Supplementary Information

The Metal-Catalyzed Reaction of N-(2-indolyl)methyl, N-bis(trimethylsilyl)methyl Diazoamides: An Entry into the β-Carboline Ring System

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General procedure for the preparation of the ester-substituted diazoamides 2, **6**, **10a**, **10b** and **14a.**

Amine (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. Ethyl diazomalonyl chloride or methyl diazomalonyl chloride (1.5 mmol) in dry CH_2Cl_2 (5 mL) was then transferred to the reaction mixture via cannula. The reaction was stirred at 0°C for 20 min, then at rt for 1 h. Then the mixture was washed successively with saturated $NaHCO_3$ (10 mL), H_2O (10 mL) and then brine (10 mL). The organic layer was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography. The ester-substituted diazoamides were obtained in a 70-83% yield.

General procedure for the preparation of the unsubstituted diazoamides 10c, 10d, 14b, 14c, 18a, 18b.

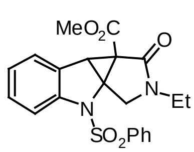
The 4-(dimethylamino)-pyridine (23.4 mg, 20mol%) and amine (0.959 mmol, 1.0 equiv) were dissolved in dry THF (5 mL) under Ar. The mixture was cooled to 0 °C in an ice-water bath. Diketene (115 µL, 1.44mmol, 1.5 equiv) in THF (3 mL) was added into the mixture via cannula. The reaction mixture was kept at 0 °C for 10 min, then stirred at rt. After 1.5 h, the mixture was diluted with CH_2Cl_2 (5 mL) and filtered through a short pad of silica gel in the sintered funnel. The filtrate was evaporated under reduced pressure to give the crude amide.

The crude acetoacetamide obtained above was dissolved in dry CH_3CN (4 mL) under Ar at 0 °C in an ice-water bath. MsN_3 (152.5 µL, 1.85 mmol, 2.0 equiv) in dry CH_3CN (3 mL) was added via cannula. DBU (276.6 µL, 1.85 mmol, 2.0 equiv) was then added and the reaction mixture was stirred at 0 °C for 1 h, then at rt for 1 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL), washed with 10% NaOH (2x5 mL) and the aqueous layer was extracted with CH_2Cl_2 (2x5 mL). The combined CH_2Cl_2 solution was washed with H_2O, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography to give the acetyl-substituted diazoamide.

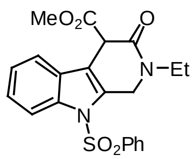
The acetyl-substituted diazoamide (0.383 mmol) was dissolved in CH_3CN (4 mL) in a 10 mL flask. Aqueous potassium hydroxide (5%, 2 mL) was added to the solution. The mixture was stirred overnight at rt under Ar. Then the mixture was concentrated under reduced pressure. Saturated aqueous solution of NH_4Cl (3mL) was added to the residue and the mixture was extracted with CH_2Cl_2 (3x5 mL). The combined organic layer was washed with water, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude products were purified by flash chromatography. The unsubstituted diazoamides were prepared in a 63-74% overall yield from the corresponding amines.

General procedure for Rh(II)-catalyzed reaction. The appropriate rhodium(II) catalyst (2mol%) was dried under high vacuum at 80^{o}C for 1 h. The diazo compound was dissolved in the dry CH_2Cl_2 and transferred to the solution of the catalyst in the dry CH_2Cl_2 at room temperature via cannula under Ar. The reaction was monitored by t.l.c.. After the reaction was complete, the solvent was removed under reduced pressure. The crude products were separated and purified by flash chromatography.
The $Rh_2(OAc)_4$-catalyzed reaction of unsubstituted diazoamides **10c**, **10d**, **14b**, **14c** and **18a**, was judged to be completed by the t.l.c. in 10 min at rt. However the $Rh_2(cap)_4$-catalyzed reaction of unsubstituted diazoamides **18a** and **18b** was complete at rt in 3 h.
The $Rh_2(OAc)_4$- and $Rh_2(tfa)_4$-catalyzed reaction of ester-substituted diazoamides **6**, **10a**, **10b** and **14a** was found to be very slow at rt compared to **10c**, **10d**, **14b**, **14c** and **18a**. Reaction times were typically 7–24h. $Rh_2(OAc)_4$ –catalyzed reaction of diazoamide **6**, at rt, was complete in 3 d. For the $Rh_2(OAc)_4$-catalyzed reaction of diazoamide **2,** after 3 h at rt, there was still a large amount of **2** detected by t.l.c.; the reaction was brought to completion by heating the mixture to reflux for 6 h.

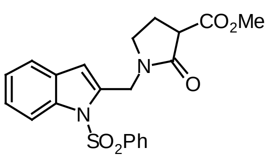
General procedure for Cu(II)-catalyzed reaction. The diazo compound was dissolved in the dry CH_2Cl_2 and transferred to the solution of the copper catalyst (5mol%) in the dry CH_2Cl_2 at rt via cannula under Ar. The reaction was monitored by t.l.c.. After the reaction was complete, the solvent was removed under reduced pressure. The crude products were separated and purified by flash chromatography.
The $Cu(hfacac)_2$-catalyzed reaction of diazoamide **10a** was complete at rt in 1.5 h. The $Cu(acac)_2$-catalyzed reaction of diazoamide **10a** was sluggish at rt, and after 48 h, substantial amount of **10a** was still present; the reaction was brought to completion by heating the mixture to reflux for 24 h. The $Cu(hfacac)_2$-catalyzed reaction of diazoamide **10b** was refluxed for 48 h for the reaction to be complete.



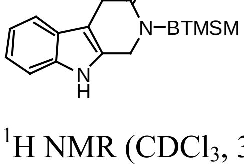
Compound **3**: unstable light yellow solid, IR (film) ν_{max}: 1733.6, 1694.1 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.85-7.94 (m, 2H, SO_2Ph*H*), 7.71 (d, 1H, *J* = 7.7 Hz, Ar*H*), 7.60 (dddd, 1H, *J* = 7.7, 7.7, 1.4, 1.4 Hz, SO_2Ph*H*), 7.45-7.54 (m, 2H, SO2Ph*H*), 7.29-7.39 (m, 2H, Ar*H*), 7.06-7.14 (m, 1H, Ar*H*), 4.82 (d, 1H, *J* = 10.9 Hz, NCH*H'*C), 3.74 (d, 1H, *J* = 10.9 Hz, NC*H*H'C), 3.55 (dq, 1H, *J* = 14.2, 7.3 Hz, NCH*H'*CH_3), 3.35 (dq, 1H, *J* = 14.2, 7.3 Hz, NC*H*H'CH_3), 3.15 (s, 1H, C*H*), 3.09 (s, 3H, OCH_3), δ 1.18 (t, 3H, *J* = 7.3 Hz, NCH_2CH_3).



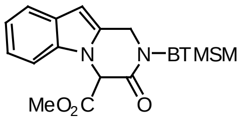
Compound **3'** was obtained from rearrangement of compound **3** in $CDCl_3$ solution: light yellow powder, mp: 177-180°C; IR (film) 1744, 1653 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 8.06-8.11 (m, 1H, indole-*H*), 7.75-7.82 (m, 2H, SO_2PhH), 7.58 (dddd, 1H, *J* = 8.0, 8.0, 2.3, 1.7 Hz, SO_2PhH), 7.45-7.52 (m, 3H, indole-*H*, SO_2PhH), 7.36(ddd, 1H, *J* = 8.6, 8.2,1.3 Hz, indole-*H*), 7.29 (dd, 1H, *J* = 8.2, 1.3 Hz, indole-*H*), 4.98 (dd, 1H, *J* = 18.6, 4.0 Hz, NC*H*H'C), 4.88 (dd, 1H, *J* = 18.6, 4.0 Hz, NCH*H'*C), 4.68 (t, 1H, *J* = 4.0 Hz, O=CC*H*C=O), 3.60-3.78 (m, 2H, NCH_2CH_3), 3.70 (s, 3H, CH_3), 1.29 (t, 3H, *J* = 6.5 Hz, NCH_2CH_3); ^{13}C NMR (75 MHz) δ 169.0, 163.0, 138.2, 136.8, 134.6, 130.0, 129.0, 127.8, 127.1, 126.0, 125.0, 119.2, 114.8, 113.9, 53.1, 48.0, 46.5, 43.5, 12.1; HRMS (EI) calcd. for $C_{21}H_{20}N_2O_5S$ 412.1093, found 412.1089.



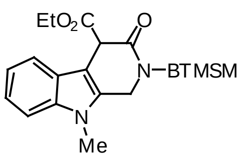
Compound **5**: colorless oil, IR (film) 1741, 1696 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 8.12 (d, 1H, *J* = 8.6 Hz, indole-*H*), 7.74-7.83 (m, 2H, SO_2PhH), 7.48-7.57 (m, 1H, SO_2PhH), 7.38-7.46 (m, 3H, indole-*H*, SO_2PhH), 7.18-7.34 (m, 2H, indole-*H*), 6.53 (s, 1H, indole-*H3*), 4.98 (d, 1H, *J* = 16.2 Hz, NCH*H'*), 4.88 (d, 1H, *J* = 16.2 Hz, NC*H*H'), 3.81 (s, 3H, OCH_3), 3.66 (ddd, 1H, *J* = 8.2, 8.2, 5.8 Hz, NCH*H'*CH_2), 3.53 (dd, 1H, *J* = 9.2, 7.3 Hz, O=CC*H*C=O), 3.45 (ddd, 1H, *J* = 8.2, 8.2, 5.8 Hz, NC*H*H'CH_2), 2.41-2.54 (m, 1H, NCH_2CH*H'*), 2.25-2.40 (m, 1H, NCH_2C*H*H'); ^{13}C NMR (75 MHz) δ 170.8, 170.0, 138.2, 137.2, 135.3, 134.0, 129.3, 126.2, 124.8, 124.0, 120.9, 114.7, 114.6, 110.6, 52.9, 48.0, 46.0, 41.5, 22.5; HRMS(EI) calcd. for $C_{21}H_{20}N_2O_5S$ 412.1093, found 412.1095.



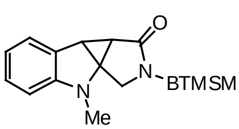
Compound **7**: light yellow solid, mp: 209-210°C; IR (film) 3456, 1740, 1614 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 8.06-8.15 (brs, 1H, indole-N*H*), 7.58 (brd, 1H, *J* = 7.7 Hz, indole-*H*), 7.32-7.37 (m, 1H, indole-*H*), 7.22 (ddd, 1H, *J* = 6.9, 6.9, 1.5 Hz, indole-*H*), 7.11-7.17 (m, 1H, indole-*H*), 4.73-4.90 (m, 2H, NCH_2), 4.45-4.57 (m, 1H, O=CC*H*C=O), 3.68 (s, 3H, OCH_3), 1.75-1.90 (brs, 1H, C*H* ($SiMe_3)_2$), 0.15-0.25 (brs, 9H, $Si(CH_3)_3$), 0.05-0.15 (brs, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 75MHz) δ 170.2, 163.8, 137.2, 127.9, 125.5, 123.1, 120.8, 119.0, 111.1, 106.0, 52.5, 51.2, 49.0, 48.1, 0.0; HRMS (EI) calcd. for $C_{20}H_{30}N_2O_3Si_2$ 402.1795, found 402.1786.



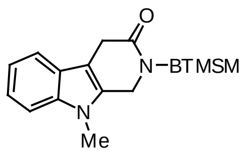
Compound **9**: white foam, IR (film) 1734, 1655 cm^{-1}; ^1H NMR (CD_3CN, 300MHz) δ 7.58 (brd, 1H, *J* = 7.7Hz, indole-*H*), 7.27-7.42 (brs, 1H, indole-*H*), 7.17 (1H, *J* = 7.7, 7.7, 1.3Hz, indole-*H*), 7.12 (ddd, 1H, *J* = 7.7, 7.7, 1.3Hz, indole-*H*), 6.31-6.57 (brs, 1H, indole-*H3*), 5.60-5.81 (brs, 1H, O=CC*H*C=O), 4.90 (brd, *J* = 16.5 Hz, NCH*H'*), 4.59 (d, *J* = 16.5 Hz, NC*H*H'), 3.92-4.10 (brs, 1H, C*H*($SiMe_3$)$_2$), 3.71 (s, 3H, OC*H_3*), -0.05-0.25 (brs, 18H, 2xSi(C*H_3*)$_3$); HRMS (EI) calcd. for $C_{20}H_{30}N_2O_3Si_2$ 402.1795, found 402.1800.



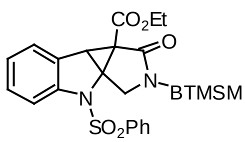
Compound **11a**: light yellow solid, mp: 144-147°C; IR (film) 1735, 1636 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 7.62 (d, 1H, *J* = 7.6Hz, indole-*H*), 7.1-7.34 (m, 2H, indole-*H*), 7.14 (ddd, IH, *J* = 7.6, 7.3, 1.5Hz, indole-*H*), 4.72-4.88(m, 2H, NCH*H'*C, O=CC*H*C=O), 4.48 (brd, 1H, NC*H*H'C), 4.04-4.26 (m, 2H, OC*H_2*CH_3), 3.67 (s, 3H, NC*H_3*), 1.78-1.96 (brs, 1H, C*H*($SiMe_3$)$_2$), 1.23(t, 3H, *J* = 7.6Hz, OCH_2C*H_3*), 04-0.30 (brs, 18H, 2xSi(C*H_3*)$_3$); ^{13}C NMR ($CDCl_3$, 75MHz) δ 169.9, 163.9, 137.8, 128.6, 124.8, 122.1, 120.0, 119.0, 109.0, 104.6, 61.7, 50.6, 48.9, 48.1, 29.8, 14.1, 0.4; HRMS (EI) calcd. for $C_{22}H_{34}N_2O_3Si_2$ 430.2108, found 430.2109.



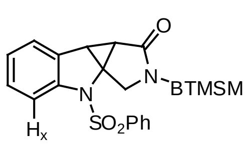
Compound **12c**: light yellow solid, mp: 162–164°C. IR (film) 1664 cm^{-1}; ^1H NMR ($CDCl_3$, 300MHz) δ 7.24 (brd, 1H, *J* = 7.6 Hz, Ar*H*), 7.16 (brt, 1H, *J* = 8.1Hz, Ar*H*), 6.83 (brt, 1H, *J* = 7.6Hz, Ar*H*), 6.69 (brd, 1H, *J* = 8.1 Hz, Ar*H*), 3.88 (d, 1H, *J* = 10.8 Hz, NCH*H'*), 3.62(dd, 1H, *J* = 10.8, 1.8 Hz, NC*H*H'), 3.07-3.14 (br s, 1H, C*H*($SiMe_3$)$_2$), 2.88 (s, 3H, NC*H_3*), 2.78-2.81 (brs, 1H, C*H*), 1.16 (t, 1H, *J* =1.8 Hz, O=CC*H*), 0.16 (s, 9H, Si(C*H_3*)$_3$), 0.12 (s, 9H, Si(C*H_3*)$_3$).



Compound **11c** was obtained from rearrangement of compound **12c** in $CDCl_3$ solution: light yellow solid, mp:182-184°C. IR (film) 1626 cm^{-1}; ^{1}H NMR (Acetone-d6, 300MHz) δ 7.46 (brd, 1H, *J* = 8.0Hz, indole-*H*), 7.37 (brd, 1H, *J* = 8.1Hz, indole-*H*), 7.18 (ddd, 1H, *J* = 8.1, 7.2, 0.9Hz, indole-*H*), 7.06 (ddd, 1H, *J* = 8.1, 7.2, 0.9Hz, indole-*H*), 4.78 (t, 2H, *J* = 3.5Hz, NCH_2C), 3.71(s, 3H, NCH_3), 3.57 (t, 2H, *J* = 3.5Hz, $O{=}CCH_2$), 1.26-1.33 (brs, 1H, $CH(SiMe_3)_2$), 0.15 (s, 18H, $2xSi(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 75MHz) δ 166.2, 137.2, 127.0, 124.8, 123.0, 119.0, 117.8, 108.4, 104.9, 48.0, 29.6, 28.2, 0.0; HRMS (EI) calcd. for $C_{18}H_{27}N_2OSi_2$ 343.1662, found 343.1661.

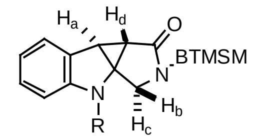


Compound **12b**: colorless oil, IR (film) 1734, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.85-7.93 (m, 2H, SO_2PhH), 7.67 (brd, 1H, *J* = 8.2 Hz, Ar*H*), 7.60 (dddd, 1H, *J* = 6.3, 6.3, 1.3, 1.3Hz, SO_2PhH), 7.45-7.54 (m, 2H, SO_2PhH), 7.36 (dd, 1H, *J* = 6.9, 1.1Hz, Ar*H*), 7.30 (ddd, 1H, *J* = 6.9, 6.9, 1.1Hz, Ar*H*), 7.10 (ddd, 1H, *J* = 6.9, 6.9, 1.1Hz, Ar*H*), 4.85 (d, 1H, *J* = 11.3 Hz, NCH*H'*), 3.69 (d, 1H, *J* = 11.3 Hz, NC*H*H'), 3.52 (dq, 1H, *J* = 11.2, 7.4 Hz, OCH*H'*CH_3), 3.39 (dq, 1H, *J* = 11.2, 7.4 Hz, OC*H*H'CH_3), 3.09 (s, 1H, C*H*), 1.25 (brs, 1H,$CH(SiMe_3)_2$), 0.72 (t, 3H, *J* = 7.4 Hz, OCH_2CH_3), 0.21 (s, 9H, $Si(CH_3)_3$), 0.17 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz) δ 166.2, 163.5, 144.2, 139.2, 133.8, 129.1, 128.2, 127.2, 126.5, 126.1, 124.0, 114.0, 61.0, 56.5, 38.0, 31.9, 29.9, 13.0, 0.1, 0.0; HRMS (EI) calcd. for $C_{26}H_{33}N_2O_3SSi_2$ 469.1437, found 469.1430.



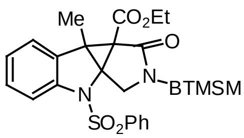
Compound **12d**: colorless solid, mp: 179-181°C. IR (film) 1672cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.87 (brd, 1H, *J* = 8.3 Hz, ArH_x), 7.64-7.71 (m, 2H, SO_2PhH), 7.53-7.61 (m, 1H, SO_2PhH), 7.36-7.46 (m, 2H, SO_2PhH), 7.20-7.34 (m, 2H, Ar*H*), 7.08 (ddd, 1H, *J* = 7.0, 7.0, 1.1 Hz, Ar*H*), 4.74 (d, 1H, *J* = 11.2 Hz, NCH*H'*), 3.76 (dd, 1H, *J* = 11.2, 1.8 Hz, NC*H*H'), 2.85-3.25 (brs, 1H, $CH(SiMe_3)_2$), 2.58 (d, 1H, *J* = 1.8 Hz, C*H*), 0.64 (t, 1H, *J* = 1.8 Hz, O=CC*H*), 0.23 (s, 9H, $Si(CH_3)_3$), 0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (75 MHz) δ 168.9, 143.7, 136.0, 134.2, 130.6, 129.6, 128.4, 128.0, 125.5, 124.8, 117.1, 52.1, 50.0, 36.9, 32.1, 23.8, 0.0; HRMS (EI) calcd. for $C_{23}H_{29}N_2O_3SSi_2$ 469.1437, found 469.1430.

A comparison of the characteristics [1]H signals of compounds **12c** and **12d**.

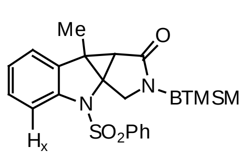


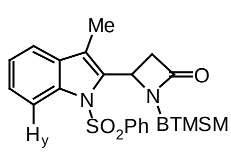
12 c, R = Me; **12d**, R = $PhSO_2$

A comparison of the chemical shifts of $H_{a,d}$ in compounds **12c,d** was informative. In **12c**, H_a was observed as a broad singlet at δ 2.79 and H_d resonated as a pseudotriplet at δ 1.16. In **12d**, however, these hydrogens resonated at lower chemical shifts with H_d being strongly shielded; H_a at δ 2.58 and H_d at δ 0.64. More importantly, the X-ray structure of **12d** revealed that the *N*-$PhSO_2$ group had adopted a conformation wherein the benzene unit resides above H_d, which explained the strong shielding experienced by H_d. This shileding effect extended as far to H_a in **12d**.



Compound **15a**: thick oil, IR (film) 1730, 1679cm^{-1}; [1]H NMR (CDCN, 300MHz) δ 7.83-7.92 (m, 2H, SO_2PhH), 7.65-7.73 (m, 1H, SO_2PhH), 7.46 (brt, 2H, *J* = 7.8 Hz, Ar*H*), 7.46 (brd, 2H, *J* = 8.0 Hz, SO_2PhH), 7.21-7.30 (m, 1H, Ar*H*), 7.15 (brt, 1H, *J* = 7.8 Hz, Ar*H*), 4.81 (d, 1H, *J* = 12.1 Hz, NCH*H'*), 3.69 (d, 1H, *J* = 12.1 Hz, NC*H*H'), 3.56-3.68 (m, 2H, OCH_2CH_3), 2.82-2.94 (brs, 1H, $CH(SiMe_3)_2$), 1.46 (s, 3H, CH_3), 0.78 (t, 3H, *J* = 7.2 Hz, OCH_2CH_3), 0.17 (s, 18H, $2xSi(CH_3)_3$); [13]C NMR (CD_3CN, 75 MHz) δ 165.9, 163.8, 141.9, 139.8, 134.2, 132.8, 129.9, 128.1, 127.2, 125.7, 124.5, 114.9, 60.9, 60.0, 48.1, 39.2, 39.1, 38.6, 13.1, 11.2, 0.0; HRMS (EI) calcd for $C_{28}H_{38}N_2O_5SSi_2$ 570.2040, found 570.2031.

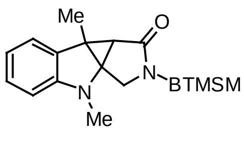




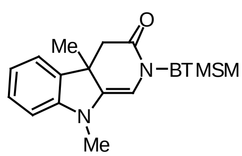
Compounds **15b** and **16b** were obtained as an inseparable mixture in 72% combined yield. The ratio of two components was calculated based on the integration of NCH*H'* in the γ-lactam **15b** and H4 in the β-lactam **16b**.

