

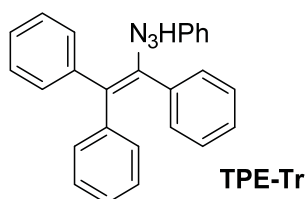
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## 1. Materials and methods

Unless otherwise stated, all *reactions* were carried out in oven-dried (110 °C) glassware under inert atmosphere of dry N<sub>2</sub> using Schlenk or glovebox techniques. All *reagents* were purchased from commercial suppliers (Sigma Aldrich, Acros, TCI, VWR, Fluorochem, ABCR) and used without additional purification. Dry *solvents* were obtained from a solvent purification system with aluminum oxide columns (Innovative Technologies). *Chromatography* was performed either manually using commercial silica gel (230–400 mesh) or on an automatic chromatography system (CombiFlash Nextgen 300+). *NMR* spectra were recorded at ambient temperature on a Bruker Avance 400 spectrometer with a BBFOz ATMA probe. Chemical shifts in ppm were aligned with respect to the residual peak of the deuterated solvent. Electrospray-ionisation *HRMS* data were acquired on a Q-ToF Ultima mass spectrometer (Waters) or a Q-ToF 6530 Accurate mass spectrometer (Agilent) operated in the positive ionization mode and fitted with a standard Z-spray ion source equipped with the Lock-Spray interface. Data from the Lock-Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Atmospheric pressure photo-ionisation (APPI) *HRMS* measurements were done on a LTQ-Orbitrap Elite instrument (ThermoFisher) operated in the positive ionization mode. *UV-Vis spectra* were recorded on a Cary 60 Spectrometer (Agilent Technologies). Quartz Suprasil cuvettes from Helma Analytics (10 x 10 mm) were used for solution spectrophotometric measurements. *Quantum yields* were measured with an Edinburgh FS5 fluorimeter equipped with an integrating sphere using powdered samples. *Quantum yields* were calculated using the Fluoracle software (Edinburgh).

## 2. Synthesis of the triazenes

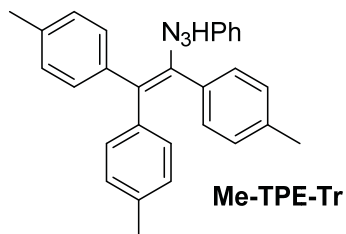
*Safety note: As many other azides, phenyl azide poses a risk of explosion, so a protective blast shield is recommended during the synthesis and purification. In the syntheses described below, PhN<sub>3</sub> was prepared following a literature procedure<sup>1</sup> and used undistilled.*



Triphenylethyne bromide (10.05 g, 30.00 mmol), magnesium powder (0.875 g, 36.00 mmol), and small amounts of I<sub>2</sub> (~0.01 eq.) were vigorously stirred in THF (30 mL) at 50 °C for 12 h. An excess of unreacted magnesium was removed by filtration. A solution of phenyl azide (4.284 g, 36.00 mmol) in THF (15 mL) was slowly added dropwise to the stirred solution of the Grignard reagent at RT (a color change to dark-red was observed). The reaction was stirred for 3 h at RT. Excess of water (20–30 mL) was added under vigorous stirring at 0 °C in air. After additional stirring at RT for 30 min, the reaction mixture was extracted with diethyl ether (3 x 100 mL). The organic phase was washed with brine, dried over MgSO<sub>4</sub>, and evaporated on rotary evaporator. The orange oily residue was exposed to high vacuum, which resulted into the formation of a yellow-orange foam. The product was recrystallized from a minimal volume of pentane at –20 °C. The product was filtered with suction, and washed with a small amount of cold pentane. The filtrate was concentrated, and recrystallization was repeated. Overall yield of **TPE-Tr** (yellow crystalline solid) from both recrystallizations = 9.300 g (83%). *Note: This and the following triazene reagents were stored in dark at –20 °C.*

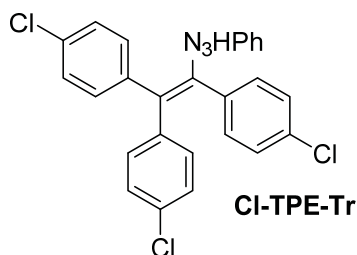
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.46 (br s, 1H), 7.48–7.22 (m, 12H), 7.16–6.98 (m, 8H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.2, 141.6, 140.9, 136.5, 131.5, 131.4, 131.2, 129.2, 128.6, 127.9, 127.8, 127.5, 126.4, 125.4, 118.5 (3 overlapped aromatic peaks). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 12.01 (s, 1H), 7.37–6.85 (m, 20H). <sup>13</sup>C NMR (100 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) δ 148.15, 141.90, 141.84, 141.37, 137.99, 136.76, 131.27, 131.06, 130.71, 129.10, 127.60, 127.53, 127.49, 126.88, 126.82, 126.36, 121.82, 113.66. HRMS (ESI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>22</sub>N<sub>3</sub><sup>+</sup> 376.1808; Found 376.1809. IR (film) cm<sup>-1</sup>: 3055, 3020, 2963, 1951, 1598, 1538, 1494, 1454, 1441, 1389, 1251,

1206, 1170, 747. **M.p.:** 103–107 °C (melts with decomposition). **Elem. Anal.** Calcd for C<sub>26</sub>H<sub>21</sub>N<sub>3</sub>: C, 83.17; H, 5.64; N, 11.19. Found: C, 83.73; H, 5.32; N, 10.77.



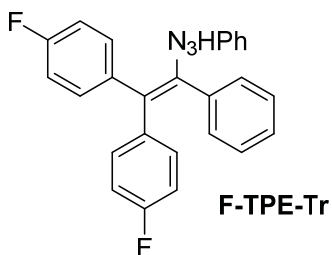
Product **Me-TPE-Tr** was obtained following the procedure described for **TPE-Tr** using tritolylolethynyl bromide<sup>2</sup> (377 mg, 1.00 mmol), Mg (30.0 mg, 1.20 mmol), and phenyl azide (143 mg, 1.20 mmol). Yield (yellow solid) = 183 mg (44%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.35 (s, 1H), 7.26–7.16 (m, 8H), 7.09–7.03 (m, 5H), 6.89–6.83 (m, 4H), 2.38 (s, 3H), 2.34 (s, 3H), 2.24 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.93, 138.29, 137.33, 137.18, 135.87, 133.53, 131.31, 131.24, 131.11, 129.28, 129.15, 128.66, 128.49, 125.32, 118.68, 21.55 (CH<sub>3</sub>), 21.42 (CH<sub>3</sub>), 21.30 (CH<sub>3</sub>) (3 overlapping aromatic peaks). **HRMS** (APCI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>28</sub>N<sub>3</sub><sup>+</sup> 418.2278; Found 418.2273.



Product **Cl-TPE-Tr** was obtained following the procedure described for **TPE-Tr** using tri(4-chlorophenyl)ethynyl bromide<sup>2</sup> (437 mg, 1.00 mmol), Mg (30.0 mg, 1.20 mmol), and phenyl azide (143 mg, 1.20 mmol). Yield (yellow solid) = 260 mg (50%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.36 (s, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.29–7.21 (m, 7H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 139.50, 138.87, 134.81, 133.89, 133.75, 132.85, 132.69, 132.65, 132.60, 129.42, 128.69, 128.45, 128.35, 125.22, 117.42 (3 overlapping aromatic peaks). **HRMS** (APCI/QTOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>19</sub>Cl<sub>3</sub>N<sub>3</sub><sup>+</sup> 478.0639; Found 478.0638.



Product **F-TPE-Tr** was obtained following the procedure described for **TPE-Tr** using tri(4-fluorophenyl)ethenyl bromide<sup>2</sup> (742 mg, 2.00 mmol), Mg (58.0 mg, 2.40 mmol), and phenyl azide (286 mg, 2.40 mmol). Yield (yellow solid) = 481 mg (59%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.34 (s, 1H), 7.30–7.21 (m, 10H), 7.10–7.04 (m, 4H), 6.94–6.91 (m, 2H), 6.77 (t, *J* = 8.7, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.08 (d, *J* = 72.9 Hz), 162.62 (d, *J* = 72.2 Hz), 137.51 (d, *J* = 3.3 Hz), 136.76 (d, *J* = 3.3 Hz), 136.47, 133.04, 132.96, 132.88, 131.37, 129.28, 128.03, 127.84, 125.05, 117.65, 115.43 (d, *J* = 21.4 Hz), 114.86 (d, *J* = 21.4 Hz) (3 overlapping aromatic peaks). HRMS (ESI/QTOF) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>20</sub>F<sub>2</sub>N<sub>3</sub><sup>+</sup> 412.1620; Found 412.1620.

### 3. Synthesis of the tetraarylethens

#### General Procedure 1 (GP1)

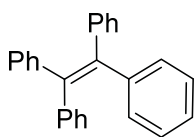
The triazene reagent (1–2.5 equiv.) and the corresponding arene (1–20 equiv.) were dissolved in DCM (0.1–0.2 M). Subsequently, triflic acid (TfOH) (2–5 equiv.) was added dropwise under vigorous stirring at RT. *The reaction is accompanied by an instantaneous color change together with active gas evolution.* After 1 h stirring at RT, the reaction mixture was filtered over a short pad of silica, and the pad was washed with DCM. After removal of all volatiles, the product was either sufficiently pure according to NMR, or it was additionally purified as described below.

#### General Procedure 2 (GP2) for heteroarenes

The triazene reagent (1 equiv.) was dissolved in the corresponding heteroarene (0.2 M). Subsequently, trifluoroacetic acid (TFA) (5 equiv.) was added dropwise under vigorous stirring at RT. *The reaction is accompanied by an instantaneous color change together with active gas evolution.* After 1 h stirring at RT, dry  $K_2CO_3$  (ca. 5 equiv.) was added under air, and the mixture was stirred for additional 30 min. The mixture was filtered through cotton wool in a Pasteur pipette, evaporated and purified as described below.

#### General Procedure 3 (GP3) for benzocrown ethers

See below the synthesis of **25**.

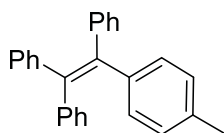


1,1,2,2-tetraphenylethene

**1**

This product was obtained following the **GPI** using **TPE-Tr** (38 mg, 0.1 mmol), benzene (180  $\mu\text{L}$ , 2 mmol, 20 equiv.) and TfOH (44  $\mu\text{L}$ , 0.5 mmol) in DCM (0.5 mL). Yield (colorless solid) = 31 mg (95%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10–7.13 (m, 12H), 7.05–7.08 (m, 8H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.85, 141.09, 131.46, 127.77, 126.54. **UV-vis** (THF,  $5 \cdot 10^{-5}$  M):  $\lambda_{\text{max}} = 310$  nm,  $\epsilon = 15600 \text{ M}^{-1} \cdot \text{cm}^{-1}$ . The NMR data are in agreement with those reported in the literature.<sup>3</sup>



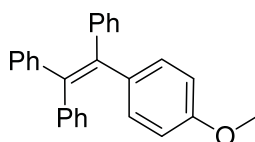
(2-(*p*-tolyl)ethene-1,1,2-triyl)tribenzene

**2**

para/meta/ortho = 75/10/15 (determined by  $^1\text{H NMR}$ )

This product was obtained following the **GPI** using **TPE-Tr** (75 mg, 0.2 mmol), toluene (424  $\mu\text{L}$ , 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). Yield (colorless solid) = 54 mg (78%). NMR data below are presented only for the major isomer.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15–6.90 (m, 19H), 2.26 (s, 3H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.08, 141.03, 140.86, 140.59, 136.18, 131.48, 131.44, 131.35, 128.50, 127.78, 127.73, 126.45, 126.41, 21.33. **UV-vis** (THF,  $1.4 \cdot 10^{-5}$  M):  $\lambda_{\text{max}} = 310$  nm,  $\epsilon = 17850 \text{ M}^{-1} \cdot \text{cm}^{-1}$ . The NMR data are in agreement with those reported in the literature.<sup>3</sup>

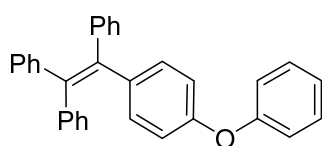


(2-(4-methoxyphenyl)ethene-1,1,2-triyl)tribenzene

**3**

This product was obtained following the **GP1** using **TPE-Tr** (75 mg, 0.2 mmol), anisole (434  $\mu\text{L}$ , 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). Yield (colorless solid) = 69 mg (95%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13–7.01 (m, 15H), 6.94 (d,  $J$  = 8.7 Hz, 1H), 6.64 (d,  $J$  = 9.6 Hz, 1H), 3.74 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.22, 144.17, 144.13, 140.66, 140.23, 136.25, 132.66, 131.52, 131.50, 131.47, 127.85, 127.73, 126.48, 126.37, 126.36, 113.17, 55.22. UV-vis (THF,  $4 \cdot 10^{-5}$  M):  $\lambda_{\text{max}}$  = 315 nm,  $\epsilon$  =  $13750 \text{ M}^{-1} \cdot \text{cm}^{-1}$ . The NMR data are in agreement with those reported in the literature.<sup>3</sup>

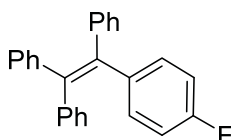


(2-(4-phenoxyphenyl)ethene-1,1,2-triyl)tribenzene

**4**

This product was obtained following the **GP1** using **TPE-Tr** (75 mg, 0.2 mmol), diphenyl ether (635  $\mu\text{L}$ , 680 mg, 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). After removal of excess of diphenyl ether using short-path distillation under high vacuum, the residue was purified by column chromatography (gradient of hexane to hexane/EtOAc=10/1). Yield (colorless solid) = 68 mg (82%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.29 (m, 2H), 7.13–7.01 (m, 15H), 6.99–6.95 (m, 4H), 6.75–6.73 (m, 2H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.27, 155.72, 143.94, 143.85, 143.78, 140.96, 140.42, 138.92, 132.85, 131.48, 131.47, 131.46, 129.79, 127.85, 127.82, 127.78, 126.62, 126.57, 126.52, 123.28, 118.92, 118.19. HRMS (APPI/LTQ-Orbitrap)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{32}\text{H}_{24}\text{O}^+$  424.1822; Found 424.1832.



(2-(4-fluorophenyl)ethene-1,1,2-triyl)tribenzene

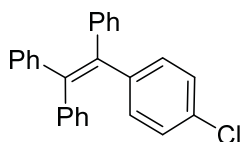
**5**

para/meta/ortho = 83/0/17 (determined by  $^{19}\text{F}$  NMR)



This product was obtained following the **GP1** using **TPE-Tr** (75 mg, 0.2 mmol), fluorobenzene (376  $\mu\text{L}$ , 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). Yield (pale yellow solid) = 42 mg (60%). NMR data below are presented only for the major isomer.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13–7.07 (m, 9H), 7.04–6.95 (m, 8H), 6.79 (t,  $J$  = 8.8 Hz, 1H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.75, 160.29, 143.70, 143.67, 143.63, 141.32, 139.95, 139.81, 139.78, 133.07, 132.99, 131.41, 127.93, 127.87, 127.81, 126.70, 126.66, 126.62, 114.87, 114.66.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.36 (ortho isomer, 0.17H), -115.60 (para isomer, 0.83H). The spectroscopic data are in agreement with those reported in the literature.<sup>4</sup>



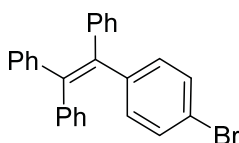
(2-(4-chlorophenyl)ethene-1,1,2-triyl)tribenzene

**6**

para/meta/ortho = 62/3/35 (determined by GC-MS)

This product was obtained following the **GP1** using **TPE-Tr** (75 mg, 0.2 mmol), chlorobenzene (407  $\mu\text{L}$ , 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). Yield (colorless solid) = 39 mg (53%). NMR data below are presented only for the major isomer.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15–6.95 (m, 19H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.56, 143.50, 143.43, 142.36, 141.72, 139.78, 132.77, 132.32, 131.42, 131.39, 131.38, 128.04, 128.00, 127.91, 127.82, 126.81, 126.77, 126.71. The spectroscopic data are in agreement with those reported in the literature.<sup>5</sup>



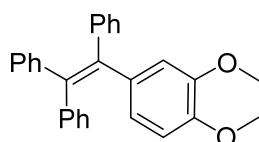
(2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene

**7**

para/meta/ortho = 62/5/33 (determined by GC-MS)

This product was obtained following the **GP1** using **TPE-Tr** (75 mg, 0.2 mmol), bromobenzene (420  $\mu\text{L}$ , 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). Yield (colorless solid) = 54 mg (66%). NMR data below are presented only for the major isomer.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 8.4$  Hz, 2H), 7.14–7.00 (m, 15H), 6.90 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.55, 143.46, 143.36, 142.84, 141.74, 139.79, 133.12, 131.43, 131.38, 131.36, 130.99, 128.02, 127.91, 127.82, 126.84, 126.78, 126.73, 120.58. The spectroscopic data are in agreement with those reported in the literature.<sup>3</sup>

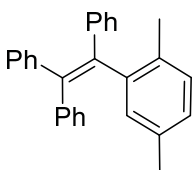


(2-(3,4-dimethoxyphenyl)ethene-1,1,2-triyl)tribenzene

**10**

This product was obtained following the **GPI** using **TPE-Tr** (450 mg, 1.2 mmol), veratrole (900  $\mu\text{L}$ , 7.1 mmol, 5.9 equiv.) and TfOH (300  $\mu\text{L}$ , 3.4 mmol) in DCM (5 mL). After removal of excess of veratrole using short-path distillation under high vacuum, the residue was suspended in hexane (ca. 4 mL), ultrasonicated for 10 min, and centrifuged. Precipitate was dried under high vacuum. Yield (colorless solid) = 390 mg (83%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.13–7.00 (m, 15H), 6.64–6.62 (m, 1H), 6.55–6.52 (m, 2H), 3.82 (s, 3H), 3.47 (s, 3H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.92, 147.69, 144.35, 143.97, 143.82, 140.81, 140.27, 136.28, 131.55, 131.45, 131.27, 127.96, 127.72, 127.71, 126.56, 126.43, 126.38, 124.09, 115.21, 110.32, 55.78, 55.64. **UV-vis** (THF,  $2 \cdot 10^{-5}$  M):  $\lambda_{\text{max}} = 325$  nm,  $\epsilon = 17500 \text{ M}^{-1} \cdot \text{cm}^{-1}$ . The NMR data are in agreement with those reported in the literature.<sup>6</sup>

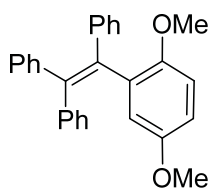


(2-(2,5-dimethylphenyl)ethene-1,1,2-triyl)tribenzene

**11**

This product was obtained following the **GPI** using **TPE-Tr** (75 mg, 0.2 mmol), p-xylene (493  $\mu\text{L}$ , 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). Excess of p-xylene was removed by short-path distillation under high vacuum. The residue was dissolved in DCM and passed over a short pad of silica in a Pasteur pipette. Removal of the solvent gave the desired product. Yield (colorless solid) = 54 mg (75%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.15–7.13 (m, 3H), 7.10–7.04 (m, 8H), 6.99–6.97 (m, 4H), 6.92–6.86 (m, 3H), 2.17 (s, 3H), 2.05 (s, 3H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 143.72, 143.59, 143.01, 142.78, 141.52, 140.31, 134.73, 133.39, 132.32, 131.59, 130.78, 130.65, 130.04, 127.86, 127.74, 127.67, 127.43, 126.60, 126.51, 126.27, 21.01, 19.84. **HRMS** (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>24</sub><sup>+</sup> 360.1873; Found 360.1873.

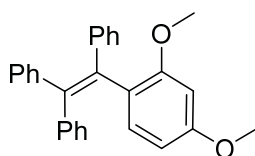


(2-(2,5-dimethoxyphenyl)ethene-1,1,2-triyl)tribenzene

**12**

This product was obtained following the **GPI** using **TPE-Tr** (75 mg, 0.2 mmol), 1,4-dimethoxybenzene (552 mg, 4 mmol, 20 equiv.) and TfOH (88 μL, 1 mmol) in DCM (1 mL). Excess of 1,4-dimethoxybenzene was removed by sublimation under high vacuum. The residue was dissolved in DCM and passed over a short pad of silica in a Pasteur pipette. Removal of the solvent gave the desired product. Yield (colorless solid) = 65 mg (83%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.12–7.03 (m, 15H), 6.67–6.65 (m, 2H), 6.60–6.58 (m, 1H), 3.59 (s, 3H), 3.36 (s, 3H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.38, 152.08, 144.05, 143.23, 143.14, 141.93, 137.38, 134.30, 131.53, 130.58, 130.47, 127.71, 127.48, 127.45, 126.53, 126.49, 126.16, 118.06, 113.42, 113.09, 77.48, 77.16, 76.84, 56.34, 55.82. **HRMS** (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>24</sub>O<sub>2</sub><sup>+</sup> 392.1771; Found 392.1771. **UV-vis** (THF, 2·10<sup>-5</sup> M): λ<sub>max</sub> = 300 nm, ε = 15500 M<sup>-1</sup>·cm<sup>-1</sup>.



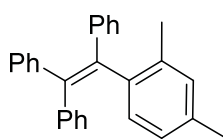
(2-(2,4-dimethoxyphenyl)ethene-1,1,2-triyl)tribenzene

**13**

This product was obtained following the **GPI** using **TPE-Tr** (75 mg, 0.2 mmol), 1,3-dimethoxybenzene (521 μL, 4 mmol, 20 equiv.) and TfOH (88 μL, 1 mmol) in DCM (1 mL).

Excess of 1,3-dimethoxybenzene was removed by short-path distillation under high vacuum. The residue was dissolved in DCM and passed over a short pad of silica in a Pasteur pipette. Removal of the solvent gave the desired product. Yield (colorless solid) = 70 mg (90%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10–7.00 (m, 3H), 6.91 (d,  $J = 7.9$  Hz, 1H), 6.32–6.29 (m, 2H), 3.75 (s, 3H), 3.41 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$   $\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.08, 158.52, 144.46, 143.73, 143.60, 141.56, 137.16, 132.95, 131.59, 130.65, 130.50, 127.66, 127.405, 127.396, 126.35, 126.22, 126.18, 126.00, 104.39, 99.12, 55.50, 55.33. **HRMS** (APPI/LTQ-Orbitrap)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{28}\text{H}_{24}\text{O}_2^+$  392.1771; Found 392.1774.

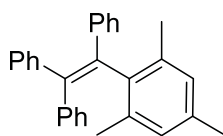


(2-(2,4-dimethylphenyl)ethene-1,1,2-triyl)tribenzene

**14**

This product was obtained following the **GP1** using **TPE-Tr** (38 mg, 0.1 mmol), *m*-xylene (246  $\mu\text{L}$ , 2 mmol, 20 equiv.) and TfOH (4  $\mu\text{L}$ , 0.5 mmol) in DCM (1 mL). Yield (colorless solid) = 25 mg (70%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.15–7.11 (m, 3H), 7.09–7.03 (m, 8H), 6.99–6.94 (m, 5H), 6.85 (s, 1H), 6.82 (d,  $J = 7.8$  Hz, 1H), 2.25 (s, 3H), 2.05 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$   $\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.87, 143.64, 143.15, 141.53, 140.32, 140.16, 136.44, 136.39, 131.72, 131.61, 131.00, 130.80, 130.70, 127.85, 127.66, 127.50, 126.58, 126.45, 126.33, 126.25, 21.25, 20.28. **HRMS** (APPI/LTQ-Orbitrap)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{28}\text{H}_{24}^+$  360.1873; Found 360.1878.

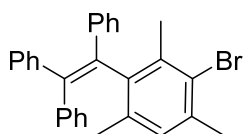


(2-mesitylethene-1,1,2-triyl)tribenzene

**15**

This product was obtained following the **GP1** using **TPE-Tr** (75 mg, 0.2 mmol), mesitylene (556  $\mu\text{L}$ , 4 mmol, 20 equiv.) and TfOH (88  $\mu\text{L}$ , 1 mmol) in DCM (1 mL). Yield (colorless solid) = 74 mg (99%).

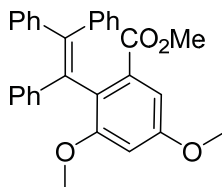
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.16–7.14 (m, 3H), 7.11–7.09 (m, 2H), 7.05–7.01 (m, 6H), 6.96–6.91 (m, 4H), 6.72 (s, 2H), 2.21 (s, 3H), 2.15 (s, 6H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 143.74, 143.69, 141.99, 141.65, 139.22, 138.52, 136.43, 136.37, 131.62, 130.53, 129.82, 128.47, 127.95, 127.57, 127.35, 126.69, 126.68, 126.18, 21.19, 20.68. **HRMS** (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>26</sub><sup>+</sup> 374.2029; Found 374.2030. **UV-vis** (THF, 2.2·10<sup>-5</sup> M): λ<sub>max</sub> = 305 nm, ε = 15450 M<sup>-1</sup>·cm<sup>-1</sup>.



(2-(3-bromo-2,4,6-trimethylphenyl)ethene-1,1,2-triyl)tribenzene  
**16**

This product was obtained following the **GPI** using **TPE-Tr** (53 mg, 0.14 mmol), bromomesitylene (200 μL, 1.3 mmol, 10 equiv.) and TfOH (44 μL, 0.5 mmol) in DCM (0.5 mL). Excess of bromomesitylene was removed by short-path distillation under high vacuum. The residue was dissolved in DCM and passed over a short pad of silica in a Pasteur pipette. Removal of the solvent gave the desired product which was recrystallized from pentane by slow evaporation. Yield (colorless cubic crystals) = 55 mg (88%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.17–6.89 (m, 15H), 6.81 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.14 (s, 3H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 143.38, 143.25, 142.15, 141.42, 141.20, 138.31, 136.81, 136.47, 135.12, 131.46, 130.47, 129.95, 129.63, 128.03, 127.70, 127.55, 126.95, 126.90, 126.45, 125.70, 24.09, 21.96, 20.48. **HRMS** (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>25</sub>Br<sup>+</sup> 452.1134; Found 452.1141.

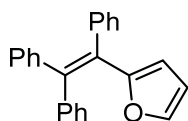


methyl 3,5-dimethoxy-2-(1,2,2-triphenylvinyl)benzoate  
**17**

This product was obtained following the **GPI** using **TPE-Tr** (45 mg, 0.12 mmol), methyl 2,6-dimethoxy benzoate (20 mg, 0.1 mmol) and TfOH (44 μL, 0.5 mmol) in DCM (0.5 mL). The crude

product was purified by column chromatography (gradient of hexane to hexane/EtOAc=10/1). Yield (colorless solid) = 31 mg (69%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12–6.97 (m, 15H), 6.72 (d,  $J = 2.4$  Hz, 1H), 6.44 (d,  $J = 2.4$  Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.54 (s, 3H).  $^{13}\text{C}$   $\{^1\text{H}\}$   $\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.21, 159.48, 159.00, 144.02, 143.44, 142.73, 141.24, 135.00, 133.52, 131.48, 130.85, 129.85, 127.68, 127.35, 127.18, 126.81, 126.56, 126.42, 125.96, 105.11, 102.49, 55.98, 55.53, 52.22. **HRMS** (APPI/LTQ-Orbitrap)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_4^+$  450.1826; Found 450.1837.

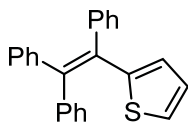


2-(1,2,2-triphenylvinyl)furan

**18**

This product was obtained following the **GP2** using **TPE-Tr** (38 mg, 0.1 mmol) and TFA (38  $\mu\text{L}$ , 0.5 mmol) in furane (1 mL). The product was obtained by recrystallization from MeOH at  $-20$   $^\circ\text{C}$ . Yield (colorless crystals) = 15 mg (48%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25–7.15 (m, 11H), 7.08–7.05 (m, 3H), 6.99–6.97 (m, 2H), 6.24 (dd,  $J = 3.3, 1.8$  Hz, 1H), 5.81 (dd,  $J = 3.3, 0.6$  Hz, 1H).  $^{13}\text{C}$   $\{^1\text{H}\}$   $\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.63, 144.17, 143.01, 141.57, 141.46, 140.82, 131.42, 131.33, 130.31, 128.06, 127.87, 127.72, 127.13, 127.02, 126.68, 112.20, 111.01. **HRMS** (APPI/LTQ-Orbitrap)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{24}\text{H}_{18}\text{O}^+$  322.1352; Found 322.1351.



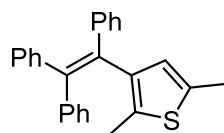
2-(1,2,2-triphenylvinyl)thiophene

**19**

$\alpha/\beta = 80/20$  (determined by  $^1\text{H NMR}$ )

This product was obtained following the **GP2** using **TPE-Tr** (38 mg, 0.1 mmol) and TFA (38  $\mu\text{L}$ , 0.5 mmol) in thiophene (1 mL). The crude product was triturated with a small amount of MeOH (1-2 mL). Yield (pale yellow solid) = 12 mg (37%). NMR data below are presented only for the major isomer.

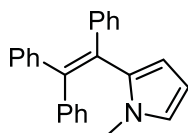
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.25–6.96 (m, 16H), 6.77 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.57 (dd, *J* = 3.6, 1.2 Hz, 1H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 146.50, 143.74, 143.30, 143.28, 141.29, 134.08, 131.40, 131.10, 131.00, 129.69, 128.36, 127.83, 127.71, 127.23, 127.06, 126.51, 126.25, 126.19. **HRMS** (nanochip-ESI/LTQ-Orbitrap) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>18</sub>S<sup>+</sup> 338.1124; Found 338.1119. The spectroscopic data are in agreement with those reported in the literature.<sup>7</sup>



2,5-dimethyl-3-(1,2,2-triphenylvinyl)thiophene  
**20**

This product was obtained following the **GP2** using **TPE-Tr** (38 mg, 0.1 mmol) and TFA (38 μL, 0.5 mmol) in 2,5-dimethylthiophene (1 mL). The crude product was purified by column chromatography (hexane/EtOAc=20/1). Yield (pale yellow solid) = 17 mg (37%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.12–7.01 (m, 15H), 6.25 (s, 1H), 2.29 (s, 3H), 1.88 (s, 3H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.05, 143.52, 142.92, 142.19, 139.54, 135.56, 135.04, 133.49, 131.66, 130.74, 130.69, 128.35, 127.81, 127.71, 127.60, 126.61, 126.53, 126.44, 15.34, 14.03. **HRMS** (APPI/LTQ-Orbitrap) *m/z*: [M]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>22</sub>S<sup>+</sup> 366.1437; Found 366.1445.

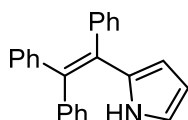


1-methyl-2-(1,2,2-triphenylvinyl)-1*H*-pyrrole  
**21**  
*α*/*β* = 70/30 (determined by <sup>1</sup>H NMR)

This product was obtained following the **GP2** using **TPE-Tr** (38 mg, 0.1 mmol) and TFA (38 μL, 0.5 mmol) in *N*-methylpyrrole (1 mL). The crude product was triturated by small amount of MeOH (1-2 mL). Yield (colorless solid) = 33 mg (99%).

**<sup>1</sup>H NMR-*α* isomer** (400 MHz, CDCl<sub>3</sub>) δ 7.30–7.00 (m, 18H), 6.48–6.45 (m, 1H), 6.02–6.01 (m, 1H), 5.80–5.78 (m, 1H). **<sup>1</sup>H NMR-*β* isomer** (400 MHz, CDCl<sub>3</sub>) δ 7.30–7.00 (m, 18H), 6.30–6.29 (m, 1H), 5.98–5.96 (m, 1H), 5.45–5.43 (m, 1H). **<sup>13</sup>C {<sup>1</sup>H} NMR-both isomers** (100 MHz, CDCl<sub>3</sub>) δ 145.26, 144.40, 144.36, 144.21, 143.36, 142.79, 142.54, 136.39, 135.33, 135.29,

132.20, 131.68, 131.62, 131.17, 131.01, 130.87, 130.52, 128.29, 127.89, 127.75, 127.70, 127.48, 127.44, 126.69, 126.62, 126.47, 126.43, 126.29, 125.56, 124.45, 122.00, 120.92, 111.87, 110.81, 107.76, 36.18 (beta), 34.62 (alpha). **HRMS** (ESI/QTOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{25}H_{22}N^+$  336.1747; Found 336.1737.



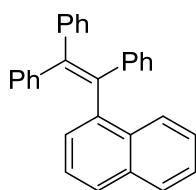
2-(1,2,2-triphenylvinyl)-1*H*-pyrrole

**22**

$\alpha/\beta$  = 85/15 (determined by  $^1H$  NMR)

This product was obtained following the **GP2** using **TPE-Tr** (375 mg, 1 mmol) and TFA (380  $\mu$ L, 5 mmol) in pyrrole (5 mL). After completion of the reaction, MeOH (3-4 mL) was added directly to the reaction mixture, resulting in precipitation of the product. The product was isolated by centrifugation, and washed with MeOH (1-2 mL) and pentane (1 mL). Yield (colorless solid) = 250 mg (78%).

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.56 (br m, 1H), 7.36–7.16 (m, 10H), 7.03–6.93 (m, 5H), 6.54–6.51 (m, 1H), 6.03 (dd,  $J$  = 6.0, 2.7 Hz, 1H), 5.72–5.68 (m, 1H).  $^{13}C$   $\{^1H\}$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  143.99, 143.57, 142.00, 136.40, 133.20, 132.32, 131.83, 131.12, 130.65, 128.84, 127.78, 127.62, 127.29, 127.04, 126.09, 118.38, 113.08, 108.58. **HRMS** (ESI/QTOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{24}H_{20}N^+$  322.1590; Found 322.1583. **UV-vis** (THF,  $3.3 \cdot 10^{-5}$  M):  $\lambda_{max}$  = 345 nm,  $\epsilon$  = 11515  $M^{-1} \cdot cm^{-1}$ . The NMR data are in agreement with those reported in the literature.<sup>8</sup>



1-(1,2,2-triphenylvinyl)naphthalene

**23**

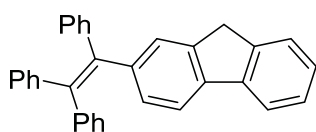
$\alpha/\beta$  = 87/13 (determined by GC-MS)

This product was obtained following the **GP1** using **TPE-Tr** (75 mg, 0.2 mmol), naphthalene (256 mg, 2 mmol, 10 equiv.) and TfOH (88  $\mu$ L, 1 mmol) in DCM (1 mL). Excess of naphthalene was



removed by sublimation under high vacuum. Yield (colorless solid) = 30 mg (43%). NMR data below are presented only for the major isomer.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01–7.99 (m, 1H), 7.72–7.70 (m, 1H), 7.64–7.61 (m, 1H), 7.33–7.29 (m, 2H), 7.26–7.25 (m, 2H), 7.17–7.10 (m, 5H), 7.07–7.00 (m, 5H), 6.92–6.85 (m, 5H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 143.80, 143.36, 143.19, 143.16, 141.26, 139.41, 133.86, 132.43, 131.59, 130.55, 130.15, 129.51, 128.38, 127.97, 127.81, 127.45, 126.81, 126.54, 126.51, 126.41, 126.01, 125.51, 125.39. The spectroscopic data are in agreement with those reported in the literature.<sup>9</sup>

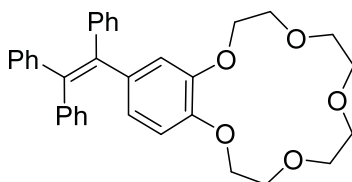


2-(1,2,2-triphenylvinyl)-9H-fluorene

**24**

This product was obtained following the **GPI** using **TPE-Tr** (38 mg, 0.1 mmol), fluorene (166 mg, 1 mmol, 10 equiv.) and TfOH (44 μL, 0.5 mmol) in DCM (1 mL). The product was isolated by column chromatography (gradient of hexane to hexane/EtOAc=10/1). First fractions contained unreacted excess of fluorene (146 mg, 98% recovered). Yield (colorless solid) = 30 mg (71%).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.29–7.04 (m, 18H), 3.72 (s, 2H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 144.09, 144.02, 144.01, 143.68, 142.79, 142.61, 141.70, 141.38, 141.02, 140.11, 131.57, 131.53, 131.49, 130.38, 128.07, 127.82, 127.80, 127.77, 126.83, 126.63, 126.55, 126.50, 126.49, 125.09, 119.95, 119.16, 36.91. **HRMS** (APPI/LTQ-Orbitrap) *m/z*: [M]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>24</sub><sup>+</sup> 420.1873; Found 420.1888. **UV-vis** (THF, 3·10<sup>-6</sup> M): λ<sub>max</sub> = 328 nm, ε = 31300 M<sup>-1</sup>·cm<sup>-1</sup>.

