Electronic Supplementary Information for:

# Highly Efficient Stabilisation of *meta*-Ethynylpyridine Polymers with Amide Side Chains in Water by Coordination of Rare-Earth Metals

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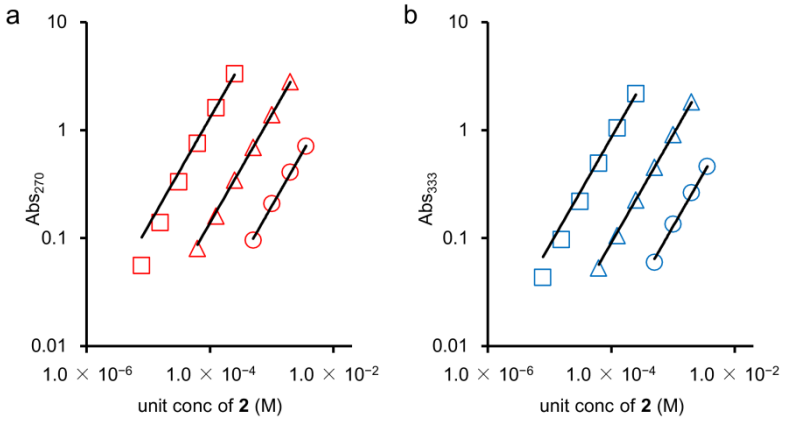


Fig. S1 The relationship between unit concentration and absorbance at (a) 270 nm and (b) 333 nm of **2** in MeCN. Conditions: **2** ($7.8 \times 10^{-6}$ to $3.6 \times 10^{-3}$ M, unit conc, $M_n = 1.2 \times 10^4$ g mol$^{-1}$, $M_w = 1.4 \times 10^4$ g mol$^{-1}$), MeCN, 25 ºC. square: path length = 10 mm; triangle: path length = 1 mm; circle: path length = 0.1 mm. Lines were fitted to the points.

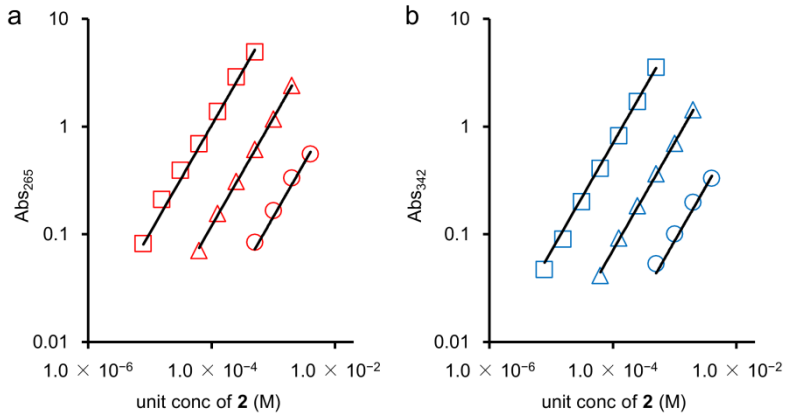


Fig. S2 The relationship between unit concentration and absorbance at (a) 265 nm and (b) 342 nm of **2** in $H_2O$. Conditions: **2** ($7.8 \times 10^{-6}$ to $4.0 \times 10^{-3}$ M, unit conc, $M_n = 1.2 \times 10^4$ g mol$^{-1}$, $M_w = 1.4 \times 10^4$ g mol$^{-1}$), $H_2O$, 25 ºC. square: path length = 10 mm; triangle: path length = 1 mm; circle: path length = 0.1 mm. Lines were fitted to points.

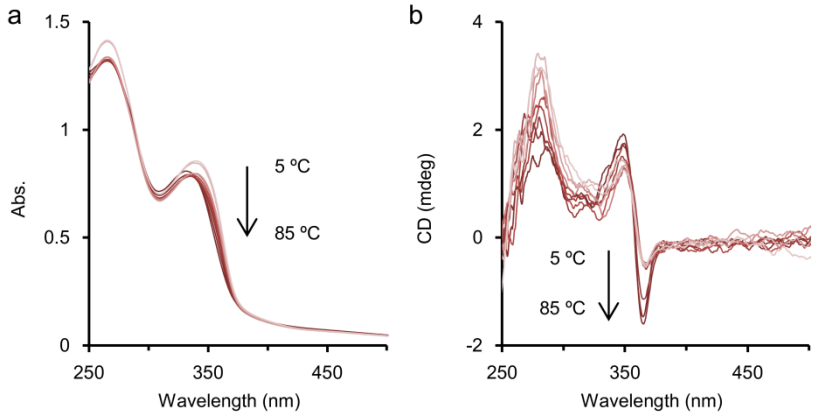


Fig. S3 Temperature dependence on UV-vis and CD spectra of **2** in $H_2O$. (a) UV-vis spectra at 5−85 ºC (b) CD spectra at 5−85 ºC. Conditions: [**2**] = $1.0 \times 10^{-3}$ M ($M_n$ = $1.2 \times 10^4$ g mol$^{-1}$, $M_w$ = $1.4 \times 10^4$ g mol$^{-1}$, unit conc), $H_2O$, path length = 1 mm.

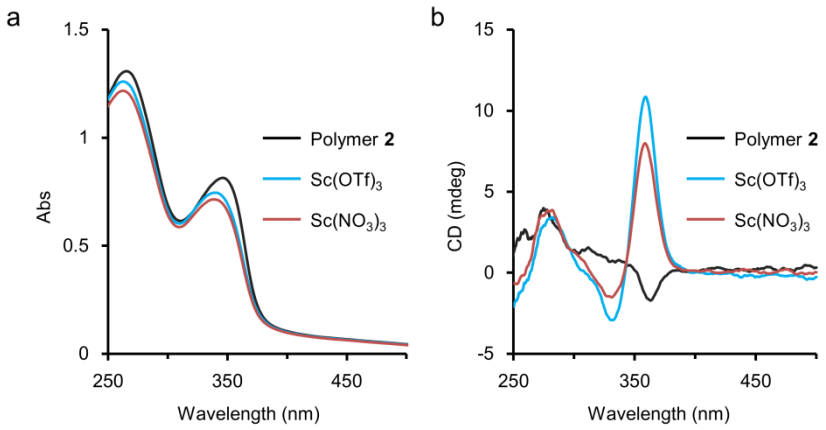


Fig. S4 Additive effects of $Sc(OTf)_2$ and $Sc(NO_3)_3$ in aqueous solutions on (a) UV-vis and (b) CD spectra. Conditions: [**2**] = $1.0 \times 10^{-3}$ M ($M_n = 5.6 \times 10^4$ g mol$^{-1}$, $M_w = 9.8 \times 10^4$ g mol$^{-1}$, unit conc), [metal salts] = $1.0 \times 10^{-3}$ M, $H_2O$, 25 °C, path length = 1 mm. These spectra were uniformly measured after 2 h from the preparation of the sample solutions (see main text).

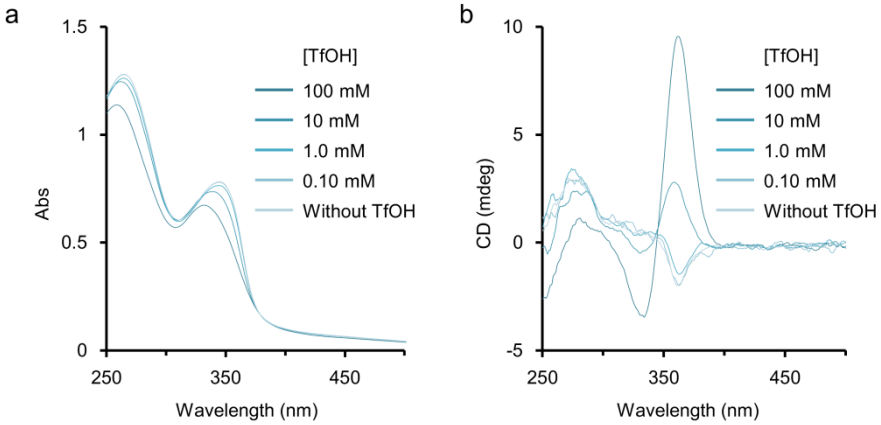


Fig. S5 Additive effects of TfOH in aqueous solutions on (a) UV-vis and (b) CD spectra. Conditions: [**2**] = $1.0 \times 10^{-3}$ M ($M_n = 5.6 \times 10^4$ g mol$^{-1}$, $M_w = 9.8 \times 10^4$ g mol$^{-1}$, unit conc), [TfOH] = $1.0 \times 10^{-4}$, $1.0 \times 10^{-3}$, $1.0 \times 10^{-2}$, or $1.0 \times 10^{-1}$ M, $H_2O$, 25 °C, path length = 1 mm. These spectra were measured after that the sample solutions reached the equilibrium state; 20 min, 100 min, 23 h, and 16 h after the addition of TfOH of $1.0 \times 10^{-4}$, $1.0 \times 10^{-3}$, $1.0 \times 10^{-2}$, and $1.0 \times 10^{-1}$ M, respectively.

