Electronic Supplementary Information

Conformational, Steric and Electronic Effects on the Site- and Chemoselectivity of the Metal-catalyzed Reaction of *N*-bis(Trimethylsilyl)methyl, *N*-(2-indolyl)methyl α-Diazoamides.

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***N*-Methoxy-*N*-methyl-1-phenylsulfonylindole-2-carboxamide (6a)**. To a stirred mixture of KOBu-*t* (61.5 mg, 0.338 mmol) and 18-crown-6 (6.5 mg, 0.025 mmol) in dry THF (2 mL) was added dropwise a solution of compound **6c** (51.0 mg, 0.25 mmol) in the same solvent (2 mL) via cannula. After cooling at 0 °C for 15 min, a solution of $PhSO_2Cl$ (44.3 mg, 32.0 μL) in dry THF (2 mL) was added dropwise. The mixture was stirred at rt for 2 h, then concentrated to a small volume and extracted with EtOAc. The organic extracts were washed with brine, dried, filtered, evaporated and the residue was purified (3:1 v/v PE–EtOAc) as the eluent to give a light brown oil (41.3 mg, 48%). IR (NaCl, film) 1670 cm^{-1}; ^1H NMR (200 MHz) δ 3.25 (s, 3 H), 3.48 (br s, 3 H), 6.60 (s, 1 H), 7.00–7.49 (m, 5 H), 7.75–8.00 (m, 4 H); ^{13}C NMR (75 MHz) δ 34.0, 62.0, 110.8, 114.6, 122.2, 124.2, 126.0, 128.2, 129.8, 133.0, 134.8, 136.0, 138.0; HRMS (EI) calcd for $C_{17}H_{16}N_2O_4S$ (M+) 344.0831, found 344.0833.

***N*-Methoxy-*N*-methyl-1-methylindole-2-carboxamide (6b)**. NaH (60%, 294 mg, 7.35 mmol, prewashed with hexane) was mixed with dry DMF (2 mL). The suspension was stirred for 10 min under Ar at rt, and then cooled to 0 °C. A solution of **6c** (1.0 g, 4.9 mmol) in dry DMF (4 mL) was added via cannula under Ar at 0 °C. The mixture was stirred for 15 min, and then MeI (0.920 mL, 14.7 mmol) was added at 0 °C. The reaction mixture was warmed to rt. The reaction was judged to be complete when TLC analysis showed that there was no starting material. Brine (6 mL) and a spatula tip full of solid NaCl was added to the reaction mixture. After stirring for 10 min, EtOAc (10 mL) was added. The mixture was transferred to a separatory funnel and extracted with EtOAc. The combined organic layers were washed with brine, dried, filtered and concentrated in vacuo. The crude product was purified (3:1 v/v PE–EtOAc) to give **6b** a pale yellow oil (0.996 g, 93%). IR (NaCl, film) 1634 cm^{-1}; ^1H NMR (200 MHz) δ 3.40 (s, 3 H), 3.60 (s, 3 H), 3.90 (s, 3 H), 7.10–7.43 (m, 5 H), 7.66 (d, 1 H, *J* = 7.5 Hz); ^{13}C NMR (50 MHz) δ 31.6, 33.8, 61.2, 106.9, 109.7, 120.0, 121.9, 123.8, 126.1, 129.4, 138.2, 162.7; HRMS (EI) calcd for $C_{12}H_{14}N_2O_2$ (M+) 218.1055, found 218.1050.

General procedure for the preparation of 2-indolecarbaldehyde 7a–c. A solution of $LiAlH_4$ in THF (1 M, 2.3 mL, 2.3 mmol) was added, dropwise, to a solution of the amide **6a–c** (1 mmol) in dry THF (8 mL) at −78 °C and the reaction was stirred for 4 h under Ar. Then 1 M aq HCl (1 mL) and brine (6 mL) was added to the reaction mixture at 0 °C. The mixture was stirred for 10 min and filtered through a pad of Celite®. The filtrate was concentrated in vacuo and the residue was extracted with CH_2Cl_2. The combined organic layers were dried, filtered, evaporated and the crude product was purified to give the known 2-indolecarbaldehydes: 1-Phenylsulfonyl-2-indolcarbaldehyde (**7a**). Chromatography: 7:1 v/v PE–EtOAc; yield: 60%. White solid, mp 141–142 °C (lit.[20a] 143.0–143.5 °C); 1-Methyl-indole-2-carbaldehyde (**7b**). Chromatography: 6:1 v/v PE–EtOAc; yield: 77%. White solid, mp 80–82 °C (lit.[20b] 84–85 °C); 1*H*-indole-2-carbaldehyde (**7c**). Chromatography: 10:1 v/v PE–EtOAc; yield: 65%. White solid, mp 138–140 °C (lit.[20c] 140 °C).

2-(*N*-Ethylaminomethyl)-1-phenylsulfonylindole (9a). To a solution of compound **7a** (77 mg, 0.27 mmol) in dry MeOH (5 mL) was added $EtNH_2$·HCl (44.0 mg, 0.54 mmol) and $NaBH_3CN$ (15.1 mg, 0.24 mmol). The resulting mixture was stirred at rt overnight. The mixture was then acidified to pH < 2

with 6 M HCl. The MeOH was evaporated in vacuo and the residue was taken up in 2 mL water, and brought to pH > 10 with 6 M aq NaOH. The aqueous phase was saturated with solid NaCl, and extracted with Et_2O. The combined extracts were dried, filtered, evaporated in vacuo. The crude product was purified (2:1 v/v PE–EtOAc) as the eluent to give a brown oil (41.8 mg, 48%). IR (NaCl, film) 3412 cm^{-1}; ^1H NMR (300 MHz) δ 1.12 (t, 3 H, *J* = 7.2 Hz), 1.98 (s, 1 H), 2.67 (q, 2 H, *J* = 7.2 Hz), 4.14 (s, 2 H), 6.58 (s, 1 H), 7.22 (ddd, 2 H, *J* = 7.7, 7.7, 1.4 Hz), 7.25–7.35 (m, 1 H), 7.36–7.47 (m, 3 H), 7.50–7.58 (m, 1 H), 7.76–7.83 (m, 2 H), 8.12–8.18 (m, 1 H); ^{13}C NMR (75 MHz) δ 12.8, 41.7, 47.8, 111.8, 115.2, 121.1, 124.2, 125.0, 126.8, 126.5, 128.0, 134.2, 137.8, 139.2, 139.5; HRMS (EI) calcd for $C_{17}H_{18}N_2O_2S$ (M+) 314.1089, found 314.1085.

Preparation of *N*-BTMSM amines 9b–d.

(i) **General procedure for the preparation of *N*-BTMSM imines**. The 2-indolecarbaldehydes **7a–c** (1 mmol) was dissolved in Et_2O (5 mL), and activated 3Å MS (300 mg) was added. Then bis(trimethylsilyl)methylamine (185 mg, 1.78 mmol) was added under Ar at rt, and then the mixture was stirred overnight. The reaction mixture was filtered through a pad of Celite®, the filtrate was washed with water, dried, filtered and evaporated in vacuo. The crude imine products were purified.

***N*-(1H-indol-2-yl)methylidene-1,1-bis(trimethylsilyl)methanamine (8a)**. Chromatography: 15:1 v/v PE–EtOAc; yield: 90%. White power, mp 78–79 °C; IR (NaCl, film) 3454 cm^{-1}; ^1H NMR (300 MHz) δ 0.10 (s, 18 H), 2.83 (s, 1 H), 6.60 (s, 1 H), 7.06–7.11 (m, 1 H), 7.15–7.25 (m, 1 H), 7.35–7.42 (m, 1 H), 7.62 (d, 1 H, *J* = 7.8 Hz), 8.02 (s, 1 H), 8.84–8.94 (br s, 1 H); ^{13}C NMR (75 MHz) δ –1.2, 59.8, 104.5, 111.1, 119.9, 121.4, 123.6, 128.5, 136.4, 147.5; HRMS (EI) calcd for $C_{16}H_{26}N_2Si_2$ (M+) 302.1635, found 302.1623.

***N*-(1-Methylindol-2-yl)methylidene-1,1-bis(trimethylsilyl)methanamine (8b)**. Chromatography: 10:1 v/v PE–EtOAc; yield: 87%. Pale yellow solid, mp 105–107 °C; IR (NaCl, film) 2743 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 2.75 (s, 1 H), 4.05 (s, 3 H), 6.55 (s, 1 H), 7.00 (ddd, 1 H, *J* = 8.0, 8.0, 1.6 Hz), 7.30 (ddd, 1 H, *J* = 8.0, 8.0, 1.6 Hz), 7.40 (d, 1 H, *J* = 8.0 Hz), 7.50 (d, 1 H, *J* = 8.0 Hz), 8.20 (s, 1 H); ^{13}C NMR (50 MHz) δ 0.0, 32.0, 61.0, 107.5, 110.0, 118.0, 120.0, 121.5, 124.6, 149.2; HRMS(EI) calcd for $C_{17}H_{28}N_2Si_2$ (M+) 316.1791, found 316.1785.

***N*-(1-Phenylsulfonylindol-2-yl)methylidene-1,1-bis(trimethylsilyl)methanamine (8c)**. Chromatography: 10:1 v/v PE–EtOAc; yield: 98%. Pale yellow oil; IR (NaCl, film) 2749 cm^{-1}; ^1H NMR (200 MHz) δ –0.10 (s, 9 H), 0.10 (s, 9 H), 1.00 (s, 1 H), 7.00 (s, 1 H), 7.10–7.40 (m, 6 H), 7.67 (d, 2 H, *J* =7.7 Hz), 8.10 (d, 1 H, *J* =7.7 Hz), 8.60 (s, 1 H); ^{13}C NMR (75 MHz) δ –1.0, 1.0, 32.0, 62.0, 113.0, 115.0, 122.0, 125.0, 126.0, 128.0, 130.0, 131.0, 134.0, 138.0, 138.5, 139.5, 149.0; HRMS (EI) calcd for $C_{22}H_{30}N_2O_2SSi_2$ (M+) 442.1562, found 442.1567.

(ii) **Reduction of imines 8a–c**. Each of the imines (1.0 mmol) was dissolved in dry MeOH (5 mL) and the solution was cooled to 0 °C under Ar. $NaBH_4$ (113 mg, 3.0 mmol) was added portionwise and the

reaction mixture was stirred under Ar at 0 °C for 30 min, at rt for 1.5 h, and then poured into saturated aq $NaHCO_3$ at 0 °C. MeOH was removed in vacuo and the resultant residue was extracted with CH_2Cl_2. The combined organic extracts were dried, filtered, concentrated and the crude amine product was purified.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1H-indol-2-yl)methyl]amine (9b)**. Chromatography: 10:1 v/v PE–Et_2O; yield: 90%. Pale yellow oil; IR (NaCl, film) 3461, 3408 cm^{-1}; ^1H NMR (200 MHz) δ 0.12 (s, 18 H), 1.05–1.20 (br s, 1 H), 1.50 (s, 1 H), 3.95 (s, 2 H), 6.34 (s, 1 H), 7.05–7.22 (m, 2 H), 7.32–7.40 (m, 1 H), 7.53–7.61 (m, 1 H), 8.38–8.47 (br s, 1 H); ^{13}C NMR (50 MHz) δ 0.0, 39.0, 51.0, 100.0, 110.8, 119.5, 120.0, 121.2, 128.2, 135.8, 138.0; HRMS (EI) calcd for $C_{16}H_{28}N_2Si_2$ (M+) 304.1791, found 304.1805.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-methyl-indol-2-yl)methyl]amine (9c)**. Chromatography: 15:1 v/v PE–EtOAc; yield: 98%. Yellow solid, mp 68–69 °C; IR (NaCl, film) 3053, 2953 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 0.80 (s, 1 H), 1.40 (s, 1 H), 3.70 (s, 3 H), 3.80 (s, 2 H), 6.28 (s, 1 H), 6.98 (ddd, 1 H, *J* = 7.7, 7.7, 1.1 Hz), 7.12 (ddd, 1 H, *J* = 7.7, 7.7, 1.1 Hz), 7.22 (d, 1 H, *J* = 7.7 Hz); ^{13}C NMR (50 MHz) δ 0.0, 29.9, 39.5, 50.2, 100.8, 119.2, 120.2, 121.1, 127.3, 139.0, 163.1; HRMS (EI) calcd for $C_{17}H_{30}N_2Si_2$ (M+) 318.1948, found: 318.1940.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-phenylsulfonylindol-2-yl)methyl]amine (9d)**. Chromatography: 12:1 v/v PE–EtOAc; yield: 87%. Pale yellow oil; IR (NaCl, film) 3079, 2947 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 1.40 (s, 1 H), 1.50–1.71 (br s, 1 H), 4.00 (s, 2 H), 6.50 (s, 1 H), 7.16–7.44 (m, 6 H), 7.70 (d, 2 H, *J* = 8.0 Hz), 8.1 (d, 1 H, *J* = 8.0 Hz); ^{13}C NMR (75 MHz) δ 0.0, 38.1, 51.2, 112.0, 115.2, 121.6, 124.2, 125.1, 127.0, 130.0, 134.2, 138.0, 139.8, 140.8; HRMS (EI) calcd for $C_{21}H_{29}N_2O_2SSi_2$ (M–15) 429.1488, found 429.1481.

Preparation of N-BTMSM α-carboalkoxy α-diazoacetamides 10a–d

The appropriate amine, **9a**–**d**, (1.0 mmol) was dissolved in dry CH_2Cl_2 (3 mL) under Ar. 2,6-Lutidine (2.0 mmol) was added to the solution and the mixture was cooled to 0 °C. A solution of methyl or ethyl diazomalonyl chloride (1.5 mmol) in dry CH_2Cl_2 (2 mL) was then transferred, via cannula, to the reaction mixture. The reaction was stirred at 0 °C for 20 min and then at rt for 1 h. The mixture was washed successively with saturated $NaHCO_3$ (5 mL), H_2O (5 mL) and brine (5 mL). The organic layer was dried, filtered, evaporated in vacuo, and the residue was purified.

***N*-Ethyl-*N*-[(1-phenylsulfonylindol-2-yl)methyl]-α-carbomethoxy-α-diazoacetamide (10a)**. Chromatography: 3:1 v/v PE–EtOAc; yield: 72%. Pale yellow oil; IR (film) 1624, 1714, 2130 cm^{-1}; ^1H NMR (300 MHz) δ 1.15 (t, 3 H, *J* = 7.3 Hz), 3.46 (q, 2 H, *J* = 7.3 Hz), 3.70 (s, 3 H), 5.00 (d, 2 H, *J* = 1.2 Hz), 6.50 (d, 1 H, *J* = 1.2 Hz), 7.20 (ddd, 1 H, *J* = 7.4, 7.4, 1.4 Hz), 7.21–7.27 (m, 1 H), 7.37–7.43 (m, 3 H), 7.50–7.58 (m, 1 H), 7.76–7.82 (m, 2 H), 8.05–8.09 (m, 1 H); ^{13}C NMR (75 MHz) δ 13.7,

29.8, 43.8, 45.0, 52.5, 110.0, 114.2, 121.0, 124.0, 124.8, 126.4, 129.3, 129.4, 133.9, 136.5, 137.2, 138.5, 161.8, 163.0; HRMS (CI) calcd for $C_{21}H_{21}N_4O_5S$ (M+1) 441.1233, found 441.1241.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1H-indol-2-yl)methyl]-α-carbomethoxy-α-diazoacetamide (10b)**. Chromatography: 5:1 v/v PE–Et2O; yield: 83%. Yellow solid; IR (film) 3404, 2132, 1702, 1619 cm^{-1}; ^1H NMR (300 MHz) δ 0.00 (s, 18 H), 2.35 (s, 1 H), 3.90 (s, 3 H), 4.50 (s, 2 H), 6.49 (s, 1 H), 7.11 (ddd, 1 H, *J* = 7.9, 7.0, 1.0 Hz), 7.21 (ddd, 1 H, *J* = 8.2, 7.0, 1.1 Hz), 7.41–7.47 (m, 1 H), 7.60 (d, 1 H, *J* = 7.9 Hz), 9.75–9.85 (br s, 1 H); ^{13}C NMR (75 MHz) δ 0.0, 44.0, 52.0, 54.0, 105.2, 112.4, 120.0, 122.1, 124.2, 128.5, 134.0, 138.5, 159.5, 165.2; HRMS (EI) calcd for $C_{19}H_{27}N_4O_3Si_2$ (M–15) 415.1622, found: 415.1629.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-methylindol-2-yl)methyl]-α-carboethoxy-α-diazoacetamide (10c)**. Chromatography: 9:1 v/v PE–EtOAc; yield: 80%. Pale yellow solid; IR (film) 2120, 1707, 1618 cm^{-1}; ^1H NMR (300 MHz) δ 0.00 (s, 18 H), 1.25 (t, 3 H, *J* = 8.2 Hz), 2.45 (s, 1 H), 3.62 (s, 3 H), 4.30 (q, 2 H, *J* = 8.2 Hz), 4.58 (s, 2 H), 6.48 (s, 1 H), 7.10 (ddd, 1 H, *J* = 8.3, 8.3, 1.6 Hz), 7.21 (ddd, 1 H, *J* = 8.3, 8.3, 1.6 Hz), 7.24 (d, 1 H, *J* = 8.3 Hz), 7.58 (d, 1 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz) δ 0.0, 14.0, 29.0, 42.5, 47.5, 61.8, 104.9, 109.0, 119.5, 120.4, 122.0, 126.8, 133.4, 136.8, 162.5; HRMS (EI) calcd for $C_{21}H_{31}N_2O_3Si_2$ (M–43) 415.1873, found 415.1877.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-phenylsulfonylindol-2-yl)methyl]-α-carboethoxy-α-diazoacetamide (10d)**. Chromatography: 5.5:1 v/v PE–EtOAc; yield: 71%. Pale yellow solid; IR (film) 2125, 1698, 1615 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 1.19 (s, 1 H), 1.24 (t, 3 H, *J* = 8.2 Hz), 4.22 (q, 2 H, *J* = 8.2 Hz), 4.83 (s, 2 H), 6.59 (s, 1 H), 7.16–7.56 (m, 8 H), 8.15 (d, 1 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz) δ 0.0, 15.0, 42.6, 50.2, 61.5, 116.0, 124.8, 126.0, 126.5, 127.0, 128.8, 129.9, 134.6, 136.5, 137.5, 138.0, 160.0; HRMS (EI) calcd for $C_{26}H_{33}N_4O_5SSi_2$ (M–15) 569.1710, found 569.1701.

Preparation of *N*-BTMSM α-acetyl α-diazoacetamides 10e,f. Amine **9c** or **9d** (1.0 mmol) and DMAP (20 mol%) were dissolved in dry THF (5 mL). The solution was cooled to 0 ^oC, and freshly redistilled diketene (1.5 mmol) in THF (3 mL) was added via cannula under Ar. The reaction was kept at 0 ^oC for 10 min, and then stirred at rt. After 1.5 h, TLC analysis showed that the reaction was complete. The mixture was diluted with CH_2Cl_2 (5 mL) and filtered through a short pad of silica gel (60Å) in a sintered funnel. The filtrate was evaporated in vacuo and the crude acetoacetamide was used without additional purification for the diazotization step.

The crude amide obtained above was dissolved in dry CH_3CN (4 mL) under Ar at 0 ^oC. MsN_3 (2.0 mmol) in dry CH_3CN (3 mL) was added via cannula. DBU (2.0 mmol) was then added, the reaction mixture was stirred at 0 ^oC for 1 h and then at rt for 1 h. The mixture was diluted with CH_2Cl_2 (5 mL), washed with 10% aq NaOH (2x5 mL) and the aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The

combined organic solution was washed with H_2O, dried, filtered, evaporated in vacuo and the crude product was purified.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-methylindo-2-lyl)methyl]-α-acetyl-α-diazoacetamide (10e)**. Chromatography: 2:1 v/v PE–EtOAc; Yield: 79%. Pale yellow solid; IR (film) 2090, 1659, 1617 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 2.40 (s, 3 H), 2.60 (s, 1 H), 3.75 (s, 3 H), 4.70 (s, 2 H), 6.49 (s, 1 H), 7.09–7.32 (m, 3 H), 7.60 (d, 1 H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz) δ 0.0, 27.2, 30.2, 43.5, 49.0, 105.1, 109.8, 120.5, 121.2, 122.6, 127.5, 134.0, 137.2, 160.0; HRMS (EI) calcd for $C_{21}H_{32}N_2O_2Si_2$ (M–28) 400.2003, found 400.1996.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-phenylsulfonylindol-2-yl)methyl]-α-acetyl-α-diazoacetamide (10f)**. Chromatography: 3.5:1 v/v PE–EtOAc; yield: 71%. Pale yellow solid; IR (film) 2108, 1648, 1624 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 1.55 (s, 1 H), 2.30 (s, 3 H), 4.80 (s, 2 H), 6.60 (s, 1 H), 7.15–7.52 (m, 8 H), 8.10 (d, 1 H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz) δ 0.0, 26.0, 42.1, 49.7, 114.120.2, 123.6, 124.8, 125.3, 128.2, 128.5, 133.3, 134.9, 137.1, 158.8; HRMS (EI) calcd for $C_{26}H_{34}N_2O_4SSi_2$ (M–28) 526.1778, found 526.1771.

Preparation of *N*-BTMSM α-diazoacetamides 10g,h

The α-diazoacetoacetamides **10e** or **10f** (1.0 mmol) was dissolved in CH_3CN (5 mL) and 5% aq KOH (3 mL) was added. The reaction mixture was vigorously stirred and reaction progress was closely monitored using TLC. The organic solvent was removed in vacuo, saturated aq NH_4Cl (2 mL) was added to the residue and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried, filtered, evaporated in vacuo, and the crude product was purified.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-methylindol-2-yl)methyl]-α-diazoacetamide (10g)**. Chromatography: 10:1 v/v PE–EtOAc; yield: 81%. Yellow solid; IR (film) 2104, 1602 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 3.60 (s, 3 H), 3.75 (s, 1 H), 4.40–4.60 (m, 2 H), 4.75–4.90 (m, 1 H), 6.48 (s, 1 H), 7.05–7.25 (m, 3 H), 7.55 (d, 1 H, *J* = 7.4 Hz); ^{13}C NMR (50 MHz) δ 0.0, 32.0, 41.0, 48.1, 49.5, 104.0, 105.1, 118.0, 120.0, 120.1, 122.0, 123.5, 128.0, 135.0, 137.5, 168.2; HRMS (EI) calcd for $C_{18}H_{27}N_4OSi_2$ (M–15) 371.1723, found 371.1726.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-phenylsulfonylindol-2-yl)methyl]-α-diazoacetamide (10h)**. Chromatography: 7:1 v/v PE–EtOAc; yield: 89%. Yellow solid; IR (film) 2107, 1609 cm^{-1}; ^1H NMR (200 MHz) δ 0.00 (s, 18 H), 4.48 (s, 1 H), 4.60 (s, 2 H), 6.55 (s, 1 H), 7.18–7.52 (m, 6 H), 7.68 (d, 2 H, *J* = 7.4 Hz), 8.11 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (Acetone-d6, 75 MHz) δ 0.0, 46.0, 111.8, 114.4, 120.8, 123.8, 124.6, 126.1, 129.2, 129.5, 134.2, 136.9, 137.2, 137.9, 164.8; HRMS (EI) calcd for $C_{23}H_{29}N_4O_3SSi_2$ (M–15) 497.1499, found 497.1515.

Rh(II)- and Cu(II)-catalyzed reactions of diazoamides 10c–h. The $Rh_2(OAc)_4$- and $Rh_2(tfa)_4$-catalyzed reaction of α-carboethoxy α-diazoamides **10c**,**d** were found to be slow at rt. Reaction times

were typically 7–24 h. The Cu(hfacac)$_2$-catalyzed reaction of diazoamide **10c** was complete at rt within 1.5 h. The Cu(acac)$_2$-catalyzed reaction of diazoamide **10c** was sluggish at rt, and after 48 h, substantial amounts of starting **10c** were still present; the reaction was brought to completion by refluxing the reaction mixture for an additional 24 h. The Cu(hfacac)$_2$-catalyzed reaction of diazoamide **10d** was refluxed for 48 h to complete the reaction. For the diazoamides **10e**,**f**, the reaction was usually complete after 24 at rt. However, the products were found to be unstable and consequently, purification of reaction products were made difficult. The $Rh_2(OAc)_4$-catalyzed reaction of unsubstituted α-diazoamides **10g**,**h** was facile and was complete within 10 min at rt. The yields of products from the reactions of **10c**–**h** are shown in Table 1 in the text.

2-[Bis(trimethylsilyl)methyl]-4-carboethoxy-9-methyl-4,9-dihydro-1*H*-pyrido[3,4-b]indol-3(2*H*)-one (18c). Chromatography: 10:1 v/v PE–EtOAc. Pale yellow solid, mp 144–147 ^{o}C; IR (film) 1735, 1636 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.04–0.30 (br s, 18 H), 1.23 (t, 3 H, *J* = 7.6 Hz), 1.78–1.96 (br s, 1 H), 3.67 (s, 3 H), 4.04–4.26 (m, 2 H), 4.48 (br d, 1 H), 4.72–4.88(m, 2 H), 7.14 (ddd, 1 H, *J* = 7.6, 7.3, 1.5 Hz), 7.1–7.34 (m, 2 H), 7.62 (d, 1 H, *J* = 7.6 Hz); ^{13}C NMR (75 MHz) δ 0.4, 14.1, 29.8, 48.1, 48.9, 50.6, 61.7, 104.6, 109.0, 119.0, 120.0, 122.1, 124.8, 128.6, 137.8, 163.9, 169.9; HRMS (EI) calcd for $C_{22}H_{34}N_2O_3Si_2$ (M^+) 430.2108, found 430.2109.

4-Acetyl-2-[bis(trimethylsilyl)methyl]-9-methyl-4,9-dihydro-1*H*-pyrido[3,4-b]indol-3(2*H*)-one (18e). Chromatography: 7:1 v/v PE-EtOAc. Pale yellow-orange oil; IR (film) 1720, 1624 cm^{-1}; ^{1}H NMR (Acetone-d$_6$, 300 MHz) δ -0.10 (s, 9H), 0.10 (s, 9H), 2.00 (s, 3H), 2.65 (s, 1H), 3.61 (s, 3H), 4.54 (t, 1H, *J* = 2.9 Hz), 4.65 (dd, 1H, *J* = 16.4, 2.9 Hz), 4.79 (dd, 1H, *J* = 16.4, 2.9 Hz), 6.90 (ddd, 1H, *J* = 8.1, 7.3, 1.4 Hz), 7.03 (ddd, 1 H, *J* = 8.1, 7.3, 1.4 Hz) 7.20 (d, 1 H, *J* = 8.1 Hz), 7.26 (m, 1 H); HRMS (EI): calcd for $C_{21}H_{32}N_2O_2Si_2$ (M^+) 400.2002 found 400.2008.

4-Acetyl-2-[bis(trimethylsilyl)methyl]-9-(phenylsulfonyl)-4,9-dihydro-1*H*-pyrido[3,4-b]indol-3(2*H*)-one (18f) and ***trans*-3-Acetyl-1-[bis(trimethylsilyl)methyl]-4-(1-phenylsulfonylindol-2-yl)-2-azetidinone (*trans*-20f)**. Compounds **18f** and **20f** were inseparable by chromatography. The ratio of **18f**:**20f** was 1:2.7, which was based on the integration of the H-4 triplet (δ 4.83) in **18f** and the H-3 doublet (δ 4.53) in **20f**. Chromatography: 4:1 v/v PE-EtOAc. Pale yellow oil; IR (film) 1749, 1714, 1633 cm^{-1}. ^{1}H NMR (300 MHz); Extensive signal overlap was observed for the resonances of the Me_3Si and indole/$PhSO_2$ units in **18f** and **20f**: *Compound **18f***: δ 0.12 (s, 9H), 0.16 (s, 9H), 2.28 (s, 3 H), 2.76 (s, 1 H), 4.83 (t, 1 H, *J* = 3.4 Hz), 4.93 (dd, 1 H, *J* = 18.3, 3.4 Hz), 5.05 (dd, 1 H, *J* = 18.3, 3.4 Hz), 7.25–7.95 (m, 7 H), 8.01–8.05 (m, 1H). *Compound **20f***: δ 0.12 (s, 9H) and 0.16 (s, 9 H) [overlap with signals of **18f**], 2.32 (s, 3 H), 2.56 (s, 1 H), 4.53 (d, 1 H, *J* = 2.3 Hz), 5.55 (dd, 1 H, *J* = 2.3, 0.9 Hz), 6.75–6.76 (m, 1 H), 7.25–7.95 (m, 7 H) and 8.08–8.13 (m, 1 H) [overlap with signals of **18f**].

Compound 18g from rearrangement of 19g in $CDCl_3$ solution. Compound **18g** was obtained as a pale yellow powder after purification (7:1 v/v,PE–EtOAc), mp 182–184 °C; IR (film) 1626 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 0.15 (s, 18 H), 1.26–1.33 (br s, 1 H), 3.57 (t, 2 H, *J* = 3.5 Hz), 3.71 (s, 3 H), 4.78 (t, 2 H, *J* = 3.5 Hz), 7.06 (ddd, 1 H, *J* = 8.1, 7.2, 0.9 Hz), 7.18 (ddd, 1 H, *J* = 8.1, 7.2, 0.9 Hz), 7.37 (br d, 1 H, *J* = 8.1 Hz), 7.46 (br d, 1 H, *J* = 8.0 Hz); ^{13}C NMR (75 MHz) δ 0.0, 28.2, 29.6, 48.0, 104.9, 108.4, 117.8, 119.0, 123.0, 124.8, 127.0, 137.2, 166.2; HRMS (EI) calcd for $C_{18}H_{27}N_2OSi_2$ (M^+) 343.1662, found 343.1661.

Ethyl 2-[bis(trimethylsilyl)methyl]-2,3,3b,8-tetrahydro-3-oxo-8-(phenylsulfonyl)-pyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3a(1*H*)-carboxylate (19d). Chromatography: 1:1 v/v PE–EtOAc. Colorless oil; IR (film) 1734, 1680 cm^{-1}; ^1H NMR (300 MHz) δ 0.17 (s, 9 H), 0.21 (s, 9 H), 0.72 (t, 3 H, *J* = 7.4 Hz), 1.25 (br s, 1 H), 3.09 (s, 1 H), 3.39 (dq, 1 H, *J* = 11.2, 7.4 Hz), 3.52 (dq, 1 H, *J* = 11.2, 7.4 Hz), 3.69 (d, 1 H, *J* = 11.3 Hz), 4.85 (d, 1 H, *J* = 11.3 Hz), 7.10 (ddd, 1 H, *J* = 6.9, 6.9, 1.1 Hz), 7.30 (ddd, 1 H, *J* = 6.9, 6.9, 1.1 Hz), 7.36 (dd, 1 H, *J* = 6.9, 1.1 Hz), 7.45–7.54 (m, 2 H), 7.56–7.62 (m, 1 H), 7.67 (br d, 1 H, *J* = 8.2 Hz), 7.85–7.93 (m, 2 H); ^{13}C NMR (75 MHz) δ 0.0, 0.1, 13.0, 29.9, 31.9, 38.0, 56.5, 61.0, 114.0, 124.0, 126.1, 126.5, 127.2, 128.2, 129.1, 133.8, 139.2, 144.2, 163.5, 166.2; HRMS (EI) calcd for $C_{21}H_{31}N_2O_3Si_2$ (M–141) 415.1873, found 415.1876.

2-[Bis(trimethylsilyl)methyl]-1,2,3b,8-tetrahydro-3-oxo-8-methyl-pyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3(3a*H*)-one (19g). Chromatography: 7:1 v/v PE–EtOAc. Pale yellow solid, mp 162–164 °C; IR (film) 1664 cm^{-1}; ^1H NMR (300 MHz) δ 0.12 (s, 9 H), 0.16 (s, 9 H), 1.16 (t, 1 H, *J* =1.8 Hz), 2.78–2.81 (br s, 1 H), 2.88 (s, 3 H), 3.07–3.14 (br s, 1 H), 3.62 (dd, 1 H, *J* = 10.8, 1.8 Hz), 3.88 (d, 1 H, *J* = 10.8 Hz), 6.69 (br d, 1 H, *J* = 8.1 Hz), 6.83 (br t, 1 H, *J* = 7.6 Hz), 7.16 (br t, 1 H, *J* = 8.1 Hz), 7.24 (br d, 1 H, *J* = 7.6 Hz).

2-[Bis(trimethylsilyl)methyl]-1,2,3b,8-tetrahydro-3-oxo-8-phenylsulfonyl-pyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3(3a*H*)-one (19h). Chromatography: 6:1 PE–EtOAc. White solid, mp 179–181 °C; IR (film) 1672 cm^{-1}; ^1H NMR (300 MHz) δ 0.14 (s, 9 H), 0.23 (s, 9 H), 0.64 (t, 1 H, *J* = 1.8 Hz), 2.58 (d, 1 H, *J* = 1.8 Hz), 2.85–3.25 (br s, 1 H), 3.76 (dd, 1 H, *J* = 11.2, 1.8 Hz), 4.74 (d, 1 H, *J* = 11.2 Hz), 7.08 (ddd, 1 H, *J* = 7.0, 7.0, 1.1 Hz), 7.87 (br d, 1 H, *J* = 8.3 Hz), 7.20–7.34 (m, 2 H), 7.36–7.46 (m, 2 H), 7.53–7.61 (m, 1 H), 7.64–7.71 (m, 2 H); ^{13}C NMR (75 MHz) δ 0.0, 23.8, 32.1, 36.9, 50.0, 52.1, 117.1, 124.8, 125.5, 128.0, 128.4, 129.6, 130.6, 134.2, 136.0, 143.7, 168.9; HRMS (EI) calcd for $C_{23}H_{29}N_2O_3SSi_2$ (M–15) 469.1437, found 469.1430.

***cis*-Ethyl 1-[bis(trimethylsilyl)methyl]-4-(1-methylindol-2-yl)-2-azetidinone-3-carboxylate (*cis*-20c)**. Chromatography: 5:1 v/v PE–EtOAc. Colorless oil; IR (film) 1731, 1760 cm^{-1}; ^1H NMR (Acetone-d_6, 300 MHz) δ 0.18 (s, 9 H), 0.35 (s, 9 H), 0.70 (t, 3 H, *J* = 7.3 Hz), 2.55 (s, 1 H), 3.62–3.72 (m, 2 H), 3.81 (s, 3H), 4.54 (d, 1 H, *J* = 5.8 Hz), 5.47 (dd, 1 H, *J* = 5.8, 0.5 Hz), 6.46 (br t, 1 H, *J* = 0.5 Hz), 7.04 (ddd, 1H, *J* = 8.5, 7.3, 1.1 Hz), 7.17 (ddd, 1 H, *J* = 8.5, 7.1, 1.2 Hz); ^{13}C NMR (Acetone-

d_6, 75 MHz) δ 0.2, 0.9, 13.9, 30.2, 38.0, 53.9, 60.0, 61.1, 101.8, 110.0, 120.2, 121.4, 122.3, 128.1, 134.6, 139.2, 162.2, 166.8; HRMS (EI) calcd for $C_{22}H_{34}N_2O_3Si_2$ (M^+) 430.2108, found 430.2110.

***cis*-Ethyl 1-[bis(trimethylsilyl)methyl]-4-(1-phenylsulfonylindol-2-yl)-2-azetidinone-3-carboxylate (*cis*-20d)**. Chromatography: 3:1 v/v PE–EtOAc. Colorless oil; IR (film) 1731, 1759 cm^{-1}; ^1H NMR (300 MHz) δ 0.10 (s, 9 H), 0.32 (s, 9 H), 0.90 (t, 3 H, *J* = 7.2 Hz), 2.33 (s, 1 H), 3.85 (q, 2H, *J* = 7.2 Hz), 4.40 (d, 1 H, *J* = 5.8 Hz), 5.64 (d, 1H, *J* = 5.8 Hz), 6.71 (s, 1 H), 7.22–7.36 (m, 2 H), 7.45 (br t, 2H, *J* = 8.4 Hz), 7.50–7.64 (m, 2 H), 7.80–7.86 (m, 2 H), 8.04 (br d, 1 H, *J* = 8.4 Hz). ^{13}C NMR (75 MHz) δ 0.0, 0.1, 13.0, 37.0, 54.0, 59.8, 60.9, 110.8, 114.0, 121.8, 123.7, 125.0, 126.0, 127.9, 129.1, 134.0, 134.2, 137.0, 138.6, 162.0, 166.0.

***trans*-Ethyl 1-[bis(trimethylsilyl)methyl]-4-(1-phenylsulfonylindol-2-yl)-2-azetidinone-3-carboxylate (*trans*-20d)**. Chromatography: 3:1 v/v PE–EtOAc. Colorless oil; IR (film) 1734, 1761 cm^{-1}; ^1H NMR (300 MHz) δ 0.10 (s, 9 H), 0.25 (s, 9 H), 1.35 (t, 3 H, *J* = 7.1 Hz), 2.30 (s, 1 H), 3.87 (d, 1H, *J* = 2.4 Hz), 4.33 (q, 2 H, *J* = 7.1 Hz), 5.41 (br d, 1 H, *J* = 2.4 Hz), 6.60–6.63 (br s, 1 H), 7.26–7.31 (m, 1 H), 7.38 (ddd, 1H, *J* = 8.2, 7.1, 1.2 Hz), 7.42–7.50 (m, 2 H), 7.52–7.62 (m, 2 H), 7.81–7.87 (m, 2H), 8.22 (br d, 1H, *J* = 8.2 Hz); ^{13}C NMR (75 MHz) δ 0.0, 0.8, 14.1, 38.2, 54.4, 61.8, 62.8, 109.2, 114.5, 121.2, 124.0, 125.3, 126.6, 128.5, 129.6, 134.1, 137.0, 137.3, 138.7, 161.9, 167.4; HRMS(CI) calcd for $C_{27}H_{36}N_2O_5SSi_2$ (M+1) 557.1962, found 557.1964.

***trans*-3-Acetyl-1-[bis(trimethylsilyl)methyl]-4-(1-methylindol-2-yl)-2-azetidinone (*trans*-20e)**. Chromatography: 7:1 v/v PE-EtOAc. Pale yellow oil; IR (film) 1750, 1712 cm^{-1}; ^1H NMR (300 MHz) δ 0.00 (s, 9H), 0.10 (s, 9H), 2.15 (s, 1 H), 2.21 (s, 3 H), 3.61 (s, 3 H), 4.00 (d, 1 H, *J* = 2.3 Hz), 5.20 (d, 1 H, *J* = 2.3 Hz), 7.00 (ddd, 1 H, *J* = 7.3, 7.3, 1.1 Hz), 7.11 (ddd, 1 H, *J* = 7.3, 7.3, 1.1 Hz), 7.19 (d, 1 H, *J* = 7.3 Hz), 7.46 (d, 1 H, *J* = 7.3 Hz); ^{13}C NMR (75 MHz) δ 0.0, 29.5, 38.0, 51.0, 71.0, 100.0, 109.0, 120.0, 121.0, 122.0, 127.0, 136.0, 138.0, 162.0, 201.0; HRMS (EI): calcd for $C_{21}H_{32}N_2O_2Si_2$ (M^+) 400.2002, found 400.1994.

Preparation of indole amines 22a,c. 2,3-Dimethyl-1-(phenylsulfonyl)indole [27a] (102 mg, 0.36 mmol) was dissolved in freshly redistilled CCl_4 and two tiny crystals of benzoyl peroxide were added. Freshly recrystallized NBS (64 mg, 0.36 mmol) was added in four portions. The first portion (18.3 mg) of NBS was added to the indole solution and the mixture was refluxed for 40 min, then cooled slightly and a second portion (21.0 mg) of NBS was added and the mixture was refluxed for 40 min. This was repeated two more times (NBS: 14.6 mg and 10 mg) and the reaction mixture was refluxed for an additional 20 min after all NBS was added (total reaction time was 3 h). The resulting mixture was cooled to rt, filtered to remove succinimide, the filtrate was evaporated and crude **21** was used without further purification in the next step.

Crude **21** was dissolved in dry DMF (1 mL) and transferred, via cannula, under Ar to a mixture of bis(trimethylsilyl)methylamine (125 mg, 0.72 mmol), Na_2CO_3 (27 mg, 0.25 mmol) and NaI (6 mg, 0.04 mmol) in dry DMF (3 mL). The resulting mixture was stirred at 65–70 ^oC in an oil bath. After 3.5 h,

the reaction mixture was cooled to rt, brine (3 mL) and a small amount of solid NaCl were added. The mixture was thoroughly extracted with EtOAc and the combined organic layers were washed with brine. The organic extract was dried, filtered and the filtrate was concentrated in vacuo. The residue was filtered through a short pad of silica gel (60 Å) using PE–Et_2O (5:1 v/v) as solvent to give the amine **22a** (97 mg) as a colorless oil; yield was 59% over two steps starting from 1-phenylsulfonyl-2,3-dimethylindole. ^{1}H NMR (300 MHz) of **22a**: δ 0.00 (s, 18 H), 1.35 (s, 1 H), 1.72–2.10 (br s, 1 H), 2.16 (s, 3 H), 3.96 (s, 2 H), 7.15–7.43 (m, 6 H), 7.63–7.72 (m, 2 H), 8.10–8.16 (m, 1 H).

For the preparation of **22c**, indole amine **22a** (88 mg, 0.19 mmol) was dissolved in a mixture of THF (2 mL) and MeOH (1 mL) at rt. Cesium carbonate (188 mg, 0.58 mmol) was added to the solution. The resulting mixture was refluxed for 96 h. Then the mixture was cooled to rt and the solvent was removed under vacuum. Water (3 mL) was added and the mixture was stirred at rt for 15 min. The resulting mixture was extracted with CH_2Cl_2, the combined organic layers were washed with brine and dried. After filtration, the solution was evaporated and the crude product was purified (1:1 v/v PE–Et_2O) to give **22b** as a colorless oil (47 mg, 77%). IR (film) 3412, 3463 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.15 (s, 18 H), 1.09–1.41 (br s, 1 H), 1.51 (s, 1 H), 2.30 (s, 3 H), 3.91 (s, 2 H), 7.12 (ddd, 1 H, *J* = 8.3, 8.3, 1.5 Hz), 7.19 (1 H, *J* = 7.1, 7.1, 1.4 Hz), 7.32–7.37 (m, 1 Hz), 7.52–7.57 (m, 1 H), 8.20–8.36 (br s, 1 H); ^{13}C NMR (75 MHz) δ –0.2, 8.2, 39.3, 48.7, 107.4, 110.5, 118.4, 119.0, 121.5, 129.1, 133.2, 135.2; HRMS (EI) calcd for $C_{17}H_{28}N_2Si_2$ (M–2) 316.1792, found 316.1796.

Indole *N*-methylation of **22b** (88 mg, 0.277 mmol) used a similar proceure as that described for the preparation of compound **6b**. The crude product was purified (5:1 v/v PE–Et2O) to give **22c** as a light yellow oil (78 mg, 85%). IR (film) 3315, 3055, 2952 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.14 (s, 18 H), 0.71–1.05 (br s, 1 H), 1.52 (s, 1 H), 2.36 (s, 3 H), 3.84 (s, 3 H), 3.88 (s, 2 H), 7.12 (ddd, 1 H, *J* = 7.9, 7.0, 1.3 Hz), 7.24 (1 H, *J* = 7.9, 7.0, 1.3 Hz), 7.27–7.33 (m, 1 H), 7.54–7.60 (m, 1 H); ^{13}C NMR (75 MHz) δ –0.6, 8.8, 29.9, 40.0, 47.6, 108.0, 108.7, 118.5, 118.6, 121.4, 127.9, 134.8, 136.8; HRMS (EI) calcd for $C_{18}H_{32}N_2Si_2$ (M+) 332.2104, found 332.2104.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-phenylsulfonyl-3-methyl-indo-2-lyl)methyl]-α-carboethoxy-α-diazoacetamide (23a)**. Diazoamide **23a** was prepared by acylation of amine **22a** (96.6 mg, 0.211 mmol) with ethyl diazomalonyl chloride (56.5 mg, 0.32 mmol) according to the procedure used for the preparation of diazoamides **10a**–**d**. Chromatography: 3:1 v/v PE–Et2O; yield: 76%. Yellow oil; IR (film) 2126, 1702, 1624 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.00 (s, 18 H), 1.36 (t, 3 H, *J* = 7.2 Hz), 2.08 (s, 1 H), 2.26 (s, 3 H), 4.35 (q, 2 H, *J* = 7.2 Hz), 4.82 (s, 2 H), 7.25–7.54 (m, 8 H), 8.23–8.27 (m, 1 H); ^{13}C NMR (75 MHz) δ 0.0, 9.6, 14.2, 40.6, 46.7, 60.6, 115.6, 118.7, 123.8, 124.0, 125.5, 125.7, 128.6, 130.3, 130.4, 133.2, 136.9, 137.4, 159.3, 163.0; HRMS (CI) calcd for $C_{28}H_{39}N_4O_5SSi_2$ (M+1) 599.2180, found 599.2198.

Preparation of diazoamides 23c,e. The appropriate indole amine **22a** or **22c** was treated with diketene and the resulting crude acetoacetamide was diazotized using MsN_3 using a similar procedure as

described for the preparation of α-unsubstituted diazoamides **10g**,**h** via **10e**,**f**. Note that the α-unsunstituted diazoamide **23c** was unstable and was used immediately, after purification, in the $Rh_2(OAc)_4$-catalyzed reaction.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-phenylsulfonyl-3-methyl-indol-2-yl)methyl]-α-diazoacetamide (23c)**. Starting from **22a** (24.6 mg, 0.054 mmol) and diketene (6 uL, 0.081 mmol), followed by diazotization yielded the corresponding α-diazoacetoacetamide **23b** as a yellow solid; yield: 23.1 mg, 76 %. Chromatography: 1:1 v/v PE–Et2O; IR (film) 2101, 1651, 1622 cm^{-1}; ^1H NMR (300 MHz) δ 0.01 (s, 18 H), 2.01 (s, 1 H), 2.27 (s, 3 H), 2.42(s, 3 H), 4.82 (s, 2 H), 7.25–7.54 (m, 8 H), 8.21 (d, 1 H, *J* = 8.6 Hz); ^{13}C NMR (75 MHz) δ 0.5, 10.1, 26.6, 41.2, 47.1, 116.2, 119.3, 124.4, 124.9, 126.0, 126.2, 129.0, 130.7, 130.9, 133.8, 137.4, 137.6, 159.5; HRMS (EI) calcd for $C_{26}H_{33}N_4O_4SSi_2$ (M–15) 553.1761, found 553.1758.

The above α-diazoacetoacetamide was deacylated (5 % aq KOH/MeCN) to give **23c** (18.3 mg, 86%) as a yellow solid; Chromatography: 2:1 v/v PE–Et2O; IR (film) 2103, 1596 cm^{-1}; ^1H NMR (Acetone-d6, 300 MHz) δ –0.02 (s, 18 H), 2.34 (s, 3 H), 2.38 (s, 1 H), 4.90 (s, 2 H), 7.26–7.34 (m, 1 H), 7.36–7.52 (m, 4 H), 7.52–7.58 (m, 1 H), 7.66–7.73 (m, 2 H), 8.18–8.22 (m, 1 H); ^{13}C NMR (Acetone-d6, 75 MHz) δ 1.0, 10.5, 42.5, 47.3, 117.1, 120.2, 125.5, 126.0, 126.8, 127.2, 130.1, 132.8, 133.2, 135.0, 137.8, 138.3, 164.8; HRMS (CI) calcd for $C_{25}H_{35}N_4O_3SSi_2$ (M+1) 527.1969, found 527.1970.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[(1-methyl-3-methyl-indo-2-lyl)methyl]-α-diazoacetamide (23e)**. The amine **22c** (60 mg, 0.181 mmol) was treated with diketene (28 uL, 0.362 mmol) followed by diazotization to yield the corresponding α-diazoacetoacetamide **23d** as a yellow solid; yield: 67.9 mg, 85% Chromatography: 3:1 v/v PE–EtOAc; IR (film) 2110, 1658, 1618 cm^{-1}; ^1H NMR (300 MHz) δ 0.00 (s, 18 H), 2.24 (s, 1 H), 2.39 (s, 3 H), 2.41 (s, 3 H), 3.53 (s, 3 H), 4.51 (s, 2 H), 7.10–7.16 (m, 1 H), 7.24–7.27 (m, 2 H), 7.55–7.60 (m, 1 H); ^{13}C NMR (75 MHz) δ 0.1, 9.5, 26.9, 29.8, 30.1, 42.0, 46.2, 109.0, 111.8, 119.0, 119.2, 122.8, 127.8, 129.3, 137.2, 158.1; HRMS (EI) calcd for $C_{22}H_{34}N_2O_2Si_2$ (M+) 414.2159, found 414.2172.

The above α-diazoacetoacetamide (67 mg) was deacylated (5% aq KOH/MeCN) to furnish an unstable **23e** (50 mg, 83%) which was immediately used in the $Rh_2(OAc)_4$-catalyzed reaction after purification (5:1 v/v PE-EtOAc).

***N*-(1-Phenylsulfonyl-3-methyl-indo-2-lyl)methylidene-1,1-bis(trimethylsilyl)methanamine (26)**. Chromatography: 2:1 v/v PE–Et_2O; yield: 16% from **23a**; 4% from **23c**. Colorless oil; IR (film) 3055, 2982 cm^{-1}; ^1H NMR (300 MHz) δ 0.11 (s, 18 H), 2.43 (s, 3 H), 3.01 (s, 1 H), 2.41 (s, 3 H), 3.53 (s, 3 H), 4.51 (s, 2 H), 7.10–7.16 (m, 1 H), 7.21–7.36 (m, 4 H), 7.40–7.48 (m, 2 H), 7.64–7.70 (m, 2 H), 8.15 (d, 1 H, *J* = 8.7 Hz); ^{13}C NMR (75 MHz) δ –1.1, 10.7, 62.0, 115.6, 119.7, 123.4, 124.1, 125.8, 126.6, 128.8, 132.2, 132.8, 133.4, 136.5, 137.7, 150.2; HRMS (EI) calcd for $C_{23}H_{32}N_2O_2Si_2S$ (M^+) 456.1723, found 456.1730.

2-[Bis(trimethylsilyl)methyl]-2,4,4a,9-tetrahydro-4a,9-dimethyl-3H-pyrido[3,4-b]indol-3-one (27). Compound **27** was obtained by standing a solution of **24c** (15 mg) in $CDCl_3$ overnight, and then purified (10:1 v/v PE–EtOAc) to give a colorless oil; yield: 98%. IR (film) 1630 cm^{-1}; ^1H NMR (300 MHz) δ 0.13 (s, 9 H), 0.16 (s, 9 H), 1.34 (s, 3 H), 2.15–2.45 (br s, 1 H), 2.70–2.90 (m, 2 H), 2.95 (s, 3 H), 5.22–5.32 (br s, 1 H), 6.56 (d, 1 H, *J* = 5.1 Hz), 6.77 (t, 1 H, *J* = 5.1 Hz), 7.02–7.07 (m, 1 H), 7.16 (ddd, 1 H, *J* = 5.1, 5.1, 0.6 Hz); ^{13}C NMR (75 MHz) δ 0.1, 24.0, 30.1, 42.0, 43.5, 106.5, 119.5, 122.3, 128.6, 135.7, 142.2, 148.9, 164.8; HRMS (EI) calcd for $C_{20}H_{32}N_2OSi_2$ (M^+) 372.2053, found 372.2054.

***N*-[Bis(trimethylsilyl)methyl]-1-(methoxymethoxy)-3-butyn-2-amine (29)**. To a solution of the trimethylsilylacetylene (710 uL, 5.0 mmol) in dry THF (8 mL), was added, slowly, n-BuLi (1.6 M in hexanes, 3.13 mL, 5.0 mmol) at –78 °C under Ar with stirring. After 1 h, $BF_3{\cdot}OEt_2$ (634 uL, 5.0 mmol) was added to the solution and the mixture was stirred for 30 min. *N*-(2-Methoxymethoxyethylidene)-1,1-bis(trimethylsilyl)methanamine [513 mg, 1.96 mmol; prepared from condensation of $BTMSMNH_2$ with 2-(methoxymethoxy)acetaldehyde, obtained via ozonolysis of the known 1,4-bis(methoxymethoxy)-2-butene (C. Saluzzo, A.-M. La Spina, D. Picq, G. Alvernhe, D. Anker, D. Wolf and G .Haufe, *Bull. Soc. Chim. France*, 1994, **131**, 831), 3Å MS, Et_2O, rt] was dissolved in dry THF (4 mL) and the solution was transferred, under Ar, via cannula to the alkynide solution. The reaction mixture was stirred for 3 h at –78 °C and then at rt for 1 h. The reaction mixture was concentrated and the residue was dissolved in dry MeOH (5 mL). The solution was cooled to 0 °C in an ice/water bath, anhydrous K_2CO_3 (2.7 g, 19.5 mmol) was added and the mixture was then stirred at rt overnight. Methanol was removed in vacuo, water (2 mL) was added and the resulting aqueous mixture was extracted thoroughly with CH_2Cl_2. The combined organic layers were dried, filtered, concentrated and the crude product was purified (15:1 v/v PE–Et_2O) to give 29 (378 mg, 67%) as a colorless oil; IR (film) 3310 cm^{-1}; ^1H NMR (300 MHz) δ 0.03 (s, 9 H), 0.05 (s, 9 H), 1.12–1.20 (br s, 1 H), 1.70 (s, 1 H), 2.25 (d, 1 H, *J* = 2.1 Hz), 3.37 (s, 3 H), 3.47–3.58 (br s, 1 H), 3.64 (d, 2 H, *J* = 4.8 Hz), 4.67 (s, 2 H); ^{13}C NMR (75 MHz) δ –0.1, 0.1, 36.8, 53.2, 55.7, 70.2, 72.0, 84.1, 96.5; HRMS (EI) calcd for $C_{12}H_{26}NO_2Si_2$ (M–15) 272.1502, found 272.1502.

***N*-[Bis(trimethylsilyl)methyl]-2-(methoxymethoxy)-1-(1-methanesulfonyl-indol-2-yl)ethanamine (30a)**. The solution of alkyne **29** (64.9 mg, 0.23 mmol) and 2-iodo-*N*-(methanesulfonyl)aniline[28] (74 mg, 0.25 mmol) in degassed DMF (1 mL) was transferred to a mixture of $PdCl_2(PPh_3)_2$ (15.9 mg, 0.023 mmol) and CuI (4 mg, 0.023 mmol) in degassed DMF (3 mL) under Ar at rt. Et_3N (1 mL) was added and argon was slowly bubbled through the resultant mixture at rt for 30 min. Then the mixture was stirred at 85–90 °C (oil bath) under Ar overnight. The mixture was poured into a separatory funnel. EtOAc (6 mL) and brine (6 mL) was added. The organic phase was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with brine and dried. After filtration, the filtrate was concentrated in vacuo and the residue was purified (2:1 v/v PE–Et_2O) to give **30a**[29b]as a colorless oil (74 mg, 72%). IR (film) 3345 cm^{-1}; ^1H NMR (300 MHz) δ 0.05 (s, 9 H), 0.15 (s, 9 H), 1.55–1.65 (br s, 1 H), 1.70 (s, 1 H), 3.04 (s, 3 H), 3.21 (s, 3 H), 3.75 (dd, 1 H, *J* = 9.6, 5.9 Hz),

3.85 (dd, 1 H, *J* = 9.6, 5.9 Hz), 4.54 (d, 1 H, *J* = 6.2 Hz), 4.58 (d, 1 H, *J* = 6.2 Hz), 4.59–4.68 (m, 1 H), 6.80 (s, 1 H), 7.24–7.35 (m, 2 H), 7.52–7.57 (m, 1 H), 7.98–8.05 (m, 1 H); ^{13}C NMR (75 MHz) δ –0.1, 0.1, 36.8, 40.3, 55.4, 58.0, 70.2, 96.5, 111.0, 114.8, 121.0, 124.0, 124.3, 129.9, 137.5, 143.8; HRMS (EI) calcd for $C_{17}H_{29}N_2O_2SSi_2$ (M–75) 381.1488, found 381.1488.

N-[Bis(trimethylsilyl)methyl]-2-(methoxymethoxy)-1-(1H-indol-2-yl)ethanamine (30b). Compound **30b** was prepared from **30a** by a similar procedure as that described for the preparation of **22b**. Chromatography: 3:1 v/v PE–Et_2O; yield: 90%. Colorless oil; IR (film) 3455, 3346 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.03 (s, 9 H), 0.14 (s, 9 H), 1.57 (s, 1 H), 1.65–1.76 (br s, 1 H), 3.38 (s, 3 H), 3.68–3.84 (m, 2 H), 4.17 (dd, 1 H, *J* = 6.3, 4.9 Hz), 4.69 (s, 2 H), 6.38–6.42 (br s, 1 H), 7.06–7.13 (m, 1 H), 7.13–7.20 (m, 1 H), 7.36 (br d, 1 H, *J* = 7.7 Hz), 7.55–7.61 (m, 1 H), 8.50–8.64 (br s, 1 H); ^{13}C NMR (75 MHz) δ –0.8, 0.1, 35.5, 55.4, 58.0, 71.1, 96.6, 100.9, 110.7, 119.5, 120.1, 121.4, 128.4, 135.6, 138.5; HRMS (EI) calcd for $C_{16}H_{27}N_2Si_2$ (M–75) 303.1713, found 303.1715.

***N*-[Bis(trimethylsilyl)methyl]-2-(methoxymethoxy)-1-[1-(methoxymethyl)-indol-2-yl]ethanamine (30c)**. Compound **30c** was prepared from **30b** by a similar procedure as that described for the preparation of **6b** except that MOMCl was used as the alkylating reagent. Chromatography: 5:1 v/v PE–Et_2O; yield: 84%. Colorless oil; IR (film) 3456 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.02 (s, 9 H), 0.14 (s, 9 H), 1.54–1.58 (br s, 1 H), 1.65 (s, 1 H), 3.31 (s, 3 H), 3.33 (s, 3 H), 3.75 (dd, 1 H, *J* = 9.9, 5.4 Hz), 3.80 (dd, 1 H, *J* = 9.9, 7.2 Hz), 4.30 (dd, 1 H, *J* = 7.2, 5.4 Hz), 4.62 (s, 2 H), 5.49 (d, 1 H, *J* = 11.2 Hz), 5.75 (d, 1 H, *J* = 11.2 Hz), 6.54 (s, 1 H), 7.09–7.16 (m, 1 H), 7.17–7.25 (m, 1 H), 7.42–7.47 (m, 1 H), 7.57–7.61 (m, 1 H); ^{13}C NMR (75 MHz) δ –0.8, 0.0, 35.9, 55.1, 55.3, 57.6, 71.0, 74.0, 96.4, 103.1, 109.1, 120.0, 120.4, 121.6, 127.8, 138.1, 140.5; HRMS (EI) calcd for $C_{21}H_{38}N_2O_3Si_2$ (M+) 422.2421, found 422.2412.

Preparation of the unsubstituted α-diazoamides 31b,d. A solution of the appropriate amine **30a** or **30b** (1.0 mmol) and DMAP (20 mol%) in dry THF (3 mL) was refluxed under Ar, and then freshly redistilled diketene (2.0 mmol) in THF (5 mL) was added dropwise via cannula. After addition was complete, the reaction was refluxed for another 30 min and then cooled to rt. The mixture was diluted with CH_2Cl_2 (5 mL) and filtered through a short pad of silica gel (60Å) in a sintered funnel. The filtrate was evaporated in vacuo to give the corresponding crude acetoacetamide, which was dissolved in dry CH_3CN (5 mL) under Ar at 0 °C. Then a solution of MsN_3 (3.0 mmol) in dry CH_3CN (2 mL) was added via cannula followed by addition of DBU (3.0 mmol) and the mixture was stirred at 0 °C for 1 h and at rt for 1 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL), washed with 10% aq NaOH (2x5 mL), and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O, dried, filtered, evaporated in vacuo, and the crude product was purified.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[[1-(1-methanesulfonyl-indol-2-yl)-2-methoxymethoxy]ethyl]-α-acetyl-α-diazoacetamide (31a)**. Chromatography: 3:1 v/v PE–EtOAc; yield: 78%. Yellow oil; IR (film) 2100, 1654, 1616 cm^{-1}; ^{1}H NMR (300 MHz) δ –0.33 (s, 9 H), 0.15 (s, 9 H), 2.31 (s, 1 H), 2.36 (s,

3 H), 2.89 (s, 3 H), 3.25 (s, 3 H), 4.01 (dd, 1 H, *J* = 10.7, 9.2 Hz), 4.19–4.39 (br s, 1 H), 4.51 (d, 1 H, *J* = 6.3 Hz), 4.63 (d, 1 H, *J* = 6.3 Hz), 5.99 (dd, 1 H, *J* = 10.7, 4.6 Hz), 7.00 (s, 1 H), 7.10–7.42 (m, 2 H), 7.58–7.65 (m, 1 H), 8.05–8.12 (m, 1 H); ^{13}C NMR (75 MHz) δ 0.6, 1.1, 26.6, 39.6, 39.7, 54.6, 55.7, 68.9, 96.6, 114.3, 116.0, 121.0, 124.8, 126.0, 129.3, 137.5, 138.2, 160.3; HRMS (EI) calcd for $C_{23}H_{35}N_4O_6SSi_2$ (M–15) 551.1816, found 551.1819.

***N*-[Bis(trimethylsilyl)methyl]-*N*-[2-methoxymethoxy-1-(1-methoxymethyl-indol-2-yl)ethyl]-α-acetyl-α-diazoacetamide (31c)**. Chromatography: 1:1 v/v PE–Et_2O; yield: 84%. Yellow oil; IR (film) 2108, 1656, 1616 cm^{-1}; ^{1}H NMR (300 MHz) δ –0.36 (s, 9 H), 0.18 (s, 9 H), 2.37 (s, 3 H), 2.57 (s, 1 H), 3.21 (s, 3 H), 3.26 (s, 3 H), 4.03 (dd, 1 H, *J* = 9.4, 8.2 Hz), 4.17 (dd, 1 H, *J* = 9.4, 6.8 Hz), 4.55 (d, 1 H, *J* = 7.1 Hz), 4.60 (d, 1 H, *J* = 7.1 Hz), 5.37 (d, 1 H, *J* = 12.1 Hz), 5.38–5.46 (m, 1 H), 5.52 (d, 1 H, *J* = 12.1 Hz), 6.69 (s, 1 H), 7.10–7.19 (m, 1 H), 7.25–7.57 (m, 2 H), 7.42 (br d, 1 H, *J* = 8.4 Hz), 7.60 (br d, 1 H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz) δ 0.5, 1.2, 26.6, 39.6, 54.9, 55.5, 56.5, 68.5, 72.8, 73.8, 96.5, 105.0, 109.2, 120.6, 120.8, 122.9, 127.2, 135.2, 137.4, 159.2, 188.7; HRMS (EI) calcd for $C_{25}H_{40}N_2O_5Si_2$ (M–28) 504.2476, found 504.2478.

