

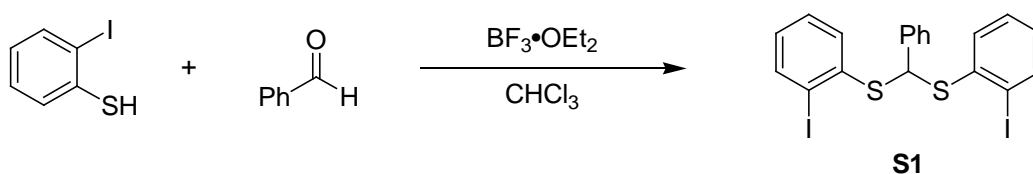
SYNTHESIS OF BIS(BENZO[*b*]THIOPHENYL)METHANES BY**GOLD-CATALYZED DOUBLE CARBOTHIOATION****Itaru Nakamura,^{*a, b} Masashi Okamoto,^b Takuma Sato,^b and Masahiro Terada^b**^a Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Sendai980-8578, Japan. ^b Department of Chemistry, Graduate School of Science, Tohoku University 980-8578, Japan.**(Supporting Information)****Contents**

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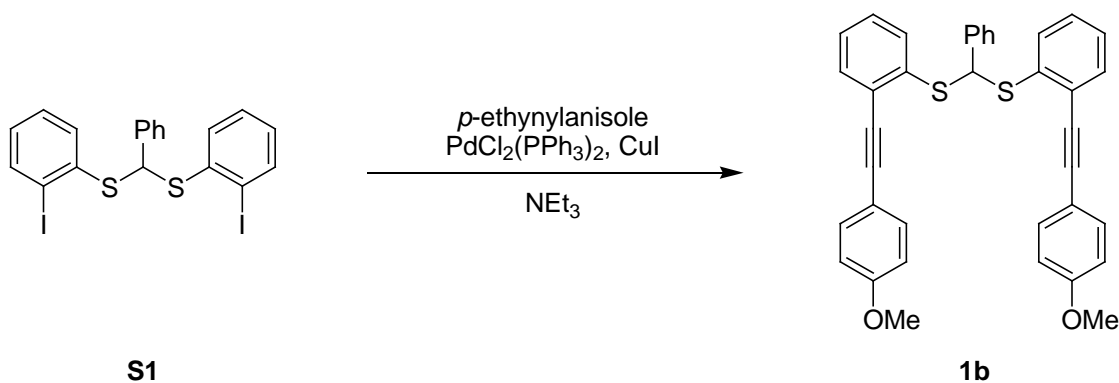
General. All reactions were carried out under argon atmosphere. Gel permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-9104 using chloroform as eluent. Spectroscopic measurements were carried out with following instruments: JEOL α -500 (NMR), JASCO FT/IR-4100 (IR), Bruker Daltonics APEX III (HRMS). Chemical shifts are reported in ppm relative to tetramethylsilane (for ^1H , δ 0.00), CDCl_3 (for ^{13}C , δ 77.00).

General procedure for the synthesis of 1.

All substrates **1a-1h** were prepared following procedure for the synthesis of **1b**.



To the mixture of *o*-iodobenzenthiol (41.0 mmol, 9.68 g) and benzaldehyde (20.0 mmol, 2.1 mL) in CHCl_3 (20 mL) was slowly added $\text{BF}_3 \cdot \text{OEt}_2$ (20.0 mmol, 2.5 mL) at 0°C , then the reaction mixture was allowed to room temperature over 30 min. After additional stirring for 1 h, the reaction was quenched with 1 N NaOH. The organic layer was extracted with CH_2Cl_2 (2×40 mL), washed with water (2×40 mL) and brine, and dried over Na_2SO_4 . After concentration, the residue was purified by column chromatography on silica gel using hexane and CH_2Cl_2 as eluent. The obtained viscous liquid was solidified at -20°C to give **S1** as a white solid in quantitative yield.



To the mixture of $\text{PdCl}_2(\text{PPh}_3)_2$ (0.18 mmol, 126mg) and CuI (0.30 mmol, 57.0 mg) was added the solution of **S1** (3.0 mmol, 1.68 g) in NEt_3 (12 mL) at room temperature. After stirring for 5 min, *p*-ethynylanisole (7.2 mmol, 1.0 mL) was added dropwise, and the solution was stirred for 2 h. The reaction mixture was quenched with sat. NH_4Cl (20 mL). The organic layer was extracted with AcOEt (2×20 mL), washed with sat. NH_4Cl (20 mL), water (20 mL) and brine, and dried over Na_2SO_4 . After concentration, the residue was purified by flash column chromatography on silica gel using hexane and AcOEt as eluent to give highly viscous oil **1b** in 82 % yield.

Analytical data of 2 and 4h.

