Synthesis

Reviews and Full Papers in Chemical Synthesis

Supporting Information

for DOI: 10.1055/a-1375-5283

Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

Thieme

Supporting Information

Iridium-Catalyzed Direct Amidation of Imidazoles at the C-2 Position with Isocyanates in the Presence of Hydrosilanes Leading to Imidazole-2-Carboxamides

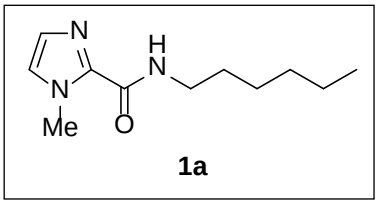
Yoshiya Fukumoto,* Motohiro Shiratani, Hikaru Noguchi, and Naoto Chatani

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

General Information. IR spectra were obtained on a Horiba FT-720 spectrometer using the transmission method; absorption data are reported in reciprocal centimeters. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer using $CDCl_3$ as the solvent. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad singlet, c = complex), coupling constant (Hz), and integration. Mass spectra (MS) were obtained using a Shimadzu GCMS-QP 2010 instrument with an ionization voltage of 70 eV. Elemental analyses and high-resolution mass spectra (HRMS) were performed by the Elemental Analysis Section of Osaka University. Analytical GC was carried out on a Shimadzu GC-2014 gas chromatograph, equipped with a flame ionization detector. GPC was carried out on a JAI LC-908 equipped with a RI detector, using chloroform as the solvent. Flash column chromatography was performed with Silicycle SiliaFlash F60 (230-400 mesh). Preparative TLC was performed with Wako-gel B-5F. Liquid reagents such as isocyanates except 1-adamantyl isocyanate, hydrosilanes, and 1-methylimidazole, are commercially available and were purified by distillation prior to use. Solid reagents, including 1-adamantyl isocyanate, 1-methylbenzimidazole, and $Ir_4(CO)_{12}$, were purchased and used without further purifications. 1-Benzylimidazole,[1] 1-methoxymethylimidazole,[2] 1-phenylimidazole,[3] 4-*tert*-butyl-1-methylimidazole,[4] 4-phenyl-1-methylimidazole,[5] 5-*tert*-butyl-1-methylimidazole,[6] 5-phenyl-1-methylimidazole,[7] 5-(4-methoxy)phenyl-1-methylimidazole,[7] 5-(4-trifluoromethyl)-phenyl-1-methylimidazole,[7] 1,4,5-trimethyl-imidazole,[8] 4-methyl-4*H*-1,2,4-triazole,[9] and 1-methyl-1*H*-1,2,4-triazole,[10] were prepared following a literature procedure.

General Procedure for the $Ir_4(CO)_{12}$-Catalyzed Coupling of Azoles with Isocyanate in the Presence of Hydrosilanes. A 10-mL reaction flask, equipped with a reflux condenser, was dried for 1 h in an oven at 150 ºC and then purged with N_2. After cooling to room temperature, $Ir_4(CO)_{12}$ (22.0 mg, 0.02 mmol), a hydrosilane (2 mmol), toluene (3 mL), an isocyanate (1 mmol), and an azole (1 mmol) were placed in the flask. The reaction mixture was refluxed in an oil-bath. After cooling to room temperature, the volatiles were removed in vacuo. The residue was passed through a silica-gel column to isolate the desired azole-2-carboxyamide. An analytically pure sample was obtained by GPC followed by bulb-to-bulb distillation.

***N*-Hexyl-1-methyl-1*H*-imidazole-2-carboxamide (1a)**



1a

Yield: 155 mg (74%); colorless oil.

R_f = 0.10 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 140 °C/8 mmHg.

IR (neat): 1664 cm^{-1}.

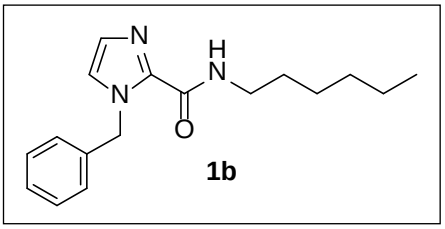
^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (br, 1H), 6.99 (s, 1H), 6.95 (s, 1H), 4.06 (s, 3H), 3.37 (q, *J* = 6.9 Hz, 2H), 1.59 (quint, *J* = 7.3 Hz, 2H), 1.28-1.47 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 139.1, 127.3, 125.3, 39.0, 35.6, 31.5, 29.6, 26.6, 22.5, 14.0.

MS (EI): *m*/*z* (%) = 209 (2, M^+), 138 (28), 110 (20), 109 (100), 100 (30), 96 (15), 82 (38), 81 (12), 54 (16).

Anal. Calcd for $C_{11}H_{19}N_3O$: C, 63.13; H, 9.15; N, 20.08. Found: C, 62.84; H, 9.04; N, 20.14.

1-Benzyl-*N*-hexyl-1*H*-imidazole-2-carboxamide (1b)



1b

Yield: 194 mg (68%); white solids, mp 81.0-81.5 °C.

R_f = 0.17 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 170 °C/0.9 mmHg.

IR (neat): 1664 cm^{-1}.

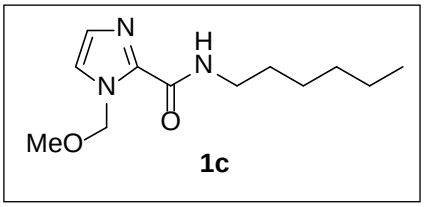
^1H NMR (400 MHz, $CDCl_3$): δ = 7.52 (br, 1H), 7.22-7.35 (m, 5H), 7.02 (s, 1H), 6.97 (s, 1H), 5.75 (s, 2H), 3.38 (q, *J* = 6.7 Hz, 2H), 1.60 (quint, *J* = 7.3 Hz, 2H), 1.28-1.41 (m, 6H), 0.88 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 138.7, 136.9, 128.7, 127.9, 127.8, 127.7, 124.1, 39.5, 31.5, 29.5, 26.6, 22.5, 14.0, one signal is obscured by overlap with other signals.

MS (EI): *m*/*z* (%) = 285 (11, M^+), 186 (19), 185 (39), 157 (51), 100 (23), 91 (100), 65 (15).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{23}N_3O$ (M^+): 285.1841; found: 285.1840.

***N*-Hexyl-1-methoxymethyl-1*H*-imidazole-2-carboxyamide (1c)**



1c

Yield: 139 mg (58%); colorless oil.

R_f = 0.10 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 160 °C/8 mmHg.

IR (neat): 1666 cm^{-1}.

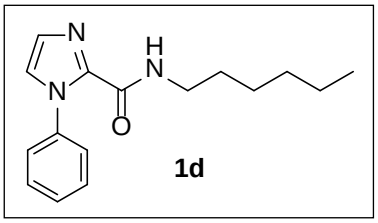
^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (br, 1H), 7.20 (s, 1H), 7.06 (s, 1H), 5.88 (s, 2H), 3.36-3.41 (m, 5H), 1.60 (quint, *J* = 7.2 Hz, 2H), 1.28-1.41 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 139.2, 128.0, 123.3, 77.9, 56.5, 39.0, 31.4, 29.4, 26.6, 22.5, 4.0.

MS (EI): *m*/*z* (%) = 239 (9, M^+), 196 (77), 194 (14), 168 (25), 140 (18), 139 (43), 138 (58), 126 (21), 124 (17), 112 (29), 109 (68), 102 (16), 100 (100), 98 (35), 96 (18), 95 (52), 94 (15), 83 (10), 82 (87), 81 (31), 74 (14), 69 (31), 68 (23), 56 (12), 55 (14), 54 (15), 53 (11).

Anal. Calcd for $C_{12}H_{21}N_3O_2$: C, 60.23; H, 8.84; N, 17.56. Found: C, 60.16; H, 8.78; N, 17.67.

***N*-Hexyl-1-phenyl-1*H*-imidazole-2-carboxyamide (1d)**



1d

Yield: 141 mg (52%); colorless oil.

R_f = 0.10 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 170 °C/1 mmHg.

IR (neat): 1672 cm^{-1}.

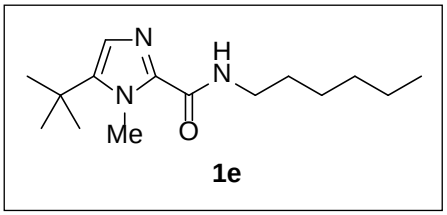
^1H NMR (400 MHz, $CDCl_3$): δ = 7.35-7.46 (m, 6H), 7.13 (d, *J* = 2.7 Hz, 2H), 3.31 (q, *J* = 6.9 Hz, 2H), 1.55 (quint, *J* = 7.3 Hz, 2H), 1.28-1.37 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.8, 139.4, 138.2, 128.5, 128.4, 127.8, 125.9, 125.6, 39.0, 31.3, 29.4, 26.5, 22.4, 13.9.

MS (EI): *m*/*z* (%) = 271 (6, M^+), 200 (30), 172 (22), 171 (100), 158 (19), 145 (12), 144 (53), 117 (37), 116 (38), 106 (15), 100 (45), 91 (14), 90 (15), 89 (16), 77 (36), 51 (15).

Anal. Calcd for $C_{16}H_{21}N_3O$: C, 70.82; H, 7.80; N, 15.49. Found: C, 70.53; H, 7.76; N, 15.27.

5-*tert*-Butyl-*N*-hexyl-1-methyl-1*H*-imidazole-2-carboxamide (1e)



1e

Yield: 119 mg (45%); colorless oil.

R_f = 0.10 in hexane/EtOAc = 4/1.

IR (neat): 1662 cm^{-1}.

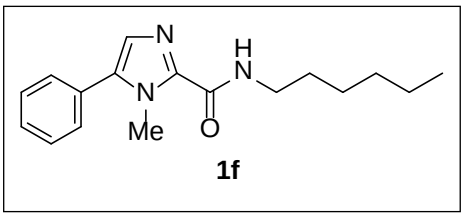
^1H NMR (400 MHz, $CDCl_3$): δ = 7.48 (br, 1H), 6.77 (s, 1H), 4.17 (s, 3H), 3.36 (q, *J* = 6.7 Hz, 2H), 1.58 (quint, *J* = 7.2 Hz, 2H), 1.28-1.43 (m, 15H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 144.5, 140.0, 123.9, 39.0, 34.3, 31.5, 31.1, 29.6, 29.4, 26.6, 22.5, 14.0.

MS (EI): *m*/*z* (%) = 265 (11, M^+), 250 (18), 222 (12), 194 (39), 166 (22), 165 (94), 152 (19), 149 (13), 139 (15), 138 (100), 123 (27), 122 (27), 100 (23), 95(10), 80 (12), 67 (12), 57 (17), 55 (13).

HRMS (EI): *m*/*z* calcd for $C_{15}H_{27}N_3O$ (M^+): 265.2154; found: 265.2151.

***N*-Hexyl-1-methyl-5-phenyl-1*H*-imidazole-2-carboxamide (1f)**



1f

Yield: 194 mg (68%); colorless oil.

R_f = 0.13 in hexane/EtOAc = 8/1.

IR (neat): 1666 cm^{-1}.

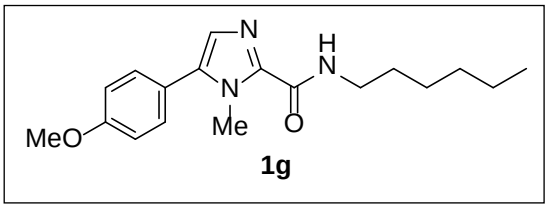
^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (br, 1H), 7.26-7.49 (m, 5H), 7.06 (s, 1H), 4.01 (s, 3H), 3.41 (q, *J* = 6.7 Hz, 2H), 1.62 (quint, *J* = 7.3 Hz, 2H), 1.29-1.41 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 139.7, 137.6, 129.0, 128.8, 128.6, 128.4, 126.5, 39.0, 33.6, 31.4, 29.5, 26.5, 22.4, 13.9.

MS (EI): *m*/*z* (%) = 285 (13, M^+), 242 (15), 214 (28), 186 (25), 185 (91), 172 (16), 159 (13), 158 (75), 157 (15), 117 (14), 116 (100), 103 (15), 102 (60), 100(33), 89 (19), 77 (15).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{23}N_3O$ (M^+): 285.1841; found: 285.1836.

***N*-Hexyl-5-(4-methoxyphenyl)-1-methyl-1*H*-imidazole-2-carboxamide (1g)**



1g

Yield: 221 mg (70%); pail yellow solids, mp 62.5-63.1 °C.

R_f = 0.09 in hexane/EtOAc = 5/1.

IR (neat): 1664 cm^{-1}.

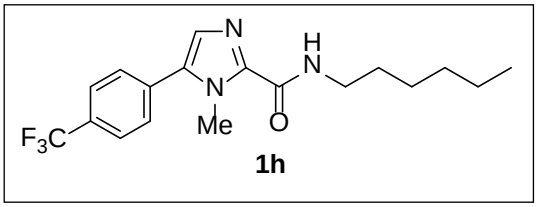
^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (br, 1H), 7.26-7.32 (m, 2H), 6.98-7.00 (m, 3H) , 3.97 (s, 3H), 3.86 (s, 3H), 3.40 (q, *J* = 6.7 Hz, 2H), 1.61 (quint, *J* = 7.3 Hz, 2H) , 1.32-1.39 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 159.4, 139.5, 137.6, 130.5, 126.3, 121.2, 114.2, 55.3, 39.0, 33.5, 31.5, 29.6, 26.6, 22.5, 14.0.

MS (EI): *m*/*z* (%) = 315 (29, M^+), 272 (12), 244 (25), 216 (27), 215 (100), 202 (19), 189 (14), 188 (85), 146 (58), 133 (11), 132 (84), 117 (15), 108 (14), 103 (11), 100 (21), 91 (11), 89 (14).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{25}N_3O_2$ (M^+): 315.1947; found: 315.1945.

***N*-Hexyl-1-methyl-5-4-(trifluoromethyl)phenyl-1*H*-imidazole-2-carboxamide (1h)**



1h

Yield: 194 mg (55%); white solids, mp 65.3-65.9 °C.

R_f = 0.14 in hexane/EtOAc = 5/1.

Bulb-to-bulb distillation (oven temp.): 160 °C/1 mmHg.

IR (neat): 1643 cm^{-1}.

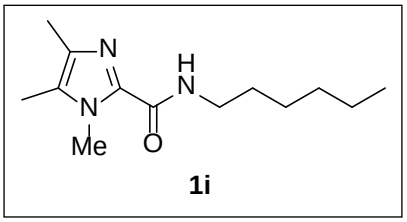
^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.2 Hz, 2H), 7.56 (br, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.12 (s, 1H), 4.04 (s, 3H), 3.42 (q, *J* = 6.9 Hz, 2H), 1.62 (quint, *J* = 7.3 Hz, 2H), 1.30-1.40 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 140.5, 136.3, 132.6, 130.5 (q, *J* = 32.6 Hz), 129.3, 127.9, 125.8 (d, *J* = 3.8 Hz), 123.8 (q, *J* = 271.1 Hz), 39.1, 33.8, 31.5, 29.6, 26.6, 22.6, 14.0.

MS (EI): *m*/*z* (%) = 353 (7, M^+), 282 (29), 254 (21), 253 (100), 240 (17), 226 (50), 225 (15), 184 (24), 100 (73).

Anal. Calcd for $C_{18}H_{22}F_3N_3O$: C, 61.18; H, 6.27; F, 16.13; N, 11.89. Found: C, 61.09; H, 6.20; F, 16.07; N, 11.73.

***N*-Hexyl-1,4,5-trimethyl-1*H*-imidazole-2-carboxamide (1i)**



1i

Yield: 95 mg (40%); colorless oil.

R_f = 0.10 in hexane/EtOAc = 4/1.

IR (neat): 1662 cm^{-1}.

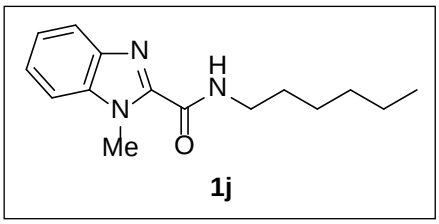
^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (br, 1H), 3.93 (s, 3H), 3.35 (q, *J* = 6.9 Hz, 2H), 2.17 (s, 3H), 2.15 (s, 3H), 1.58 (quint, *J* = 7.2 Hz, 2H), 1.25-1.38 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 136.5, 132.6, 127.9, 38.9, 32.2, 31.4, 29.5, 26.6, 22.5, 14.0, 12.3, 8.8.

MS (EI): *m*/*z* (%) = 237 (11, M^+), 166 (19), 138 (21), 137 (83), 124 (19), 111 (11), 110 (100), 109 (14), 56 (44), 55 (11).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{23}N_3O$ (M^+): 237.1841; found: 237.1845.

***N*-Hexyl-1-methyl-1*H*-benzo[*d*]imidazole-2-carboxamide (1j)**



1j

Yield: 174 mg (67%); colorless oil.

R_f = 0.18 in hexane/EtOAc = 8/1.

Bulb-to-bulb distillation (oven temp.): 127 °C/0.9 mmHg.

IR (neat): 1672 cm^{-1}.

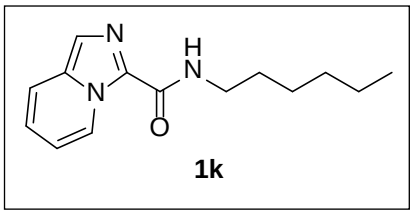
^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.2 Hz, 2H), 7.33-7.46 (m, 3H), 4.24 (s, 3H), 3.45 (q, *J* = 6.9 Hz, 2H), 1.65 (quint, *J* = 7.3 Hz, 2H), 1.33-1.43 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl^3$): δ = 159.6, 143.5, 140.8, 136.9, 124.4, 123.4, 120.4, 110.4, 39.3, 32.0, 31.4, 29.5, 26.6, 22.5, 14.0.

