Supplementary Information for:

Copper(II)-mediated chiral helicity amplification and inversion of *meta*-ethynylpyridine polymers with metal coordination sites

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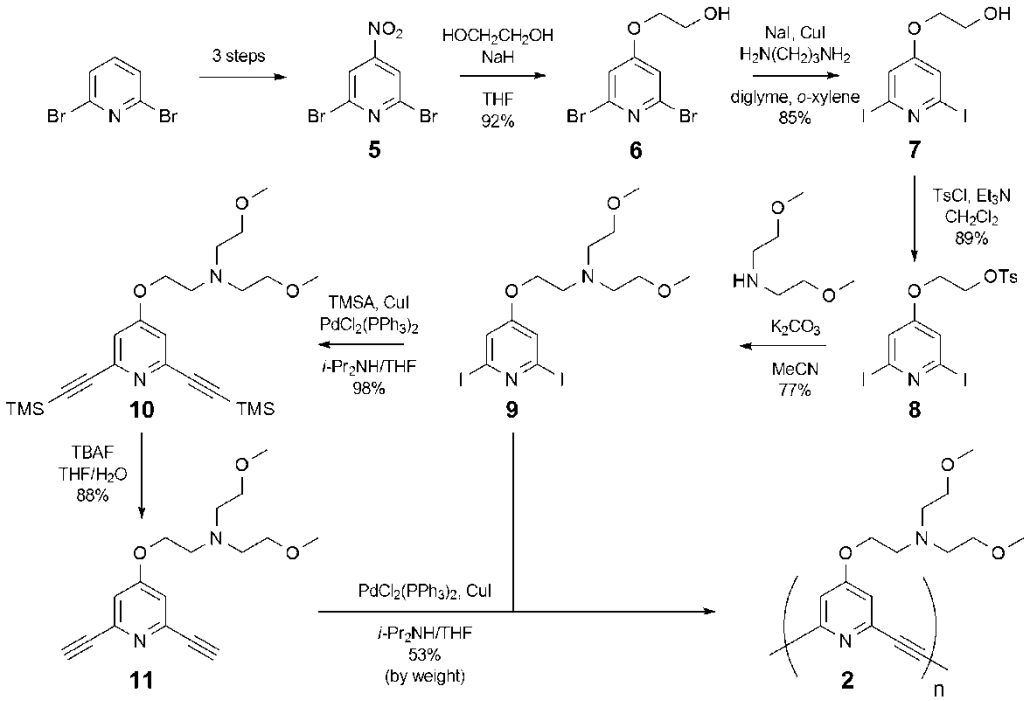
Experimental Section

General. NMR spectra were recorded on a Varian Gemini 300 spectrometer using tetramethylsilane (TMS) as an internal reference. ESI-HRMS analyses were carried out on a JEOL JMS-T100LC mass spectrometer. IR, UV-vis, and CD spectra were obtained by a JASCO spectrometers FT/IR-460plus, V-560, J-720WI, respectively. Melting points were determined with Yanako MP-500D and not corrected. THF was freshly distilled from sodium benzophenone ketyl before use. CH_2Cl_2 used for the spectroscopic analyses was purchased from Aldrich (anhydrous grade). 2,6-Dibromo-4-nitropyridine[1] (**5**) was prepared according to the procedure in the literature. Halogen exchange reactions to obtain **7**, **13a**,**b** were carried out according to the procedure reported by Buchwald et al.[2]

Preparation of Polymer 2



2,6-Dibromo-4-(2-hydroxyethyloxy)pyridine (6). To a suspension of NaH (0.99 g, 23 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) in THF (100 mL) was slowly added ethylene glycol (13 g, 0.21 mol) at 0 °C, and subsequently **5** (6.0 g, 21 mmol) was added to the mixture in one portion at the same temperature. The reaction mixture was stirred for 2

h at 0 °C and additionally for 12 h at room temperature. The resulting mixture was quenched with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (60 mL × 3). The combined organic layer was dried over $MgSO_4$, and concentrated by a rotary evaporator. The resulting syrup was subjected to silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield **6** (4.3 g, 92%) as a white solid. Mp 85−86 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.99 (s, 2 H), 4.16 (t, J = 4.2 Hz, 2 H), 4.01 (t, J = 4.2 Hz, 2 H), 3.24 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.6, 140.7, 113.7, 70.3, 60.3; IR (KBr) ν_{max} 3305, 3116, 3084, 2957, 2925, 2869, 1577, 1537 cm^{-1}; HRMS (ESI−TOF) calcd for $C_7H_7Br_2NNaO_2$ (M + Na$^+$): 319.8721; found: 319.8764.

4-(2-Hydroxyethyloxy)-2,6-diiodopyridine (7). A mixture of **6** (10 g, 35 mmol), CuI (0.67 g, 3.5 mmol), NaI (26 g, 0.18 mol), 1,3-diaminopropane (0.52 g, 7.0 mmol), diglyme (60 mL), and *o*-xylene (140 mL) was stirred at 110 °C for 24 h. The resulting suspension was allowed to reach room temperature, and then diluted with water (100 mL). The resulting mixture was extracted with AcOEt (100 mL × 3), and the combined organic layer was washed with water and brine subsequently, dried over Na_2SO_4, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield **7** (12 g, 85%) as a white solid. Mp 104−106 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (s, 2 H), 4.10 (t, J = 4.5 Hz, 2 H), 3.97 (br s, 2 H), 2.00 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.3, 121.1, 115.8, 69.9, 60.8; IR (KBr) ν_{max} 3323, 3101, 3069, 2966, 2925, 2852, 1563, 1520 cm^{-1}; HRMS (ESI−TOF) calcd for $C_7H_8I_2NO_2$ (M + H$^+$): 391.88644; found: 391.8635.

Tosylate 8. To a CH_2Cl_2 (450 mL) solution of **7** (11 g, 29 mmol) were added *p*-toluenesulfonyl chloride (15 g, 78 mmol) and triethylamine (91 g, 0.90 mol) at 0 °C. The reaction mixture was stirred for 2 h at that temperature, and additionally stirred for 12 h at room temperature. The resulting mixture was evaporated by a rotary evaporator and the resulting residue was dissolved in $CHCl_3$ (1 L). This solution was washed with 1N HCl and brine subsequently, dried over Na_2SO_4, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 3:1) to yield **8** (14.3 g, 89%) as a pale yellow solid. Mp 104−105 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.78 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 8.3 Hz, 2 H), 7.07

(s, 2 H), 4.37 (t, J = 4.4 Hz, 2 H), 4.15 (t, J = 4.4 Hz, 2 H), 2.48 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.4, 145.1, 132.4, 129.8, 127.8, 120.9, 115.7, 67.1, 65.8, 21.8; IR (KBr) ν_{max} 3098, 3068, 2955, 2922, 1594, 1559, 1522, 1362, 1174 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{14}H_{14}I_2NO_4S$ (M + H^+): 545.8733; found: 545.8734.

Tertiary Amine 9. A mixture of **8** (14 g, 26 mmol), bis(2-methoxyethyl)amine (4.2 g, 31 mmol), and K_2CO_3 (4.3 g, 31 mmol) in MeCN (200 mL) was stirred under reflux for 4 days. After cooling to room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield **9** (10 g, 77%) as a yellowish brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24 (s, 2 H), 4.07 (t, J = 6.0 Hz, 2 H), 3.47 (t, J = 5.6 Hz, 4 H), 3.34 (s, 6 H), 3.01 (t, J = 6.0 Hz, 2 H), 2.81 (t, J = 5.6 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.4, 121.0, 115.5, 71.1, 67.4, 58.7, 54.6, 53.3; IR (neat) ν_{max} 3098, 3061, 2924, 2875, 2825, 1560, 1521 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{13}H_{21}I_2N_2O_3$ (M + H^+): 506.9642; found: 506.9678.

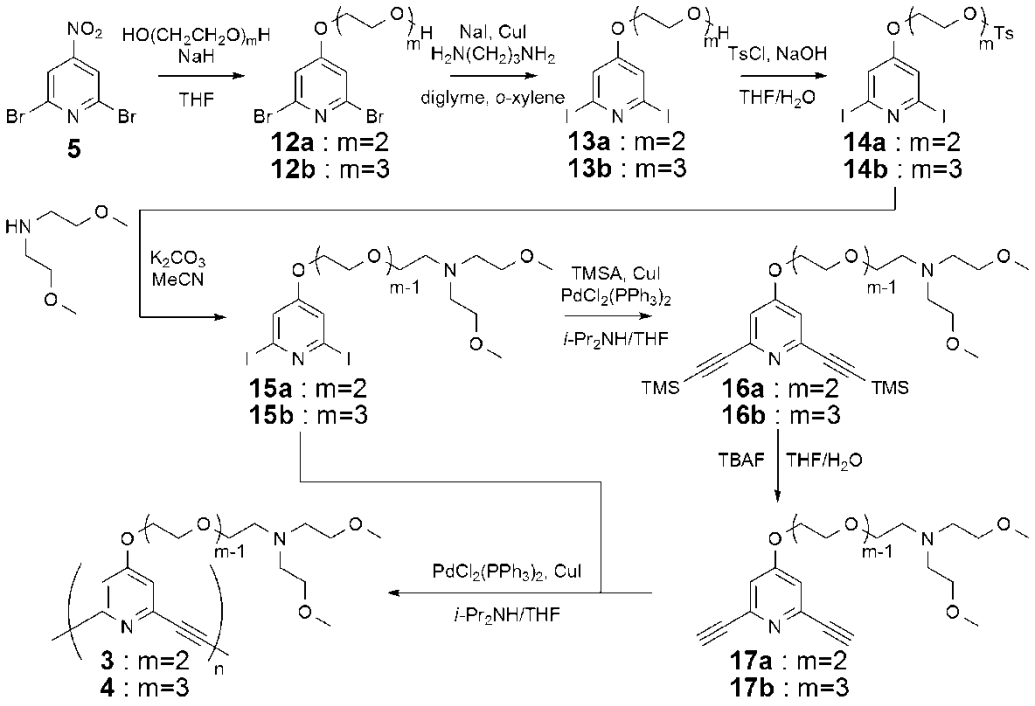
Bis(TMS-acetylene) 10. A mixture of **9** (0.14 g, 0.27 mmol), $PdCl_2(PPh_3)_2$ (9.5 mg, 14 μmol), and CuI (2.1 mg, 11 μmol) in i-Pr_2NH (2 mL) and THF (2 mL) was stirred for 30 min at room temperature. To this mixture was added trimethylsilylacetylene (TMSA, 0.11 g, 1.1 mmol) dropwise, and the reaction mixture was additionally stirred for 3 h at room temperature. The resulting mixture was diluted with ether (5 mL) and filtered. The filtrate was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt) to yield **10** (0.12 g, 98%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.94 (s, 2 H), 4.10 (t, J = 5.9 Hz, 2 H), 3.48 (t, J = 5.5 Hz, 4 H), 3.35 (s, 6 H), 3.02 (t, J = 5.9 Hz, 2 H), 2.83 (t, J = 5.5 Hz, 4 H), 0.25 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.7, 144.1, 113.5, 103.1, 94.6, 71.3, 67.0, 58.8, 54.7, 53.4, −0.27; IR (neat) ν_{max} 2957, 2925, 2876, 2823, 2164, 1579, 1550 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{23}H_{39}N_2O_3Si_2$ (M + H^+): 447.2499; found: 447.2498.

Diacetylene 11. To a THF (4 mL) solution of **10** (0.12 g, 0.26 mmol) were added tetrabutylammonium fluoride (TBAF, 1.0 M solution in THF, 0.52 mL, 0.52 mmol) and a few drops

of water. After stirring for 1 h at room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: hexane/AcOEt = 1:1 to AcOEt) to yield **11** (70 mg, 88%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.00 (s, 2 H), 4.11 (t, J = 5.9 Hz, 2 H), 3.48 (t, J = 5.8 Hz, 4 H), 3.34 (s, 6 H), 3.12 (s, 2 H), 3.03 (t, J = 5.9 Hz, 2 H), 2.83 (t, J = 5.8 Hz, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 143.4, 114.0, 82.1, 77.1, 71.3, 67.2, 58.8, 54.8, 53.5; IR (neat) ν_{max} 3286, 2925, 2874, 2824, 2103, 1578, 1550 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{17}H_{22}N_2NaO_3$ (M + Na^+): 325.1528; found: 325.1568.

Polymer 2. Co-polymerization of 9 and 11. A mixture of **9** (43 mg, 84 μmol), **11** (32 mg, 0.11 mmol), $PdCl_2(PPh_3)_2$ (3.7 mg, 5.3 μmol), and CuI (0.8 mg, 4.2 μmol) in *i*-Pr_2NH (4 mL) and THF (4 mL) was stirred for 3 days at room temperature. The reaction mixture was concentrated by a rotary evaporator and the resulting residue was treated with a Sephadex LH-20 column (eluent: $CHCl_3$). The crude product of **2** was subjected to GPC (Shodex K-2002 and K-2002.5; eluent: $CHCl_3$) and divided into four fractions as brown oils. The sum of the weights of these fractions was 40 mg (53% yield by weight). One fraction of M_n = 12,700 g/mol (corresponding to 46-mer) was used for the experiments to evaluate additive effects of Cu(II) ion. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17 (s, 2n H), 4.13 (br s, 2n H), 3.53 (t, J = 5.5 Hz, 4n H), 3.34 (br s, 6n H), 3.12 (br s, 2n H), 2.87 (t, J = 5.5 Hz, 4n H); IR (KBr) ν_{max} 2924, 2873, 1579, 1550 cm^{-1}.

Preparation of Polymers 3 and 4



2,6-Dibromo-4-[2-(2-hydroxyethyloxy)ethyloxy]pyridine (12a). To a suspension of NaH (94 mg, 3.9 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) in THF (20 mL) was slowly added diethylene glycol (7.5 g, 71 mmol) at 0 °C, and subsequently **5** (1.0 g, 3.5 mmol) was added to the mixture in one portion at the same temperature. The reaction mixture was stirred for 2 h at 0 °C and additionally for 12 h at room temperature. The resulting mixture was quenched with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was dried over $MgSO_4$, and concentrated by a rotary evaporator. The resulting syrup was subjected to silica gel column chromatography (eluent; CH_2Cl_2 to hexane/AcOEt = 1:1) to yield **12a** (1.1 g, 95%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (s, 2 H), 4.20 (t, J = 4.4 Hz, 2 H), 3.86 (t, J = 4.4 Hz, 2 H), 3.76 (t, J = 4.6 Hz, 2 H), 3.65 (t, J = 4.6 Hz, 2 H), 2.63 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.4, 140.7, 113.6, 72.6, 68.7, 68.2, 61.5; IR (neat) ν_{max} 3414, 3115, 3081, 2932, 2874, 1574, 1536 cm^{-1}; HRMS (ESI−TOF) calcd for $C_9H_{11}Br_2NNaO_3$ ($M + Na^+$): 363.8983; found: 363.8971.

2,6-Dibromo-4-[2-[2-(2-hydroxyethyloxy)ethyloxy]ethyloxy]pyridine (12b). To a suspension of NaH (0.38 g, 15 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) in THF (60 mL) was slowly added triethylene glycol (42 g, 0.28 mol) at 0 °C, and subsequently **5** (4.0 g, 14 mmol) was added to the mixture in one portion at the same temperature. The reaction mixture was stirred for 2 h at 0 °C and additionally for 12 h at room temperature. The resulting mixture was quenched with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (40 mL × 3). The combined organic layer was dried over $MgSO_4$, and concentrated by a rotary evaporator. The resulting syrup was subjected to silica gel column chromatography (eluent; CH_2Cl_2 to CH_2Cl_2/MeOH = 100:3) to yield **12b** (5.0 g, 92%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.03 (s, 2 H), 4.20 (t, J = 4.4 Hz, 2 H), 3.86 (t, J = 4.4 Hz, 2 H), 3.76−3.63 (m, 6 H), 3.60 (t, J = 4.5 Hz, 2 H), 3.35 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.4, 140.6, 113.6, 72.3, 70.6, 69.9, 68.7, 68.2, 61.3; IR (neat) ν_{max} 3414, 3115, 3081, 2875, 1575, 1536 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{11}H_{15}Br_2NNaO_4$ (M + Na^+): 407.9246; found: 407.9279.

4-[2-(2-Hydroxyethyloxy)ethyloxy]-2,6-diiodopyridine (13a). A mixture of **12a** (2.6 g, 7.6 mmol), CuI (0.14 g, 0.76 mmol), NaI (5.7 g, 38 mmol), 1,3-diaminopropane (0.11 g, 1.5 mmol), diglyme (18 mL), and *o*-xylene (42 mL) was stirred at 110 °C for 24 h. The resulting suspension was allowed to reach room temperature, and then diluted with water (50 mL). The resulting mixture was extracted with AcOEt (50 mL × 3), and the combined organic layer was washed with water and brine, subsequently, dried over Na_2SO_4, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield **13a** (2.7 g, 83%) as a yellow solid. Mp 63−66 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (s, 2 H), 4.17 (t, J = 4.3 Hz, 2 H), 3.85 (t, J = 4.3 Hz, 2 H), 3.76 (br s, 2 H), 3.70−3.62 (br m, 2 H), 3.01 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.1, 120.9, 115.6, 72.5, 68.6, 67.9, 61.3; IR (KBr) ν_{max} 3370, 3107, 3075, 2952, 2920, 2872, 2852, 1565, 1523 cm^{-1}; HRMS (ESI−TOF) calcd for $C_9H_{11}I_2NNaO_3$ (M + Na^+): 457.8726; found: 457.8713.