3,3'-(Phenylmethylene)bis(2-(4-methoxyphenyl)benzo[*b*]thiophene) 2a. ^1H NMR (500 MHz, CDCl_3) δ 3.71 (s, 6H), 6.26 (s, 1H), 6.53-6.56 (m, 4H), 6.91-6.94 (m, 4H), 6.95-7.01 (m, 4H), 7.11-7.12 (m, 2H), 7.15-7.20 (m, 5H), 7.70 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 44.70, 55.15, 113.20, 121.58, 123.35, 123.72, 124.13, 126.25, 126.44, 128.36, 129.20, 130.55, 131.86, 138.75, 140.05, 141.26, 142.21, 159.02. IR (neat) 3060, 2955, 2835, 1608, 1497, 1433, 1291, 1248, 1175, 1033, 829 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 591.1423, found. 591.1422.

3,3'-(Phenylmethylene)bis(2-phenylbenzo[*b*]thiophene) 2b. ^1H NMR (500 MHz, CDCl_3) δ 6.28 (s, 1H), 6.96-7.04 (m, 13H), 7.06-7.10 (m, 2H), 7.16-7.19 (m, 6H), 7.70 (d, $J = 7.9$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 44.82, 121.68, 123.56, 123.82, 124.18, 126.52, 127.64, 128.37, 129.27, 129.43, 132.01, 133.97, 138.90, 140.01, 141.38, 142.10. IR (neat) 3728, 3705, 3628, 3590, 3048, 3022, 1600, 1434, 1077, 1027 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 531.1212, found. 531.1211.

3,3'-(Phenylmethylene)bis(2-(4-(trifluoromethyl)phenyl)benzo[*b*]thiophene) 2c. ^1H NMR (500 MHz, CDCl_3) δ 6.24 (s, 1H), 7.01-7.03 (m, 4H), 7.07 (d, $J = 8.1$ Hz, 4H), 7.12-7.14 (m, 2H), 7.21-7.25 (m, 5H), 7.27 (d, $J = 8.1$ Hz, 4H), 7.72 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 44.79, 121.93, 123.86 (q, $^1J(\text{C}, \text{F}) = 272.8$ Hz), 124.19, 124.25, 124.29, 234.65 (q, $^3J(\text{C}, \text{F}) = 3.8$ Hz), 127.01, 128.67, 129.16, 129.59, 129.73 (q, $^2J(\text{C}, \text{F}) = 32.7$ Hz), 132.78, 137.57, 138.94, 139.53, 139.58, 141.18. IR (neat) 3060, 1615, 1320, 1164, 1127, 1066, 1018 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 667.0959, found. 667.0956.

3,3'-(Phenylmethylene)bis(2-propylbenzo[*b*]thiophene) 2d. ^1H NMR (500 MHz, CDCl_3) δ 0.63 (t, $J = 7.3$ Hz, 6H), 1.29-1.46 (m, 4H), 2.36-2.48 (m, 4H), 6.34 (s, 1H), 7.08-7.11 (m, 2H), 7.16-7.12 (m, 6H), 7.25-7.28 (m, 3H), 7.75 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 13.84, 24.46, 31.10, 44.30, 121.99, 122.24, 123.28, 123.83, 126.74, 128.51, 129.08, 130.17, 137.95, 140.54, 141.27, 143.76. IR (neat) 3060, 2958, 2929, 2870, 1601, 1493, 1456, 1435, 1151, 1027 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 463.1525, found. 463.1522.

3,3'-(Phenylmethylene)bis(2-cyclohexylbenzo[*b*]thiophene) 2e. ^1H NMR (500 MHz, CDCl_3) δ 0.59 (dtt, $J = 12.8, 12.8, 3.4$ Hz, 2H), 0.68 (dtt, $J = 12.8, 12.8, 3.4$ Hz, 2H), 1.05 (dtt, $J = 12.8, 12.8, 12.8, 3.4, 3.4$ Hz, 2H), 1.16-1.24 (m, 2H), 1.26-1.34 (m, 4H), 1.45-1.59 (m, 8H), 2.60 (tt, $J = 11.8, 3.4$ Hz, 2H), 6.42 (s, 1H), 7.08-7.13 (m, 4H), 7.18 (ddd, $J = 8.1, 6.4, 1.7$ Hz, 1H), 7.20 (ddd, $J = 8.1, 6.4, 1.7$ Hz, 1H), 7.24-7.31 (m, 5H), 7.76 (d, $J = 7.7$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 25.71, 26.24, 26.39, 35.19, 35.48, 38.30, 44.34, 122.22, 122.45, 123.15, 123.66, 126.79, 128.58, 129.05, 129.36, 137.82, 140.10, 141.21, 150.31. IR (neat) 3061, 2925, 2850, 1494, 1448, 1153, 1025 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 543.2151, found. 543.2150.

