

Supporting Information

Smooth Isoindolinone Formation from Isopropyl Carbamates via Bischler-Napieralski-type Cyclization

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General Information

The melting points were determined on a micro hot-stage Yanaco MP-S3 and were uncorrected. Optical rotations were measured on a JASCO P-2100 polarimeter. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Varian MERCURY plus 300 or a JEOL ECA-500. Chemical shifts of ^1H NMR spectra were expressed in ppm relative to tetramethylsilane = 0.00 in CDCl_3 unless noted. Chemical shifts of ^{13}C NMR spectra were expressed in ppm relative to the solvent signal in CDCl_3 (77.00 ppm), $(\text{CD}_3)_2\text{SO}$ (39.50 ppm), or $(\text{CD}_3)_2\text{CO}$ (29.85 ppm). High- and low-resolution mass spectra were recorded on a JEOL GC mate (EI). Analytical thin layer chromatography (TLC) was performed using Merck TLC 60F-254 plates (0.25 mm), and visualization was accomplished with ethanolic phosphomolybdic acid. Column chromatography was performed on Fuji silysia PSQ 100B silica gel. Experiments requiring anhydrous conditions were performed under an argon atmosphere. Organic solvents were distilled by appropriate procedure and stored under argon atmosphere.

Experimental Procedures

General Procedures for Synthesis of Carbamates

Method A

Preparation of carbamates **1a**, **1b**, **1c**, **1d**, **1f**, **9b**, and **15b**.

To a stirred solution of amine (2.10 mmol) in a mixture of 1:1:1 THF–acetone– H_2O (10.0 mL) was added at 0 °C ClCO_2R (3.78 mmol). After 2 h at rt, saturated aqueous NaHCO_3 (10 mL) was added at 0 °C and the mixture was extracted with EtOAc (10 mL \times 3). The extracts were washed with saturated aqueous NaCl (10 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford carbamates **1a**, **1b**, **1c**, **1d**, **1f**, **9b**, and **15b**.

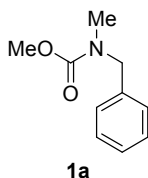
Method B

Preparation of carbamates **5b**, **6b**, **7b**, **S1**, **S4**, **10b**, **11b**, **12b**, **13b**, **13c**, **13f**, **13g**, **14b**, and **14g**.

To a stirred solution of aldehyde (2.10 mmol) in MeOH (10.5 mL) was added at rt a 40% MeOH solution of MeNH_2 (0.429 mL, 4.20 mmol). After 1 h at rt, NaBH_4 (159 mg, 4.20 mmol) was added at 0 °C and the mixture was stirred at rt for 30 min. The reaction mixture was quenched with acetone (20 mL) at 0 °C and the new mixture was concentrated under reduced pressure. The residual white solids were used for the next step without purification. To a stirred solution of the residue in a mixture of 1:1:1 THF–acetone– H_2O (10.0 mL) was added at 0 °C ClCO_2R (3.78 mmol) or FmocOSu (1.28 g, 3.78 mmol, for **17g** and **S15**). After 2 h at rt, saturated aqueous NaHCO_3 (10 mL) was added at 0 °C and the mixture was extracted with EtOAc (10 mL \times 3). The extracts were washed with saturated aqueous NaCl (10 mL), dried over Na_2SO_4 , and concentrated under reduced

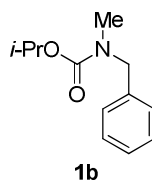
pressure. The residue was purified by column chromatography on silica gel to afford carbamates **5b**, **6b**, **7b**, **S1**, **S4**, **10b**, **11b**, **12b**, **13b**, **13c**, **13f**, **13g**, **14b**, and **14g**.

Methyl benzyl(methyl)carbamate (1a) (known)¹



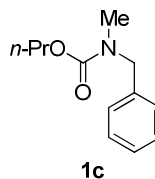
1a was prepared from *N*-methylbenzylamine in 90% yield (Method A): colorless syrup; R_f = 0.44 (2:1 hexane–EtOAc); IR (neat, cm^{-1}) 3030, 2955, 1705, 1484, 1454, 1394, 1222, 1146, 771, 701; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 2.81 (3H, s), 3.65 (3H, s), 4.43 (2H, s), 7.21–7.29 (3H, m), 7.32–7.37 (2H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 33.4, 51.4, 51.9, 126.7, 126.9, 128.1, 137.4, 156.0.

Isopropyl benzyl(methyl)carbamate (1b) (known)¹



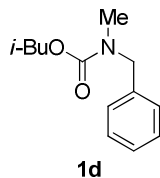
1b was prepared from *N*-methylbenzylamine in 99% yield (Method A): colorless syrup; R_f = 0.43 (4:1 hexane–EtOAc); IR (neat, cm^{-1}) 2980, 2934, 1696, 1471, 1454, 1401, 1237, 1145, 1120, 926, 701; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.21 (6H, d, J = 6.3 Hz), 2.80 (3H, s), 4.41 (2H, s), 4.84 (1H, sept, J = 6.3 Hz), 7.21–7.29 (3H, m), 7.32–7.37 (2H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 21.5, 33.3, 51.2, 67.6, 126.6, 126.9, 128.0, 137.6, 155.1.

***n*-Propyl benzyl(methyl)carbamate (1c)** (known)²



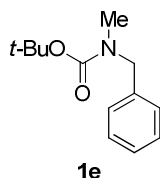
1c was prepared from *N*-methylbenzylamine in 99% yield (Method A): colorless syrup; R_f = 0.41 (4:1 hexane–EtOAc); IR (neat, cm^{-1}) 2968, 1702, 1454, 1405, 1235, 1219, 1143, 700; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 0.89 (3H, t, J = 7.4 Hz), 1.61 (2H, tq, J = 7.4, 6.6 Hz), 2.82 (3H, s), 4.02 (2H, t, J = 6.6 Hz), 4.43 (2H, s), 7.22–7.29 (3H, m), 7.32–7.37 (2H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 9.6, 21.6, 33.3, 51.3, 66.0, 126.6, 126.8, 128.0, 137.5, 155.6.

Isobutyl benzyl(methyl)carbamate (**1d**) (known)³



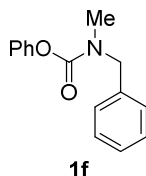
1d was prepared from *N*-methylbenzylamine in 95% yield (Method A): colorless syrup; $R_f = 0.41$ (4:1 hexane–EtOAc); IR (neat, cm^{-1}) 2962, 1703, 1454, 1405, 1387, 1234, 1219, 1144, 701; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 0.89 (6H, d, $J = 6.6$ Hz), 1.89 (1H, t-sept, $J = 6.6, 6.6$ Hz), 2.83 (3H, s), 3.85 (2H, d, $J = 6.6$ Hz), 4.44 (2H, s), 7.21–7.29 (3H, m), 7.32–7.37 (2H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 18.4, 27.2, 33.4, 51.3, 70.5, 126.7, 126.8, 128.0, 137.5, 155.6; LRMS (EI) m/z (M)⁺ 221.0; HRMS (EI) m/z (M)⁺ calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$ 221.1416, found 221.1411.

tert-Butyl benzyl(methyl)carbamate (**1e**) (known)⁴



To a stirred solution of *N*-methylbenzylamine (250 mg, 2.06 mmol) in THF (10.0 mL) were added at 0 °C 4-(dimethylamino)pyridine (252 mg, 2.06 mmol) and Boc_2O (0.567 mL, 2.47 mmol). After 1 h at rt, H_2O (10 mL) was added at 0 °C and the mixture was extracted with EtOAc (10 mL \times 3). The extracts were washed with saturated aqueous NaCl (10 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (25 g, 4:1 hexane–EtOAc) to afford **1e** (397 mg, 87%) as a colorless syrup; $R_f = 0.46$ (4:1 hexane–EtOAc); IR (neat, cm^{-1}) 2977, 2930, 1698, 1453, 1393, 1244, 1175, 1145, 878, 700; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.43 (9H, s), 2.77 (3H, s), 4.38 (2H, s), 7.21–7.28 (3H, m), 7.32–7.37 (2H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 27.7, 33.4, 51.3, 78.4, 126.6, 126.8, 128.0, 137.9, 154.7; LRMS (EI) m/z (M)⁺ 221.1; HRMS (EI) m/z (M)⁺ calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_2$ 221.1416, found 221.1419.

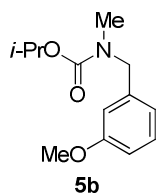
Phenyl benzyl(methyl)carbamate (**1f**)



1f was prepared from *N*-methylbenzylamine in 98% yield (Method A): colorless syrup; $R_f = 0.52$

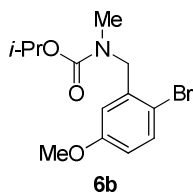
(2:1 hexane–EtOAc); IR (neat, cm^{-1}) 3032, 1722, 1474, 1454, 1399, 1206, 1129, 754, 692; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 2.98 (3H, s), 4.58 (2H, s), 7.11–7.24 (3H, m), 7.29–7.43 (7H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 34.0, 51.8, 121.2, 124.6, 126.9, 127.0, 128.2, 128.7, 137.0, 151.1, 153.8; LRMS (EI) m/z (M) $^+$ 240.9; HRMS (EI) m/z (M) $^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$ 241.1103, found 241.1102.

Isopropyl 3-methoxybenzyl(methyl)carbamate (5b)



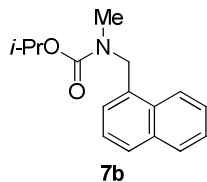
5b was prepared from 3-methoxybenzaldehyde in 92% yield (Method B): colorless syrup; R_f = 0.34 (3:1 hexane–EtOAc); IR (neat, cm^{-1}) 2980, 1698, 1602, 1490, 1457, 1400, 1262, 1234, 1151, 1113; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.21 (6H, d, J = 6.3 Hz), 2.80 (3H, s), 3.76 (3H, s), 4.38 (2H, s), 4.84 (1H, sept, J = 6.3 Hz), 6.77–6.86 (3H, m), 7.26 (1H, dd, J = 7.8, 7.8 Hz); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 21.5, 33.4, 51.2, 54.7, 67.6, 112.3, 112.8, 119.1, 129.1, 139.2, 155.1, 159.2; LRMS (EI) m/z (M) $^+$ 237.1; HRMS (EI) m/z (M) $^+$ calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_3$ 237.1365, found 237.1361.

Isopropyl 2-bromo-5-methoxybenzyl(methyl)carbamate (6b)



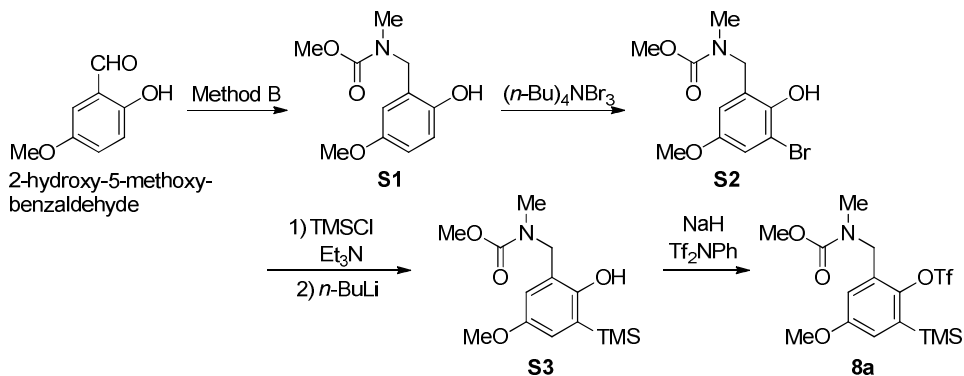
6b was prepared from 2-bromo-5-methoxybenzaldehyde⁵ in 92% yield (Method B): colorless syrup; R_f = 0.36 (3:1 hexane–EtOAc); IR (neat, cm^{-1}) 2980, 1700, 1470, 1399, 1296, 1238, 1159, 1112, 1019; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.20 (6H, d, J = 6.3 Hz), 2.85 (3H, s), 3.76 (3H, s), 4.44 (2H, s), 4.83 (1H, sept, J = 6.3 Hz), 6.73 (1H, d, J = 2.9 Hz), 6.84 (1H, dd, J = 8.9, 2.9 Hz), 7.50 (1H, d, J = 8.9 Hz); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 21.5, 33.8, 51.6, 55.0, 67.8, 112.2, 114.1, 114.2, 133.0, 137.3, 155.1, 158.8; LRMS (EI) m/z (M) $^+$ 315.1; HRMS (EI) m/z (M) $^+$ calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_3\text{Br}$ 315.0470, found 315.0493.

Isopropyl methyl(naphthalen-1-ylmethyl)carbamate (7b)



7b was prepared from 1-naphthaldehyde in 82% yield (Method B): colorless syrup; $R_f = 0.40$ (4:1 hexane–EtOAc); IR (neat, cm^{-1}) 2979, 1696, 1471, 1399, 1250, 1147, 1112, 773; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.23 (6H, d, $J = 6.3$ Hz), 2.79 (3H, s), 4.89 (1H, sept, $J = 6.3$ Hz), 4.91 (2H, s), 7.35 (1H, d, $J = 7.2$ Hz), 7.49 (1H, dd, $J = 8.1, 7.2$ Hz), 7.51–7.58 (2H, m), 7.86 (1H, d, $J = 8.1$ Hz), 7.95 (1H, m), 8.12 (1H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 21.6, 33.0, 49.0, 67.7, 122.8, 124.9, 125.0, 125.4, 125.8, 127.4, 128.2, 130.8, 132.7, 133.2, 155.1; LRMS (EI) m/z (M^+) 257.1; HRMS (EI) m/z (M^+) calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2$ 257.1416, found 257.1414.

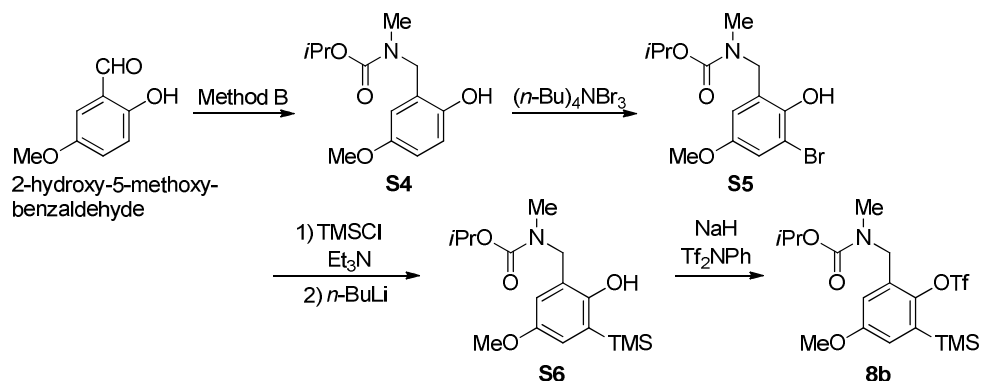
Synthesis of 4-methoxy-2-(((methoxycarbonyl)(methyl)amino)methyl)-6-(trimethylsilyl)-phenyl trifluoromethanesulfonate (8a)



Methyl 2-hydroxy-5-methoxybenzyl(methyl)carbamate (**S1**) was prepared from 2-hydroxy-5-methoxybenzaldehyde (322 mg, 2.12 mmol) (Method B). To a stirred solution of the crude **S1** (478 mg) in MeOH (5.30 mL) and CH_2Cl_2 (10.6 mL) was added at 0 °C $(n\text{-Bu})_4\text{NBr}_3$ (1.23 g, 2.55 mmol). After 1 h at rt, saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL) was added at 0 °C and the mixture was extracted with CHCl_3 (8 mL \times 3). The extracts were washed with saturated aqueous NaCl (15 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (20 g, 3:1 hexane–EtOAc) to afford methyl 3-bromo-2-hydroxy-5-methoxybenzyl(methyl)carbamate (**S2**) (397 mg, 62%) as a brown syrup; $R_f = 0.47$ (2:1 hexane–EtOAc); mp 73–77 °C (not recrystallized); IR (KBr, cm^{-1}) 2960, 1652, 1489, 1451, 1436, 1392, 1259, 1224, 1102, 1047, 776; ^1H NMR (500 MHz, CDCl_3 , solvent residual peak = 7.26) δ 2.91 (3H, s), 3.72 (3H, s), 3.73 (3H, s), 4.34 (2H, s), 6.64 (1H, d, $J = 3.2$ Hz), 7.02 (1H, br), 8.96 (1H, br s); ^{13}C NMR (125 MHz, CDCl_3) δ 33.9, 50.0, 53.5, 55.8, 111.3, 116.6, 117.7,

124.0, 146.5, 152.4, 158.8; LRMS (EI) m/z (M)⁺ 303.3; HRMS (EI) m/z (M)⁺ calcd for C₁₁H₁₄NO₄Br 303.0106, found 303.0114. To a stirred solution of **S2** (188 mg, 0.617 mmol) in dry CH₂Cl₂ (3.10 mL) were slowly added at 0 °C Et₃N (0.128 mL, 0.925 mmol) and TMSCl (0.0935 mL, 0.740 mmol). After 1 h at rt, the reaction mixture was filtrated with celite and the filter cake was washed with CHCl₃. The filtrate and washings were concentrated under reduced pressure. The residue was used for the next step without purification. To a stirred solution of the residue in dry THF (4.10 mL) was added at -78 °C 1.65 M *n*-BuLi (0.432 mL, 0.679 mmol). After the solution was slowly warm to rt over 2.5 h, saturated aqueous NH₄Cl (4 mL) was added at 0 °C and the mixture was extracted with EtOAc (3 mL × 3). The extracts were washed with saturated aqueous NaCl (4 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (10 g, 5:1 hexane–EtOAc) to afford methyl 2-hydroxy-5-methoxy-3-(trimethylsilyl)benzyl(methyl)carbamate (**S3**) (176 mg, 96%) as a colorless syrup; R_f = 0.65 (3:1 hexane–EtOAc); IR (neat, cm⁻¹) 3217, 2953, 1669, 1496, 1466, 1416, 1396, 1218, 1131, 879, 840; ¹H NMR (500 MHz, CDCl₃, solvent residual peak = 7.26) δ 0.30 (9H, s), 2.97 (3H, s), 3.75 (3H, s), 3.78 (3H, s), 4.31 (2H, s), 6.68 (1H, d, J = 3.2 Hz), 6.92 (1H, d, J = 3.2 Hz), 8.71 (1H, br s); ¹³C NMR (125 MHz, CDCl₃) δ -1.0, 34.0, 50.1, 53.5, 55.8, 117.7, 120.4, 122.0, 128.9, 152.1, 154.6, 158.7; LRMS (EI) m/z (M)⁺ 297.0; HRMS (EI) m/z (M)⁺ calcd for C₁₄H₂₃NO₄Si 297.1396, found 297.1398. To a stirred solution of **S3** (185 g, 0.620 mmol) in dry THF (3.10 mL) were added at 0 °C NaH (40.6 mg, 0.931 mmol, 55% oil dispersion) and PhNTf₂ (333 g, 0.931 mmol). After 30 min at rt, saturated aqueous NH₄Cl (5 mL) was added at 0 °C and the mixture was extracted with EtOAc (3 mL × 3). The extracts were washed with saturated aqueous NaCl (5 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (45 g, 6:1 hexane–EtOAc) to afford **8a** (257 g, 96%) as a colorless syrup; R_f = 0.58 (3:1 hexane–EtOAc); IR (neat, cm⁻¹) 2958, 1713, 1582, 1400, 1253, 1216, 1157, 1141, 1042, 879, 846; ¹H NMR (500 MHz, CDCl₃, solvent residual peak = 7.26) δ 0.37 (9H, s), 2.95 (3H, s), 3.65 (3H, s), 3.82 (3H, s), 4.51 (2H, s), 6.79 (1H, d, J = 3.2 Hz), 7.04 (1H, d, J = 3.2 Hz); ¹³C NMR (125 MHz, CDCl₃) δ -0.5, 34.0, 46.7, 52.2, 55.3, 114.6, 117.8 (q, $J_{C,F}$ = 318 Hz), 120.0, 132.3, 135.7, 141.8, 156.1, 158.4; LRMS (EI) m/z (M–Me)⁺ 414.1; HRMS (EI) m/z (M–Me)⁺ calcd for C₁₄H₁₉NO₆F₃SiS 414.0654, found 414.0655.

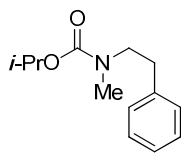
Synthesis of 2-(((isopropoxycarbonyl)(methyl)amino)methyl)-4-methoxy-6-(trimethylsilyl)-phenyl trifluoromethanesulfonate (8b)



Isopropyl 2-hydroxy-5-methoxybenzyl(methyl)carbamate (**S4**) was prepared from 2-hydroxy-5-methoxybenzaldehyde in 99% yield (Method B): colorless syrup; $R_f = 0.45$ (2:1 hexane–EtOAc); IR (neat, cm^{-1}) 3277, 2982, 1661, 1500, 1405, 1211, 1153, 1110, 1044; ^1H NMR (500 MHz, CDCl_3) δ 1.25 (6H, d, $J = 6.3$ Hz), 2.92 (3H, s), 3.76 (3H, s), 4.31 (2H, s), 4.95 (1H, sept, $J = 6.3$ Hz), 6.67 (1H, d, $J = 2.9$ Hz), 6.80 (1H, dd, $J = 8.9, 2.9$ Hz), 6.88 (1H, d, $J = 8.9$ Hz), 8.83 (1H, br s); ^{13}C NMR (125 MHz, CDCl_3) δ 22.1, 33.8, 49.7, 55.8, 70.2, 114.7, 116.8, 118.0, 123.1, 149.9, 152.5, 158.2; LRMS (EI) m/z (M^+) 252.8; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_4$ 253.1314, found 253.1314. To a stirred solution of **S4** (253 mg, 1.00 mmol) in MeOH (5.0 mL) and CH_2Cl_2 (2.5 mL) was added at 0 °C $(n\text{-Bu})_4\text{NBr}_3$ (579 mg, 1.20 mmol). After 1 h at rt, saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (3 mL) was added at 0 °C and the mixture was extracted with CHCl_3 (3 mL \times 3). The extracts were washed with saturated aqueous NaCl (3 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (60 g, 3:1 hexane–EtOAc) to afford isopropyl 3-bromo-2-hydroxy-5-methoxybenzyl(methyl)carbamate (**S5**) (176 mg, 53%) as a brown syrup: $R_f = 0.50$ (2:1 hexane–EtOAc); IR (neat, cm^{-1}) 3130, 2982, 1652, 1483, 1404, 1294, 1220, 1109, 1050, 773; ^1H NMR (500 MHz, CDCl_3) δ 1.26 (6H, d, $J = 6.3$ Hz), 2.91 (3H, s), 3.75 (3H, s), 4.35 (2H, s), 4.97 (1H, sept, $J = 6.3$ Hz), 6.65 (1H, d, $J = 3.2$ Hz), 7.04 (1H, d, $J = 3.2$ Hz), 9.25 (1H, br s); ^{13}C NMR (125 MHz, CDCl_3) δ 22.2, 33.8, 50.0, 55.9, 70.4, 111.4, 116.8, 117.7, 124.1, 147.0, 152.4, 158.2; LRMS (EI) m/z (M^+) 330.7; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_4\text{Br}$ 331.0419, found 331.0431. To a stirred solution of **S5** (346 mg, 1.04 mmol) in dry CH_2Cl_2 (5.2 mL) were slowly added at 0 °C Et_3N (0.217 mL, 1.56 mmol) and TMSCl (0.157 mL, 1.25 mmol). After 1 h at rt, the reaction mixture was filtrated with celite and the filter cake was washed with CHCl_3 . The filtrate and washings were concentrated under reduced pressure. The residue was used for the next step without purification. To a stirred solution of the residue in dry THF (6.90 mL) was added at -78 °C 1.65 M $n\text{-BuLi}$ (0.691 mL, 1.14 mmol). After the solution was slowly warm to rt over 2.5 h, saturated aqueous NH_4Cl (6 mL) was added at 0 °C and the mixture was extracted with EtOAc (6 mL \times 3). The extracts were washed with saturated aqueous NaCl (6

mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (20 g, 5:1 hexane–EtOAc) to afford isopropyl 2-hydroxy-5-methoxy-3-(trimethylsilyl)benzyl(methyl)-carbamate (**S6**) (257 mg, 74%) as a colorless syrup; *R_f* = 0.63 (3:1 hexane–EtOAc); IR (neat, cm⁻¹) 3203, 2952, 1657, 1467, 1406, 1231, 1215, 1110, 881, 840; ¹H NMR (500 MHz, CDCl₃, solvent residual peak = 7.26) δ 0.30 (9H, s), 1.25 (6H, d, *J* = 6.0 Hz), 2.94 (3H, s), 3.78 (3H, s), 4.30 (2H, s), 4.94 (1H, sept, *J* = 6.0 Hz), 6.68 (1H, d, *J* = 2.9 Hz), 6.92 (1H, d, *J* = 2.9 Hz), 8.90 (1H, br s); ¹³C NMR (125 MHz, CDCl₃) δ -1.1, 22.1, 33.9, 49.9, 55.9, 70.2, 117.9, 120.3, 122.1, 128.8, 152.1, 154.8, 158.1; LRMS (EI) *m/z* (M)⁺ 325.1; HRMS (EI) *m/z* (M)⁺ calcd for C₁₆H₂₇NO₄Si 325.1709, found 325.1709. To a stirred solution of **S6** (2.61 g, 8.02 mmol) in dry THF (40.1 mL) were added at 0 °C NaH (525 mg, 12.0 mmol, 55% oil dispersion) and PhNTf₂ (3.44 g, 9.62 mmol). After 30 min at rt, saturated aqueous NH₄Cl (50 mL) was added at 0 °C and the mixture was extracted with EtOAc (50 mL × 3). The extracts were washed with saturated aqueous NaCl (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (500 g, 6:1 hexane–EtOAc) to afford **8b** (3.67 g, 100%) as a colorless syrup; *R_f* = 0.42 (3:1 hexane–EtOAc); IR (neat, cm⁻¹) 2981, 1705, 1400, 1252, 1216, 1157, 1142, 881, 846; ¹H NMR (500 MHz, (CD₃)₂SO, 80 °C, solvent residual peak = 2.50) δ 0.37 (9H, s), 1.16 (6H, d, *J* = 6.3 Hz), 2.87 (3H, s), 3.81 (3H, s), 4.48 (2H, s), 4.81 (1H, sept, *J* = 6.3 Hz), 6.78 (1H, d, *J* = 2.9 Hz), 7.04 (1H, d, *J* = 2.9 Hz); ¹³C NMR (125 MHz, 80 °C, (CD₃)₂SO) δ -0.5, 21.4, 34.2, 46.5, 55.3, 67.9, 114.4, 117.8 (q, *J*_{C,F} = 318 Hz), 120.1, 132.7, 135.6, 141.8, 155.1, 158.3; LRMS (EI) *m/z* (M)⁺ 457.2; HRMS (EI) *m/z* (M)⁺ calcd for C₁₇H₂₆NO₆F₃SiS 457.1202, found 457.1180.

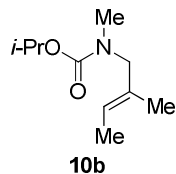
Isopropyl methyl(phenethyl)carbamate (**9b**)



9b

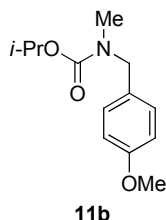
9b was prepared from *N*-methylphenethylamine in 87% yield (Method A): colorless syrup; *R_f* = 0.36 (4:1 hexane–EtOAc); IR (neat, cm⁻¹) 2979, 2933, 1697, 1455, 1401, 1203, 1114, 700; ¹H NMR (500 MHz, (CD₃)₂SO, 80 °C, solvent residual peak = 2.50) δ 1.15 (6H, d, *J* = 6.3 Hz), 2.78 (3H, s), 2.78 (2H, t, *J* = 7.5 Hz), 3.43 (2H, t, *J* = 7.5 Hz), 4.73 (1H, sept, *J* = 6.3 Hz), 7.18–7.22 (3H, m), 7.26–7.31 (2H, m); ¹³C NMR (125 MHz, 80 °C, (CD₃)₂SO) δ 21.5, 33.3, 33.6, 49.3, 67.1, 125.6, 127.8, 128.2, 138.8, 154.7; LRMS (EI) *m/z* (M)⁺ 221.2; HRMS (EI) *m/z* (M)⁺ calcd for C₁₃H₁₉NO₂ 221.1416, found 221.1419.

(E)-Isopropyl methyl(2-methylbut-2-en-1-yl)carbamate (10b)



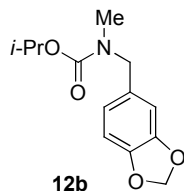
10b was prepared from tiglic aldehyde in 62% yield (Method B): colorless syrup; $R_f = 0.39$ (5:1 hexane–EtOAc); IR (neat, cm^{-1}) 2980, 2923, 1701, 1401, 1385, 1240, 1155, 1114, 923, 771; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.19 (6H, d, $J = 6.3$ Hz), 1.51 (3H, s), 1.59 (3H, d, $J = 6.6$ Hz), 2.71 (3H, s), 3.73 (2H, s), 4.79 (1H, sept, $J = 6.3$ Hz), 5.31 (1H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 12.4, 12.9, 21.5, 32.5, 54.8, 67.2, 120.2, 131.2, 155.1; LRMS (EI) m/z (M^+) 185.2; HRMS (EI) m/z (M^+) calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_2$ 185.1416, found 185.1393.

Isopropyl 4-methoxybenzyl(methyl)carbamate (11b)



11b was prepared from 4-methoxybenzaldehyde in 82% yield (Method B): colorless syrup; $R_f = 0.28$ (4:1 hexane–EtOAc); IR (neat, cm^{-1}) 2980, 1695, 1514, 1449, 1400, 1248, 1177, 1146, 1109, 1036; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.21 (6H, d, $J = 6.3$ Hz), 2.76 (3H, s), 3.75 (3H, s), 4.33 (2H, s), 4.83 (1H, sept, $J = 6.3$ Hz), 6.90 (2H, d, $J = 8.3$ Hz), 7.16 (2H, d, $J = 8.3$ Hz); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 21.6, 33.0, 50.6, 54.8, 67.5, 113.7, 128.3, 129.5, 155.1, 158.3; LRMS (EI) m/z (M^+) 236.9; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_3$ 237.1365, found 237.1359.

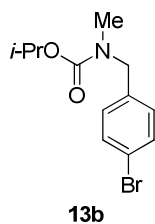
Isopropyl (benzo[1,3]dioxol-5-ylmethyl)(methyl)carbamate (12b)



12b was prepared from heliotropine in 88% yield (Method B): colorless syrup; $R_f = 0.48$ (2:1 hexane–EtOAc); IR (neat, cm^{-1}) 2980, 1696, 1491, 1445, 1401, 1248, 1146, 1113, 1040, 929; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.21 (6H, d, $J = 6.3$ Hz), 2.77 (3H, s), 4.31 (2H, s), 4.83 (1H, sept, $J = 6.3$ Hz), 5.98 (2H, s), 6.72 (1H, br d, $J = 8.0$ Hz), 6.76 (1H, br s), 6.85 (1H, d, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 21.6, 33.1, 51.0, 67.6,

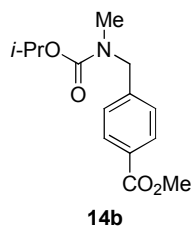
100.5, 107.5, 107.7, 120.4, 131.4, 146.1, 147.1, 155.0; LRMS (EI) m/z (M)⁺ 251.0; HRMS (EI) m/z (M)⁺ calcd for C₁₃H₁₇NO₄ 251.1158, found 251.1160.

Isopropyl 4-bromobenzyl(methyl)carbamate (**13b**)



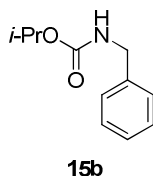
13b was prepared from 4-bromobenzaldehyde in 87% yield (Method B): colorless syrup; R_f = 0.42 (4:1 hexane–EtOAc); IR (neat, cm⁻¹) 2980, 1697, 1488, 1399, 1228, 1146, 1112, 1012; ¹H NMR (500 MHz, (CD₃)₂SO, 80 °C, solvent residual peak = 2.50) δ 1.20 (6H, d, J = 6.3 Hz), 2.80 (3H, s), 4.38 (2H, s), 4.82 (1H, sept, J = 6.3 Hz), 7.19 (2H, d, J = 8.3 Hz), 7.52 (2H, d, J = 8.3 Hz); ¹³C NMR (125 MHz, 80 °C, (CD₃)₂SO) δ 21.5, 33.4, 50.7, 67.7, 119.8, 129.1, 130.9, 137.1, 155.1; LRMS (EI) m/z (M)⁺ 285.0; HRMS (EI) m/z (M)⁺ calcd for C₁₂H₁₆NO₂Br 285.0364, found 285.0356.

Methyl 4-(((isopropoxycarbonyl)methyl)amino)methyl)benzoate (**14b**)



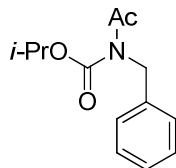
14b was prepared from methyl 4-formylbenzoate in 96% yield (Method B): colorless syrup; R_f = 0.39 (2:1 hexane–EtOAc); IR (neat, cm⁻¹) 2981, 1724, 1697, 1436, 1397, 1280, 1242, 1179, 1147, 1109; ¹H NMR (500 MHz, (CD₃)₂SO, 80 °C, solvent residual peak = 2.50) δ 1.20 (6H, d, J = 6.3 Hz), 2.83 (3H, s), 3.86 (3H, s), 4.49 (2H, s), 4.83 (1H, sept, J = 6.3 Hz), 7.36 (2H, d, J = 8.3 Hz), 7.94 (2H, d, J = 8.3 Hz); ¹³C NMR (125 MHz, 80 °C, (CD₃)₂SO) δ 21.5, 33.6, 51.1, 51.5, 67.8, 127.0, 128.4, 129.0, 143.2, 155.1, 165.7; LRMS (EI) m/z (M)⁺ 265.2; HRMS (EI) m/z (M)⁺ calcd for C₁₄H₁₉NO₄ 265.1314, found 265.1332.

Isopropyl benzylcarbamate (**15b**) (known)⁶



15b was prepared from benzylamine in 99% yield (Method A): white solids; $R_f = 0.43$ (3:1 hexane–EtOAc); mp 33–34 °C (not recrystallized); IR (KBr, cm^{-1}) 3320, 2978, 1682, 1528, 1257, 1131, 1047, 749, 697; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 1.19 (6H, d, $J = 6.3$ Hz), 4.19 (2H, d, $J = 5.9$ Hz), 4.80 (1H, sept, $J = 6.3$ Hz), 7.20–7.33 (5H, m); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 21.6, 43.6, 66.5, 126.2, 126.6, 127.7, 139.6, 155.7; LRMS (EI) m/z (M^+) 193.1; HRMS (EI) m/z (M^+) calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_2$ 193.1103, found 193.1129.

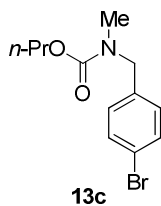
Isopropyl acetyl(benzyl) carbamate (**16b**)



16b

To a stirred solution of **15b** (249 mg, 1.29 mmol) in Ac_2O (1.60 mL) was added at 0 °C ZnCl_2 ^[9] (5.3 mg, 0.039 mmol). After 6 h at rt, H_2O (3 mL) was added at 0 °C and the mixture was extracted with CHCl_3 (3 mL \times 3). The extracts were washed with saturated aqueous NaCl (3 mL \times 3), dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (20 g, 4:1 hexane–EtOAc) to afford **16b** (269 mg, 89%) as a colorless syrup; $R_f = 0.57$ (3:1 hexane–EtOAc); IR (neat, cm^{-1}) 2984, 1736, 1701, 1373, 1215, 1106, 979, 702; ^1H NMR (500 MHz, CDCl_3) δ 1.22 (6H, d, $J = 6.3$ Hz), 2.56 (3H, s), 4.92 (2H, s), 4.98 (1H, sept, $J = 6.3$ Hz), 7.21–7.31 (5H, m); ^{13}C NMR (125 MHz, CDCl_3) δ 21.6, 26.8, 46.8, 71.1, 127.2, 127.8, 128.2, 137.9, 154.0, 173.0; LRMS (EI) m/z (M^+) 234.9; HRMS (EI) m/z (M^+) calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3$ 235.1208, found 235.1202.

n-Propyl 4-bromobenzyl(methyl)carbamate (**13c**)

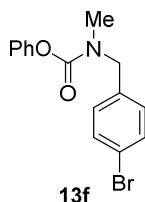


13c

13c was prepared from 4-bromobenzaldehyde in 92% yield (Method B): colorless syrup; $R_f = 0.34$ (4:1 hexane–EtOAc); IR (neat, cm^{-1}) 2968, 1701, 1488, 1403, 1380, 1221, 1146, 1071, 794; ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, 80 °C, solvent residual peak = 2.50) δ 0.88 (3H, t, $J = 7.5$ Hz), 1.59 (2H, tq, $J = 7.5, 6.6$ Hz), 2.82 (3H, s), 4.00 (2H, t, $J = 6.6$ Hz), 4.40 (2H, s), 7.19 (2H, d, $J = 8.3$ Hz), 7.52 (2H, d, $J = 8.3$ Hz); ^{13}C NMR (125 MHz, 80 °C, $(\text{CD}_3)_2\text{SO}$) δ 9.7, 21.5, 33.5, 50.8, 66.1, 119.8, 129.1, 131.0, 137.0, 155.5; LRMS (EI) m/z (M^+) 285.0; HRMS (EI) m/z (M^+) calcd for

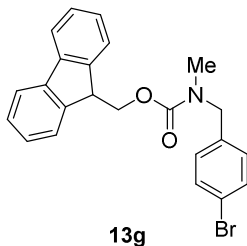
C₁₂H₁₆NO₂Br 285.0364, found 285.0345.

Phenyl 4-bromobenzyl(methyl)carbamate (**13f**)



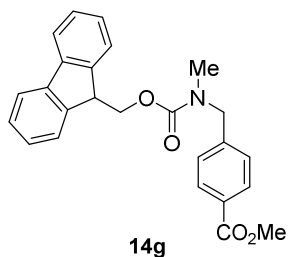
13f was prepared from 4-bromobenzaldehyde in 90% yield (Method B): colorless syrup; R_f = 0.34 (5:1 hexane–EtOAc); IR (neat, cm⁻¹) 3044, 2933, 1721, 1594, 1488, 1474, 1397, 1205, 1130, 753; ¹H NMR (500 MHz, (CD₃)₂SO, 80 °C, solvent residual peak = 2.50) δ 2.98 (3H, s), 4.55 (2H, s), 7.14 (2H, d, J = 8.3 Hz), 7.21 (1H, t, J = 7.2 Hz), 7.30 (2H, d, J = 7.8 Hz), 7.39 (2H, dd, J = 7.8, 7.2 Hz), 7.57 (2H, d, J = 8.3 Hz); ¹³C NMR (125 MHz, 80 °C, (CD₃)₂SO) δ 34.1, 51.2, 120.0, 121.2, 124.6, 128.7, 129.2, 131.1, 136.5, 151.0, 153.7; LRMS (EI) m/z (M)⁺ 319.0; HRMS (EI) m/z (M)⁺ calcd for C₁₅H₁₄NO₂Br 319.0208, found 319.0194.

(9H-Fluoren-9-yl)methyl 4-bromobenzyl(methyl)carbamate (**13g**)



13g was prepared from 4-bromobenzaldehyde in 88% yield (Method B): white solids; R_f = 0.45 (2:1 hexane–EtOAc); mp 90–91 °C (not recrystallized); IR (KBr, cm⁻¹) 2925, 1696, 1485, 1451, 1430, 1404, 1228, 1141, 742; ¹H NMR (500 MHz, C₆D₆, solvent residual peak = 7.16, 1:1 mixture of rotamers) δ 2.29 (1.5H, br s), 2.50 (1.5H, br s), 3.61 (1H, br s), 3.85 (0.5H, br), 3.99 (0.5H, br), 4.05 (1H, br s), 4.52 (2H, br), 6.32 (1H, br), 6.68 (1H, br), 7.04–7.30 (7H, m), 7.38–7.60 (3H, m); ¹³C NMR (125 MHz, (CD₃)₂CO, 1:1 mixture of rotamers) δ 33.9, 34.6, 48.2, 48.3, 51.9, 52.2, 67.5, 67.7, 120.8, 121.38, 121.41, 125.7, 125.9, 128.0, 128.5, 130.3, 130.6, 132.4, 138.2, 138.3, 142.2, 145.2, 156.3, 157.1; LRMS (EI) m/z (M)⁺ 421.2; HRMS (EI) m/z (M)⁺ calcd for C₂₃H₂₀NO₂Br 421.0677, found 421.0704.

Methyl 4-((((9H-fluoren-9-yl)methoxy)carbonyl)(methyl)amino)methyl)benzoate (14g)

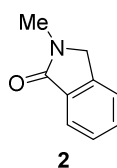


14g was prepared methyl 4-formylbenzoate in 85% yield (Method B): white solids; $R_f = 0.45$ (2:1 hexane–EtOAc); mp 78–81 °C (not recrystallized); IR (KBr, cm^{-1}) 2953, 1712, 1693, 1437, 1407, 1291, 1234, 1140, 1113, 739; ^1H NMR (500 MHz, C_6D_6 , solvent residual peak = 7.16, 1:1 mixture of rotamers) δ 2.33 (1.5H, br s), 2.55 (1.5H, br s), 3.51 (1.5H, s), 3.54 (1.5H, s), 3.78 (1H, br s), 3.88 (0.5H, br), 4.00 (0.5H, br), 4.18 (1H, br s), 4.52 (2H d, $J = 5.8$ Hz), 6.66 (1H, br), 6.97 (1H, br), 7.05–7.32 (5H, m), 7.38–7.62 (3H, m), 7.96–8.09 (2H, m); ^{13}C NMR (125 MHz, $(\text{CD}_3)_2\text{CO}$, 1:1 mixture of rotamers) δ 34.0, 34.8, 48.1, 48.3, 52.3, 52.6, 67.6, 67.7, 120.8, 125.7, 125.9, 127.9, 128.1, 128.4, 130.1, 130.5, 142.2, 144.2, 144.3, 145.1, 156.4, 157.1, 167.0; LRMS (EI) m/z (M) $^+$ 401.2; HRMS (EI) m/z (M) $^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{NO}_4$ 401.1627, found 401.1634.

General Procedure for Bischler-Napieralski-Type Cyclization of Carbamates

To a stirred solution of carbamate (0.100 mmol) in CH₂Cl₂ (1.7 mL) was added at 0 °C phosphorus pentoxide (142 mg, 1.00 mmol). After the reaction time at the reaction temperature indicated in tables and schemes, 1 M aqueous NaOH (2 mL) was added at 0 °C and the mixture was extracted with CHCl₃ (2 mL × 3). The extracts were washed with saturated aqueous NaCl (2 mL × 3), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the corresponding *N*-methylisoindolinone, 3,4-dihydroisoquinolinone, or pyrrolinone.

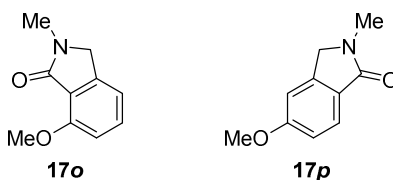
2-Methylisoindolin-1-one (**2**) (known)⁷



2: white solids; $R_f = 0.40$ (5:1 CHCl₃–acetone); mp 113–114 °C (not recrystallized); IR (KBr, cm⁻¹) 2919, 1673, 1483, 1445, 1422, 1398, 1277, 1208, 1054, 743; ¹H NMR (500 MHz, CDCl₃) δ 3.20 (3H, s), 4.37 (2H, s), 7.42–7.48 (2H, m), 7.50–7.54 (1H, m), 7.84 (1H, d, $J = 7.8$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 29.4, 51.9, 122.5, 123.5, 127.9, 131.1, 132.8, 140.9, 168.6; LRMS (EI) m/z (M)⁺ 147.0; HRMS (EI) m/z (M)⁺ calcd for C₉H₉NO 147.0684, found 147.0680.

7-Methoxy-2-methylisoindolin-1-one (**17o**) (known)⁸

and 5-methoxy-2-methylisoindolin-1-one (**17p**) (known)⁹

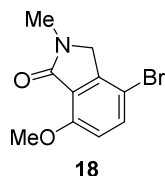


17o: 19% yield; white solids from **5b**; $R_f = 0.29$ (5:1 CHCl₃–acetone); mp 96–97 °C (not recrystallized); IR (KBr, cm⁻¹) 2921, 1672, 1613, 1490, 1266, 1066, 778; ¹H NMR (500 MHz, CDCl₃) δ 3.14 (3H, s), 3.96 (3H, s), 4.31 (2H, s), 6.88 (1H, d, $J = 8.3$ Hz), 6.98 (1H, d, $J = 7.5$ Hz), 7.44 (1H, dd, $J = 8.3, 7.5$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 29.3, 51.5, 55.8, 110.1, 114.7, 120.2, 132.7, 143.8, 157.3, 167.5; LRMS (EI) m/z (M)⁺ 177.1; HRMS (EI) m/z (M)⁺ calcd for C₁₀H₁₁NO₂ 177.0790, found 177.0790.

17p: 67% yield; white solids from **5b**; $R_f = 0.35$ (5:1 CHCl₃–acetone); mp 135–137 °C (not recrystallized); IR (KBr, cm⁻¹) 2912, 1674, 1612, 1487, 1450, 1400, 1260, 1056, 867, 772; ¹H NMR (500 MHz, CDCl₃) δ 3.16 (3H, s), 3.86 (3H, s), 4.30 (2H, s), 6.91 (1H, d, $J = 2.3$ Hz), 6.96 (1H, dd, $J = 8.3, 2.3$ Hz), 7.73 (1H, d, $J = 8.3$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 29.3, 51.7, 55.5, 107.5,

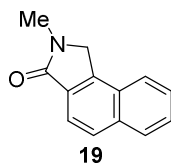
114.3, 124.7, 125.5, 143.1, 162.4, 168.4; LRMS (EI) m/z (M)⁺ 177.1; HRMS (EI) m/z (M)⁺ calcd for C₁₀H₁₁NO₂ 177.0790, found 177.0762.

4-Bromo-7-methoxy-2-methylisoindolin-1-one (18)



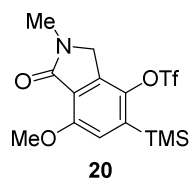
18: 86% yield from **6b**; white solids; R_f = 0.50 (5:1 CHCl₃–acetone); mp 72–73 °C (not recrystallized); IR (KBr, cm⁻¹) 2924, 1682, 1652, 1482, 1453, 1282, 1260, 1052, 959, 805; ¹H NMR (500 MHz, CDCl₃) δ 3.16 (3H, s), 3.95 (3H, s), 4.21 (2H, s), 6.81 (1H, d, J = 8.9 Hz), 7.52 (1H, d, J = 8.9 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 29.3, 52.2, 56.1, 107.4, 112.5, 122.0, 135.2, 143.5, 156.6, 166.7; LRMS (EI) m/z (M)⁺ 254.8; HRMS (EI) m/z (M)⁺ calcd for C₁₀H₁₀NO₂Br 254.9895, found 254.9894.

2-Methyl-benzo[*e*]isoindolin-1-one (19) (known)¹⁰



19: 85% yield from **7b**; white solids; R_f = 0.42 (5:1 CHCl₃–acetone); mp 137–140 °C (not recrystallized); IR (KBr, cm⁻¹) 2914, 1674, 1484, 1444, 1420, 1393, 816, 780, 753; ¹H NMR (500 MHz, CDCl₃) δ 3.28 (3H, s), 4.69 (2H, s), 7.57–7.62 (2H, m), 7.81–7.87 (2H, m), 7.90 (1H, m), 7.96 (1H, m); ¹³C NMR (125 MHz, CDCl₃) δ 29.6, 51.2, 120.1, 123.0, 127.1, 127.5, 127.8, 128.9, 129.1, 130.4, 134.8, 140.0, 169.3; LRMS (EI) m/z (M)⁺ 197.1; HRMS (EI) m/z (M)⁺ calcd for C₁₃H₁₁NO 197.0841, found 197.0841.

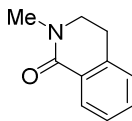
7-Methoxy-2-methyl-1-oxo-5-(trimethylsilyl)isoindolin-4-yl trifluoromethanesulfonate (20)



20: 40% yield from **8a**, 78% yield from **8b**; white solids; R_f = 0.18 (9:1 CHCl₃–acetone); mp 133–134 °C (not recrystallized); IR (KBr, cm⁻¹) 2961, 1690, 1404, 1252, 1214, 1141, 997, 901, 867, 843; ¹H NMR (300 MHz, CDCl₃ solvent residual peak = 7.26) δ 0.41 (9H, s), 3.15 (3H, s), 4.00 (3H, s), 4.42 (2H, s), 7.01 (1H, s); ¹³C NMR (125 MHz, CDCl₃) δ -0.4, 29.3, 49.5, 56.3, 118.0, 118.5 (q,

$J_{C,F}$ = 318 Hz), 123.6, 135.7, 140.0, 140.1, 155.9, 165.7; LRMS (EI) m/z (M)⁺ 397.0; HRMS (EI) m/z (M)⁺ calcd for C₁₄H₁₈F₃NO₅SSi 397.0627, found 397.0616.

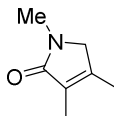
2-Methyl-3,4-dihydroisoquinolin-1-one (21) (known)¹¹



21

21: 96% yield from **9b**; colorless syrup; R_f = 0.46 (9:1 CHCl₃-acetone); IR (neat, cm⁻¹) 2943, 1647, 1605, 1579, 1496, 1439, 1399, 1337, 1265, 746; ¹H NMR (300 MHz, CDCl₃) δ 2.99 (2H, t, J = 6.0 Hz), 3.16 (3H, s), 3.57 (2H, t, J = 6.0 Hz), 7.17 (1H, d, J = 8.0 Hz), 7.29–7.44 (2H, m), 8.08 (1H, dd, J = 8.0, 2.0 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 27.7, 35.0, 48.0, 126.7, 126.8, 127.9, 129.2, 131.4, 137.8, 164.6; LRMS (EI) m/z (M)⁺ 161.0; HRMS (EI) m/z (M)⁺ calcd for C₁₀H₁₁NO 161.0841, found 161.0854.

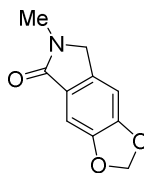
1,3,4-Trimethyl-3-pyrrolin-2-one (22)¹²



22

22: 71% yield; colorless syrup from **10b**; R_f = 0.38 (5:1 CHCl₃-acetone); IR (neat, cm⁻¹) 2920, 1676, 1481, 1452, 1427, 1403, 1225, 755; ¹H NMR (500 MHz, CDCl₃) δ 1.79 (3H, s), 1.95 (3H, s), 3.01 (3H, s), 3.72 (2H, s); ¹³C NMR (125 MHz, CDCl₃) δ 8.5, 12.7, 28.8, 56.0, 128.7, 144.9, 172.7; LRMS (EI) m/z (M)⁺ 125.1; HRMS (EI) m/z (M)⁺ calcd for C₇H₁₁NO 125.0841, found 125.0824.

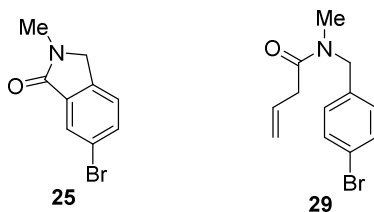
2-Methyl-5,6-(methylenedioxy)isoindoline-1-one (24) (known)¹³



24

24: 83% yield from **12b**; white solids; R_f = 0.40 (5:1 CHCl₃-acetone); mp 180–181 °C (not recrystallized); IR (KBr, cm⁻¹) 2920, 1677, 1476, 1464, 1395, 1300, 1242, 1021, 936, 927; ¹H NMR (500 MHz, CDCl₃) δ 3.16 (3H, s), 4.25 (2H, s), 6.05 (2H, s), 6.83 (1H, d, J = 0.6 Hz), 7.22 (1H, br s); ¹³C NMR (125 MHz, CDCl₃) δ 29.5, 51.7, 101.8, 102.9, 103.5, 126.9, 136.3, 148.2, 151.0, 168.3; LRMS (EI) m/z (M)⁺ 191.1; HRMS (EI) m/z (M)⁺ calcd for C₁₀H₉NO₃ 191.0582, found 191.0584.

