Synthesis of Chiral Dotriacontanaphthalenes:

How many naphthalene units can be elaborately connected?

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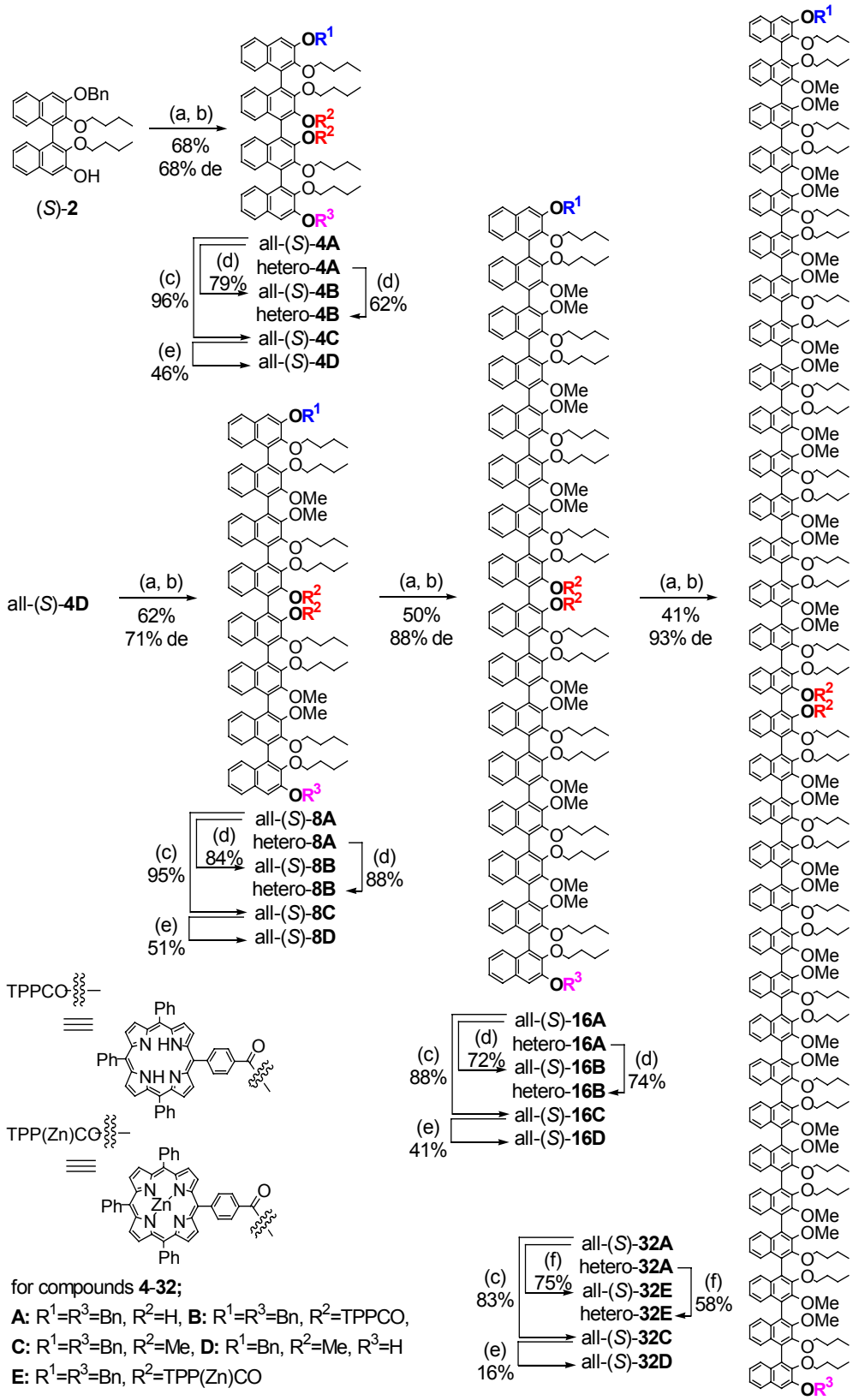
Pages 42-44: Figure SI-2. NMR spectra of all-(*S*)-**8a**, hetero-**8a** and all-(*S*)-**4d** in various concentration.

Page 45: Figure SI-3. Fluorescence spectra of all-(*S*)-**4C**, **8C**, **16C,** and **32C**.

Experimental Section

Synthetic route of oligonaphthalenes is outlined in Scheme 1.



General Procedure for the Synthesis of A Series Compounds:

The preparation of **16A** is typical. To a mixture of $CuCl_2$ (29 mg, 216.6 μmol) in methanol (1 ml), *i*-propylamine (23 μl, 270.8 μmol) was added under argon atmosphere under ice-bath cooling. After 45 min, a solution of all-(*S*)-**8d** (204.8 mg, 108.3 μmol) in dichloromethane (1 ml) was added and the reaction mixture was stirred for 5h at 0 °C to rt. The reaction mixture was poured into the mixed solvent of 1 M hydrochloric acid solution and $CHCl_3$. The aqueous layer was extracted with chloroform (twice). The organic layer was combined, washed with brine, and dried over sodium sulfate and evaporated to give a residue. The residue was purified by column chromatography (SiO_2 hexane/chloroform/ethyl acetate = 10/1/1) to afford to all-(*S*)-**16A** (96.6 mg, 47%) and hetero-**16A** (17.5 mg, 5.4%).

all-(*S*)-16A: yellow powder; mp. 296 °C; $[\alpha]_D^{20}$ = -164 (c = 0.70, $CHCl_3$); IR (KBr) 3505, 2956, 2933, 1376, 1344, 1237, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.65-1.70 (m, 106H), 3.73-4.38 (m, 68H), 5.39 (s, 4H), 6.41 (s, 2H), 7.12-7.53 (m, 68 H), 7.55-7.67 (m, 6H), 7.83 (d, *J* = 8.2, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0 14.2, 14.24, 14.33, 19.1, 19.5, 15.6, 19.7, 30.2, 32.7, 32.8, 32.9, 33.0, 33.1, 61.3, 70.9, 73.4, 73.5, 73.7, 74.3, 109.3, 115.7, 124.6, 125.5, 125.7, 125.9, 126.1, 126.2, 126.4, 126.7, 126.8, 126.9, 127.0, 127.1, 127.3, 127.4, 127.58, 127.62, 127.7, 128.3, 129.0, 129.8, 129.9, 131.4, 131.5, 131.6, 131.8, 137.5, 146.1, 146.9, 147.9, 150.8, 151.1, 151.6, 151.7, 152.3; MS (MALDI-TOF, dithranol matrix) 3776 (M^+); *Anal*. Calcd for $C_{250}H_{262}O_{32}\cdot1.75CHCl_3$: C, 75.83; H, 6.67. Found: C, 75.87; H, 6.62.

hetero-16A: yellow powder; mp. 249 °C; $[\alpha]_D^{20}$ = -154 (c = 1.20, $CHCl_3$); IR (KBr) 3518, 2956, 2933, 1376, 1345, 1237, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.60-1.80 (m, 106H), 3.60-4.40 (m, 68H), 5.38 (s, 4H), 6.09 (brs, 2H), 7.10-7.55 (m, 74H), 7.82 (d, *J* = 8.3, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.1, 14.25, 14.34, 19.1, 19.4, 19.6, 19.7, 30.2, 32.7, 32.8, 32.9, 33.1, 61.3, 70.9, 73.4, 73.5, 73.7, 74.1, 115.3, 124.6, 125.4, 125.5, 125.7, 125.9, 126.2, 126.4, 126.7, 126.8, 126.9, 127.0, 127.1, 127.35, 127.39, 127.47, 127.55, 127.6, 127.8, 128.4, 129.0, 129.8, 129.9, 131.4, 131.5, 131.6, 131.7, 131.8, 137.5, 146.3, 147.4, 147.9, 150.79, 150.84, 151.1, 151.6, 151.8, 152.3; MS (MALDI-TOF, dithranol matrix) 3778 (M^+); *Anal*. Calcd for $C_{250}H_{262}O_{32}\cdot1.5CHCl_3$: C, 76.32; H, 6.71. Found: C, 76.30; H, 6.94.

all-(*S*)-32A: yellow powder; mp. ＞300 °C; $[\alpha]_D^{20}$ = -196 (c = 0.993, $CHCl_3$); IR (KBr) 2956, 2871, 1375, 1343, 1236,758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.59-1.80 (m, 218H), 3.70-4.50 (m, 148H), 5.38 (s, 4H), 6.41 (s, 2H), 7.10-7.45 (m, 134H), 7.60 (d, *J* = 7.8,H), 7.82 (d, *J* = 8.3, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 11.4, 14.0, 14.3, 14.5, 19.1, 19.7, 20.2, 23.2, 23.4, 24.2, 27.7, 29.4, 29.8, 30.2, 30.8, 32.7, 32.9, 33.1, 39.2, 61.3, 68.6, 73.5, 125.6, 127.0, 127.69, 127.76, 129.0, 129.3, 131.4, 131.6, 131.8, 137.5, 150.8, 151.7; MS (MALDI-TOF, dithranol matrix) 7426 (M^+); HPLC tR=22.07 min (COSMOSIL 5SL-II, 20×250 nm, $CHCl_3$: Et_2O = 50:1, 3.0 ml/min). *Anal*. Calcd for $C_{490}H_{516}O_{64}\cdot1.5CHCl_3$: C, 77.57; H, 6.88. Found: C, 77.42; H, 7.06.

hetero-32A: yellow powder; mp. ＞300 °C; $[\alpha]_D^{20}$ = -184 (c = 0.257, $CHCl_3$); IR (KBr) 2956, 2933, 1376, 1343, 1236, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.60-1.80 (m, 218H), 3.70-4.40 (m, 148H), 5.38 (s, 4H), 6.10 (s, 2H), 7.10-7.65 (m, 138H), 7.83 (d, *J* = 8.7, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.2, 14.4, 14.6, 19.2, 19.6, 19.7, 23.2, 29.9, 30.2, 32.4, 32.7, 32.9, 33.2, 61.3, 71.0, 73.6, 125.6, 126.4, 126.8, 127.0, 127.7, 127.8, 128.4, 129.1, 131.6, 131.8, 137.6, 148.0, 150.9, 151.7, 152.4; MS (MALDI-TOF, dithranol matrix) 7428 (M^+); HPLC tR=28.51 min (COSMOSIL 5SL-II, 20×250 nm, $CHCl_3$: Et_2O = 50:1, 3.0 ml/min).

all-(*S*)-**4A**, hetero-**4A**, all-(*S*)-**8A**, and hetero-**8A** were known. Tsubaki, K. et al. *J. Org. Chem*., **2006**, *71*, 6579-6587.

General Procedure for the Synthesis of B and E Series Compounds:

The preparation of all-(*S*)-**16B** is typical. A solution of all-(*S*)-**16A** (61.8 mg, 16.35 μmol) in CH_2Cl_2 (6 ml), TPP(H_2)CO_2H (**5**) (54 mg, 81.75 μmol), WSC·HCl (63 mg, 327 μmol) and DMAP (5 mg, 40 μmol) were added. The reaction mixture was stirred at reflux temperature for 29 hr. The reaction mixture was poured into the mixed solvent of 1 M hydrochloric acid solution and chloroform. The aqueous layer was extracted with chloroform (twice). The organic layer was combined, washed with brine, and dried over sodium sulfate and evaporated to give a residue. The residue was purified by column chromatography (SiO_2 chloroform) to give a crude material which was further purified by recycling preparative HPLC (Japan Analytical Industry Co., Ltd. LC-908) with connected JAIGEL-1H (20 x 600 mm) and JAIGEL-2H (20 x 600 mm) under the conditions of 3.5 ml/min of flow rate with chloroform detected by UV (254 nm) and RI (refractive index) to afford all-(*S*)-**16B** (59.5 mg, 72%).

all-(*S*)-16B: purple powder; mp. 237 °C; $[\alpha]_D^{20}$ = -1905 (c = 4.74×10^{-2}, $CHCl_3$); IR (KBr) 3429, 2955, 2931, 1744, 1238, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ -2.78 (s, 4H), 0.40-1.80 (m, 112H), 3.70-4.60 (m, 68H), 5.38 (s, 4H), 6.69 (brs, 1H), 6.91 (brs, 1H), 7.15-8.00 (m, 98H), 8.10-8.28 (m, 10H), 8.30-8.65 (m, 6H), 8.68-8.95 (m, 14H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.29, 14.33, 14.36, 14.5, 19.2, 19.6, 19.70, 19.73, 30.2, 32.7, 32.9, 33.0, 33.2, 61.27, 61.31, 70.9, 73.45, 73.53, 73.9, 74.5, 109.3, 120.9, 121.1, 121.9, 124.6, 125.6, 126.4, 126.8, 127.0, 127.2, 127.37, 127.42, 127.58, 127.63, 127.8, 128.0, 128.3, 128.4, 128.9, 129.0, 129.7, 129.9, 130.9, 131.4, 131.6, 131.7, 131.8, 132.1, 132.6, 132.6, 132.9, 133.3, 134.9, 135.0, 135.2, 137.5, 142.4, 142.5, 143.1, 147.8, 148.0, 149.9, 150.0, 150.0, 150.8, 151.2, 151.7, 152.3, 164.7; MS (MALDI-TOF, dithranol matrix) 5058 (M^+); *Anal*. Calcd for $C_{340}H_{318}N_8O_{34}\cdot CHCl_3$: C, 79.07; H, 6.21; N, 2.16. Found: C, 79.18; H, 6.35; N, 1.98.

heteo-4B: 62% yield; purple solid; mp = 202 °C; $[\alpha]_D^{20}$ = -1245 (c = 0.048, $CHCl_3$); IR (KBr) 2955, 1745, 1597, 1350 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ -2.84 (s, 4H), 0.30 (t, *J* = 6.4 Hz, 6H), 0.54 (t, *J* = 7.1 Hz, 6H), 0.6-1.0 (m, 8H), 1.1-1.4 (m, 8H), 3.7-4.2 (m, 8H), 5.28 (s, 4H), 7.1-7.8 (m, 44H), 7.83 (d, *J* = 7.8 Hz, 2H), 8.15-8.25 (m, 12 H), 8.27 (d, *J* = 7.8 Hz, 4H), 8.56 (brs, 4H), 8.73 (d, *J* = 4.5 Hz, 4H), 8.75-8.9 (m, 12H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 13.7, 14.2, 14.6, 18.8, 19.3, 23.2, 29.9, 30.2, 31.9, 32.3, 32.4, 32.7, 36.9, 70.9, 73.4, 74.4, 78.1, 109.9, 119.0, 120.8, 121.0, 125.2, 125.7, 126.1, 126.3, 126.4, 126.6, 126.7, 127.2, 127.6, 127.8, 128.20, 128.24, 128.9, 129.5, 129.9, 130.9, 131.5, 132.7, 133.1, 134.3, 135.0, 135.1, 137.4, 142.5, 143.7, 147.7, 148.3, 149.5, 152.1, 163.0; MS (FAB^+) *m/z* 2320 ($M+H^+$); *Anal*. Calcd for $C_{160}H_{126}N_8O_{10}\cdot 3H_2O$: C, 80.92; H, 5.60; N, 4.70. Found: C, 80.95; H, 5.90; N, 4.39.

all-(*S*)-8B: 84% yield; purple solid; mp = 231 °C; $[\alpha]_D^{20}$ = -1941 (c = 0.049, $CHCl_3$); IR (KBr) 2955, 1745, 1598, 1345 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ -2.79 (s, 4H), 0.49 (t, *J* = 7.4 Hz, 6H), 0.55 (t, *J* = 7.3 Hz, 6H), 0.6-1.6 (m, 44H), 3.81 (s, 6H), 3.91 (s, 6H), 3.7-4.35 (m, 14H), 4.44 (dt, *J* = 8.7 Hz, 6.0 Hz, 2H), 5.37 (s, 4H), 6.65 (brs, 2H), 6.90 (brs, 2H), 7.1-7.75 (m, 56H), 7.82 (d, *J* = 8.2 Hz, 2H), 8.1-8.2 (m, 12 H), 8.36 (d, *J* = 8.3 Hz, 4H), 8.52 (brs, 4H), 8.7-8.9 (m, 16H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.2, 14.3, 14.5, 19.2, 19.5, 19.7, 32.7, 32.9, 33.0, 33.2, 61.26, 61.33, 70.9, 73.4, 73.4, 73.9, 74.5, 109.3, 118.9, 120.9, 121.1, 124.6, 125.3, 125.5, 126.1, 126.3, 126.5, 126.7, 126.8, 127.0, 127.2, 127.3, 127.5, 127.8, 128.2, 128.4, 128.9, 129.0, 129.7, 129.9, 130.9, 131.3, 131.5, 131.7, 132.1, 133.3, 135.0, 135.2, 137.5, 142.4, 142.5, 143.5, 147.8, 147.9, 149.8, 150.8, 151.2, 151.6, 151.7, 152.3, 164.6; MS (FAB^+) *m/z* 3233 ($M+H^+$); *Anal*. Calcd for $C_{220}H_{190}N_8O_{18}\cdot 0.5CHCl_3$: C, 80.41; H, 5.83; N, 3.40. Found: C, 80.36; H, 6.02; N, 3.38.

hetero-8B: 88% yield; purple solid; mp = 198 °C; $[\alpha]_D^{20}$ = -3120 (c = 0.054, $CHCl_3$); IR (KBr) 2956, 1745, 1598, 1348 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ -2.79 (s, 4H), 0.49 (t, *J* = 7.4 Hz, 6H), 0.55 (t, *J* = 7.3 Hz, 6H), 0.6-1.6 (m, 44H), 3.81 (s, 6H), 3.91 (s, 6H), 3.7-4.35 (m, 14H), 4.44 (dt, *J* = 8.7 Hz, 6.0 Hz, 2H), 5.37 (s, 4H), 6.65 (brs, 2H), 6.90 (brs, 2H), 7.1-7.75 (m, 56H), 7.82 (d, *J* = 8.2 Hz, 2H), 8.1-8.2 (m, 12 H), 8.36 (d, *J* = 8.3 Hz, 4H), 8.52 (brs, 4H), 8.7-8.9 (m, 16H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 1.5, 11.5, 13.8, 14.1, 14.3, 14.4, 14.57, 14.64, 18.9, 19.2, 19.6, 19.8, 23.2, 23.5, 24.2, 27.6, 29.4, 29.9, 30.2, 30.5, 30.8, 31.7, 32.5, 32.8, 32.9, 33.2, 37.6, 38.6, 39.2, 61.1, 61.3, 68.6, 71.0, 73.5, 109.3, 118.9, 120.8, 121.1, 124.6, 125.4, 125.5, 125.8, 126.3, 126.5, 126.7, 126.8, 127.1, 127.4, 127.5, 127.6, 127.8, 128.2, 128.4, 129.1, 129.3, 129.5, 130.0, 131.1, 131.4, 131.5, 131.7, 131.8, 132.9, 133.2, 134.9, 135.0, 135.2, 137.5, 142.4, 142.5, 143.8, 147.9, 148.0, 149.5, 150.8, 151.0, 151.5, 151.6, 152.4, 168.3.; MS (FAB^+) *m/z* 3232 (M^+). *Anal*. Calcd for $C_{220}H_{190}N_8O_{18}\cdot 2H_2O$: C, 80.81; H, 5.98; N, 3.43. Found: C, 80.93; H, 6.06; N, 3.44.

hetero-16B: purple powder; mp. 196 °C; $[\alpha]_D^{20}$ = -3150 (c = 5.50×10^{-2}, $CHCl_3$); IR (KBr) 3428, 2929, 1742, 1239, 759 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ -2.79 (s, 4H), 0.40-0.50 (m, 6H), 0.59 (t, *J* = 7.3 6H), 0.65-1.70 (m, 100H), 3.60-4.50 (m, 68H), 5.41 (s, 4H), 7.10-8.00 (m, 96H), 8.10-8.30 (m, 11H), 8.39 (d, *J* = 7.8, 4H), 8.60-8.90 (m, 19H) ; ^{13}C-NMR (100MHz, $CDCl_3$) δ 13.8, 14.0, 14.3, 14.4, 14.6, 18.9, 19.1, 19.6, 19.7, 19.8, 30.2, 32.5, 32.7, 32.9, 33.0, 33.2, 60.9, 61.1, 61.28, 61.33, 70.9, 73.46, 73.54, 109.3, 120.8, 121.1, 121.8, 124.6 125.6, 125.9, 126.4, 126.5, 126.8, 126.9, 127.0, 127.2, 127.37, 127.41, 127.6, 127.8, 128.0, 128.2, 128.4, 129.0, 129.9, 131.2, 131.4, 131.6, 131.7, 131.8, 132.5, 132.6, 133.3, 134.8, 134.9, 135.0, 135.2, 137.5, 142.4, 143.1, 147.9, 149.6, 149.9, 150.6, 150.8, 150.9, 151.6, 151.7, 152.3, 165.0; MS (MALDI-TOF, dithranol matrix) 5060 (M^+); *Anal*. Calcd for $C_{340}H_{318}N_8O_{34}\cdot 1.5CHCl_3$: C, 78.29; H, 6.15; N, 2.14. Found: C, 78.65; H, 6.44; N, 2.16.

all-(*S*)-32E: purple powder; mp. > 300 °C; $[\alpha]_D^{20}$ = -1481 (c = 6.67×10^{-3}, $CHCl_3$); IR (KBr) 2956, 2929, 1376, 1237, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, 7.3 6H), 0.60-1.70 (m, 218H), 3.60-4.40 (m, 148H), 5.38 (s, 4H), 7.10-7.90 (m, 180H), 8.10-8.30 (m, 6H), 8.75-9.00 (m, 8H). ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.4, 19.1, 19.7, 30.2, 33.2, 61.3, 73.6, 125.6, 127.0, 127.7, 127.8, 129.1, 131.6, 131.8, 150.9, 151.7

hetero-32E: purple powder; mp. > 300 °C; $[\alpha]_D^{20}$ = -3802 (c = 1.67×10^{-2}, $CHCl_3$); IR (KBr) 2956, 2926, 1376, 1344, 1237, 759 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.60-1.70 (m, 218H), 3.60-4.45 (m, 148H), 5.38 (s, 4H), 7.00-7.85 (m, 175H), 8.06-8.40 (m, 9H), 8.80-9.05 (m, 10H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.3, 14.4, 19.1, 19.6, 19.7, 30.2, 32.7, 32.9, 33.2, 61.3, 73.6, 125.6, 125.8, 126.5, 126.8, 127.0, 127.4, 127.7, 127.8, 128.4, 129.1, 131.6, 131.8, 134.9, 150.9, 131.7.

all-(*S*)-**4B** was known. Tsubaki, K. et al. *J. Org. Chem*., **2008**, *73*, 4279-7282.

