Microwave-assisted synthesis of a new series of resorcin[4]arene cavitand-capped porphyrin capsules.

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General Experimental Methods, Experimental Procedures and Characterisation Data: S1-S6

Electronic Copies of ^{1}H NMR, ^{13}C NMR and COSY NMR Spectra of Compounds 3, 4, 14-25: S7-S47

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General

All solvents and reagents were obtained from Acros, Aldrich, Fluka, Merck or Alfa-Aesar. Unless otherwise stated, these were used without further purification. Microwave synthesis was completed using a CEM Liberty microwave peptide synthesiser, using sealed borosilicate tubes. Yields for the MW-assisted reaction are reported as average yield *per* reaction. Thin-layer chromatography (TLC) was conducted on aluminium-backed, precoated silica gel plates (Merck, silica gel 60, 20 cm x 20 cm). Column chromatography was performed with silica gel 60 (Merck, particle size 0.040-0.063 mm). Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded using a Bruker Avance spectrometer, operating at ambient temperatures, at 400 MHz for ^{1}H experiments, and 100 MHz for ^{13}C experiments. Chemical shifts are reported in parts per million (ppm). Ultraviolet-Visible spectra were recorded at 298 K on a Varian Cary 50 CONC single beam UV-Vis spectrophotometer, using a quartz cell of 1 cm path length and an analyte concentration of approximately 100 ppm. Infrared (IR) spectra were recorded on a Nicolet Impact 400 spectrophotometer at 293 K, as KBr discs. All melting points are uncorrected.

7,11,15,28-Tetrakis(bromomethyl)-1,21,23,25-tetramethyl-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin Stereoisomer (1)

Vacuum dried methyl cavitand[1] (1.00 g, 1.54 mmol) and *N*-bromosuccinimide (1.10 g, 6.31 mmol) were added to CCl_4 (100 mL). A catalytic amount of benzoyl peroxide was added to the solution, and the solution allowed to reflux overnight. The light orange solution was then allowed to cool to room temperature, during which time a succinimide precipitate formed. The precipitate was filtered off, and the yellow filtrate concentrated on a rotary evaporator. The resulting solid was chromatographed on silica gel using a mobile phase of 3:1 hexane-ethyl acetate. The fractions that were collected were concentrated on a rotary evaporator, and the yellow solid product that resulted stirred in methanol overnight. The solution was then filtered to yield **1** (0.96 g, 69 %) as an off-white powder; mp >300 $^{\circ}$C. ν_{max}(KBr)/cm^{-1} 2980, 2940, 2875, 1595, 1415, 1440, 1400, 1345, 1305, 1250, 1205, 1145, 1100, 1095, 1050, 1010, 980, 935, 895, 805, 750, 695, 600, 560, 490, 480; δ_H(400 MHz, $CDCl_3$) 1.74 (d, 12 H, CH_3), 4.43 (s, 8 H, CH_2Br), 4.56 (d, 4 H, inner of OCH_2O), 5.01 (q, 4 H, CHCH$_3$), 6.02 (d, 4 H, outer of OCH_2O), 7.26 (s, 4 H, Ar *H*); δ_C(100 MHz, $CDCl_3$) 153.1, 138.9, 124.4, 120.4, 99.0, 31.1, 22.9, 16.0.

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7,11,15,28-Tetrakis(bromomethyl)-1,21,23,25-tetrapentyl-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin Stereoisomer (2)

Procedure as *per* that for **1** described, using methyl cavitand[2] (1.00 g, 1.15 mmol) and *N*-bromosuccinimide (0.90 g, 5.04 mmol) in CCl_4 (100 mL). The material was purified using column chromatography on silica gel, employing a chloroform mobile phase. The purified product was stirred in methanol overnight, before drying to yield **2** (1.03 g, 76 %) as a dark orange powder; mp 280-282 °C (from ethyl acetate/hexane). ν_{max}(KBr)/cm^{-1} 2926, 2858, 1589, 1470, 1453, 1398, 1241, 1147, 1056, 1013, 970, 936, 784, 683, 607, 583, 559, 474; δ_H(400 MHz, $CDCl_3$) 0.89 (t, 12 H, C*H*$_3$), 1.28-1.50 (m, 24 H, (C*H*$_2$)$_3$), 2.15-2.22 (m, 8 H, C*H*$_2$), 4.40 (s, 8 H, C*H*$_2$Br), 4.55 (d, 4 H, inner of OC*H*$_2$O), 4.76 (t, 4 H, C*H*(CH$_2$)$_4$CH$_3$), 6.02 (d, 4 H, outer of OC*H*$_2$O), 7.11 (s, 4 H, Ar *H*); δ_C(100 MHz, $CDCl_3$) 153.5, 138.1, 124.5, 121.1, 98.1, 36.8 32.6, 31.9, 30.0, 27.5, 22.6, 14.1.

5,10,15,20-Tetrakis(2-hydroxyphenyl)-21H,23H-porphyrin (*o*-hydroxy TPP)[3, 4]

To dry, freshly distilled CH_2Cl_2 (50 mL), tetramethoxyporphyrin (2.00 g, 2.72 mmol) was added as a solid under a nitrogen atmosphere to give a purple solution. To this, BBr_3 (8.7 mL, 0.093 mol) was added to the solution via syringe, and the reaction vessel shielded from light. After stirring for 5 hours, water (30 mL) was carefully added to the bright green solution to neutralise excess acid, and the product precipitated from solution. The contents of the reaction vessel were transferred to a 500 mL beaker, and the solution treated carefully with a saturated solution of $NaHCO_3$, so turning the solution purple. Once effervescence subsided, the solution was subjected to extraction using ethyl acetate. The organic layers were collected and dried over anhydrous Na_2SO_4 before gravity filtration. The solution was concentrated on a rotary evaporator, suspended in a small amount of hexane and filtered. The retained dark purple material was washed further with hexane to give the product compound (1.68 g, 91 %) as a purple solid; mp >300 °C. TLC (SiO_2, 9:1 $CHCl_3$-Et_2O): R_f 0.19 ($\alpha\alpha\alpha\alpha$ isomer), 0.33 ($\alpha\alpha\alpha\beta$), 0.46 ($\alpha\alpha\beta\beta$), 0.59 ($\alpha\beta\alpha\beta$).ν_{max}(KBr)/cm^{-1} 3630-3220, 3120, 2925, 1690, 1650, 1640, 1625, 1610, 1585, 1560, 1455, 1350, 1290, 1220, 1160, 1100, 965, 755, 650. δ_H(400 MHz, $CDCl_3$) 4.93 (br. s, 4 H, O*H*), 7.32-7.39 (m, 8 H, 4 *H*C(3'), 4 *H*C(5')), 7.68-7.76 (t, 4 H, *H*C(4')), 7.95 (m, 4 H, *H*C(6')), 8.91 (s, 8 H, *H*C(β) of pyrrole). δ_C(100 MHz, $CDCl_3$) 155.5, 135.0, 130.6, 127.3, 119.6, 115.6.

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7,11,15,28-Tetrabromo-1,21,23,25-tetrapentyl-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin Stereoisomer (7)

To a solution of CH_2BrCl (12 mL, 0.179 mol) and oven-dried (110 °C) K_2CO_3 (38.00 g, 0.274 mol) in dry, degassed DMF (200 mL), bromoresorcin[4]arene[5] (10.00 g, 9.2 mmol) in DMF (50 mL) was added over 1.5 hours. After stirring for 24 hours at room temperature under a nitrogen atmosphere, CH_2BrCl (12 mL, 0.179 mol) was added and the solution heated to 45 °C. After a further 24 hours, a further aliquot of CH_2BrCl (12 mL, 0.179 mol) was added, and the solution heated to 63 °C. After 48 hours at 63 °C, the light brown solution was cooled to room temperature, and the K_2CO_3 neutralised by the addition of a 6 % HCl solution. The crude product simultaneously precipitated from solution, and was collected on filtration of the neutralized reaction mixture. The brown solid was suspended in methanol and stirred for 24 hours, before being filtered from the methanol and dried. The material was chromatographed on silica gel using a 1:2 hexane:dichloromethane mobile phase, before being stirred once again in methanol, filtered and dried to give **7** (7.21 g, 69 %) as a white solid; mp 280 °C (dec). ν_{max}(KBr)/cm^{-1} 2926, 2858, 1688, 1473, 1450, 1285, 1240, 1155, 1090, 1019, 973, 858, 751; δ_H(400 MHz, $CDCl_3$) 0.91 (t, 12 H, C*H*$_3$), 1.31-1.44 (m, 24 H, (C*H*$_2$)$_3$), 2.17-2.23 (m, 8 H, C*H*$_2$), 4.40 (d, 4 H, inner of OC*H*$_2$O), 4.85 (t, 4 H, C*H*(CH$_2$)$_4$CH$_3$), 5.95 (d, 4 H, outer of OC*H*$_2$O), 7.03 (s, 4 H, Ar *H*); δ_C(100 MHz, $CDCl_3$) 152.1, 139.3, 119.0, 113.5, 98.5, 37.7, 31.9, 27.4, 22.7, 14.0.

7,11,15,28-Tetrabromo-1,21,23,25-tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin Stereoisomer (8)

Application of the described procedure for the preparation of **7**, to aliquots of CH_2BrCl (16.3 mL, 0.243 mol *per* addition), oven-dried (110 °C) K_2CO_3 (99.25 g, 0.718 mol), and bromoresorcin[4]arene[5] (25.00 g, 20.5 mmol), in dry, degassed DMF (800 mL). The crude product was purified *via* silica gel chromatography using a chloroform mobile phase, before being stirred in methanol, filtered and dried to give **8** (25.90 g, 70 %) as an off-white solid; mp 285-290 °C (dec). ν_{max}(KBr)/cm^{-1} 2939, 1729, 1602, 1469, 1452, 1415, 1299, 1234, 1091, 1057, 1017, 984, 957, 790, 745, 699, 586; δ_H(400 MHz, $CDCl_3$) 2.47-2.49 (m, 8 H, C*H*$_2$CH$_2$Ar), 2.62-2.64 (m, 8 H, CH$_2$C*H*$_2$Ar), 4.41 (d, 4 H, inner of OC*H*$_2$O), 4.94 (t, 4 H, C*H*CH$_2$CH$_2$Ar), 5.95 (d, 4 H, outer of OC*H*$_2$O), 7.09-7.24 (m, 24 H, Ar *H* and CH$_2$CH$_2$C$_6$*H*$_5$);

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δ_C(100 MHz, $CDCl_3$) 152.8, 141.7, 139.6, 129.2, 128.9, 126.8, 119.5, 114.4, 99.0, 38.3, 34.7, 32.8.

1,21,23,25-Tetrapentyl-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin-7,11,15,28-tetrol Stereoisomer (9)

A solution of vacuum-dried **7** (5.01 g, 4.41 mmol) in dry THF (800 mL) was set to stir in an oven-dried round-bottomed flask under a nitrogen atmosphere, sealed with a septum. The solution was cooled to -80 °C, and treated with *n*-butyllithium (~ 1.6 M solution in hexane, 46.0 mL, 73.6 mmol), which was rapidly added *via* the septum using a syringe. After one minute, trimethyl borate (4.5 mL, 39.4 mmol) was added, so turning the solution into a dark yellow emulsion. The flask and its contents were removed from the cooling bath, and allowed to attain room temperature slowly, during which time the emulsion disappeared to yield a yellow solution. After stirring at room temperature for one hour, the solution was again cooled to -80 °C, and treated with 1:1 15 % H_2O_2:1.5 M NaOH (100 mL) to give a viscous, white reaction mixture. The solution was allowed to warm to ambient temperature and stirred overnight, over which time it cleared to give a clear, slightly yellow solution. Thereafter, excess $Na_2S_2O_5$ (20 g, 0.105 mol) was carefully added to the stirring solution, which resulted in the formation of two layers. The THF was subsequently removed *in vacuo* to yield a white solid in the residual water, which was filtered. The mixture of alcohols was preadsorbed onto silica before being subjected to chromatography on silica gel. The gravity column (30 cm in length x 5.5 cm in diameter) was gradient eluted, starting with 100 % chloroform, accompanied by the slow addition of methanol towards a final chloroform-methanol ratio of 85:15. Tetrol **9** was exclusively isolated (1.56 g, 40 %) in the form of a white solid as the most polar fraction (R_f 0.17, by TLC in 85:15 chloroform:methanol); mp 280 °C (dec). TLC (SiO_2, 3:1 EtOAc-Hexane): R_f 0.16 (tetrol), 0.35 (triol), 0.55 (diol), 0.72 (mono-ol). ν_{max}(KBr)/cm^{-1} 3343, 2924, 2853, 1697, 1584, 1443, , 1285, 1245, 1161, 1090, 1019, 975, 864, 757; δ_H(400 MHz, d_6-DMSO) 0.88 (t, 12 H, C*H*$_3$), 1.40-1.28 (m, 24 H, (C*H*$_2$)$_3$), 2.23-2.27 (m, 8 H, C*H*$_2$), 4.20 (d, 4 H, inner of OC*H*$_2$O), 4.50 (t, 4 H, C*H*$(CH_2)_4CH_3$), 5.74 (d, 4 H, outer of OC*H*$_2$O), 6.91 (s, 4 H, Ar *H*), 8.75 (s, 4 H, OH); δ_C(100 MHz, d_6-DMSO) 142.2, 138.1, 110.0, 99.5, 36.7, 31.5, 28.9, 27.4, 22.2, 13.9.

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1,21,23,25-Tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']-bis[1,3]benzodioxocin-7,11,15,28-tetrol Stereoisomer (10)

As *per* the preparation of **9**, applied to vacuum-dried **8** (5.00 g, 3.94 mmol) in dry THF (800 mL), adding *n*-butyllithium (~ 1.6 M solution in hexane, 40.0 mL, 64 mmol), trimethyl borate (12 mL, 105 mmol), and treated with 1:1 15 % H_2O_2:1.5 M NaOH (100 mL). A gravity column employing gradient elution yielded tetrol **10** (1.80 g, 45 %) as the most polar fraction (R_f 0.16, by TLC in 85:15 chloroform:methanol) in the form of a white solid; mp >300 °C dec. TLC (SiO_2, 3:1 EtOAc-Hexane): R_f 0.14 (tetrol), 0.34 (triol), 0.56 (diol), 0.70 (mono-ol). ν_{max}(KBr)/cm^{-1} 3368 (OH), 2938, 1587, 1492, 1468, 1446, 1320, 1150, 1106, 1066, 1018, 983, 969, 735, 697, 692, 591, 511; δ_H(400 MHz, d_6-$(CH_3)_2CO$) 2.55-2.2.61 (m, 8 H, C*H*$_2$CH$_2$Ar), 2.63-2.68 (m, 8 H, CH$_2$C*H*$_2$Ar), 4.42 (d, 4 H, inner of OC*H*$_2$O), 4.79 (t, 4 H, C*H*CH$_2$CH$_2$Ar), 5.83 (d, 4 H, outer of OC*H*$_2$O), 7.18-7.25 (m, 24 H, Ar *H* and CH$_2$CH$_2$C$_6$*H*$_5$), 7.96 (s, 4 H, Ar O*H*); δ_C(100 MHz, d_6-$(CH_3)_2CO$) 143.5, 143.4, 143.3, 139.4, 129.3, 129.2, 126, 6, 111.3, 100.7, 38.1, 35.2, 33.0.

General procedure for preparation of aldehyde reagents 11-13,[6] and 26[7]

To a stirring solution of oven-dried (110 °C) K_2CO_3 (13.00 g, 0.0941 mol) in dry DMF (80 mL), salicylaldehyde (10.00 g, 0.0819 mol) was added so turning the solution bright yellow. After ten minutes of stirring at room temperature, the respective dibromoalkane was added and the reaction mixture left to stir for three days. Thereafter, the mixture was poured into water, and the liberated oil extracted from the aqueous emulsion with diethyl ether. The organic layer was treated with 10 % NaOH (three times) followed by washing with water (twice) before being dried over Na_2SO_4. The diethyl ether was evaporated, and the excess dibromoalkane reagent removed *via* high vacuum distillation.

2-(2-bromobutoxy)benzaldehyde (11)

Application of the general procedure, using 1,4-dibromobutane (141.42 g, 0.655 mol), yielded **11** (16.15 g, 77 %) as a yellow oil; ν_{max}(KBr)/cm^{-1} 2867, 1686, 1598, 1487, 1453, 1389, 1280, 1250, 1181, 1155, 1104, 1027, 931, 840, 751, 651, 602, 562; δ_H(400 MHz, $CDCl_3$) 1.83-2.12 (m, 4 H, OCH$_2$(C*H*$_2$)$_2$CH$_2$Br), 3.45 (t, 2 H, O(CH$_2$)$_3$C*H*$_2$Br), 4.20 (t, 2 H, OC*H*$_2$(CH$_2$)$_3$Br), 6.97-7.05 (m, 2 H, Ar *H*), 7.53 (td, 1 H, Ar *H*), 7.84 (dd, 1 H, Ar *H*), 10.50 (s, 1 H, Ar C*H*O); δ_C(100 MHz, $CDCl_3$) 189.7, 161.0, 136.0, 128.4, 124.9, 120.8, 112.4, 67.0, 32.9, 29.3, 27.7.

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2-(2-bromopropoxy)benzaldehyde (12)

Application of the general procedure, using 1,3-dibromopropane (132.26 g, 0.655 mol), yielded **12** (19.29 g, 97 %) as a yellow oil; ν_{max}(KBr)/cm^{-1} 2870, 1683, 1597, 1485, 1456, 1386, 1283, 1237, 1189, 1160, 1102, 1021, 928, 836, 753, 647, 599, 563, 501, 439; δ_H(400 MHz, $CDCl_3$) 2.37 (m, 2 H, $OCH_2CH_2CH_2Br$), 3.60 (t, 2 H, $O(CH_2)_2CH_2Br$), 4.21 (t, 2 H, $OCH_2(CH_2)_2Br$), 6.97-7.03 (m, 2 H, Ar *H*), 7.52 (td, 1 H, Ar *H*), 7.81 (dd, 1 H, Ar *H*), 10.45 (s, 1 H, Ar C*H*O); δ_C(100 MHz, $CDCl_3$) 189.5, 161.0, 136.1, 128.6, 124.9, 121.0, 112.5, 65.9, 32.1, 29.7.

2-(2-bromoethoxy)benzaldehyde (13)

Application of the general procedure to 1,2-dibromoethane (123.07 g, 0.655 mol). After extraction and removal of excess 1,2-dibromoethane, **13** was obtained (13.11 g, 70 %) as a yellow oil, which, upon cooling to room temperature gave a yellow, crystalline solid; mp 50-52 °C. ν_{max}(KBr)/cm^{-1} 2863, 1676, 1596, 1581, 1482, 1452, 1396, 1382, 1289, 1188, 1163, 1104, 1011, 944, 878, 827, 763, 653, 567, 497, 448, 407; δ_H(400 MHz, $CDCl_3$) 3.69 (t, 2 H, OCH_2CH_2Br), 4.40 (t, 2 H, OCH_2CH_2Br), 6.94 (d, 1 H, Ar *H*), 7.04 (t, 1 H, Ar *H*), 7.52 (td, 1 H, Ar *H*), 7.81 (dd, 1 H, Ar *H*), 10.41 (s, 1 H, Ar C*H*O); δ_C(100 MHz, $CDCl_3$) 189.6, 160.4, 135.9, 128.4, 125.2, 121.5, 112.7, 68.2, 28.8.

2-chloromethoxybenzaldehyde 26

Application of the general procedure, using K_2CO_3 (6.50 g, 0.0471 mol), DMF (80 mL), salicylaldehyde (5.0 g, 0.0410 mol) and bromochloromethane (42.44 g, 0.328 mol). This yielded **26** (4.68 g, 67 %) as a white, crystalline solid; mp 118-120 °C. ν_{max}(KBr)/cm^{-1} 2863, 1687, 1597, 1582*sh*, 1479, 1459, 1414, 1388, 1284, 1215, 1194, 1159, 1101, 1004, 829, 753, 643, 580, 41414, 1388, 1284, 1215, 1194, 1159, 1101, 1004, 829, 753, 643, 580, 479, 438; δ_H(400 MHz, $CDCl_3$) 6.02 (s, 2 H, CH_2), 7.14-7.20 (m, 1 H, Ar *H*), 7.34-7.43 (m, 1 H, Ar *H*), 7.58-7.66 (m, 1 H, Ar *H*), 7.85-7.94 (m, 1 H, Ar *H*), 10.47 (s, 1 H, Ar C*H*O); δ_C(100 MHz, $CDCl_3$) 189.5, 157.3, 136.3, 128.9, 126.4, 123.0, 115.7, 91.5.

