Electronic Supplementary Information

The Asymmetric Reduction of Imidazolinones with Trichlorosilane

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Electronic Supplementary Information

Experimental procedures, analytical data and copies of ^{1}H, ^{13}C NMR-spectra and HPLC-traces

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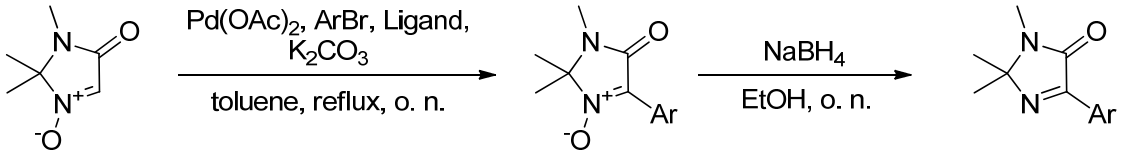
General Experimental Details

All commercially available chemicals were used without further purification. Moisture sensitive reactions were performed using standard Schlenk-techniques under an atmosphere of nitrogen. Methylene chloride (CH_2Cl_2), diethyl ether (Et_2O) and tetrahydrofuran (THF) were dried using an SPS-800 from M. Braun. ^{1}H NMR spectra were obtained on Bruker 600 MHz FT-NMR and 400 MHz FT-NMR spectrometers. ^{13}C NMR spectra were recorded at 151 MHz and 101 MHz. Chemical shifts are reported in ppm relative to the solvent signal. Multiplicity is indicated as follows: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets), etc. GC-MS analysis (EI) was performed on an Agilent Technologies 7890A with an MSD 5975C detector; high resolution mass spectra were obtained on a Bruker Daltonics micrOTOF (ESI). IR spectra were recorded on a Bruker ALPHA spectrometer using ATR technique. Flash chromatography was performed with E. Merck silica gel (43−60 μm). The employed eluent is reported in parentheses (PE = petroleum ether, CH = cyclohexane). Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (Merck Kieselgel 60 F_{254}), and components were visualized by observation under UV light or by treating the plates with $KMnO_4$ or CAM (cerium ammonium molybdate in diluted sulfuric acid) or Ninhydrin (in ethanol with acetic acid) solution followed by heating. Enantiomeric purities were determined using chiral HPLC (Chiralpak-column with solvent mixtures consisting of heptane and isopropanol or ethanol) or achiral HPLC (Kromasil RP 18-column with solvent mixtures consisting of acetonitrile and TFA (0.1%, aq.)) after derivatization with a chiral reagent. Optical rotations were obtained on a Perkin-Elmer Polarimeter 241.

Substrate synthesis

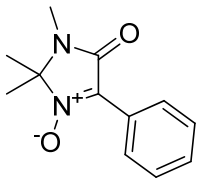
Aromatic substrates (1a-i)



General procedure for the palladium-catalyzed direct arylation of nitrones

The direct arylations were conducted according to an optimised procedure of Zhao and Wang *et al.*[1] The nitrone, potassium carbonate (2.0 eq.), P(*o*-Tol)$_3$ (0.15 eq., PPh$_3$ if Bromobenzene was used) and the corresponding aryl bromide were dissolved in toluene (0.1 M solution), and palladium acetate (0.05 eq.) was added. The reaction mixture was heated under reflux to satisfying conversion (controlled by TLC), i.e. over night in most cases. The mixture was filtrated through a pad of Celite® and flushed with ethyl acetate. Purification was performed by column chromatography. The corresponding eluent is stated for the particular product.

1,2,2-Trimethyl-5-oxo-4-phenyl-2,5-dihydro-1*H*-imidazole 3-oxide

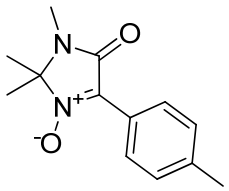


$C_{12}H_{14}N_2O_2$
218,2518

The title compound was obtained as a yellowish solid (747 mg, 3.42 mmol, 97%). (PE:EtOAc = 8:2 → 1:1)

R_f (EtOAc): 0.49 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.79 – 8.75 (m, 2H), 7.46 – 7.42 (m, 3H), 3.06 (s, 3H), 1.65 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 161.9, 130.9, 129.7, 128.3, 127.6, 126.2, 86.9, 25.5, 24.3 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3064, 2988, 2936, 1697, 1553, 1488, 1424, 1401, 1382, 1356, 1304, 1288, 1218, 1200, 1153, 1117, 1075, 1022, 999, 952, 929. 898, 824, 777, 740, 690, 666, 649, 605, 552, 520, 454, 420. **LRMS (EI):** *m/z* (%) 218 (8) [M^+], 202 (1) [$(M\text{-}O)^+$], 187 (1) [$((M\text{-}O)^+\text{-}CH_3)$], 119 (12), 104 (9), 89 (10), 71 (20), 56 (100). **HRMS (ESI):** *m/z* 262.1542 [262.1550 calculated for $C_{14}H_{20}N_3O_2^+$ ($M+H^+$)].

1,2,2-Trimethyl-5-oxo-4-(*p*-tolyl)-2,5-dihydro-1*H*-imidazole 3-oxide

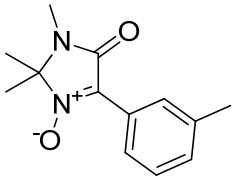


$C_{13}H_{16}N_2O_2$
232,2783

The title compound was obtained as a pale yellow solid (192 mg, 0.83 mmol, 59%). (CH:EtOAc = 7:3)

R_f (EtOAc): 0.46 [UV]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.75 – 8.69 (m, 2H), 7.30 – 7.26 (m, 2H), 3.09 (s, 3H), 2.39 (s, 3H), 1.68 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 162.1, 141.5, 129.8, 129.1, 127.6, 123.6, 86.7, 25.5, 24.3, 21.9 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3080, 3052, 2995, 2937, 1703, 1612, 1553, 1506, 1433, 1397, 1357, 1320, 1305, 1287, 1266, 1212, 1188, 1155, 1116, 1021, 959, 901, 844, 819, 733, 702, 662, 639, 617, 570, 554, 522, 491, 460, 419. **LRMS (EI):** *m/z* (%) 232 (100) [M^+], 201 (15) [$((M-O)^+-CH_3)$], 133 (48), 103 (22), 73 (23), 56 (73). **HRMS (ESI):** *m/z* 255.1104 [255.1104 calculated for $C_{13}H_{16}N_2O_2Na^+$ ($M+Na^+$)].

1,2,2-Trimethyl-5-oxo-4-(*m*-tolyl)-2,5-dihydro-1*H*-imidazole 3-oxide



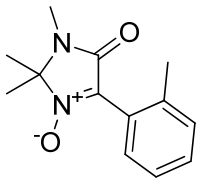
$C_{13}H_{16}N_2O_2$
232,2783

The title compound was obtained as a pale yellow solid (645 mg, 2.78 mmol, 93%). (CH:EtOAc = 7:3)

R_f (EtOAc): 0.46 [UV]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.64 – 8.61 (m, 1H), 8.59 – 8.55 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 3.08 (s, 3H), 2.40 (d, *J* = 0.7 Hz, 3H), 1.67 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 161.9, 137.9, 131.8, 129.9, 128.2, 127.9, 126.1, 124.8, 86.8, 25.5, 24.3, 21.7 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3067, 2989, 2918, 1697, 1600, 1579, 1551, 1476, 1429, 1395, 1382, 1352, 1307, 1284, 1229, 1200, 1188, 1171, 1147, 1112, 1026, 963, 918, 900, 872, 796, 767, 735, 694, 663, 607, 552, 439, 420. **LRMS**

(EI): 232 (65) [M^+], 201 (11) [$((M-O)^+-CH_3)$], 133 (38), 118 (13), 103 (15), 77 (15), 71 (18), 56 (100). **HRMS (ESI):** *m/z* 255.1101 [255.1104 calculated for $C_{13}H_{16}N_2O_2Na^+$ ($M+Na^+$)].

1,2,2-Trimethyl-5-oxo-4-(*o*-tolyl)-2,5-dihydro-1*H*-imidazole 3-oxide

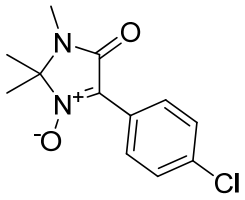


$C_{13}H_{16}N_2O_2$
232,2783

The title compound was obtained as a yellowish solid (630 mg, 2.72 mmol, 90%). (CH:EtOAc = 7:3 → 1:1)

R_f (EtOAc): 0.35 [UV]. **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 7.44 – 7.42 (m, 1H), 7.38 – 7.34 (m, 1H), 7.29 – 7.26 (m, 2H), 3.11 (s, 3H), 2.28 (s, 3H), 1.71 (s, 6H) ppm. **^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 161.8, 139.1, 134.2, 130.7, 130.6, 130.0, 125.7, 123.9, 87.8, 25.7, 24.4, 20.1 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3054, 2987, 2936, 1699, 1604, 1567, 1492, 1425, 1398, 1383, 1356, 1303, 1284, 1268, 1227, 1204, 1189, 1159, 1133, 1101, 1022, 953, 902, 838, 769, 731, 700, 672, 648, 610, 555, 446, 413. **LRMS (EI):** *m/z* (%) 215 (10) [$(M-O)^+$], 201 (7) [$((M-O)^+-CH_3)$], 72 (10), 56 (100). **HRMS (ESI):** *m/z* 255.1103 [255.1104 calculated for $C_{13}H_{16}N_2O_2Na^+$ ($M+Na^+$)].

4-(4-Chlorophenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazole 3-oxide



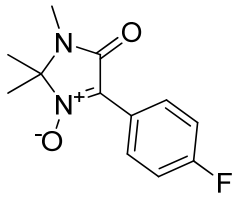
$C_{12}H_{13}ClN_2O_2$
252,6968

The title compound was obtained as a pale yellowish solid (663 mg, 2.62 mmol, 87%). (CH:EtOAc = 7:3)

R_f (EtOAc): 0.46 [UV]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.84 – 8.78 (m, 2H), 7.46 – 7.40 (m, 2H), 3.09 (s, 3H), 1.68 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 161.7, 136.8, 128.9, 128.7, 124.8, 87.2, 25.6, 24.3 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3083, 2994, 2937, 1699, 1590, 1560, 1543, 1486, 1434, 1393, 1358, 1315, 1293, 1214, 1202, 1178, 1158, 1118, 1087,

1031, 1012, 957, 902, 827, 736, 705, 690, 662, 613, 556, 517, 489, 460, 412. **LRMS (EI):** *m/z* (%) 252 (9) [M^+], 236 (4) [$(M\text{-}O)^+$], 221 (8) [$((M\text{-}O)^+\text{-}CH_3)$], 138 (8), 71 (20), 56 (100). **HRMS (ESI):** *m/z* 253.0738 [253.0738 calculated for $C_{12}H_{14}N_2O_2Cl^+$ ($M+H^+$)].

4-(4-fluorophenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazole 3-oxide

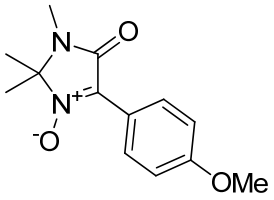


$C_{12}H_{13}FN_2O_2$
236,2422

The title compound was obtained as a light yellowish solid (624 mg, 2.64 mmol, 88%). (CH:EtOAc = 7:3)

R_f (EtOAc): 0.46 [UV]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.93 – 8.85 (m, 2H), 7.19 – 7.11 (m, 2H), 3.10 (s, 3H), 1.69 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 165.1, 162.20 (d, *J* = 77.6 Hz), 130.11 (d, *J* = 8.4 Hz), 122.66 (d, *J* = 3.3 Hz), 115.53 (d, *J* = 21.5 Hz), 87.0, 25.6, 24.3 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3054, 2989, 1699, 1602, 1558, 1504, 1434, 1415, 1397, 1384, 1358, 1313, 1298, 1265, 1237, 1213, 1162, 1117, 1100, 1016, 954, 899, 843, 786, 732, 703, 664, 632, 619, 569, 551, 528, 467, 417. **LRMS (EI):** *m/z* (%) 236 (29) [M^+], 220 (4) [$(M\text{-}O)^+$], 205 (9) [$((M\text{-}O)^+\text{-}CH_3)$], 137 (8), 122 (10), 107 (9), 71 (30), 56 (100). **HRMS (ESI):** *m/z* 237.1035 [237.1034 calculated for $C_{12}H_{14}N_2O_2F^+$ ($M+H^+$)].