Each of the above-described α-acetyl-α-diazoacetamides was deacetylated using 5% aq KOH in MeCN, according to the procedure employed for the preparation of α- unsubstituted diazoamides **23b**,**c**, to give **31b** (90%) and **31d** (89%). Diazoamides **31b**,**d** were found to be quite unstable and were used immediately after purification in the subsequent metal-catalyzed reactions.

Metal-catalyzed reaction of α-unsubstituted diazoamides 31b,d. Diazoamides **31b**,**d** were treated with the appropriate Rh(II) catalyst (2 mol%) or Cu(II) catalyst (4 mol%) as described for the reactions of diazoamides **10**. Some general observations were as follows: The $Rh_2(OAc)_4$- and $Cu(hfacac)_2$-catalyzed reactions were complete within 10 min at rt. The $Rh_2(cap)_4$-catalyzed reaction was complete at rt within 3 h. The $Rh_2(tfa)_4$-catalyzed reaction of diazoamide **31b** was slower, but was complete within 6 h at rt. Yields are shown in Table 2 in the text.

2-[Bis(trimethylsilyl)methyl]-1,2,3b,8-tetrahydro-1-[(methoxymethoxy)methyl]-8-(methanesulfonyl)pyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3(3a*H*)-one (32b). Chromatography: 3:1 v/v PE–EtOAc. White solid, mp 146–147 °C; IR (film) 1678 cm^{-1}; ^{1}H NMR (300 MHz) δ 0.13 (s, 9 H), 0.18 (s, 9 H), 1.68 (d, 1 H, *J* = 1.7 Hz), 2.38 (s, 1 H), 2.81 (s, 3 H), 2.96 (br d, 1 H, *J* = 1.7 Hz), 3.26 (s, 3 H), 3.70 (dd, 1 H, *J* = 11.3, 5.5 Hz), 3.88 (dd, 1 H, *J* = 11.3, 5.5 Hz), 4.58 (s, 2 H), 4.90 (dd, 1 H, *J* = 5.5, 3.0 Hz), 7.12 (ddd, 1 H, *J* = 7.6, 7.6, 0.8 Hz), 7.26 (ddd, 1 H, *J* = 7.6, 7.6, 1.5 Hz), 7.36–7.41 (m, 1 H), 7.55 (br d, 1 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz) δ 0.5, 0.8, 23.3, 30.4, 36.2, 37.7, 52.9, 55.5, 61.4, 67.1, 96.6, 115.7, 125.0, 125.6, 128.5, 129.6, 143.4, 169.4; HRMS (EI) calcd for $C_{22}H_{36}N_2O_5SSi_2$ (M^+) 496.1884, found 496.1879.

2-[Bis(trimethylsilyl)methyl]-1,2,3b,8-tetrahydro-1-[(methoxymethoxy)methyl]-8-(methoxymethyl)pyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3(3a*H*)-one (32d). Chromatography: 2:1

v/v PE–Et_2O. Colorless oil; IR (film) 1674 cm^{-1}; ^1H NMR (300 MHz) δ 0.14 (s, 9 H), 0.18 (s, 9 H), 1.18 (d, 1 H, *J* = 1.3 Hz), 2.48 (s, 1 H), 2.83–2.87 (br s, 1 H), 3.30 (s, 3 H), 3.37 (s, 3 H), 3.59 (dd, 1 H, *J* = 11.0, 6.5 Hz), 3.84 (dd, 1 H, *J* = 11.0, 2.9 Hz), 4.32 (dd, 1 H, *J* = 6.5, 2.9 Hz), 4.58 (s, 2 H), 4.75 (d, 1 H, *J* = 11.0 Hz), 4.75 (d, 1 H, *J* = 11.0 Hz), 6.78–6.88 (m, 2 H), 7.15 (ddd, 1 H, *J* = 8.0, 8.0, 1.1 Hz), 7.29 (br d, 1 H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz) δ 0.6, 0.7, 2.08, 29.8, 37.5, 52.9, 55.3, 56.0, 60.0, 68.9, 79.3, 96.6, 109.5, 120.0, 125.2, 127.5, 128.1, 148.8, 171.8; HRMS (EI) calcd for $C_{23}H_{38}N_2O_4Si_2$ (M^+) 462.2370, found 462.2379.

1-[Bis(trimethylsilyl)methyl]-4-(methoxymethoxy)-5-[1-(methanesulfonyl)-indol-2-yl]-2-pyrrolidinone (33b). Chromatography: 1:1 v/v PE–EtOAc; obtained as two separable diastereomers, *cis*-**33b** and *trans*-**33b**.

cis-**33b**: Colorless oil; IR (film) 1677 cm^{-1}; ^1H NMR (300 MHz) δ 0.10 (s, 9H), 0.20 (s, 9H), 2.20 (s, 1 H), 2.64 (dd, 1 H, *J* = 16.3, 7.9 Hz), 2.71 (dd, 1 H, *J* = 16.3, 8.5 Hz), 3.19 (s, 3 H), 3.28 (s, 3 H), 4.52 (d, 1 H, *J* = 6.8 Hz), 4.61 (d, 1 H, *J* = 6.8 Hz), 4.68 (br q, 1 H, *J* = 8.5 Hz), 5.83 (d, 1 H, *J* = 8.5 Hz), 6.71 (s, 1 H), 7.28–7.42 (m, 2 H), 7.55–7.62 (m, 1 H), 7.94–8.00 (m, 1 H); ^{13}C NMR (75 MHz) δ 0.1, 2.0, 36.0, 38.5, 40.5, 56.0, 61.8, 72.2, 96.0, 110.5, 114.0, 121.8, 124.0, 125.0, 129.0, 137.2, 170.9; HRMS (EI) calcd for $C_{22}H_{36}N_2O_5SSi_2$ (M^+) 496.1884, found 496.1880.

trans-**33b**: Colorless oil; IR (film) 1683 cm^{-1}; ^1H NMR (300 MHz) δ 0.15 (s, 9 H), 0.20 (s, 9 H, 2.16 (s, 1 H), 2.39 (br d, 1 H, *J* = 17.3 Hz), 2.84 (dd, 1 H, *J* = 17.3, 5.8 Hz), 3.18 (s, 3 H), 3.40 (s, 3 H), 4.24 (br d, 1 H, *J* = 5.8 Hz), 4.66 (d, 1 H, *J* = 7.2 Hz), 4.89 (d, 1 H, *J* = 7.2 Hz), 5.55–5.59 (br s, 1 H), 6.66 (s, 1 H), 7.29–7.42 (m, 2 H, 7.53–7.59 (m, 1 H), 8.02 (br d, 1 H, *J* =7.2 Hz); ^{13}C NMR (75 MHz) δ 0.1, 2.0, 36.0, 38.5, 41.0, 56.0, 61.8, 75.9, 95.0, 110.0, 114.2, 121.2, 124.2, 125.6, 128.6, 137.2, 172.0; HRMS (EI) calcd for $C_{22}H_{36}N_2O_5SSi_2$ (M^+) 496.1884, found: 496.1880.

2-[Bis(trimethylsilyl)methyl]-1,2,3b,8-tetrahydro-1-(hydroxymethyl)-8-(methanesulfonyl)pyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3(3a*H*)-one (34). Concentrated HCl (37%, 4 drops) and MeOH (2 mL) were added to compound **32b** (11 mg, 0.022 mmol). The resulting mixture was refluxed for 3 h, then the reaction mixture was cooled to rt, and saturated aq $NaHCO_3$ was slowly added until pH > 7. Methanol was removed in vacuo and the residue was extracted with CH_2Cl_2 (3x2 mL). The combined organic layers were washed with brine, dried, filtered and evaporated. The residue was purified (3:1 v/v PE–EtOAc) to give **34** (9 mg, 90%) as a white solid. Subsequent recrystallization (hexane–EtOAc) gave colorless crystals (8.4 mg, 84%). mp 179–181 °C; IR (film) 1671, 3385 cm^{-1}; ^1H NMR (300 MHz) δ 0.18 (s, 9 H), 0.20 (s, 9 H), 1.63 (dd, 1 H, *J* = 4.1, 5.6 Hz), 1.67 (d, 1 H, *J* = 1.8 Hz), 2.36 (s, 1 H), 2.81 (s, 3 H), 3.03 (d, 1 H, *J* = 1.8 Hz), 3.87 (ddd, 1 H, *J* = 12.2, 5.6, 5.6 Hz), 3.87 (ddd, 1H, *J* = 12.2, 4.1, 4.1 Hz), 4.80 (t, 1 H, *J* = 5.2 Hz), 7.14 (ddd, 1 H, *J* = 7.4, 7.4, 0.9 Hz), 7.27 (ddd, 1 H, *J* = 7.4, 7.4, 1.4 Hz), 7.40 (d, 1 H, *J* = 7.4 Hz), 7.56 (d, 1 H, *J* = 7.4 Hz); ^{13}C NMR (75 MHz) δ 0.8, 1.0, 23.5, 30.5, 36.4, 38.3, 53.3, 62.6, 63.1, 116.1, 125.3, 126.1, 128.8, 129.9, 143.5, 169.7; HRMS (EI) calcd for $C_{20}H_{32}N_2O_4SSi_2$ (M^+) 452.1621, found 452.1623.

2-[Bis(trimethylsilyl)methyl]-1,2,4,9-tetrahydro-1-[(methoxymethoxy)methyl]-4*H*-pyrido(3,4-b]indol-3-one (36). To a solution of compound **32b** (32 mg, 0.069 mmol) in $CHCl_3$ (2 mL) was added silica gel (100 mg, 60Å) at rt. Then two drops of 6 M aq HCl was added. After stirring at rt overnight, silica gel was filtered out. The mixture was neutralized by slowly adding saturated aq $NaHCO_3$. The aqueous solution was extracted with CH_2Cl_2 (2x3 mL). The combined organic layers were washed with brine, dried, filtered and evaporated in vacuo. The residue was purified (2:1 v/v PE–Et_2O) to give a white solid (24 mg, 84%). mp 217–219 ^oC; IR (film) 1674 cm^{-1}; ^1H NMR (300 MHz) δ 0.11 (s, 9 H), 0.21 (s, 9 H), 2.11 (s, 1 H), 3.25 (s, 3 H), 3.47–3.58 (m, 2 H), 3.68 (dd, 1 H, *J* = 20.7, 2.1 Hz), 3.88 (dd, 1 H, *J* = 9.4, 4.2 Hz), 4.58–4.67 (m, 3 H), 6.98–7.02 (m, 1 H), 7.10 (ddd, 1 H, *J* = 7.3, 7.3, 1.1 Hz), 7.26 (br d, 1 H, *J* = 7.9 Hz), 7.38 (br d, 1 H, *J* = 7.9 Hz), 8.89 (s, 1 H); ^{13}C NMR (75 MHz) δ 0.5, 1.5, 29.6, 46.0, 55.8, 60.0, 70.0, 96.9, 106.4, 110.2, 118.2, 119.9, 122.4, 125.8, 129.9, 137.2, 168.0; HRMS (EI) calcd for $C_{21}H_{34}N_2O_3Si_2$ (M^+) 418.2108, found 418.2110.

2*H*-1,2,3b,8-Tetrahydro-3-oxo-8-phenylsulfonylpyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3(3a*H*)-one (39). A solution of CAN (307 mg, 0.56 mmol) in distilled water (2 mL) was added, under Ar, to a solution of compound **19h** (66.5 mg, 0.137 mmol) in CH_3CN at 0 ^oC. The mixture was stirred at 0 ^oC for 30 min. Then 40% aq $NaHSO_3$ (3 mL) was added, and the mixture was stirred for 10 min at rt. The mixture was extracted with EtOAc (3x2 mL). The combined organic layers were dried, filtered and evaporated in vacuo. The crude product was filtered through a short pad of silica gel (60Å) using PE–EtOAc (4:1) as the eluent. The crude product (37.5 mg, 0.11 mmol) was dissolved in MeOH (2 mL), Na_2CO_3 (17.5 mg, 0.165 mmol) was added and the mixture was stirred at rt for 30 min. Then MeOH was removed in vacuo and the residue was extracted with CH_2Cl_2 (3x2 mL). The combined organic layers were dried and filtered. The filtrate was concentrated in vacuo and the crude product was purified (4:1 v/v CH_2Cl_2–acetone) to give a white solid (22.8 mg, 51% over two steps). mp 230–241 ^oC; IR (film) 3437, 1704 cm^{-1}; ^1H NMR (300 MHz) δ 0.42 (dd, 1 H, *J* = 3.2, 1.8 Hz), 2.74 (d, 1 H, *J* = 2.0 Hz), 3.79 (dd, 1 H, *J* = 10.9, 1.8 Hz), 4.66 (d, 1 H, *J* = 10.9 Hz), 6.38 (s, 1 H), 7.08 (ddd, 1 H, *J* = 7.2, 7.2, 1.2, Hz), 7.22–7.34 (m, 2 H), 7.41–7.49 (m, 2 H), 7.52–7.60 (m, 1 H), 7.66–7.73 (m, 2 H), 7.88 (d, 1 H, *J* = 8.3 Hz); ^{13}C NMR (75 MHz) δ 22.9, 32.0, 45.1, 52.2, 116.8, 125.0, 125.2, 127.5, 128.3, 129.2, 129.9, 134.2, 135.2, 143.1, 173.6; HRMS (EI) calcd for $C_{17}H_{14}N_2O_3S$ (M^+) 326.0725, found 326.0727.

2-(1-Butenyl)-1,2,3b,8-tetrahydro-3-oxo-8-phenylsulfonylpyrrolo[3',4':1,3]cycloprop[1,2-b]indol-3(3a*H*)-one (40). NaH (60%, 4 mg, 0.09 mmol, prewashed with hexane) was suspended in dry THF (1 mL). The mixture was stirred for 10 min under Ar at rt, and then Bu_4NI (2.2 mg, 0.006 mmol) was added. The mixture was cooled to 0 ^oC, and a solution of **39** (21 mg, 0.06 mmol) in dry THF (2 mL) was transferred under Ar via cannula. The mixture was stirred at 0 ^oC for 15 min and then 4-bromo-1-butene (24.3 mg, 0.18 mmol) was added. The reaction mixture was warmed to rt and stirred at rt for 1 h. Brine (2 mL) was added to the reaction mixture. After stirring for another 10 min, EtOAc (2 mL) was added. The mixture was transferred into a separatory funnel and extracted with EtOAc (2x2 mL).

The combined extracts were dried, filtered and evaporated in vacuo. The crude product was purified (1:1 v/v PE–EtOAc) to afford a colorless oil (16 mg, 69%). IR (film) 1684 cm^{-1}; ^1H NMR (300 MHz) δ 0.51 (br t, 1 H, *J* = 2.0 Hz), 2.30–2.42 (m, 2 H), 2.64 (d, 1 H, *J* = 2.0 Hz), 3.38 (ddd, 1 H, *J* = 18.2, 11.5, 6.8 Hz), 3.45 (ddd, 1 H, *J* = 18.2, 11.5, 6.8 Hz), 3.74 (dd, 1 H, *J* = 10.8, 2.0 Hz), 4.66 (d, 1 H, *J* = 10.8 Hz), 5.10–5.23 (m, 2 H), 5.79 (dddd, 1 H, *J* = 16.9, 10.5, 6.8, 6.8 Hz), 7.07 (ddd, 1 H, *J* = 7.4, 7.4, 1.0, Hz), 7.20–7.32 (m, 2 H), 7.40–7.48 (m, 2 H), 7.52–7.60 (m, 1 H), 7.63–7.69 (m, 2 H), 7.87 (d, 1 H, *J* = 8.2 Hz); ^{13}C NMR (75 MHz) δ 23.7, 32.1, 32.4, 41.2, 49.6, 49.9, 116.8, 117.4, 124.8, 125.3, 127.6, 128.3, 129.4, 130.0, 134.3, 134.9, 135.4, 143.3, 170.1; HRMS (EI) calcd for $C_{21}H_{20}N_2O_3S$ (M^+) 380.1195, found 380.1182.

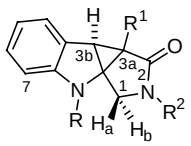
1,2,4,9-Tetrahydro-9-phenylsulfonyl-4*H*-pyrido[3,4-b]indol-3(9*H*)-one (41b). Two drops of $BF_3{\cdot}OEt_2$ was added to a solution of **39** (6 mg, 0.018 mmol) in $ClCH_2CH_2Cl$ (2 mL). The reaction mixture was refluxed for 80 h. Then it was cooled to rt and diluted with CH_2Cl_2 (2 mL). To the mixture was added saturated aq $NaHCO_3$ (2 mL). The aqueous layer was extracted with CH_2Cl_2 (2x2 mL). The combined organic layers were dried, filtered and evaporated in vacuo. The residue was purified (4:1 v/v CH_2Cl_2–acetone) to give a pale yellow solid (4.3 mg, 69%). mp 238–241 °C; IR (film) 3300, 1624 cm^{-1}; ^1H NMR (300 MHz) δ 3.58 (br t, 2 H, *J* = 3.3 Hz), 4.93 (br t, 2 H, *J* = 3.3 Hz), 6.41–6.50 (br s, 1 H), 7.25–7.61 (m, 6 H), 7.78 (d, 2 H, *J* = 8.3 Hz), 8.13 (d, 2 H, *J* = 8.6 Hz); ^{13}C NMR (75 MHz) δ 29.8, 42.9, 114.2, 118.8, 124.0, 125.6, 126.2, 126.7, 126.9, 128.0, 129.5, 134.2, 136.9, 138.1; HRMS (EI) calcd for $C_{17}H_{14}N_2O_3S$ (M^+) 326.0725, found 326.0734.

Summary of ^{1}H NMR data for tetracyclic-γ-lactams 11, 19d, 19g and 19h, and tricyclic products 14, 15, 18c and 18g.

^{1}H NMR data for 11, 19d, 19g and 19h.

Table 1 shows the salient features in the ^{1}H NMR spectra of the tetracyclic γ-lactams: the signals of the C(3a) (for **19g**,**h**), C(1) and C(3b) hydrogens are diagnostically useful. In general, it was found that the chemical shift positions of the C(1)-methylene hydrogens of the *N*-PhSO$_2$ substituted tetracyclic γ-lactams **11**, **19d** and **19h** occurred at lower field than those for the *N*-Me substituted compound **19g**.

Table 1. Characteristic ^{1}H NMR signals for the tetracyclic-γ-lactams **11**, **19d**, **19g** and **19h**.[a]



11: R = SO_2Ph, R^1 = CO_2Me, R^2 = Et
19d: R = SO_2Ph, R^1 = CO_2Et, R^2 = BTMSM
19g: R = Me, R^1 = H_c, R^2 = BTMSM
19h: R = SO_2Ph, R^1 = H_c, R^2 = BTMSM

	Chemical Shift (δ)			
	11	**19d**	**19g**	**19h**
C(1)-H_a	4.82 (d, 1H, *J* = 10.9 Hz)	4.85 (d, 1H, *J* = 11.3 Hz)	3.88 (d, 1H, *J* = 10.8 Hz)	4.74 (d, 1H, *J* = 11.2 Hz)
C(1)-H_b	3.74 (d, 1H, *J* = 10.9 Hz)	3.69 (d, 1H, *J* = 11.3 Hz)	3.62 (dd, 1H, *J* = 10.8, 1.8 Hz)	3.76 (dd, 1H, *J* = 11.2, 1.8 Hz)
C(3a)-H	na[b]	na[b]	1.16 (t, 1H, *J* = 1.8 Hz)	0.64 (t, 1H, *J* = 1.8 Hz)
C(3b)-H	3.15 (s, 1H)	3.09 (s, 1H)	3.07-3.14 (br s, 1H)	2.58 (d, 1H, *J* = 1.8 Hz)

[a]Chemical shifts of aromatic groups, CH_3 and CH groups in BTMSM, and Et (or Me) group in R, R^1 and R^2 are not included. [b]Not applicable.

In the case of **11** and **19d**, C(1)-H_a appeared in the range δ 4.82–4.85, C(1)-H_b at δ 3.69–3.74 and C(3b)-H at δ 3.09–3.15. Both C(1)-H_a,H_b resonated as doublets (J_{gem} ~ 10.8 Hz) and were not coupled to C(3b)-H, which was observed as a singlet (δ 3.15 for **11**; δ 3.09 for **19d**).

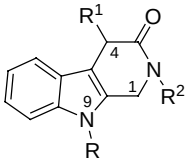
For **19g**, C(1)-H_a was observed as a doublet, centred at δ 3.88, due to coupling to H_b ($J_{Ha,Hb}$ = 10.8 Hz), and no long-range coupling between C(1)-H_a and C(3a)-H was observed. The C(1)-H_b signal

appeared as a double doublet at δ 3.62 due to coupling to C(1)-H_a and long range coupling to C(3a)-H ($J_{Hb,Ha}$ = 10.8 Hz, $J_{Hb,H3a}$ = 1.8 Hz). The C(3a)-H signal was observed as a triplet ($J_{H3a,Hb}$ = $J_{H3a,H3b}$ = 1.8 Hz) at δ 1.16 and was ascribed to coupling to C(1)-H_b and C(3b)-H. The resonance for C(3b)-H was seen at δ 2.78 as a broad singlet. A similar signal pattern was also observed for compound **19h** except for significant differences in chemical shifts for C(3a)-H and C(3b)-H. As expected, the C(1)-H_a,H_b resonances were found within the chemical shift range as was observed in compounds **11** and **19d**; C(1)-H_a resonated at δ 4.74 (d, $J_{Ha,Hb}$ = 11.2 Hz) and C(1)-H_b appeared at δ 3.76 (dd, $J_{Hb,Ha}$ = 11.2 Hz, $J_{Hb,H3a}$ = 1.8 Hz). Surprisingly, the C(3a)-H and C(3b)-H signals were observed at lower chemical shifts with the C(3a)-H triplet ($J_{H3a,Ha}$ = $J_{H3a,H3b}$ = 1.8 Hz) being very strongly shielded and resonated at δ 0.64, and the C(3b)-H doublet ($J_{H3b,H3a}$ = 1.8 Hz) occurred at δ 2.58.

^{1}H NMR data for the tricyclic products **14**, **15**, **18c** and **18g**.

Table 2 summarizes the characteristic ^{1}H NMR signals of **14**, **15**, **18c** and **18g**.

Table 2. ^{1}H NMR signals for **14**, **15**, **18c** and **18g**.[a]

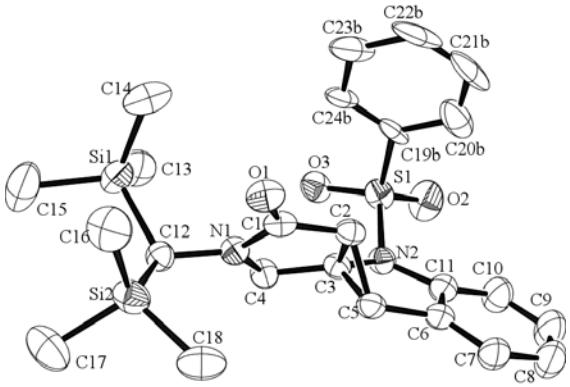


14: R = SO_2Ph, R^1 = CO_2Me, R^2 = Et
15: R = H, R^1 = CO_2Et, R^2 = BTMSM
18c: R = Me, R^1 = CO_2Et, R^2 = BTMSM
18g: R = Me, R^1 = H, R^2 = BTMSM

	Chemical Shift (δ)			
	14	**15**	**18c**	**18g**
C(1)-H	4.88 (d, 1H, *J* = 18.6, 4.0 Hz) 4.98 (d, 1H, *J* = 18.6, 4.0 Hz)	4.45-4.57 (m, 1H) 4.73-4.90 (m, 1H)	4.48 (br d, 1H), 4.72-4.88 (m, 1H)	4.78 (t, 2H, *J* = 3.5 Hz) na[b]
C(4)-H	4.68 (t, 1H, *J* = 4.0 Hz)	4.73-4.90 (m, 1H)	4.72-4.88 (m, 1H)	3.57 (t, 2H, *J* = 3.5 Hz)

[a]Chemical shifts of aromatic groups, CH_3 and CH groups in BTMSM, and Et (or Me) group in R, R^1 and R^2 are not included.

Figure ESI-1. ORTEP drawing of **19h**

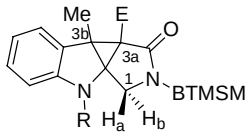


The X-ray structure of **19h** confirmed its assigned structure and, by corollary, compounds **11**, **19d** and **19g**. The crystal structure also revealed that the *N*-PhSO$_2$ group had adopted a conformation wherein the phenyl unit resided directly above C(3a)-H and the distal C(3b)-H. The C(3a)-H being closest to the phenyl moiety would experience the strongest shielding and therefore resonated at δ 0.64 whereas this effect would be less, but still significant, for C(3b)-H, which resonated at δ 2.58. Furthermore, the X-ray structure also showed that C(1)-H$_a$ bond is positioned close to one of the S–O units of the *N*-PhSO$_2$ group and therefore would experience additional deshielding, in addition to the electron-withdrawing inductive effect of the nitrogen centers, due to the anisotropy of the SO$_2$ moiety.[1] This would explain why C(1)-H$_a$ is more strongly deshielded than C(1)-H$_b$ in compounds **11**, **19d** and **19h**.

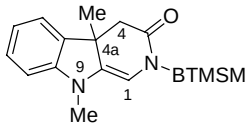
Summary of ^{1}H NMR data for tetracyclic-γ-lactams 24a,c,e and the tricycle 27.

The characteristic 1H NMR signals are collected in Table 3.

Table 3. Characteristic ^{1}H NMR signals for **24a**,**c**,**e** and the tricycle **27**.[a]



24 a: R = SO_2Ph, E = CO_2Et
c: R = SO_2Ph, E = H
e: R = Me, E = H



27

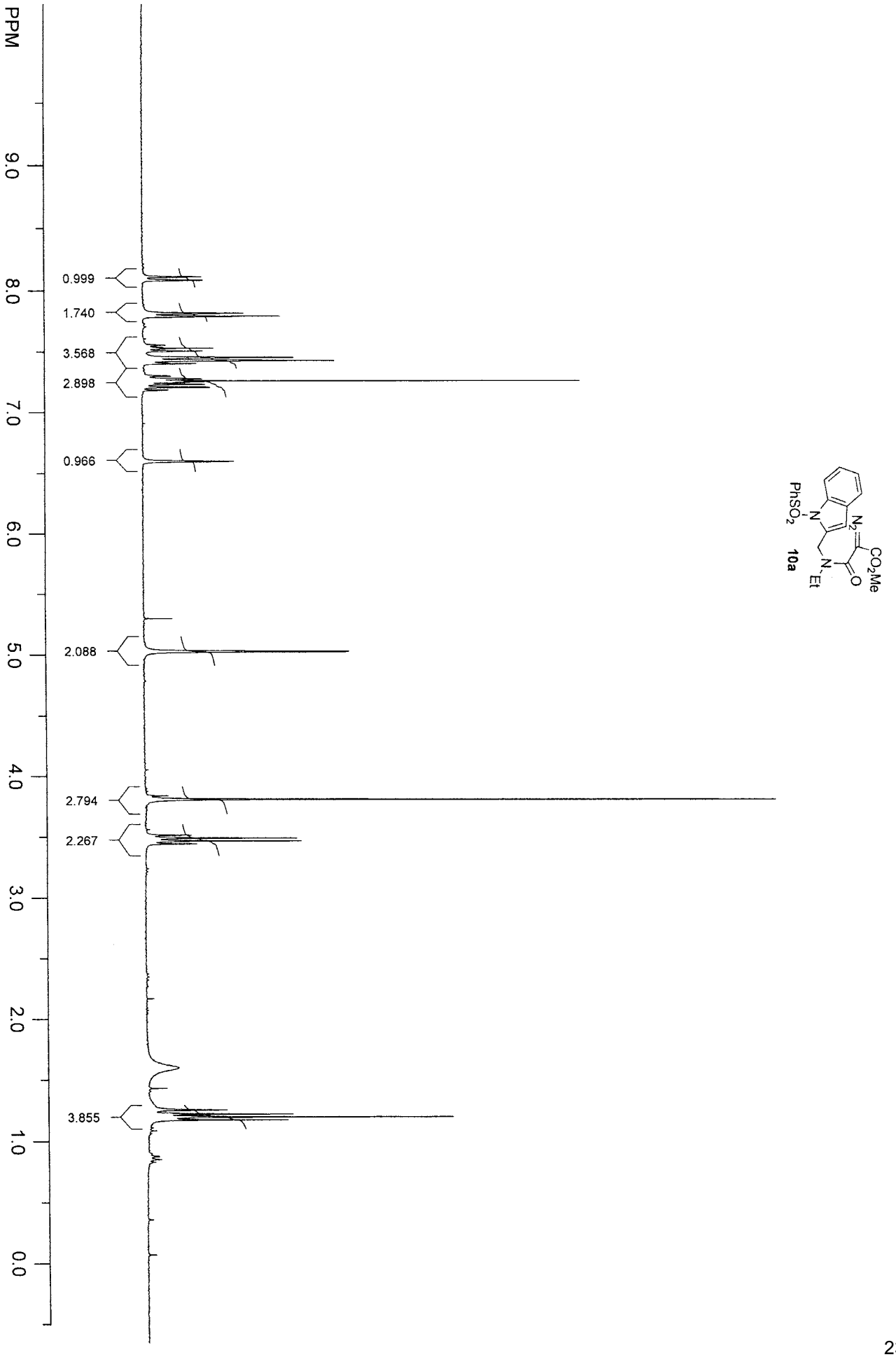
	Chemical Shift (δ)			
	24a	**24c**	**24e**	**27**
C(1)-H	4.81 (d, 1H, J = 12.1 Hz, H_a) 3.69 (d, 1H, J = 12.1 Hz, H_b)	4.85 (d, 1H, J = 11.1 Hz, H_a) 3.65 (dd, 1H, J = 11.1, 1.9 Hz, H_b)	3.80 (d, 1H, J = 11.3 Hz, H_a) 3.55 (dd, 1H, J = 11.3, 1.8 Hz, H_b)	5.22-5.32 (br s, 1H) na[b]
C(3a)-H	na[b]	0.85 (d, 1H, J = 1.9 Hz)	1.21 (d, 1H, J = 1.8 Hz)	na[b]
C(3b)-H	1.46 (s, 3H)	1.41 (s, 3H)	1.54 (s, 3H)	na[b]
C(4)-H	na[b]	na[b]	na[b]	2.70-2.90 (m, 2H)
C(4a)-Me	na[b]	na[b]	na[b]	1.34 (s, 3H)

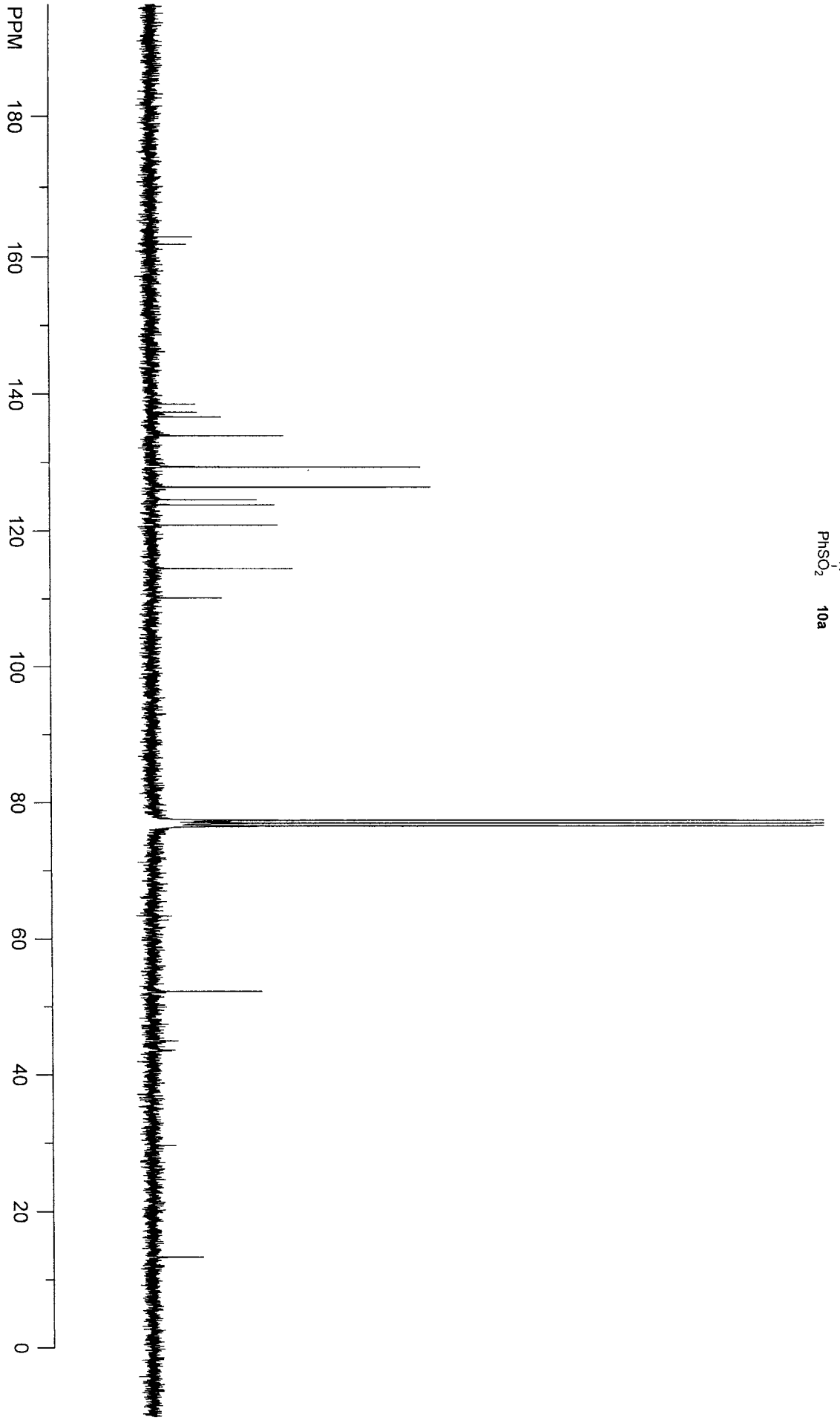
[a]Chemical shifts of aromatic groups, CH_3 and CH groups in BTMSM, Et group in CO_2Et and *N*-Me on the indoline moiety are not included. [b]Not applicable.

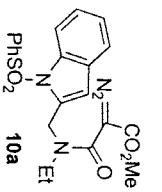
The C(1)-methylene hydrogens in **24a**,**c** were more deshielded than those in **24e**. In **24a,** C(1)-H_a appeared as a lower field doublet at δ 4.81 ($J_{Ha,Hb}$ = 12.1 Hz) and C(1)-H_b showed up as a higher field doublet centered at δ 3.69. The C(3b)-Me singlet was observed at δ 1.46. For **24c**, similar chemical shift positions were observed for C(1)-H_a (δ 4.81) and C(1)-H_b (δ 3.65), but the latter signal now resonated as a double doublet ($J_{Hb,Ha}$ = 11.1 Hz, $J_{Hb,H3a}$ = 1.9 Hz) due to coupling to C(3a)-H. The C(3a)-H doublet occurred at δ 0.85 ($J_{Hb,H3a}$ = 1.9 Hz) and the C(3b)-Me singlet appeared at δ 1.41. For the *N*-Me derivative **24e**, the doublet at δ 3.80 ($J_{Ha,Hb}$ = 11.3 Hz) and the double doublet at δ 3.55

($J_{Hb,Ha}$ = 11.3, $J_{Hb,H3a}$ = 1.8 Hz) were ascribed to C(1)-H_a and C(1)-H_b, respectively. The C(3a)-H doublet was observed at δ 1.21 ($J_{Hb,H3a}$ = 1.8 Hz) and the C(3b)-Me singlet appeared at δ 1.54. A comparison of the chemical shift positions for C(3a)-H signal in **24c** and of the C(3b)-Me singlet in **24a**,**c** to those of **24e** clearly indicates that the anisotrpy of the *N*-$PhSO_2$ moiety in **24a**,**c** strongly shields the C(3a)-H (in **24c**) and to a lesser extent the C(3b)-Me (in **24a**,**c**).

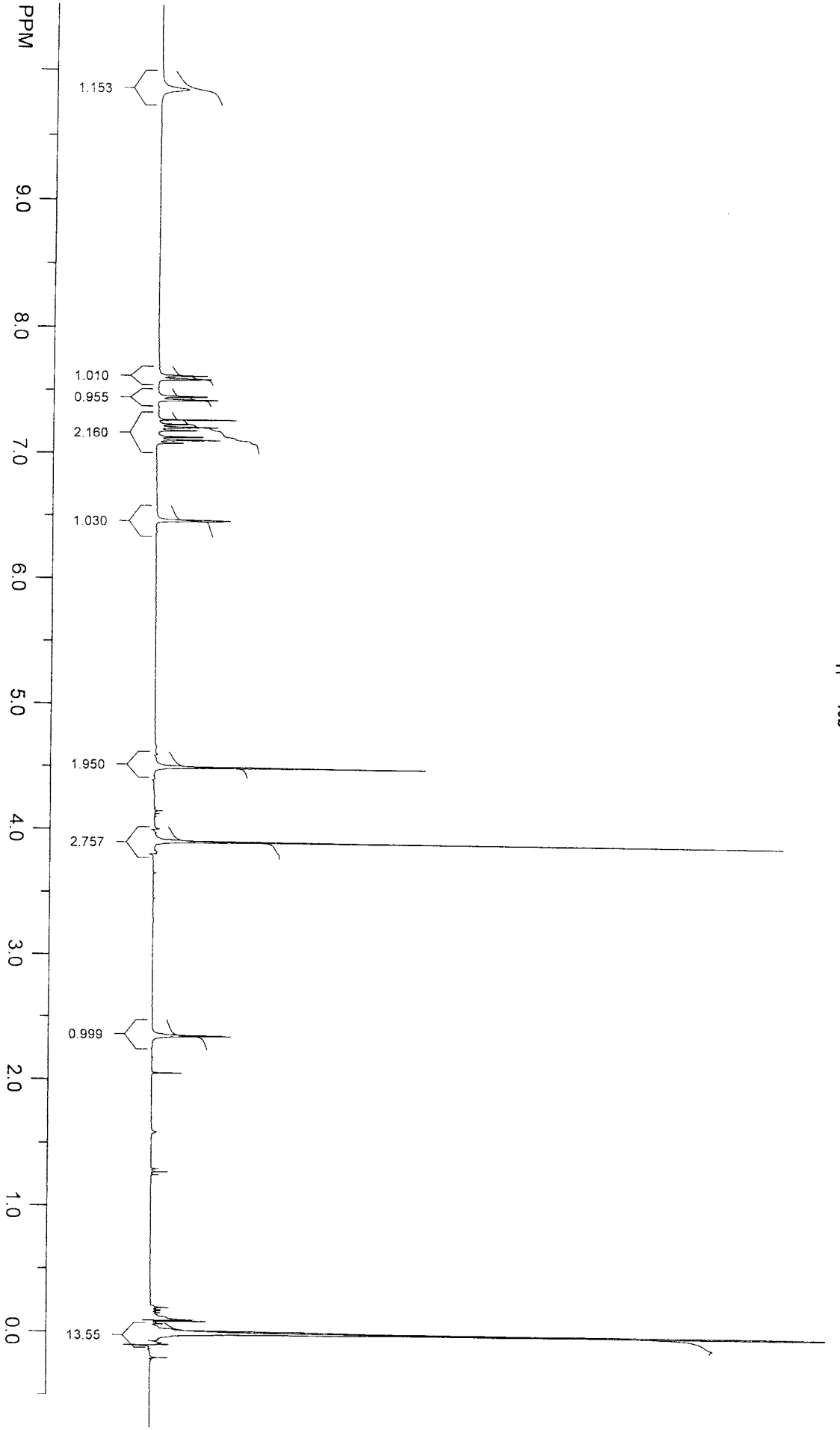
In the ^{1}H NMR spectrum of **27**, the characteristic signals at δ 3.55 (dd) and δ 3.80 (d) due to the C(4)-methylene hydrogens in **24e** were replaced by a broad singlet at δ 5.22–5.32, which was ascribed to the C(1)-olefinic proton.

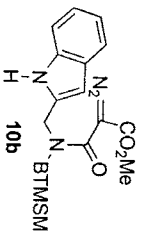




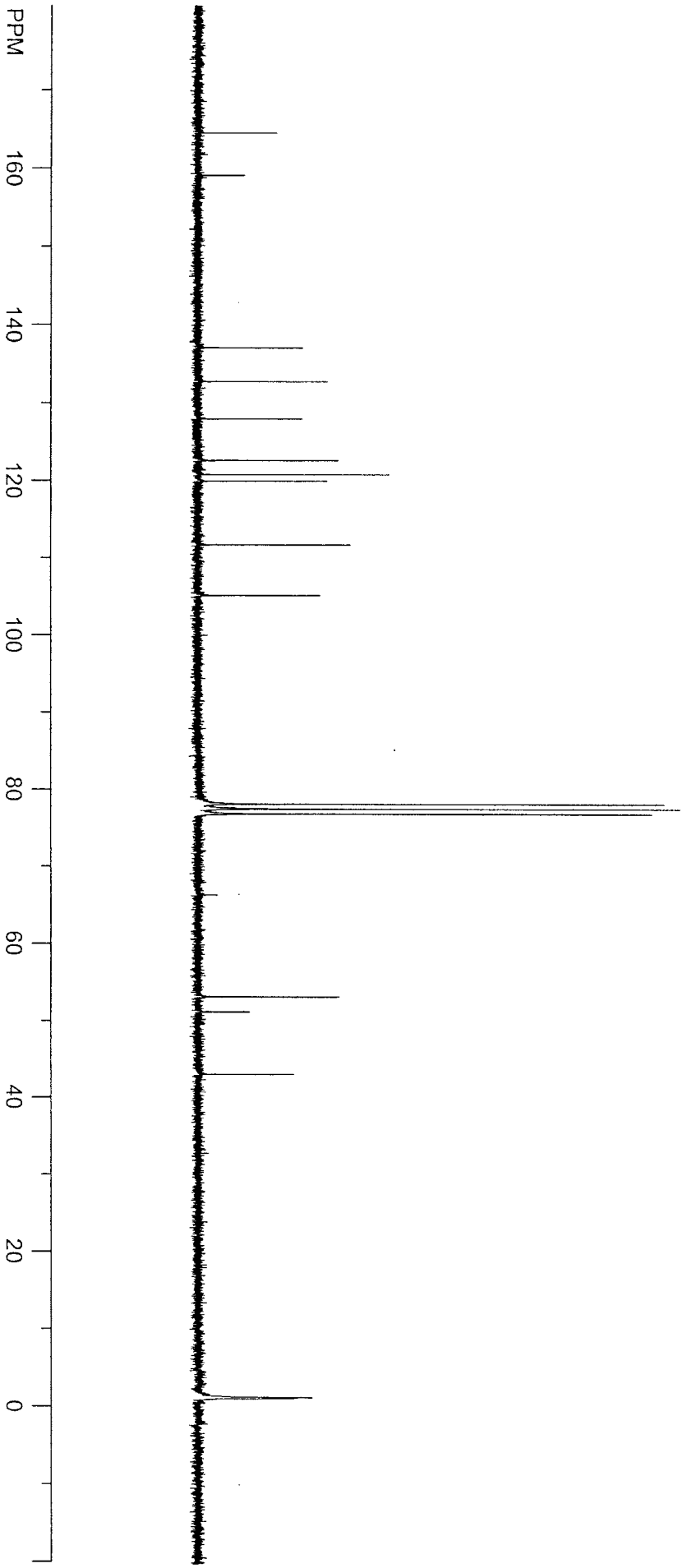


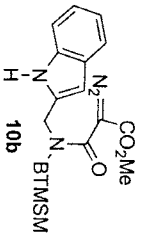
10a



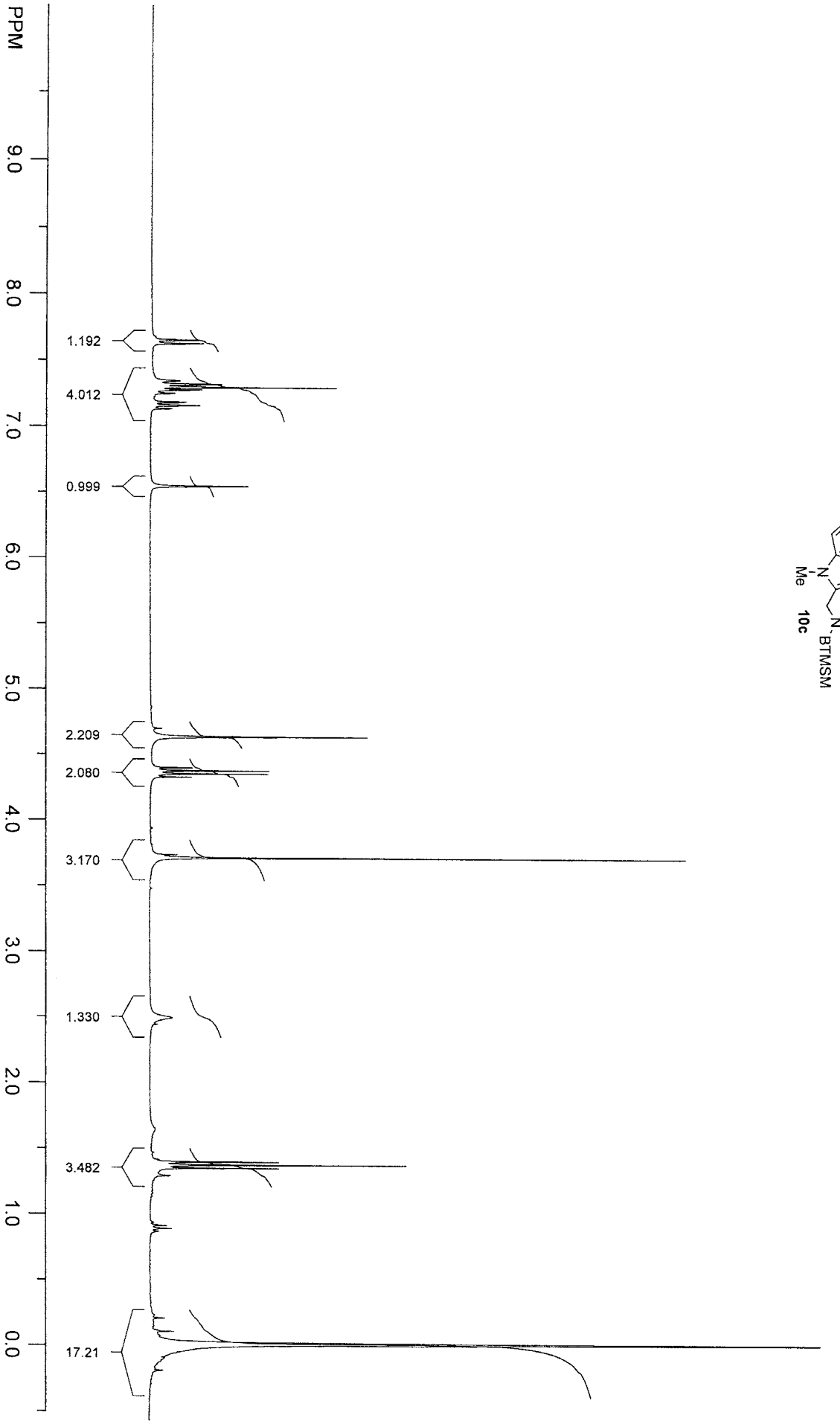


10b





10b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2.209
2.080
3.170
1.330
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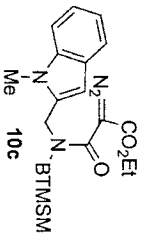
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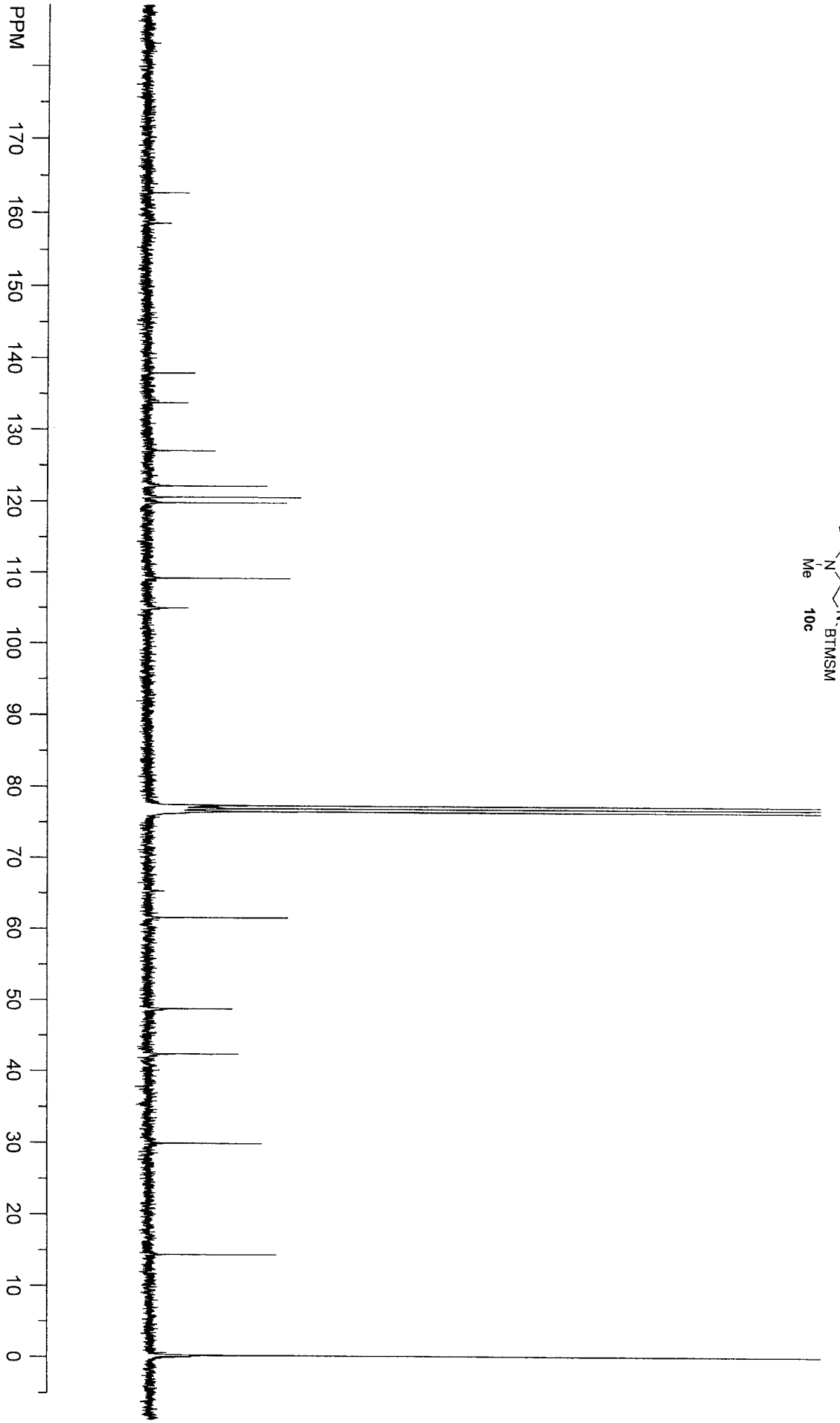

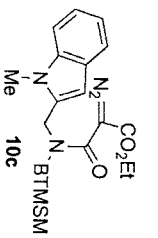

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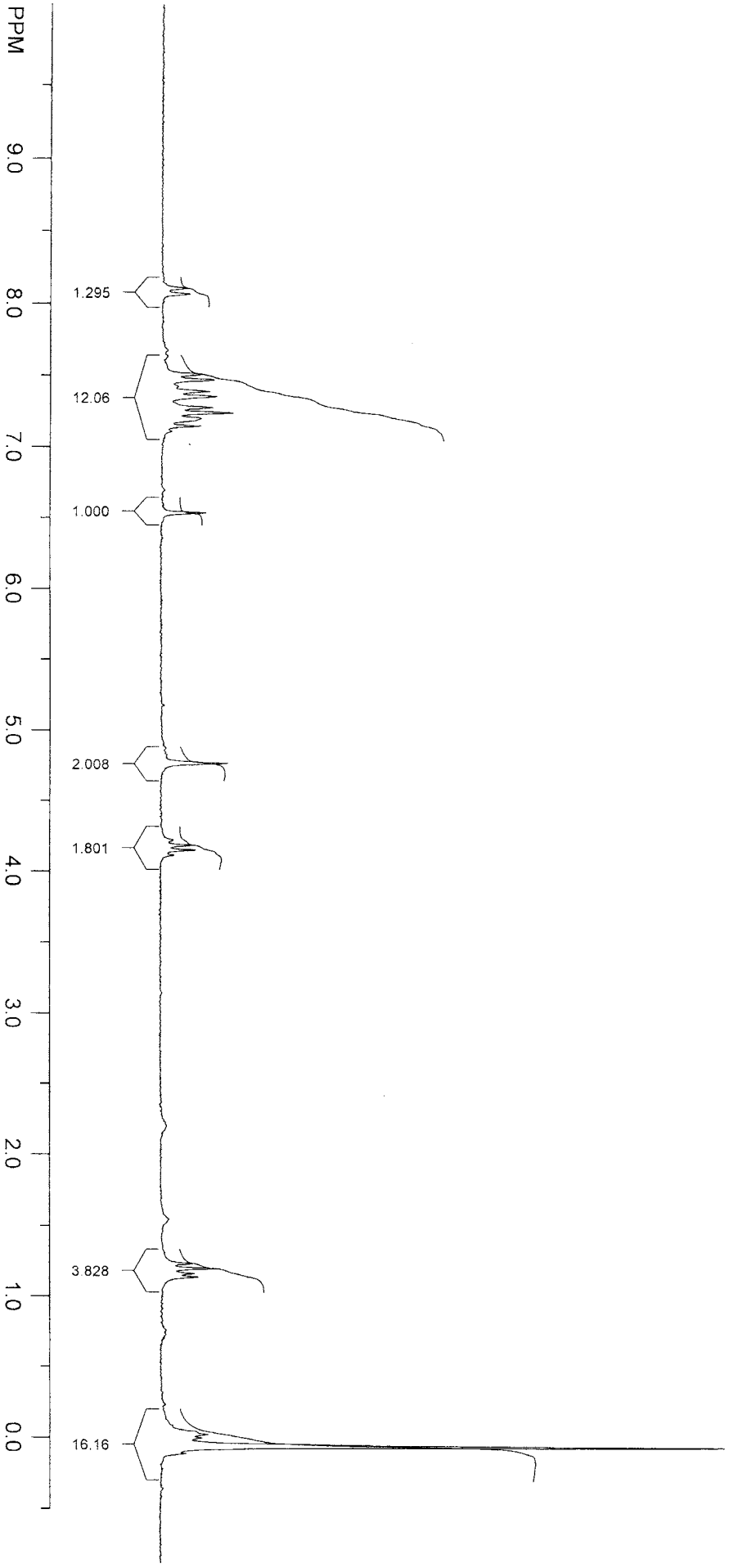

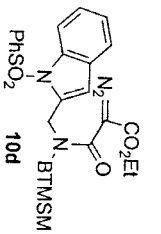

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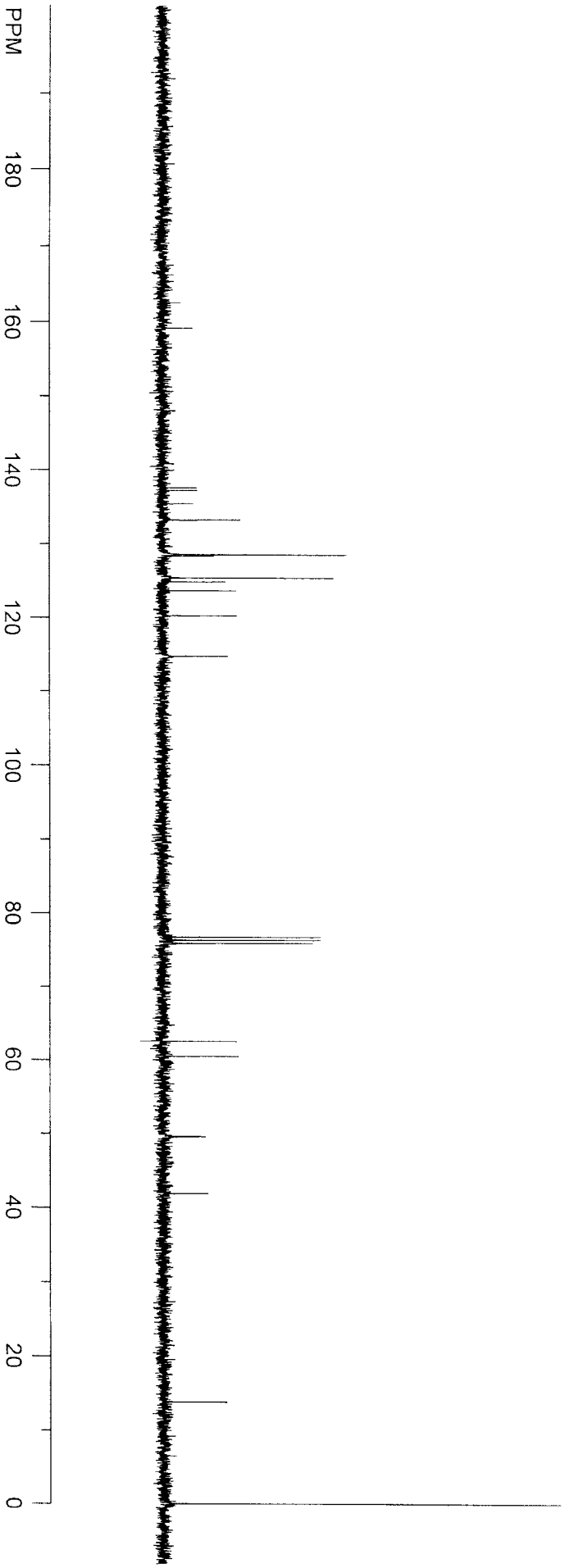

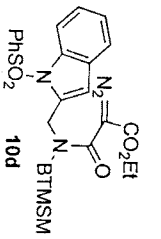

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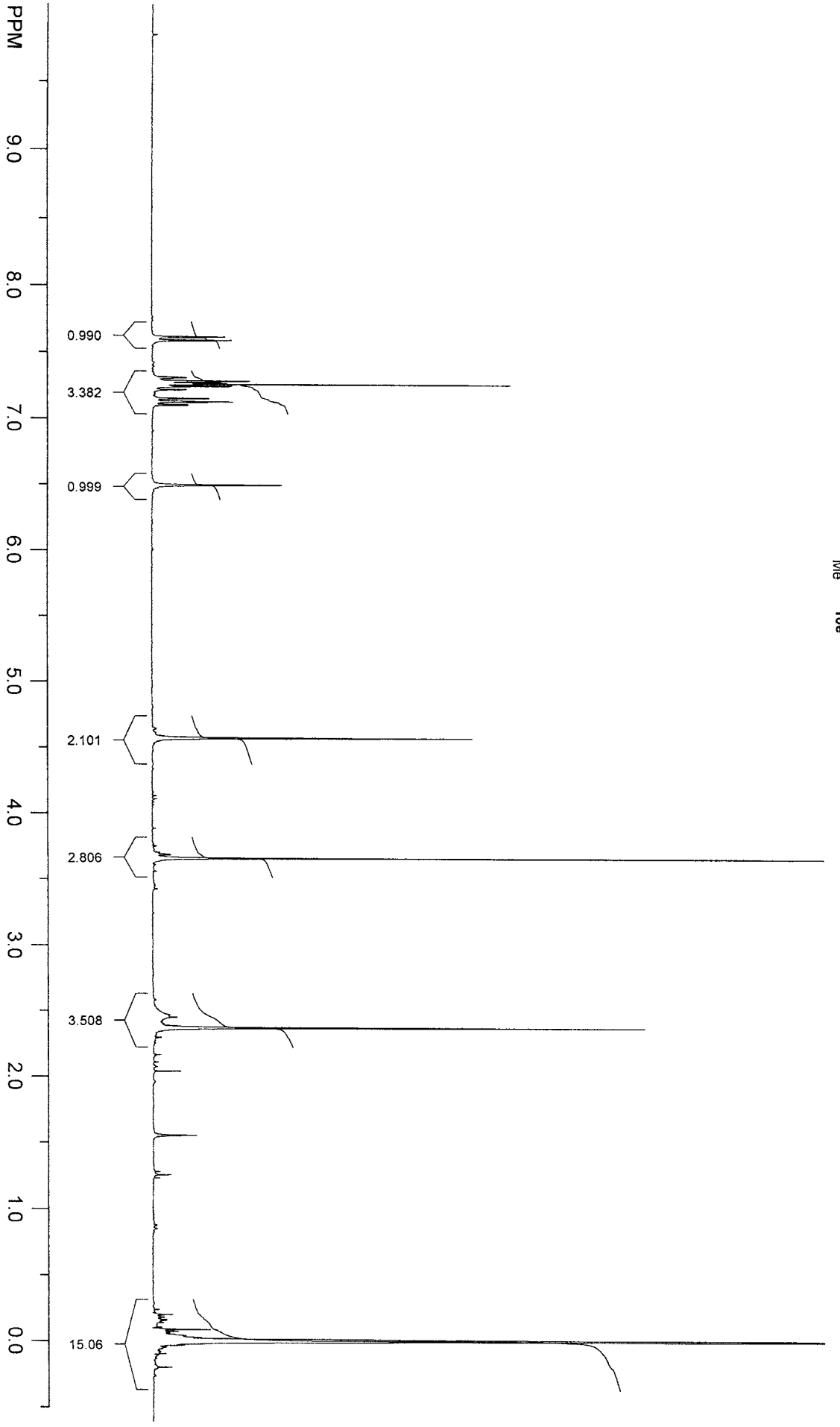