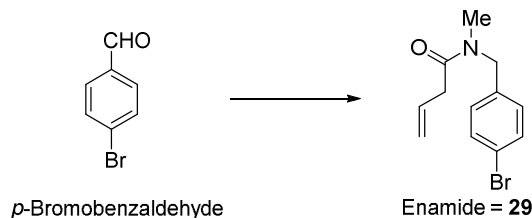
6-Bromo-2-methylisoindolin-1-one (25) (known)¹⁴
and ***N*-(4-bromobenzyl)-*N*-methylbut-3-enamide (29)**



25: 28% yield from **13b**; white solids; $R_f = 0.44$ (9:1 CHCl₃-acetone); mp 119–121 °C (not recrystallized); IR (KBr, cm⁻¹) 2923, 1677, 1460, 1398, 824, 763; ¹H NMR (500 MHz, CDCl₃) δ 3.20 (3H, s), 4.33 (2H, s), 7.31 (1H, d, $J = 8.0$ Hz), 7.65 (1H, dd, $J = 8.0, 2.0$ Hz), 7.97 (1H, d, $J = 2.0$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 29.5, 51.7, 122.1, 124.1, 126.8, 134.1, 135.0, 139.5, 167.1; LRMS (EI) m/z (M)⁺ 225.0; HRMS (EI) m/z (M)⁺ calcd for C₉H₈NOBr 224.9789, found 224.9798.

29: 30% yield; colorless syrup from **13b**; $R_f = 0.34$ (1:1 hexane-EtOAc); IR (neat, cm⁻¹) 2930, 1649, 1488, 1401, 1071, 1011, 921, 793, 754; ¹H NMR (500 MHz, CDCl₃ 2:1 mixture of rotamers) δ 2.92 (2H, s), 2.93 (1H, s), 3.17 (0.7H, br d, $J = 6.6$ Hz), 3.20 (1.3H, dt, $J = 6.6, 1.5$ Hz), 4.49 (0.7H, s), 4.53 (1.3H, s), 5.07–5.22 (2H, m), 5.99 (1H, m), 7.05 (0.7H, d, $J = 8.3$ Hz), 7.13 (1.3H, d, $J = 8.3$ Hz), 7.44 (1.3H, d, $J = 8.3$ Hz), 7.49 (0.7H, d, $J = 8.3$ Hz); ¹³C NMR (125 MHz, CDCl₃ 2:1 mixture of rotamers) δ 33.8, 34.9, 38.5, 38.8, 50.3, 52.9, 117.9, 118.0, 121.2, 121.5, 128.0, 129.8, 131.2, 131.5, 131.6, 132.0, 135.5, 136.3, 171.0, 171.2; LRMS (EI) m/z (M)⁺ 267.1; HRMS (EI) m/z (M)⁺ calcd for C₁₂H₁₄NOBr 267.0259, found 267.0279.

Determination of the structure of amide 29

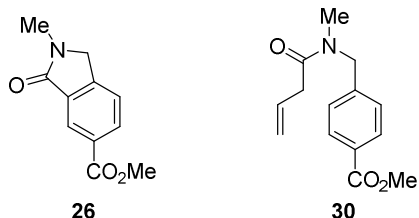


To a stirred solution of *p*-bromobenzaldehyde (500 mg, 2.70 mmol) in MeOH (14.0 mL) was added at rt a 40% MeOH solution of MeNH₂ (0.418 mL, 4.05 mmol). After 1 h at rt, NaBH₄ (155 mg, 4.05 mmol) was added at 0 °C and the mixture was stirred at rt for 30 min. The reaction mixture was quenched with acetone (18 mL) at 0 °C and the new mixture was concentrated under reduced pressure. The residual white solids were used for the next step without purification. To a stirred solution of the residue in CH₂Cl₂ (50.0 mL) were added at 0 °C 3-butenic acid (0.251 mL, 2.97 mmol), EDCI (1.55 g, 8.10 mmol), and HOBt (36.5 mg, 0.27 mmol). After 30 min at rt, H₂O (30 mL) was added at 0 °C and the mixture was extracted with CHCl₃ (30 mL \times 3). The extracts were washed with saturated aqueous NaCl (30 mL), dried over Na₂SO₄, and concentrated under

reduced pressure. The residue was purified by column chromatography on silica gel (20 g, 1:1 hexane–EtOAc) to afford *N*-(4-bromobenzyl)-*N*-methylbut-3-enamide (594 mg, 82%). The spectral data of this enamide were identical with those of **29**.

Methyl 6-(2-methyl-1-oxoisindoline)carboxylate (**26**)

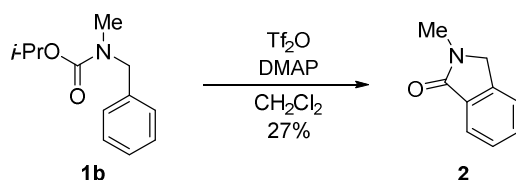
and methyl 4-((*N*-methylbut-3-enamido)methyl)benzoate (**30**)



26: 18% yield; white solids from **14b**; $R_f = 0.22$ (9:1 CHCl₃–acetone); mp 134–136 °C (not recrystallized); IR (KBr, cm⁻¹) 2953, 1723, 1672, 1482, 1300, 1265, 1200, 1114, 749; ¹H NMR (500 MHz, CDCl₃) δ 3.22 (3H, s), 3.95 (3H, s), 4.44 (2H, s), 7.51 (1H, d, $J = 8.6$ Hz), 8.23 (1H, dd, $J = 8.6, 1.5$ Hz), 8.49 (1H, d, $J = 1.5$ Hz); ¹³C NMR (125 MHz, CDCl₃) δ 29.5, 52.0, 52.3, 122.7, 125.0, 130.5, 132.4, 133.3, 145.4, 166.4, 167.6; LRMS (EI) m/z (M)⁺ 205.1; HRMS (EI) m/z (M)⁺ calcd for C₁₁H₁₁NO₃ 205.0739, found 205.0751.

30: 28% yield; colorless syrup from **14b**; $R_f = 0.44$ (9:1 CHCl₃–acetone); IR (neat, cm⁻¹) 2953, 1721, 1648, 1614, 1436, 1402, 1280, 1179, 1110, 755; ¹H NMR (500 MHz, CDCl₃, 2:1 mixture of rotamers) δ 2.95 (2H, s), 2.96 (1H, s), 3.17 (1.3H, br d, $J = 6.6$ Hz), 3.23 (0.7H, dt, $J = 6.6, 1.7$ Hz), 3.91 (2H, s), 3.92 (1H, s), 4.60 (0.7H, s), 4.65 (1.3H, s), 5.07–5.23 (2H, m), 6.00 (1H, m), 7.25 (0.7H, d, $J = 8.6$ Hz), 7.31 (1.3H, d, $J = 8.6$ Hz), 8.00 (1.3H, d, $J = 8.6$ Hz), 8.04 (0.7H, d, $J = 8.6$ Hz); ¹³C NMR (125 MHz, CDCl₃, 2:1 mixture of rotamers) δ 34.0, 35.0, 38.5, 38.8, 50.6, 52.0, 52.1, 53.2, 117.9, 118.0, 126.2, 127.8, 129.2, 129.6, 129.8, 130.2, 131.2, 131.4, 141.7, 142.5, 166.5, 166.7, 171.1, 171.3; LRMS (EI) m/z (M)⁺ 247.1; HRMS (EI) m/z (M)⁺ calcd for C₁₄H₁₇NO₃ 247.1208, found 247.1201.

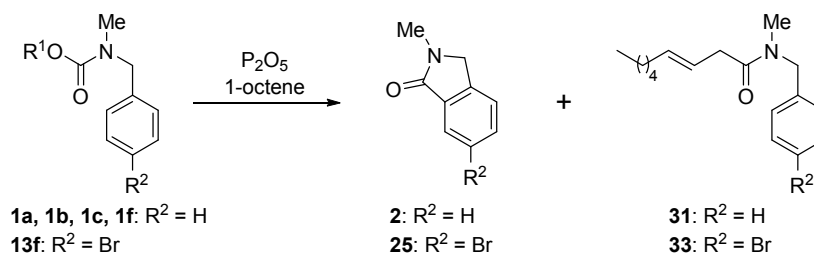
Cyclization of isopropyl carbamate **1b** using Tf₂O/DMAP



To a solution of **1b** (20.7 mg, 0.100 mmol) and DMAP (36.7 mg, 0.300 mmol) in dry CH₂Cl₂ (1.67 mL) was added dropwise triflic anhydride (0.084 mL, 0.500 mmol) over 5 min at 0 °C. The mixture was warmed to rt in 30 min. Saturated aqueous NaHCO₃ (2 mL) was added at 0 °C and the mixture was extracted with CHCl₃ (2 mL × 3). The extracts were washed with saturated aqueous

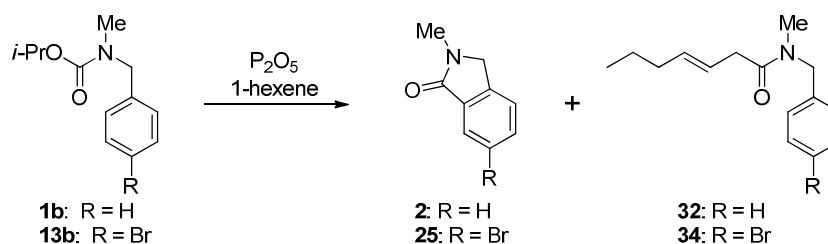
NaCl (2 mL \times 3), dried over Na₂SO₄, and concentrated under reduced pressure. ¹H NMR spectrum of the residue included detectable amounts of benzylmethylamine (>29%). The crude product was purified by column chromatography on silica gel (1.0 g, 10:1 CHCl₃–EtOAc) to afford **2** (4.0 mg, 27%) and *N*-benzyl-*N*-methyltrifluoromethanesulfonamide¹⁵ (0.4 mg, 2%).

Competition experiment in method A



To a stirred solution of carbamate **1a**, **1b**, **1c**, **1f**, or **13f** (0.100 mmol) in CH₂Cl₂ (1.7 mL) were successively added at 0 °C 1-octene (0.157 mL, 1.00 mmol) and phosphorus pentoxide (142 mg, 1.00 mmol). After 1 d at 84 °C, 1 M aqueous NaOH (2 mL) was added at 0 °C and the mixture was extracted with CHCl₃ (2 mL \times 3). The extracts were washed with saturated aqueous NaCl (2 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford isoindolinone **2** or **25**, and 3-enamide **31**. (*E*)-*N*-benzyl-*N*-methyl-non-3-enamide (**31**): colorless syrup; *R_f* = 0.69 (2:1 hexane–EtOAc); IR (neat, cm⁻¹) 2956, 2927, 1644, 1453, 1403, 1262, 1114, 732, 699; ¹H NMR (500 MHz, CDCl₃ 2:1 mixture of rotamers) δ 0.87 (1H, t, *J* = 7.2 Hz), 0.88 (2H, t, *J* = 7.2 Hz), 1.21–1.41 (6H, m), 1.97–2.10 (2H, m), 2.92 (2H, s), 2.93 (1H, s), 3.12–3.17 (2H, m), 4.54 (0.7H, s), 4.59 (1.3H, s), 5.45–5.64 (2H, m), 7.14–7.39 (5H, m); ¹³C NMR (125 MHz, CDCl₃ 2:1 mixture of rotamers) δ 14.1, 22.6, 28.95, 29.03, 31.46, 31.48, 32.59, 32.63, 34.0, 35.0, 37.9, 38.1, 50.9, 53.6, 122.6, 122.9, 126.5, 127.4, 127.7, 128.2, 128.6, 129.0, 134.3, 134.4, 136.7, 137.5, 171.8, 172.2; LRMS (EI) *m/z* (M)⁺ 259.2; HRMS (EI) *m/z* (M)⁺ calcd for C₁₇H₂₅NO 259.1936, found 259.1938.

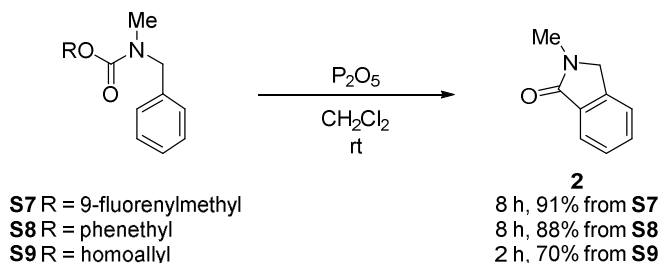
Competition experiment in method B



To a stirred solution of carbamate **1b** or **13b** (0.100 mmol) in CH₂Cl₂ (1.7 mL) were successively added at 0 °C 1-hexene (0.125 mL, 1.00 mmol) and phosphorus pentoxide (142 mg, 1.00 mmol). After 1 h at rt, 1 M aqueous NaOH (2 mL) was added at 0 °C and the mixture was extracted with

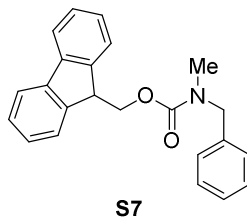
CHCl₃ (2 mL × 3). The extracts were washed with saturated aqueous NaCl (2 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford isoindolinone **2** or **25**, and enamide **32** or **34**. (*E*)-*N*-benzyl-*N*-methyl-hept-3-enamide (**32**): colorless syrup; *R*_f = 0.32 (2:1 hexane–EtOAc); IR (neat, cm⁻¹) 2959, 2929, 1647, 1453, 1401, 1111, 970, 733, 699; ¹H NMR (500 MHz, CDCl₃ 2:1 mixture of rotamers) δ 0.88 (1H, t, *J* = 7.2 Hz), 0.89 (2H, t, *J* = 7.2 Hz), 1.32–1.44 (2H, m), 1.96–2.08 (2H, m), 2.92 (2H, s), 2.93 (1H, s), 3.12–3.17 (2H, m), 4.54 (0.7H, s), 4.59 (1.3H, s), 5.45–5.64 (2H, m), 7.13–7.38 (5H, m); ¹³C NMR (125 MHz, CDCl₃ 2:1 mixture of rotamers) δ 13.6, 22.25, 22.32, 33.8, 34.5, 34.6, 34.8, 37.7, 37.9, 50.7, 53.4, 122.7, 123.0, 126.3, 127.2, 127.5, 128.0, 128.5, 128.8, 133.86, 133.92, 136.6, 137.4, 171.6, 172.0; LRMS (EI) *m/z* (M)⁺ 231.0; HRMS (EI) *m/z* (M)⁺ calcd for C₁₅H₂₁NO 231.1623, found 231.1629. (*E*)-*N*-(4-Bromobenzyl)-*N*-methylhept-3-enamide (**34**): colorless syrup; *R*_f = 0.25 (2:1 hexane–EtOAc); IR (neat, cm⁻¹) 2958, 2928, 1647, 1488, 1400, 1071, 1011, 969, 794; ¹H NMR (500 MHz, CDCl₃ 2:1 mixture of rotamers) δ 0.88 (1H, t, *J* = 7.2 Hz), δ 0.89 (2H, t, *J* = 7.2 Hz), 1.33–1.45 (2H, m), 1.96–2.06 (2H, m), 2.92 (3H, s), 3.09–3.16 (2H, m), 4.49 (0.7H, s), 4.53 (1.3H, s), 5.45–5.62 (2H, m), 7.05 (0.7H, d, *J* = 8.3 Hz), 7.12 (1.3H, d, *J* = 8.3 Hz), 7.43 (1.3H, d, *J* = 8.3 Hz), 7.49 (0.7H, d, *J* = 8.3 Hz); ¹³C NMR (125 MHz, CDCl₃ 2:1 mixture of rotamers) δ 13.6, 22.25, 22.33, 33.8, 34.5, 34.6, 34.9, 37.7, 37.9, 50.3, 52.9, 121.2, 121.4, 122.5, 122.8, 128.1, 129.8, 131.6, 132.0, 134.06, 134.12, 135.7, 136.4, 171.7, 171.9; LRMS (EI) *m/z* (M)⁺ 308.9; HRMS (EI) *m/z* (M)⁺ calcd for C₁₅H₂₀NOBr 309.0728, found 309.0729.

Cyclization of 9-fluorenylmethyl carbamate **S7**, phenethyl carbamate **S8** and homoallyl carbamate **S9**



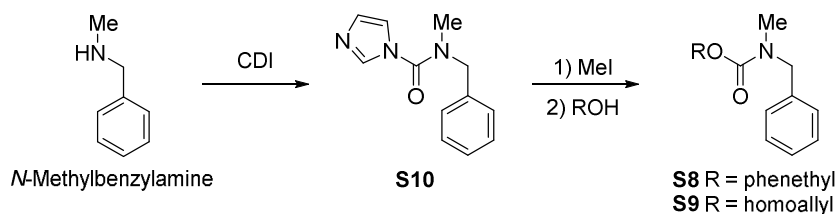
To examine the reactivity of 9-fluorenylmethyl carbamate, phenethyl carbamate, and homoallyl carbamate in the cyclization, the cyclization of benzyl carbamate **S7**, **S8**, and **S9** were conducted under the above reaction. As the results, 9-fluorenylmethyl carbamate **S7** was the best from the points of the cyclization and easy preparation shown below.

(9H-Fluoren-9-yl)methyl benzyl(methyl)carbamate (S7)



To a stirred solution of *N*-methylbenzylamine (0.271 mL, 2.10 mmol) in a mixture of 1:1:1 THF–acetone–H₂O (10.0 mL) was added at 0 °C FmocOSu (1.28 g, 3.78 mmol). After 2 h at rt, saturated aqueous NaHCO₃ (10 mL) was added at 0 °C and the mixture was extracted with EtOAc (10 mL × 3). The extracts were washed with saturated aqueous NaCl (10 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford **S7** (591 mg, 82%) as white solids; *R*_f = 0.58 (3:1 hexane–EtOAc); mp 87–89 °C (not recrystallized); IR (KBr, cm⁻¹) 2924, 1691, 1452, 1426, 1230, 1136, 742, 704; ¹H NMR (500 MHz, C₆D₆, solvent residual peak = 7.16, 1:1 mixture of rotamers) δ 2.42 (1.5H, br s), 2.63 (1.5H, br s), 3.95 (1H, br s), 4.05 (1H, br t, *J* = 6.3 Hz), 4.29 (1H, br s), 4.51 (2H, br d, *J* = 6.3 Hz), 6.80 (1H, br), 7.02–7.25 (8H, m), 7.31 (1H, m), 7.45 (1H, m), 7.50–7.60 (2H, m); ¹³C NMR (125 MHz, (CD₃)₂CO, 1:1 mixture of rotamers) δ 33.8, 34.5, 48.2, 48.3, 52.5, 52.8, 67.6, 67.7, 120.8, 125.8, 125.9, 127.95, 128.03, 128.3, 128.5, 129.4, 138.8, 138.9, 142.2, 145.2, 156.4, 157.1, 206.1; LRMS (EI) *m/z* (M)⁺ 343.2; HRMS (EI) *m/z* (M)⁺ calcd for C₂₃H₂₁NO₂ 343.1572, found 343.1598.

Preparation of carbamates S8, and S9.¹⁶



To a stirred solution of *N*-methylbenzylamine (1.21 g, 10.0 mmol) in dry THF (20.0 mL) was added at 0 °C 1,1'-carbonyldiimidazole (2.43 g, 15.0 mmol). After 30 min at rt, H₂O (20 mL) was slowly added at 0 °C and the mixture was extracted with EtOAc (20 mL × 3). The extracts were washed with saturated aqueous NaCl (20 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (40 g, 1:3 hexane–EtOAc) to afford **S10** (1.98 g, 92%).

To a stirred solution of **S10** (2.00 g, 9.30 mmol) in MeCN (19.0 mL) was added at rt MeI (2.32 g, 37.2 mmol). After 1 d at rt, the reaction mixture was concentrated under reduced pressure. The residual yellow solids were used for the next step without purification. To a stirred solution of the

residue in MeCN (47.0 mL) were added at 0 °C ROH (9.30 mmol) and Et₃N (1.56 mL, 11.2 mmol). After 8 h at 80 °C, H₂O (50 mL) was added at 0 °C and the mixture was extracted with EtOAc (50 mL × 3). The extracts were washed with saturated aqueous NaCl (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford carbamates **S8** (77%) and **S9** (12%).

Phenethyl benzyl(methyl)carbamate (**S8**): colorless syrup; *R_f* = 0.43 (3:1 hexane–EtOAc); IR (neat, cm⁻¹) 3029, 2955, 1702, 1454, 1404, 1234, 1144, 700; ¹H NMR (500 MHz, (CD₃)₂SO, 80 °C, solvent residual peak = 2.50) δ 2.76 (3H, s), 2.92 (2H, t, *J* = 6.6 Hz), 4.28 (2H, t, *J* = 6.6 Hz), 4.38 (2H, s), 7.13–7.35 (10H, m); ¹³C NMR (125 MHz, 80 °C, (CD₃)₂SO) δ 33.3, 34.6, 51.3, 65.0, 125.8, 126.7, 126.9, 127.8, 128.0, 128.3, 137.3, 137.9, 155.4; LRMS (EI) *m/z* (M)⁺ 269.1; HRMS (EI) *m/z* (M)⁺ calcd for C₁₇H₁₉NO₂ 269.1416, found 269.1414.

But-3-en-1-yl benzyl(methyl)carbamate (**S9**): colorless syrup; *R_f* = 0.46 (3:1 hexane–EtOAc); IR (neat, cm⁻¹) 2956, 1703, 1484, 1454, 1404, 1234, 1143, 701; ¹H NMR (500 MHz, (CD₃)₂SO, 80 °C, solvent residual peak = 2.50) δ 2.35 (2H, dt, *J* = 6.6, 6.6 Hz), 2.80 (3H, s), 4.11 (2H, t, *J* = 6.6 Hz), 4.42 (2H, s), 5.05 (1H, d, *J* = 10.3 Hz), 5.10 (1H, d, *J* = 17.2 Hz), 5.80 (1H, m), 7.22–7.37 (5H, m); ¹³C NMR (125 MHz, 80 °C, (CD₃)₂SO) δ 32.7, 33.4, 51.3, 63.5, 116.3, 126.7, 126.9, 128.0, 134.3, 137.4, 155.4; LRMS (EI) *m/z* (M)⁺ 219.0; HRMS (EI) *m/z* (M)⁺ calcd for C₁₃H₁₇NO₂ 219.1259, found 219.1254.

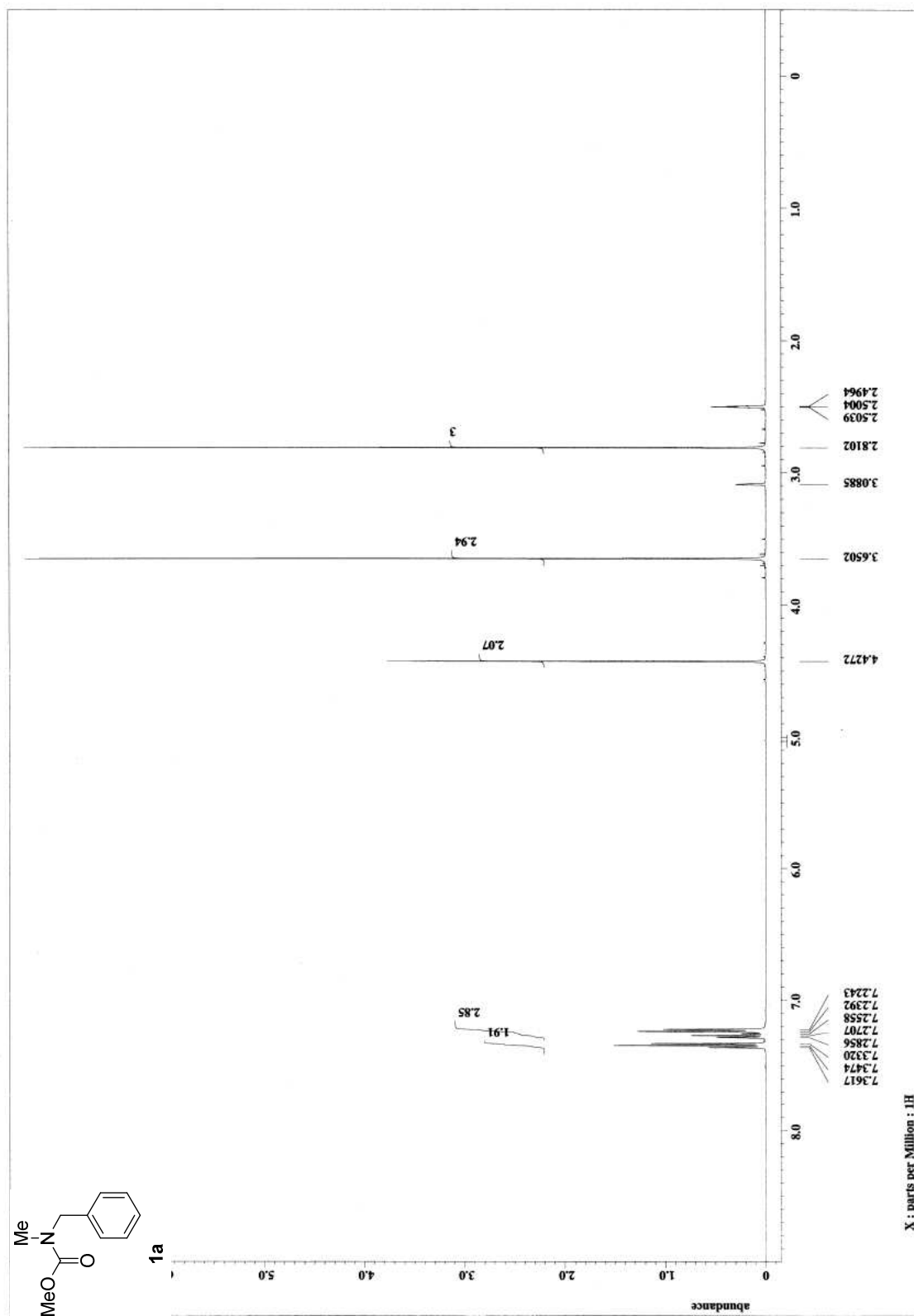
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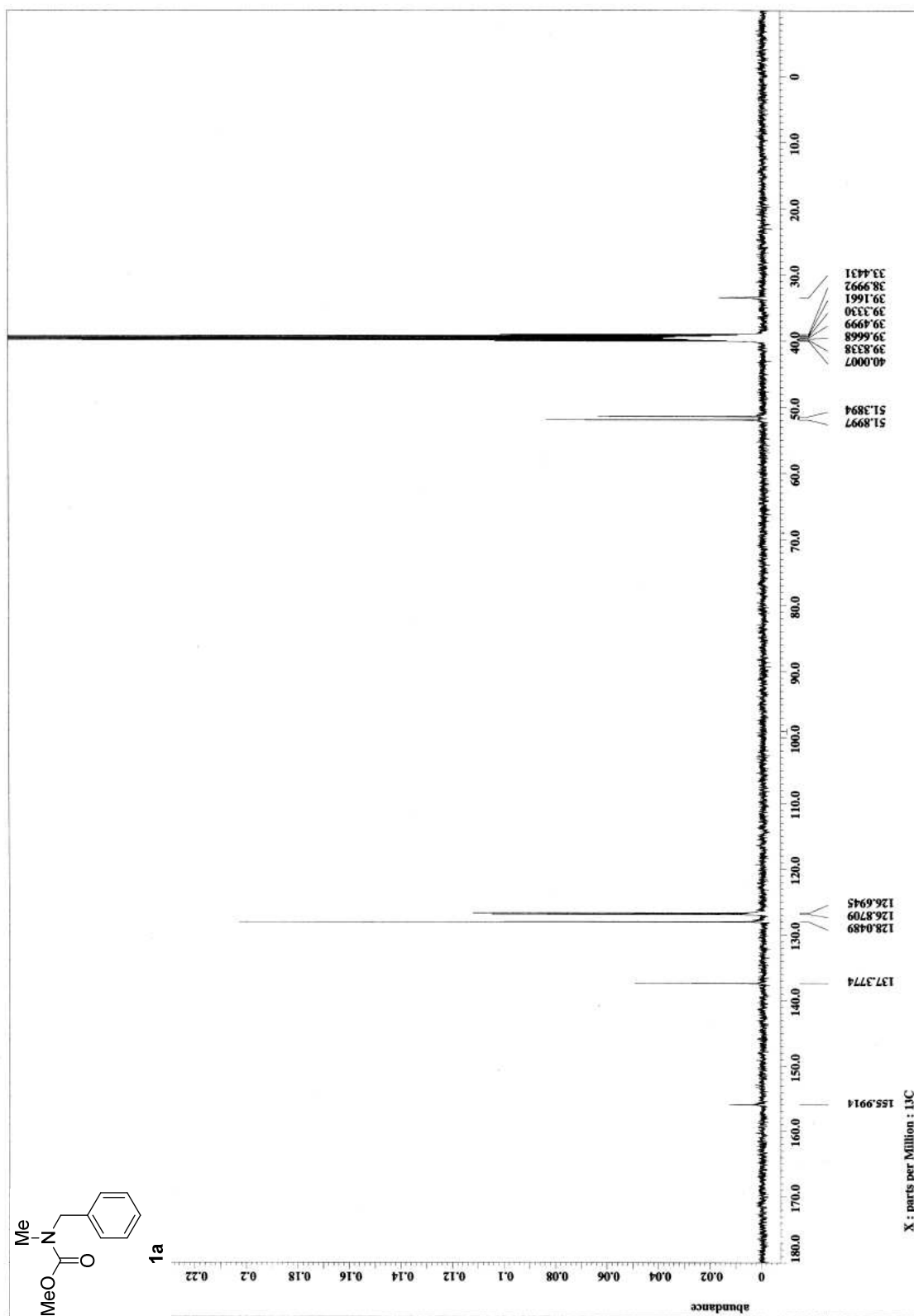
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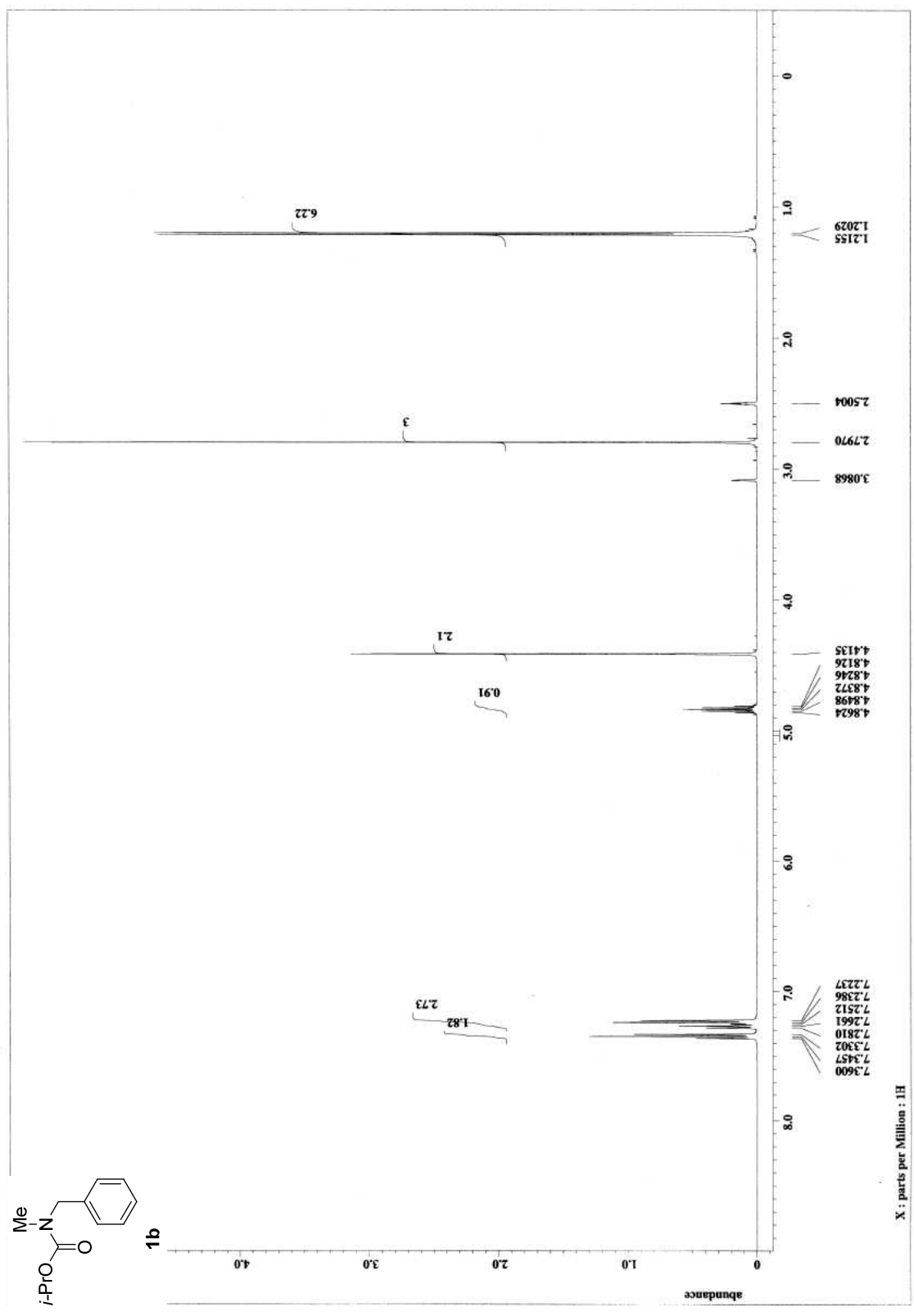
NMR spectra ¹H NMR spectrum of 1a



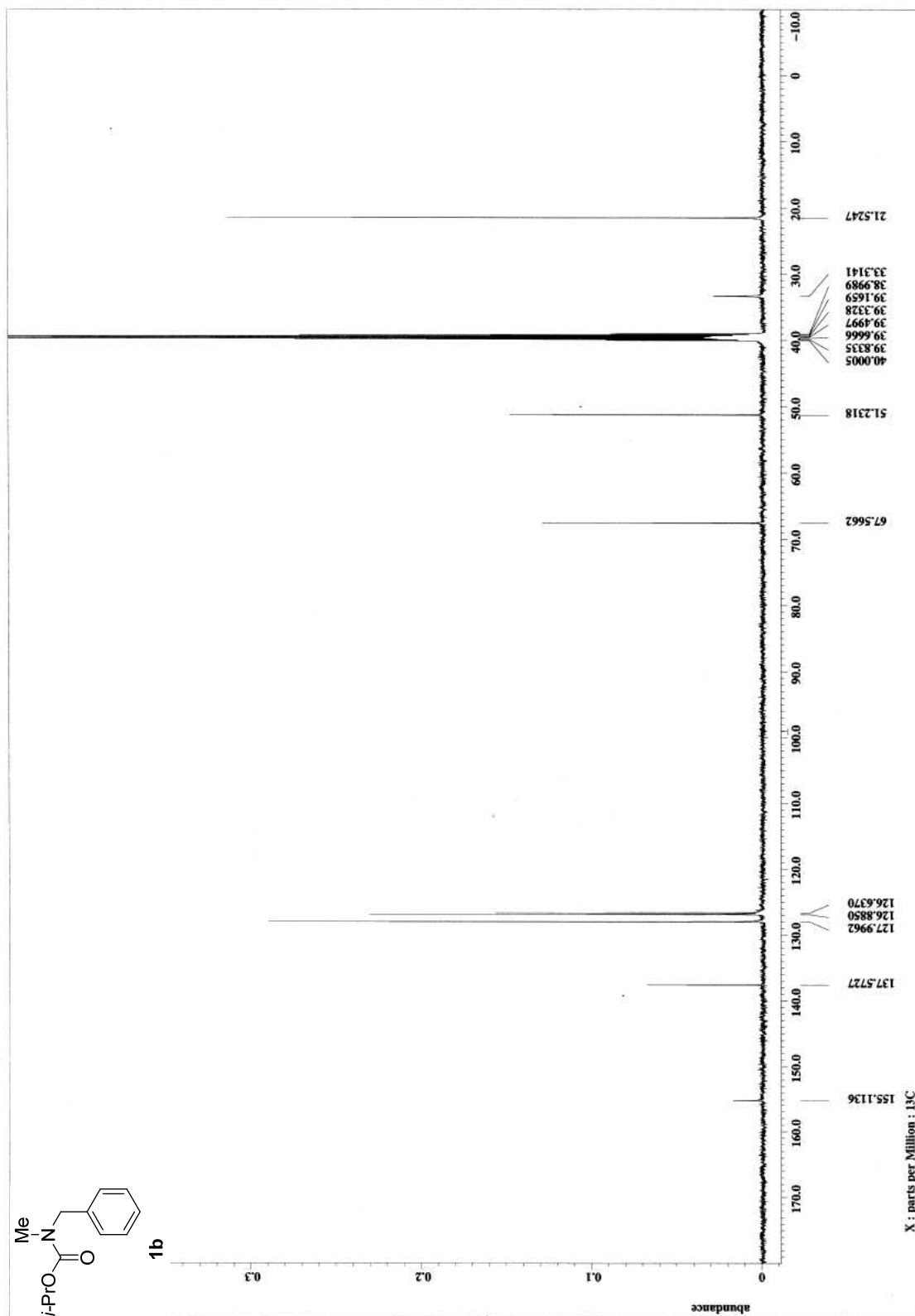
¹³C NMR spectrum of **1a**



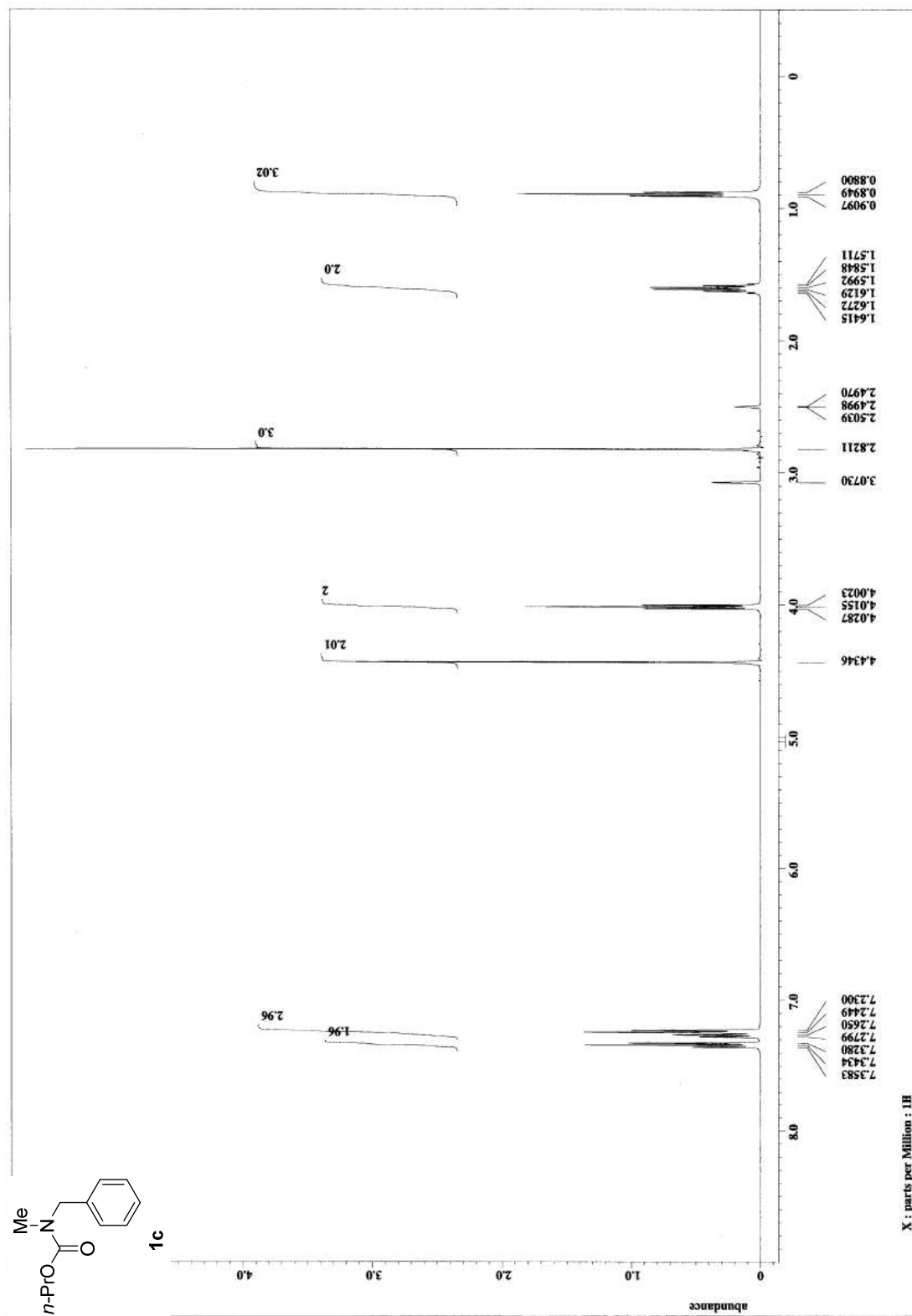
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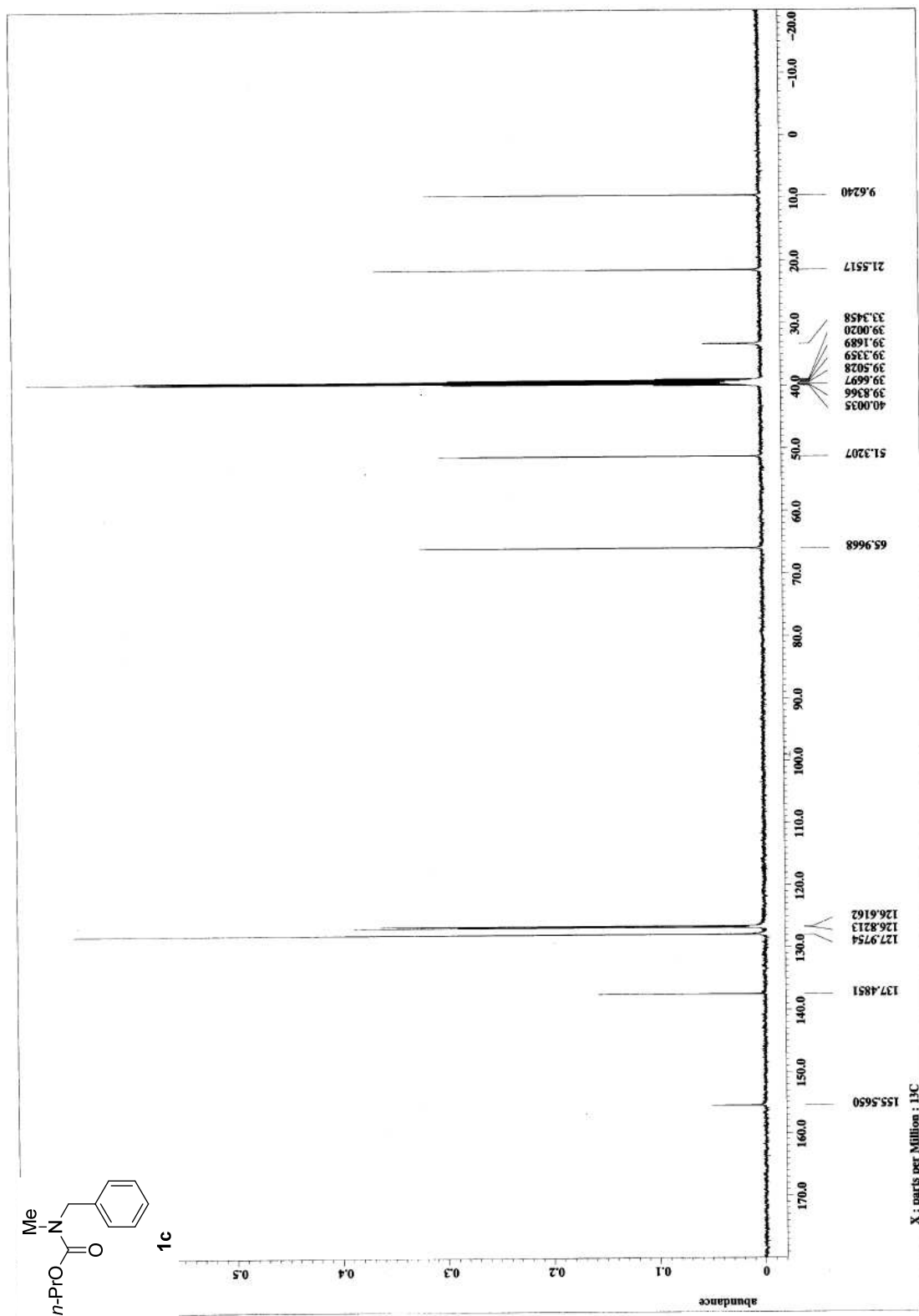
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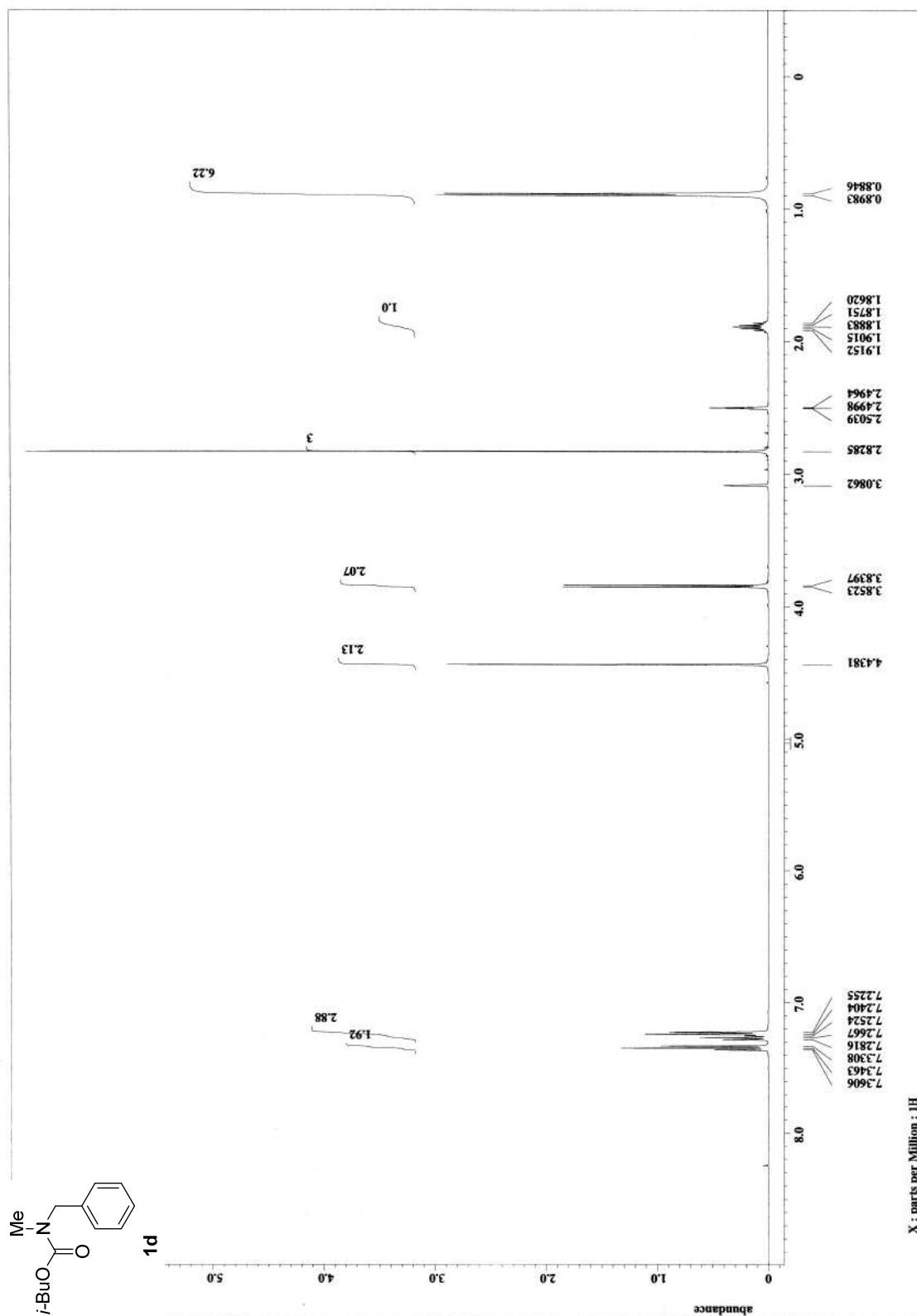
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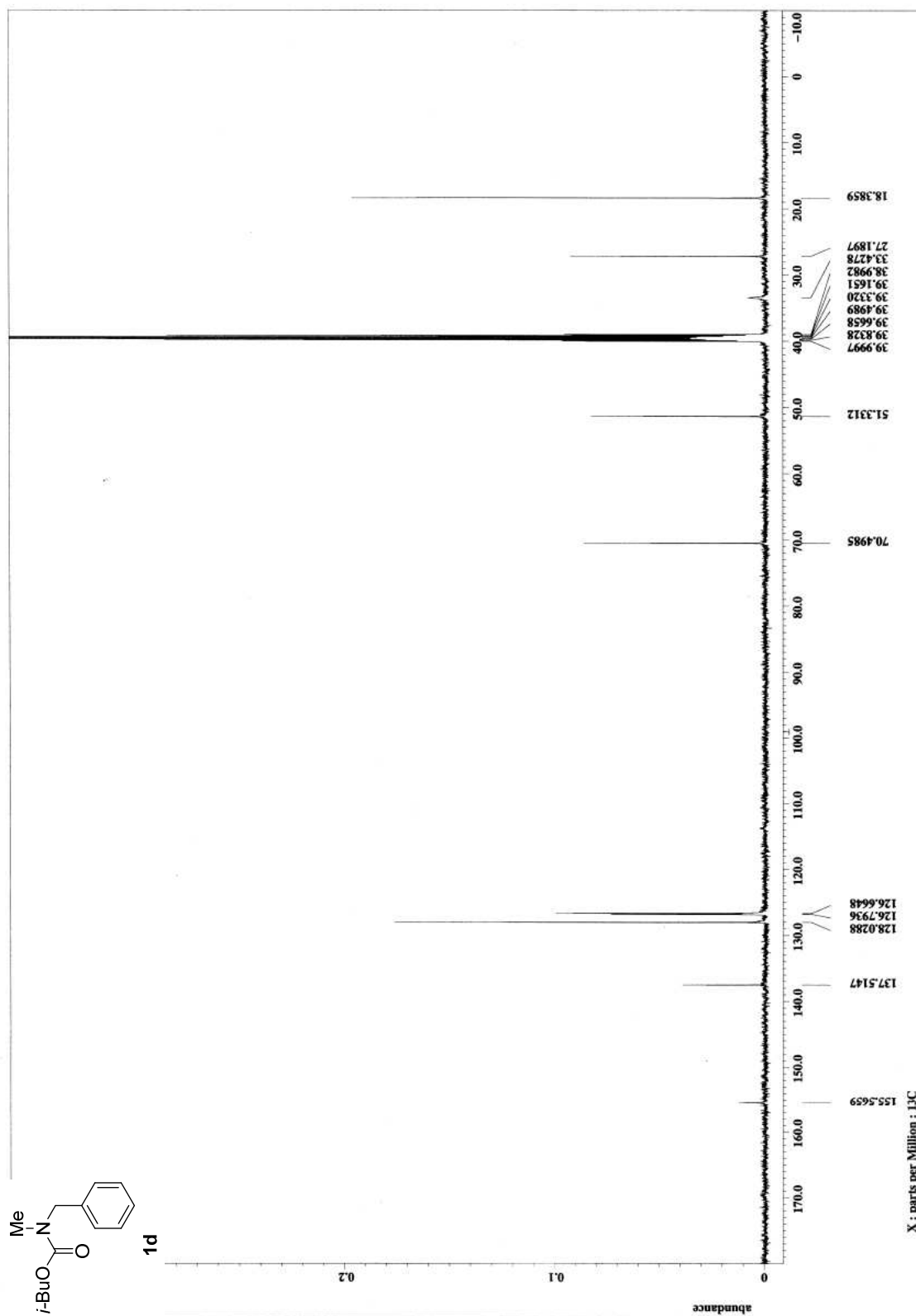
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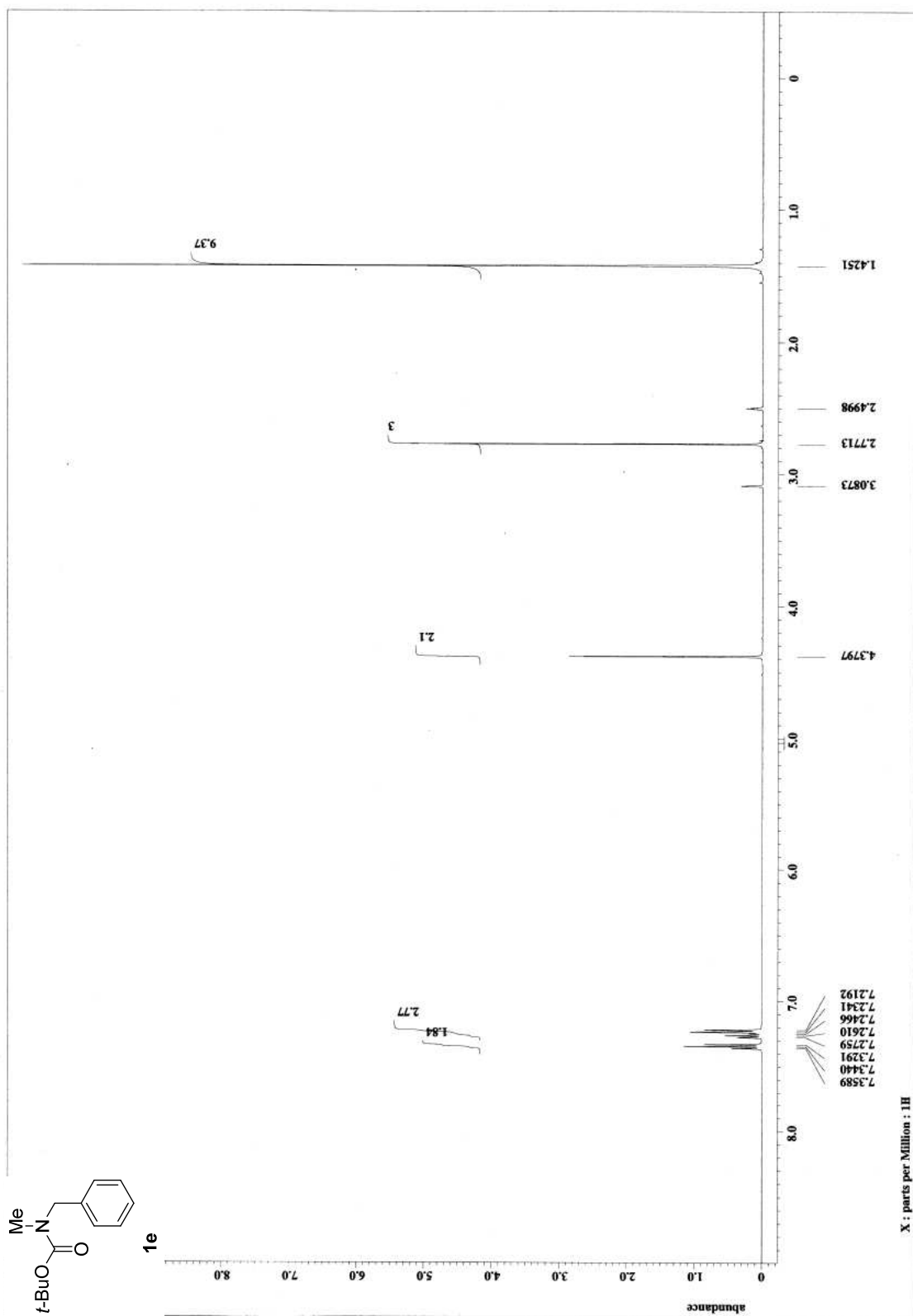
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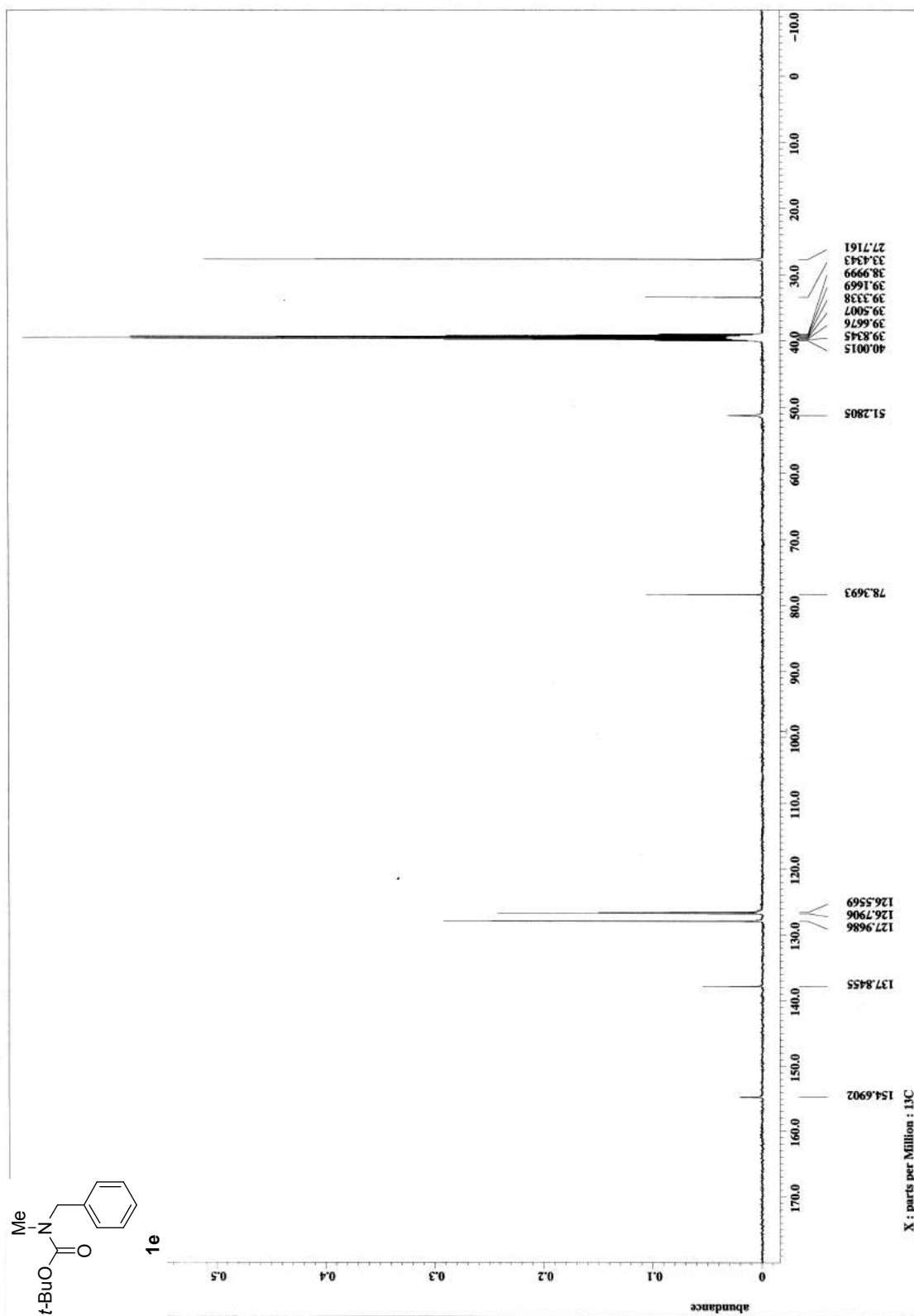
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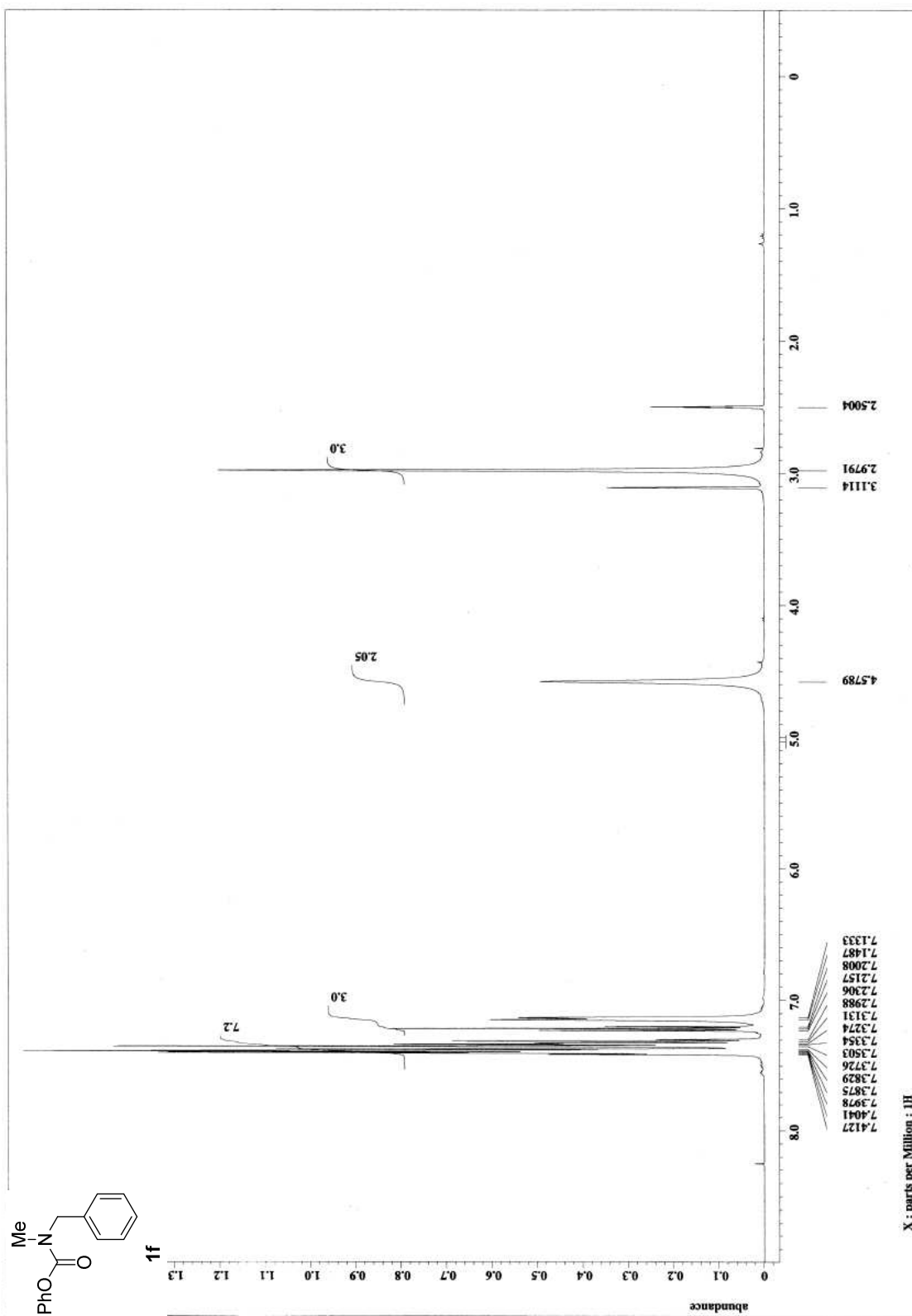
^1H NM spectrum of **1e**



