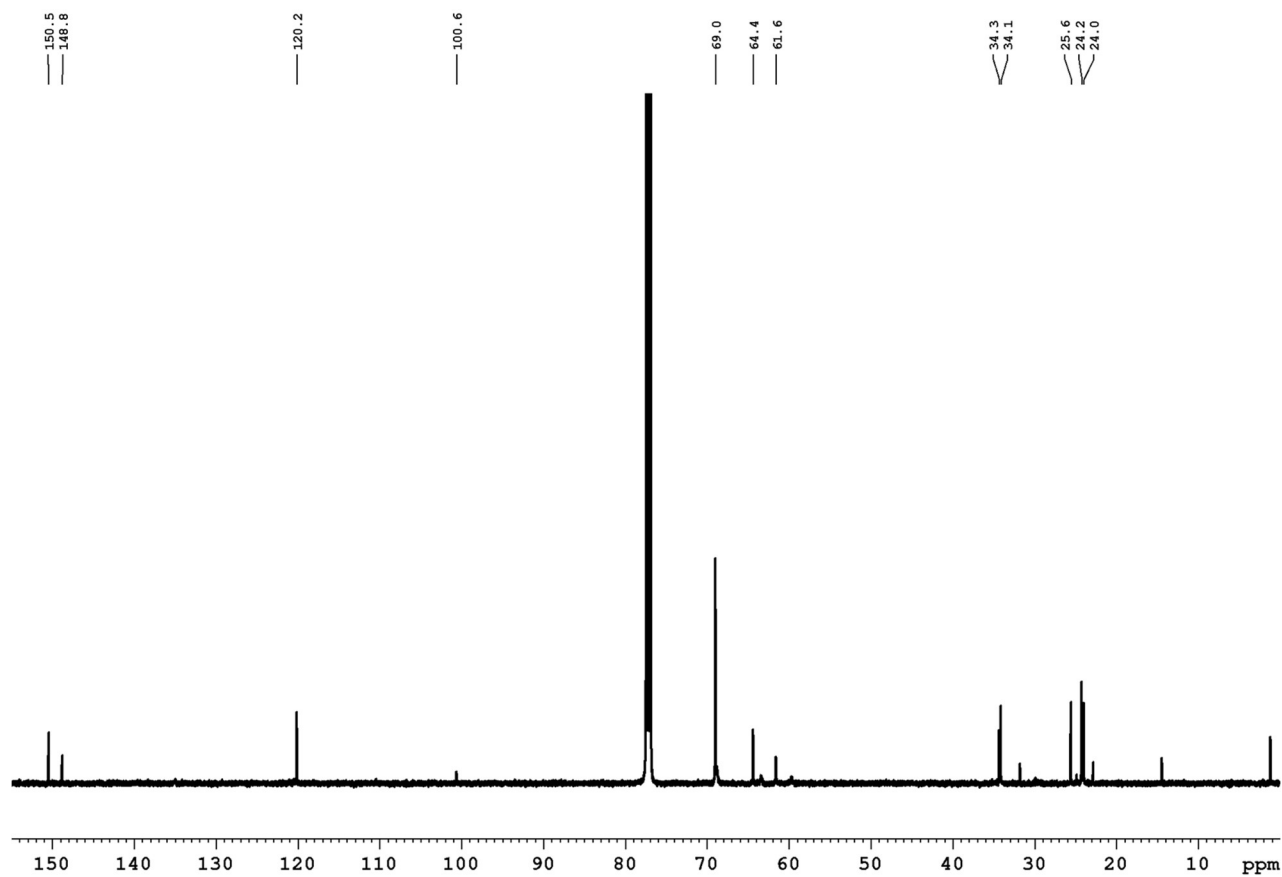


Figure S26.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $7^{\text{Tp}}$  (125 MHz, in  $\text{CDCl}_3$ , at  $-30^\circ\text{C}$ ).

# SUPPORTING INFORMATION

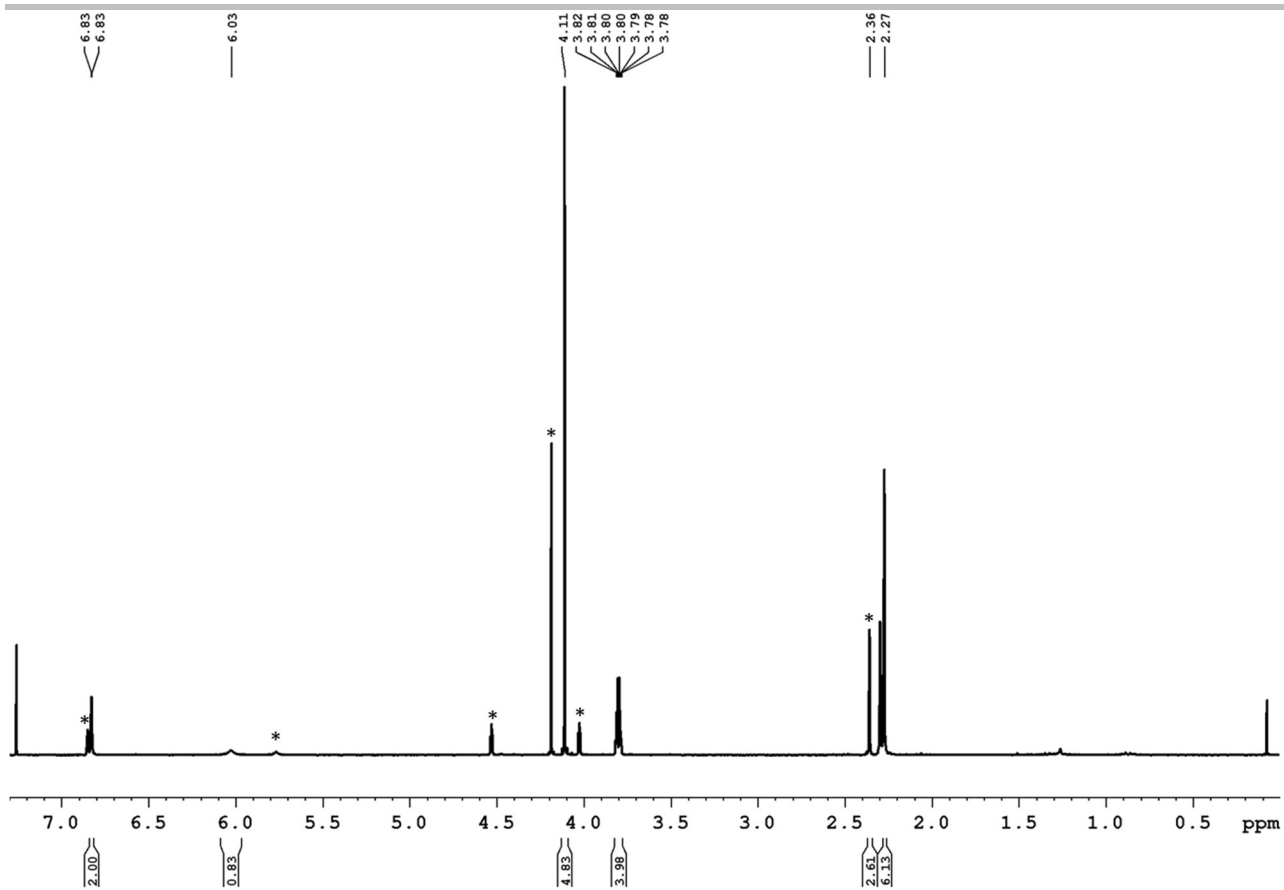


Figure S27.  $^1\text{H}$  NMR spectrum of  $8^{\text{Mes}}$  (300 MHz, in  $\text{CDCl}_3$ ); \* = minor isomer of the isomeric mixture.

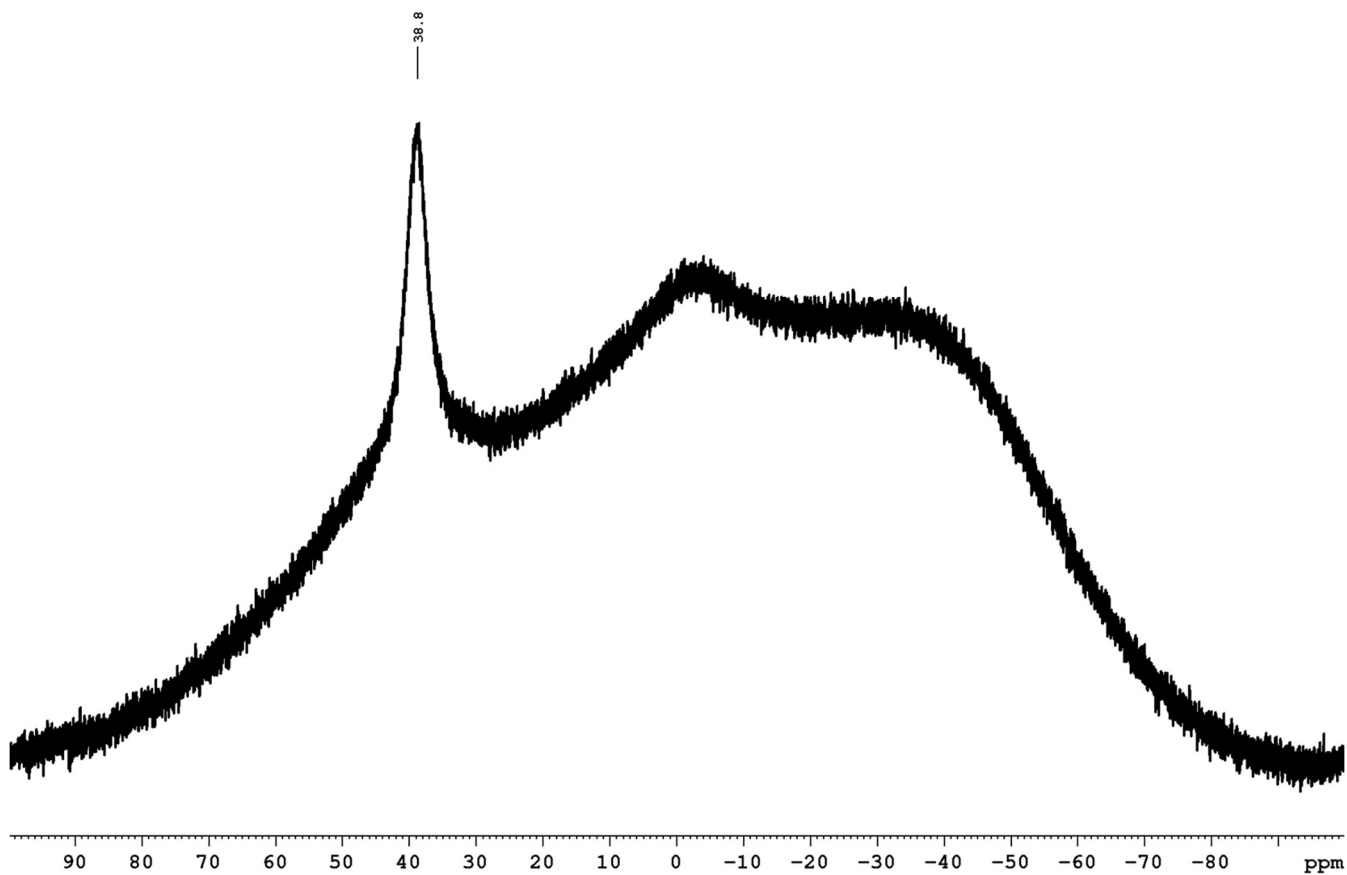


Figure S28.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $8^{\text{Mes}}$  (96 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

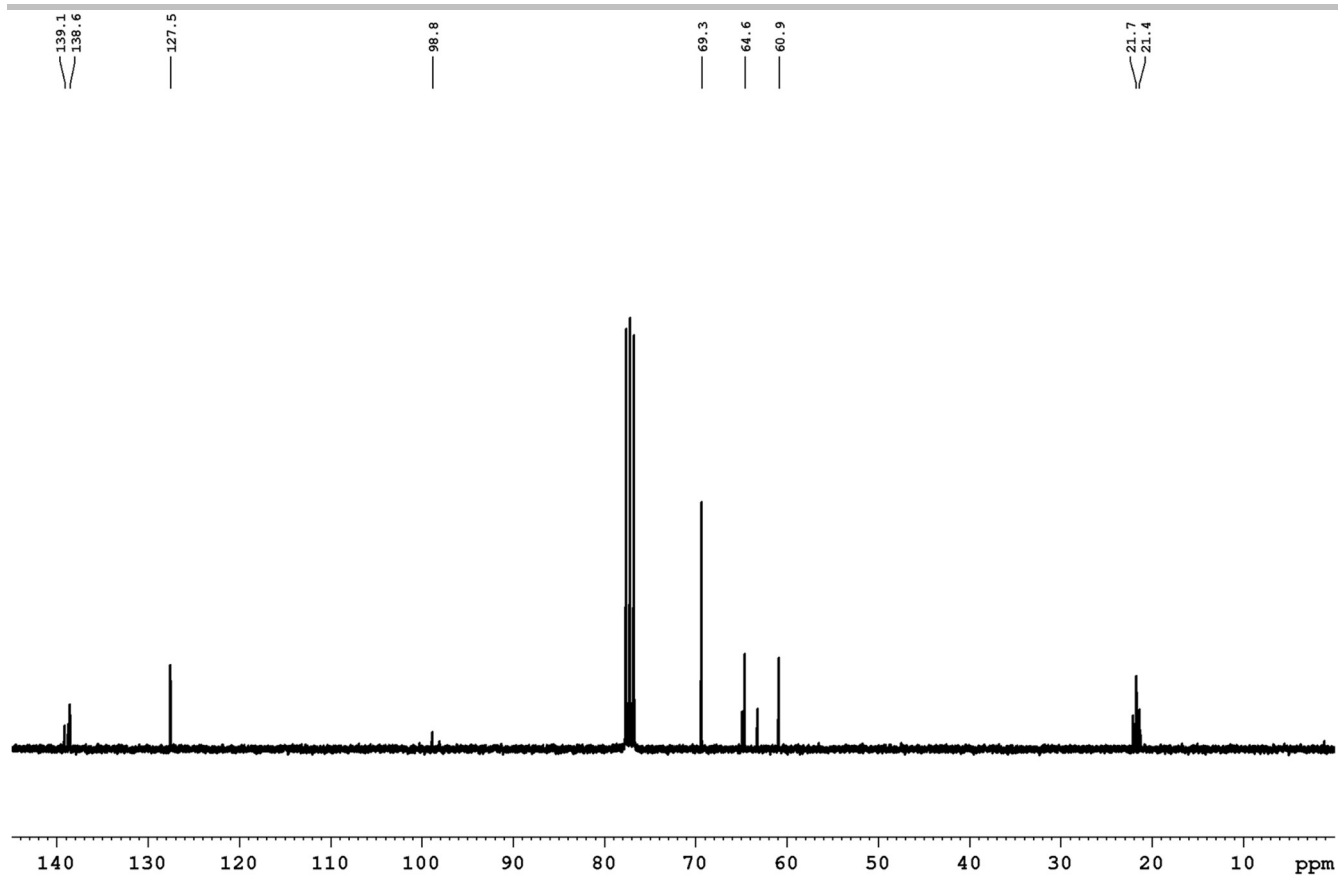


Figure S29.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $8^{\text{Mes}}$  (76 MHz, in  $\text{CDCl}_3$ ).