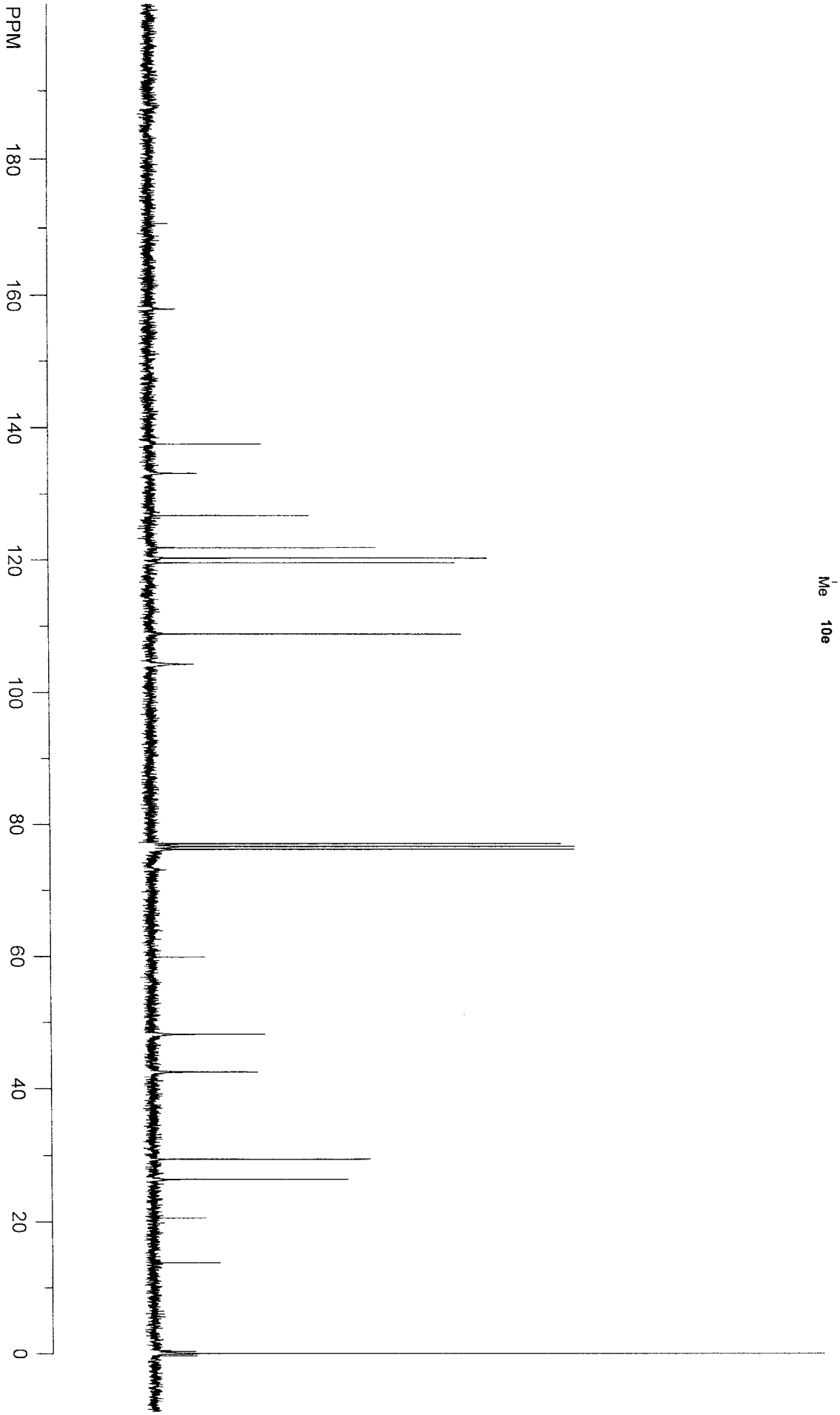

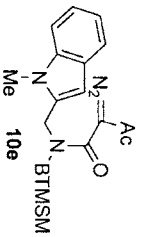

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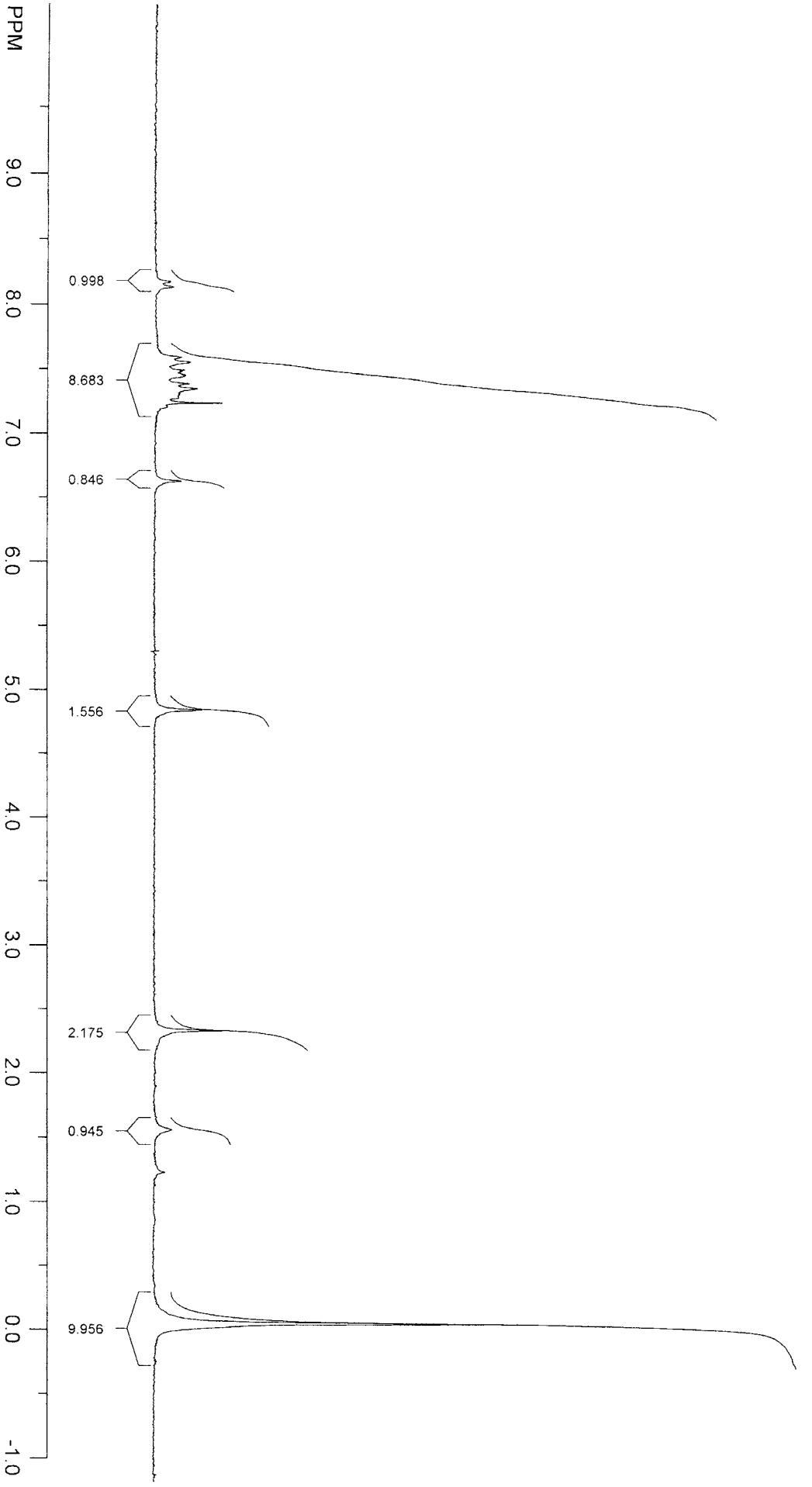

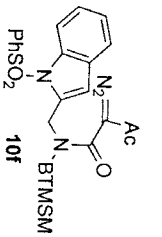

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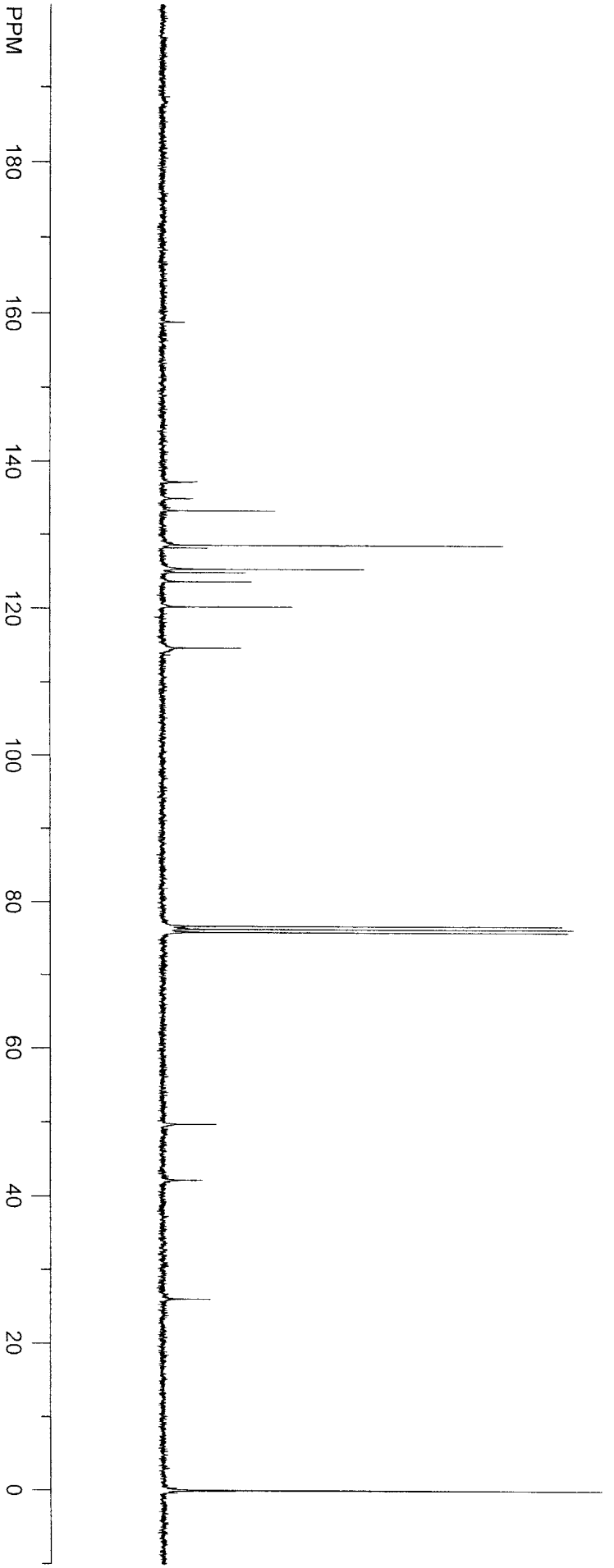

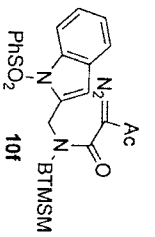

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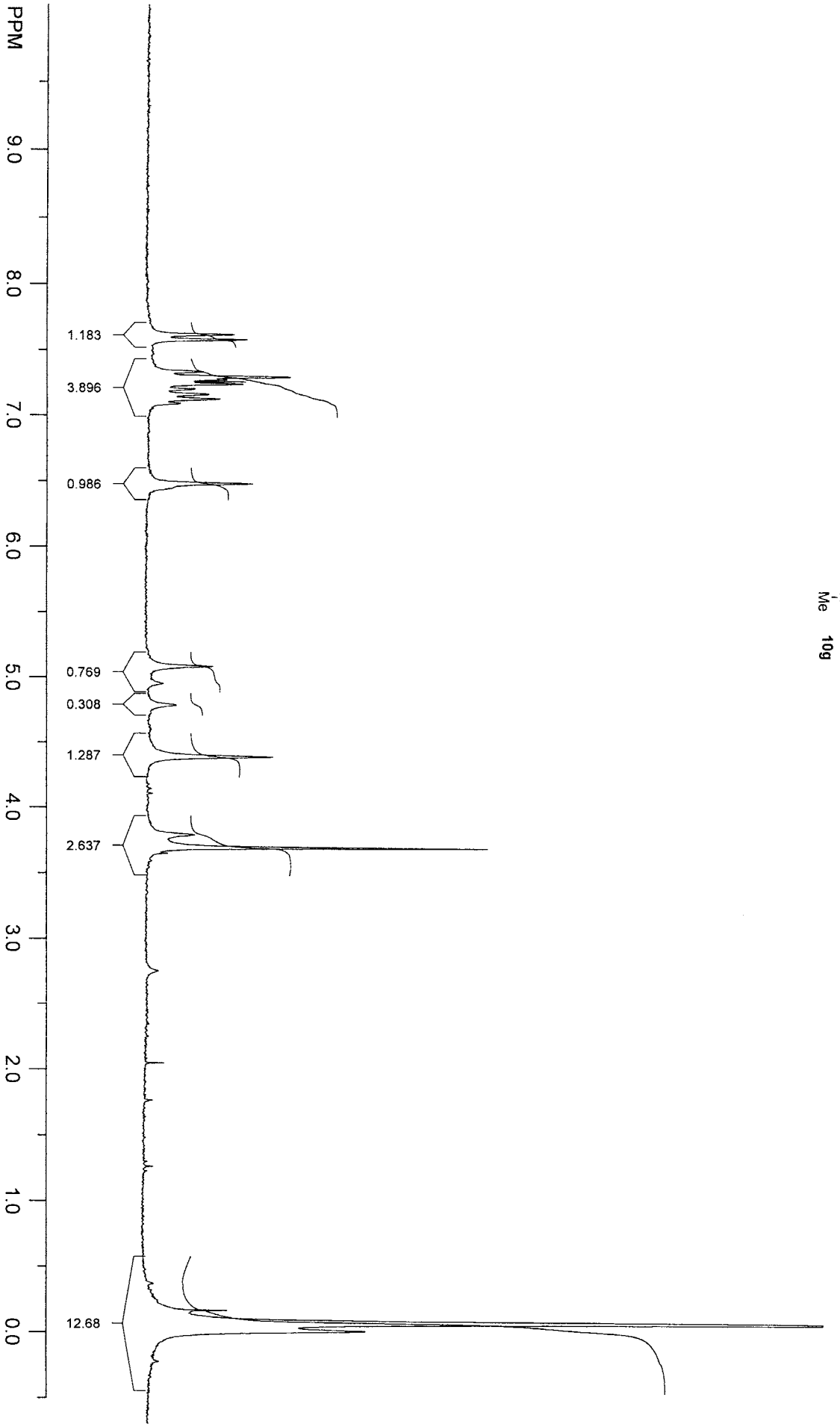

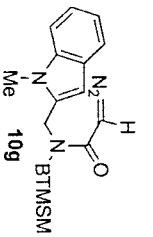

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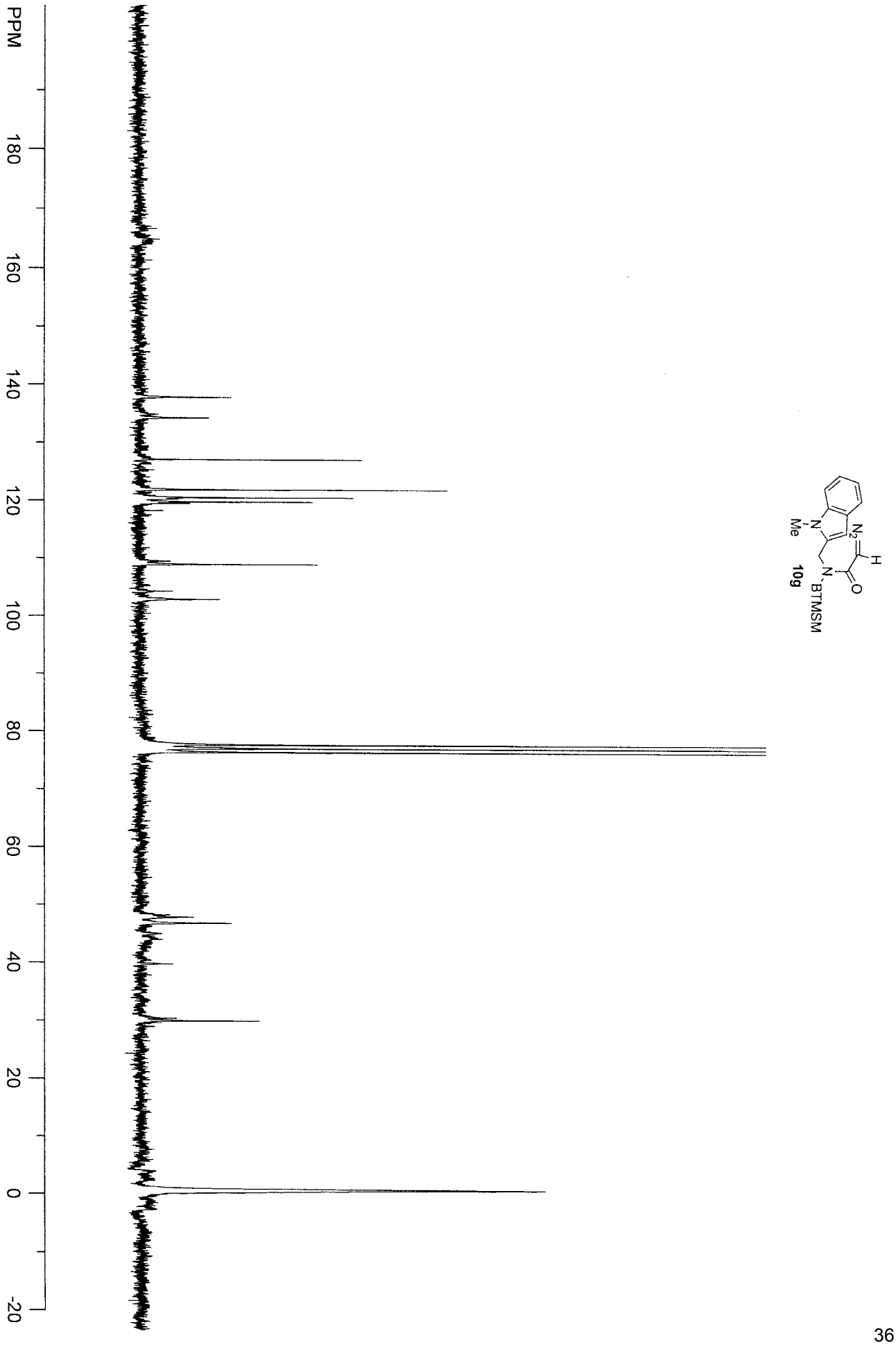

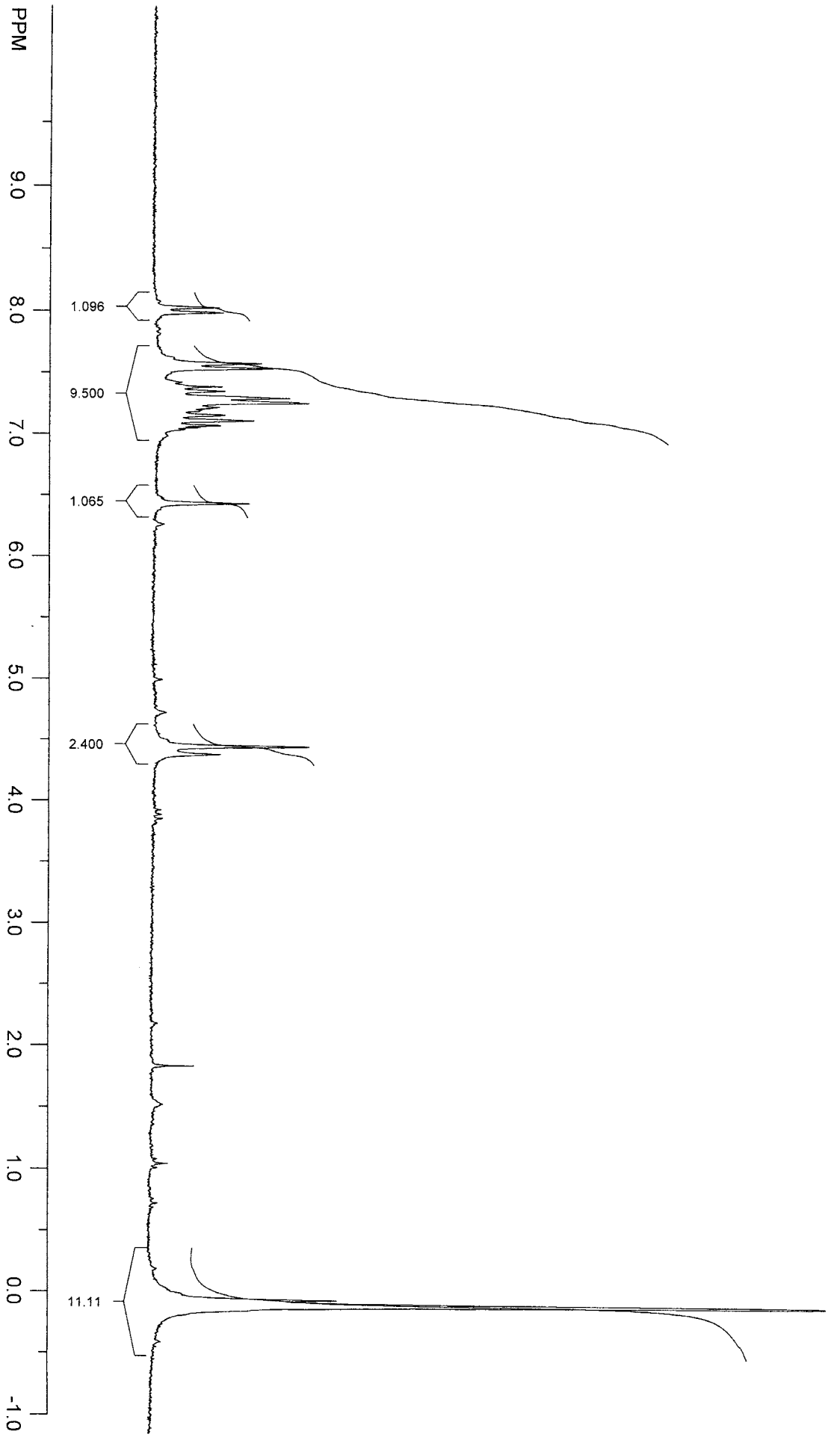

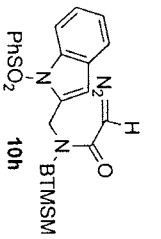

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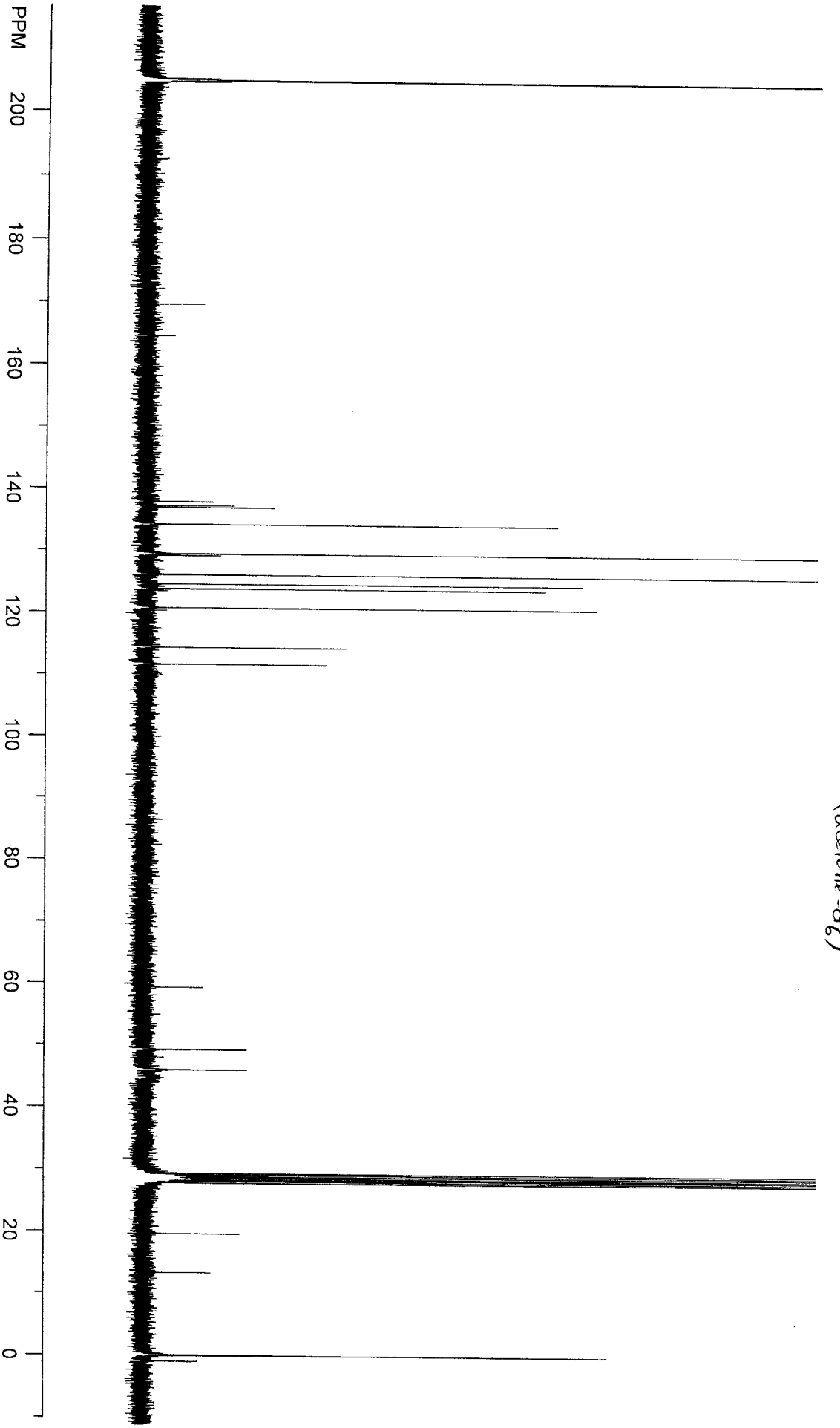

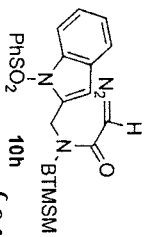

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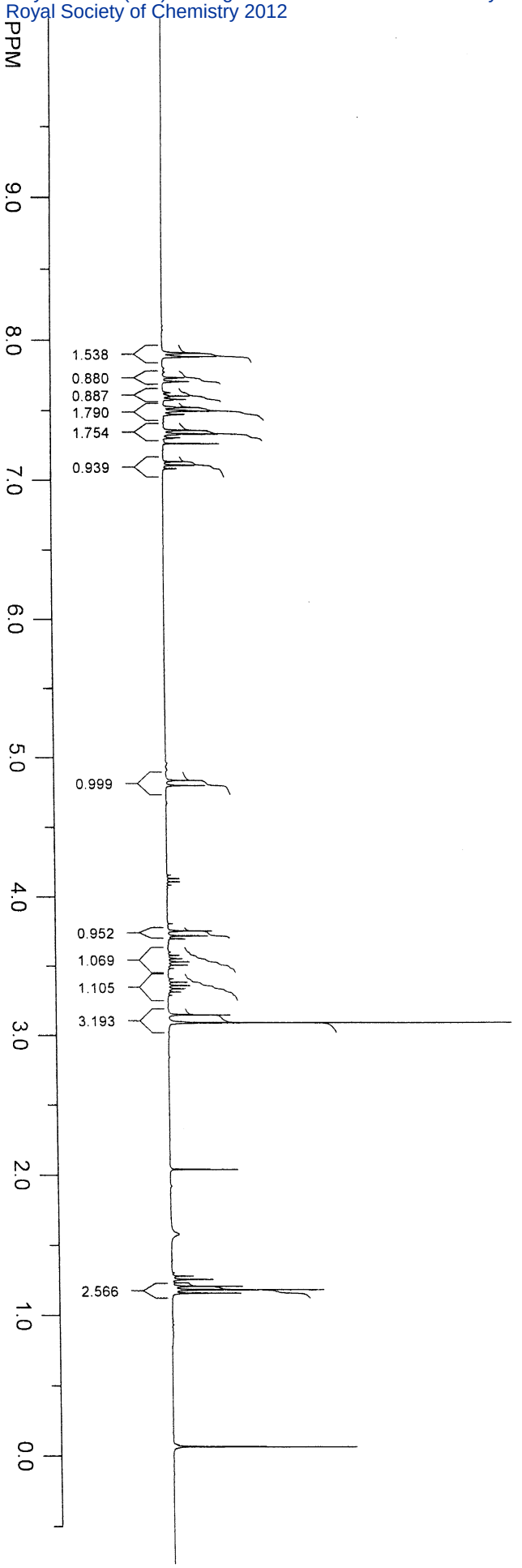

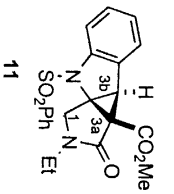

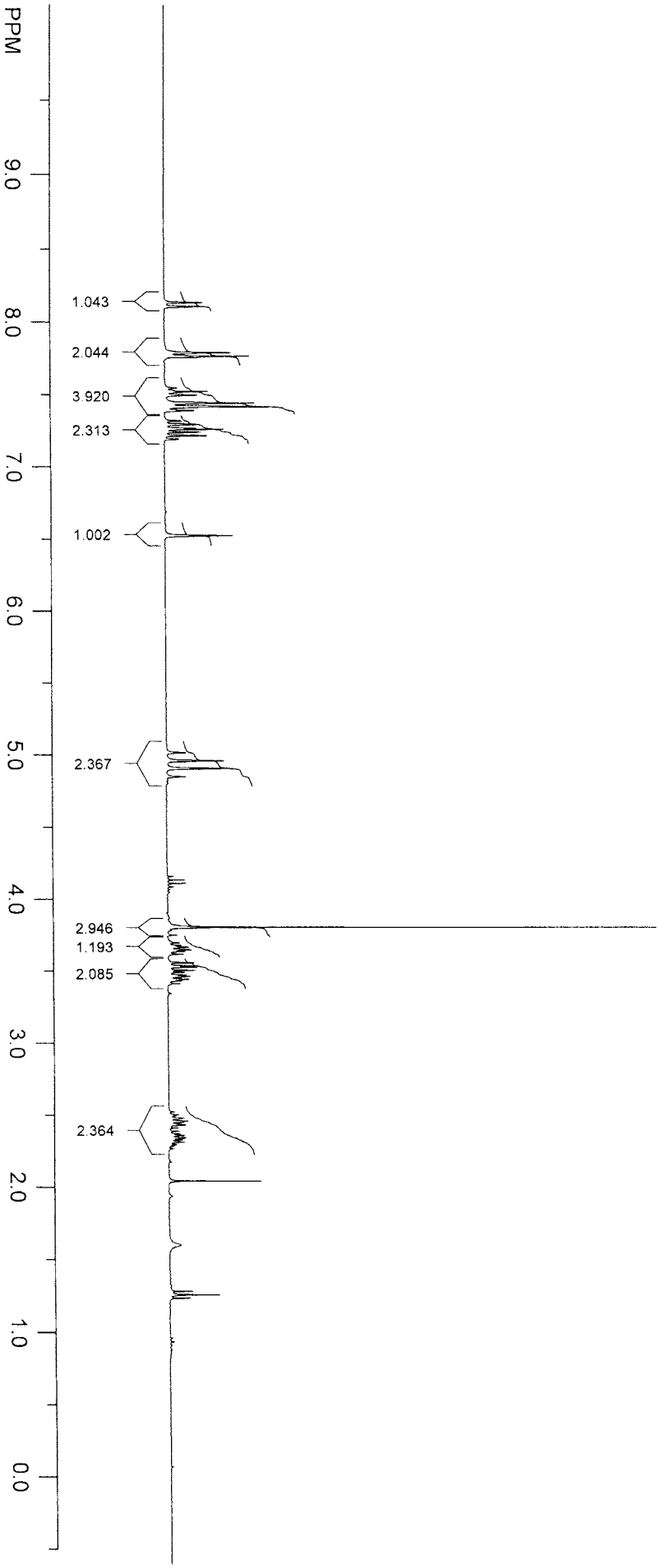

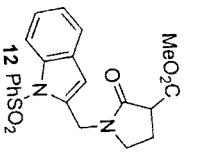

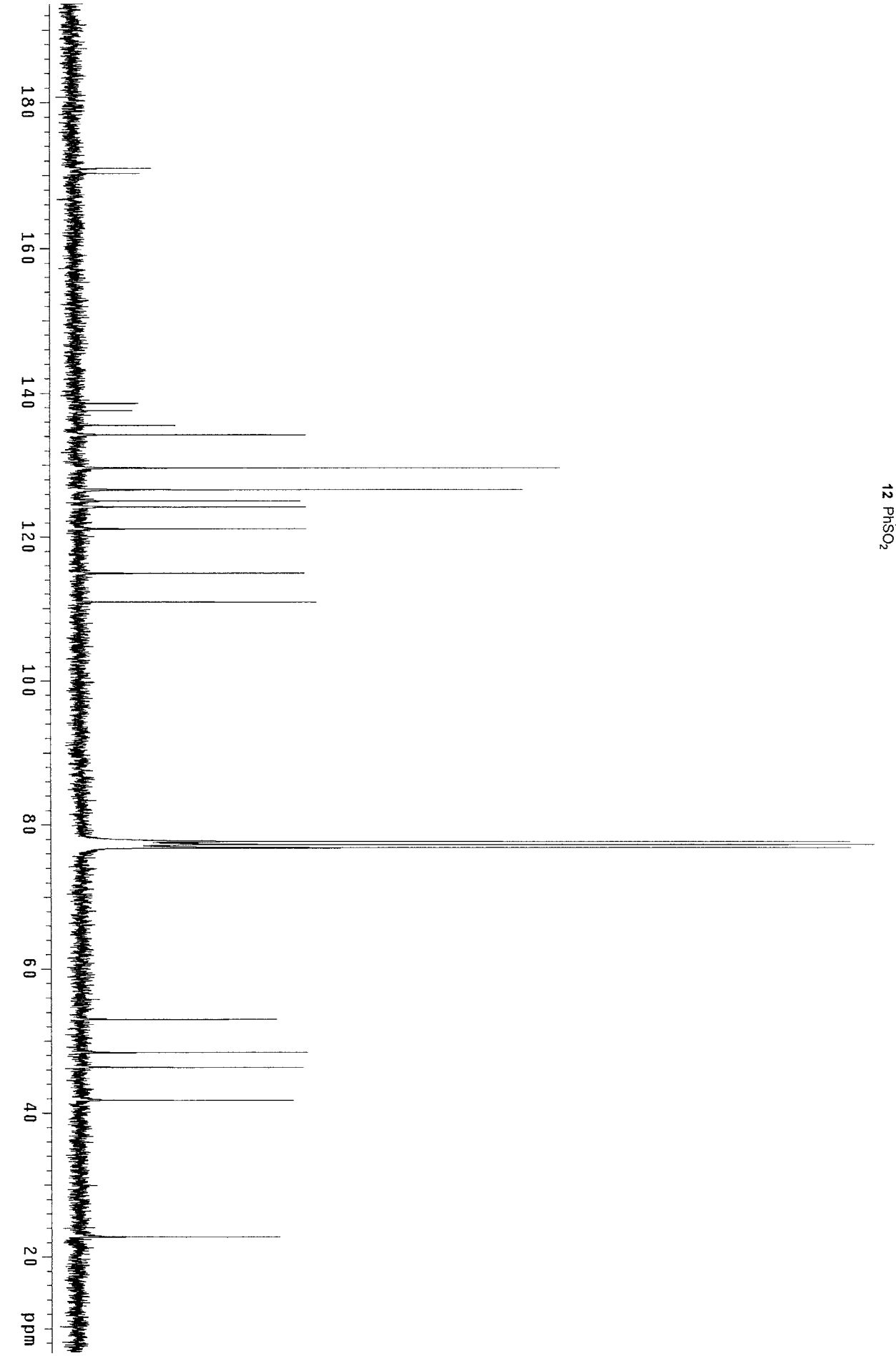

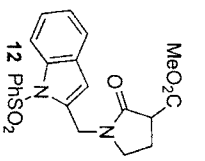

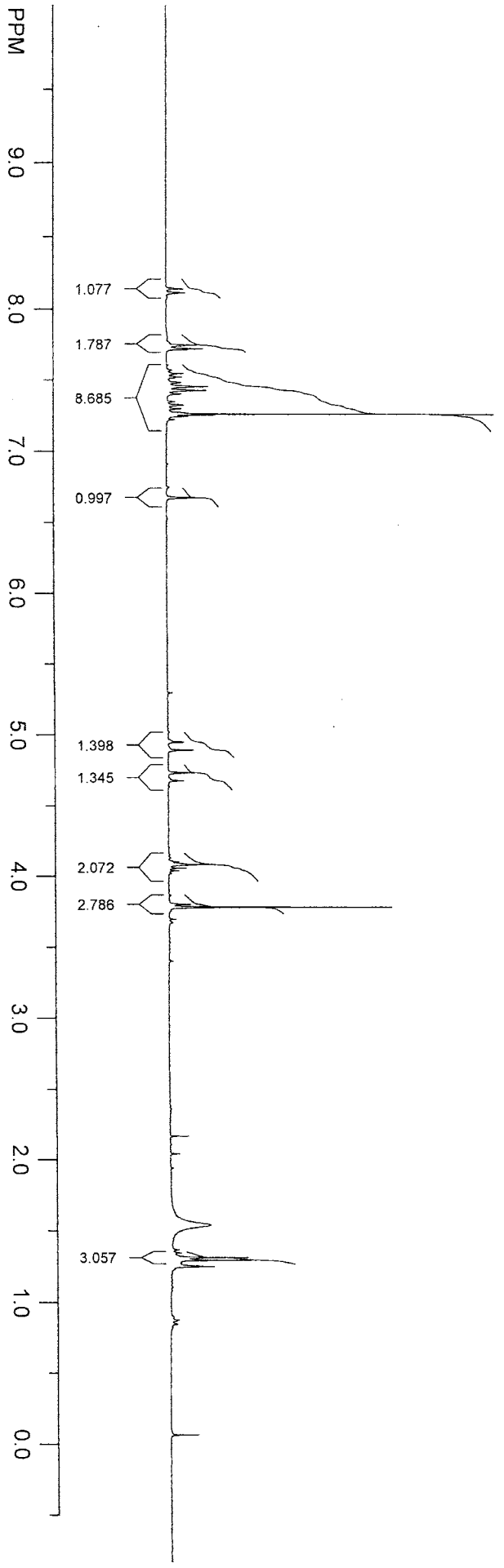

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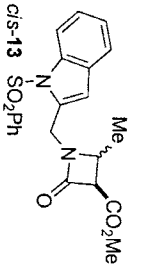

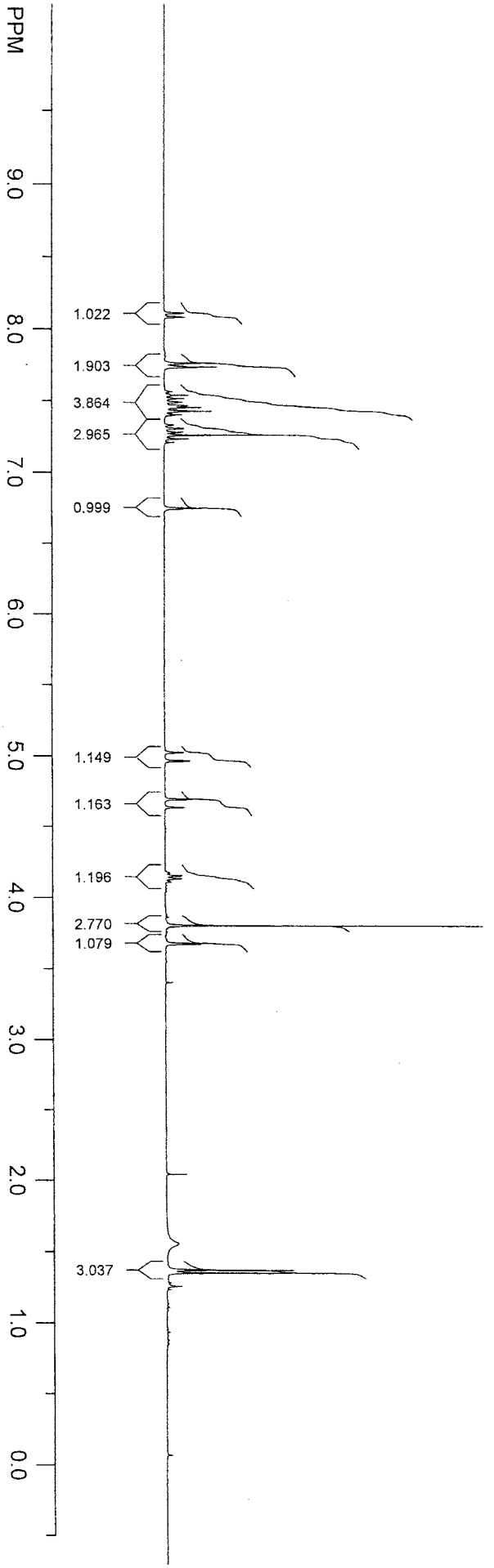

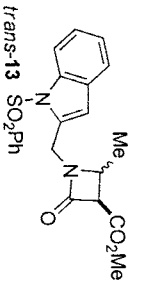

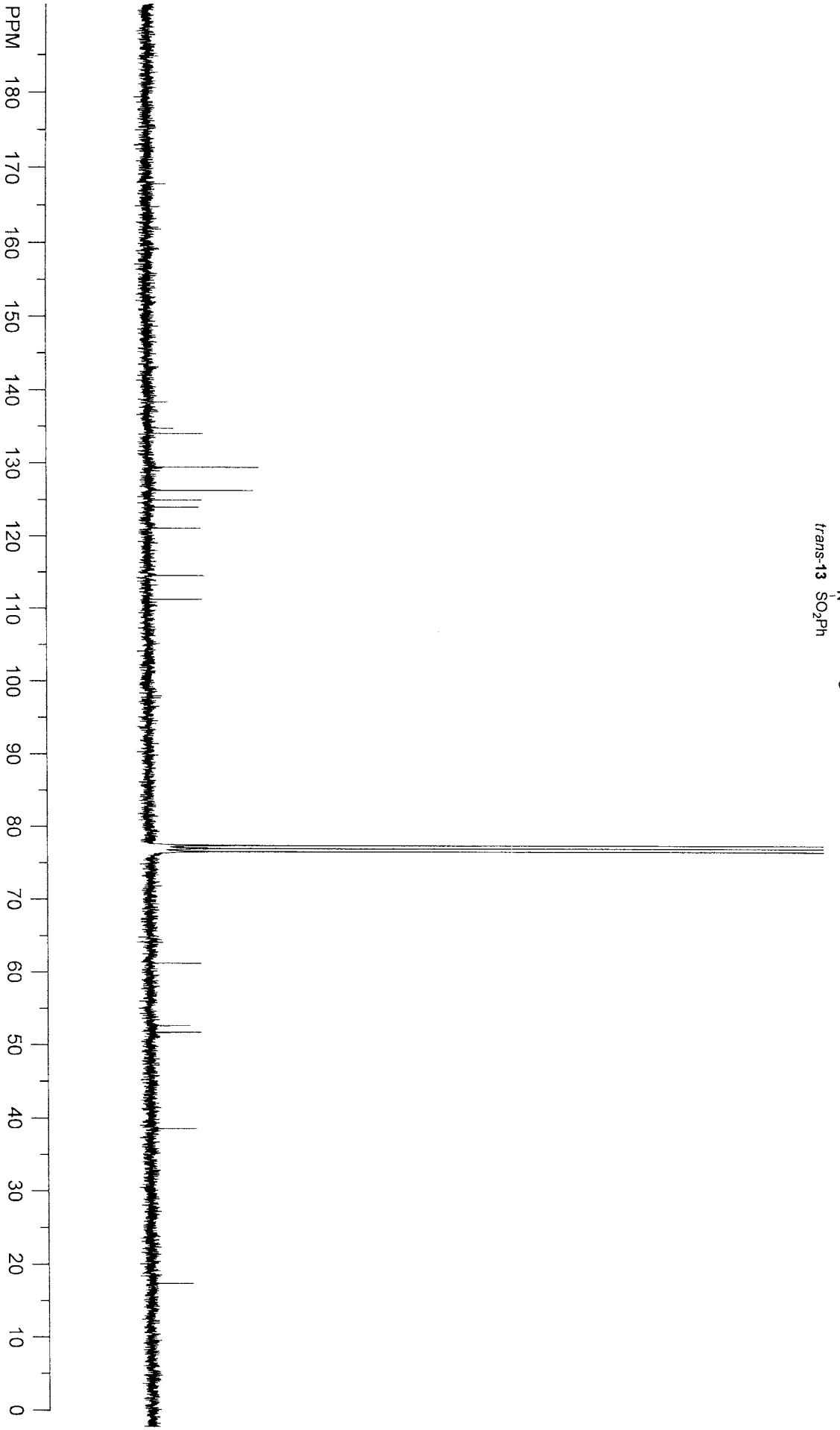

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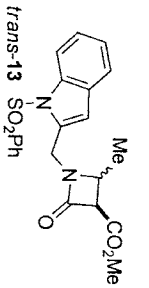

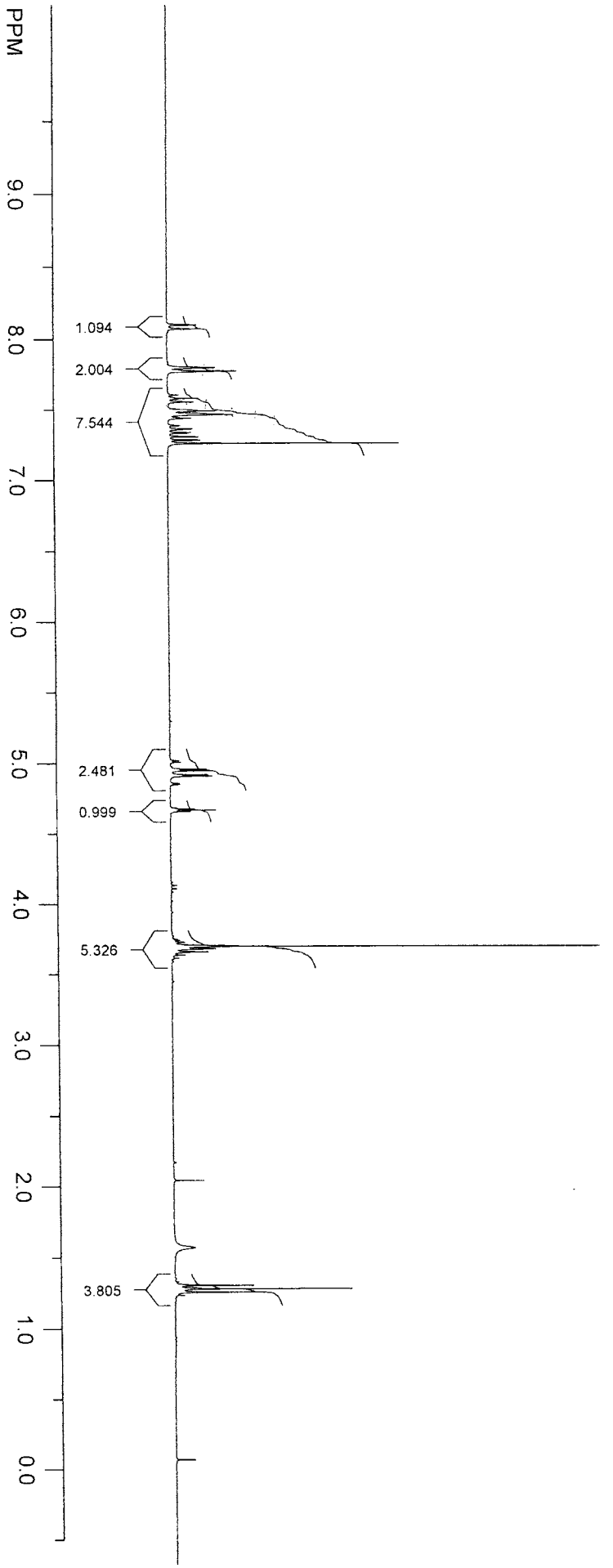

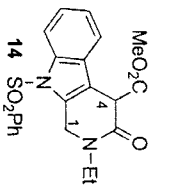

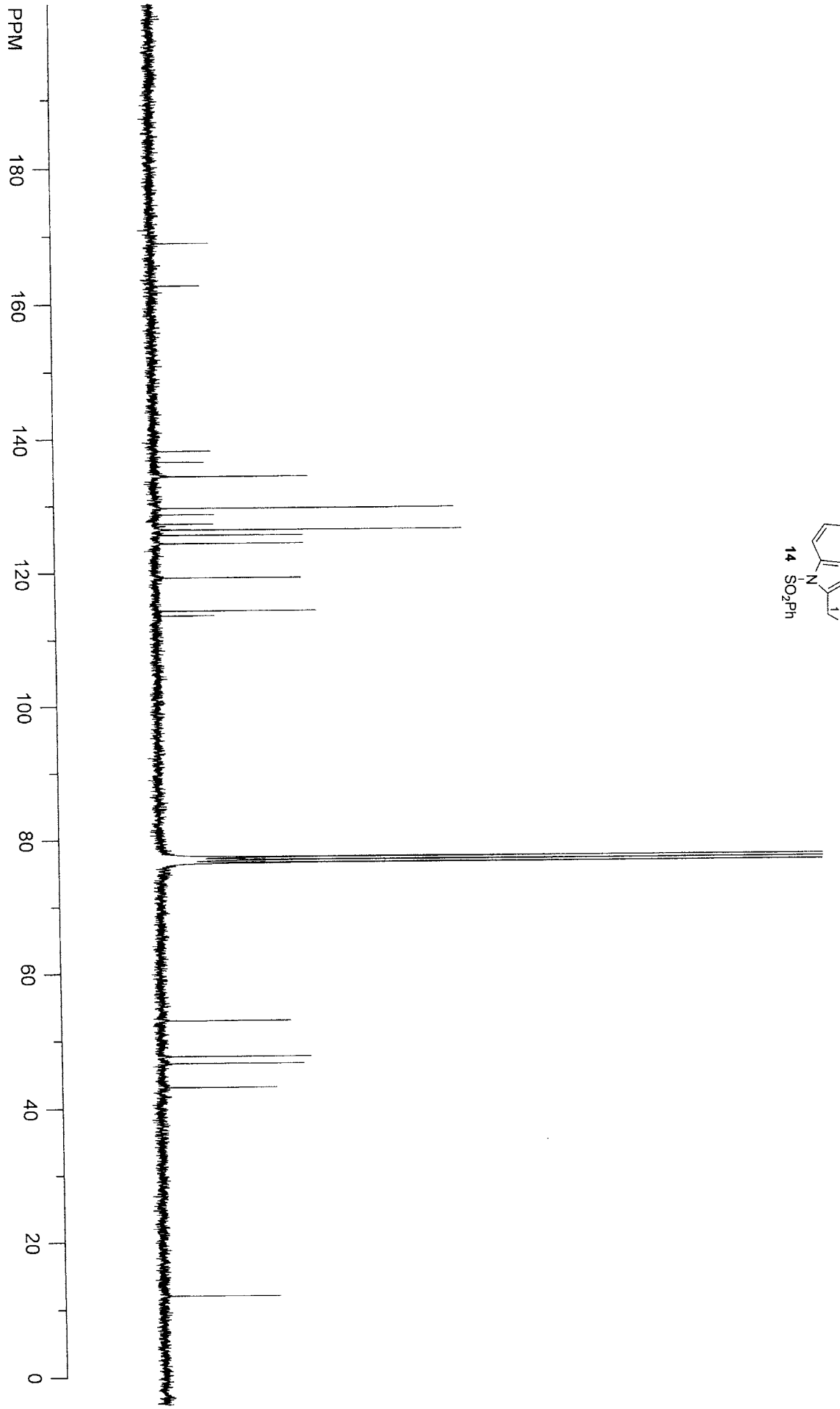

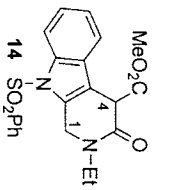

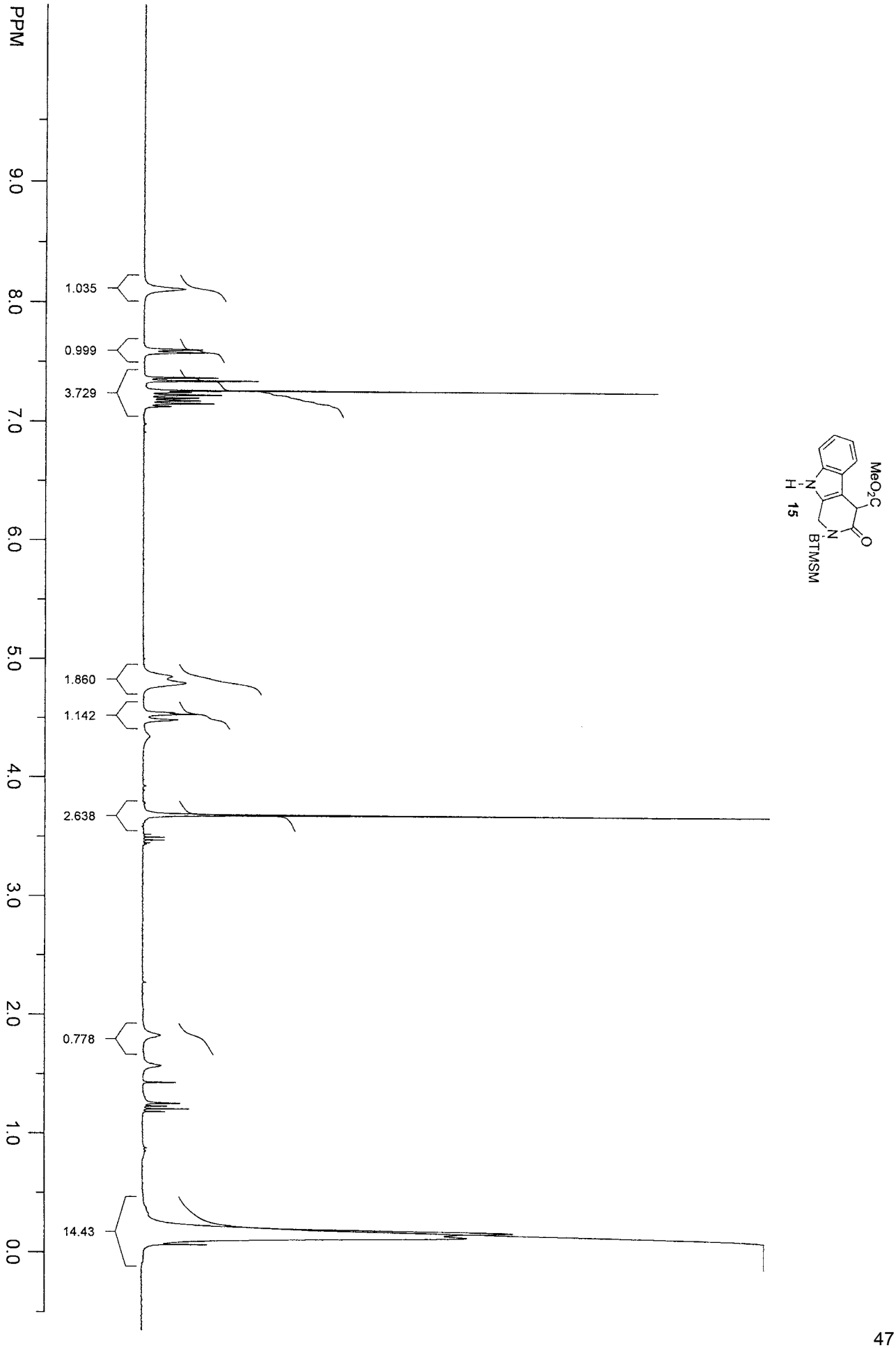

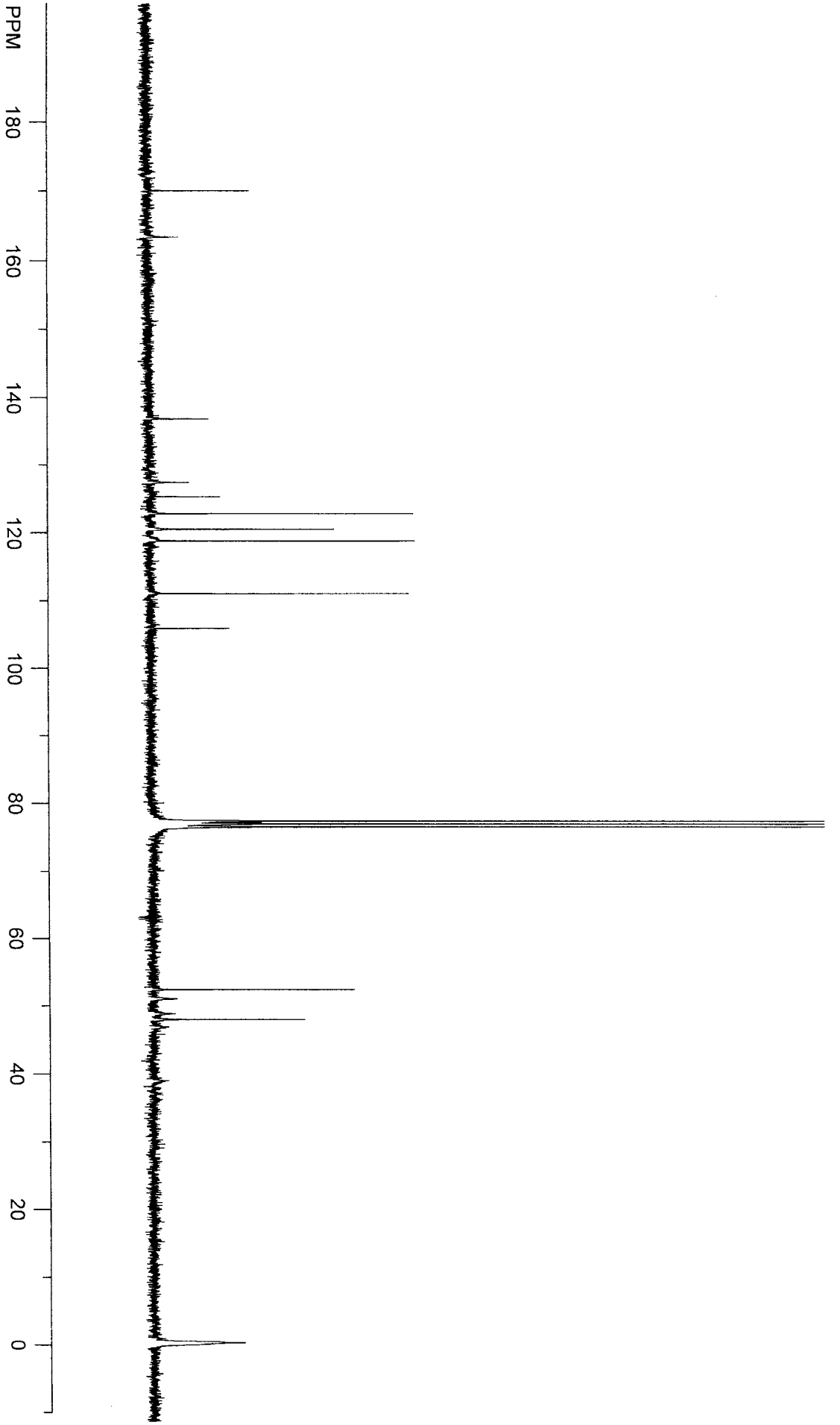

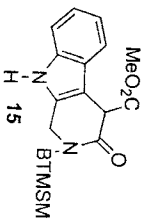

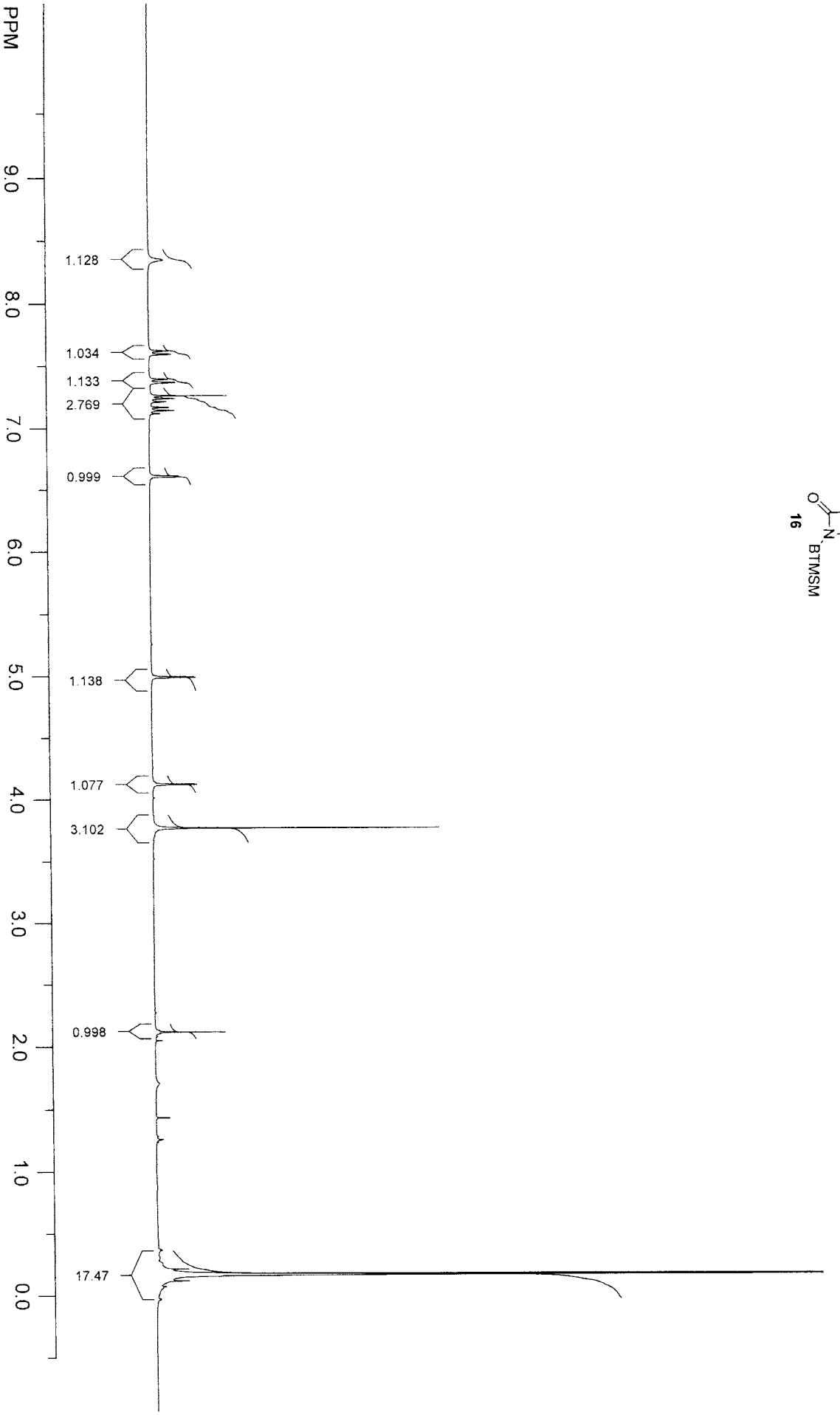

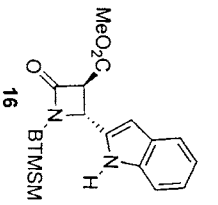

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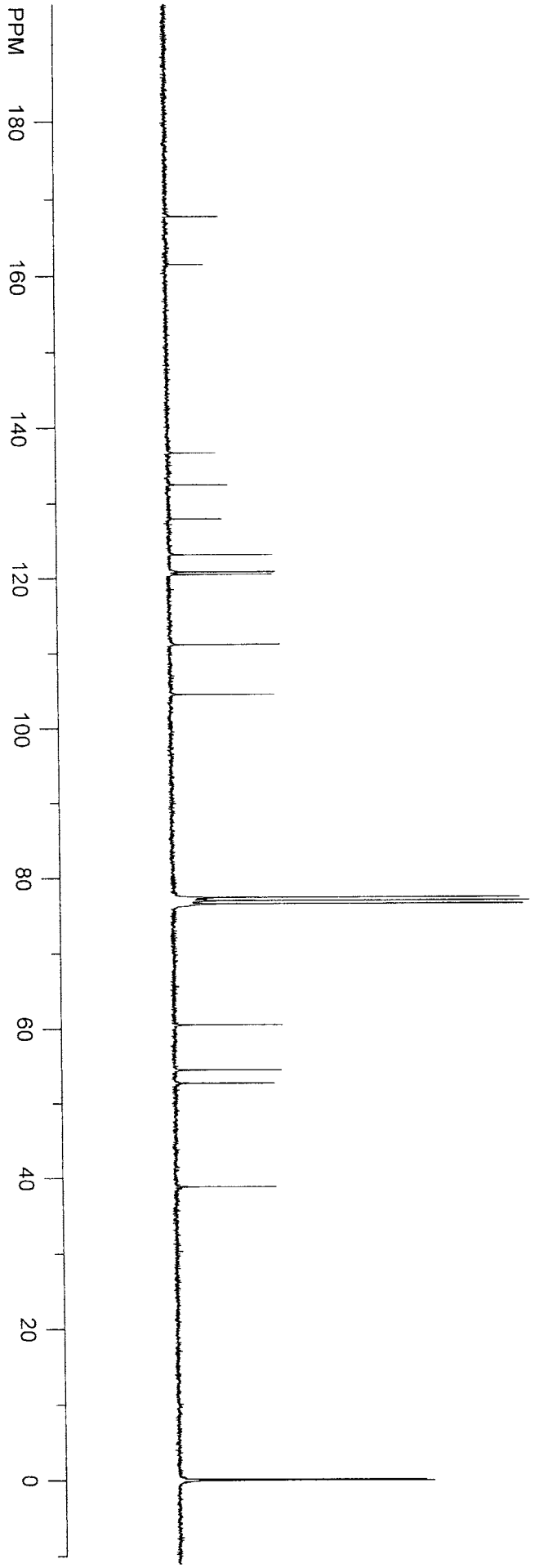

