

## Supporting Information

### Synthesis and Ring Size Effect of Macrocyclic Ethynylhelicene Oligomers

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## General experimental methods

Reagents were purchased from commercial suppliers, and were used without further purification. Solvents were purchased from commercial suppliers, and were purified as follows before use: Dry *N,N*-dimethylformamide was purchased, and was used without further purification. Triethylamine was distilled from calcium hydride. Toluene was distilled from calcium hydride, and stored over 4Å molecular sieves. Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to use. <sup>1</sup>H NMR spectra taken in CDCl<sub>3</sub> were referenced to tetramethylsilane ( $\delta$ 0.00) as an internal standard. <sup>13</sup>C NMR spectra taken in CDCl<sub>3</sub> were referenced to the residual solvent ( $\delta$ 77.0). MALDI-TOF mass spectra were recorded using  $\alpha$ -cyano-4-hydroxycinnamic acid as a matrix. Vapor pressure osmometry (VPO) was conducted using benzil as a standard.

### Characterization data for compounds 1b–1d, and 2f

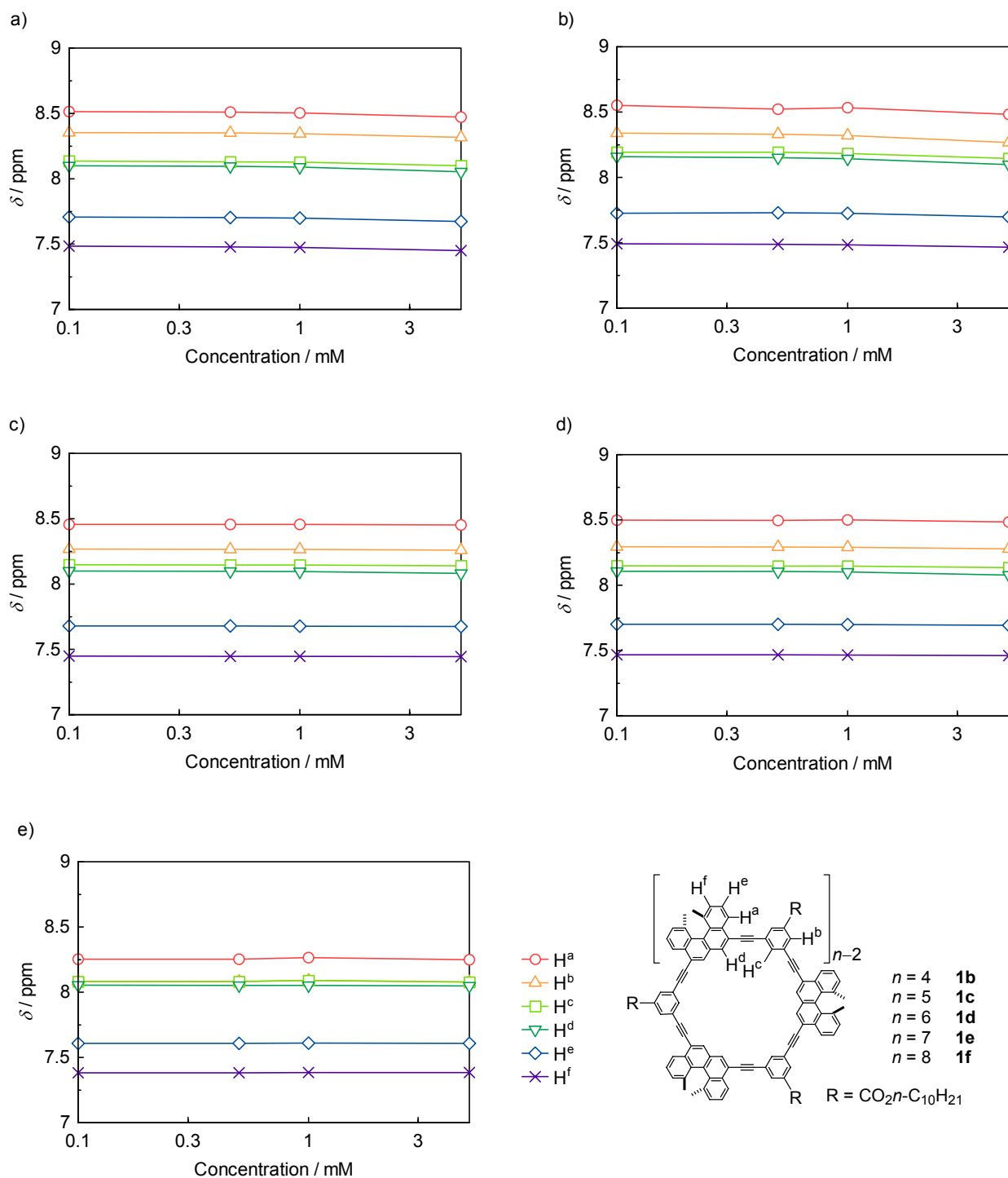
**[4+4]Cycloalkyne 1b.** The compound (23.8 mg, 0.0106 mmol, 42%) was prepared from desilylated acyclic tetramer **2b**<sup>4</sup> (50 mg, 0.0251 mmol): mp 192–194 °C (toluene–methanol);  $[\alpha]_D^{22}$  –995 (*c* 0.10, CHCl<sub>3</sub>); MALDI-TOF MS *m/z* calcd for  $[M+H]^+$  2252.0, found 2251.8; VPO (CHCl<sub>3</sub>, 5.4 mM, 35 °C) 2150 g·mol<sup>–1</sup>; UV–vis (CHCl<sub>3</sub>, 1 μM, 25 °C)  $\lambda_{\max}$  ( $\epsilon$ ) 335 nm ( $3.2 \times 10^5$ ); CD (CHCl<sub>3</sub>, 5 μM, 25 °C)  $\lambda$  ( $\Delta\epsilon$ ) 266 nm (191), 290 nm (–13), 331 nm (324), 354 nm (–305), 389 nm (–273); IR (KBr) 2204, 1724 cm<sup>–1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 5 mM, 25 °C)  $\delta$  0.84 (12H, t, *J* = 6.8 Hz), 1.19–1.43 (48H, m), 1.43–1.52 (8H, m), 1.84 (8H, tt, *J* = 8.7, 6.7 Hz), 1.95 (24H, s), 4.41 (8H, t, *J* = 6.7 Hz), 7.45 (8H, d, *J* = 7.0 Hz), 7.67 (8H, dd, *J* = 8.2, 7.0 Hz), 8.05 (8H, s), 8.10 (4H, d, *J* = 1.6 Hz), 8.31 (8H, d, *J* = 1.6 Hz), 8.47 (8H, d, *J* = 8.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 5 mM, 25 °C)  $\delta$  14.2, 22.8, 23.3, 26.2, 28.9, 29.41, 29.44, 29.7, 32.0, 65.9, 89.2, 92.8, 119.7, 123.5, 124.1, 126.7, 126.9, 129.1, 129.7, 130.8, 130.9, 131.3, 132.0, 132.3, 136.8, 138.3, 165.2. Anal. (C<sub>164</sub>H<sub>152</sub>O<sub>8</sub>) Calcd: C, 87.51; H, 6.81. Found: C, 87.81; H, 6.89.