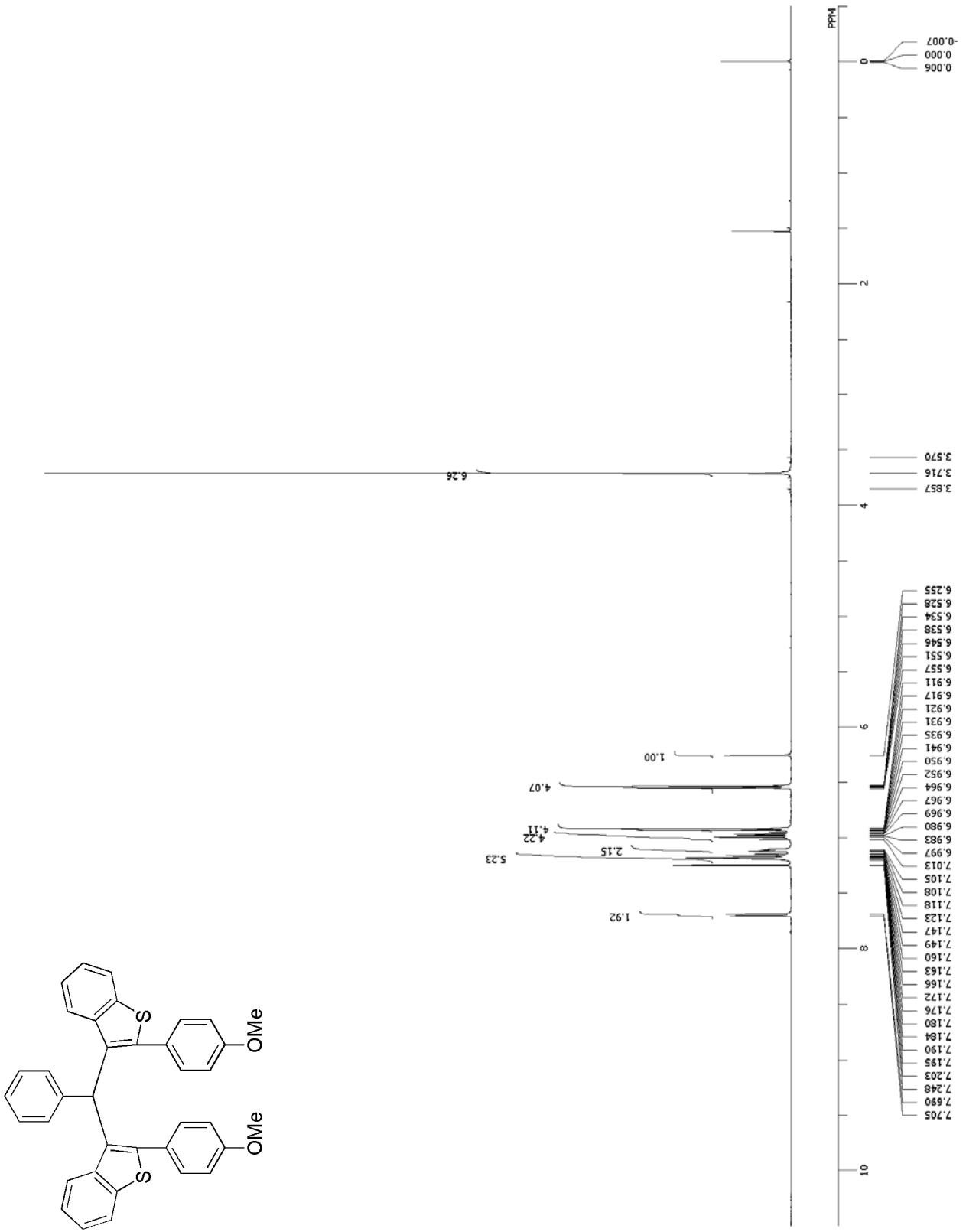
3,3'-((4-Chlorophenyl)methylene)bis(2-phenylbenzo[*b*]thiophene) 2f. ^1H NMR (500 MHz, CDCl_3) δ 6.23 (s, 1H), 6.97-6.99 (m, 4H), 7.01-7.07 (m, 10H), 7.08-7.12 (m, 4H), 7.20 (ddd, $J = 8.0, 6.3, 1.3$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 44.35, 121.77, 123.73, 123.90, 123.98, 127.72, 128.46, 129.42,

