Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Palladium/Norbornene Chemistry: An Unexpected Route to Methanocarbazole Derivatives via Three Csp^3-Csp^2/Csp^3-N/Csp^2-N Bond Formation in a Single Synthetic Sequence

Farnaz Jafarpour, Nafiseh Jalalimanesh, Mahdieh Teimouri, and Mitra Shamsianpour*

School of Chemistry, College of Science, University of Tehran, P.O. Box 14155-6455, Tehran, Iran

jafarpour@ut.ac.ir

Contents

1 General remarks

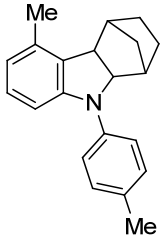
The following includes general experimental procedures, specific details for representative reactions and spectroscopic information for new compounds. Palladium catalysts and ligands were commercially available and used as received. The reactions were carried out in a sand bath using microwave vials (2-5 mL). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on 500, 400 and 300 MHz spectrometers using $CDCl_3$ as the NMR solvent. ^{1}H NMR spectra are referenced to tetramethylsilane (0.00 ppm) and ^{13}C NMR spectra are referenced from the solvent central peak (77.23 ppm). Chemical shifts are given in ppm. IR is reported as characteristic bands (cm^{-1}) in their maximal intensity.

2 General experimental procedure for palladium-catalyzed annulation reaction

A vial equipped with a stir bar was charged with aromatic amine (0.2 mmol, 1 equiv), haloarene (0.40 mmol, 2 equiv), $Pd(OAc)_2$ (0.02 mmol, 10 mol%), PPh_3 (0.044 mmol, 22 mol%), norbornene (0.4 mmol, 2 equiv), K_2CO_3 (0.4 mmol, 2 equiv) and dry DMF (0.1 M) was added and the vial was capped. The resulting mixture was heated in a sand bath at 140°C for 24 h, cooled then filtered through a short plug of silica. Removal of the solvent gave a crude mixture which was purified by column chromatography (hexane/EtOAc gradient).

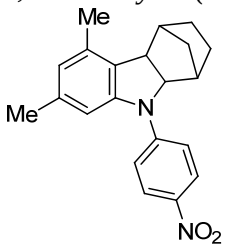
3 Experimental characterization data

5-Methyl-9-(p-tolyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3a)**



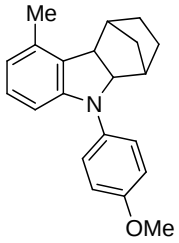
Green solid; Yield = 63% (36 mg); m.p.= 89-84 °C; Eluent: Hexane.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (d, *J* = 10.0 Hz, 1H), 1.29-1.32 (m, 1H), 1.44-1.47 (m, 1H), 1.51-1.60 (m, 3H), 2.33 (s, 3H), 2.37 (s, 3H), 2.50 (s, 2H), 3.28 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5, 20.8, 25.0, 28.9, 32.4, 40.6, 41.3, 49.7, 71.1, 104.9, 119.6, 120.5, 127.4, 129.7, 131.0, 131.2, 134.5, 141.0, 149.4; IR 725, 759, 812, 1248, 1299, 1373, 1461, 1511, 1588, 2869, 2957 cm^{-1}; MS, m/z (%) 289 (M•+, 100%), 248 (31), 222 (68), 67 (20). Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84. Found: C, 87.45; H, 8.15; N, 5.01.

5,7-Dimethyl-9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3b)**



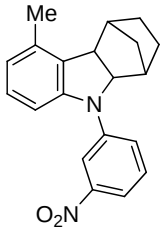
Red solid; Yield = 81% (54 mg); m.p. = 110-115 °C; Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13-1.17 (m, 1H), 1.35-1.48 (m, 3H), 1.63-1.66 (m, 2H), 2.21 (s, 3H), 2.31 (s, 3H), 2.50 (s, 1H), 2.60 (s, 1H), 3.29 (d, *J* = 8.0 Hz, 1H), 4.34 (d, *J* = 8.0 Hz, 1H), 6.59 (s, 1H), 6.94 (s, 1H), 7.33 (d, *J* = 9.6 Hz, 2H), 8.22 (d, *J* = 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 21.7, 25.0, 28.5, 32.3, 40.3, 41.0, 49.3, 70.9, 108.8, 116.4, 123.9, 125.6, 129.9, 134.9, 137.4, 139.6, 146.1, 149.1; IR 808, 1105, 1291, 1378, 1460, 1496, 1580, 2870, 2958 cm^{-1}; MS, m/z (%) 334 (M•+, 100%), 293 (28), 267 (56), 221 (11). Anal. Calcd for $C_{21}H_{22}N_2O_2$: C, 75.42; H, 6.63; N, 8.38. Found: C, 75.71; H, 6.73; N, 8.54.

9-(4-Methoxyphenyl)-5-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3c)**



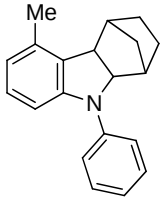
Green oil; Yield = 58% (35 mg); Eluent: Hexane.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (d, *J* = 10.1 Hz, 1H), 1.21-1.32 (m, 1H), 1.39-1.50 (m, 1H), 1.58-1.66 (m, 3H), 2.31 (s, 3H), 2.43 (s, 1H), 2.48 (s, 1H), 3.28 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 4.24 (d, *J* = 8.1 Hz, 1H), 6.48 (d, *J* = 7.4 Hz, 1H), 6.55 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 3H), 7.25 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 24.9, 28.9, 32.4, 40.8, 41.3, 49.8, 55.5, 71.8, 104.2, 114.5, 119.1, 123.1, 127.4, 130.6, 134.4, 136.9, 150.3, 155.2; IR 763, 827, 1036, 1239, 1462, 1591, 2952 cm^{-1}; MS, m/z (%) 305 (M•+, 100%), 264 (21), 238 (79), 67 (25). Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.92; H, 7.73; N, 4.78.

5-Methyl-9-(3-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3d)**



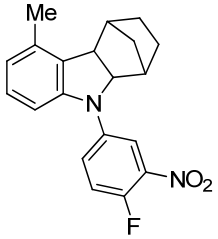
Orange solid; Yield = 48% (31 mg); m.p. = 143-146 °C; Eluent: Hexane.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (d, *J* = 10.2 Hz, 1H), 1.25-1.50 (m, 3H), 1.50-1.62 (m, 2H), 2.32 (s, 3H), 2.50 (s, 1H), 2.52 (s, 1H), 3.30 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 7.00-7.05 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 8.14 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 25.0, 28.6, 32.4, 40.3, 41.1, 49.7, 70.7, 106.1, 112.8, 115.0, 121.8, 124.1, 127.5, 129.7, 131.7, 135.1, 144.6, 147.0, 149.1; IR 667, 733, 795, 1245, 1339, 1461, 1515, 2868, 2967 cm^{-1}; MS, m/z (%) 320 (M•+, 100%), 290 (30), 279 (35), 253 (91), 207 (36), 191 (32), 178 (34), 165 (34), 67 (37). Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.71 H, 6.18; N, 8.54.

5-Methyl-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3e)**



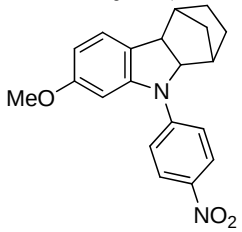
Gray solid; Yield = 44% (24 mg); m.p.= 96-100 °C; Eluent: Hexane.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, *J* = 6.0 Hz, 1H), 1.28 (m, 1H), 1.41 (m, 1H), 1.56-1.60 (m, 3H), 2.30 (s, 3H), 2.47 (s, 1H), 2.52 (s, 1H), 3.28 (d, *J* = 8.0 Hz, 1H), 4.32 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 7.0 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.94-6.99 (m, 2H), 7.33-7.34 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5, 25.0, 28.8, 32.5, 40.6, 41.3, 49.7, 70.9, 105.4, 119.8, 120.0, 121.4, 127.4, 129.1, 131.3, 134.6, 143.5, 148.8; IR 763, 827, 1036, 1238, 1462, 1506, 1591, 2952 cm^{-1}; MS, m/z (%) 275 (M•+, 100%), 234 (38), 208 (82), 77 (18), 67 (23). Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09. Found: C, 87.55; H, 7.83; N, 5.30.

9-(4-Fluoro-3-nitrophenyl)-5-methyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3f)**



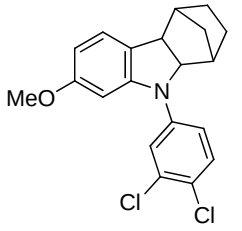
Purple oil; Yield = 57% (39 mg); Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.10-1.42 (m, 3H), 1.54-1.60 (m, 3H), 2.30 (s, 3H), 2.63 (s, 1H), 2.74 (s, 1H), 3.29 (d, *J* = 8.0 Hz, 1H), 4.24 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.95-7.15 (m, 2H), 7.56-7.59 (m, 1H), 7.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 24.9, 28.7, 32.3, 40.6, 41.1, 49.8, 71.3, 104.9, 114.5, 120.4, 120.9, 127.5, 130.3, 130.9, 131.1, 134.9, 136.8, 148.2, 150.1; IR 760, 1180, 1243, 1293, 1463, 1534, 1592, 2869, 2954 cm^{-1}; MS, m/z (%) 338 (M•+, 76%), 290 (22), 269 (48), 207 (56), 165 (46), 149 (34), 67 (100). Anal. Calcd for $C_{20}H_{19}FN_2O_2$: C, 70.99; H, 5.66; N, 8.28. Found: C, 80.27; H, 5.77; N, 8.44.

7-Methoxy-9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3g)**



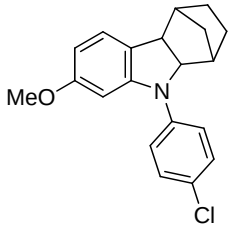
Red Oil; Yield = 73% (49 mg); Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 0.91-0.92 (m, 1H), 1.14-1.30 (m, 1H), 1.29-1.46 (m, 2H), 1.64-1.67 (m, 2H), 2.38 (s, 1H), 2.61 (s, 1H), 3.34 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H) 4.30 (d, *J*= 8.0 Hz, 1H), 6.47 (dd, *J*= 8.0, 2.4 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 9.6 Hz, 2H), 8.35 (d, *J* = 9.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 28.5, 32.3, 40.3, 43.2, 49.5, 55.4, 71.9, 96.2, 103.8, 116.4, 125.0, 125.6, 126.3, 146.1, 148.1, 150.1, 159.6; IR 749, 827, 1033, 1109, 1239, 1297, 1451, 1400, 1585, 2869, 2949 cm^{-1}; MS, m/z (%) 336 (M•+, 4%), 319 (12), 201 (24), 147 (37), 121 (100), 67 (93). Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.69; H, 6.11; N, 8.50.

9-(3,4-Dichlorophenyl)-7-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3h)**



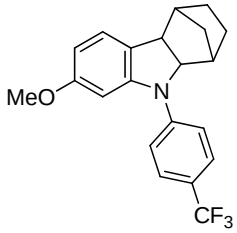
Green oil; Yield = 50% (36 mg); Eluent: Hexane.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, *J* = 10.2 Hz, 1H), 1.23-1.29 (m, 1H), 1.37-1.47 (m, 2H), 1.59-1.61 (m, 2H), 2.32 (s, 1H), 2.46 (s, 1H), 3.25 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 4.19 (d, *J* = 8.0 Hz, 1H), 6.32 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.55 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.15 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.33-7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 28.2, 32.2, 40.8, 43.3, 49.6, 55.4, 71.9, 96.1, 103.6, 118.5, 120.5, 123.9, 125.2, 126.3, 130.5, 132.8, 143.0, 148.7, 159.6; IR 809, 1133, 1159, 1206, 1474, 1583, 2952 cm^{-1}; MS, m/z (%) 359 (M•+, 100%), 318 (48), 292 (63), 187 (16), 84 (27), 67 (33). Anal. Calcd for $C_{20}H_{19}Cl_2NO$: C, 66.67; H, 5.32; N, 3.89. Found: C, 66.93; H, 5.41; N, 4.07.

9-(4-Chlorophenyl)-7-methoxy-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3i)**



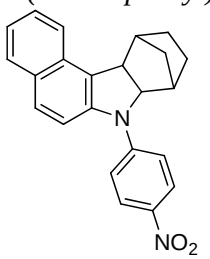
Green solid; Yield = 45% (29 mg); m.p. = 96-100 °C; Eluent: Hexane.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (d, *J* = 10.1 Hz, 1H), 1.22-1.43 (m, 2H), 1.52 (d, *J* = 10.1 Hz, 1H), 1.58-1.61 (m, 2H), 2.34 (s, 1H), 2.46 (s, 1H), 3.26 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 4.24 (d, *J* = 8.0 Hz, 1H), 6.29 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.25-7.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.1, 28.3, 32.2, 40.8, 43.4, 49.6, 55.4, 71.9, 95.5, 102.9, 120.8, 125.0, 126.2, 129.1, 141.9, 149.6, 159.6; IR 818, 1093, 1160, 1204, 1272, 1376, 1492, 1589, 2869, 2952 cm^{-1}; MS, m/z (%) 325 (M•+, 100%), 296 (23), 284 (69), 258 (83), 242 (23), 159 (21), 67 (42). Anal. Calcd for $C_{20}H_{20}ClNO$: C, 73.72; H, 6.19; N, 4.30. Found: C, 74.01; H, 6.31; N, 4.47.

7-Methoxy-9-(4-(trifluoromethyl)phenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3j)**



Green oil; Yield = 48% (35 mg); Eluent: Hexane.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, *J* = 10.1 Hz, 1H), 1.26-1.31 (m, 1H), 1.38-1.48 (m, 2H), 1.56-1.62 (m, 2H), 2.34 (s, 1H), 2.51 (s, 1H), 3.28 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 4.29 (d, *J* = 8.0 Hz, 1H), 6.35 (m, 1H), 6.69 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 28.2, 29.7, 32.2, 40.7, 43.3, 49.6, 55.5, 71.5, 96.7, 104.0, 117.8, 122.1 (q, J_{CF} = 32.5 Hz), 125.2, 126.3 (q, J_{CF} = 3.7 Hz), 126.6, 146.3, 148.4, 159.5; IR 822, 1063, 1109, 1159, 1318, 1451, 1493, 1520, 1603, 2954 cm^{-1}; MS, m/z (%) 359 (M•+, 100%), 330 (16), 318 (62), 292 (75), 276 (21), 67 (37). Anal. Calcd for $C_{21}H_{20}F_3NO$: C, 70.18; H, 5.61; N, 3.90. Found: C, 70.50; H, 5.74; N, 4.14.