**[5+5]Cycloalkyne 1c.** The compound (23.0 mg, 0.00818 mmol, 42%) was prepared from desilylated acyclic pentamer **2c**<sup>4</sup> (50 mg, 0.0196 mmol): mp 212–214 °C (toluene–methanol);  $[\alpha]_D^{22}$  –768 (*c* 0.10, CHCl<sub>3</sub>); MALDI-TOF MS *m/z* calcd for  $[M+H]^+$  2814.7, found 2814.6; VPO (CHCl<sub>3</sub>, 5.3 mM, 35 °C) 2780 g·mol<sup>–1</sup>; UV–vis (CHCl<sub>3</sub>, 1 μM, 25 °C)  $\lambda_{\max}$  ( $\epsilon$ ) 341 nm ( $3.9 \times 10^5$ ); CD (CHCl<sub>3</sub>, 5 μM, 25 °C)  $\lambda$  ( $\Delta\epsilon$ ) 266 nm (303), 297 nm (–28), 335 nm (281), 390 nm (–320); IR (KBr) 2204, 1723 cm<sup>–1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 5 mM, 25 °C)  $\delta$  0.85 (15H, t, *J* = 6.7 Hz), 1.20–1.43 (60H, m), 1.43–1.52 (10H, m), 1.83 (10H, tt, *J* = 7.8, 6.8 Hz), 1.96 (30H, s), 4.38 (10H, t, *J* = 6.8 Hz), 7.47 (10H, d, *J* = 7.0 Hz), 7.70 (10H, dd, *J* = 8.2, 7.0 Hz), 8.10 (10H, s), 8.15 (5H, d, *J* = 1.5 Hz), 8.27 (10H, d, *J* = 1.5 Hz), 8.48 (10H, d, *J* = 8.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 5 mM, 25 °C)  $\delta$  14.3, 22.8, 23.4, 26.2, 28.9, 29.4, 29.5, 29.7, 32.0, 65.8, 89.3, 93.0, 119.8, 123.5, 124.1, 126.7, 126.9, 129.2, 129.8, 130.8, 131.0, 131.20, 131.25, 132.0, 136.8, 138.3, 165.2. Anal. (C<sub>205</sub>H<sub>190</sub>O<sub>10</sub>) Calcd: C, 87.51; H, 6.81. Found: C, 87.33; H, 6.89.

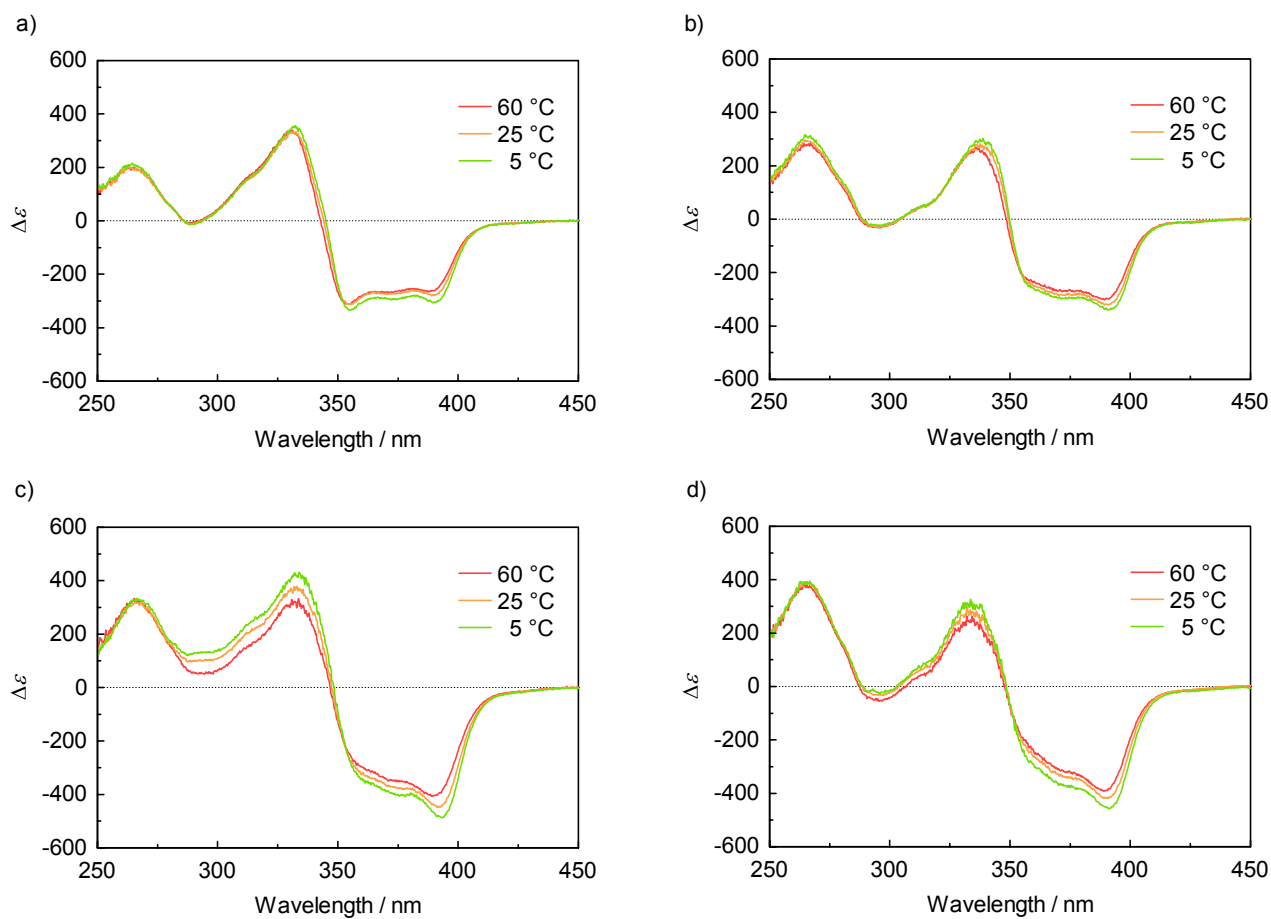
**[6+6]Cycloalkyne 1d.** The compound (21.4 mg, 0.00634 mmol, 40%) was prepared from desilylated acyclic hexamer **2d**<sup>4</sup> (50 mg, 0.0160 mmol): mp 206–208 °C (toluene–methanol);  $[\alpha]_D^{22}$  –872 (*c* 0.10, CHCl<sub>3</sub>); MALDI-TOF MS *m/z* calcd for  $[M+H]^+$  3377.4, found: 3377.7; VPO (CHCl<sub>3</sub>, 5.3 mM, 35 °C) 3300 g·mol<sup>–1</sup>; UV–vis (CHCl<sub>3</sub>, 1 μM, 25 °C)  $\lambda_{\max}$  ( $\epsilon$ ) 340 nm ( $4.4 \times 10^5$ ); CD (CHCl<sub>3</sub>, 5 μM, 25 °C)  $\lambda$  ( $\Delta\epsilon$ ) 267 nm (318), 288 nm (94), 332 nm (382), 392 nm (–448); IR (KBr)