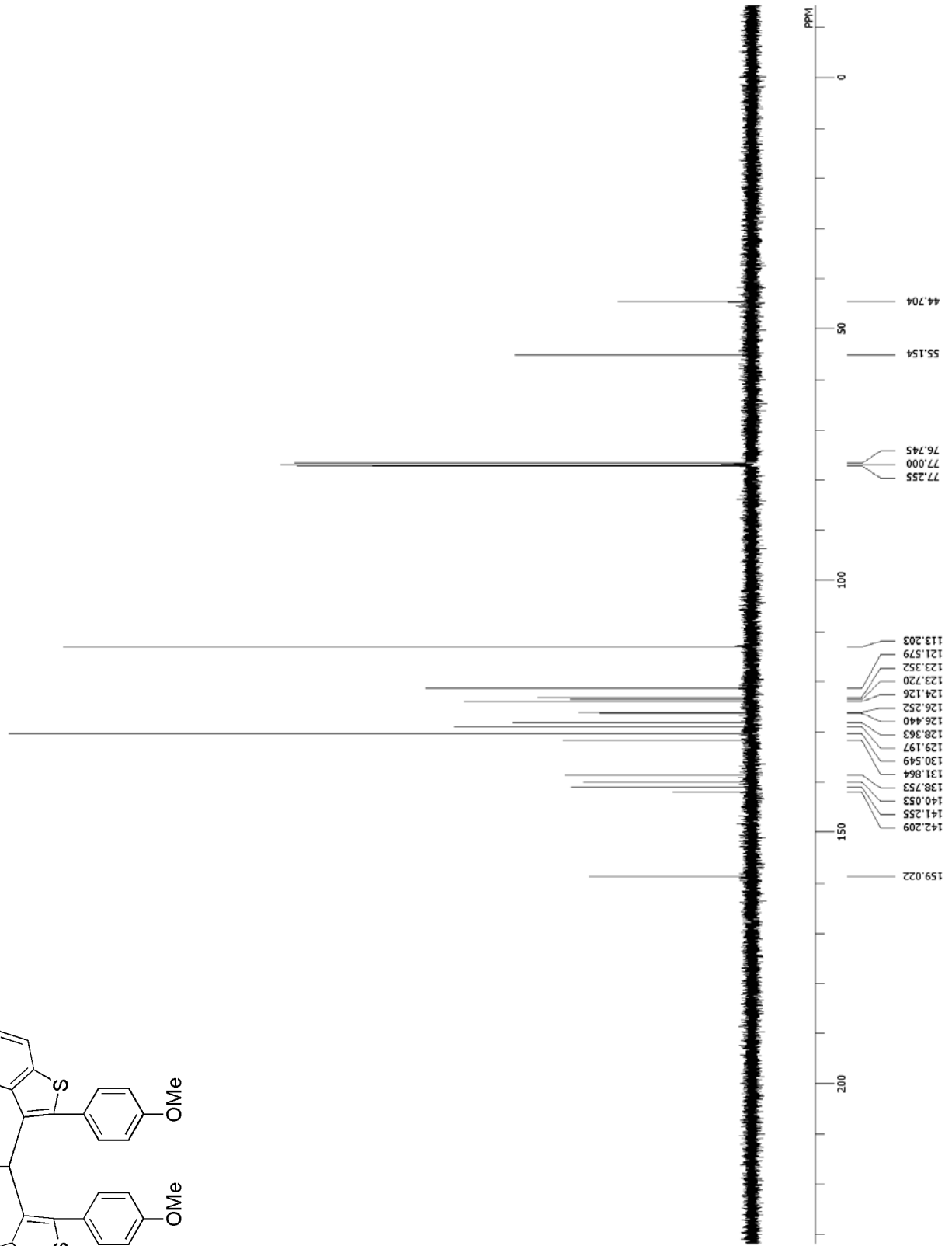
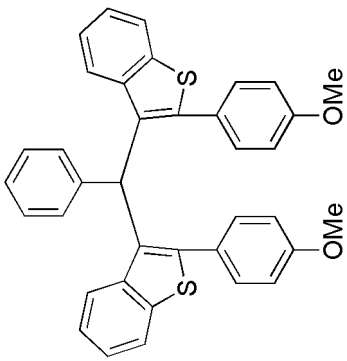
130.59, 131.35, 132.24, 133.79, 138.90, 139.74, 140.57, 141.62. IR (neat) 3060, 3025, 1600, 1488, 1432, 1092, 1014, 823 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 565.0822, found. 565.0821.

