SUPPORTING INFORMATION

Total Synthesis of Dictyodendrin B

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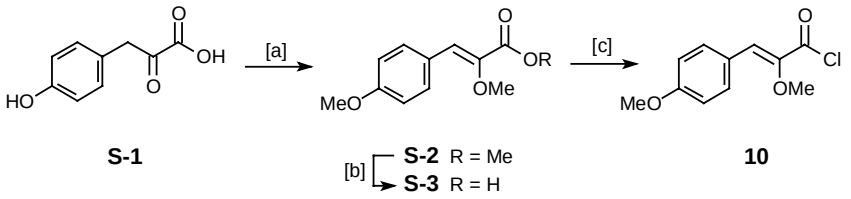
General: All reactions were carried out in flame-dried glassware under Ar. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O, DME (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N (CaH_2), MeOH (Mg), DMF (Desmodur®, dibutyltin dilaurate), hexane, toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

NMR: Spectra were recorded on a Bruker DPX 300, AV 400, or DMX 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual CH_2Cl_2 in CD_2Cl_2: $\delta_H \equiv 5.32$ ppm; residual CHD_2OD in CD_3OD: $\delta_H \equiv 3.31$ ppm; CD_3OD: $\delta_C \equiv 49.0$ ppm). *The coupling constants were not averaged. The proton spectra of the para-disubstituted phenyl groups are of AA'XX' spin systems. The splitting of signals of greatest intensity is quoted as the value of the coupling constant* $^3J_{(AX)}$*, assuming that* $^5J_{(AX')}$ *is zero. Where indicated, the signal assignments are unambiguous*; the numbering scheme is arbitrary and is shown in the inserts. The assignments are based upon

1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs* and *cosydqtp*); HSQC (*invietgssi*) optimized for ^{1}J(C,H) = 145 Hz; HMBC (*inv4gslplrnd*) for correlations via ^{n}J(C,H); HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms.

STARTING MATERIALS



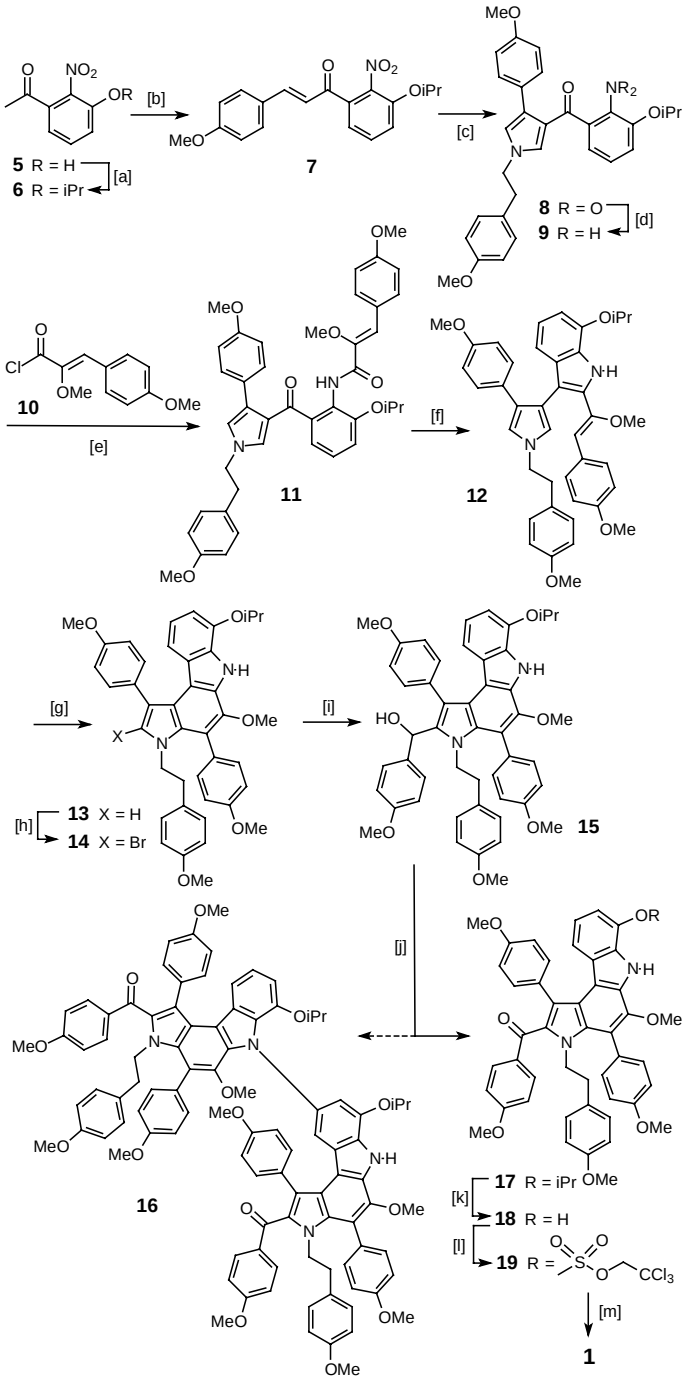
Scheme S-1. Conditions: [a] (i) NaH, DMF, 2h; (ii) dimethyl sulfate, DMF, 67%; [b] NaOH, MeOH/H_2O (2:1), 87%; [c] oxalyl chloride, DMF cat., CH_2Cl_2, quant.

Methyl 2-methoxy-3-(4-methoxyphenyl)-2-propenoate (S-2).[1] To a suspension of NaH (1.60 g, 66.6 mmol) in dry DMF (15 mL) was added a solution of 4-hydroxyphenylpyruvic acid (2.00 g, 11.1 mmol) in dry DMF (10 mL) at 0°C. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. Dimethyl sulfate (8.35 mL, 88.8 mmol) was then added and the mixture was stirred for another 2 h. After completion of the reaction, water was introduced, the aqueous layer was extracted with EtOAc (3 x 20 mL), the combined organic layers were washed with water and dried (Na_2SO_4). Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 1:4) afforded the title compound **S-2** as a pale yellow oil (1.66 g, 67%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.72 (d, J = 8.9 Hz, 2 H), 6.94 (s, 1 H), 6.91 (d, J = 8.9 Hz, 2 H), 3.82 (s, 3 H), 3.81 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 160.6, 144.3, 132.1, 126.5, 124.0, 114.3, 59.3, 55.6, 52.2; IR (film): $\tilde{\nu}$ = 3001, 2952, 2910, 2841, 1717, 1634, 1605, 1571, 1511, 1437, 1354, 1315, 1301, 1252, 1175, 1102, 1030, 834, 552, 521 cm^{-1}; MS (EI): *m/z* (%): 222 (100 $[M]^+$), 179 (52), 151 (53), 120 (18), 91 (14), 77 (16), 59 (9), 51 (11); HRMS (EI) *calcd.* for

[1] Kotsuki, H.; Saito, I.; Matsuura, T. *Tetrahedron Lett.* **1981**, *22*, 469-472.

$C_{12}H_{14}O_3$: 222.0892; *found*: 222.0894. *The stereochemical assignment of the configuration of the double bond is tentative*.

2-Methoxy-3-(4-methoxyphenyl)-2-propenoic acid (S-3). A solution of compound **S-2** (246 mg, 1.19 mmol) in MeOH (2.4 mL) and aq. NaOH (2 M, 1.2 mL) was stirred at ambient temperature for 2 h. For work up, the solution was acidified with aq. HCl (1 M) and the product was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried (Na_2SO_4) and evaporated, and the residue was dried under high vacuum for several hours to afford the title acid **S-3** (216 mg, 87 %) as a white solid. mp = 168-169°C. ^{1}H NMR (300 MHz, CD_3OD): δ = 7.70 (d, J = 8.9 Hz, 2 H), 6.98 (s, 1 H), 6.91 (d, J = 8.9 Hz, 2 H), 3.02 (s, 3 H), 3.72 (s, 3 H); ^{13}C NMR (75 MHz, CD_3OD): δ = 167.8, 161.8, 145.3, 132.8, 127.4, 125.2, 115.1, 59.3, 55.7; IR (film): $\tilde{\nu}$ = 3000, 2975, 2938, 2837, 2515, 1684, 1603, 1569, 1509, 1443, 1425, 1249, 1175, 929, 822 cm^{-1}; MS (EI): *m/z* (%): 208 (100 $[M]^+$), 165 (36), 148 (18), 137 (20), 121 (14), 91 (11), 77 (18), 63 (6), 51 (11); HRMS (EI) *calcd.* for $C_{11}H_{12}O_4$: 208.0735; *found*: 208.0733. *The stereochemical assignment of the configuration of the double bond is tentative*.



[a] Conditions: [a] 2-bromopropane, K_2CO_3, DMF, 100°C, 99%; [b] *p*-$MeOC_6H_4CHO$, NaOMe, MeOH, 70°C, 74%; [c] (i) TosMIC, NaH, THF, –30°C; (ii) *p*-$MeOC_6H_4(CH_2)_2Br$, reflux, 83%; [d] Fe powder, aq. HCl, EtOH, 96%; [e] **10**, CH_2Cl_2, Et_3N, DMAP cat., 89%; [f] $TiCl_3$/2 KC_8, DME, pyridine, reflux, 71-93%; [g] hν, MeCN, Pd/C cat., $C_6H_5NO_2$, 81%; [h] NBS, THF, 0°C, 69%; [i] (i) MeLi, THF, –78°C; (ii) *n*-BuLi, –78°C; (iii) *p*-$MeOC_6H_4CHO$, –78°C→rt, 97%; [j] TPAP (10%), NMO, MS 4Å, CH_2Cl_2 (0.01 M), 66% (**17**), 16% (**16**); [k] BCl_3, CH_2Cl_2, –20°C, 85%; [l] $Cl_3CCH_2OSO_2Cl$, DABCO, CH_2Cl_2, 92%; [m] (i) BCl_3, TBAI, CH_2Cl_2, 0°C→rt; (ii) Zn, $HCOONH_4$, MeOH, 58%.

3-Hydroxy-2-nitrophenylethanone (5).[2] 3-Hydroxyacetophenone (10.0 g, 73.4 mmol) was dissolved in ice-cold concentrated H_2SO_4 (30 mL). The resulting solution was cooled to –20°C before a mixture of concentrated H_2SO_4 (4 mL) and HNO_3 (5 mL) was slowly added over 15 min. Once the addition was complete, the mixture was stirred for another 10 min before it was carefully poured on ice. After stirring for another 30 min, the yellow precipitate was filtered off and recrystallized twice from ethanol to yield compound **5** as a beige solid (3.81 g, 29 %). mp = 134-135°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.5 (s, 1 H), 7.60 (dd, J = 8.5, 7.4 Hz, 1 H), 7.22 (dd, J = 8.5, 1.3 Hz, 1 H), 6.84 (dd, J = 7.4, 1.3 Hz, 1 H), 2.52 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4, 155.1, 140.6, 137.0, 121.1, 118.1, 30.3; IR (film): $\tilde{\nu}$ 3093, 1666, 1582, 1530, 1472, 1376, 1290, 798 cm^{-1}; MS (EI): *m/z* (%): 181 (48 $[M]^+$), 166 (100), 139 (13), 92 (36), 77 (8), 66 (24), 43 (97), 39 (35).

3-Isopropoxy-2-nitrophenylethanone (6). A suspension of ketone **5** (1.00 g, 5.52 mmol), isopropyl bromide (0.64 mL, 6.79 mmol) and K_2CO_3 (2.67 g, 19 mmol) in DMF (12 mL) was stirred at 100 °C for 3 h. For work up, water (80 mL) was added, the aqueous layer was extracted with *tert*-butyl methyl ether (3 x 20 mL), the combined organic layers were washed with water (5 x 20 mL) and aq. NaOH (2 M, 20 mL) before they were dried (Na_2SO_4) and evaporated, thus affording the title compound **6** as brown syrup which solidified upon standing at ambient temperature (1.22 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49 (m, 1 H), 7.35 (m, 1 H), 7.24 (m, 1 H), 4.65 (hept, J = 6.1 Hz, 1 H), 2.57 (s, 3 H), 1.35 (d, J = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.5, 150.0, 131.5, 130.8, 120.7, 119.4, 73.2, 27.9, 21.7; IR (film): $\tilde{\nu}$ = 3090, 2982, 2935, 1697, 1579, 1544, 1446, 1375, 1286, 1106, 949, 851, 790 cm^{-1}; MS (EI): *m/z* (%): 223 (8 $[M]^+$), 181 (30), 166 (100), 139 (9), 92 (8), 77 (3), 66 (8), 51 (3), 43 (63), 39 (11); HRMS (EI) *calcd.* for $C_{11}H_{13}NO_4$ (M): 223.0844; *found*: 223.0846.

(2*E*)-3-Isopropoxy-2-nitrophenyl-3-(4-methoxyphenyl)-2-propenone (7). Sodium (294 mg, 12.8 mmol) was dissolved in MeOH (10 mL) before a solution of *p*-methoxybenzaldehyde (6.20 mL, 51.1 mmol) and ketone **6** (5.70 g, 25.6 mmol) in MeOH (10 mL) was added. The mixture was stirred at 70 °C for 2 h before it was slowly cooled to ambient temperature. The resulting precipitate was filtered off, washed successively with water (20 mL) and MeOH (20 mL), and dried under high vacuum to give chalcone **7** as a

[2] Butenandt, A.; Hallmann, G.; Beckmann, R. *Chem. Ber*. **1957**, *90*, 1120-1124.

white solid (6.44 g, 74 %). mp = 111-112°C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 15.9 Hz, 1 H), 7.54-7.47 (m, 3 H), 7.26-7.20 (m, 2 H), 6.99 (d, *J* = 15.9 Hz, 1 H), 6.91 (m, 2 H), 4.67 (hept, *J* = 6.1 Hz, 1 H), 3.85 (s, 3 H), 1.37 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.6, 162.2, 150.1, 147.0, 134.3, 131.1, 130.6, 126.9, 121.4, 120.2, 118.1, 114.5, 73.1, 55.4, 21.8; IR (film): $\tilde{\nu}$ = 2980, 2935, 2839, 1664, 1642, 1589, 1572, 1541, 1512, 1466, 1444, 1424, 1374, 1259, 1174, 1029, 977, 830, 799 cm^{-1}; MS (EI): *m/z* (%): 341 (14 $[M]^+$), 188 (23), 176 (8), 163 (55), 149 (38), 135 (38), 121 (100), 107 (17), 90 (9), 77 (11), 63 (3), 43 (18). HRMS (EI) *calcd.* for $C_{19}H_{19}NNaO_5$ (M+Na): 364.1160; *found*: 364.1157.

2-Bromoethyl-4-methoxybenzene.[3] A mixture of 2-(methoxyphenyl)ethanol (18.2 g, 119 mmol) and PBr_3 (3.74 mL, 39.8 mmol) in toluene was refluxed for 2 h before it was allowed to cool to ambient temperature. The organic phase was washed with sat. aq. $Na_2S_2O_3$/$NaHCO_3$ (1:1, 3 x 20 mL) and dried (Na_2SO_4) before the solvent was evaporated to give the title bromide as a colorless liquid (24.3 g, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 8.6 Hz, 2 H), 6.84 (d, *J* = 8.6 Hz, 2 H), 3.78 (s, 3 H), 3.51 (t, *J* = 7.6 Hz, 2 H), 3.08 (t, *J* = 7.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.5, 130.9, 129.6, 113.9, 55.2, 38.5, 33.3; IR (film): $\tilde{\nu}$ = 3031, 3002, 2957, 2935, 2908, 2834, 1611, 1584, 1513, 1464, 1441, 1302, 1247, 1179, 1035, 821 cm^{-1}; MS (EI): *m/z* (%): 216 (16), 214 (17 $[M]^+$), 135 (19), 121 (100), 91 (7), 77 (6), 65 (4), 51 (3), 39 (3).