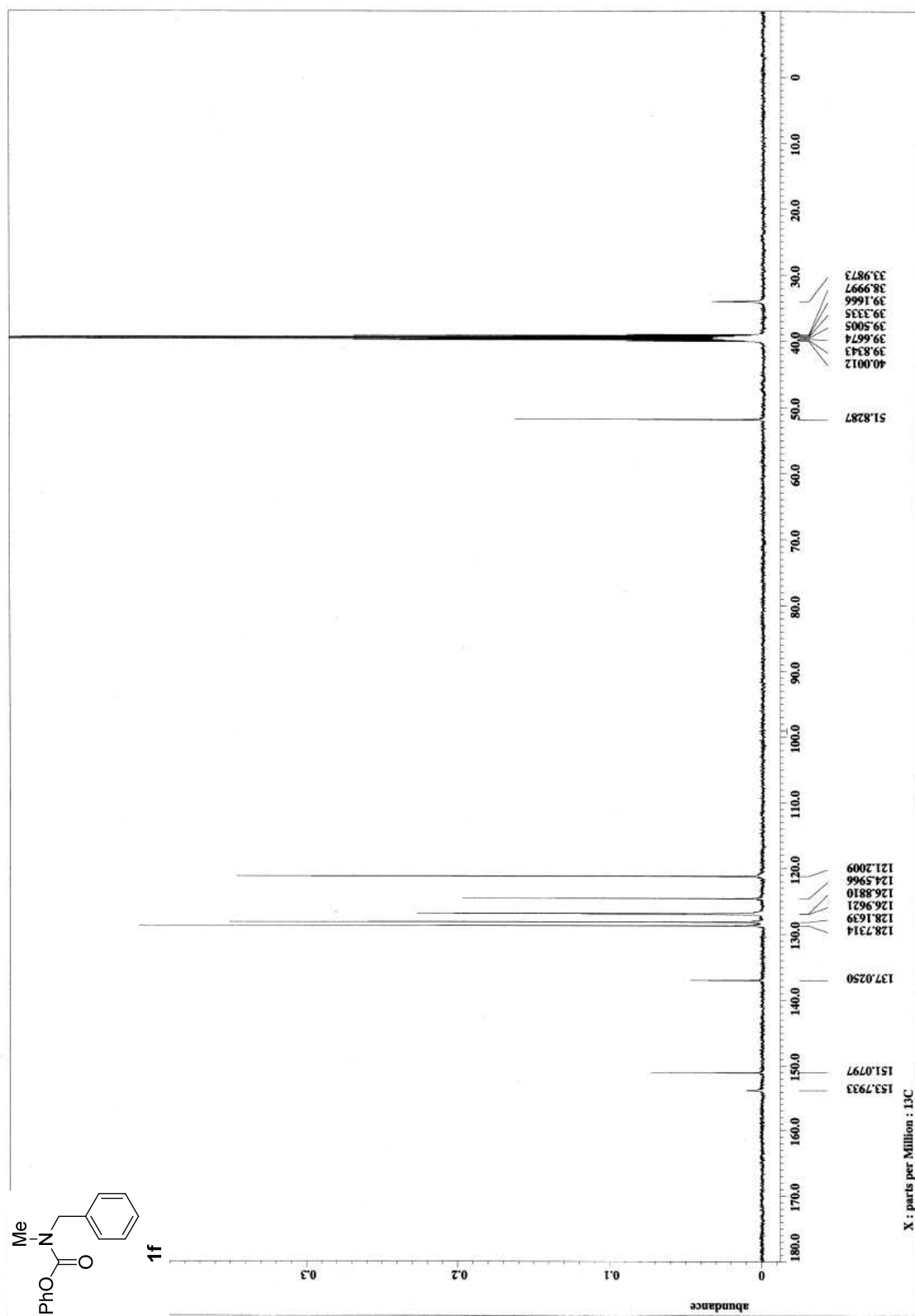
^{13}C NMR spectrum of **1e**



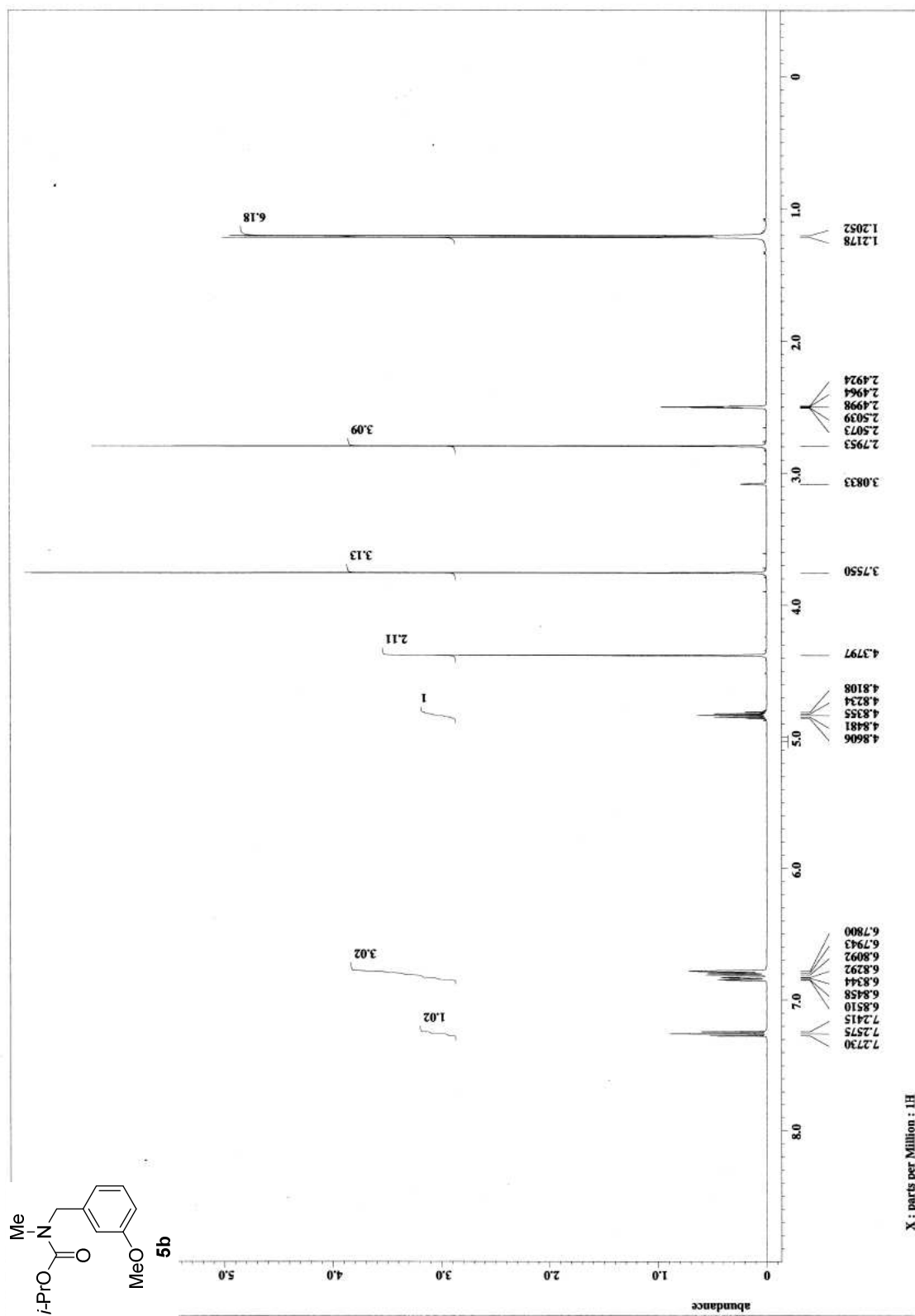
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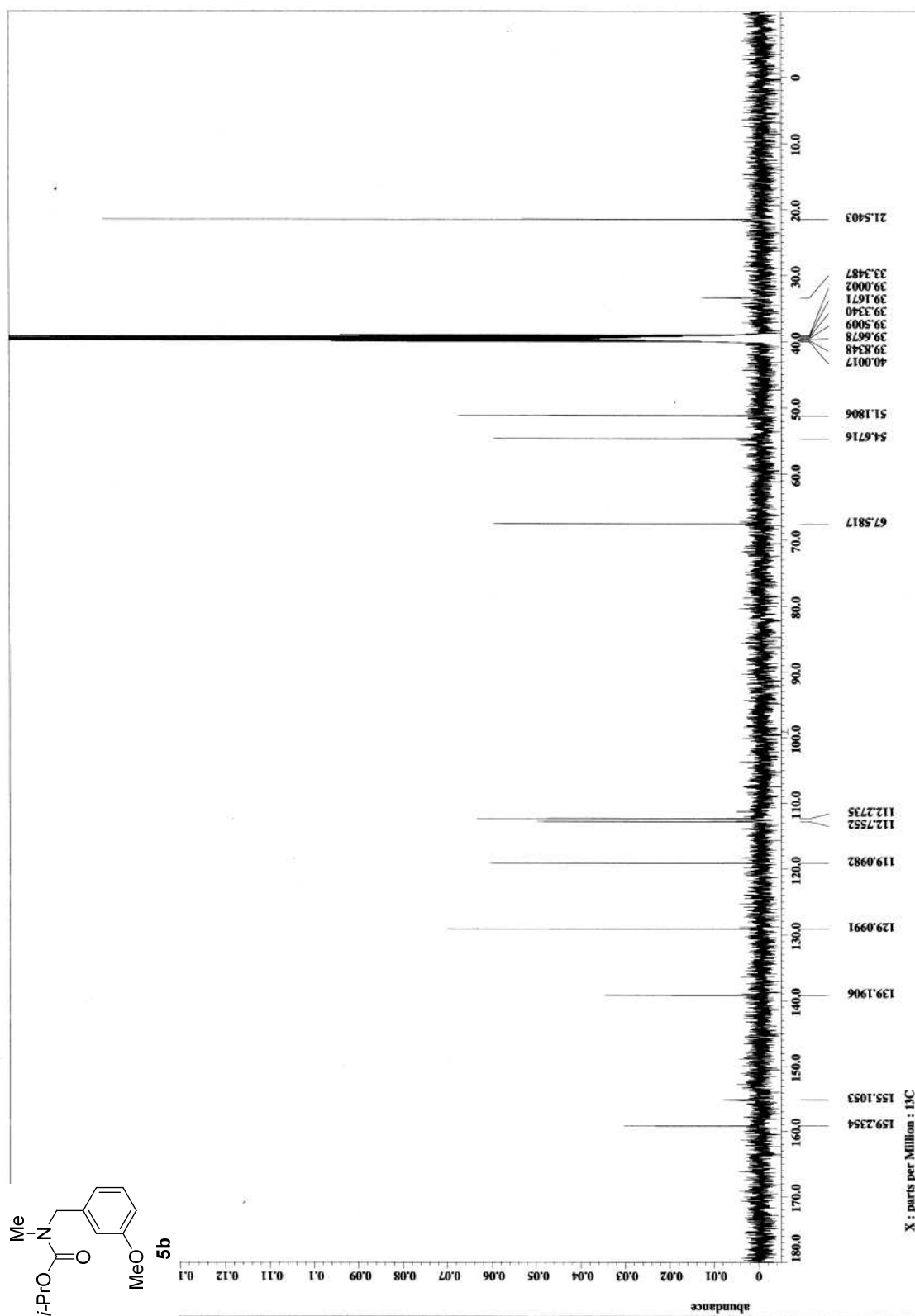
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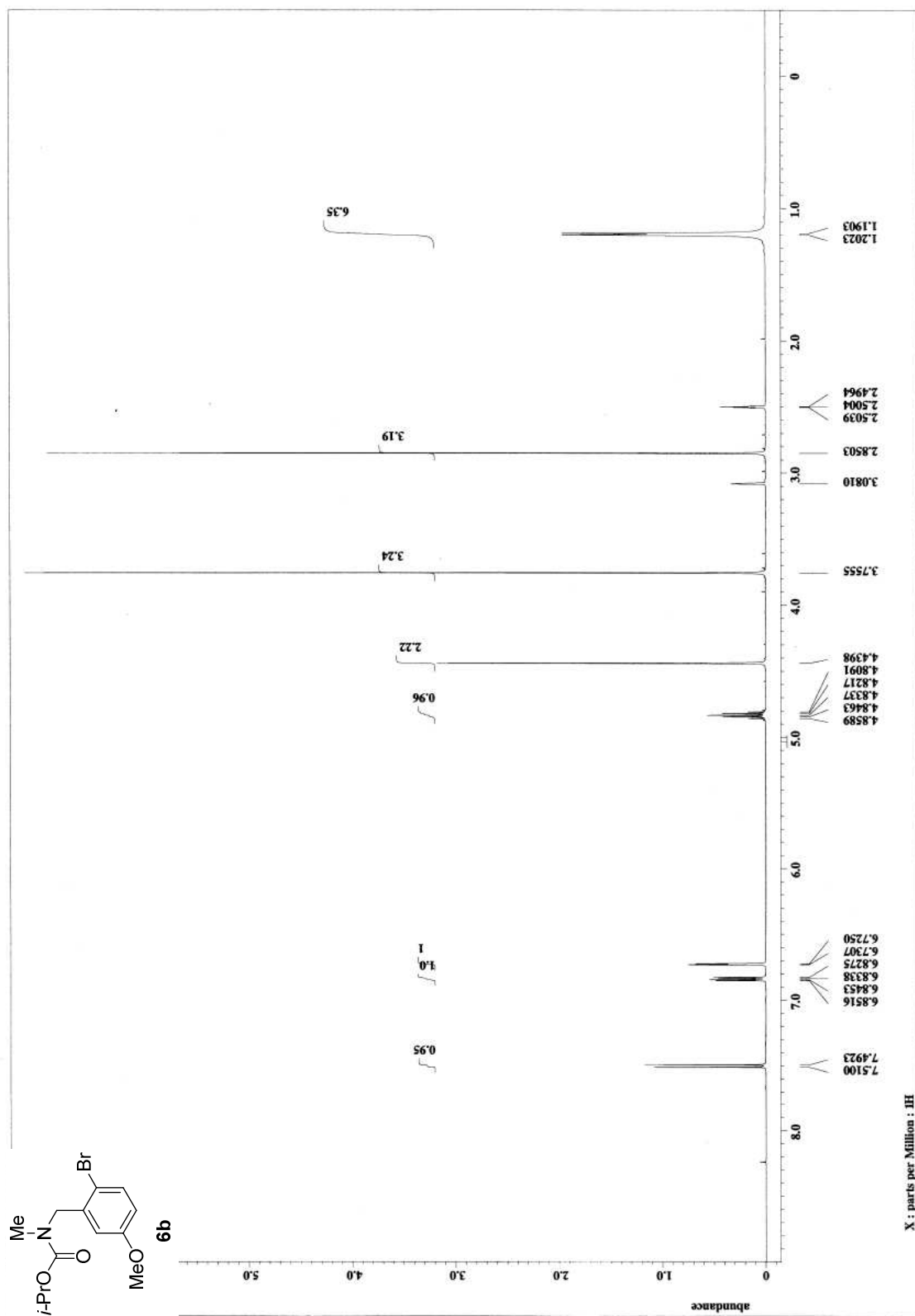
¹H NMR spectrum of **5b**



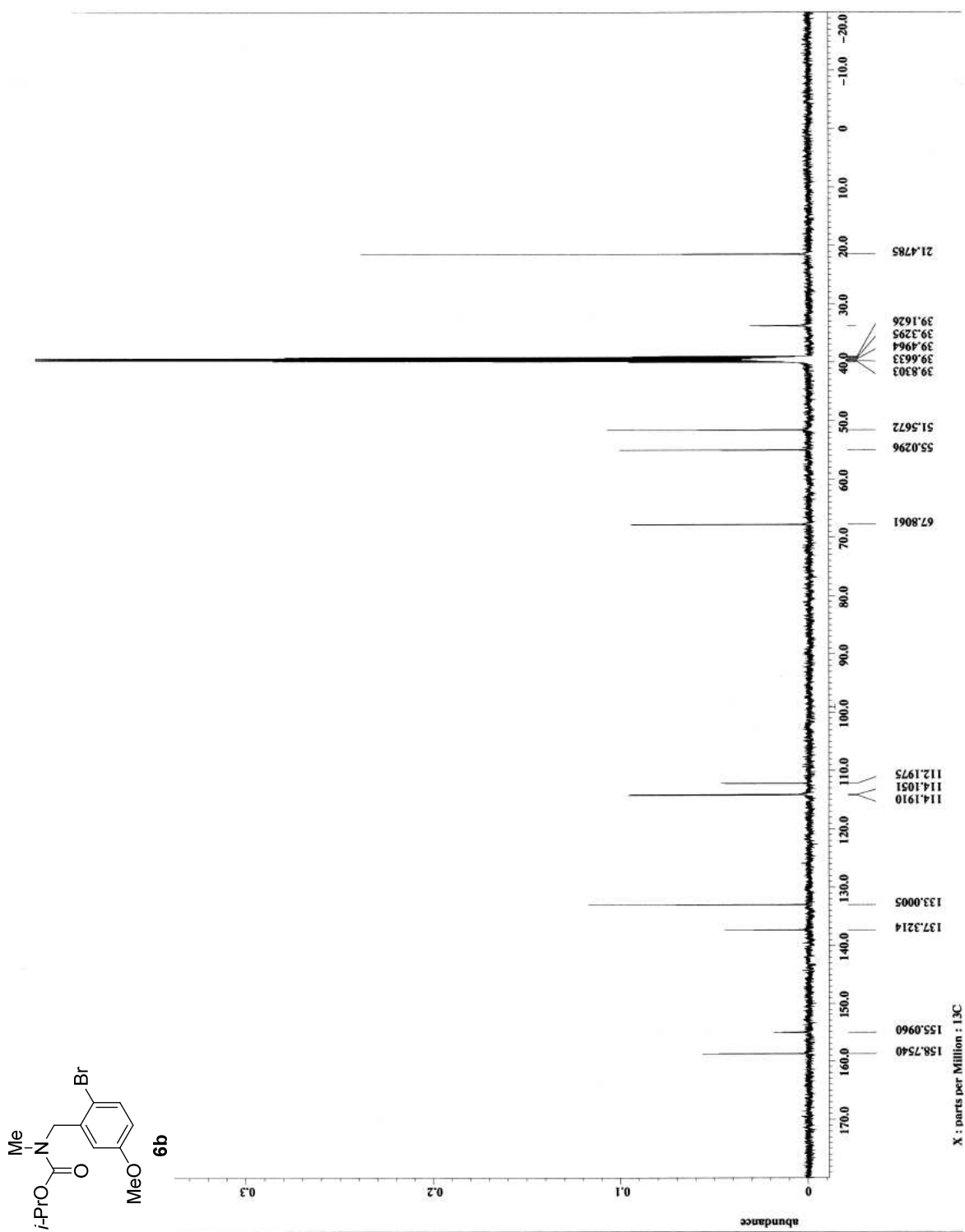
^{13}C NMR spectrum of **5b**



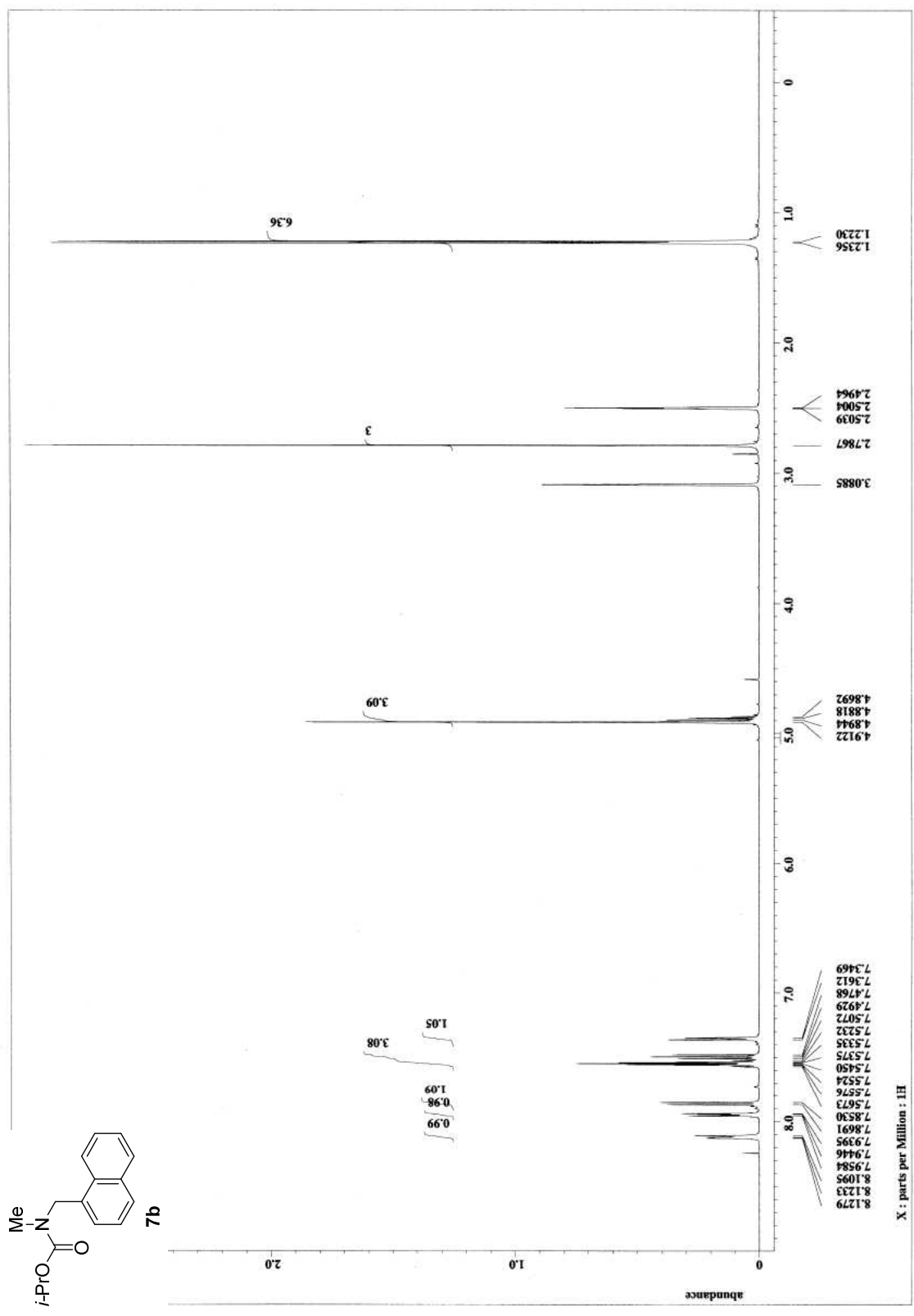
¹H NMR spectrum of **6b**



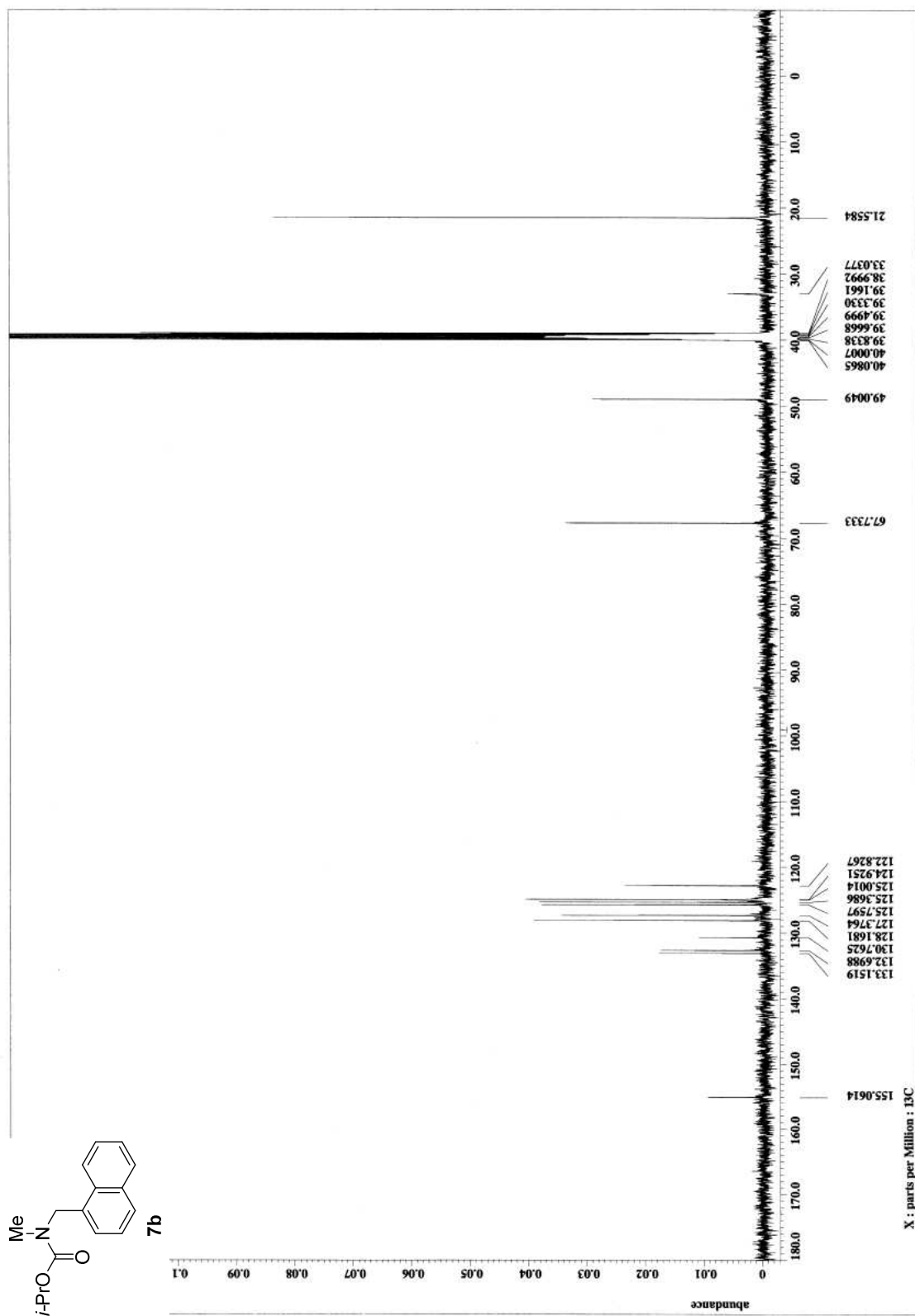
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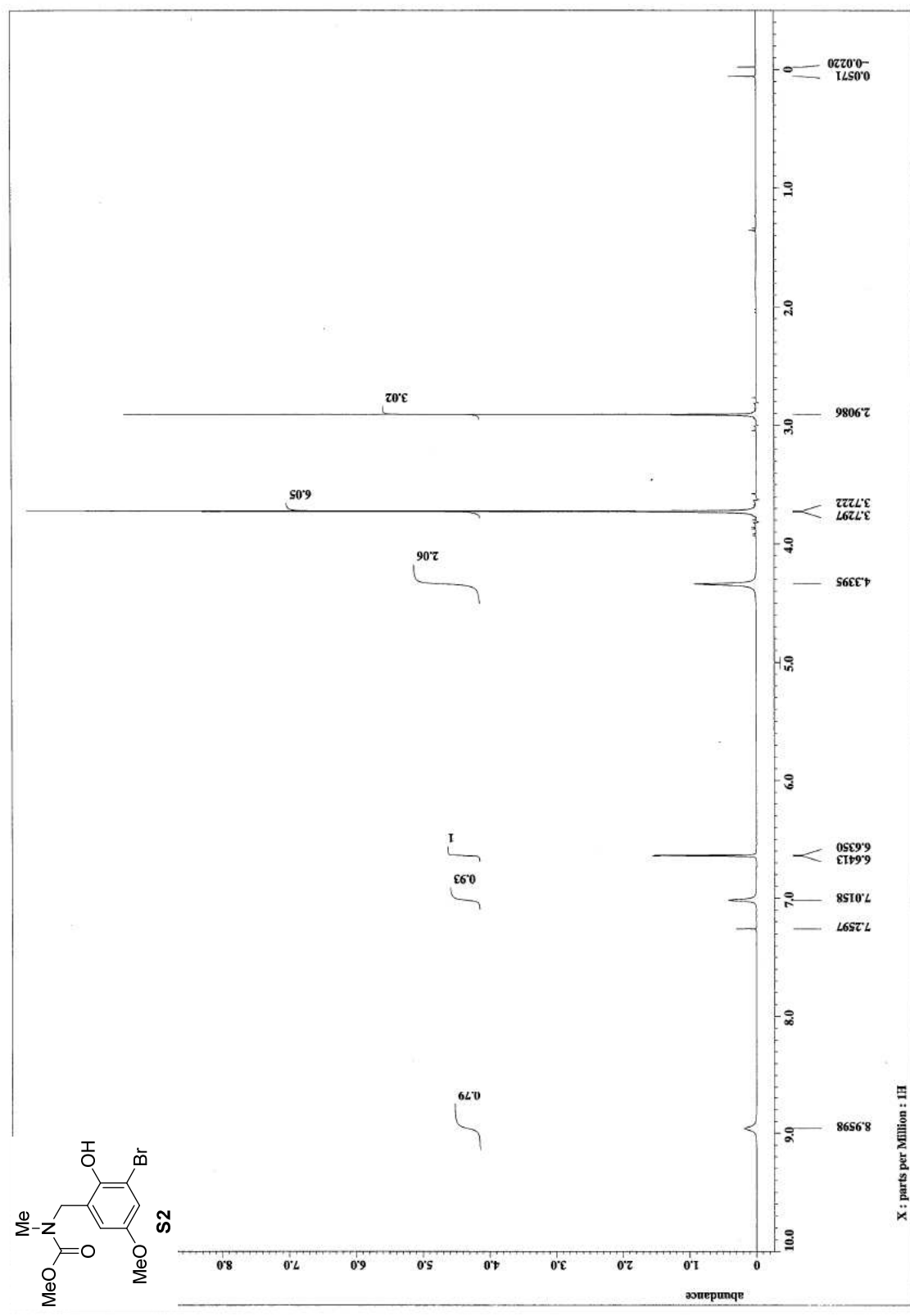
¹H NMR spectrum of **7b**



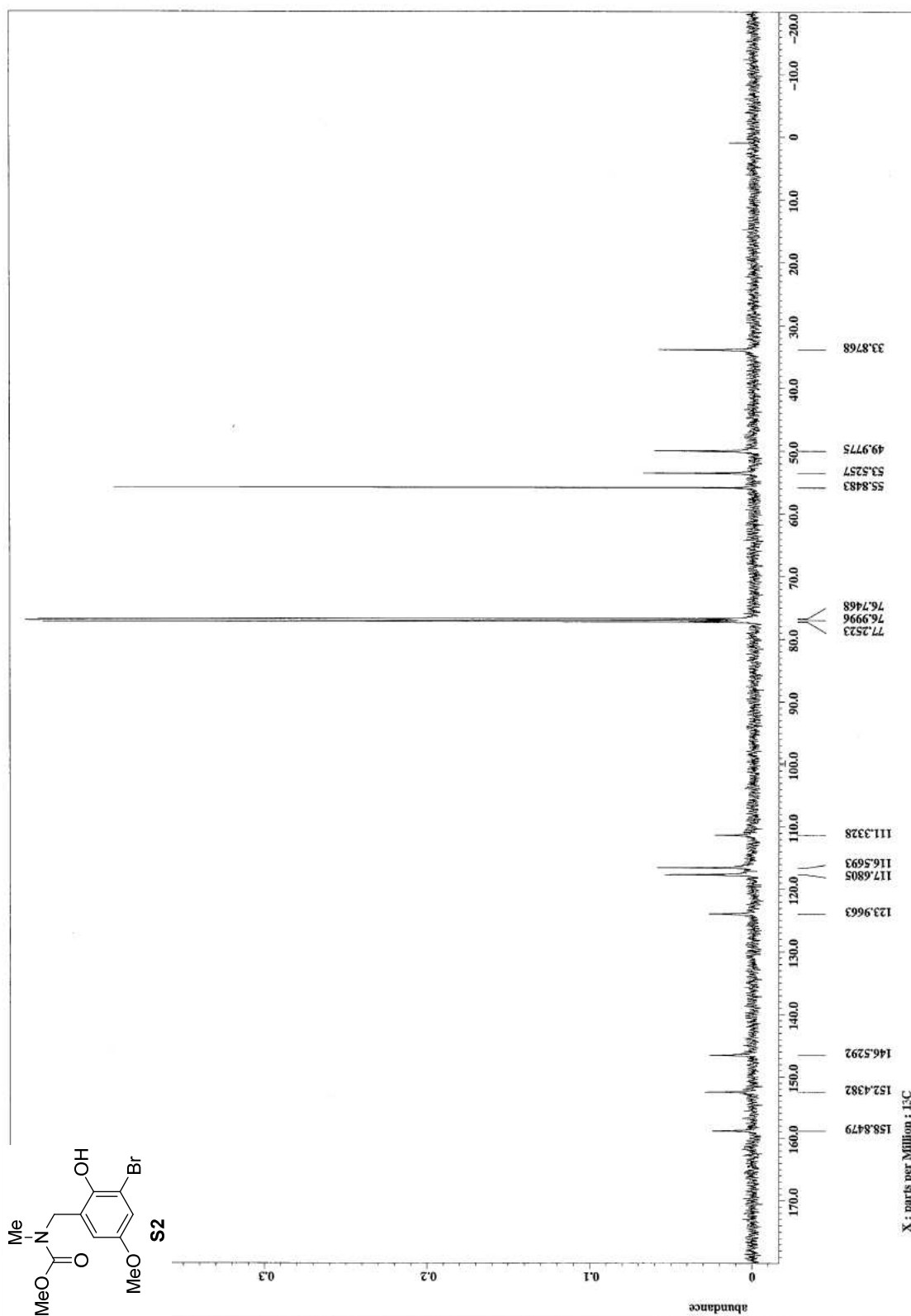
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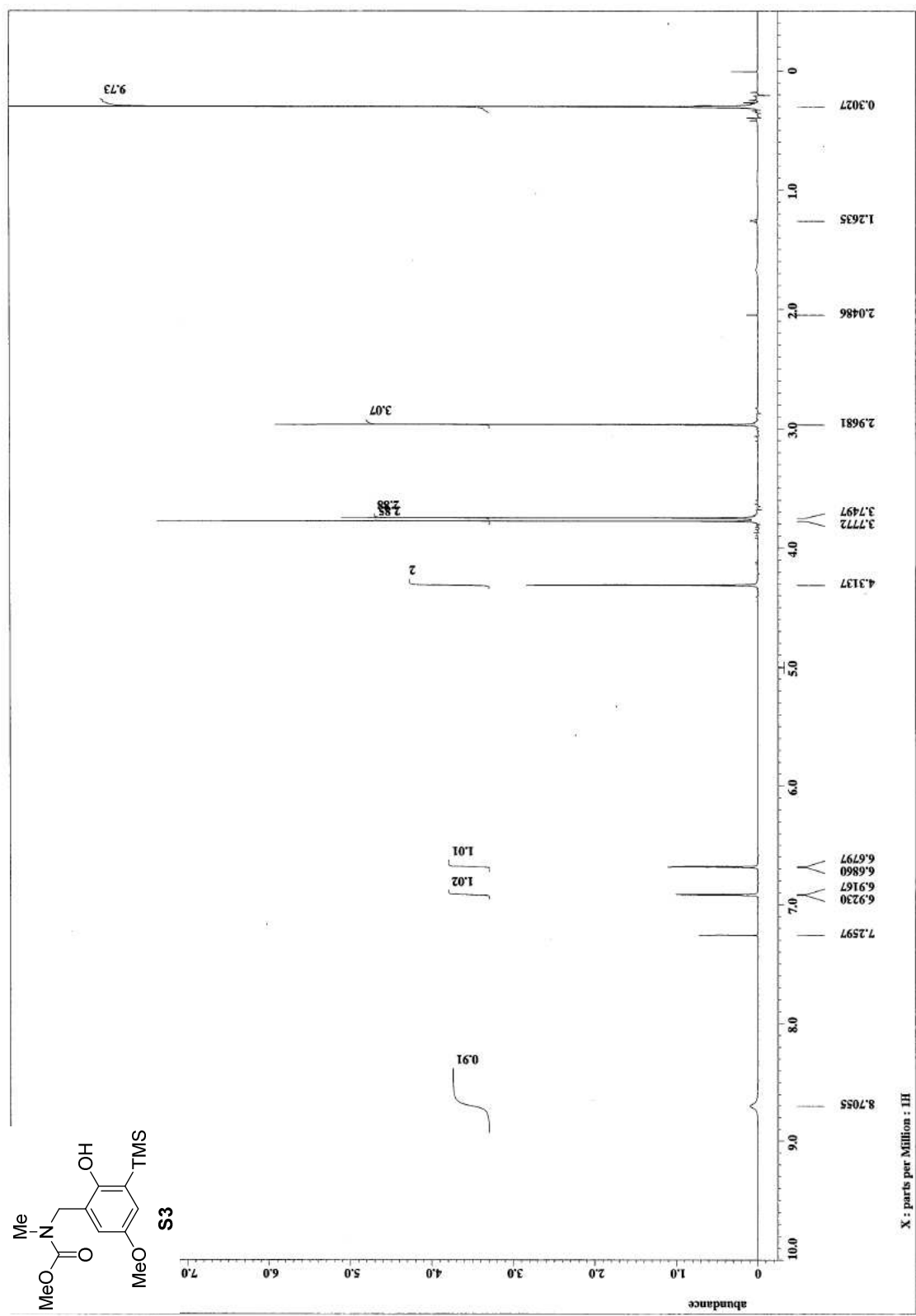
¹H NMR spectrum of S2