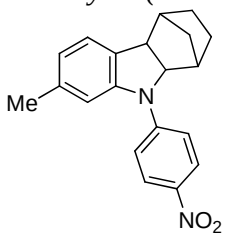
7-(4-Nitrophenyl)-7a,8,9,10,11,11a-hexahydro-7H-8,11-methanobenzo[c]carbazole (**3k)**



Red solid; Yield = 74% (53 mg); m.p. = 90-91 °C; Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.15-1.17 (m, 1H), 1.27-1.28 (m, 1H), 1.40-1.48 (m, 2H), 1.65-1.75 (m, 2H), 2.69 (s, 1H), 2.77 (s, 1H), 3.79 (d, *J* = 8.3 Hz, 1H), 4.46 (d, *J*= 7.8 Hz, 1H), 7.31-7.36 (m, 1H), 7.35 (d, *J* = 9.3 Hz, 2H), 7.47-7.50 (m, 1H), 7.51 (d, *J* = 8.9 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.8 (d, *J* = 8.1, 1H), 8.21 (d, *J* = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.7, 28.9, 30.3, 38.7, 41.2, 50.0, 70.1, 107.9, 112.1, 116.0, 122.8, 124.0, 125.7, 126.7, 128.4, 128.8, 130.9, 132.7, 142.8, 144.7, 150.0; IR 736, 802, 842, 1106, 1294, 1370, 1464, 1489, 1583, 2869, 2952 cm^{-1}; MS, m/z (%) 356

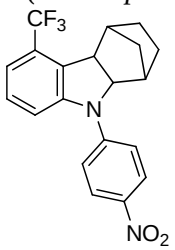
(M•+, 100%), 315 (40), 289 (92), 241 (100), 67 (100). Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.76; H, 5.75; N, 8.02.

7-Methyl-9-(4-nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3l)**



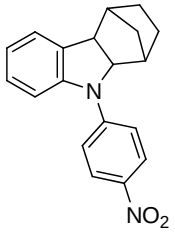
Orange solid; Yield = 62% (40 mg); m.p. = 115-120 °C; Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14-1.17 (m, 1H), 1.37-1.49 (m, 3H), 1.65-1.68 (m, 2H), 2.35 (s, 3H), 2.40 (s, 1H), 2.61 (s, 1H), 3.36 (d, *J* = 7.6 Hz, 1H), 4.27 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 7.09-7.11 (m, 2H), 7.33 (d, *J* = 9.6 Hz, 2H), 8.22 (d, *J* = 9.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 25.3, 28.4, 32.5, 40.3, 41.5, 49.6, 70.5, 107.8, 116.9, 123.4, 125.4, 125.7, 129.8, 134.7, 139.6, 146.6, 149.4; IR 748, 835, 898, 1107, 1292, 1379, 1442, 1497, 1582, 2871, 2948 cm^{-1}; MS, m/z (%) 320 (M•+, 100%), 291 (24), 279 (45), 253 (79), 121 (40). Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 75.27; H, 6.41; N, 8.96.

9-(4-Nitrophenyl)-5-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3m)**



Yellow oil; Yield = 47% (35.2 mg); Eluent: Hexane/EtOAc 98:2.
(%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15-1.19 (m, 2H), 1.25-1.50 (m, 2H), 1.50-1.66 (m, 2H), 2.57(s, 1H), 2.62 (s, 1H), 3.56 (d, *J* = 7.8 Hz, 1H), 4.42 (d, *J* = 8.1 Hz, 1H), 7.1 (d, *J* = 7.6 Hz, 1H), 7.19-7.27 (m, 1H), 7.34 (d, *J* = 9.1 Hz, 3H), 8.22 (d, *J* = 9.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.6, 28.7, 32.2, 40.4, 43.0, 49.4, 71.0, 112.4, 117.4, 118.2 (q, *J* = 5.0 Hz), 121.1 (q, *J* = 202.0 Hz) 125.5, 128.0 (q, *J* = 31.7 Hz), 128.1, 132.0, 140.8, 147.7, 148.2; IR 1107, 1290, 1376, 1460, 1501, 1588, 2872, 2951 cm^{-1}; MS, m/z (%) 374 (M•+, 41%), 283 (77), 256 (100), 215 (71), 169 (37). Anal. Calcd for $C_{20}H_{17}F_3N_2O_2$: C, 64.17; H, 4.58; N, 7.48. Found: C, 64.44; H, 4.68; N, 7.66.

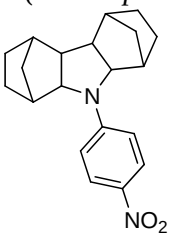
9-(4-Nitrophenyl)-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanocarbazole (**3n)**



Red oil; Yield = 56% (34 mg); Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11-1.16 (m, 2H), 1.43-1.49 (m, 2H), 1.63-1.67 (m, 2H), 2.41(s, 1H), 2.61 (s, 1H), 3.39 (d, *J* = 8.0 Hz, 1H), 4.26 (d, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 7.13-7.24 (m, 3H), 7.33 (d, *J* = 9.3 Hz, 2H), 8.19 (d, *J* = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.3, 28.1, 32.3, 40.8, 43.1, 50.3, 71.8, 110.7, 115.7, 121.6, 125.4, 125.6, 127.3, 134.9, 139.7, 145.8, 149.1; IR 744, 1108, 1294,

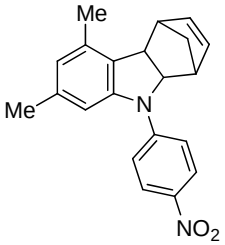
1379, 1458, 1499, 1583, 2872, 2954 cm^{-1}; MS, m/z (%) 306 (M•+, 100%), 277 (41), 265 (57), 239 (100), 193 (52). Anal. Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.79; H, 6.05; N, 9.36.

9-(4-Nitrophenyl)dodecahydro-1H-1,4:5,8-dimethanocarbazole (**4**)



Yellow oil; Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (d, J = 10.3 Hz, 2H), 1.14 (d, J = 10.3 Hz, 2H), 1.13-1.21 (m, 4H), 1.52-1.54 (m, 4H), 1.97 (d, J = 6.7 Hz, 2H), 2.21 (s, 2H), 2.50 (s, 2H), 3.64 (d, J = 6.7 Hz, 2H), 6.58 (d, J = 9.3 Hz, 2H), 8.14 (d, J = 9.3, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.6, 27.5, 33.1, 38.7, 42.7, 54.1, 70.5, 112.6, 125.9, 127.4, 150.1. Anal. Calcd for $C_{20}H_{24}N_2O_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.32; H, 7.57; N, 8.81.

5,7-Dimethyl-9-(4-nitrophenyl)-4,4a,9,9a-tetrahydro-1H-1,4-methanocarbazole (**5)**

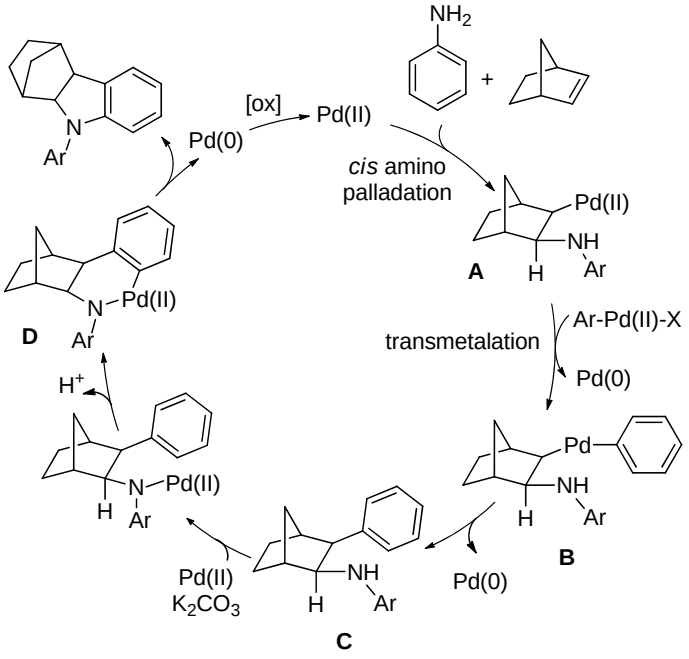


Red oil; Yield = 57% (38 mg); Eluent: Hexane/EtOAc 98:2.
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47-1.54 (m, 2H), 2.32 (s, 6H), 3.10 (s, 1H), 3.22(s, 1H), 3.46 (d, J = 7.9 Hz, 1H), 4.42 (d, J = 7.9 Hz, 1H), 6.18 (dd, J = 5.7, 3.2 Hz 1H), 6.42 (dd, J = 5.7, 3.0 Hz, 1H), 6.58 (s, 1H), 6.94 (s, 1H), 7.38 (d, J = 9.3 Hz, 2H), 8.22 (d, J = 9.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 21.7, 42.4, 46.1, 46.8, 47.4, 69.9, 109.5, 116.2, 123.9, 125.6, 127.9, 134.5, 134.7, 137.6, 139.8, 140.6, 147.7, 149.2; IR 823, 1111, 1305, 1373, 1454, 1499, 1582, 2927 cm^{-1}; MS, m/z (%) 332 (M•+, 12%), 266 (100), 220 (66), 205 (83), 148 (57), 84 (33). Anal. Calcd for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43. Found: C, 76.16; H, 6.18; N, 8.60.

4 Alternative reaction mechanisms

Mechanism A

Based on known Pd-catalyzed amination of alkenes and C-H bond activation/amination reactions,[1] an alternative mechanism was hypothesized for the present domino Pd-catalysed Csp^3-Csp^2/Csp^3-N/Csp^2-N bond formation reaction (Scheme S1). In this mechanism, *cis*-aminopalladation of initially activated norbornene by palladium(II), leads to norbornylpalladium species **A**. Transmetallation between two Pd(II) centers produces the intermediate **B** which on subsequent reductive elimination affords intermediate **C.** Next electrophilic palladation of **C** and aromatic C-H activation leads to formation of six membered palladacycle **D.** Subsequent reductive elimination leads to anticipated product and Pd(0). The latter is reoxidized to palladium(II) by oxidant to complete this catalytic cycle. However, the last intramolecular oxidative C-H amination step would be difficult as the reaction was conducted in absence of any oxidants. Furthermore, the reaction was well conducted under argon atmosphere (in absence of air or O_2 as oxidants).

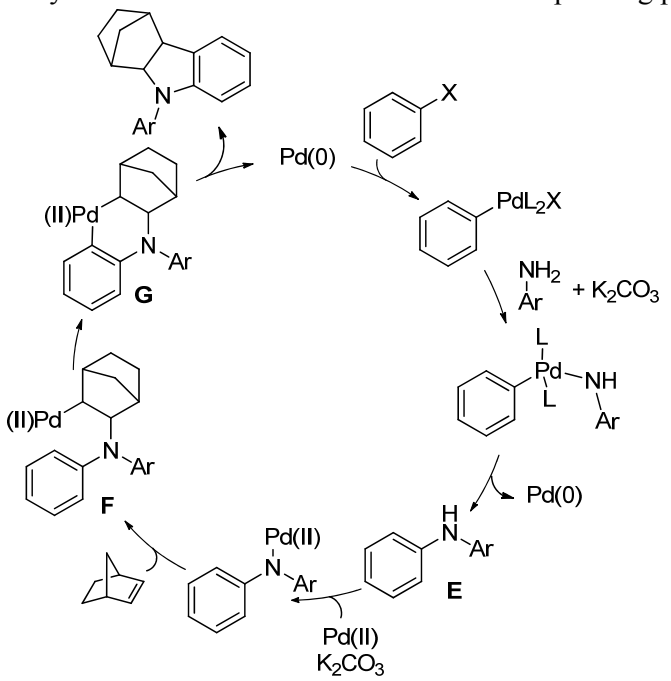


Scheme S1. Alternative mechanism for the annulation reaction

[1] a) G. He, Y. Zhao, S. Zhang, C. Lu, G. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 3-6; b) J. Kim, S. Chang, *J. Am. Chem. Soc.* **2010**, 132, 10272-10274; c) T.-S. Mei, X. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 10806-10807; d) K. Muniz, C. H. Hovelmann, J. Streuff, *J. Am. Chem. Soc.* **2008**, 130, 763-773.

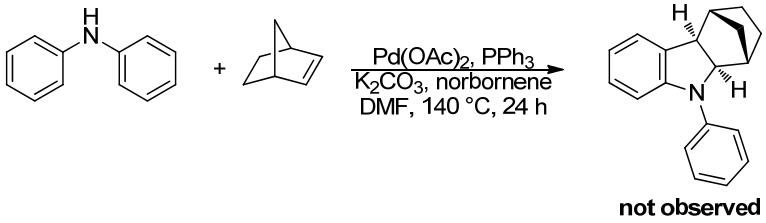
Mechanism B

An alternative path to the desired methanocarbazoles may consist of an initial N-arylation of haloarene, followed by aminopalladation of norbornene (**F**) (Scheme S2). Subsequent intramolecular C-H bond activation (**G**) followed by reductive elimination leads to the corresponding product.



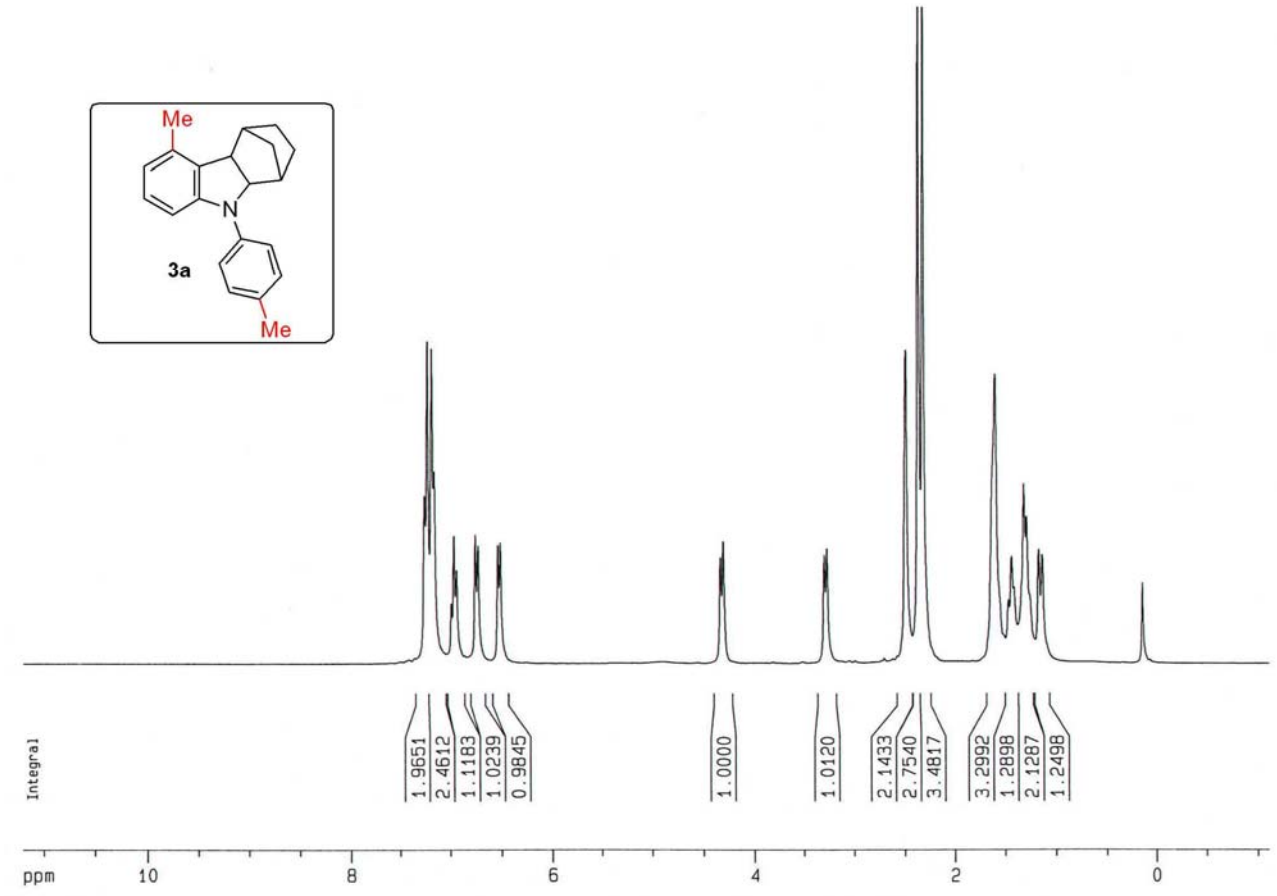
Scheme S2. Alternative mechanism for the annulation reaction

