Supporting Information

for

Palladium[II] Catalysed C(sp^3)–H Oxidation of Dimethyl Carbamoyl Tetrahydrocarbazoles

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SI-1. Experimental Procedures

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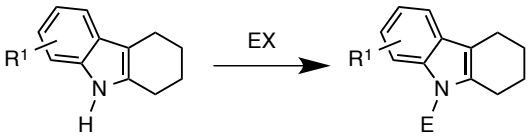
I General Procedures

NMR spectra were recorded in $CDCl_3$ on a Bruker DRX400 NMR spectrometer operating at 400 MHz for proton, and 100 MHz for carbon nuclei. Residual $CHCl_3$ was used as the internal standard for proton NMR spectra (7.26 ppm), and the central peak in $CDCl_3$ triplet used for carbon NMR spectra (77.16 ppm). NMR data recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) *J* (Hz), relative integral], where multiplicity is defined: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof, and prefixed br = broad. Infrared spectra (υ_{max}) were recorded on a Agilent Cary 630 FTIR spectrometer. High resolution mass spectrometry (HRMS) was performed on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. Melting points (Mp) were measured on a Stanford Research Systems Digimelt MPA 161 apparatus. Flash column chromatography was performed on silica gel (Davsil LC60A, 40-63 μm silica media) using compressed air. Thin layer chromatography (TLC) was performed using aluminium-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F254 plates). Eluted plates were visualised using a 254 nm UV lamp and/or by developing with a suitable stain following heating.

Starting materials and reagents were purchased from Sigma-Aldrich, Oakwood Chemicals, Merck or Alfa-Aesar and were used as supplied without further purification. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl. Concentration under reduced pressure was performed on a rotary evaporator with a water bath temperature of 40°C.

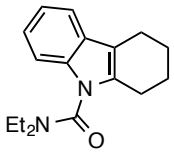
II Synthesis of *N*-protected 1,2,3,4-tetrahydrocarbazoles 6



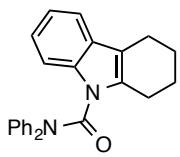
Method A: to a stirred suspension of NaH (0.12 g of a 60% dispersion in mineral oil, 3 mmol) in anhydrous THF (20 mL) at 0 °C was added portion-wise 1,2,3,4-tetrahydrocarbazole (0.34 g, 2 mmol). The resulting solution was stirred at 0 °C for a further hour, before an appropriate electrophile (EX, 3 mmol) was added at once. The reaction mixture was bought up to room temperature and stirred overnight before a solution of saturated NH_4Cl was added. The aqueous layer was separated and extracted with diethyl ether (20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and evaporated. The crude residue was purified *via* column chromatography.

Method B: to a stirred solution of 1,2,3,4-tetrahydrocarbazole (0.34 g, 2 mmol) in anhydrous THF (20 mL) at –78 °C was added drop-wise a solution of *n*-BuLi (1.67 mL of a 1.6 M solution in hexanes, 3 mmol). The resulting solution was stirred at –78 °C for a further hour, before an appropriate electrophile (RX, 3 mmol) was added at once. The reaction mixture was bought up to room temperature and stirred overnight before a solution of saturated NH_4Cl was added. The aqueous layer was separated and extracted with diethyl ether (20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered and evaporated. The crude residue was purified *via* column chromatography.

***N*,*N*-Diethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide** (**6a**) was prepared as a brown oil following method A, using diethyl carbamoylchloride as electrophile (0.51 g, 94%). $\mathbf{R_f}$ 0.43 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 1H), 7.26–7.23 (m, 1H), 7.17 (td, *J* = 7.2, 1.2 Hz, 1H), 7.13 (td, *J* = 7.2, 1.2 Hz, 1H), 3.50 (m, 4H), 2.78–2.75 (m, 2H), 2.72–2.68 (m, 2H), 1.94–1.85 (m, 4H), 1.20 (t, *J* = 7.2 Hz, 6H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.0, 135.3, 128.7, 122.3, 120.7, 118.2, 113.5, 110.8, 42.5, 23.2, 23.0, 22.9, 21.1, 13.9, 1 peak missing or superimposed; **IR** υ_{max} 2970, 2932, 2844, 1682, 1456, 1418, 1303, 1303, 1269, 1229, 1133, 1095, 858, 741; **HRMS** found $(M+H)^+$, 271.1804, $C_{17}H_{22}N_2O$ requires $(M+H)^+$, 271.1805.



***N*,*N*-Diphenyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide** (**6b**) was prepared as a yellow solid following method A, using diphenyl carbamoylchloride as electrophile (0.61 g, 83%). $\mathbf{R_f}$ 0.45 (1:4, v/v EtOAc : hexanes); **Mp** 128.7–131.2 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.62–7.60 (m, 1H), 7.32–7.29 (m, 1H), 7.27–7.22 (m, 4H), 7.15–7.11 (m, 2H), 7.10–7.05 (m, 6H), 2.87–2.83 (m, 2H), 2.62–2.58 (m, 2H), 1.86–1.73 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.8, 143.4, 135.1, 135.0, 129.3, 129.2, 126.2, 125.8, 122.6, 121.6, 117.8, 115.8, 112.8, 24.1, 23.4, 22.7, 21.0; **IR** υ_{max} 2927, 2847, 1679, 1589, 1489, 1453, 1357, 1224, 1143, 833, 750, 695; **HRMS** found $(M+H)^+$, 367.1806, $C_{25}H_{22}N_2O$ requires $(M+H)^+$, 367.1805.



Pyrrolidin-1-yl(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)methanone (**6c**) was prepared as a brown oil following method A, using pyrrodoyl chloride as electrophile (0.44 g, 81%). $\mathbf{R_f}$ 0.18 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.35–7.32 (m, 1H), 7.13–7.11 (m, 1H), 7.07 (td, *J* = 7.2, 1.2 Hz, 1H), 7.01 (td, *J* = 7.2, 1.2 Hz, 1H), 3.43–3.32 (m, 4H), 2.72 (broad s, 2H), 2.60–2.57 (m, 2H), 1.83–1.75 (m, 8H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 151.9, 134.0, 133.4, 127.6, 121.0, 119.5, 117.1, 112.4, 110.3, 46.7, 24.3, 22.1, 22.0, 21.8, 19.9; **IR** υ_{max} 2926, 1672, 1454, 1393, 1340, 1300, 1225, 1014, 913, 839, 739; **HRMS** found $(M+H)^+$, 269.1651, $C_{17}H_{20}N_2O$ requires $(M+H)^+$, 269.1648.

***N*,*N*-Dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide** (**6d**) was prepared as a white solid following method A, using dimethyl carbamoylchloride as electrophile (0.38 g, 79%). $\mathbf{R_f}$ 0.26 (1:4, v/v EtOAc : hexanes); **Mp** 79.8–82.4 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45–7.43 (m, 1H), 7.24–7.22 (m, 1H), 7.18 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 3.05 (s, 6H), 2.80–2.78 (m, 2H), 2.71–2.68 (m, 2H), 1.92–1.86 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.7, 135.5, 135.2, 128.8, 122.3, 120.9, 118.2, 113.9, 111.5, 38.0, 23.2, 23.1, 22.9, 21.0; **IR** υ_{max} 2925, 2891, 1676, 1489, 1454, 1382, 1359, 1304, 1224, 1189, 1107, 1020, 752; **HRMS** found $(M+H)^+$, 243.1493, $C_{15}H_{18}N_2O$ requires $(M+H)^+$, 243.1492.

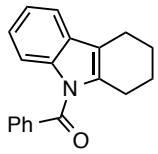
***tert*-Butyl 1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxylate** (**6e**).[1] To a stirred solution of 1,2,3,4-tetrahydrocarbazole (0.17 g, 1.0 mmol) and 4-dimethylaminopyridine (12.4 mg, 0.1 mmol) in DMF (5 mL) was added di-*tert*-butyl-dicarbonate (0.33 g, 1.5 mmol) and triethylamine (0.25 mL, 1.8 mmol). The reaction mixture was stirred for 2.5 hours at room temperature before being diluted with brine (50 mL) and extracted with EtOAc (2 x 50 mL). The combined organic layers were dried ($MgSO_4$), filtered, concentrated and purified *via* flash column chromatography (1:4 v/v EtOAC:hexanes on SiO_2) to yield the title compound as a yellow oil (0.25 g, 91%). $\mathbf{R_f}$ 0.62 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.39 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.26–7.18 (m, 2H), 3.01–2.98 (m, 2H), 2.66–2.63 (m, 2H), 1.92–1.80 (m, 4H), 1.67 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 150.6, 135.8, 135.5, 129.8, 123.3, 122.3, 117.4, 116.5, 115.4, 83.0, 28.3, 25.9, 23.7, 22.2, 21.1; **IR** υ_{max} 2934, 2856, 1726, 1457, 1360, 1326, 1143, 1017, 852, 745.

1-(1,2,3,4-Tetrahydro-9*H*-carbazol-9-yl)ethan-1-one (**6f**).[2] Acetyl chloride (0.31 mL, 4.3 mmol) was added dropwise to a stirred solution of 1,2,3,4-tetrahydrocarbazole (0.43 g, 2.5 mmol), tetrabutylammonium hydrogensulfate (42.1 mg, 0.12 mmol), and sodium hydroxide (0.21 g, 5 mmol) in dichloromethane (25 mL). The mixture was stirred for 2 hours at room temperature before a saturated solution of ammonium chloride (25 mL) was added. The organic phase was separated, and aqueous phase extracted with dichloromethane (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered and evaporated. The crude residue was purified *via* flash column chromatography (1:4 v/v EtOAC:hexanes on SiO_2) to yield title compound as a yellow solid (0.12 g, 23%). $\mathbf{R_f}$ 0.38 (1:4, v/v EtOAc : hexanes); **Mp** 71.9–74.1 °C (lit:[1] 76–77 °C); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.08–8.05 (m, 1H), 7.42–7.40

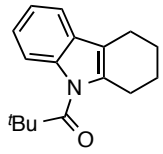
1) P. A. Wender, A. W. White *Tetrahedron Lett.* **1981**, *22*, 1475.
2) T. Benkovics *Angew. Chem. Int. Ed.* **2010**, *49*, 9153.

(m, 1H), 7.30–7.23 (m, 2H), 3.02–2.98 (m, 2H), 2.69 (s, 3H), 2.70–2.66 (m, 2H), 1.95–1.82 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 170.0, 136.1, 135.4, 130.5, 124.0, 123.1, 118.4, 117.9, 115.6, 27.3, 26.8, 24.0, 22.1, 21.3; **IR** υ_{max} 2929, 2851, 1686, 1610, 1450, 1363, 1313, 1200, 1134, 1010, 740, 666.

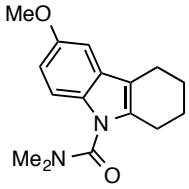
Phenyl(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)methanone (**6g**) was prepared as a dark brown oil following method A, using benzoyl chloride as electrophile (0.40 g, 71%). **R_f** 0.58 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.71–7.68 (m, 2H), 7.63–7.59 (m, 1H), 7.51–7.46 (m, 2H), 7.43–7.41 (m, 1H), 7.20–7.16 (m, 2H), 7.09–7.05 (m, 1H), 2.71–2.61 (m, 4H), 1.89–1.78 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.3, 136.6, 136.1, 132.3, 131.4, 130.1, 129.4, 129.0, 128.6, 123.2, 122.6, 117.8, 114.7, 25.7, 23.6, 22.3, 21.1; **IR** υ_{max} 2924, 2847, 1675, 1451, 1356, 1302, 1215, 1153, 1061, 925, 741, 697; **HRMS** found $(M+Na)^+$, 298.1203, $C_{19}H_{17}NO$ requires $(M+Na)^+$, 298.1202.



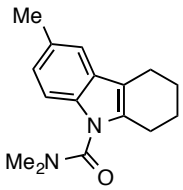
2,2-Dimethyl-1-(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)propan-1-one (**6h**)[3] was prepared as a brown oil following method A, using pivaloyl chloride as electrophile (0.22 g, 43%). **R_f** 0.60 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 1H), 7.39–7.36 (m, 1H), 7.17 (td, *J* = 7.2, 1.6 Hz, 1H), 7.13 (td, *J* = 7.2, 1.6 Hz, 1H), 2.71–2.69 (m, 4H), 1.88–1.87 (m, 4H), 1.44 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 184.9, 135.9, 135.6, 129.0, 122.1, 121.0, 118.1, 114.6, 112.9, 28.4, 26.6, 24.3, 23.5, 22.7, 21.1; **IR** υ_{max} 2931, 1697, 1458, 1301, 1197, 935, 866, 736.



6-Methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**6db**) was prepared as a brown oil following method A, using dimethyl carbamoylchloride as electrophile (0.13 g, 24%). **R_f** 0.34 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 2.8 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.85 (s, 3H), 3.03 (s, 6H), 2.80–2.77 (m, 2H), 2.66–2.64 (m, 2H), 1.92–1.84 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.8, 154.6, 136.1, 129.9, 129.2, 113.6, 112.0, 111.0, 100.7, 55.6, 37.8, 23.0(4), 23.0(0), 22.7, 20.8; **IR** υ_{max} 2928, 2843, 1675, 1458, 1437, 1383, 1254, 1222, 1110, 1036, 901, 799, 767, 700; **HRMS** found $(M+H)^+$, 273.1599, $C_{16}H_{20}N_2O_2$ requires $(M+H)^+$, 273.1598.

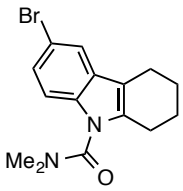


***N*,*N*,-Trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide** (**6dc**) was prepared as a colourless oil following general procedure A, using dimethyl carbamoylchloride as electrophile (0.18 g, 36%). **R_f** 0.31 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 1.2 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.00 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.04 (s, 6H), 2.79–2.64 (m, 4H), 2.44 (s, 3H), 1.90–1.85 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.8, 135.5, 133.4, 130.1, 128.9, 123.6, 118.1, 113.6, 111.2, 38.0, 23.2, 23.1, 22.8, 21.3, 21.0; **IR** υ_{max} 2927, 2854, 2678, 1461, 1387, 1310, 1285, 1228, 1198, 1116, 798; **HRMS** found $(M+H)^+$, 257.1648, $C_{16}H_{20}N_2O$ requires $(M+H)^+$, 257.1648.



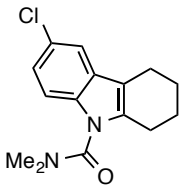
3) P. A. Wender, A. W. White *Tetrahedron* 1983, **39**, 3767

6-Bromo-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**6dd**) was



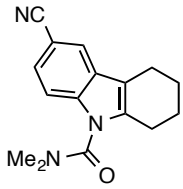
prepared as a brown oil following method A, using dimethyl carbamoylchloride as electrophile (0.22 g, 34%). $\mathbf{R_f}$ 0.26 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.0 Hz, 1H), 7.26 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.02 (s, 6H), 2.78–2.62 (m, 4H), 1.92–1.83 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.2, 136.8, 133.8, 130.4, 124.9, 120.9, 114.0, 113.4, 112.8, 37.9, 23.0(0), 22.9(8), 22.7, 20.8; **IR** υ_{max} 2927, 2845, 1683, 1438, 1382, 1309, 1261, 1225, 1190, 1118, 1050, 991, 887, 861, 794, 750; **HRMS** found $(M+H)^+$, 321.0592, $C_{15}H_{17}{}^{79}BrN_2O$ requires $(M+H)^+$, 321.0597.

6-Chloro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9- carboxamide (**6de**) was



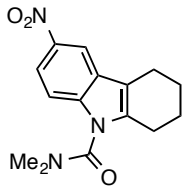
prepared as a yellow oil following method A, using dimethyl carbamoylchloride as electrophile (0.32 g, 56%). $\mathbf{R_f}$ 0.21 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 2.0, 0.8 Hz, 1H), 7.13 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.01 (s, 6H), 2.77–2.61 (m, 4H), 1.91–1.82 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.2, 137.0, 133.5, 129.9, 126.5, 122.3, 117.8, 113.5, 112.3, 38.0, 23.1, 23.0, 22.7, 20.8; **IR** υ_{max} 2931, 2847, 1685, 1441, 1386, 1311, 1263, 1226, 1193, 1121, 1063, 997, 799, 757, 662; **HRMS** found $(M+Na)^+$, 299.0924, $C_{15}H_{17}{}^{35}ClN_2O$ requires $(M+Na)^+$, 299.0922.

6-Cyano-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**6df**) was



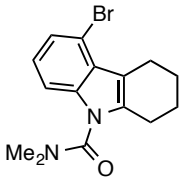
prepared as a yellow solid following method A, using dimethyl carbamoylchloride as electrophile (0.19 g, 36%). $\mathbf{R_f}$ 0.49 (1:1, v/v EtOAc : hexanes); **Mp** 120.7–121.5 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.43 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.28 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.04 (s, 6H), 2.78–2.67 (m, 4H), 1.95–1.86 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.6, 137.9, 136.9, 128.7, 125.6, 123.4, 120.5, 114.1, 112.0, 104.1, 38.0, 23.0, 22.9, 22.6, 20.8; **IR** υ_{max} 2916, 2844, 2214, 1687, 1454, 1387, 1304, 1112, 870, 822, 761; **HRMS** found $(M+Na)^+$, 290.1250, $C_{16}H_{17}N_3O$ requires $(M+H)^+$, 290.1264.

***N*,*N*-Dimethyl-6-nitro-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide** (**6dg**) was



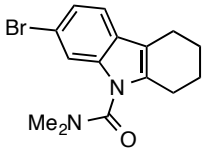
prepared as a brown solid following method A, using dimethyl carbamoylchloride as electrophile (0.15 g, 27%). $\mathbf{R_f}$ 0.14 (1:4, v/v EtOAc : hexanes); **Mp** 108.7–110.9 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.4 Hz, 1H), 8.10 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 3.06 (s, 6H), 2.79–2.72 (m, 4H), 1.95–1.89 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.4, 142.6, 138.8, 138.1, 128.3, 118.0, 115.3, 115.1, 111.1, 38.0, 23.0, 22.9, 22.6, 20.8; **IR** υ_{max} 3088, 2933, 2853, 1680, 1505, 1462, 1379, 1316, 1195, 1127, 886, 819, 735; **HRMS** found $(M+Na)^+$, 310.1160, $C_{15}H_{17}N_3O_3$ requires $(M+Na)^+$, 310.1162.

5-Bromo-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**6dh**) was



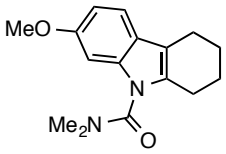
prepared as a brown oil following method B, using dimethyl carbamoylchloride as electrophile (0.35 g, 55%). $\mathbf{R_f}$ 0.36 (1:1, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.15 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 3.11–3.06 (m, 2H), 3.02 (s, 6H), 2.79–2.69 (m, 2H), 1.88–1.85 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.9, 136.3, 136.0, 127.1, 124.9, 123.0, 114.0, 113.9, 110.3, 37.8, 23.3, 23.1, 23.0, 22.5; **IR** υ_{max} 2930, 2849, 1683, 1488, 1427, 1385, 1315, 1267, 1186, 1112, 769, 735; **HRMS** found $(M+H)^+$, 321.0589, $C_{15}H_{17}{}^{79}BrN_2O$ requires $(M+H)^+$, 321.0597.

7-Bromo-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**6di**) was



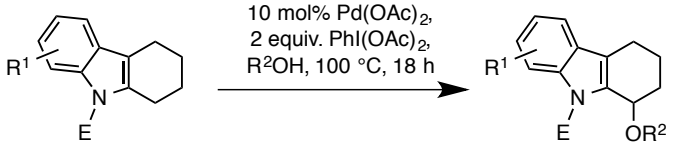
prepared as brown oil following general procedure B, using dimethyl carbamoylchloride as electrophile (0.48 g, 76%). $\mathbf{R_f}$ 0.13 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 1.6 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.24 (dd, *J* = 8.4, 1.6 Hz, 1H), 3.04 (s, 6H), 2.75–2.64 (m, 4H), 1.91–1.84 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.0, 136.0, 135.8, 127.5, 123.9, 119.3, 115.6, 114.3, 113.7, 37.9, 22.9, 22.6, 20.7 (1 peak missing or superimposed); **IR** υ_{max} 2928, 2845, 1678, 1463, 1381, 1305, 1224, 1190, 1136, 1112, 1053, 986, 799, 762, 735; **HRMS** found $(M+Na)^+$, 343.0417, $C_{15}H_{17}{}^{79}BrN_2O$ requires $(M+Na)^+$, 343.0416.

7-Methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**6dj**) was



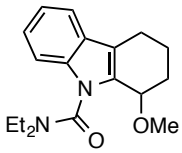
prepared as brown oil following method B, using dimethyl carbamoylchloride as electrophile (0.55 g, 99%). $\mathbf{R_f}$ 0.26 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 6.4 Hz, 1H), 6.72 (s, 1H), 6.71 (d, *J* = 6.4 Hz, 1H), 3.77 (s, 3H), 2.97 (s, 6H), 2.67–2.56 (m, 4H), 1.82–1.76 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 156.7, 154.7, 136.0, 133.9, 123.0, 118.4, 113.6, 109.1, 96.7, 55.8, 37.9, 23.1, 23.0, 22.8, 20.9; **IR** υ_{max} 2930, 2839, 1674, 1618, 1488, 1439, 1384, 1310, 1230, 1156, 1108 1033, 907, 803, 726, 667; **HRMS** found $(M+Na)^+$, 295.1420, $C_{16}H_{20}N_2O_2$ requires $(M+Na)^+$, 295.1417.

III C–H oxidation of 1,2,3,4-tetrahydrocarbazoles



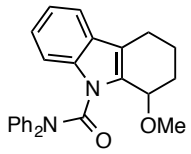
General method: a sealed tube vessel fitted with a Teflon screw lid was charged with the carbazole (0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $PhI(OAc)_2$ (322.1 mg, 1.0 mmol) and an alcohol (5 mL). The mixture was stirred at room temperature for 15 minutes, and then at 100 °C for 18 hours. The reaction mixture was then cooled to ambient temperature before the solvent was removed under reduced pressure. The crude residue was purified *via* column chromatography.

***N*,*N*-Diethyl-1-methoxy-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide** (**7a**) was



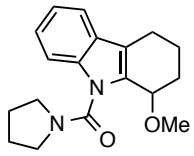
prepared yellow solid from **6a** following the general C–H oxidation procedure described (101.8 mg, 65%). $\mathbf{R_f}$ 0.26 (1:4, v/v EtOAc : hexanes); **Mp** 60.4–62.0 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 1H), 7.25–7.19 (m, 2H), 7.13 (ddd, *J* = 8.0, 6.4, 1.6 Hz, 1H), 4.74 (t, *J* = 4.8 Hz, 1H), 3.80–3.71 (m, 1H), 3.50–3.41 (m, 2H), 3.42 (s, 3H), 3.21–3.12 (m, 1H), 2.75 (dt, *J* = 16.0, 5.2 Hz, 1H), 2.66–2.59 (m, 1H), 2.11–1.92 (m, 3H), 1.88–1.79 (m, 1H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.1, 135.7, 135.2, 127.7, 123.2, 120.6, 119.3, 115.9, 110.9, 71.4, 56.7, 43.9, 41.1, 28.0, 21.2, 19.8, 13.8, 13.3; **IR** υ_{max} 2923, 1677, 1412, 1368, 1301, 1079, 908, 849, 738; **HRMS** found $(M+Na)^+$, 323.1725, $C_{18}H_{24}N_2O_2$ requires $(M+Na)^+$, 323.1730.