4-(4-Methoxyphenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazole 3-oxide



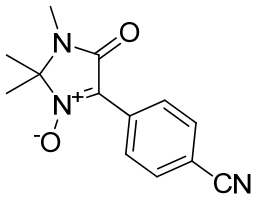
$C_{13}H_{16}N_2O_3$
248,2777

The title compound was obtained as a white solid (250 mg, 1.01 mmol, 84%). (PE:EtOAc = 8:2 → 2:3)

R_f (PE:EtOAc = 1:1): 0.20 [UV]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.87 – 8.82 (m, 2H), 6.99 – 6.94 (m, 2H), 3.84 (s, 3H), 3.08 (s, 3H), 1.66 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 162.1, 161.4, 129.9, 129.5, 119.1, 113.7, 86.4 55.4 25.5, 24.2 ppm. **IR (film):**

ν_{max} [cm^{-1}] = 3078, 3002, 2929, 2854, 2562, 1696, 1604, 1557, 1504, 1442, 1399, 1381, 1358, 1317, 1295, 1259, 1212, 1177, 1158, 1117, 1108, 1023, 955, 904, 836, 809, 776, 733, 689, 659, 634, 579, 556, 531, 470. **LRMS (EI):** *m/z* (%) 248 (52) [M^+], 233 (2) [$(M-CH_3)^+$], 217 (5) [$(M-CH_3-O)^+$], 203 (5), 149 (51), 147 (58), 134 (12), 119 (48), 106 (8), 71 (25), 56 (100). **HRMS (ESI):** *m/z* 271.1052 [271.1053 calculated for $C_{13}H_{16}N_2O_3Na^+$ ($M+Na^+$)].

4-(4-Cyanophenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazole 3-oxide

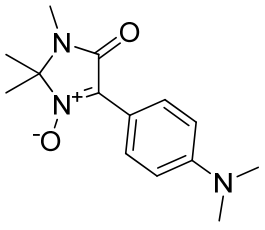


$C_{13}H_{13}N_3O_2$
243,2612

The title compound was obtained as a yellow solid (343 mg, 1.41 mmol, 94%). (CH:EtOAc = 7:3 → 1:1)

R_f (EtOAc): 0.39 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.98 – 8.91 (m, 2H), 7.75 – 7.69 (m, 2H), 3.10 (s, 3H), 1.69 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 161.3, 132.0, 130.2, 128.3, 127.6, 118.5, 113.8, 87.9, 25.6, 24.3 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3086, 3065, 3048, 2996, 2940, 2229, 1694, 1606, 1547, 1502, 1438, 1416, 1398, 1385, 1364, 1306, 1220, 1201, 1188, 1152, 1117, 1020, 997, 952, 900, 855, 732, 668, 643, 614, 556, 527, 451, 417. **LRMS (EI):** *m/z* (%) 243 (18) [M^+], 228 (2) [$(M- CH_3)^+$], 213 (4), 144 (5), 114 (6), 71 (25), 56 (100). **HRMS ESI:** *m/z* 266.0898 [266.0900 calculated for $C_{13}H_{13}N_3O_2Na^+$ ($M+Na^+$)].

4-(4-(Dimethylamino)phenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazol-3-oxide



$C_{14}H_{19}N_3O_2$
261,3196

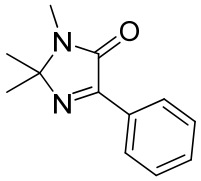
The title compound was obtained as a yellow solid (476 mg, 1.82 mmol, 73%). (PE:EtOAc = 8:2 → EtOAc).

R_f (EtOAc): 0.38 [UV, Ninhydrin, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.86 – 8.81 (m, 2H), 6.75 – 6.71 (m, 2H), 3.08 (s, 3H), 3.04 (s, 6H), 1.66 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 162.5, 151.7, 129.8, 129.1, 114.3, 111.1, 85.7, 40.1, 25.4, 24.2 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3090, 2986, 2934, 2812, 1694, 1601, 1559, 1517, 1444, 1423, 1398, 1350, 1324, 1294, 1214, 1202, 1154, 1111, 1066, 1023, 944, 902, 823, 734, 652, 634, 566, 553, 532, 410. **LRMS (EI):** *m/z* (%) 261 (9) [M^+], 245 (7) [$(M\text{-}O)^+$], 230 (14) [$((M\text{-}O)^+\text{-}CH_3)$], 207 (11), 162 (28), 145 (15), 132 (34), 115 (11), 90 (11), 73 (17), 56 (100). **HRMS (ESI):** *m/z* 219.1131 [219.1128 calculated for $C_{12}H_{15}N_2O_2^+$ ($M+H^+$)].

General procedure for the deoxygenation of the nitrones with $NaBH_4$

Sodium borohydride (3.0 eq.) was added to a solution of the nitrone in ethanol (abs., 0.04 M solution) and the resulting reaction mixture was stirred at the corresponding temperature (room temperature in most cases) until satisfying conversion (controlled by TLC) was visible (in most cases over night). It was diluted with ethyl acetate and brine, the layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification was performed by column chromatography. (PE:EtOAc = 1:0 → 0:1)

1,2,2-Trimethyl-4-phenyl-1*H*-imidazol-5(2*H*)-one (1a)



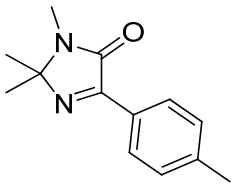
$C_{12}H_{14}N_2O$
202,2524

The title compound was obtained as a white solid (411.0 mg, 2.03 mmol, 66%).

R_f (EtOAc): 0.46 [UV, $KMnO_4$]. **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 8.47 – 8.44 (m, 2H), 7.54 – 7.51 (m, 1H), 7.50 – 7.46 (m, 2H), 3.06 (s, 3H), 1.52 (s, 6H) ppm. **^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 162.4, 161.3, 131.5, 130.8, 128.4, 128.4, 83.2, 25.6, 24.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3068, 2980, 2931, 1696, 1604, 1572, 1494, 1449, 1421, 1396, 1380, 1363, 1325, 1305, 1272, 1196, 1182, 1154, 1100, 1073, 1029, 997, 965, 916, 806, 751, 693, 657, 631, 616, 580, 557, 535. **LRMS (EI):** *m/z* (%) 202 (4) [M^+], 187 (11) [$(M\text{-}CH_3)^+$], 145 (5) [$((M\text{-}CH_3)^+\text{-}$

C_3H_6)], 104 (21), 77 (8), 71 (26), 56 (100). **HRMS (ESI):** *m/z* 203.1178 [203.1179 calculated for $C_{12}H_{15}N_2O^+$ ($M+H^+$)].

1,2,2-Trimethyl-4-(*p*-tolyl)-1*H*-imidazol-5(2*H*)-one (1b)

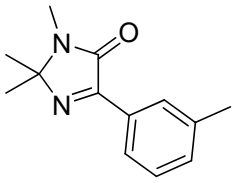


$C_{13}H_{16}N_2O$
216,2789

The title compound was obtained as a colourless solid (89 mg, 0.41 mmol, 96%).

R_f (CH:EtOAc = 1:1): 0.34 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.36 – 8.30 (m, 2H), 7.28 – 7.23 (m, 2H), 3.01 (s, 3H), 2.39 (s, 3H), 1.47 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 162.7, 161.2, 142.0, 129.3, 128.4, 128.2, 83.1, 25.7, 24.6, 21.7 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2980, 2931, 1694, 1612, 1601, 1565, 1513, 1455, 1422, 1396, 1380, 1363, 1343, 1321, 1303, 1274, 1192, 1182, 1155, 1100, 1039, 1023, 1001, 964, 917, 832, 784, 715, 641, 625, 600, 556, 535. **LRMS (EI):** *m/z* (%) 216 (44) [M^+], 201 (67) [$(M-CH_3)^+$], 159 (14), 118 (30), 71 (36), 56 (100). **HRMS (ESI):** *m/z* 239.1154 [239.1155 calculated for $C_{13}H_{16}N_2ONa^+$ ($M+Na^+$)].

1,2,2-Trimethyl-4-(*m*-tolyl)-1*H*-imidazol-5(2*H*)-one (1c)



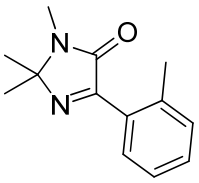
$C_{13}H_{16}N_2O$
216,2789

The title compound was obtained as a colourless solid (256 mg, 1.18 mmol, 68%).

R_f (CH:EtOAc = 1:1): 0.37 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.28 – 8.24 (m, 1H), 8.21 – 8.19 (m, 1H), 7.37 – 7.29 (m, 2H), 3.03 (s, 3H), 2.41 (s, 3H), 1.49 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 162.6, 161.6, 138.3, 132.5, 130.8, 128.8, 128.5, 125.8, 83.3, 25.7, 24.7, 21.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2981, 2931, 1697, 1597, 1584, 1456, 1421, 1399, 1380, 1362, 1327, 1311, 1274, 1205, 1195, 1153, 1089, 1011, 917, 895, 809, 774, 734, 692, 659, 630, 584, 554, 450. **LRMS (EI):** *m/z* (%) 216 (49) [M^+], 201 (64)

[(M-CH_3)$^+$], 159 (21), 118 (37), 71 (42), 56 (100). **HRMS (ESI):** *m/z* 239.1156 [239.1155 calculated for $C_{13}H_{16}N_2ONa^+$ (M+Na^+)].

1,2,2-Trimethyl-4-(*o*-tolyl)-1*H*-imidazol-5(2*H*)-one (1d)

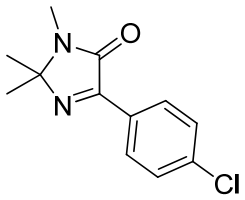


$C_{13}H_{16}N_2O$
216,2789

The title compound was obtained as a colourless solid (345 mg, 1.59 mmol, 73%).

R_f (CH:EtOAc = 1:1): 0.35 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.30 – 7.25 (m, 2H), 3.04 (s, 3H), 2.49 (s, 3H), 1.52 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 164.6, 162.6, 138.2, 131.1, 130.3, 130.1, 129.9, 125.7, 83.9, 25.9, 24.8, 20.8 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2981, 2931, 1696, 1612, 1493, 1455, 1422, 1400, 1380, 1363, 1309, 1267, 1196, 1157, 1087, 998, 966, 914, 803, 777, 733, 723, 701, 652, 629, 584, 560, 466**. LRMS (EI):** *m/z* (%) 216 (92) [M^+], 201 (100) [(M-CH_3)$^+$], 185 (13), 158 (27), 144 (24), 117 (32), 72 (25), 56 (86). **HRMS (ESI):** *m/z* 239.1159 [239.1155 calculated for $C_{13}H_{16}N_2ONa^+$ (M+Na^+)].

4-(4-Chlorophenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1e)



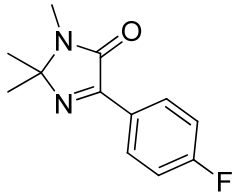
$C_{12}H_{13}ClN_2O$
236,6974

The title compound was obtained as a colourless solid (243 mg, 1.03 mmol, 55%).

R_f (CH:EtOAc = 1:1): 0.30 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.43 – 8.37 (m, 2H), 7.46 – 7.40 (m, 2H), 3.03 (s, 3H), 1.49 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 162.3, 160.5, 138.0, 129.9, 129.4, 128.9, 83.5, 25.8, 24.6 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2981, 2932, 1697, 1605, 1563, 1486, 1456, 1423, 1396, 1380, 1363, 1314, 1297, 1271, 1189, 1175, 1155, 1088, 1016, 999, 964, 916, 842, 824, 786, 713, 637, 621, 585, 556, 533, 490.

LRMS (EI): *m/z* (%) 236 (19) [M^+], 221 (38) [$(M- CH_3)^+$], 138 (19), 137 (21), 102 (12), 71 (18), 56 (100). **HRMS (ESI):** *m/z* 237.0785 [237.0789 calculated for $C_{12}H_{14}N_2OCl^+$ ($M+H^+$)].

4-(4-Fluorophenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1f)

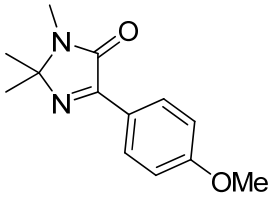


$C_{12}H_{13}FN_2O$
220,2428

The title compound was obtained as a colourless solid (264 mg, 1.19 mmol, 66%).

R_f (CH:EtOAc = 1:1): 0.30 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.50 – 8.45 (m, 2H), 7.17 – 7.10 (m, 2H), 3.03 (s, 3H), 1.49 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 166.3, 163.14 (d, *J* = 136.5 Hz), 160.3, 130.87 (d, *J* = 8.8 Hz), 127.24 (d, *J* = 3.3 Hz), 115.73 (d, *J* = 21.6 Hz), 83.4, 25.8, 24.6 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2983, 2934, 1696, 1608, 1508, 1457, 1426, 1411, 1400, 1380, 1364, 1317, 1296, 1266, 1225, 1192, 1155, 1094, 1000, 966, 918, 848, 790, 732, 702, 639, 621, 599, 558, 539. **LRMS (EI):** *m/z* (%) 220 (22) [M^+], 205 (67) [$(M- CH_3)^+$], 213 (4), 163 (10), 122 (41), 71 (22), 56 (100). **HRMS (ESI):** *m/z* 221.1085 [221.1085 calculated for $C_{12}H_{14}N_2OF^+$ ($M+H^+$)].

