Nanomechanical properties of molecular-scale bridges as visualised by intramolecular electronic energy transfer

Delphine Hablot, Raymond Ziessel, Mohammed A. H. Alamiry, Effat Bahraidah, and Anthony Harriman

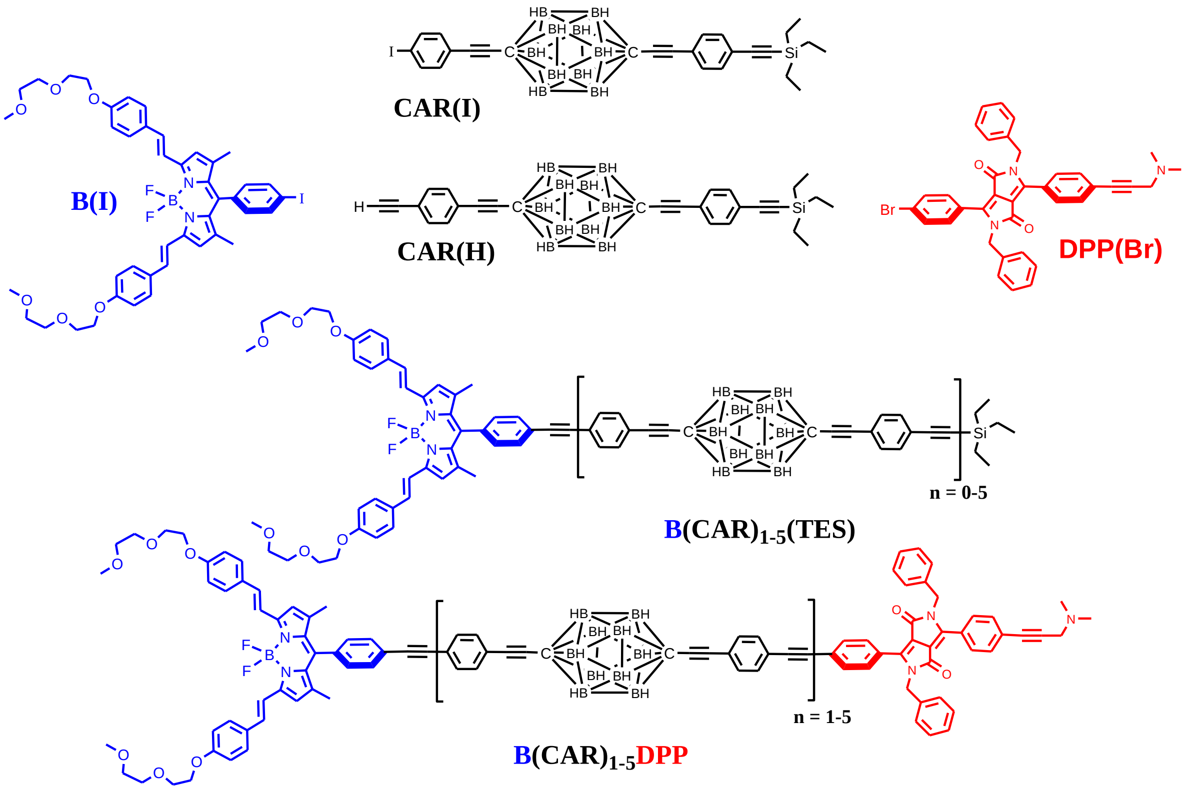
Supporting Information (total 50 pages)

Table of Contents Pages

1) General Methods

All reactions were performed under an atmosphere of dried argon using standard Schlenk tube techniques. All chemicals were used as received from commercial sources unless stated otherwise. CH_2Cl_2 was distilled from P_2O_5 under an argon atmosphere. THF was distilled from sodium and benzophenone under an argon atmosphere. ^1H NMR (300.1 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded at rt on a Bruker Advance 300 MHz spectrometer, ^1H NMR (200.1 MHz) and ^{13}C NMR (50.5 MHz) spectra were recorded at rt on a Bruker Advance 200 MHz spectrometer using perdeuteriated solvents as internal standards. Fast atom bombardment (FAB, positive mode) mass spectra were recorded with a ZAB-HF-VB analytical apparatus using m-nitrobenzyl alcohol (m-NBA) as matrix. Chromatographic purifications were performed using silica gel (40-63 µm). TLC was performed on silica gel plates coated with fluorescent indicator.

2) Synthetic Experimental Part for the B(CAR)$_x$DPP



Chemical formulae's of the molecules involved in the synthesis of the carborane bridged donor-acceptor dyads.

General Procedure N°1 for the Sonogashira cross-coupling reaction with [Pd(PPh$_3$)$_4$]. To a degassed solution of starting material iodide (1 eq) and starting material acetylene (1 eq) in benzene and triethylamine was added [Pd(PPh$_3$)$_4$] (0.05 eq). The reaction mixture was heated to 60°C overnight (16h) then was cooled to room temperature. The reaction mixture was concentrated under reduce pressure. The remaining solid was dissolved in dichloromethane. The solution was washed with water then extracted with dichloromethane (3x) and dried over

$MgSO_4$. The solvent was filtered and evaporated. The crude product was purified by silica gel column chromatography.

General Procedure N°2 for the Sonogashira cross-coupling reaction with [Pd(PPh_3)$_4$]. To a degassed solution of starting material iodide or bromide (1.1 eq or 1.05 eq or 1 eq or 0.95 eq) and starting material acetylene (1 eq) in THF and triethylamine was added [Pd(PPh_3)$_4$] (0.05 eq). The reaction mixture was heated to 60°C overnight (16h) then was cooled to room temperature. The reaction mixture was concentrated under reduce pressure. The remaining solid was dissolved in dichloromethane. The solution was washed with water then extracted with dichloromethane (3x) and dried over $MgSO_4$. The solvent was filtered and evaporated. The crude product was purified by silica gel column chromatography.

General Procedure N°3 for the Sonogashira cross-coupling reaction with [Pd(PPh_3)$_4$]. To a degassed solution of starting material iodide or bromide (1.05 eq or 0.95 eq or 0.61 eq) and starting material acetylene (1 eq) in THF and triethylamine was added [Pd(PPh_3)$_4$] (0.05 eq). The reaction mixture was heated to 70°C overnight (16h) then was cooled to room temperature. The reaction mixture was concentrated under reduce pressure. The crude product was purified by silica gel column chromatography.

B(CAR)$_1$(TES): was prepared according to the general procedure N°1 for Sonogashira cross-coupling reaction with [Pd(PPh_3)$_4$]: Starting material iodide **B(I)** (0.1962 g, 0.2275 mmol) and starting material acetylene **CAR(H)** (0.1153 g, 0.2275 mmol). The crude product was purified on silica gel eluting with ethyle acetate/petroleum ether (gradient from 1:1 to 7:3) to afford 0.2505 g (0.2018 mmol, 89%) of **B(CAR)$_1$(TES)** as a blue compound. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.50-7.70 (4 lines m, 8H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.28-7.40 (4 lines m, 6H), 7.14-7.27 (5 lines m, 4H), 6.94 (d, *J* = 8.9 Hz, 4H), 6.61 (s, 2H), 4.09-4.27 (3 lines m, 4H), 3.82-3.94 (3 lines m, 4H), 3.68-3.78 (4 lines m, 4H), 3.54-3.64 (4 lines m, 4H), 3.41 (s, 6H), 3.62-1.57 (large m, 10H, BH), 1.47 (s, 6H), 1.04 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (75.46 MHz, $CDCl_3$), δ (ppm): 159.64, 152.90, 141.46, 136.90, 135.98, 135.62, 132.86, 132.19, 131.92, 131.79, 131.65, 131.41, 129.61, 129.02, 128.86, 124.06, 123.59, 123.55, 121.21, 120.94, 117.65, 117.16, 114.91, 105.44, 94.43, 90.96, 90.04, 87.18, 86.90, 80.10, 79.97, 71.93, 70.76, 69.67, 67.47, 59.06, 14.79, 7.43, 4.30.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 1241.5 ([M+H], 100).

Elemental analysis calcd (%) for $C_{71}H_{79}B_{11}F_2N_2O_6Si$: C 68.69, H 6.41, N 2.26. Found: C 68.45, H 6.23, N 2.08

B(CAR)$_1$(H): to a solution of **B(CAR)$_1$(TES)** (0.2027 g, 1 eq, 0.1633 mmol) in THF (40 mL) was added a solution of NaOH (0.6074 g, 93 eq, 15.1854 mmol) in water. The reaction mixture was stirred at room temperature overnight (15h) then was concentrated under reduce pressure. The remaining solid was dissolved in dichloromethane. The solution was washed with NH_4Cl saturated then extracted with dichloromethane (3x) and dried over $MgSO_4$. The solvent was filtered and evaporated. The crude product was purified by silica gel with dichloromethane then dichloromethane/EtOH (gradient from 99.8:0.2 to 99:1) to afford 0.1571 g (0.1394 mmol, 85%) of **B(CAR)$_1$(H)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.1307 g (0.1159 mmol, 71%) of **B(CAR)$_1$(H)** as blue crystals. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 7.08-7.74 (14 lines m, 20H), 6.93 (d, *J* = 8.8 Hz, 4H), 6.60 (s, 2H), 4.06-4.32 (3 lines m, 4H), 3.80-3.95 (3 lines m, 4H), 3.66-3.78 (4 lines m, 4H), 3.49-3.64 (4 lines m, 4H), 3.40 (s, 6H), 3.17 (s, 1H), 3.62-1.57 (large m, 10H, BH), 1.45 (s, 6H).

ESI-MS in dichloromethane, positif mode, *m/z* (%): 1127.5 ([M+H], 100).

Elemental analysis calcd (%) for $C_{65}H_{65}B_{11}F_2N_2O_6$: C 69.26, H 5.81, N 2.49.

Found: C 69.04, H 5.63, N 2.16.

B(CAR)$_1$DPP: was prepared according to the general procedure N°2 for Sonogashira cross-coupling reaction with [Pd(PPh_3)$_4$]: Starting material bromide **DPP(Br)** (0.0191 g, 1.1 eq, 0.0304 mmol) and starting material acetylene **B(CAR)$_1$(H)** (0.0311 g, 1 eq, 0.0276 mmol). The crude product was purified on silica gel eluting with dichloromethane then dichloromethane/MeOH (95:5) to afford 0.0400 g (0.0239 mmol, 87%) of **B(CAR)$_1$DPP** as a gray compound. Finally, this compound was recrystallized by evaporation of THF/EtOH to afford 0.0335 g (0.0200 mmol, 72%) of **B(CAR)$_1$DPP** as gray crystals. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.43-7.63 (10 lines m, 14H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.22-7.35 (10 lines m, 12H), 7.18 (d, *J* = 7.4 Hz, 4H), 6.97 (d, *J* = 8.6 Hz, 4H), 6.66 (s, 2H), 4.98 (s, 4H), 4.11-4.22 (3 lines m, 4H), 3.77-3.89 (3 lines m, 4H), 3.63-3.72 (4 lines m, 4H), 3.51-3.58 (4 lines m, 4H), 3.49 (s, 2H), 3.35 (s, 6H), 2.34 (s, 6H), 3.62-1.57 (large m, 10H, BH), 1.51 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 163.05, 160.45, 153,32, 148.75, 148.40, 142.57, 138.11, 137.96, 136.59, 136.13, 133.52, 132.86, 132.48, 132.46, 132.40, 132.17, 130.13, 129.63, 129.55, 129.34, 128.36, 127.97, 127.13, 126.97, 126.36, 124.37, 124.21, 121.88, 121.72, 118.15, 117.46, 115.50, 110.91, 110.75, 92.05, 91.58, 90.34, 87.62, 80.67, 72.53, 71.26, 70.14, 68.26, 66.85, 59.26, 49.04, 46.12, 44.48, 15.21.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 1675.6 ([M+H], 100).

Elemental analysis calcd (%) for $C_{102}H_{94}B_{11}F_2N_5O_8$: C 73.15, H 5.66, N 4.18.

Found: C 72.83, H 5.41, N 3.86.

B(CAR)$_2$(TES): was prepared according to the general procedure N°2 for Sonogashira cross-coupling reaction with [Pd(PPh$_3$)$_4$]: Starting material iodide **CAR(I)** (0.1859 g, 1.05 eq, 0.3054 mmol) and starting material acetylene **B(CAR)$_1$(H)** (0.3278 g, 1 eq, 0.2908 mmol). The crude product was purified on silica gel eluting with dichloromethane then dichloromethane/EtOH (gradient from 99.5:0.5 to 99:1) to afford 0.4489 g (0.2792 mmol, 96%) of **B(CAR)$_2$(TES)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.4120 g (0.2562 mmol, 88%) of **B(CAR)$_2$(TES)** as blue crystals. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$), δ (ppm): 7.67 (d, *J* = 7.9 Hz, 2H), 7.53-7.63 (3 lines m, 6H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 4H), 7.15-7.38 (7 lines m, 14H), 6.96 (d, *J* = 8.6 Hz, 4H), 6.65 (s, 2H), 4.07-4.22 (3 lines m, 4H), 3.76-3.90 (3 lines m, 4H), 3.61-3.72 (4 lines m, 4H), 3.48-3.58 (4 lines m, 4H), 3.35 (s, 6H), 3.62-1.57 (large m, 20H, BH), 1.49 (s, 6H), 1.02 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 8.1 Hz, 6H). ^{13}C NMR (75.46 MHz, CD$_2$Cl$_2$), δ (ppm): 160.43, 153.30, 142.53, 137.91, 136.58, 136.10, 133.50, 132.85, 132.46, 132.42, 132.04, 130.10, 129.54, 124.73, 124.24, 124.18, 121.71, 121.49, 118.15, 117.45, 115.46, 105.88, 95.11, 91.43, 90.34, 87.61, 80.65, 72.50, 71.24, 70.11, 68.22, 66.79, 59.24, 15.21, 7.79, 4.83.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 1608.0 ([M+H], 100).

Elemental analysis calcd (%) for $C_{91}H_{97}B_{21}F_2N_2O_6Si$: C 67.98, H 6.08, N 1.74.

Found: C 67.62, H 5.73, N 1.55.

B(CAR)$_2$(H): To a solution of **B(CAR)$_2$(TES)** (0.4120 g, 1 eq, 0.2562 mmol) in THF (63 mL) was added a solution of NaOH (0.9532 g, 93 eq, 23.8303 mmol) in water. The reaction mixture was heated to 60°C overnight (16h) then was cooled to room temperature. It was concentrated under reduce pressure. The remaining solid was dissolved in dichloromethane. The solution was washed with NH$_4$Cl saturated then extracted with dichloromethane (3x) and dried over $MgSO_4$. The solvent was filtered and evaporated. The crude product was purified by silica gel with dichloromethane then dichloromethane/EtOH (gradient from 99.5:0.5 to 99:1) to afford 0.3149 g (0.2108 mmol, 82%) of **B(CAR)$_2$(H)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.2835 g (0.1898 mmol, 74%) of **B(CAR)$_2$(H)** as blue crystals. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 7.08-7.76 (14 lines m, 28H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.62 (s, 2H), 4.12-4.26 (3 lines m, 4H), 3.82-3.97 (3 lines m, 4H), 3.69-3.81 (4 lines m, 4H), 3.51-3.66 (4 lines m, 4H), 3.41 (s, 6H), 3.16 (s, 1H), 3.62-1.57 (large m, 20H, BH), 1.48 (s, 6H).

ESI-MS in dichloromethane, positif mode, *m/z* (%): 1495.0 ([M+H], 100).

Elemental analysis calcd (%) for $C_{85}H_{83}B_{21}F_2N_2O_6$: C 68.35, H 5.60, N 1.88.

Found: C 68.13, H 5.32, N 1.65.

B(CAR)$_2$DPP: was prepared according to the general procedure N°2 for Sonogashira cross-coupling reaction with [Pd(PPh_3)$_4$]: Starting material bromide **DPP(Br)** (0.0126 g, 1 eq, 0.0201 mmol) and starting material acetylene **B(CAR)$_2$(H)** (0.0300 g, 1 eq, 0.0201 mmol). The crude product was purified on silica gel eluting with dichloromethane then dichloromethane/EtOH (gradient from 99.5:0.5 to 9:1) to afford 0.0354 g (0.0173 mmol, 86%) of **B(CAR)$_2$DPP** as a gray compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.0275 g (0.0135 mmol, 67%) of **B(CAR)$_2$DPP** as gray crystals. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.40-7.63 (11 lines m, 18H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.22-7.35 (8 lines m, 16H), 7.18 (d, *J* = 7.4 Hz, 4H), 6.97 (d, *J* = 8.6 Hz, 4H), 6.66 (s, 2H), 4.98 (s, 4H), 4.10-4.22 (3 lines m, 4H), 3.78-3.88 (3 lines m, 4H), 3.62-3.73 (4 lines m, 4H), 3.50-3.59 (4 lines m, 4H), 3.47 (s, 2H), 3.36 (s, 6H), 2.32 (s, 6H), 3.62-1.57 (large m, 20H, BH), 1.51 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 163.07, 160.46, 153.34, 148.76, 148.37, 142.56, 138.12, 137.95, 136.60, 136.13, 133.53, 132.86, 132.47, 132.43, 132.40, 132.16, 132.08, 132.06, 130.15, 129.63, 129.54, 129.34, 128.37, 127.97, 127.77, 127.15, 127.14, 127.07, 126.35, 125.98, 124.37, 124.26, 124.22, 124.18, 121.88, 121.75, 118.16, 117.48, 115.51, 110.92, 110.74, 92.06, 91.59, 91.45, 90.35, 89.05, 87.71, 87.63, 85.03, 80.66, 72.53, 71.27, 70.15, 68.34, 68.26, 66.84, 59.26, 49.08, 46.13, 44.54, 15.21.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 2040.0 ([M+H], 100).

Elemental analysis calcd (%) for $C_{122}H_{112}B_{21}F_2N_5O_8$: C 71.78, H 5.53, N 3.43.

Found: C 71.52, H 5.23, N 3.18.

B(CAR)$_3$(TES): To a degassed solution of starting material iodide **CAR(I)** (0.1213 g, 1.05 eq, 0.1993 mmol) and starting material acetylene **B(CAR)$_2$(H)** (0.2835 g, 1 eq, 0.1898 mmol) in THF and triethylamine was added [Pd(PPh$_3$)$_4$] (0.0110 g, 0.05 eq, 0.0095 mmol). The reaction mixture was heated to 60°C during 48h then was cooled to room temperature. The reaction mixture was concentrated under reduce pressure. The remaining solid was dissolved in dichloromethane. The solution was washed with water then extracted with dichloromethane (3x) and dried over $MgSO_4$. The solvent was filtered and evaporated. The crude product was purified on silica gel eluting with dichloromethane then dichloromethane/EtOH (gradient from 99.8:0.2 to 95:5) to afford 0.3179 g (0.1610 mmol, 85%) of **B(CAR)$_3$(TES)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.1499 g (0.0759 mmol, 40%) of **B(CAR)$_3$(TES)** as blue crystals. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (ppm): 7.15-7.76 (18 lines m, 36H), 6.96 (d, *J* = 8.9 Hz, 4H), 6.64 (s, 2H), 4.04-4.25 (3 lines m, 4H), 3.75-3.91 (3 lines m, 4H), 3.61-3.73 (4 lines m, 4H), 3.49-3.60 (4 lines m, 4H), 3.35 (s, 6H), 3.62-1.57 (large m, 30H, BH), 1.49 (s, 6H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (75.46 MHz, CD_2Cl_2), δ (ppm): 160.43, 153.30, 142.51, 137.89, 136.59, 136.10, 133.50, 132.85, 132.46, 132.42, 132.04, 130.10, 129.54, 124.73, 124.36, 124.24, 124.18, 121.71, 118.16, 117.45, 115.46, 105.89, 95.11, 91.45, 87.61, 80.66, 72.50, 71.24, 70.12, 68.22, 66.82, 59.25, 15.21, 7.80, 4.84.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 1974.1 ([M+H], 100).

Elemental analysis calcd (%) for $C_{111}H_{115}B_{31}F_2N_2O_6Si$: C 67.53, H 5.87, N 1.42.

Found: C 67.35, H 5.63, N 1.21.

B(CAR)$_3$(H): To a solution of **B(CAR)$_3$(TES)** (0.3179 g, 1 eq, 0.1610 mmol) in THF (40 mL) was added a solution of NaOH (0.5990 g, 93 eq, 14.9745 mmol) in water. The reaction mixture was heated to 60°C overnight (16h) then was cooled to room temperature. It was concentrated under reduce pressure. The remaining solid was dissolved in dichloromethane. The solution was washed with NH_4Cl saturated then extracted with dichloromethane (3x) and dried over $MgSO_4$. The solvent was filtered and evaporated. The crude product was purified by silica gel with dichloromethane then dichloromethane/EtOH (99.8:0.2) to afford 0.2619 g (0.1408 mmol, 87%) of **B(CAR)$_3$(H)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.2200 g (0.1183 mmol, 73%) of **B(CAR)$_3$(H)** as blue crystals. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 7.08-7.77 (14 lines m, 36H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.62 (s, 2H), 4.06-4.29 (3 lines m, 4H), 3.82-4.01 (3 lines m, 4H), 3.67-3.81 (4 lines m, 4H), 3.49-3.66 (4 lines m, 4H), 3.41 (s, 6H), 3.17 (s, 1H), 3.62-1.57 (large m, 30H, BH), 1.47 (s, 6H).

ESI-MS in dichloromethane, positif mode, *m/z* (%): 1861.0 ([M+H], 100).

Elemental analysis calcd (%) for $C_{105}H_{101}B_{31}F_2N_2O_6$: C 67.80, H 5.47, N 1.51.

Found: C 67.63, H 5.31, N 1.37.

B(CAR)$_3$DPP: was prepared according to the general procedure N°2 for Sonogashira cross-coupling reaction with $[Pd(PPh_3)_4]$: Starting material bromide **DPP(Br)** (0.0192 g, 0.95

eq, 0.0305 mmol) and starting material acetylene **B(CAR)$_3$(H)** (0.0598 g, 1 eq, 0.0321 mmol). The crude product was purified on silica gel eluting with dichloromethane then dichloromethane/EtOH (gradient from 99.8:0.2 to 97:3) to afford 0.0510 g (0.0212 mmol, 69%) of **B(CAR)$_3$DPP** as a gray compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.0263 g (0.0109 mmol, 36%) of **B(CAR)$_3$DPP** as gray crystals. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.40-7.64 (10 lines m, 22H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.22-7.35 (8 lines m, 20H), 7.19 (d, *J* = 7.4 Hz, 4H), 6.97 (d, *J* = 7.8 Hz, 4H), 6.66 (s, 2H), 4.99 (s, 4H), 4.11-4.23 (3 lines m, 4H), 3.78-3.90 (3 lines m, 4H), 3.63-3.73 (4 lines m, 4H), 3.52-3.59 (4 lines m, 4H), 3.48 (s, 2H), 3.36 (s, 6H), 2.33 (s, 6H), 3.62-1.57 (large m, 30H, BH), 1.51 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 163.09, 160.48, 153,36, 152.07, 148.78, 148.39, 142.57, 138.14, 136.62, 136.46, 136.15, 133.55, 132.88, 132.49, 132.45, 132.19, 132.07, 130.17, 129.65, 129.56, 129.36, 128.90, 128.00, 127.17, 127.16, 126.00, 124.29, 121.77, 118.18, 117.51, 115.54, 110.94, 110.77, 92.09, 91.61, 91.47, 90.38, 88.98, 87.66, 85.09, 80.69, 72.55, 71.28, 70.16, 68.29, 66.86, 59.27, 49.05, 46.15, 44.51, 15.22.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 2409.2 ([M+H], 100).

Elemental analysis calcd (%) for $C_{142}H_{130}B_{31}F_2N_5O_8$: C 70.84, H 5.44, N 2.91.

Found: C 70.67, H 5.25, N 2.71.

B(CAR)$_4$(TES): was prepared according to the general procedure N°2 for Sonogashira cross-coupling reaction with [$Pd(PPh_3)_4$]: Starting material iodide **CAR(I)** (0.0835 g, 1.05 eq, 0.1372 mmol) and starting material acetylene **B(CAR)$_3$(H)** (0.2430 g, 1 eq, 0.1306 mmol). The crude product was purified on silica gel eluting with dichloromethane then dichloromethane/EtOH (gradient from 99.9:0.1 to 99:1) to afford 0.2735 g (0.1168 mmol, 89%) of **B(CAR)$_4$(TES)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.2168 g (0.0926 mmol, 71%) of **B(CAR)$_4$(TES)** as blue crystals. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (ppm): 7.13-7.82 (m, 44H), 6.97 (d, *J* = 7.9 Hz, 4H), 6.66 (s, 2H), 4.06-4.28 (m, 4H), 3.77-3.95 (m, 4H), 3.62-3.75 (m, 4H), 3.48-3.60 (m, 4H), 3.36 (s, 6H), 3.62-1.57 (large m, 40H, BH), 1.51 (s, 6H), 1.03 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (75.46 MHz, CD_2Cl_2), δ (ppm): 160.45, 153.33, 142.54, 137.71, 136.40, 133.56, 132.43, 132.05, 129.56, 125.98, 124.75, 124.26, 121.74, 115.50, 100.58, 96.71, 91.43, 87.61, 80.65, 72.52, 71.25, 70.12, 68.23, 67.46, 59.26, 15.22, 7.79, 4.83.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 2340.2 ([M+H], 100).