IR (film) 1737, 1668cm^{-1}; [1]H NMR ($CDCl_3$, 300MHz) (major component: γ-lactam) δ 7.19-7.62 (m, 5H, extensive aromatic hydrogens), 7.84 (d, 1H, *J* = 11.4 Hz, ArH_x), 7.68-7.72 (m, 2H, SO_2PhH), 7.10 (ddd, 1H, *J* = 8.0, 8.0, 0.6 Hz, Ar*H*), 4.81 (d, 1H, *J* = 11.1 Hz, NCH*H'*), 3.65 (dd, 1H, *J* = 11.1, 1.9 Hz, NC*H*H'), 2.85-2.95 (brs, 1H, $CH(SiMe_3)_2$), 1.41 (s, 3H, CH_3), 0.85 (d, 1H, *J* = 1.9Hz, O=CC*H*), 0.30 (s, 9H, $Si(CH_3)_3$), 0.27 (s, 9H, $Si(CH_3)_3$) /(minor component: β-lactam) δ 8.21 (d, *J* = 11.4 Hz, indole-

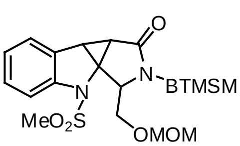
H_y), discernible signals for β-lactam 7.19-7.62 (m, 8H, extensive overlap signals of aromatic hydrogens), 5.61 (dd, 1H, *J* = 5.6, 2.8 Hz, NC*H*CH_2), 3.27 (dd, 1H, *J* = 13.9, 5.6Hz, O=CCH*H'*), 3.01 (dd, 1H, *J* = 13.9, 2.8 Hz, O=CC*H*H'), 2.30 (s, 3H, C*H_3*), 2.13 (s, 1H, C*H*$(SiMe_3)_2$), 0.20 (s, 9H, Si(C*H_3*)$_3$), 0.10 (s, 9H, Si(C*H_3*)$_3$); ^{13}C NMR (75 MHz) (major component: γ-lactam) δ 168.2, 142.2, 135.9, 135.0, 134.0, 129.2, 128.1, 127.8, 124.9, 124.1, 116.9, 53.8, 49.8, 38.1, 34.7, 26.9, 11.0, 0.9, 0.6. /(minor component: β-lactam) δ 167.1, 137.3, 133.8, 132.1, 131.7, 129.1, 127.8, 126.1, 125.7, 124.1, 118.8, 116.8, 115.9, 43.4, 39.8, 30.3, 10.0, 0.3.



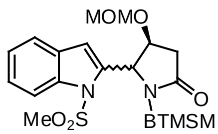
Compound **15c**: white solid, mp: 148-150°C; IR (film) 1664 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.28 (d, 1H, *J* = 7.5 Hz, Ar*H*), 7.16 (ddd, 1H, *J* = 7.5, 7.5, 0.9Hz, Ar*H*), 6.86 (ddd, 1H, *J* = 7.5, 7.5, 0.9Hz, Ar*H*), 6.70 (brd, 1H, *J* = 7.5 Hz, Ar*H*), 3.80 (d, 1H, *J* = 11.3 Hz, NCH*H'*), 3.55(dd, 1H, *J* = 11.3, 1.8 Hz, NC*H*H'), 3.08-3.18 (brs, 1H, C*H* $(SiMe_3)_2$), 2.86 (s, 3H, NC*H_3*), 1.54 (s, 3H, C*H_3*), 1.21 (d, 1H, *J* =1.8 Hz, O=CC*H*), 0.18 (s, 9H, Si(C*H_3*)$_3$), 0.16 (s, 9H, Si(C*H_3*)$_3$); ^{13}C NMR (75 MHz), δ 169.2, 149.5, 134.2, 128.0, 124.0, 120.2, 111.0, 56.2, 47.8, 37.2, 33.8, 34.1, 24.0, 10.8, 1.2; HRMS (EI) calcd. for $C_{20}H_{32}N_2OSi_2$ 372.2053, found 372.2928.



Compound **17**: colorless oil, IR (film) 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.16 (ddd, 1H, *J* = 5.1, 5.1, 0.6 Hz, Ar*H*), 7.02-7.07 (m, 1H, Ar*H*), 6.77 (t, 1H, *J* = 5.1 Hz, Ar*H*), 6.56 (d, 1H, *J* = 5.1 Hz, Ar*H*), 5.22-5.32 (brs, 1H, C=C*H*), 2.95 (s, 3H, NC*H_3*), 2.70-2.90 (m, 2H, O=CC*H_2*), 2.15-2.45 (brs, 1H, C*H*$(SiMe_3)_2$), 1.34 (s, 3H, C*H_3*), 0.16 (s, 9H, Si(C*H_3*)$_3$), 0.13 (s, 9H, Si(C*H_3*)$_3$); ^{13}C NMR (75 MHz) δ 164.8, 148.9, 142.2, 135.7, 128.6, 122.3, 119.5, 106.5, 43.5, 42.0, 30.1, 24.0, 0.1; HRMS (EI) calcd. for $C_{20}H_{32}N_2OSi_2$ 372.2053, found 372.2054.



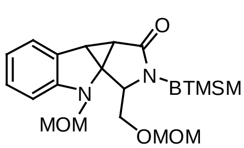
Compound **19a**: white solid, mp: 146-147°C. IR (film) 1678 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.55 (brd, 1H, *J* = 8.3 Hz, Ar*H*), 7.36-7.41 (m, 1H, Ar*H*), 7.26 (ddd, 1H, *J* = 7.6, 7.6, 1.5 Hz, Ar*H*), 7.12 (ddd, 1H, *J* = 7.6, 7.6, 0.8 Hz, Ar*H*), 4.90 (dd, 1H, *J* = 5.5, 3.0 Hz, NC*H*), 4.58 (s, 2H, MOC*H_2*), 3.88 (dd, 1H, *J* = 11.3, 5.5 Hz, MOMOCH*H'*), 3.70 (dd, 1H, *J* = 11.3, 5.5 Hz, MOMOC*H*H'), 2.96 (brd, 1H, *J* = 1.7 Hz, C*H*), 3.26 (s, 3H, OC*H*$_3$), 2.81 (s, 3H, SO$_2$C*H*$_3$), 2.38 (s, 1H, C*H*(SiMe$_3$)$_2$), 1.68 (d, 1H, *J* =1.7 Hz, O=CC*H*), 0.18 (s, 9H, Si(C*H*$_3$)$_3$), 0.13 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR (75 MHz) δ 169.4, 143.4, 129.6, 128.5, 125.6, 125.0, 115.7, 96.6, 67.1, 61.4, 55.5, 52.9, 37.7, 36.2, 30.4, 23.3, 0.8, 0.5; HRMS (EI) calcd. for $C_{22}H_{36}N_2O_5SSi_2$ 496.1884, found 496.1879.



Compound **20a** was obtained in about 1: 1 ratio based on the separated yield.

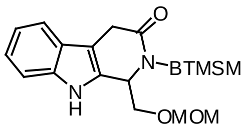
Stereoisomer 1: colorless oil, IR (film) 1677 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300MHz) δ 7.94-8.00 (m, 1H, indole-*H*), 7.55-7.62 (m, 1H, indole-*H*), 7.28-7.42 (m, 2H, indole-*H*), 6.71(s, 1H, indole-*H3*), 5.83 (d, 1H, *J* = 8.5 Hz, NC*H*), 4.68 (q, 1H, *J* = 8.5 Hz, MOMOC*H*), 4.61 (d, 1H, *J* =6.8 Hz, MOCH*H'*), 4.52 (d, 1H, *J* =6.8 Hz, MOC*H*H'), 3.28 (s, 3H, OC*H*$_3$), 3.19 (s, 3H, SO$_2$C*H*$_3$), 2.71 (dd, 1H, *J* =16.3, 8.5 Hz, O=CCH*H'*), 2.64 (dd, 1H, *J* =16.3, 7.9 Hz, O=CC*H*H'), 2.20 (s, 1H, C*H*(SiMe$_3$)$_2$), 0.10 (s, 9H, Si(C*H*$_3$)$_3$), 0.20 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR (75 MHz) δ 170.9, 137.2, 129.0, 125.0, 124.0, 121.8, 114.0, 110.5, 96.0, 72.2, 61.8, 56.0, 40.5, 38.5, 36.0, 2.0, 0.1; HRMS (EI) calcd. for $C_{22}H_{36}N_2O_5SSi_2$ 496.1884, found 496.1880.

Stereoisomer 2: colorless oil, IR (film) 1683 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300MHz) δ 8.02 (brd, 1H, *J* =7.2 Hz, indole-*H*), 7.53-7.59 (m, 1H, indole-*H*), 7.29-7.42 (m, 2H, indole-*H*), 6.66(s, 2H, indole-*H3*), 5.55-5.59 (brs, 1H, NC*H*), 4.89 (d, 1H, *J* =7.2 Hz, MOCH*H'*), 4.66 (d, 1H, *J* =7.2 Hz, MOC*H*H'), 4.24 (brd, 1H, *J* =5.8 Hz, MOMOC*H*), 3.40 (s, 3H, OC*H*$_3$), 3.18 (s, 3H, SO$_2$C*H*$_3$), 2.84 (dd, 1H, *J* =17.3, 5.8 Hz, O=CCH*H'*), 2.39 (brd, 1H, *J* =17.3Hz, O=CC*H*H'), 2.16 (s, 1H, C*H*(SiMe$_3$)$_2$), 0.20 (s, 9H, Si(C*H*$_3$)$_3$), 0.15 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR (75 MHz) δ 172.0, 137.2, 128.6, 125.6, 124.2, 121.2, 114.2, 110.0, 95.0, 75.9, 61.8, 56.0, 41.0, 38.5, 36.0, 2.0, 0.1; HRMS (EI) calcd. for $C_{22}H_{36}N_2O_5SSi_2$ 496.1884, found 496.1880.

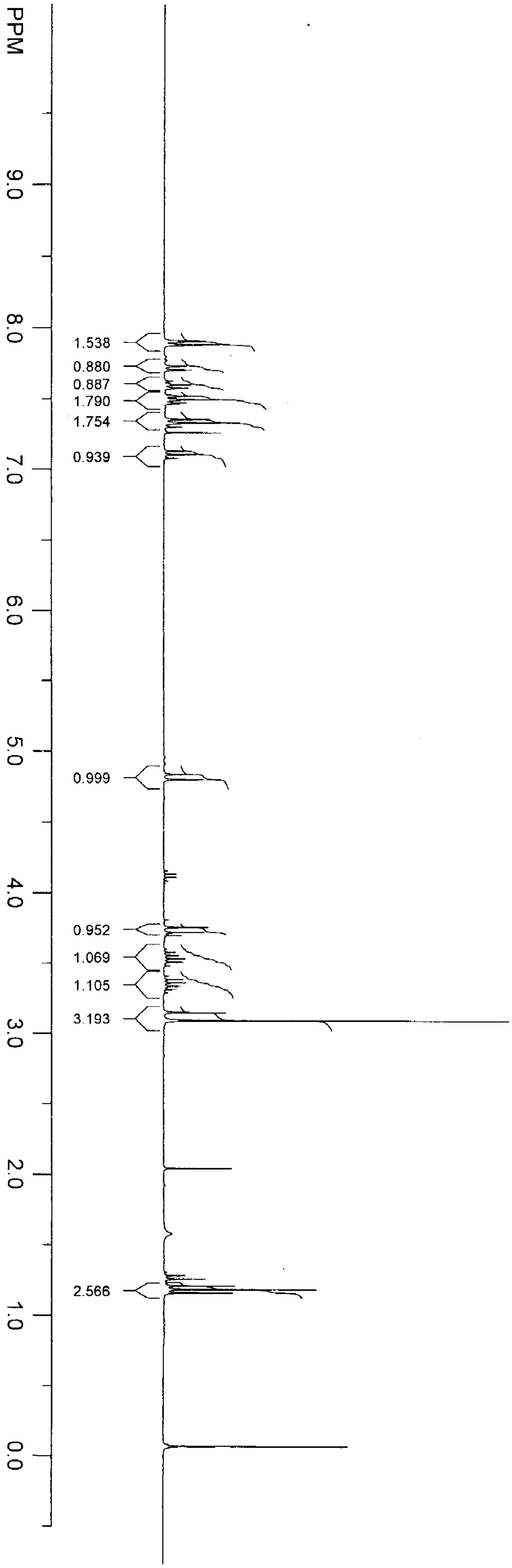


Compound **19b**: colorless oil, IR (film) 1674 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300MHz) δ 7.29 (brd, 1H, *J* = 7.4 Hz, Ar*H*), 7.15 (ddd, 1H, *J* = 8.0, 8.0, 1.1 Hz, Ar*H*), 6.78-6.88 (m, 2H, Ar*H*), 4.75 (d, 1H, *J* = 11.0 Hz, NCH*H'*OM), 4.75 (d, 1H, *J* = 11.0 Hz, NC*H*H'OM), 4.58 (s, 2H, MOC*H*$_2$), 4.32 (dd, 1H, *J* = 6.5, 2.9 Hz, NC*H*), 3.84 (dd, 1H, *J* = 11.0, 2.9 Hz, MOMOCH*H'*), 3.59 (dd, 1H, *J* = 11.0, 6.5 Hz, MOMOC*H*H'), 3.37 (s, 3H, OC*H*$_3$), 3.30 (s, 3H, OC*H*$_3$), 2.83-2.87 (brs, 1H, C*H*), 2.48 (s, 1H, C*H*(SiMe$_3$)$_2$), 1.18 (d, 1H, *J* =1.3 Hz, O=CC*H*), 0.18 (s, 9H, Si(C*H*$_3$)$_3$), 0.14 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C

NMR (75 MHz) δ 171.8, 148.8, 128.1, 127.5, 125.2, 120.0, 109.5, 96.6, 79.3, 68.9, 60.0, 56.0, 55.3, 52.9, 37.5, 29.8, 2.08, 0.7, 0.6; HRMS (EI) calcd. for $C_{23}H_{38}N_2O_4SSi_2$ 462.2370, found 462.2379.



Compound **21**: white solid, mp: 217-219°C; IR (film) 1674 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.89 (s, 1H, indole-N*H*), 7.38 (brd, 1H, *J* = 7.9 Hz, indole-*H*), 7.26 (brd, 1H, *J* = 7.9 Hz, indole-*H*), 7.10 (ddd, 1H, *J* = 7.3, 7.3, 1.1 Hz, indole-*H*), 6.98-7.02 (m, 1H, indole-*H*), 4.58-4.67 (brs, 3H, MOC*H*$_2$, NC*H*), 3.88 (dd, 1H, *J* =9.4, 4.2 Hz, MOMOCH*H'*), 3.68 (dd, 1H, *J* =20.7, 2.1 Hz, O=CCH*H'*), 3.47-3.58 (m, 2H, O=CC*H*H', MOMOC*H*H'), 3.25 (s, 3H, OC*H*$_3$), 2.11 (s, 1H, C*H*($SiMe_3$)$_2$), 0.21 (s, 9H, Si(C*H*$_3$)$_3$), 0.11 (s, 9H, Si(C*H*$_3$)$_3$); ^{13}C NMR (75 MHz) δ 168.0, 137.2, 129.9, 125.8, 122.4, 119.9, 118.2, 110.2, 106.4, 96.9, 70.0, 60.0, 55.8, 46.0, 29.6, 1.5, 0.5; HRMS (EI) calcd. for $C_{23}H_{38}N_2O_4SSi_2$ 418.2108, found 418.2110.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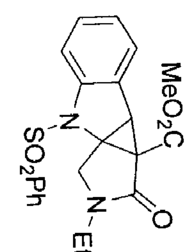
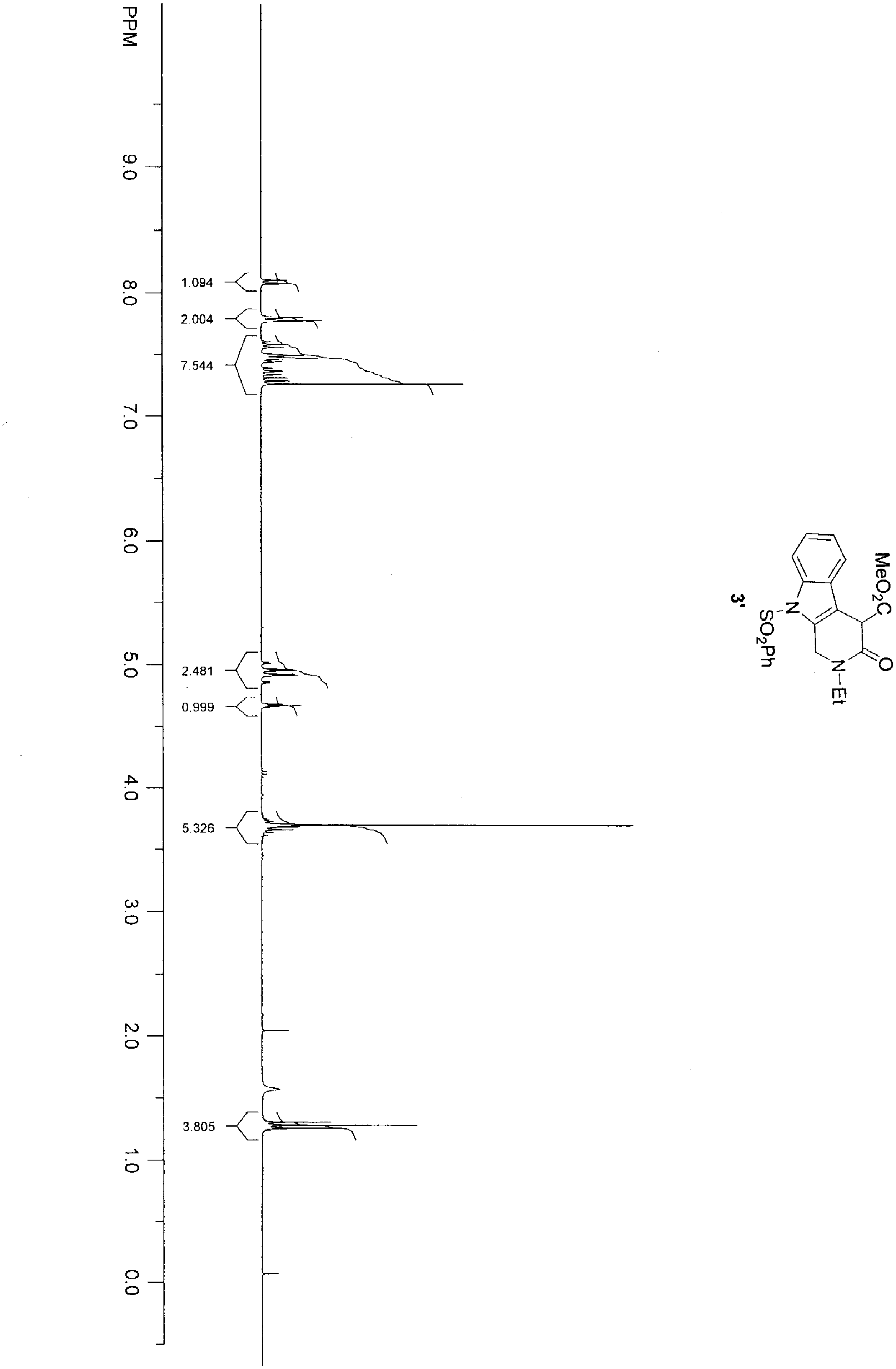
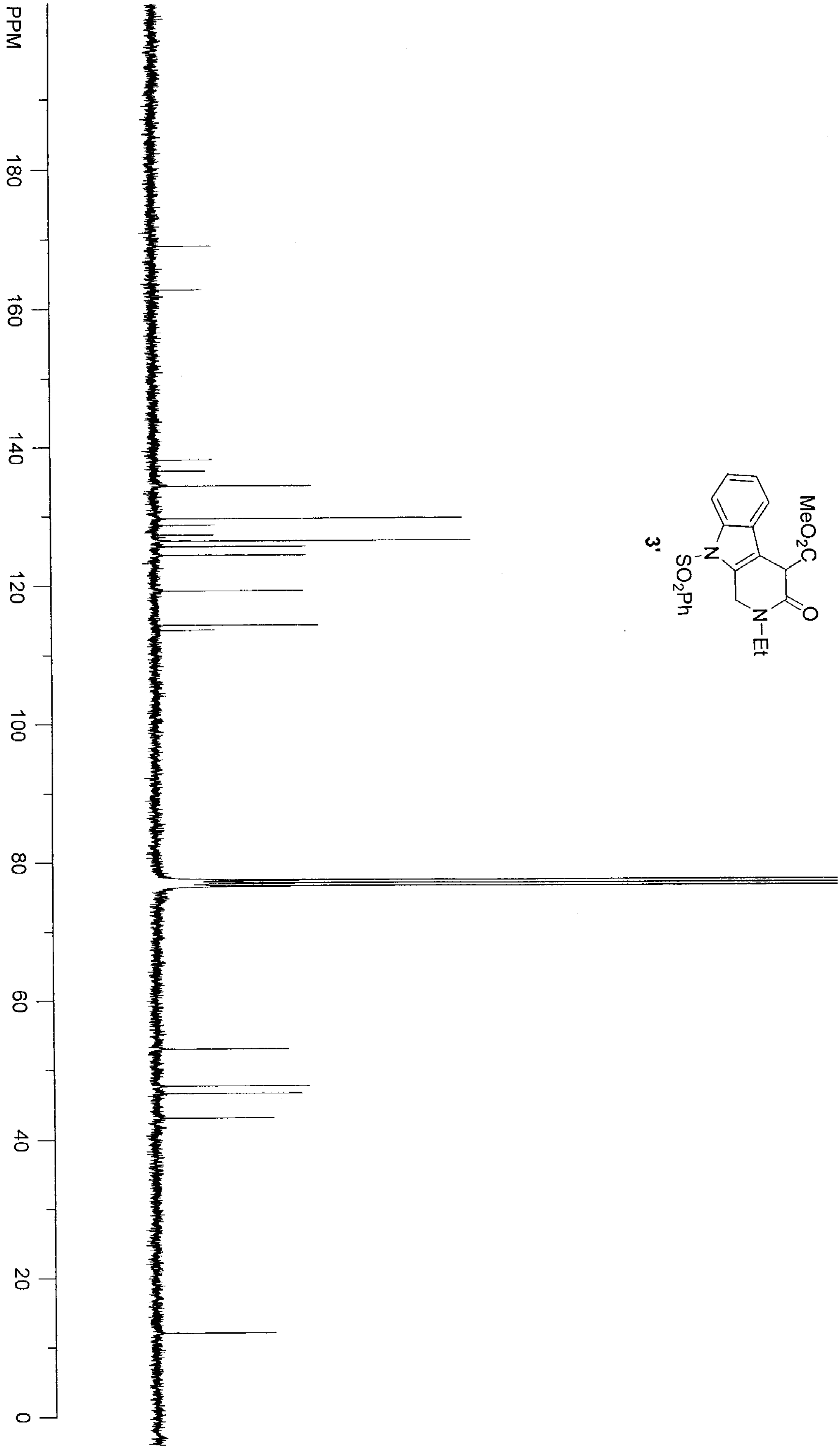
0.939
0.999
0.952
1.069
1.105
3.193
2.566