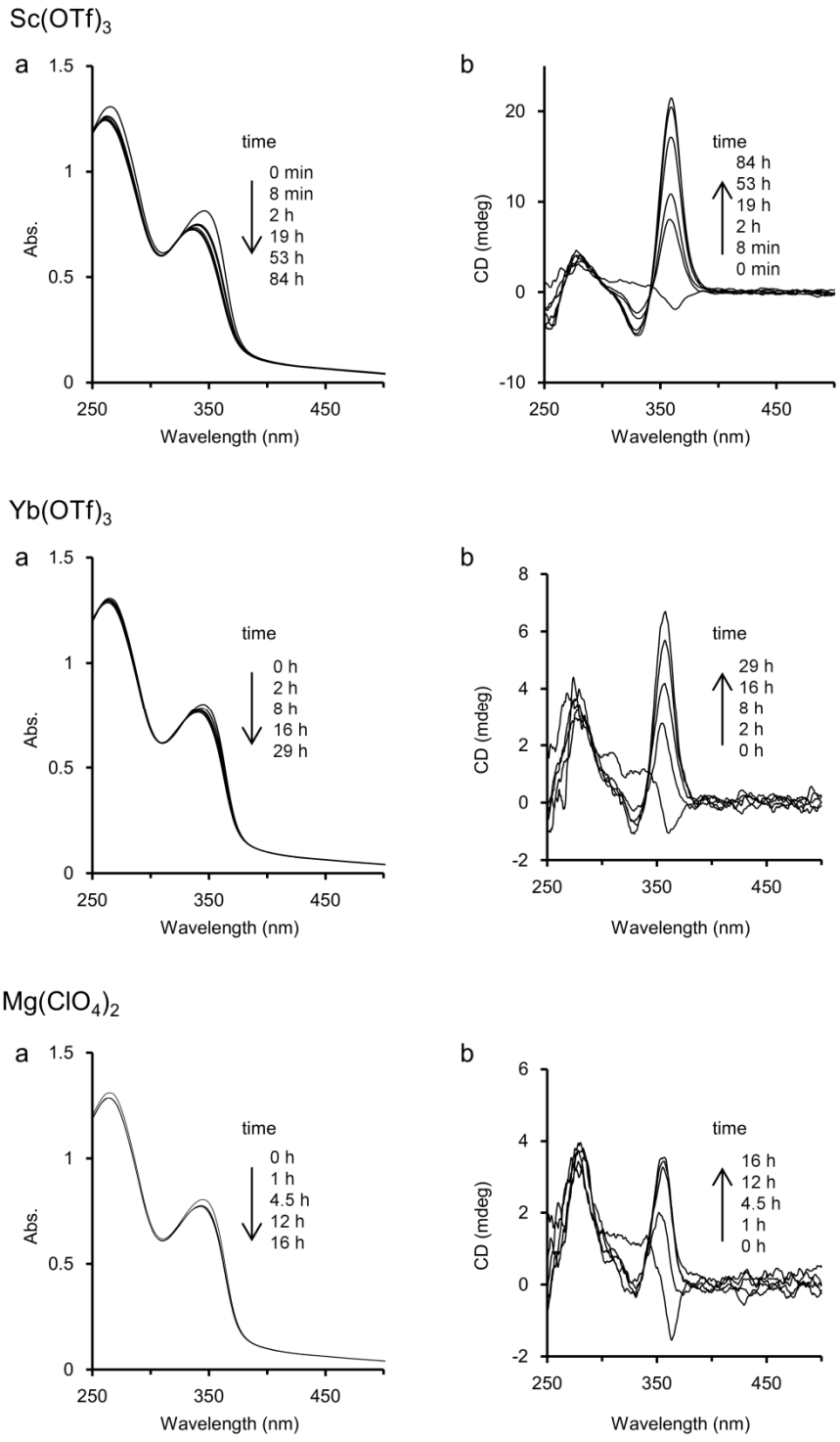


Fig. S6 Time-dependence on (a) UV-vis and (b) CD spectra of **2** treated with an equimolar amount of (top) $Sc(OTf)_3$, (middle) $Yb(OTf)_3$, and (bottom) $Mg(ClO_4)_2$ in $H_2O$. Conditions: [**2**] = $1.0 \times 10^{-3}$ M ($M_n$ = $5.6 \times 10^4$ g mol$^{-1}$, $M_w$ = $9.8 \times 10^4$ g mol$^{-1}$, unit conc), [metal salt] = $1.0 \times 10^{-3}$ M, $H_2O$, 25 °C, path length = 1 mm.

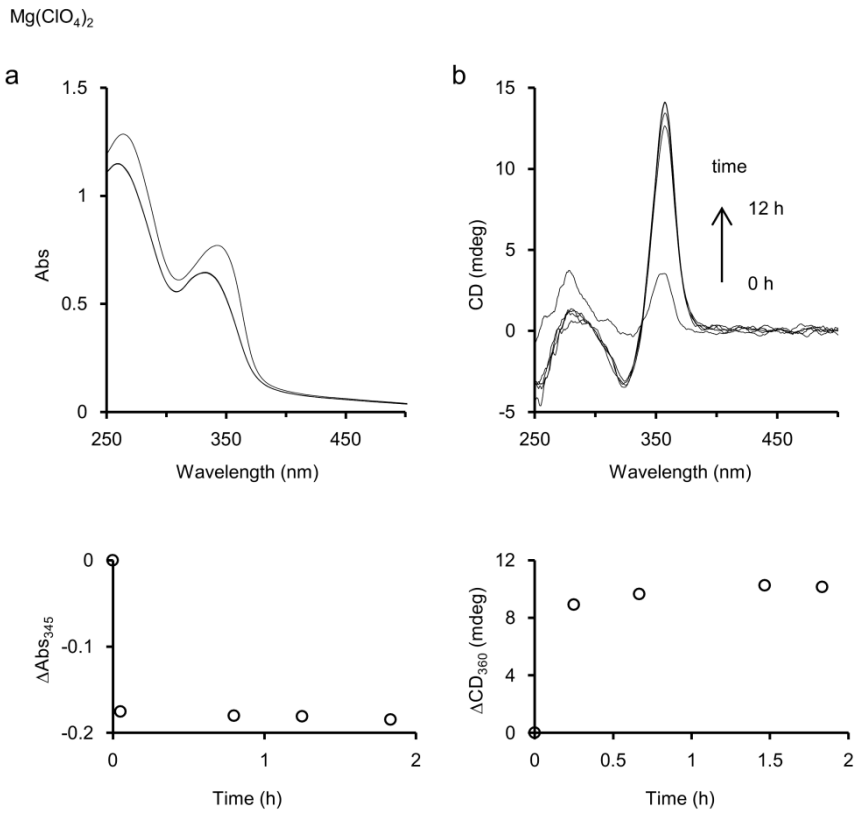


Fig. S7 Time-dependence on (left) UV-vis and (right) CD spectra of **2** treated with a large excess amount of $Mg(ClO_4)_2$ in $H_2O$. Conditions: [**2**] = $1.0 \times 10^{-3}$ M ($M_n = 5.6 \times 10^4$ g mol$^{-1}$, $M_w = 9.8 \times 10^4$ g mol$^{-1}$, unit conc), [$Mg(ClO_4)_2$] = 1.0 M, $H_2O$, 25 °C, path length = 1 mm. 0−12 h. Plots show the changes of absorbance at 345 nm and CD at 360 nm in initial two hours.

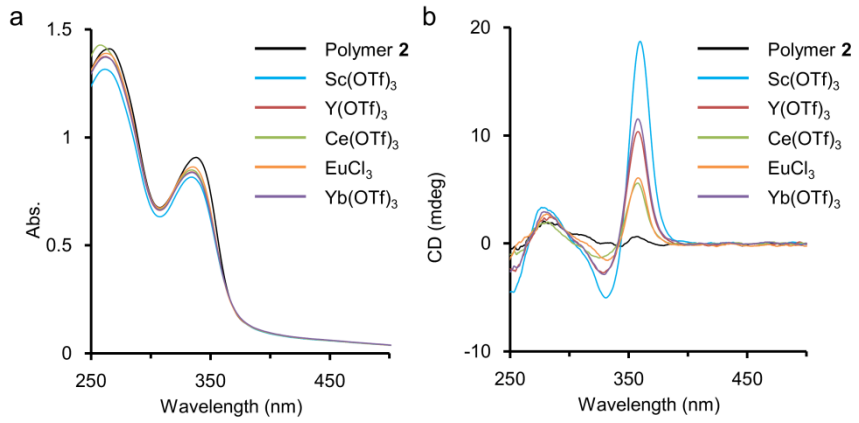


Fig. S8 Additive effects of rare-earth metal salts in aqueous EtOH solutions of **2** on (a) UV-vis and (b) CD spectra. Conditions: [**2**] = $1.0 \times 10^{-3}$ M ($M_n = 5.6 \times 10^4$ g mol$^{-1}$, $M_w = 9.8 \times 10^4$ g mol$^{-1}$, unit conc), [metal salts] = $1.0 \times 10^{-3}$ M, EtOH−$H_2O$ = 9:1, 25 ºC, path length = 1 mm.

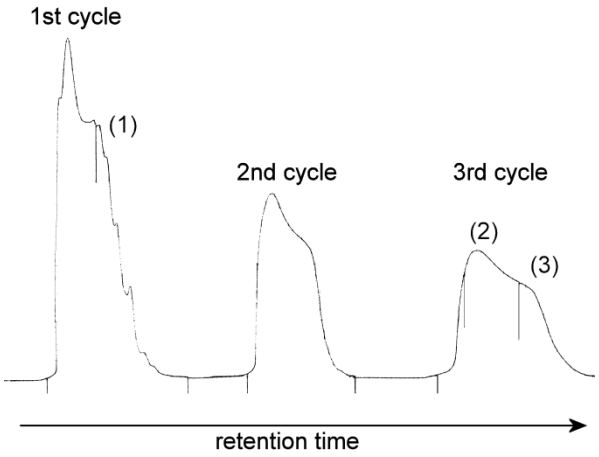


Figure S9. A GPC chart in fractionation of **2** by a preparative GPC (Shodex K-2002 and K-2002.5) in recycle mode using $CHCl_3$ as eluent.

Table S1. Molecular weights of fractions of the polymer **2** applied as a substrate in this report.[a]

| lot | $M_n$ (g mol$^{-1}$) | $M_w$ (g mol$^{-1}$) | $M_w$ / $M_n$ |
|---|---|---|---|
| 1 | $1.9 \times 10^4$ | $2.7 \times 10^4$ | 1.4 |
| 2 | $1.2 \times 10^4$ | $1.4 \times 10^4$ | 1.1 |
| 3 | $5.6 \times 10^4$ | $9.8 \times 10^4$ | 1.7 |
| 4 | $5.3 \times 10^4$ | $1.0 \times 10^5$ | 1.9 |

[a] Molecular weights versus polystyrene standards. Estimated by GPC using TOSOH TSKgel G2000HHR and TSKgel G3000HHR columns with a DMF solution of 0.1 M LiBr as eluent.

**Experimental Details of Preparation of 2**

**General**

$^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian GEMINI 300 spectrometer by using tetramethylsilane (TMS) as an internal reference. ESI-HRMS analyses were carried out on a JEOL JMS-T100LC mass spectrometer by using MeOH solutions of the analytes. IR, UV-vis, and CD spectra were measured by JASCO spectrometers FT/IR-460 plus, V-560, and J-720WI, respectively. Optical rotation was measured on a JASCO P-2100 polarimeter. All reactions were carried out under an argon atmosphere. 2,6-Dibromo-4-nitropyridine (**3**),[S1] 10-iodo-2,5,8-trioxadecane (**7**),[S2] and methyl 2,6-dibromoisonicotinate (**10**)[S3] were prepared according to the procedures in the literature.

**Heptaethylene glycol monomethyl ether**[S4]

This compound was prepared from tetraethylene glycol and triethylene glycol monomethyl ether monotosylate in a similar way to the preparation of hexaethylene glycol monomethyl ether.[S5]

To a mixture of tetraethylene glycol (193 g, 1.0 mol) and triethylene glycol monomethyl ether monotosylate[S6.] (60 g, 0.19 mmol) was added freshly ground KOH (33 g, 0.58 mol), and this mixture was stirred at 100 °C for 18 h. The resulting solution was allowed to reach to room temperature, diluted with $H_2O$ (50 mL), and extracted with $CH_2Cl_2$ (250 mL × 3). The combined organic layer was dried over $Na_2SO_4$ and concentrated by a rotary evaporator. The residual oil was purified by distillation under reduced pressure (1.0 mmHg, bp: 220−240 ºC) to give heptaethylene glycol monomethyl ether (37 g, 57%) as a colourless oil. $^{1}H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 3.37 (s, 3 H), 3.54−3.55 (m, 2 H), 3.62−3.73 (m, 26 H). The $^{1}H$ NMR spectrum was in accordance with that in the literature.[S4]

**2,6-Dibromo-4-(1,4,7,10,13,16,19,22-octaoxatricosanyl)pyridine (4)**

This compound was prepared from 2,6-dibromo-4-nitropyridine and heptaethylene glycol monomethyl ether in a similar way to the preparation of 2,6-dibromo-4-(1,4,7,10-tetraoxaundecyl)pyridine.[S7]

To a suspension of NaH (2.0 g, 84 mmol, 60% dispersion in oil was washed thoroughly with hexane (10 mL × 2) before use) in THF (250 mL) was added heptaethylene glycol monomethyl ether (24 g, 71 mmol) dropwise over a period of 1.5 h at 0 °C. Subsequently, 2,6-dibromo-4-nitropyridine (**3**) (20 g, 71 mmol) was added to the mixture in one portion at that temperature. The reaction mixture was stirred for 3.5 h at room temperature, and then quenched with saturated aqueous $NH_4Cl$ solution (10 mL). The volatile components were removed by a rotary evaporator, and the resulting mixture was diluted with $H_2O$ (250 mL) and extracted with $CH_2Cl_2$ (200 mL × 3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated by a rotary evaporator to

give **4** as a yellowish oil (39 g, 94% crude yield). This crude product was practically pure and could be used at the next step without further purification. If you wish, further purification was carried out by silica gel column chromatography (eluent; AcOEt) to afford analytically pure **4** as a yellowish oil. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.38 (s, 3 H), 3.53−3.56 (m, 2 H), 3.63−3.71 (m, 22 H), 3.83−3.86 (m, 2 H), 4.18 (t, $J$ = 4.5 Hz, 2 H), 7.02 (s, 2 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 59.1, 68.5, 69.1, 70.5, 70.56, 70.62, 71.0, 71.9, 113.9, 140.9, 166.7; IR (neat) $\nu$ 2875, 1574, 1536 cm$^{-1}$; ESI-HRMS $m/z$ calcd for $C_{20}H_{33}{}^{79}Br^{81}BrNNaO_8$ (M + Na$^+$): 598.0452; found: 598.0450.