MS (EI): *m*/*z* (%) = 259 (18, M^+), 216 (10), 188 (41), 160 (22), 159 (88), 146 (20), 133 (18), 132 (100), 131 (38), 104 (29), 100 (42), 90 (11), 77 (33).

HRMS (EI): *m*/*z* calcd for $C_{15}H_{21}N_3O$ (M^+): 259.1685; found: 259.1676.

***N*-Hexylimidazo[1,5-*a*]pyridine-3-carboxamide (1k)**



1k

Yield: 169 mg (69%); colorless oil.

R_f = 0.13 in hexane/EtOAc = 8/1.

Bulb-to-bulb distillation (oven temp.): 155 °C/1.5 mmHg.

IR (neat): 1652 cm^{-1}.

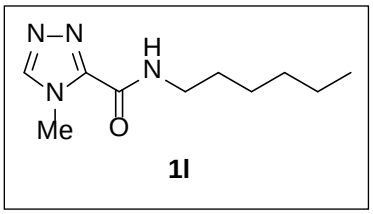
^1H NMR (400 MHz, $CDCl_3$): δ = 9.48 (d, *J* = 7.3 Hz, 1H), 7.55 (dd, *J* = 8.9, 1.1 Hz, 1H), 7.45 (s, 1H), 7.37 (br, 1H), 6.96 (s, 1H), 6.81 (t, *J* = 6.9 Hz, 1H), 3.47 (q, *J* = 6.7 Hz, 2H), 1.64 (quint, *J* = 7.4 Hz, 2H), 1.30-1.44 (m, 6H), 0.89 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 133.4, 129.8, 125.5, 121.3, 120.1, 117.8, 114.4, 39.0, 31.5, 29.7, 26.6, 22.5, 14.0.

MS (EI): *m*/*z* (%) = 245 (23, M^+), 174 (14), 146 (14), 145 (73), 132 (10), 119 (16), 118 (100), 117 (39), 100 (37), 91 (18), 90 (28), 78 (12), 64 (12), 63 (14).

HRMS (EI): *m*/*z* calcd for $C_{14}H_{19}N_3O$ (M^+): 245.1528; found: 245.1527.

***N*-Hexyl-1-methyl-1*H*-1,2,4-triazole-5-carboxamide (1l)**



1l

Yield: 147 mg (70%); colorless oil.

R_f = 0.07 in hexane/EtOAc = 1/1.

Bulb-to-bulb distillation (oven temp.): 200 °C/8 mmHg.

IR (neat): 1680 cm^{-1}.

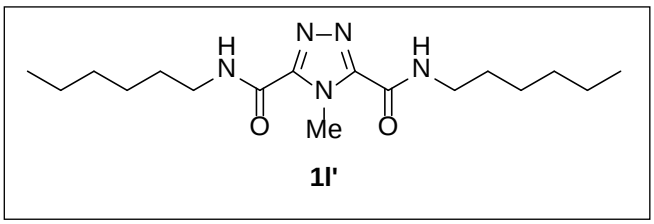
^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (s, 1H), 7.50 (br, 1H), 4.04 (s, 3H), 3.42 (q, *J* = 6.9 Hz, 2H), 1.61 (quint, *J* = 7.2 Hz, 2H), 1.25-1.38 (m, 6H), 0.89 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 146.7, 39.2, 33.3, 31.3, 29.3, 26.5, 22.5, 14.0, one signal is obscured by overlap with other signals.

MS (EI): *m*/*z* (%) = 210 (1, M^+), 139 (73), 111 (16), 110 (100), 100 (89), 97 (16), 84 (14), 83 (28), 56 (23), 55 (15).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{18}N_4O$ (M^+): 210.1481; found: 209.1480.

***N*^{3},*N*^{5}-Dihexyl-4-methyl-4*H*-1,2,4-triazole-3,5-dicarboxamide (1l')**



1l'

This reaction was carried out using 4-methyl-4*H*-1,2,4-triazole (83.1 mg, 1mmol), hexyl isocyanate (318.0 mg, 2.5 mmol), $Ir_4(CO)_{12}$ (27.6 mg, 0.025 mmol), and $HSiEt_2Me$ (511.3 mg, 5 mmol) in toluene (3 mL) at 110 ˚C for 6 h. The product was isolated by preparative TLC (R_f = 0.61 in hexane/AcOEt = 1/1) in 75% yield (253 mg). An analytically pure sample was obtained by GPC in 48% yield (163 mg).

White solids, mp 105.5-106.0 °C.

IR (neat): 1672 cm^{-1}.

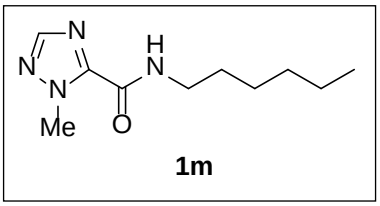
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (bs, 2H), 4.39 (s, 3H), 3.43 (q, *J* = 6.8 Hz, 4H), 1.62 (quint, *J* = 7.1 Hz, 4H), 1.26-1.42 (m, 12H), 0.89 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 148.6, 39.2, 33.7, 31.2, 29.1, 26.3, 22.3, 13.8.

MS (EI): *m*/*z* (%) = 337 (1, M^+), 266 (33), 237 (31), 110 (12), 100 (100), 83 (11).

HRMS (DART): *m*/*z* calcd for $C_{17}H_{32}N_5O_2$ (M^+): 338.2551; found: 338.2549.

***N*-Hexyl-4-methyl-4*H*-1,2,4-triazole-3-carboxamide (1m)**



1m

Yield: 175 mg (83%); colorless oil.

R_f = 0.10 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 160 °C/8 mmHg.

IR (neat): 1660 cm^{-1}.

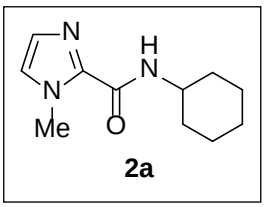
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1H), 7.35 (br, 1H), 4.28 (s, 3H), 3.41 (q, *J* = 6.7 Hz, 2H), 1.61 (quint, *J* = 7.2 Hz, 2H), 1.29-1.39 (m, 6H), 0.89 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 149.2, 146.2, 39.3, 38.2, 31.4, 29.3, 26.5, 22.5, 14.0.

MS (EI): *m*/*z* (%) = 210 (1, M^+), 139 (67), 111 (15), 110 (77), 100 (100), 97 (17), 84 (30), 83 (41), 56 (24), 55 (14).

Anal. Calcd for $C_{10}H_{18}N_4O$: C, 57.12; H, 8.63; N, 26.64. Found: C, 57.07; H, 8.46; N, 26.55.

***N*-Cyclohexyl-1-methyl-1*H*-imidazole-2-carboxamide (2a)**



2a

Yield: 172 mg (83%); white solids, mp 73.4-74.0 °C.

R_f = 0.10 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 160 °C/8 mmHg.

IR (neat): 1668 cm^{-1}.

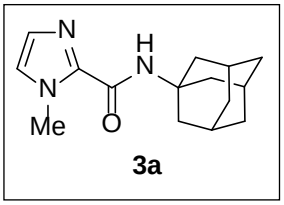
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (br, 1H), 6.99 (s, 1H), 6.95 (s, 1H), 4.06 (s, 3H), 3.83-3.90 (m, 1H), 1.98 (c, 2H), 1.76 (c, 2H), 1.64 (c, 1H), 1.18-1.45 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 139.0, 127.1, 125.1, 47.8, 35.4, 32.9, 25.3, 24.7.

MS (EI): *m*/*z* (%) = 207 (4, M^+), 179 (13), 164 (26), 150 (43), 110 (15), 109 (98), 98 (100), 97 (12), 96 (18), 83 (12), 82 (56), 81 (28), 56 (13), 55 (15), 54 (30).

Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.46; H, 8.01; N, 20.29.

***N*-(1-Adamantyl)-1-methyl-1*H*-imidazole-2-carboxamide (3a)**



3a

Yield: 207 mg (80%); white solids, mp 115.0-115.5 °C.

R_f = 0.17 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 170 °C/8 mmHg.

IR (neat): 1673 cm^{-1}.

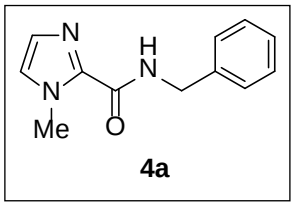
^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (br, 1H), 6.96 (s, 1H), 6.92 (s, 1H) , 4.03 (s, 3H), 2.11 (br, 9H), 1.67-1.74 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 139.0, 127.1, 125.1, 51.8, 41.5, 36.2, 35.7, 29.3.

MS (EI): *m*/*z* (%) = 259 (3, M^+), 231 (57), 216 (19), 215 (10), 214 (53), 202 (18), 150 (12), 136 (11), 120 (12), 109 (100), 96 (38), 93 (10), 91 (14), 83 (36), 82 (30), 81 (24), 79 (14), 77 (12), 55 (11), 54 (21).

Anal. Calcd for $C_{15}H_{21}N_3O$: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.56; H, 8.08; N, 16.16.

***N*-Benzyl-1-methyl-1*H*-imidazole-2-carboxamide (4a)**



4a

Yield: 207 mg (66%); white solids, mp 102.0-102.4 °C.

R_f = 0.10 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 170 °C/8 mmHg.

IR (neat): 1662 cm^{-1}.

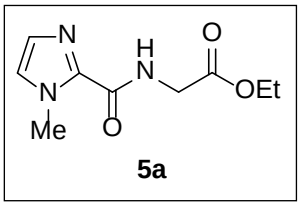
^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (br, 1H), 7.26-7.34 (m, 5H), 6.99 (s, 1H), 6.96 (s, 1H), 4.57 (d, *J* = 5.9 Hz, 2H), 4.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 138.9, 137.9, 128.6, 127.7, 127.5, 127.3, 125.4, 42.9, 35.6.

MS (EI): *m*/*z* (%) = 215 (2, M^+), 172 (36), 109 (24), 106 (100), 91 (17), 82 (77), 81 (29), 79 (11), 65 (11), 54 (15).

Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.88; H, 6.05; N, 19.52.

Ethyl 2-(1-methyl-1*H*-imidazole-2-carboxamido)acetate (5a)



5a

Yield: 139 mg (66%); white solids, mp 92.0-93.0 °C.

R_f = 0.10 in hexane/EtOAc = 4/1.

Bulb-to-bulb distillation (oven temp.): 180 °C/8 mmHg.

IR (neat): 1749, 1670 cm^{-1}.

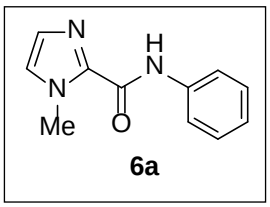
^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (br, 1H), 7.03 (s, 1H), 6.98 (s, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.15 (d, *J* = 5.9 Hz, 2H), 4.05 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.4, 159.3, 138.4, 127.7, 125.5, 61.3, 40.8, 35.4, 14.1.

MS (EI): *m*/*z* (%) = 259 (3, M^+), 231 (57), 216 (19), 215 (10), 214 (53), 202 (18), 150 (12), 136 (11), 120 (12), 109 (100), 96 (38), 93 (10), 91 (14), 83 (36), 82 (30), 81 (24), 79 (14), 77 (12), 55 (11), 54 (21).

Anal. Calcd for $C_9H_{13}N_3O_3$: C, 51.18; H, 6.20; N, 19.89. Found: C, 51.17; H, 6.01; N, 19.82.

1-Methyl-*N*-phenyl-1*H*-imidazole-2-carboxamide (6a)



6a

Yield: 48 mg (24%); colorless oil.

R_f = 0.54 in hexane/EtOAc = 5/1.

IR (neat): 1680 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.24 (br, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 7.02 (s, 1H), 4.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 138.8, 137.5, 128.9, 127.6, 126.1, 124.1, 119. 5, 47.8, 35.8.

MS (EI): *m*/*z* (%) = 201 (60, M^+), 200 (51), 109 (35), 106 (11), 83 (14), 82 (100), 81 (100), 77 (12), 65 (14), 56 (26), 55 (21), 54 (39), 51 (12).

HRMS (EI): *m*/*z* calcd for $C_{11}H_{11}N_3O$ (M^+): 201.0902; found: 201.0894.

References.

(1) Owen, C. P.; Dhanani, S.; Patel, C. H.; Shahid, I.; Ahmed, S. *Bioorg. Med. Chem. Lett*. **2006**, *16*, 4011.

(2) Lan, J. -Bo.; Yu, X. -Q.; You, J. -S.; Xie, R. -G. *Chem. Commun*. **2004**, *2*, 188.

(3) Manoharan, T. S.; Brown, R. S. *J. Org. Chem*. **1989**, *54*, 1439.

(4) Hilf, C.; Bosold, F.; Harms, K.; Lohrenz, J. C. W.; Marsch, M.; Schimeczek, M.; Boche, G. *Chem. Ber*. **1997**, *130*, 1201.

(5) Poon, F. S.; St. Jean, D.; Harrington, P. E.; Henley, C. III,; Davis, J.; Morony, S.; Lott, F. D.; Reagan, J. D.; Ying-Lin, L. J.; Yang, Y.; Fotsch, C. *J. Med. Chem*. **2009**, *52*, 6535.

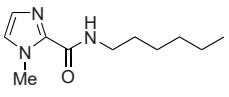
(6) van Leusen, A. M.; Wildeman, J.; Oldenziel, O. H. *J. Org. Chem*. **1977**, *42*, 1153.

(7) Bellina, F.; Cauteruccio, S.; Di Fiore, A.; Rossi, R. *Eur. J. Org. Chem*. **2008**, *32*, 5436.

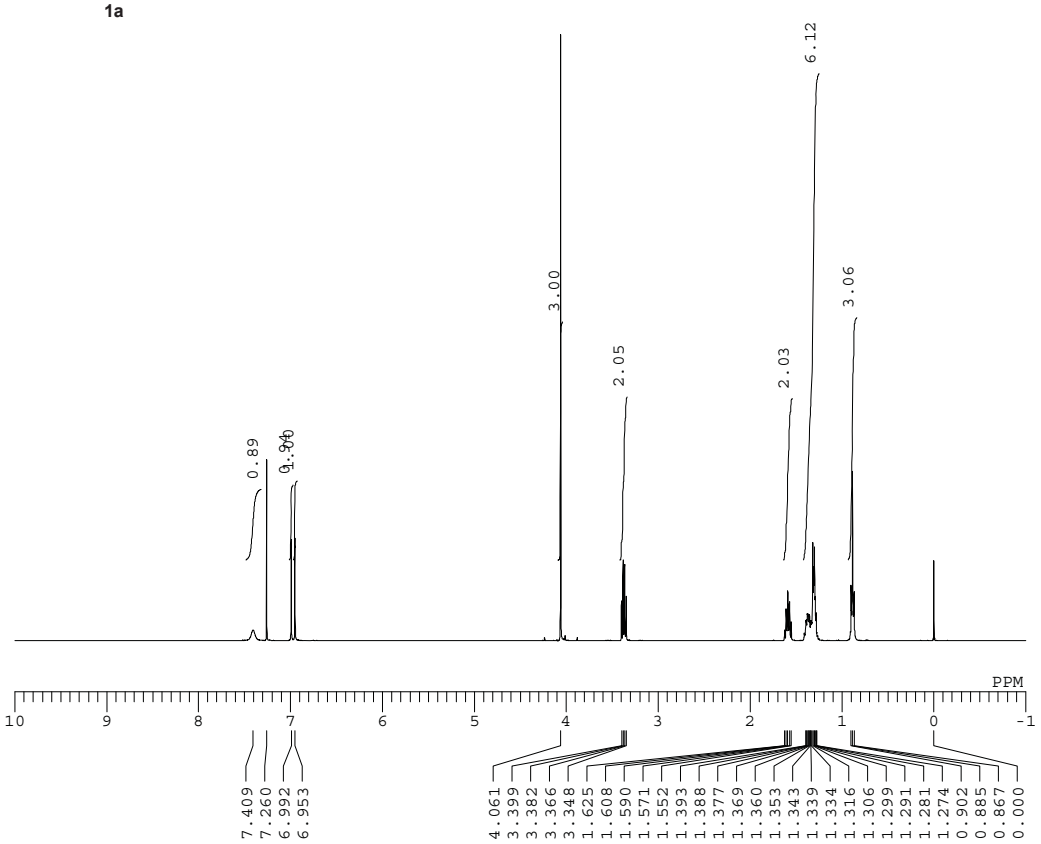
(8) E. I. du Pont de Nemours and Company **Patent:**US6177575 B1, **2001**.

(9) Bulger, P. G.; Cottrell, I. F.; Cowden, C. J.; Davies, A. J.; Dolling, U.-H. *Tetrahedron Lett.* **2000**, *41*, 1297.

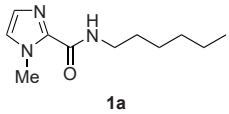
(10) Olofson, R. A.; Kendall, R. V.; *J. Org. Chem*. **1975**, *35*, 2246.