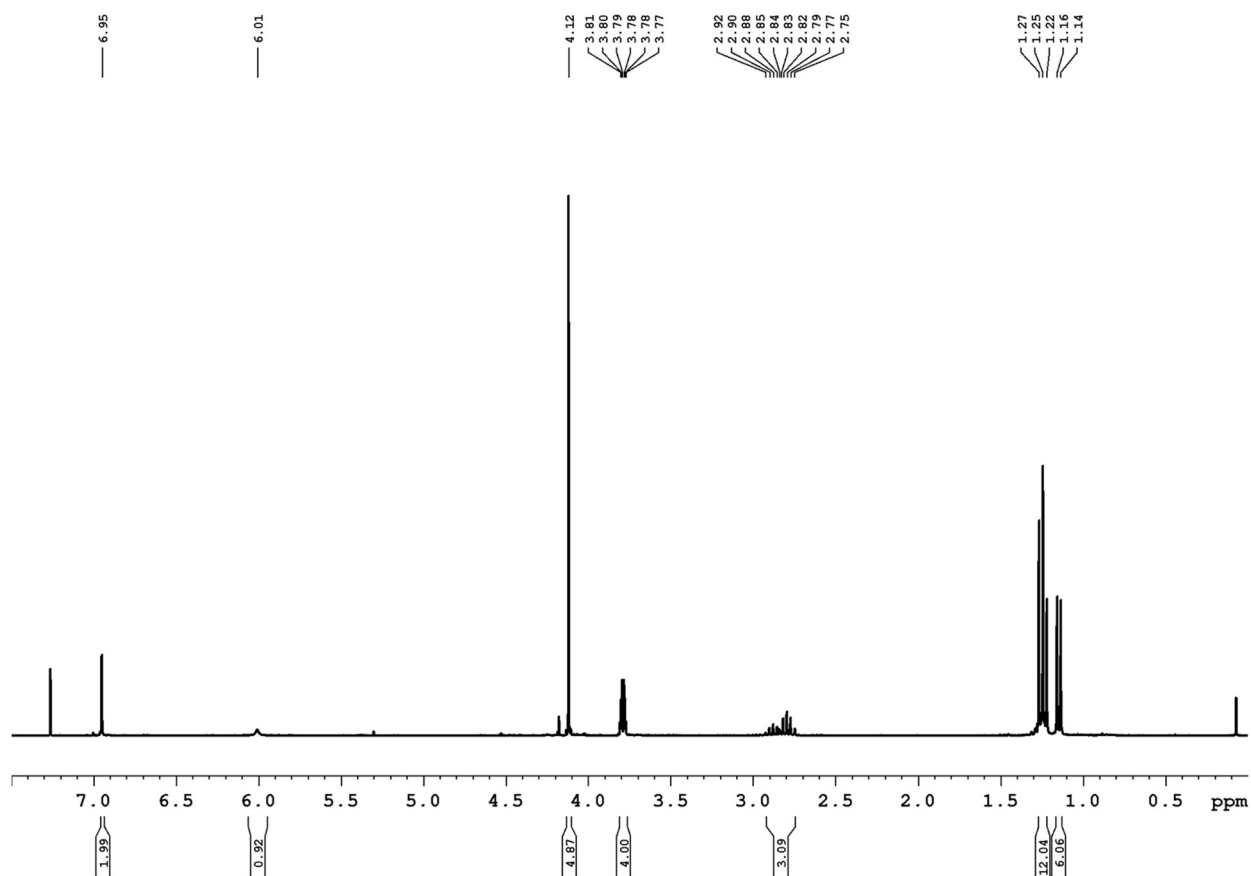


Figure S30.  $^1\text{H}$  NMR spectrum of  $8^{\text{TIP}}$  (300 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

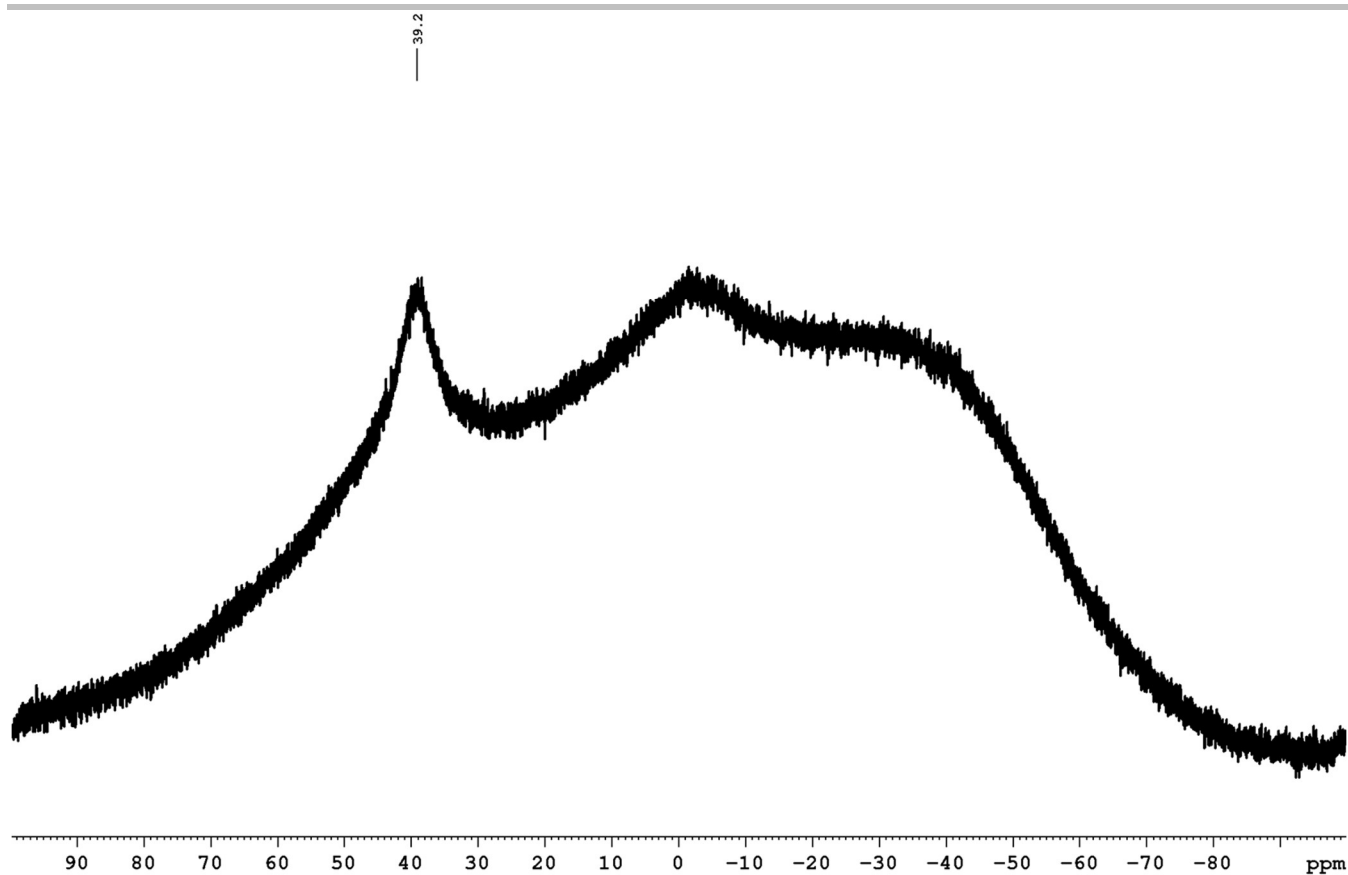


Figure S31.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $8^{\text{TP}}$  (96 MHz, in  $\text{CDCl}_3$ ).

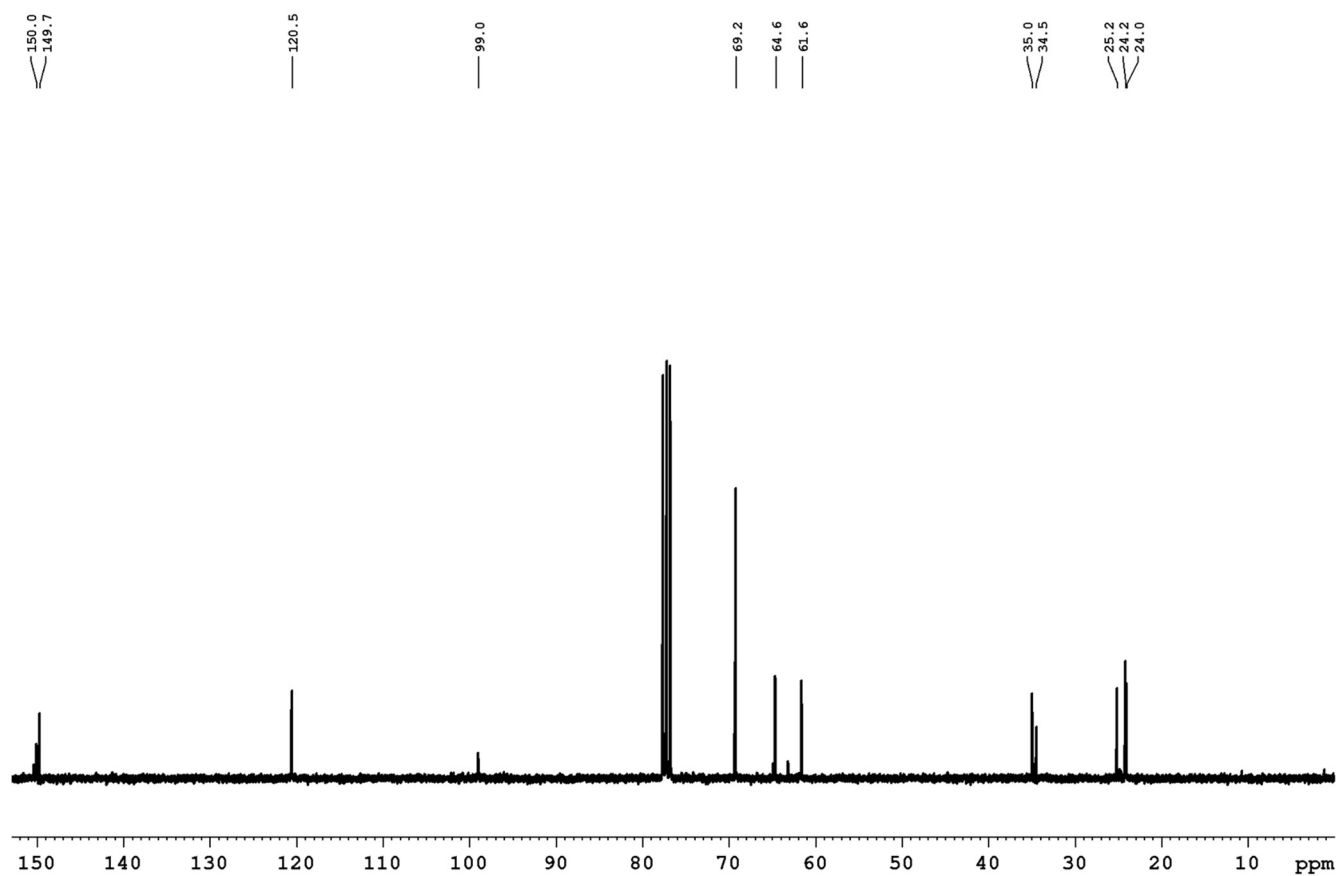


Figure S32.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $8^{\text{TP}}$  (76 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

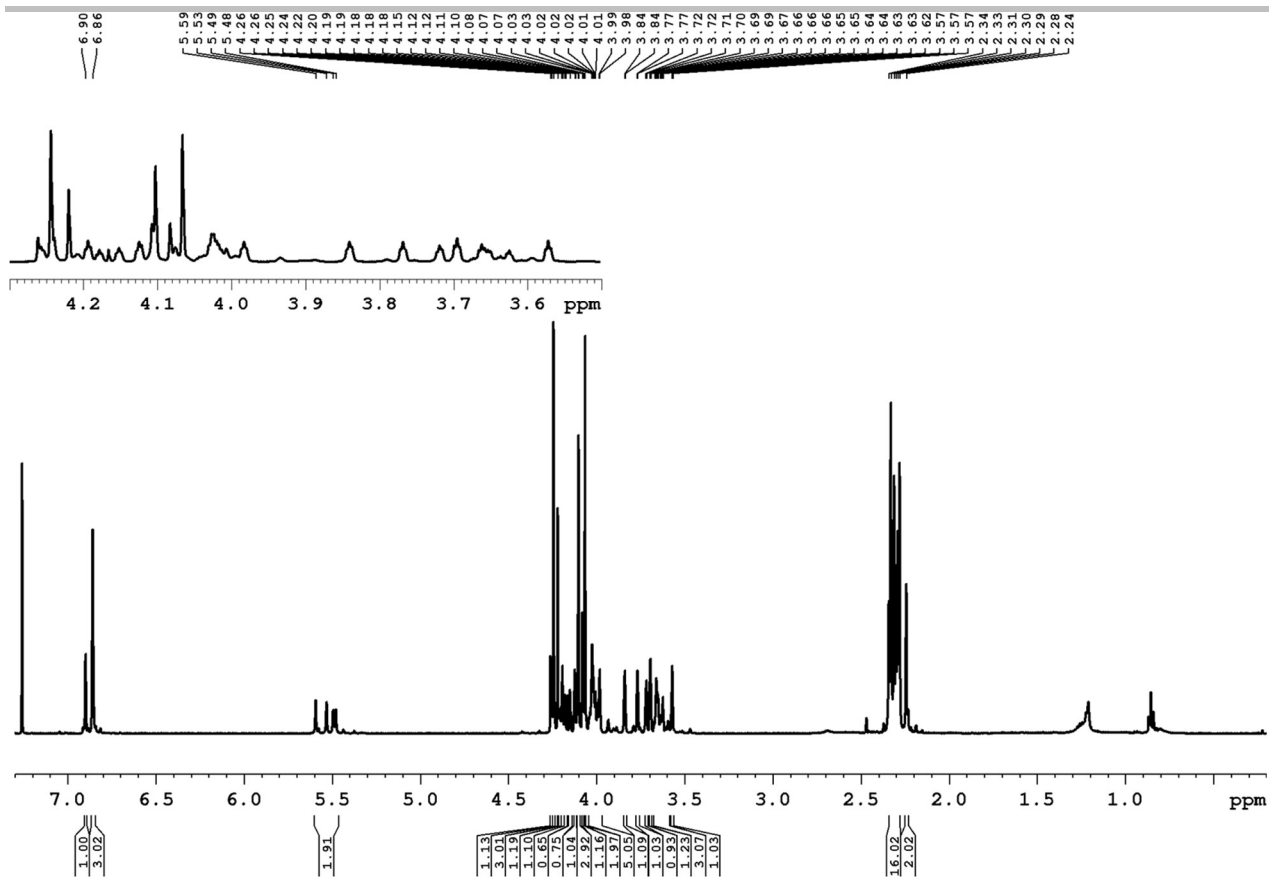


Figure S33.  $^1\text{H}$  NMR spectrum of  $9^{\text{Mes}}$  (500 MHz, in  $\text{CDCl}_3$ , at  $-40^\circ\text{C}$ ).

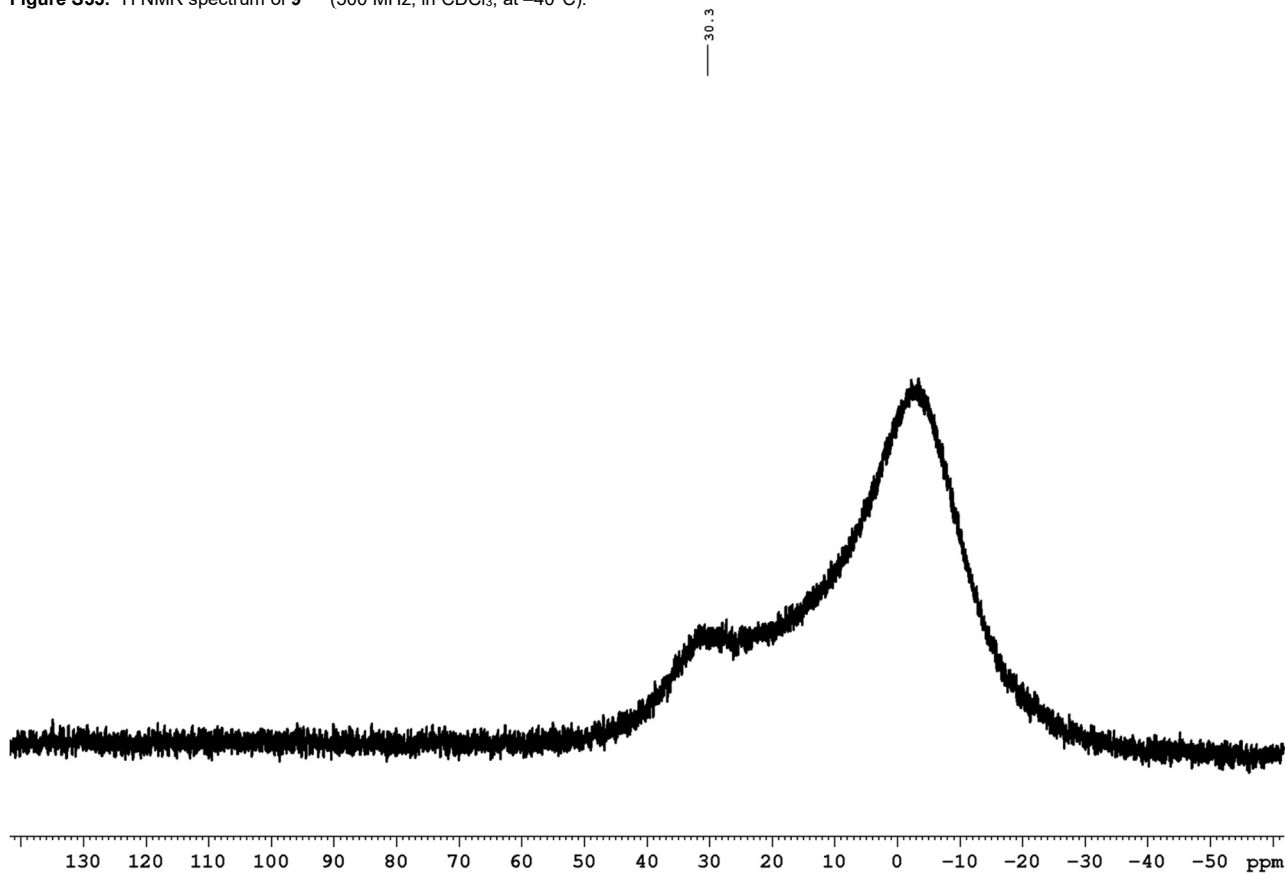


Figure S34.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $9^{\text{Mes}}$  (160 MHz, in  $\text{CDCl}_3$ , at  $-40^\circ\text{C}$ ).

