Fragment Parameters for the Calibration of Molecular Weights of Rod-Like Oligomers/Polymers by Gel Permeation Chromatography

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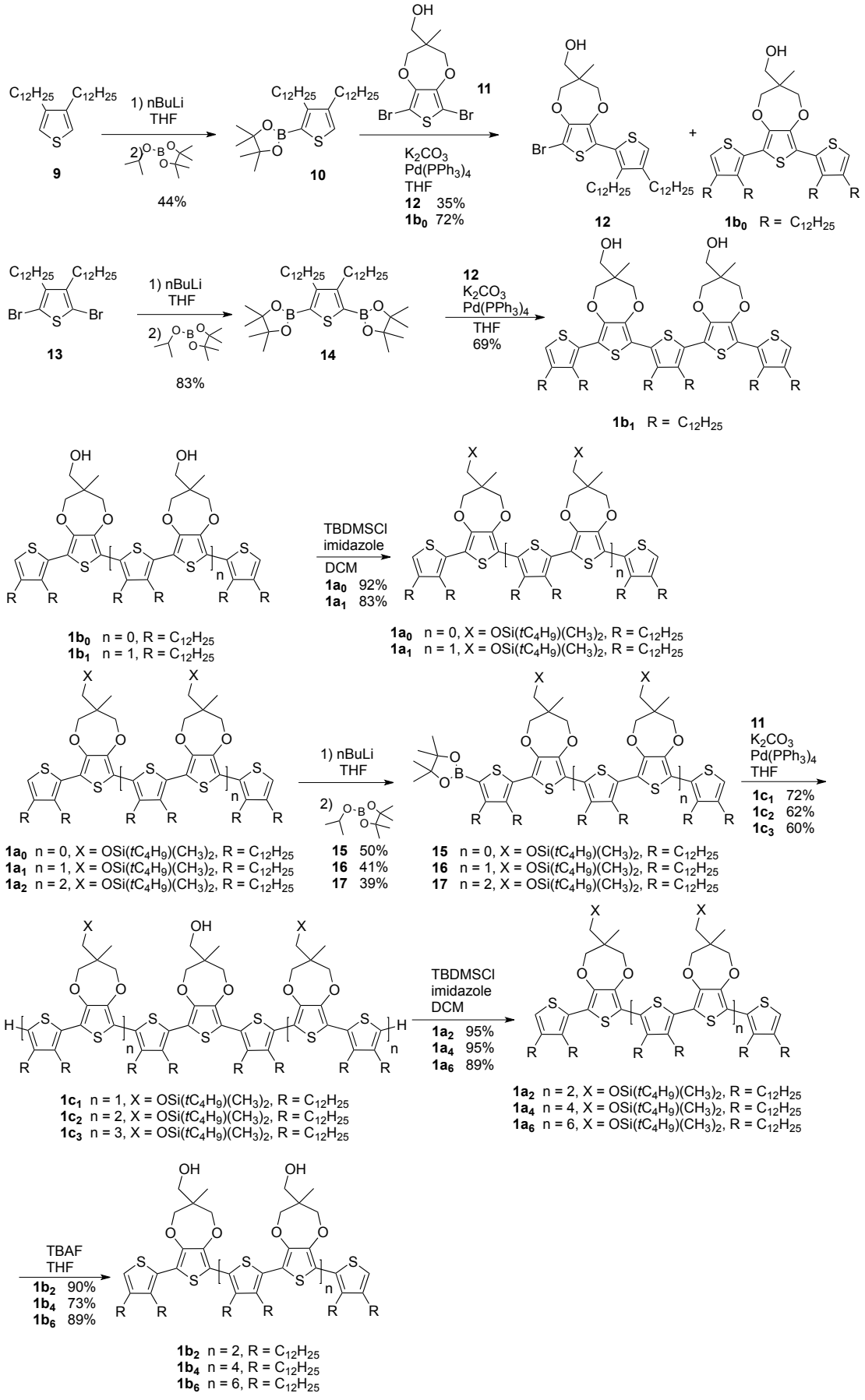
Supporting Information

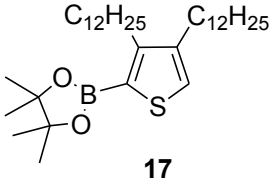
1. Experimental details for the synthesis of **1a**, **1b**, and **1c**.
2. ^{1}H and ^{13}C NMR spectra for all new compounds shown in Scheme S1.
3. GPC profiles for **1a**, **1b**, and **1c**.
4. Plots of M_n, and M_c against M_r values for **1-15**.

Scheme S1 Synthetic scheme



General. All melting points were recorded on a Fargo MP-ID equipment and were uncorrected. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 Unity plus (400 MHz) at ambient temperature. Chemical shifts (δ) and coupling constants (*J*) were expressed in unit of ppm and Hz, respectively. Samples for ^{1}H and ^{13}C NMR measurements were dissolved in $CDCl_3$. Infrared Spectra were taken on a Bio-Rad FTS-40 infrared spectrophotometer using KBr palate for solid samples. MALDI-mass spectra were conducted on an Applied Biosystem 4800 Proteomics Analyzer equipped with an Nd/YAG laser (335 nm) operating at repetition rate of 200 Hz. EI and Fab-mass spectra were collected on a JMS-700 double focusing mass spectrometer. Electrospray ionization (ESI) mass spectra were measured on a Waters LCT premier/XE mass spectrometer analyzer.

3,4-Didodecyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)thiophene (17)

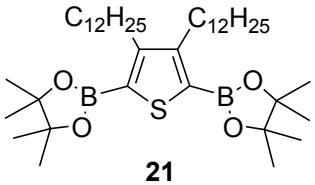


17

Under N_2, to a THF solution (180 mL) of **16**[S1] (11.1 g, 26.4 mmol) was added dropwise ^{n}BuLi (2.5 M in hexane, 12.7 mL, 31.7 mmol) at -78 ^{o}C. After stirring at rt for 3 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.9 g, 26.2 mmol) was added dropwise at -78 ^{o}C and the mixture was stirred at rt overnight. Water (10 mL) was added, and the mixture was extracted with EA (30 mL). The organic layer was washed with saturated NH_4Cl (50 mL x 3), brine (50 mL), dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (hexane) to afford **17** as a colorless oil (12 g, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 6 H), 1.26-1.36 (m, 48 H), 1.46 (quint, *J* = 7.7 Hz, 2 H), 1.60 (quint, *J* = 7.7 Hz, 2 H), 2.52 (t, *J* = 7.7 Hz, 2 H), 2.80 (t, *J* = 7.7 Hz, 2 H), 7.16 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 24.8, 28.6, 29.37, 29.47, 29.54, 29.62, 29.68, 29.72, 30.1, 32.0, 83.4, 127.0, 143.9, 153.4; IR (KBr) ν 2976, 2924, 2853,

1541, 1457, 1378, 1371, 1339, 1305, 1145, 856, 758, 659 cm^{-1}; HRMS (ESI) (M + Na) calcd for $C_{34}H_{63}BNaO_2S$: 569.4540; found: 569.4537.

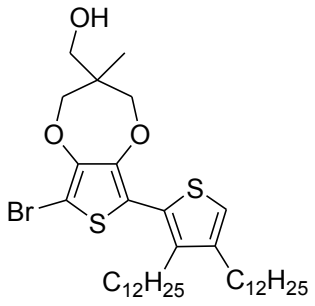
3,4-Didodecyl-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)thiophene (21)



21

In a manner similar to that described for the synthesis of **17**, a mixture of **20**[S1] (3.4 g, 5.9 mmol), ^{n}BuLi (2.5 M in hexane, 9.4 mL, 23.5 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.3 g, 17.6 mmol) was transformed into **21** as a colorless oil (1.7 g, 44%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.8 Hz, 6 H), 1.26-1.36 (m, 60 H), 1.46 (quint, *J* = 7.5 Hz, 4 H), 2.78 (t, *J* = 7.5 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 24.8, 28.5, 29.38, 29.48, 29.68, 29.73, 29.8, 31.9, 32.5, 83.4, 154.0; IR (KBr) ν 2924, 2853, 1527, 1467, 1371, 1341, 1305, 1270, 1167, 1136, 1104, 857, 684 cm^{-1}; HRMS (MALDI) (M + Na) calcd for $C_{40}H_{74}B_2NaO_4S$: 695.5392; found: 695.5386.

Hydroxymethyl-substituted 2-(3,4-didodecyl-2-thienyl)-5-bromo-3,4-dioxythiophene (19)

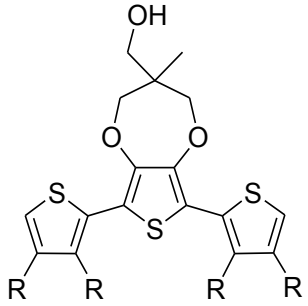


19

A mixture of **18**[S2] (6.4 g, 17.9 mmol), **17** (9.4 g, 17.2 mmol), aqueous K_2CO_3 (2 M, 34 mL), and $Pd(PPh_3)_4$ (990 mg, 0.86 mmol) in THF (170 mL) was degassed with freeze-pump-thaw method and the mixture was stirred at 70 ^{o}C for 2 days. Water (10 mL) was added, and the mixture was extracted with EA (30 mL). The organic layer was washed with saturated NH_4Cl (50 mL x 3), brine (50 mL), dried ($MgSO_4$),

filtered and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (EA/hexane = 8/92) to afford **1b$_0$** (1.12 g, 9%) and **19** as a white solid (4.23 g, 35%): mp 59-60 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 0.98 (s, 3 H), 1.26-1.50 (m, 38 H), 1.55-1.60 (m, 1 H), 1.64 (quint, *J* = 7.7 Hz, 2 H), 2.50 (t, *J* = 7.7 Hz, 2 H), 2.57 (t, *J* = 8.0 Hz, 2 H), 3.71-3.77 (m, 2 H) 3.78 (d, *J* = 12.0 Hz, 1 H), 3.84 (d, *J* = 12.0 Hz, 1 H), 4.12 (d, *J* = 12.0 Hz, 1 H), 4.19 (d, *J* = 12.0 Hz, 1 H), 6.93 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 17.0, 22.7, 27.80, 29.2, 29.36, 29.54, 29.62, 29.66, 29.7, 29.8, 30.3, 31.2, 44.0, 65.5, 76.6, 109.0, 120.7, 126.2, 141.0, 142.7, 144.8, 145.3; IR (KBr) ν 3335, 2954, 2920, 2849, 1546, 1502, 1468, 1434, 1389, 1370, 1052, 1024, 873, 762, 734, 720 cm^{-1}; HRMS (EI) (M) calcd for $C_{37}H_{61}BrO_3S_2$: 696.3245; found: 696.3256.

Hydroxymethyl-substituted 2,5-[bis(3,4-didodecyl-2-thienyl)]-3,4-dioxythiophene (1b$_0$)

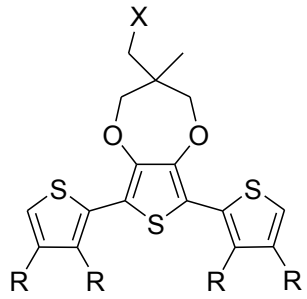


1b$_0$ R = $C_{12}H_{25}$

In a manner similar to that described for the synthesis of **19**, a mixture of **18**[S2] (1.8 g, 5.0 mmol), **17** (6.0 g, 10.9 mmol), aqueous K_2CO_3 (2 M, 20 mL), and $Pd(PPh_3)_4$ (287 mg, 0.25 mmol) was transformed into **1b$_0$** as a pale yellow solid (3.7 g, 72%): mp 56-57 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.8 Hz, 6 H), 0.88 (t, *J* = 6.8 Hz, 6 H), 0.97 (s, 3 H), 1.24-1.44 (m, 72 H), 1.50 (quint, *J* = 7.8 Hz, 4 H), 1.59 (t, *J* = 5.8 Hz, 1 H), 1.65 (quint, *J* = 7.7 Hz, 4 H), 2.51 (t, *J* = 7.7 Hz, 4 H), 2.65 (t, *J* = 7.8 Hz, 4 H), 3.78 (d, *J* = 5.8.0 Hz, 2 H), 3.80 (d, *J* = 12.0 Hz, 2 H), 4.17 (d, *J* = 12.0 Hz, 2 H), 6.93 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 16.9, 22.7, 28.0, 29.2, 29.37, 29.46, 29.4, 29.55, 29.69, 29.73, 29.94, 30.4, 32.0, 43.9, 65.6, 76.5, 115.0, 120.3, 127.3, 140.1, 142.7, 145.7; IR (KBr) ν 3345, 2954, 2920, 2850, 1544, 1530, 1494, 1468,

1427, 1392, 1366, 1210, 1081, 1043, 964, 878, 721 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{65}H_{112}O_3S_3$: 1036.7768; found: 1036.7774; GPC (THF): M_n = 1733, PDI = 1.01.

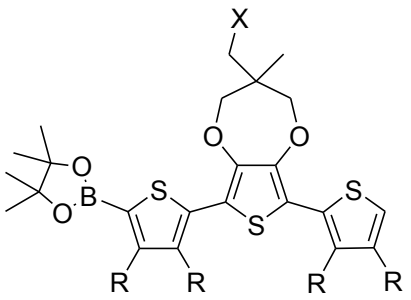
TBS-protected hydroxymethyl-substituted 2,5-[bis(3,4-didodecyl-2-thienyl)]-3,4-dioxythiophene ($1a_0$)



$1a_0$ X = $OSi(^tC_4H_9)(CH_3)_2$, R = $C_{12}H_{25}$

Under N_2, a DCM solution (10 mL) of **$1b_0$** (1.0 g, 1.0 mmol), imidazole (203 mg, 3.0 mmol), and tert-butyldimethylsilyl chloride (195 mg, 1.3 mmol) was stirred at rt overnight. Water (10 mL) was added, and the mixture was extracted with DCM (20 mL). The organic layer was washed with saturated NH_4Cl (20 mL x 3), brine (20 mL), dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel (DCM/hexane = 10/90) to afford **$1a_0$** as a yellow oil (1.05 g, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.88 (t, *J* = 6.8 Hz, 6 H), 0.89 (t, *J* = 6.8 Hz, 6 H), 0.90 (s, 9 H), 0.99 (s, 3 H), 1.24-1.44 (m, 72 H), 1.51 (quint, *J* = 7.7 Hz, 4 H), 1.65 (quint, *J* = 7.6 Hz, 4 H), 2.52 (t, *J* = 7.6 Hz, 4 H), 2.67 (t, *J* = 7.7 Hz, 4 H), 3.67 (s, 2 H), 3.81 (d, *J* = 12.0 Hz, 2 H), 4.06 (d, *J* = 12.0 Hz, 2 H), 6.93 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.5, 14.1, 17.1, 18.3, 22.7, 25.9, 28.0, 29.2, 29.20, 29.39, 29.47, 29.57, 29.67, 29.70, 29.74, 30.0, 30.3, 32.0, 44.2, 65.8, 76.5, 114.6, 120.2, 127.6, 140.0, 142.6, 145.9; IR (KBr) ν 2957, 2925, 2853, 1496, 1464, 1426, 1391, 1373, 1256, 1102, 1075, 1006, 837, 775, 721 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{71}H_{126}O_3S_3Si$: 1150.8638; found: 1150.8654; GPC (THF): M_n = 1816, PDI = 1.01.

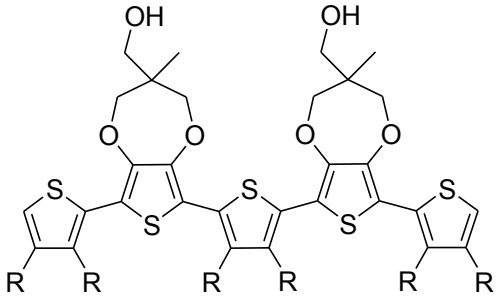
4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl-substituted $1a_0$ (22)



22 X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **17**, a mixture of **1a$_0$** (6.4 g, 5.6 mmol), ^{n}BuLi (2.5 M in hexane, 2.6 mL, 6.5 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (1.0 g, 5.4 mmol) was transformed into **22** as a yellow oil (3.7 g, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 6 H), 0.93 (t, *J* = 6.8 Hz, 6 H), 0.94 (t, *J* = 6.8 Hz, 6 H), 0.95 (s, 9 H), 1.04 (s, 3 H), 1.25-1.49 (m, 84 H), 1.52-1.63 (m, 6 H), 1.70 (quint, *J* = 7.6 Hz, 2 H), 2.57 (t, *J* = 7.6 Hz, 2 H), 2.73 (t, *J* = 8.8 Hz, 2 H), 2.75 (t, *J* = 8.8 Hz, 2 H), 2.85 (t, *J* = 7.8 Hz, 2 H), 3.69 (d, *J* = 10.0 Hz, 1 H), 3.75 (d, *J* = 10.0 Hz, 1 H), 3.86 (d, *J* = 12.0 Hz, 1 H), 3.89 (d, *J* = 12.0 Hz, 1 H), 4.06 (d, *J* = 12.0 Hz, 1 H), 4.07 (d, *J* = 12.0 Hz, 1 H) 6.67 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.6, 14.1, 17.1, 22.7, 24.8, 25.9, 28.0, 29.2, 29.4, 29.48, 29.57, 29.71, 29.74, 30.0, 30.3, 30.7, 31.9, 32.5, 44.2, 65.9, 76.4, 83.4, 114.5, 114.9, 120.2, 127.7, 140.0, 141.4, 142.6, 145.9, 154.0; IR (KBr) ν 2955, 2922, 2853, 1495, 1465, 1390, 1371, 1339, 1305, 1271, 1257, 1144, 1077, 776, 721, 670 cm^{-1}; HRMS (FAB) (M) calcd for $C_{77}H_{137}BO_5S_3Si$: 1276.9491; found: 1276.9510.

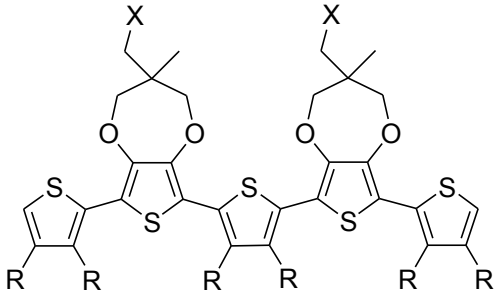
Alternating tris-(3,4-didodecylthiophene)-bis-(hydroxymethyl-substituted-3,4-dioxythiophene) pentamer (1b$_1$)



1b$_1$ R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **19**, a mixture of **19** (3.2 g, 4.6 mmol), **21**(1.4 g, 2.1 mmol), aqueous K_2CO_3 (2 M, 4.8 mL), and $Pd(PPh_3)_4$ (120 mg, 0.1 mmol) was transformed into **1b$_1$** as a yellow solid (2.34 g, 69%): mp 96-98 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 6.8 Hz, 6 H), 0.87 (t, *J* = 6.8 Hz, 6 H), 0.88 (t, *J* = 6.8 Hz, 6 H), 0.97 (s, 3 H), 0.98 (s, 3 H), 1.20-1.45 (m, 108 H), 1.47-1.58 (m, 8 H), 1.59-1.70 (m, 6 H), 2.52 (t, *J* = 7.8 Hz, 4 H) , 2.62-2.71 (m, 8 H), 3.79 (d, *J* = 6.0 Hz, 4 H), 3.81 (d, *J* = 12.4 Hz, 2 H), 3.82 (d, *J* = 12.0 Hz, 2 H), 4.18 (d, *J* = 12.0 Hz, 2 H), 4.19 (d, *J* = 12.4 Hz, 2 H), 6.95 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 16.9, 22.7, 28.2, 28.4, 28.5, 28.6, 29.2, 29.38, 29.45, 29.51, 29.57, 29.66, 29.70, 29.74, 30.0, 30.1, 30.4, 30.7, 31.9, 43.9, 65.7, 76.5, 114.5, 115.2, 120.3, 127.3, 127.7, 140.1, 140.6, 142.7, 145.7, 145.8; IR (KBr) ν 3421, 2955, 2920, 2850, 1496, 1467, 1457, 1429, 1364, 1051, 897, 721 cm^{-1}; MS (MALDI) (M) calcd for $C_{102}H_{172}O_6S_5$: 1653.1757; found: 1653.1692; GPC (THF): M_n = 2668, PDI = 1.01.