2204, 1723  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 5 mM, 25  $^\circ\text{C}$ )  $\delta$  0.85 (18H, t,  $J$  = 6.6 Hz), 1.18–1.49 (84H, m), 1.77–1.88 (12H, m), 1.88 (36H, s), 4.30–4.41 (12H, m), 7.45 (12H, d,  $J$  = 7.0 Hz), 7.68 (12H, dd,  $J$  = 7.5, 7.0 Hz), 8.08 (12H, s), 8.14 (6H, d,  $J$  = 0.9 Hz), 8.26 (12H, d,  $J$  = 0.9 Hz), 8.45 (12H, d,  $J$  = 7.5 Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 5 mM, 25  $^\circ\text{C}$ )  $\delta$  14.3, 22.8, 23.3, 26.2, 28.9, 29.4, 29.5, 29.7, 32.0, 65.8, 89.4, 93.1, 119.7, 123.5, 124.1, 126.6, 126.8, 129.1, 129.9, 130.7, 130.9, 131.2, 131.9, 132.1, 136.7, 138.1, 165.2. Anal. ( $\text{C}_{246}\text{H}_{228}\text{O}_{12}$ ) Calcd: C, 87.51; H, 6.81. Found: C, 87.32; H, 6.89.

**Desilylated acyclic octamer 2f.** To a solution of bis(trimethylsilyl)-protected acyclic octamer<sup>4</sup> (90 mg, 0.0205 mmol) in tetrahydrofuran (3.0 mL) was added 1.0 M tetrabutylammonium fluoride (3.0 equiv, 0.0615 mmol, 0.0615 mL) in tetrahydrofuran at 0  $^\circ\text{C}$ . After being stirred for 10 min at that temperature, saturated aqueous ammonium chloride was added. The organic materials were extracted with toluene. The organic layer was washed with brine, and dried over anhydrous magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel flash column chromatography ( $\text{CHCl}_3$ ) gave **2f** (83.5 mg, 0.0197 mmol, 96%): mp > 155  $^\circ\text{C}$  dec (toluene–methanol);  $[\alpha]_D^{22}$  +4974 ( $c$  0.10,  $\alpha,\alpha,\alpha$ -trifluoromethylbenzene, within 30 min after dissolution); MALDI-TOF MS  $m/z$  calcd for  $[\text{M}+\text{H}]^+$  4244.6, found 4244.8; UV–vis ( $\alpha,\alpha,\alpha$ -trifluoromethylbenzene, 1  $\mu\text{M}$ , within 10 min after dissolution, 25  $^\circ\text{C}$ )  $\lambda_{\text{max}}$  ( $\epsilon$ ) 323 nm ( $3.0 \times 10^5$ ); IR (KBr) 3306, 2205, 1722  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 1 mM, observed at 60  $^\circ\text{C}$  after being heated at 60  $^\circ\text{C}$  for 3 h)  $\delta$  0.85 (21H, t,  $J$  = 7.3 Hz), 1.20–1.46 (84H, m), 1.46–1.54 (14H, m), 1.81–1.88 (14H, m), 1.94 (6H, s), 1.95 (6H, s), 1.98 (36H, s), 3.52 (2H, s), 4.39–4.43 (14H, m), 7.43 (2H, d,  $J$  = 6.9 Hz), 7.44–7.50 (14H, m), 7.63 (2H, dd,  $J$  = 8.3, 6.9 Hz), 7.67–7.73 (14H, m), 8.04 (2H, s), 8.07 (2H, s), 8.11 (4H, s), 8.12 (8H, s), 8.15–8.17 (2H, m), 8.17–8.19 (5H, m), 8.31–8.33 (2H, m), 8.33–8.36 (12H, m), 8.43 (2H, d,  $J$  = 8.3 Hz), 8.50–8.56 (14H, m);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ , 1 mM, observed at 60  $^\circ\text{C}$  after being heated at 60  $^\circ\text{C}$  for 3 h)  $\delta$  14.0, 22.7, 23.08, 23.13, 26.1, 28.9, 29.30, 29.34, 29.6, 31.9, 65.8, 89.5, 93.1, 120.1, 123.7, 124.5, 126.96, 127.03, 127.1, 129.3, 130.0, 130.5, 131.0, 131.16, 131.22, 131.8, 132.4, 137.1, 138.3, 165.5. Anal. ( $\text{C}_{311}\text{H}_{282}\text{O}_{14}$ ) Calcd: C, 88.02; H, 6.70. Found: C, 87.91; H, 6.73.



**Figure S1.** Concentration dependences (0.1–5.0 mM) of chemical shifts for aromatic protons of  $[n+n]$ cycloalkynes ( $n = 4$ – $8$ ) measured by  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ). a) **1b**, b) **1c**, c) **1d**, d) **1e**, and e) **1f**.



**Figure S2.** CD spectra ( $\text{CHCl}_3$ , 5  $\mu\text{M}$ ) of  $[n+n]$ cycloalkynes ( $n = 4-7$ ) observed at 60 °C (red line), 25 °C (orange line), and 5 °C (light green line). a) **1b**, b) **1c**, c) **1d**, and d) **1e**.