**2,6-Diiodo-4-(1,4,7,10,13,16,19,22-octaoxatricosanyl)pyridine (5)**

This diiodide was obtained by copper-catalyzed halogen exchange reaction from **4** according to the procedure reported by Buchwald et al.[S8]

A mixture of 1,3-diaminopropane (0.17 g, 2.3 mmol), CuI (0.22 g, 1.2 mmol), and NaI (8.8 g, 59 mmol) in diglyme (7.0 mL) was stirred for 20 min at room temperature. An *o*-xylene solution (18 mL) of dibromide **4** (6.7 g, 12 mmol) was added to the mixture, which was then stirred for 10 h at 110 ºC. The resulting suspension was allowed to reach to room temperature, diluted with $H_2O$ (150 mL), and extracted with AcOEt (100 mL × 3). The combined organic layer was washed with $H_2O$ and brine subsequently, dried over $Na_2SO_4$, and concentrated by a rotary evaporator. The residue was purified by silica gel column chromatography (eluent; hexane−AcOEt = 2:1, then $CH_2Cl_2$−MeOH = 30:1) to yield **5** (6.5 g, 83%) as a yellowish oil. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 3.38 (s, 3 H), 3.53−3.56 (m, 2 H), 3.63−3.67 (m, 22 H), 3.81−3.84 (m, 2 H), 4.13 (t, $J$ = 4.2 Hz, 2 H), 7.26 (s, 2 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 59.1, 68.2, 69.1, 70.5, 70.6, 71.0, 71.9, 115.6, 121.2, 164.5; IR (neat) $\nu$ 2873, 1560, 1521 cm$^{-1}$; ESI-HRMS $m/z$ calcd for $C_{20}H_{33}I_2NNaO_8$ (M + Na$^+$): 692.0193; found: 692.0173

***N*-Boc-(*S*)-2,5,8,11-tetraoxatetradecan-13-amine (8)**

To a suspension of NaH (0.98 g, 25 mmol, 60% dispersion in oil was washed thoroughly with hexane (10 mL × 2) before use) in THF (82 mL) was added *N*-Boc-L-alaninol **6** (2.9 g, 16 mmol) at 0 °C, and the mixture was stirred for 10 min at 0 ºC. Then, 10-iodo-2,5,8-trioxadecane (**7**) (9.0 g, 33 mmol) was added to this mixture, which was further stirred for 16.5 h at room temperature. During this stirring, additional amounts of NaH and **7** were provided into the reaction mixture to improve the conversion. NaH was added at the points of 14 h (0.59 g, 15 mmol) and 15 h (1.2 g, 30 mmol) without washing out mineral oil. Iodide **7** was added at the point of 14 h (4.5 g, 16 mmol). The resulting mixture was carefully quenched with $H_2O$ (5.0 mL), diluted with $H_2O$ (200 mL), and extracted with hexane−AcOEt (1:1) (200 mL × 3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated by a rotary evaporator. The resulting residue was purified by silica gel column chromatography (eluent; hexane−AcOEt = 1:1 to 1:2) to yield **8** (3.1 g,

60%) as a colourless oil. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.16 (d, $J$ = 6.6 Hz, 3 H), 1.44 (s, 9 H), 3.38 (s, 3 H), 3.43 (d, $J$ = 4.8 Hz, 2 H), 3.54−3.56 (m, 2 H), 3.60−3.67 (m, 10 H), 3.80 (m, 1 H), 4.82 (br s, 1 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 18.1, 28.6, 59.1, 70.6, 70.7, 72.0, 74.5, 79.1, 155.3; IR (neat) $\nu$ 3342, 2977, 2925, 2875, 1712, 1523 cm$^{-1}$; ESI-HRMS $m/z$ calcd for $C_{15}H_{31}NNaO_6$ (M + $Na^+$): 344.2049; found: 344.2050; $[\alpha]_D^{25}$ −16.0 ($c$ = 1.0, EtOH).

**(*S*)-2,5,8,11-Tetraoxatetradecan-13-amine (9)**

To an AcOEt (17 mL) solution of **8** (1.1 g, 3.5 mmol) was added conc HCl (2.9 mL), and the mixture was stirred for 15 min at room temperature. The reaction mixture was concentrated by a rotary evaporator, and the residual oil was dissolved in $CH_2Cl_2$ (34 mL). This solution was treated with $K_2CO_3$ (7.6 g, 55 mmol), and the resulting insoluble materials were filtered off. The filtrate was concentrated by a rotary evaporator to yield **9** (0.72 g, 94% crude yield) as a yellowish oil. This crude product was used at the next step without further purification. Further purification could be carried out by bulb-to-bulb distillation (2.5 mmHg, 110−120 ºC) to afford analytically pure **9** as a colourless oil. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.03 (d, $J$ = 6.0 Hz, 3 H), 1.53 (br s, 2 H), 3.09−3.19 (m, 2 H), 3.36−3.42 (m, 4 H), 3.53−3.56 (m, 2 H), 3.59−3.68 (m, 10 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 19.8, 46.4, 59.0, 70.46, 70.53, 70.54, 70.61, 70.64, 78.3; ESI-HRMS $m/z$ calcd for $C_{10}H_{24}NO_4$ (M + $H^+$): 222.1705; found: 222.1700; $[\alpha]_D^{24}$ +13.7 ($c$ = 1.1, EtOH). The $^1$H NMR spectrum was identical to that reported in the literature.[S9]

**2,6-Dibromoisonicotinic acid (11)**[S3]

To a solution of methyl 2,6-dibromoisonicotinate (**10**) (4.4 g, 15 mmol) in THF (25 mL) and $H_2O$ (25 mL) was added $LiOH \cdot H_2O$ (0.76 g, 18 mmol), and the mixture was stirred for 15 min at room temperature. The resulting mixture was cooled to 0 ºC and neutralised by the addition of conc HCl (1.5 mL). The volatile components were removed by a rotary evaporator, and the resulting mixture was extracted with AcOEt (30 mL × 3). The combined organic layer was washed with brine, dried over $Na_2SO_4$, and concentrated by a rotary evaporator to yield **11** (4.0 g, 95%) as a colourless solid. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 8.05 (s, 2 H), 8.35 (br s, 1 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 126.9, 140.3, 141.7, 166.9. The $^1$H NMR spectrum was identical to that reported in the literature. [S3]

***N*-((*S*)-1-Methyl-3,6,9,12-tetraoxatridecyl)-2,6-dibromoisonicotinamide (12)**

To a $CH_2Cl_2$ (15 mL) solution of **11** (0.86 g, 3.1 mmol) and chiral amine **9** (0.72 g, 3.2 mmol) were added $i$Pr$_2$NEt (0.41 g, 3.2 mmol), DCC (0.83 g, 4.0 mmol), and $HOBt \cdot H_2O$ (0.67 g, 4.4 mmol) at −15 ºC. This mixture was stirred for 20 min at that temperature, additionally for 1 h at 0 ºC, and for 2 h at room temperature. The resulting reaction mixture was diluted with $CH_2Cl_2$ (15 mL), and filtered through a celite bed. The filtrate was concentrated by a rotary evaporator, and the residual oil was

dissolved into toluene (40 mL). The toluene solution was washed with a saturated aqueous $NaHCO_3$ solution (20 mL × 1 and 5 mL × 1) and brine (10 mL) subsequently, dried over $Na_2SO_4$, and concentrated by a rotary evaporator. The residue was subjected to silica gel column chromatography (eluent; hexane−AcOEt = 2:1 to 1:2) to yield **12** (1.2 g, 78%) as a colourless oil. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.29 (d, $J$ = 6.6 Hz, 3 H), 3.30 (s, 3 H), 3.48−3.51 (m, 2 H), 3.55−3.70 (m, 12 H), 4.27−4.35 (m, 1 H), 7.37 (d, $J$ = 7.2 Hz, 1 H), 7.90 (s, 2 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 17.2, 46.5, 58.7, 70.3, 70.4, 70.5, 70.6, 71.7, 73.6, 125.0, 141.0, 146.3, 162.0; IR (neat) $\nu$ 3319, 2875, 1667, 1528 cm$^{-1}$; ESI-HRMS $m/z$ calcd for $C_{16}H_{24}{}^{79}Br^{81}BrN_2NaO_5$ (M + $Na^+$): 506.9930; found: 506.9942.

***N*-((*S*)-1-Methyl-3,6,9,12-tetraoxatridecyl)-2,6-bis(trimethylsilylethynyl)isonicotinamide (13)**

A mixture of **12** (0.70 g, 1.4 mmol), $PdCl_2(PPh_3)_2$ (30 mg, 43 μmol), and CuI (4.1 mg, 22 μmol) in $i$Pr$_2$NH (4.8 mL) and THF (9.6 mL) was stirred for 5 min at room temperature. Trimethylsilylacetylene (TMSA, 0.14 g, 1.4 mmol) was added to this mixture, which was then stirred for 1 h at room temperature. Subsequently, an additional amount of TMSA (0.99 g, 10 mmol) was added to the mixture, which was additionally stirred for 1.5 h under reflux. The resulting mixture was allowed to reach to room temperature, diluted with $Et_2O$ (14 mL), and filtered through a Florisil bed. The filtrate was concentrated by a rotary evaporator, and the residual oil was purified by silica gel column chromatography (eluent; hexane−AcOEt = 5:1 to 2:1) to yield **13** (0.71 g, 96%) as a yellowish oil. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 0.26 (s, 18 H), 1.29 (d, $J$ = 6.9 Hz, 3 H), 3.30 (s, 3 H), 3.48−3.50 (m, 2 H), 3.58−3.67 (m, 12 H), 4.31 (m, 1 H), 7.04 (d, $J$ = 7.2 Hz, 1 H), 7.76 (s, 2 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ −0.21, 17.5, 46.3, 58.9, 70.5, 70.6, 70.8, 71.9, 73.9, 77.2, 96.4, 102.7, 124.2, 142.6, 143.8, 163.6; IR (neat) $\nu$ 3318, 2959, 2897, 2873, 1669, 1539 cm$^{-1}$; ESI-HRMS $m/z$ calcd for $C_{26}H_{42}N_2NaO_5Si_2$ (M + $Na^+$): 541.2530; found: 541.2543.