1-Methoxy-*N*,*N*-diphenyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**7b**) was



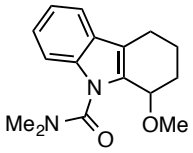
prepared as a brown solid from **6b** following the general C–H oxidation procedure described (82.9 mg, 30%). $\mathbf{R_f}$ 0.32 (1:4, v/v EtOAc : hexanes); **Mp** 148.4–152.9 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.50–7.48 (m, 1H), 7.40–7.36 (m, 2H), 7.33–7.31 (m, 1H), 7.28–7.23 (m, 5H), 7.12–7.08 (m, 2H), 7.04 (td, *J* = 7.6, 1.2 Hz, 1H), 7.00 (td, *J* = 7.6, 1.2 Hz, 1H), 6.97–6.93 (m, 1H), 4.88 (t, *J* = 4.4 Hz, 1H), 3.51 (s, 3H), 2.71 (dt, *J* = 16.4, 4.0 Hz, 1H), 2.58–2.51 (m, 1H), 2.10–1.93 (m, 3H), 1.82–1.75 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.8, 143.7, 143.4, 135.0, 134.6, 129.5, 128.9, 127.8, 126.7, 126.6, 125.8, 125.6, 123.3, 121.2, 118.8, 118.2, 112.6, 71.2, 57.0, 27.8, 21.2, 19.5; **IR** υ_{max} 2927, 1689, 1590, 1490, 1452, 1410, 1359, 1306, 1272, 1229, 1074, 974, 906, 838, 744, 695; **HRMS** found $(M+Na)^+$, 419.1739, $C_{26}H_{24}N_2O_2$ requires $(M+Na)^+$, 419.1730.

(1-Methoxy-1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)(pyrrolidin-1-yl)methanone (**7c**) was



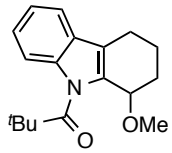
prepared as a white solid from **6c** following the general C–H oxidation procedure described (70.3 mg, 45%). $\mathbf{R_f}$ 0.13 (1:4, v/v EtOAc : hexanes); **Mp** 124.3–126.1 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.50–7.48 (m, 1H), 7.23–7.22 (m, 2H), 7.12 (ddd, *J* = 8.0, 5.6, 2.4 Hz, 1H), 4.77 (t, *J* = 4.8 Hz, 1H), 3.82–3.75 (m, 1H), 3.64–3.59 (m, 1H), 3.42 (s, 3H), 3.39–3.35 (m, 1H), 3.21–3.16 (m, 1H), 2.75 (dt, *J* = 16.0, 5.2 Hz, 1H), 2.66–2.58 (m, 1H), 2.07–1.99 (m, 8H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.4, 135.0, 134.3, 127.6, 123.2, 120.5, 119.4, 115.6, 111.2, 71.2, 57.0, 48.3, 47.1, 28.0, 26.0, 25.2, 21.1, 19.8; **IR** υ_{max} 2921, 2884, 1677, 1405, 1370, 1338, 1304, 1231, 1186, 1165, 1077, 973, 908, 744, 699; **HRMS** found $(M+Na)^+$, 321.1579, $C_{18}H_{22}N_2O_2$ requires $(M+Na)^+$, 321.1573.

1-Methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**7d**) was



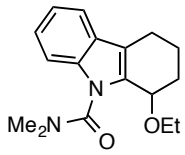
prepared as a white solid from **6d** the general C–H oxidation procedure described (118.4 mg, 86%). $\mathbf{R_f}$ 0.17 (1:4, v/v EtOAc : hexanes); **Mp** 92.6–93.9 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.30–7.24 (m, 2H), 7.18 (ddd, *J* = 7.6, 6.0, 2.0 Hz, 1H), 4.80 (t, *J* = 4.8 Hz, 1H), 3.47 (s, 3H), 3.21 (s, 3H), 2.95 (s, 3H), 2.80 (dt, *J* = 16.0, 5.6 Hz, 1H), 2.71–2.63 (m, 1H), 2.15–1.96 (m, 3H), 1.93–1.84 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.9, 135.5, 134.8, 127.6, 123.4, 120.7, 119.3, 116.2, 111.2, 71.2, 56.9, 38.8, 36.9, 28.0, 21.1, 19.8; **IR** υ_{max} 2925, 1683, 1449, 1368, 1316, 1233, 1196, 1131, 1110, 1078, 1021, 904, 743, 690; **HRMS** found $(M+Na)^+$, 295.1421, $C_{16}H_{20}N_2O_2$ requires $(M+Na)^+$, 295.1417.

1-(1-Methoxy-1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)-2,2-dimethylpropan-1-one (**7h**) was



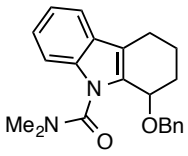
prepared as brown oil from **6h** following the general C–H oxidation procedure described (63.7 mg, 44%). $\mathbf{R_f}$ 0.61 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 1H), 7.40–7.38 (m, 1H), 7.22 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.13 (ddd, *J* = 8.4, 7.2, 0.8 Hz, 1H), 4.68 (t, *J* = 4.0 Hz, 1H), 3.33 (s, 3H), 2.71–2.64 (m, 1H), 2.59–2.52 (m, 1H), 2.02–1.85 (m, 3H), 1.78–1.70 (m, 1H), 1.38 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 185.7, 136.0, 135.7, 128.0, 123.1, 120.8, 119.3, 116.8, 113.0, 71.3, 56.2, 43.5, 28.4, 27.6, 21.3, 19.7; **IR** υ_{max} 2932, 1702, 1454, 1298, 1260, 1170, 1082, 1020, 801, 739; **HRMS** found $(M+H)^+$, 308.1621, $C_{18}H_{22}NO_2$ requires $(M+Na)^+$, 308.1621.

1-Ethoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**8d**) was

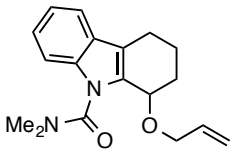


prepared as a brown from **6d** following the general C–H oxidation procedure described (91.6 mg, 64%). $\mathbf{R_f}$ 0.23 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 4.0 Hz, 1H), 7.24–7.19 (m, 2H), 7.15–7.11 (m, 1H), 4.85, (t, *J* = 5.2 Hz, 1H), 3.77–3.70 (m, 1H), 3.56–3.48 (m, 1H), 3.17 (s, 3H), 2.91 (s, 3H), 2.73 (dt, *J* = 15.6, 5.2 Hz, 1H), 2.67–2.60 (m, 1H), 2.15–2.09 (m, 1H), 2.03–1.90 (m, 3H), 1.87–1.78 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.9, 135.4, 135.1, 127.7, 123.2, 120.6, 119.3, 115.9, 111.0, 70.2, 64.6, 38.8, 36.9, 28.9, 21.1, 20.1, 15.9; **IR** υ_{max} 2928, 1682, 1485, 1451, 1386, 1301, 1230, 1197, 1133, 1081, 1018, 740; **HRMS** found $(M+Na)^+$, 309.1571, $C_{17}H_{22}N_2O_2$ requires $(M+Na)^+$, 309.1573.

1-(Benzyloxy)-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**9d**) was



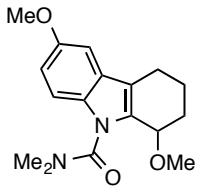
prepared as a low melting solid from **6d** following the general C–H oxidation procedure described (155.4 mg, 89%). $\mathbf{R_f}$ 0.30 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.50–7.48 (m, 1H), 7.36–7.28 (m, 5H), 7.23–7.17 (m, 2H), 7.13 (ddd, *J* = 8.0, 6.8, 1.6 Hz, 1H), 5.08 (t, *J* = 4.8 Hz, 1H), 4.72 and 4.54 (ABq, J_{AB} = 10.4 Hz, 2H), 3.03 (s, 3H), 2.79–2.62 (m, 2H), 2.74 (s, 3H), 2.23–2.15 (m, 1H), 2.09–1.99 (m, 2H), 1.91–1.82 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.8, 139.0, 135.4, 134.8, 128.2, 127.9, 127.6, 127.5, 123.3, 120.6, 119.3, 116.2, 111.1, 71.6, 70.7, 38.7, 36.6, 28.8, 21.1, 20.0; **IR** υ_{max} 2916, 2854, 1681, 1484, 1452, 1384, 1306, 1227, 1193, 1157, 1111, 1076, 1049, 1021, 929, 736, 695; **HRMS** found $(M+Na)^+$, 371.1736, $C_{22}H_{24}N_2O_2$ requires $(M+Na)^+$, 371.1730.



1-(Allyloxy)-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**10d**) was prepared as a colourless oil from **6d** following the general C–H oxidation procedure described (62.3 mg, 42%). $\mathbf{R_f}$ 0.21 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.50–7.48 (m, 1H), 7.23–7.19 (m, 2H), 7.06 (ddd, *J* = 8.0, 6.4, 2.0 Hz, 1H), 5.93 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.26 (ddt, *J* = 17.2, 2.0, 1.6 Hz, 1H), 5.14 (ddt, *J* = 10.4, 2.0, 1.6 Hz, 1H), 4.91 (t, *J* = 5.2 Hz, 1H), 4.18 and 4.04 (ABq dt, J_{AB} = 12.4 Hz, *J* = 5.6, 1.6 Hz, 2H), 3.14 (s, 3H), 2.89 (s, 3H), 2.74 (dt, *J* = 8.0, 5.2 Hz, 1H), 2.67–2.60 (m, 1H), 2.17–2.08 (m, 1H), 2.05–1.93 (m, 2H), 1.88–1.79 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.9, 135.6, 135.5, 134.9, 127.7, 123.3, 120.7, 119.3, 116.1(9), 116.1(5), 111.1, 70.4, 70.2, 38.9, 26.9, 28.9, 21.1, 20.1; **IR** υ_{max}

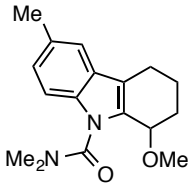
2928, 2849, 1679, 1489, 1451, 1387, 1302, 1227, 1191, 1132, 1109, 1061, 1020, 927, 741; **HRMS** found $(M+Na)^+$, 321.1578, $C_{18}H_{22}N_2O_2$ requires $(M+Na)^+$, 321.1573.

1,6-Dimethoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**7db**) was



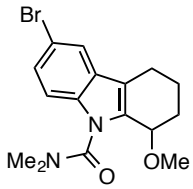
prepared as a brown oil from **6db** the general C–H oxidation procedure described (81.6 mg, 54%). $\mathbf{R_f}$ 0.14 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.8 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.75 (t, *J* = 4.8 Hz, 1H), 3.85 (s, 3H), 3.41 (s, 3H), 3.14 (s, 3H), 2.91 (s, 3H), 2.71 (dt, *J* = 16.0, 4.8 Hz, 1H), 2.62–2.55 (m, 1H), 2.06–1.91 (m, 3H), 1.87–1.79 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 155.1, 154.8, 135.6, 130.6, 128.3, 116.1, 112.8, 112.1, 101.7, 71.2, 56.9, 56.0, 38.9, 37.0, 28.0, 21.2, 19.7; **IR** υ_{max} 2930, 2828, 1679, 1437, 1385, 1226, 1192, 1115, 1079, 1033, 799; **HRMS** found $(M+Na)^+$, 325.1525, $C_{17}H_{22}N_2O_3$ requires $(M+Na)^+$, 325.1523.

1-Methoxy-*N*,*N*,6-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (**7dc**) was



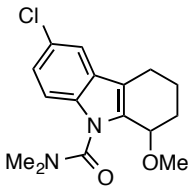
prepared as a brown oil from **6dc** following the general C–H oxidation procedure described (123.5 mg, 86%). $\mathbf{R_f}$ 0.19 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 1.6 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.76 (t, *J* = 4.8 Hz, 1H), 3.41 (s, 3H), 3.15 (s, 3H), 2.90 (s, 3H), 2.72 (dt, *J* = 16.0, 4.8 Hz, 1H), 2.62–2.55 (m, 1H), 2.43 (s, 3H), 2.05–1.90 (m, 3H), 1.87–1.78 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 155.0, 134.8, 133.8, 130.0, 127.8, 124.7, 119.1, 115.8, 110.9, 71.1, 56.7, 38.8, 26.8, 28.0, 21.4, 21.1, 19.7; **IR** υ_{max} 2926, 1670, 1443, 1387, 1307, 1181, 1117, 1027, 907, 798, 727; **HRMS** found $(M+Na)^+$, 309.1576, $C_{17}H_{22}N_2O_2$ requires $(M+Na)^+$, 309.1573.

6-Bromo-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide



(**7dd**) was prepared as pale crystals from **6dd** following the general C–H oxidation procedure described (126.7 mg, 72%). $\mathbf{R_f}$ 0.10 (1:4, v/v EtOAc : hexanes); **Mp** 101.1–103.2 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.0 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.08 (d, *J* = 8.8 Hz), 4.72 (t, *J* = 4.8 Hz, 1H), 3.41 (s, 3H), 3.15 (s, 3H), 2.87 (s, 3H), 2.69 (dt, *J* = 16.0, 5.6 Hz, 1H), 2.61–2.54 (m, 1H), 2.10–2.02 (m, 1H), 2.01–1.90 (m, 2H), 1.87–1.78 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.3, 136.1, 134.0, 129.2, 126.0, 122.0, 115.4, 113.8, 112.5, 71.0, 56.9, 38.6, 36.9, 27.8, 20.9, 19.6; **IR** υ_{max} 2927, 1690, 1436, 1385, 1313, 1265, 1230, 1198, 1122, 1078, 993, 904, 866, 805, 737, 690; **HRMS** found $(M+Na)^+$, 373.0521, $C_{16}H_{19}{}^{79}BrN_2O_2$ requires $(M+Na)^+$, 373.0522.

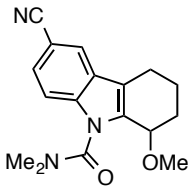
6-Chloro-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide



(**7de**) was prepared as a yellow oil from **6de** following the general C–H oxidation procedure described (100.9 mg, 66%). $\mathbf{R_f}$ 0.34 (1:1, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1 H), 4.72 (t, *J* = 5.2 Hz, 1H), 3.42 (s, 3H), 3.16 (s, 3H), 2.88 (s, 3H), 2.69 (dt, *J* = 16.0, 5.2 Hz, 1H), 2.62–2.54 (m, 1H), 2.11–1.91 (m 3H), 1.87–1.78 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.3, 136.2, 133.7, 128.6, 126.2, 123.4, 118.9, 115.5, 112.0, 71.0, 56.8, 38.6, 36.9, 27.8, 20.9, 19.6; **IR** υ_{max} 2929, 1684, 1440, 1385, 1313, 1262, 1230, 1194, 1123,

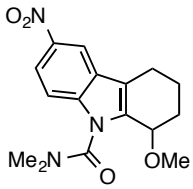
1081, 1060, 998, 907, 859, 798, 730; **HRMS** found $(M+Na)^+$, 329.1028, $C_{16}H_{19}{}^{35}ClN_2O_2$ requires $(M+Na)^+$, 329.1027.

6-Cyano-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7df)



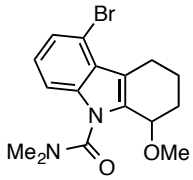
was prepared as a white solid from **6df** following the general C–H oxidation procedure described (93.8 mg, 62%). $\mathbf{R_f}$ 0.39 (1:1, v/v EtOAc : hexanes); **Mp** 126.3–127.9 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.2 Hz, 1H), 7.46 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 4.69 (t, *J* = 4.8 Hz, 1H), 3.42 (s, 3H), 3.17 (s, 3H), 2.86 (s, 3H), 2.73 (dt, J = 16.0, 5.2 Hz, 1H), 2.66–2.58 (m, 1H) 2.13–2.17 (m, 1H), 1.99–1.93 (m, 2H), 1.88–1.82 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153. 6, 137.2, 136.9, 127.4, 126.3, 124.6, 120.3, 116.0, 111.7, 103.8, 71.0, 57.0, 38.5, 37.0, 27.7, 20.8, 19.6; **IR** υ_{max} 2927, 2857, 2822, 2215, 1687, 1439, 1384, 1361, 1320, 1231, 1198, 1161, 1119, 1083, 905, 801, 732; **HRMS** found $(M+Na)^+$, 320.1371, $C_{17}H_{19}N_3O_3$ requires $(M+Na)^+$, 320.1369.

1-Methoxy-*N*,*N*-dimethyl-6-nitro-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7dg)



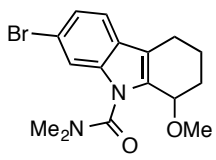
was prepared as a brown oil from **6dg** following the general C–H oxidation procedure described (109.6 mg, 69%). $\mathbf{R_f}$ 0.26 (1:1, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.0 Hz, 1H), 8.14 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.25 (d, *J* = 2.0 Hz, 1H), 4.70 (t, *J* = 5.2 Hz, 1H), 3.43 (s, 3H), 3.20 (s, 3H), 2.87 (s, 3H), 2.78 (dt, *J* = 16.0, 5.2 Hz, 1H), 2.71–2.64 (m, 1H), 2.17–2.09 (m, 1H), 2.04–1.94 (m, 2H), 1.94–1.84 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 153.6, 142.4, 138.2(1), 138.1(8), 127.1, 118.9, 117.3, 116.4, 110.8, 71.1, 57.1, 38.6, 37.1, 27.8, 20.9, 19.7; **IR** υ_{max} 2930, 1691, 1512, 1457, 1389, 1314, 1262, 1195, 1122, 1074, 905, 817, 733; **HRMS** found $(M+Na)^+$, 340.1271, $C_{16}H_{19}N_3O_4$ requires $(M+Na)^+$, 340.1268.

5-Bromo-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide



(**7dh**) was prepared as a yellow solid from **6dh** following the general C–H oxidation procedure described (111.8 mg, 63%). $\mathbf{R_f}$ 0.35 (1:1, v/v EtOAc : hexanes); **Mp** 104.8–107.8 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.14 (dd, 8.0, 0.8 Hz, 1H), 7.03 (dd, *J* = 8.0, 7.6 Hz, 1H), 4.68 (t, *J* = 4.8 Hz, 1H), 3.41 (s, 3H), 3.18–3.11 (m, 4H), 3.04–2.97 (m, 1H), 2.85 (s, 3H), 2.10–2.02 (m, 1H), 2.00–1.88 (m, 2H), 1.86–1.78 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.2, 136.3, 135.9, 126.2, 124.8, 123.9, 116.1, 115.0, 110.0, 71.3, 56.9, 38.5, 36.9, 27.4, 23.3, 19.9; **IR** υ_{max} 2928, 1684, 1392, 1307, 1261, 1185, 1114, 1078, 988, 780, 740, 657; **HRMS** found $(M+Na)^+$, 373.0527, $C_{16}H_{19}{}^{79}BrN_2O_2$ requires $(M+Na)^+$, 373.0522.

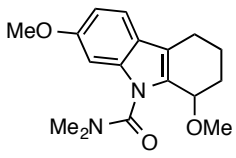
7-Bromo-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7di)



was prepared as a white solid from **6di** following the general C–H oxidation procedure described (140.0 mg, 79%). $\mathbf{R_f}$ 0.12 (1:4, v/v EtOAc : hexanes); **Mp** 174.1–174.9 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.24 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.70 (t, *J* = 4.8 Hz, 1H), 3.41 (s, 3H), 3.17 (s, 3H), 2.90 (s, 3H), 2.71 (dt, *J* = 16.0, 5.6 Hz, 1H), 2.63–2.56 (m, 1H), 2.10–2.03 (m, 1H), 2.01–1.93 (m, 2H), 1.87–1.79 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 154.3, 136.0, 135.5, 126.5, 123.9, 120.5, 116.8,

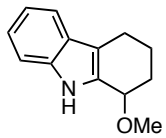
115.9, 114.0, 71.1, 56.9, 38.7, 37.0, 27.8, 20.9, 19.7; **IR** υ_{max} 2929, 2824, 1686, 1458, 1372, 1302, 1225, 1195, 1161, 1113, 1073, 1050, 932, 907, 847, 790; **HRMS** found $(M+Na)^+$, 373.0527, $C_{16}H_{19}{}^{79}BrN_2O_2$ requires $(M+Na)^+$, 373.0522.

1,7-Dimethoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7dj) was prepared as a brown oil from **6dj** following the general C–H oxidation procedure described (76.4 mg, 51%). $\mathbf{R_f}$ 0.20 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 4.71 (t, *J* = 4.8 Hz, 1H), 3.84 (s, 3H), 3.40 (s, 3H), 3.15 (s, 3H), 2.92 (s, 3H), 2.71 (dt, *J* = 16.0 Hz, 5.2 Hz, 1H), 2.62–2.54 (m, 1H), 2.04–1.89 (m, 3H), 1.86–1.78 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 157.5, 155.0, 136.4, 133.6, 121.9, 119.8, 116.1, 109.4, 96.0, 71.2, 56.7, 55.9, 38.8, 37.0, 27.9, 21.2, 19.7; **IR** υ_{max} 2933, 1735, 1678, 1489, 1439, 1387, 1311, 1235, 1161, 1113, 1079, 1033, 907, 726; **HRMS** found $(M+Na)^+$, 325.1522, $C_{17}H_{22}N_2O_3$ requires $(M+Na)^+$, 325.1523.



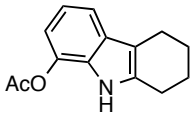
1-Methoxy-2,3,4,9-tetrahydro-1*H*-carbazole (**15**) Using procedures developed by Fagnou[4] a screw cap vial fitted with a silicone cap was charged with carbazole methyl ether **7d** (90.3 mg), EtOH (3 mL) and KOH (2 mL of a 15% aqueous solution). The vial was sealed and lowered into an oil bath preheated at 120 °C. After 36 hours the reaction mixture was partitioned between EtOAc (~10 mL) and saturated aqueous NH_4Cl solution (~10 mL). The aqueous layer was separated and extracted with EtOAc (2 x 5 mL), and the combined organic layers washed with brine (10 mL), dried (Na_2SO_4), filtered and evaporated to provide a brown oil. The crude product was purified via column chromatography to furnish the deprotected carbazole **16** as a yellow oil (38.1 mg, 58%) whose spectral data matched those previously reported.[5] $\mathbf{R_f}$ 0.07 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.05 (brs, 1H), 7.50 (d, *J* = 10.0 Hz, 1H), 7.32 (d, *J* = 10 Hz, 1H), 7.18–7.08 (m, 2H), 4.57 (t, *J* = 4.0 Hz, 1H), 3.47 (s, 3H), 2.93–2.87 (m, 1H), 2.76–2.70 (m, 1H), 2.01–1.82 (m, 4H).

1-Methoxy-2,3,4,9-tetrahydro-1*H*-carbazole (**15**) and **2,3,4,9-Tetrahydro-1*H*-carbazol-8-yl acetate** (**16**). A sealed tube vessel fitted with a Teflon screw lid was charged with the carbazole (0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $PhI(OAc)_2$ (644 mg, 2.0 mmol) and methanol (5 mL). The mixture was stirred at room temperature for 15 minutes, and then at 100 °C for 18 hours. The reaction mixture was then cooled to ambient temperature before the solvent was removed under reduced pressure. The crude residue was purified *via* column chromatography to provide a mixture of products which were subsequently deprotected using conditions reported by Carretero.[6] Purification of the resultant residue afforded the carbazoles **15** and **16**. **15**[5]: $\mathbf{R_f}$ 0.07 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.05 (brs, 1H), 7.50 (d, *J* = 10.0 Hz, 1H), 7.32 (d, *J* = 10 Hz, 1H), 7.18–7.08 (m, 2H), 4.57 (t, *J* = 4.0 Hz, 1H), 3.47 (s, 3H), 2.93–2.87 (m, 1H), 2.76–2.70 (m, 1H), 2.01–1.82 (m, 4H).