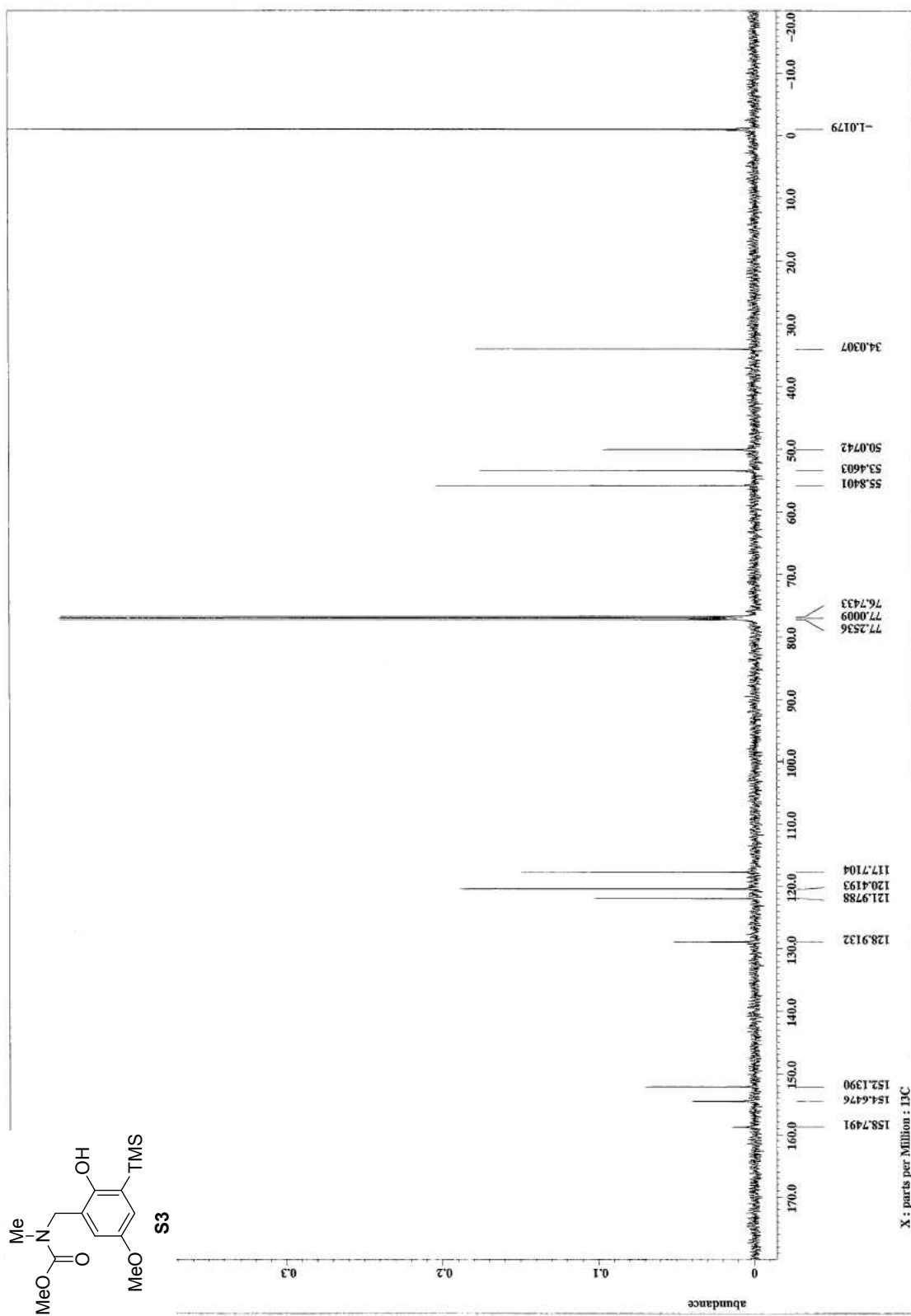
¹³C NMR spectrum of S2



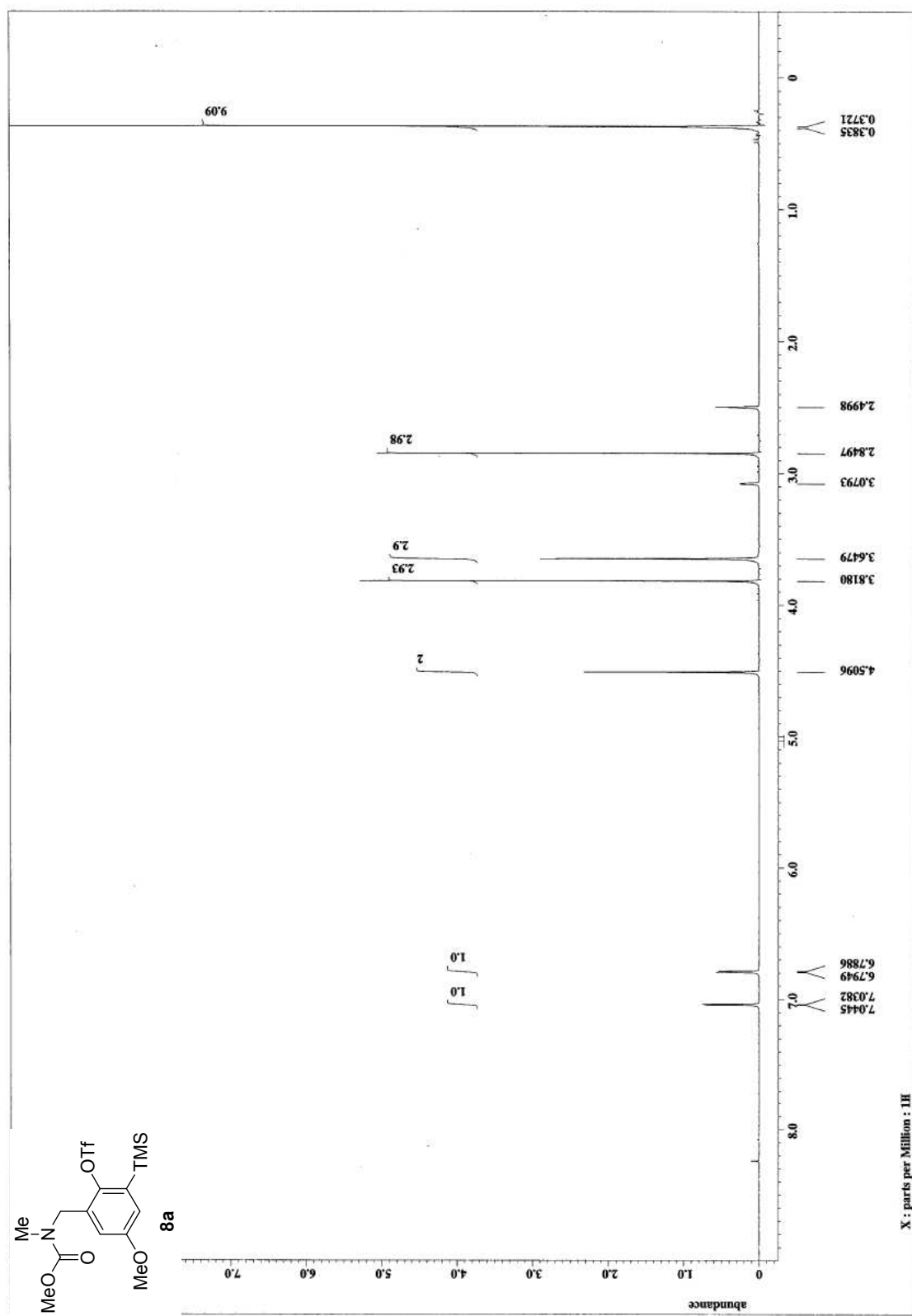
¹H NMR spectrum of S3



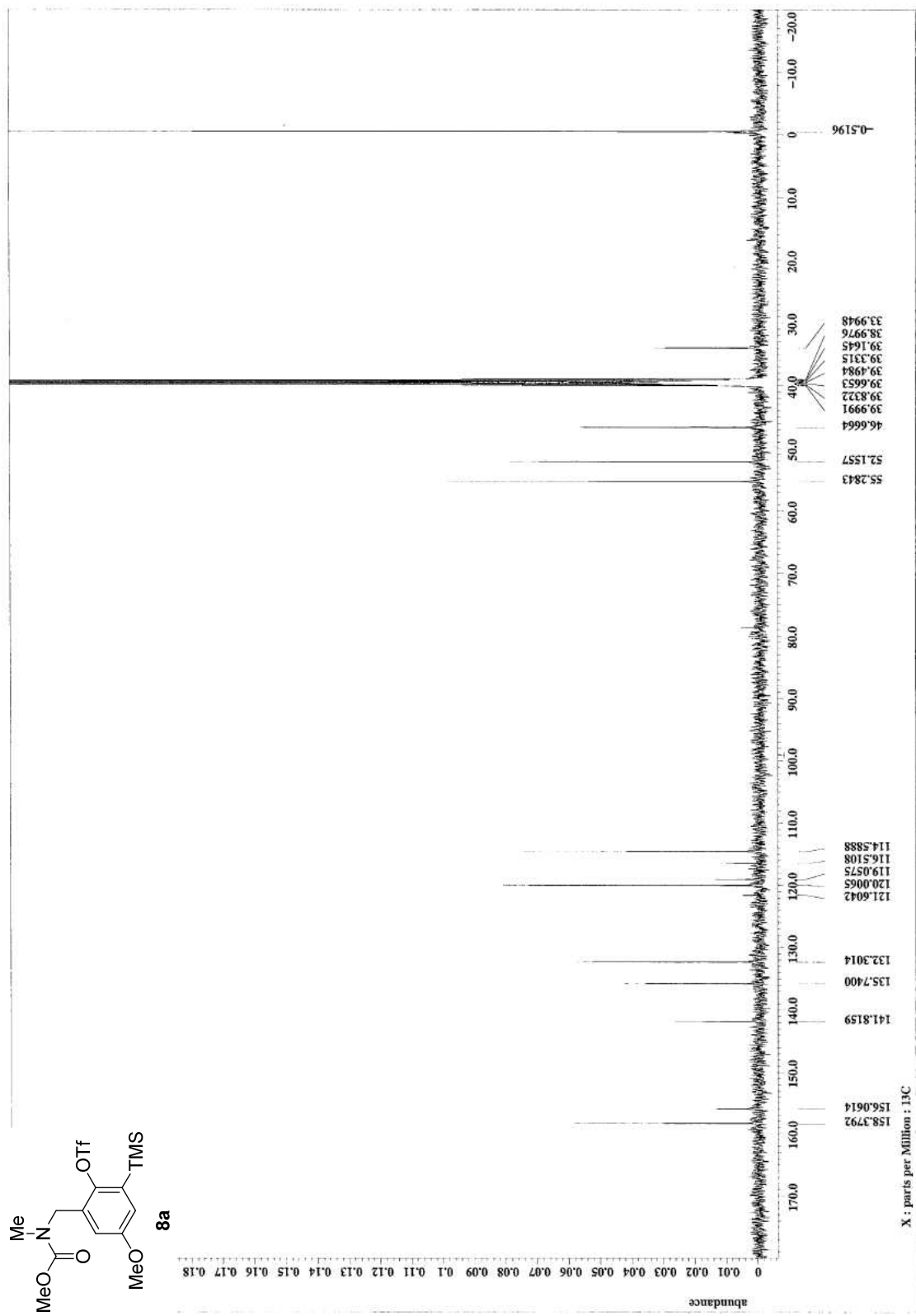
¹³C NMR spectrum of S3



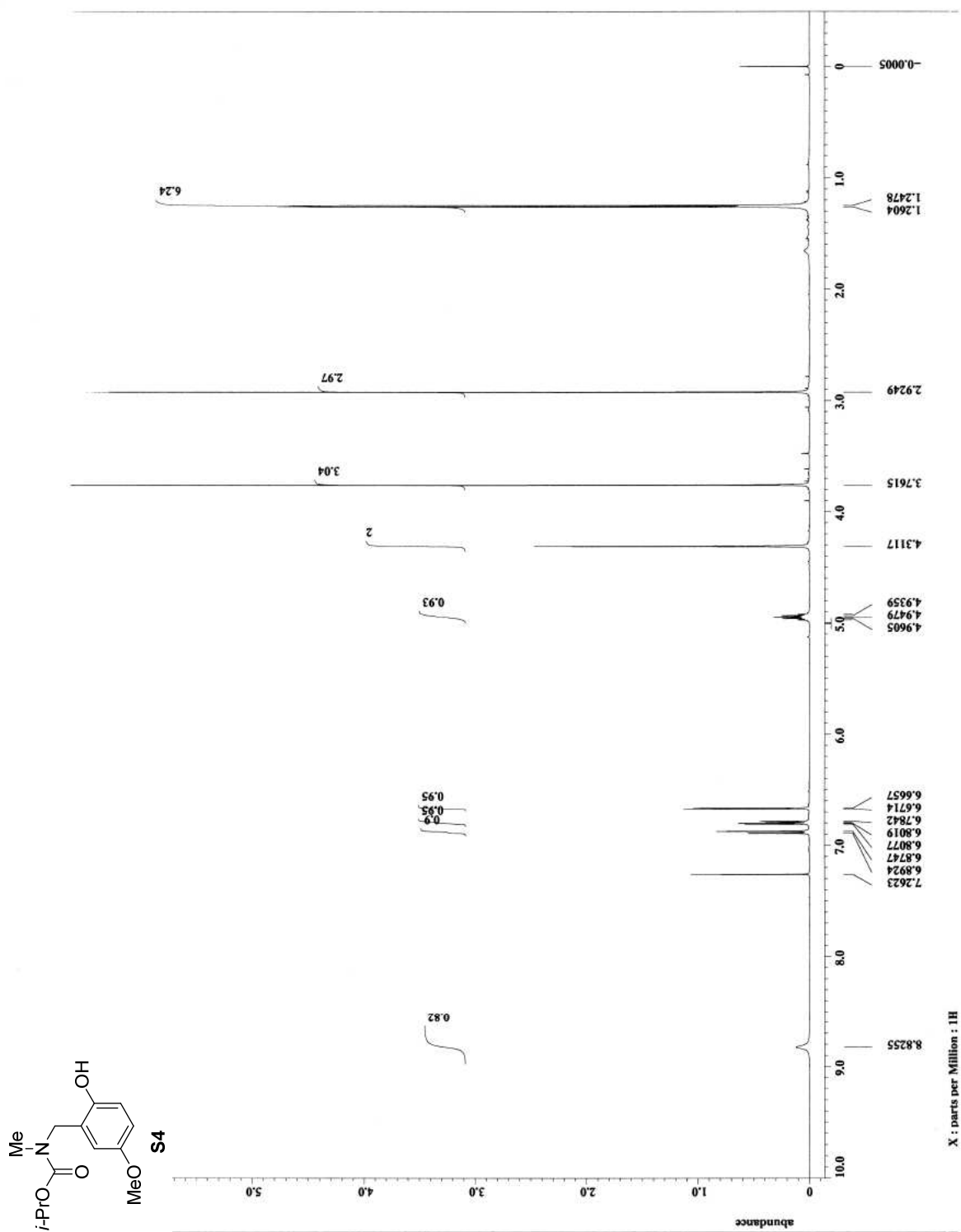
¹H NMR spectrum of **8a**



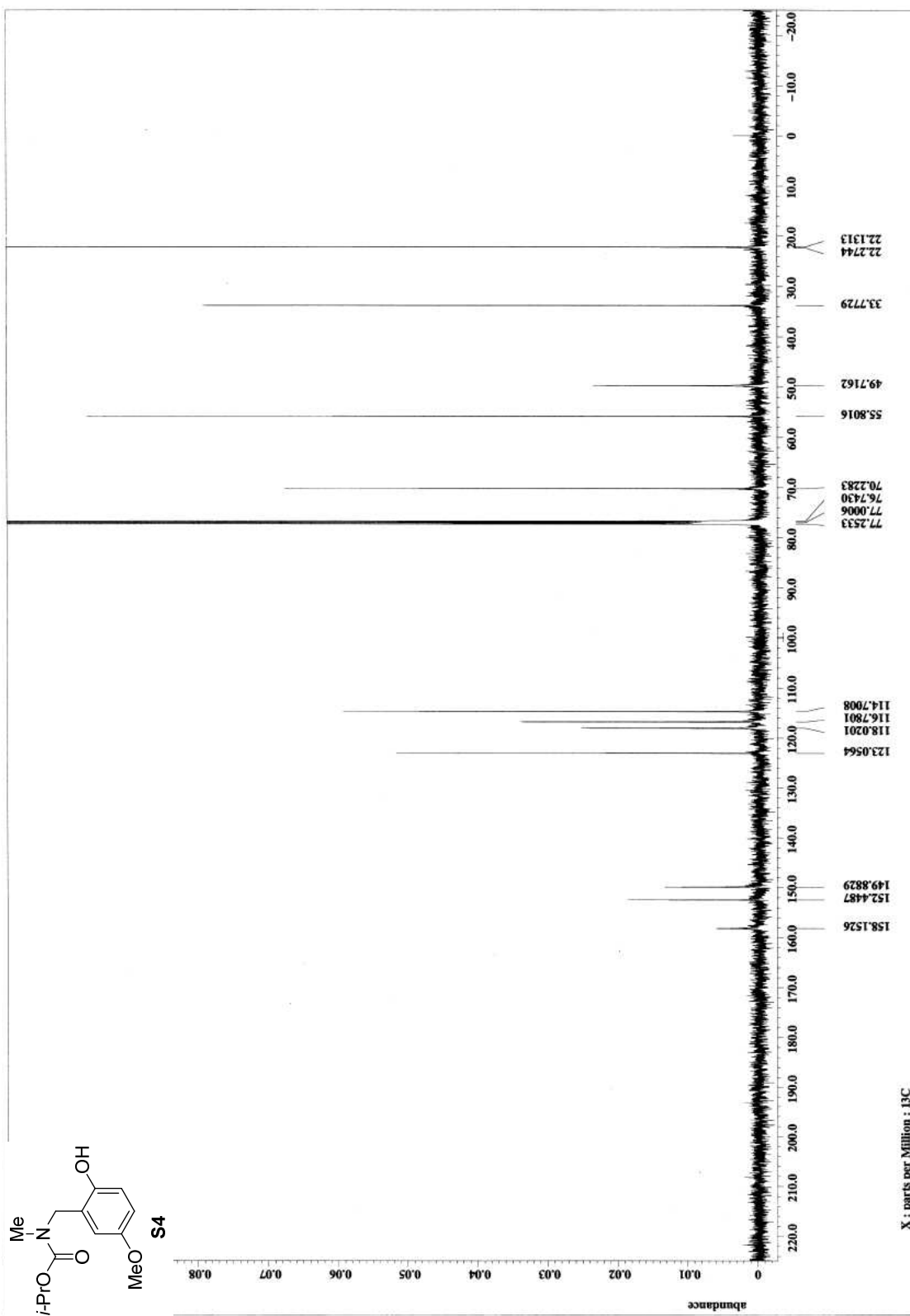
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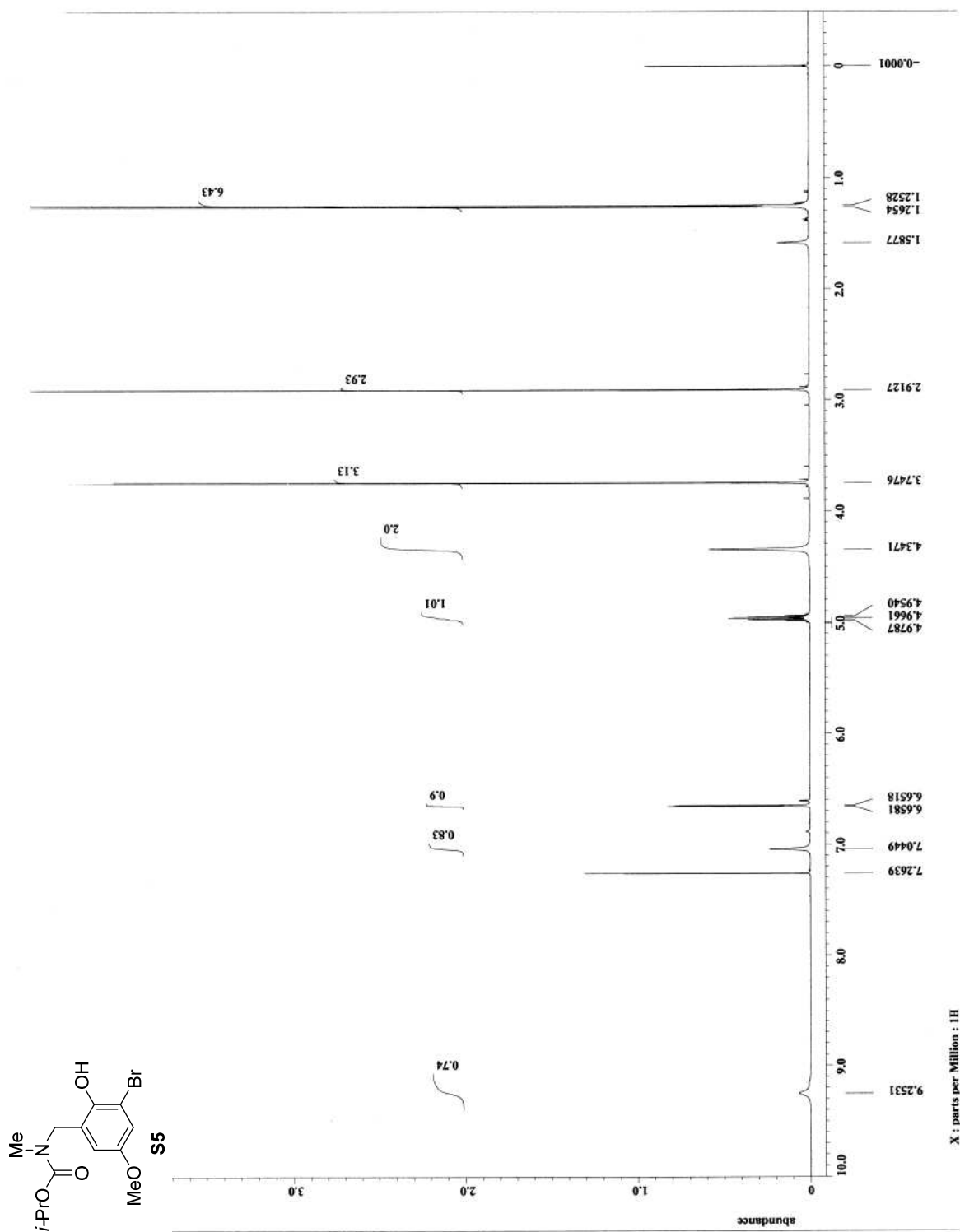
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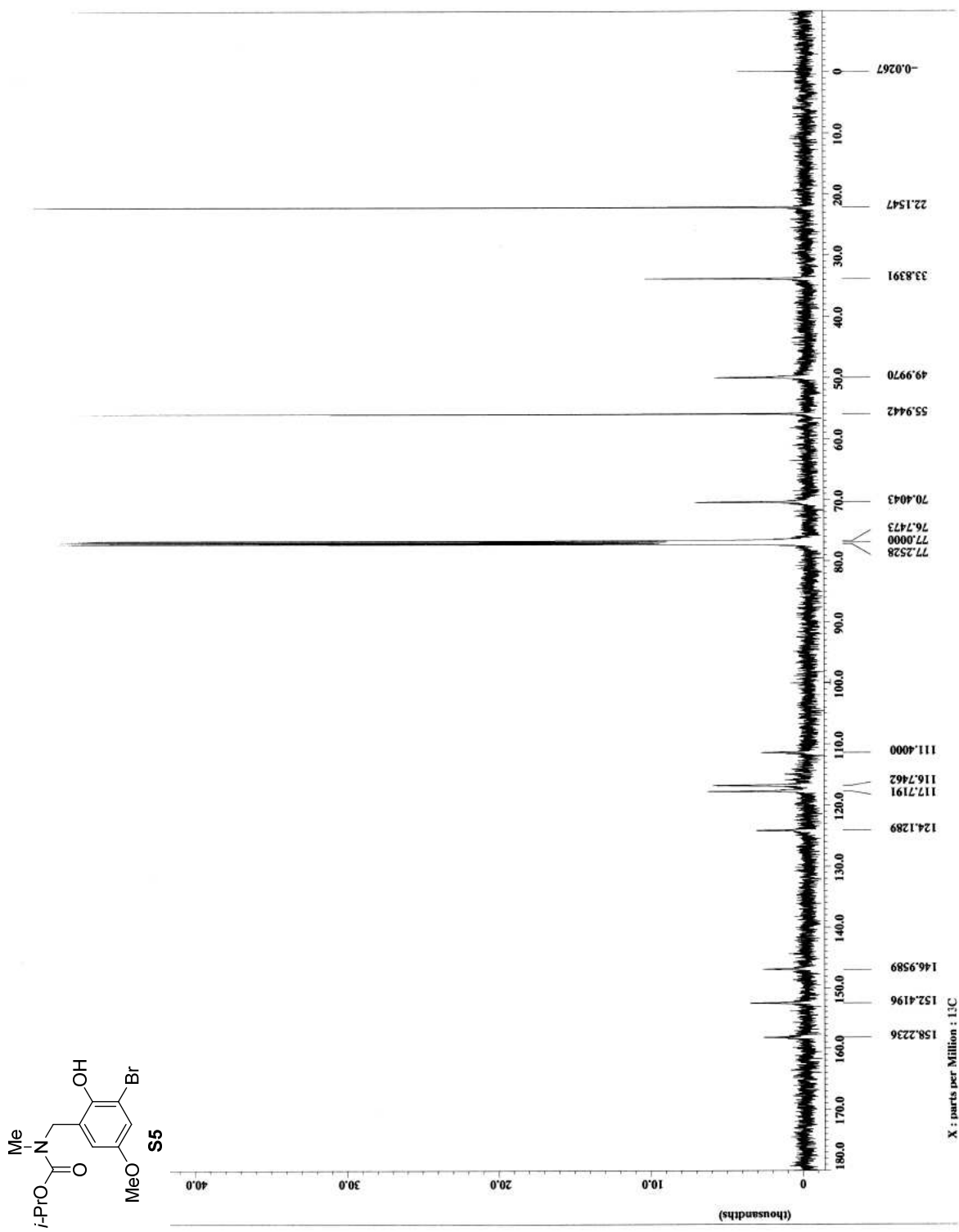
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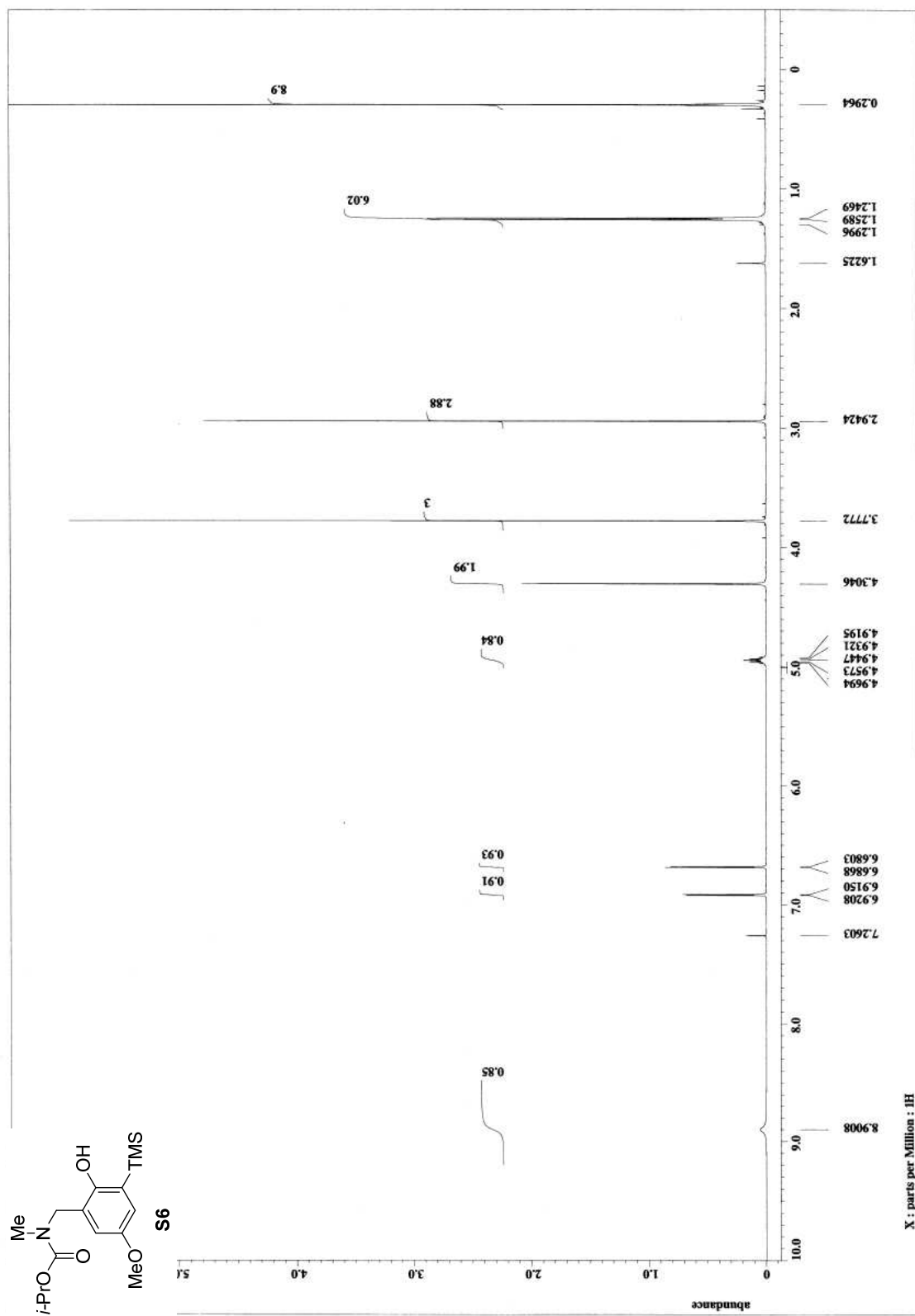
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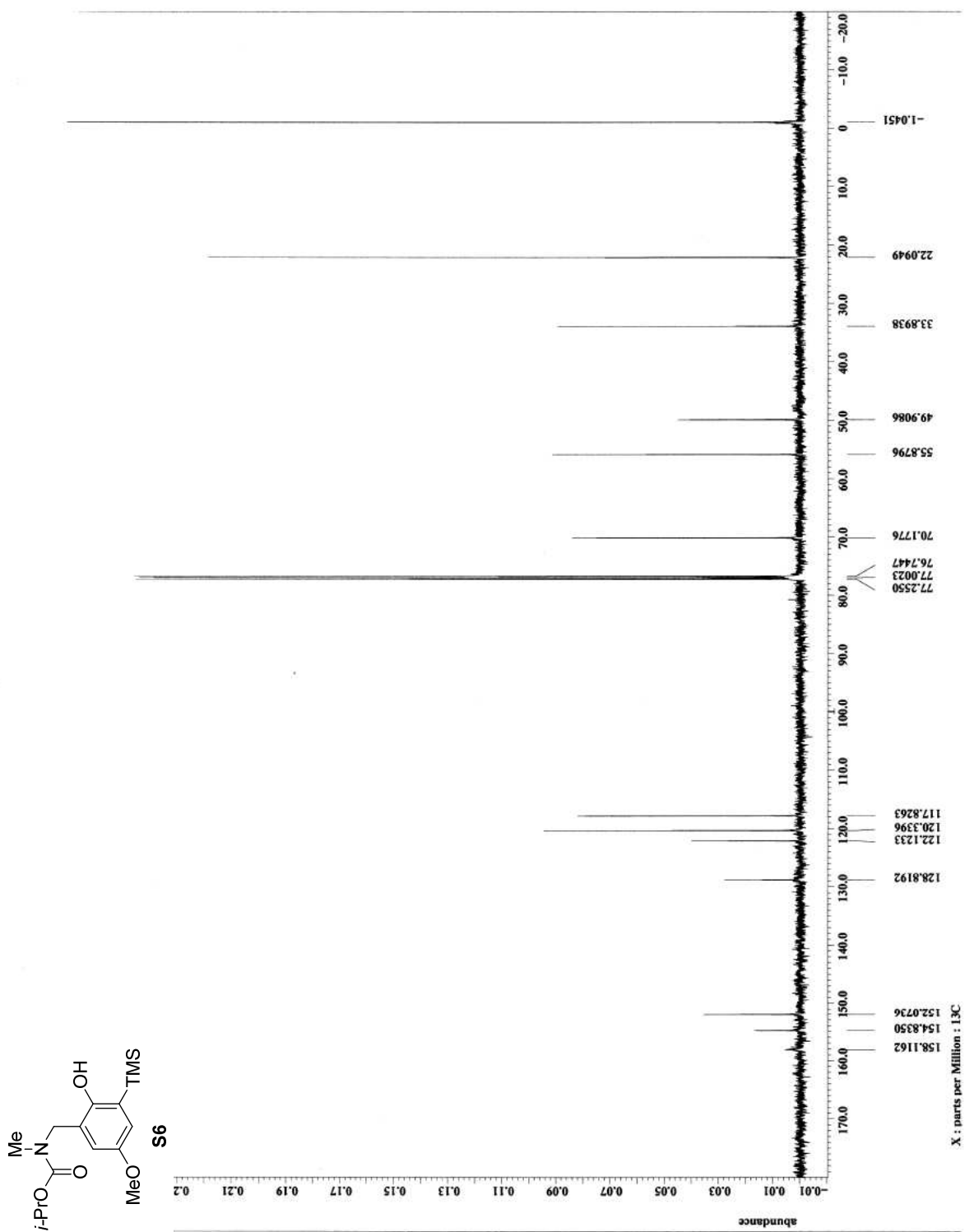
¹³C NMR spectrum of S5



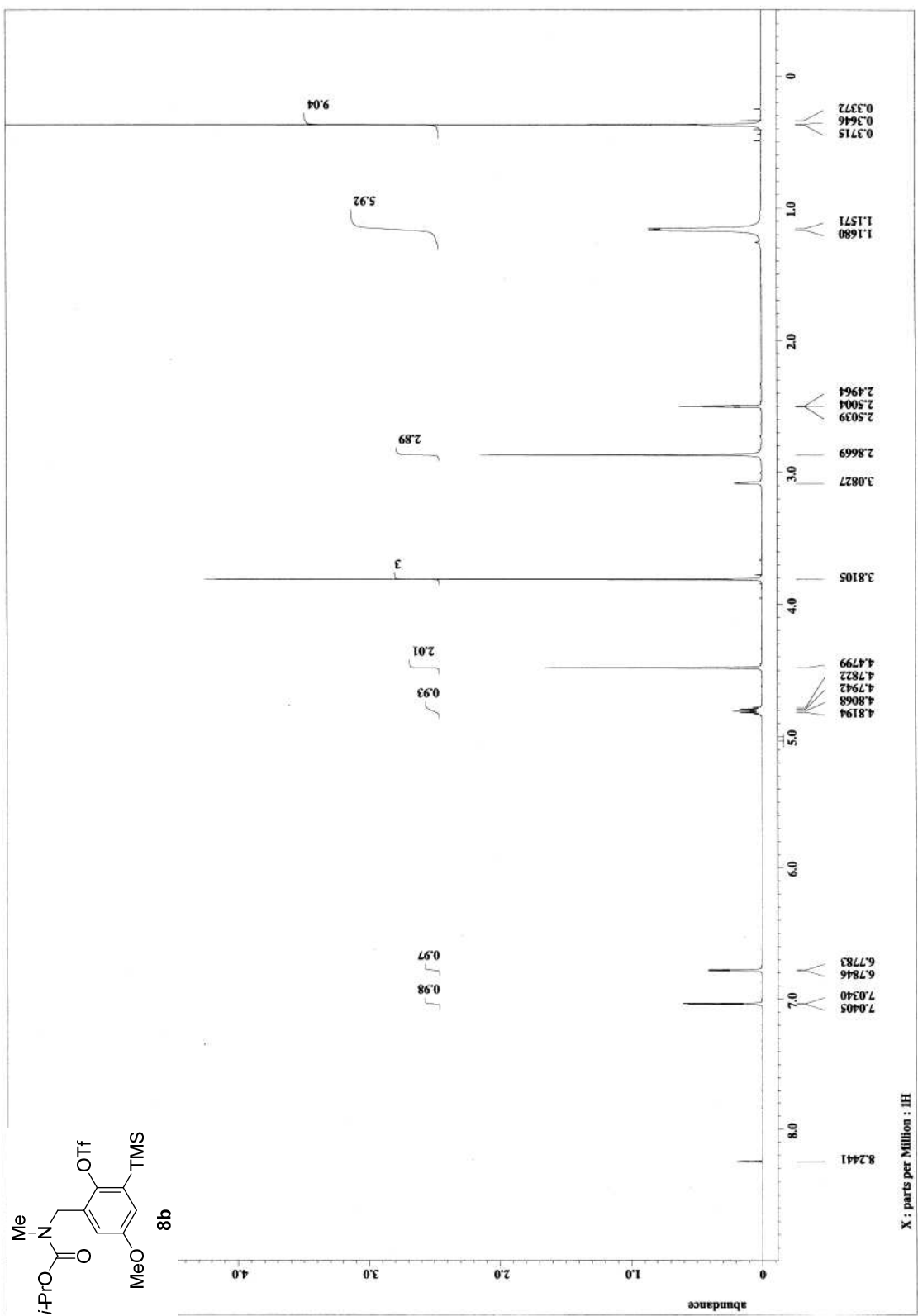
^1H NMR spectrum of S6



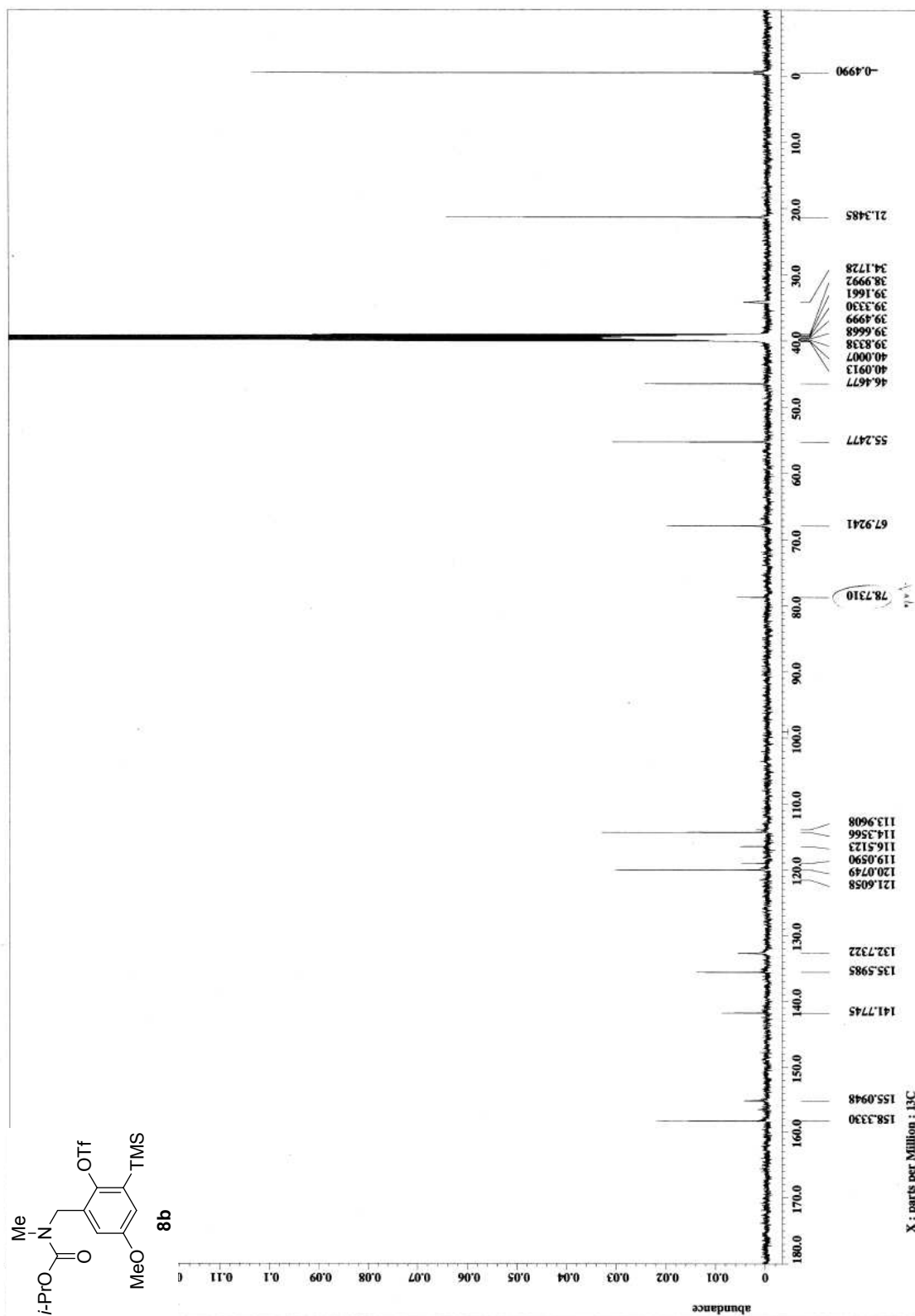
¹³C NMR spectrum of S6



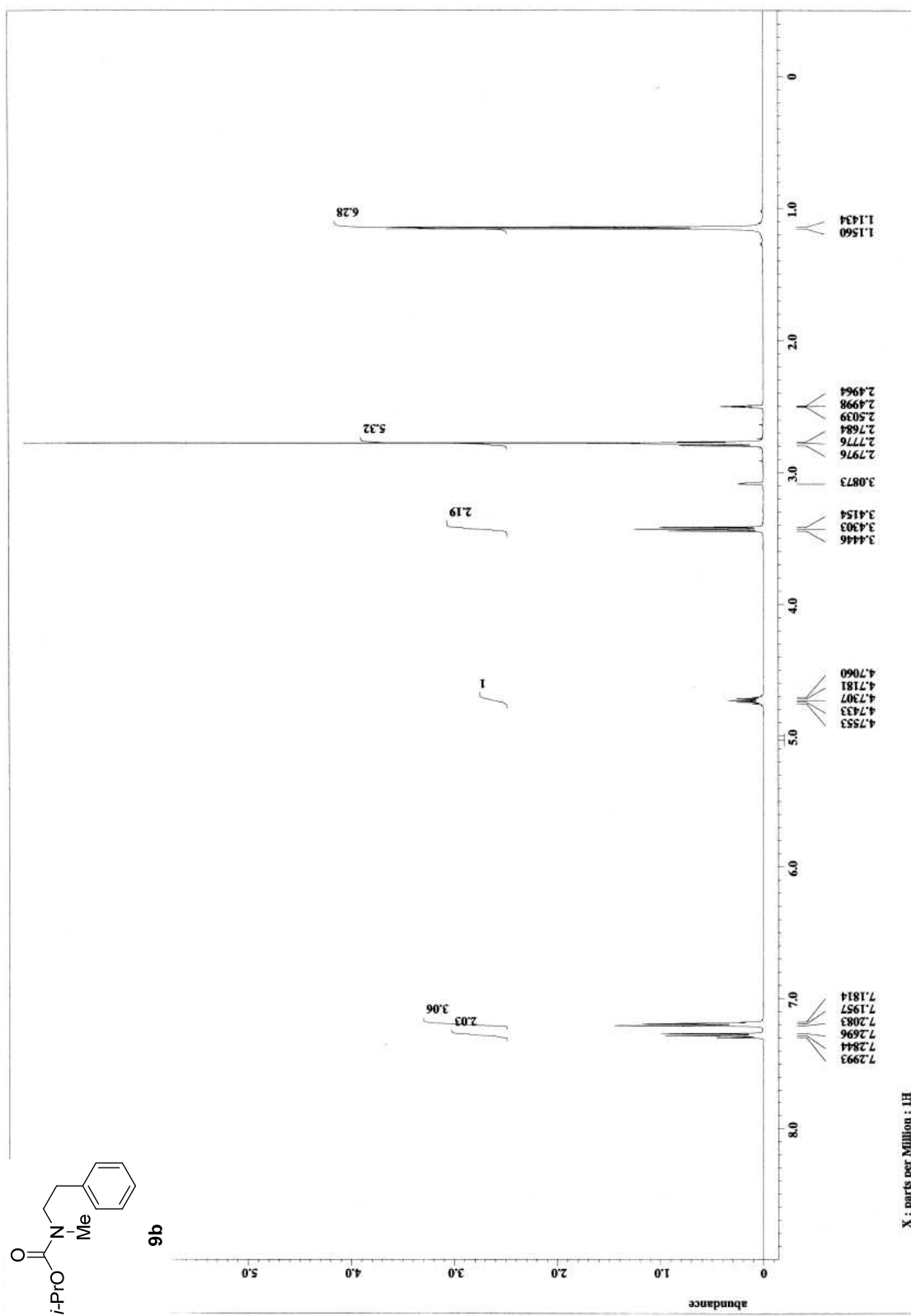
¹H NMR spectrum of **8b**



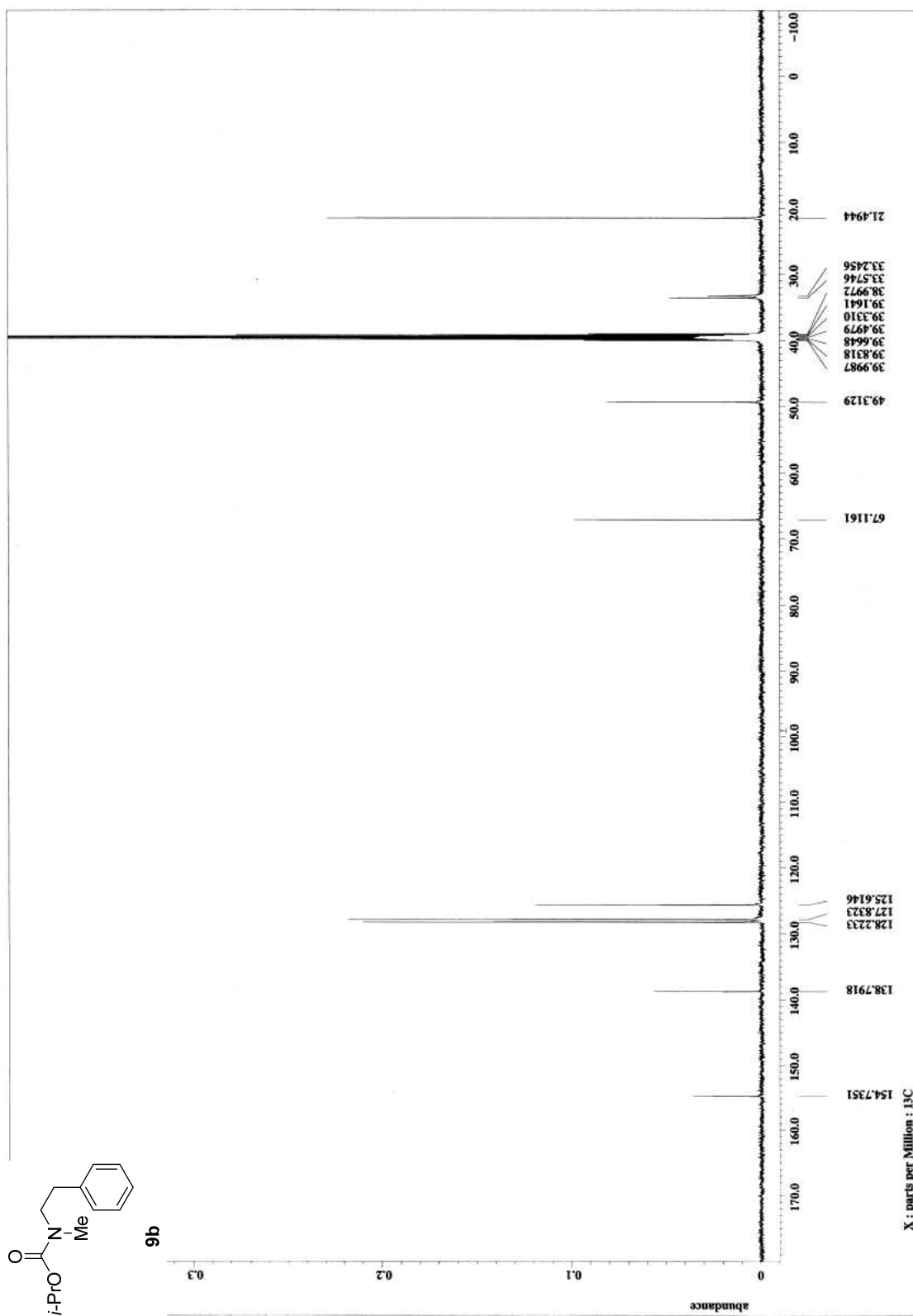
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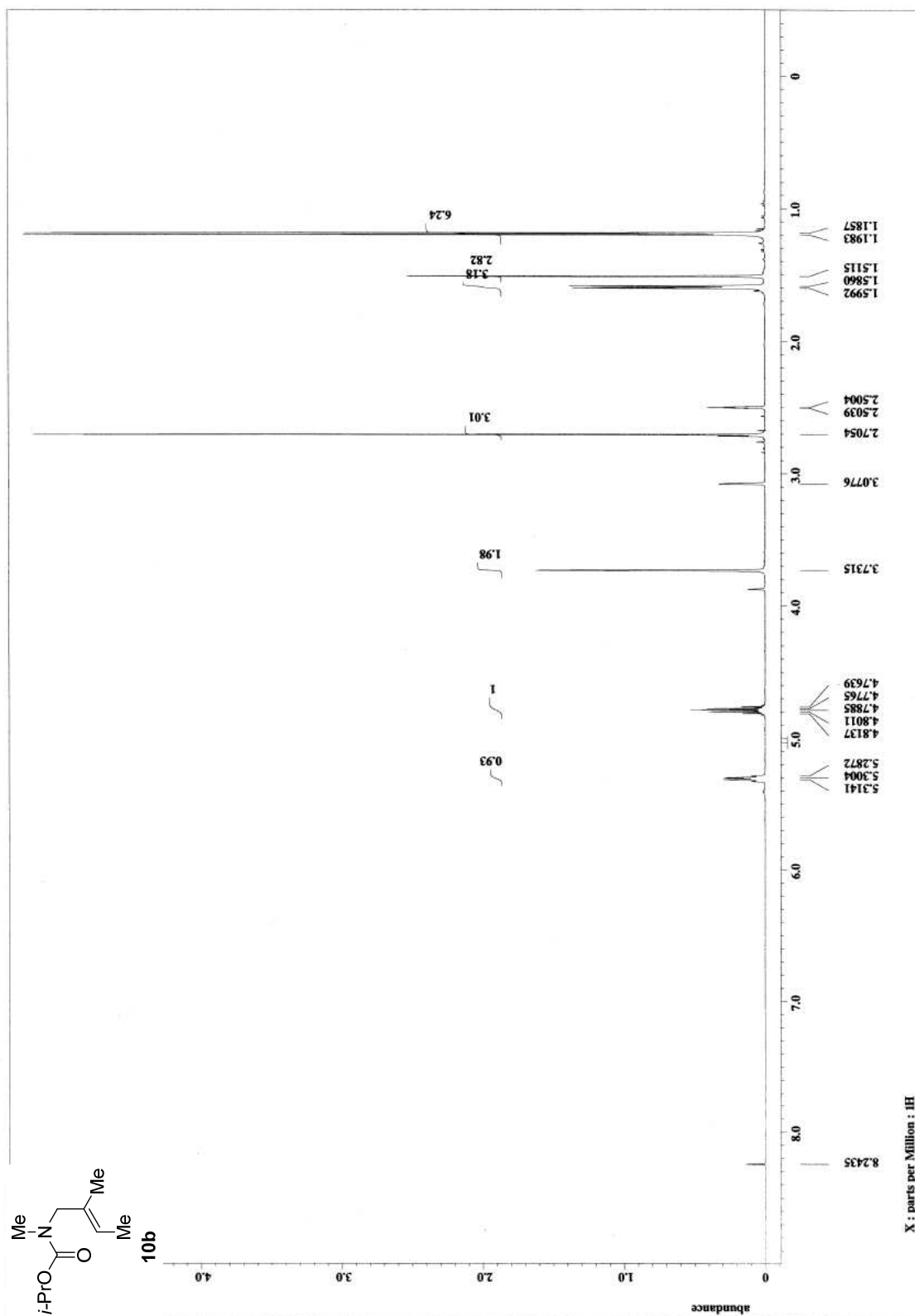
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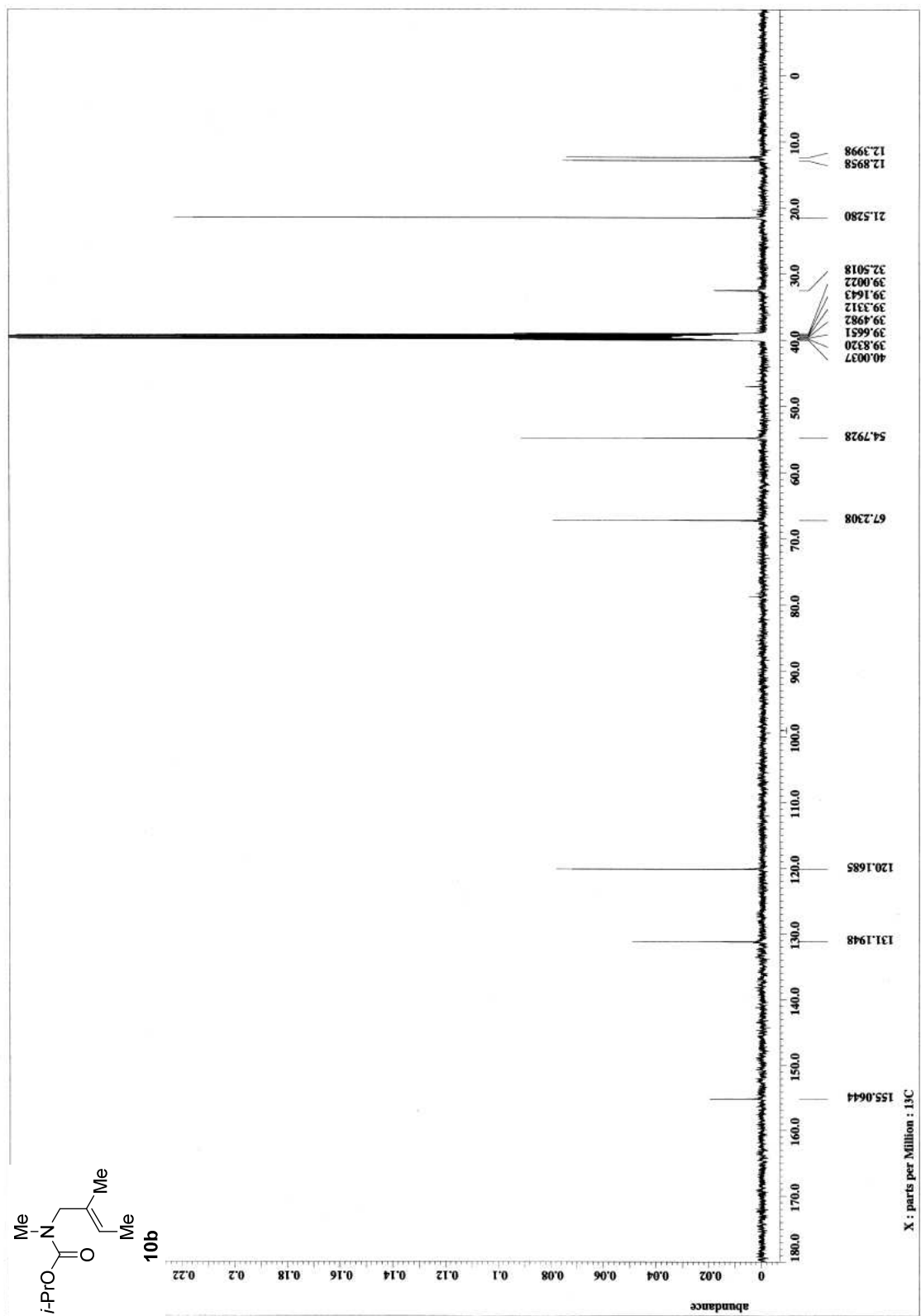
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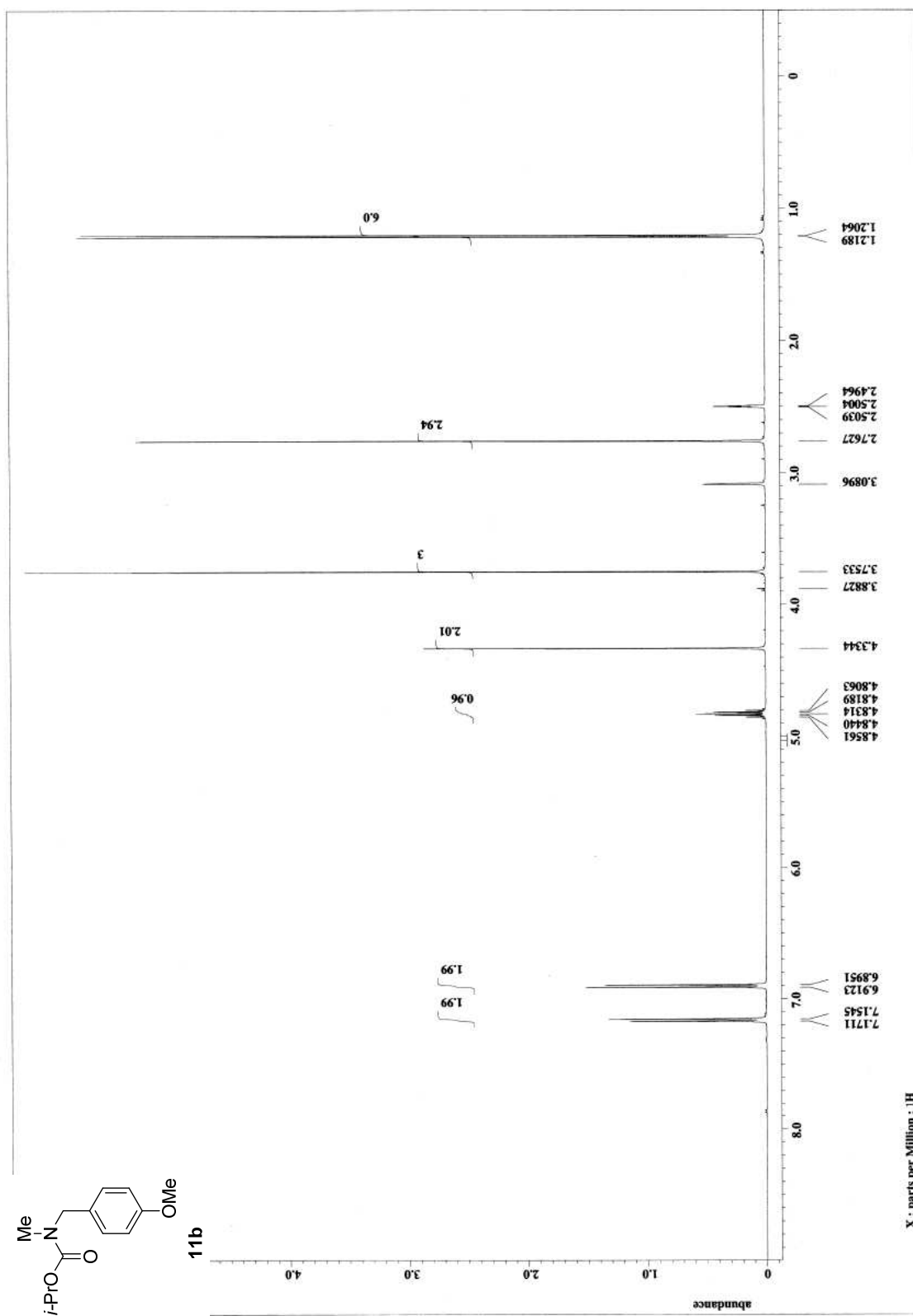
¹H NMR spectrum of **10b**