TBS-protected 1b$_1$ (1a$_1$)

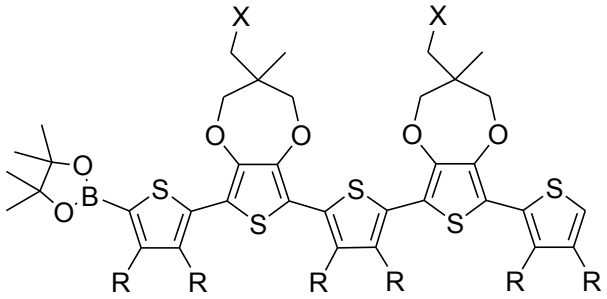


1a$_1$ X = $OSi(^tC_4H_9)(CH_3)_2$, R = $C_{12}H_{25}$

In a manner similar to that described for the synthesis of **1a$_0$**, a mixture of **1b$_1$** (309 mg, 0.2 mmol), imidazole (76 mg, 1.1 mmol), and tert-butyldimethylsilyl chloride (73 mg, 0.5 mmol) was transformed into **1a$_1$** as a yellow solid (282 mg, 83%): mp 37-39 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 12 H), 0.90 (t, *J* = 6.8 Hz, 6 H), 0.91 (t, *J* = 6.8 Hz, 6 H), 0.92 (t, *J* = 6.8 Hz, 6 H), 0.94 (s, 18 H) 1.03 (s, 6 H), 1.20-1.49 (m, 108 H), 1.52-1.63 (m, 8 H), 1.69 (quint, *J* = 7.6 Hz, 4 H), 2.56 (t, *J* = 7.6 Hz, 4 H), 2.67-2.79 (m, 8 H), 3.72 (s, 4 H), 3.85 (d, *J* = 12.0 Hz, 2 H), 3.86 (d, *J* = 12.0 Hz , 2 H), 4.10 (d, *J* = 12.0 Hz, 2 H), 4.12 (d, *J* = 12.0 Hz, 2 H), 6.96 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.55, -5.52, 14.1, 17.1, 18.3, 22.7, 25.9, 28.0, 28.3, 29.2, 29.39,

29.46, 29.51, 29.58, 29.65, 29.68, 29.72, 29.76, 30.0, 30.1, 30.3, 30.6, 31.9, 44.2, 65.9, 76.6, 114.3, 114.8, 120.2, 127.7, 127.8, 139.9, 140.4, 142.6, 145.8, 145.9; IR (KBr) ν 2957, 2922, 2851, 1494, 1469, 1427, 1374, 1363, 1258, 1104, 1077, 1030, 837, 774, 720 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{114}H_{200}O_6S_5Si_2$: 1881.3487; found: 1881.3459; GPC (THF): M_n = 2755, PDI = 1.01.

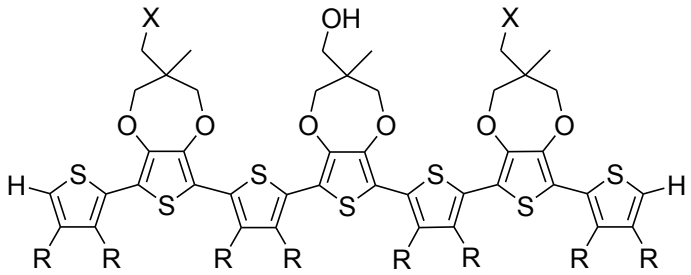
4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl-substituted $1a_1$ (23)



23 X = $OSi(^tC_4H_9)(CH_3)_2$, R = $C_{12}H_{25}$

In a manner similar to that described for the synthesis of **17**, a mixture of **$1a_1$** (2.28 g, 1.2 mmol), ^{n}BuLi (2.5 M in hexane, 0.58 mL, 1.5 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (225 mg, 1.2 mmol) was transformed into **23** as a yellow oil (1 g, 41%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 12 H), 0.87-0.95 (m, 36 H), 1.02 (s, 6 H), 1.22-1.48 (m, 120 H), 1.50-1.61 (m, 10 H), 1.68 (quint, J = 7.6 Hz, 2 H), 2.55 (t, J = 7.6 Hz, 2 H), 2.66-2.76 (m, 8 H), 2.82 (t, J = 7.8 Hz, 2 H), 3.63-3.78 (m, 4 H), 3.79-3.92 (m, 4 H), 4.04-4.16 (m, 4 H), 6.95 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.56, -5.53, 14.1, 17.1, 18.3, 22.7, 24.8, 25.9, 28.0, 28.3, 29.2, 29.39, 29.48, 29.57, 29.70, 29.76, 29.95, 30.0 , 30.1, 30.3, 30.6, 30.7, 31.9, 44.2, 66.0, 76.5, 83.4, 114.33, 114.34, 114.64, 114.65, 114.69, 114.74, 120.2, 127.7, 127.8, 127.9, 134.3, 139.9, 140.4, 140.5, 141.4, 142.6, 145.9, 154.1; IR (KBr) ν 2953, 2924, 2853, 1467, 1427, 1390, 1371, 1338, 1257, 1144, 1076, 838, 776, 671 cm^{-1}; HRMS (MALDI) (M + H) calcd for $C_{120}H_{212}BO_8S_5Si_2$: 2008.4417; found: 2008.4391.

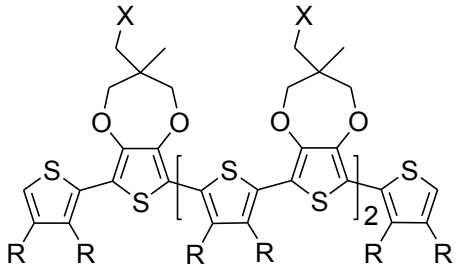
Bis-TBS-protected alternating tetrakis-(3,4-didodecylthiophene)-tris-(hydroxy-methyl-substituted-3,4- dioxythiophene) heptamer ($1c_1$)



1c$_1$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **19**, a mixture of **18** [S2] (0.4 g, 1.17 mmol), **22** (4.5 g, 3.52 mmol), aqueous K_2CO_3 (2 M, 4.5 mL), and $Pd(PPh_3)_4$ (70 mg, 0.06 mmol) was transformed into **1c$_1$** as a red solid (2.1 g, 72%): mp 67-68 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 12 H), 0.89-0.96 (m, 24 H), 0.95 (s, 18 H) 1.02 (s, 3 H), 1.04 (s, 6 H) 1.25-1.49 (m, 144 H), 1.52-1.65 (m, 12 H), 1.70 (quint, *J* = 7.7 Hz, 4 H), 1.76 (t, *J* = 6.8 Hz, 1 H) 2.57 (t, *J* = 7.7 Hz, 4 H), 2.68-2.80 (m, 12 H), 3.73 (s, 4 H), 3.84-3.89 (m, 8 H), 4.12 (d, *J* = 12.0 Hz, 2 H), 4.14 (d, *J* = 12.0 Hz, 2 H), 4.24 (d, *J* = 12.0 Hz, 2 H), 6.97 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.57, -5.54, 14.1, 19.2, 17.0, 18.2, 22.7, 25.9, 28.0, 28.3, 29.2, 29.39, 29.44, 29.50, 29.56, 29.64, 29.70, 29.75, 29.99, 30.1, 30.3, 30.6, 30.7, 31.9, 43.9, 44.2, 65.6, 65.9, 76.5, 114.2, 114.7, 114.8, 114.9, 120.2, 127.6, 127.7, 128.0, 140.0, 140.4, 140.5, 142.6, 145.7, 145.8, 145.9; IR (KBr) ν 3440, 2954, 2919, 2850, 1494, 1469, 1426, 1375, 1256, 1075, 838, 775 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{151}H_{260}O_9S_7Si_2$: 2497.7471; found: 2497.7513; GPC (THF): M_n = 3710, PDI = 1.01.

TBS-protected 1b$_2$ (1a$_2$)

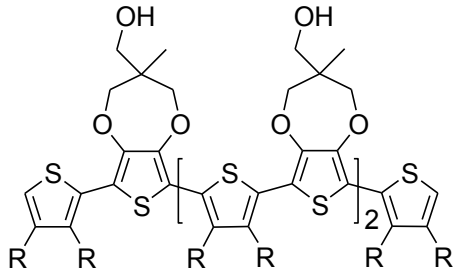


1a$_2$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **1a$_0$**, a mixture of **1c$_1$** (2.1 g, 0.8 mmol), imidazole (170 mg, 2.5 mmol), and tert-butyldimethylsilyl chloride (190

mg, 1.3 mmol) was transformed into **1a$_2$** as a red solid (2.1 g, 95%): mp 48-50 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05-0.13 (ms, 18 H), 0.93-0.92 (m, 51 H), 1.00-1.05 (ms, 9 H), 1.20-1.45 (m, 144 H), 1.49-1.60 (m, 12 H), 1.66 (quint, *J* = 7.5 Hz, 4 H), 2.52 (t, *J* = 7.5 Hz, 4 H), 2.62-2.76 (m, 12 H), 3.66-3.70 (m, 6 H), 3.78-3.87 (m, 6 H), 4.04-4.12 (m, 6 H). 6.93 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.55, -5.52, 14.1, 17.1, 18.3, 22.7, 25.9, 28.0, 28.4, 29.2, 29.40, 29.47, 29.51, 29.57, 29.67, 29.71, 29.77, 30.0, 30.1, 30.2, 30.3, 30.6, 31.9, 44.2, 65.9, 76.5, 114.3, 114.5, 114.8, 120.2, 127.7, 127.8, 139.9, 140.41, 140.44, 142.6, 145.88, 145.91; IR (KBr) ν 2955, 2924, 2853, 1467, 1373, 1256, 1103, 1074, 838, 776 cm^{-1}; HRMS (MALDI) (M + H) calcd for $C_{157}H_{275}O_9S_7Si_3$: 2612.8414; found: 2612.8359; GPC (THF): M_n = 3589, PDI = 1.01.

Alternating tetrakis-(3,4-didodecylthiophene)-tris-(hydroxy-methyl-substituted-3,4-dioxythiophene) heptamer (1b$_2$)

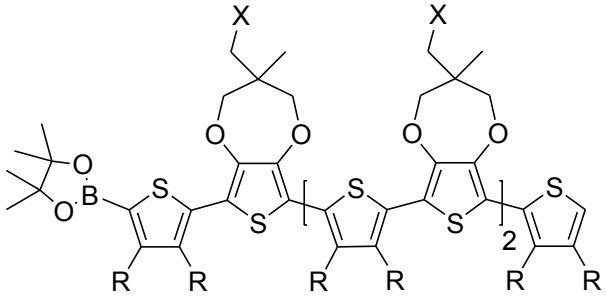


1b$_2$ R = $C_{12}H_{25}$

Under N_2, a THF solution (5 mL) of **1a$_2$** (170 mg, 0.07 mmol), and tetra-n-butylammonium fluoride (1 M in THF, 0.39 mL, 0.39 mmol) was stirred at rt for 3 h. Water (5 mL) was added, and the mixture was extracted with DCM (10 mL). The organic layer was washed with saturated NH_4Cl (10 mL x 3), brine (10 mL), dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The residue was recrystallized with ethanol/chloroform to afford **1b$_2$** as a red solid (154 mg, 90%): mp 117-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.92 (m, 24 H), 0.94-1.03 (ms, 9 H), 1.12-1.46 (m, 144 H), 1.48-1.61 (m, 12 H), 1.66 (quint, *J* = 7.7 Hz, 4 H), 1.76-1.92 (ms, 3 H), 2.53 (t, *J* = 7.7 Hz, 4 H), 2.62-2.80 (m, 12 H), 3.75-3.89 (m, 12 H), 4.16-4.26 (m, 6 H), 6.95 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 16.9, 22.7, 28.0, 28.3, 29.2, 29.38, 29.45, 29.45, 29.56, 29.70, 29.75, 29.98, 30.0, 30.1, 30.4, 30.7,

31.9, 43.9, 65.6, 76.5, 114.5, 114.7, 115.2, 120.3, 127.3, 127.7, 127.7, 140.1, 140.58, 140.59, 142.7, 145.66, 145.72, 145.8; IR (KBr) ν 3428, 2957, 2919, 2850, 1493, 1469, 1421, 1364, 1050, 949, 875, 720 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{139}H_{232}O_9S_7$: 2269.5714; found: 2269.5724; GPC (THF): M_n = 3461, PDI = 1.01.

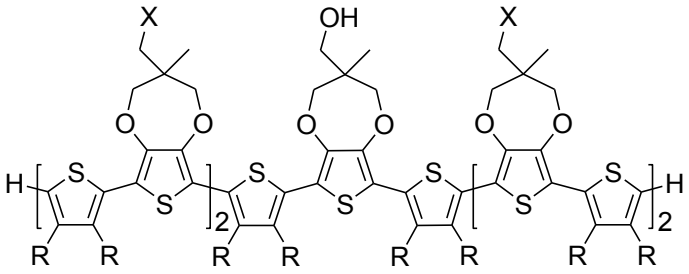
4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl-substituted 1a$_2$ (24)



24 X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **17**, a mixture of **1a$_2$** (2.1 g, 0.8 mmol), ^{n}BuLi (2.5 M in hexane, 0.39 mL, 0.98 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (150 mg, 0.8 mmol) was transformed into **24** as an orange oil (0.86 g, 39%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03-0.13 (ms, 18 H), 0.87-0.94 (m, 51 H), 0.98-1.05 (ms, 9 H), 1.20-1.48 (m, 156 H), 1.49-1.63 (m, 14 H), 1.68 (quint, J = 7.7 Hz, 2 H), 2.54 (t, J = 7.7 Hz, 2 H), 2.62-2.77 (m, 12 H), 2.78-2.86 (m, 2 H), 3.63-3.75 (m, 6 H), 3.80-3.92 (m, 6 H), 4.05-4.18 (m, 6 H), 6.95 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.55, -5.52, 14.1, 17.1, 18.3, 22.7, 24.8, 25.9, 28.0, 28.3, 29.2, 29.39, 29.48, 29.57, 29.65, 29.67, 29.71, 29.76, 29.95, 30.0, 30.1, 30.2, 30.3, 30.6, 31.9, 44.2, 65.9, 76.6, 114.3, 114.5, 114.66, 114.71, 114.8, 120.2, 127.7, 127.8, 139.9, 140.40, 140.44, 142.6, 145.9, 154.1; IR (KBr) ν 2953, 2924, 2853, 1466, 1426, 1390, 1372, 1339, 1256, 1101, 1074, 837, 775, 671 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{163}H_{285}BO_{11}S_7Si_3$: 2737.9188; found: 2737.9226.

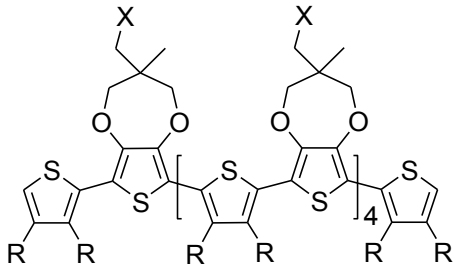
Tetrakis-TBS-protected alternating hexakis-(3,4-didodecylthiophene)-pentakis-(hydroxy-methyl-substituted-3,4-dioxythiophene) undecamer (1c$_2$)



1c$_2$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **19**, a mixture of **18**[S2] (53 mg, 0.15 mmol), **23** (900 mg, 0.45 mmol), aqueous K_2CO_3 (2 M, 0.6 mL), and $Pd(PPh_3)_4$ (10 mg, 0.01 mmol) was transformed into **1c$_2$** as a red solid (363 mg, 62%): mp 65-66 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 12 H), 0.11 (s, 12 H), 0.86-0.96 (m, 72 H), 0.98-1.07 (ms, 15H), 1.21-1.50 (m, 216 H), 1.50-1.75 (m, 25 H), 2.51-2.60 (t, *J* = 7.6 Hz, 4 H), 2.65-2.85 (m, 20 H), 3.67-3.78 (m, 8 H), 3.80-3.94 (m, 12 H), 4.07-4.18 (m, 8 H), 4.24 (d, *J* = 12.0 Hz, 2 H), 6.96 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.56, -5.53, 14.1, 16.9, 17.1, 18.3, 22.7, 25.9, 28.0, 28.4, 29.2, 29.3, 29.39, 29.46, 29.50, 29.56, 29.64, 29.67, 29.71, 29.76, 30.0, 30.1, 30.3, 30.6, 31.9, 44.2, 65.9, 76.6, 114.3, 114.37, 114.41, 114.6, 114.79, 114.83, 120.18, 120.19, 127.7, 127.8, 139.93, 139.96, 140.4, 140.6, 142.66, 145.7, 145.8, 145.87, 145.95; IR (KBr) ν 3428, 2957, 2919, 2849, 1492, 1469, 1421, 1392, 1374, 1256, 1068, 837, 815, 774, 720 cm^{-1}; HRMS (MALDI) (M + H) calcd for $C_{237}H_{409}O_{15}S_{11}Si_4$: 3959.7246; found: 3959.7152 ; GPC (THF): M_n = 5231, PDI = 1.01

TBS-protected 1b$_4$ (1a$_4$)

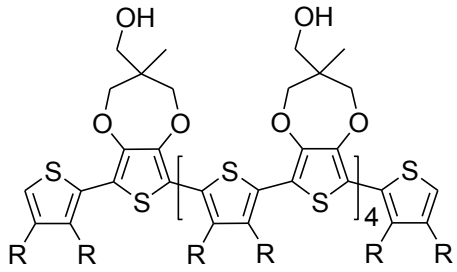


1a$_4$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **1a$_0$**, a mixture of **1c$_2$** (250 mg, 0.06 mmol), imidazole (13 mg, 0.19 mmol), and tert-butyldimethylsilyl chloride

(14 mg, 0.09 mmol) was transformed into **1a$_4$** as a red solid (244 mg, 95%): mp 59-60 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03-0.12 (ms, 30 H), 0.84-0.97 (m, 81 H), 0.97-1.06 (ms, 15 H), 1.17-1.48 (m, 216 H), 1.48-1.63 (m, 20 H), 1.67 (quint, *J* = 7.5 Hz, 4 H), 2.54 (t, *J* = 7.5 Hz, 4 H), 2.60-2.84 (m, 20 H), 3.64-3.75 (m, 10 H), 3.77-3.92 (m, 10 H), 4.03-4.18 (m, 10 H), 6.94 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.54, -5.51, 14.1, 17.1, 18.3, 22.7, 25.9, 27.2, 28.0, 28.4, 29.2, 29.4, 29.47, 29.51, 29.57, 29.65, 29.67, 29.78, 30.1, 30.3, 30.7, 32.0, 44.2, 65.9, 76.6, 114.3, 114.5, 114.8, 120.2, 127.7, 127.9, 140.4, 142.6, 145.9; IR (KBr) ν 2954, 2920, 2851, 1492, 1468, 1422, 1391, 1374, 1258, 1102, 1067, 838, 775, 720 cm^{-1}; HRMS (MALDI) (M + H) calcd for $C_{243}H_{423}O_{15}S_{11}Si_5$: 4073.8111; found: 4073.8056; GPC (THF): M_n = 5460, PDI = 1.01.