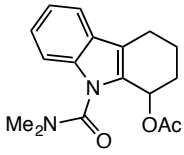


4) D. J. Schipper, M. Hutchinson and K. Fagnou *J. Am. Chem. Soc.* 2010, **132**, 6910.
5) R. J. Owellen *J. Org. Chem.* 1974, **39**, 69.
6) B. Urones, R. G. Arrayás and J. C. Carretero *Org. Lett.* 2013, **15**, 1120

16: $\mathbf{R_f}$ 0.11 (1:4, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.68 (brs, 1H), 7.31 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.88 (dd, *J* = 7.6, 0.8 Hz, 1H), 2.74–2.68 (m, 4H), 2.39 (s, 3H), 1.94–1.83 (m, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 169.2, 135.8, 135.0, 131.1, 127.6, 119.4, 115.8, 113.3, 111.2, 23.4, 23.2(9), 23.2(6), 21.3, 21.1; **IR** υ_{max} 3324, 2926, 1754, 1703, 1635, 1367, 1195, 1013, 906, 798, 729.



9-(Dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl acetate 17.



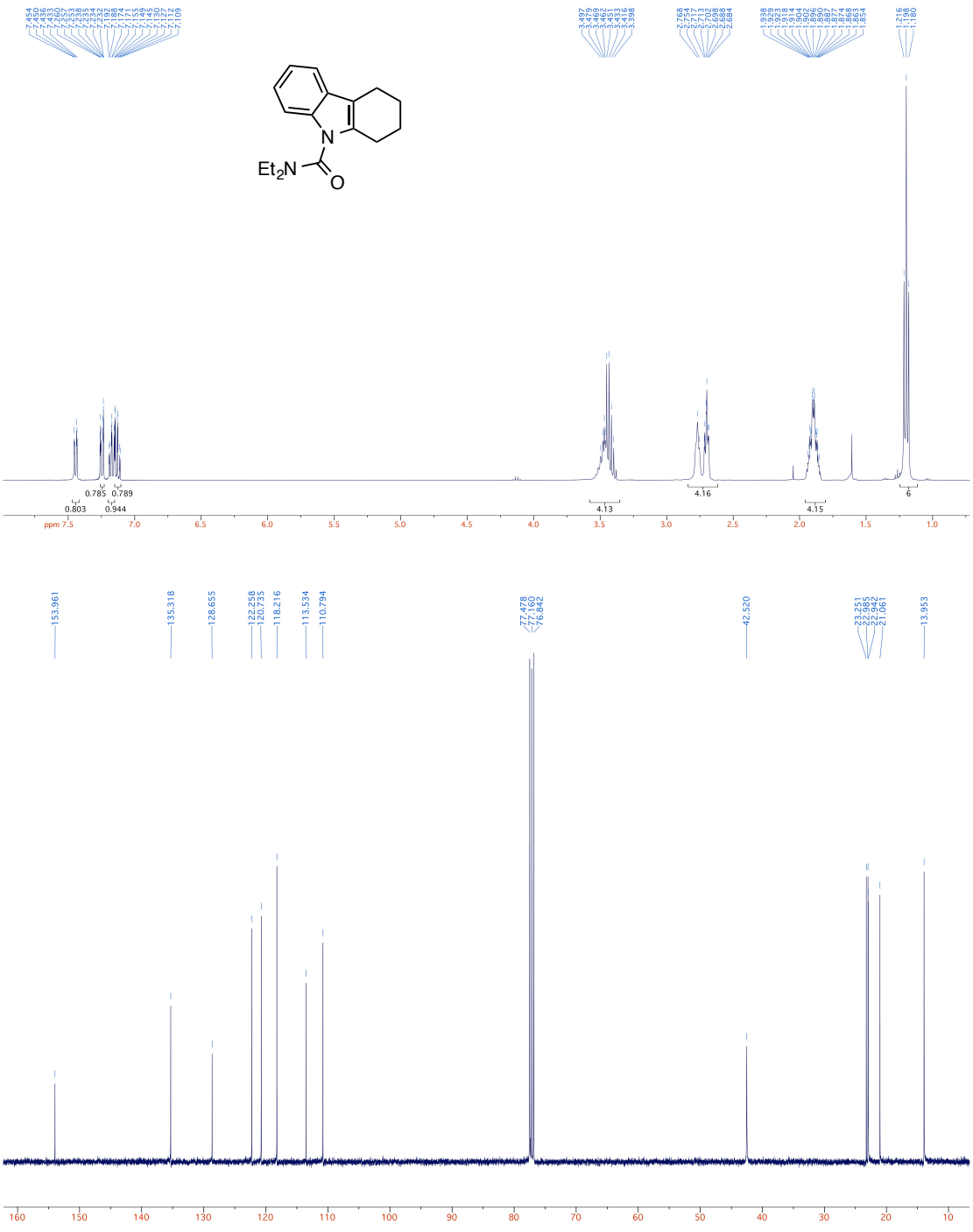
17

Prepared following modified procedures reported by Taniguchi et al.[7] To a stirred solution of the carbazole (1.22 g, 5.0 mmol) and TBAI (0.37 g, 1.0 mmol) in CH_2Cl_2:AcOH (1:1, 50 mL) at –10 °C (salt-ice bath) under an atmosphere of air was added portionwise $PhI(OAc)_2$ (2.42 g, 7.5 mmol) over 10 minutes. An immediate brown colour change was observed. The reaction mixture was stirred a further 15 minutes before being quenched by a 10% aqueous solution of Na_2SO_3 (20 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3 x 25 mL). The combined organic layers were washed with brine (75 mL), dried over Na_2SO_4, filtered, evaporated, and purified by column chromatography to give the title acetate as a pale yellow solid (1.00 g, 66%). $\mathbf{R_f}$ 0.38 (1:1, v/v EtOAc : hexanes); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.52 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.27–7.25 (m, 2H), 7.19–7.15 (m, 1H), 6.22 (t, *J* = 4.8 Hz, 1H), 3.07 (s, 3H), 2.99 (s, 3H), 2.83 (dt, *J* = 16.0, 4.8 Hz, 1H), 2.72–2.64 (m, 1H), 2.32–2.15 (m, 1H), 2.06–1.87 (m, 3H), 2.03 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$) δ 170.2, 154.4, 135.8, 131.9, 127.5, 124.0, 121.1, 119.4, 118.2, 111.7, 65.3, 38.3, 37.5, 29.8, 21.2, 20.9, 19.4; **IR** υ_{max} 2932, 1737, 1688, 1487, 1452, 1389, 1306, 1236, 1197, 746; **HRMS** found $(M+Na)^+$, 323.1368, $C_{17}H_{20}N_2O_3$ requires $(M+Na)^+$, 323.1366.

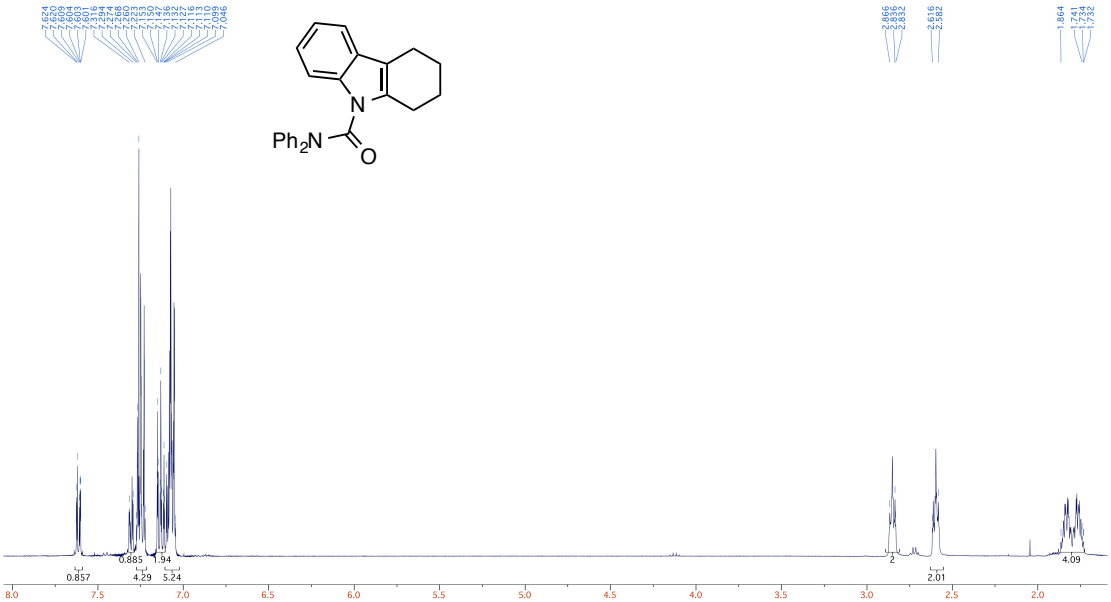
7) H. Zaimoku, T. Hatta, T. Taniguchi, H. Ishibashi *Org. Lett.* 2012, **14**, 6088.

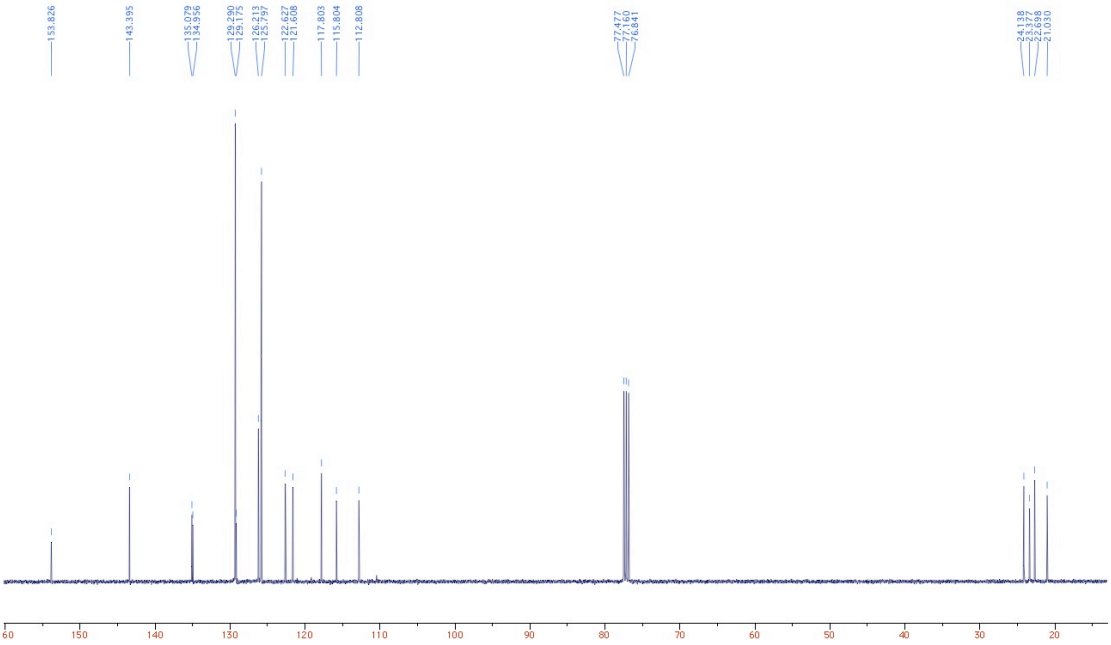
IV ^{1}H-NMR and ^{13}C-NMR Spectra

N,*N*-Diethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (6a)

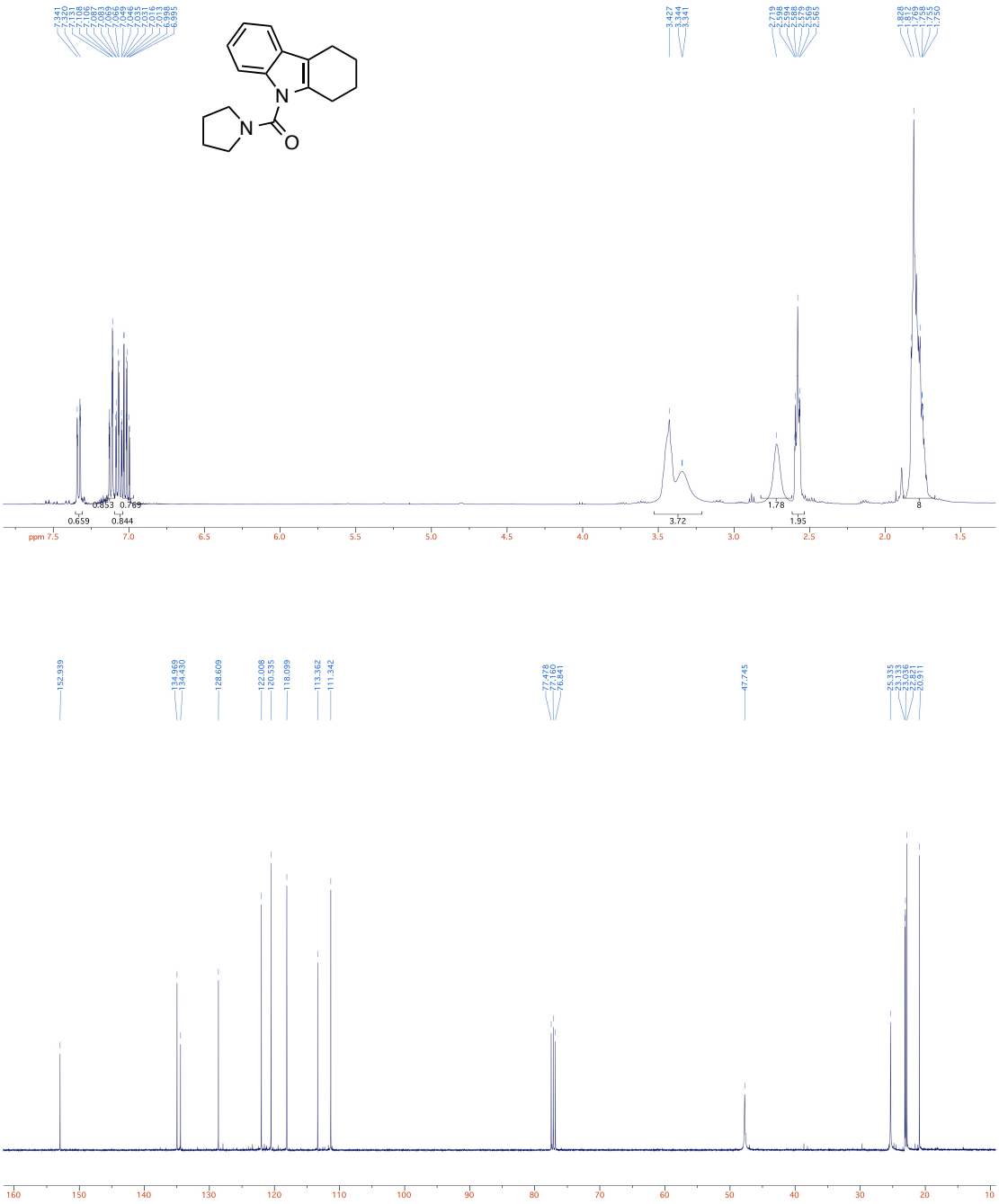


_N_,_N_-Diphenyl-1,2,3,4-tetrahydro-9_H_-carbazole-9-carboxamide (6b)

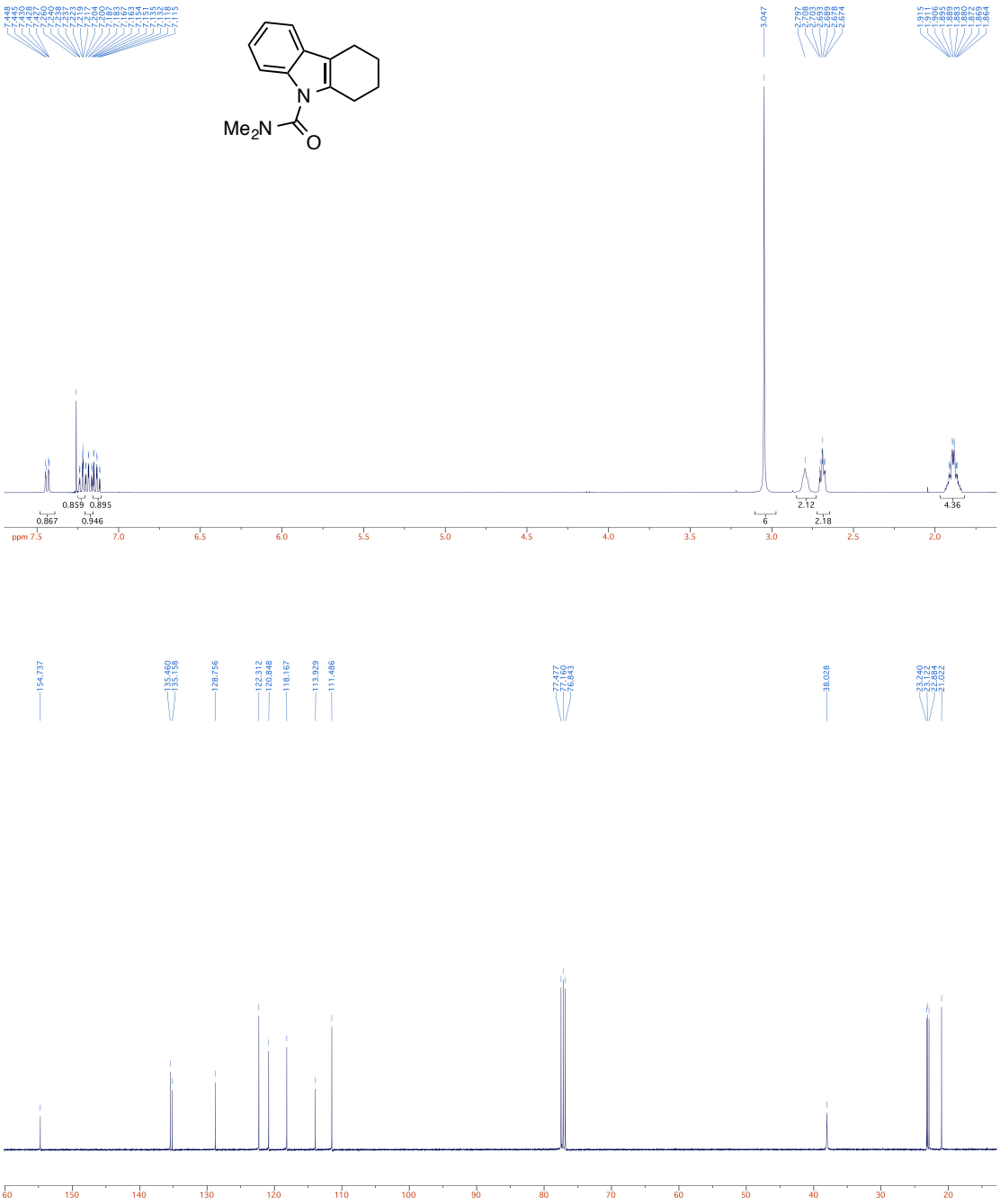




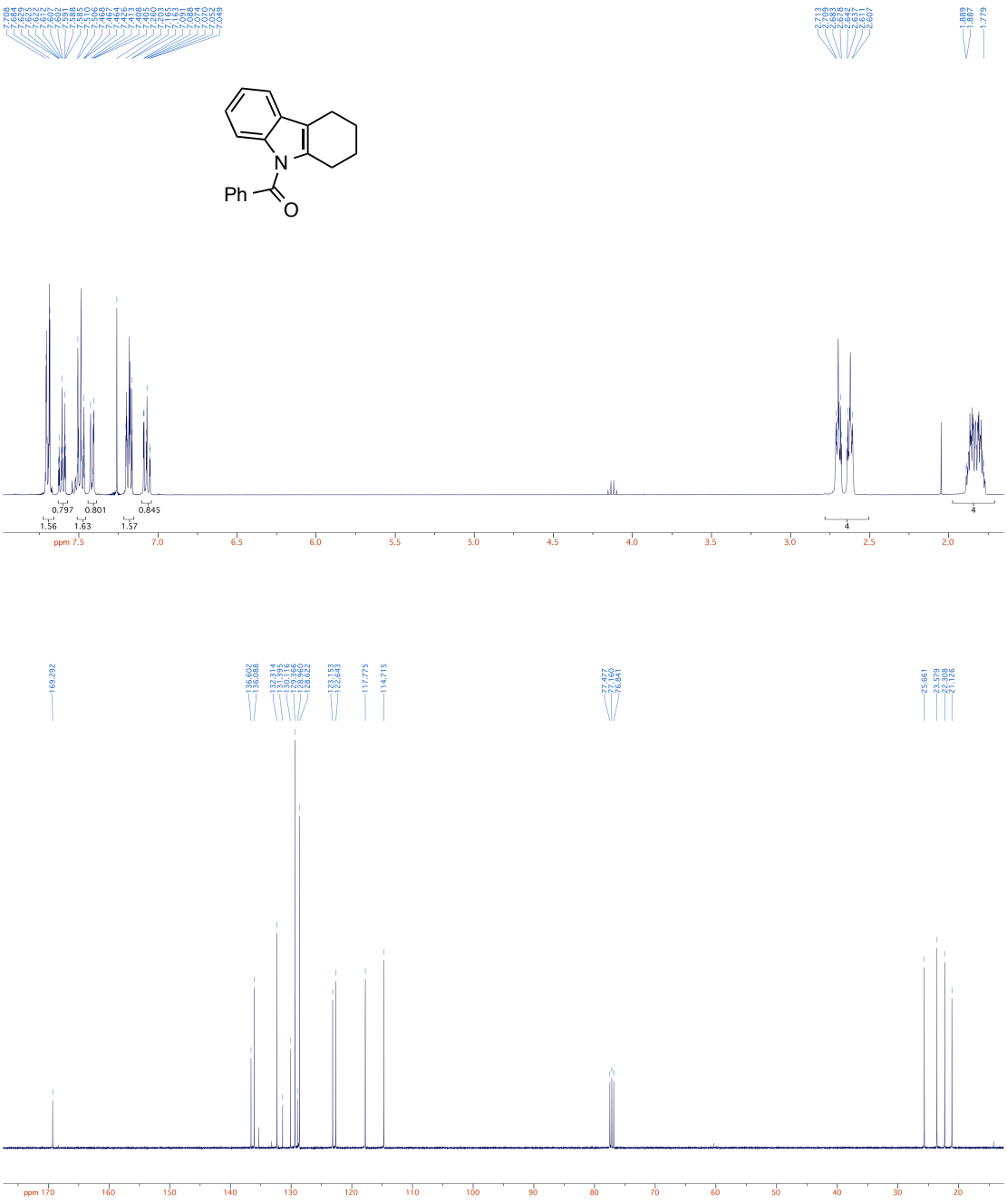
Pyrrolidin-1-yl(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)methanone (6c)



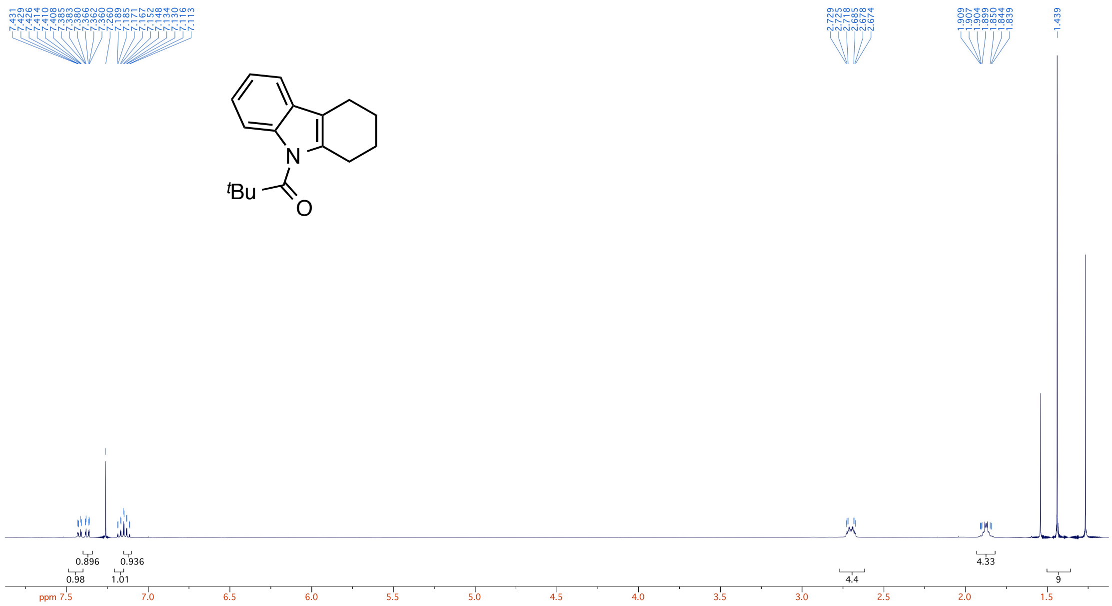
_N_,_N_-Dimethyl-1,2,3,4-tetrahydro-9_H_-carbazole-9-carboxamide (6d)