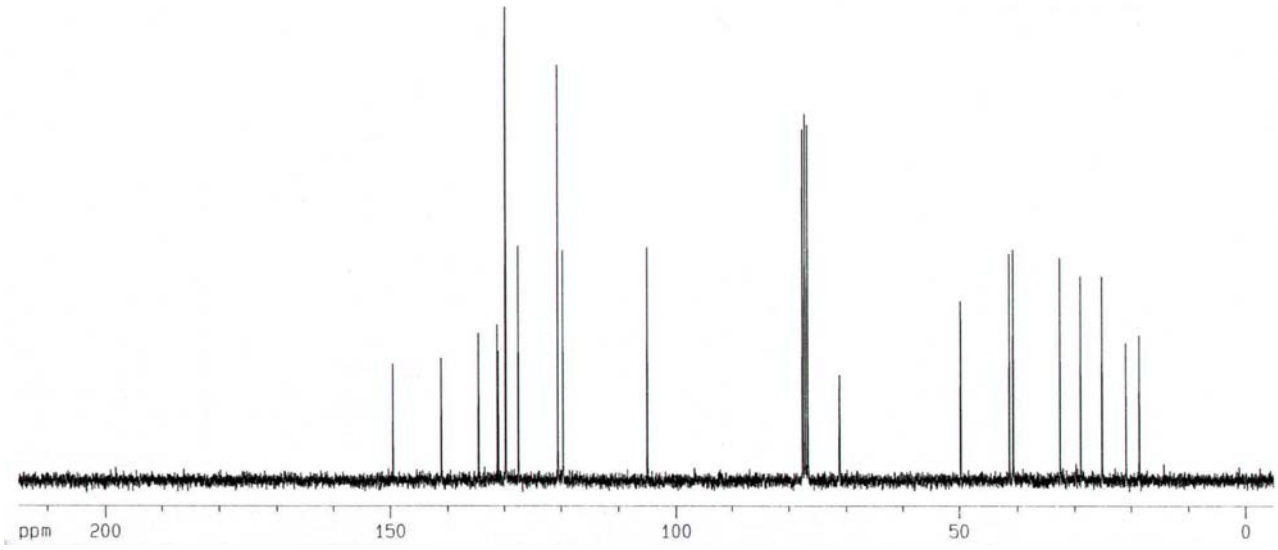
To clarify the participation of competing pathway of N-arylation/norbornene aminopalladation/intramolecular C-H bond activation in this protocol, we explored the reaction of diphenylamine and norbornene under the optimized reaction conditions (Scheme S3). However, the desired methanocarbazole product was not observed in the reaction mixture. This result confirms that this pathway is also unlikely to proceed.

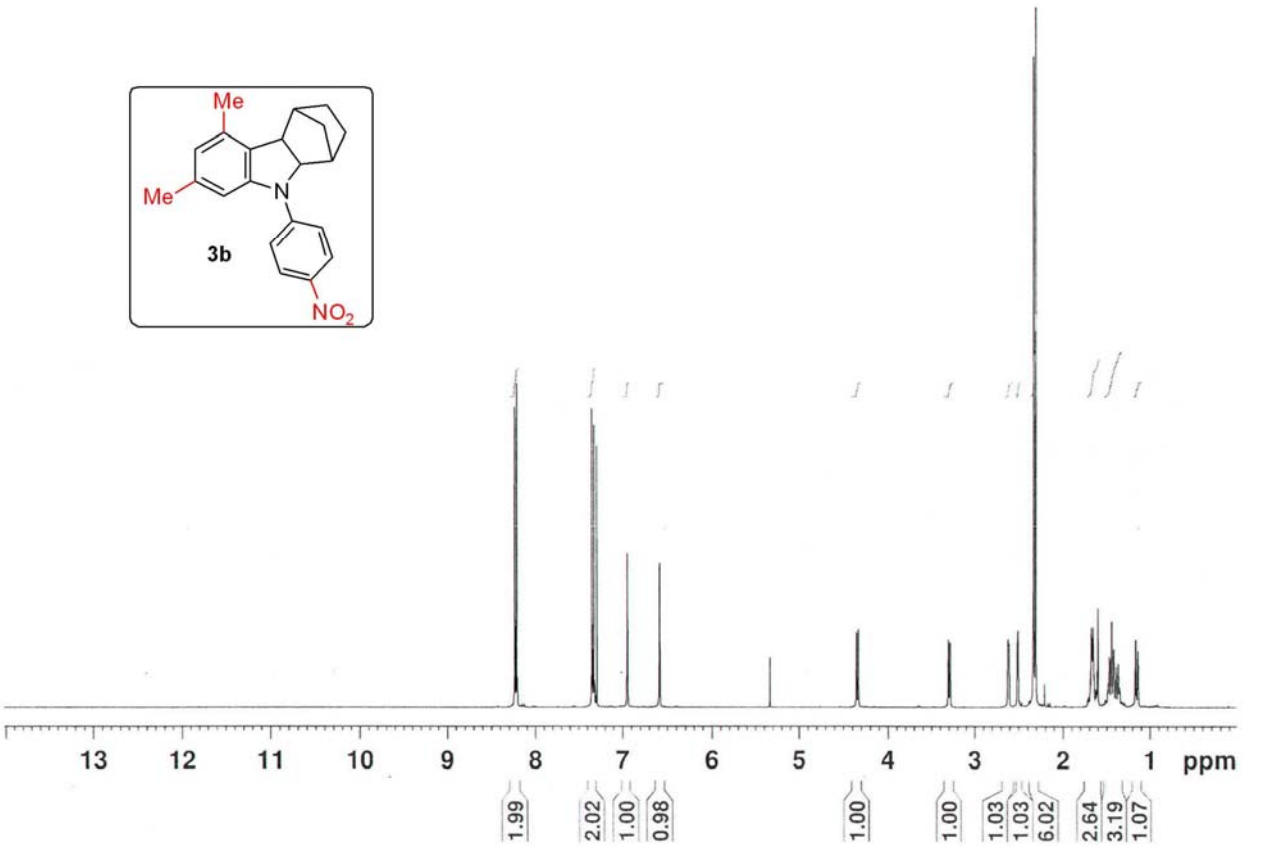


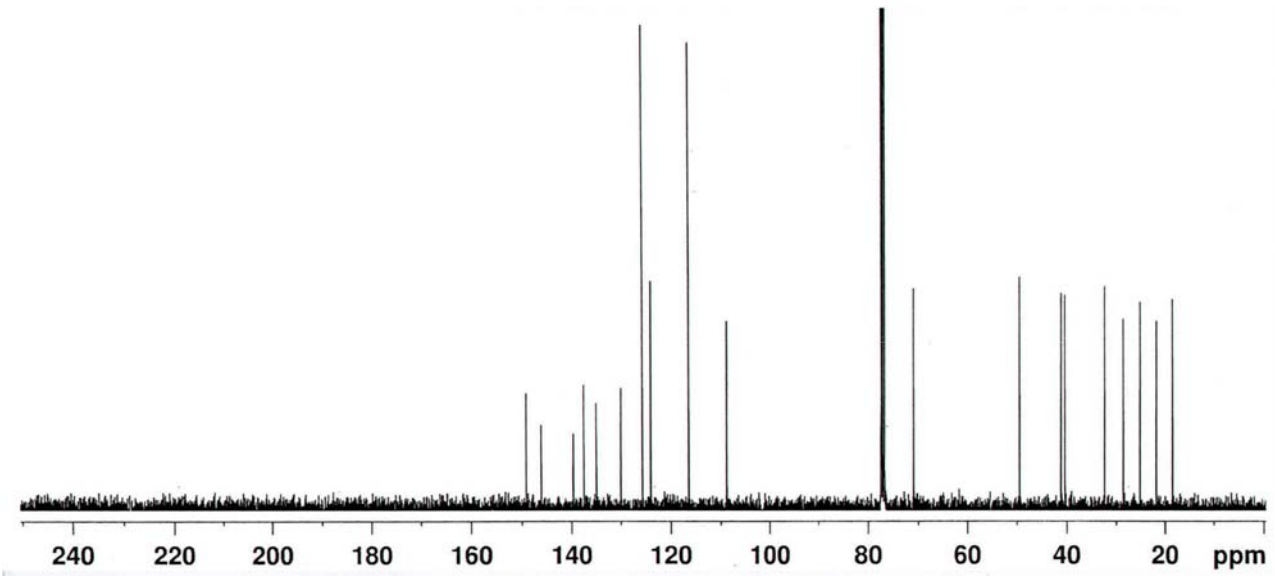
Scheme S3. The reaction of diphenylamine and norbornene under the optimized reaction condition .

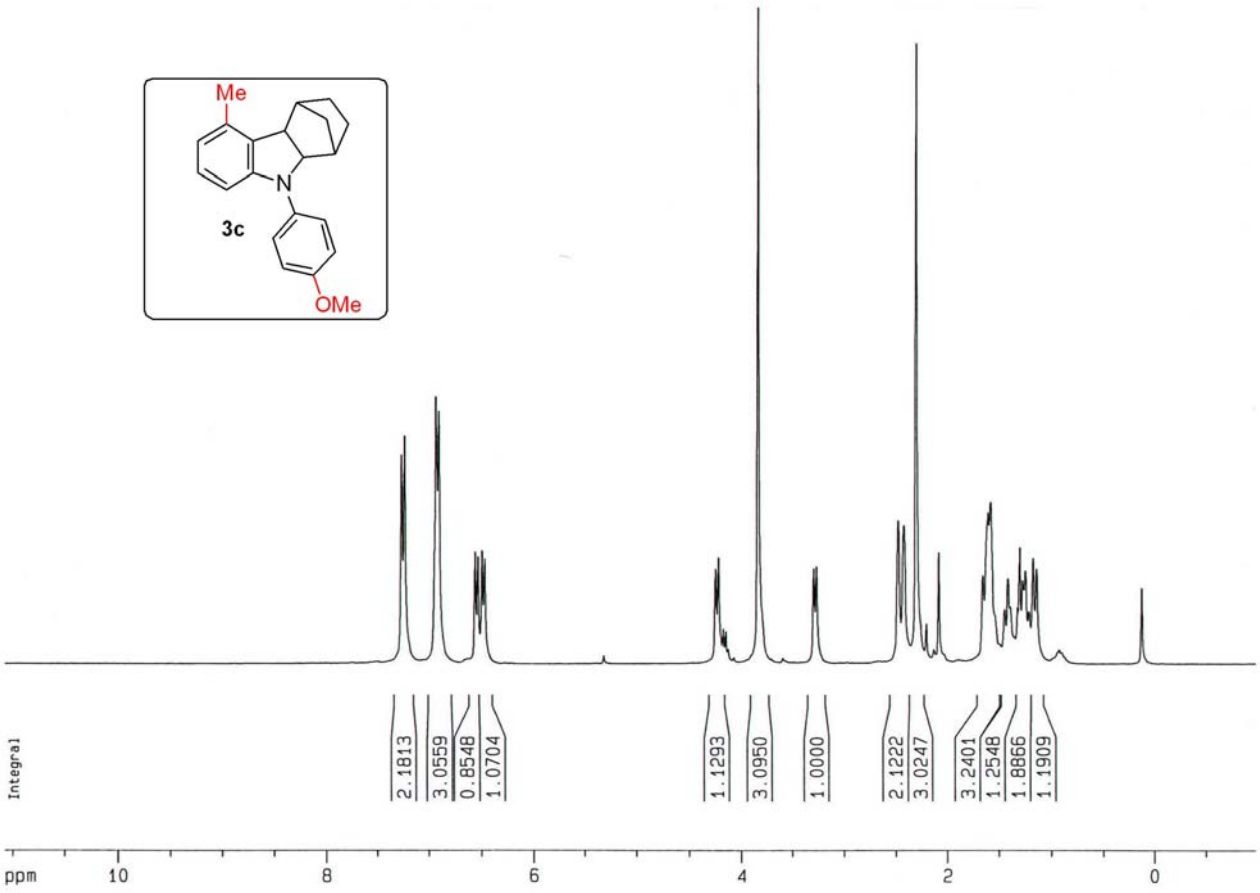
5 Copies of ^{1}H and ^{13}C NMR Spectra