Alternating hexakis-(3,4-didodecylthiophene)-pentakis- (hydroxymethyl-substituted-3,4-dioxythiophene) undecamer (1b$_4$)

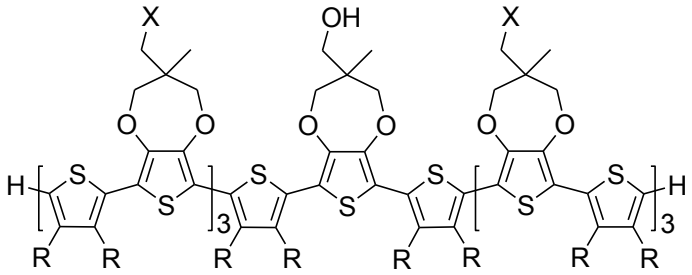


1b$_4$ R = $C_{12}H_{25}$

In a manner similar to that described for the synthesis of **1b$_2$**, a mixture of **1a$_4$** (240 mg, 0.06 mmol), and tetra-n-butylammonium fluoride (1 M in THF, 0.59 mL, 0.59 mmol) was transformed into **1b$_4$** as a red solid (152 mg, 73%): mp 147-148 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81-0.93 (m, 36 H), 0.95-1.04 (ms, 15 H), 1.17-1.47 (m, 216 H), 1.48-1.61 (m, 20 H), 1.66 (quint, *J* = 7.6 Hz, 4 H), 1.76-1.95 (ms, 5H), 2.53 (t, *J* = 7.6 Hz, 4 H), 2.58-2.82 (m, 20 H), 3.75-3.90 (m, 20 H), 4.13-4.27 (m, 10 H), 6.95 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 16.9, 22.7, 28.0, 28.4, 29.2, 29.38, 29.45, 29.49, 29.55, 29.69, 29.75, 30.0, 30.1, 30.4, 30.7, 31.9, 43.9, 65.7, 76.5, 114.5, 114.7, 115.2, 120.3, 127.3, 127.7, 140.1, 140.6, 142.7, 145.7; IR (KBr) ν 3421, 2955, 2920, 2850, 1494, 1468, 1420, 1364, 1263, 1049, 955, 720 cm^{-1}; HRMS (MALDI) (M

calcd for $C_{213}H_{352}O_{15}S_{11}$: 3502.3709; found: 3502.3747; GPC (THF): M_n = 4931, PDI = 1.01.

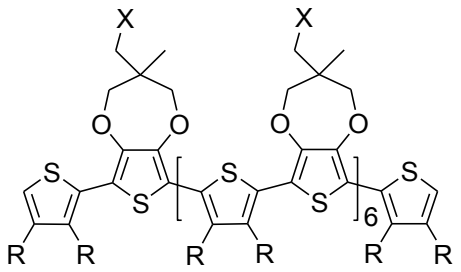
Hexakis-TBS-protected alternating octakis-(3,4-didodecylthiophene)-heptakis-(hydroxy-methyl-substituted-3,4-dioxythiophene) pentadecamer ($\mathbf{1c_3}$)



$\mathbf{1c_3}$ X = $OSi(^tC_4H_9)(CH_3)_2$, R = $C_{12}H_{25}$

In a manner similar to that described for the synthesis of **19**, a mixture of **18**[S2] (270 mg, 0.08 mmol), **24** (480 mg, 0.18 mmol), aqueous K_2CO_3 (2 M, 0.3 mL), and $Pd(PPh_3)_4$ (5 mg, 0.004 mmol) was transformed into **$\mathbf{1c_3}$** as a red solid (246 mg, 60%): mp 71-72 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 12 H), 0.09 (s, 12 H), 0.10 (s, 12 H), 0.82-0.97 (m, 102 H), 0.98-1.07 (ms, 21 H), 1.19-1.49 (m, 288 H), 1.51-1.75 (m, 33 H), 2.55 (t, J = 7.6 Hz, 4 H), 2.63-2.84 (m, 28 H), 3.67-3.77 (m, 12 H), 3.80-3.93 (m, 16 H), 4.06-4.17 (m, 12 H), 4.23 (t, J = 12.0 Hz, 2 H), 6.95 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.5, 14.1, 16.9, 17.1, 18.3, 22.7, 25.9, 28.0, 28.4, 29.2, 29.4, 29.50, 29.56, 29.64, 29.71, 29.77, 30.0, 30.1, 30.3, 30.6, 32.0, 43.9, 44.2, 65.7, 65.9, 76.6, 114.32, 114.34, 114.39, 114.50, 114.53, 114.60, 114.77, 114.85, 120.2, 127.6, 127.7, 127.8, 127.9, 128.0, 139.9,140.5, 140.61, 140.64, 142.6, 145.7, 145.90, 145.96; IR (KBr) ν 3445, 2955, 2920, 2850, 1467, 1255, 1068, 837, 775, 720 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{323}H_{556}O_{21}S_{15}Si_6$: 5419.6865; found: 5419.7009; GPC (THF): M_n = 6840, PDI = 1.01.

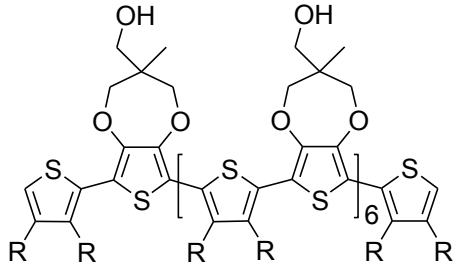
TBS-protected $\mathbf{1b_6}$ ($\mathbf{1a_6}$)



1a$_6$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **1a$_0$**, a mixture of **1c$_3$** (246 mg, 0.05 mmol), imidazole (12 mg, 0.18 mmol), and tert-butyldimethylsilyl chloride (13 mg, 0.09 mmol) was transformed into **1a$_6$** as a red solid (224 mg, 89%): mp 78-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02-0.18 (ms, 42 H), 0.82-1.00 (m, 111 H), 0.99-1.09 (ms, 21 H), 1.20-1.50 (m, 288 H), 1.50-1.65 (m, 28 H), 1.68 (quint, J = 7.5 Hz, 4 H), 2.55 (t, J = 7.5 Hz, 4 H), 2.63-2.95 (m, 28 H), 3.65-3.79 (m, 14 H), 3.80-3.96 (m, 14 H), 4.05-4.24 (m, 14 H), 6.97 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -5.5, 14.1, 17.0, 18.1, 18.3, 25.6, 26.7, 25.9, 28.0, 28.4, 29.2, 29.4, 29.5, 29.6, 29.67, 29.71, 29.8, 30.0, 30.1, 30.4, 30.6, 32.0, 44.2, 65.9, 76.6, 114.3, 114.5, 114.8, 120.2, 127.7, 127.9, 139.9, 140.0, 142.6, 145.9; IR (KBr) ν 2957, 2920, 2851, 1467, 1340, 1378, 1257, 1197, 1183, 1047, 957, 850, 721 cm^{-1}; HRMS (MALDI) (M) calcd for $C_{329}H_{570}O_{21}S_{15}Si_7$: 5533.7730; found: 5533.7913; GPC (THF): M_n = 6635, PDI = 1.01.

Alternating octakis-(3,4-didodecylthiophene)-heptakis- (hydroxymethyl-substituted-3,4-dioxythiophene) pentadecamer (1b$_6$)



1b$_6$ R = C$_{12}$H$_{25}$

In a manner similar to that described for the synthesis of **1b$_2$**, a mixture of **1a$_6$** (224 mg, 0.04 mmol), and tetra-n-butylammonium fluoride (1 M in THF, 0.56 mL, 0.56

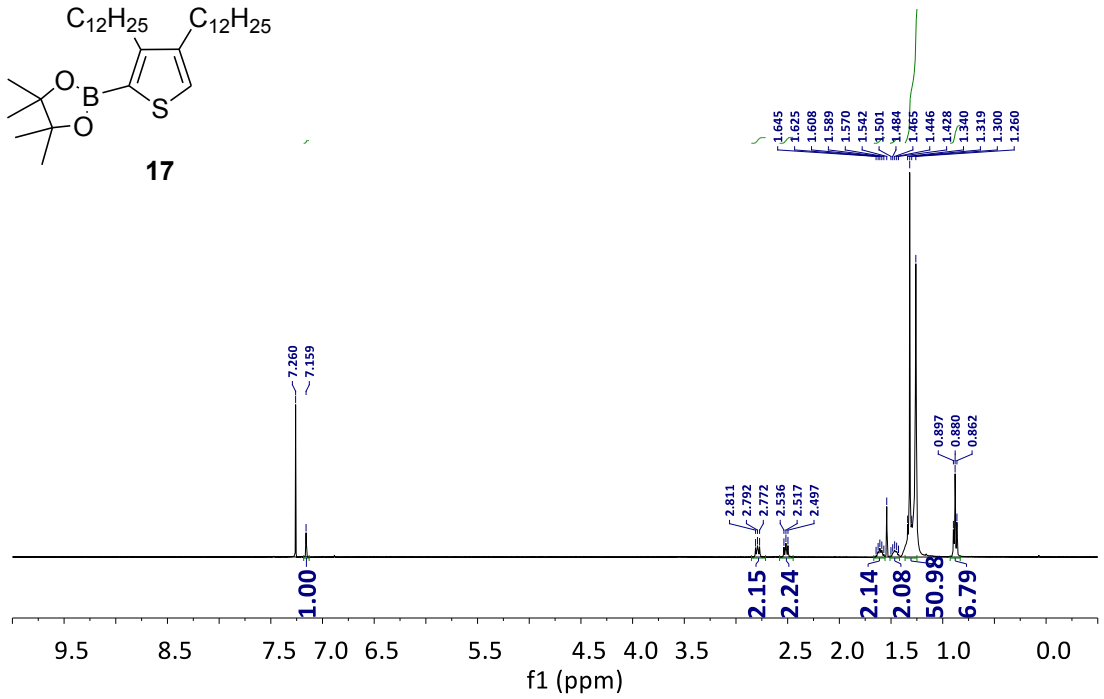
mmol) was transformed into **1b$_6$** as a red solid (170 mg, 89%): mp 158-159 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.93 (m, 48 H), 0.89-0.95 (ms, 21 H), 1.17-1.46 (m, 288 H), 1.48-17.5 (m, 39 H), 2.45 (t, J = 7.8 Hz, 4 H), 2.59-2.80 (m, 28 H), 3.74-3.91 (m, 28 H), 4.14-4.29 (m, 14 H), 6.94 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 17.0, 22.7, 28.0, 28.4, 29.2, 29.4, 29.49, 29.55, 29.69, 29.75, 30.0, 30.1, 30.4, 30.7, 31.9, 43.9, 65.7, 76.5, 114.5, 114.8, 115.2, 120.3, 127.3, 127.7, 140.2, 140.6, 140.7, 142.7, 145.67, 145.75; IR (KBr) ν 3424, 2955, 2920, 2849, 1493, 1468, 1421, 1378, 1364, 1261, 1157, 1047, 954, 926, 876, 720 cm^{-1}; HRMS (MALDI) (M + H) calcd for $C_{287}H_{473}O_{21}S_{15}$: 4736.1755; found: 4736.1749; GPC (THF): M_n = 6356, PDI = 1.01.

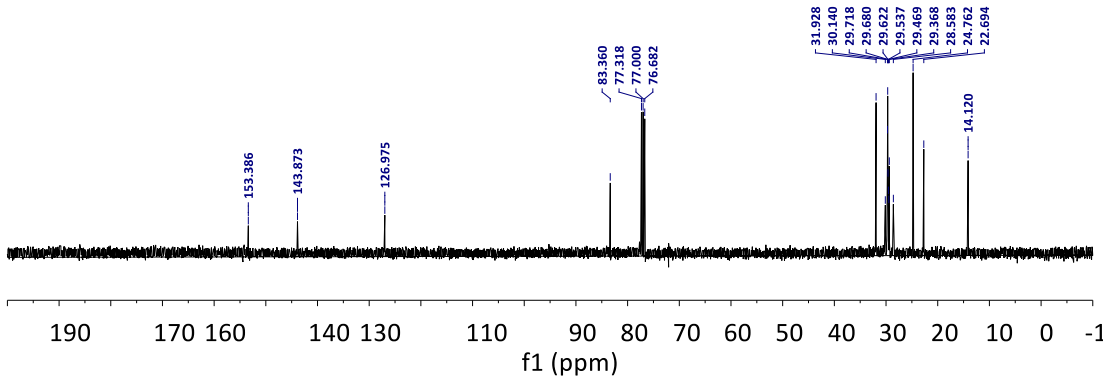
References

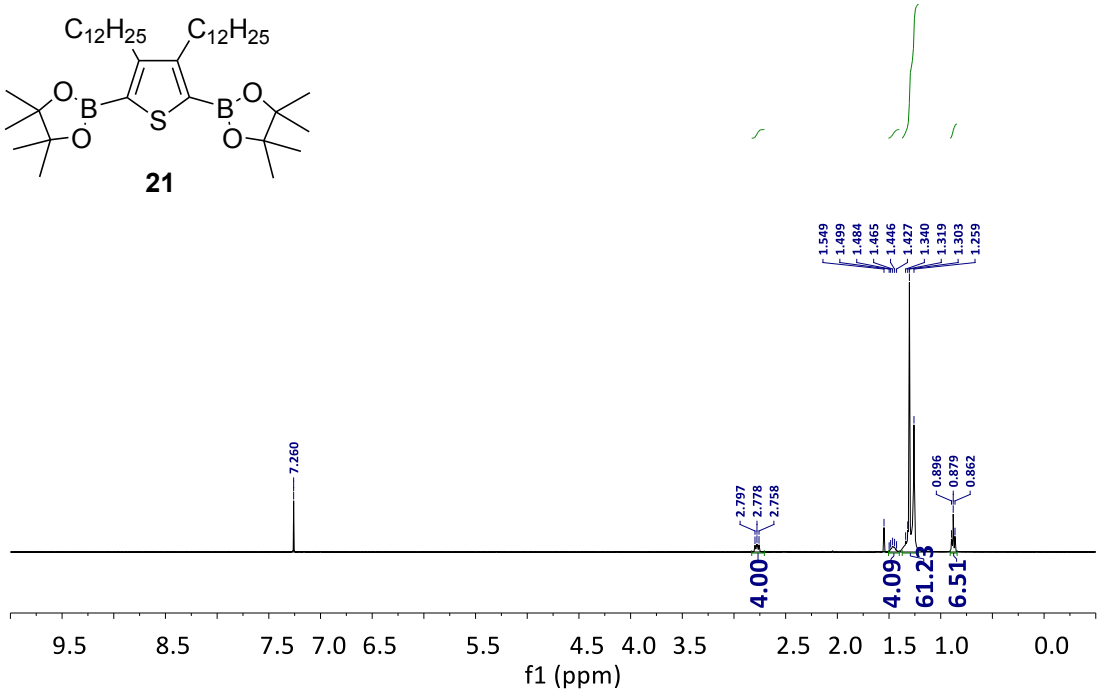
S1. Ko, S.; Verploegen, E.; Hong, S.; Mondal, R.; Hoke, E. T.; Toney, M. F.; McGehee, M. D.; Bao, Z. *J. Am. Chem. Soc.* **2011**, *133*, 16722–16725.

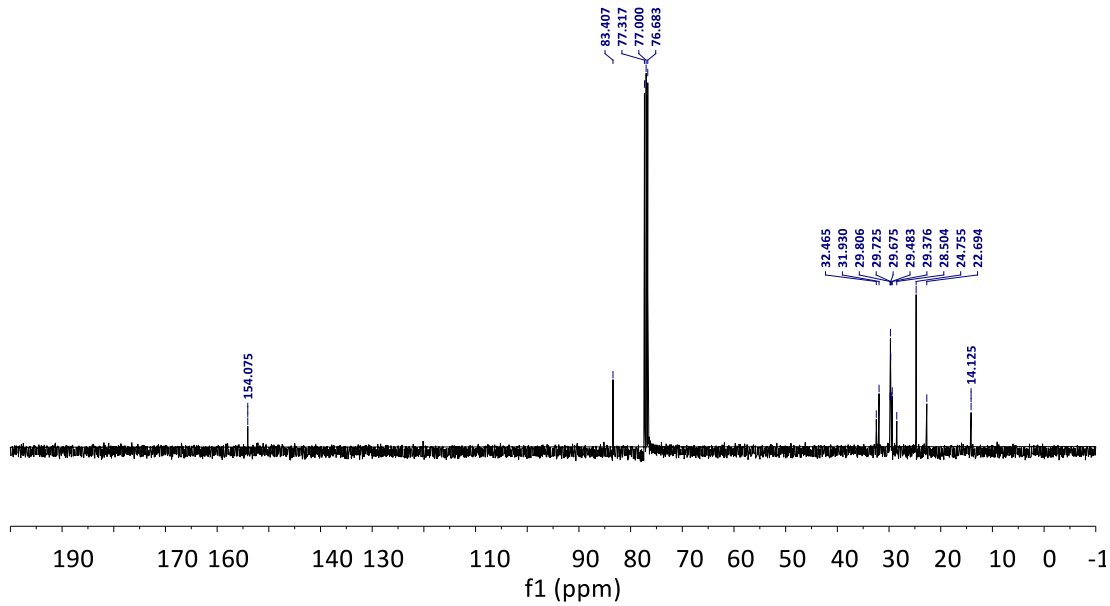
S2. Nantalaksakul, A.; Krishnamoorthy, K.; Thayumanavan, S. *Macromolecules* **2010**, *43*, 37–43.