***N*-((*S*)-1-Methyl-3,6,9,12-tetraoxatridecyl)-2,6-diethynylisonicotinamide (14)**

To a solution of **13** (0.71 g, 1.4 mmol) in $CH_2Cl_2$ (12 mL) and MeOH (1.2 mL) was added $K_2CO_3$ (0.57 g, 4.1 mmol), and the mixture was stirred for 5 h at room temperature. The resulting mixture was diluted with $CH_2Cl_2$ (12 mL) and filtered through a celite bed. The filtrate was concentrated by a rotary evaporator, and the residual oil was purified by silica gel column chromatography (eluent; hexane−AcOEt = 5:1 to AcOEt) to yield **14** as a yellowish oil (0.48 g, 93%). $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.30 (d, $J$ = 6.9 Hz, 3 H), 3.22 (s, 2 H), 3.31 (s, 3 H), 3.47−3.67 (m, 14 H), 4.30−4.37 (m, 1 H), 7.28 (d, $J$ = 7.2 Hz, 1 H), 7.86 (s, 2 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 17.4, 46.4, 58.9, 70.4, 70.6, 70.7, 71.8, 73.7, 78.5, 81.8, 124.7, 142.9, 143.1, 163.3; IR (neat) $\nu$ 3502, 3229, 2972, 2877, 2109, 1656, 1543 cm$^{-1}$; ESI-HRMS $m/z$ calcd for $C_{20}H_{26}N_2NaO_5$ (M + $Na^+$): 397.1739; found: 397.1739.

**Trimeric block 15**

To **14** (0.28 g, 0.75 mmol) and **5** (3.0 g, 4.5 mmol) was added a mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ (16 mg, 0.015 mmol), $PPh_3$ (16 mg, 0.060 mmol), and CuI (2.9 mg, 0.015 mmol) in $i$Pr$_2$NEt (6.0 mL) and THF (12 mL). This reaction mixture was stirred for 23 h at 30 ºC, diluted with AcOEt (20 mL), and filtered through a celite bed. The filtrate was concentrated by a rotary evaporator, and resulting residual oil was purified by silica gel column chromatography (eluent; hexane−AcOEt = 5:1 to AcOEt then $CH_2Cl_2$−MeOH = 100:1 to 20:1) to give recovered **5** (2.3 g, 76% recovery) and **15** (0.73 g, 67%) as a yellowish oil. $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$ 1.32 (d, $J$ = 6.9 Hz, 3 H), 3.30 (s, 3 H), 3.37 (s, 6 H), 3.49−3.73 (m, 62 H), 3.85−3.88 (m, 4 H), 4.16−4.19 (m, 4 H), 4.32−4.39 (m, 1 H), 7.06 (d, $J$ = 7.2, 1 H), 7.13 (d, $J$ = 2.1 Hz, 2 H), 7.31 (d, $J$ = 2.1 Hz, 2 H), 8.00 (s, 2 H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 17.5, 46.4, 58.9, 59.1, 68.2, 69.1, 70.46, 70.54, 70.6, 70.7, 70.8, 71.0, 71.9, 72.0, 73.8, 87.5, 87.8, 114.7, 117.7, 121.5, 125.2, 142.9, 143.2, 143.3, 163.0, 164.6; IR (neat) $\nu$ 3521, 2874, 1662, 1575, 1532 cm$^{-1}$; ESI-HRMS $m/z$ calcd for $C_{60}H_{90}I_2N_4NaO_{21}$ (M + $Na^+$): 1479.4065; found: 1479.4085.

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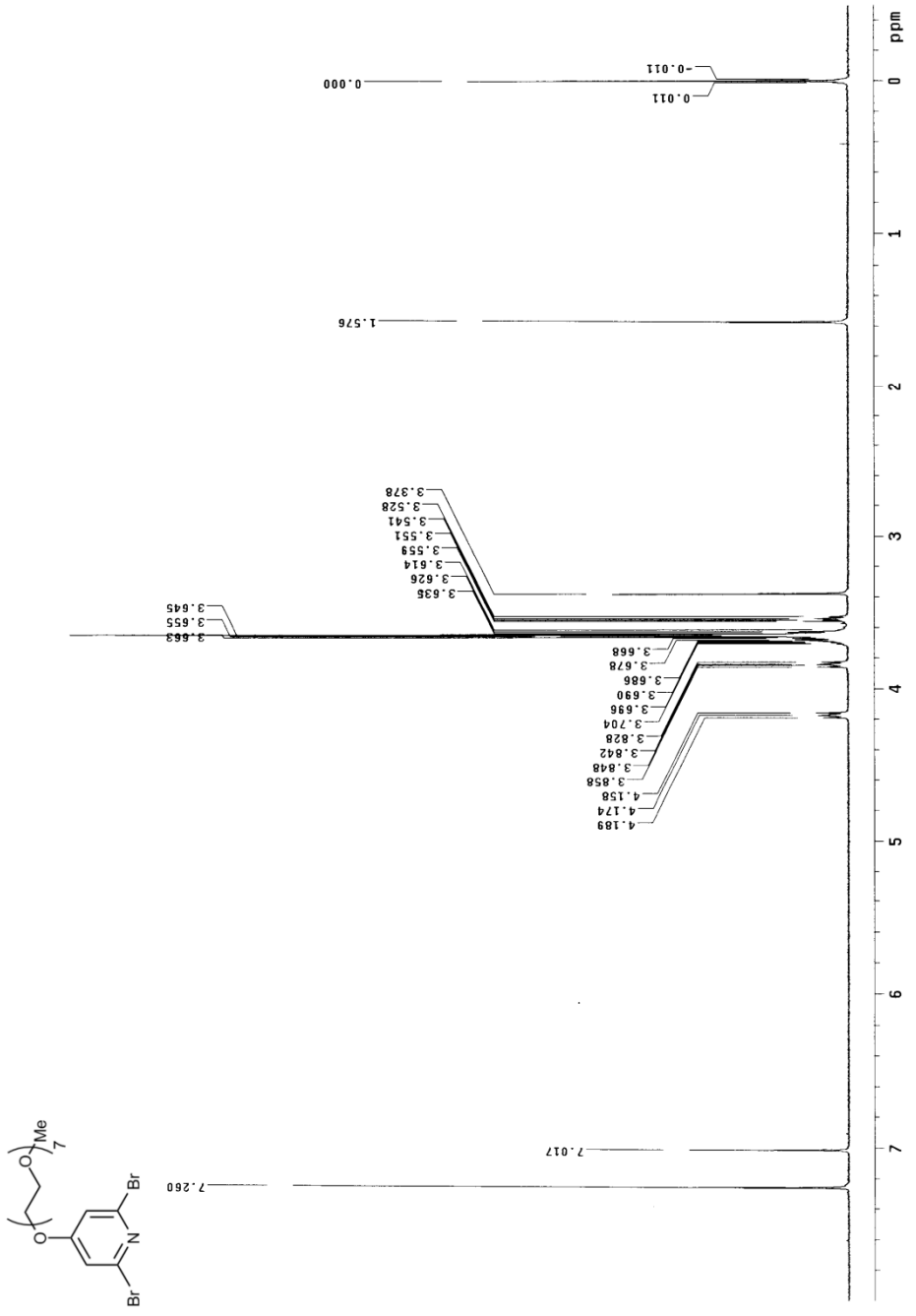
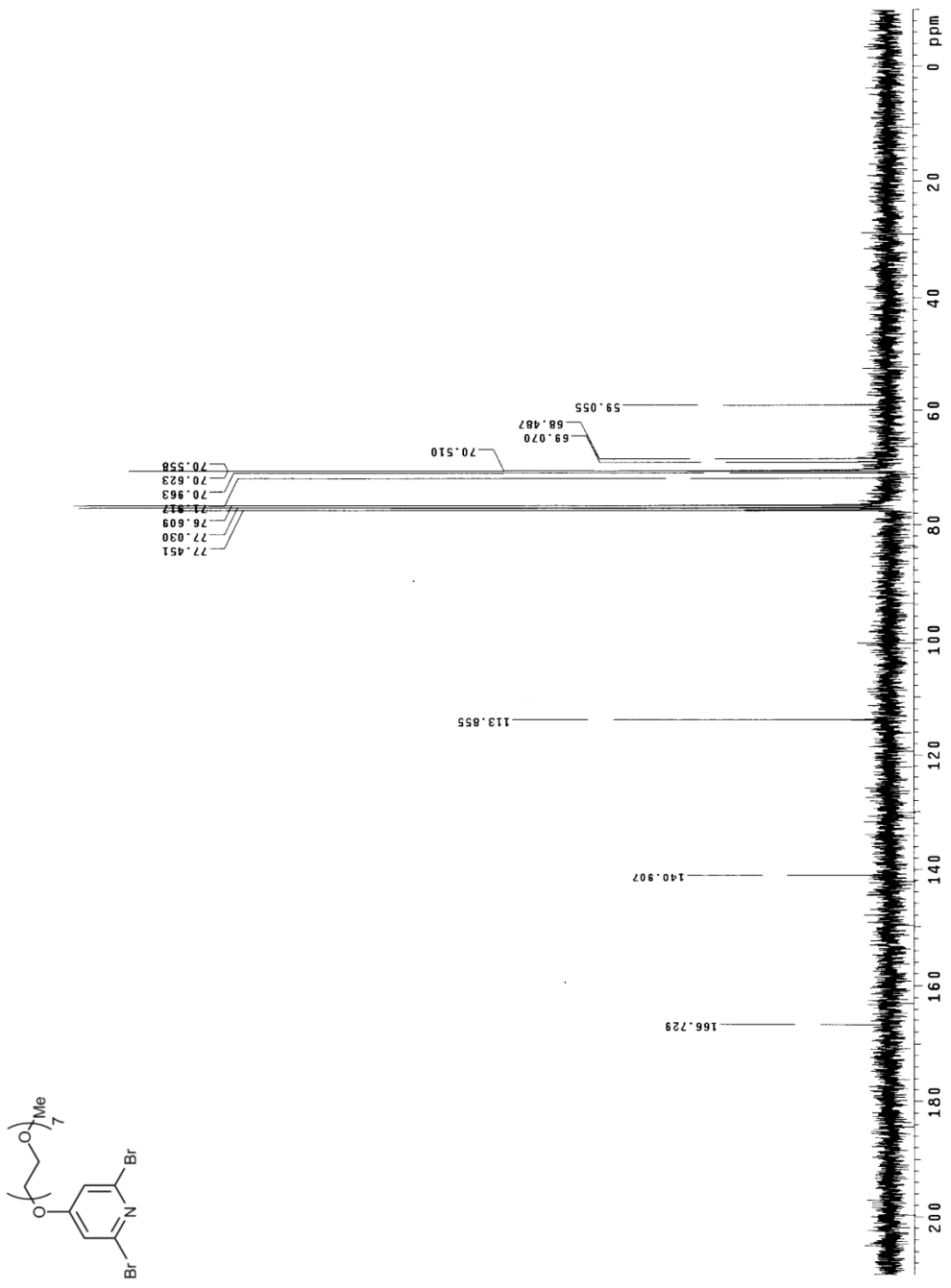
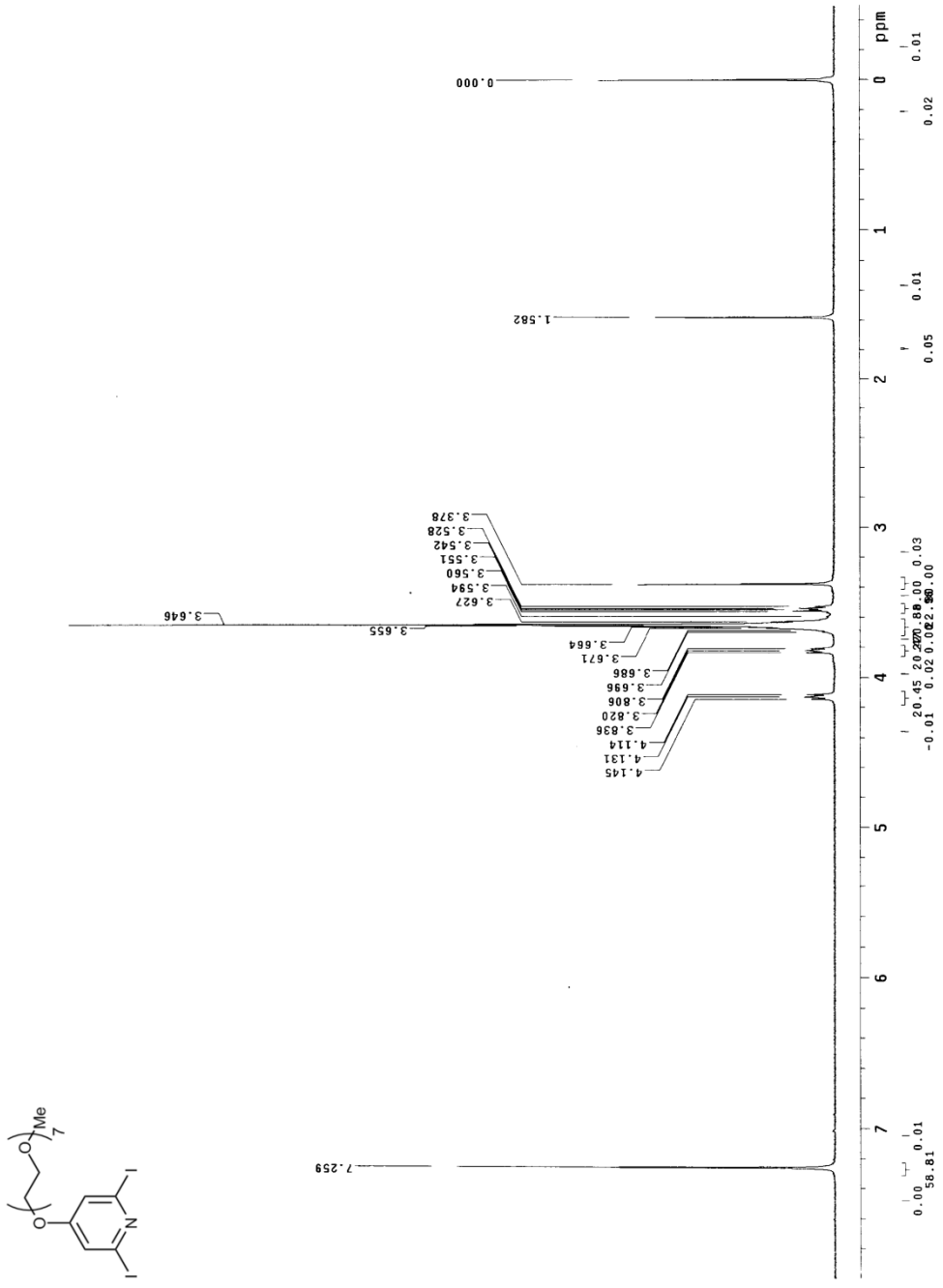
$^1$H NMR spectrum of **4**