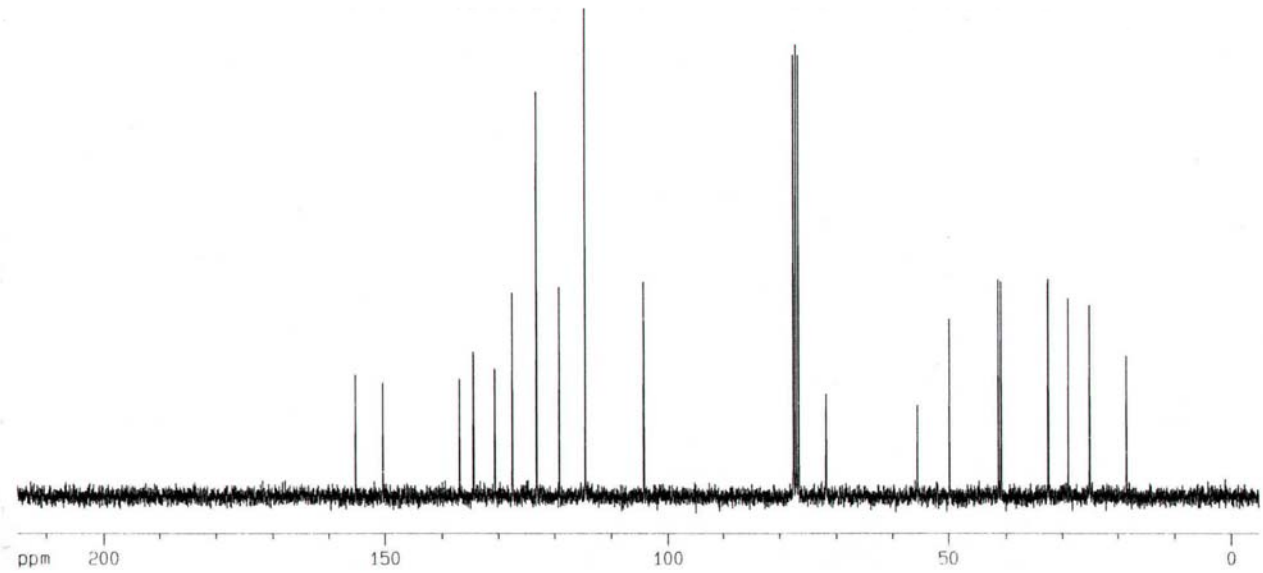


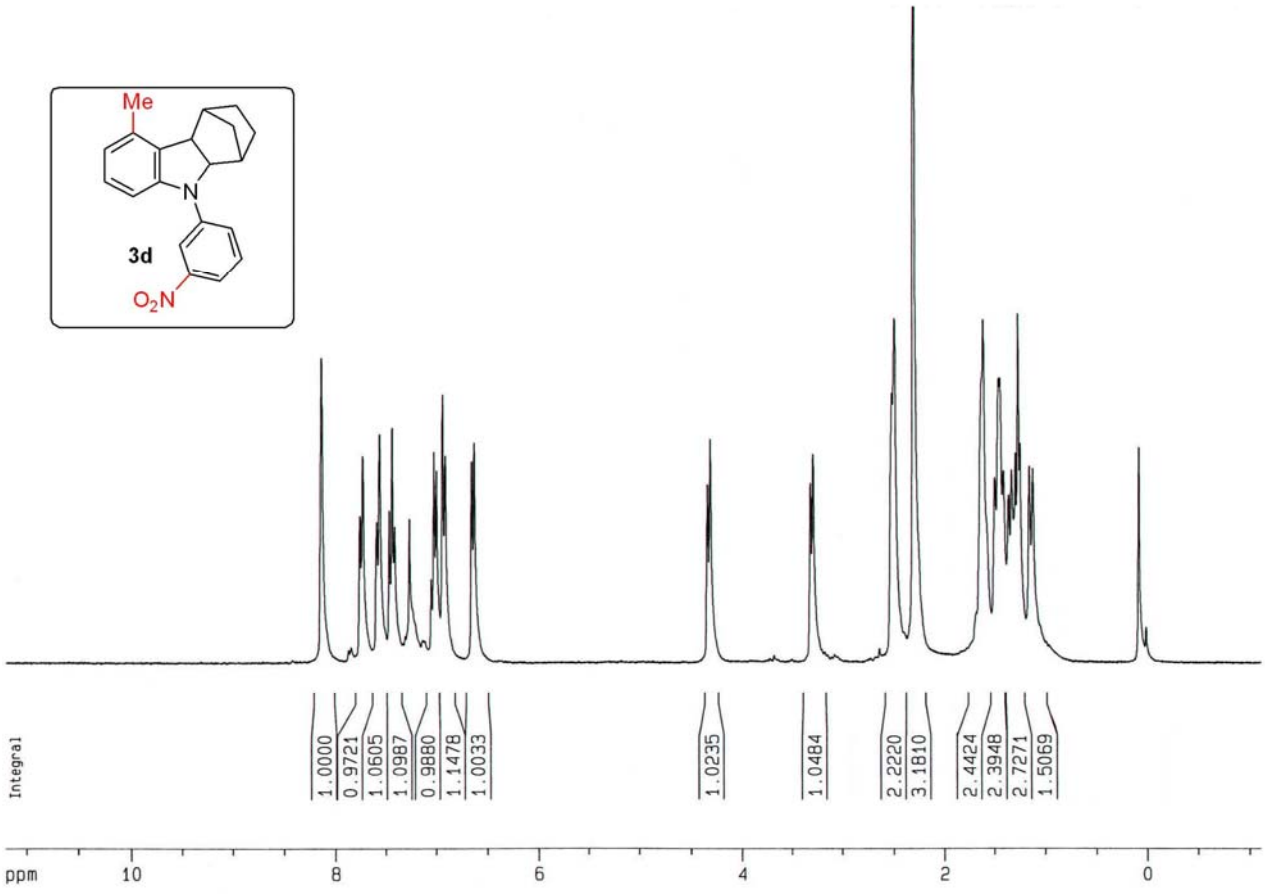


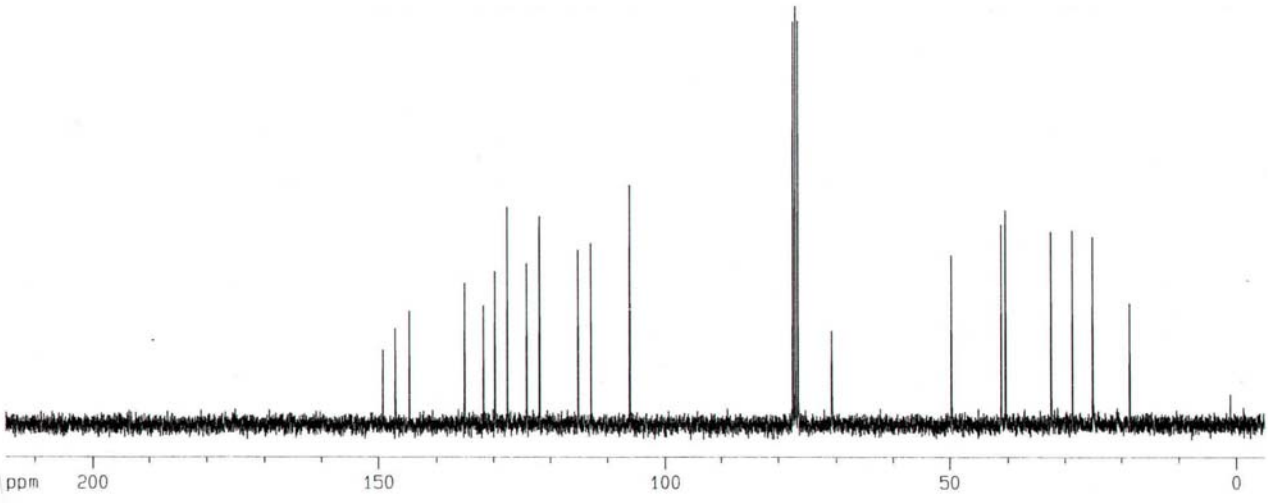

Me
Me
N
3b
NO2
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.99
2.02
1.00
0.98
1.00
1.00
1.03
1.03
6.02
2.64
3.19
1.07

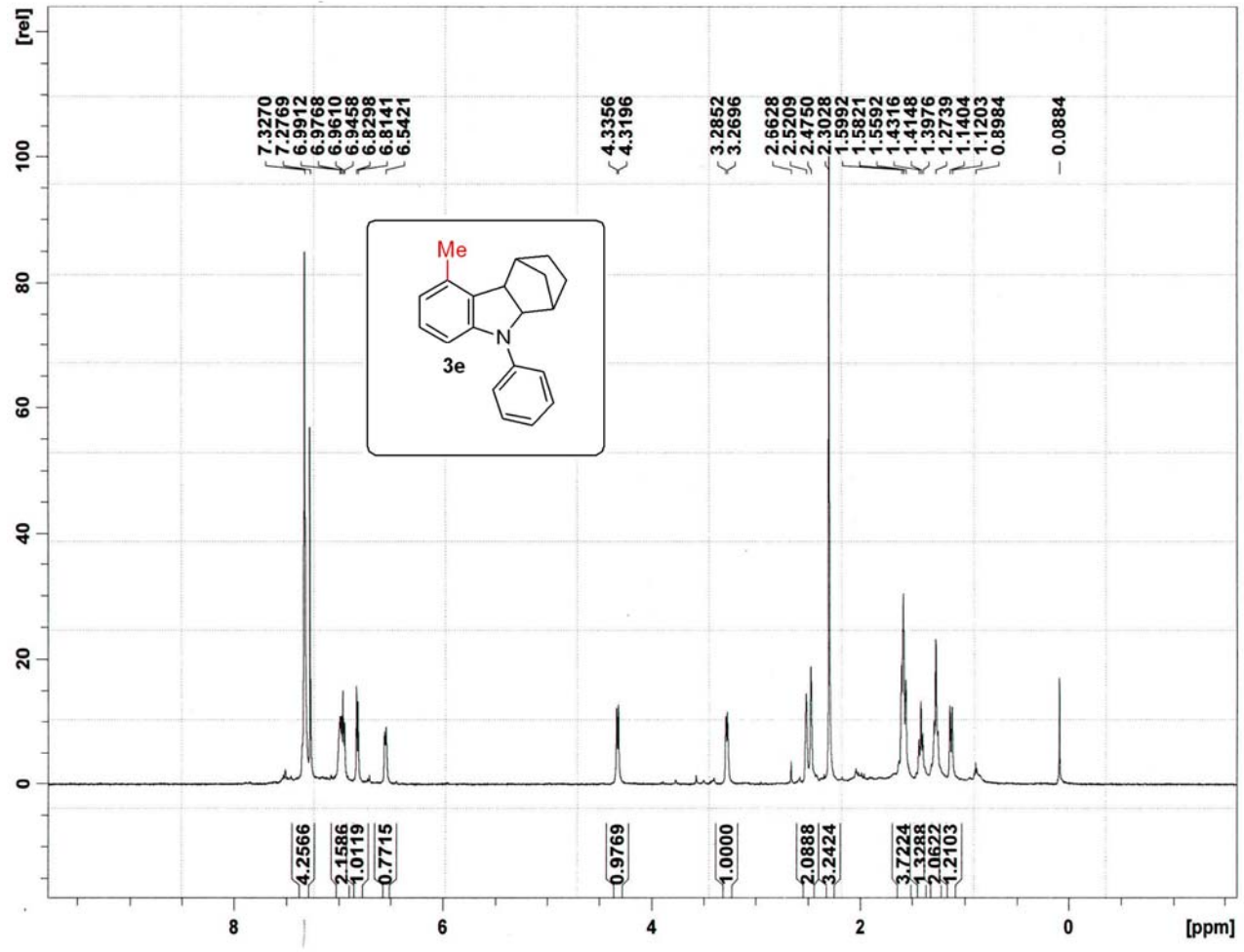

240 220 200 180 160 140 120 100 80 60 40 20 ppm

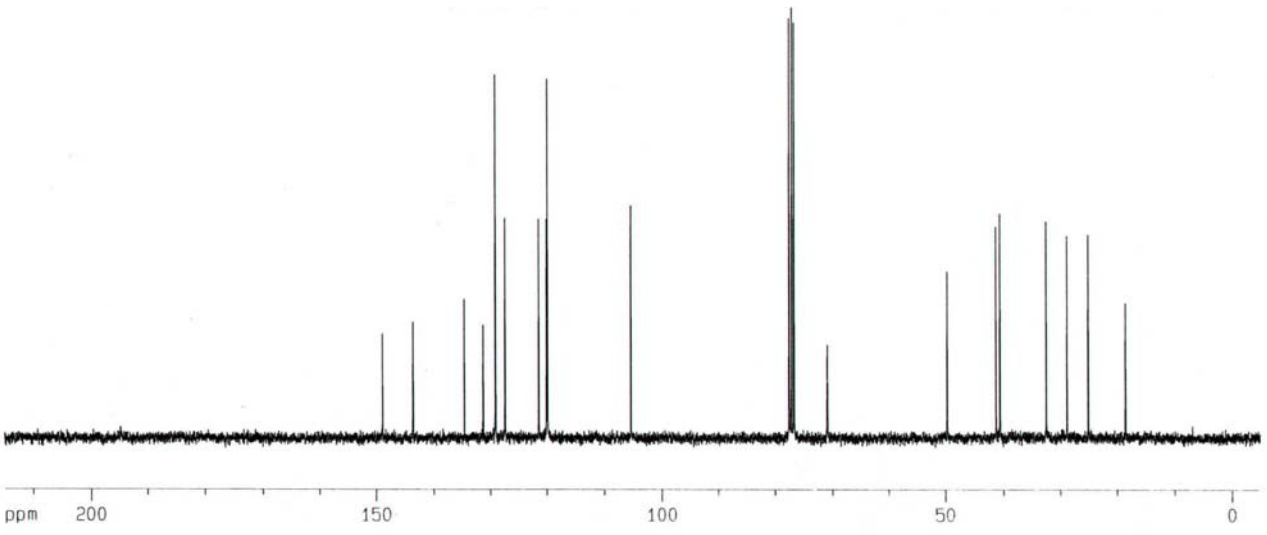

Me
3c
OMe
Integral
2.1813
3.0559
0.8548
1.0704
1.1293
3.0950
1.0000
2.1222
3.0247
3.2401
1.2548
1.8866
1.1909
ppm
10
8
6
4
2
0

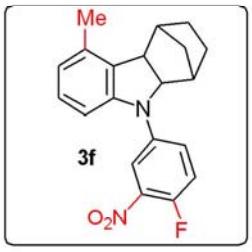

ppm
200
150
100
50
0


Me
N
3d
O2N
Integral
1.0000
0.9721
1.0605
1.0987
0.9880
1.1478
1.0033
1.0235
1.0484
2.2220
3.1810
2.4424
2.3948
2.7271
1.5069
ppm
10
8
6
4
2
0