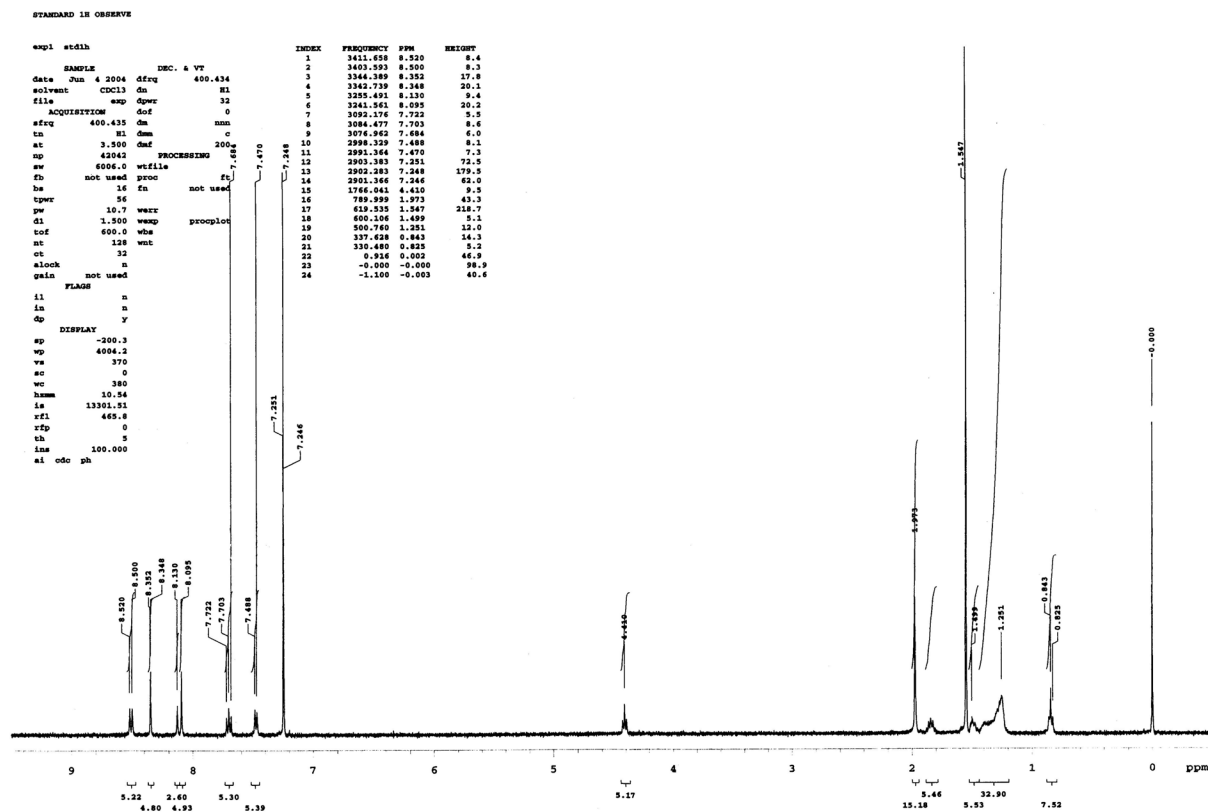


Figure S3.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 0.5 mM, 25  $^\circ\text{C}$ ) spectrum of **1b**.

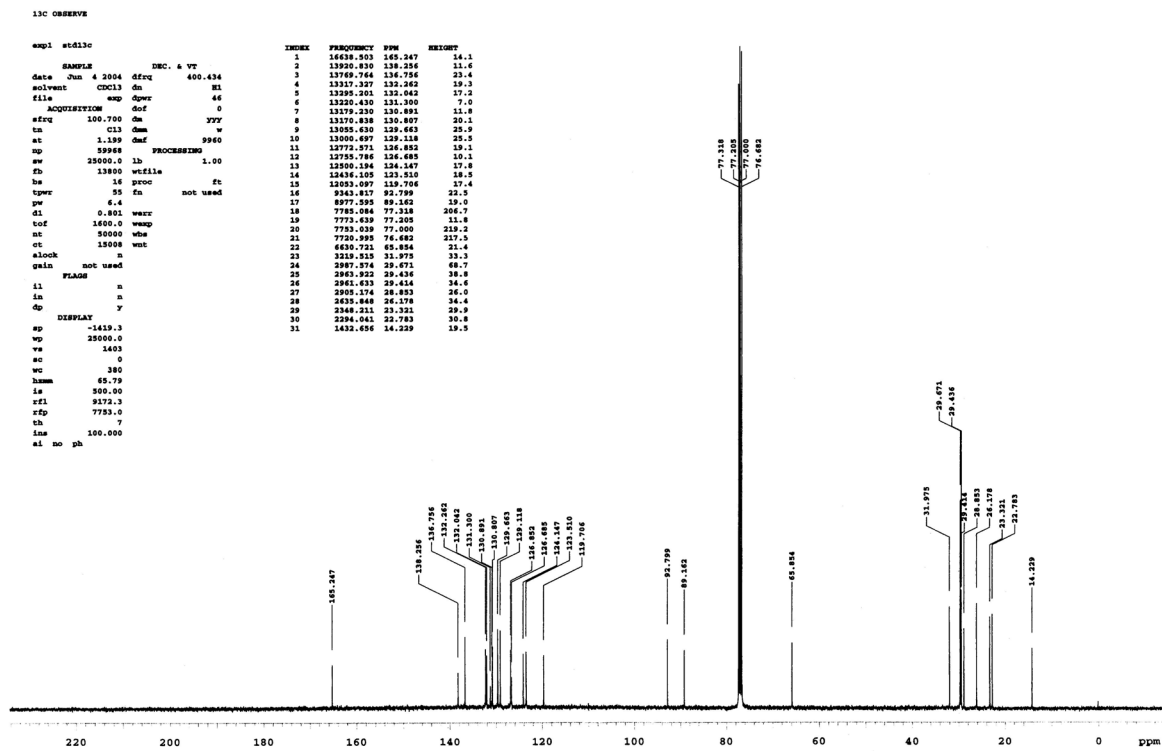


Figure S4.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 5 mM, 25  $^\circ\text{C}$ ) spectrum of **1b**.

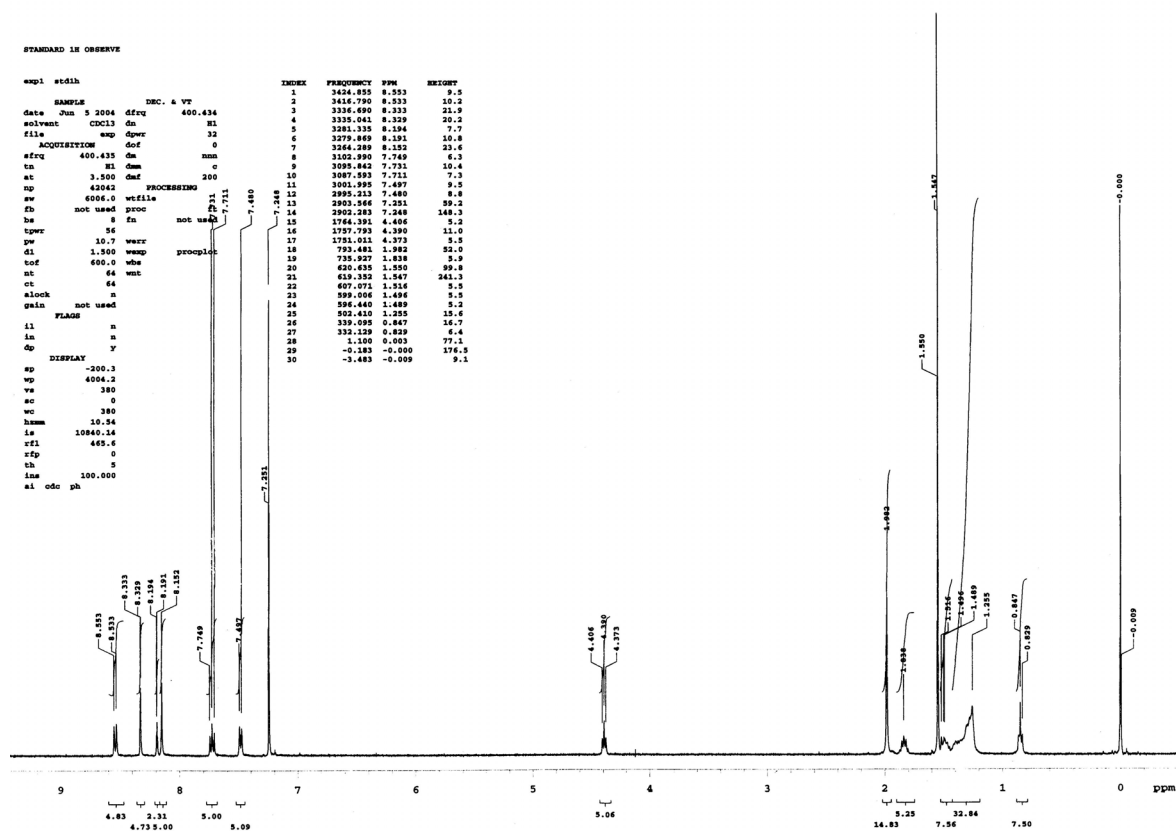


Figure S5.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 0.5 mM, 25  $^\circ\text{C}$ ) spectrum of **1c**.