4-(4-Methoxyphenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1g)



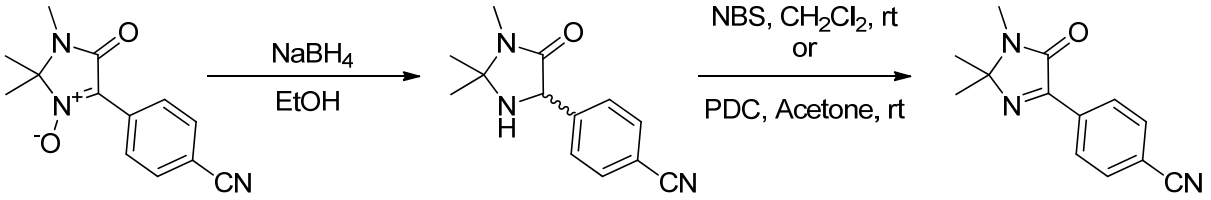
$C_{13}H_{16}N_2O_2$
232,2783

The title compound was obtained as a white solid (49 mg, 0.21 mmol, 63%). The reaction was carried out 45 °C.

R_f (PE:EtOAc = 1:1): 0.31 [UV]. **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 8.45 – 8.40 (m, 2H), 6.98 – 6.93 (m, 2H), 3.85 (s, 3H), 3.01 (s, 3H), 1.47 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 162.8, 162.4, 160.5, 130.3, 123.7, 114.0, 83.0, 55.5, 25.7, 24.7 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3077, 2978, 2931, 2839, 1693, 1605, 1569, 1510, 1458, 1442, 1417, 1397, 1380, 1363, 1324, 1304, 1250, 1173, 1157, 1100, 1029, 998, 965, 918, 842, 791, 776, 641, 621, 603,

557, 544, 485. **LRMS (EI):** *m/z* (%) 232 (14) [M^+], 217 (27) [$(M\text{-}CH_3)^+$], 134 (10), 71 (16), 56 (100). **HRMS (ESI):** *m/z* 233.1285 [233.1285 calculated for $C_{13}H_{17}N_2O_2^+$ ($M+H^+$)].

4-(1,2,2-Trimethyl-5-oxo-2,5-dihydro-1*H*-imidazol-4-yl)benzonitrile (1h)



The reduction of the nitrone led to the formation of the corresponding amine quantitatively. It could be oxidized to the desired imine either by using *N*-Bromosuccinimide or PDC.

Oxidation using *N*-bromosuccinimide

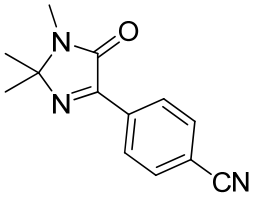
N-Bromosuccinimide (85.4 mg, 0.48 mmol, 1.1 eq.) was added to a solution of the amine (100.0 mg, 0.44 mmol) in methylene chloride (abs., 14 ml). The reaction mixture was stirred at room temperature for 5 h and quenched with $Na_2S_2O_3$ solution (saturated, aq.). The layers were separated and the aqueous layer was extracted with methylene chloride. The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography. (PE:EtOAc = 1:1 → 2:8)

The title compound was obtained as a white solid (50 mg, 0.22 mmol, 50%).

Oxidation using pyridiniumdichromate

Pyridiniumdichromate (116.5 mg, 0,31 mmol, 0.71 eq.) was added to a solution of the amine (100.0 mg, 0.44 mmol) in acetone (5 ml). The resulting mixture was stirred at room temperature over night and filtrated through a pad of Celite®. After concentration under reduced pressure, the crude product was purified by column chromatography. (PE:EtOAc = 1:1 → 2:8)

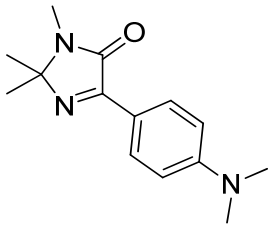
The title compound was obtained as a white solid (79 mg, 0.35 mmol, 80%).



$C_{13}H_{13}N_3O$
227,2618

R_f (EtOAc): 0.39 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 8.98 – 8.91 (m, 2H), 7.75 – 7.69 (m, 2H), 3.10 (s, 3H), 1.69 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 161.3, 132.0, 130.2, 128.3, 127.6, 118.5, 113.8, 87.9, 25.6, 24.3 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3086, 3065, 3048, 2996, 2940, 2229, 1694, 1606, 1547, 1502, 1438, 1416, 1398, 1385, 1364, 1306, 1220, 1201, 1188, 1152, 1117, 1020, 997, 952, 900, 855, 732, 668, 643, 614, 556, 527, 451, 417. **LRMS (EI):** *m/z* (%) 243 (18) [M^+], 228 (2) [$(M- CH_3)^+$], 213 (4), 144 (5), 114 (6), 71 (25), 56 (100). **HRMS ESI:** *m/z* 266.0898 [266.0900 calculated for $C_{13}H_{13}N_3ONa^+$ ($M+Na^+$)].

4-(4-(Dimethylamino)phenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1i)



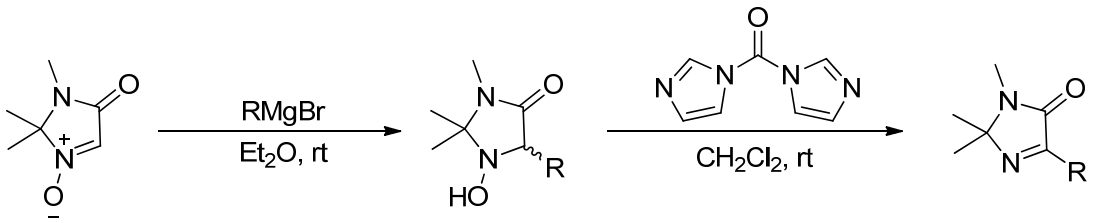
$C_{14}H_{19}N_3O$
245,3202

The title compound was obtained as a yellowish solid (100 mg, 0.41 mmol, 51%). The reaction was carried out 60 °C.

R_f (EtOAc): 0.55 [UV, $KMnO_4$] **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 8.40 – 8.35 (m, 2H), 6.74 – 6.68 (m, 2H), 3.03 (s, 6H), 3.00 (s, 3H), 1.46 (s, 6H) ppm. **^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 163.4, 160.3, 152.6, 129.9, 118.8, 111.5, 82.7, 77.4, 40.2, 25.6, 24.9 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3511, 3080, 2977, 2928, 2809, 1688), 1606, 1588, 1521, 1476, 1446, 1421, 1397, 1360, 1328, 1302, 1272, 1230, 1191, 1156, 1127, 1098, 1064, 1011, 997, 944, 918, 827, 791, 742, 726, 641, 622, 594, 555, 539, 483. **LRMS (EI):** *m/z* (%) 245 (4) [M^+], 230 (9) [$(M-CH_3)^+$], 146 (7), 145 (8), 56 (100). **HRMS (ESI):** *m/z* 246.1595 [246.1601 calculated for $C_{14}H_{20}N_3O_1^+$ ($M+H^+$)].

Aliphatic substrates

The aliphatic substrates were synthesized according to an optimised procedure of Blandin and Chavant *et al*.[2]

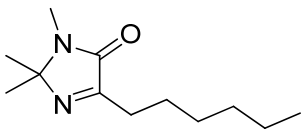


General procedure for the synthesis of the aliphatic substrates

A freshly prepared solution of Grignard-reagent (2.0 M in diethyl ether, 3.0 ml, 2.0 eq.) was added to a suspension of the nitrone (213.2 mg, 1.5 mmol) in diethyl ether (8 ml, abs.). The resulting suspension was stirred at room temperature until satisfying conversion was determined (controlled by TLC). Ammonium chloride solution (saturated, aq.) was added and the layers were separated. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried over $MgSO_4$, filtrated and concentrated under reduced pressure. At this stage, the hydroxylamine was partly dehydratised to the corresponding imine. Thus, the crude product was shortly filtrated over a pad of silica gel and flushed with ethyl acetate. After evaporation of the solvent the residue was directly used in the following step without further purification.

The crude product was solved in methylene chloride (abs., 0.16 M solution) and carbonyldiimidazole (1.5 eq. based on the crude mass) was added. The resulting solution was stirred at room temperature until satisfying conversion was determined (controlled by TLC) and was concentrated under reduced pressure. The crude mixture was purified by column chromatography. (PE:EtOAc = 1:0 → 0:1)

4-Hexyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1j)

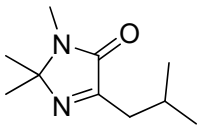


$C_{12}H_{22}N_2O$
210,3159

The title compound was obtained as a pale yellow liquid **(**151 mg, 0.72 mmol, 48% over 2 steps).

R_f (EtOAc): 0.39 [UV, CAM, $KMnO_4$] **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 2.93 (s, 3H), 2.58 – 2.50 (m, 2H), 1.68 (tt, *J* = 7.7, 6.7 Hz, 2H), 1.37 (s, 6H), 1.36 – 1.25 (m, 6H), 0.90 – 0.81 (m, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 168.8, 162.9, 84.2, 31.5, 29.0, 28.6, 25.7, 25.5, 24.4, 22.6, 14.1 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2955, 2929, 2858, 1701, 1634, 1458, 1424, 1402, 1379, 1364, 1279, 1197, 1151, 1038, 911, 726, 679, 659, 607, 556. **LRMS (EI):** *m/z* (%) 210 (3) [M^+], 195 (40) [(M- CH_3)$^+$], 140 (19), 125 (90), 82 (9), 71 (17), 56 (100). **HRMS (ESI):** *m/z* 211.1794 [211.1805 calculated for $C_{12}H_{23}N_2O^+$ ($M+H^+$)].

4-Isobutyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1k)

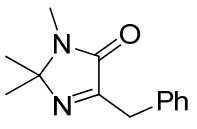


$C_{10}H_{18}N_2O$
182,2627

The title compound was obtained as a yellowish liquid (132 mg, 0.72 mmol, 48% over 2 steps)

R_f (EtOAc): 0.37 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 2.93 (s, 3H), 2.42 (d, *J* = 7.2 Hz, 2H), 2.17 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.37 (s, 6H), 0.94 (d, *J* = 6.6 Hz, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 168.1, 163.1, 84.2, 37.2, 26.1, 25.6, 24.5, 22.6 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2957, 2932, 2871, 1750, 1701, 1633, 1464, 1424, 1402, 1365, 1306, 1271, 1195, 1167, 1151, 1037, 919, 682, 662, 606, 556. **LRMS (EI):** *m/z* (%) 182 (8) [M^+], 167 (31) [(M-CH_3)$^+$], 140 (21), 125 (67), 82 (16), 71 (19), 56 (100). **HRMS (ESI):** *m/z* 183.1492 [183.1492 calculated for $C_{10}H_{19}N_2O^+$ ($M+H^+$)].

4-Benzyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (2l)



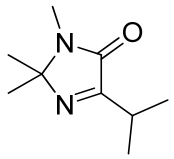
$C_{13}H_{16}N_2O$
216,2789

The title compound was obtained as a yellow liquid that crystallised upon storage (162 mg, 0.75 mmol, 50% over 2 steps).

R_f (EtOAc): 0.41 [UV, $KMnO_4$] **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.37 – 7.33 (m, 2H), 7.34 – 7.25 (m, 2H), 7.25 – 7.19 (m, 1H), 3.90 (s, 2H), 2.93 (s, 3H), 1.38 (s, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 167.0, 162.5, 135.3, 129.3, 128.6, 126.8, 84.3, 34.8, 25.5, 24.2 ppm.

IR (film): ν_{max} [cm^{-1}] = 3062, 3030, 2980, 2931, 1699, 1633, 1601, 1495, 1454, 1423, 1401, 1381, 1363, 1306,1273, 1194, 1150, 1036, 948, 750, 698, 679, 657, 639, 604, 585, 556, 463, 420. **LRMS (EI):** *m/z* (%) 216 (27) [M^+], 215 (21), 201 (21) [$(M\text{-}CH_3)^+$], 144 (10), 117 (12), 91 (28), 71 (14), 56 (100). **HRMS (ESI):** *m/z* 217.1327 [217.1335 calculated for $C_{13}H_{17}N_2O^+$ ($M+H^+$)].

4-Isopropyl-1,2,2-trimethyl-1H-imidazol-5(2H)-one (1m)

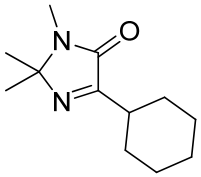


$C_9H_{16}N_2O$
168,2361

The title compound was obtained as a yellow liquid (382 mg, 2.27 mmol, 50% over 2 steps).

R_f (EtOAc): 0.29 [UV, CAM, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ =3.01 – 2.93 (m, 1H), 2.92 (s, 3H), 1.36 (s, 6H), 1.23 (d, *J* = 6.9 Hz, 6H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ =172.6, 162.5, 83.9, 28.1, 25.4, 24.5, 19.4 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3481, 2973, 2933, 2875, 1774, 1697, 1631, 1459, 1424, 1399, 1382, 1365, 1283, 1269, 1222, 1197, 1162, 1147,1097, 1018, 910, 826, 796, 701, 638, 611, 584, 557, 504. **LRMS (EI):** *m/z* (%) 168 (8) [M^+], 153 (14) [$(M\text{-}CH_3)^+$], 140 (11), 96 (18), 71 (33), 56 (100).**HRMS (ESI):** *m/z* 169.1336 [169.1335 calculated for $C_9H_{17}N_2O^+$ ($M+H^+$)].