(3-Isopropoxy-2-nitrophenyl){4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]1*H*-pyrrol-3-yl}methanone (8). To a stirred suspension of NaH (2.11 g, 87.9 mmol) in dry THF (60 mL) was added a solution of TosMIC (5.70 g, 29.3 mmol) and chalcone **7** (5.00 g, 14.7 mmol) in THF (40 mL) at –30°C. The mixture was stirred at –30 °C for 1 h and at ambient temperature for 2 h. After completion of the reaction, 2-bromoethyl-4-methoxybenzene (15.8 g, 73.3 mmol) was introduced and the solution was refluxed for 2 h. For work up, the reaction was quenched with water (20 mL) and the product was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 1:3) afforded pyrrole **8** as a pale yellow foam (6.27 g, 83 %). mp = 68-69°C; ^{1}H NMR (400 MHz, $CDCl_3$):

[3] Hori, M.; Ozeki, H.; Iwamura, T.; Shimizu, H.; Kataoka, T.; Iwata, N. *Heterocycles* **1990**, *31*, 23-26.

δ = 7.33 (m, 2 H), 7.25 (t, *J* = 8.0 Hz, 1 H), 7.05 (m, 1 H), 6.97 (m, 2 H), 6.88 (dd, *J* = 1.0, 7.6 Hz, 1 H), 6.84-6.78 (m, 5 H), 6.56 (m, 1 H), 4.61 (hep, *J* = 6.1 Hz, 1 H), 4.01 (t, *J* = 7.0 Hz, 2 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 2.98 (t, *J* = 7.0 Hz, 2 H), 1.34 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.4, 158.6, 158.4, 149.7, 141.0, 136.1, 130.7, 130.5, 129.9, 129.7, 129.5, 127.1, 126.7, 121.5, 121.2, 120.7, 117.3, 114.1, 113.3, 73.0, 55.2, 55.2, 52.0, 36.8, 21.8; IR (film): $\tilde{\nu}$ = 3124, 2979, 2935, 2836, 1643, 1611, 1537, 1514, 1465, 1443, 1383, 1288, 1247, 1179, 1034, 833 cm^{-1}; MS (EI): *m/z* (%): 514 (100 $[M]^+$), 322 (23), 160 (10), 135 (48), 121 (41), 105 (9), 77 (4), 43 (6); HRMS (EI) *calcd.* for $C_{30}H_{30}N_2NaO_6$ (M+Na): 537.2001; *found*: 537.1997.

(2-Amino-3-isopropoxyphenyl){4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]1*H*-pyrrol-3-yl}methanone (9). Aq. HCl (0.6 M, 21 mL, 12.5 mmol) was added to a suspension of compound **8** (4.67 g, 9.08 mmol) and iron powder (5.07 g, 90.8 mmol) in EtOH (90 mL) and the resulting suspension was refluxed for 2 h with vigorous stirring. The mixture was cooled to ambient temperature and filtered through a pad of Celite, the filtrate was diluted with EtOAc (200 mL) and successively washed with sat. aq. $NaHCO_3$ (50 mL) and brine (30 mL). Drying of the organic layer over Na_2SO_4 followed by evaporation of the solvent gave aniline **9** as a yellow foam (4.24 g, 96 %). mp = 54-55°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 2 H), 7.13 (dd, *J* = 1.2, 8.1 Hz, 1 H), 6.98 (m, 2 H), 6.86-6.81 (m, 5 H), 6.72 (d, *J* = 2.3 Hz, 1 H), 6.64 (d, *J* = 2.3 Hz, 1 H), 6.43 (m, 1 H), 6.02 (s, 2 H), 4.51 (hept, *J* = 6.1 Hz, 1 H), 4.03 (t, *J* = 7.0 Hz, 2 H), 3.78 (s, 3 H), 3.77 (s, 3 H), 2.98 (t, *J* = 7.0 Hz, 2 H), 1.35 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.3, 158.5, 158.0, 144.9, 141.7, 129.7, 129.6, 129.2, 128.4, 127.5, 126.7, 125.3, 122.0, 120.8, 120.0, 115.5, 114.0, 113.6, 113.5, 70.9, 55.2, 55.1, 51.7, 37.0, 22.1; IR (film): $\tilde{\nu}$ = 3488, 3358, 3119, 3034, 2975, 2933, 2834, 1612, 1541, 1513, 1454, 1385, 1246, 1220, 1036, 833 cm^{-1}; MS (EI): *m/z* (%): 484 (69 $[M]^+$), 441 (10), 363 (100), 321 (42), 186 (15), 135 (23); HRMS (EI) *calcd.* for $C_{30}H_{33}N_2O_4$ (M+H): 485.2440; *found*: 485.2441.

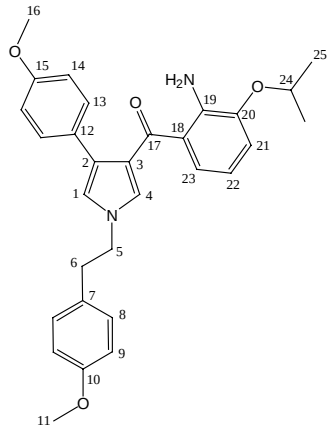


Table S-1. Tabular survey of the NMR data of amine **9** recorded in CD_2Cl_2. All assignments are unambiguous, cf. General; numbering scheme as indicated in the insert.

Position	δ_C [ppm] (150 MHz)	δ_H [ppm] (600 MHz)
1	120.5	6.68 (d, *J* = 2.3 Hz, 1H)
2	126.7	
3	122.4	
4	128.6	6.72 (d, *J* = 2.3 Hz, 1H)
5	52.1	4.08 (t, *J* = 7.0 Hz, 2H)
6	37.3	3.02 (t, *J* = 7.0 Hz, 2H)
7	130.4	
8	130.1	7.04 (m, 2H)
9	114.4	6.86 (m, 2H)
10	159.0	
11	55.5	3.794 (s, 3H)
12	128.2	
13	129.6	7.27 (m, 2H)
14	113.7	6.83 (m, 2H)
15	158.5	
16	55.5	3.792 (s, 3H)
17	193.5	
18	121.2	
19	142.1	
20	145.4	
21	116.0	6.87 (m, 1H)
22	114.0	6.46 (m, 1H)
23	125.7	7.13 (dd, *J* = 1.2, 8.1 Hz, 1H)
24	71.5	4.55 (sep, *J* = 6.1 Hz, 1H)
25	22.3	1.36 (d, *J* = 6.1 Hz, 6H)
NH_2		6.01 (s, 2H),

2-*N*-[2-Isopropoxy-6-({4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]-1*H*-pyrrol-3-yl}carbonyl)phenyl]-2-methoxy-3-(4-methoxyphenyl)-2-propenamide (11). Freshly distilled oxalyl chloride (0.70 mL, 8.26 mmol) was added dropwise to a suspension of acid **S–3** (1.29 g, 6.19 mmol) in CH_2Cl_2 (20 mL) at 0 °C under argon, followed by 4 drops of dry DMF. After 5 min, the cooling bath was removed and the mixture was stirred at ambient temperature for 1 h. The solvent was evaporated and the residue was dried *in vacuo*.

The crude acid chloride **10** thus formed was dissolved in CH_2Cl_2 (10 mL) and the resulting solution was added dropwise to a stirred solution containing aniline **9** (2.00 g, 4.13 mmol), freshly distilled Et_3N (2.90 mL, 20.7 mmol) and DMAP (50 mg, 0.619 mmol) in CH_2Cl_2 (20 mL) at ambient temperature. The mixture was stirred for 30 min before it was quenched with sat. aq. $NaHCO_3$ (5 mL). The layers were separated, the organic phase was washed successively with aq. HCl (3 M, 10 mL), sat. aq. $NaHCO_3$ (10 mL) and brine (5 mL) before it was dried over $MgSO_4$. Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 3:7 → 1:1) afforded amide **11** as a yellow foam (2.49 g, 89 %). mp = 69-70°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (s, 1 H), 7.61 (m, 2 H), 7.37 (m, 2 H), 7.08 (m, 1H), 7.00-6.94 (m, 6 H), 6.88-6.78 (m, 6 H), 6.54 (m, 1 H), 4.55 (hept, *J* = 6.1 Hz, 1 H), 4.00 (t, *J* = 7.1 Hz, 2 H), 3.81 (s, 3 H), 3.77 (s, 6 H), 3.66 (s, 3 H), 2.98 (t, *J* = 7.1 Hz, 2 H), 1.34 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.0, 162.1, 159.7, 158.5, 158.1, 151.4, 147.4, 137.6, 131.4, 131.0, 129.8, 129.7, 127.4, 126.8, 126.2, 125.3, 124.5, 121.8, 121.3, 120.8, 120.2, 115.2, 114.0, 114.0, 113.2, 71.1, 59.2, 55.2, 51.8, 36.9, 22.1; IR (KBr): $\tilde{\nu}$ = 3406, 3122, 2974, 2935, 2836, 1683, 1638, 1604, 1512, 1465, 1442, 1247, 1147, 1032, 851, 833, 785 cm^{-1}; MS (EI): *m/z* (%): 674 (51 [M]$^+$), 630 (8), 469 (12), 334 (40), 308 (16), 162 (17), 148 (100), 121 (22), 120 (18), 105 (8); HRMS (EI) *calcd.* for $C_{41}H_{42}N_2NaO_7$ (M+Na) 697.2889; *found*: 697.2886.

7-Isopropoxy-2-[methoxy-2-(4-methoxyphenyl)ethenyl]-3-{4-(4-methoxyphenyl)-1-[2-(4-methoxyphenyl)ethyl]-1*H*-pyrrol-3-yl}-1*H*-indole (12). Dry DME (40 mL) was carefully added (*exothermic*!) to a mixture of $TiCl_3$ (2.85 g, 18.5 mmol) and C_8K (4.96 g, 36.7 mmol) at 0 °C under argon and the resulting suspension was refluxed for 1.5 h. Dry pyridine (1.5 mL, 18.5 mmol) was introduced and reflux was continued for another 15 min. A solution of ketoamide **11** (2.49 g, 3.69 mmol) in dry DME (10 mL) was then introduced and the mixture was refluxed until TLC indicated complete conversion of the substrate (ca. 1.5 h). After reaching ambient temperature, the mixture was filtered through a plug of Celite layered on silica, which was carefully rinsed with EtOAc/PhMe (1:1, 150 mL), and the combined

filtrates were concentrated *in vacuo*. Purification of the residue by flash chromatography (EtOAc/hexanes, 1:6 + 1% 6 M NH_3/MeOH) yielded indole **12** as a yellow oil (1.68 g, 71 %). The yield was raised to 93% when this reaction was performed on a somewhat smaller scale (278 mg of ketoamide **11**). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.55 (s, 1 H), 7.35 (m, 2 H), 7.08-7.02 (m, 4 H), 6.97-6.90 (m, 2 H), 6.82-6.76 (m, 5 H), 6.67-6.57 (m, 4 H), 5.93 (m, 1 H), 4.75 (hep, *J* = 6.1 Hz, 1 H), 4.15 (t, *J* = 7.0 Hz, 2 H), 3.79 (s, 3 H), 3.73 (s, 3 H), 3.64 (s, 3 H), 3.34 (s, 3 H), 3.08 (t, *J* = 7.0 Hz, 2 H), 1.44 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 158.6, 157.9, 147.3, 144.4, 132.1, 131.1, 130.9, 130.2, 130.1, 129.8, 128.8, 128.3, 126.9, 124.6, 121.9, 120.4, 118.9, 114.5, 114.2, 113.9, 113.7, 112.7, 105.0, 70.8, 58.5, 55.5, 55.4, 52.0, 37.7, 22.5; IR (KBr): $\tilde{\nu}$ = 3480, 3429, 2974, 2933, 2834, 1609, 1575, 1547, 1511, 1463, 1454, 1441, 1248, 1177, 1034, 832, 784 cm^{-1}; MS (EI): *m/z* (%): 642 (44 [M]$^+$), 627 (100), 135 (36), 121 (11), 43 (2). HRMS (EI) *calcd.* for $C_{41}H_{42}N_2NaO_5$ (M+Na): 665.2991; *found*: 665.2987.

7-Isopropoxy-5-methoxy-1,4-bis-(4-methoxy-phenyl)-3-[2-(4-methoxy-phenyl)-ethyl]-3,6-dihydro-pyrrolo[2,3-*c*]carbazole (13). In a water-cooled photoreactor, a solution of indole **12** (450 mg, 0.70 mmol) and nitrobenzene (1 mL) in MeCN (140 mL) was purged with argon for 30 min. After that time, Pd/C (10% w/w, 370 mg, 0.350 mmol) was added and the resulting suspension was irradiated with a medium pressure Hg-lamp (Hanovia, 250 W) (cooled by a stream of cold water) for 2.5 h. After completion of the reaction, the suspension was filtered through a silica/Celite pad, which was carefully rinsed with EtOAc/PhMe (1:1, 100 mL). The filtrate was evaporated and the residue was purified by flash chromatography (EtOAc/hexanes, 1:6) to afford pyrrolocarbazole **13** as a yellow solid (365 mg, 81 %). mp = 173-174 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 8.54 (br s, 1 H), 7.53 (d, *J* = 8.8 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H), 7.09 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 6.90 (s, 1 H), 6.79 (d, *J* = 7.6 Hz, 1 H), 6.73 (dd, *J* = 8.0, 7.6 Hz, 1 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.23 (d, *J* = 7.6 Hz, 1 H), 4.76 (hept, *J* = 6.0 Hz, 1 H), 3.93 (s, 3 H), 3.92 (s, 3 H), 3.84 (m, 2 H), 3.74 (s, 3 H), 3.66 (s, 3 H), 2.63 (m, 2 H), 1.45 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 159.6, 159.1, 158.4, 143.7, 140.6, 132.4, 132.0, 130.7, 130.6, 130.3, 129.8, 129.1, 128.9, 127.8, 124.9, 119.4, 118.7, 118.1, 117.1, 117.0, 115.2, 113.8, 113.7, 113.4, 106.9, 70.9, 61.4, 55.5, 55.3, 50.2, 37.0, 22.2; IR (film) $\tilde{\nu}$ = 3328, 2935, 2831, 1614, 1572, 1544, 1513, 1455, 1436, 1404, 1369, 1340, 1304, 1276, 1236, 1174, 1135, 1117, 1038, 1024, 1004, 931, 913, 874, 859, 834, 819, 783, 770, 734, 678 cm^{-1}. MS (EI): *m/z* (%): 484 (69 [M$^+$]), 441 (10), 363 (100), 321 (42), 186 (15), 135 (23).