General Procedure for the Synthesis of C Series Compounds:

The preparation of all-(*S*)-**16C** is typical. To a suspension of all-(*S*)-**16A** (100 mg, 26.5 μmol) and potassium carbonate (73 mg, 530 μmol) in DMF (1 ml) and THF (1 ml), iodomethane (32 μl, 530 μmol) was added. The reaction mixture was stirred for 24 h under reflux condition. The reaction mixture was poured into the mixed solvent of 1 M hydrochloric acid solution and chloroform. The aqueous layer was extracted with chloroform (twice). The organic layer was combined, washed with brine, and dried over sodium sulfate and evaporated to give a residue. The residue was purified by column chromatography (SiO_2 chloroform/hexane/Et_2O=50/10/1) to afford all-(*S*)-**16C** (88.3 mg, 88%).

all-(*S*)-16C: yellow powder; mp. > 300 °C; $[\alpha]_D^{20}$ = -192 (c = 0.452, $CHCl_3$); IR (KBr) 2956, 2931, 1445, 1376, 759 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.60-1.65 (m, 106H), 3.70-4.40 (m, 74H), 5.38 (s, 4H), 7.10-7.45 (m, 70H), 7.60 (d, *J* = 7.8, 4H), 7.82 (d, *J* = 8.3 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.25, 14.34, 14.6, 19.1, 19.6, 19.7, 30.2, 32.4, 32.7, 32.9, 33.1, 61.2, 61.3, 70.9, 73.4, 73.5, 124.6, 125.5, 126.4, 126.8, 126.9, 127.4, 127.5, 127.67, 127.74, 128.3, 129.0, 129.3, 129.9, 131.4, 131.55, 131.63, 131.8, 137.5, 147.9 150.8, 151.7, 152.3; MS (MALDI-TOF, dithranol matrix) 3805 (M^+); *Anal*. Calcd for $C_{252}H_{266}O_{32}\cdot 0.8CHCl_3$: C, 77.81; H, 6.89. Found: C, 77.93; H, 7.04.

all-(*S*)-8C: 95%; white solid; mp = 84 °C; $[\alpha]_D^{20}$ = -145 (c = 0.58, $CHCl_3$); IR (KBr) 2956, 2932, 2871, 1596, 1442, 1376, 1239 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.54 (t, *J* = 7.3 Hz, 6H), 0.68 (t, *J* = 7.8 Hz, 6H), 0.73 (t, *J* = 6.9 Hz, 6H), 0.74 (t, *J* = 7.3 Hz, 6H), 0.8-1.6 (m, 32H), 3.7-4.4 (m, 16H), 3.82 (s, 6H), 3.86 (s, 6H), 3.89 (s, 6H), 5.37 (s, 4H), 7.15-7.45 (m, 38H), 7.59 (d, *J* = 7.8 Hz, 4H), 7.82 (d, *J* = 8.2 Hz, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.24, 14.30, 14.32, 14.5, 14.6, 19.1, 19.55,19.66, 19.68, 23.2, 29.8, 30.2, 32.4, 32.7, 32.9, 33.1, 61.2, 70.9, 73.4, 73.5, 109.2, 124.5, 125.4, 125.5, 126.2, 126.4, 126.5, 126.8, 126.9, 127.1, 127.3, 127.4, 127.5, 127.67, 127.74, 128.3, 129.0, 129.9, 131.4, 131.5, 131.6, 131.7, 131.8, 137.5, 147.9, 150.8, 151.6, 152.3; MS (FAB^+) *m/z* 1979 (M^+); *Anal*. Calcd for $C_{132}H_{138}O_{16}\cdot H_2O$: C, 79.33; H, 7.06. Found: C, 79.44; H, 7.21.

all-(*S*)-32C: yellow powder; mp. > 300 °C; $[\alpha]_D^{20}$ = -180 (c = 0.50, $CHCl_3$); IR (KBr) 2956, 2933, 1376, 1343, 1237, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.60-1.80 (m, 218H), 3.70-4.50 (m, 154H), 5.38 (s, 4H), 7.00-7.57 (m, 134H), 7.60 (d, *J* = 7.3, 4H), 7.82 (d, *J* = 8.2, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 14.0, 14.4, 14.6, 19.1, 19.6, 19.7, 20.2, 23.2, 27.7, 29.8, 30.2, 32.4, 32.7, 32.9, 33.2, 61.3, 70.9, 73.6, 125.6, 126.3, 126.8, 127.0, 127.4, 127.7, 127.8, 128.4, 129.0, 131.4, 131.6, 131.8, 137.6, 150.9, 151.7, 152.3. *Anal*. Calcd for $C_{490}H_{522}O_{64}\cdot 6H_2O$: C, 78.09; H, 7.11. Found: C, 78.37; H, 7.44.

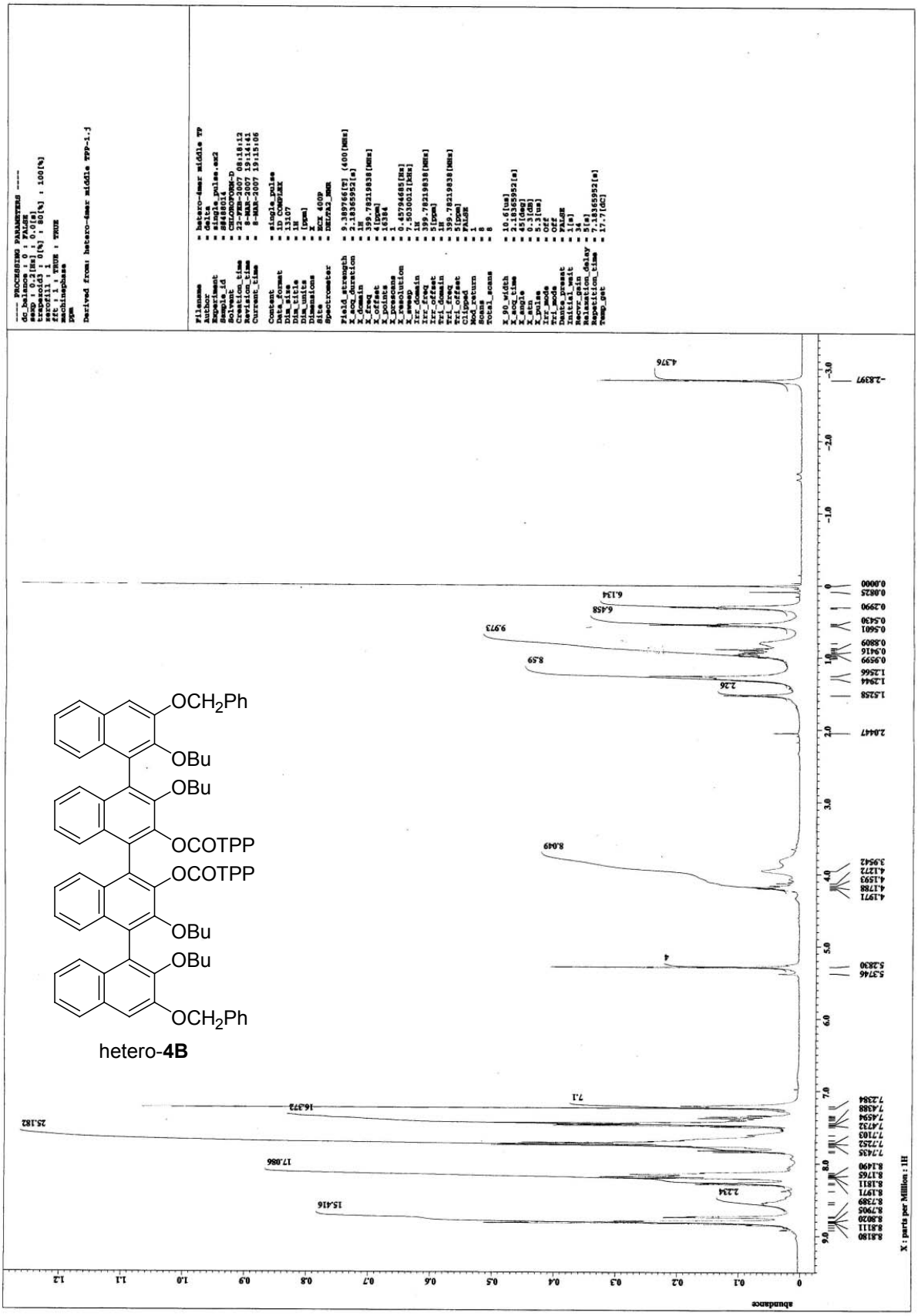
General Procedure for the Synthesis of D Series Compounds:

The preparation of all-(*S*)-**16D** is typical. A suspension of all-(*S*)-**16C** (2.57 g, 0.68 mmol) and $Pd(OH)_2$ (500 mg) in THF (80 ml) was stirred under hydrogen atmosphere for 4 h at room temperature with monitoring the reaction by TLC (hexane/AcOEt/chloroform = 5/1/2). After $Pd(OH)_2$ was filtered off, the filtrate was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, hexane/diethyl ether/chloroform = 5/1/2, twice) to afford all-(*S*)-**16D** (1.02 g, 41%) and recovered all-(*S*)-**16C** (0.80 g).

all-(*S*)-16D: yellow powder; mp. > 300 °C; $[\alpha]_D^{20}$ = -176 (c = 0.408, $CHCl_3$); IR (KBr) 3438, 2957, 2934, 1376, 1343, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.548 (t, *J* = 7.3, 3H), 0.552 (t, *J* = 7.3, 6H), 0.64-1.70 (m, 106H), 3.60-4.05 (m, 74H), 5.39 (s, 2H), 6.24 (s, 1H), 7.10-7.45 (m, 67H), 7.60 (d, *J* = 7.4, 2H), 7.78-7.85 (m, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 13.98, 14.03, 14.2, 14.4, 19.1, 19.6, 19.7, 30.2, 32.6, 32.7, 32.9, 33.1, 61.26, 61.33, 70.9, 73.5, 74.3, 125.2, 125.6, 126.4, 126.8, 126.9, 127.6, 127.7, 127.8, 128.4, 129.0, 131.3, 131.6, 131.8, 137.5, 146.1, 148.6, 150.8, 151.0, 151.7; MS (MALDI-TOF, dithranol matrix) 3716 (M^+); *Anal*. Calcd for $C_{245}H_{260}O_{32}\cdot 0.25CHCl_3$: C, 78.62; H, 7.00. Found: C, 78.22; H, 7.07.

all-(*S*)-8D: yellow foam; mp. 121-123 °C; $[\alpha]_D^{20}$ = -146 (c = 1.04, $CHCl_3$); IR (KBr) 3518, 3009, 2958, 1444, 1238, 908, 758 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.548 (t, *J* = 7.3, 3H), 0.553 (t, *J* = 7.3, 3H), 0.62-1.65 (m, 50H), 3.60-4.05 (m, 28H), 4.05-4.40 (m, 6H), 5.38 (s, 2H), 6.26 (s, 1H), 7.10-7.54 (m, 35H), 7.60 (d, *J* =7.3, 2H), 7.76-7.86 (m, 2H); ^{13}C-NMR (100MHz, $CDCl_3$) δ 13.95, 14.00, 14.1, 14.2, 14.28, 14.31, 19.07, 19.11, 19.5, 19.6, 19.7, 32.6, 32.7, 32.9, 33.1, 61.2, 70.9, 73.4, 73.5, 73.6, 74.2, 109.2, 110.4, 124.2, 124.5, 125.2, 125.5, 125.9, 126.1, 126.4, 126.5, 126.6, 126.7, 126.77, 126.84, 127.0, 127.1, 127.3, 127.4, 127.5, 127.7, 128.3, 129.0, 129.5, 129.9, 131.32, 131.36, 131.40, 131.5, 131.6, 131.7, 131.8, 132.1, 137.5, 146.1, 147.9, 148.6, 150.8, 151.0, 151.6, 152.3; MS (FAB) 1889 (M^+); *Anal*. Calcd for $C_{125}H_{132}O_{16}\cdot H_2O$: C, 78.67; H, 7.08. Found: C, 78.72; H, 7.07.