Elemental analysis calcd (%) for $C_{131}H_{133}B_{41}F_2N_2O_6Si$: C 67.22, H 5.73, N 1.20.

Found: C 66.92, H 5.56, N 1.04.

B(CAR)$_4$(H): To a solution of **B(CAR)$_4$(TES)** (0.2735 g, 1 eq, 0.1168 mmol) in THF (29 mL) was added a solution of NaOH (0.4346 g, 93 eq, 10.8661 mmol) in water. The reaction mixture was heated to 60°C during 20h30 then was cooled to room temperature. It was concentrated under reduce pressure. The crude product was purified by silica gel with petroleum ether/THF (gradient from 8:2 to 2:8) to afford 0.2583 g (0.1160 mmol, 99%) of **B(CAR)$_4$(H)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.2151 g (0.0966 mmol, 83%) of **B(CAR)$_4$(H)** as blue crystals. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 7.11-7.75 (12 lines m, 44H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.62 (s, 2H), 4.11-4.27 (3 lines m, 4H), 3.82-3.98 (3 lines m, 4H), 3.67-3.81 (4 lines m, 4H), 3.51-3.66 (4 lines m, 4H), 3.41 (s, 6H), 3.16 (s, 1H), 3.62-1.57 (large m, 40H, BH), 1.48 (s, 6H).

ESI-MS in dichloromethane, positif mode, *m/z* (%): 2227.2 ([M+H], 100).

Elemental analysis calcd (%) for $C_{125}H_{119}B_{41}F_2N_2O_6$: C 67.43, H 5.39, N 1.26.

Found: C 67.23, H 5.18, N 0.95.

B(CAR)$_4$DPP: was prepared according to the general procedure N°3 for Sonogashira cross-coupling reaction with [Pd(PPh$_3$)$_4$]: Starting material bromide **DPP(Br)** (0.0108 g, 0.95 eq, 0.0172 mmol) and starting material acetylene **B(CAR)$_4$(H)** (0.0404 g, 1 eq, 0.0181 mmol). The reaction mixture was concentrated under reduce pressure. The remaining solid was dissolved in dichloromethane. The solution was washed with water then extracted with dichloromethane (3x) and dried over MgSO$_4$. The solvent was filtered and evaporated. The crude product was purified on silica gel eluting with dichloromethane then dichloromethane/EtOH (gradient from 99.8:0.2 to 8:2) to afford 0.0332 g (0.0120 mmol, 69%) of **B(CAR)$_4$DPP** as a gray compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford some gray crystals of **B(CAR)$_4$DPP**. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$), δ (ppm): 7.78 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.40-7.64 (m, 26H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.22-7.35 (m, 24H), 7.19 (d, *J* = 7.4 Hz, 4H), 6.97 (d, *J* = 8.6 Hz, 4H), 6.66 (s, 2H), 4.98 (s, 4H), 4.09-4.24 (3 lines m, 4H), 3.76-3.89 (3 lines m, 4H), 3.63-3.73 (4 lines m, 4H), 3.50-3.59 (4 lines m, 4H), 3.47 (s, 2H), 3.36 (s, 6H), 2.32 (s, 6H), 3.62-1.57 (large m, 40H, BH), 1.51 (s, 6H). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$), δ (ppm): 163.06, 160.47, 153,35, 152.06, 148.78, 148.38, 142.57, 138.13, 136.61, 136.44, 136.14, 133.55, 132.87, 132.44, 132.17, 132.06, 130.16, 129.64, 129.55, 129.35, 128.89, 127.98, 127.16, 126.37, 125.99, 124.27, 121.75, 118.18, 117.49, 115.52, 110.92, 110.75, 91.45, 87.63, 80.67, 72.53, 71.28, 70.15, 68.27, 66.85, 59.27, 49.08, 46.14, 44.55, 15.21.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 2775.3 ([M+H], 100).

Elemental analysis calcd (%) for $C_{162}H_{148}B_{41}F_2N_5O_8$: C 70.14, H 5.38, N 2.52.

Found: C 69.83, H 5.04, N 2.31.

B(CAR)$_5$(TES): was prepared according to the general procedure N°3 for Sonogashira cross-coupling reaction with [Pd(PPh$_3$)$_4$]: Starting material iodide **CAR(I)** (0.0501 g, 1.05 eq, 0.0824 mmol) and starting material acetylene **B(CAR)$_4$(H)** (0.1747 g, 1 eq, 0.0785 mmol). The crude product was purified on silica gel eluting with THF/petroleum ether (gradient from 1:9 to 8:2) then THF to afford 0.2103 g (0.0777 mmol, 99%) of **B(CAR)$_5$(TES)** as a blue compound. Finally, this compound was recrystallized several times by evaporation of THF/pentane to afford some blue crystals of **B(CAR)$_5$(TES)**. ^{1}H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.54-7.70 (4 lines m, 10H), 7.18-7.52 (12 lines m, 42H), 6.96 (d, *J* = 8.6 Hz, 4H), 6.62 (s, 2H), 4.14-4.27 (3 lines m, 4H), 3.86-3.96 (3 lines m, 4H), 3.70-3.80 (4 lines m, 4H), 3.56-3.66 (4 lines m, 4H), 3.42 (s, 6H), 3.62-1.57 (large m, 50H, BH), 1.49 (s, 6H), 1.04 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 159.65, 152.94, 151.49, 141.47, 135.99, 135.77, 132.90, 131.89, 131.40, 129.65, 129.04, 128.24, 125.49, 123.60, 121.20, 117.68, 114.95, 105.43, 91.00, 87.20, 80.00, 71.96, 70.80, 69.70, 67.51, 66.18, 59.08, 53.38, 14.82, 7.44, 4.33.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 2706.5 ([M+H], 100).

Elemental analysis calcd (%) for $C_{151}H_{151}B_{51}F_2N_2O_6Si$: C 66.99, H 5.62, N 1.03.

Found: C 66.72, H 5.48, N 0.72.

B(CAR)$_5$(H): To a solution of **B(CAR)$_5$(TES)** (0.1982 g, 1 eq, 0.0732 mmol) in THF (30 mL) was added a solution of NaOH (0.2928 g, 100 eq, 7.3210 mmol) in water (10 mL). The reaction mixture was heated to 60°C during 24h then was cooled to room temperature. It was concentrated under reduce pressure. The crude product was purified by silica gel with petroleum ether/THF (gradient from 9:1 to 1:9) to afford 0.1481 g (0.0571 mmol, 78%) of **B(CAR)$_5$(H)** as a blue compound. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.1113 g (0.0429 mmol, 59%) of **B(CAR)$_5$(H)** as blue crystals. ^{1}H

NMR (200 MHz, $CDCl_3$), δ (ppm): 7.08-7.75 (m, 52H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.61 (s, 2H), 4.11-4.28 (3 lines m, 4H), 3.82-3.96 (3 lines m, 4H), 3.67-3.80 (4 lines m, 4H), 3.51-3.65 (4 lines m, 4H), 3.41 (s, 6H), 3.16 (s, 1H), 3.62-1.57 (large m, 50H, BH), 1.47 (s, 6H).

ESI-MS in dichloromethane, positif mode, *m/z* (%): 2593.4 ([M+H], 100).

Elemental analysis calcd (%) for $C_{145}H_{137}B_{51}F_2N_2O_6$: C 67.16, H 5.33, N 1.08.

Found: C 66.83, H 5.03, N 0.78.

B(CAR)$_5$DPP: was prepared according to the general procedure N°3 for Sonogashira cross-coupling reaction with [Pd(PPh_3)$_4$]: Starting material bromide **DPP(Br)** (0.0069 g, 0.61 eq, 0.0110 mmol) and starting material acetylene **B(CAR)$_5$(H)** (0.0470 g, 1 eq, 0.0181 mmol). The crude product was purified on silica gel eluting with petroleum ether then petroleum ether/THF (gradient from 8:2 to 2:8) and then THF to afford a gray compound of **B(CAR)$_5$DPP**. Finally, this compound was recrystallized by evaporation of THF/pentane to afford 0.0220 g (0.0070 mmol, 64%) of **B(CAR)$_5$DPP** as gray crystals. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.78 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.22-7.69 (m, 62H), 7.20 (d, *J* = 7.4 Hz, 4H), 6.96 (d, *J* = 8.5 Hz, 4H), 6.62 (s, 2H), 5.00 (s, 4H), 4.13-4.28 (3 lines m, 4H), 3.84-3.96 (3 lines m, 4H), 3.69-3.82 (4 lines m, 4H), 3.57-3.66 (4 lines m, 4H), 3.52 (s, 2H), 3.42 (s, 6H), 2.39 (s, 6H), 3.62-1.57 (large m, 50H, BH), 1.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 162.67, 159.69, 152,97, 148.43, 148.12, 141.50, 137.28, 136.00, 132.93, 132.22, 132.07, 131.90, 131.41, 129.69, 129.05, 128.87, 127.51, 126.63, 123.62, 121.23, 117.68, 117.29, 114.98, 110.23, 108.44, 91.02, 87.53, 87.20, 80.04, 71.99, 70.82, 69.72, 67.97, 67.54, 66.20, 59.09, 44.16, 14.83.

ESI-MS in dichloromethane, positif mode, *m/z* (%): 3142.6 ([M+H], 100).

Elemental analysis calcd (%) for $C_{182}H_{166}B_{51}F_2N_5O_8$: C 69.60, H 5.33, N 2.23.

Found: C 69.42, H 5.17, N 1.85.

3) NMR Traces

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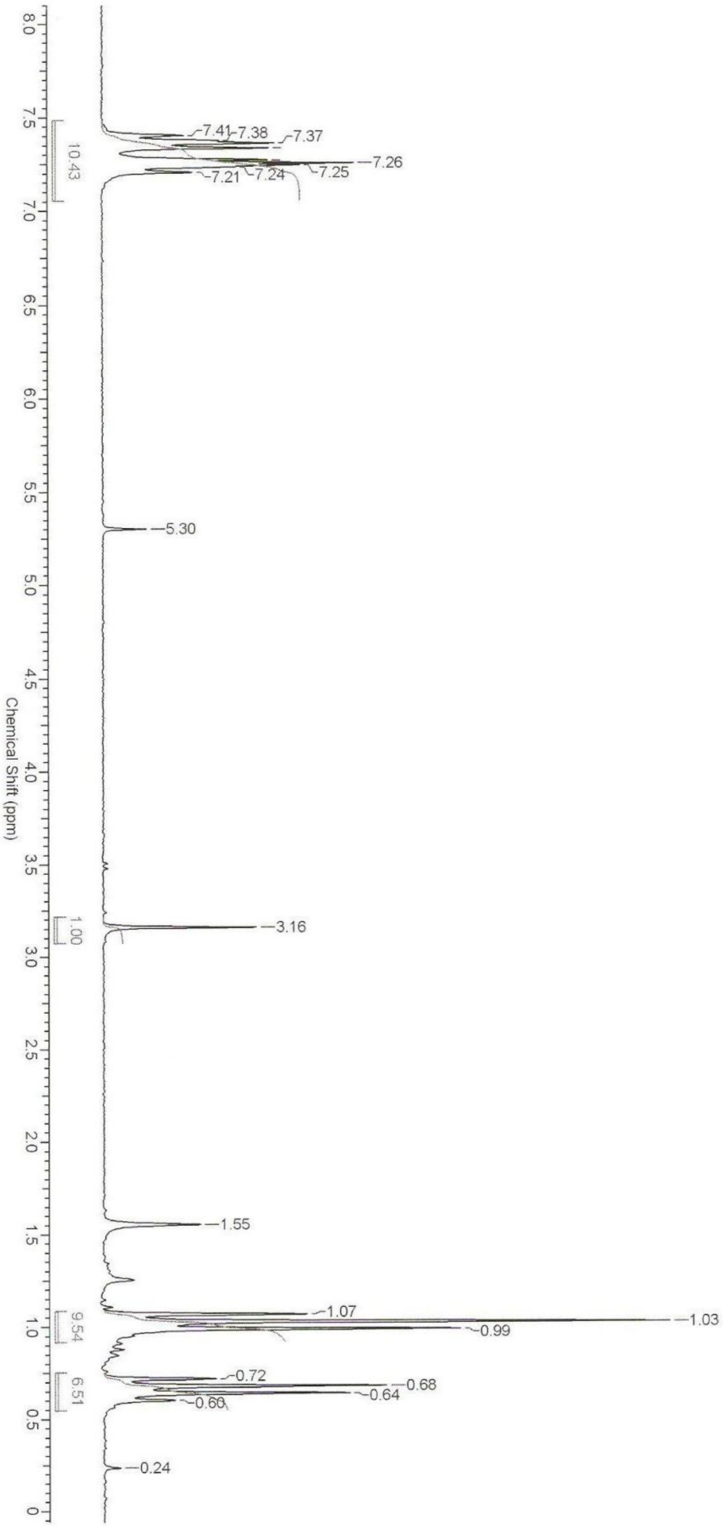