2-Bromo-7-isopropoxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)-ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazole (14). NBS (230 mg, 1.29 mmol) was added in one portion to a stirred solution of the pyrrolocarbazole **13** (830 mg, 1.29 mmol) in THF (26 mL) at 0°C. After stirring for 30 min, the cooling bath was removed and the solution was allowed to reach ambient temperature over 10 min. The mixture was concentrated under reduced pressure to ca. 1/5 of the original volume and passed through a silica pad, which was rinsed with EtOAc/hexanes (1:2). The combined filtrates were evaporated and the solid thus obtained was recrystallized from hot EtOAc/hexanes to give the title compound **14** as an off-white solid (639 mg, 69%). *The compound should be stored in a refrigerator to avoid migration of the bromine along the periphery of the heteroarene system*. mp = 201-202 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.54 (s, 1 H), 7.54 (d, *J* = 8.6 Hz, 2 H), 7.41 (d, *J* = 8.6 Hz, 2 H), 7.10 (d, *J* = 8.1 Hz, 2 H), 7.08 (d, *J* = 8.1 Hz, 2 H), 6.77 (d, *J* = 7.7 Hz, 1 H), 6.72 (br s, 4 H), 6.67 (t, *J* = 8.0 Hz, 1 H), 5.85 (d, *J* = 8.1 Hz, 1 H), 4.74 (hept, *J* = 6.1 Hz, 1 H), 3.99 (m, 2 H), 3.95 (s, 3 H), 3.93 (s, 3 H), 3.75 (s, 3 H), 3.65 (s, 3 H), 2.58 (m, 2 H), 1.43 (d, *J* = 6.1 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 160.0, 159.9, 158.8, 144.0, 141.0, 133.3, 132.7, 131.1, 130.6, 130.1, 129.8, 129.6, 127.8, 124.9, 120.2, 119.2, 118.3, 118.1, 116.7, 114.9, 114.4, 114.2, 114.1, 114.0, 107.4, 71.2, 61.6, 55.8, 55.8, 55.6, 48.7, 36.0, 22.5; IR (film): $\tilde{\nu}$ = 3353, 2932, 2831, 1613, 1573, 1547, 1511, 1498, 1455, 1440, 1408, 1356, 1338, 1317, 1302, 1285, 1244, 1170, 1141, 1123, 1104, 1027, 1007, 933, 916, 862, 840, 820, 786, 753, 740, 686, 659 cm^{-1} ; MS (EI): *m/z* (%): 722 (10), 721 (42), 720 (100 [M^+]), 719 (43), 718 (93), 556 (14), 554 (13), 541 (12), 539 (11), 518 (10), 461 (8), 135 (56); HRMS (ESI^+) *calcd.* for $C_{41}H_{39}Br_1N_2O_5Na$ (M+Na): 741.1940; *found*: 741.1937.

{7-Isopropoxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-c]carbazol-2-yl}-(4-methoxyphenyl)methanol (15). MeLi (1.6 M in Et_2O, 0.59 mL, 0.946 mmol) was added dropwise to a stirred solution of the bromo-pyrrolocarbazole **14** (619 mg, 0.860 mmol) in dry THF (33 mL) at –78 °C under argon. After stirring for 15 min, *n*-BuLi (1.6 M in hexanes, 0.59 mL, 0.946 mmol) was added dropwise and stirring was continued for another 15 min before a solution of *p*-methoxybenzaldehyde (0.26 mL, 2.15 mmol) in dry THF (1 mL) was slowly introduced. After 15 min, the cooling bath was removed and the mixture was allowed to reach ambient temperature over 30 min. For work up, the reaction was carefully quenched with aq. NH_4Cl (1 mL) and brine (1 mL), the organic layer was dried ($MgSO_4$) and evaporated, and the residue was purified by flash

chromatography (EtOAc/hexanes, 1:4) to furnish compound **15** as a white foam (647 mg, 97 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.58 (s, 1 H), 7.54-7.45 (m, 4 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 7.07-7.02 (m, 3 H), 6.98 (dd, *J* = 8.4, 2.8 Hz, 1 H), 6.84 (d, *J* = 8.8 Hz, 2 H), 6.78 (d, *J* = 7.6 Hz, 1 H), 6.69 (dd, *J* = 8.0, 8.0 Hz, 1 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.31 (d, *J* = 8.8 Hz, 2 H), 6.03 (d, *J* = 2.8 Hz, 1 H), 5.80 (d, *J* = 8.0 Hz, 1 H), 4.76 (hept, J = 6.4 Hz, 1 H), 3.92 (s, 3 H), 3.87 (s, 3 H), 3.82 (m, 2 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 3.57 (s, 3 H), 2.54 (m, 1 H), 2.46 (d, *J* = 3.7 Hz, 1 H), 2.09 (m, 1 H), 1.45 (dd, *J* = 6.1, 1.4 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ =159.9, 159.8, 159.1, 158.4, 144.0, 141.4, 137.8, 134.8, 133.6, 133.5, 133.1, 133.0, 131.1, 130.2, 129.9, 129.5, 129.5, 127.9, 127.1, 125.1, 120.3, 119.2, 118.4, 118.4, 116.8, 115.7, 114.3, 114.1, 114.1, 113.9, 113.8, 113.6, 114.3, 114.1, 114.1, 113.9, 113.8, 113.6, 107.3, 71.2, 68.0, 61.3, 55.9, 55.8, 55.6, 55.5, 47.6, 36.0, 22.5; IR (film): $\tilde{\nu}$ = 3451, 2969, 2934, 2835, 1729, 1610, 1573, 1547, 1510, 1463, 1440, 1402, 1371, 1318, 1301, 1284, 1240, 1171, 1106, 1064, 1030, 1007, 953, 918, 875, 837, 804, 789, 770, 734, 709, 677 cm^{-1}; MS (EI): *m/z* (%): 778 (10), 777 (34), 776 (66 [M^+]), 655 (12), 626 (14), 612 (9), 534 (7), 506 (16), 449 (7), 135 (63), 134 (44), 121 (100), 119 (19), 91 (15), 65 (8); HRMS (ESI^+) *calcd.* for $C_{49}H_{48}N_2O_7Na$ (M+Na): 799.3359; *found*: 799.3352.

{7-Isopropoxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazol-2-yl}-(4-methoxyphenyl) methanone (17). TPAP (9.1 mg, 0.026 mmol) was added to a suspension of alcohol **15** (202 mg, 0.260 mmol), NMO (61.0 mg, 0.520 mmol) and activated molecular sieves (4Å, 600 mg) in dry CH_2Cl_2 under argon. The mixture was vigorously stirred for 2 h before it was filtered through a pad of Celite and the filtrate was evaporated. Purification of the residue by flash chromatography (EtOAc/hexanes, 1:4) afforded ketone **17** as a yellow foam (129 mg, 66 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.68 (s, 1 H), 7.59 (d, *J* = 8.8 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.66 (dd, *J* = 8.4, 8.4 Hz, 1 H), 6.62 (d, *J* = 8.8 Hz, 2 H), 6.54 (d, *J* = 8.4 Hz, 2 H), 5.81 (d, *J* = 8.0 Hz, 1 H), 4.76 (hept, *J* = 6.0 Hz, 1 H), 3.96 (m, 2 H), 3.92 (s, 3 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 2.55 (m, 2 H), 1.45 (d, *J* = 6.0 Hz, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 189.7, 163.3, 159.7, 159.2, 158.3, 143.8, 143.0, 136.3, 133.2, 132.4, 132.3, 131.8, 131.2, 130.8, 130.5, 129.7, 129.6, 128.8, 127.4, 124.6, 121.8, 119.5, 118.9, 118.2, 116.9, 115.7, 113.9, 113.6, 113.3, 113.3, 107.0, 70.9, 61.3, 55.5, 55.5, 55.5, 55.2, 47.6, 36.7, 22.2; IR (film): $\tilde{\nu}$ = 3344, 2969, 1934, 1835, 1596, 1572, 1533, 1510, 1462, 1439, 1420, 1384, 1371, 1350, 1316, 1285, 1239, 1170, 1153, 1106, 1063, 1028, 1008, 971,

932, 922, 905, 869, 836, 795, 781, 773, 733, 704 cm^{-1}; MS (EI): *m/z* (%): 775 (32), 774 (58 [M^+]), 654 (15), 653 (33), 640 (14), 595 (16), 135 (100), 121 (25); HRMS (ESI^+) *calcd.* for $C_{49}H_{47}N_2O_7$ (M+H): 775.3370; *found*: 775.3378.

{7-Hydroxy-5-methoxy-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazol-2-yl}-(4-methoxyphenyl)methanone (18). BCl_3 (1 M in heptanes, 1.32 mL, 1.32 mmol) was added dropwise to a stirred solution of compound **15** (256 mg, 0.330 mmol) in CH_2Cl_2 (16 mL) at –20 °C. After 1 h the reaction was quenched at that temperature with sat. aq. $NaHCO_3$ (3 mL) with vigorous stirring and the mixture was allowed to warm to ambient temperature over 30 min. The organic layer was washed with brine (3 mL), dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (EtOAc/hexanes, 2:3) to afford compound **18** as a yellow oil (206 mg, 85 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.68 (s, 1 H), 7.58 (d, *J* = 8.8 Hz, 2 H), 7.56 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 7.05 (d, *J* = 8.4 Hz, 2 H), 6.78 (d, *J* = 8.4 Hz, 2 H), 6.70 (d, *J* = 8.8 Hz, 2 H), 6.69 (d, *J* = 7.2 Hz, 1 H), 6.60 (d, *J* = 8.8 Hz, 2 H), 6.58 (t, *J* = 8.0 Hz, 1 H), 6.52 (d, *J* = 8.8 Hz, 2 H), 5.81 (d, *J* = 8.0 Hz, 1 H), 5.25 (s, 1 H), 3.96 (m, 2 H), 3.91 (s, 3 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.69 (s, 3 H), 3.65 (s, 3 H), 2.52 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 190.3, 163.7, 159.9, 159.5, 158.6, 143.4, 141.6, 136.6, 133.5, 132.7, 132.6, 132.0, 131.8, 131.5, 130.8, 130.4, 129.9, 129.3, 129.0, 127.6, 125.6, 122.6, 119.9, 119.3, 118.7, 117.6, 116.0, 114.2, 113.9, 113.6, 109.561.5, 55.8, 55.8, 55.8, 55.5, 64.4, 47.9, 36.9; IR (film): $\tilde{\nu}$ = 3359, 2935, 1609, 1595, 1577, 1532, 1512, 1463, 1438, 1422, 1287, 1245, 1174, 1107, 1067, 1034, 966, 835 cm^{-1}; MS (EI): *m/z* (%): 733 (15), 732 (30 [M^+]), 612 (10), 611 (25), 598 (17), 135 (100), 121 (29), 105 (7); HRMS (ESI^+) *calcd.* for $C_{46}H_{41}N_2O_7$ (M+H): 733.2913; *found*: 733.2908.

Sulfuric acid 5-methoxy-2-(4-methoxybenzoyl)-1,4-bis-(4-methoxyphenyl)-3-[2-(4-methoxyphenyl)ethyl]-3,6-dihydropyrrolo[2,3-*c*]carbazol-7-yl ester 2,2,2-trichloroethyl ester (19). A solution of 2,2,2-trichloroethyl chlorosulfate (91 mg, 0.37 mmol) in CH_2Cl_2 (1 mL) was added in one portion to a stirred solution of phenol **18** (180 mg, 0.243 mmol) and DABCO (83 mg, 0.37 mmol) in CH_2Cl_2 (24 mL) at ambient temperature. After completion of the reaction (2 h), sat. aq. NH_4Cl (4 mL) was added, the layers were separated, and the organic layer was washed with brine (2 mL) before being dried over Na_2SO_4. Evaporation of the solvent followed by flash chromatography of the residue (EtOAc/hexanes, 1:3) gave compound **19** as a yellow foam (214 mg, 92 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.82 (s, 1

H), 7.58 (d, *J* = 8.8 Hz, 2 H), 7.57 (d, *J* = 8.8 Hz, 2 H), 7.30 (dd, *J* = 8.0, 0.6 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.11 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 6.77 (dd, *J* = 8.4, 8.0 Hz, 1 H), 6.71 (d, *J* = 8.8 Hz, 2 H), 6.61 (d, *J* = 8.8 Hz, 2 H), 6.52 (d, *J* = 8.8 Hz, 2 H), 6.19 (d, *J* = 8.4 Hz, 1 H), 4.85 (s, 2 H), 3.95 (m, 2 H), 3.91 (s, 3 H), 3.81 (s, 3 H), 3.79 (s, 3 H), 3.69 (s, 3 H), 3.65 (s, 3 H), 2.53 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 189.9, 163.8, 160.1, 159.7, 142.9, 137.0, 135.2, 133.5, 132.6, 131.9, 131.8, 131.1, 130.6, 129.9, 128.7, 127.6, 127.2, 124.7, 121.7, 120.0, 119.6, 119.1, 116.3, 115.4, 114.3, 113.9, 113.8, 113.7, 81.3, 61.7, 55.8, 55.8, 55.8, 55.5, 48.0, 37.0; IR (film): $\tilde{\nu}$ = 2935, 2835, 1597, 1572, 1533, 1511, 1462, 1442, 1417, 1351, 1311, 1286, 1243, 1193, 1173, 1158, 1106, 1068, 1030, 996, 965, 926, 885, 867, 836, 812, 794, 782, 770, 724 cm^{-1}; HRMS (ESI$^+$) *calcd.* for $C_{48}H_{42}Cl_3N_2O_{10}S_1$ (M+H): 943.1622; *found*: 943.1622.

Dictyodendrin B (1). BCl_3 (1 M in heptanes, 0.76 mL, 0.76 mmol) was added dropwise to a stirred solution of compound **19** (60 mg, 0.064 mmol) and (*n*-Bu)$_4$NI (282 mg, 0.0764 mmol) in CH_2Cl_2 (6.4 mL) at 0 °C under argon. The cooling bath was removed and the solution was stirred at ambient temperature for 1.5 h. The reaction was quenched with water (10 mL) and the resulting mixture was vigorously stirred for 1 h before it was diluted with EtOAc (20 mL). The organic layer was successively washed with sat. aq. Na_2SO_3 (5 mL) and brine (2 mL) before it was dried over Na_2SO_4 and evaporated. The residue was passed through a pad of reverse-phase chromatography gel (LiChroprep RP-18, E. Merck, Darmstadt, 5 g), eluting with 3:1 MeOH/H_2O, and the product thus obtained was immediately processed in the next step without further characterization.