3


MeO2C
O
N
Et
N
SO2Ph

Supplementary Material (ESI) for Chemical Communications

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O
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N
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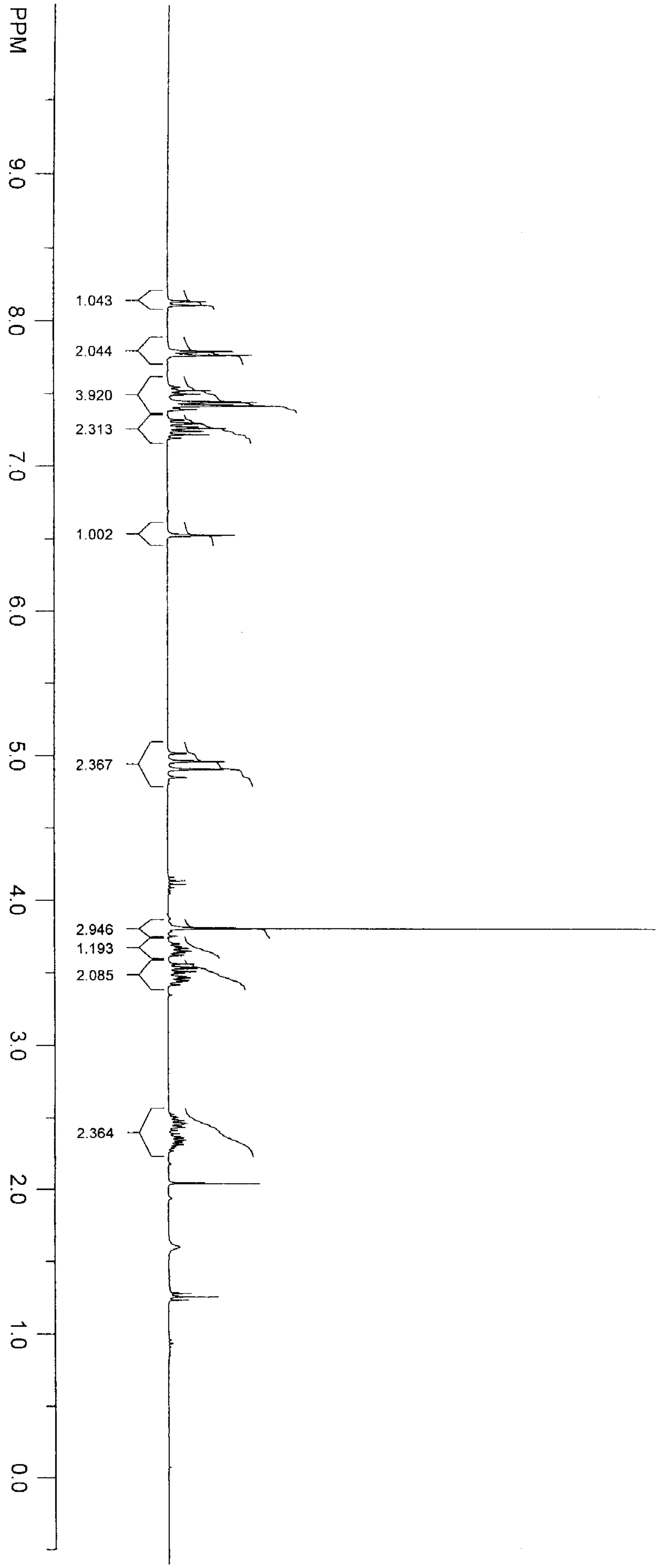
3'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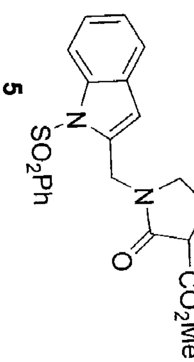
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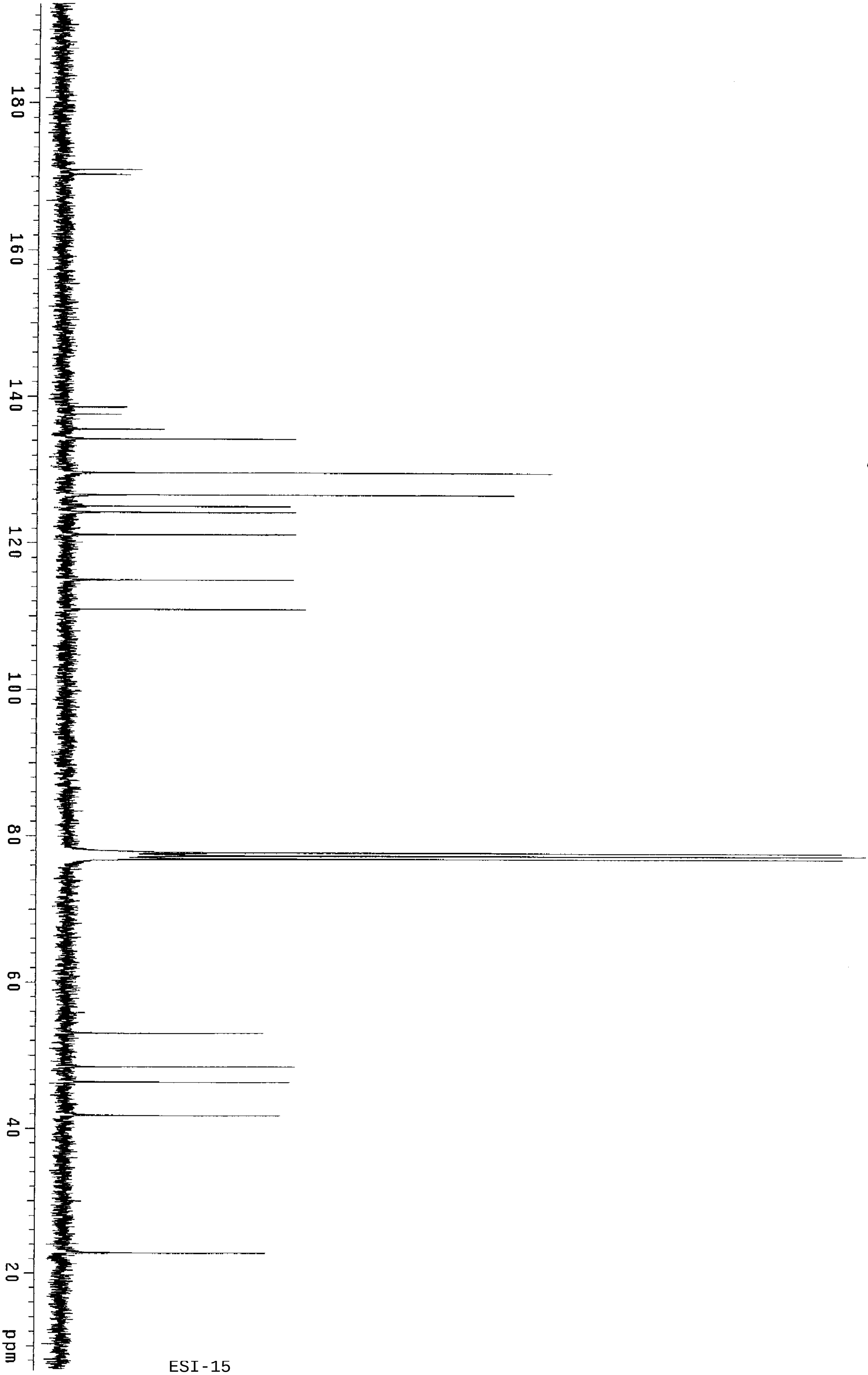
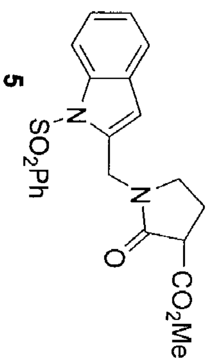
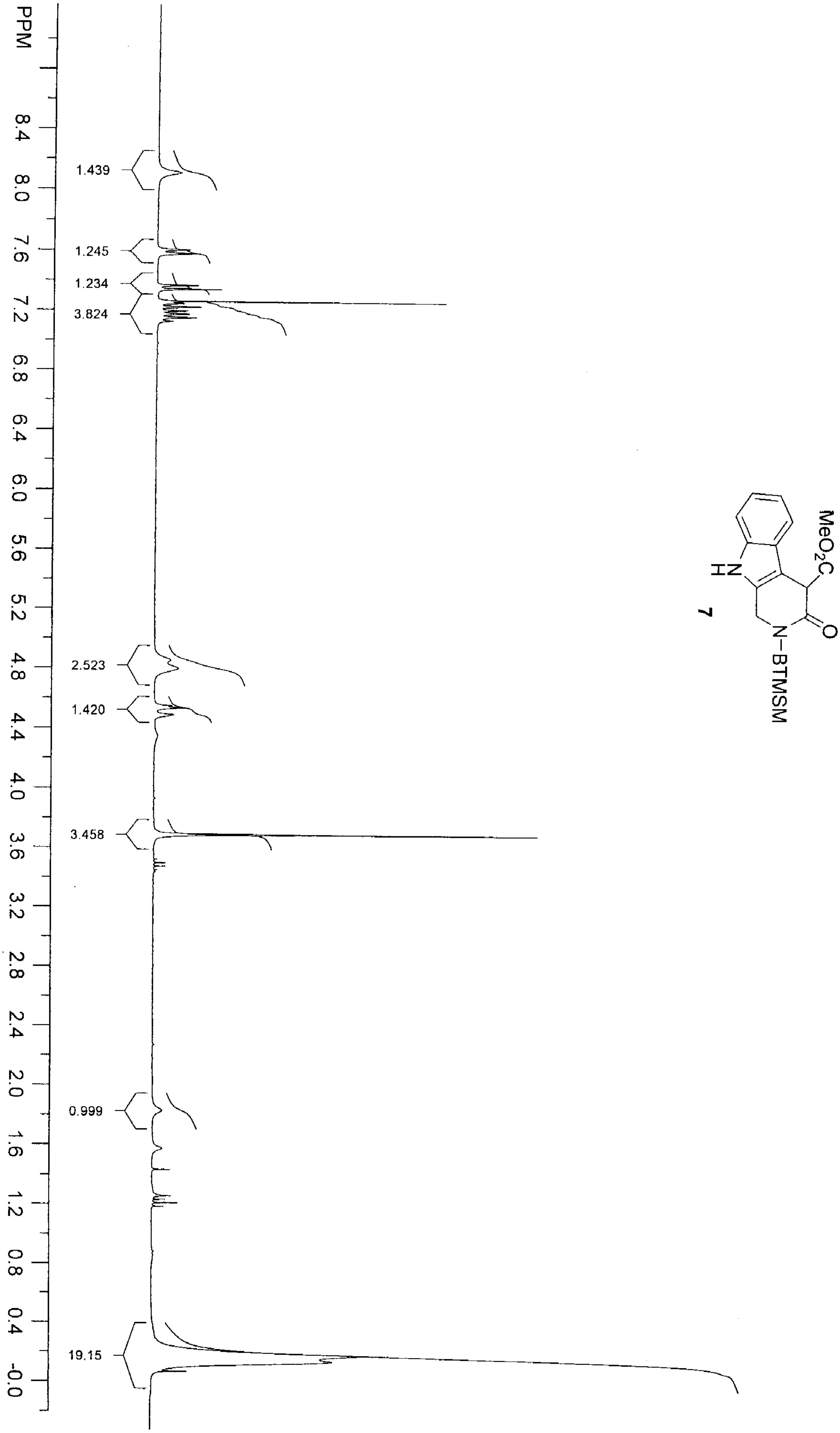
SO$_2$Ph
N
O
CO$_2$Me

5





5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3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
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1.245
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3.824
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1.420
3.458
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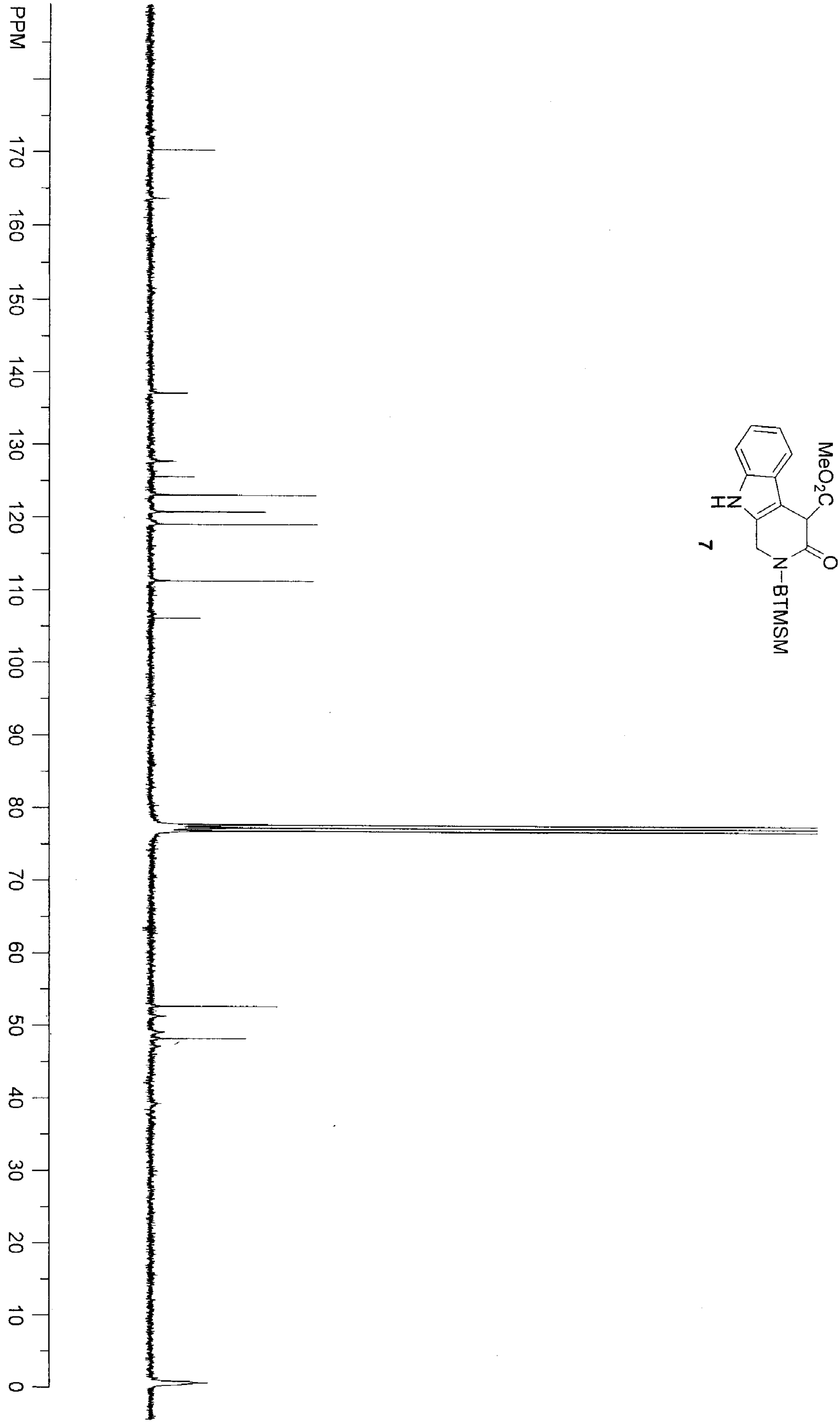
MeO2C
N–BTMSM
O
N
H
7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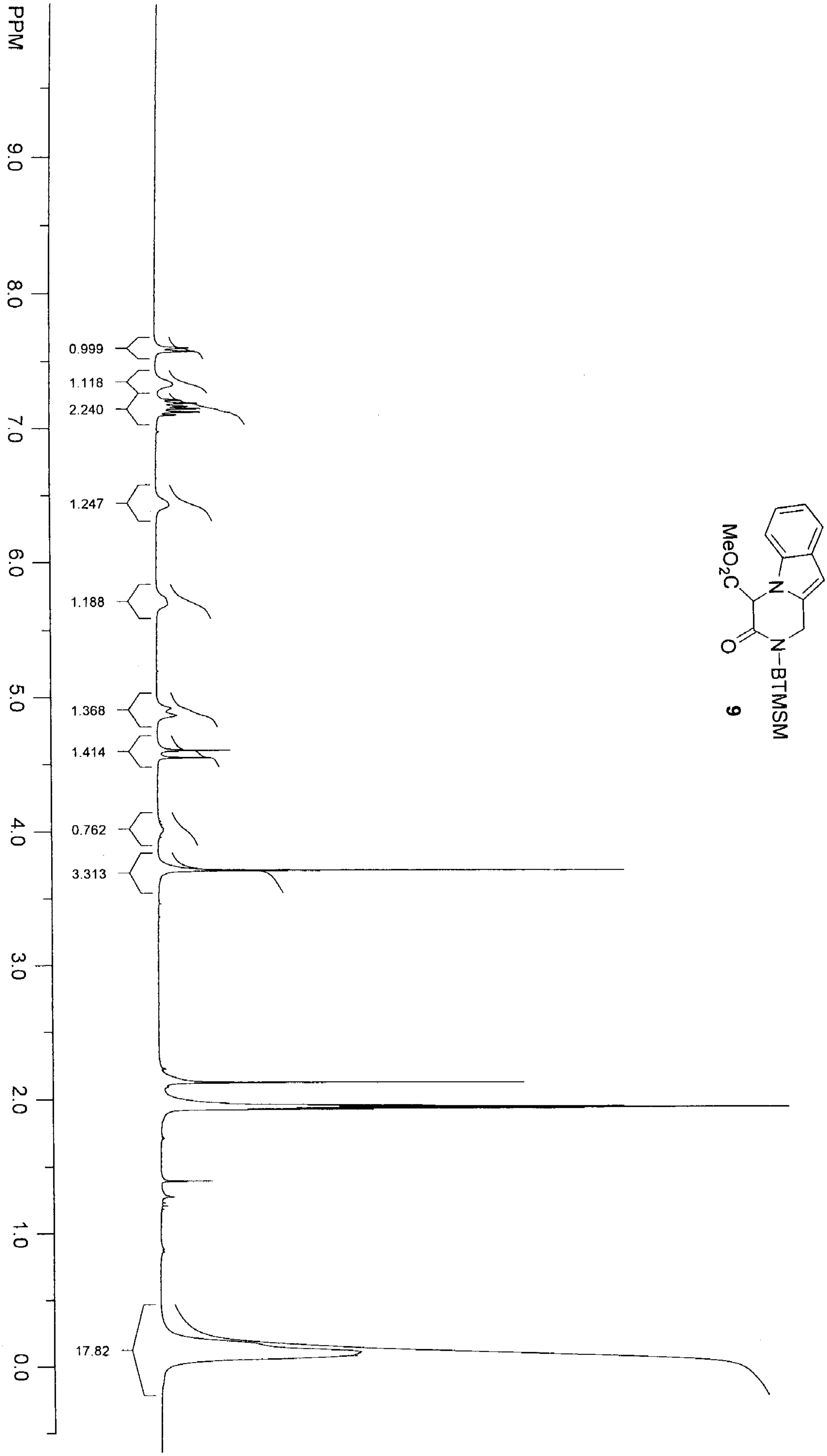
N
H
7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N–BTMSM
O
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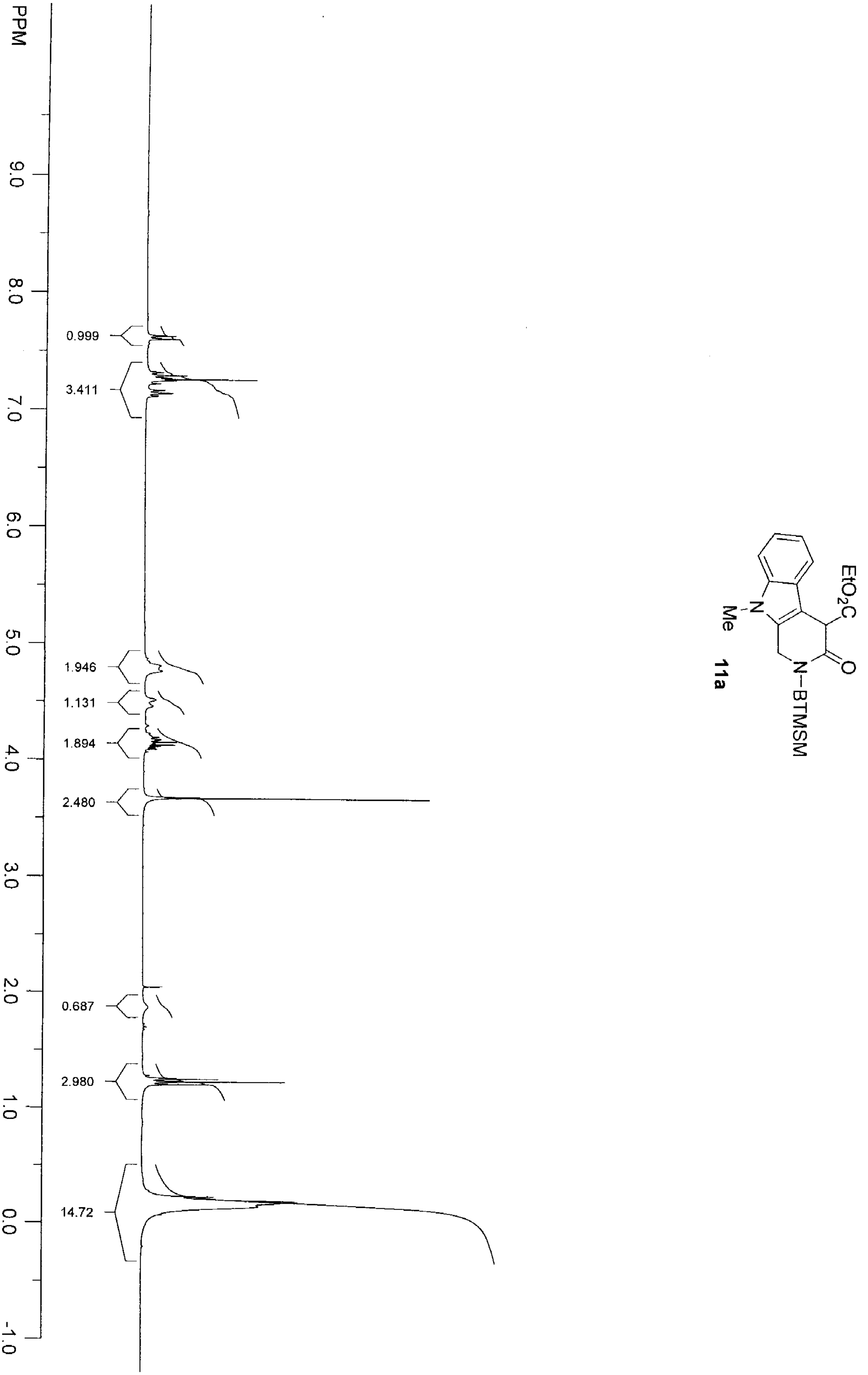
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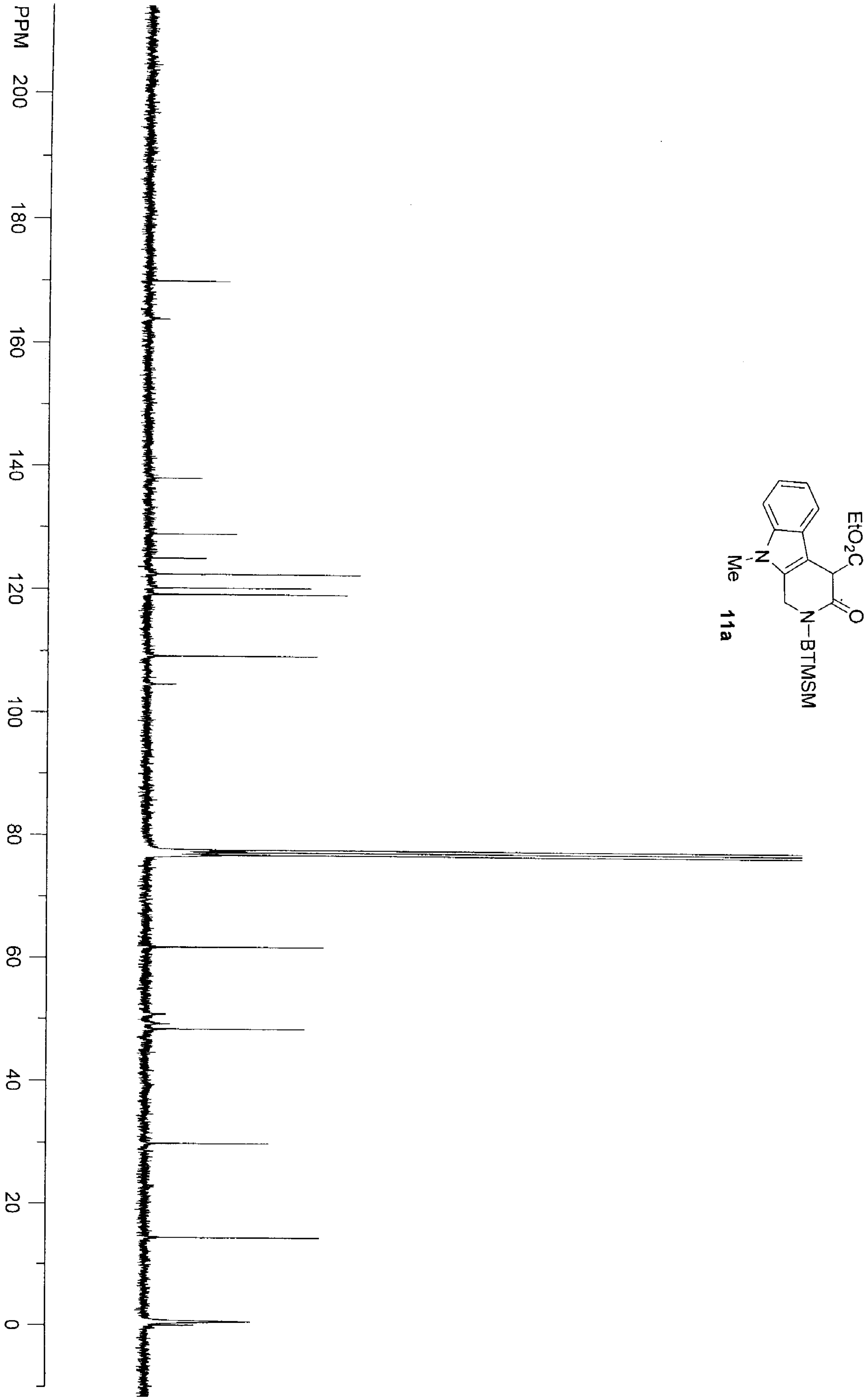
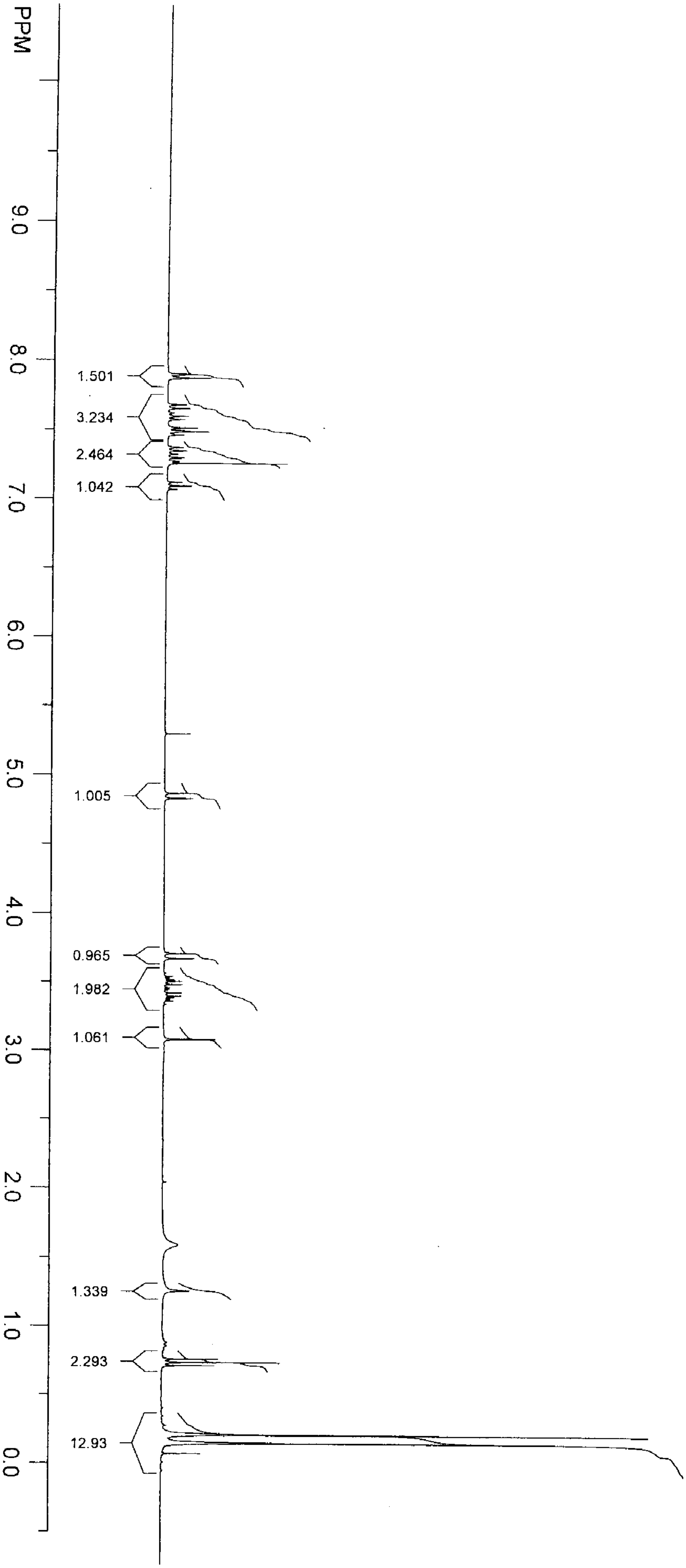
N
Me
11a