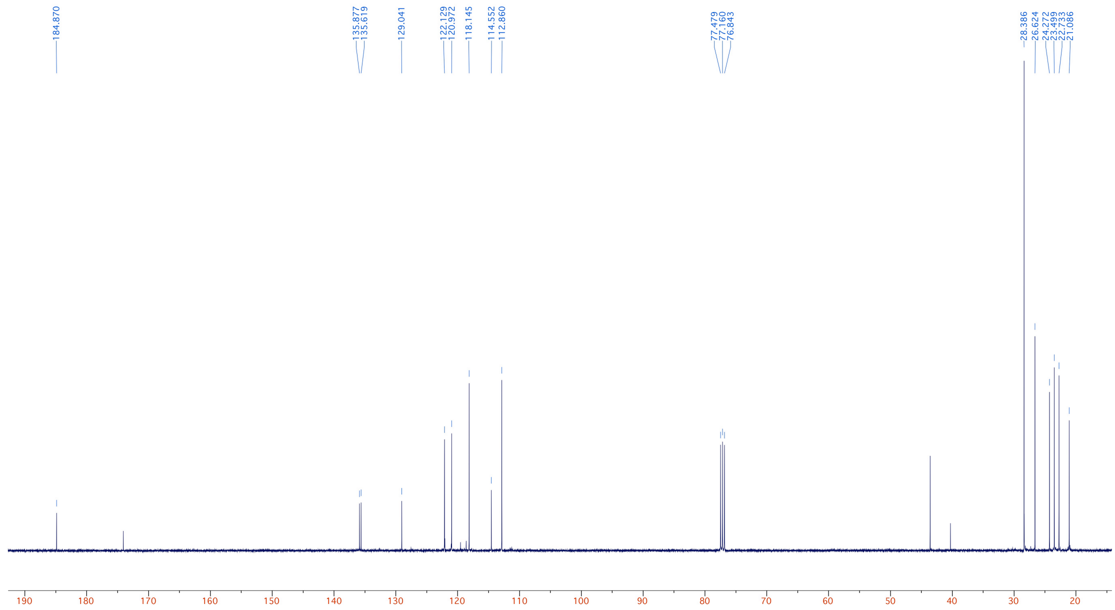


Phenyl(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)methanone (6g)

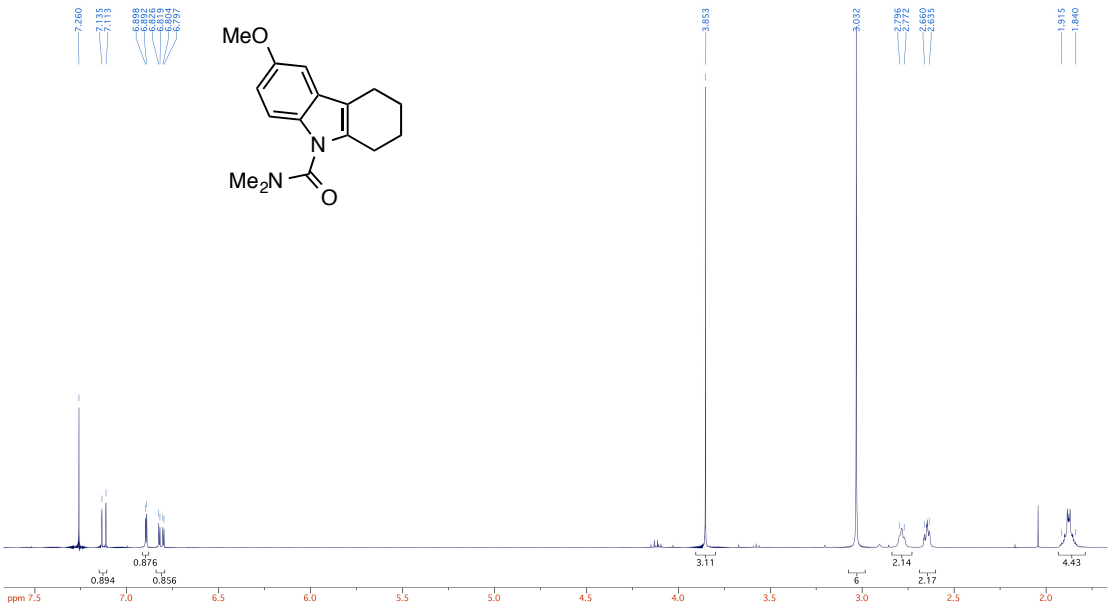


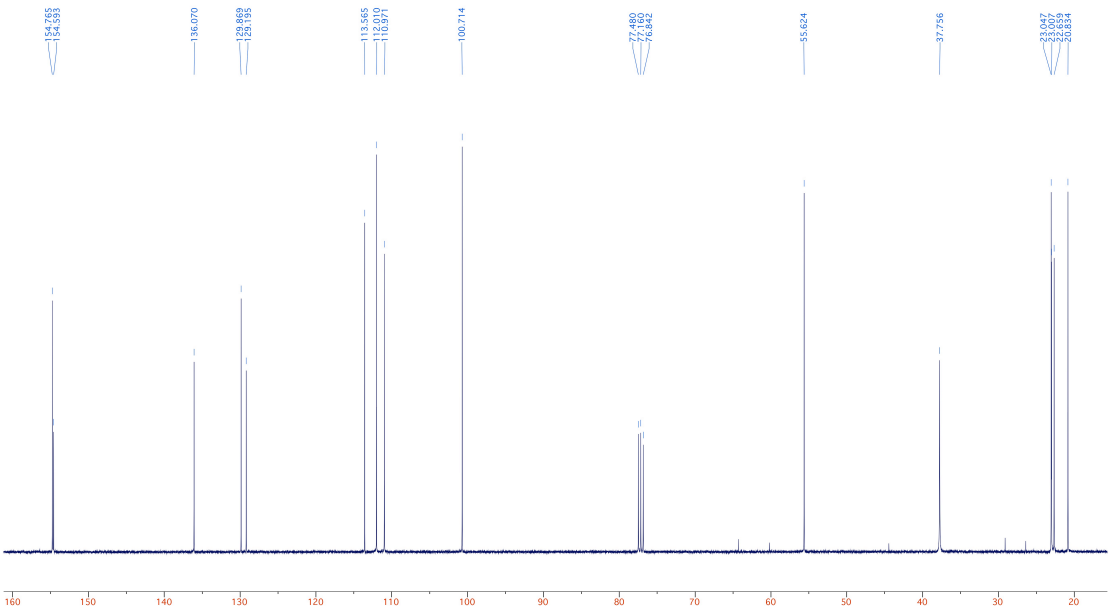
2,2-Dimethyl-1-(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)propan-1-one (6h)



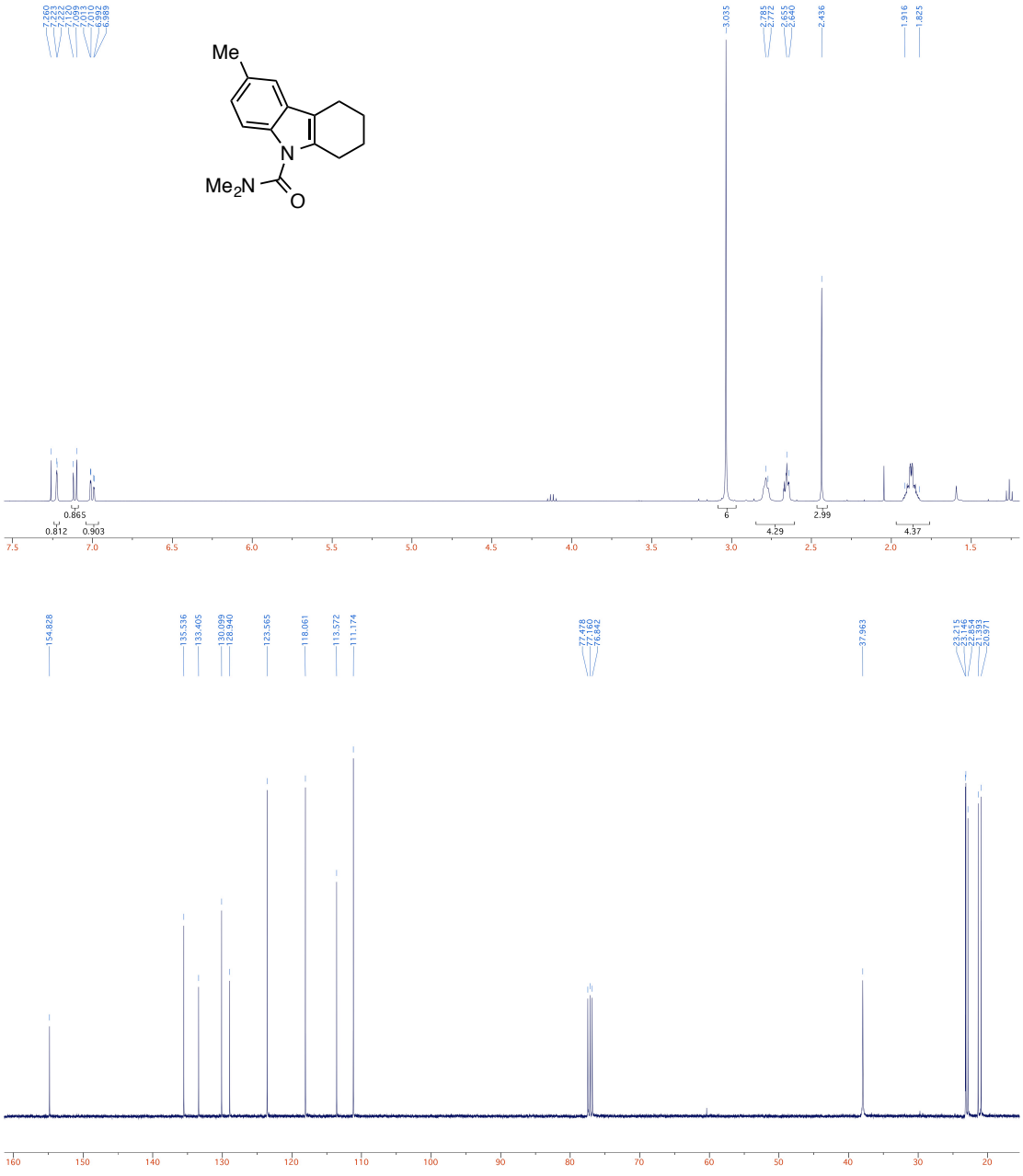


6-Methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (6db)

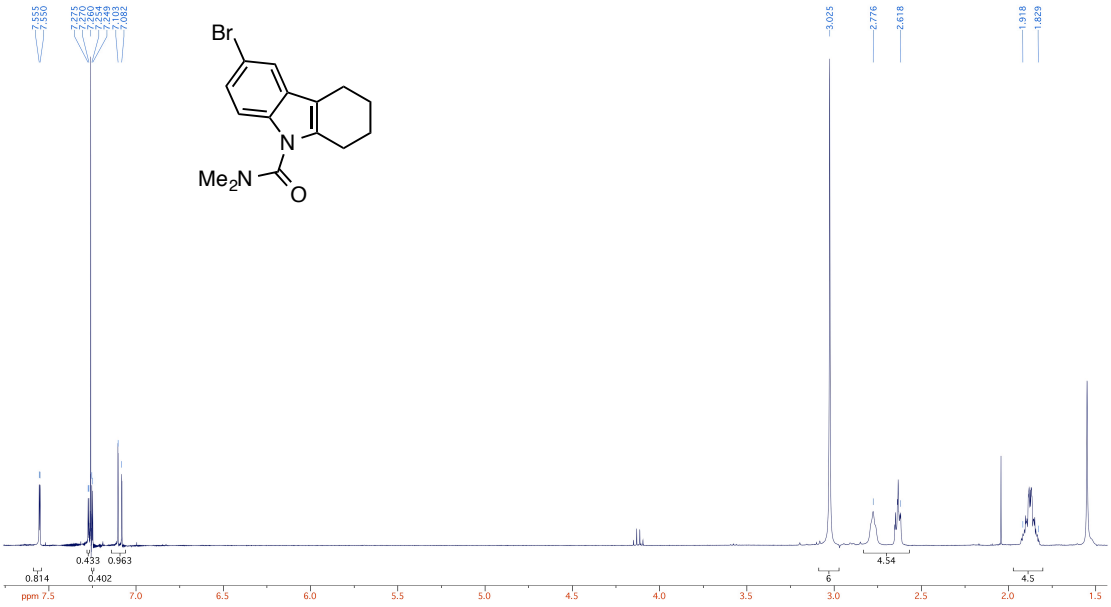


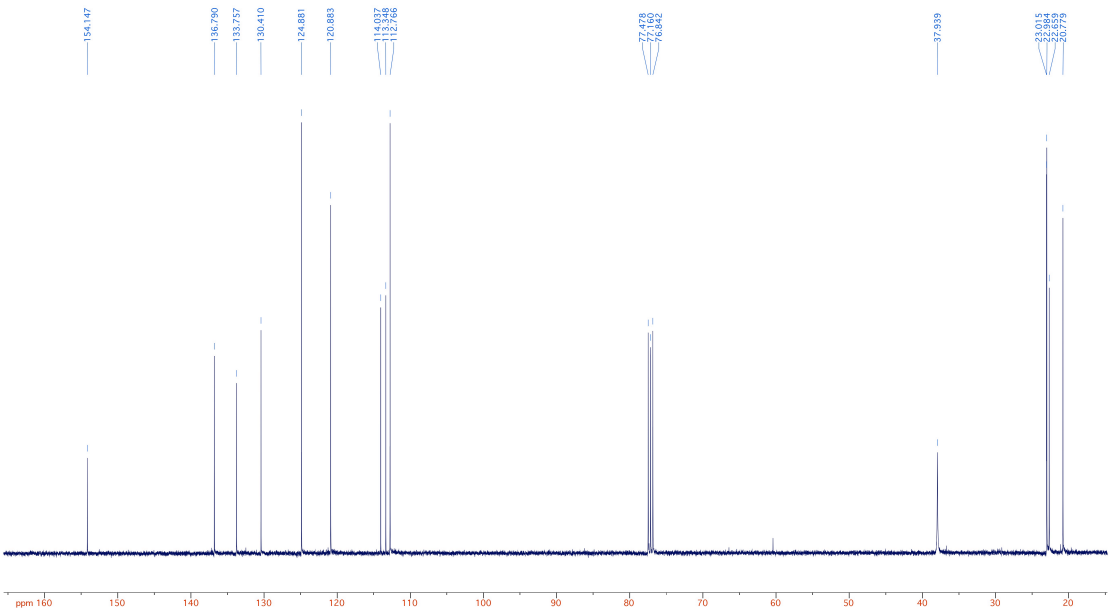


_N_,_N_,-Trimethyl-1,2,3,4-tetrahydro-9_H_-carbazole-9-carboxamide (6dc)

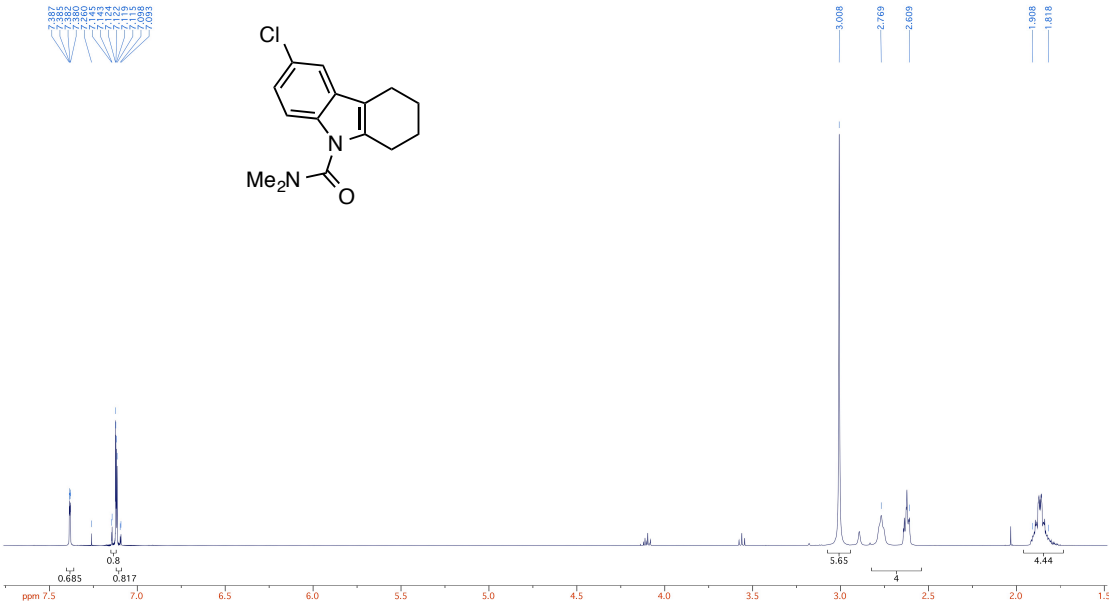


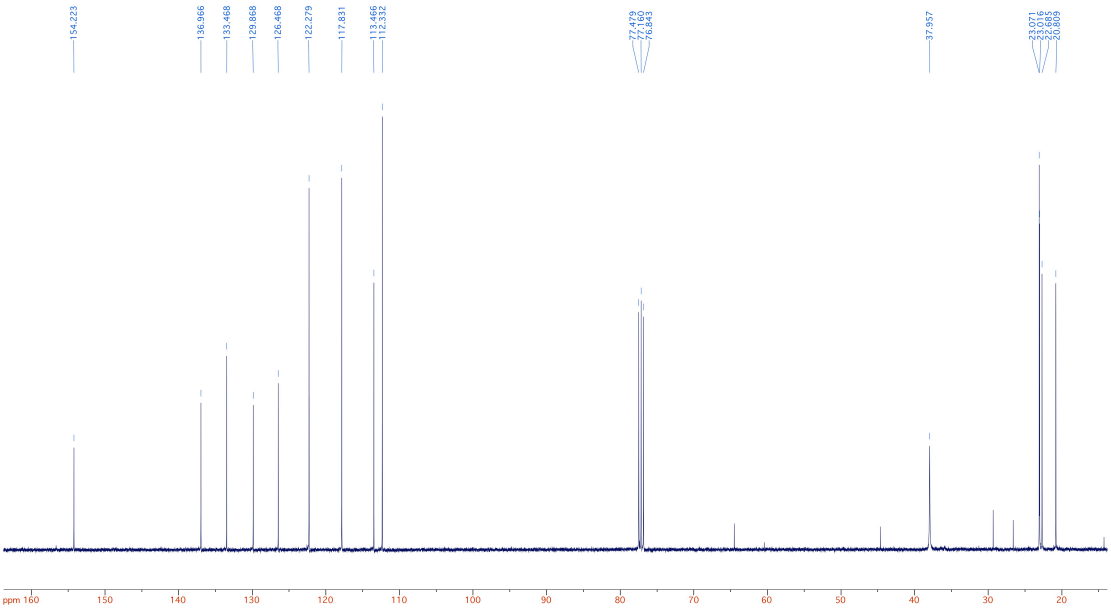
6-Bromo-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (6dd)



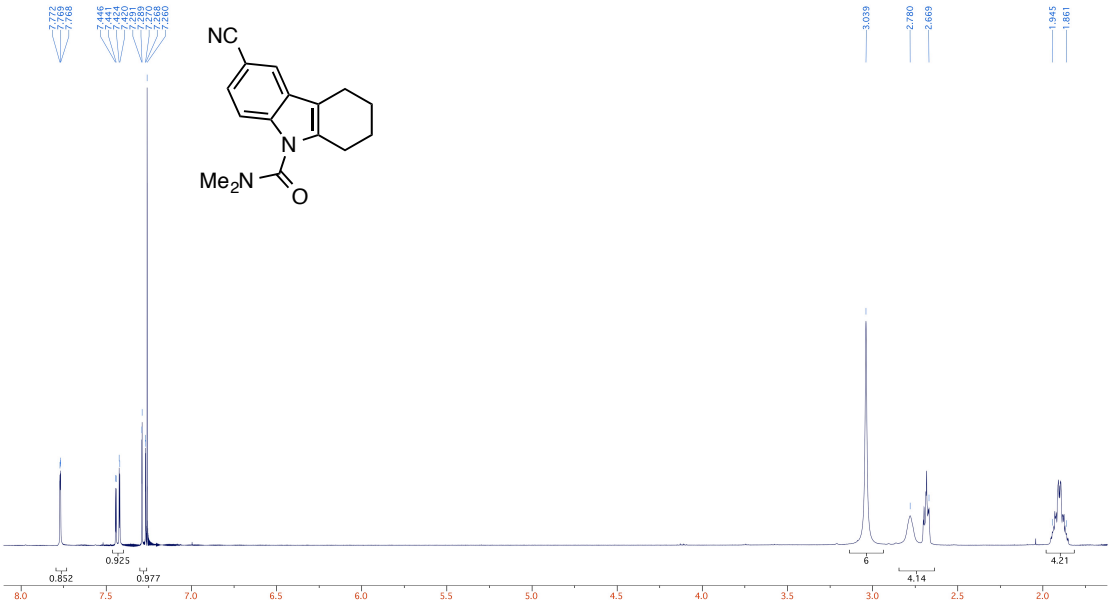


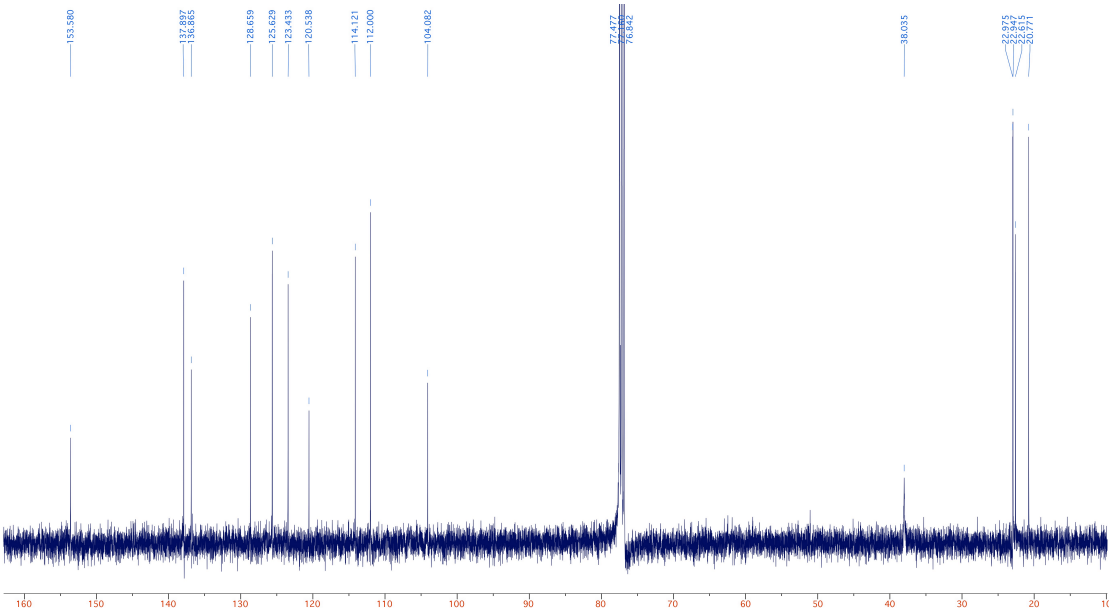
6-Chloro-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9- carboxamide (6de)