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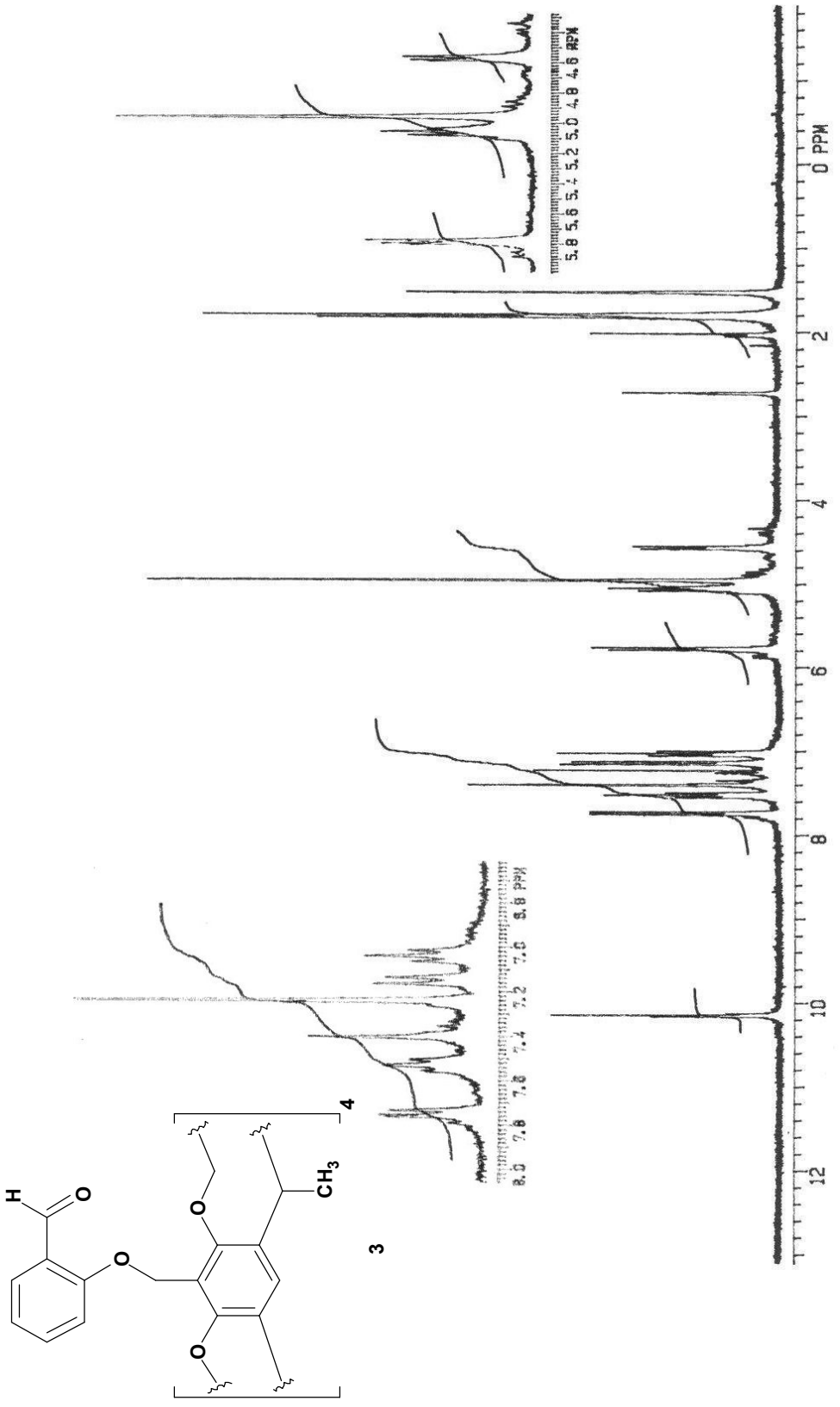

^{1}H NMR spectrum of 3 in $CDCl_3$ (400 MHz)

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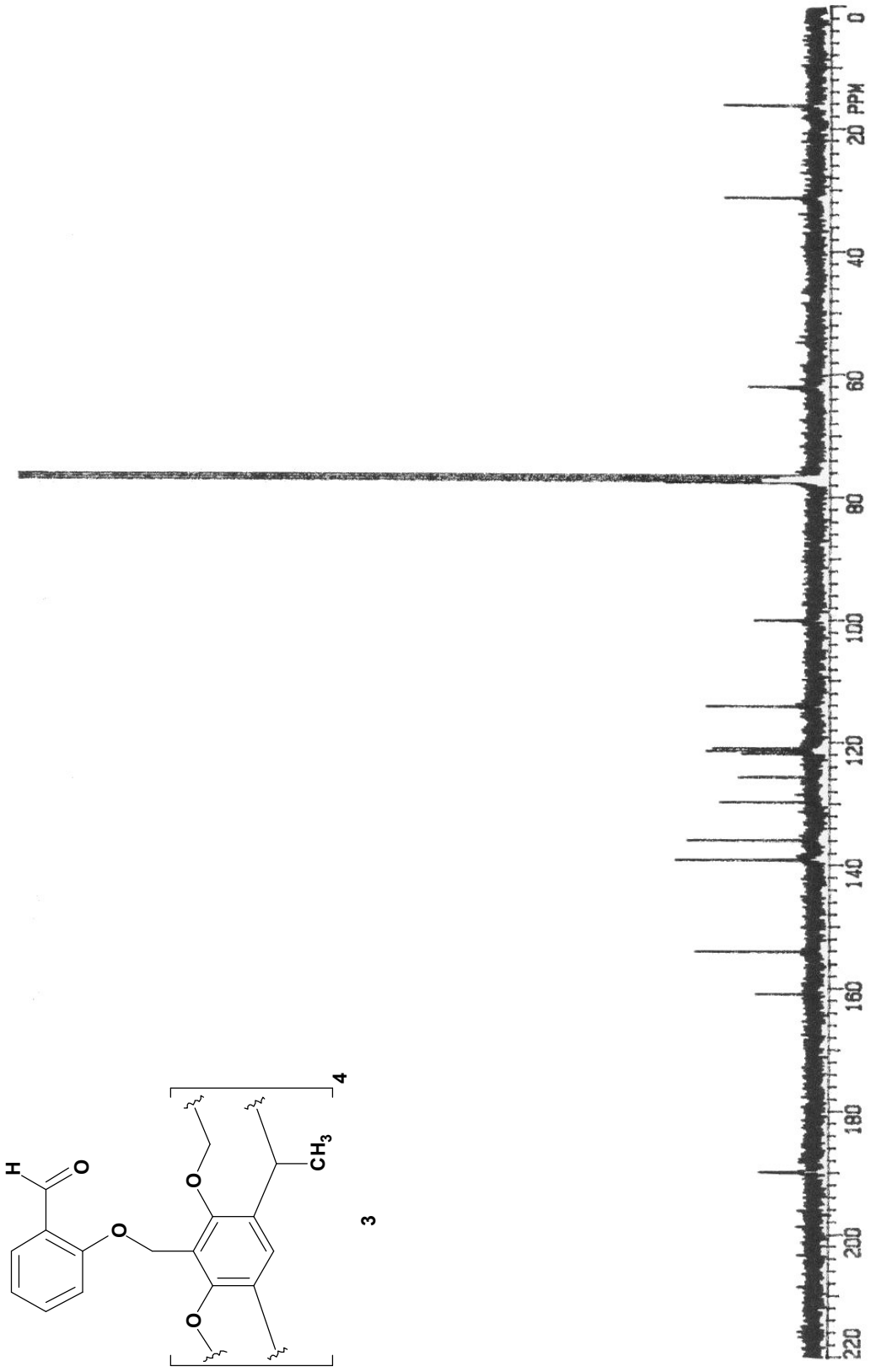

^{13}C NMR spectrum of 3 in $CDCl_3$ (100 MHz)

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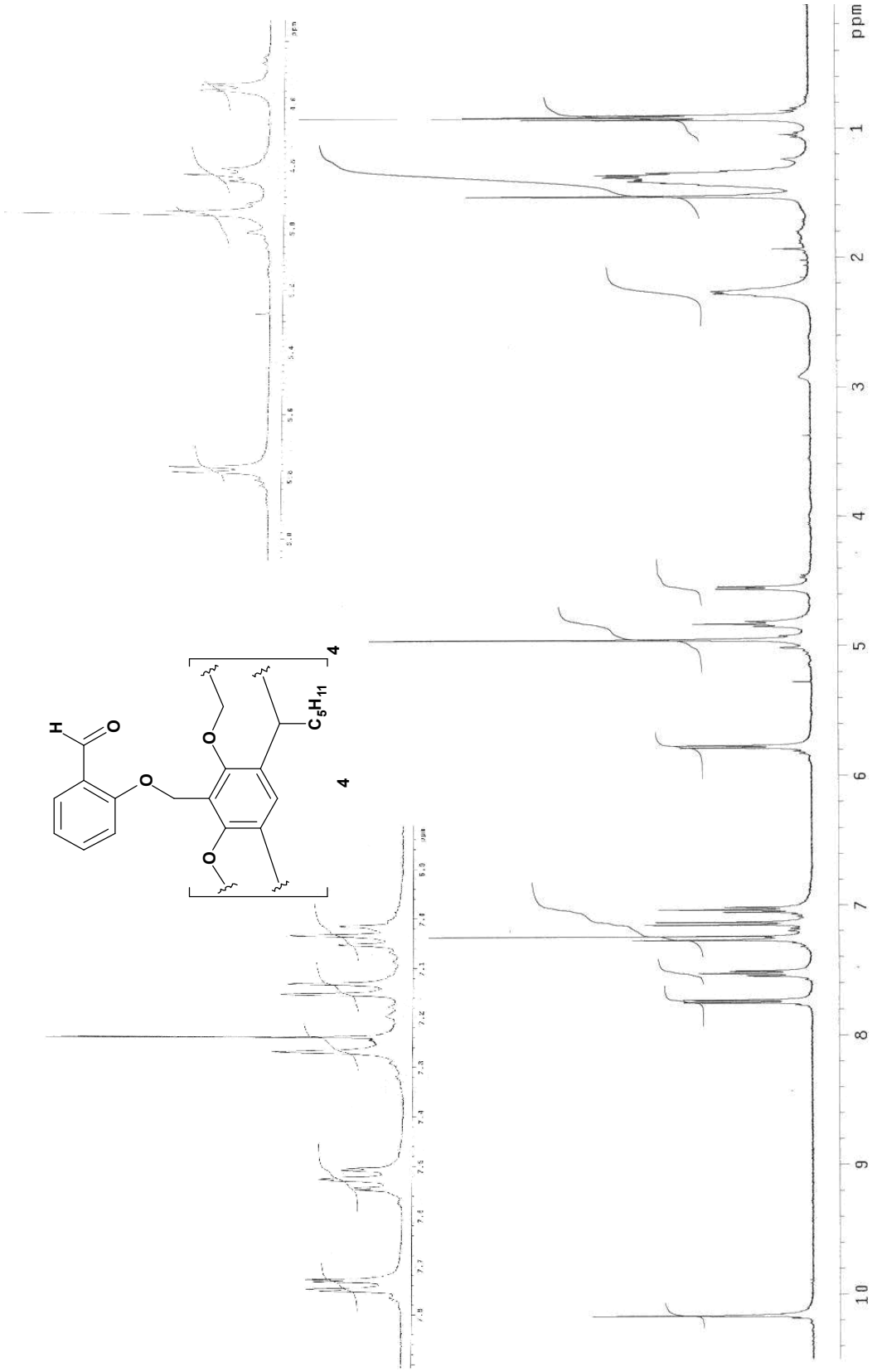

^{1}H NMR spectrum of 4 in $CDCl_3$ (400 MHz)

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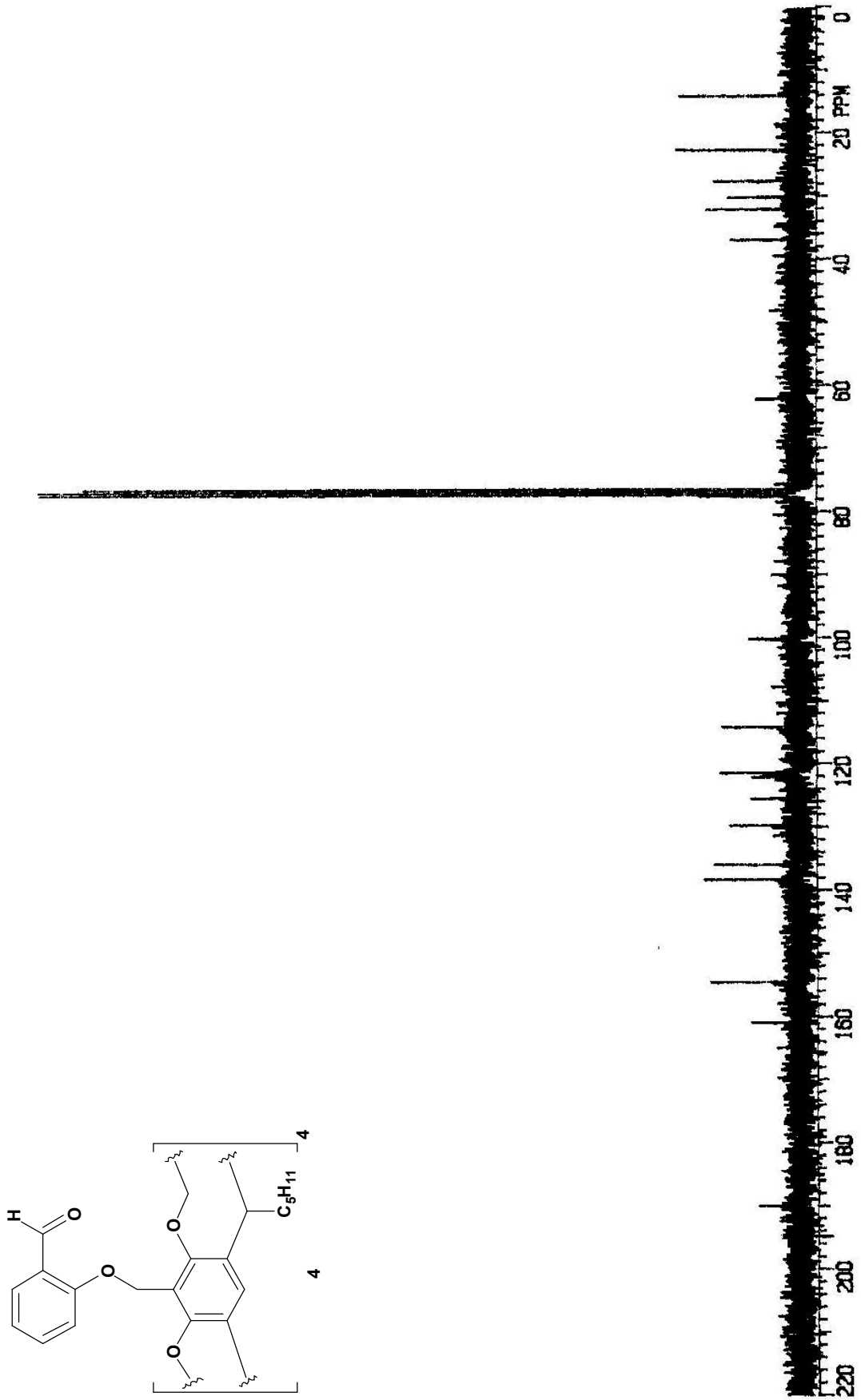

^{13}C NMR spectrum of 4 in $CDCl_3$ (100 MHz)

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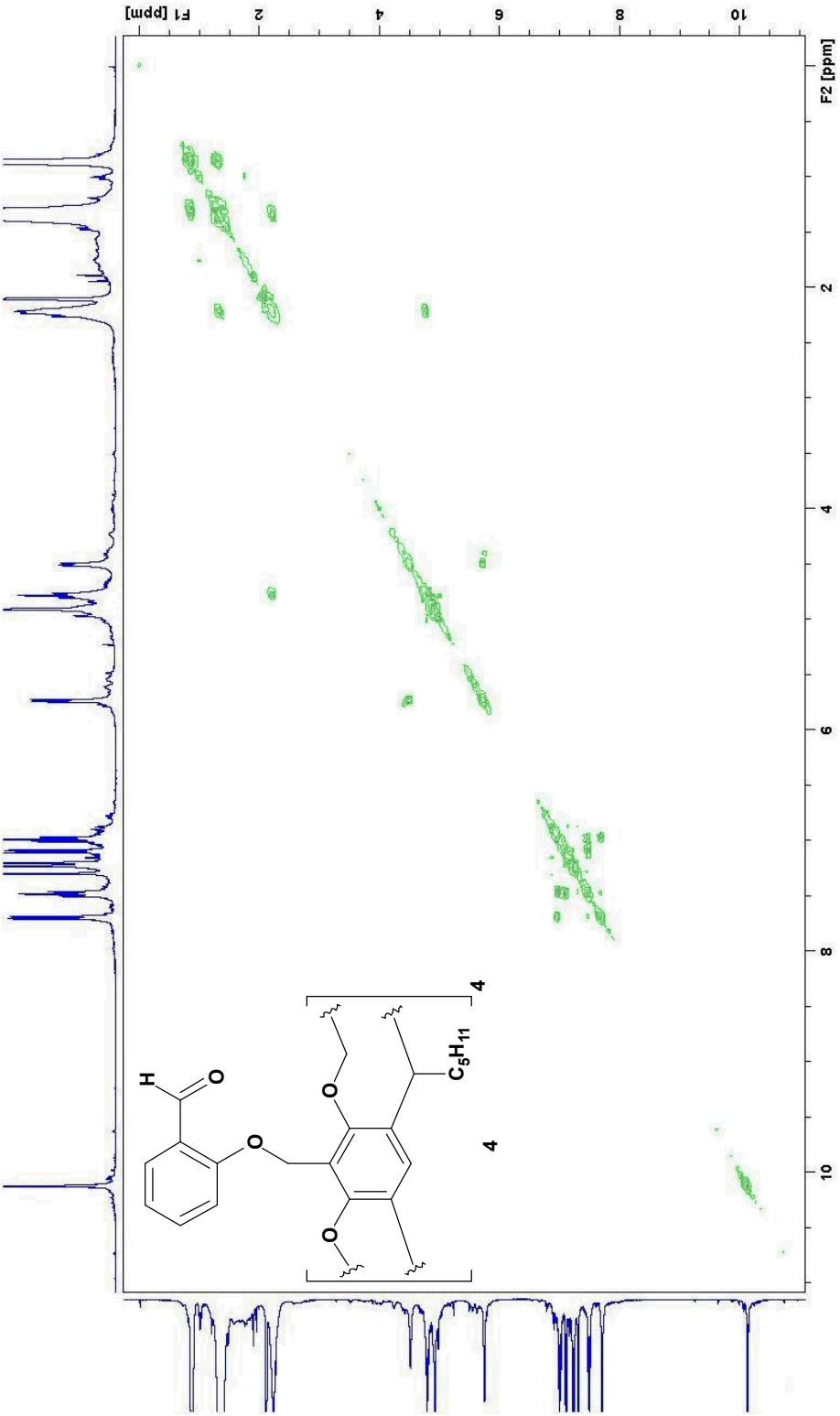

COSY NMR spectrum of 4 in $CDCl_3$ (400 MHz)

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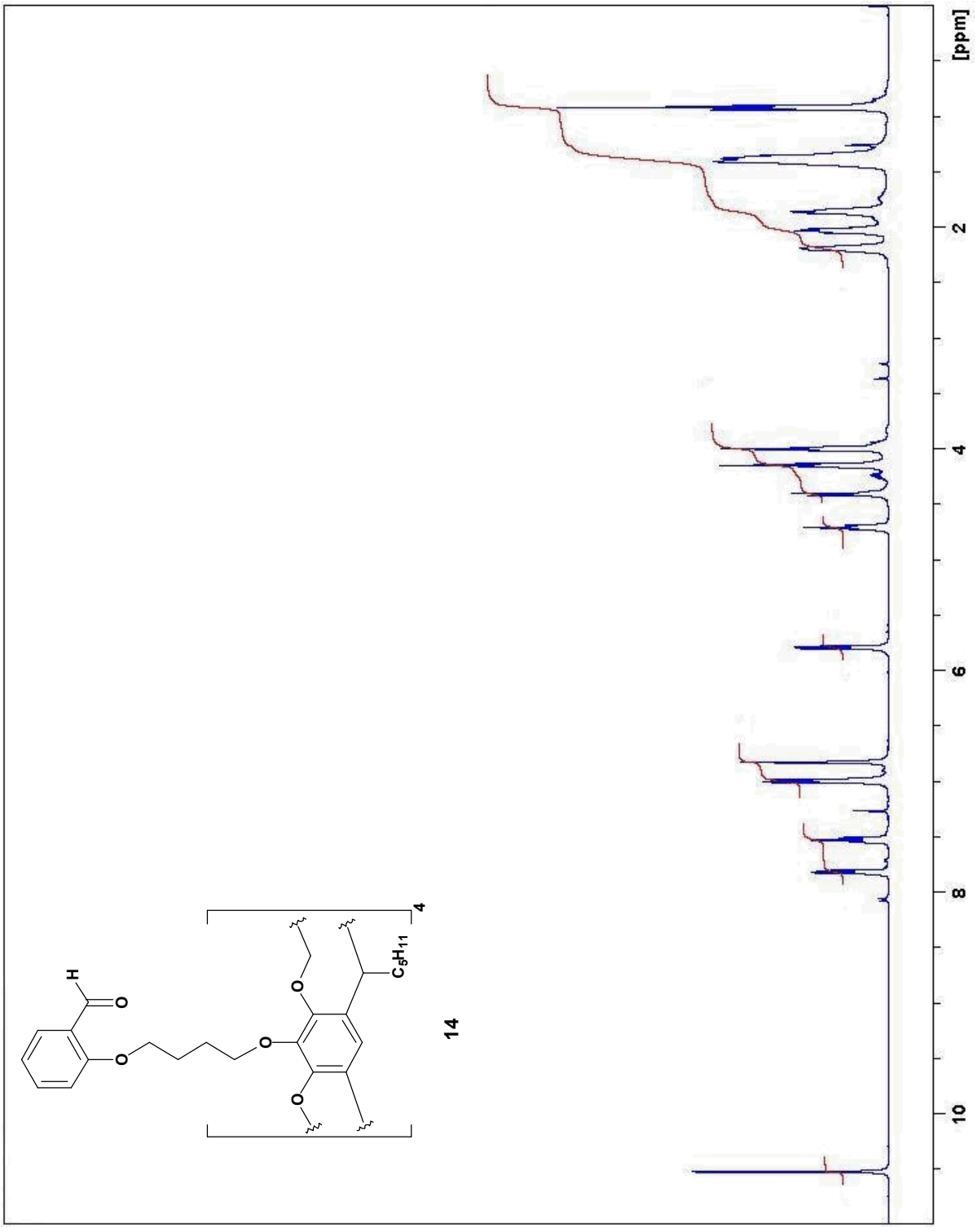

^{1}H NMR spectrum of 14 in $CDCl_3$ (400 MHz)