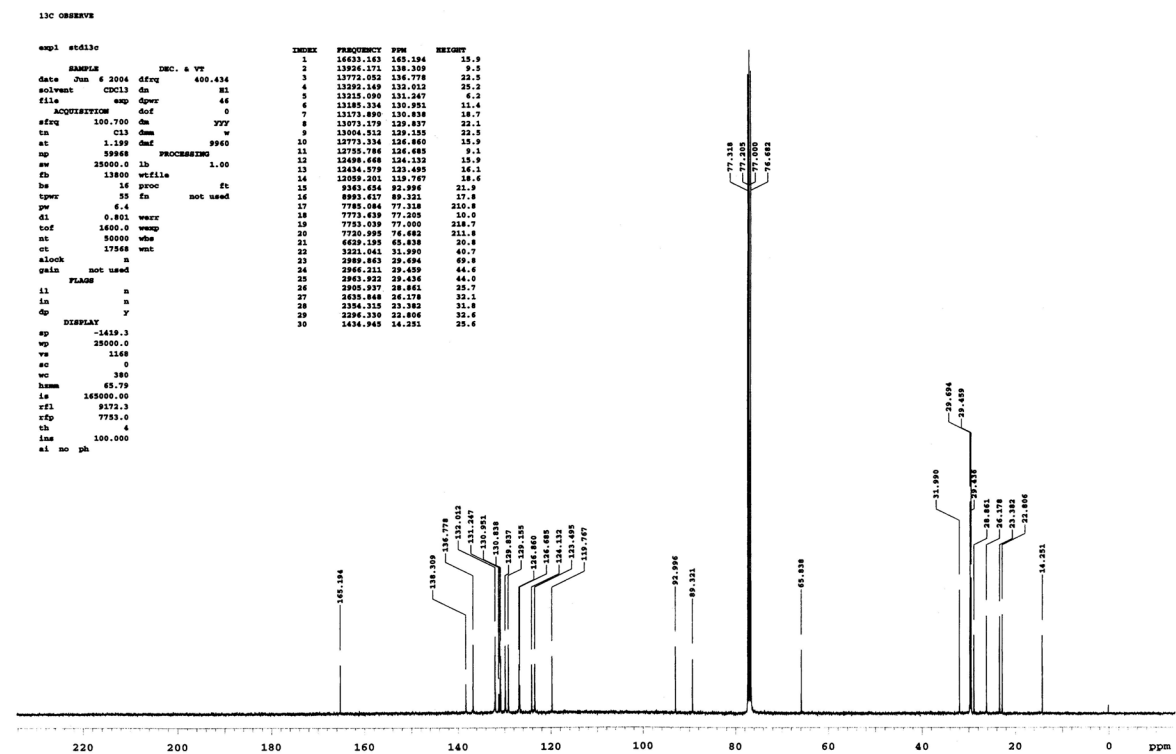


Figure S6.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 5 mM, 25  $^\circ\text{C}$ ) spectrum of **1c**.



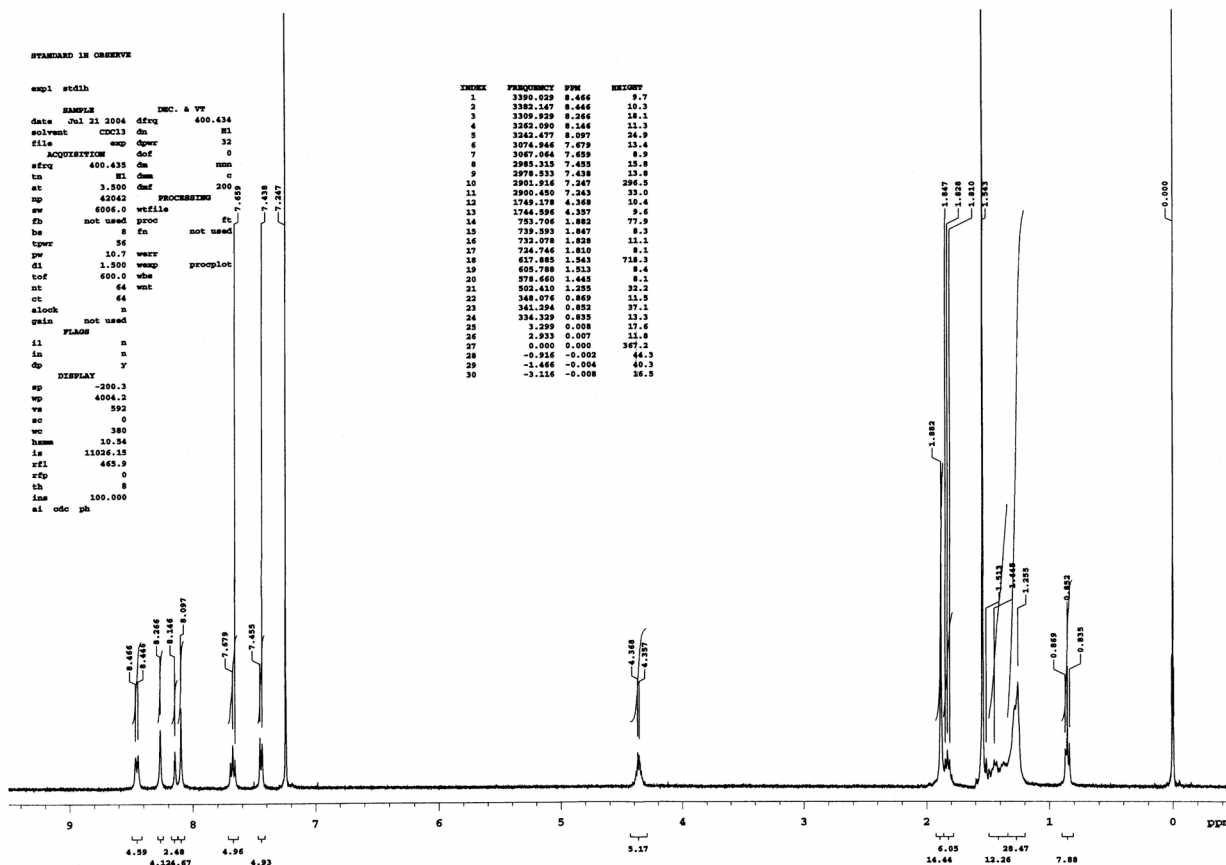


Figure S7.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 0.5 mM, 25  $^\circ\text{C}$ ) spectrum of **1d**.