To a solution of this crude material and HCO_2NH_4 (24 mg, 0.38 mmol) in dry MeOH (6.4 mL) was added activated zinc (8.3 mg, 0.13 mmol). The suspension was vigorously stirred for 1 h before excess zinc was filtered off through a pad of Celite. The filtrate was evaporated and the residue purified by flash chromatography (CH_2Cl_2/MeOH, 9:1 → 4:1). The pooled fractions were concentrated, and the residue was dissolved in water (1 mL). 4 Drops of ammonia (7 M in MeOH) were added, and the product was lyophilized to afford dicytodendrin B **1** (28 mg, 58% over both steps) as a yellow foam. ^{1}H NMR (600 MHz, CD_3OD): δ = 8.48 (s, 1 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 9.0 Hz, 2 H), 7.18 (d, *J* = 7.8, 1.2 Hz, 1 H); 7.05 (d, *J* = 8.4 Hz, 2 H), 7.03 (d, *J* = 8.4 Hz, 2 H), 6.65 (d, *J* = 9.0 Hz, 2 H), 6.57 (dd, *J* = 7.8, 7.8 Hz, 1 H), 6.56 (d, *J* = 9.0 Hz, 2 H), 6.47 (d, *J* = 9.0 Hz, 2 H), 6.41 (d, *J* = 8.4 Hz, 2 H), 6.02 (dd, *J* = 8.4, 0.6 Hz, 1 H), 3.96 (t, *J* = 7.2 Hz, 2 H), 2.47 (t, *J* = 7.2 Hz, 2 H); ^{13}C NMR (150 MHz, CD_3OD) δ = 192.0, 163.1, 158.7, 157.7, 156.8, 141.7, 138.8,

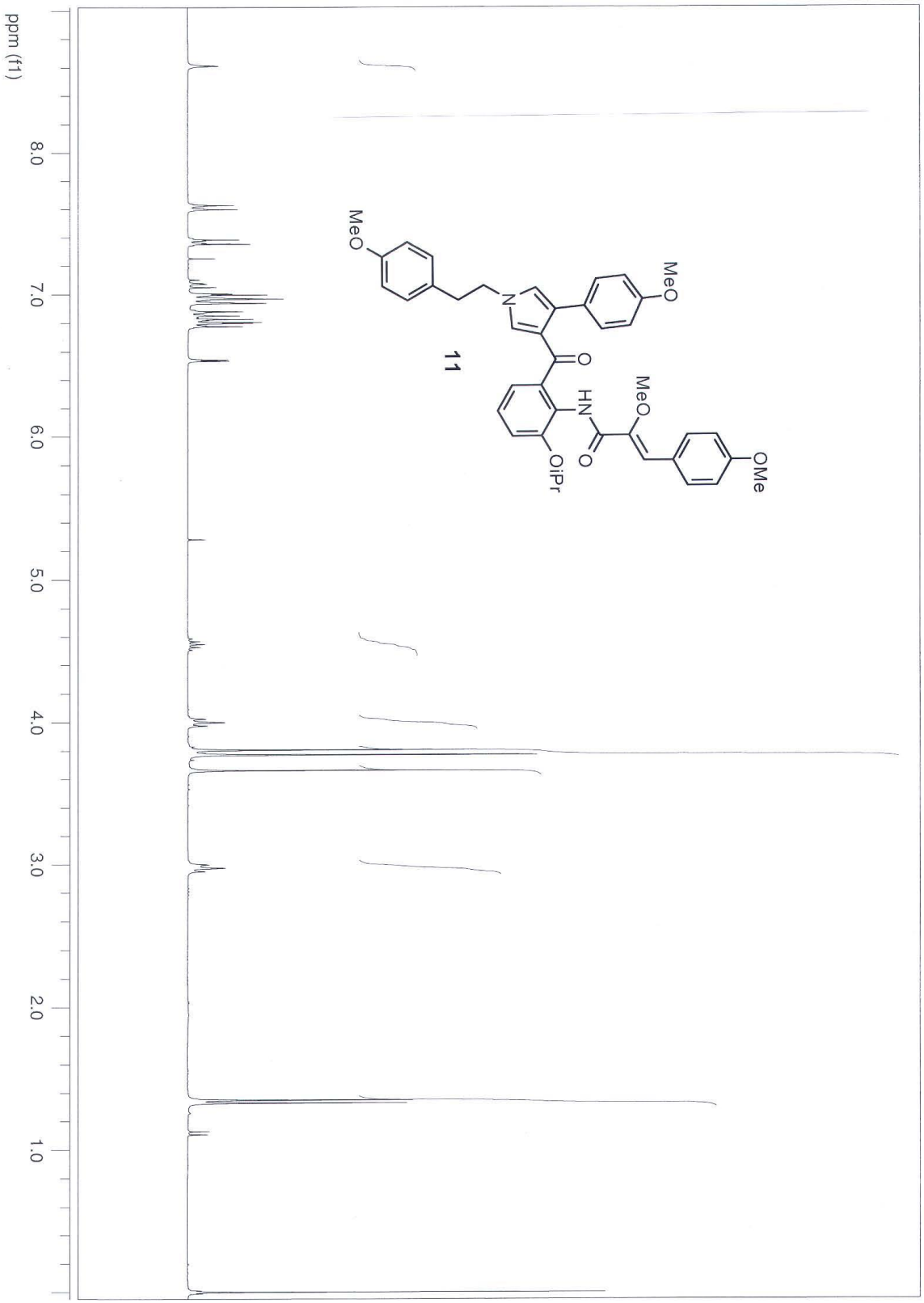
136.2, 134.3, 134.3, 134.0, 133.8, 132.0, 130.6, 129.3, 129.2, 127.1, 126.8, 125.8, 122.7, 118.9, 118.2, 117.2, 116.8, 116.1, 116.0, 115.6, 112.6, 48.4, 37.7; IR (film): $\tilde{\nu}$ = 3250, 1673, 1593, 1535, 1513, 1441, 1369, 1325, 1204, 1157, 1104, 1053, 1004, 921, 838, 798, 764, 724, 679 cm^{-1}. MS (ESI^-) *m/z*: 741 [M - H]; HRMS (ESI^-) *calcd.* for $C_{41}H_{29}N_2O_{10}S_1$ (M-H): 741.1549; *found*: 741.1549.

2,2,2-Trichloroacetyl chlorosulfate.[4] SO_2Cl_2 (5.0 mL, 62 mmol) was added dropwise to a stirred solution of 2,2,2-trichloroethanol (6.0 mL, 62 mmol) and pyridine (5.0 mL, 62 mmol) in Et_2O (120 mL) at –20 °C. Once the addition was complete, the mixture was warmed to ambient temperature, and stirring was continued for 1 h. For work up, the reaction was carefully quenched with water (20 mL), the layers were separated, and the organic layer was dried ($MgSO_4$) and evaporated. The crude product thus obtained was purified by distillation, yielding the title compound as a colorless oil (10.6 g, 69 %, bp = 38 °C/0.04 mbar). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.92 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 91.3, 81.2; IR (film): $\tilde{\nu}$ 3021, 2963, 1420, 1376, 1193, 1088, 1045, 993, 875, 780, 729, 597 cm^{-1}; MS (EI): *m/z* (%): 213 (35), 129 (100), 119 (43), 117 (44), 99 (23), 77 (12), 61 (12), 49 (14), 29 (12).

7-Hydroxy-1,4-bis(4-hydroxyphenyl)-3-[2-(4-hydroxyphenyl)ethyl]pyrrolo[2,3-*c*]-carbazol-2,5(3*H*,6*H*)-dione (20). A solution of BBr_3 (1 M in CH_2Cl_2, 0.31 mL, 0.31 mmol) is added to a solution of compound **13** (20 mg, 0.031 mmol) and cyclohexene (0.063 mL, 0.620 mmol) in CH_2Cl_2 (8 mL) at −78°C and the resulting mixture is allowed to slowly reach ambient temperature over the course of 8 h. The reaction is quenched with aq. $KHSO_4$ (10% *w/w*, 2 mL) and NaOH (20% *w/w*, 1 mL) and the organic phase is washed with water. The aqueous phase is acidified with conc. HCl (2 mL) and extracted with *tert*-butyl methyl ether, the combined organic layers are washed with brine, dried over Na_2SO_4 and evaporated. Purification of the residue by preparative reverse-phase HPLC (Nucleodur 100-16-C-18/A, MeOH/H_2O) afforded the compound **20** as a green-brown solid (8.5 mg, 49%). ^{1}H NMR (600 MHz, d_6-acetone): δ = 7.40 (m, 2 H), 7.32 (m, 2H), 6.98 (m, 2 H), 6.96 (m, 2 H), 6.68 (m, 2 H), 6.66 (dd, *J* = 7.8, 1.1 Hz, 1 H), 6.63 (t, *J* = 7.8 Hz, 1 H), 6.62 (m, 2 H), 5.95 (dd, *J* = 7.8, 1.1 Hz, 1 H), 3.45 (m, 2 H), 2.43 (m, 2 H); ^{13}C NMR (150 MHz, d_6-acetone): δ = 179.4, 171.8, 159.5, 158.5, 156.7, 149.6, 145.5, 134.8, 133.7, 133.3, 133.1, 130.6, 129.8, 129.8, 129.3, 126.2, 124.4, 123.9, 122.8, 118.1, 116.2, 115.9, 115.8, 115.6, 113.4, 110.2, 43.7, 34.6.

[4] Liu, Y.; Lien, I. F.; Ruttgaizer, S.; Dove, P.; Taylor, S. D. *Org. Lett.* **2004**, *6*, 209-212.

