Supplementary Information for

Ring Expansion of Sulfur Substituted *p*-Quinamines: Regiospecific Synthesis of 4-Aminotropones

M. Carmen Carreño,* M. Jesús Sanz-Cuesta and María Ribagorda

[*]Prof. M. C. Carreño, M. Jesús Sanz-Cuesta, Dr. M. Ribagorda

Dpto. de Química Orgánica (C-I), Universidad Autónoma, Cantoblanco, 28049-Madrid (Spain), FAX: 34 91 497 3966, E-mail: carmen.carrenno@uam.es

Experimental Procedures

Melting points were obtained in open capillary tubes. ^{1}H-NMR spectra were recorded at 500 or 300 MHz, ^{13}C-NMR spectra were recorded at 125 or 75 MHz. All reactions were monitored by TLC, which was performed on precoated silica gel 60 F_{254} plates. Flash column chromatography was effected with silica gel 60 (230-240 mesh) of Macherey-Nagel. HRMS were measured at 70 eV. Diisopropylamine was used freshly distilled over KOH in each case. NaH was washed before use with several portions of hexane. MCPBA was dried over $MgSO_4$ in CH_2Cl_2 solution. Reagent quality solvents as THF, diethyl ether and acetonitrile were dry purchased and kept under an argon atmosphere over activated 4Å molecular sieves. For toluene and benzene, activated 3Å molecular sieves were used. CH_2Cl_2 was predried over $CaCl_2$, distilled over P_2O_5 and carefully kept under an argon atmosphere.

General Procedure A. Synthesis of 4-Aminotropones from sulfur substituted *p*-Quinamines. To a 0.2 M THF solution of the corresponding *p*-quinamine, under an argon atmosphere, 4 equiv of NaH were added. After the time indicated in each case, the mixture was diluted with CH_3CN and filtered over Celite. The solvents were removed under reduced pressure and the crude purified by flash column chromatography (eluents indicated in each case).

***N*-(*tert*-Butoxycarbonyl)-4-aminotropone (9a).** From (±)-*N*-(*tert*-butoxycarbonyl)-4-amino-4-[(*p*-tolylsulfinyl)methyl]-2,5-cyclo hexadienone (**5a**): Following general procedure A from 50 mg (0.14 mmol, 1 equiv) of (±)-*N*-(*tert*-butoxycarbonyl)-4-amino-4-[(*p*-tolylsulfinyl)methyl]-2,5-cyclohexadienone (**5a**), 0.7 mL of THF and 13.2 mg (0.55 mmol, 4 equiv) of NaH. Reaction time: 3 h. Purified by column chromatography in a mixture Hexane:AcOEt (1:1). Tropone **9a** was obtained in a 99% yield as pale yellow crystals. When IMe (1.1 equiv) is added to the reaction mixture, **9a** and MeSOTol **3** were formed and separated by column chromatography (Hexane:AcOEt 1:1 to AcOEt), in 99% (**9a**) and 84%

(**3**). M.p.140-142 ºC ($CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 9H, ^{t}Bu), 6.83 (dd, J_d = 11.9 and J_d = 2.6 Hz, 1H, H_7), 6.89 (brs, 1H, NH), 7.01-7.40 (ABXY system, J_{AB} = 12.9, J_{AX} = 2.6 and J_{BY} = 2.2 Hz, Δν =20.1 Hz, 2H, H_2 and H_3), 7.12 (dd, J_d = 12.1 and J_d = 9.6 Hz, 1H, H_6), 7.43 (dd, J_d = 9.7 and J_d = 2.0 Hz, 1H, H_5); ^{1}H-RMN (300 MHz, MeOD-d_4) δ 1.54 (s, 9H, ^{t}Bu), 6.83 (dd, J_d = 11.9 and J_d = 3.0 Hz, 1H, H_7), 7.05-7.50 (ABXY system, J_{AB} = 12.9, J_{AX} = 3.0 and J_{BY} = 2.4 Hz, Δν =111.3 Hz, 2H, H_2 and H_3), 7.38 (dd, J_d = 11.9 and J_d = 9.9 Hz, 1H, H_6), 7.72 (dd, J_d = 9.9 and J_d = 2.4 Hz, 1H, H_5); ^{13}C-RMN (75 MHz, $CDCl_3$) δ 28.1 (3 C, ^{t}Bu), 82.0 (-C-^{t}Bu), 118.6, 132.8, 136.6, 137.2, 142.0, 144.3, 152.0, 186.8 (C=O); MS (m/z) 57 (100), 93 (13), 121 (5), 148 (8), 221 (M^+, 7); HRMS (EI) Calcd. for $C_{12}H_{15}NO_3$ 221.10519, Found 221.10573; Anal. Calcd. for $C_{12}H_{15}NO_3$ C, 65.14; H, 6.83; N, 6.33. Found C, 65.05; H, 6.47; N, 6.20; IR (neat) ν 3055, 2986, 1728, 1645, 1596, 1547, 1510, 1455, 1423, 1370, 1238, 1212, 1153, 1070, 896, 870 cm^{-1}; UV (0.12 mM in CH_3CN) 327 (0.68 AU). From *N-(tert*-butoxycarbonyl)-4-amino-4-[(*p*-tolylsulfonyl)methyl]-2,5 cyclohexadienone **(6a)**: Following general procedure A from 45 mg (0.12 mmol, 1 equiv) of *N-(tert*-butoxycarbonyl)-4-amino-4-[(*p*-tolylsulfonyl)methyl]-2,5-cyclohexadienone (**6a**), 0.7 mL of THF and 11 mg (0.5 mmol, 4 equiv) of NaH. Reaction time: 2 h. Purified by column chromatography in a mixture Hexane:AcOEt (1:1), 97 % yield.

***N*-(*tert*-Butoxycarbonyl)-4-amino-3-methyltropone (9b)**. Following the general procedure A from 30 mg (0.06 mmol, 1 equiv) of (±)-*N-(tert*-butoxycarbonyl)-4-amino-3-methyl-4-[(*p*-tolylsulfonyl)methyl]-2,5-cyclohexadienone **(5b)**, 0.4 mL of THF and 6 mg (0.16 mmol, 4 equiv) of NaH. Reaction time: 1 h. Purified by column chromatography in a mixture Hexane:AcOEt (1:1). Tropone **9b** was obtained pure in a 77% yield as pale yellow crystals. M.p. 148-150 ºC (Acetone); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 9H, ^{t}Bu), 2.31 (s, 3H, CH_3-), 6.31-6.43 (brs, 1H, NHBOC), 6.83 (ddd, J_d = 11.9, J_d = 2.8 and J_d = 0.8 Hz, 1H, H_7), 7.12 (dd, J_d = 11.7 and J_d = 9.9 Hz, 1H, H_6), 7.14 (brs, 1H, H_2), 7.74 (d, J_d = 9.9 Hz, 1H, H_5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 23.8 (CH_3-), 28.2 (3 C, ^{t}Bu), 82.0 (-C-^{t}Bu), 120.7, 136.1, 136.9, 140.2, 142.9, 143.3, 152.1, 186.2 (C=O); MS (m/z) 57 (100), 59 (22), 77 (11), 104 (14), 106 (16), 107 (23), 133 (11), 135 (10), 151 (11), 162 (11), 179 (12), 235 (M^+, 8); HRMS (EI) Calcd. for $C_{13}H_{17}NO_3$ 235.1208, Found 235.1204.

***N*-(*tert*-Butoxycarbonyl)-4-amino-5-methyltropone (9c)**. Following the general procedure A from 35 mg (0.09 mmol, 1 equiv) of (±)-*N-(tert*-butoxycarbonyl)-4-amino-4-[1´-methyl-1´-benzenesulfonyl)methyl]-2,5-cyclohexadienone **(5c)**, 0.5 mL of THF and 9 mg (0.36 mmol, 4 equiv) of NaH. Reaction time: 4 h. Purified by coulmn chromatography in a mixture Hexane:AcOEt (1:1). Tropone **9c** was obtained pure in a 94% yield as a yellowish oil: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 9H, ^{t}Bu), 2.25 (s, 3H, CH_3-), 6.27 (brs, 1H, NHBOC), 6.79-7.10 (ABX system, J_{AB} = 12.5 and J_{AX} = 3.0 Hz, Δν =72.7 Hz, 2H, H_6 and H_7),

6.91-7.73 (ABX system, J_{AB} = 13.3 and J_{AX} = 2.8 Hz, Δν =221.1 Hz, 2H, H_2 and H_3); ^{13}C-NMR (125 MHz, $CDCl_3$) (Double signals are observed since a keto-imine equilibrium is possible to occur) δ 22.1 (CH_3-), 22.3 (CH_3-), 28.21 (3 C, ^{t}Bu), 28.23 (3 C, ^{t}Bu), 81.9 (-C-^{t}Bu), 130.1, 132.1, 134.9, 135.0, 137.5, 137.9, 138.5, 138.6, 139.8, 140.3, 140.8, 141.0, 152.5 (^{t}BuO-C(O)-), 153.6 (^{t}BuO-C(O)-), 186.40 (C=O), 186.44 (C=O); MS (m/z) 57 (100), 59 (13), 77 (14), 78 (11), 83 (19), 85 (12), 104 (14), 106 (18), 107 (35), 108 (14), 133 (10), 135 (16), 151 (19), 162 (13), 179 (15), 207 (M^+, 13); HRMS (EI) Calcd. for $C_{13}H_{17}NO_3$ 235.1208, Found 235.1200.

***N,N´*-Dimethyl-4-aminotropone (9d)**. Following the general procedure A from 7 mg (0.02 mmol, 1 equiv) of (±)-*N,N´*-dimethyl-4-amino-4-[(*p*-tolylsulfinyl)methyl]-2,5-cyclohexadienone **(5d),** 0.1 mL of THF and 3 mg (0.10 mmol, 4 equiv) of NaH. Reaction time: 2 h. Purified by chromatography on 500 mg silica gel for amines prepacked cartridges [BondElut LRC-SCX in CH_2Cl_2 and 2.0 M solution of ammonia in MeOH]. Tropone **9d** was obtained pure in a 99% yield as a yellowish oil: ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.86 (s, 3H, CH_3N), 2.87 (s, 3H, CH_3N), 5.80 (dd, J_d = 9.9 and J_d = 2.4 Hz, 1H, H_5), 6.50 (dd, J_d = 11.8 and J_d = 2.7 Hz, 1H, H_7), 6.60-7.00 (ABXY system, J_{AB} = 12.9, J_{AX} = 2.8 and J_{AX} = 2.7 Hz, Δν= 175.9 Hz, 2H, H_2 and H_3), 7.09 (dd, J_d = 11.8 and J_d = 9.9 Hz, 1H, H_6); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 30.2 ($2CH_3N$), 104.5, 128.0, 132.2, 139.1, 142.3, 153.9, 186.2 (C=O); MS (m/z) 55 (14), 76 (21), 77 (10), 88 (20), 89 (14), 91 (15), 93 (16), 107 (26), 120 (13), 121 (10), 124 (13), 135 (80), 137 (70), 139 (38), 150 (M^++1, 7); HRMS (FAB+) Calcd. for C_8H_9NO 135.0684, Found 135.0689.

***N*-Methyl-4-aminotropone (9e)**. Following the general procedure A from 13 mg (0.05 mmol, 1 equiv) of (±)-*N*-methyl-4-amino-4-[(*p*-tolylsulfinyl)methyl]-2,5-cyclohexadienone **(5e)**, 0.3 mL of THF and 5 mg (0.20 mmol, 4 equiv) of NaH. Reaction time: 2 h. Purified by chromatography on 500 mg silica gel for amines prepacked cartridges [BondElut LRC-SCX in CH_2Cl_2 and 2.0 M solution of ammonia in MeOH]. Tropone **9e** was obtained pure in a 70% yield as a yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.13 (s, 3H, CH_3NH), 6.00 (dd, J_d = 9.9 and J_d = 1.9 Hz, 1H, H_5), 6.51 (dd, J_d = 11.1 and J_d = 2.0 Hz, 1H, H_7), 7.08-7.11 (m, 2H, H_2 and H_3), 7.09 (dd, J_d = 11.1 and J_d = 9.9 Hz, 1H, H_6); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 29.7 (CH_3-), 108.6, 128.1, 128.2, 138.5, 142.2, 155.6, 185.8 (C=O); MS (m/z) 55 (26), 57 (33), 65 (18), 68 (19), 71 (14), 71 (22), 77 (34), 84 (17), 106 (100), 107 (76), 120 (20), 135 (M^+, 38); HRMS (EI) Calcd. for C_8H_9NO 135.0684, Found 135.0689.

***N*-Benzyl-4-aminotropone (9f)**. Following the general procedure A from 23 mg (0.07 mmol, 1 equiv) of (±)-*N*-benzyl-4-amino-4-[(*p*-tolylsulfinyl)methyl]-2,5-cyclohexadienone **(9f)**, 0.3 mL of THF and 6 mg (0.26 mmol, 4 equiv) of NaH. Reaction time: 2 h. Purified by chromatography on 500 mg silica gel for amines prepacked cartridges [BondElut LRC-SCX

in CH_2Cl_2 and 2.0 M solution of ammonia in MeOH]. Tropone **9f** was obtained in a 99% yield as green-yellowish oil, that slowly decomposes on standing at rt. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.31 (s, 2H, CH_2-Ph), 5.87 (dd, J_d = 10.5 and J_d = 2.9 Hz, 1H, H_5), 6.51 (dd, J_d = 12.3 and J_d = 2.7 Hz, 1H, H_7), 6.63-7.03 (ABX system, J_{AB} = 12.4, J_{AX} = 2.7 Hz, Δν =64.0 Hz, 2H, H_2 and H_3), 7.06 (dd, J_d = 12.4 and J_d = 10.5 Hz, 1H, H_6), 7.31-7.42 (m, 5H, Ph); MS (m/z) 57 (12), 60 (12), 65 (19), 66 (34), 91 (100), 121 (M^+-91, 36); HRMS (EI) Calcd. for $C_{14}H_{13}NO$ –C_7H_7 121.0528, Found 121.0522.

4-Aminotropone (10a). Following the general procedure A from 77 mg (0.28 mmol, 1 equiv) of 4-amino-4-[(*p*-tolylsulfonyl)methyl]-2,5-cyclohexadienone **(8a)**, 1.4 mL of THF and 27 mg (1.11 mmol, 4 equiv) of NaH. Reaction time: 6 h. Purified by chromatography on 500 mg silica gel for amines prepacked cartridges [BondElut LRC-SCX in CH_2Cl_2 and 2.0 M solution of ammonia in MeOH]. Tropone **10a** was obtained pure in a 99% yield as a yellowish oil: ^{1}H-NMR (300 MHz, MeOD-d_4) δ 6.38 (dd, J_d = 10.3 and J_d = 1.2 Hz, 1H, H_5), 6.47 (dd, J_d = 11.5 and J_d = 2.0 Hz, 1H, H_7), 7.06-7.16 (AB system, J_{AB} = 14.1 Hz, Δν =2.1 Hz, 2H, H_2 and H_3), 7.20 (dd, J_d = 11.3 and J_d = 10.3 Hz, 1H, H_6); ^{13}C-RMN (75 MHz, MeOD-d_4) δ 113.1, 127.2, 134.6, 144.1, 144.9, 161.3, 187.5 (C=O); MS (m/z) 57 (12), 60 (12), 65 (19), 66 (34), 93 (100), 121 (M^+, 36); HRMS (EI) Calcd. for C_7H_7NO 121.0527, Found 121.0533.