11a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1.005
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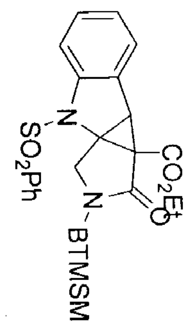
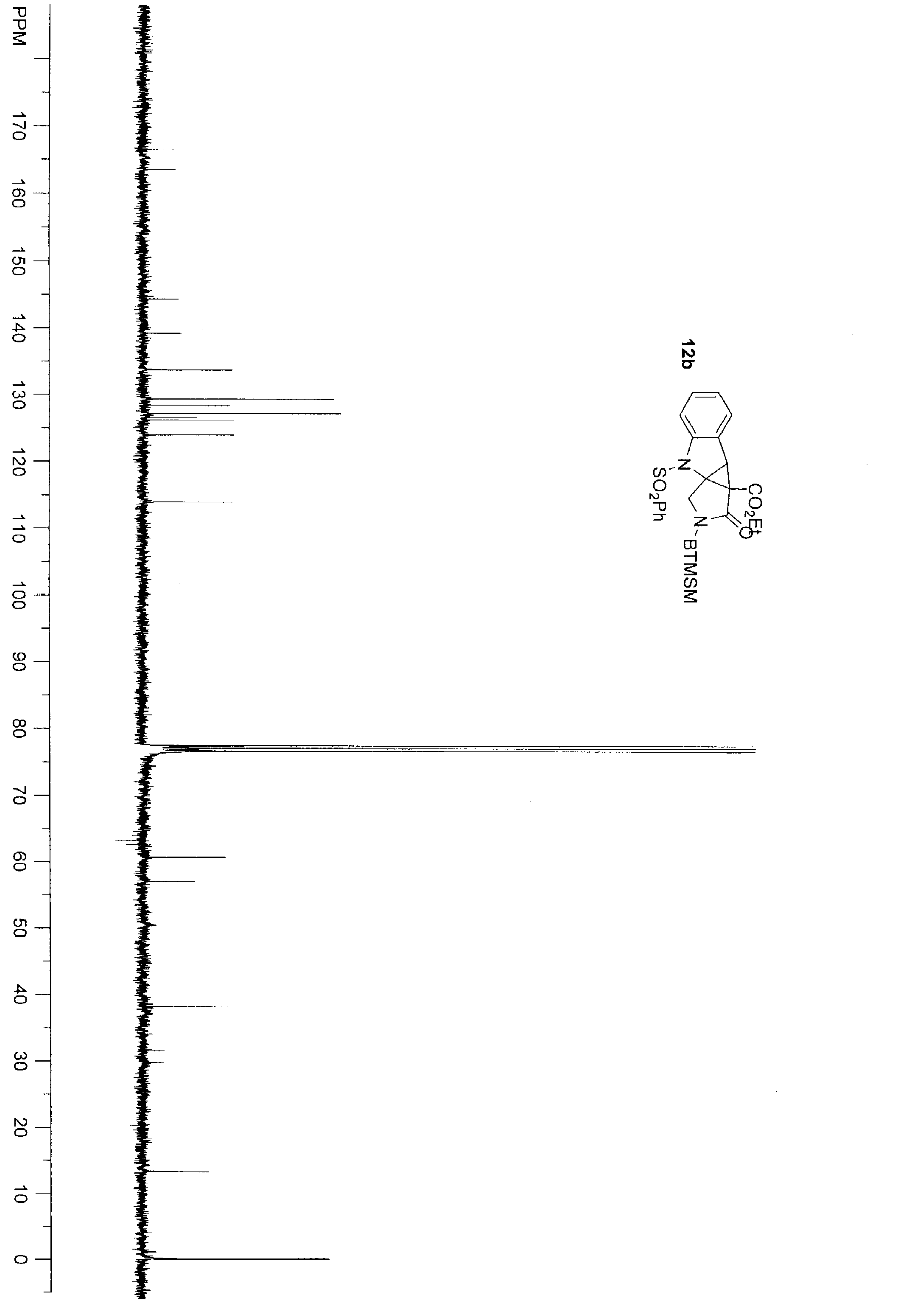
1.982
1.061
1.339
2.293
12.93

12b


CO2Et
O
N
BTMSM
N
SO2Ph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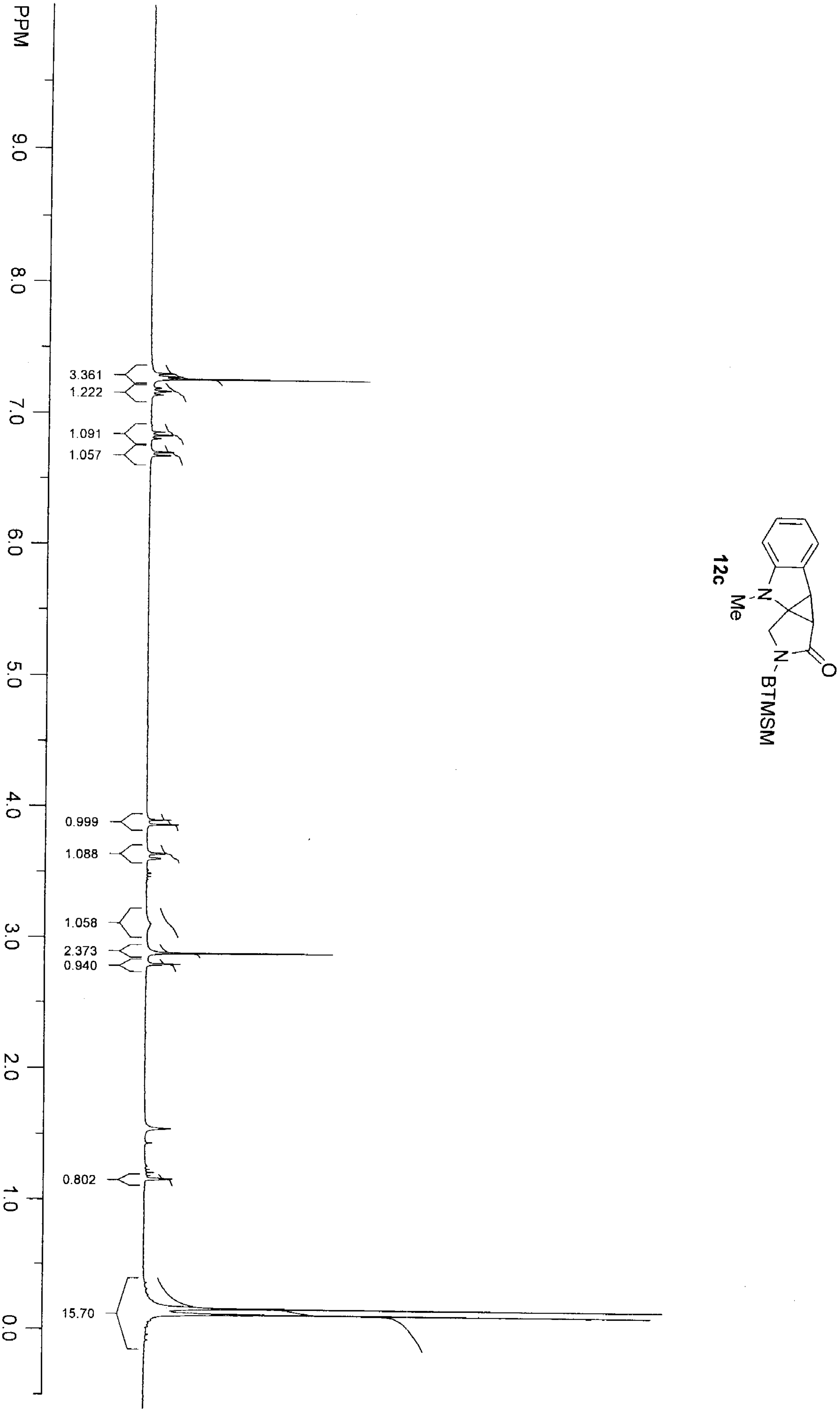
SO_2Ph
CO_2Et
O
N
BTMSM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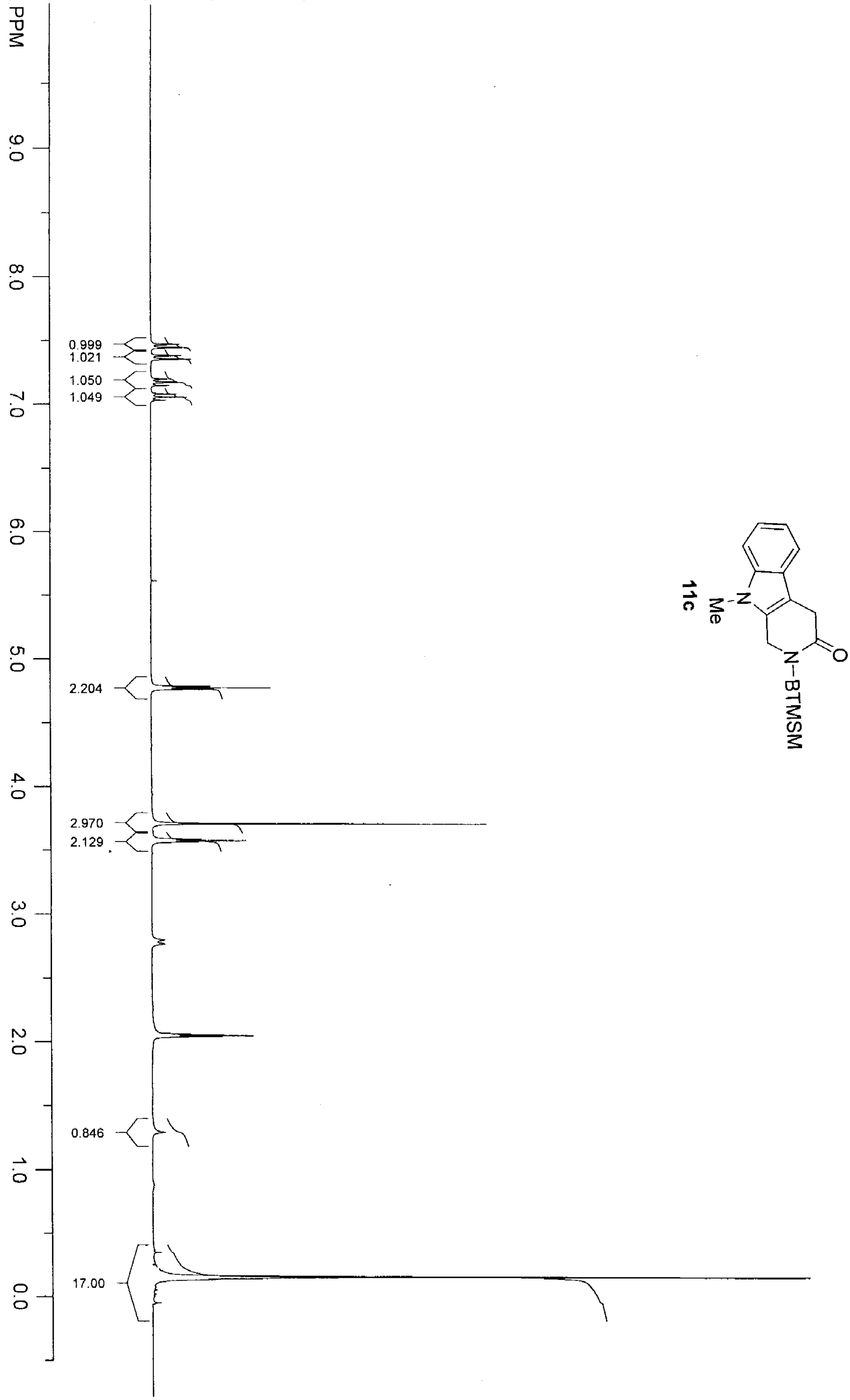
Me
N
BTMSM
O
12c


PPM
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4.0
3.0
2.0
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17.00
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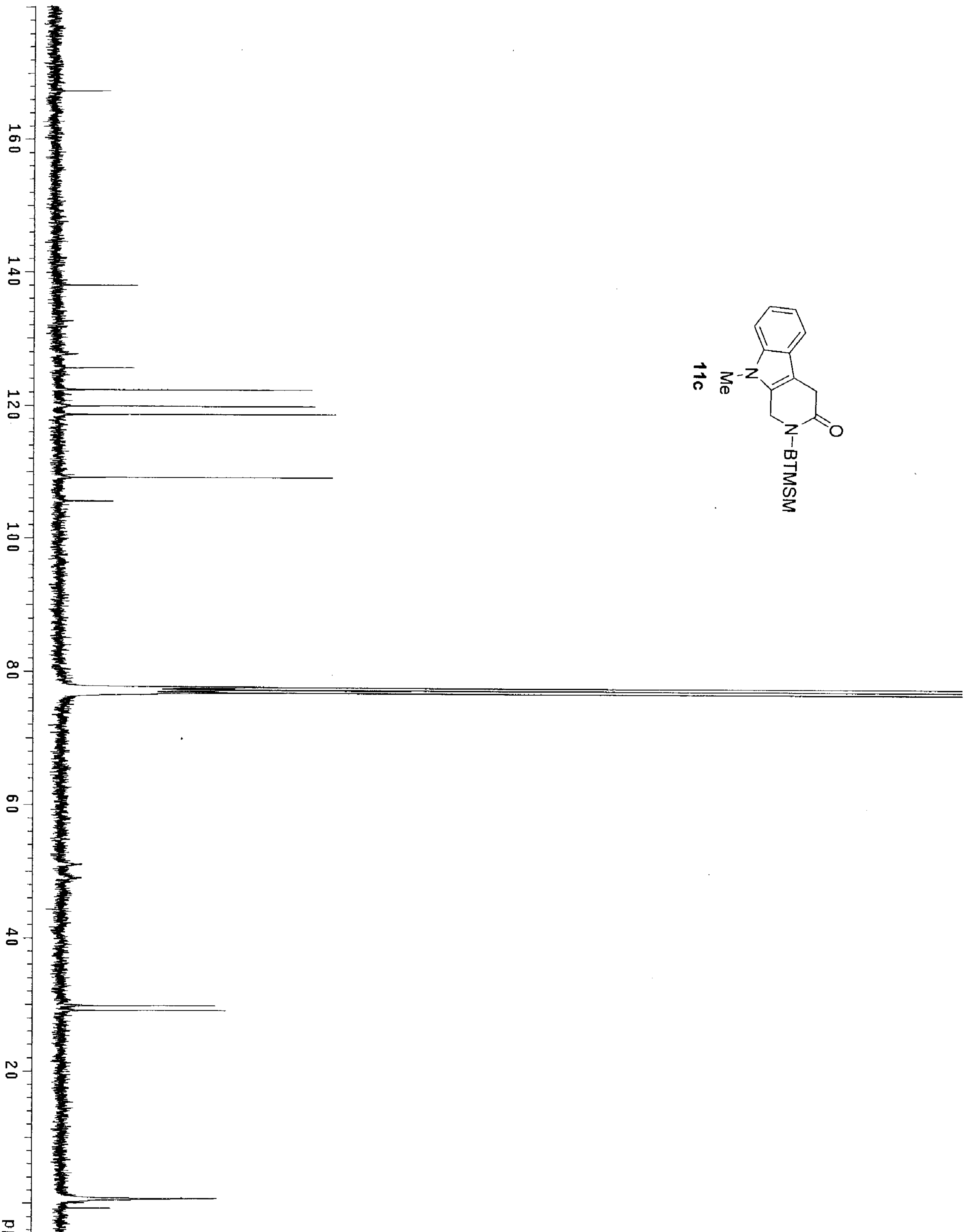
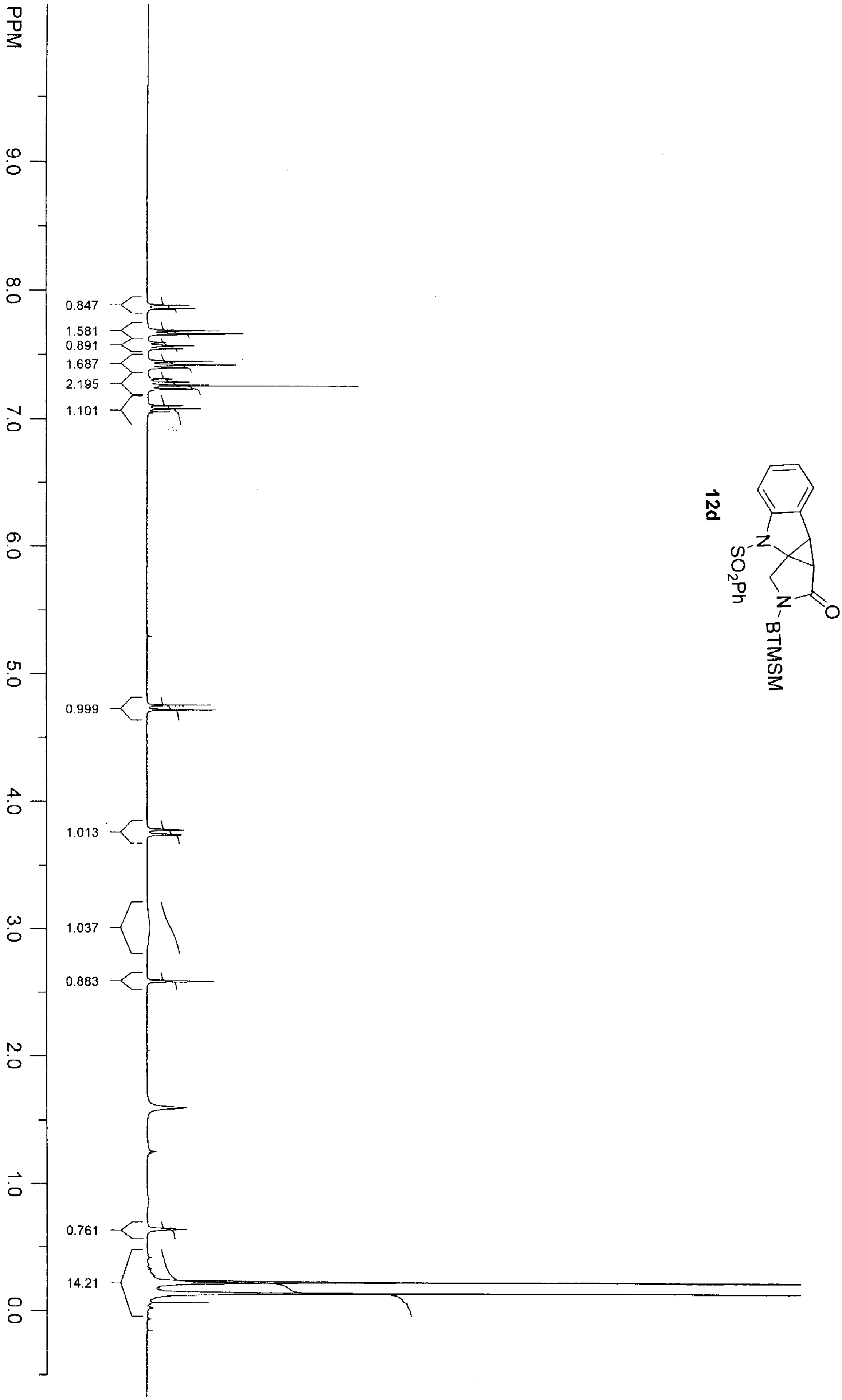
Me
N–BTMSM
O
11c