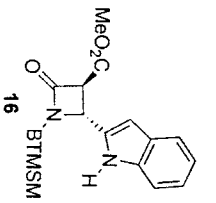

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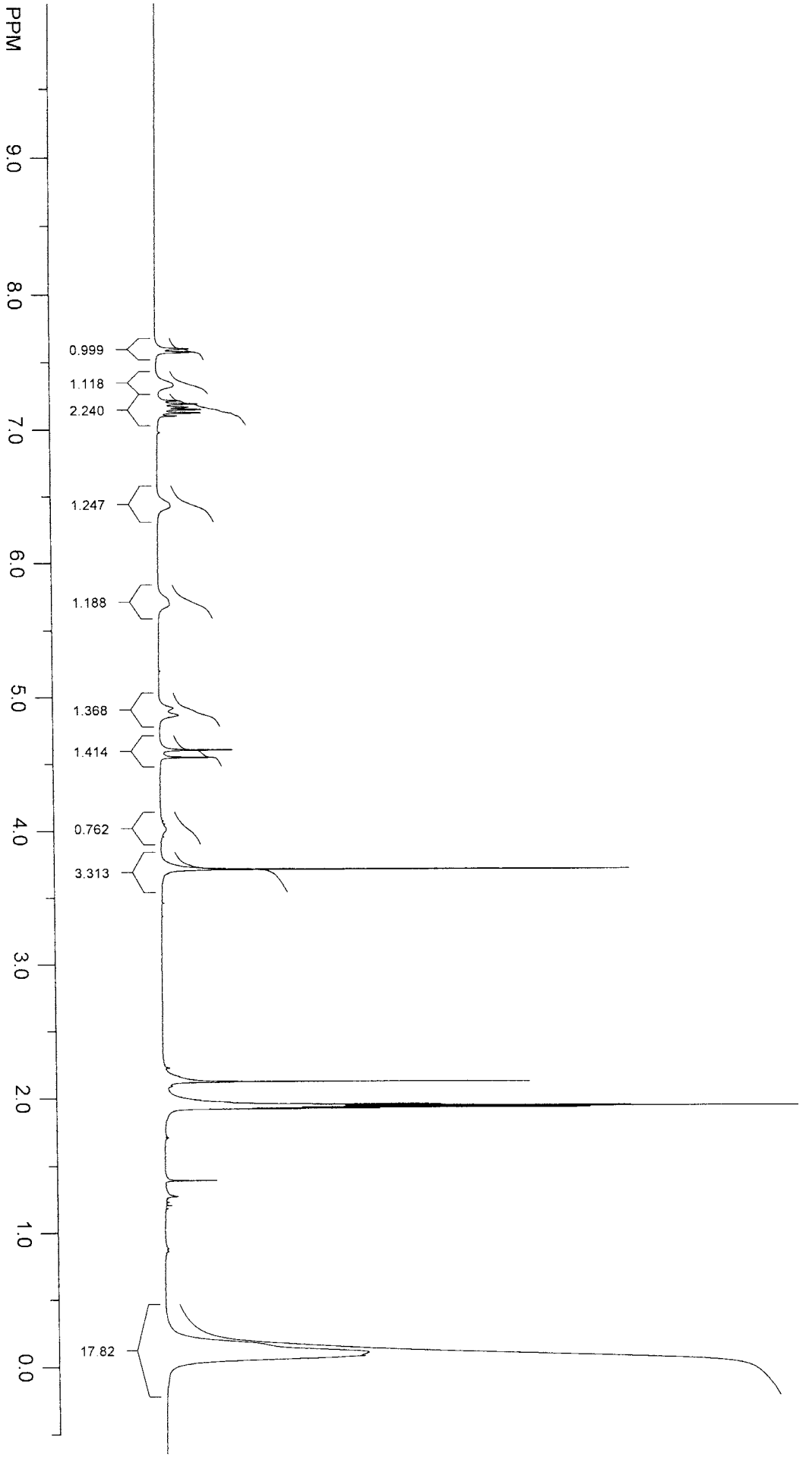

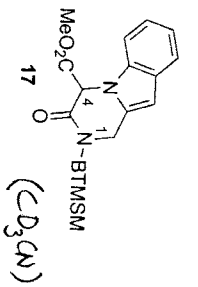

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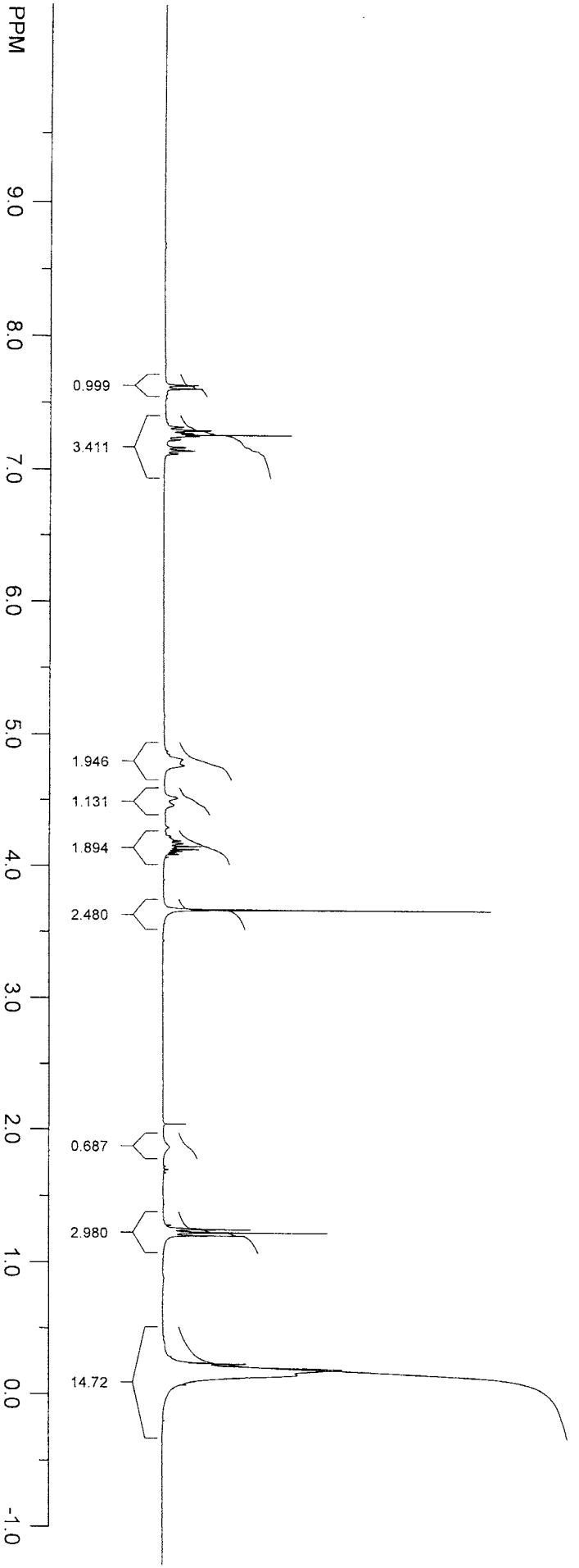

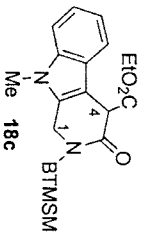

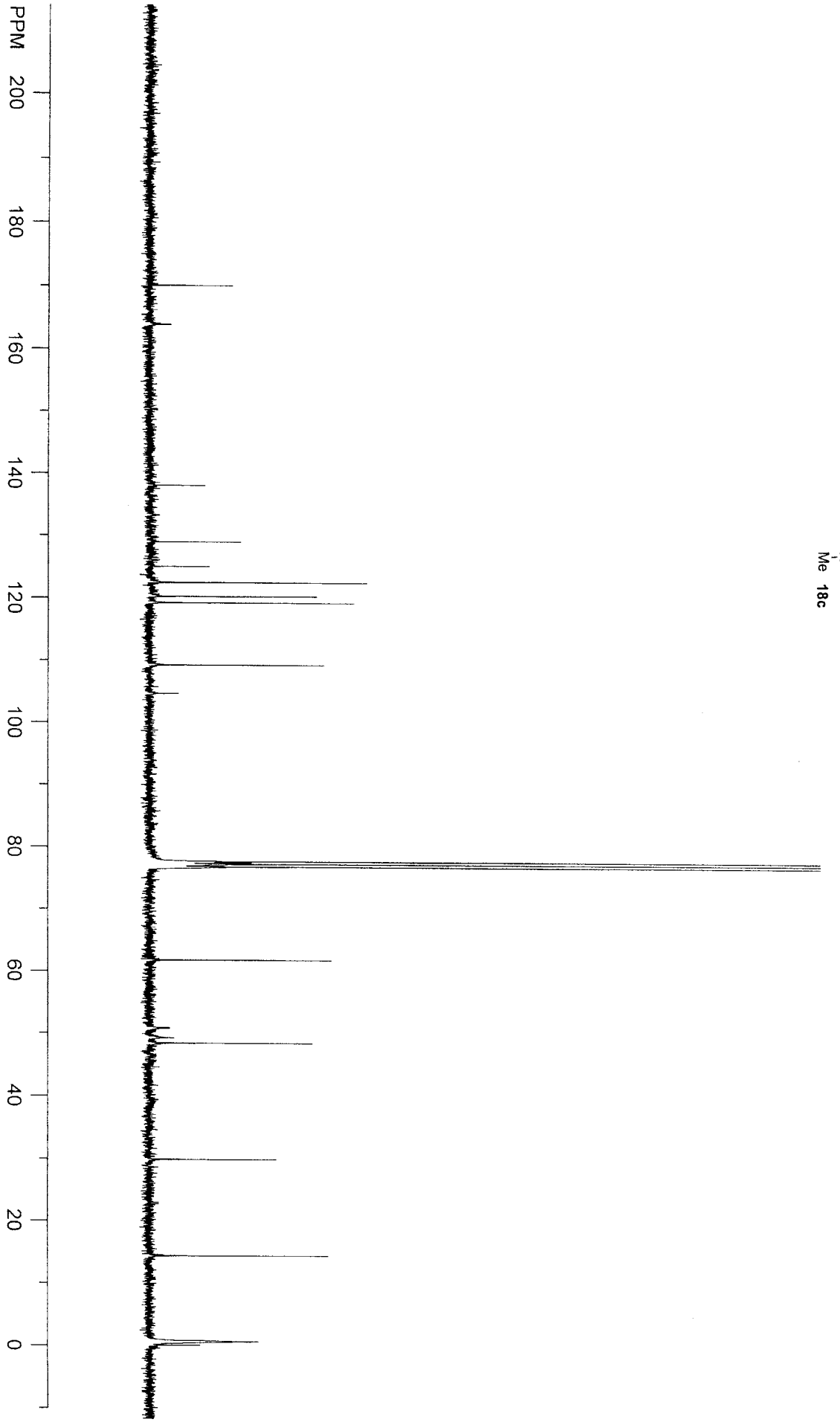

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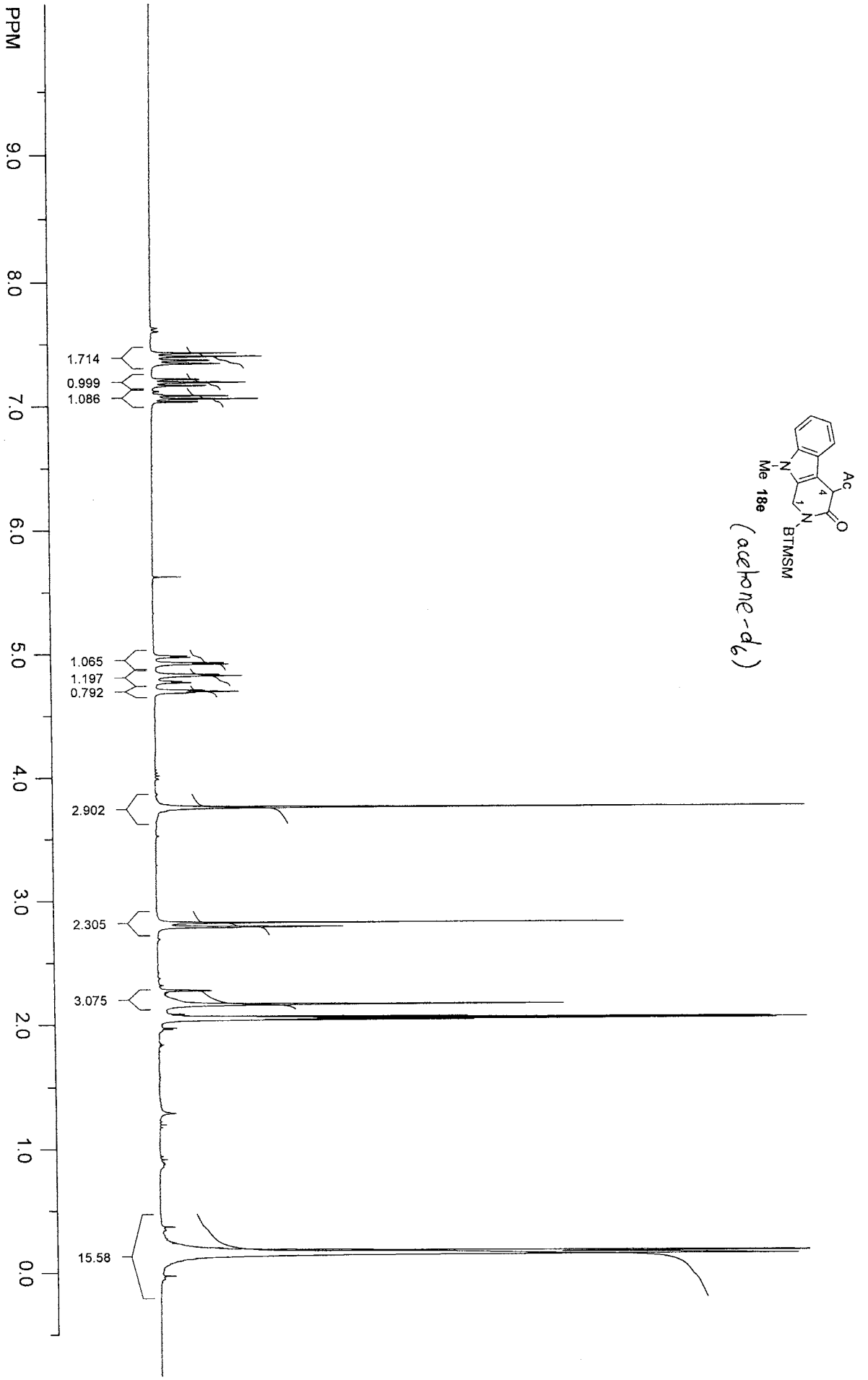

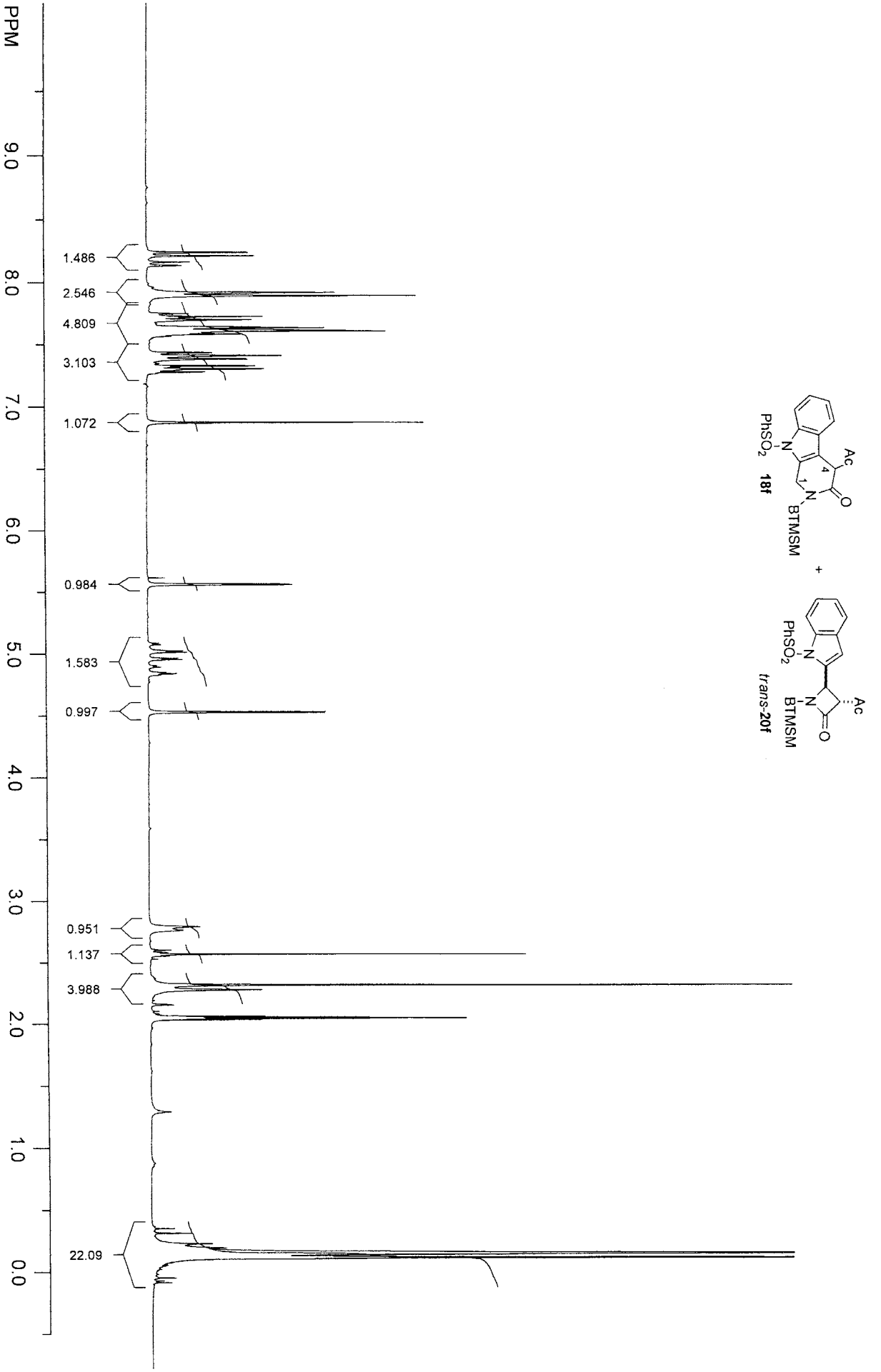

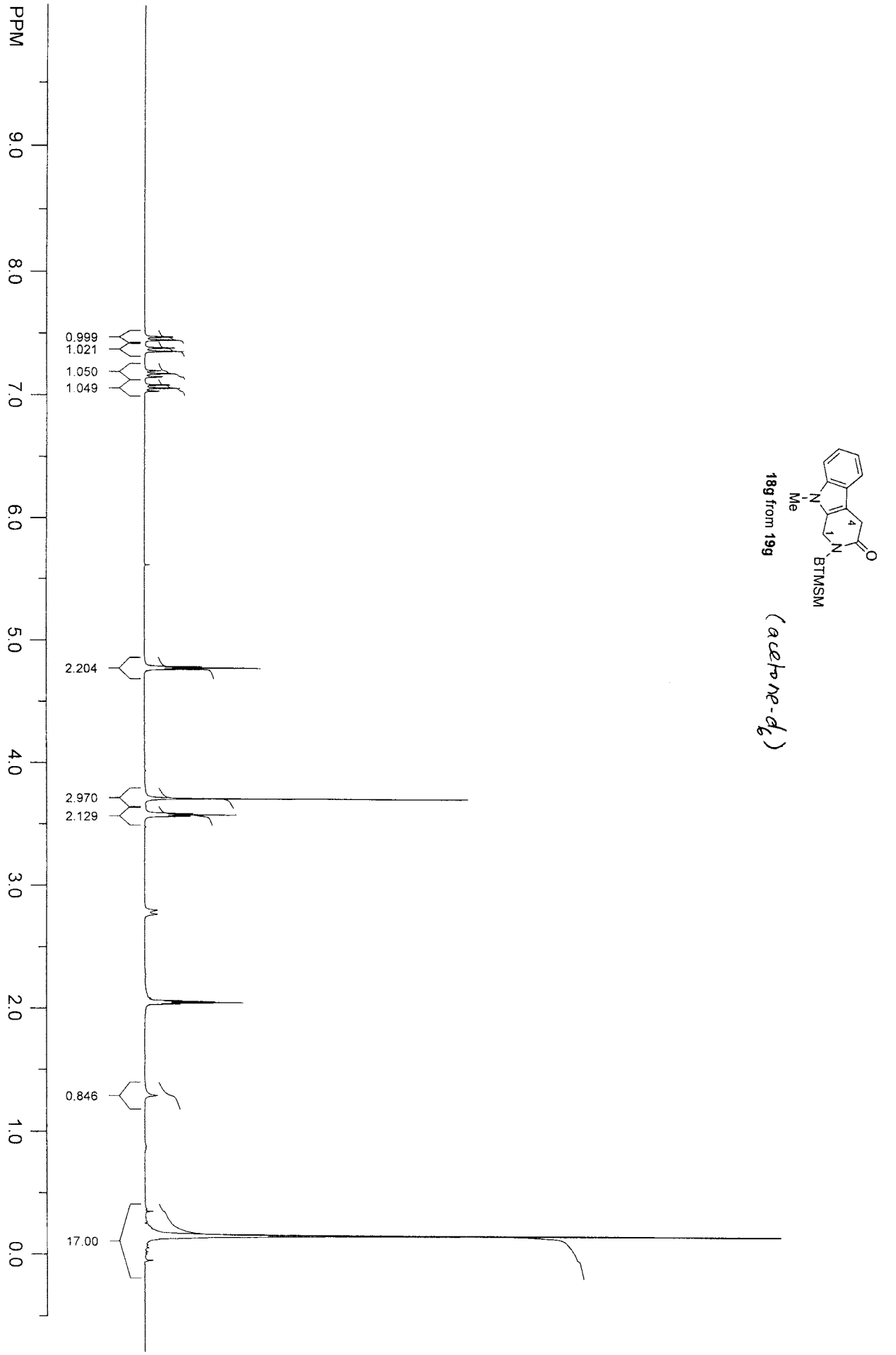

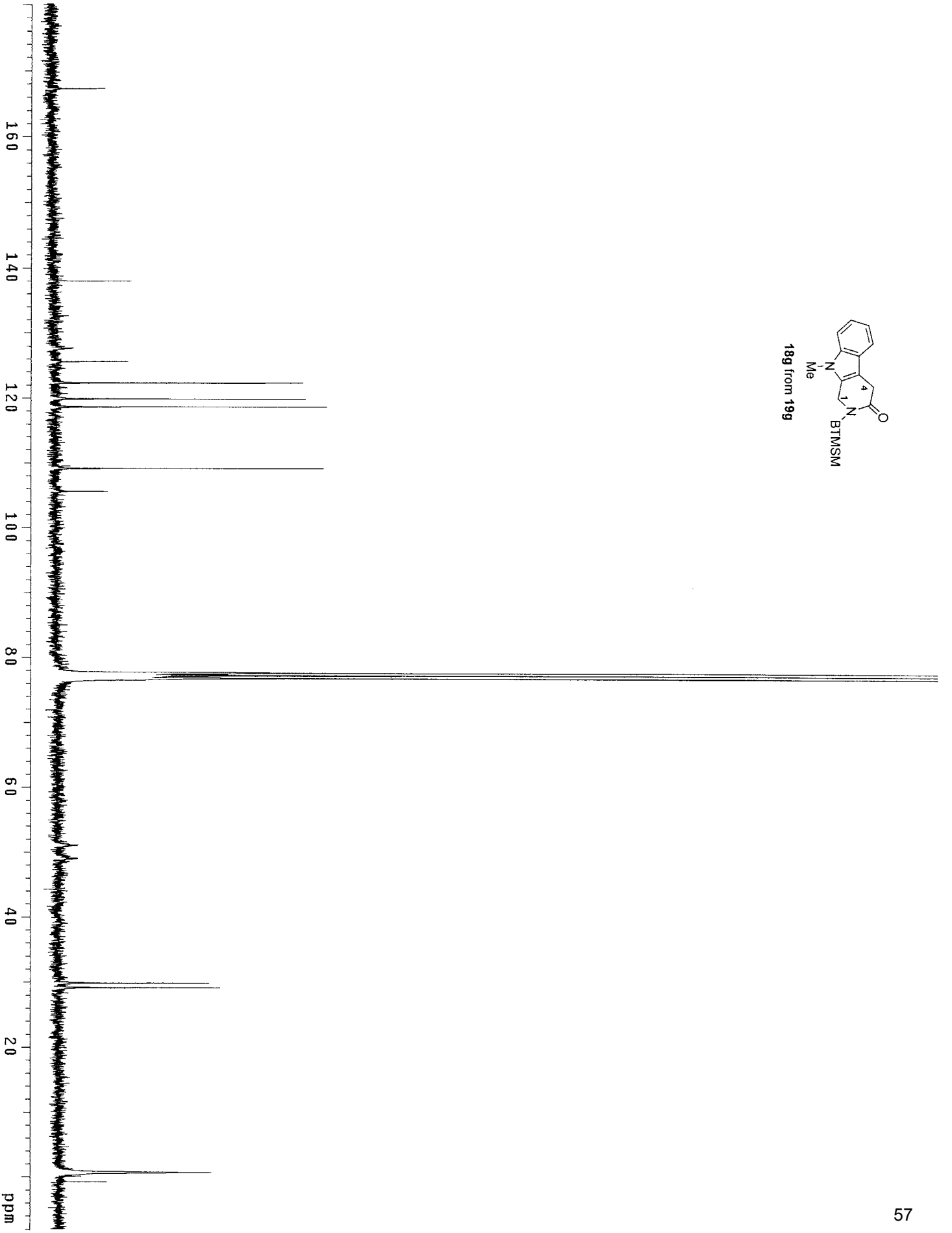

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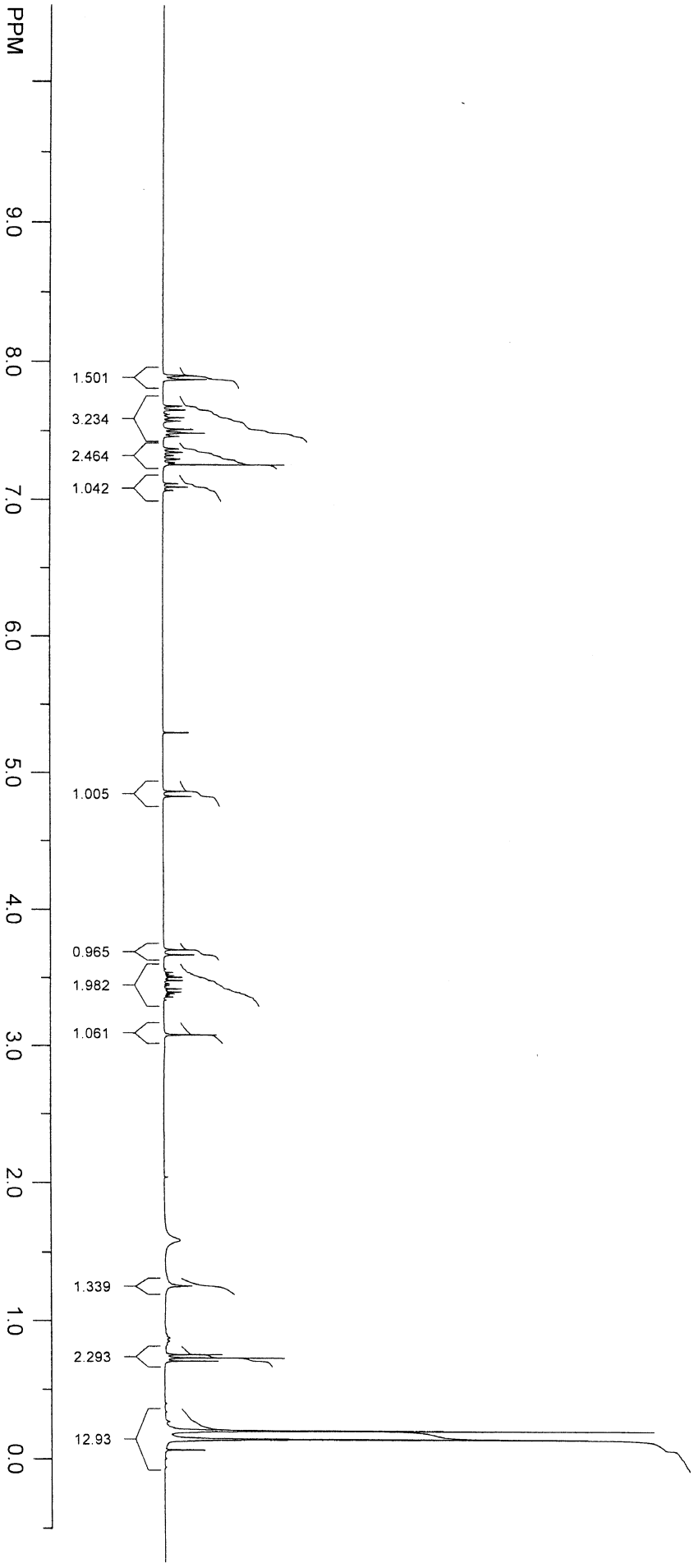

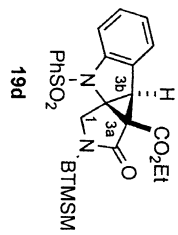

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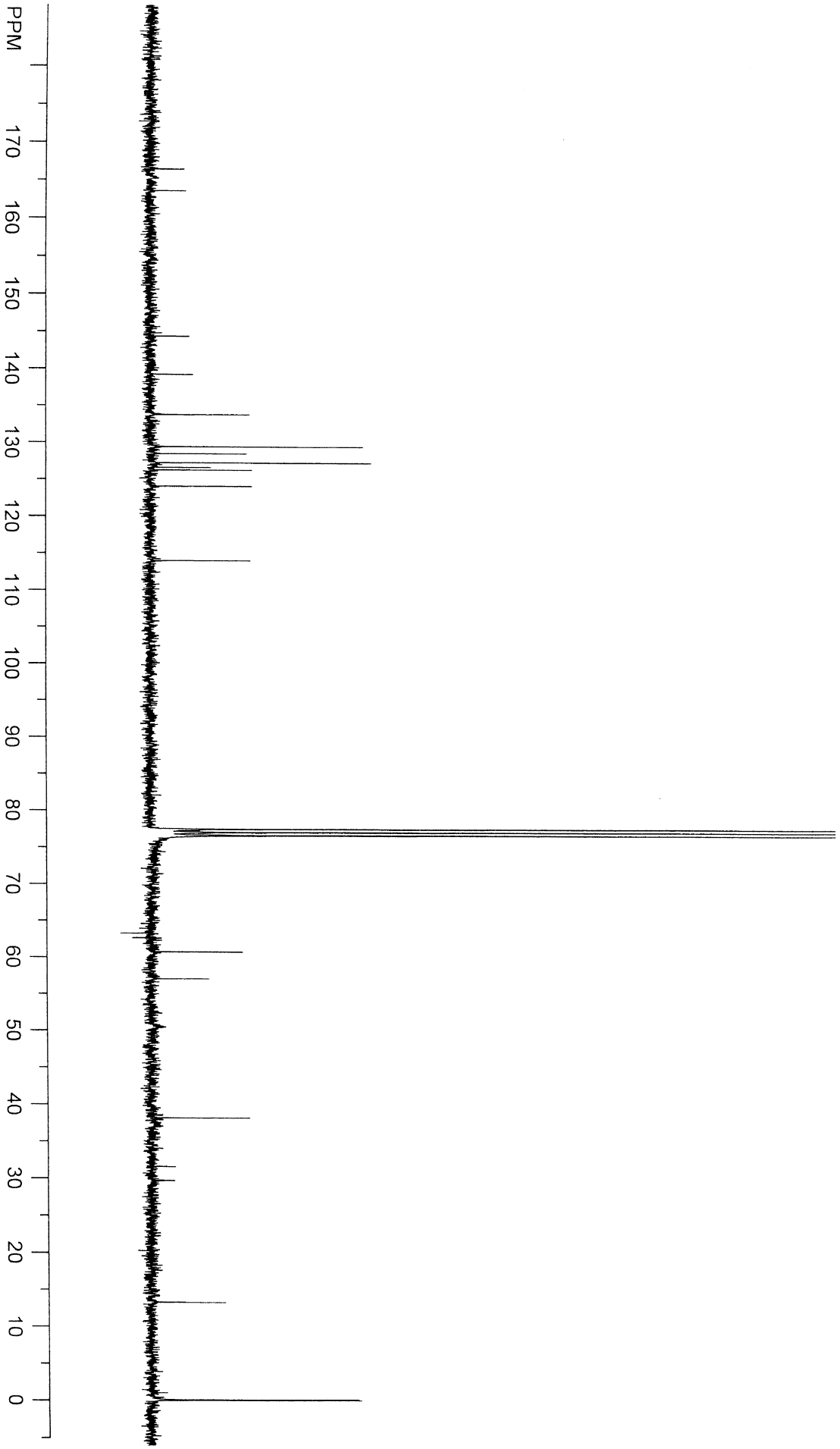

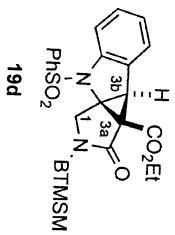

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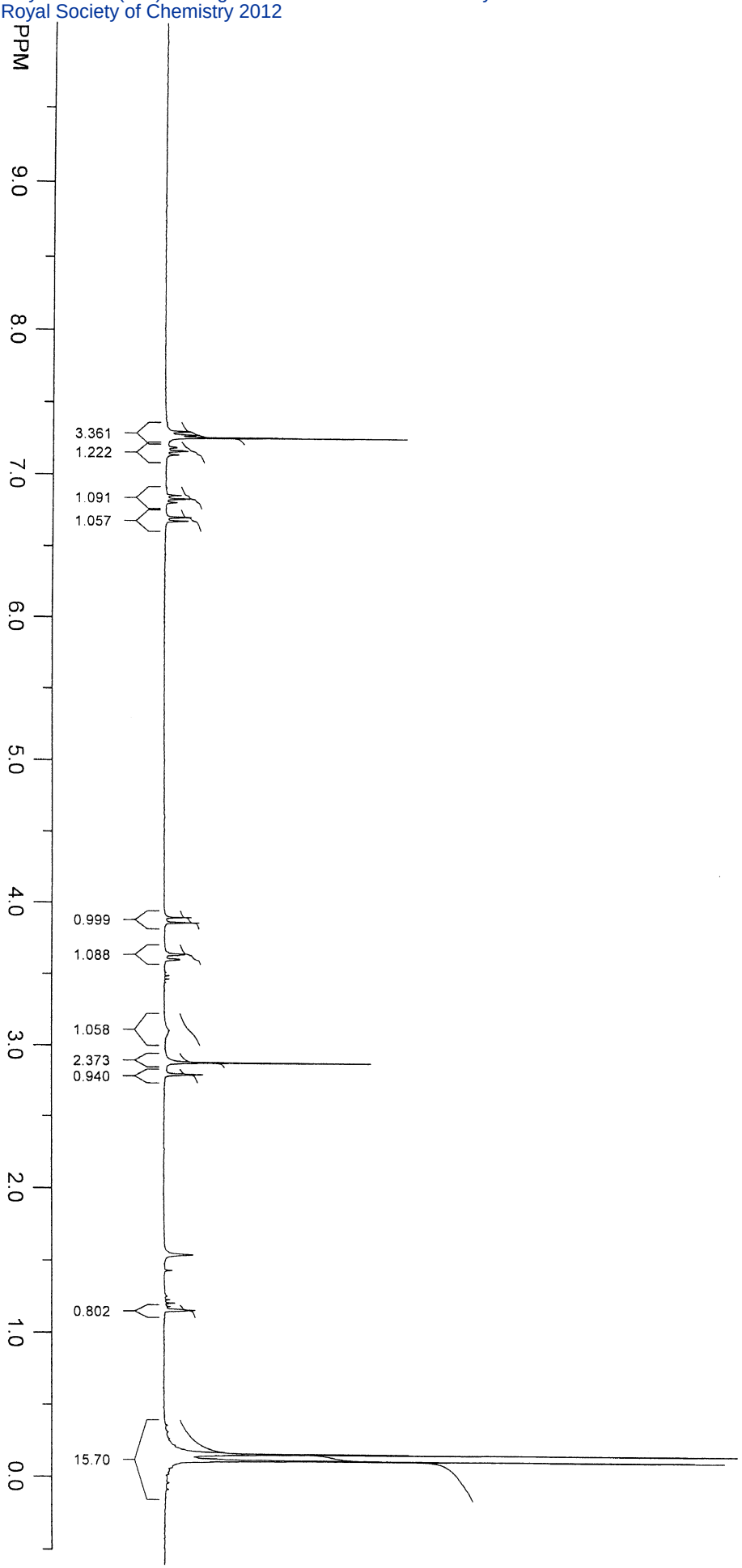

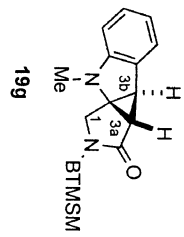

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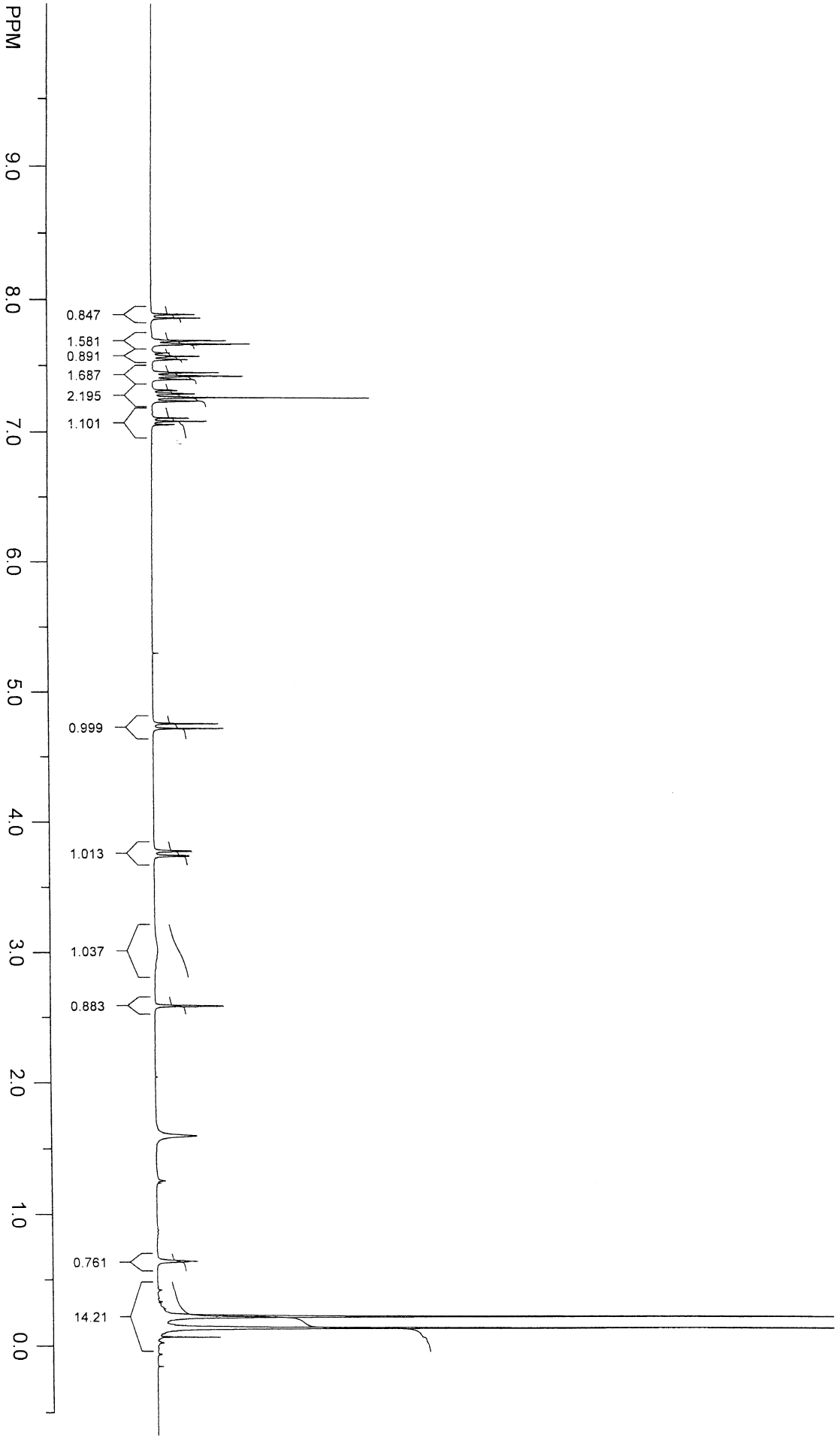

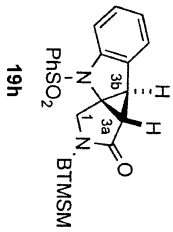

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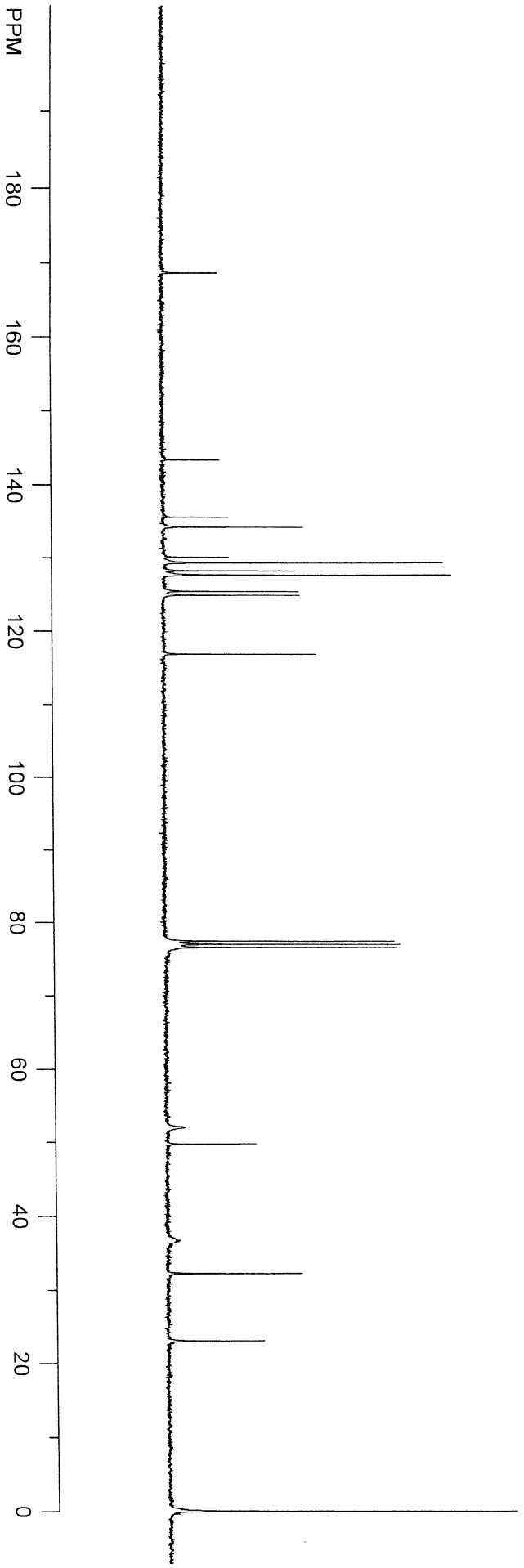

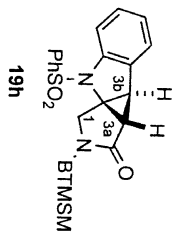

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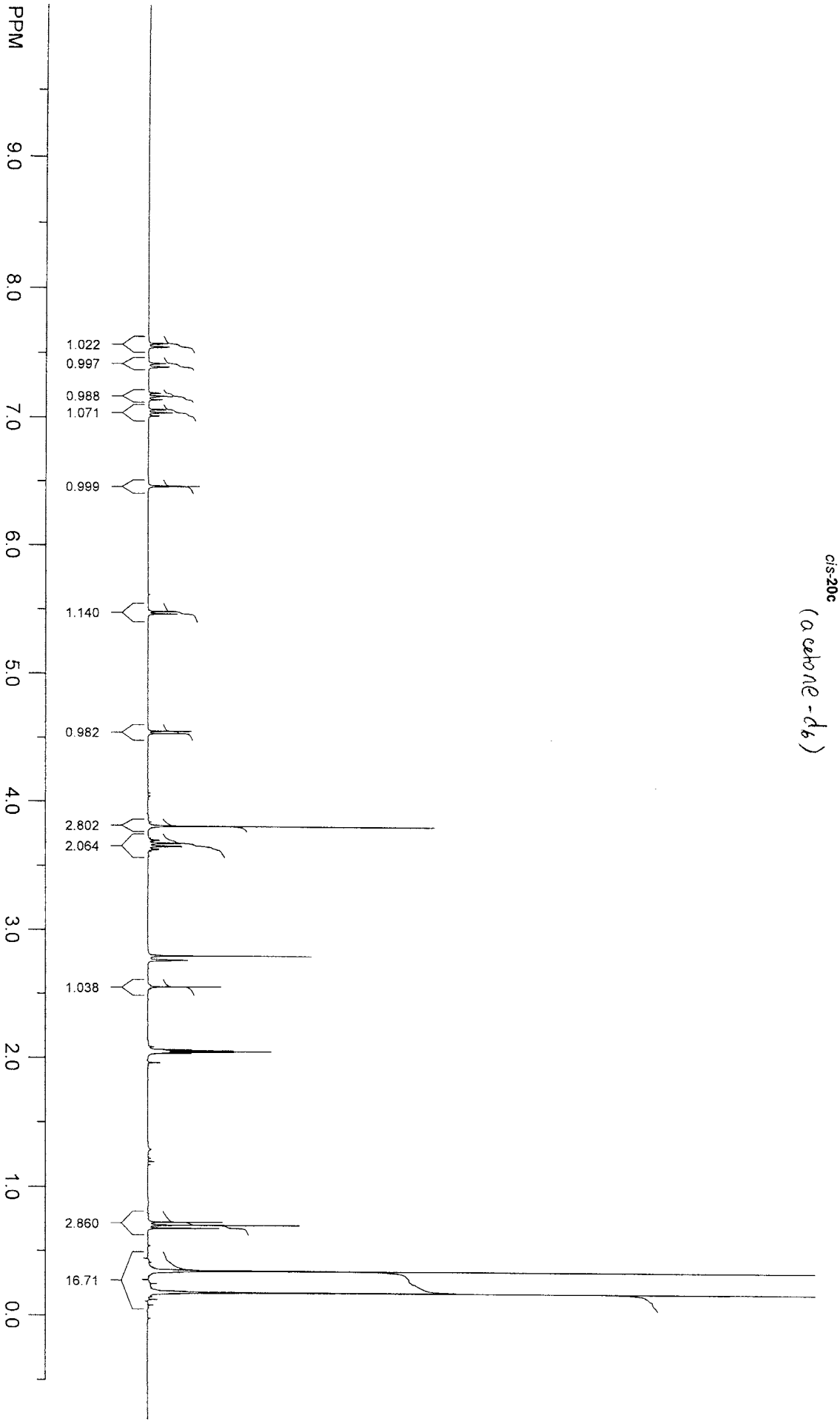

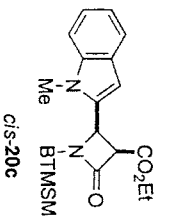

cis-**20c**

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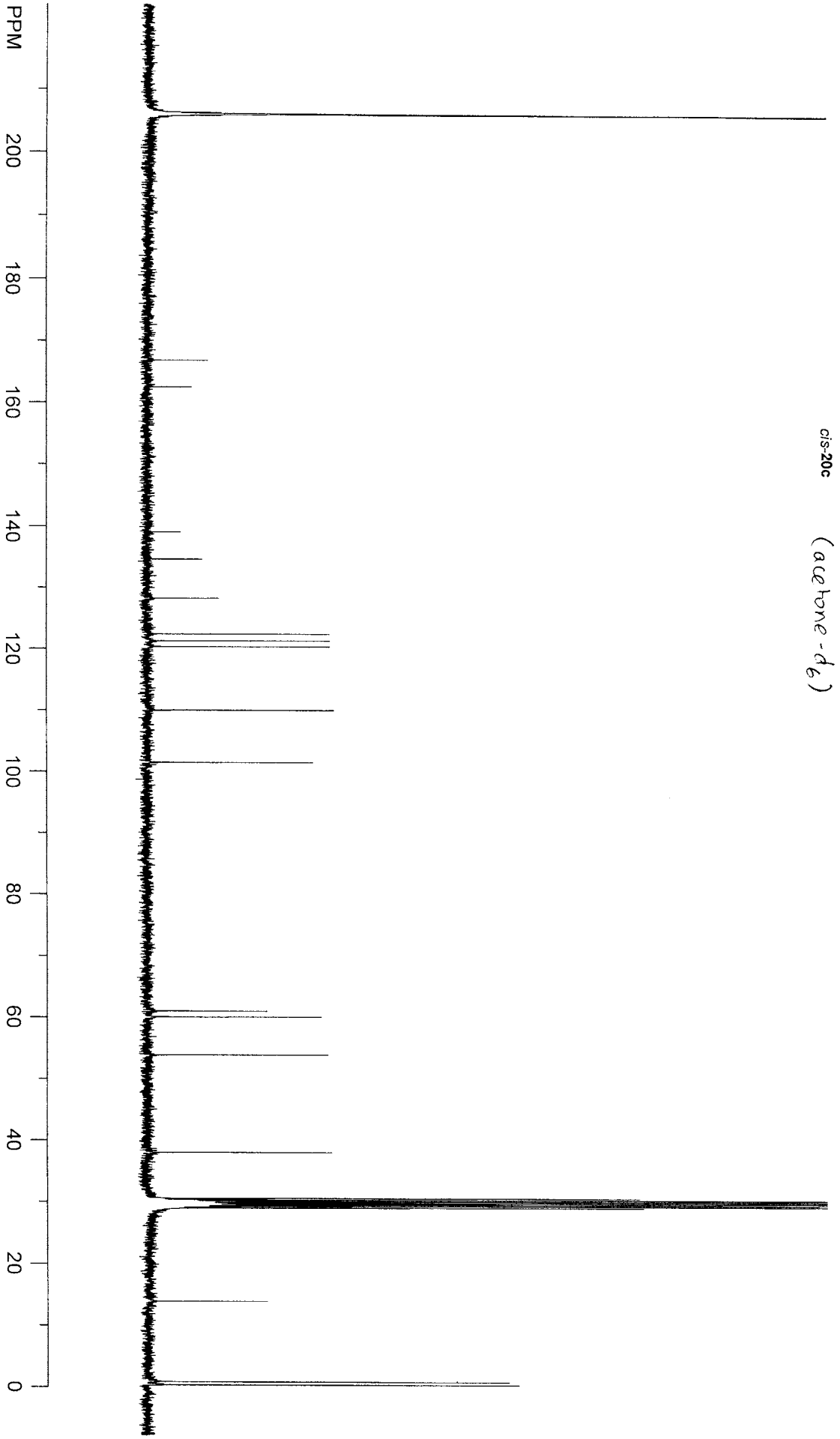

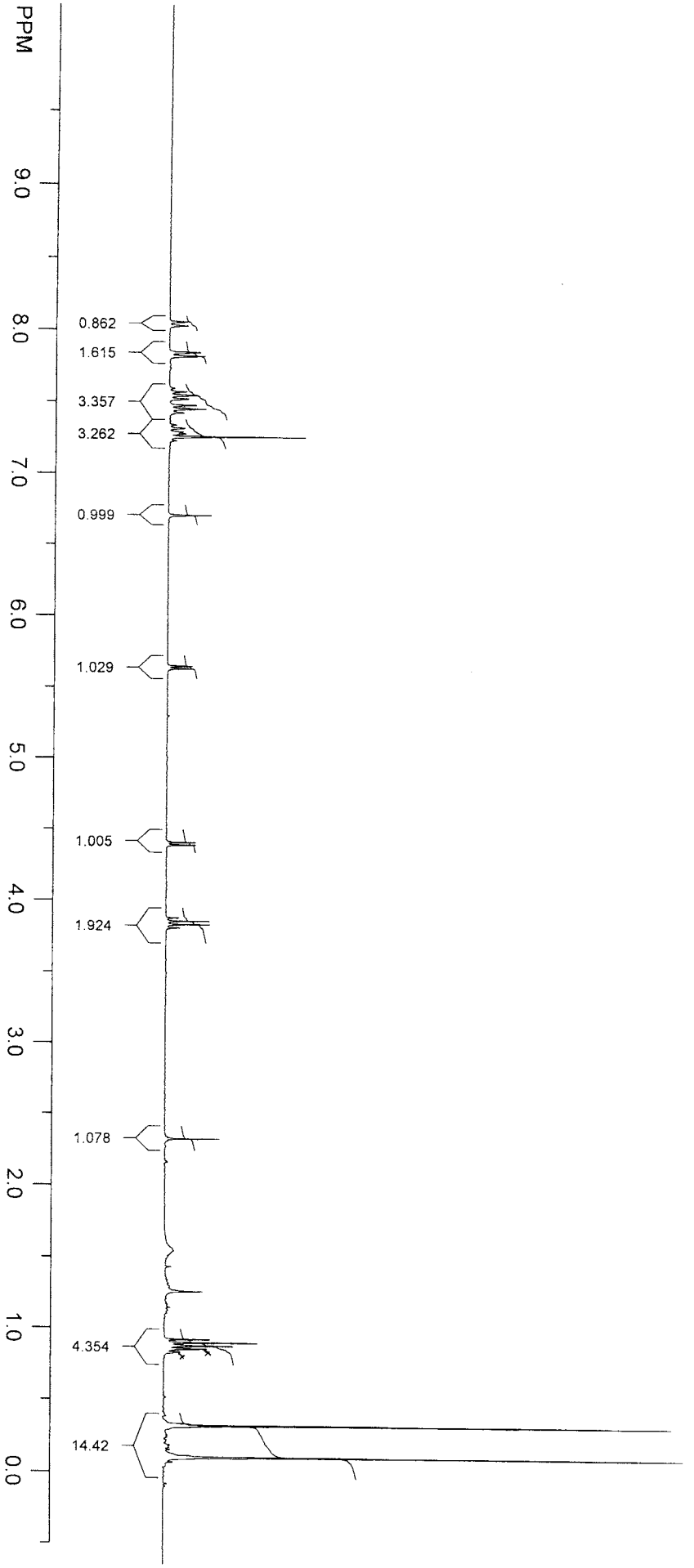
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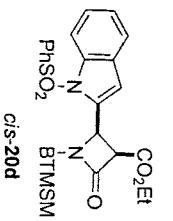
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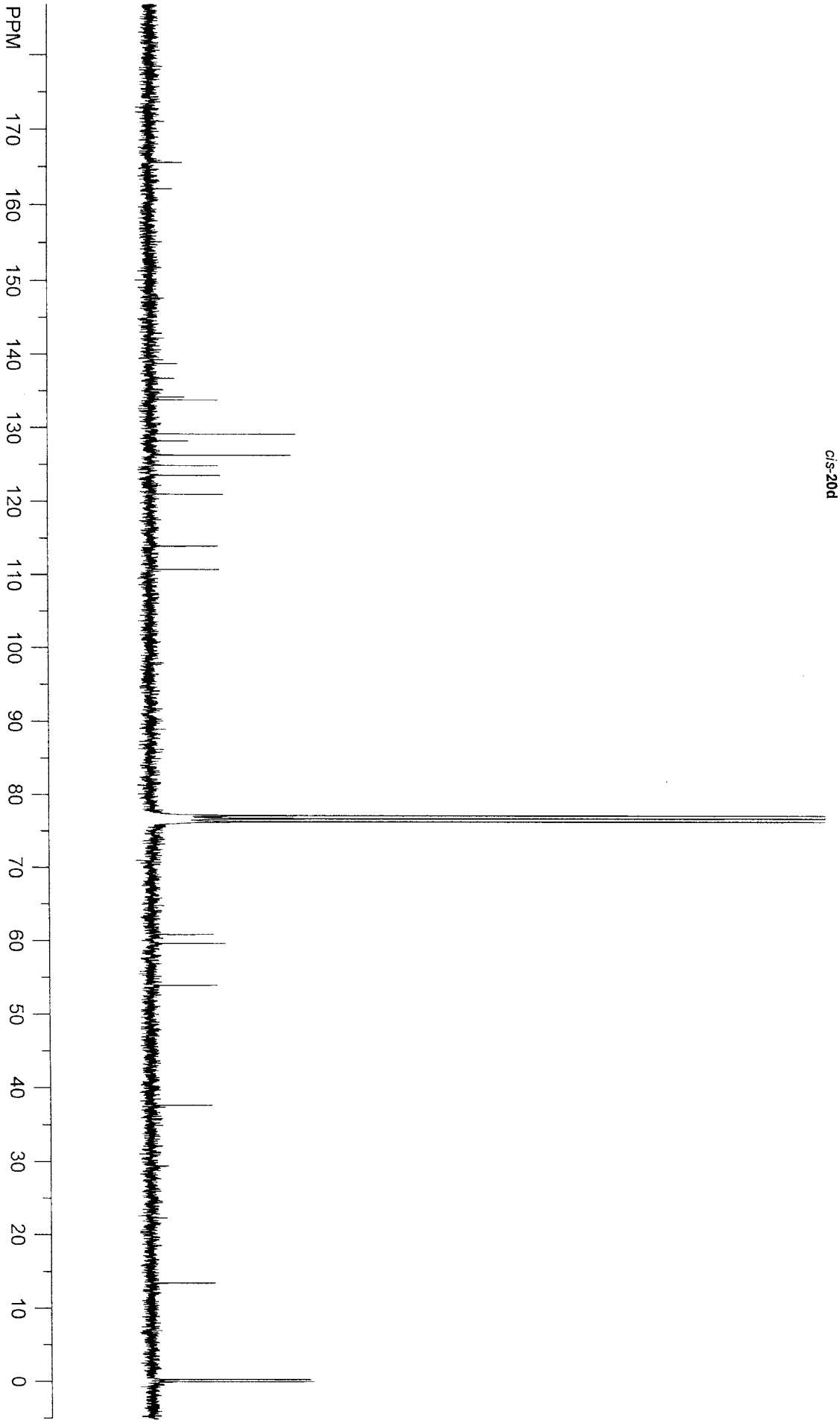
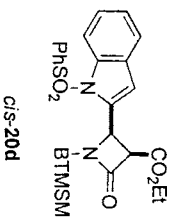
cis-**20d**