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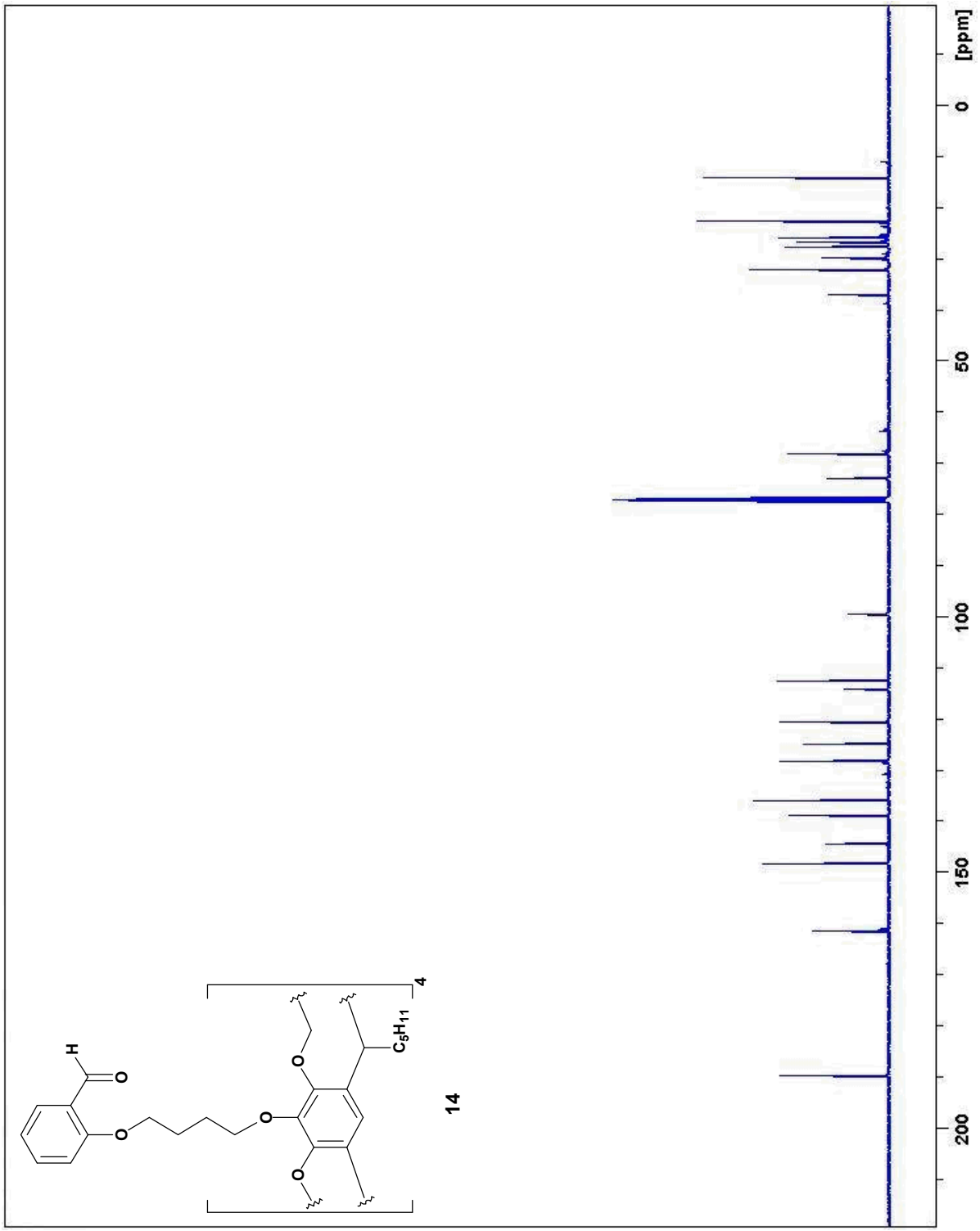

^{13}C NMR spectrum of 14 in $CDCl_3$ (100 MHz)

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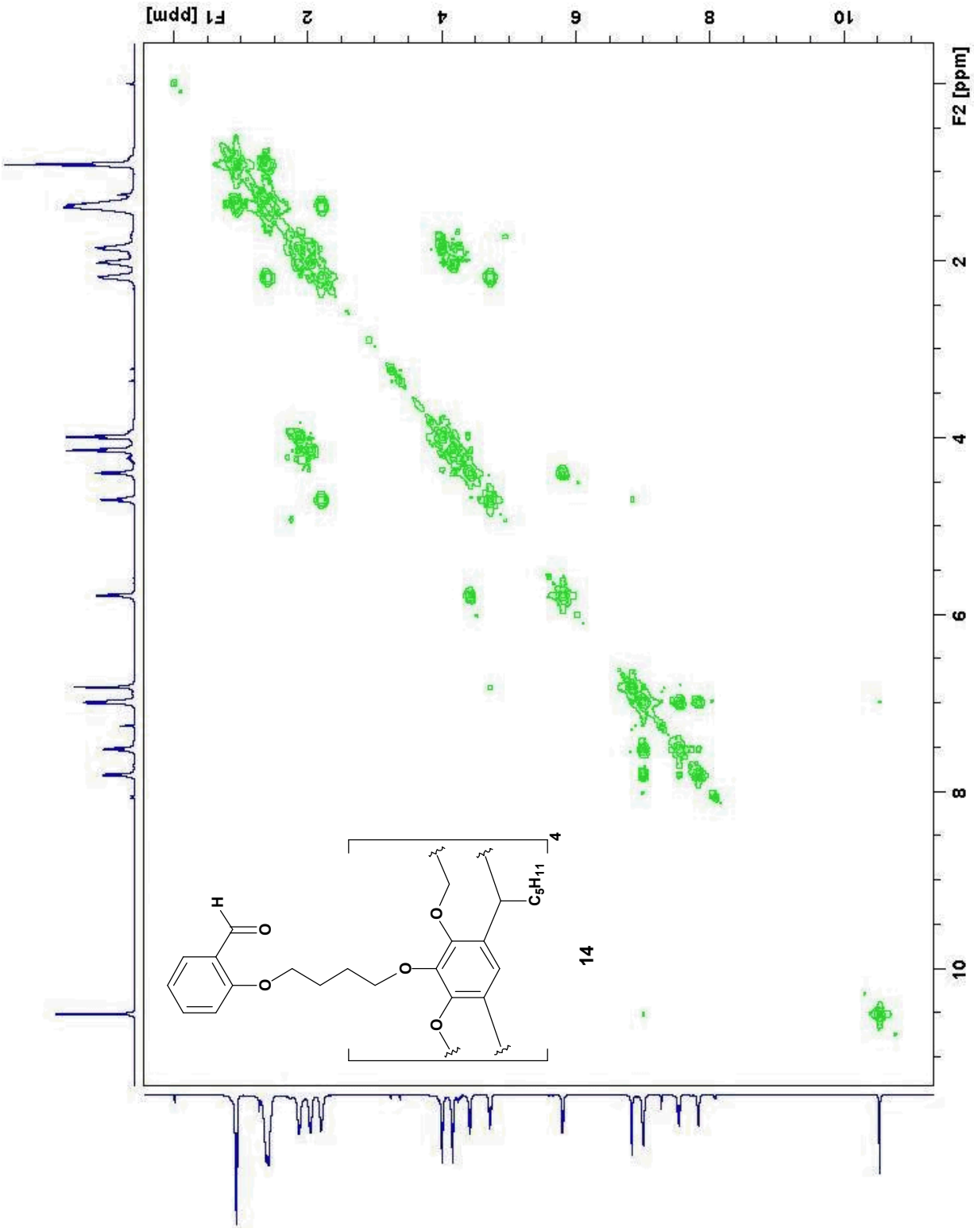

COSY NMR spectrum of 14 in $CDCl_3$ (400 MHz)

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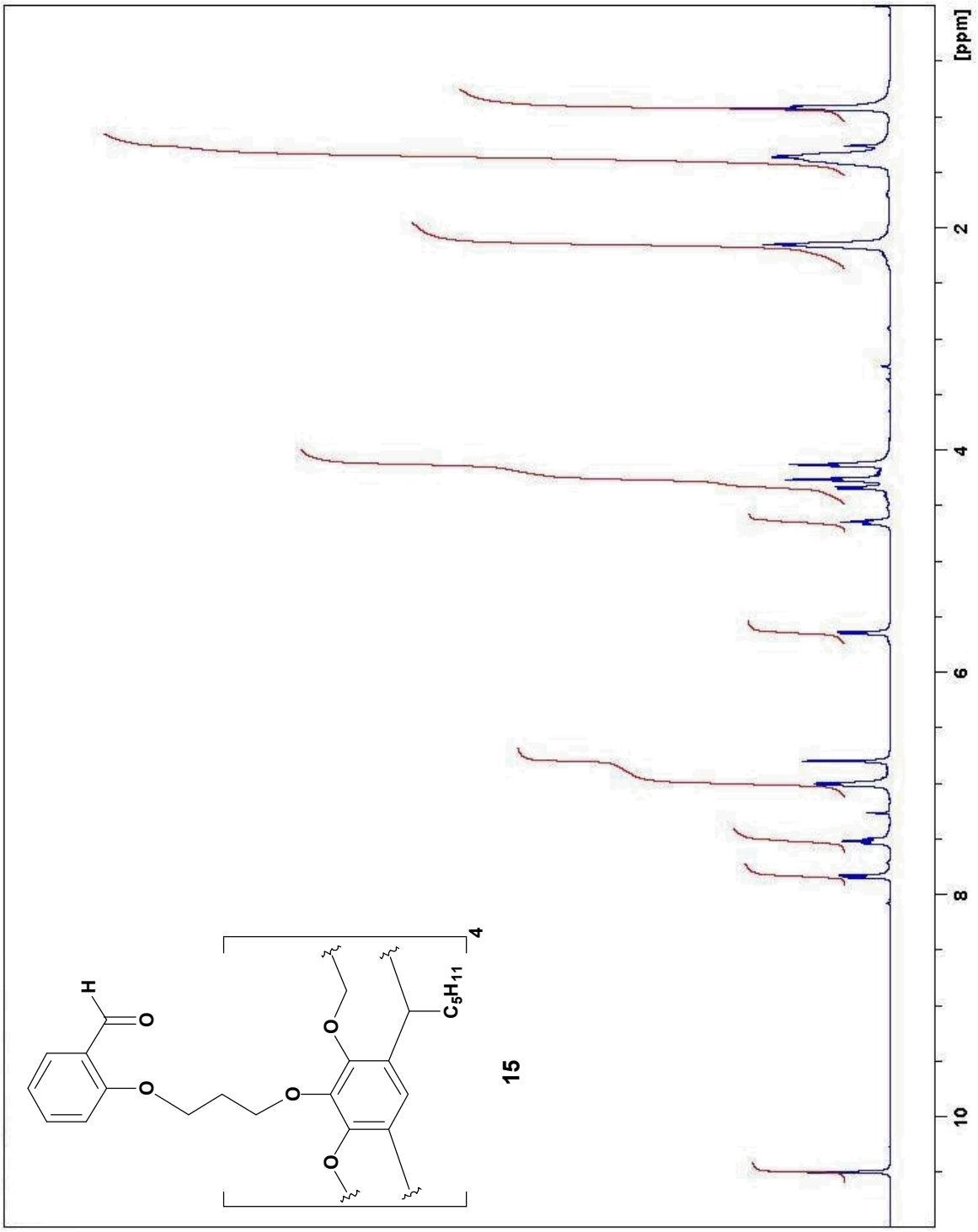

^{1}H NMR spectrum of 15 in $CDCl_3$ (400 MHz)

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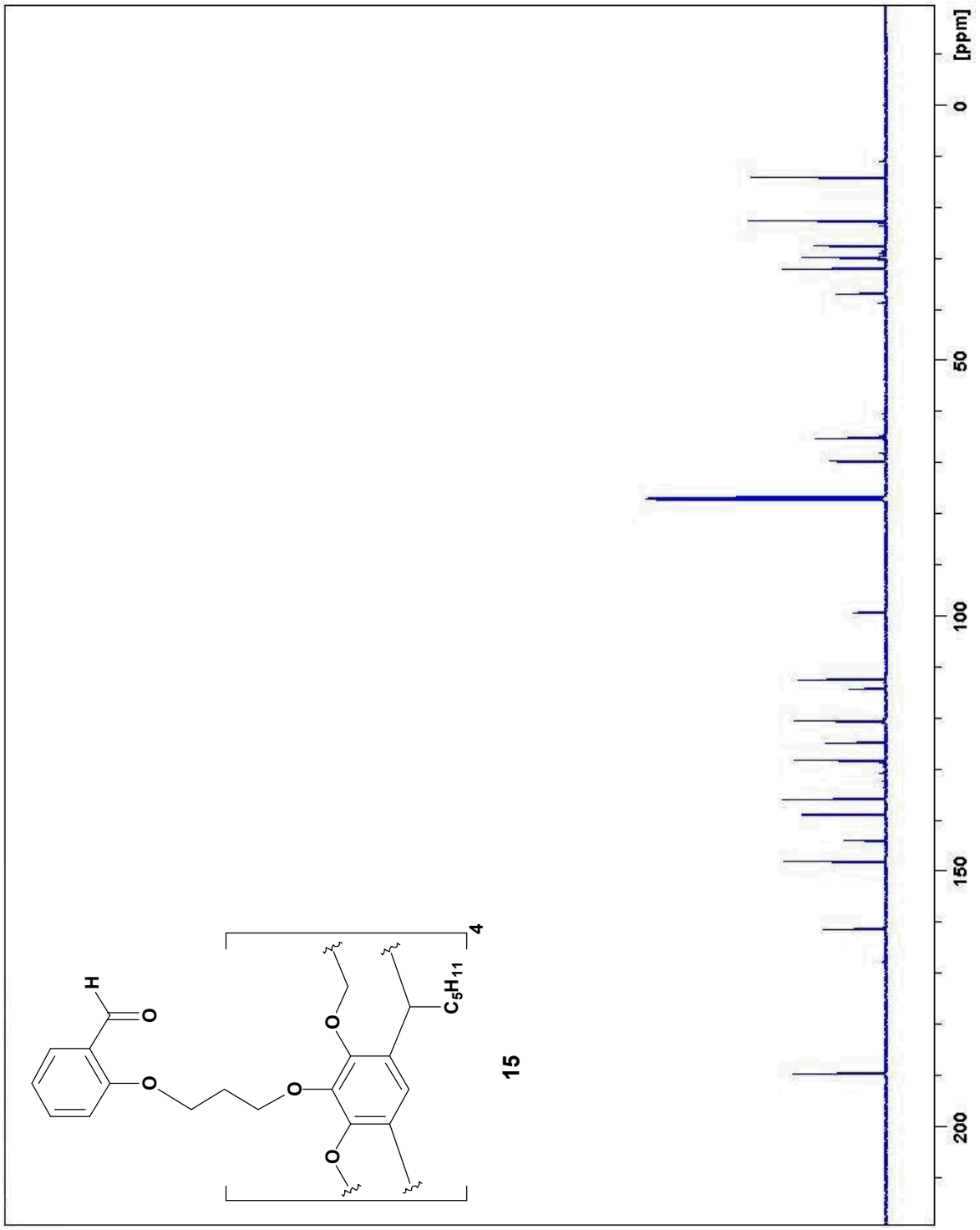

^{13}C NMR spectrum of 15 in $CDCl_3$ (100 MHz)

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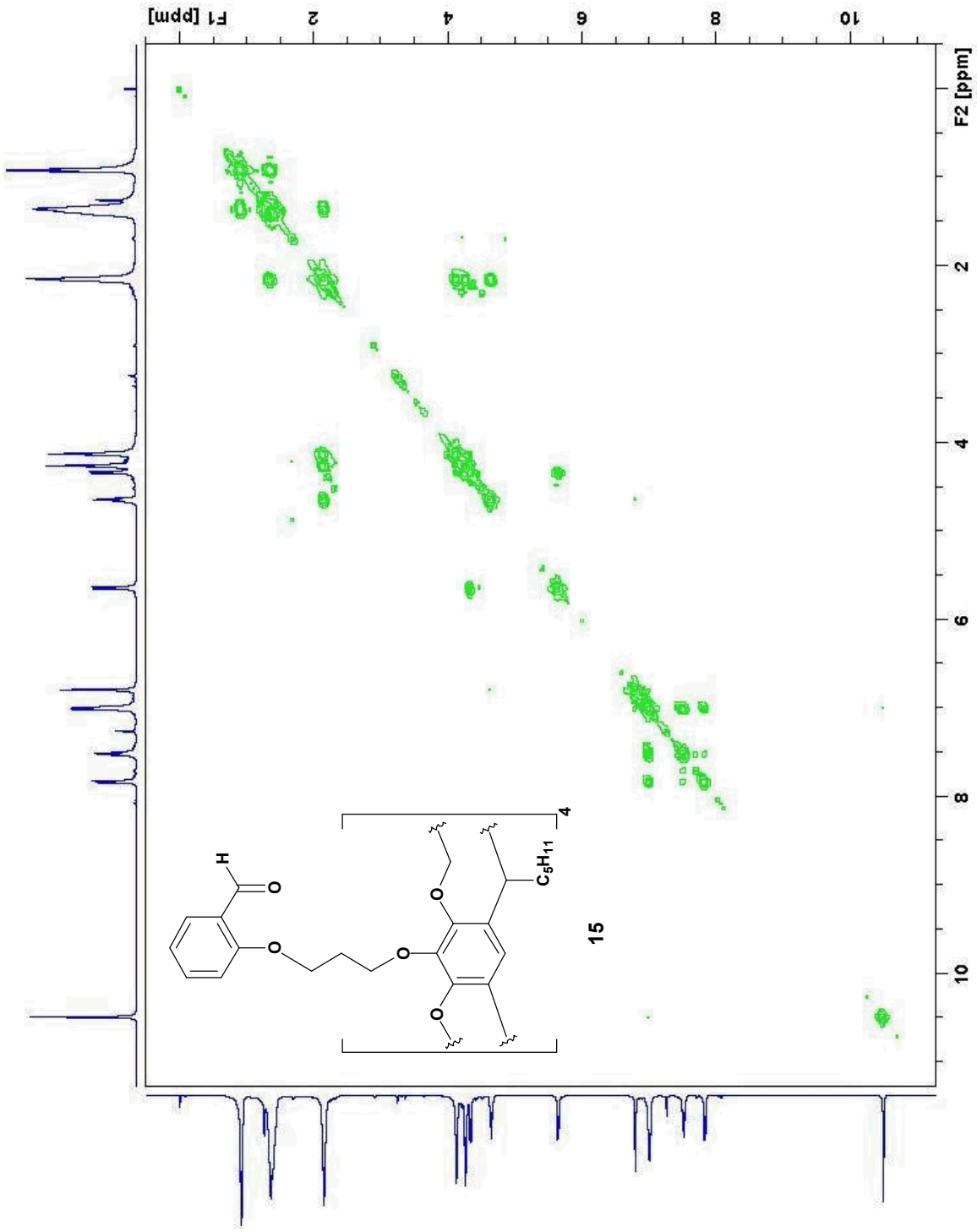

COSY NMR spectrum of 15 in $CDCl_3$ (400 MHz)

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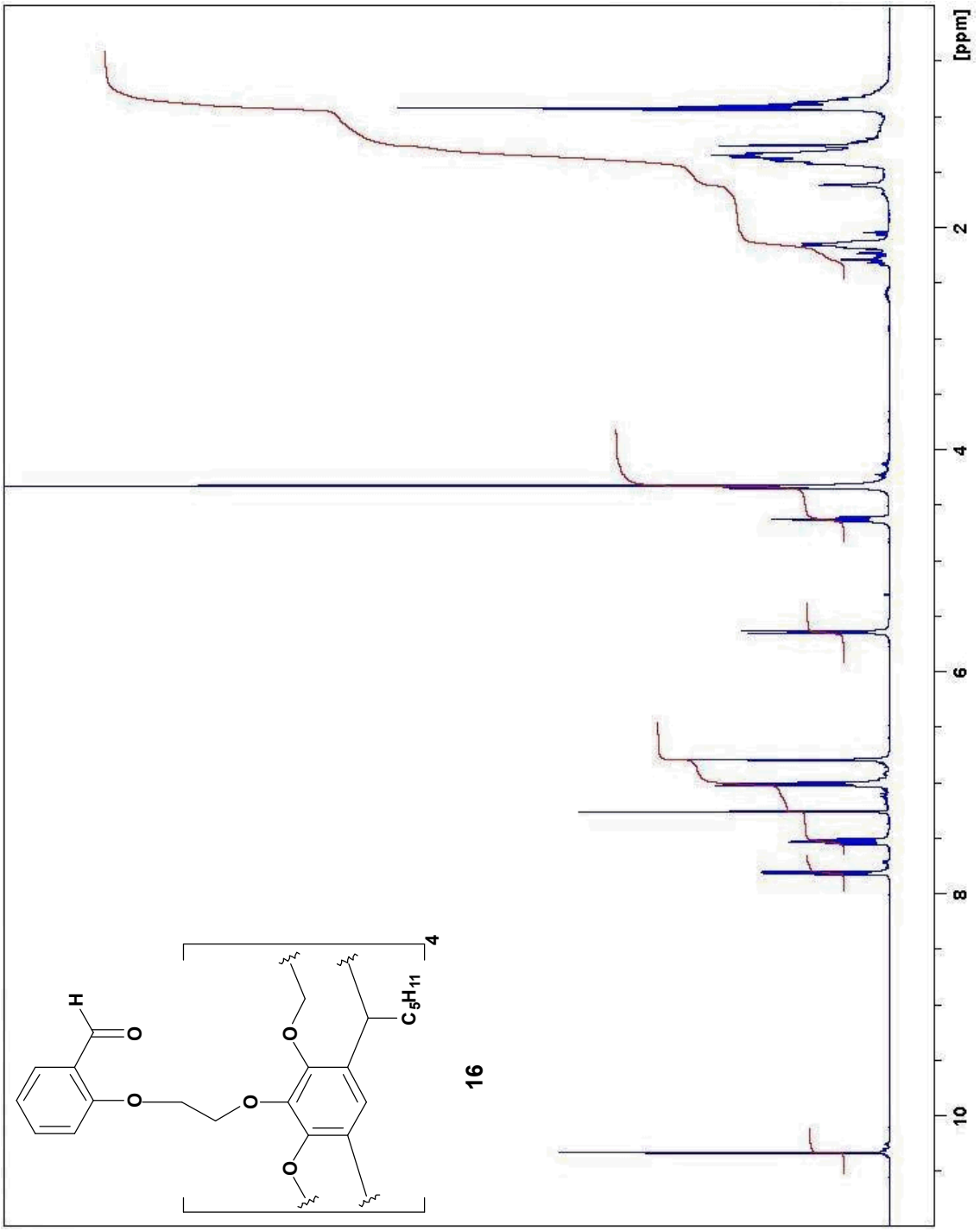

^{1}H NMR spectrum of 16 in $CDCl_3$ (400 MHz)