4-[2-[2-(2-Hydroxyethyloxy)ethyloxy]ethyloxy]-2,6-diiodopyridine (13b). A mixture of **12b** (0.1 g, 0.26 mmol), CuI (4.9 mg, 26 μmol), NaI (0.19 g, 1.3 mmol), 1,3-diaminopropane (3.9 mg, 52

μmol), diglyme (0.6 mL) and *o*-xylene (1.4 mL) was stirred at 110 °C for 24 h. The resulting suspension was allowed to reach room temperature, and then diluted with water (2 mL). The resulting mixture was extracted with AcOEt (2 mL × 3), and the combined organic layer was washed with water and brine, subsequently, dried over Na_2SO_4, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield **13b** (96 mg, 77%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (s, 2 H), 4.12 (t, J = 4.6 Hz, 2 H), 3.83 (t, J = 4.6 Hz, 2 H), 3.79−3.65 (m, 6 H), 3.61 (t, J = 4.5 Hz, 2 H), 2.41 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.3, 121.1, 115.6, 72.4, 70.7, 70.1, 68.8, 67.9, 61.5; IR (neat) ν_{max} 3420, 3098, 3064, 2875, 1561, 1520 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{11}H_{15}I_2NNaO_4$ (M + Na^+): 501.8988; found: 501.8976.

Tosylate 14a. A water (5 mL) solution of NaOH (1.0 g, 26 mmol) and a THF (5 mL) solution of **13a** (1.1 g, 2.6 mmol) were mixed and cooled to 0 °C. To this mixture was added a THF (5 mL) solution of *p*-toluenesulfonyl chloride (0.6 g, 3.1 mmol) dropwise and the reaction mixture was stirred for 2 h, being kept at the same temperature. The resulting mixture was poured into ice-water (50 mL) and extracted with CH_2Cl_2 (25 mL × 3). The combined organic layer was dried over $MgSO_4$, and concentrated by a rotary evaporator, and the crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 3:2) to yield **14a** (1.3 g, 87%) as a white solid. Mp 110−111 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (d, J = 8.3 Hz, 2 H), 7.33 (d, J = 8.3 Hz, 2 H), 7.22 (s, 2 H), 4.18 (t, J = 4.6 Hz, 2 H), 4.05 (t, J = 4.6 Hz, 2 H), 3.80−3.71 (m, 4 H), 2.45 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.2, 144.7, 129.7, 127.7, 121.0, 115.6, 69.0, 68.9, 67.8, 21.7; IR (KBr) ν_{max} 3100, 3068, 2995, 2895, 2870, 1597, 1559, 1522, 1357, 1175 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{16}H_{17}I_2NNaO_5S$ (M + Na^+): 611.8814; found: 611.8846.

Tosylate 14b. A water (25 mL) solution of NaOH (3.3 g, 82 mmol) and a THF (25 mL) solution of **13b** (13 g, 2.6 mmol) were mixed and cooled to 0 °C. To this mixture was added a THF (25 mL) solution of *p*-toluenesulfonyl chloride (7.8 g, 41 mmol) dropwise and the reaction mixture was stirred for 2 h, being kept at the same temperature. The resulting mixture was poured into ice-water (250 mL) and extracted with CH_2Cl_2 (100 mL × 3). The combined organic layer was dried over

$MgSO_4$, and concentrated by a rotary evaporator, and the crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield **14b** (16 g, 94%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (d, J = 8.1 Hz, 2 H), 7.34 (d, J = 8.1 Hz, 2 H), 7.25 (s, 2 H), 4.18−4.10 (m, 4 H), 3.80 (t, J = 4.5 Hz, 2 H), 3.69 (t, J = 4.5 Hz, 2 H), 3.62 (s, 4 H), 2.45 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.4, 144.7, 132.7, 129.7, 127.7, 121.2, 115.6, 70.7, 69.2, 69.1, 68.7, 68.1, 21.7; IR (neat) ν_{max} 3101, 3065, 2878, 1597, 1560, 1522, 1362, 1175 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{18}H_{21}I_2NNaO_6S$ (M + Na^+): 655.9077; found: 655.9052.

Tertiary Amine 15a. A mixture of **14a** (1.3 g, 2.3 mmol), bis(2-methoxyethyl)amine (0.37 g, 2.7 mmol), and K_2CO_3 (0.38 g, 2.7 mmol) in MeCN (60 mL) was stirred under reflux for 4 days. After cooling to room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1 to AcOEt) to yield **15a** (0.98 g, 77%) as a yellowish brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (s, 2 H), 4.12 (t, J = 4.5 Hz, 2 H), 3.78 (t, J = 4.5 Hz, 2 H), 3.61 (t, J = 6.0 Hz, 2 H), 3.46 (t, J = 6.0 Hz, 4 H), 3.33 (s, 6 H), 2.84−2.76 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.4, 121.1, 115.6, 70.9, 70.0, 68.7, 68.0, 58.8, 54.4, 54.3; IR (neat) ν_{max} 3102, 3060, 2925, 2875, 2822, 1561, 1523 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{15}H_{24}I_2N_2NaO_4$ (M + Na^+): 572.9723; found: 572.9677.

Tertiary Amine 15b. A mixture of **14b** (2.6 g, 4.1 mmol), bis(2-methoxyethyl)amine (0.61 g, 4.6 mmol), and K_2CO_3 (0.63 g, 4.6 mmol) in MeCN (110 mL) was stirred under reflux for 5 days. After cooling to room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1 to AcOEt) to yield **15b** (1.7 g, 70%) as a yellowish brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.27 (s, 2 H), 4.15 (t, J = 4.4 Hz, 2 H), 3.83 (t, J = 4.4 Hz, 2 H), 3.71−3.52 (m, 6 H), 3.47 (t, J = 5.7 Hz, 4 H), 3.33 (s, 6 H), 2.82−2.74 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.3, 121.0, 115.5, 70.8, 70.7, 70.2, 69.5, 68.9, 68.0, 58.7, 54.3, 54.2; IR (neat) ν_{max} 3100, 3061, 2923, 2873, 1560, 1523 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{17}H_{28}I_2N_2NaO_5$ (M + Na^+): 616.9985; found: 616.9973.

Bis(TMS-acetylene) 16a. A mixture of **15a** (0.21 g, 0.39 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 19 μmol),

and CuI (3.0 mg, 16 μmol) in *i*-Pr_2NH (3 mL) and THF (3 mL) was stirred for 30 min at room temperature. To this mixture was added TMSA (0.15 g, 1.6 mmol) dropwise, and the reaction mixture was additionally stirred for 3 h at room temperature. The resulting mixture was diluted with ether (10 mL) and filtered. The filtrate was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt to AcOEt/MeOH = 50:1) to yield **16a** (0.17 g, 88%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.94 (s, 2 H), 4.15 (t, J = 4.6 Hz, 2 H), 3.79 (t, J = 4.6 Hz, 2 H), 3.62 (t, J = 5.9 Hz, 2 H), 3.47 (t, J = 5.9 Hz, 4 H), 3.33 (s, 6 H), 2.86−2.76 (m, 6 H), 0.24 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.66, 144.15, 113.52, 103.0, 94.7, 71.0, 70.0, 68.8, 67.6, 58.8, 54.5, 54.4, −0.26; IR (neat) ν_{max} 2957, 2926, 2875, 2165, 1579, 1550 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{25}H_{42}N_2NaO_4Si_2$ (M + Na^+): 513.2581; found: 513.2617.

Bis(TMS-acetylene) 16b. A mixture of **15b** (0.12 g, 0.20 mmol), $PdCl_2(PPh_3)_2$ (6.9 mg, 9.8 μmol), and CuI (1.5 mg, 7.8 μmol) in *i*-Pr_2NH (2 mL) and THF (2 mL) was stirred for 30 min at room temperature. To this mixture was added TMSA (77 mg, 0.78 mmol) dropwise, and the reaction mixture was additionally stirred for 3 h at room temperature. The resulting mixture was diluted with ether (5 mL) and filtered. The filtrate was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt to AcOEt/MeOH = 50:1) to yield **16b** (98 mg, 94%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.95 (s, 2 H), 4.17 (t, J = 4.8 Hz, 2 H), 3.85 (t, J = 4.8 Hz, 2 H), 3.72−3.50 (m, 6 H), 3.47 (t, J = 5.9 Hz, 4 H), 3.33 (s, 6 H), 2.84−2.76 (m, 6 H), 0.24 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.5, 144.0, 113.4, 102.9, 94.6, 70.9, 70.8, 70.3, 69.5, 69.0, 67.6, 58.7, 54.4, 54.3, −0.35; IR (neat) ν_{max} 2956, 2926, 2875, 2165, 1580, 1551 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{27}H_{47}N_2O_5Si_2$ (M + H^+): 535.3023; found: 535.3045.

Diacetylene 17a. To a THF (4 mL) solution of **16a** (0.17 g, 0.34 mmol) were added TBAF (1.0 M solution in THF, 0.68 mL, 0.68 mmol) and a few drops of water. After stirring for 1 h at room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt/MeOH = 50:1 to 20:1) to yield

17a (86 mg, 75%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (s, 2 H), 4.16 (t, J = 4.7 Hz, 2 H), 3.81 (t, J = 4.7 Hz, 2 H), 3.62 (t, J = 5.9 Hz, 2 H), 3.46 (t, J = 5.9 Hz, 4 H), 3.33 (s, 6 H), 3.10 (s, 2 H), 2.86−2.76 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 143.5, 114.0, 82.1, 77.2, 71.0, 70.1, 68.9, 67.8, 58.8, 54.5, 54.4; IR (neat) ν_{max} 3249, 2956, 2929, 2873, 2112, 1580, 1556 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{19}H_{26}N_2NaO_4$ (M + Na$^+$): 369.1790; found: 369.1785.

Diacetylene 17b. To a THF (4 mL) solution of **16b** (0.17 g, 0.34 mmol) were added TBAF (1.0 M solution in THF, 0.63 mL, 0.63 mmol) and a few drops of water. After stirring for 1 h at room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt/MeOH = 50:1 to 20:1) to yield **17b** (82 mg, 67%) as a brown oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.01 (s, 2 H), 4.18 (t, J = 4.5 Hz, 2 H), 3.86 (t, J = 4.4 Hz, 2 H), 3.72−3.55 (m, 6 H), 3.46 (t, J = 5.9 Hz, 4 H), 3.33 (s, 6 H), 3.11 (s, 2 H), 2.86−2.76 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.8, 143.5, 114.0, 82.1, 77.2, 71.0, 70.9, 70.4, 69.7, 69.1, 67.8, 58.8, 54.5, 54.4; IR (neat) ν_{max} 3229, 2926, 2875, 2111, 1581, 1556 cm^{-1}; HRMS (ESI−TOF) calcd for $C_{21}H_{30}N_2NaO_5$ (M + Na$^+$): 413.2052; found: 413.2063.

Polymer 3. Co-polymerization of 15a and 17a. A mixture of **15a** (57 mg, 0.10 mmol), **17a** (45 mg, 0.13 mmol), $PdCl_2(PPh_3)_2$ (4.5 mg, 6.5 μmol), and CuI (1.0 mg, 5.2 μmol) in i-Pr_2NH (4 mL) and THF (4 mL) was stirred for 3 days at room temperature. The reaction mixture was concentrated by a rotary evaporator and the resulting residue was treated with a Sephadex LH-20 column (eluent: $CHCl_3$). The crude product of **3** was subjected to GPC (Shodex K-2002 and K-2002.5; eluent: $CHCl_3$) and divided into four fractions as brown oils. The sum of the weights of these fractions was 24 mg (24% yield by weight). One fraction of M_n = 12,500 g/mol (corresponding to 39-mer) was used for the experiments to evaluate additive effects of Cu(II) ion. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19 (s, 2n H), 4.19 (br s, 2n H), 3.84 (br s, 2n H), 3.64 (s, 2n H), 3.48 (t, J = 5.6 Hz, 4n H), 3.34 (s, 6n H), 2.88−2.76 (m, 6n H); IR (KBr) ν_{max} 2924, 2853, 1578, 1559 cm^{-1}.

Polymer 4. Co-polymerization of 15b and 17b. A mixture of **15b** (57 mg, 95 μmol), **17b** (46

mg, 0.12 mmol), $PdCl_2(PPh_3)_2$ (4.2 mg, 5.9 μmol), and CuI (0.9 mg, 4.8 μmol) in *i*-Pr_2NH (4 mL) and THF (4 mL) was stirred for 3 days at room temperature. The reaction mixture was concentrated by a rotary evaporator and the resulting residue was treated with a Sephadex LH-20 column (eluent: $CHCl_3$). The crude product was subjected to GPC (Shodex K-2002 and K-2002.5; eluent: $CHCl_3$) and divided into four fractions as brown oils. The sum of the weights of these fractions was 69 mg (67% yield by weight). One fraction of M_n = 16,200 g/mol (corresponding to 45-mer) was used for the experiments to evaluate additive effects of Cu(II) ion. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19 (s, 2n H), 4.22 (br s, 2n H), 3.90 (br s, 2n H), 3.82−3.46 (m, 10n H), 3.33 (s, 6n H), 2.95 (br s, 6n H); IR (neat) ν_{max} 2923, 2852, 1578, 1541 cm^{-1}.

Evaluation of binding affinity of 2 with glucosides. Polymer **2** (1.0×10^{-3} M, unit concentration) was dissolved in CH_2Cl_2 (commercially available anhydrous grade). This solution was titrated with a solution of β-D-glucopyranoside (**β-D-Glc**), and the observed ellipticity was plotted versus the concentration of the **β-D-Glc**. The formal binding constants were obtained by curve fitting measurements based on the equation[3] and the assumption that the molecular weight of the polymer **2** was uniform in length and that the polymer and the guest associate in a 1:1 ratio.

Equation:

$$\theta_{obs} = \frac{\theta_{11}}{2K_{11}[2]_0}\left[1 + K_{11}[2]_0 + K_{11}[G]_0 - \{(1 + K_{11}[2]_0 + K_{11}[G]_0)^2 - 4K_{11}^2[2]_0[G]_0\}^{1/2}\right]$$

K_{11}: 1:1 binding constant of **2** with glycosides

θ_{obs}: observed ellipticity

θ_{11}: ellipticity of the 1:1 host-guest complex (at the saturation point)

$[\mathbf{2}]_0$: total concentration of **2**

$[G]_0$: total concentration of guest glycoside

References

1) U. Neumann and F. Vögtle, *Chem. Ber.*, 1989, **122**, 589−591.

2) A. Klapars and S. L. Buchwald, *J. Am. Chem. Soc.*, 2002, **124**, 14844−14845.

3) K. A. Connors, *Binding Constants*, John Wiley & Sons, New York, 1987.