all-(*S*)-32D: mp. > 300 °C; $[\alpha]_D^{20}$ = -195 (c = 0.25, $CHCl_3$); IR (KBr) 3374, 2934, 1692, 1477 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$) δ 0.55 (t, *J* = 7.3, 6H), 0.60-1.70 (m, 218H), 3.70-4.40 (m, 154H), 5.38 (s, 2H), 6.21 (s, 1H), 7.10-7.63 (m, 133H), 7.82 (d, *J* = 8.2, 2H). MS (MALDI-TOF, dithranol matrix) 7369 (M^+); *Anal*. Calcd for $C_{485}H_{516}O_{64}\cdot CHCl_3$: C, 77.95; H, 6.96. Found: C, 77.95; H, 7.06.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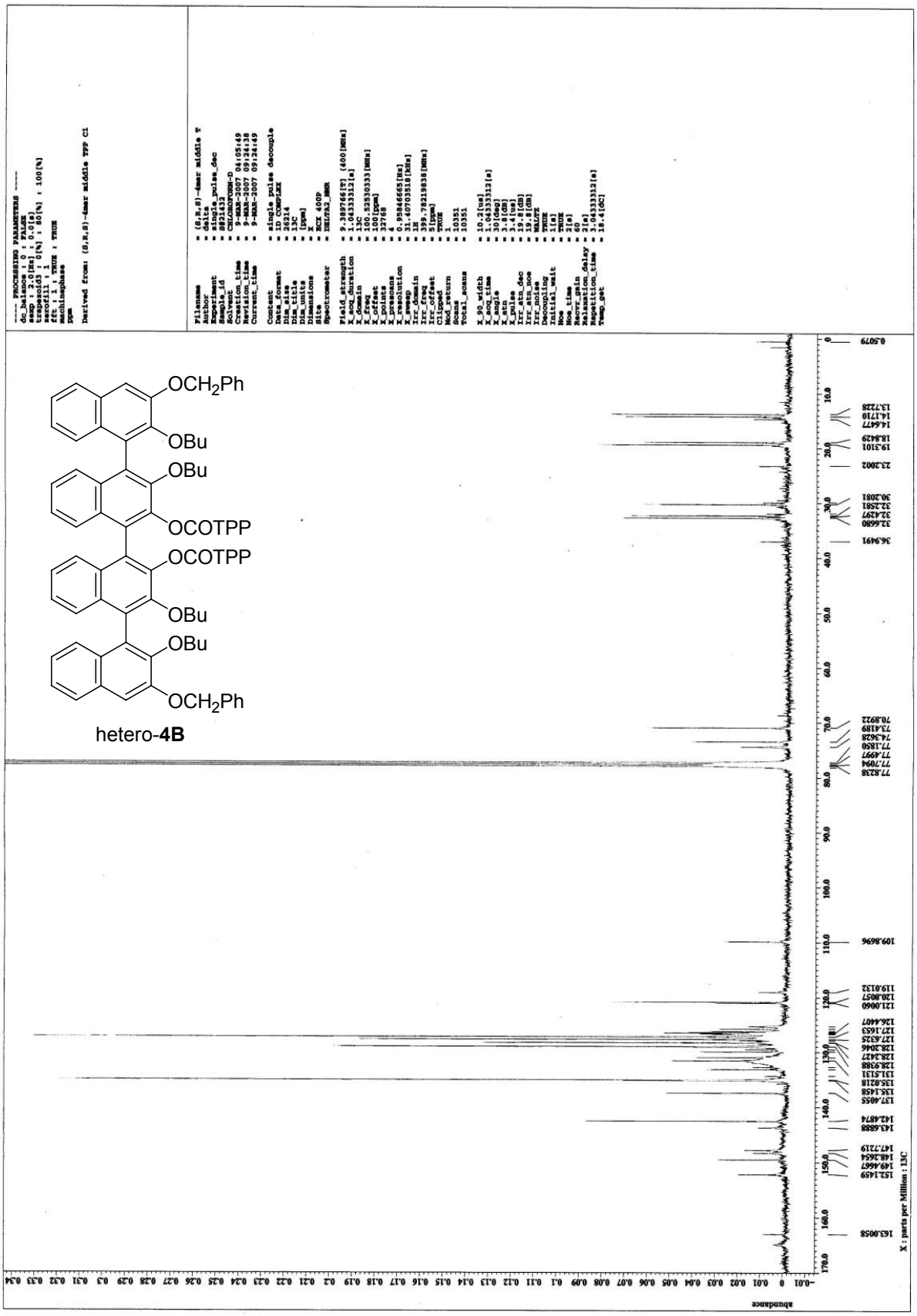
OBu
OCOTPP
OCOTPP
OBu
OBu
OCH2Ph
hetero-4B
X : parts per Million : 1H
abundance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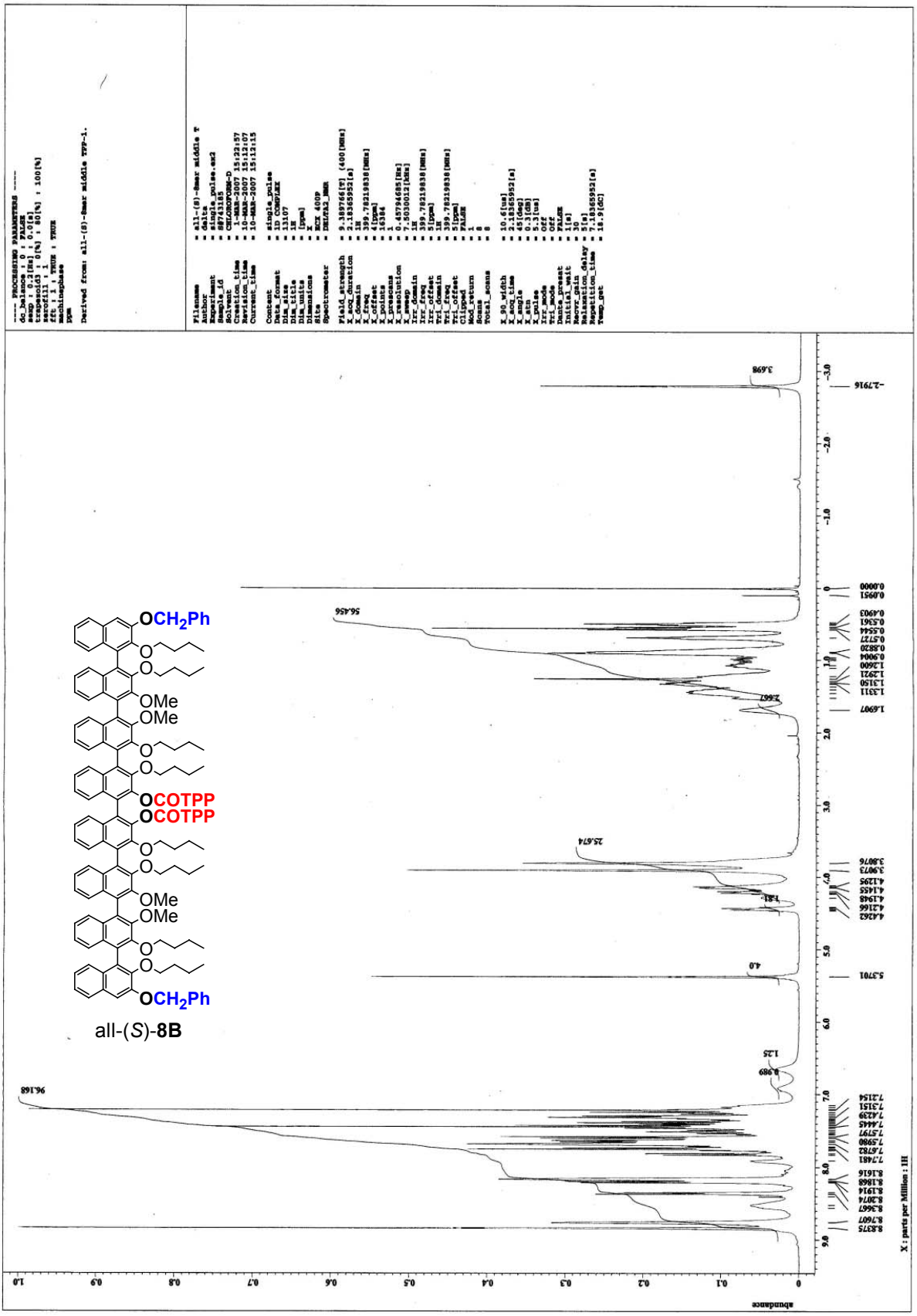
OCH2Ph
hetero-4B
X : parts per Million : 13C
Abundance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OMe
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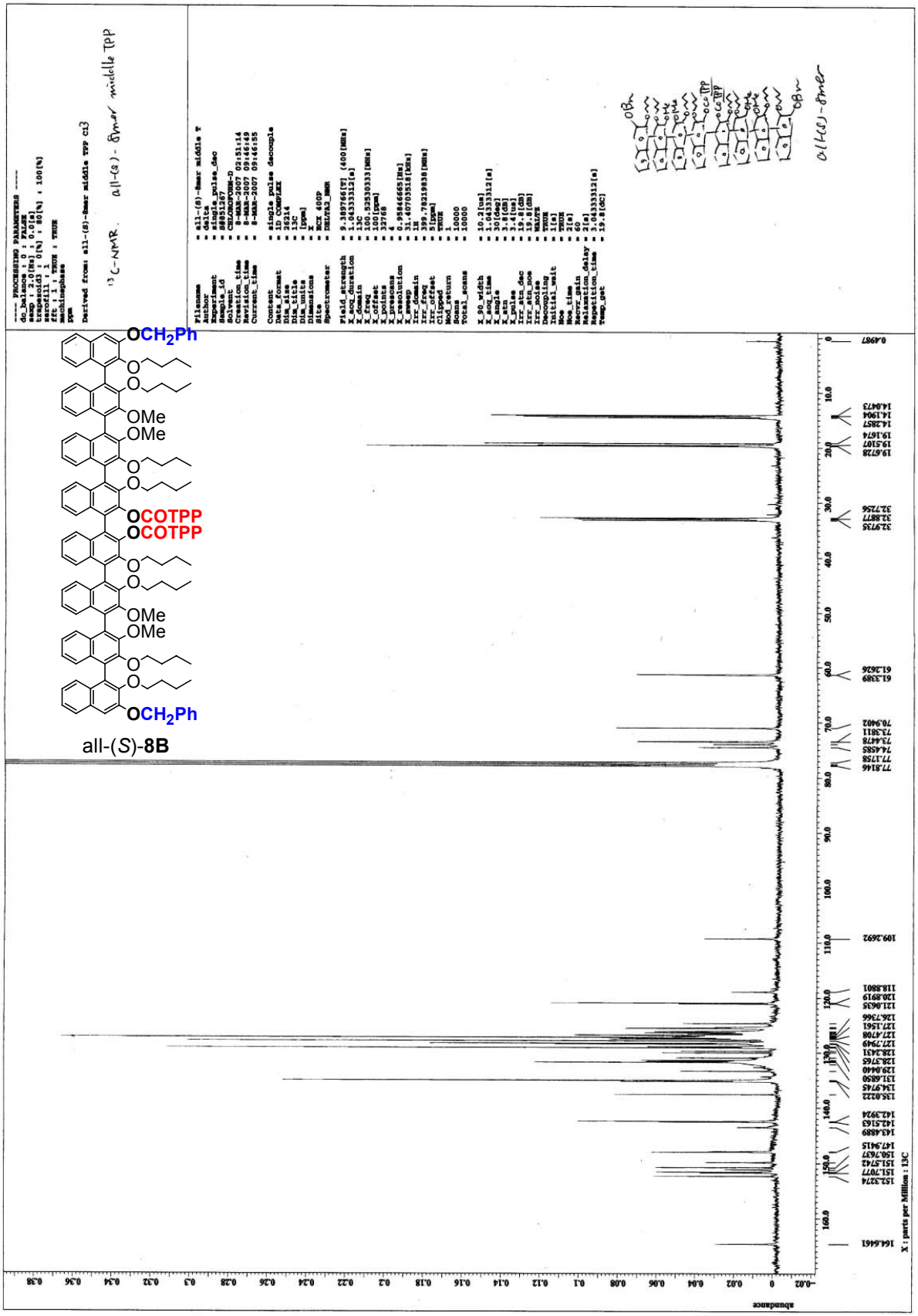
OCOTPP
OMe
OMe
OCH2Ph
all-(S)-8B
X : parts per Million : 1H
abundance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OMe
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OCOTPP
OMe
OMe
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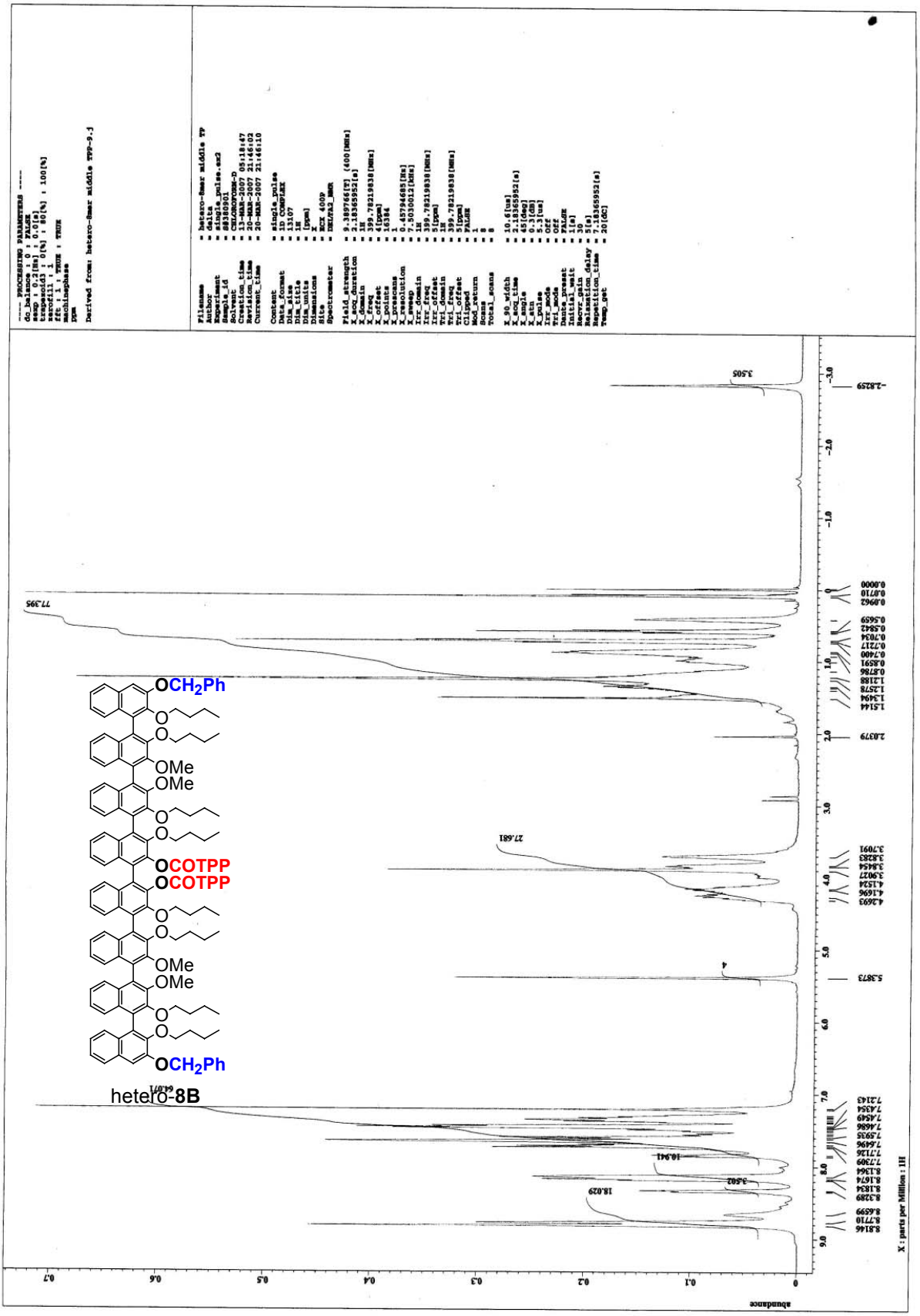
all-(S)-8B
13C-NMR. all-(S)-8mer middle TPP
all-(S)-8mer
X : parts per Million : 13C
Abundance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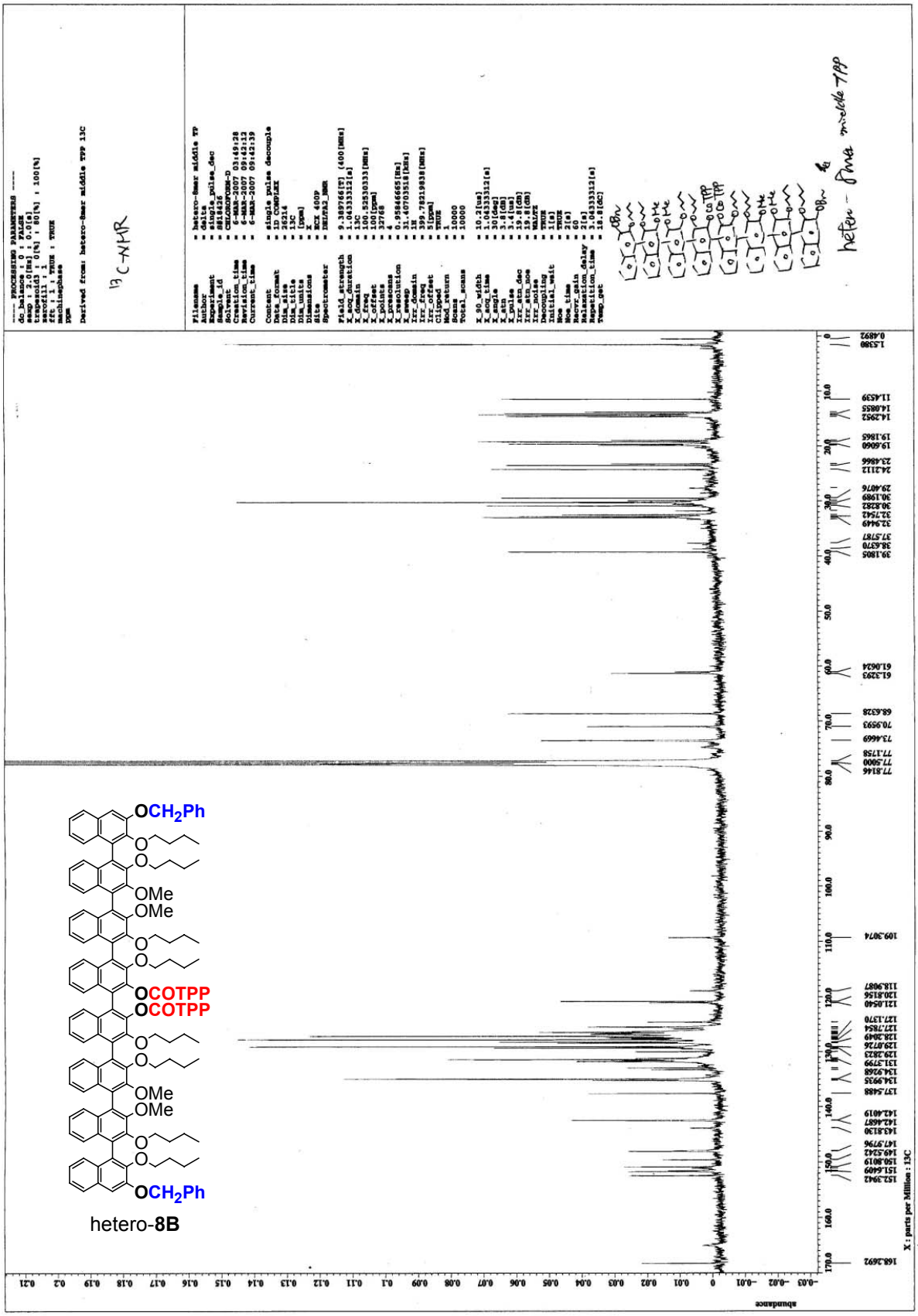
OCOTPP
OCOTPP
OMe
OMe
OCH2Ph
hetero-8B
X : parts per Million : 1H
abundance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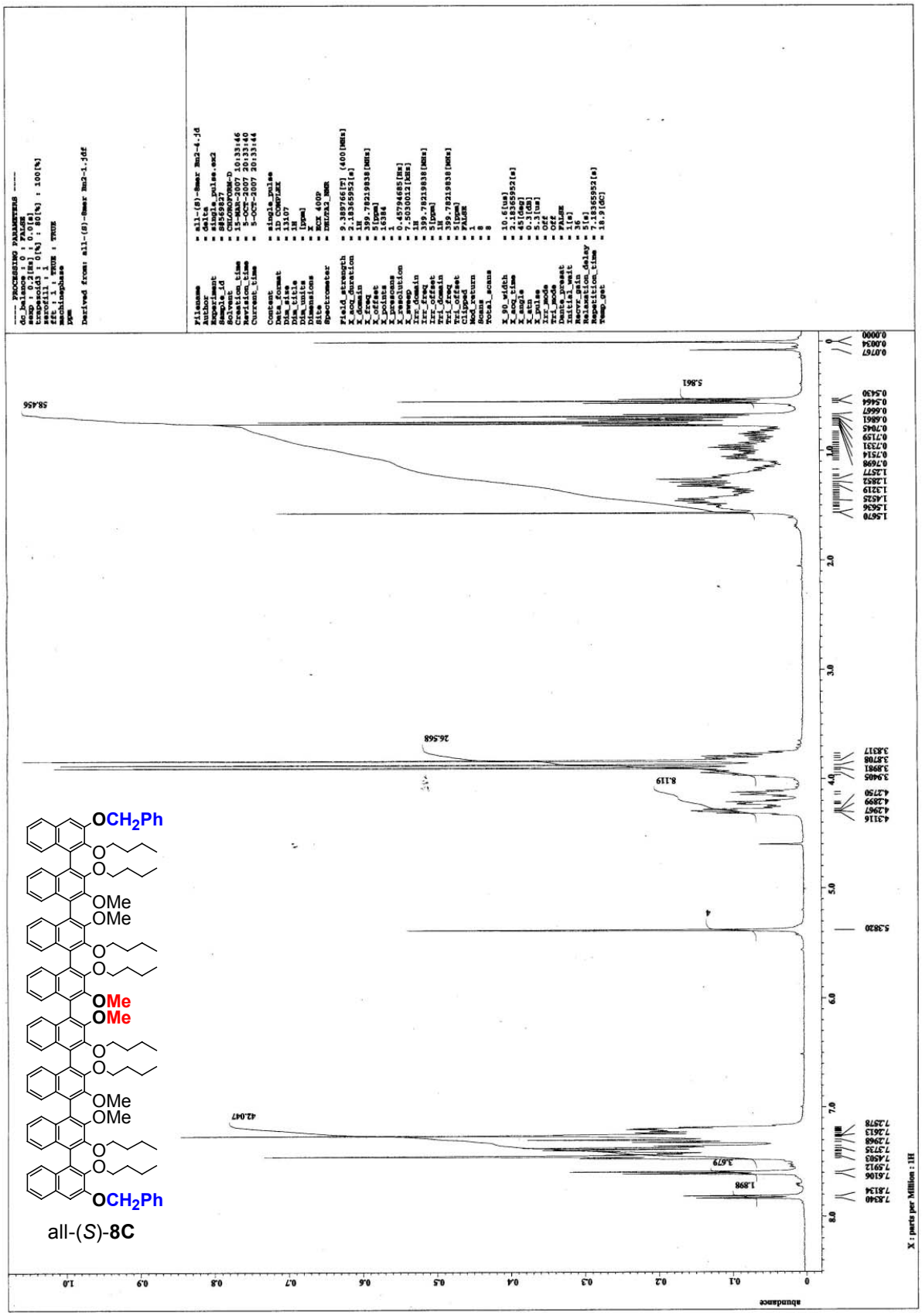
OMe
OMe
OCH2Ph
hetero-8B
13C-NMR
X : parts per Million : 13C
abundance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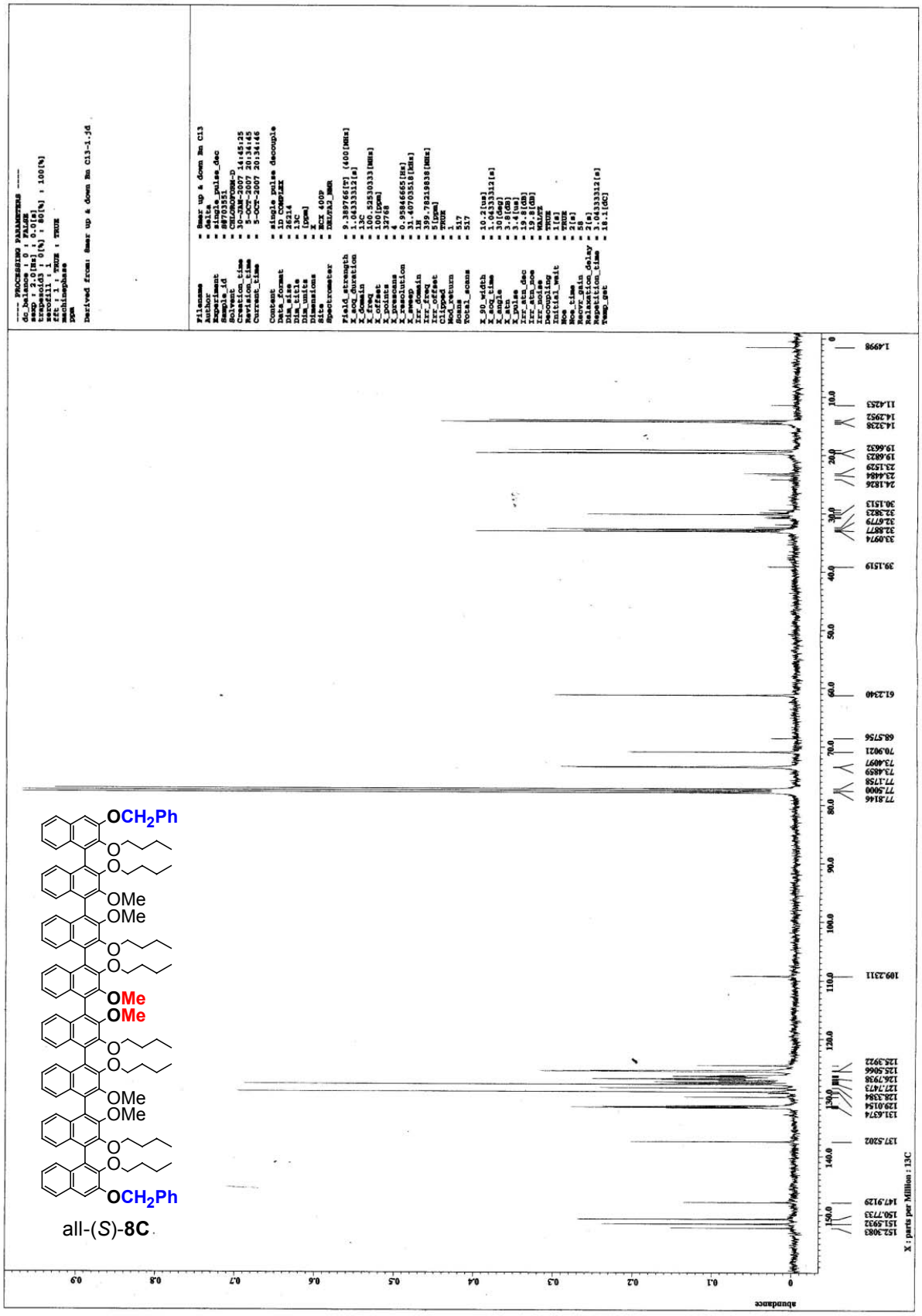
OMe
OMe
OMe
OMe
OMe
OCH2Ph
all-(S)-8C
X : parts per Million : 1H
Abundance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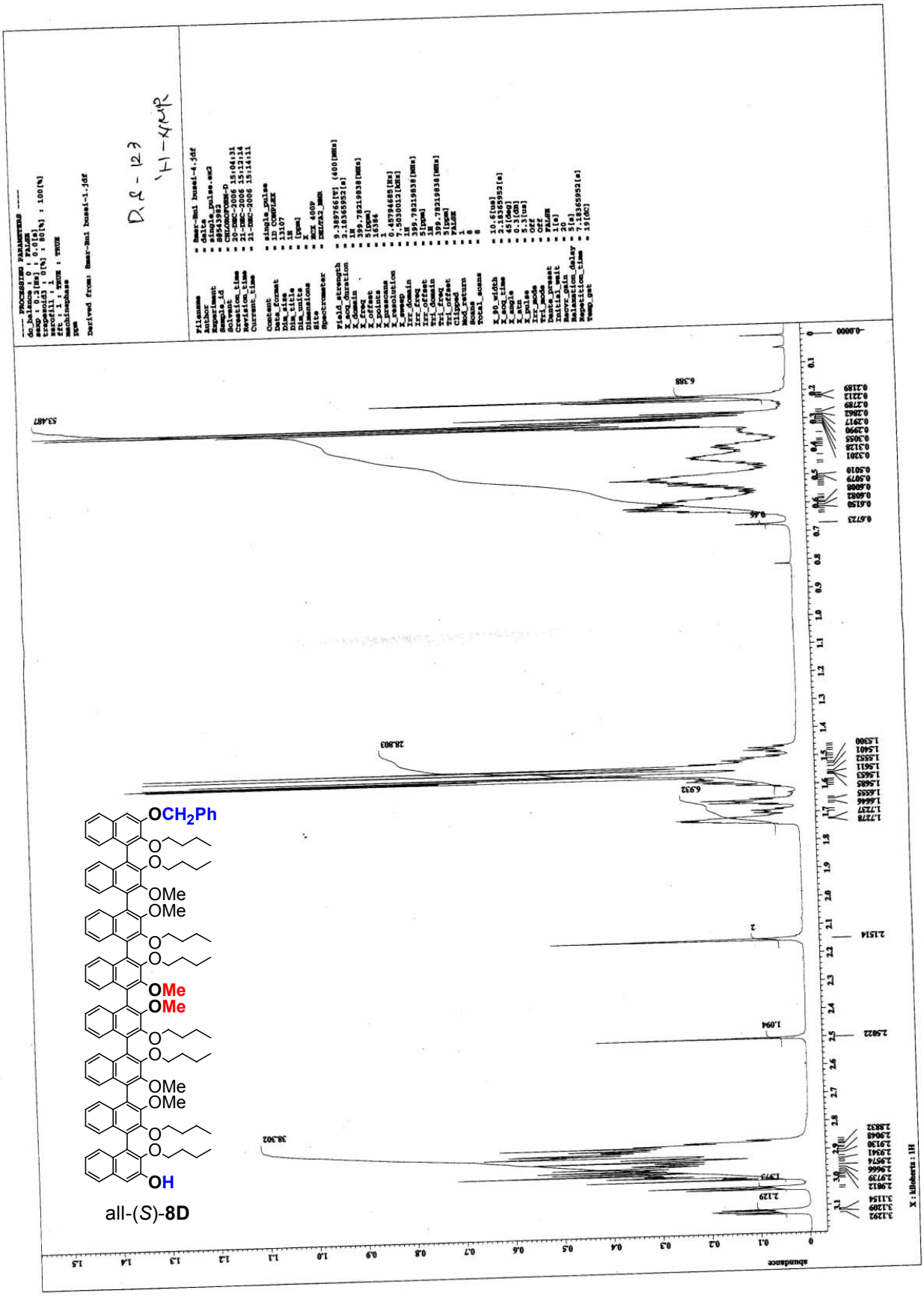
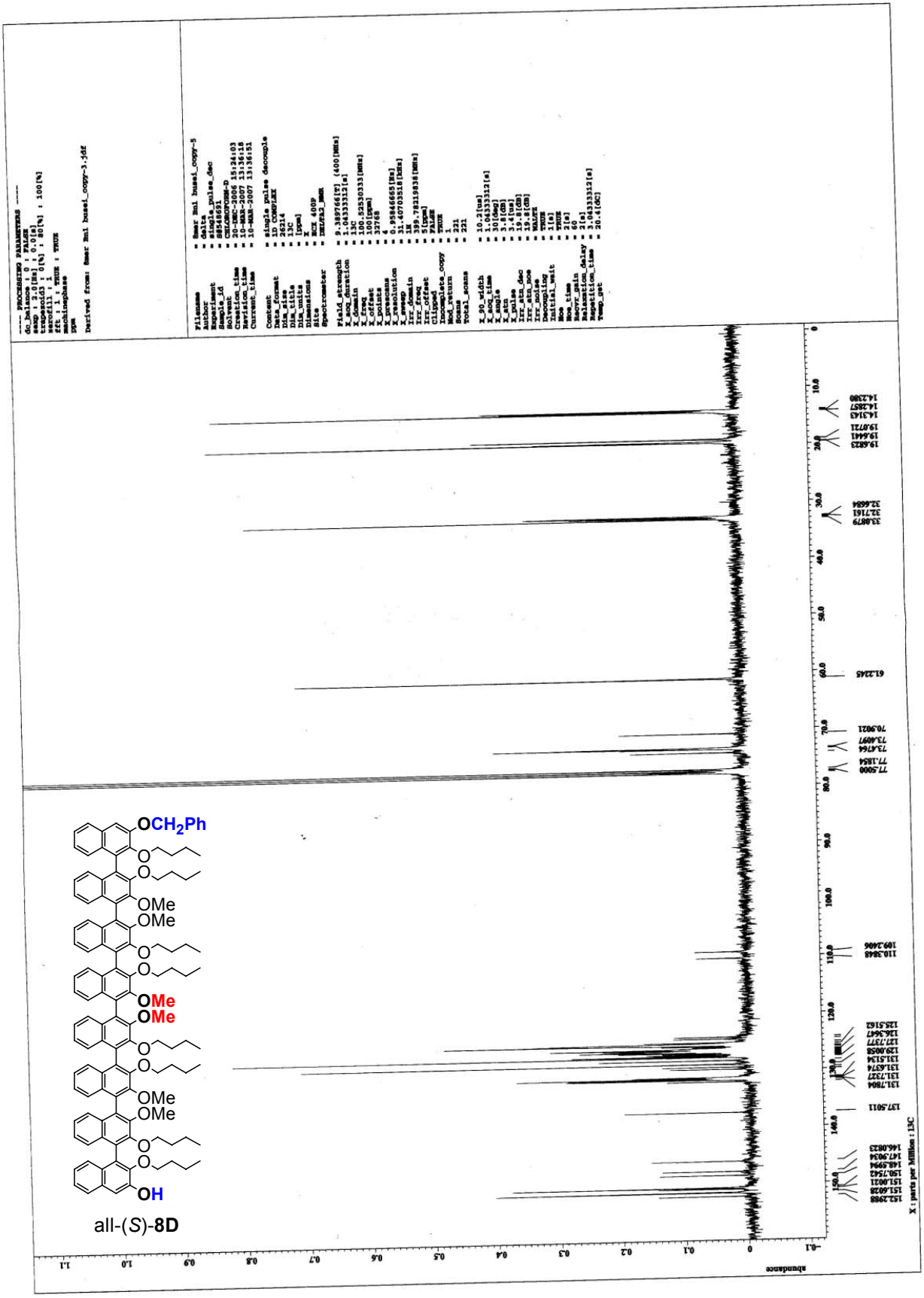
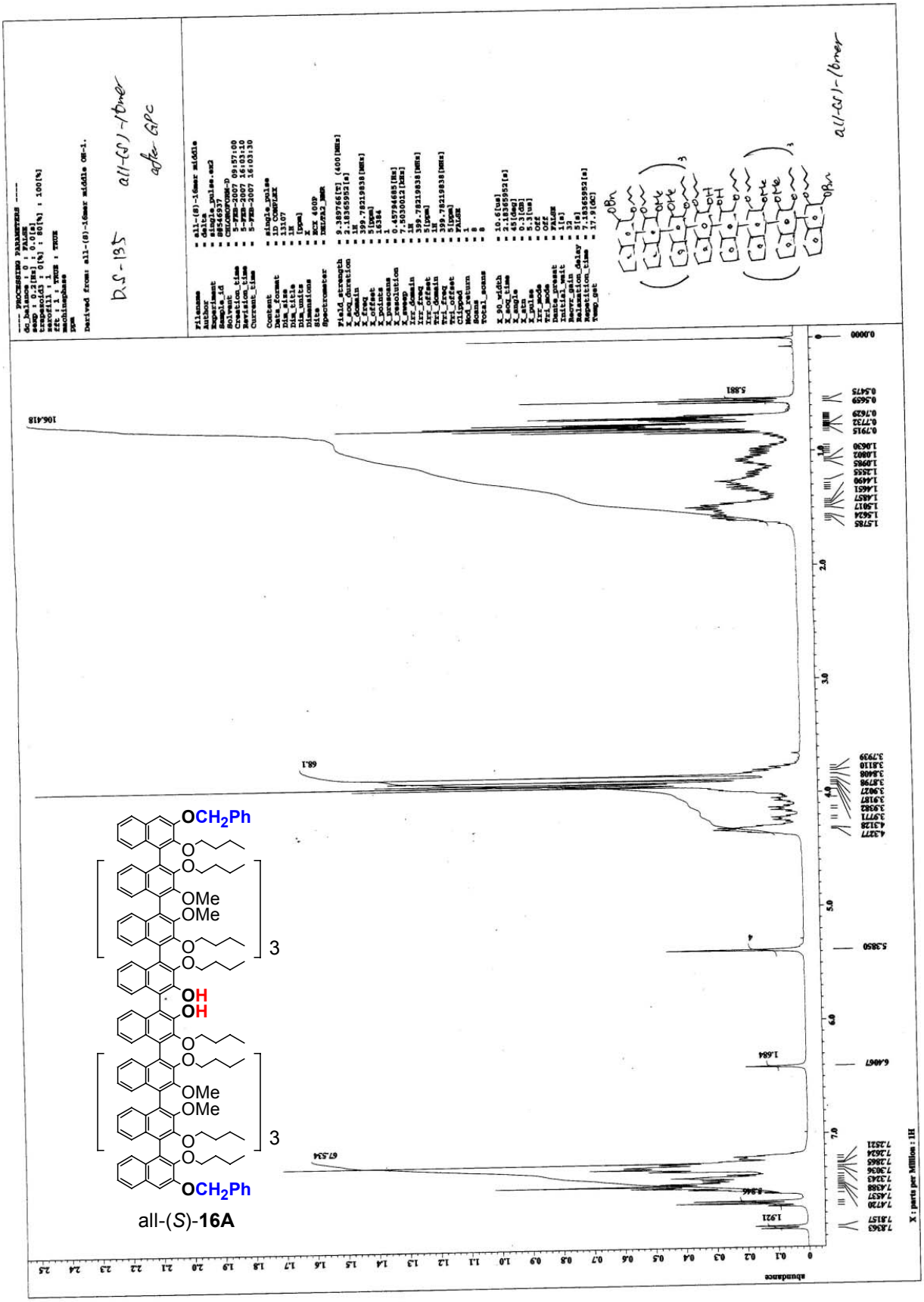
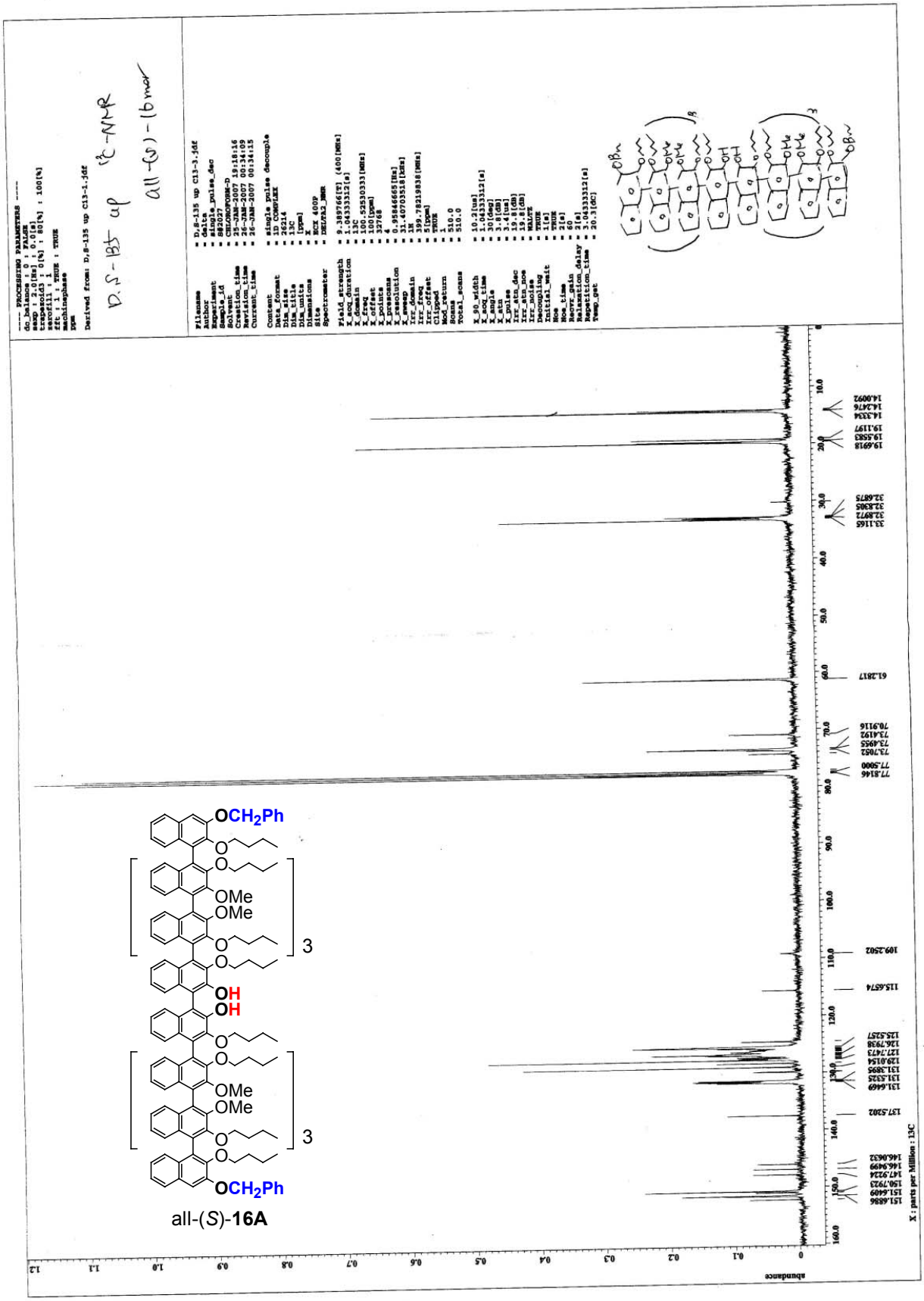
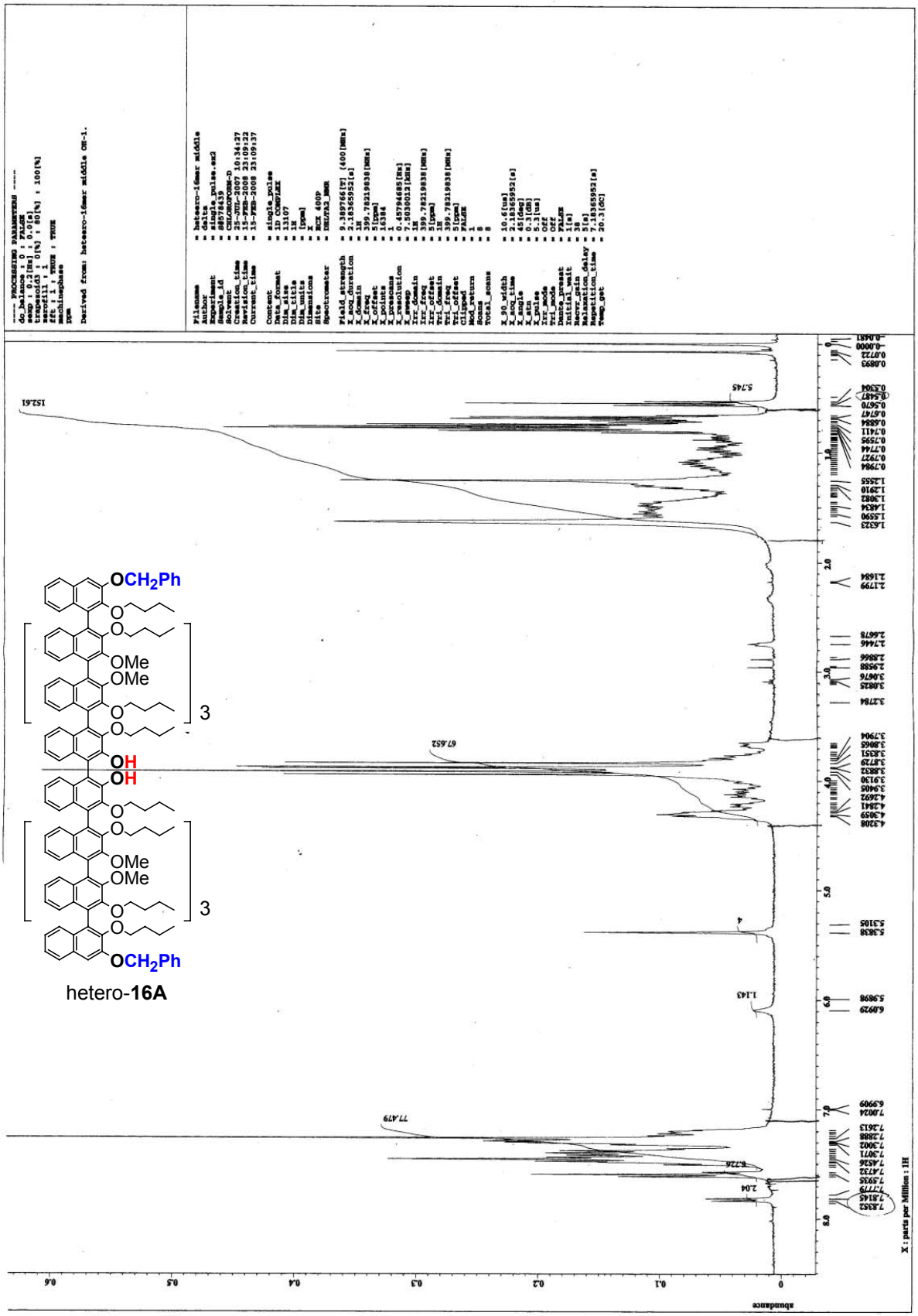
OMe
OMe
OMe
OMe
OMe
OCH2Ph
all-(S)-8C
X : parts per Million : 13C
abundance