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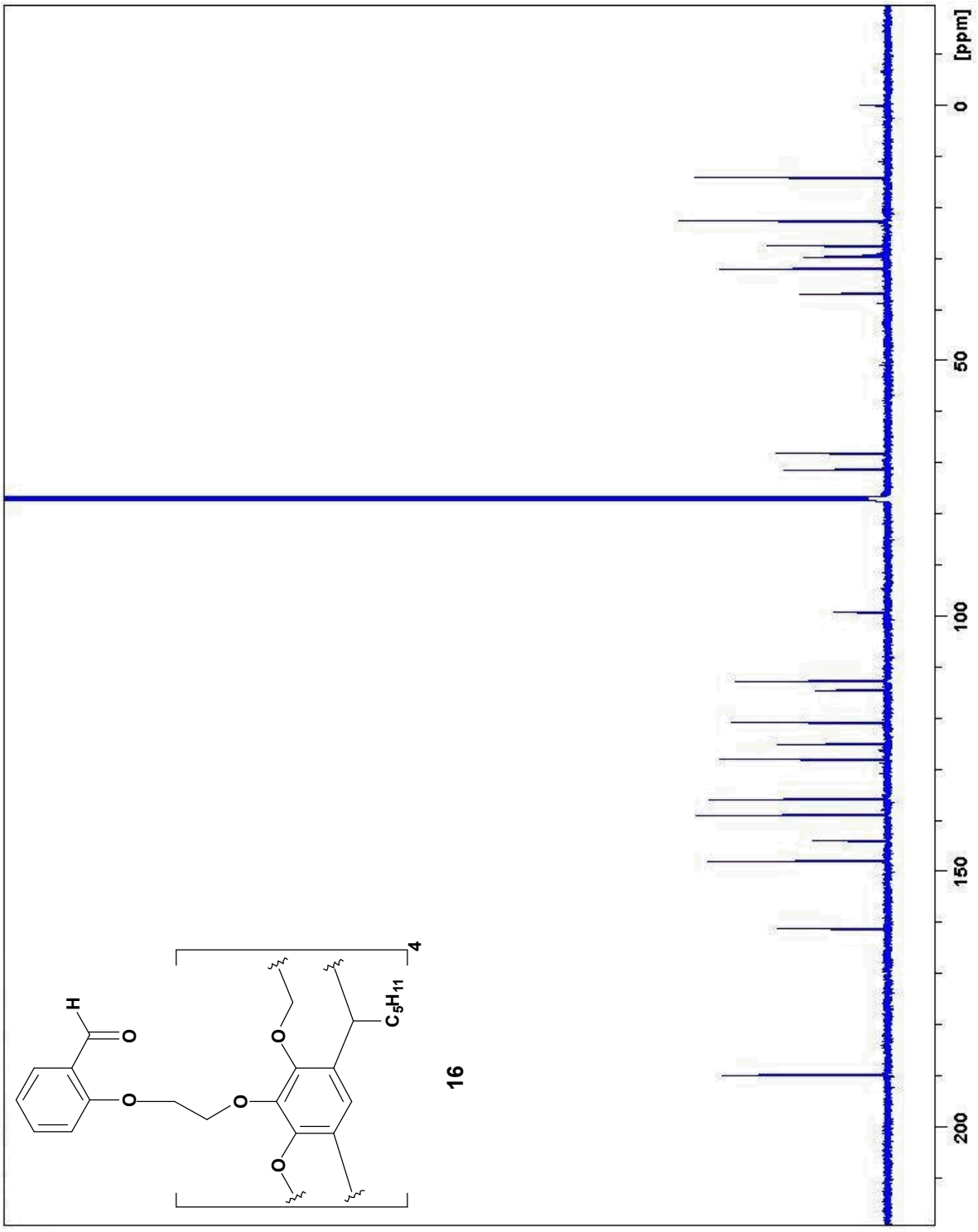

^{13}C NMR spectrum of 16 in $CDCl_3$ (100 MHz)

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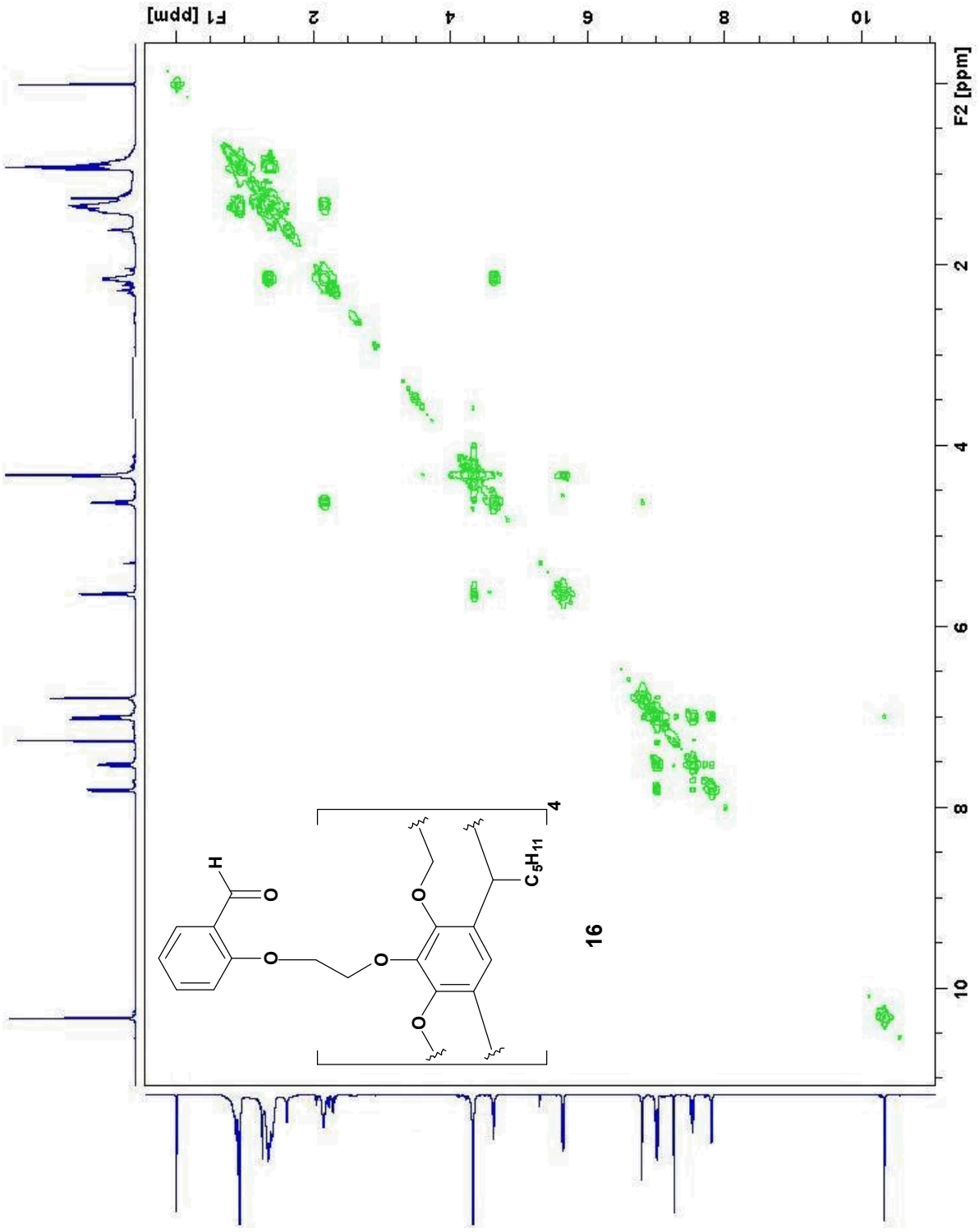

COSY NMR spectrum of 16 in $CDCl_3$ (400 MHz)

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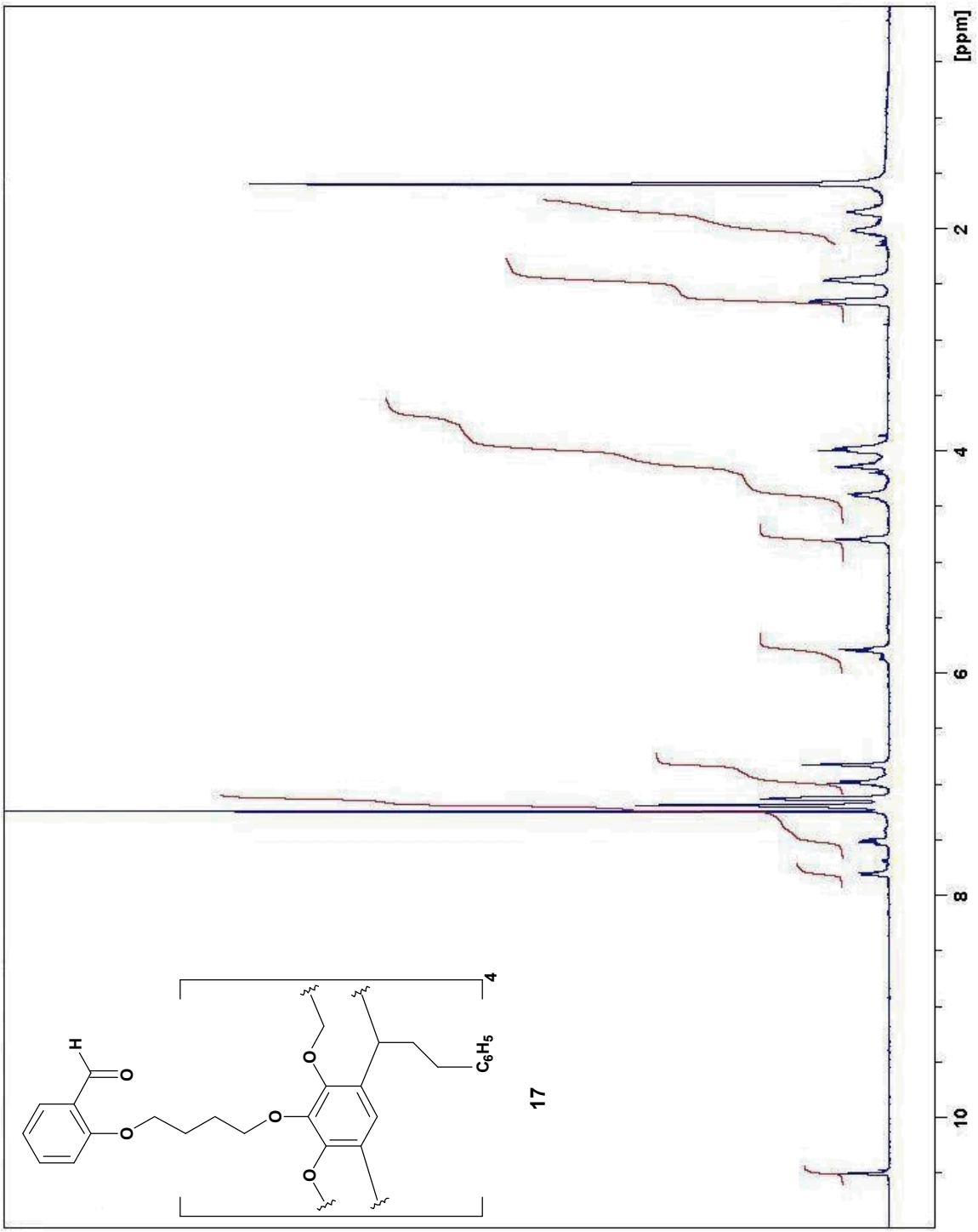

^{1}H NMR spectrum of 17 in $CDCl_3$ (400 MHz)

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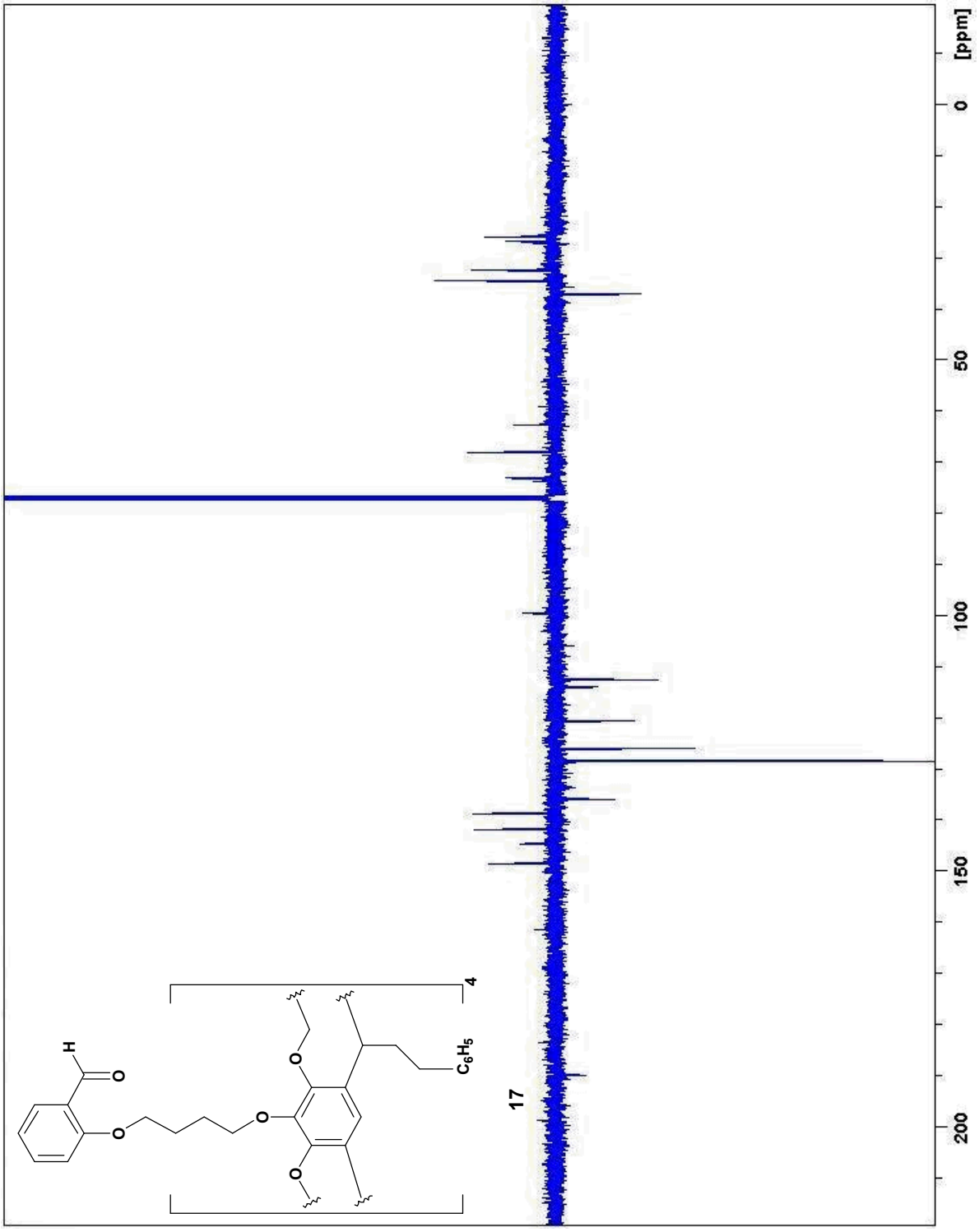

^{13}C APT NMR spectrum of 17 in $CDCl_3$ (100 MHz)

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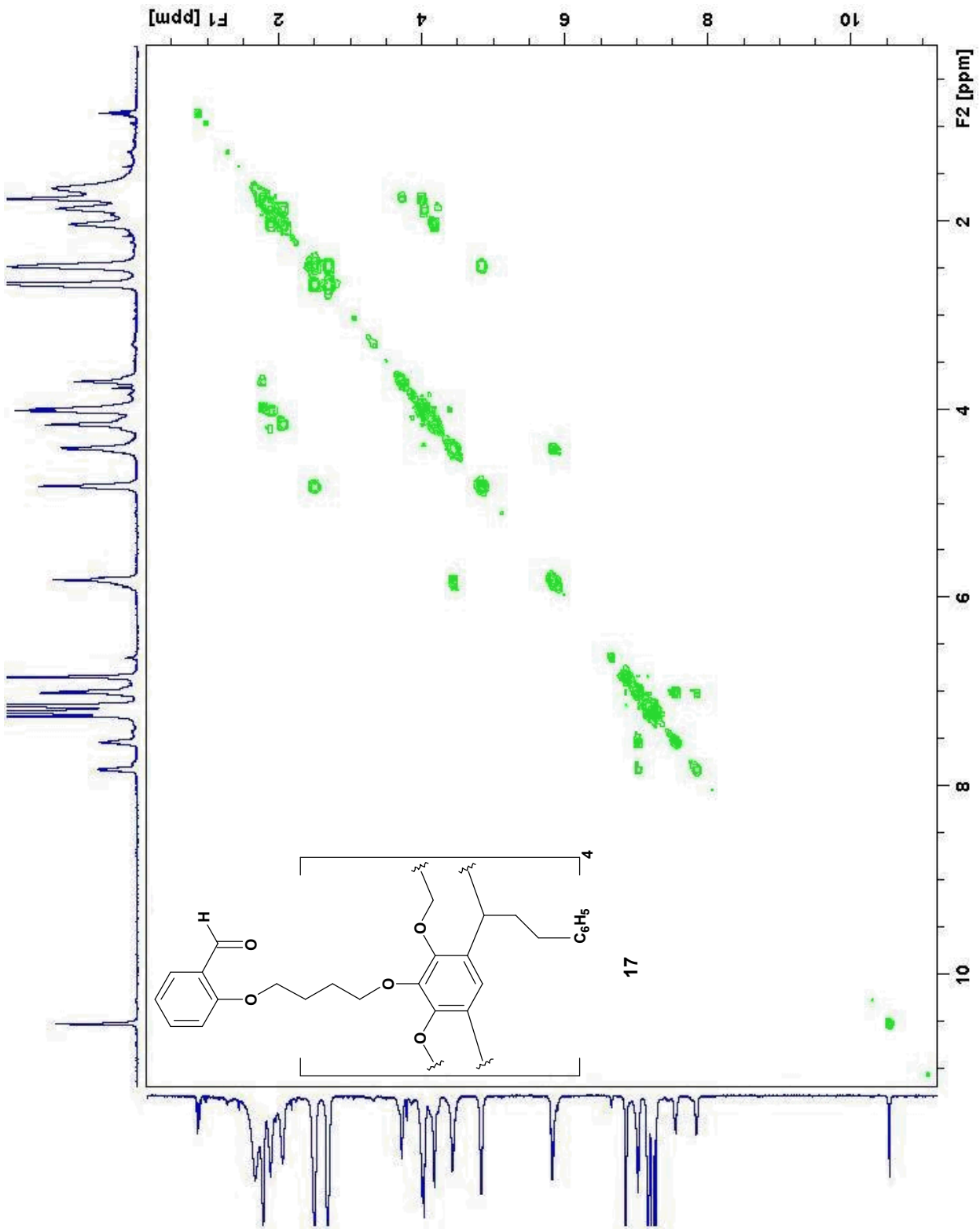

COSY NMR spectrum of 17 in $CDCl_3$ (400 MHz)

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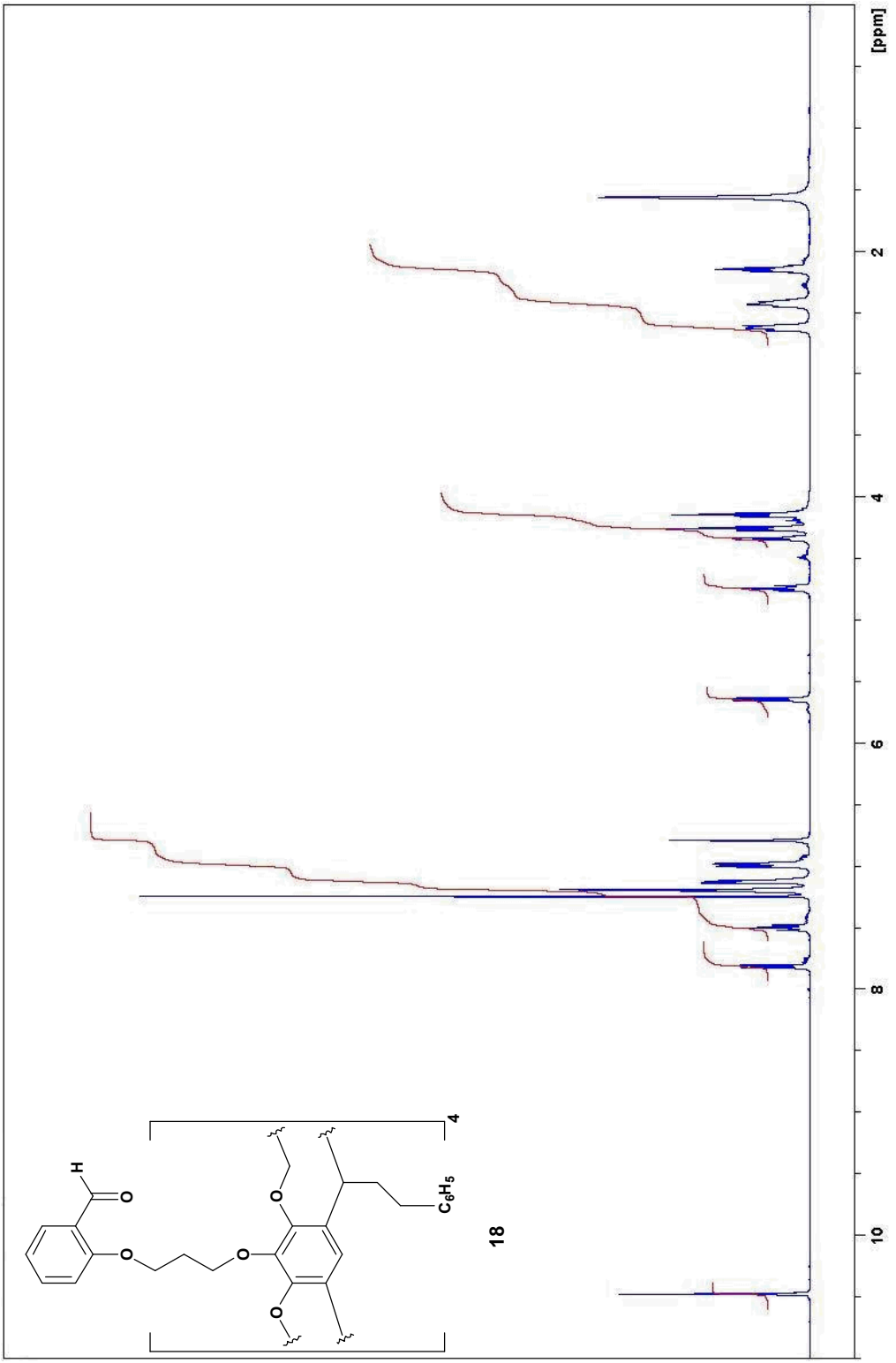