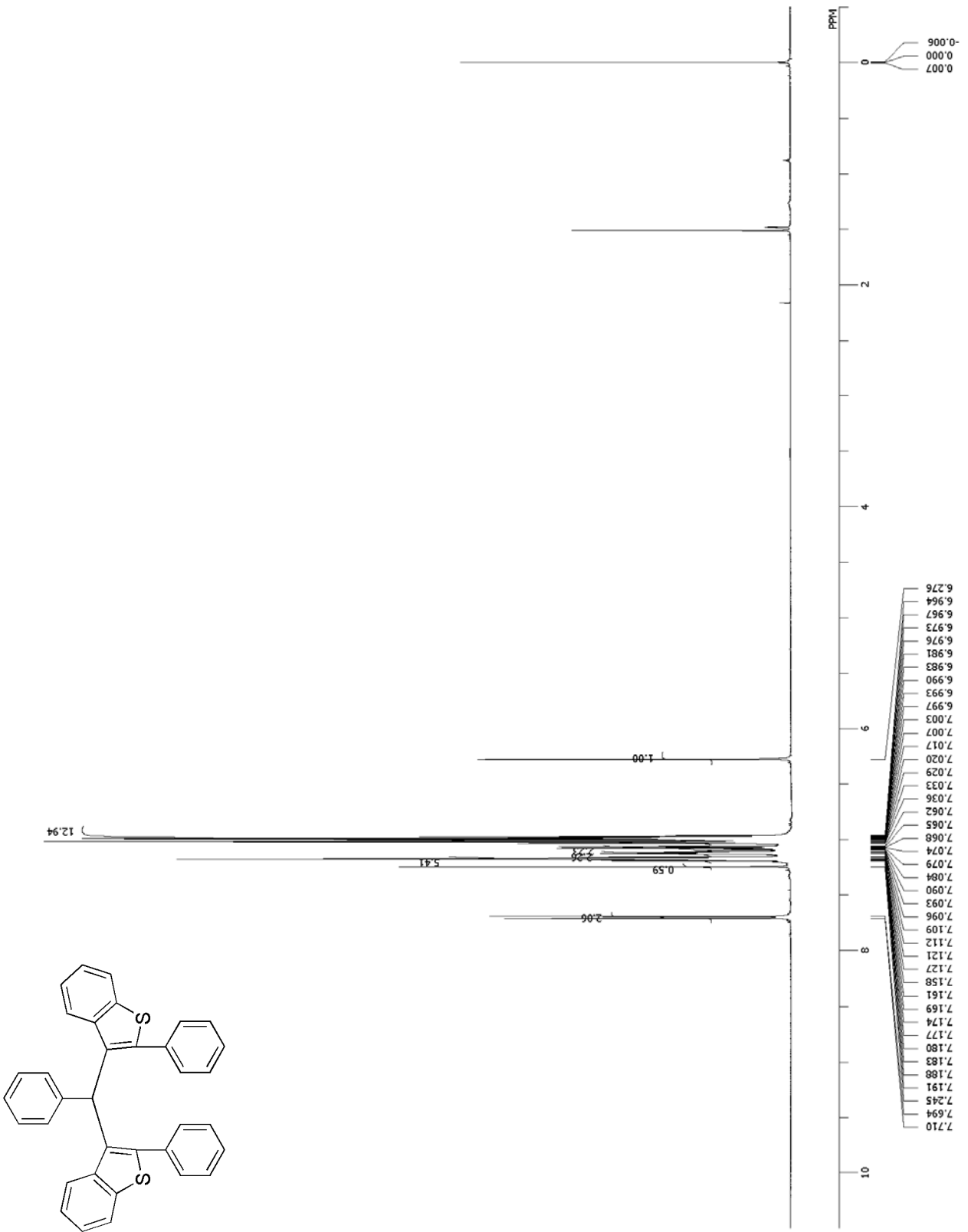
3,3'-(Butane-1,1-diyl)bis(2-phenylbenzo[*b*]thiophene) 2g. ^1H NMR (500 MHz, CDCl_3) δ 0.58 (t, $J = 7.3$ Hz, 3H), 1.05-1.15 (m, 2H), 2.09-2.14 (m, 2H), 4.96 (t, $J = 7.8$ Hz, 1H), 7.07-7.18 (m, 12H), 7.22-7.23 (m, 2H), 7.60 (d, $J = 8.1$ Hz, 2H), 7.72 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 13.61, 21.39, 36.14, 19.91, 121.71, 123.40, 123.59, 123.87, 127.64, 127.73, 129.88, 133.28, 134.76, 138.88, 139.79, 140.27. IR (neat) 3060, 2958, 2871, 1601, 1456, 1434, 1212, 1075, 1028 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 497.1368, found. 497.1368.