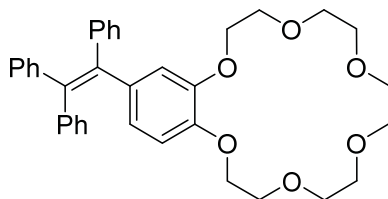


15-(1,2,2-triphenylvinyl)-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecine

**25**

Benzo-15-crown-5 (75 mg, 0.28 mmol) and **TPE-Tr** (125 mg, 0.33 mmol) were dissolved in DCM (1.7 mL). Triflic acid (147  $\mu$ L, 1.66 mmol) was added slowly and the resulting mixture was stirred at room temperature for 1 h. An instantaneous colour change along with a strong gas evolution was observed. The reaction mixture was quenched with a saturated Na<sub>2</sub>CO<sub>3</sub> solution (5 mL). The organic layer was washed with water (2 x 10 mL), dried over MgSO<sub>4</sub>, and the solvent was evaporated. The product was purified by column chromatography (EtOAc/hexane 1:1 then MeOH). Yield (pale yellow solid) = 102 mg (70%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20–6.94 (m, 15H), 6.61 (d, *J* = 8.2 Hz, 1H), 6.55 (d, *J* = 10.8 Hz, 2H), 4.08 (t, *J* = 4.4 Hz, 2H), 3.90 (t, *J* = 4.4 Hz, 2H), 3.81–3.68 (m, 12H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.11, 146.90, 144.04, 143.73, 143.52, 140.47, 140.34, 137.07, 131.40, 131.31, 131.17, 127.90, 127.63 (broad peak for 2 aromatic C), 126.51, 126.43, 126.35, 124.86, 117.00, 112.22, 70.21 (2 CH<sub>2</sub>), 69.91 (2 CH<sub>2</sub>), 68.65 (2 CH<sub>2</sub>), 67.83 (2 CH<sub>2</sub>). HRMS (ESI/QTOF) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>34</sub>NaO<sub>5</sub><sup>+</sup> 545.2298; Found 545.2314. UV-vis (THF):  $\lambda_{\text{max}}$  = 321 nm.

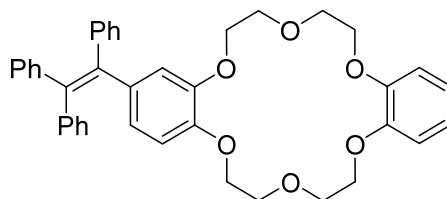


18-(1,2,2-triphenylvinyl)-2,3,5,6,8,9,11,12,14,15-decahydrobenzo[*b*][1,4,7,10,13,16]hexaoxacyclooctadecine

**26**

This product was obtained following the **GP3** using benzo-18-crown-6 (87 mg, 0.28 mmol), **TPE-Tr** (125 mg, 0.33 mmol), triflic acid (147  $\mu$ L, 1.66 mmol) and DCM (1.7 mL). Yield (pale beige solid) = 112 mg (71%).

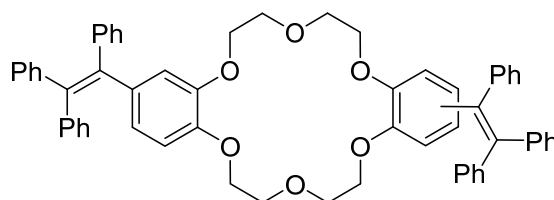
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.13–6.99 (m, 15H), 6.61 (d, *J* = 8.8 Hz, 1H), 6.54–6.50 (m, 2H), 4.09–4.07 (m, 2H), 3.90 (t, *J* = 4.5 Hz, 2H), 3.80–3.61 (m, 16H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.40, 147.26, 144.25, 143.93, 143.74, 140.67, 140.37, 136.84, 131.52, 131.45, 131.30, 127.98, 127.73, 127.72, 126.57, 126.47, 126.41, 124.65, 117.11, 112.33, 70.51 (br, 4 CH<sub>2</sub>), 69.43 (2 CH<sub>2</sub>), 69.22 (2 CH<sub>2</sub>), 68.20 (br, 2 CH<sub>2</sub>). HRMS (ESI/QTOF) *m/z*: [M + Na]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>38</sub>NaO<sub>6</sub><sup>+</sup> 589.2561; Found 589.2568.



2-(1,2,2-triphenylvinyl)-6,7,9,10,17,18,20,21-  
octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecine  
**27**

This product was obtained following the **GP3** using dibenzo-18-crown-6 (33 mg, 0.092 mmol), **TPE-Tr** (38 mg, 0.10 mmol), triflic acid (44  $\mu$ L, 0.50 mmol) and DCM (0.5 mL). The product was purified by column chromatography (EtOAc/hexane 1:1 then DCM/MeOH 96:4) Yield (pale beige solid) = 32 mg (56%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10–7.00 (m, 15H), 6.91–6.84 (m, 4H), 6.60–6.57 (m, 1H), 6.54–6.50 (m, 2H), 4.18–3.74 (m, 16H).  $^{13}\text{C}$   $\{^1\text{H}\}$   $\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.88, 147.65, 147.41, 144.26, 143.99, 143.81, 140.77, 140.28, 136.73, 131.53, 131.48, 131.31, 127.96, 127.73, 127.70, 126.54, 126.45, 126.39, 124.54, 121.46, 121.44, 116.95 (br, 2  $\text{C}_{\text{ar}}$ ), 113.76 (br, 2  $\text{C}_{\text{ar}}$ ), 112.24 (br, 2  $\text{C}_{\text{ar}}$ ), 70.05 (br, 2  $\text{CH}_2$ ), 69.76 (br, 2  $\text{CH}_2$ ), 68.86 (br, 2  $\text{CH}_2$ ), 68.43 (br, 2  $\text{CH}_2$ ). **HRMS** (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{40}\text{H}_{38}\text{NaO}_6^+$  637.2561; Found 637.2562.

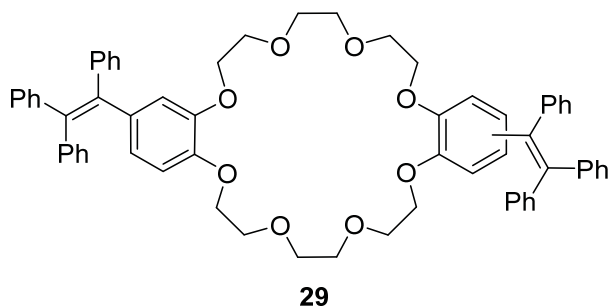


**28**

This product was obtained following the **GP3** using dibenzo-18-crown-6 (60 mg, 0.17 mmol), **TPE-Tr** (150 mg, 0.40 mmol), triflic acid (176  $\mu$ L, 2.0 mmol) and DCM (2 mL). The product was purified by column chromatography ( $\text{SiO}_2$ , EtOAc/hexane 1:1 then DCM/MeOH 98:2). Yield (pale beige solid) = 53 mg (37%).

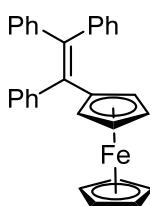
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.12–7.00 (m, 30H), 6.61 (d,  $J = 8.2$  Hz, 2H), 6.52 (d,  $J = 7.8$  Hz, 4H), 4.09–4.05 (m, 4H), 3.97–3.90 (m, 4H), 3.81–3.74 (m, 8H).  $^{13}\text{C}$   $\{^1\text{H}\}$   $\text{NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13C  $\text{NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.75, 147.49, 144.28, 144.02, 143.83, 140.81, 140.25, 136.73, 131.54, 131.49, 131.32, 127.95, 127.73, 127.70, 126.54, 126.43, 126.39, 124.54, 116.99, 112.33,

70.02, 69.96, 69.83, 69.77, 68.58, 68.50, 68.47, 68.39. **HRMS** (ESI/QTOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{60}H_{52}NaO_6^+$  891.3656; Found 891.3649. **UV-vis** (THF):  $\lambda_{max} = 323$  nm.



This product was obtained following the **GP3** using dibenzo-24-crown-8 (74 mg, 0.17 mmol), **TPE-Tr** (150 mg, 0.40 mmol), triflic acid (176  $\mu$ L, 2.0 mmol) and DCM (2 mL). The product was purified by column chromatography ( $SiO_2$ , EtOAc/hexane 1:1 then DCM/MeOH 98:2). Yield (pale yellow solid) = 130 mg (79%).

**$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.13–6.99 (m, 30H), 6.61–6.59 (m, 2H), 6.54–6.50 (m, 4H), 4.17–3.70 (m, 24H).  **$^{13}C$  { $^1H$ } NMR** (100 MHz,  $CDCl_3$ )  $\delta$  147.80, 147.62, 144.28, 143.97, 143.79, 140.75, 140.32, 136.85, 131.53, 131.47, 131.32, 127.95, 127.74, 127.72, 126.56, 126.46, 126.40, 124.66, 117.50, 112.76, 77.48, 77.16, 76.84, 71.49, 71.46, 71.36, 71.33, 70.03 (br, 2  $CH_2$ ), 69.83 (br, 2  $CH_2$ ), 69.32, 69.27, 69.24, 69.19. **HRMS** (ESI/QTOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{64}H_{60}NaO_8^+$  979.4180; Found 979.4175. **UV-vis** (THF):  $\lambda_{max} = 320$  nm.

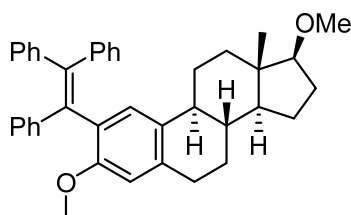


1,2,2-triphenylvinylferrocene  
**30**

This product was obtained following the **GP1** using **TPE-Tr** (38 mg, 0.1 mmol), ferrocene (186 mg, 1 mmol, 10 equiv.) and TfOH (44  $\mu$ L, 0.5 mmol) in DCM (1 mL). Excess of ferrocene was removed by sublimation under high vacuum. The product was purified by column chromatography (gradient of hexane to hexane/EtOAc=10/1). Yield (red-orange solid) = 25 mg (57%).

*Note: This product is air-sensitive. The NMR spectra were recorded under inert atmosphere in degassed CDCl<sub>3</sub>.*

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.44–7.01 (m, 15H), 4.12 (s, 5H), 4.04–4.03 (m, 2H), 3.47–3.46 (m, 2H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 144.77, 144.68, 142.69, 139.51, 138.86, 131.62, 130.41, 129.98, 129.23, 127.92, 127.83, 127.40, 126.78, 126.10, 86.25, 70.41, 69.87, 69.10. **HRMS** (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>30</sub>H<sub>24</sub>Fe<sup>+</sup> 440.1222; Found 440.1221. **UV-vis** (THF, 6·10<sup>-5</sup> M): λ<sub>max1</sub> = 300 nm, ε<sub>1</sub> = 8500 M<sup>-1</sup>·cm<sup>-1</sup>; λ<sub>max2</sub> = 461 nm, ε<sub>2</sub> = 550 M<sup>-1</sup>·cm<sup>-1</sup>.



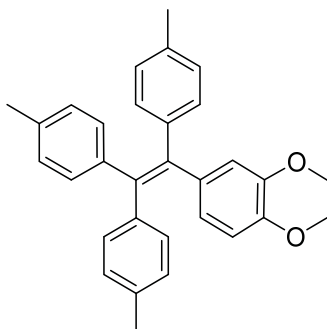
(8*R*,9*S*,13*S*,14*S*,17*S*)-3,17-dimethoxy-13-methyl-2-(1,2,2-triphenylvinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene

**31**

This product was obtained following the **GP1** using **TPE-Tr** (38 mg, 0.1 mmol), Me<sub>2</sub>-estradiol (150 mg, 0.5 mmol, 5 equiv.) and TfOH (44 μL, 0.5 mmol) in DCM (1 mL). The product was purified using a preparative TLC plate (SiO<sub>2</sub>, eluent: toluene). Yield (colorless solid) = 36 mg (64%).

*Note: Starting dimethyl-substituted estradiol derivative (Me<sub>2</sub>-estradiol) was obtained following the literature procedure.<sup>10</sup>*

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.10–7.01 (m, 15H), 6.86 (s, 1H), 6.40 (s, 1H), 3.37 (s, 3H), 3.36 (s, 3H), 3.27 (t, *J* = 8.3 Hz, 1H), 2.80–2.72 (m, 2H), 2.09–1.90 (m, 4H), 1.83–1.78 (m, 1H), 1.69–1.61 (m, 1H), 1.54–1.44 (m, 2H), 1.36–1.22 (m, 4H), 1.16–1.08 (m, 1H), 0.73 (s, 3H). **<sup>13</sup>C {<sup>1</sup>H} NMR** (100 MHz, CDCl<sub>3</sub>) δ 155.55, 144.50, 143.66, 143.58, 141.47, 138.19, 136.64, 132.28, 131.59, 130.56, 130.55, 130.34, 127.64, 127.40, 127.37, 126.30, 126.09, 125.92, 111.98, 90.95, 58.03, 55.71, 50.36, 43.78, 43.34, 38.70, 38.09, 29.77, 27.91, 27.29, 26.44, 23.19, 11.67. **HRMS** (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>40</sub>H<sub>42</sub>O<sub>2</sub><sup>+</sup> 554.3179; Found 554.3187.

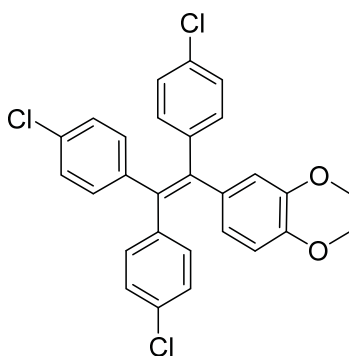


4,4',4''-(2-(3,4-dimethoxyphenyl)ethene-1,1,2-triyl)tris(methylbenzene)

**32**

This product was obtained following the **GP1** using **Me-TPE-Tr** (20 mg, 0.05 mmol), veratrole (130  $\mu$ L, 1 mmol, 20 equiv.) and TfOH (22  $\mu$ L, 0.25 mmol) in DCM (0.5 mL). Excess of veratrole was removed by short-path distillation under high vacuum. The product was purified using a preparative TLC plate (SiO<sub>2</sub>, eluent: hexane/EtOAc=10/1). Yield (colorless solid) = 18 mg (82%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.93–6.90 (m, 12H), 6.63–6.62 (m, 1H), 6.55–6.52 (m, 2H), 3.82 (s, 3H), 3.47 (s, 3H), 2.27 (s, 3H), 2.25 (s, 3H), 2.25 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  147.82, 147.44, 141.82, 141.33, 141.15, 139.83, 139.73, 136.98, 135.94, 135.83, 135.81, 131.42, 131.33, 131.22, 128.59, 128.45, 124.00, 115.34, 110.24, 55.77, 55.61, 21.35, 21.33, 21.25 (1 overlapped aromatic peak). **HRMS** (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>31</sub>H<sub>30</sub>O<sub>2</sub><sup>+</sup> 434.2240; Found 434.2240.



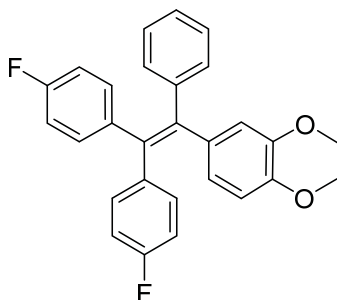
4,4',4''-(2-(3,4-dimethoxyphenyl)ethene-1,1,2-triyl)tris(chlorobenzene)

**33**

This product was obtained following the **GP1** using **Cl-TPE-Tr** (24 mg, 0.05 mmol), veratrole (130  $\mu$ L, 1 mmol, 20 equiv.) and TfOH (22  $\mu$ L, 0.25 mmol) in DCM (0.5 mL). Excess of veratrole was removed by short-path distillation under high vacuum. The product was purified using a

preparative TLC plate (SiO<sub>2</sub>, eluent: hexane/EtOAc=10/1). Yield (pale yellow solid) = 16 mg (64%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.12–6.90 (m, 12H), 6.65–6.63 (m, 1H), 6.52–6.45 (m, 2H), 3.83 (s, 3H), 3.53 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 148.28, 142.14, 141.67, 140.81, 138.24, 135.20, 132.87, 132.77, 132.74, 132.69, 132.68, 132.54, 128.39, 128.35, 128.28, 124.17, 114.78, 110.61, 55.87, 55.77 (2 overlapped aromatic peaks). HRMS (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>21</sub>Cl<sub>3</sub>O<sub>2</sub><sup>+</sup> 494.0602; Found 494.0616.

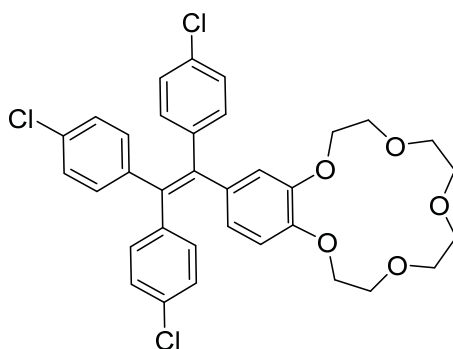


4,4'-(2-(3,4-dimethoxyphenyl)-2-phenylethene-1,1-diyl)bis(fluorobenzene)

**34**

This product was obtained following the **GP1** using **F-TPE-Tr** (41 mg, 0.1 mmol), veratrole (255 μL, 2 mmol, 20 equiv.) and TfOH (44 μL, 0.5 mmol) in DCM (0.5 mL). Excess of veratrole was removed by short-path distillation under high vacuum. The product was purified using a preparative TLC plate (SiO<sub>2</sub>, eluent: hexane/EtOAc=10/1). Yield (colorless solid) = 30 mg (70%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.13–7.11 (m, 3H), 7.04–6.99 (m, 6H), 6.85–6.76 (m, 4H), 6.65–6.63 (m, 1H), 6.54–6.50 (m, 2H), 3.83 (s, 3H), 3.52 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 162.74, 162.72, 160.29, 160.27, 148.13, 147.90, 143.49, 141.30, 140.07, 140.04, 139.71, 139.68, 137.99, 135.97, 133.03, 132.95, 132.89, 132.81, 131.43, 127.91, 126.79, 124.13, 115.10, 114.94, 114.92, 114.89, 114.73, 110.49, 55.83, 55.73. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -115.36, -115.42. HRMS (APPI/LTQ-Orbitrap) m/z: [M]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>22</sub>F<sub>2</sub>O<sub>2</sub><sup>+</sup> 428.1582; Found 428.1577.



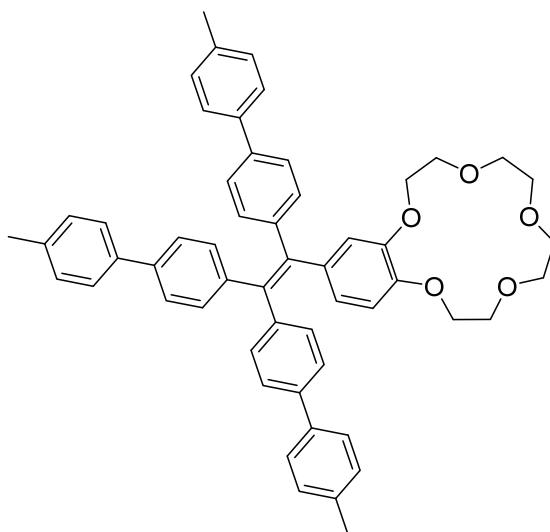
15-(1,2,2-tris(4-chlorophenyl)vinyl)-2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecine

**35**

This product was obtained following the **GP3** using benzo-15-crown-5 (22 mg, 0.08  $\mu\text{mol}$ ), **Cl-TPE-Tr** (48 mg, 0.1 mmol), triflic acid (44  $\mu\text{L}$ , 0.5 mmol) and DCM (0.5 mL). The product was purified by column chromatography ( $\text{SiO}_2$ , hexane/EtOAc 1:1 then DCM/MeOH 95:5). Yield (brown solid) = 25 mg, 48%.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10–7.08 (m, 6H), 6.94–6.89 (m, 6H), 6.62 (d,  $J = 8.3$  Hz, 1H), 6.52–6.45 (m, 2H), 4.11–4.06 (m, 2H), 3.88 (t,  $J = 4.3$  Hz, 2H), 3.80–3.67 (m, 12H).  $^{13}\text{C } \{^1\text{H}\}$  **NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.29, 148.27, 142.09, 141.68, 141.64, 140.75, 138.24, 135.64, 132.85, 132.77, 132.72, 132.70, 132.66, 132.58, 128.39, 128.35, 128.27, 124.73, 117.38, 112.94, 71.21 (br, 2  $\text{CH}_2$ ), 70.54 (2  $\text{CH}_2$ ), 69.55 (br, 2  $\text{CH}_2$ ), 68.83 (br, 2  $\text{CH}_2$ ). **HRMS** (ESI/QTOF)  $m/z$ :  $[\text{M} + \text{Na}]^+$  Calcd for  $\text{C}_{34}\text{H}_{31}\text{Cl}_3\text{NaO}_5^+$  647.1129; Found 647.1141.





15-(1,2,2-tris(4'-methyl-[1,1'-biphenyl]-4-yl)vinyl)-2,3,5,6,8,9,11,12-octahydrobenzo[*b*][1,4,7,10,13]pentaoxacyclopentadecine

**36**

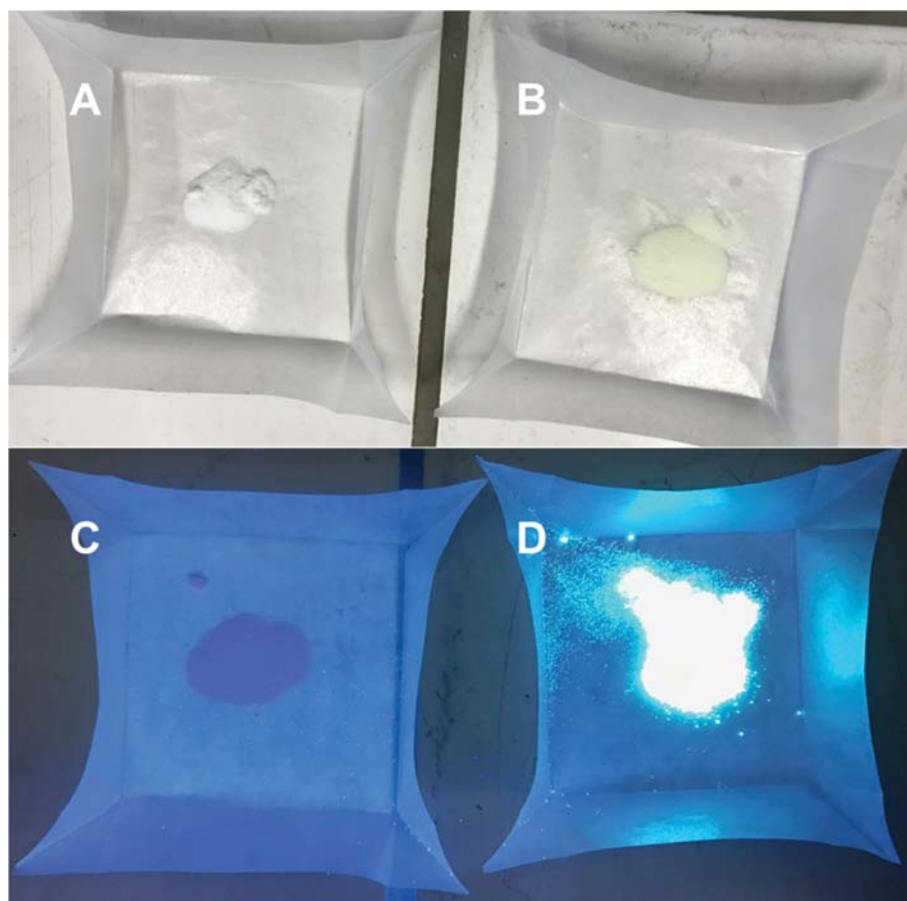
Cl-TPE-15-crown-5 (**35**) (25 mg, 40  $\mu$ mol), tolylboronic acid (65 mg, 0.48 mmol), tris(dibenzylideneacetone)dipalladium (7.3 mg, 8  $\mu$ mol), SPhos (6.6 mg, 16  $\mu$ mol) and potassium phosphate (51 mg, 0.24 mmol) were mixed in 1,4-dioxane (2 mL). The mixture was heated to 100 °C for 20 h. The mixture was cooled down, and 1,4-dioxane was evaporated. The residue was dissolved in DCM (20 mL) and filtered over Celite. The filtrate was washed with a saturated solution of NaHCO<sub>3</sub> (20 mL) and with distilled water (2 x 20 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent was evaporated. The product was purified by column chromatography (SiO<sub>2</sub>, DCM/MeOH 94:6). It was further purified with preparative TLC (SiO<sub>2</sub>, DCM/MeOH 94:6 then DCM/MeOH 97:3). Yield (pale yellow solid) = 12 mg (38%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47–7.45 (m, 6H), 7.39–7.35 (m, 6H), 7.24–7.17 (m, 6H), 7.14–7.10 (m, 6H), 6.64–6.61 (m, 3H), 4.11–4.05 (m, 2H), 3.88 (t, *J* = 4.3 Hz, 2H), 3.78–3.59 (m, 12H), 2.39–2.37 (m, 9H). <sup>13</sup>C {<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.10, 148.06, 143.19, 142.76, 142.59, 140.57, 139.61, 138.95, 138.93, 138.89, 137.91, 137.88, 137.86, 137.04, 137.01, 136.91, 132.04, 132.00, 131.91, 129.54, 126.84, 126.81, 126.80, 126.29, 126.19, 126.09, 124.92, 118.09, 112.96, 71.26, 71.06, 70.61, 70.57, 69.75, 69.44, 68.88, 68.82, 38.75, 37.19, 33.81. (4 overlapped aromatic peaks). HRMS (nanochip-ESI/LTQ-Orbitrap) *m/z*: [M + H]<sup>+</sup> Calcd for C<sub>55</sub>H<sub>53</sub>O<sub>5</sub><sup>+</sup> 793.3888; Found 793.3900.

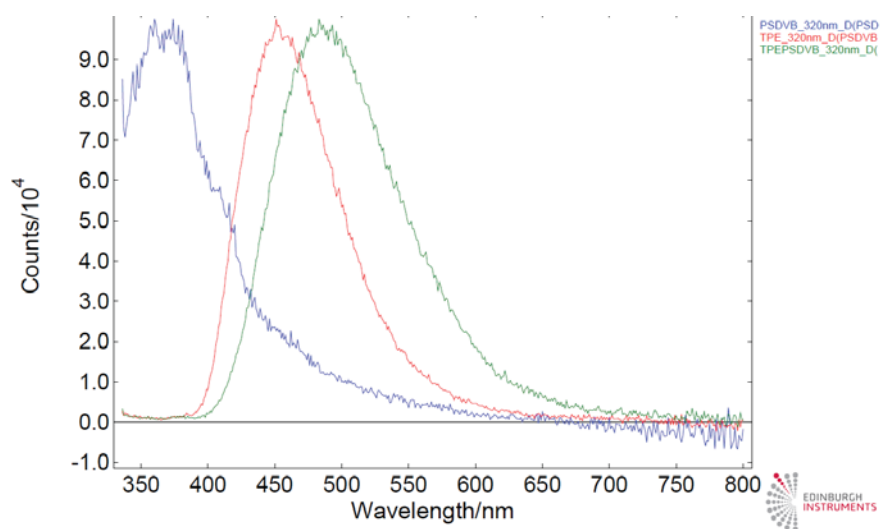
#### 4. Functionalization of polymers

##### *Functionalization of crosslinked polystyrene (from Sigma Aldrich)*

**TPE-Tr** (375 mg, 1 mmol) and a polystyrene-divinylbenzene (1%) copolymer (powder, 1040 mg, ca. 10 mmol per monomer) were mixed in DCM (20 mL) and stirred for 15 min. Triflic acid (0.44 mL, 750 mg, 5 mmol) was added dropwise under vigorous stirring. The mixture was stirred for 1 h and excess of MeOH (20 mL) was added. The mixture was filtered with suction. The resulting solid was washed with an excess of MeOH, diethyl ether, DCM, acetone, water, acetone, and diethylether. The polymer was left drying in air. Weight of dry product (**TPE-PS**) = ca. 1000 mg. **Elem. Anal.** C, 93.07; H, 8.04; N, 0.00.



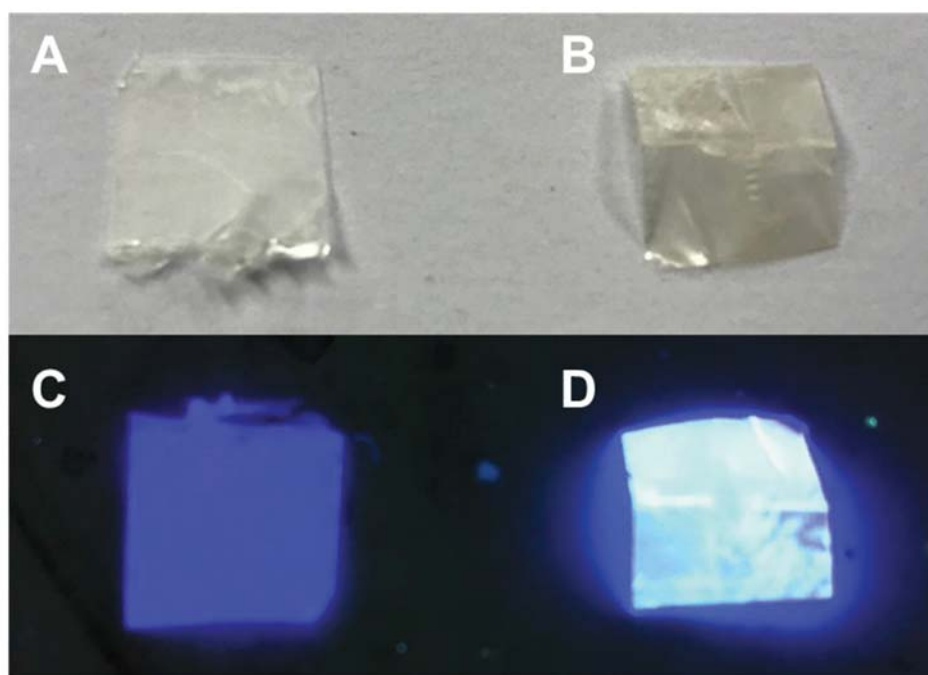
**Figure S4-1.** Starting polystyrene (A, C) and **TPE-PS** (B, D) under visible light (top) and UV-365 nm (bottom).



**Figure S4-2.** Normalized emission spectra ( $\lambda_{\text{exc}} = 320$  nm) of starting polystyrene (blue line,  $\lambda_{\text{em}} = 360$  nm), tetraphenylethylene (red line,  $\lambda_{\text{em}} = 460$  nm) and **TPE-PS** (green line,  $\lambda_{\text{em}} = 500$  nm).

*Functionalization of parylene C (from parylene deposition system Comelec C-30-S)*

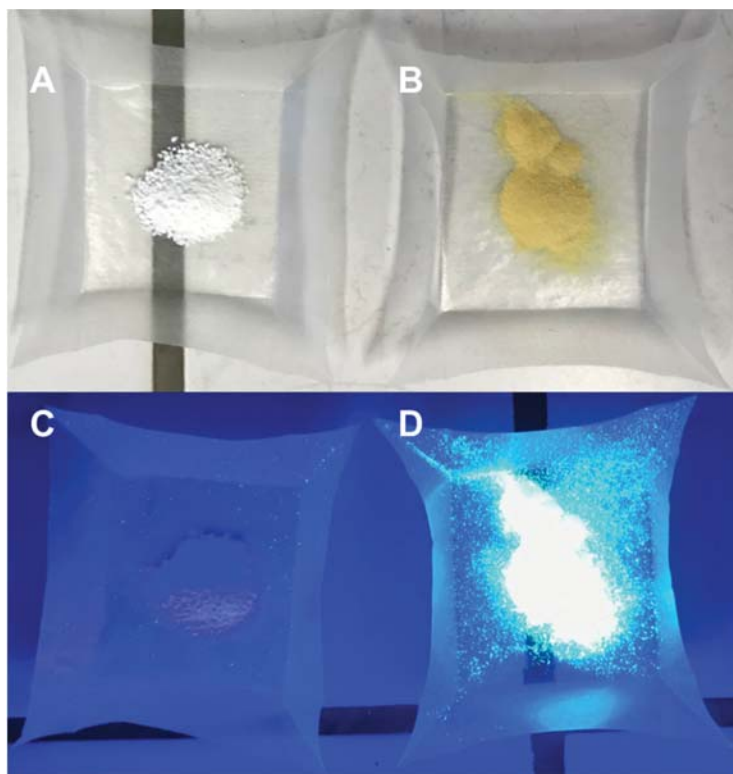
**TPE-Tr** (38 mg, 0.1 mmol) was dissolved in DCM (1.5 mL). A film of parylene C (1 cm x 1 cm, 15 mg) was added into the reaction vessel in a way that it was completely covered by solution. Upon medium stirring, TfOH (44  $\mu$ L, 75 mg, 0.5 mmol) was added dropwise. The mixture was stirred for 1 h, and then the polymer film was removed with tweezers and washed with excess of MeOH, DCM, acetone, water and acetone. Weight of dry film (**TPE-PC**) = ca. 15 mg. **Elem. Anal.** C, 70.30; H, 5.94; N, 0.00.