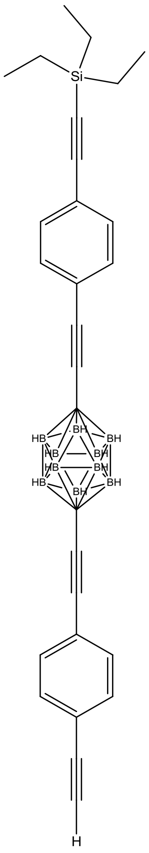

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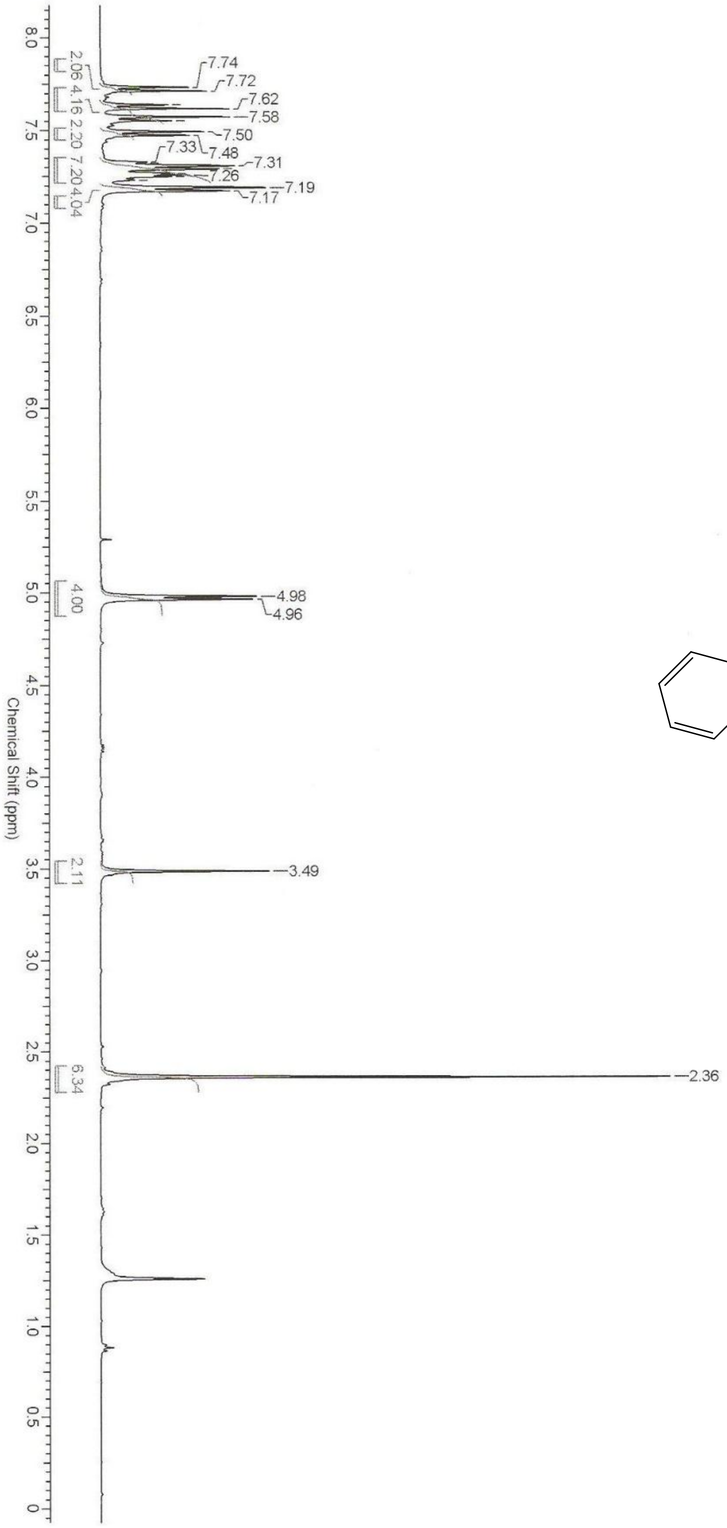
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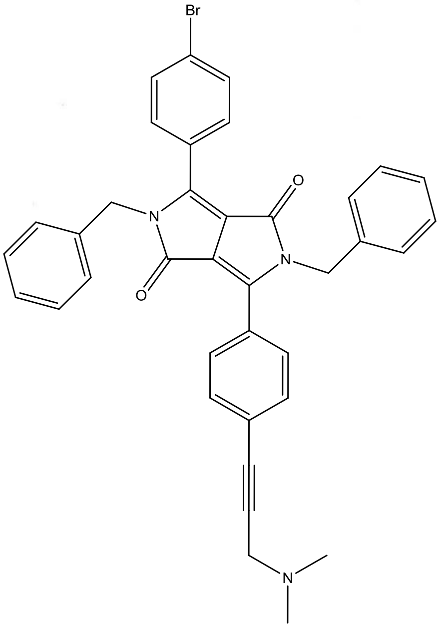
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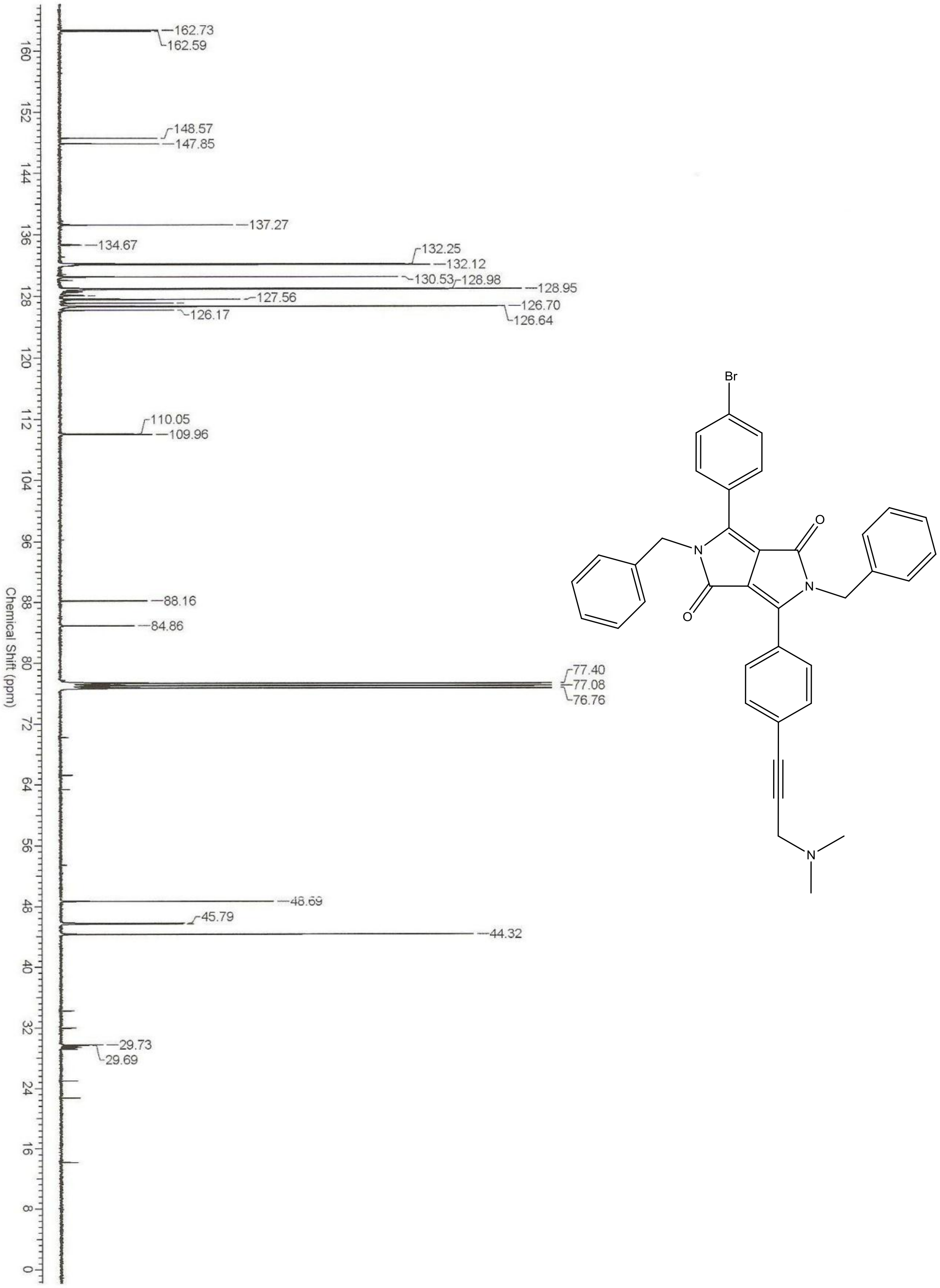
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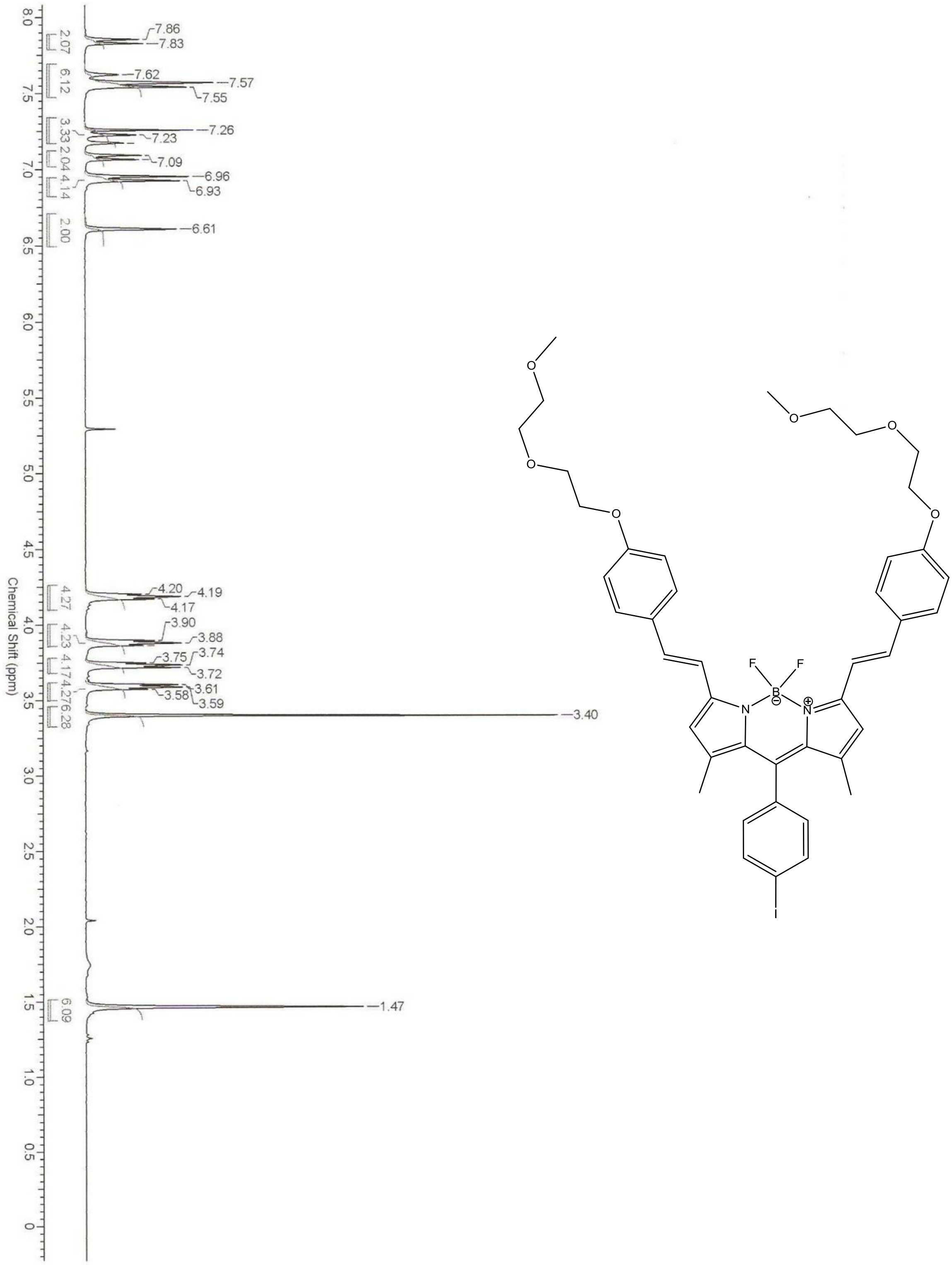
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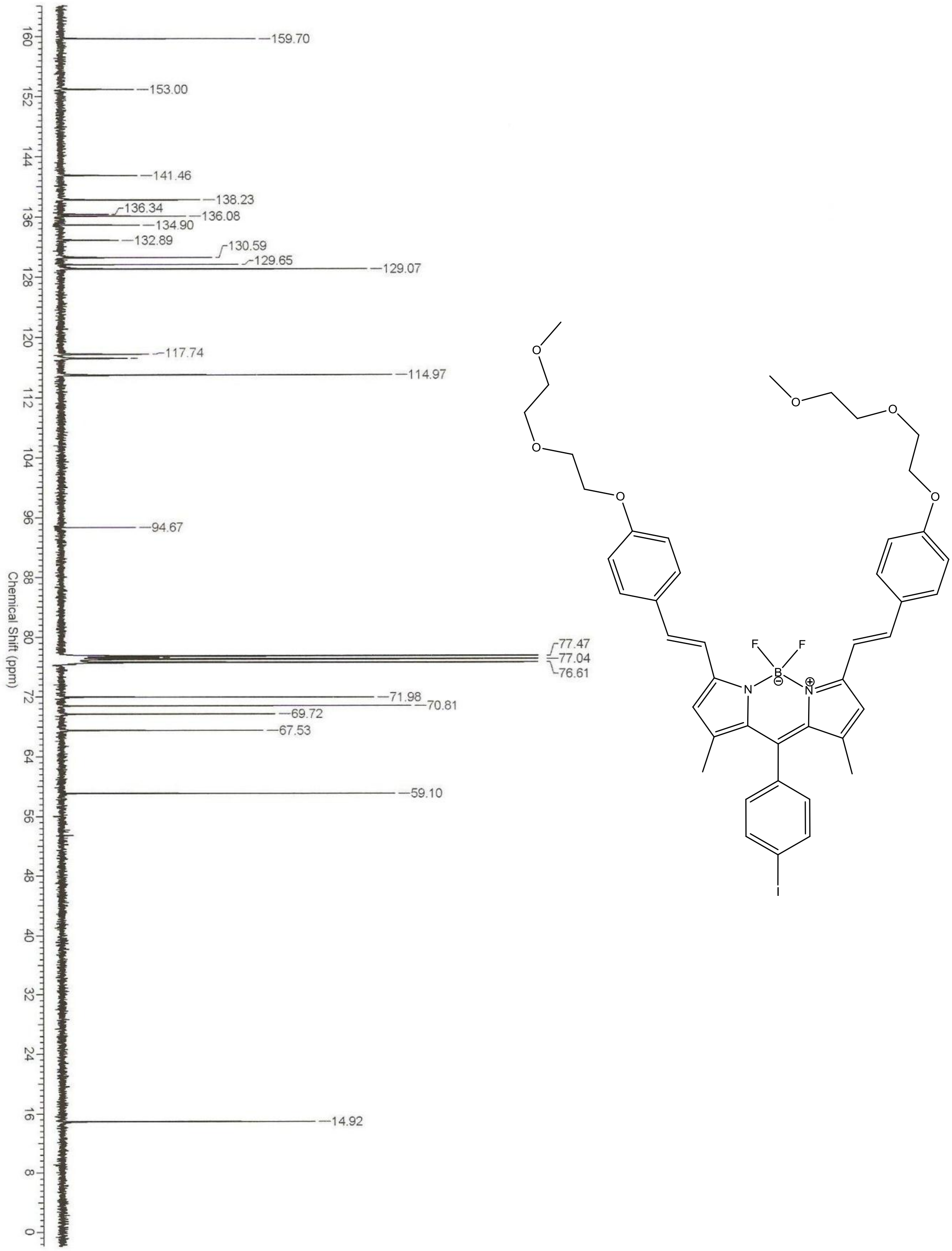
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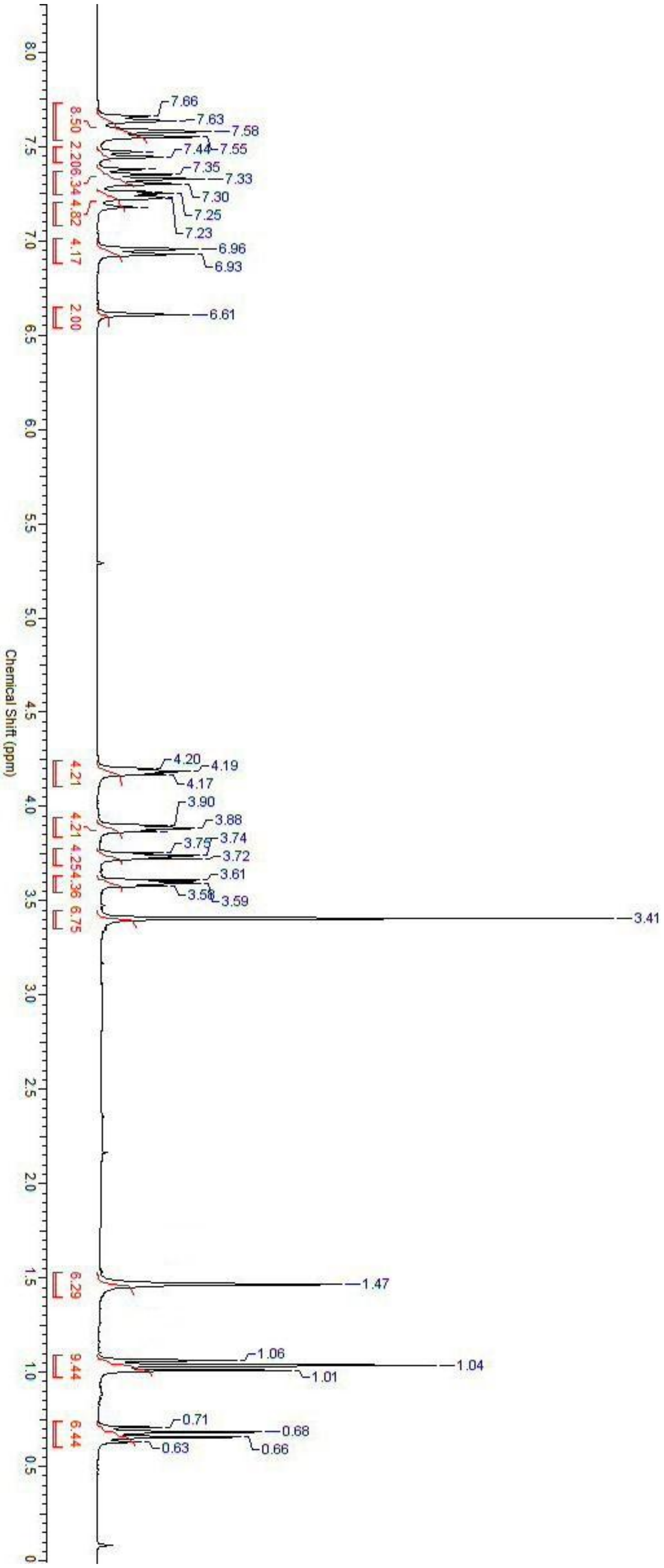
B(CAR)$_1$(TES)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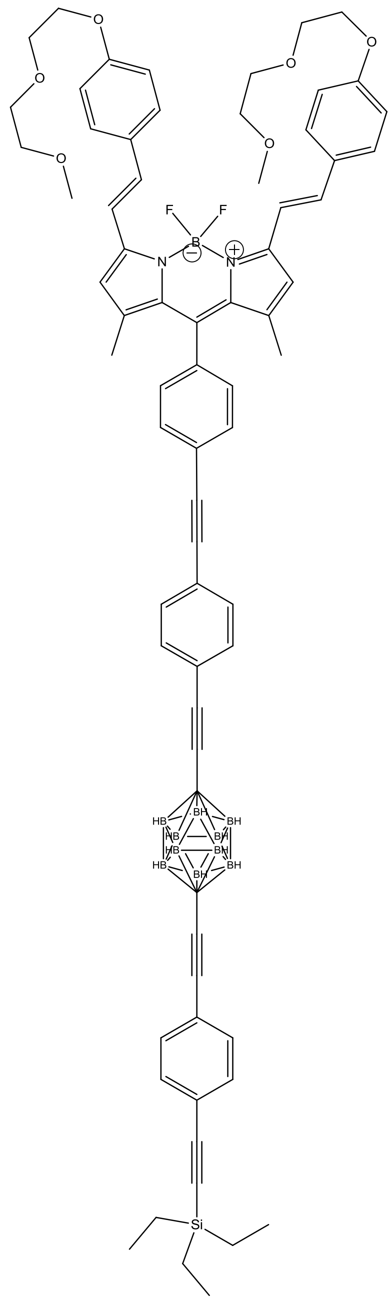
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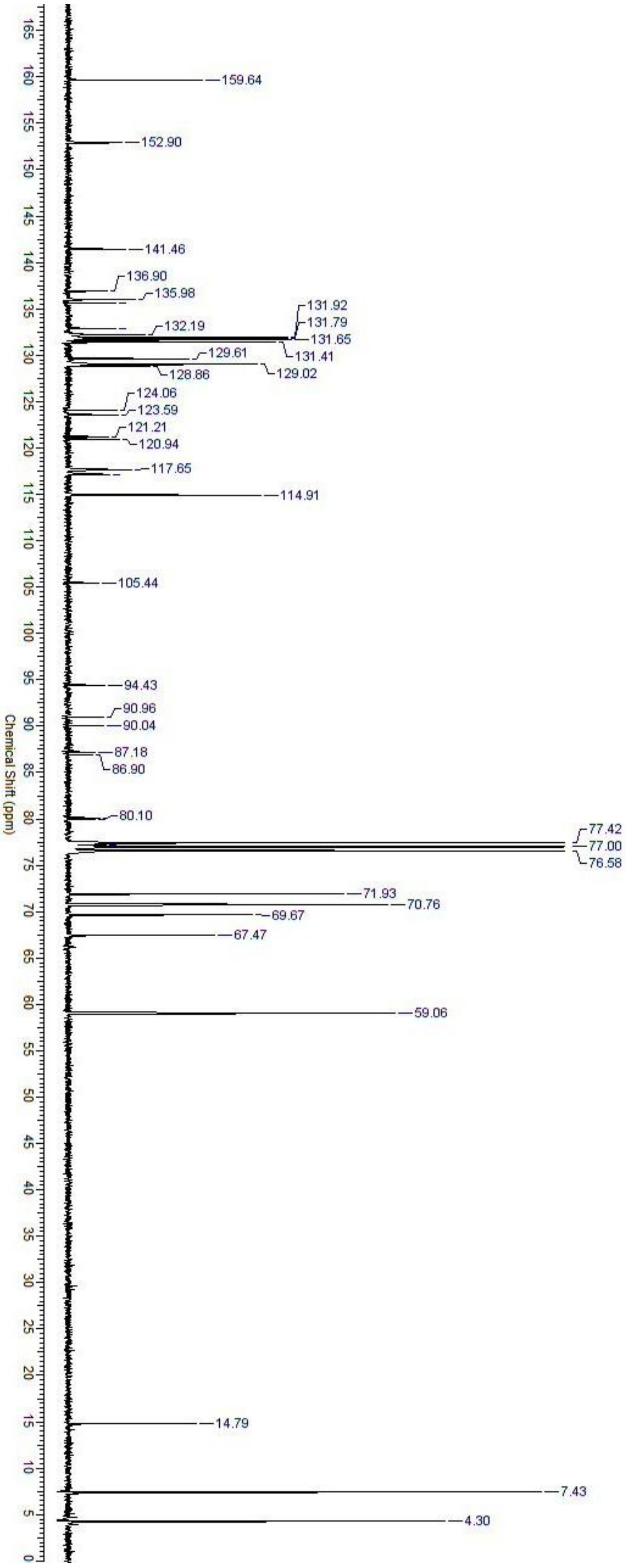
B(CAR)$_1$(TES)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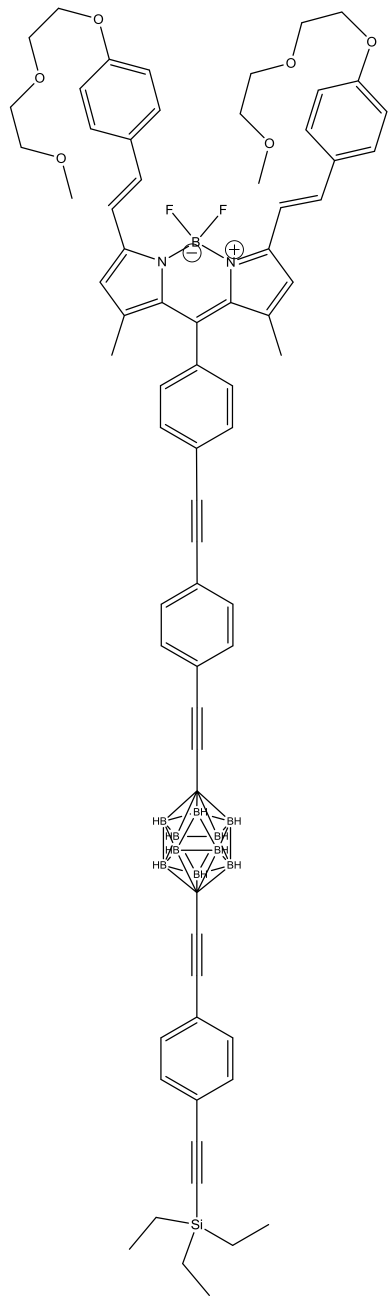
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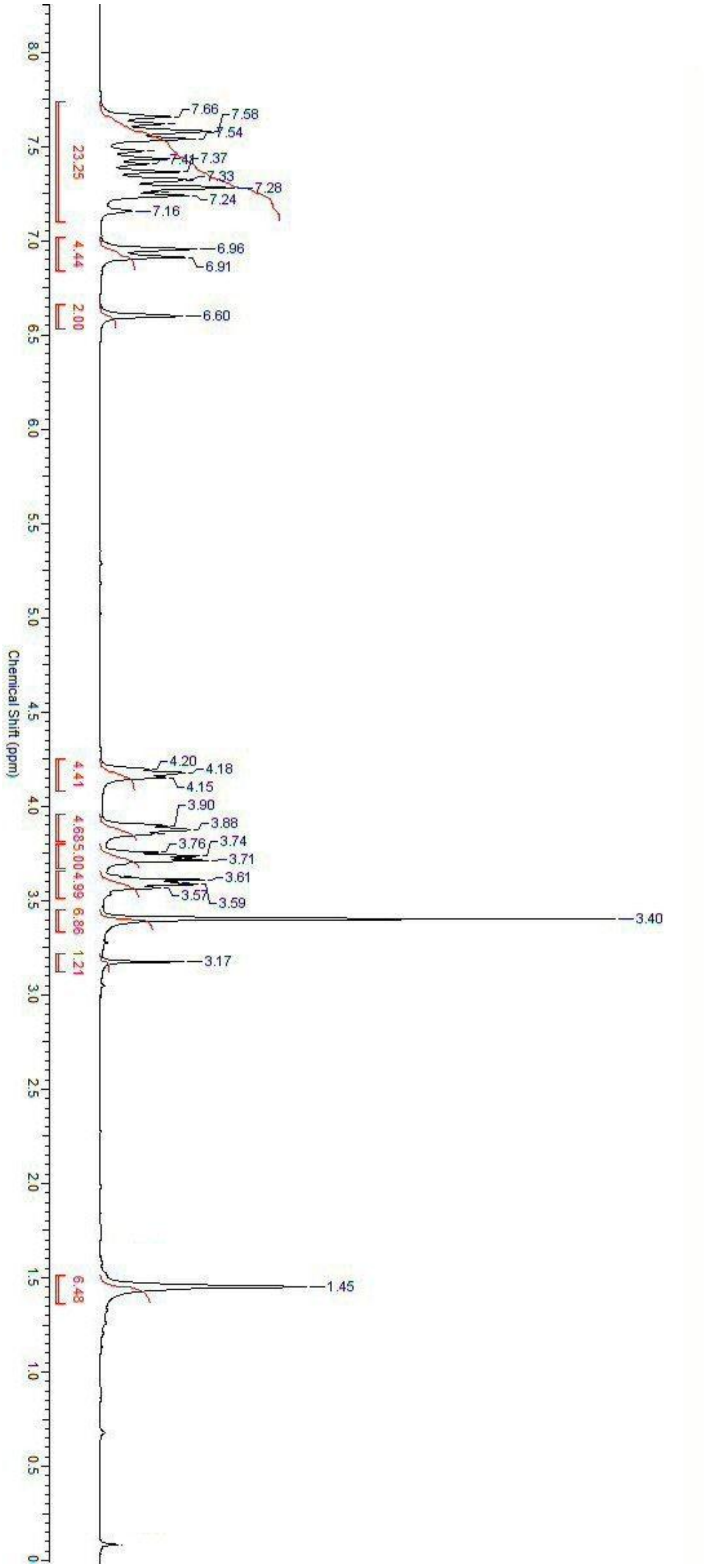
B(CAR)$_1$(H)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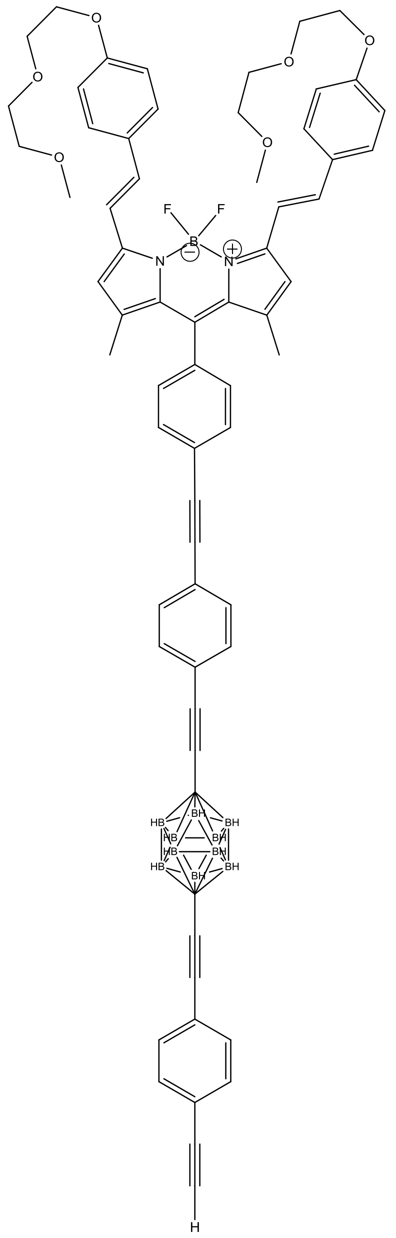
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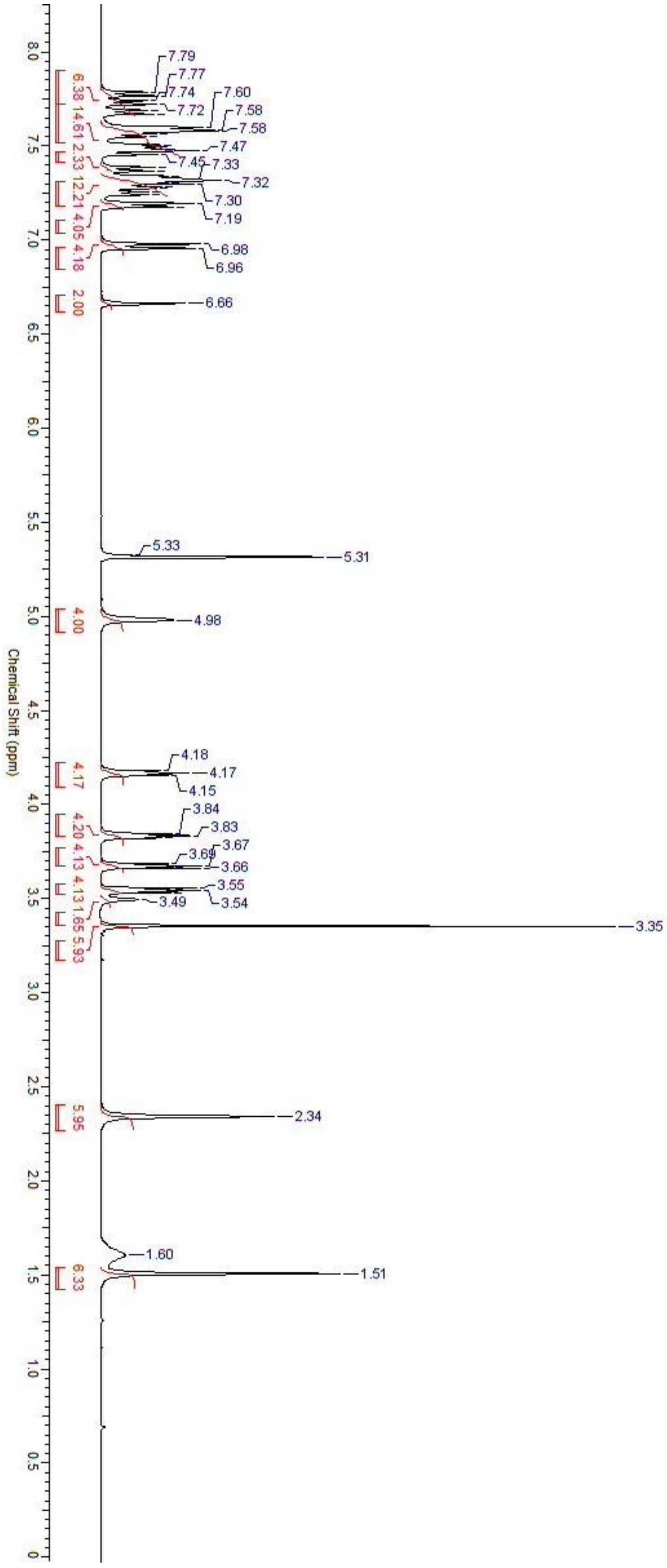
B(CAR)$_1$DPP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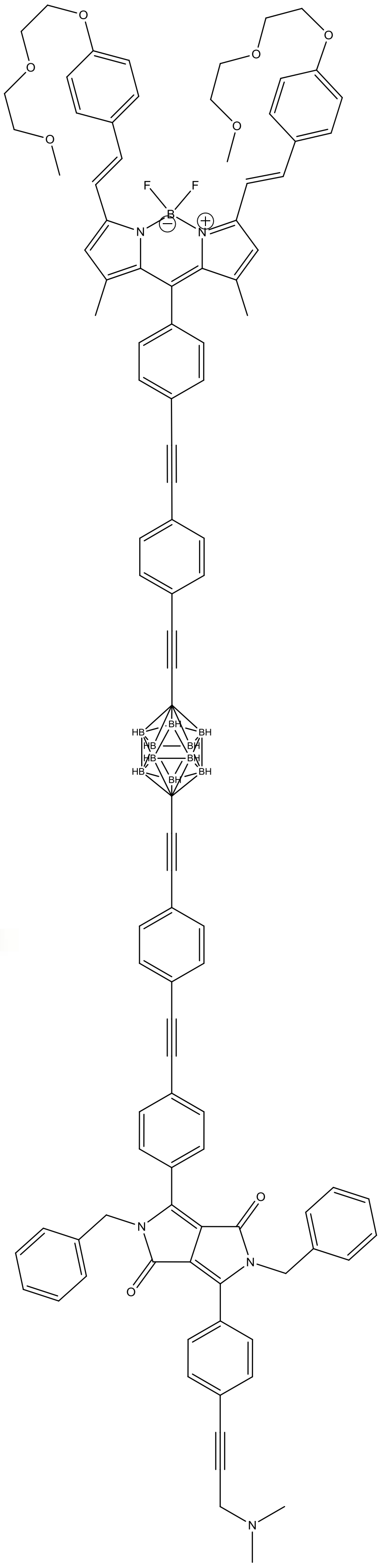
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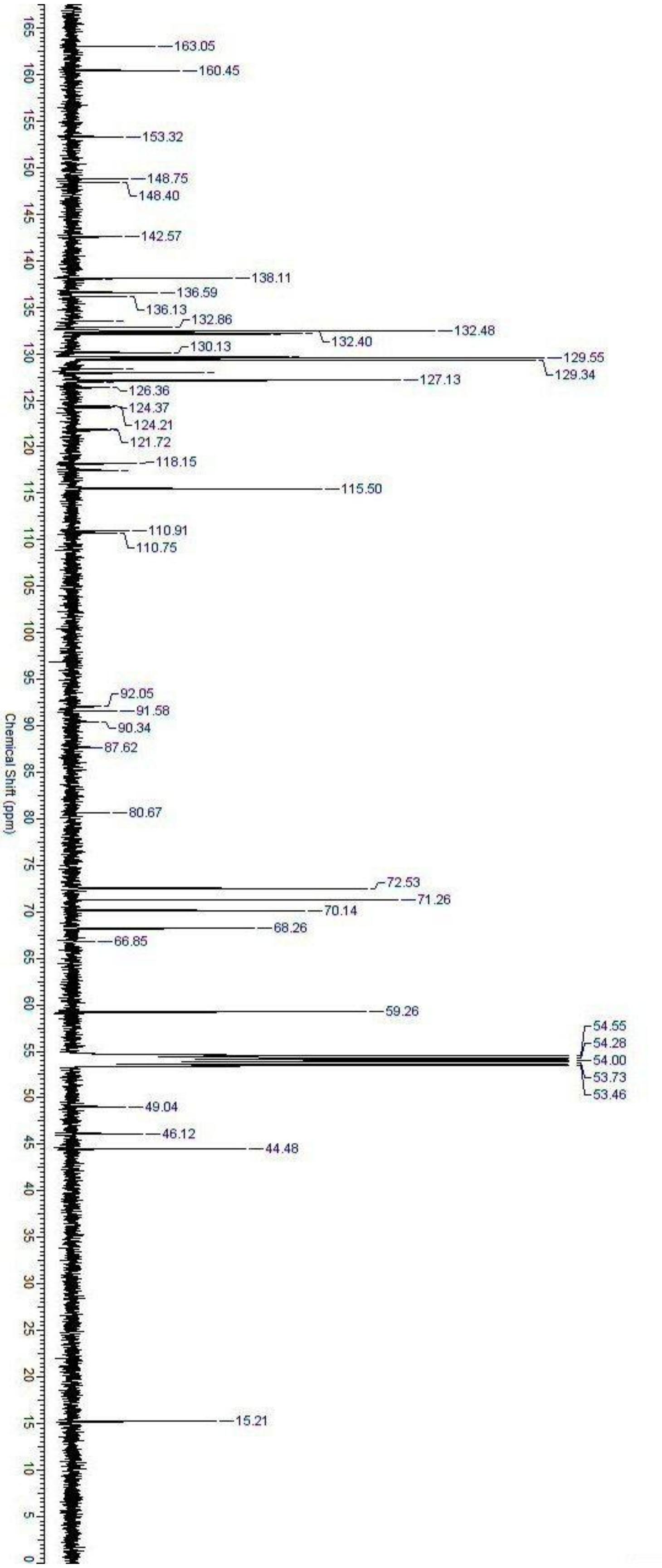
B(CAR)$_1$DPP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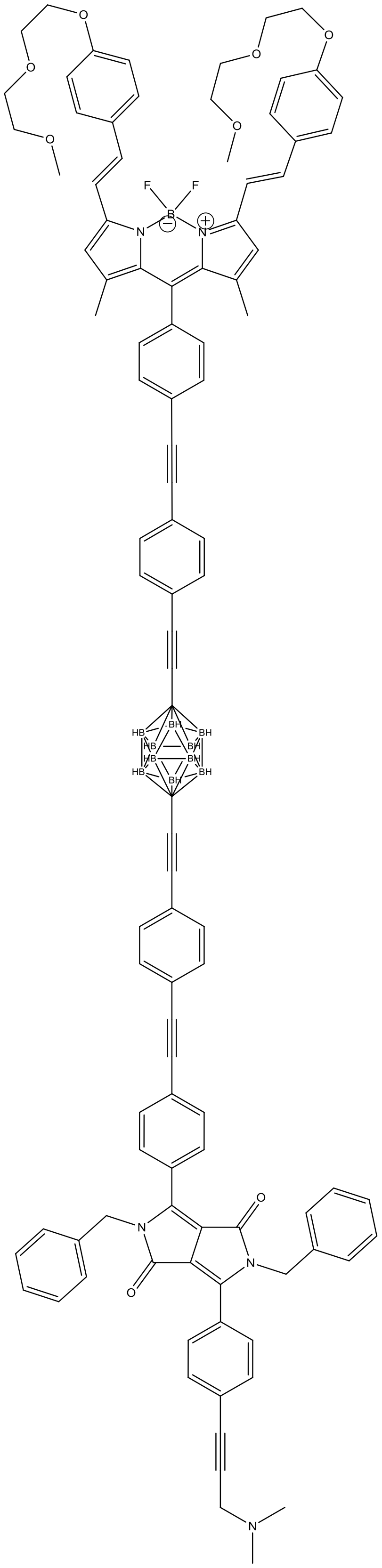
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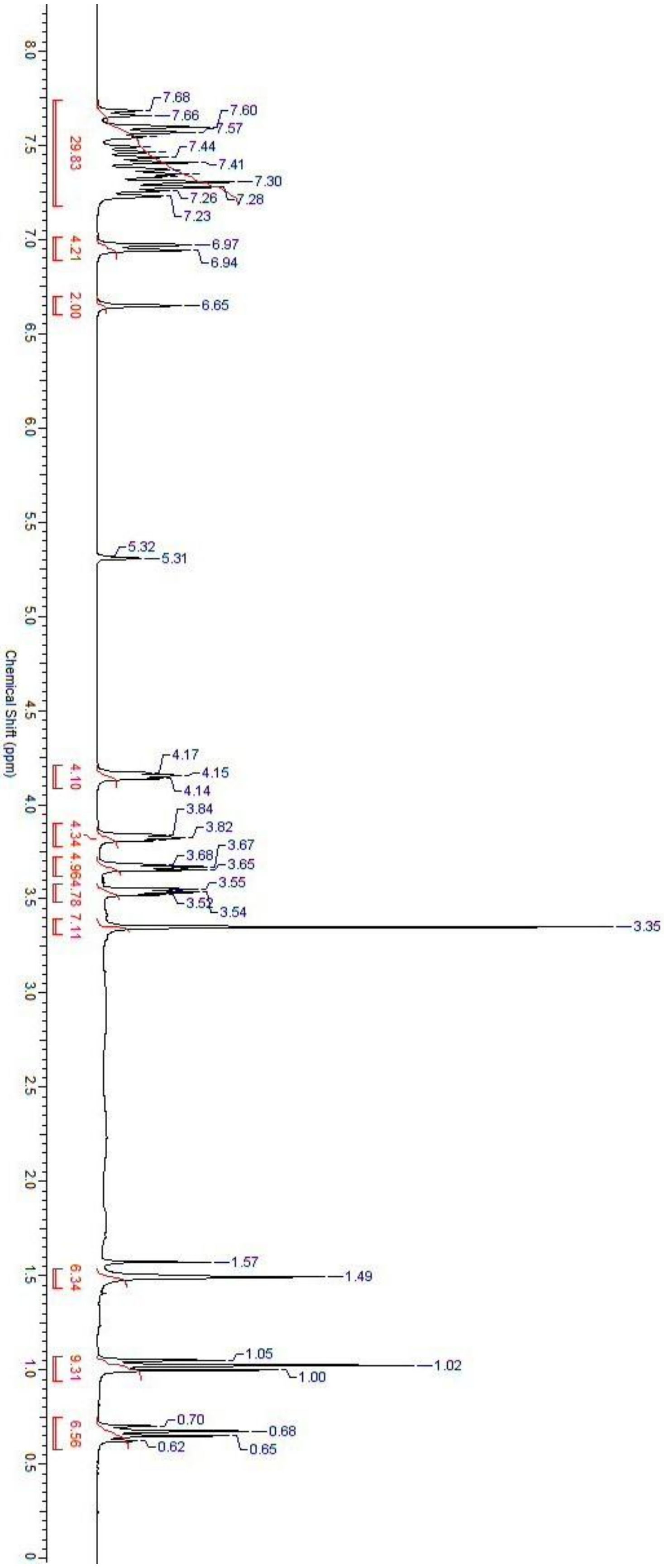
B(CAR)$_2$(TES)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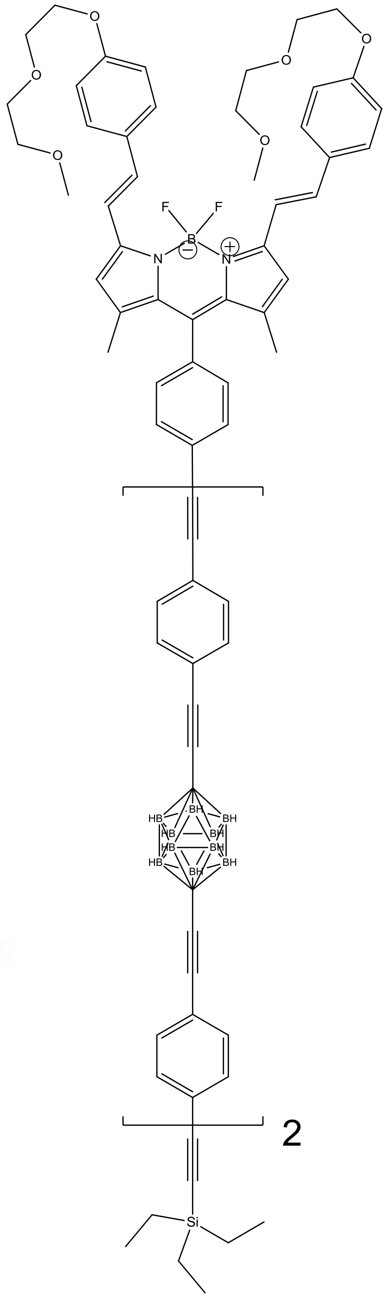
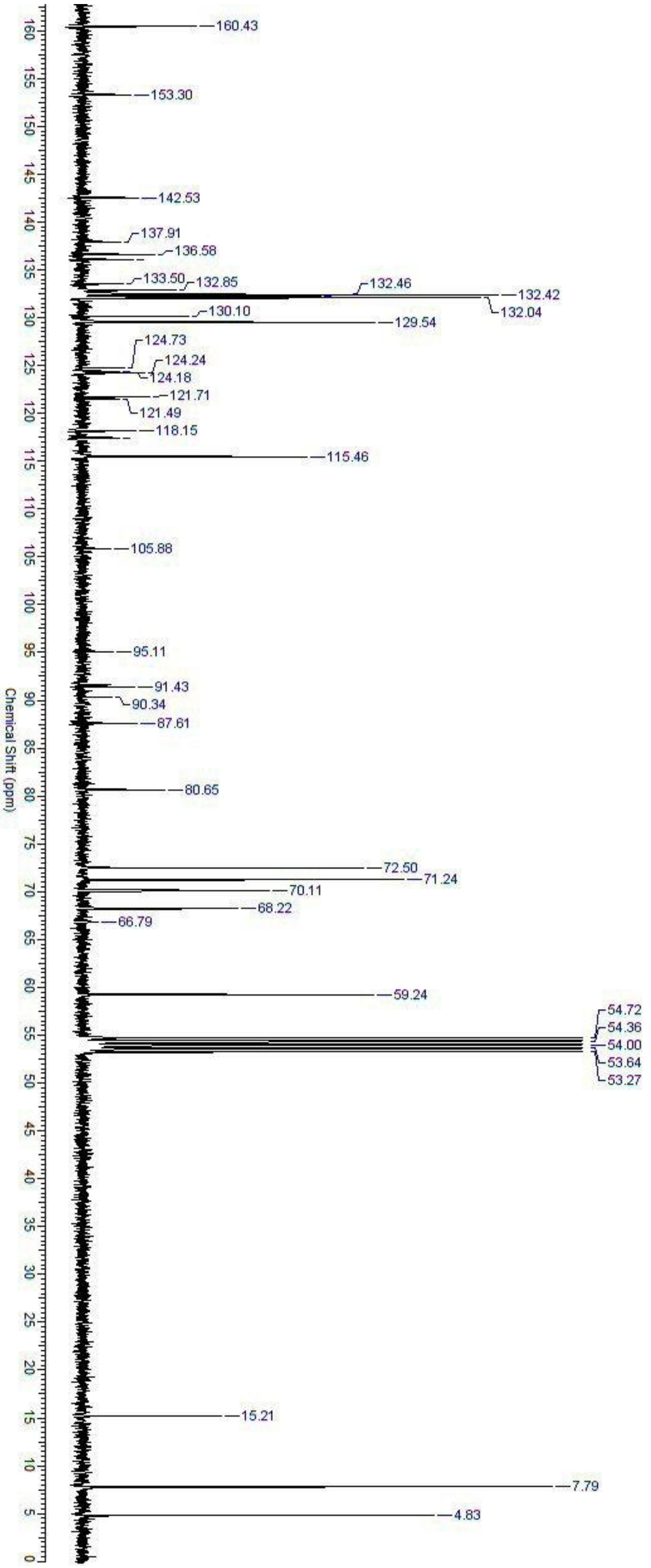
4.78
7.11
6.34
9.31
6.56
7.68
7.66
7.60
7.57
7.44
7.41
7.30
7.26
7.28
7.23
6.97
6.94
6.65
5.32
5.31
4.17
4.15
4.14
3.84
3.82
3.67
3.68
3.65
3.55
3.52
3.54
3.35
1.57
1.49
1.05
1.02
1.00
0.70
0.68
0.62
0.65