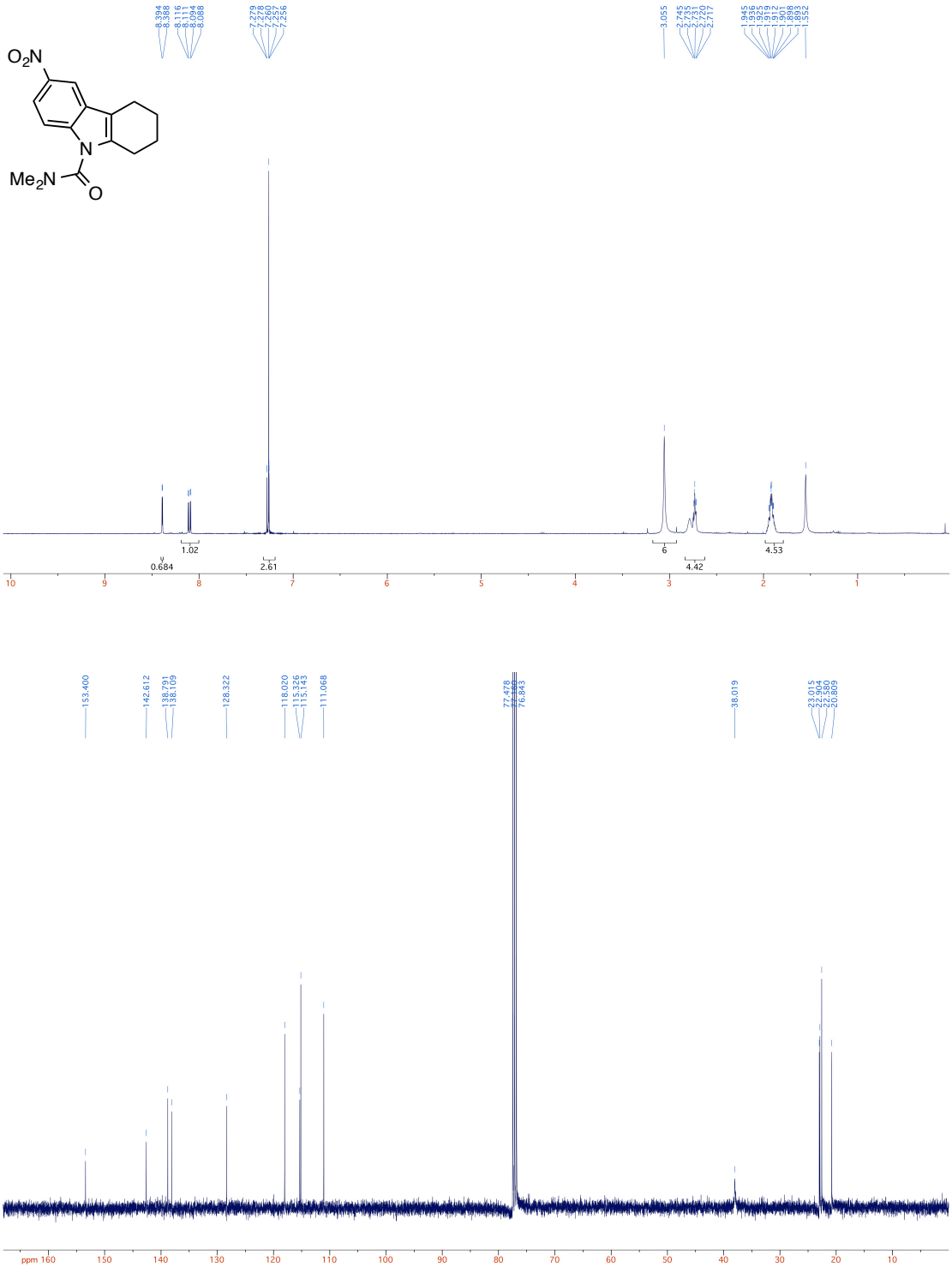


6-Cyano-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (6df)

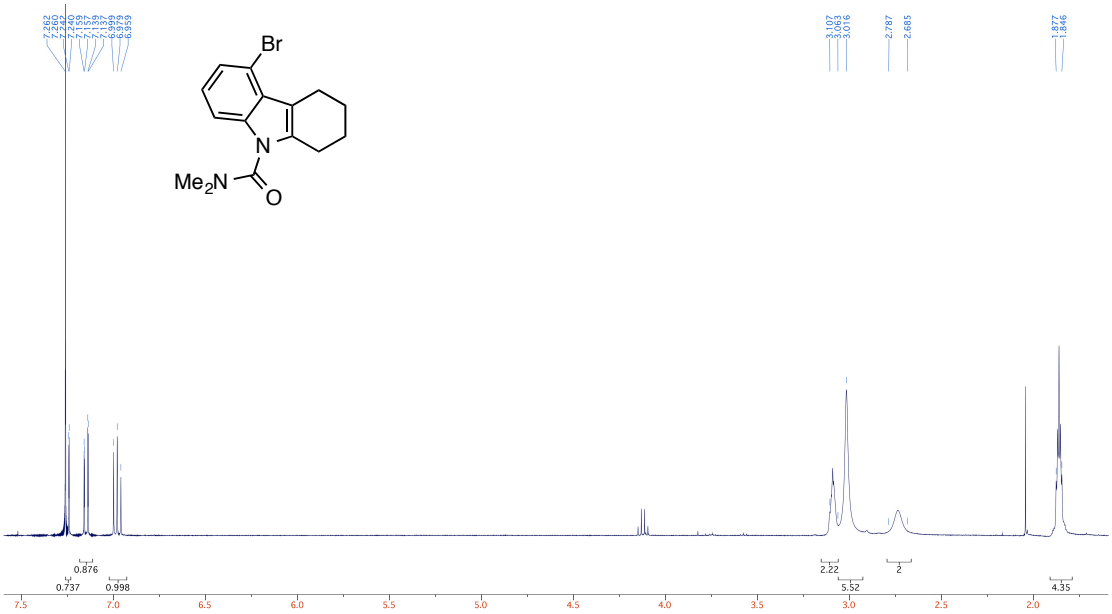


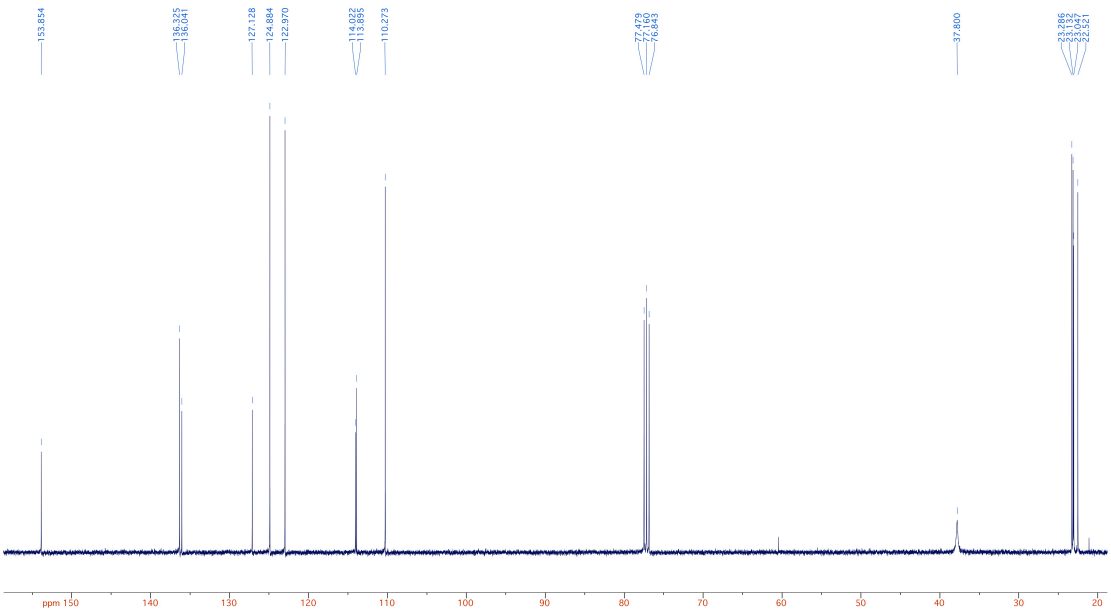


_N_,_N_-Dimethyl-6-nitro-1,2,3,4-tetrahydro-9_H_-carbazole-9-carboxamide (6dg)

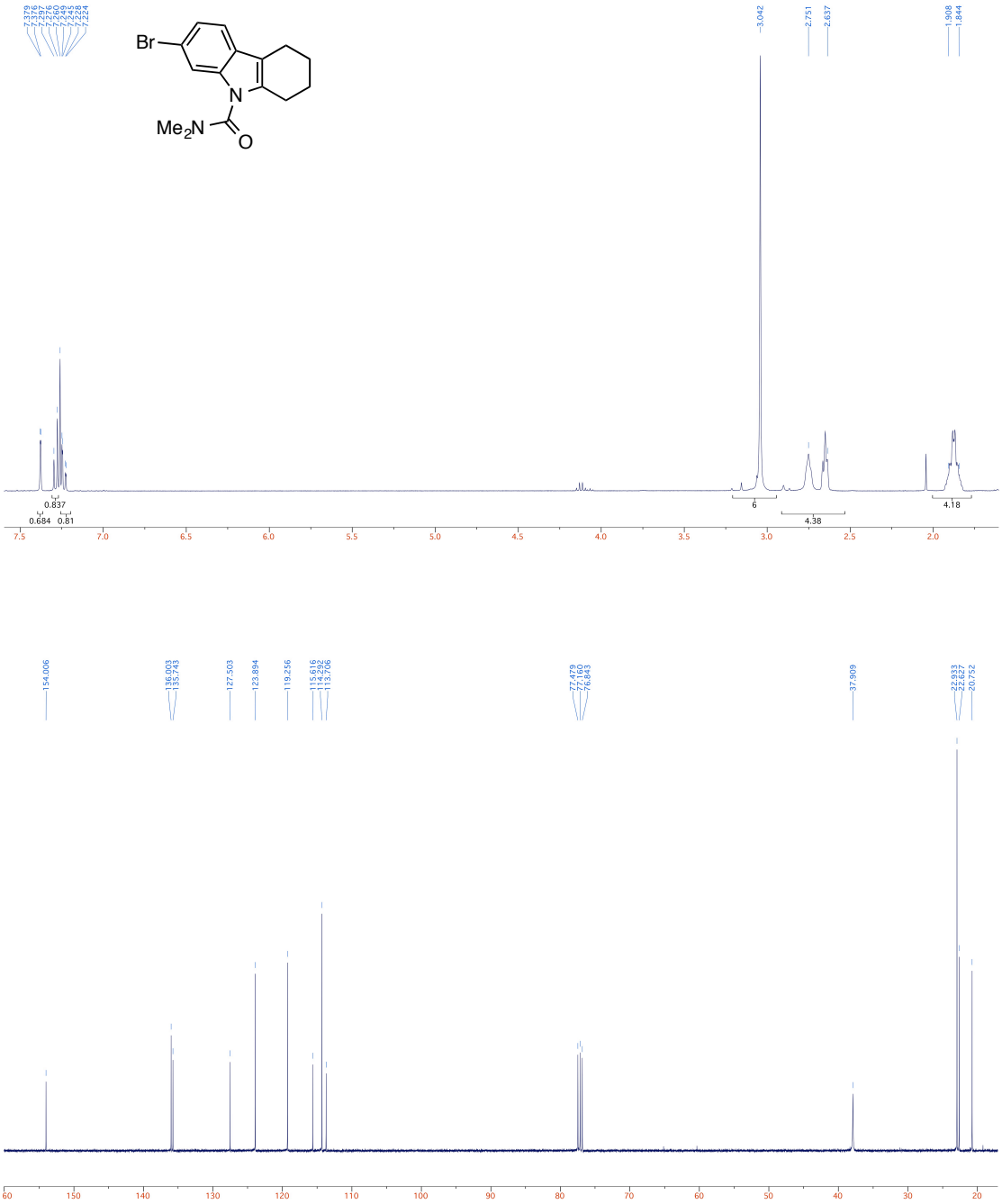


5-Bromo-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (6dh)

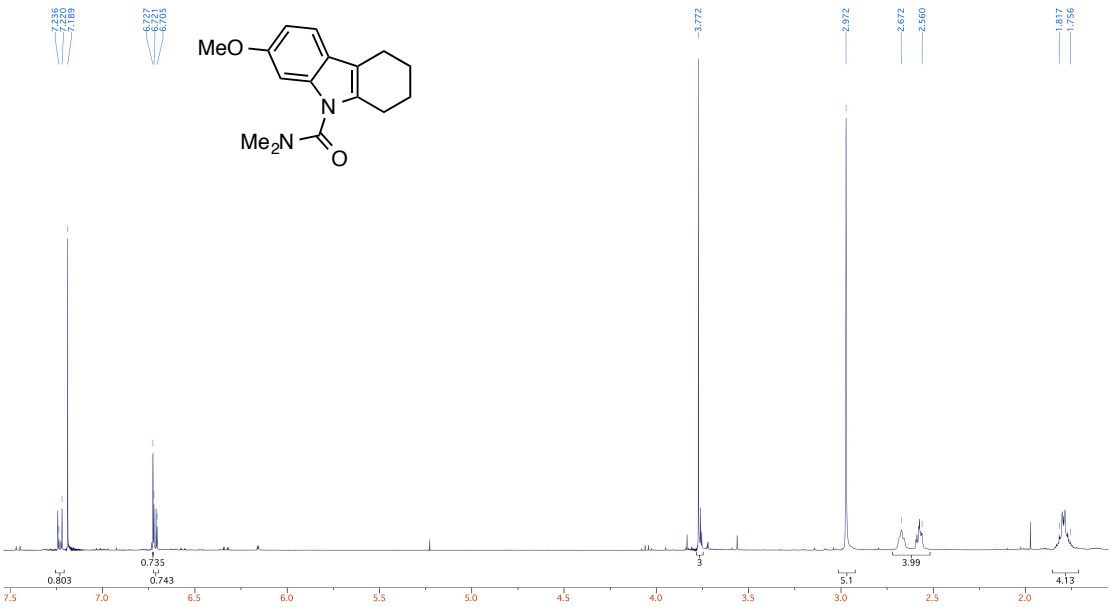


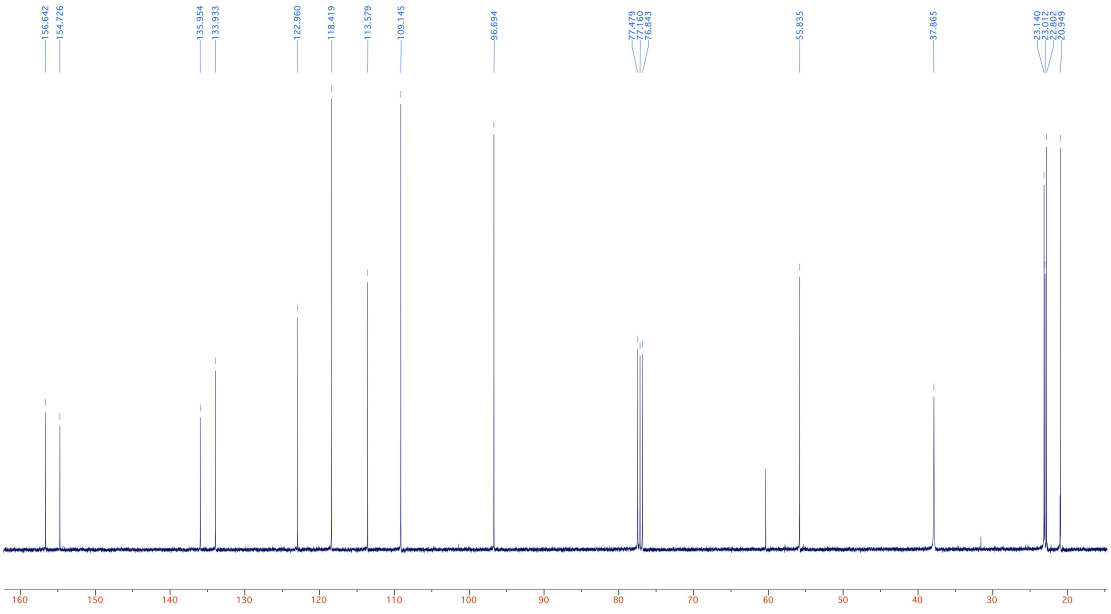


7-Bromo-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (6di)

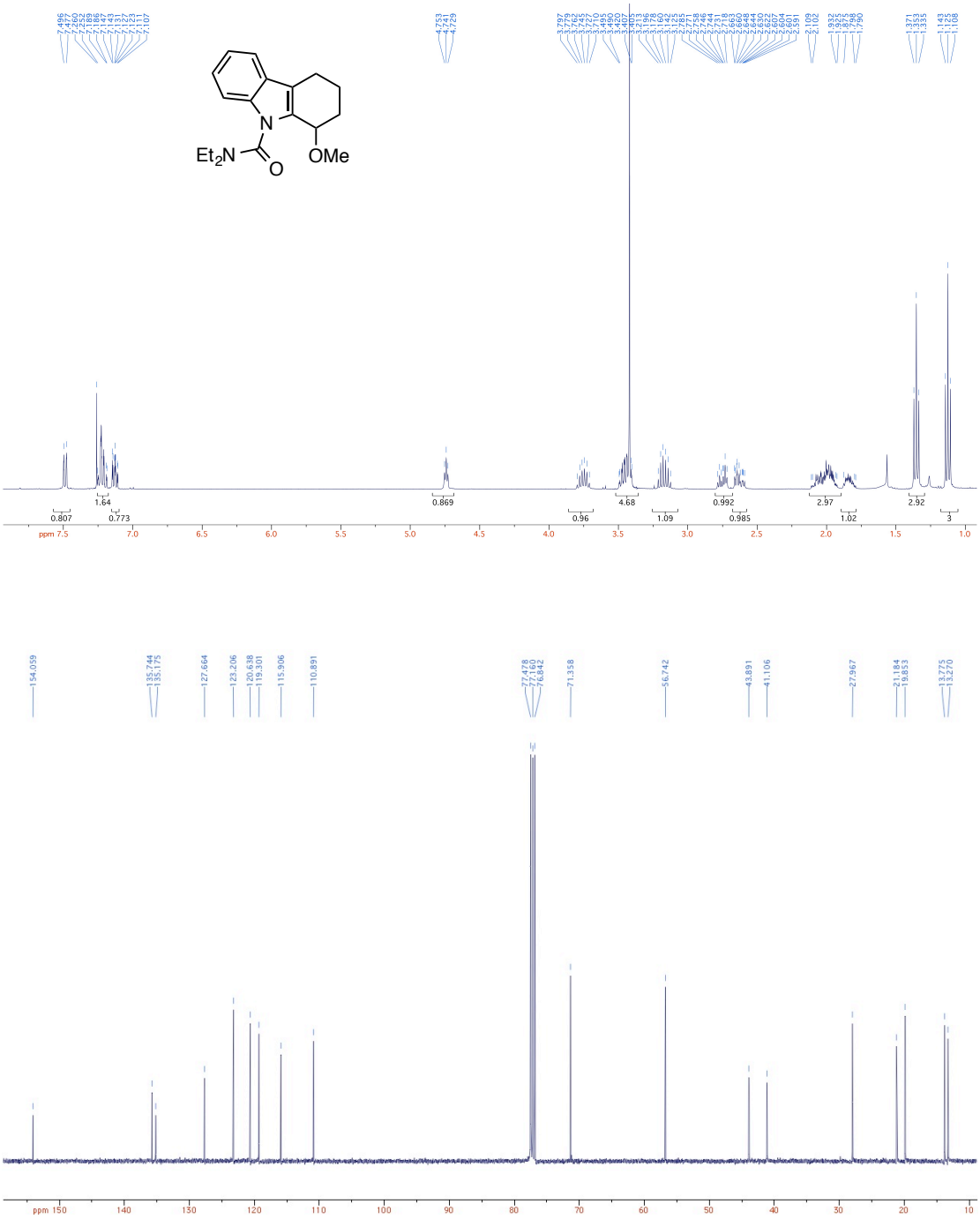


7-Methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (6dj)

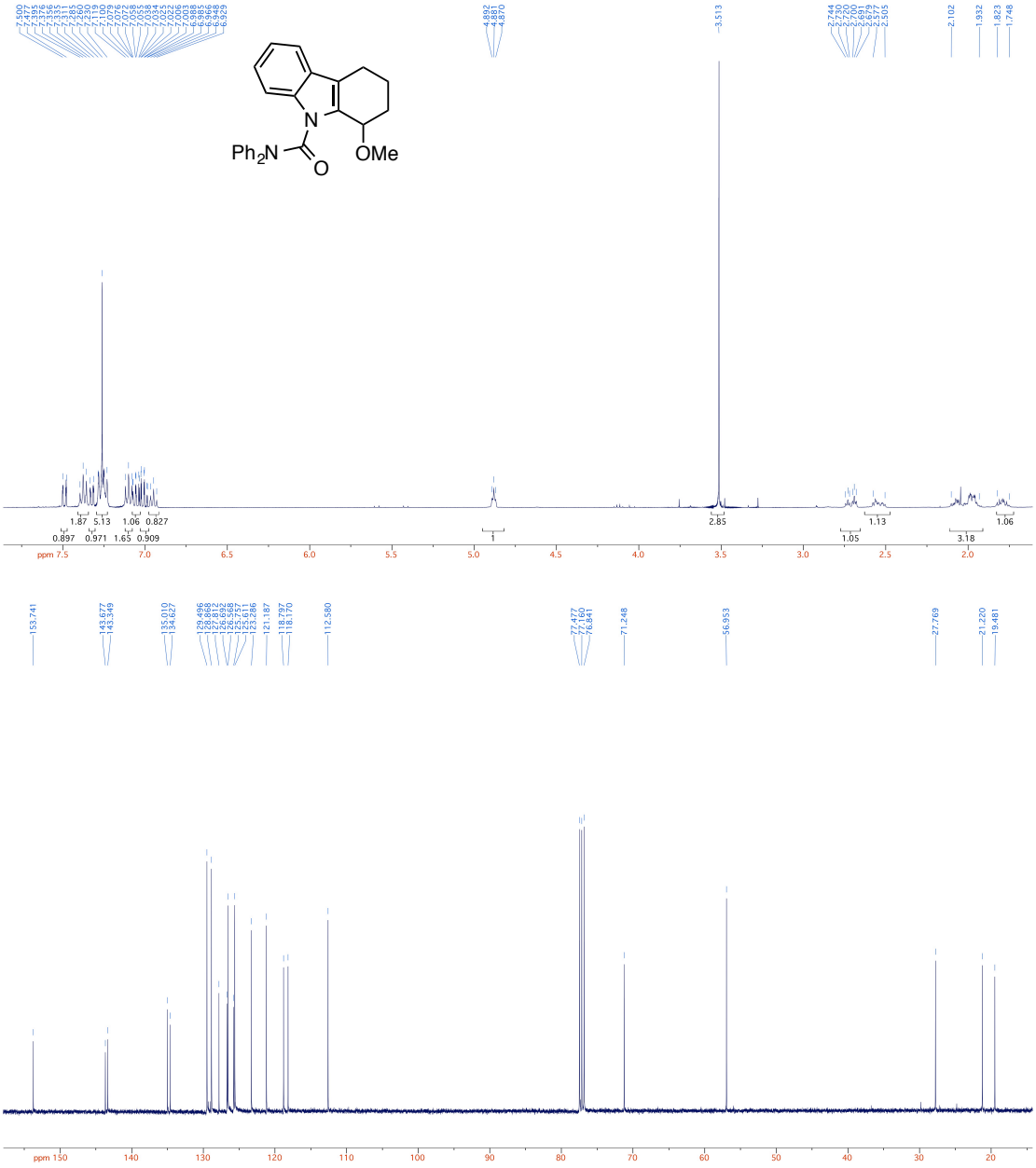




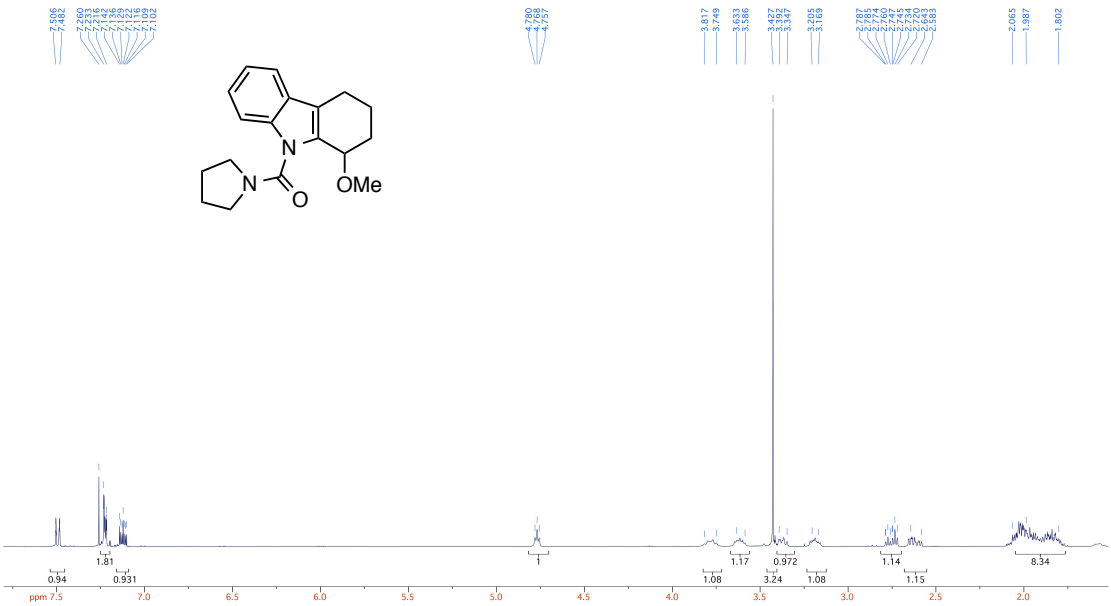
_N_,_N_-Diethyl-1-methoxy-1,2,3,4-tetrahydro-9_H_-carbazole-9-carboxamide (7a)