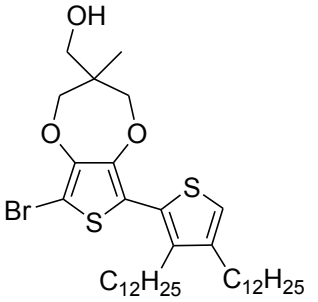
^{1}H and ^{13}C NMR spectra for all new compounds





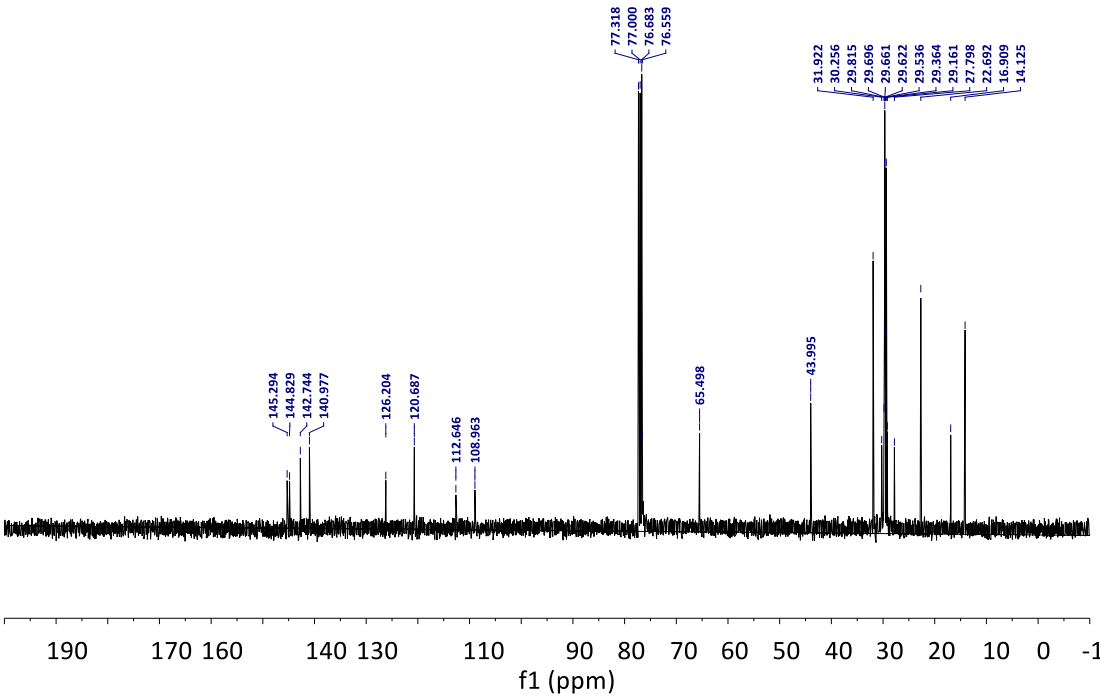

C12H25
C12H25
O
B
O
S
B
O
O
21
7.260
2.797
2.778
2.758
1.549
1.499
1.484
1.465
1.446
1.427
1.340
1.319
1.303
1.259
0.896
0.879
0.862
4.00
4.09
61.23
6.51
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
2.0
1.5
1.0
0.0
f1 (ppm)

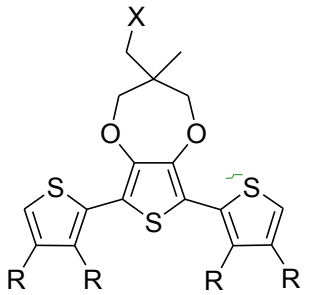

83.407
77.317
77.000
76.683
154.075
32.465
31.930
29.806
29.725
29.675
29.483
29.376
28.504
24.755
22.694
14.125
190
170
160
140
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


OH
O
O
S
Br
S
$C_{12}H_{25}$
$C_{12}H_{25}$

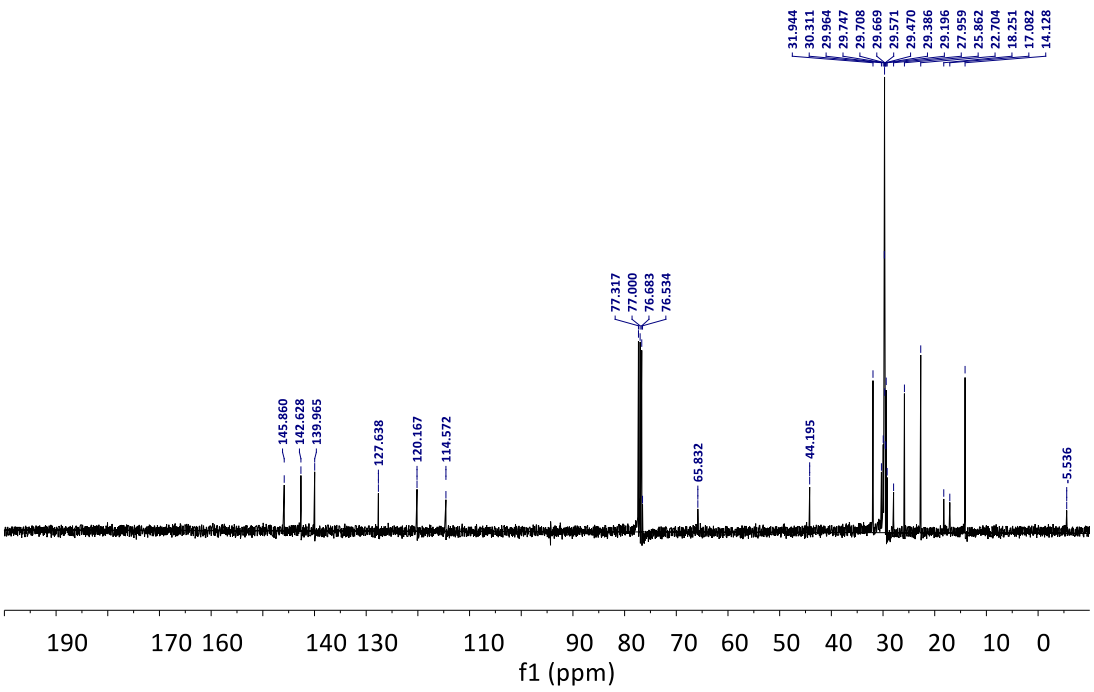
19

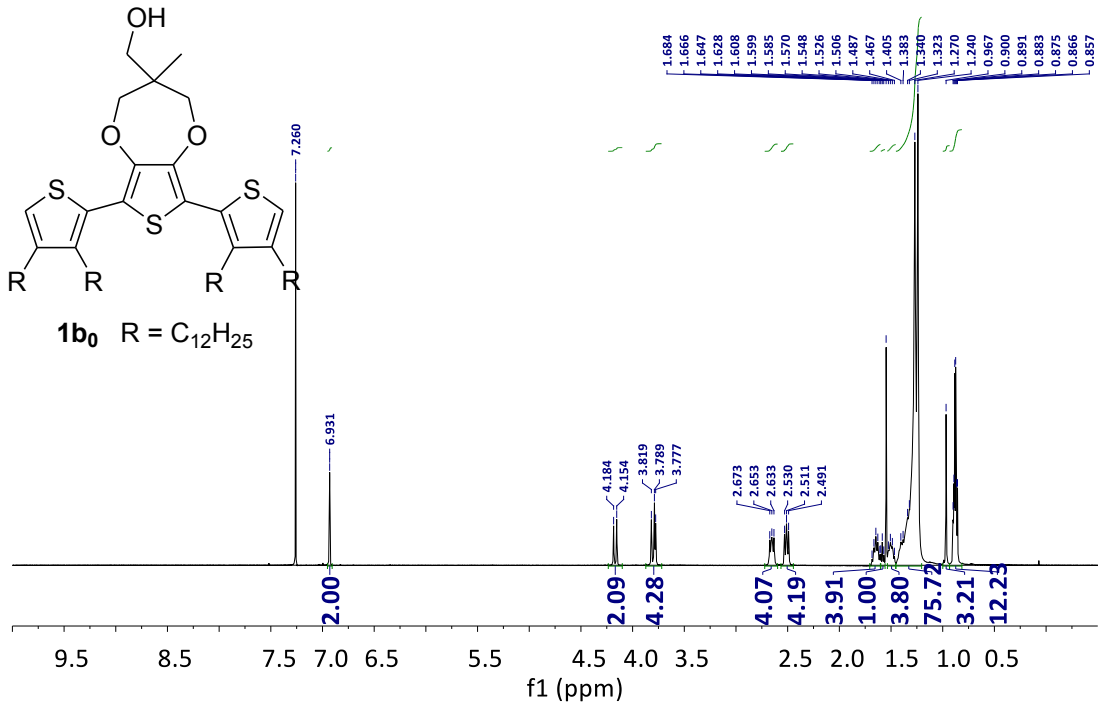
1.672
1.653
1.635
1.616
1.596
1.582
1.560
1.476
1.459
1.448
1.439
1.418
1.395
1.376
1.319
1.303
1.269
1.259
0.980
0.899
0.884
0.882
0.866
7.260
6.931
4.210
4.179
4.135
4.105
3.856
3.825
3.795
3.764
3.757
3.751
2.589
2.570
2.549
2.515
2.496
2.476
1.00
1.05
1.03
4.18
2.04
2.03
3.49
39.63
2.96
5.89
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

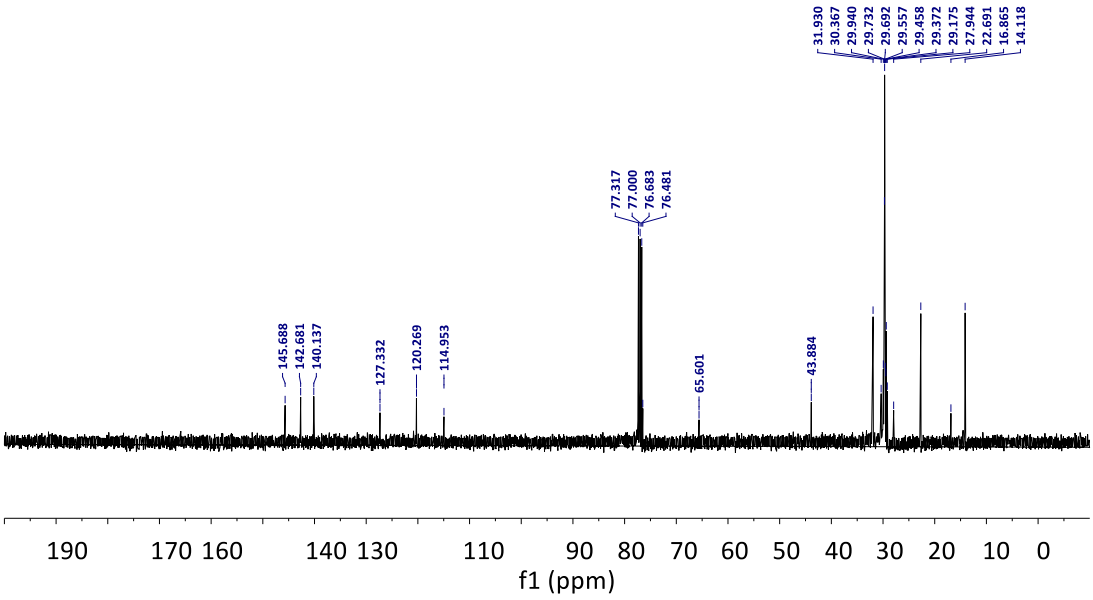

77.318
77.000
76.683
76.559
31.922
30.256
29.815
29.696
29.661
29.622
29.536
29.364
29.161
27.798
22.692
16.909
14.125
145.294
144.829
142.744
140.977
126.204
120.687
112.646
108.963
65.498
43.995
190
170
160
140
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

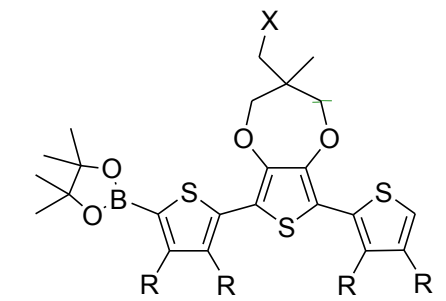


1a$_0$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

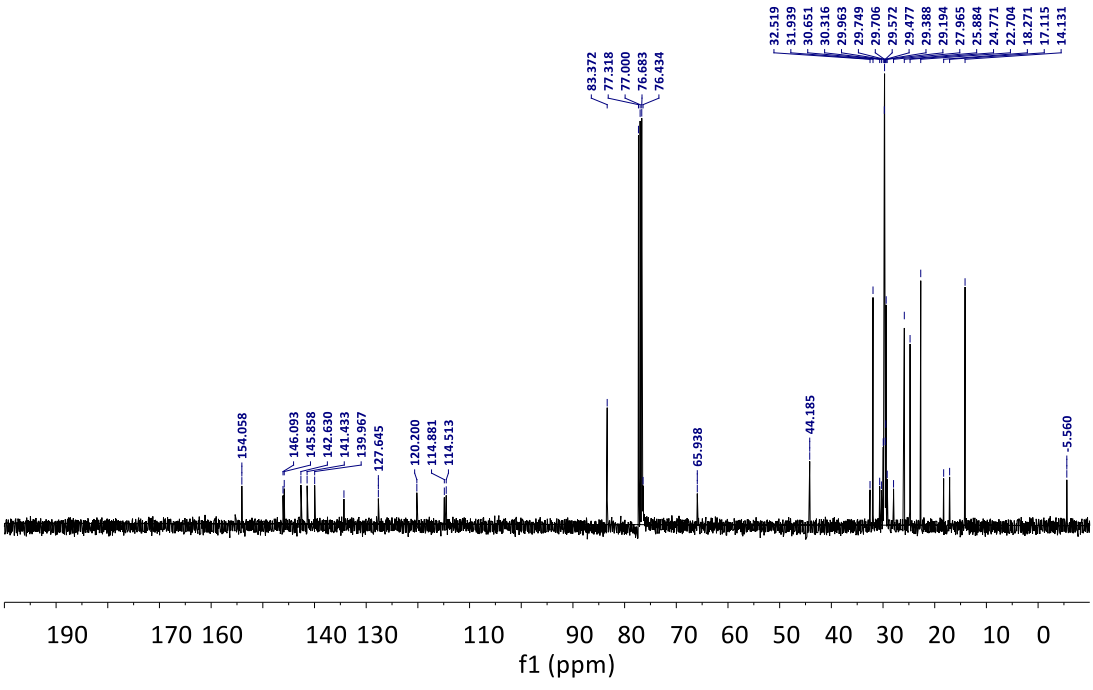


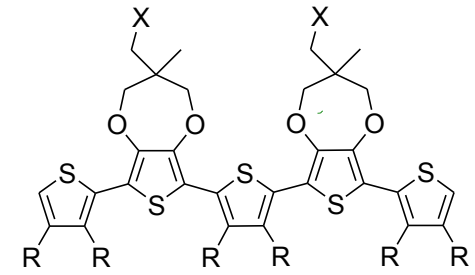

OH
O
O
S
S
S
R
R
R
R
1b0 R = C12H25
7.260
6.931
4.184
4.154
3.819
3.789
3.777
2.673
2.653
2.633
2.530
2.511
2.491
1.684
1.666
1.647
1.628
1.608
1.599
1.585
1.570
1.548
1.526
1.506
1.487
1.467
1.405
1.383
1.340
1.323
1.270
1.240
0.967
0.900
0.891
0.883
0.875
0.866
0.857
2.00
2.09
4.28
4.07
4.19
3.91
1.00
3.80
75.72
3.21
12.23
9.5 8.5 7.5 7.0 6.5 5.5 4.5 4.0 3.5 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


31.930
30.367
29.940
29.732
29.692
29.557
29.458
29.372
29.175
27.944
22.691
16.865
14.118
77.317
77.000
76.683
76.481
145.688
142.681
140.137
127.332
120.269
114.953
65.601
43.884
190 170 160 140 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

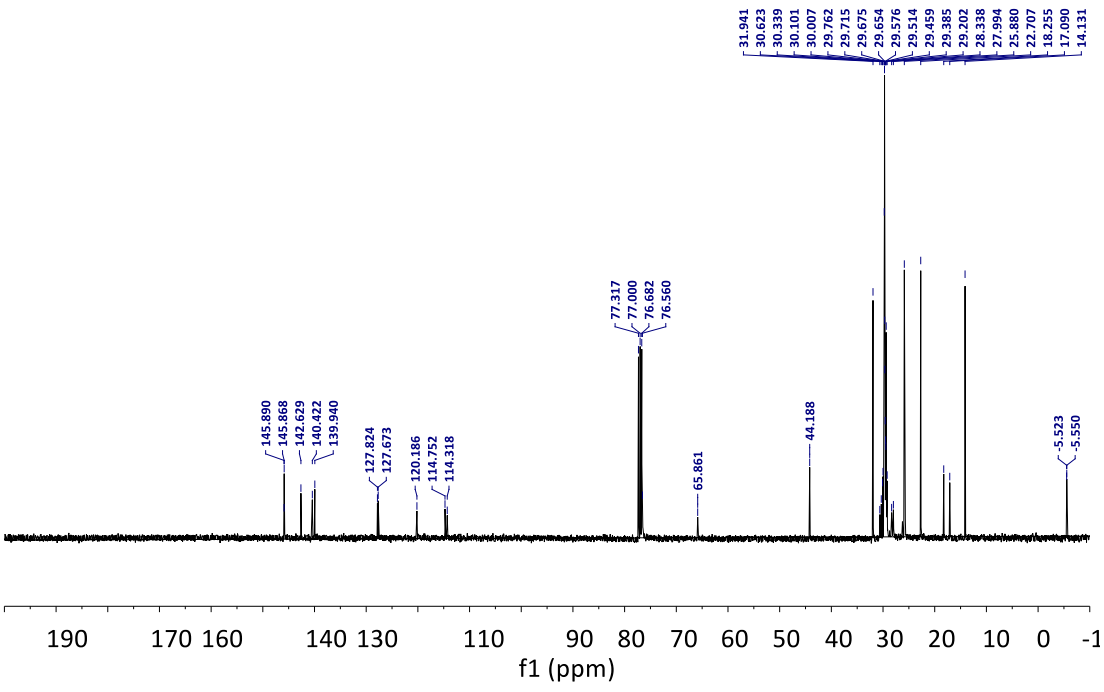


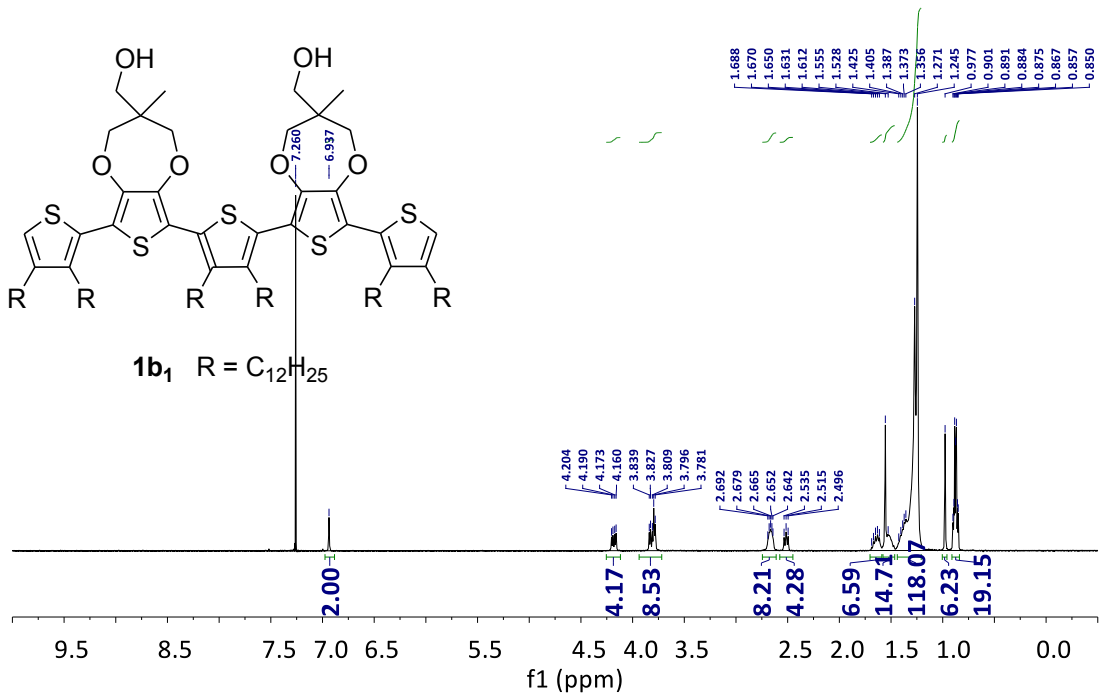
22 X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