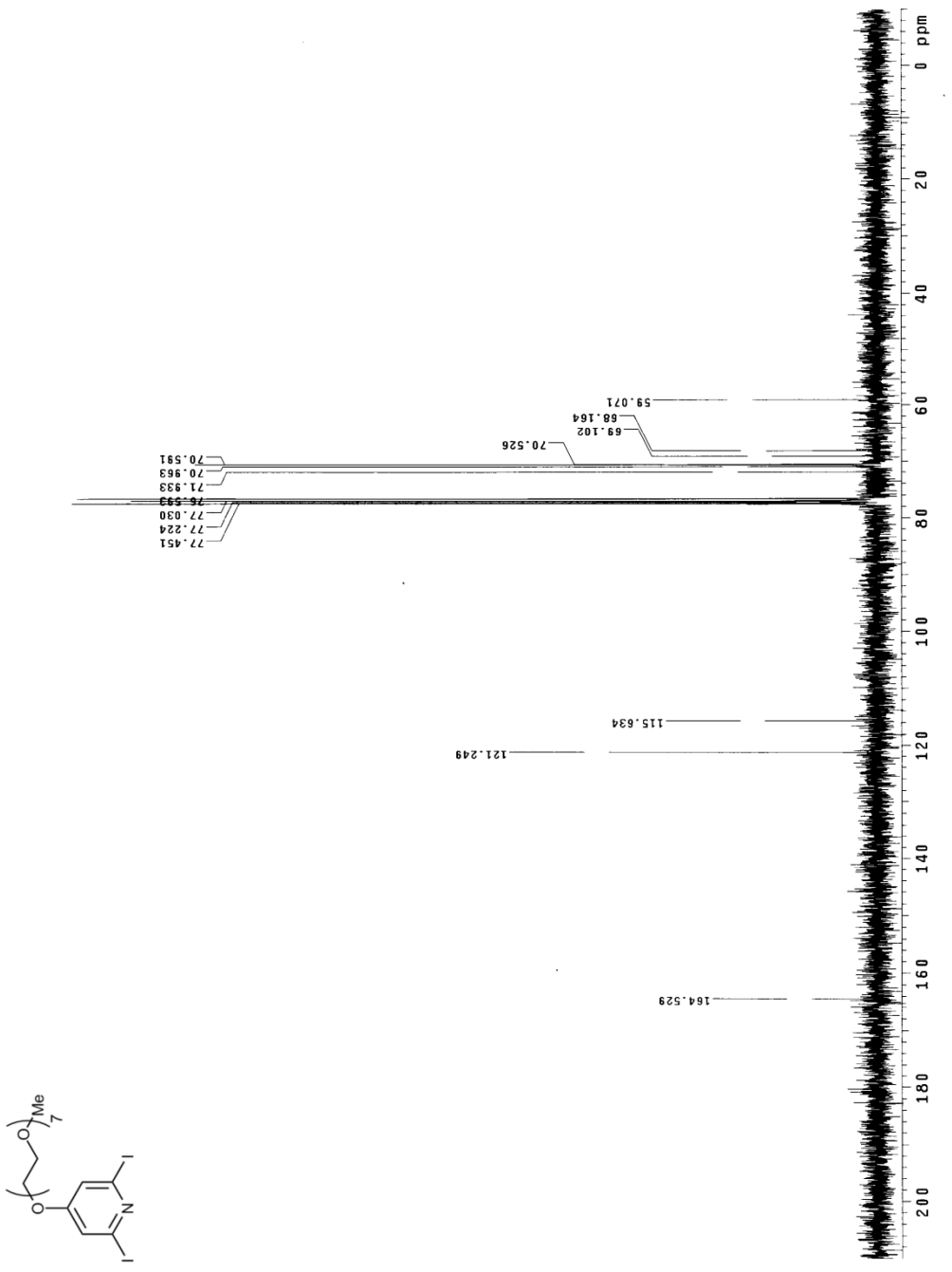
$^{13}$C NMR spectrum of **4**



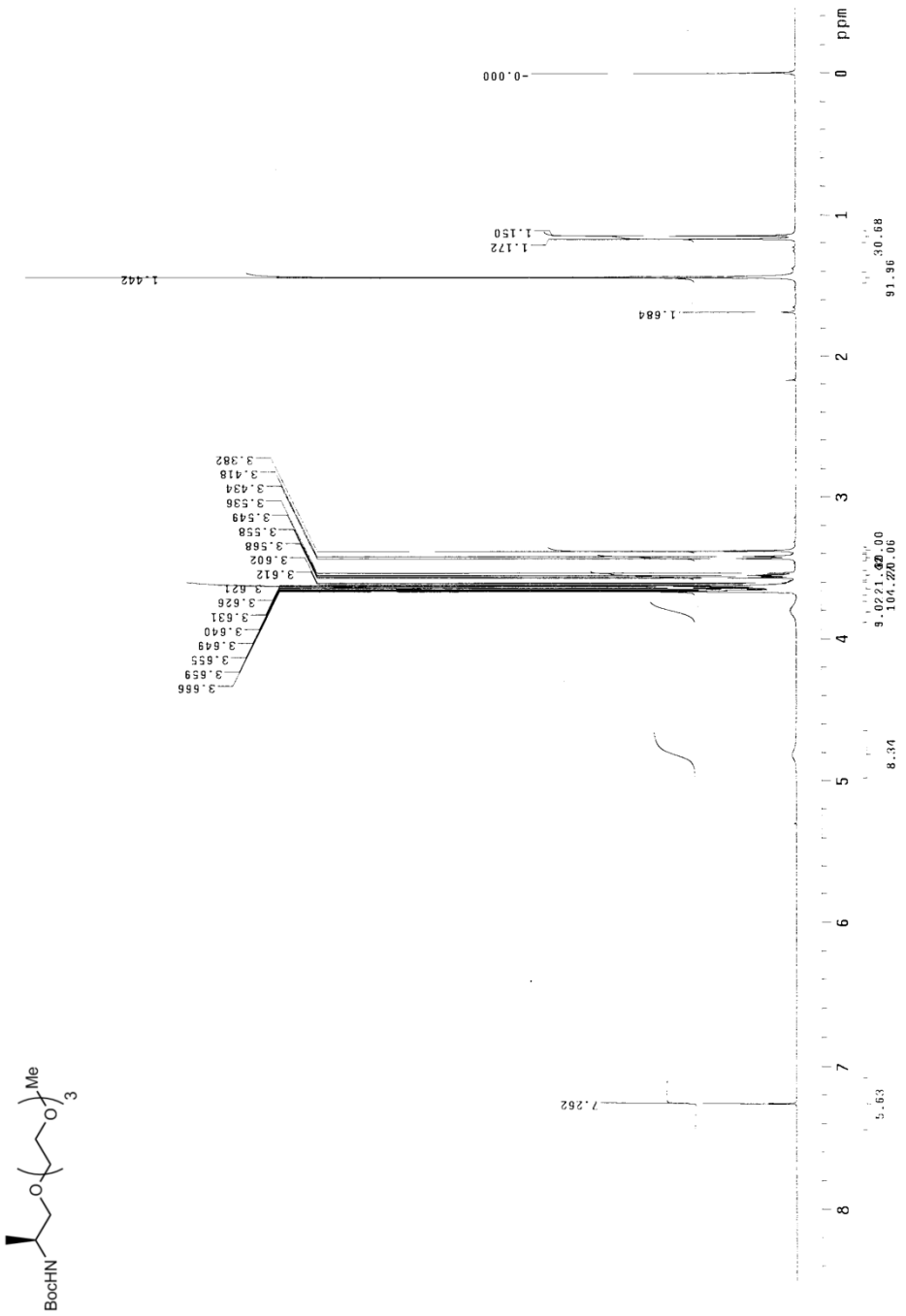
$^{1}$H NMR spectrum of **5**



$^{13}$C NMR spectrum of **5**



$^1$H NMR spectrum of **8**