IR (film): $\tilde{\nu}$ = 3312, 2925, 1687, 1582, 1511, 1436, 1392, 1357, 1217, 1168, 1106, 1080, 827, 780 cm^{-1}. MS (EI): *m/z* (%): 557 ([M+H]). HRMS (EI) *calcd*. for $C_{34}H_{24}N_2NaO_6$: 579.15321 (M+Na); *found*: 579.15271 (M+Na).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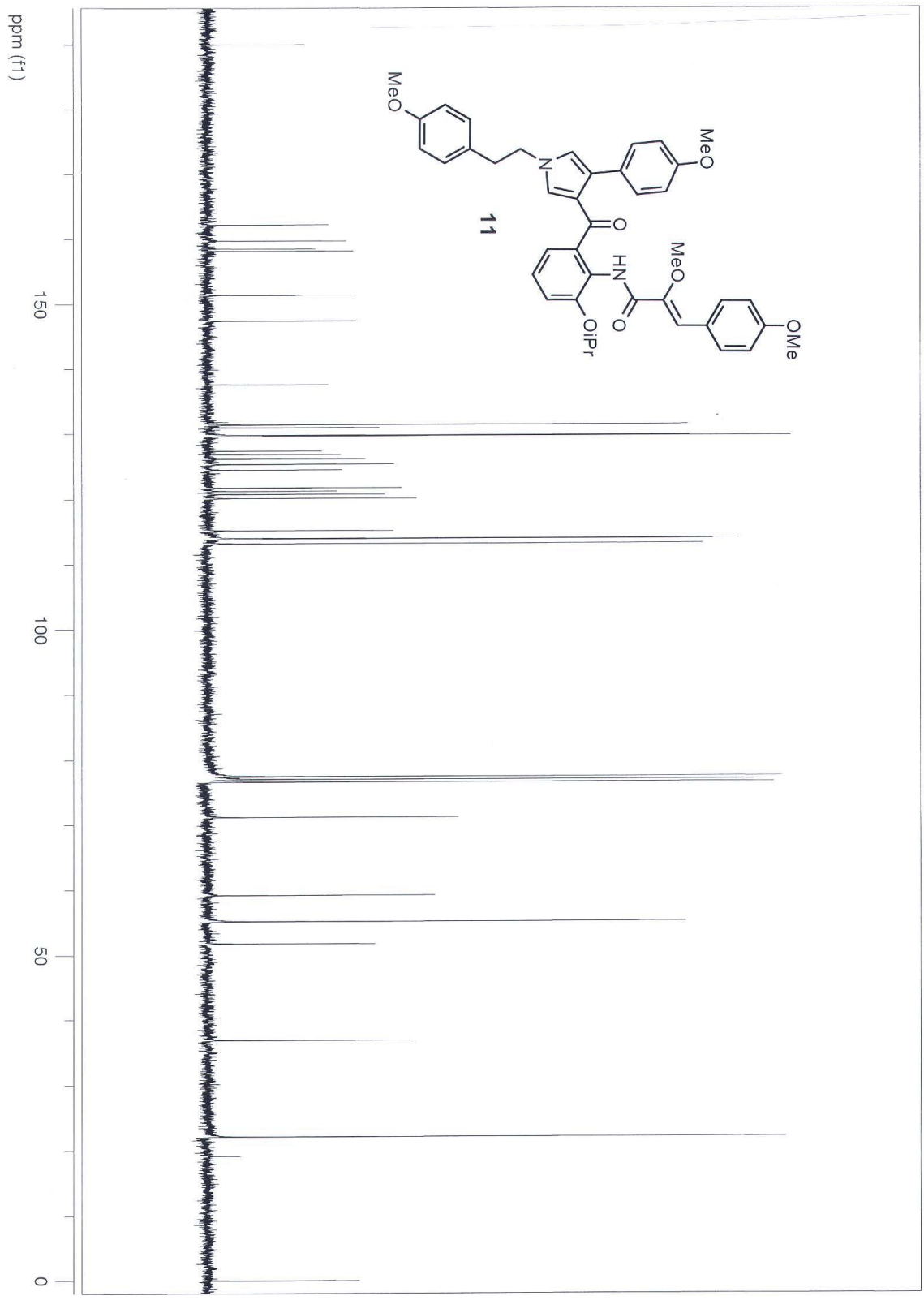
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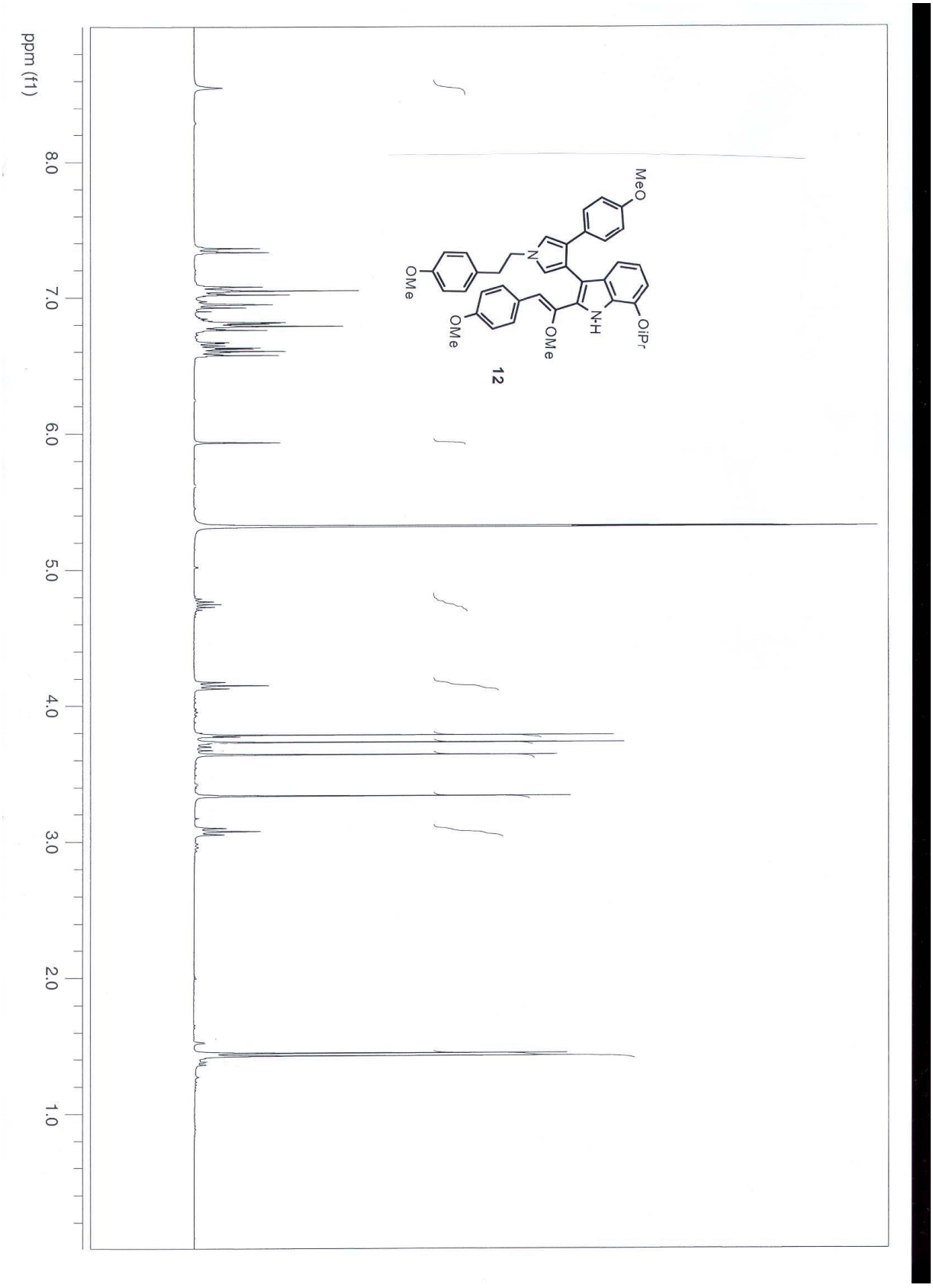
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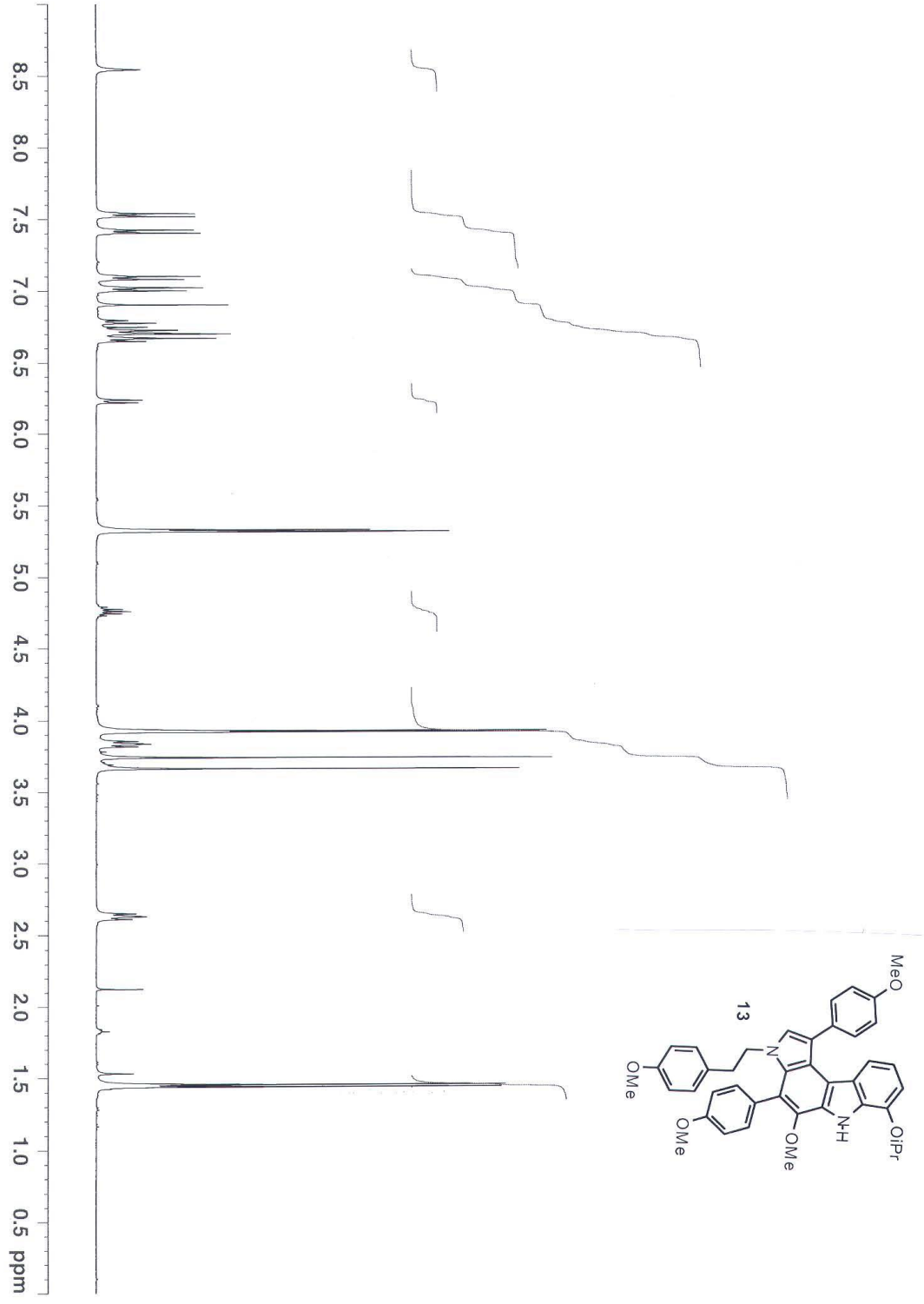