4-Amino-3-methyltropone (10b). Following the general procedure A from 13 mg (0.04 mmol, 1 equiv) of (±)-4-amino-3-methyl-4-[(*p*-tolylsulfonyl)methyl]-2,5-cyclohexadienone **(8b)**, in 0.3 mL of THF and 5 mg (0.18 mmol, 4 equiv) of NaH. Reaction time: 24 h. Purified by chromatography on 500 mg silica gel for amines prepacked cartridges [BondElut LRC-SCX in CH_2Cl_2 and 2.0 M solution of ammonia in MeOH]. Topone **10b** was obtained pure in a 97% yield as a yellowish oil: ^{1}H-NMR (300 MHz, Acetone-d_6) δ 2.33 (d, J_d= 1.0 Hz, 3H, CH_3-), 6.06-6.25 (brs, 2H, NH_2), 6.39 (d, J_d = 10.3 Hz, 1H, H_5), 6.44 (dd, J_d = 11.3 and J_d = 2.8 Hz, 1H, H_7), 7.02 (dd, J_d = 11.5 and J_d = 10.3 Hz, 1H, H_6), 7.14 (J_d = 2.1 and J_d = 1.0 Hz, 1H, H_2); ^{13}C-NMR (75 MHz, Acetone-d_6) δ 24.6 (CH_3-), 111.0, 128.7, 140.1, 146.0, 157.7, 163.0, 185.4 (C=O); MS (m/z) 55 (20), 57 (19), 58 (64), 63 (13), 65 (19), 69 (54), 77 (23), 91 (70), 92 (25), 107 (20), 123 (22), 124 (51), 135 (M^+, 5); HRMS (EI) Calcd. for C_8H_9NO 135.0684, Found 135.0687.

4-Amino-5-methyltropone (10c). Following the general procedure A from 17 mg (0.06 mmol, 1 equiv) of (±)-4-amino-4-[1´-methyl-1´-benzenesulfonyl)methyl]-2,5-cyclohexadienone **(8c)**, 0.3 mL of THF and 6 mg (0.24 mmol, 4 equiv) of NaH. Reaction time: 2 h and the crude was purified by chromatography on 500 mg silica gel for amines prepacked cartridges [BondElut LRC-SCX in CH_2Cl_2 and 2.0 M solution of ammonia in MeOH]. Tropone **10c** was obtained in a 99% yield as pale yellow crystals: M.p. 148-150 ºC

(acetone), ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.20 (s, 3H, CH_3-), 4-20-4.40 (brs, 2H, NH_2), 6.58-7.08 (ABX system, J_{AB} = 12.3 and J_{AX} = 3.0 Hz, Δν =140.8 Hz, 2H, H_2 and H_3), 6.74-7.02 (dd, J_d = 12.9 and J_d = 3.0 Hz, 2H, H_6 and H_7); ^{13}C-RMN (125 MHz, Acetone-d_6) δ 22.3 (CH_3-), 117.7, 128.8, 133.6, 142.2, 144.4, 153.0, 185.7 (C=O); MS (m/z) 55 (13), 57 (15), 77 (19), 79 (14), 80 (10), 106 (100), 107 (86), 135 (M^+, 45); HRMS (EI) Calcd. for C_8H_9NO 135.0684, Found 135.0690.

Diels-Alder Adduct (11). To a solution of 50 mg (0.23 mmol, 1 equiv) *N-(tert*-butoxycarbonyl)-4-aminotropone **(9a)** in 2 mL of toluene, 44 mg (0.45 mmol, 2 equiv) of maleimide were added under an argon atmosphere. The reaction mixture was allowed to reflux for 24 h. After removal of the solvent at reduced pressure, the crude was purified by column chromatography on silica gel (eluent Hexane:AcOEt, 1:1). Compound **11** was obtained in 74% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.49 (s, 9H, ^{t}Bu), 3.37 (d, J_d = 7.6 Hz, 1H, H_6), 3.69 (d, J_d = 8.8 Hz, 1H, H_2), 3.95 (d, J_d = 7.4 Hz, 1H, H_7), 5.75 (dd, J_d = 11.5 and J_d = 1.9 Hz, 1H, H_{12}), 6.10 (t, J_t = 7.7 Hz, 1H, H_9), 6.48 (d, J_d = 8.7 Hz, 1H, H_{10}), 6.70 (brs, 1H, NHBOC), 7.19 (d, J_d = 11.5 Hz, 1H, H_{11}), 8.18 (s, 1H,-C(O)-NH-C(O)-); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 28.3 (3C, ^{t}Bu), 42.4, 48.4, 53.0, 58.9, 81.0 (^{t}BuOC(O)-), 124.0, 125.9, 135.1, 140.9, 156.5, 175.0 (C=O), 175.4 (C=O), 191.6 (C=O); MS (m/z) 57 (100), 59 (13), 65 (11), 69 (15), 77 (11), 93 (45), 97 (24), 119 (14), 121 (10), 130 (159), 131 (10), 146 (13), 149 (14), 173 (16), 190 (12), 201 (14), 217 (25), 218 (29), 245 (11), 262 (M^+-56, 6). HRMS (EI) Calcd. for $C_{12}H_{10}N_2O_5$ 262.0589, Found 262.0582.

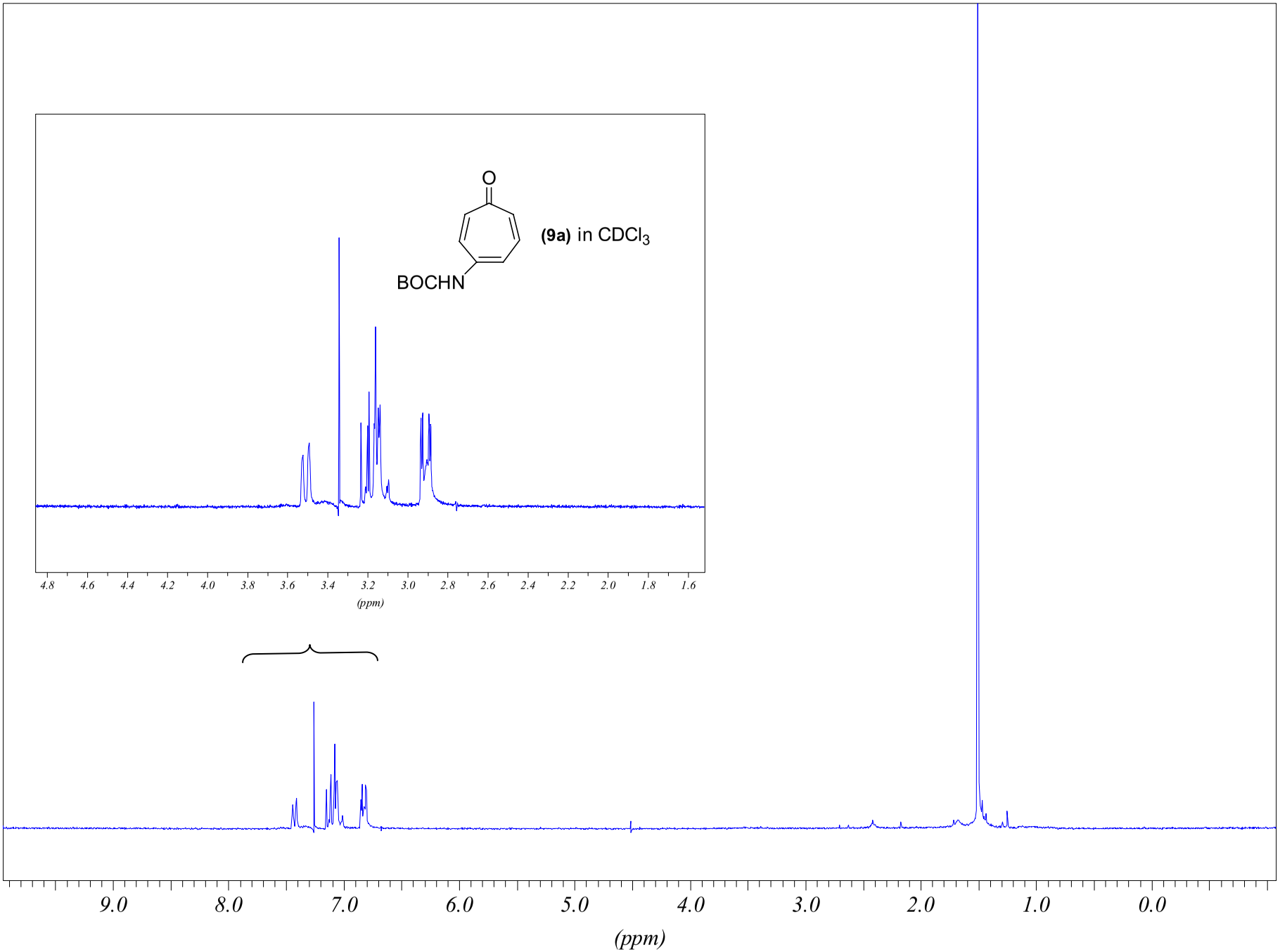
(±)-*N-(tert*-Butoxycarbonyl)-1-amino-[3.2.0]hepta-2,6-dien-4-ona (12). A solution of 50 mg (0.23 mmol, 1 equiv) *N-(tert*-butoxycarbonyl)-4-aminotropone **(9a)** in 2 mL of CH_3CN was degasified with a stream of dry argon for 15 min. Then, the reaction mixture was irradiated with a high pressure Hg lamp (400 W) under continuous stirring for 4 h at room temperature (overheating was not detected). The reaction was monitored by TLC and after 4 h the solvent was removed in vacuo without overheating the water bath, (water bath temperature 20-25 ºC since the 4π-electrocyclic reaction is reversible). The bicyclic dienone **12** was obtained in a 60% yield after flash column chromatography on silica gel (CH_2Cl_2:AcOEt, 9:1): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.43 (s, 9H, ^{t}Bu), 3.33 (s, 1H, H_5), 5.12 (brs, 1H, NHBOC), 5.96 (d, J_d = 6.9 Hz, 2H, H_3), 6.54 (d, J_d = 2.2 Hz, 2H, H_6), 6.67 (s, 1H, H_7),), 7.57 (d, J_d = 6.9 Hz, 2H, H_2); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 28.7 (3C, ^{t}Bu), 58.7, 68.3, 81.0 (^{t}BuOC(O)-), 131.6, 139.6, 143.1, 155.1, 161.3, 200.6 (C=O); MS (m/z) 58 (21), 59 (37), 64 (10), 65 (259, 66 (22), 77 (15), 83 (129, 91 (16), 93 (100), 105 (13), 119 (17), 121 (24), 137 (27), 147 (25), 221 (M^{+1}, 0.28); HRMS (EI) Calcd. for $C_{12}H_{15}NO_3$ 221.10519, Found 221.10469; IR (neat) 3055, 2931, 2306, 1706, 1597, 1548, 1485, 1422, 1394, 1369, 1238, 1159, 1061, 896 cm^{-1}.