**Figure S4-3.** Starting parylene (A, C) and **TPE-PC** (B, D) under visible light (top) and UV-365 nm (bottom).

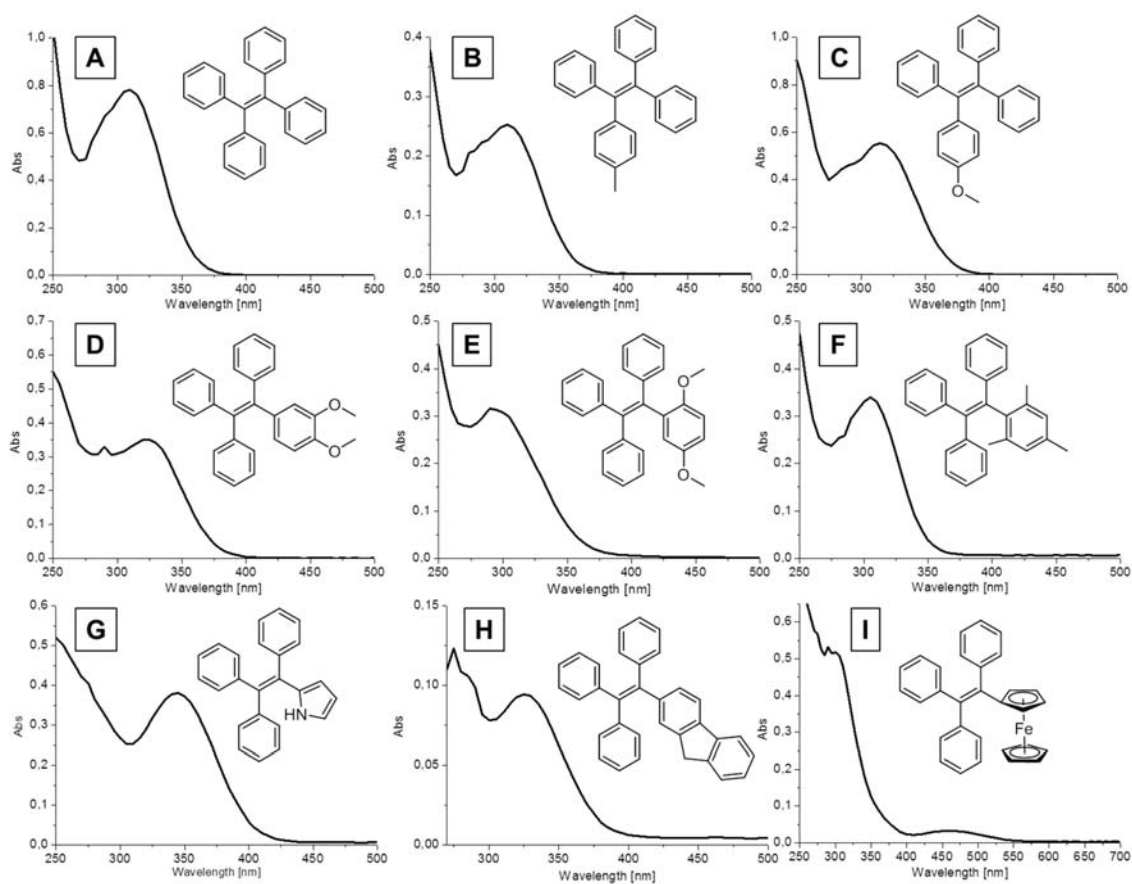
*Functionalization of polyvinylcarbazole (from TCI)*

**TPE-Tr** (38 mg, 0.1 mmol) and polyvinylcarbazole (powder, 20 mg, ca. 0.1 mmol per monomer) were mixed in DCM (20 mL) and vigorously stirred for 1 h. Triflic acid (0.44 mL, 750 mg, 5 mmol) was added dropwise to the resulting viscous mixture under vigorous stirring. The mixture was stirred for 1 h and excess of MeOH (10 mL) was added upon stirring. A gummy-like substance precipitated out from the reaction mixture. The solution was removed, and the resinous precipitate was placed in a tube with MeOH (10 mL) and ultrasonicated for 15 min. The resulting suspension was centrifuged and the procedure with sonication and centrifuging with MeOH was repeated 2 more times. The resulting yellow polymer was dried under high vacuum. Weight of dry product (**TPE-PVK**) = ca. 30 mg. **Elem. Anal. (product)** C, 90.29; H, 6.05; N, 4.19. **Elem. Anal. (starting polyvinylcarbazole)** Calcd for C<sub>14</sub>H<sub>11</sub>N: C, 87.01; H, 5.74; N, 7.25. Found: C, 88.92; H, 6.17; N, 7.31. Coupling efficiency ca. 50%.



**Figure S4-3.** Starting polyvinylcarbazole (A, C) and **TPE-PVK** (B, D) under visible light (top) and UV-365 nm (bottom).

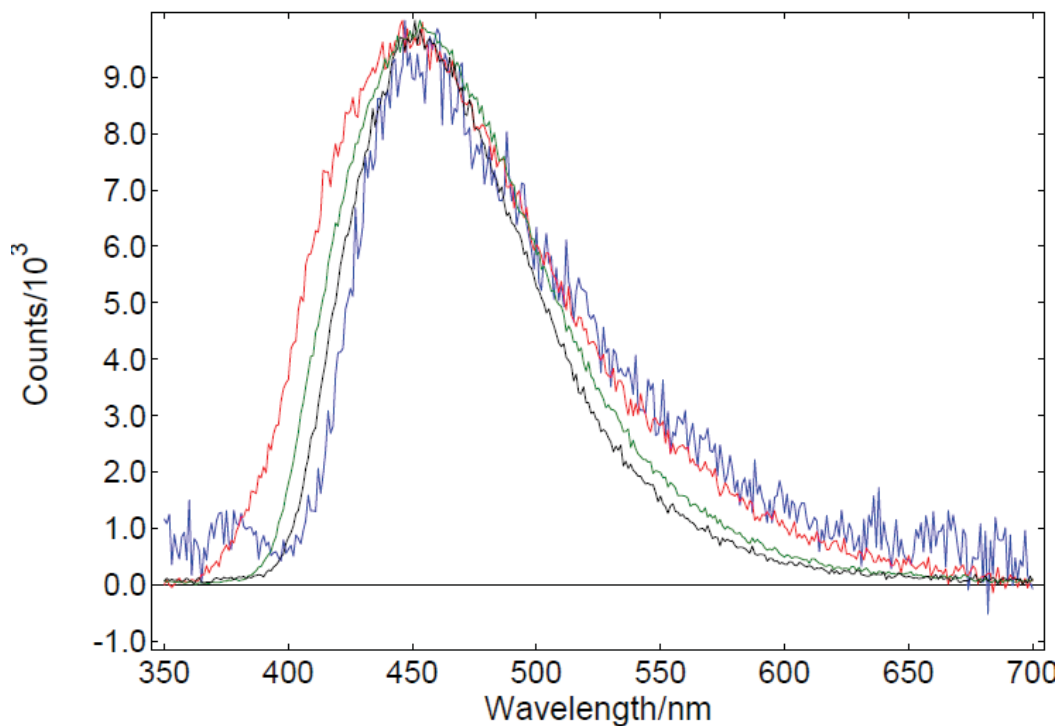
## 5. Photophysical properties of some tetraarylethenes



**Figure S5-1.** UV-vis absorption spectra of **1** (A), **2** (B), **3** (C), **10** (D), **12** (E), **15** (F), **22** (G), **24** (H) and **30** (I) measured in THF.

**Table S5-1.** Absorption maxima ( $\lambda_{abs}$ ) and molar extinction coefficients ( $\epsilon$ ) of tetraarylethenes measured in THF.

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>10</b>	<b>12</b>	<b>15</b>	<b>22</b>	<b>24</b>	<b>30</b>
$\lambda_{abs}$ [nm]	310	310	315	325	300	305	345	328	300, 461
$\epsilon$ [ $M^{-1}cm^{-1}$ ]	15600	17857	13750	17500	15500	15454	11515	31300	8500, 550



**Figure S5-2.** Stacked and normalized solid state emission spectra ( $\lambda_{exc} = 320$  nm) of **1** (black line), **10** (green line), **12** (red line) and **22** (blue line).

**Table S5-2.** Solid state fluorescence quantum yields ( $\Phi_{solid}$ ) of tetraarylethenes ( $\lambda_{exc} = 320$  nm).

Compound	<b>10</b>	<b>12</b>	<b>22</b>	<b>TPE-PS</b>
$\Phi_{solid}$ [%]	30.3	9	1.3	24

*Remark: The compound 22 was found to be highly photosensitive. During QY measurements we observed color change of the sample to reddish under UV irradiation. This UV degradation may explain unusually low QY value for 22.*

## 6. Some optimization details

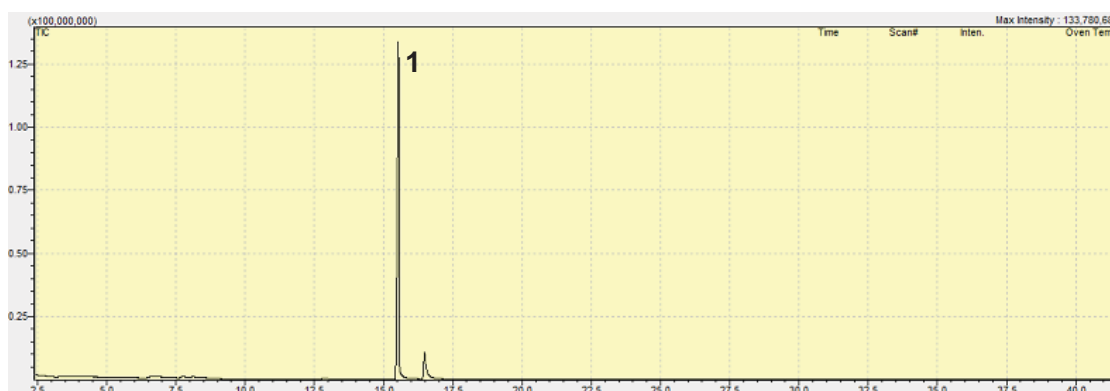
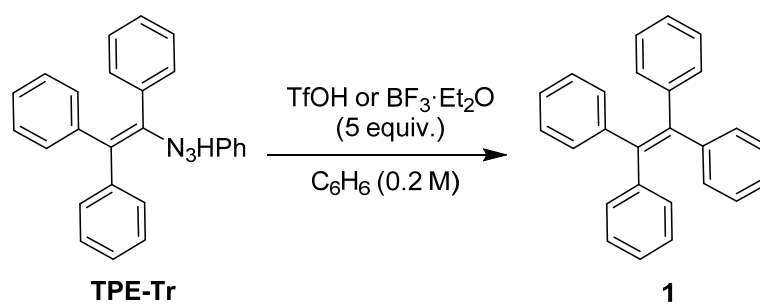


Figure S6-1. GC-MS chromatogram of the reaction mixture with TfOH.

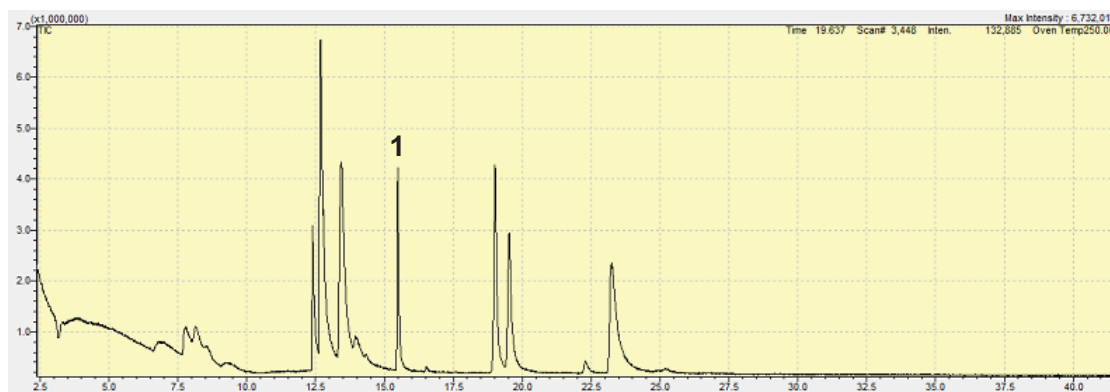
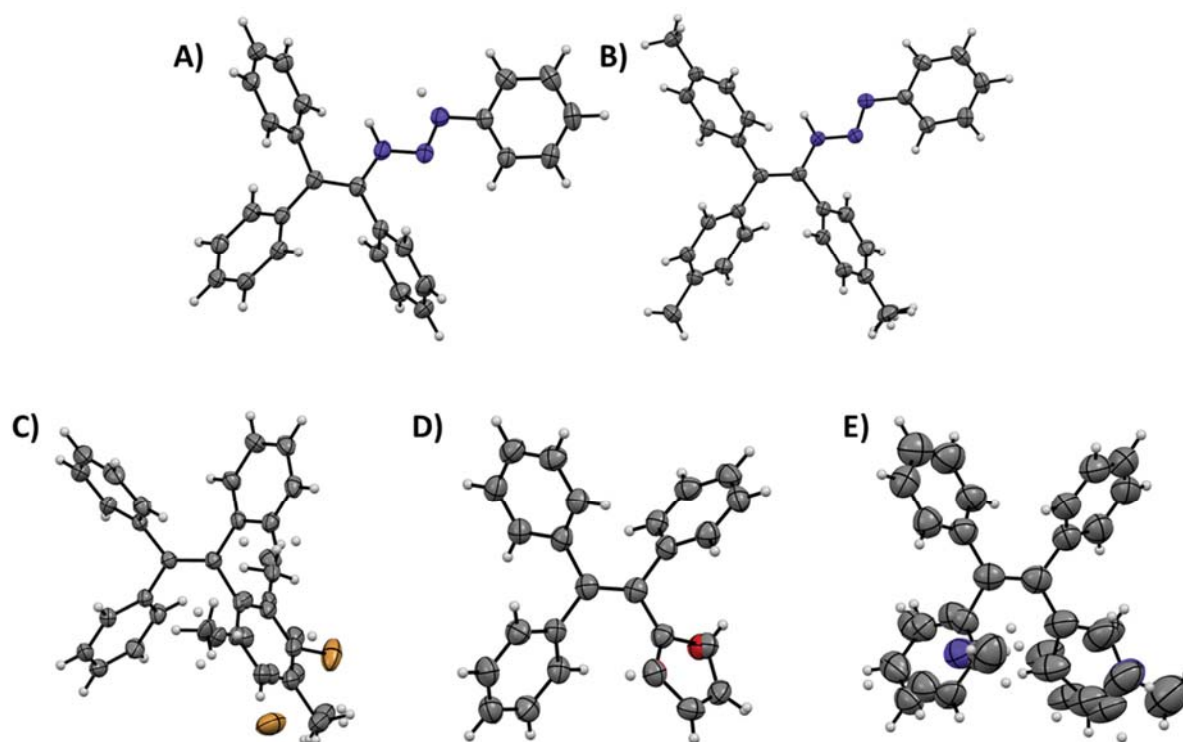


Figure S6-2. GC-MS chromatogram of the reaction mixture with  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ .



## 7. Crystallographic data



**Figure S7.** ORTEP view (probability level = 50%) of **TPE-Tr** (A), **Me-TPE-Tr** (B), **17** (C), **18** (D) and **21** (E).

### Experimental details

Bragg-intensities of **TPE-Tr**, **Me-TPE-Tr**, **17**, **18** and **21** were collected at low temperature (See [Table S6](#)) using  $\text{CuK}\alpha$  radiation. A Rigaku SuperNova dual system diffractometer with an Atlas CCD detector was used for compounds **TPE-Tr**, **Me-TPE-Tr** and **17**, and one equipped with an Atlas S2 CCD detector for compounds **18** and **21**. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis<sup>Pro</sup>*.<sup>11</sup>

The solutions and refinements of the structures were performed by the latest available version of *ShelXT<sup>12</sup>* and *ShelXL*.<sup>13</sup> All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on  $|F|^2$ . The hydrogen atoms were placed at calculated positions by means of the “riding” model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2  $U_{\text{eq}}$  of its parent C-atom (1.5  $U_{\text{eq}}$  for the methyl groups), but in the structures of **TPE-Tr** and **Me-TPE-Tr**, hydrogen atom positions were found in a difference map and refined freely. Crystallographic and refinement data are summarized in [Table S6](#). Crystallographic data have been deposited to the CCDC and correspond to the following codes: **TPE-Tr** (1938618), **Me-TPE-Tr** (1938619), **17** (1938622), **18** (1938621) and **21** (1938620). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). In the structure **TPE-Tr**, the hydrogen of NH group occupies two positions on N1 and N3 found in a difference map. These were freely refined using fixed isotropic displacement parameters corresponding to a value of 1.2  $U_{\text{eq}}$  of their parent N-atom; this yielded site occupancies of 0.80(3)/0.20(3).

The structure **Me-TPE-Tr** was refined as a two-component twin, yielding a BASF parameter of 0.411(3).

In the structure **17**, the bromo-phenyl ring is disordered over two orientations found in a difference map. These were anisotropically refined imposing distance and similarity constraint and restraints (AFIX 66, SADI and SIMU) for the least-squares refinement; this yielded site occupancies of 0.581(2)/ 0.419(2).

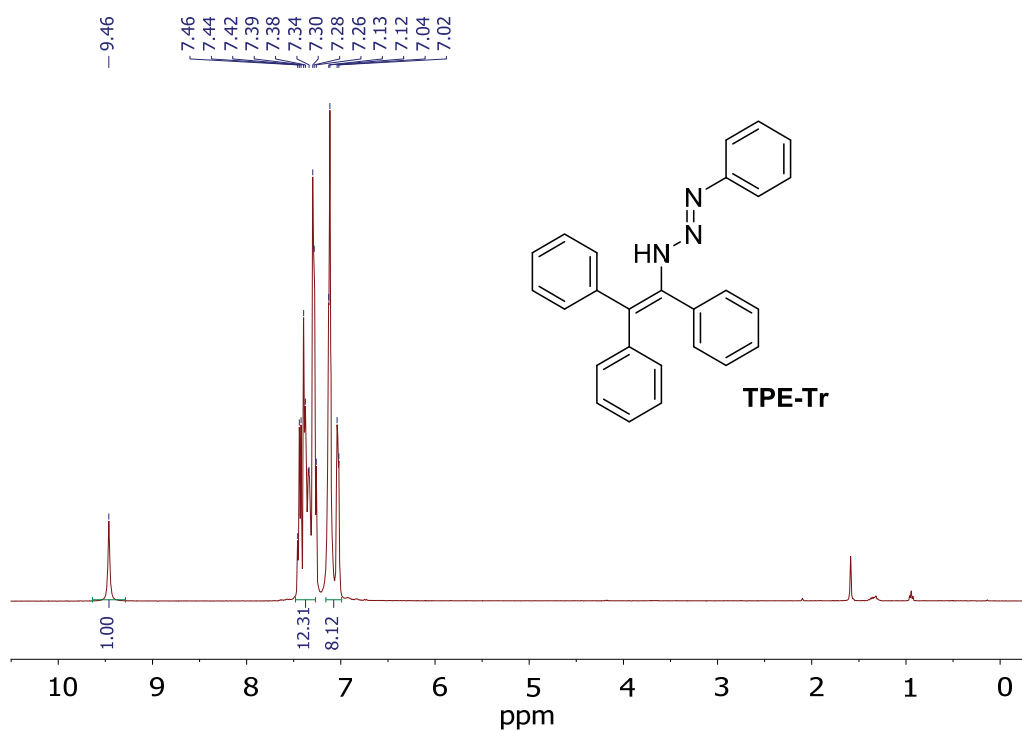
The structure **18** was refined as a two-component twin, yielding a BASF parameter of 0.332(5). A difference-map revealed the furan-ring to be disordered by a twofold rotation about the C-C bond to the alpha-carbon; accordingly, the superimposed C and O atoms were treated by EADP in the least-squares refinement which yielded site occupancies of 0.54(1)/ 0.46(1).

In the structure **21**, the Me-pyrrol and phenyl rings are disordered over two orientations each, found in a difference map. These were anisotropically refined imposing distance and similarity constraint and restraints (AFIX 66, SADI and SIMU) for the least-squares refinement which yielded site occupancies of 0.573(7)/ 0.427(7).

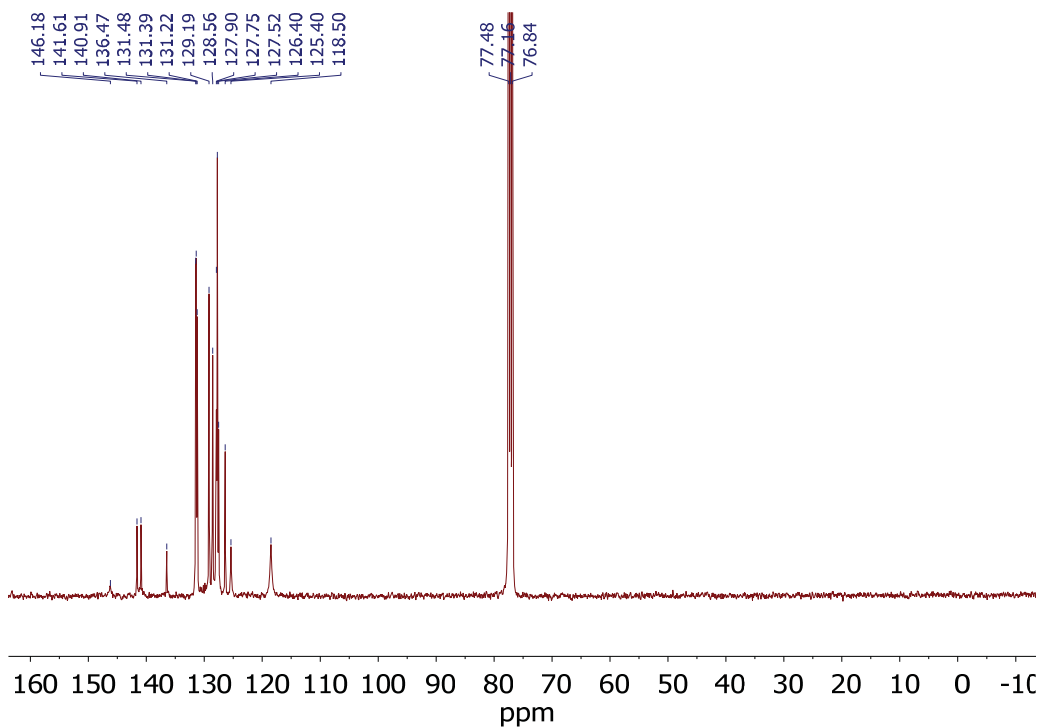
**Table S7.** Crystallographic data of **TPE-Tr**, **Me-TPE-Tr**, **17**, **18** and **21**.

<b>Compound</b>	<b>TPE-Tr</b>	<b>Me-TPE-Tr</b>	<b>17</b>	<b>18</b>	<b>21</b>
Formula	C <sub>26</sub> H <sub>21</sub> N <sub>3</sub>	C <sub>29</sub> H <sub>27</sub> N <sub>3</sub>	C <sub>29</sub> H <sub>25</sub> Br	C <sub>24</sub> H <sub>18</sub> O	C <sub>25</sub> H <sub>21</sub> N
$D_{calc}/g\text{ cm}^{-3}$	1.252	1.214	1.329	1.249	1.190
$\mu/\text{mm}^{-1}$	0.576	0.550	2.546	0.577	0.520
Formula Weight	375.46	417.53	453.40	322.38	335.43
Colour	yellow	yellow	clear colourless	clear pale green	clear colourless
Shape	prism	prism	prism	prism	prism
Size/mm <sup>3</sup>	0.121 x 0.098 x 0.091	0.597 x 0.527 x 0.274	0.27x0.21x0.13	0.44x0.27x0.20	0.46x0.40x0.25
$T/\text{K}$	140.00(10)	140.00(10)	140.01(10)	140.00(10)	100.00(10)
Crystal System	triclinic	Triclinic	orthorhombic	triclinic	monoclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P2_1$
$a/\text{\AA}$	9.1435(7)	9.1758(6)	9.3953(2)	8.4901(7)	9.8348(8)
$b/\text{\AA}$	9.8141(8)	10.5158(5)	13.6981(3)	9.4614(7)	9.4972(5)
$c/\text{\AA}$	12.3430(11)	12.8588(9)	17.6052(4)	11.1438(9)	10.4082(7)
$\alpha/^\circ$	68.198(8).	82.920(5).	90	75.944(7)	90
$\beta/^\circ$	80.142(7)	69.936(6)	90	87.169(6)	105.700(8)
$\gamma/^\circ$	76.673(7)	79.219(4)	90	80.874(7)	90
$V/\text{\AA}^3$	996.18(16)	1142.54(13)	2265.75(9)	857.31(12)	935.89(11)
$Z$	2	2	4	2	2
$Z'$	1	1	1	1	1
Wavelength/ $\text{\AA}$	1.54184	1.54184	1.54184	1.54184	1.54184
Radiation type	CuK $\alpha$	CuK $\alpha$	CuK $\alpha$	CuK $\alpha$	CuK $\alpha$
$\theta_{min}/^\circ$	3.875	3.667	5.024	4.090	4.670
$\theta_{max}/^\circ$	75.227	75.248	73.564	73.752	74.629
Measured Refl.	6844	4709	15322	3449	14160
Independent Refl.	3970	4709	4485	3449	3727
Reflections with $I > 2(I)$	3193	3896	4295	2781	3409
$R_{int}$	0.0191	n/a	0.0336	n/a	0.0327
Parameters	350	389	344	234	303
Restraints	1	0	330	0	460
Largest Peak/ $e\text{\AA}^{-3}$	0.211	0.207	0.401	0.358	0.257
Deepest Hole/ $e\text{\AA}^{-3}$	-0.206	-0.267	-0.744	-0.212	-0.300
GooF	1.011	1.031	1.071	1.052	1.059
$wR_2$ (all data)	0.1021	0.1318	0.1691	0.2038	0.2362
$wR_2$	0.0938	0.1250	0.1666	0.1963	0.2304
$R_1$ (all data)	0.0498	0.0538	0.0572	0.0769	0.0782
$R_1$	0.0374	0.0447	0.0554	0.0669	0.0753
CCDC code	1938618	1938619	1938622	1938621	1938620

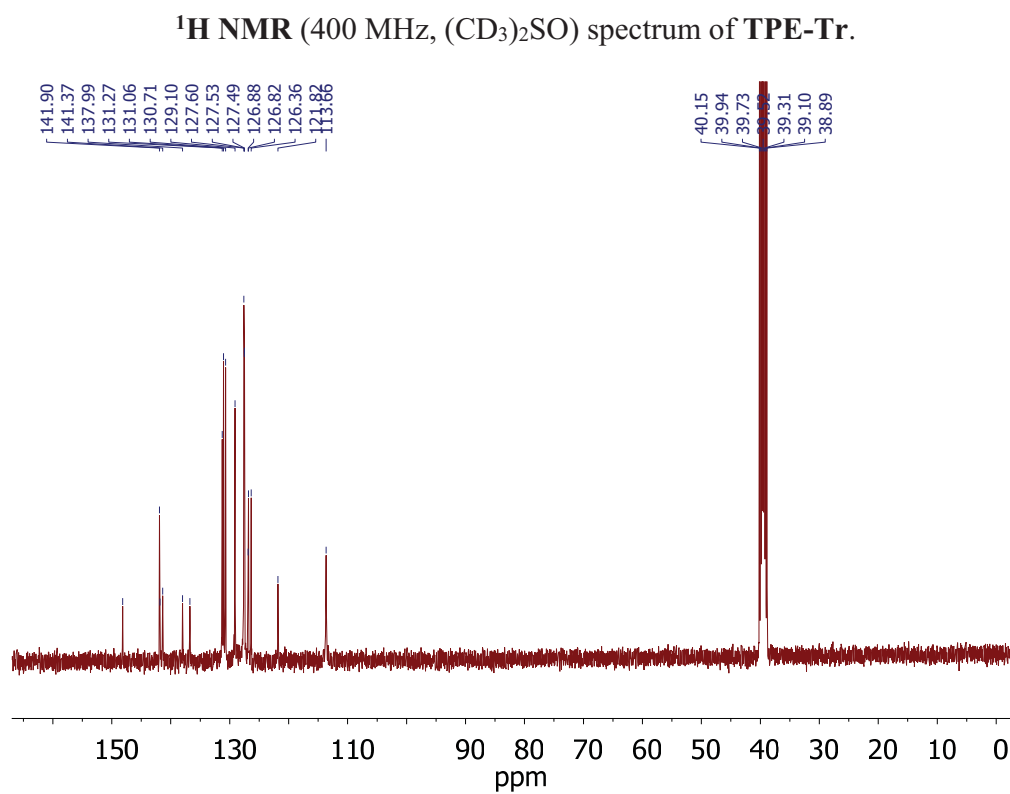
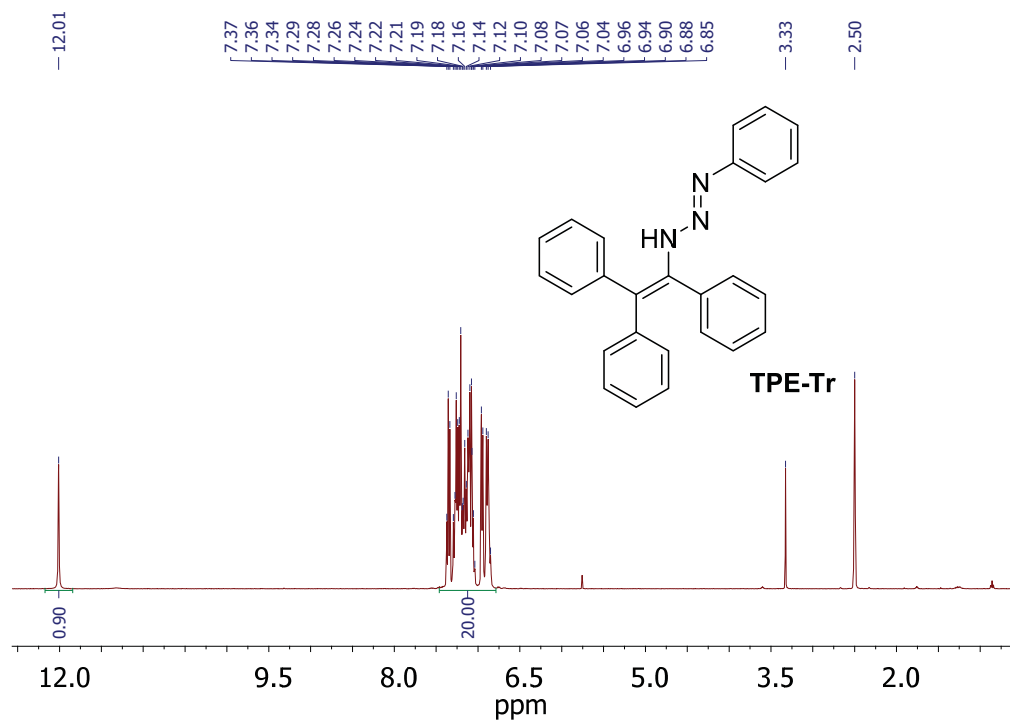
## 8. NMR spectra.

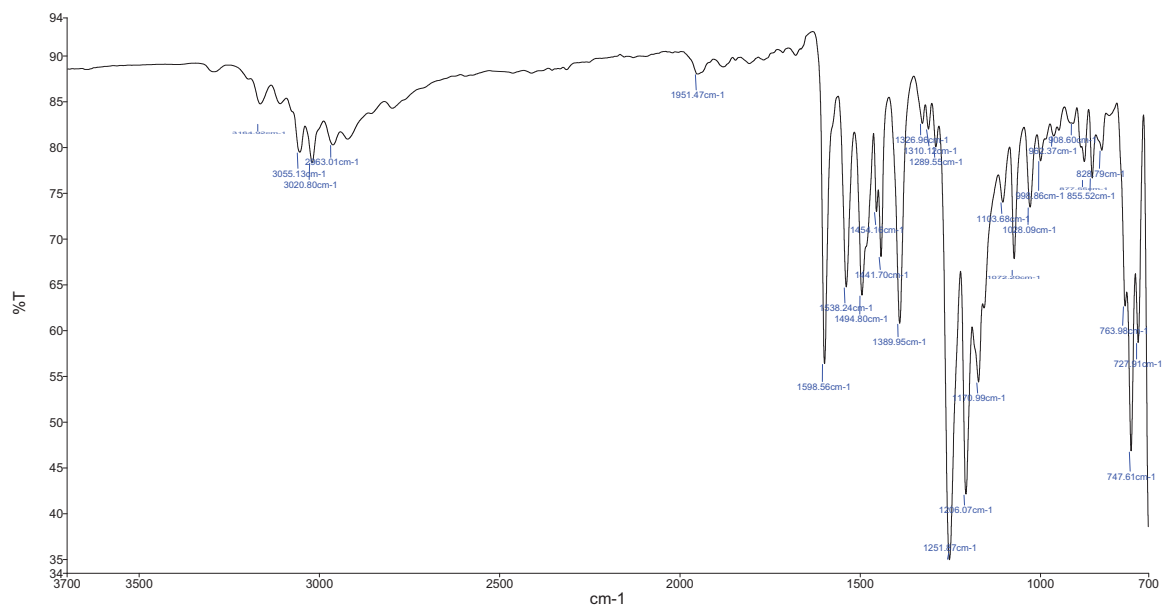


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of TPE-Tr.

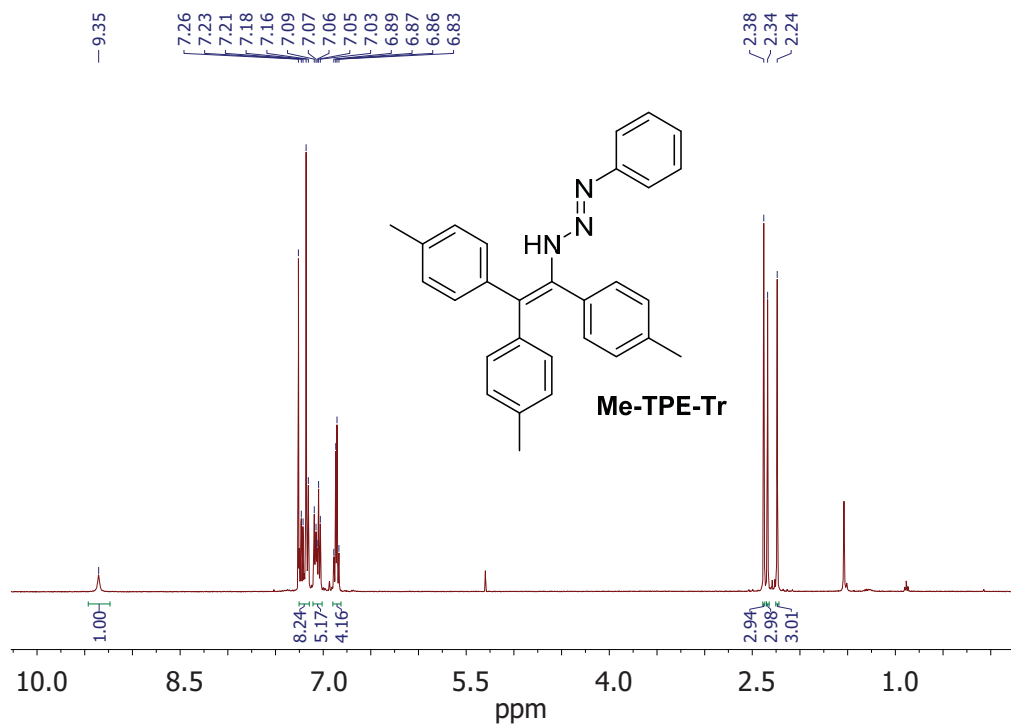


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of TPE-Tr.