# SUPPORTING INFORMATION

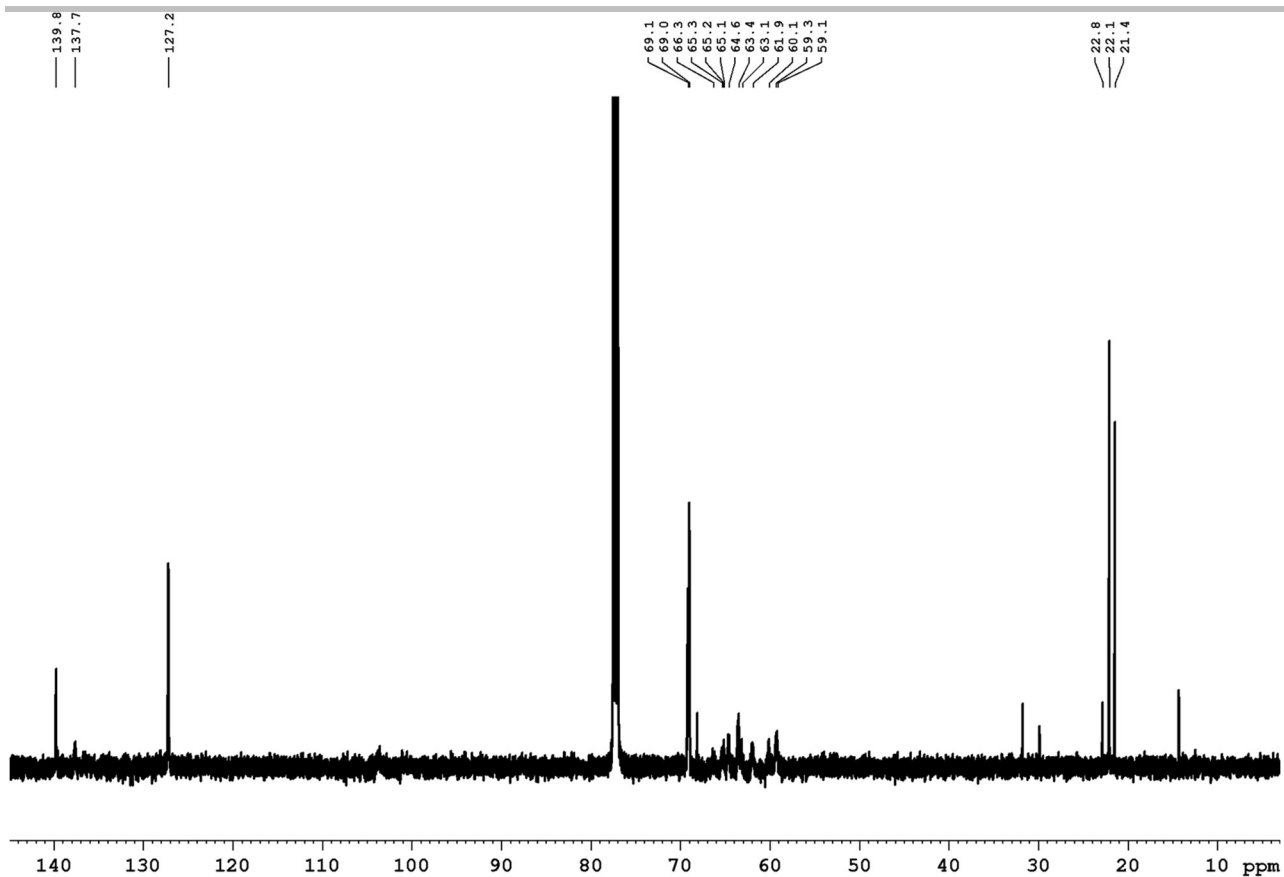


Figure S35.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $9^{\text{Mes}}$  (125 MHz, in  $\text{CDCl}_3$ ).

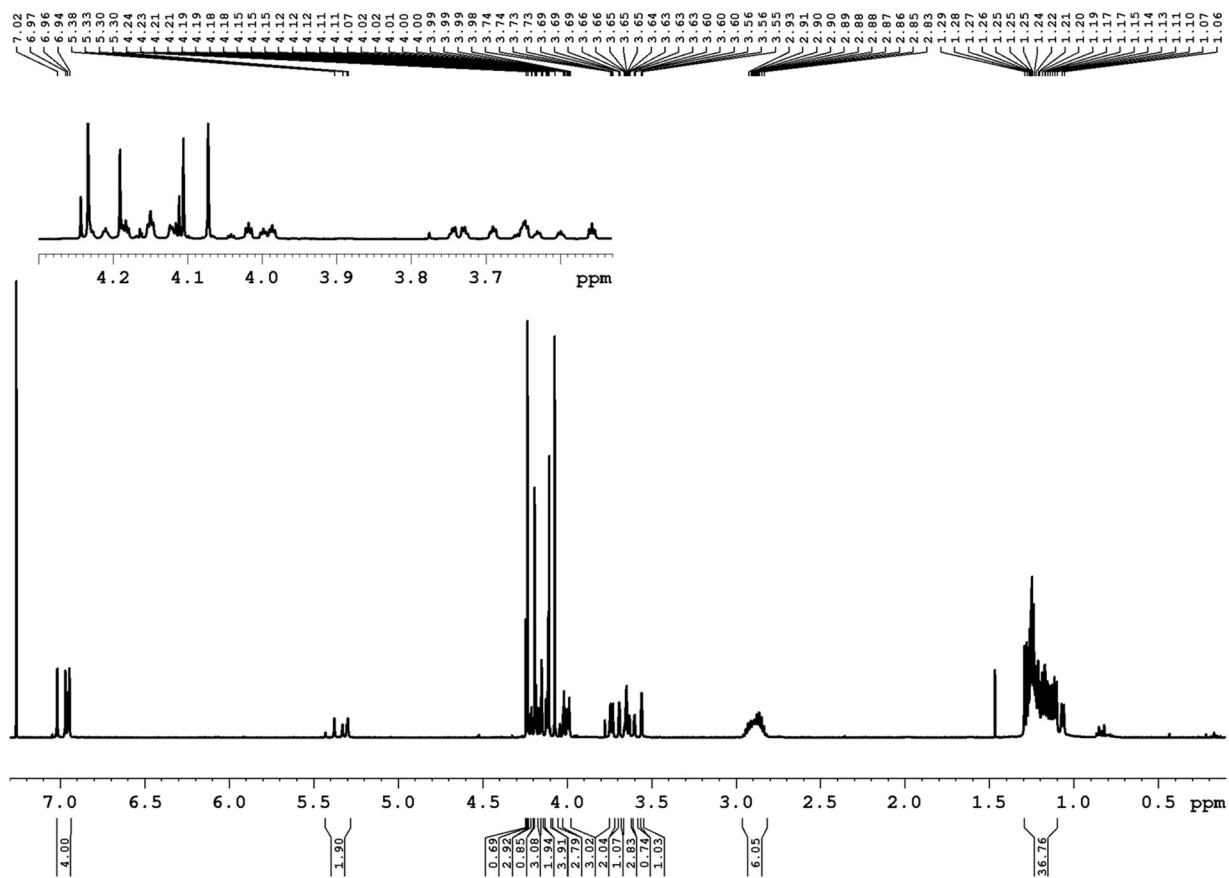


Figure S36.  $^1\text{H}$  NMR spectrum of  $9^{\text{TIP}}$  (500 MHz, in  $\text{CDCl}_3$ , at  $-40^\circ\text{C}$ ).



# SUPPORTING INFORMATION

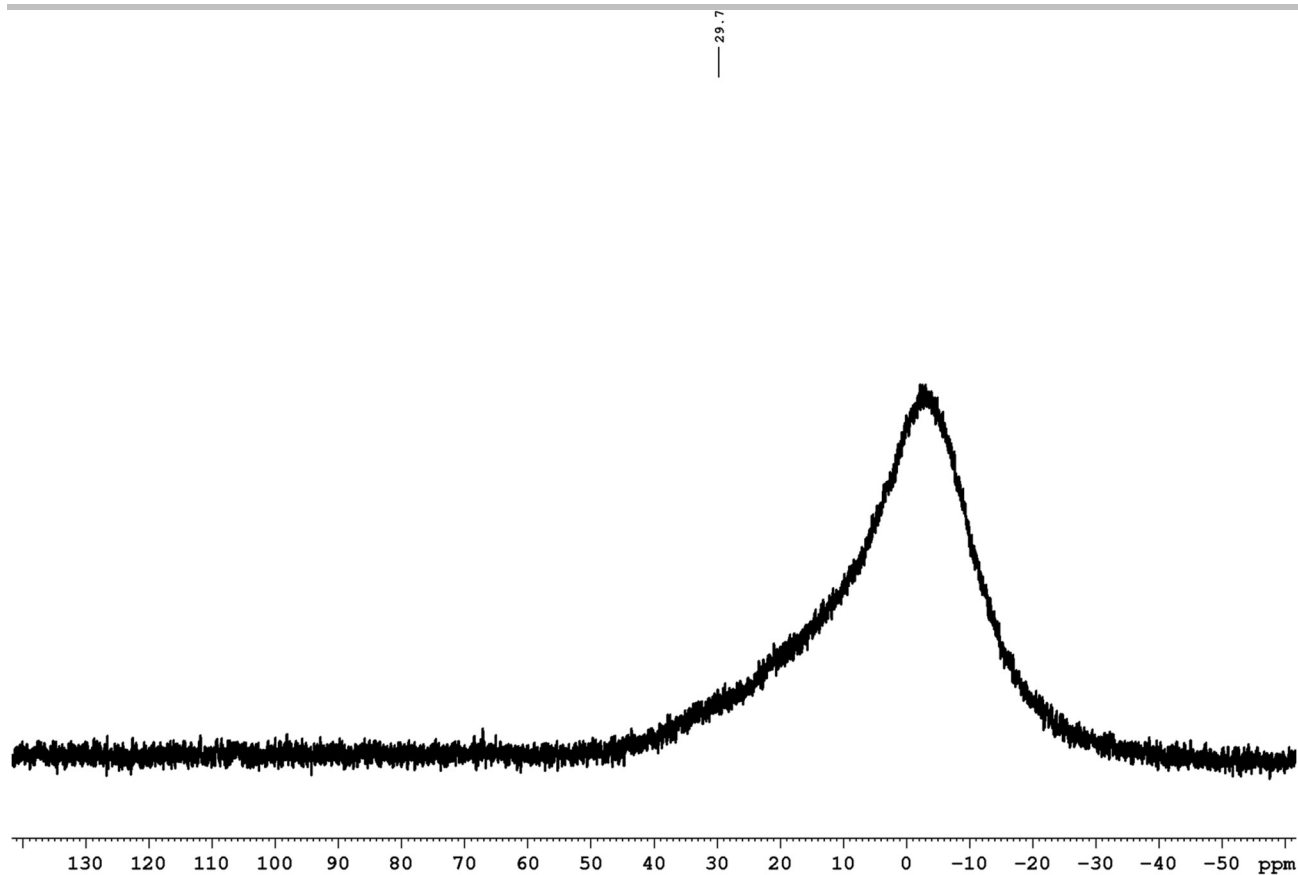


Figure S37.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $9^{\text{Tp}}$  (160 MHz, in  $\text{CDCl}_3$ , at  $-40^\circ\text{C}$ ).

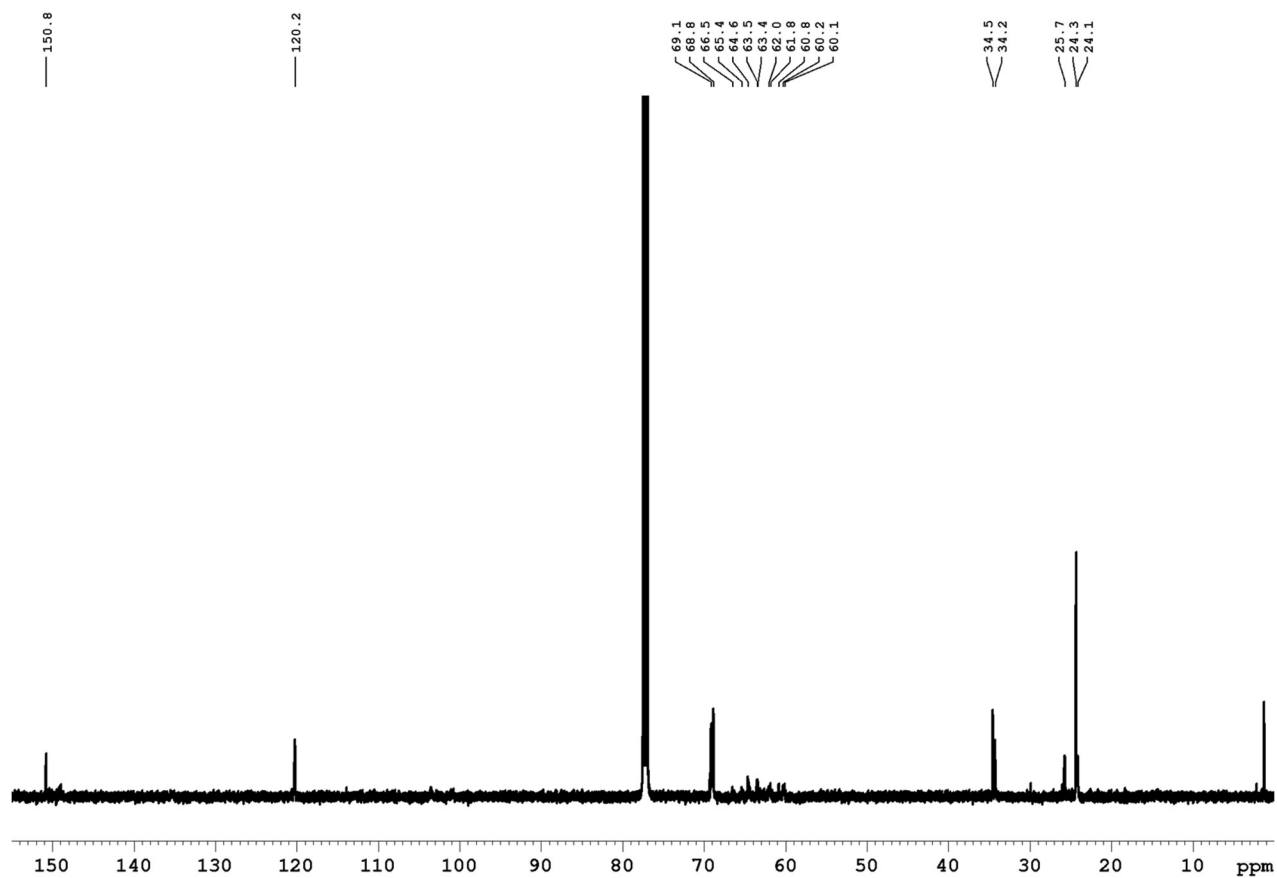


Figure S38.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $9^{\text{Tp}}$  (125 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

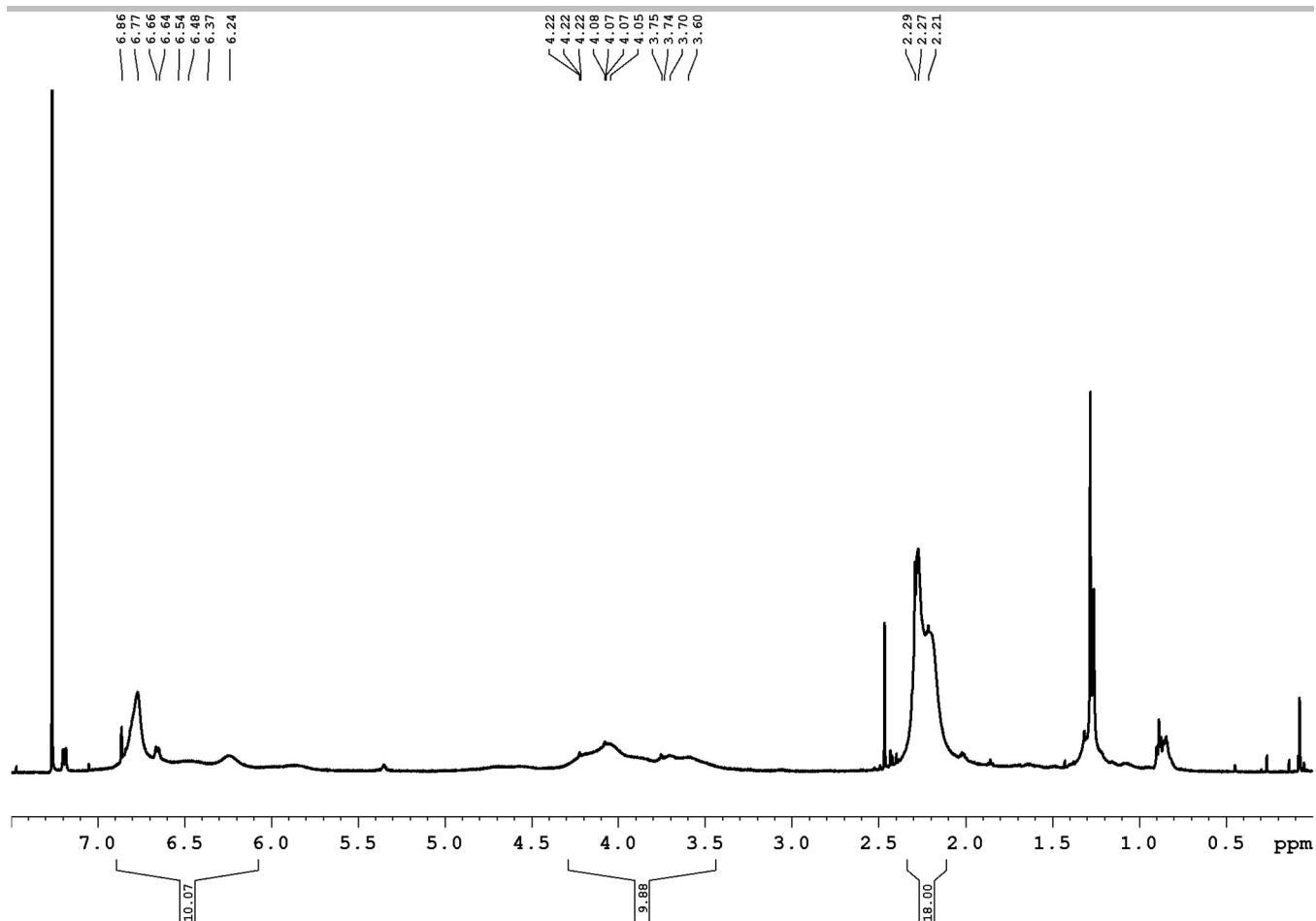


Figure S39.  $^1\text{H}$  NMR spectrum of **10** (500 MHz, in  $\text{CDCl}_3$ ).