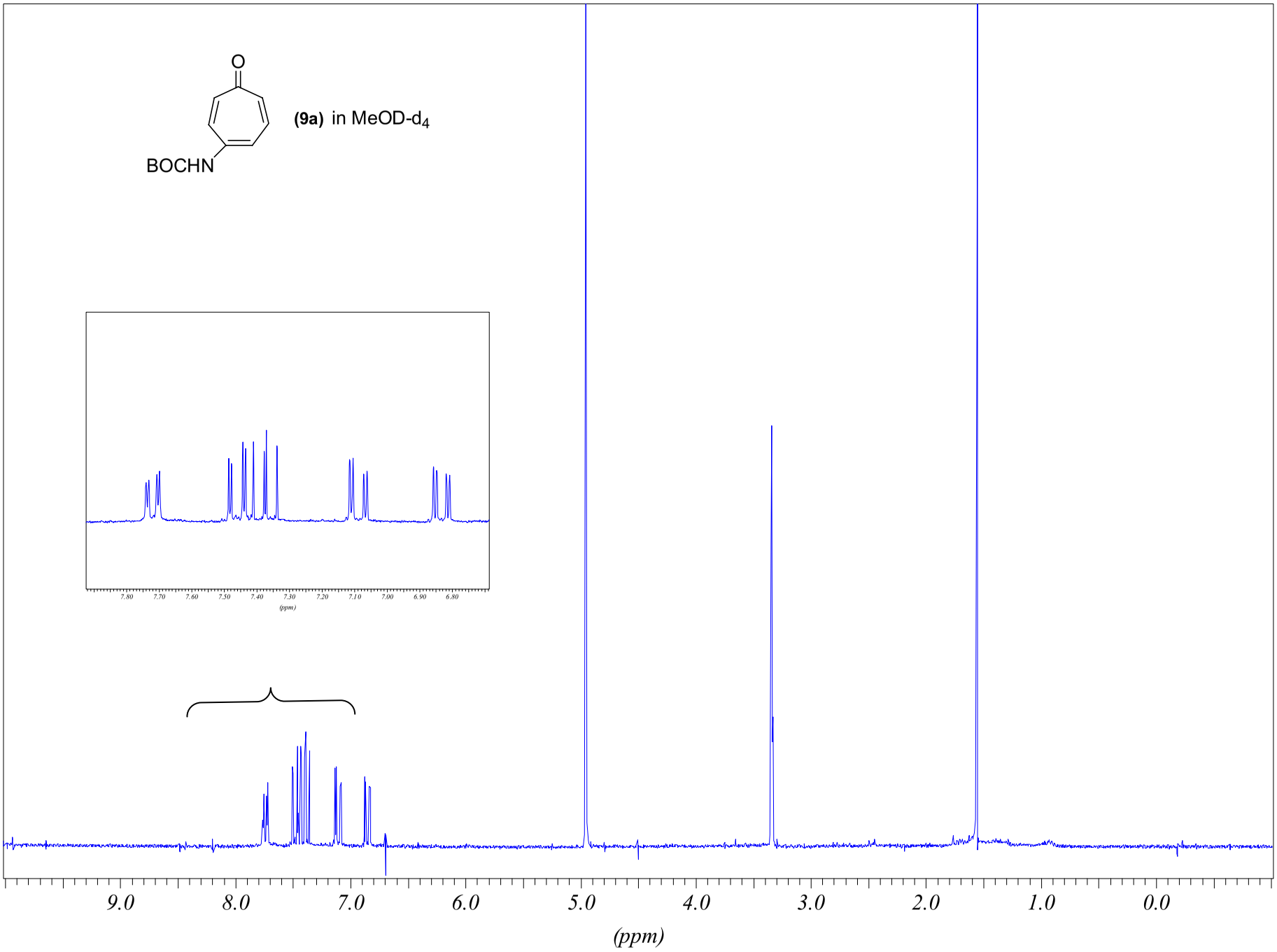
SUPPORTING INFORMATION FOR

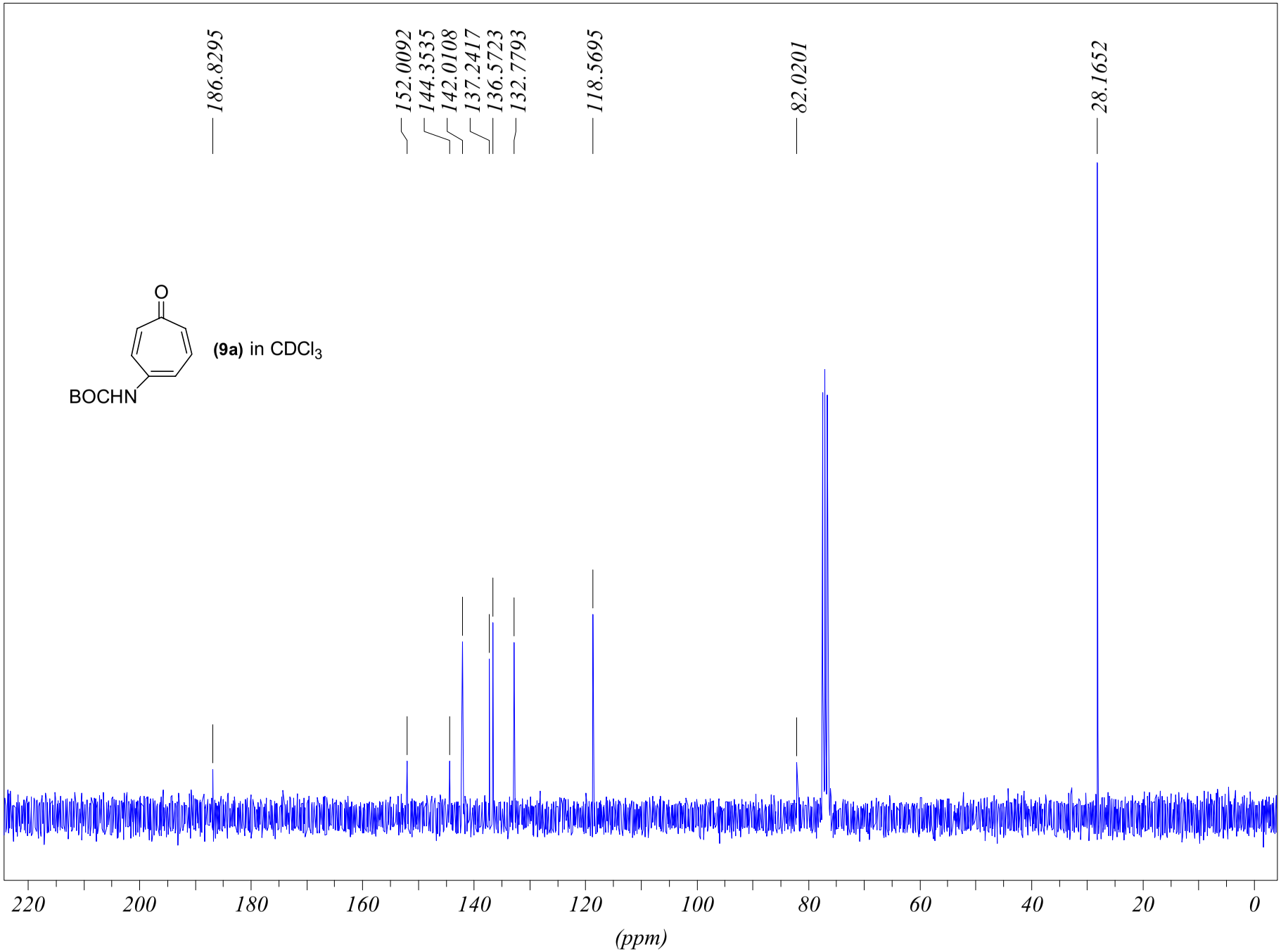
Regiospecific Synthesis of 4-Aminotropones by Ring Expansion of Sulfur Substituted *p*-Quinamines

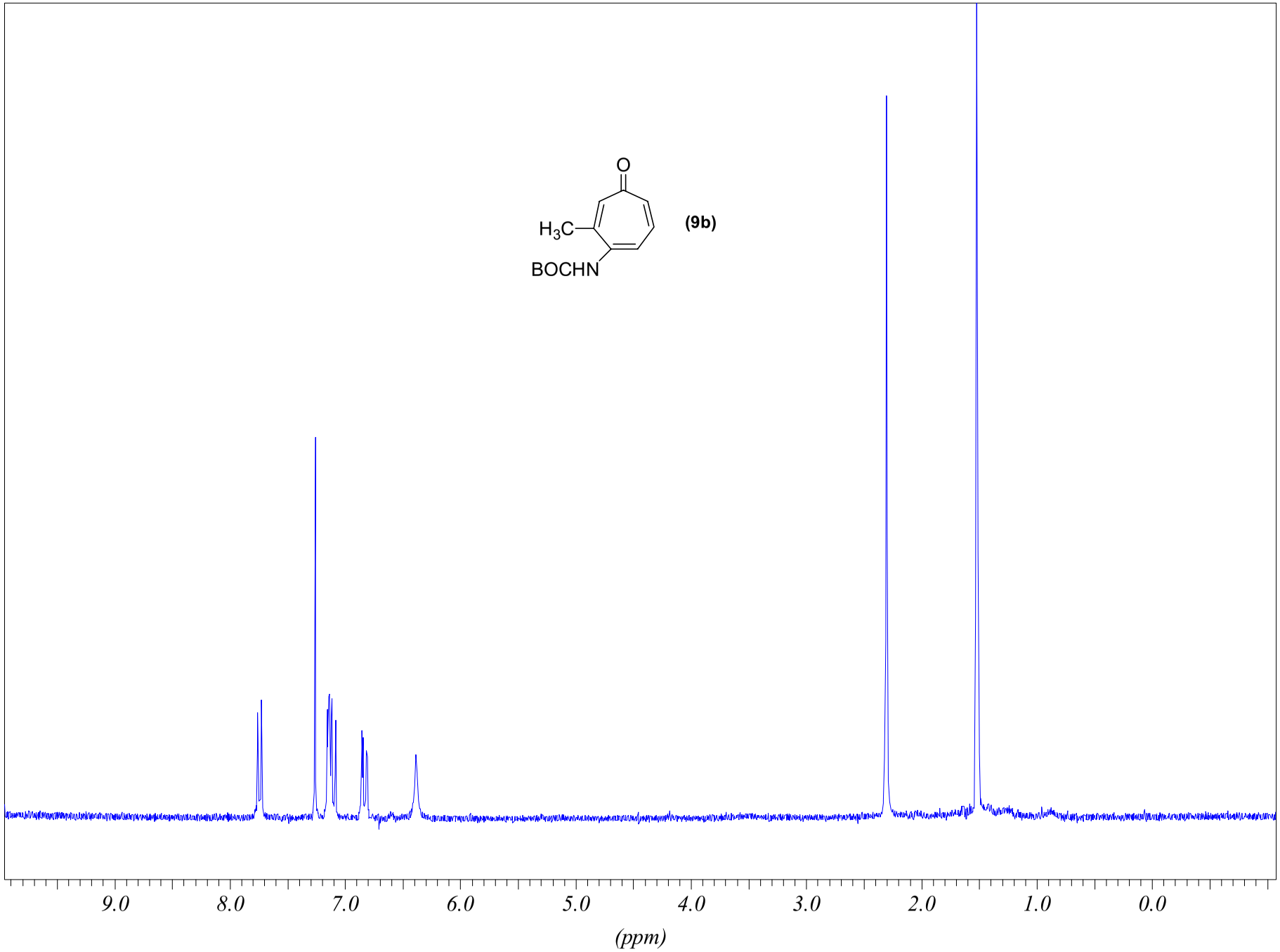
M. Carmen Carreño, M. Jesús Sanz-Cuesta, María Ribagorda*

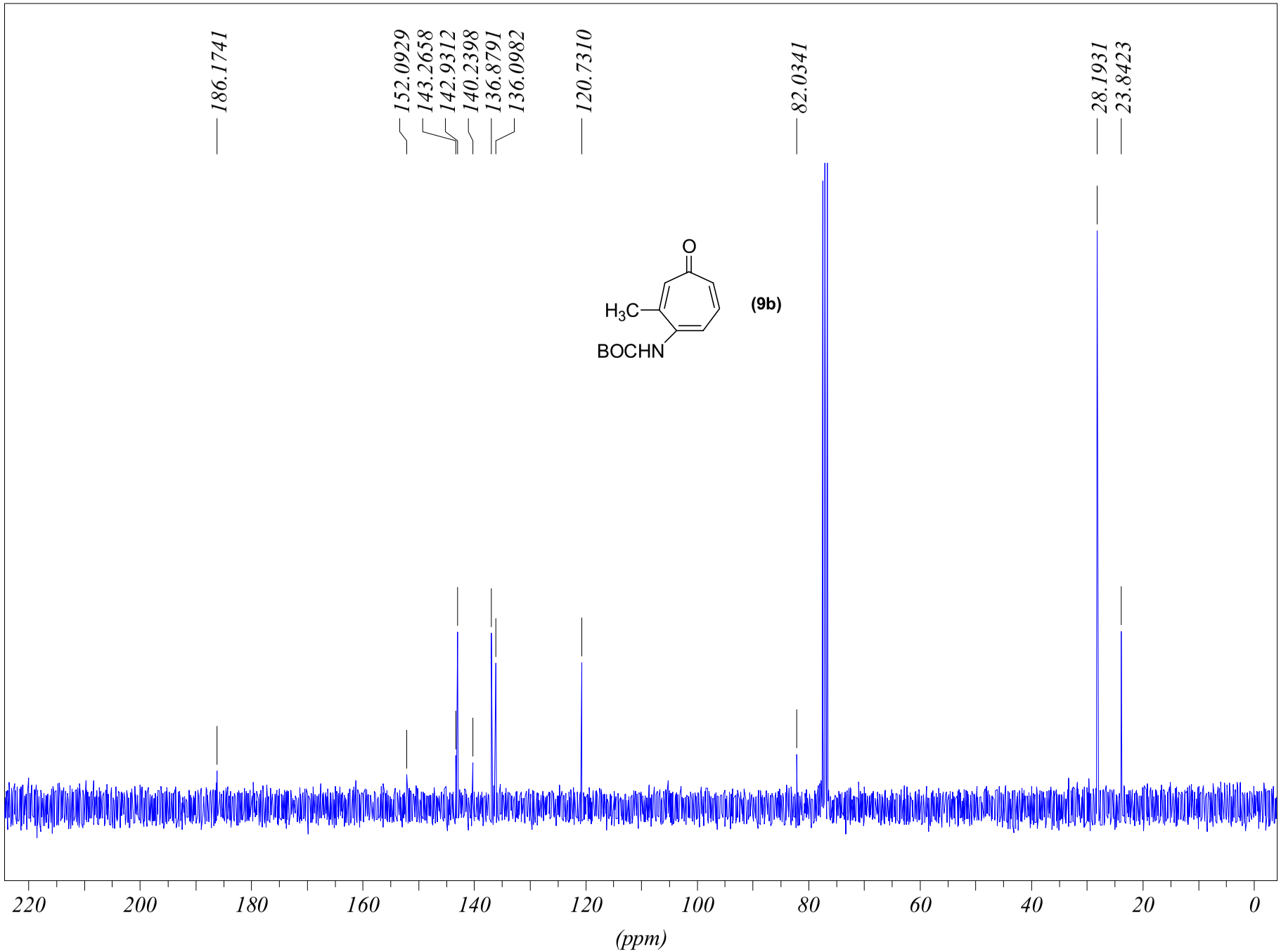
Table of contents

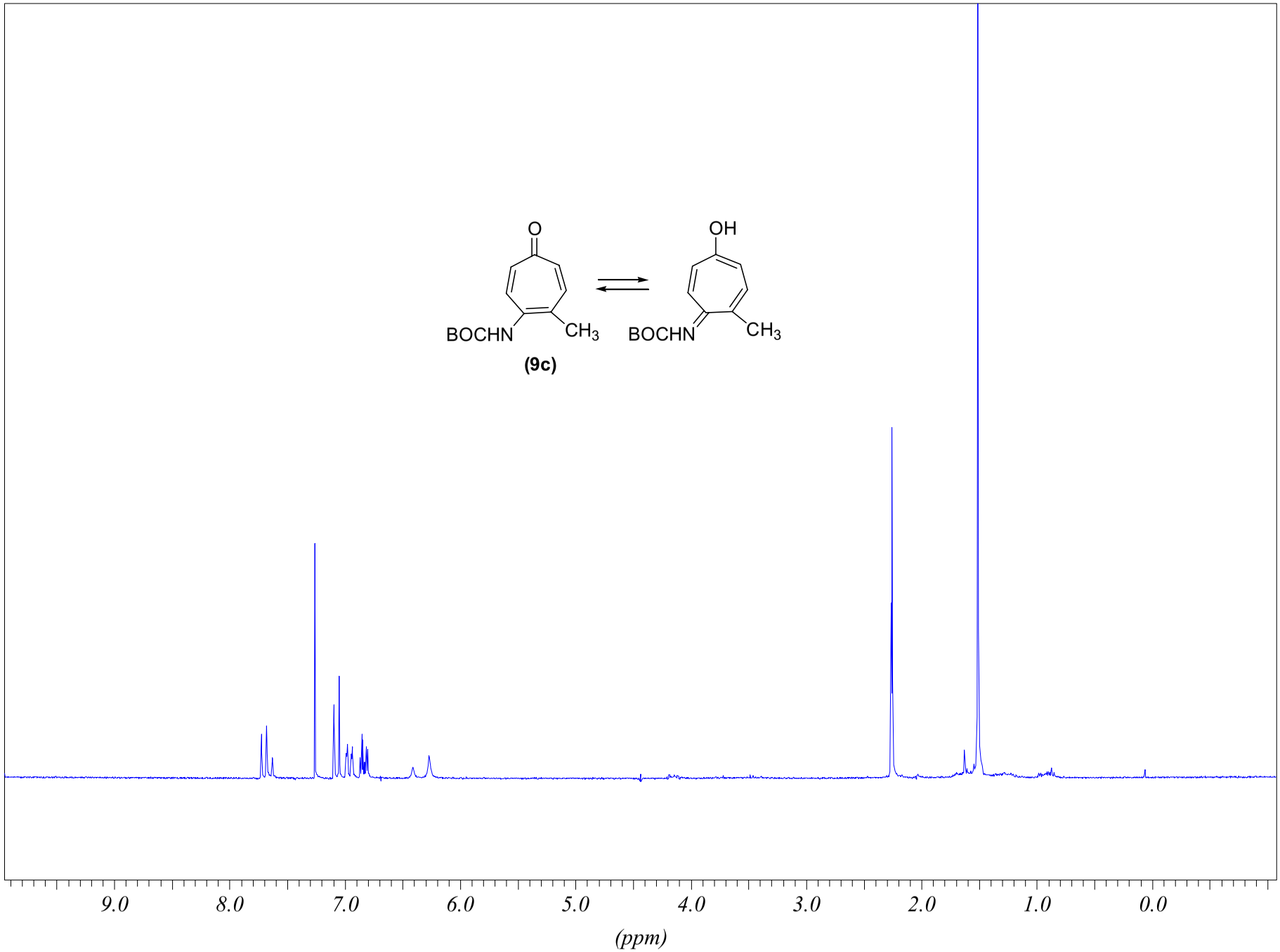

O
BOCHN
(9a) in CDCl3
4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
(ppm)
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
(ppm)