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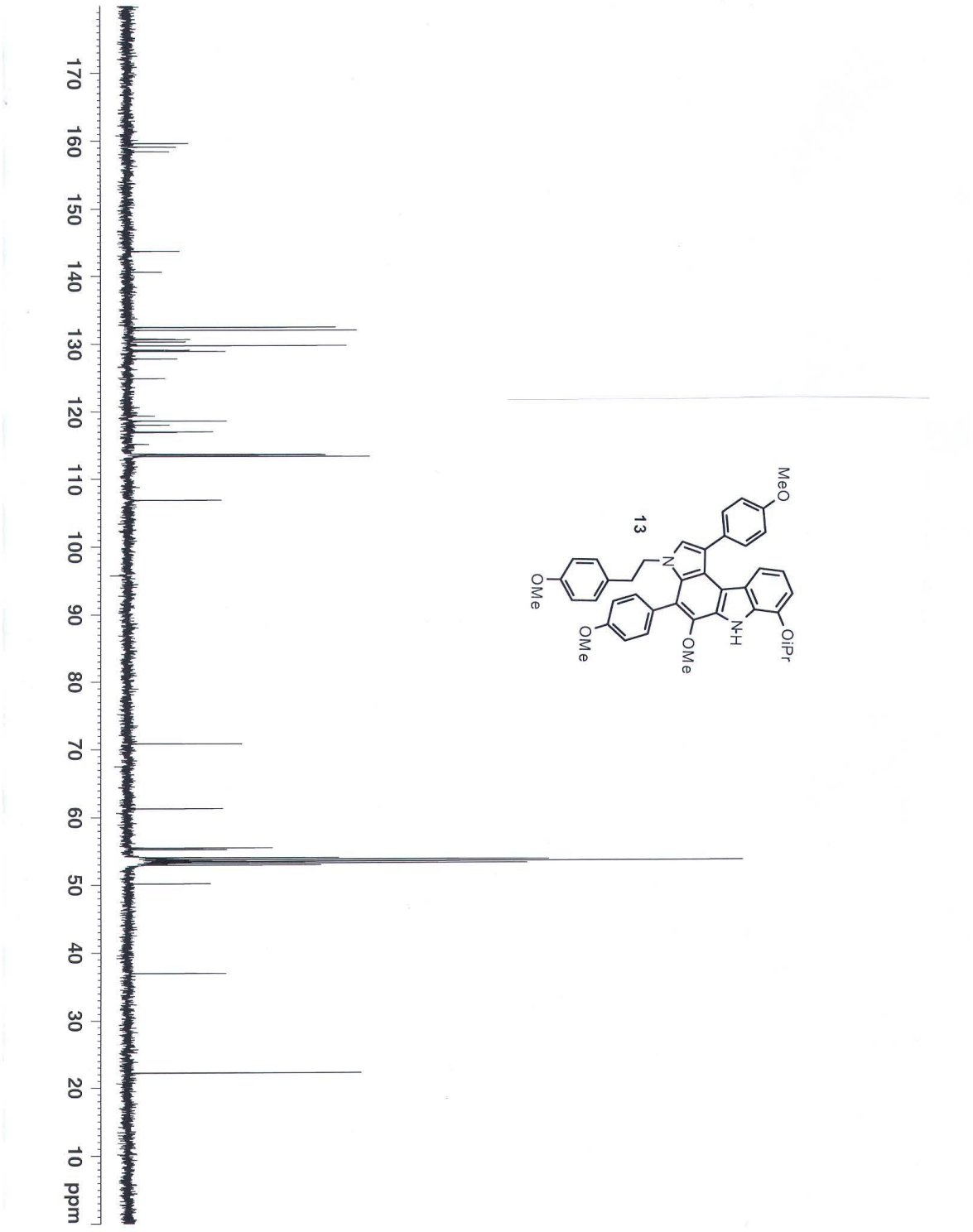
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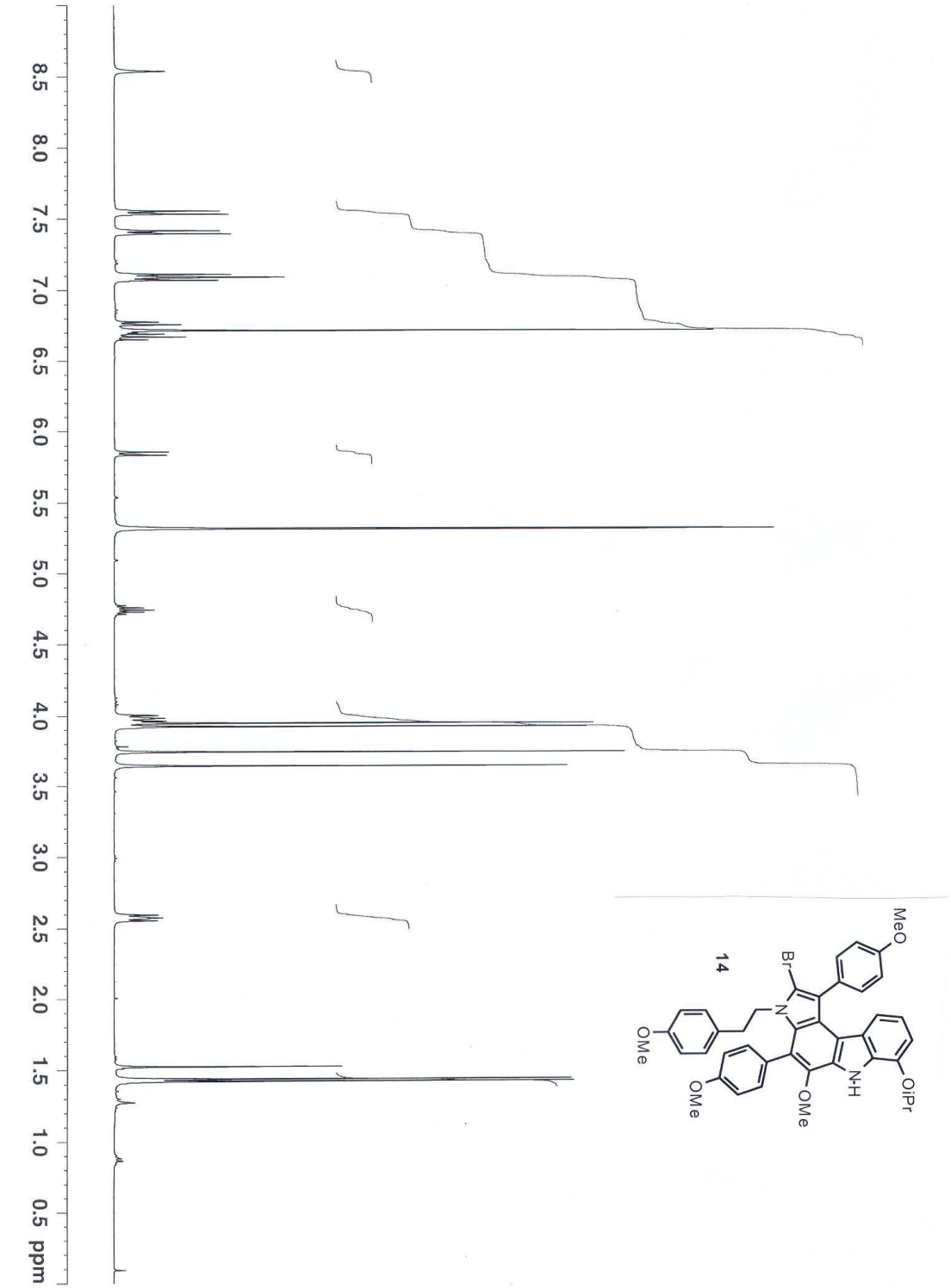
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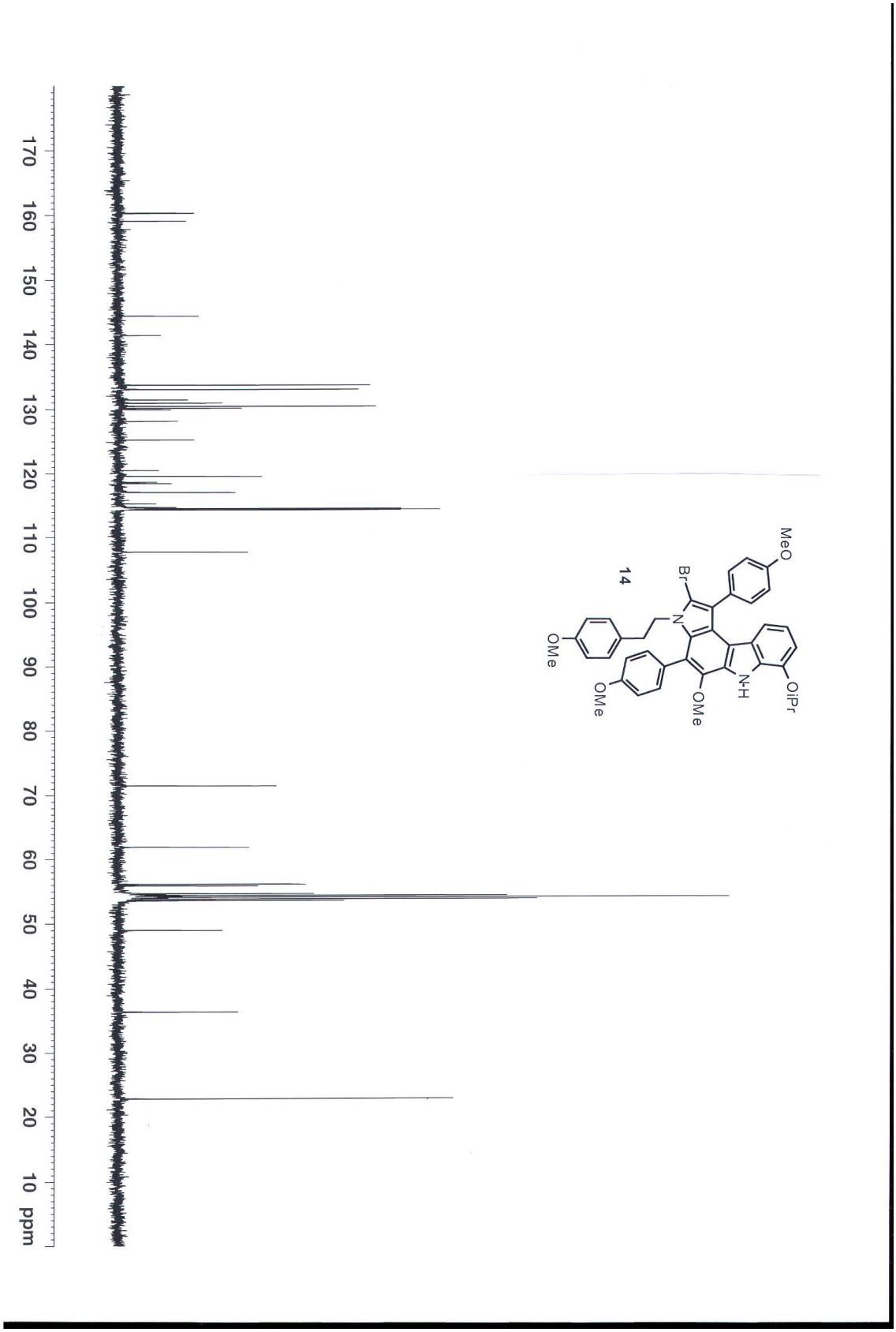
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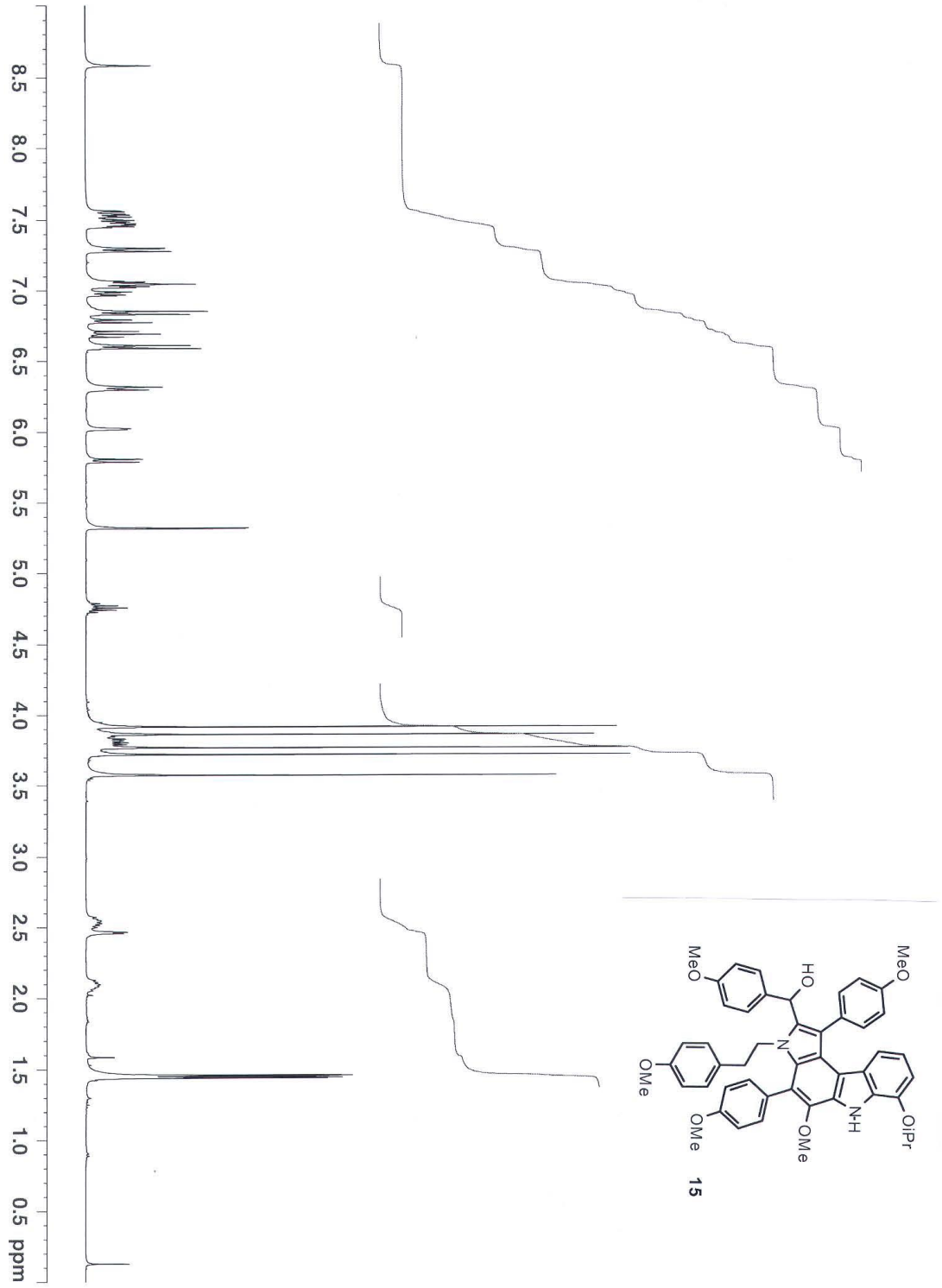
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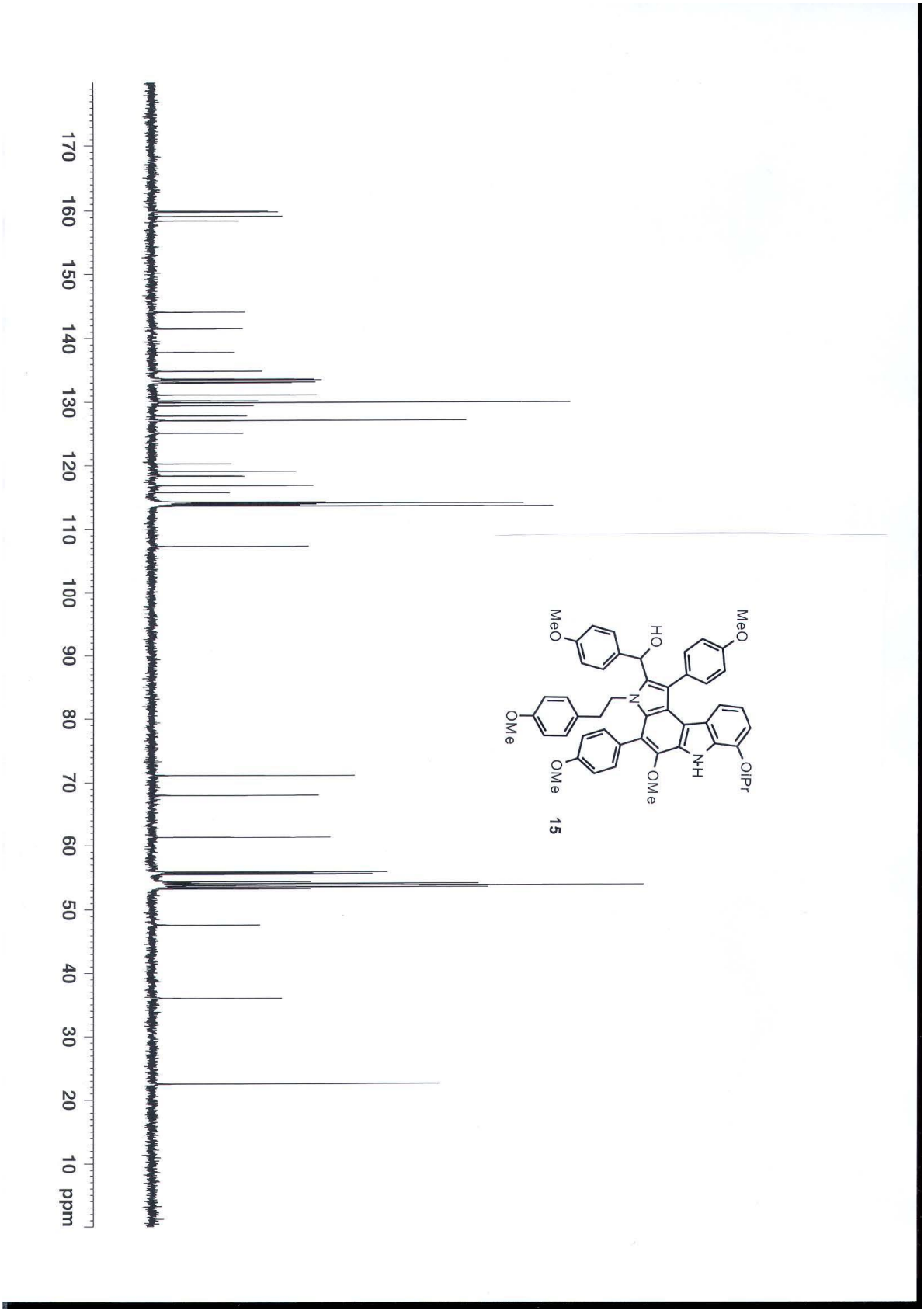