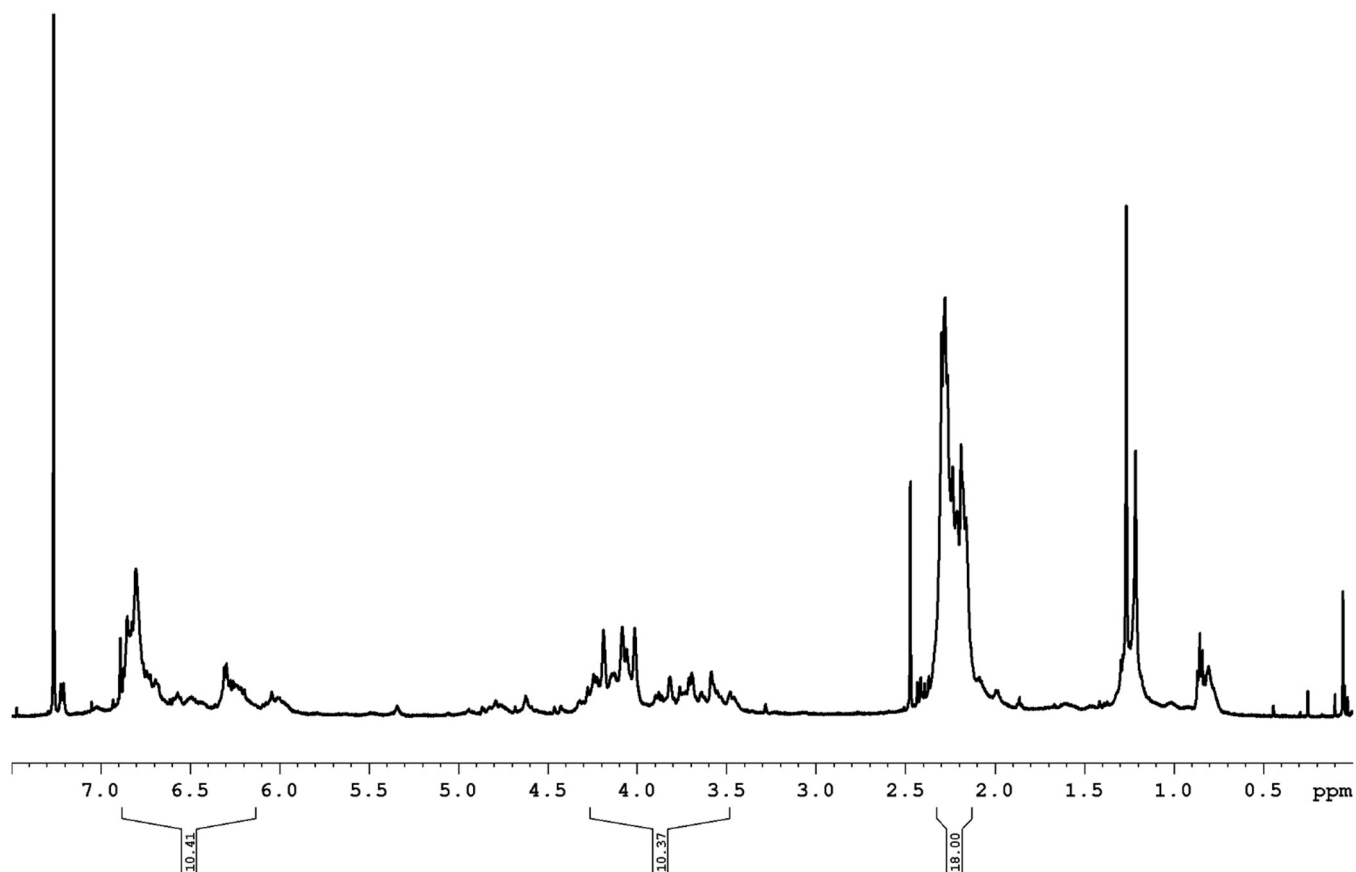
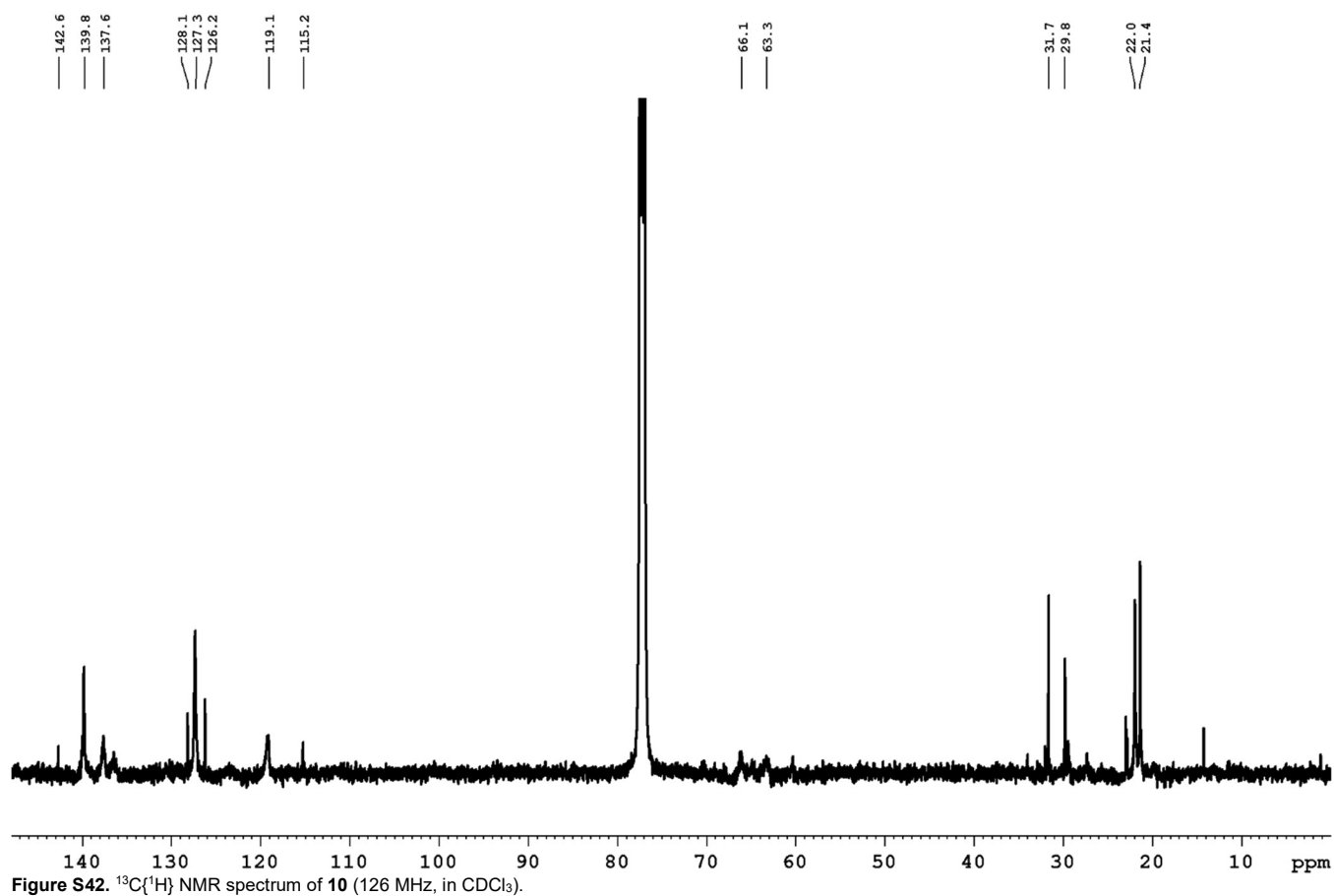
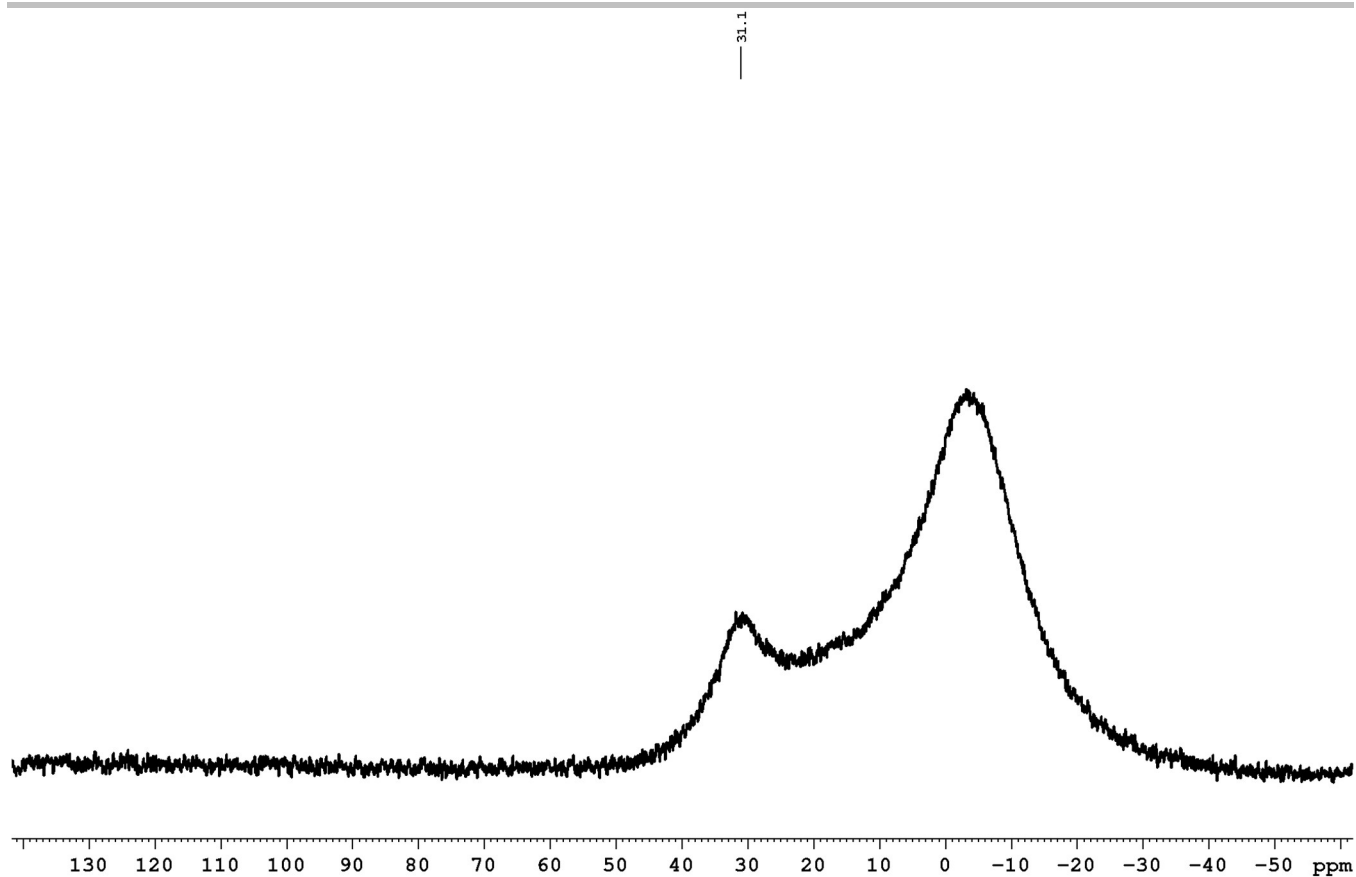


Figure S40.  $^1\text{H}$  NMR spectrum of **10** (500 MHz, in  $\text{CDCl}_3$ , at  $-40^\circ\text{C}$ ).

# SUPPORTING INFORMATION



# SUPPORTING INFORMATION

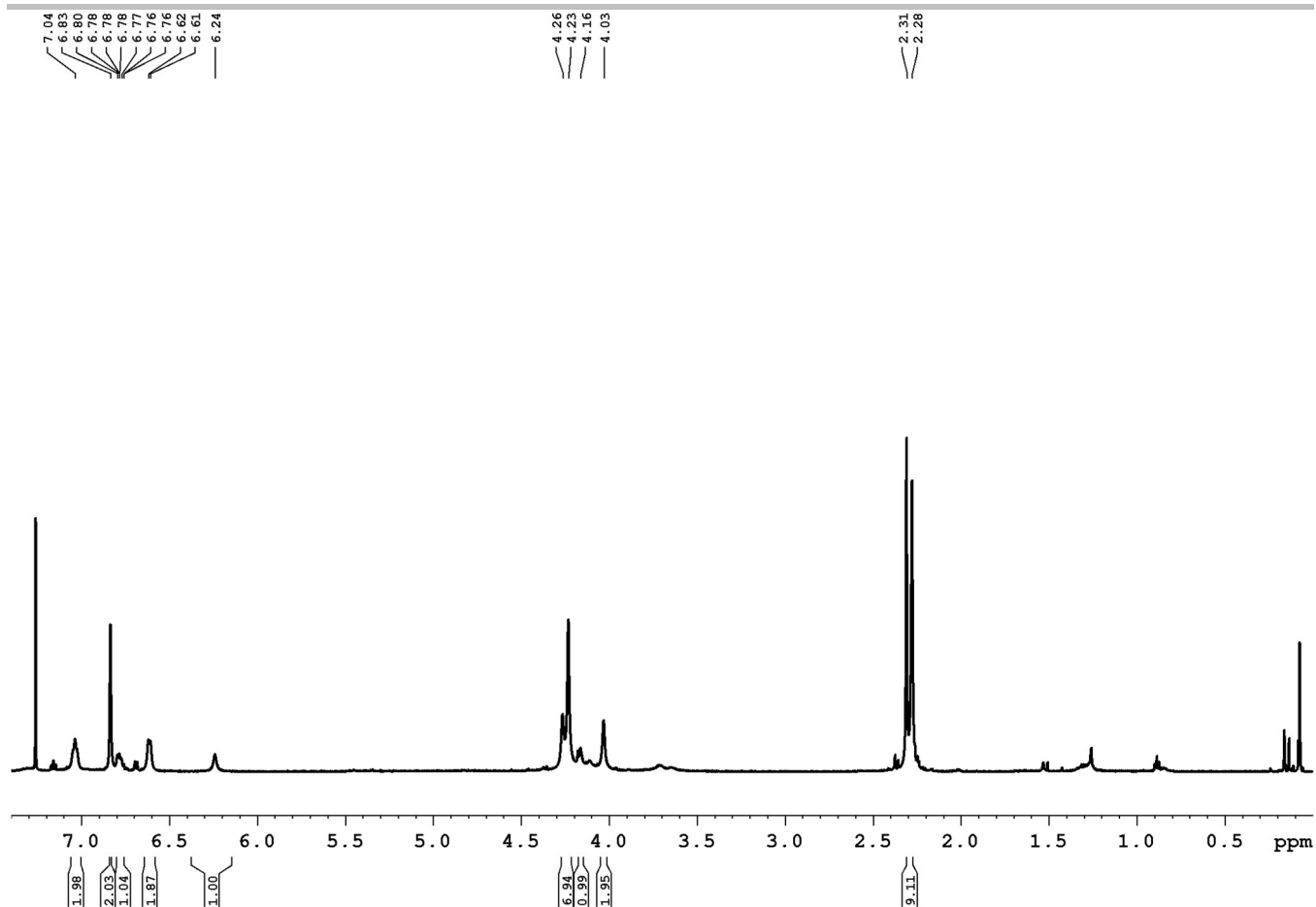


Figure S43.  $^1\text{H}$  NMR spectrum of **11** (600 MHz, in  $\text{CDCl}_3$ ).