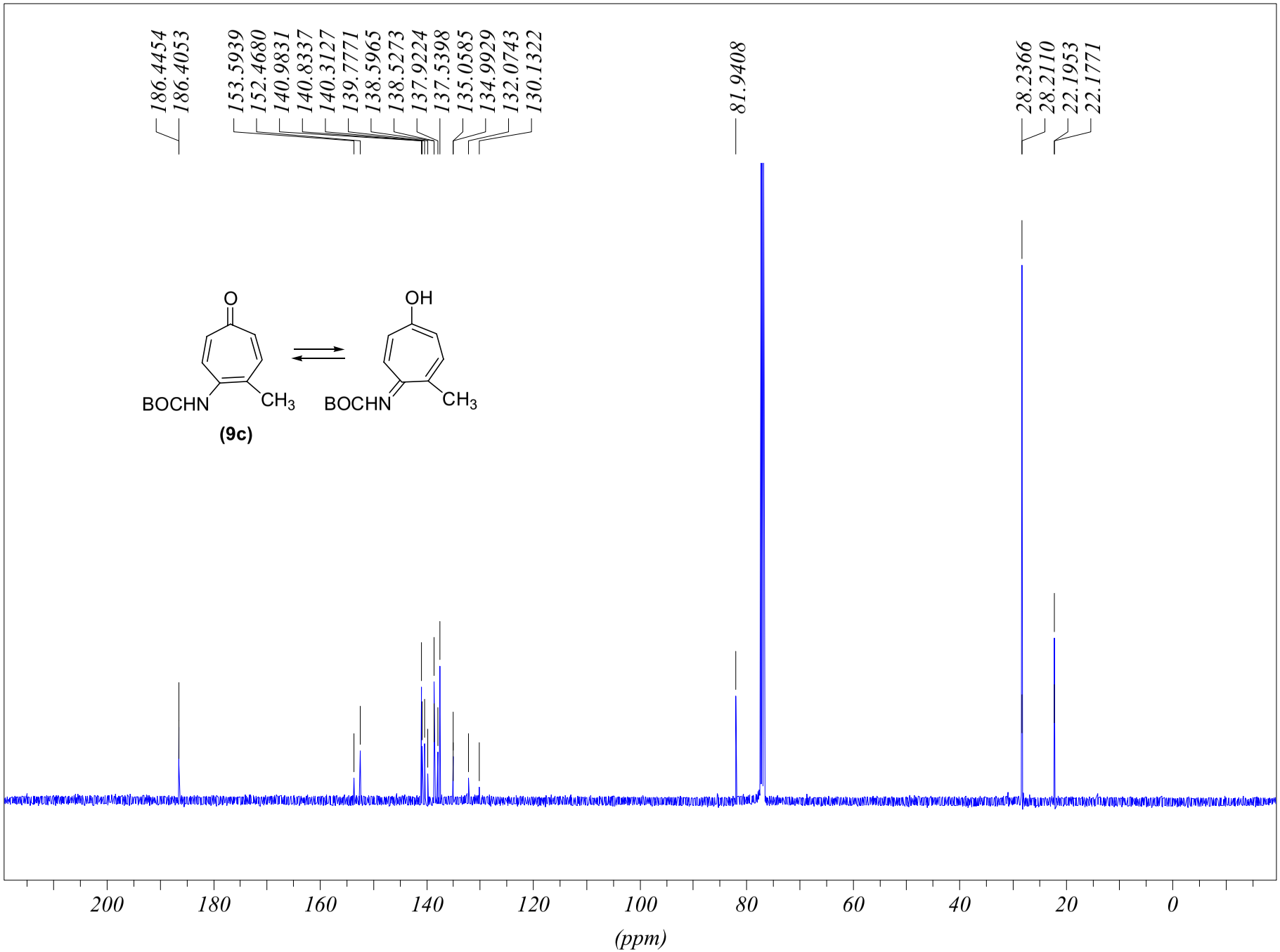

O
BOCHN
(9a) in MeOD-d4
7.80 7.70 7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80
(ppm)
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
(ppm)

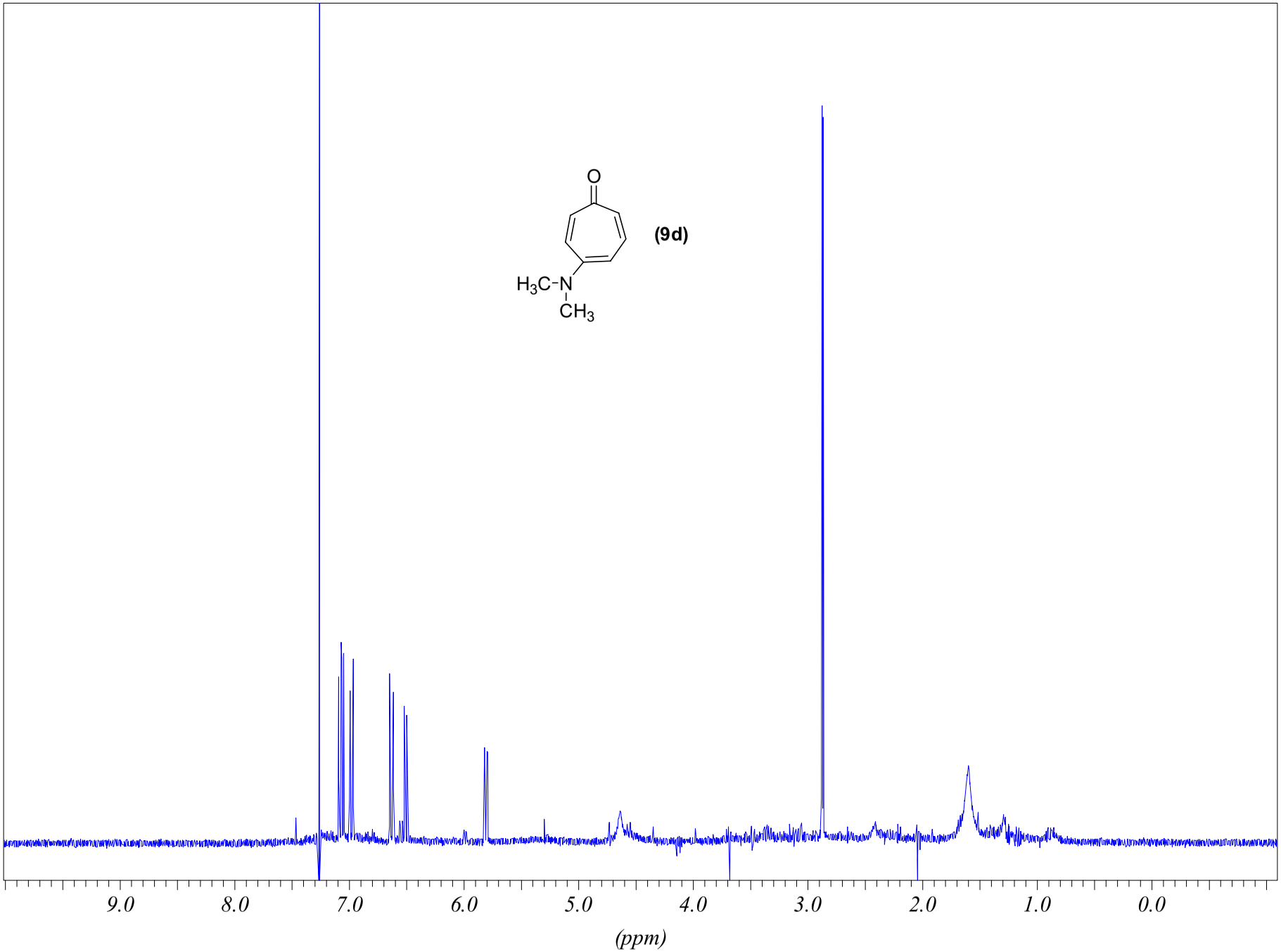

186.8295
152.0092
144.3535
142.0108
137.2417
136.5723
132.7793
118.5695
82.0201
28.1652
O
BOCHN
(9a) in CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

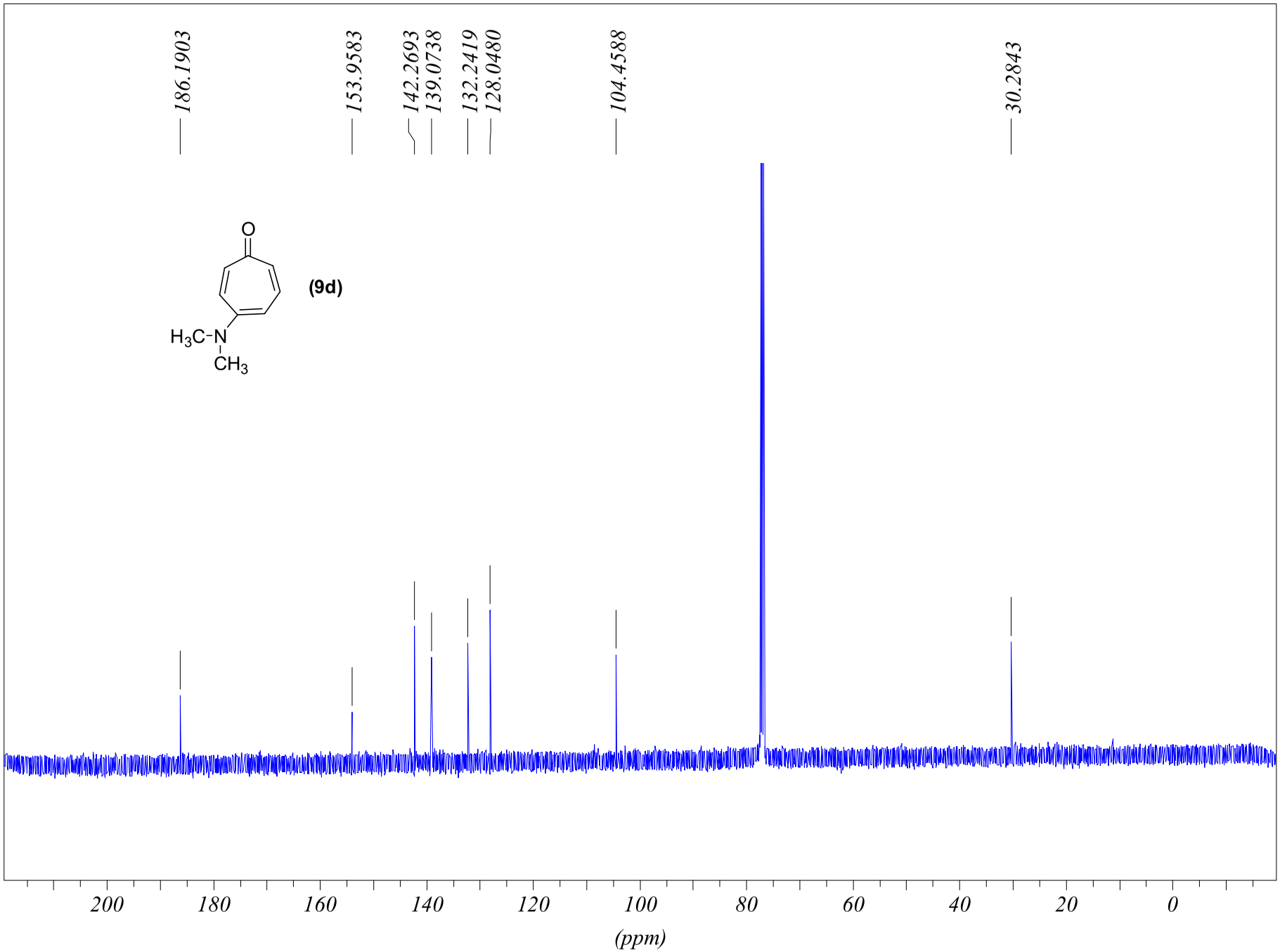

O
H3C
BOCHN
(9b)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

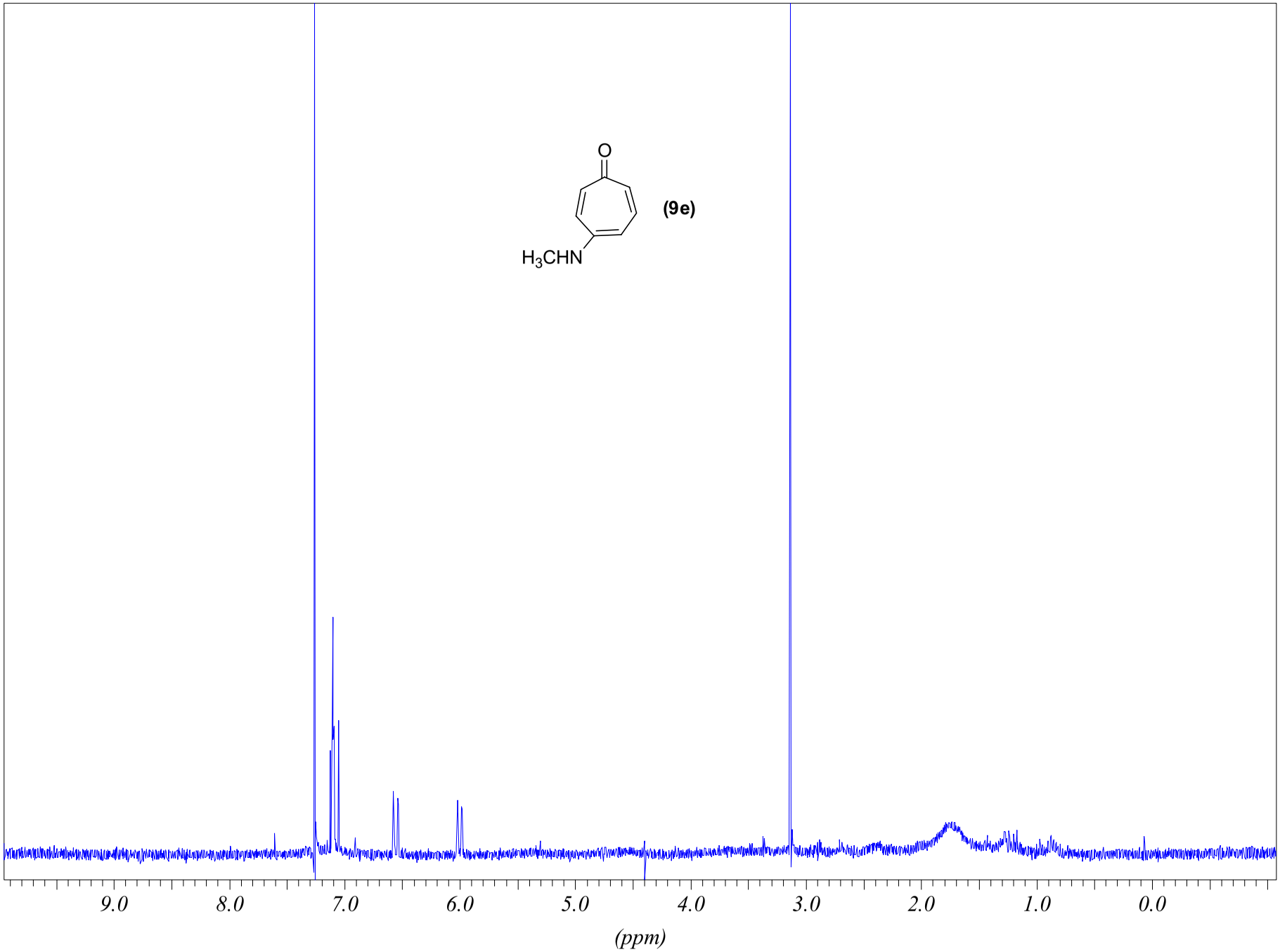

186.1741
152.0929
143.2658
142.9312
140.2398
136.8791
136.0982
120.7310
82.0341
28.1931
23.8423
O
H3C
BOCHN
(9b)
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