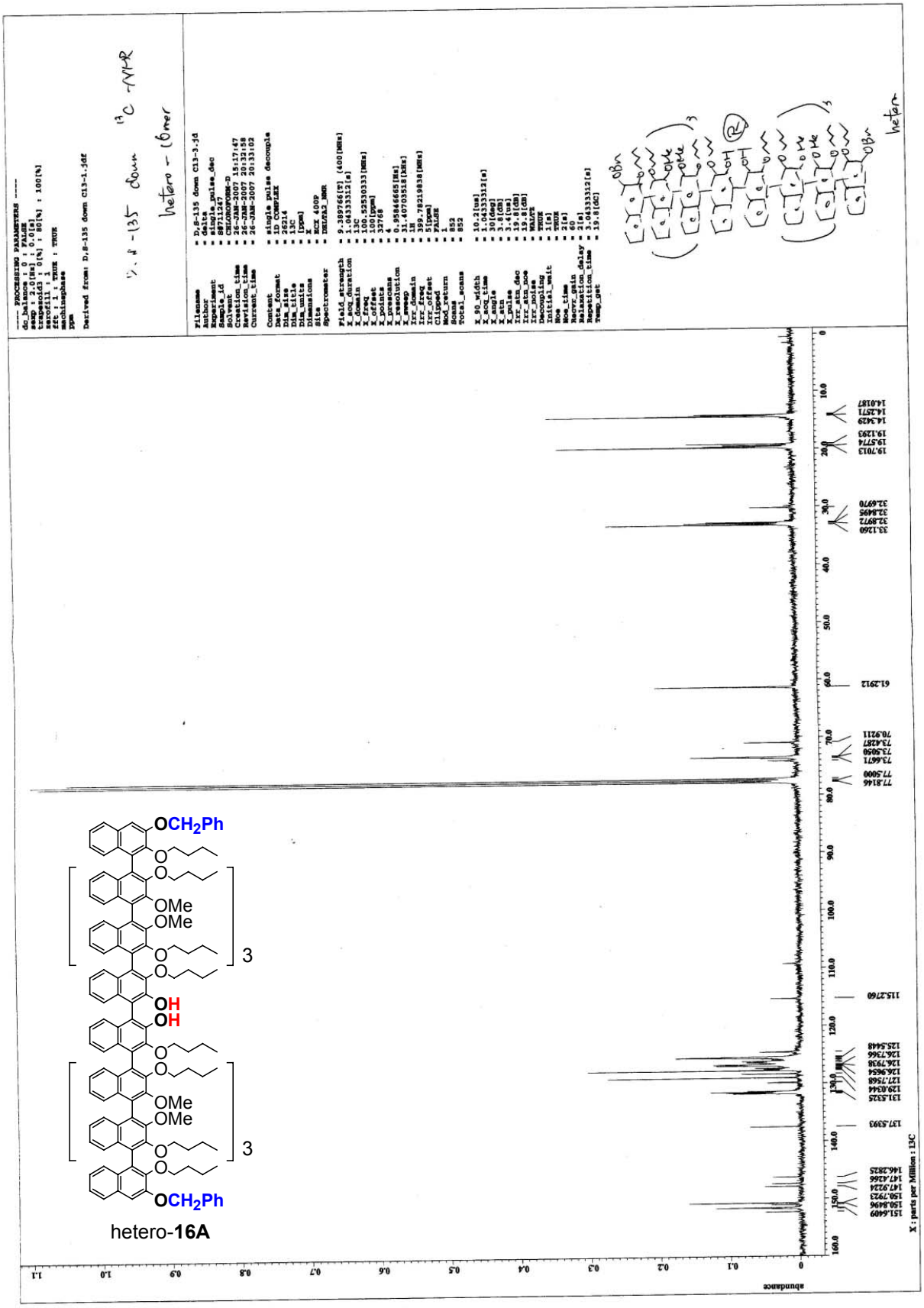

OCH2Ph
OMe
OMe
OMe
OMe
OMe
OMe
OH
all-(S)-8D
X : kilohertz : 1H
abundance

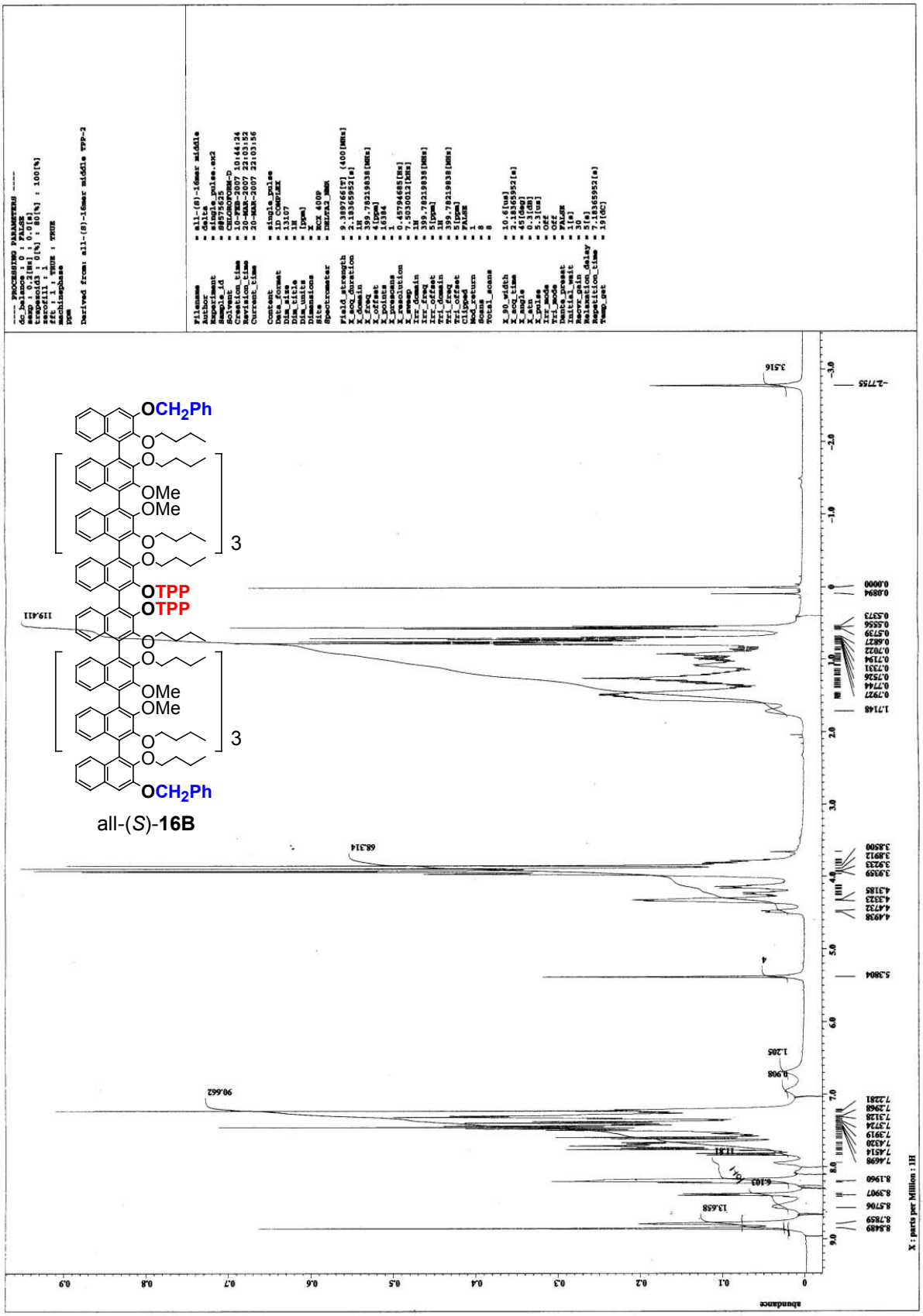

OCH2Ph
OMe
OMe
OMe
OMe
OMe
OMe
OH
all-(S)-8D
X : parts per Million : 13C
Abundance


all-(S)-16A
OCH2Ph
OMe
OH
3
all-(S)-16mer
after GPC
X : parts per Million : 1H
abundance