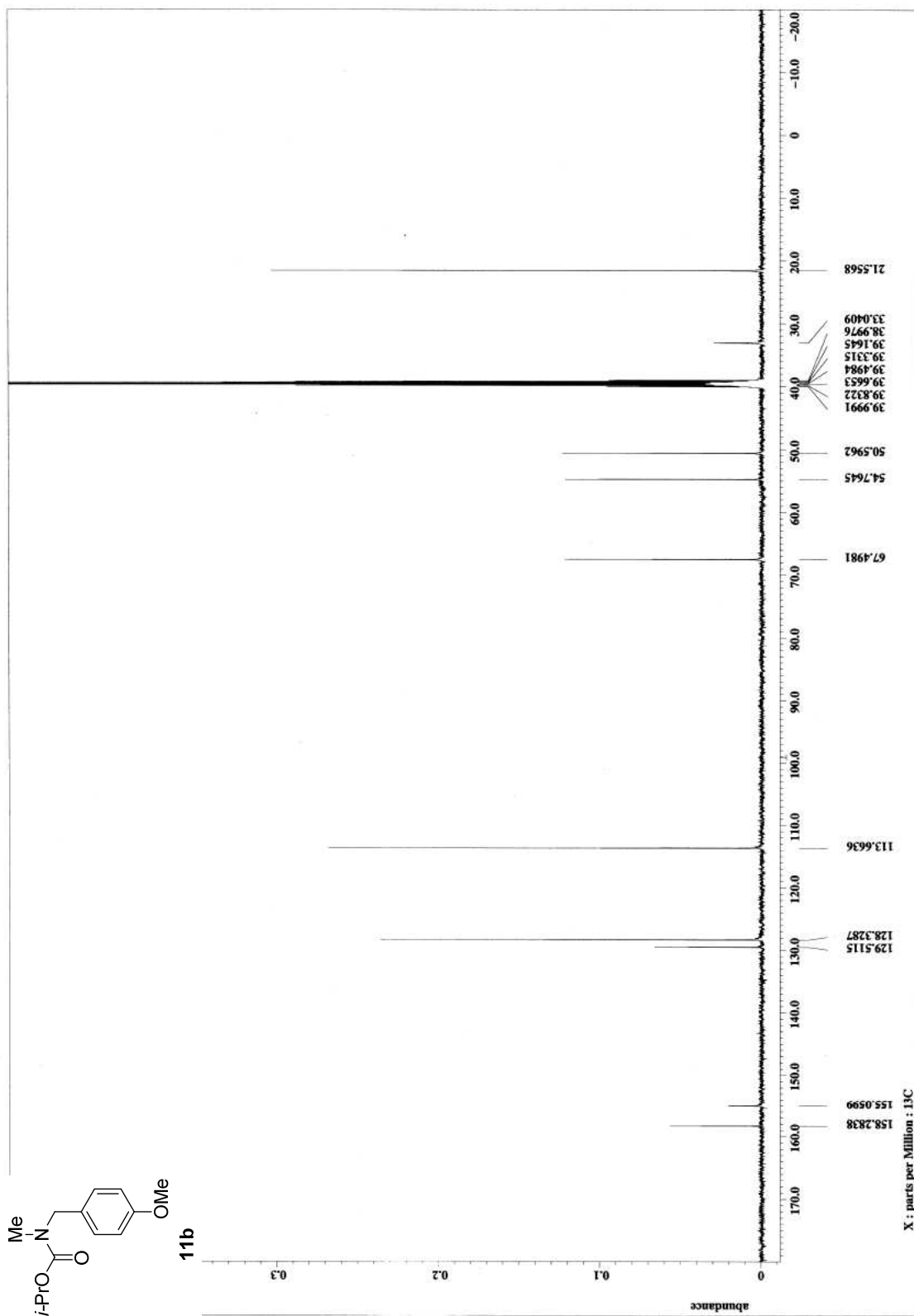
¹³C NMR spectrum of **10b**



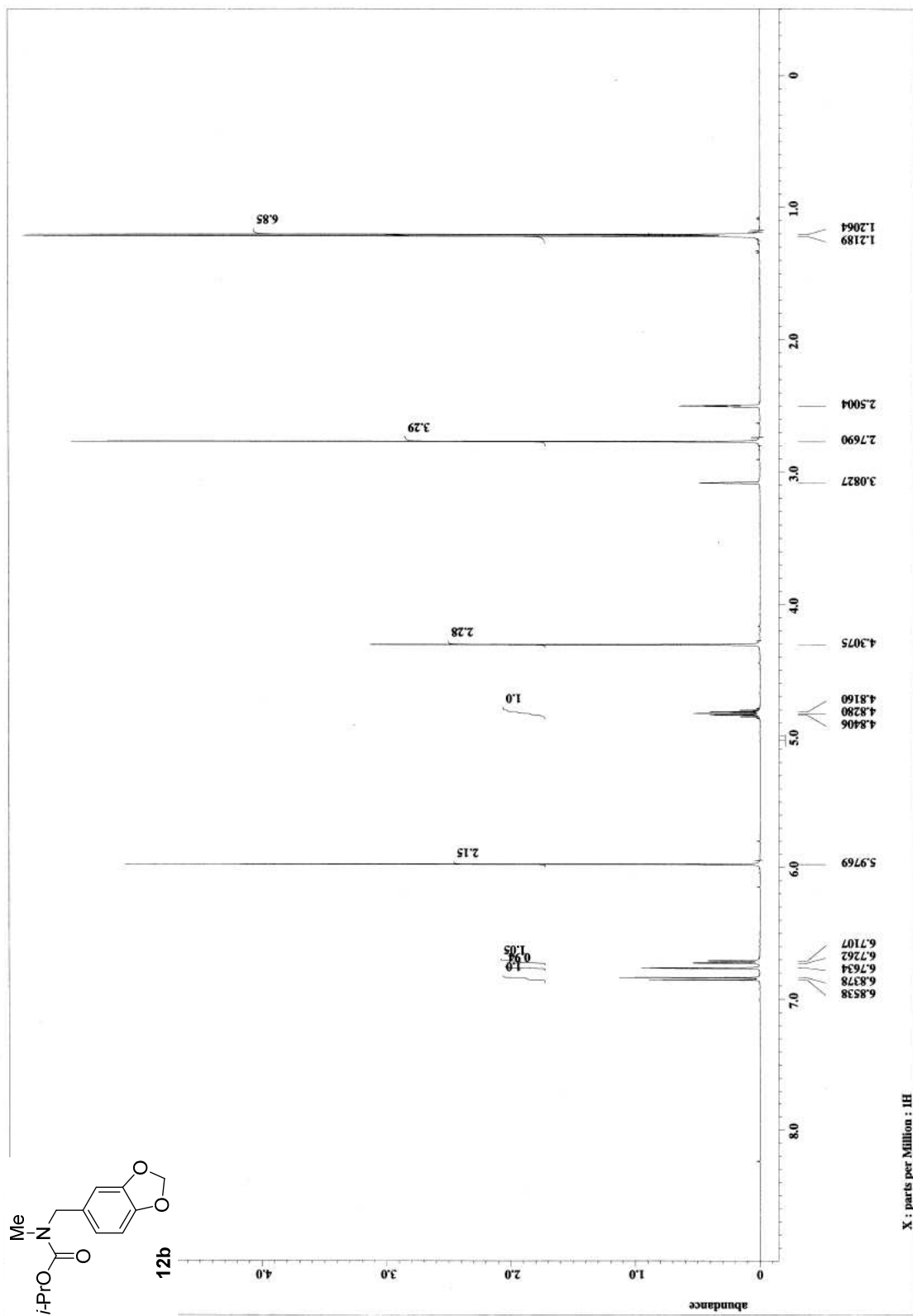
¹H NMR spectrum of S11b



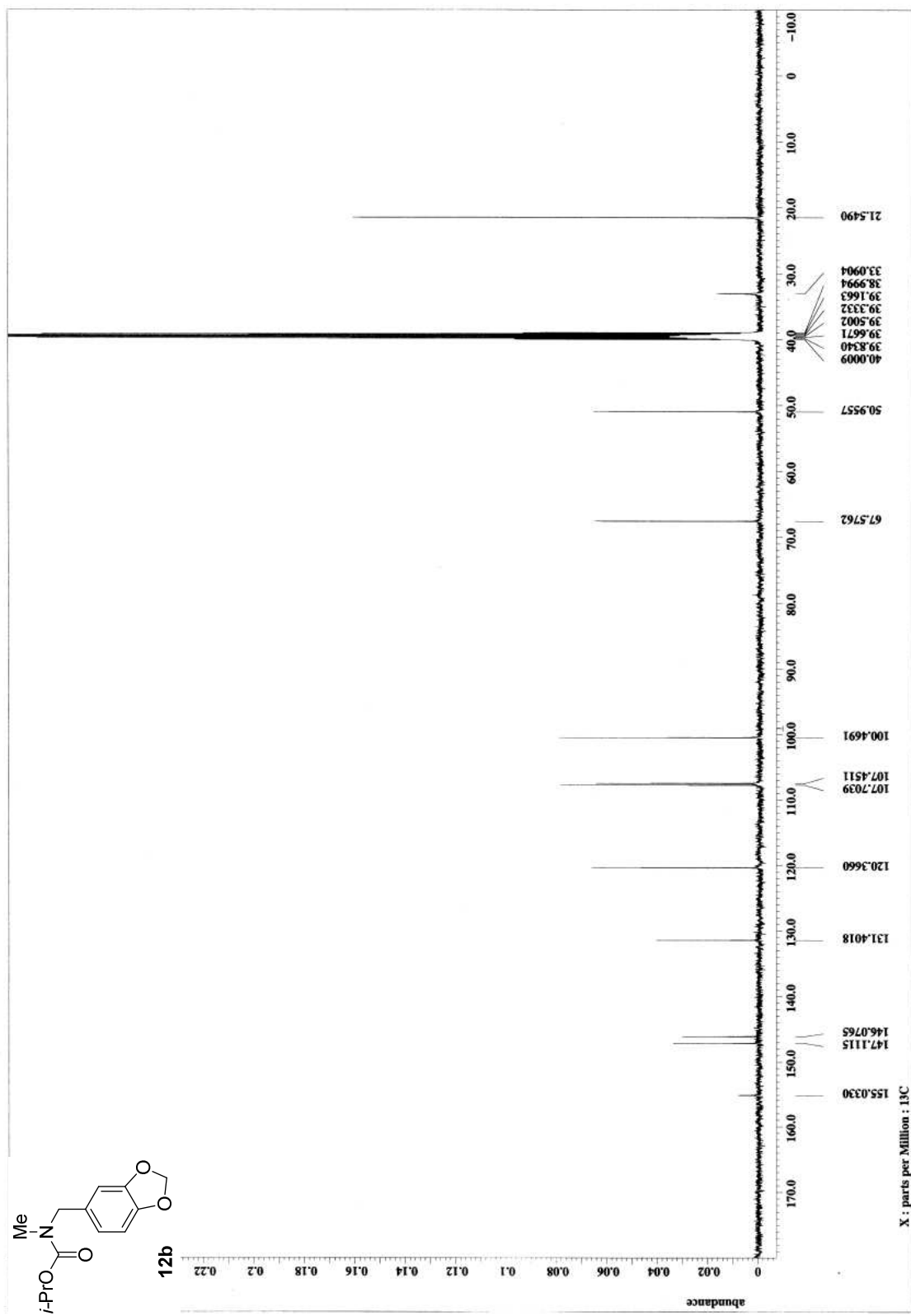
¹³C NMR spectrum of **11b**



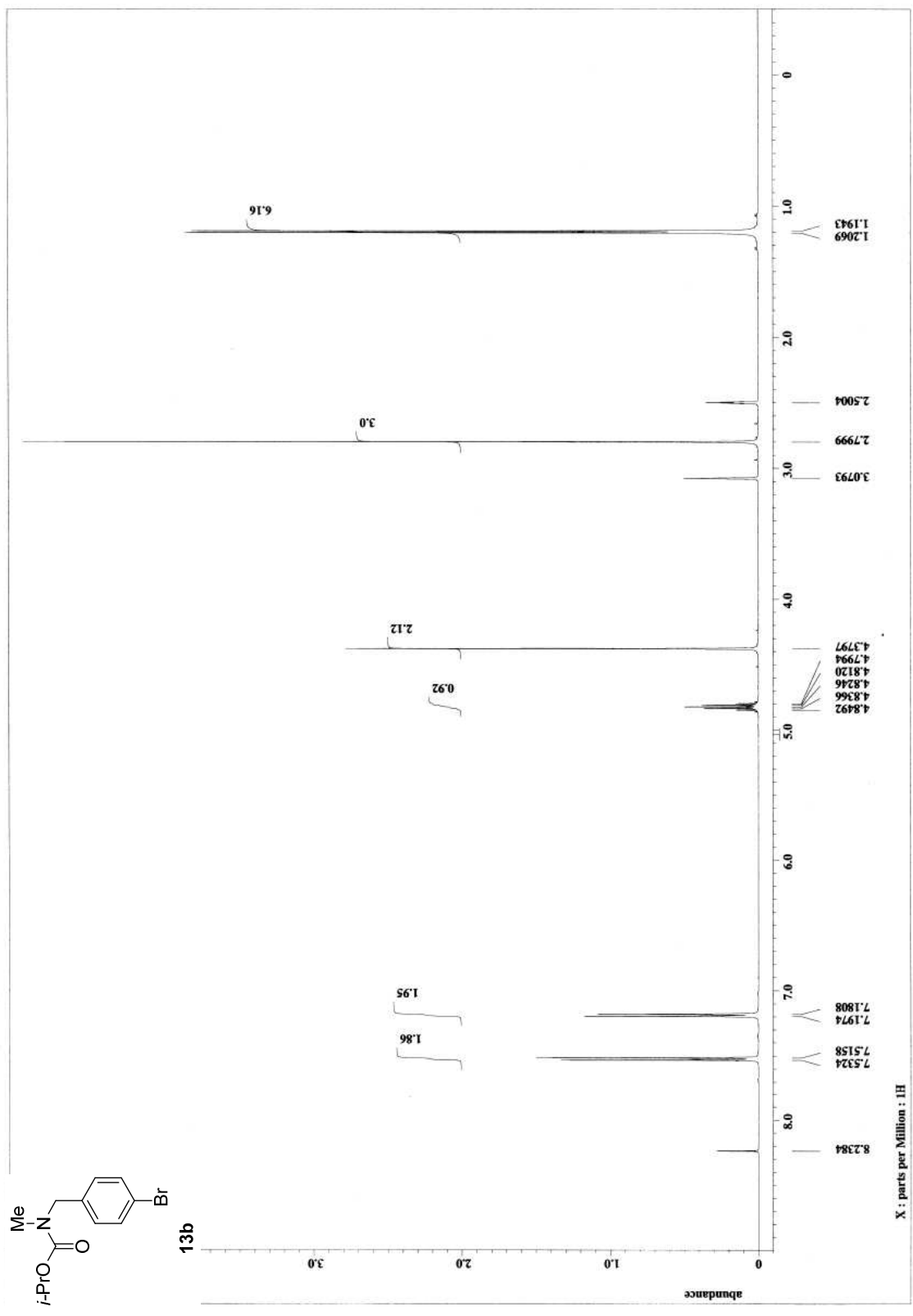
H NMR spectrum of **12b**



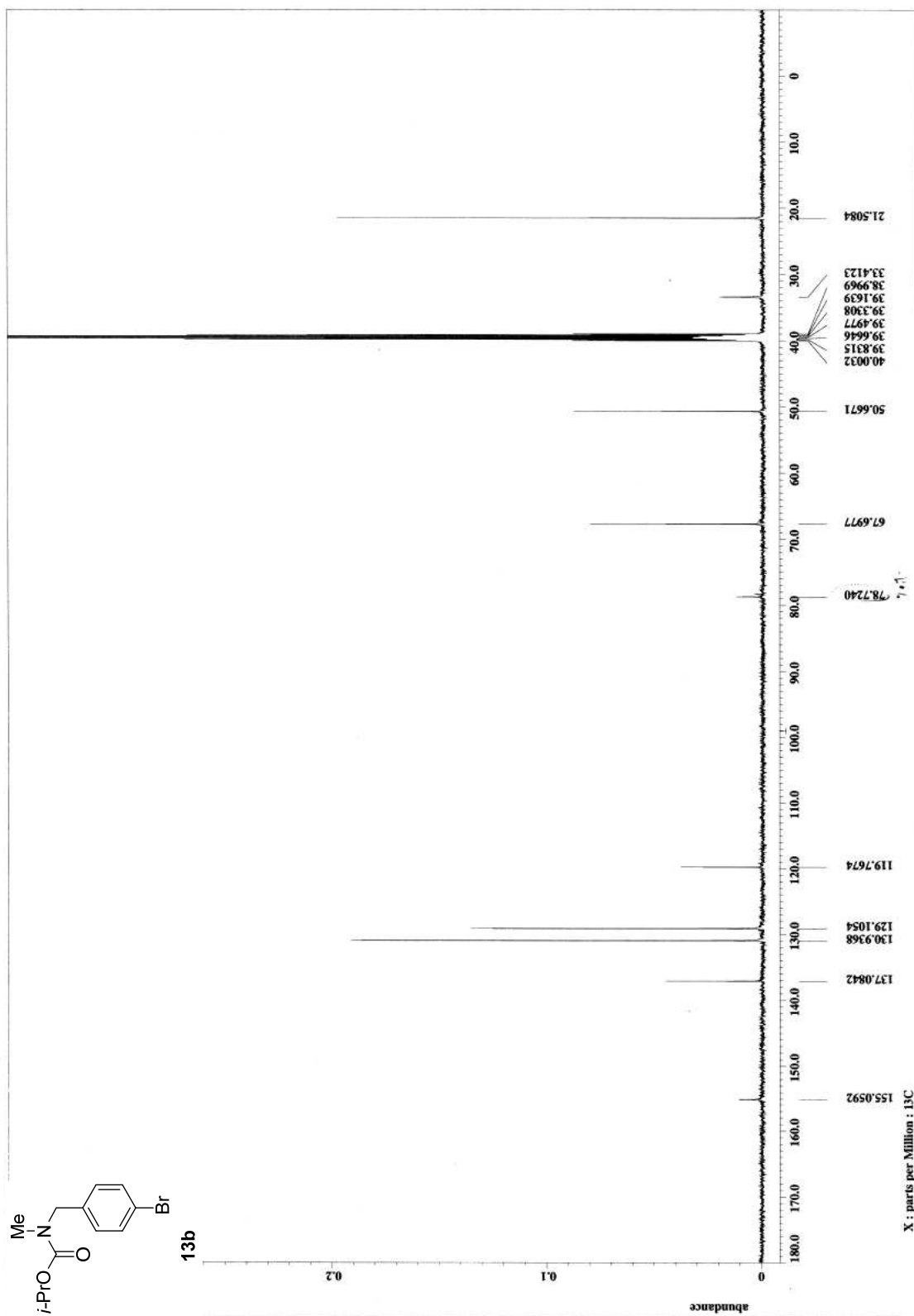
¹³C NMR spectrum of **12b**



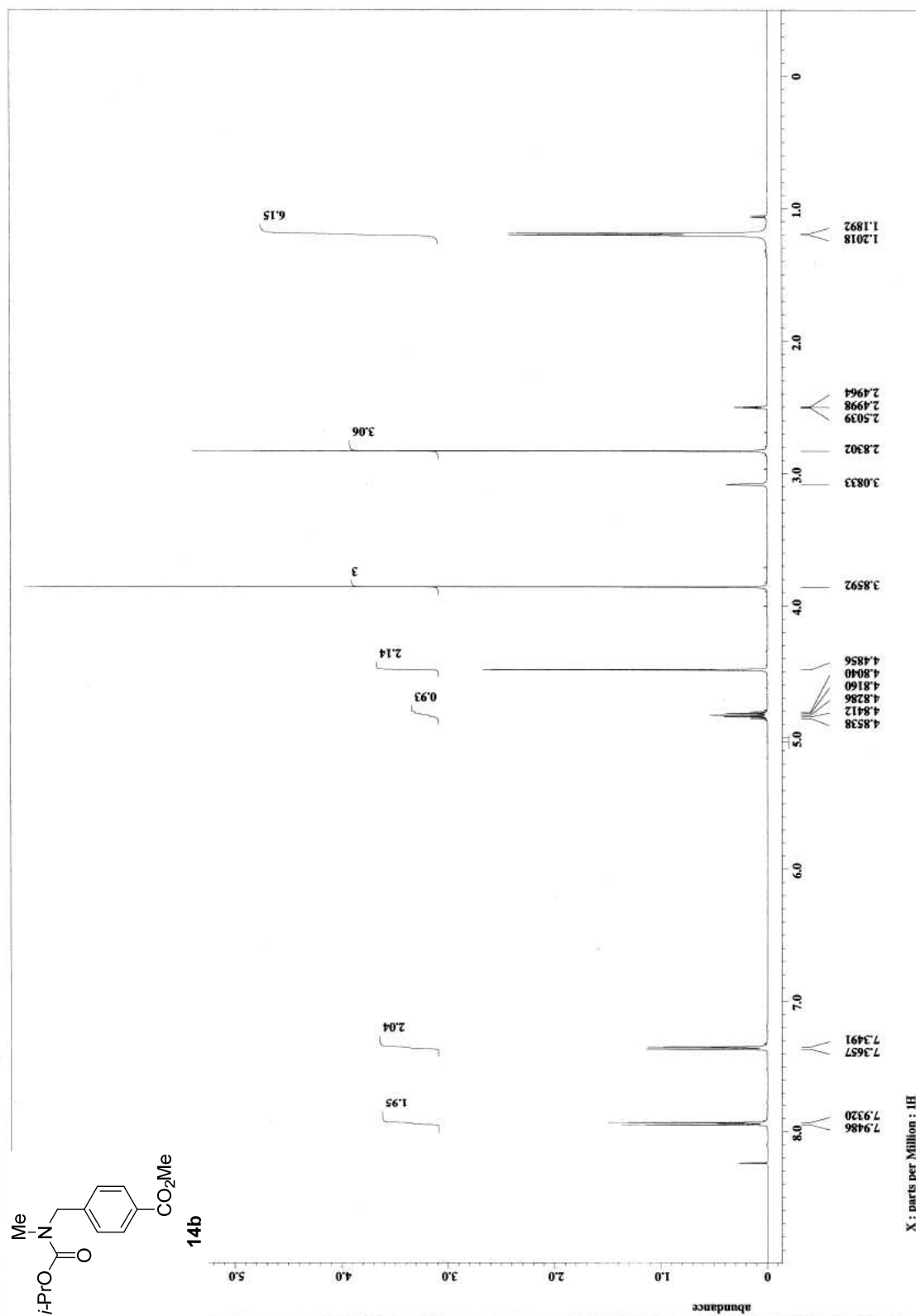
¹H NMR spectrum of 13b



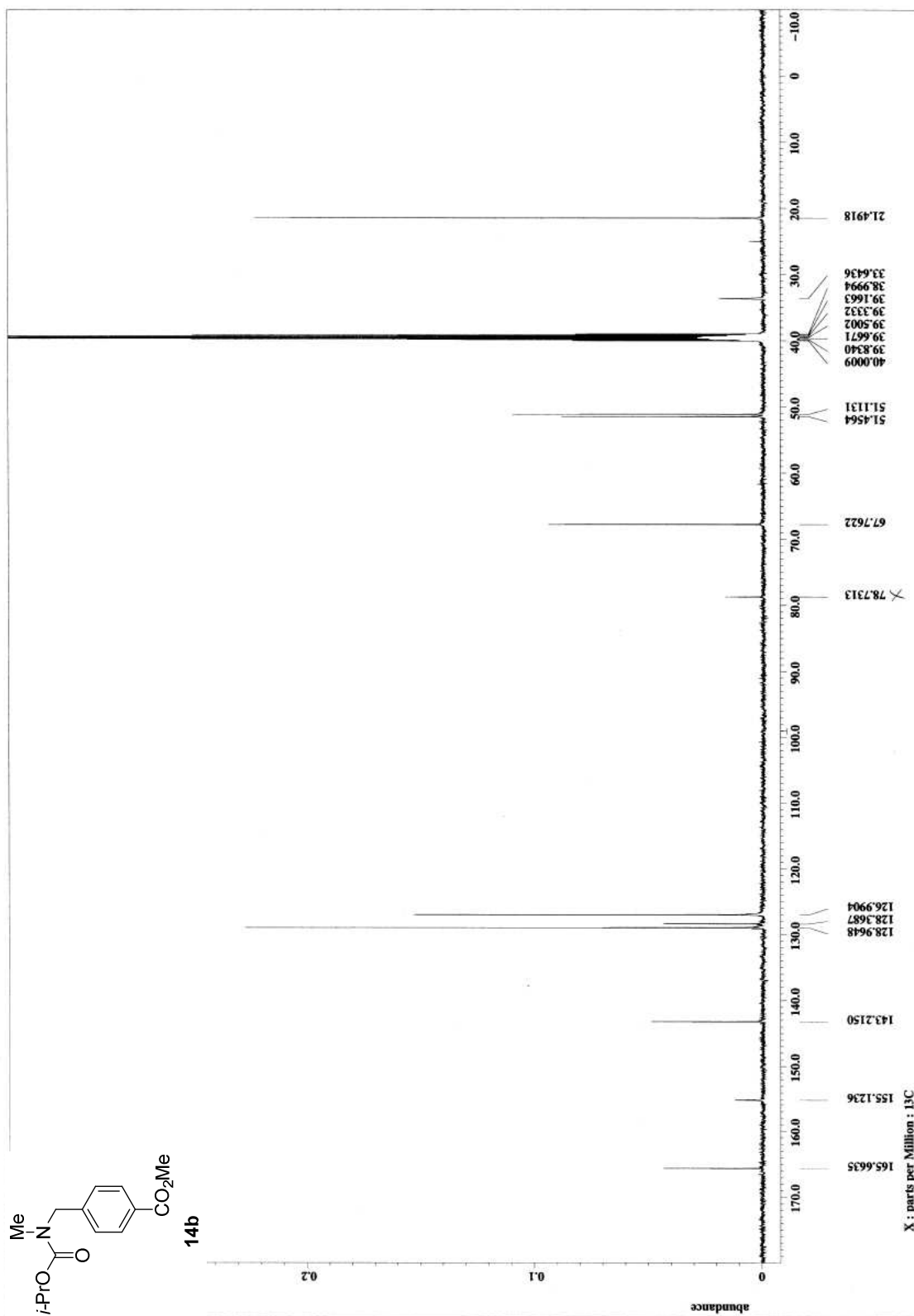
^{13}C NMR spectrum of **13b**



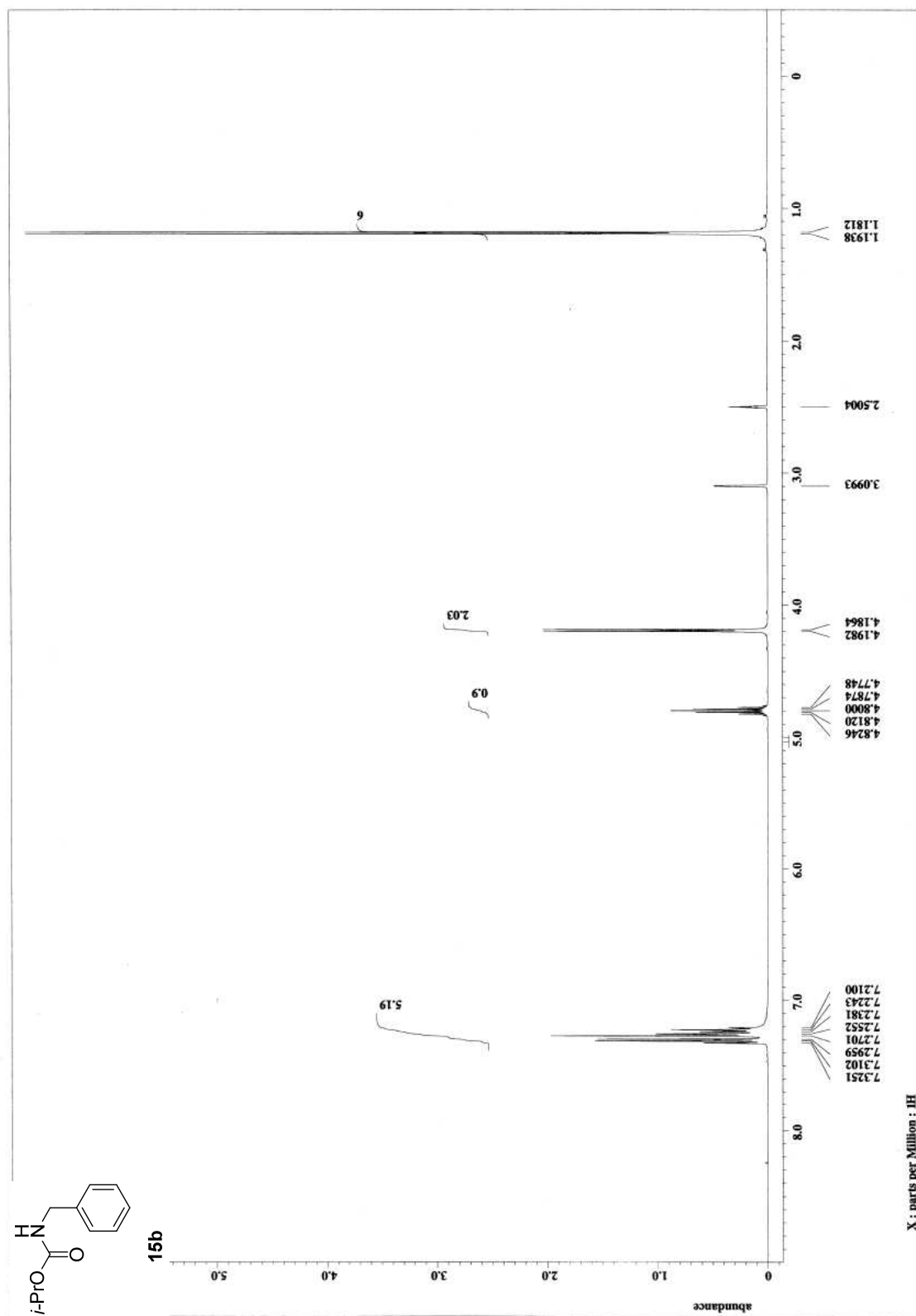
¹H NMR spectrum of 14b



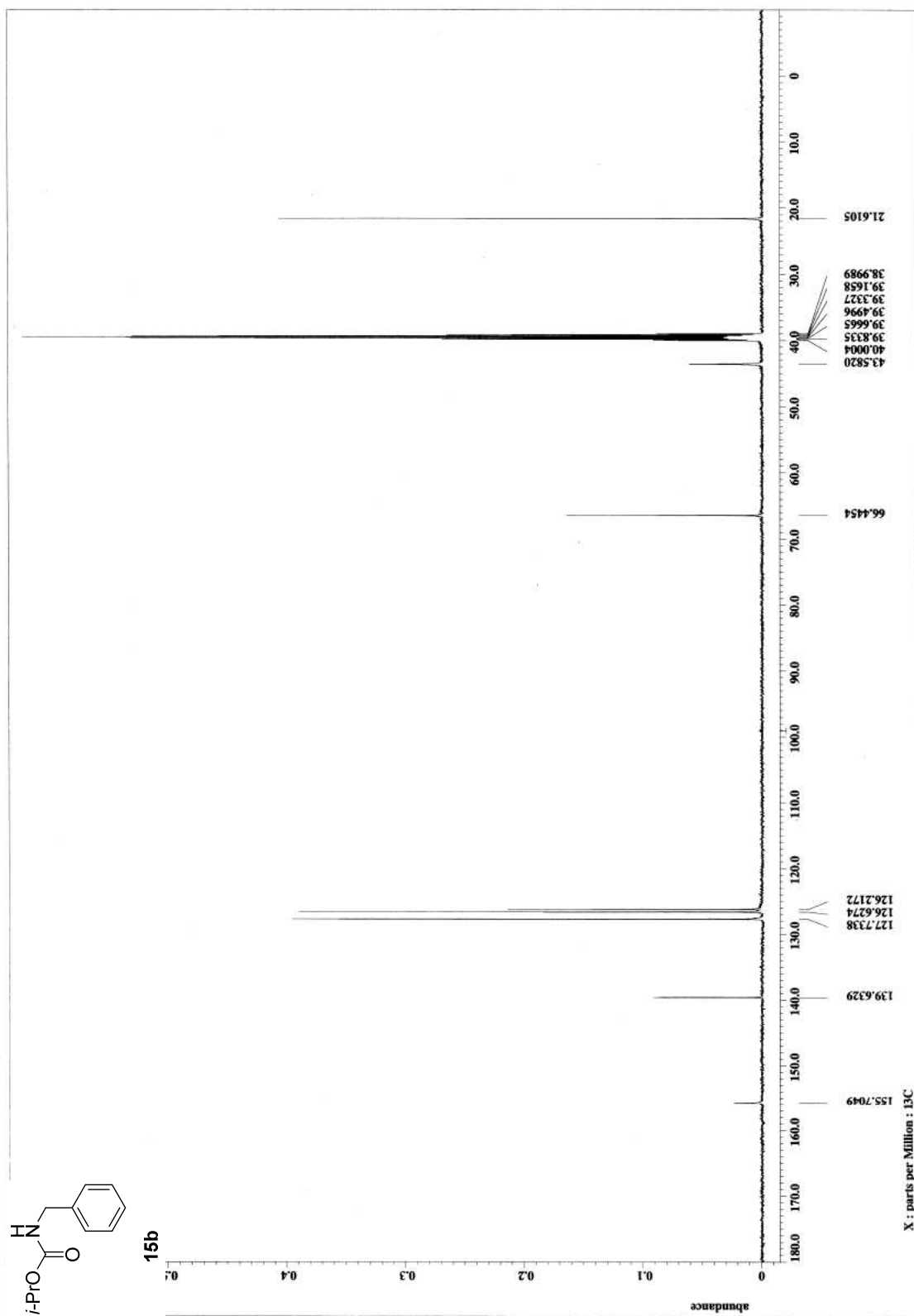
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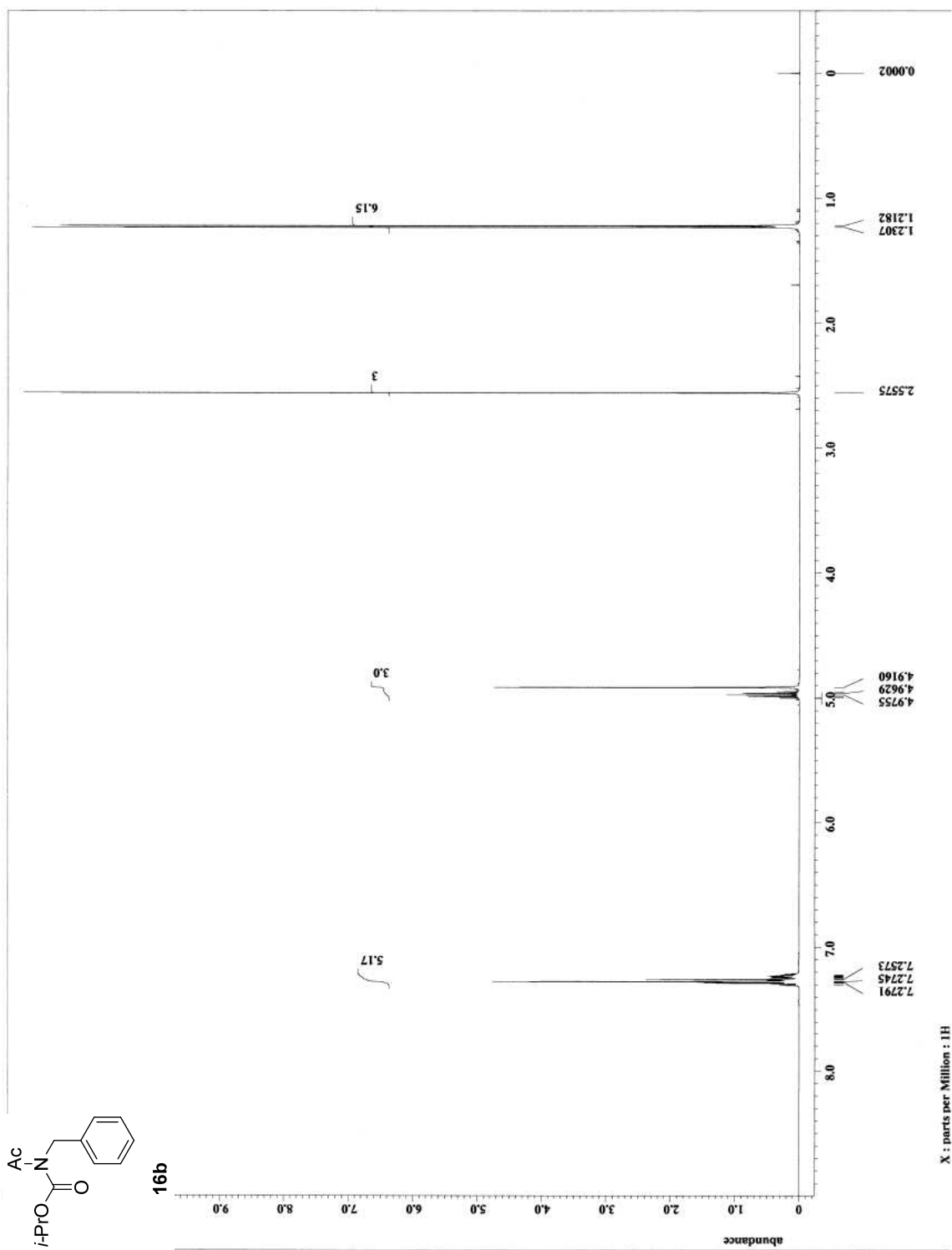
¹H NMR spectrum of **15b**