4-Cyclohexyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1n)



$C_{12}H_{20}N_2O$
208,3000

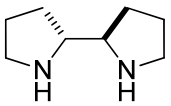
The title compound was obtained as a colourless liquid (179 mg, 0.86 mmol, 57% over 2 steps).

R_f (EtOAc): 0.42 [UV, $KMnO_4$]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 2.94 (s, 3H), 2.78 – 2.64 (m, 1H), 2.02 – 1.90 (m, 2H), 1.85 – 1.78 (m, 2H), 1.76 – 1.68 (m, 1H), 1.52 – 1.30 (m, 5H), 1.38 (s, 6H) ppm.**^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 171.7, 162.6, 84.0, 37.2, 29.7, 26.0, 25.9, 25.4, 24.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 2979, 2928, 2853, 1698, 1629, 1449, 1423,

1401, 1379, 1364, 1319, 1295, 1273, 1196, 1178, 1152, 1054, 1001, 979, 912, 891, 842, 716, 678, 621, 571, 557, 507. **LRMS (EI):** *m/z* (%) 208 (14) [M^+], 193 (95) [$(M\text{-}CH_3)^+$], 165 (10), 153 (10), 125 (14), 71 (24), 56 (100). **HRMS (ESI):** *m/z* 209.1648 [209.1648 calculated for $C_{12}H_{21}N_2O^+$ ($M+H^+$)].

Catalyst synthesis

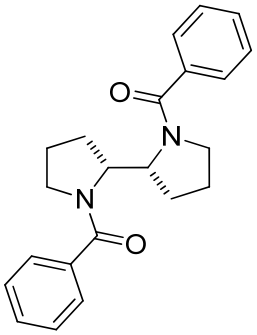
2,2'-Bispyrrolidine



$C_8H_{16}N_2$
140,2260

The title compound was synthesized in accordance to a procedure published by Denmark *et al.*[3] The obtained enantiomers were stored as the corresponding ammonium tartrate which could be isolated as white solids and liberated for further use in the synthesis of the catalysts. The characterization and the determination of the enantiomeric excess were accomplished using the benzoylated derivatives.

[2,2'-Bispyrrolidine]-1,1'-diyl bis(phenylmethanone)



$C_{22}H_{24}N_2O_2$
348,4382

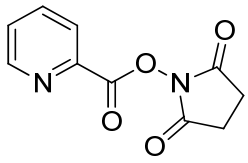
The benzoylated derivatives were synthesized in accordance to a procedure published by Denmark *et al.*[3] Triethylamine (0.8 M in CH_2Cl_2, 0.5 ml, 2.0 eq.) and benzoyl chloride (0.8 M in CH_2Cl_2, 0.5 ml, 2.0 eq.) were added to a solution of bispyrrolidine (28 mg, 0.20 mmol) in CH_2Cl_2 (1.0 ml) at 0 °C and the reaction mixture was stirred at room temperature over night. Ethyl acetate (10 ml) and dist. water (2 ml) were added, the aqueous layer was removed and extracted with ethyl acetate. The combined organic layers were washed with $NaHCO_3$ solution (saturated, aq., 3 ml), dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The crude product was purified by column chromatography. (PE: Isopropanol = 6:1)

The title compound was obtained as a white solid (57 mg, 0.16 mmol, 82% for the (*R*, *R*)- and 49 mg, 0.14 mmol, 49% for the (*S*, *S*)-enantiomer).

R_f (PE:Isopropanol = 6:1): 0.38 [UV] **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.45 – 7.38 (m, 4H), 7.34 – 7.21 (m, 6H), 4.65 – 4.58 (m, 2H), 3.80 (ddd, *J* = 10.6, 8.7, 5.1 Hz, 2H), 3.20 (ddd, *J* = 10.5, 8.0, 6.8 Hz, 2H), 2.30 – 2.16 (m, 2H), 2.08 – 1.97 (m, 2H), 1.96 – 1.85 (m, 2H), 1.83 – 1.74 (m, 2H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 171.1, 137.4, 129.7, 128.3, 127.3, 59.0, 49.3, 28.4, 24.3 ppm.

The analytical data are in agreement with the literature.[3]

2,5-Dioxopyrrolidin-1-yl picolinate



$C_{10}H_8N_2O_4$
220,1815

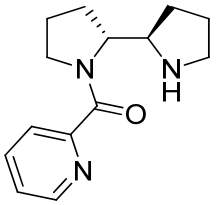
The title compound was synthesized according to a procedure published by Christensen *et al.*[4] Within 15 minutes triethylamine (28.333 ml, 20.683 g, 204.4 mmol, 2.8 eq.) was added to a suspension of picolinoyl chloride hydrochloride (12.995 g, 73.0 mmol) and *N*-hydroxysuccinimide (8.401 g, 73.0 mmol, 1.0 eq.) in THF (150 ml, abs.). The reaction mixture was stirred at room temperature over night before it was filtrated and rinsed with ethyl acetate. The filtrate was concentrated under reduced pressure to a volume of approximately 300 ml. Activated charcoal was added, the mixture was filtrated and concentrated under reduced pressure. The residue was recrystallised from isopropanol.

The title compound was obtained as a yellowish solid (3.319 g, 15.07 mmol, 21%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 4.9 Hz, 1H), 8.25 (d, *J* = 7.9, 1.1 Hz, 1H), 7.98 (td, *J* = 7.7, 1.6 Hz, 1H), 7.61 (ddd, *J* = 7.7, 4.9, 1.2 Hz, 1H), 2.74 (s, 4H) ppm.

The analytical data are in agreement with the literature.[4]

(2*R*,2'*R*)-[2,2'-Bipyrrolidin]-1-yl(pyridin-2-yl)methanone



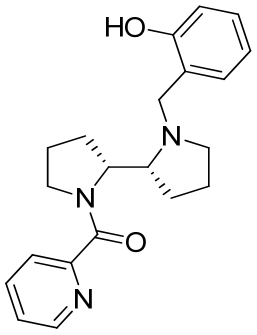
$C_{14}H_{19}N_3O$
245,3202

The enantiomerically pure (2*R*,2'*R*)-2,2'-bipyrrolidine (512 mg, 3.65 mmol), which was freshly liberated from the corresponding tartrate (according to the literature procedure by Denmark *et al.*)[3], was dissolved in a mixture of distilled water (3.56 ml) and hydrochloric acid (1 M, 3.56 ml, 1.0 eq.). 2,5-Dioxopyrrolidin-1-yl picolinate (804 g, 3.65 mmol, 1.0 eq.) was added. A small amount of acetone was used to rinse the weighing paper. The reaction mixture was stirred at room temperature over night. The aqueous layer was extracted 3 times with CH_2Cl_2 and the organic layer was discarded. The aqueos layer was basified with NaOH solution (aq., 10%, 20 ml) and saturated with sodium chloride. The aqueous layer was then extracted with methylene chloride. The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under reduced pressure. The crude product was used in the following step without further purification.

General procedure for the reductive amination of the catalyst's precursor with different aldehydes

The catalyst's precurser was weighed in, solved in methylene chlorid (10.2 M solution, abs.) and transferred to a flame-dried flask. The corresponding aldehyde (2.0 eq.) was added and the reaction mixture was stirred at room temperature for 0.5 h. Subsequently, tetramethylammonium triacetoxyborohydride (2.0 eq.) was added and the reaction mixture was stirred at room temperature over night. The solvent was removed under reduced pressure and the residue was purified by column chromatography. (PE:EtOAc 9:1 → 7:3 + 5% triethylamine)

((2*R*,2'*R*)-1'-(2-hydroxybenzyl)-[2,2'-bipyrrolidin]-1-yl)(pyridin-2-yl)methanon (Catalyst E)



$C_{21}H_{25}N_3O_2$
351,4421

The title compound was obtained as a yellowish solid (426.4 mg, 1.21 mmol, 70% over 2 steps).

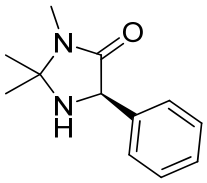
Two rotamers (ratio 8:2) were observed in the NMR-spectra.

R_f (PE:EtOAc = 7:3 + 5% Et_3N): 0.24 [UV, CAM, Ninhydrin]. **$[\alpha]^{20}_D$ =** +173.7 (c = 1.00, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 11.10 (br s, 1H), 8.61 – 8.58 (m, 0.8H), 8.58 – 8.55 (m, 0.2H), 7.88 – 7.76 (m, 2.0H), 7.42 – 7.37 (m, 0.2H), 7.36 – 7.31 (m, 0.8H), 7.18 – 7.12 (m, 1.0H), 7.04 – 7.00 (d, *J* = 7.3 Hz, 0.8H), 6.89 – 6.85 (d, *J* = 7.3 Hz, 0.2H), 6.82 – 6.72 (m, 2.0H), 5.29 – 5.24 (m, 0.2H), 4.73 – 4.66 (m, 0.8H), 4.55 – 4.49 (d, *J* = 14.0 Hz, 0.8H), 4.15 – 4.07 (m, 0.4H), 3.78 – 3.73 (m, 1.6H), 3.70 – 3.63 (m, 0.8H), 3.54 – 3.46 (m, 1.0H), 3.12 – 3.04 (m, 0.8H), 2.98 – 2.90 (m, 0.4H), 2.48 – 2.42 (m, 0.2H), 2.32 – 2.19 (m, 1.8H), 2.08 – 1.86 (m, 3.2H), 1.85 – 1.62 (m, 4.0H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$, major rotamer):** δ = 167.4, 157.7, 154.6, 148.2, 136.9, 128.6, 128.3, 124.9, 124.1, 122.7, 119.2, 115.9, 63.7, 58.8, 58.2, 54.6, 51.1, 25.6, 25.4, 25.2, 23.3 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3072, 3042, 2964, 2922, 2881, 2852, 2741, 2724, 2650, 1623, 1588, 1474, 1448, 1410, 1257, 1096, 756, 720. **LRMS (ESI):** *m*/z (%) 352 (100) [($M+H^+$)]. **HRMS (ESI):** *m*/z 352.2022 [352.2020 calculated for $C_{21}H_{26}N_3O_2^+$ ($M+H^+$)].

General procedure for the asymmetric organocatalytic reduction of aromatic imidazolinones

The imidazolinone (0.1 mmol) was placed in the reaction vessel. Successively, stock solutions of the catalyst (0.4 ml, 5.0 mM in chloroform, 0.02 eq.), acetic acid (0.4 ml, 0.5 M in chloroform, 2.0 eq.) and trichlorosilane (0.2 ml, 1.25 M in chloroform, 2.5 eq.) were added. After 24 h, methylene chloride, sodium bicarbonate solution (aq., sat., 1.6 ml) and sodium hydroxide solution (aq., 10%, 1.2 ml) were added. The organic layer was removed and the aqueous layer was extracted with methylene chloride. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified with column chromatography. (PE:EtOAc = 6:4 → 0:1).

(*R*)-2,2,3-Trimethyl-5-phenylimidazolidin-4-on (2a)



$C_{12}H_{16}N_2O$
204,2682

The title compound was obtained as a colourless viscous liquid (19.8 mg, 0.10 mmol, 97%, 96% *ee*).

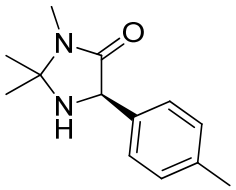
R_f (EtOAc): 0.26 [UV, Ninhydrin]. **R_f (EtOAc:MeOH = 9:1):** 0.35 [UV, Ninhydrin]. **$[\alpha]^{20}_D$** = -17.9 (c = 1.00, MeOH). **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 7.47 – 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 4.63 (s, 1H), 2.84 (d, *J* = 0.9 Hz, 3H), 2.16 (br s, 1H), 1.44 (s, 3H), 1.40 (s, 3H) ppm. **^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 172.5, 138.6, 128.7, 128.0, 127.7, 75.7, 62.2, 27.8, 25.7, 25.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3324, 3062, 3030, 2975, 2930, 1681, 1603, 1493, 1475, 1449, 1422, 1395, 1366, 1326, 1304, 1280, 1205, 1182, 1148, 1095, 1064, 1029, 1005, 980, 937, 917, 858, 806, 776, 753, 729, 696, 658, 632, 611, 561, 526. **LRMS (EI):** *m/z* (%) 189 (51) [M^+-CH_3], 146 (19),104 (14), 91 (14), 77 (12), 56 (100). **HRMS (ESI):** *m/z* 227.1153 [227.1155 calculated for $C_{12}H_{16}N_2NaO^+$ ($M+Na^+$)]. **HPLC** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 90:10; 220 nm) 96% *ee* (*R*-enantiomer t_r = 10.66 min; *S*-enantiomer t_r = 12.84 min).