Figures S1 – S12

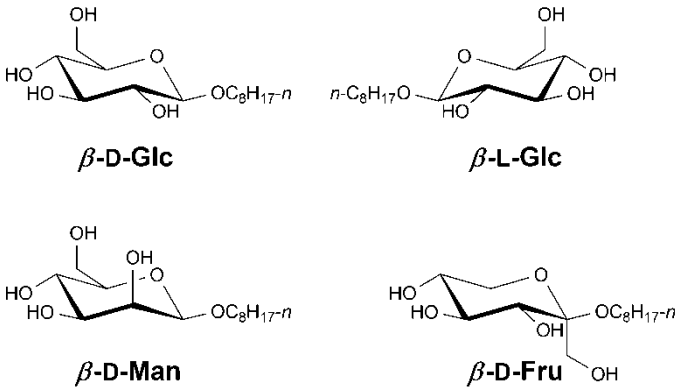


Fig S1 *n*-Octyl glycosides subjected as a guest saccharide

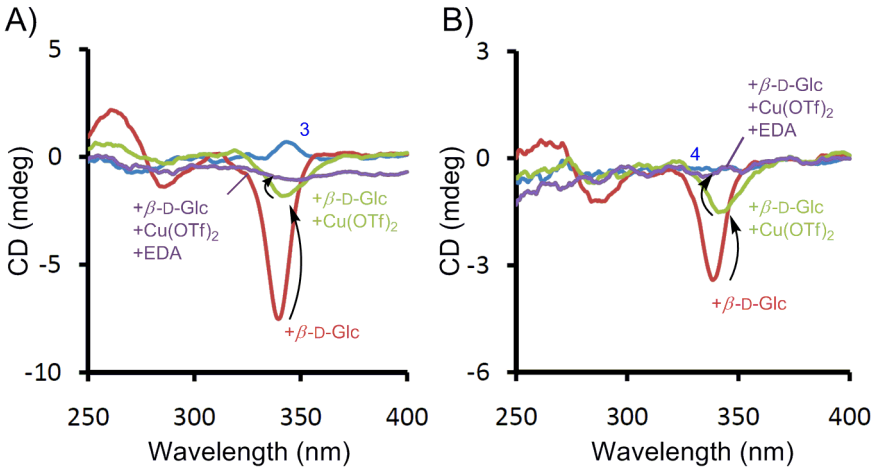


Fig S2 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the ICDs of host polymer **3** and **4** associated with octyl *β*-D-glucopyranoside (***β*-D-Glc**). (A) host polymer: **3** (B) host polymer: **4**. Blue: host polymer; red: host polymer + ***β*-D-Glc**; green: host polymer + ***β*-D-Glc**

+ $Cu(OTf)_2$; purple: host polymer + **β-D-Glc** + $Cu(OTf)_2$ + EDA. Conditions: host polymer (1.0×10^{-3} M, unit conc.), **β-D-Glc** (2.0×10^{-3} M), $Cu(OTf)_2$ (5.0×10^{-4} M), EDA (5.0×10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

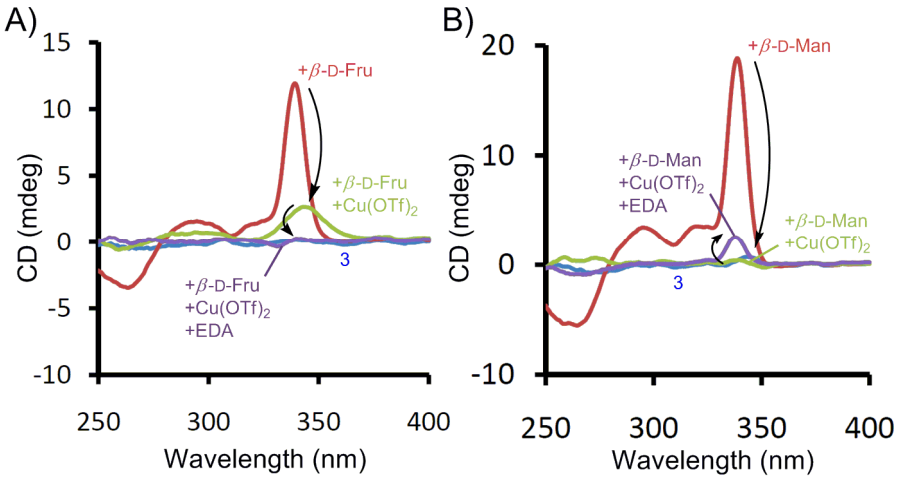


Fig S3 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the ICDs of host polymer **3** associated with (A) octyl β-fructopyranoside (**β-D-Fru**) and (B) octyl β-mannopyranoside (**β-D-Man**). Blue: **3**; red: **3** + glycoside; green: **3** + glycoside + $Cu(OTf)_2$; purple: **3** + glycoside + $Cu(OTf)_2$ + EDA. Conditions: **3** (1.0×10^{-3} M, unit conc.), glycoside (2.0×10^{-3} M), $Cu(OTf)_2$ (5.0×10^{-4} M), EDA (5.0×10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

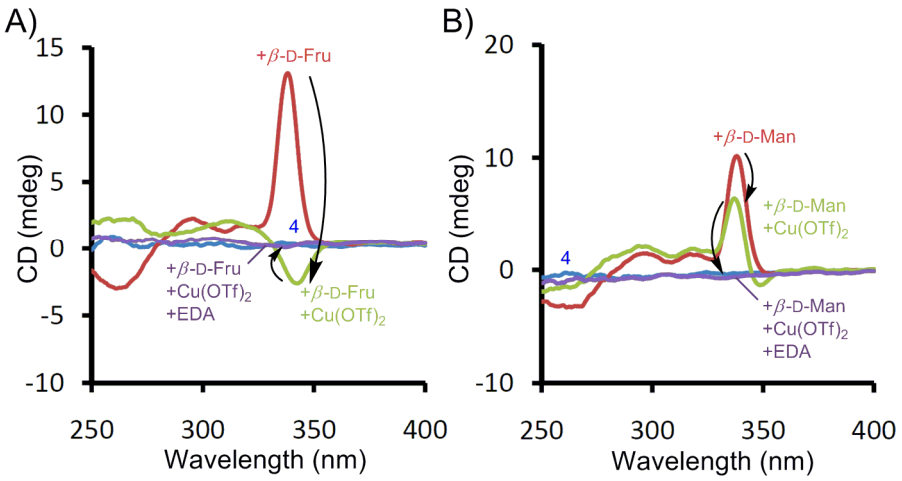


Fig S4 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the ICDs of host polymer **4** associated with (A) octyl *β*-fructopyranoside (***β*-D-Fru**) and (B) octyl *β*-mannopyranoside (***β*-D-Man**). Blue: **4**; red: **4** + glycoside; green: **4** + glycoside + $Cu(OTf)_2$; purple: **4** + glycoside + $Cu(OTf)_2$ + EDA. Conditions: **4** (1.0×10^{-3} M, unit conc.), glycoside (2.0×10^{-3} M), $Cu(OTf)_2$ (5.0×10^{-4} M), EDA (5.0×10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

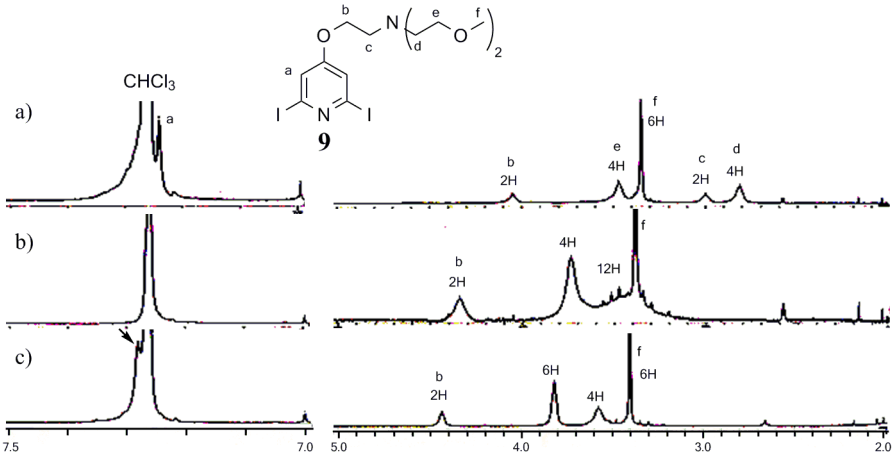


Fig S5 The additive effect of Cu(II) triflate on the ^{1}H NMR (300 MHz) spectrum of tertiary amine **9**. The chemical shifts for the side chains shifted upfield by the addition of $Cu(OTf)_2$. a) **9** (1.0×10^{-3} M); b) **9** (1.0×10^{-3} M) + $Cu(OTf)_2$ (5.0×10^{-4} M); c) **9** (1.0×10^{-3} M) + $Cu(OTf)_2$ (1.0×10^{-3} M). Conditions: 300 MHz, $CDCl_3$/DMSO-d_6 = 300:1, 22 °C.

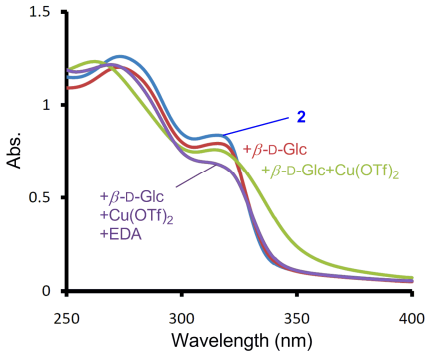


Fig S6 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectrum of host polymer **2** associated with octyl *β*-D-glucopyranoside (***β*-D-Glc**). Blue: **2**; red: **2** + ***β*-D-Glc**; green: **2** + ***β*-D-Glc** + $Cu(OTf)_2$; purple: **2** + ***β*-D-Glc** + $Cu(OTf)_2$ + EDA. Conditions: **2** (1.0×10^{-3} M, unit conc.), ***β*-D-Glc** (2.0×10^{-3} M), $Cu(OTf)_2$ (5.0×10^{-4} M), EDA (5.0×10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

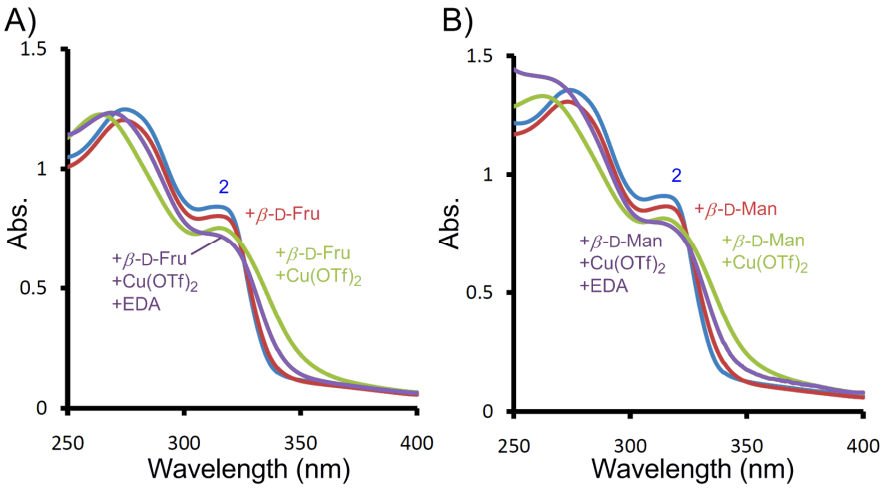


Fig S7 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer **2** associated with (A) octyl *β*-fructopyranoside (***β*-D-Fru**) and (B) octyl *β*-mannopyranoside (***β*-D-Man**). Blue: **2**; red: **2** + glycoside; green: **2** + glycoside + $Cu(OTf)_2$; purple: **2** + glycoside + $Cu(OTf)_2$ + EDA. Conditions: **2** (1.0×10^{-3} M, unit conc.), glycoside (2.0×10^{-3} M), $Cu(OTf)_2$ (5.0×10^{-4} M), EDA (5.0×10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

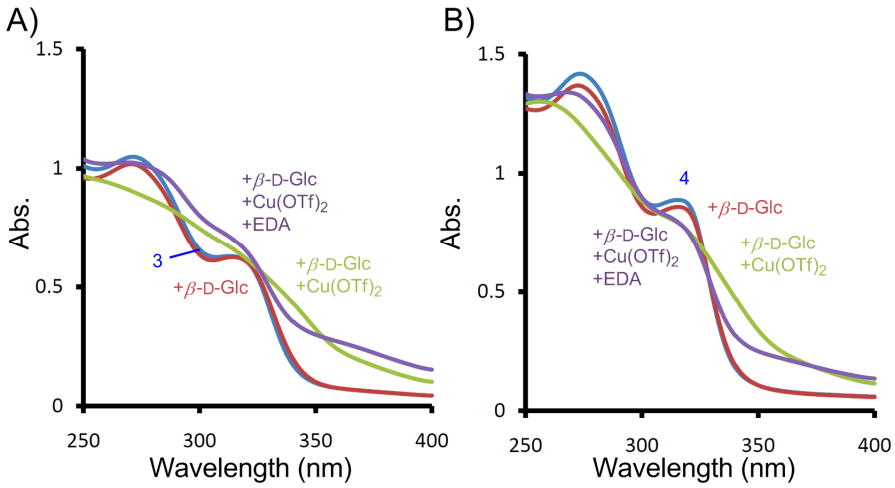


Fig S8 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer **3** and **4** associated with octyl β-D-glucopyranoside (**β-D-Glc**). (A) host polymer: **3** (B) host polymer: **4**. Blue: host polymer; red: host polymer + **β-D-Glc**; green: host polymer + **β-D-Glc** + $Cu(OTf)_2$; purple: host polymer + **β-D-Glc** + $Cu(OTf)_2$ + EDA. Conditions: host polymer (1.0×10^{-3} M, unit conc.), **β-D-Glc** (2.0×10^{-3} M), $Cu(OTf)_2$ (5.0×10^{-4} M), EDA (5.0×10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

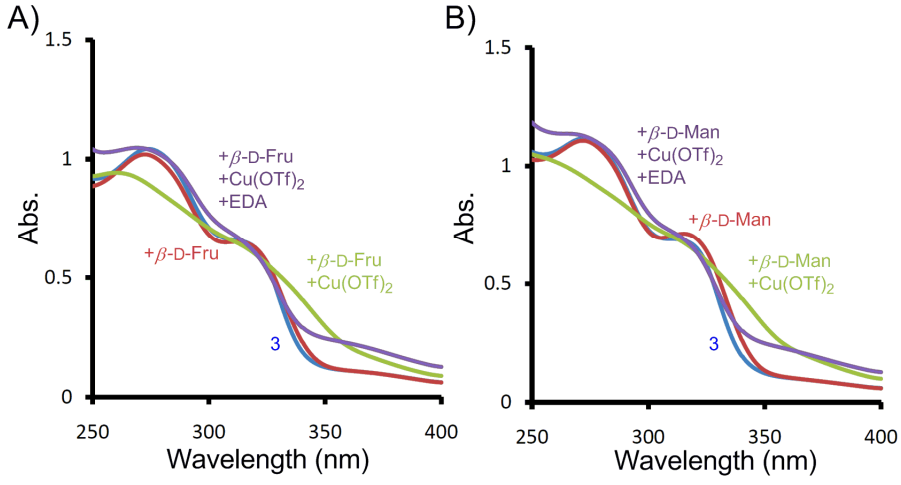


Fig S9 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer **3** associated with (A) octyl β-fructopyranoside (**β-D-Fru**) and (B) octyl β-mannopyranoside (**β-D-Man**). Blue: **3**; red: **3** + glycoside; green: **3** + glycoside + $Cu(OTf)_2$; purple: **3** + glycoside + $Cu(OTf)_2$ + EDA. Conditions: **3** (1.0×10^{-3} M, unit conc.), glycoside (2.0

× 10^{-3} M), $Cu(OTf)_2$ (5.0 × 10^{-4} M), EDA (5.0 × 10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

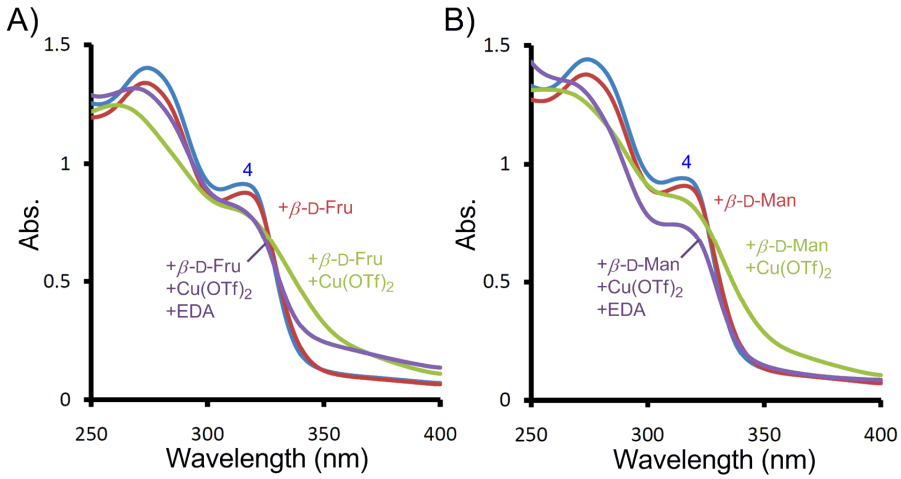


Fig S10 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer **4** associated with (A) octyl β-fructopyranoside (**β-D-Fru**) and (B) octyl β-mannopyranoside (**β-D-Man**). Blue: **4**; red: **4** + glycoside; green: **4** + glycoside + $Cu(OTf)_2$; purple: **4** + glycoside + $Cu(OTf)_2$ + EDA. Conditions: **4** (1.0 × 10^{-3} M, unit conc.), glycoside (2.0 × 10^{-3} M), $Cu(OTf)_2$ (5.0 × 10^{-4} M), EDA (5.0 × 10^{-4} M), CH_2Cl_2, 25 °C, path length = 1 mm. $Cu(OTf)_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

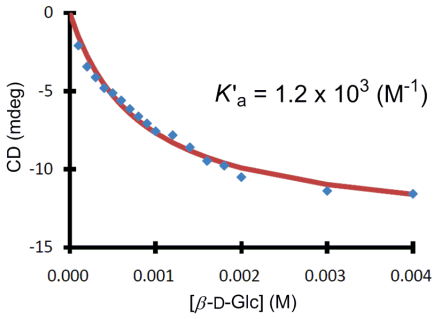


Fig S11 The titration curve for CD at 339 nm of the mixture of **2** and β-D-glucopyranoside (**β-D-Glc**). **β-D-Glc** was used as titrant. The formal binding constant *K'* was obtained by curve fitting measurements based on the equation mentioned above and the assumption that the molecular

weight of the polymer **2** was uniform in length and that the polymer and the guest associate in a 1:1 ratio. Conditions: **2** (1.0×10^{-3} M, unit conc.), ***β*-D-Glc**, CH_2Cl_2, 25 °C, path length = 1 mm.