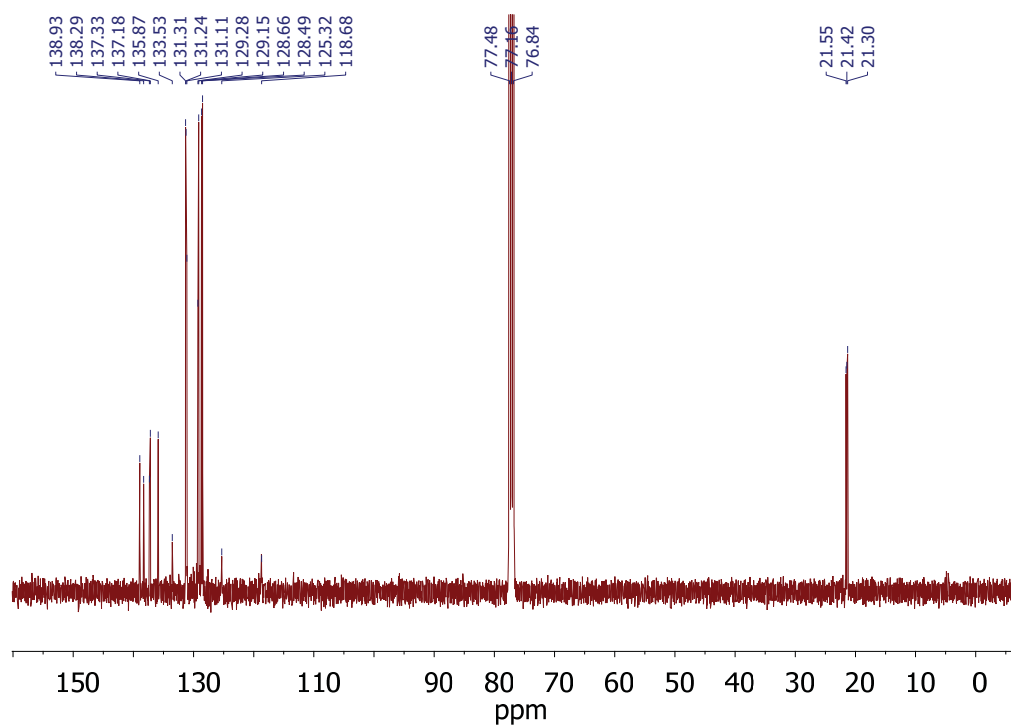




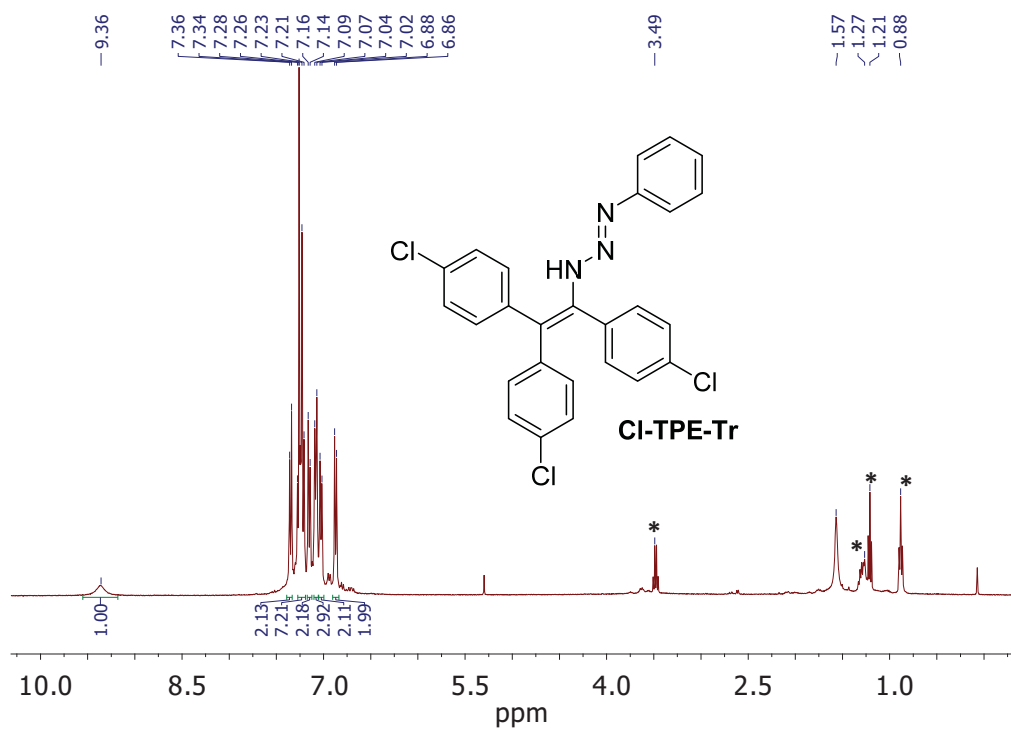
IR (film) spectrum of TPE-Tr.



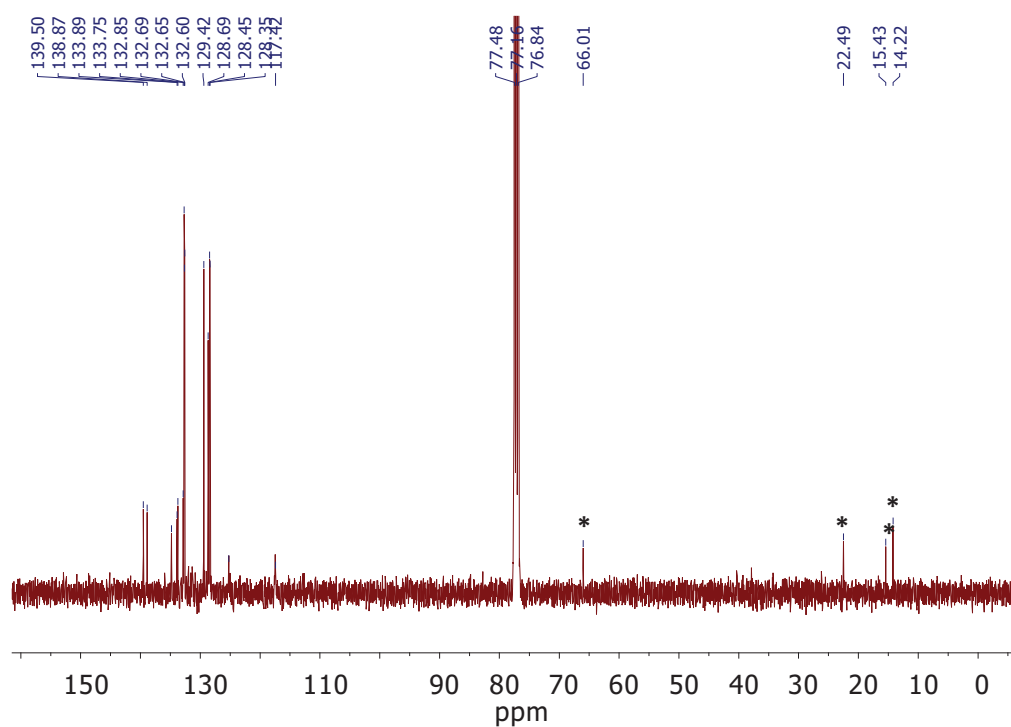
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of Me-TPE-Tr.



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of Me-TPE-Tr.

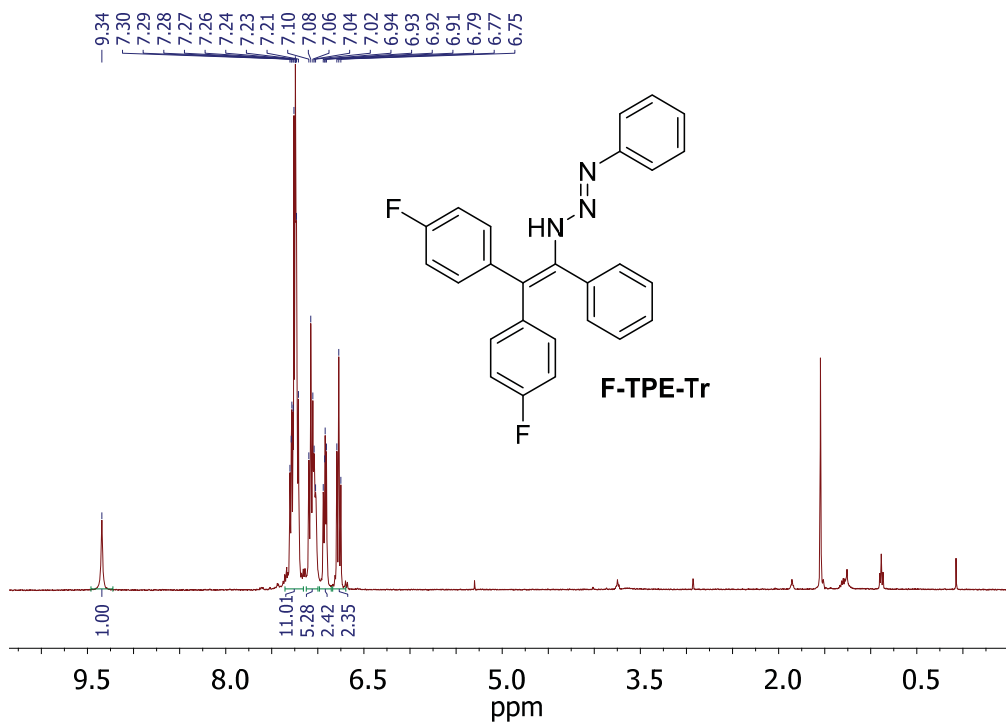


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of Cl-TPE-Tr (\* peaks of pentane and Et<sub>2</sub>O).

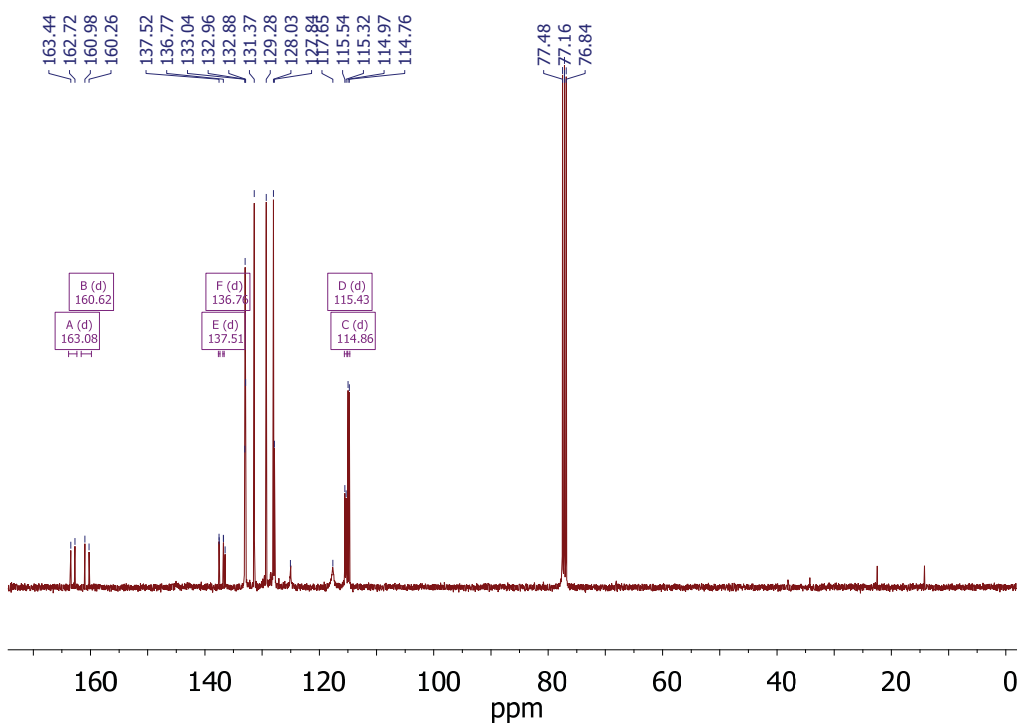


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of Cl-TPE-Tr (\* peaks of pentane and Et<sub>2</sub>O).

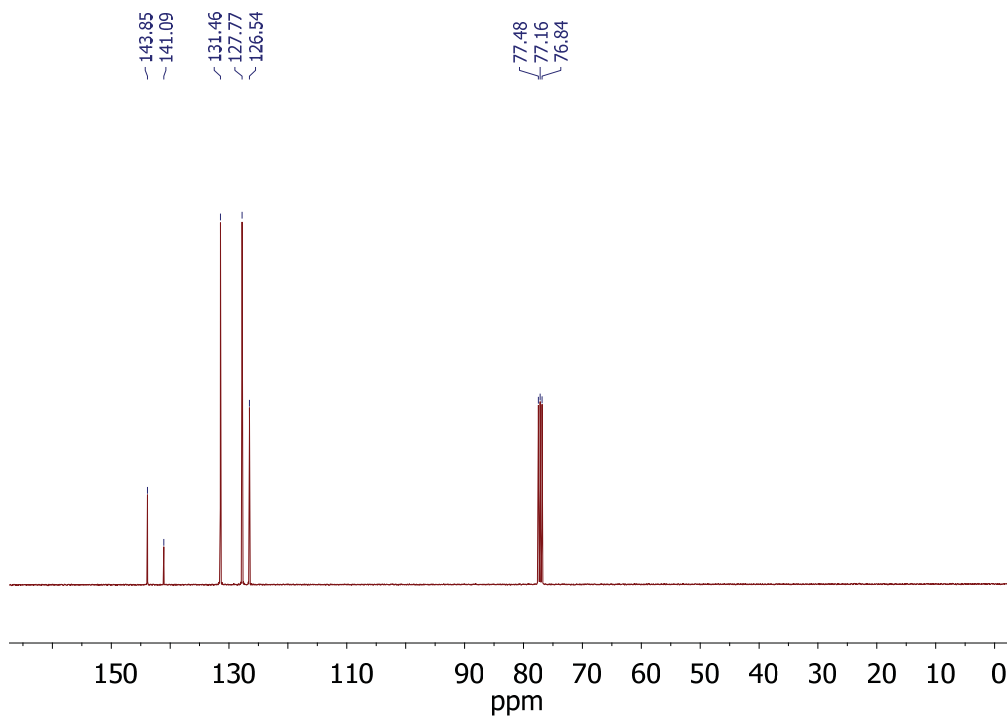
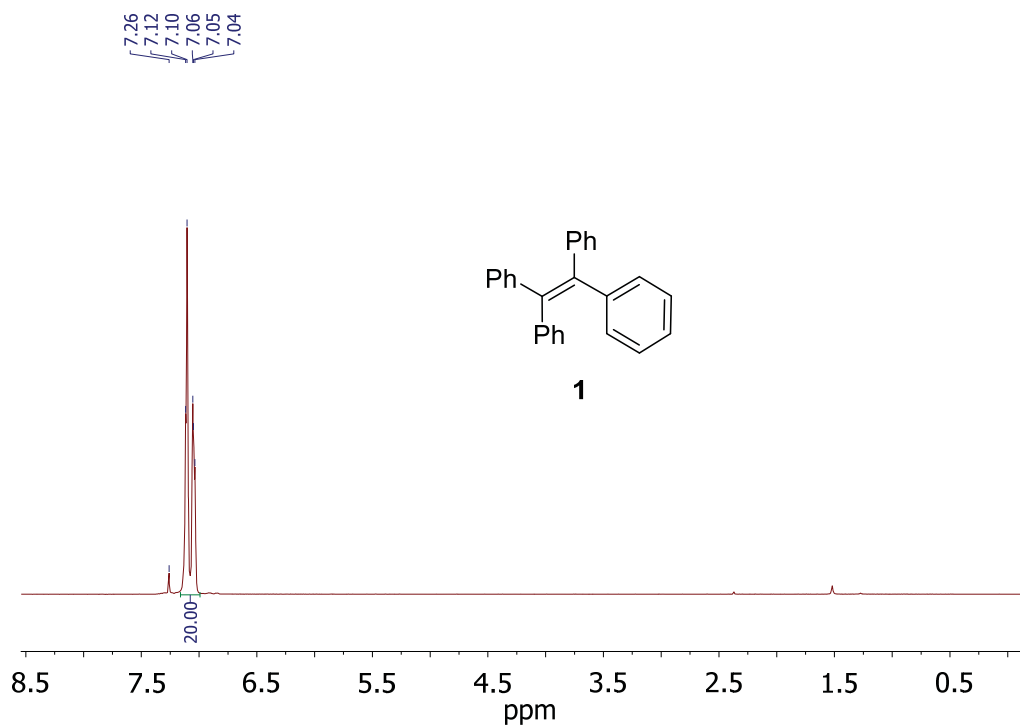


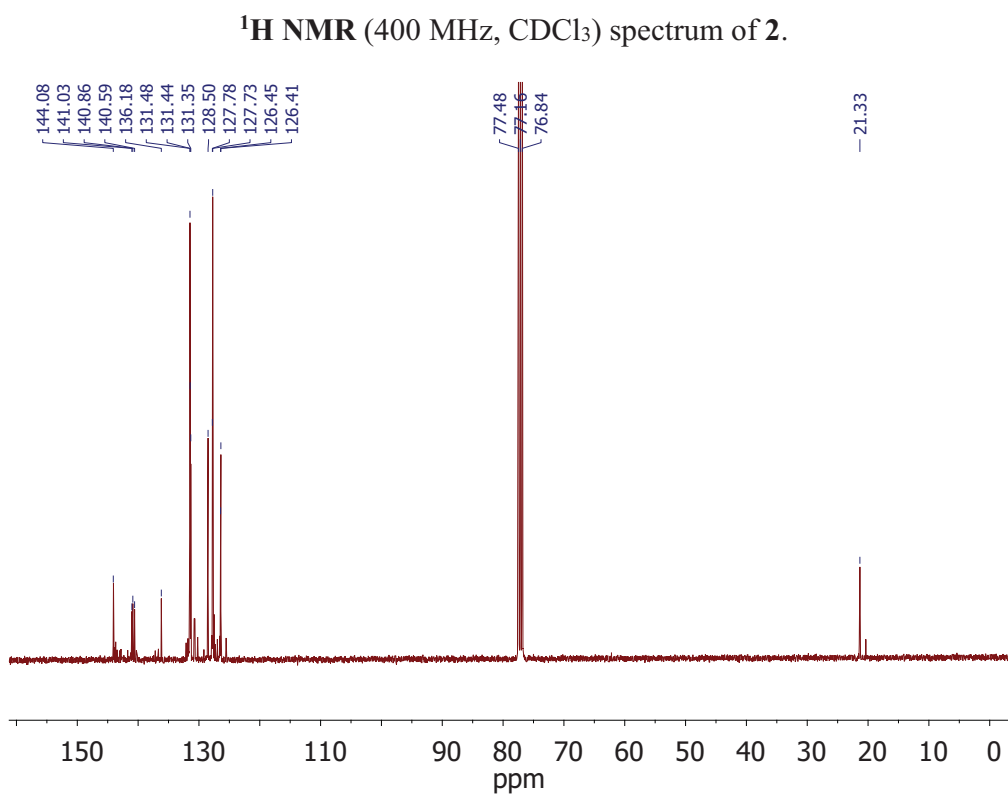
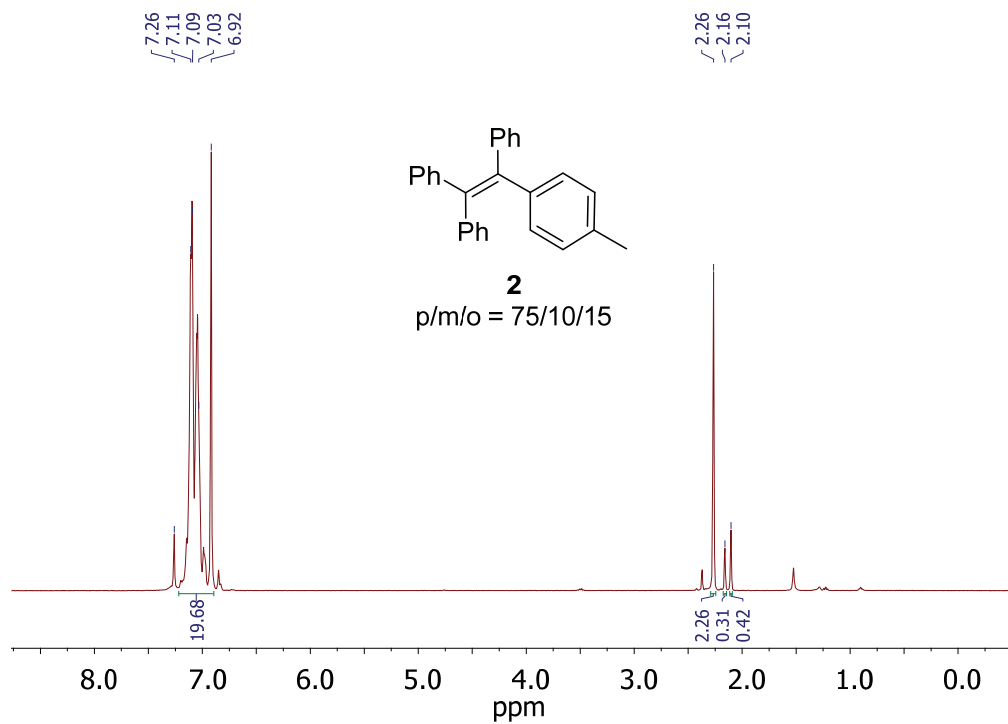


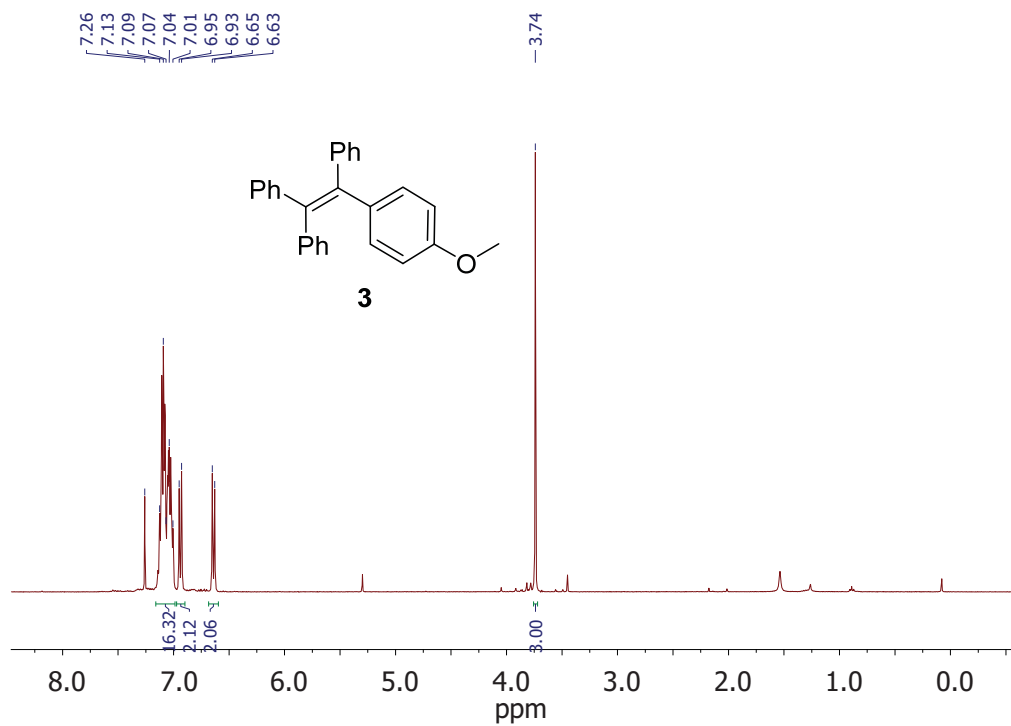
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of F-TPE-Tr.



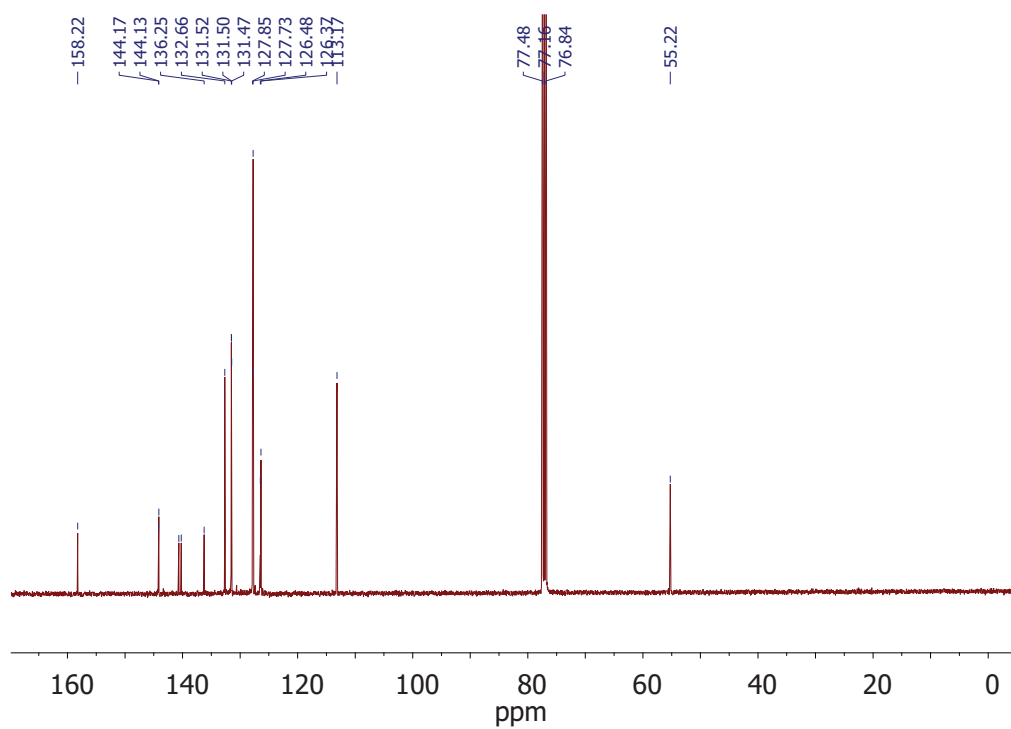
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of F-TPE-Tr.



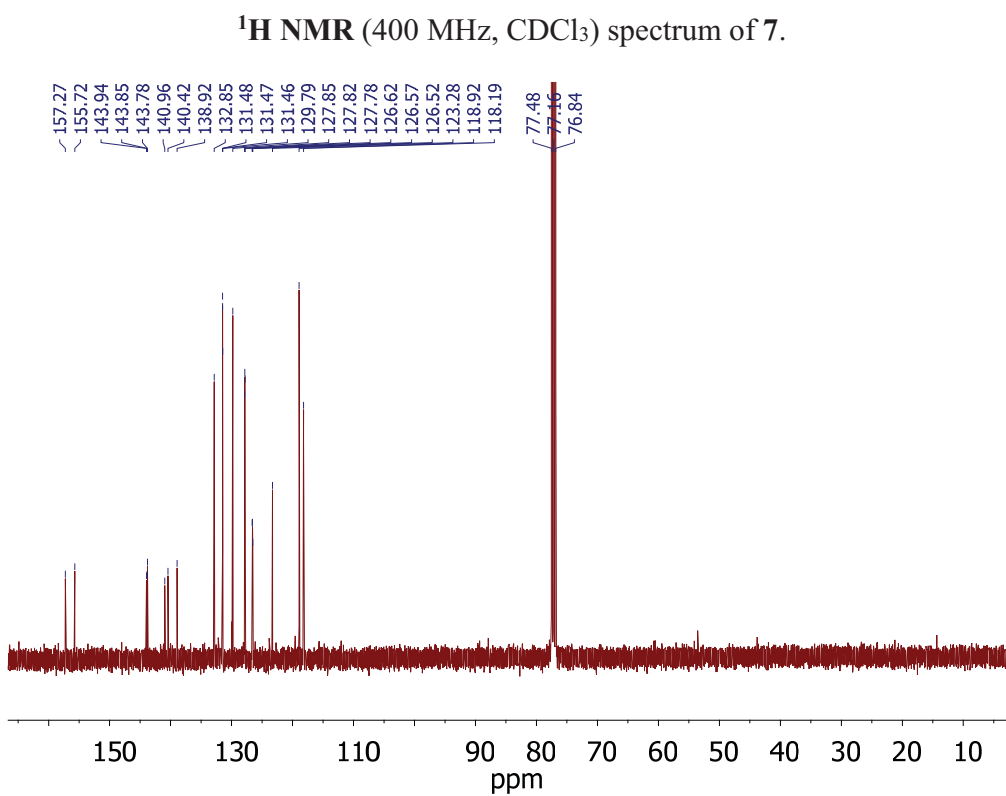
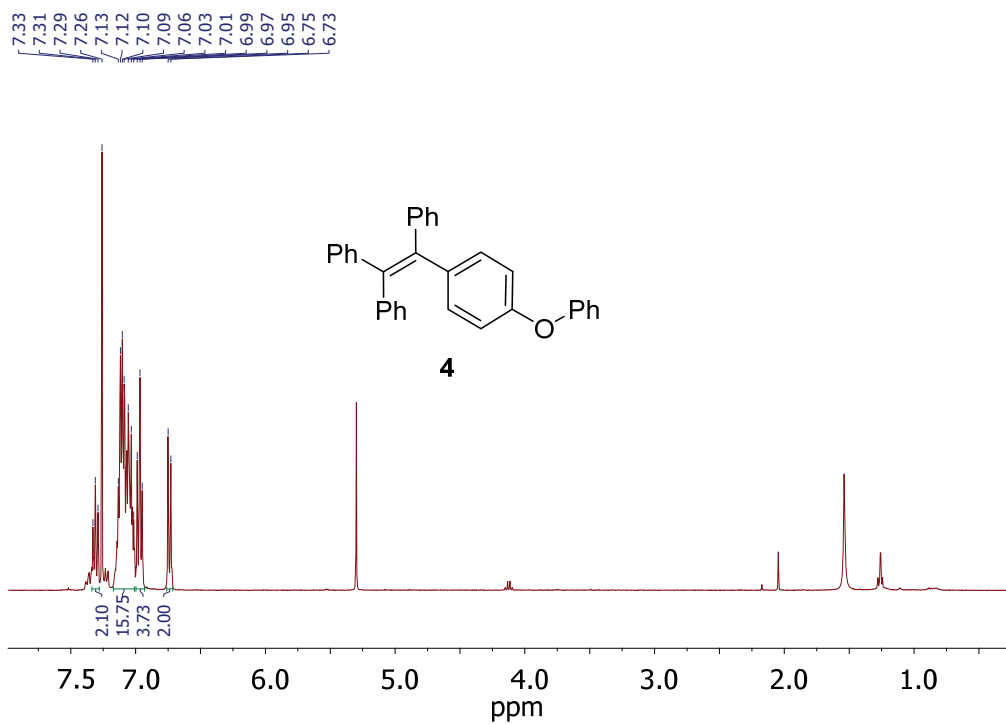


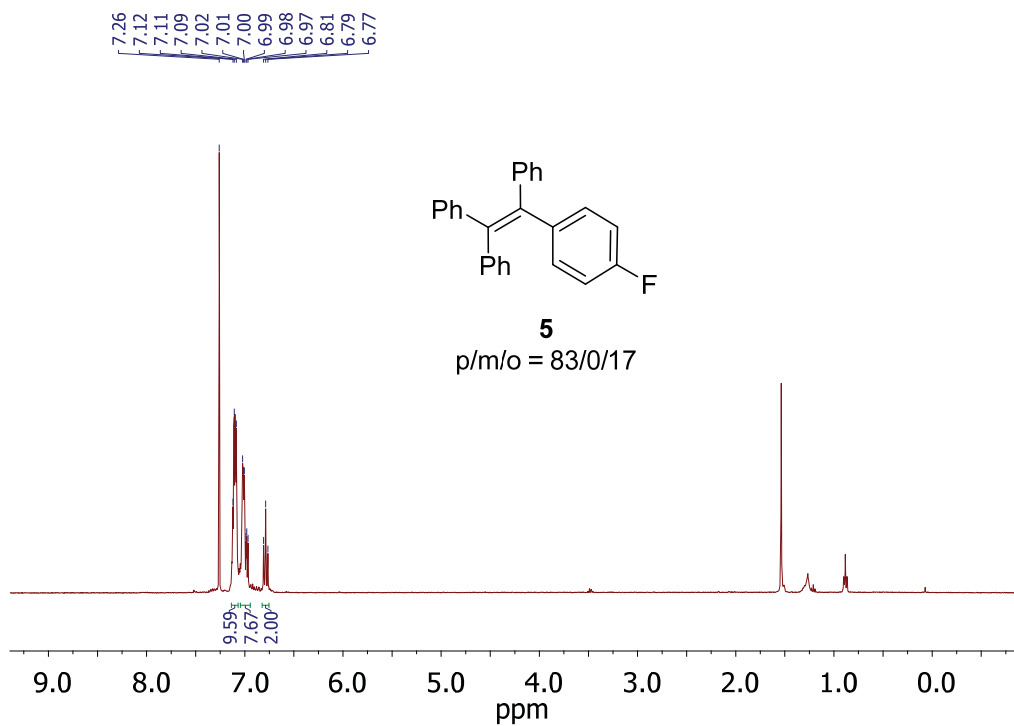


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3**.

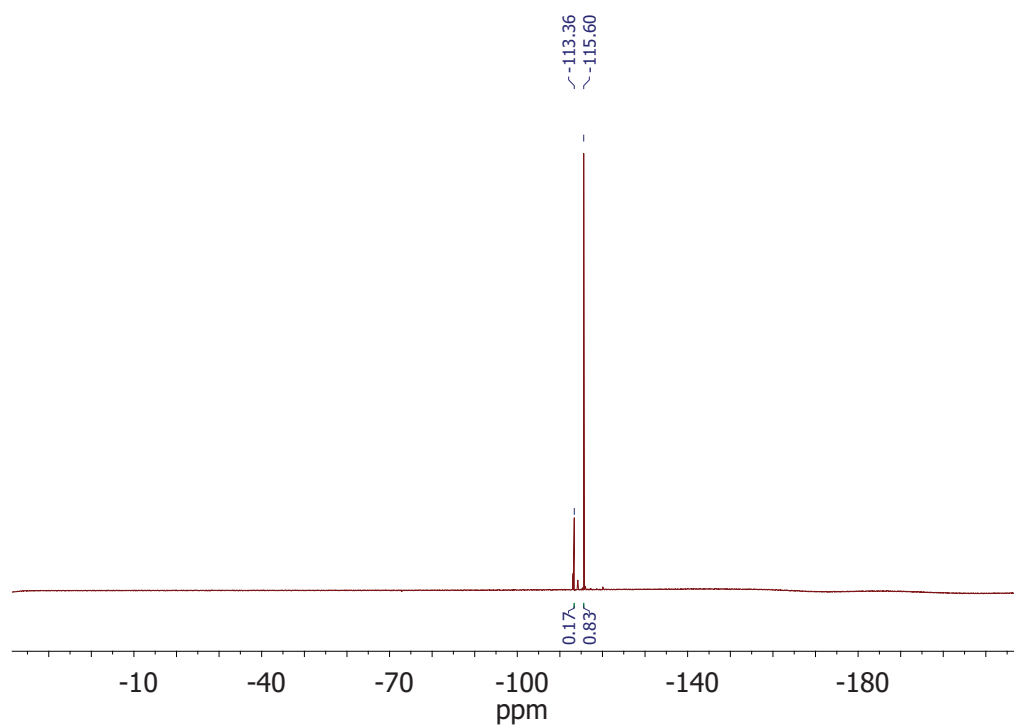


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **3**.