O
O
O
O
O
O
F
F
B
N
N
HB
BH
BH
HB
BH
HB
BH
HB
BH
BH
2
Si

B(CAR)$_2$(TES)


160.43
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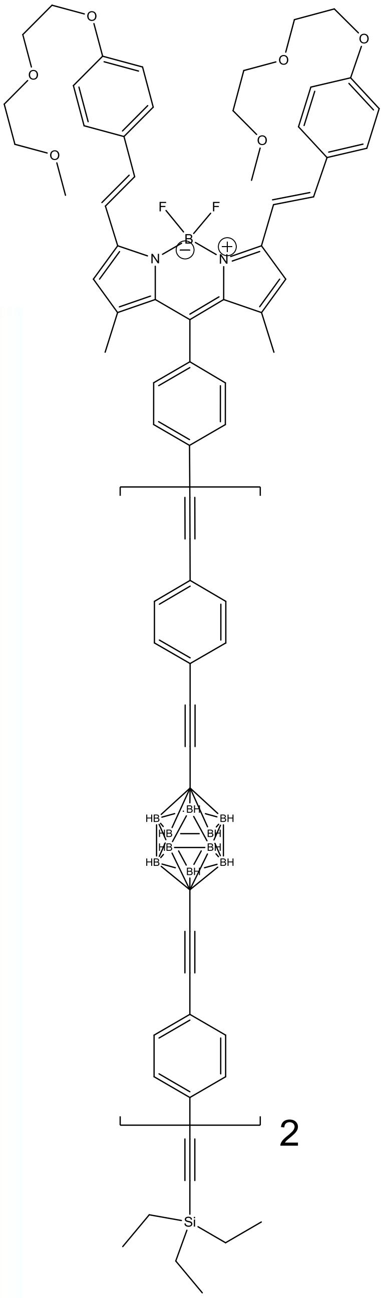
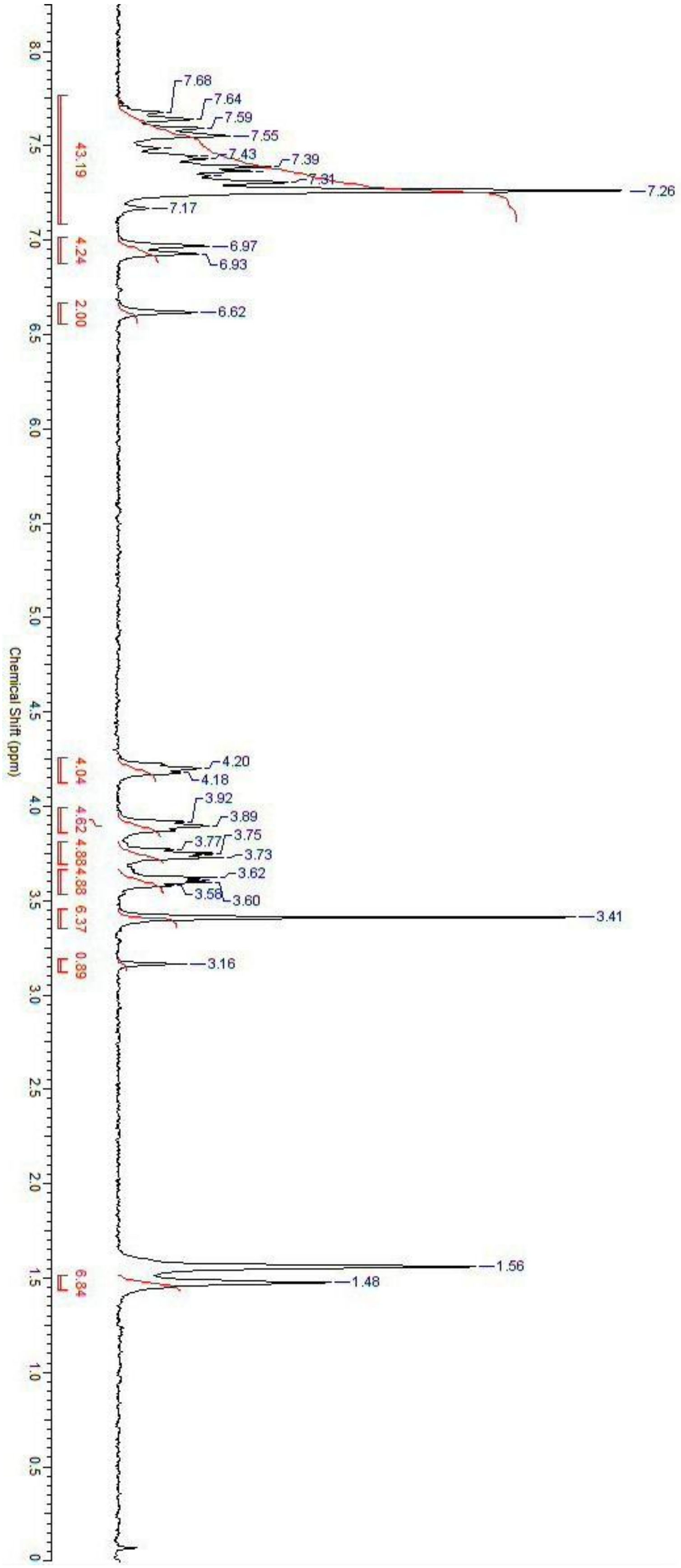
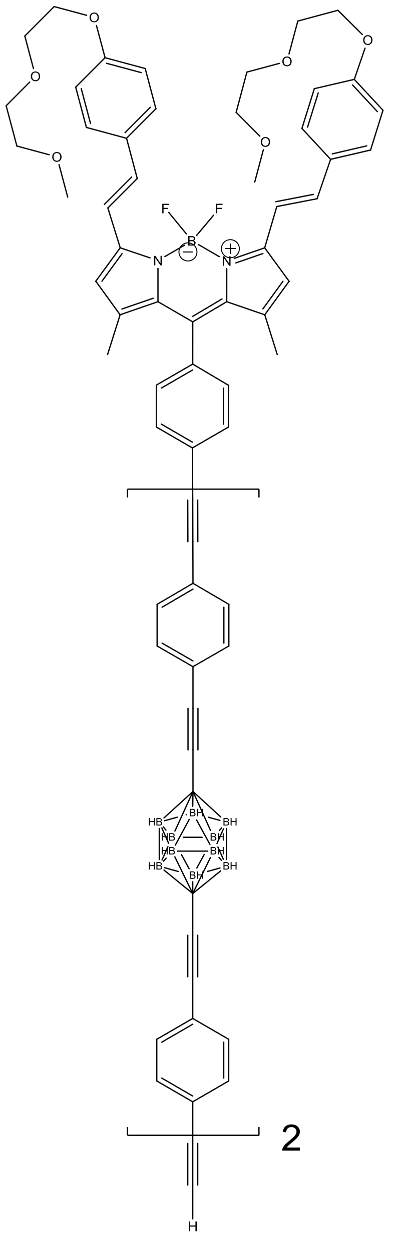
142.53
137.91
136.58
133.50
132.85
132.46
132.42
132.04
130.10
129.54
124.73
124.24
124.18
121.71
121.49
118.15
115.46
105.88
95.11
91.43
90.34
87.61
80.65
72.50
71.24
70.11
68.22
66.79
59.24
54.72
54.36
54.00
53.64
53.27
15.21
7.79
4.83
Chemical Shift (ppm)
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0

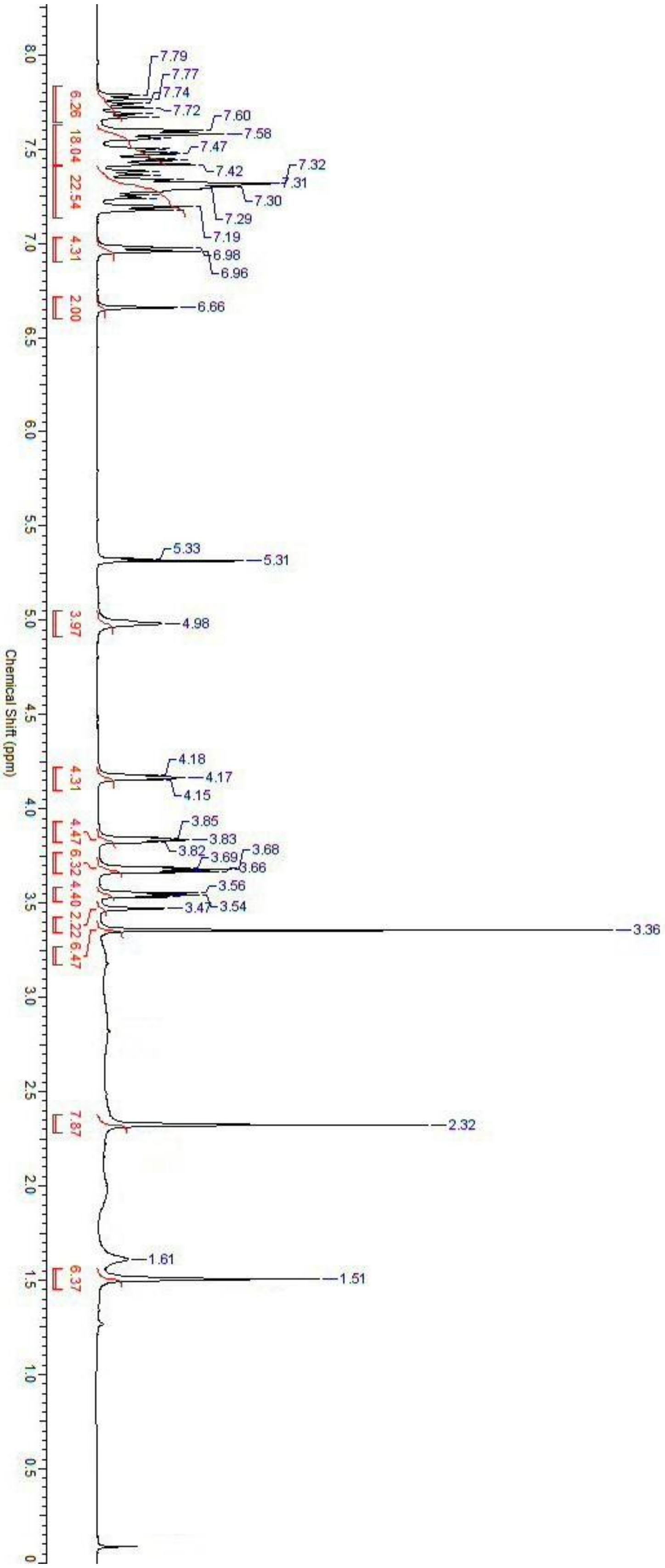

O
F
F
B
N
N
HB
BH
Si
2

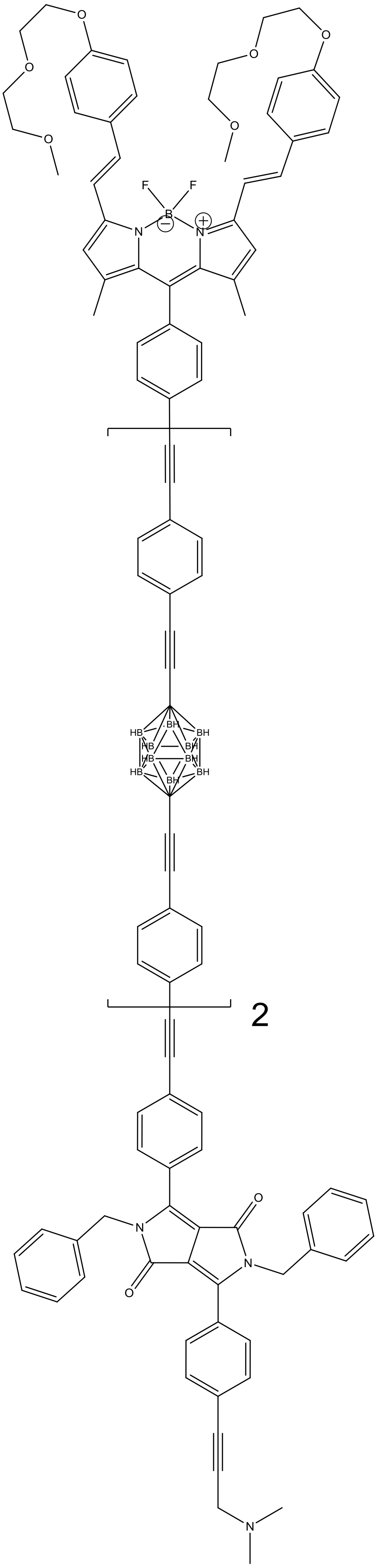
B(CAR)$_2$(H)


7.68
7.64
7.59
7.55
7.43
7.39
7.31
7.26
7.17
6.97
6.93
6.62
4.20
4.18
3.92
3.89
3.77
3.75
3.73
3.62
3.58
3.60
3.41
3.16
1.56
1.48
43.19
4.24
2.00
4.04
4.62
4.88
4.88
6.37
0.89
6.84
Chemical Shift (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