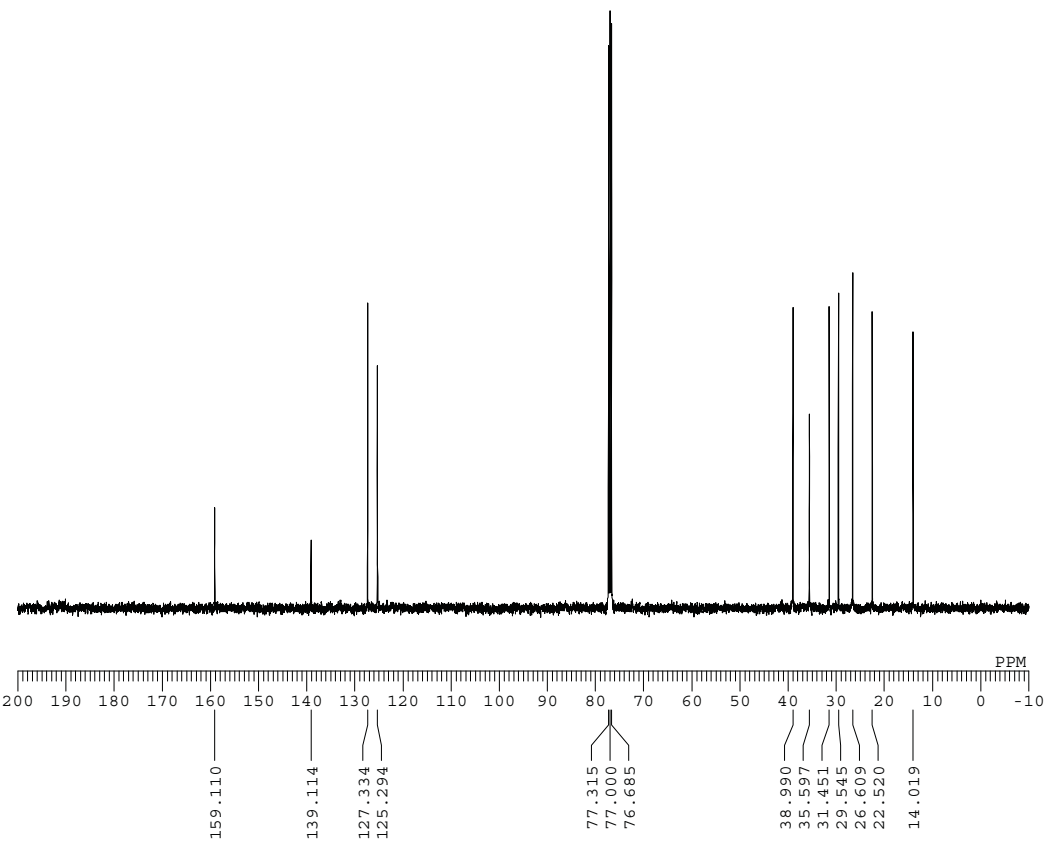
1a



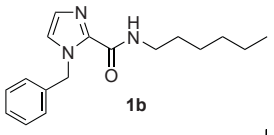

```
DFILE  MS084-a-1.jdf
COMNT  MS084
DATIM  2010-12-01 23:56:51
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           16.3 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             44
```



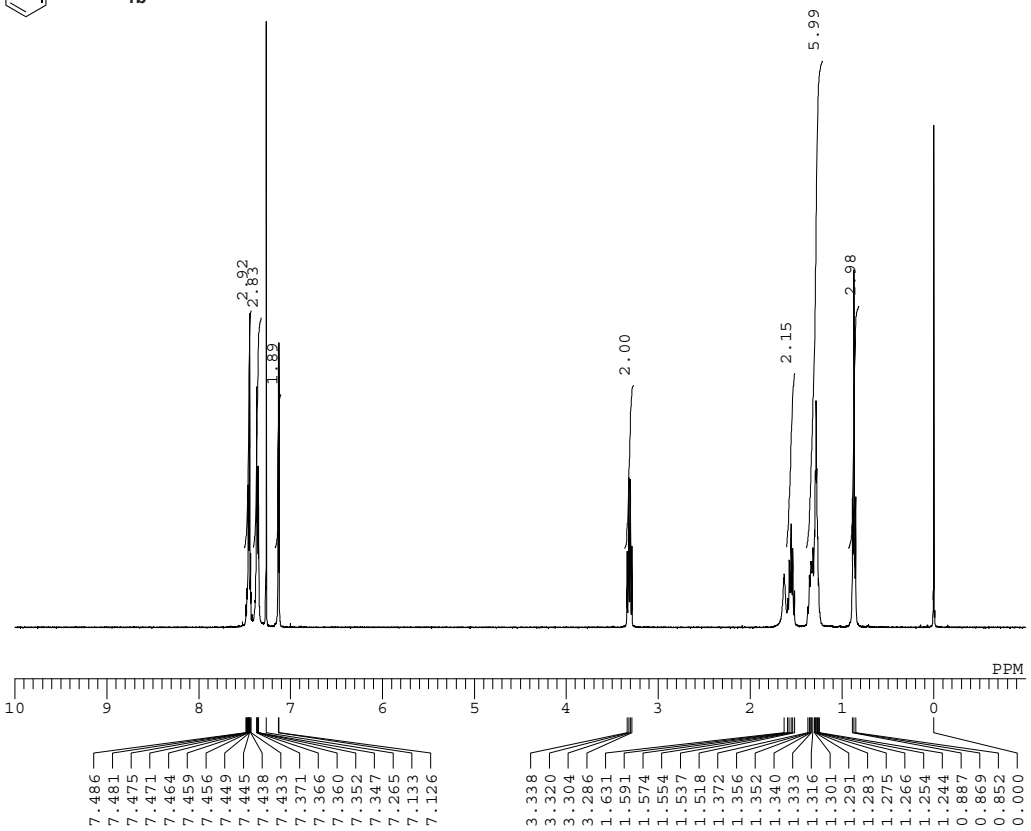
1a



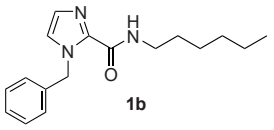

```
DFILE  1a.als
COMNT
DATIM  2010-12-02 00:15:40
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.17 usec
IRNUC  1H
CTEMP           16.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



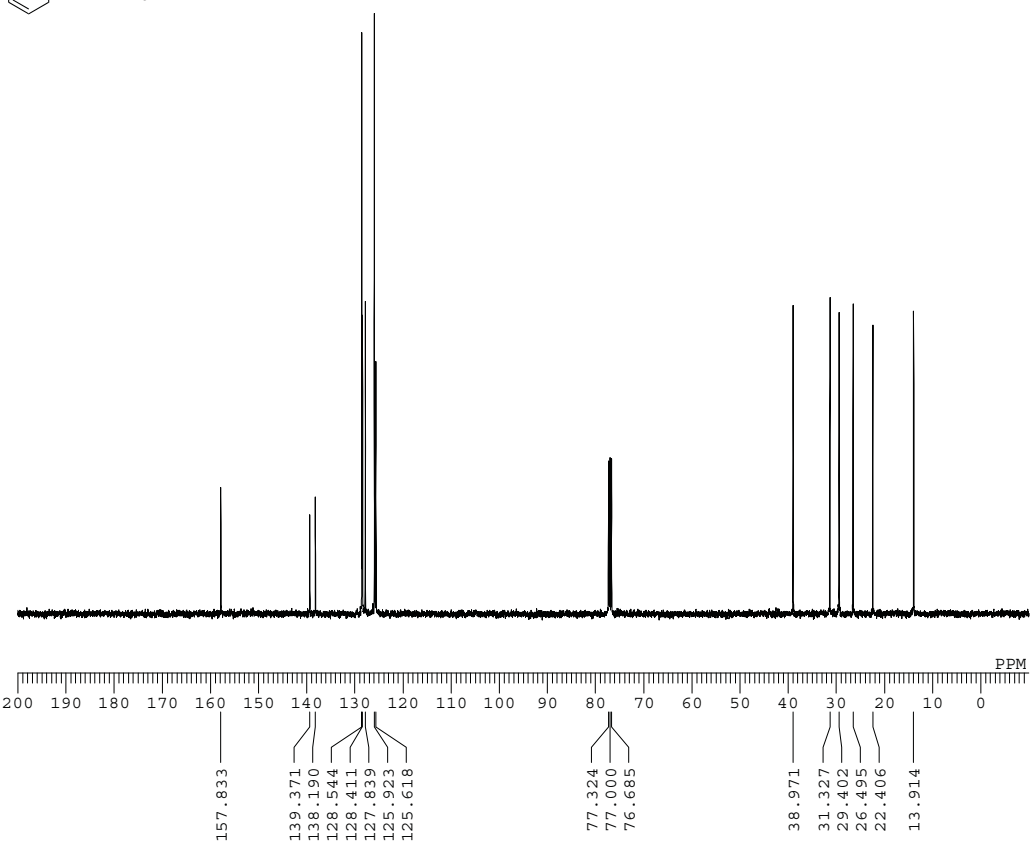
1b



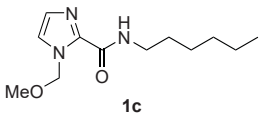

```
DFILE  N-phenyl imidazole product.jdf
COMNT  MS220 reaction mixture
DATIM  2011-02-25 18:12:31
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16384
FREQU       7503.00 Hz
SCANS              8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.00 usec
IRNUC  1H
CTEMP           17.1 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             38
```



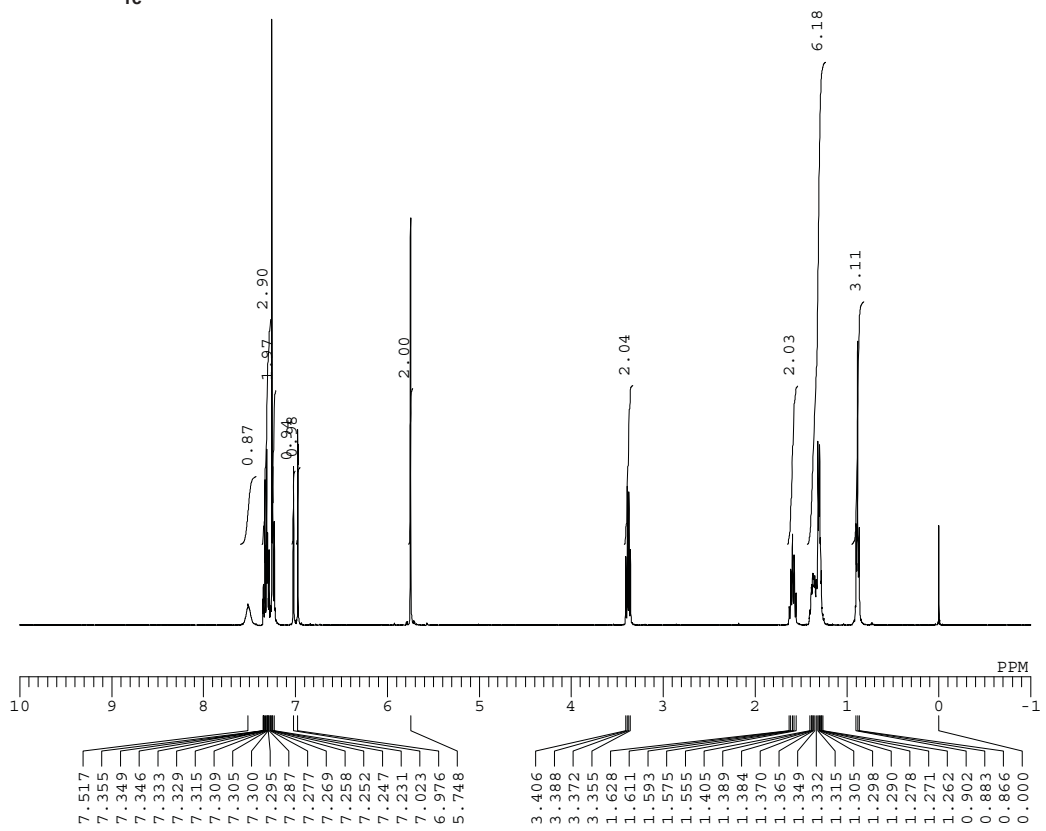
1b



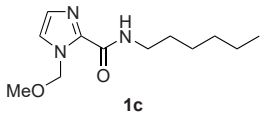

```
DFILE  1b.als
COMNT  N-phenyl imidazole product
DATIM  2011-02-25 22:03:06
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           101
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             4.00 usec
IRNUC  1H
CTEMP           17.3 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



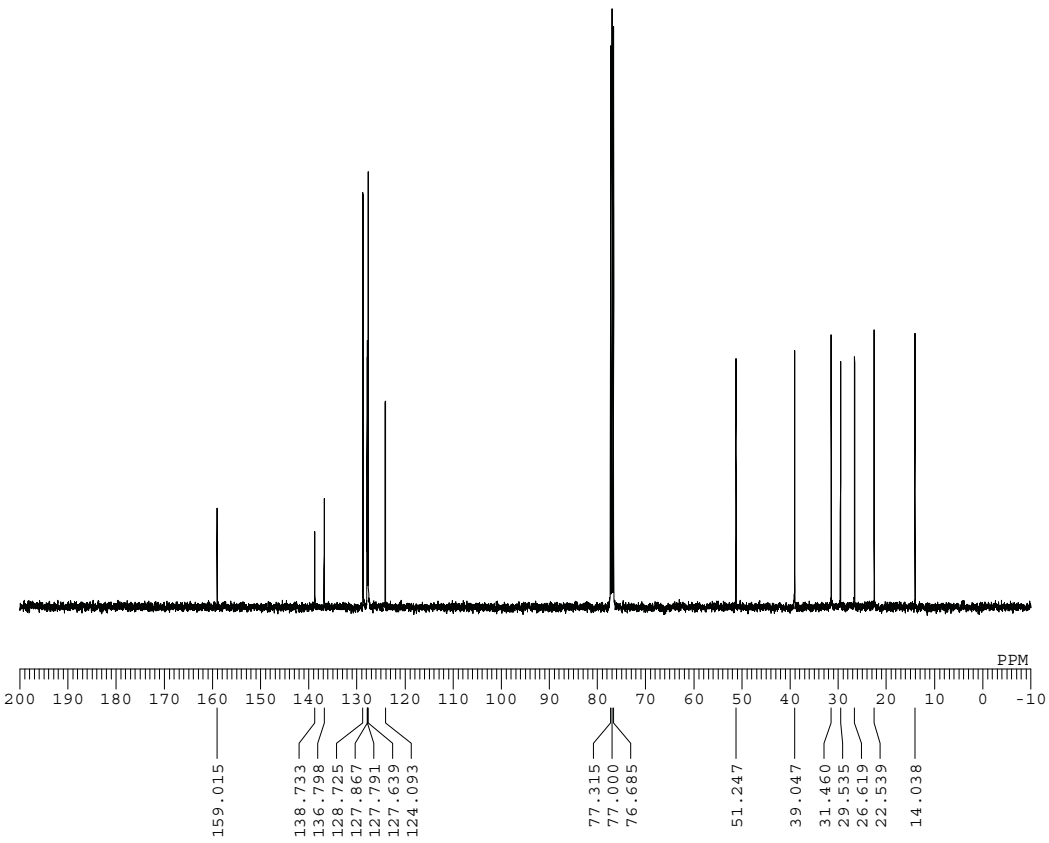
1c



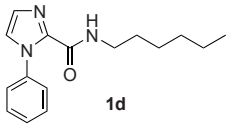
DFILE MS144-1.jdf
COMNT MS144 1H NMR
DATIM 2010-12-09 16:27:48
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.15 usec
IRNUC 1H
CTEMP 15.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 46



1c

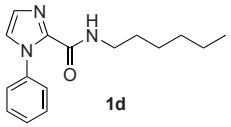


DFILE 1c.als
COMNT MS144 13C NMR
DATIM 2010-12-09 16:41:57
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 15.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

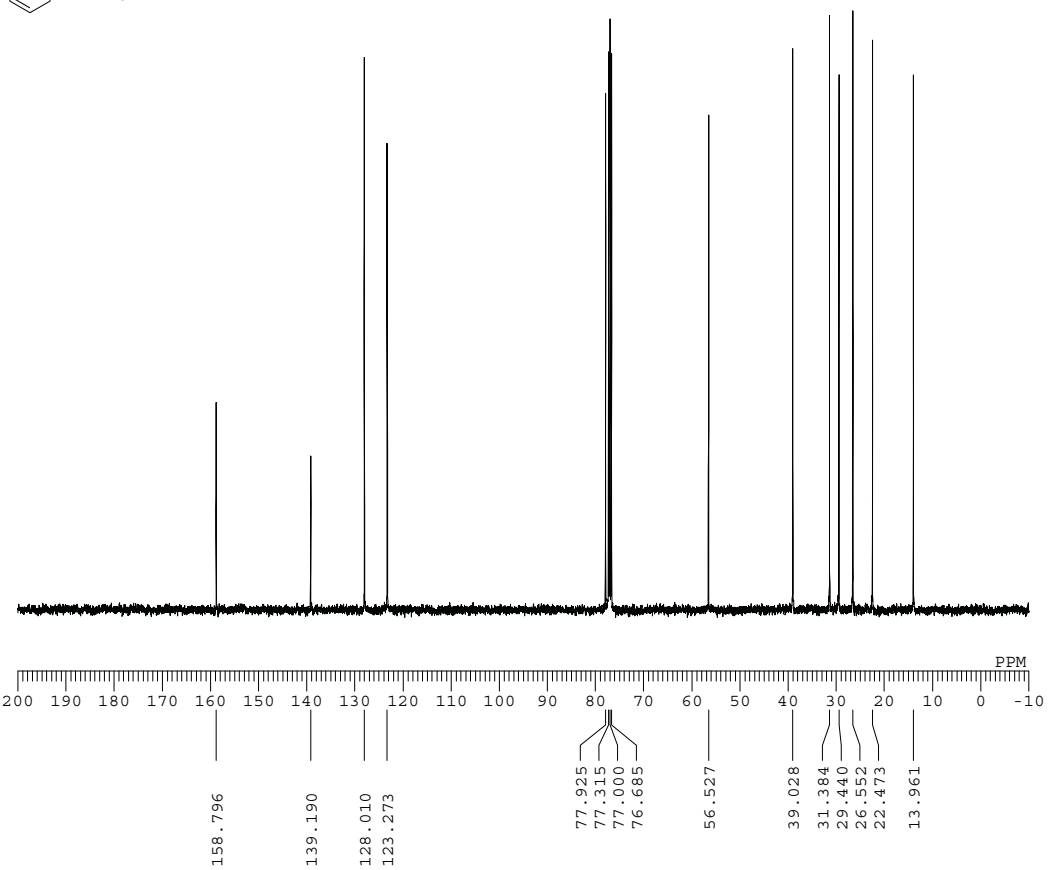


1d

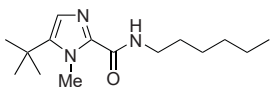
DFILE MS146-1.jdf
COMNT MS146
DATIM 2010-12-03 20:32:12
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.15 usec
IRNUC 1H
CTEMP 16.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44