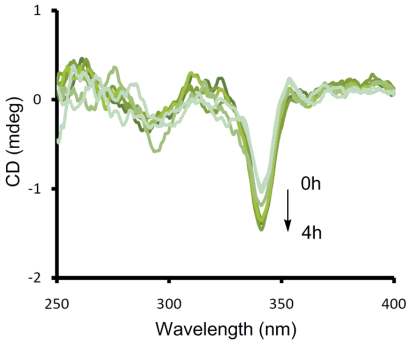
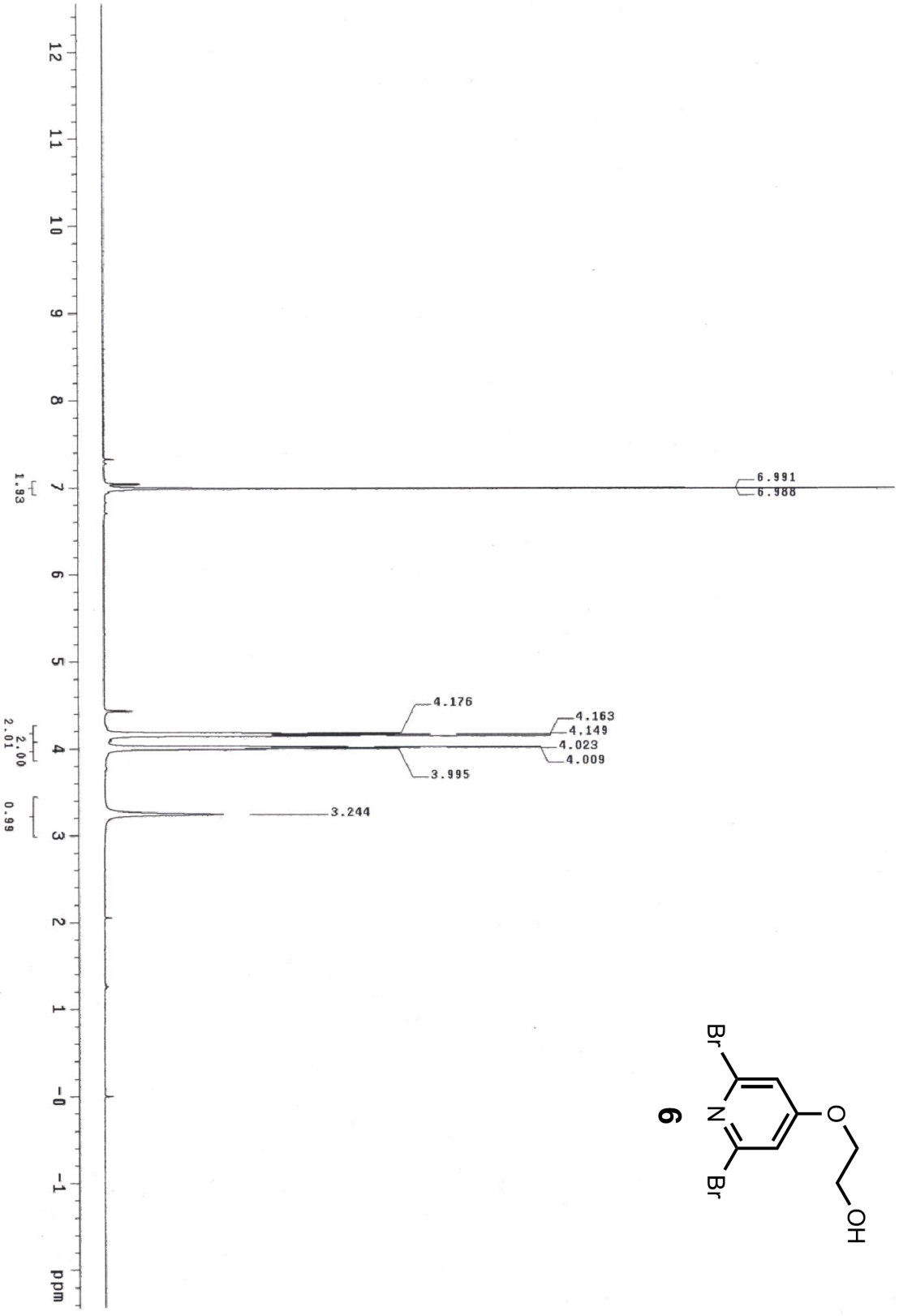
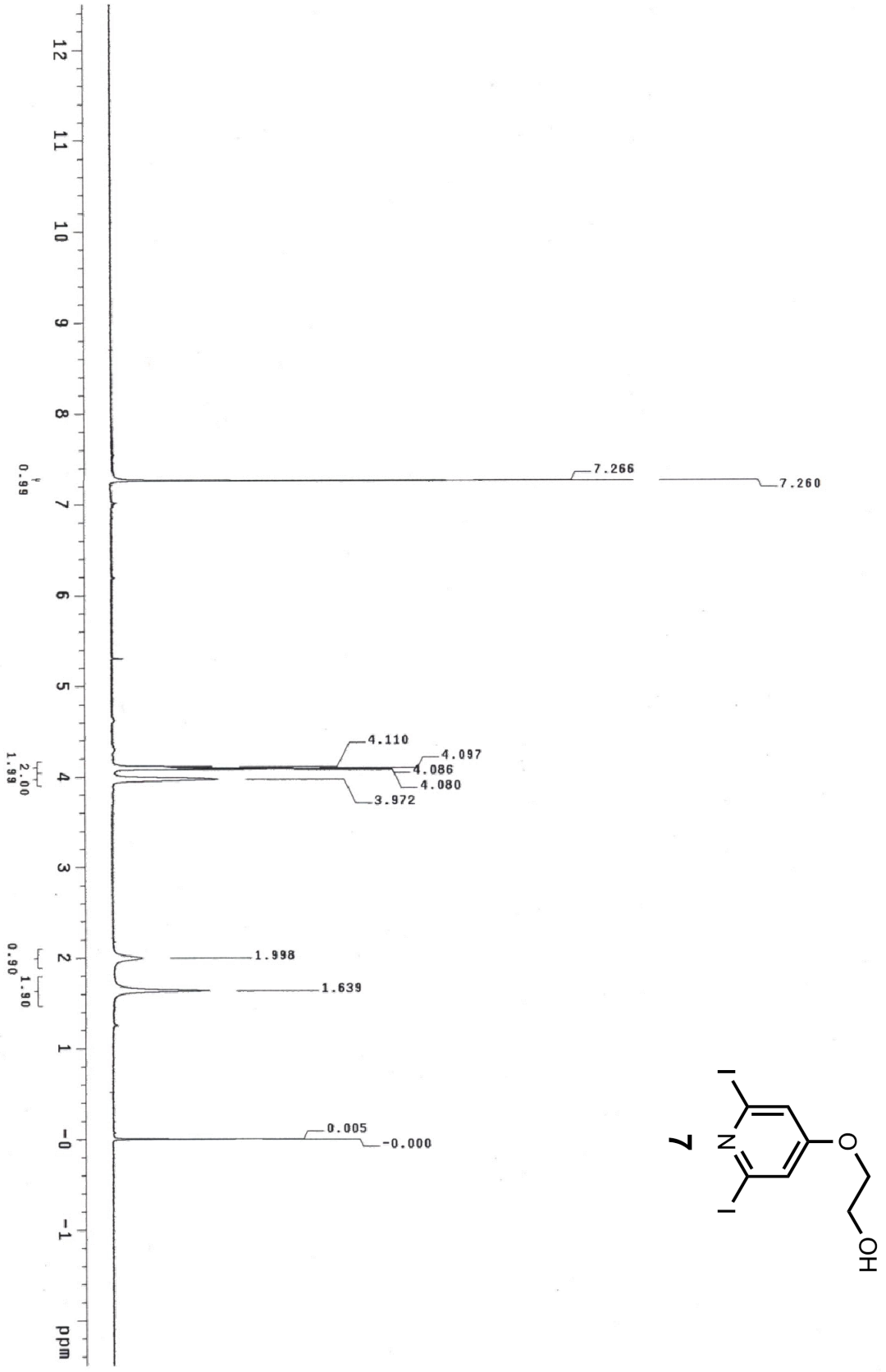


Fig S12 A CD spectral change in the reverse-order experiment. *β*-D-glucopyranoside (***β*-D-Glc**) was added to the mixture of host polymer **2** and Cu(II) triflate. A small ICD band was retained even after reaching equilibrium in four hours upon the addition of ***β*-D-Glc**. The ICD was five times smaller than that shown in Fig. 3. Conditions: **2** (1.0×10^{-3} M, unit conc.), ***β*-D-Glc** (2.0×10^{-3} M), $Cu(OTf)_2$ (5.0×10^{-4} M), CH_2Cl_2:DMSO = 300:1, 25 °C, path length = 1 mm.

^{1}H NMR spectra (300 MHz in $CDCl_3$)