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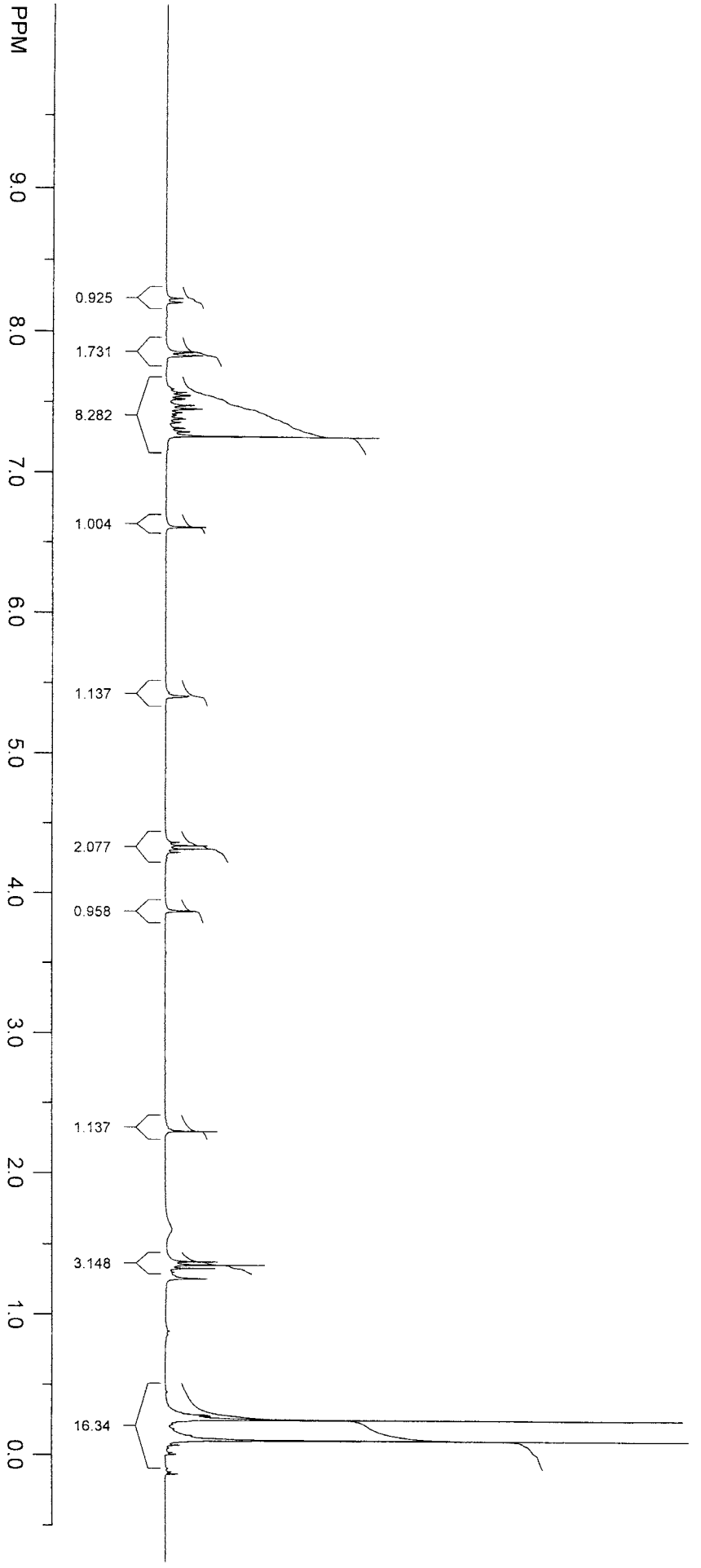

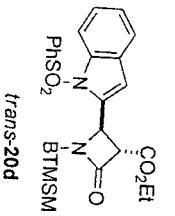

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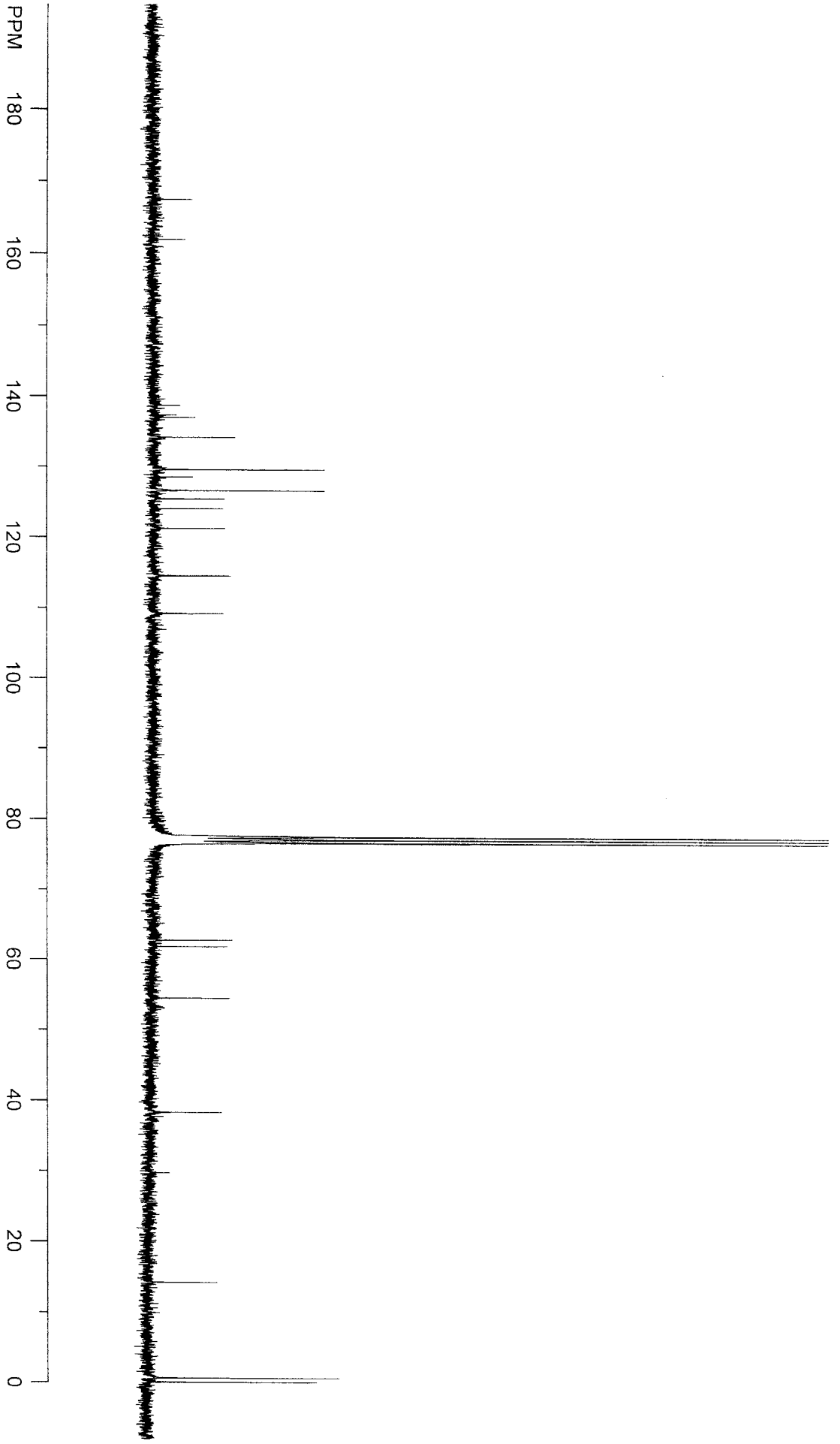

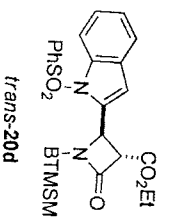

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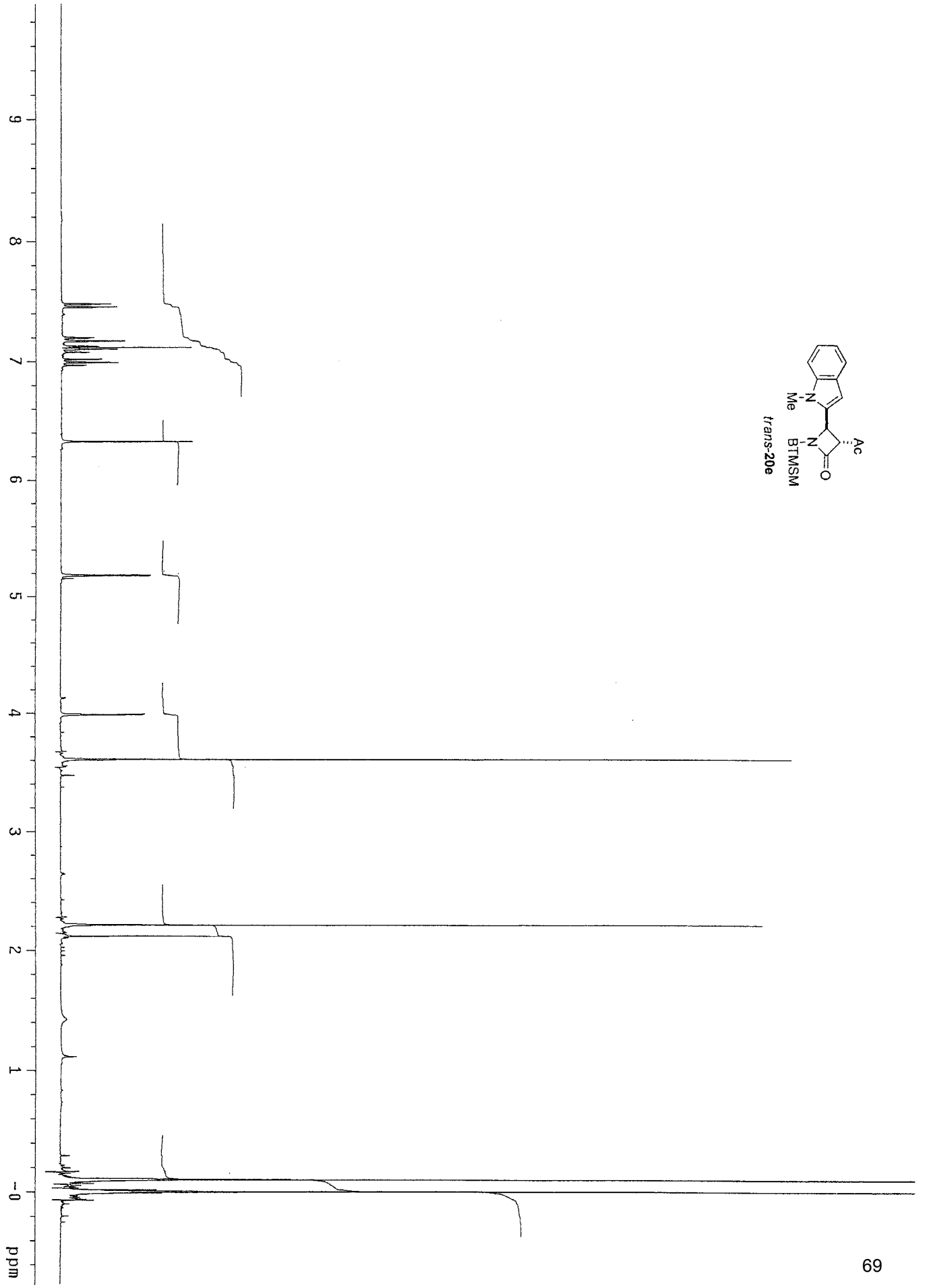

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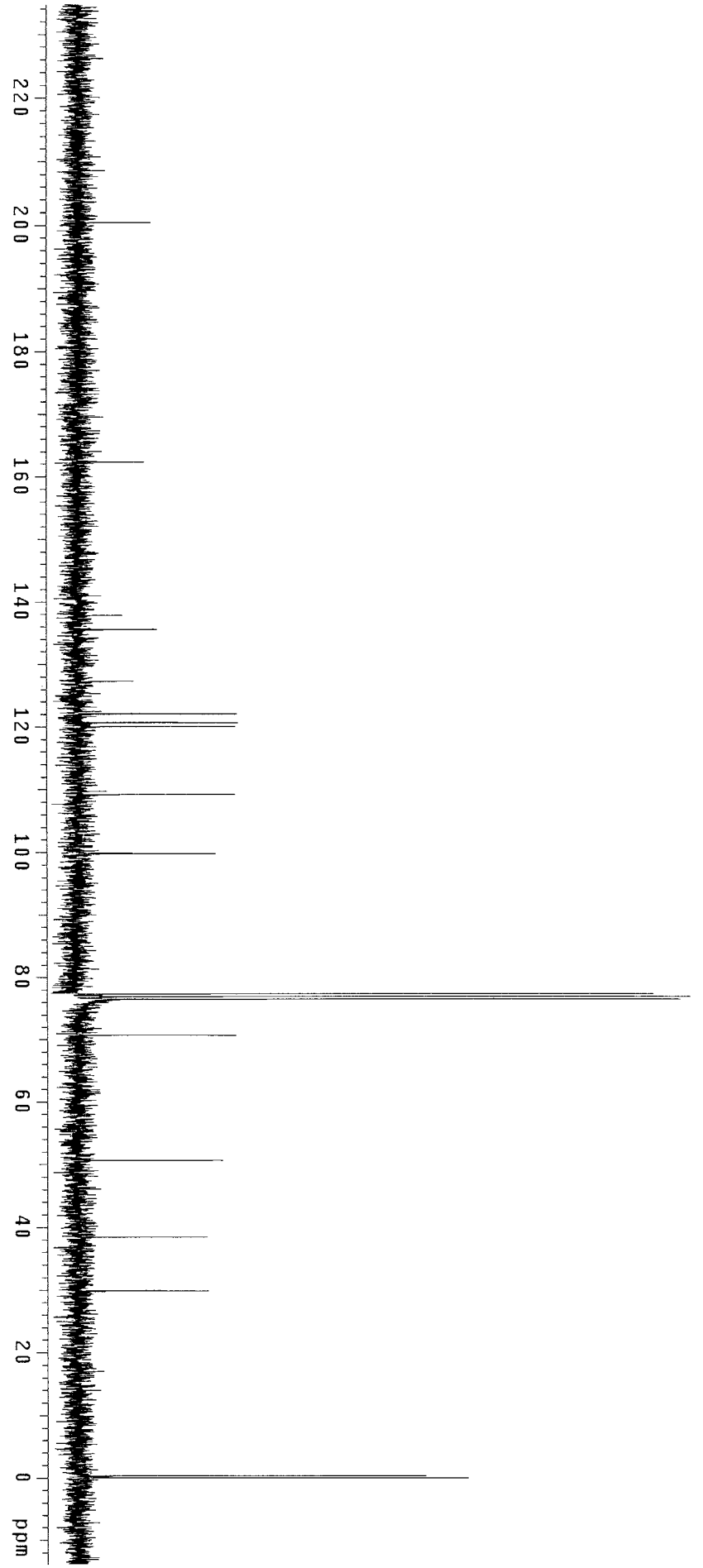

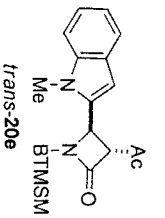

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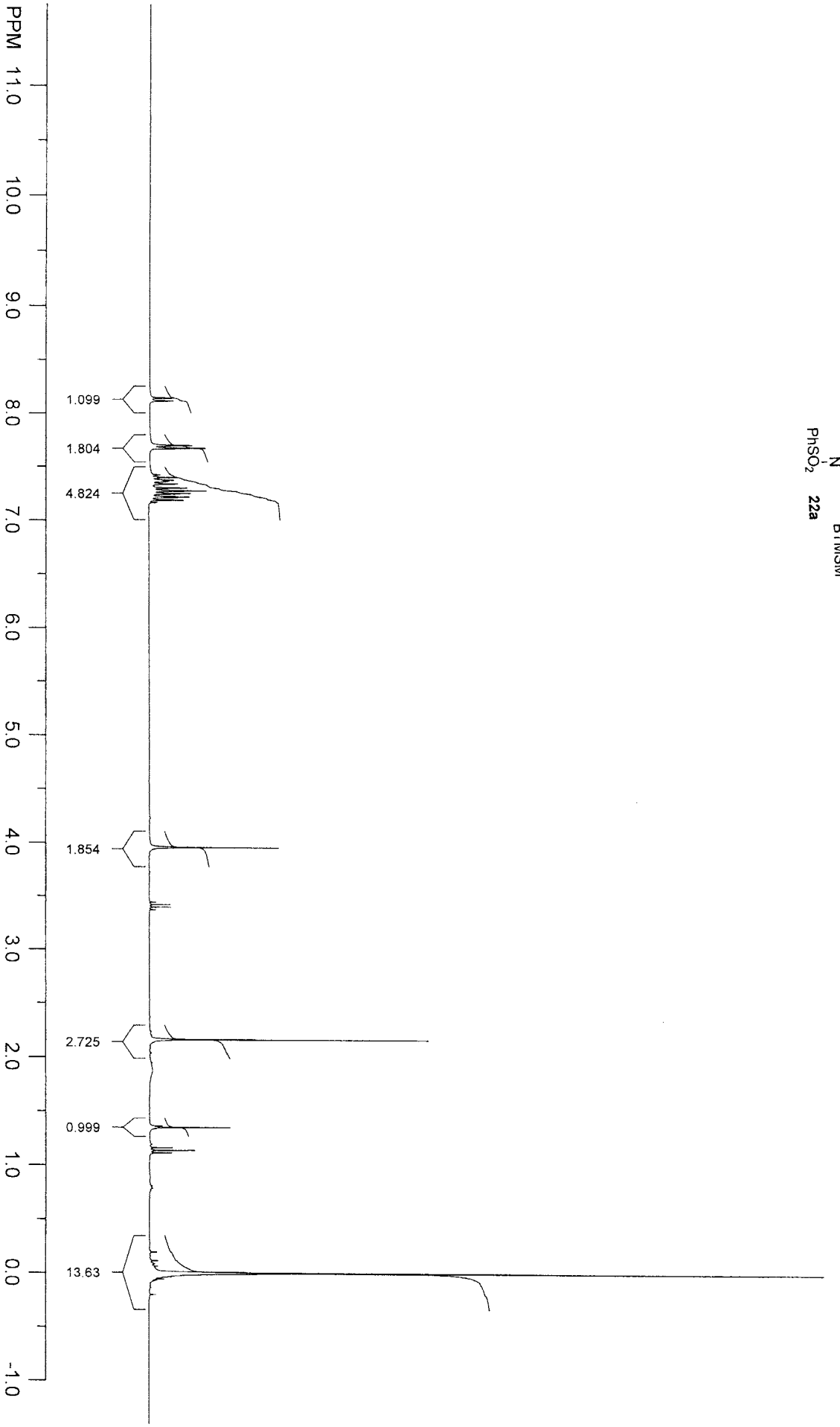

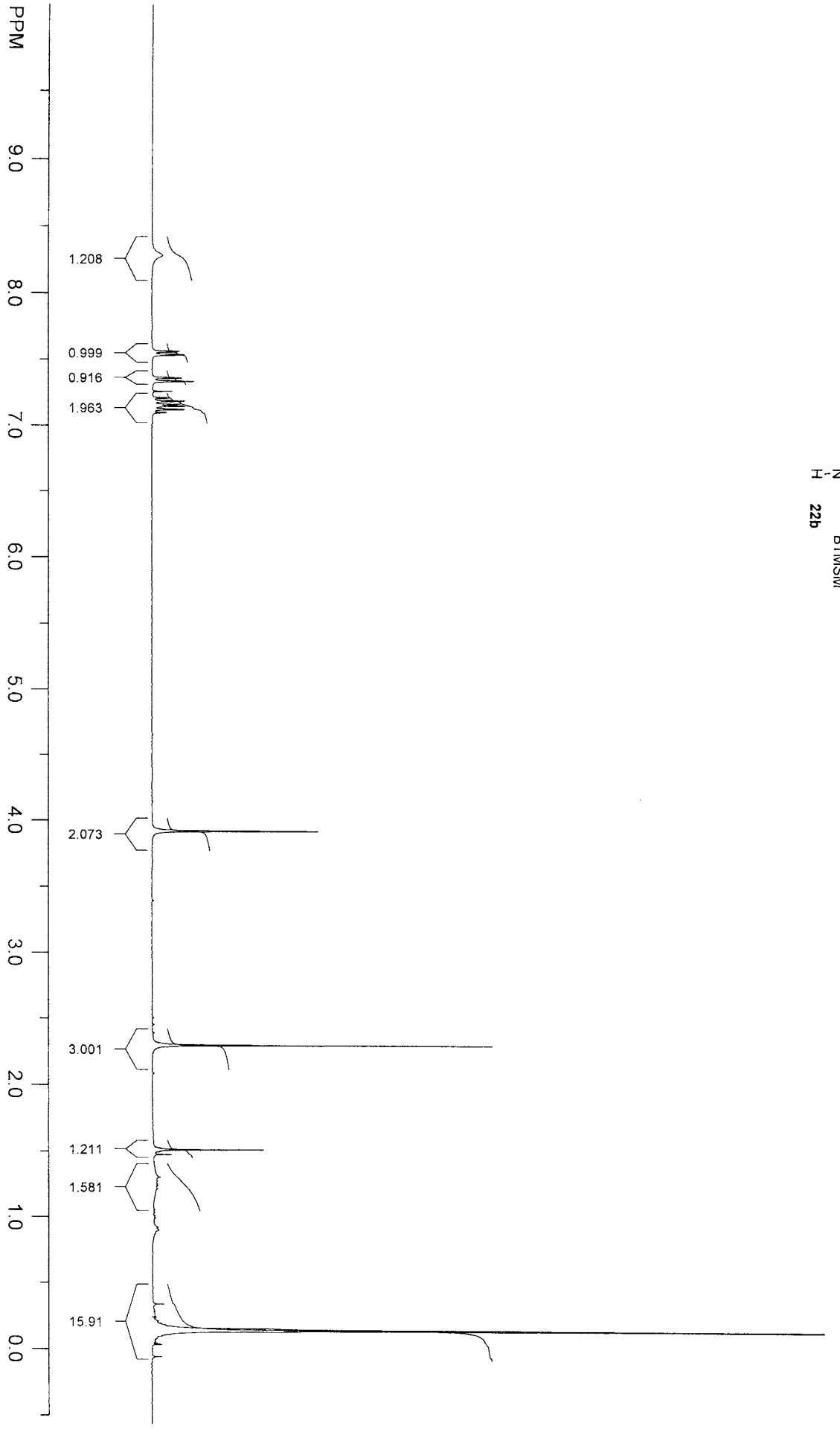

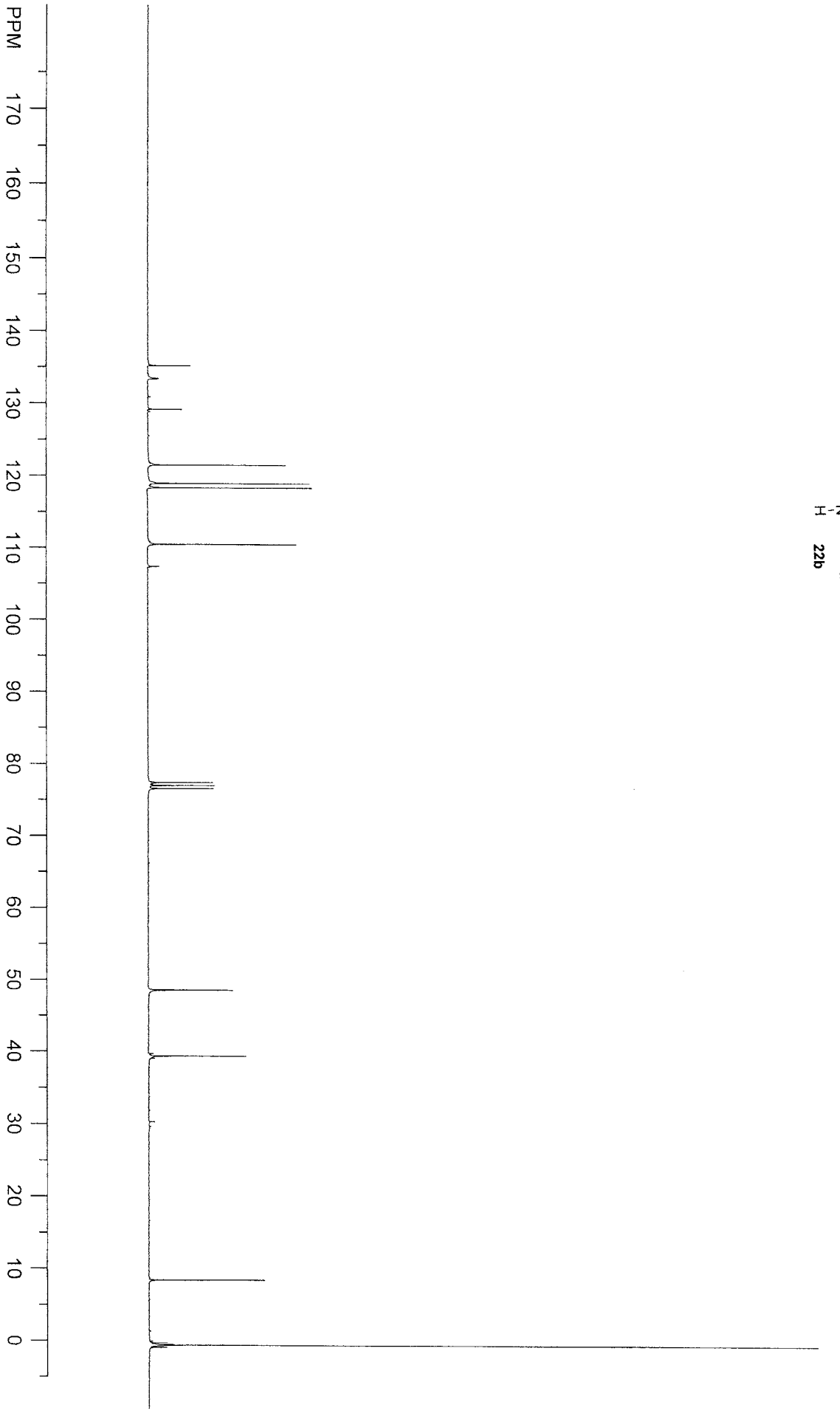

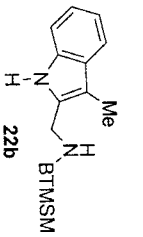

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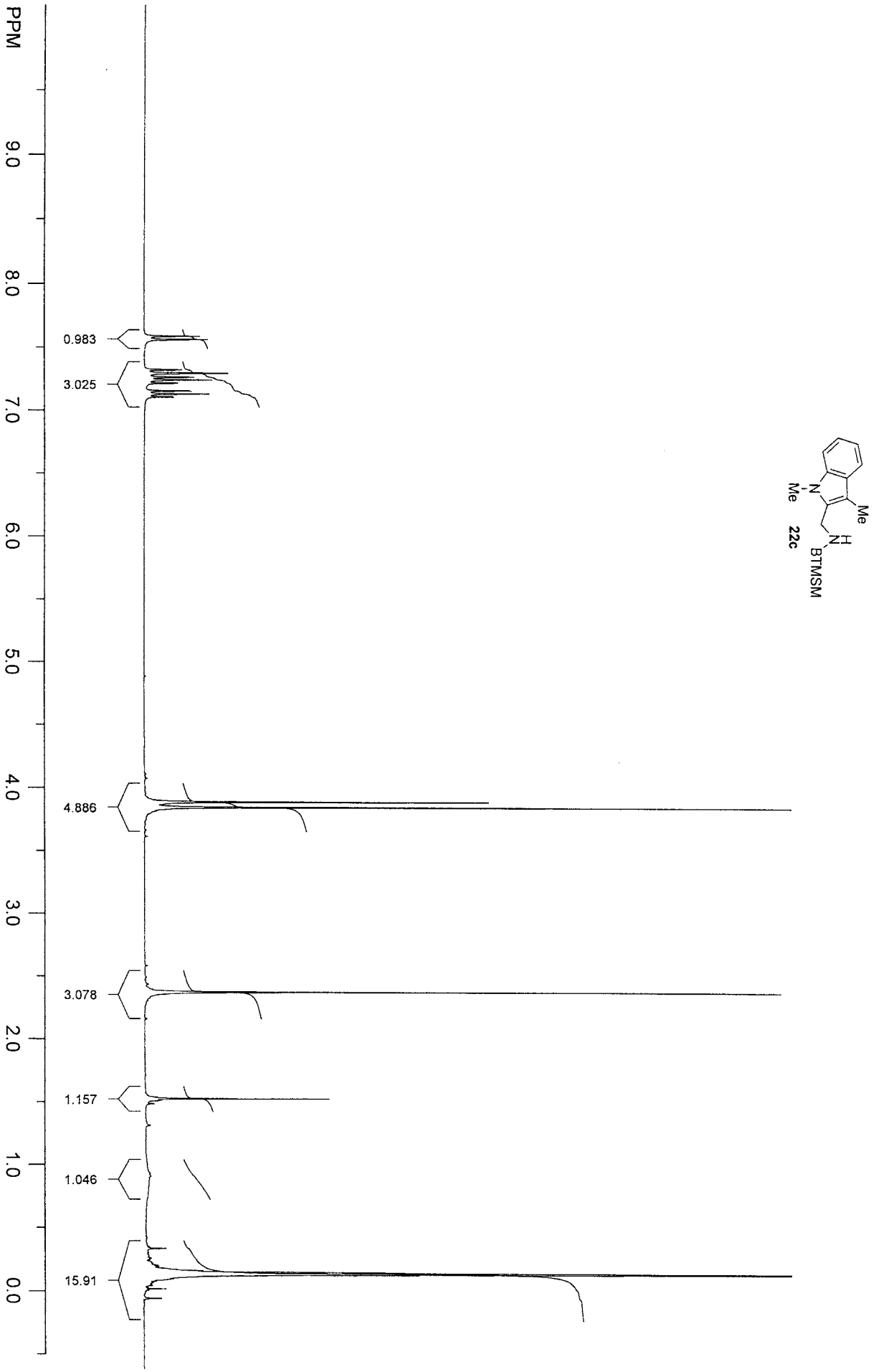
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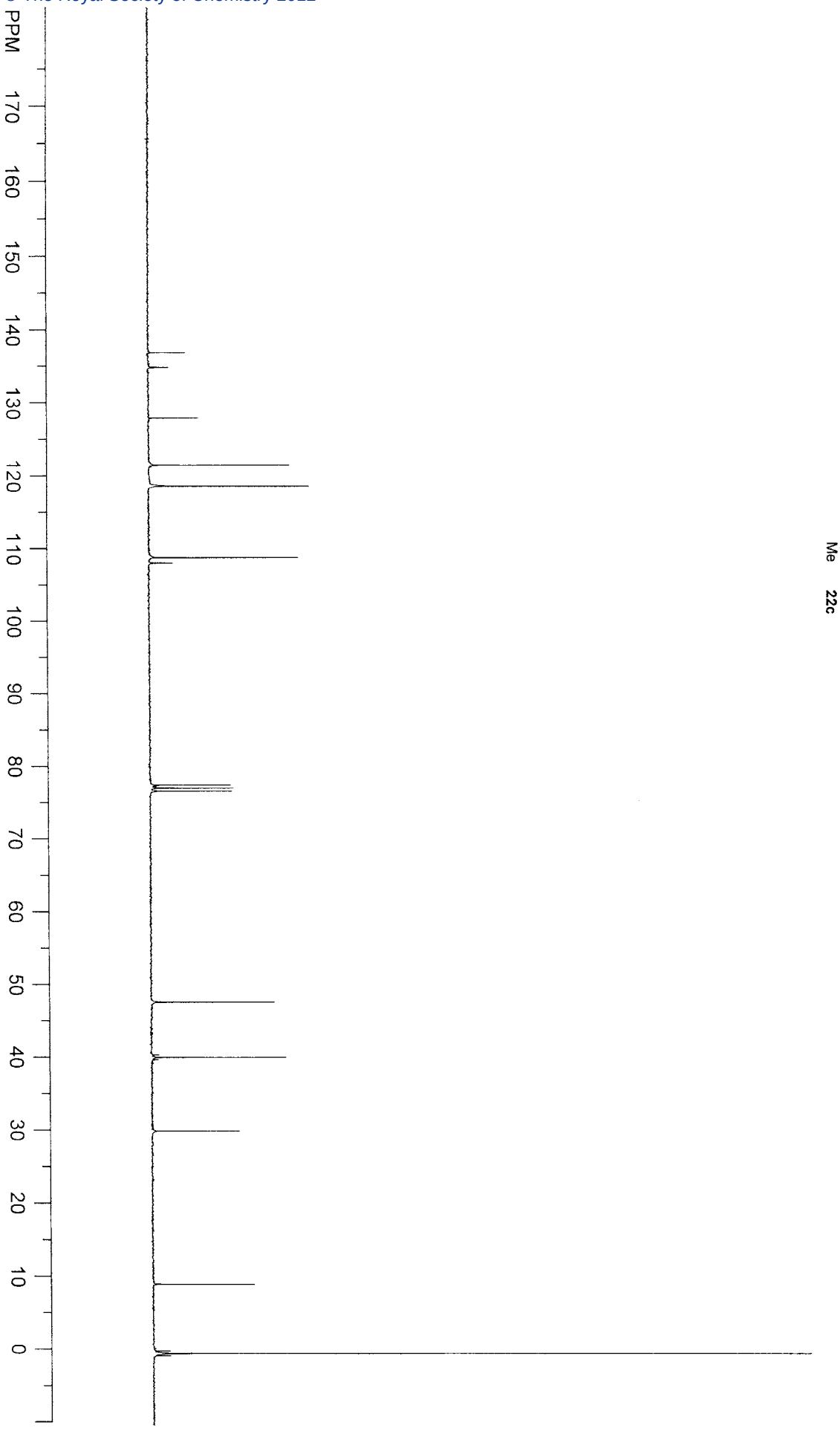

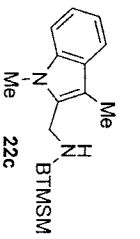

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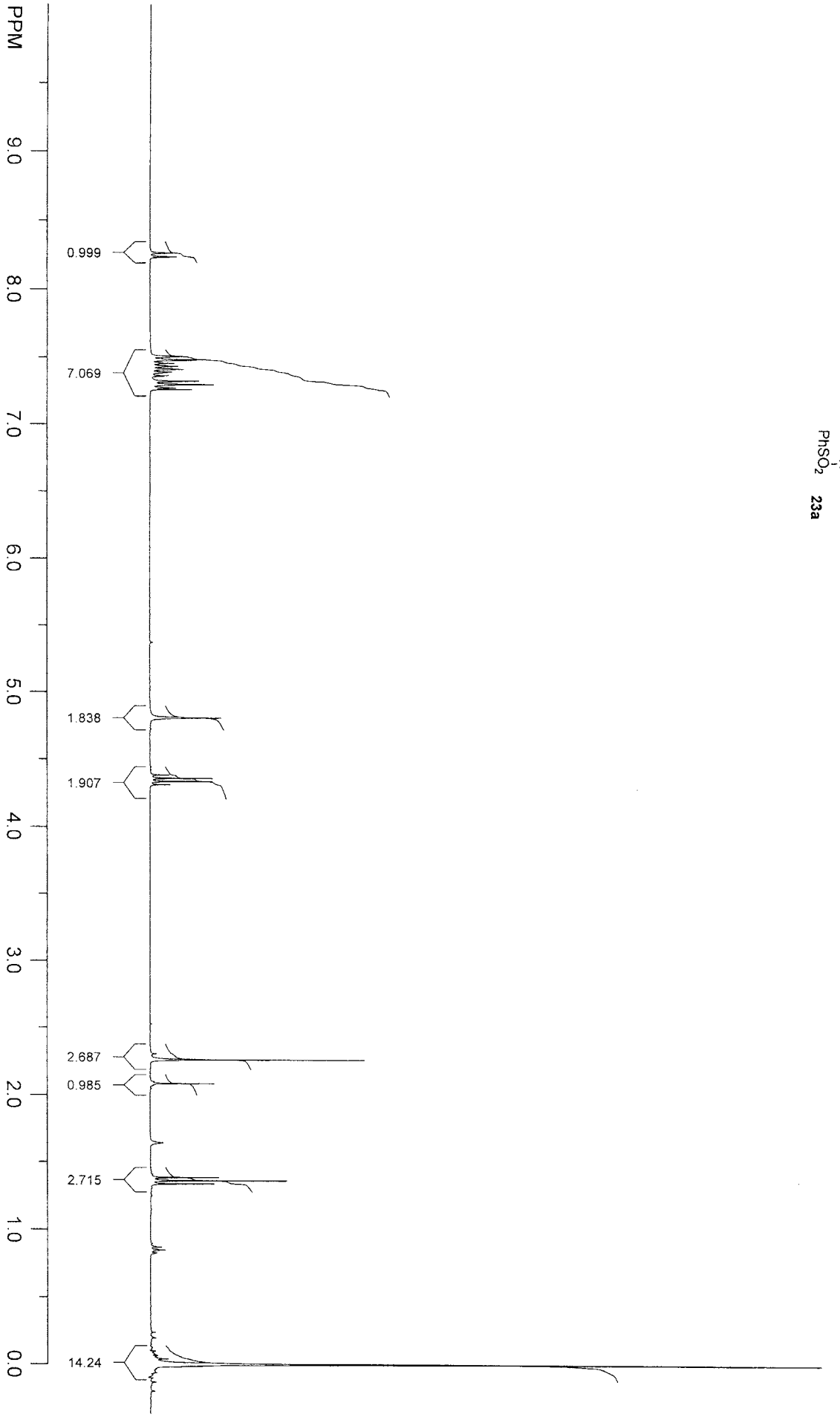

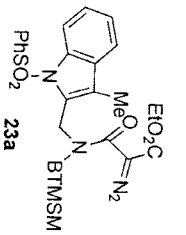

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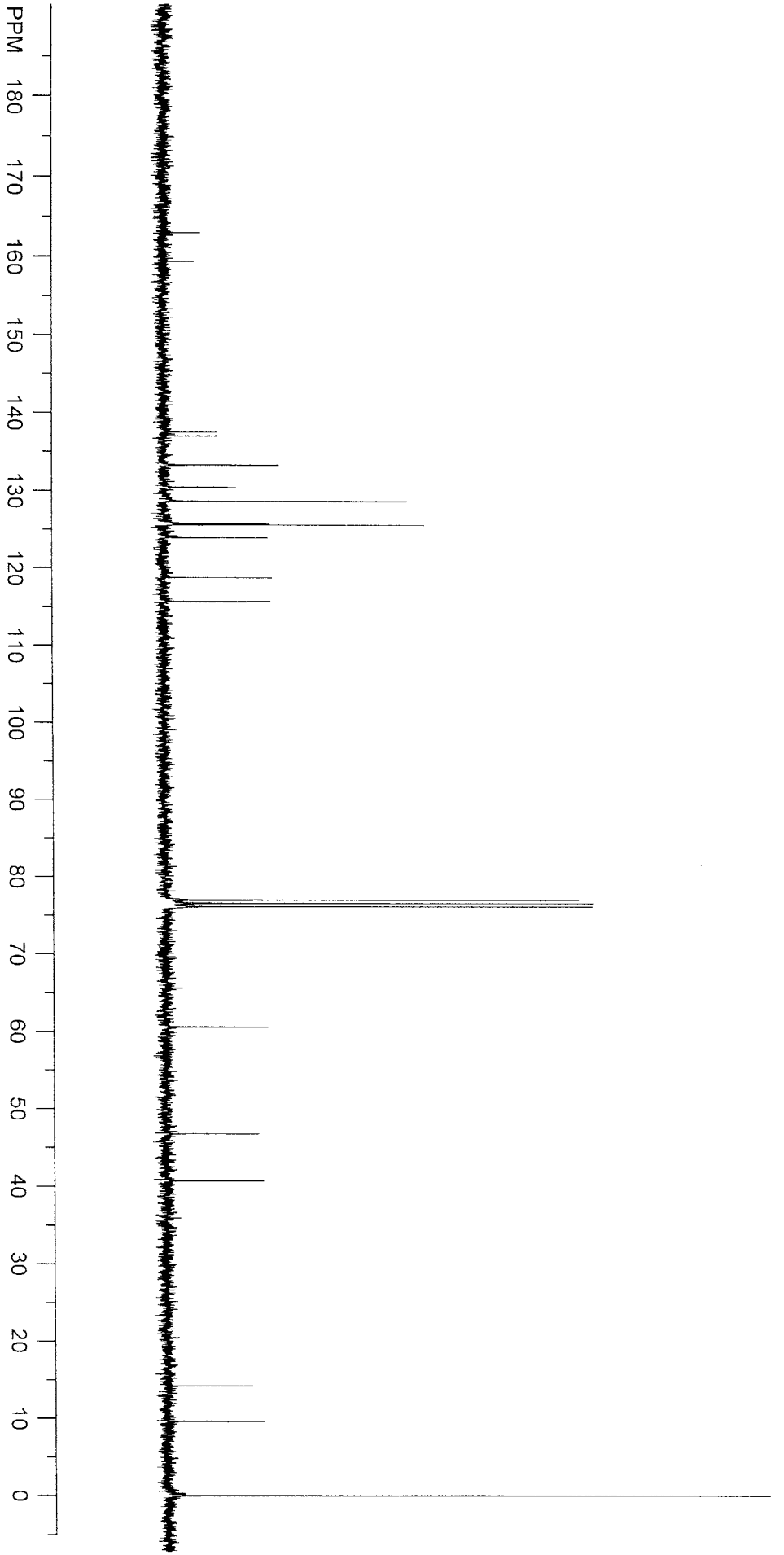

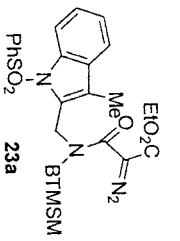

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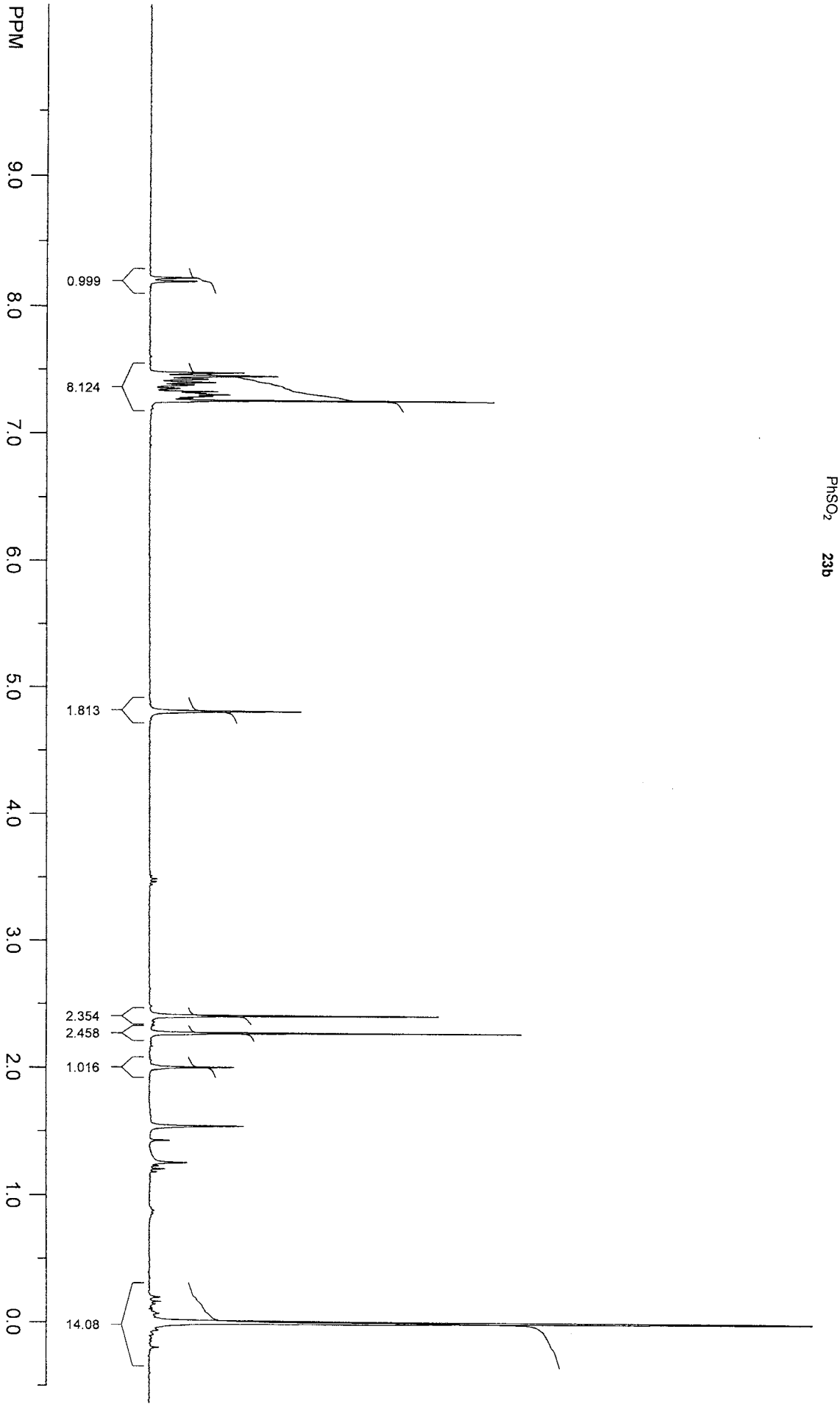

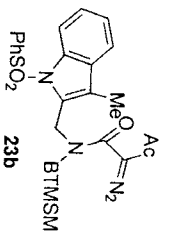

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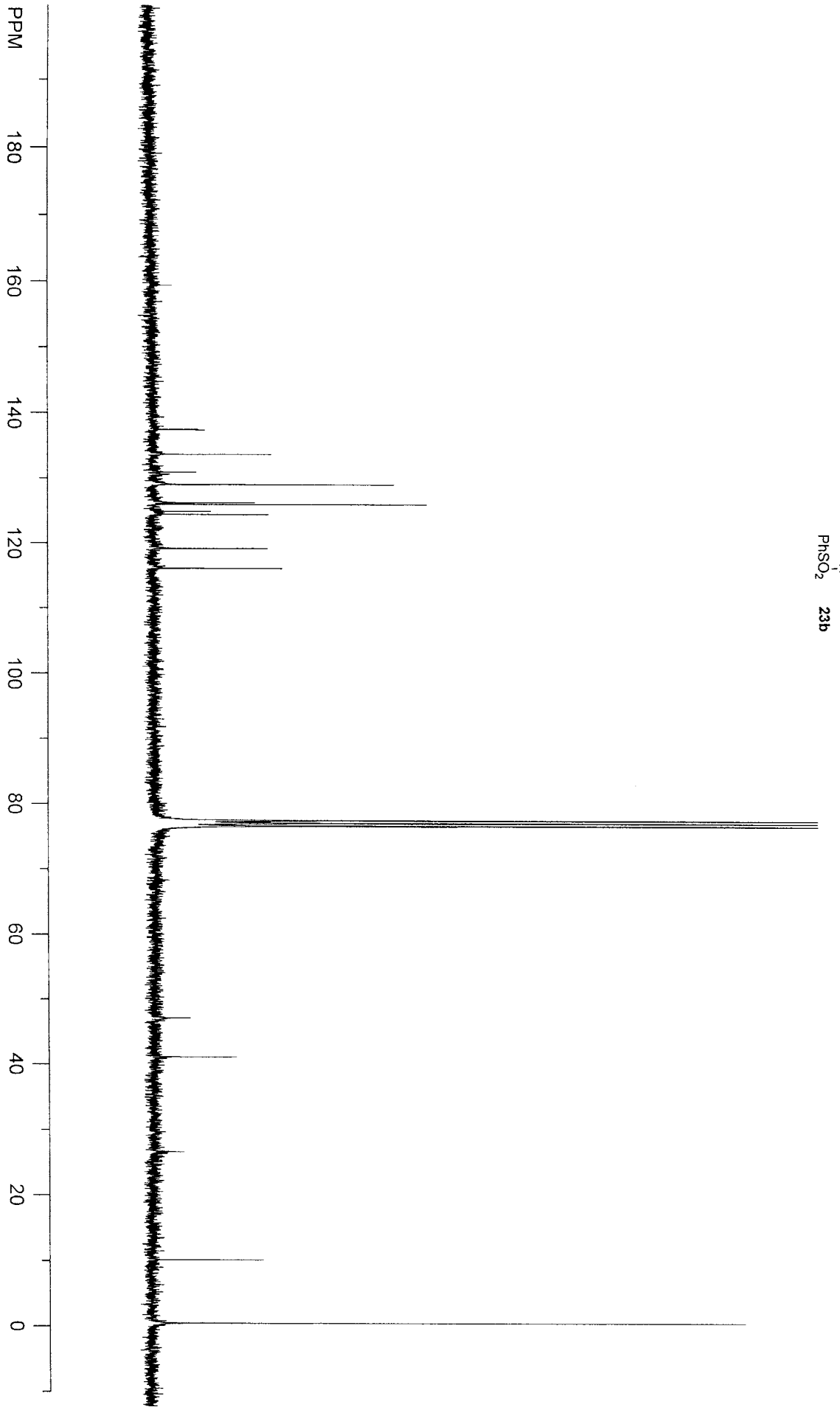

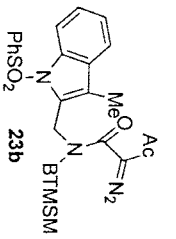

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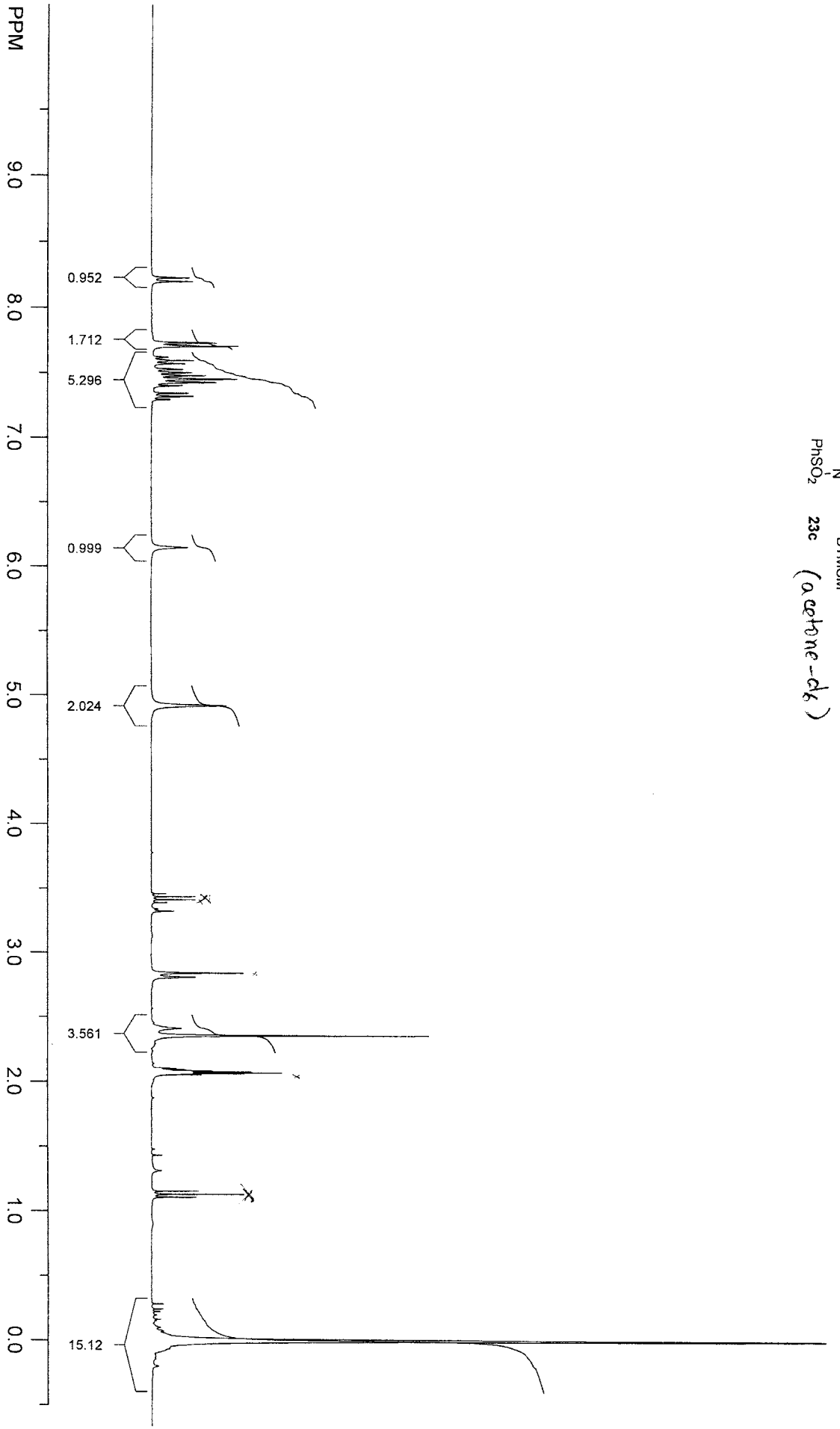

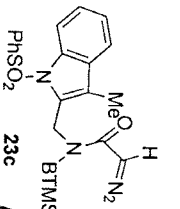

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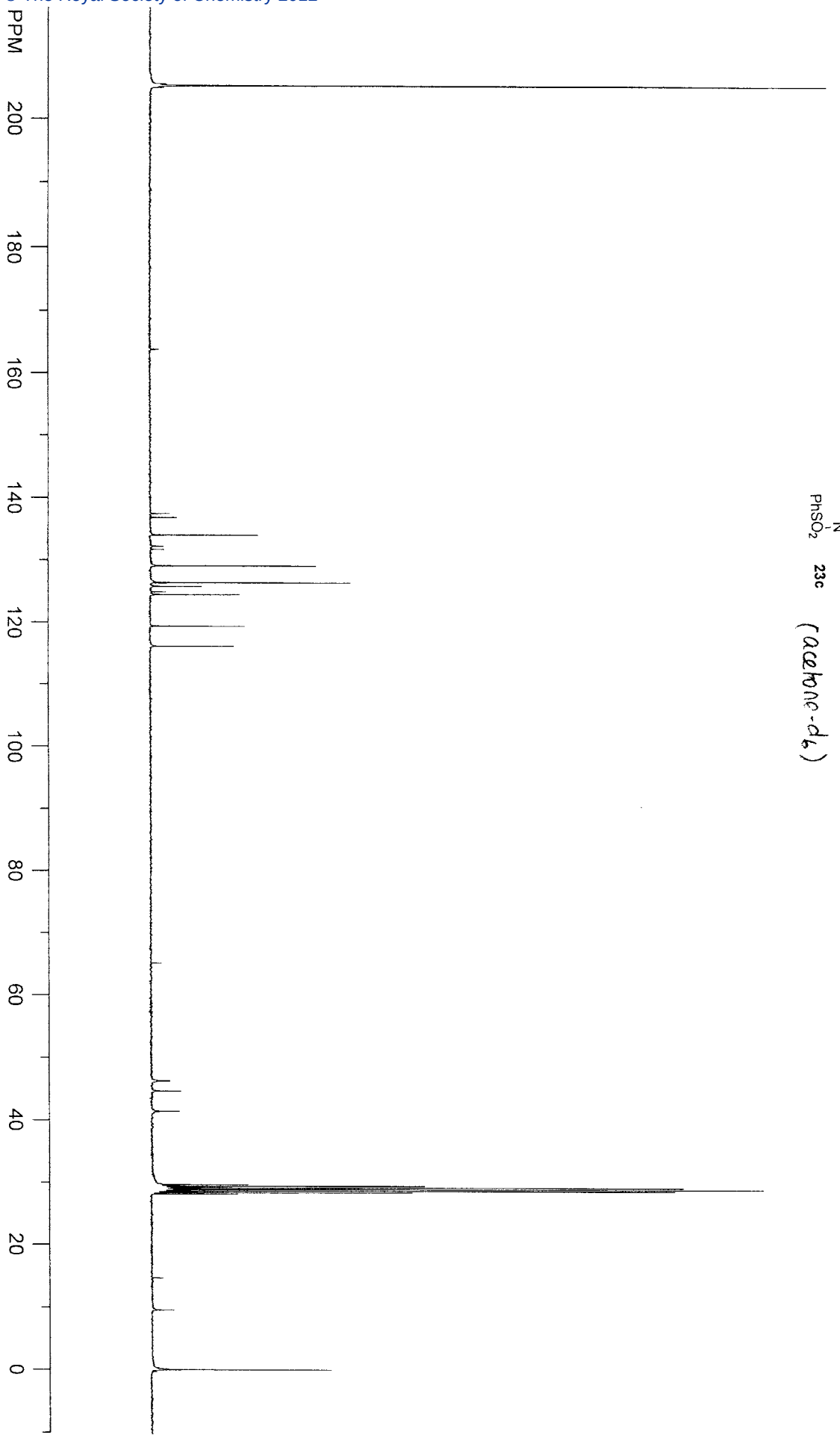

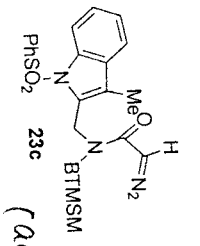

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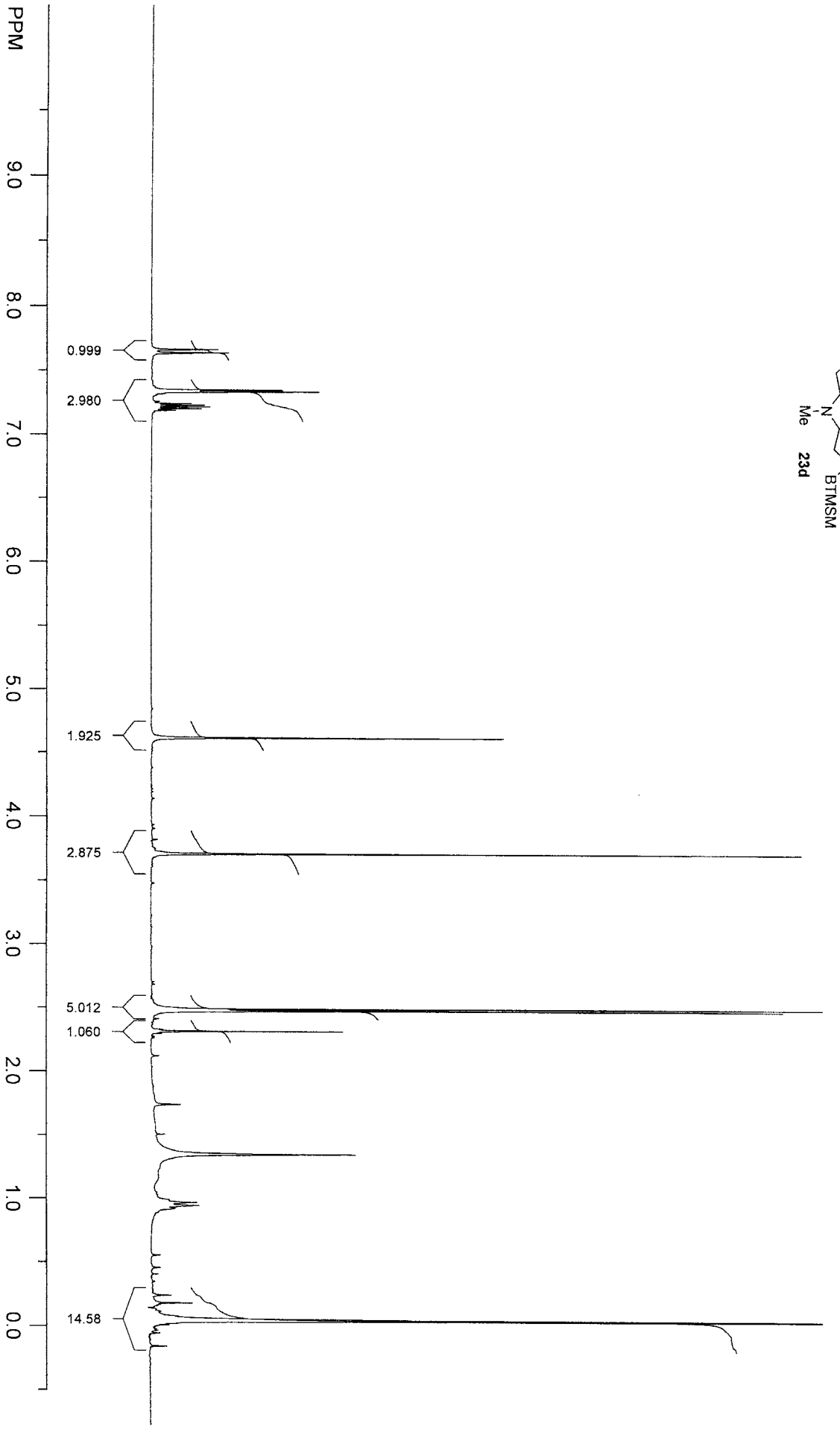