1d

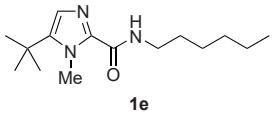


DFILE 1d.als
COMNT MS146
DATIM 2010-12-03 22:35:28
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 203
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 16.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

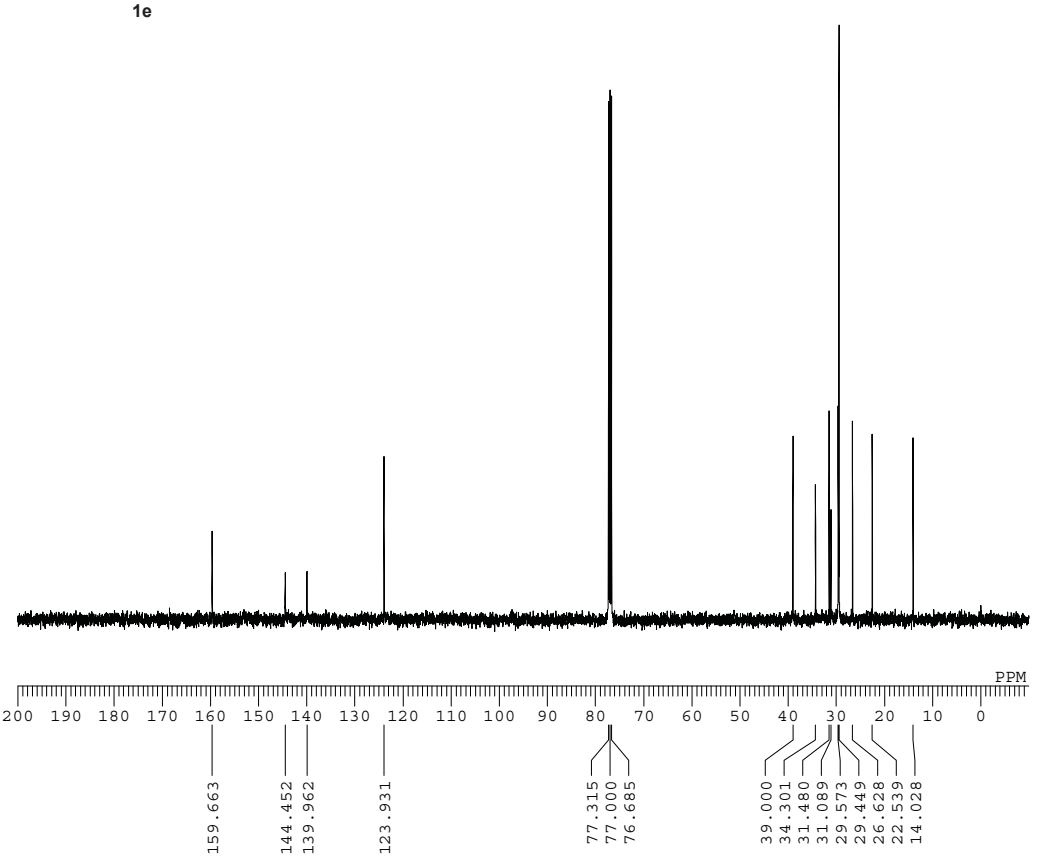


1e

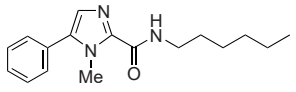

```
DFILE  MS184-1.jdf
COMNT  MS184 1H NMR
DATIM  2010-12-11 19:11:34
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           16.8 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             44
```



1e

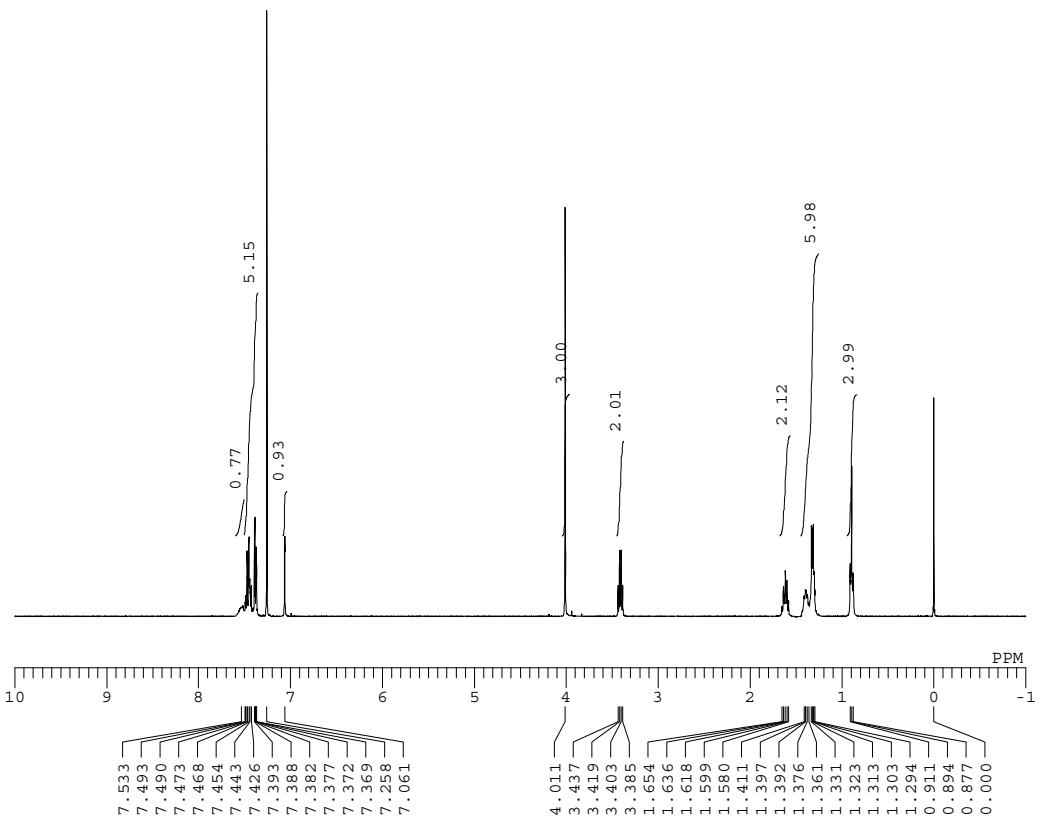



```
DFILE  1e.als
COMNT  MS184
DATIM  2011-04-22 14:25:59
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           158
ACQTM         0.0000 sec
PD            2.0000 sec
PW1             3.07 usec
IRNUC  1H
CTEMP           17.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



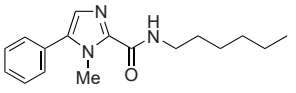
1f

```
DFILE  MS156-2-1.jdf
COMNT  MS156
DATIM  2011-02-08 20:57:52
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           16.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             40
```



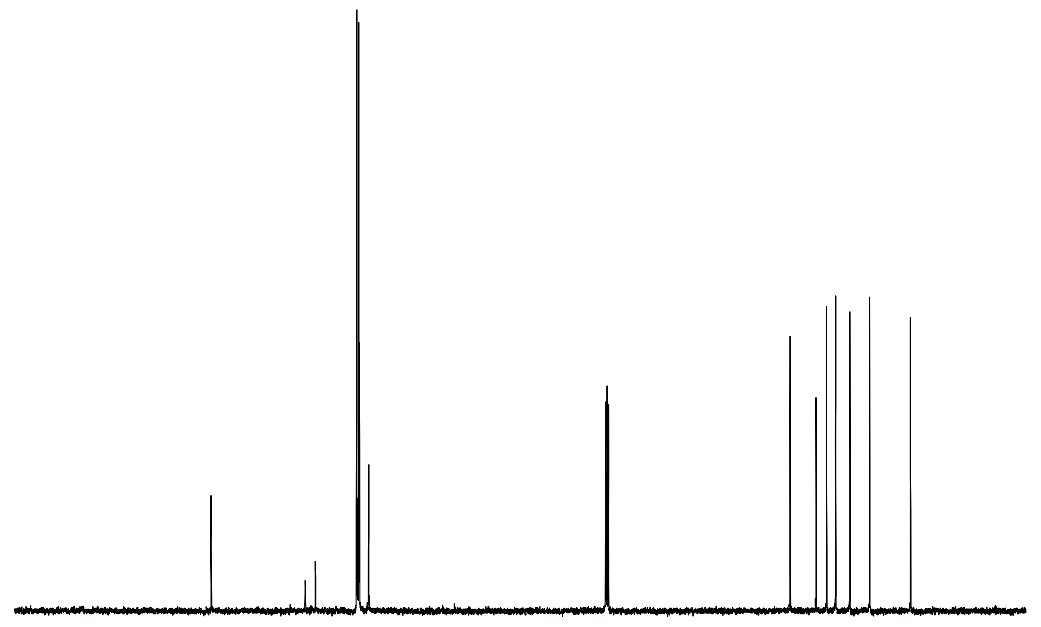
7.533 7.493 7.490 7.473 7.468 7.454 7.443 7.426 7.393 7.388 7.382 7.377 7.372 7.369 7.258 7.061

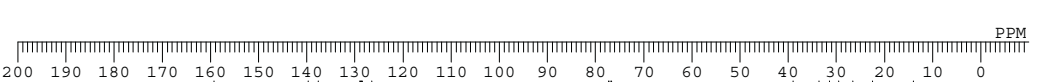
4.011 3.437 3.419 3.403 3.385 1.654 1.636 1.618 1.599 1.580 1.411 1.397 1.392 1.376 1.361 1.331 1.323 1.313 1.303 1.294 0.911 0.894 0.877 0.000



1f

```
DFILE  MS156-3-1.jdf
COMNT  MS156 13C NMR
DATIM  2010-12-11 00:39:13
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS            65
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.17 usec
IRNUC  1H
CTEMP           15.8 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



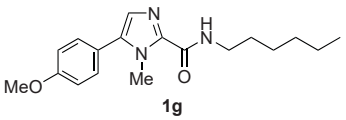


159.215

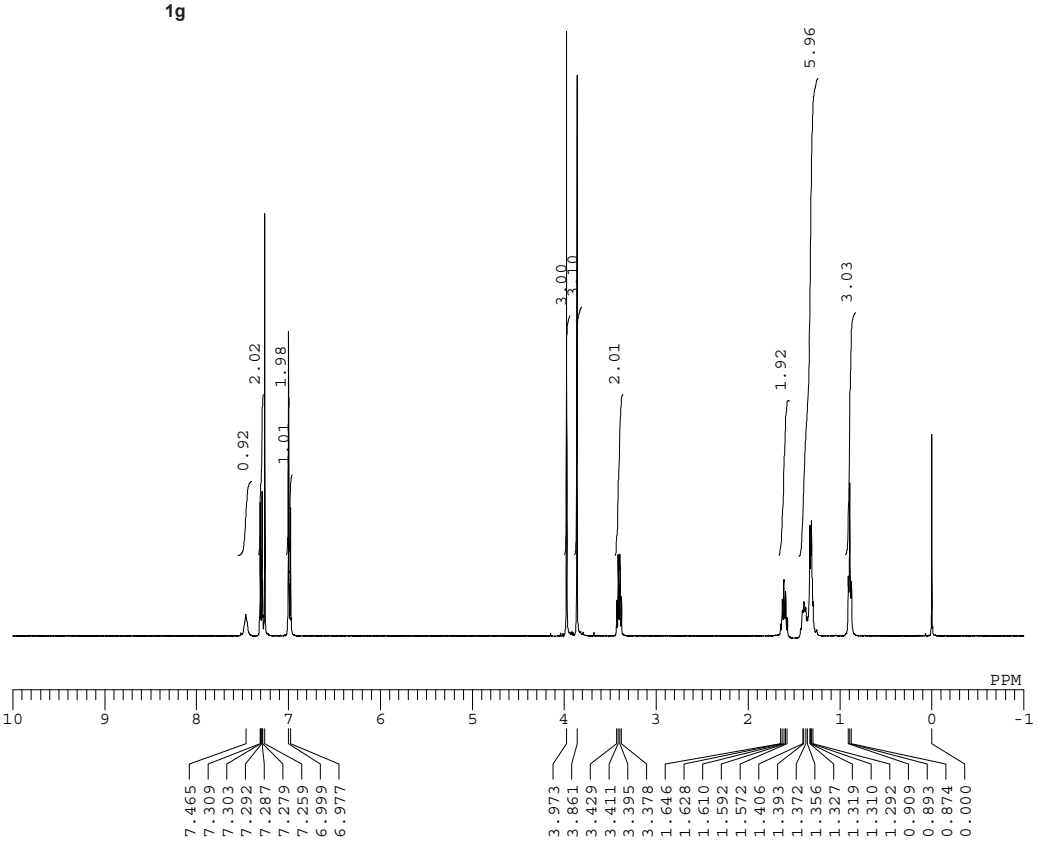
139.696 137.561 129.011 128.792 128.592 128.420 126.495

77.315 77.000 76.685

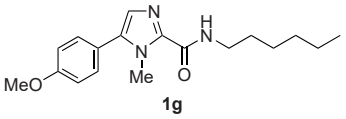
38.952 33.567 31.365 29.478 26.514 22.425 13.923



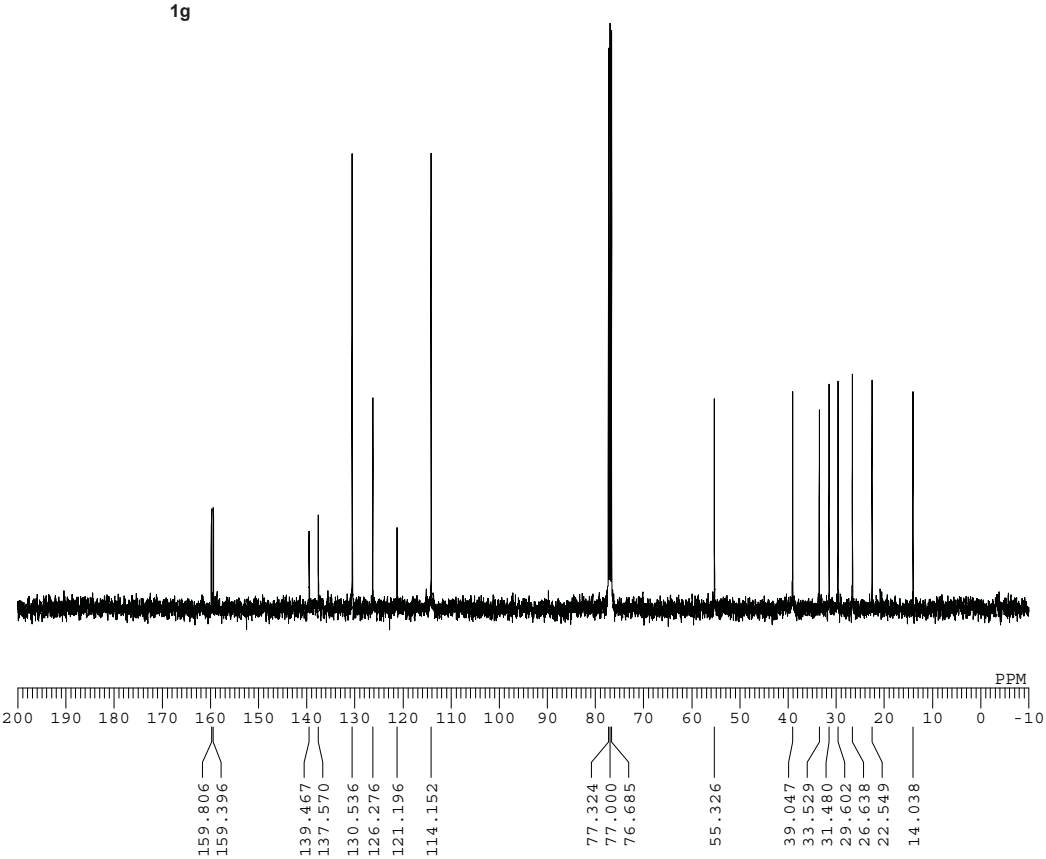
1g



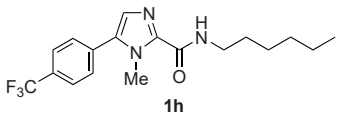

```
DFILE  MS166-1.jdf
COMNT  MS166
DATIM  2011-02-09 00:22:54
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           16.2 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             40
```