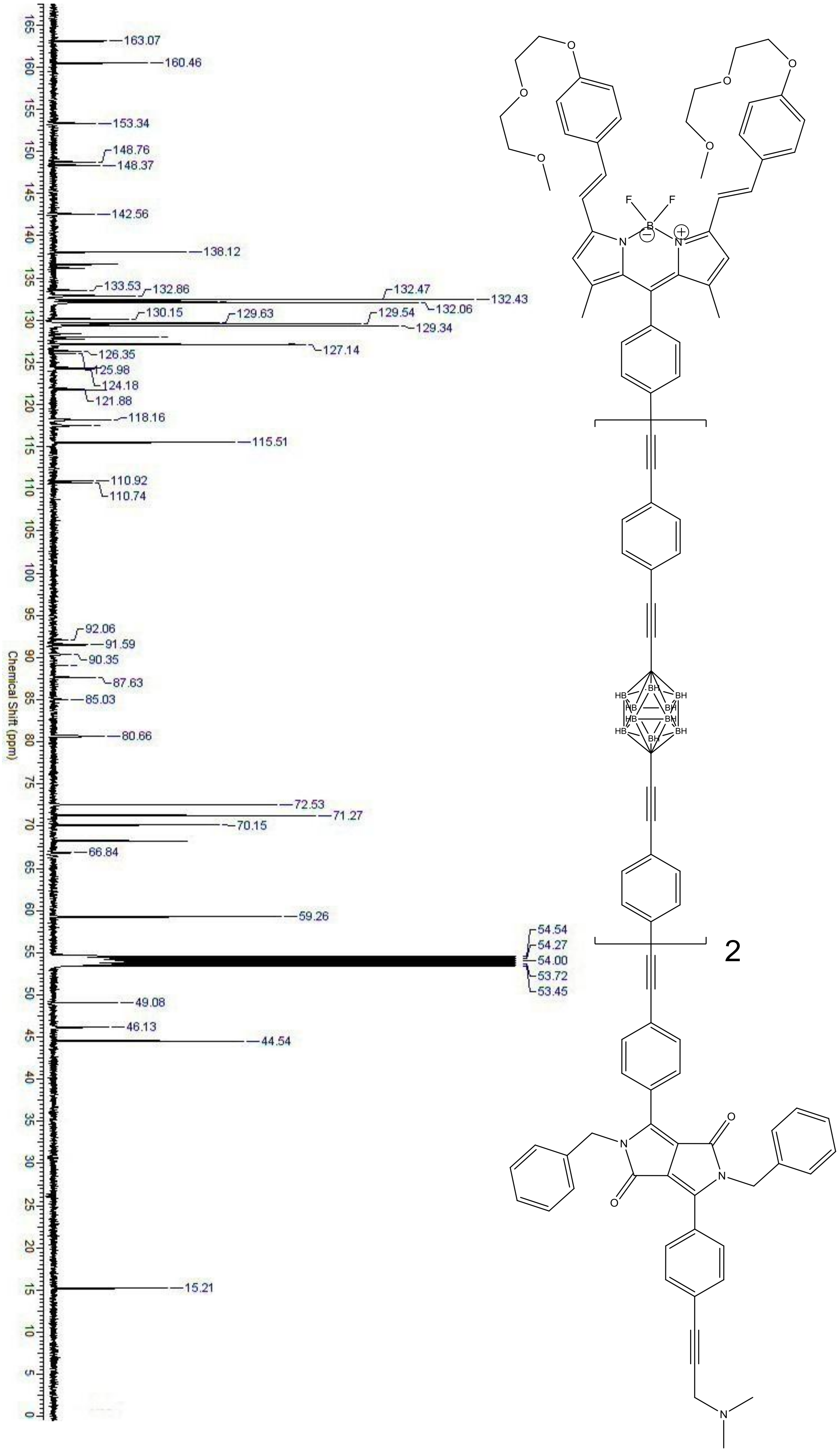

O
F
B
N
HB
BH
H
2

B(CAR)$_2$DPP


Chemical Shift (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
6.26
18.04
22.54
4.31
2.00
3.97
4.31
4.47
6.32
4.40
2.22
6.47
7.87
6.37
7.79
7.77
7.74
7.72
7.60
7.58
7.47
7.42
7.32
7.31
7.30
7.29
7.19
6.98
6.96
6.66
5.33
5.31
4.98
4.18
4.17
4.15
3.85
3.83
3.82
3.69
3.68
3.66
3.56
3.47
3.54
3.36
2.32
1.61
1.51


O
O
O
O
O
O
F
F
B
N
N
HB
BH
2
O
O
N
N
N

B(CAR)$_2$DPP


163.07
160.46
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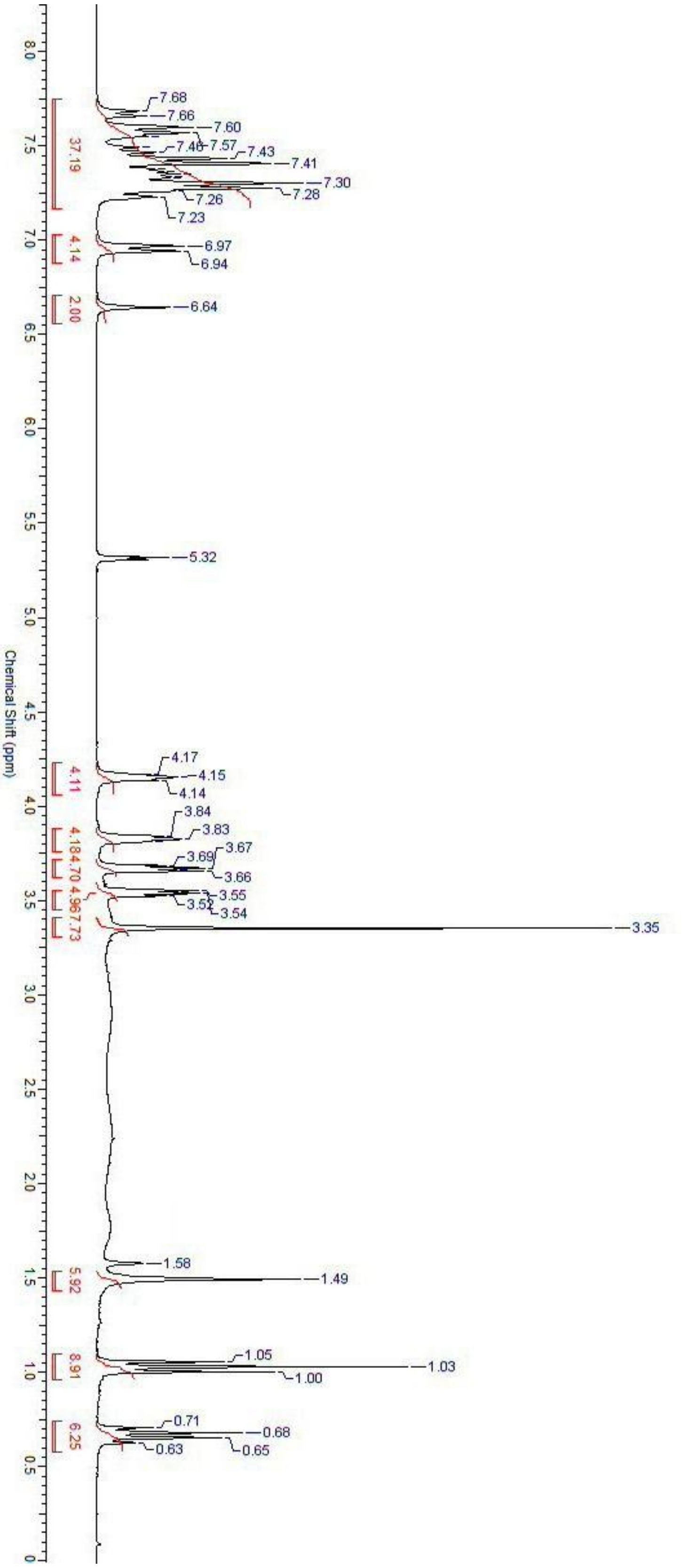
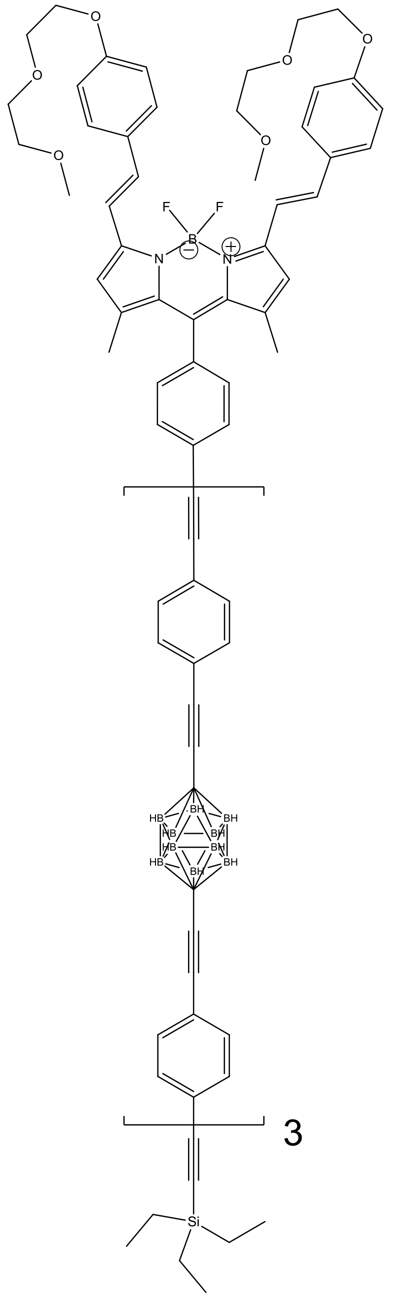
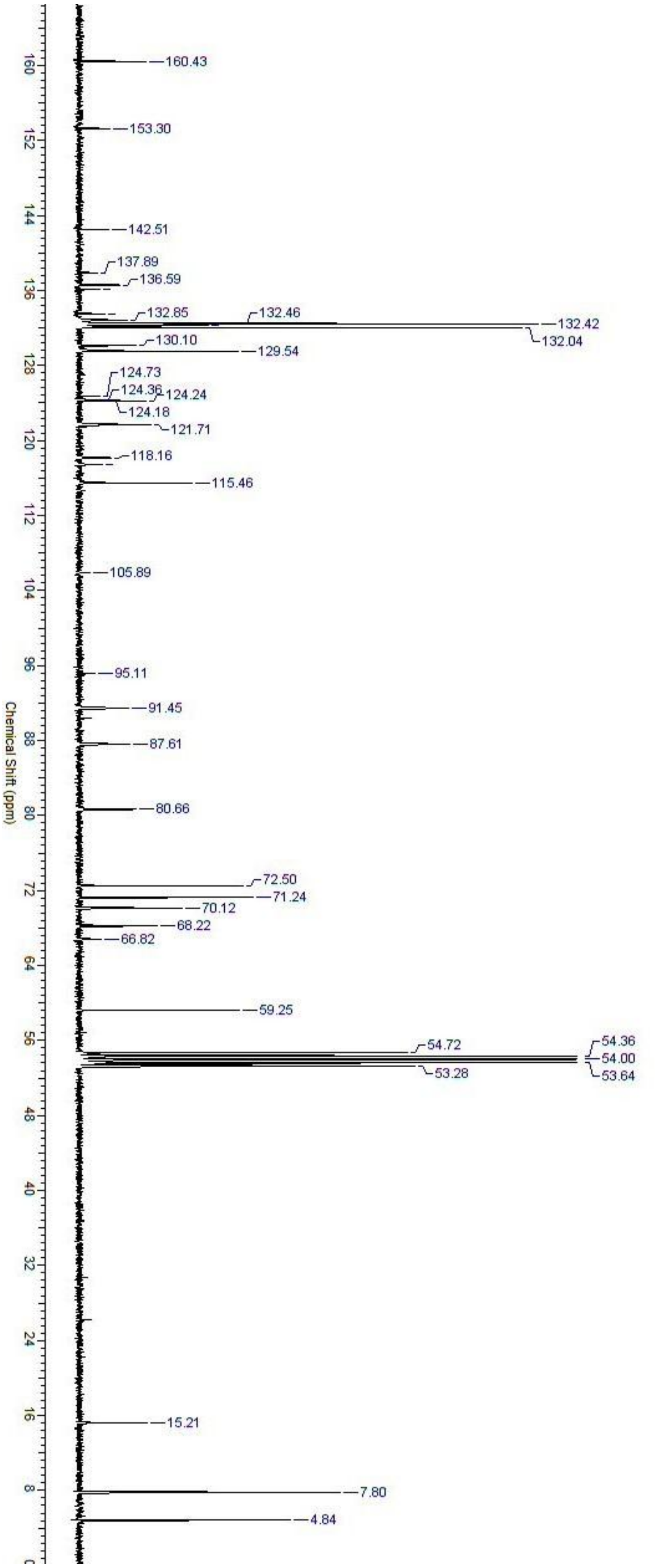
148.37
142.56
138.12
133.53
132.86
132.47
132.43
132.06
130.15
129.63
129.54
129.34
127.14
126.35
125.98
124.18
121.88
118.16
115.51
110.92
110.74
92.06
91.59
90.35
87.63
85.03
80.66
72.53
71.27
70.15
66.84
59.26
54.54
54.27
54.00
53.72
53.45
49.08
46.13
44.54
15.21
Chemical Shift (ppm)
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
O
F
B
N
HB
BH
2

B(CAR)$_3$(TES)


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
37.19
4.14
2.00
4.11
4.18
4.70
4.96
7.73
5.92
8.91
6.25
7.68
7.66
7.60
7.46
7.57
7.43
7.41
7.30
7.28
7.26
7.23
6.97
6.94
6.64
5.32
4.17
4.15
4.14
3.84
3.83
3.67
3.69
3.66
3.55
3.52
3.54
3.35
1.58
1.49
1.05
1.03
1.00
0.71
0.68
0.63
0.65


O
O
O
O
O
O
F
F
B
N
N
HB
BH
BH
HB
BH
HB
BH
HB
BH
BH
3
Si

B(CAR)$_3$(TES)


160.43
153.30
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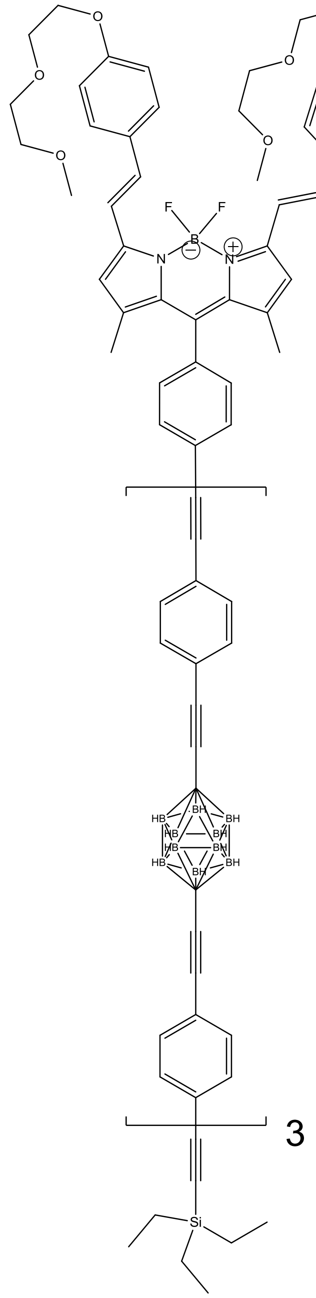
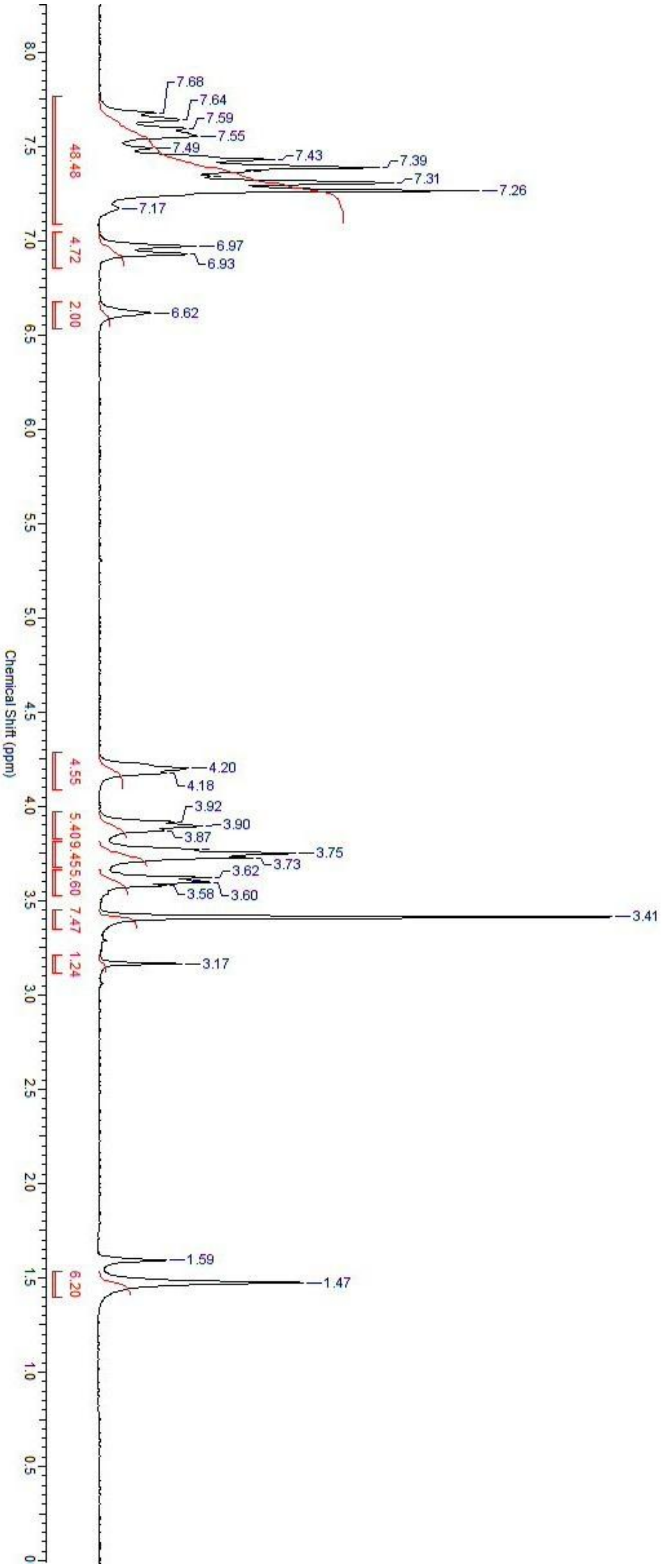
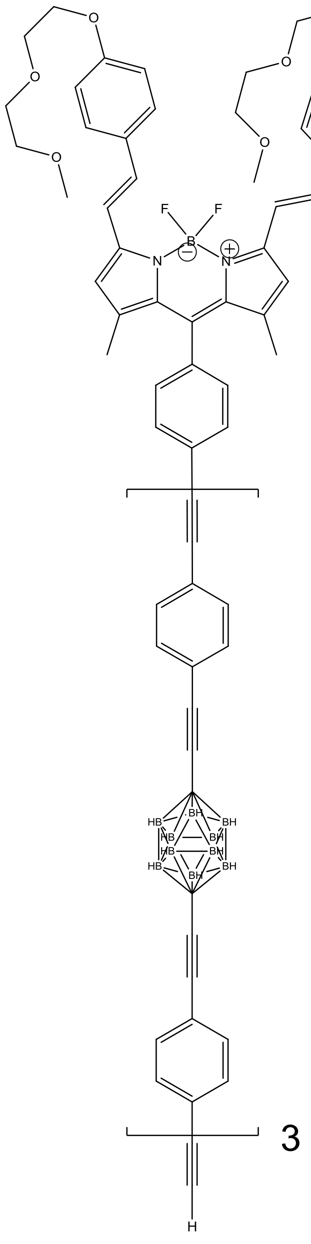
137.89
136.59
132.85
132.46
132.42
132.04
130.10
129.54
124.73
124.36
124.24
124.18
121.71
118.16
115.46
105.89
95.11
91.45
87.61
80.66
72.50
71.24
70.12
68.22
66.82
59.25
54.72
54.36
54.00
53.64
53.28
15.21
7.80
4.84
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

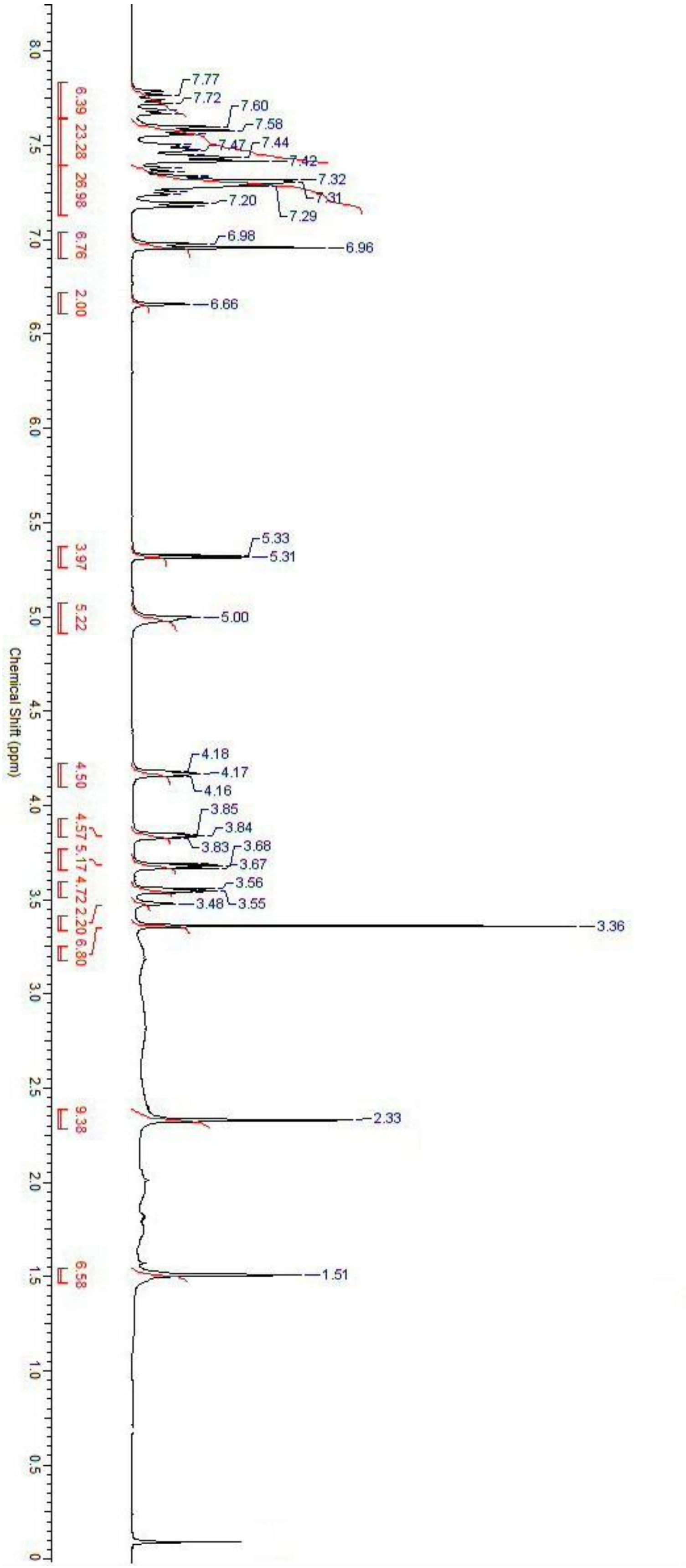

O
O
O
O
O
O
F
F
B
N
N
HB
BH
BH
3
Si

B(CAR)$_3$(H)


Chemical Shift (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
48.48
4.72
2.00
4.55
5.40
9.45
5.60
7.47
1.24
6.20
7.68
7.64
7.59
7.55
7.49
7.43
7.39
7.31
7.26
7.17
6.97
6.93
6.62
4.20
4.18
3.92
3.90
3.87
3.75
3.73
3.62
3.58
3.60
3.41
3.17
1.59
1.47