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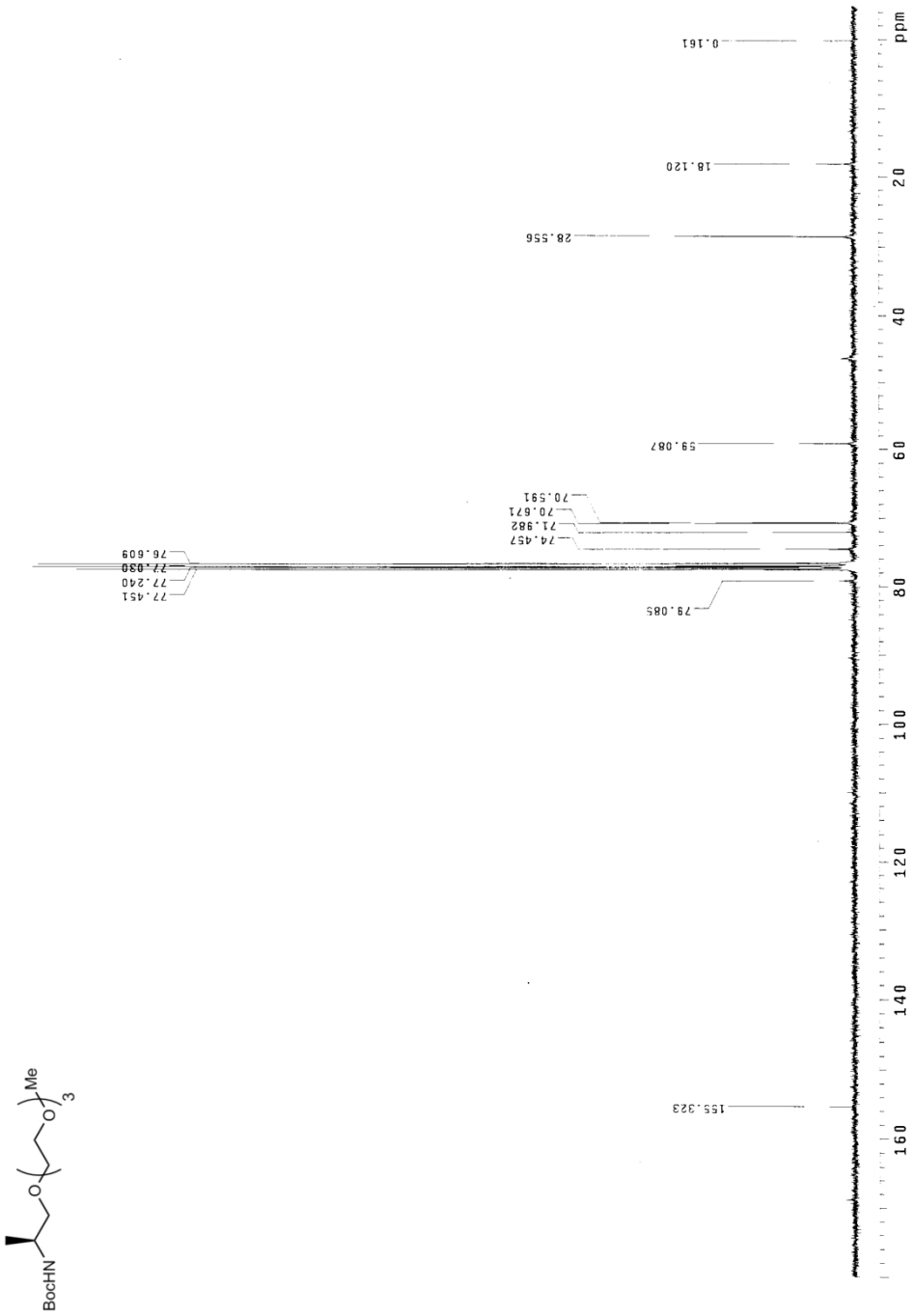
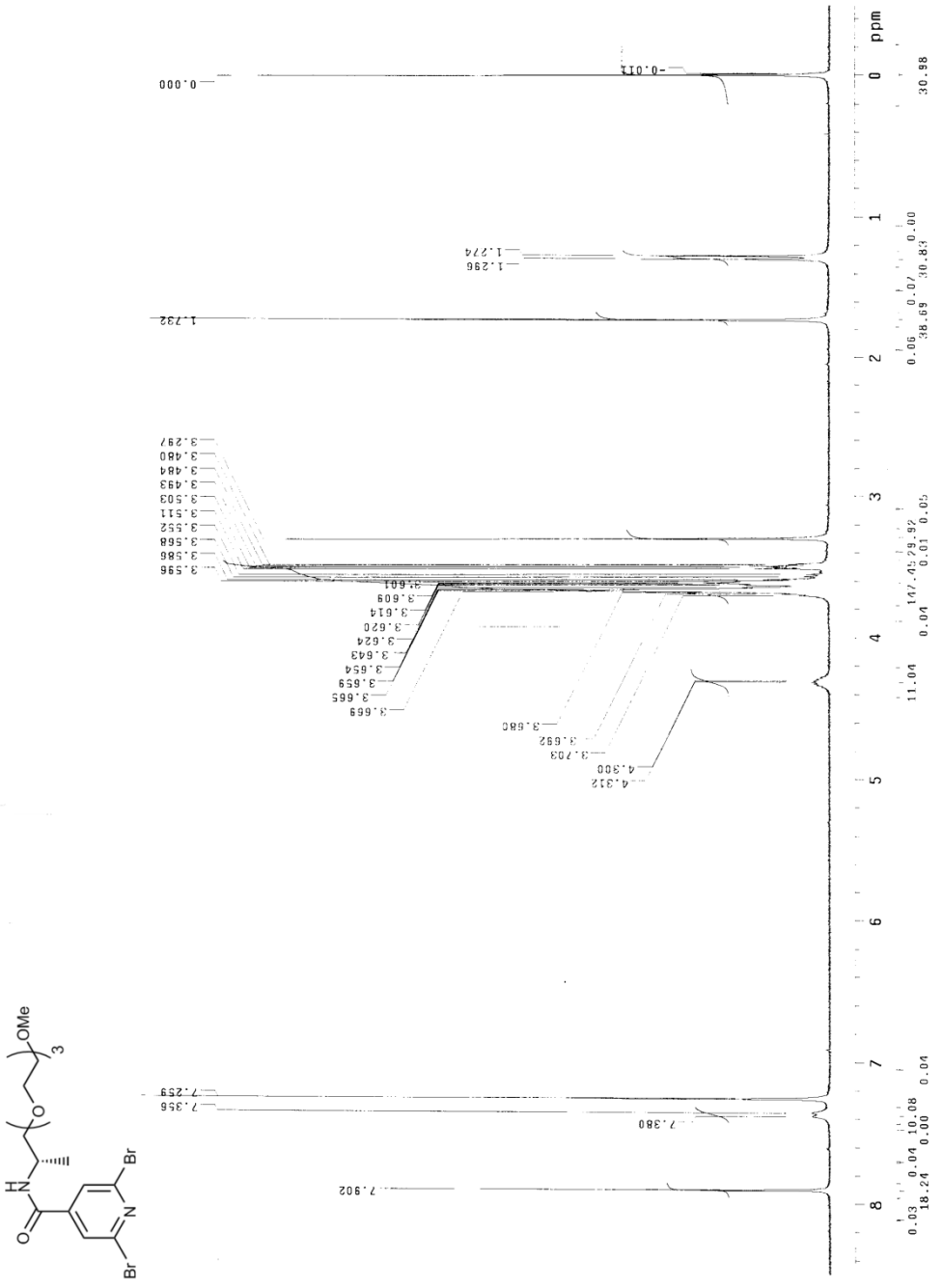


$^1$H NMR spectrum of **12**



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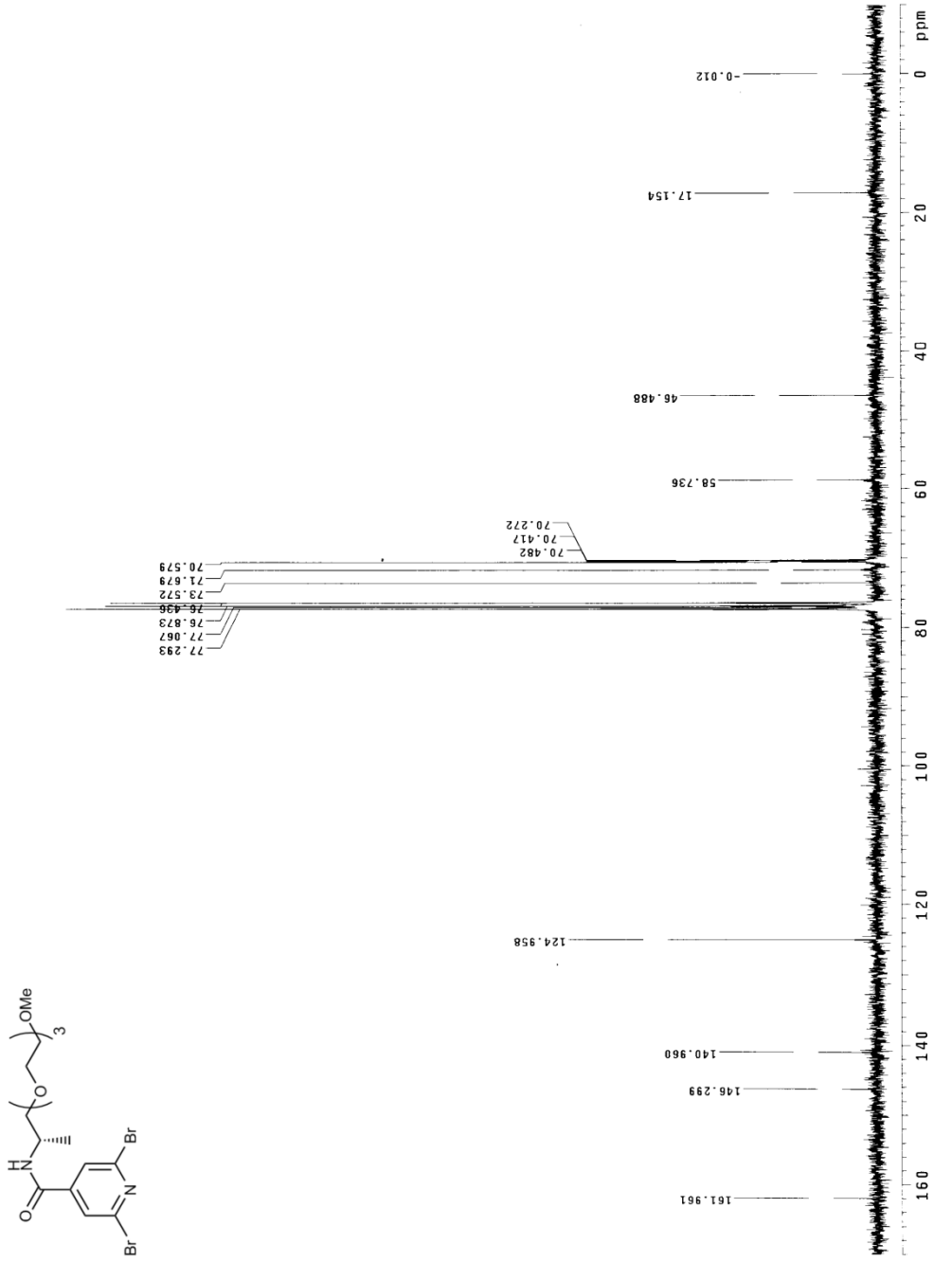