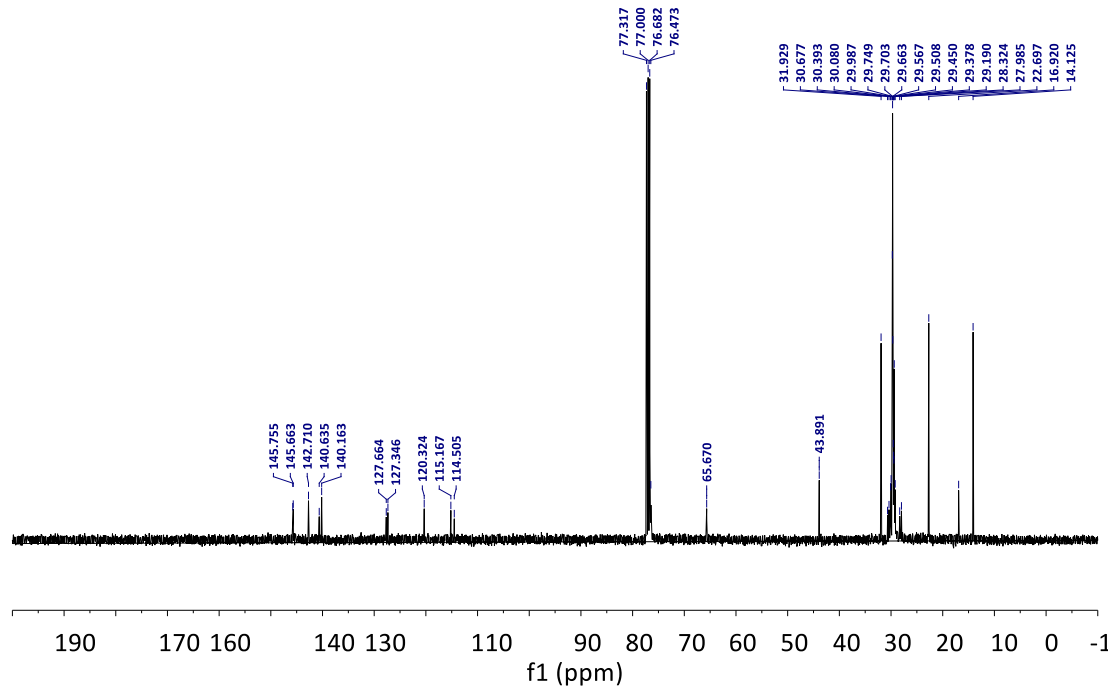


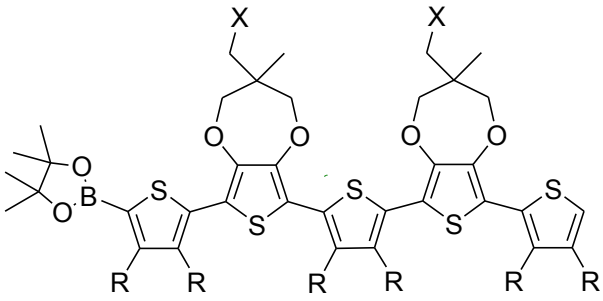


1a$_1$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

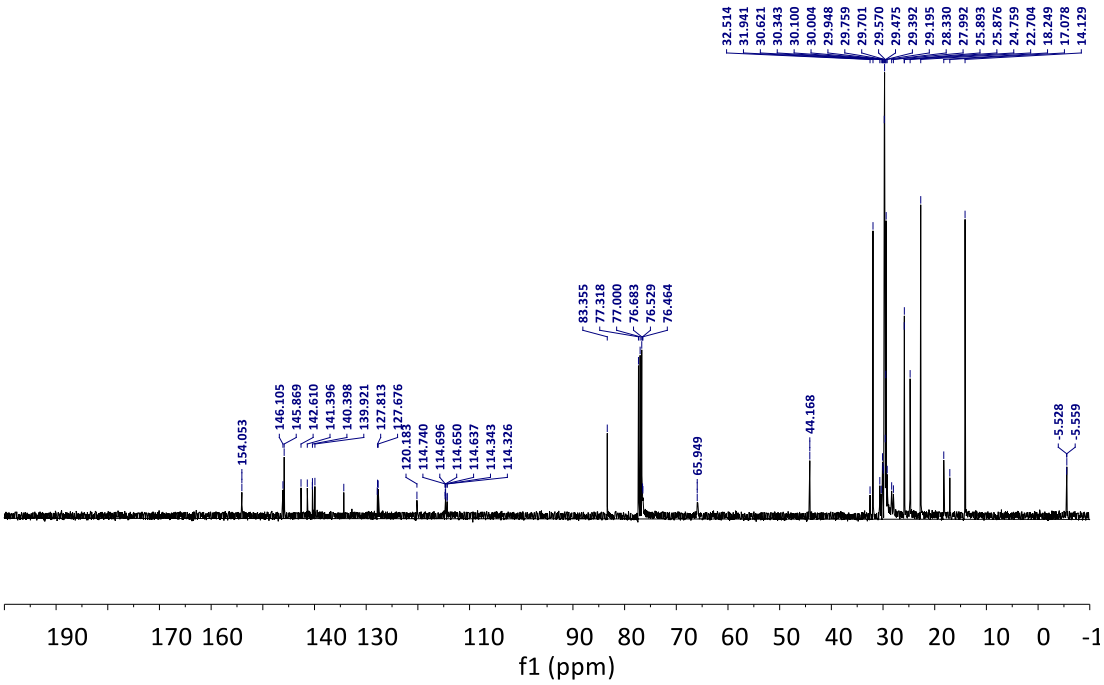


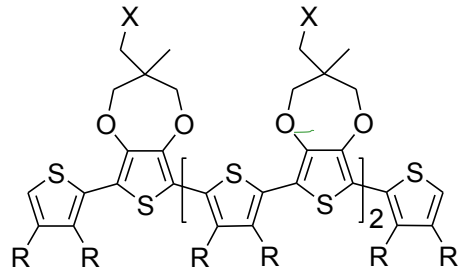

OH
OH
O
O
O
O
S
S
S
S
S
S
R
R
R
R
R
R
7.260
6.937
1b1 R = C12H25
1.688
1.670
1.650
1.631
1.612
1.555
1.528
1.425
1.405
1.387
1.373
1.356
1.271
1.245
0.977
0.901
0.891
0.884
0.875
0.867
0.857
0.850
4.204
4.190
4.173
4.160
3.839
3.827
3.809
3.796
3.781
2.692
2.679
2.665
2.652
2.642
2.535
2.515
2.496
2.00
4.17
8.53
8.21
4.28
6.59
14.71
118.07
6.23
19.15
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
2.0
1.5
1.0
0.0
f1 (ppm)


77.317
77.000
76.682
76.473
31.929
30.677
30.393
30.080
29.987
29.749
29.703
29.663
29.567
29.508
29.450
29.378
29.190
28.324
27.985
22.697
16.920
14.125
145.755
145.663
142.710
140.635
140.163
127.664
127.346
120.324
115.167
114.505
65.670
43.891
190
170
160
140
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

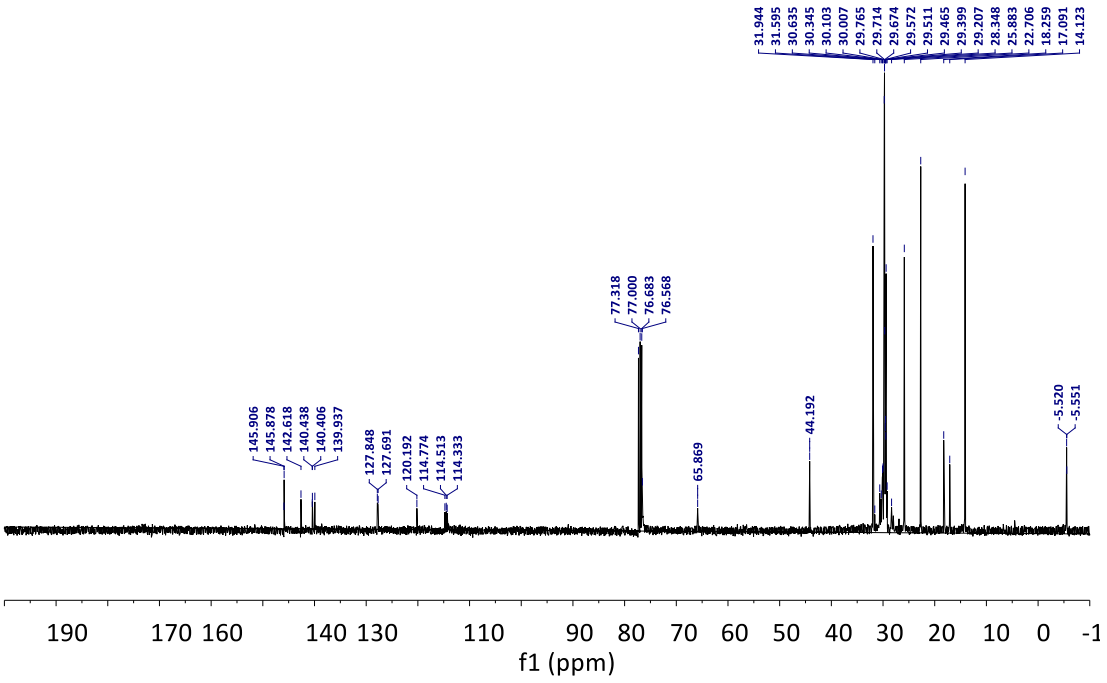


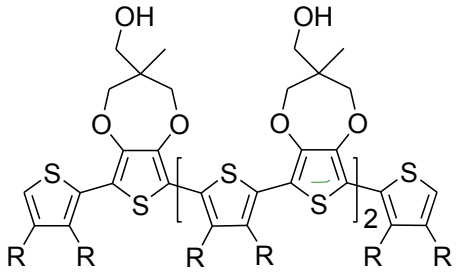
23 X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$





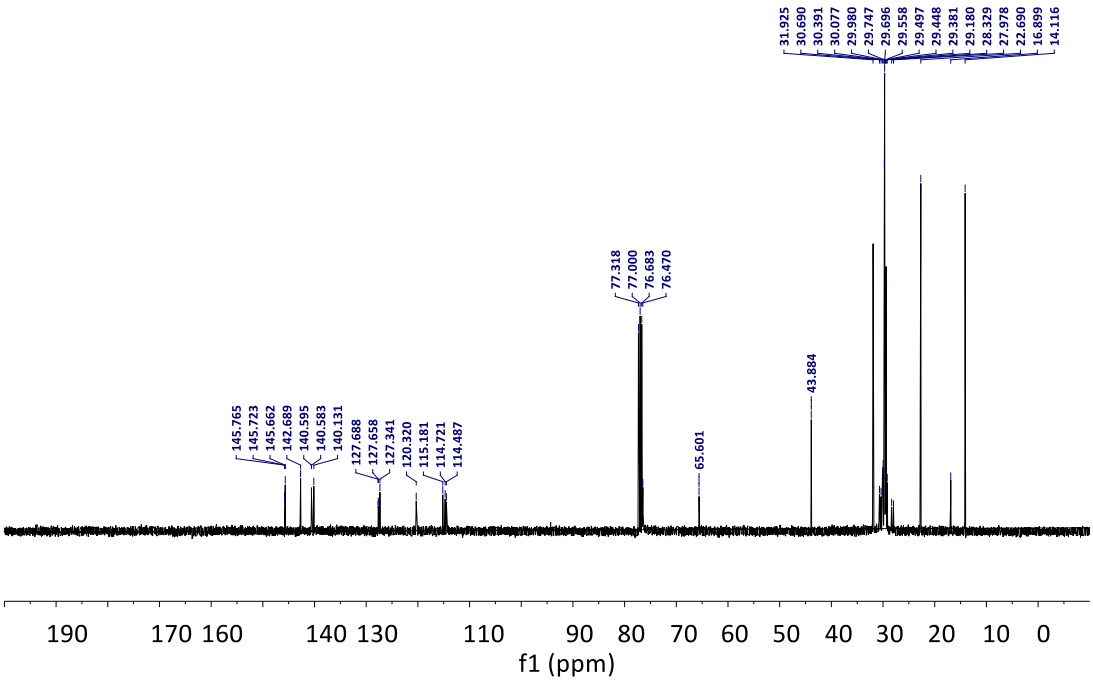
1a$_2$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

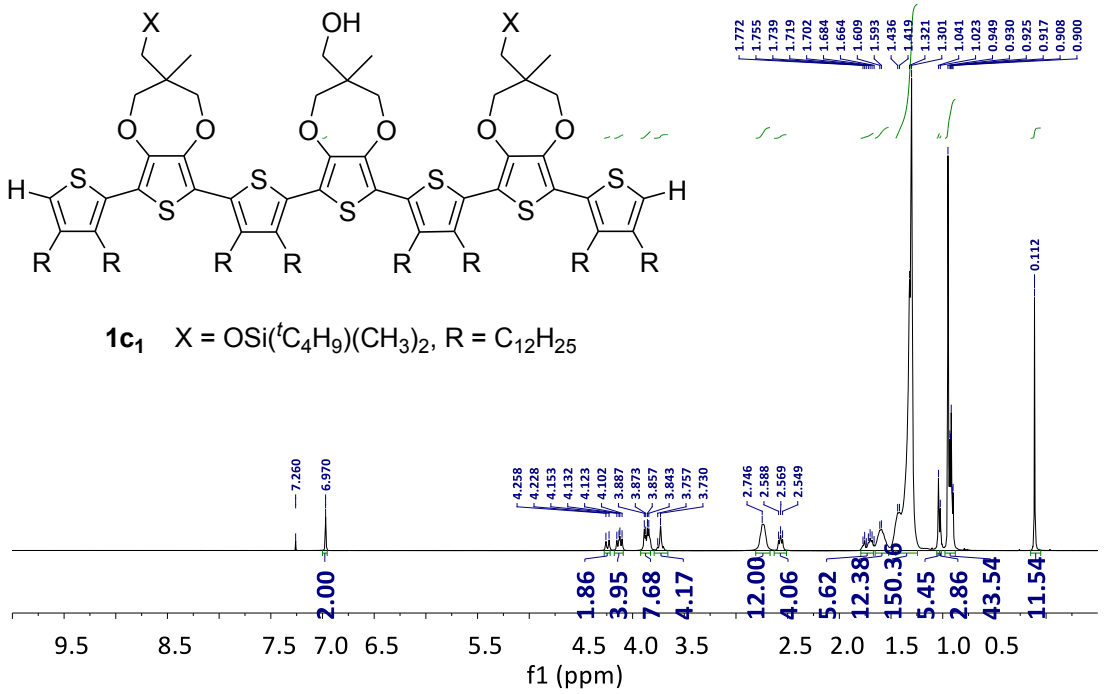



OH
OH
O
O
O
O
S
S
S
S
S
2
R
R
R
R
R
R

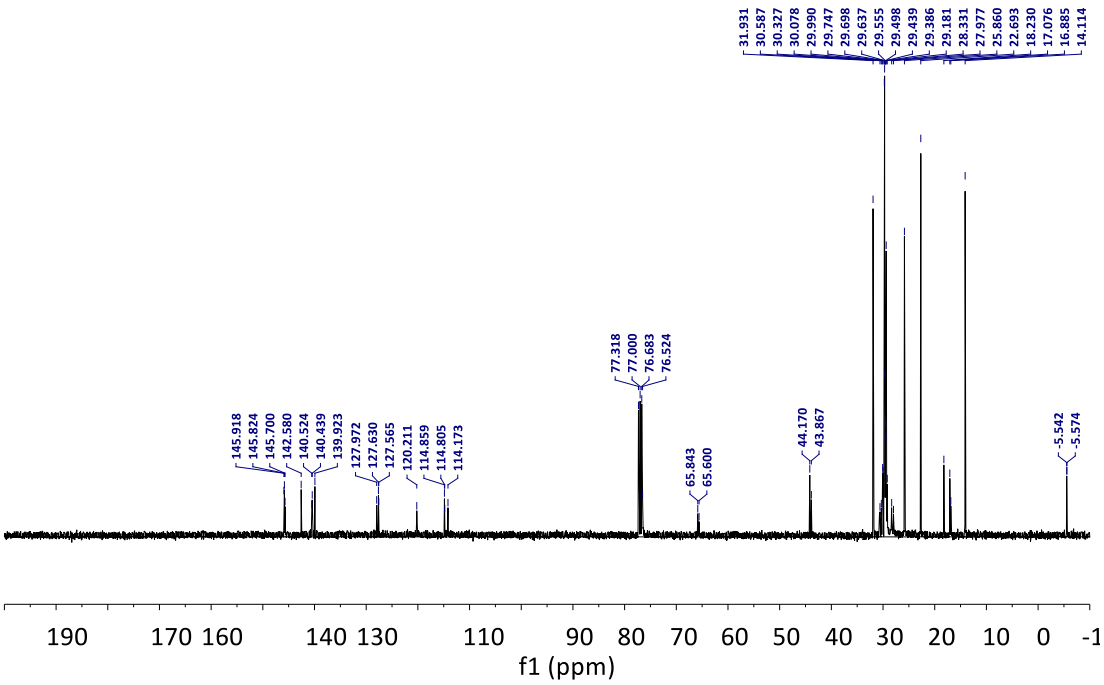
1b$_2$ R = $C_{12}H_{25}$

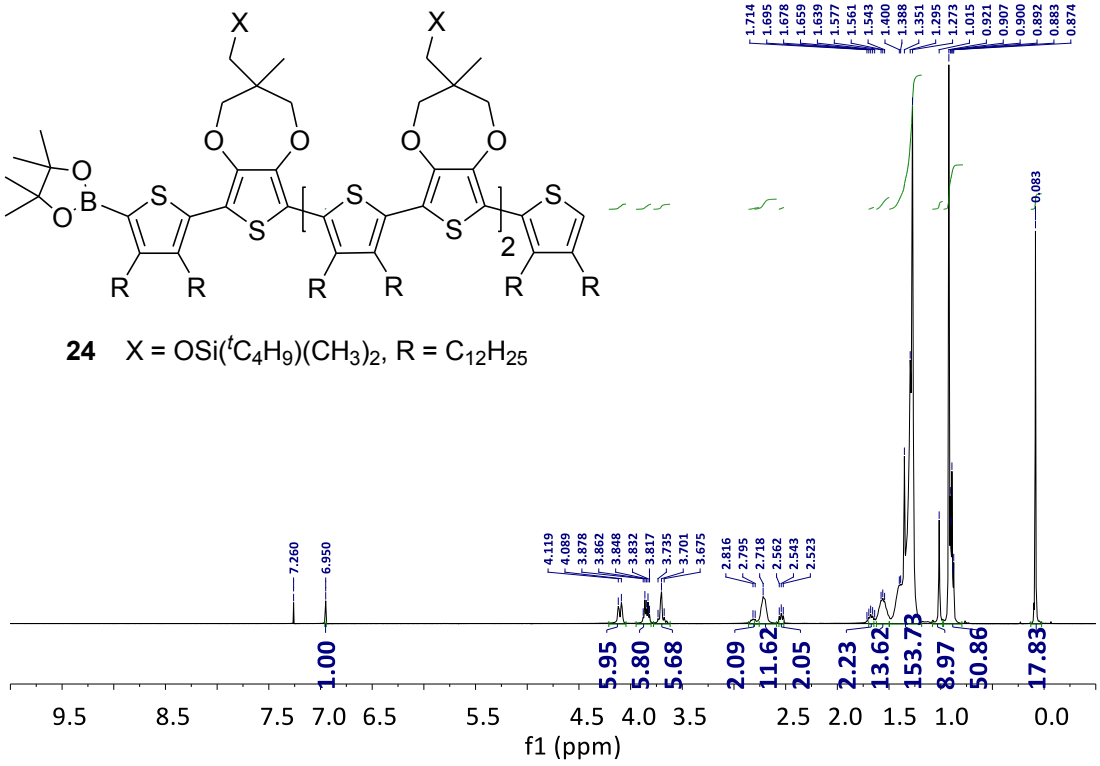
1.832
1.699
1.680
1.662
1.644
1.624
1.564
1.548
1.385
1.373
1.283
0.984
0.895
0.887
0.879
0.870
0.862
7.260
6.945
4.220
4.190
4.167
3.848
3.831
3.818
3.798
2.697
2.547
2.528
2.508
2.00
6.06
11.81
11.51
3.77
3.00
3.63
11.30
145.89
8.80
25.11
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


31.925
30.690
30.391
30.077
29.980
29.747
29.696
29.558
29.497
29.448
29.381
29.180
28.329
27.978
22.690
16.899
14.116
77.318
77.000
76.683
76.470
145.765
145.723
145.662
142.689
140.595
140.583
140.131
127.688
127.658
127.341
120.320
115.181
114.721
114.487
65.601
43.884
190
170
160
140
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