N-BTMSM
Me
11c
160
140
120
100
80
60
40
20
ppm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4.0
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0.0
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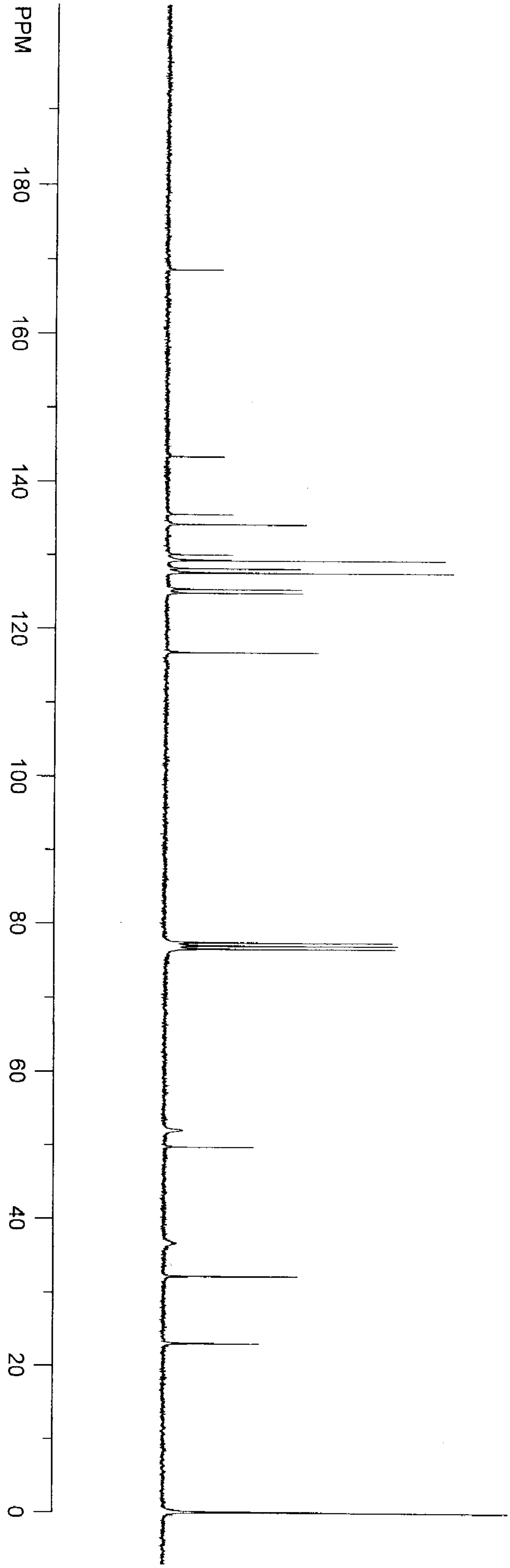
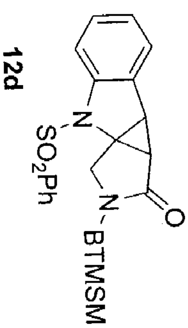
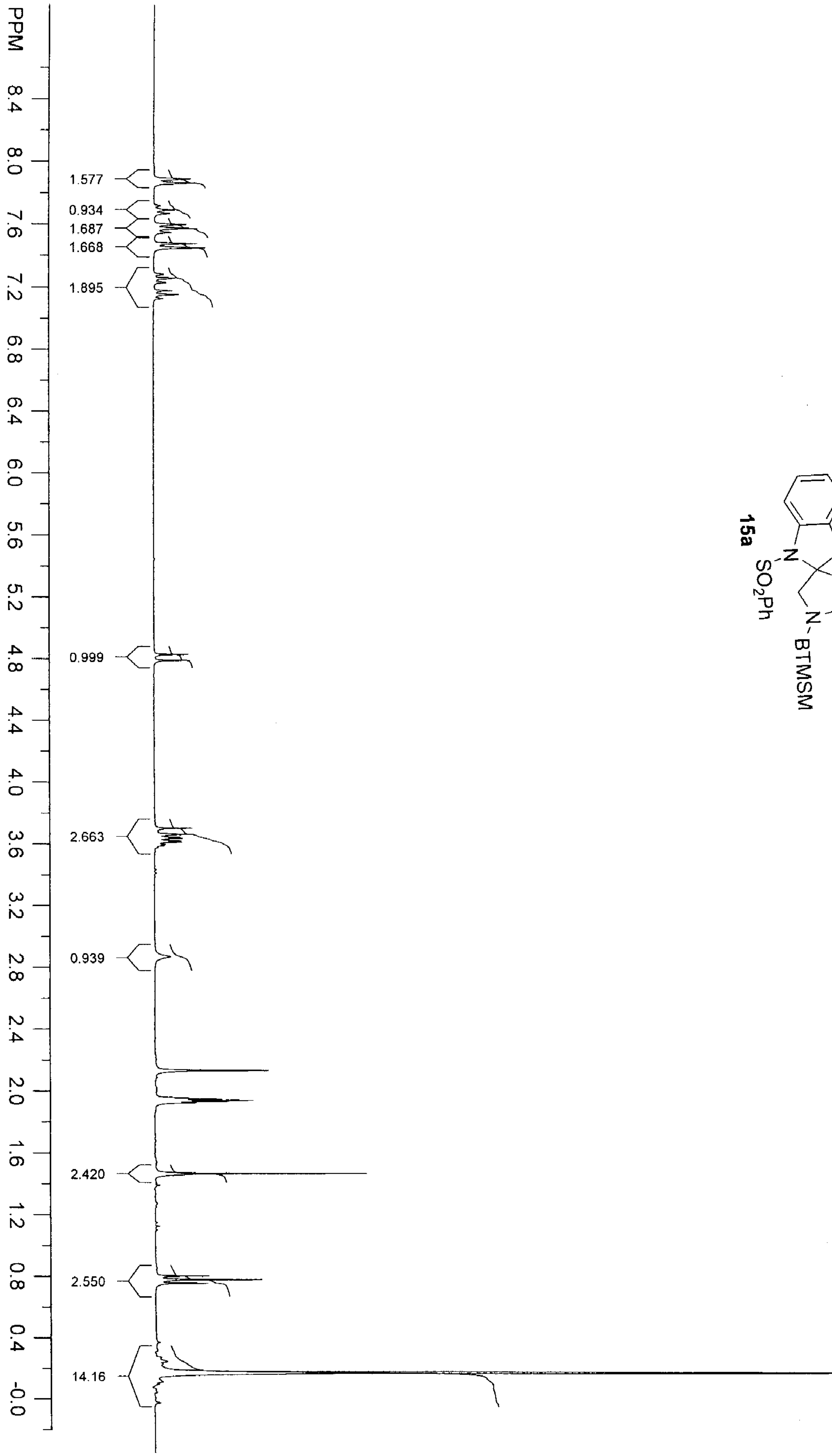
1.581
0.891
1.687
2.195
1.101
0.999
1.013
1.037
0.883
0.761
14.21
12d
N
SO2Ph
N
BTMSM
O





12d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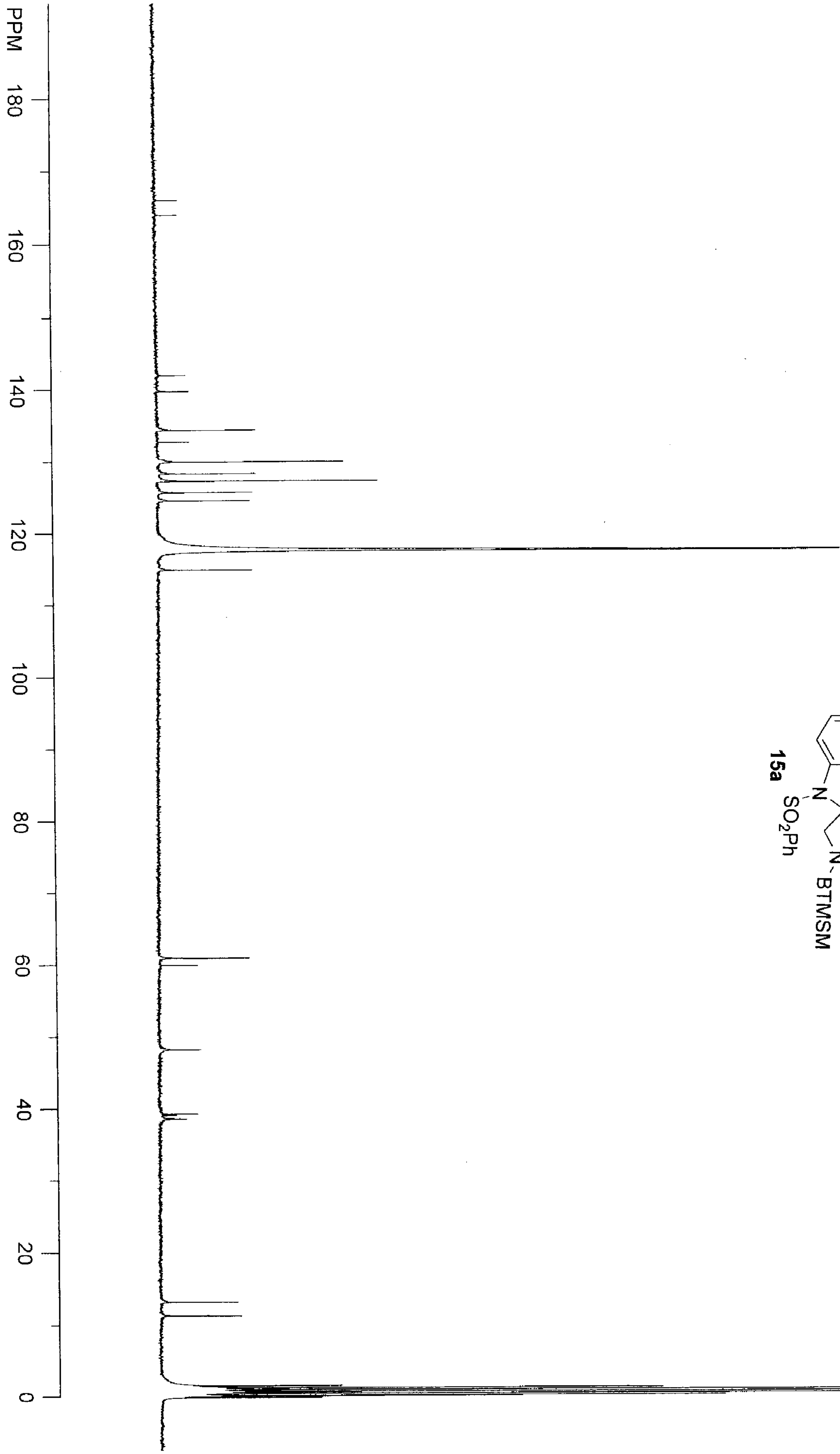
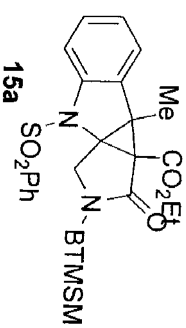
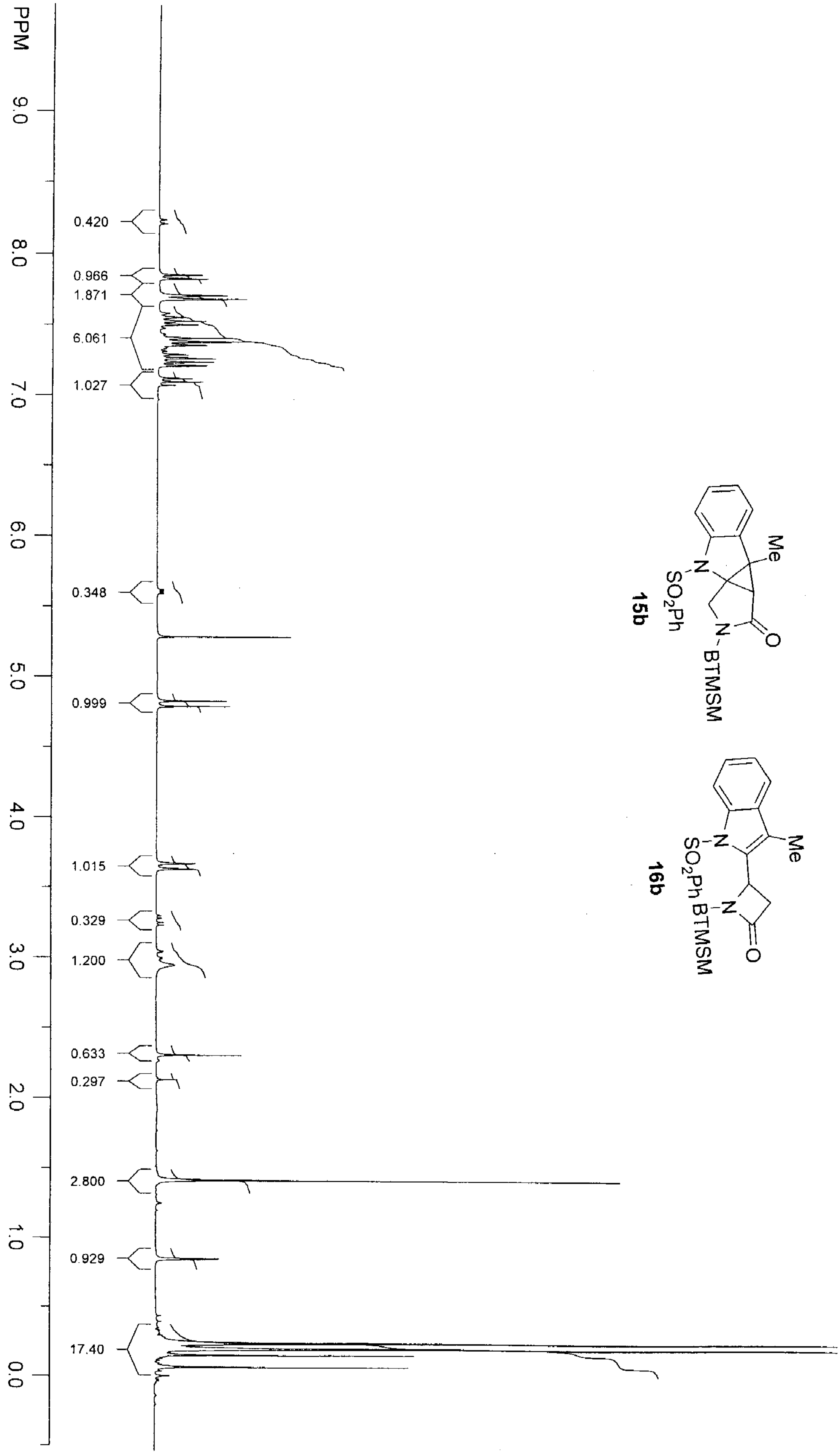
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
1.577
0.934
1.687
1.668
1.895
0.999
2.663
0.939
2.420
2.550
14.16
Me
CO2Et
N
SO2Ph
N
BTMSM
O
15a





15a


PPM
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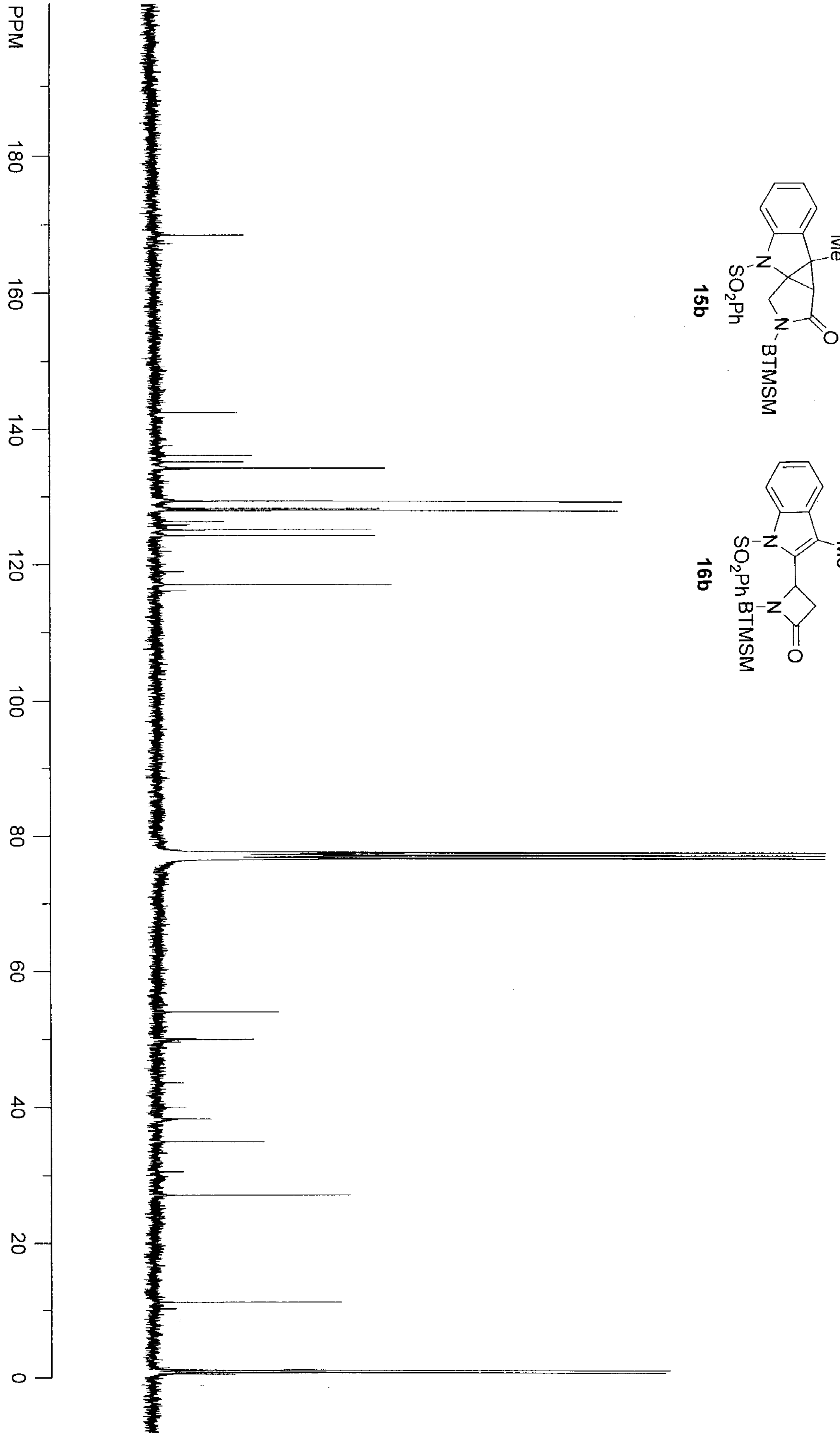
5.0
4.0
3.0
2.0
1.0
0.0
0.420
0.966
1.871
6.061
1.027
0.348
0.999
1.015
0.329
1.200
0.633
0.297
2.800
0.929
17.40
Me
N
SO_2Ph
N
BTMSM
O
15b
Me
N
SO_2Ph
N
BTMSM
O
16b