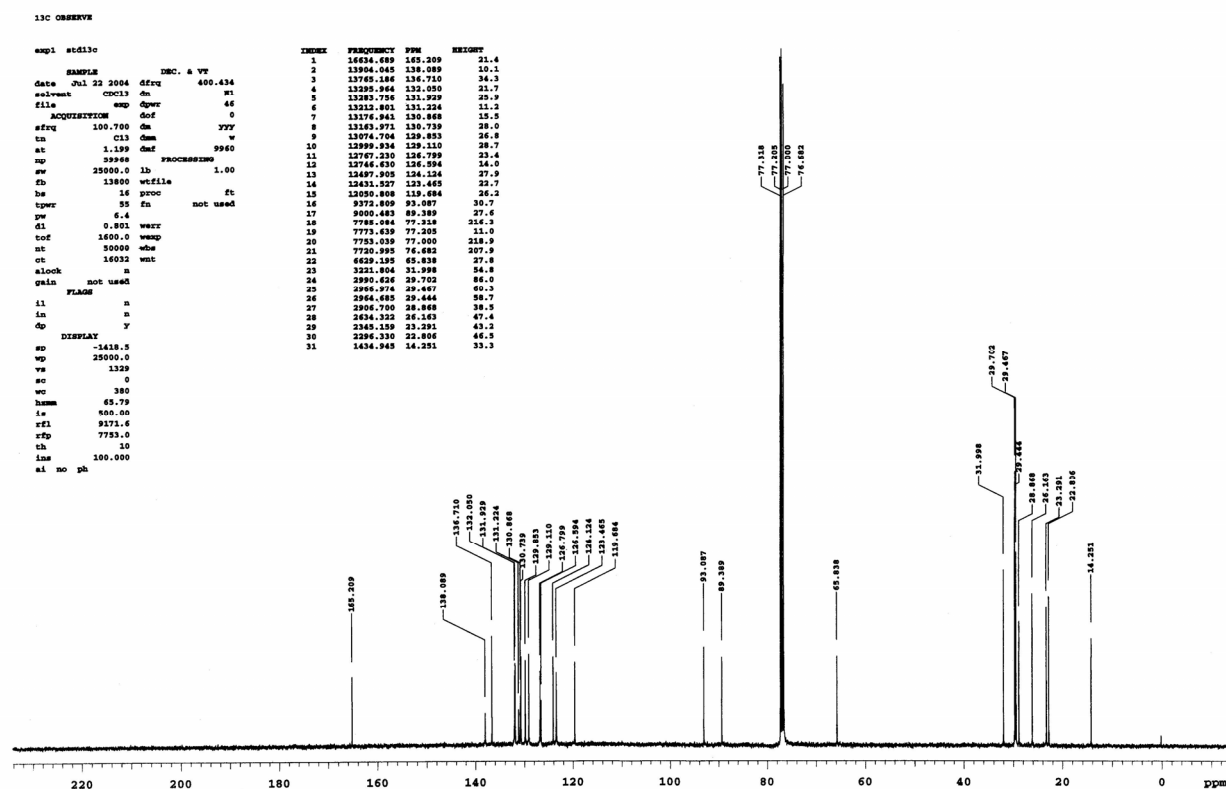


Figure S8.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 5 mM, 25  $^\circ\text{C}$ ) spectrum of **1d**.

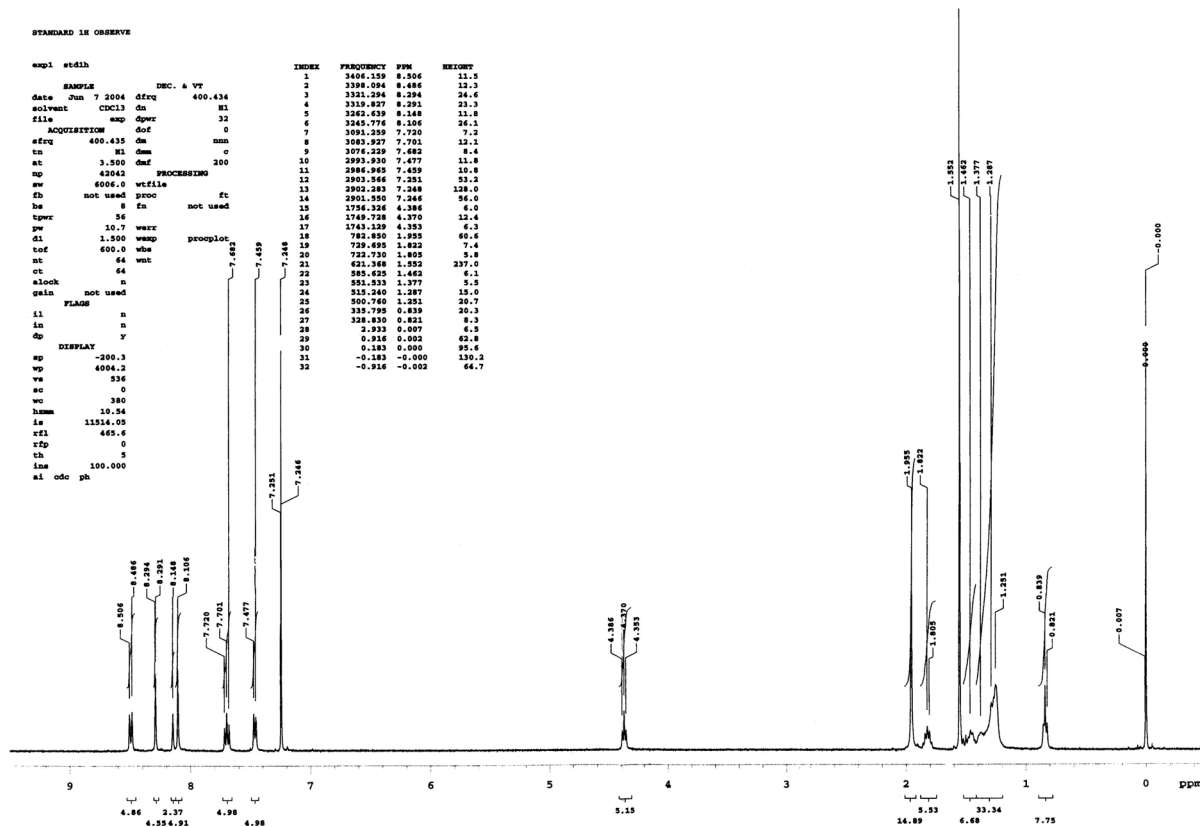


Figure S9.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 0.5 mM, 25  $^\circ\text{C}$ ) spectrum of **1e**.