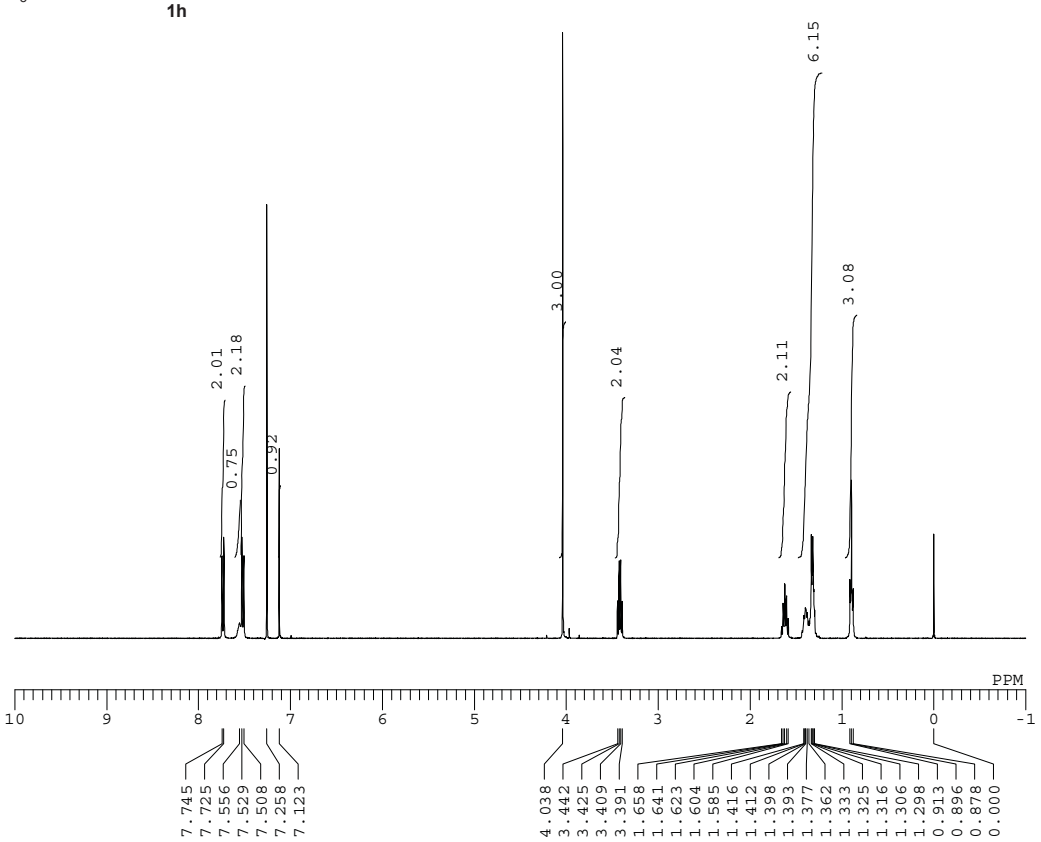
1g



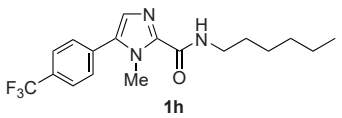

```
DFILE  MS166-2-1.jdf
COMNT  MS166
DATIM  2011-03-02 11:29:28
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           108
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             4.00 usec
IRNUC  1H
CTEMP           17.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



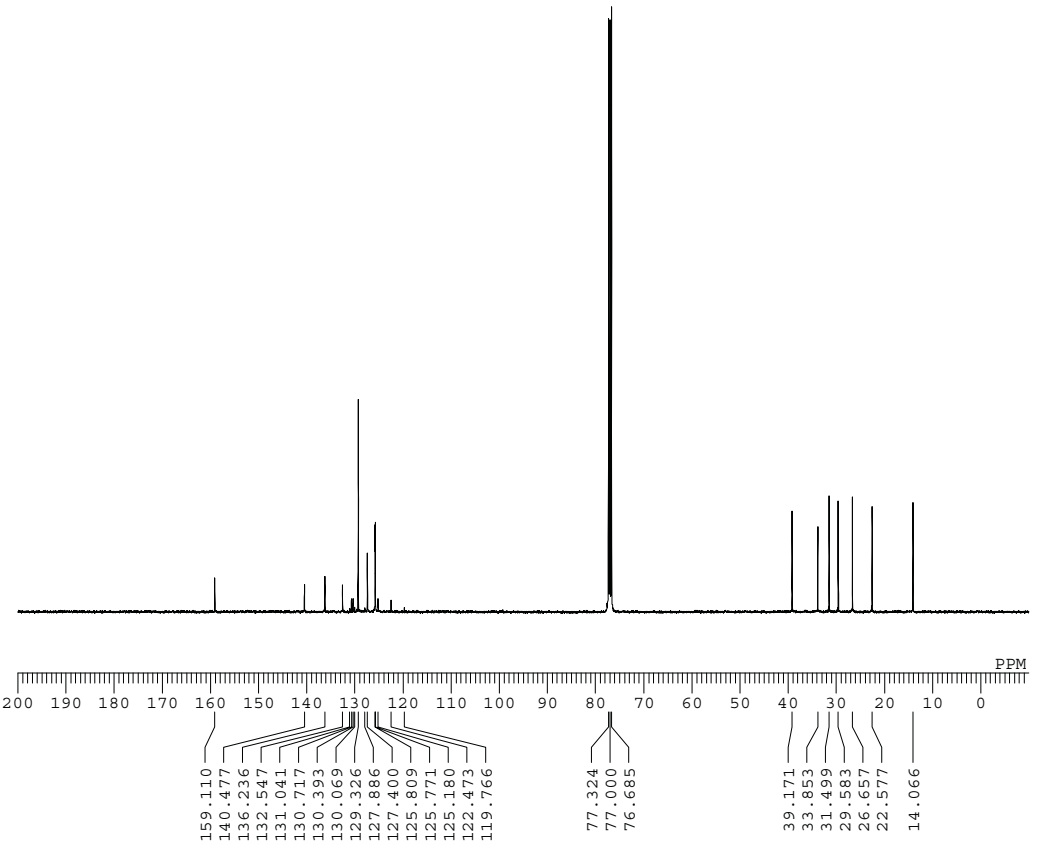
1h



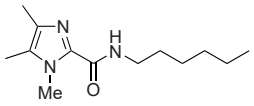

```
DFILE  MS167.jdf
COMNT  MS177
DATIM  2010-11-26 13:28:40
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM        2.1837 sec
PD           5.0000 sec
PW1            5.15 usec
IRNUC  1H
CTEMP          16.3 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            50
```



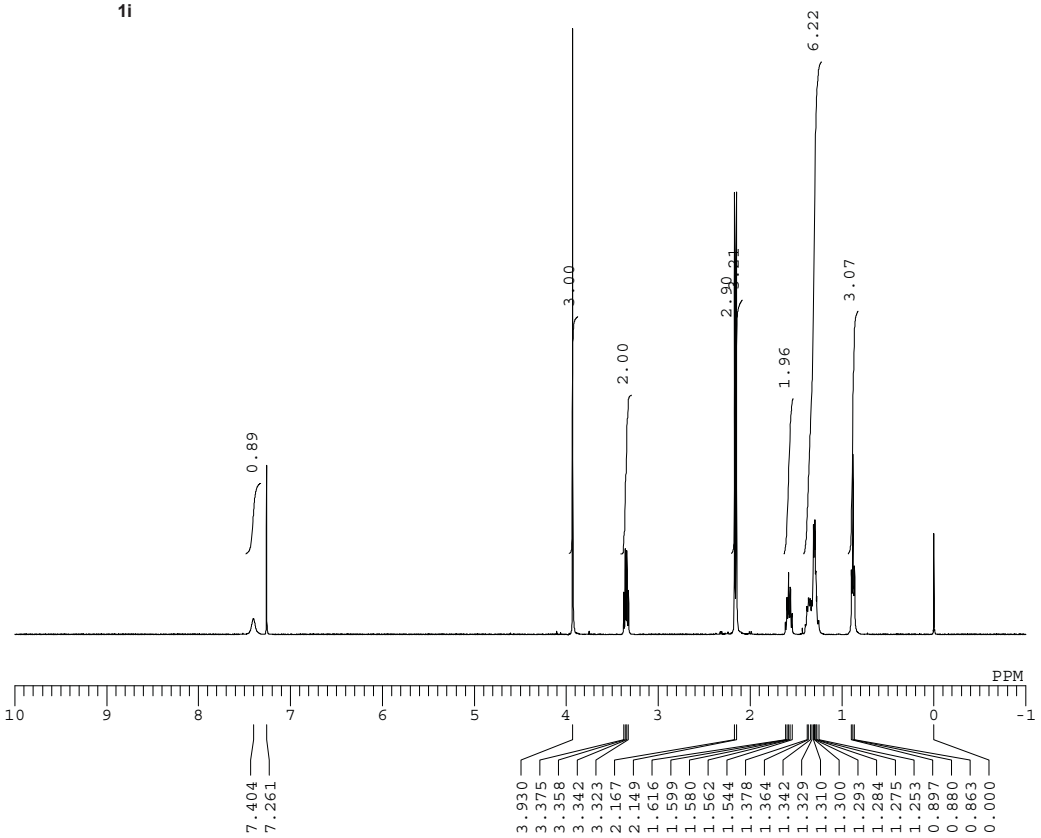
1h



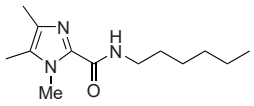

```
DFILE  1h.als
COMNT  MS159
DATIM  2011-02-09 00:31:36
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS          9000
ACQTM        1.0433 sec
PD           2.0000 sec
PW1            4.00 usec
IRNUC  1H
CTEMP          17.2 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            60
```



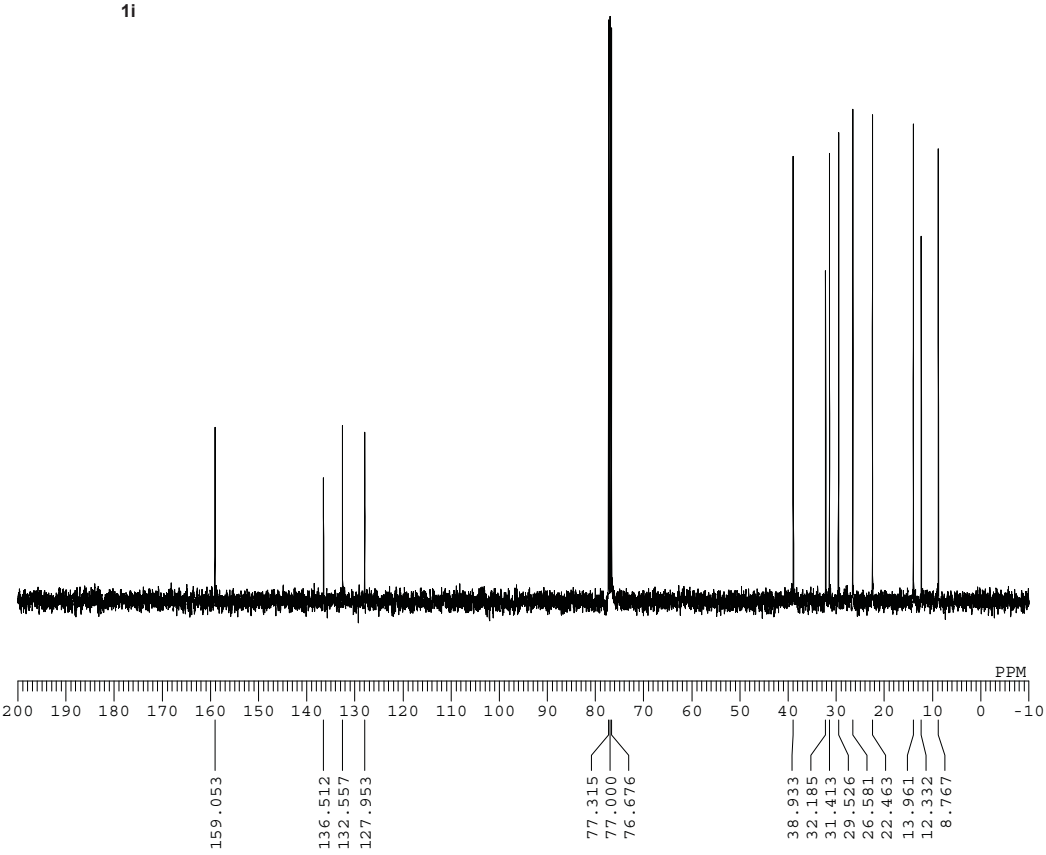
1i



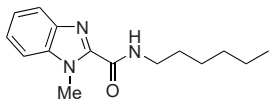

```
DFILE  MS248 GPC2-2-1-1.jdf
COMNT  MS248 GPC2-2
DATIM  2011-06-01 20:39:34
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS              8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.00 usec
IRNUC  1H
CTEMP           18.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             40
```



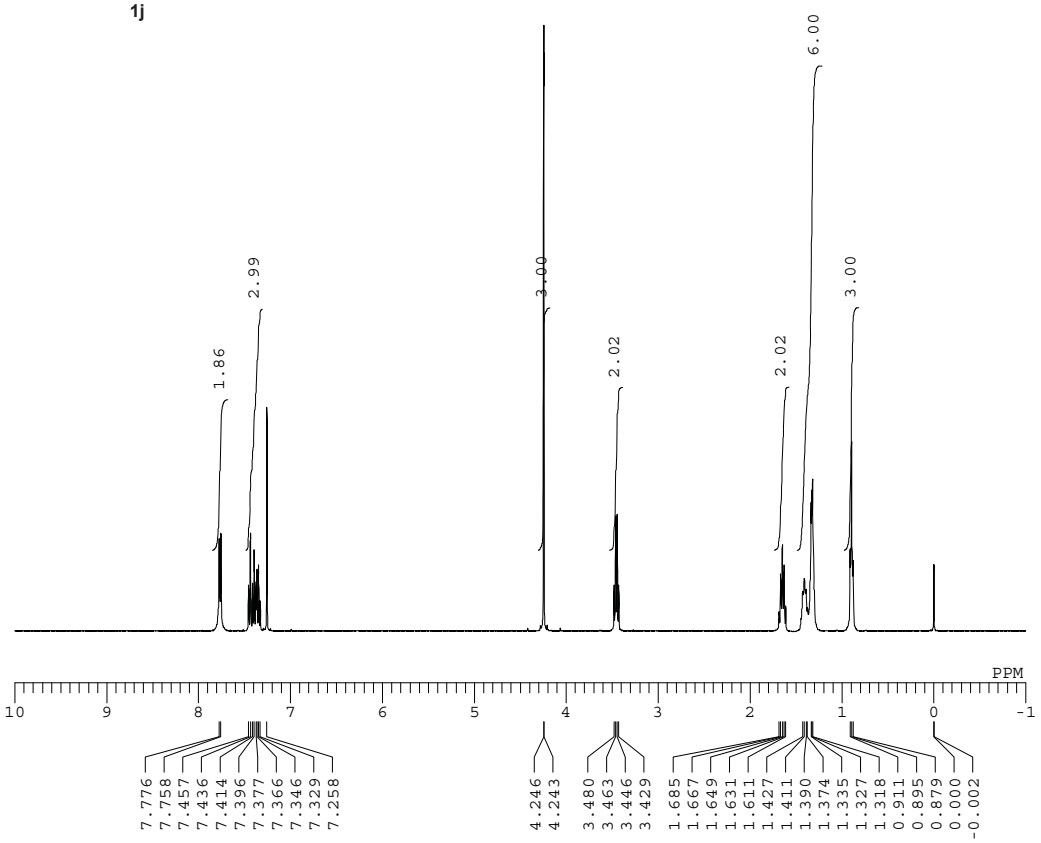
1i



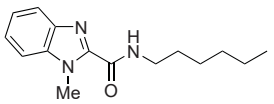

```
DFILE  trimethylimidazole product_cop
COMNT  trimethylimidazole product
DATIM  2011-04-22 13:27:07
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS            34
ACQTM         0.0000 sec
PD            2.0000 sec
PW1             3.07 usec
IRNUC  1H
CTEMP           17.5 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



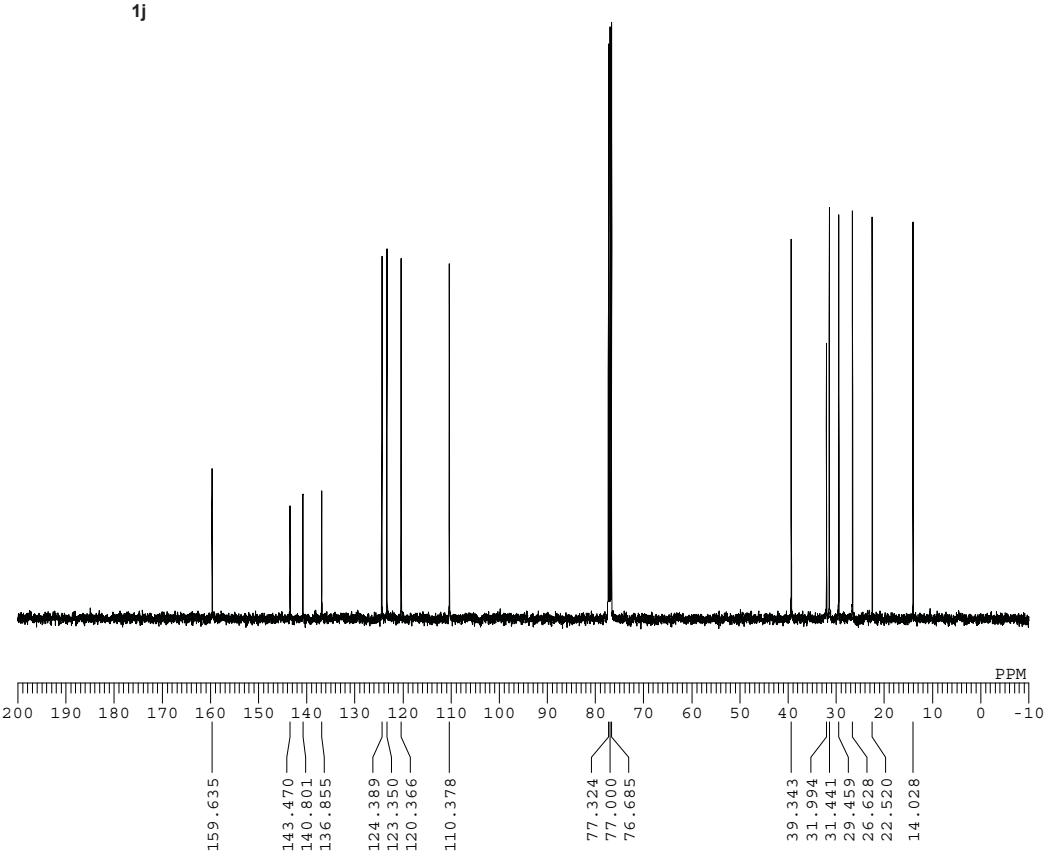
1j



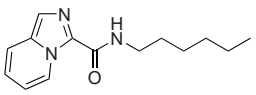

```
DFILE  MS147-1-1.jdf
COMNT  MS147 1H NMR
DATIM  2010-12-10 14:59:41
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           15.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             46
```