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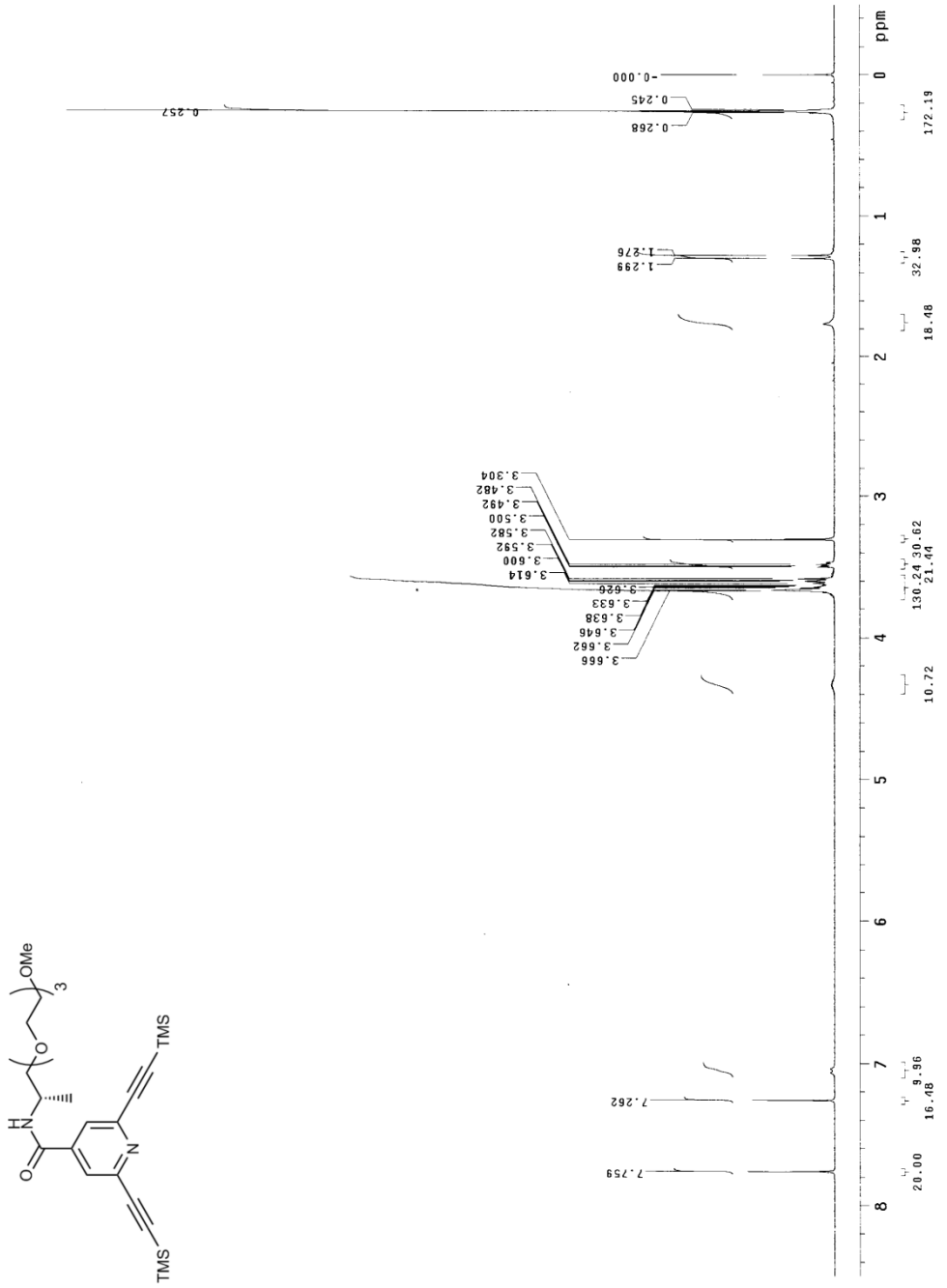

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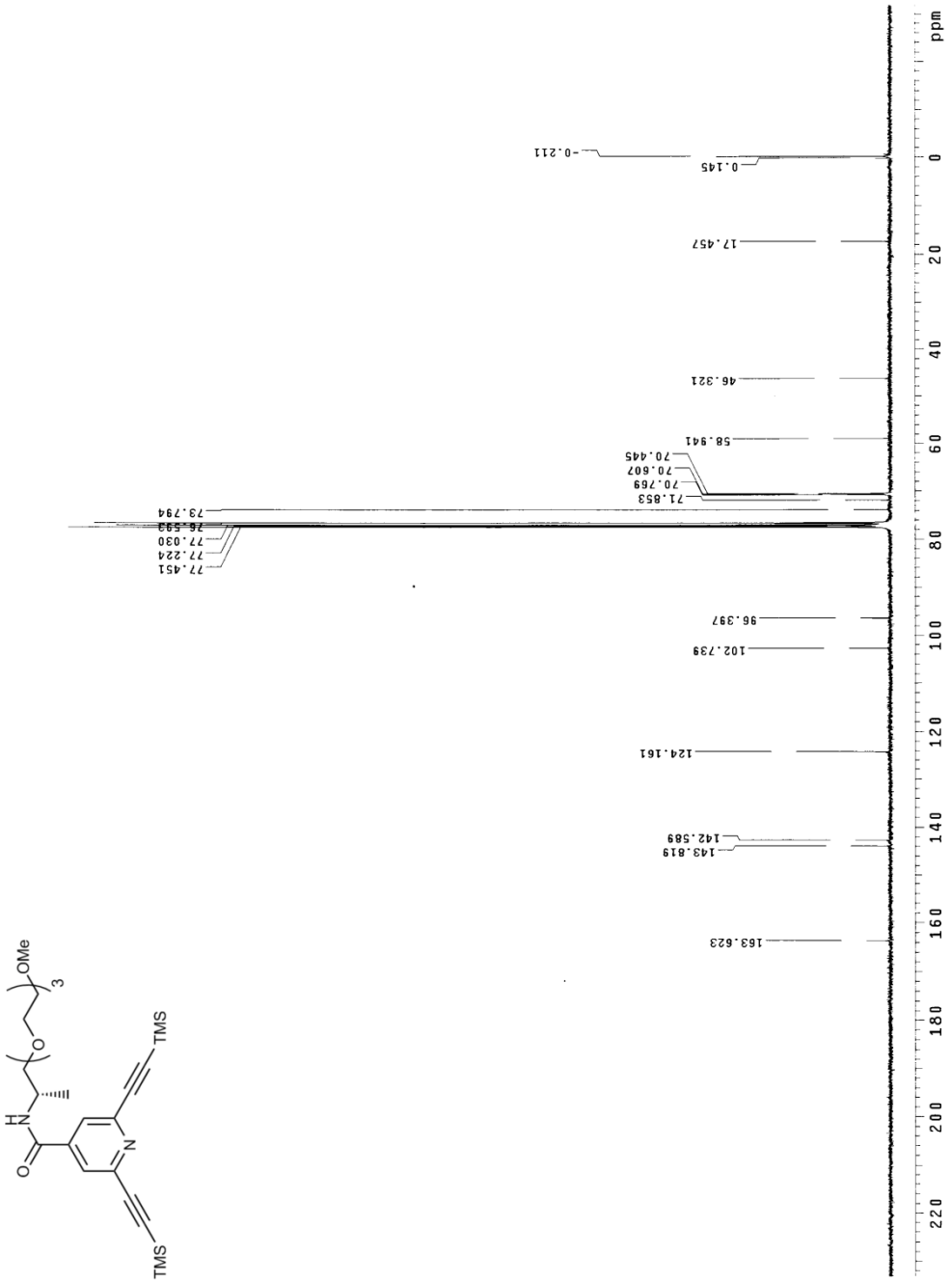

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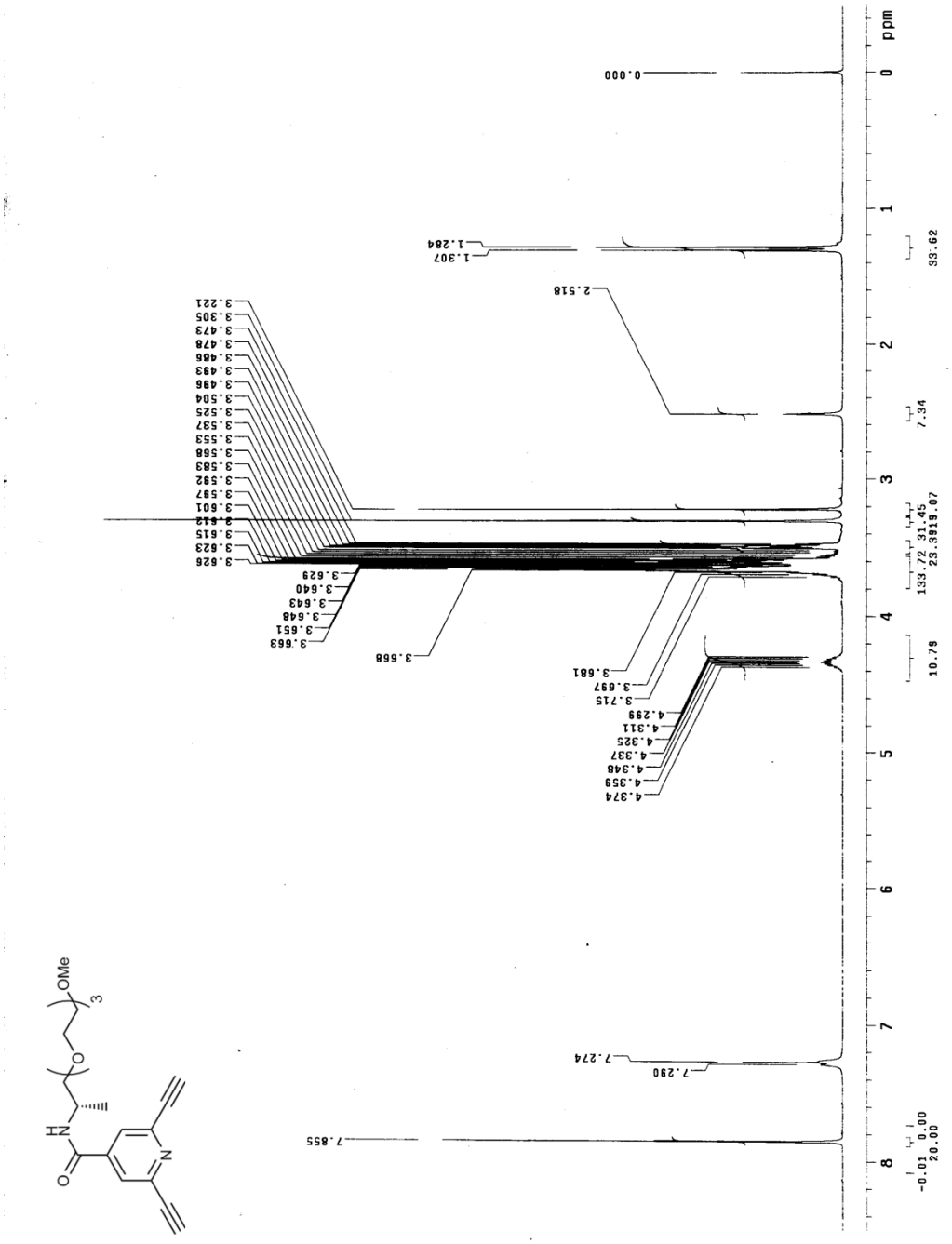