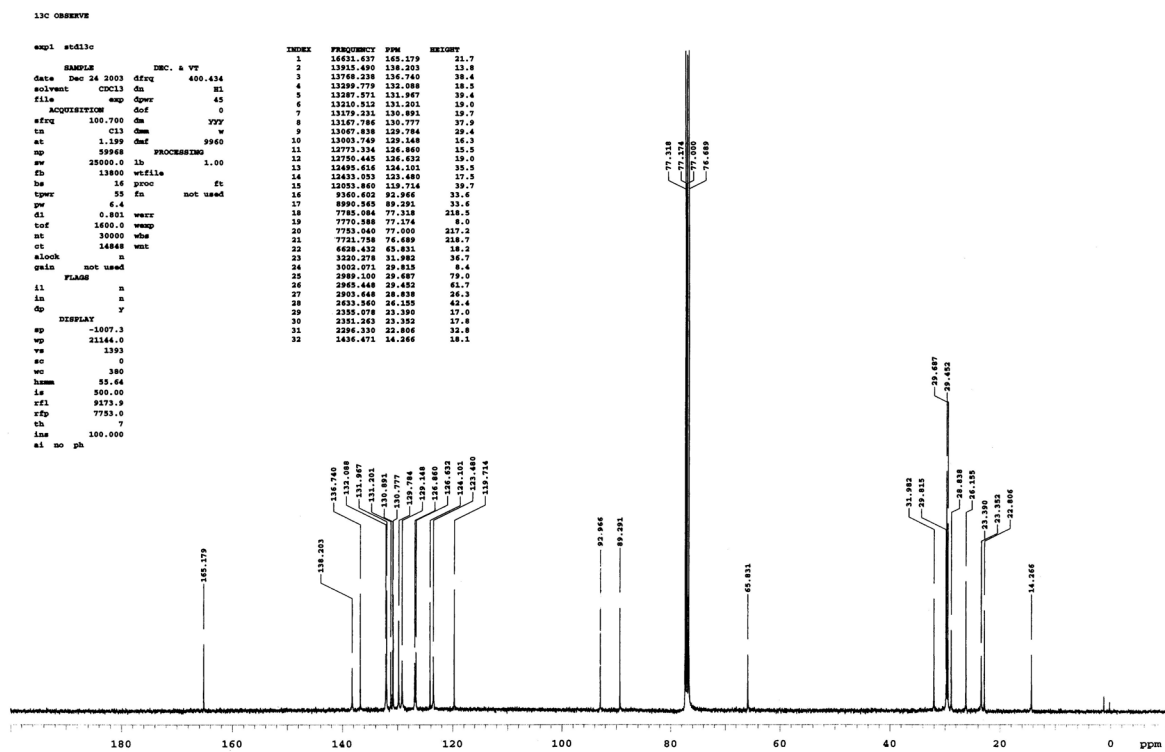


Figure S10.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 5 mM, 25  $^\circ\text{C}$ ) spectrum of **1e**.

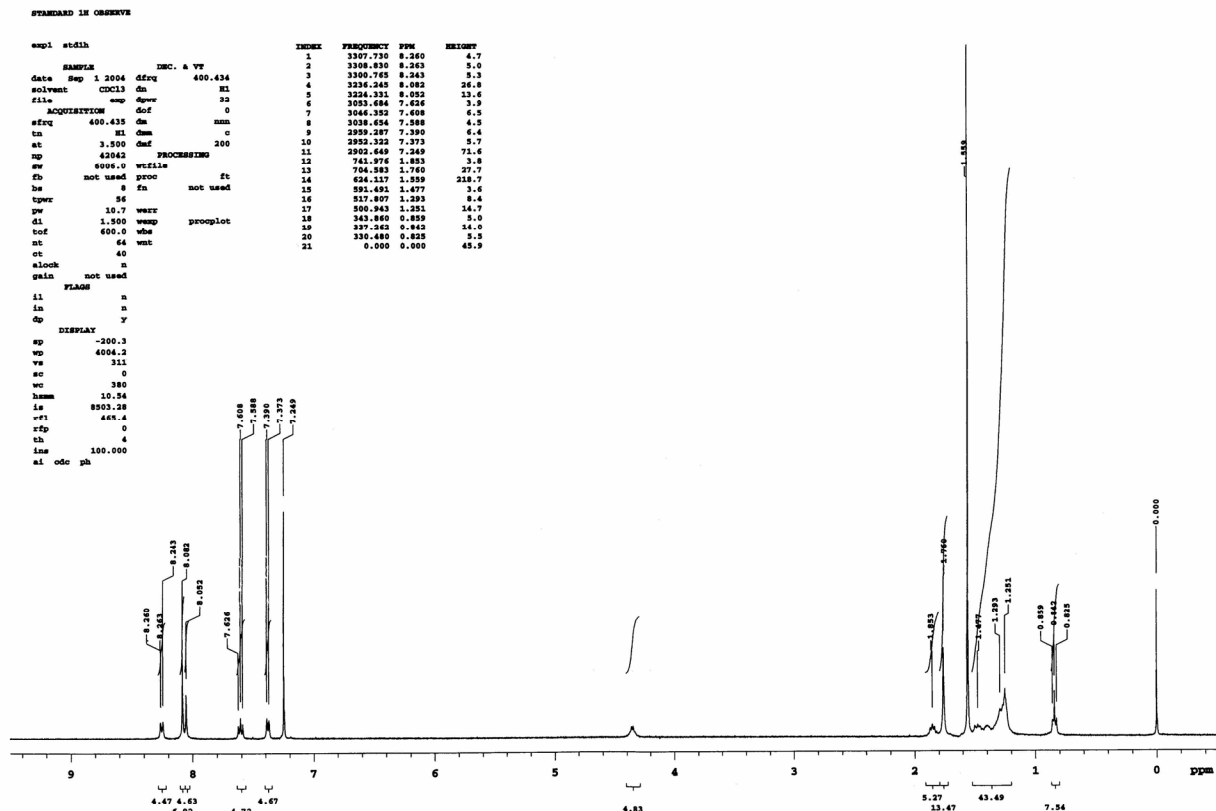


Figure S11.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 0.5 mM, 25  $^\circ\text{C}$ ) spectrum of **1f**.