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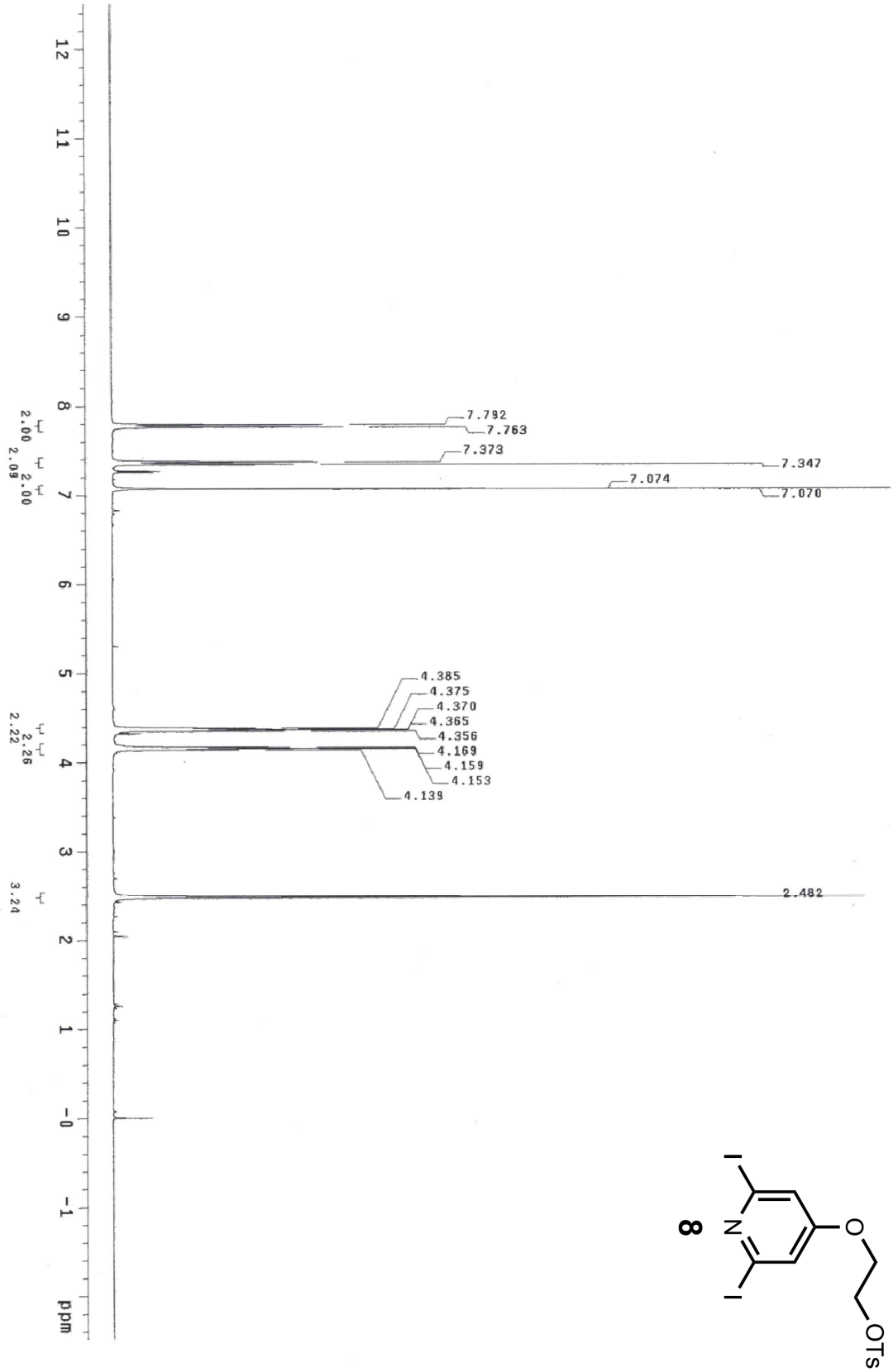
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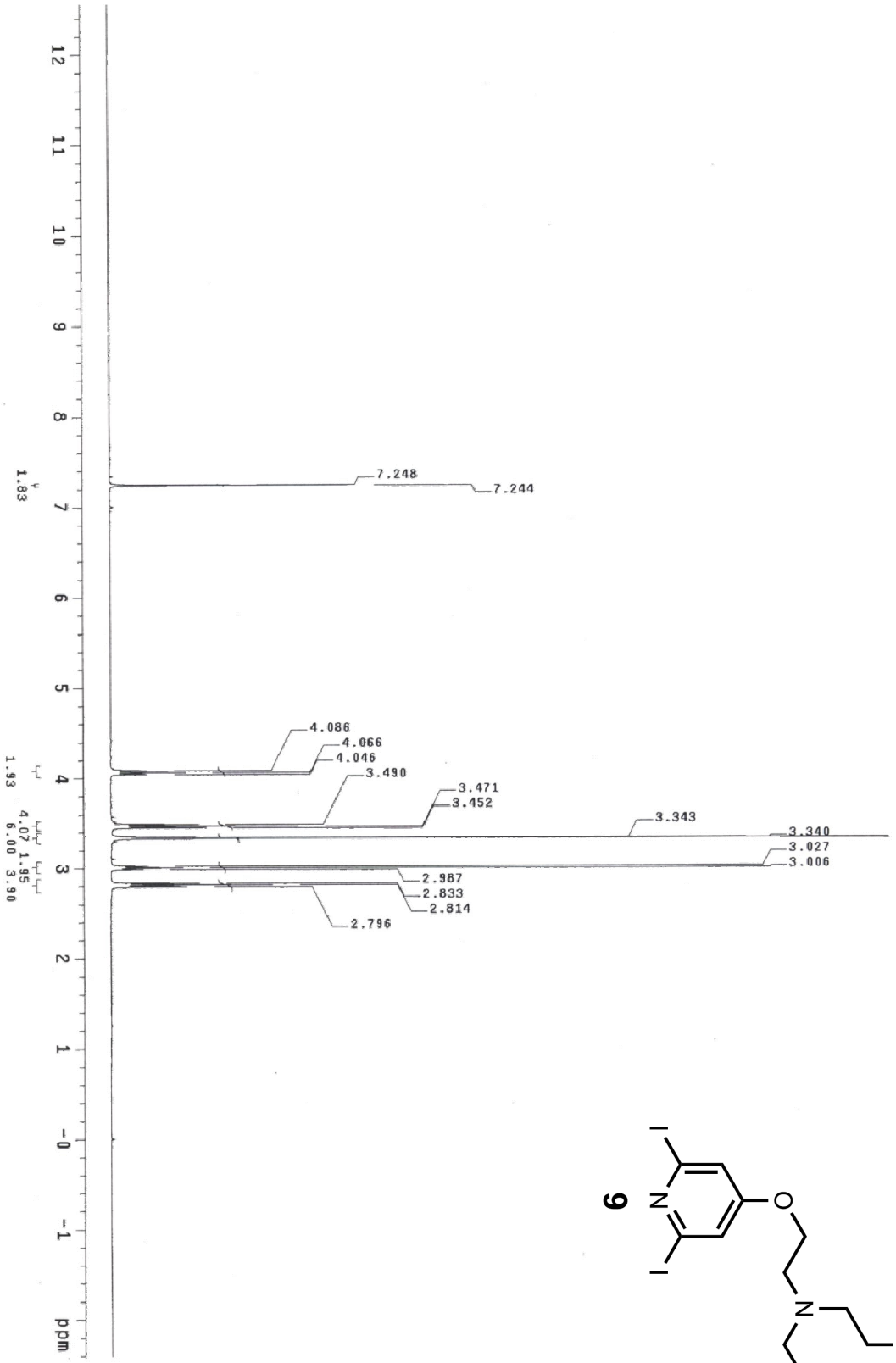
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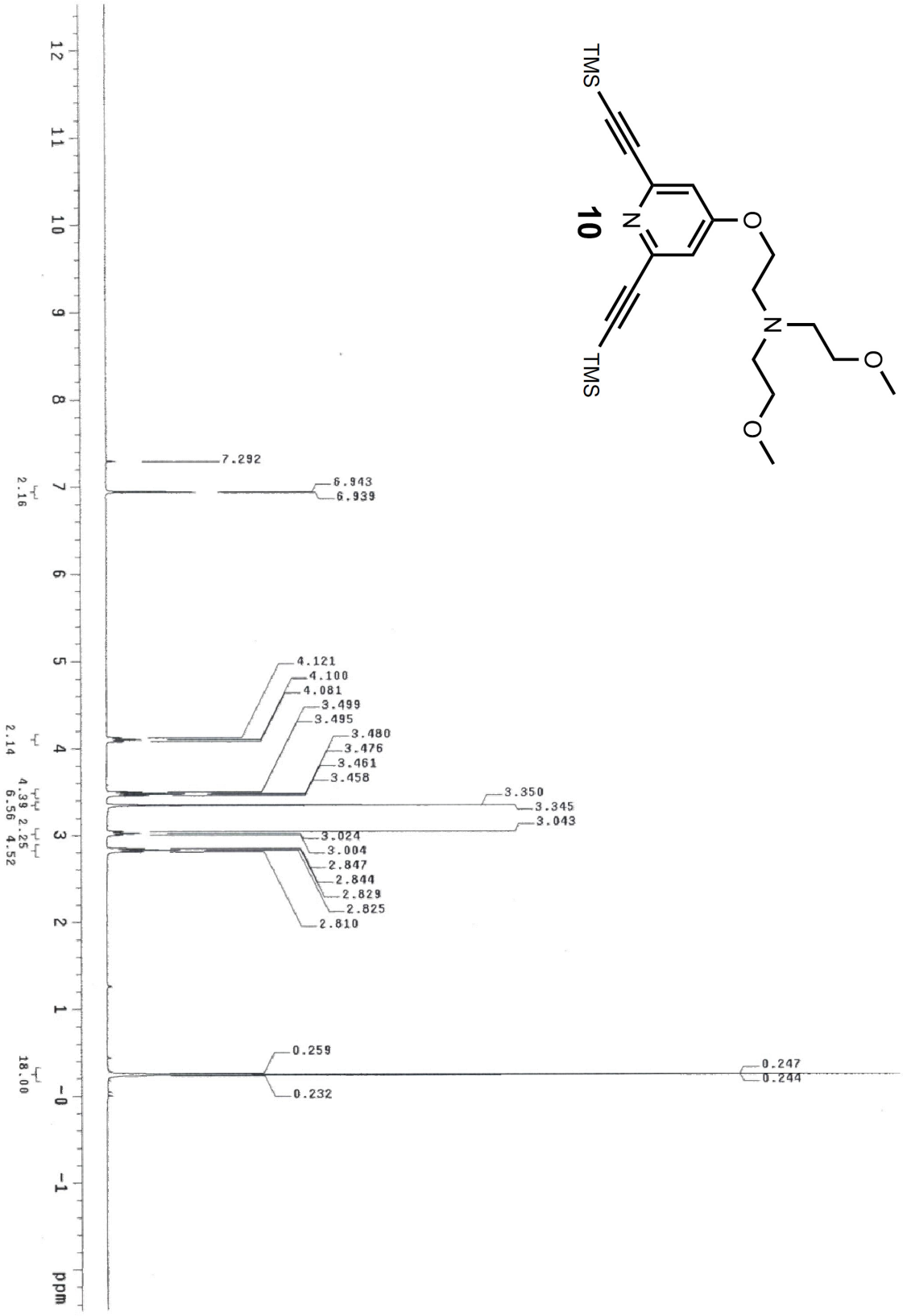
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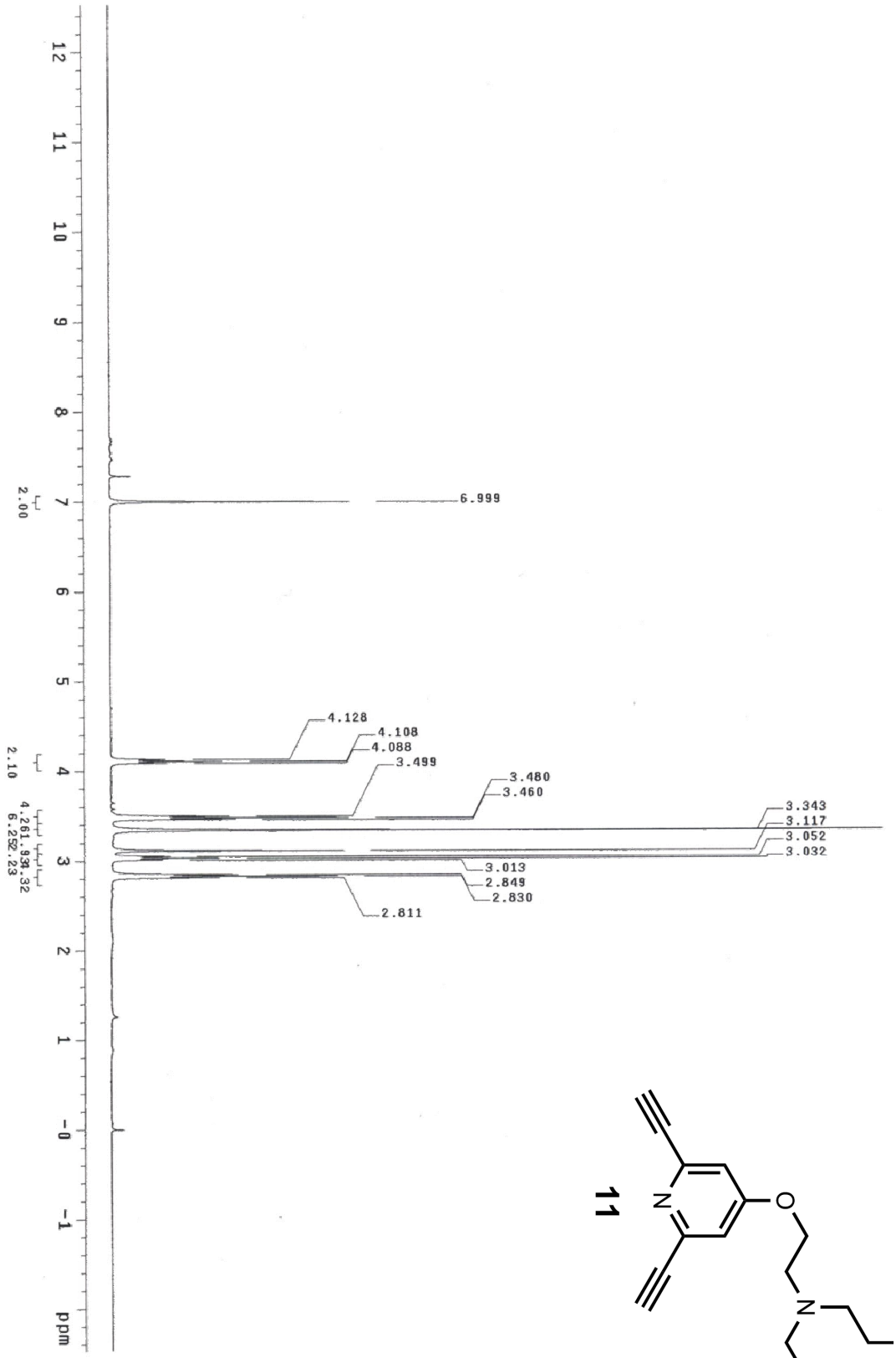
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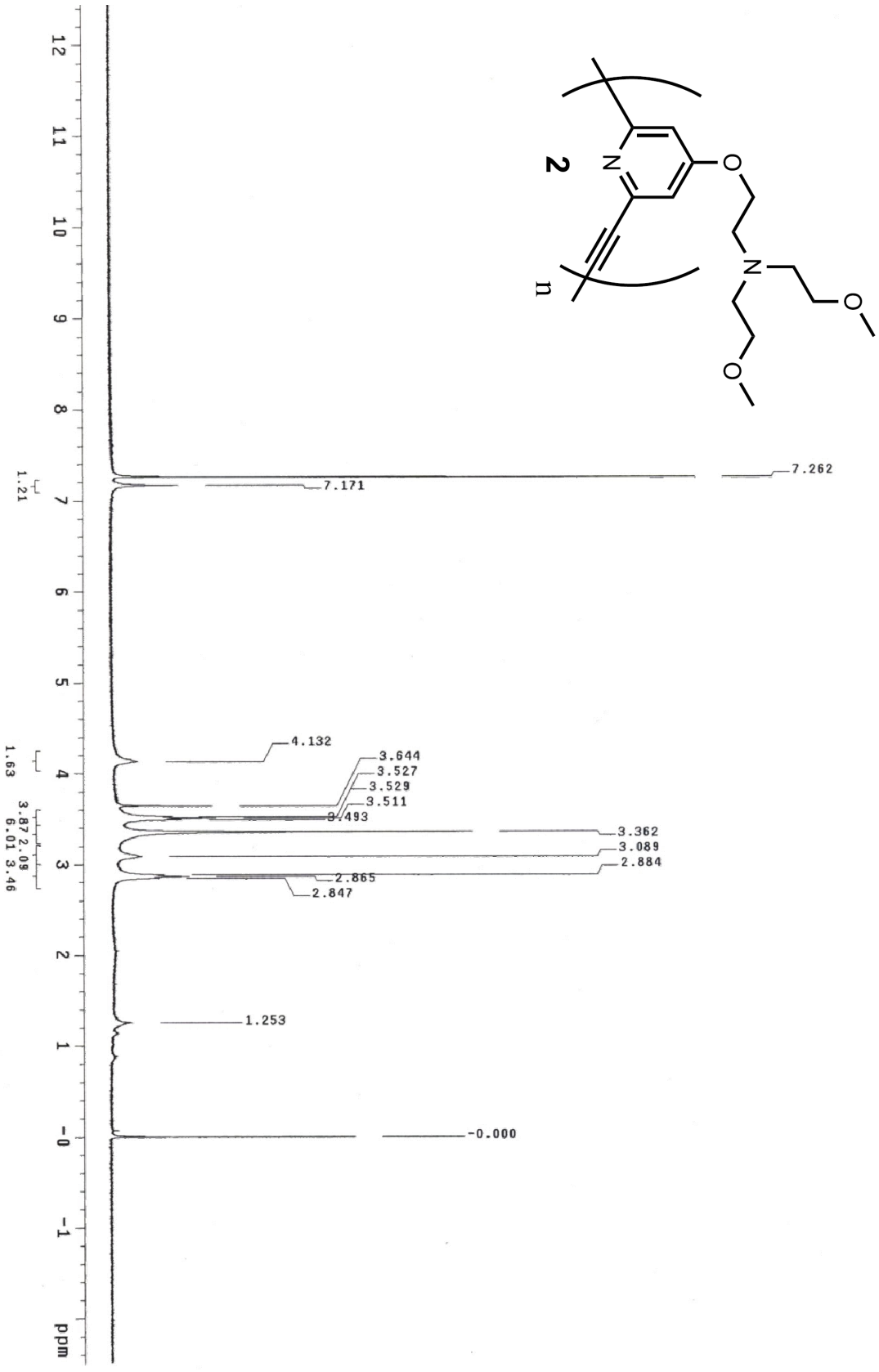
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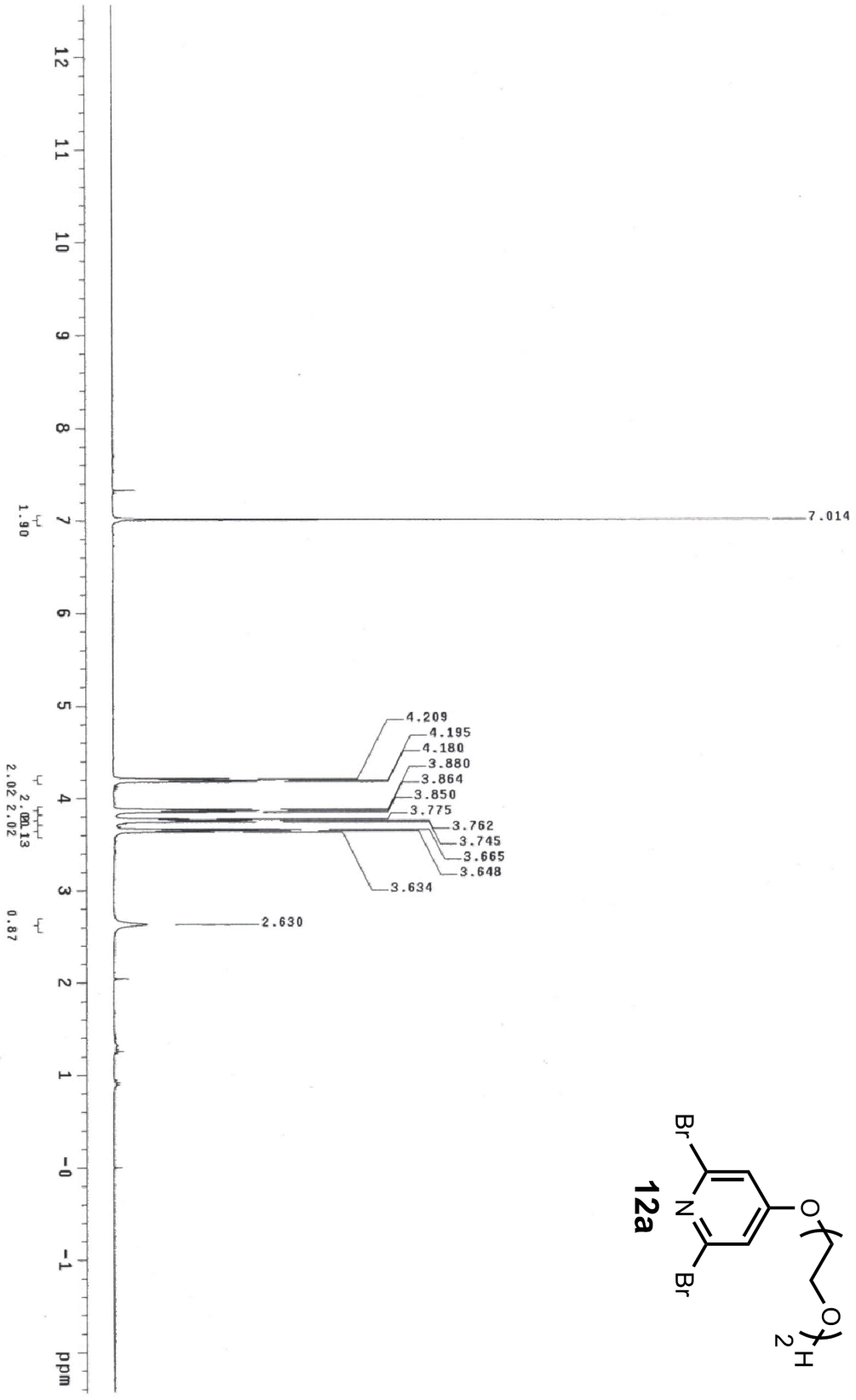
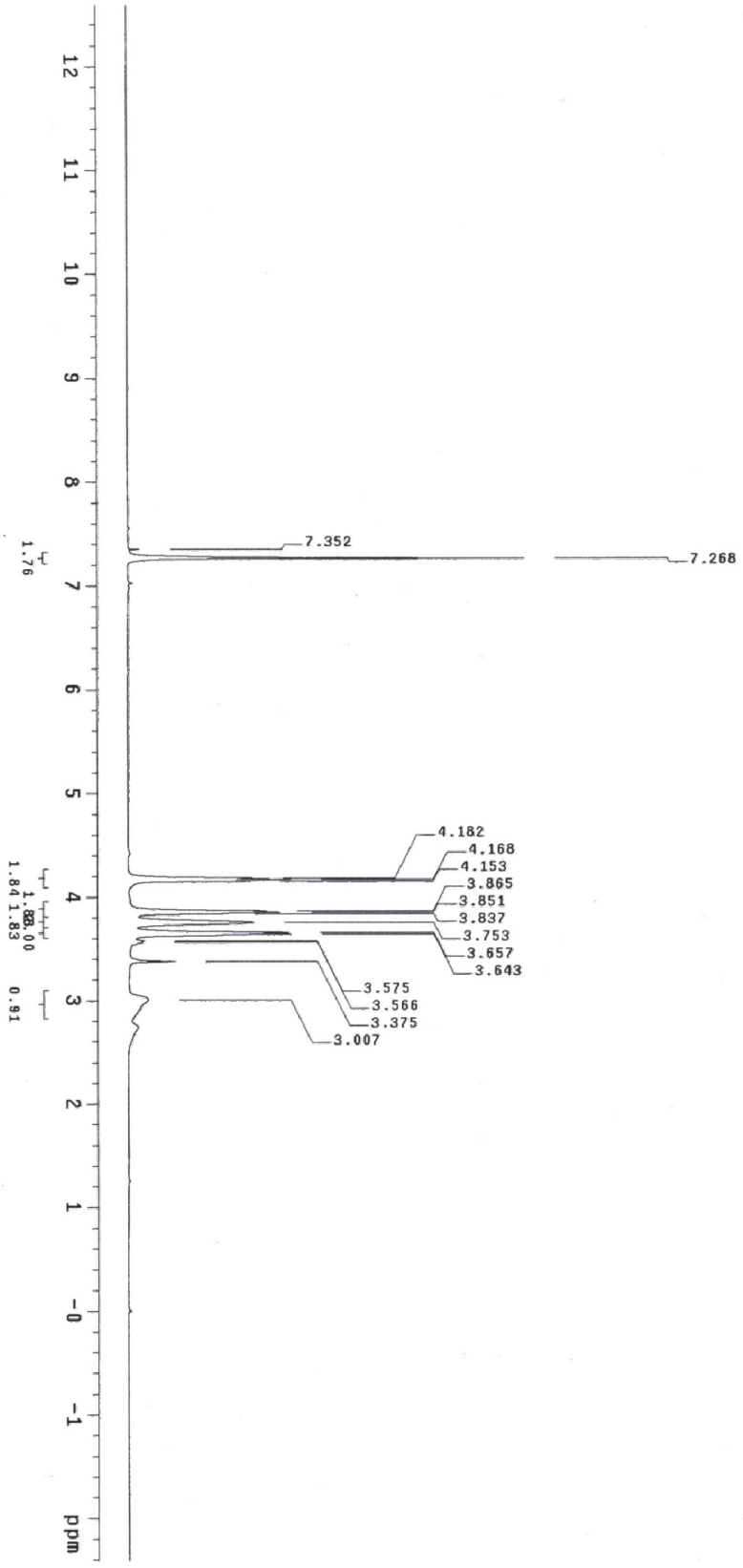
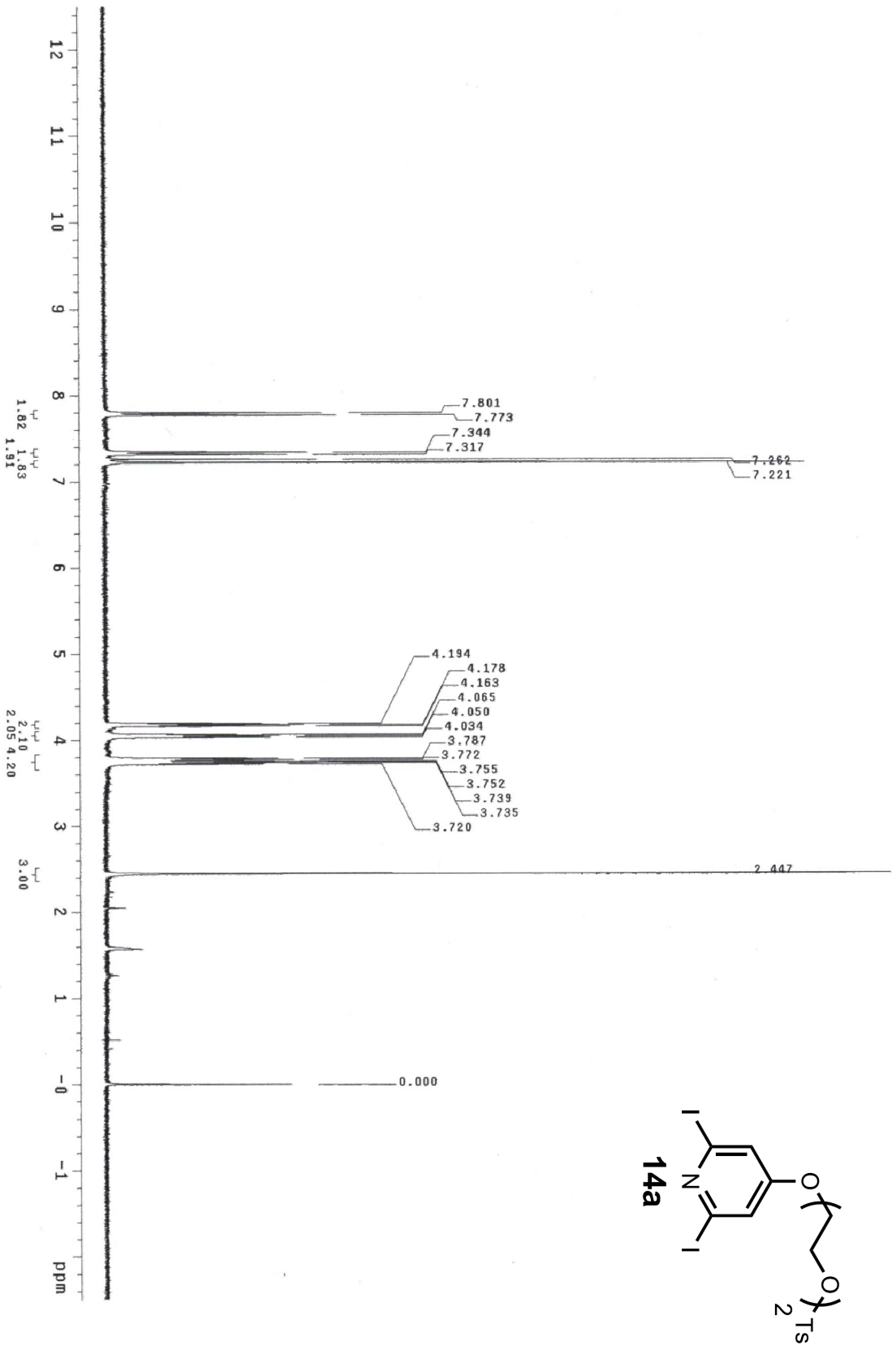
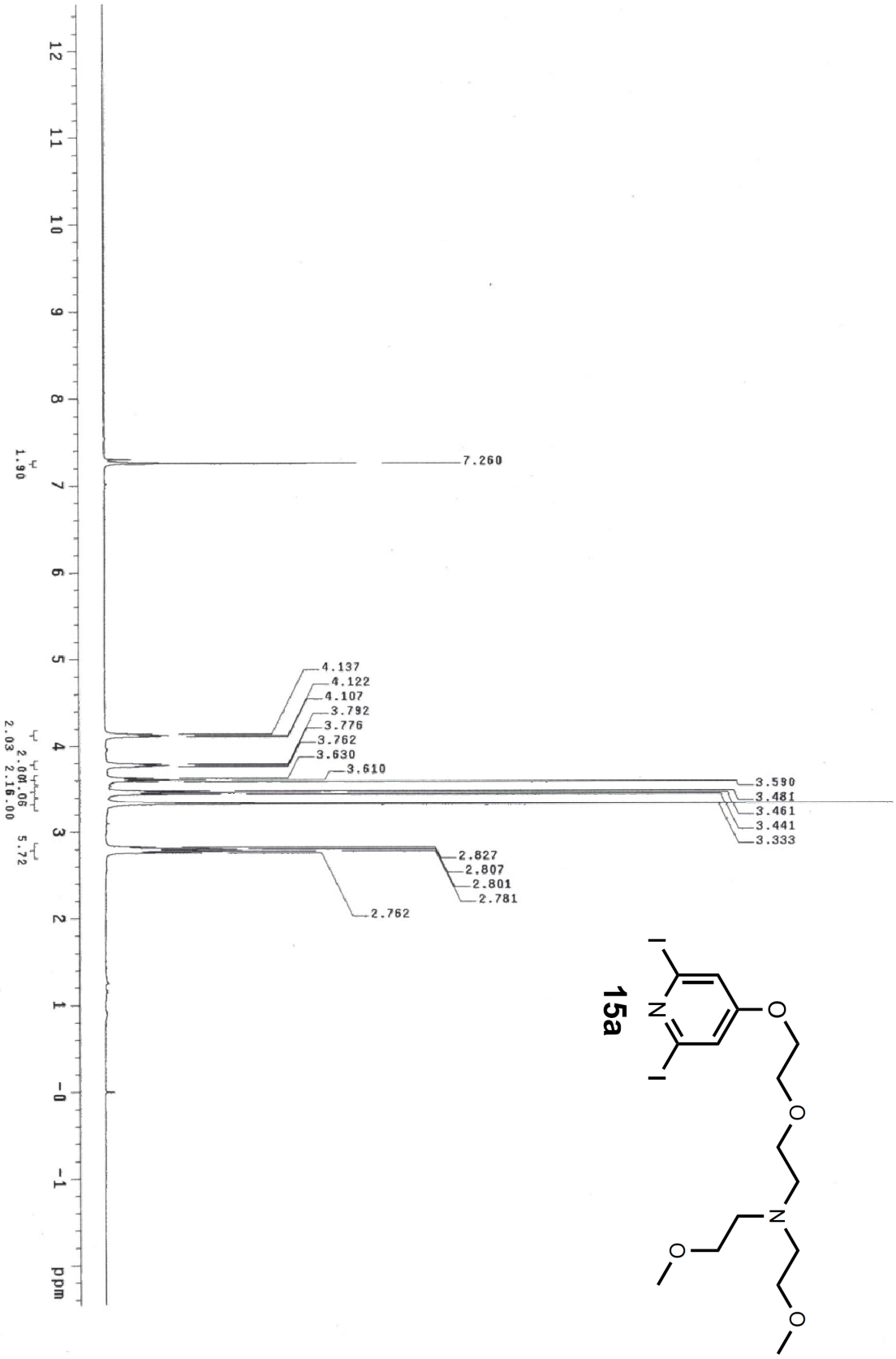
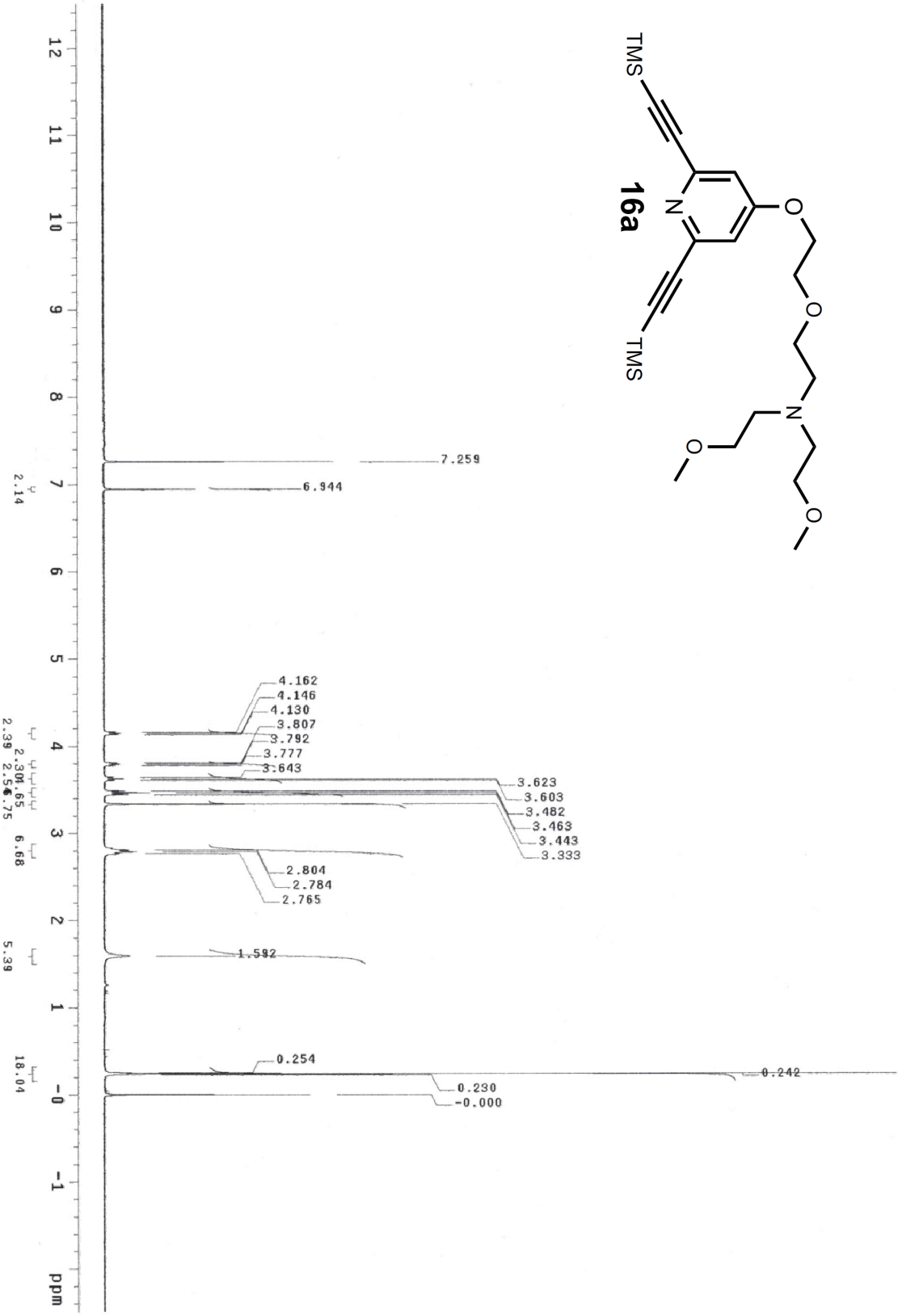