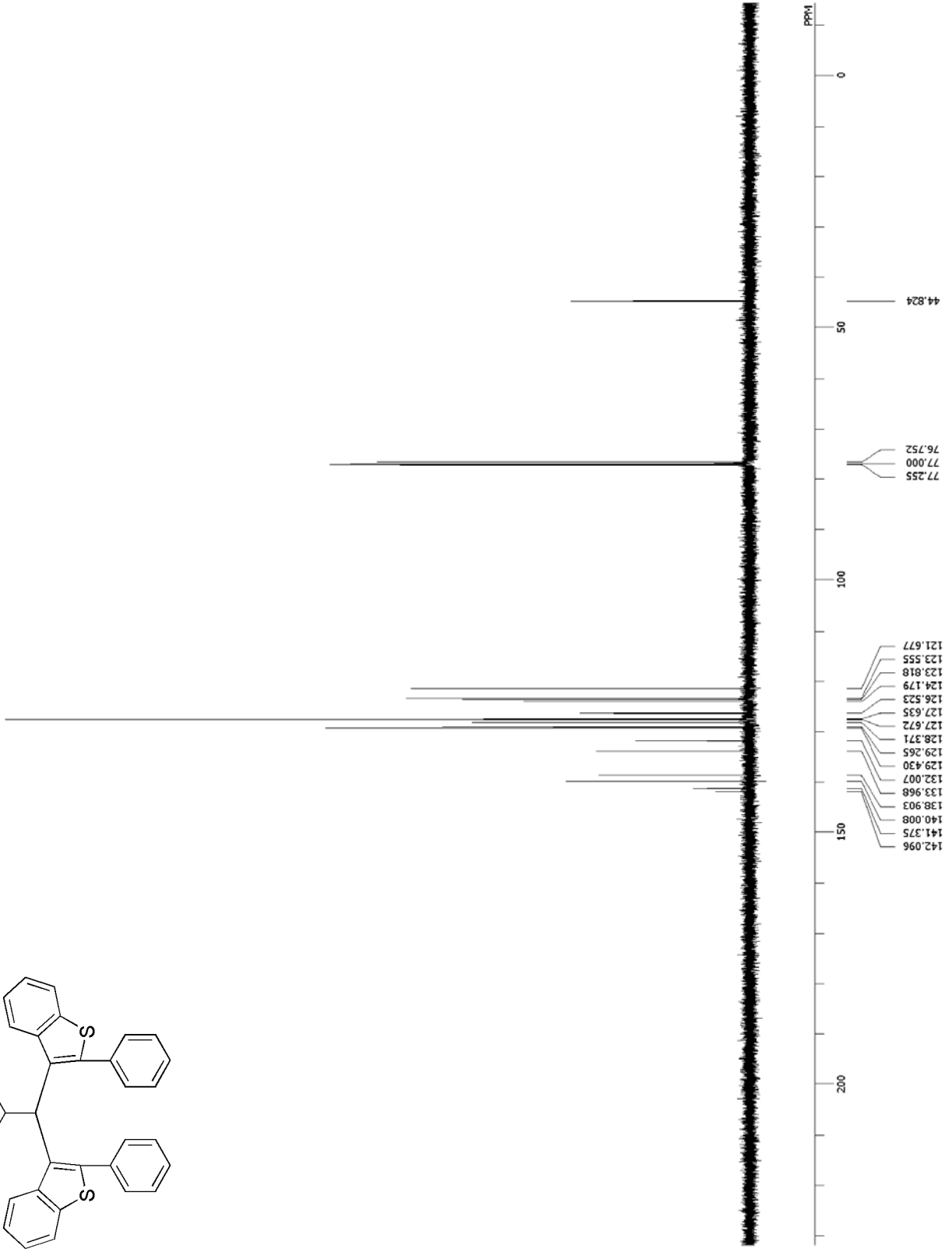
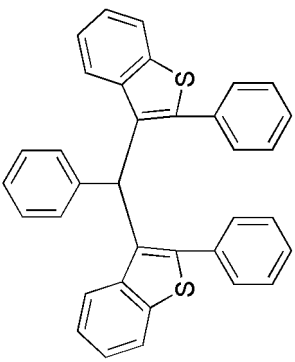
2,2'-(Phenylmethylene)dibenzo[*b*]thiophene 6h. ^1H NMR (500 MHz, CDCl_3) δ 5.94 (s, 1H), 7.08 (s, 2H), 7.21-7.31 (m, 5H), 7.33-7.36 (m, 2H), 7.38-7.40 (m, 2H), 7.64 (d, $J = 6.8$ Hz, 2H), 7.73 (dd, $J = 7.9, 0.4$ Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 48.81, 122.20, 123.11, 123.44, 124.13, 124.26, 127.54, 128.57, 128.66, 139.47, 139.93, 142.10, 147.30. IR (neat) 3058, 3027, 1600, 1493, 1456, 1434, 1154, 1071, 859 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$, 379.0586, found. 379.0586.