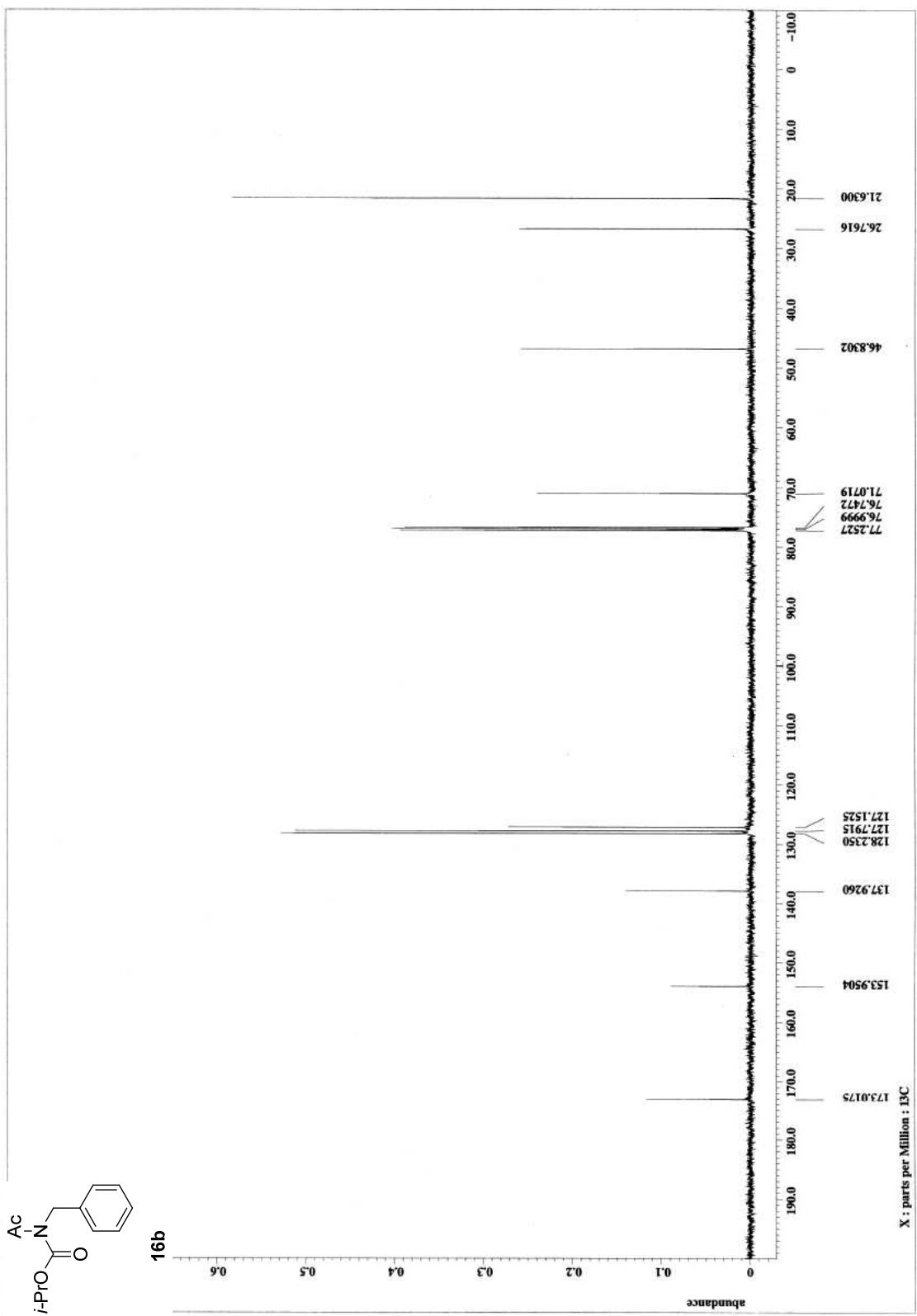
¹³C NMR spectrum of **15b**



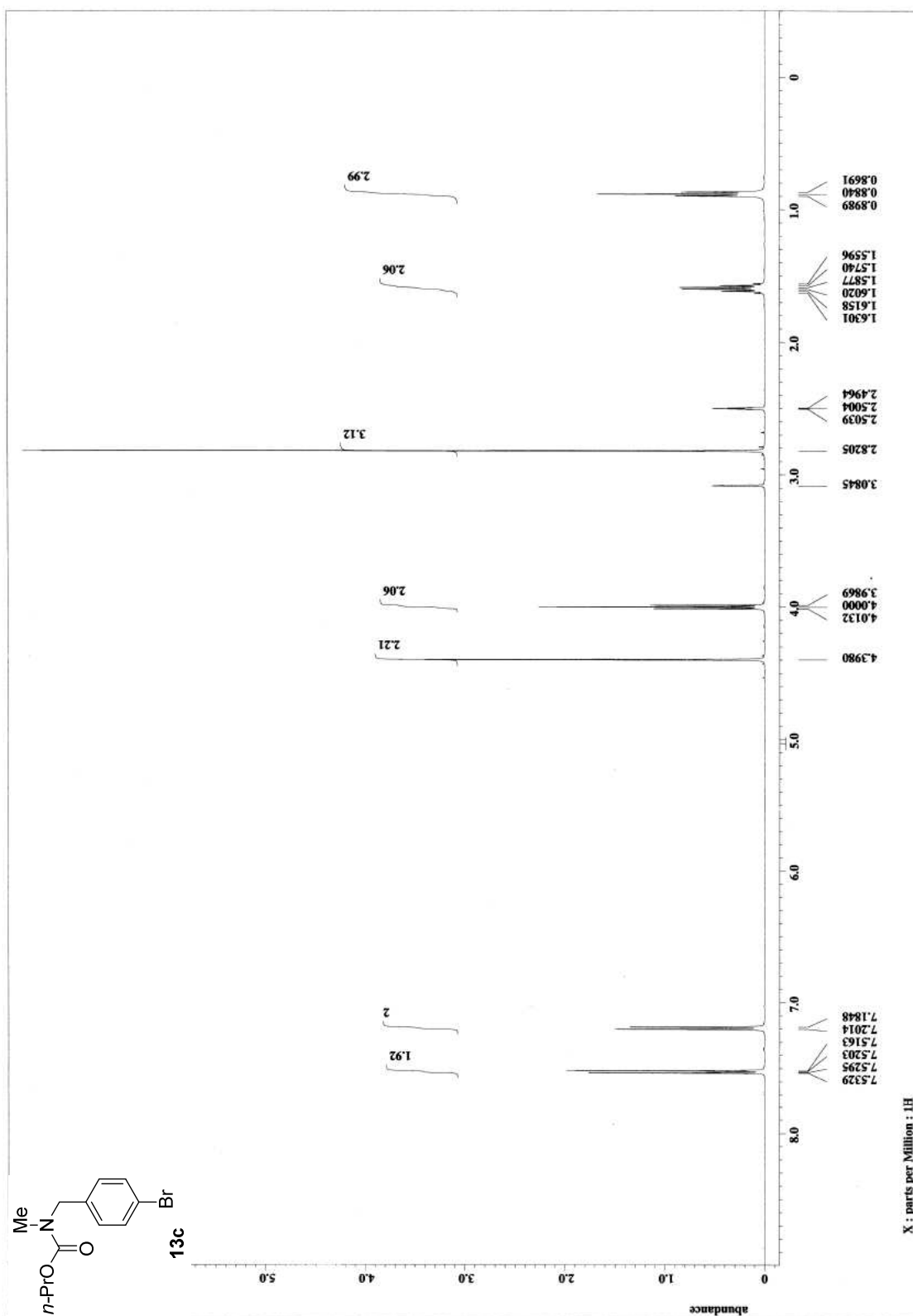
¹H NMR spectrum of S16b



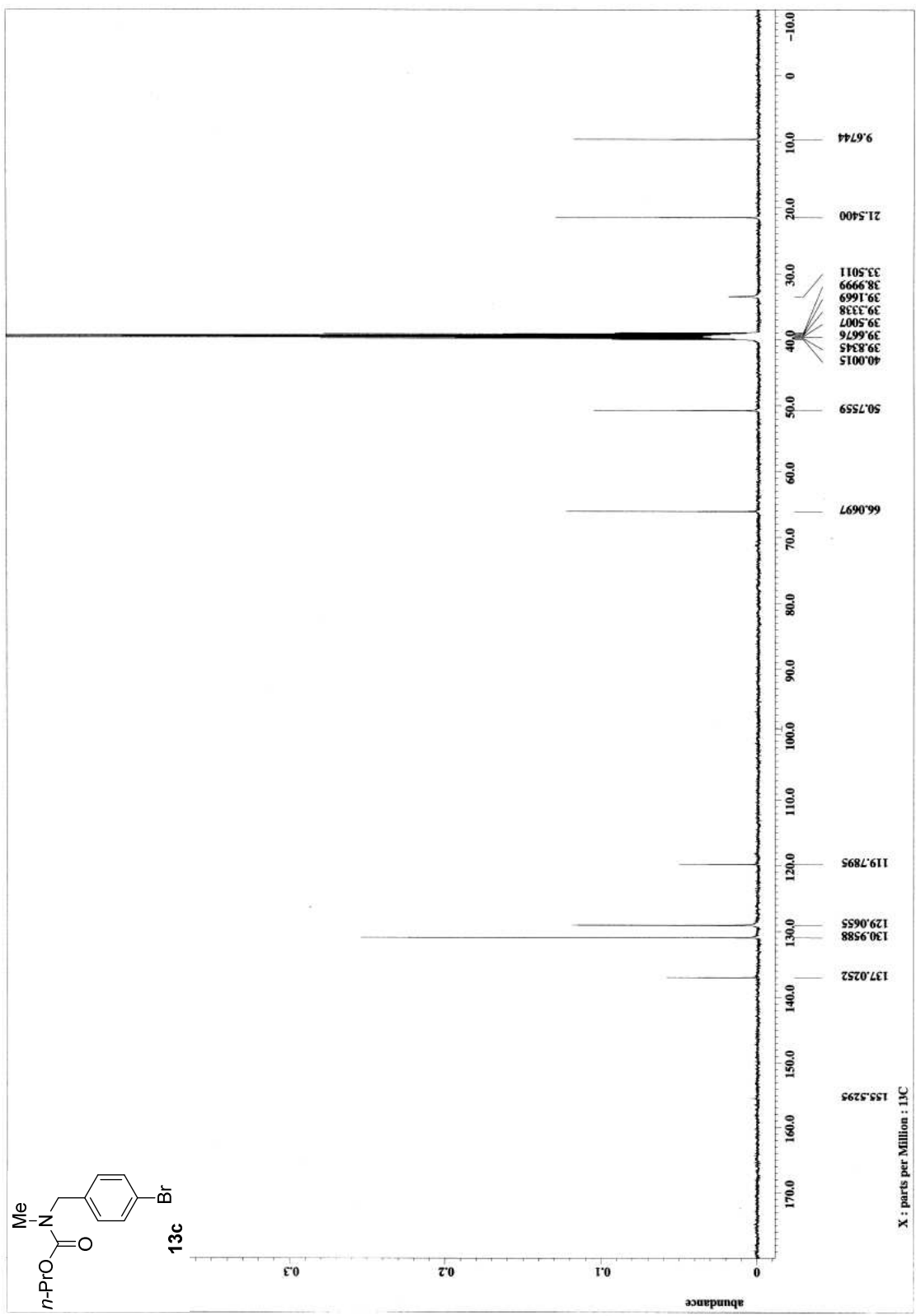
¹³C NMR spectrum of **16b**



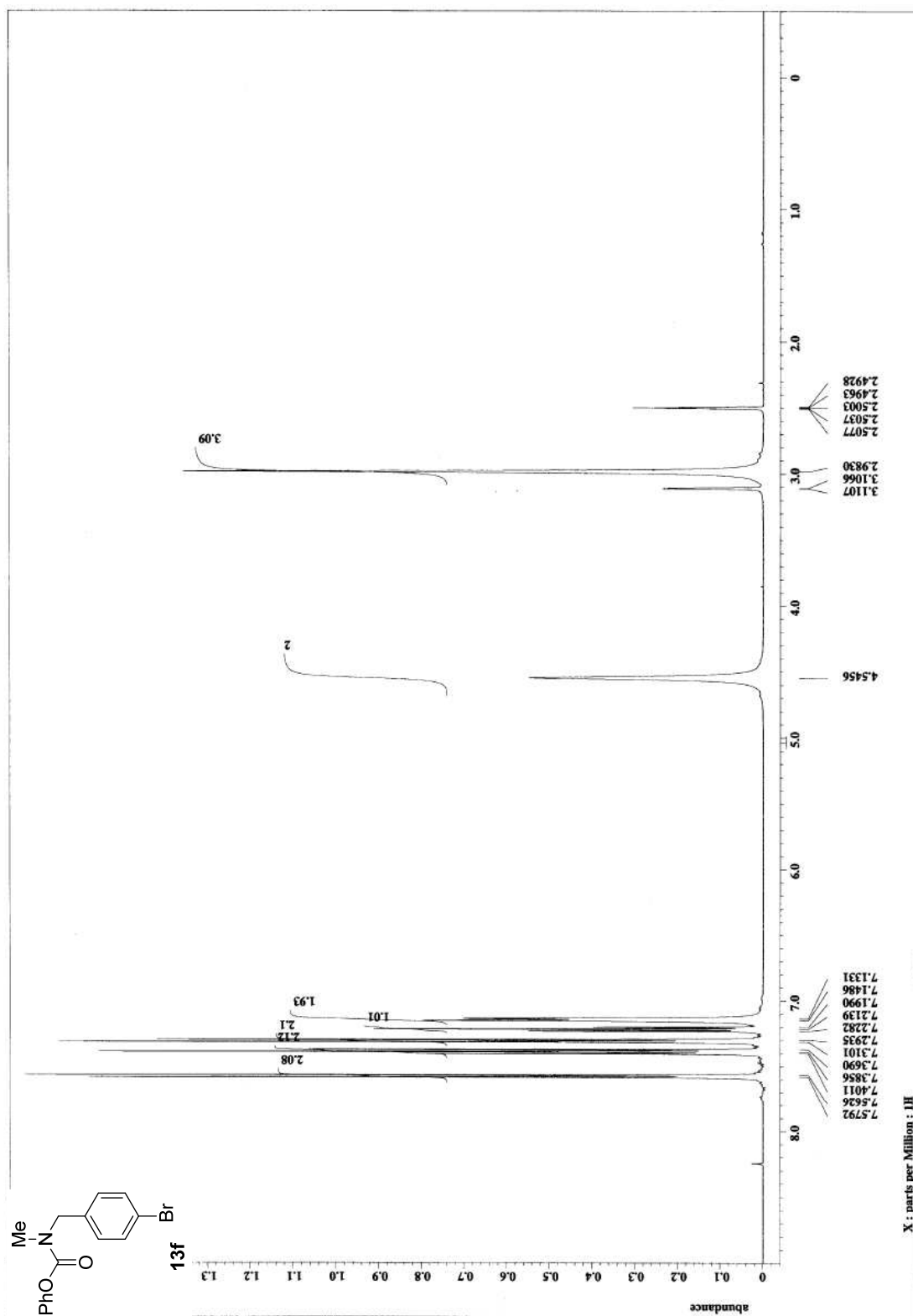
¹H NMR spectrum of 13c



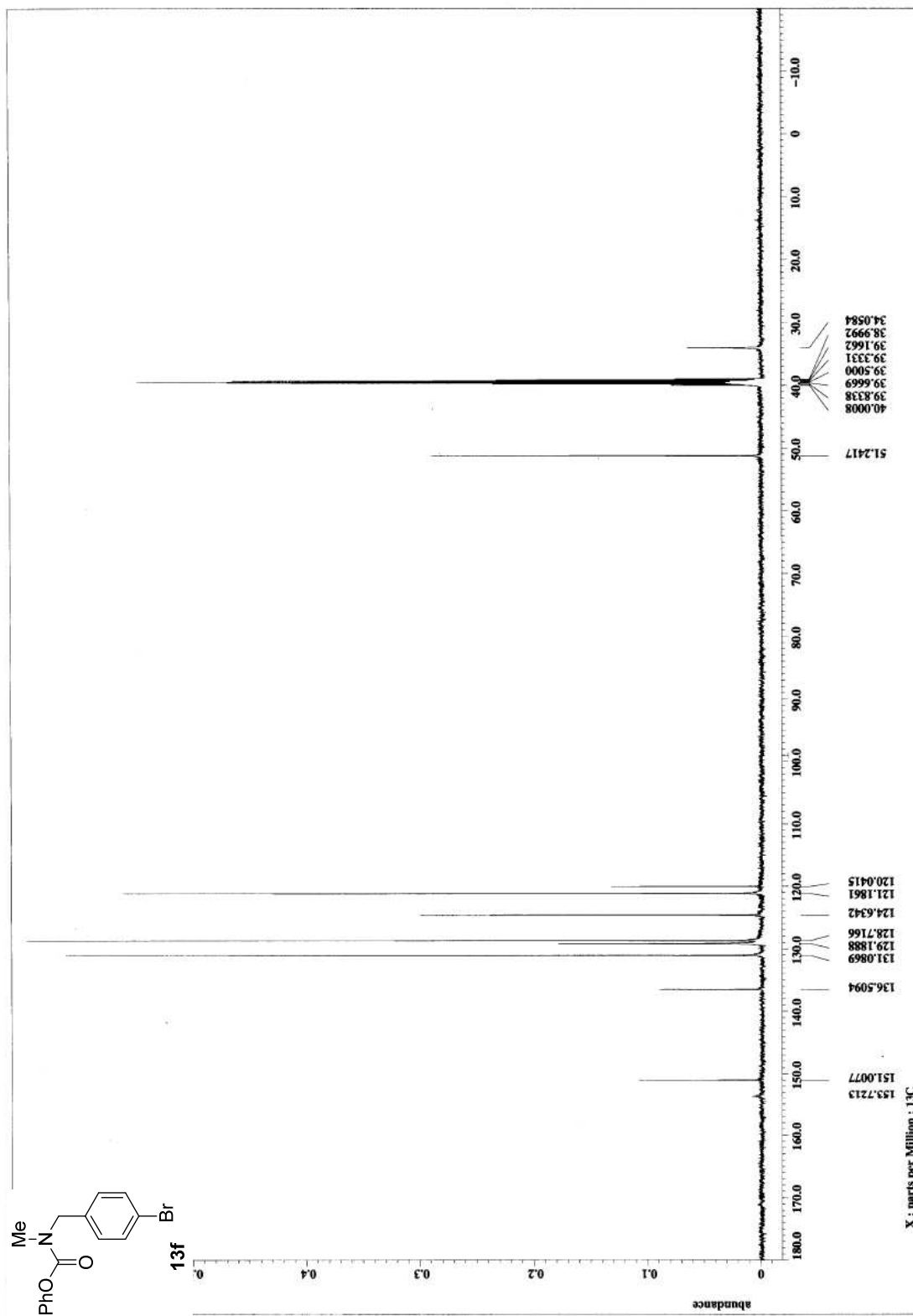
¹³C NMR spectrum of **13c**



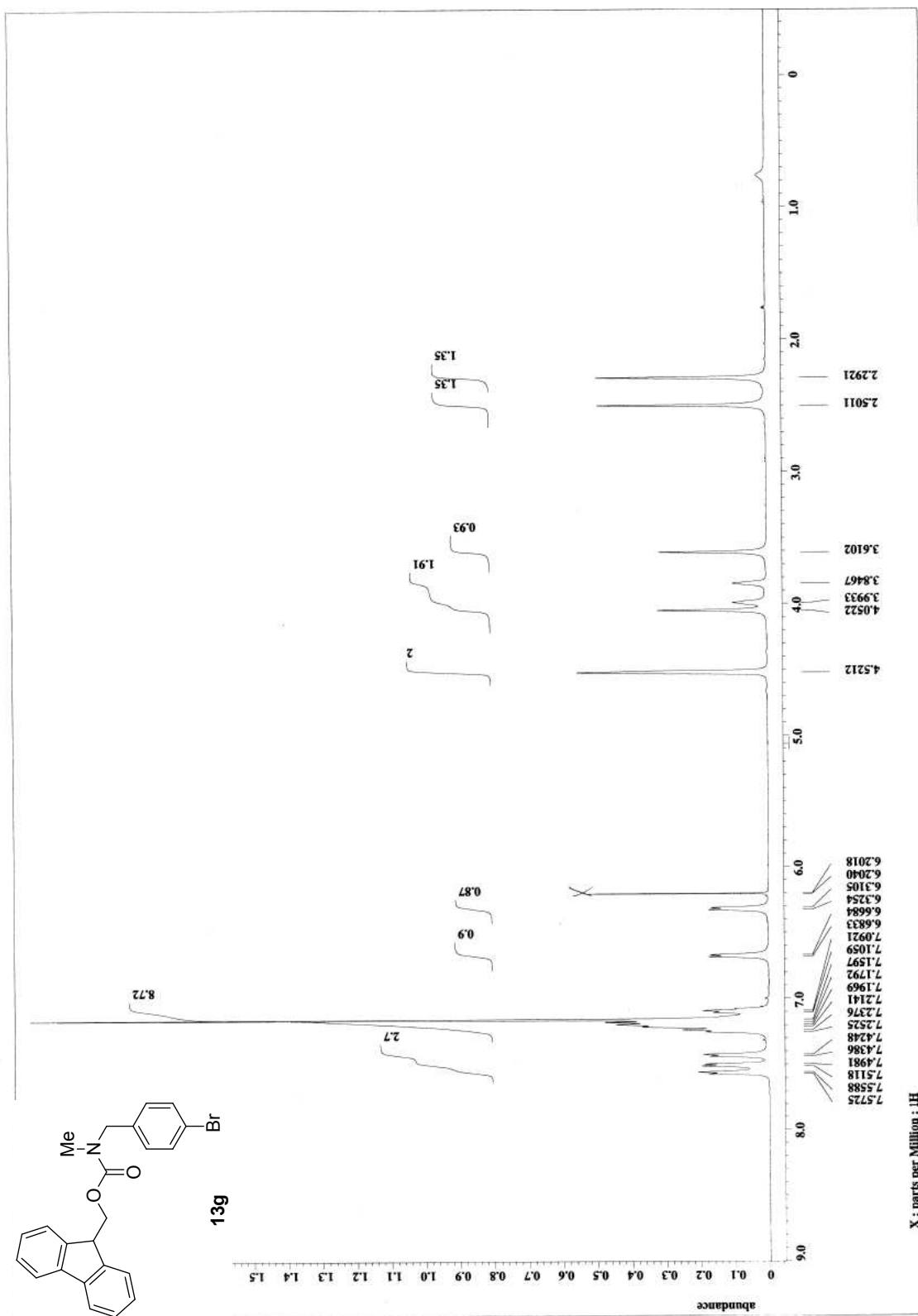
¹H NMR spectrum of 13f



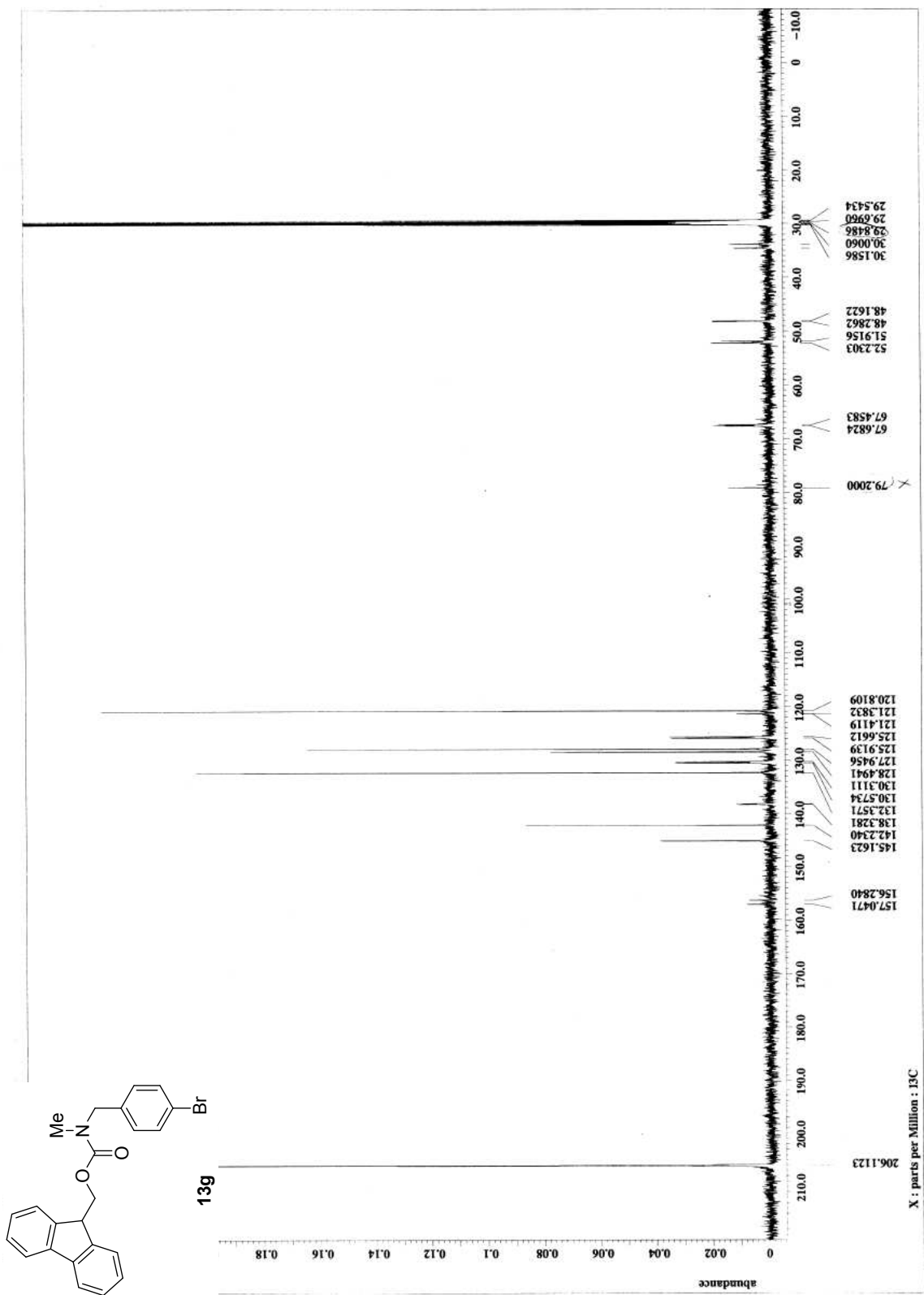
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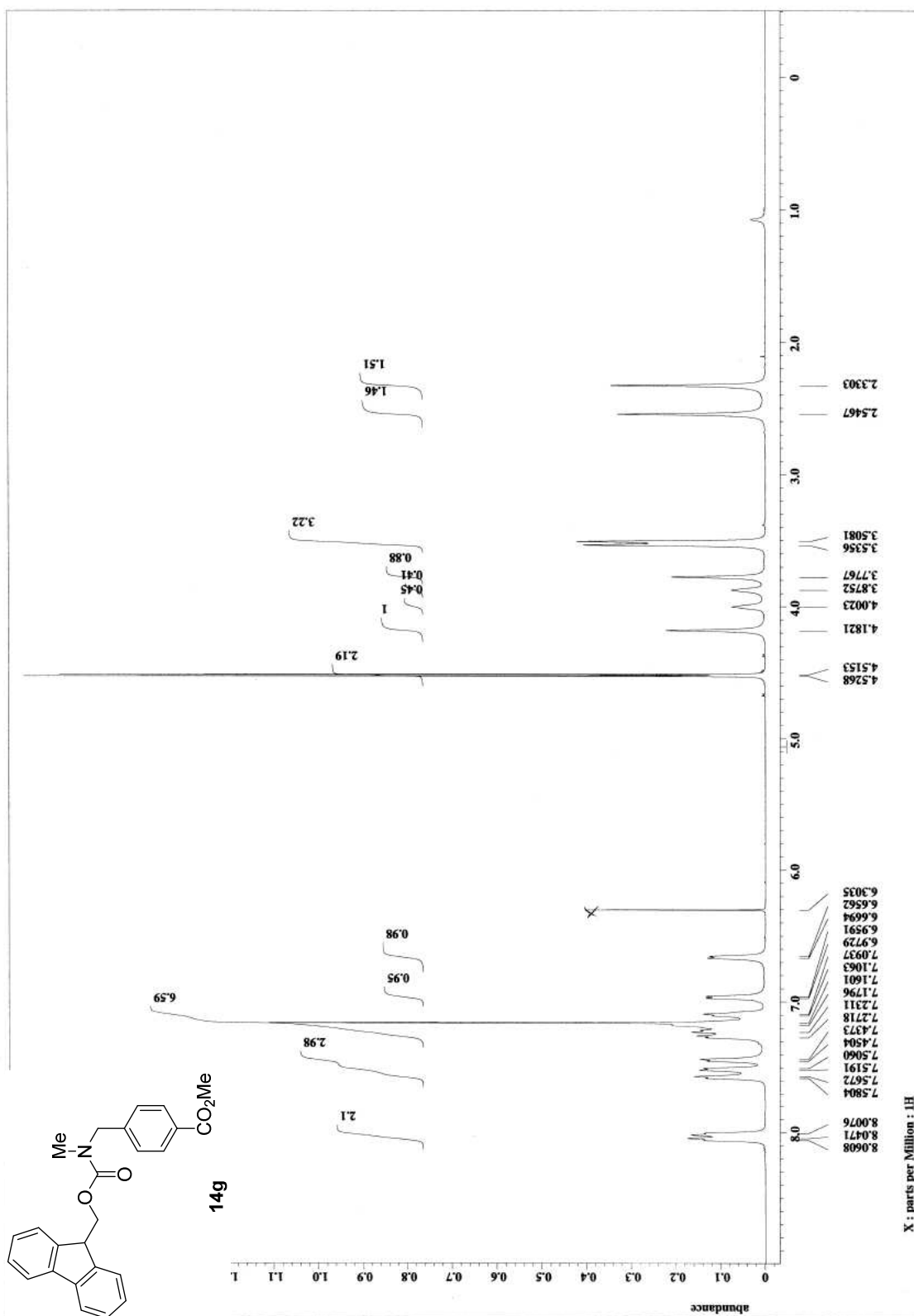
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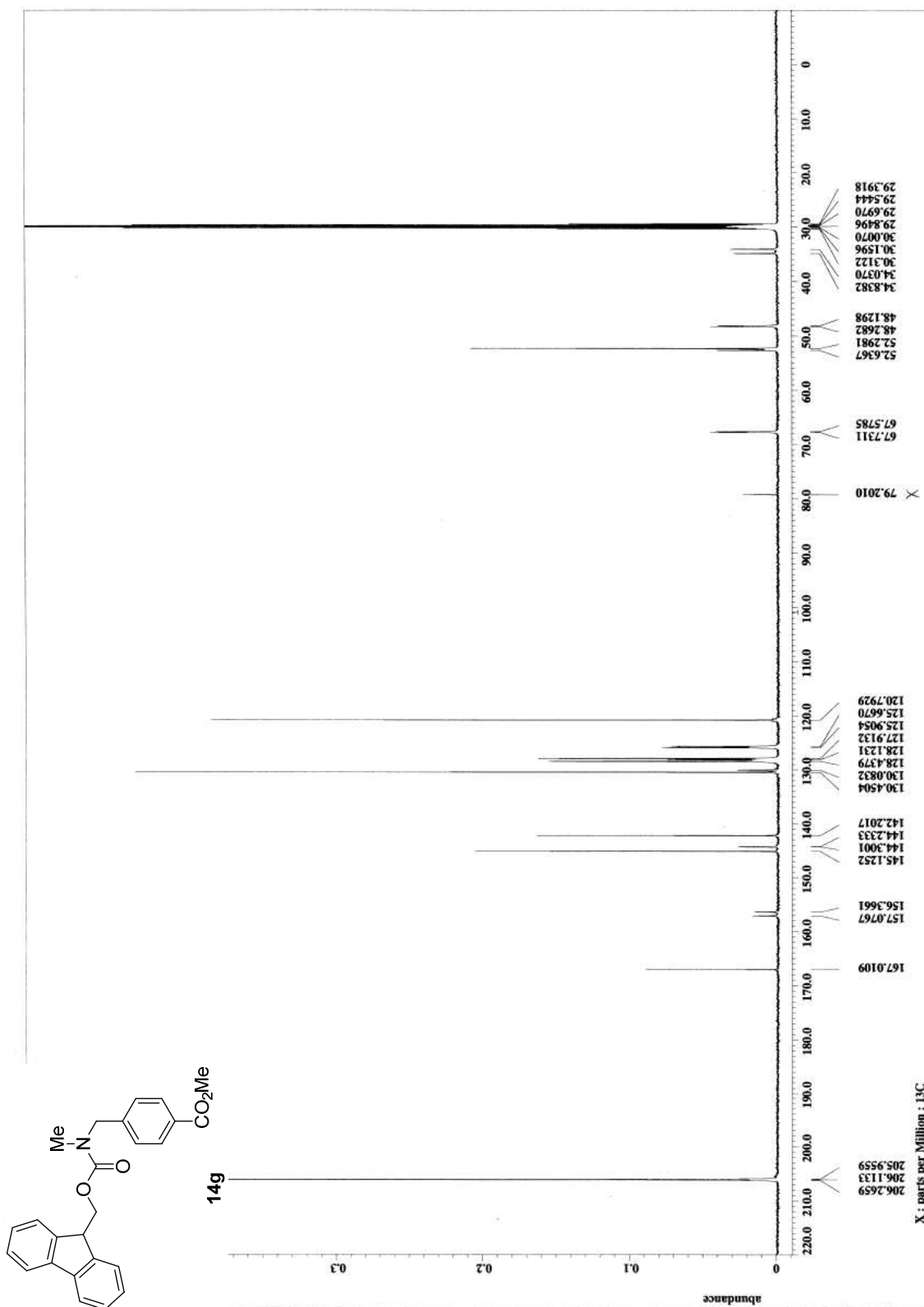
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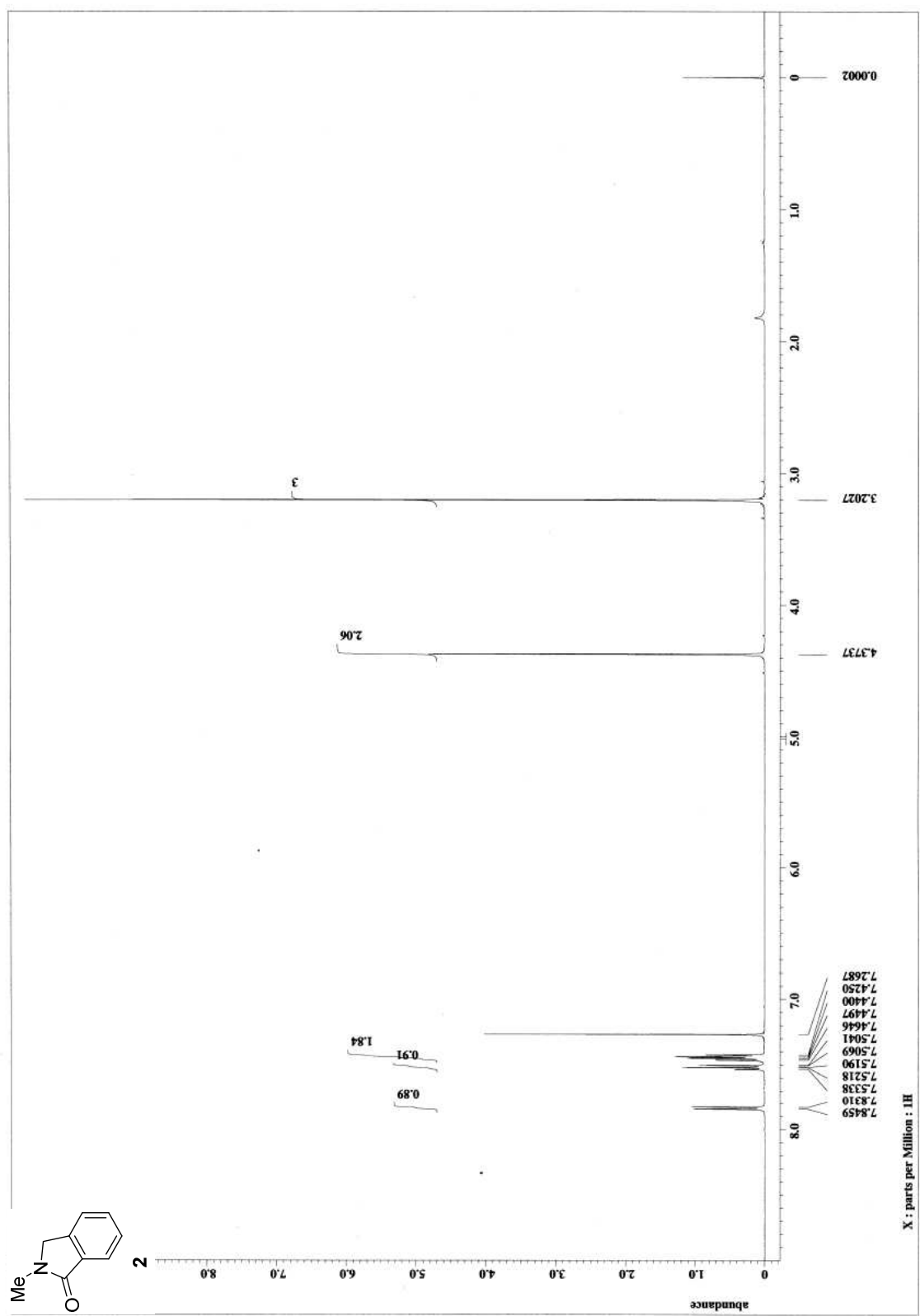
¹H NMR spectrum of 14g