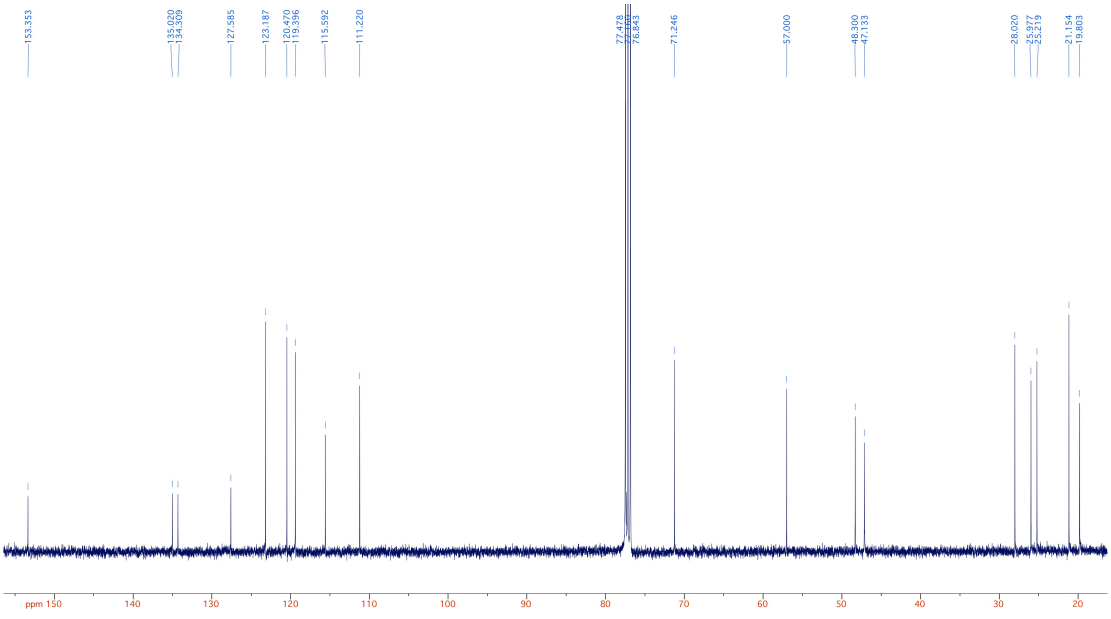


1-Methoxy-*N*,*N*-diphenyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7b)

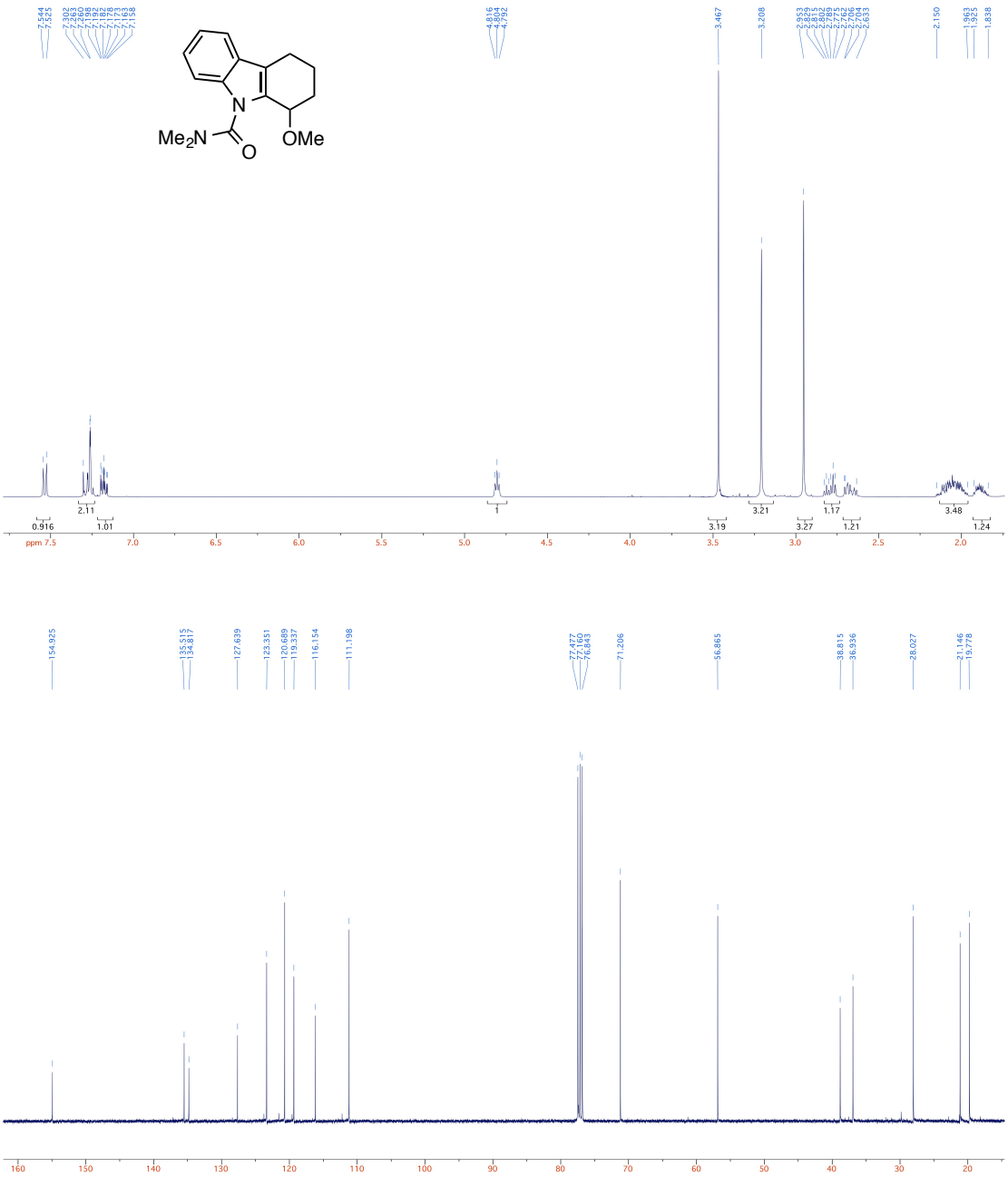


(1-Methoxy-1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)(pyrrolidin-1-yl)methanone (7c)

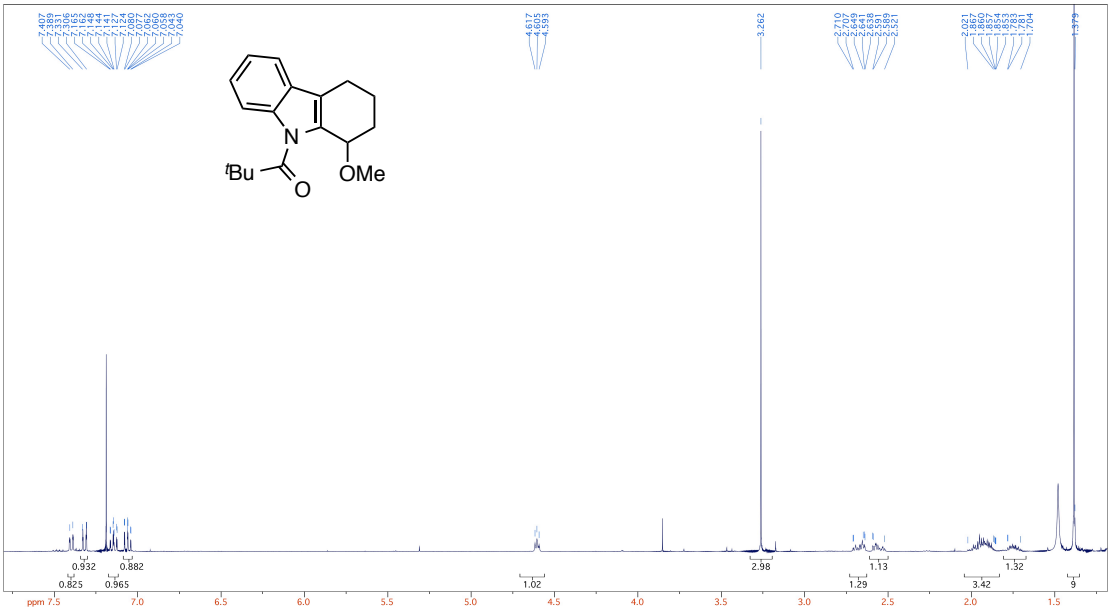


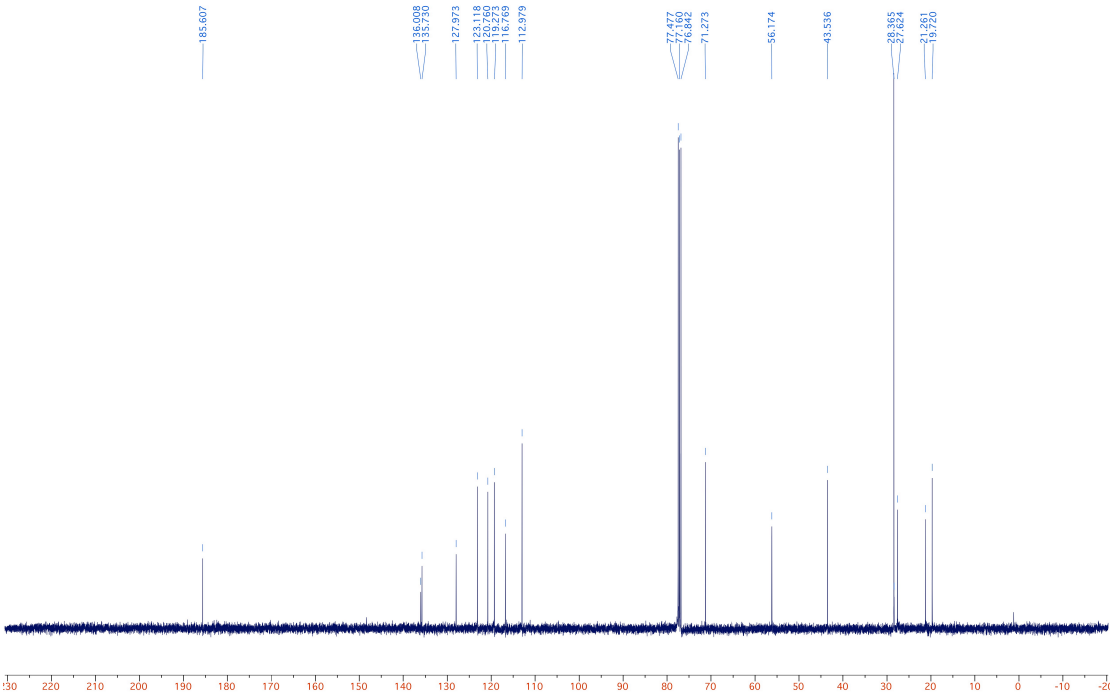


1-Methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7d)

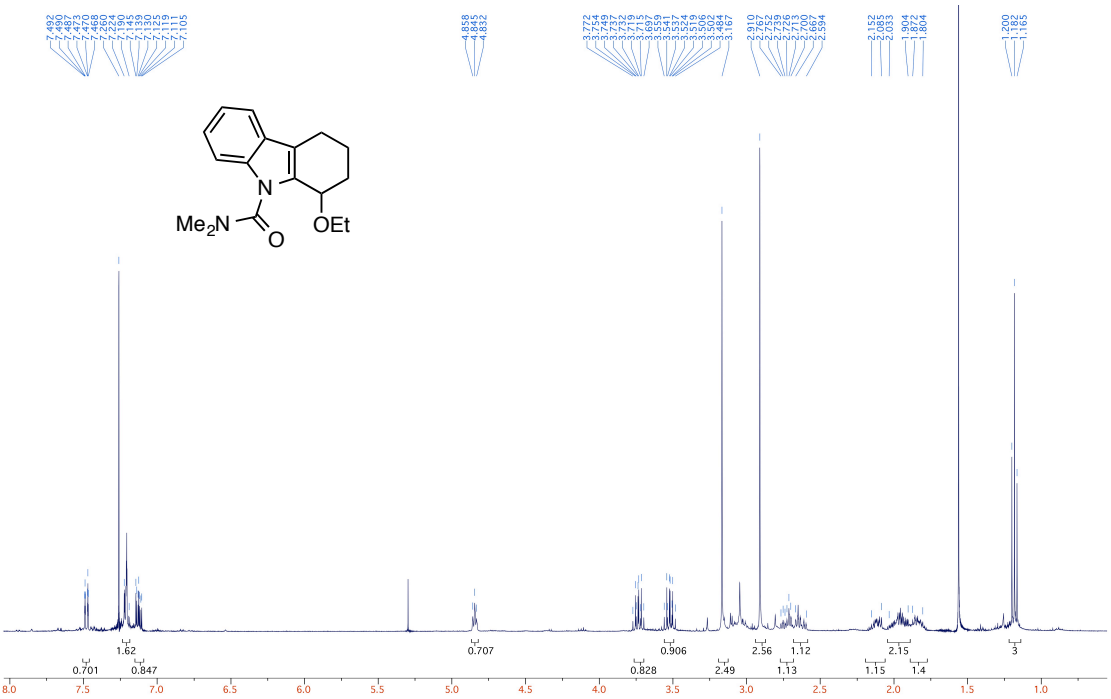


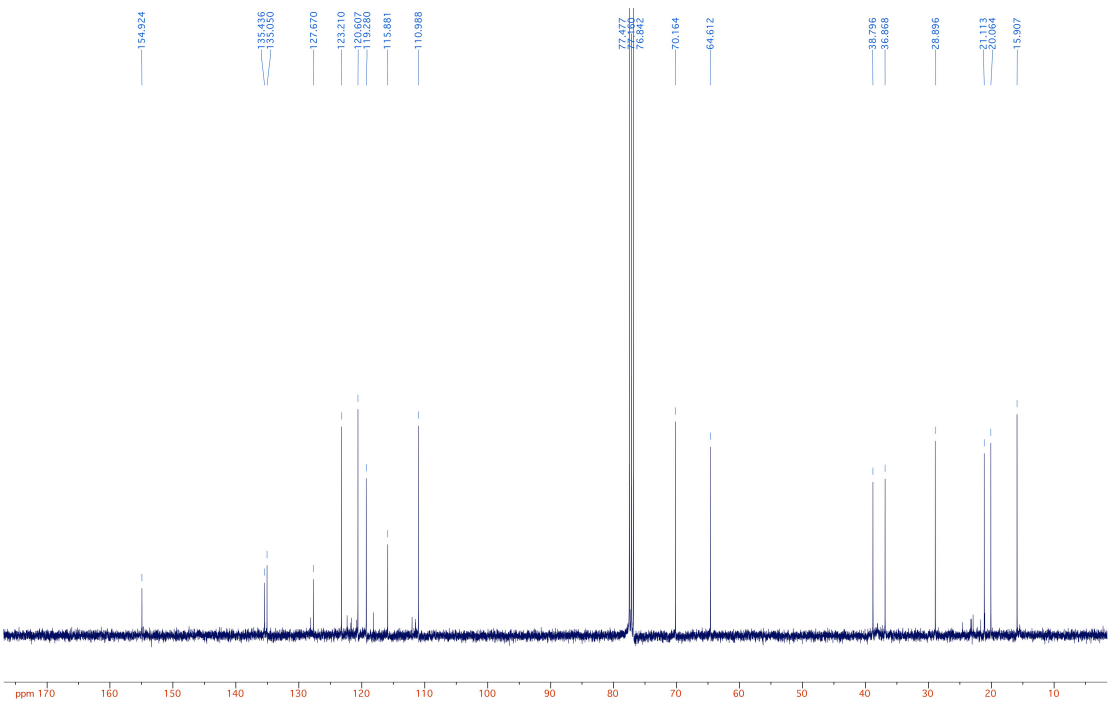
1-(1-Methoxy-1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)-2,2-dimethylpropan-1-one (7h)



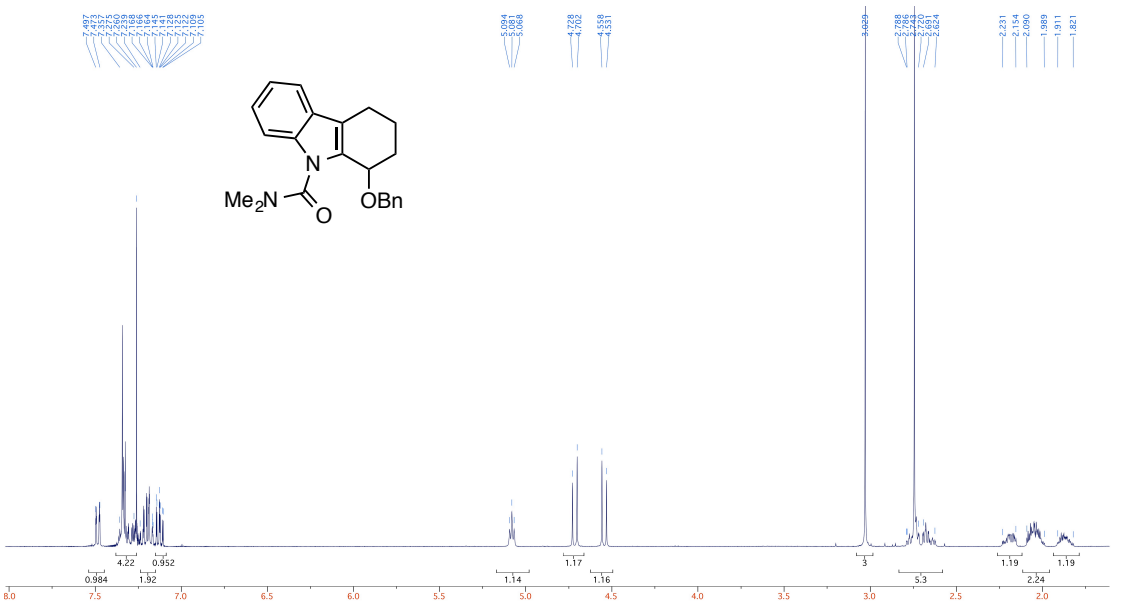


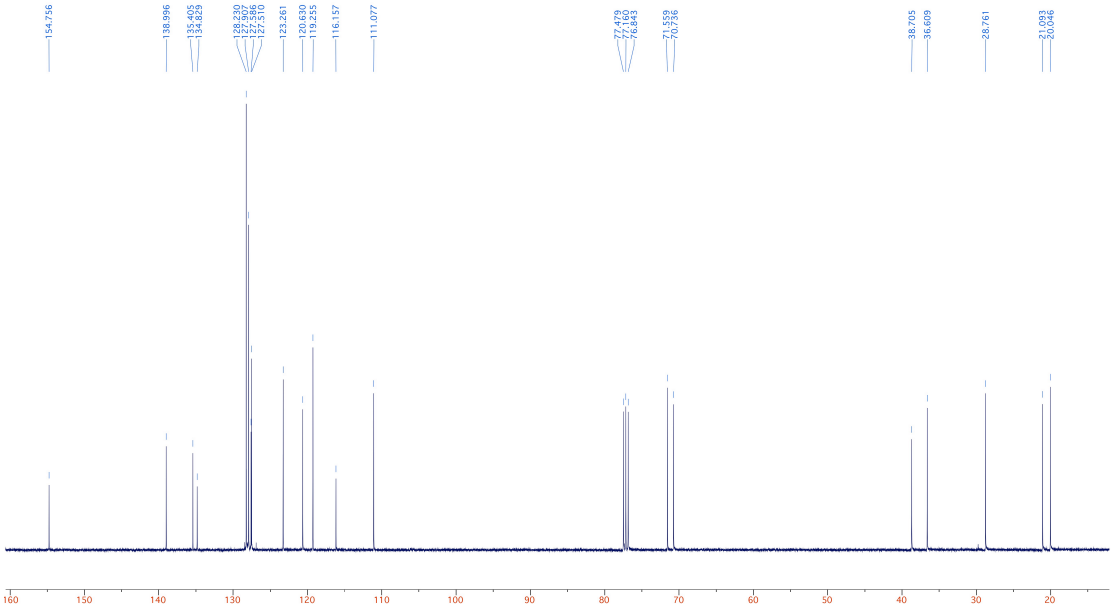
1-Ethoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (8d)