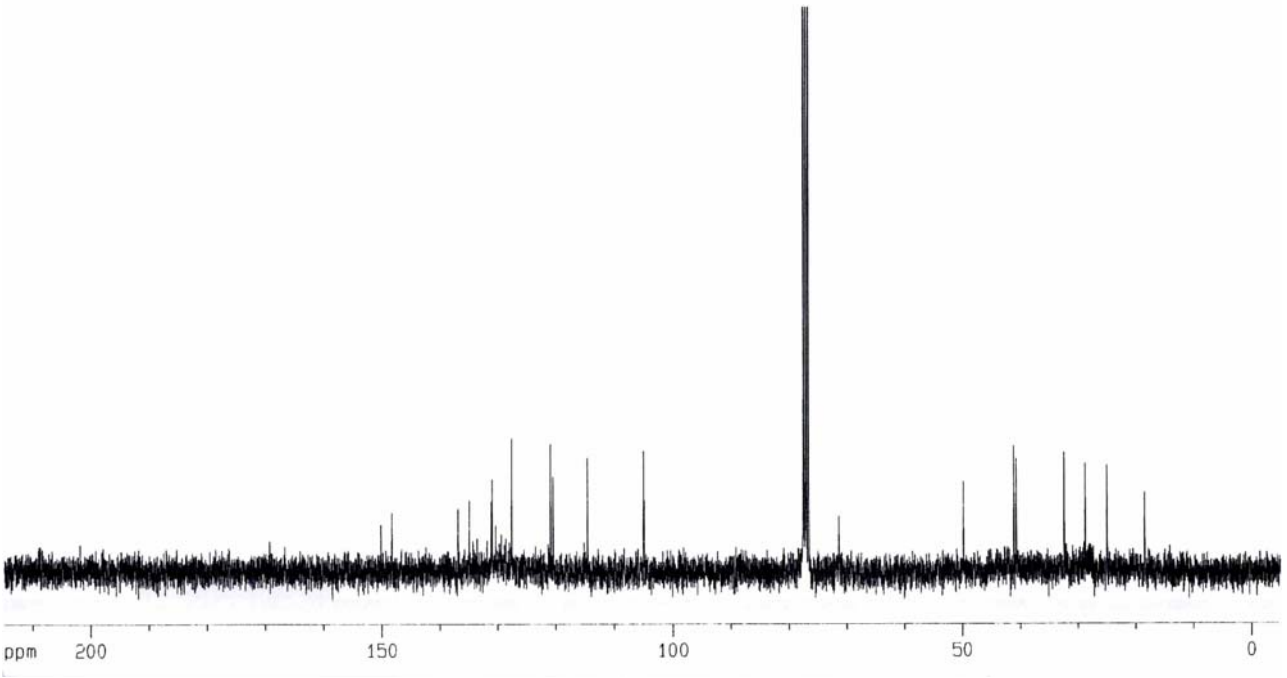

ppm
200
150
100
50
0

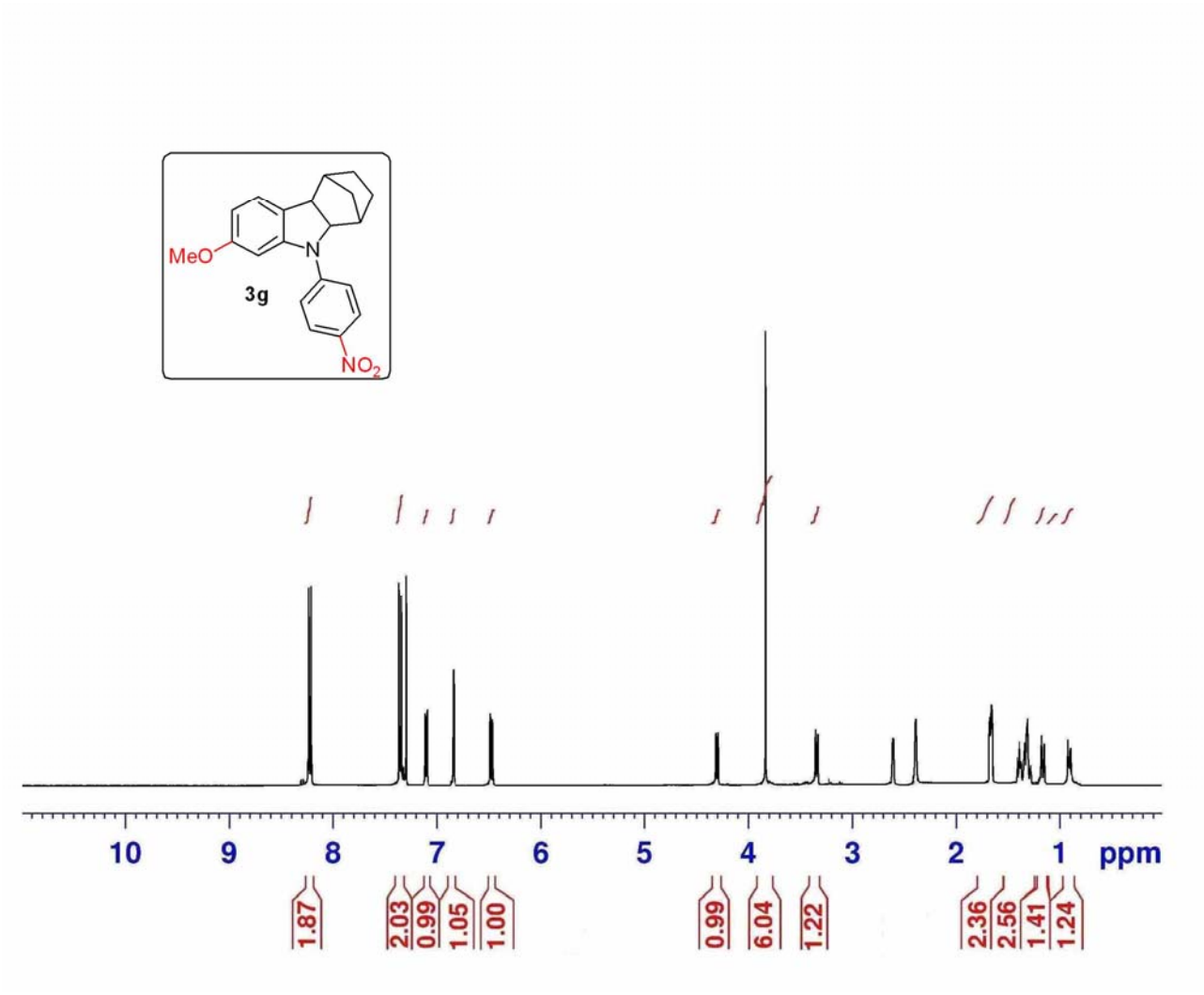

[rel]
7.3270
7.2769
6.9912
6.9768
6.9610
6.9458
6.8298
6.8141
6.5421
4.3356
4.3196
3.2852
3.2696
2.6628
2.5209
2.4750
2.3028
1.5992
1.5821
1.5592
1.4316
1.4148
1.3976
1.2739
1.1404
1.1203
0.8984
0.0884
Me
N
3e
4.2566
2.1586
1.0119
0.7715
0.9769
1.0000
2.0888
3.2424
3.7224
1.3288
2.0622
1.2103
8
6
4
2
0
[ppm]

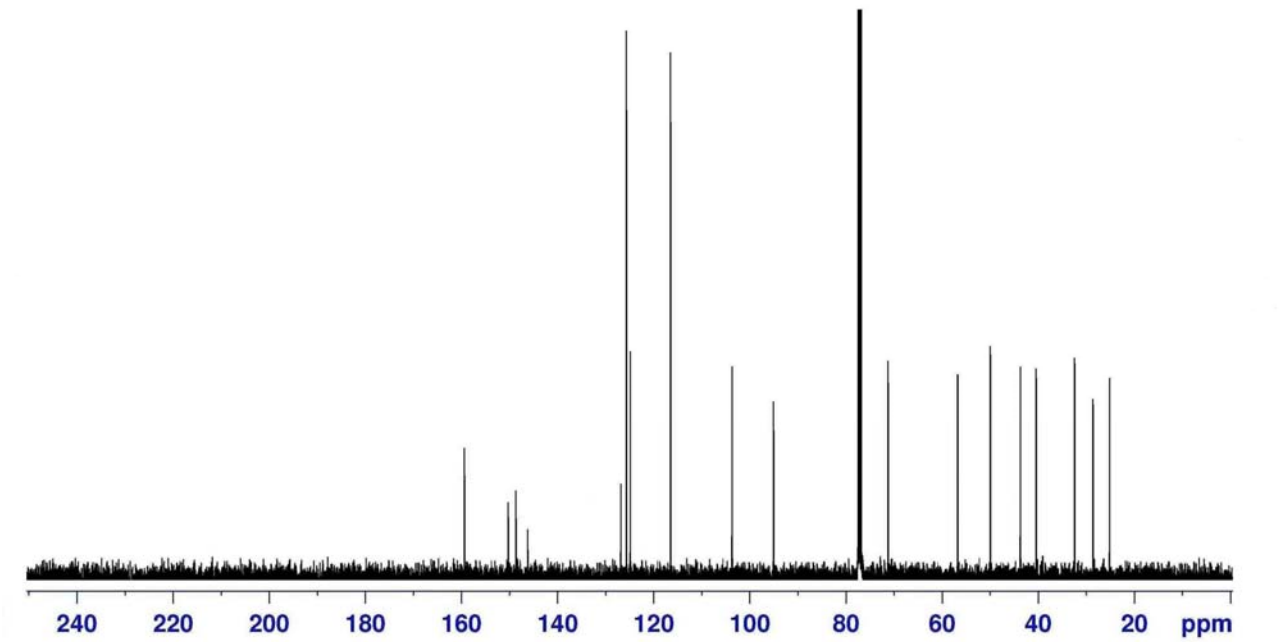

ppm
200
150
100
50
0

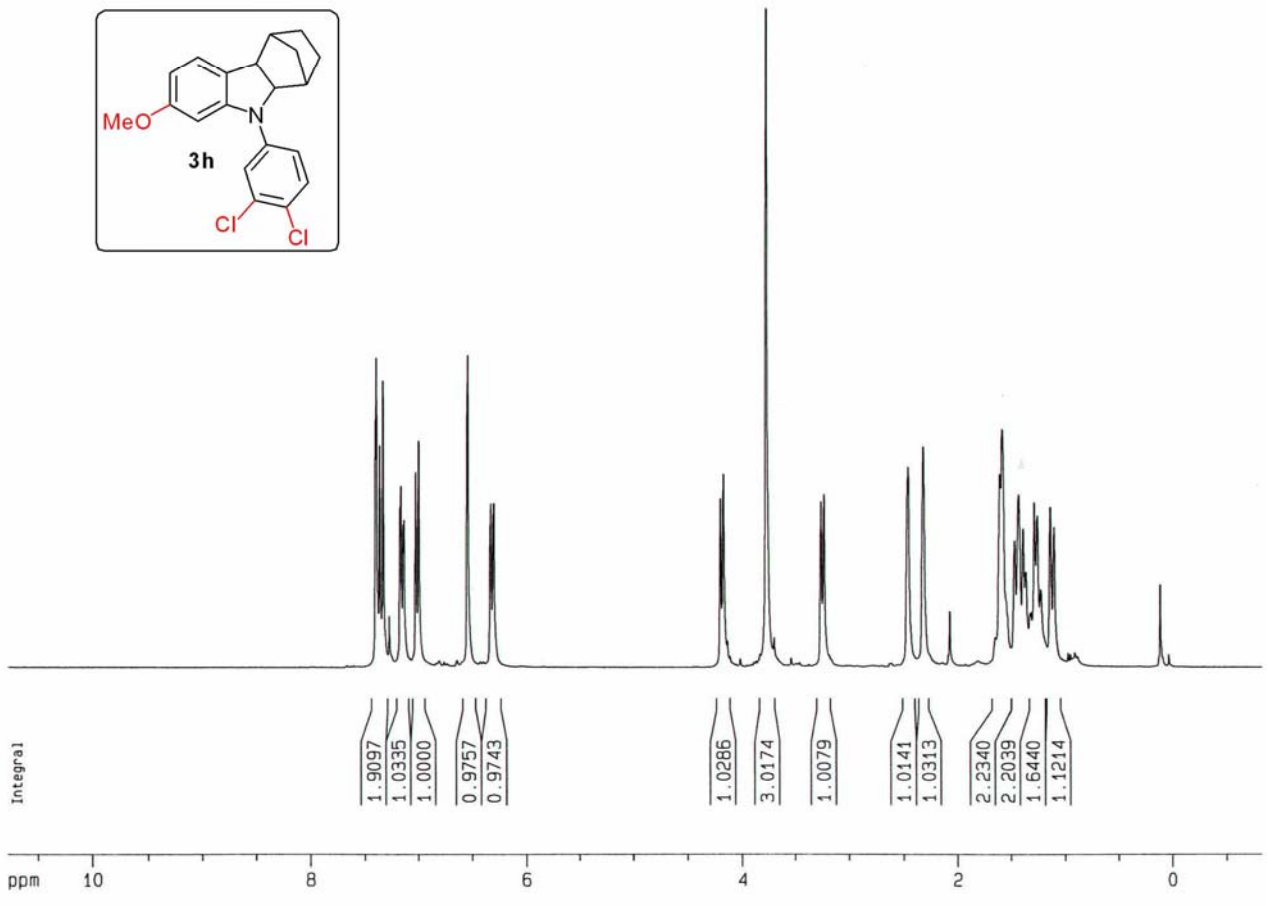

Me
N
3f
O2N
F

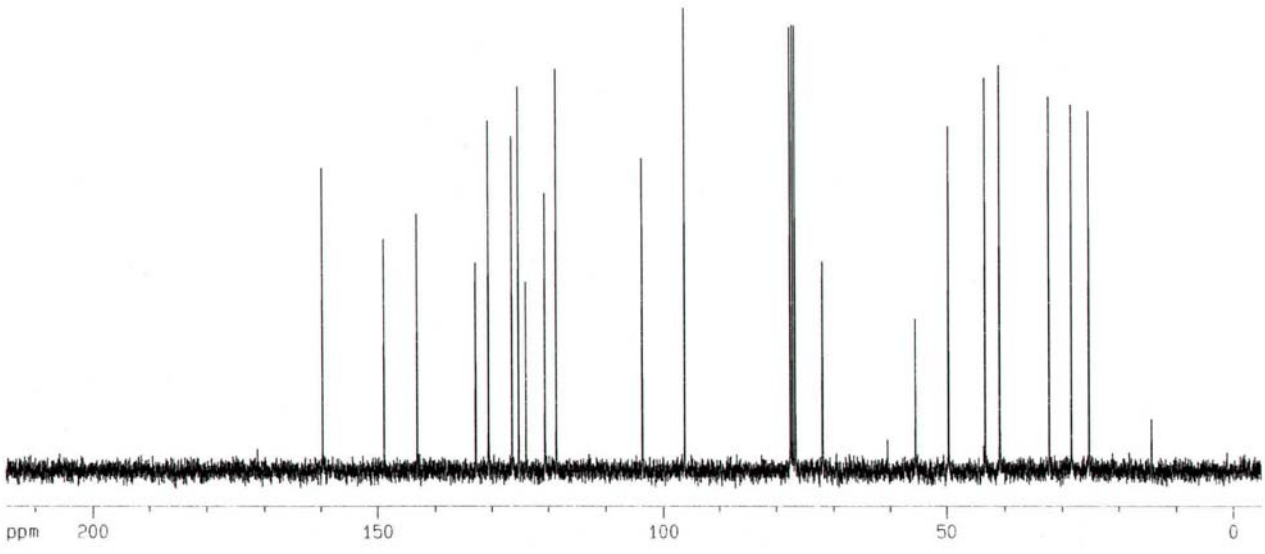
Integral
1.239
1.183
1.721
1.791
1.375
1.643
1.431
1.183
1.304
1.493
3.367
3.2451
1.2641
1.5764
1.1909
ppm
10
8
6
4
2
0