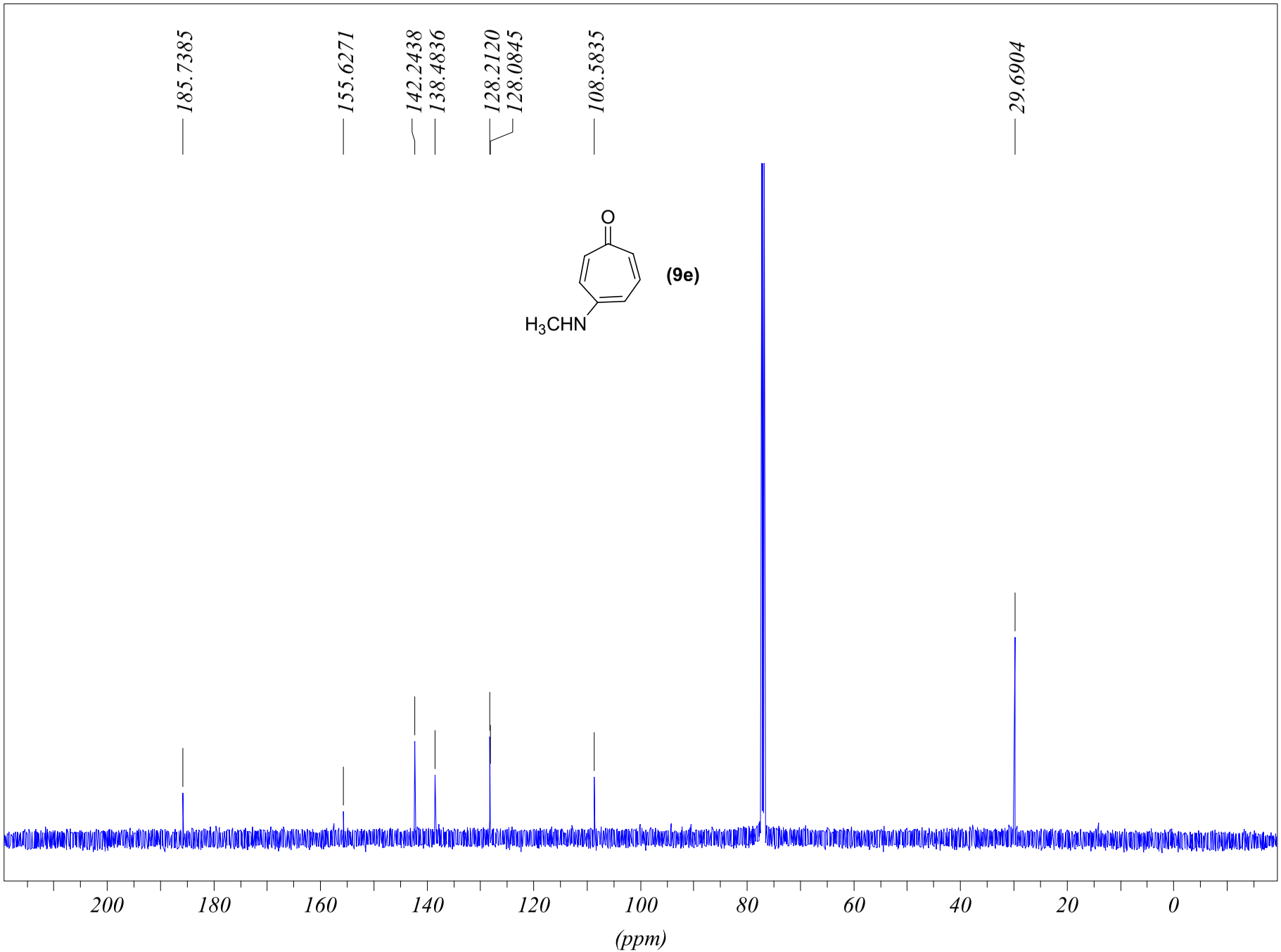

O
OH
BOCHN
CH3
BOCHN
CH3
(9c)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

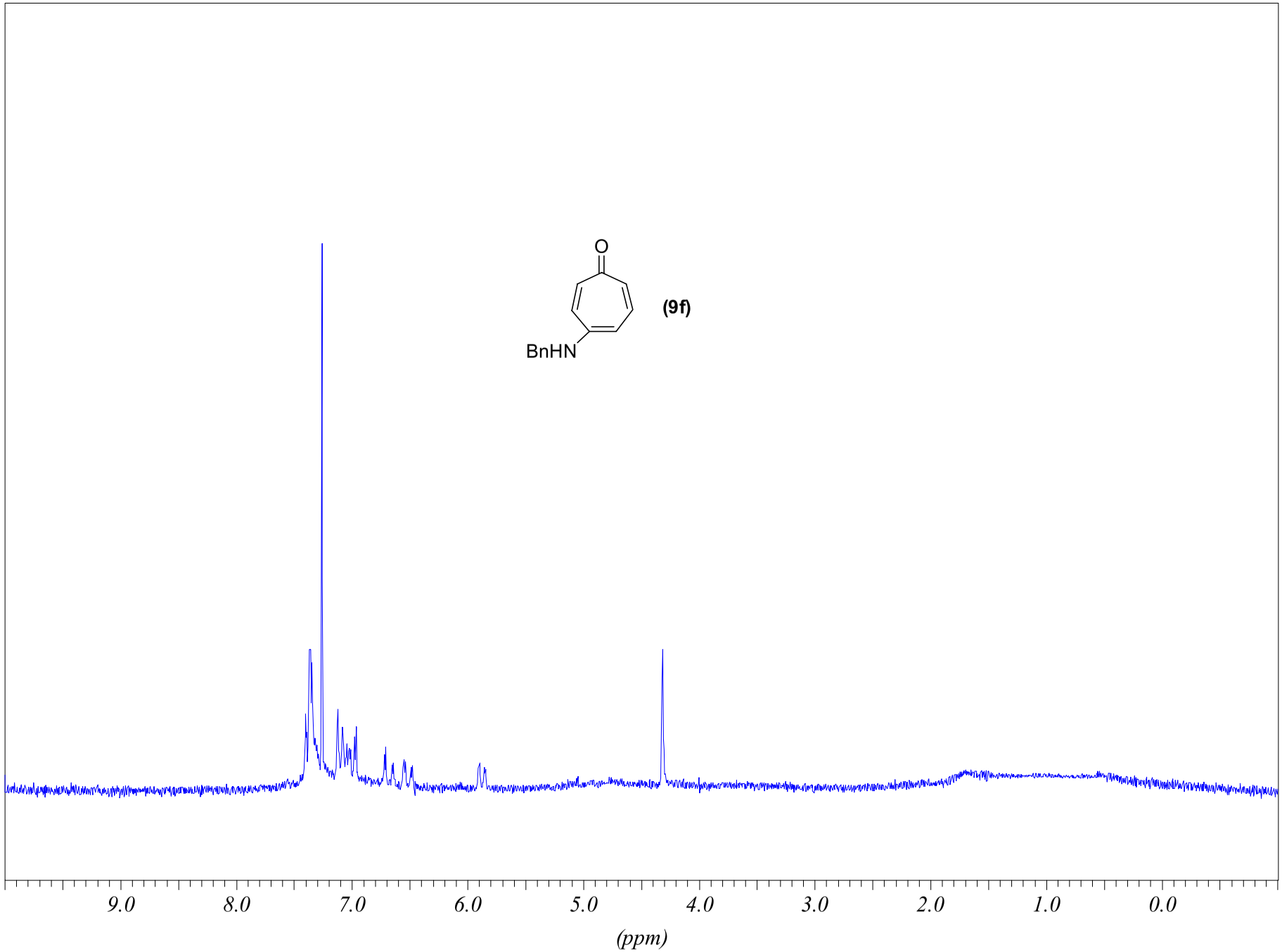

186.4454
186.4053
153.5939
152.4680
140.9831
140.8337
140.3127
139.7771
138.5965
138.5273
137.9224
137.5398
135.0585
134.9929
132.0743
130.1322
81.9408
28.2366
28.2110
22.1953
22.1771
O
OH
BOCHN
CH3
BOCHN
CH3
(9c)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

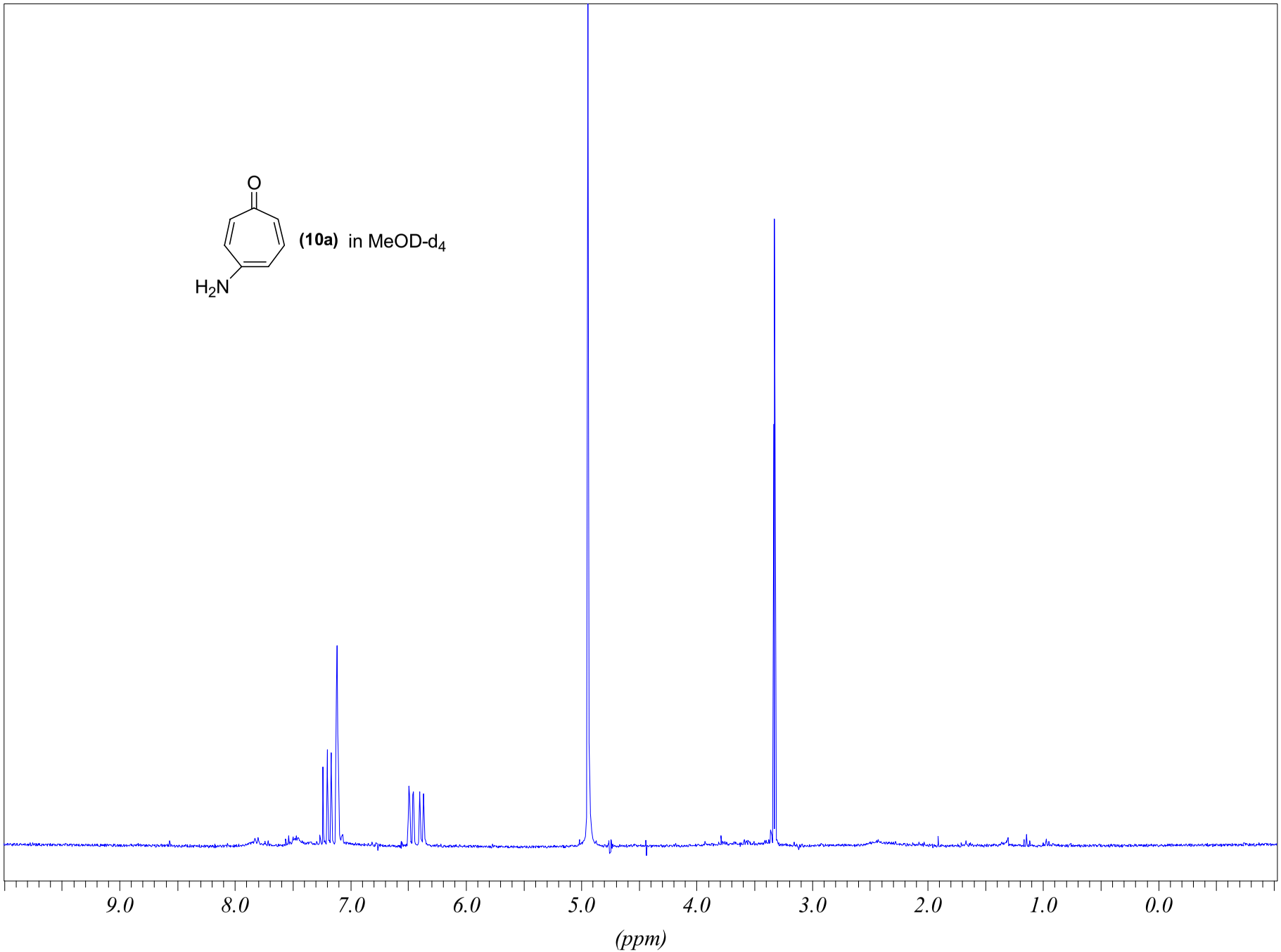

O
H3C-N
CH3
(9d)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

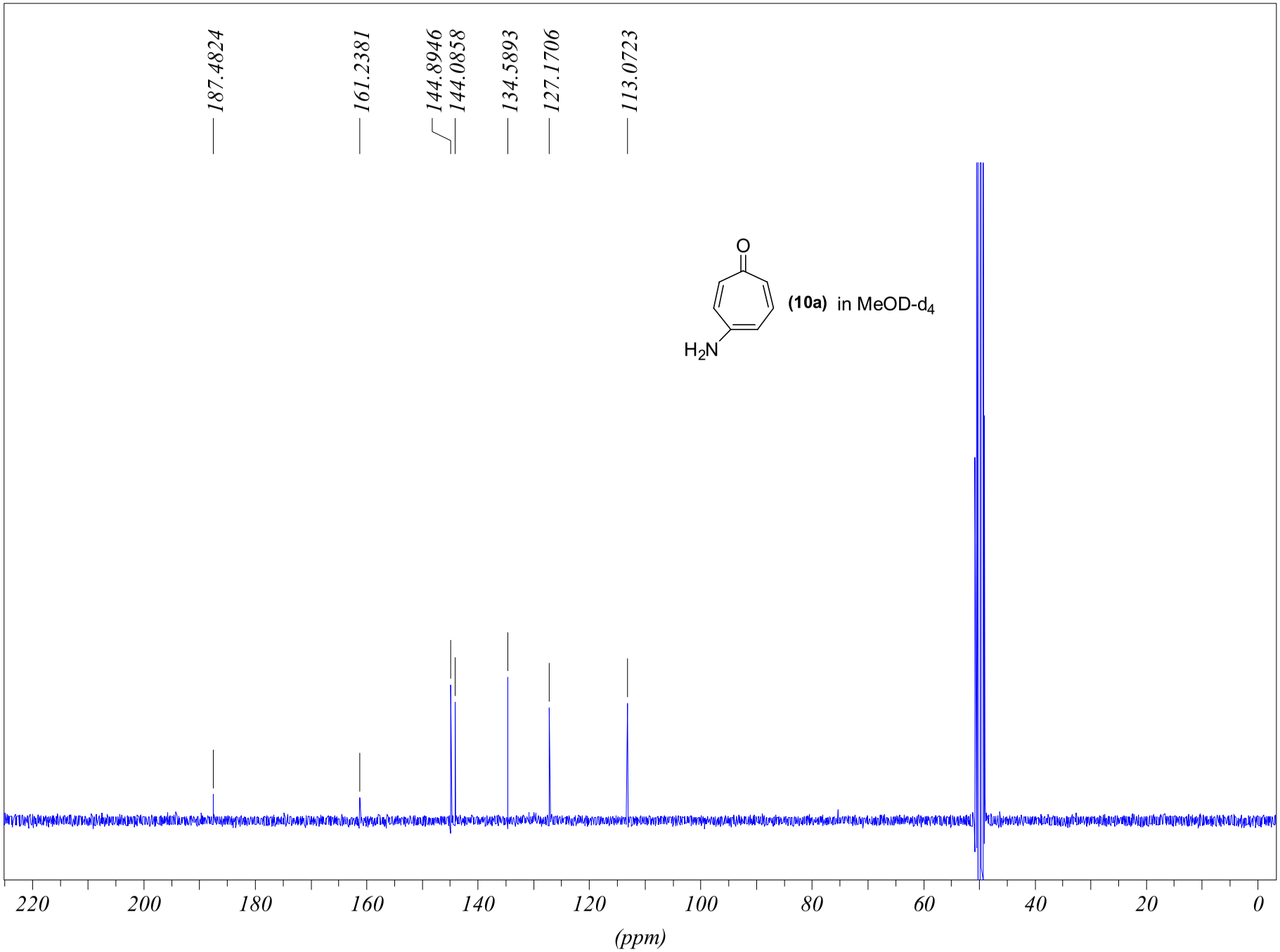

186.1903
153.9583
142.2693
139.0738
132.2419
128.0480
104.4588
30.2843
O
H3C-N
CH3
(9d)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