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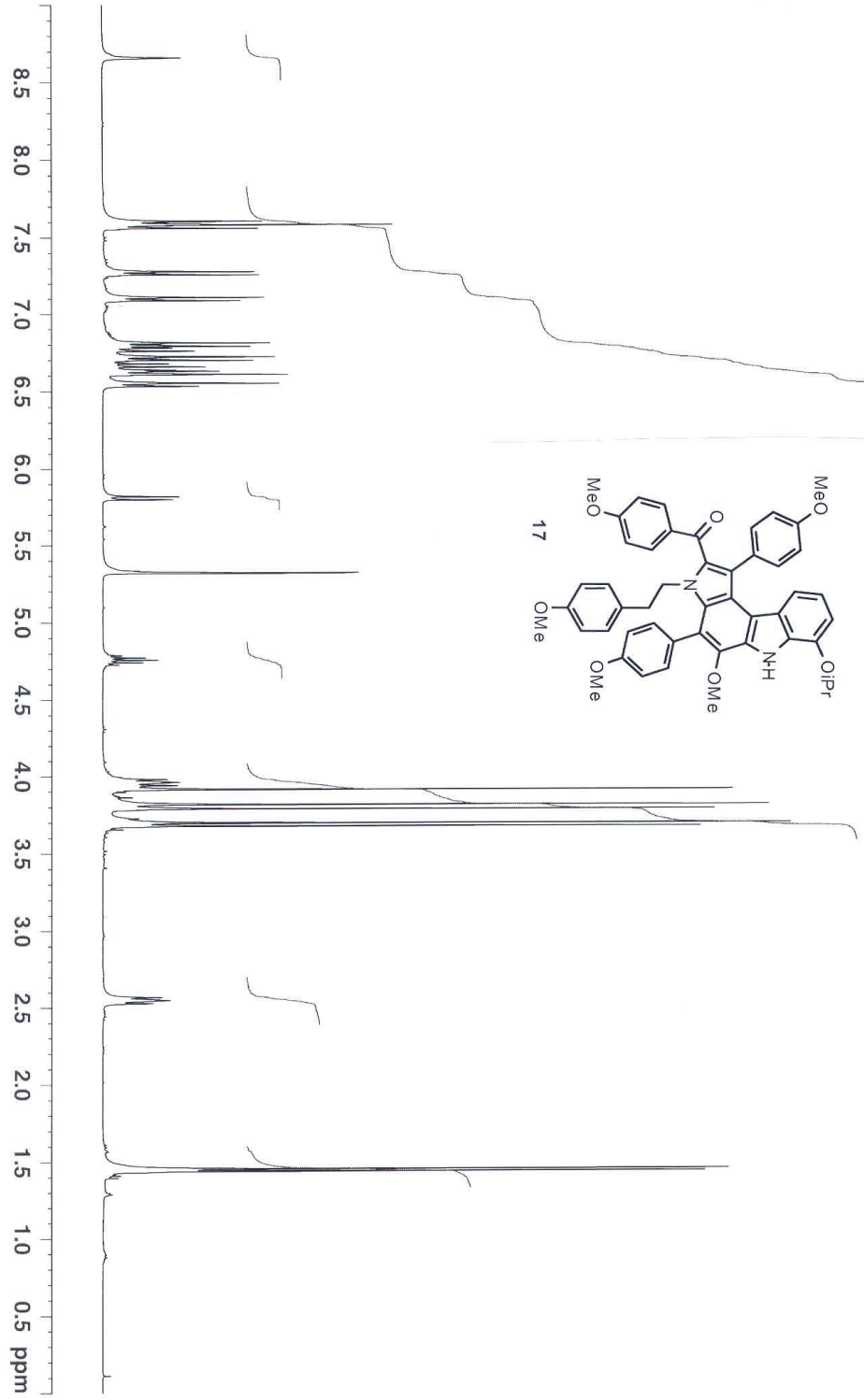
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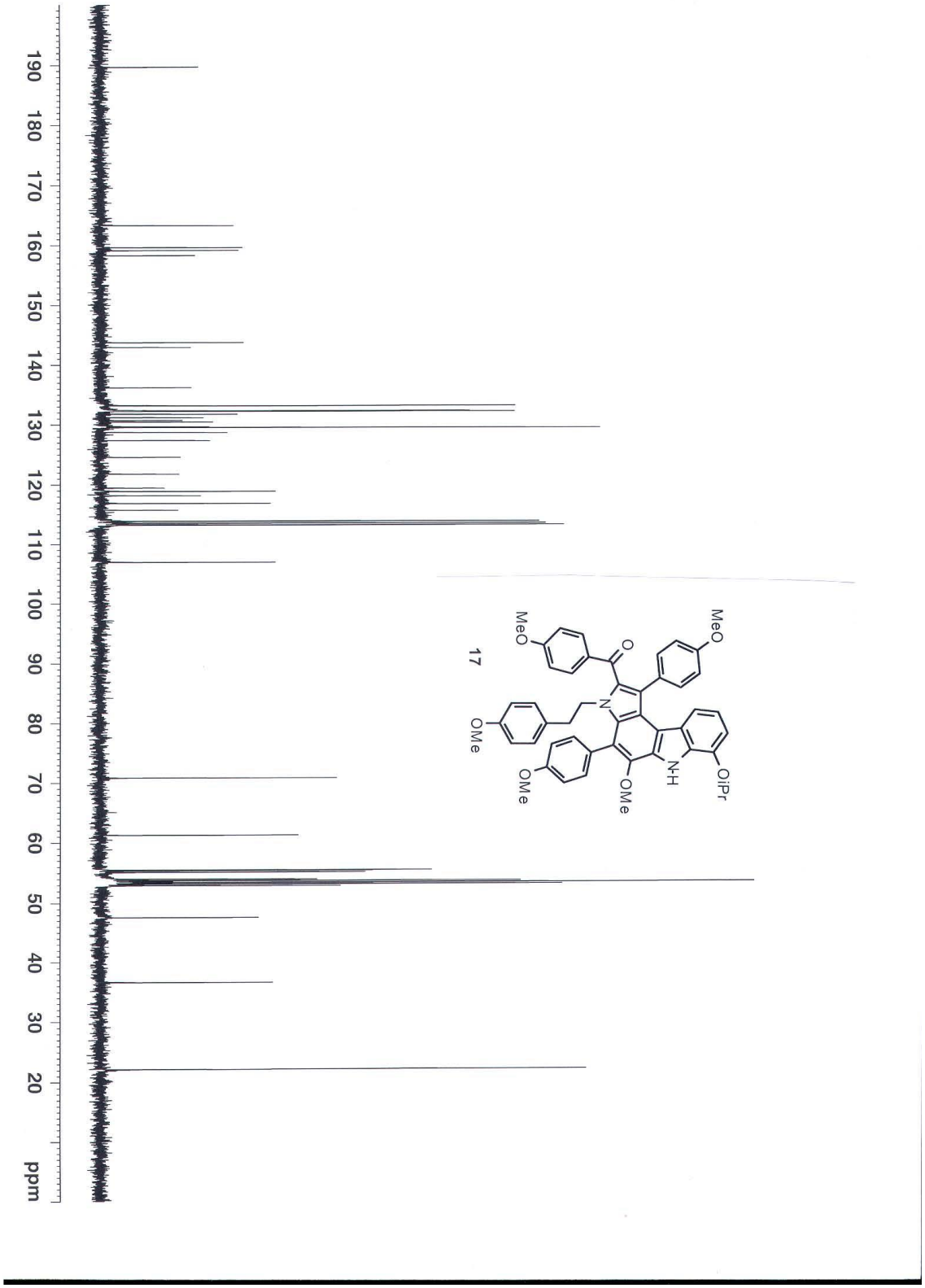
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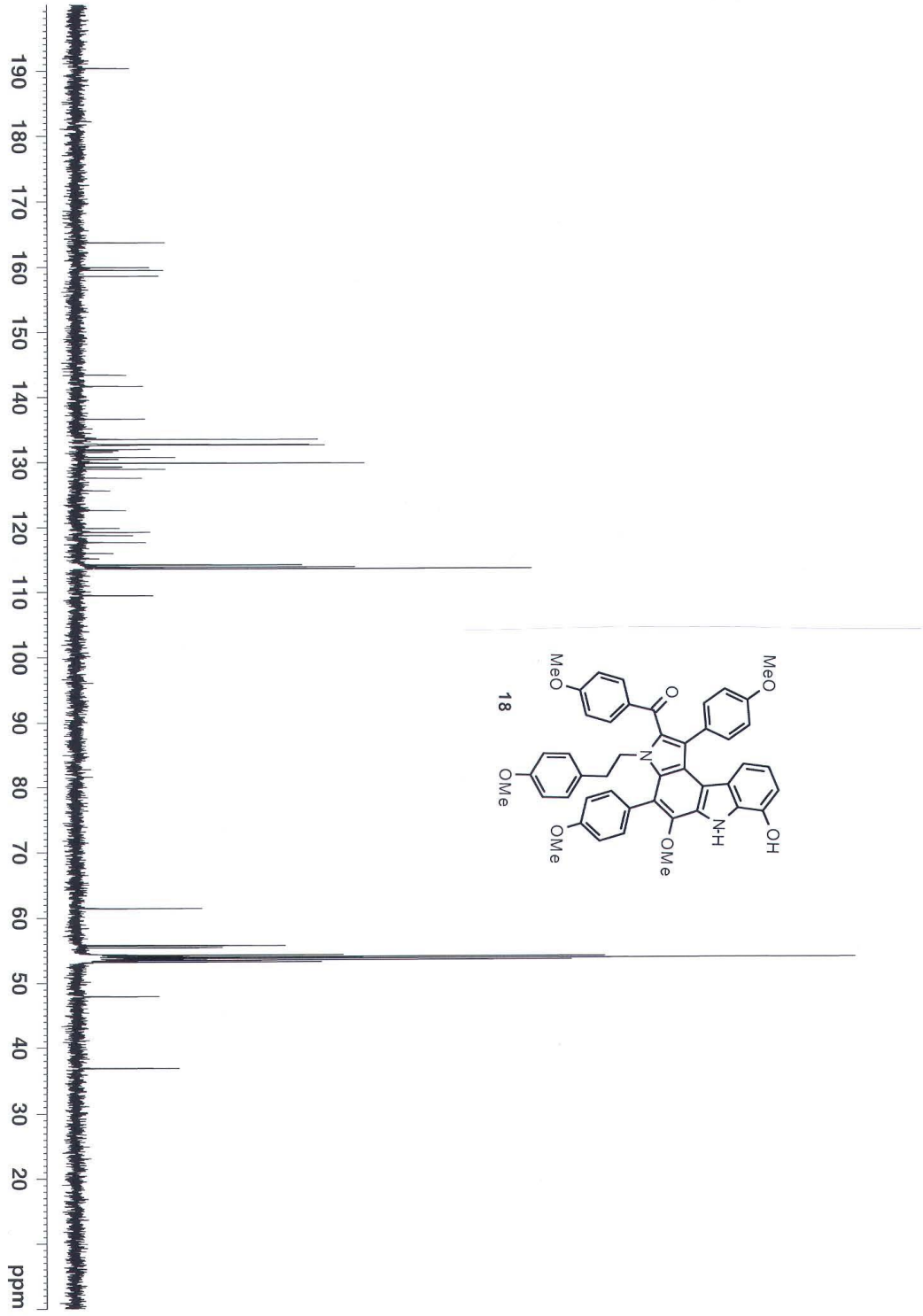
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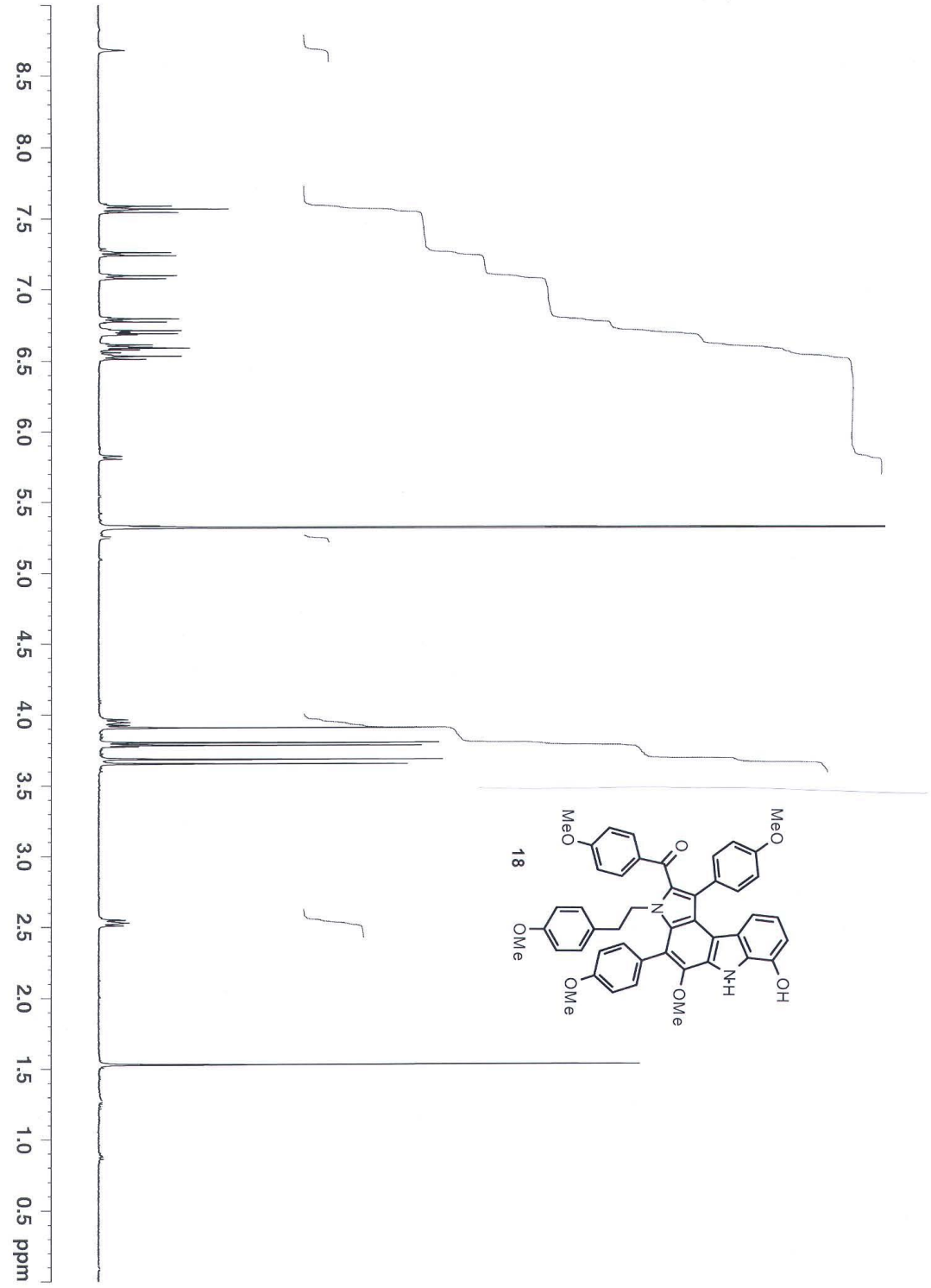
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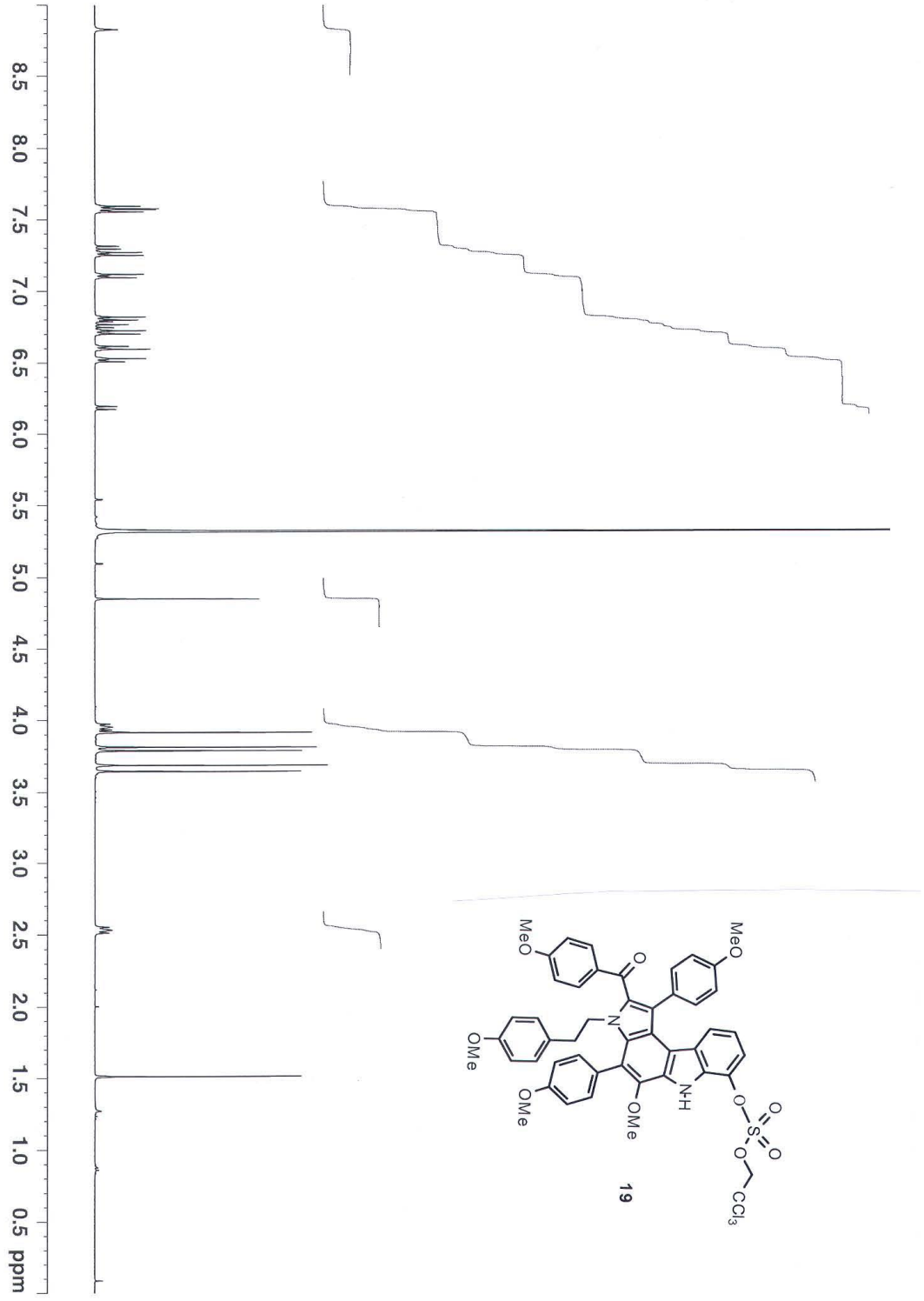