OCH2Ph
OMe
OMe
3
OH
OH
OMe
OMe
3
OCH2Ph
all-(S)-16A
X : parts per Million : 13C
Abundance


OCH2Ph
OMe
OMe
3
OH
OH
OMe
OMe
3
OCH2Ph
hetero-16A
X : parts per Million : 1H
abundance


OCH2Ph
OMe
OMe
3
OH
OH
OMe
OMe
3
OCH2Ph
hetero-16A
X : parts per Million : 13C
abundance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OTPP
OTPP
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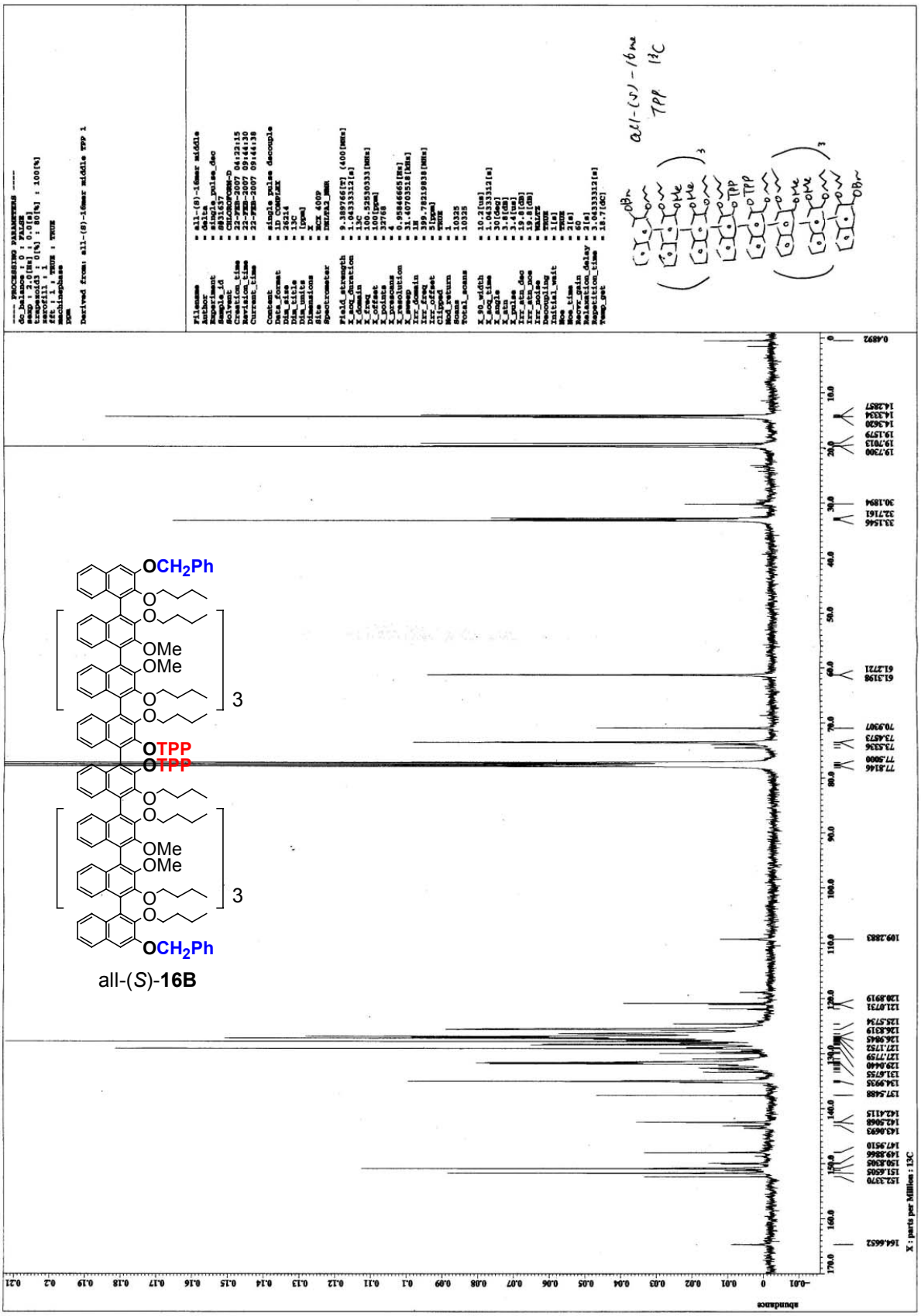
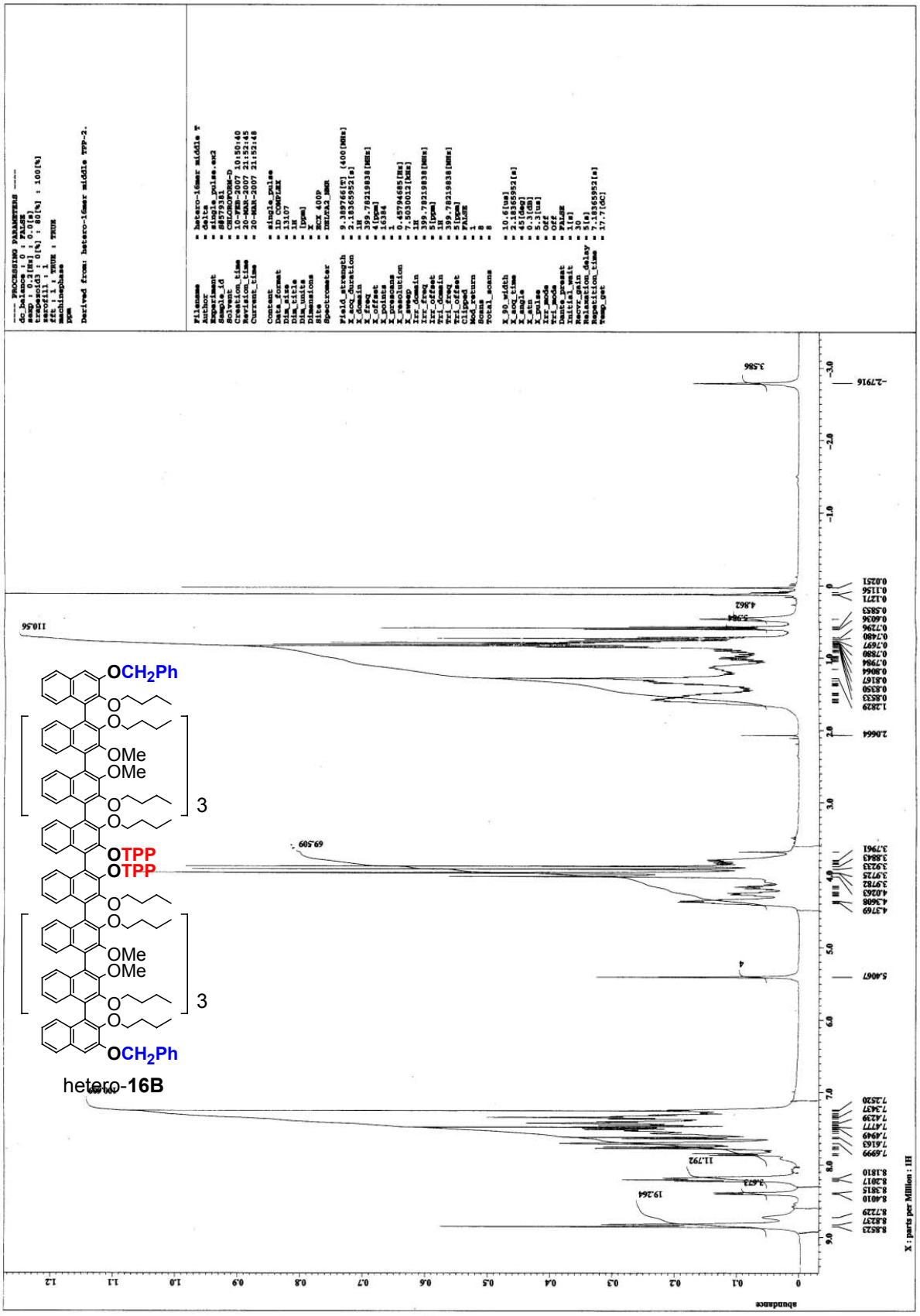
3
OCH2Ph
all-(S)-16B
X : parts per Million : 1H
Abundance


OCH2Ph
OMe
OMe
3
OTPP
OTPP
OMe
OMe
3
OCH2Ph
all-(S)-16B
all-(S)-16
TPP
13C
X : parts per Million : 13C
abundance


OCH2Ph
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OMe
3
OTPP
OTPP
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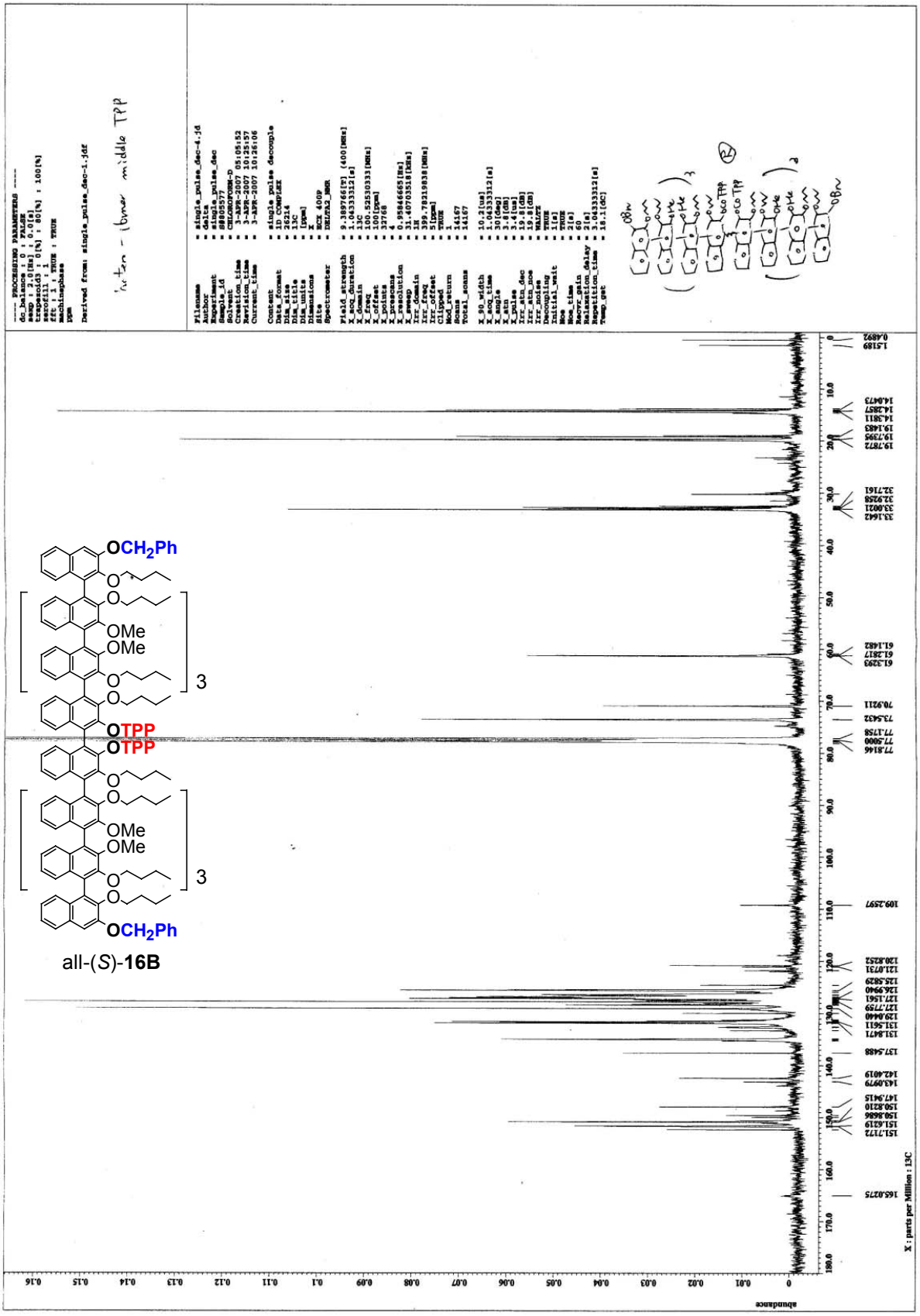
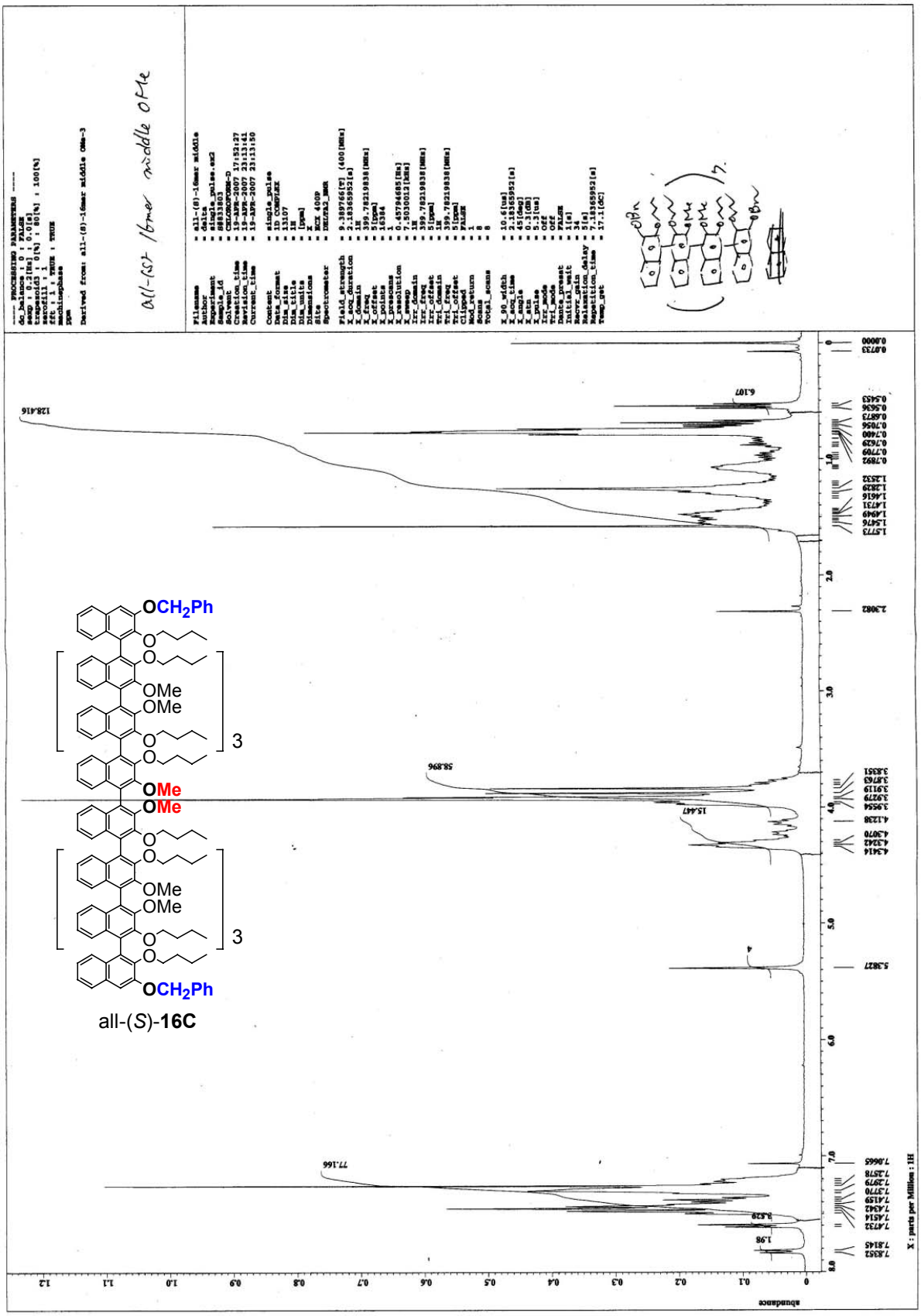
OMe
3
OCH2Ph
hetero-16B
X : parts per Million : 1H
abundance


OCH2Ph
OMe
OMe
3
OTPP
OTPP
OMe
OMe
3
OCH2Ph
all-(S)-16B
X : parts per Million : 13C
abundance