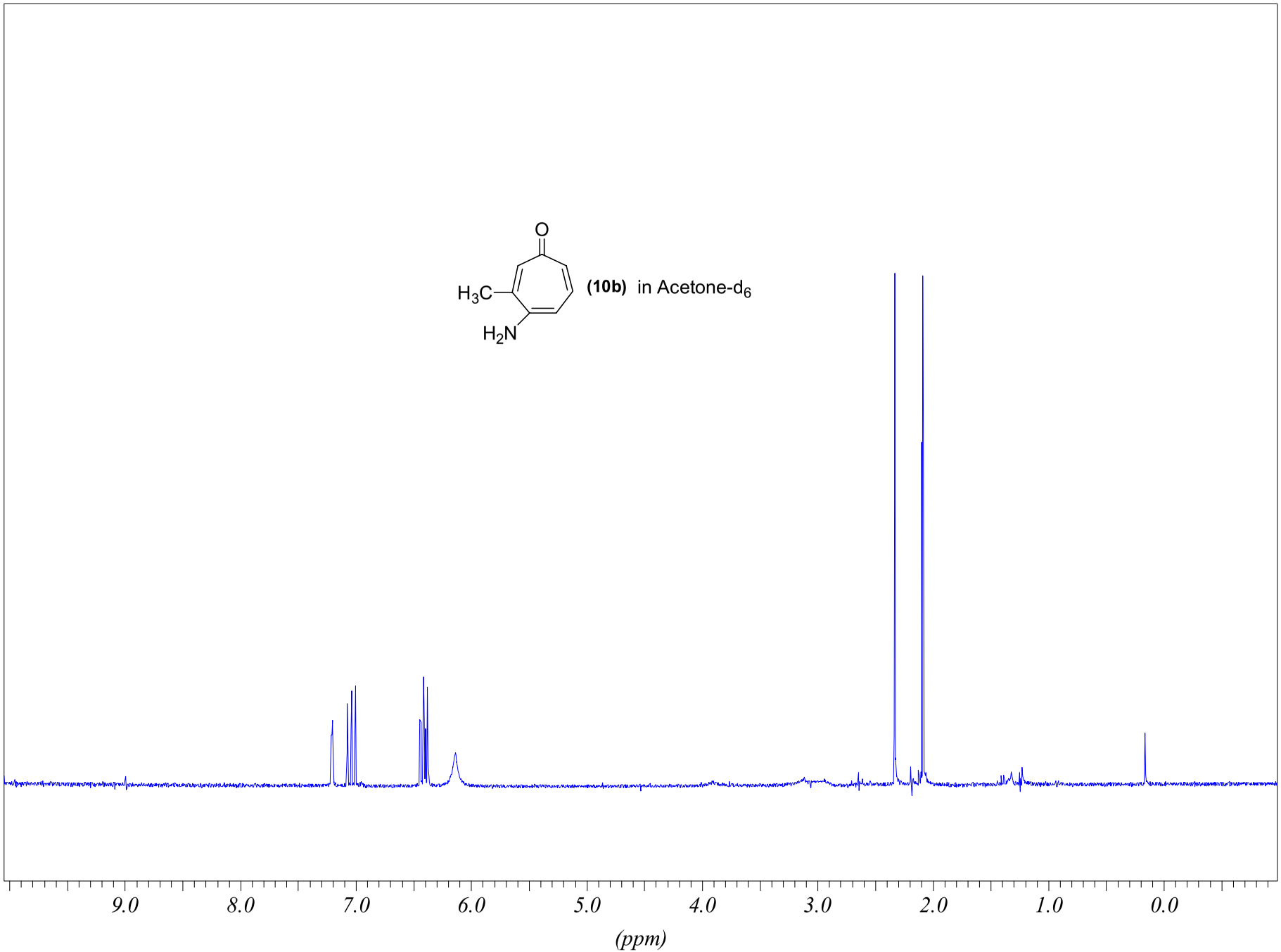

O
H3CHN
(9e)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

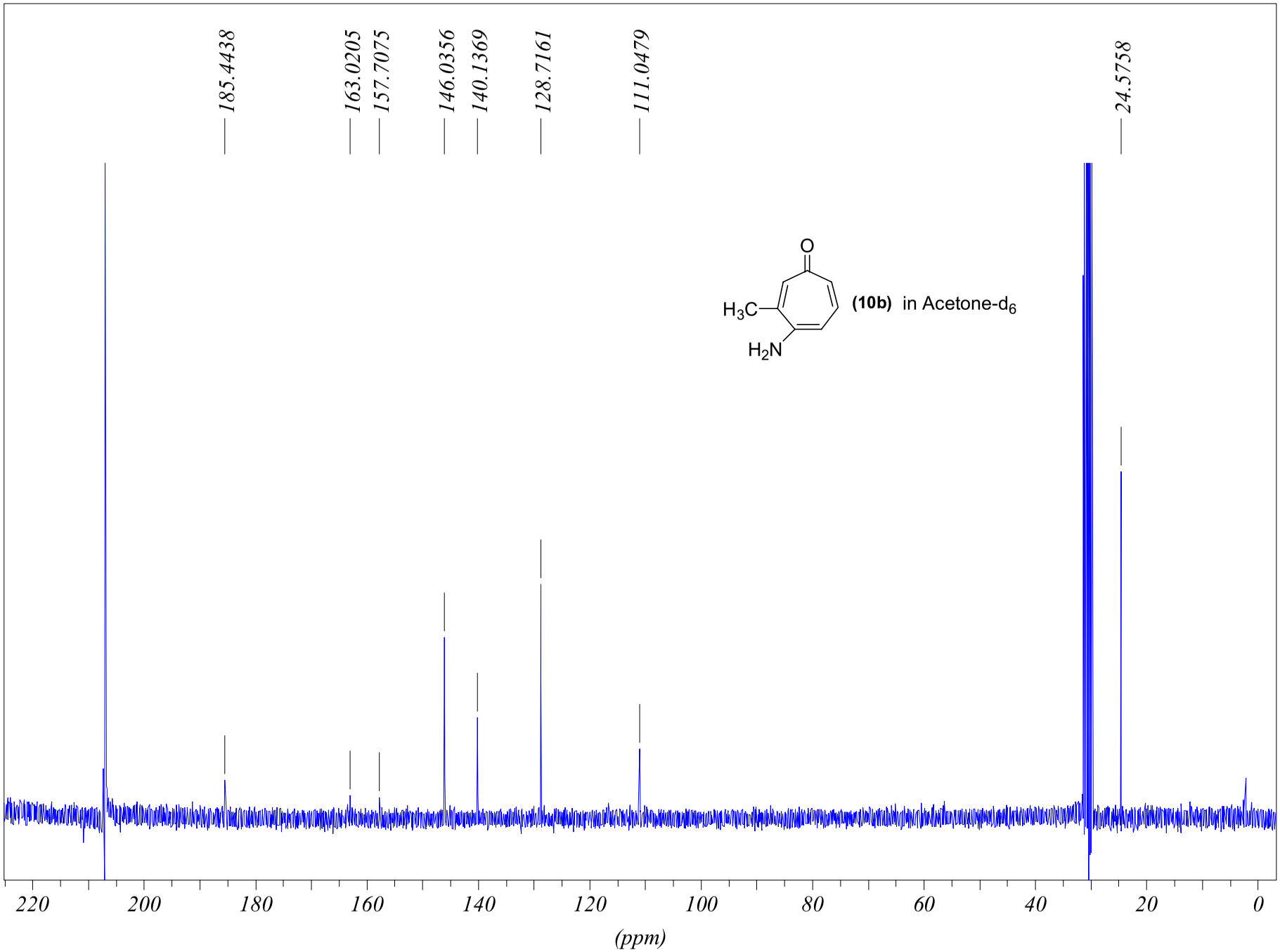

185.7385
155.6271
142.2438
138.4836
128.2120
128.0845
108.5835
29.6904
O
H3CHN
(9e)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