PPM
180
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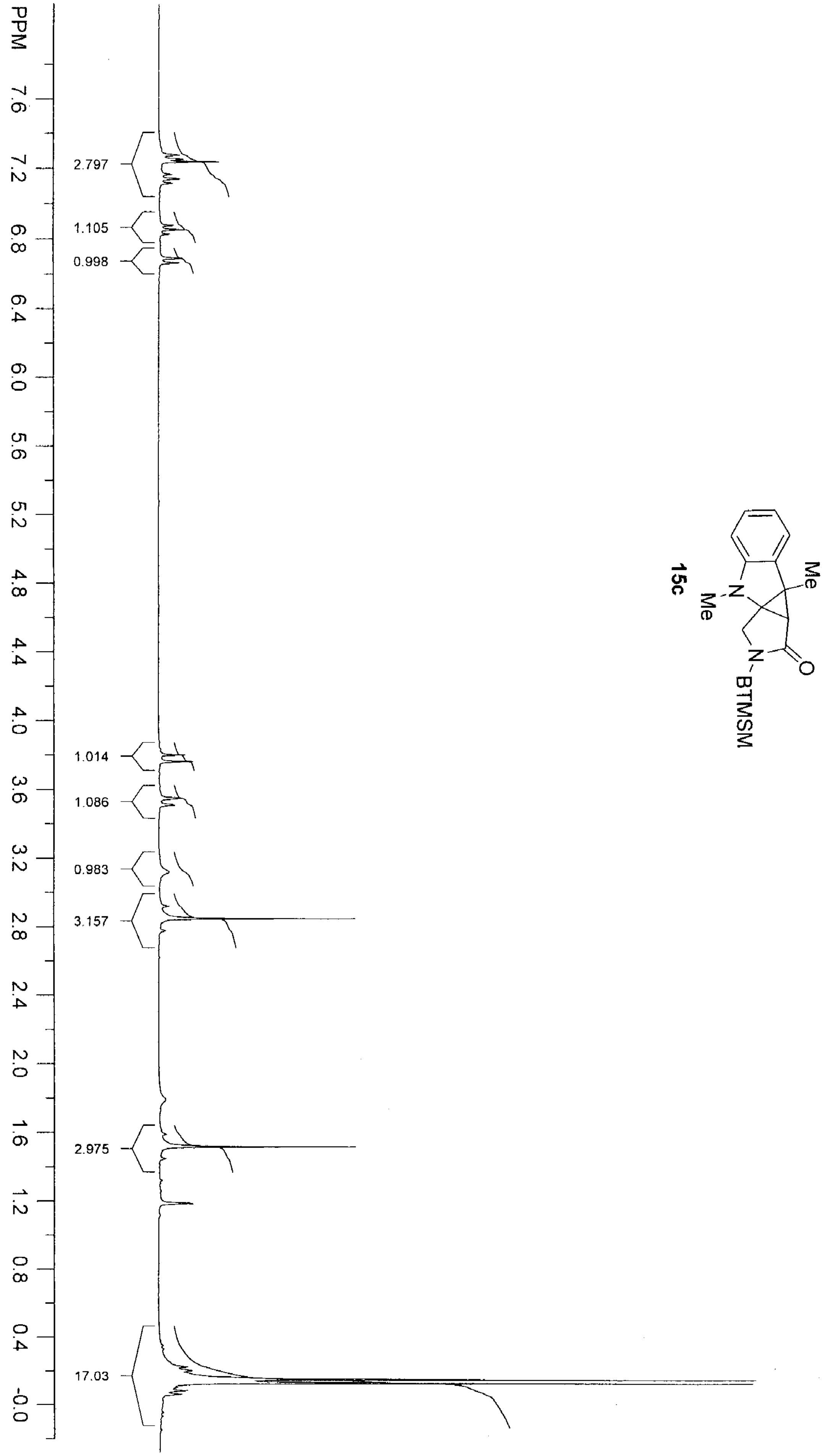
140
120
100
80
60
40
20
0
Me
N
SO2Ph
N
BTMSM
O
15b
Me
N
SO2Ph
N
BTMSM
O
16b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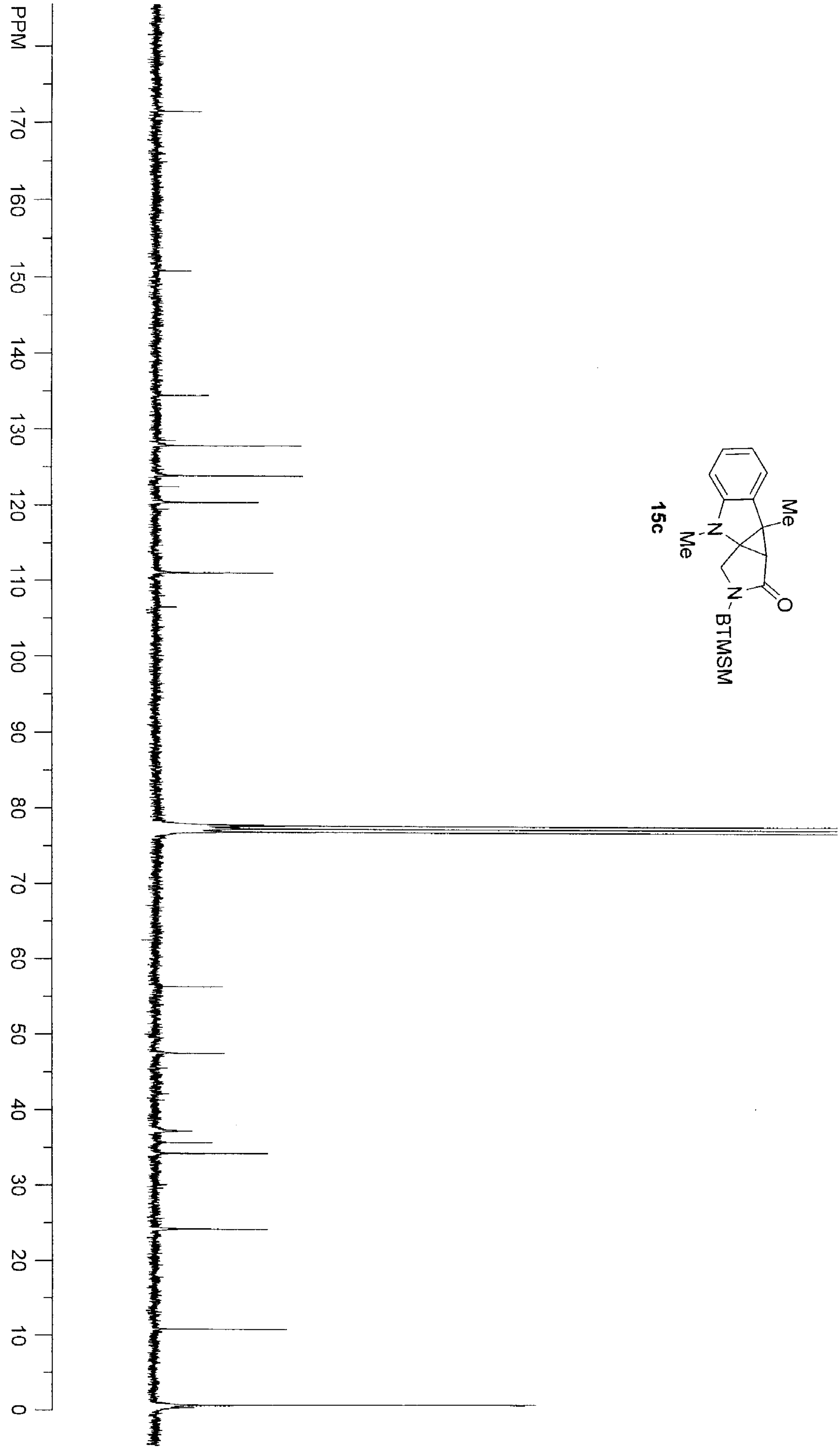
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
2.797
1.105
0.998
1.014
1.086
0.983
3.157
2.975
17.03
Me
N
Me
N
O
BTMSM
15c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150
140
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110
100
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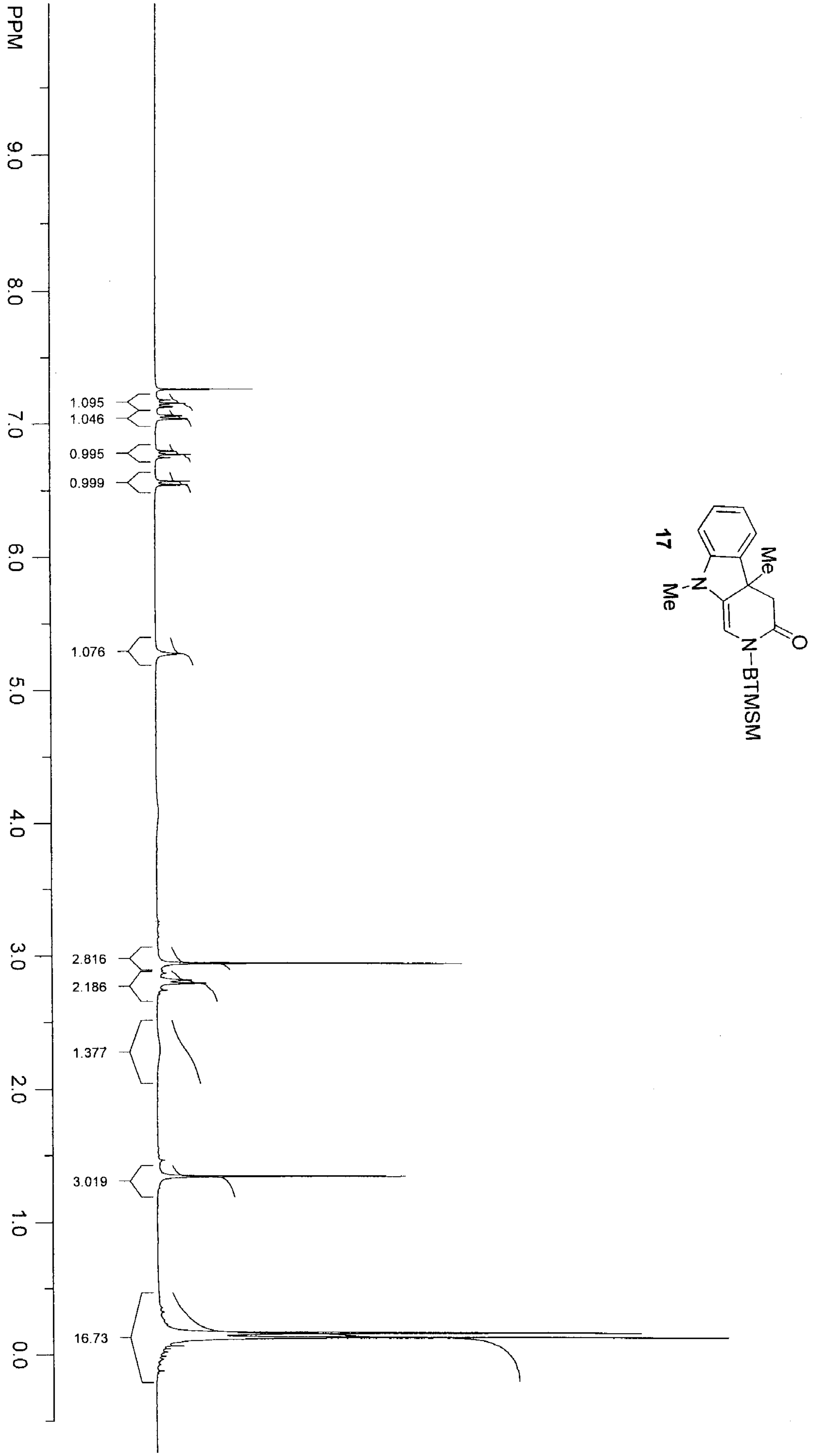
80
70
60
50
40
30
20
10
0
Me
N
Me
N
O
BTMSM

15c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1.0
0.0
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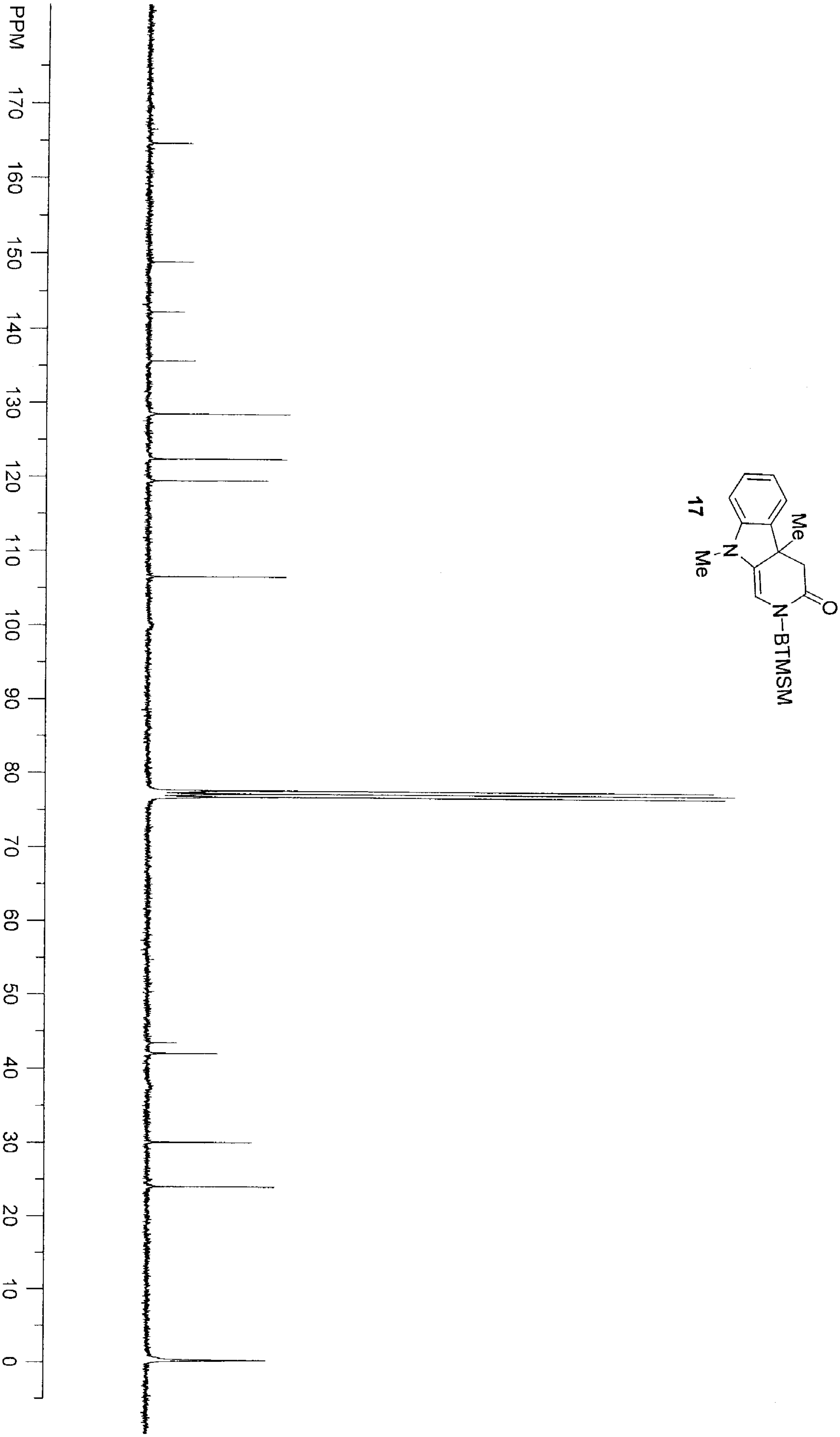
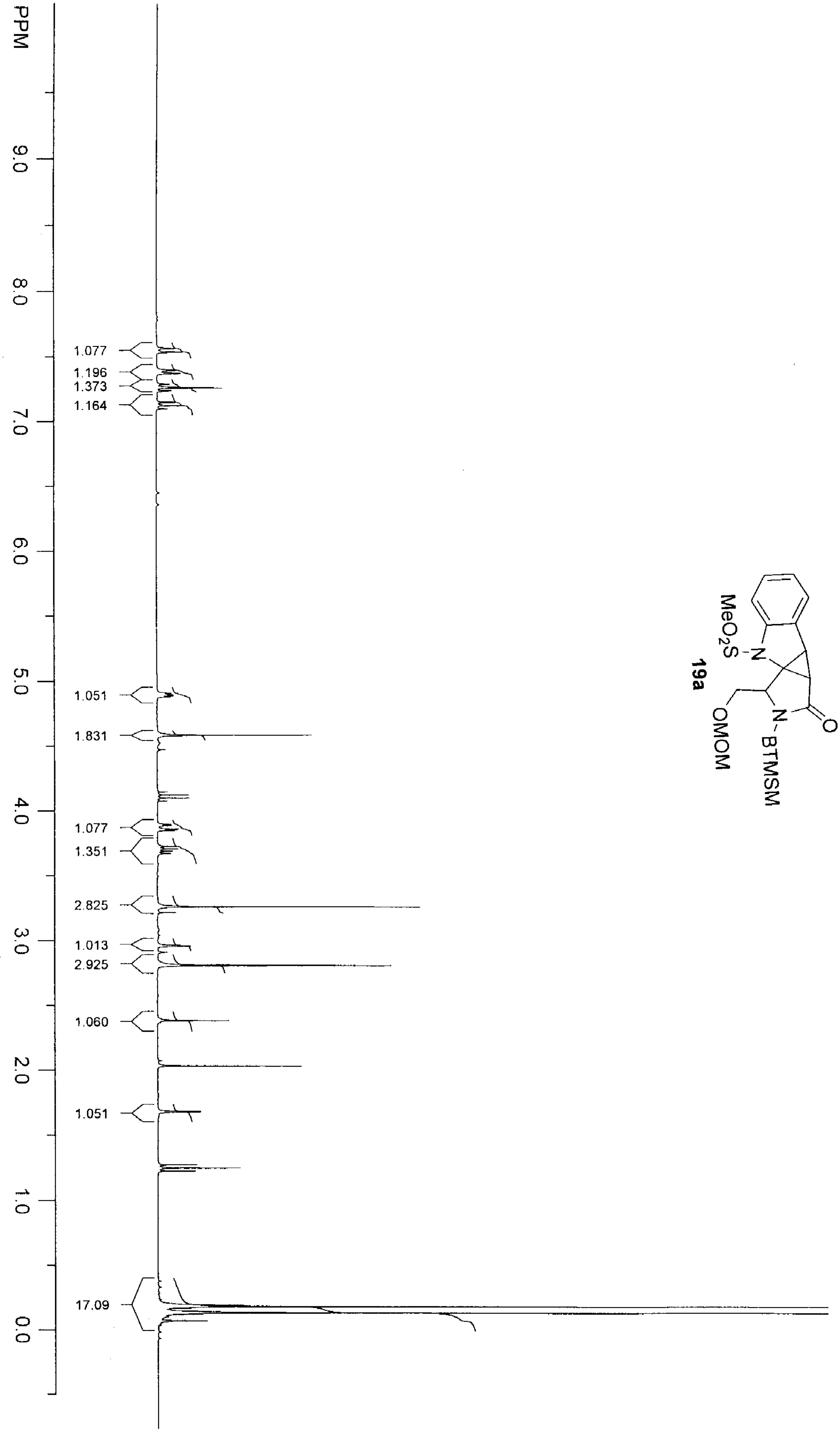
1.046
0.995
0.999
1.076
2.816
2.186
1.377
3.019
16.73
17
Me
N
Me
O
N–BTMSM


PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Me
N
Me
O
N–BTMSM
17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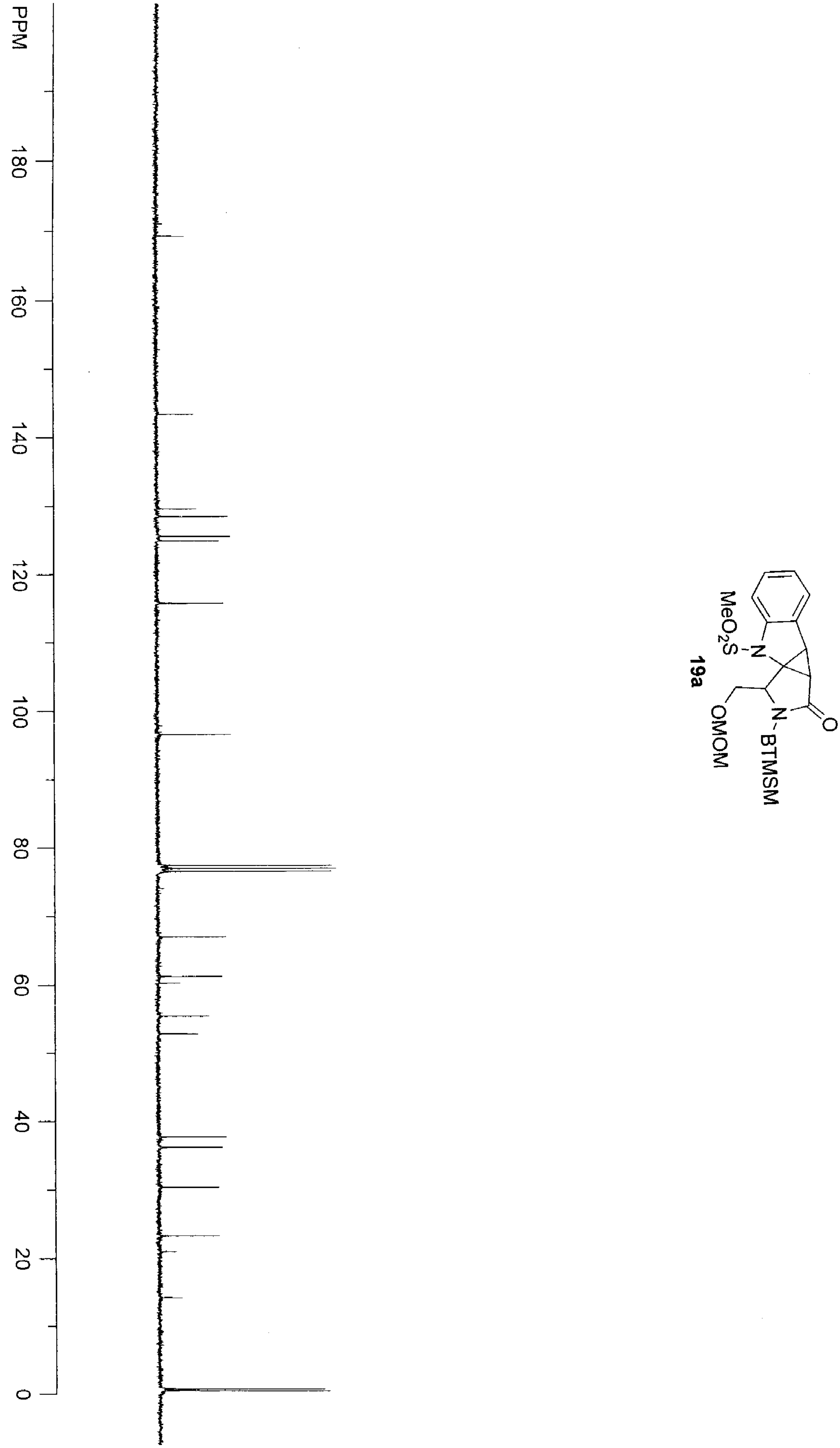
1.077
1.196
1.373
1.164
1.051
1.831
1.077
1.351
2.825
1.013
2.925
1.060
1.051
17.09
MeO2S
N
N
BTMSM
OMOM
O
19a