Procedure for the asymmetric organocatalytic reduction of 1a on a scale of 1.0 mmol

1a (202.3 mg, 1.0 mmol) was placed in the reaction flask and stock solutions of the catalyst (4.0 ml, 5.0 mM in chloroform, 0.02 eq.), acetic acid (4.0 ml, 0.5 M in chloroform, 2.0 eq.), and trichlorosilane (2.0 ml, 1.25 M in chloroform, 2.5 eq.) were successively added. The reaction was stirred at room temperature for 24 h. Methylene chloride, sodium bicarbonate solution (aq., sat., 16.0 ml) and sodium hydroxide solution (aq., 10%, 12.0 ml) were added, the organic layer was removed and the aqueous layer was extracted with methylene chloride. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified with column chromatography. (PE:EtOAc = 6:4 → 0:1).

The title compound was obtained as a colourless viscous liquid (204.4 mg, 1.00 mmol, 99%, 94% *ee*).

(*R*)-2,2,3-Trimethyl-5-(*p*-tolyl)imidazolidin-4-on (2b)

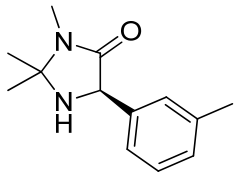


$C_{13}H_{18}N_2O$
218,2948

The title compound was obtained as a yellow viscous liquid (20.4 mg, 0.09 mmol, 93%, 96% *ee*).

R_f (EtOAc): 0.33 [UV, Ninhydrin]. **$[\alpha]^{20}_D$ =** -11.9 (c = 1.00, MeOH). **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 7.32 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 4.60 (s, 1H), 2.86 (s, 3H), 2.33 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 172.8, 137.7, 135.6, 129.4, 127.6, 75.6, 62.1, 27.8, 25.6, 25.5, 21.2 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3324, 2973, 2924, 1684, 1512, 1421, 1394, 1366, 1275, 1205, 1182, 1147, 1096, 1022, 1005, 980, 933, 850, 808, 774, 752, 705, 654, 642, 565, 518. **LRMS (EI):** *m/z* (%) 203 (100) [(M-CH_3)$^+$], 161 (31), 160 (25), 146 (12), 120 (18), 105 (17), 91 (10), 56 (45). **HRMS:** *m/z* 241.1313 [241.1311 calculated for $C_{13}H_{18}N_2ONa^+$ (M+Na^+)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 90:10; 220 nm) 96% *ee* (*R*-enantiomer t_r = 11.12 min; *S*-enantiomer t_r = 13.48 min).

(*R*)-2,2,3-Trimethyl-5-(*m*-tolyl)imidazolidin-4-on (2c)

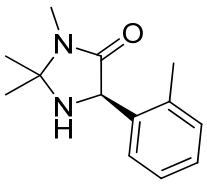


$C_{13}H_{18}N_2O$
218,2948

The title compound was obtained as a colourless viscous liquid (22.4 mg, 0.10 mmol, quant., 96% *ee*).

R_f (EtOAc): 0.33 [UV, Ninhydrin]. **$[\alpha]^{20}_D$ =** -18.0 (c = 1.00, MeOH). **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 7.25 – 7.16 (m, 4H), 4.59 (s, 1H), 2.86 (s, 3H), 2.35 (s, 3H), 1.47 (s, 3H), 1.41 (s, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 172.8, 138.4, 138.4, 128.8, 128.7, 128.4, 124.8, 75.7, 62.4, 27.7, 25.6, 25.6, 21.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3324, 2974, 2924, 2856, 1685, 1608, 1422, 1395, 1366, 1328, 1278, 1253, 1206, 1148, 1096, 1002, 980, 938, 810, 749, 696, 663, 636, 618, 574, 539, 507, 437. **LRMS (EI):** *m/z* (%) 203 (97) [(M- CH_3)$^+$], 161 (26), 160 (25), 146 (14), 120 (18), 105 (17), 91 (18), 56 (100). **HRMS:** *m/z* 241.1307 [241.1311 calculated for $C_{13}H_{18}N_2ONa^+$ (M+Na^+)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 90:10; 220 nm) 96% *ee* (*R*-enantiomer t_r = 9.89 min; *S*-enantiomer t_r = 12.54 min).

(*R*)-2,2,3-Trimethyl-5-(*o*-tolyl)imidazolidin-4-on (2d)



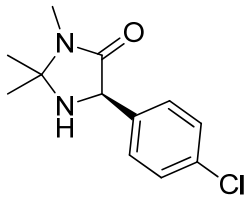
$C_{13}H_{18}N_2O$
218,2948

The reaction was carried out at a longer reaction time of 48 h.

The title compound was obtained as a colourless viscous liquid (9.6 mg, 0.04 mmol, 44%, 64% *ee*).

R_f (EtOAc): 0.30 [UV, Ninhydrin]. **$[\alpha]^{20}_D$ =** +35.7 (c = 0.08, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.25 – 7.17 (m, 4H), 4.82 (s, 1H), 2.90 (d, *J* = 0.6 Hz, 3H), 2.45 (s, 3H), 1.48 (s, 3H), 1.41 (s, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 173.3, 137.6, 136.7, 130.8, 128.2, 127.6, 126.6, 75.7, 60.0, 27.6, 25.6, 25.3, 19.4 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3324, 2971, 2924, 2853, 1685, 1605, 1463, 1422, 1395, 1367, 1278, 1254, 1208, 1181, 1149, 1095, 1072, 1050, 1006, 980, 936, 859, 806, 746, 725, 659, 632, 614, 576, 560, 501, 447. **LRMS (EI):** *m/z* (%) 203 (34) [(M- CH_3)$^+$], 160 (61), 146 (22), 118 (17), 104 (21), 91 (19), 56 (100). **HRMS:** *m/z* 241.1314 [241.1311 calculated for $C_{13}H_{18}N_2ONa^+$ (M+Na^+)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 90:10; 220 nm) 64% *ee* (*R*-Enantiomer t_r = 8.31 min; *S*-Enantiomer t_r = 8.85 min).

(*R*)-5-(4-Chlorophenyl)-2,2,3-trimethylimidazolidin-4-on (2e)

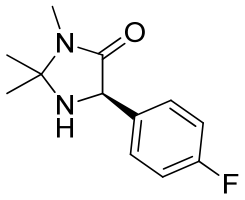


$C_{12}H_{15}ClN_2O$
238,7133

The title compound was obtained as a yellow viscous liquid (22.8 mg, 0.10 mmol, 96%, 94% *ee*).

R_f (EtOAc): 0.28 [UV, Ninhydrin]. **$[\alpha]^{20}_D$ =** -36.8 (c = 0.72, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.47 – 7.42 (m, 2H), 7.34 – 7.29 (m, 2H), 4.64 (s, 1H), 2.84 (d, *J* = 0.7 Hz, 3H), 1.43 (s, 3H), 1.43 (s, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 171.9, 137.2, 133.8, 128.9, 128.8, 75.8, 61.3, 28.0, 26.0, 25.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3324, 2973, 2926, 1680, 1596, 1488, 1422, 1396, 1367, 1334, 1290, 1271, 1251, 1206, 1182, 1148, 1086, 1014, 981, 933, 911, 848, 821, 799, 772, 696, 651, 634, 568, 546, 497, 455. **LRMS (EI):** *m/z* (%) 223 (50) [(M- CH_3)$^+$], 181 (20), 138 (11), 125 (11), 89 (10), 56 (100). **HRMS (ESI):** *m/z* 267.0768 [267.0765 calculated for $C_{12}H_{15}ClN_2ONa^+$ (M+Na^+)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 90:10; 220 nm) 94% *ee* (*R*-enantiomer t_r = 11.02 min; *S*-enantiomer t_r = 15.41 min).

(*R*)-5-(4-Fluorophenyl)-2,2,3-trimethylimidazolidin-4-on (2f)

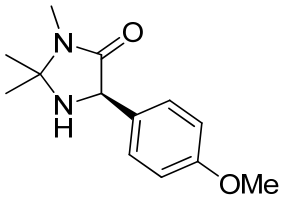


$C_{12}H_{15}FN_2O$
222,2587

The title compound was obtained as a colourless viscous liquid (21.5 mg, 0.10 mmol, 97%, 96% *ee*).

R_f (EtOAc): 0.27 [UV, Ninhydrin]. **$[\alpha]^{20}_D$ =** -23.9 (c = 1.00, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.49 – 7.43 (m, 2H), 7.08 – 7.00 (m, 2H), 4.64 (s, 1H), 2.85 (d, *J* = 0.6 Hz, 3H), 1.44 (s, 3H), 1.43 (s, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 172.19, 162.52 (d, *J* = 246.0 Hz), 134.43 (d, *J* = 3.2 Hz), 129.26 (d, *J* = 8.1 Hz), 115.47 (d, *J* = 21.6 Hz), 75.66, 61.30, 27.94, 25.78, 25.50 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3324, 2975, 2927, 1682, 1604, 1506, 1475, 1423, 1396, 1367, 1331, 1279, 1217, 1182, 1152, 1096, 1079, 1015, 980, 933, 835, 787, 701, 656, 637, 599, 565, 522. **LRMS (EI):** *m/z* (%) 207 (60) [(M- CH_3)$^+$], 165 (21), 122 (23), 109 (21), 56 (100). **HRMS (ESI):** *m/z* 245.1057 [245.1061 calcuated for $C_{12}H_{15}FN_2ONa^+$ ($M+Na^+$)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 90:10; 220 nm) 96% *ee* (*R*-enantiomer t_r = 9.95 min; *S*-enantiomer t_r = 13.59 min).

(*R*)-5-(4-Methoxyphenyl)-2,2,3-trimethylimidazolidin-4-on (2g)



$C_{13}H_{18}N_2O_2$
234,2942

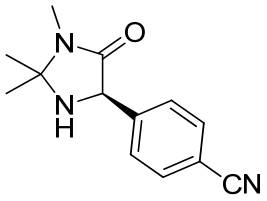
The reaction was carried out at an elevated temperature of 45 °C.

The title compound was obtained as a colourless viscous liquid (20.1 mg, 0.09 mmol, 86%, 95% *ee*).

R_f (EtOAc): 0.25 [UV, Ninhydrin]. **$[\alpha]^{20}_D$ =** -9.0 (c = 0.74, MeOH). **^{1}H-NMR (600 MHz, $CDCl_3$):** δ = 7.37 – 7.33 (m, 2H), 6.91 – 6.87 (m, 2H), 4.61 (s, 1H), 3.79 (s, 3H), 2.86 (d, *J* =

0.7 Hz, 3H), 1.46 (s, 3H), 1.42 (s, 3H) ppm.**^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 173.0, 159.6, 130.6, 129.0, 114.3, 75.6, 61.9, 55.4, 29.8, 27.8, 25.6 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3320, 2971, 2927, 2837, 1683, 1611, 1585, 1510, 1462, 1421, 1395, 1366, 1288, 1243, 1207, 1177, 1148, 1095, 1030, 980, 933, 907, 828, 810, 785, 709, 656, 639, 587, 567, 534. **LRMS (EI):** *m/z* (%) 234 (6) [M^+], 219 (40) [(M- $CH_3)^+$], 177 (24), 136 (20), 121 (25), 77 (10), 56 (100). **HRMS (ESI):** *m/z* 235.1440 [235.1441 calculated for $C_{13}H_{19}N_2O_2^+$ ($M+H^+$)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 90:10; 220 nm) 95% *ee* (*R*-enantiomer t_r = 22.32 min; *S*-enantiomer t_r = 26.66 min).

(*R*)-4-(1,2,2-Trimethyl-5-oxoimidazolidin-4-yl)benzonitril (2h)

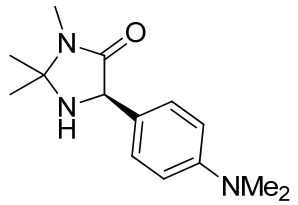


$C_{13}H_{15}N_3O$
229,2777

The title compound was obtained as a colourless viscous liquid (22.5 mg, 0.10 mmol, 98%, 90% *ee*).

R_f (EtOAc): 0.31 [UV, Ninhydrin]. **$[\alpha]^{20}_D$ =** -45.5 (c = 1.00, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.74 – 7.70 (m, 2H), 7.66 – 7.62 (m, 2H), 4.77 (s, 1H), 2.83 (d, *J* = 0.6 Hz, 3H), 1.48 (s, 3H), 1.42 (s, 3H) ppm. **^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 170.7, 144.4, 132.2, 128.0, 119.0, 111.6, 76.0, 61.0, 28.3, 26.4, 25.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3336, 2976, 2929, 2227, 1684, 1608, 1501, 1475, 1424, 1398, 1367, 1338, 1278, 1208, 1183, 1148, 1097, 1020, 980, 935, 855, 831, 748,708, 665, 645, 592, 552, 501. **LRMS (EI):** *m/z* (%) 214 (55) [(M- $CH_3)^+$], 172 (20), 129 (9), 116 (10), 56 (100). **HRMS (ESI):** *m/z* 230.1292 [230.1288 calculated for $C_{13}H_{16}ClN_3O^+$ ($M+H^+$)]. **HPLC:** (Chiralpak IA; flow: 0.8 ml/min; Heptane:EtOH = 80:20; 220 nm) 90% *ee* (*R*-enantiomer t_r = 11.84 min; *S*-enantiomer t_r = 16.43 min).

(*R*)-5-(4-(Dimethylamino)phenyl)-2,2,3-trimethylimidazolidin-4-on (2i)



$C_{14}H_{21}N_3O$
247,3360

The reaction was carried out at an elevated temperature of 45 °C and with 10 mol% of catalyst.