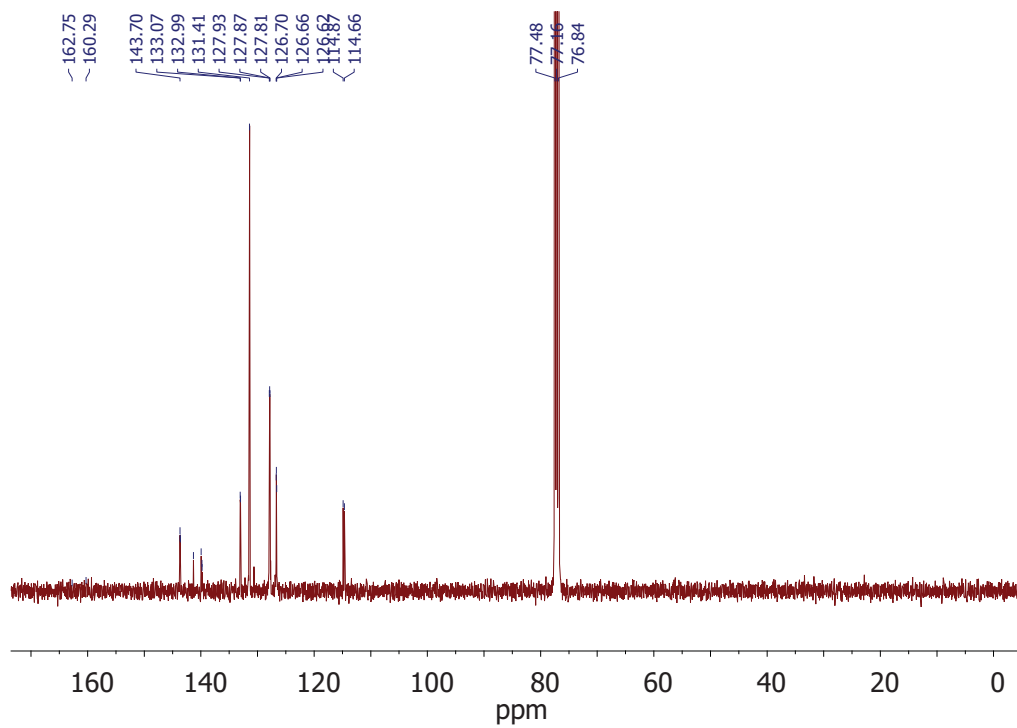




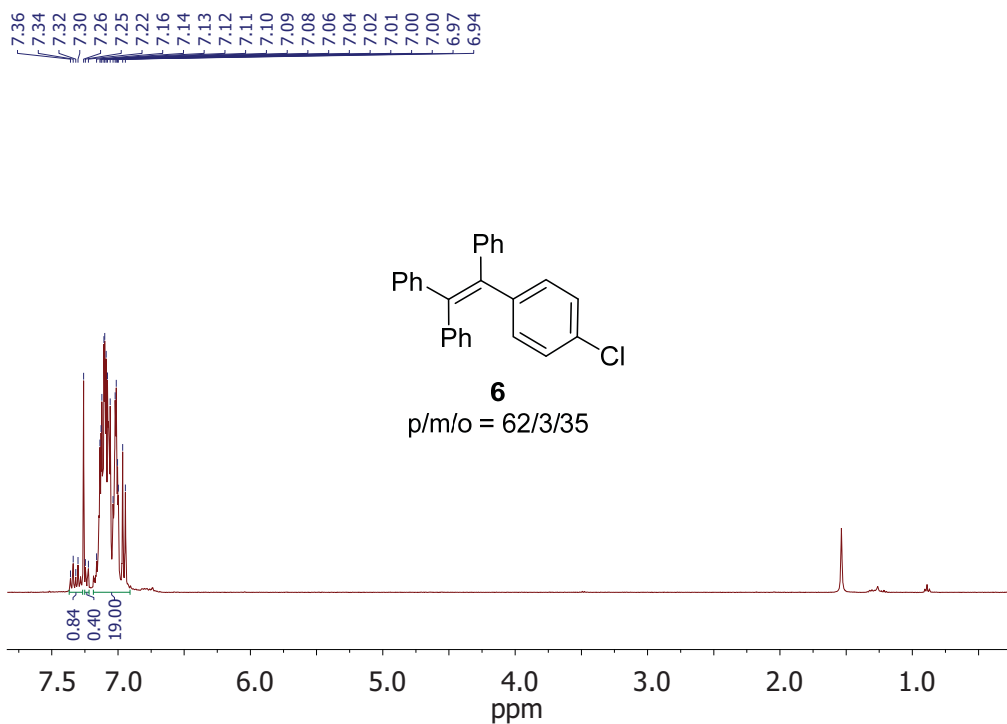
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **5**.



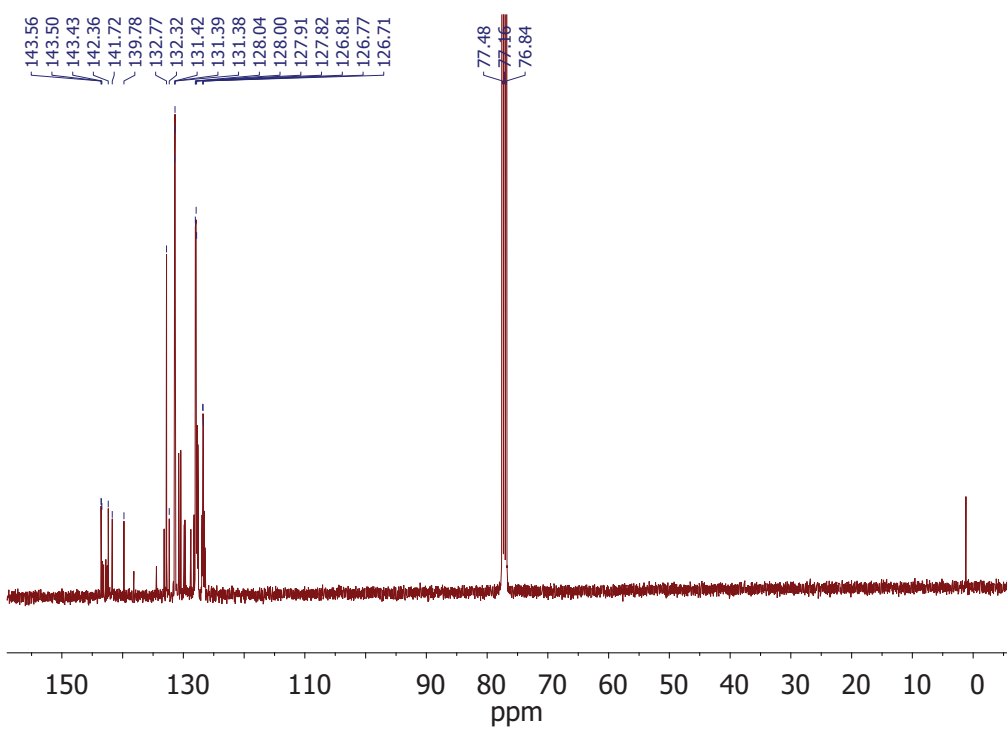
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectrum of **5**.



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **5**.

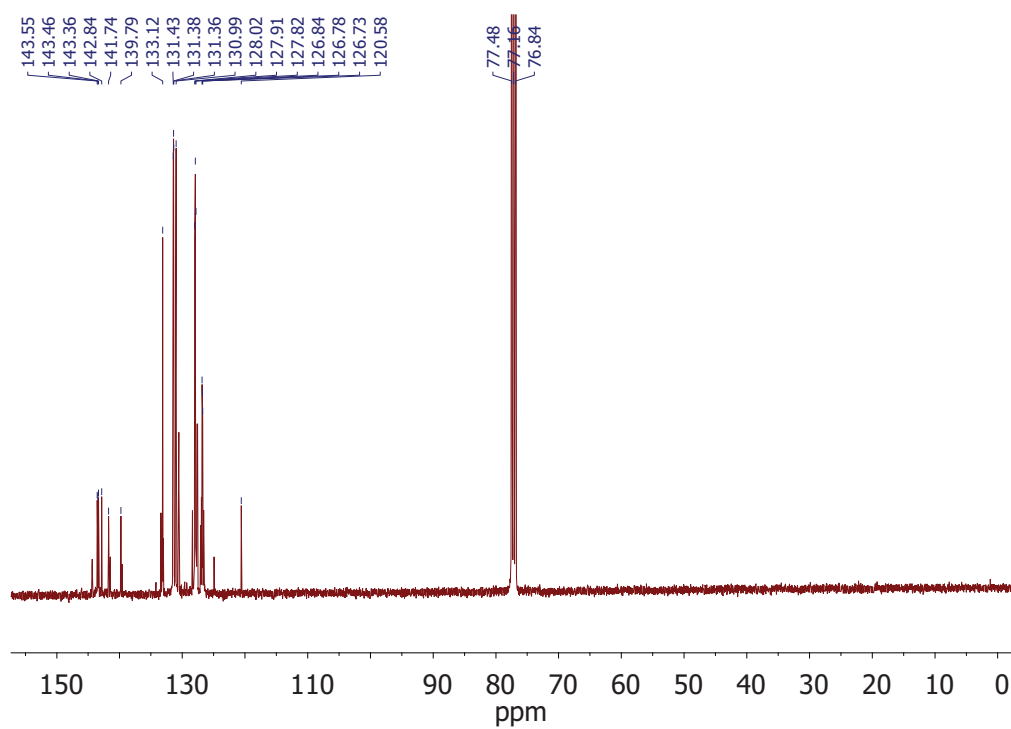
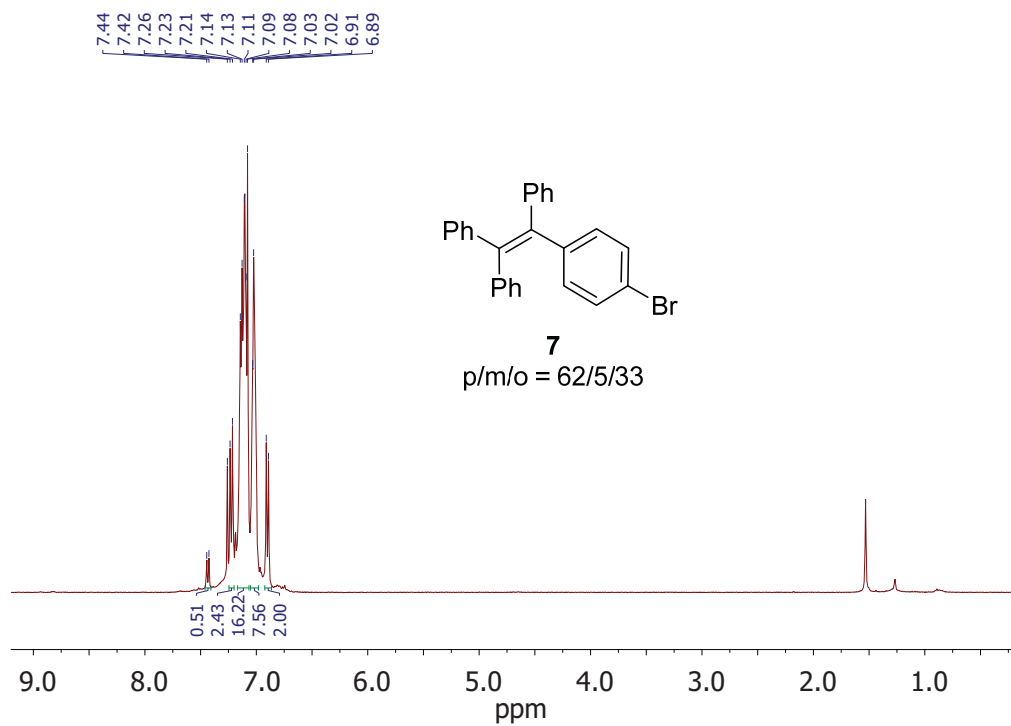


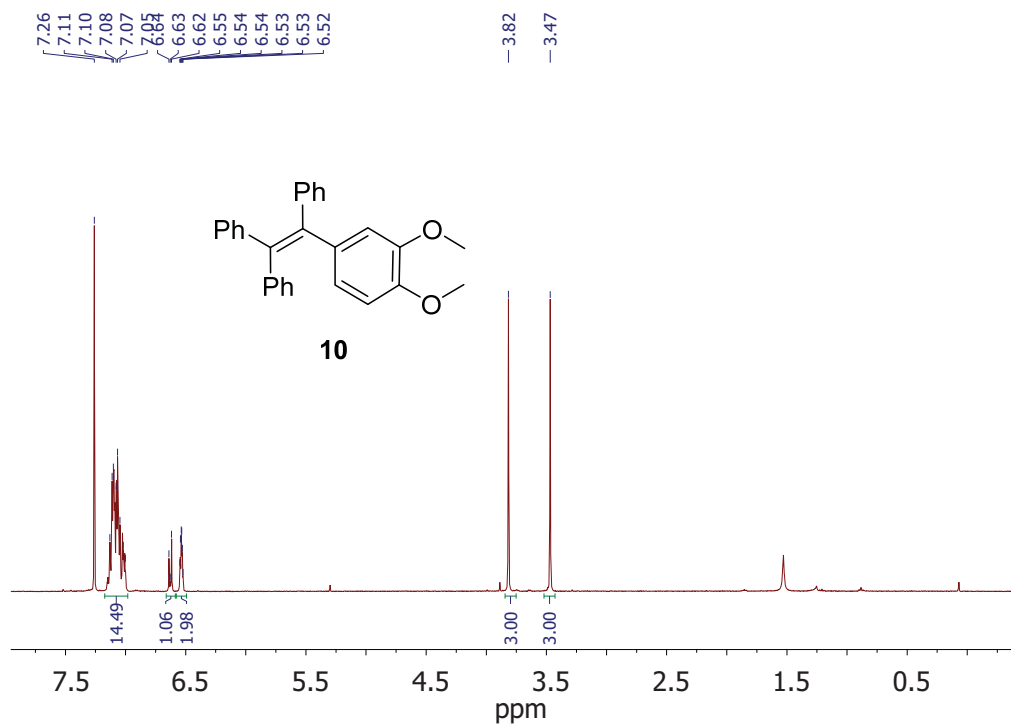
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **6**.



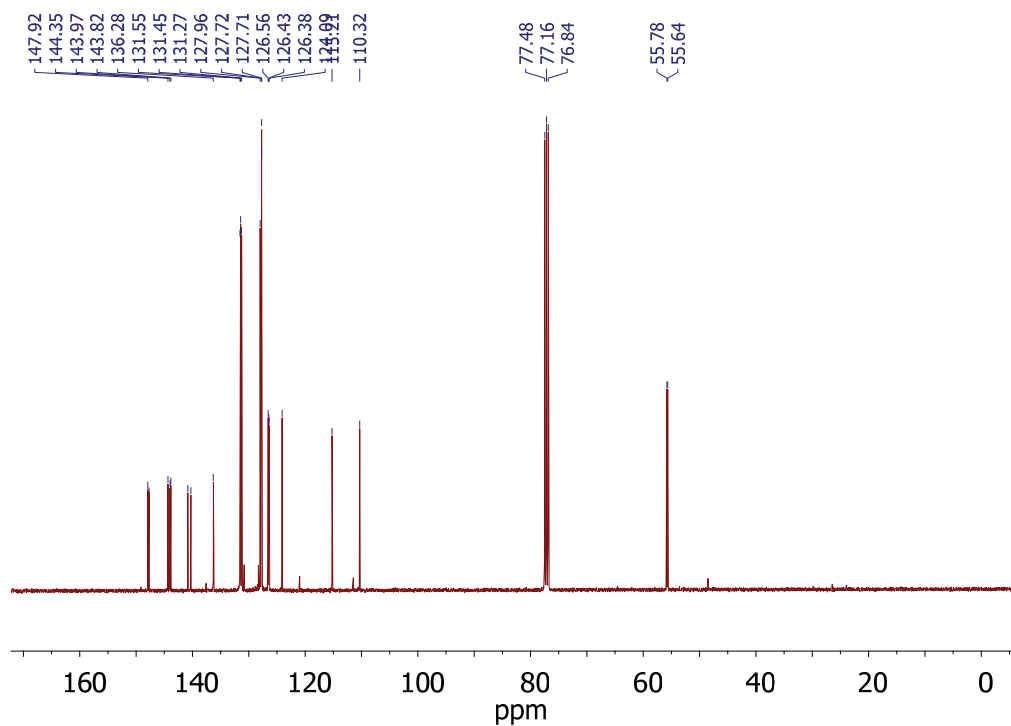
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **6**.



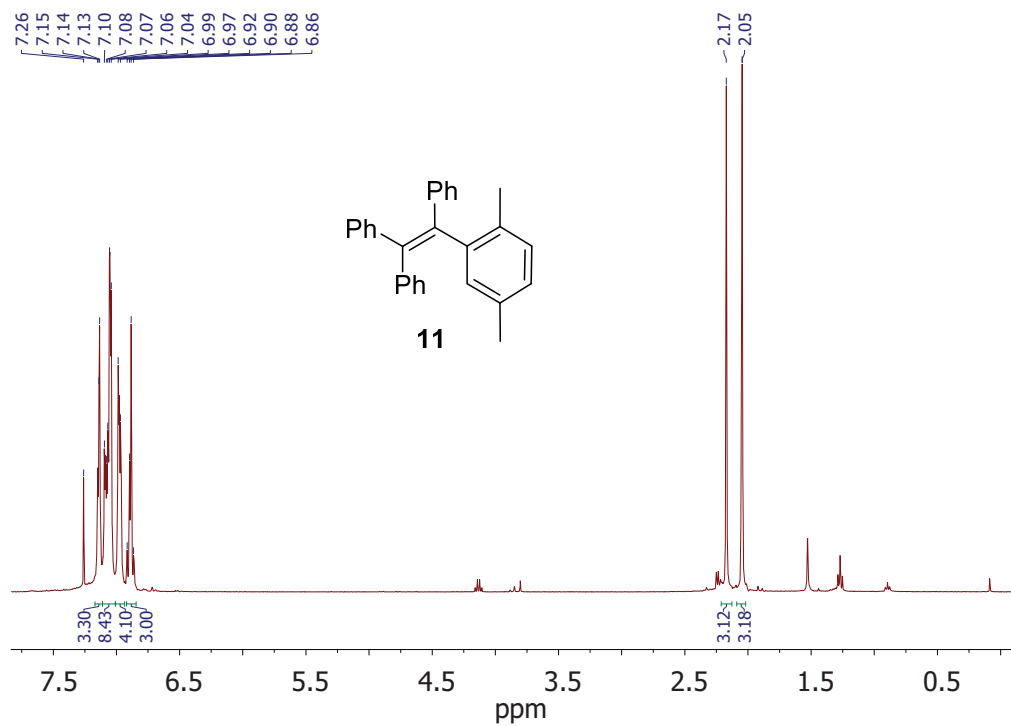




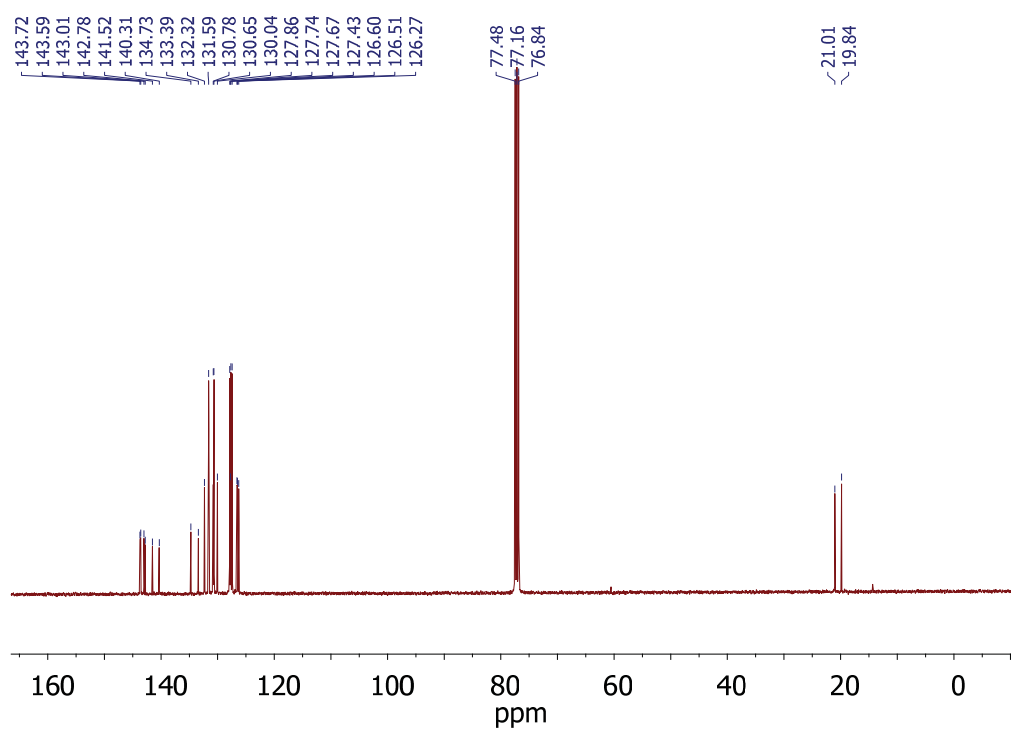
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **10**.



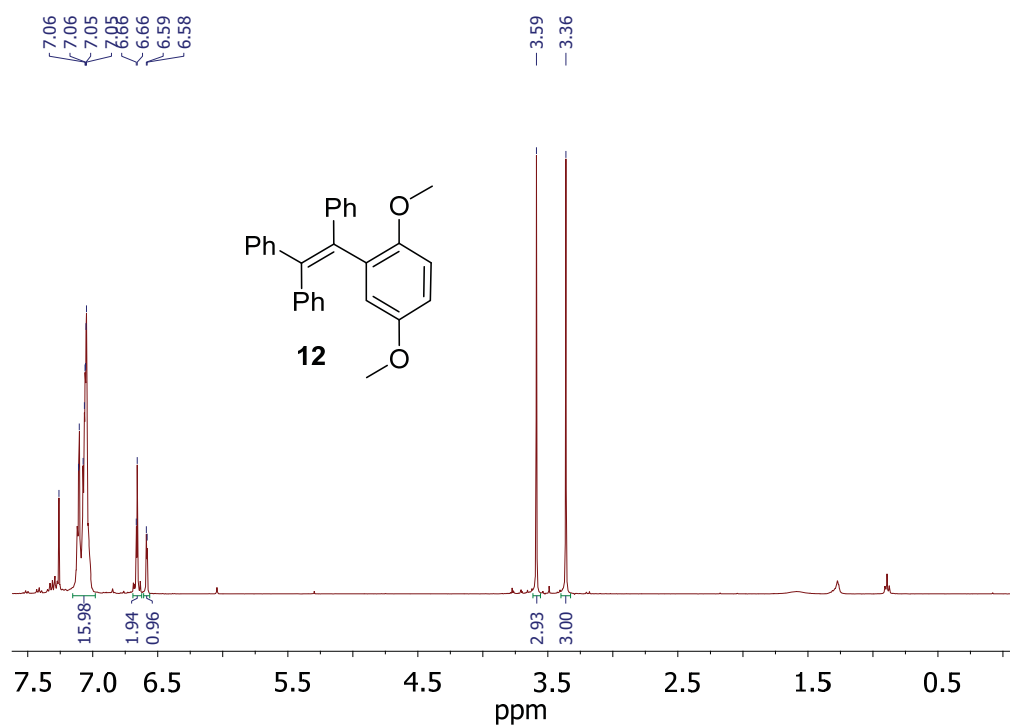
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **10**.



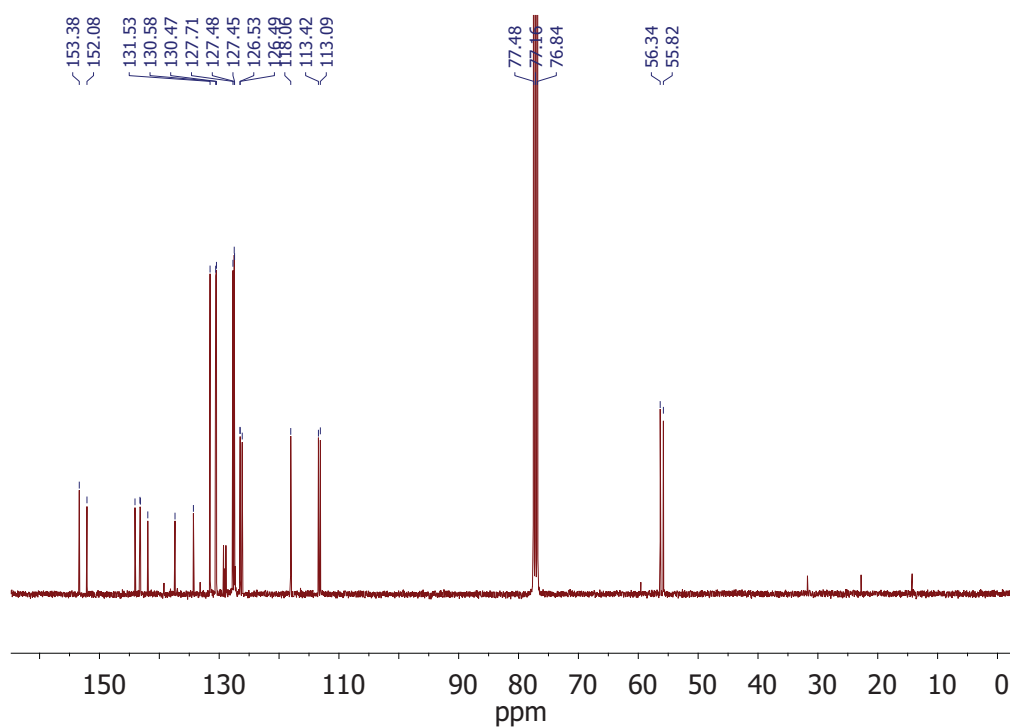
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **11**.



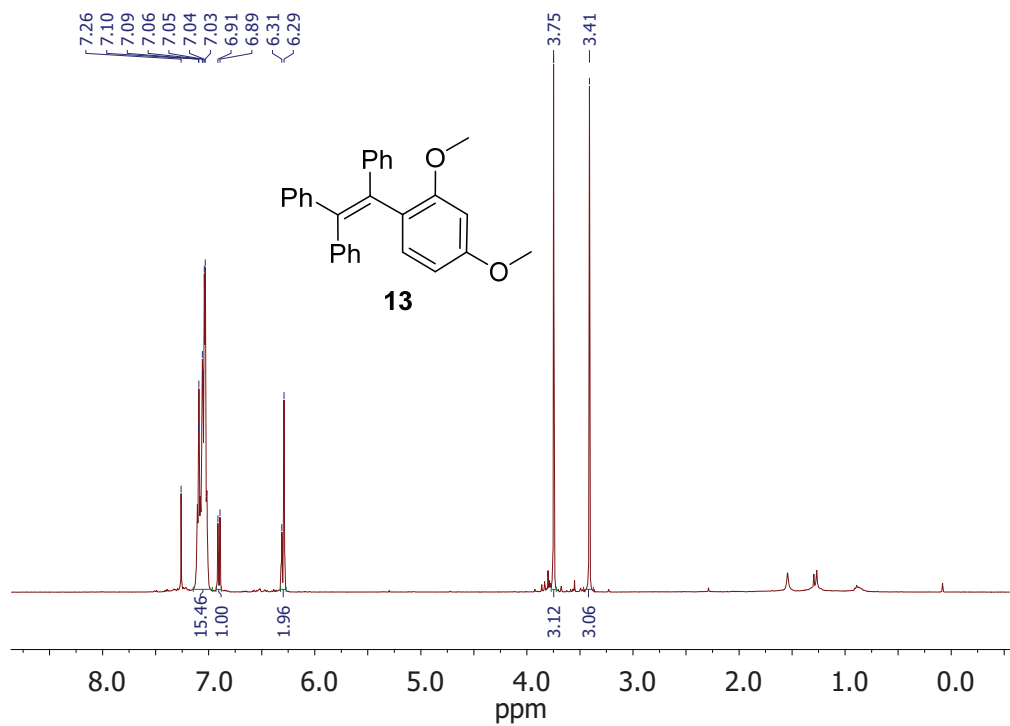
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **11**.



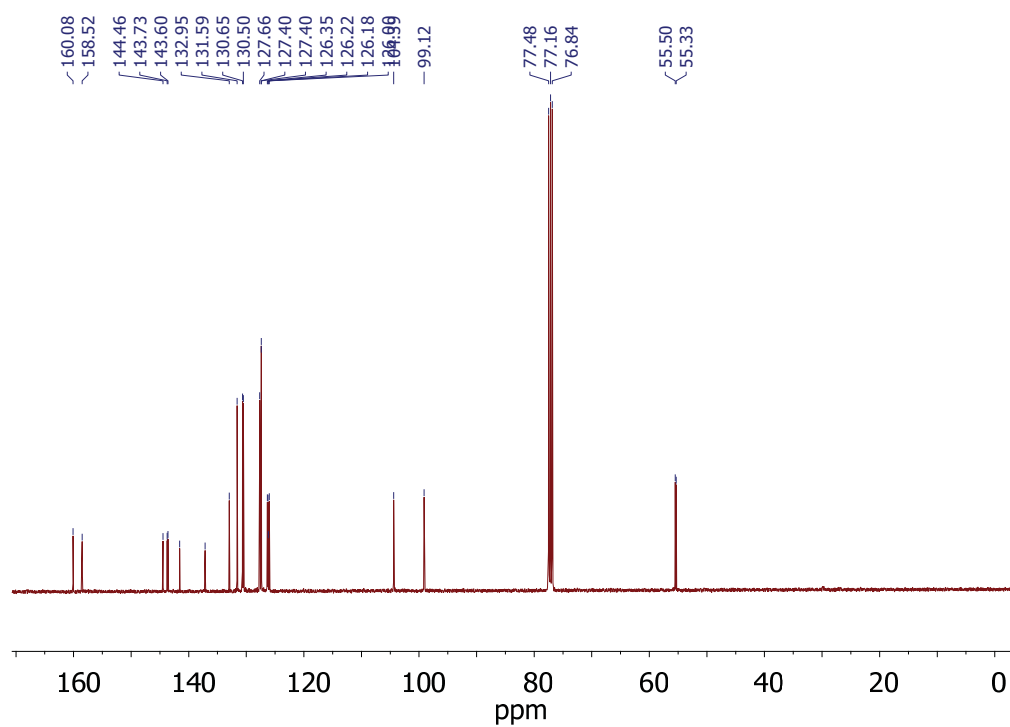
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **12**.



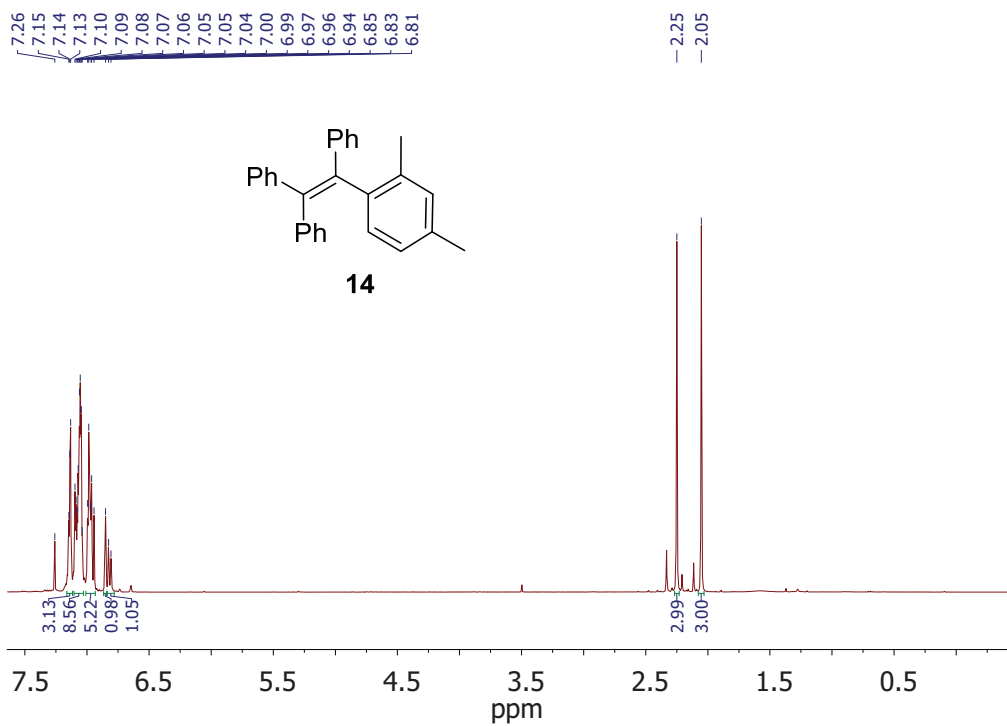
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **12**.



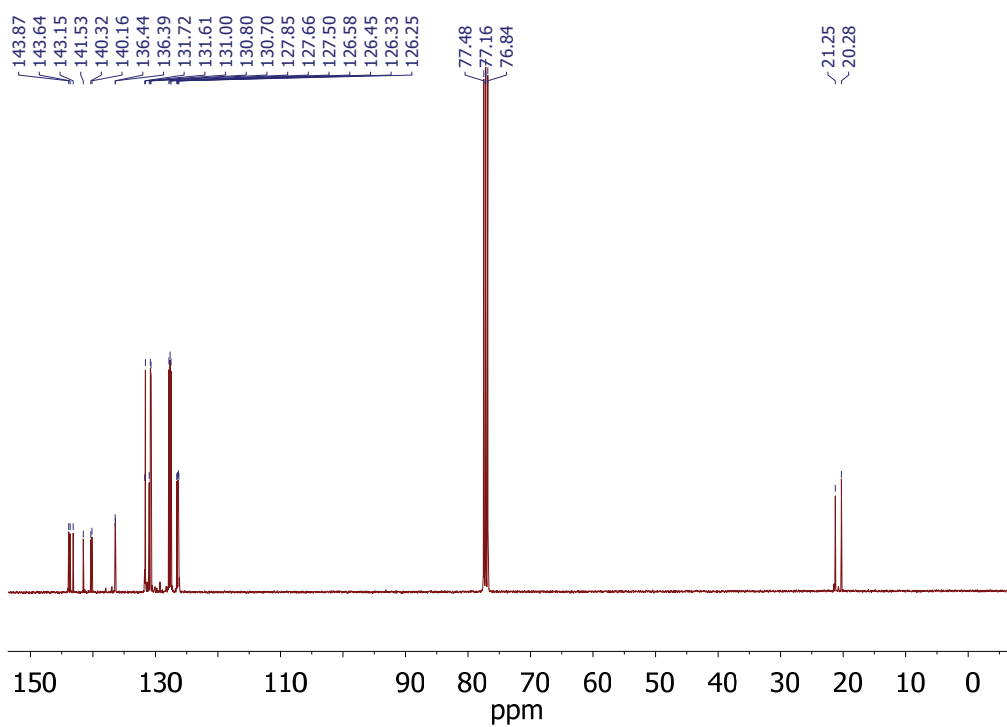
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) spectrum of **13**.