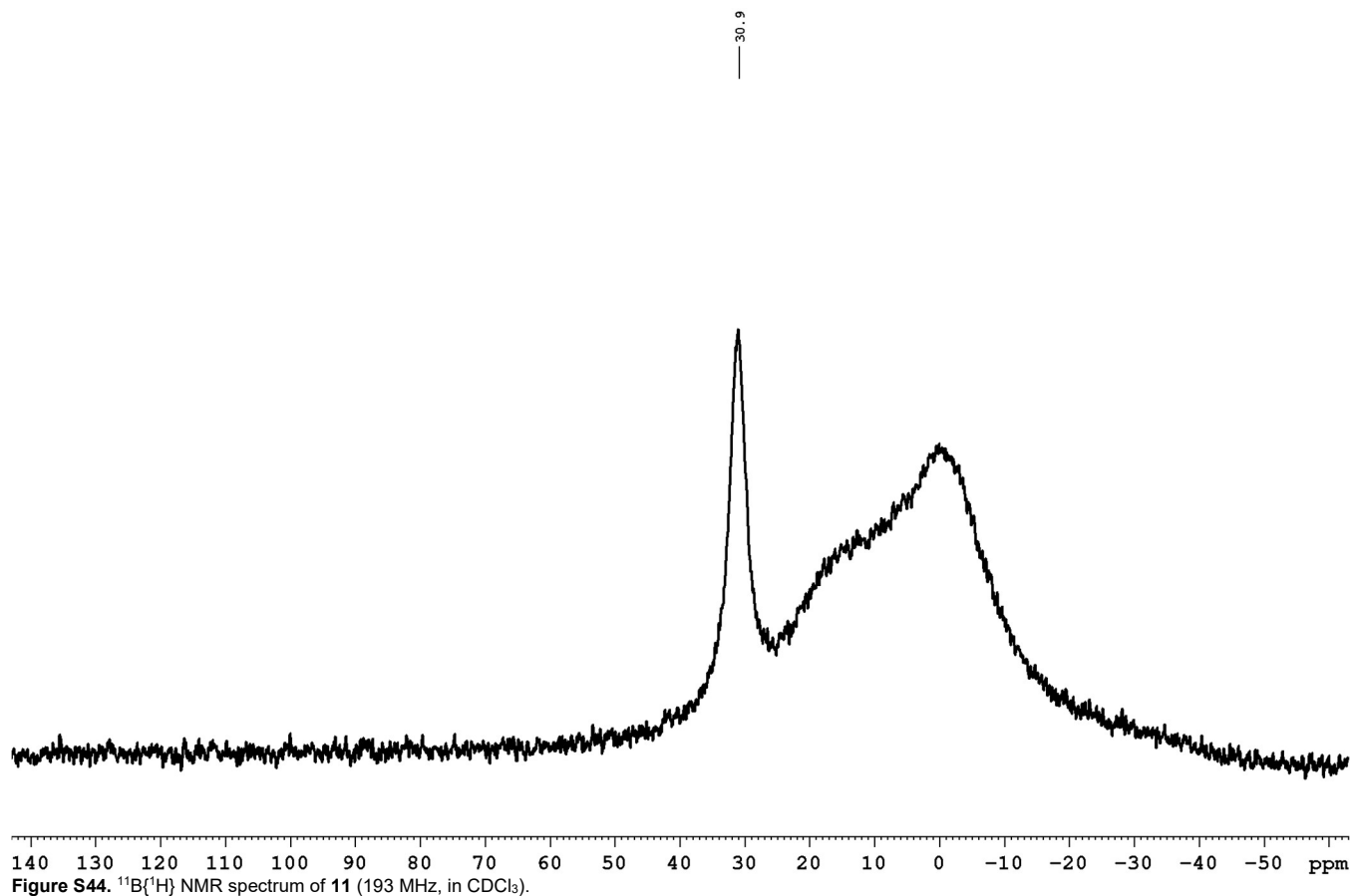


Figure S44.  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **11** (193 MHz, in  $\text{CDCl}_3$ ).

# SUPPORTING INFORMATION

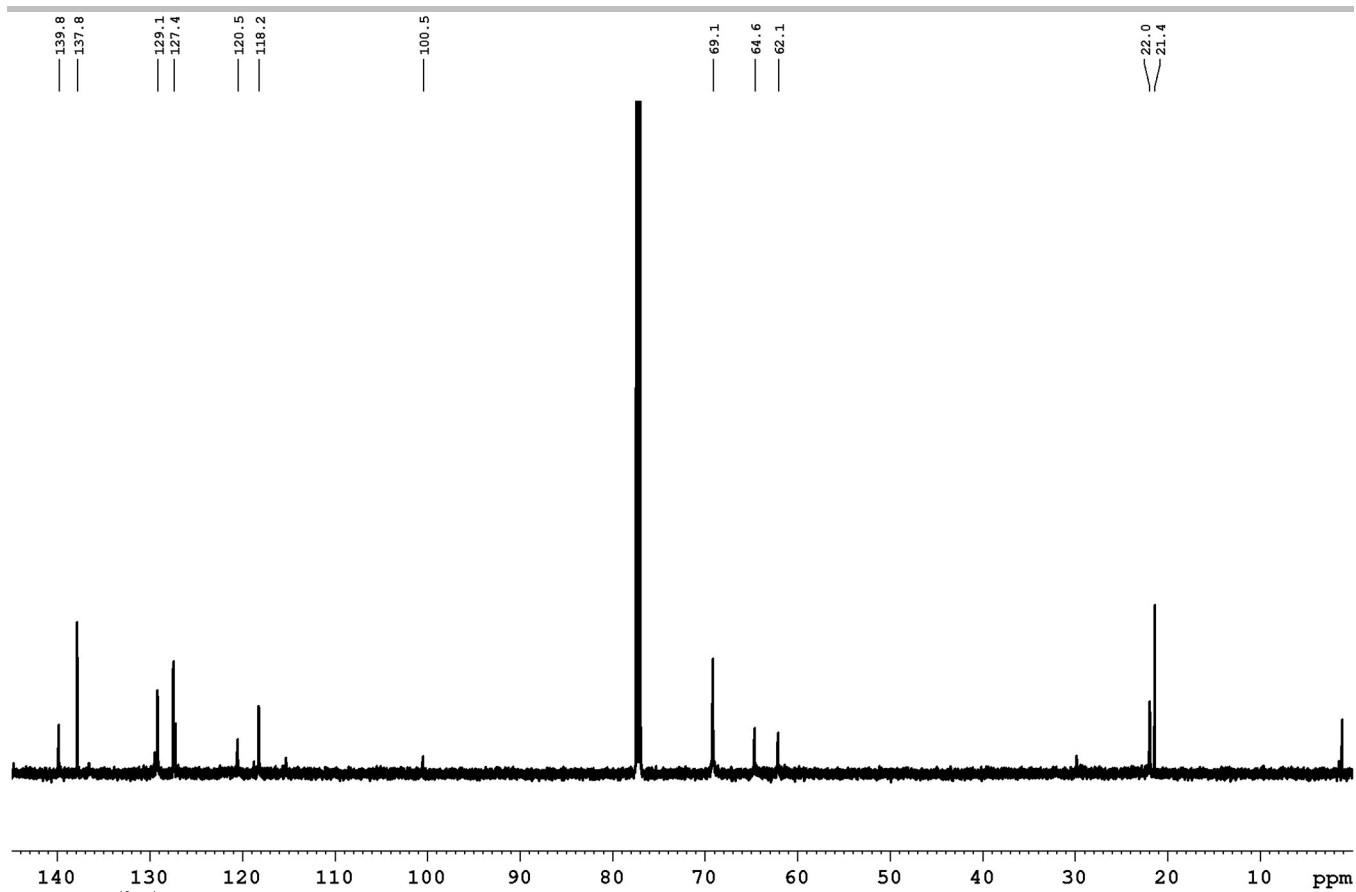


Figure S45.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of 11 (151 MHz, in  $\text{CDCl}_3$ ).

## SUPPORTING INFORMATION

### High resolution mass spectra

The mass spectra were processed using the Qual Browser of the XCalibur software. The figures show the total spectrum in the upper part, the product peak with isotope distribution in the middle and a corresponding simulation in the lower part.

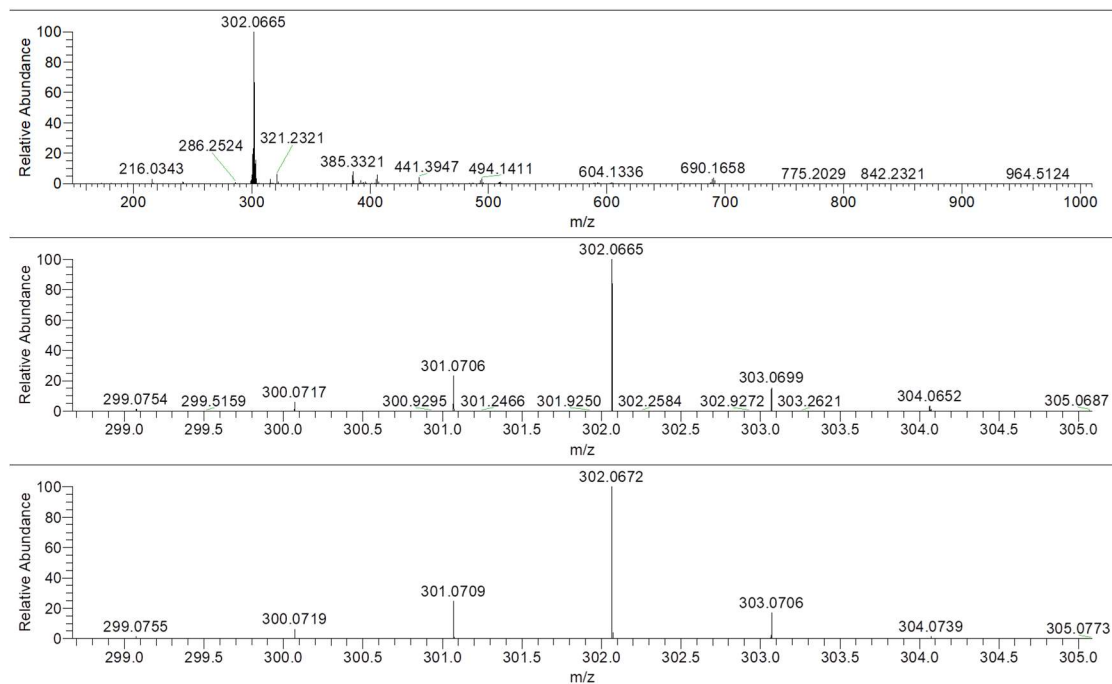


Figure S46. LIFDI spectrum of  $2^{\text{Ph}}$ .

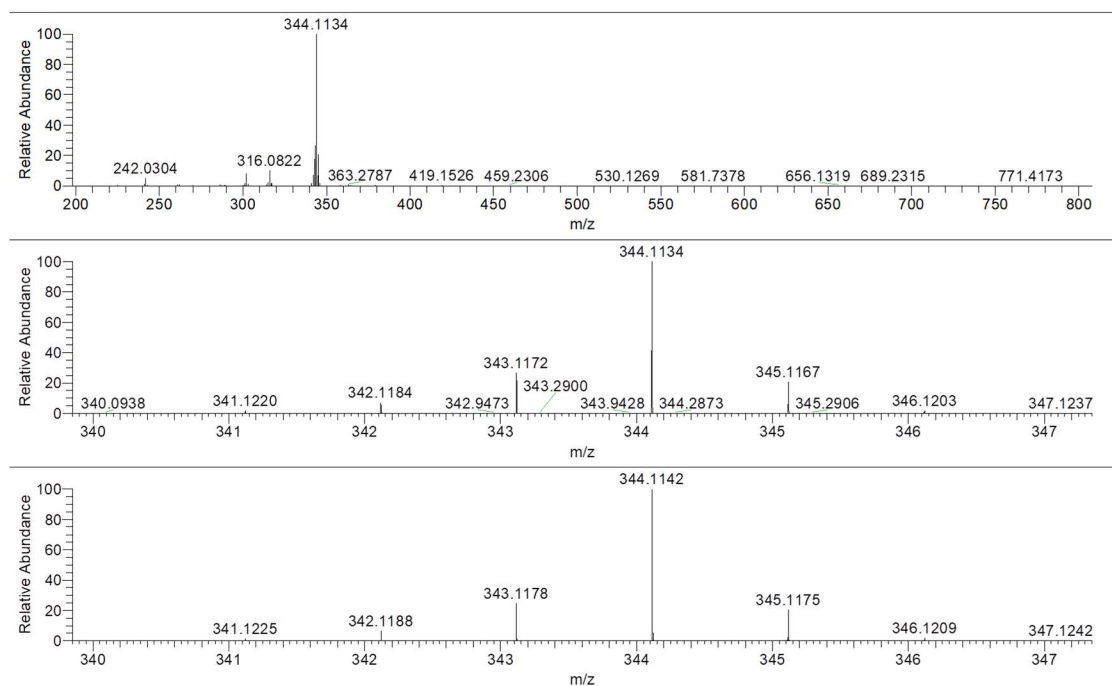


Figure S47. LIFDI spectrum of  $2^{\text{Mes}}$ .

# SUPPORTING INFORMATION

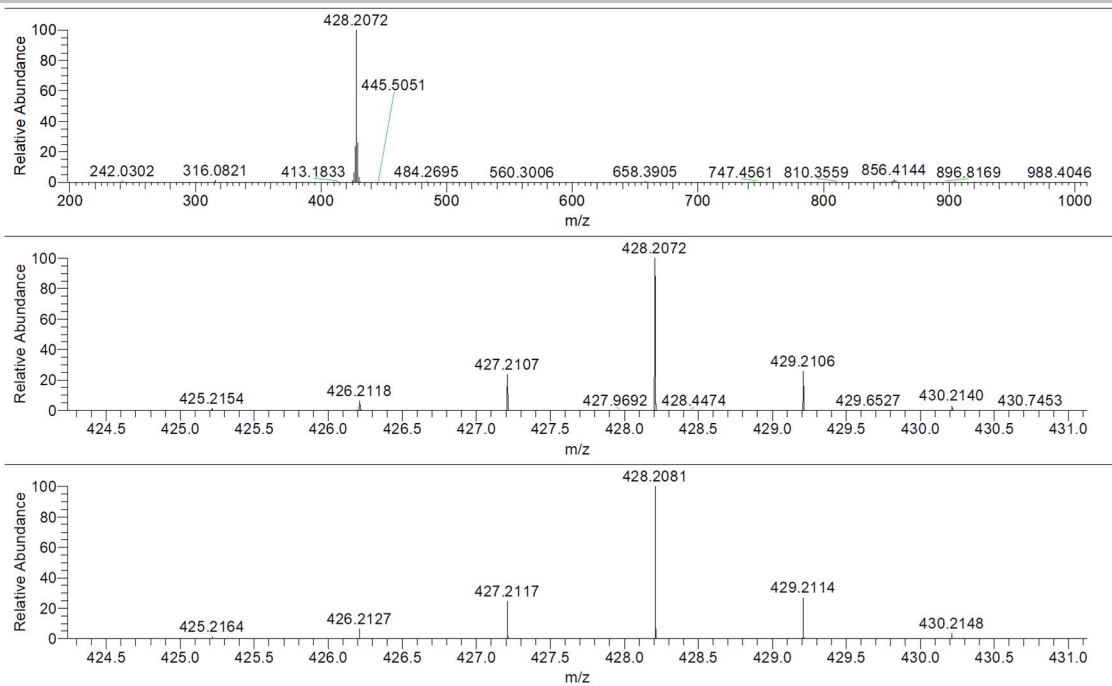


Figure S48. LIFDI spectrum of 2<sup>Tp</sup>.