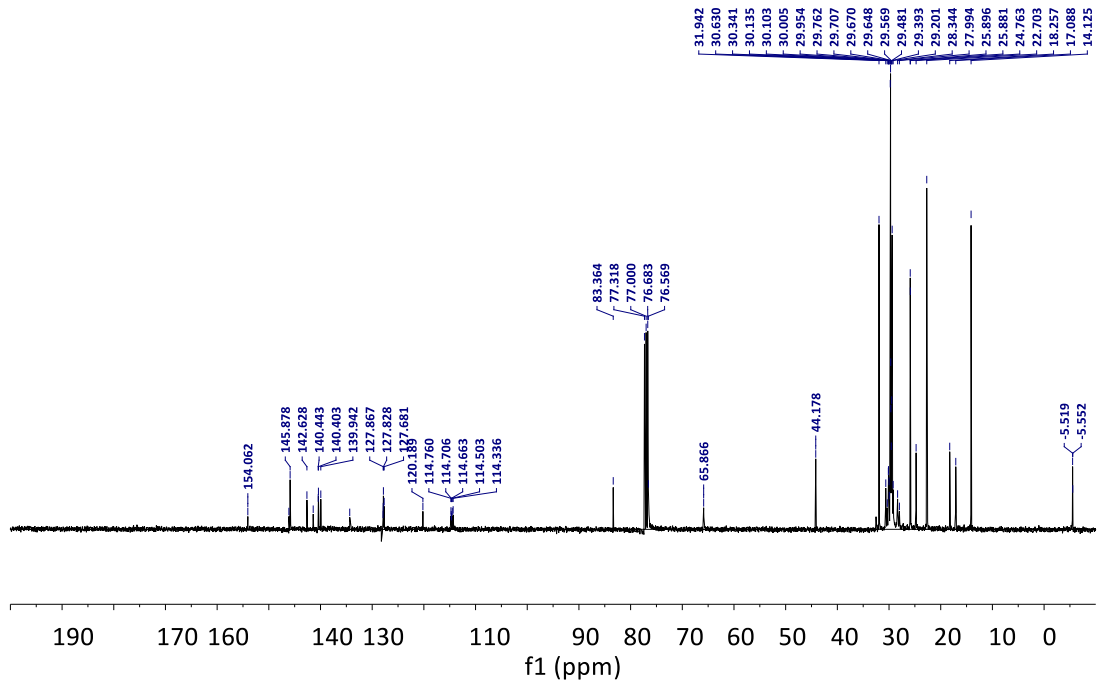


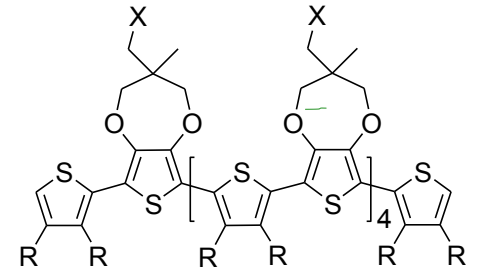
1c$_1$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$



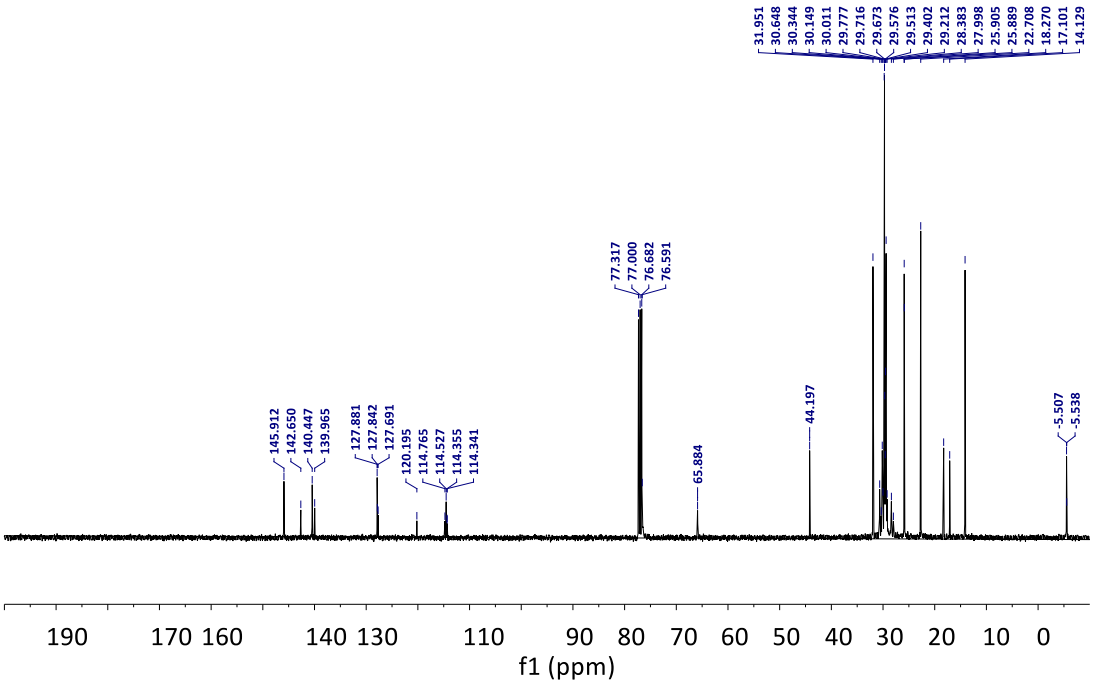


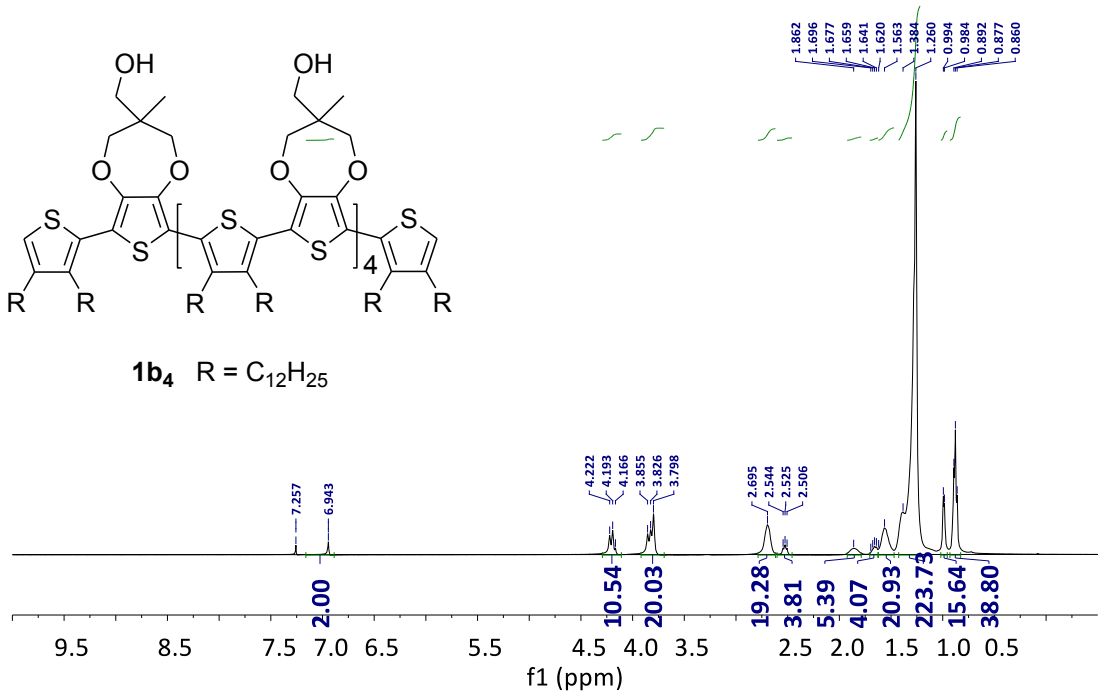
24 X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

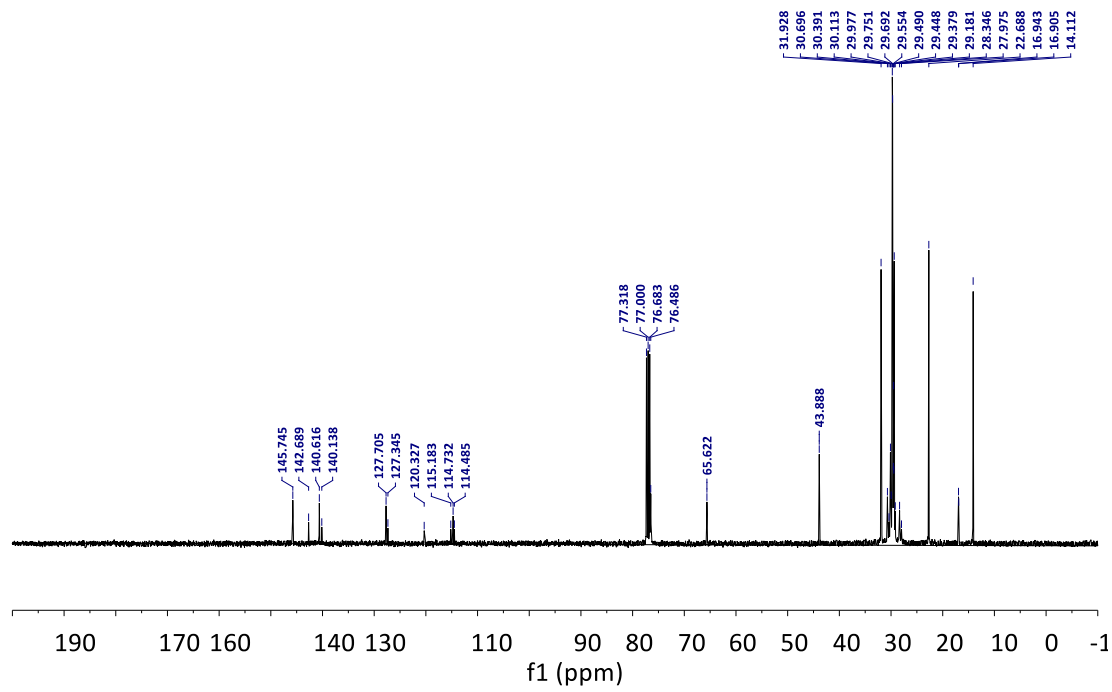


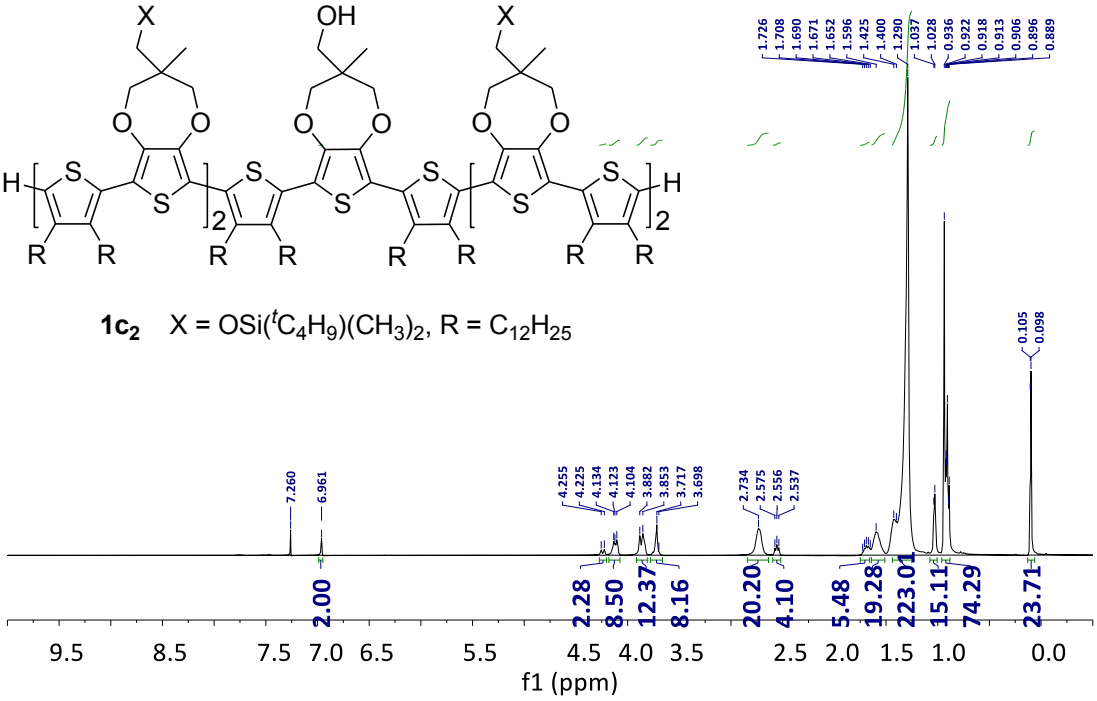


1a$_4$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

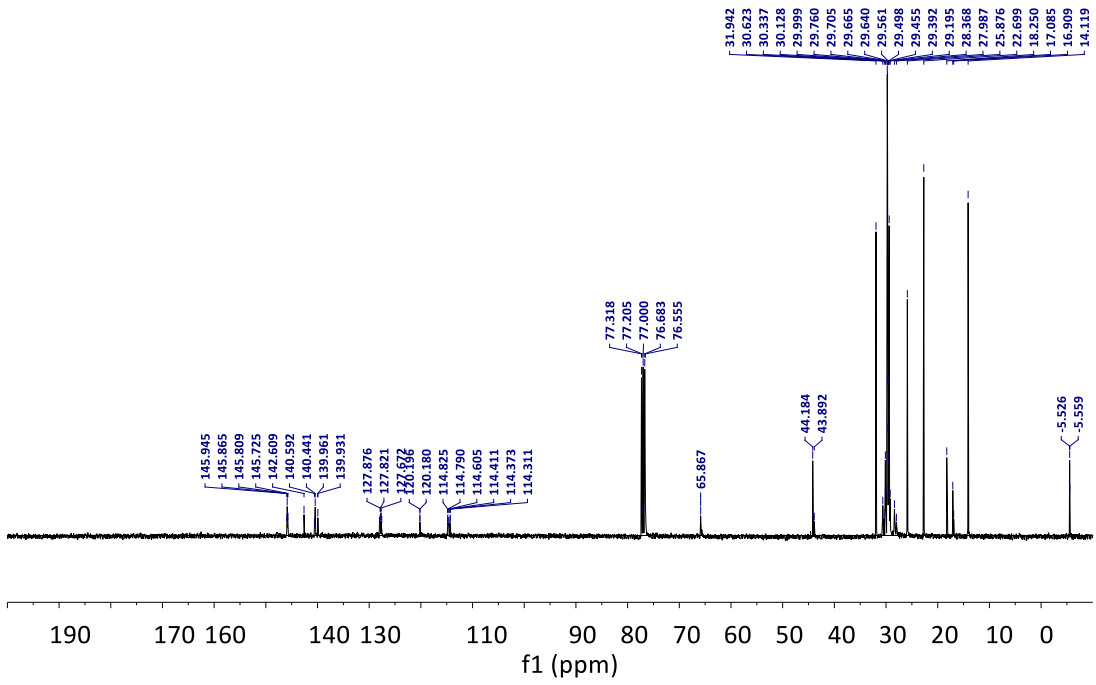


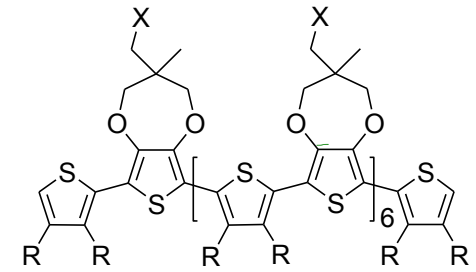

OH
OH
O
O
O
O
S
S
S
S
S
S
4
R
R
R
R
R
R
1b4 R = C12H25
1.862
1.696
1.677
1.659
1.641
1.620
1.563
1.384
1.260
0.994
0.984
0.892
0.877
0.860
7.257
6.943
4.222
4.193
4.166
3.855
3.826
3.798
2.695
2.544
2.525
2.506
2.00
10.54
20.03
19.28
3.81
5.39
4.07
20.93
223.75
15.64
38.80
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


31.928
30.696
30.391
30.113
29.977
29.751
29.692
29.554
29.490
29.448
29.379
29.181
28.346
27.975
22.688
16.943
16.905
14.112
77.318
77.000
76.683
76.486
65.622
43.888
145.745
142.689
140.616
140.138
127.705
127.345
120.327
115.183
114.732
114.485
190
170
160
140
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

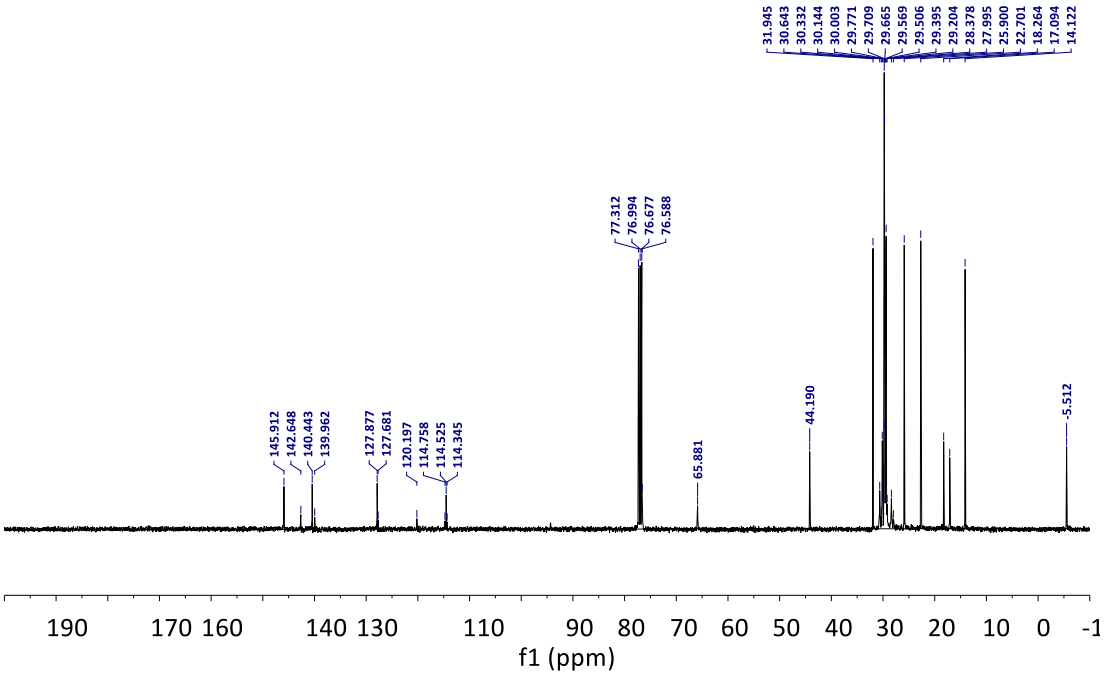


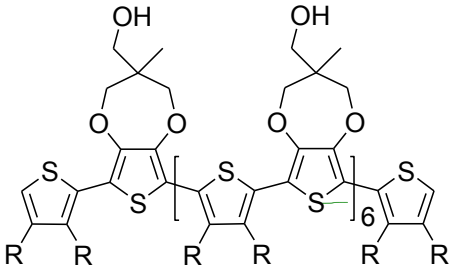
1c$_2$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$