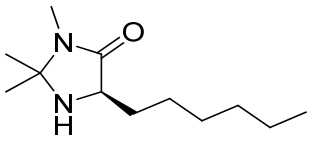
The title compound was obtained as a yellow viscous liquid (14.3 mg, 0.06 mmol, 58%, 86% *ee*).

R_f (EtOAc:MeOH = 95:5): 0.23 [Ninhydrin]. **$[\alpha]^{20}_D$ =** -13.8 (c = 0.50, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.27 – 7.21 (m, 2H), 6.74 – 6.67 (m, 2H), 4.53 (s, 1H), 2.93 (s, 6H), 2.86 (s, 3H), 1.46 (s, 3H), 1.39 (s, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 173.6, 150.6, 128.7, 126.2, 113.0, 75.4, 62.2, 40.7, 27.71, 25.7, 25.5 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3324, 2972, 2923, 2800, 1684, 1614, 1567, 1520, 1476, 1444, 1420, 1393, 1347, 1284, 1211, 1188, 1164, 1147, 1095, 1062, 1008, 980, 946, 906, 864, 811, 778, 725, 655, 640, 613, 566, 530. **LRMS (EI):** *m/z* (%) 247 (50) [M^+], 232 (13) [$(M- CH_3)^+$], 190 (50), 175 (13), 148 (100), 134 (74), 116 (18), 95 (12), 72 (22), 56 (88). **HRMS (ESI):** *m/z* 248.1758 [248.1757 calculated for $C_{14}H_{22}N_3O^+$ ($M+H^+$)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:^{i}PrOH = 80:20; 220 nm) 86%*ee* (*R*-enantiomer t_r = 9.77 min; *S*-enantiomer t_r = 13.62 min).

General Procedure for the asymmetric organocatalytic reduction of aliphatic imidazolinones

The imidazolinone (0.1 mmol) was placed in the reaction vessel and solved in chloroform (9.0 ml). Successively, stock solutions of the catalyst (0.4 ml, 25.0 mM in chloroform, 0.10 eq.), additive (0.4 ml, 0.5 M in chloroform, 2.0 eq.) and trichlorosilane (0.2 ml, 1.25 M in chloroform, 2.5 eq.) were added. After 24 h, methylene chloride, sodium bicarbonate solution (aq., sat., 1.6 ml) and sodium hydroxide solution (aq., 10%, 1.2 ml) were added. The organic layer was removed and the aqueous layer was extracted twice with methylene chloride. The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified with column chromatography. (PE:EtOAc 6:4 → 0:1 → EtOAc:MeOH 9:1).

(*R*)-5-Hexyl-2,2,3-trimethylimidazolidin-4-on (2j)

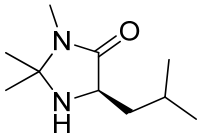


$C_{12}H_{24}N_2O$
212,3318

The title compound was obtained as a colourless viscous liquid (21.3 mg, 0.10 mmol, quant., 96% *ee*).

R_f (EtOAc:MeOH = 95:5): 0.32 [Ninhydrin]. **$[\alpha]^{20}_D$ =** +10.1 (c = 1.00, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 3.47 (dd, *J* = 7.8, 3.8 Hz, 1H), 2.79 (s, 3H), 1.96 (ddt, *J* = 10.4, 8.1, 4.2 Hz, 1H), 1.52 – 1.39 (m, 3H), 1.42 (s, 3H), 1.39 – 1.24 (m, 7H), 1.31 (s, 3H), 0.93 – 0.85 (m, 3H) ppm. **^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 174.7, 75.6, 58.6, 32.6, 31.8, 29.3, 27.6, 26.2, 25.3, 25.1, 22.7, 14.2 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3325, 2955, 2925, 2856, 1682, 1423, 1396, 1366, 1266, 1205, 1150, 1079, 1043, 1000, 971, 885, 819, 767, 725, 662, 618, 587, 552, 505. **LRMS (ESI):** *m/z* (%) 213 (100) [$(M+H^+)$]. **HRMS (ESI):** *m/z* 213.1965 [213.1961 calcuated for $C_{12}H_{25}N_2O^+$ $(M+H^+)$]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 95:5; 220 nm) 93% *ee* (*R*-enantiomer t_r = 9.50 min; *S*-enantiomer t_r = 10.65 min).

(*R*)-5-Isobutyl-2,2,3-trimethylimidazolidin-4-one (2k)



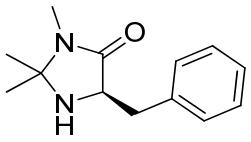
$C_{10}H_{20}N_2O$
184,2786

The title compound was obtained as a yellowish viscous liquid (19.7 mg, 0.10 mmol, quant., 93% *ee*).

R_f (EtOAc:MeOH = 95:5): 0.30 [Ninhydrin]. **$[\alpha]^{20}_D$ =** +9.3 (c = 1.00, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 3.48 (dd, *J* = 9.9, 3.2 Hz, 1H), 2.78 (s, 3H), 1.90 – 1.76 (m, 2H), 1.41 (s, 3H), 1.30 (s, 3H), 0.96 (dd, *J* = 8.1, 6.2 Hz, 6H), 0.91 – 0.77 (m, 1H) ppm. **^{13}C-NMR (151 MHz, $CDCl_3$):** δ = 175.2, 75.7, 56.8, 42.0, 27.6, 25.5, 25.4, 24.9, 23.5, 21.7 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3325, 2955, 2928, 2869, 1681, 1468, 1423, 1396, 1366, 1307, 1267, 1205, 1151, 1079, 1008, 979, 930, 889, 801, 750, 666, 620, 587, 552, 505. **LRMS (EI):** *m/z* (%) 169 (75) [$(M- CH_3)^+$], 127 (8), 84 (12), 72 (9), 56 (100). **HRMS (ESI):** *m/z* 185.1649 [185.1648

calcuated for $C_{10}H_{21}N_2O^+$ ($M+H^+$)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 95:5; 220 nm) 93% *ee* (*R*-Enantiomer t_r = 9.36 min; *S*-Enantiomer t_r = 10.84 min).

(*R*)-5-Benzyl-2,2,3-trimethylimidazolidin-4-on (2l)



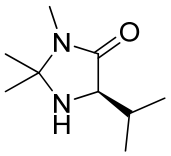
$C_{13}H_{18}N_2O$
218,29

The title compound was obtained as a colourless viscous liquid (22.2 mg, 0.10 mmol, quant., 84% *ee*).

R_f (EtOAc:MeOH = 95:5): 0.32 [Ninhydrin]. **$[\alpha]^{20}_D$ =** +69.3 (c = 0.50, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.32 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 3.81 – 3.76 (m, 1H), 3.14 (dd, *J* = 14.2, 4.4 Hz, 1H), 3.00 (dd, *J* = 14.2, 6.9 Hz, 1H), 2.75 (d, *J* = 0.6 Hz, 3H), 1.25 (s, 3H), 1.15 (s, 3H). ppm. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 95:5; 220 nm) 84% *ee* (*R*-Enantiomer t_r = 13.65 min; *S*-Enantiomer t_r = 13.05 min).

The analytical data are in agreement with the literature.[5]

(*R*)-5-Isopropyl-2,2,3-trimethylimidazolidin-4-one (2m)



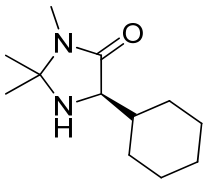
$C_9H_{18}N_2O$
170,2520

The title compound was obtained as a yellowish viscous liquid (12.4 mg, 0.07 mmol, 73%, 96% *ee*).

R_f (EtOAc:MeOH = 95:5): 0.29 [Ninhydrin]. **$[\alpha]^{20}_D$ =** +27.2 (c = 0.23, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 3.46 – 3.42 (m, 1H), 2.76 (d, *J* = 0.7 Hz, 3H), 2.17 (pd, *J* = 6.9, 4.0 Hz, 1H), 1.39 (s, 3H), 1.29 (s, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 173.7, 75.2, 63.4, 29.1, 27.6, 25.5, 25.1, 19.5, 16.9 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3337, 2965, 2932, 2872, 1676, 1468, 1425, 1398, 1383, 1366, 1281, 1261, 1203, 1179, 1154, 1045, 766, 653, 612, 559, 513. **LRMS (EI):** *m/z* (%) 155 (57) [M^+-CH_3], 127 (20), 113 (13), 98 (10), 72 (12), 56 (100). **HRMS (ESI):** *m/z* 171.1487 [171.1492

calculated for $C_9H_{19}N_2O^+$ ($M+H^+$)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 95:5; 220 nm) 96% *ee* (*R*-enantiomer t_r = 8.54 min; *S*-enantiomer t_r = 13.55 min).

(*R*)-5-Cyclohexyl-2,2,3-trimethylimidazolidin-4-one (2n)



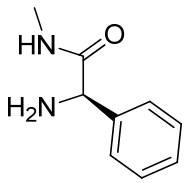
$C_{12}H_{22}N_2O$
210,3159

The title compound was obtained as a yellowish viscous liquid (20.2 mg, 0.10 mmol, 96%, 96% *ee*).

R_f (EtOAc:MeOH = 95:5): 0.32 [Ninhydrin]. **$[\alpha]^{20}_D$ =** +12.0 (c = 1.00, MeOH). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 3.42 (d, *J* = 3.8 Hz, 1H), 2.76 (s, 3H), 1.84 – 1.70 (m, 5H), 1.69 – 1.63 (m, 1H), 1.55 – 1.48 (m, *J* = 12.8 Hz, 1H), 1.38 (s, 3H), 1.29 (s, 3H), 1.26 – 1.08 (m, 4H). **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 173.7, 75.3, 63.0, 39.1, 30.2, 27.6, 27.3, 26.6, 26.4, 26.2, 25.5, 25.2 ppm. **IR (film):** ν_{max} [cm^{-1}] = 3337, 2971, 2922, 2851, 1679, 1448, 1423, 1396, 1364, 1320, 1263, 1204, 1181, 1152, 1099, 1074, 1008, 982, 892, 813, 792, 754, 676, 643, 587, 558, 534, 496. **LRMS (ESI):** *m/z* (%) 211 (100) [($M+H^+$)]. **HRMS (ESI):** *m/z* 211.1806 [211.1805 calcuated for $C_{12}H_{23}N_2O^+$ ($M+H^+$)]. **HPLC:** (Chiralpak IA; flow: 1.0 ml/min; Heptane:EtOH = 95:5; 220 nm) 96% *ee* (*R*-enantiomer t_r = 9.84 min; *S*-enantiomer t_r = 13.22 min).

Synthesis of amino acid derivatives

Liberation of D-phenylglycine methyl amide (5)



$C_9H_{12}N_2O$
164,20

2a (53.1 mg, 0.26 mmol, 94% *ee*) was dissolved in toluene (0.76 ml). Acetic acid (1.0 ml) and hydrochloric acid (1 M, 4.0 ml) were added, and the resulting mixture was stirred under

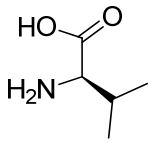
microwave radiation at 100 °C for 1 h. The reaction mixture was cooled to 0 °C and, under continuous stirring, methylene chloride and NaOH (1.5 g, in small portions) were added. The aqueous phase was extracted with methylene chloride. The combined organic phases were dried over $MgSO_4$, filtrated, and the solvent was removed under reduced pressure. The crude product was purified with column chromatography. (PE:EtOAc 1:1 → 0:1 → EtOAc:MeOH 9:1). The determination of the enantiomeric excess was accomplished after derivatisation according to literature.[6]

The title compound was obtained as a yellowish viscous liquid (27.4 mg, 0.17 mmol, 64%, 93% *ee*).

R_f (EtOAc:MeOH = 9:1): 0.20 [UV, Ninhydrin]. **^{1}H-NMR (400 MHz, $CDCl_3$):** δ = 7.40 – 7.27 (m, 5H), 7.05 (br s, 1H), 4.52 (s, 1H), 2.80 (d, *J* = 5.0 Hz, 3H), 2.20 (br s, 2H) ppm. **^{13}C-NMR (101 MHz, $CDCl_3$):** δ = 173.6, 141.1, 128.9, 128.1, 127.0, 59.9, 26.2 ppm. **HPLC:** (Kromasil RP 18; flow: 0.6 ml/min; ACN:TFA (0.1%, aq.) = 50:50 → 80:20 (60 min); 254 nm) 93% *ee* (*R*-enantiomer t_r = 24.11 min; *S*-enantiomer t_r = 27.84 min).

The analytical data are in agreement with the literature.[7]

Liberation of D-valine (4)



$C_5H_{11}NO_2$
117,08

2m (350.4 mg, 2.0 mmol, >99% *ee*) was dissolved in toluene (4.5 ml). Acetic acid (7.2 ml) and hydrochloric acid (conc., 28.6 ml) were added, and the resulting mixture was stirred at 105 °C for 42 h. The reaction mixture was cooled to room temperature and the crude product was purified with an ion exchange resin (DOWEX® 50W8-100) which was filled in a column. The acidic reaction mixture was poured onto the resin and it was flushed with water (dist.), ethanol, and again with water until an almost neutral pH-value could be measured. Afterwards, the column was flushed with ammonia solution (aq., 10%) until thin layer chromatography showed no positive result to staining with ninhydrin. The determination of the enantiomeric excess was accomplished after derivatisation according to literature.[6]

The title compound was obtained as a white solid (149.5 mg, 1.28 mmol, 64%, 99% *ee*).