7.014
4.209
4.195
4.180
3.880
3.864
3.850
3.775
3.762
3.745
3.665
3.648
3.634
2.630
1.90
2.02 2.02 2.13
0.87
ppm
12a
Br
N
Br
O
O
H
2

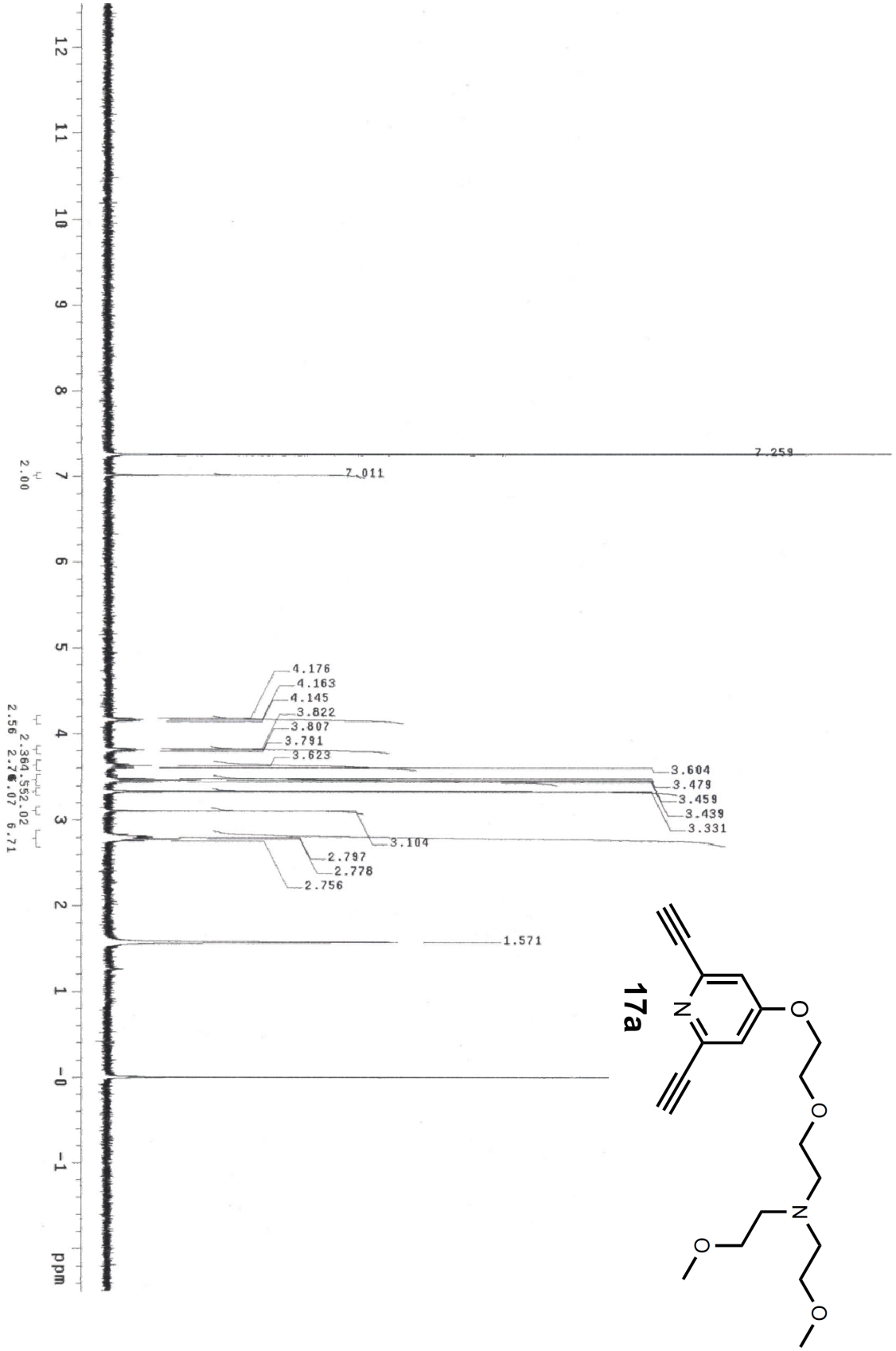

7.352
7.268
4.182
4.168
4.153
3.865
3.851
3.837
3.753
3.657
3.643
3.575
3.566
3.375
3.007
1.76
1.84
1.83
0.91
ppm