^{1}H NMR spectrum of 18 in $CDCl_3$ (400 MHz)

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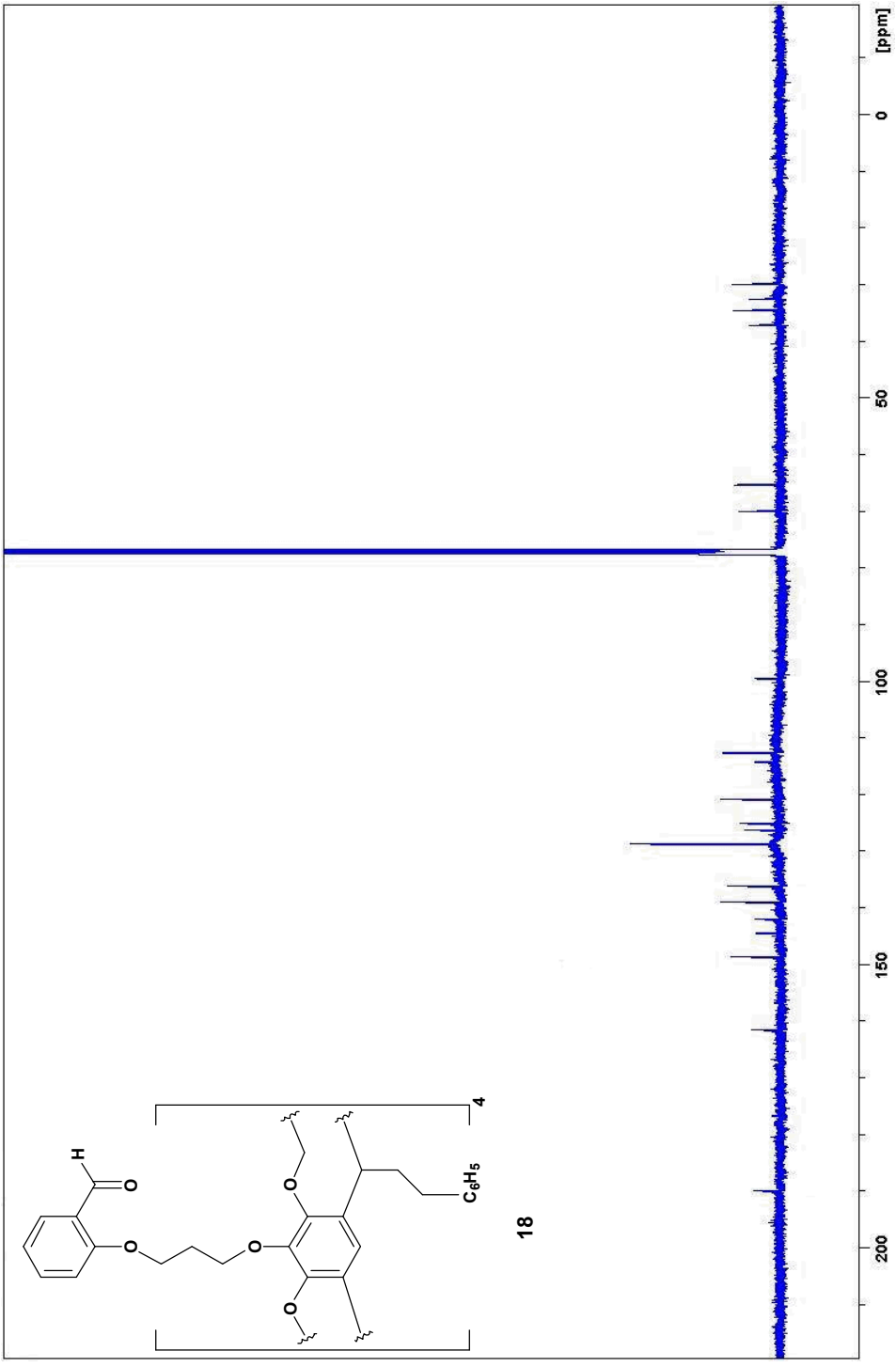

^{13}C NMR spectrum of 18 in $CDCl_3$ (100 MHz)

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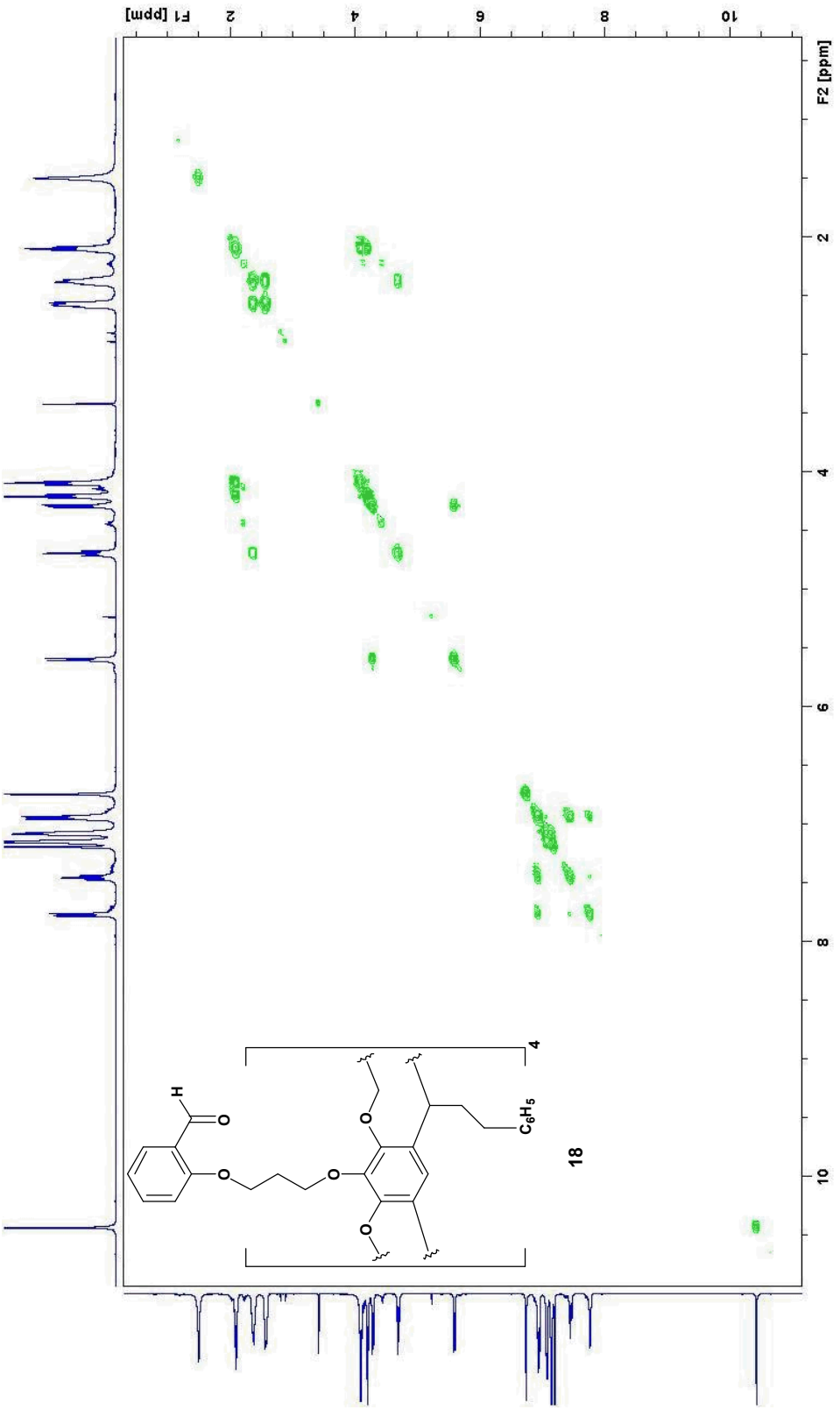

COSY NMR spectrum of 18 in $CDCl_3$ (400 MHz)

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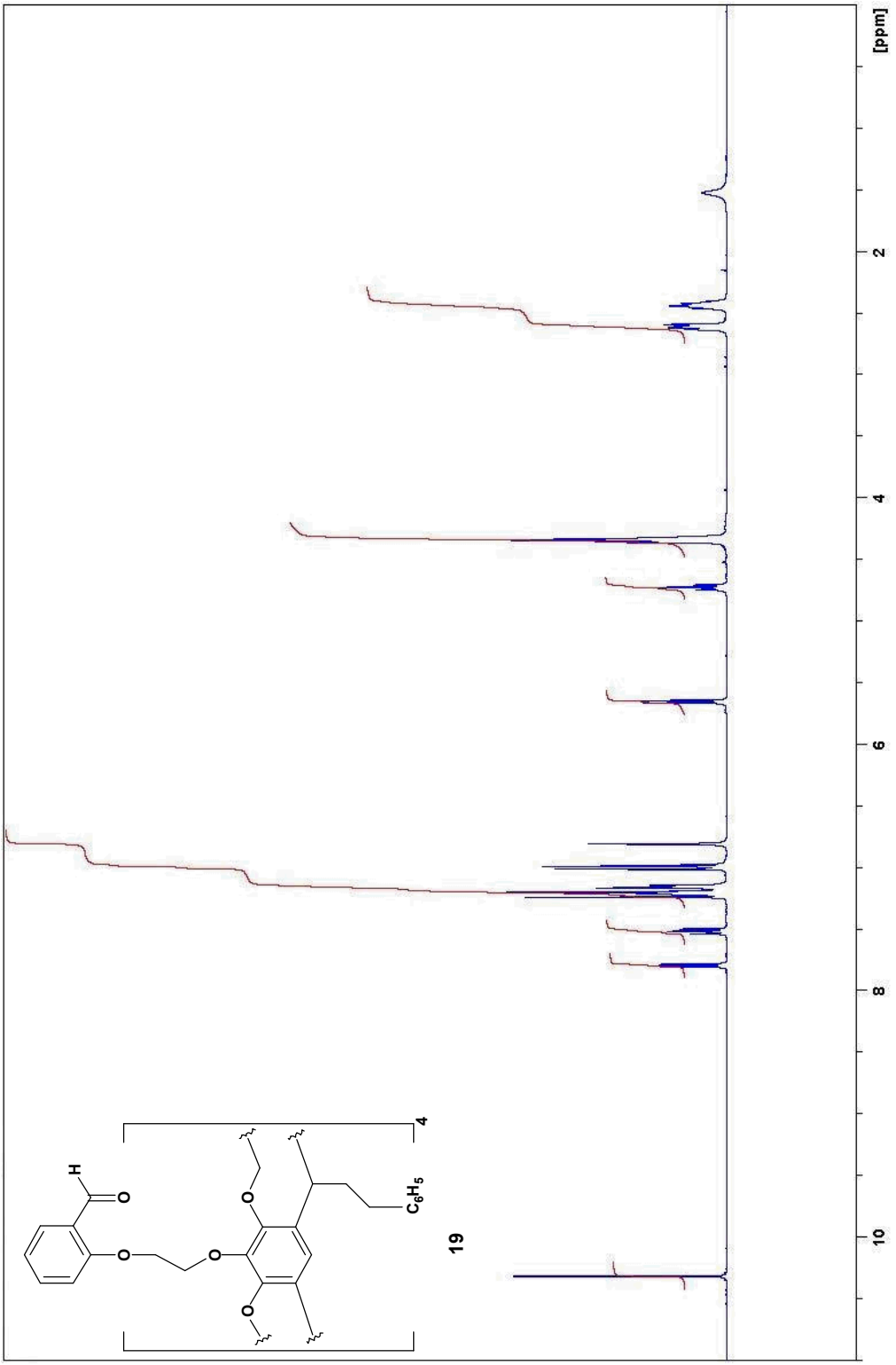

^{1}H NMR spectrum of 19 in $CDCl_3$ (400 MHz)

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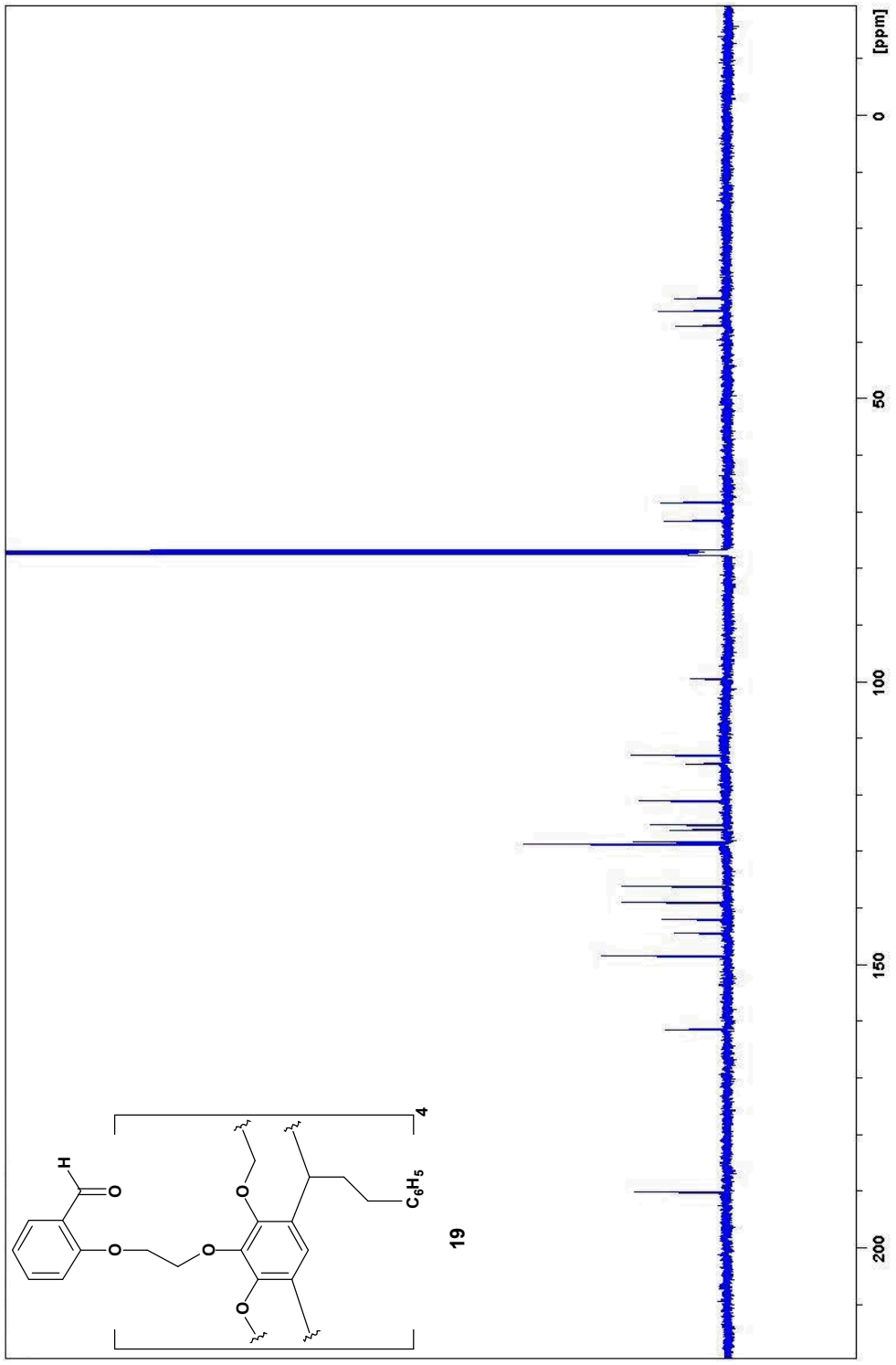

^{13}C NMR spectrum of 19 in $CDCl_3$ (100 MHz)

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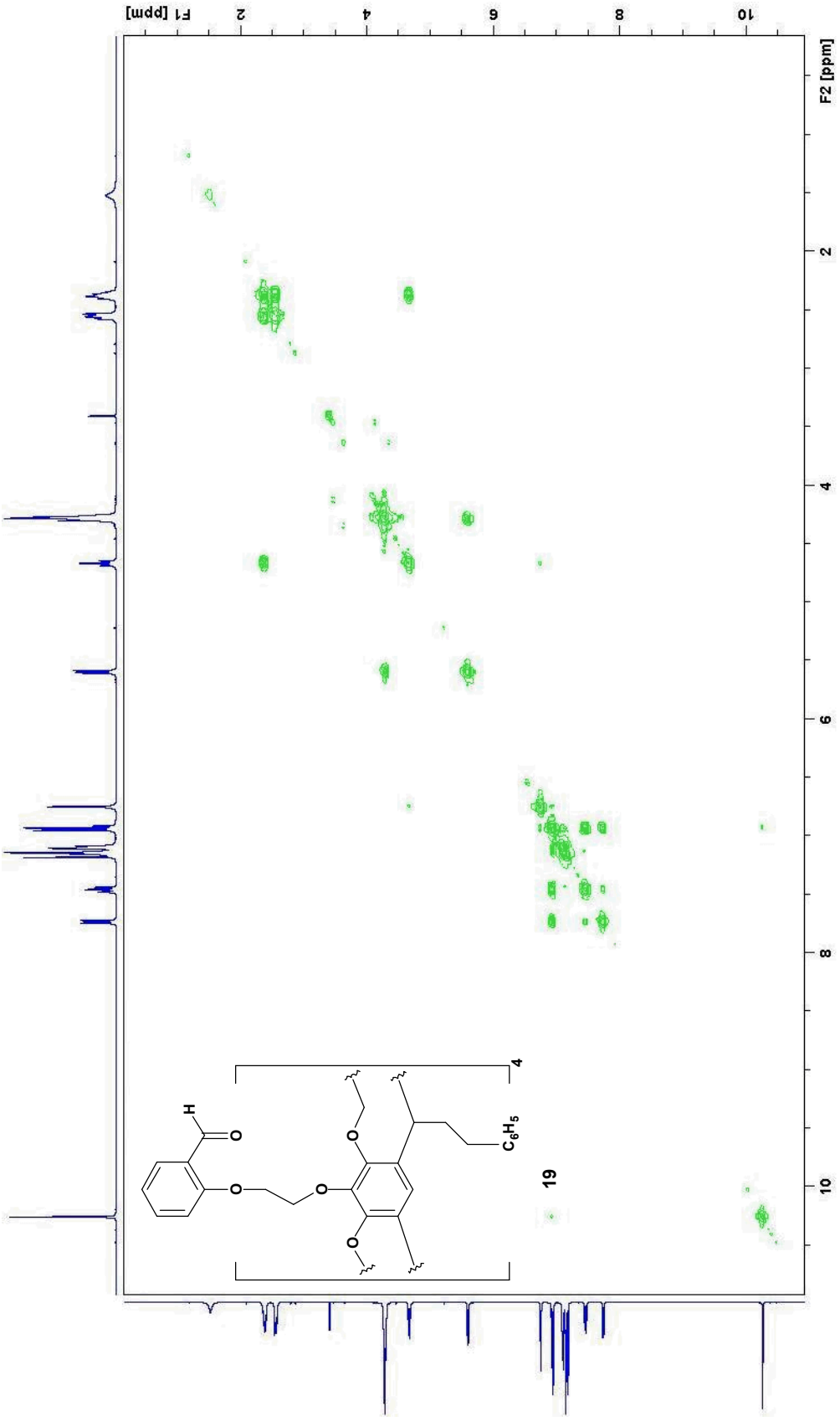

COSY NMR spectrum of 19 in $CDCl_3$ (400 MHz)

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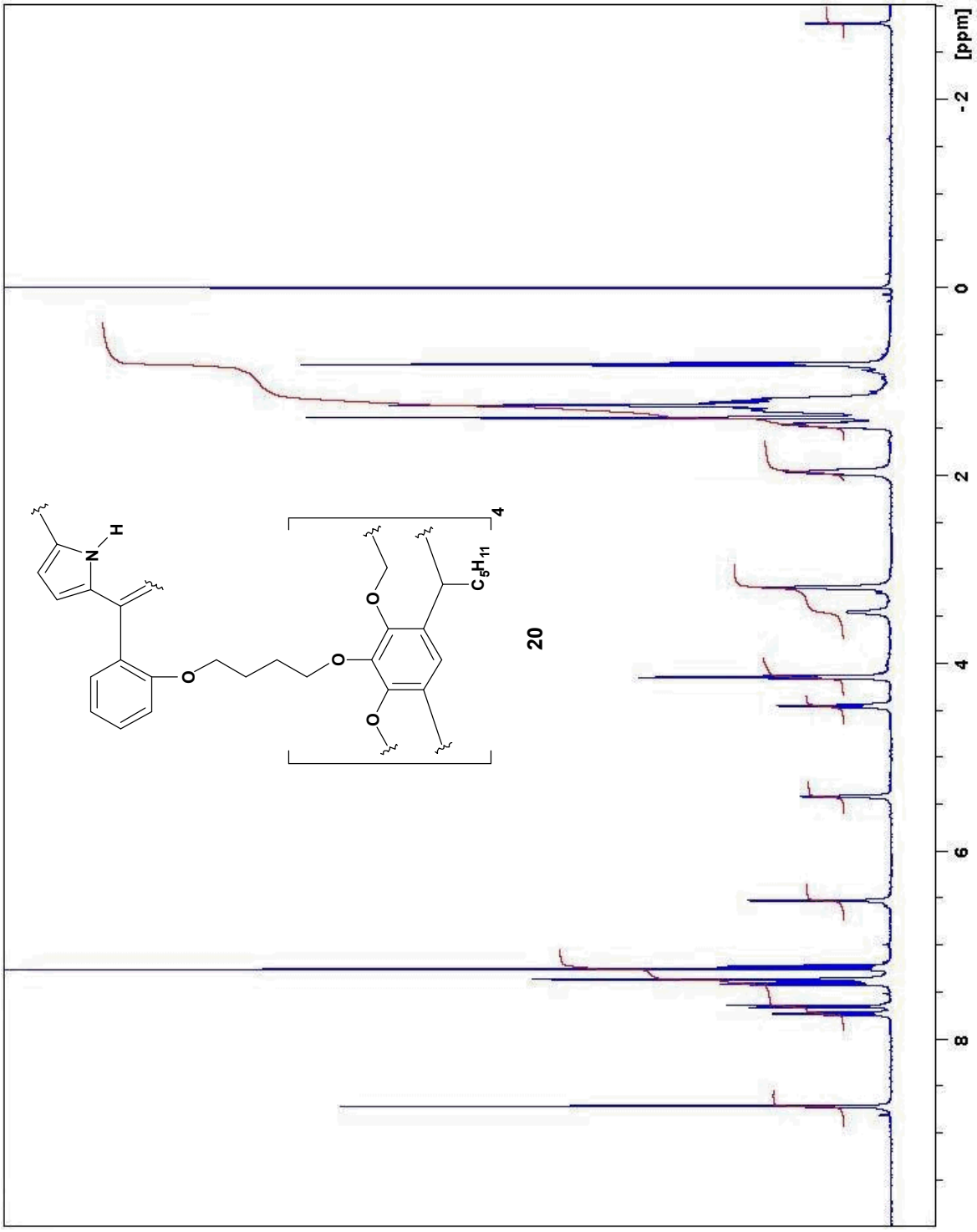