^{1}H-NMR (400 MHz, D_2O): δ = 3.62 (d, *J* = 2.2 Hz, 1H), 2.33 – 2.25 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H) ppm. **HPLC:** (Kromasil RP 18; flow: 0.6 ml/min; ACN:TFA (0.1%, aq.) = 50:50 → 80:20 (60 min); 254 nm) 99% *ee* (*R*-enantiomer t_r = 22.27 min; *S*-enantiomer t_r = 35.31 min).

The analytical data are in agreement with the literature.[8]

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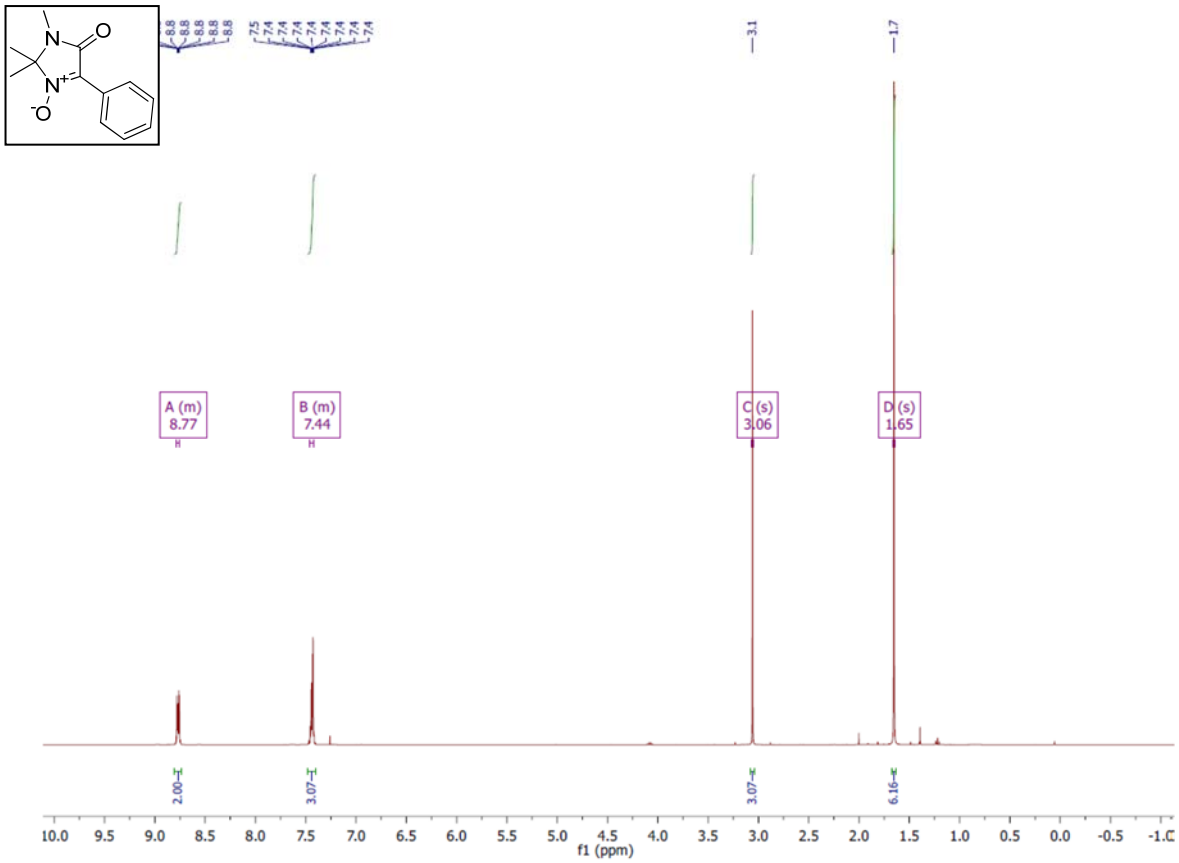
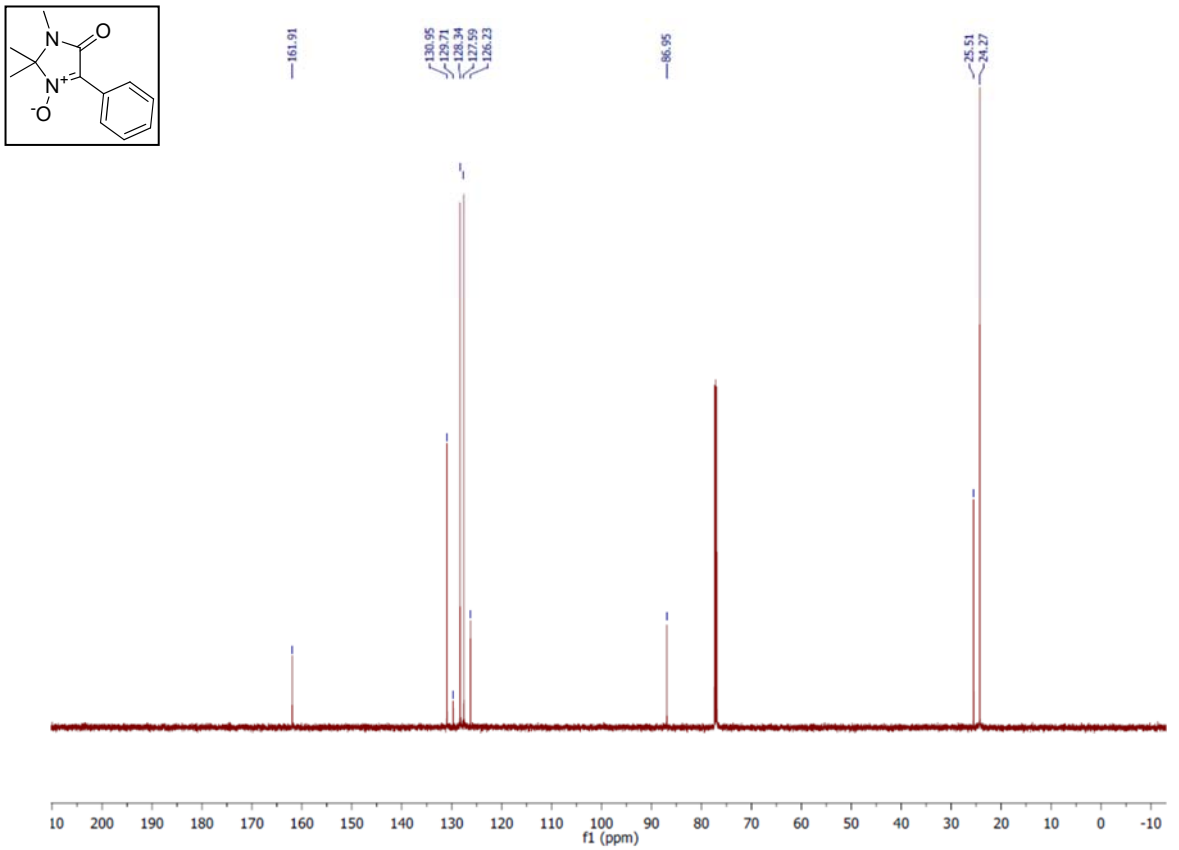
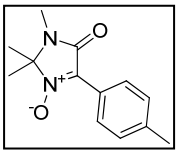
Copies of ^{1}H and ^{13}C NMR Spectra and HPLC Chromatograms

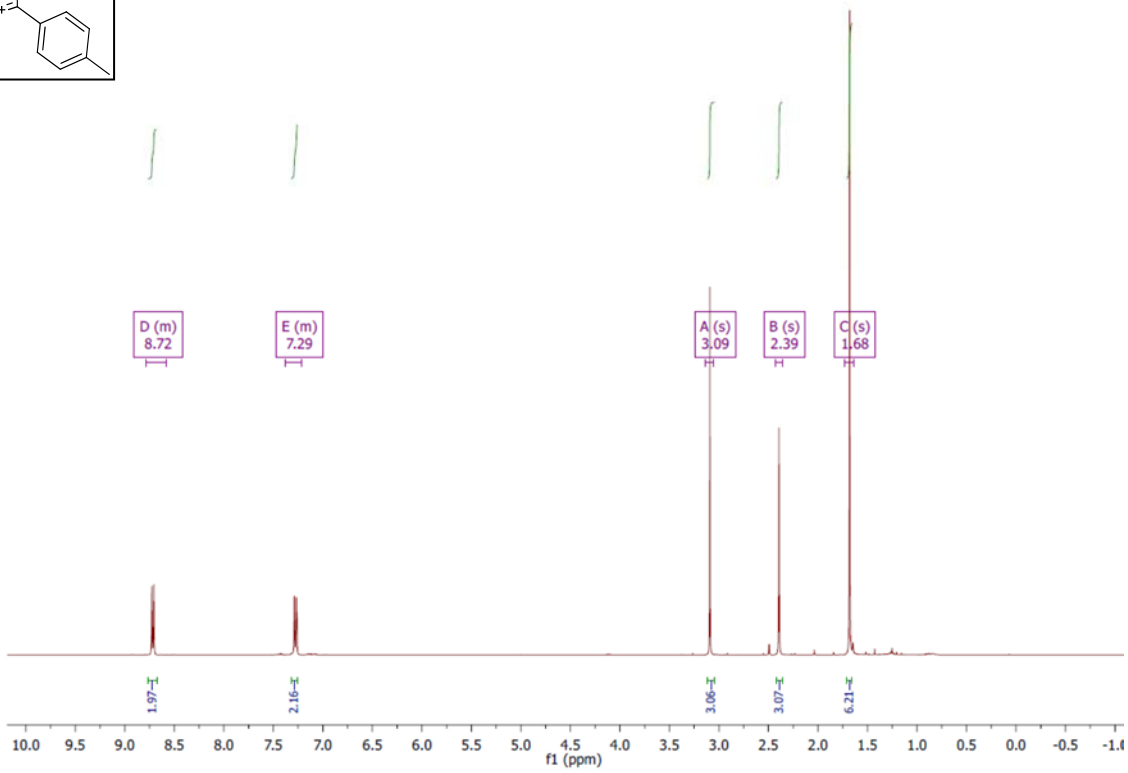
1,2,2-Trimethyl-5-oxo-4-phenyl-2,5-dihydro-1*H*-imidazole 3-oxide

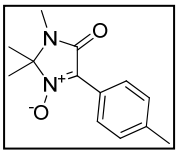




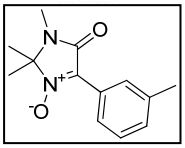
1,2,2-Trimethyl-5-oxo-4-(*p*-tolyl)-2,5-dihydro-1*H*-imidazole 3-oxide

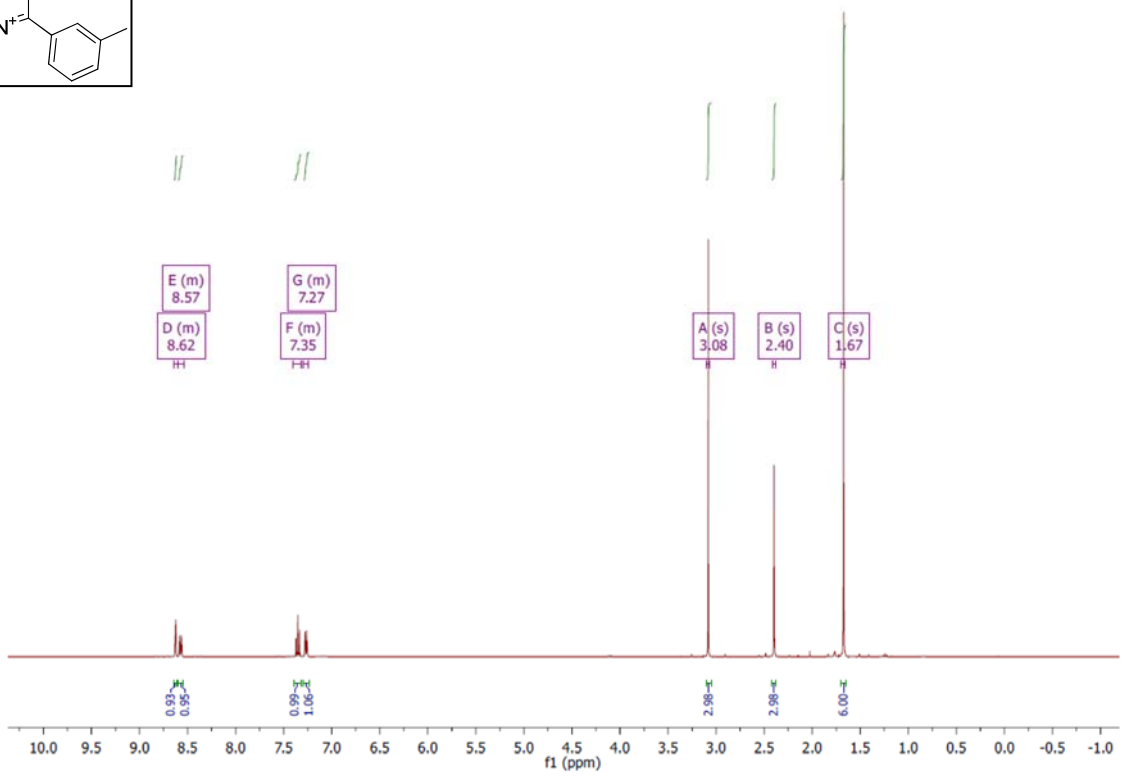


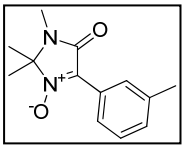




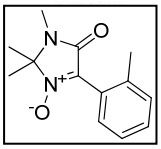
1,2,2-Trimethyl-5-oxo-4-(*m*-tolyl)-2,5-dihydro-1*H*-imidazole 3-oxide