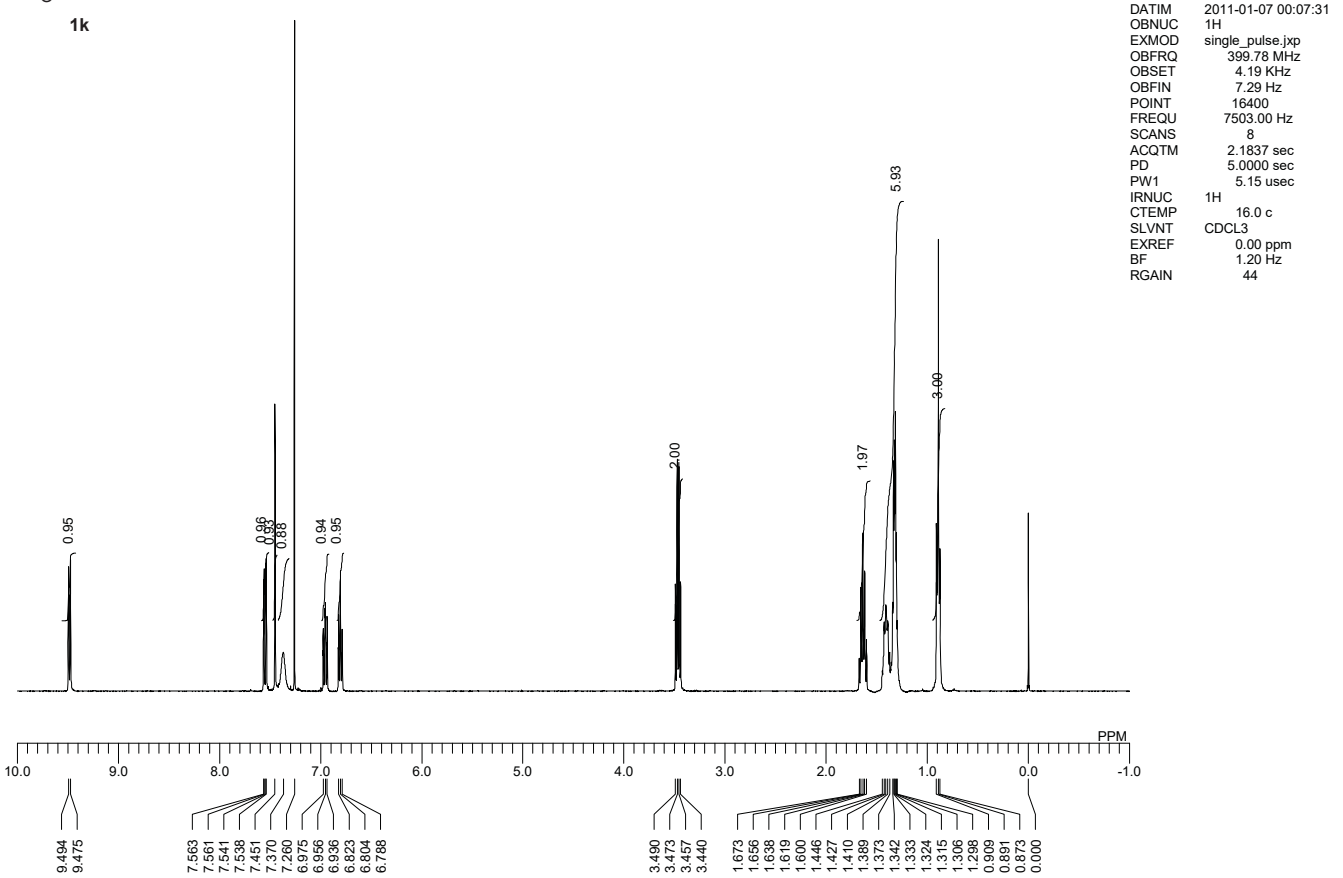
1j



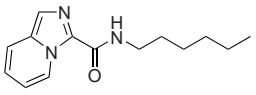

```
DFILE  MS147-1.jdf
COMNT  MS147
DATIM  2010-12-10 15:17:39
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.17 usec
IRNUC  1H
CTEMP           15.7 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



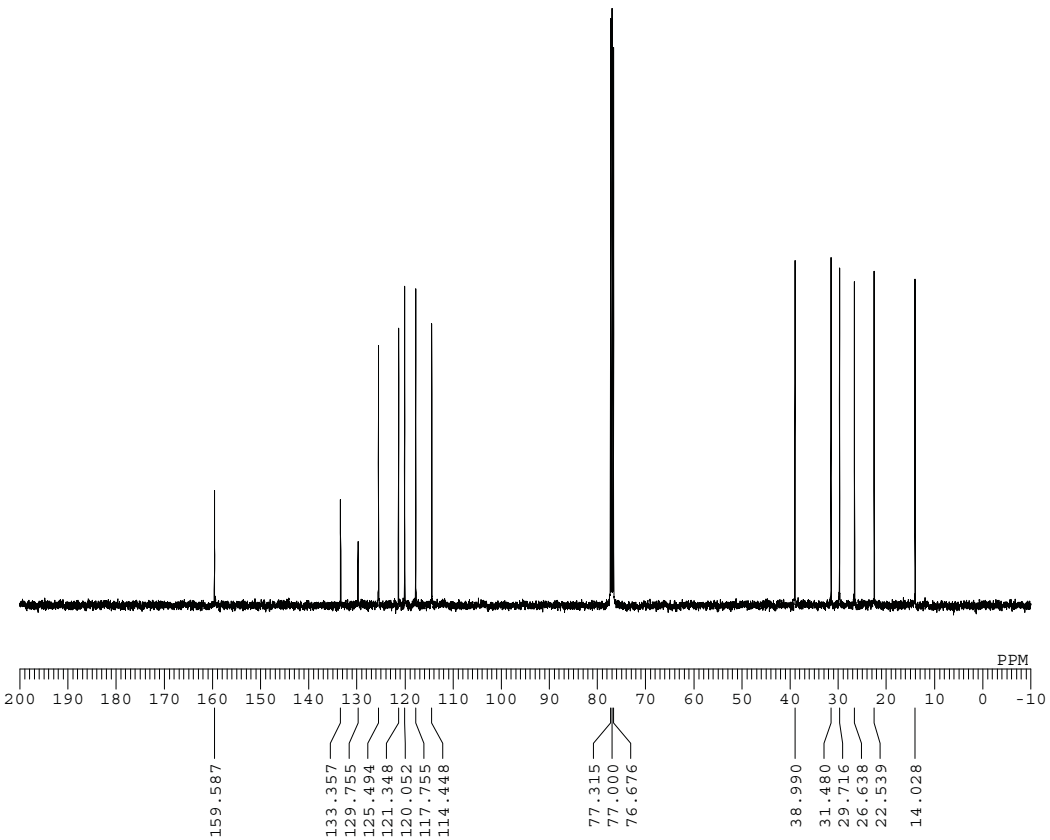
1k



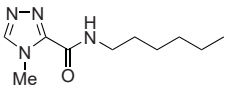
DFILE MS190 1H NMR-1.jdf
COMNT MS190 1H NMR
DATIM 2011-01-07 00:07:31
OBNUC 1H
EXMOD single_pulse.jxp
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 16400
FREQU 7503.00 Hz
SCANS 8
ACQTM 2.1837 sec
PD 5.0000 sec
PW1 5.15 usec
IRNUC 1H
CTEMP 16.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 44



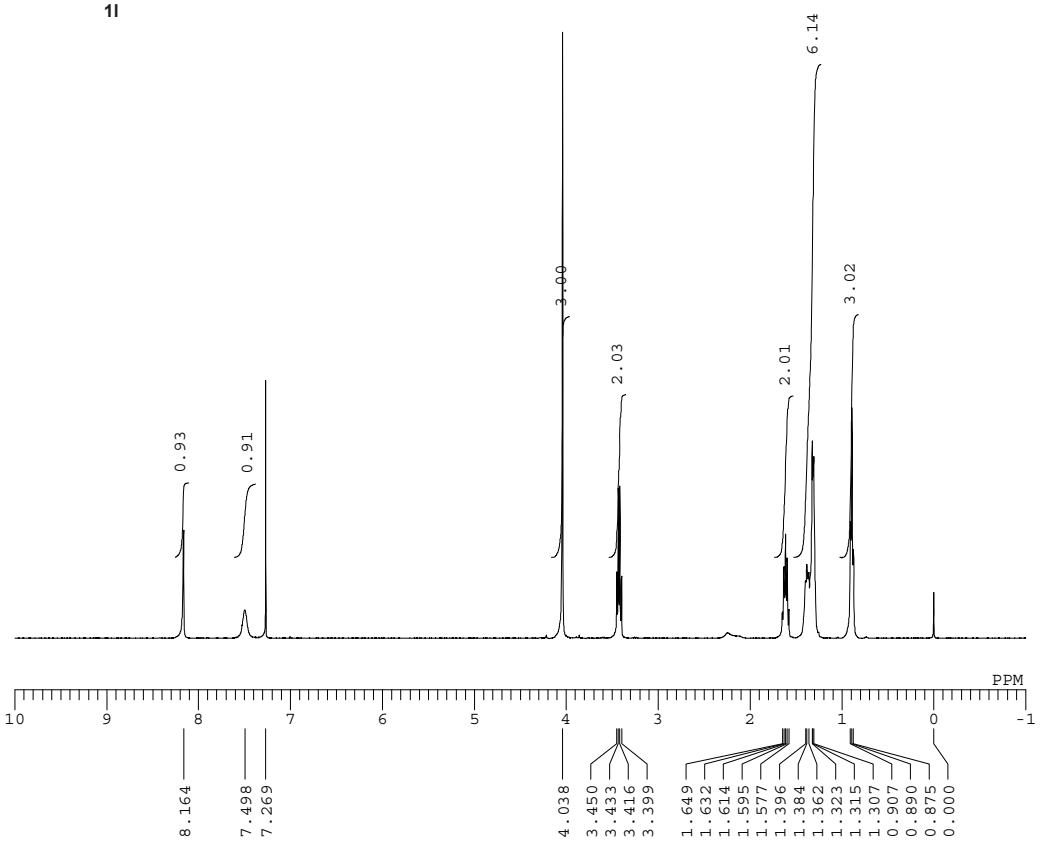
1k



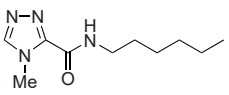
DFILE 1k.als
COMNT MS190 13C NMR
DATIM 2011-01-07 00:30:55
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 32780
FREQU 31407.04 Hz
SCANS 256
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.17 usec
IRNUC 1H
CTEMP 16.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



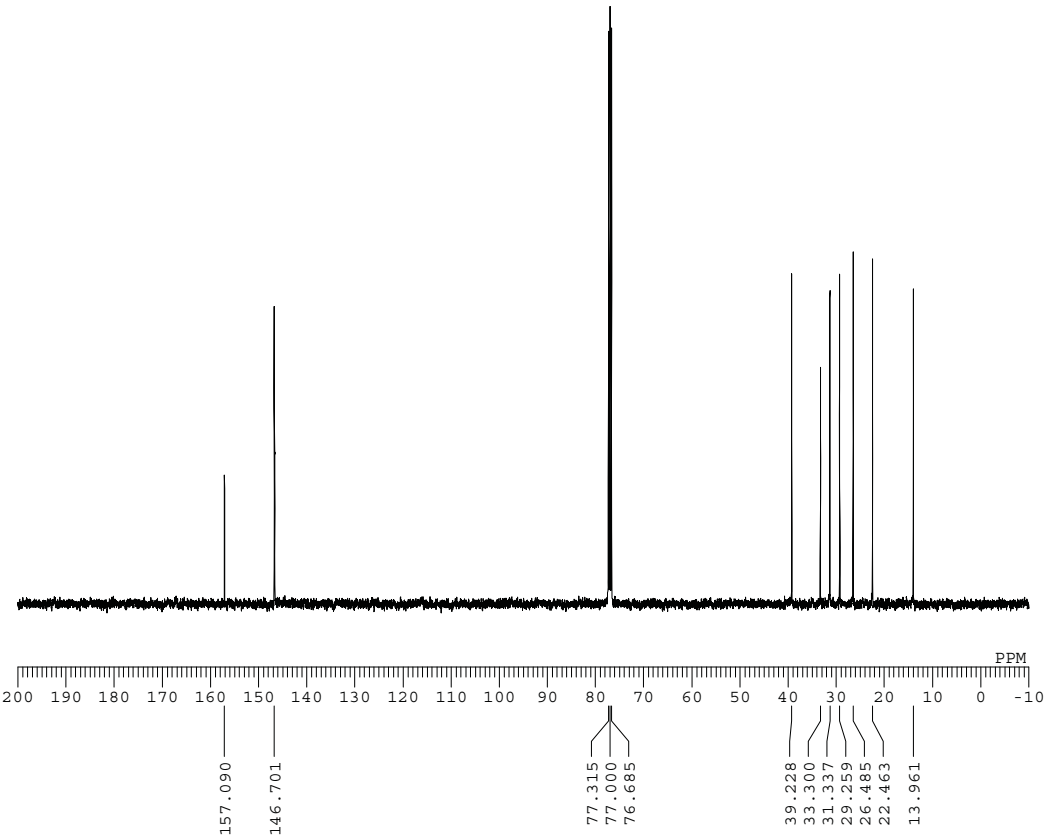
1l



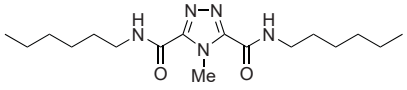

```
DFILE  MS136-1.jdf
COMNT  MS136
DATIM  2010-11-26 21:59:51
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           16.0 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             42
```



1l

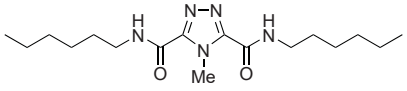



```
DFILE  1l.als
COMNT  MS136
DATIM  2010-11-26 23:28:23
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.17 usec
IRNUC  1H
CTEMP           16.6 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



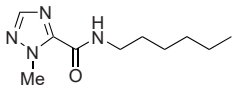
1l'


```
Filename                = nh#4045-GPC2-1 1_1H-1
Author                  = delta
Experiment              = proton.jxp
Sample_Id               = nh#4045-GPC2-1 1
Solvent                 = CHLOROFORM-D
Actual_Start_Time       =  3-DEC-2020 10:48:26
Revision_Time           =  4-DEC-2020 09:40:45

Comment                 = nh#4045-GPC2-1 1_1H
Data_Format             = 1D COMPLEX
Dim_Size                = 26214
X_Domain                = Proton
Dim_Title               = Proton
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ400S/L1

Field_Strength          = 9.389766[T] (400[MHz]
X_Acq_Duration          = 4.37256192[s]
X_Domain                = Proton
X_Freq                  = 399.78219838[MHz]
X_Offset                = 5[ppm]
X_Points                = 32768
X_Prescans              = 0
X_Resolution            = 0.22869888[Hz]
X_Sweep                 = 7.4940048[kHz]
X_Sweep_Clipped         = 5.99520384[kHz]
Irr_Domain              = Proton
Irr_Freq                = 399.78219838[MHz]
Irr_Offset              = 5[ppm]
Tri_Domain              = Proton
Tri_Freq                = 399.78219838[MHz]
Tri_Offset              = 5[ppm]
Blanking                = 2[us]
Clipped                 = FALSE
Scans                   = 8
Total_Scans             = 8

Relaxation_Delay        = 5[s]
Recvr_Gain              = 62
Temp_Get                = 18.2[dC]
X_90_Width              = 6.4[us]
X_Acq_Time              = 4.37256192[s]
X_Angle                 = 90[deg]
X_Atn                   = 1[dB]
X_Pulse                 = 6.4[us]
Irr_Mode                = Off
Tri_Mode                = Off
Dante_Loop              = 500
Dante_Presat            = FALSE
Decimation_Rate         = 0
Experiment_Path         = c:\Program Files\JEOL
Initial_Wait            = 1[s]
Phase                   = {0, 90, 270, 180, 180
Presat_Time             = 5[s]
Presat_Time_Flag        = FALSE
Relaxation_Delay_Calc   = 0[s]
Relaxation_Delay_Temp   = 5[s]
Repetition_Time         = 9.37256192[s]
```

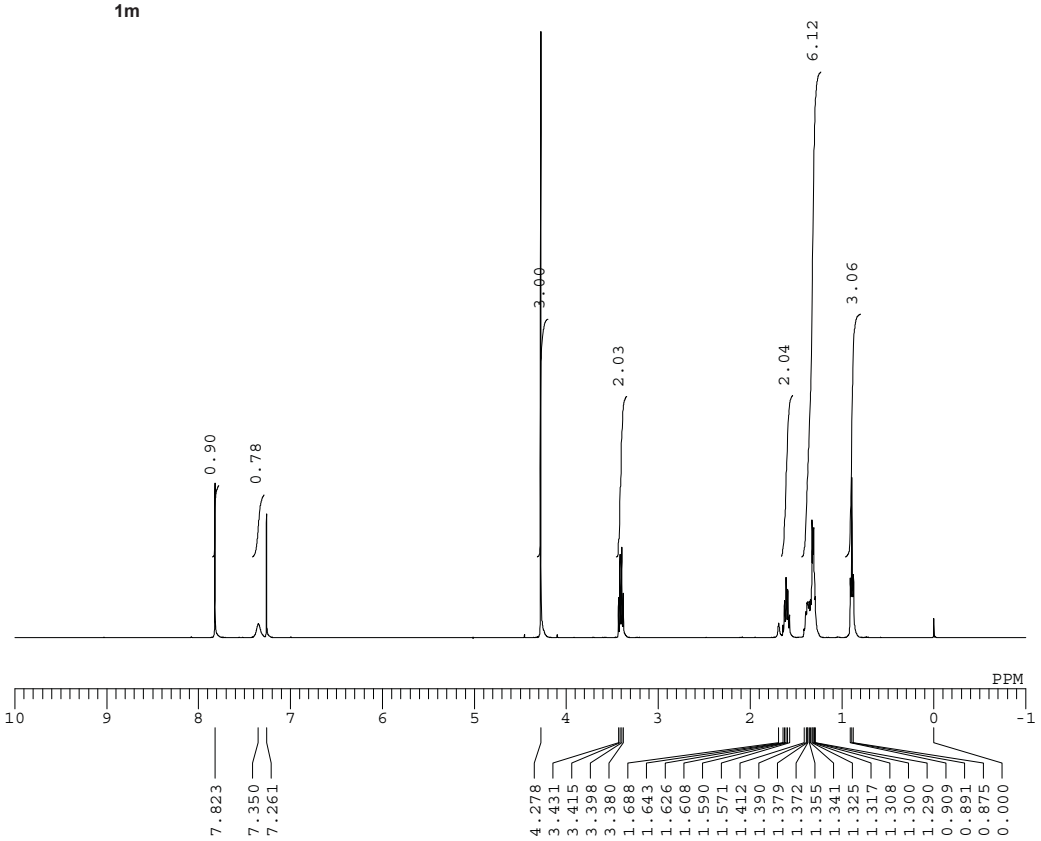


1l'