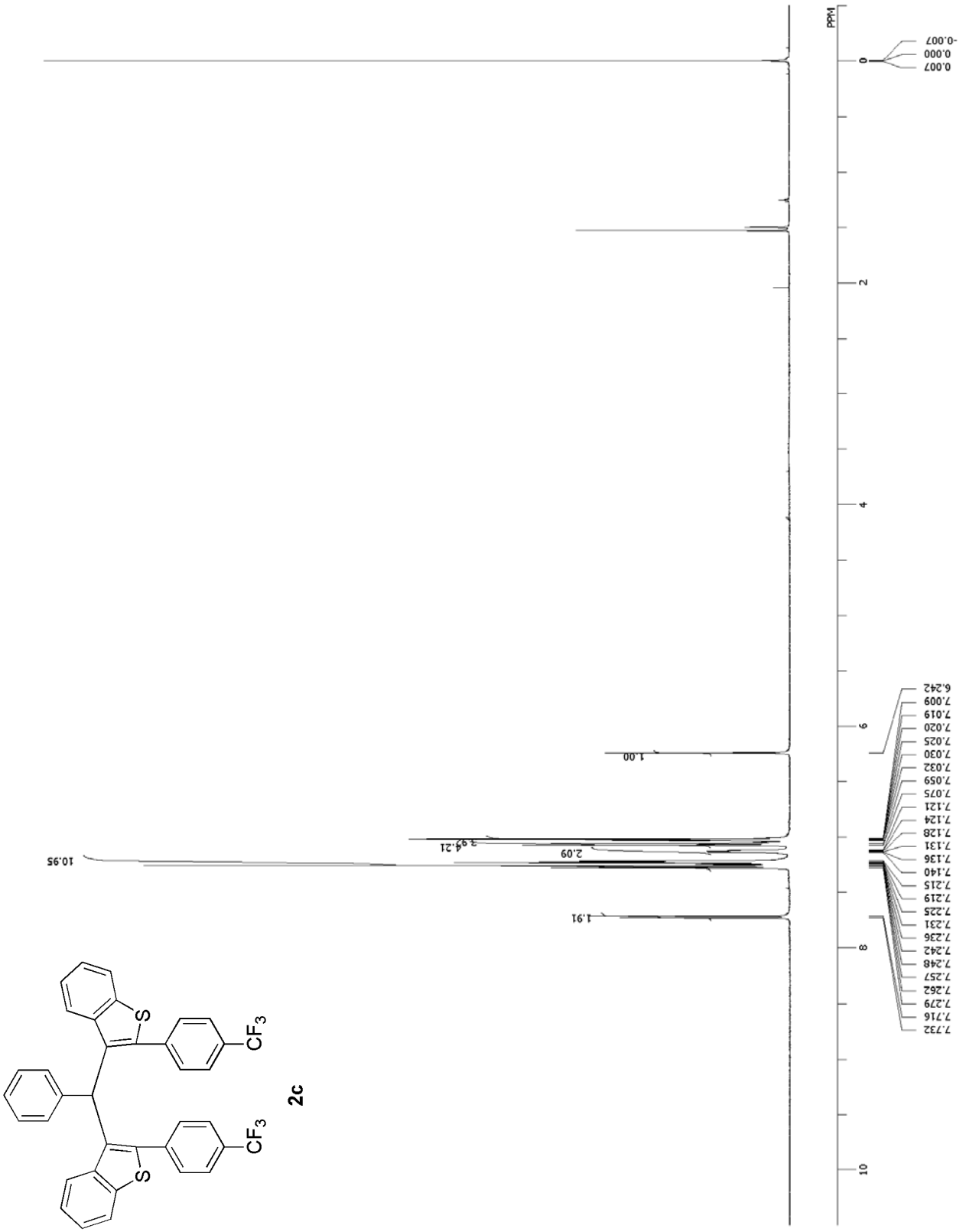
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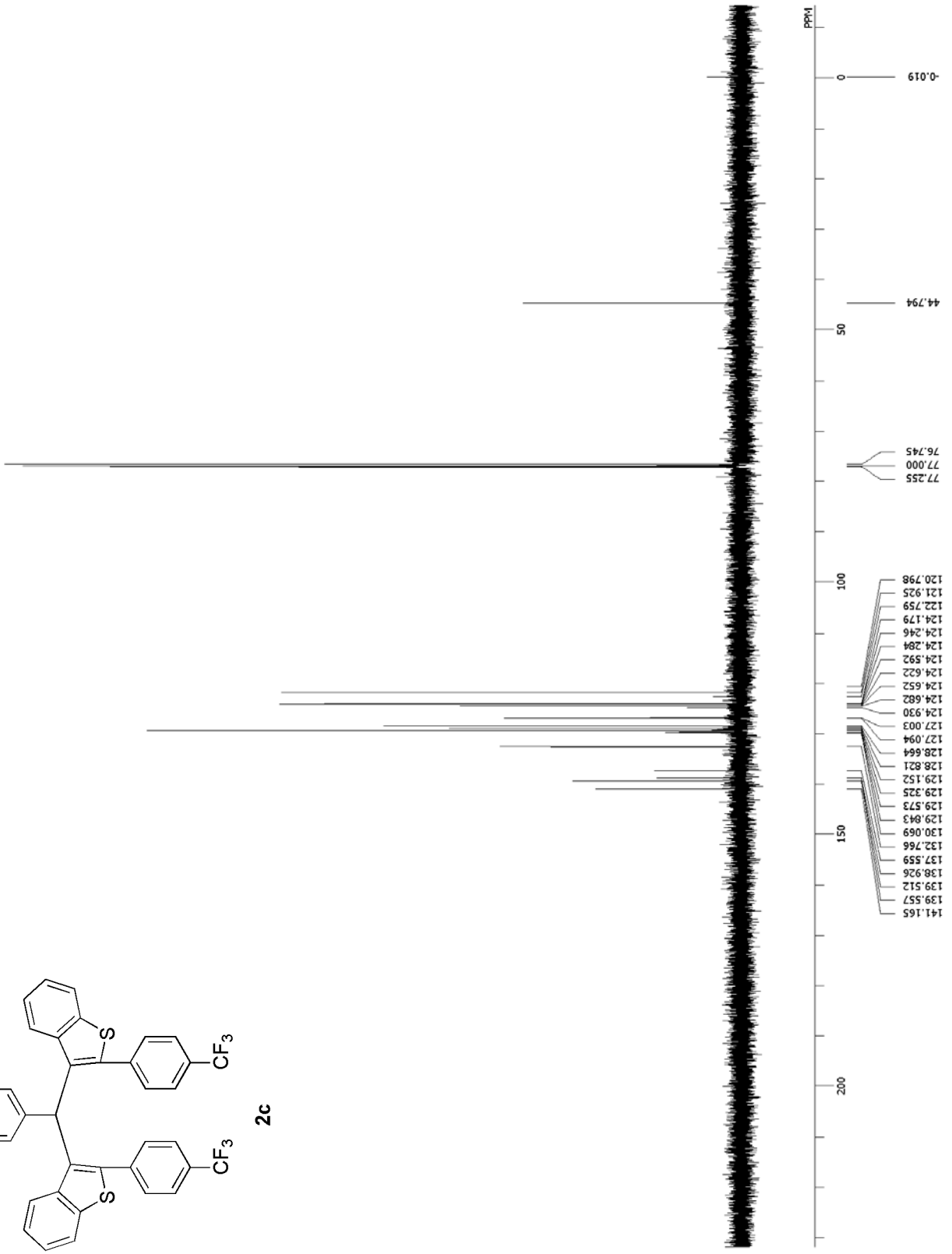
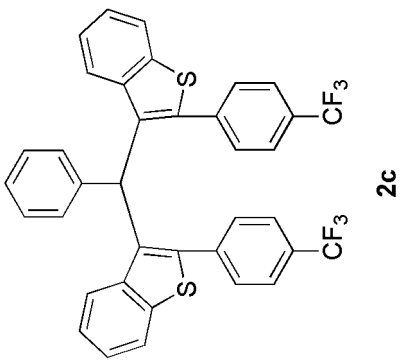