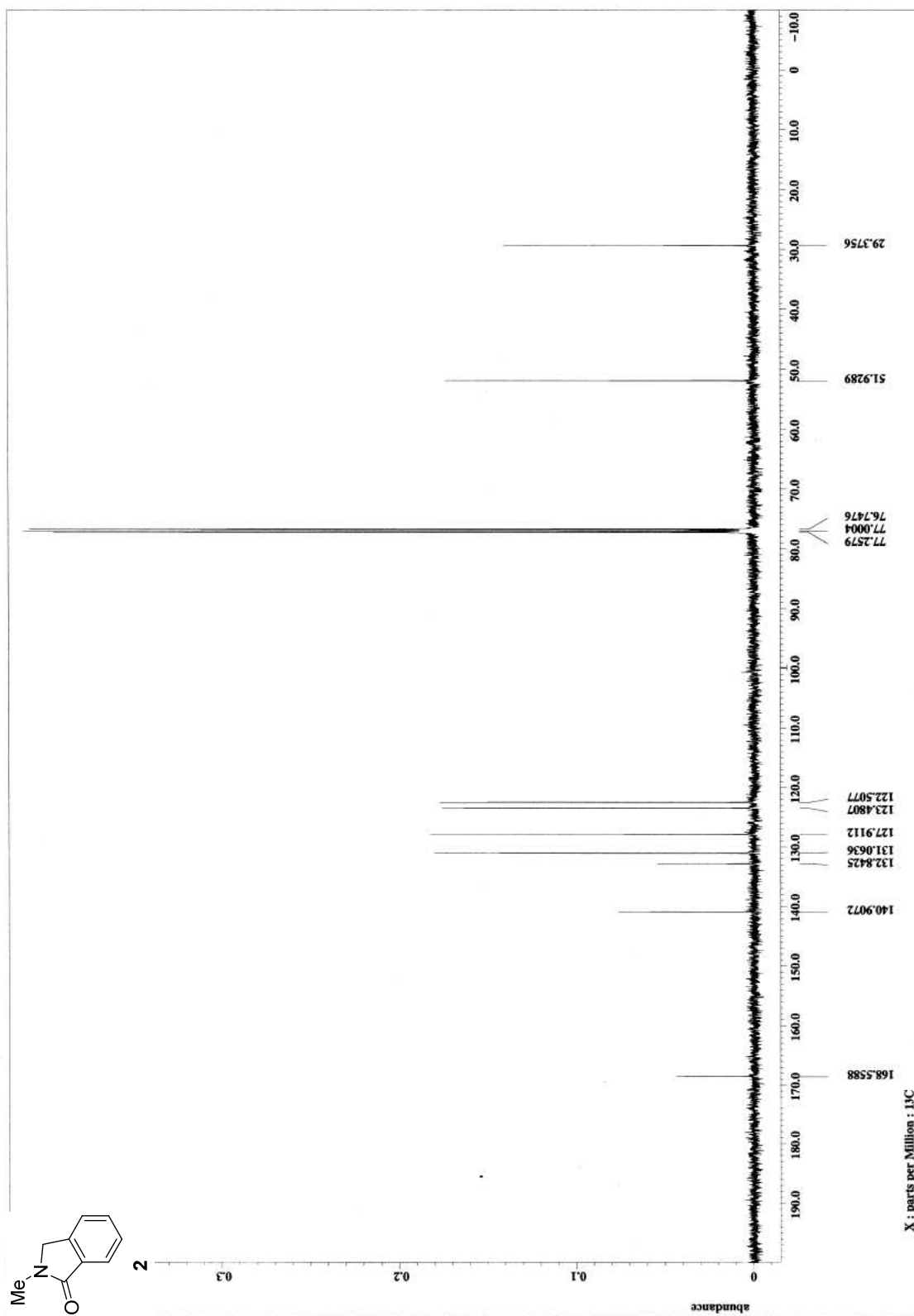
¹³C NMR spectrum of **14g**



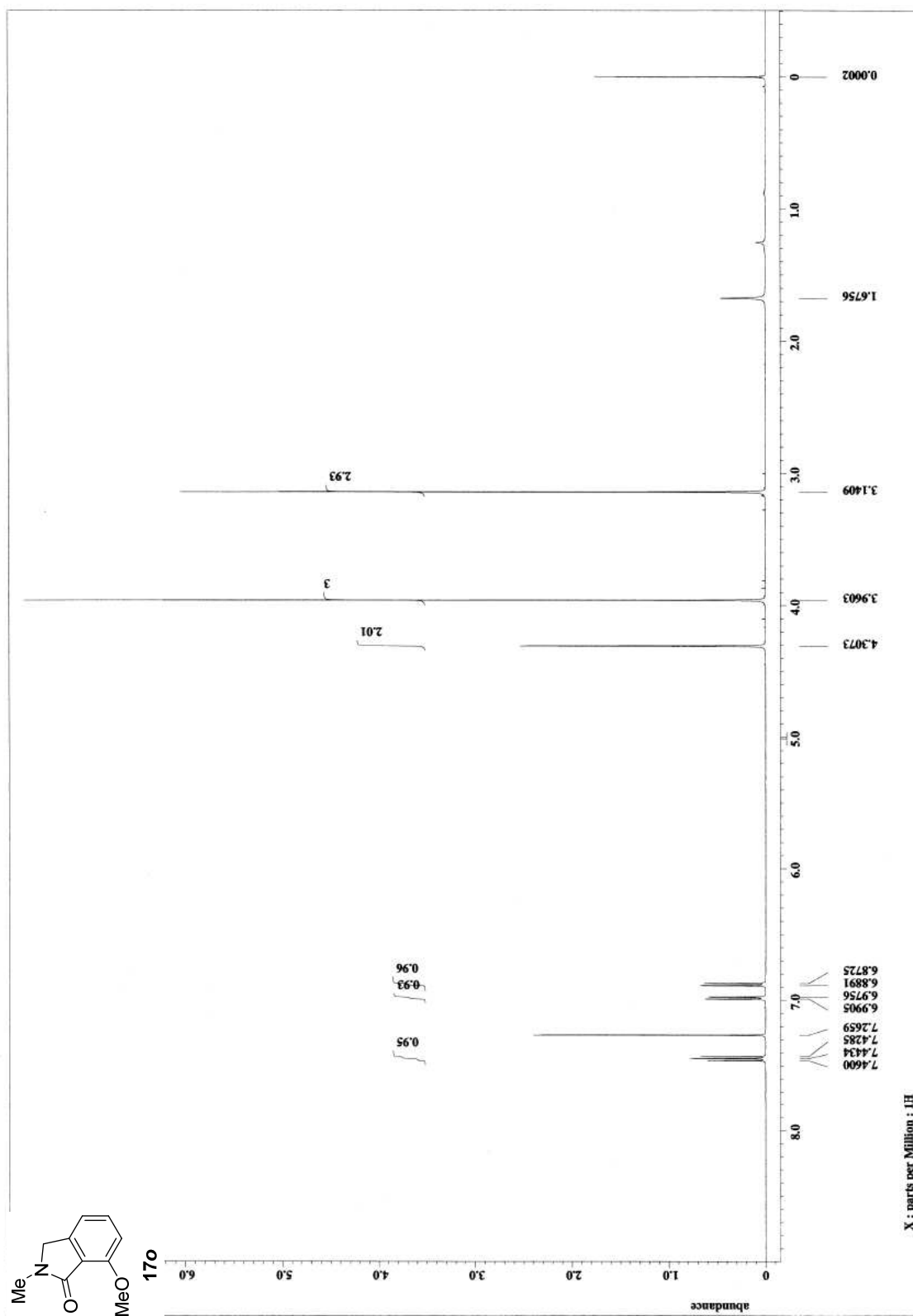
^1H NMR spectrum of **2**



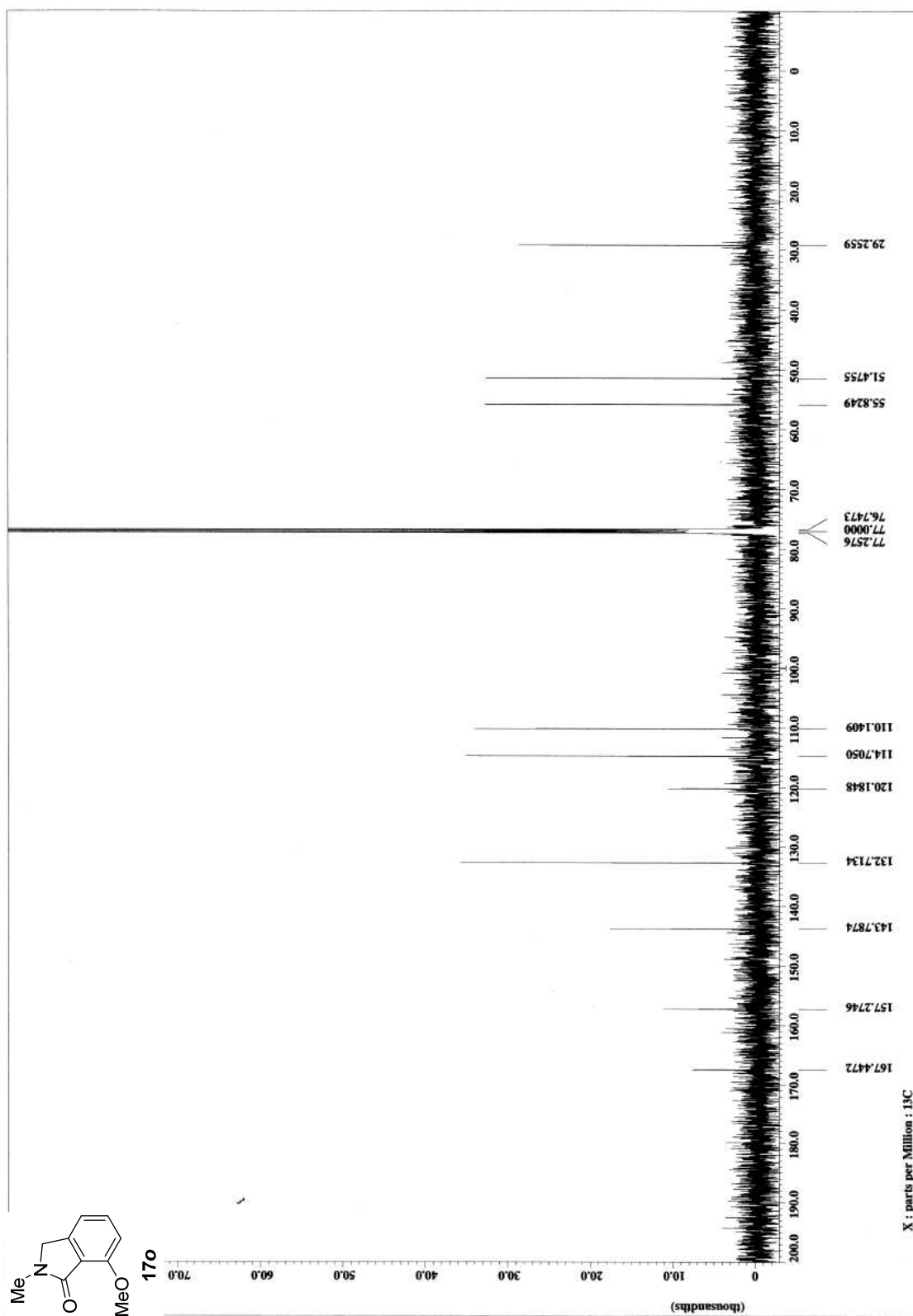
¹³C NMR spectrum of 2



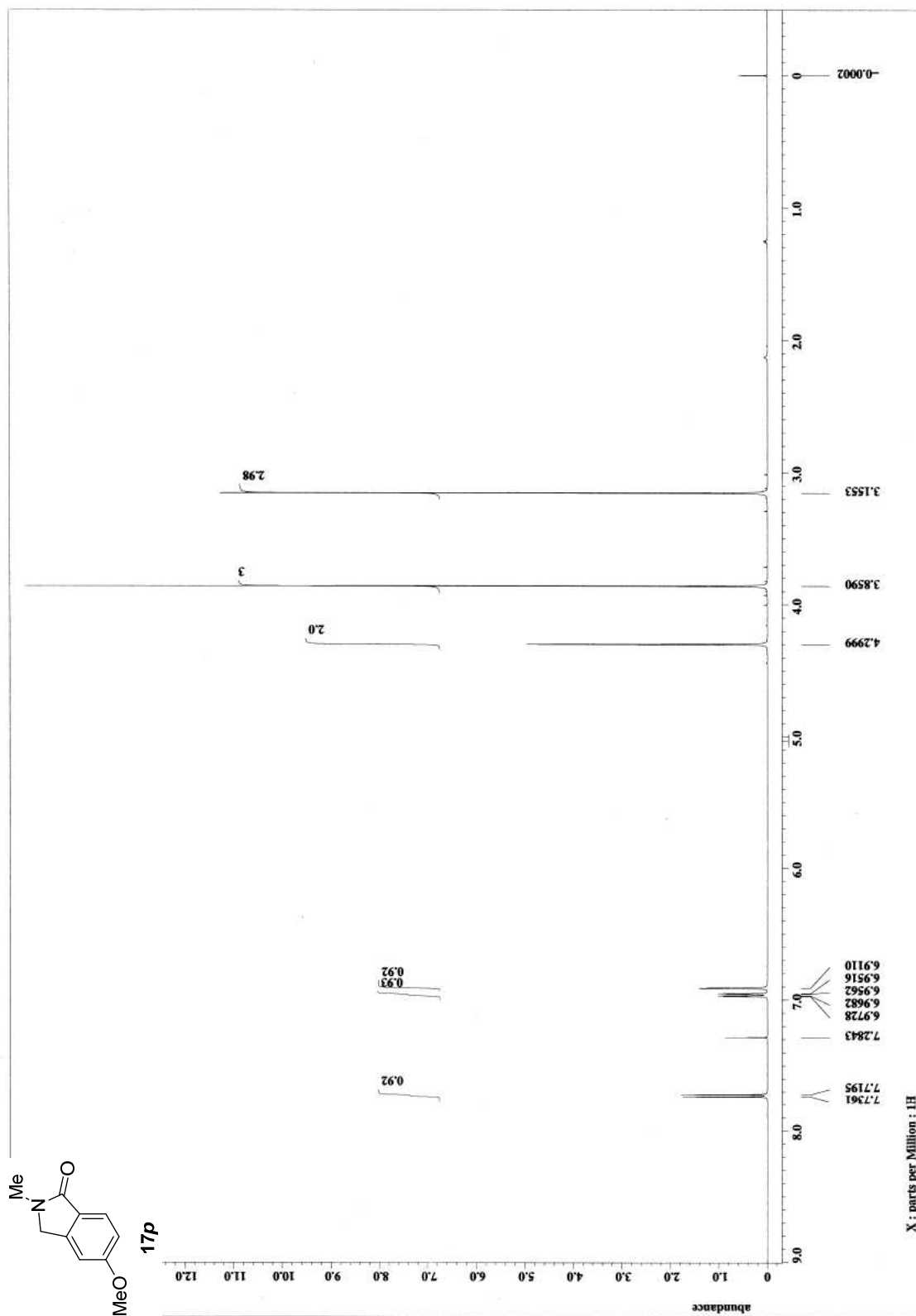
¹H NMR spectrum of **17o**



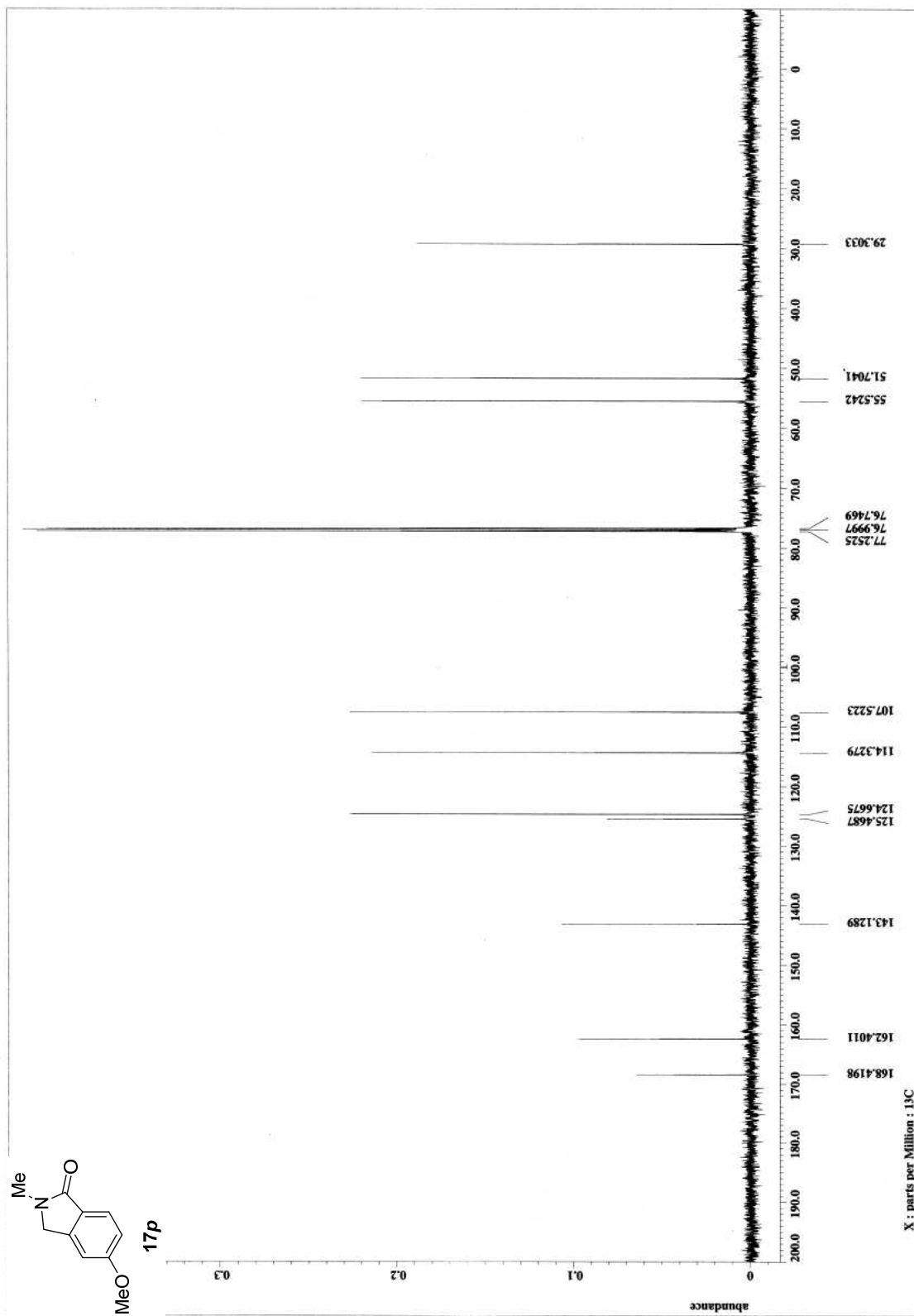
¹³C NMR spectrum of **17o**



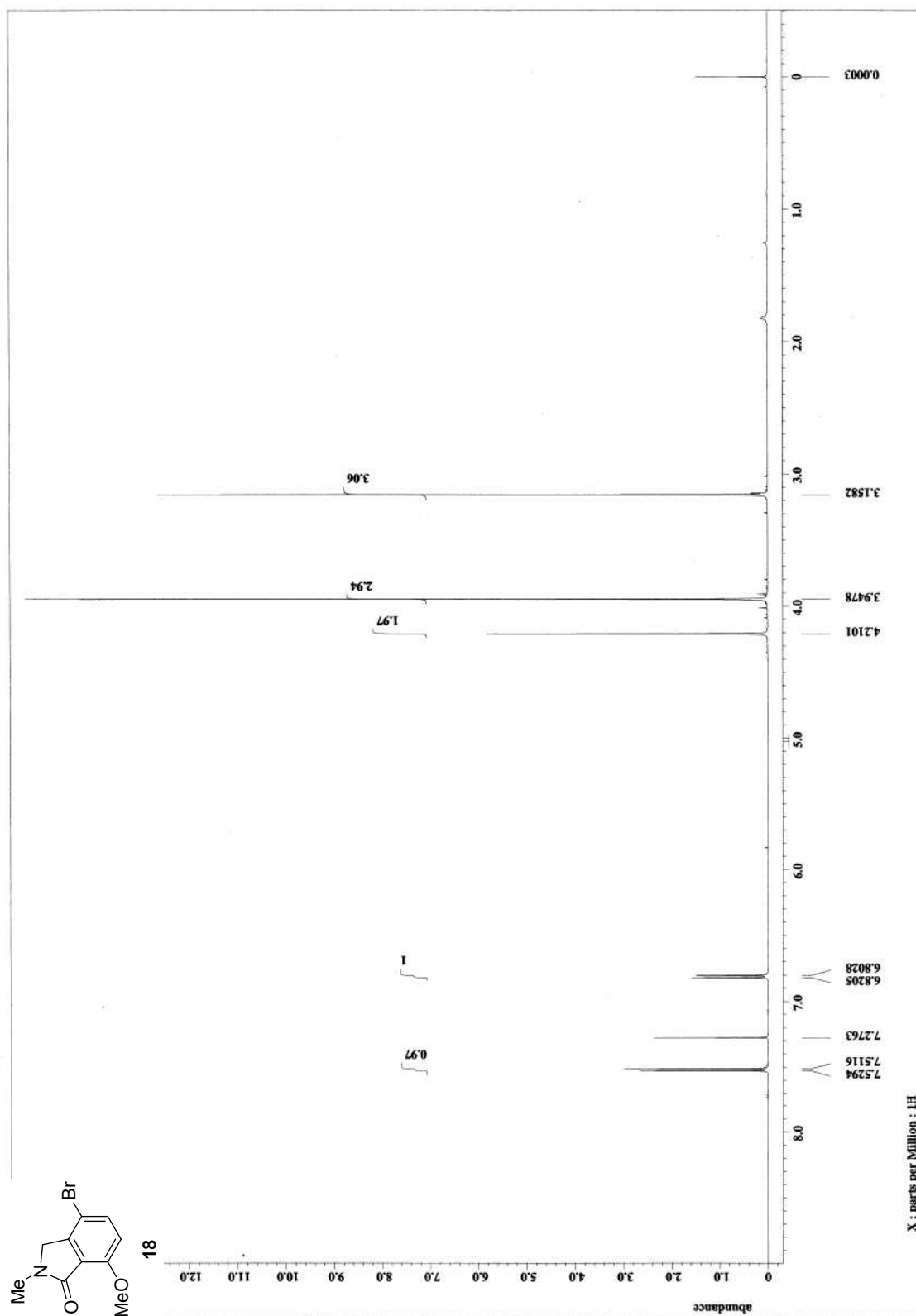
¹H NMR spectrum of 17p



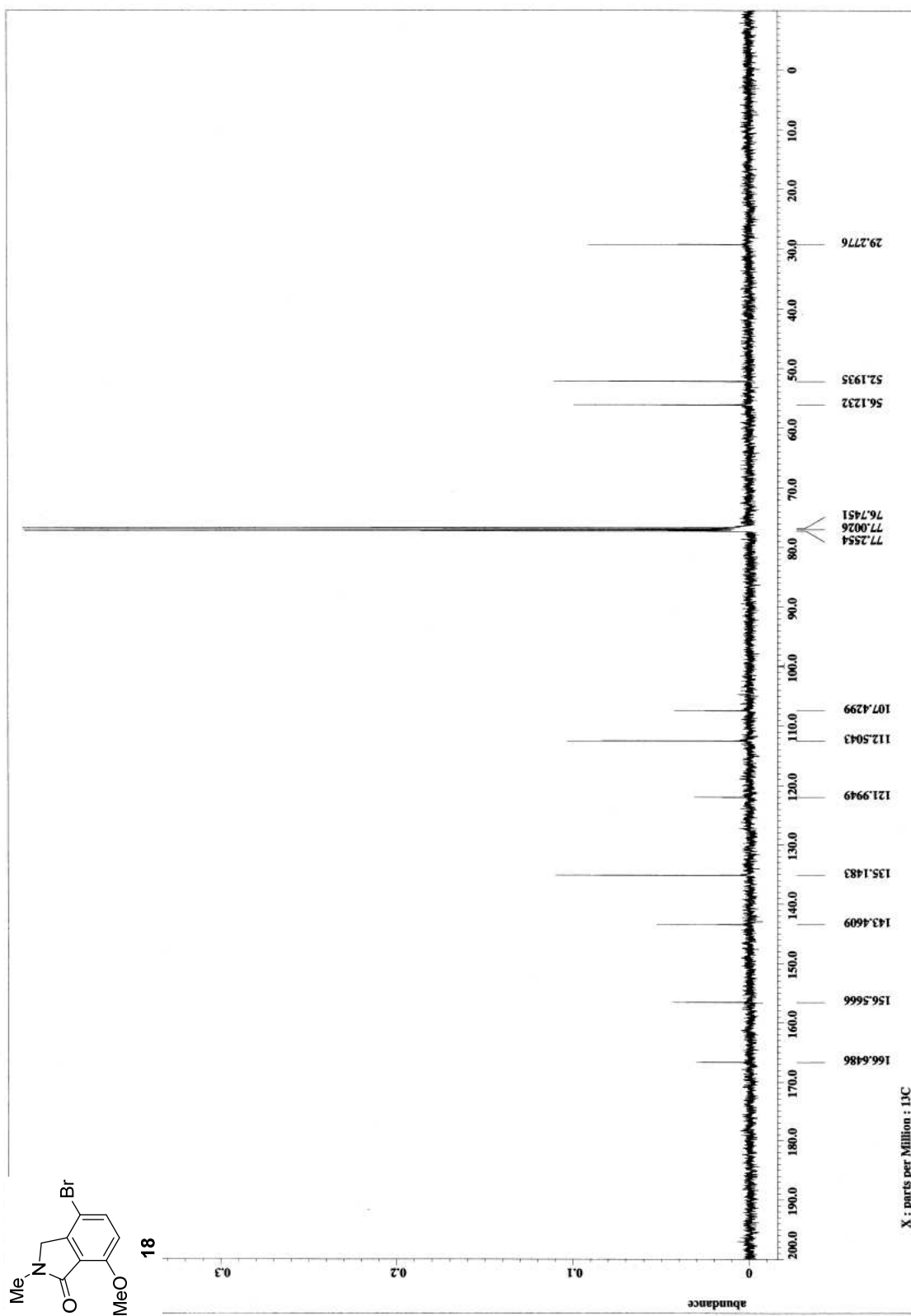
¹³C NMR spectrum of **17p**



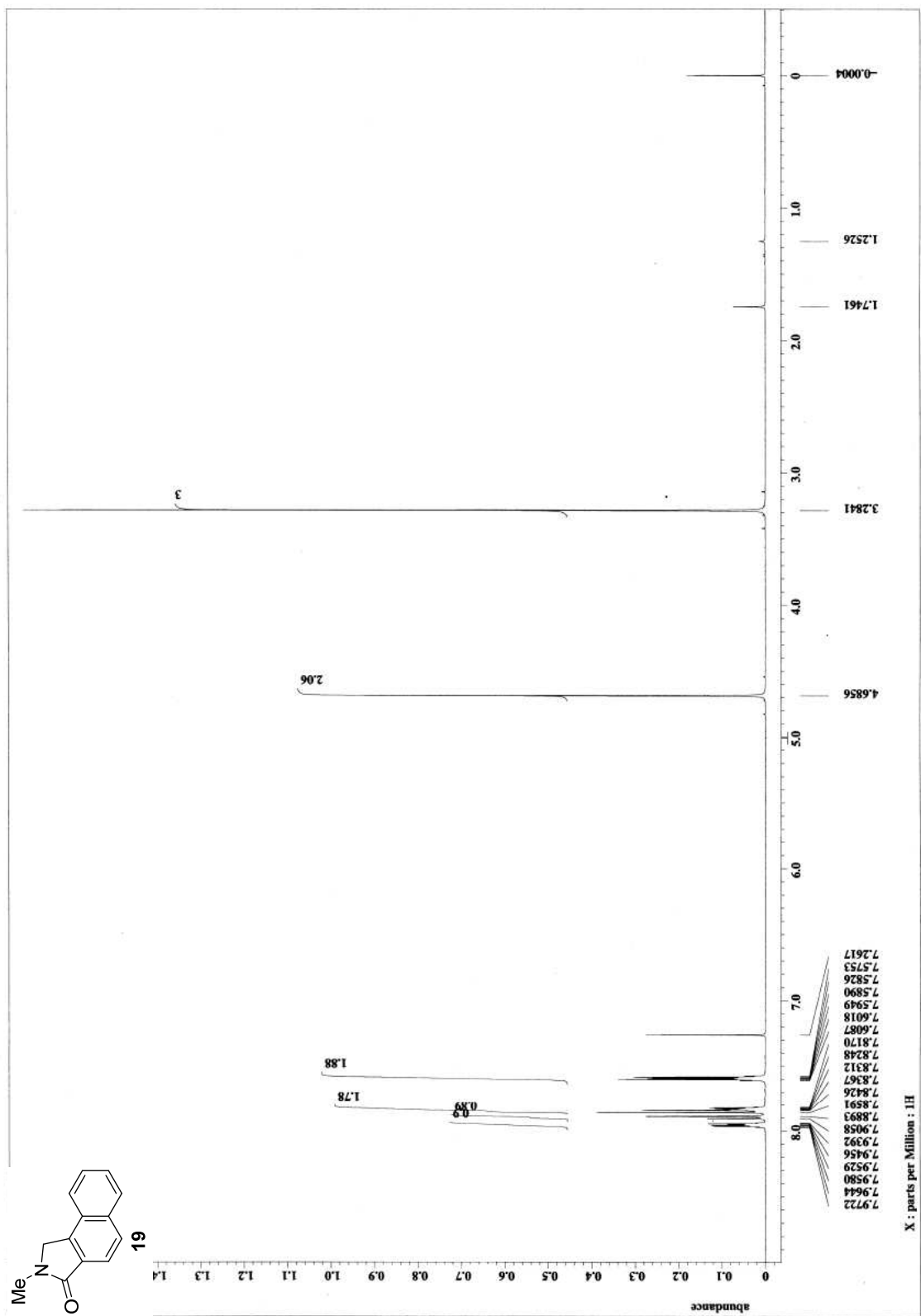
¹H NMR spectrum of 18



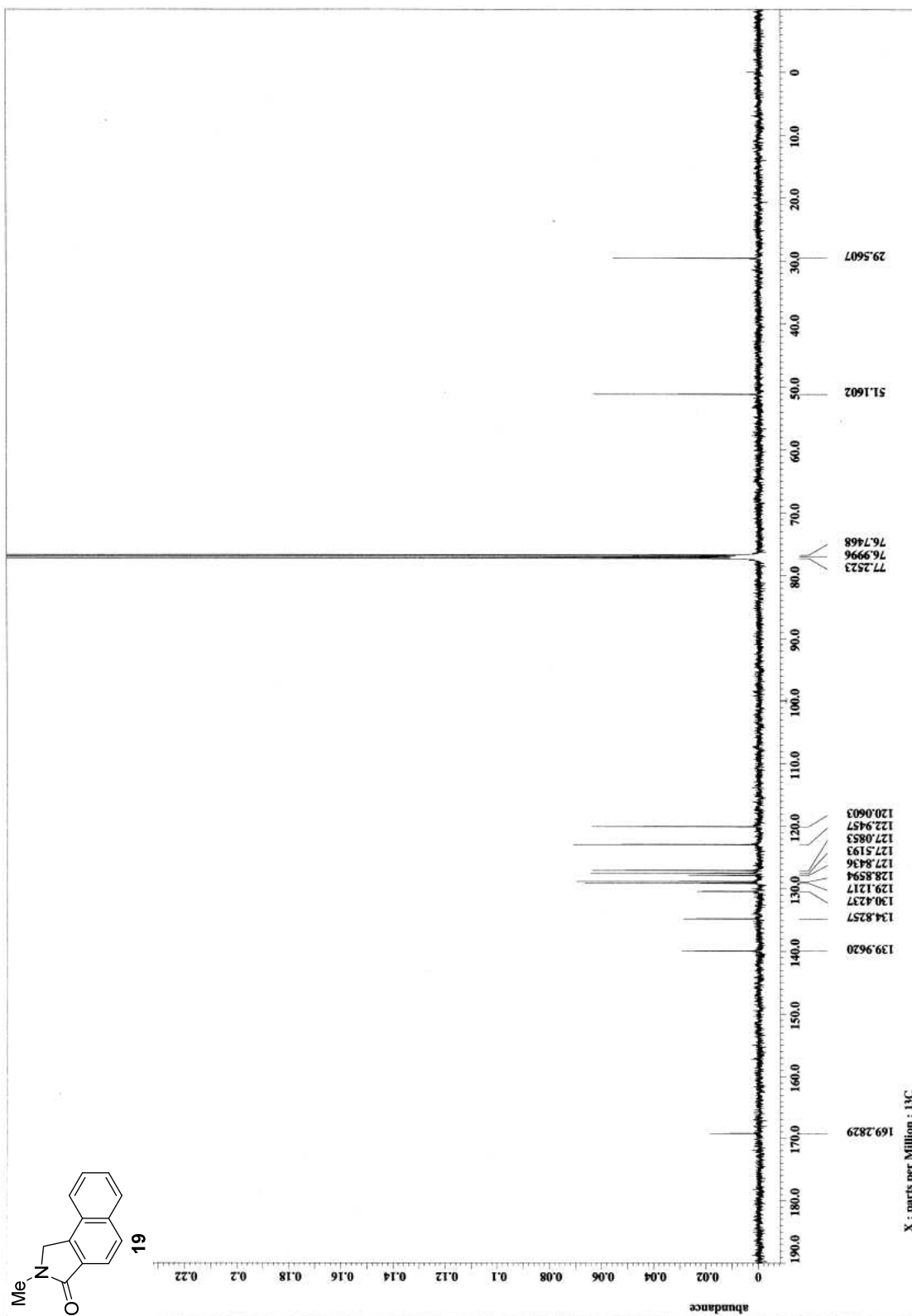
¹³C NMR spectrum of **18**



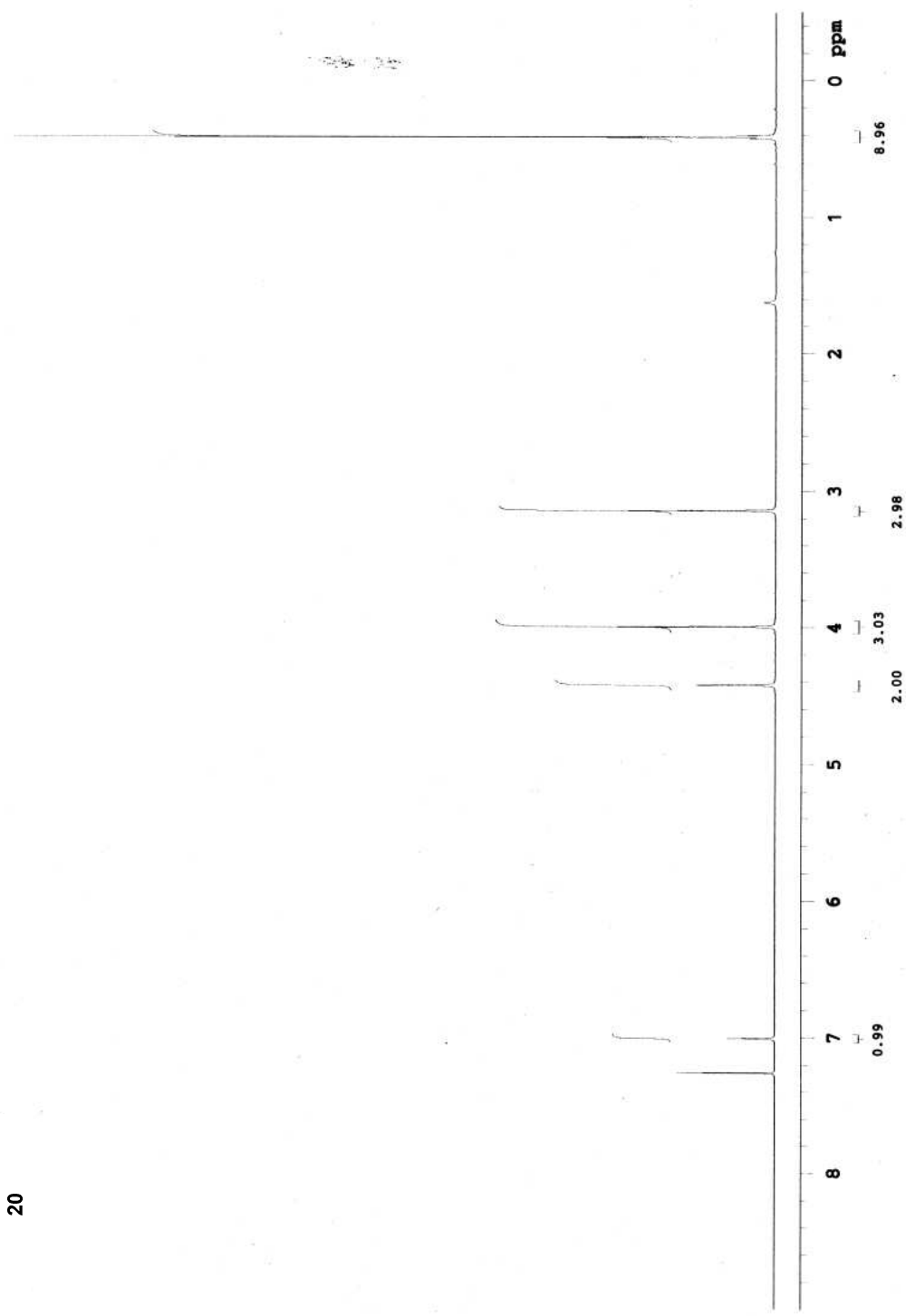
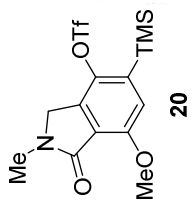
¹H NMR spectrum of 19



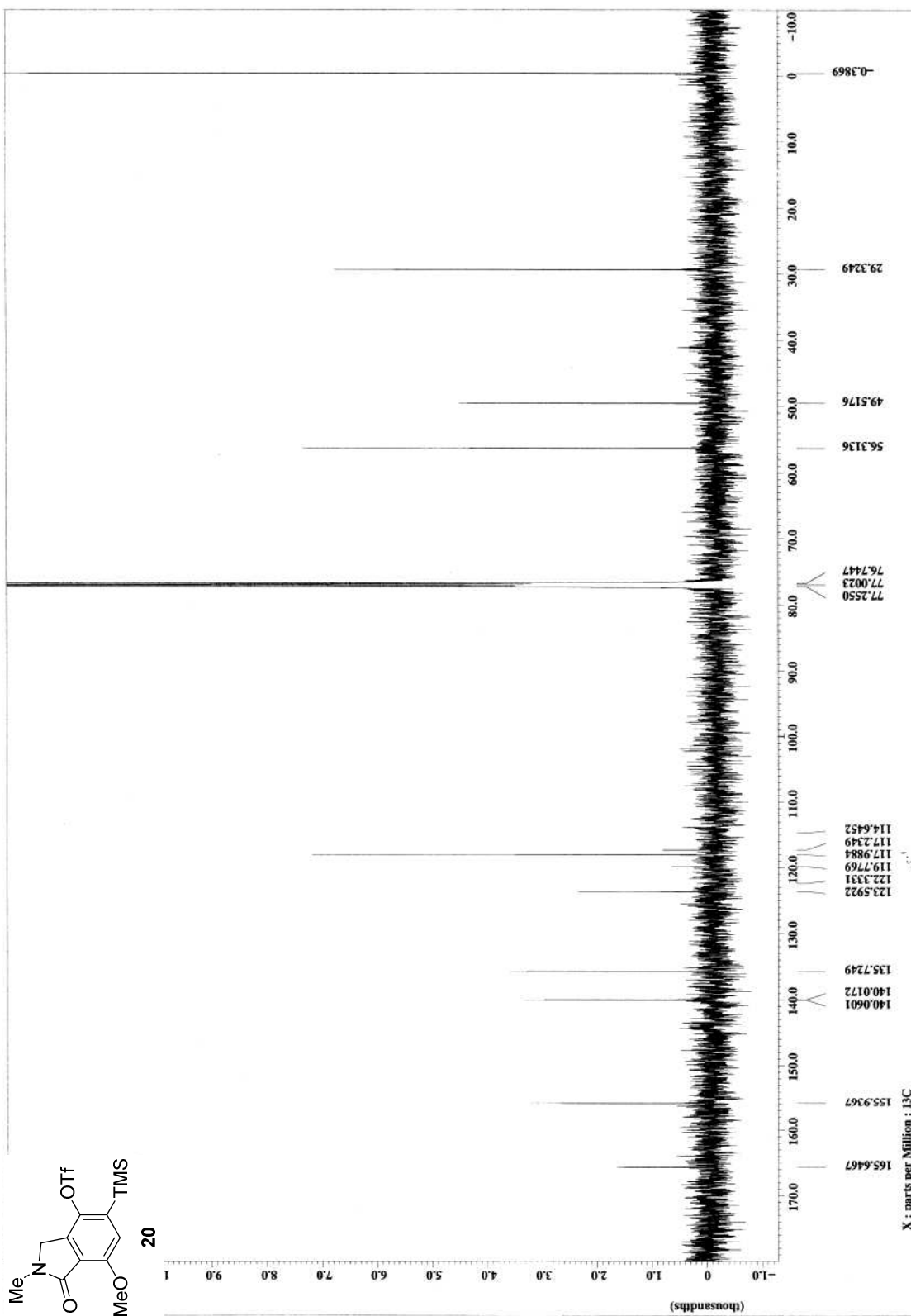
¹³C NMR spectrum of 19



¹H NMR spectrum of **20**

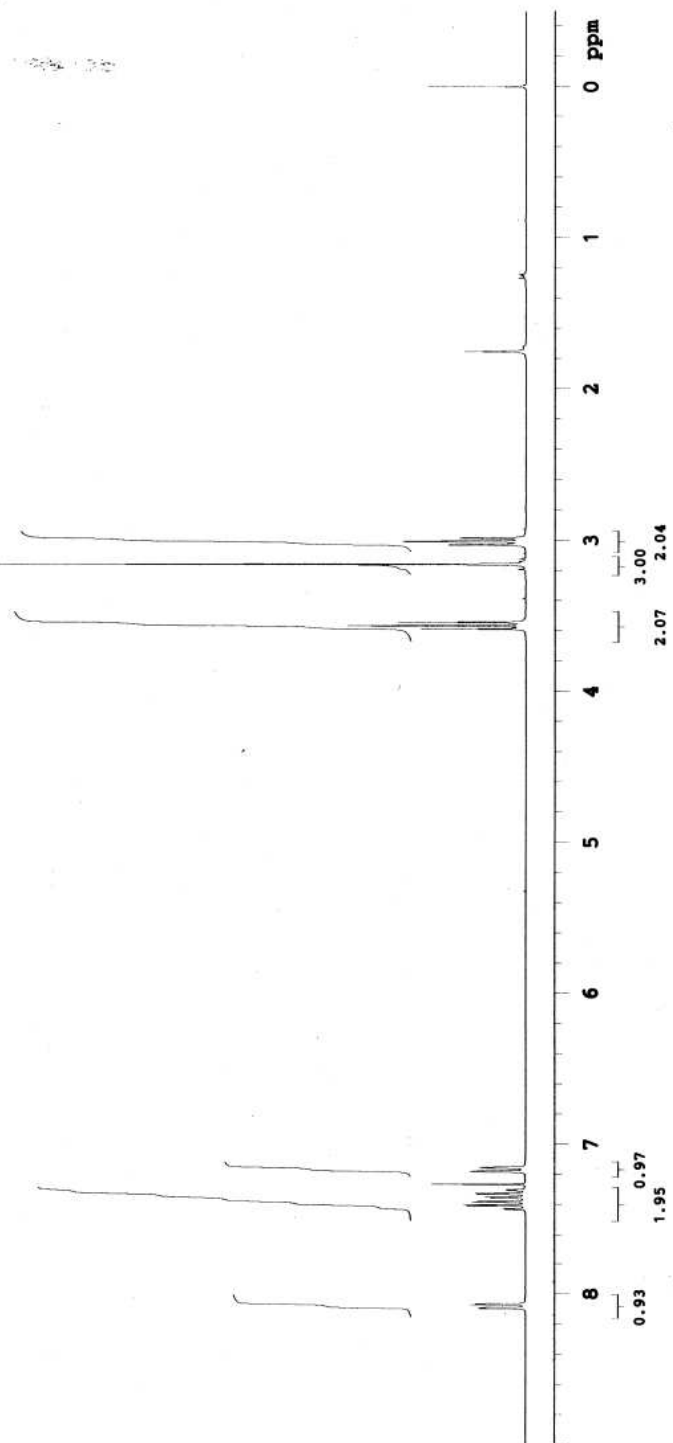
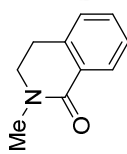