PPM
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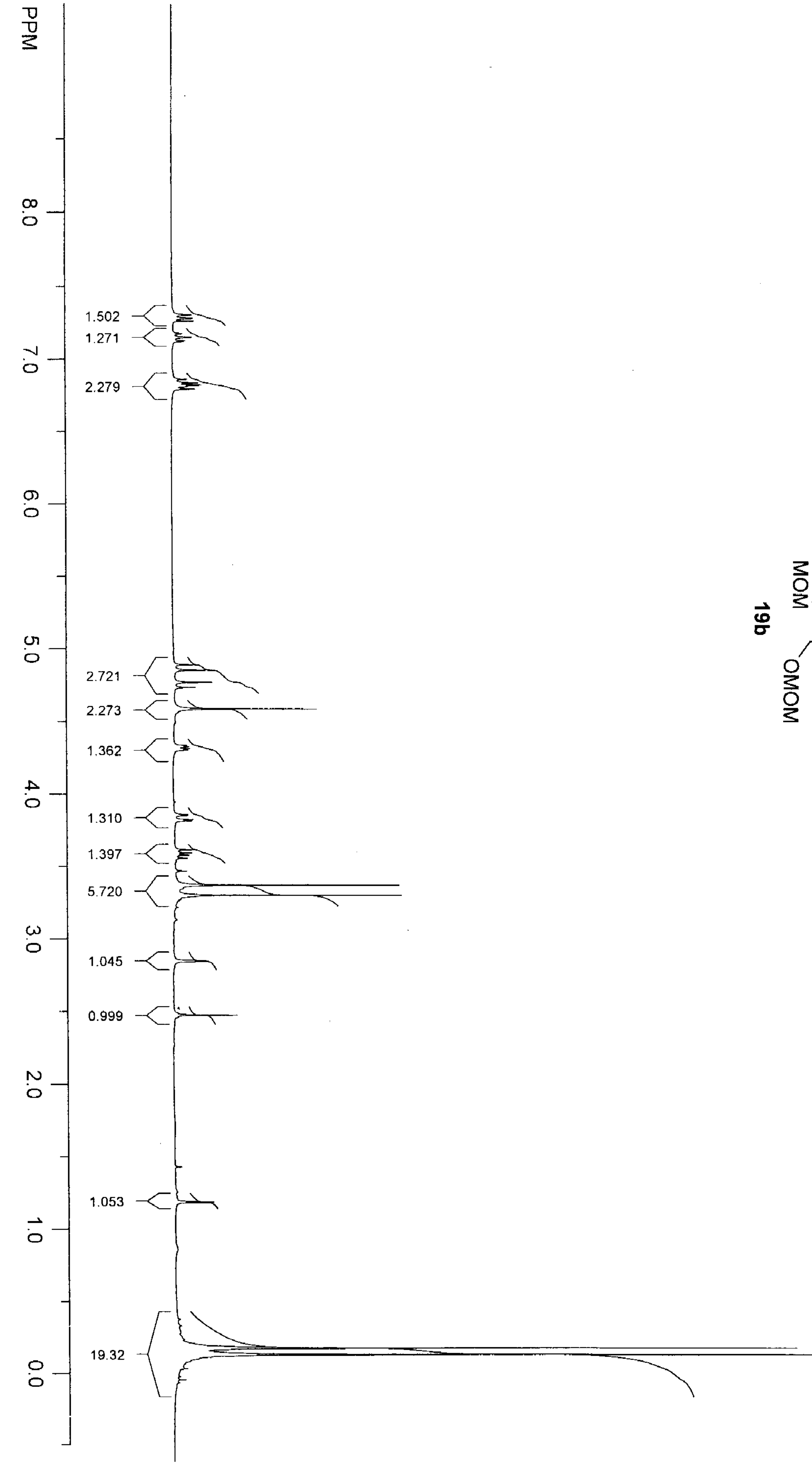
160
140
120
100
80
60
40
20
0
MeO2S
N
N
BTMSM
O
OMOM
19a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8.0
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4.0
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2.0
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0.0
1.502
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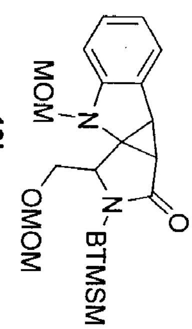
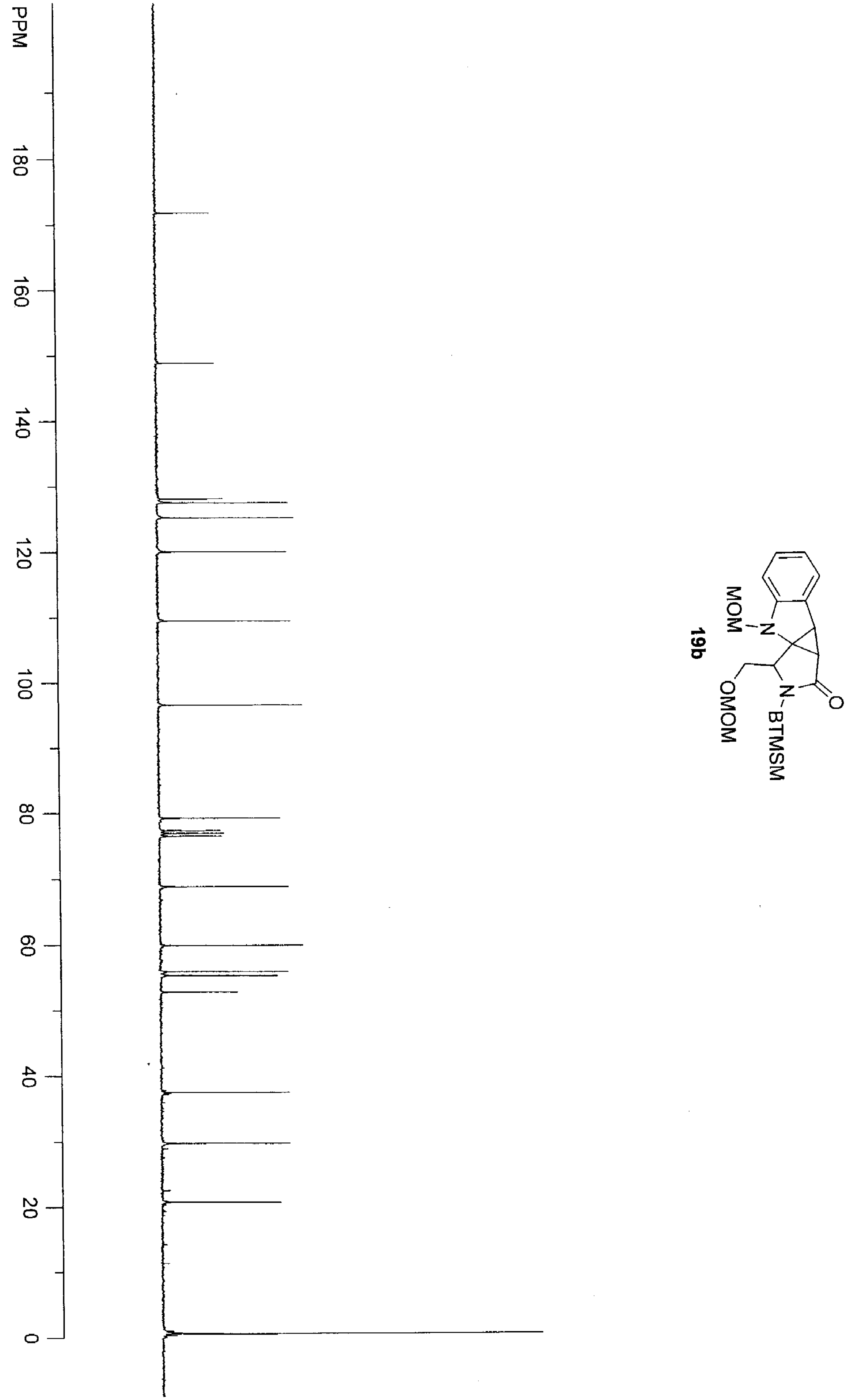
2.279
2.721
2.273
1.362
1.310
1.397
5.720
1.045
0.999
1.053
19.32


MOM
N
N
BTMSM
O
OMOM

19b


PPM
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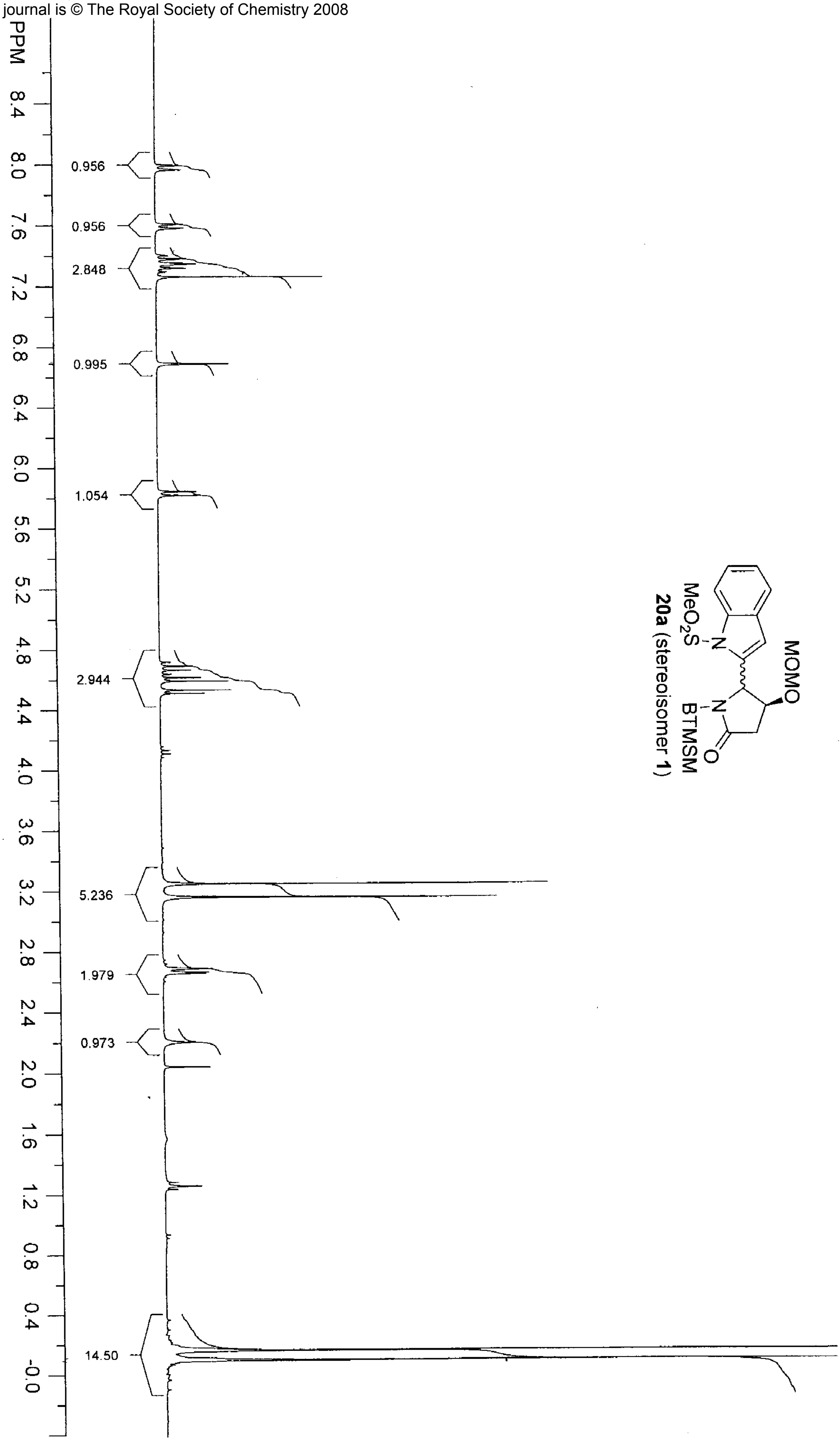
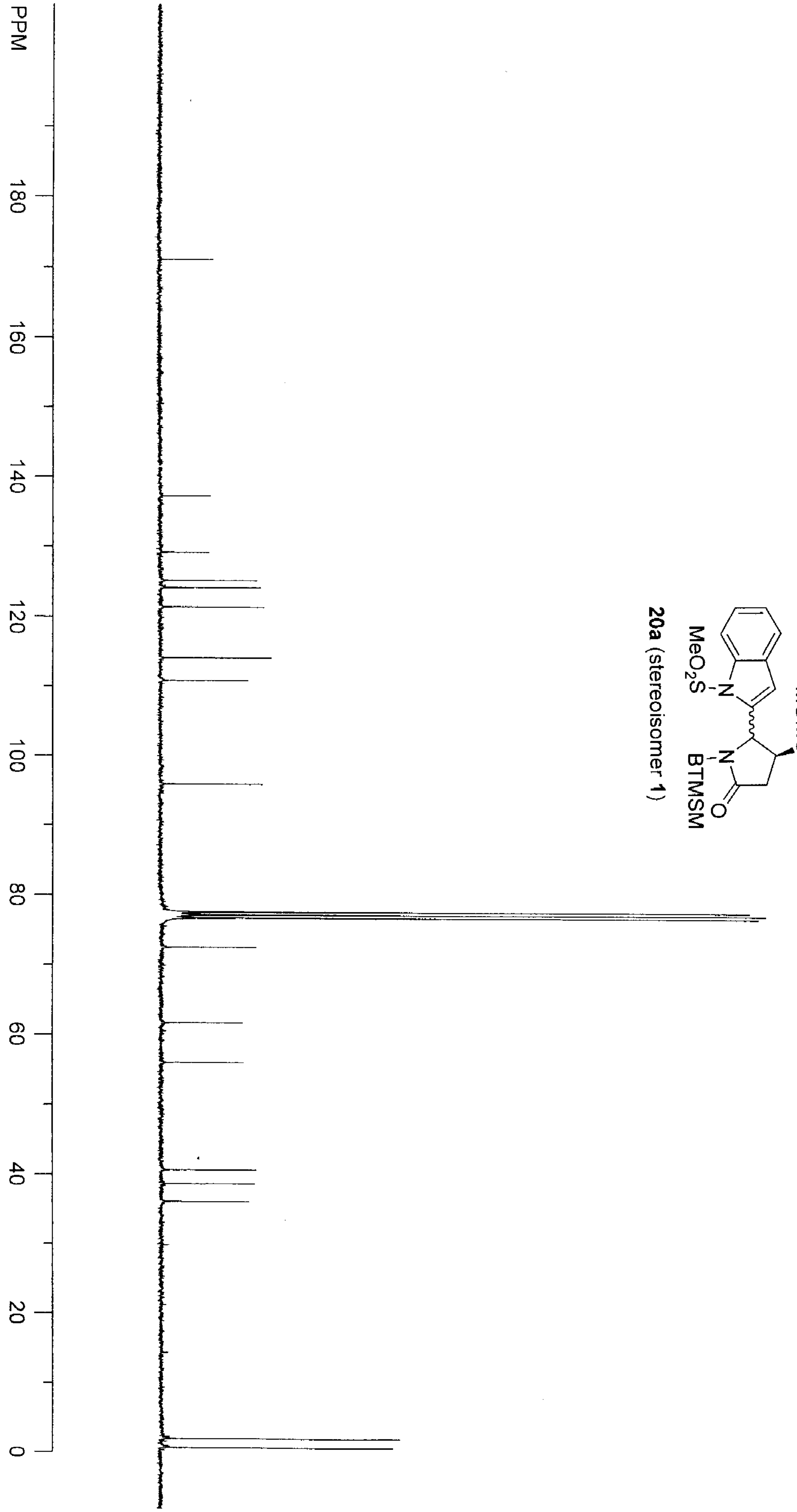
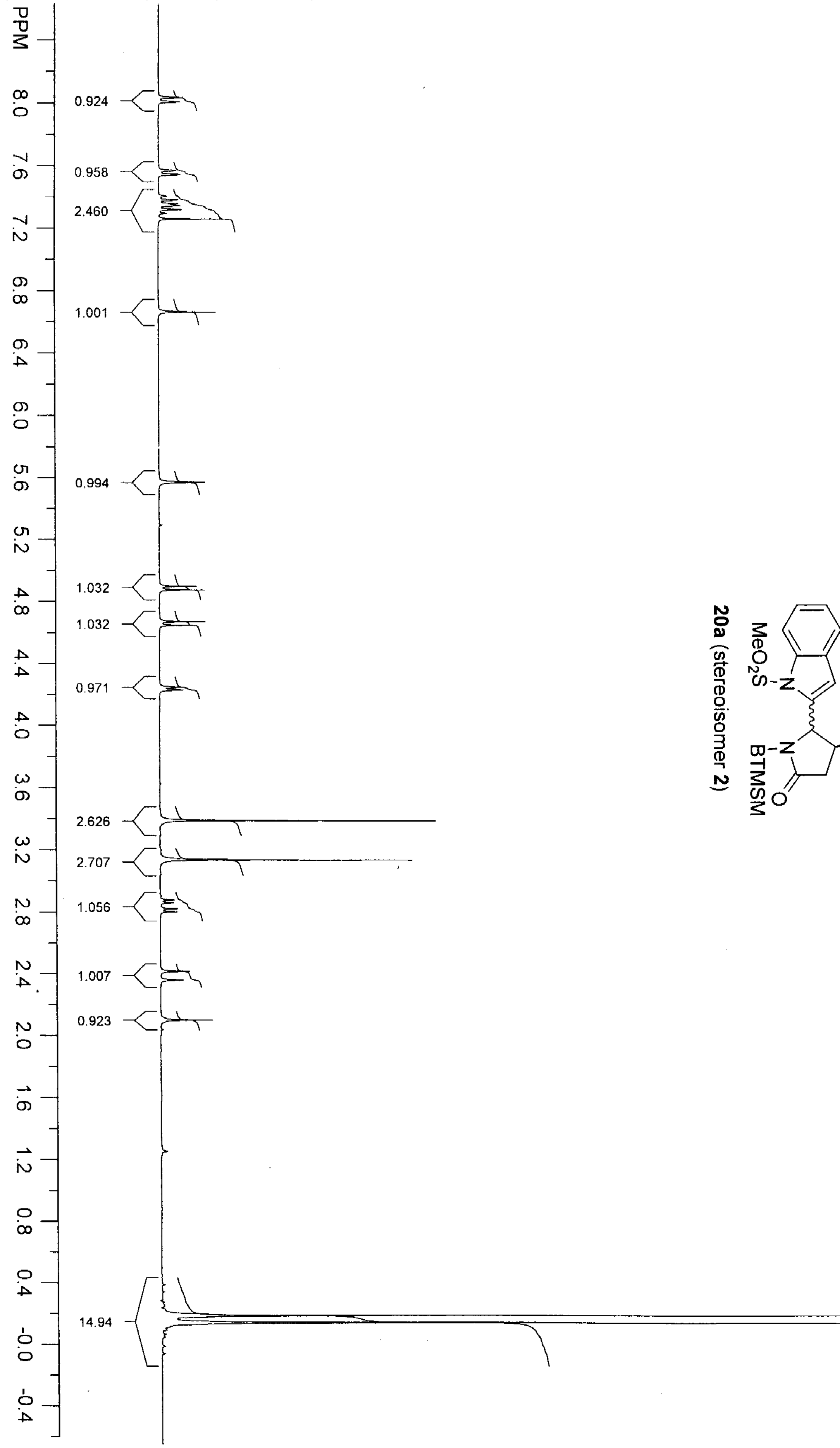
160
140
120
100
80
60
40
20
0
MOM
N
O
N
BTMSM
OMOM
19b


PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
0.956
0.956
2.848
0.995
1.054
2.944
5.236
1.979
0.973
14.50
MOMO
MeO_2S
N
N
BTMSM
O
20a (stereoisomer **1**)



20a (stereoisomer **1**)


PPM
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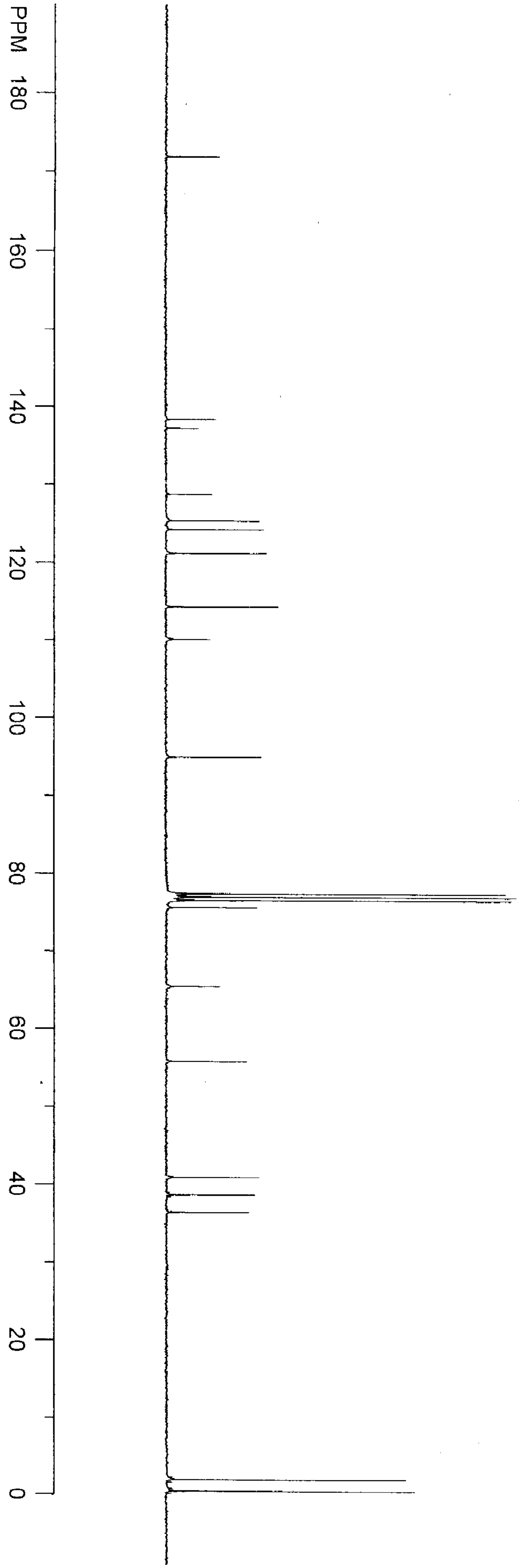
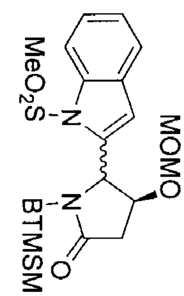
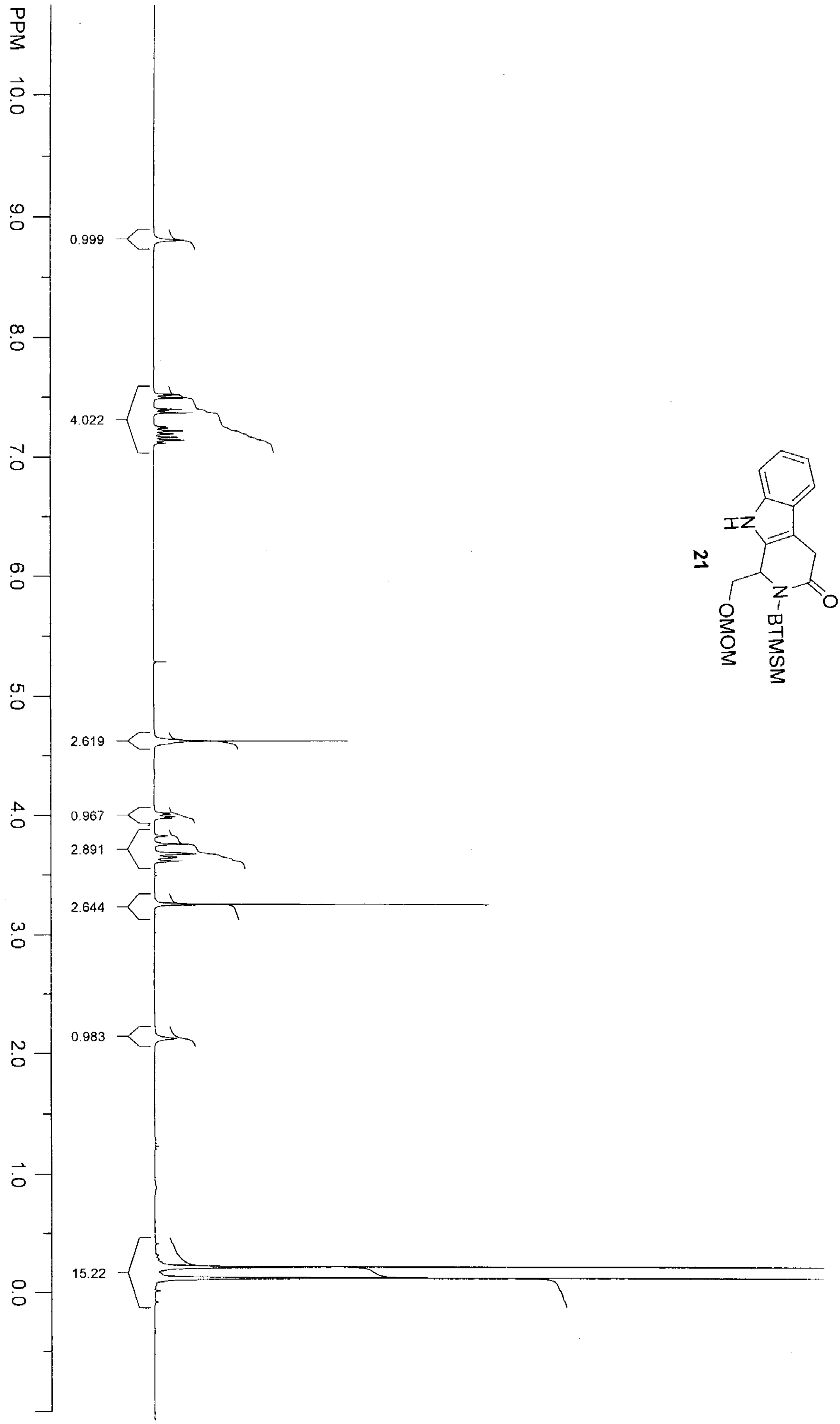
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
-0.4
0.924
0.958
2.460
1.001
0.994
1.032
1.032
0.971
2.626
2.707
1.056
1.007
0.923
14.94
MOMO
MeO2S
N
N
BTMSM
O
20a (stereoisomer 2)





20a (stereoisomer **2**)