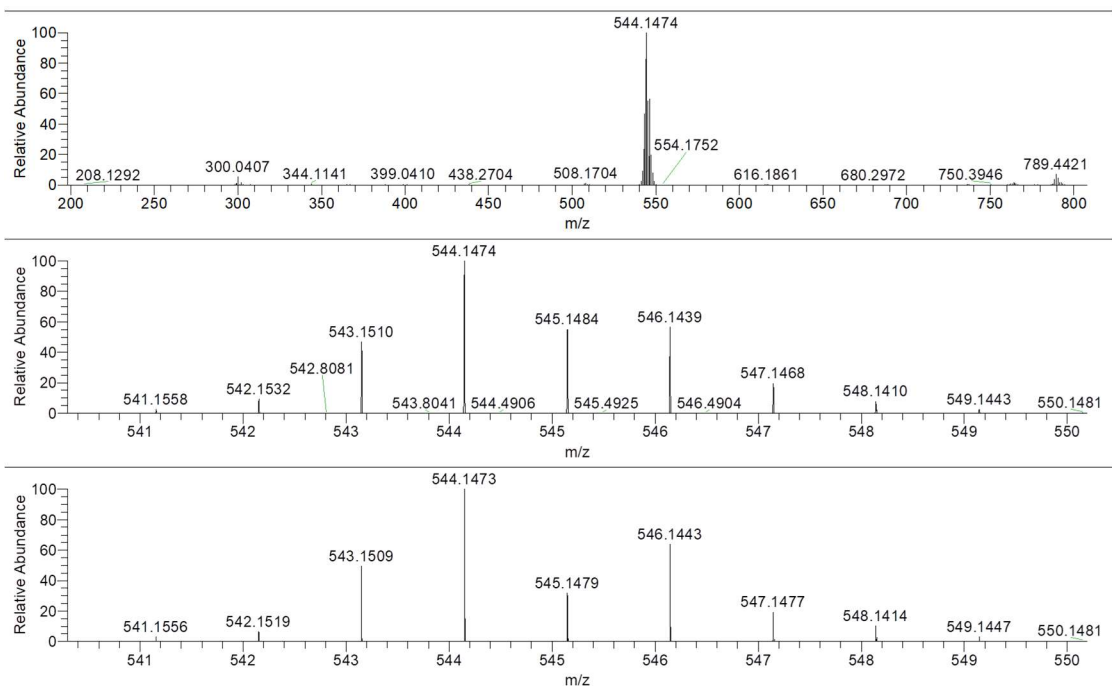
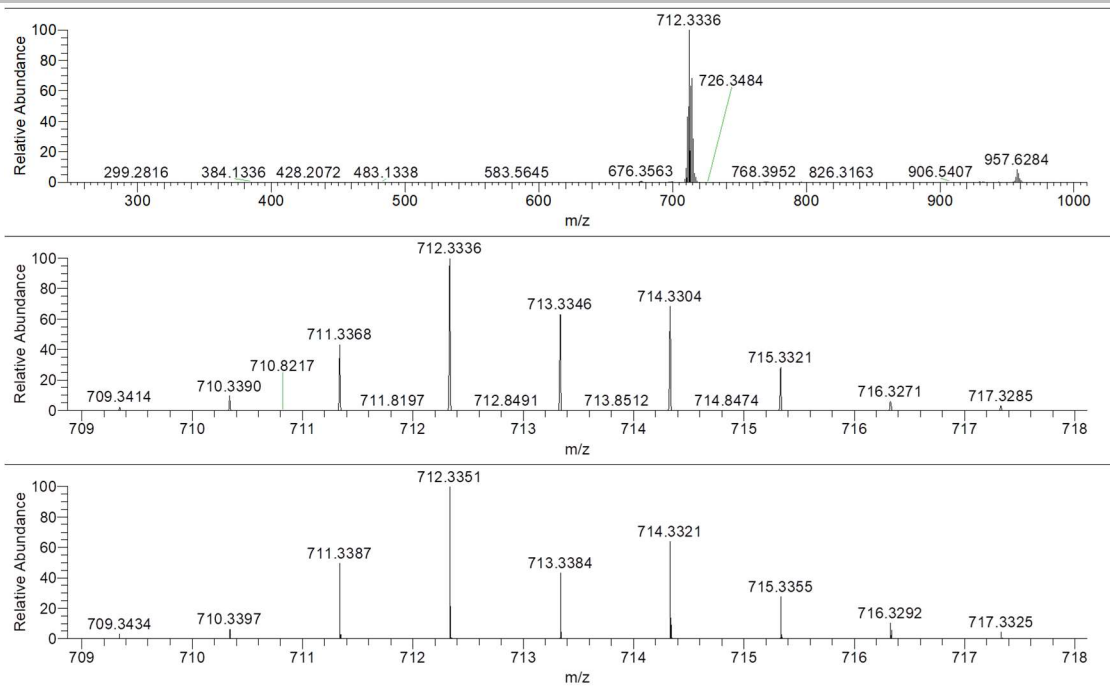
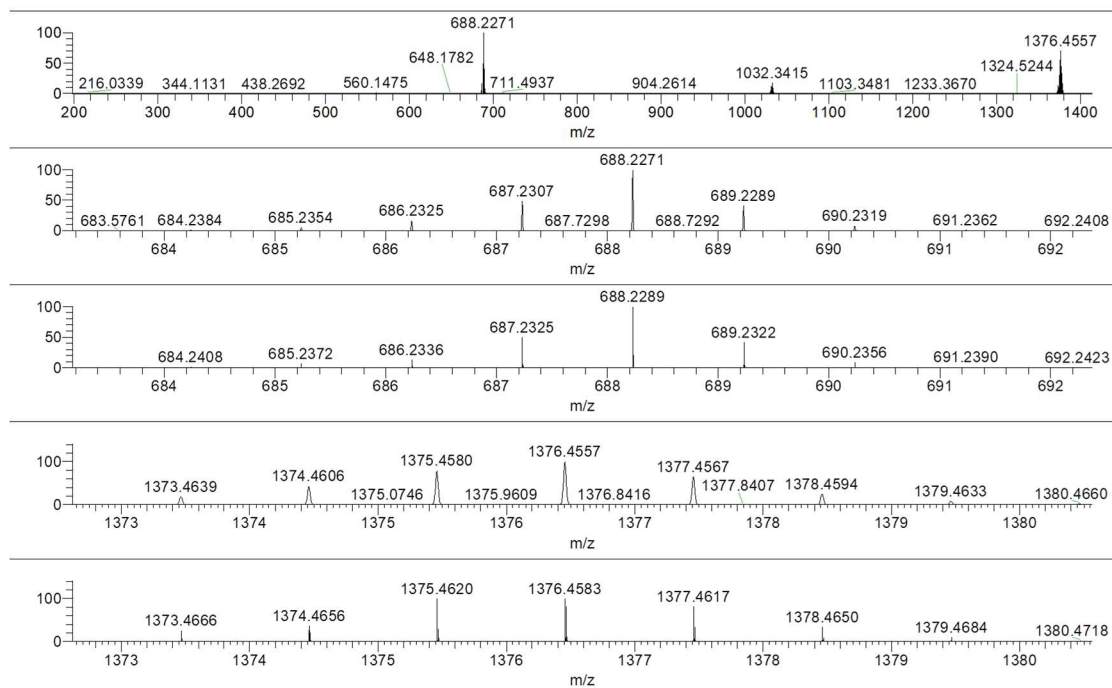


Figure S49. LIFDI spectrum of 3<sup>Mes</sup>.

# SUPPORTING INFORMATION



**Figure S50.** LIFDI spectrum of 3<sup>TIP</sup>.



**Figure S51.** LIFDI spectrum from the product mixture of the reaction of 1 with 3<sup>Mes</sup>, showing peaks of the molecular ions of 4<sup>Mes</sup> (m/z = 688.2271) and other ferrocenophane species 5<sup>Mes</sup> ([-NHfcNHB(Mes)-]<sub>3</sub> m/z = 1032.3415; [-NHfcNHB(Mes)-]<sub>4</sub> m/z = 1376.4557).



# SUPPORTING INFORMATION

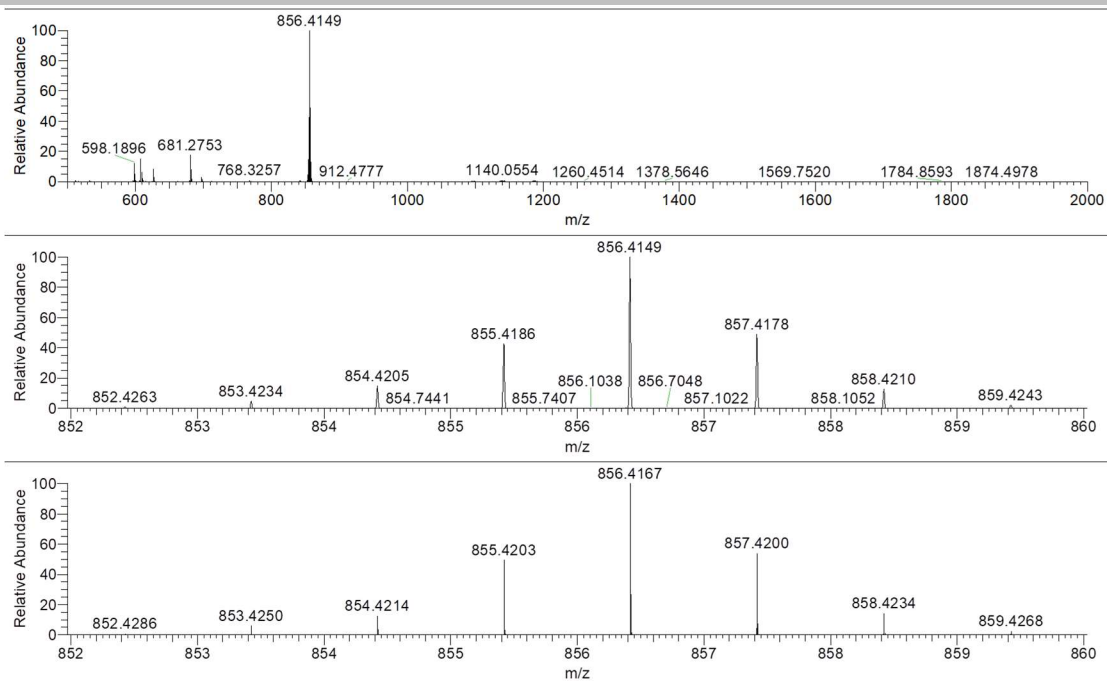


Figure S52. LIFDI spectrum of  $4^{TIP}$ .

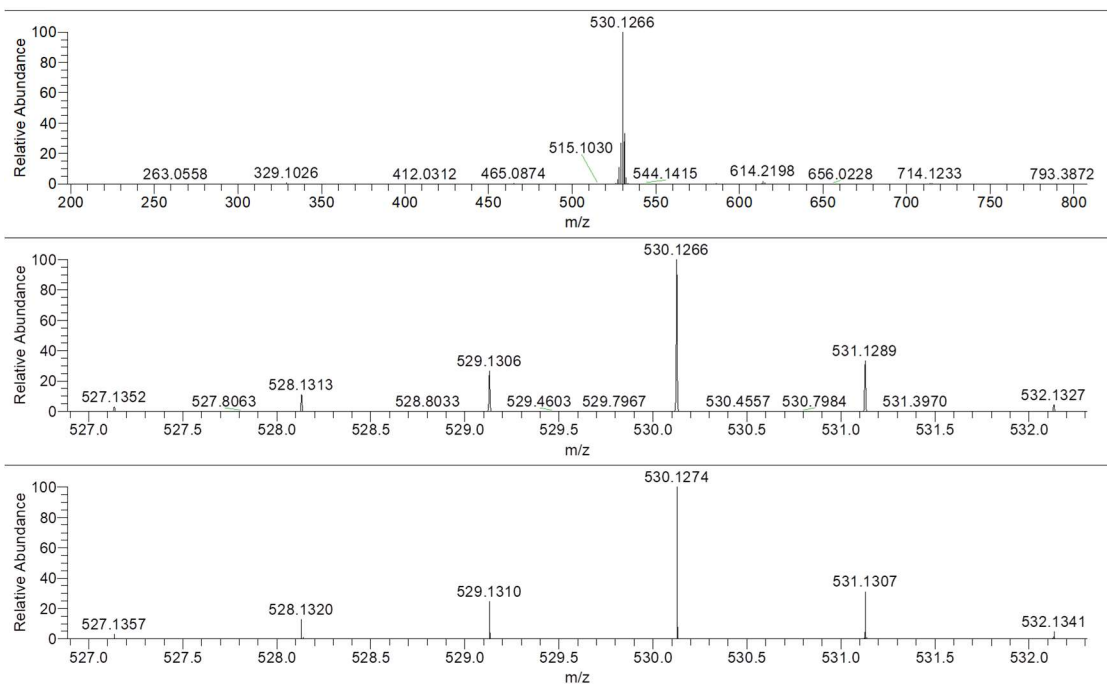


Figure S53. LIFDI spectrum of  $7^{Mes}$ .

# SUPPORTING INFORMATION

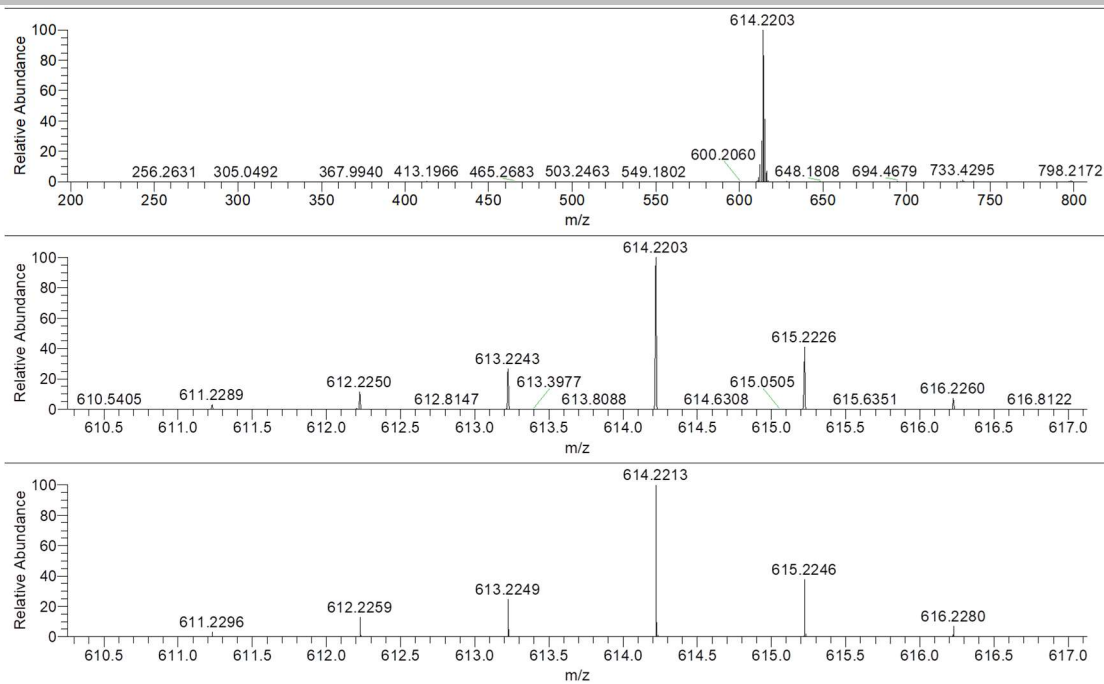


Figure S54. LIFDI spectrum of 7<sup>TIP</sup>.

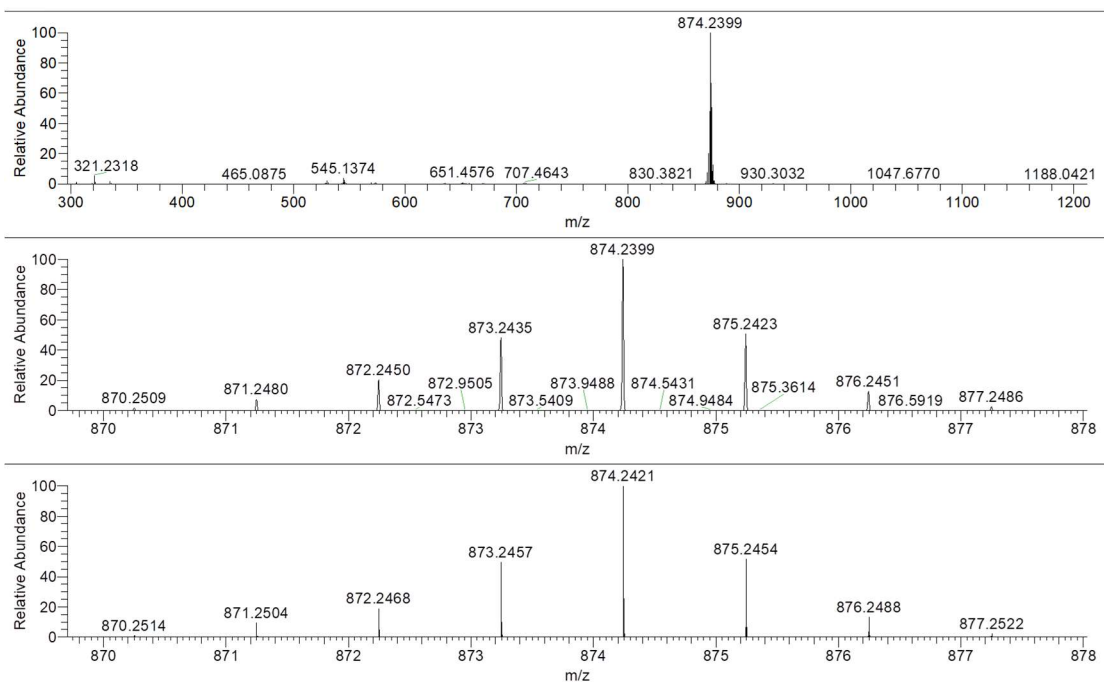
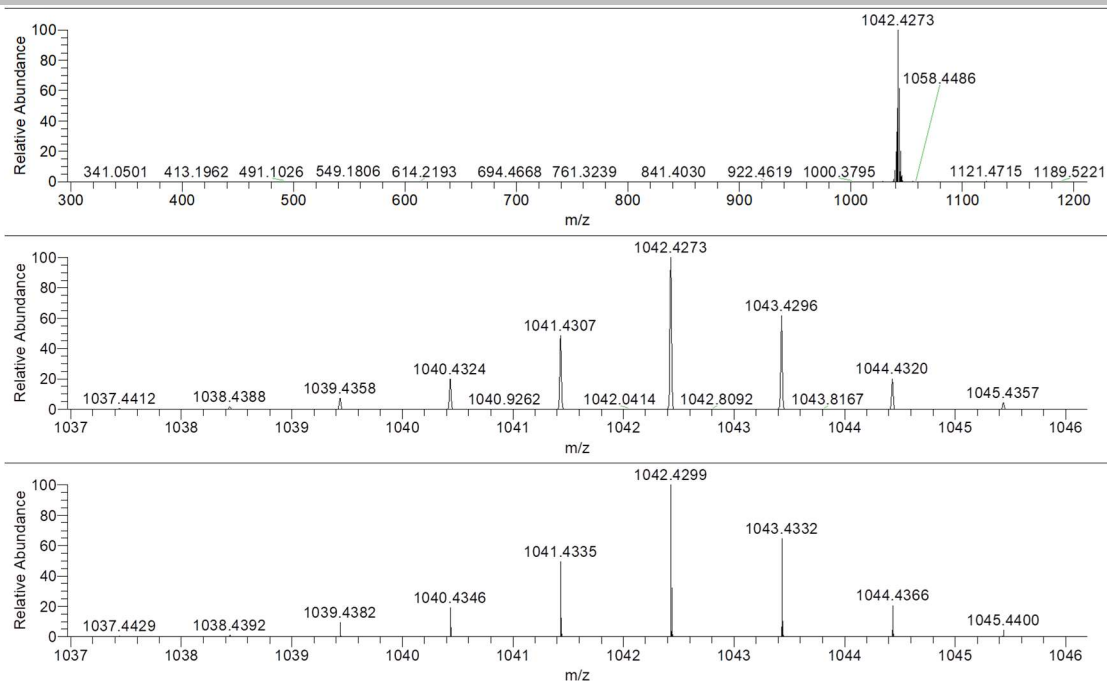
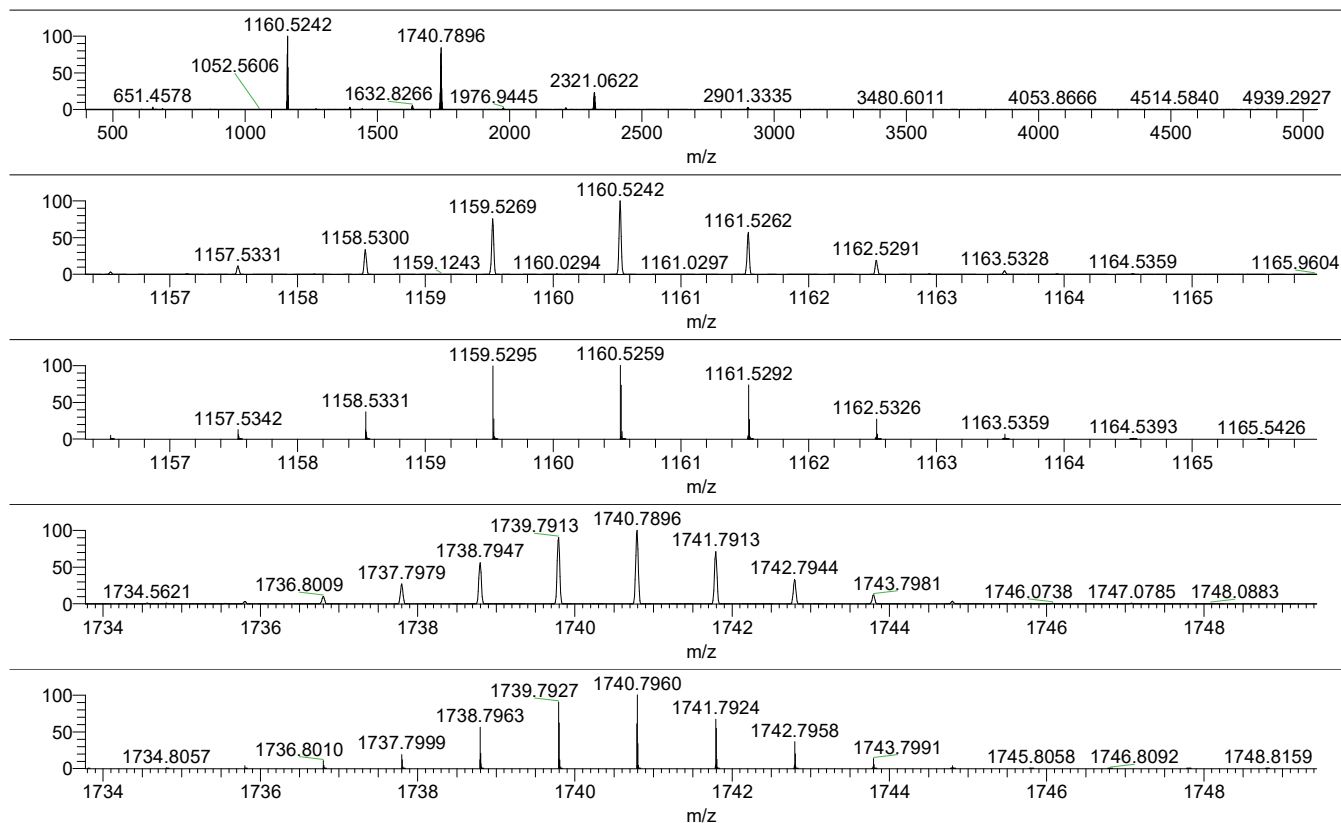