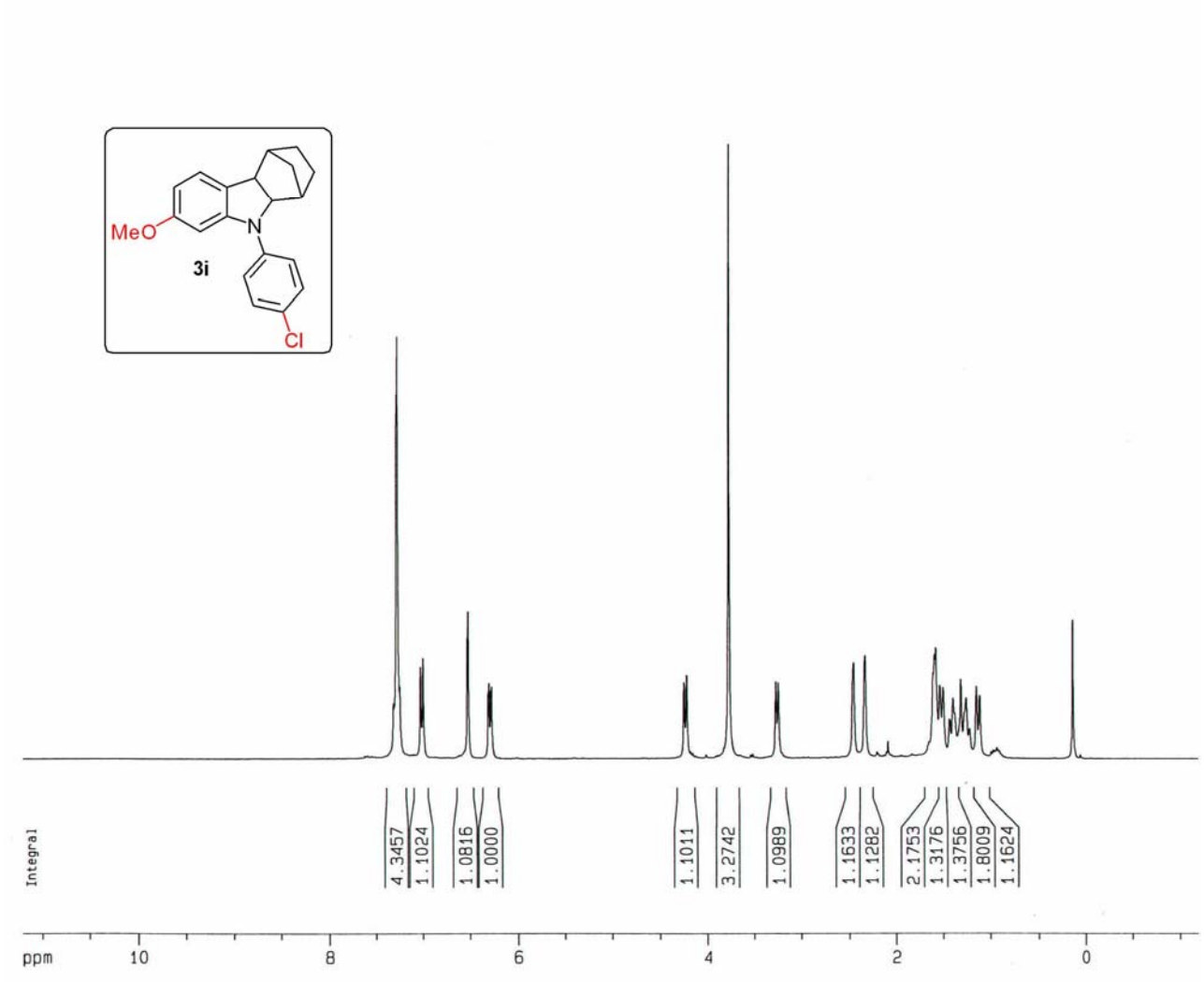

ppm
200
150
100
50
0

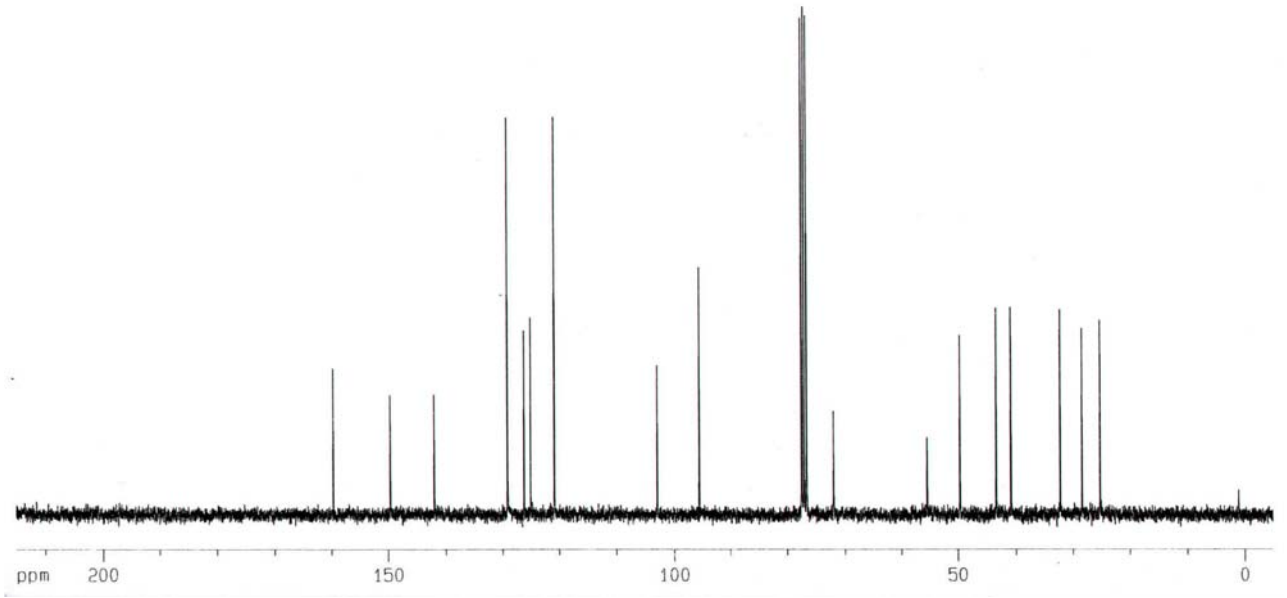

MeO
N
3g
NO2
10
9
8
7
6
5
4
3
2
1
ppm
1.87
2.03
0.99
1.05
1.00
0.99
6.04
1.22
2.36
2.56
1.41
1.24

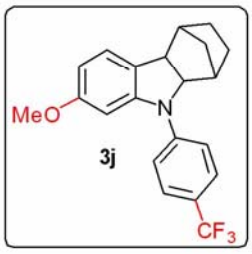

240
220
200
180
160
140
120
100
80
60
40
20
ppm


MeO
3h
Cl
Cl
Integral
1.9097
1.0335
1.0000
0.9757
0.9743
1.0286
3.0174
1.0079
1.0141
1.0313
2.2340
2.2039
1.6440
1.1214
ppm
10
8
6
4
2
0

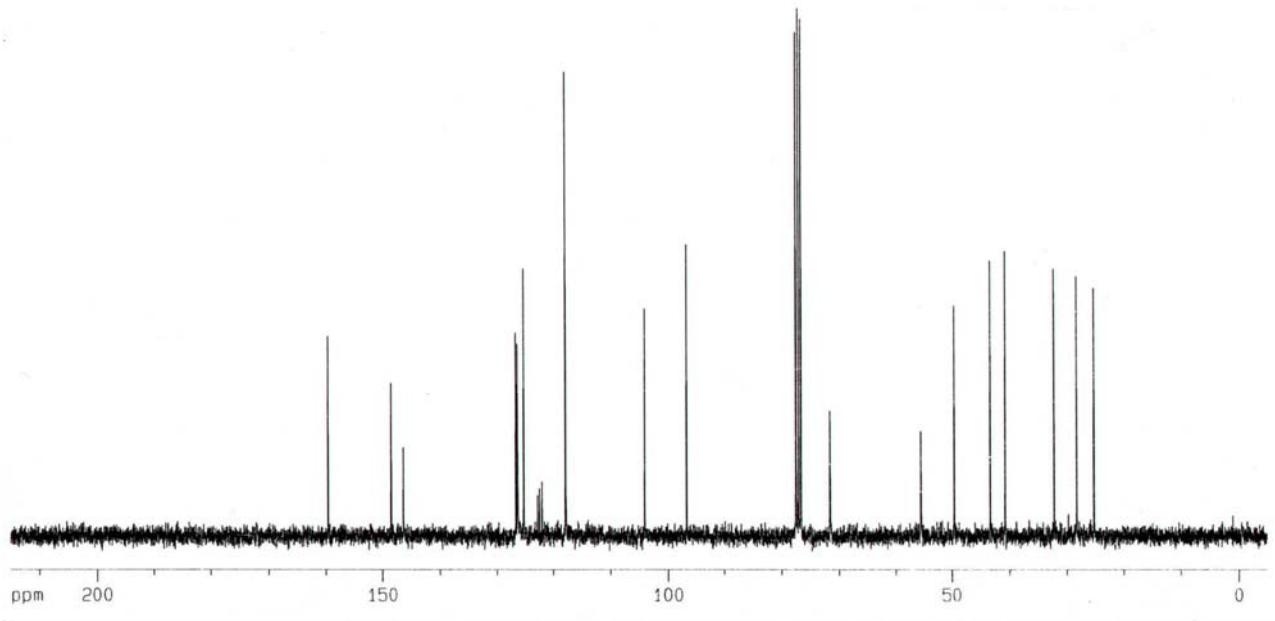

ppm
200
150
100
50
0

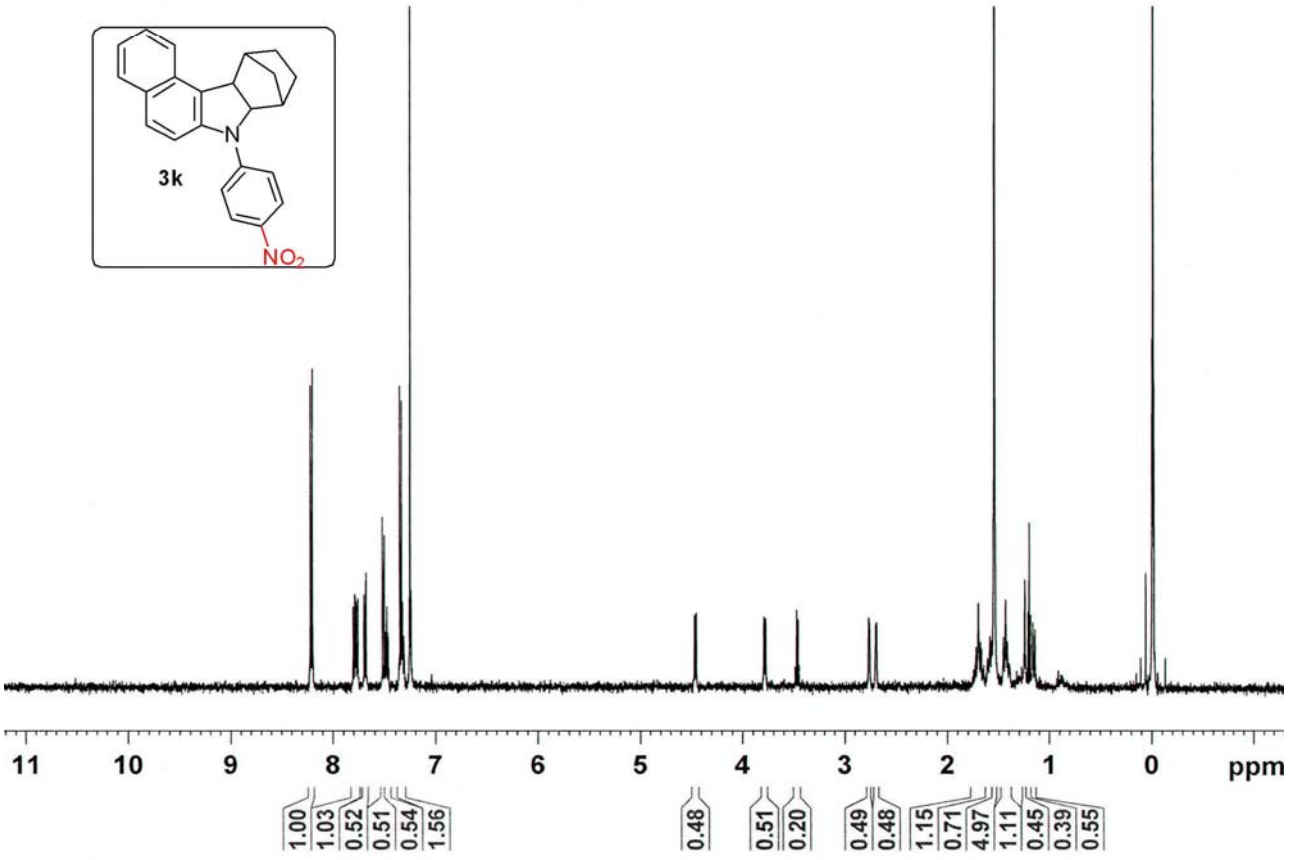

MeO
N
Cl
3i
Integral
4.3457
1.1024
1.0816
1.0000
1.1011
3.2742
1.0989
1.1633
1.1282
2.1753
1.3176
1.3756
1.8009
1.1624
ppm
10
8
6
4
2
0