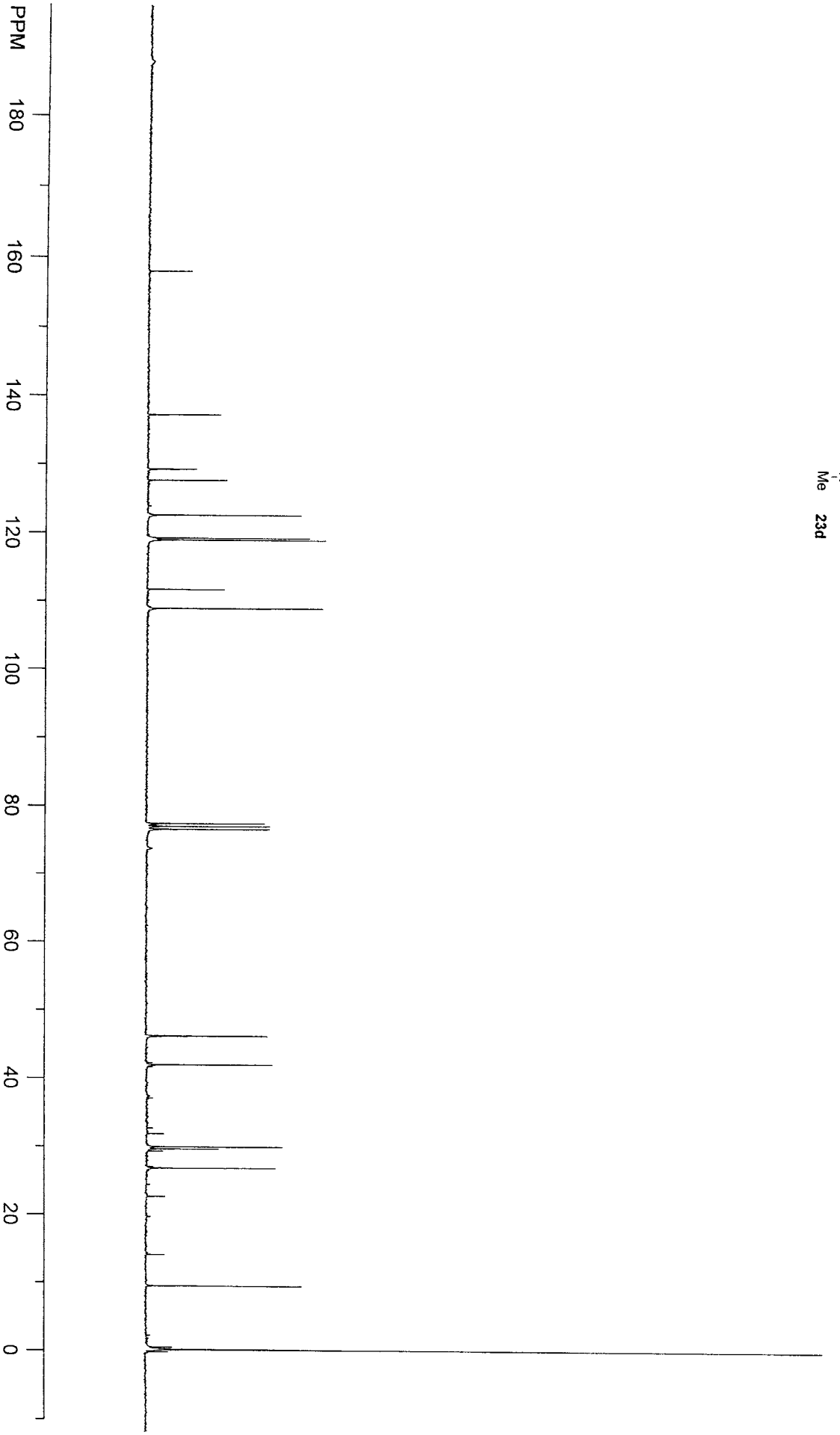

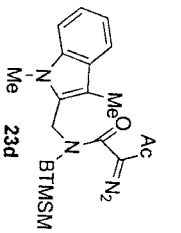

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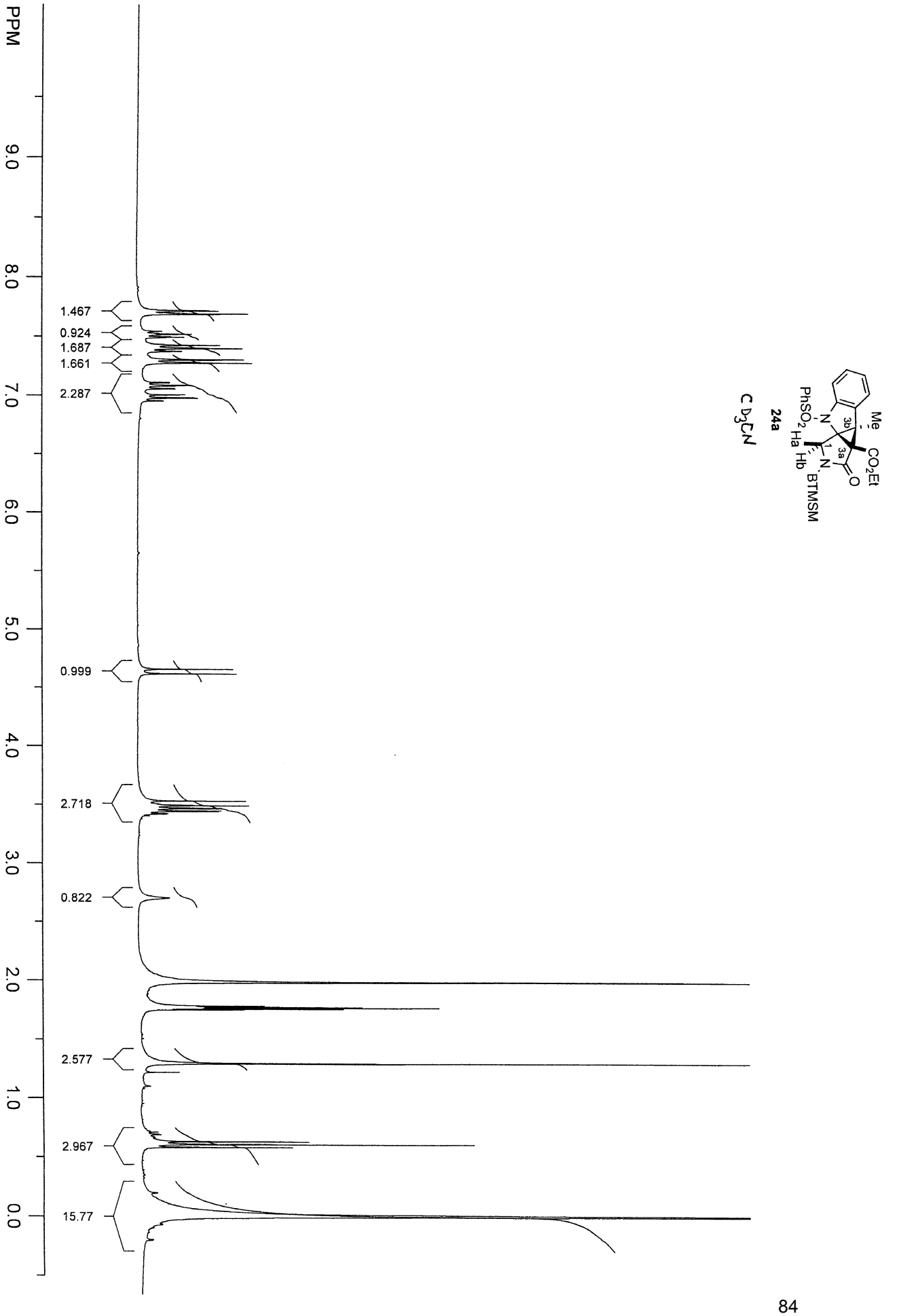

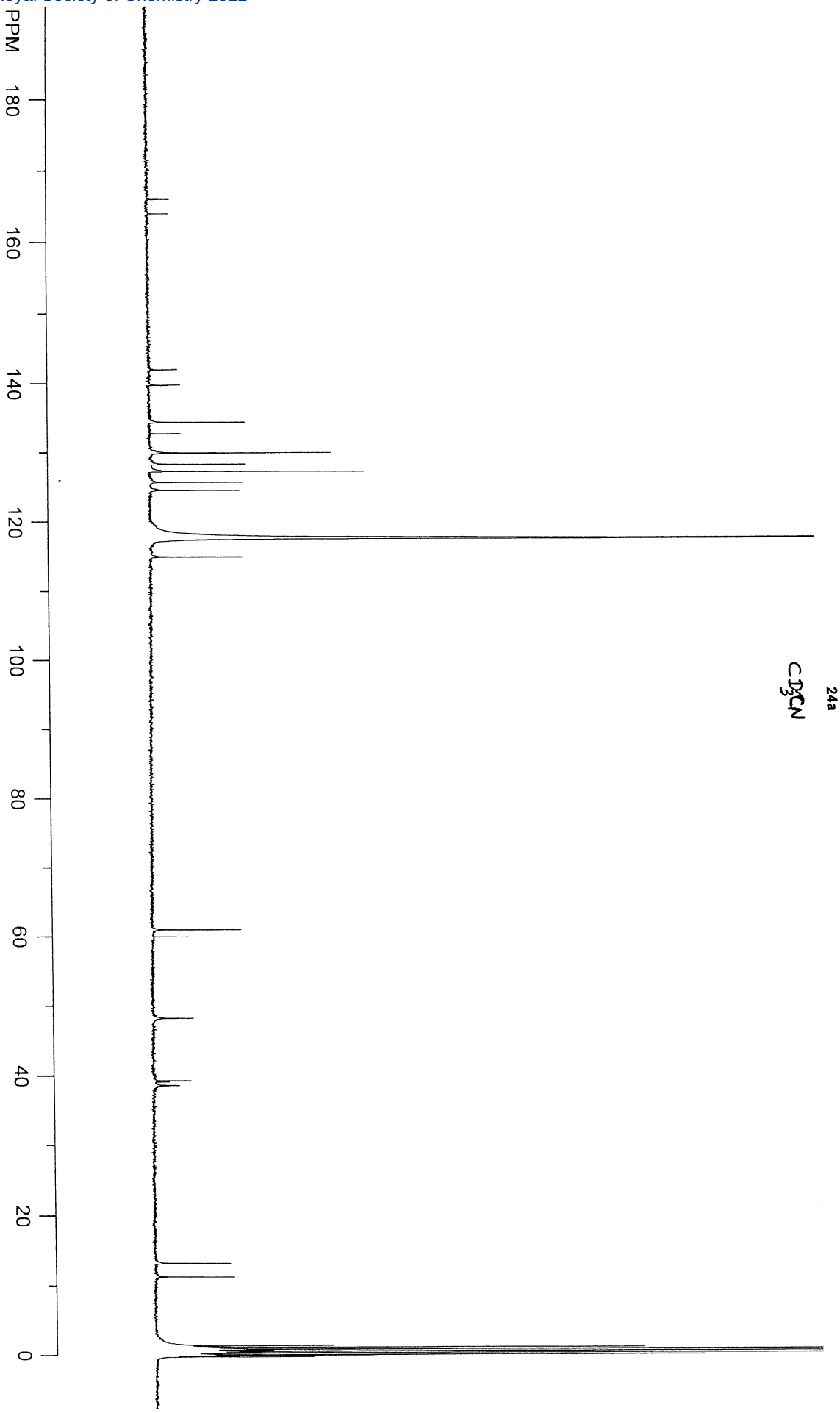

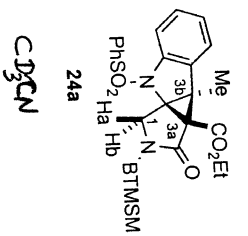

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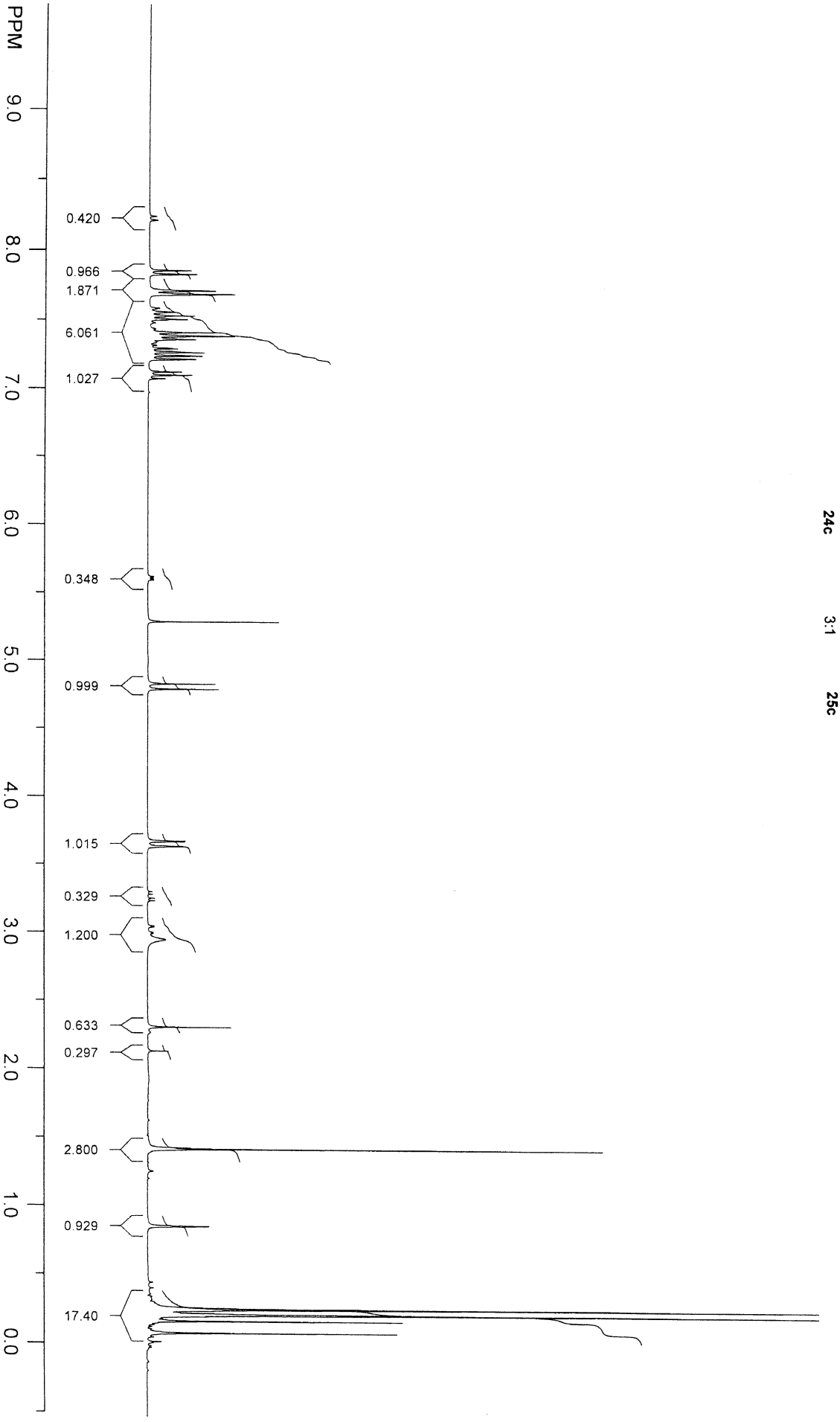

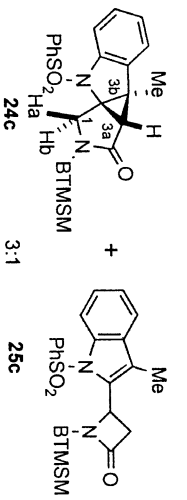

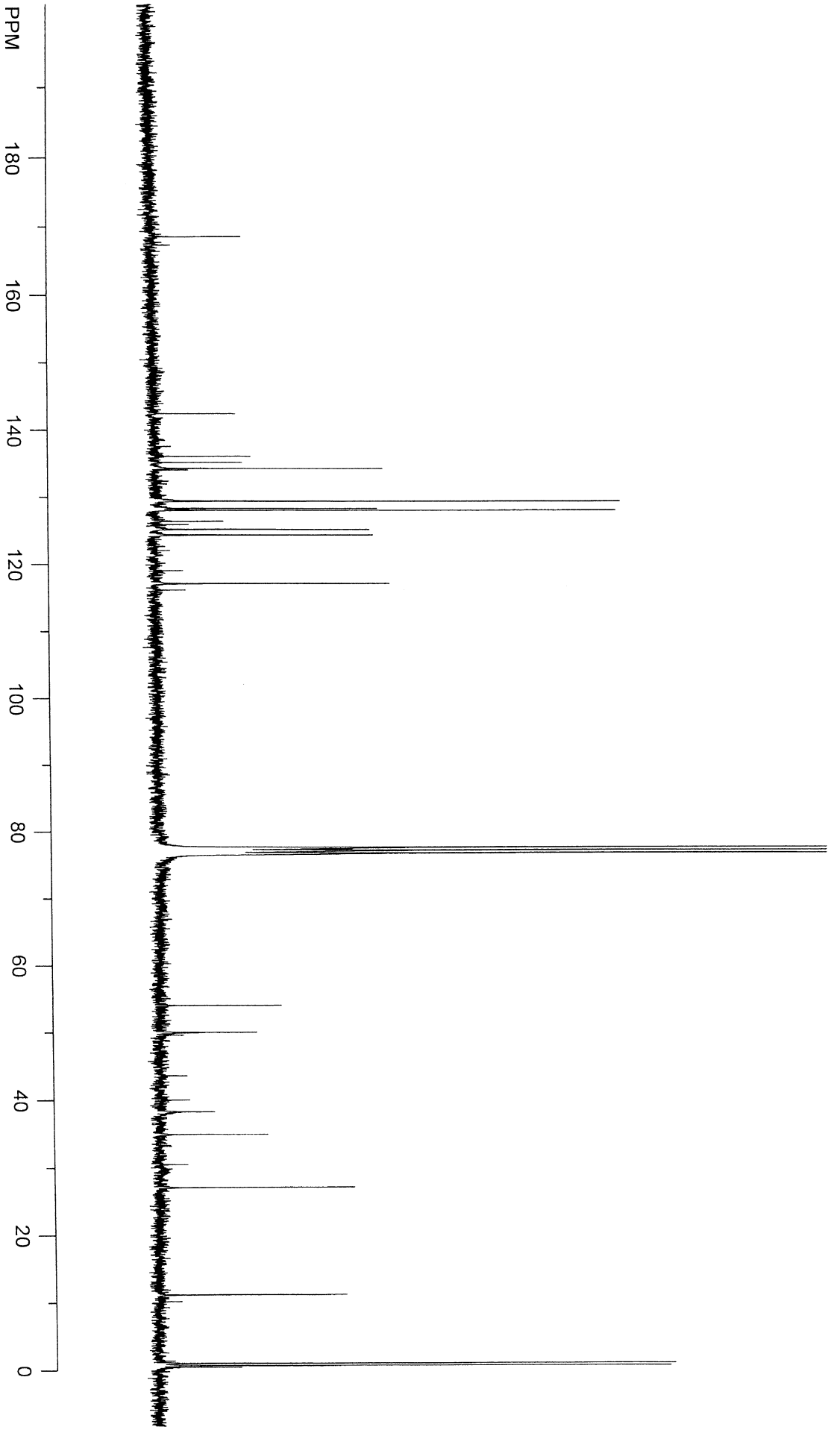

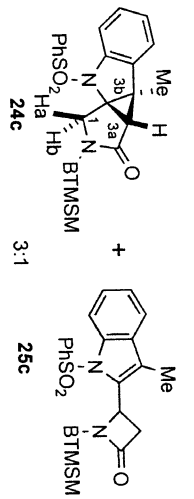

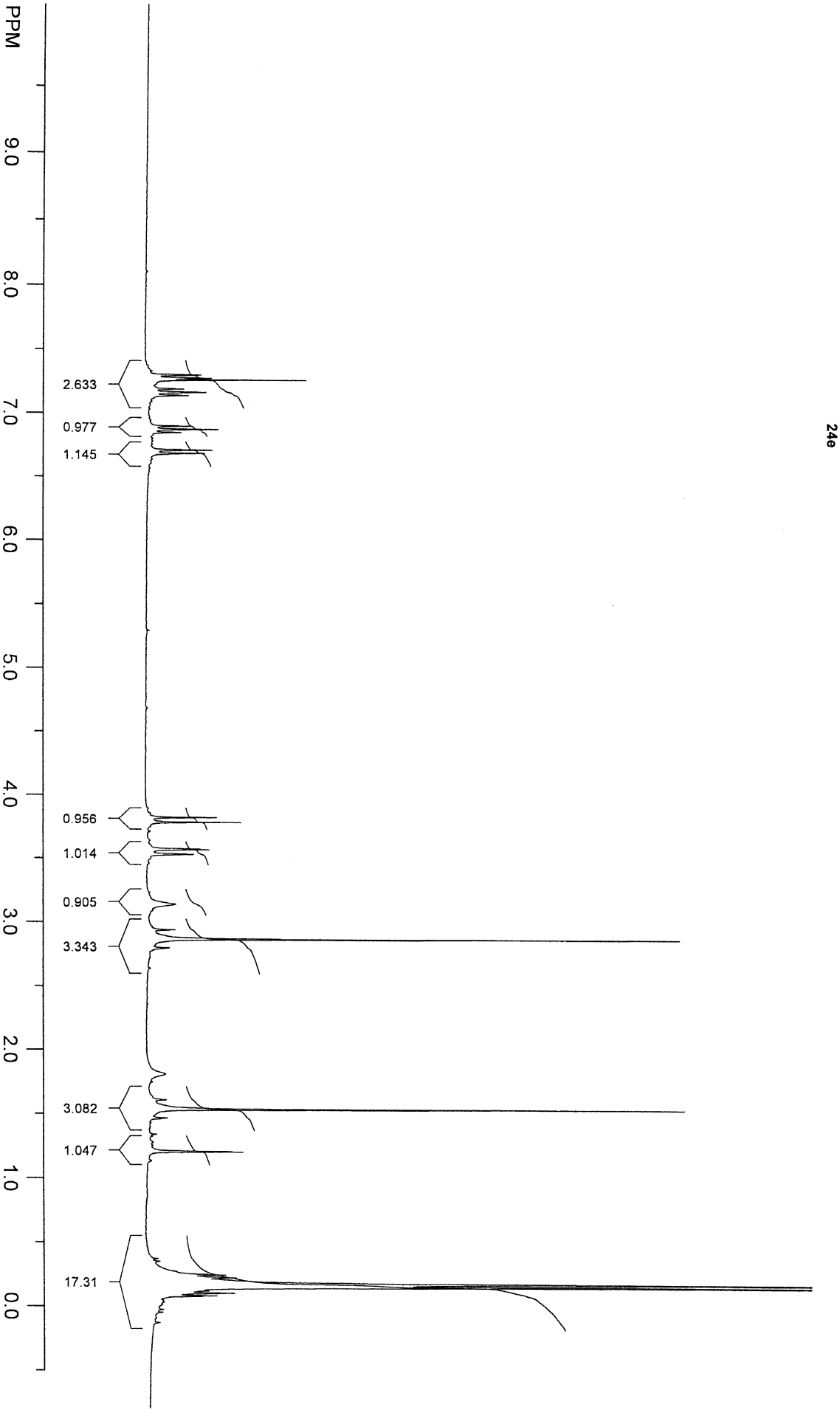

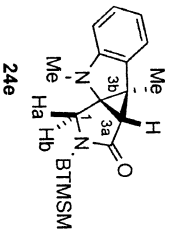

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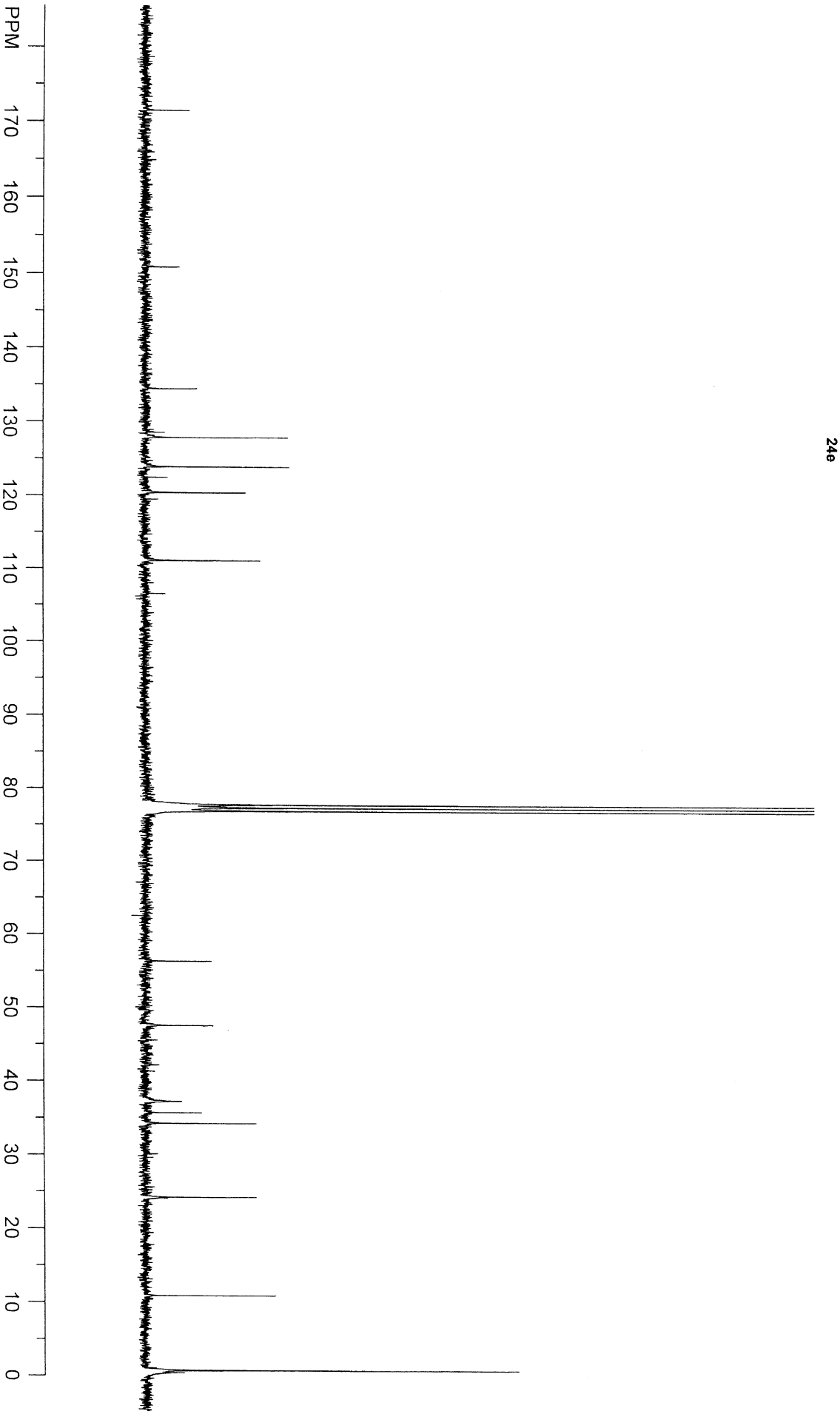

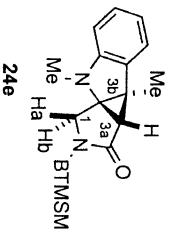

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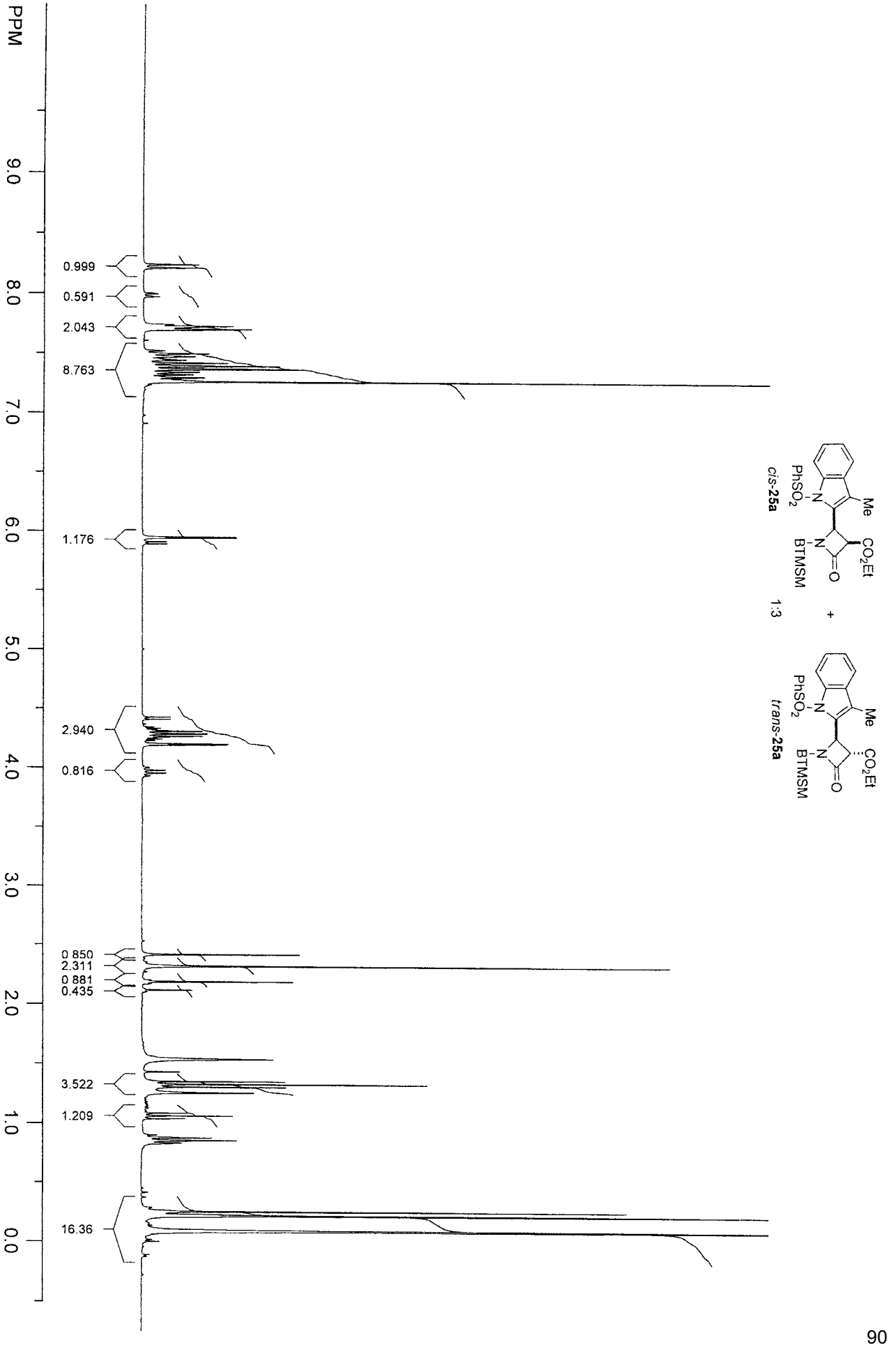

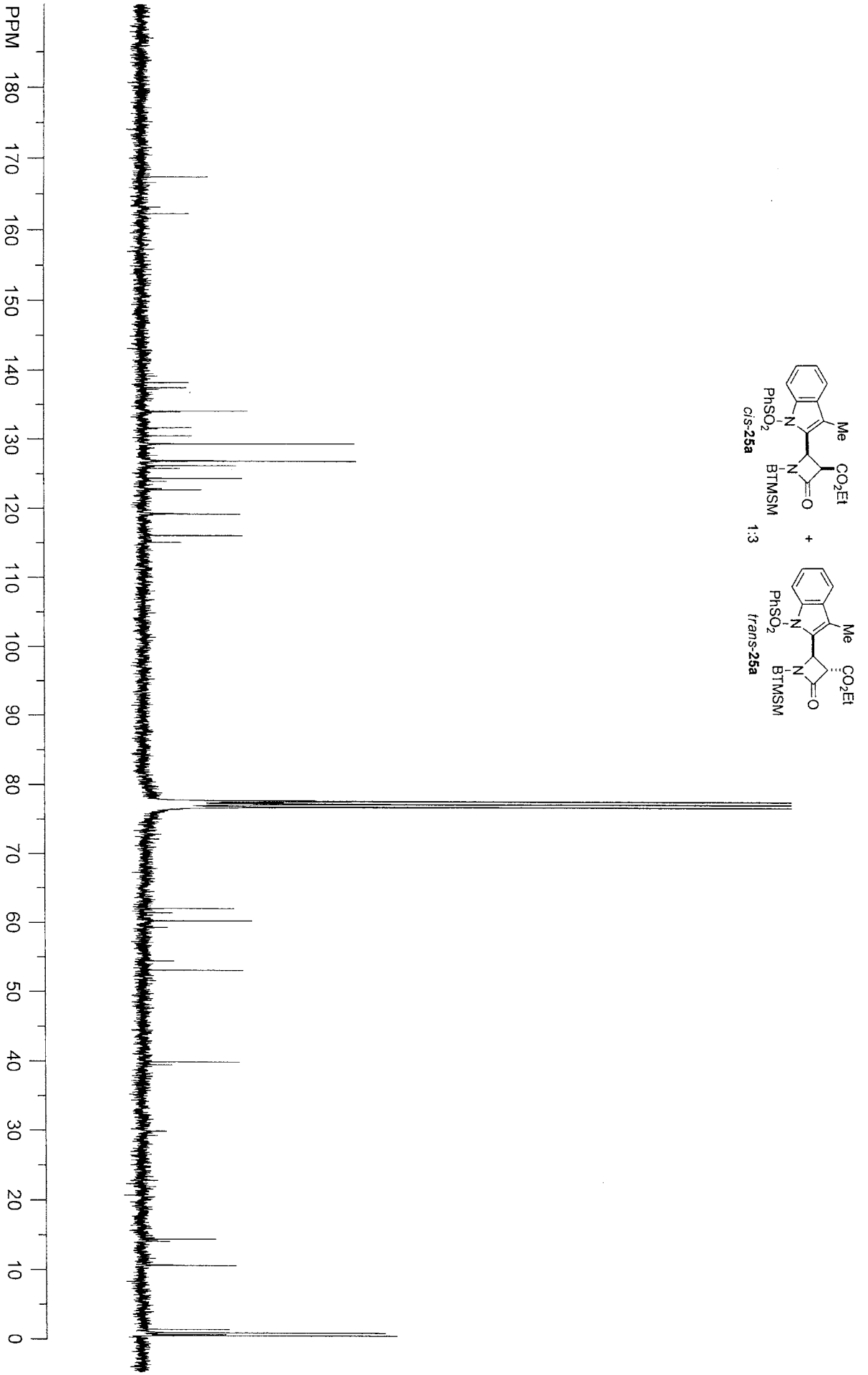
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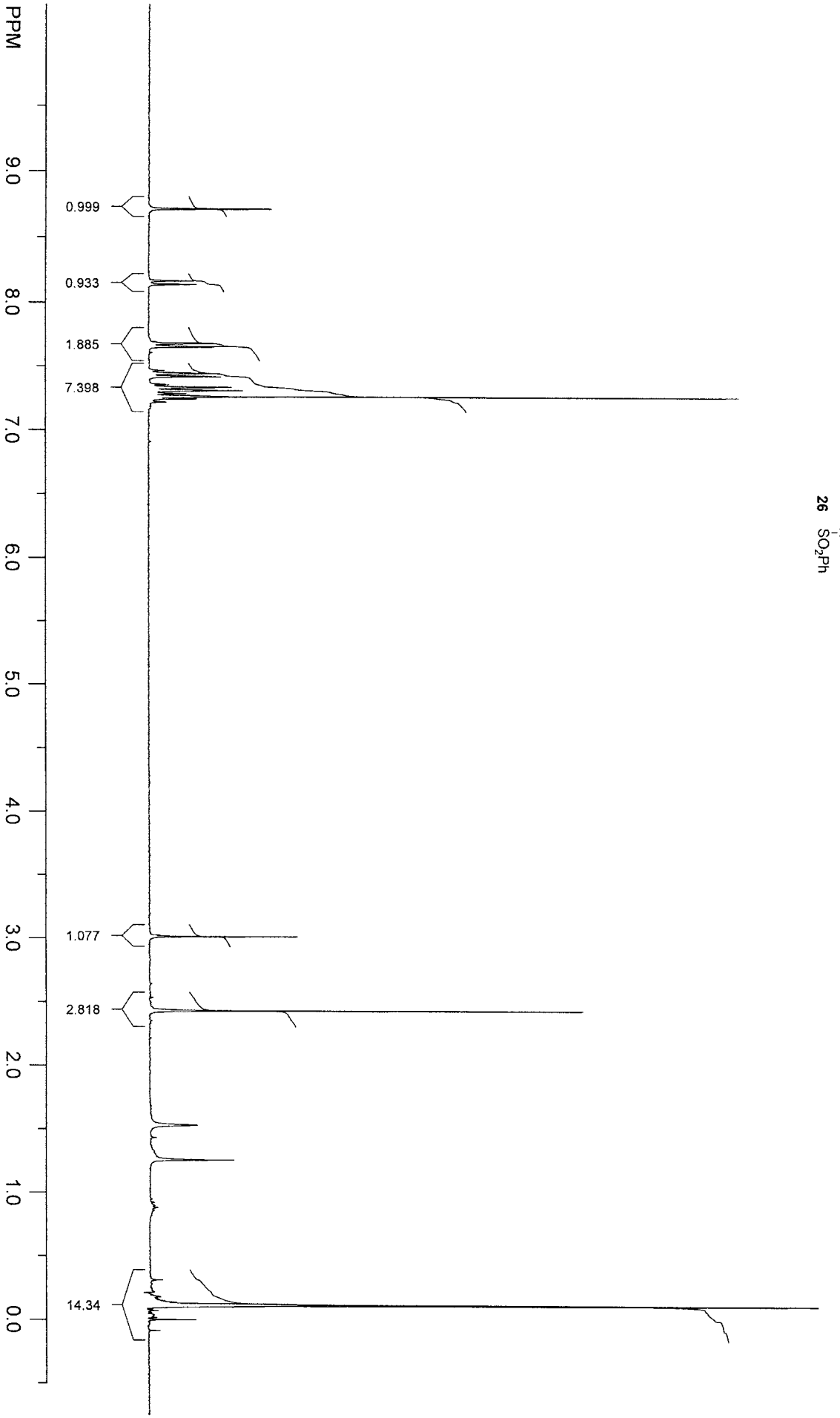
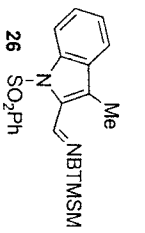
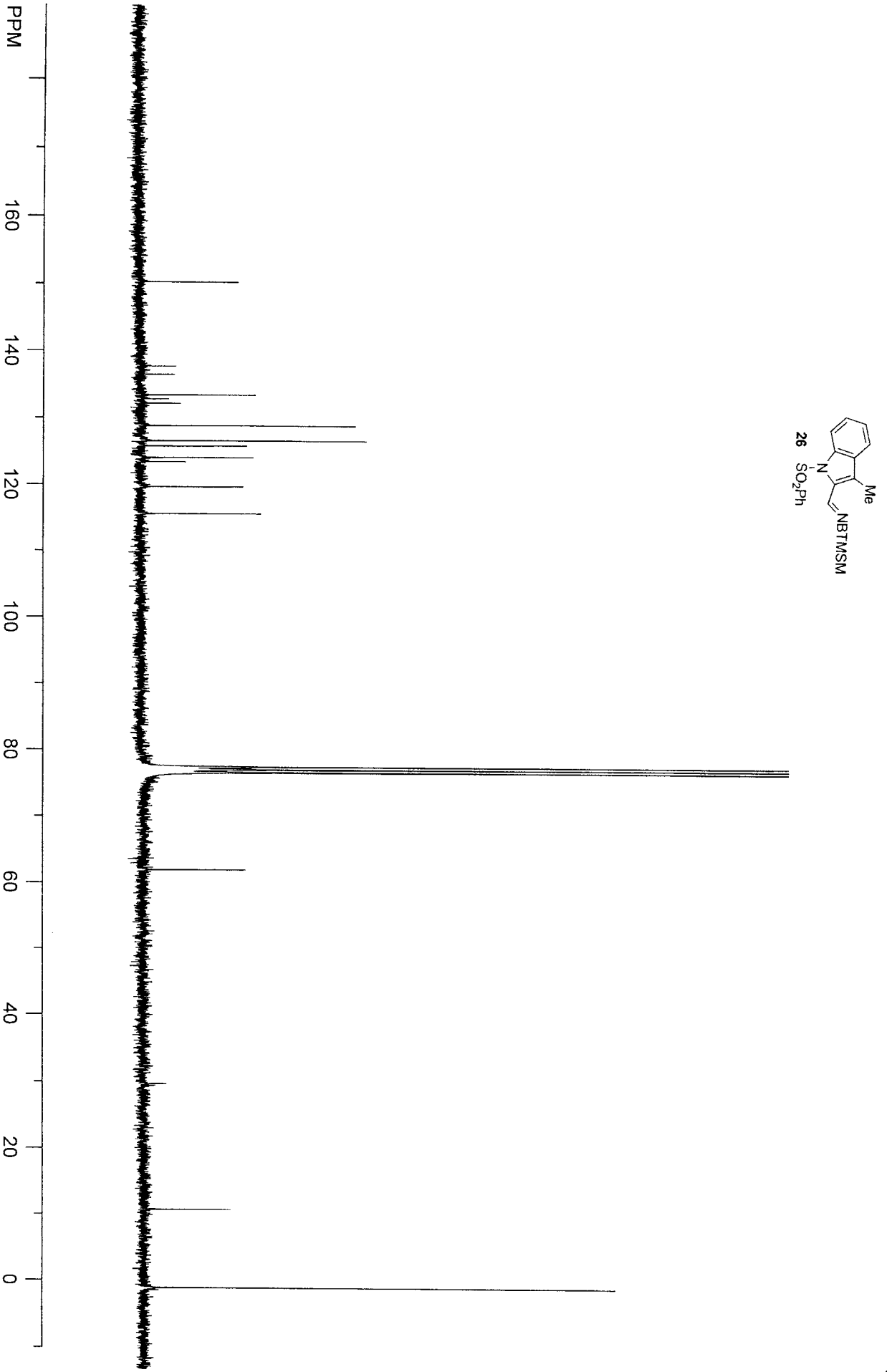
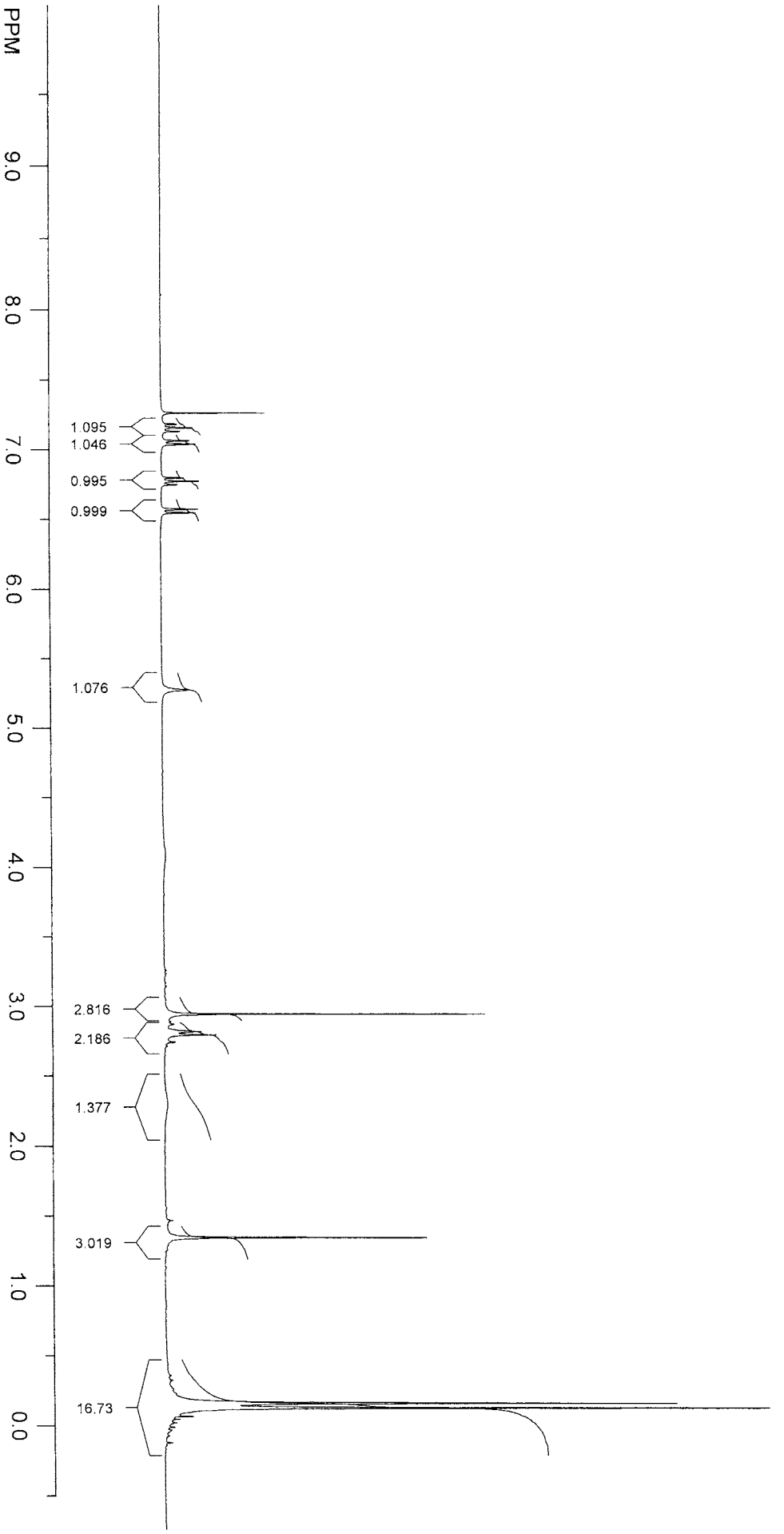
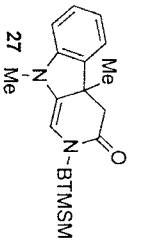
trans-25a

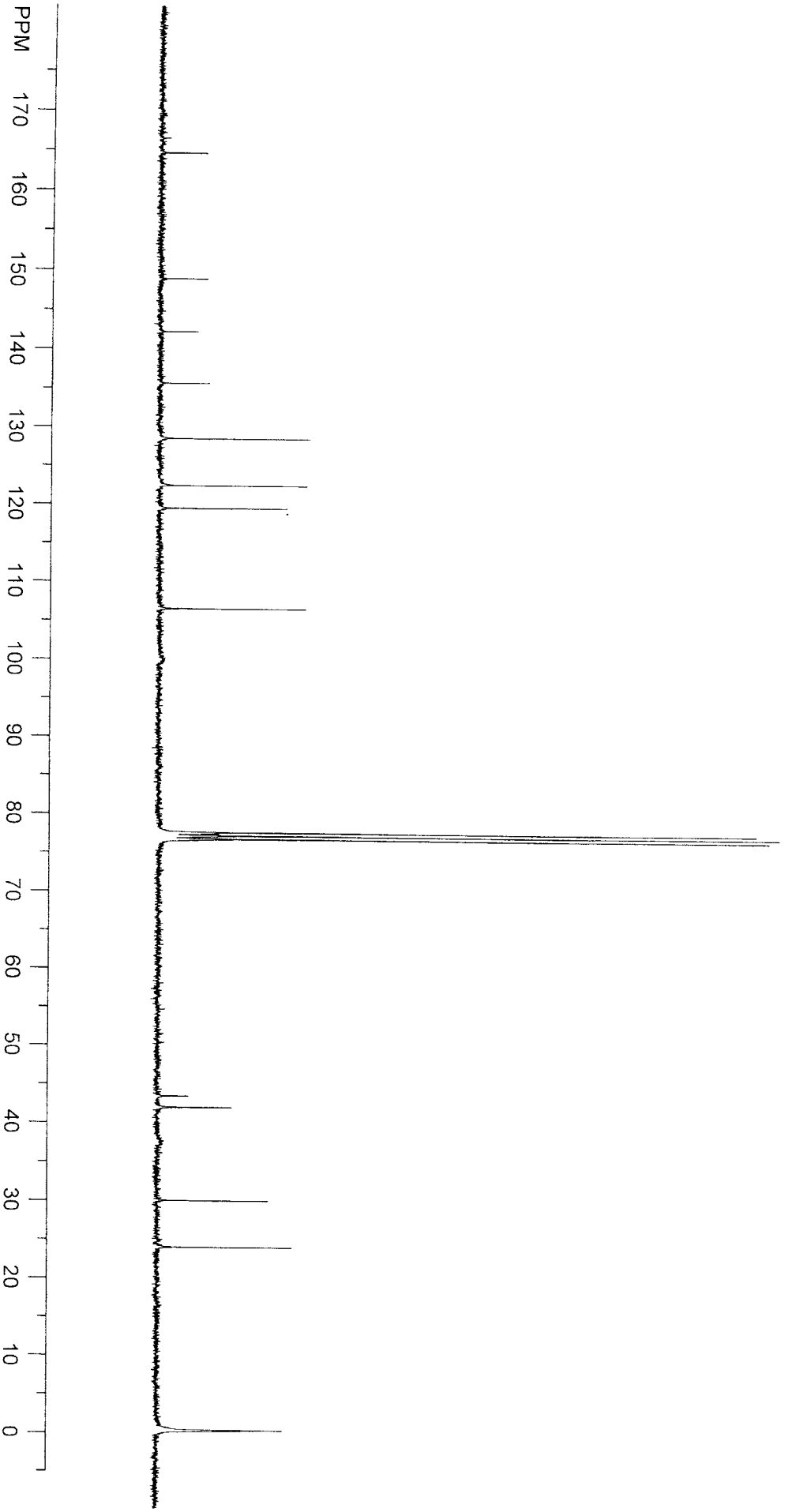


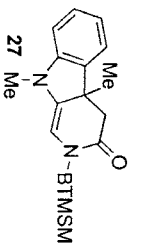




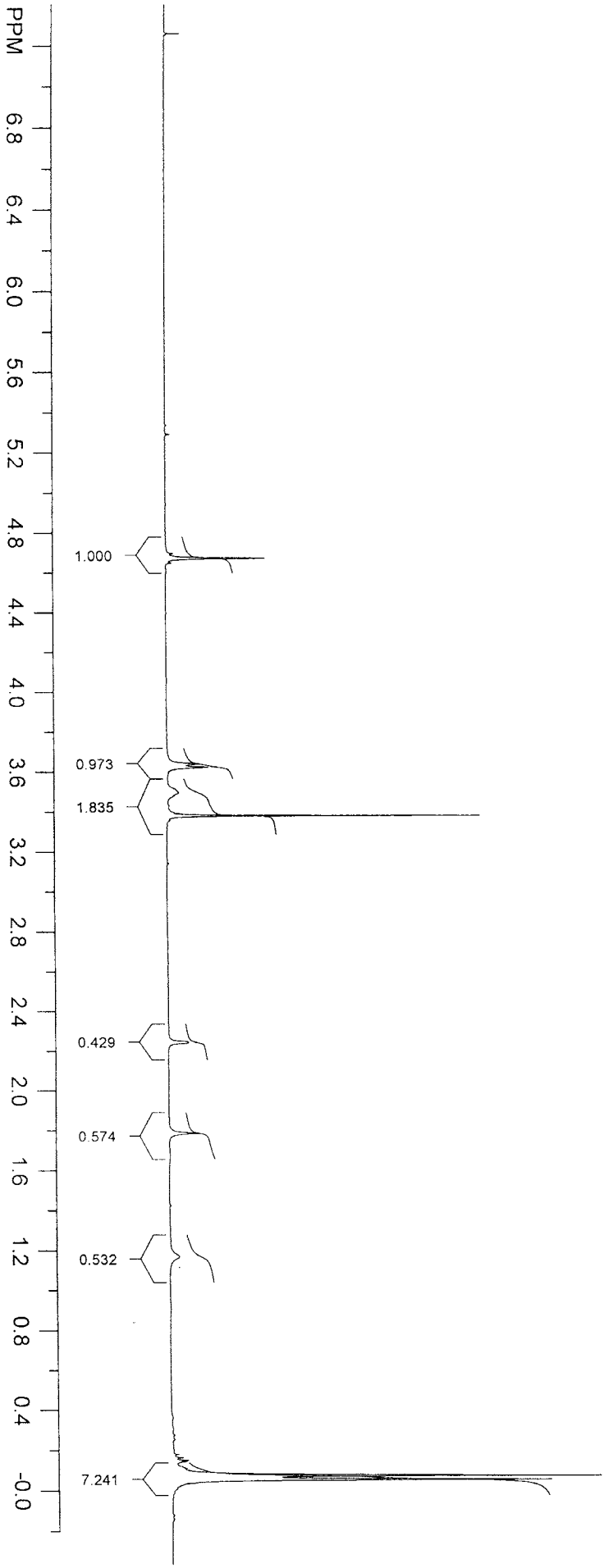


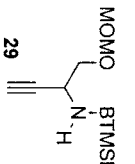


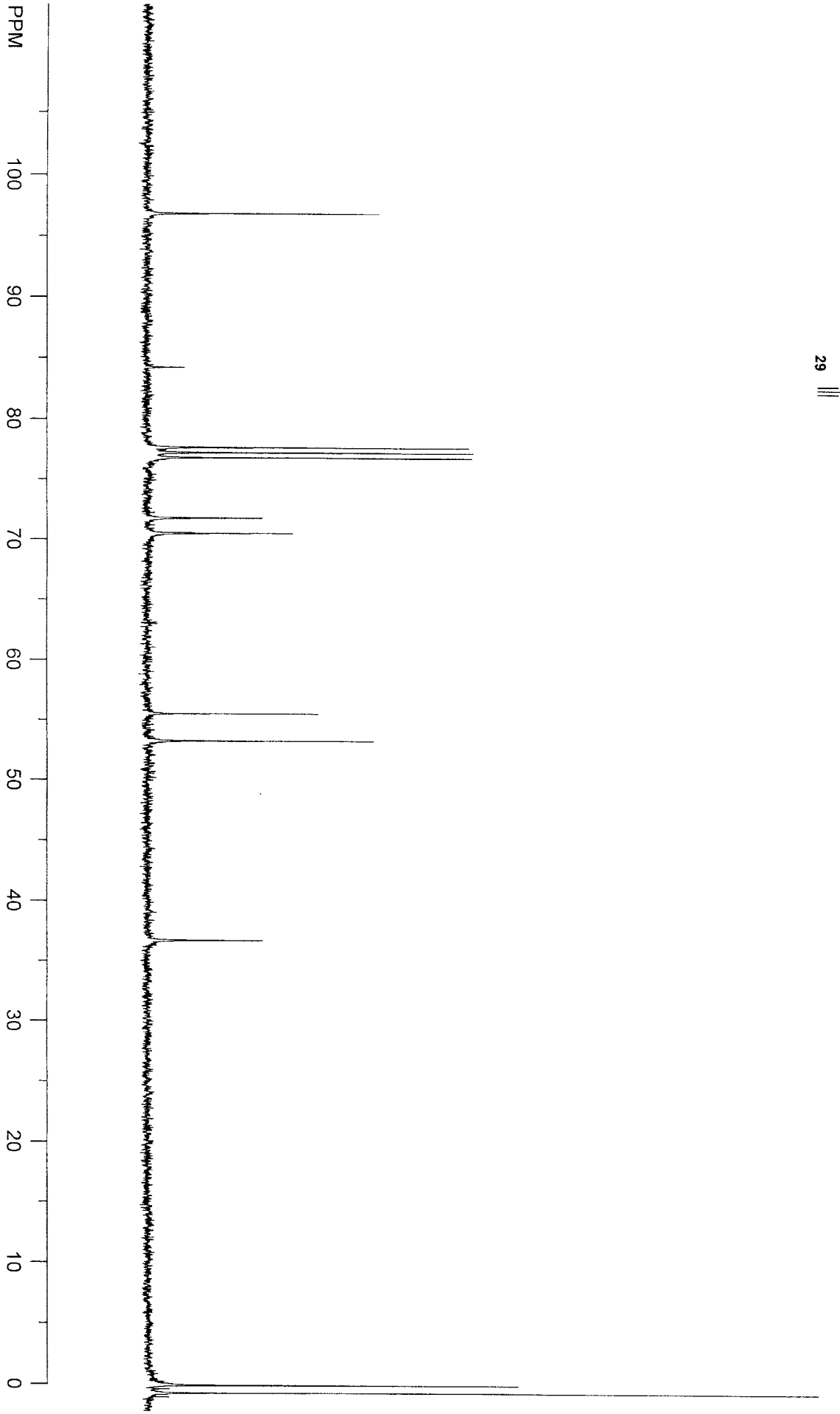


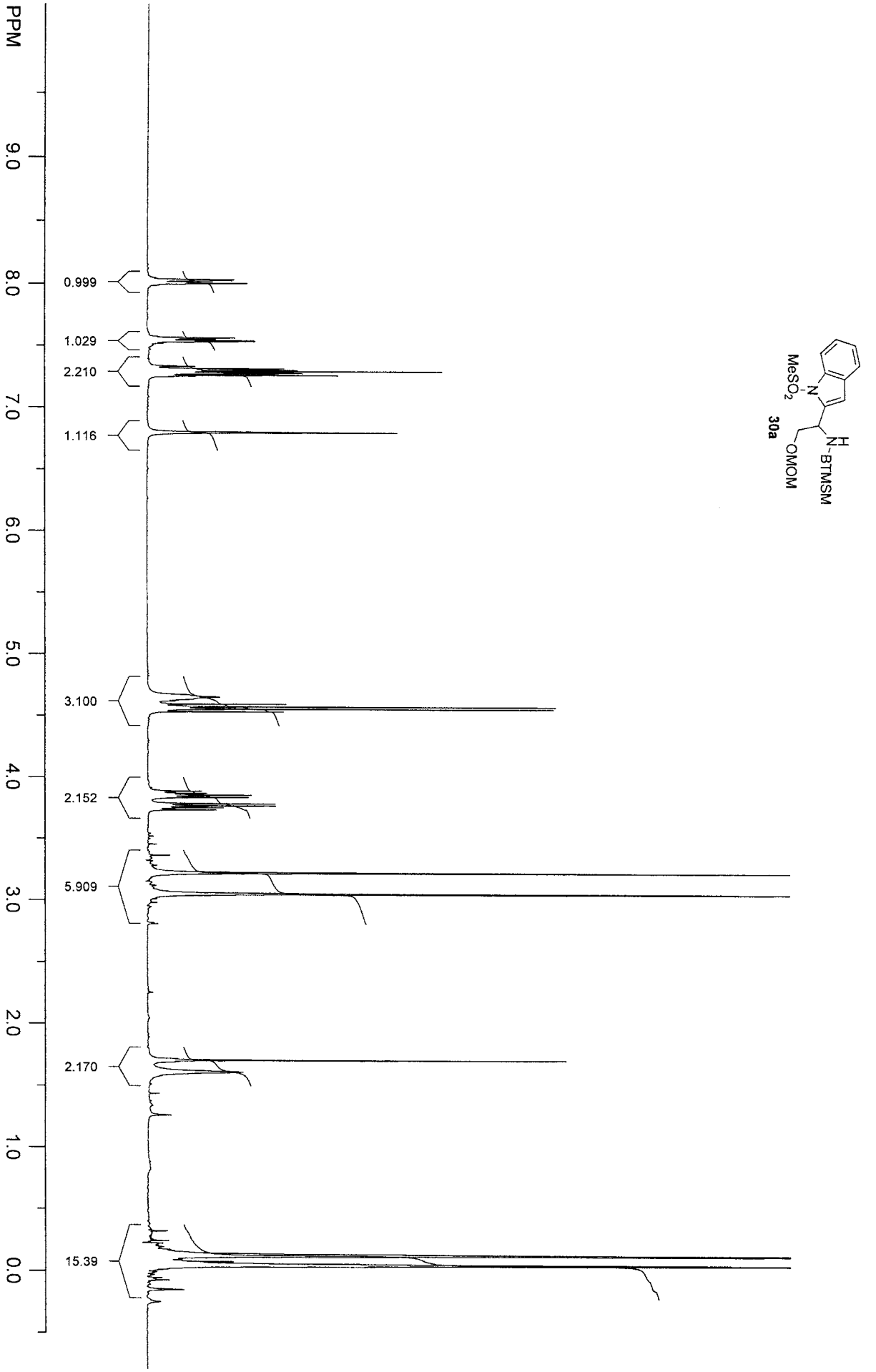


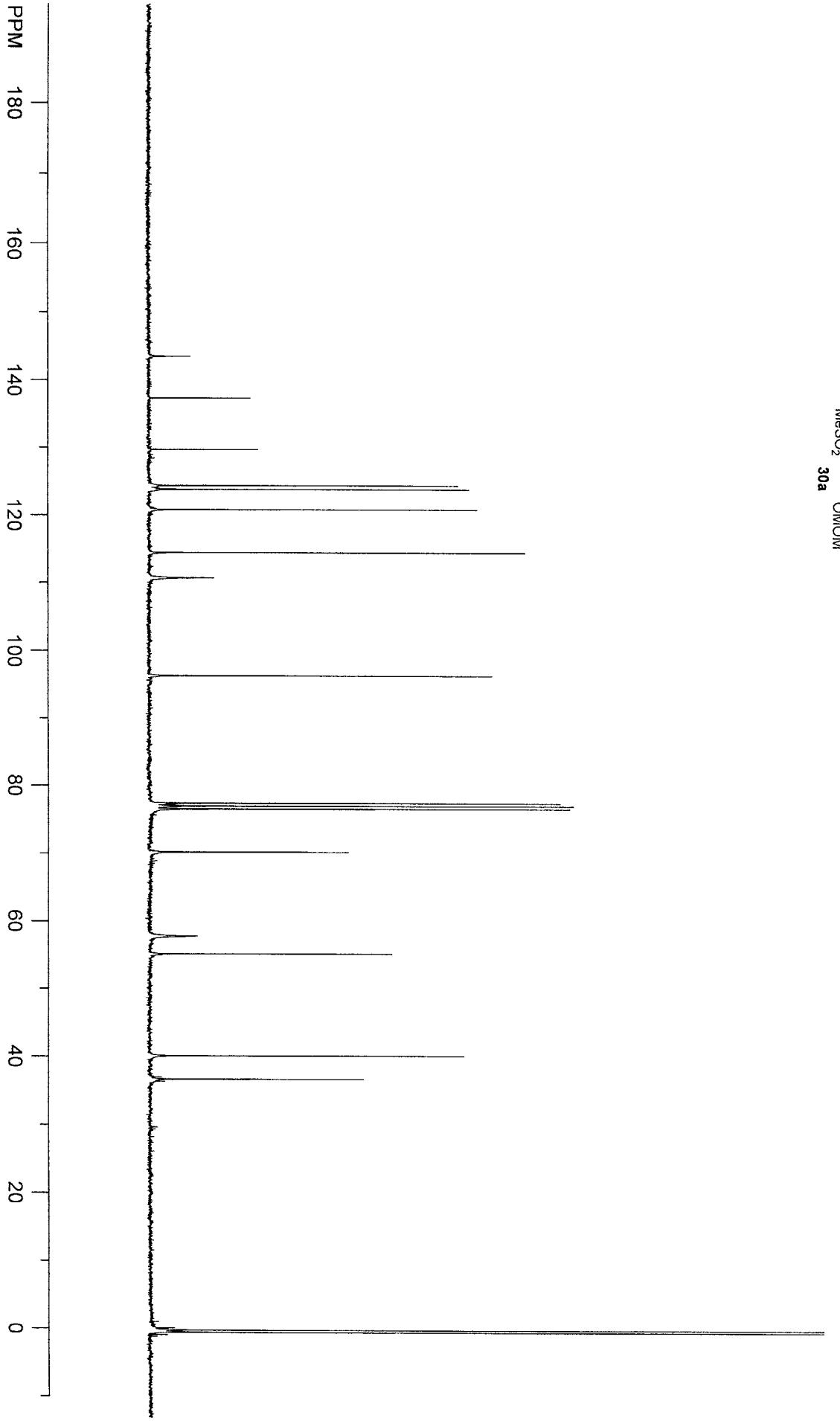
27

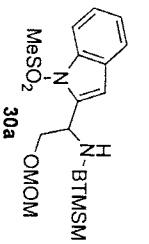












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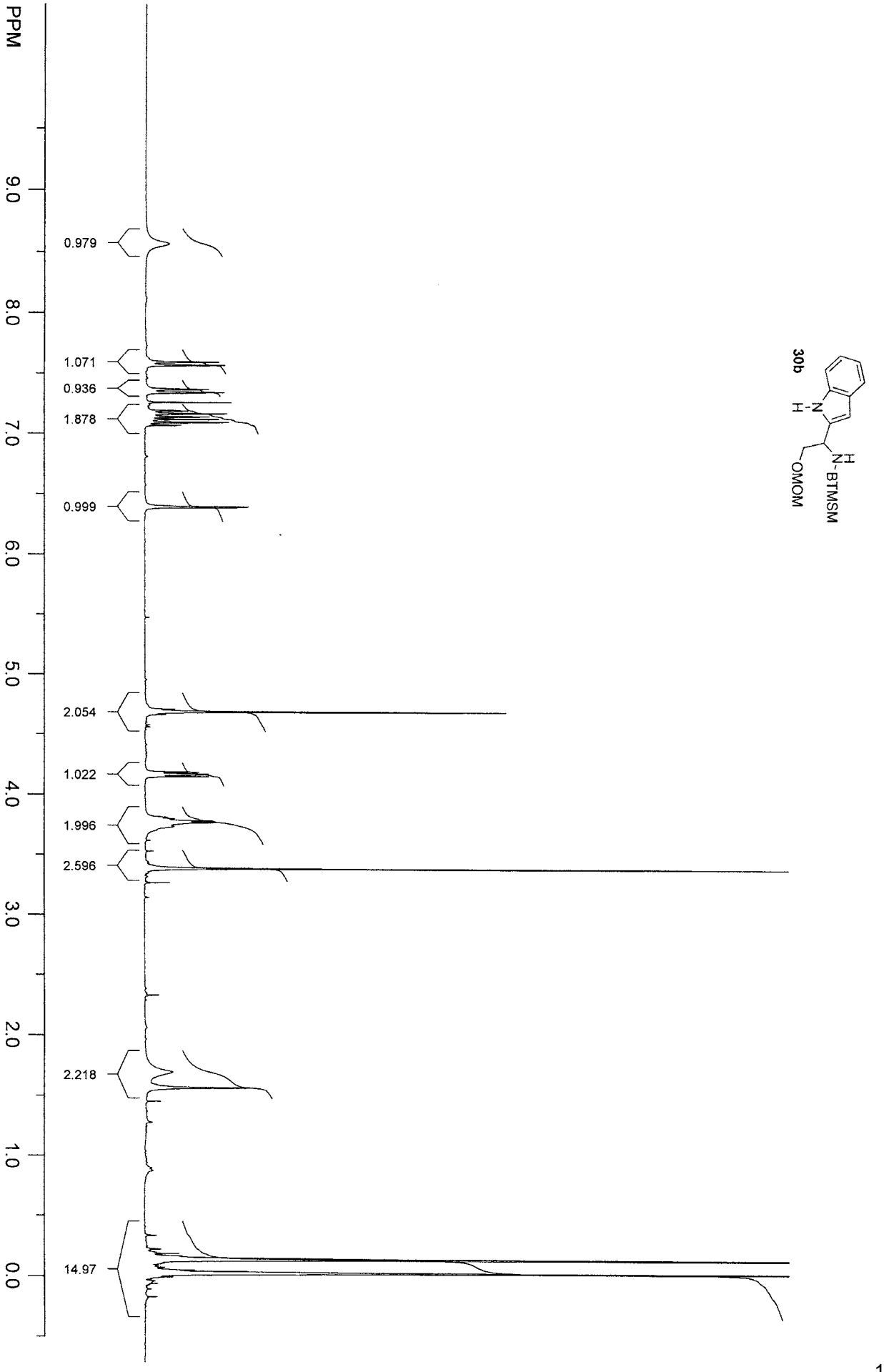