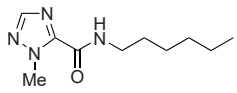

```
Filename                = nh#4045 2_13C-1-2.
Author                  = delta
Experiment              = carbon.jxp
Sample_Id               = nh#4045 2
Solvent                 = CHLOROFORM-D
Actual_Start_Time       =  2-DEC-2020 11:23:
Revision_Time           =  2-DEC-2020 11:19:

Comment                 = nh#4045 2_13C
Data_Format             = 1D COMPLEX
Dim_Size                = 26214
X_Domain                = Carbon13
Dim_Title               = Carbon13
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ400S/L1

Field_Strength          = 9.389766[T] (400[M
X_Acq_Duration          = 1.03809024[s]
X_Domain                = Carbon13
X_Freq                  = 100.52530333[MHz]
X_Offset                = 100[ppm]
X_Points                = 32768
X_Prescans              = 4
X_Resolution            = 0.96330739[Hz]
X_Sweep                 = 31.56565657[kHz]
X_Sweep_Clipped         = 25.25252525[kHz]
Irr_Domain              = Proton
Irr_Freq                = 399.78219838[MHz]
Irr_Offset              = 5[ppm]
Blanking                = 5[us]
Clipped                 = TRUE
Scans                   = 256
Total_Scans             = 256

Relaxation_Delay        = 2[s]
Recvr_Gain              = 56
Temp_Get                = 18.4[dC]
X_90_Width              = 10.3[us]
X_Acq_Time              = 1.03809024[s]
X_Angle                 = 30[deg]
X_Atn                   = 5[dB]
X_Pulse                 = 3.43333333[us]
Irr_Atn_Dec             = 26.09[dB]
Irr_Atn_Dec_Calc        = 26.09[dB]
Irr_Atn_Dec_Default_Calc = 26.09[dB]
Irr_Atn_Noe             = 26.09[dB]
Irr_Dec_Bandwidth_Hz    = 4.7826087[kHz]
Irr_Dec_Bandwidth_Ppm   = 11.96303566[ppm]
Irr_Dec_Freq            = 399.78219838[MHz]
Irr_Dec_Merit_Factor    = 2.2
Irr_Decoupling          = TRUE
Irr_Noe                 = TRUE
Irr_Noise               = WALTZ
Irr_Offset_Default      = 5[ppm]
Irr_Pwidth              = 0.115[ms]
Irr_Pwidth_Default      = 0.115[ms]
Irr_Pwidth_Default_Calc = 0.115[ms]
Irr_Pwidth_Temp1        = 0.115[ms]
Irr_Wurst               = FALSE
Decimation_Rate         = 0
Experiment_Path         = c:\Program Files\J
Initial_Wait            = 1[s]
Noe_Time                = 2[s]
Noe_Time_Flag           = FALSE
Relaxation_Delay_Calc   = 0[s]
Relaxation_Delay_Temp   = 2[s]
Repetition_Time         = 3.03809024[s]
```



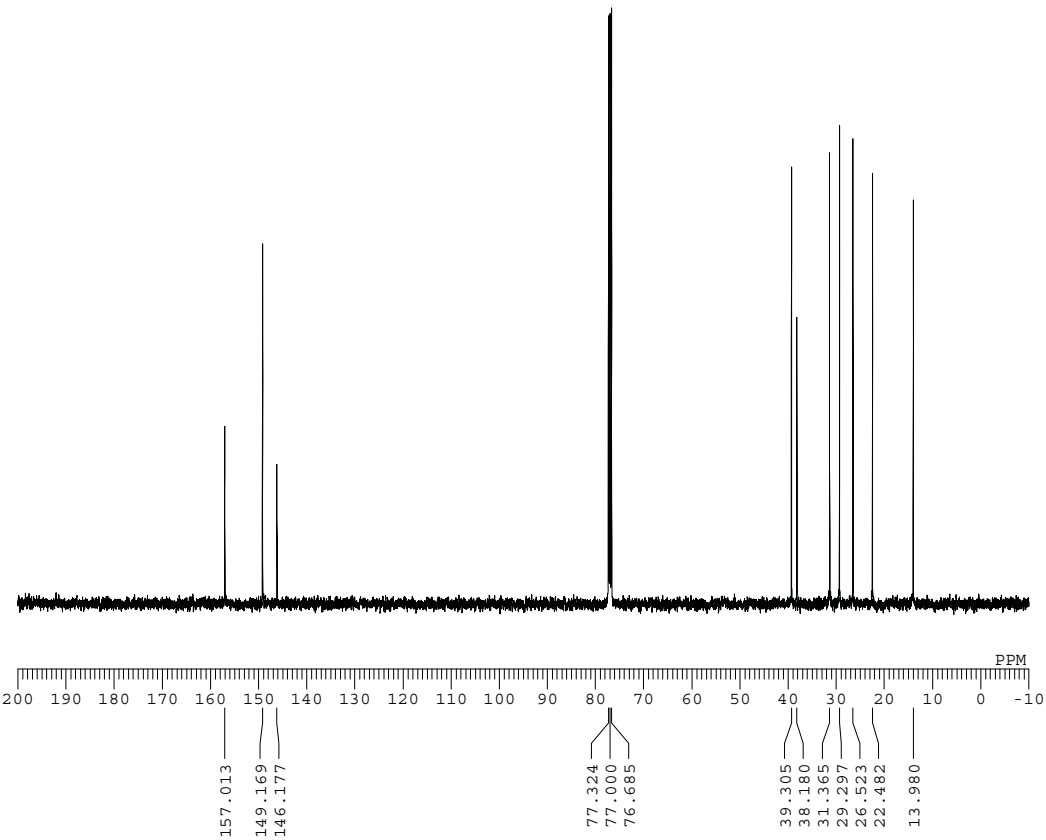
1m



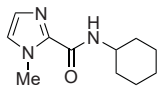

```
DFILE  MS138-1.jdf
COMNT  MS138
DATIM  2010-12-01 15:19:01
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           16.0 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             44
```



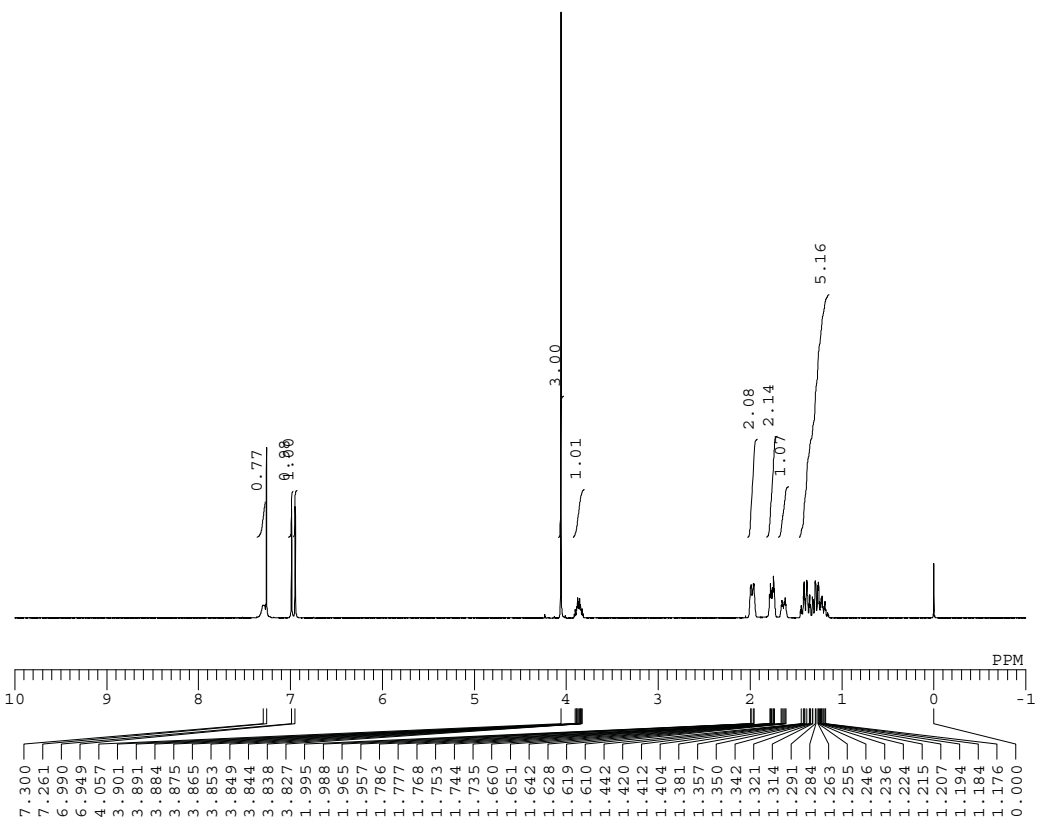
1m



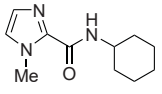

```
DFILE  1m.als
COMNT  MS138
DATIM  2010-12-01 16:04:24
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.17 usec
IRNUC  1H
CTEMP           16.5 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



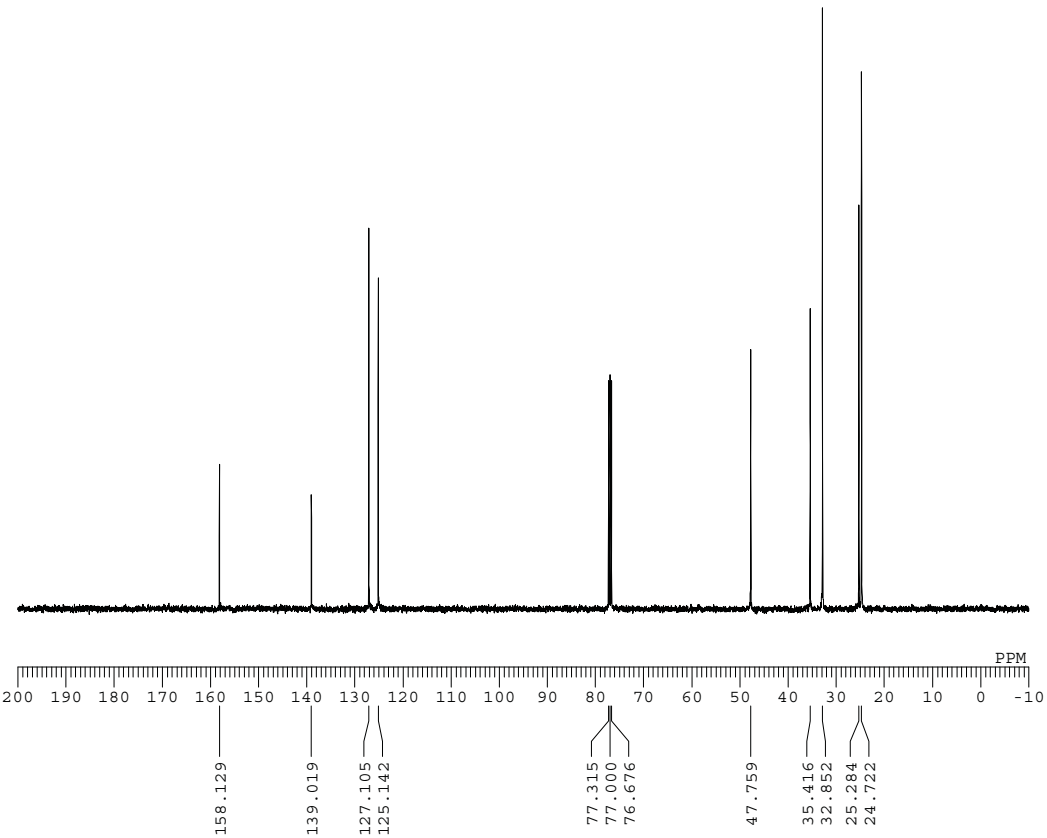
2a



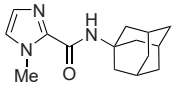

```
DFILE  MS102.jdf
COMNT  MS102 GPC
DATIM  2010-11-26 15:38:40
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           16.2 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             44
```



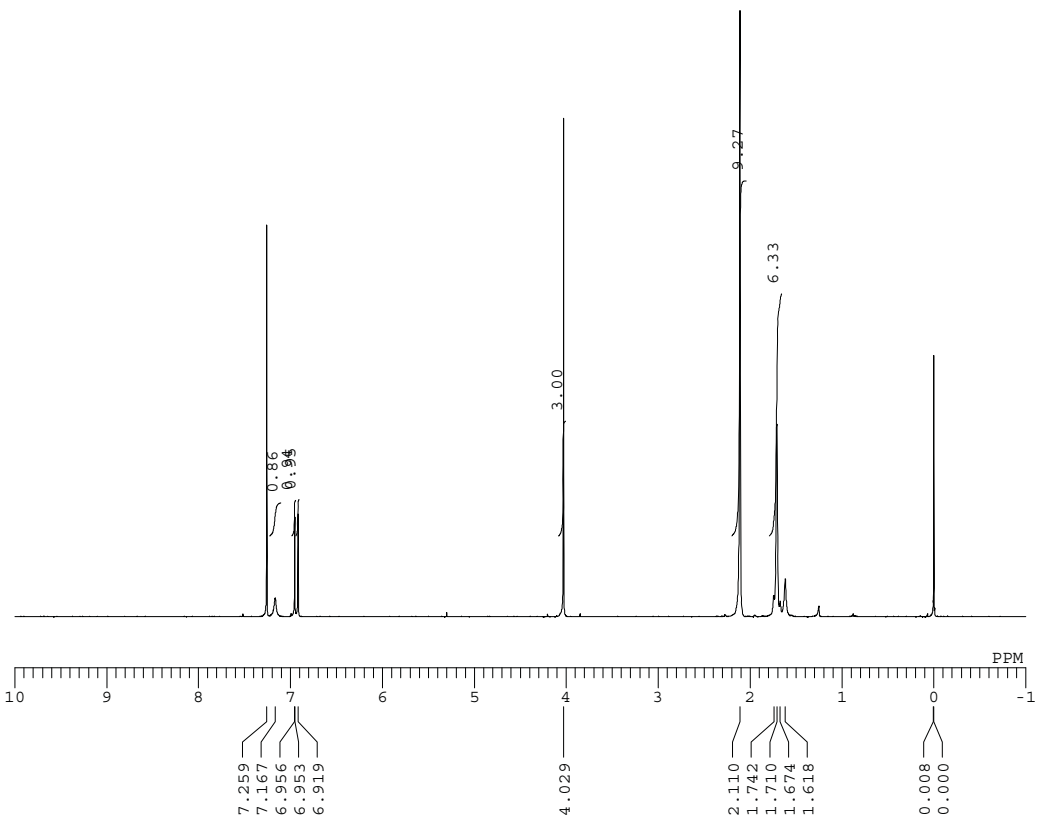
2a



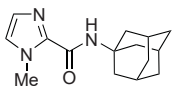

```
DFILE  2a.als
COMNT  MS102
DATIM  2011-02-17 13:54:47
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           101
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             4.00 usec
IRNUC  1H
CTEMP           17.0 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



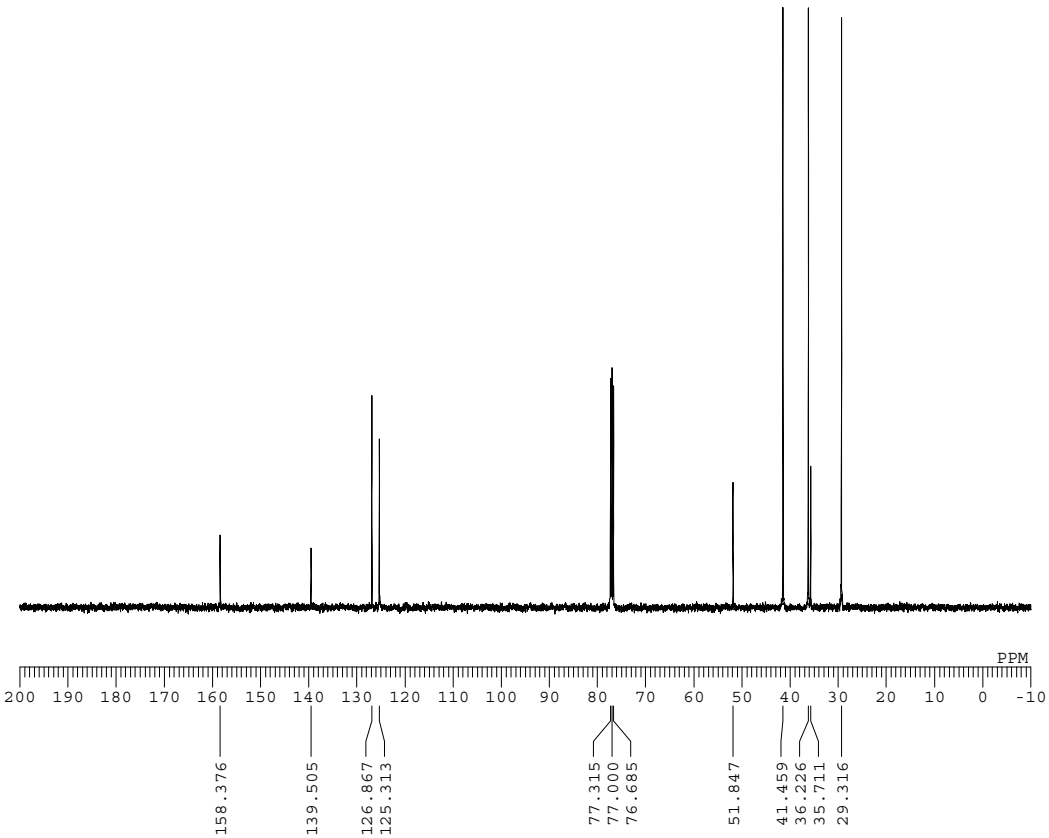
3a



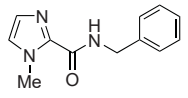

```
DFILE  MS169-1.jdf
COMNT  MS169
DATIM  2011-02-16 19:37:03
OBNUC  1H
EXMOD  proton.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             6.00 usec
IRNUC  1H
CTEMP           15.6 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             38
```