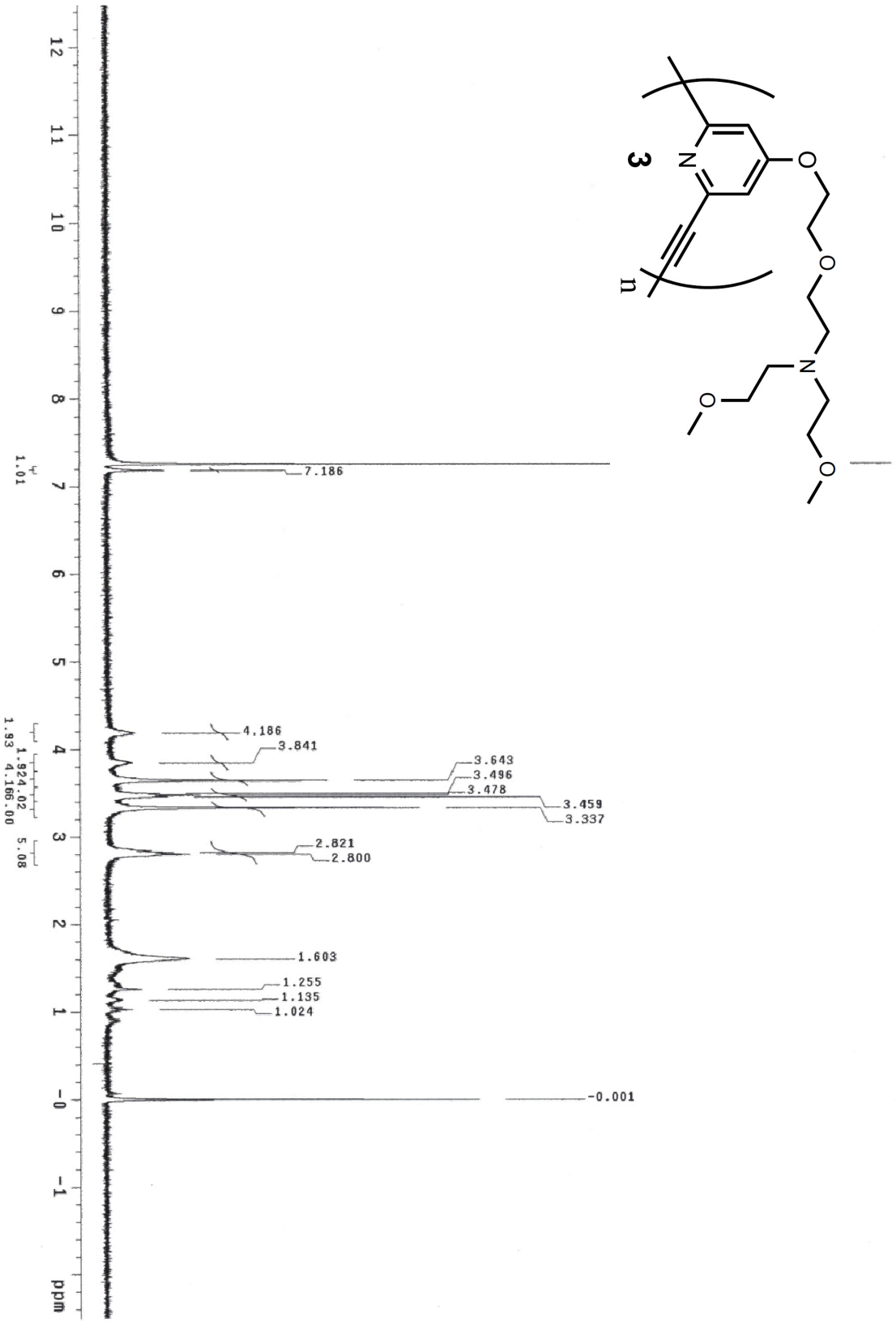
13a

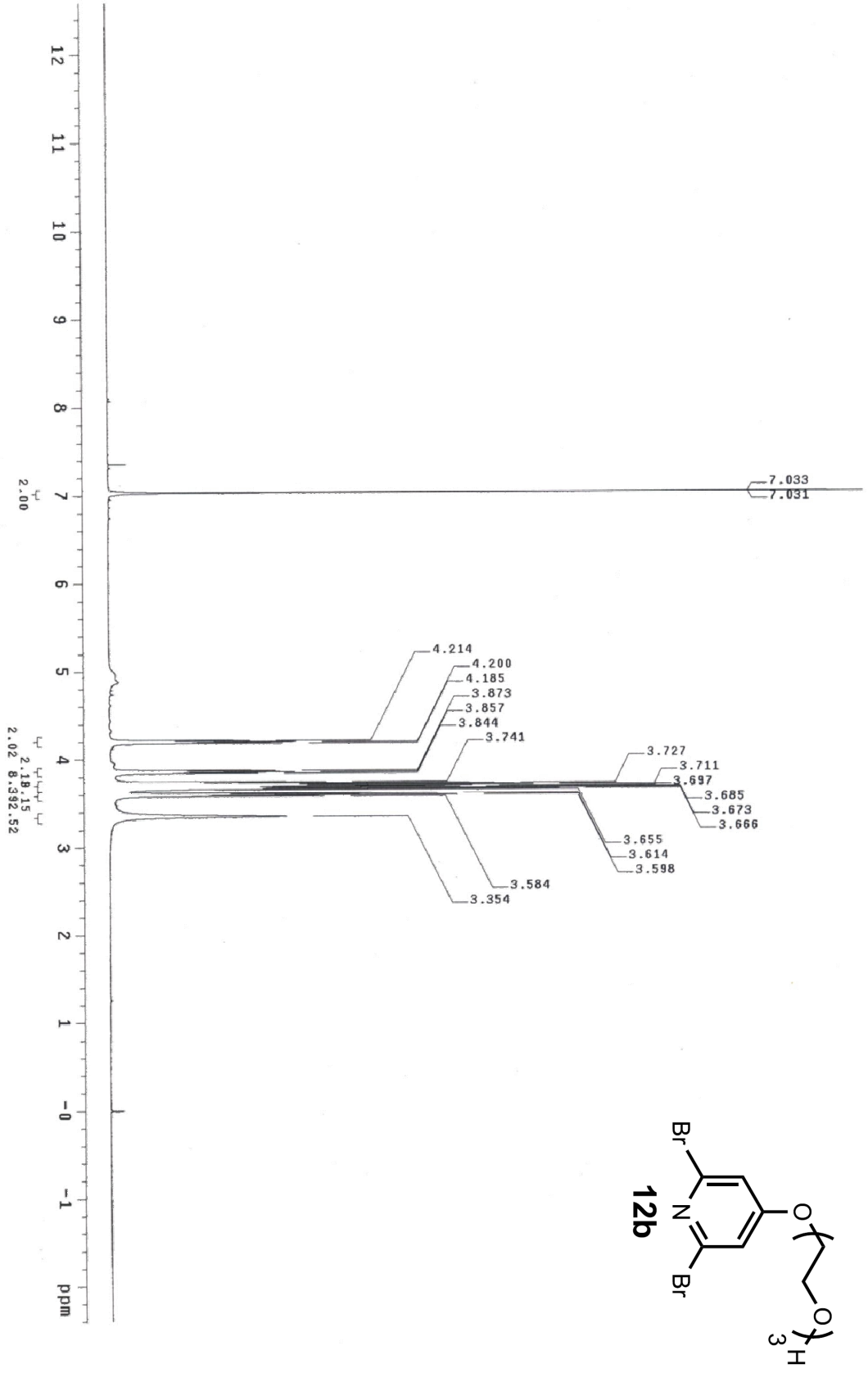

7.801
7.773
7.344
7.317
7.262
7.221
4.194
4.178
4.163
4.065
4.050
4.034
3.787
3.772
3.755
3.752
3.739
3.735
3.720
2.447
0.000
1.82
1.83
1.91
2.10
2.05
4.20
3.00
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
14a
N
O
O
O
Ts
2

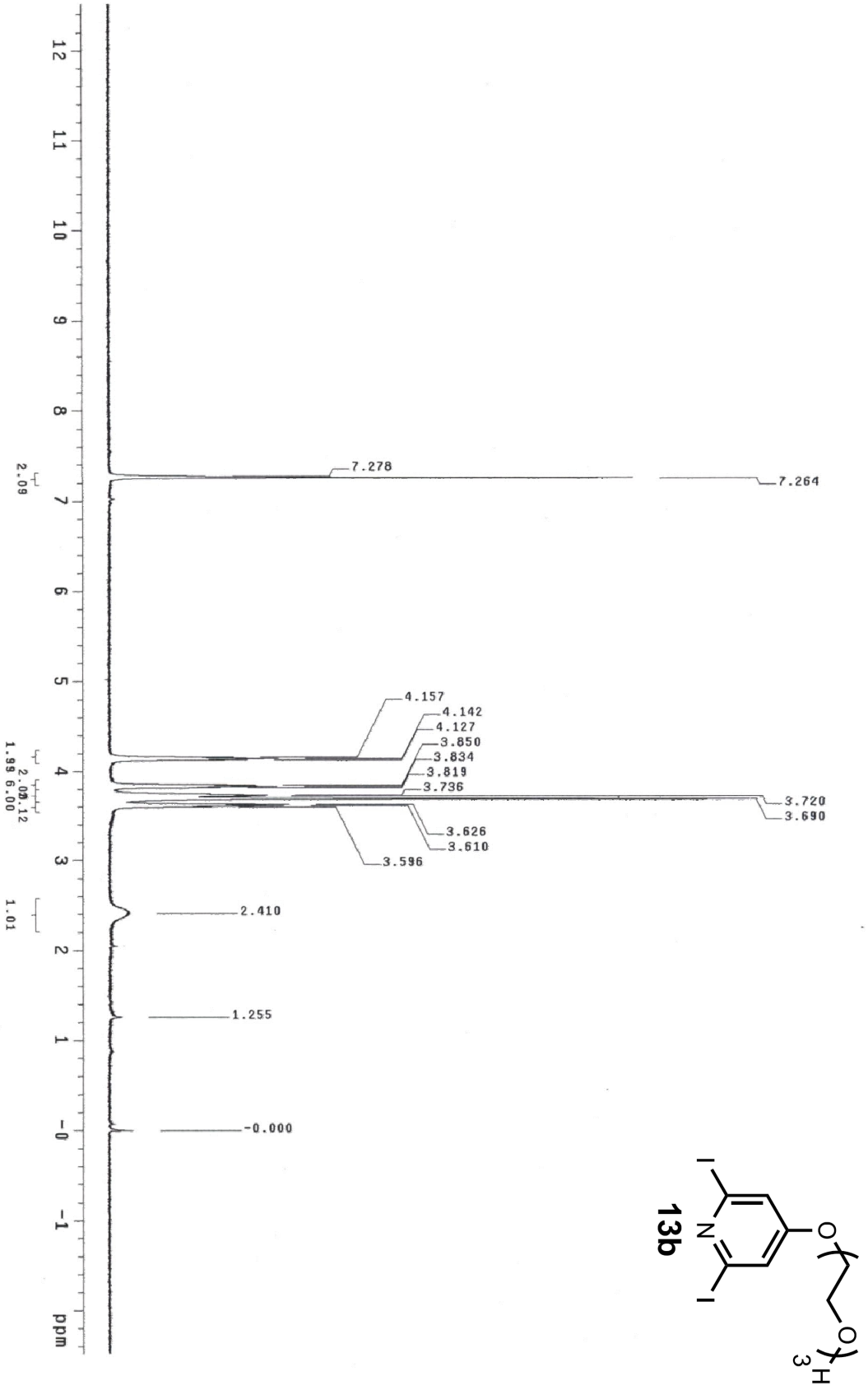

7.260
4.137
4.122
4.107
3.792
3.776
3.762
3.630
3.610
3.590
3.481
3.461
3.441
3.333
2.827
2.807
2.801
2.781
2.762
1.90
2.03
2.00
2.16
6.06
5.72
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
15a
N
O
O
N
O
O

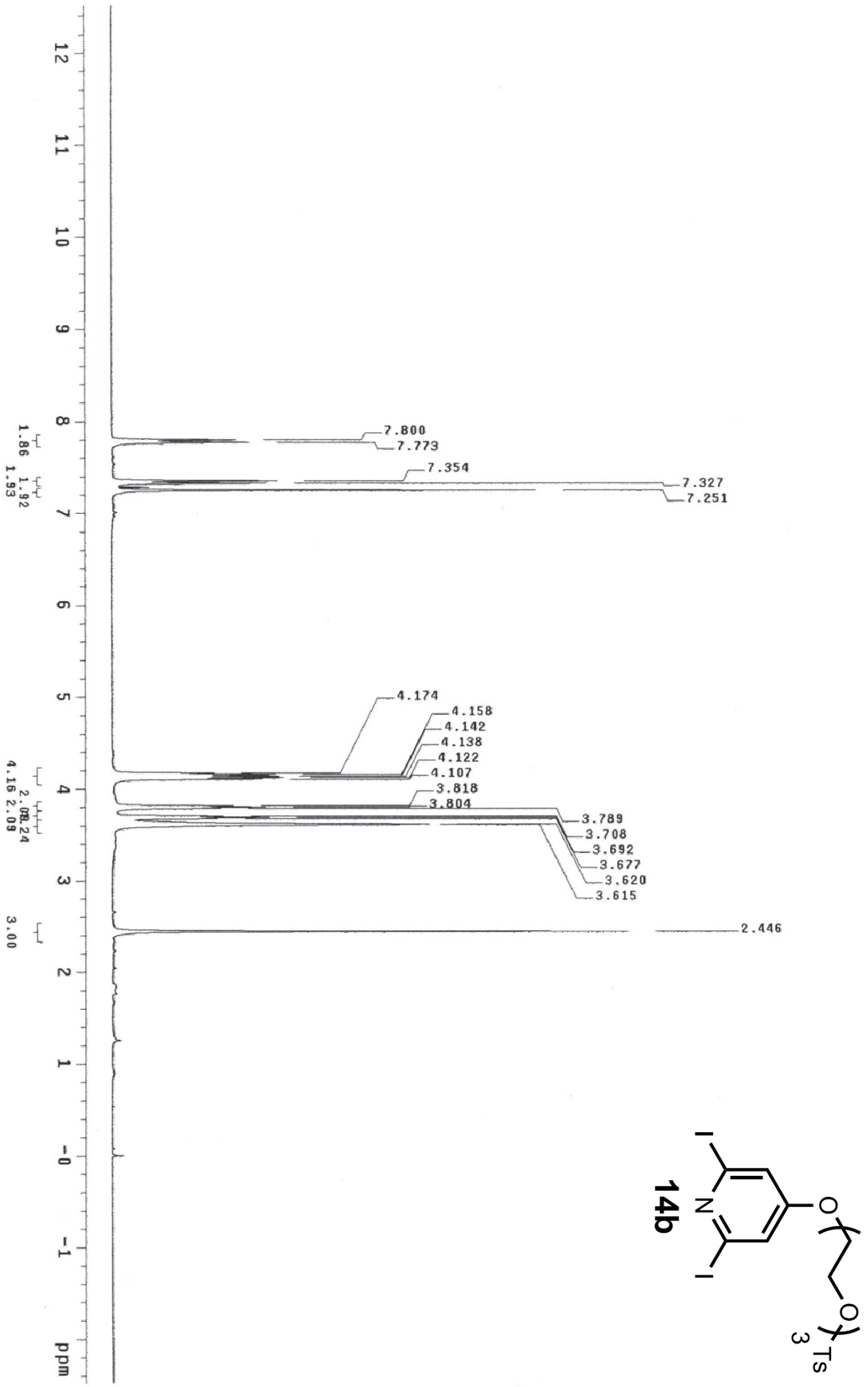

TMS
16a
N
O
O
O
N
O
O
TMS
7.259
6.944
4.162
4.146
4.130
3.807
3.792
3.777
3.643
3.623
3.603
3.482
3.463
3.443
3.333
2.804
2.784
2.765
1.592
0.254
0.242
0.230
-0.000
2.14
2.39
2.30
2.56
1.65
6.75
6.68
5.39
18.04
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