^{1}H NMR spectrum of 20 in $CDCl_3$ (400 MHz)

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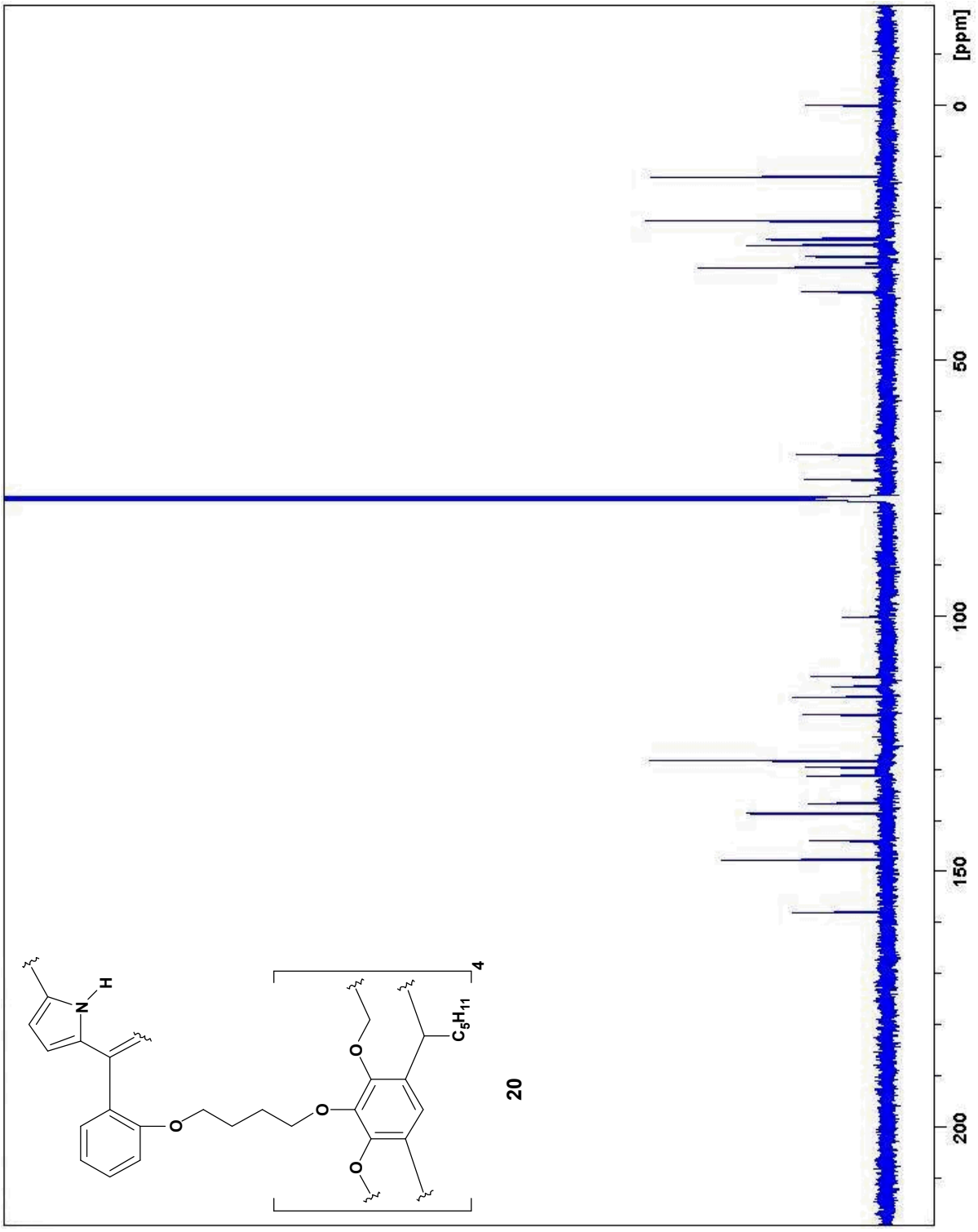

^{13}C NMR spectrum of 20 in $CDCl_3$ (100 MHz)

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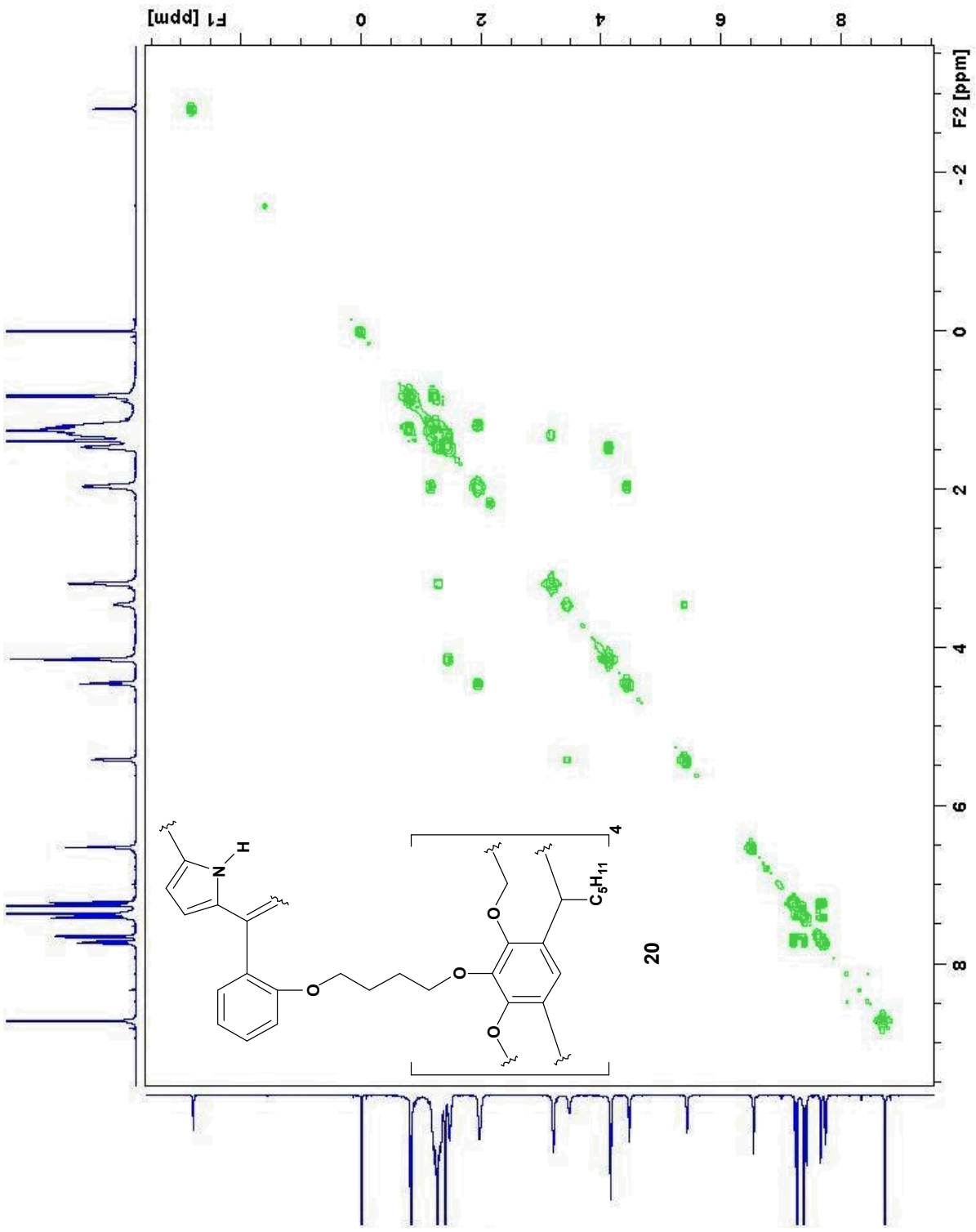

COSY NMR spectrum of 20 in $CDCl_3$ (400 MHz)

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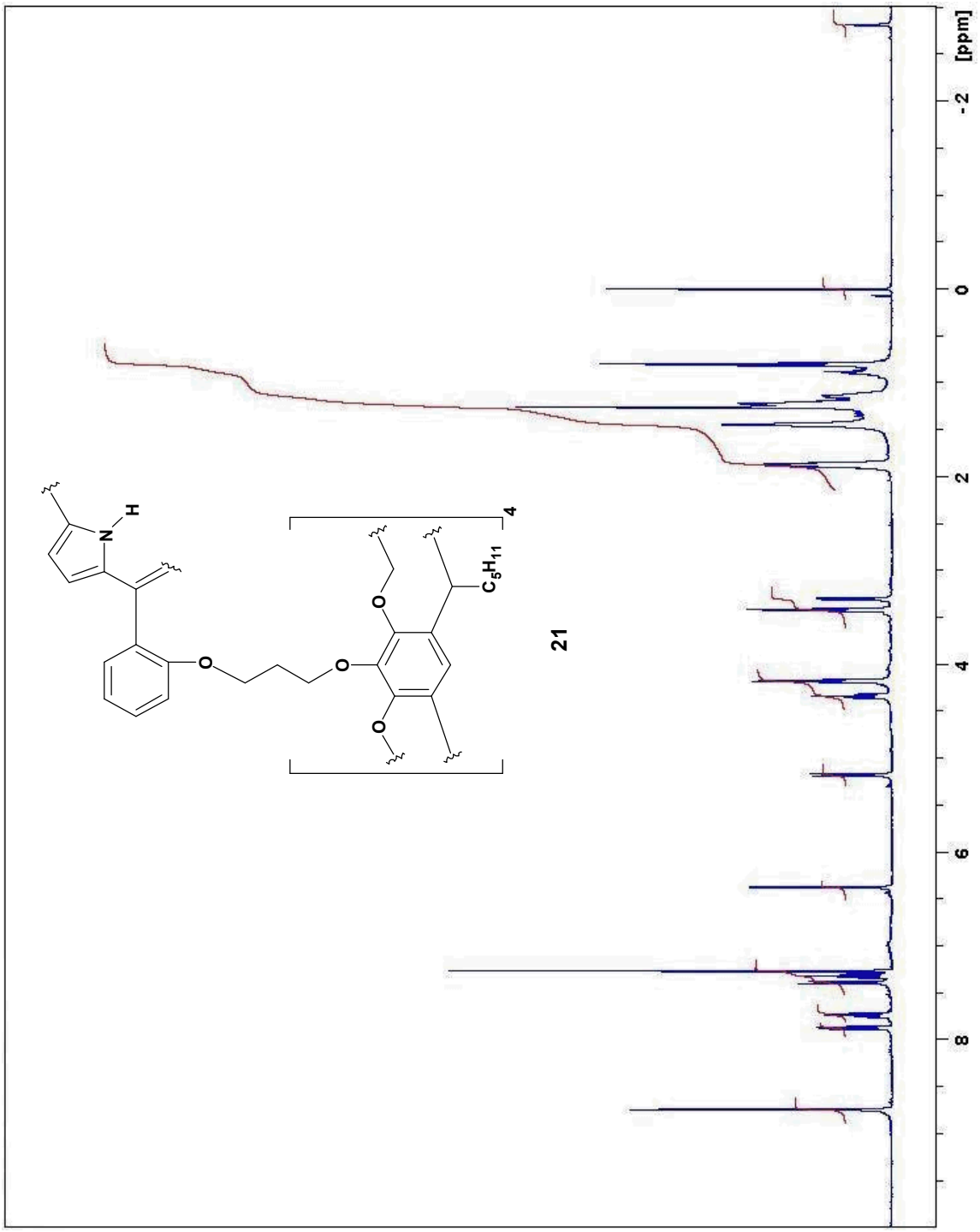

^{1}H NMR spectrum of 21 in $CDCl_3$ (400 MHz)

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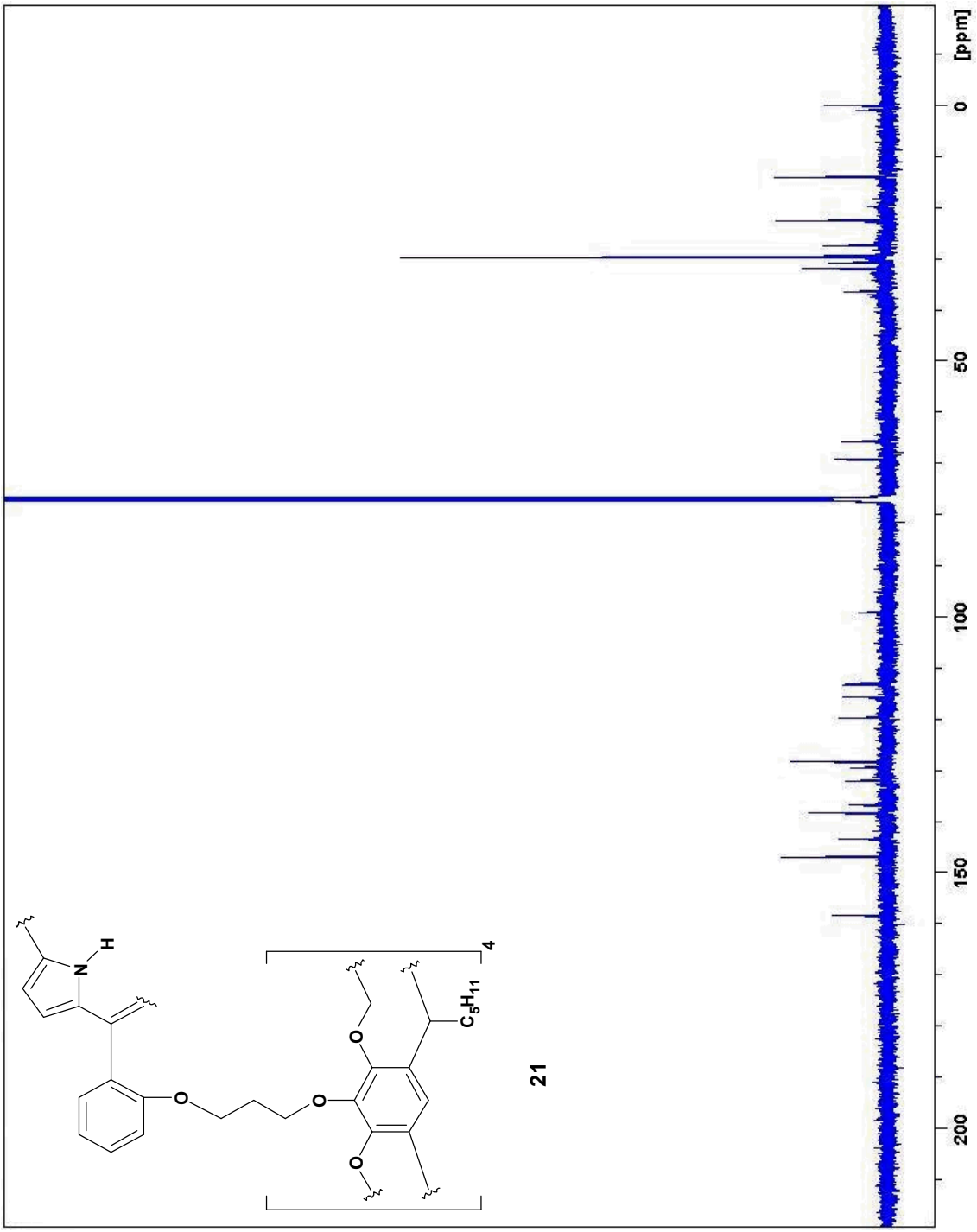

^{13}C NMR spectrum of 21 in $CDCl_3$ (100 MHz)

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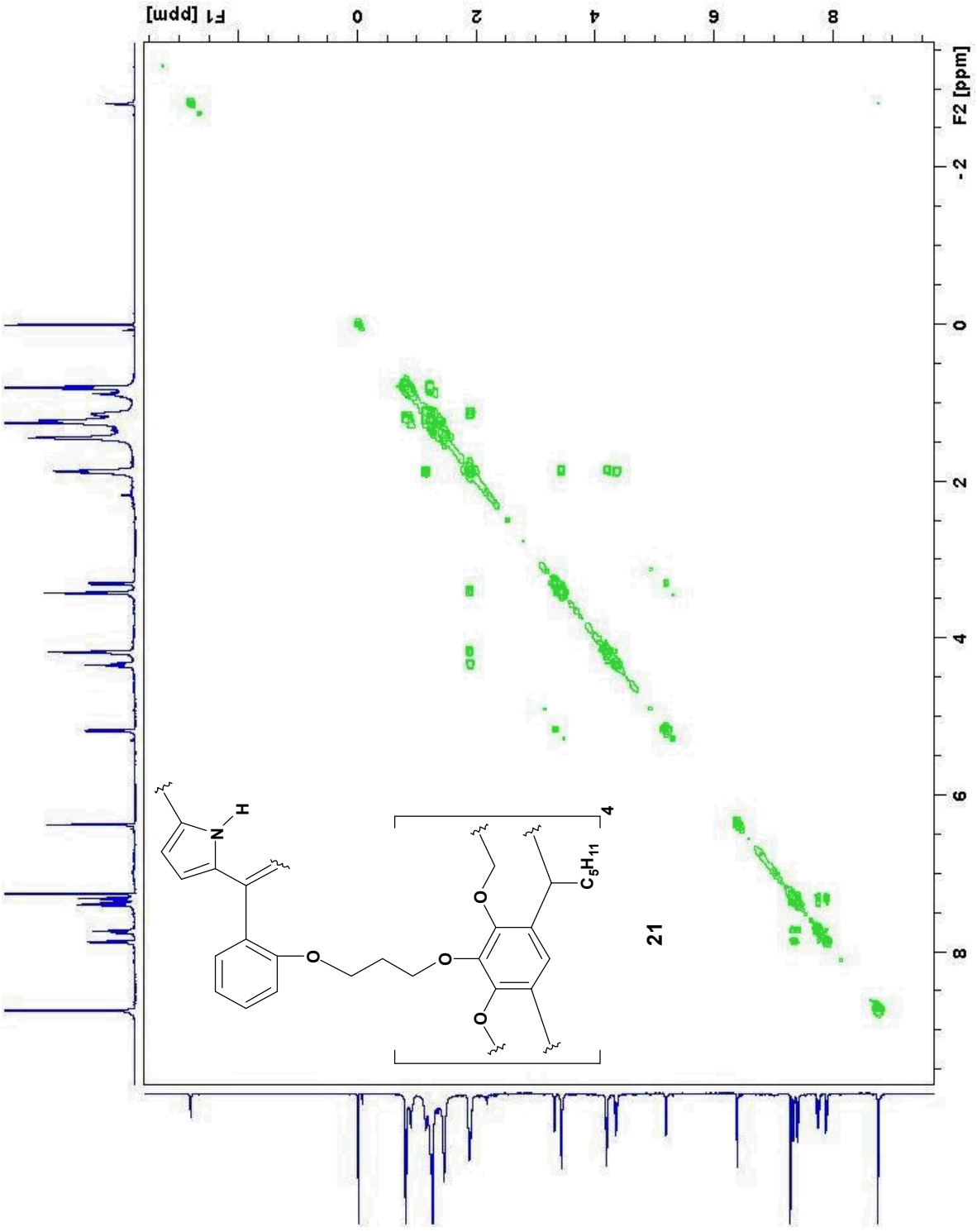

COSY NMR spectrum of 21 in $CDCl_3$ (400 MHz)