OCH2Ph
OMe
OMe
3
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OMe
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3
OCH2Ph
all-(S)-16C
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6.107
1.98
8.529
7.8652
7.8145
7.4732
7.4514
7.4342
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7.3579
7.3578
7.0665
5.3827
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1.2522
0.7892
0.7629
0.7799
0.7400
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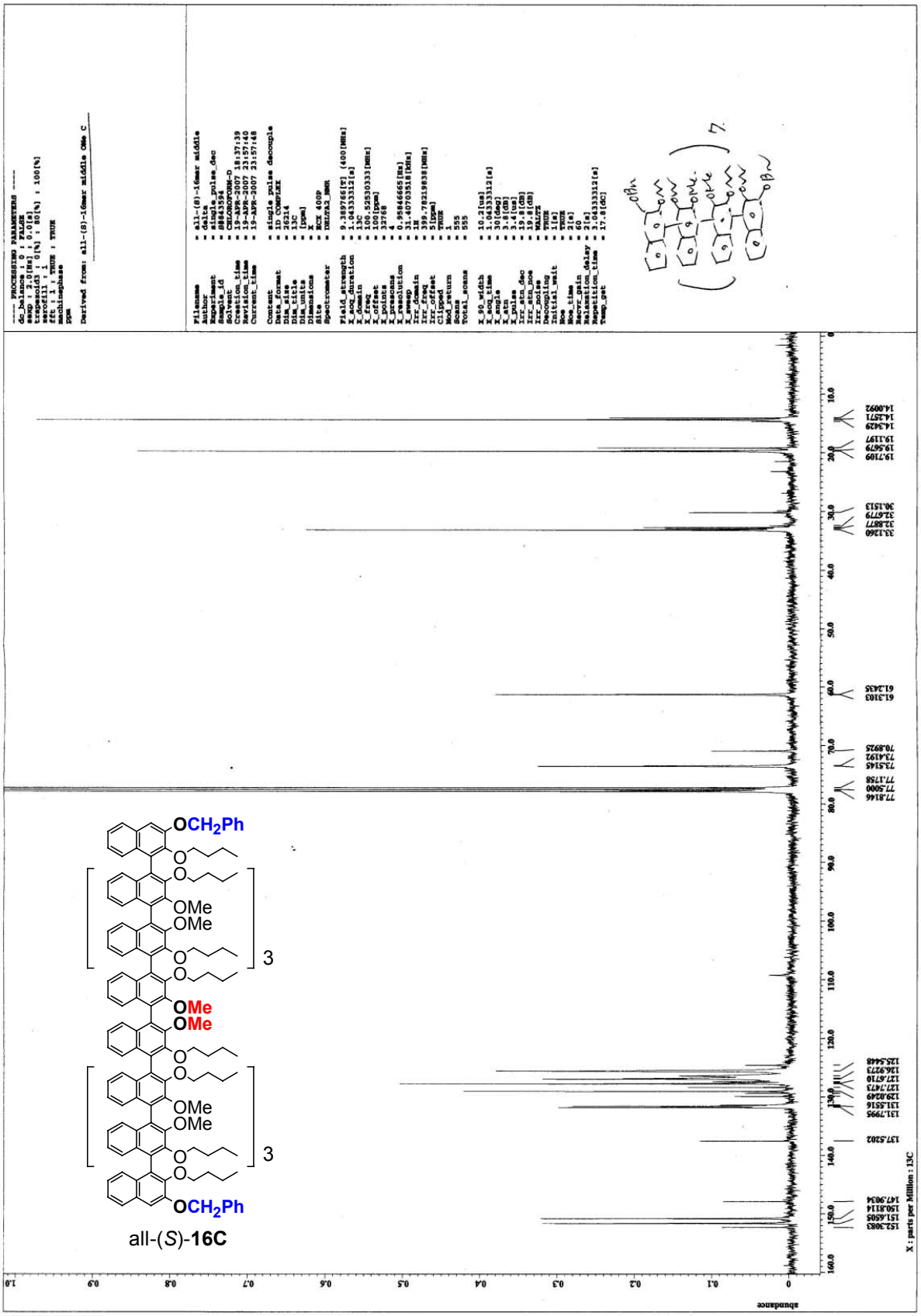
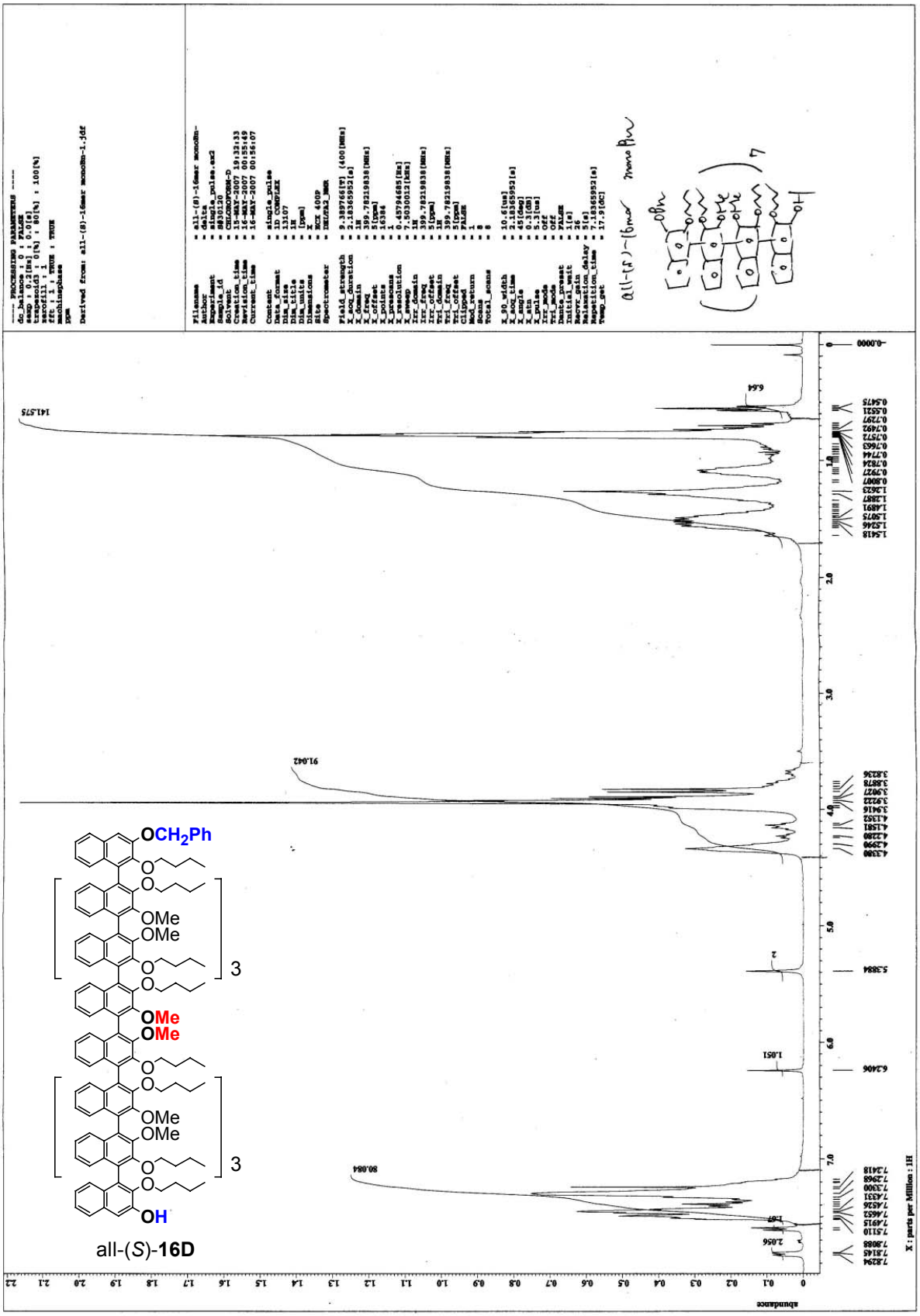
0.0000
X : parts per Million : 1H
abundance


OCH2Ph
OMe
OMe
3
OMe
OMe
OMe
OMe
3
OCH2Ph
all-(S)-16C
X : parts per Million : 13C
abundance


OCH2Ph
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3
OMe
OMe
OMe
OMe
3
OH
all-(S)-16D
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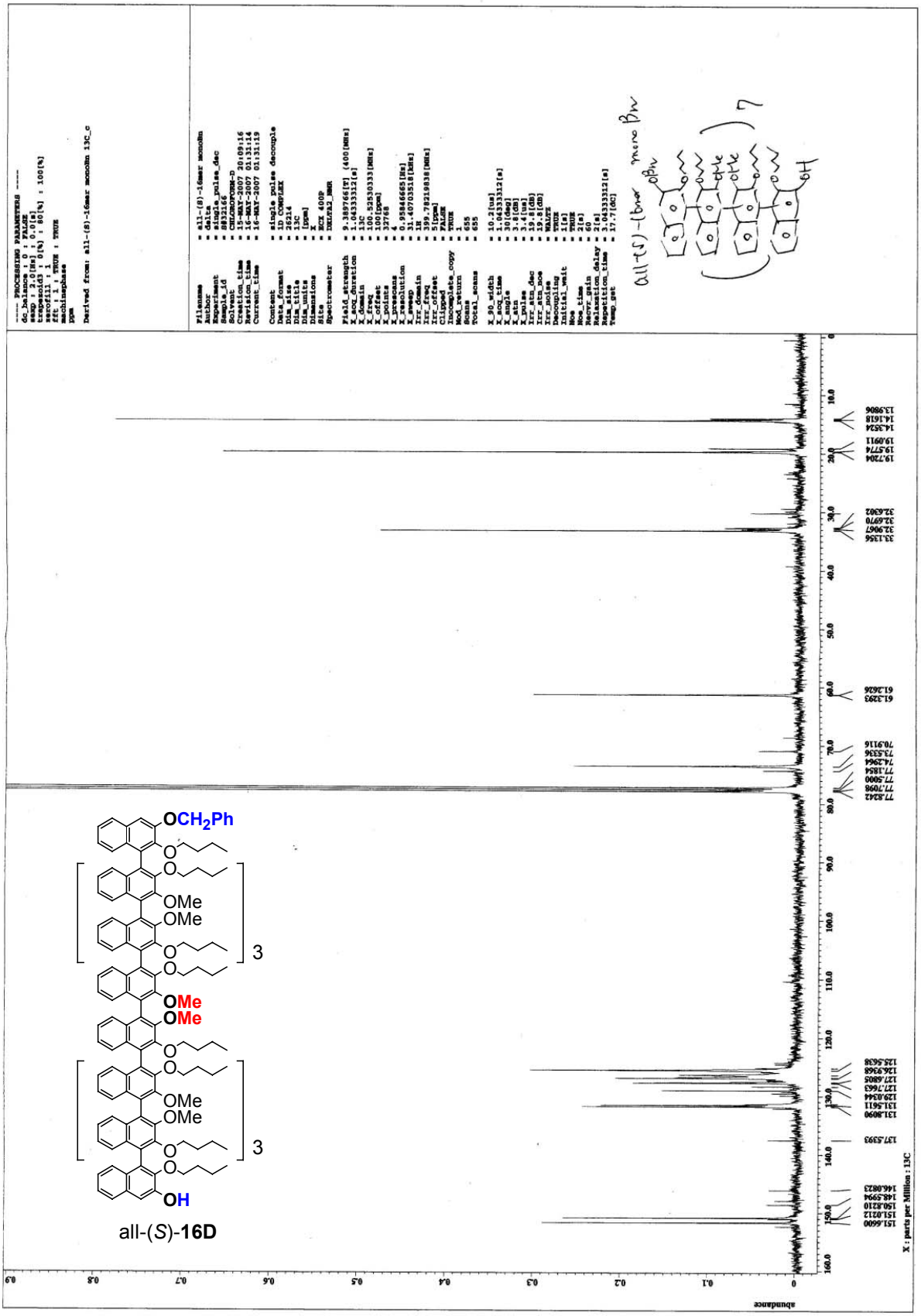
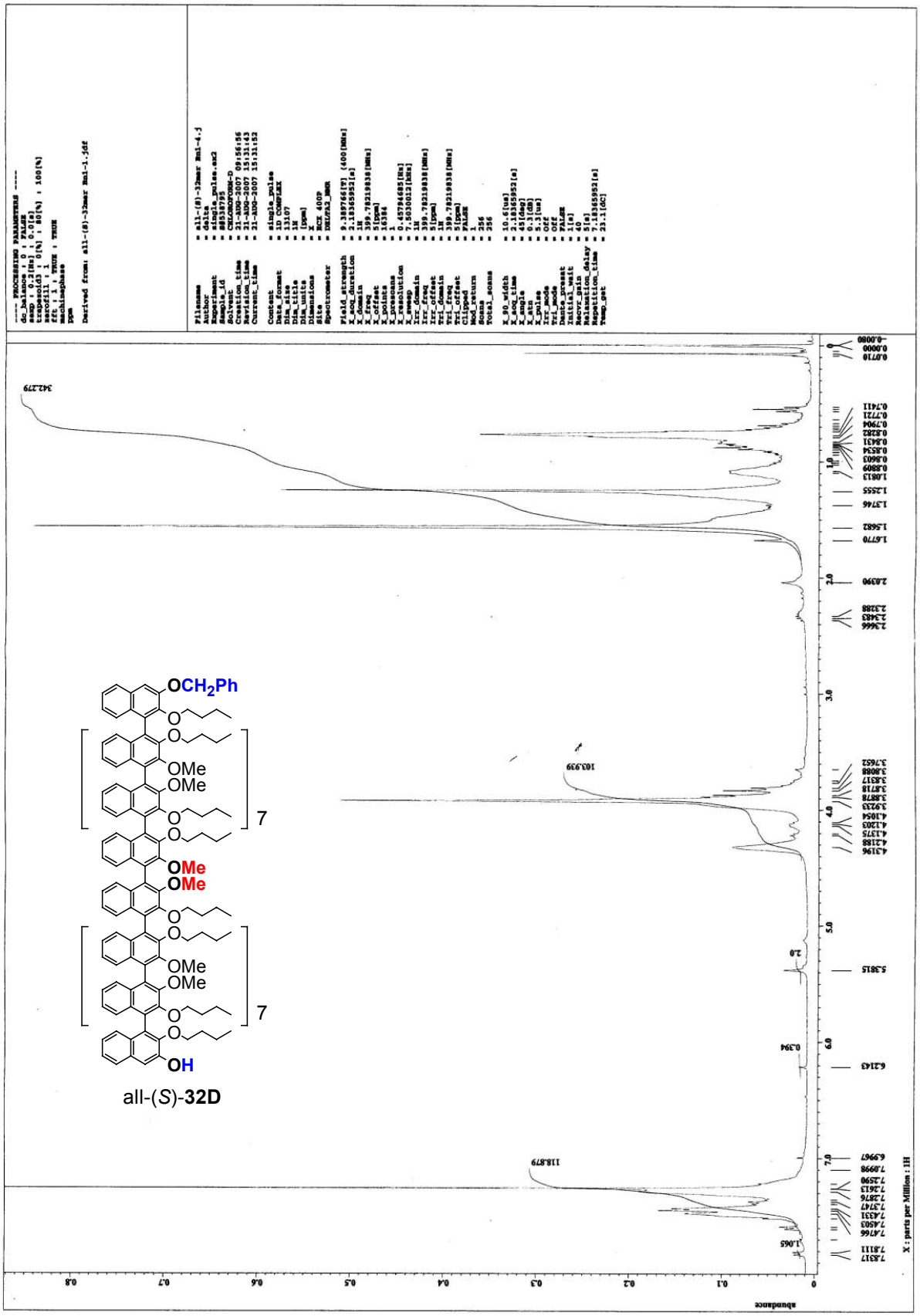
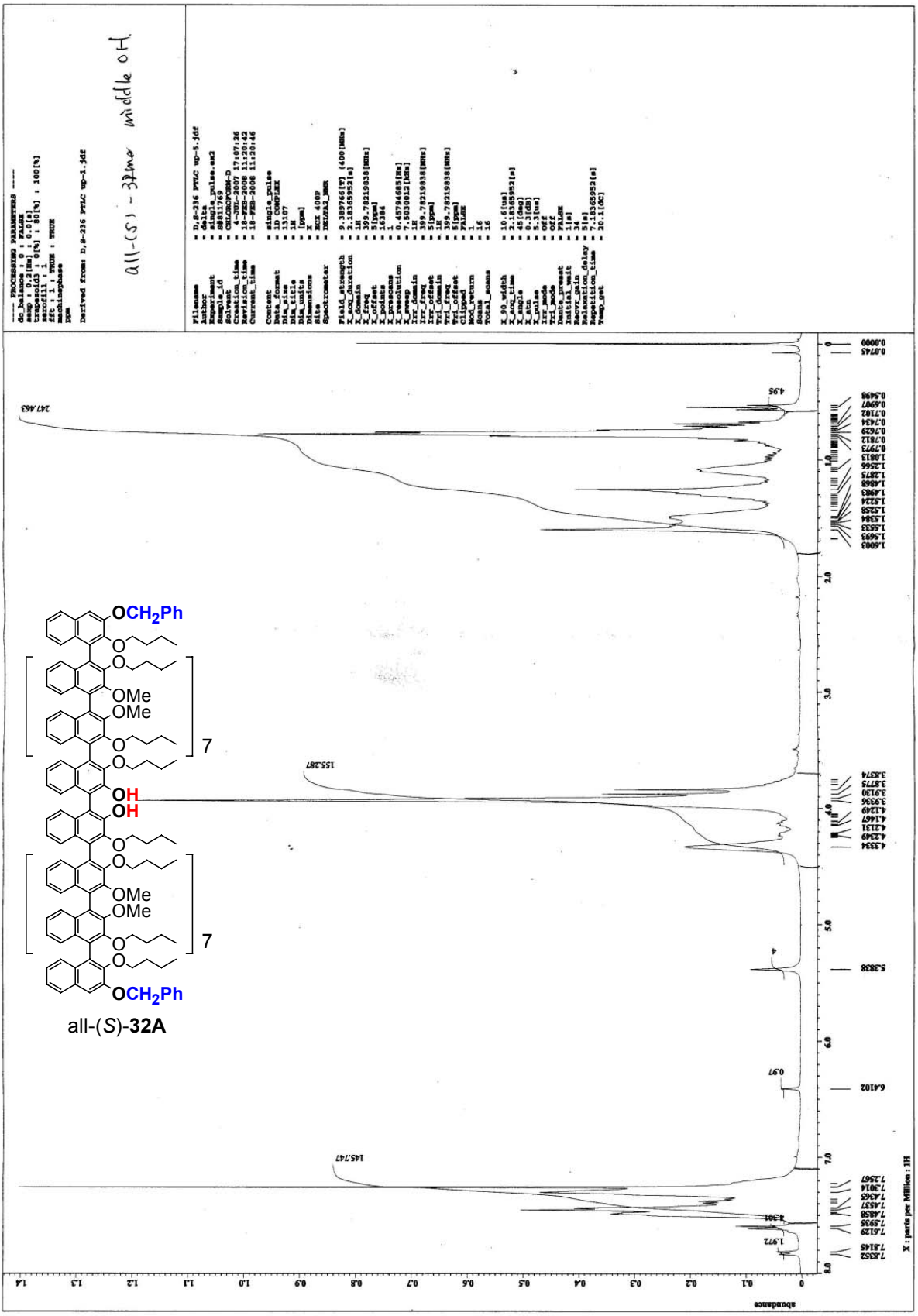
80.084
6.64
5.3884
6.2406
1.051
2
2.056
1.87
X : parts per Million : 1H
abundance


OCH2Ph
OMe
OMe
OMe
OMe
OMe
OMe
OH
3
3
all-(S)-16D
all-(S)-16mer monoBn
X : parts per Million : 13C
abundance