¹³C NMR spectrum of 20

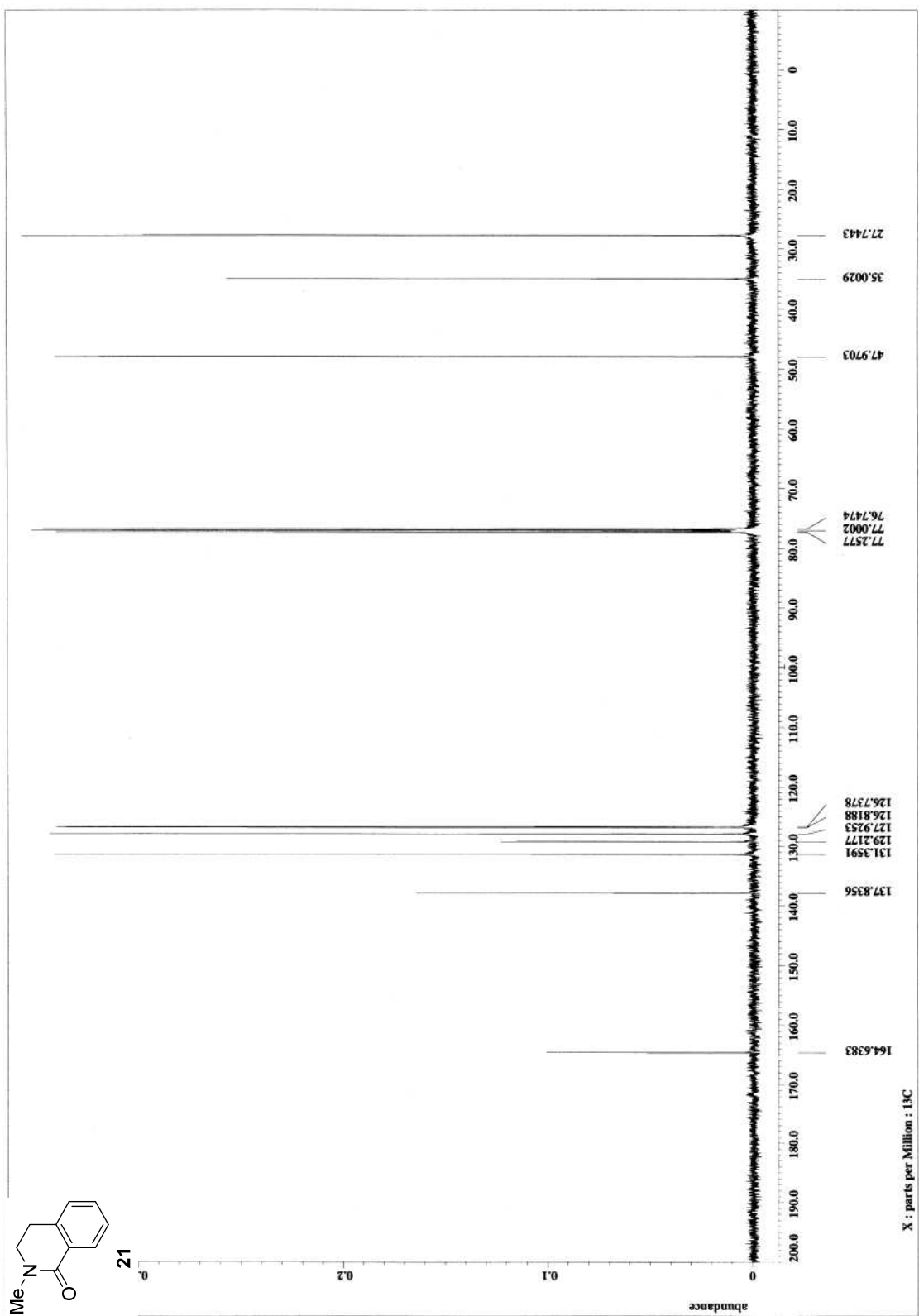


¹H NMR spectrum of 21

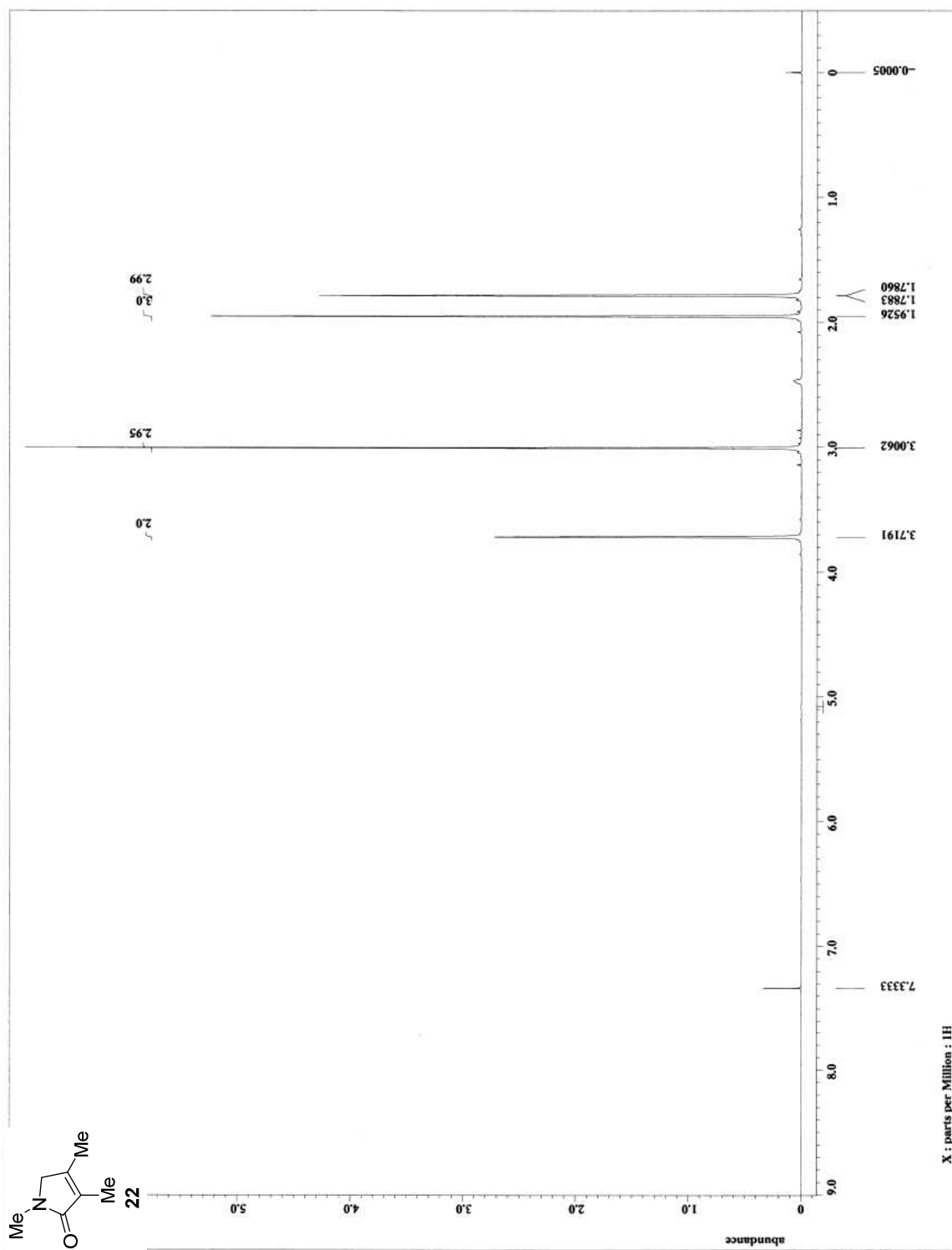
Pulse Sequence: s2pul



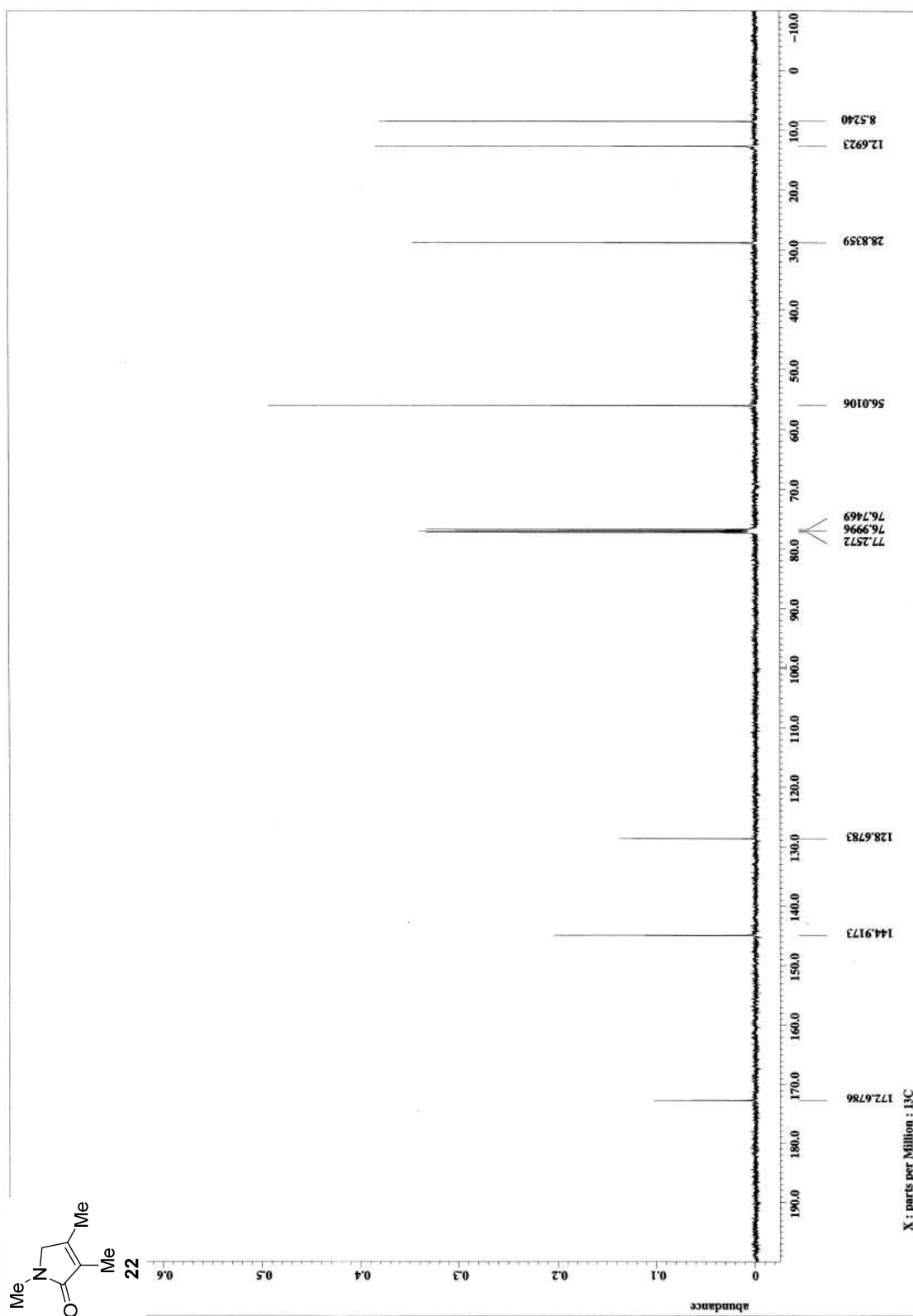
¹³C NMR spectrum of 21



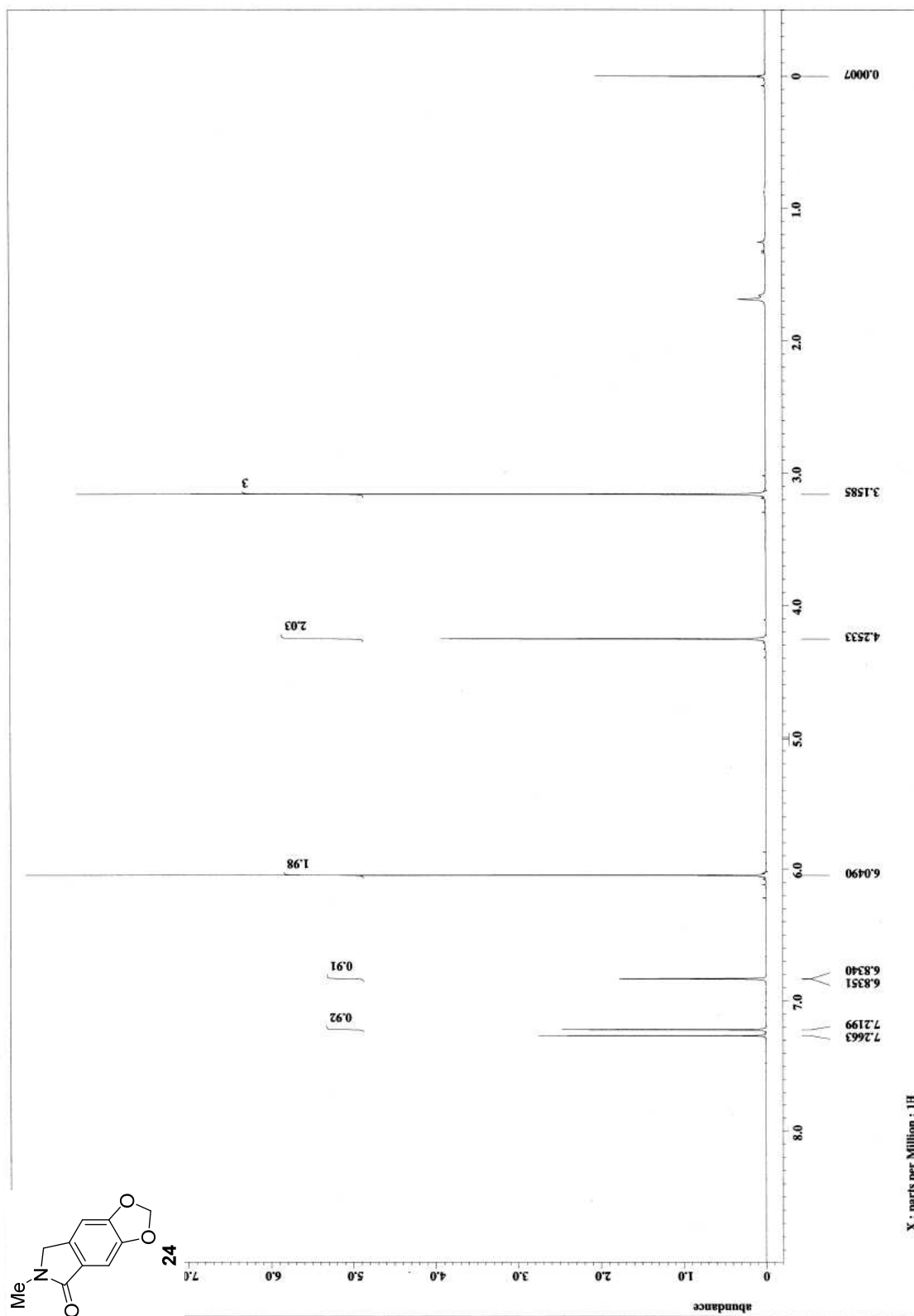
^1H NMR spectrum of **22**



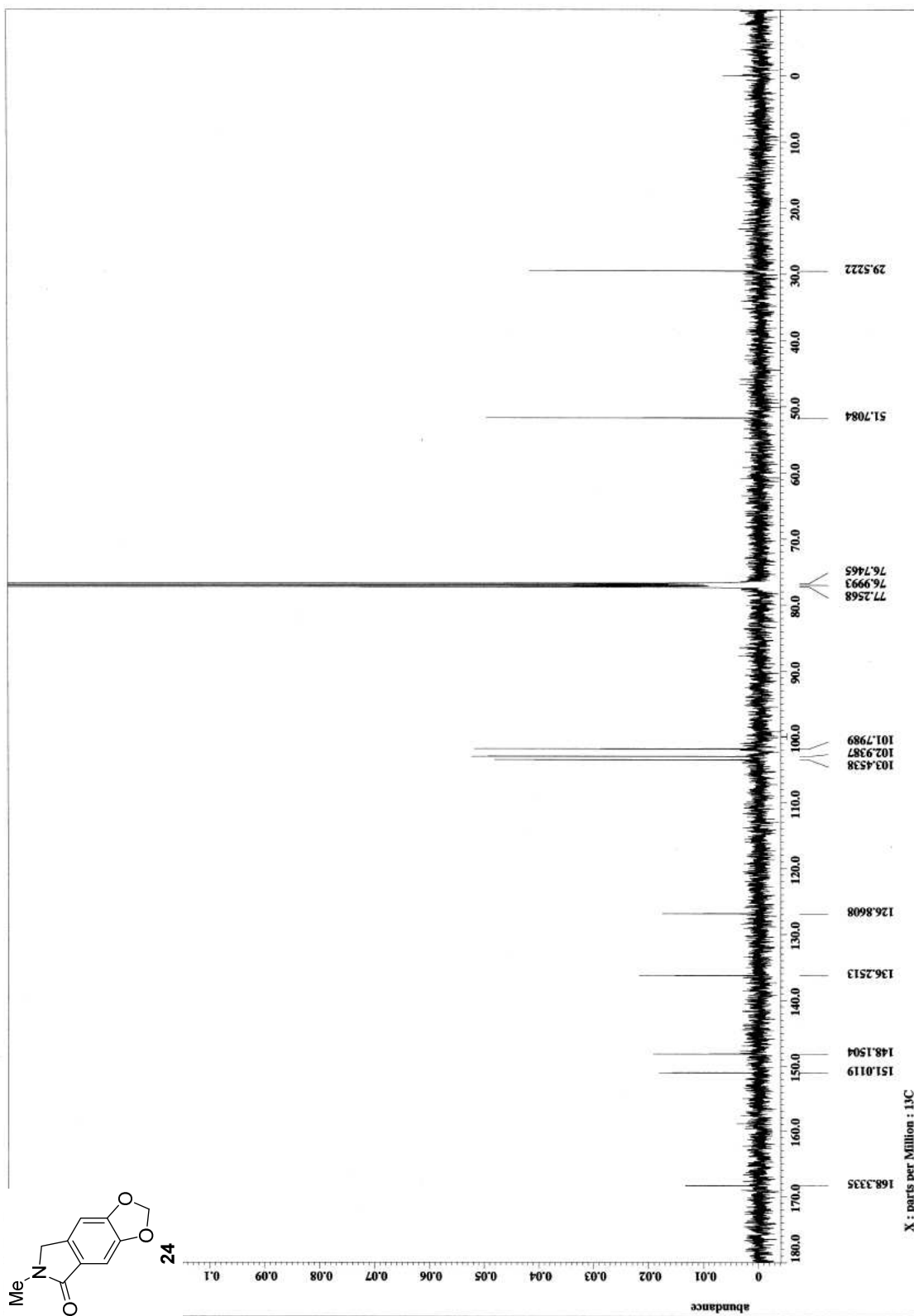
^{13}C NMR spectrum of 22



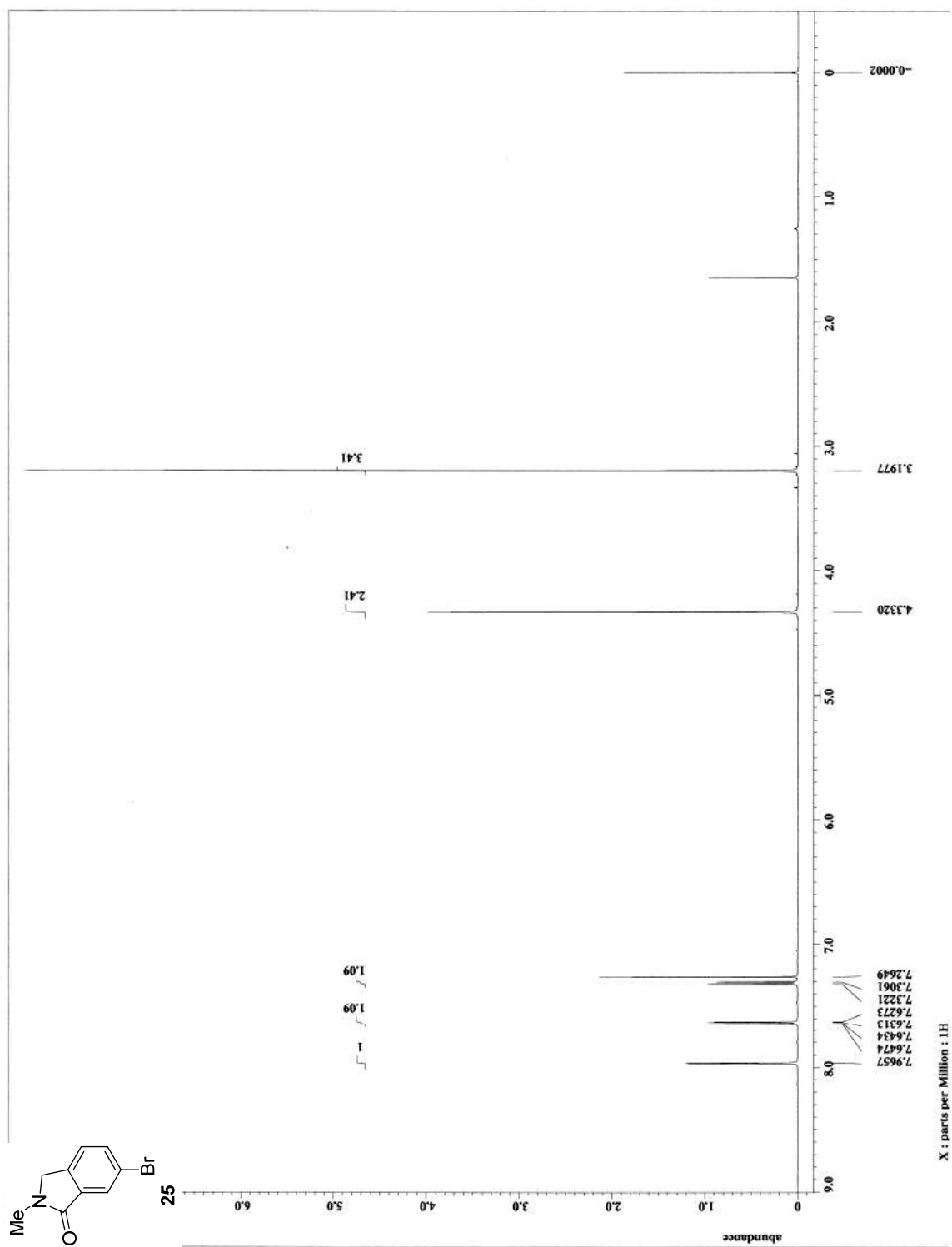
¹H NMR spectrum of 24



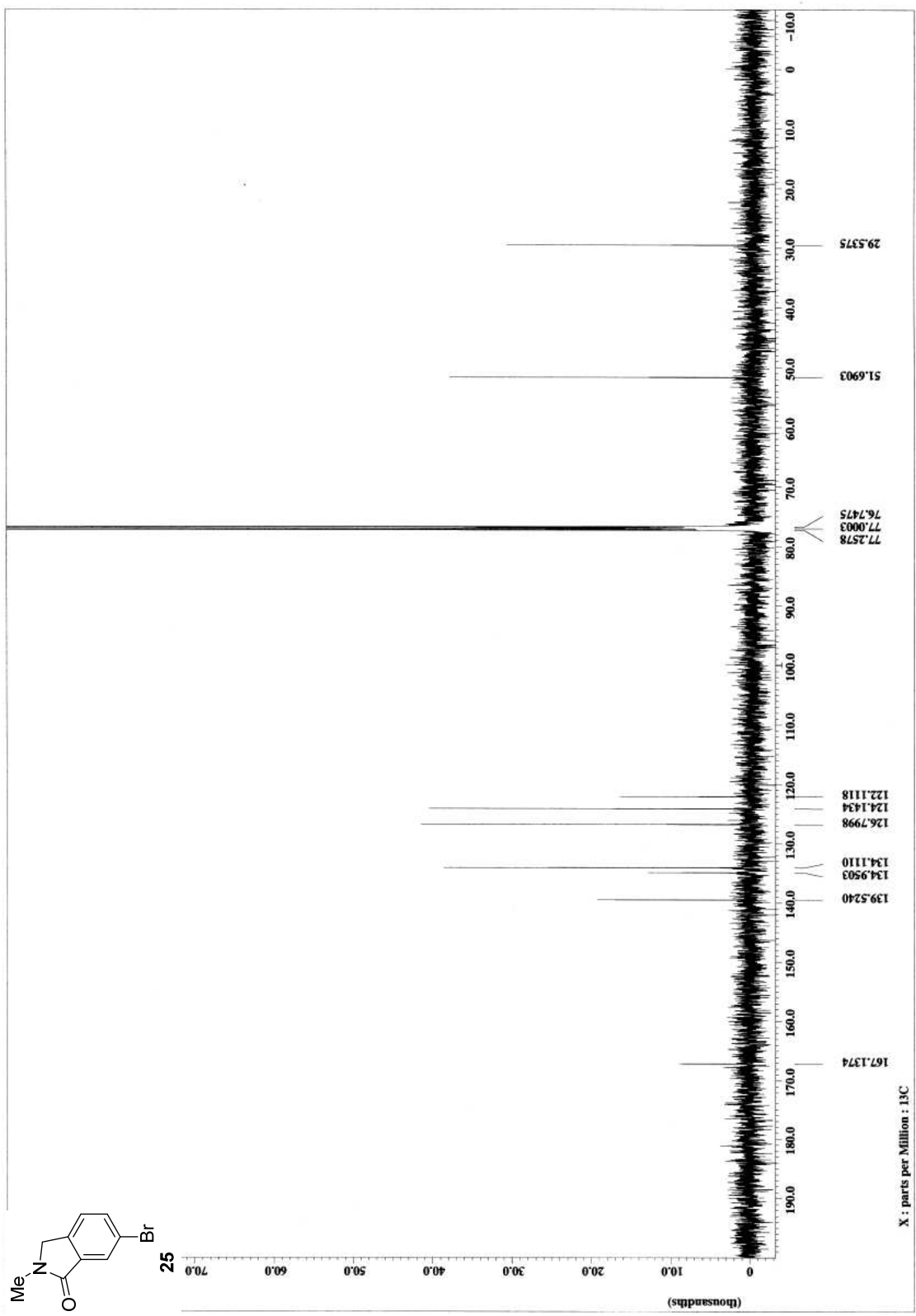
¹³C NMR spectrum of 24



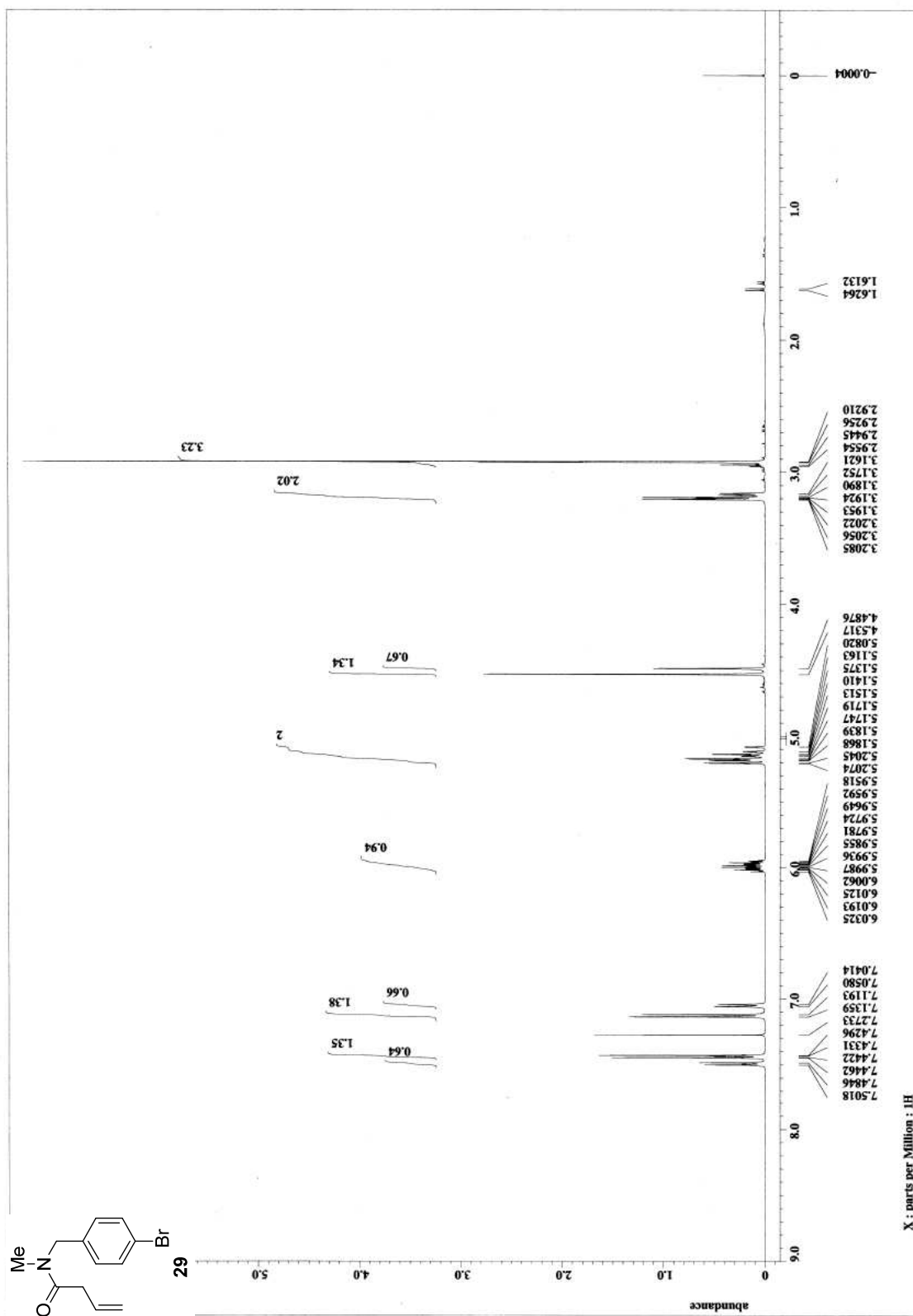
^1H NMR spectrum of **25**



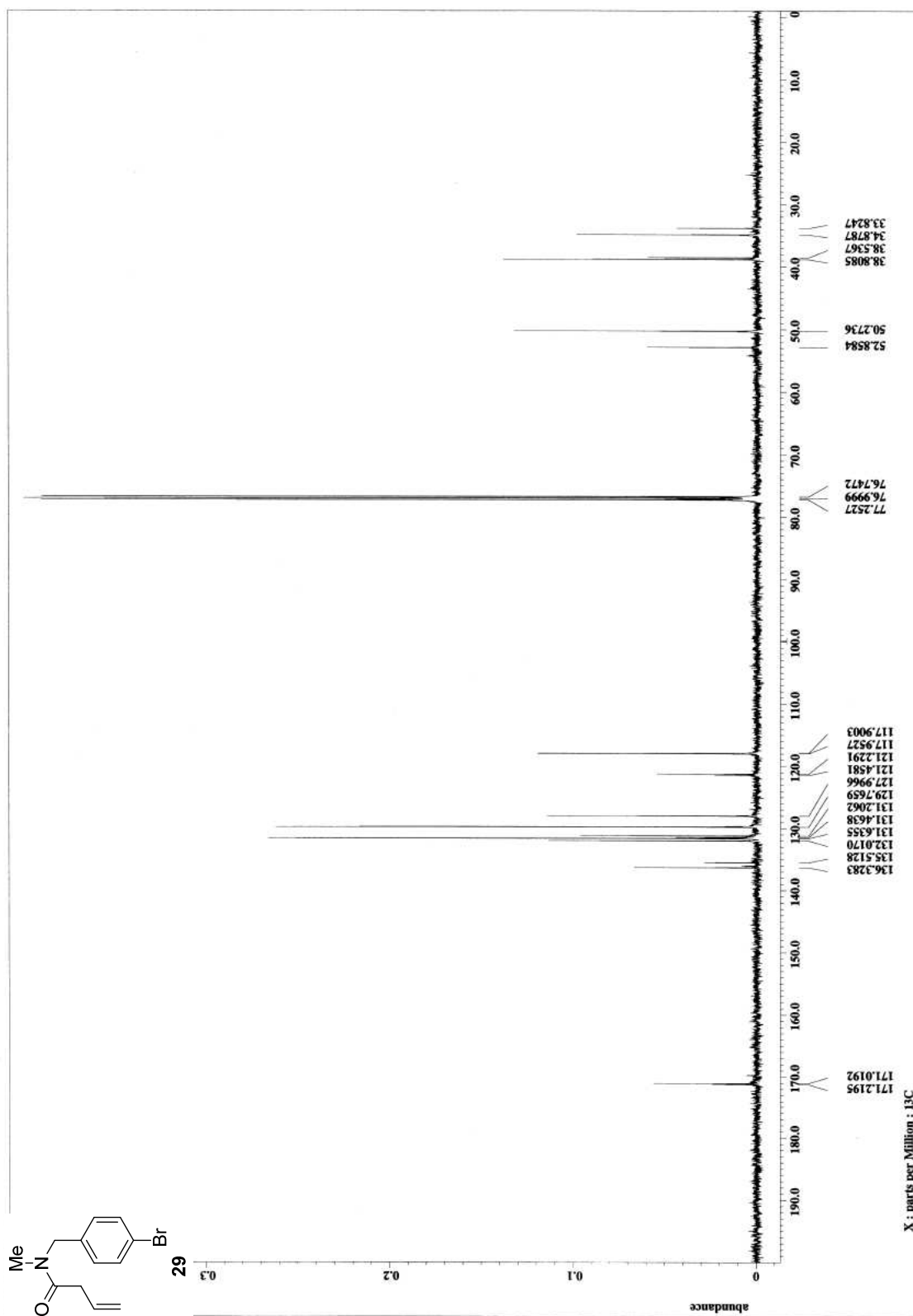
¹³C NMR spectrum of 25



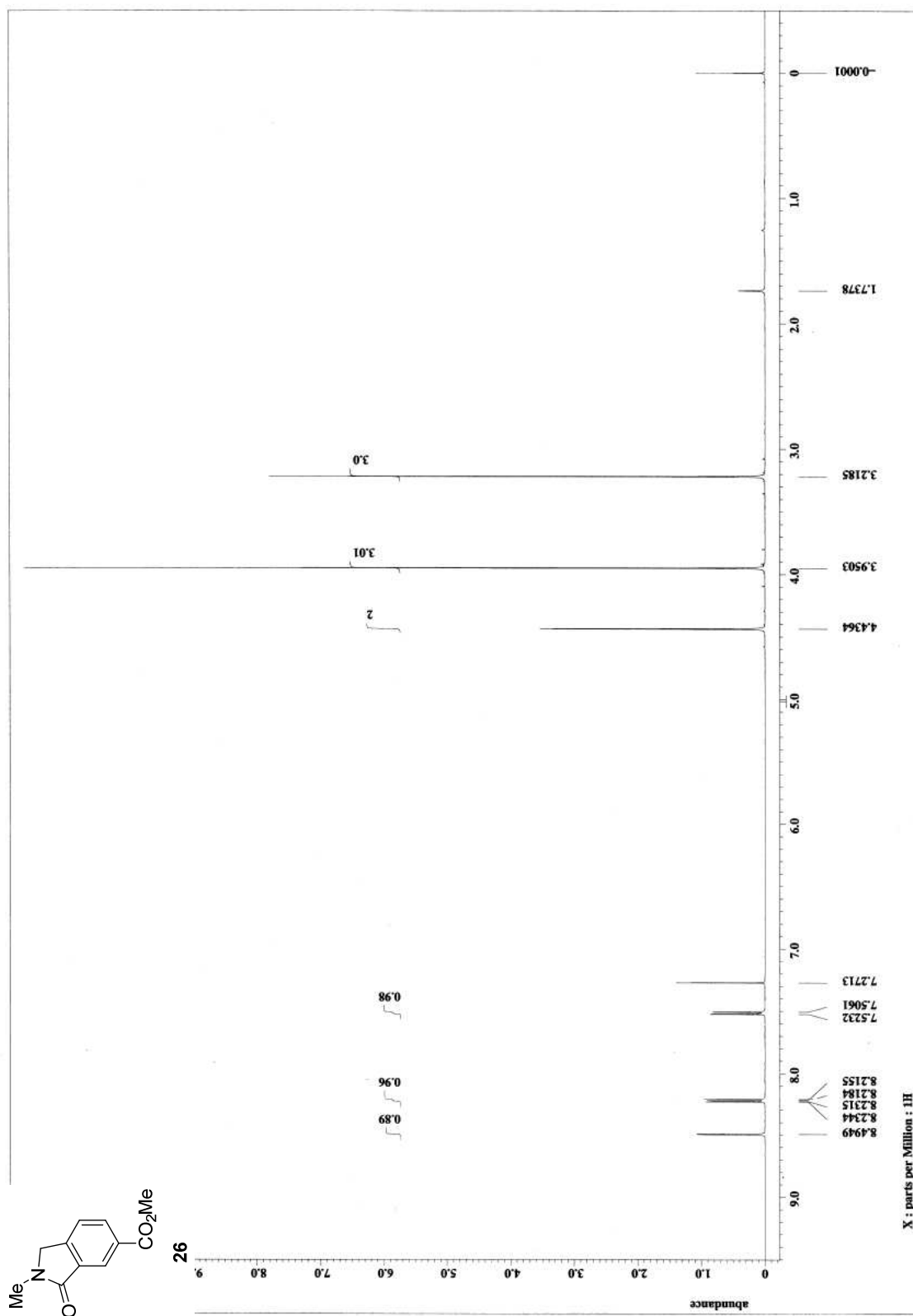
¹H NMR spectrum of 29



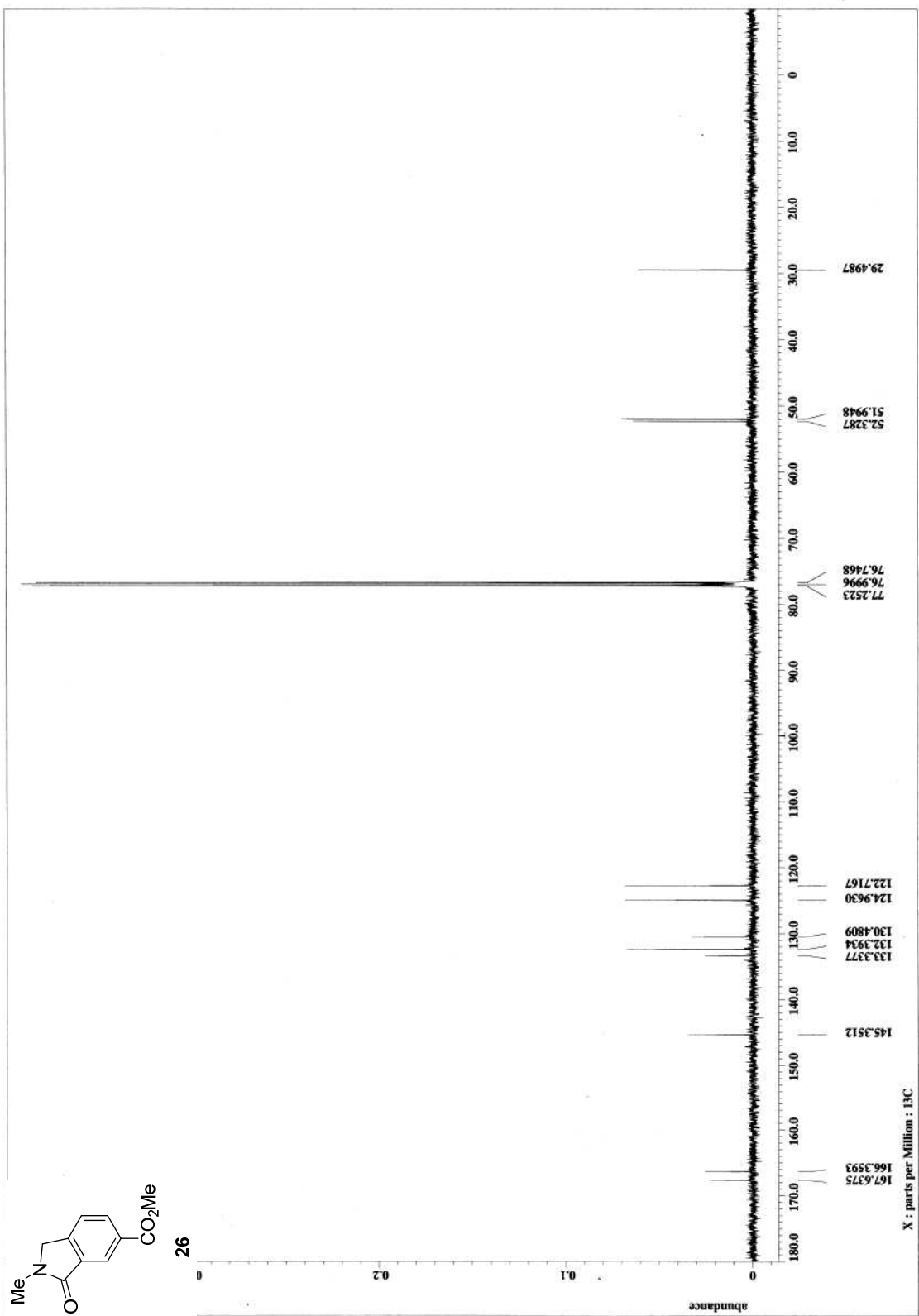
¹³C NMR spectrum of 29



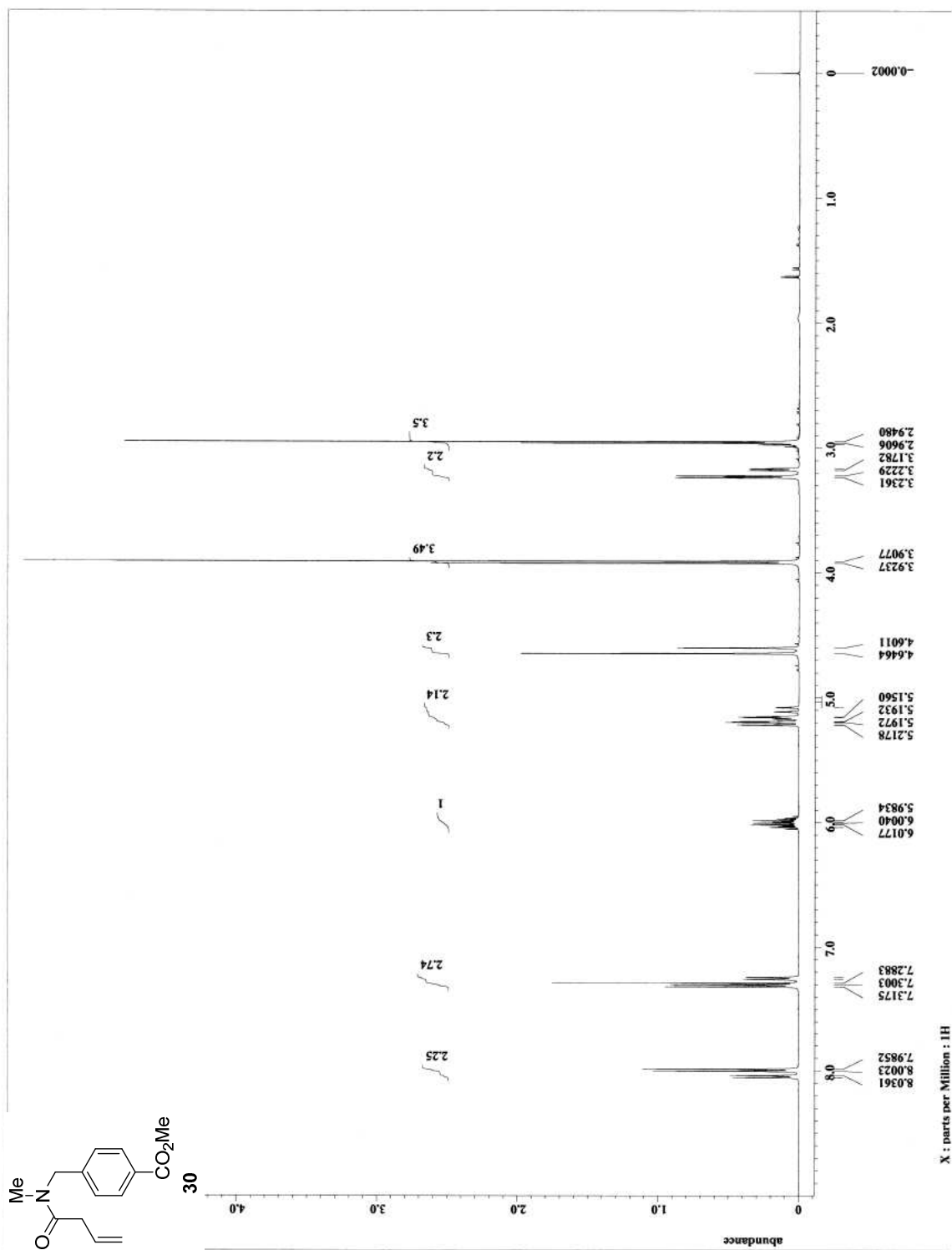
¹H NMR spectrum of 26



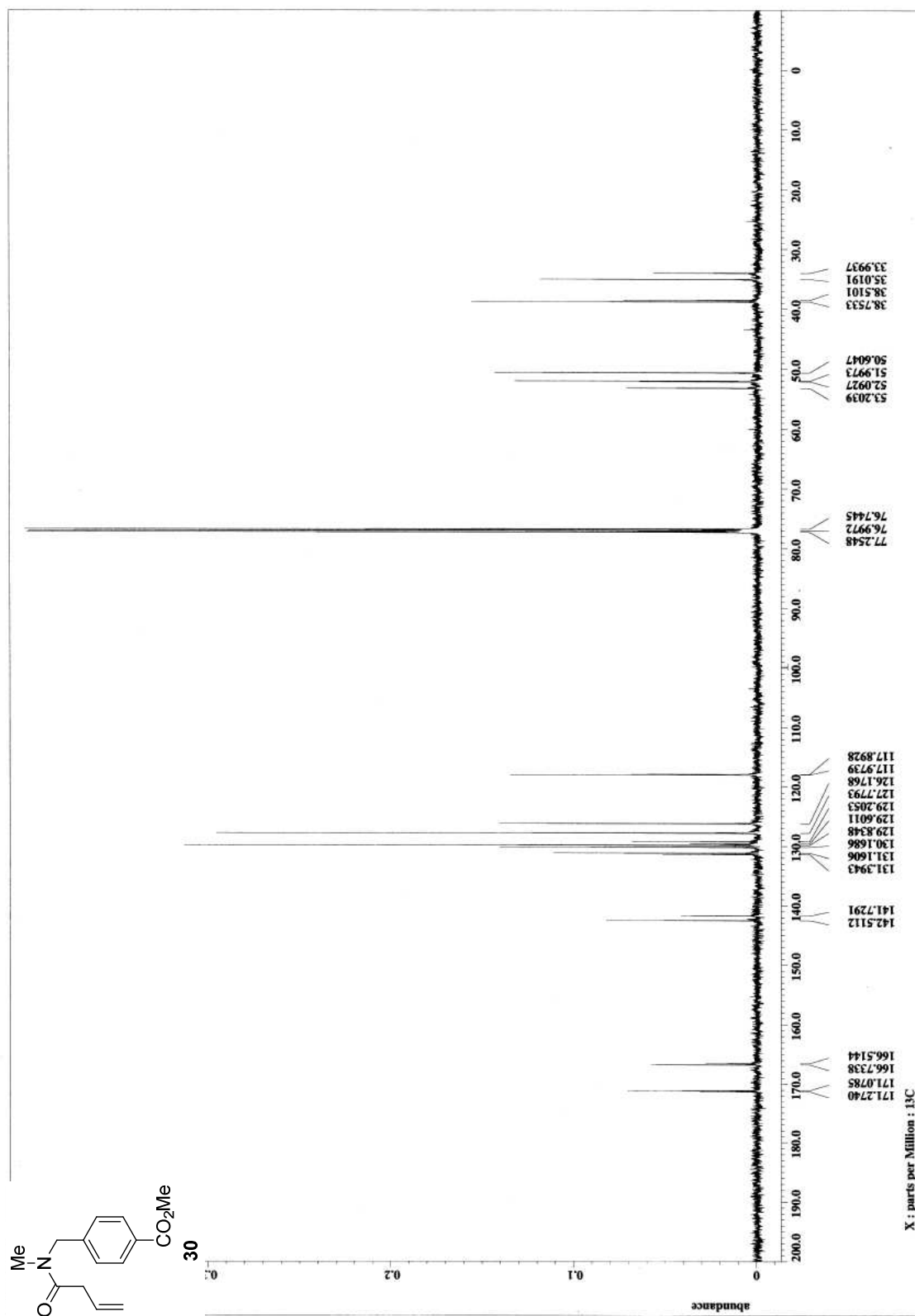
¹³C NMR spectrum of 26



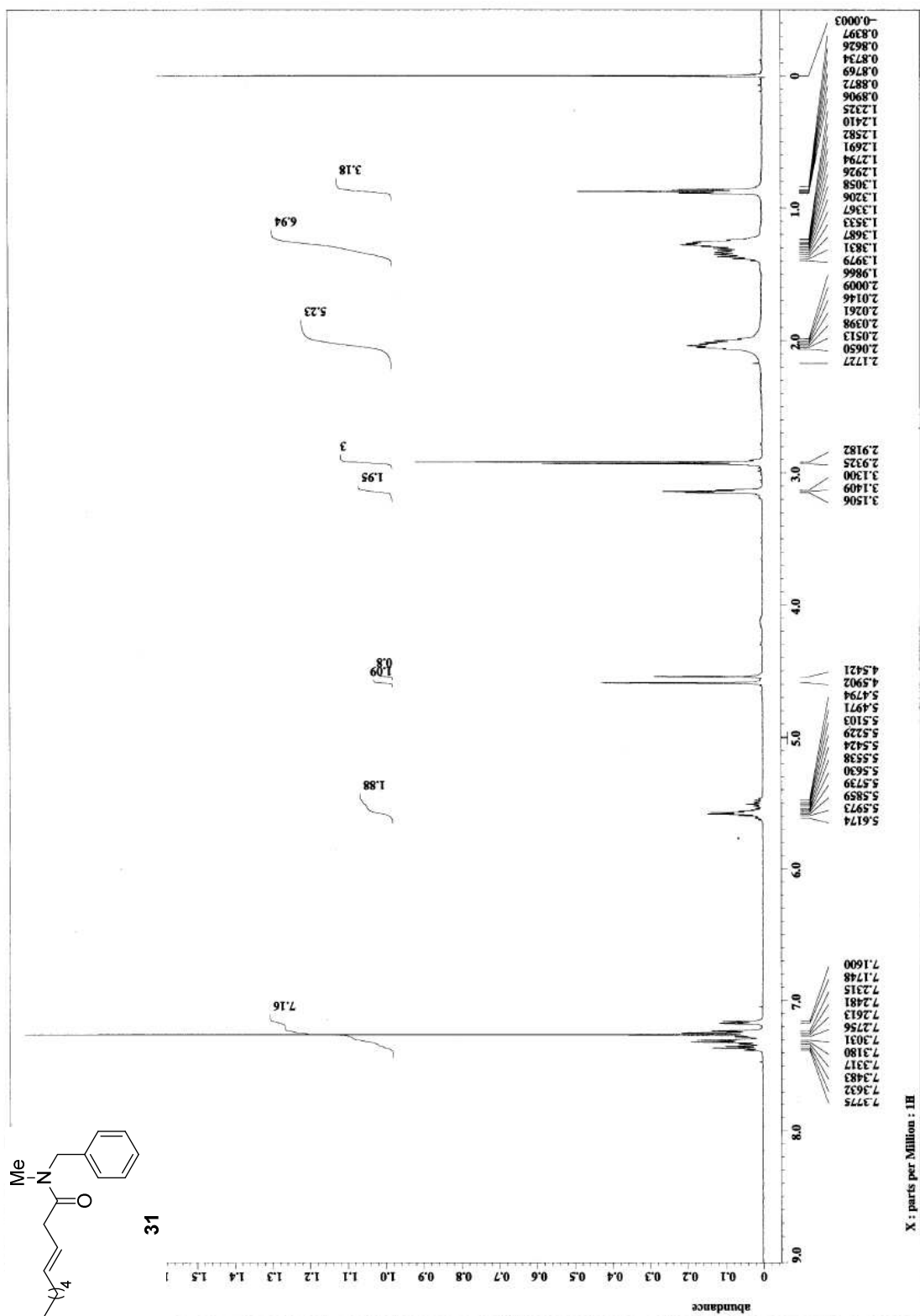
^1H NMR spectrum of **30**



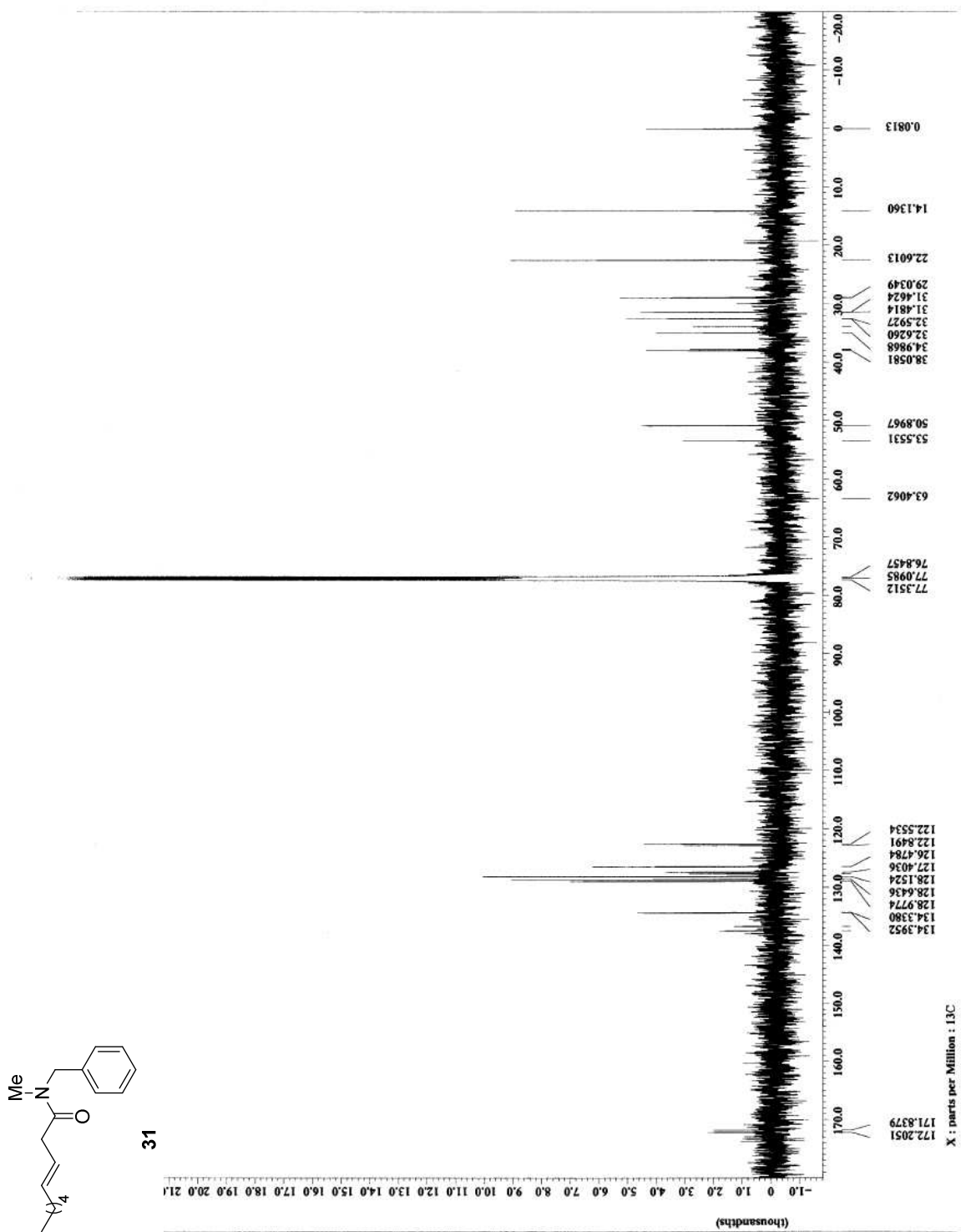
¹³C NMR spectrum of 30



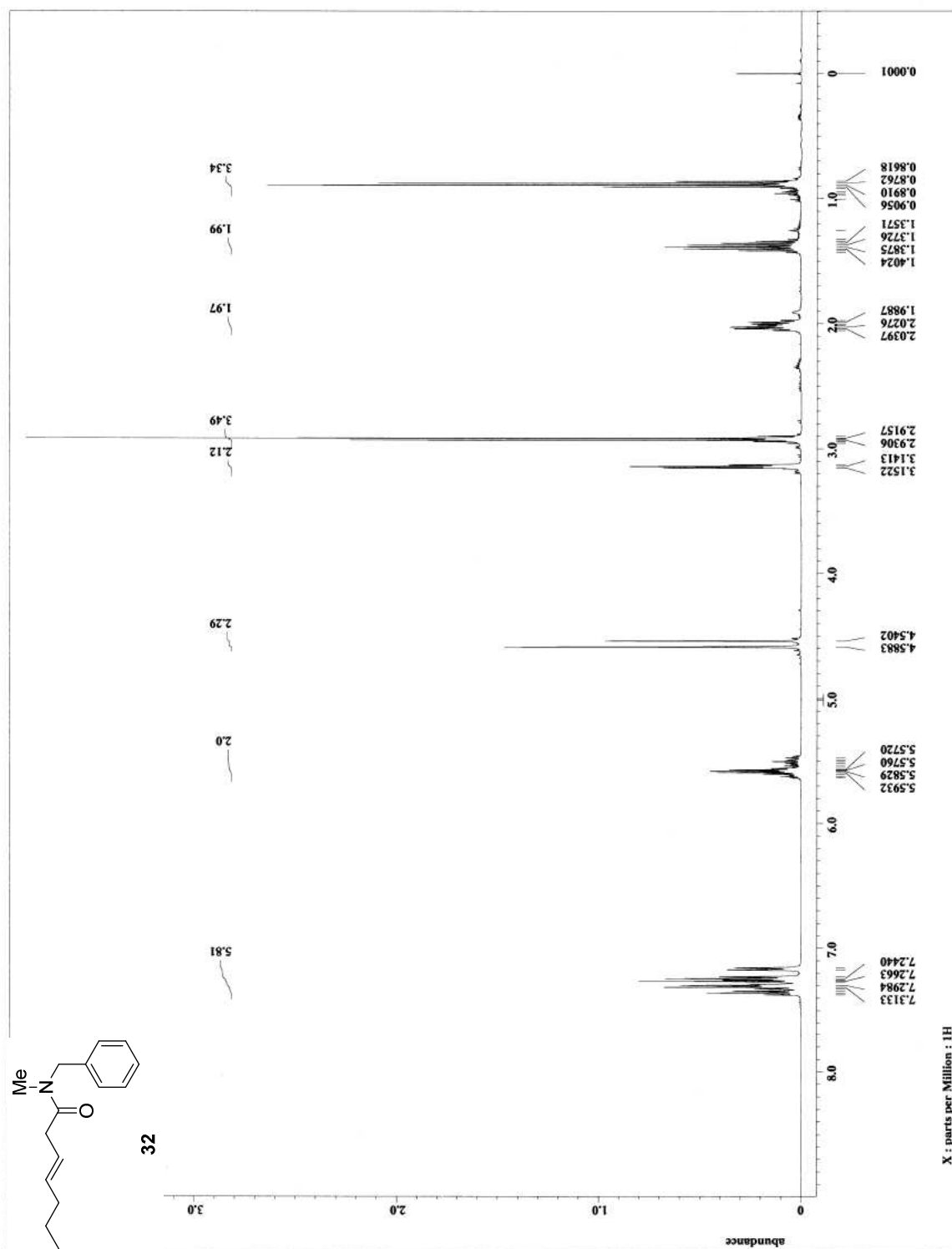
¹H NMR spectrum of 31



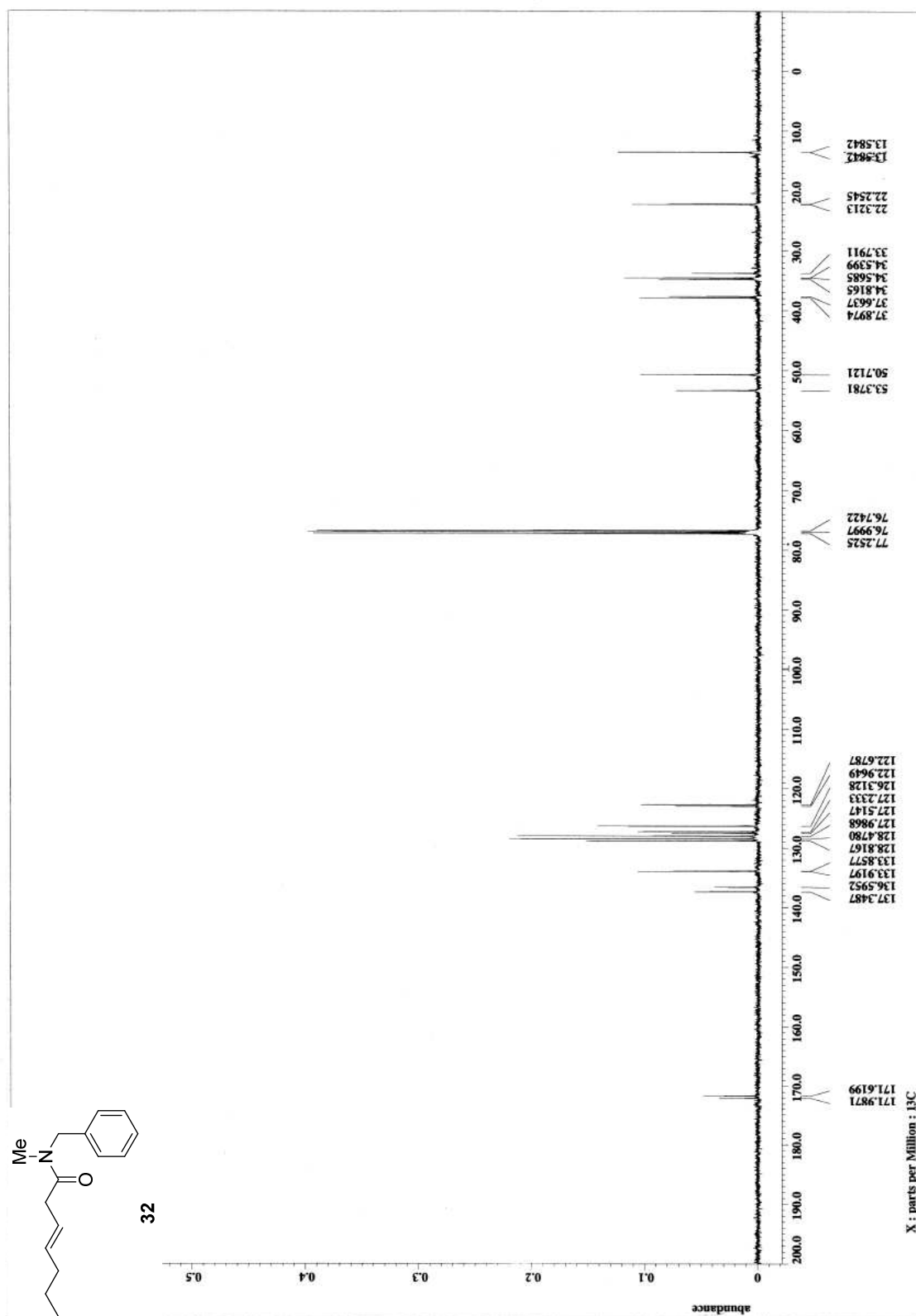
¹³C NMR spectrum of **31**



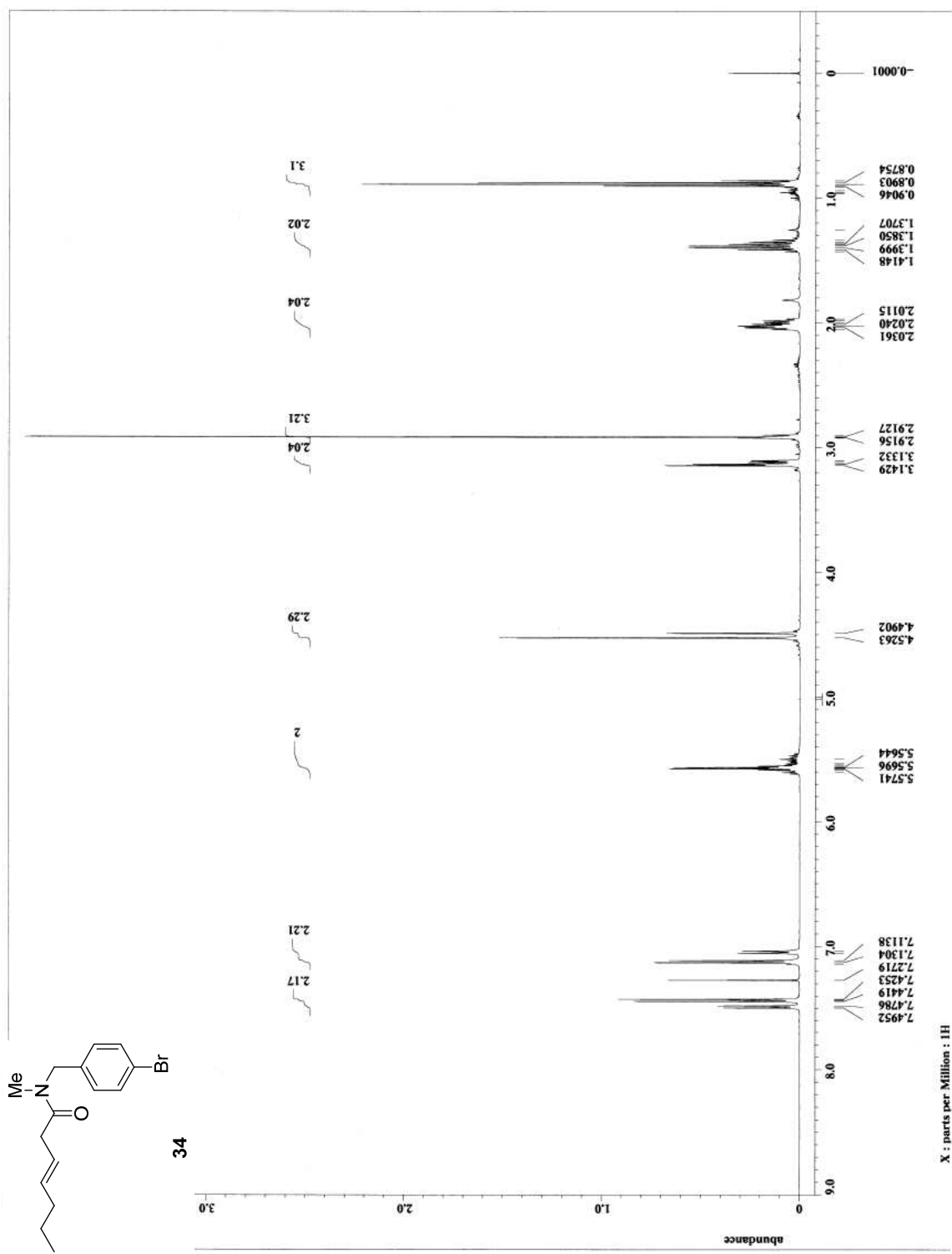
^1H NMR spectrum of **32**



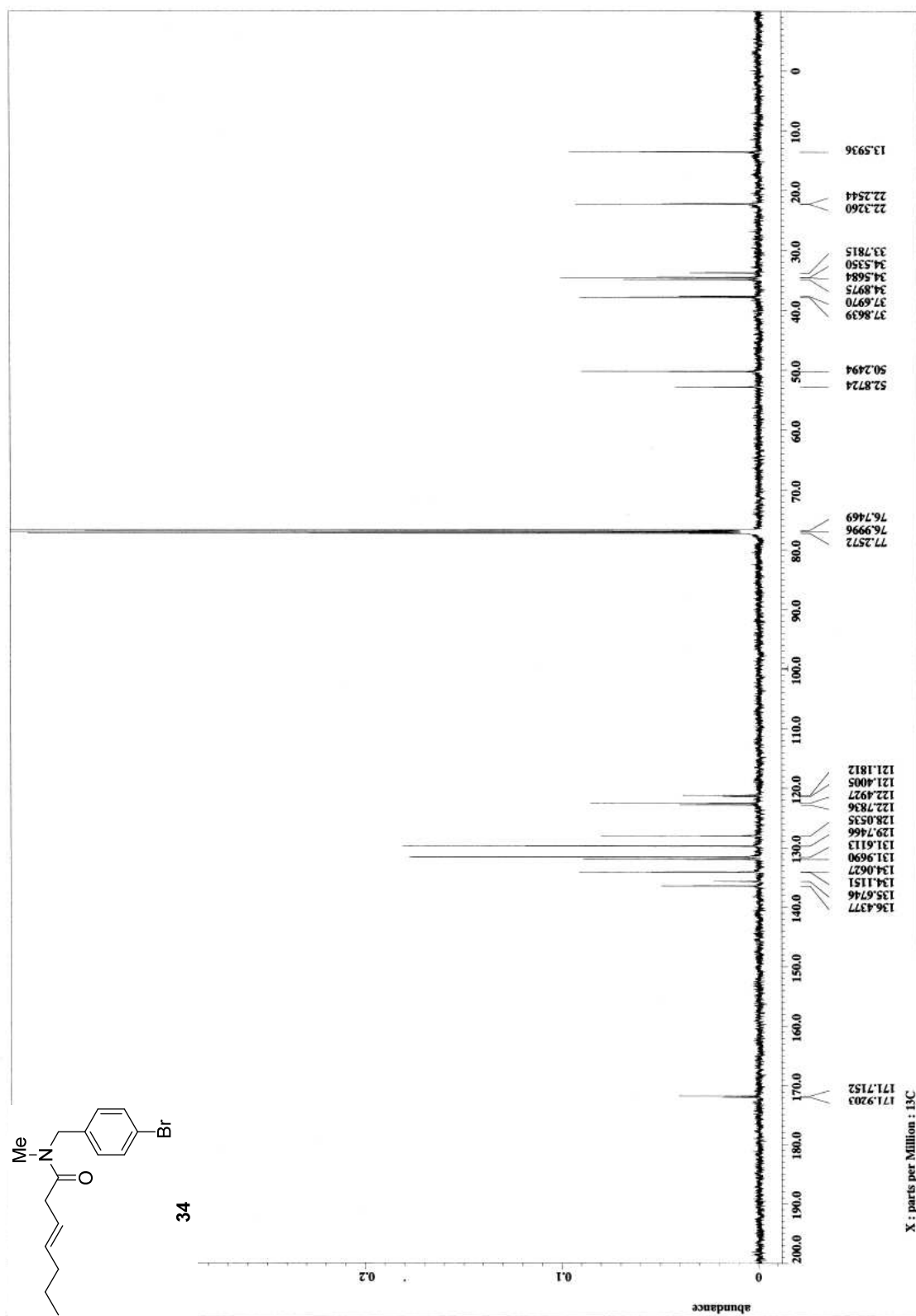
¹³C NMR spectrum of 32



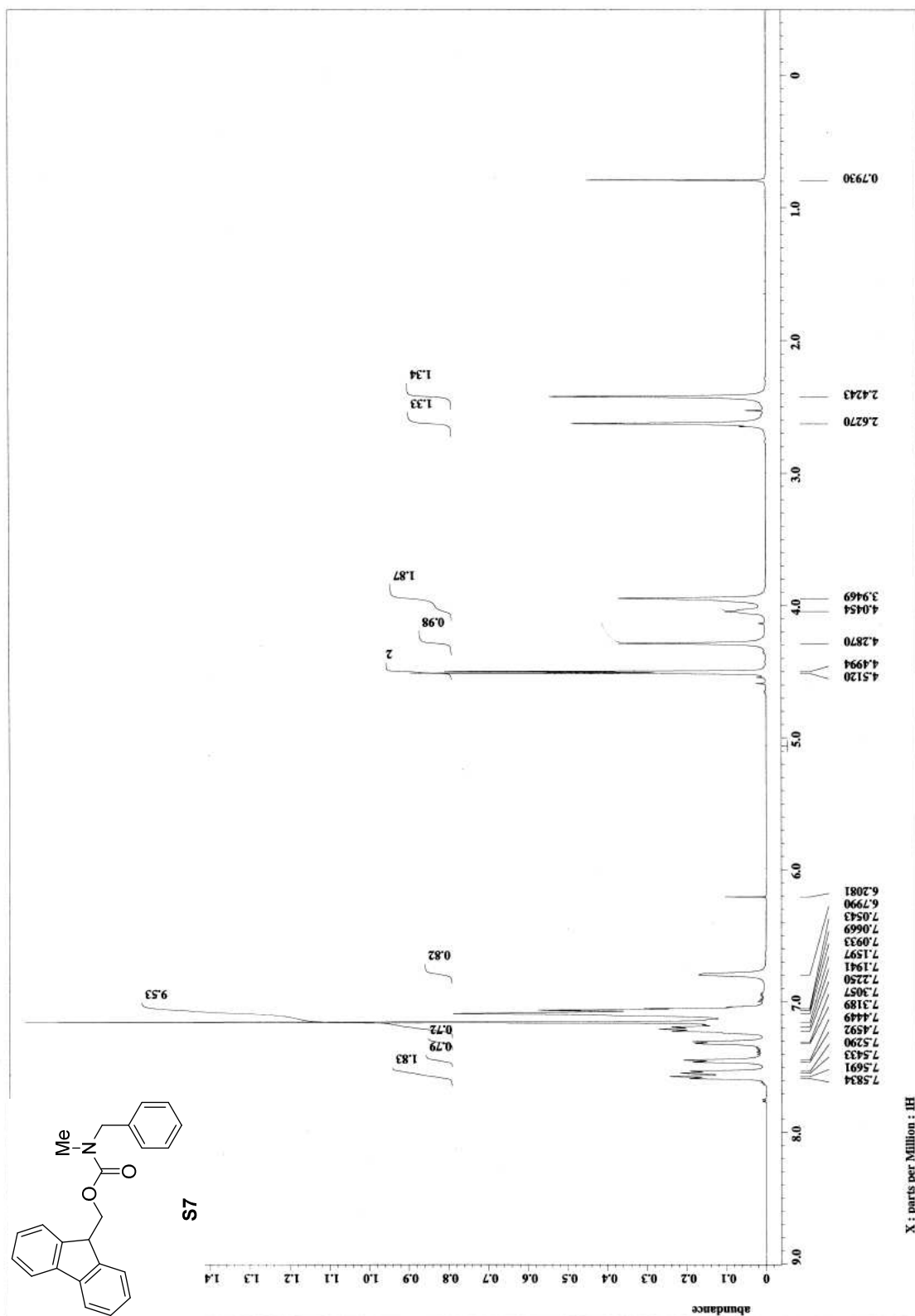
^1H NMR spectrum of **34**



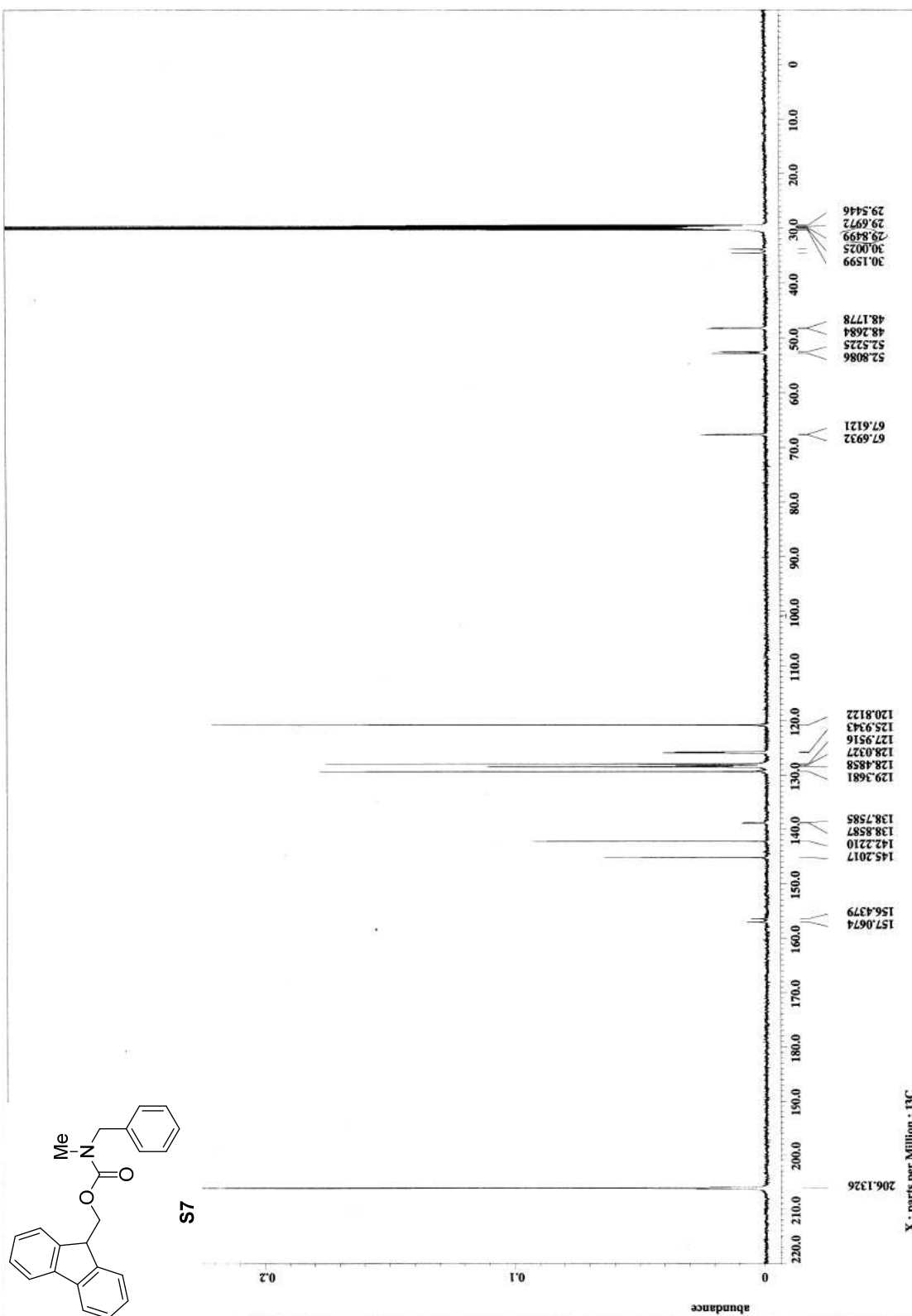
¹³C NMR spectrum of 34



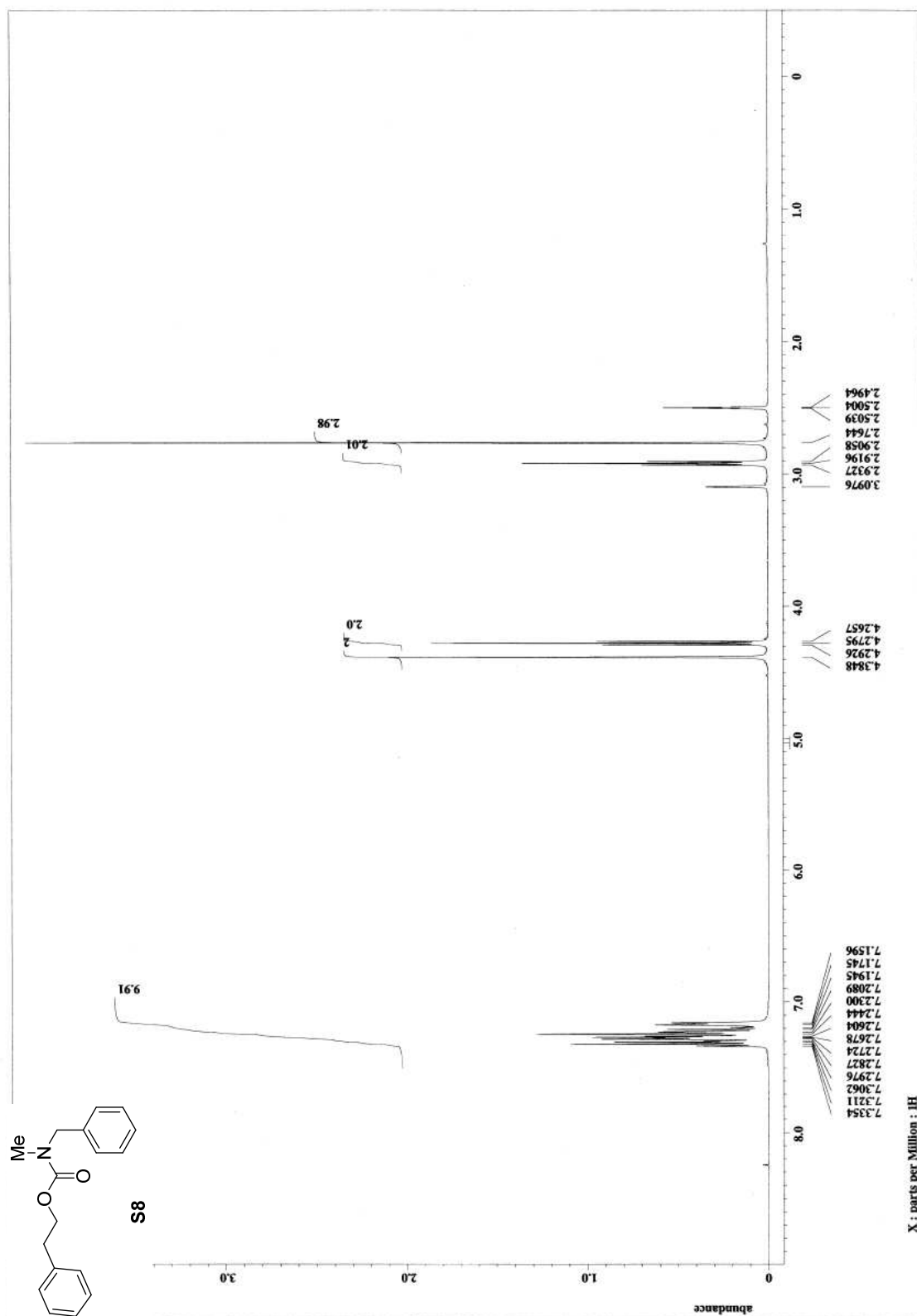
^1H NMR spectrum of S7



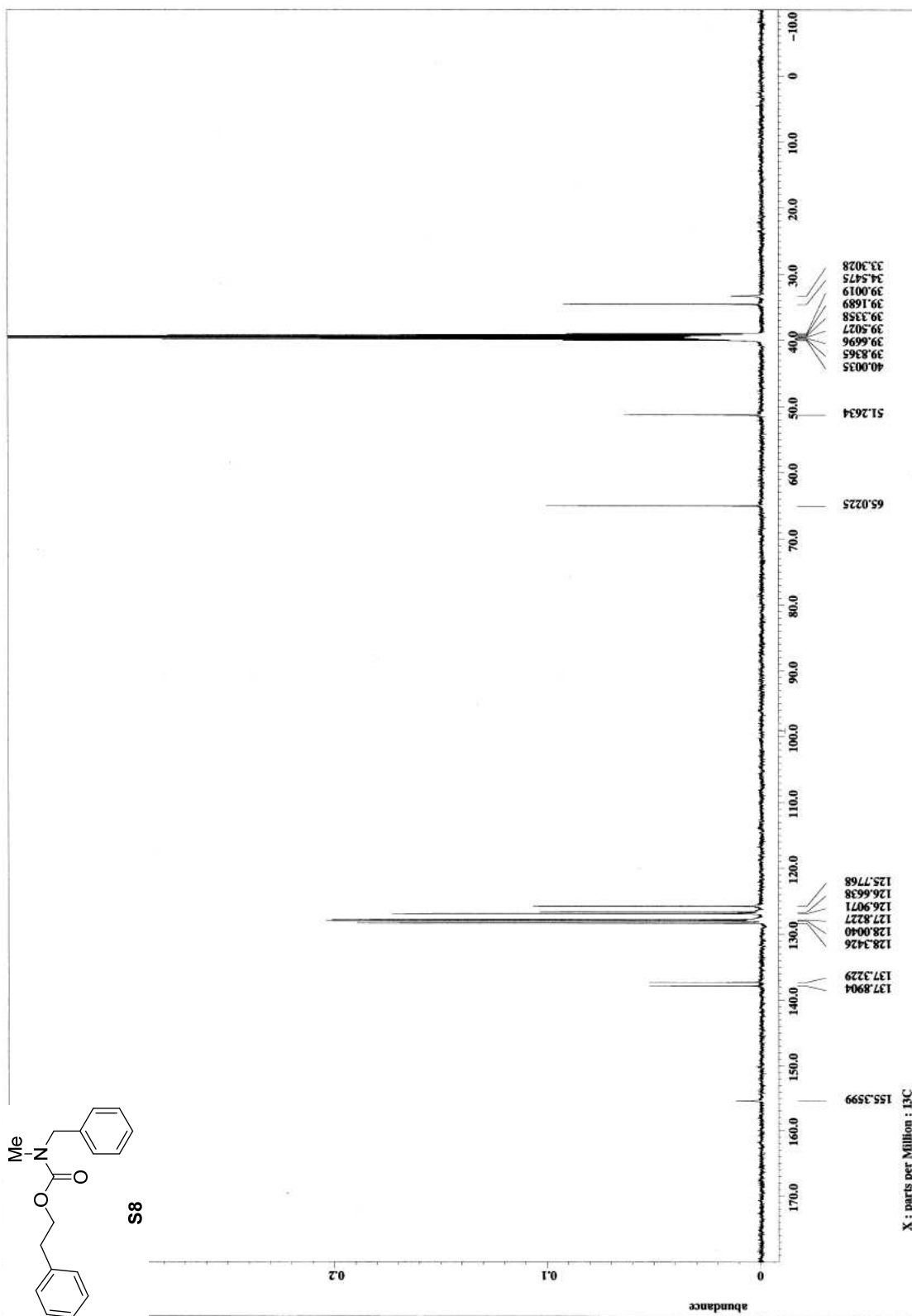
¹³C NMR spectrum of S7



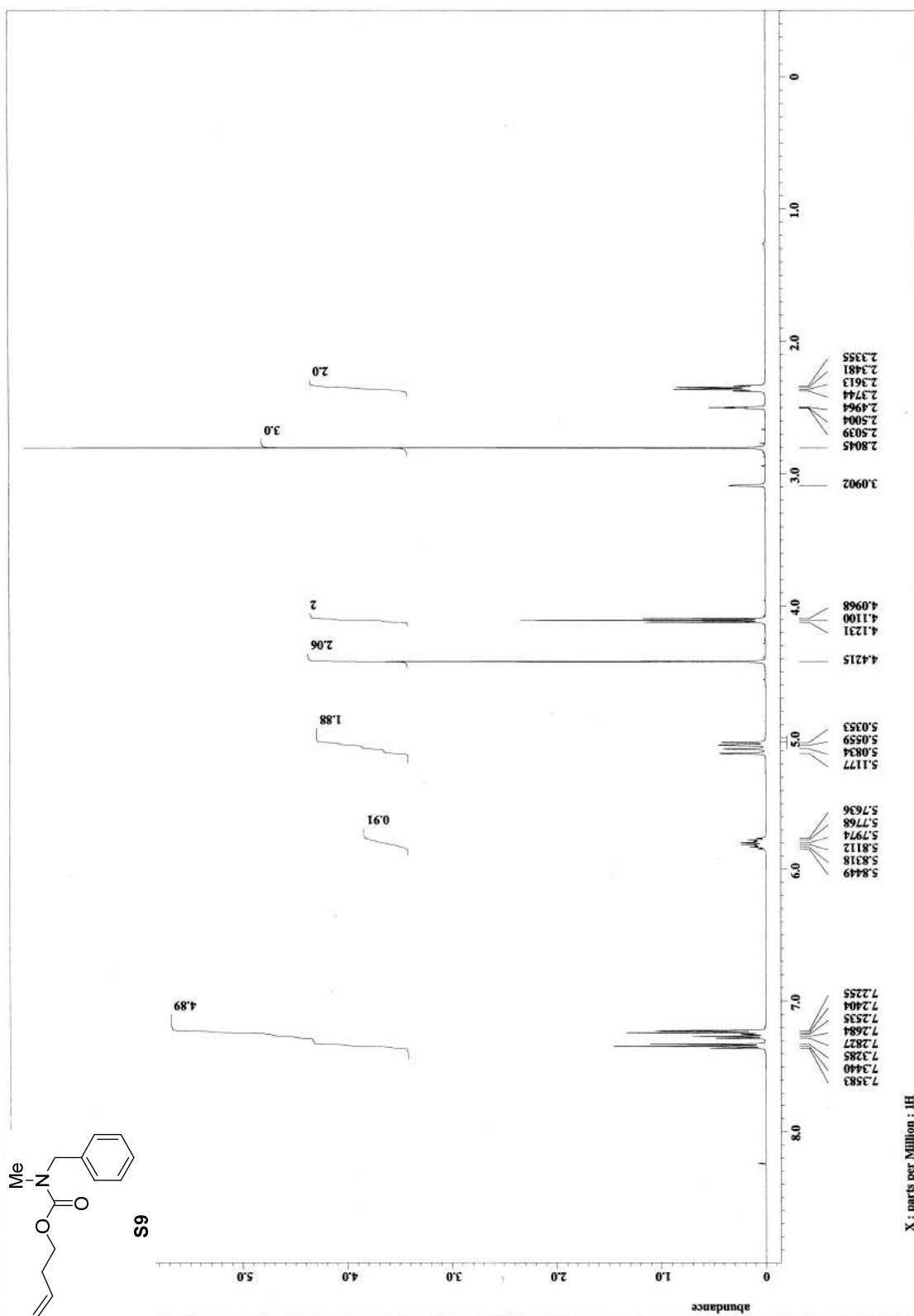
^1H NMR spectrum of S8



¹³C NMR spectrum of S8



¹H NMR spectrum of S9



¹³C NMR spectrum of S9