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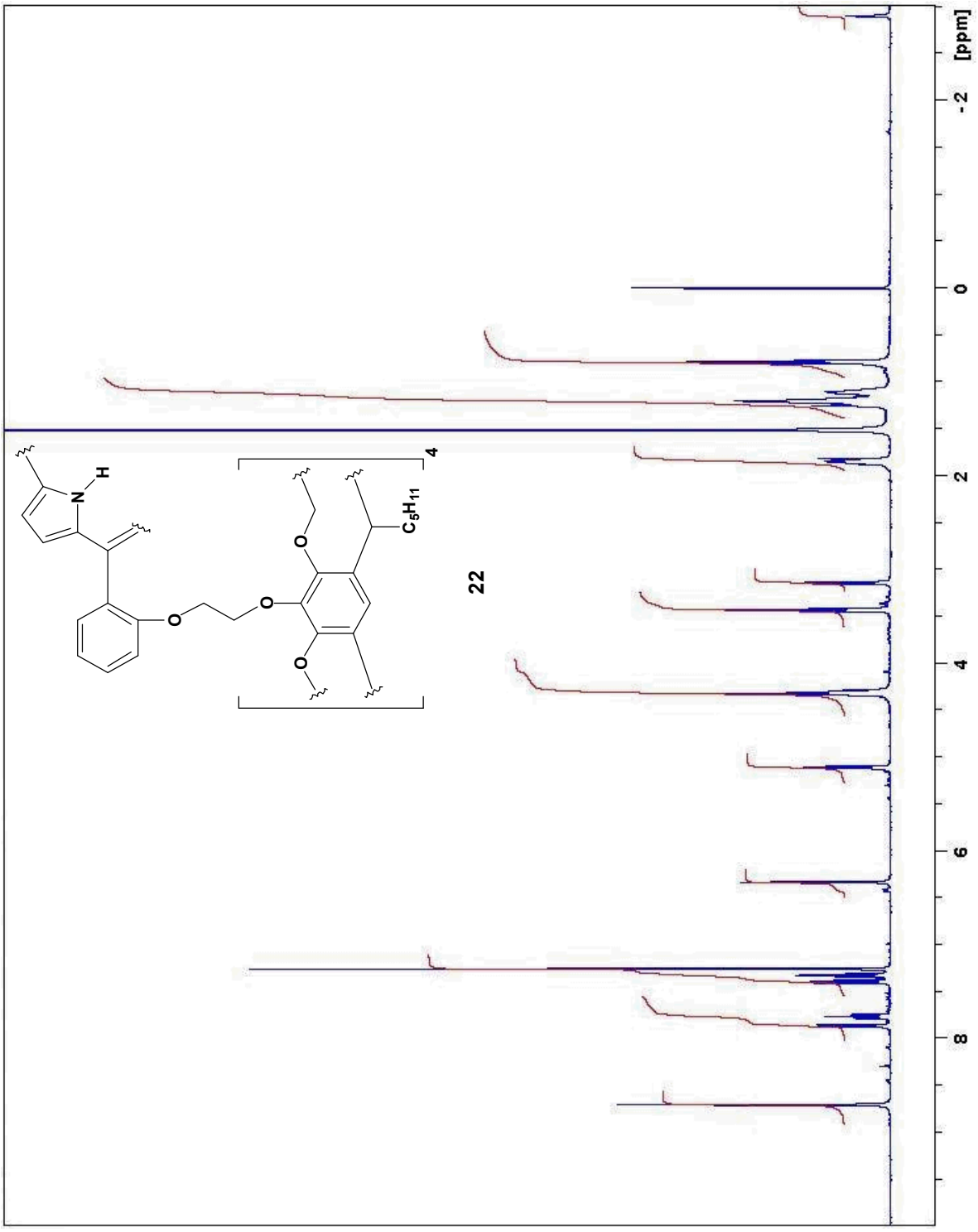

^{1}H NMR spectrum of 22 in $CDCl_3$ (400 MHz)

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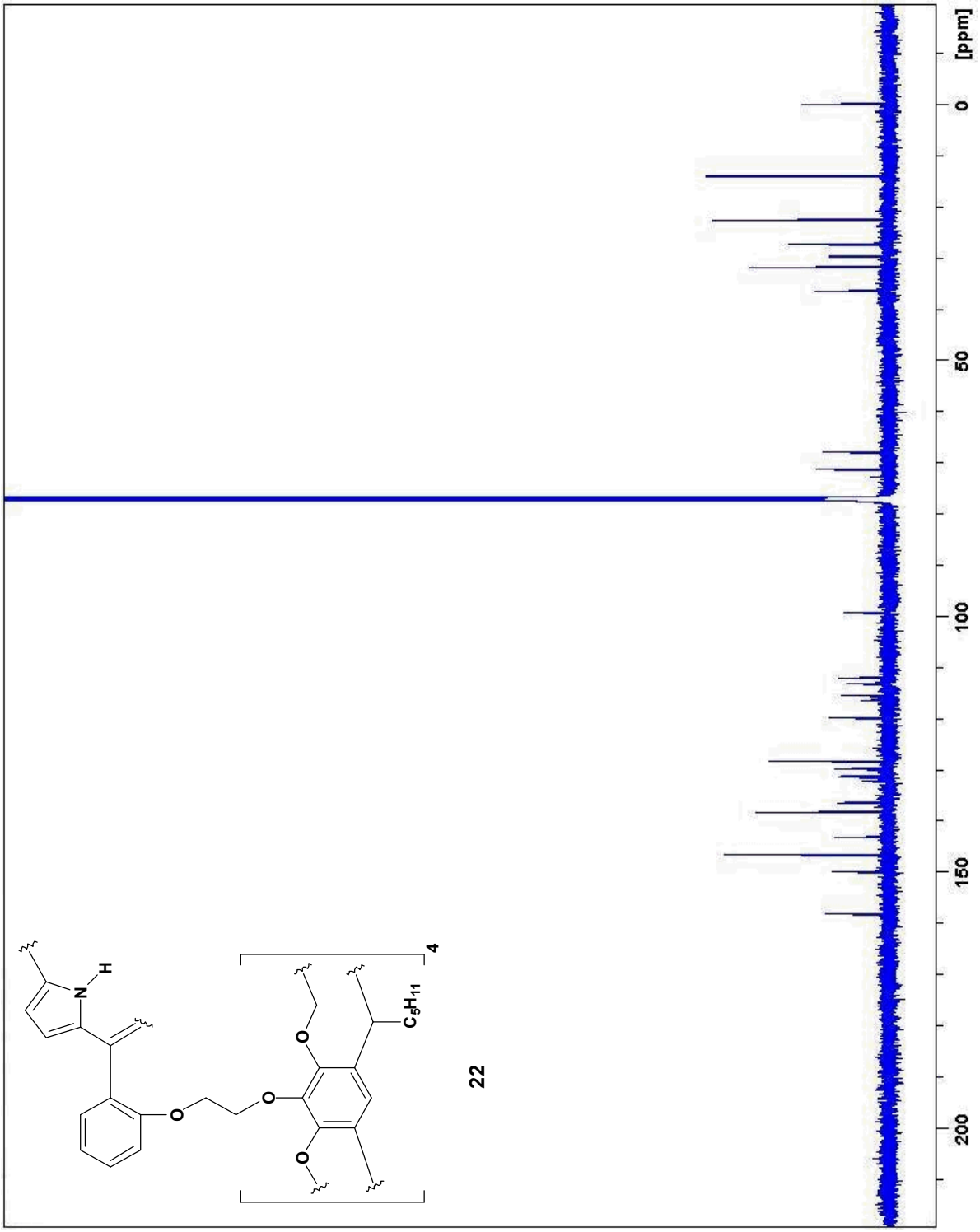

^{13}C NMR spectrum of 22 in $CDCl_3$ (100 MHz)

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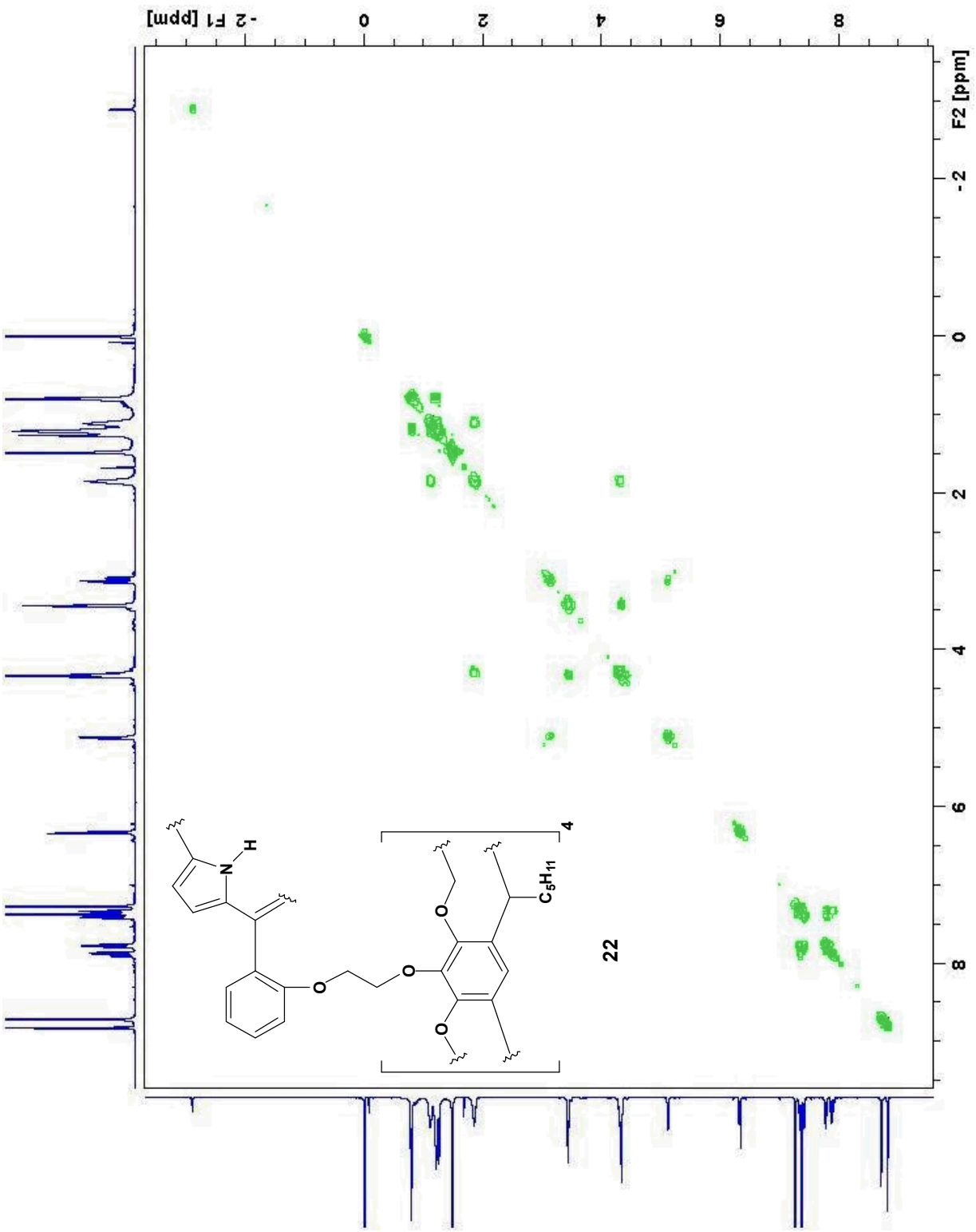

COSY NMR spectrum of 22 in $CDCl_3$ (400 MHz)

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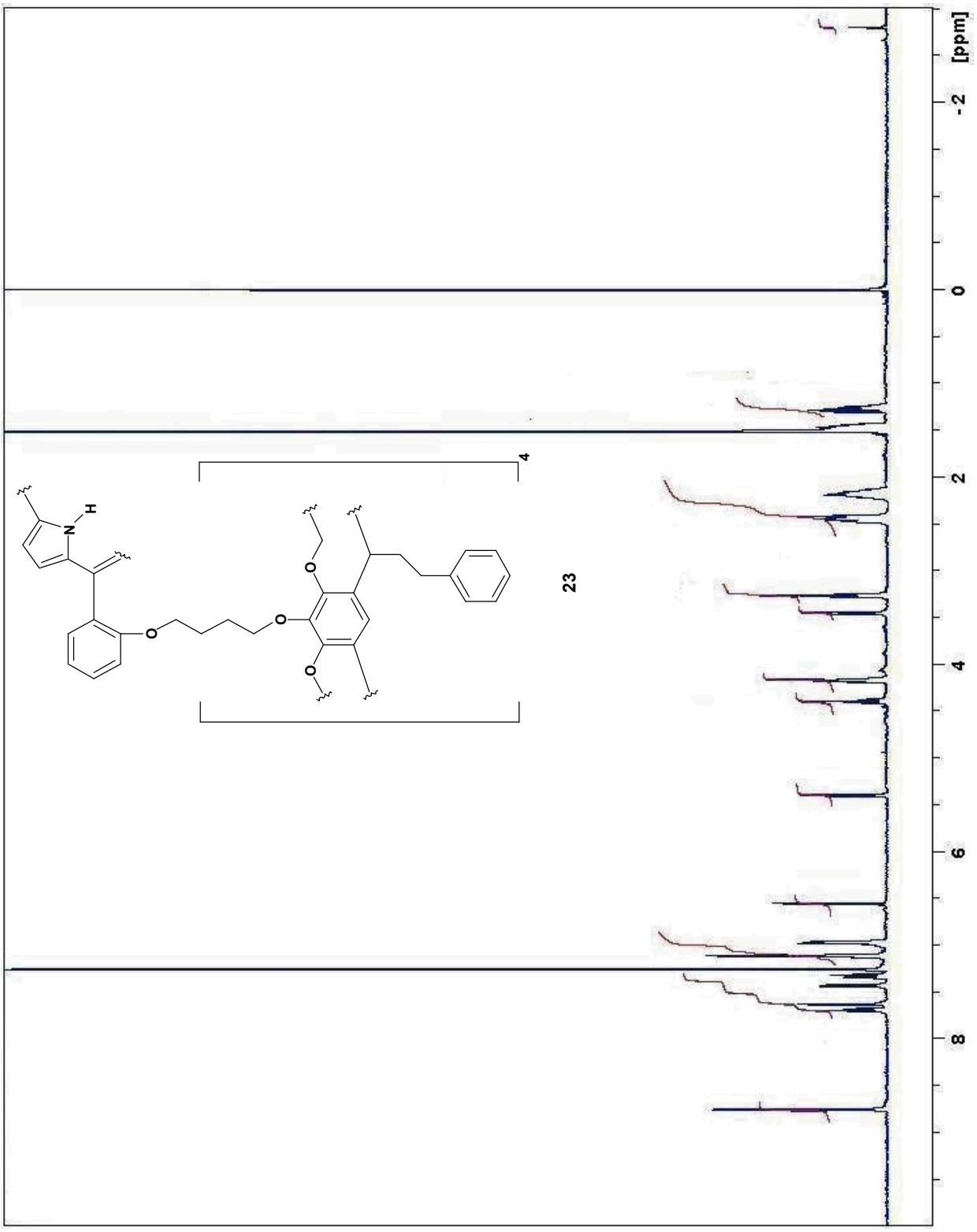

^{1}H NMR spectrum of 23 in $CDCl_3$ (400 MHz)

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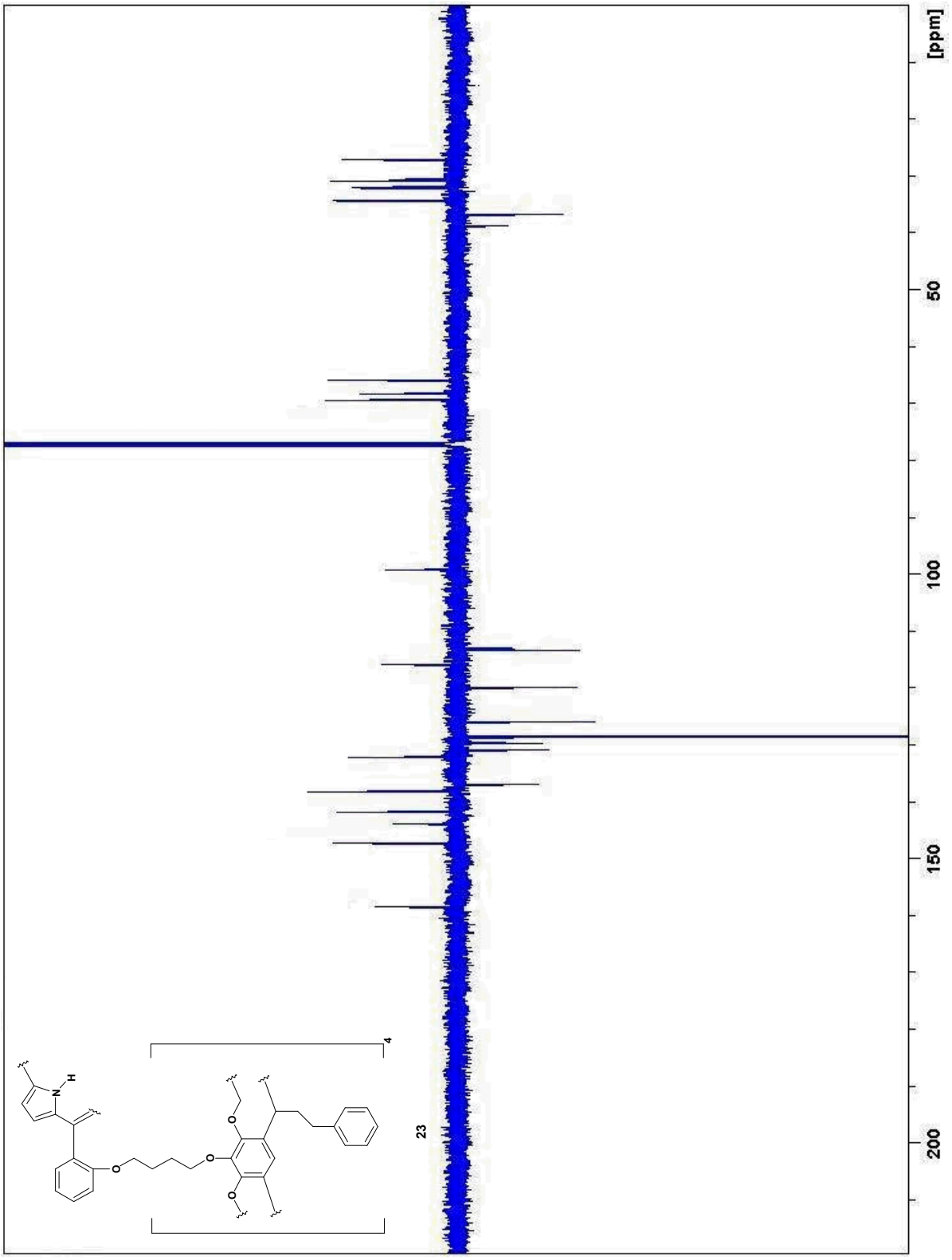

^{13}C APT NMR spectrum of 23 in $CDCl_3$ (100 MHz)

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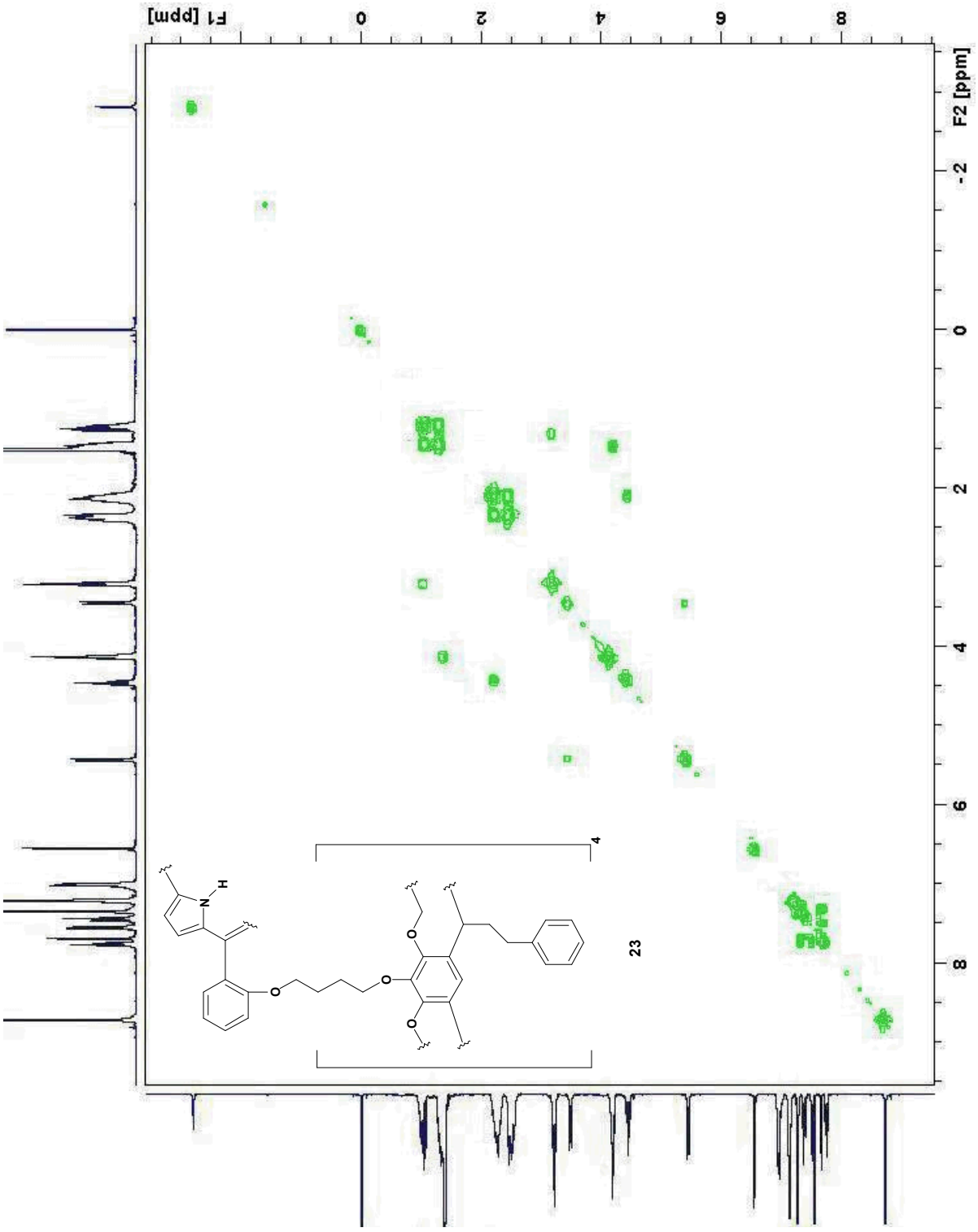

COSY NMR spectrum of 23 in $CDCl_3$ (400 MHz)