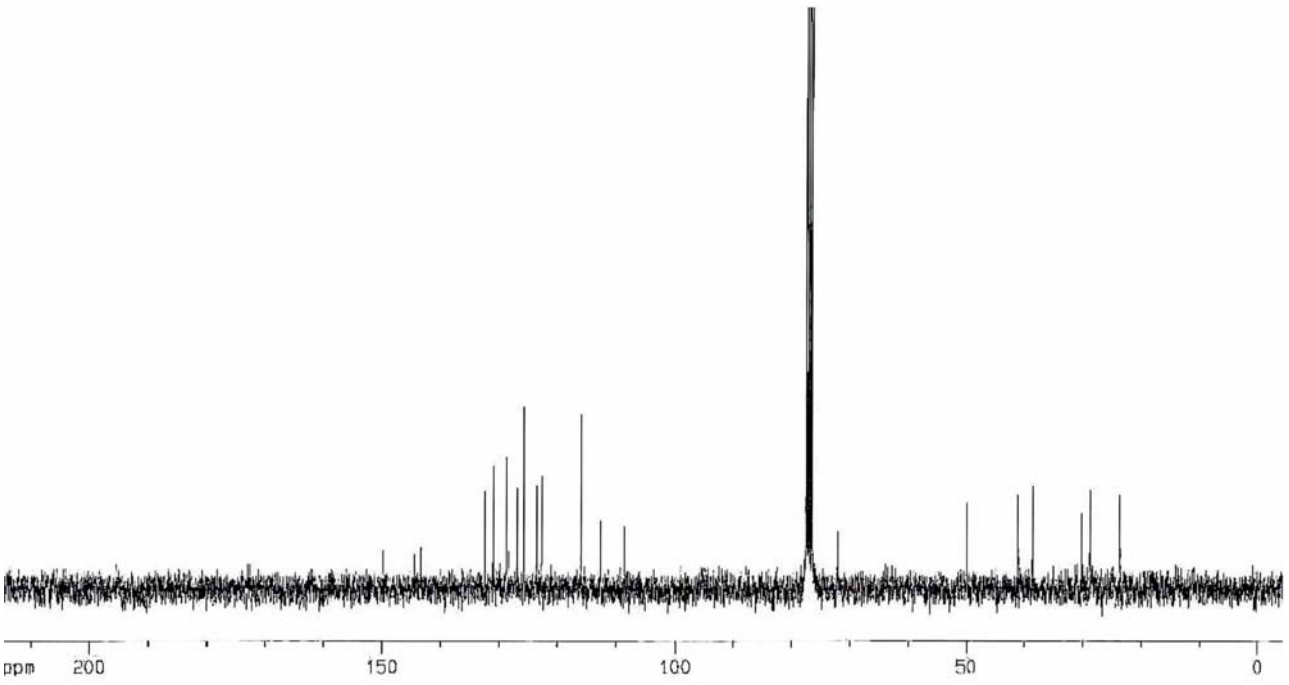

ppm
200
150
100
50
0

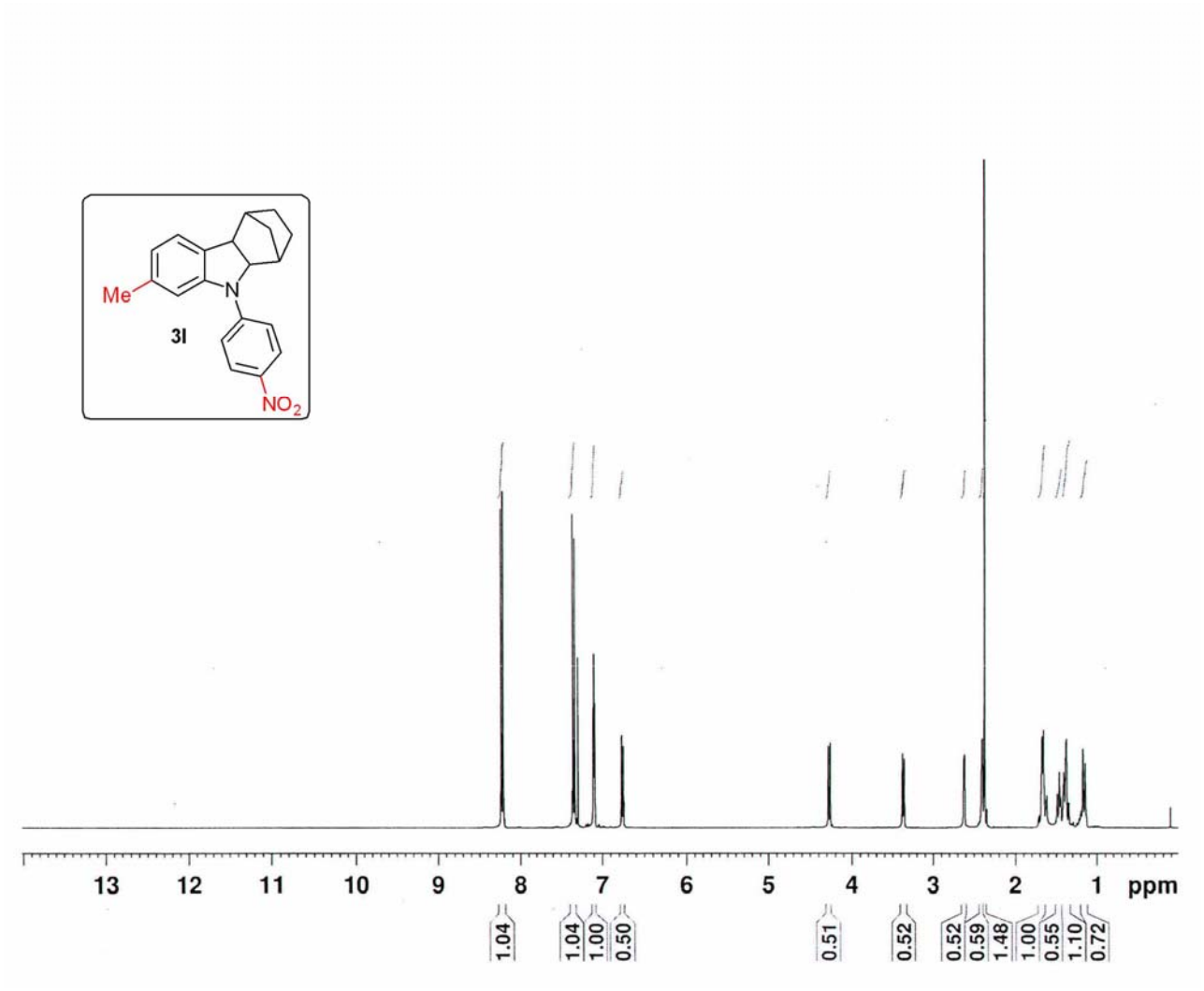

MeO
N
3j
CF3

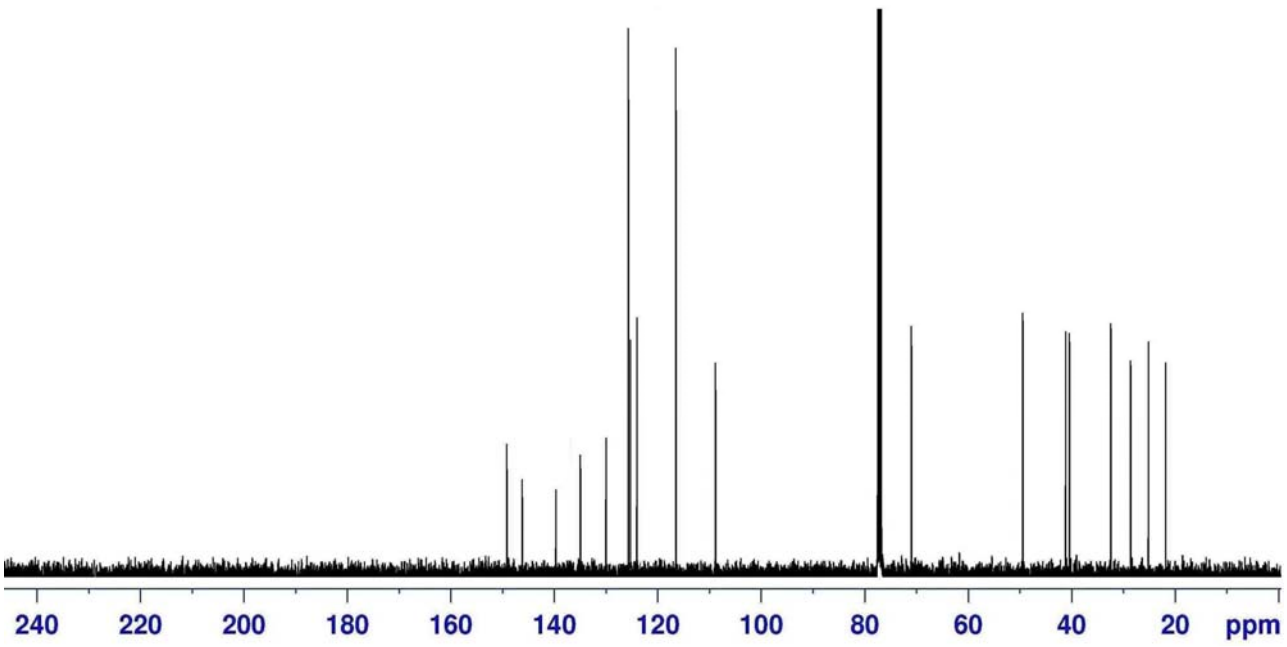
Integral
1.9800
2.0083
1.0000
0.9686
0.9361
0.9884
3.1206
1.0001
1.0260
1.0859
2.3710
2.2837
1.9324
1.1245
ppm 10
8
6
4
2
0

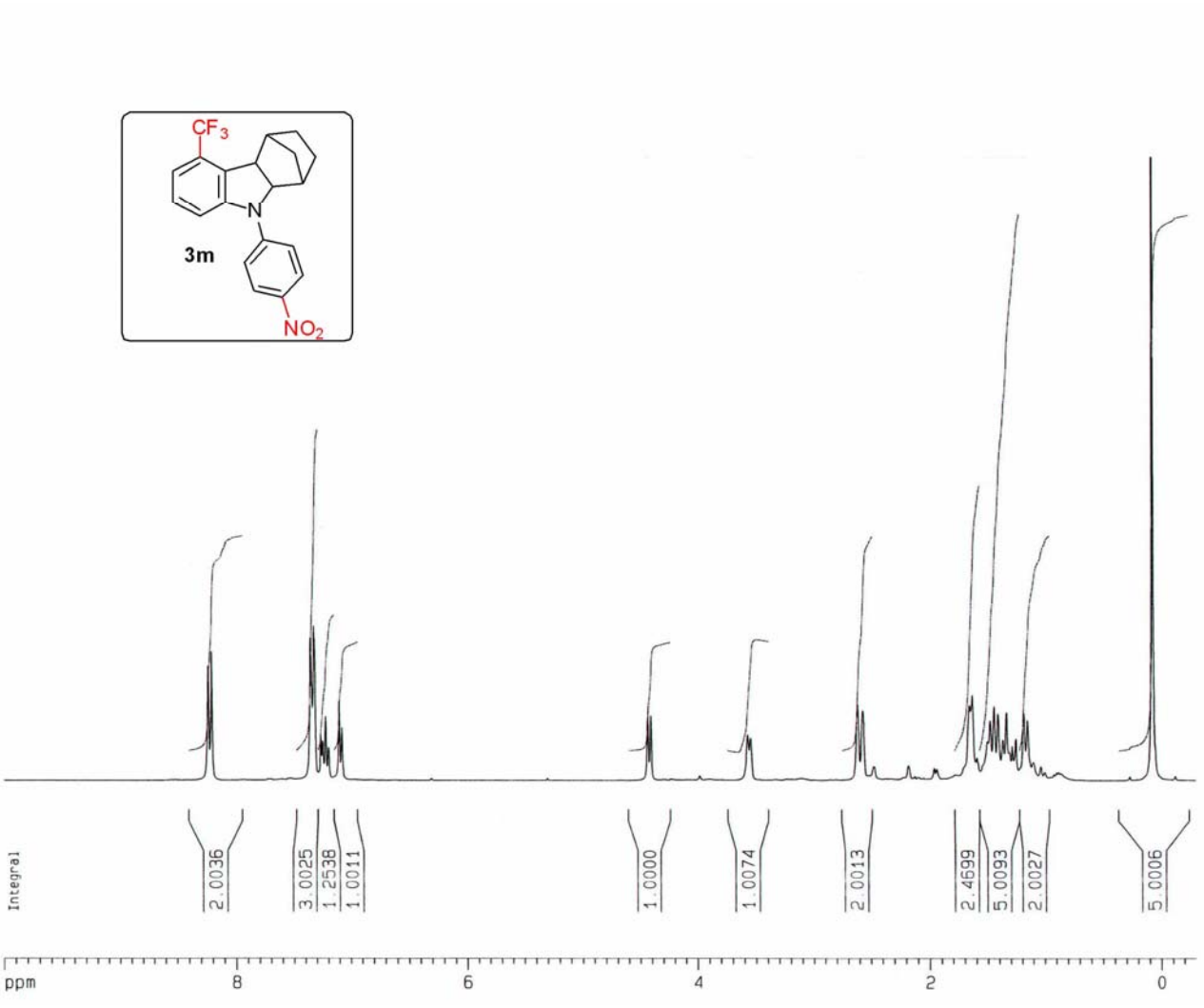

ppm 200
150
100
50
0

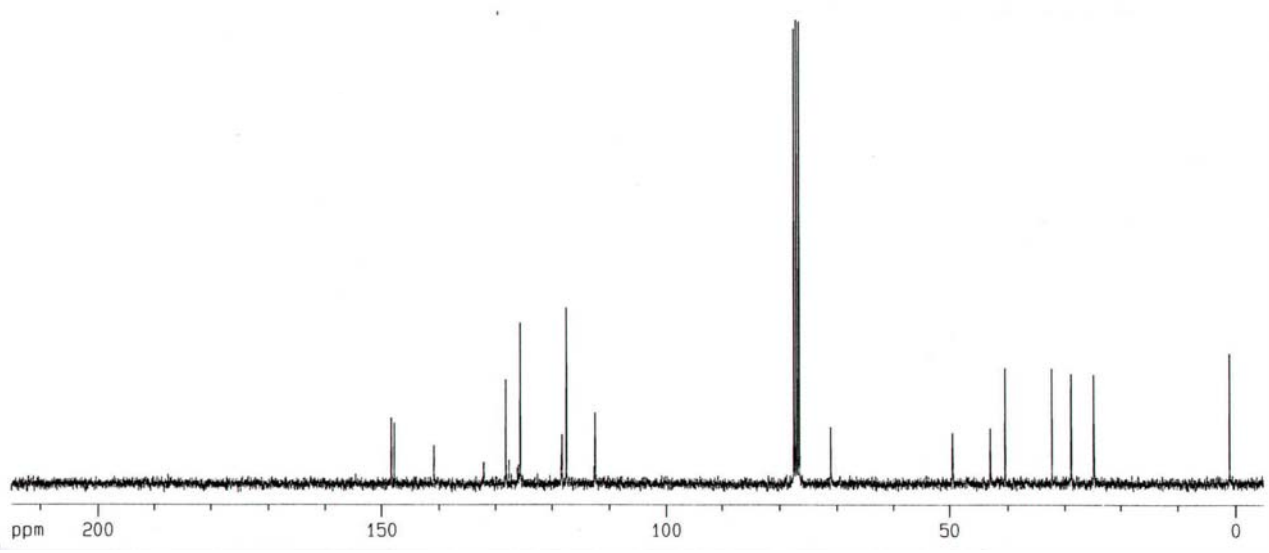

3k
N
NO2
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
0.52
0.51
0.54
1.56
0.48
0.51
0.20
0.49
0.48
1.15
0.71
4.97
1.11
0.45
0.39
0.55