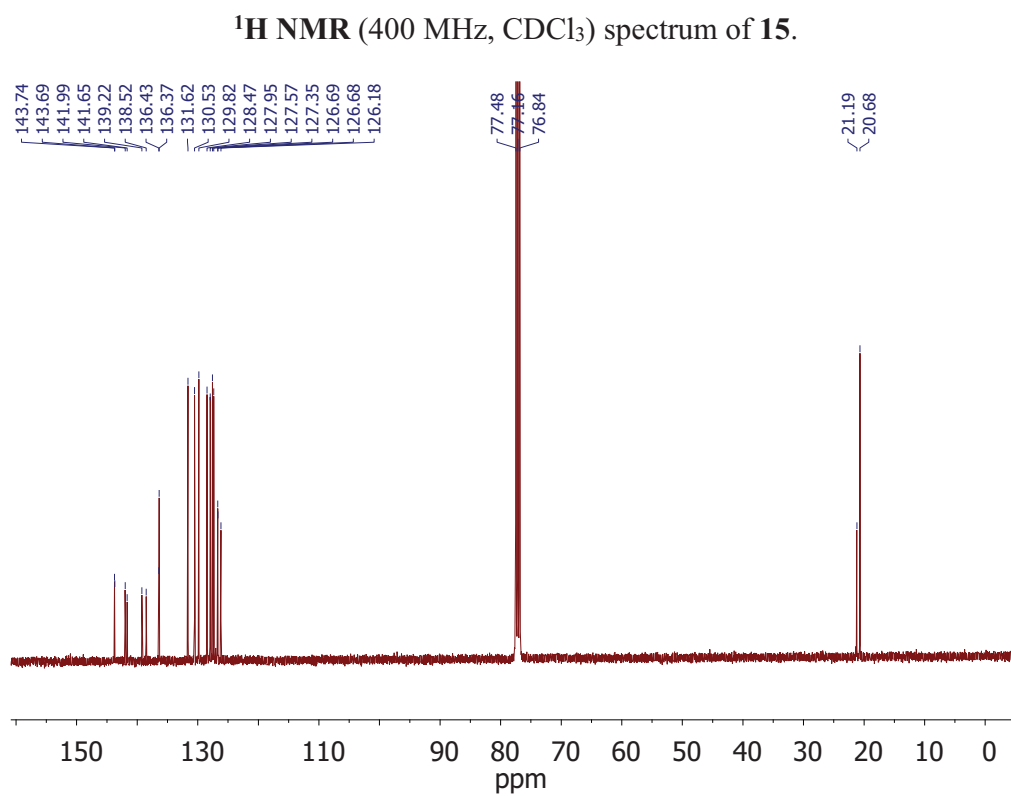
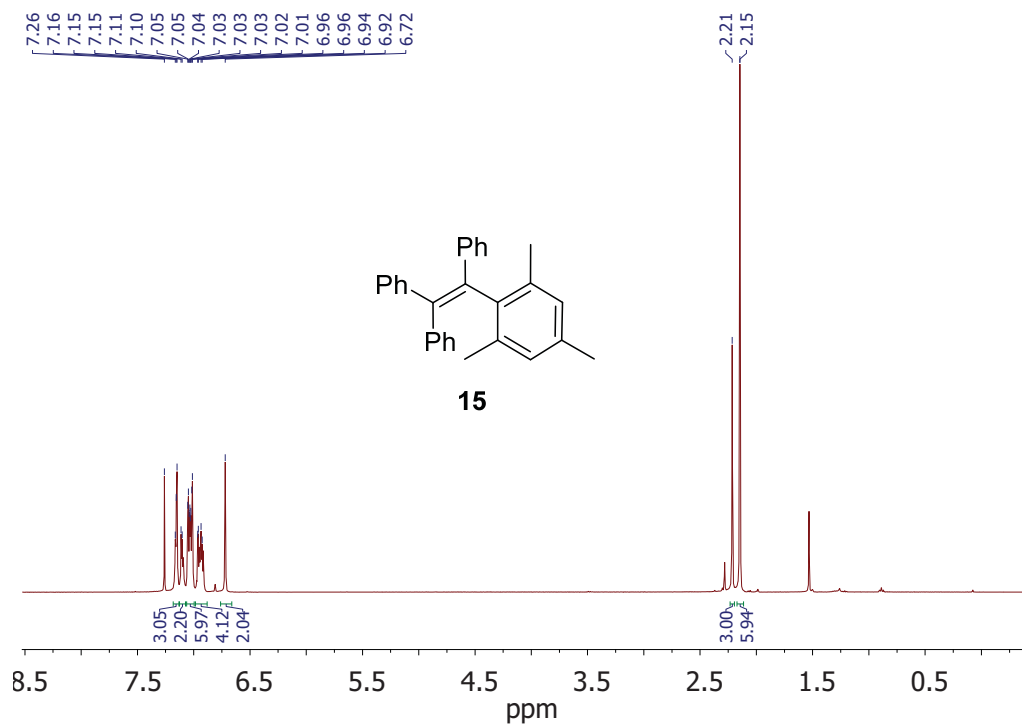
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) spectrum of **13**.

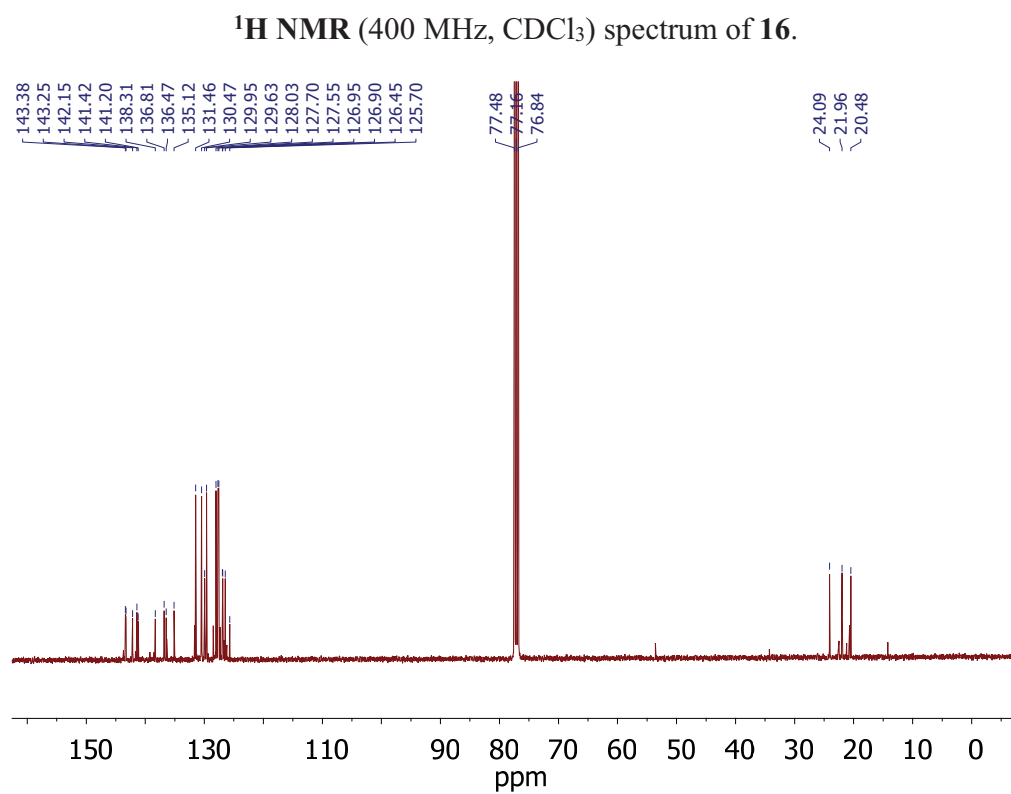
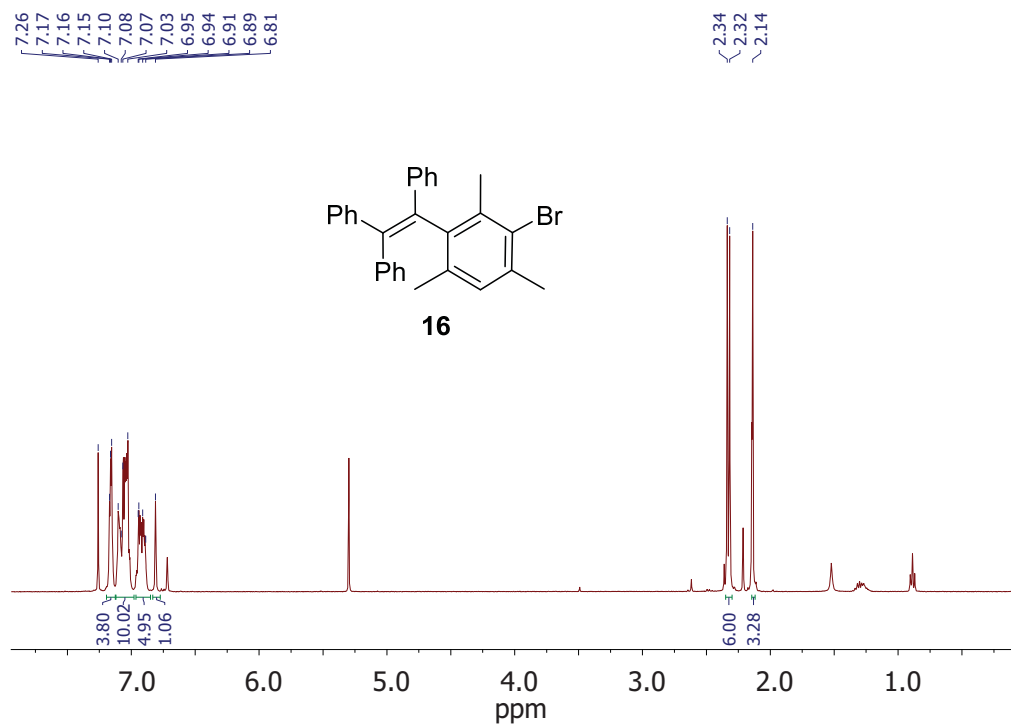


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **14**.

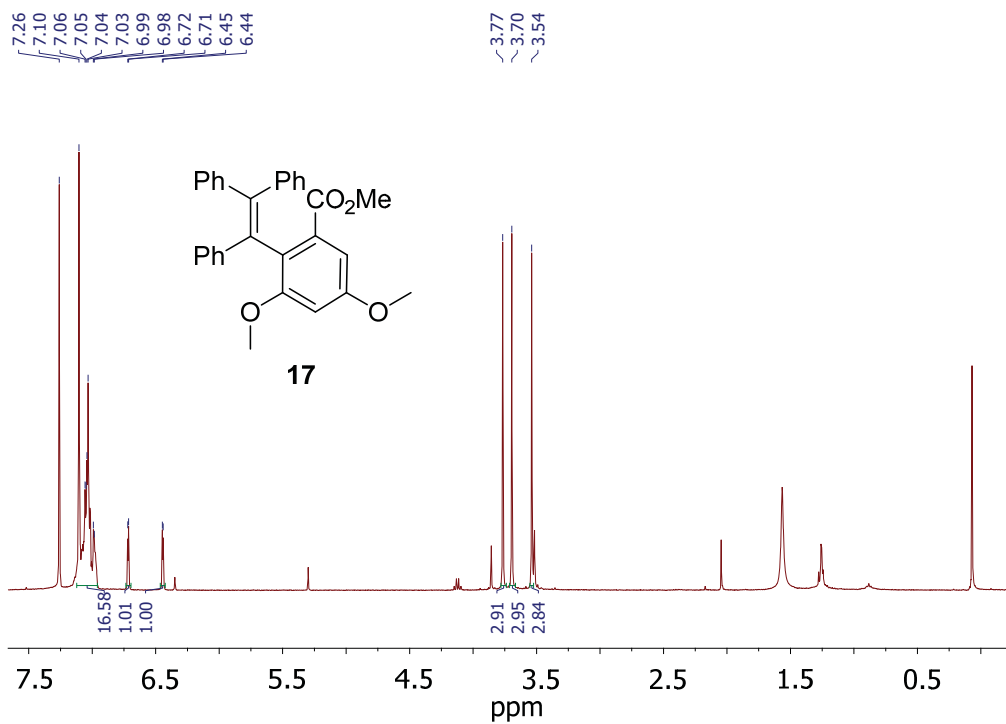


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **14**.

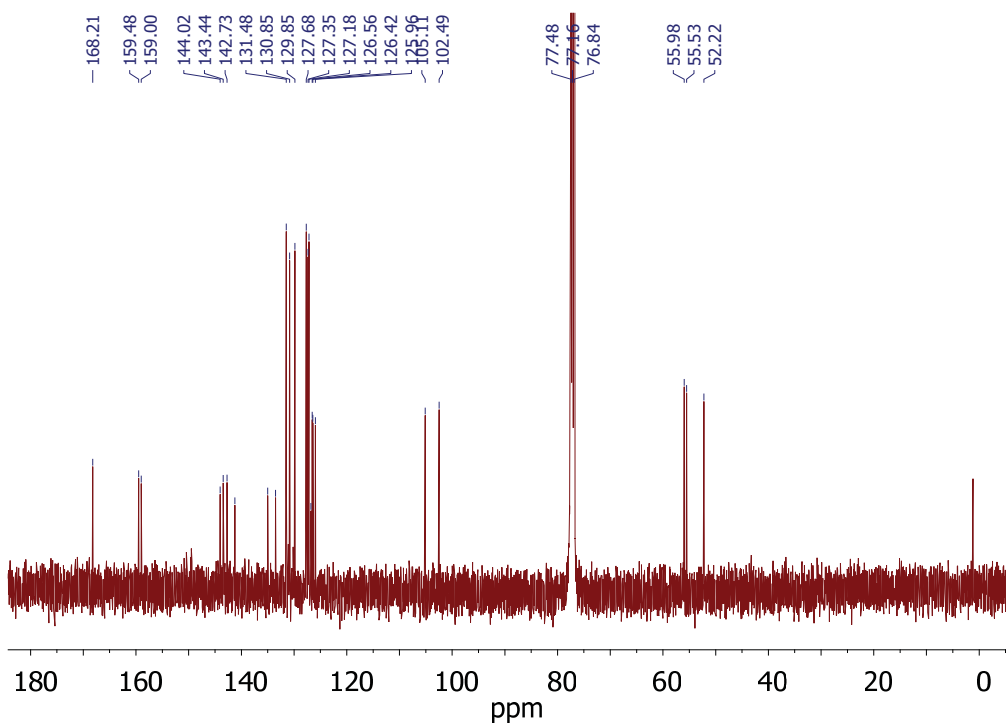




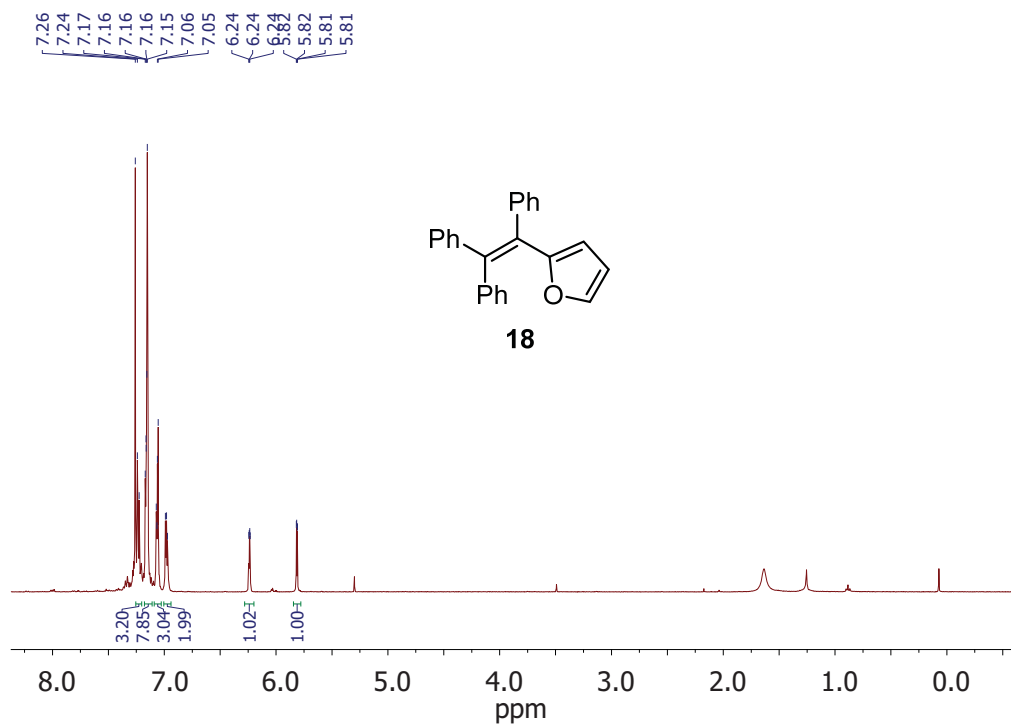




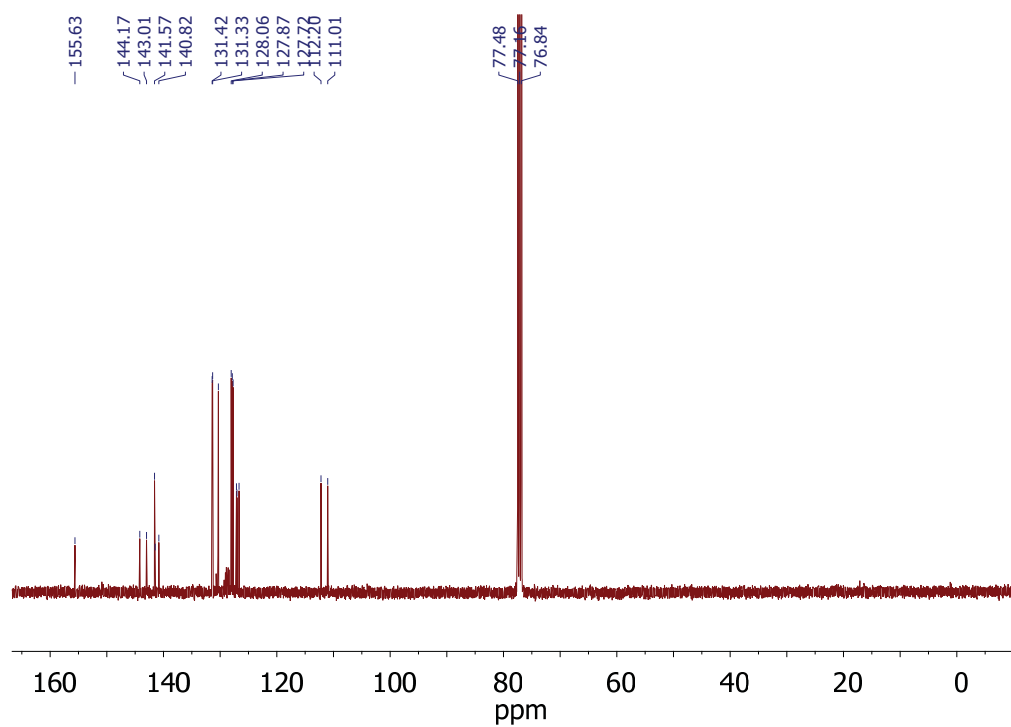
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **17**.



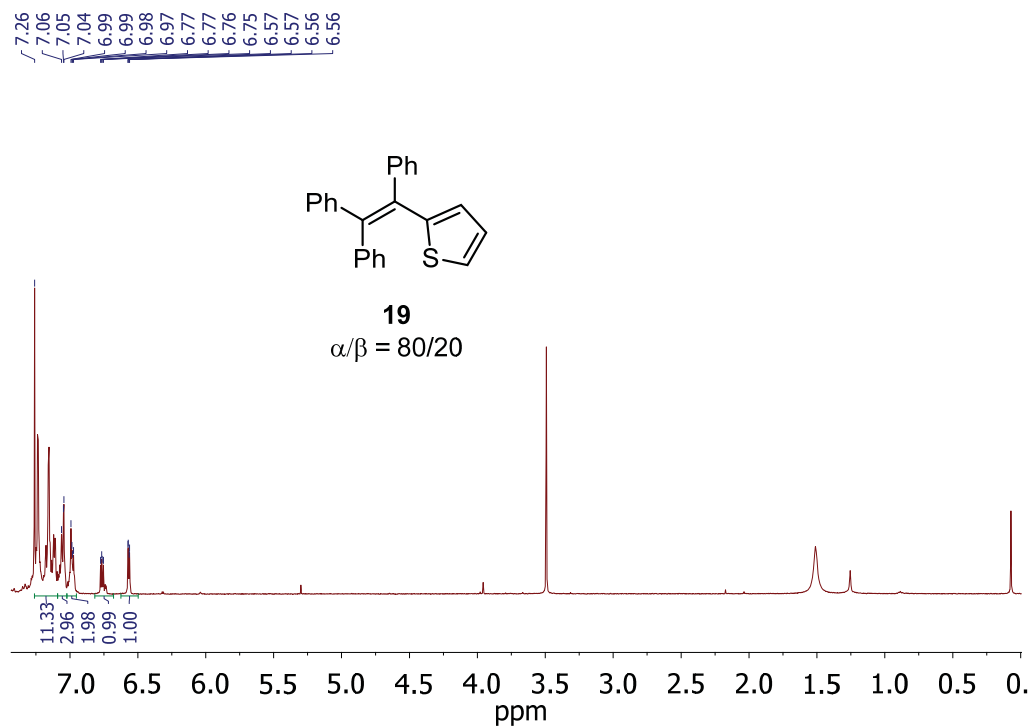
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **17**.



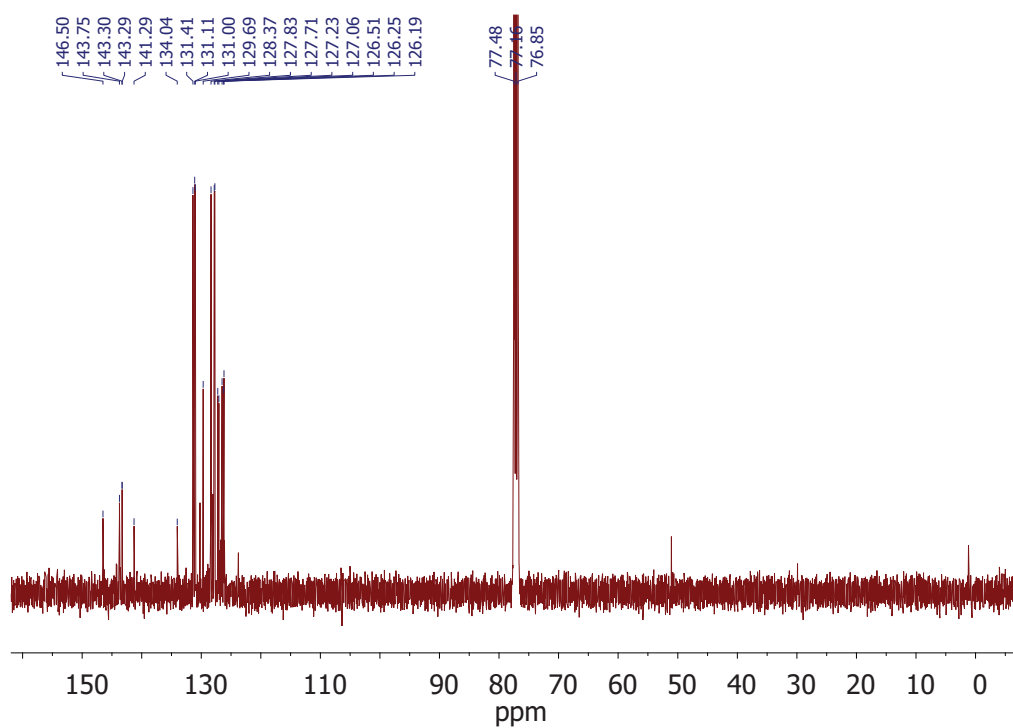
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **18**.



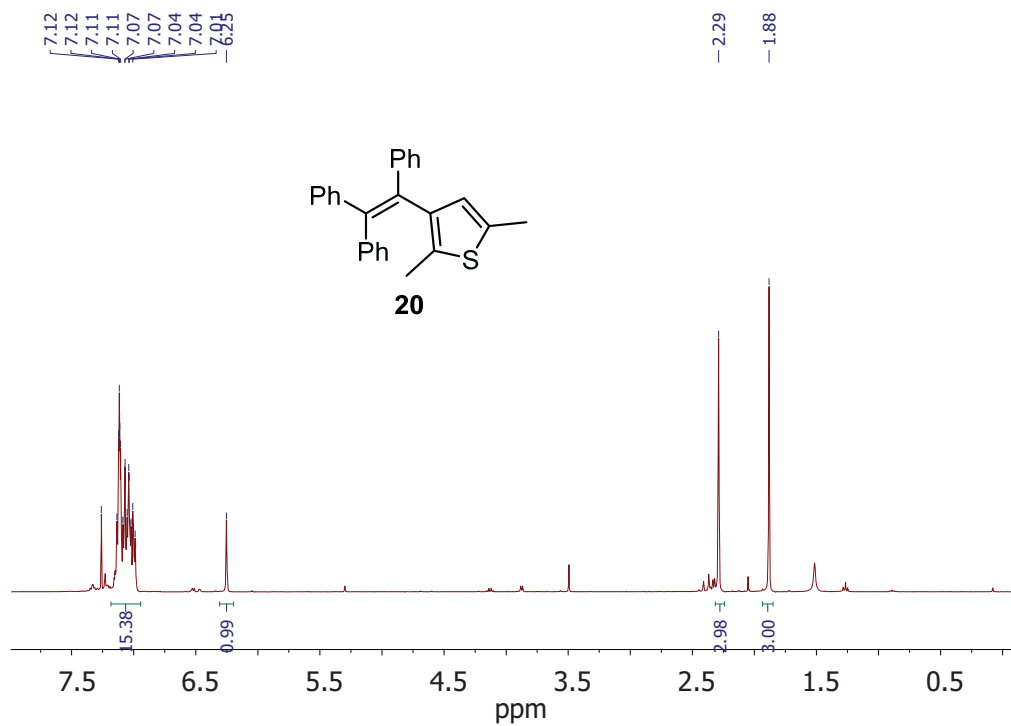
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **18**.



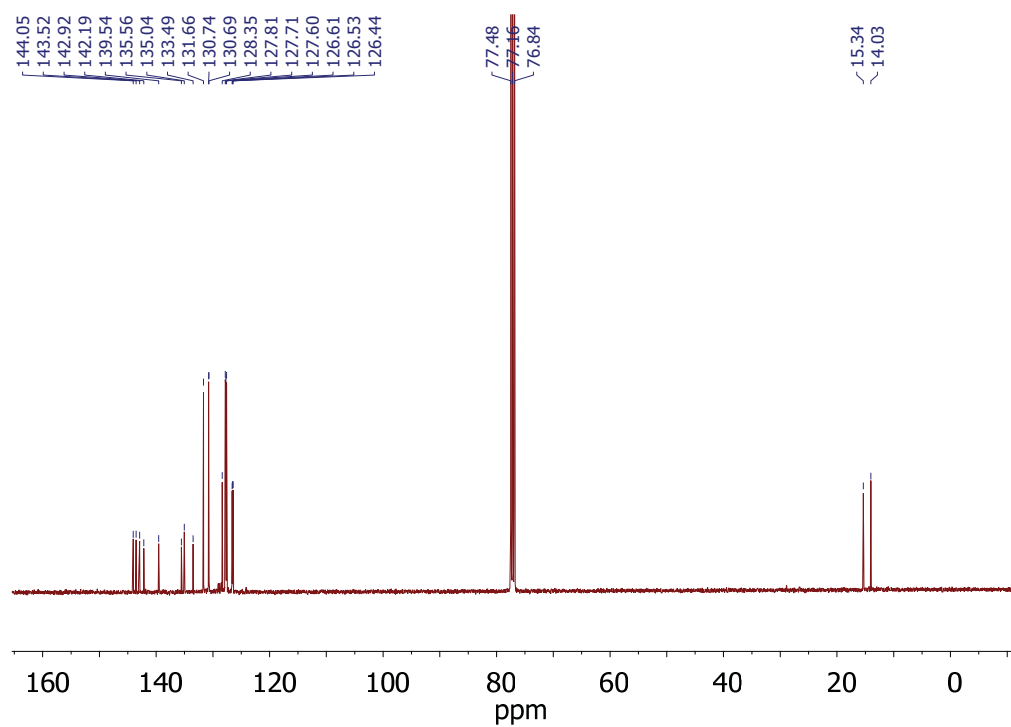
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **19**.



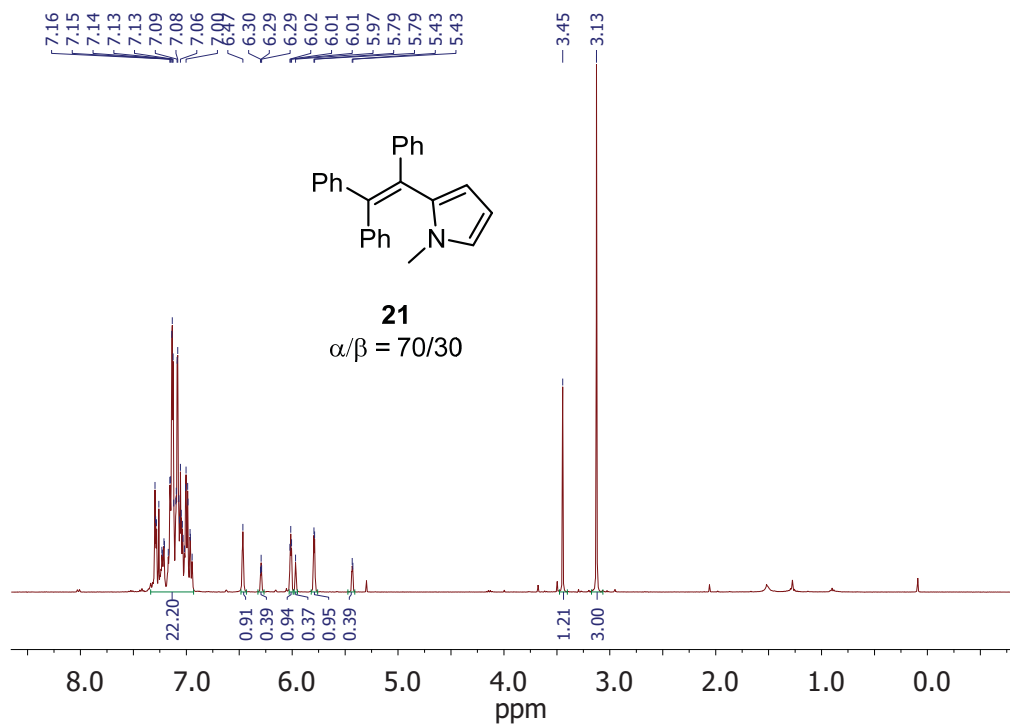
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **19**.



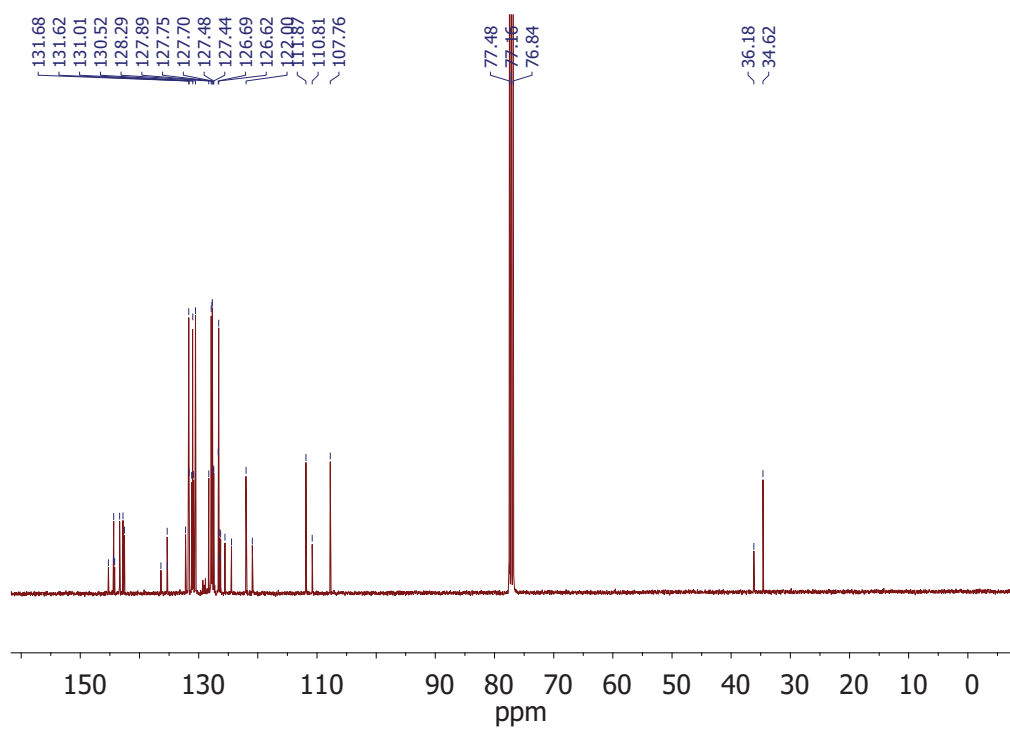
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **20**.



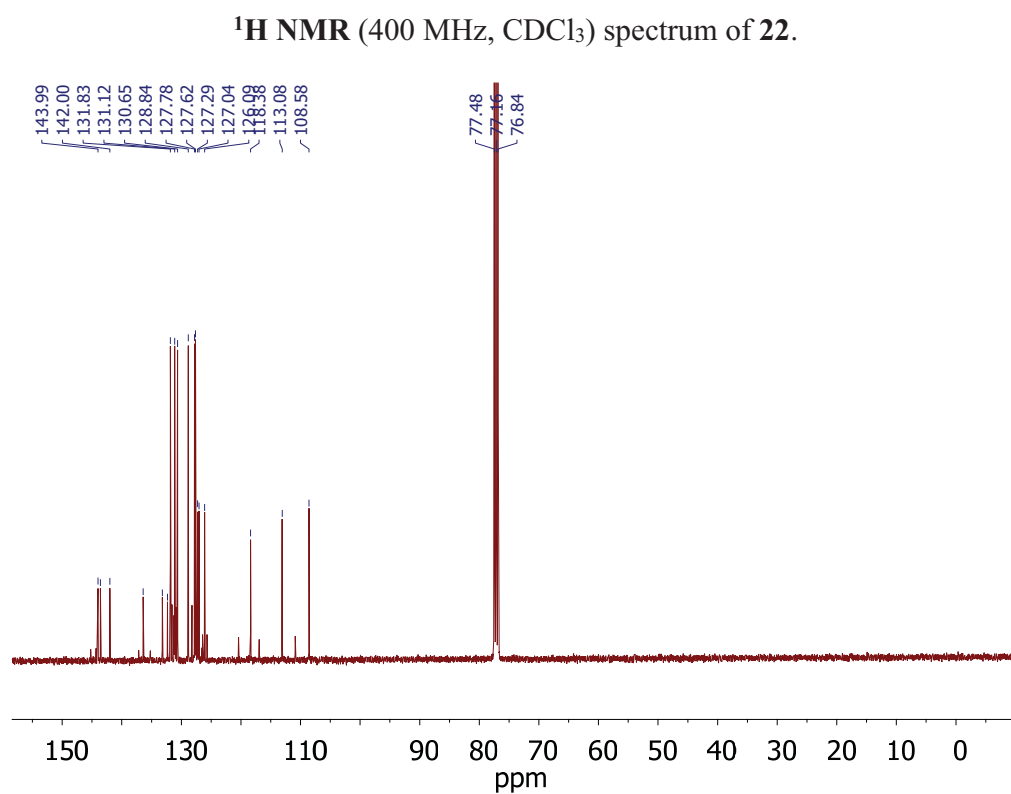
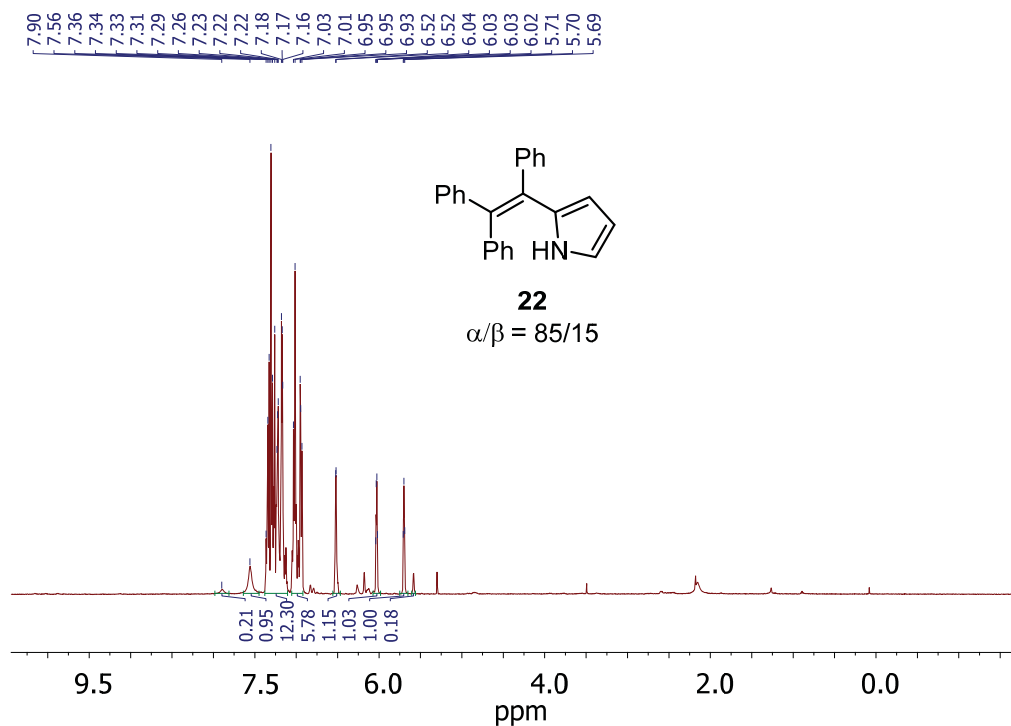
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **20**.