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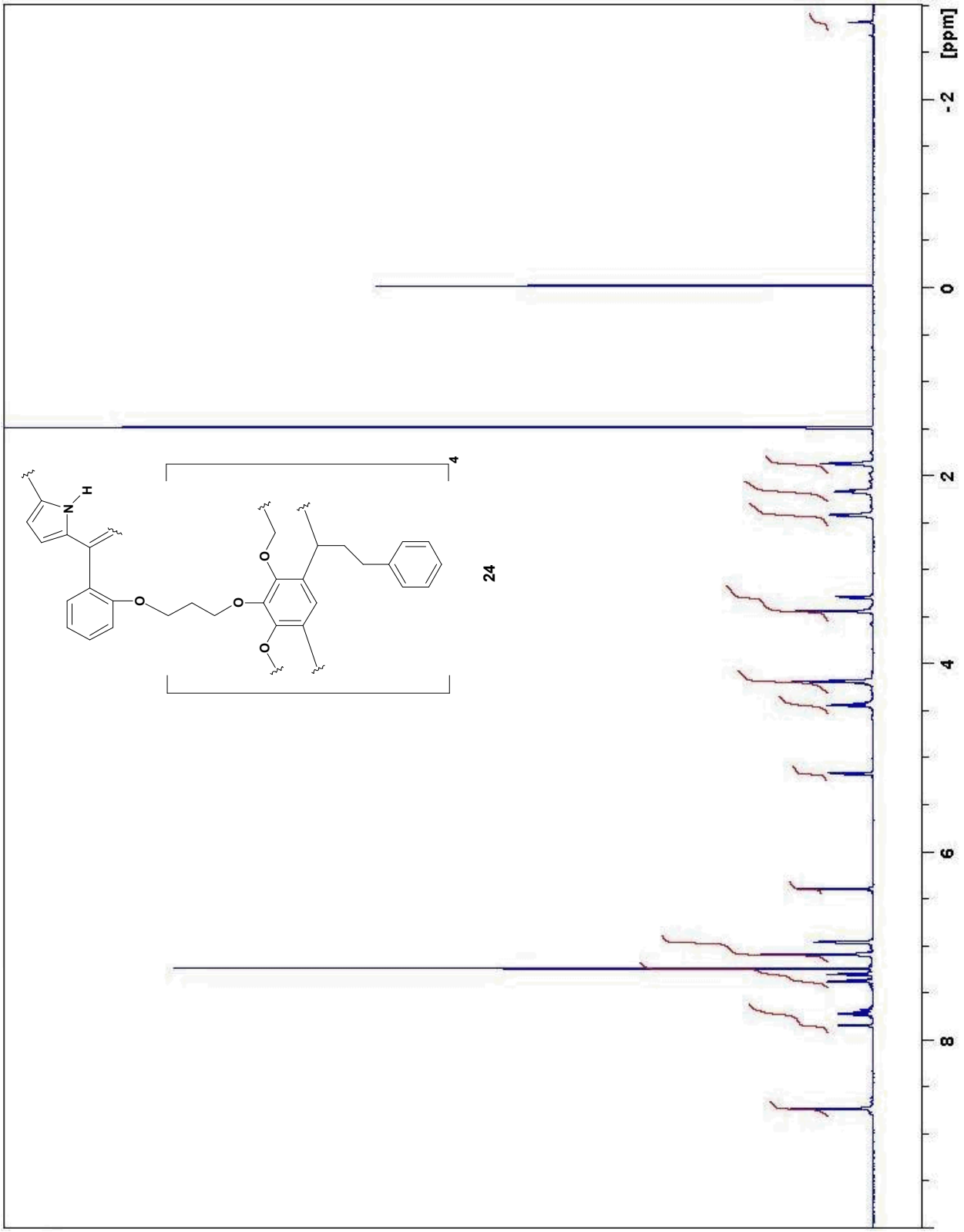

^{1}H NMR spectrum of 24 in $CDCl_3$ (400 MHz)

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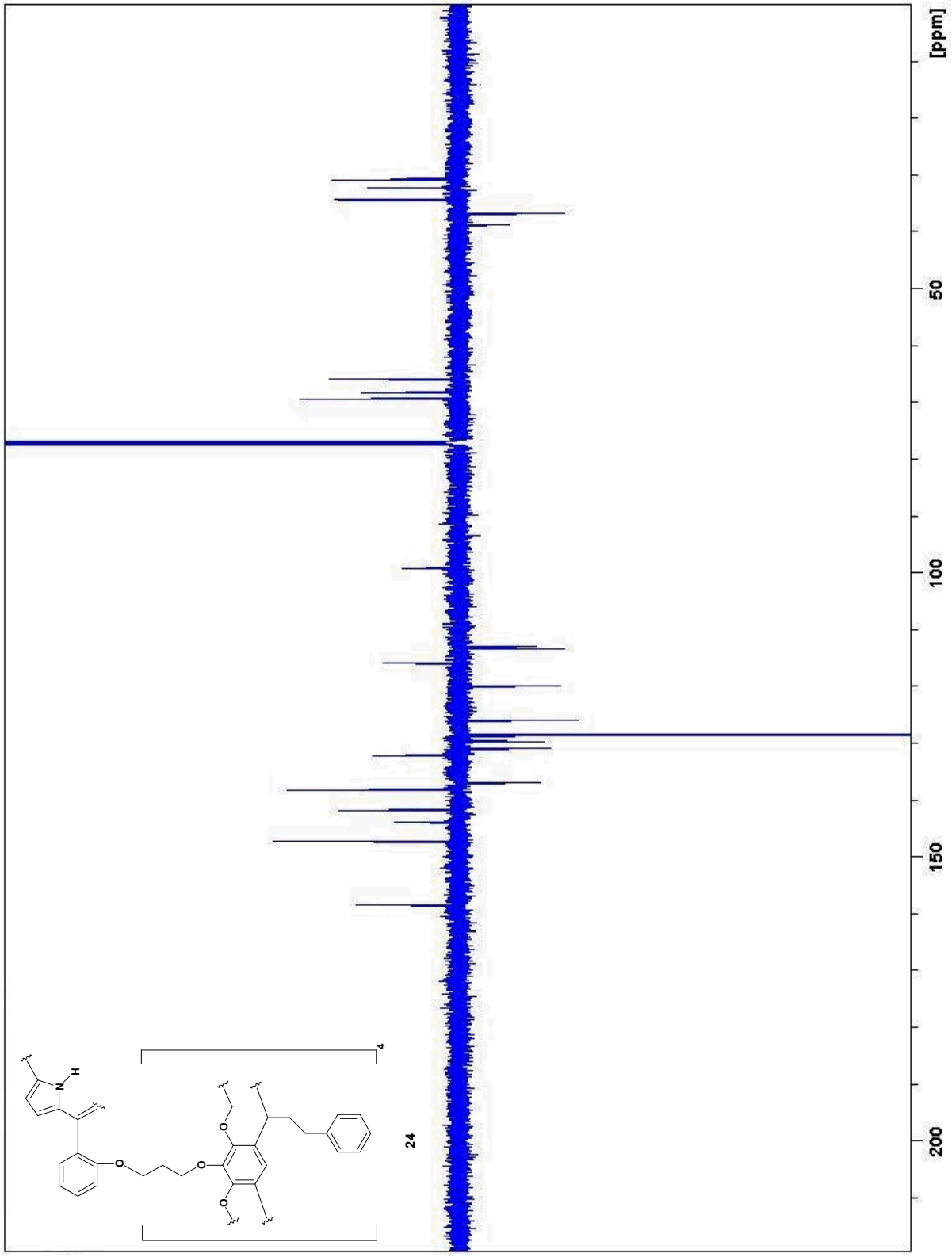

^{13}C APT NMR spectrum of 24 in $CDCl_3$ (100 MHz)

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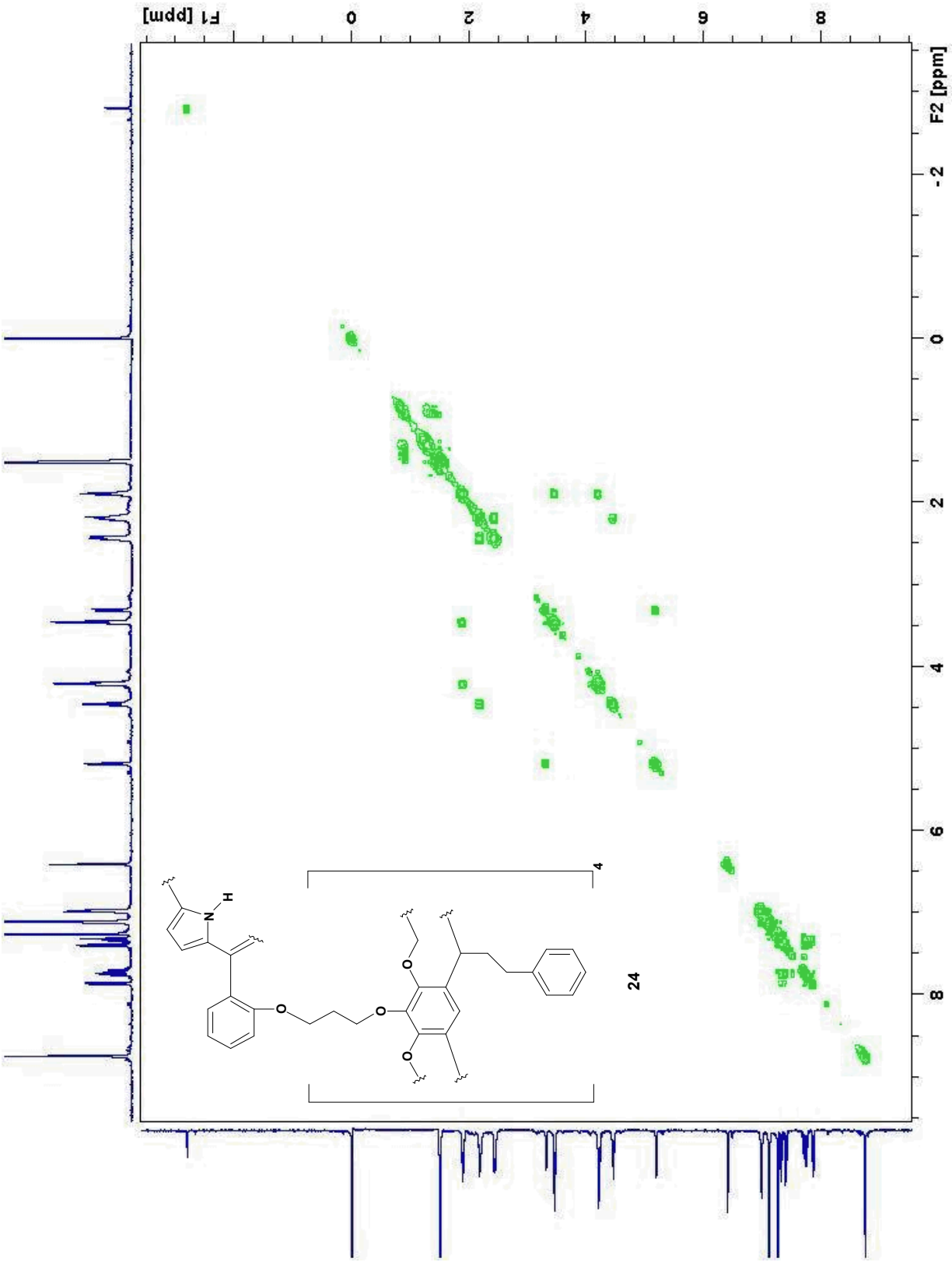

COSY NMR spectrum of 24 in $CDCl_3$ (400 MHz)

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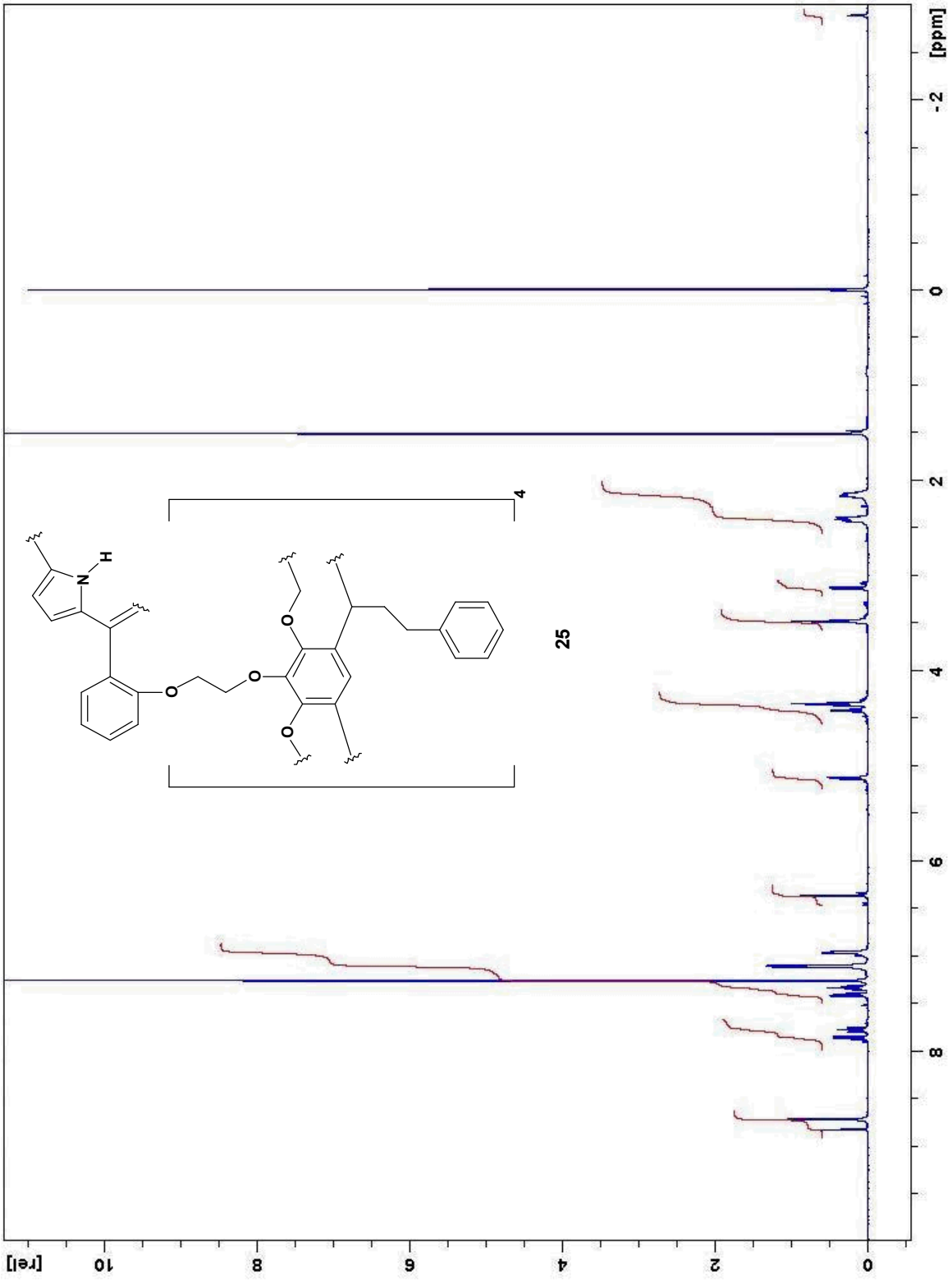

^{1}H NMR spectrum of 25 in $CDCl_3$ (400 MHz)

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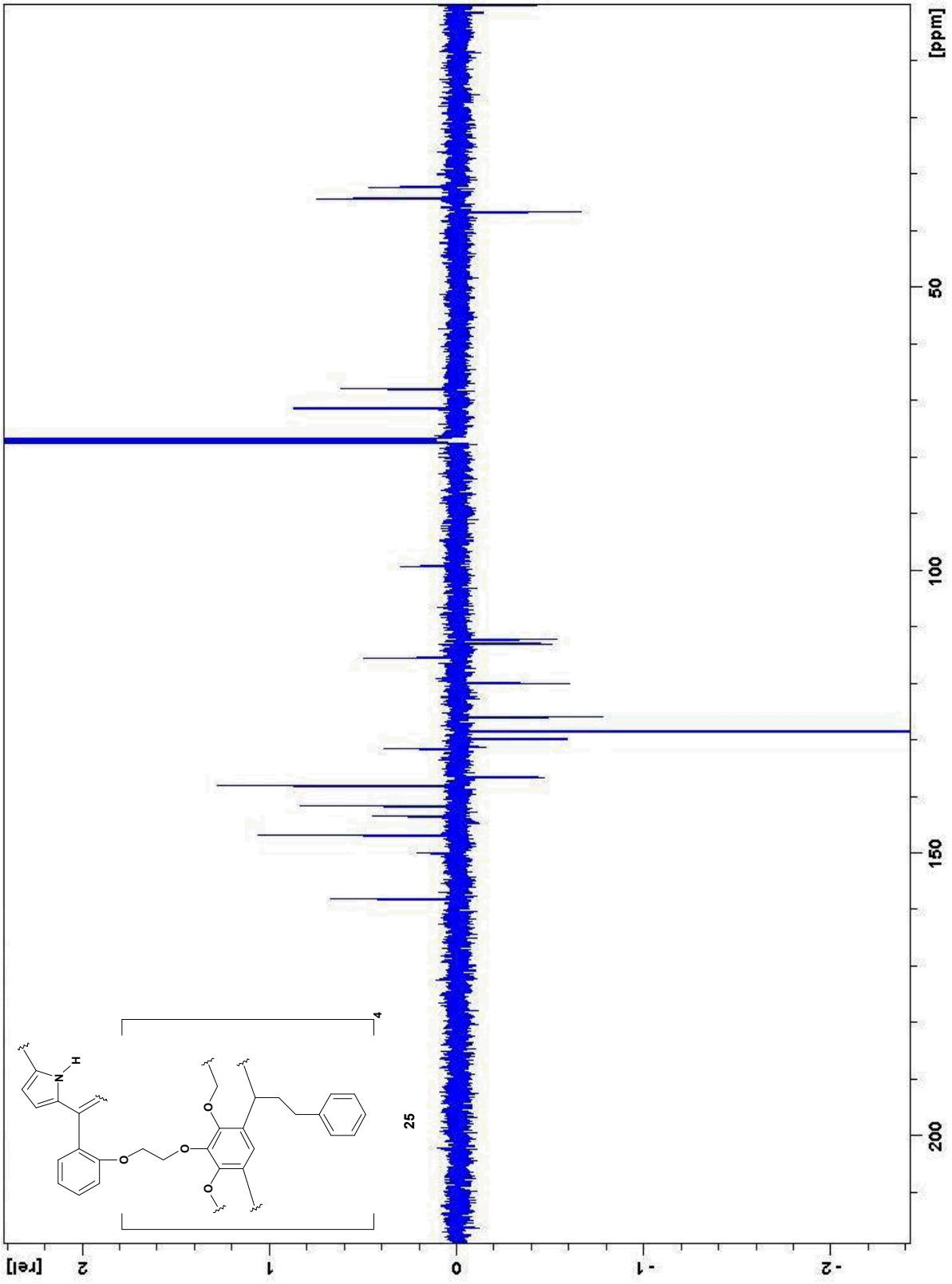

^{13}C APT NMR spectrum of 25 in $CDCl_3$ (100 MHz)

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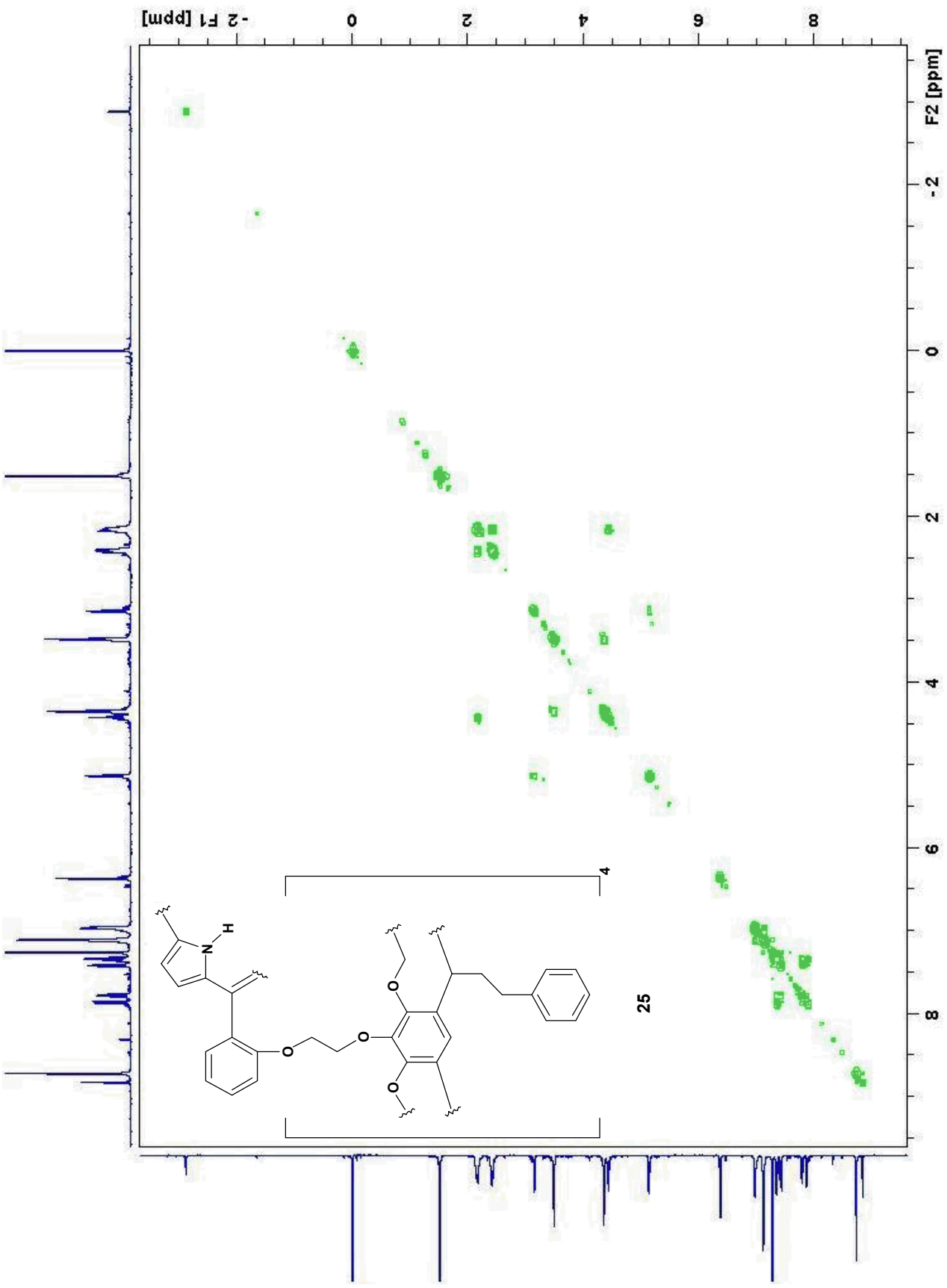

COSY NMR spectrum of 25 in $CDCl_3$ (400 MHz)

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