O
O
O
O
O
O
F
F
B
N
N
HB
BH
BH
3
H

B(CAR)$_3$DPP


Chemical Shift (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
6.39
23.28
26.98
6.76
2.00
3.97
5.22
4.50
4.57
5.17
4.72
2.20
6.80
9.38
6.58
7.77
7.72
7.60
7.58
7.47
7.44
7.42
7.32
7.31
7.20
7.29
6.98
6.96
6.66
5.33
5.31
5.00
4.18
4.17
4.16
3.85
3.84
3.83
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3.67
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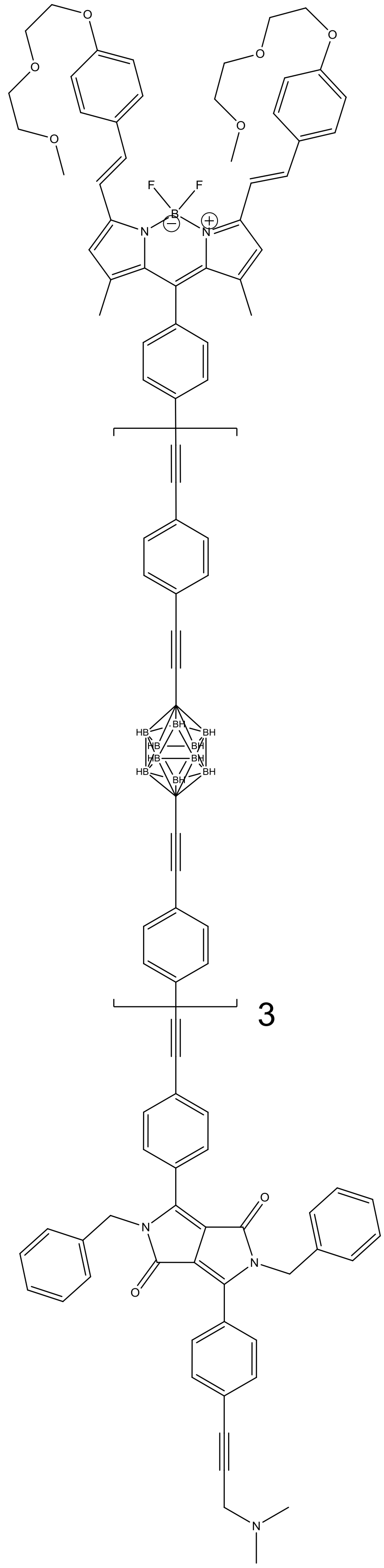
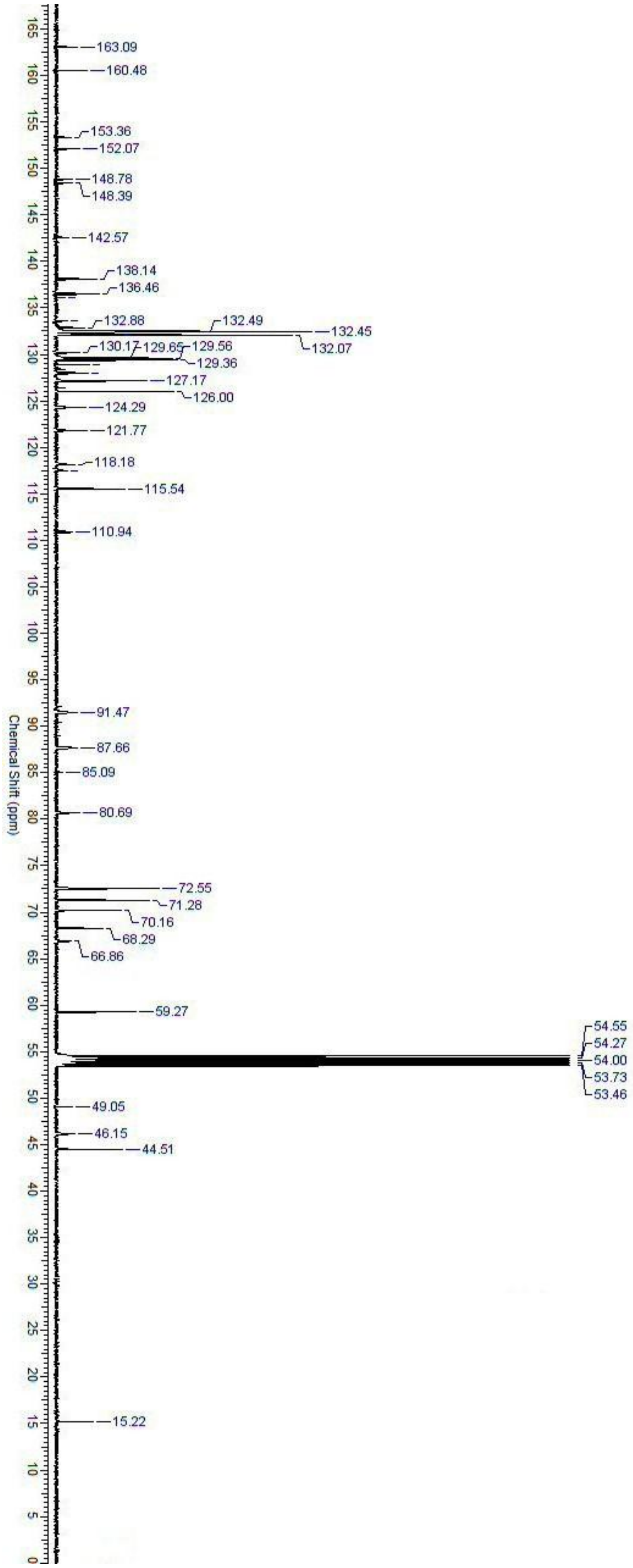
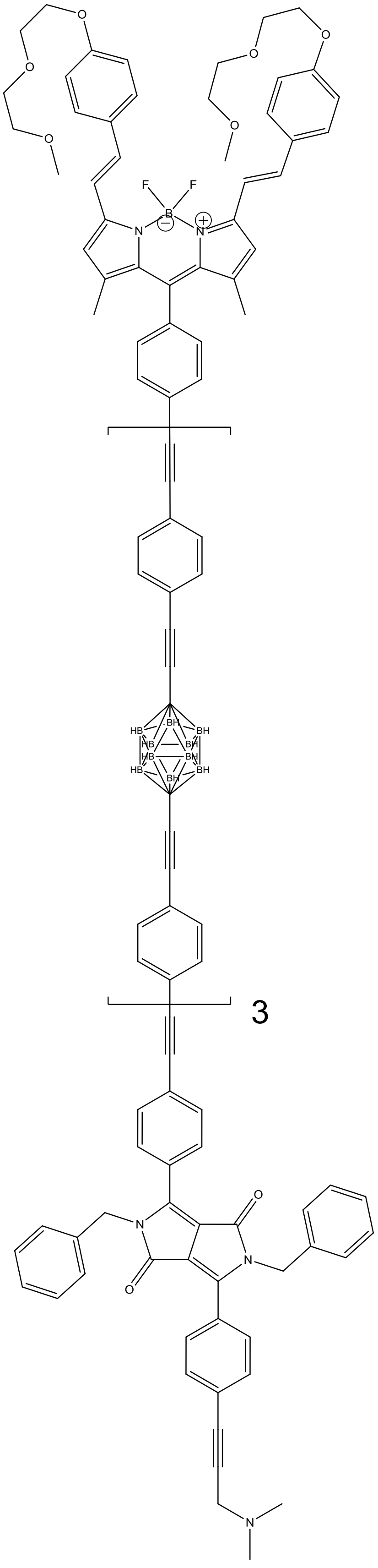
3.55
3.36
2.33
1.51

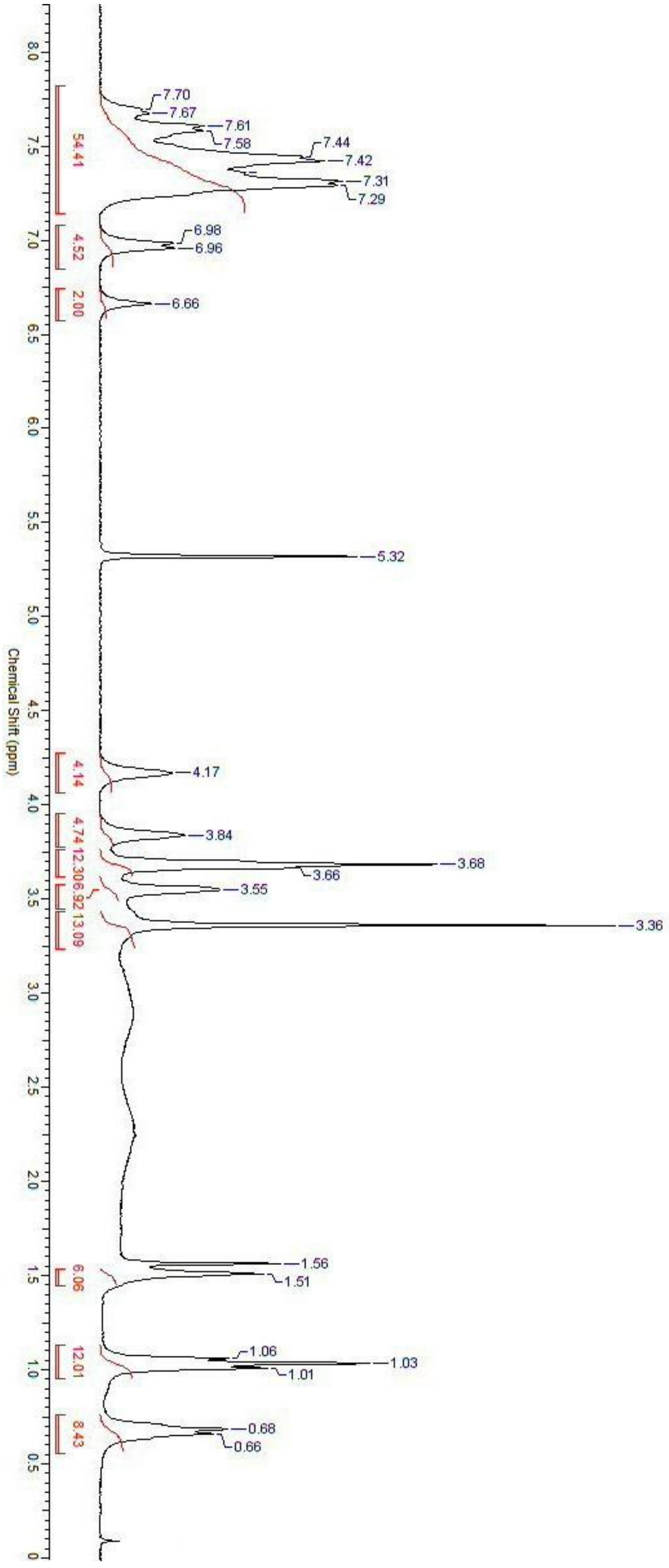

O
O
O
O
O
O
F
F
B
N
N
BH
HB
BH
HB
BH
HB
BH
HB
BH
BH
3
N
O
O
N
N

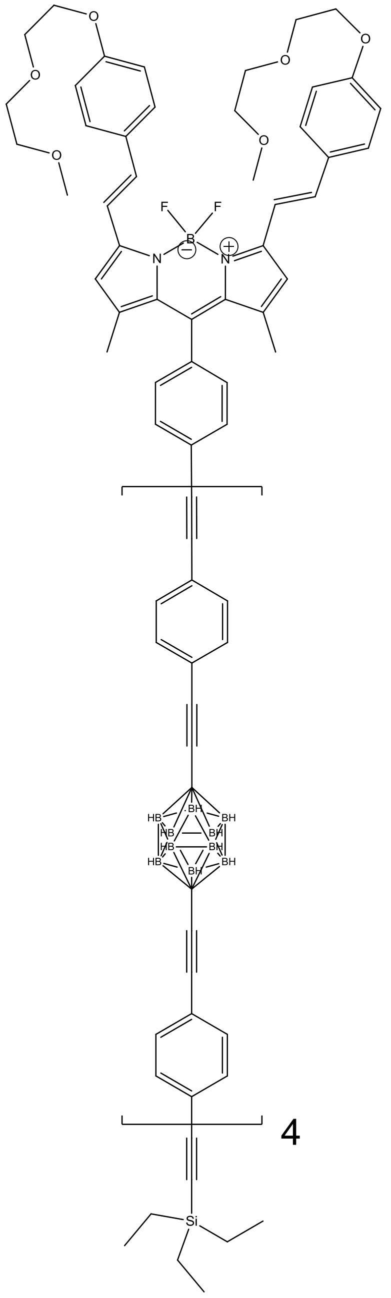
B(CAR)$_3$DPP


163.09
160.48
153.36
152.07
148.78
148.39
142.57
138.14
136.46
132.88
132.49
132.45
132.07
130.17
129.65
129.56
129.36
127.17
126.00
124.29
121.77
118.18
115.54
110.94
91.47
87.66
85.09
80.69
72.55
71.28
70.16
68.29
66.86
59.27
54.55
54.27
54.00
53.73
53.46
49.05
46.15
44.51
15.22
Chemical Shift (ppm)
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0

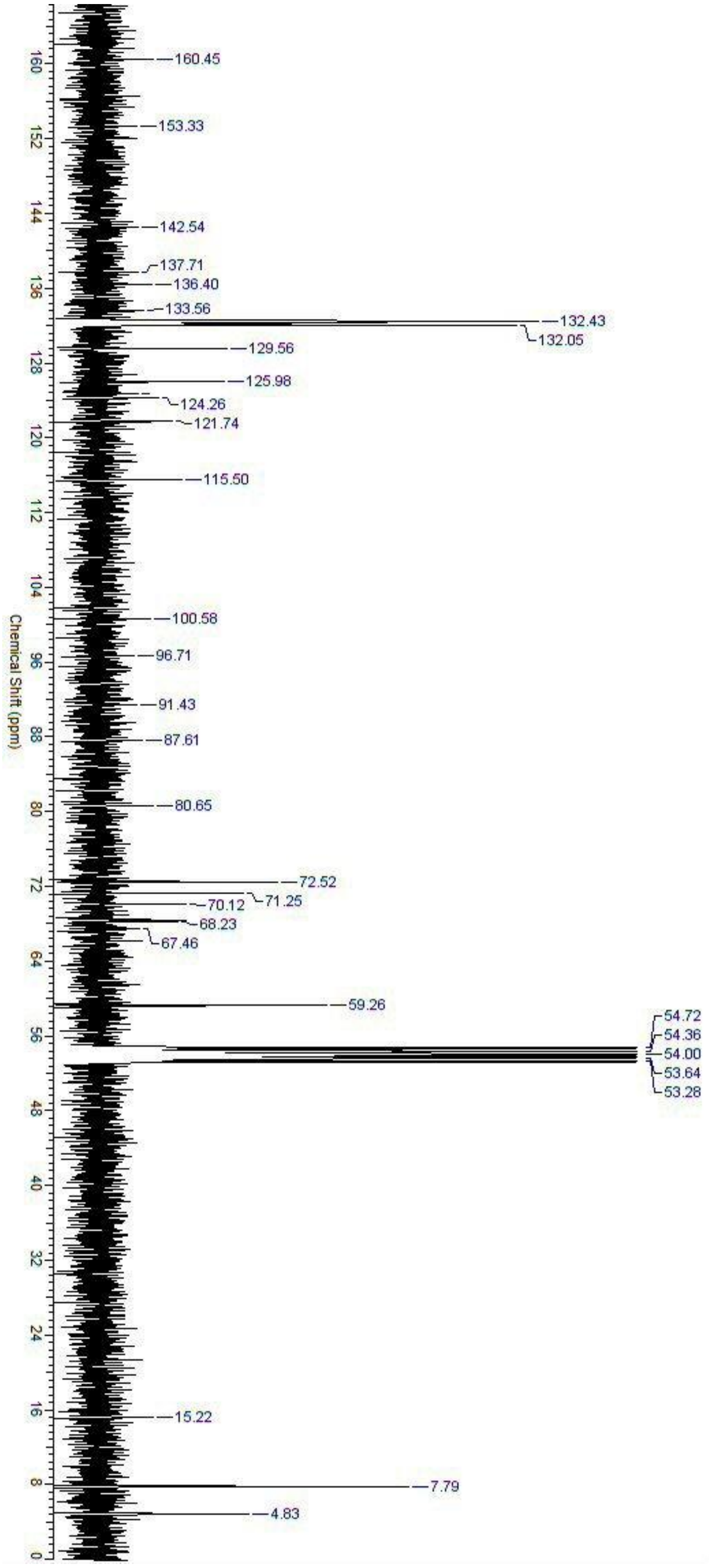

O
O
O
O
O
O
F
F
B
N
N
BH
HB
3
O
O
N
N
N

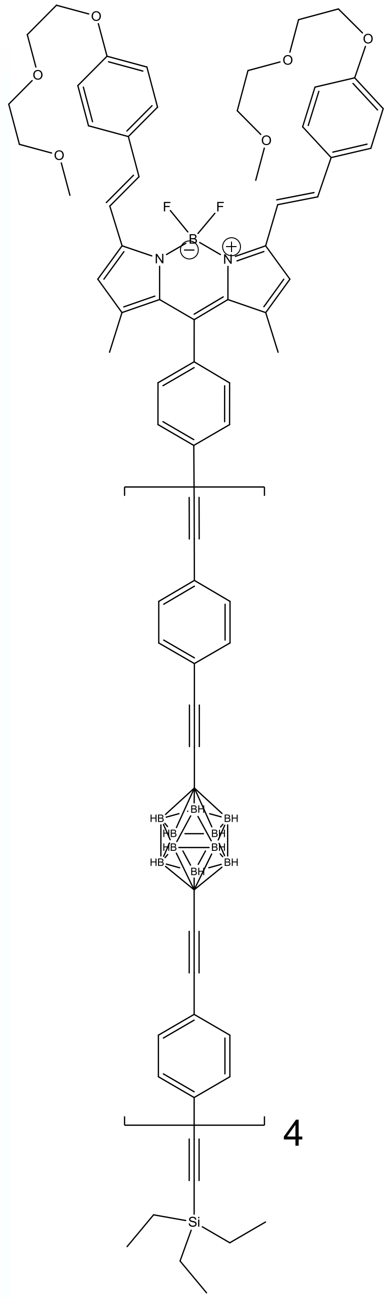
B(CAR)$_4$(TES)


Chemical Shift (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
54.41
4.52
2.00
4.14
4.74
12.30
6.92
13.09
6.06
12.01
8.43
7.70
7.67
7.61
7.58
7.44
7.42
7.31
7.29
6.98
6.96
6.66
5.32
4.17
3.84
3.68
3.66
3.55
3.36
1.56
1.51
1.06
1.03
1.01
0.68
0.66

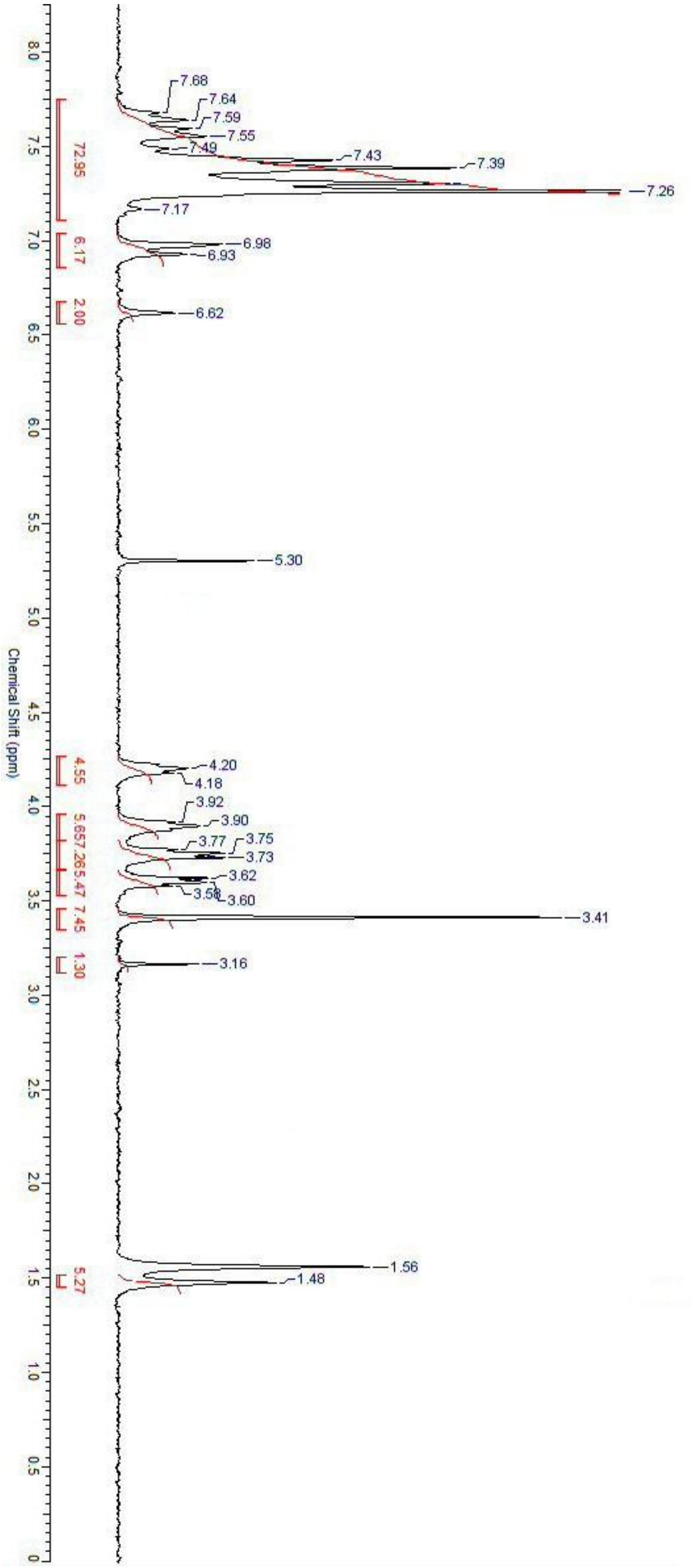

O
O
O
O
O
O
F
F
B
N
N
HB
BH
BH
4
Si

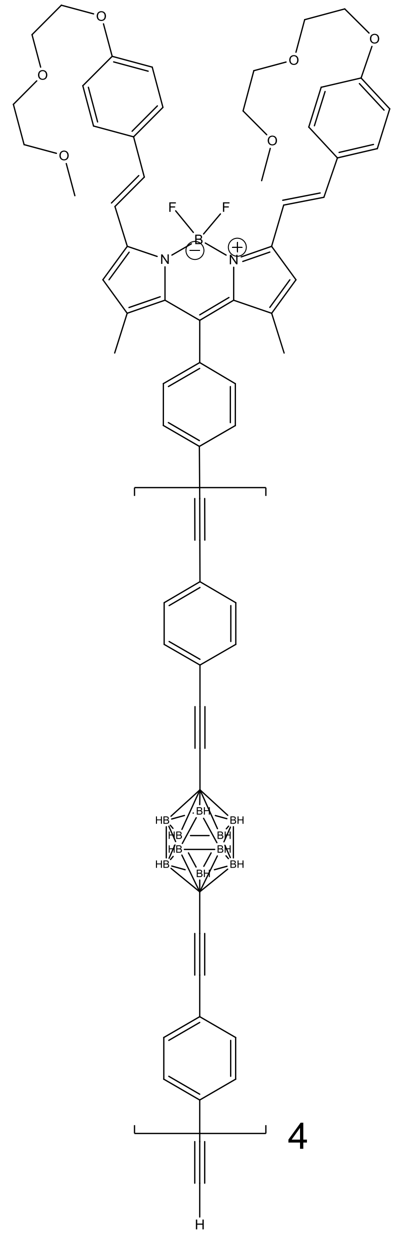
B(CAR)$_4$(TES)


160.45
153.33
142.54
137.71
136.40
133.56
132.43
132.05
129.56
125.98
124.26
121.74
115.50
100.58
96.71
91.43
87.61
80.65
72.52
71.25
70.12
68.23
67.46
59.26
54.72
54.36
54.00
53.64
53.28
15.22
7.79
4.83
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