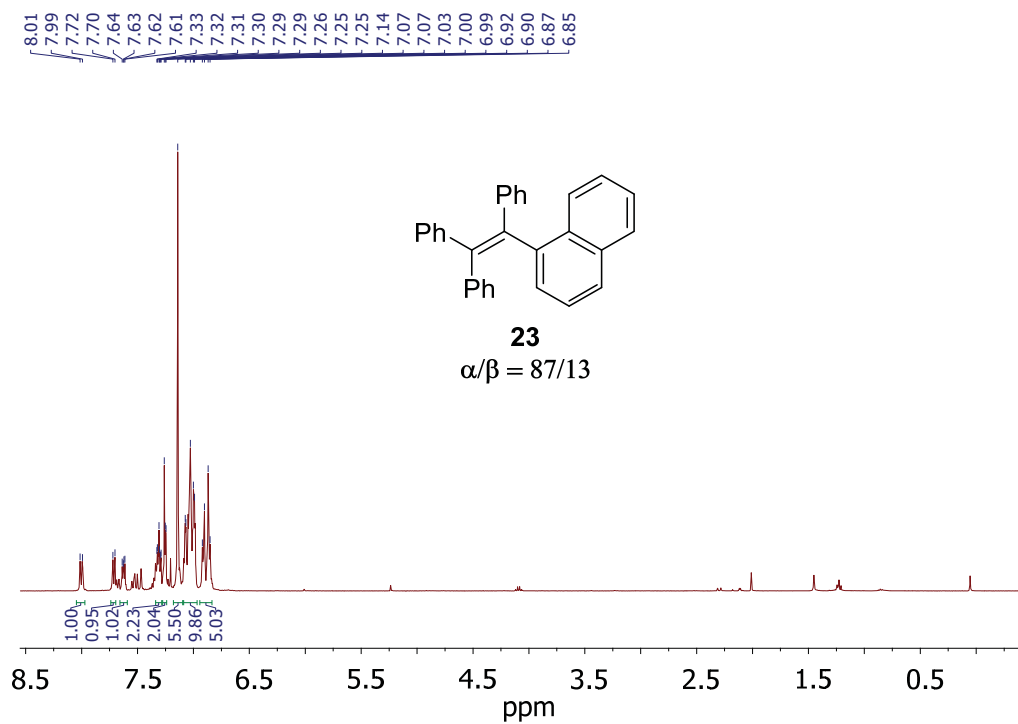


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **21**.

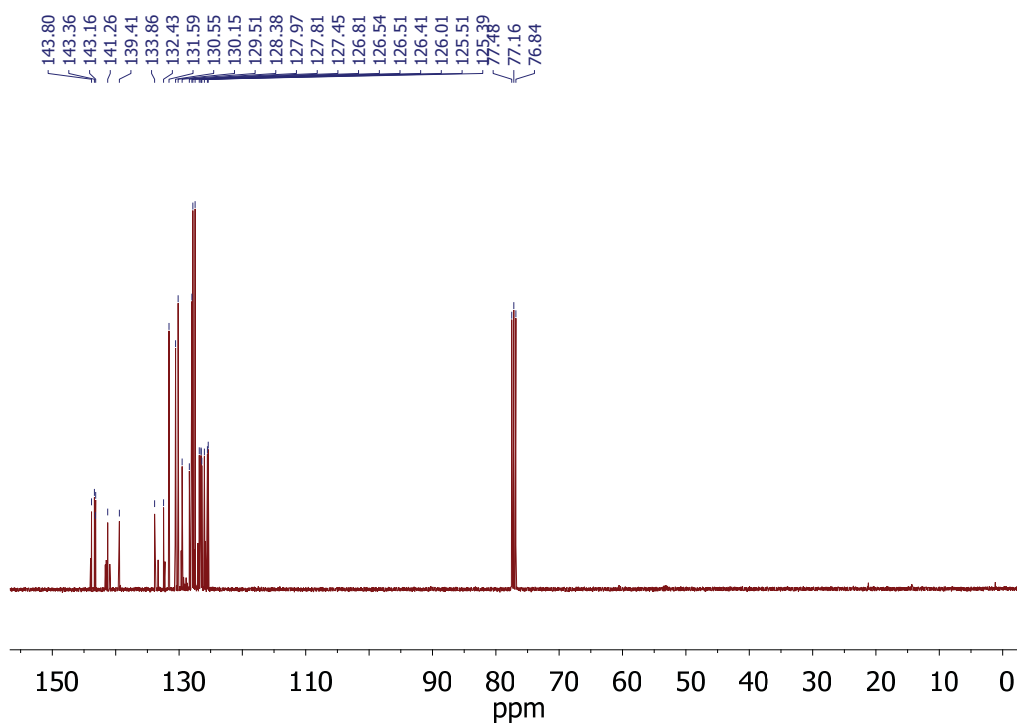


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **21**.

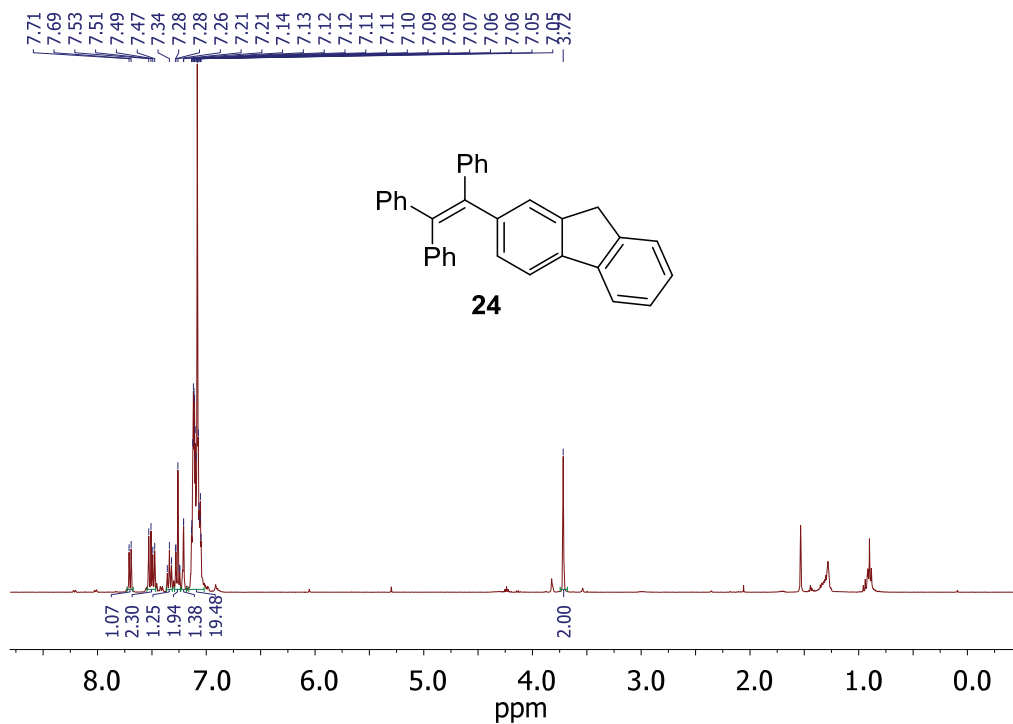




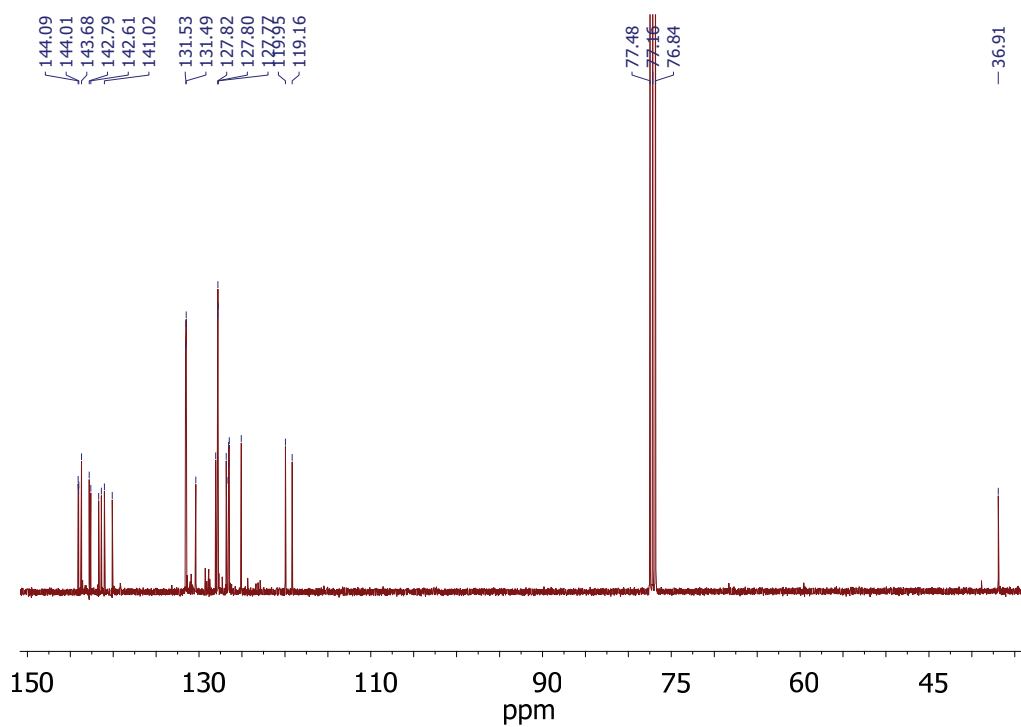
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) spectrum of **23**.



$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) spectrum of **23**.

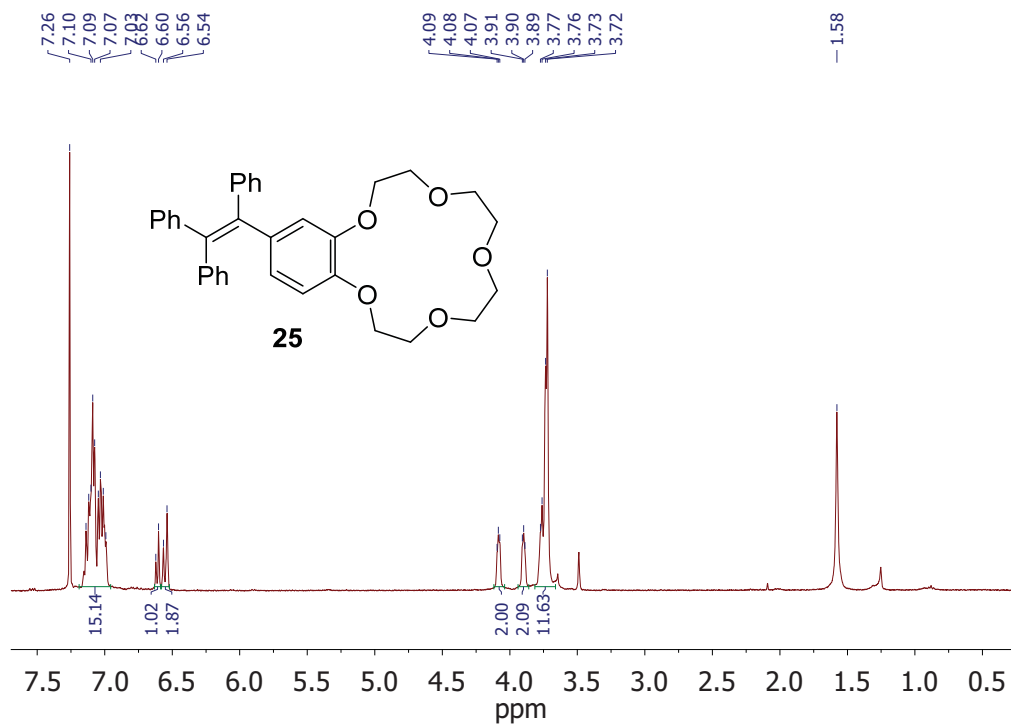


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **24**.

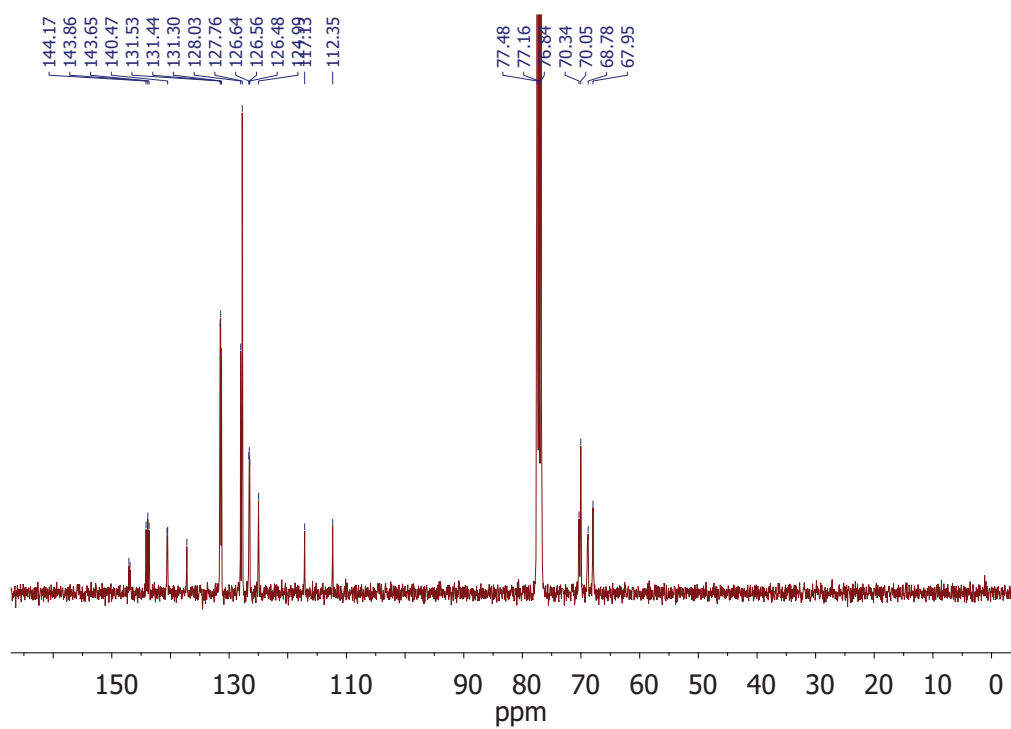


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **24**.

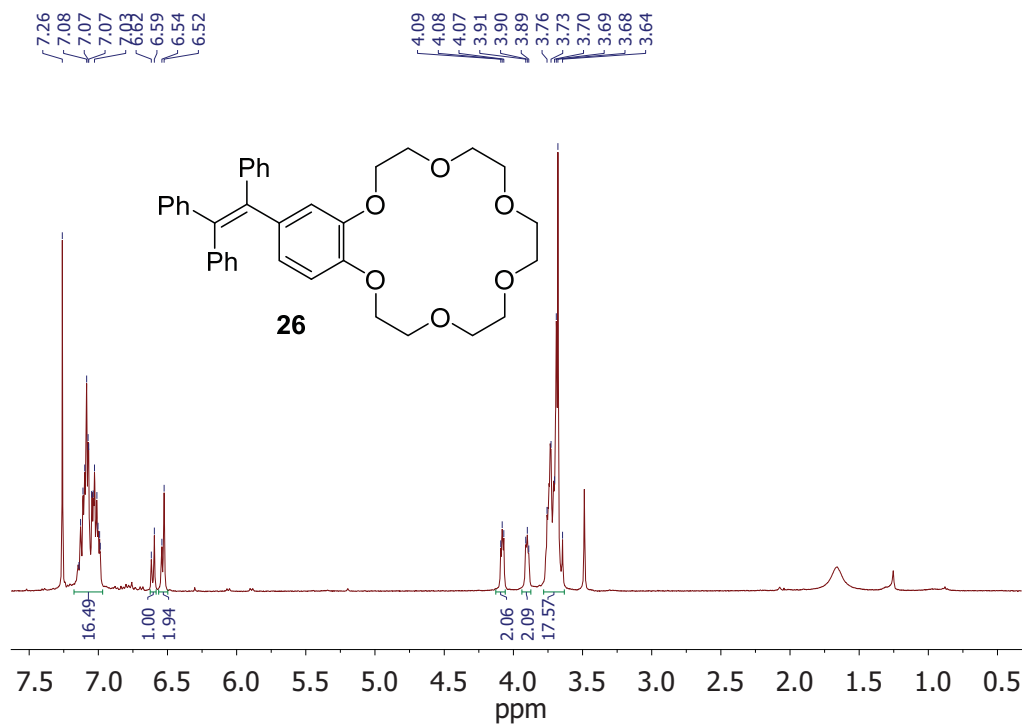




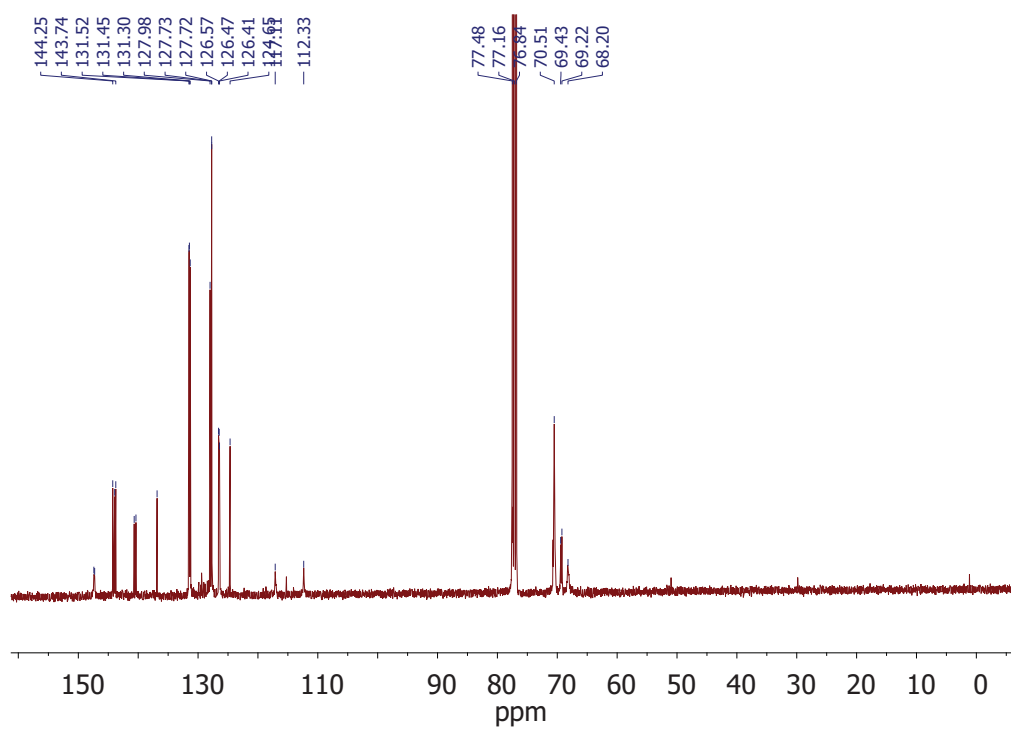
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) spectrum of **25**.



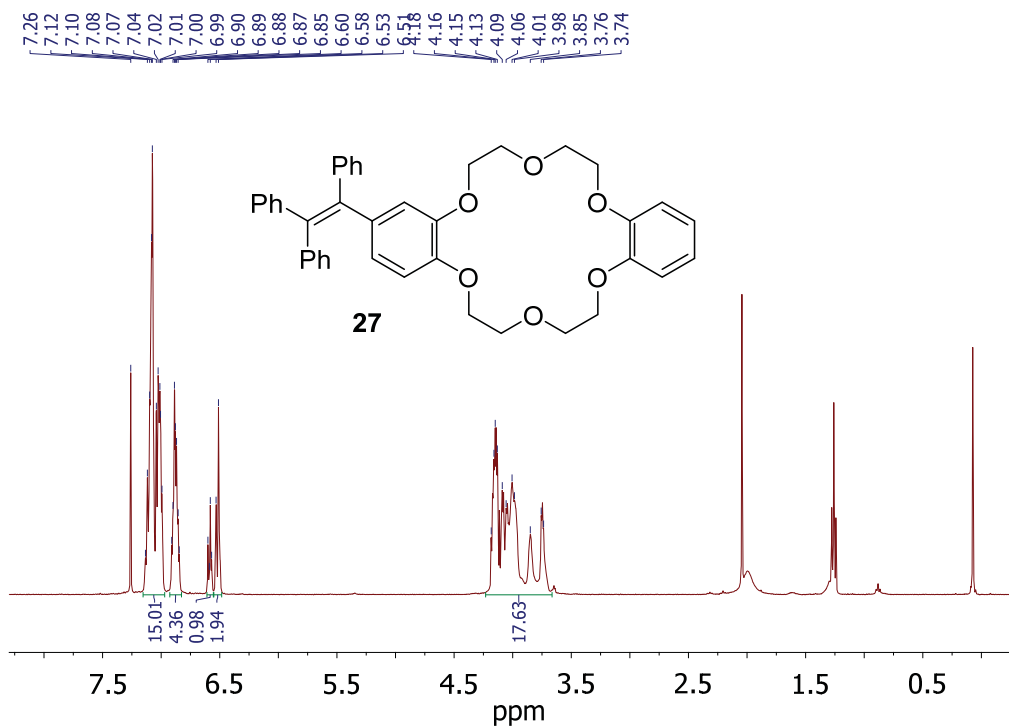
$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) spectrum of **25**.



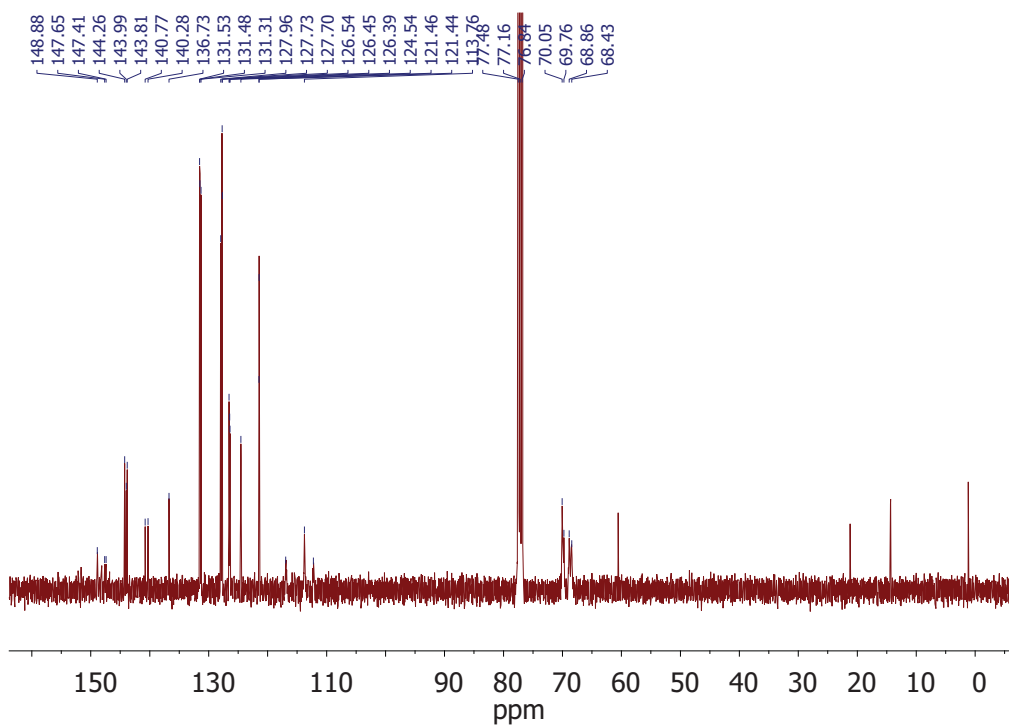
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **26**.



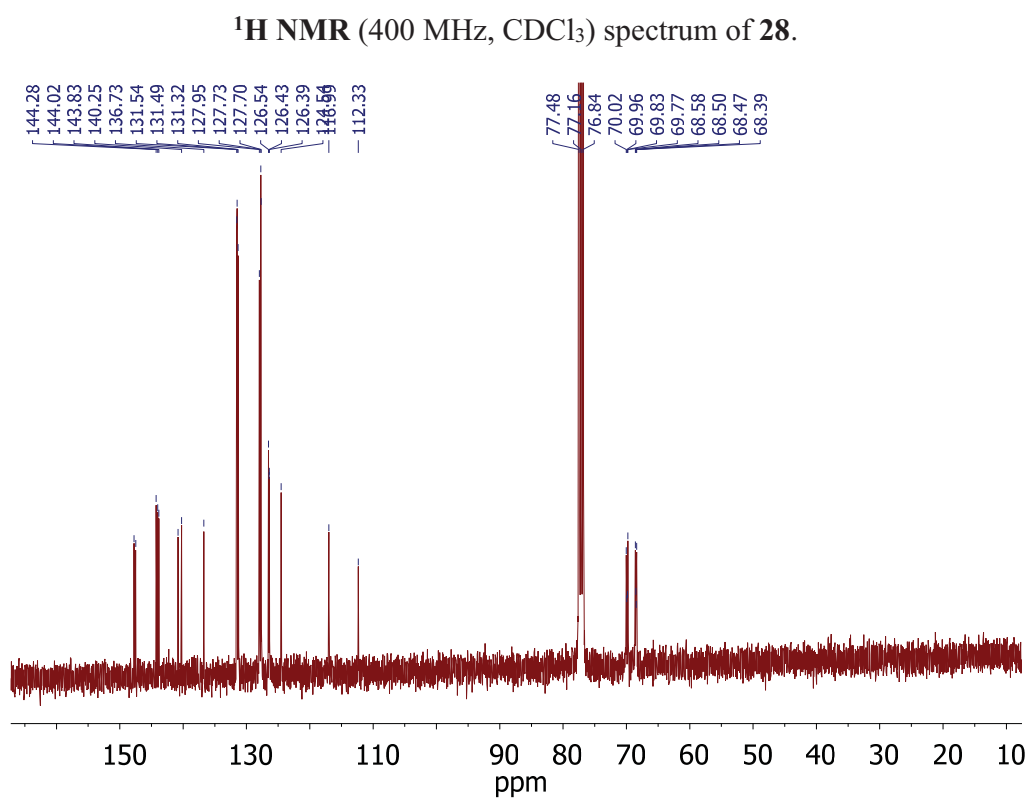
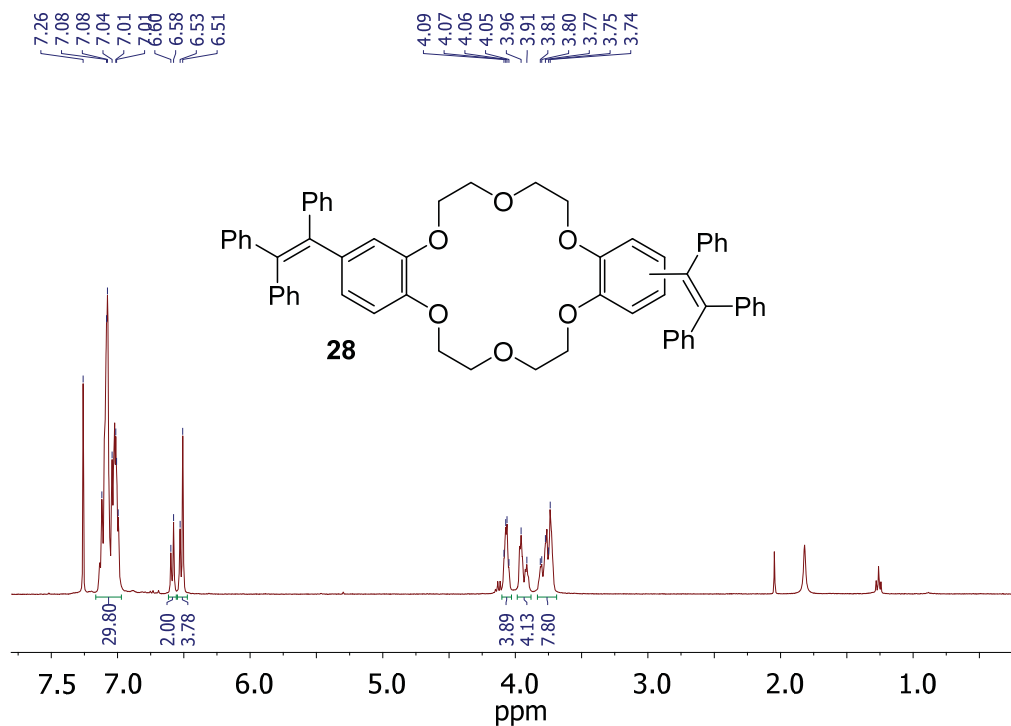
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **26**.

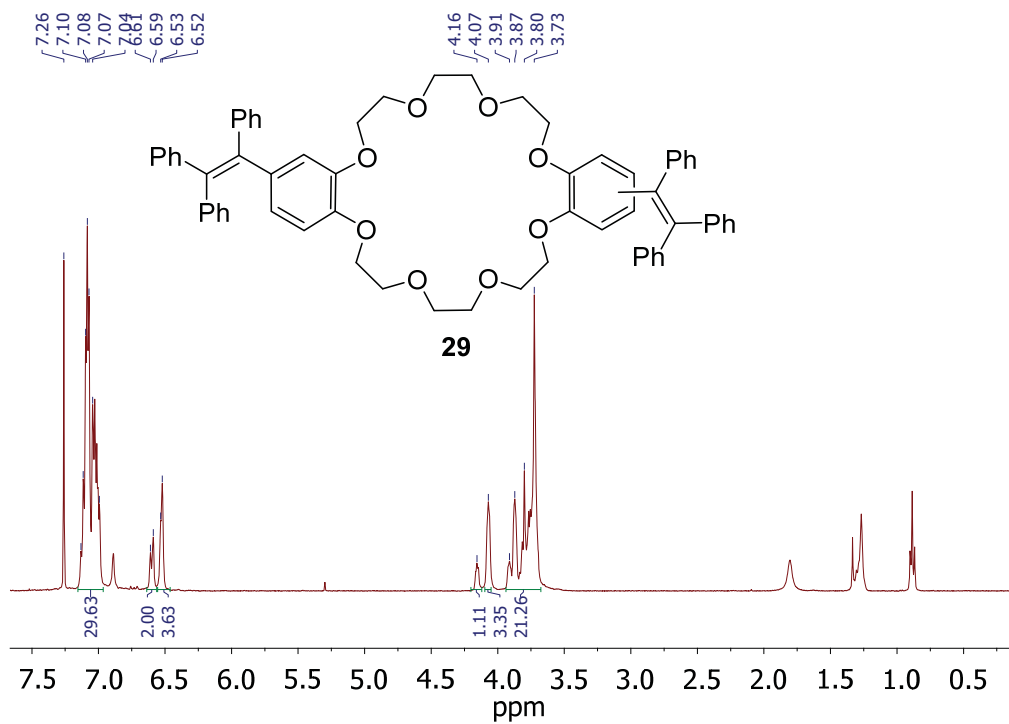


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **27**

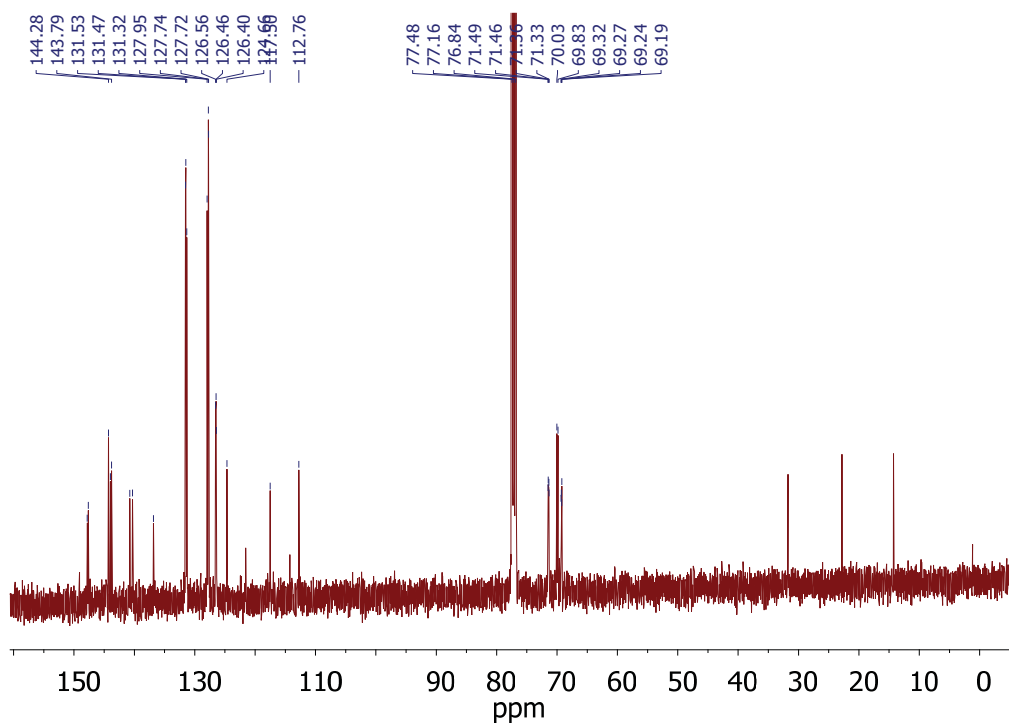


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **27**.