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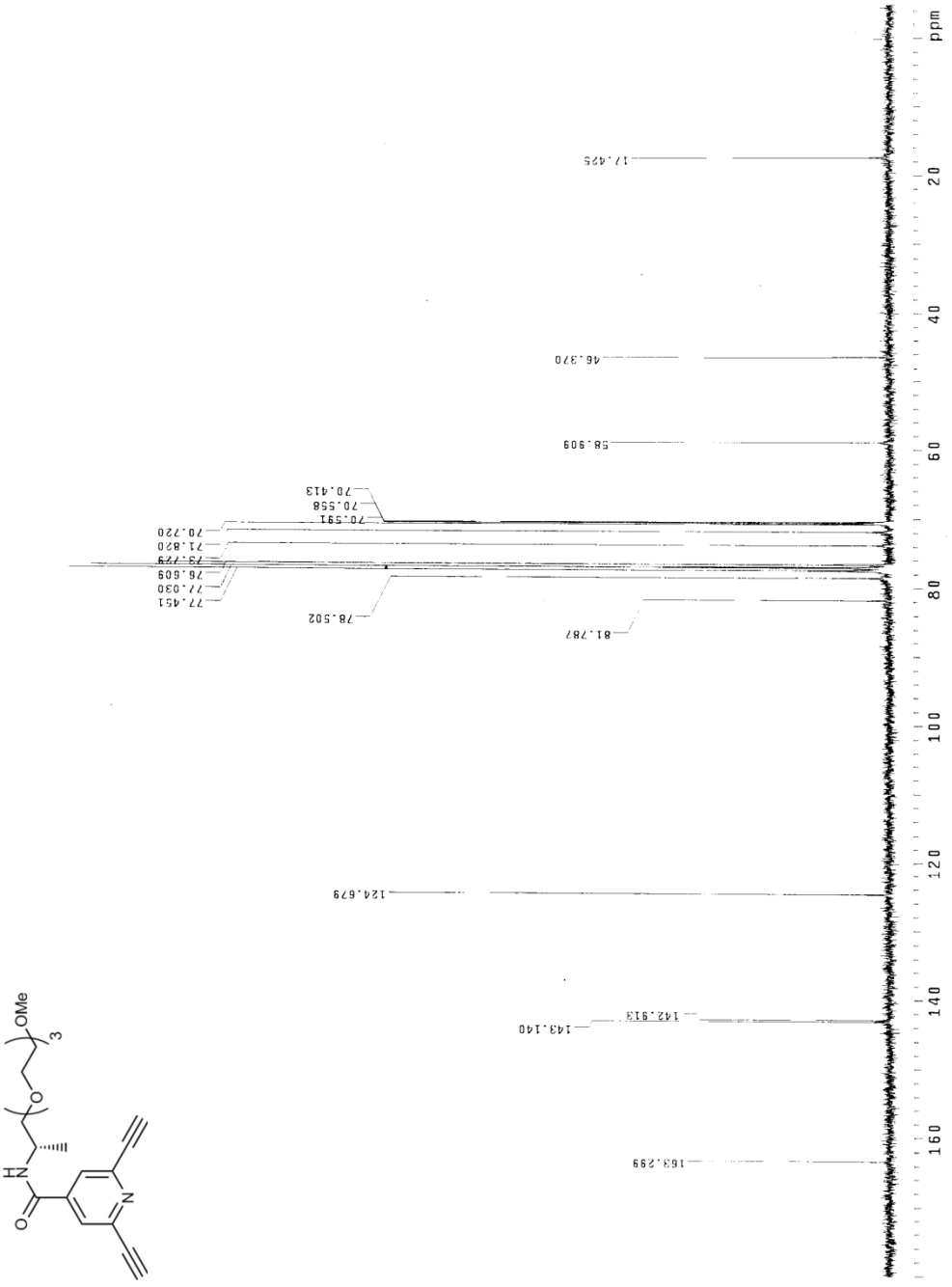

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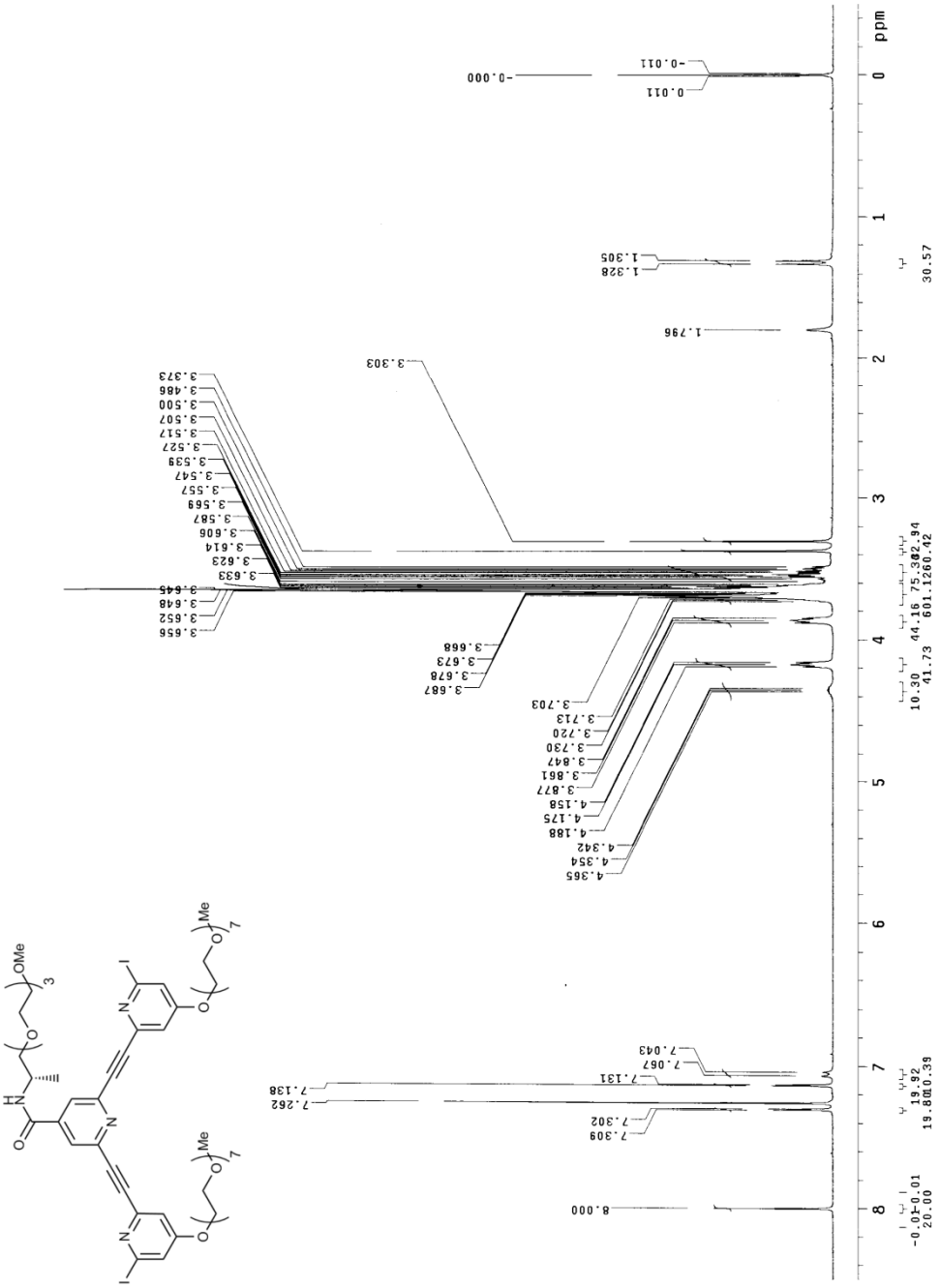

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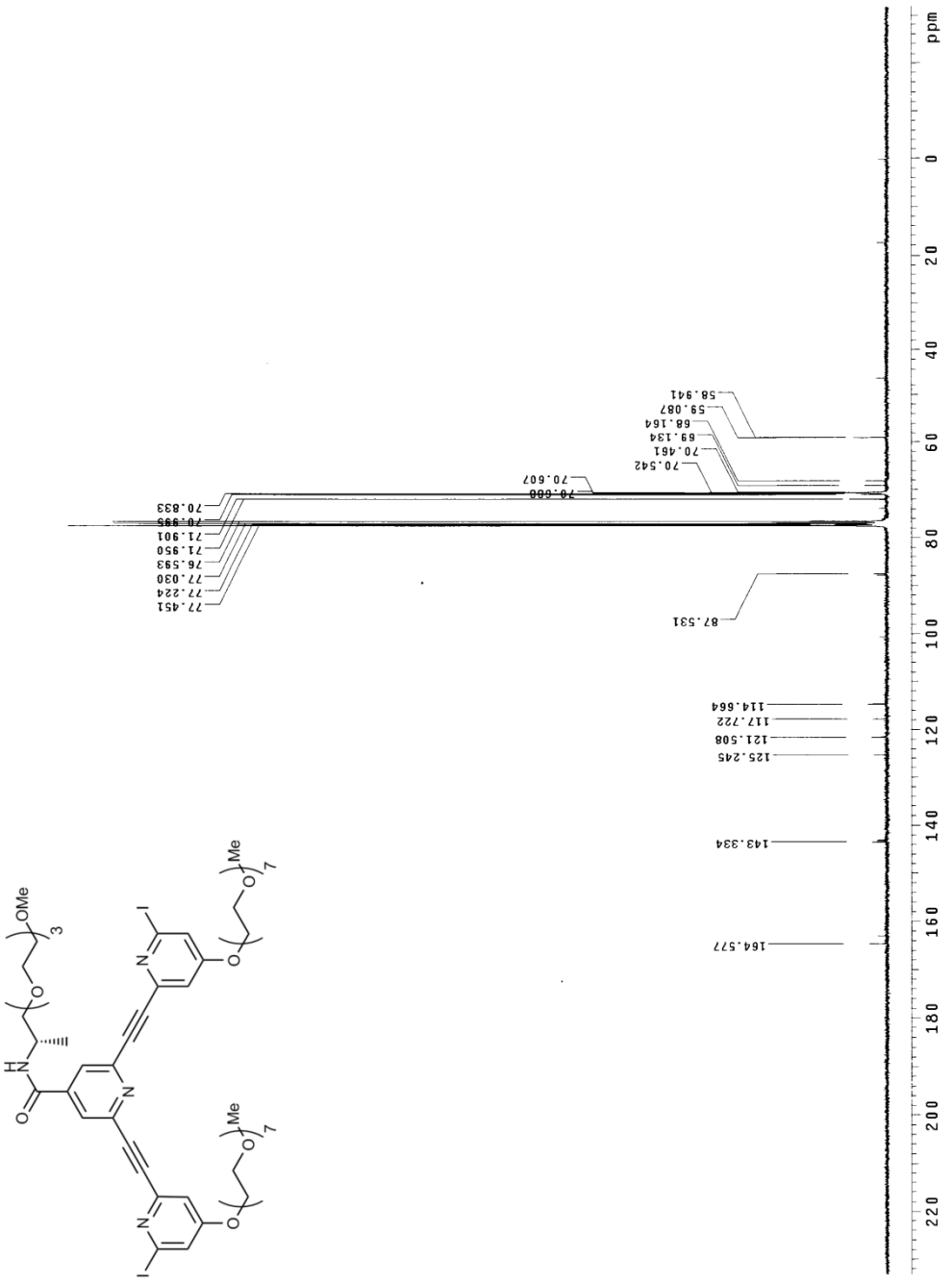

$^{1}$H NMR spectrum of **2**