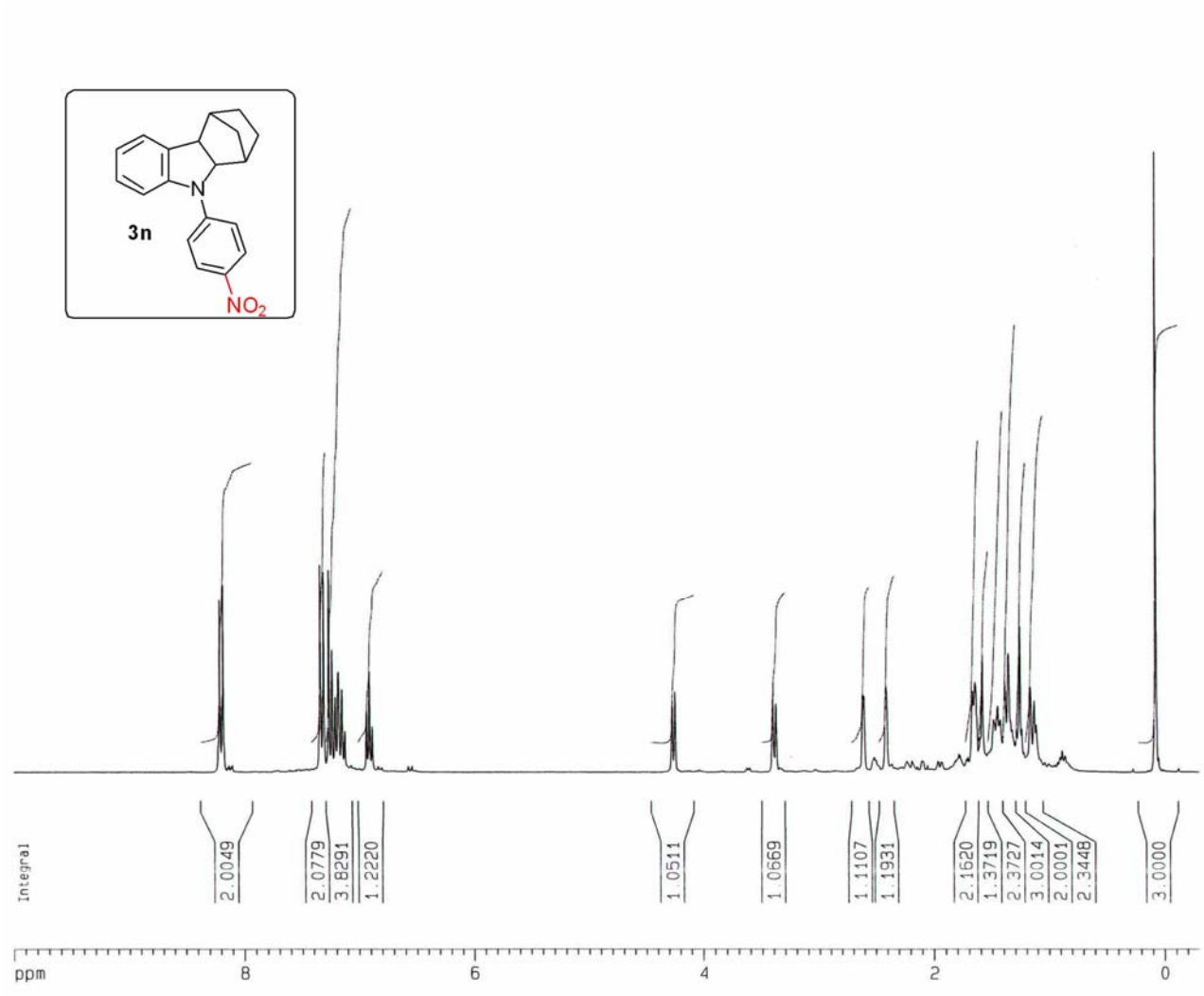

ppm
200
150
100
50
0

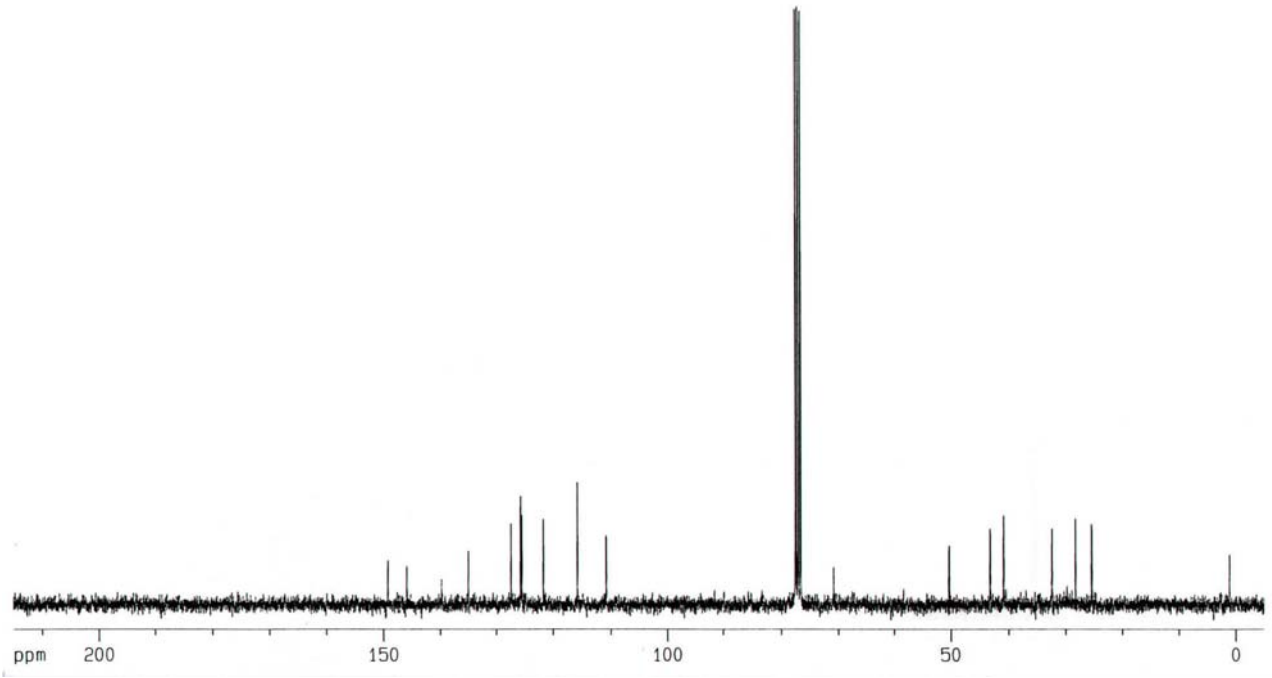

Me
N
3l
NO2
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.04
1.04
1.00
0.50
0.51
0.52
0.52
0.59
1.48
1.00
0.55
1.10
0.72

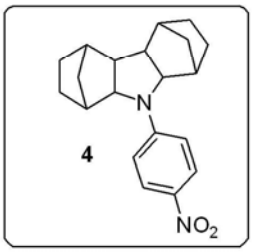

240
220
200
180
160
140
120
100
80
60
40
20
ppm

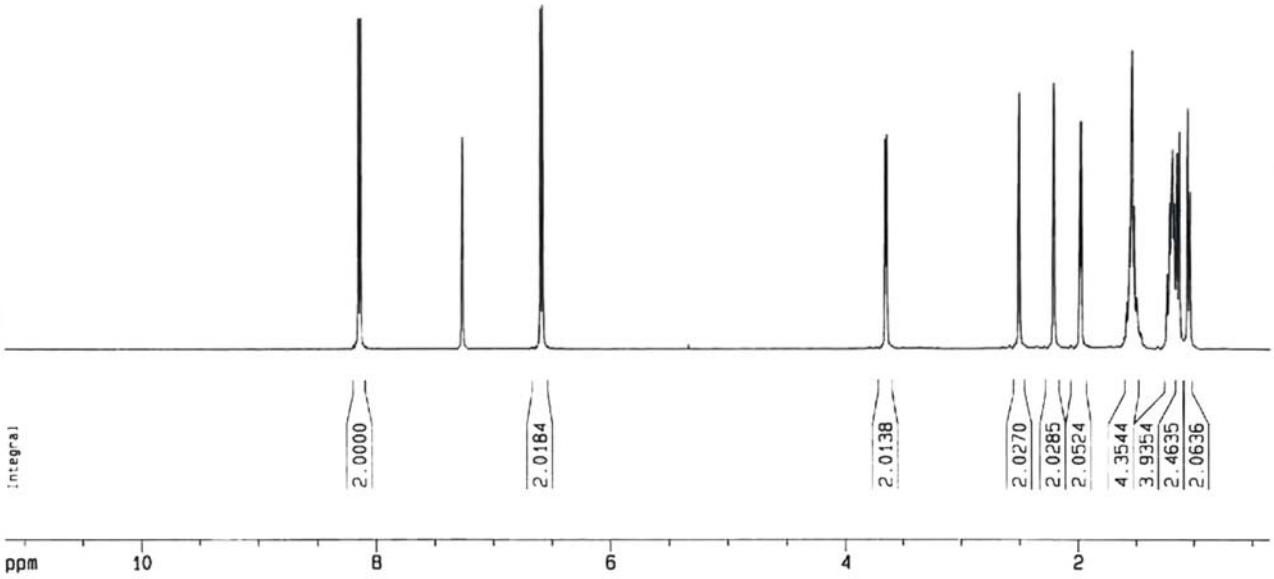

CF3
N
3m
NO2
Integral
2.0036
3.0025
1.2538
1.0011
1.0000
1.0074
2.0013
2.4699
5.0093
2.0027
5.0006
ppm
8
6
4
2
0

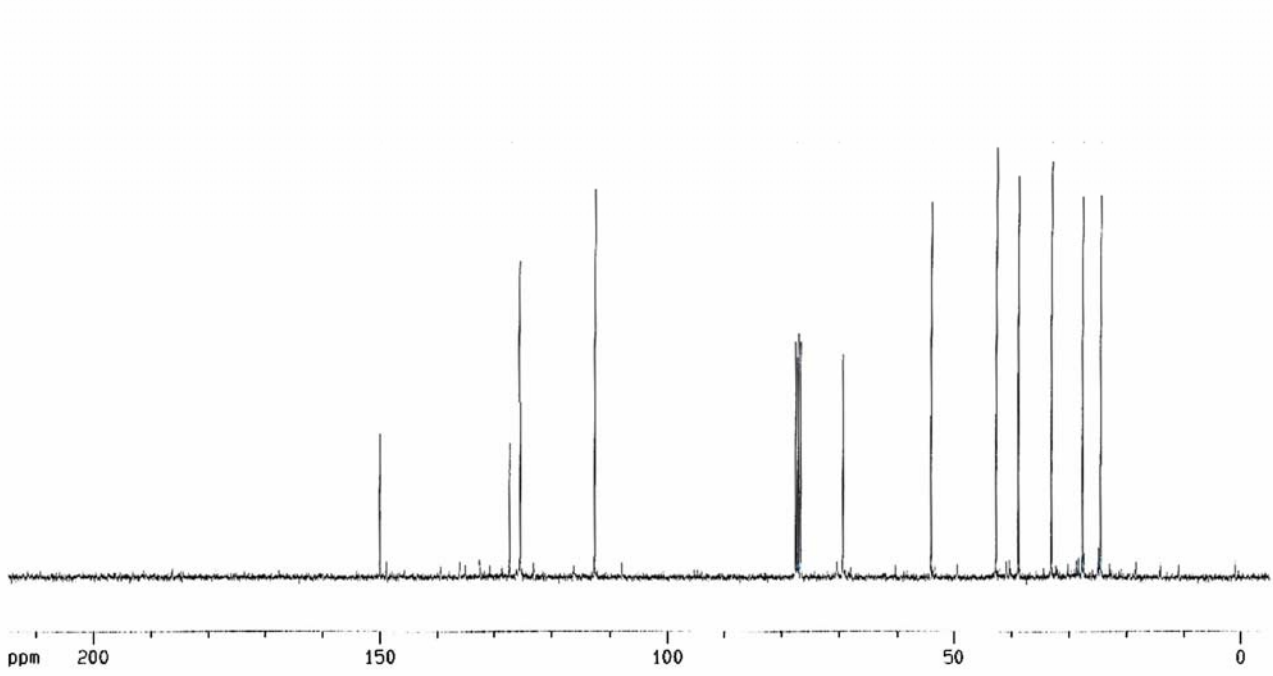

ppm
200
150
100
50
0

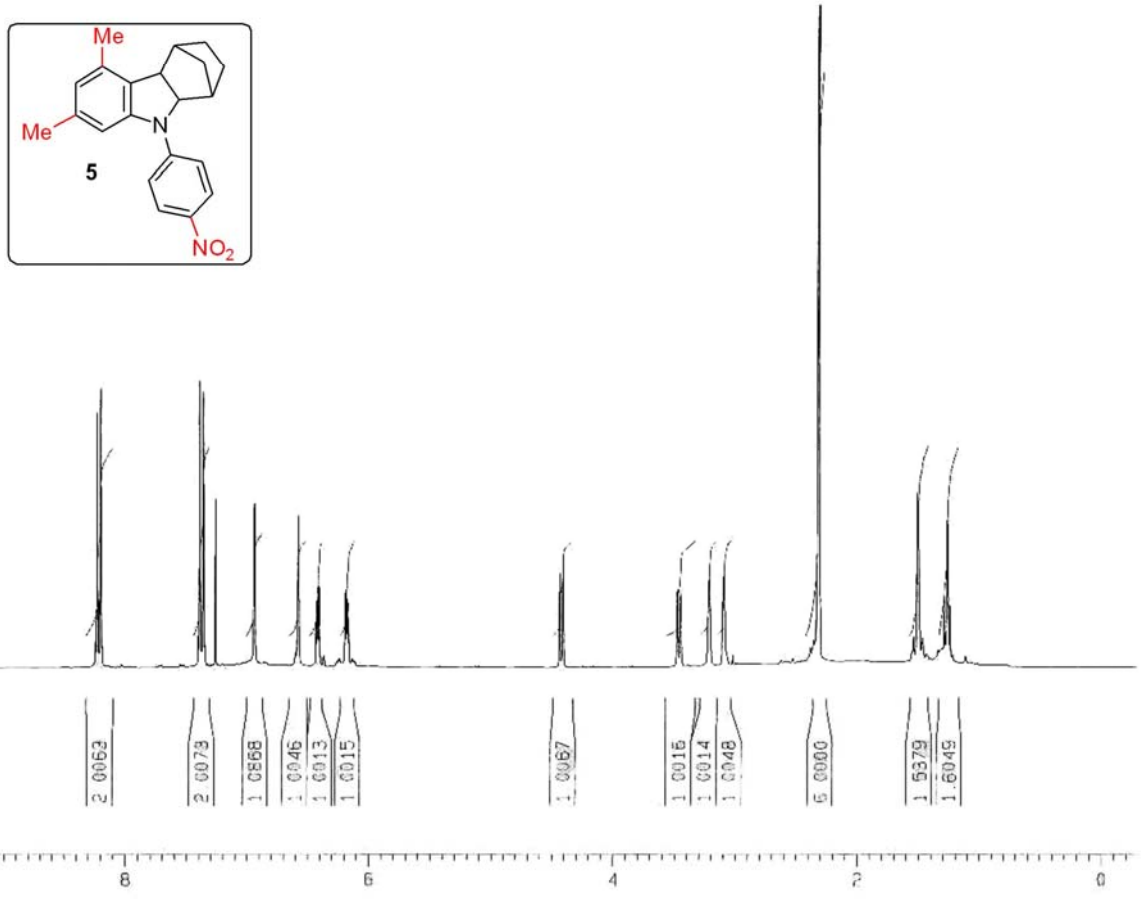

3n
NO2
Integral
2.0049
2.0779
3.8291
1.2220
1.0511
1.0669
1.1107
1.1931
2.1620
1.3719
2.3727
3.0014
2.0001
2.3448
3.0000
ppm
8
6
4
2
0

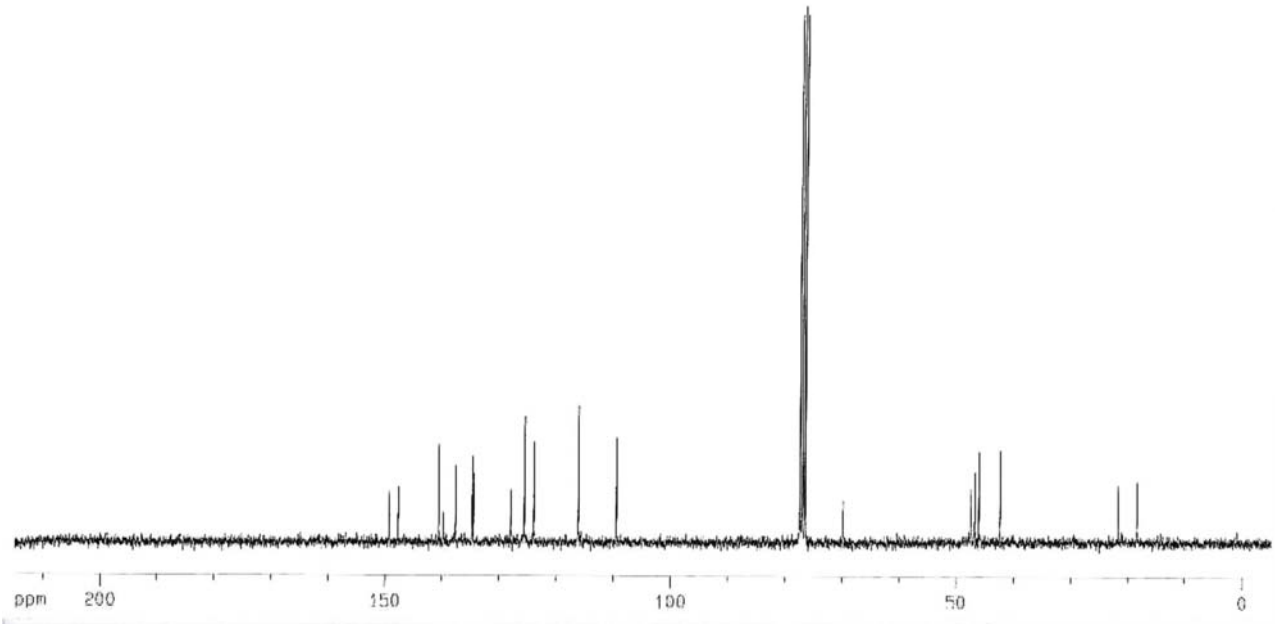

ppm
200
150
100
50
0


N
4
NO2


Integral
2.0000
2.0184
2.0138
2.0270
2.0285
2.0524
4.3544
3.9354
2.4635
2.0636
ppm
10
8
6
4
2


ppm
200
150
100
50
0


Me
Me
N
5
NO2
Integral
2.0062
2.0079
1.0868
1.0046
1.0013
1.0015
1.0067
1.0016
1.0014
1.0048
6.0000
1.5379
1.6049
ppm
8
6
4
2
0


ppm
200
150
100
50
0

6 2D NMR Spectrum for compound 3a