PPM
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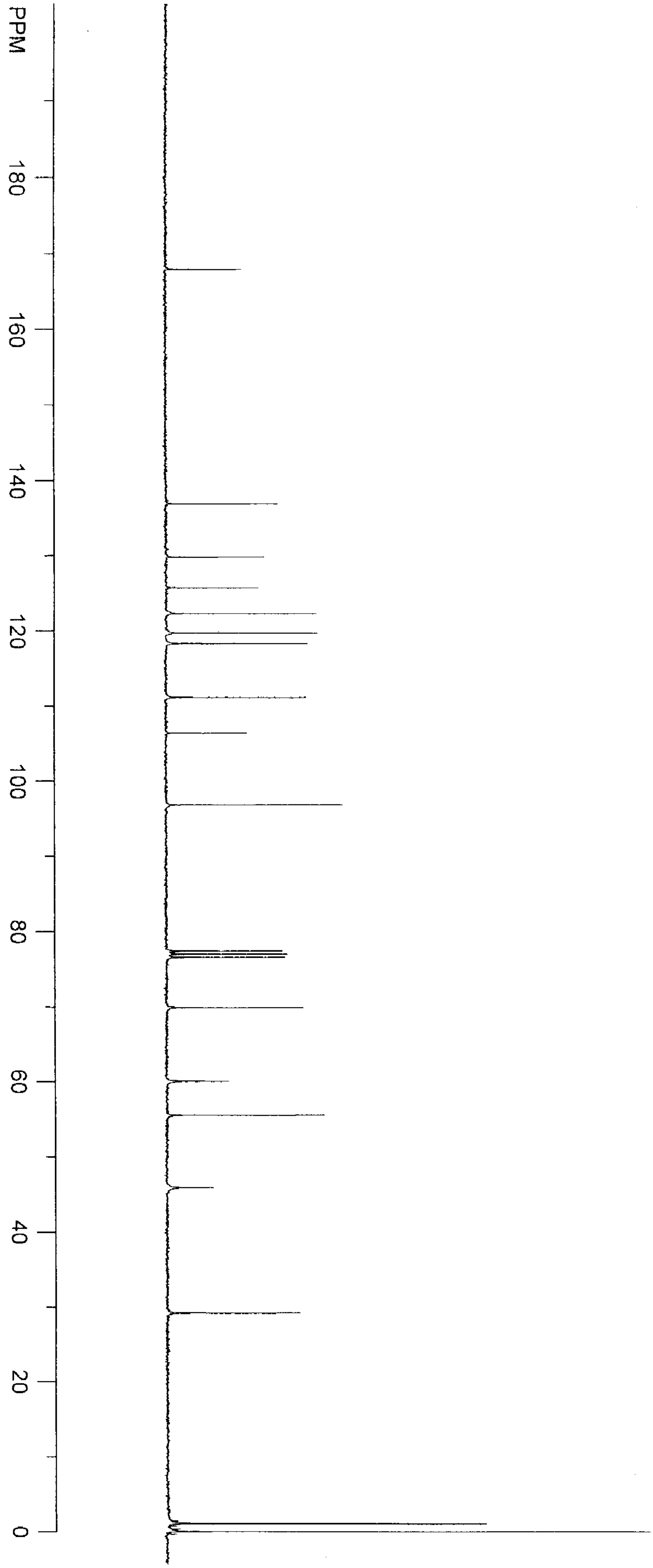
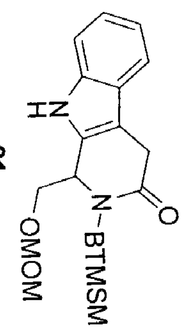
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.999
4.022
2.619
0.967
2.891
2.644
0.983
15.22
N
H
21
N-BTMSM
OMOM
O





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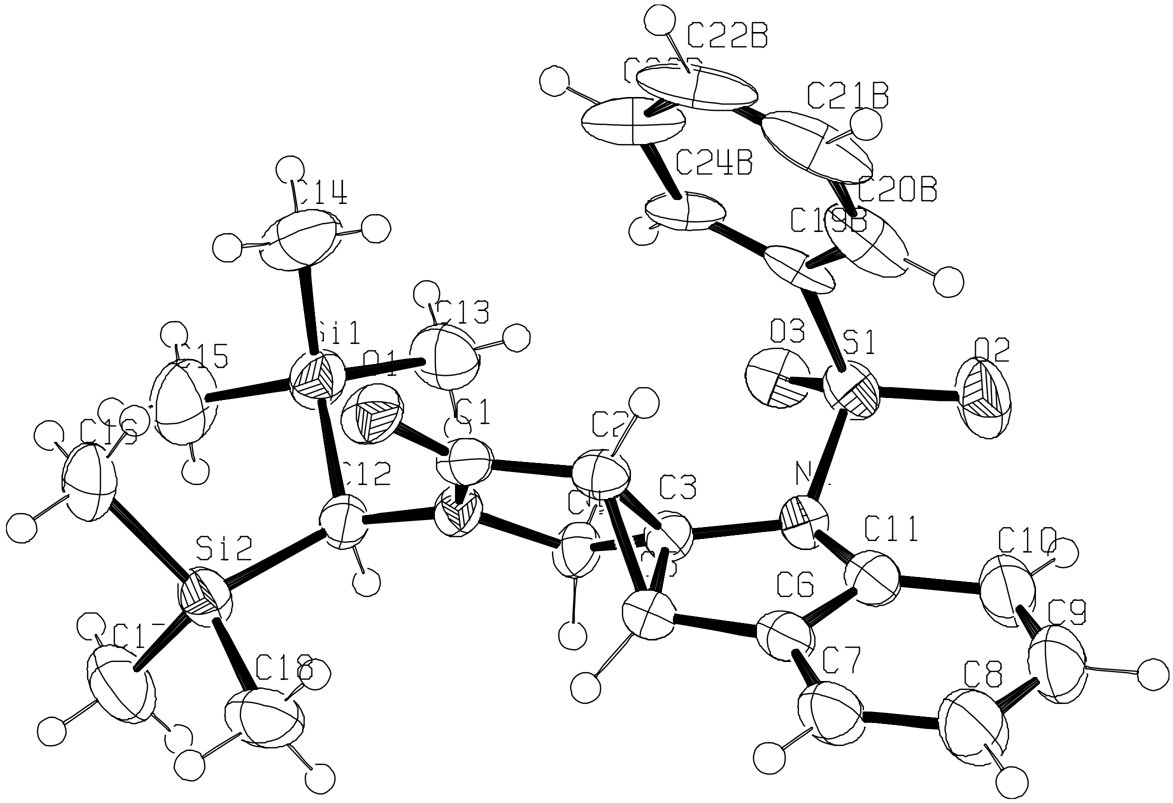
ORTEP Drawing of compound **12d**



Data was collected at -100°C on a Nonius Kappa CCD diffractometer, using the COLLECT program (Nonius, 1998). Cell refinement and data reductions used the programs DENZO and SCALEPACK (Otwinowski & Minor, 1997). SIR97 (Altomare et al., 1999) was used to solve the structure and SHELXL97 (Sheldrick, 1997) was used to refine the structure. ORTEP-3 for Windows (Farrugia , 1997) was used for molecular graphics and PLATON (Spek, 2001) was used to prepare material for publication. H atoms were placed in calculated positions with U_{iso} constrained to be 1.5 times U_{eq} of the carrier atom for methyl protons and 1.2 times U_{eq} of the carrier atom for all other hydrogen atoms.

The phenyl group of the benzene sulfonate moiety was found to be disordered. The phenyl group was modelled as rigid phenyl groups in two different positions. The occupancies were approximately 48 and 52%. The ORTEP diagram was drawn using only the higher occupancy phenyl position.

References:

A, Altomare, M. C. Burla, M. Camalli, G. Cascarano, C, Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna, R. *J. Appl. Cryst*., 1999, **32**, 115.

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L. J. Farrugia, *J. Appl. Cryst*. 1997, **30**, 565. (one page only)

Nonius (1998). COLLECT. Nonius BV, Delft, The Netherlands

Z. Otwinowski and W. Minor, *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C.W. Carter and R.M. Sweet, pp. 307-326. London: Academic Press, 1997.

Sheldrick, G.M. (1997). SHELXL-97. University of Göttingen. Germany.

Spek, A.L. (2001). PLATON. University of Utrecht, The Netherlands.

Table 1. Crystal data and structure refinement for 384.

Identification code	384	
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	$P2_1/c$	
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 384. 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 384.

S(1)-O(2)	1.4248(15)	C(5)-C(6)	1.484(2)	C(17)-H(17C)	0.9800
S(1)-O(3)	1.4255(14)	C(5)-H(5)	1.0000	C(18)-H(18A)	0.9800
S(1)-N(2)	1.6702(16)	C(6)-C(7)	1.386(3)	C(18)-H(18B)	0.9800
S(1)-C(19A)	1.746(3)	C(6)-C(11)	1.388(3)	C(18)-H(18C)	0.9800
S(1)-C(19B)	1.756(2)	C(7)-C(8)	1.391(3)	C(19A)-C(20A)	1.3799
Si(1)-C(14)	1.860(3)	C(7)-H(7)	0.9500	C(19A)-C(24A)	1.3799
Si(1)-C(13)	1.861(2)	C(8)-C(9)	1.379(3)	C(20A)-C(21A)	1.3800
Si(1)-C(15)	1.864(3)	C(8)-H(8)	0.9500	C(20A)-H(20A)	0.9500
Si(1)-C(12)	1.8984(19)	C(9)-C(10)	1.386(3)	C(21A)-C(22A)	1.3799
Si(2)-C(16)	1.866(2)	C(9)-H(9)	0.9500	C(21A)-H(21A)	0.9500
Si(2)-C(18)	1.868(2)	C(10)-C(11)	1.389(3)	C(22A)-C(23A)	1.3799
Si(2)-C(17)	1.874(3)	C(10)-H(10)	0.9500	C(22A)-H(22A)	0.9500
Si(2)-C(12)	1.9057(19)	C(12)-H(12)	1.0000	C(23A)-C(24A)	1.3800
O(1)-C(1)	1.233(2)	C(13)-H(13A)	0.9800	C(23A)-H(23A)	0.9500
N(1)-C(1)	1.348(2)	C(13)-H(13B)	0.9800	C(24A)-H(24A)	0.9500
N(1)-C(4)	1.469(2)	C(13)-H(13C)	0.9800	C(19B)-C(20B)	1.3799
N(1)-C(12)	1.483(2)	C(14)-H(14A)	0.9800	C(19B)-C(24B)	1.3799
N(2)-C(11)	1.446(2)	C(14)-H(14B)	0.9800	C(20B)-C(21B)	1.3800
N(2)-C(3)	1.467(2)	C(14)-H(14C)	0.9800	C(20B)-H(20B)	0.9500
C(1)-C(2)	1.491(2)	C(15)-H(15A)	0.9800	C(21B)-C(22B)	1.3799
C(2)-C(3)	1.512(2)	C(15)-H(15B)	0.9800	C(21B)-H(21B)	0.9500
C(2)-C(5)	1.521(2)	C(15)-H(15C)	0.9800	C(22B)-C(23B)	1.3799
C(2)-H(2)	1.0000	C(16)-H(16A)	0.9800	C(22B)-H(22B)	0.9500
C(3)-C(5)	1.496(3)	C(16)-H(16B)	0.9800	C(23B)-C(24B)	1.3800
C(3)-C(4)	1.510(2)	C(16)-H(16C)	0.9800	C(23B)-H(23B)	0.9500
C(4)-H(4A)	0.9900	C(17)-H(17A)	0.9800	C(24B)-H(24B)	0.9500
C(4)-H(4B)	0.9900	C(17)-H(17B)	0.9800		
O(2)-S(1)-O(3)	120.17(10)	N(1)-C(1)-C(2)	109.41(15)	C(6)-C(7)-H(7)	120.8
O(2)-S(1)-N(2)	106.50(9)	C(1)-C(2)-C(3)	104.32(14)	C(8)-C(7)-H(7)	120.8
O(3)-S(1)-N(2)	106.08(8)	C(1)-C(2)-C(5)	114.28(15)	C(9)-C(8)-C(7)	120.6(2)
O(2)-S(1)-C(19A)	104.6(5)	C(3)-C(2)-C(5)	59.09(12)	C(9)-C(8)-H(8)	119.7
O(3)-S(1)-C(19A)	111.9(5)	C(1)-C(2)-H(2)	120.8	C(7)-C(8)-H(8)	119.7
N(2)-S(1)-C(19A)	106.9(5)	C(3)-C(2)-H(2)	120.8	C(8)-C(9)-C(10)	121.8(2)
O(2)-S(1)-C(19B)	114.1(5)	C(5)-C(2)-H(2)	120.8	C(8)-C(9)-H(9)	119.1
O(3)-S(1)-C(19B)	104.8(4)	N(2)-C(3)-C(5)	108.50(14)	C(10)-C(9)-H(9)	119.1
N(2)-S(1)-C(19B)	103.9(4)	N(2)-C(3)-C(4)	122.36(15)	C(9)-C(10)-C(11)	117.2(2)
C(14)-Si(1)-C(13)	108.37(13)	C(5)-C(3)-C(4)	118.87(15)	C(9)-C(10)-H(10)	121.4
C(14)-Si(1)-C(15)	111.14(14)	N(2)-C(3)-C(2)	122.39(15)	C(11)-C(10)-H(10)	121.4
C(13)-Si(1)-C(15)	108.13(13)	C(5)-C(3)-C(2)	60.76(12)	C(6)-C(11)-C(10)	121.60(19)
C(14)-Si(1)-C(12)	111.15(11)	C(4)-C(3)-C(2)	108.89(14)	C(6)-C(11)-N(2)	110.31(16)
C(13)-Si(1)-C(12)	109.29(10)	N(1)-C(4)-C(3)	102.36(14)	C(10)-C(11)-N(2)	127.79(19)
C(15)-Si(1)-C(12)	108.70(11)	N(1)-C(4)-H(4A)	111.3	N(1)-C(12)-Si(1)	110.87(12)
C(16)-Si(2)-C(18)	111.79(12)	C(3)-C(4)-H(4A)	111.3	N(1)-C(12)-Si(2)	113.64(13)
C(16)-Si(2)-C(17)	107.83(12)	N(1)-C(4)-H(4B)	111.3	Si(1)-C(12)-Si(2)	118.76(9)
C(18)-Si(2)-C(17)	107.40(13)	C(3)-C(4)-H(4B)	111.3	N(1)-C(12)-H(12)	103.9
C(16)-Si(2)-C(12)	114.07(10)	H(4A)-C(4)-H(4B)	109.2	Si(1)-C(12)-H(12)	103.9
C(18)-Si(2)-C(12)	108.72(10)	C(6)-C(5)-C(3)	104.14(15)	Si(2)-C(12)-H(12)	103.9
C(17)-Si(2)-C(12)	106.69(11)	C(6)-C(5)-C(2)	116.82(15)	Si(1)-C(13)-H(13A)	109.5
C(1)-N(1)-C(4)	114.59(14)	C(3)-C(5)-C(2)	60.15(11)	Si(1)-C(13)-H(13B)	109.5
C(1)-N(1)-C(12)	125.24(15)	C(6)-C(5)-H(5)	119.9	H(13A)-C(13)-H(13B)	109.5
C(4)-N(1)-C(12)	120.15(14)	C(3)-C(5)-H(5)	119.9	Si(1)-C(13)-H(13C)	109.5
C(11)-N(2)-C(3)	106.54(14)	C(2)-C(5)-H(5)	119.9	H(13A)-C(13)-H(13C)	109.5
C(11)-N(2)-S(1)	121.08(12)	C(7)-C(6)-C(11)	120.43(18)	H(13B)-C(13)-H(13C)	109.5
C(3)-N(2)-S(1)	117.66(12)	C(7)-C(6)-C(5)	129.18(18)	Si(1)-C(14)-H(14A)	109.5
O(1)-C(1)-N(1)	124.96(17)	C(11)-C(6)-C(5)	110.23(17)	Si(1)-C(14)-H(14B)	109.5
O(1)-C(1)-C(2)	125.61(17)	C(6)-C(7)-C(8)	118.3(2)	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 384. 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 384.

	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

Table 6. Torsion angles [°] for 384.

O(2)-S(1)-N(2)-C(11)	43.19(17)	C(9)-C(10)-C(11)-N(2)	-173.6(2)
O(3)-S(1)-N(2)-C(11)	172.30(14)	C(3)-N(2)-C(11)-C(6)	4.6(2)
C(19A)-S(1)-N(2)-C(11)	-68.2(5)	S(1)-N(2)-C(11)-C(6)	142.66(14)
C(19B)-S(1)-N(2)-C(11)	-77.6(5)	C(3)-N(2)-C(11)-C(10)	178.3(2)
O(2)-S(1)-N(2)-C(3)	176.91(14)	S(1)-N(2)-C(11)-C(10)	-43.6(3)
O(3)-S(1)-N(2)-C(3)	-53.98(15)	C(1)-N(1)-C(12)-Si(1)	87.89(19)
C(19A)-S(1)-N(2)-C(3)	65.5(5)	C(4)-N(1)-C(12)-Si(1)	-91.11(17)
C(19B)-S(1)-N(2)-C(3)	56.2(5)	C(1)-N(1)-C(12)-Si(2)	-48.9(2)
C(4)-N(1)-C(1)-O(1)	176.08(17)	C(4)-N(1)-C(12)-Si(2)	132.08(15)
C(12)-N(1)-C(1)-O(1)	-3.0(3)	C(14)-Si(1)-C(12)-N(1)	-58.33(16)
C(4)-N(1)-C(1)-C(2)	-5.0(2)	C(13)-Si(1)-C(12)-N(1)	61.23(16)
C(12)-N(1)-C(1)-C(2)	175.94(15)	C(15)-Si(1)-C(12)-N(1)	179.05(15)
O(1)-C(1)-C(2)-C(3)	179.83(17)	C(14)-Si(1)-C(12)-Si(2)	76.00(14)
N(1)-C(1)-C(2)-C(3)	0.94(19)	C(13)-Si(1)-C(12)-Si(2)	-164.43(12)
O(1)-C(1)-C(2)-C(5)	117.6(2)	C(15)-Si(1)-C(12)-Si(2)	-46.62(16)
N(1)-C(1)-C(2)-C(5)	-61.3(2)	C(16)-Si(2)-C(12)-N(1)	94.43(15)
C(11)-N(2)-C(3)-C(5)	-5.47(18)	C(18)-Si(2)-C(12)-N(1)	-31.07(16)
S(1)-N(2)-C(3)-C(5)	-145.25(13)	C(17)-Si(2)-C(12)-N(1)	-146.61(15)
C(11)-N(2)-C(3)-C(4)	-150.04(16)	C(16)-Si(2)-C(12)-Si(1)	-38.71(15)
S(1)-N(2)-C(3)-C(4)	70.18(19)	C(18)-Si(2)-C(12)-Si(1)	-164.22(12)
C(11)-N(2)-C(3)-C(2)	61.1(2)	C(17)-Si(2)-C(12)-Si(1)	80.24(15)
S(1)-N(2)-C(3)-C(2)	-78.68(19)	O(2)-S(1)-C(19A)-C(20A)	-36.9(8)
C(1)-C(2)-C(3)-N(2)	155.68(15)	O(3)-S(1)-C(19A)-C(20A)	-168.5(6)
C(5)-C(2)-C(3)-N(2)	-94.33(18)	N(2)-S(1)-C(19A)-C(20A)	75.8(7)
C(1)-C(2)-C(3)-C(5)	-109.98(15)	C(19B)-S(1)-C(19A)-C(20A)	149(6)
C(1)-C(2)-C(3)-C(4)	3.18(19)	O(2)-S(1)-C(19A)-C(24A)	151.7(5)
C(5)-C(2)-C(3)-C(4)	113.16(16)	O(3)-S(1)-C(19A)-C(24A)	20.1(7)
C(1)-N(1)-C(4)-C(3)	6.7(2)	N(2)-S(1)-C(19A)-C(24A)	-95.6(6)
C(12)-N(1)-C(4)-C(3)	-174.19(15)	C(19B)-S(1)-C(19A)-C(24A)	-23(5)
N(2)-C(3)-C(4)-N(1)	-158.20(15)	C(24A)-C(19A)-C(20A)-C(21A)	0.0
C(5)-C(3)-C(4)-N(1)	60.68(19)	S(1)-C(19A)-C(20A)-C(21A)	-171.3(10)
C(2)-C(3)-C(4)-N(1)	-5.69(19)	C(19A)-C(20A)-C(21A)-C(22A)	0.0
N(2)-C(3)-C(5)-C(6)	4.31(18)	C(20A)-C(21A)-C(22A)-C(23A)	0.0
C(4)-C(3)-C(5)-C(6)	150.32(15)	C(21A)-C(22A)-C(23A)-C(24A)	0.0
C(2)-C(3)-C(5)-C(6)	-113.07(16)	C(20A)-C(19A)-C(24A)-C(23A)	0.0
N(2)-C(3)-C(5)-C(2)	117.39(15)	S(1)-C(19A)-C(24A)-C(23A)	171.5(10)
C(4)-C(3)-C(5)-C(2)	-96.61(17)	C(22A)-C(23A)-C(24A)-C(19A)	0.0
C(1)-C(2)-C(5)-C(6)	-175.89(16)	O(2)-S(1)-C(19B)-C(20B)	-37.9(7)
C(3)-C(2)-C(5)-C(6)	91.46(18)	O(3)-S(1)-C(19B)-C(20B)	-171.3(5)
C(1)-C(2)-C(5)-C(3)	92.65(16)	N(2)-S(1)-C(19B)-C(20B)	77.6(6)
C(3)-C(5)-C(6)-C(7)	-176.8(2)	C(19A)-S(1)-C(19B)-C(20B)	-32(5)
C(2)-C(5)-C(6)-C(7)	119.8(2)	O(2)-S(1)-C(19B)-C(24B)	149.2(4)
C(3)-C(5)-C(6)-C(11)	-1.5(2)	O(3)-S(1)-C(19B)-C(24B)	15.8(6)
C(2)-C(5)-C(6)-C(11)	-65.0(2)	N(2)-S(1)-C(19B)-C(24B)	-95.3(5)
C(11)-C(6)-C(7)-C(8)	0.8(3)	C(19A)-S(1)-C(19B)-C(24B)	155(6)
C(5)-C(6)-C(7)-C(8)	175.6(2)	C(24B)-C(19B)-C(20B)-C(21B)	0.0
C(6)-C(7)-C(8)-C(9)	-0.4(4)	S(1)-C(19B)-C(20B)-C(21B)	-172.9(9)
C(7)-C(8)-C(9)-C(10)	-0.5(4)	C(19B)-C(20B)-C(21B)-C(22B)	0.0
C(8)-C(9)-C(10)-C(11)	0.9(4)	C(20B)-C(21B)-C(22B)-C(23B)	0.0
C(7)-C(6)-C(11)-C(10)	-0.4(3)	C(21B)-C(22B)-C(23B)-C(24B)	0.0
C(5)-C(6)-C(11)-C(10)	-176.05(19)	C(20B)-C(19B)-C(24B)-C(23B)	0.0
C(7)-C(6)-C(11)-N(2)	173.84(18)	S(1)-C(19B)-C(24B)-C(23B)	172.8(9)
C(5)-C(6)-C(11)-N(2)	-1.9(2)	C(22B)-C(23B)-C(24B)-C(19B)	0.0
C(9)-C(10)-C(11)-C(6)	-0.5(3)		