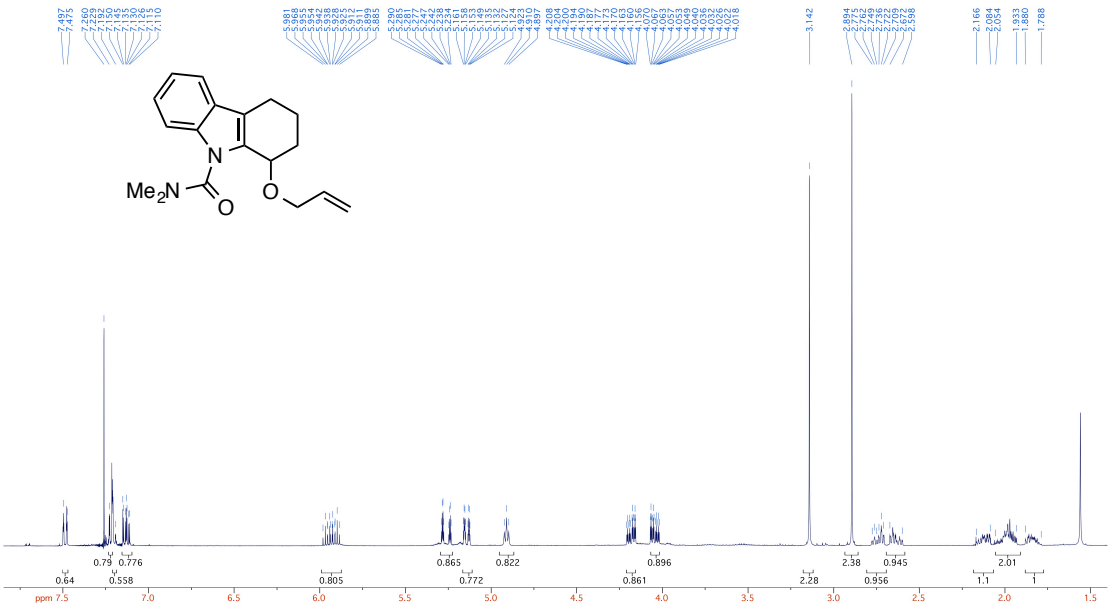


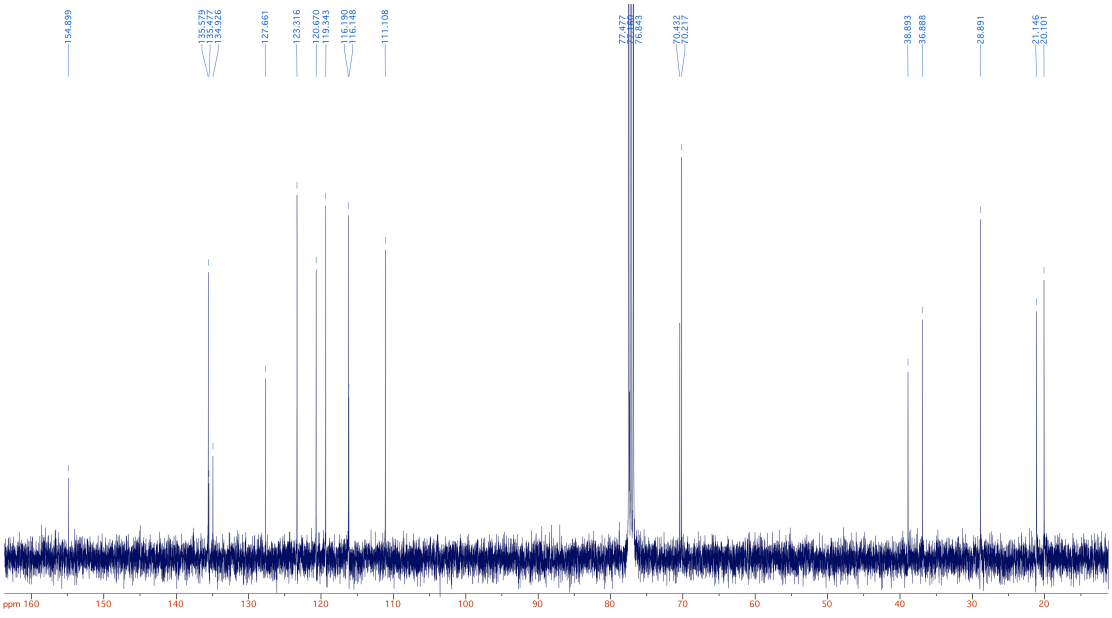
1-(Benzyloxy)-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (9d)



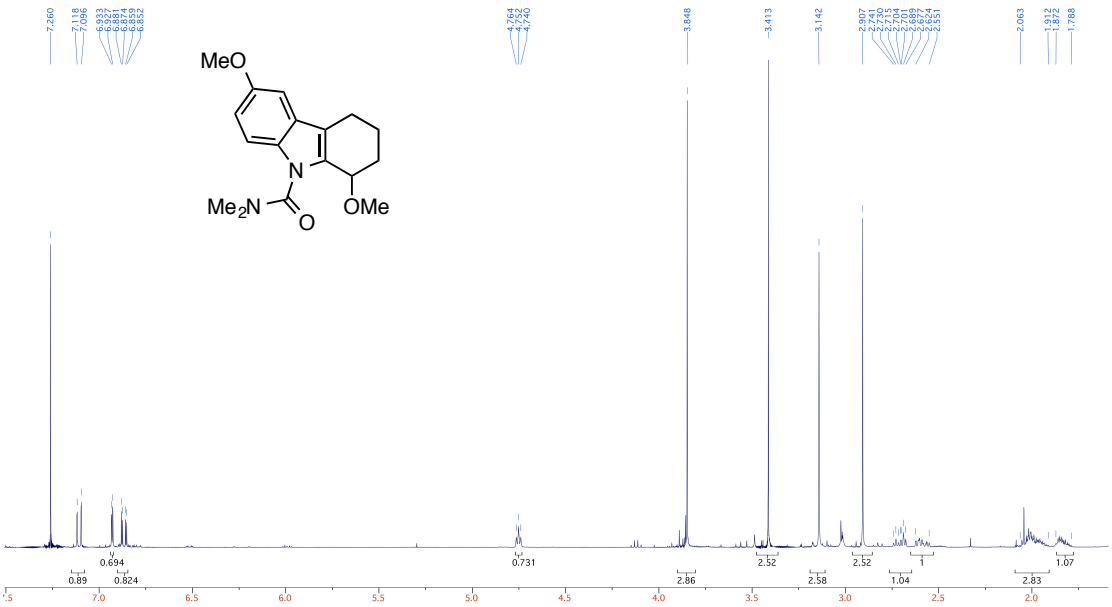


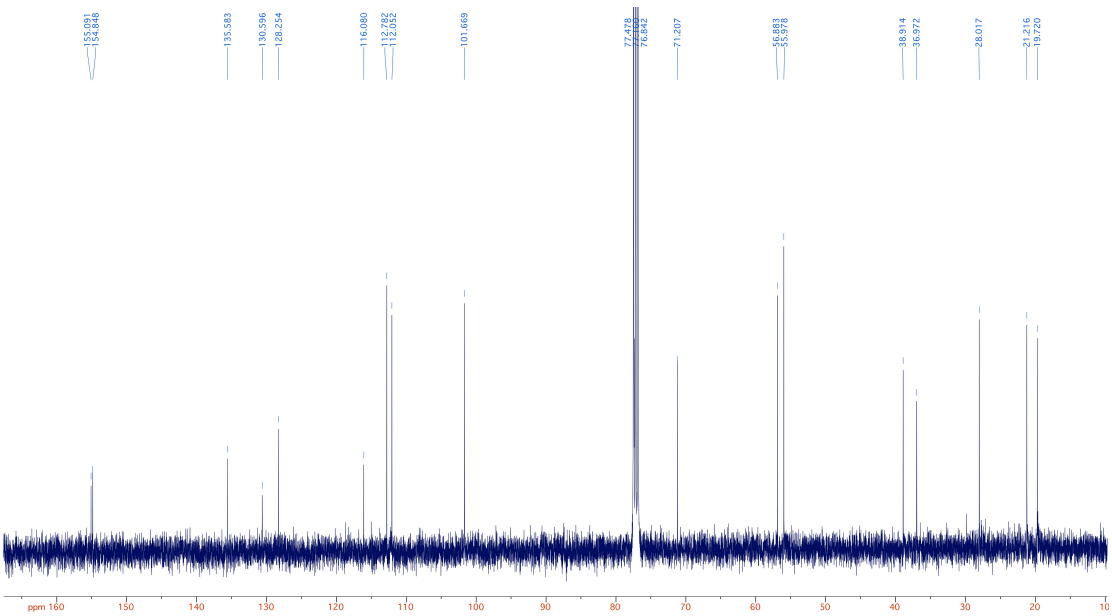
1-(Allyloxy)-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (10d)



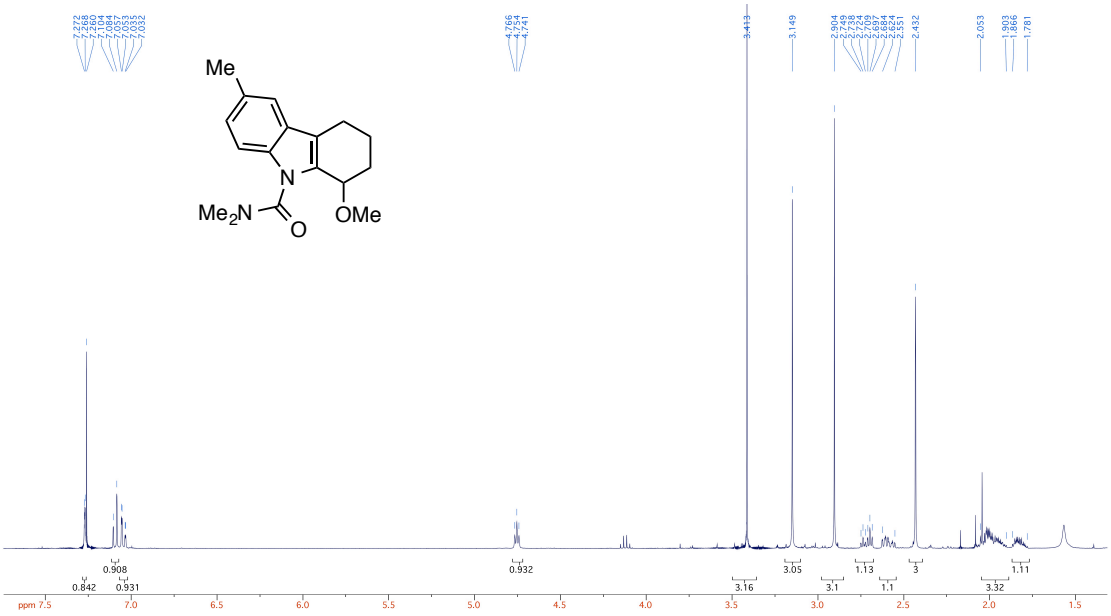


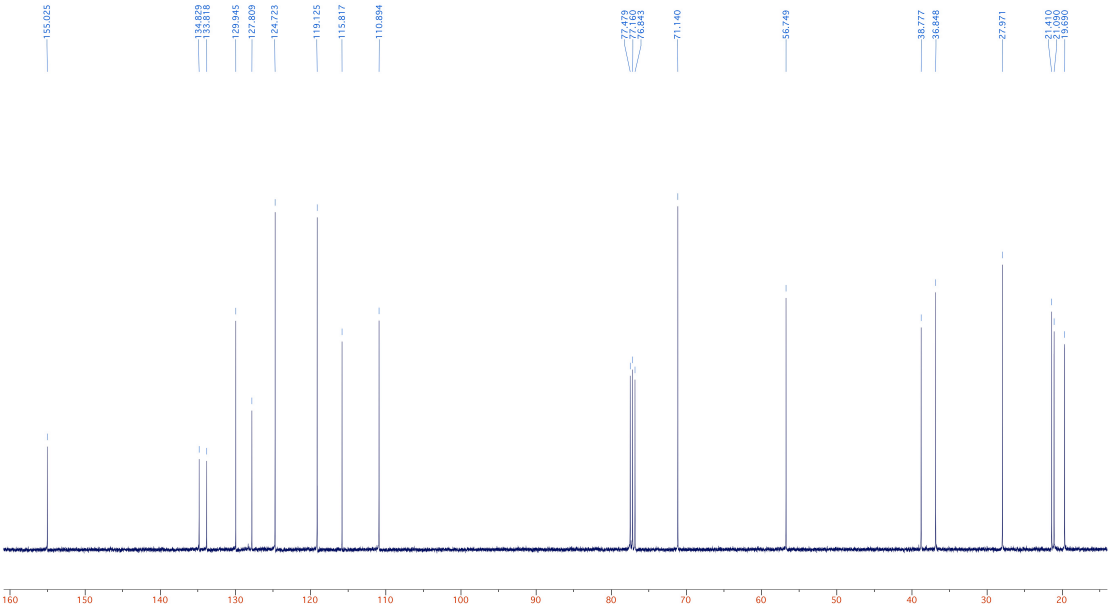
1,6-Dimethoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7db)



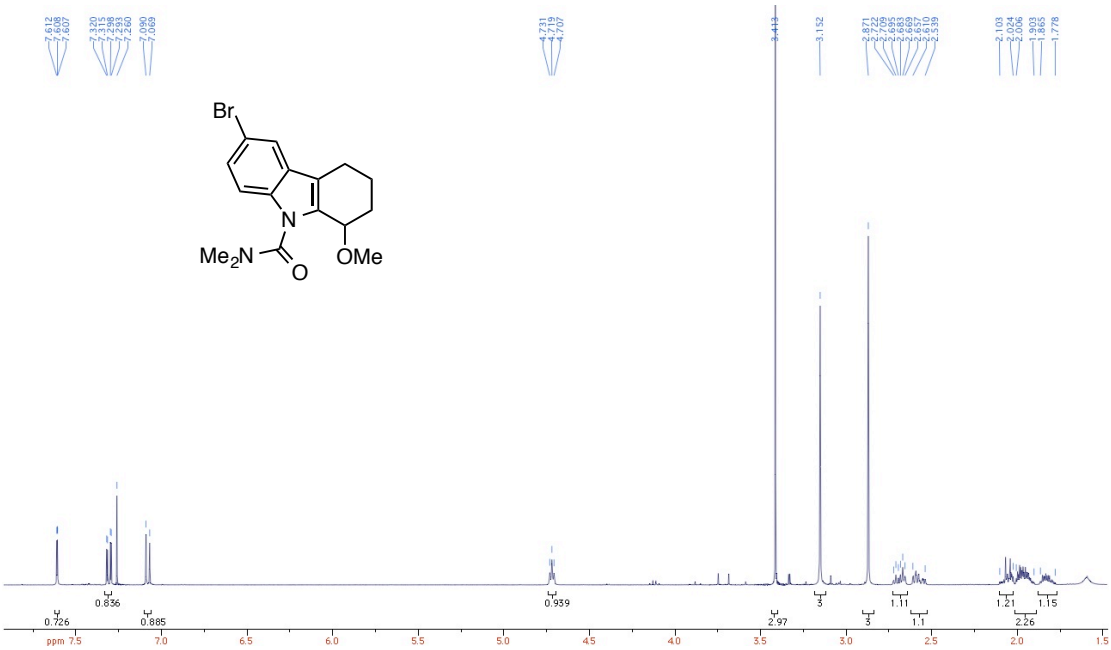


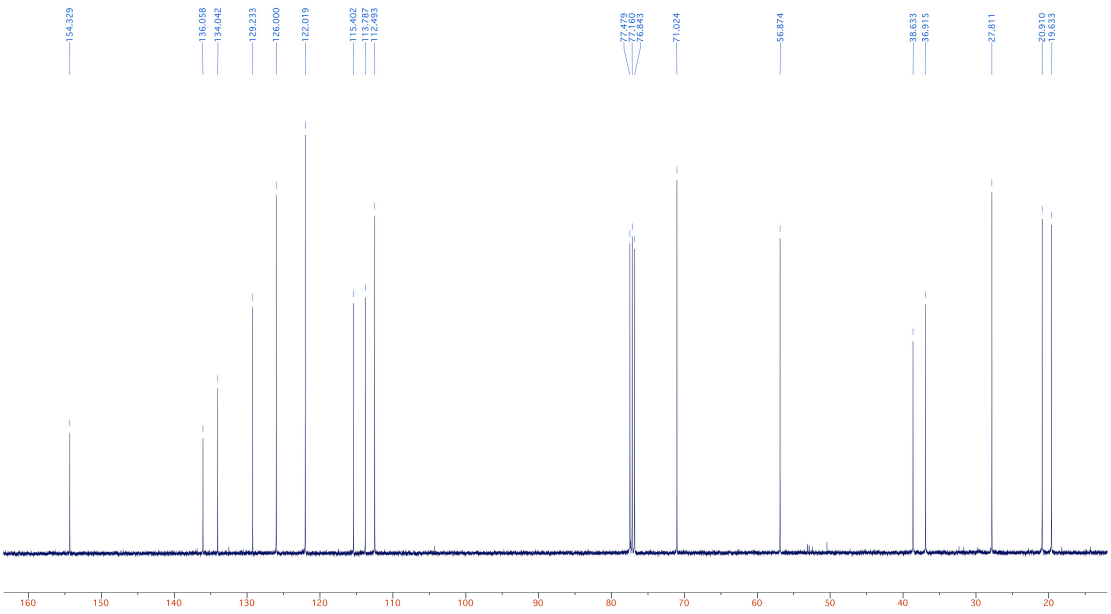
1-Methoxy-*N*,*N*,6-trimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7dc)



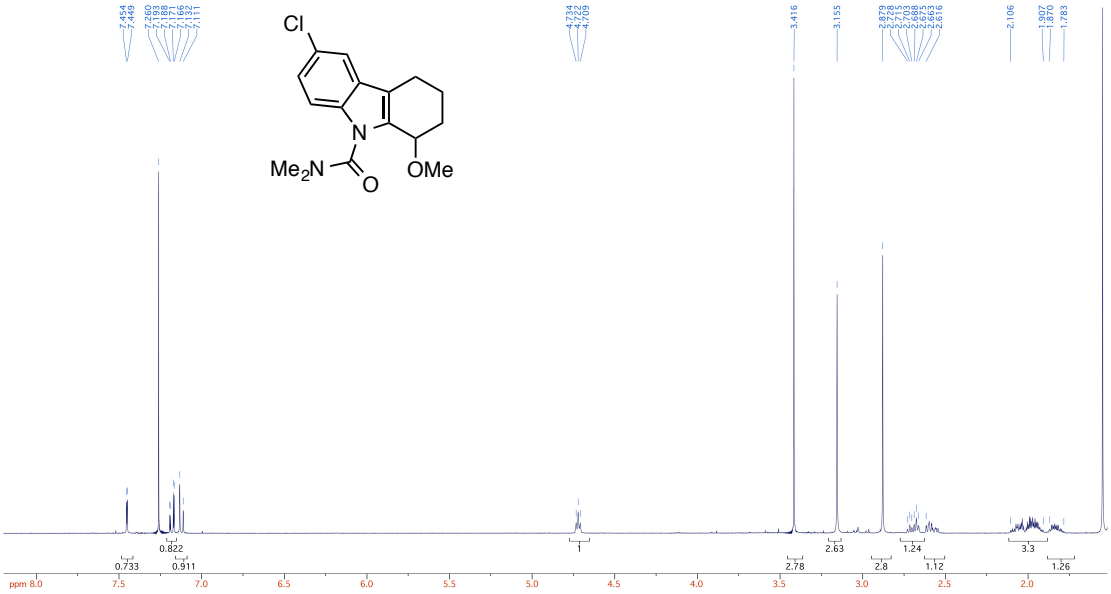


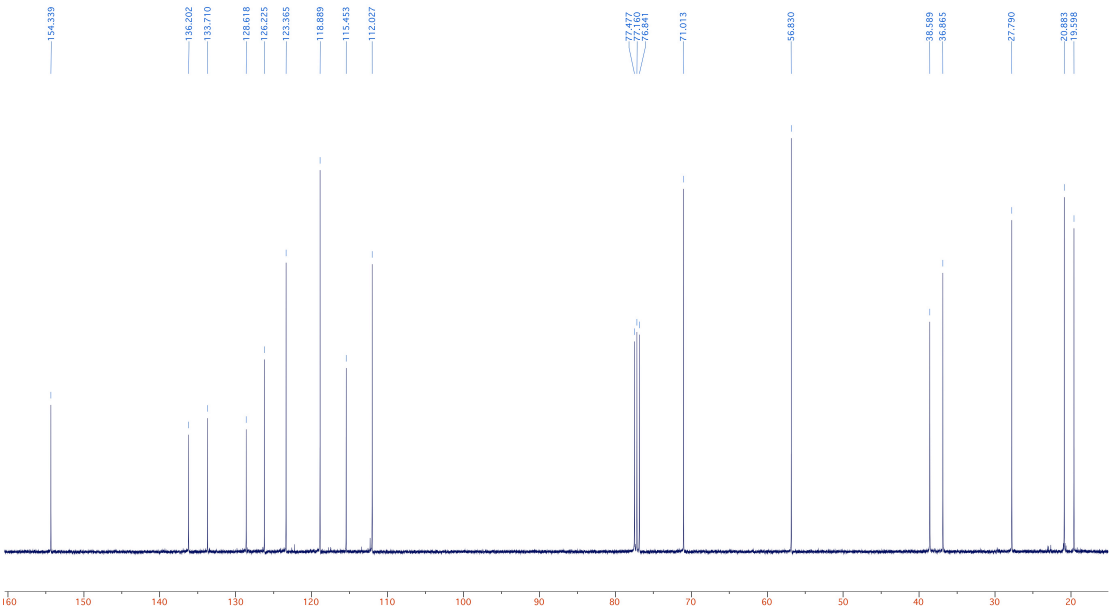
6-Bromo-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7dd)



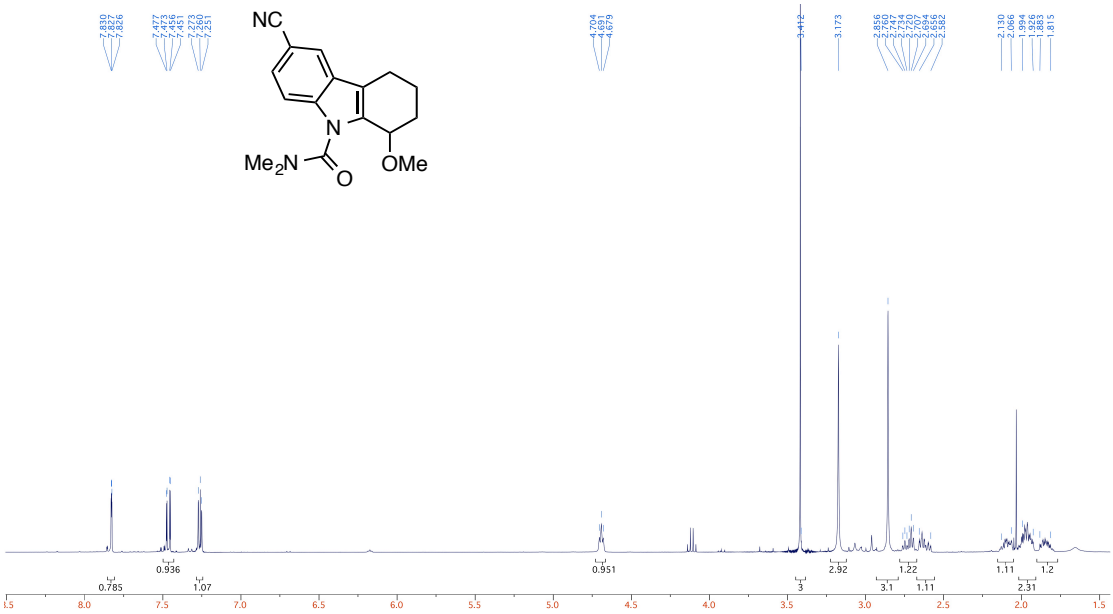


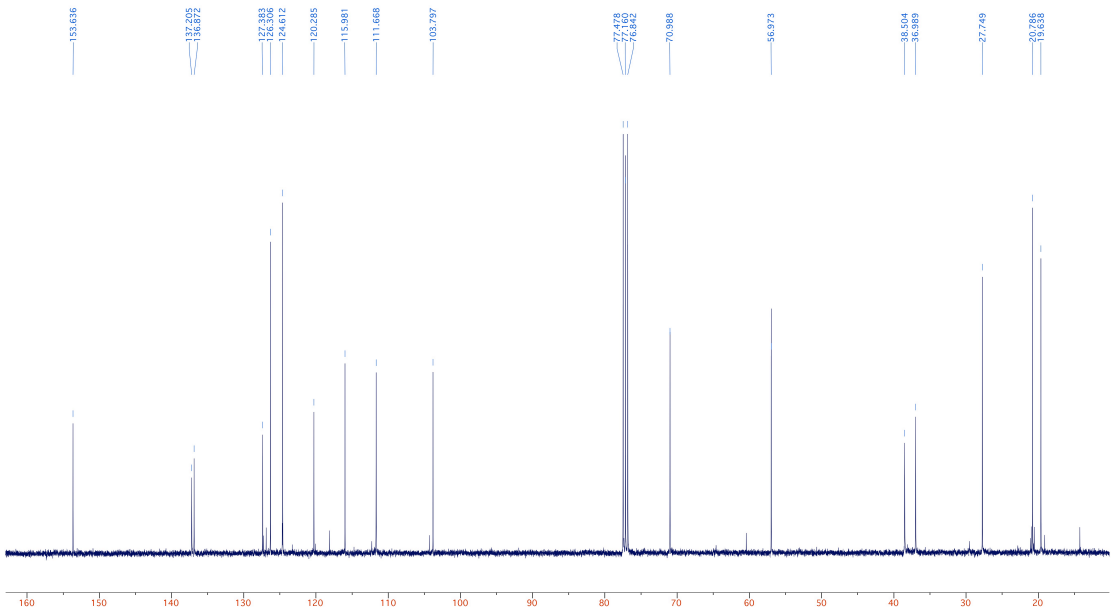
6-Chloro-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7de)