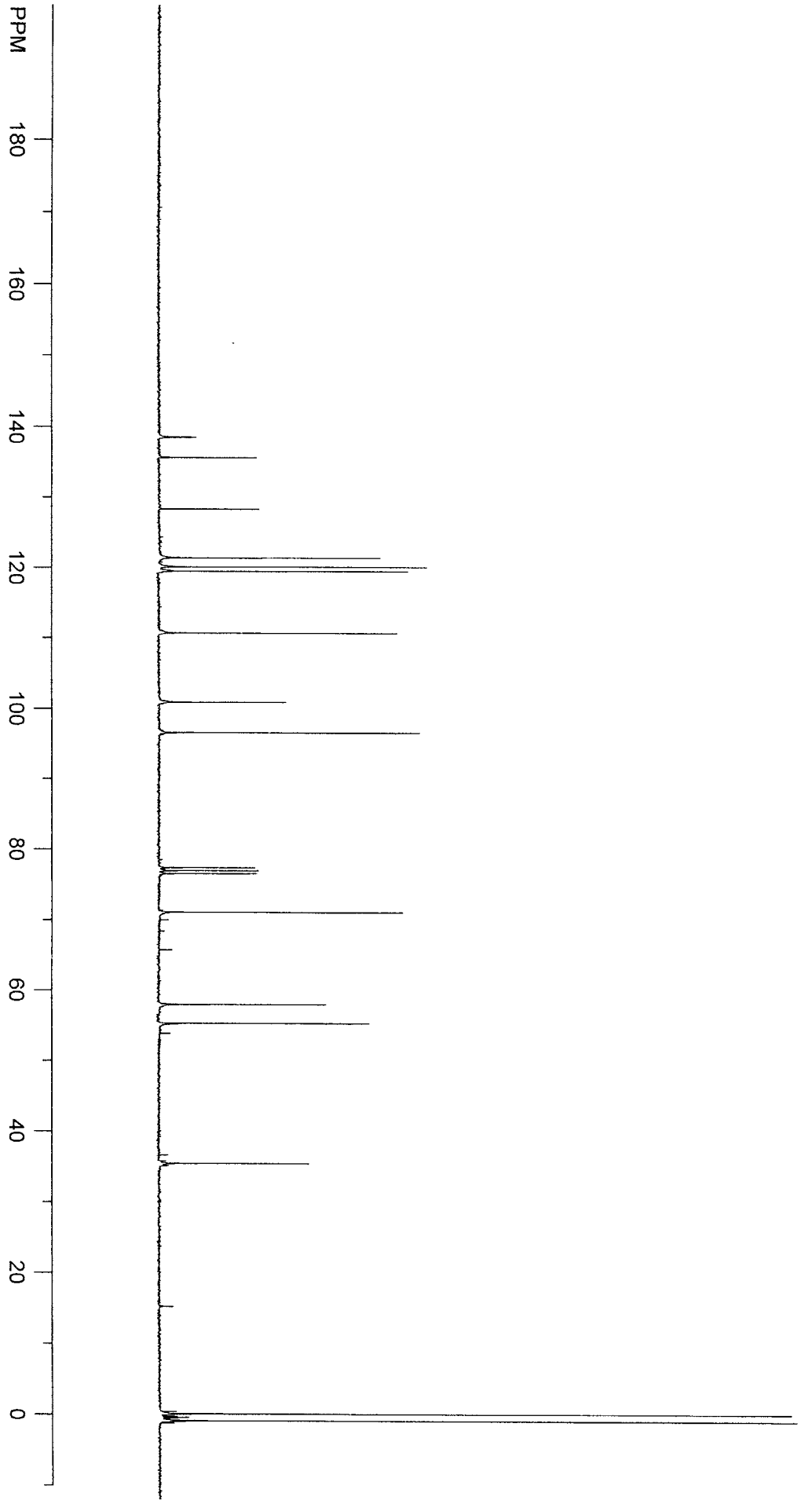

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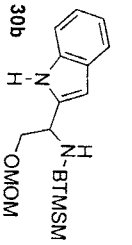

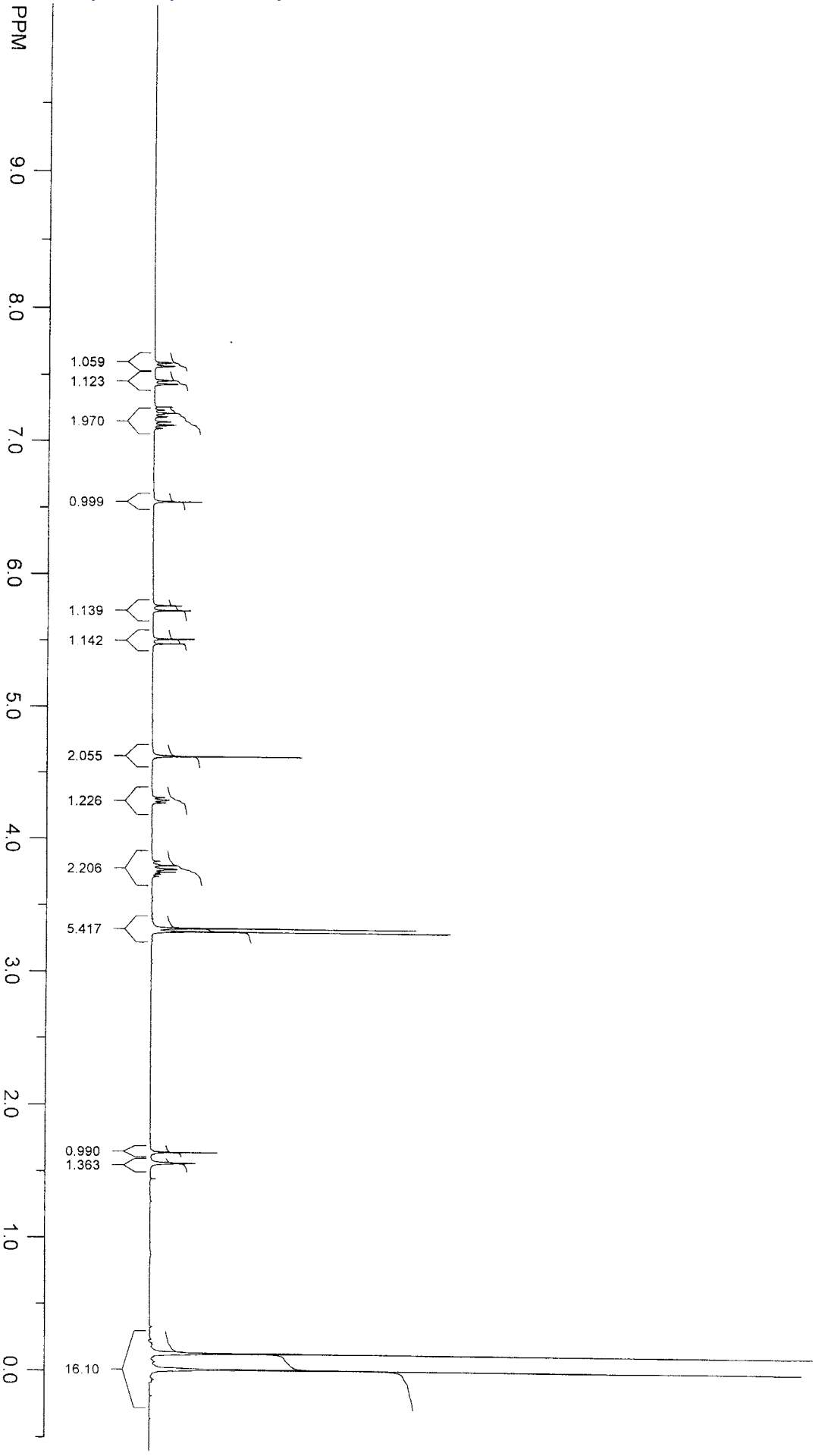

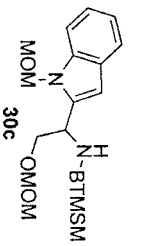

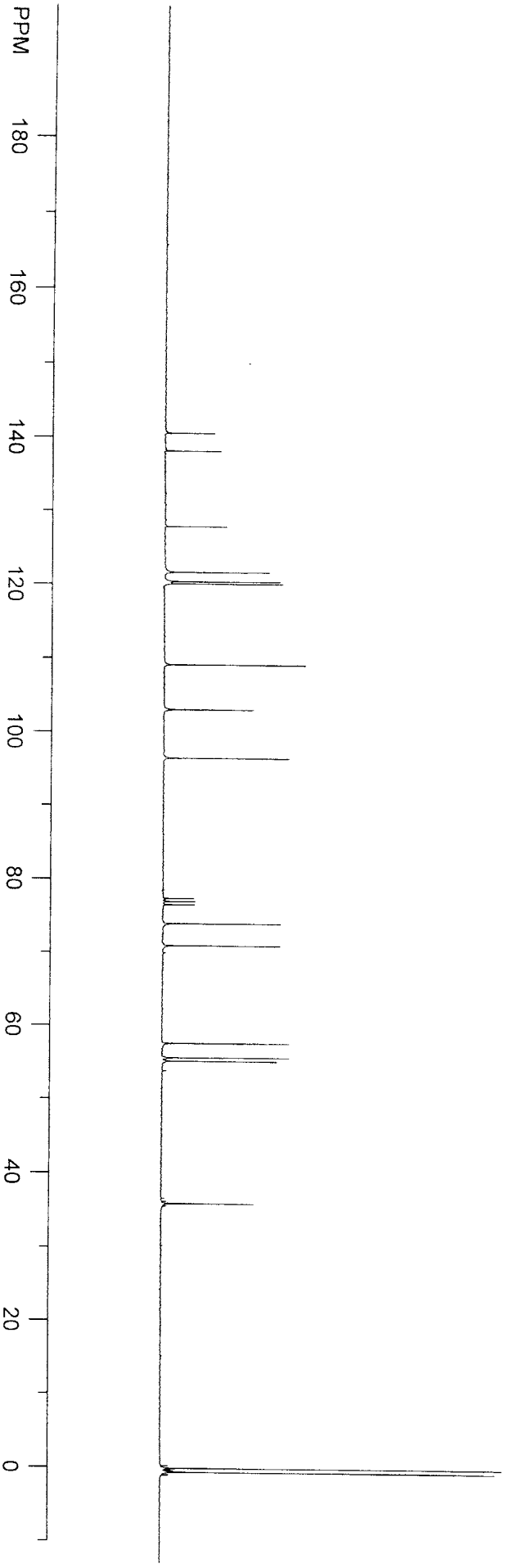

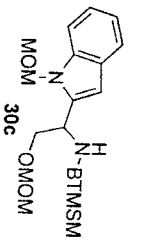

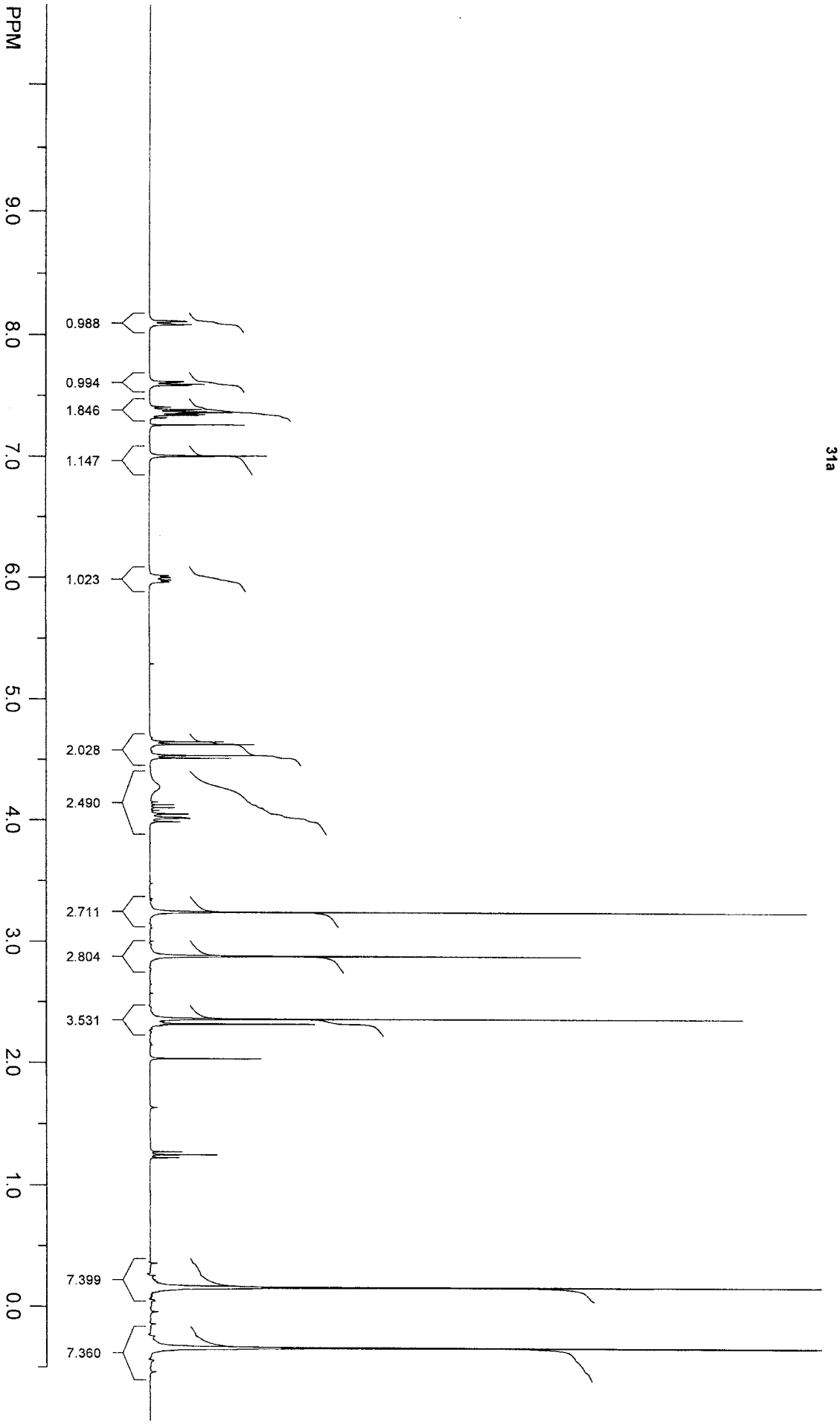

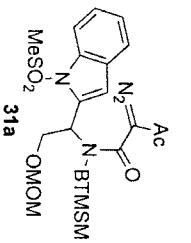

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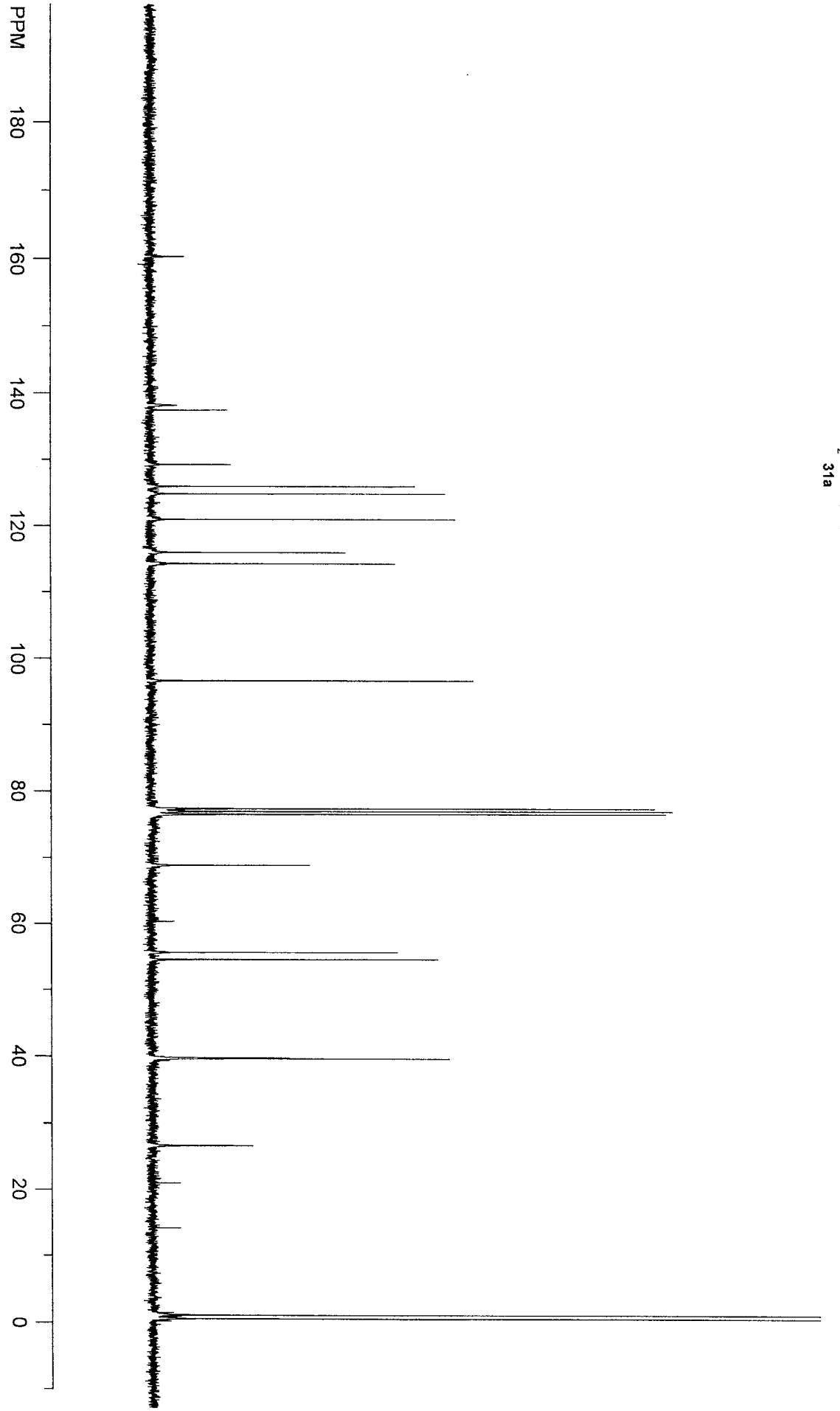

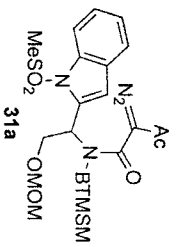

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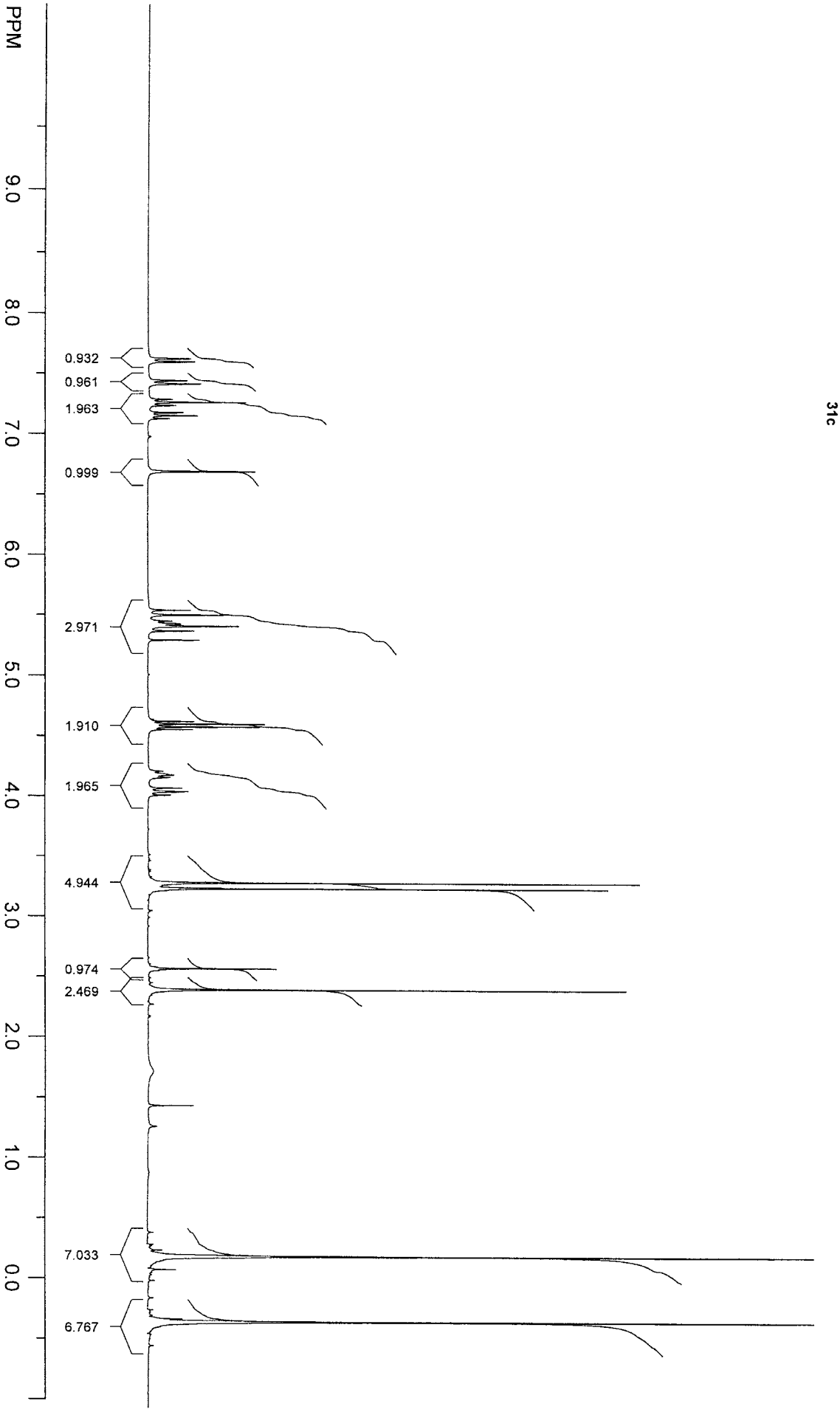

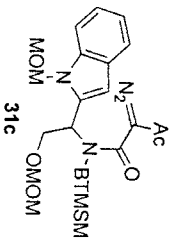

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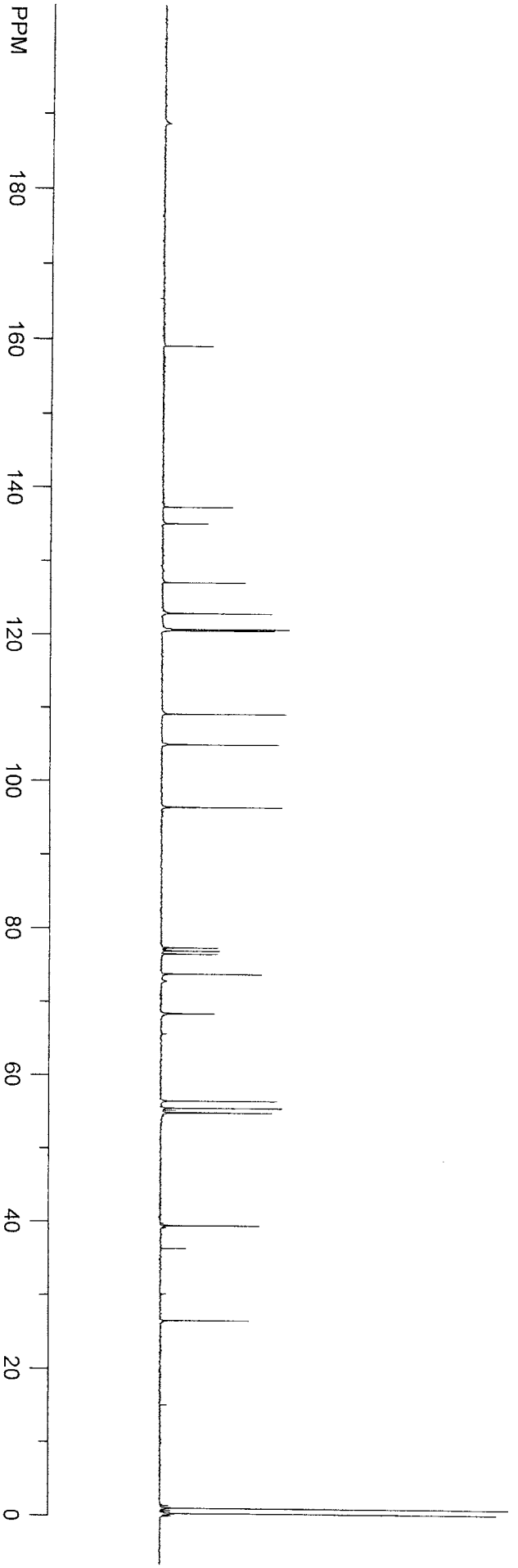

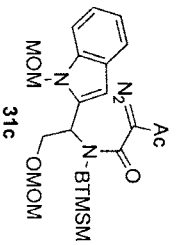

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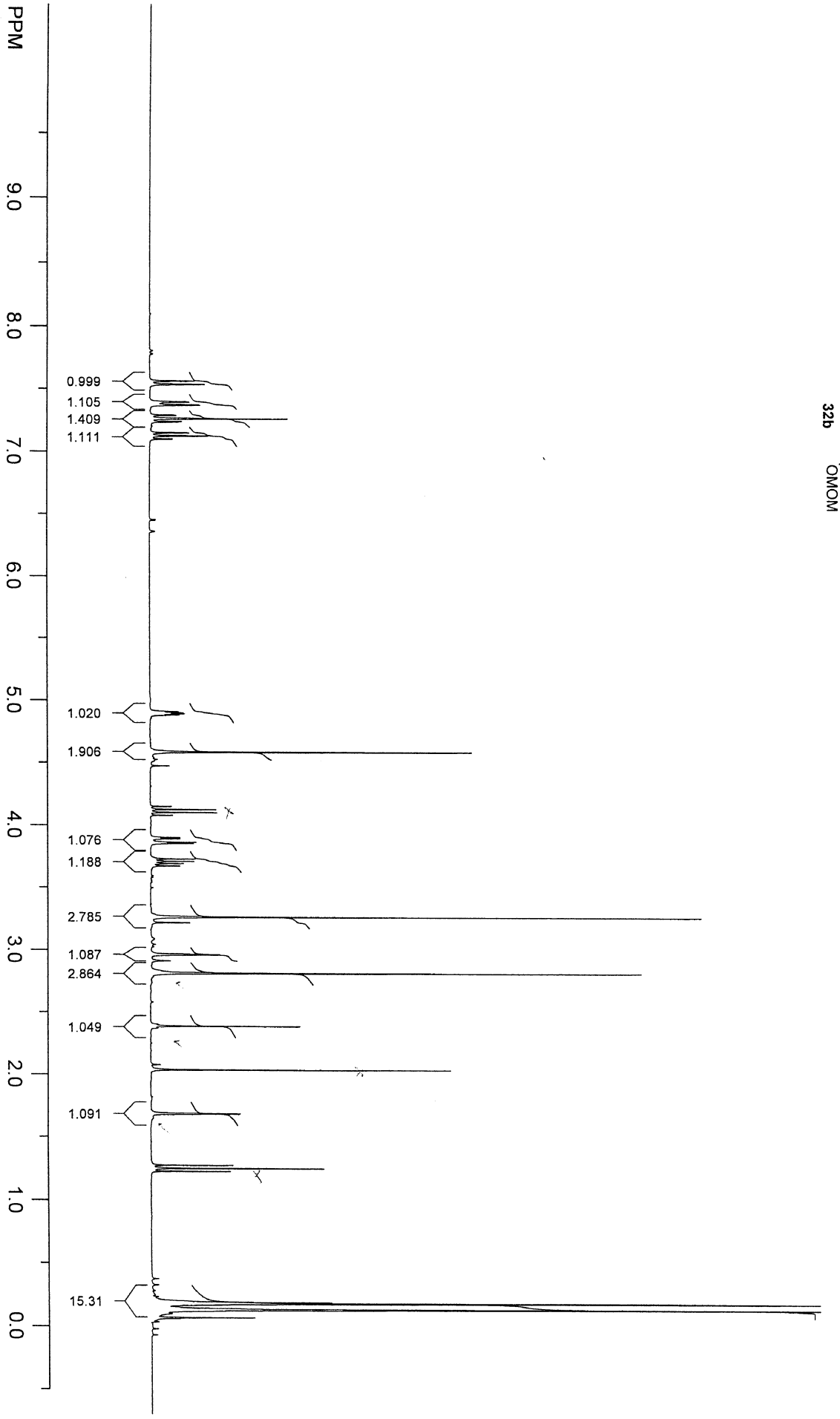
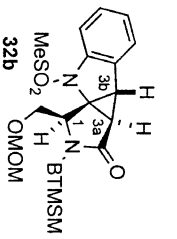
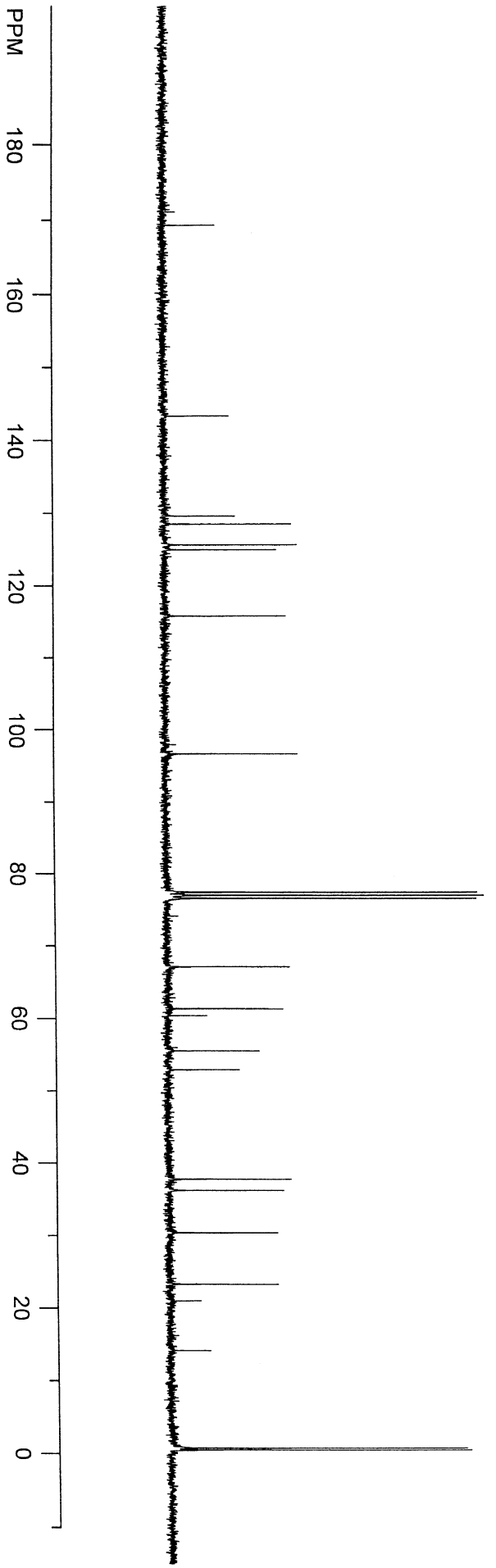
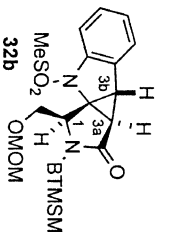
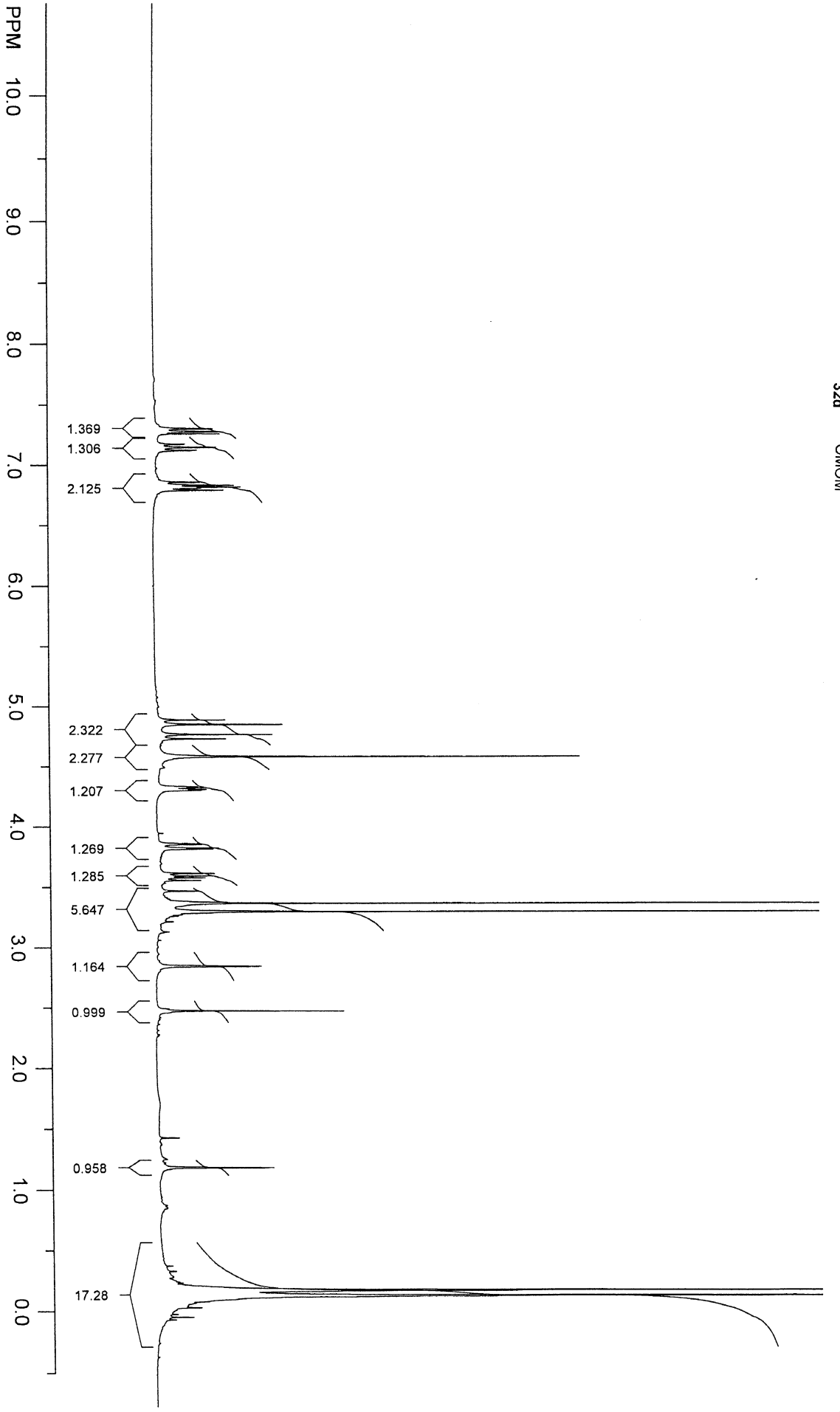


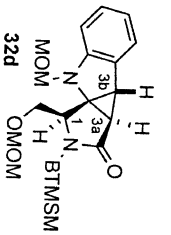


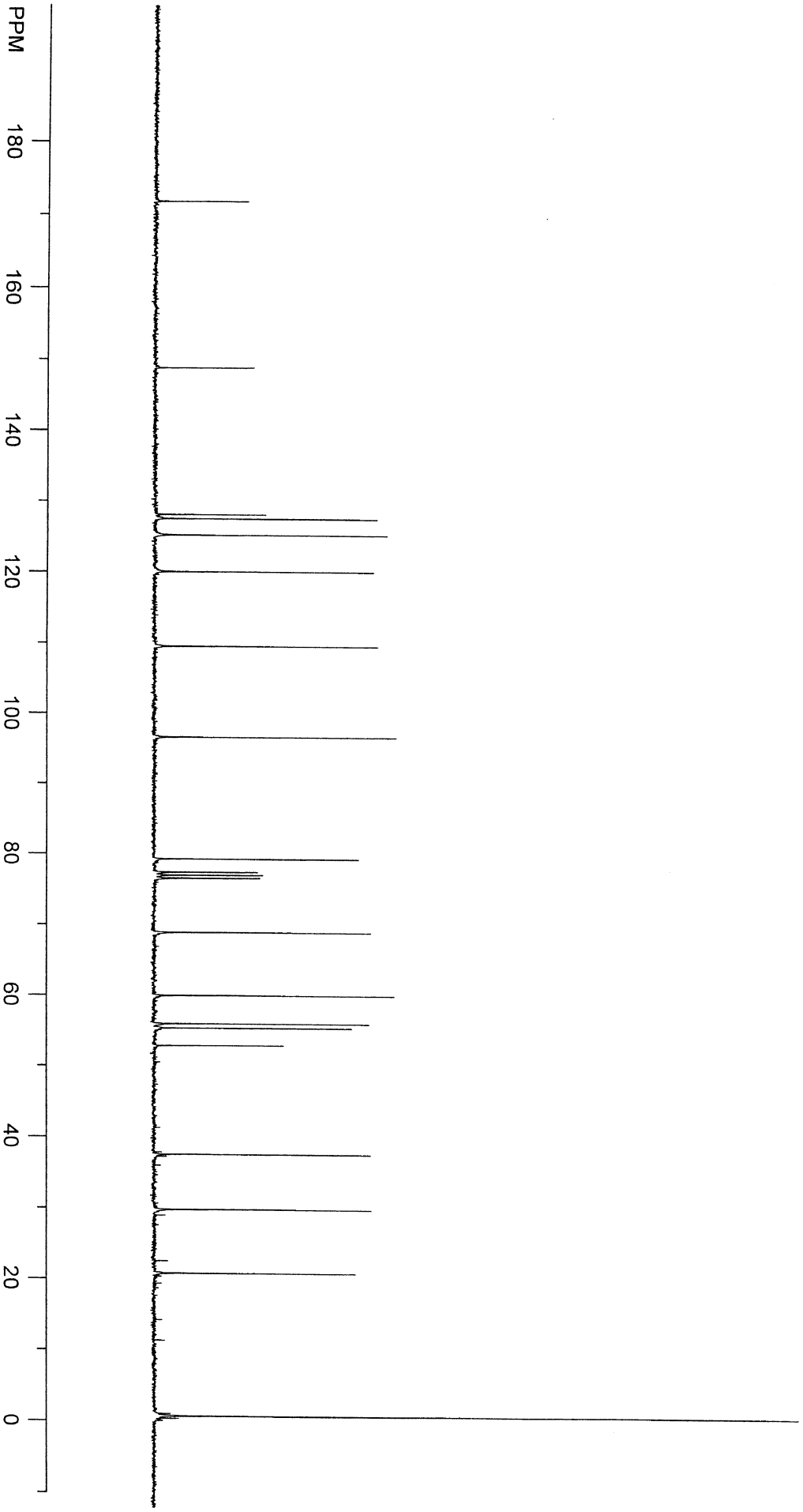


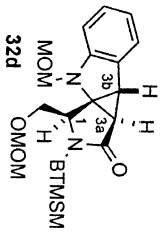


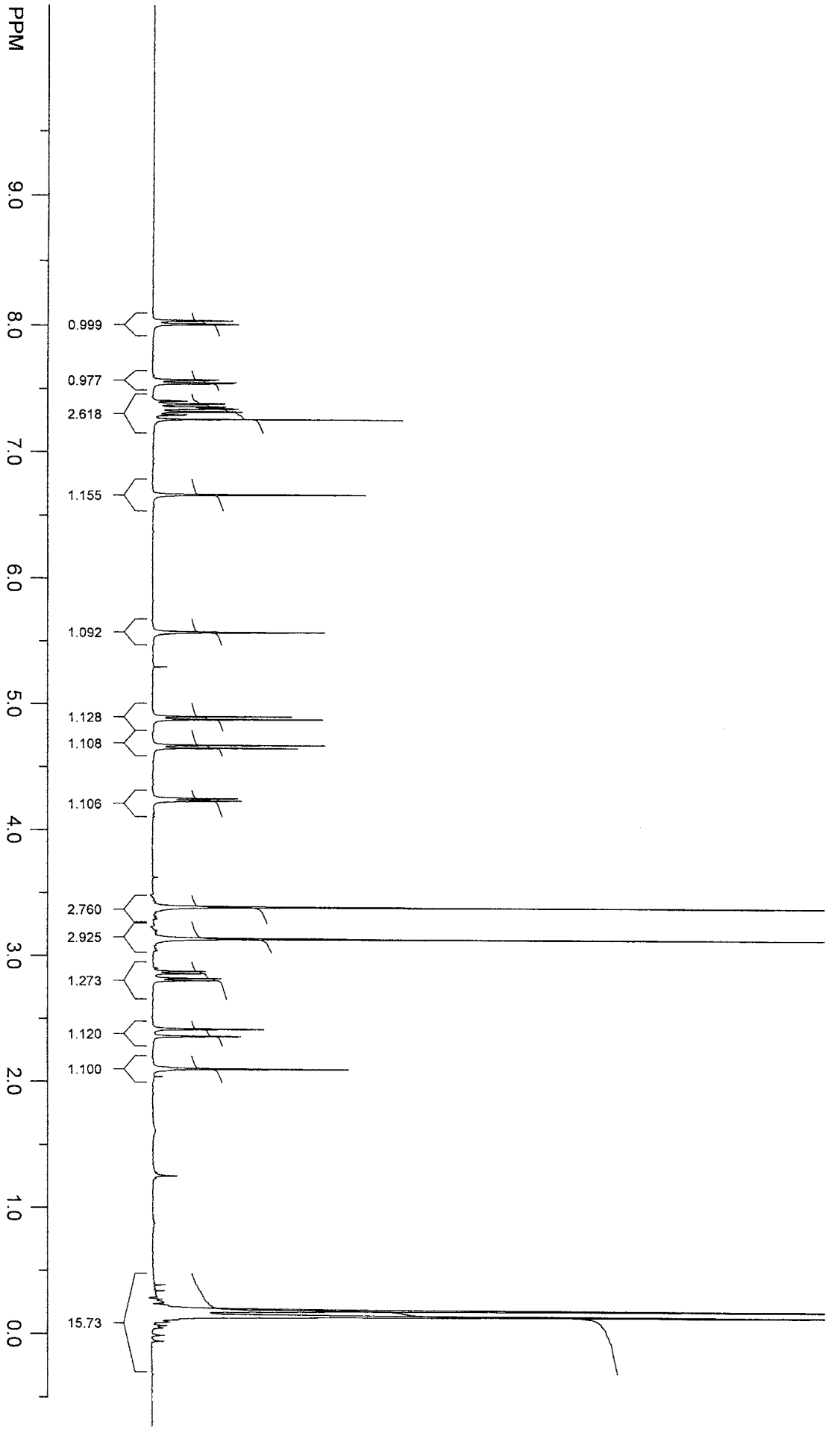
32b

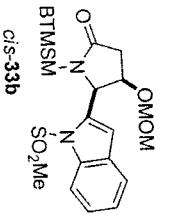




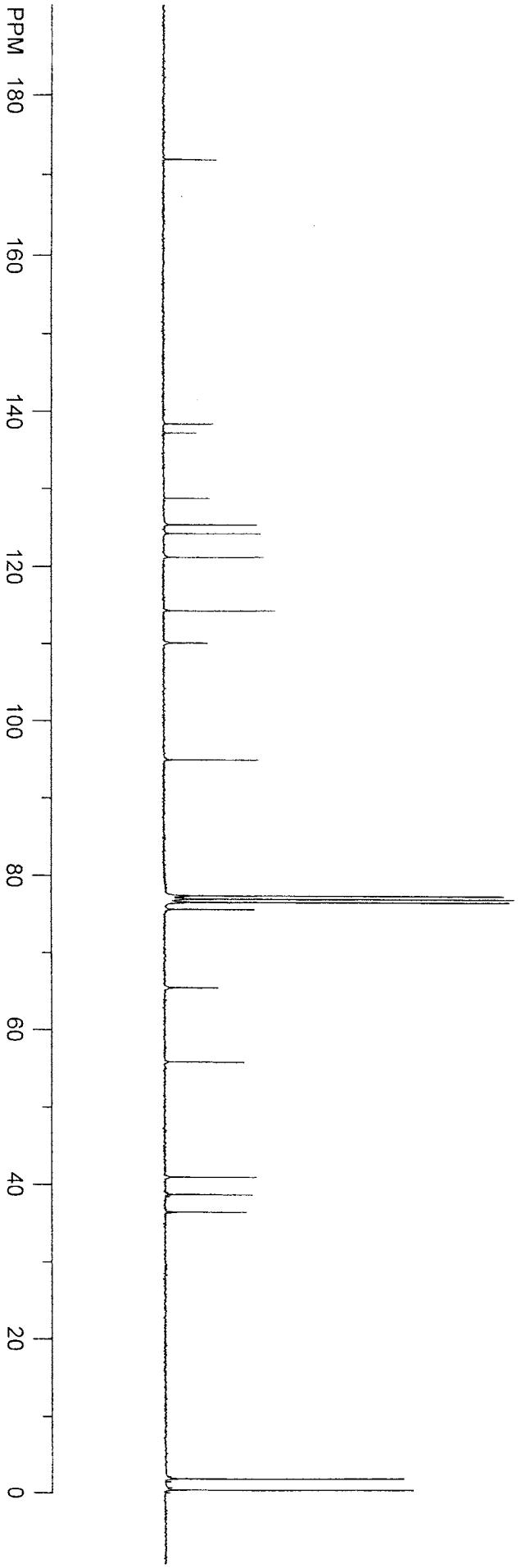


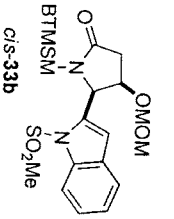




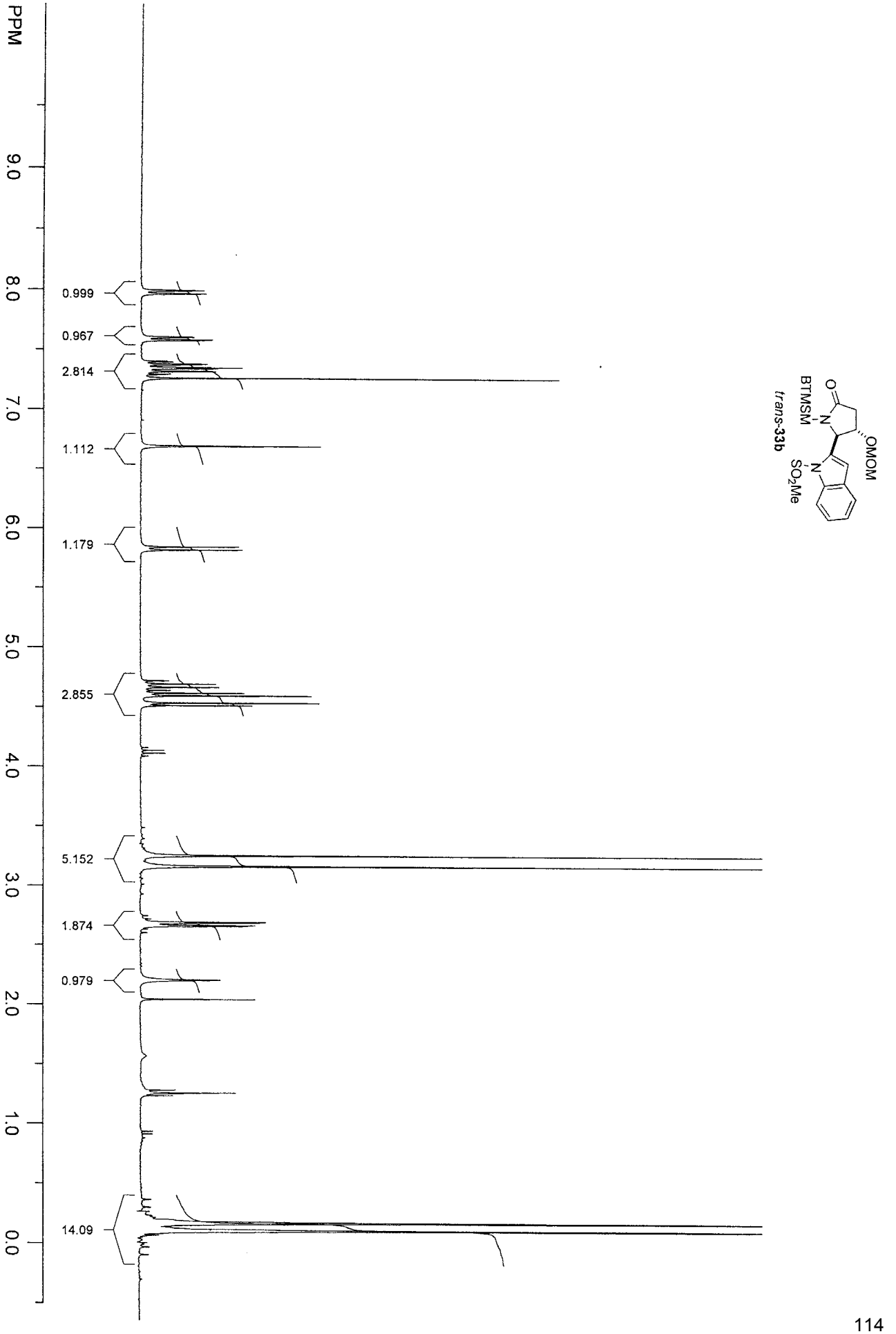


cis-**33b**





cis-**33b**



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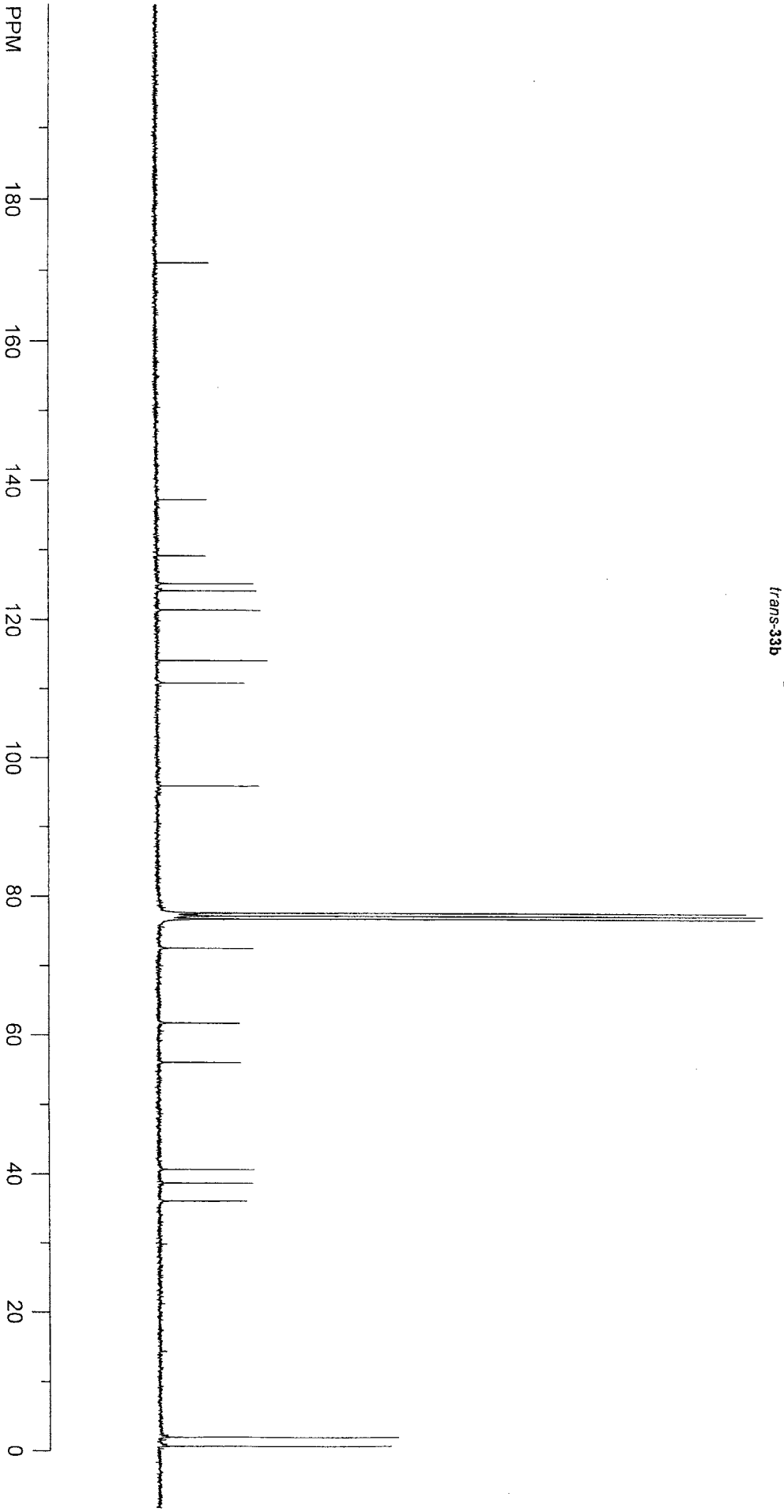

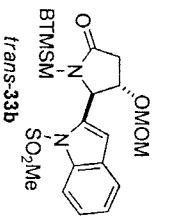

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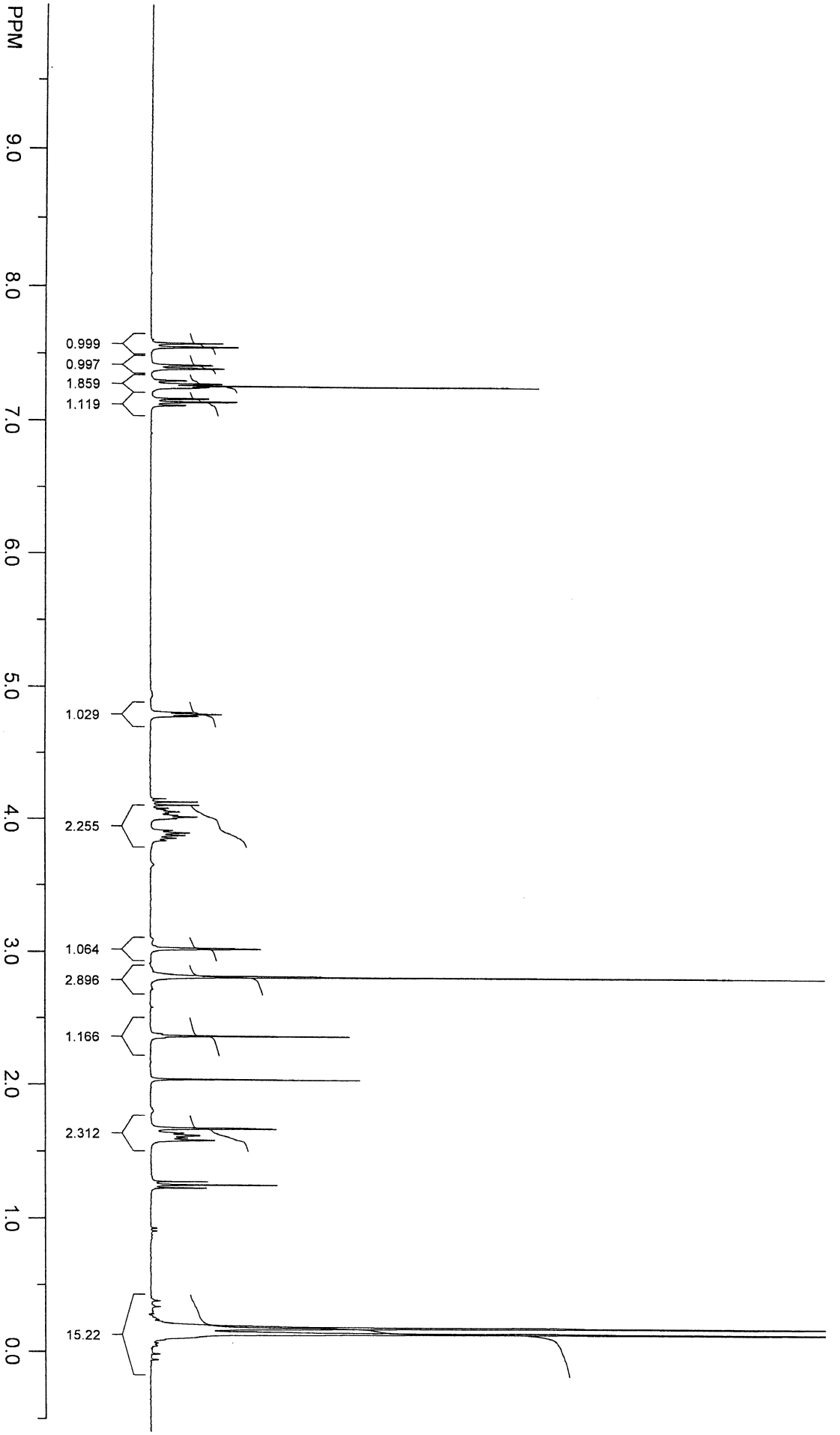