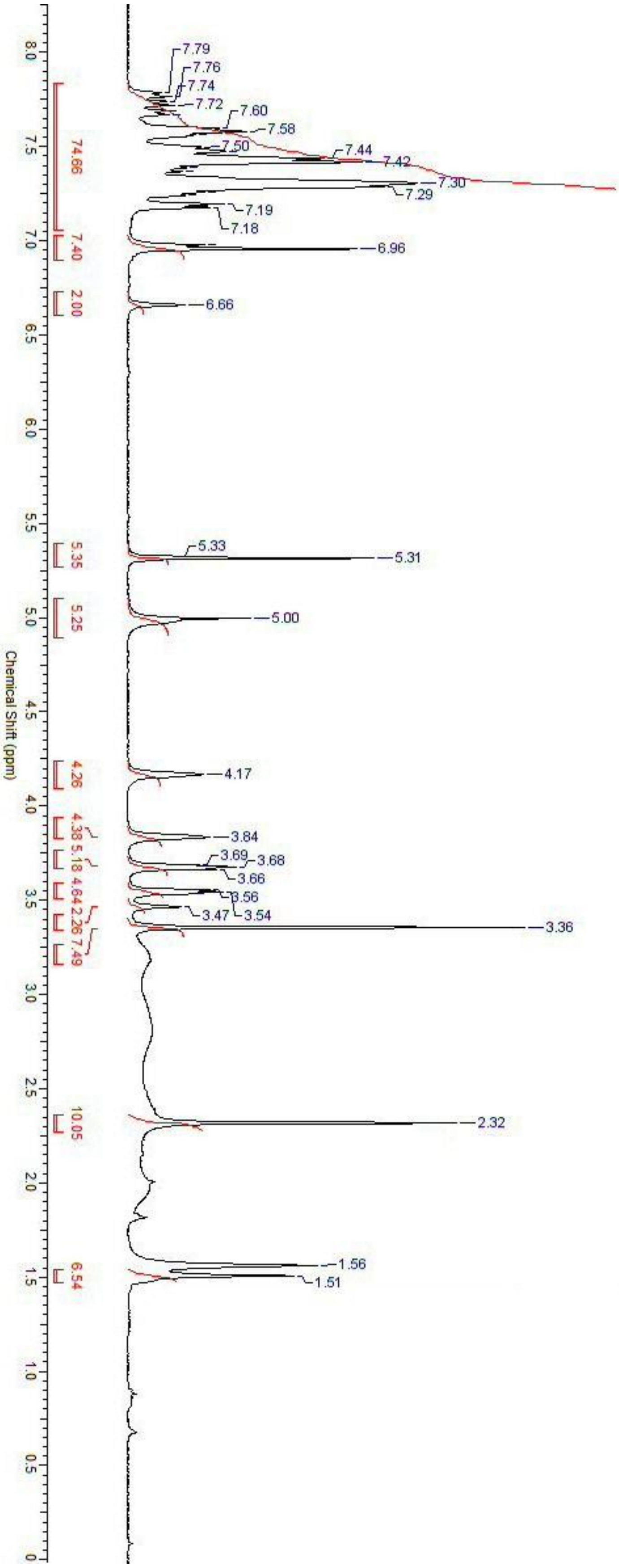

O
O
O
O
O
O
O
O
F
F
B
N
N
HB
BH
BH
HB
BH
HB
BH
HB
BH
BH
4
Si

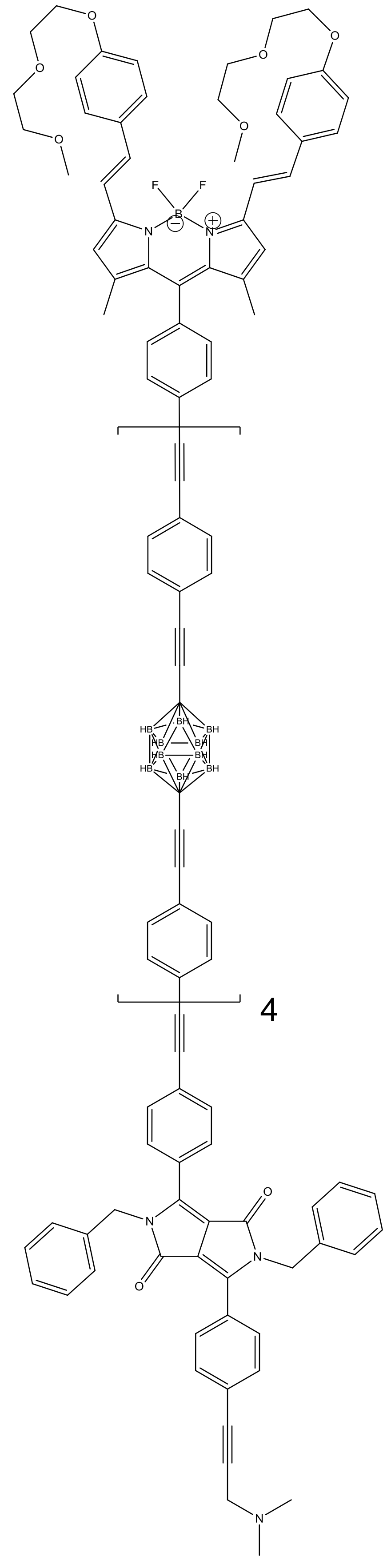
B(CAR)$_4$(H)


7.68
7.64
7.59
7.55
7.49
7.43
7.39
7.26
7.17
6.98
6.93
6.62
5.30
4.20
4.18
3.92
3.90
3.77
3.75
3.73
3.62
3.58
3.60
3.41
3.16
1.56
1.48
72.95
6.17
2.00
4.55
5.65
7.26
5.47
7.45
1.30
5.27
Chemical Shift (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

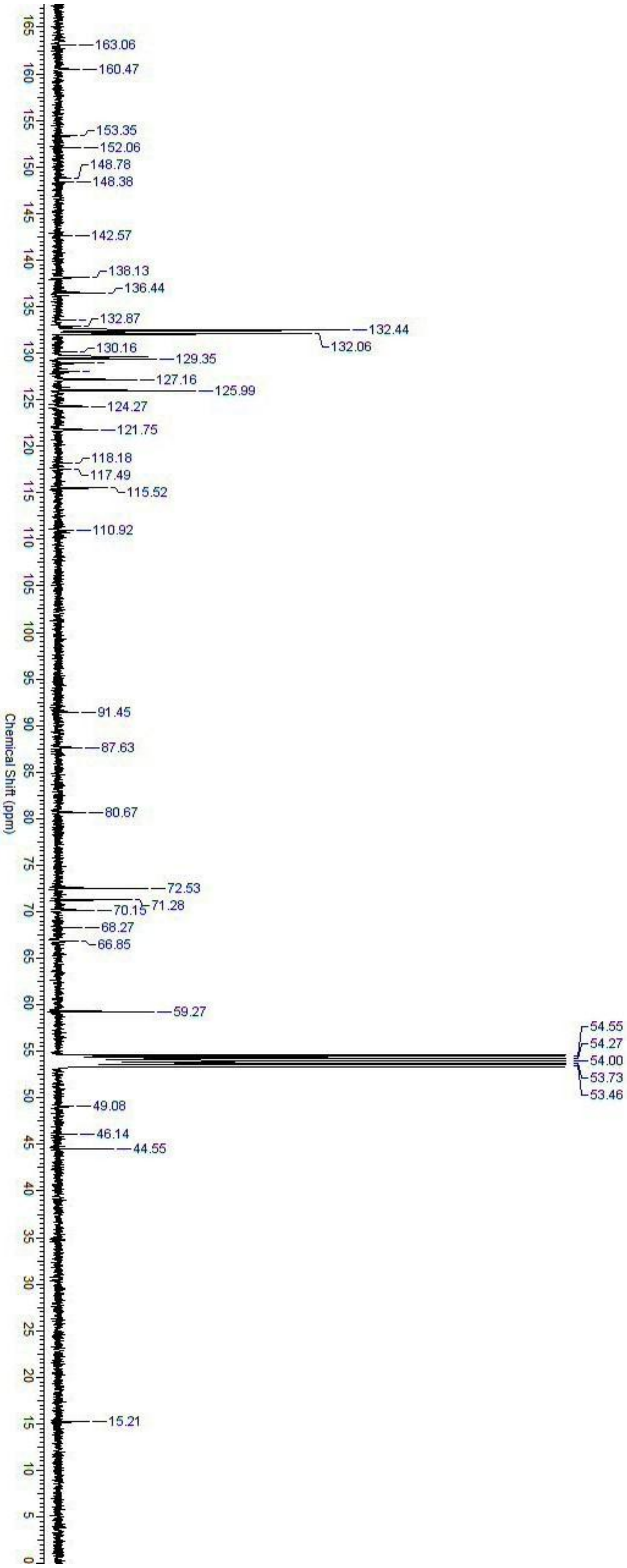

O
O
O
O
O
O
F
F
B
N
N
HB
BH
BH
HB
BH
HB
BH
BH
BH
4
H

B(CAR)$_4$DPP


7.79
7.76
7.74
7.72
7.60
7.58
7.50
7.44
7.42
7.30
7.29
7.19
7.18
6.96
6.66
5.33
5.31
5.00
4.17
3.84
3.69
3.68
3.66
3.56
3.47
3.54
3.36
2.32
1.56
1.51
74.66
7.40
2.00
5.35
5.25
4.26
4.38
5.18
4.64
2.26
7.49
10.05
6.54
Chemical Shift (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0


O
F
F
B
N
N
HB
BH
4
N
O
N

B(CAR)$_4$DPP


163.06
160.47
153.35
152.06
148.78
148.38
142.57
138.13
136.44
132.87
132.44
132.06
130.16
129.35
127.16
125.99
124.27
121.75
118.18
117.49
115.52
110.92
91.45
87.63
80.67
72.53
71.28
70.15
68.27
66.85
59.27
54.55
54.27
54.00
53.73
53.46
49.08
46.14
44.55
15.21
Chemical Shift (ppm)
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
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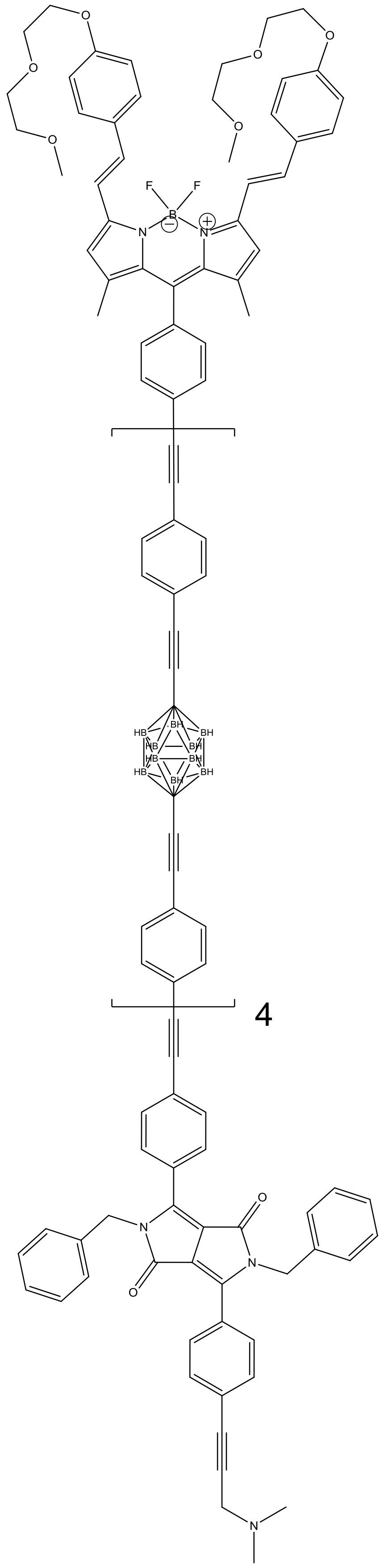
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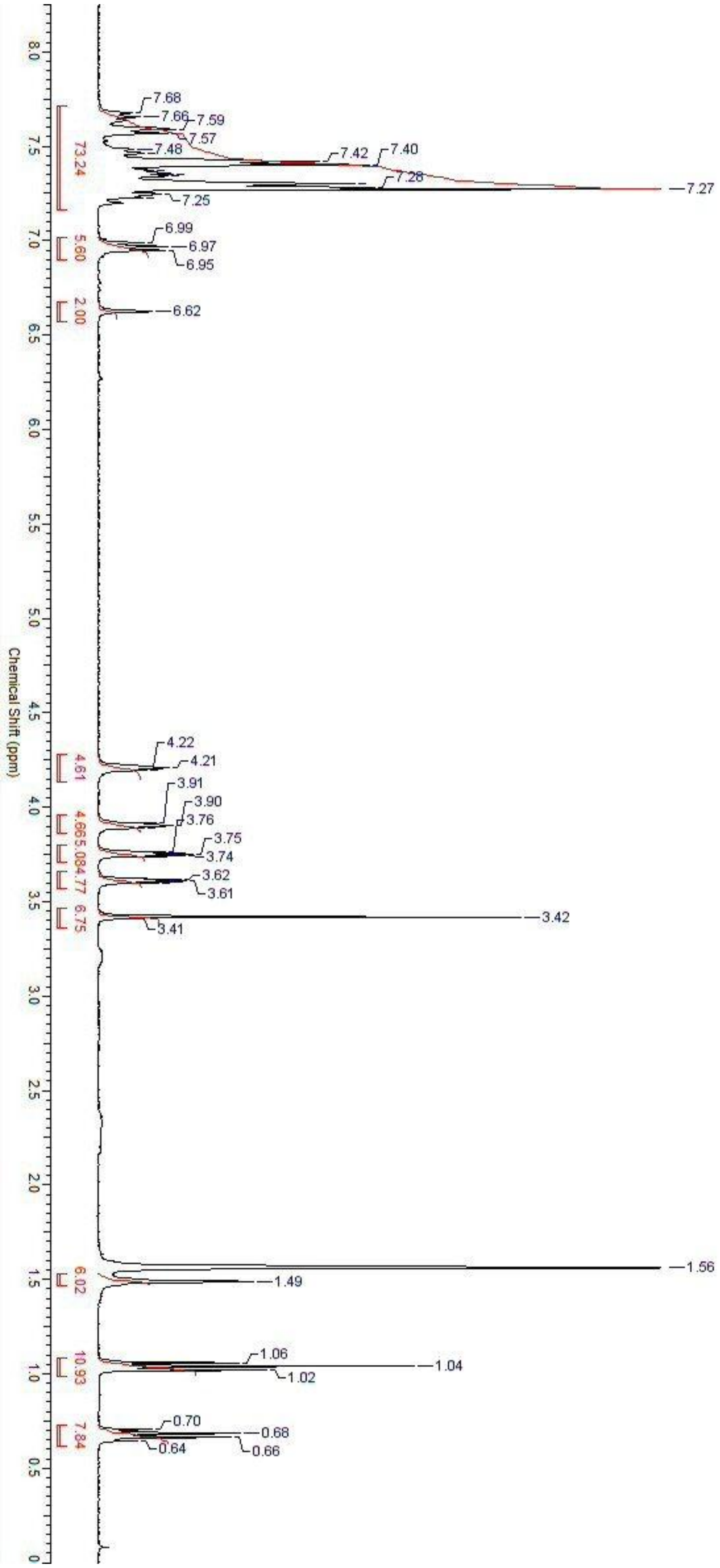
N
4
HB
BH

B(CAR)$_5$(TES)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2.00
4.61
4.66
5.08
4.77
6.75
6.02
10.93
7.84
7.68
7.66
7.59
7.57
7.48
7.42
7.40
7.28
7.27
7.25
6.99
6.97
6.95
6.62
4.22
4.21
3.91
3.90
3.76
3.75
3.74
3.62
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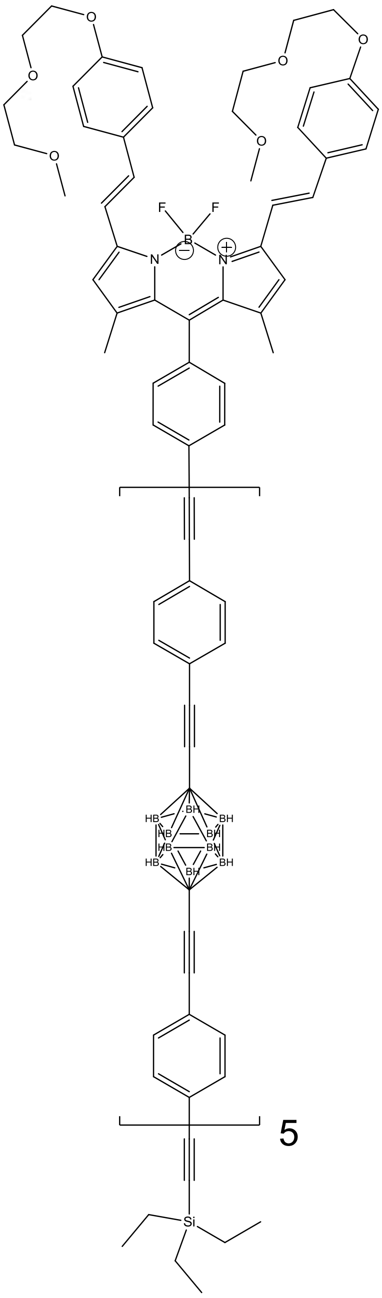
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HB
BH
Si
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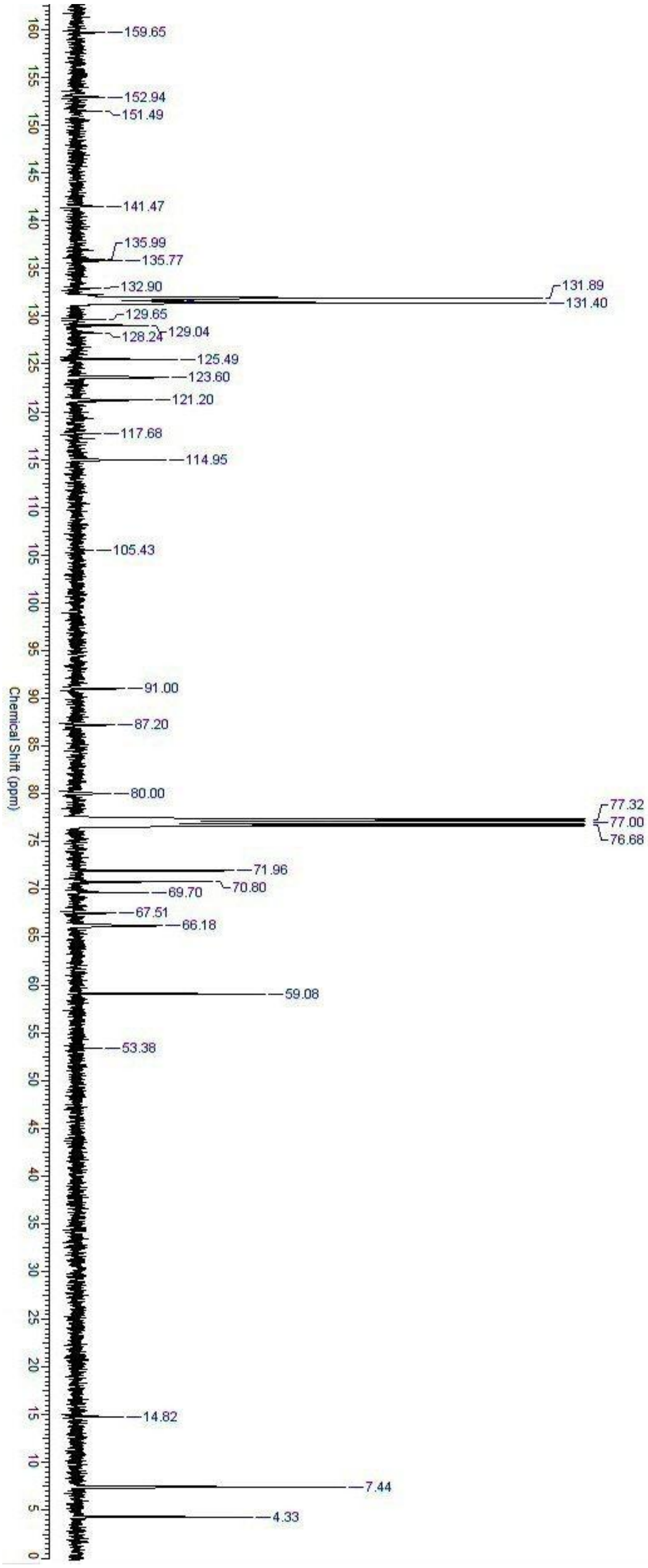
B(CAR)$_5$(TES)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123.60
121.20
117.68
114.95
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91.00
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4.33
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150
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140
135
130
125
120
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110
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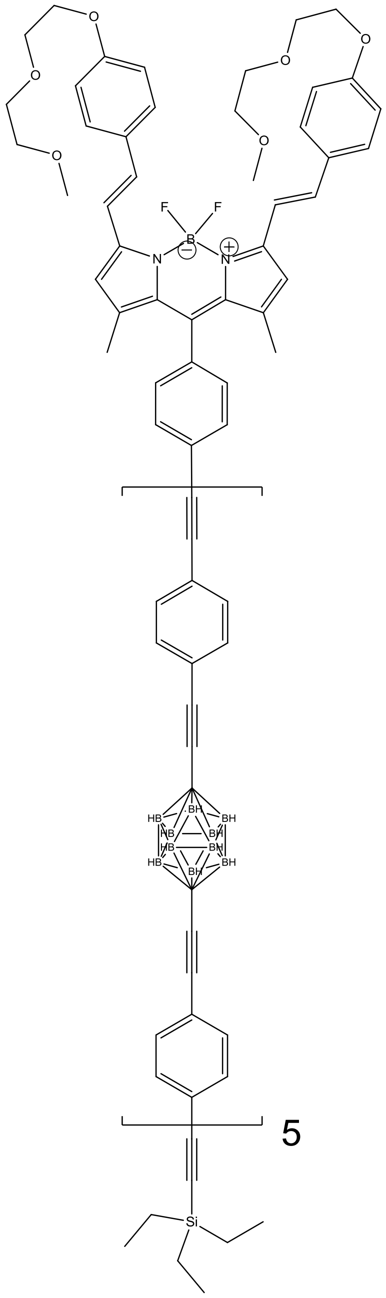
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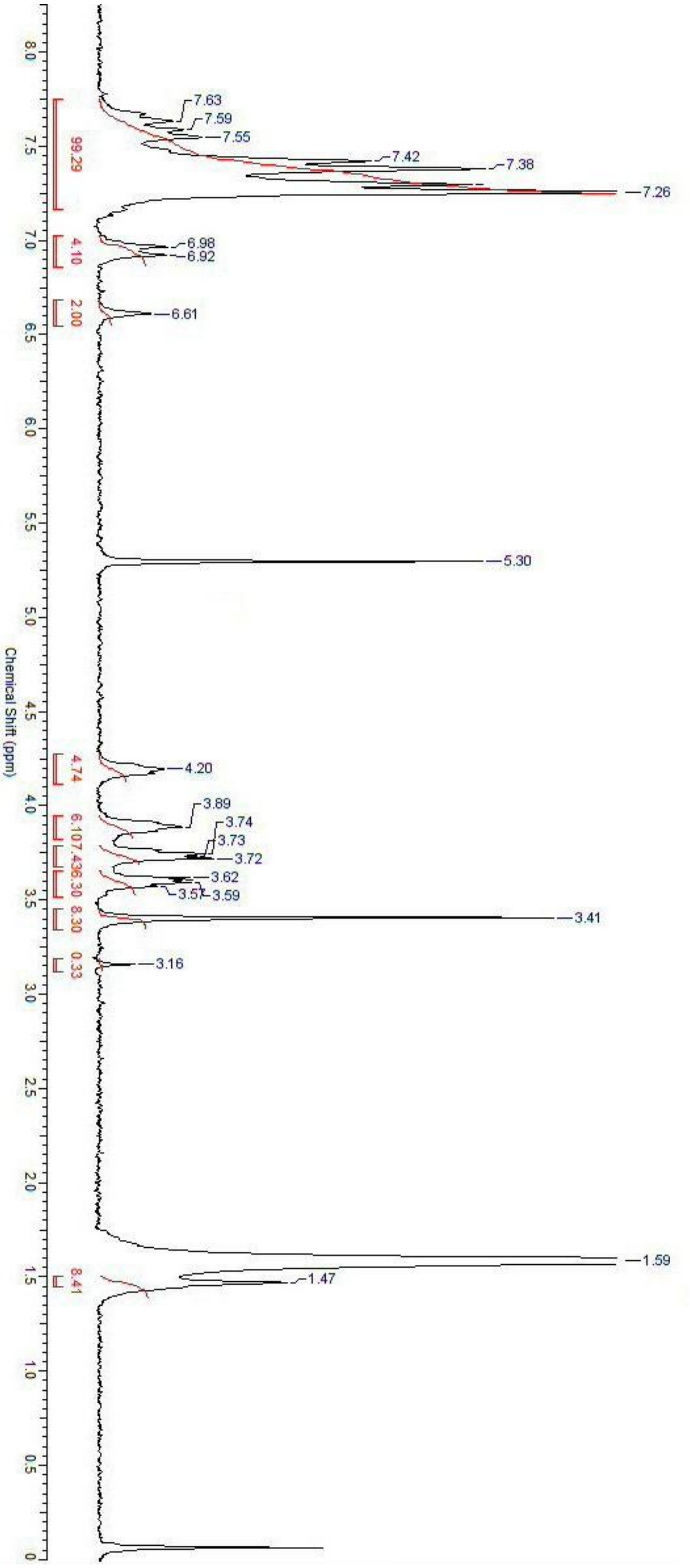
BH
5
Si