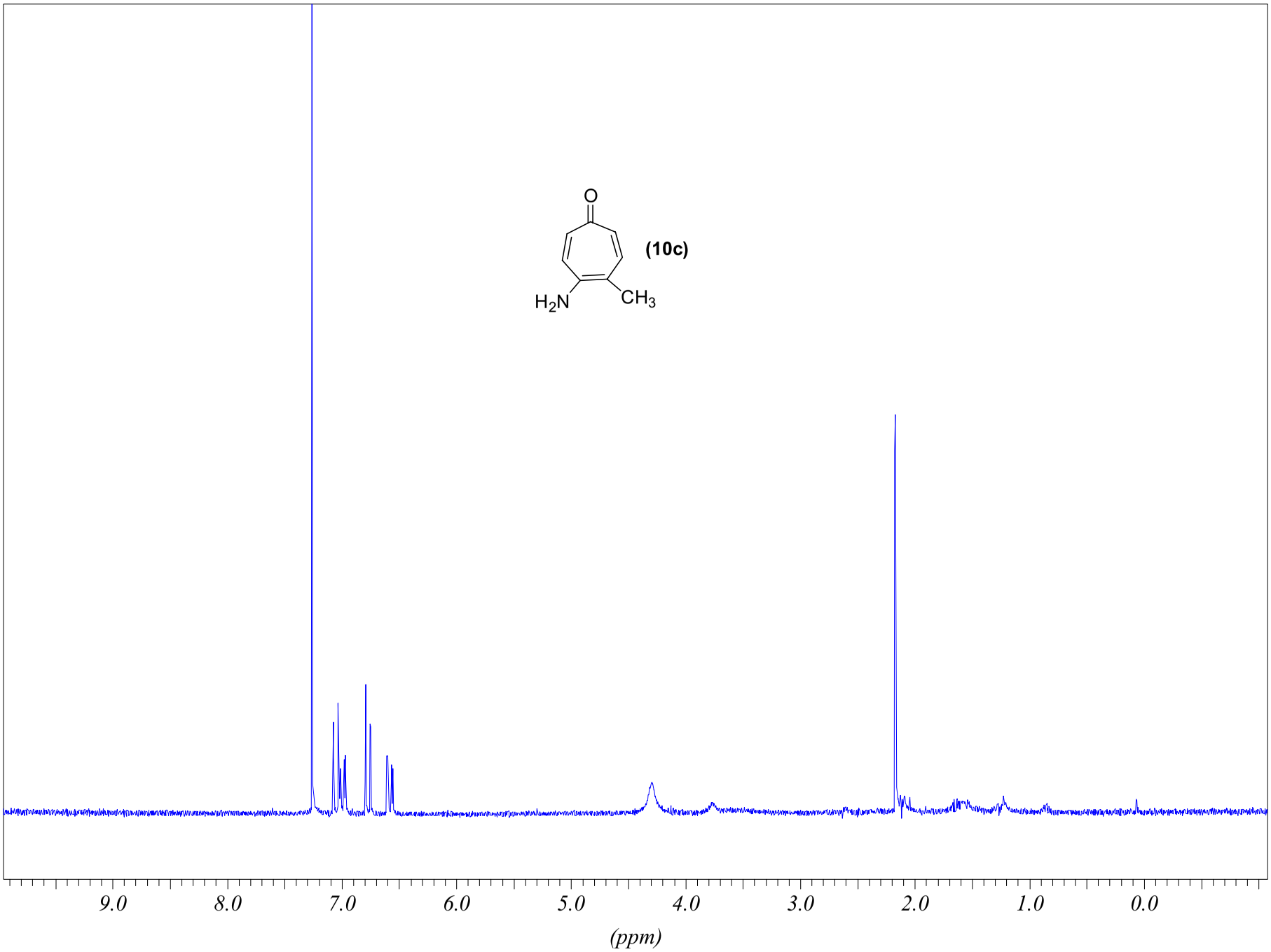

O
BnHN
(9f)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

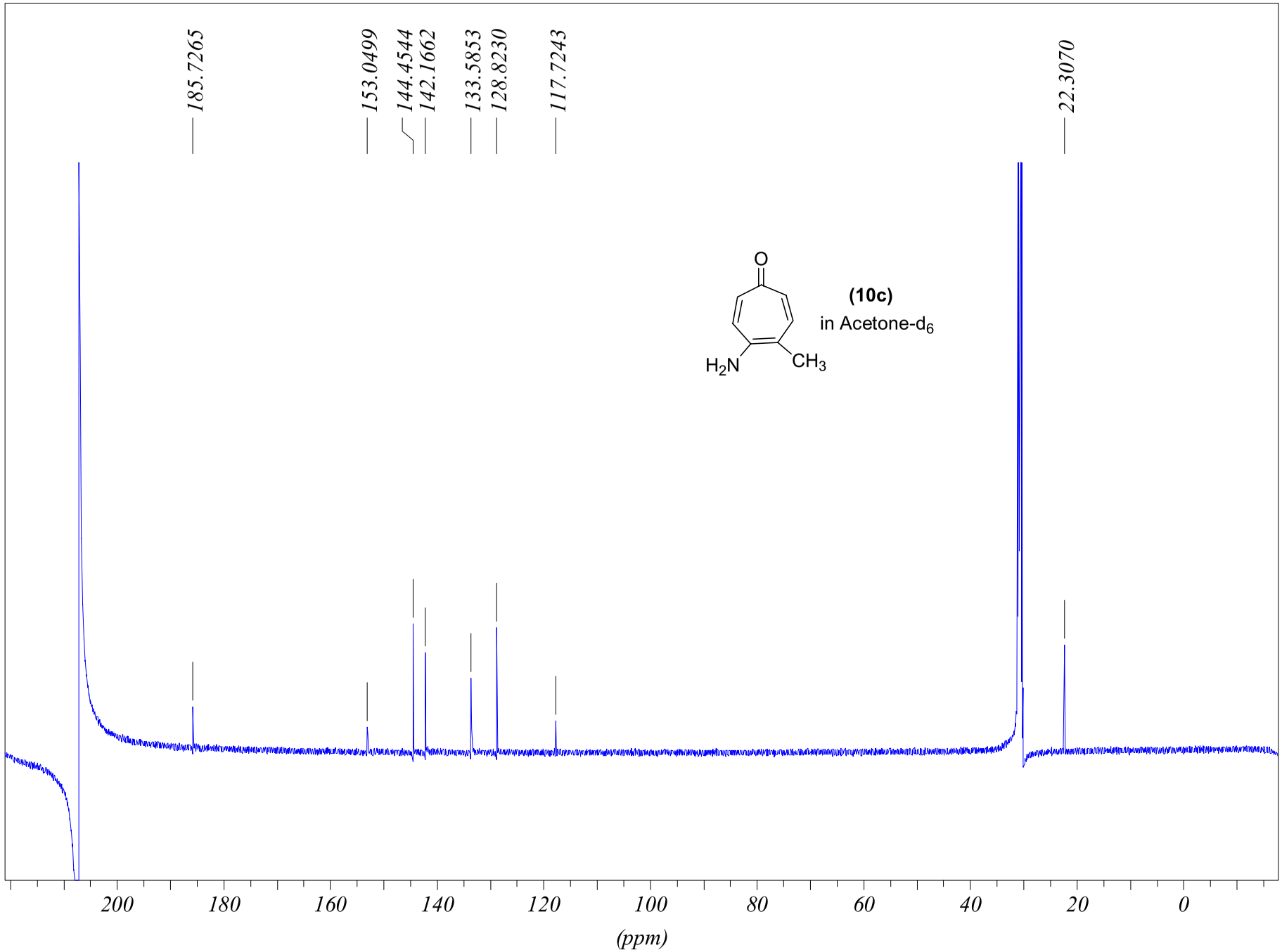

O
H2N
(10a) in MeOD-d4
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

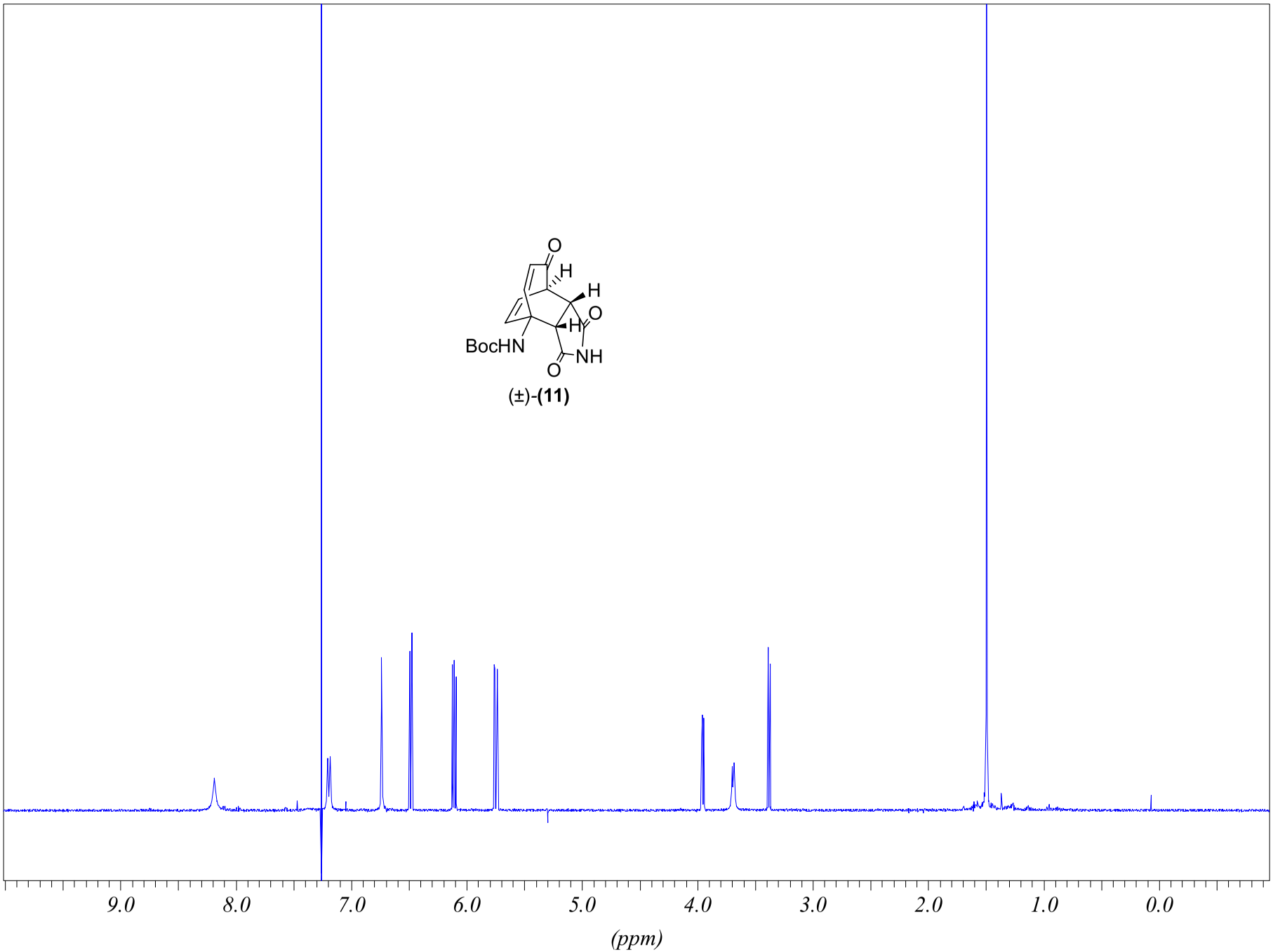

187.4824
161.2381
144.8946
144.0858
134.5893
127.1706
113.0723
O
H2N
(10a) in MeOD-d4
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)


O
H3C
H2N
(10b) in Acetone-d6
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

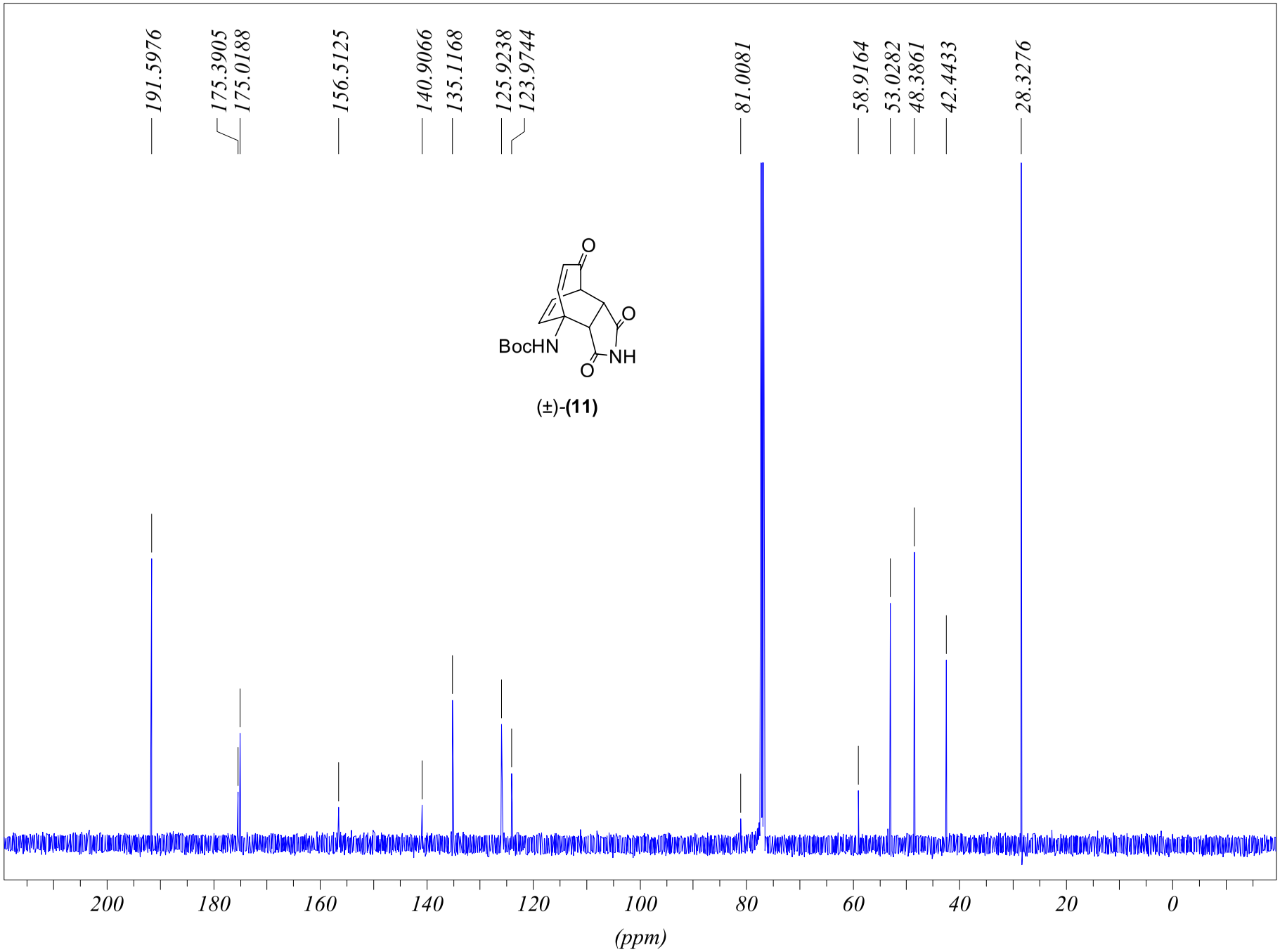

185.4438
163.0205
157.7075
146.0356
140.1369
128.7161
111.0479
24.5758
O
H3C
H2N
(10b) in Acetone-d6
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

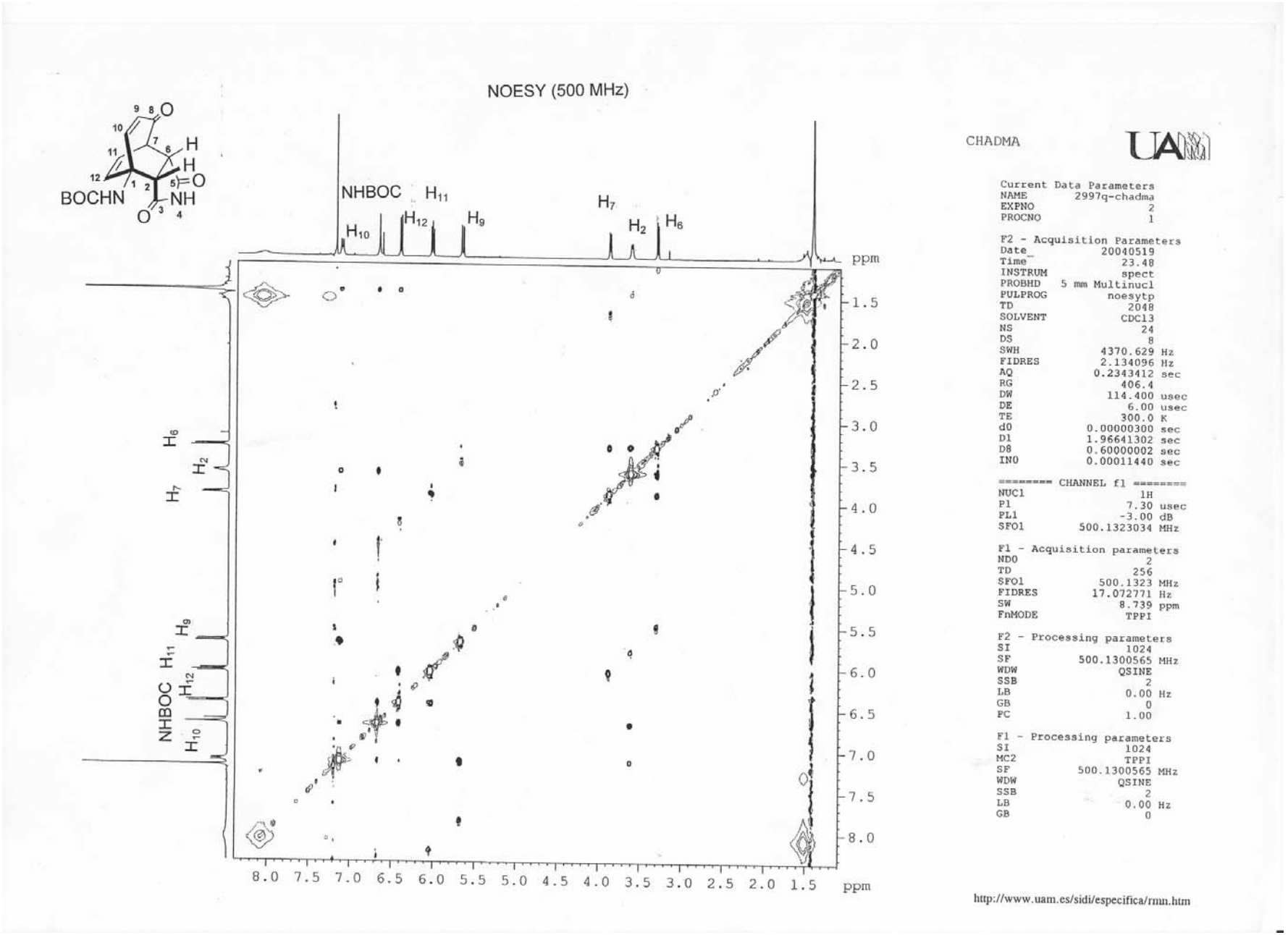

O
(10c)
H2N
CH3
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


185.7265
153.0499
144.4544
142.1662
133.5853
128.8230
117.7243
22.3070
O
H2N
CH3
(10c)
in Acetone-d6
200
180
160
140
120
100
80
60
40
20
0
(ppm)



(±)-**(11)**


191.5976
175.3905
175.0188
156.5125
140.9066
135.1168
125.9238
123.9744
81.0081
58.9164
53.0282
48.3861
42.4433
28.3276
BocHN
NH
O
O
O
O
(±)-(11)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

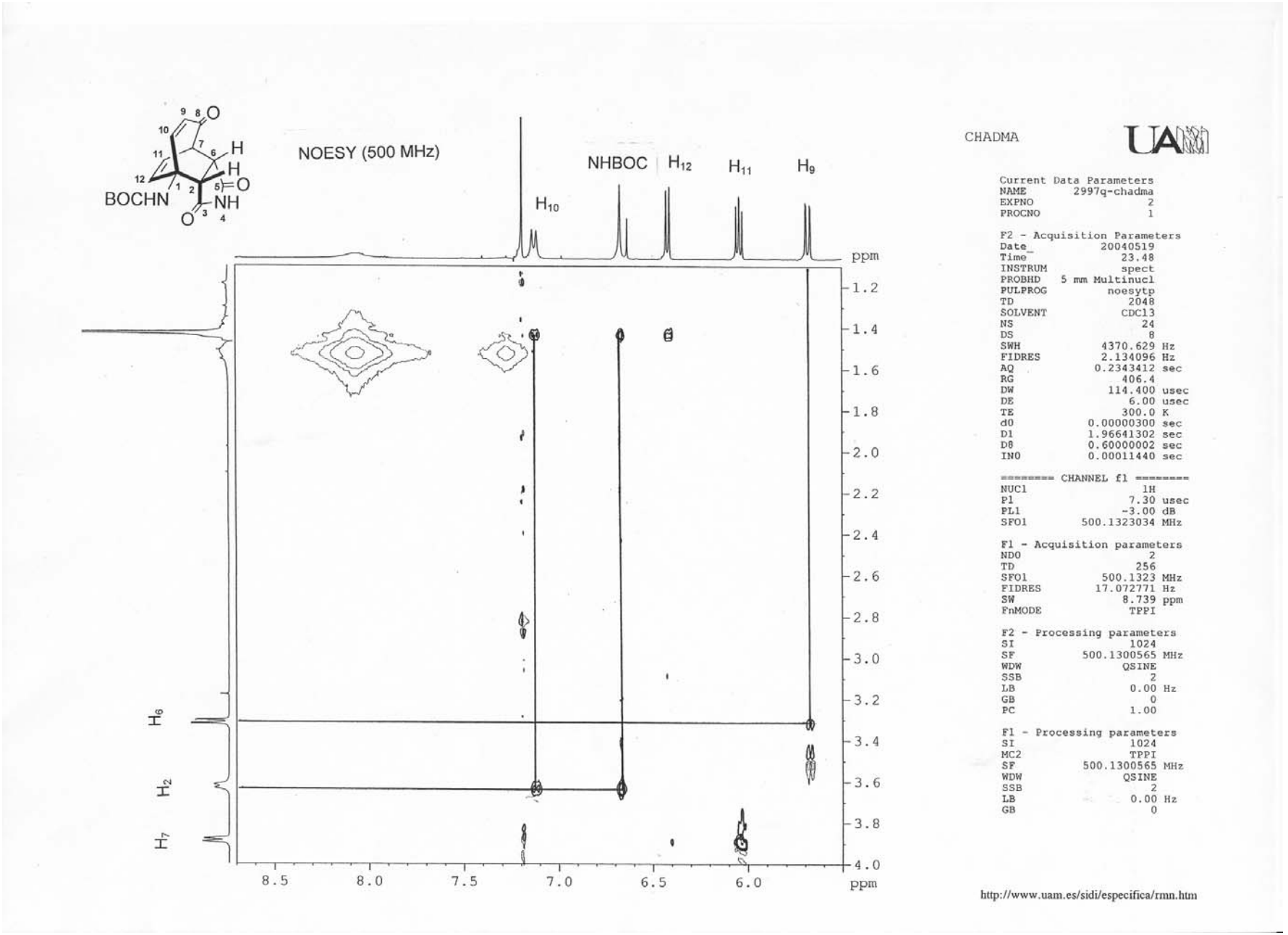


CHADMA

UAM

```
Current Data Parameters
NAME          2997q-chadma
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20040519
Time                 23.48
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG           noesytp
TD                    2048
SOLVENT              CDCl3
NS                      24
DS                       8
SWH              4370.629 Hz
FIDRES           2.134096 Hz
AQ               0.2343412 sec
RG                   406.4
DW               114.400 usec
DE                 6.00 usec
TE                 300.0 K
d0               0.00000300 sec
D1               1.96641302 sec
D8               0.60000002 sec
IN0              0.00011440 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                 7.30 usec
PL1                -3.00 dB
SFO1          500.1323034 MHz

F1 - Acquisition parameters
ND0                      2
TD                     256
SFO1          500.1323 MHz
FIDRES        17.072771 Hz
SW                8.739 ppm
FnMODE             TPPI

F2 - Processing parameters
SI                    1024
SF            500.1300565 MHz
WDW                  QSINE
SSB                      2
LB                 0.00 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
SI                    1024
MC2                  TPPI
SF            500.1300565 MHz
WDW                  QSINE
SSB                      2
LB                 0.00 Hz
GB                       0
```