Figure S55. LIFDI spectrum of 9<sup>Mes</sup>.

# SUPPORTING INFORMATION

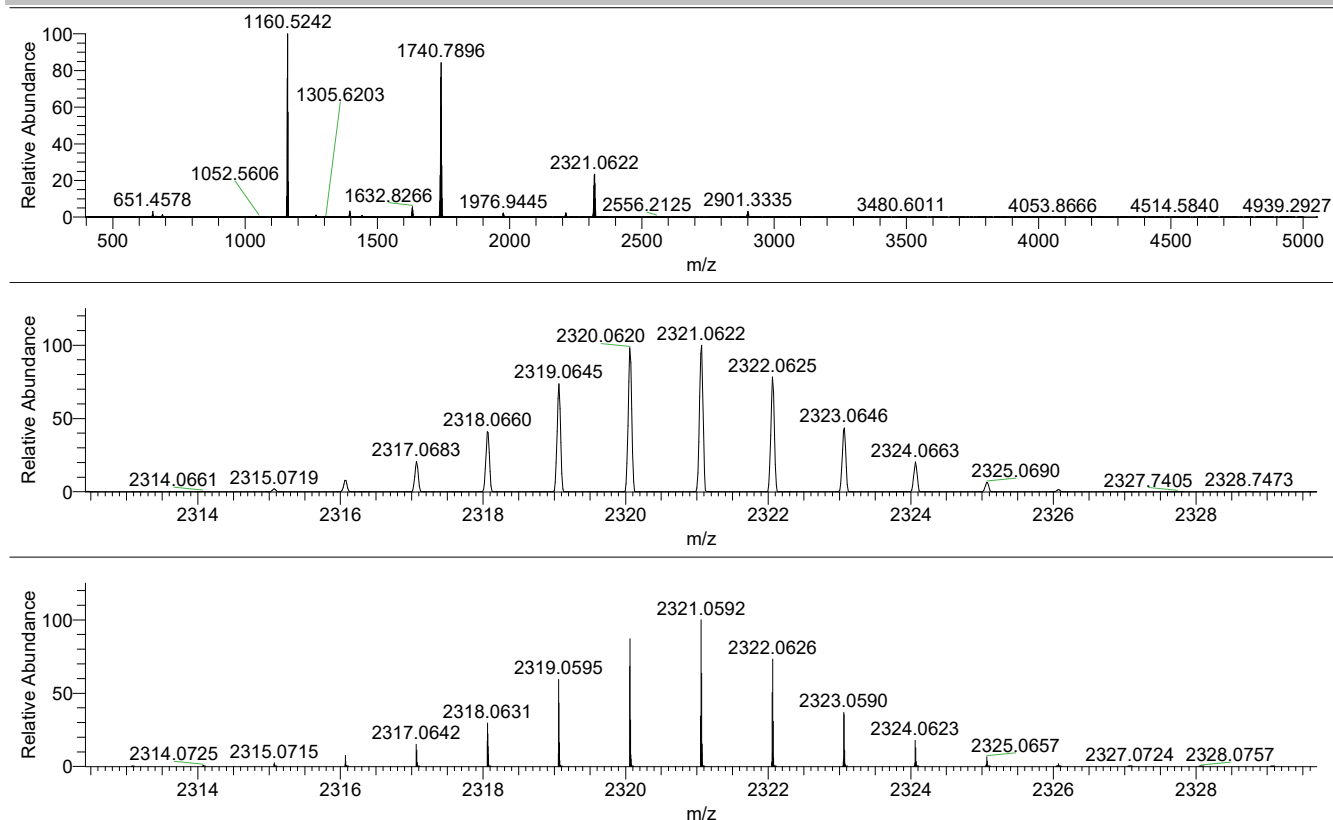


**Figure S56.** LIFDI spectrum of 9TIP.

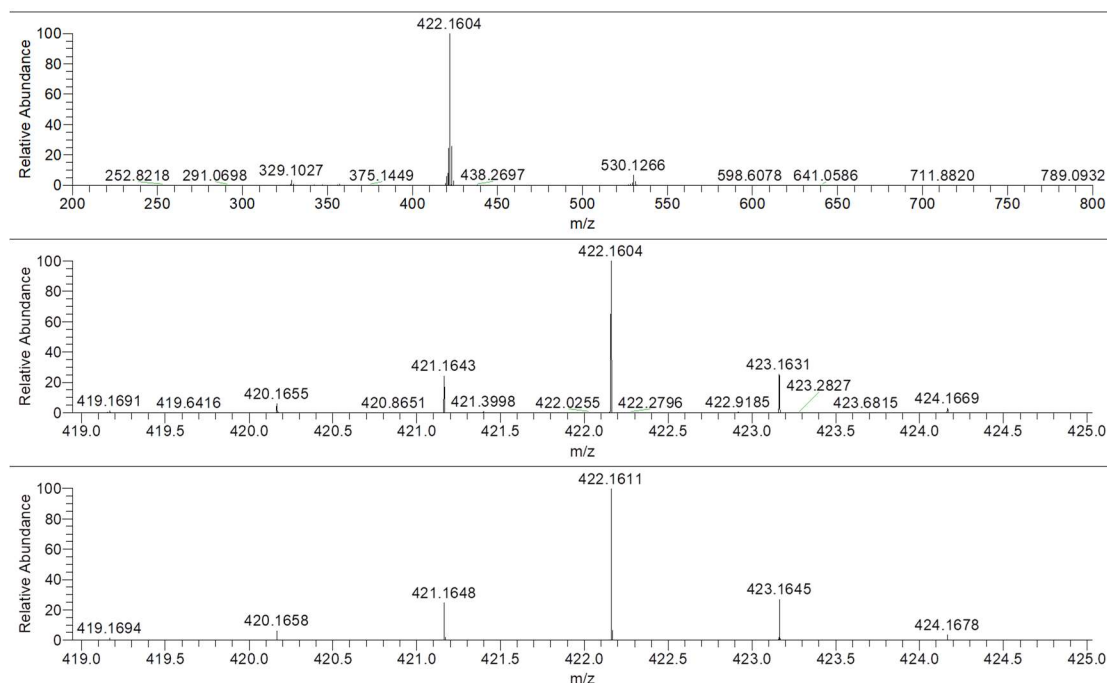


**Figure S57.** LIFDI spectrum of 10 ( $m/z = 580.1710$ , repeating unit) and further copolymer chain lengths ( $[(\text{repeating unit})_2]$   $m/z = 1160.5242$ );  $[(\text{repeating unit})_3]$   $m/z = 1740.7896$ ).

# SUPPORTING INFORMATION



**Figure S58.** LIFDI spectrum of **10** ( $m/z = 580.1710$ , repeating unit) further copolymer chain lengths ([repeating unit] $_n$ ,  $m/z = 2321.0622$ ).



**Figure S59.** LIFDI spectrum of **11**.

# SUPPORTING INFORMATION

## GPC trace

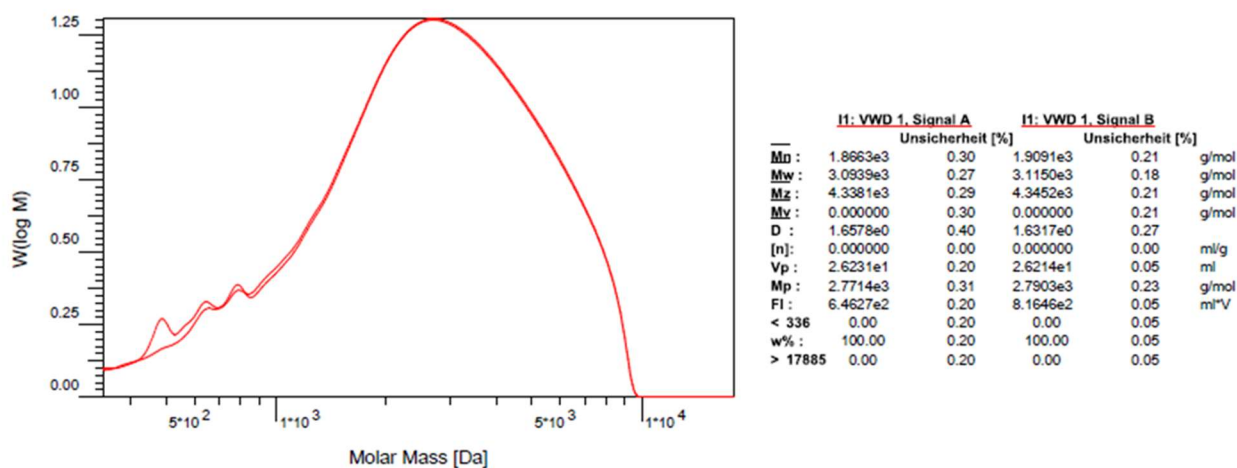


Figure S60. GPC trace of **10** (in THF, vs. polystyrene standard).

## Electrochemical studies

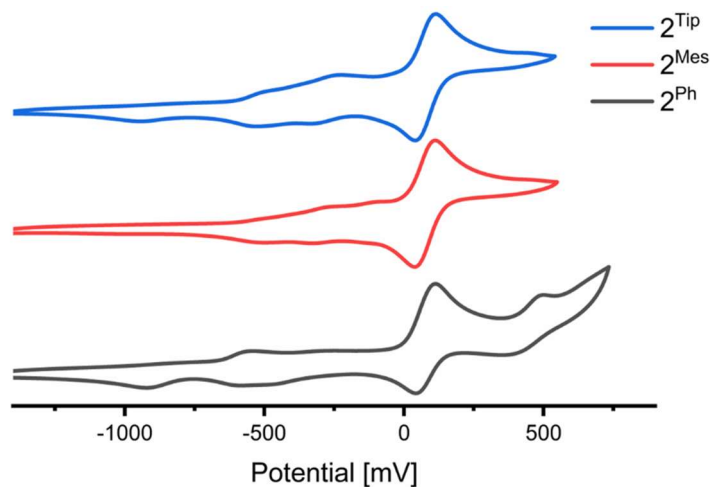


Figure S61. Cyclic voltammogram of **2<sup>Ar</sup>** (Ar = Ph, Mes, Tip) recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate: 250  $\text{mVs}^{-1}$ .

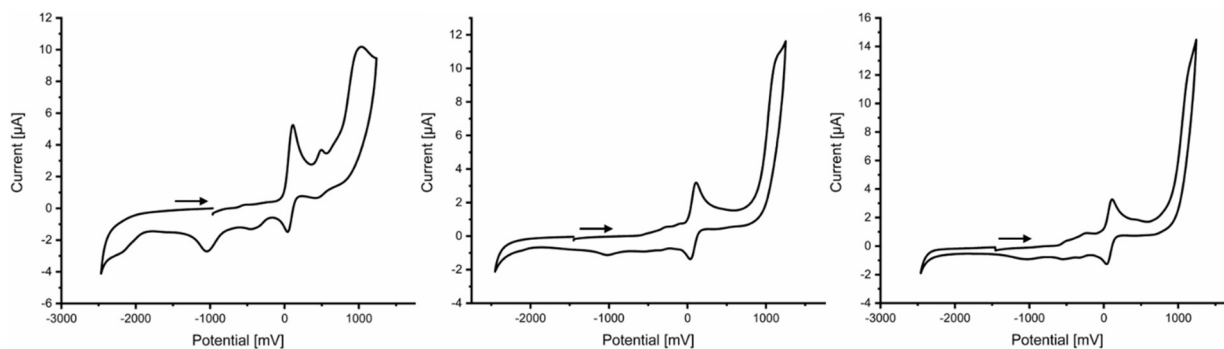
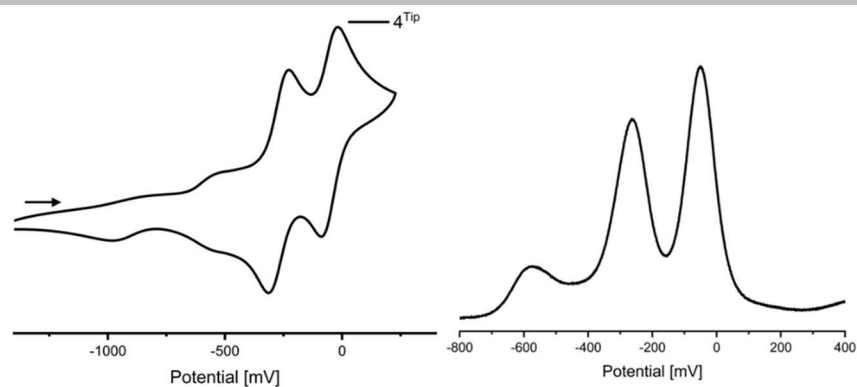
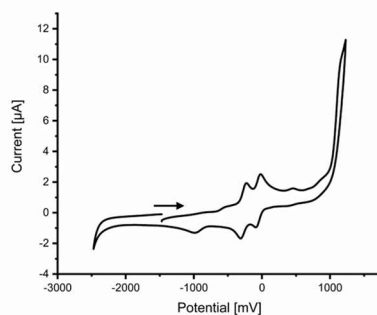


Figure S62. Cyclic voltammogram of **2<sup>Ph</sup>** (left), **2<sup>Mes</sup>** (middle), **2<sup>Tip</sup>** (right) recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate: 250  $\text{mVs}^{-1}$ .