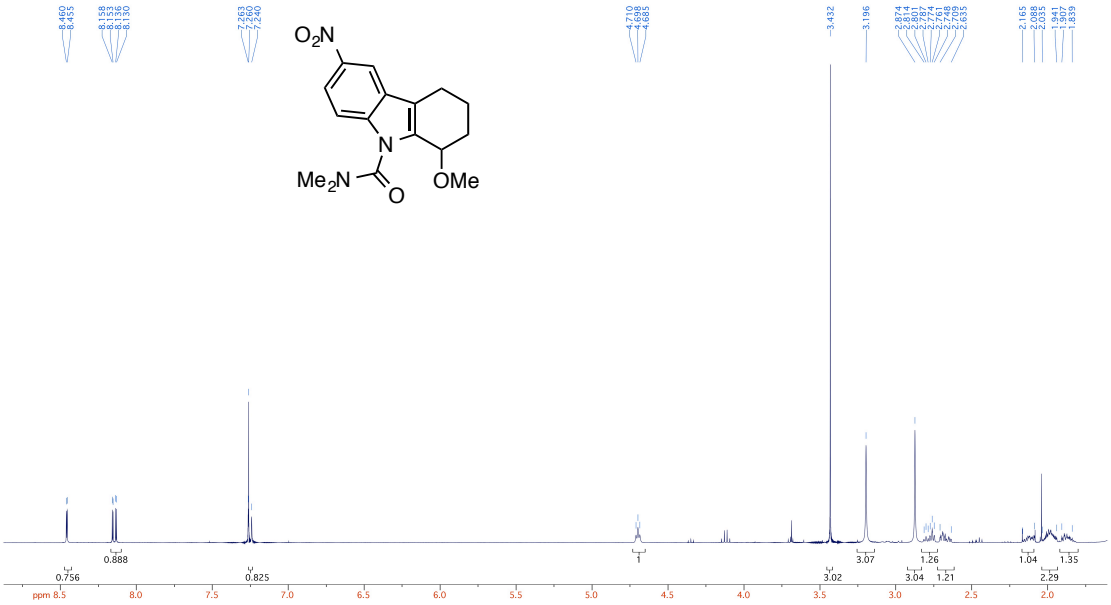


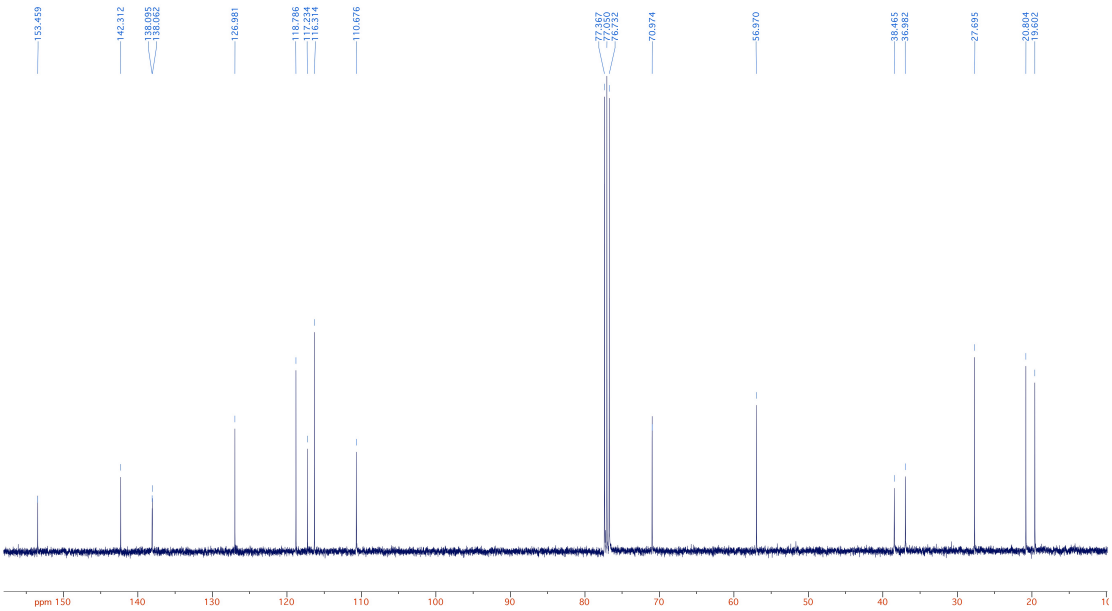
6-Cyano-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7df)



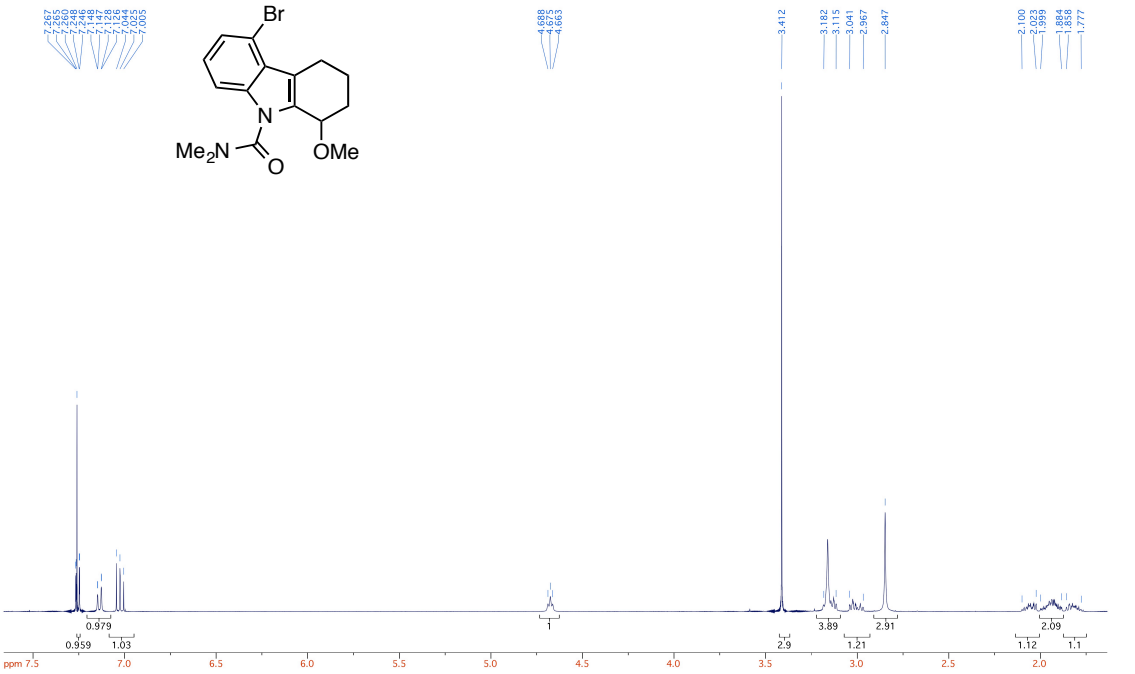


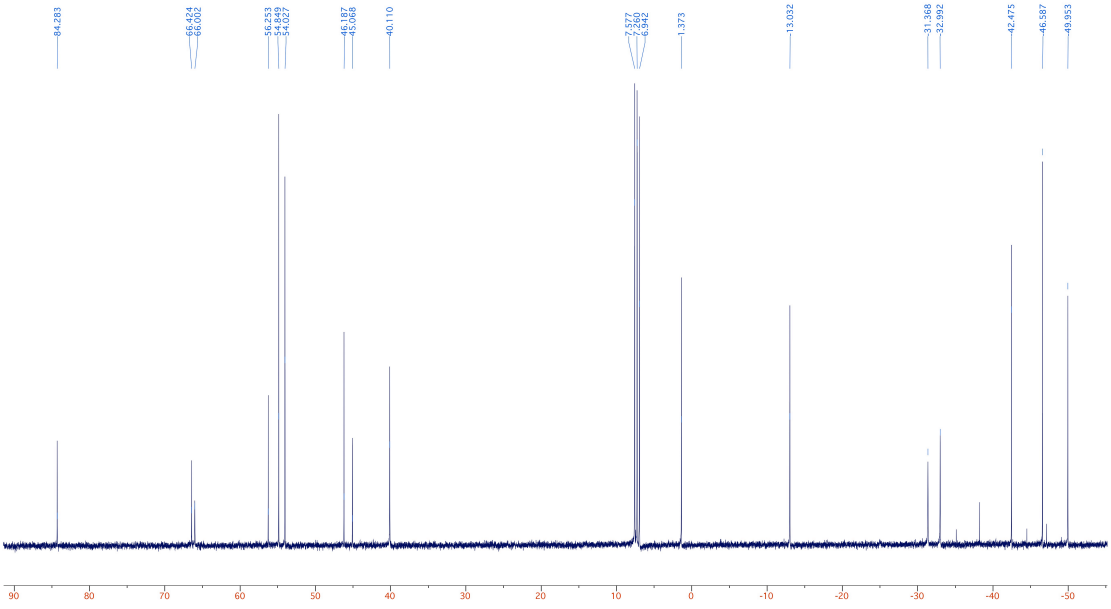
1-Methoxy-*N*,*N*-dimethyl-6-nitro-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7dg)



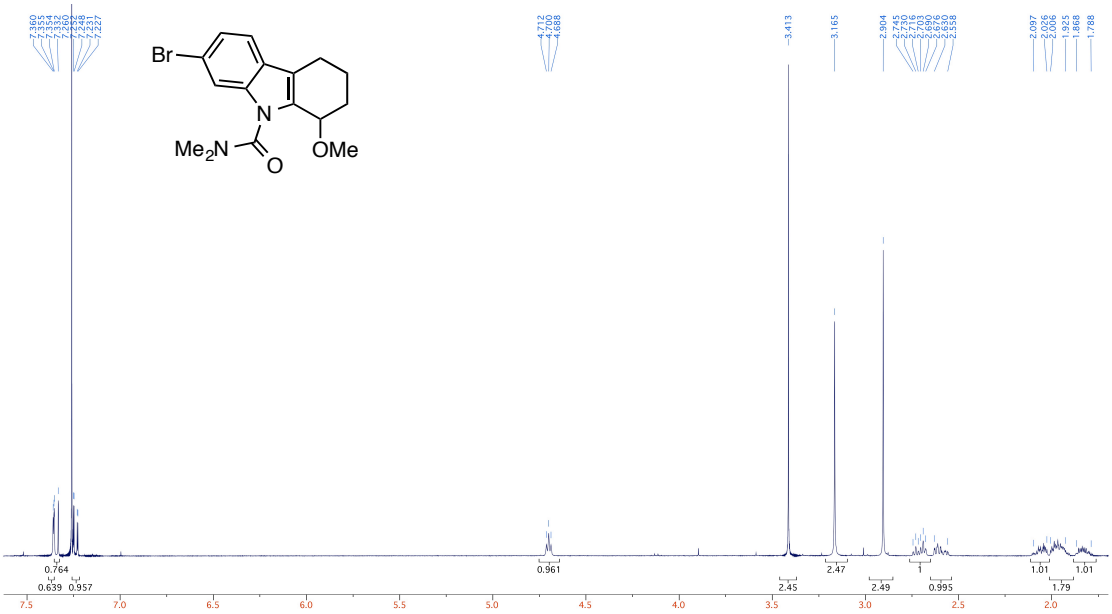


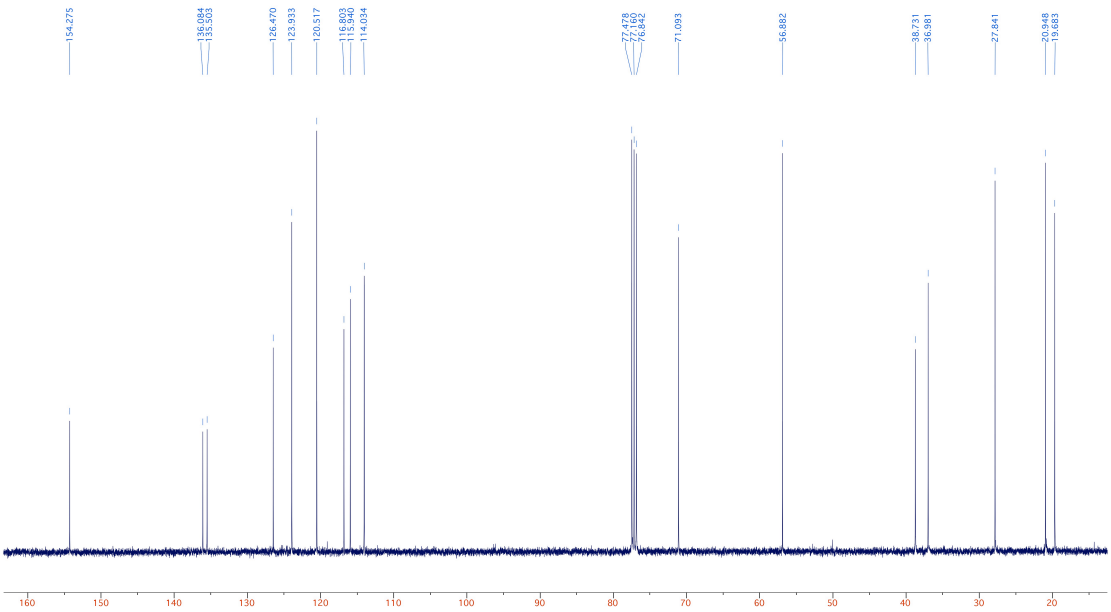
5-Bromo-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7dh)



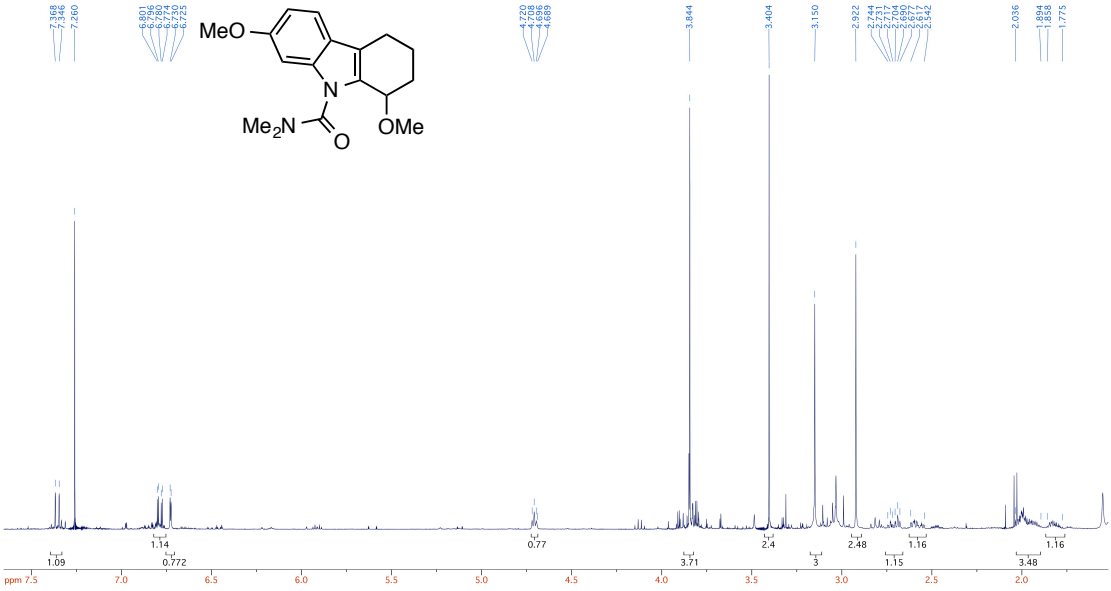


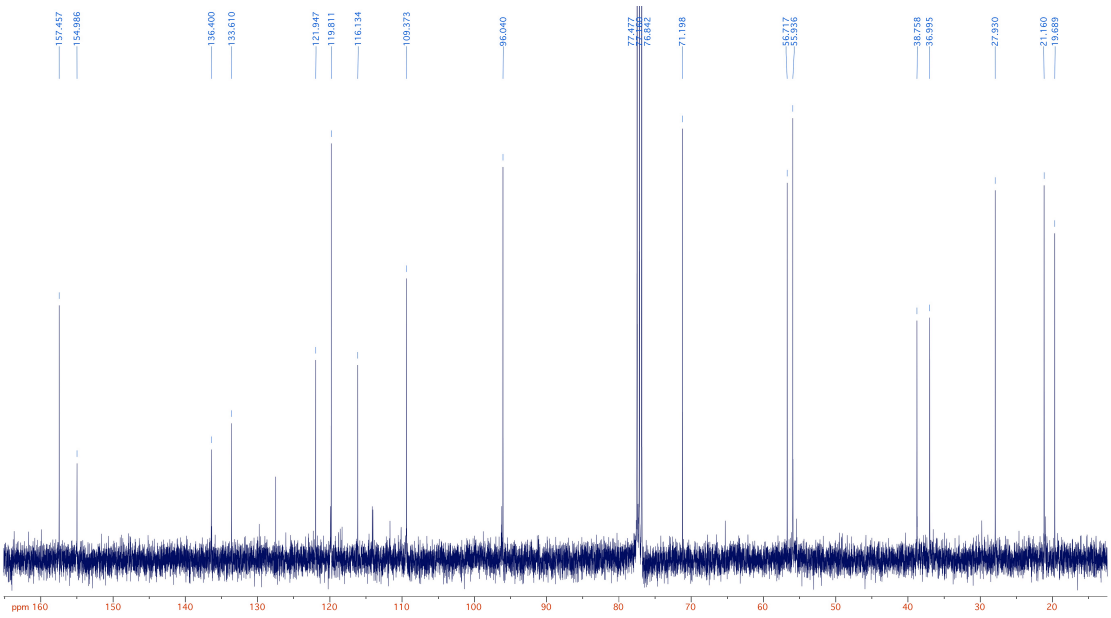
7-Bromo-1-methoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7di)



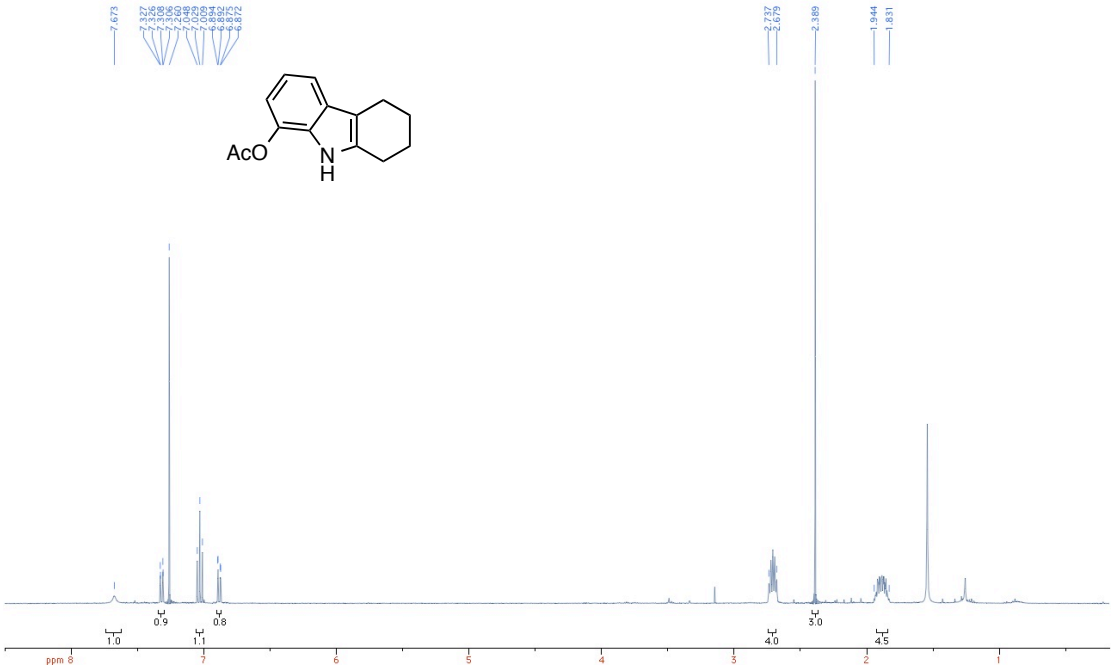


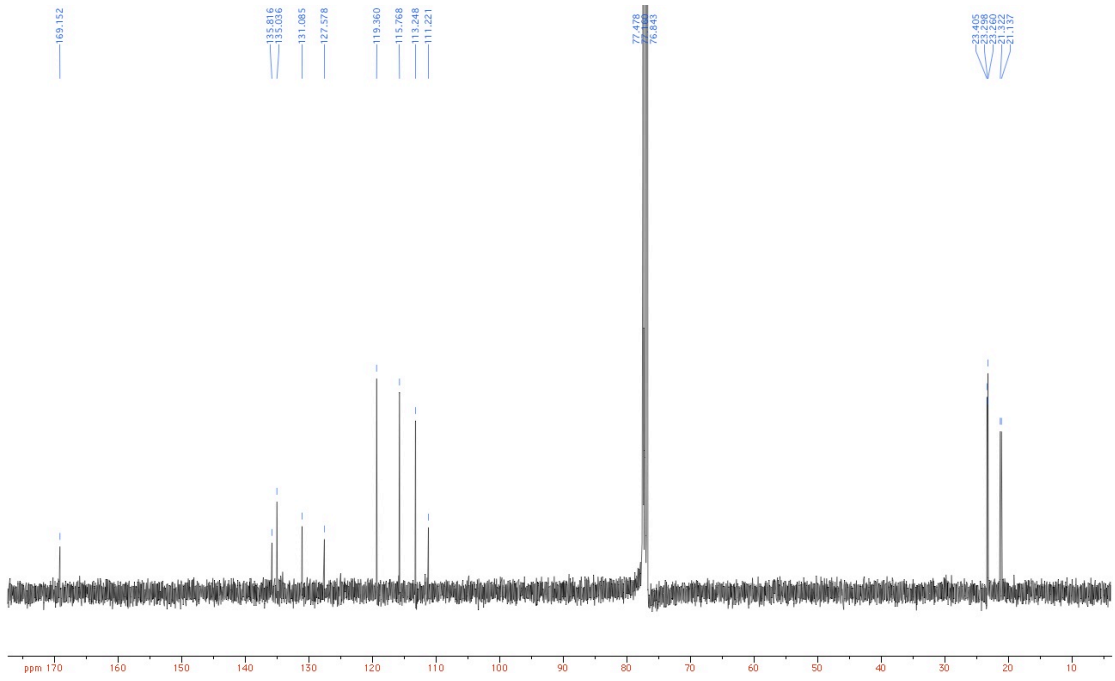
1,7-Dimethoxy-*N*,*N*-dimethyl-1,2,3,4-tetrahydro-9*H*-carbazole-9-carboxamide (7dj)





2,3,4,9-Tetrahydro-1*H*-carbazol-8-yl acetate (16)





9-(Dimethylcarbamoyl)-2,3,4,9-tetrahydro-1*H*-carbazol-1-yl acetate (17)