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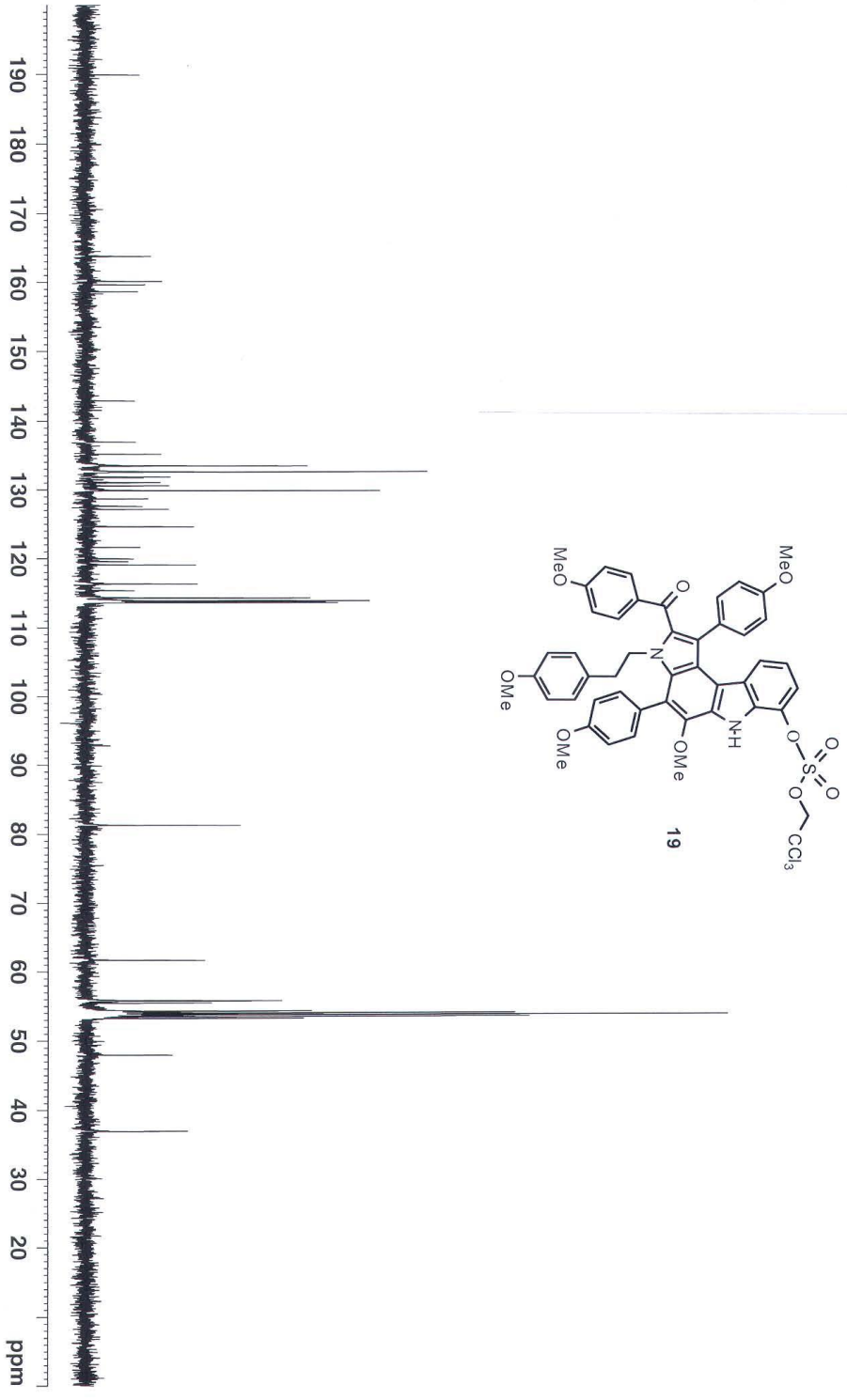
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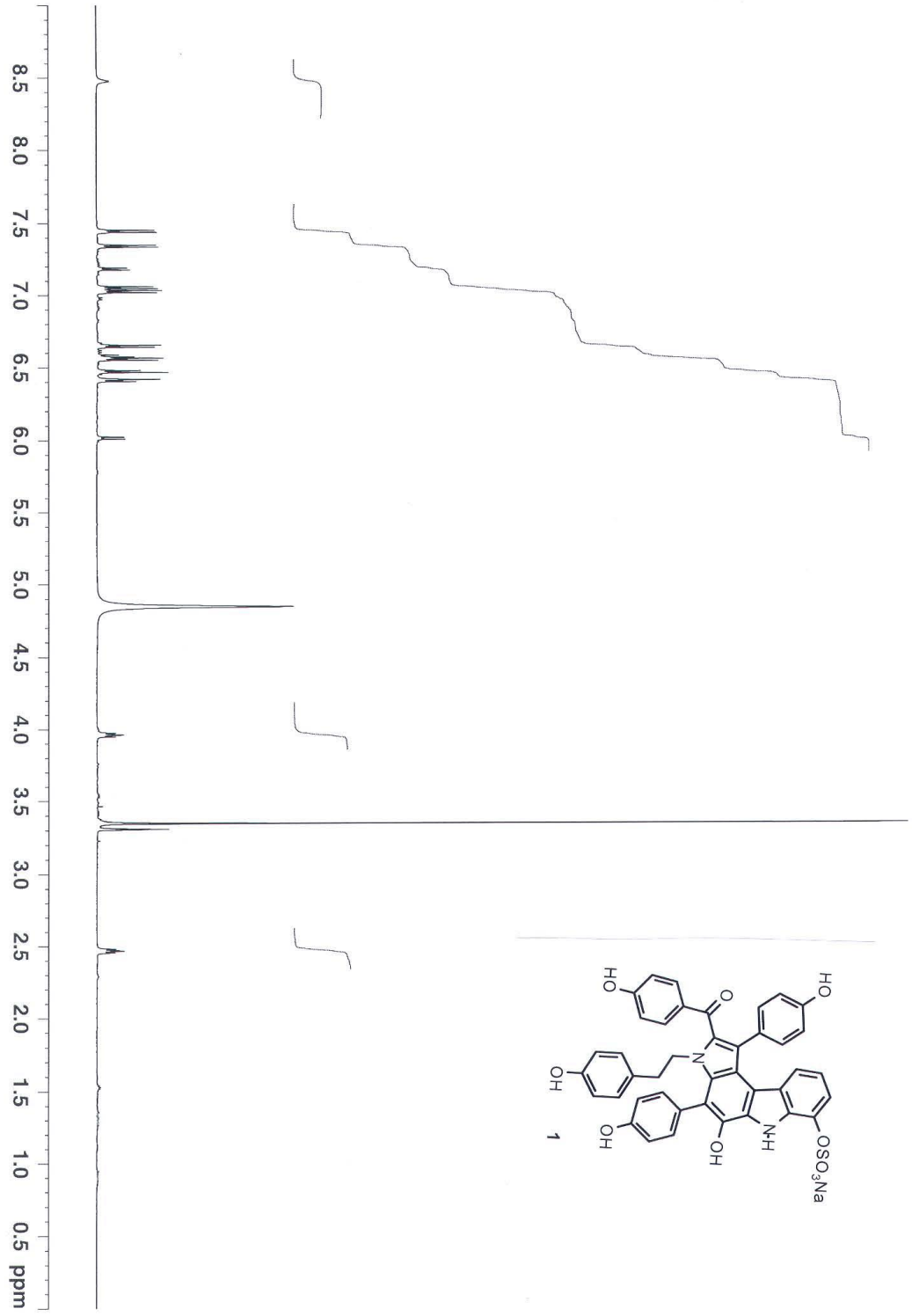
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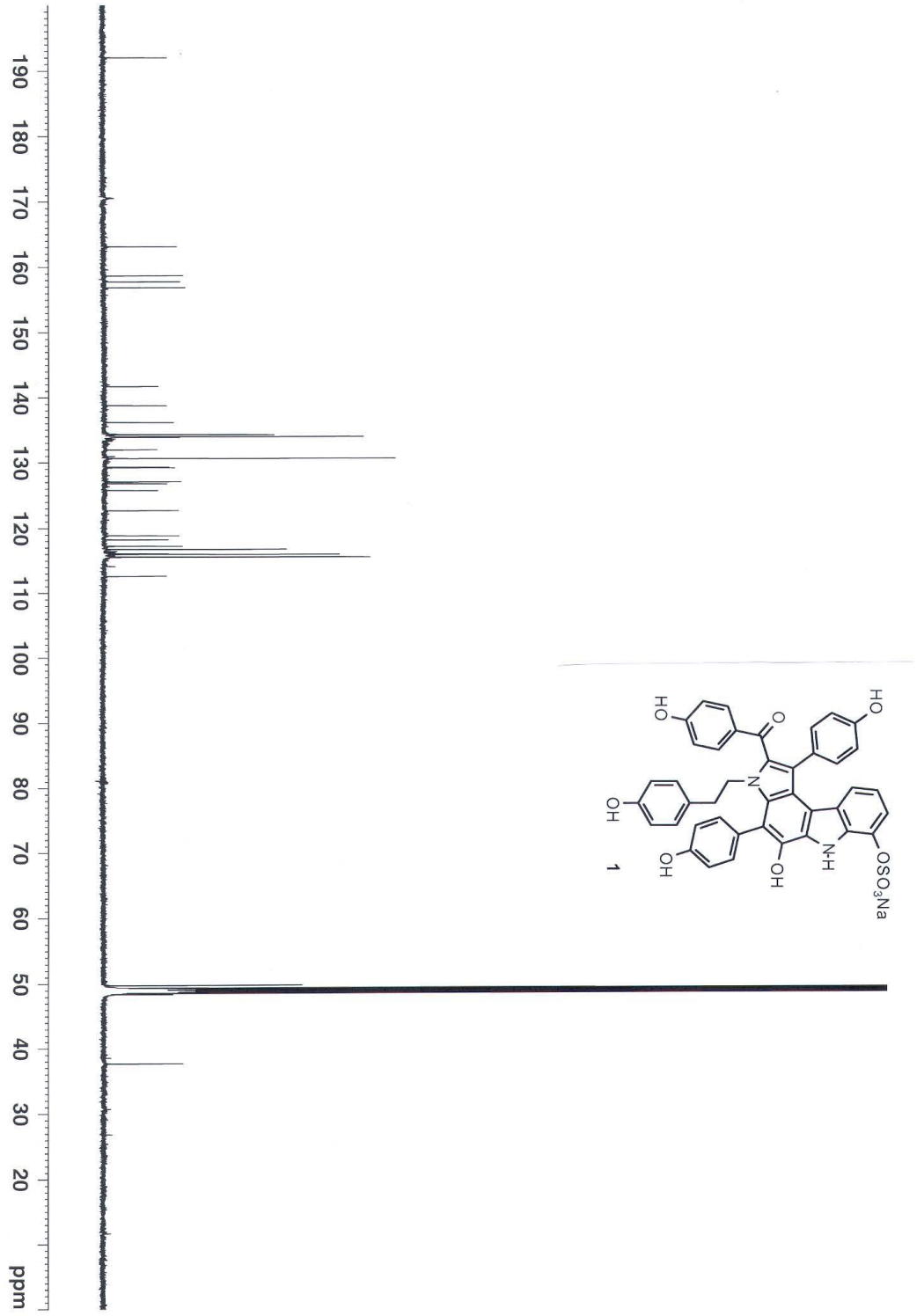
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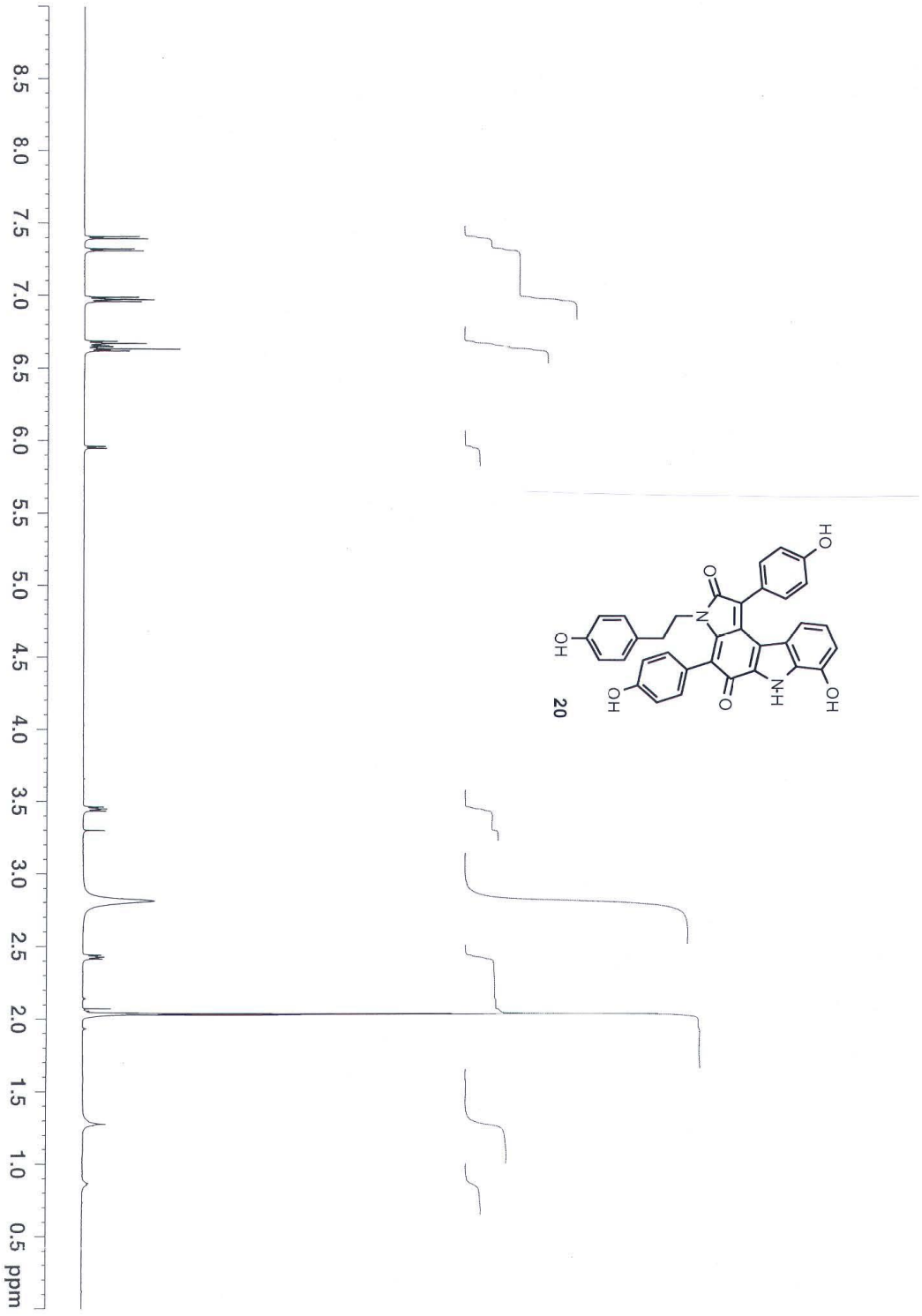
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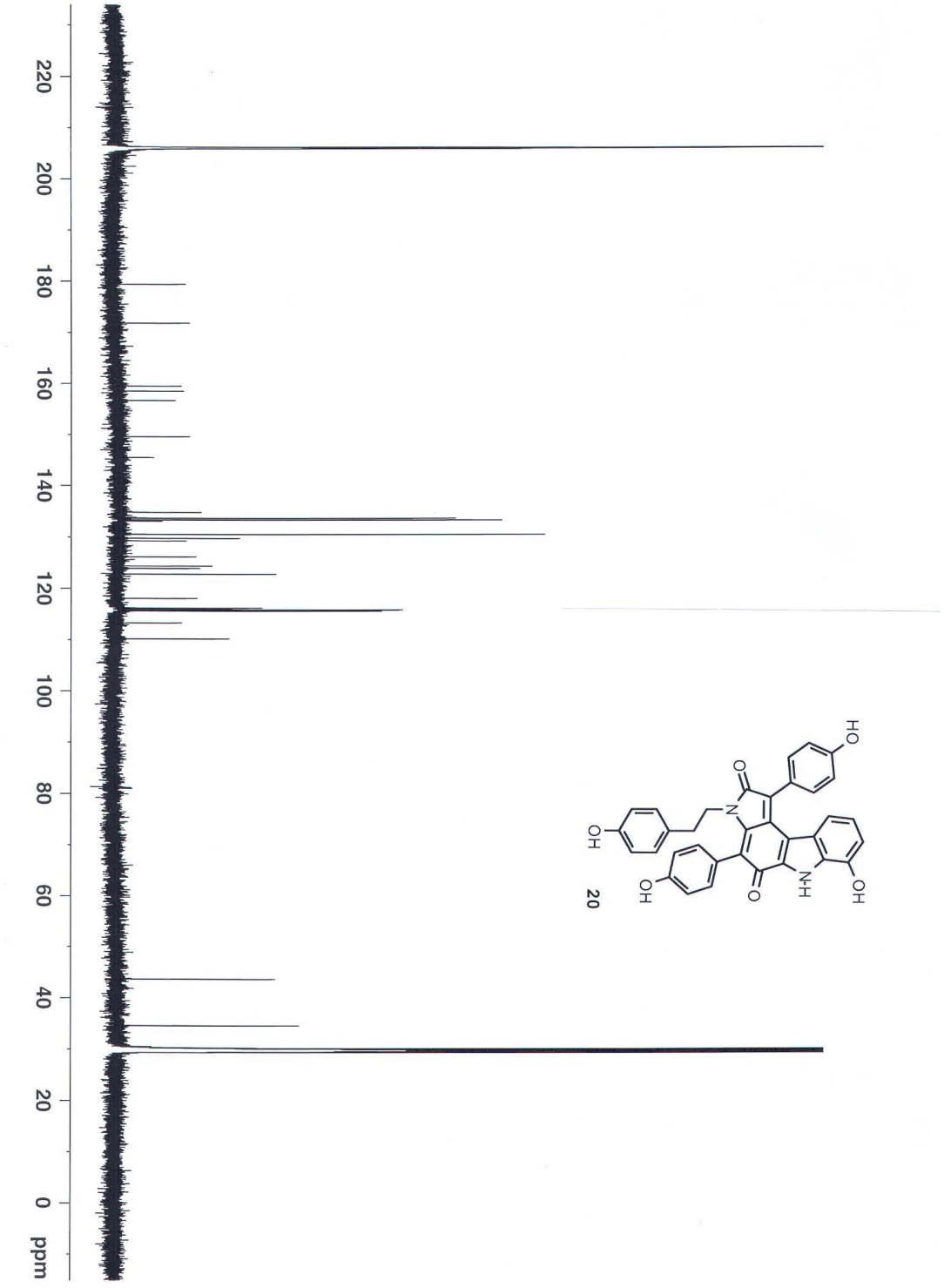
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