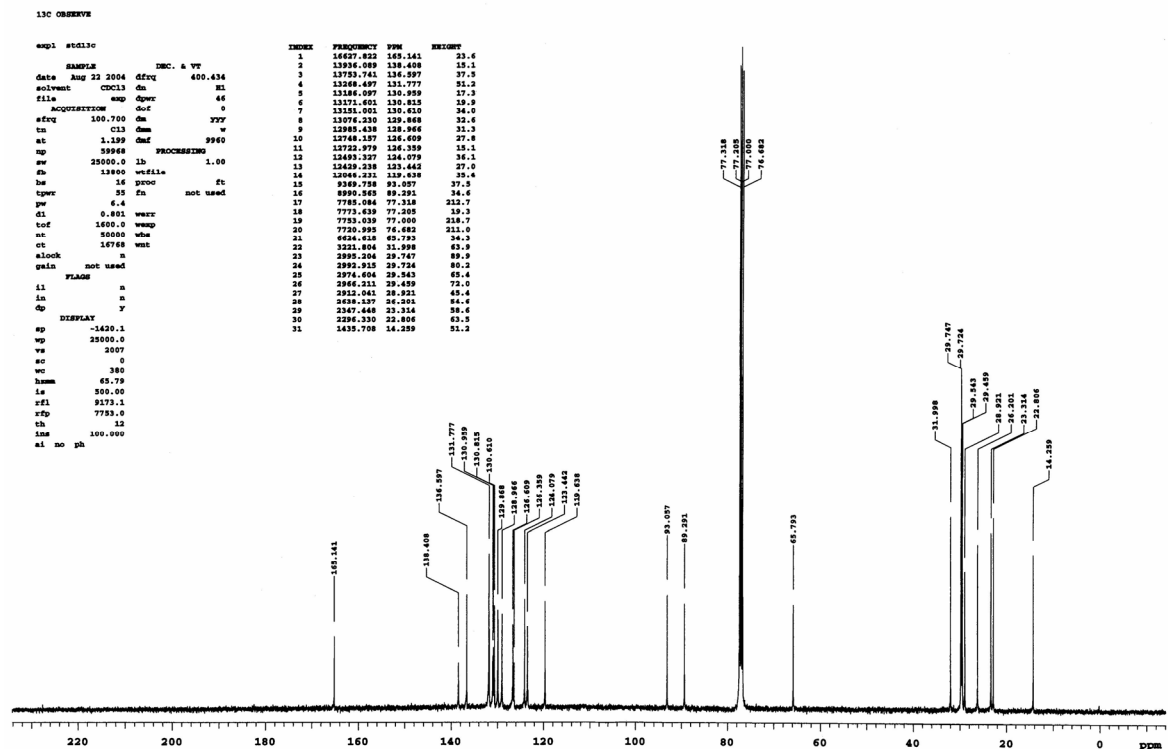
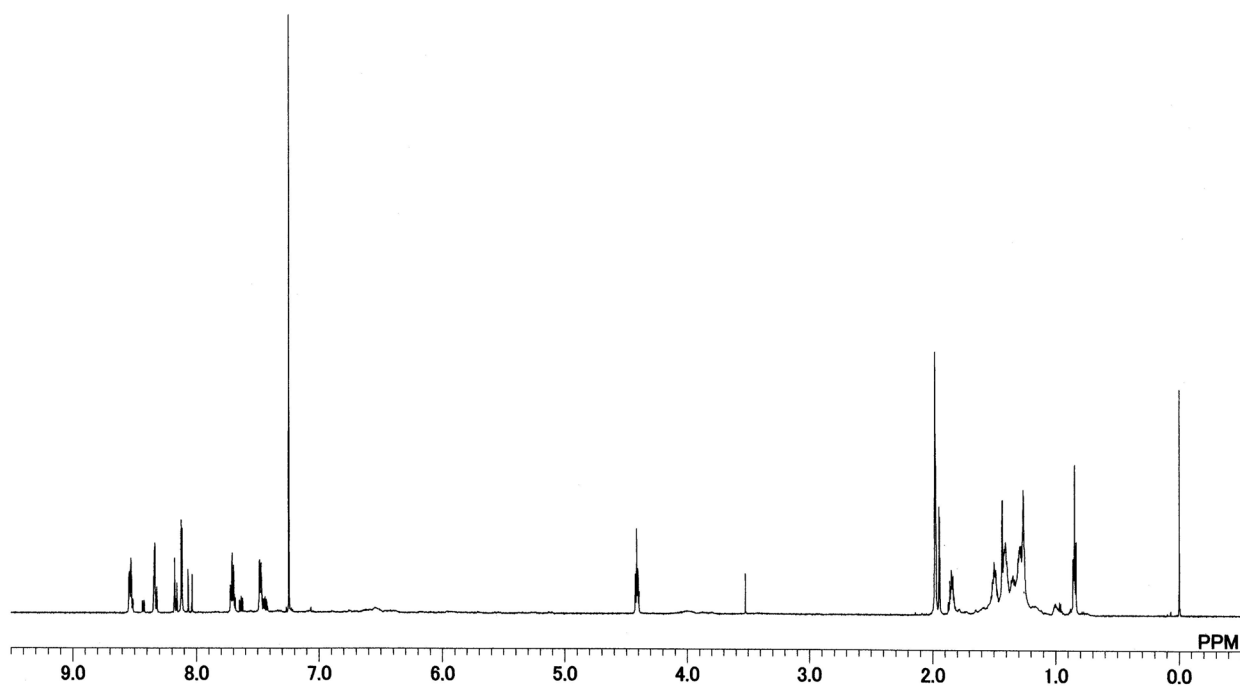
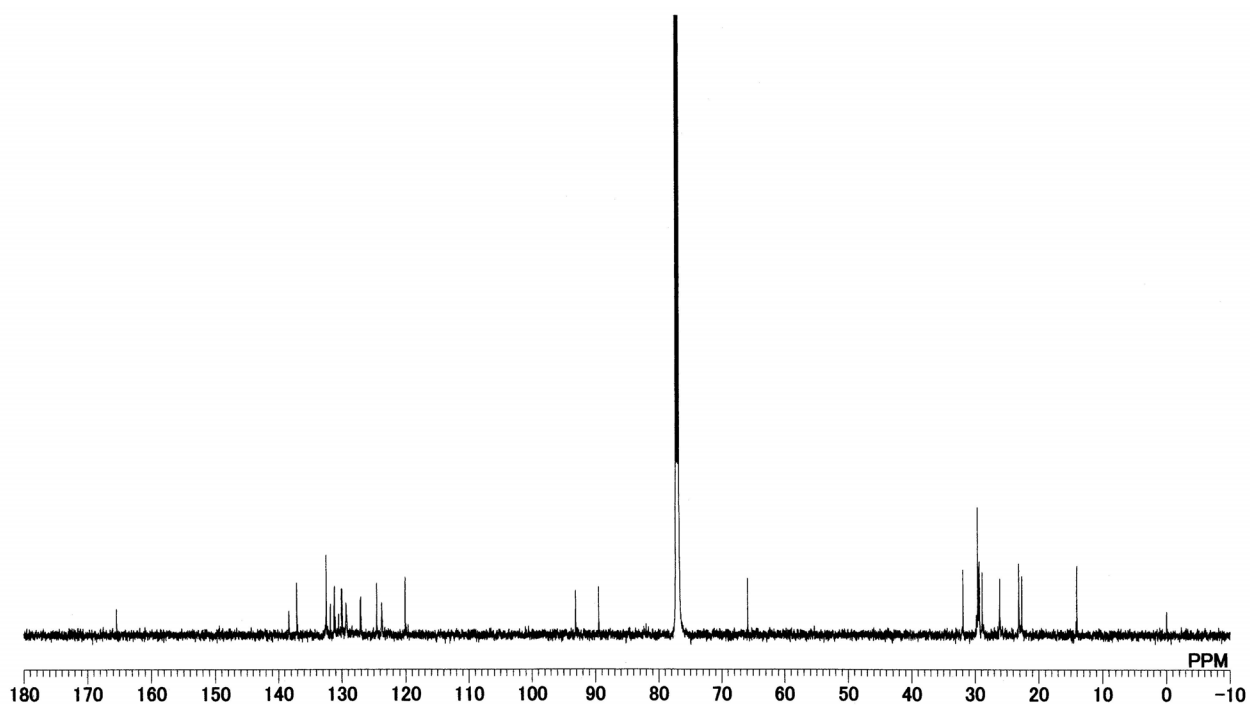


Figure S12.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 5 mM, 25  $^\circ\text{C}$ ) spectrum of **1f**.



**Figure S13.**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 1 mM, observed at 60 °C after being heated at 60 °C for 3 h) spectrum of **2f**.



**Figure S14.**  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ , 1 mM, observed at 60 °C after being heated at 60 °C for 3 h) spectrum of **2f**.