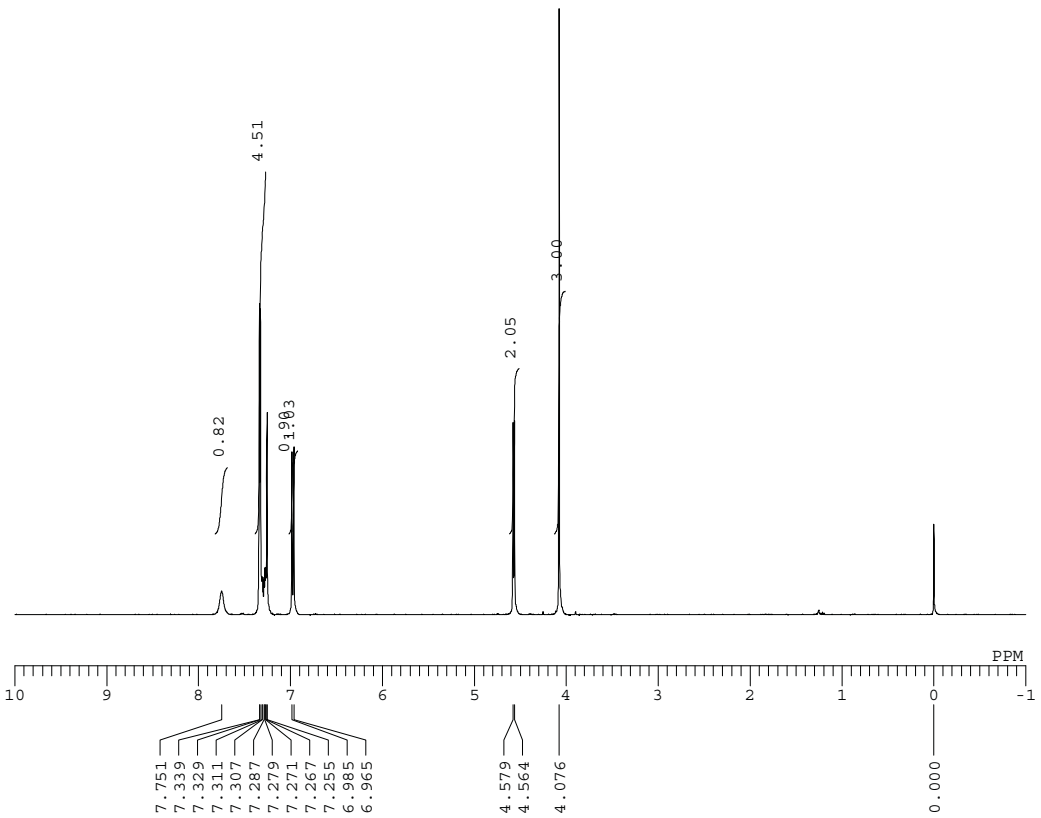
3a



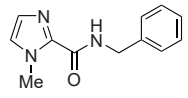

```
DFILE  MS169-1.jdf
COMNT  MS169
DATIM  2011-02-16 20:26:03
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           101
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             4.00 usec
IRNUC  1H
CTEMP           16.2 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



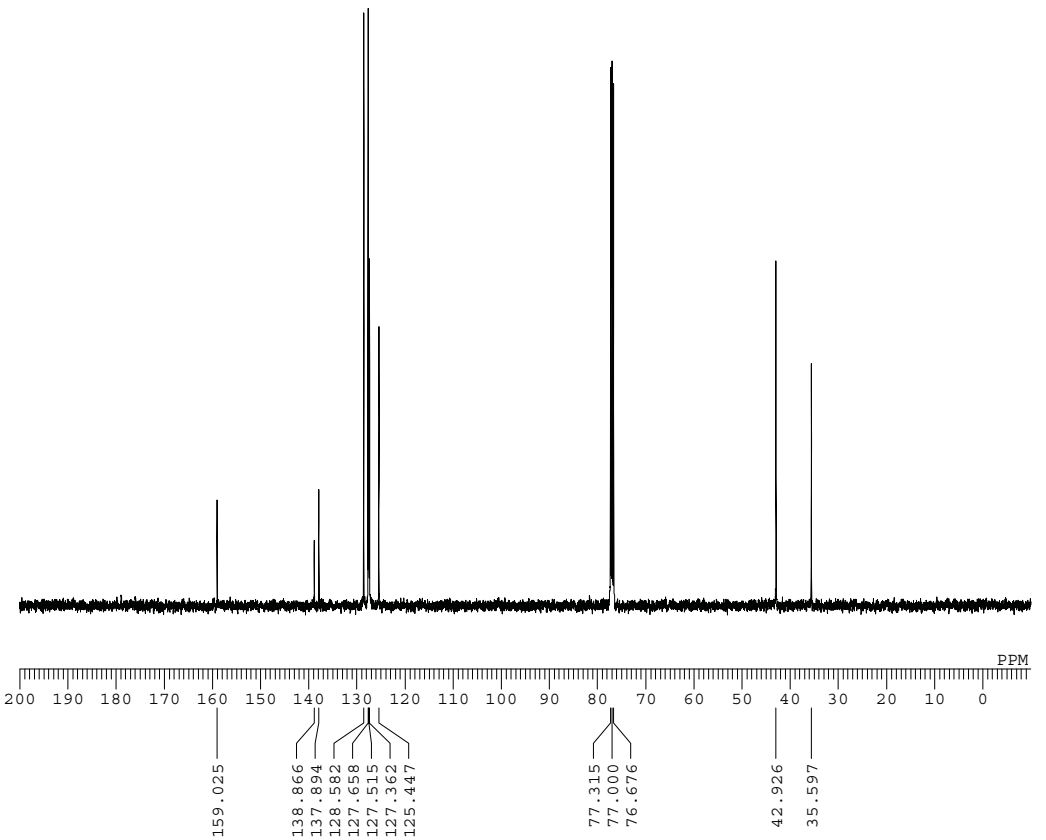
4a



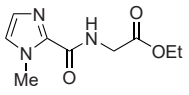

```
DFILE  MS076-1.jdf
COMNT  MS076
DATIM  2010-12-04 13:46:14
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           16.1 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             46
```



4a

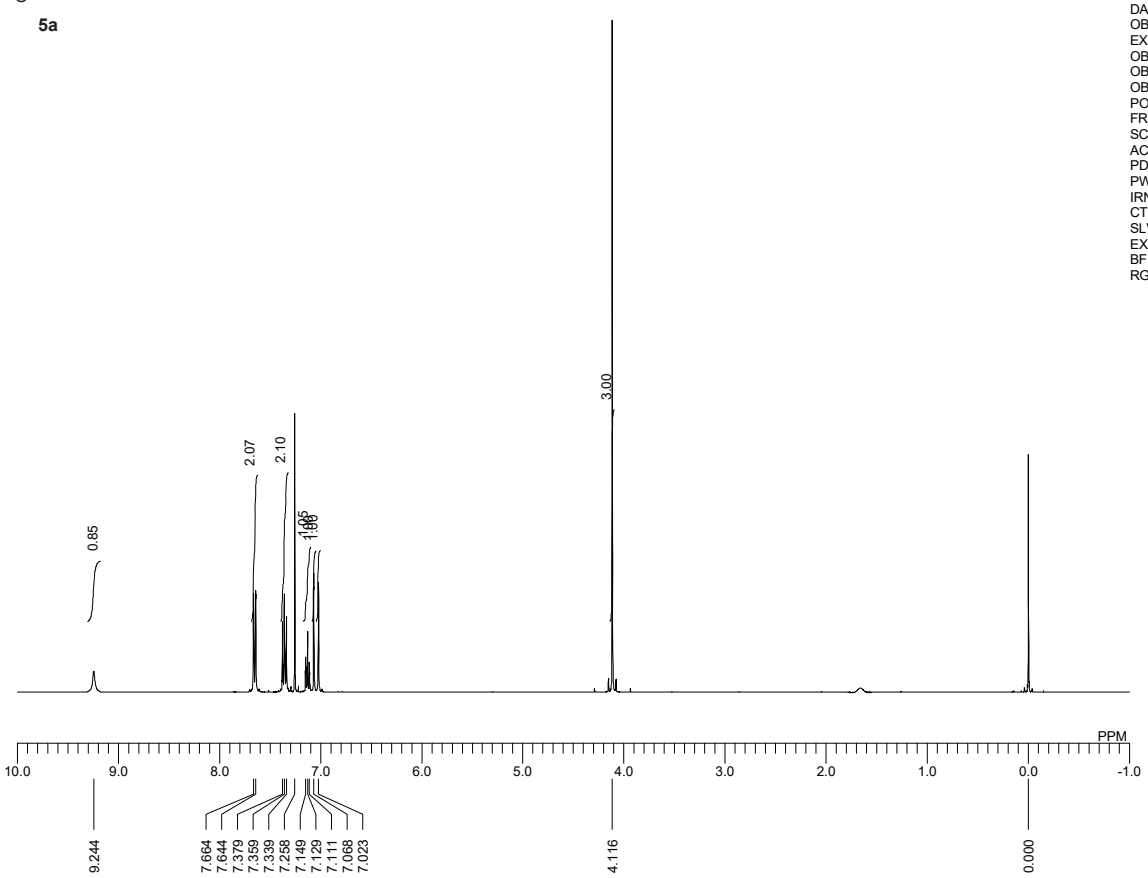


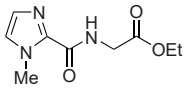

```
DFILE  5aa.als
COMNT  MS076 13C NMR
DATIM  2010-12-04 14:20:46
OBNUC  13C
EXMOD  single_pulse_dec
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         26224
FREQU      25125.63 Hz
SCANS           256
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             3.17 usec
IRNUC  1H
CTEMP           16.4 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```



5a

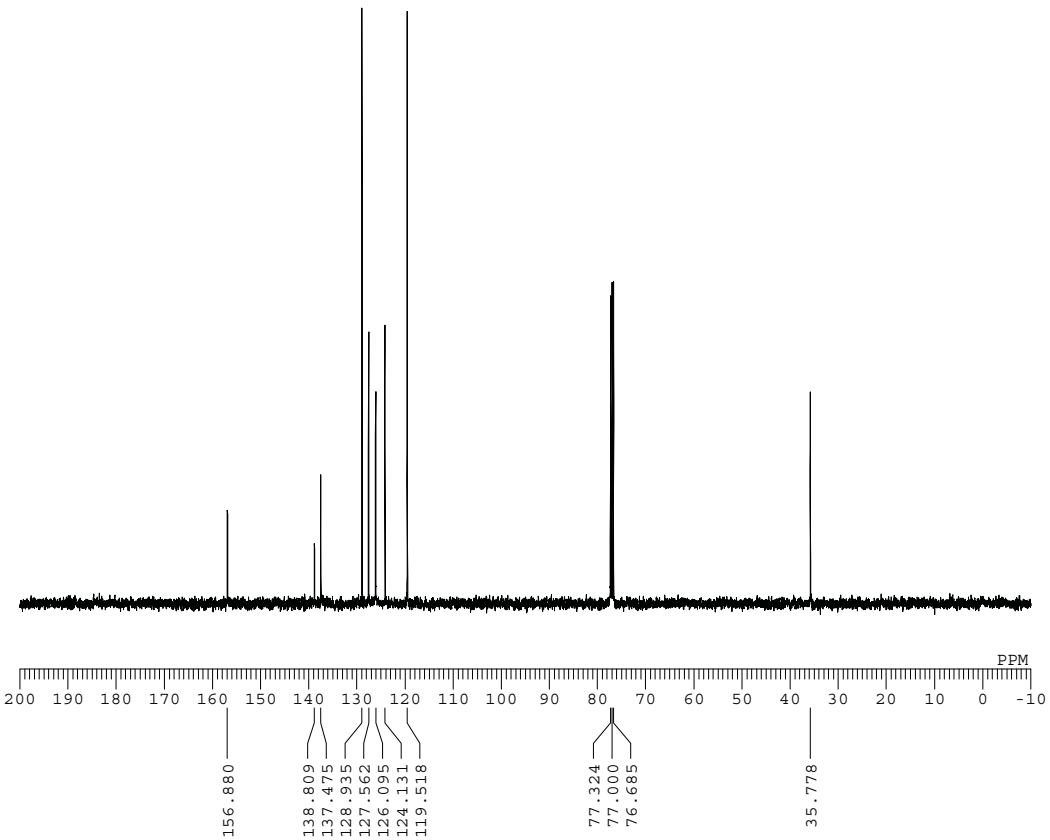
DFILE	MS194-1.jdf
COMNT	MS194
DATIM	2011-02-02 13:38:02
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	399.78 MHz
OBSET	4.19 KHz
OBFIN	7.29 Hz
POINT	16400
FREQU	7503.00 Hz
SCANS	8
ACQTM	2.1837 sec
PD	5.0000 sec
PW1	5.15 usec
IRNUC	1H
CTEMP	16.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.20 Hz
RGAIN	50

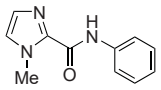




5a

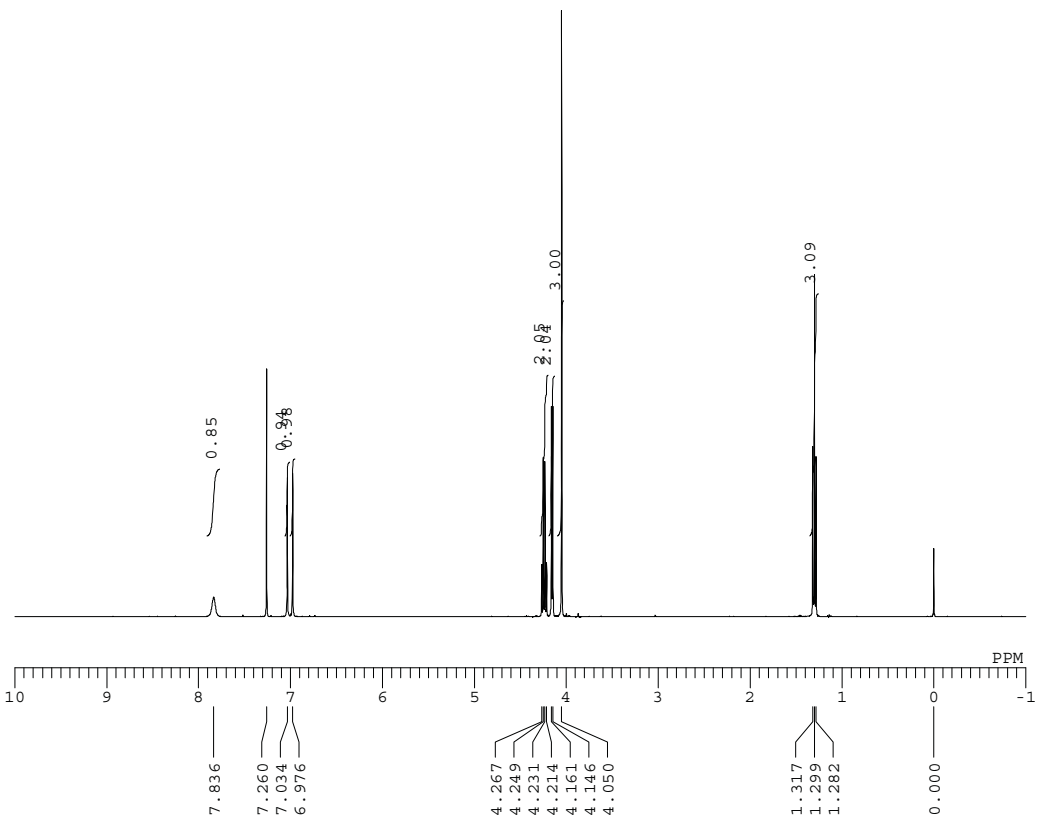
```
DFILE  4a.als
COMNT  MS194
DATIM  2011-02-02 13:50:14
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS            43
ACQTM         0.0000 sec
PD            2.0000 sec
PW1             3.17 usec
IRNUC  1H
CTEMP           16.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             0.12 Hz
RGAIN            60
```

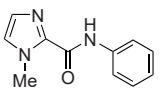




6a

```
DFILE  MS183-1.jdf
COMNT  MS183
DATIM  2010-12-03 22:30:10
OBNUC  1H
EXMOD  single_pulse.jxp
OBFRQ        399.78 MHz
OBSET          4.19 KHz
OBFIN          7.29 Hz
POINT         16400
FREQU       7503.00 Hz
SCANS             8
ACQTM         2.1837 sec
PD            5.0000 sec
PW1             5.15 usec
IRNUC  1H
CTEMP           16.7 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             48
```





6a

```
DFILE  MS183-2-1.jdf
COMNT  MS183
DATIM  2011-02-16 20:37:43
OBNUC  13C
EXMOD  carbon.jxp
OBFRQ        100.53 MHz
OBSET          5.35 KHz
OBFIN          5.86 Hz
POINT         32780
FREQU      31407.04 Hz
SCANS           101
ACQTM         1.0433 sec
PD            2.0000 sec
PW1             4.00 usec
IRNUC  1H
CTEMP           15.8 c
SLVNT  CDCL3
EXREF          77.00 ppm
BF              0.12 Hz
RGAIN             60
```