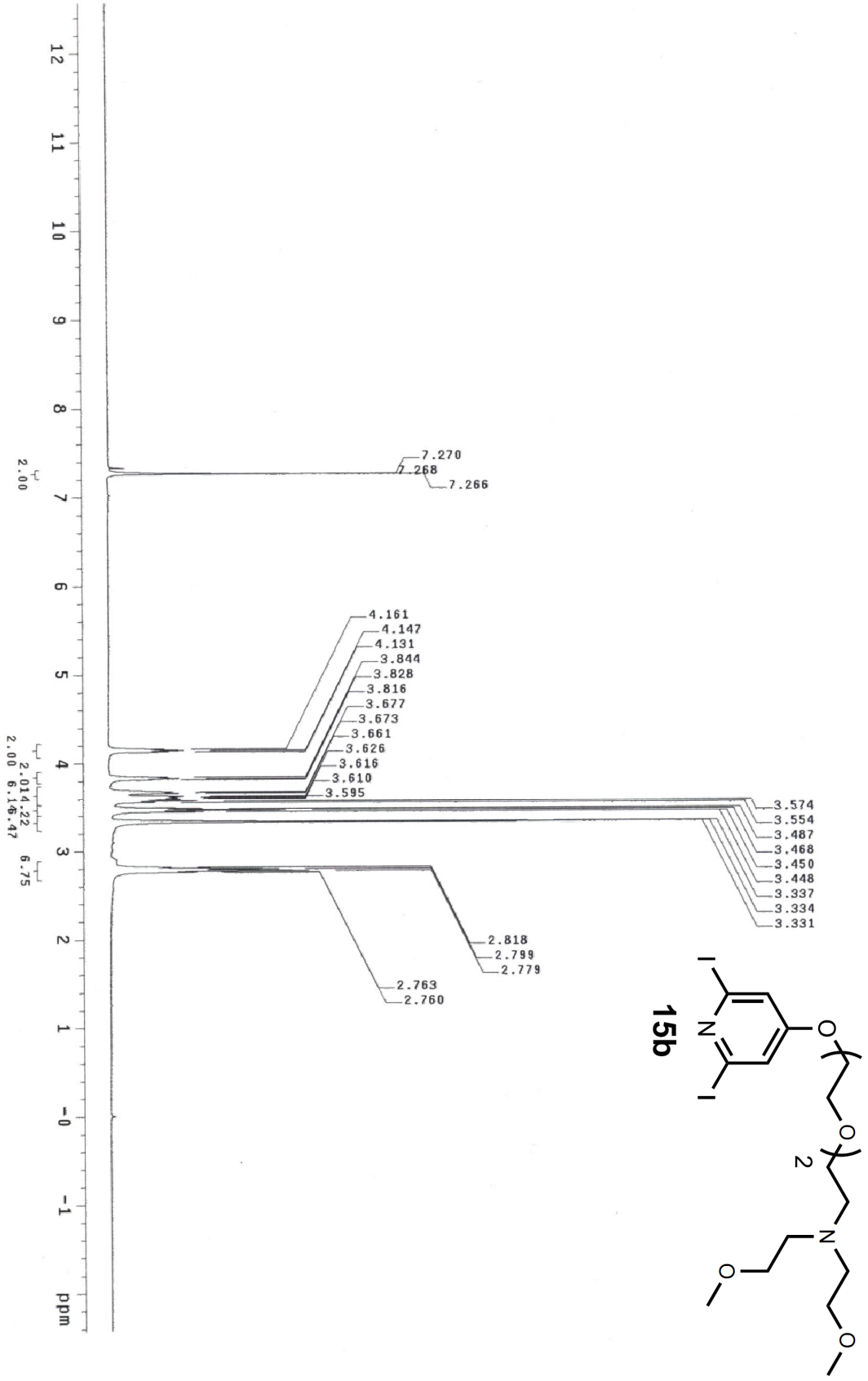

7.259
7.011
4.176
4.163
4.145
3.822
3.807
3.791
3.623
3.604
3.479
3.459
3.439
3.331
3.104
2.797
2.778
2.756
1.571
ppm
17a

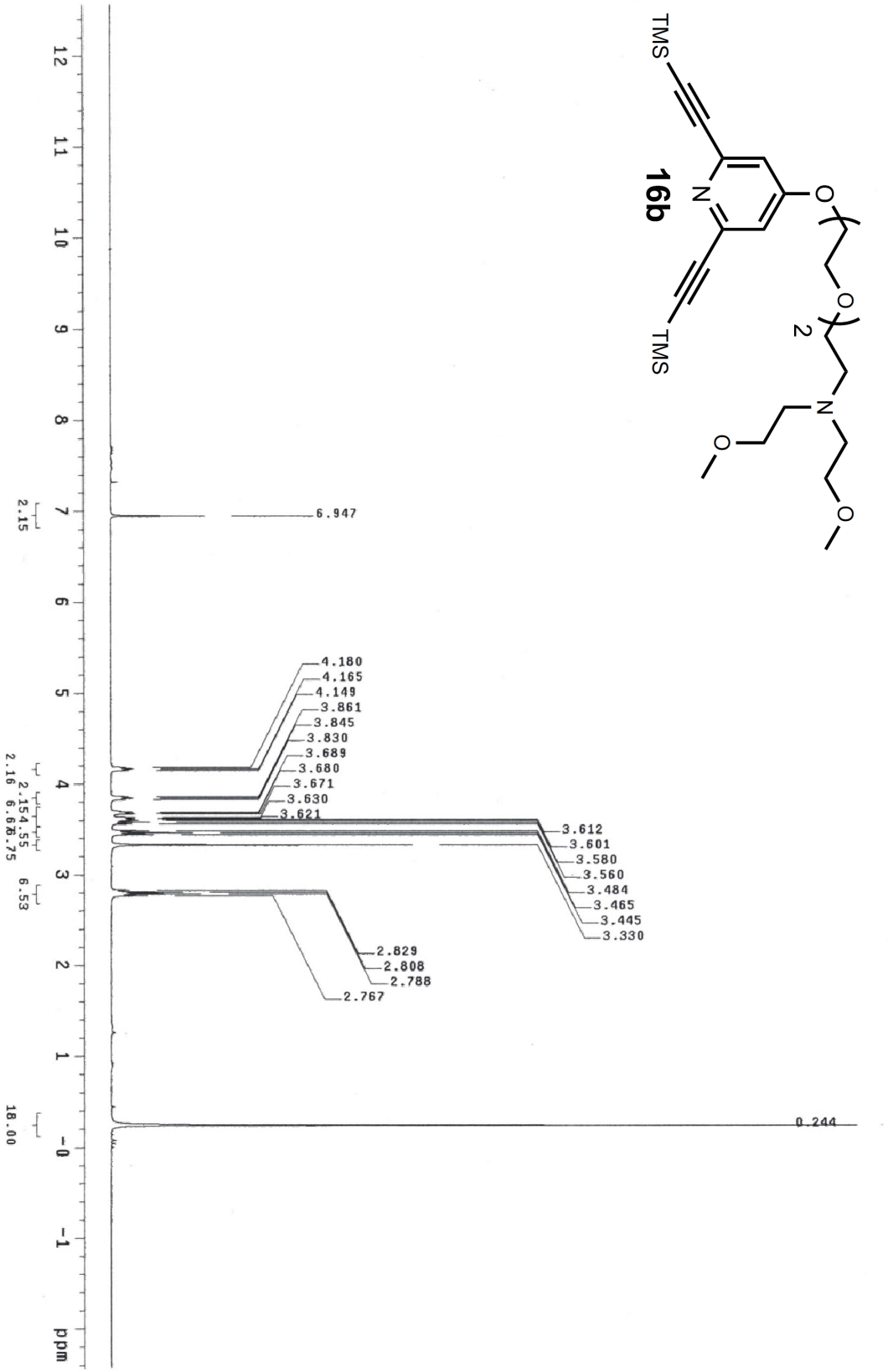

7.186
4.186
3.841
3.643
3.496
3.478
3.459
3.337
2.821
2.800
1.603
1.255
1.135
1.024
-0.001
1.01
1.93
1.924.02
4.166.00
5.08
ppm

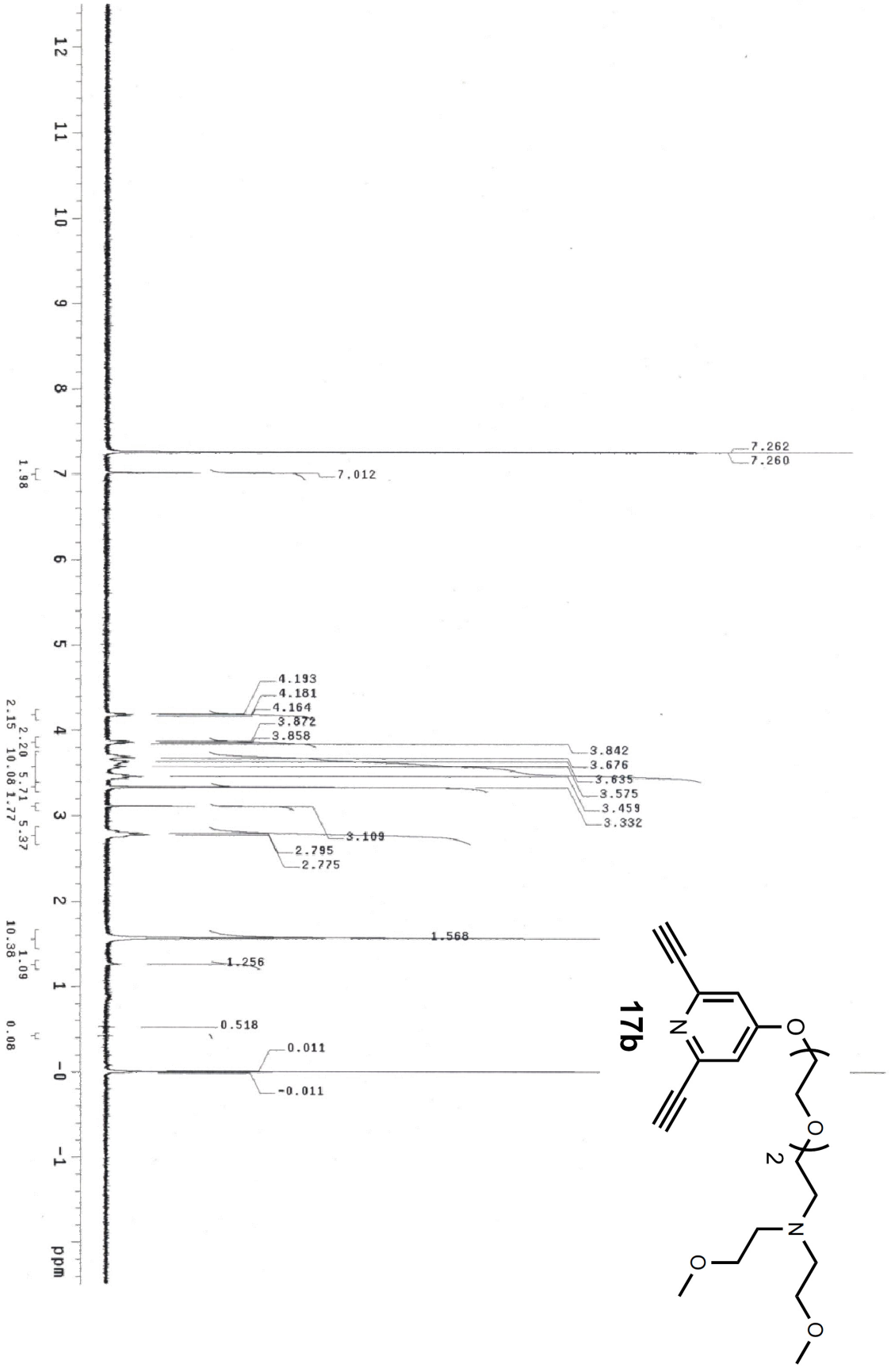

7.033
7.031
4.214
4.200
4.185
3.873
3.857
3.844
3.741
3.727
3.711
3.697
3.685
3.673
3.666
3.655
3.614
3.598
3.584
3.354
2.00
2.18
2.02
8.392.52
ppm
12b
Br
N
Br
O
O
H
3

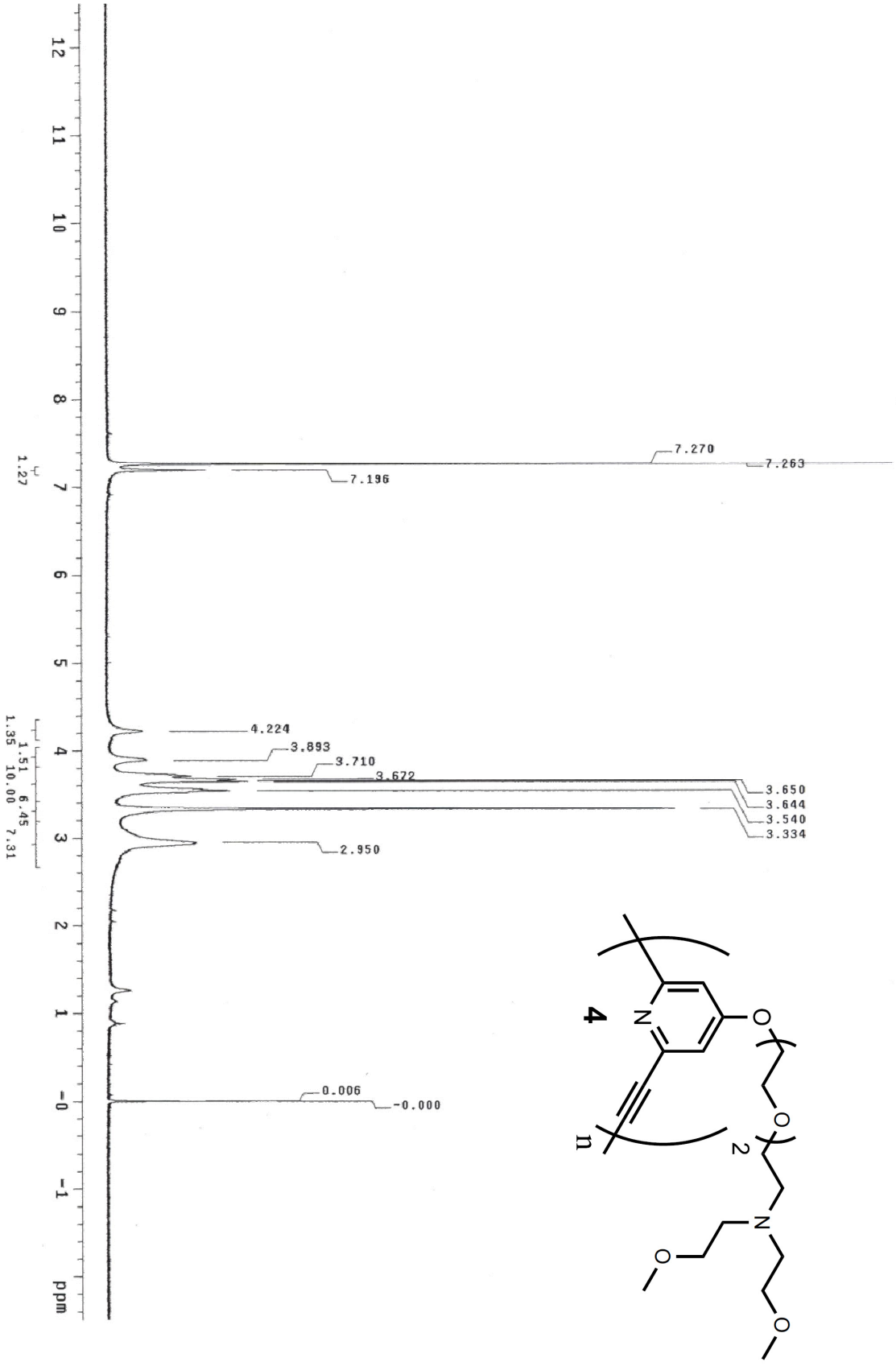

7.278
7.264
4.157
4.142
4.127
3.850
3.834
3.819
3.736
3.720
3.690
3.626
3.610
3.596
2.410
1.255
-0.000
ppm
13b


7.800
7.773
7.354
7.327
7.251
4.174
4.158
4.142
4.138
4.122
4.107
3.818
3.804
3.789
3.708
3.692
3.677
3.620
3.615
2.446
1.86
1.92
1.93
4.16
2.09
3.00
ppm
14b
I
N
I
O
O
3
Ts


7.270
7.268
7.266
4.161
4.147
4.131
3.844
3.828
3.816
3.677
3.673
3.661
3.626
3.616
3.610
3.595
3.574
3.554
3.487
3.468
3.450
3.448
3.337
3.334
3.331
2.818
2.799
2.779
2.763
2.760
2.00
2.00 2.01 4.22 6.16 6.47 6.75
12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
15b
I
N
I
O
O
2
N
O
O


16b
TMS
TMS
N
O
O
O
2
N
O
O
6.947
4.180
4.165
4.149
3.861
3.845
3.830
3.689
3.680
3.671
3.630
3.621
3.612
3.601
3.580
3.560
3.484
3.465
3.445
3.330
2.829
2.808
2.788
2.767
0.244
2.15
2.16
6.53
18.00
ppm


7.262
7.260
7.012
4.193
4.181
4.164
3.872
3.858
3.842
3.676
3.635
3.575
3.459
3.332
3.109
2.795
2.775
1.568
1.256
0.518
0.011
-0.011
1.98
2.15
10.08
2.20
1.77
5.71
5.37
10.38
1.09
0.08
ppm
17b
N
O
O
2
N
O
O


7.270
7.263
7.196
4.224
3.893
3.710
3.672
3.650
3.644
3.540
3.334
2.950
0.006
-0.000
1.27
1.35
1.51
10.00
6.45
7.31
ppm
4
n
2
N
O
N
O