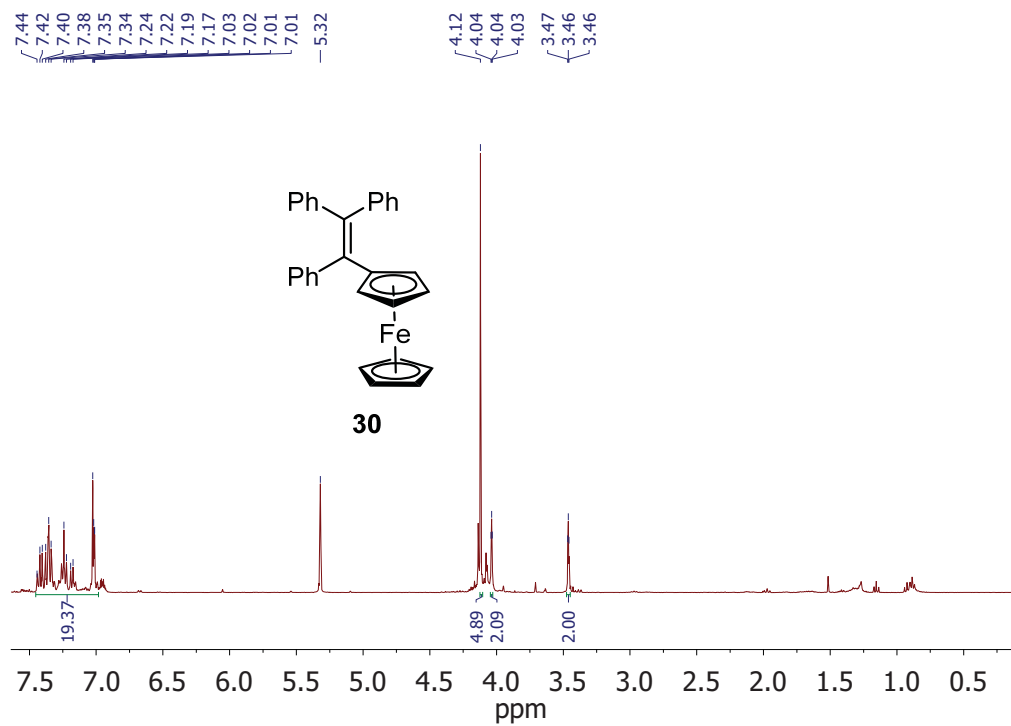




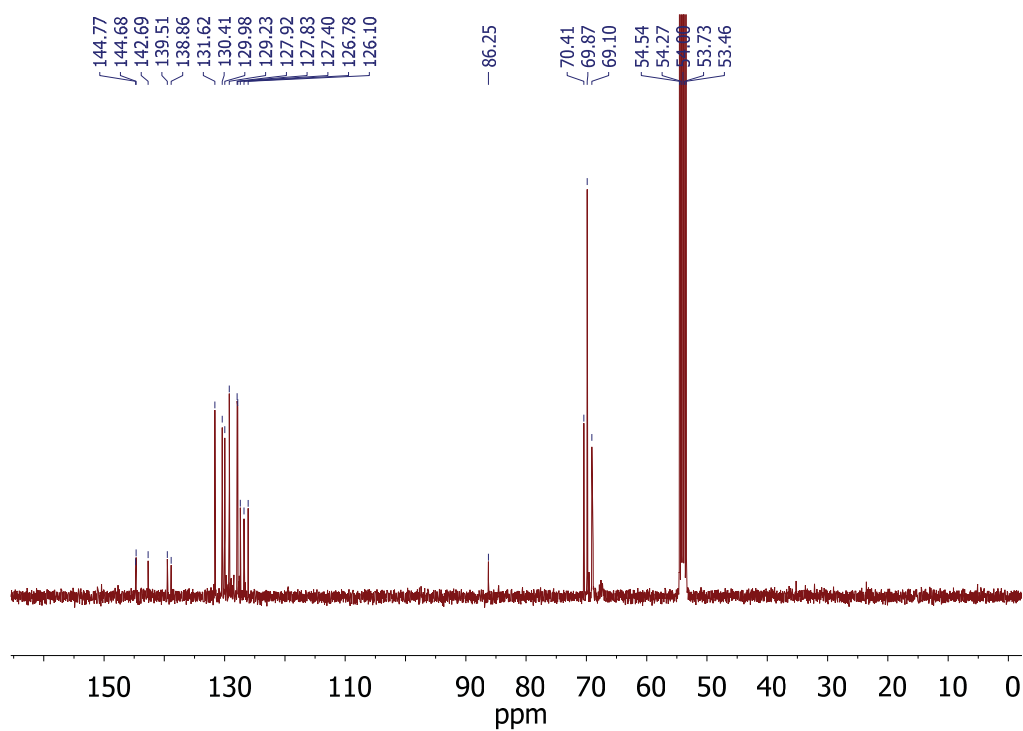
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **29**.



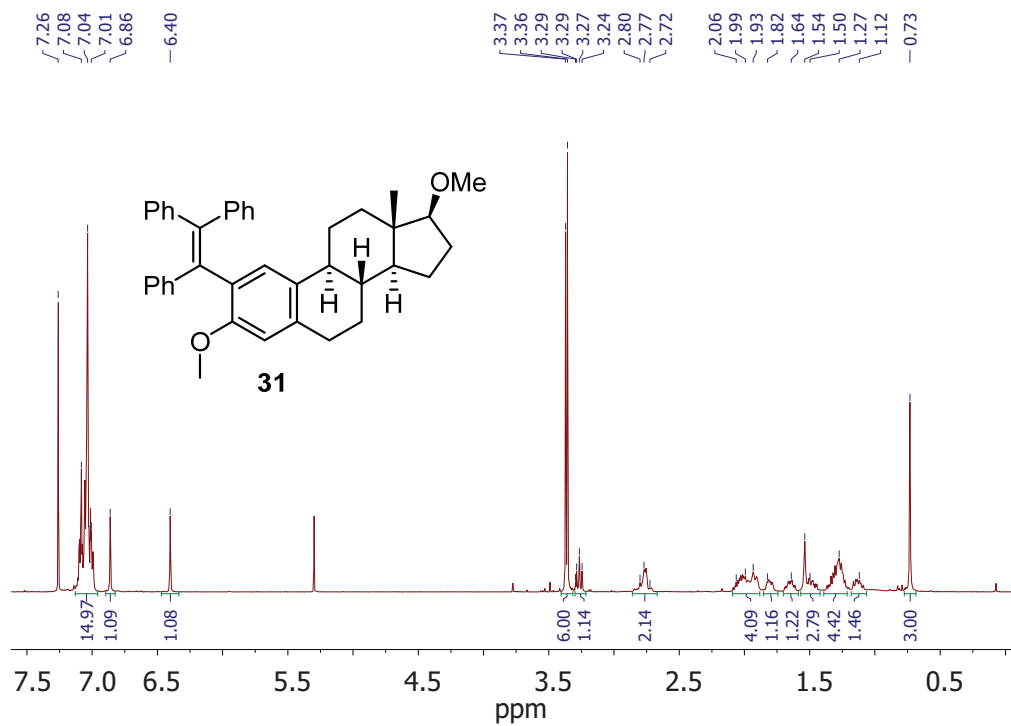
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **29**.



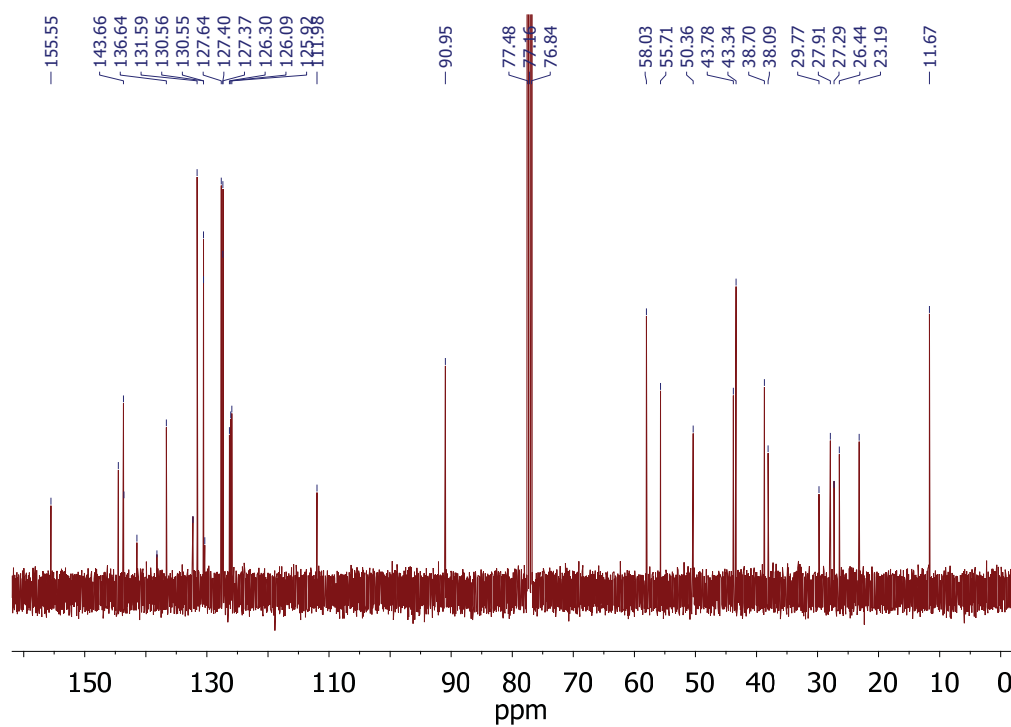
<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of **30**.



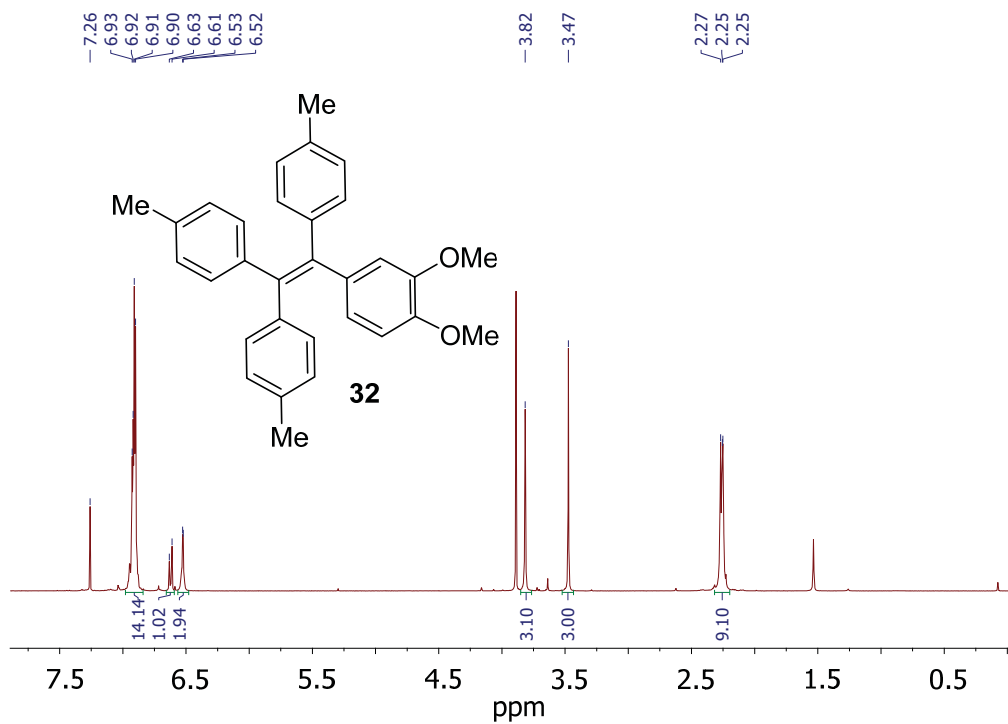
<sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) spectrum of **30**.



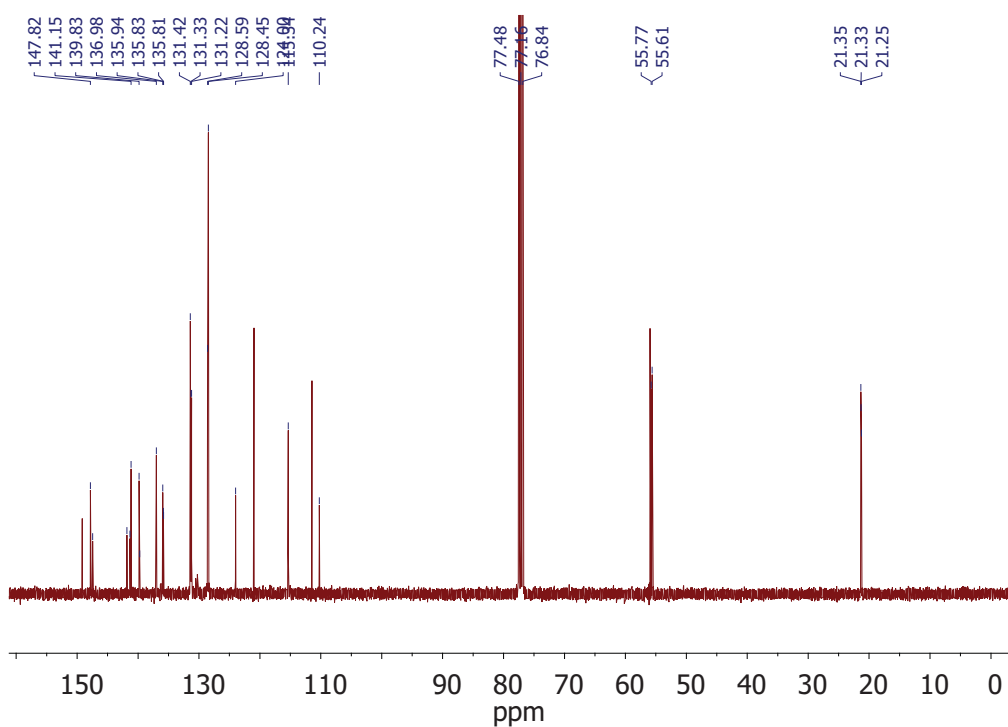
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of 31.



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of 31.

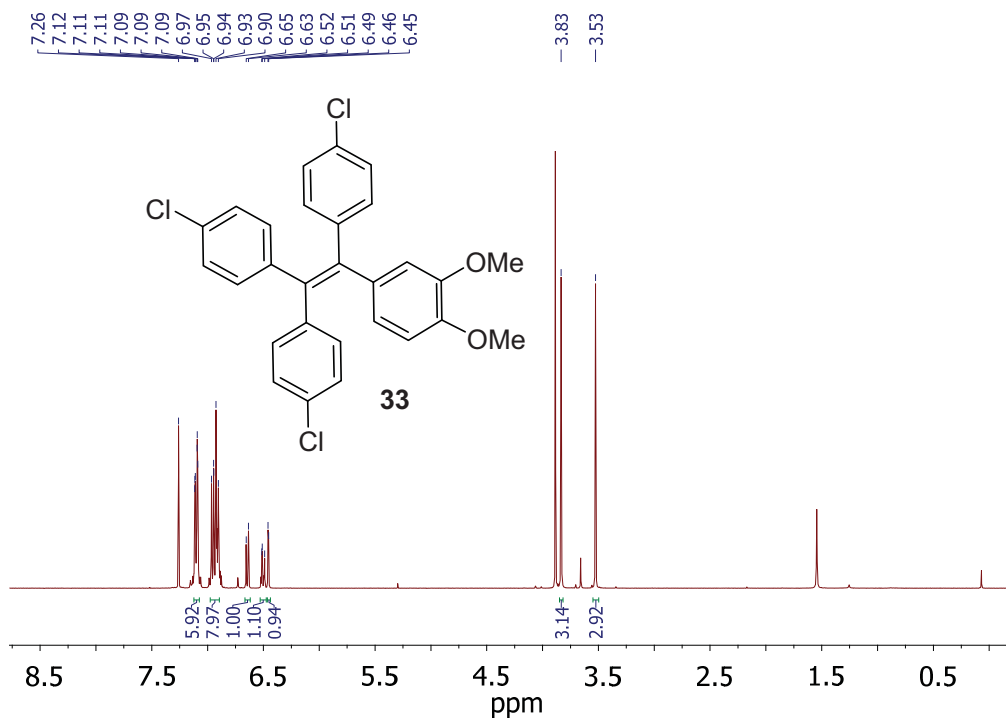


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **32**.

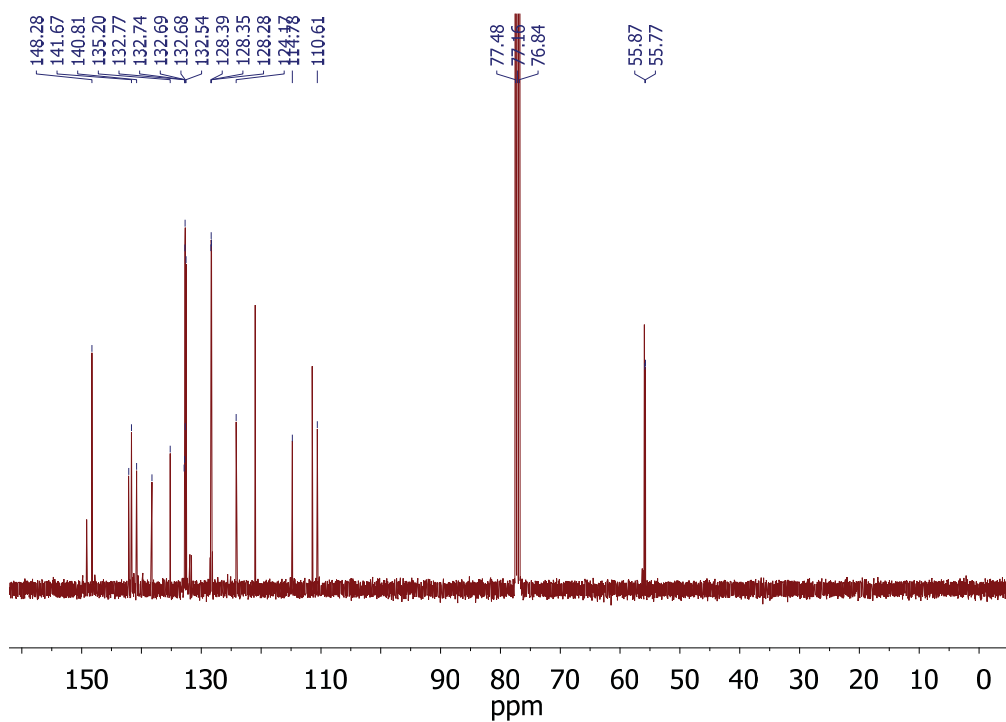


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **32**.

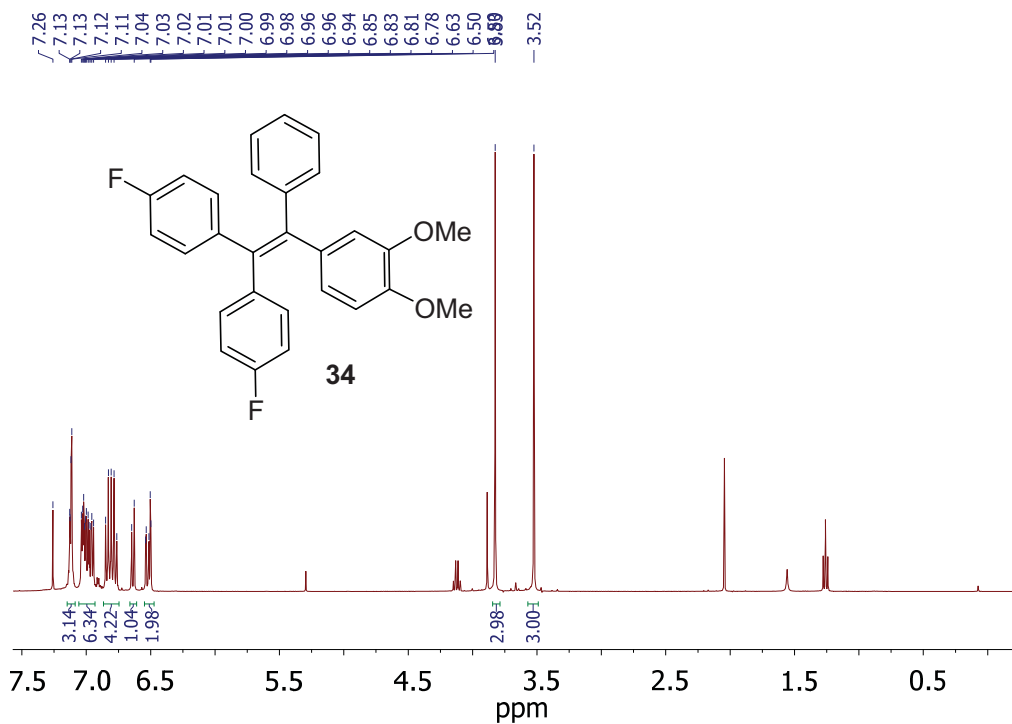




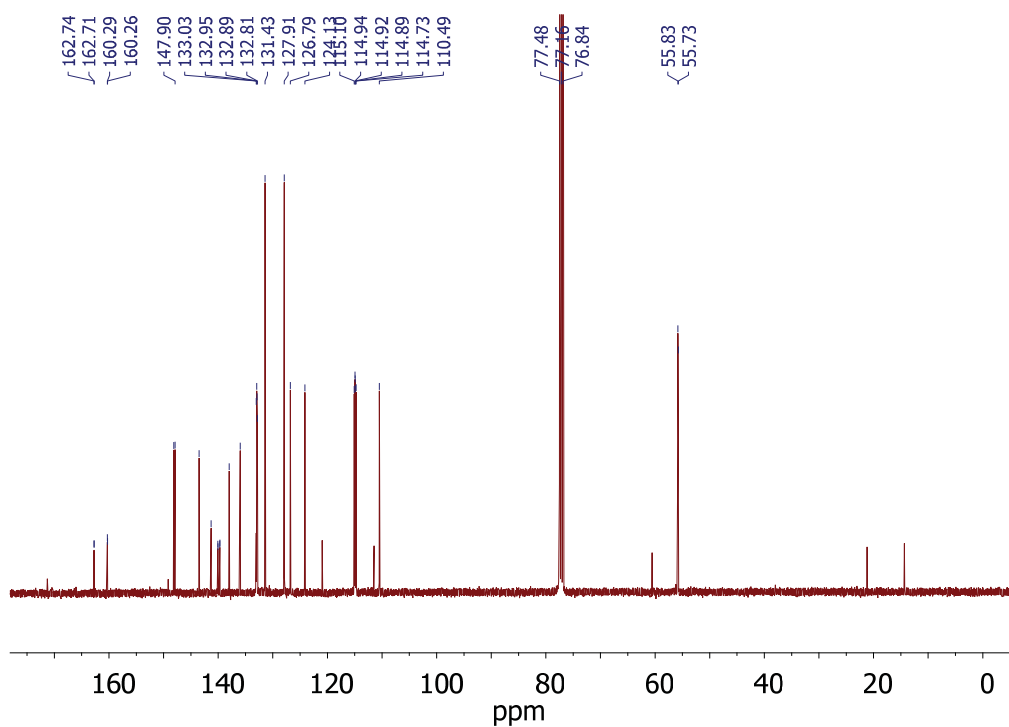
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **33**.



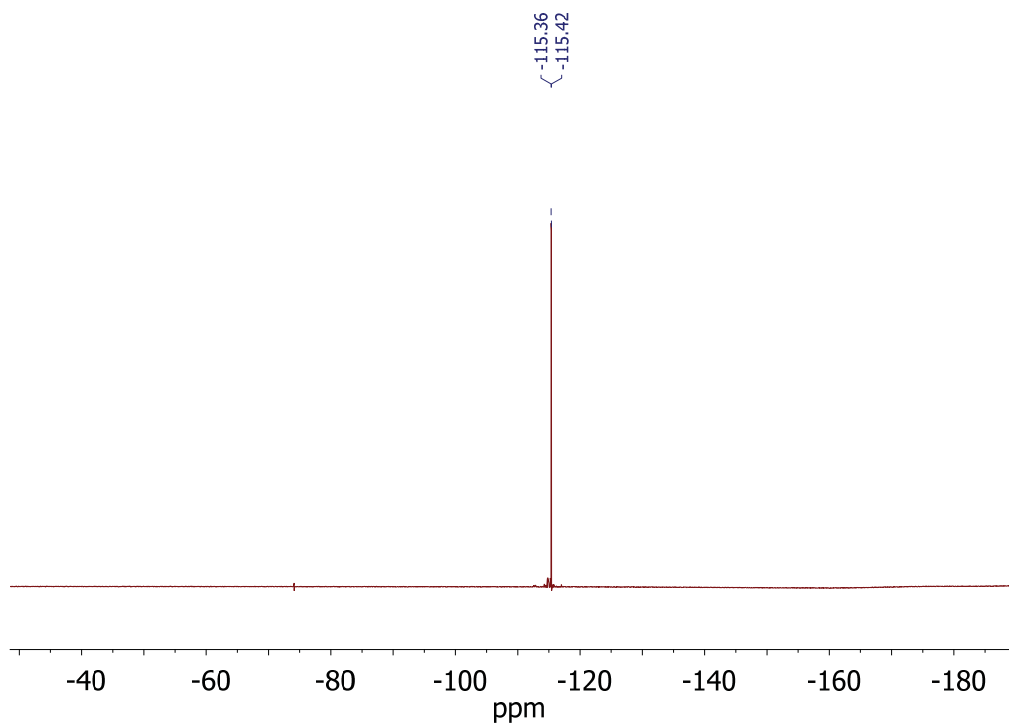
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **33**.



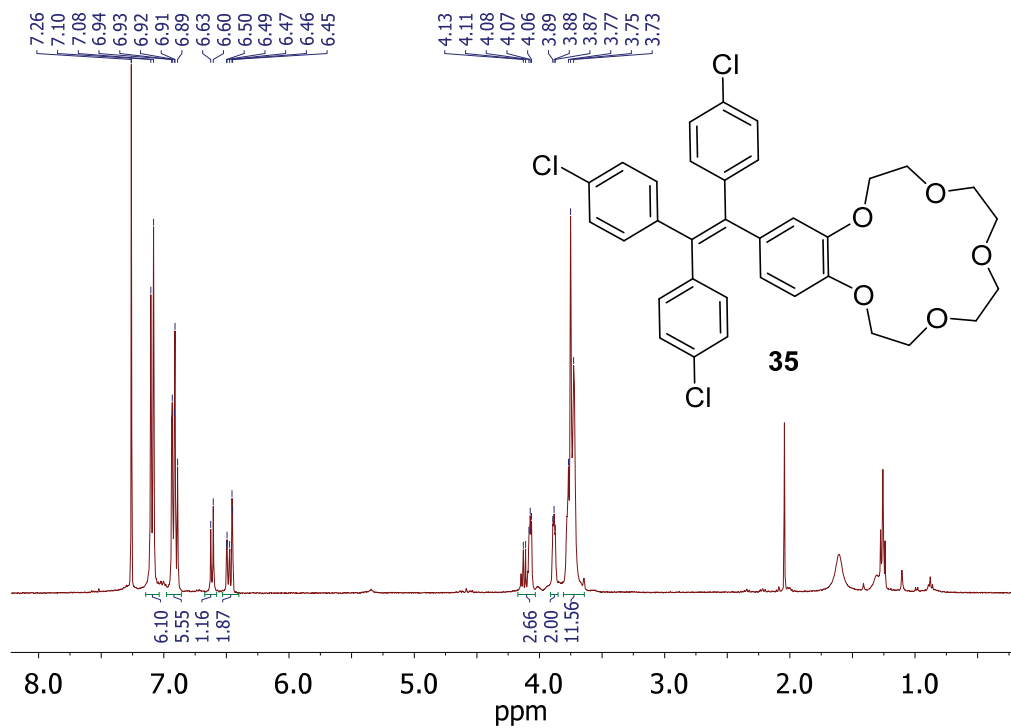
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **34**.



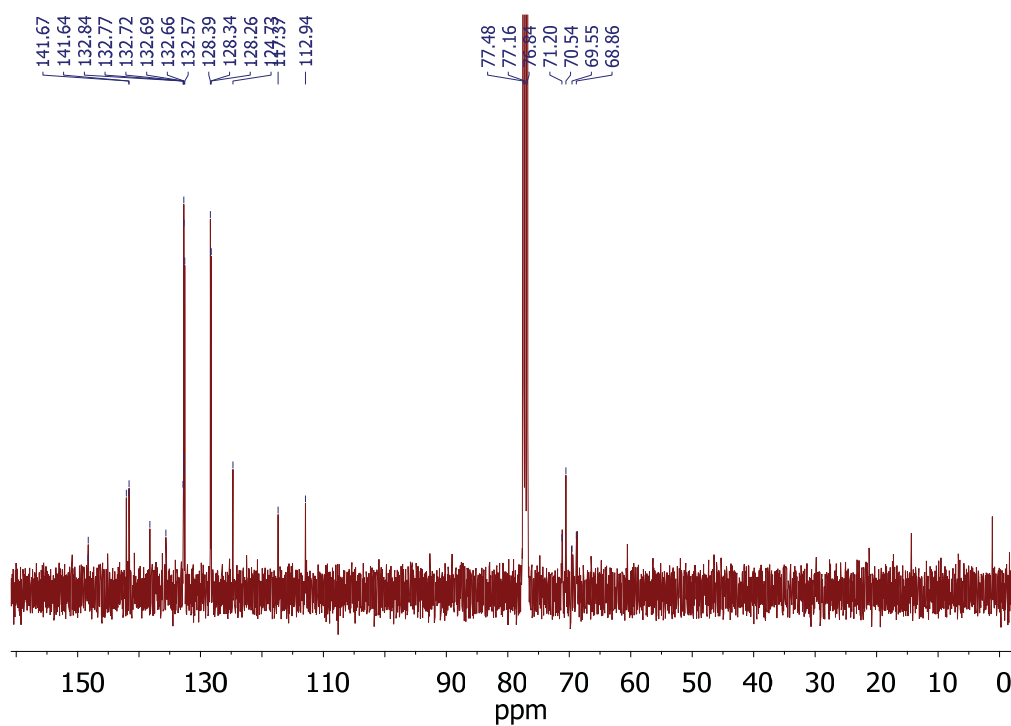
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **34**.



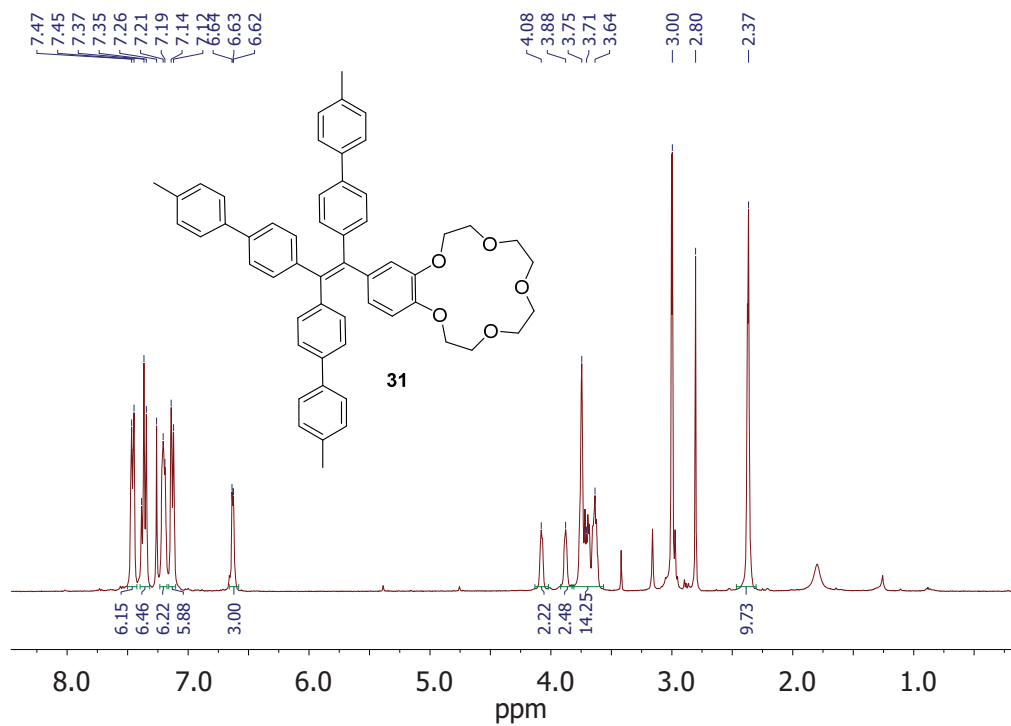
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) spectrum of **34**



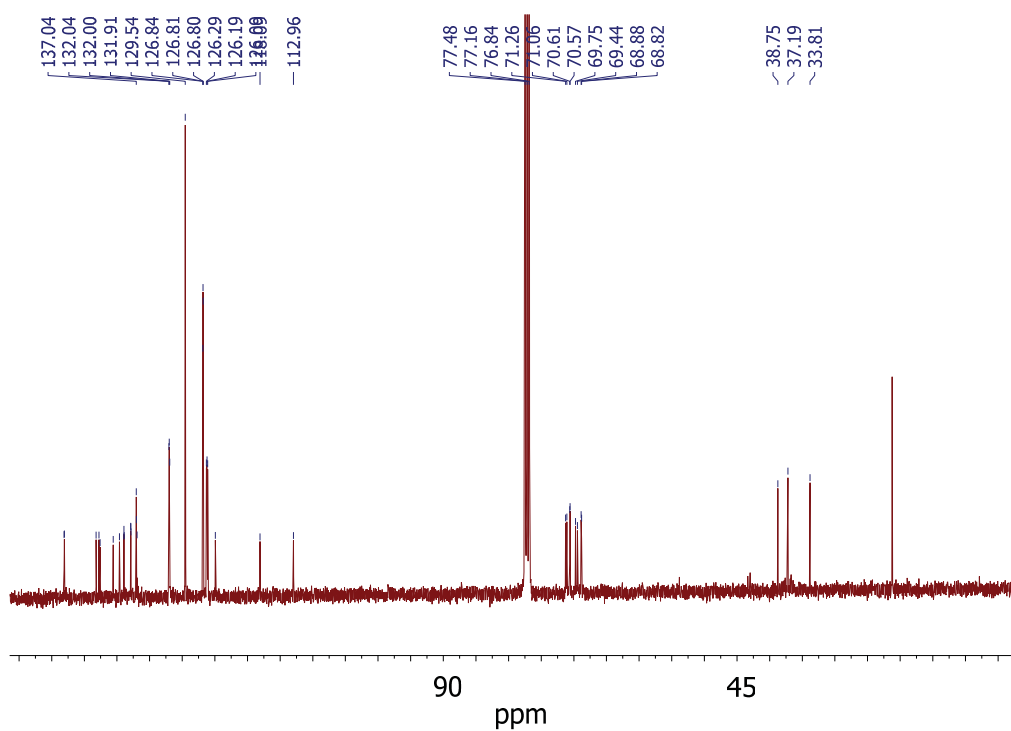
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **35**.



<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum of **35**.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of **36**.



$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **36**.

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