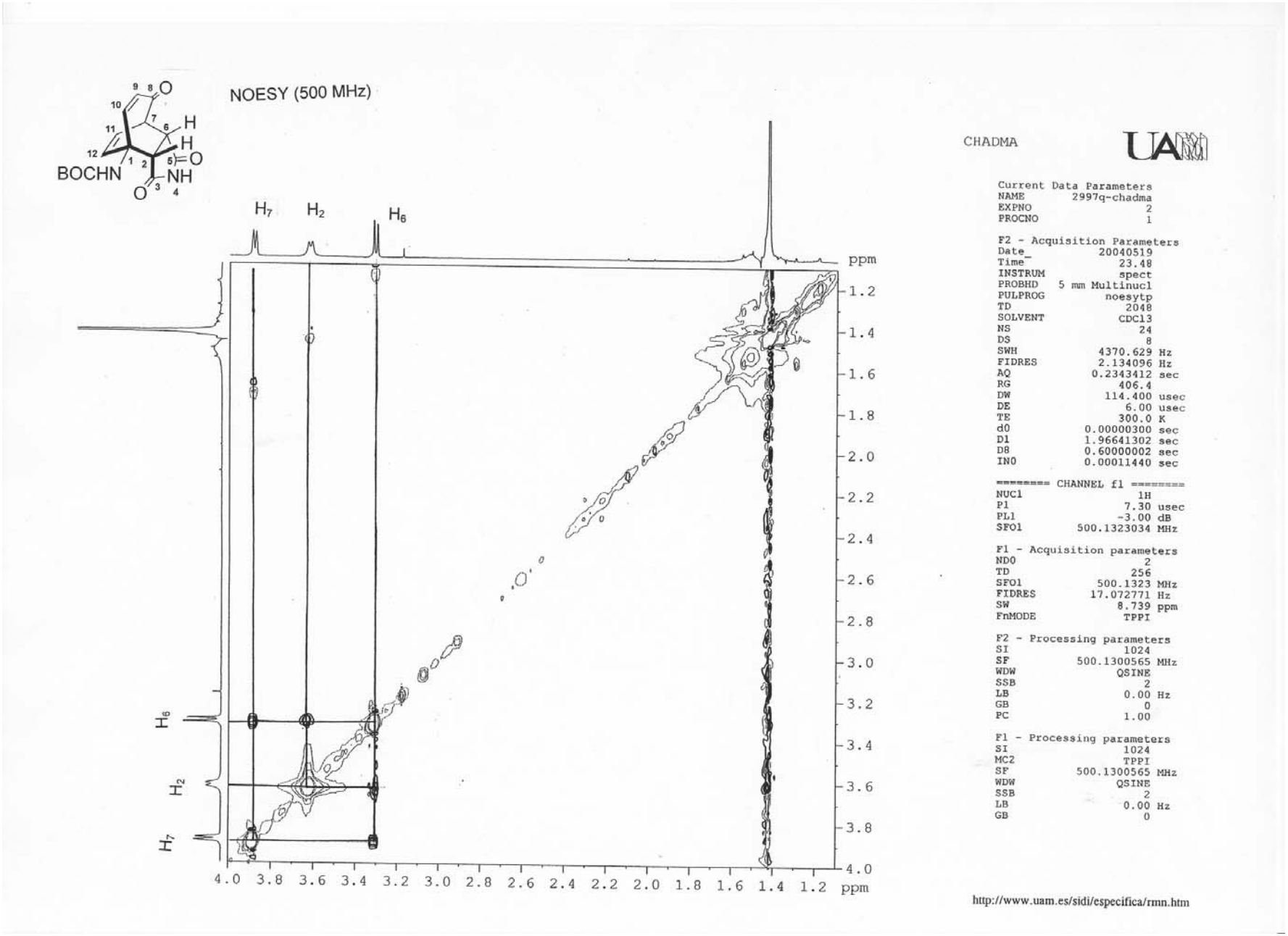
http://www.uam.es/sidi/especifica/rmn.htm



CHADMA

```
Current Data Parameters
NAME          2997q-chadma
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20040519
Time                 23.48
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG           noesytp
TD                    2048
SOLVENT               CDCl3
NS                      24
DS                       8
SWH              4370.629 Hz
FIDRES           2.134096 Hz
AQ               0.2343412 sec
RG                   406.4
DW                 114.400 usec
DE                   6.00 usec
TE                  300.0 K
d0               0.00000300 sec
D1               1.96641302 sec
D8               0.60000002 sec
IN0              0.00011440 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.30 usec
PL1                 -3.00 dB
SFO1          500.1323034 MHz

F1 - Acquisition parameters
ND0                      2
TD                     256
SFO1           500.1323 MHz
FIDRES         17.072771 Hz
SW                 8.739 ppm
FnMODE              TPPI

F2 - Processing parameters
SI                    1024
SF           500.1300565 MHz
WDW                 QSINE
SSB                      2
LB                0.00 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
SI                    1024
MC2                 TPPI
SF           500.1300565 MHz
WDW                 QSINE
SSB                      2
LB                0.00 Hz
GB                       0
```

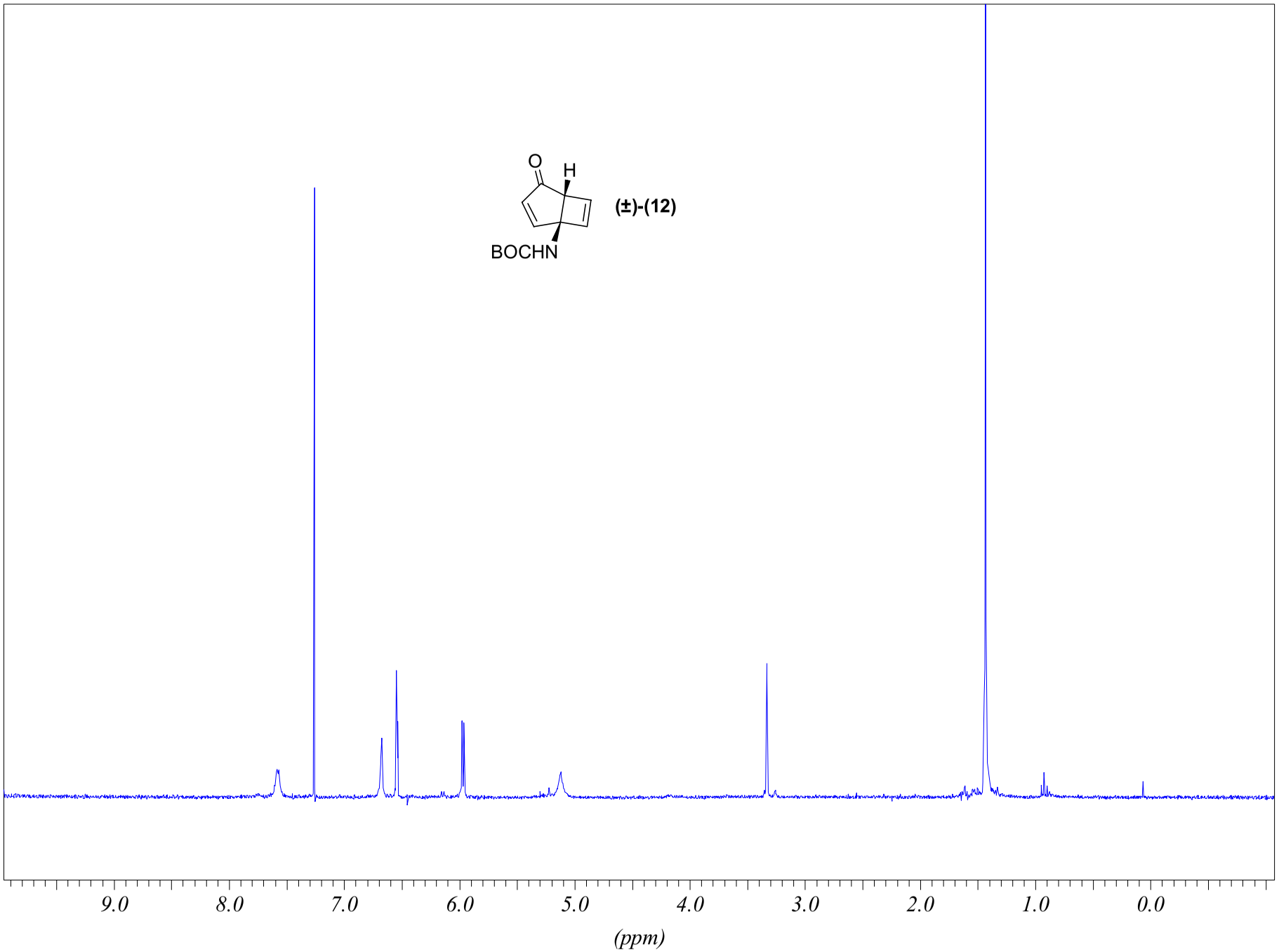
http://www.uam.es/sidi/especifica/rmn.htm

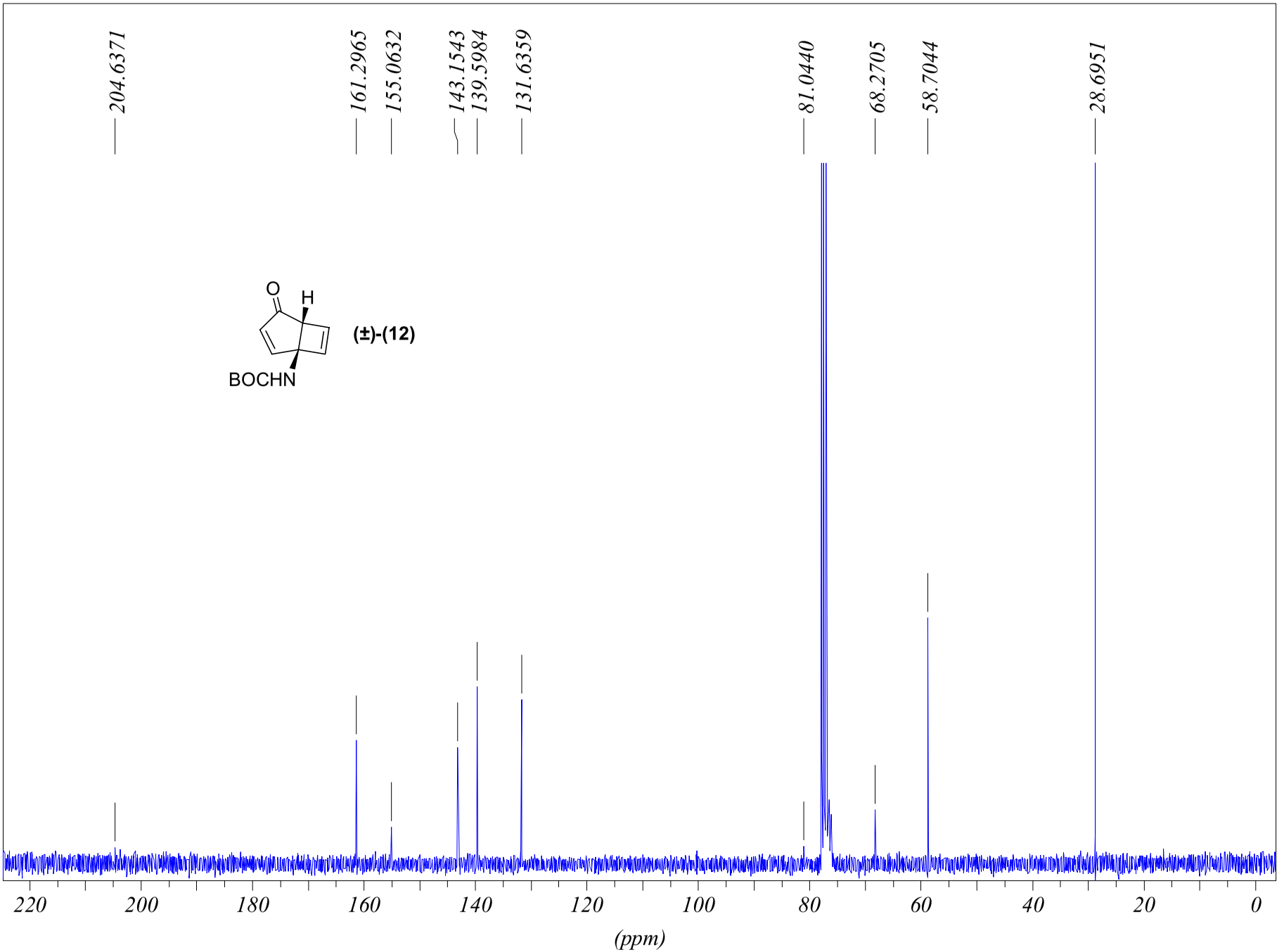


CHADMA

```
Current Data Parameters
NAME          2997q-chadma
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20040519
Time                 23.48
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG           noesytp
TD                    2048
SOLVENT              CDCl3
NS                      24
DS                       8
SWH               4370.629 Hz
FIDRES            2.134096 Hz
AQ                0.2343412 sec
RG                    406.4
DW                  114.400 usec
DE                    6.00 usec
TE                   300.0 K
d0              0.00000300 sec
D1              1.96641302 sec
D8              0.60000002 sec
IN0             0.00011440 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                    7.30 usec
PL1                  -3.00 dB
SFO1           500.1323034 MHz

F1 - Acquisition parameters
ND0                      2
TD                     256
SFO1            500.1323 MHz
FIDRES         17.072771 Hz
SW                 8.739 ppm
FnMODE              TPPI

F2 - Processing parameters
SI                    1024
SF             500.1300565 MHz
WDW                 QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    1.00

F1 - Processing parameters
SI                    1024
MC2                 TPPI
SF             500.1300565 MHz
WDW                 QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
```

http://www.uam.es/sidi/especifica/rmn.htm


O
H
BOCHN
(±)-(12)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


204.6371
161.2965
155.0632
143.1543
139.5984
131.6359
81.0440
68.2705
58.7044
28.6951
O
H
BOCHN
(±)-(12)
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

S-27

X-Ray ORTEP for compound 9a
CCDC 247411