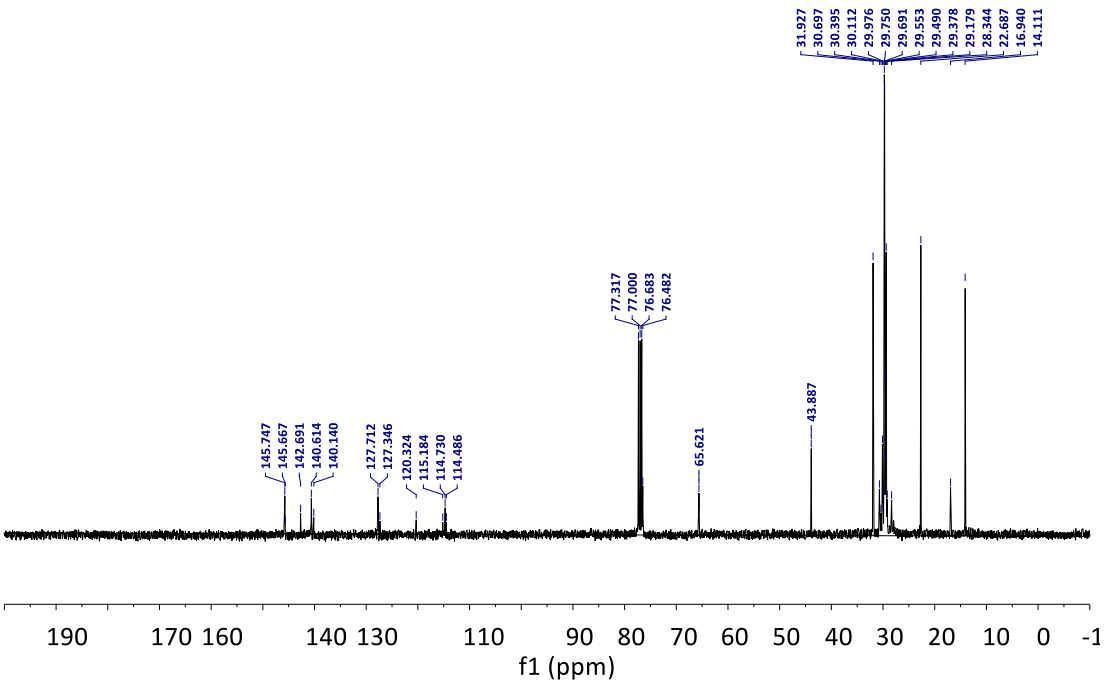
1a$_6$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

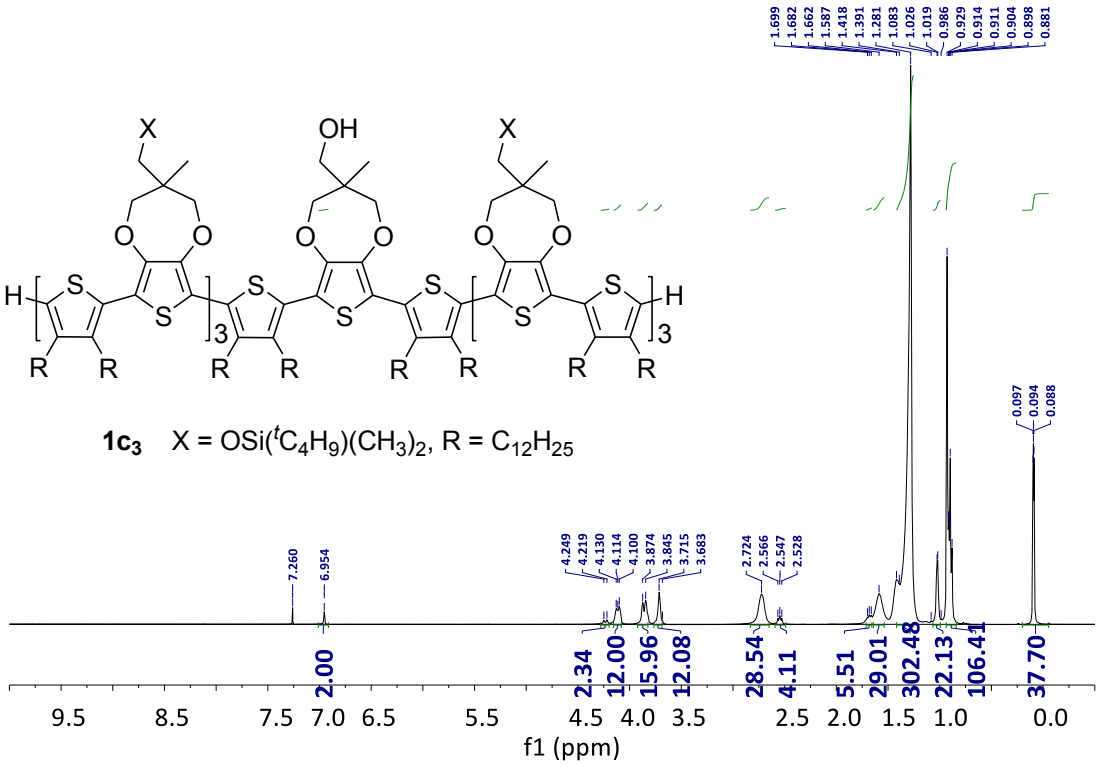


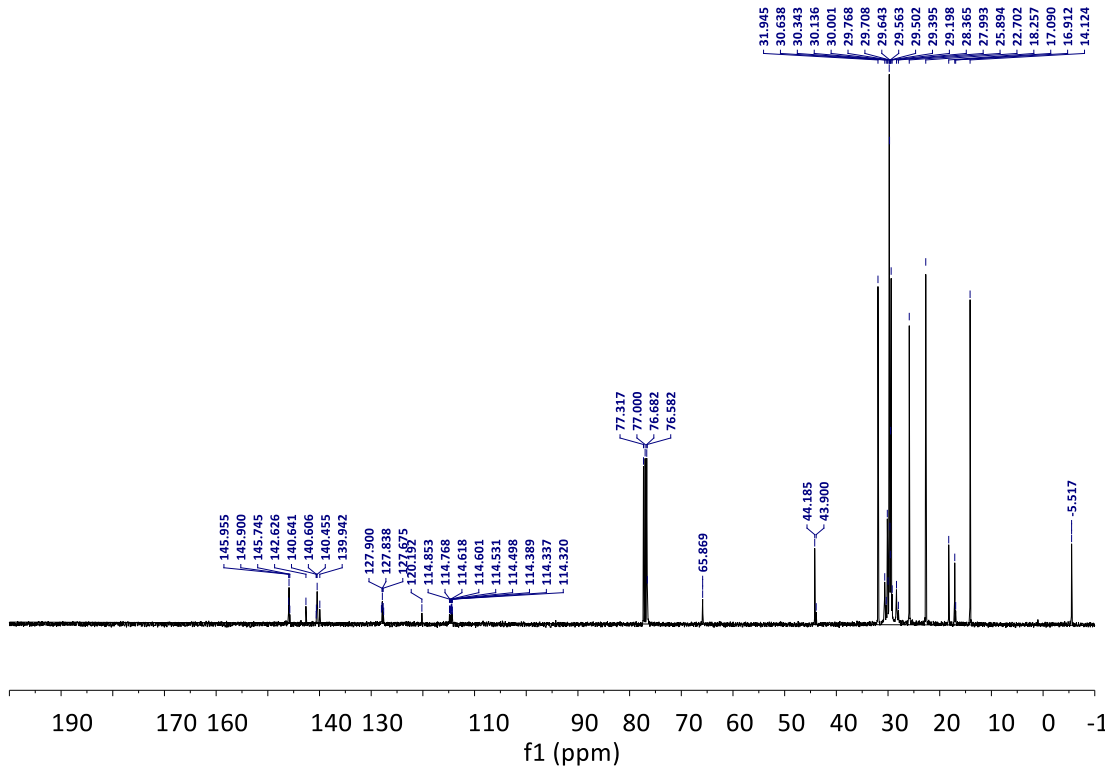

OH
OH
O
O
O
O
S
S
S
S
S
S
6
R
R
R
R
R
R

1b$_6$ R = $C_{12}H_{25}$

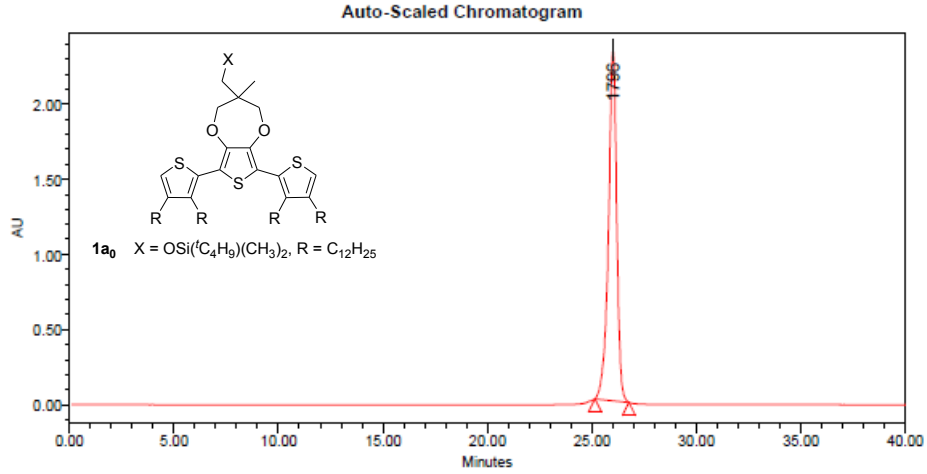
1.648
1.583
1.565
1.488
1.319
1.183
0.923
0.912
0.816
0.801
0.783
7.189
6.870
4.148
4.120
4.093
3.783
3.753
3.729
2.615
2.468
2.448
2.429
2.00
14.65
29.74
28.05
4.42
42.15
315.85
23.22
51.04
9.5
8.5
7.5
7.0
6.5
5.5
4.5
4.0
3.5
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


31.927
30.697
30.395
30.112
29.976
29.750
29.691
29.553
29.490
29.378
29.179
28.344
22.687
16.940
14.111
77.317
77.000
76.683
76.482
145.747
145.667
142.691
140.614
140.140
127.712
127.346
120.324
115.184
114.730
114.486
65.621
43.887
190
170
160
140
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


X
OH
X
H
R
3
1c3 X = OSi(tC4H9)(CH3)2, R = C12H25
f1 (ppm)

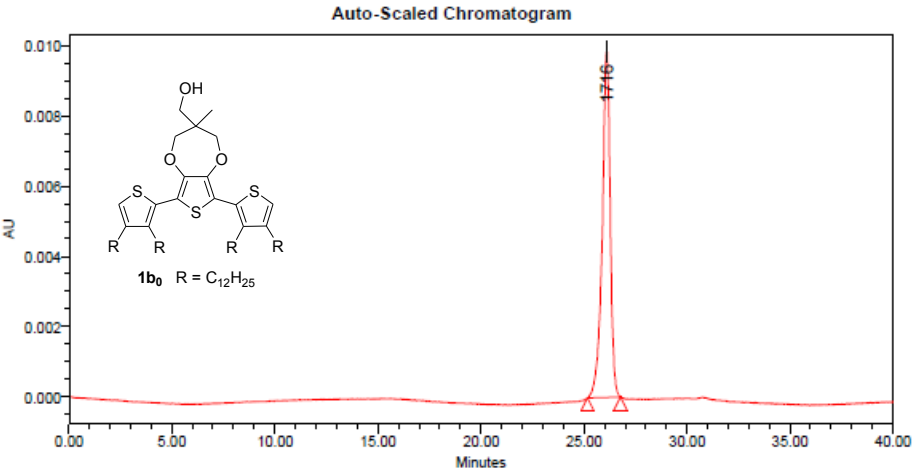

f1 (ppm)

GPC profiles for **1a**, **1b**, and **1c**.



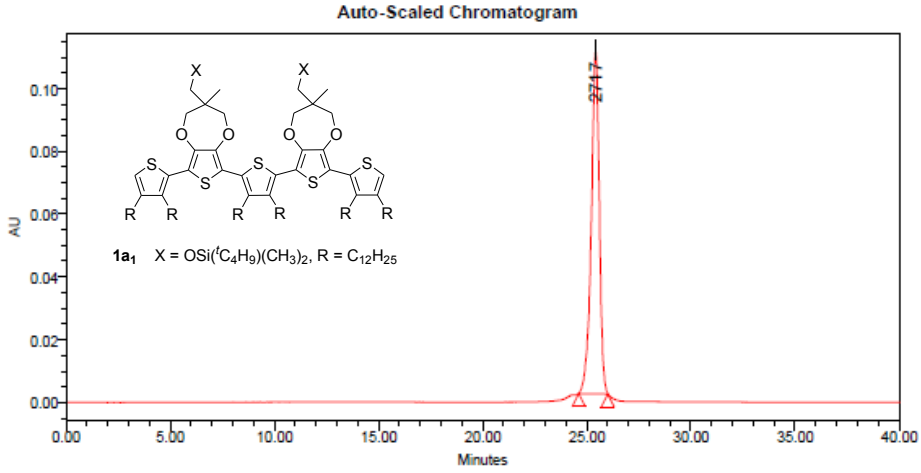
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		1816	1839	1796	1863	1888		1.012570		



GPC Results

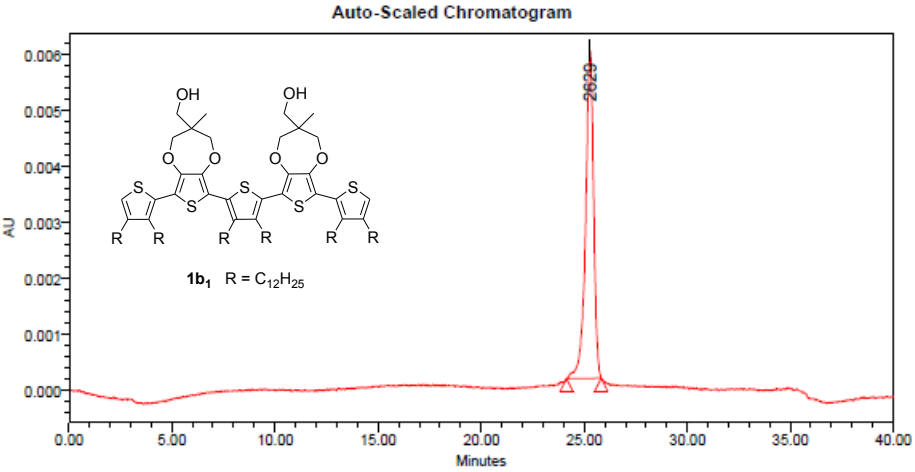
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		1733	1756	1716	1779	1804		1.012802		



1a$_1$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

GPC Results

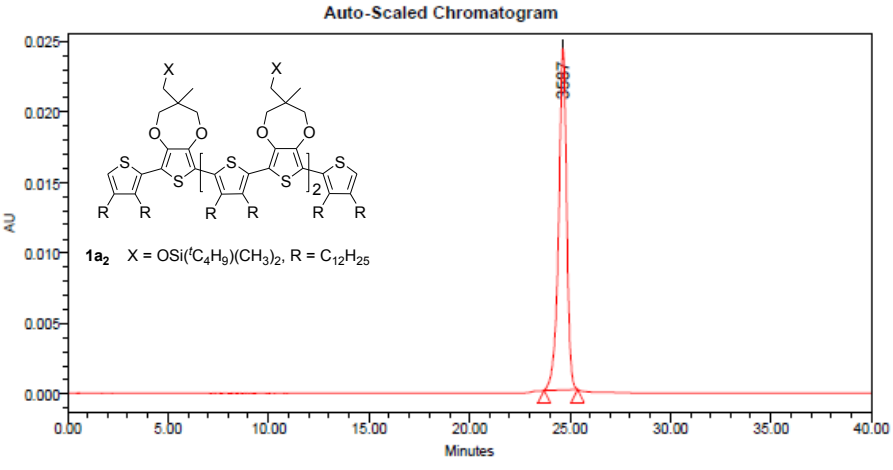
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		2755	2778	2717	2802	2827		1.008368		



1b$_1$ R = C$_{12}$H$_{25}$

GPC Results

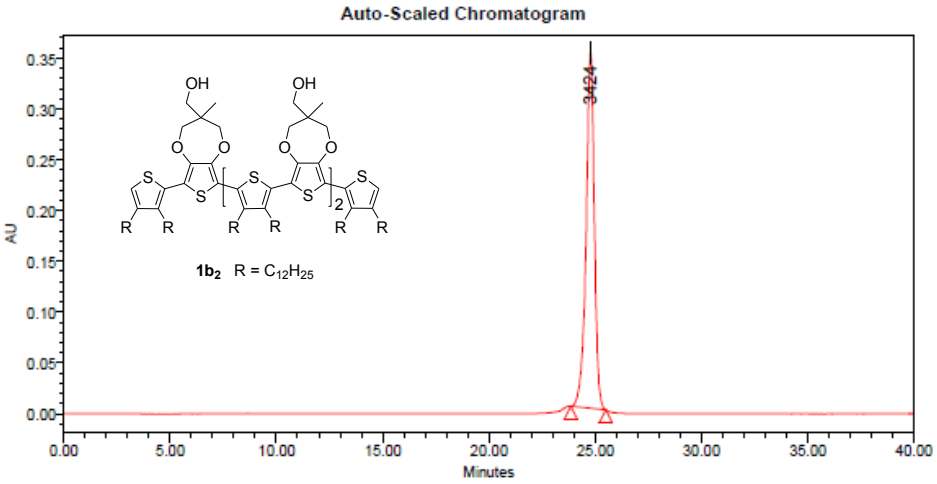
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		2668	2698	2629	2731	2769		1.011284		



1a$_2$ X = OSi(^{t}C$_4$H$_9$)(CH$_3$)$_2$, R = C$_{12}$H$_{25}$

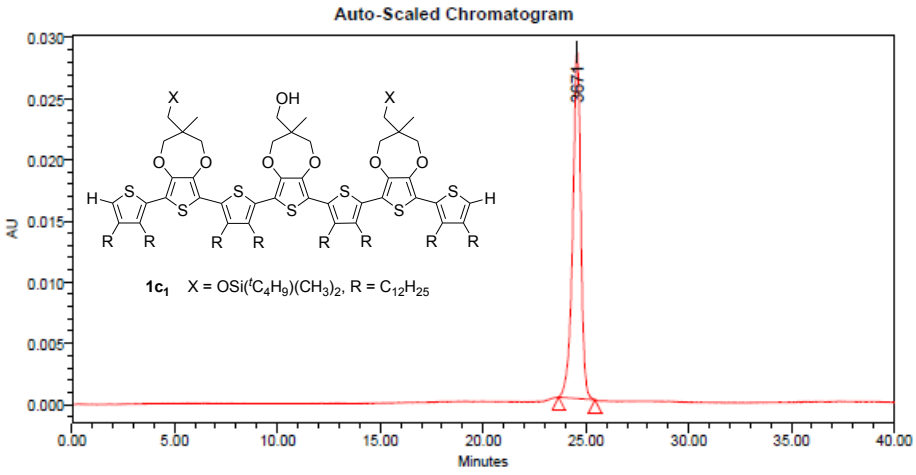
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		3589	3621	3587	3654	3687		1.008947		



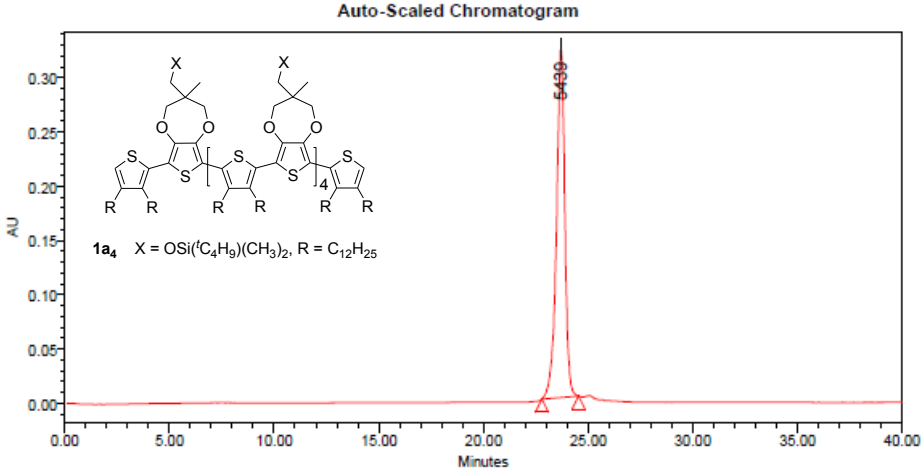
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		3461	3495	3424	3531	3568		1.010083		