OCH2Ph
OMe
OMe
7
OMe
OMe
OMe
OMe
7
OH
all-(S)-32D
X : parts per Million : 1H
abundance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OH
OH
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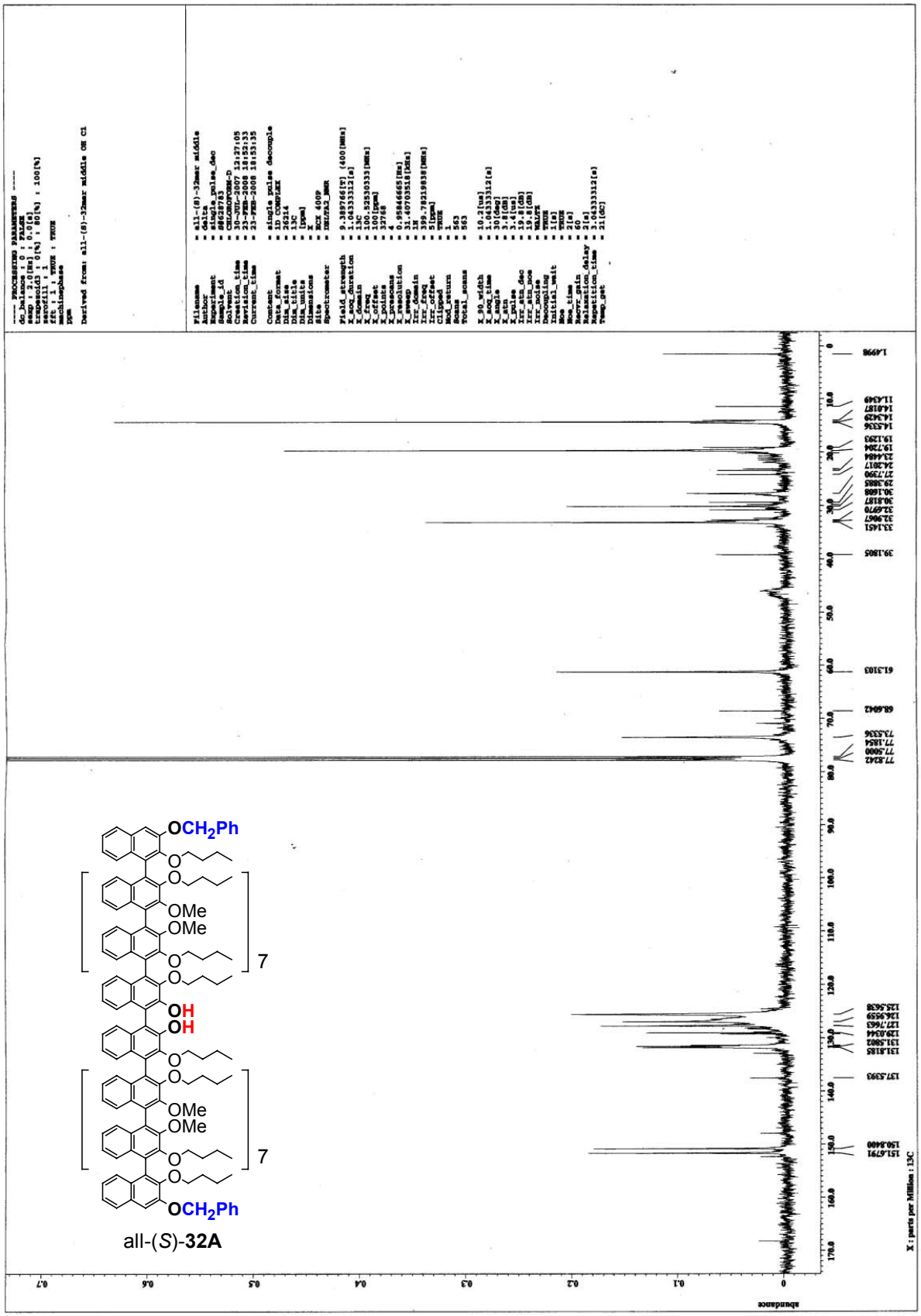
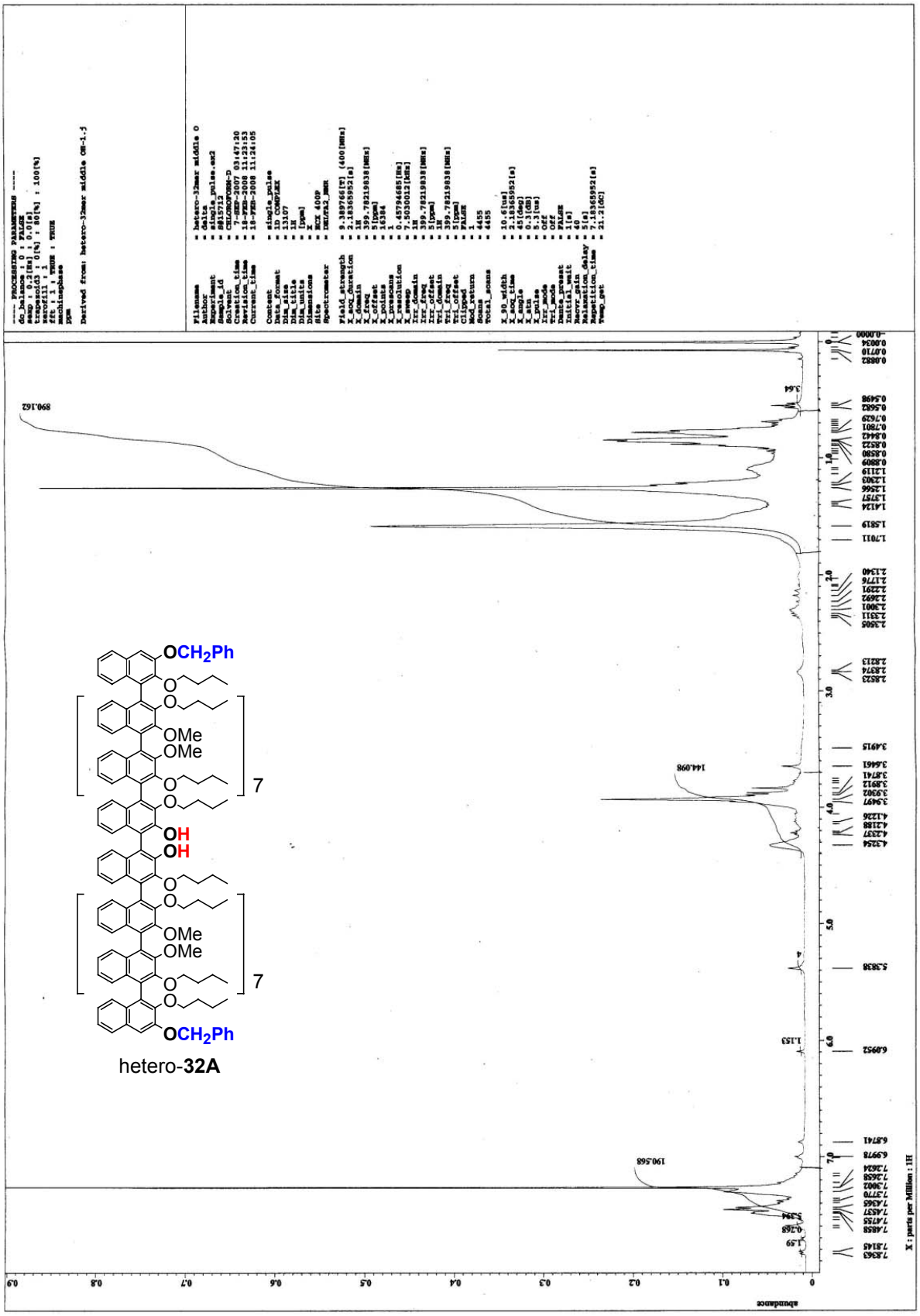
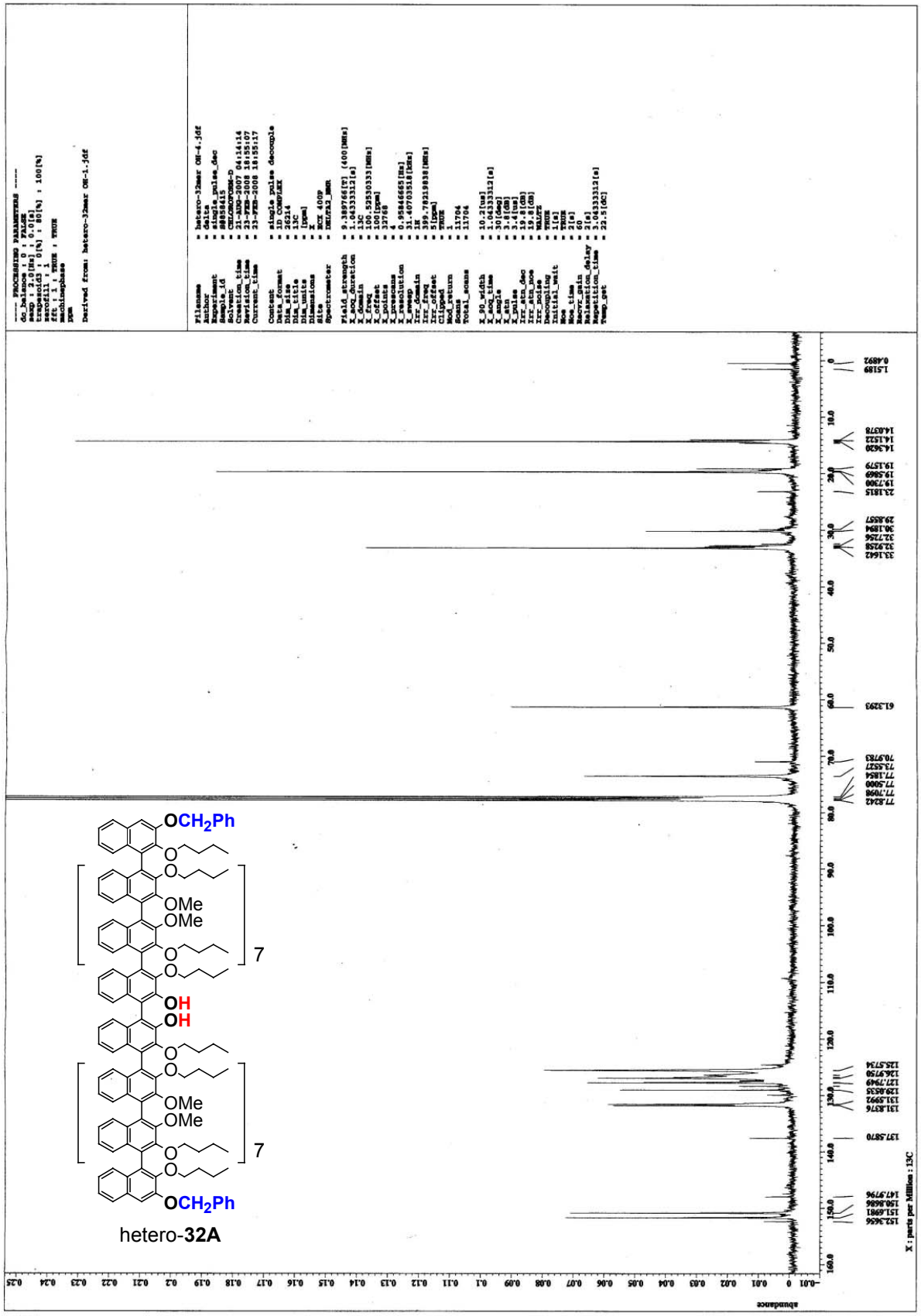
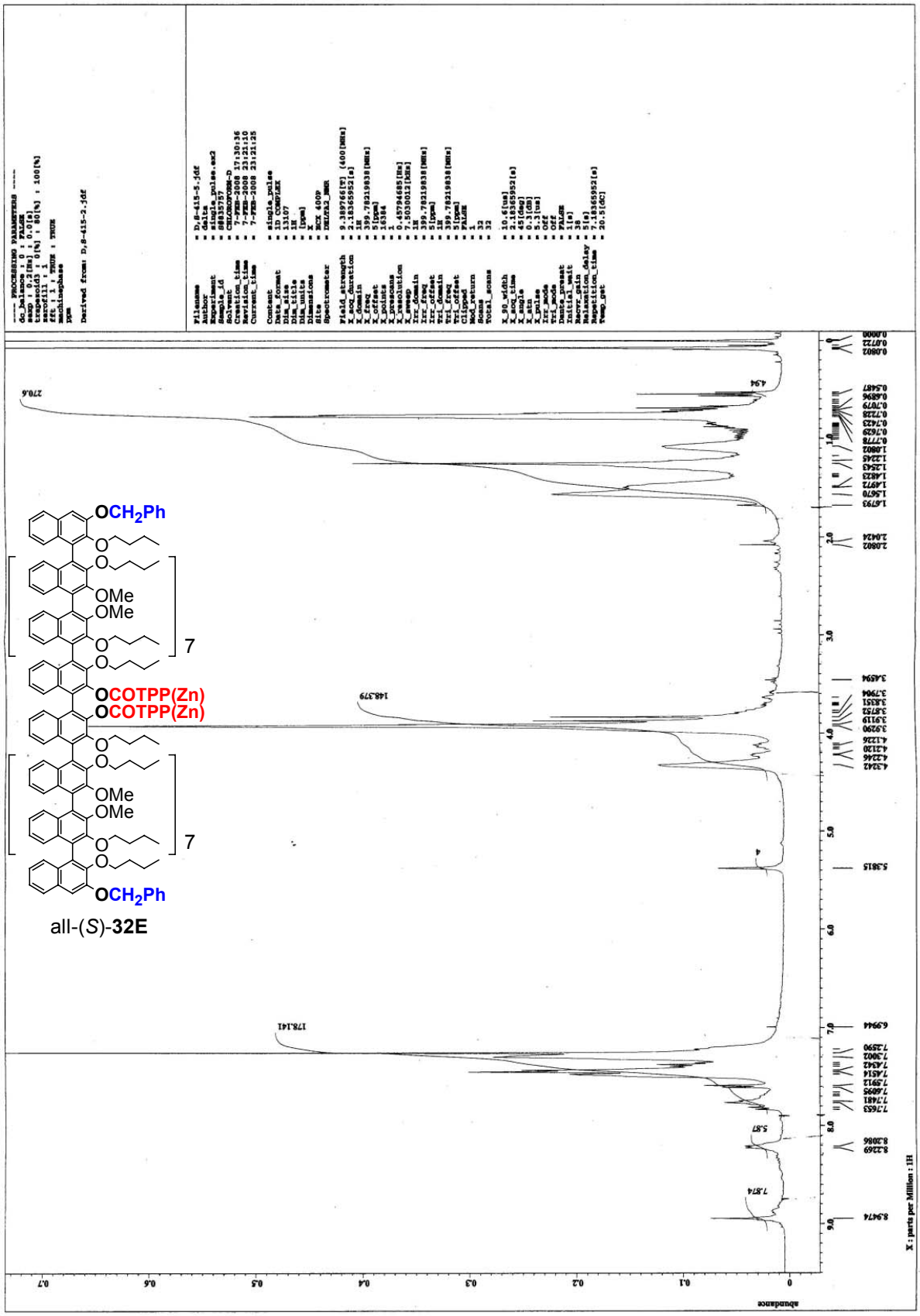
0.97
1.972
4.301
5.3838
6.4102
X : parts per Million : 1H
abundance

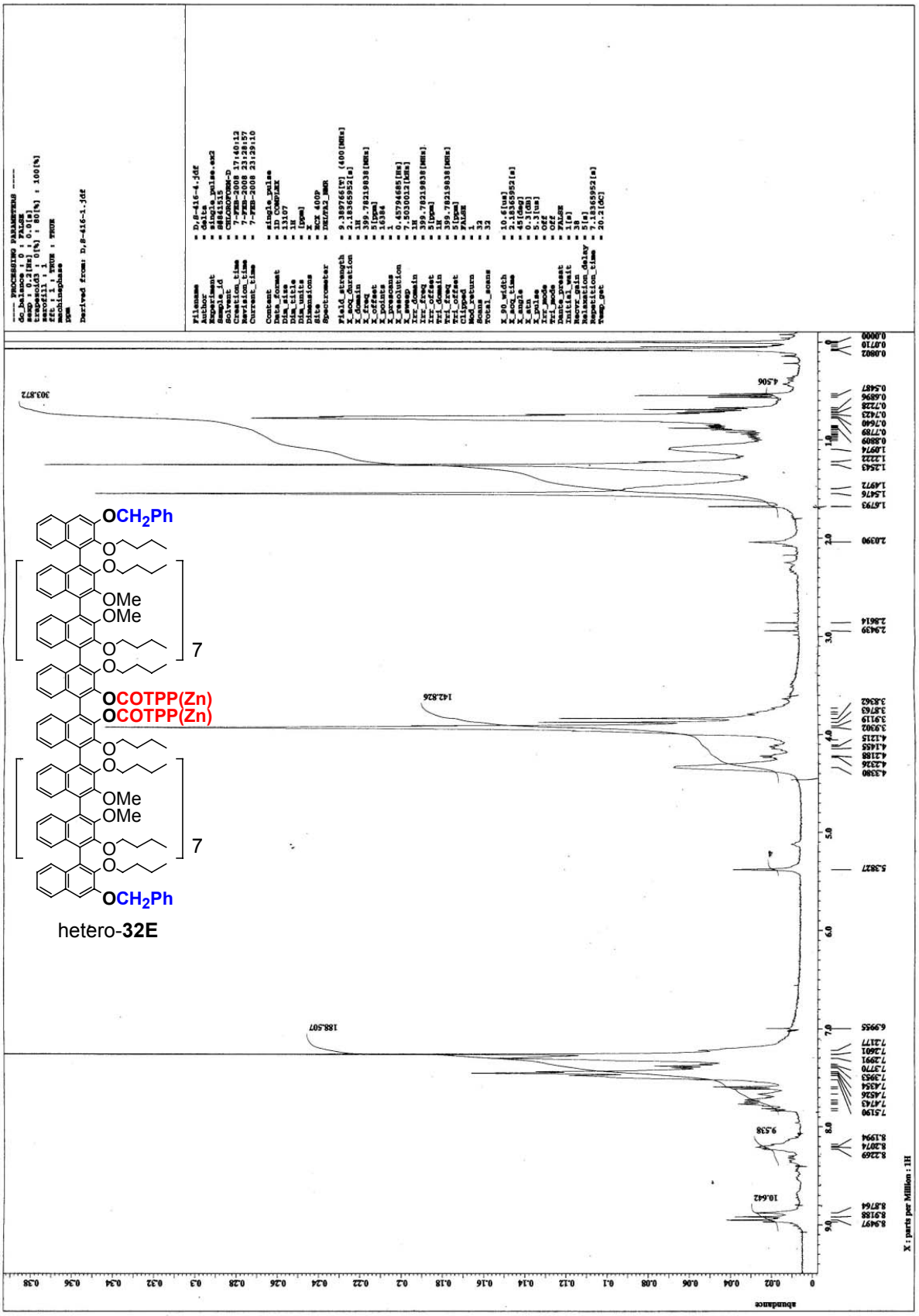

OCH2Ph
OMe
OMe
7
OH
OH
OMe
OMe
7
OCH2Ph
all-(S)-32A
X : parts per Million : 13C
abundance

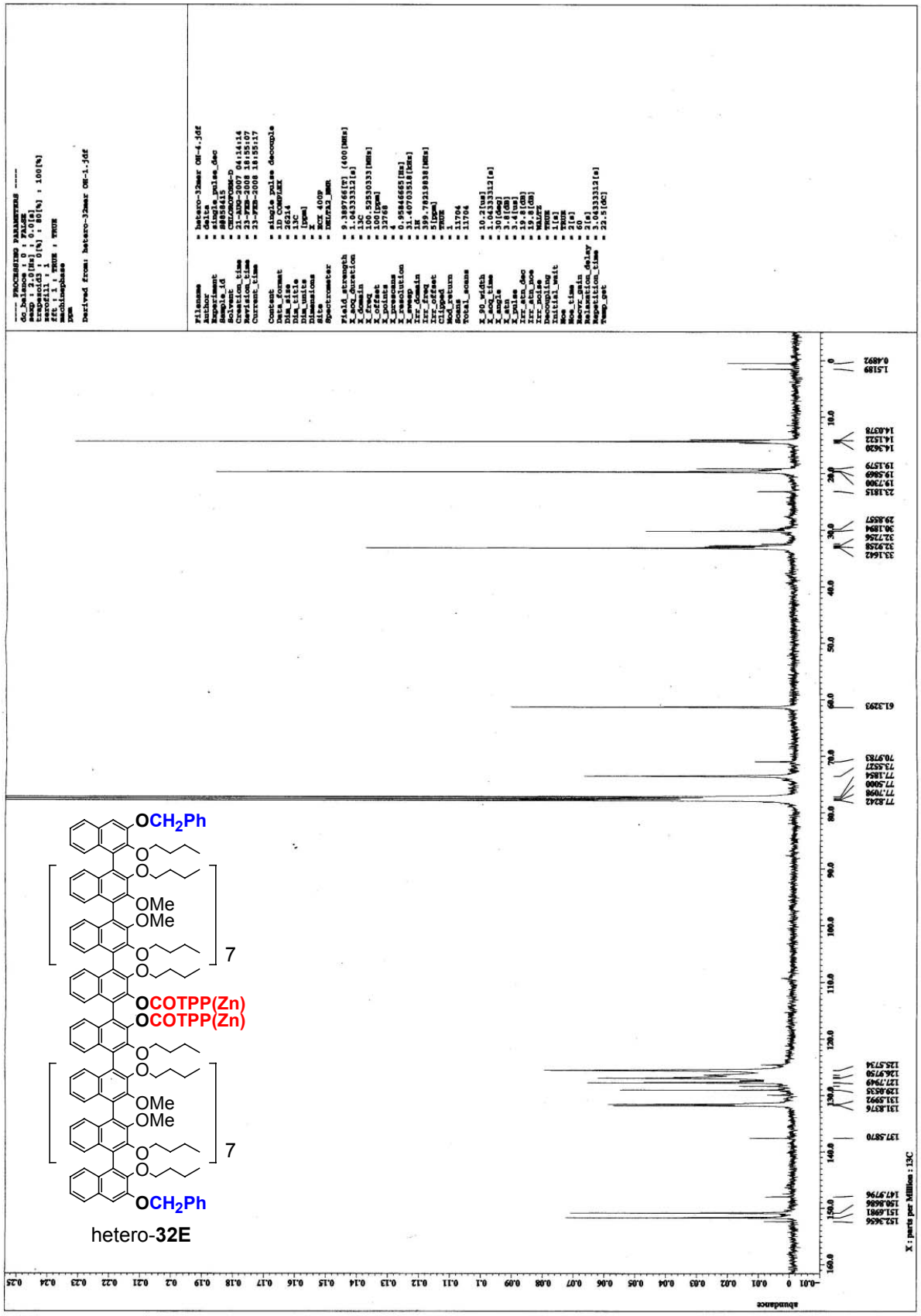

OCH2Ph
O
O
OMe
OMe
O
O
7
OH
OH
O
O
OMe
OMe
O
O
7
OCH2Ph
hetero-32A
890.162
144.098
190.568
1.153
3.64
1.59
0.768
5.294
X : parts per Million : 1H
abundance

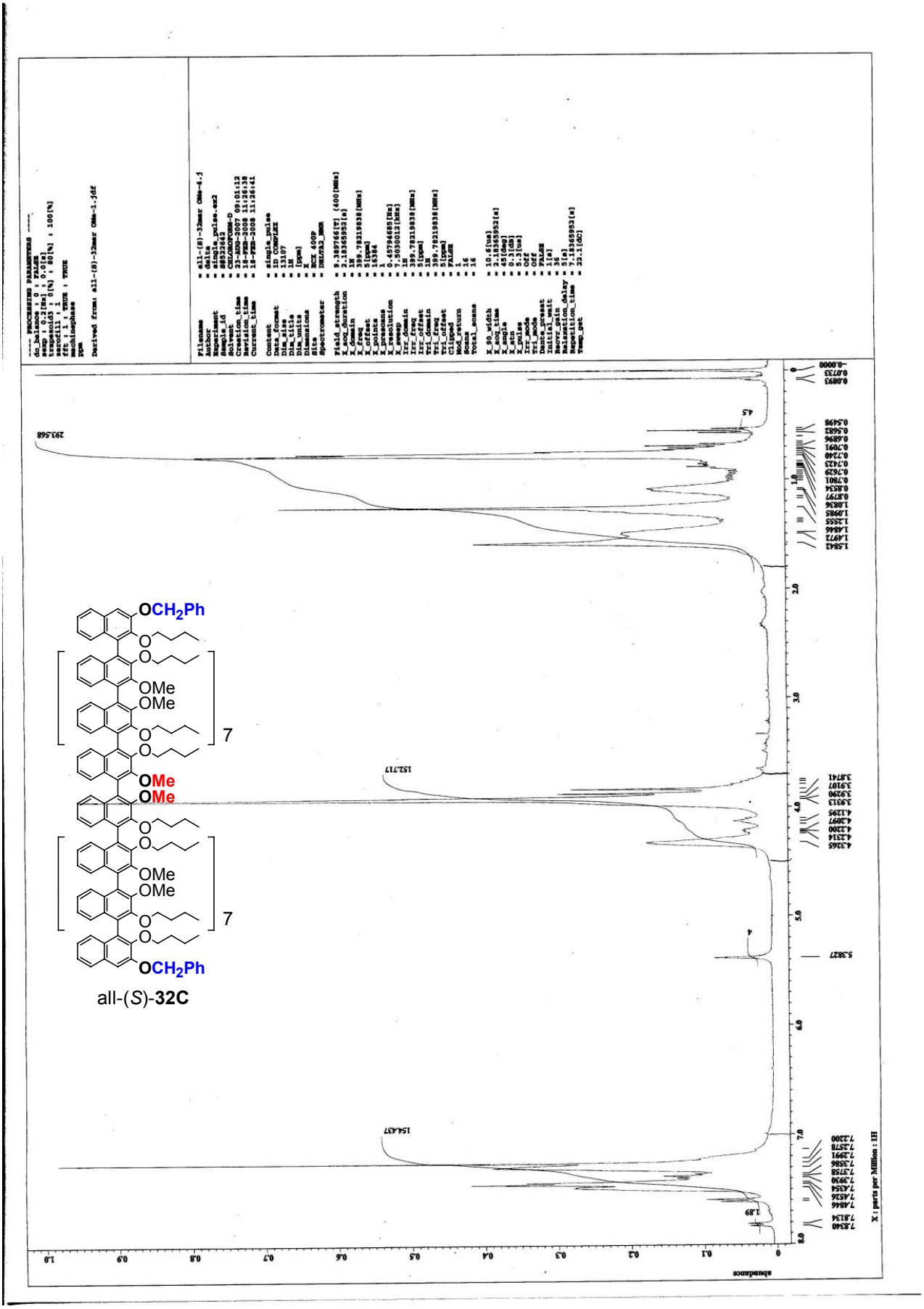

OCH2Ph
OMe
OMe
7
OH
OH
OMe
OMe
7
OCH2Ph
hetero-32A
X : parts per Million : 13C
abundance


OCH2Ph
OMe
OMe
7
OCOTPP(Zn)
OCOTPP(Zn)
OMe
OMe
7
OCH2Ph
all-(S)-32E
X : parts per Million : 1H
abundance

OCH2Ph
OMe
OMe
7
OCOTPP(Zn)
OCOTPP(Zn)
OMe
OMe
7
OCH2Ph
all-(S)-32E
X : parts per Million : 13C
(thousandths)