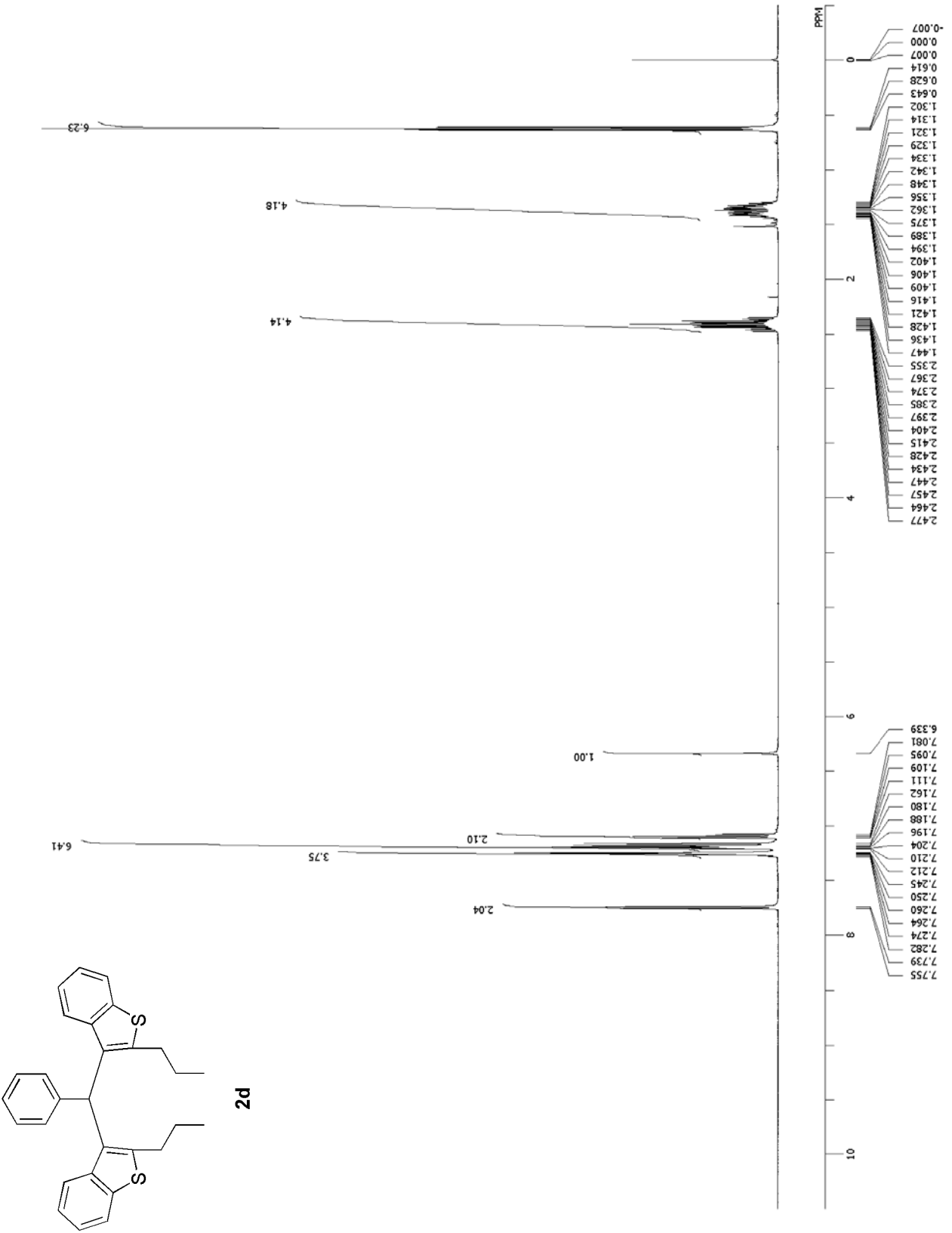


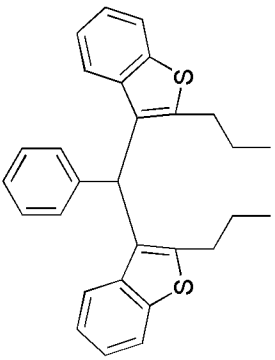












2d