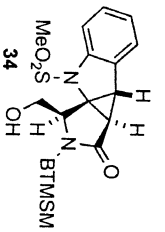

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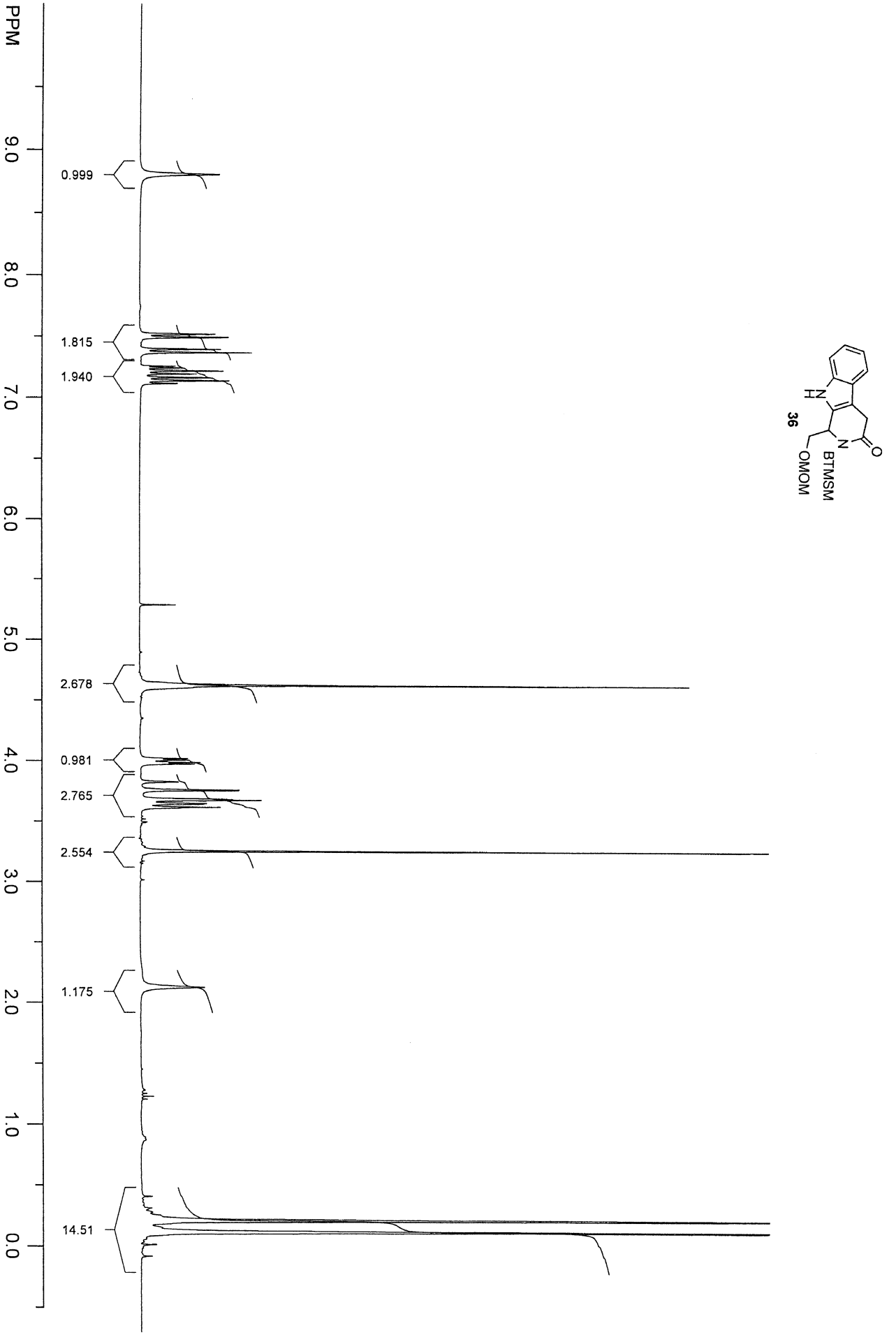

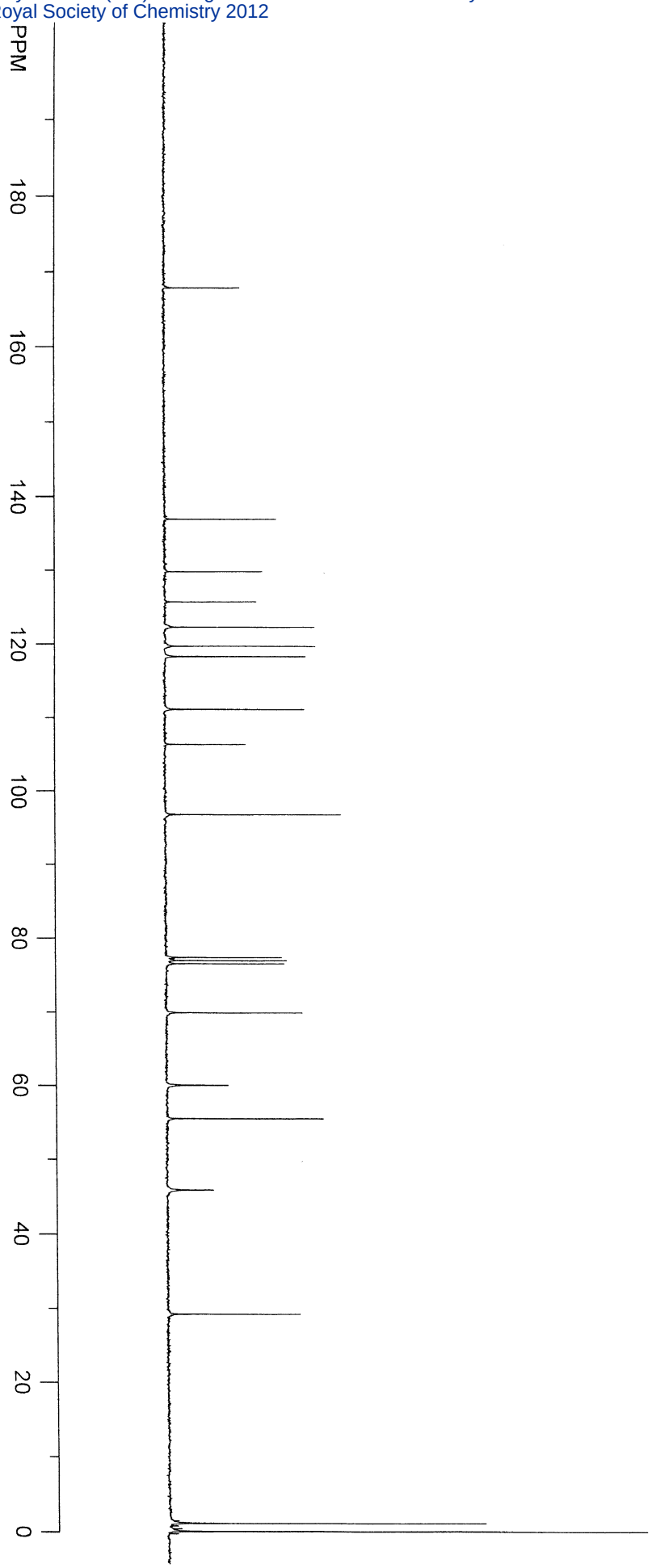

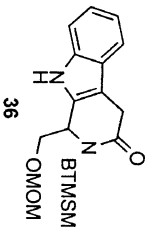

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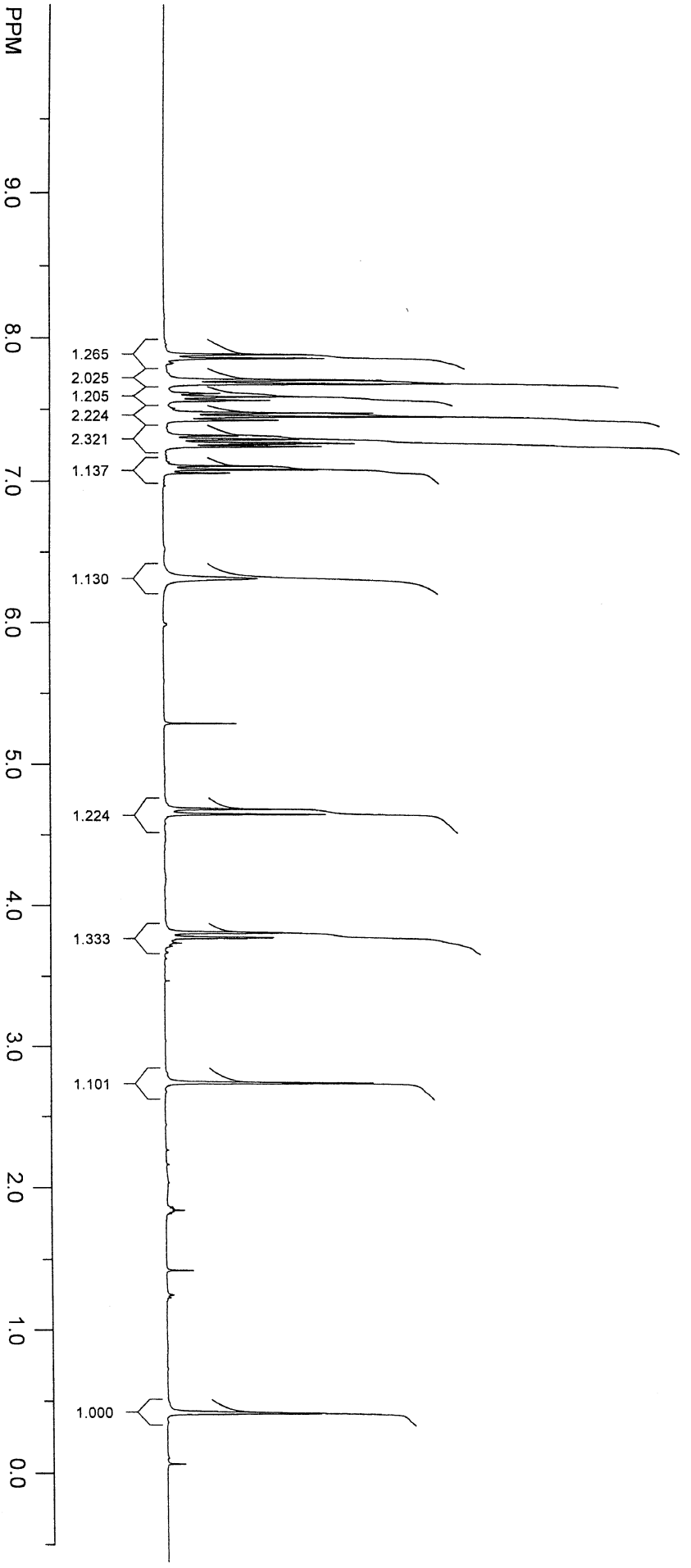

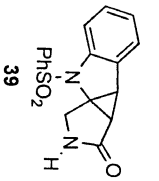

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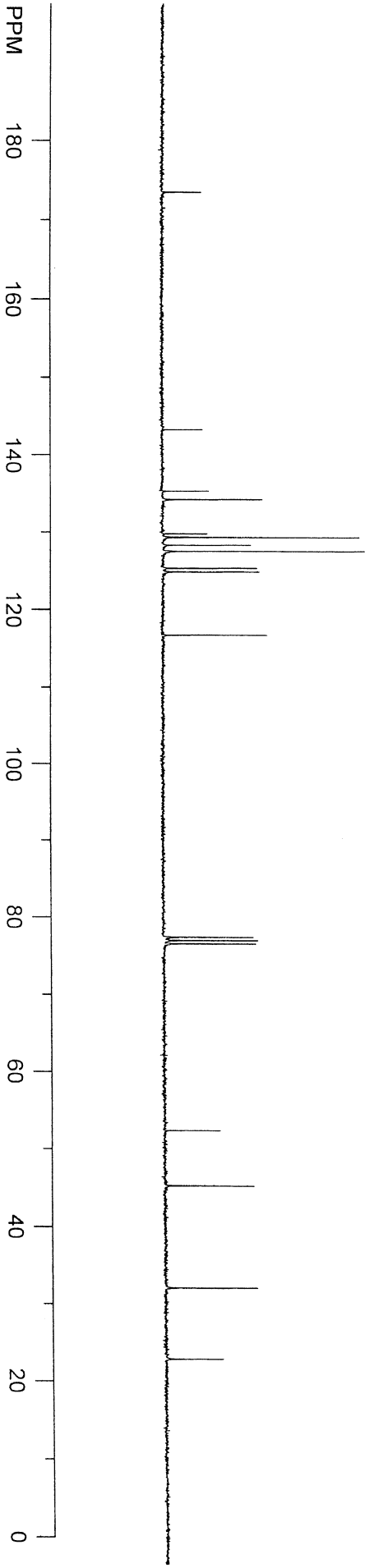

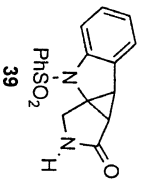

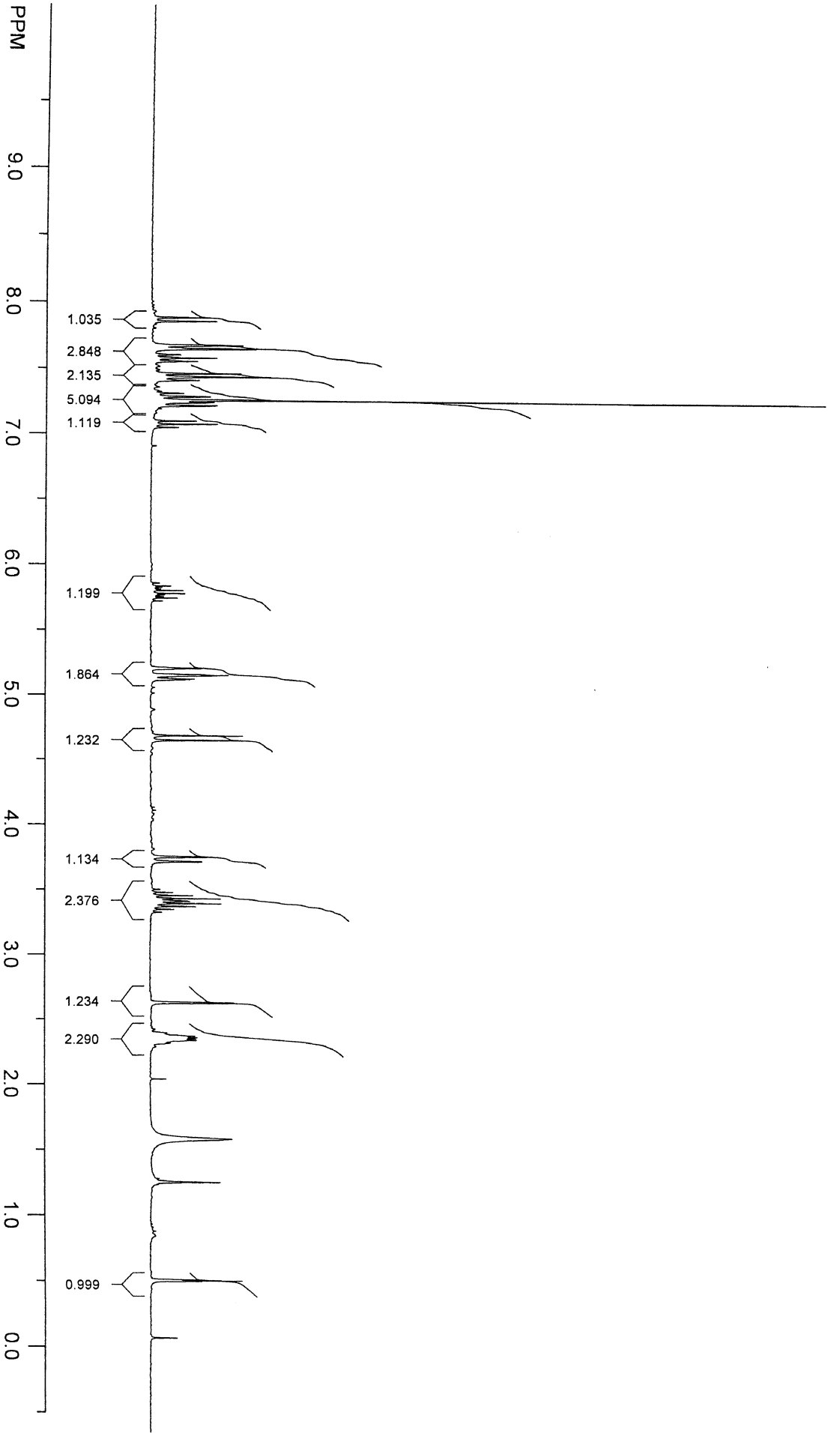

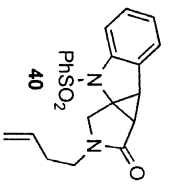

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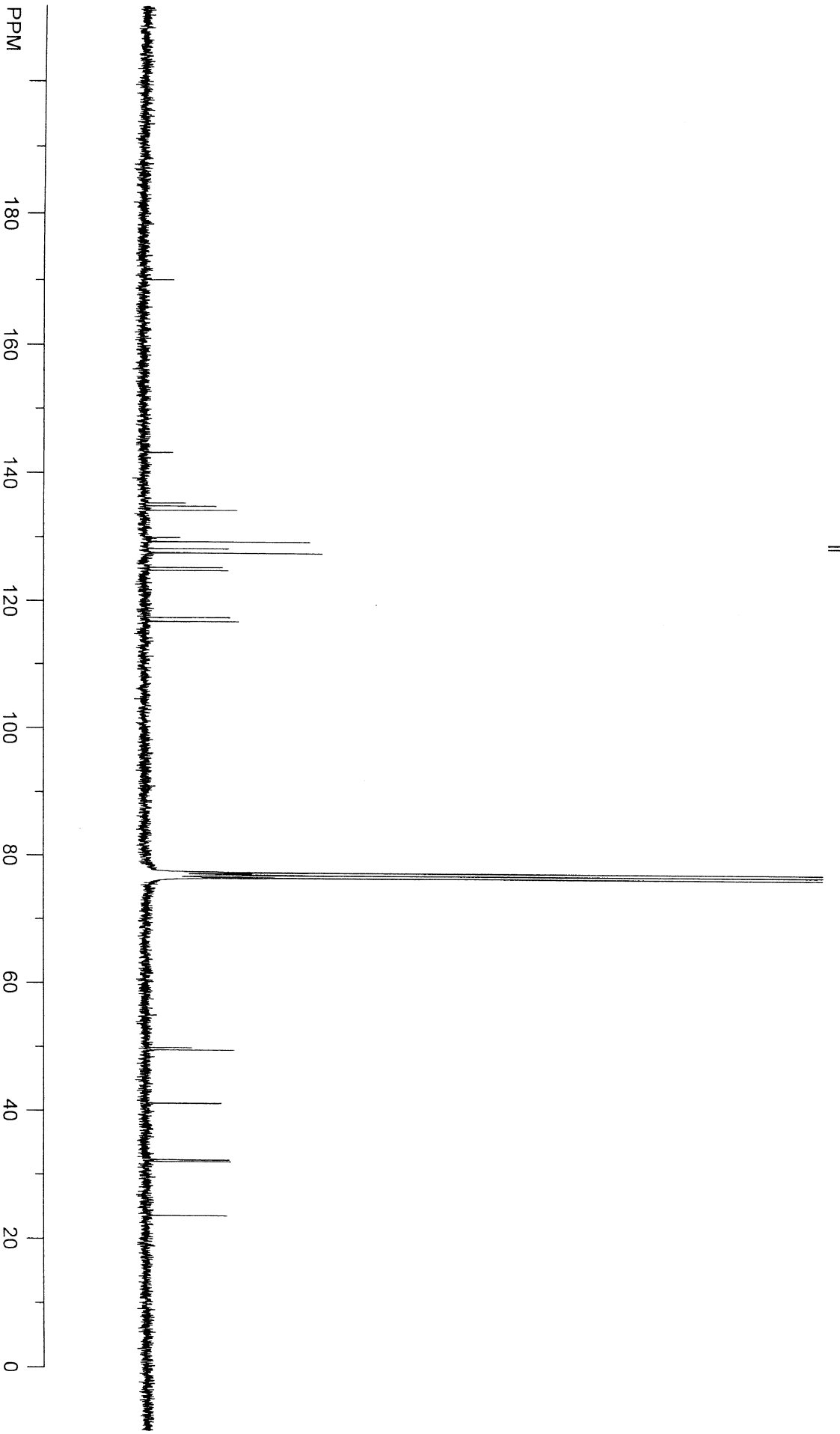

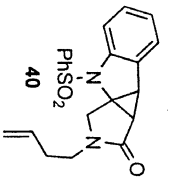

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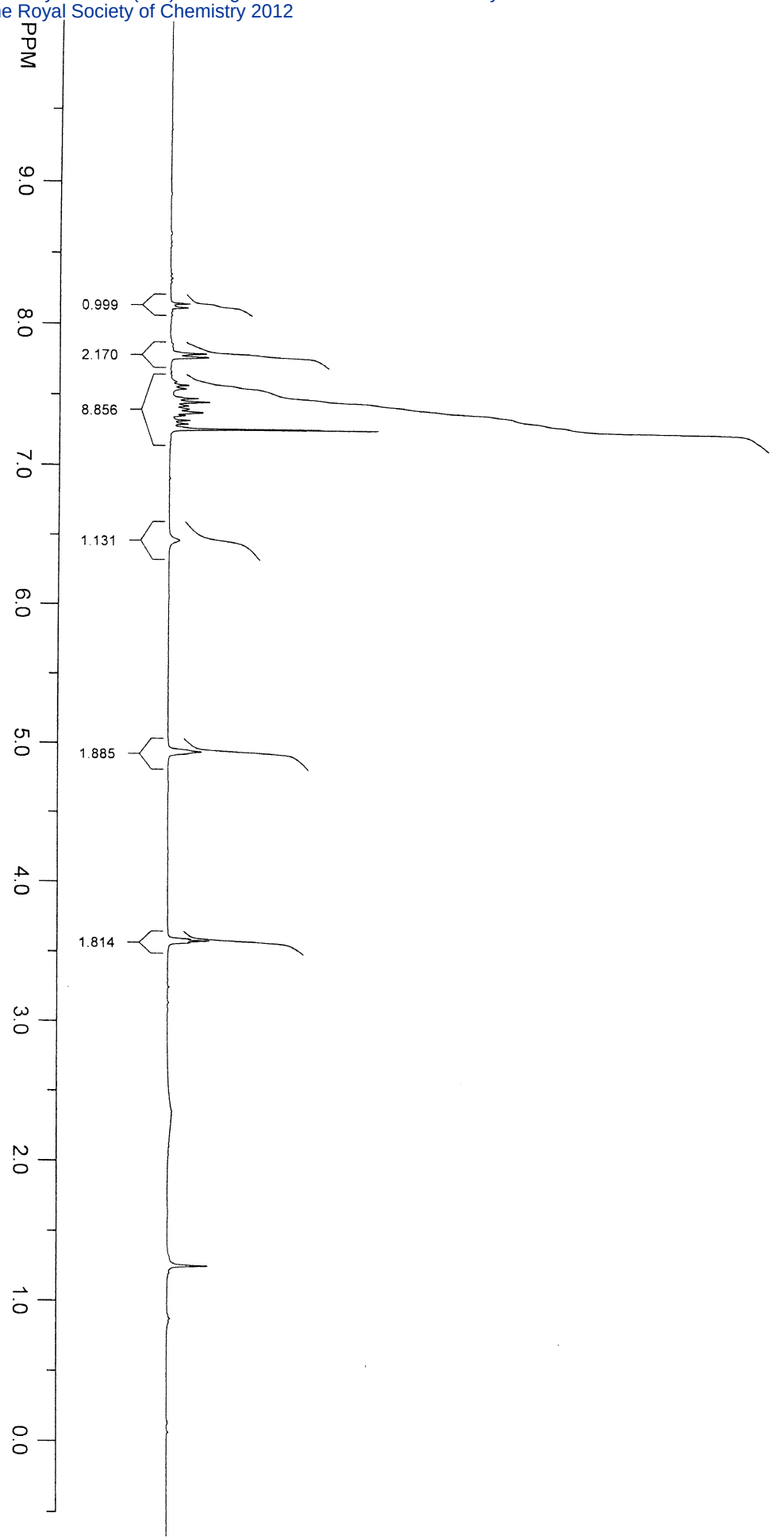
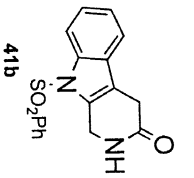
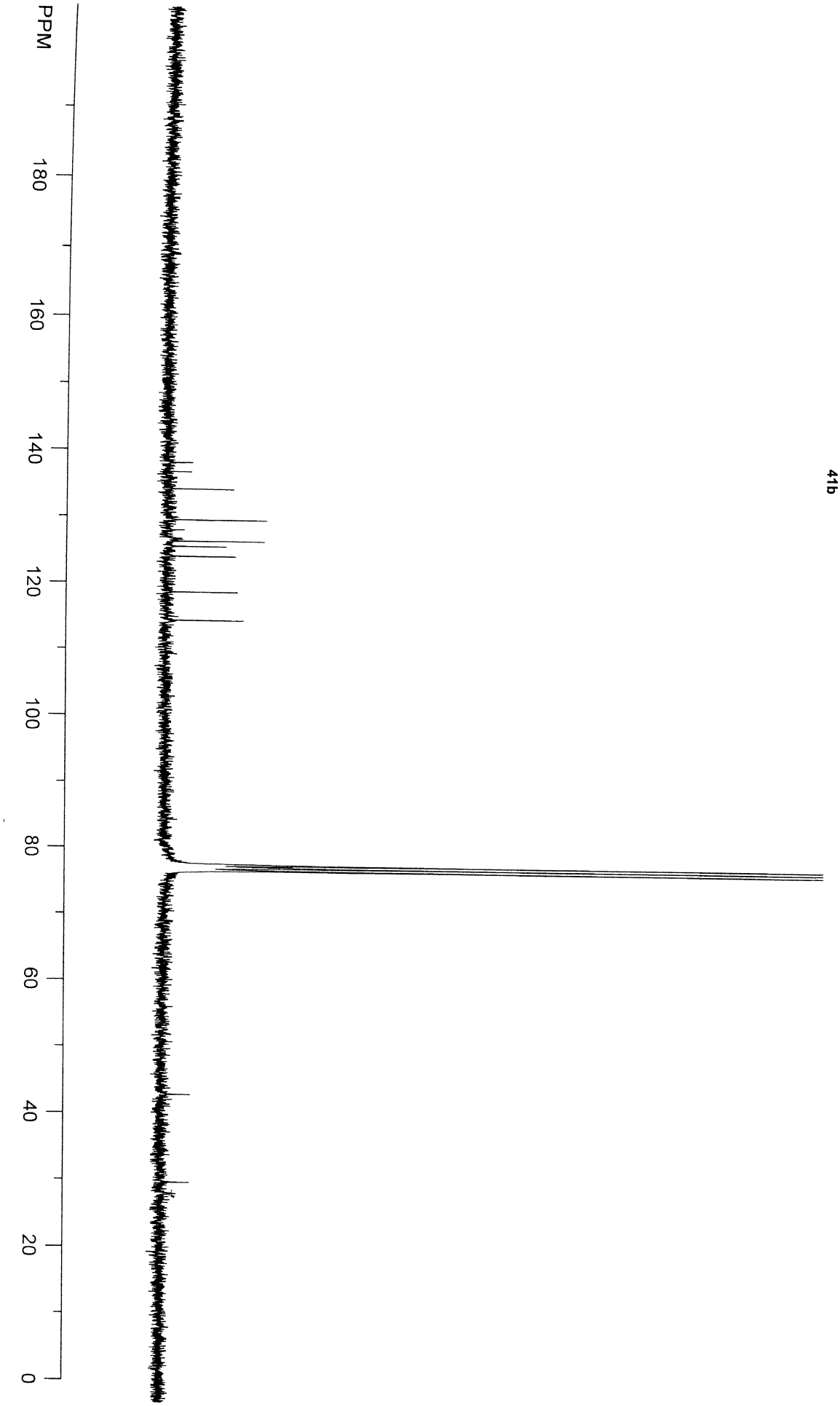
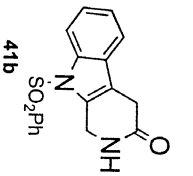


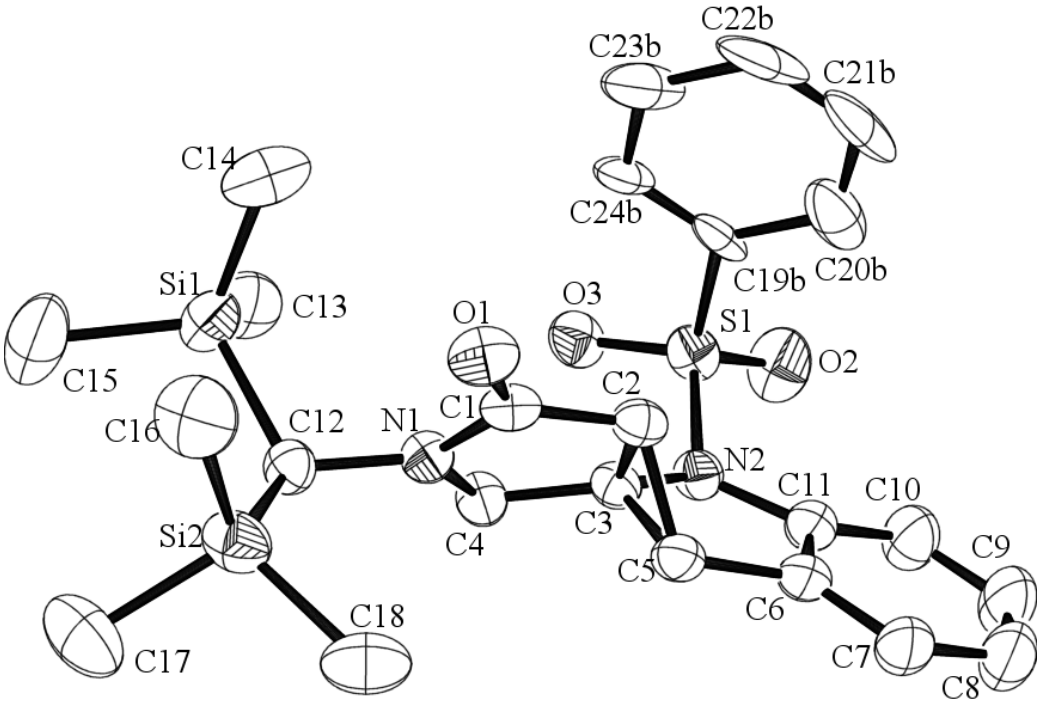






41b

Crystallographic data for **19h**



Crystal data for **19h**: $C_{24}H_{32}N_2O_3SSi_2$, *M*r = 484.76, monoclinic, space group $P2_1/c$, a = 16.8073(4), b = 9.1044(2), c = 23.0328(5) Å, β = 131.7160(10)°, V = 2630.86(10) Å^3, T = 173(2) K, Z = 4, D_{calc} = 1.224 Mg m^{-3}, F(000) = 1032, μ = 0.241 mm^{-1}. 40367 reflections were measured on a Nonius Kappa CCD diffractometer, 4992 were independent (I>2σ(I)). Final R1 = 0.0403, wR2 = 0.0938. CCDC 691157.

Table 1. Crystal data and structure refinement for **19h**.

Identification code	**19h**	
Empirical formula	C24 H32 N2 O3 S Si2	
Formula weight	484.76	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 16.8073(4) Å	α= 90°.
	b = 9.1044(2) Å	β= 131.7160(10)°.
	c = 23.0328(5) Å	γ = 90°.
Volume	2630.86(10) $Å^3$	
Z	4	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	1032	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.37 to 25.68°.	
Index ranges	-20<=h<=20, -11<=k<=11, -28<=l<=27	
Reflections collected	40367	
Independent reflections	4992 [R(int) = 0.0543]	
Completeness to theta = 25.68°	99.9 %	
Absorption correction	Psi-scan	
Max. and min. transmission	0.976 and 0.917	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4992 / 170 / 326	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0938	
R indices (all data)	R1 = 0.0543, wR2 = 0.1019	
Largest diff. peak and hole	0.197 and -0.453 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **19h**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	3305(1)	2224(1)	-437(1)	39(1)
Si(1)	8071(1)	2919(1)	2022(1)	46(1)
Si(2)	8183(1)	5367(1)	3116(1)	45(1)
O(1)	6610(1)	2854(1)	2737(1)	41(1)
O(2)	2224(1)	2153(2)	-1149(1)	63(1)
O(3)	4145(1)	2285(2)	-446(1)	44(1)
N(1)	6299(1)	4083(2)	1736(1)	32(1)
N(2)	3417(1)	3745(2)	18(1)	34(1)
C(1)	5997(1)	3353(2)	2070(1)	33(1)
C(2)	4810(1)	3272(2)	1515(1)	32(1)
C(3)	4451(1)	4042(2)	793(1)	30(1)
C(4)	5422(1)	4480(2)	918(1)	34(1)
C(5)	4259(1)	4759(2)	1275(1)	34(1)
C(6)	3081(1)	4750(2)	766(1)	38(1)
C(7)	2457(2)	5336(2)	901(1)	50(1)
C(8)	1355(2)	5274(3)	306(2)	65(1)
C(9)	899(2)	4652(3)	-402(2)	65(1)
C(10)	1512(2)	4078(3)	-550(1)	54(1)
C(11)	2612(2)	4135(2)	49(1)	39(1)
C(12)	7414(1)	4466(2)	2124(1)	35(1)
C(13)	7327(2)	2606(3)	973(1)	61(1)
C(14)	8065(2)	1181(3)	2444(2)	70(1)
C(15)	9457(2)	3482(4)	2507(2)	81(1)
C(16)	8986(2)	4058(3)	3950(1)	63(1)
C(17)	9125(2)	6711(3)	3232(2)	75(1)
C(18)	7228(2)	6440(3)	3108(1)	61(1)
C(19A)	3451(11)	736(11)	106(7)	43(2)
C(20A)	2639(13)	318(9)	80(10)	56(2)
C(21A)	2824(19)	-729(11)	591(13)	85(3)
C(22A)	3820(20)	-1358(12)	1128(11)	83(4)
C(23A)	4632(16)	-940(12)	1153(8)	67(3)
C(24A)	4447(12)	107(13)	642(7)	48(2)
C(19B)	3676(11)	809(10)	221(7)	36(2)
C(20B)	2961(12)	328(9)	286(8)	62(2)
C(21B)	3280(15)	-666(9)	859(8)	71(3)
C(22B)	4315(16)	-1179(10)	1366(7)	75(3)
C(23B)	5031(14)	-697(11)	1300(7)	63(2)
C(24B)	4711(12)	296(12)	727(7)	42(2)

Table 3. Bond lengths [Å] and angles [°] for **19h**.

S(1)-O(2)	1.4248(15)
S(1)-O(3)	1.4255(14)
S(1)-N(2)	1.6702(16)
S(1)-C(19A)	1.746(3)
S(1)-C(19B)	1.756(2)
Si(1)-C(14)	1.860(3)
Si(1)-C(13)	1.861(2)
Si(1)-C(15)	1.864(3)
Si(1)-C(12)	1.8984(19)
Si(2)-C(16)	1.866(2)
Si(2)-C(18)	1.868(2)
Si(2)-C(17)	1.874(3)
Si(2)-C(12)	1.9057(19)
O(1)-C(1)	1.233(2)
N(1)-C(1)	1.348(2)
N(1)-C(4)	1.469(2)
N(1)-C(12)	1.483(2)
N(2)-C(11)	1.446(2)
N(2)-C(3)	1.467(2)
C(1)-C(2)	1.491(2)
C(2)-C(3)	1.512(2)
C(2)-C(5)	1.521(2)
C(2)-H(2)	1.0000
C(3)-C(5)	1.496(3)
C(3)-C(4)	1.510(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.484(2)
C(5)-H(5)	1.0000
C(6)-C(7)	1.386(3)
C(6)-C(11)	1.388(3)
C(7)-C(8)	1.391(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.379(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.386(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.389(3)
C(10)-H(10)	0.9500
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800

C(18)-H(18C)	0.9800
C(19A)-C(20A)	1.3799
C(19A)-C(24A)	1.3799
C(20A)-C(21A)	1.3800
C(20A)-H(20A)	0.9500
C(21A)-C(22A)	1.3799
C(21A)-H(21A)	0.9500
C(22A)-C(23A)	1.3799
C(22A)-H(22A)	0.9500
C(23A)-C(24A)	1.3800
C(23A)-H(23A)	0.9500
C(24A)-H(24A)	0.9500
C(19B)-C(20B)	1.3799
C(19B)-C(24B)	1.3799
C(20B)-C(21B)	1.3800
C(20B)-H(20B)	0.9500
C(21B)-C(22B)	1.3799
C(21B)-H(21B)	0.9500
C(22B)-C(23B)	1.3799
C(22B)-H(22B)	0.9500
C(23B)-C(24B)	1.3800
C(23B)-H(23B)	0.9500
C(24B)-H(24B)	0.9500
O(2)-S(1)-O(3)	120.17(10)
O(2)-S(1)-N(2)	106.50(9)
O(3)-S(1)-N(2)	106.08(8)
O(2)-S(1)-C(19A)	104.6(5)
O(3)-S(1)-C(19A)	111.9(5)
N(2)-S(1)-C(19A)	106.9(5)
O(2)-S(1)-C(19B)	114.1(5)
O(3)-S(1)-C(19B)	104.8(4)
N(2)-S(1)-C(19B)	103.9(4)
C(14)-Si(1)-C(13)	108.37(13)
C(14)-Si(1)-C(15)	111.14(14)
C(13)-Si(1)-C(15)	108.13(13)
C(14)-Si(1)-C(12)	111.15(11)
C(13)-Si(1)-C(12)	109.29(10)
C(15)-Si(1)-C(12)	108.70(11)
C(16)-Si(2)-C(18)	111.79(12)
C(16)-Si(2)-C(17)	107.83(12)
C(18)-Si(2)-C(17)	107.40(13)
C(16)-Si(2)-C(12)	114.07(10)
C(18)-Si(2)-C(12)	108.72(10)
C(17)-Si(2)-C(12)	106.69(11)
C(1)-N(1)-C(4)	114.59(14)
C(1)-N(1)-C(12)	125.24(15)
C(4)-N(1)-C(12)	120.15(14)
C(11)-N(2)-C(3)	106.54(14)
C(11)-N(2)-S(1)	121.08(12)
C(3)-N(2)-S(1)	117.66(12)
O(1)-C(1)-N(1)	124.96(17)
O(1)-C(1)-C(2)	125.61(17)
N(1)-C(1)-C(2)	109.41(15)
C(1)-C(2)-C(3)	104.32(14)
C(1)-C(2)-C(5)	114.28(15)
C(3)-C(2)-C(5)	59.09(12)
C(1)-C(2)-H(2)	120.8
C(3)-C(2)-H(2)	120.8
C(5)-C(2)-H(2)	120.8

N(2)-C(3)-C(5)	108.50(14)
N(2)-C(3)-C(4)	122.36(15)
C(5)-C(3)-C(4)	118.87(15)
N(2)-C(3)-C(2)	122.39(15)
C(5)-C(3)-C(2)	60.76(12)
C(4)-C(3)-C(2)	108.89(14)
N(1)-C(4)-C(3)	102.36(14)
N(1)-C(4)-H(4A)	111.3
C(3)-C(4)-H(4A)	111.3
N(1)-C(4)-H(4B)	111.3
C(3)-C(4)-H(4B)	111.3
H(4A)-C(4)-H(4B)	109.2
C(6)-C(5)-C(3)	104.14(15)
C(6)-C(5)-C(2)	116.82(15)
C(3)-C(5)-C(2)	60.15(11)
C(6)-C(5)-H(5)	119.9
C(3)-C(5)-H(5)	119.9
C(2)-C(5)-H(5)	119.9
C(7)-C(6)-C(11)	120.43(18)
C(7)-C(6)-C(5)	129.18(18)
C(11)-C(6)-C(5)	110.23(17)
C(6)-C(7)-C(8)	118.3(2)
C(6)-C(7)-H(7)	120.8
C(8)-C(7)-H(7)	120.8
C(9)-C(8)-C(7)	120.6(2)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(8)-C(9)-C(10)	121.8(2)
C(8)-C(9)-H(9)	119.1
C(10)-C(9)-H(9)	119.1
C(9)-C(10)-C(11)	117.2(2)
C(9)-C(10)-H(10)	121.4
C(11)-C(10)-H(10)	121.4
C(6)-C(11)-C(10)	121.60(19)
C(6)-C(11)-N(2)	110.31(16)
C(10)-C(11)-N(2)	127.79(19)
N(1)-C(12)-Si(1)	110.87(12)
N(1)-C(12)-Si(2)	113.64(13)
Si(1)-C(12)-Si(2)	118.76(9)
N(1)-C(12)-H(12)	103.9
Si(1)-C(12)-H(12)	103.9
Si(2)-C(12)-H(12)	103.9
Si(1)-C(13)-H(13A)	109.5
Si(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
Si(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
Si(1)-C(14)-H(14A)	109.5
Si(1)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
Si(1)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Si(1)-C(15)-H(15A)	109.5
Si(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
Si(2)-C(16)-H(16A)	109.5
Si(2)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
Si(2)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
Si(2)-C(17)-H(17A)	109.5
Si(2)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
Si(2)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
Si(2)-C(18)-H(18A)	109.5
Si(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
Si(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20A)-C(19A)-C(24A)	120.0
C(20A)-C(19A)-S(1)	121.4(6)
C(24A)-C(19A)-S(1)	118.1(6)
C(19A)-C(20A)-C(21A)	120.0
C(19A)-C(20A)-H(20A)	120.0
C(21A)-C(20A)-H(20A)	120.0
C(22A)-C(21A)-C(20A)	120.0
C(22A)-C(21A)-H(21A)	120.0
C(20A)-C(21A)-H(21A)	120.0
C(23A)-C(22A)-C(21A)	120.0
C(23A)-C(22A)-H(22A)	120.0
C(21A)-C(22A)-H(22A)	120.0
C(22A)-C(23A)-C(24A)	120.0
C(22A)-C(23A)-H(23A)	120.0
C(24A)-C(23A)-H(23A)	120.0
C(19A)-C(24A)-C(23A)	120.0
C(19A)-C(24A)-H(24A)	120.0
C(23A)-C(24A)-H(24A)	120.0
C(20B)-C(19B)-C(24B)	120.0
C(20B)-C(19B)-S(1)	119.5(5)
C(24B)-C(19B)-S(1)	120.1(5)
C(19B)-C(20B)-C(21B)	120.0
C(19B)-C(20B)-H(20B)	120.0
C(21B)-C(20B)-H(20B)	120.0
C(22B)-C(21B)-C(20B)	120.0
C(22B)-C(21B)-H(21B)	120.0
C(20B)-C(21B)-H(21B)	120.0
C(21B)-C(22B)-C(23B)	120.0
C(21B)-C(22B)-H(22B)	120.0
C(23B)-C(22B)-H(22B)	120.0
C(22B)-C(23B)-C(24B)	120.0
C(22B)-C(23B)-H(23B)	120.0
C(24B)-C(23B)-H(23B)	120.0
C(19B)-C(24B)-C(23B)	120.0
C(19B)-C(24B)-H(24B)	120.0
C(23B)-C(24B)-H(24B)	120.0

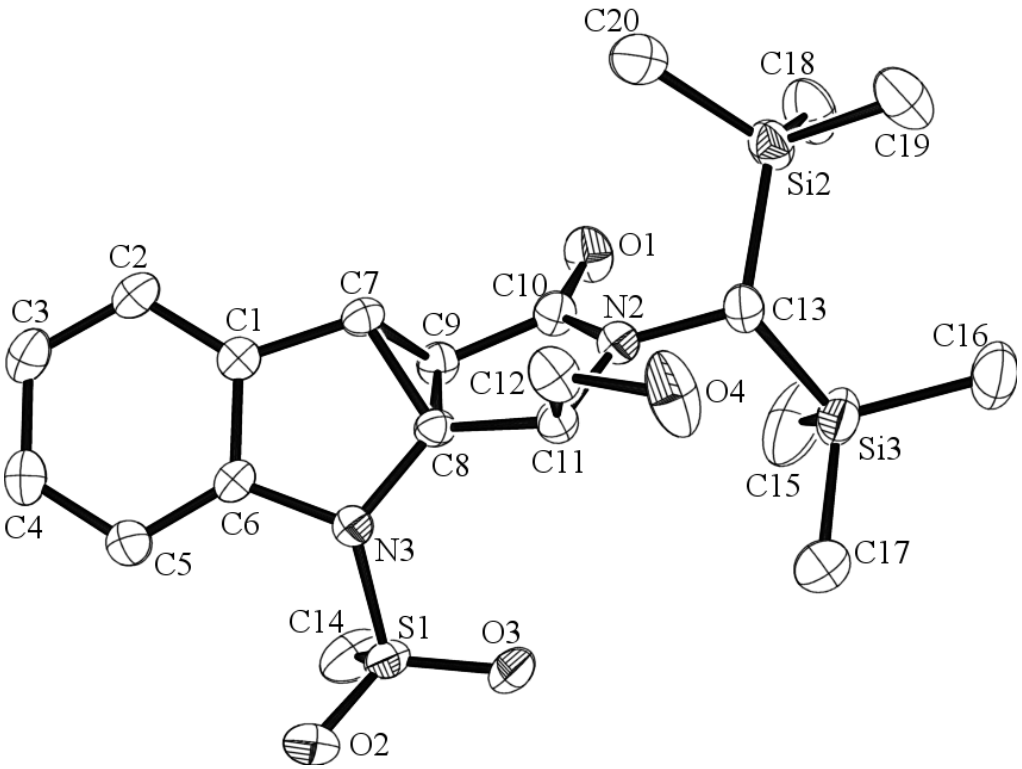
Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **19h**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	44(1)	42(1)	36(1)	-8(1)	28(1)	-8(1)
Si(1)	41(1)	50(1)	44(1)	-1(1)	27(1)	7(1)
Si(2)	46(1)	41(1)	34(1)	-6(1)	21(1)	-7(1)
O(1)	49(1)	41(1)	29(1)	9(1)	25(1)	8(1)
O(2)	44(1)	83(1)	42(1)	-27(1)	21(1)	-11(1)
O(3)	55(1)	45(1)	48(1)	0(1)	41(1)	-4(1)
N(1)	31(1)	33(1)	25(1)	5(1)	16(1)	2(1)
N(2)	31(1)	34(1)	30(1)	-3(1)	18(1)	-2(1)
C(1)	42(1)	27(1)	31(1)	1(1)	24(1)	4(1)
C(2)	40(1)	28(1)	33(1)	1(1)	26(1)	0(1)
C(3)	31(1)	28(1)	27(1)	1(1)	18(1)	-1(1)
C(4)	31(1)	38(1)	28(1)	7(1)	17(1)	1(1)
C(5)	34(1)	28(1)	36(1)	-4(1)	22(1)	-2(1)
C(6)	37(1)	28(1)	45(1)	-8(1)	26(1)	-4(1)
C(7)	45(1)	44(1)	63(1)	-19(1)	37(1)	-6(1)
C(8)	45(1)	65(2)	84(2)	-29(1)	43(1)	-9(1)
C(9)	34(1)	69(2)	74(2)	-24(1)	29(1)	-8(1)
C(10)	37(1)	60(1)	51(1)	-16(1)	24(1)	-7(1)
C(11)	36(1)	35(1)	44(1)	-6(1)	25(1)	-3(1)
C(12)	31(1)	37(1)	31(1)	2(1)	18(1)	0(1)
C(13)	70(2)	61(2)	60(2)	-12(1)	47(1)	0(1)
C(14)	85(2)	52(1)	76(2)	13(1)	54(2)	27(1)
C(15)	47(1)	107(2)	83(2)	-11(2)	41(1)	7(2)
C(16)	53(1)	70(2)	31(1)	-1(1)	14(1)	-3(1)
C(17)	70(2)	68(2)	68(2)	-17(1)	37(2)	-29(1)
C(18)	83(2)	43(1)	57(1)	-7(1)	47(1)	3(1)
C(19A)	56(4)	34(4)	58(4)	-17(3)	46(4)	-17(3)
C(20A)	78(5)	39(3)	100(6)	-36(3)	79(5)	-34(3)
C(21A)	144(8)	41(4)	166(9)	-40(5)	143(8)	-43(5)
C(22A)	173(11)	34(5)	140(7)	-3(5)	145(8)	-7(5)
C(23A)	115(7)	30(3)	96(6)	11(3)	87(6)	2(4)
C(24A)	73(5)	33(4)	59(4)	-8(3)	53(4)	-16(3)
C(19B)	63(5)	21(3)	50(4)	-17(2)	49(4)	-21(3)
C(20B)	80(5)	53(4)	86(5)	-35(3)	69(5)	-34(3)
C(21B)	132(7)	44(4)	113(6)	-32(4)	114(6)	-46(4)
C(22B)	157(9)	19(3)	122(6)	-1(3)	124(6)	-12(4)
C(23B)	115(6)	27(3)	96(5)	10(3)	91(5)	10(4)
C(24B)	71(5)	17(3)	68(4)	4(3)	60(4)	0(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **19h**.

	x	y	z	U(eq)
H(2)	4442	2364	1475	38
H(4A)	5464	3928	569	41
H(4B)	5422	5546	833	41
H(5)	4674	5653	1587	41
H(7)	2773	5769	1388	60
H(8)	911	5664	388	77
H(9)	144	4616	-798	78
H(10)	1193	3664	-1041	64
H(12)	7335	5269	1793	42
H(13A)	7712	1892	921	92
H(13B)	7262	3535	730	92
H(13C)	6615	2226	716	92
H(14A)	8389	396	2370	105
H(14B)	7329	915	2183	105
H(14C)	8474	1317	3001	105
H(15A)	9792	2715	2433	121
H(15B)	9870	3625	3064	121
H(15C)	9438	4403	2277	121
H(16A)	9275	4571	4430	94
H(16B)	9573	3670	4000	94
H(16C)	8530	3246	3858	94
H(17A)	9495	7263	3716	113
H(17B)	8725	7392	2791	113
H(17C)	9648	6180	3250	113
H(18A)	7621	6957	3605	91
H(18B)	6710	5770	3034	91
H(18C)	6853	7155	2683	91
H(20A)	1953	751	-289	67
H(21A)	2265	-1017	574	102
H(22A)	3947	-2079	1479	100
H(23A)	5317	-1372	1522	80
H(24A)	5006	396	659	57
H(20B)	2248	681	-62	74
H(21B)	2788	-997	904	85
H(22B)	4535	-1863	1760	89
H(23B)	5743	-1050	1649	75
H(24B)	5204	628	682	50

Crystallographic data for **34**.



Crystal data for **34**: $C_{20}H_{32}N_2O_4SSi_2$, *M*r = 452.72, monoclinic, space group $P2_1/n$, a = 9.0478(9), b = 18.6125(18), c = 14.1521(14) Å, β = 96.3590(10)°, V = 2368.6(4) Å^3, T = 193(2) K, Z = 4, D_{calc} = 1.270 Mg m^{-3}, F(000) = 968, μ = 0.265 mm^{-1}. 15535 reflections were measured on a Nonius Kappa CCD diffractometer, 5381 were independent (I>2σ(I)). Final R1 = 0.0410, wR2 = 0.1103.

Table 1. Crystal data and structure refinement for **34**.

Identification code	**34**	
Empirical formula	C20 H32 N2 O4 S Si2	
Formula weight	452.72	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 9.0478(9) Å	α= 90°.
	b = 18.6125(18) Å	β= 96.3590(10)°.
	c = 14.1521(14) Å	γ = 90°.
Volume	2368.6(4) $Å^3$	
Z	4	
Density (calculated)	1.270 Mg/m^3	
Absorption coefficient	0.265 mm^{-1}	
F(000)	968	
Crystal size	0.60 x 0.47 x 0.31 mm^3	
Theta range for data collection	1.81 to 27.48°.	
Index ranges	-11<=h<=11, -24<=k<=23, -18<=l<=18	
Reflections collected	15535	
Independent reflections	5381 [R(int) = 0.0176]	
Completeness to theta = 27.48°	99.0 %	
Max. and min. transmission	0.9223 and 0.8570	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5381 / 0 / 252	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.1103	
R indices (all data)	R1 = 0.0487, wR2 = 0.1172	
Largest diff. peak and hole	0.445 and -0.420 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **34**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4593(2)	622(1)	6751(1)	24(1)
C(2)	3192(2)	399(1)	6930(1)	29(1)
C(3)	3022(2)	-290(1)	7290(1)	35(1)
C(4)	4242(2)	-742(1)	7461(1)	36(1)
C(5)	5670(2)	-518(1)	7302(1)	31(1)
C(6)	5820(2)	171(1)	6962(1)	23(1)
C(7)	5068(2)	1313(1)	6356(1)	24(1)
C(8)	6727(2)	1227(1)	6332(1)	22(1)
C(9)	5720(2)	1261(1)	5405(1)	25(1)
C(10)	6064(2)	1974(1)	4998(1)	26(1)
C(11)	7717(2)	1886(1)	6420(1)	24(1)
C(12)	7644(2)	2277(1)	7361(1)	32(1)
C(13)	7760(2)	3012(1)	5342(1)	27(1)
C(14)	7881(2)	-402(1)	5429(2)	46(1)
C(15)	8643(3)	2423(2)	3432(2)	79(1)
C(16)	10124(3)	3781(1)	4310(2)	52(1)
C(17)	10837(3)	2346(1)	5217(2)	68(1)
C(18)	5734(3)	3846(1)	3701(1)	49(1)
C(19)	7127(3)	4605(1)	5430(2)	48(1)
C(20)	4652(2)	3544(1)	5665(2)	49(1)
N(2)	7133(1)	2303(1)	5571(1)	25(1)
N(3)	7163(1)	545(1)	6788(1)	22(1)
O(1)	5445(1)	2227(1)	4248(1)	37(1)
O(2)	9040(1)	-417(1)	7184(1)	40(1)
O(3)	9617(1)	601(1)	6170(1)	36(1)
O(4)	8801(2)	2789(1)	7498(1)	51(1)
S(1)	8582(1)	82(1)	6445(1)	26(1)
Si(2)	6285(1)	3731(1)	4999(1)	32(1)
Si(3)	9321(1)	2891(1)	4561(1)	41(1)

Table 3. Bond lengths [Å] and angles [°] for **34**.

C(1)-C(2)	1.384(2)
C(1)-C(6)	1.397(2)
C(1)-C(7)	1.484(2)
C(2)-C(3)	1.394(3)
C(3)-C(4)	1.388(3)
C(4)-C(5)	1.399(2)
C(5)-C(6)	1.383(2)
C(6)-N(3)	1.4448(19)
C(7)-C(8)	1.514(2)
C(7)-C(9)	1.531(2)
C(8)-N(3)	1.4589(18)
C(8)-C(9)	1.5137(19)
C(8)-C(11)	1.515(2)
C(9)-C(10)	1.492(2)
C(10)-O(1)	1.2372(19)
C(10)-N(2)	1.341(2)
C(11)-N(2)	1.4783(19)
C(11)-C(12)	1.525(2)
C(12)-O(4)	1.413(2)
C(13)-N(2)	1.4863(19)
C(13)-Si(3)	1.9008(18)
C(13)-Si(2)	1.9136(17)
C(14)-S(1)	1.7550(19)
C(15)-Si(3)	1.862(3)
C(16)-Si(3)	1.859(2)
C(17)-Si(3)	1.867(3)
C(18)-Si(2)	1.862(2)
C(19)-Si(2)	1.870(2)
C(20)-Si(2)	1.871(2)
N(3)-S(1)	1.6624(13)
O(2)-S(1)	1.4249(13)
O(3)-S(1)	1.4286(13)
C(2)-C(1)-C(6)	120.18(15)
C(2)-C(1)-C(7)	129.64(14)
C(6)-C(1)-C(7)	110.17(13)
C(1)-C(2)-C(3)	118.90(15)
C(4)-C(3)-C(2)	120.23(16)
C(3)-C(4)-C(5)	121.46(16)
C(6)-C(5)-C(4)	117.44(15)
C(5)-C(6)-C(1)	121.70(14)
C(5)-C(6)-N(3)	128.53(14)
C(1)-C(6)-N(3)	109.76(13)
C(1)-C(7)-C(8)	104.23(12)
C(1)-C(7)-C(9)	115.66(13)
C(8)-C(7)-C(9)	59.63(9)

N(3)-C(8)-C(9)	121.83(12)
N(3)-C(8)-C(7)	107.60(12)
C(9)-C(8)-C(7)	60.73(10)
N(3)-C(8)-C(11)	122.64(12)
C(9)-C(8)-C(11)	109.32(12)
C(7)-C(8)-C(11)	119.46(13)
C(10)-C(9)-C(8)	103.96(12)
C(10)-C(9)-C(7)	113.68(13)
C(8)-C(9)-C(7)	59.64(9)
O(1)-C(10)-N(2)	124.89(15)
O(1)-C(10)-C(9)	125.24(14)
N(2)-C(10)-C(9)	109.86(13)
N(2)-C(11)-C(8)	101.74(11)
N(2)-C(11)-C(12)	114.34(13)
C(8)-C(11)-C(12)	112.06(13)
O(4)-C(12)-C(11)	109.84(15)
N(2)-C(13)-Si(3)	110.38(11)
N(2)-C(13)-Si(2)	113.79(11)
Si(3)-C(13)-Si(2)	118.53(8)
C(10)-N(2)-C(11)	114.88(13)
C(10)-N(2)-C(13)	122.77(13)
C(11)-N(2)-C(13)	122.22(12)
C(6)-N(3)-C(8)	107.62(11)
C(6)-N(3)-S(1)	119.47(10)
C(8)-N(3)-S(1)	120.11(10)
O(2)-S(1)-O(3)	119.59(8)
O(2)-S(1)-N(3)	107.12(7)
O(3)-S(1)-N(3)	106.27(7)
O(2)-S(1)-C(14)	108.45(10)
O(3)-S(1)-C(14)	108.17(10)
N(3)-S(1)-C(14)	106.53(8)
C(18)-Si(2)-C(19)	106.04(10)
C(18)-Si(2)-C(20)	112.22(11)
C(19)-Si(2)-C(20)	108.26(11)
C(18)-Si(2)-C(13)	115.72(9)
C(19)-Si(2)-C(13)	106.14(8)
C(20)-Si(2)-C(13)	108.06(8)
C(16)-Si(3)-C(15)	110.55(13)
C(16)-Si(3)-C(17)	107.33(11)
C(15)-Si(3)-C(17)	109.07(16)
C(16)-Si(3)-C(13)	109.69(9)
C(15)-Si(3)-C(13)	111.02(10)
C(17)-Si(3)-C(13)	109.10(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **34**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(1)	26(1)	22(1)	-2(1)	2(1)	-1(1)
C(2)	21(1)	38(1)	29(1)	-2(1)	3(1)	-1(1)
C(3)	26(1)	42(1)	38(1)	1(1)	6(1)	-8(1)
C(4)	35(1)	32(1)	43(1)	5(1)	8(1)	-8(1)
C(5)	28(1)	28(1)	38(1)	3(1)	3(1)	0(1)
C(6)	19(1)	27(1)	23(1)	-2(1)	3(1)	-2(1)
C(7)	18(1)	27(1)	26(1)	1(1)	1(1)	1(1)
C(8)	19(1)	23(1)	23(1)	-1(1)	0(1)	1(1)
C(9)	23(1)	27(1)	24(1)	-1(1)	-1(1)	-3(1)
C(10)	26(1)	30(1)	24(1)	1(1)	1(1)	-2(1)
C(11)	22(1)	24(1)	25(1)	1(1)	-1(1)	-2(1)
C(12)	39(1)	29(1)	26(1)	-2(1)	-4(1)	-4(1)
C(13)	28(1)	26(1)	27(1)	3(1)	1(1)	-5(1)
C(14)	35(1)	56(1)	47(1)	-26(1)	5(1)	2(1)
C(15)	74(2)	100(2)	72(2)	-41(2)	42(2)	-34(2)
C(16)	47(1)	54(1)	58(1)	11(1)	14(1)	-15(1)
C(17)	44(1)	52(1)	113(2)	20(1)	35(1)	10(1)
C(18)	59(1)	45(1)	39(1)	14(1)	-10(1)	-7(1)
C(19)	61(1)	30(1)	51(1)	4(1)	-6(1)	0(1)
C(20)	45(1)	44(1)	60(1)	12(1)	14(1)	11(1)
O(1)	40(1)	40(1)	26(1)	7(1)	-8(1)	-5(1)
O(2)	32(1)	37(1)	49(1)	9(1)	3(1)	11(1)
O(3)	22(1)	36(1)	50(1)	0(1)	11(1)	0(1)
O(4)	76(1)	40(1)	32(1)	4(1)	-19(1)	-28(1)
S(1)	19(1)	28(1)	31(1)	-3(1)	2(1)	2(1)
Si(2)	35(1)	29(1)	32(1)	8(1)	-1(1)	-1(1)
Si(3)	37(1)	40(1)	48(1)	-2(1)	16(1)	-10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **34**.

	x	y	z	U(eq)
H(2)	2359	709	6809	35
H(3)	2068	-450	7420	42
H(4)	4105	-1215	7690	43
H(5)	6504	-828	7423	37
H(7)	4650	1777	6562	29
H(9)	5545	828	4990	30
H(11)	8768	1740	6363	29
H(12A)	6671	2520	7356	38
H(12B)	7743	1926	7890	38
H(13)	8276	3183	5962	33
H(14A)	7563	-66	4912	69
H(14B)	7029	-692	5572	69
H(14C)	8658	-718	5234	69
H(15A)	8221	1957	3578	119
H(15B)	9474	2351	3054	119
H(15C)	7876	2717	3072	119
H(16A)	10491	4015	4910	78
H(16B)	9356	4081	3963	78
H(16C)	10948	3715	3923	78
H(17A)	10448	1873	5364	102
H(17B)	11205	2592	5809	102
H(17C)	11652	2288	4821	102
H(18A)	6621	3940	3381	73
H(18B)	5044	4251	3597	73
H(18C)	5247	3407	3442	73
H(19A)	7989	4711	5091	72
H(19B)	7445	4573	6114	72
H(19C)	6389	4989	5312	72
H(20A)	4194	3087	5448	73
H(20B)	3922	3932	5548	73
H(20C)	4984	3515	6347	73
H(4)	8755	3003	8017	77