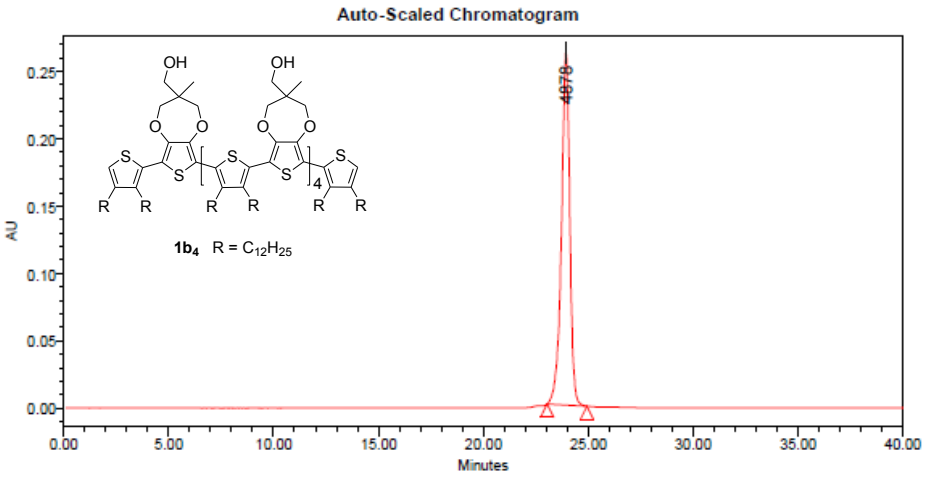
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		3710	3743	3671	3778	3815		1.009086		



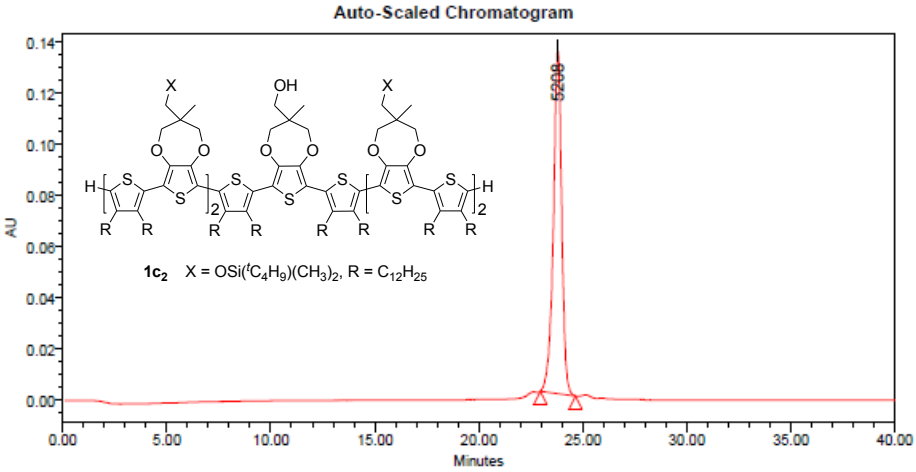
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		5460	5505	5439	5552	5600		1.008245		



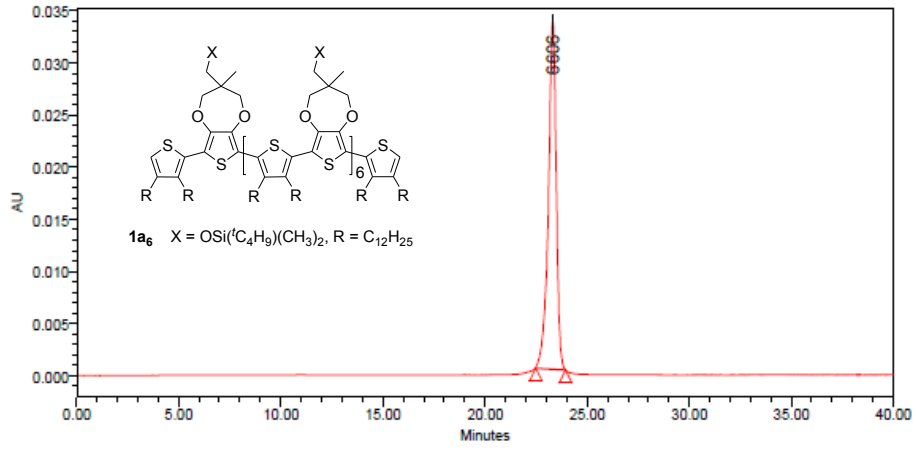
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	
1		4931	4973	4878	5016	5061		1.008474	MW Marker 2	



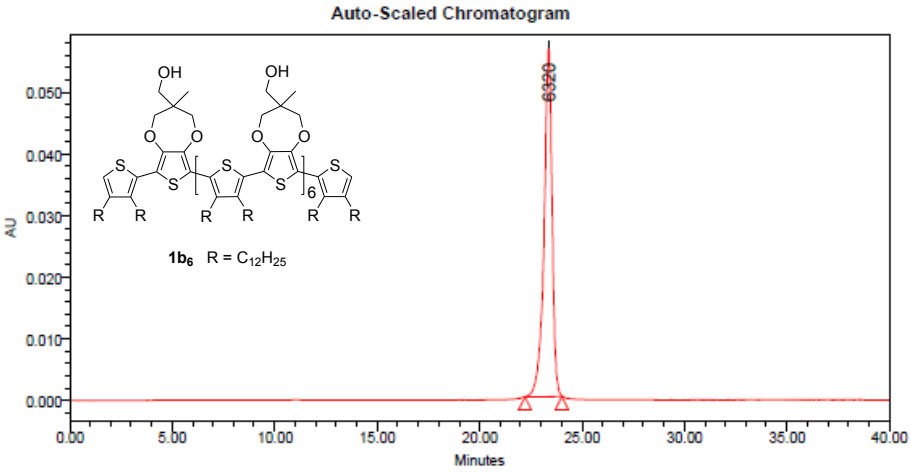
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		5231	5273	5208	5317	5362		1.008088		



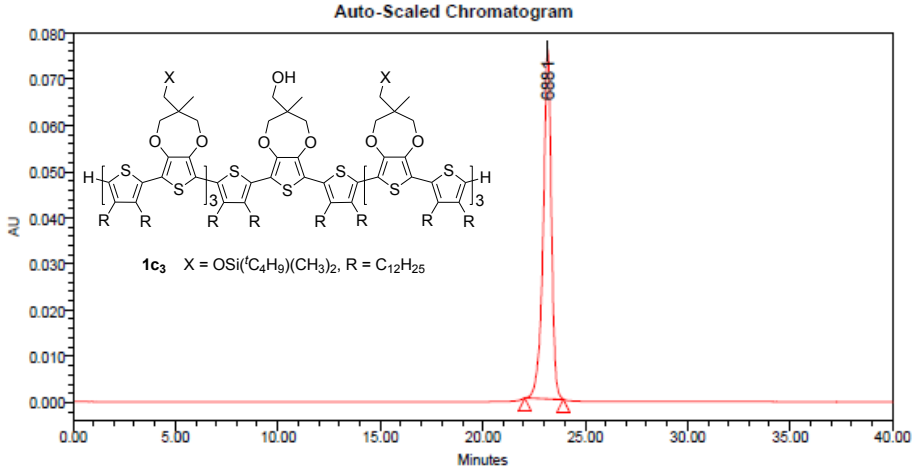
GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		6635	6717	6606	6751	6814		1.012307		



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		6356	6411	6320	6469	6529		1.008687		



GPC Results

	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		6840	6911	6881	6976	7042		1.010348		

Plots of M_n, and M_c against M_r values for **1-15**.

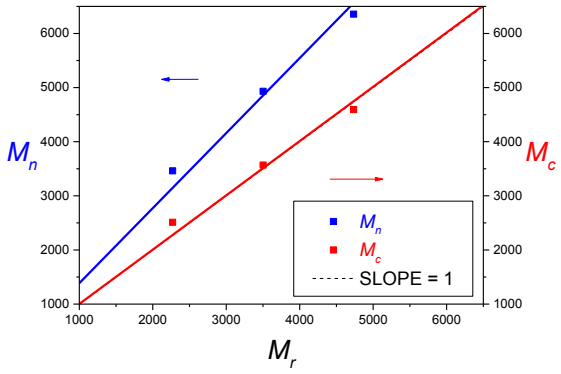


Figure S1. M_r vs M_n and M_r vs M_c for **1b$_n$** (SLOPE (M_n) = 1.39, R^2 = 0.99; SLOPE (M_c) = 1.00, R^2 = 0.99).

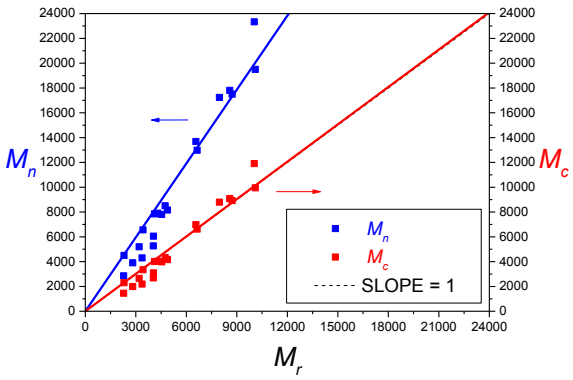


Figure S2. M_r vs M_n and M_r vs M_c for **2$_n$** (SLOPE (M_n) = 1.98, R^2 = 0.94; SLOPE (M_c) = 1.00, R^2 = 0.94).

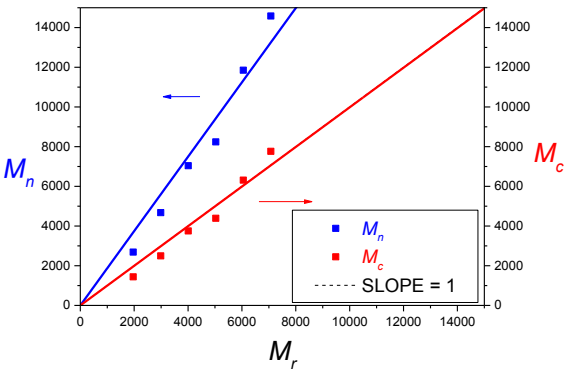


Figure S3. M_r vs M_n and M_r vs M_c for **3$_n$** (SLOPE (M_n) = 1.87, R^2 = 0.96; SLOPE (M_c) = 1.00, R^2 = 0.96).

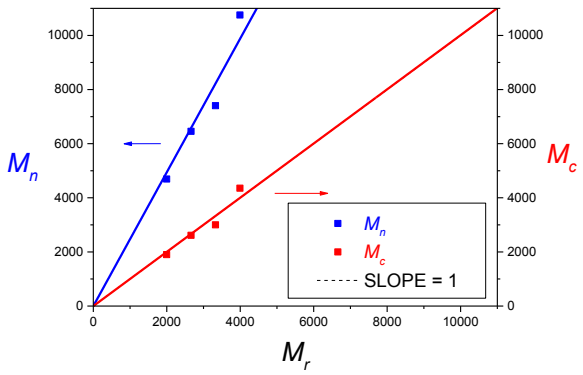


Figure S4. M_r vs M_n and M_r vs M_c for $\mathbf{4_n}$ (SLOPE (M_n) = 2.47, R^2 = 0.98; SLOPE (M_c) = 1.00, R^2 = 0.98).

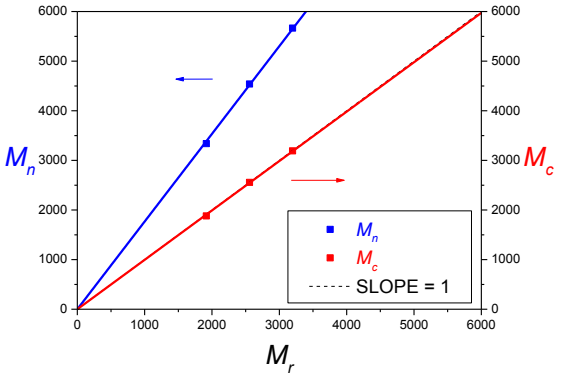


Figure S5. M_r vs M_n and M_r vs M_c for $\mathbf{5_n}$ (SLOPE (M_n) = 1.77, R^2 = 1.00; SLOPE (M_c) = 1.00, R^2 = 1.00).

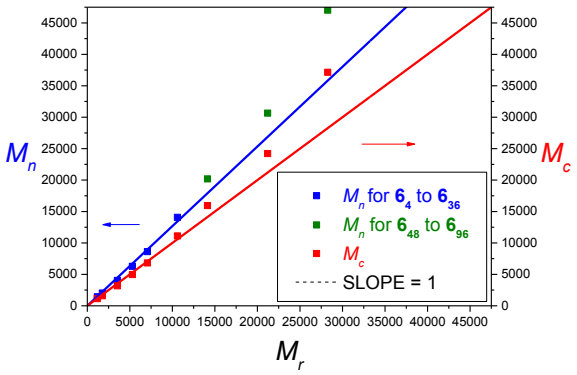


Figure S6a. M_r vs M_n and M_r vs M_c for $\mathbf{6_4}$ to $\mathbf{6_{36}}$ (SLOPE (M_n) = 1.27, R^2 = 0.99; SLOPE (M_c) = 1.00, R^2 = 0.99).

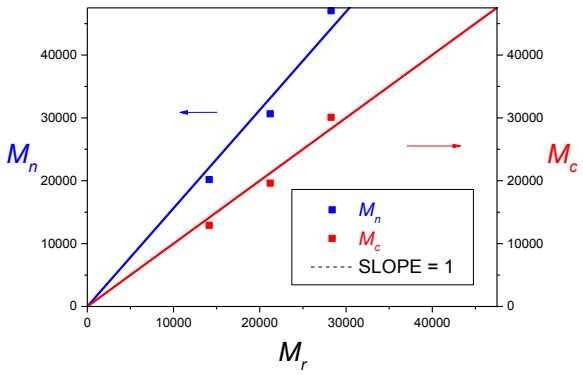


Figure S6b. M_r vs M_n and M_r vs M_c for $\mathbf{6_{48}}$ to $\mathbf{6_{96}}$ (SLOPE (M_n) = 1.56, R^2 = 0.95; SLOPE (M_c) = 1.00, R^2 = 0.95).

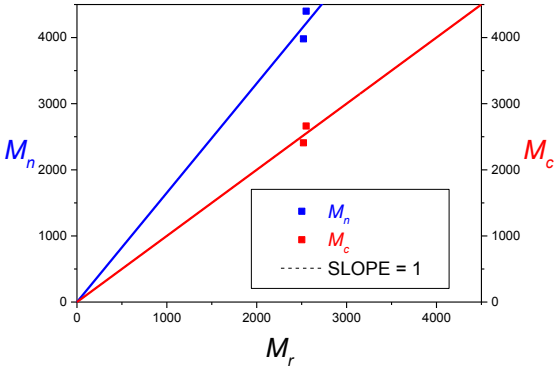


Figure S7. M_r vs M_n and M_r vs M_c for $\mathbf{7_5}$ and $\mathbf{8_6}$ (SLOPE (M_n) = 1.65, R^2 = 0.99; SLOPE (M_c) = 1.00, R^2 = 0.99).

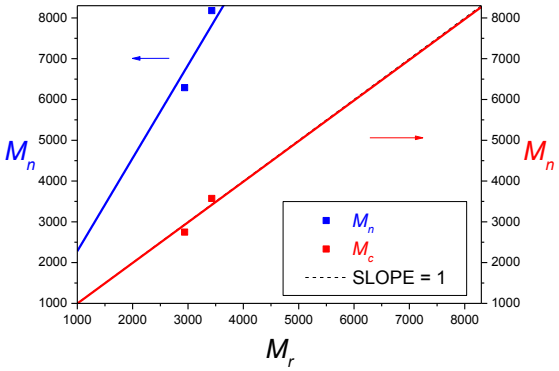


Figure S8. M_r vs M_n and M_r vs M_c for $\mathbf{9_n}$ (SLOPE (M_n) = 2.28, R^2 = 0.83; SLOPE (M_c) = 1.00, R^2 = 0.83).

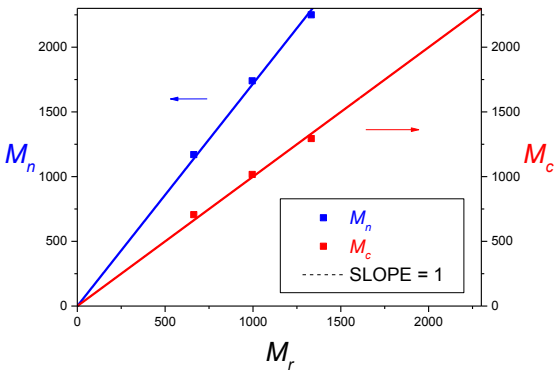


Figure S9. M_r vs M_n and M_r vs M_c for $\mathbf{11_n}$ (SLOPE (M_n) = 1.72, R^2 = 0.99; SLOPE (M_c) = 1.00, R^2 = 0.99).

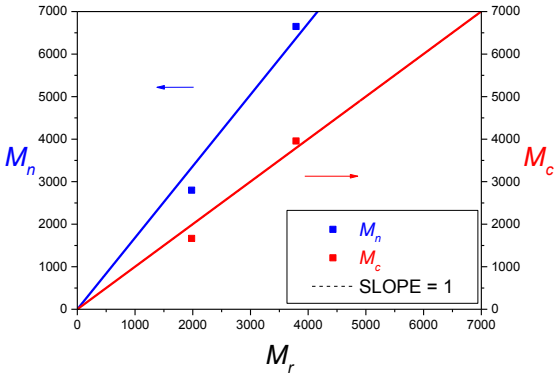


Figure S10. M_r vs M_n and M_r vs M_c for $\mathbf{13_n}$ (SLOPE (M_n) = 1.68, R^2 = 0.95; SLOPE (M_c) = 1.00, R^2 = 0.95).

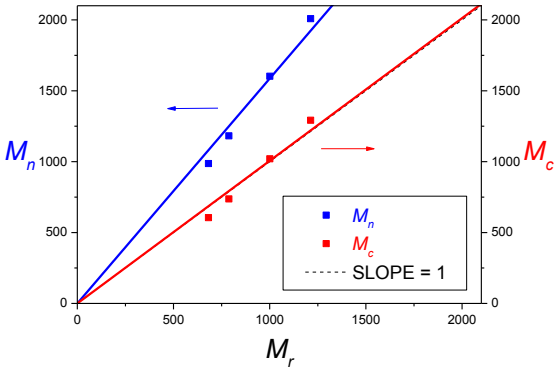


Figure S11. M_r vs M_n and M_r vs M_c for $\mathbf{14_n}$ (SLOPE (M_n) = 1.59, R^2 = 0.97; SLOPE (M_c) = 1.00, R^2 = 0.97).

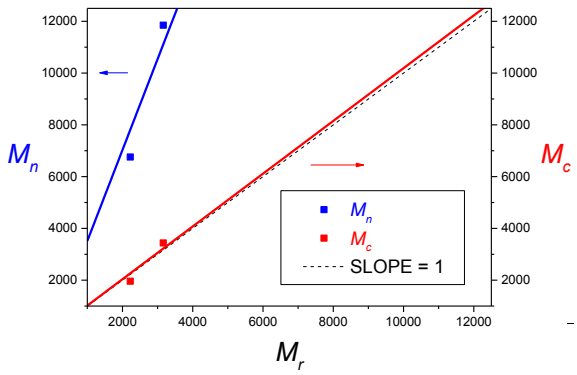


Figure S12. M_r vs M_n and M_r vs M_c for $\mathbf{15_n}$ (SLOPE (M_n) = 3.51, R^2 = 0.87; SLOPE (M_c) = 1.01, R^2 = 0.87).