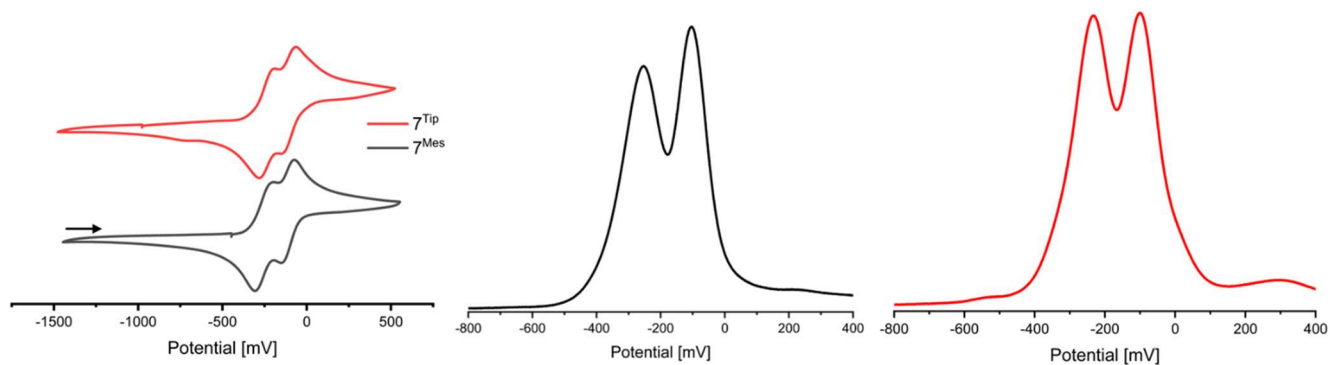
## SUPPORTING INFORMATION



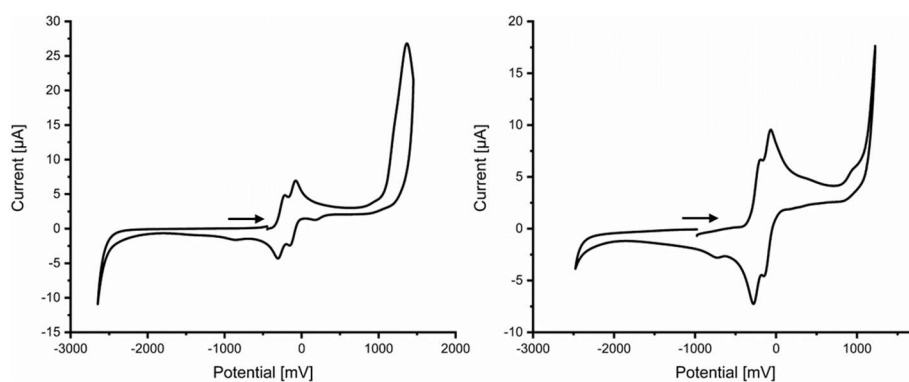
**Figure S63.** Cyclic voltammogram (left) and square wave voltammogram (right) of  $4^{\text{Tip}}$  recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .



**Figure S64.** Cyclic voltammogram of  $4^{\text{Tip}}$  recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .

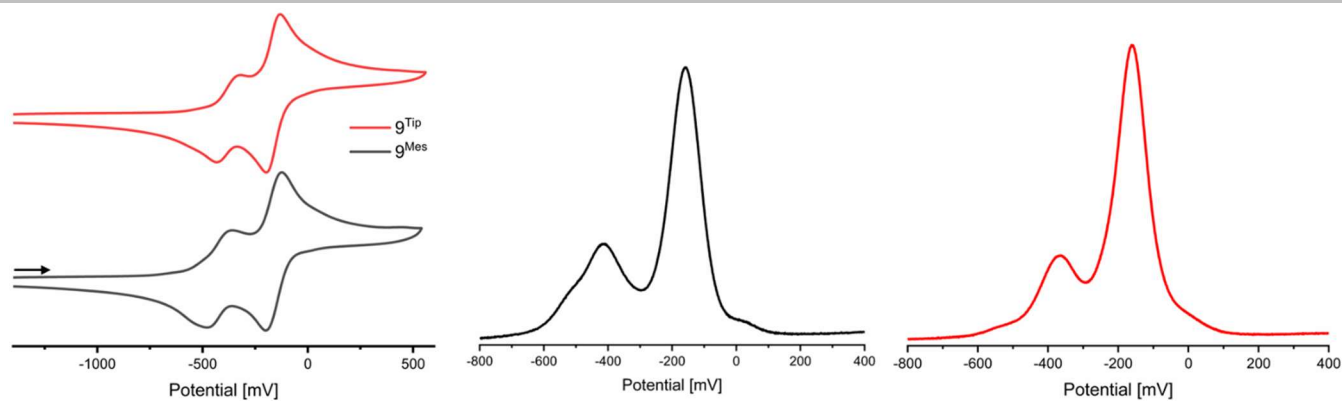


**Figure S65.** Cyclic voltammogram (left) and square wave voltammogram (middle, right) of  $7^{\text{Ar}}$  ( $\text{Ar} = \text{Mes}, \text{Tip}$ ) recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .

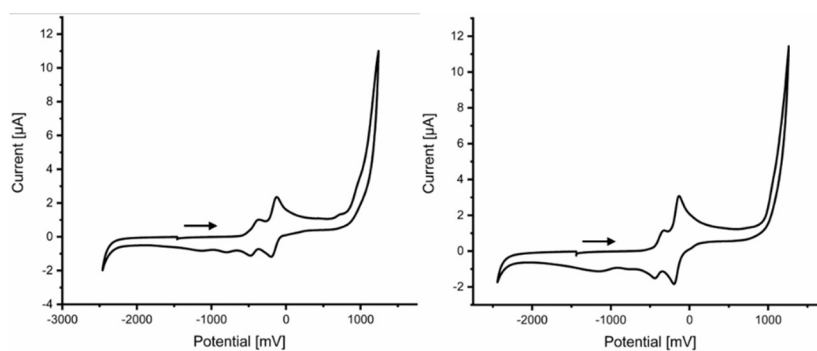


**Figure S66.** Cyclic voltammogram of  $1^{\text{Mes}}$  (left),  $1^{\text{Tip}}$  (right) recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .

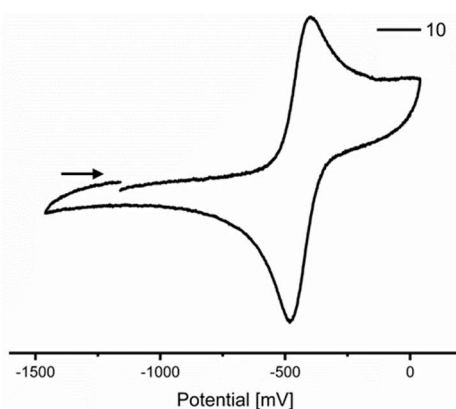
## SUPPORTING INFORMATION



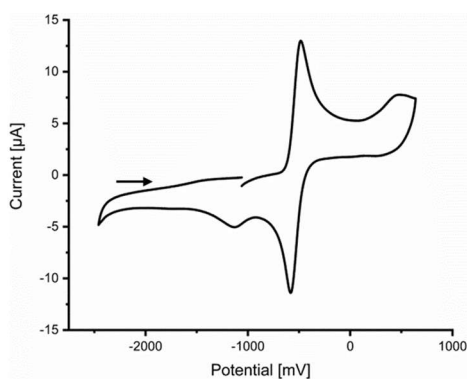
**Figure S67.** Cyclic voltammogram (left) and square wave voltammogram (middle, right) of  $9^{\text{Ar}}$  (Ar = Mes, Tip) recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .



**Figure S68.** Cyclic voltammogram of  $9^{\text{Mes}}$  (left),  $9^{\text{Tip}}$  (right) recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .

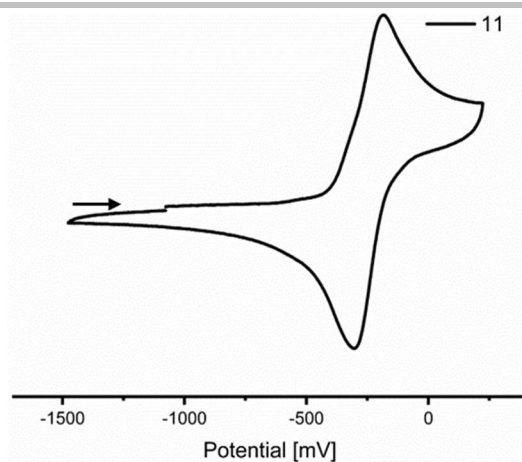


**Figure S69.** Cyclic voltammogram of **10** recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .

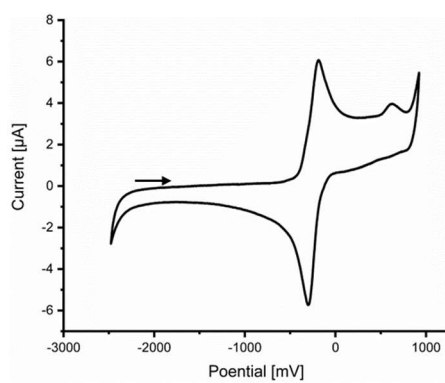


**Figure S70.** Cyclic voltammogram of **10** recorded in DCM containing 0.1 M  $[n\text{-Bu}_4\text{N}][\text{PF}_6]$  and referenced to  $[\text{Fc}]^{0/+}$ ; scan rate:  $250 \text{ mVs}^{-1}$ .

## SUPPORTING INFORMATION



**Figure S71.** Cyclic voltammogram of **11** recorded in DCM containing 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] and referenced to [Fc]<sup>0/+</sup>; scan rate: 250 mVs<sup>-1</sup>.



**Figure S72.** Cyclic voltammogram of **11** recorded in DCM containing 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] and referenced to [Fc]<sup>0/+</sup>; scan rate: 250 mVs<sup>-1</sup>.



## SUPPORTING INFORMATION

### X-ray crystallography

Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen or polyimide microloops. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-K $\alpha$  radiation. The crystals were cooled using an Oxford Cryostreams low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)<sup>[10]</sup> and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against  $F^2$  of all data, using SHELXL<sup>[11]</sup> software and the SHELXLE graphical user interface.<sup>[12]</sup> Crystal data and experimental details are listed in Table S1 and Table S2; full structural information has been deposited with the Cambridge Crystallographic Data Centre. CCDC-2374123 – 2374126.

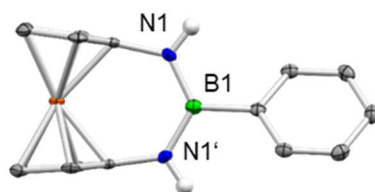
Table S1. Single crystal X-ray diffraction data and structure refinements of **2<sup>Ph</sup>** and **2<sup>Mes</sup>**.

| Compound  | <b>2<sup>Ph</sup></b>                             | <b>2<sup>Mes</sup></b>                            |
|---|---|---|
| CCDC number   | 2374123   | 2374124   |
| Empirical formula   | C <sub>16</sub> H <sub>15</sub> BFeN <sub>2</sub> | C <sub>19</sub> H <sub>21</sub> BFeN <sub>2</sub> |
| $M_r$   | 301.96  | 344.04  |
| $T / K$   | 100(2)  | 100(2)  |
| Radiation, $\lambda / \text{\AA}$                           | MoK $\alpha$ , 0.71073                            | MoK $\alpha$ , 0.71073                            |
| Crystal size / mm <sup>3</sup>                              | 0.188 x 0.210 x 0.689                             | 0.148 x 0.174 x 0.388                             |
| Crystal color, habit  | orange, block                                     | orange, needle                                    |
| Crystal system  | monoclinic  | monoclinic  |
| Space group   | C 2/c   | P 21/c  |
| $a / \text{\AA}$  | 11.325(3)   | 11.157(5)   |
| $b / \text{\AA}$  | 12.058(4)   | 17.255(6)   |
| $c / \text{\AA}$  | 10.190(4)   | 17.651(8)   |
| $\alpha / ^\circ$   | 90  | 90  |
| $\beta / ^\circ$  | 110.437(12)                                       | 104.88(3)   |
| $\gamma / ^\circ$   | 90  | 90  |
| Volume / $\text{\AA}^3$                                     | 1304.0(7)   | 3284(2)   |
| $Z$   | 4   | 8   |
| $\rho_{\text{calc}} / \text{g cm}^{-3}$                     | 1.538   | 1.392   |
| $\mu / \text{mm}^{-1}$                                      | 1.144   | 0.918   |
| $F(000)$  | 624   | 1440  |
| $\theta$ range / $^\circ$                                   | 2.557 – 26.409                                    | 1.679 – 26.536                                    |
| Completeness  | 1.000   | 0.990   |
| Reflections collected                                       | 8616  | 34121   |
| Unique reflections  | 1294  | 4854  |
| $R_{\text{int}}$  | 0.0349  | 0.0833  |
| Parameters / restraints                                     | 93 / 0  | 421 / 0   |
| GooF on $F^2$   | 1.134   | 1.027   |
| $R_1 [I \geq 2\sigma(I)]$                                   | 0.0277  | 0.0454  |
| $wR_2$ [all data]   | 0.0714  | 0.1125  |
| Max. / min. residual electron density / $e \text{\AA}^{-3}$ | 0.828 / -0.250                                    | 0.666 / -0.366                                    |

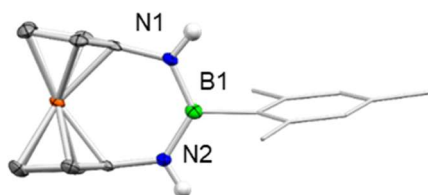
## SUPPORTING INFORMATION

Table S2. Single crystal X-ray diffraction data and structure refinements of **4<sup>TIP</sup>** and **7<sup>Mes</sup>**.

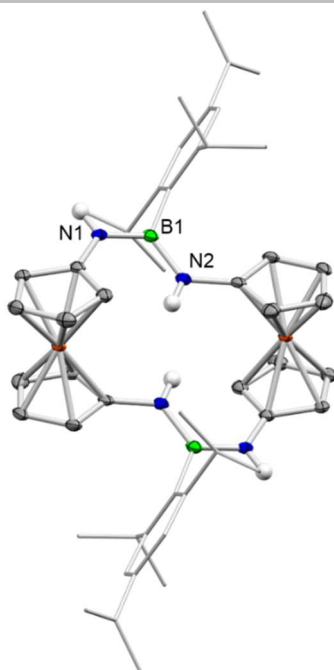
| Compound  | <b>4<sup>TIP</sup></b>  | <b>7<sup>Mes</sup></b>   |
|---|---|--|
| CCDC number   | 2374215   | 2374216  |
| Empirical formula   | C <sub>50</sub> H <sub>66</sub> B <sub>2</sub> Fe <sub>2</sub> N <sub>4</sub> | C <sub>29</sub> H <sub>31</sub> B Fe <sub>2</sub> N <sub>2</sub> |
| <i>M<sub>r</sub></i>                                      | 856.38  | 530.07   |
| <i>T</i> / K  | 100(2)  | 100(2)   |
| Radiation, $\lambda$ / Å                                  | MoK $\alpha$ , 0.71073  | MoK $\alpha$ , 0.71073   |
| Crystal size / mm <sup>3</sup>                            | 0.141 x 0.145 x 0.453   | 0.280 x 0.377 x 0.595  |
| Crystal color, habit                                      | yellow, block   | orange, block  |
| Crystal system  | triclinic   | monoclinic   |
| Space group   | P -1  | P 21/n   |
| <i>a</i> / Å  | 8.9103(19)  | 11.278(2)  |
| <i>b</i> / Å  | 11.730(3)   | 11.1383(15)  |
| <i>c</i> / Å  | 12.368(4)   | 19.453(6)  |
| $\alpha$ / °  | 65.001(13)  | 90   |
| $\beta$ / °   | 71.807(16)  | 95.180(12)   |
| $\gamma$ / °  | 78.23(3)  | 90   |
| Volume / Å <sup>3</sup>                                   | 1109.2(5)   | 2433.6(10)   |
| <i>Z</i>  | 1   | 4  |
| $\rho_{\text{calc}}$ / g cm <sup>-3</sup>                 | 1.282   | 1.447  |
| $\mu$ / mm <sup>-1</sup>                                  | 0.693   | 1.213  |
| <i>F</i> (000)  | 456   | 1104   |
| $\theta$ range / °  | 1.879 – 26.469  | 2.012 – 26.445   |
| Completeness  | 0.996   | 0.999  |
| Reflections collected                                     | 23488   | 35548  |
| Unique reflections  | 3961  | 4470   |
| <i>R</i> <sub>int</sub>                                   | 0.0428  | 0.0509   |
| Parameters / restraints                                   | 294 / 315   | 310 / 0  |
| Goof on <i>F</i> <sup>2</sup>                             | 1.056   | 1.035  |
| <i>R</i> <sub>1</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]        | 0.0420  | 0.0306   |
| w <i>R</i> <sub>2</sub> [all data]                        | 0.1024  | 0.0820   |
| Max. / min. residual electron density / e Å <sup>-3</sup> | 1.249 / -1.007  | 0.799 / -0.315   |



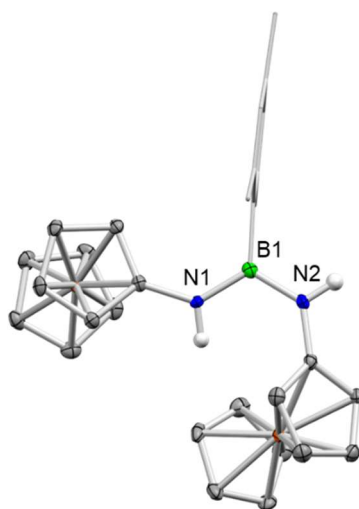
**Figure S73.** Structure of **2<sup>Ph</sup>** in the solid state in two different views (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bonded H omitted for clarity).



**Figure S74.** Structure of **2<sup>Mes</sup>** in the solid state in two different views (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bonded H omitted for clarity).



**Figure S75.** Structure of **4<sup>TP</sup>** in the solid state in two different views (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bonded H omitted for clarity).



**Figure S76.** Structure of **7<sup>Mes</sup>** in the solid state in two different views (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bonded H omitted for clarity).

### **Author Contributions**

J.S. carried out all syntheses and the characterization of the products, including X-ray crystal structure analyses. H.H. provided the resources and performed the conceptualization, funding acquisition, supervision, and administration of the project. The manuscript was written by J.S. and H.H.

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