B(CAR)$_5$(H)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3.62
3.57
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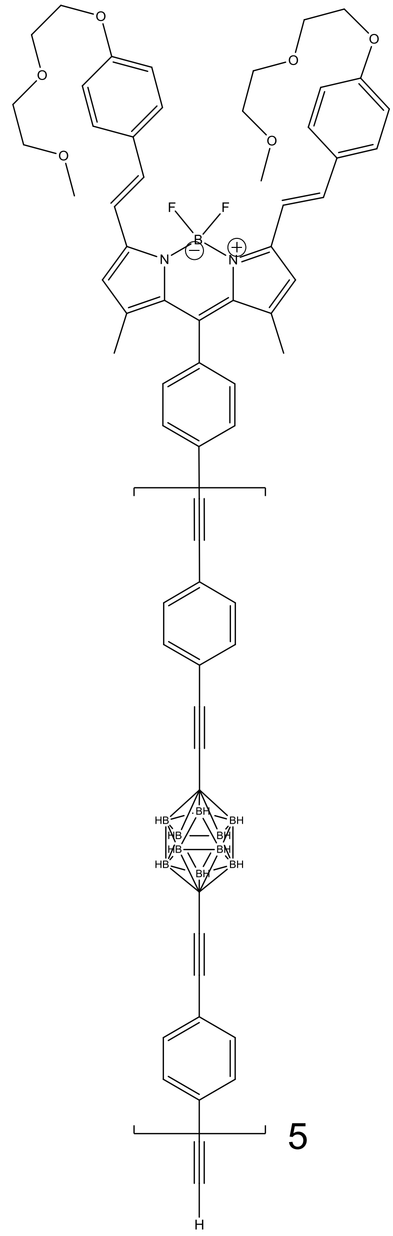
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BH
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HB
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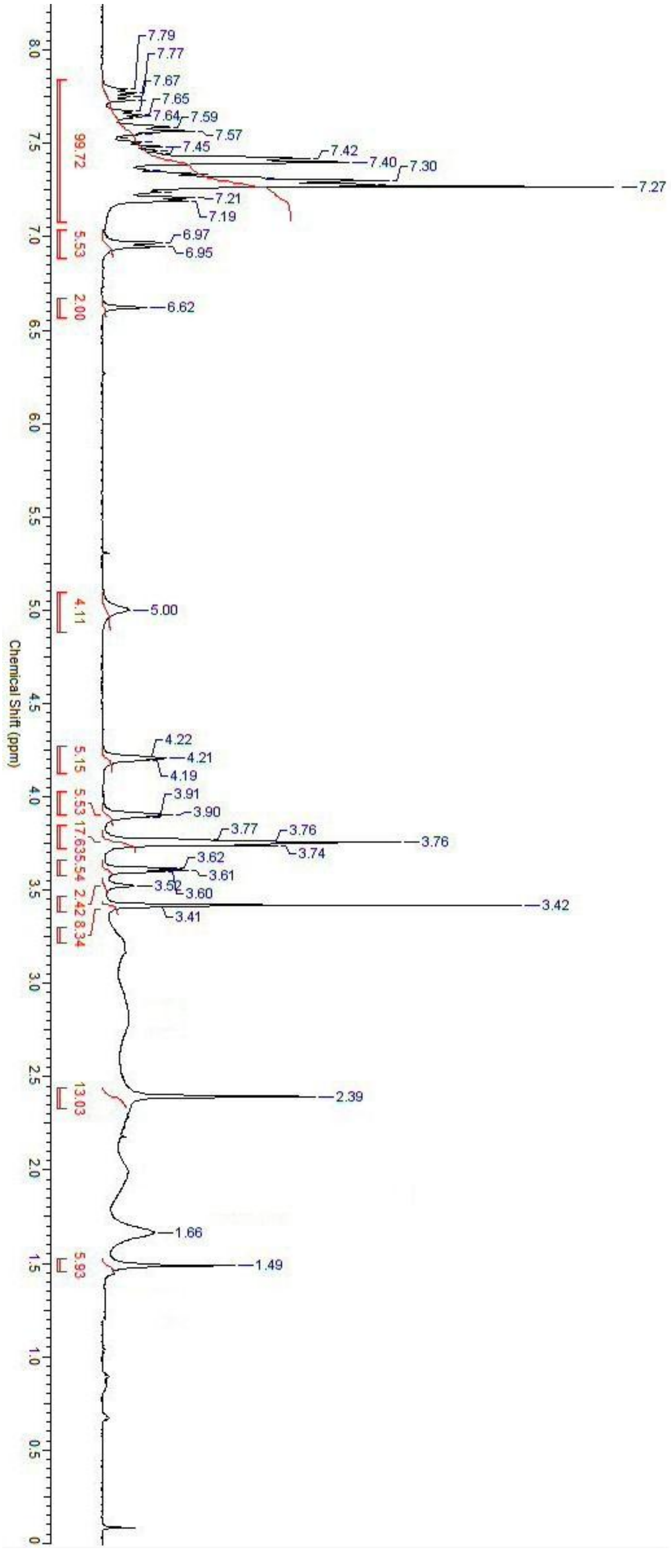
BH
5
H

B(CAR)$_5$DPP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1.0
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2.00
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5.53
17.63
5.54
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13.03
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3.90
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3.41
2.39
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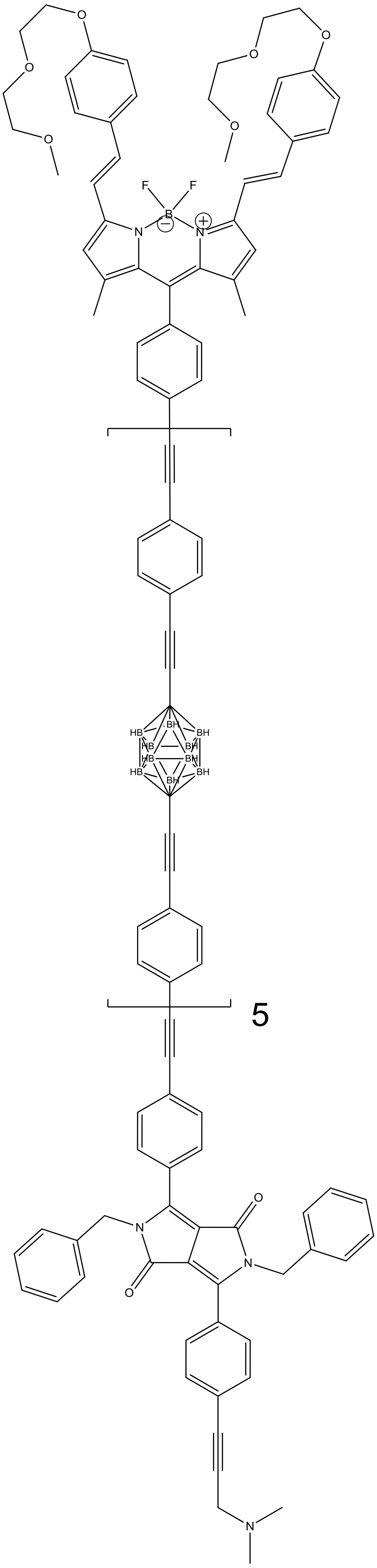
1.49


O
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B
N
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HB
BH
BH
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N
N
O
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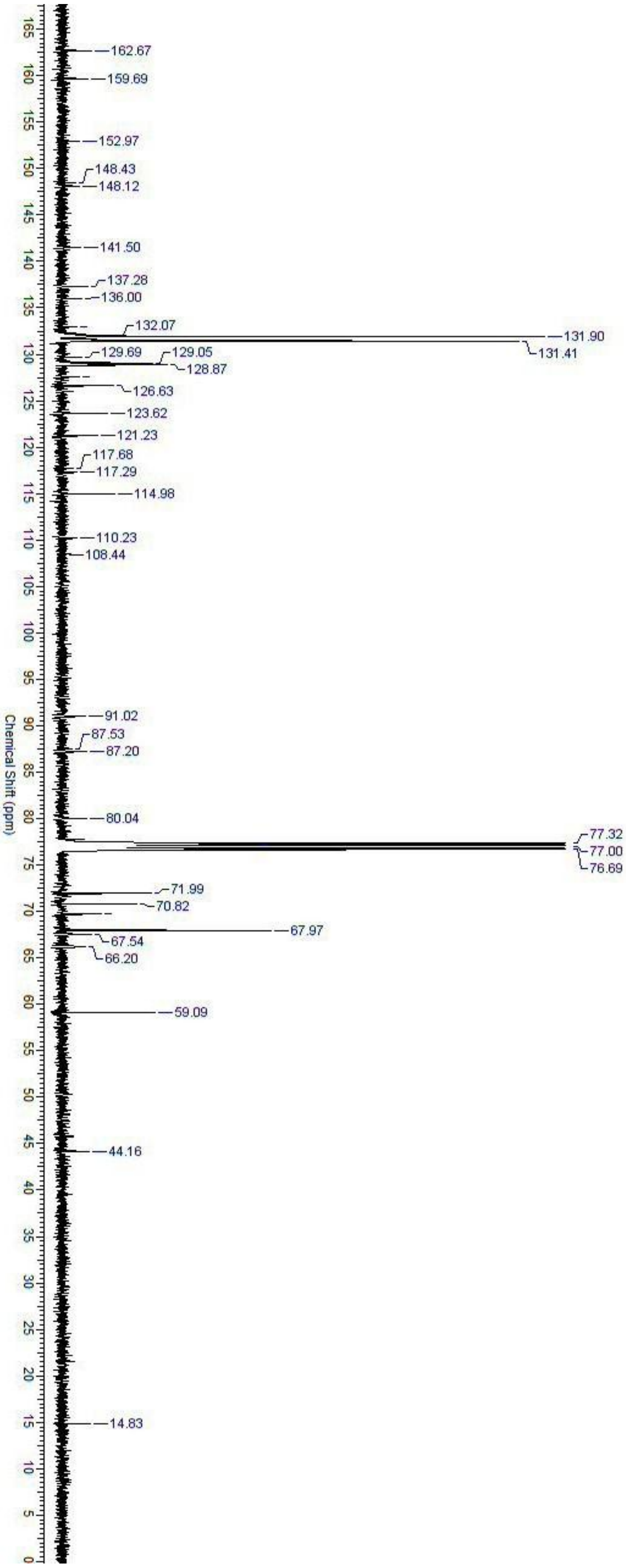
N

B(CAR)$_5$DPP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121.23
117.68
117.29
114.98
110.23
108.44
91.02
87.53
87.20
80.04
77.32
77.00
76.69
71.99
70.82
67.97
67.54
66.20
59.09
44.16
14.83
165
160
155
150
145
140
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130
125
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110
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100
95
90
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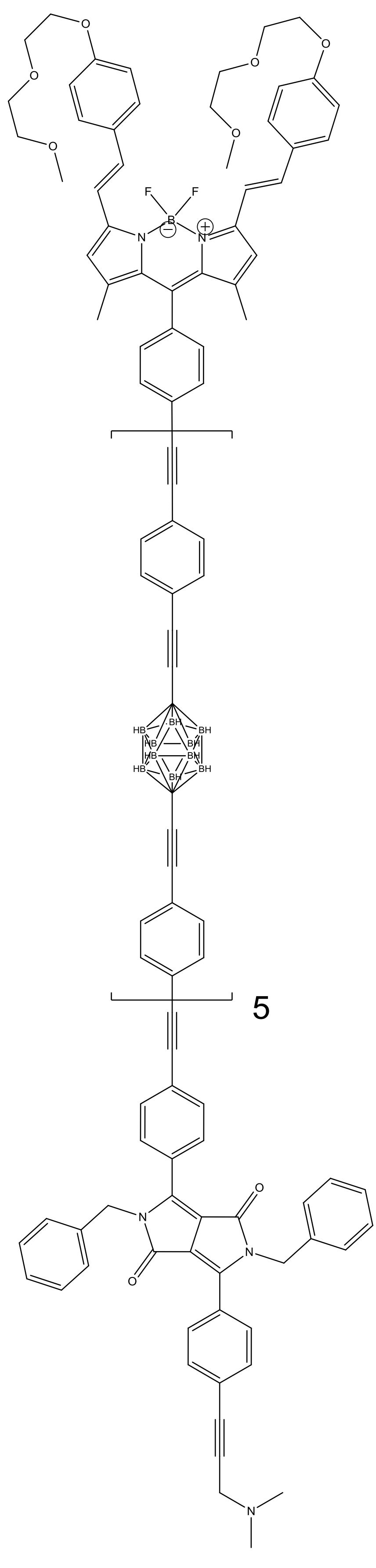
Chemical Shift (ppm)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F
B
N
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BH
HB
5
O
O
N
N
N

Extended dipole approxamation

The calculations relating to molecular length were repeated using the extended dipole method introduced by Kuhn in place of the conventional IDA. This particular approach is less problematic in terms of defining the center of the transition dipole moment vector. Instead, the transition dipole moment resident on the donor (μ_D), measured by absorption spectroscopy to be 4.56 D, is associated with a characteristic length (l_D = 7.14 Å), measured along the dipole vector. On the basis of Equation S1, the electronic charges at the extremities of this vector (q_D = ±0.64 D/Å) can be assigned. The same operation can be performed for the acceptor (μ_A = 8.06 D; l_A = 10.17 Å) to give q_A = ±0.79 D/Å, after due allowance for the degeneracy. This gives a set of six charges, two associated with the donor and four characteristic of the acceptor, each assigned to a particular atom whose location is known from molecular modelling. The electronic coupling matrix element (V_{XTD}) can now be calculated by summation of the eight electrostatic-type interactions using the computed separation distances (R_{DA}) between pairs of charges on donor and acceptor (Equation S2). The derived V_{XTD} can be refined for the effects of Brownian motion by allowing the donor to rotate around the molecular axis but fixing the position of the acceptor.

$$\mu_D = q_D . l_D \qquad \text{(S1)}$$

$$V_{XTD} = \frac{q_D q_A}{4\pi\varepsilon_0} \sum \left(\frac{1}{R_{DA}} \right) \qquad \text{(S2)}$$

It is difficult, in this case, to be precise about the dipole length associated with the acceptor but this particular value can be adjusted by matching the experimental and calculated coupling matrix elements for n=1. Perfect agreement is reached when the length of the acceptor-based transition dipole moment vector is set equal to 9.43 Å. These various parameters are now fixed and the calculation repeated for the longer analogues in order to find the effective repeat length of the carborane-based connector. At 77 K, the extended dipole approach leads to an effective repeat length of 17.6 ± 0.9 Å across the series.

Pressure effect on spectroscopic properties of the control dyes

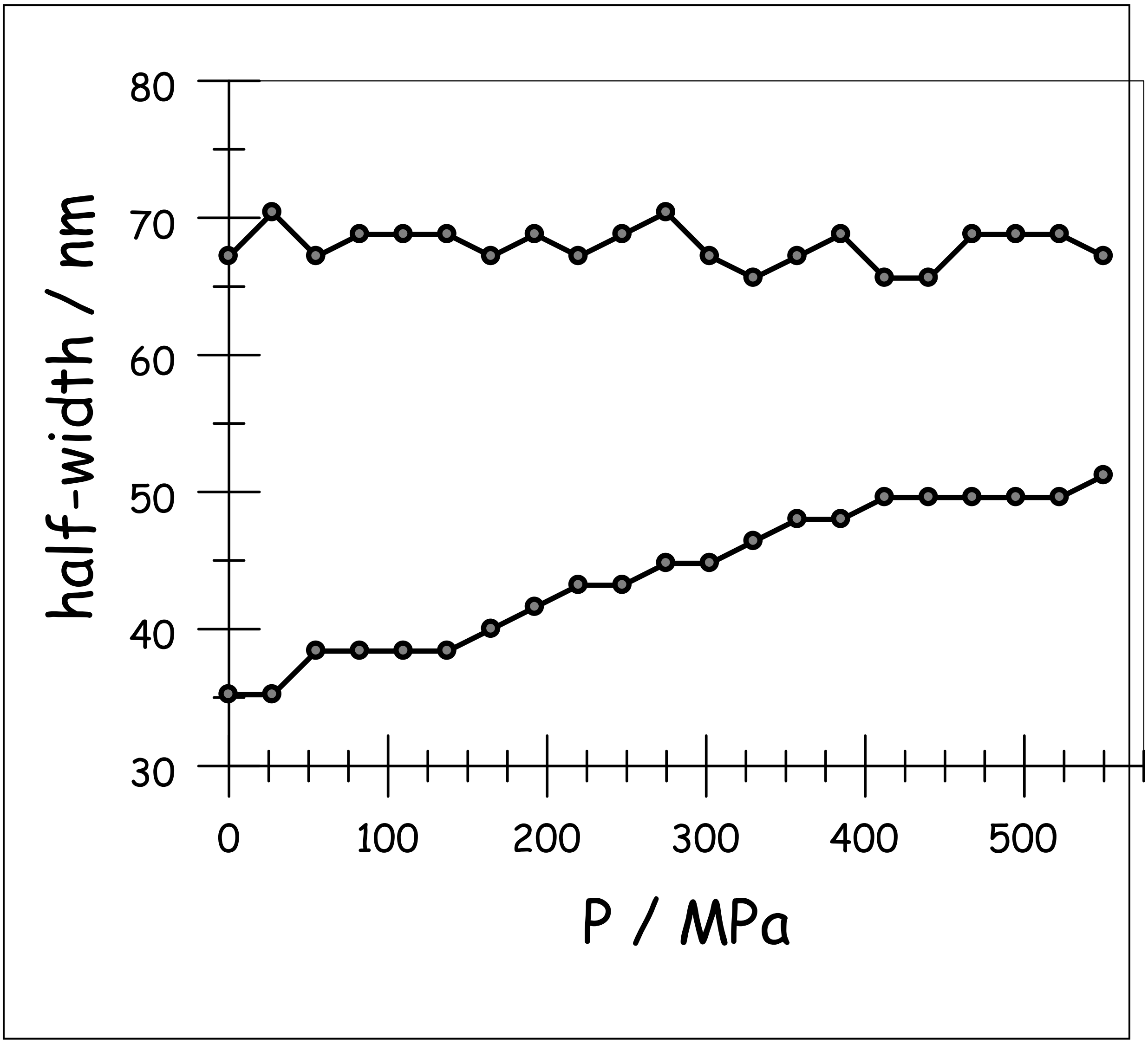

Figure S1 Effect of applied pressure on the deconvoluted band half-widths measured in MTHF at 20 ^{0}C. The data refer to N=5, the upper trace being for the DPP subunit and the lower trace being for B.

Table S1. Effect of applied pressure on the fluorescence spectral half-width recorded for the B subunit in the molecular dyads in MTHF at 20 ^{0}C.

Pressure / MPa	N=1	N=2	N=3	N=4	N=5
0	33.6	38.4	38.4	44.8	35.2
27.5	33.6	38.4	38.4	48	35.2
55	33.6	38.4	40	49.6	38.4
82.5	33.6	36.8	40	51.2	38.4
110	33.6	38.4	41.6	51.2	38.4
137.5	33.6	38.4	43.2	51.2	38.4
165	33.6	36.8	43.2	54.4	40
192.5	33.6	38.4	44.8	57.6	41.6
220	35.2	38.4	44.8	54.4	43.2
247.5	33.6	38.4	46.4	57.6	43.2
275	35.2	38.4	48	59.2	44.8
302.5	33.6	38.4	48	60.8	44.8
330	33.6	38.4	48	51.2	46.4
357.5	35.2	38.4	49.6	51.2	48
385	33.6	38.4	51.2	52.8	48
412.5	33.6	40	51.2	54.4	49.6
440	35.2	38.4	52.8	54.4	49.6
467.5	33.6	40	52.8	56	49.6
495	33.6	40	52.8	54.4	49.6
522.5	35.2	38.4	54.4	54.4	49.6
550	35.2	40	54.4	57.6	51.2

Table S2. Effect of applied pressure on the fluorescence spectral half-width recorded for the DPP subunit in the molecular dyads in MTHF at 20 ^{0}C.

Pressure / MPa	N=2	N=3	N=4	N=5
0	76.8	72	72	67.2
27.5	78.4	73.6	73.6	70.4
55	76.8	72	72	67.2
82.5	73.6	70.4	70.4	68.8
110	73.6	70.4	70.4	68.8
137.5	75.2	72	72	68.8
165	73.6	70.4	70.4	67.2
192.5	73.6	70.4	72	68.8
220	72	70.4	72	67.2
247.5	72	70.4	70.4	68.8
275	73.6	68.8	72	70.4
302.5	72	70.4	70.4	67.2
330	72	72	73.6	65.6
357.5	73.6	70.4	72	67.2
385	72	70.4	72	68.8
412.5	73.6	70.4	73.6	65.6
440	70.4	70.4	72	65.6
467.5	72	72	73.6	68.8
495	73.6	70.4	72	68.8
522.5	73.6	68.8	72	68.8
550	73.6	70.4	72	67.2

Temperature effect on the probability of electronic energy transfer measured in MTHF

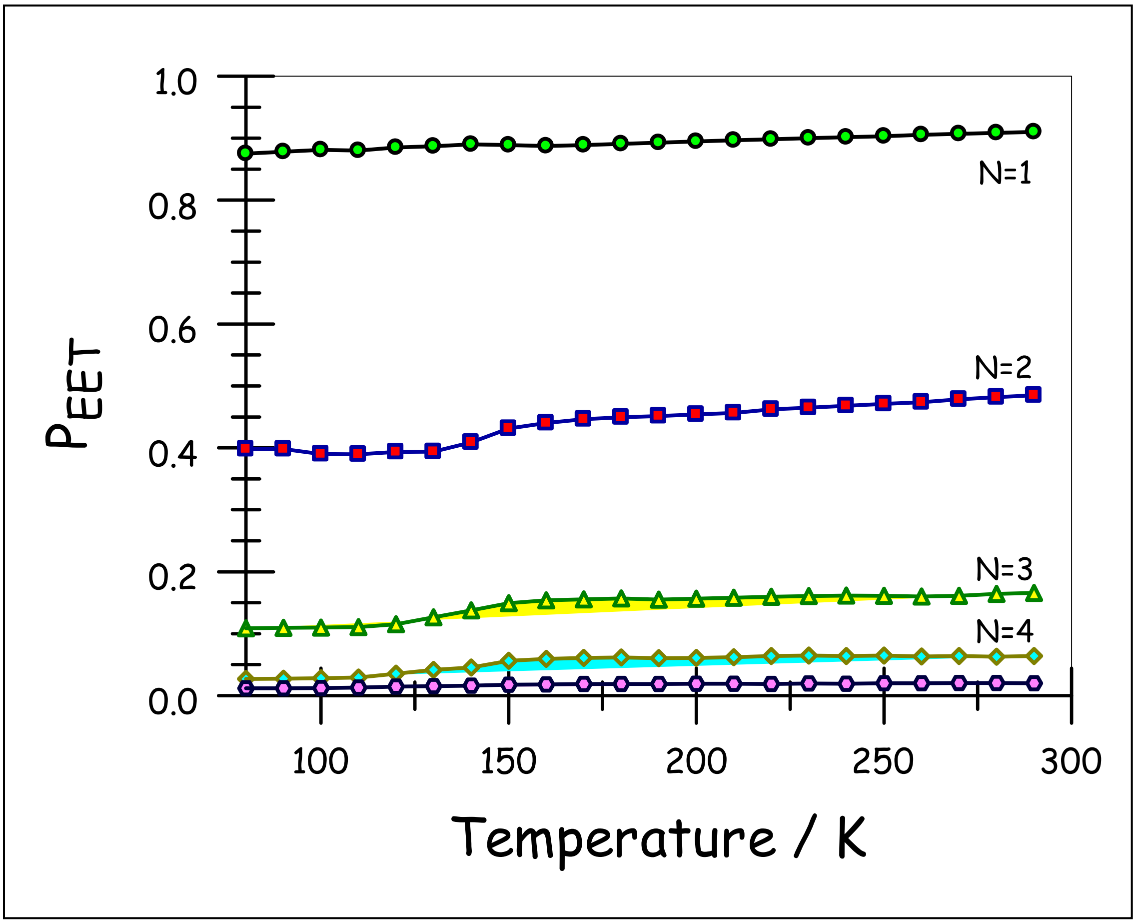

Figure S2. Effect of temperature on the probability of EET across the molecular dyad in MTHF as measured from the fluorescence ratio. The data are collected in Table S3.

Table S3. Effect of temperature on the probability of ETT (P_{EET}) measured by the fluorescence ratio method in MTHF.

T / K	N=1	N=2	N=3	N=4	N=5
80	0.875	0.398	0.109	0.027	0.0120
90	0.878	0.398	0.110	0.0275	0.0119
100	0.881	0.390	0.110	0.028	0.0125
110	0.880	0.390	0.111	0.0295	0.0132
120	0.885	0.394	0.112	0.0355	0.0146
130	0.887	0.394	0.123	0.0415	0.0155
140	0.89	0.409	0.138	0.0455	0.0163
150	0.889	0.431	0.149	0.0562	0.0178
160	0.887	0.440	0.154	0.0593	0.0181
170	0.889	0.446	0.156	0.0610	0.0189
180	0.891	0.450	0.157	0.0617	0.0190
190	0.893	0.451	0.155	0.0606	0.0191
200	0.895	0.454	0.156	0.0608	0.0193
210	0.897	0.456	0.158	0.0622	0.0192
220	0.898	0.462	0.160	0.0639	0.0191
230	0.900	0.465	0.161	0.0649	0.0195
240	0.902	0.469	0.162	0.0650	0.0195
250	0.903	0.471	0.161	0.0649	0.0201
260	0.905	0.474	0.160	0.0631	0.0200
270	0.907	0.478	0.161	0.0641	0.0204
280	0.909	0.482	0.164	0.0628	0.0206
290	0.910	0.485	0.166	0.0640	0.0201

Calculation of the transition dipole moments in MTHF

The transition dipole moments for donor and acceptor in dilute MTHF solution were calculated from Equation S3. Molar absorption coefficients (ε) were measured by conventional methods, taking three separate averages and ensuring complete dissolution of the sample by mild sonication. The spectra were reduced (ε/ν) and converted from wavelength (λ) to wavenumber (ν) before integration. The integral was taken over the entire S_0-S_1 envelope, including vibrational satellites. The solvent refractive index (n) was measured with an Abbé refractometer at atmospheric pressure while the solvent screening factor, s, is explained in the text. Remaining terms in Equation S3 refer to Avogadro’s constant (N_A), the speed of light (c), reduced Plancks constant (□) and the permittivity of free space (ε). Applied pressure causes only a small perturbation of the derived values, partly because of compensation effects, and this was taken into account during the subsequent calculations.

$$\frac{\left|\mu_D\right|^2}{4\pi\varepsilon_0} = \left(\frac{3000\ln 10\hbar c}{8\pi^3 N_A}\right)\left(\frac{n}{s^2}\right)\int\left(\frac{\varepsilon}{\nu}\right)d\nu \qquad \text{(S3)}$$