OCH2Ph
OMe
OMe
7
OCOTPP(Zn)
OCOTPP(Zn)
OMe
OMe
7
OCH2Ph
hetero-32E
X : parts per Million : 1H
abundance


OCH2Ph
OMe
OMe
7
OCOTPP(Zn)
OCOTPP(Zn)
OMe
OMe
7
OCH2Ph
hetero-32E
X : parts per Million : 13C
abundance


OCH2Ph
OMe
OMe
7
OMe
OMe
OMe
OMe
7
OCH2Ph
all-(S)-32C
X : parts per Million : 1H
abundance

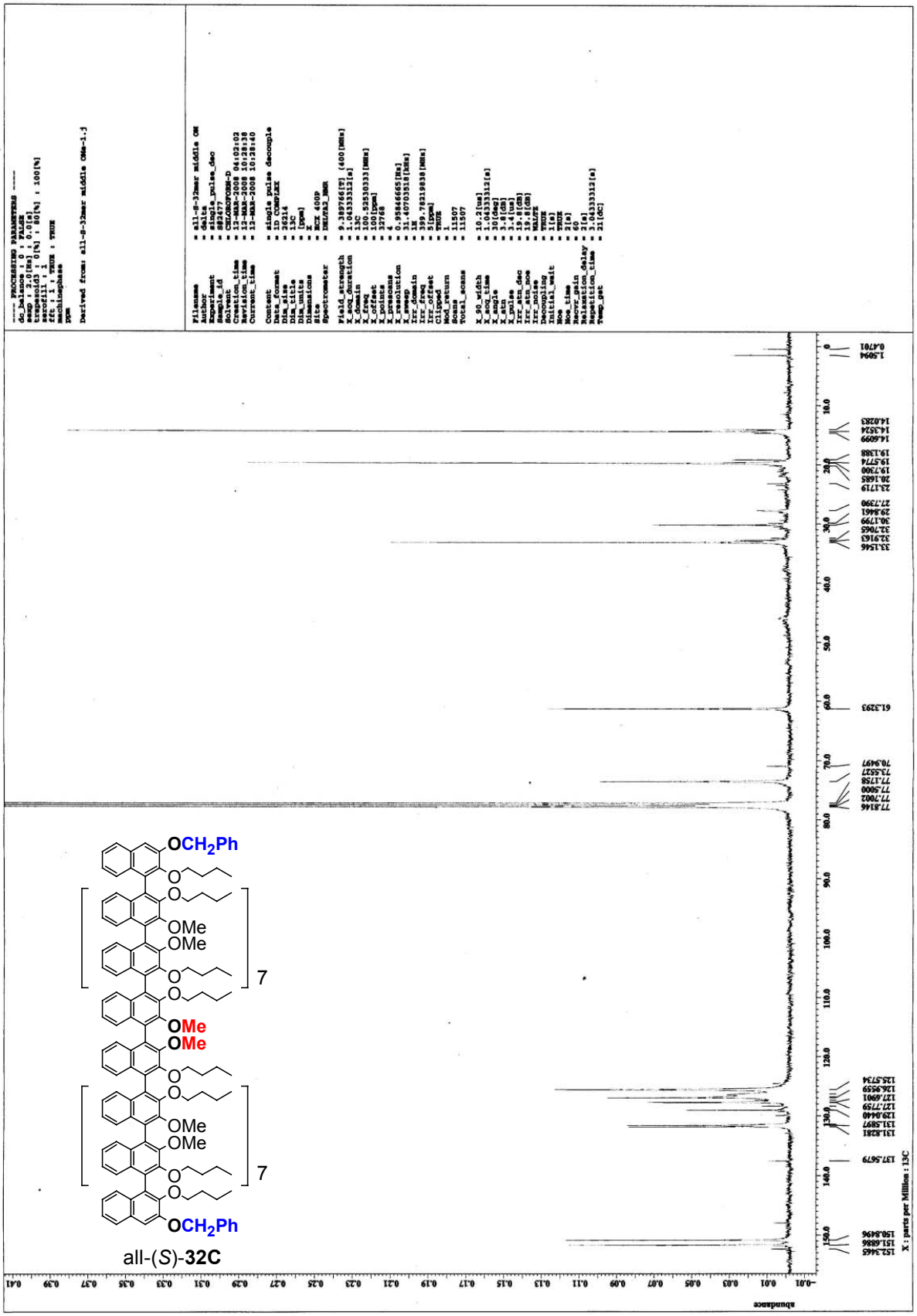
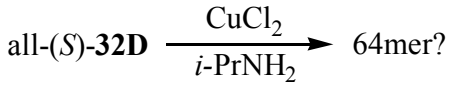
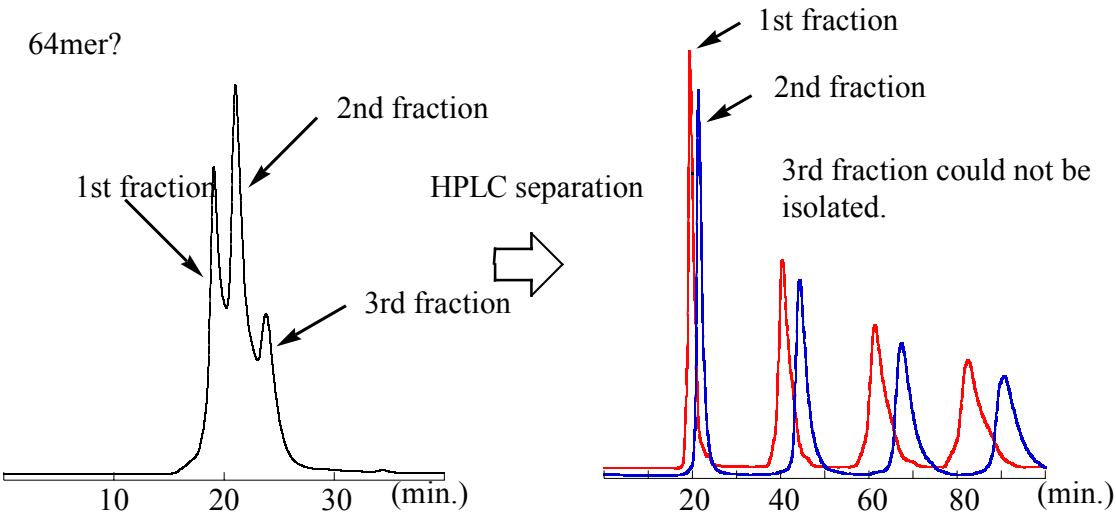

OCH2Ph
OMe
OMe
7
OMe
OMe
OMe
OMe
7
OCH2Ph
all-(S)-32C
X : parts per Million : 13C
abundance

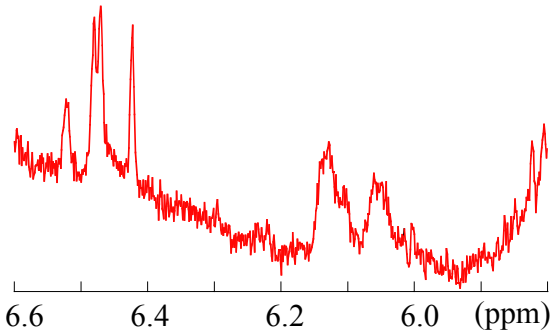
Figure SI-1. Attempt for higher order oligonaphthalenes using **32D** as a starting material





Recycling HPLC chart of 64mer?

Partial ^{1}H NMR spectra of 1st fraction



Partial ^{1}H NMR spectra of 2nd fraction

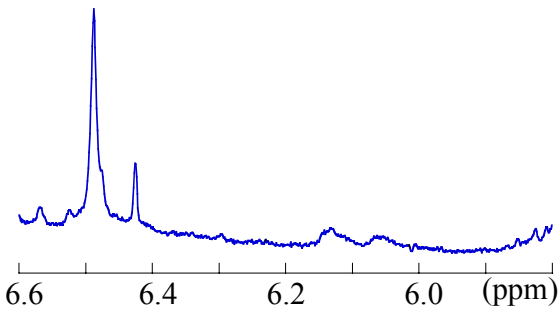
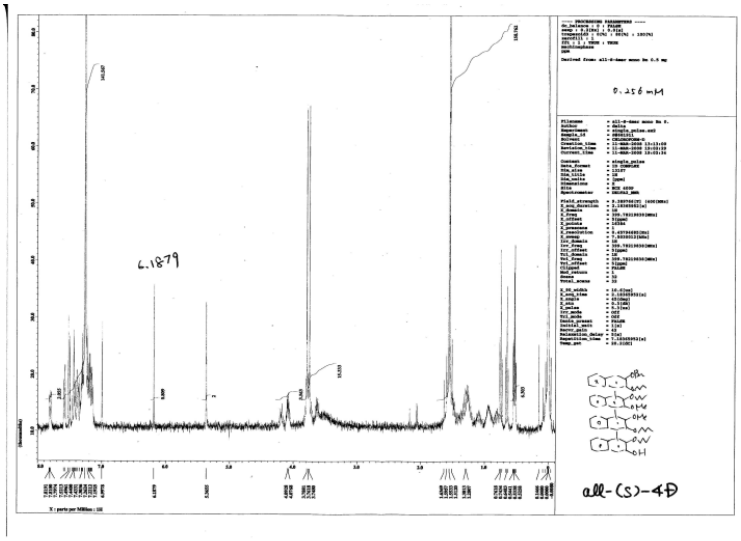
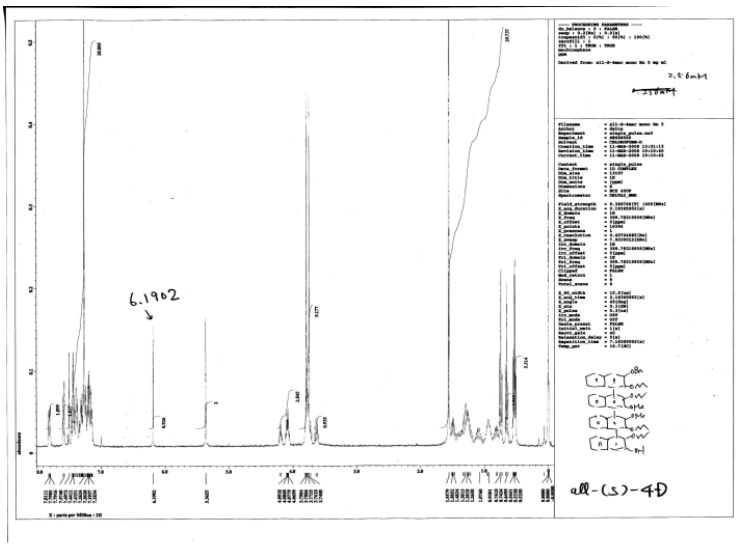


Figure SI-2a. NMR spectra of all-(*S*)-**4d** in various concentration.

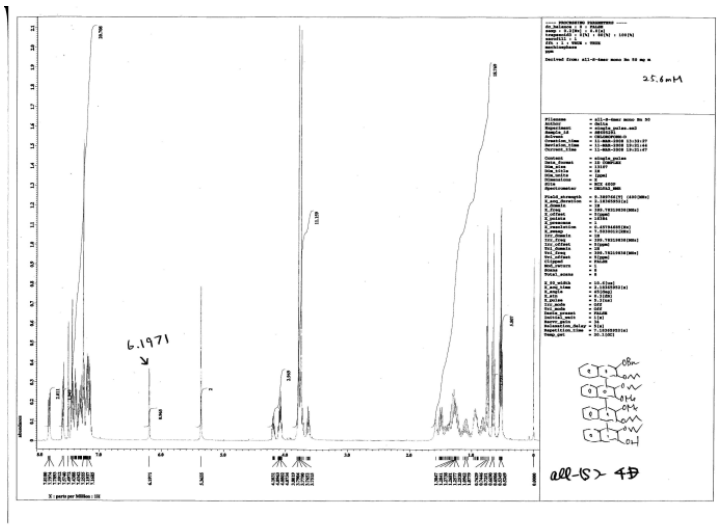
(a)



(b)



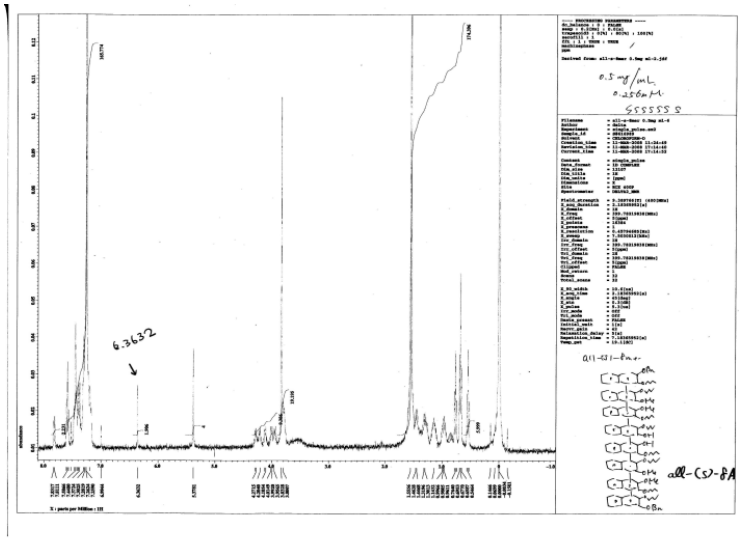
(c)



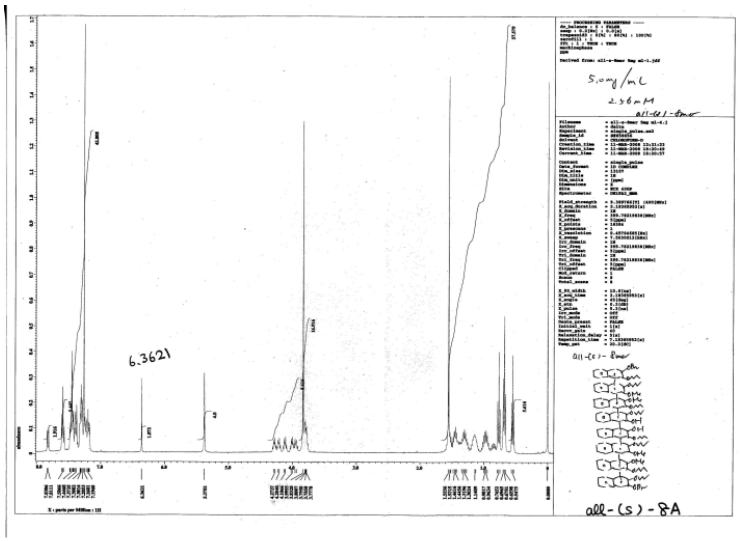
(a) 0.256 mM, (b) 2.56 mM, (c) 25.6 mM in $CDCl_3$.

Figure SI-2b. NMR spectra of all-(*S*)-**8a** in various concentration.

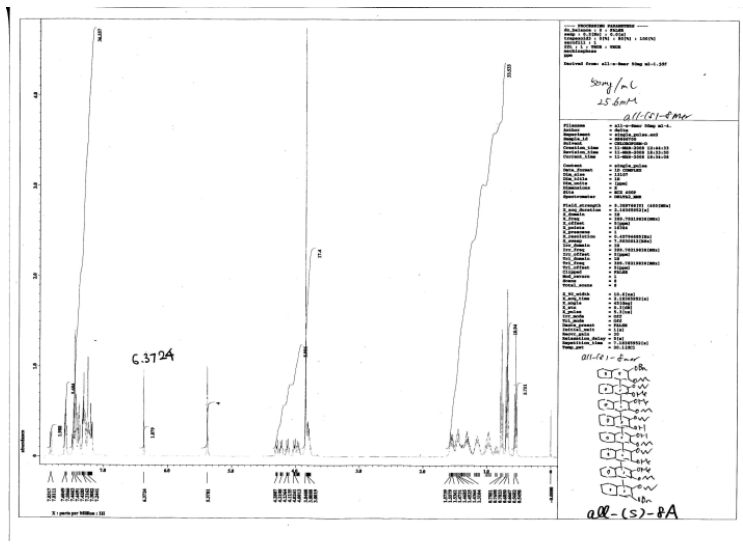
(a)



(b)



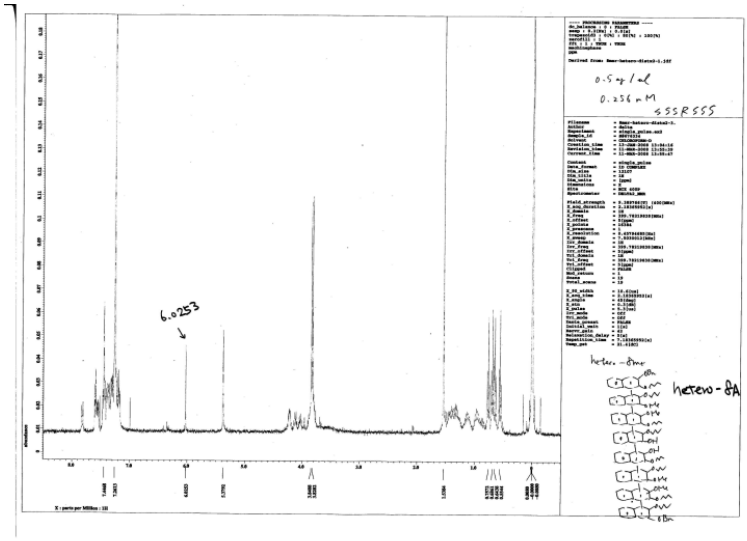
(c)



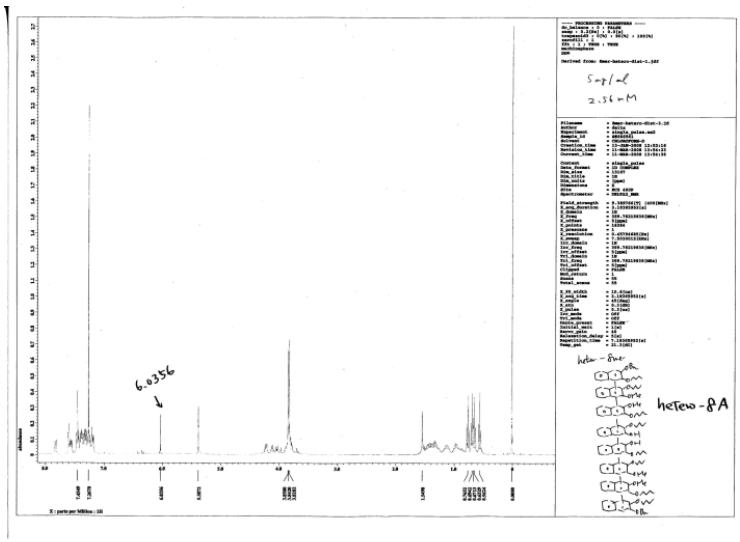
(a) 0.256 mM, (b) 2.56 mM, (c) 25.6 mM in $CDCl_3$.

Figure SI-2c. NMR spectra of hetero-**8a** in various concentration.

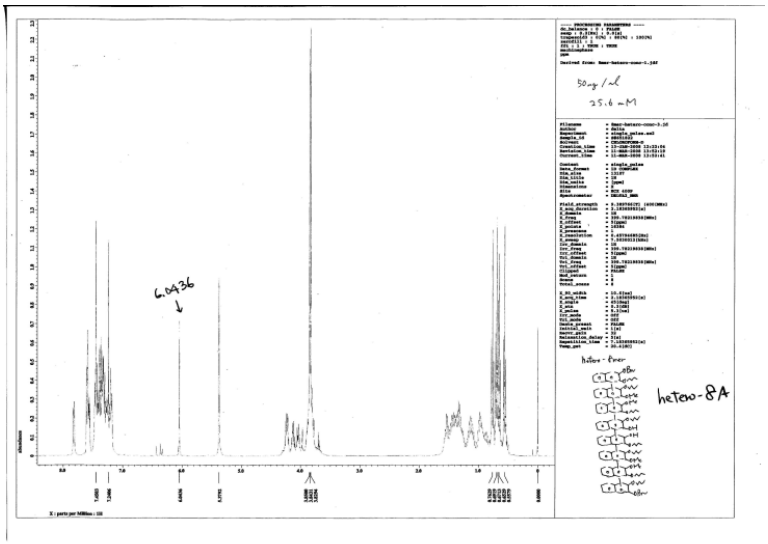
(a)



(b)

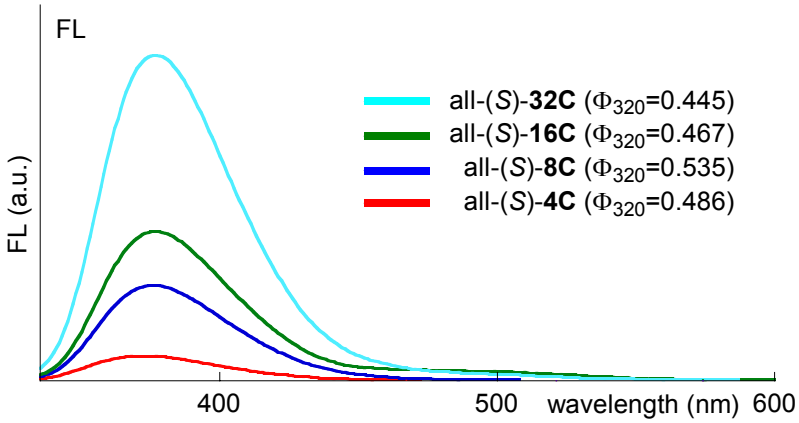


(c)



(a) 0.256 mM, (b) 2.56 mM, (c) 25.6 mM in $CDCl_3$.

Figure SI-3. Fluorescence spectra of all-(*S*)-**4C**, **8C**, **16C,** and **32C**.



conditions, CH_2Cl_2, 20 °C, light path length 10 mm. λ_{ext} = 320 nm. Fluorescence quantum yield (Φ) excited at 320 nm using a solution of quinine sulfate in 1 N H_2SO_4 as a reference standard (Φ = 0.546) in parenthesis.