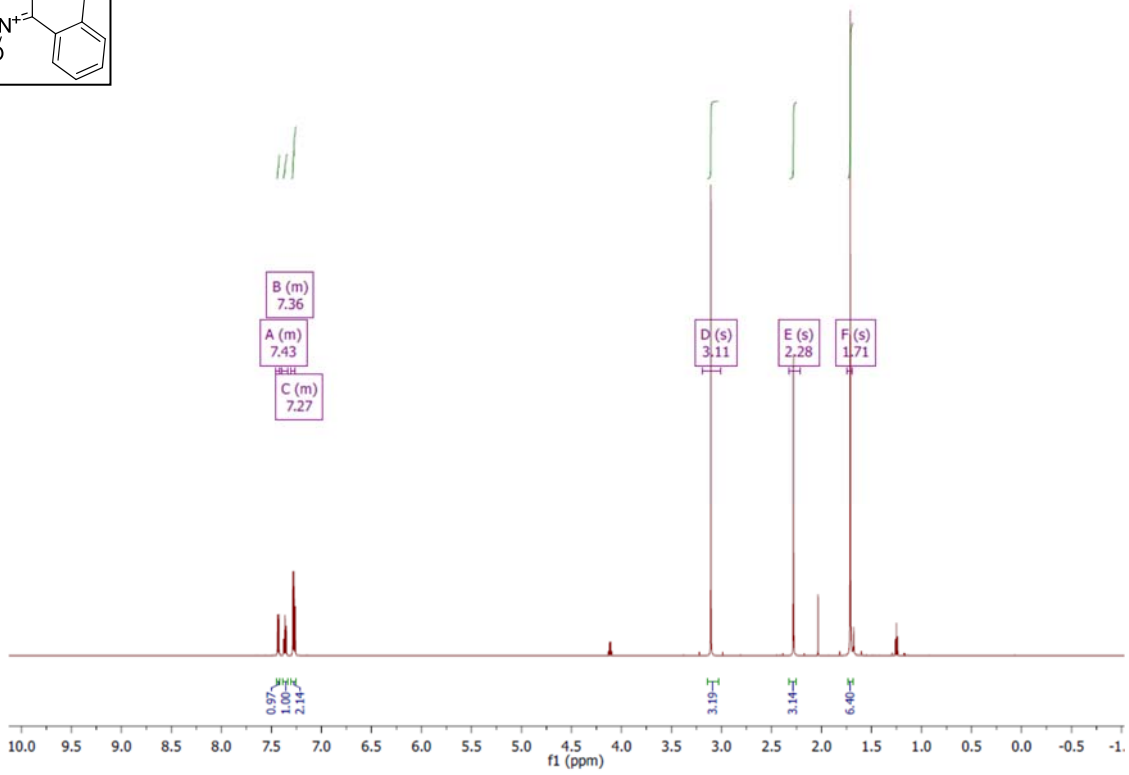


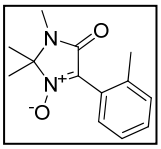




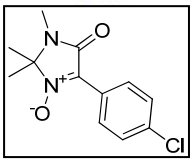
1,2,2-Trimethyl-5-oxo-4-(*o*-tolyl)-2,5-dihydro-1*H*-imidazole 3-oxide

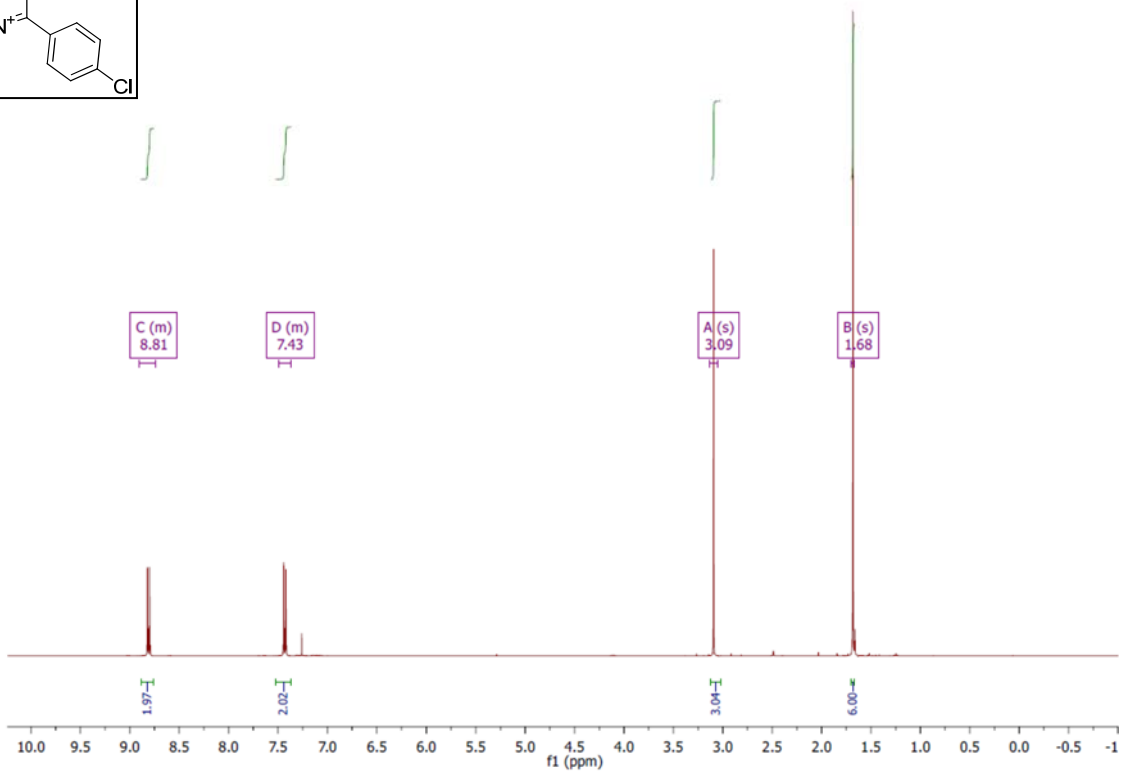


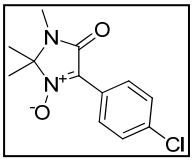




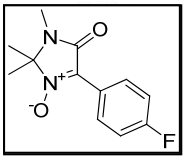
4-(4-Chlorophenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazole 3-oxide

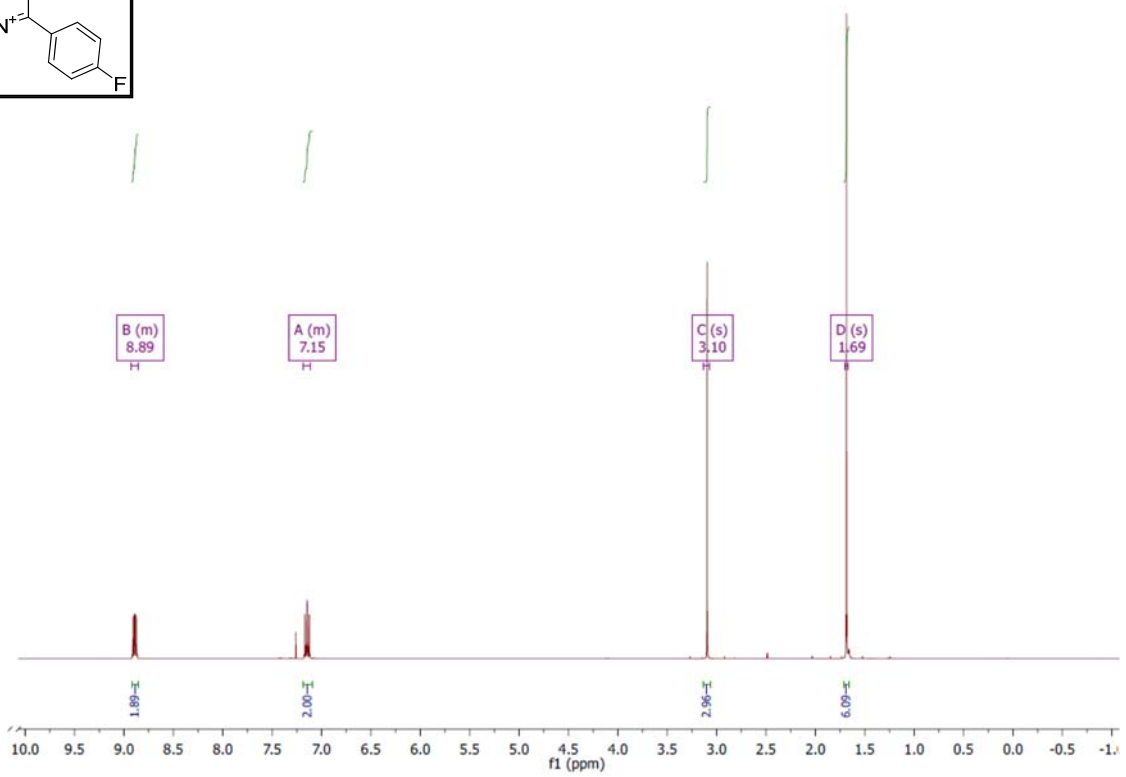


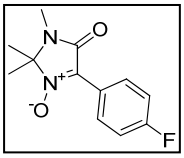


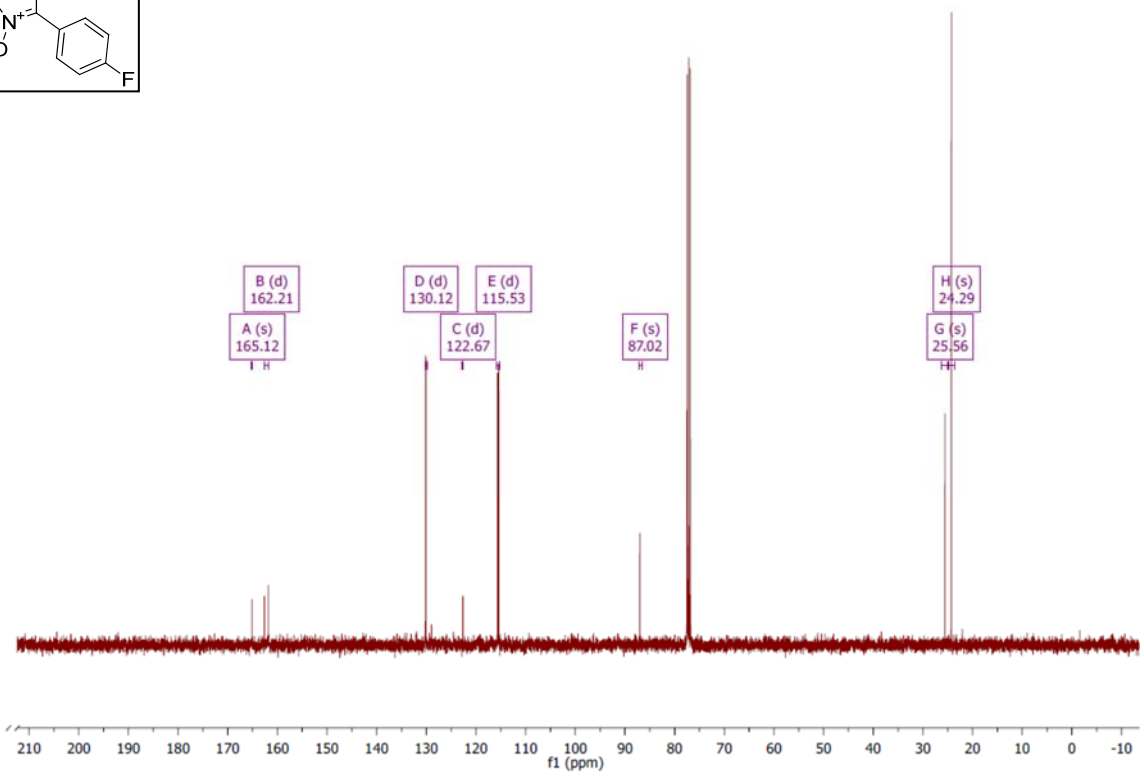


5-(4-Fluorophenyl)-2,2,3-trimethylimidazolidin-4-on

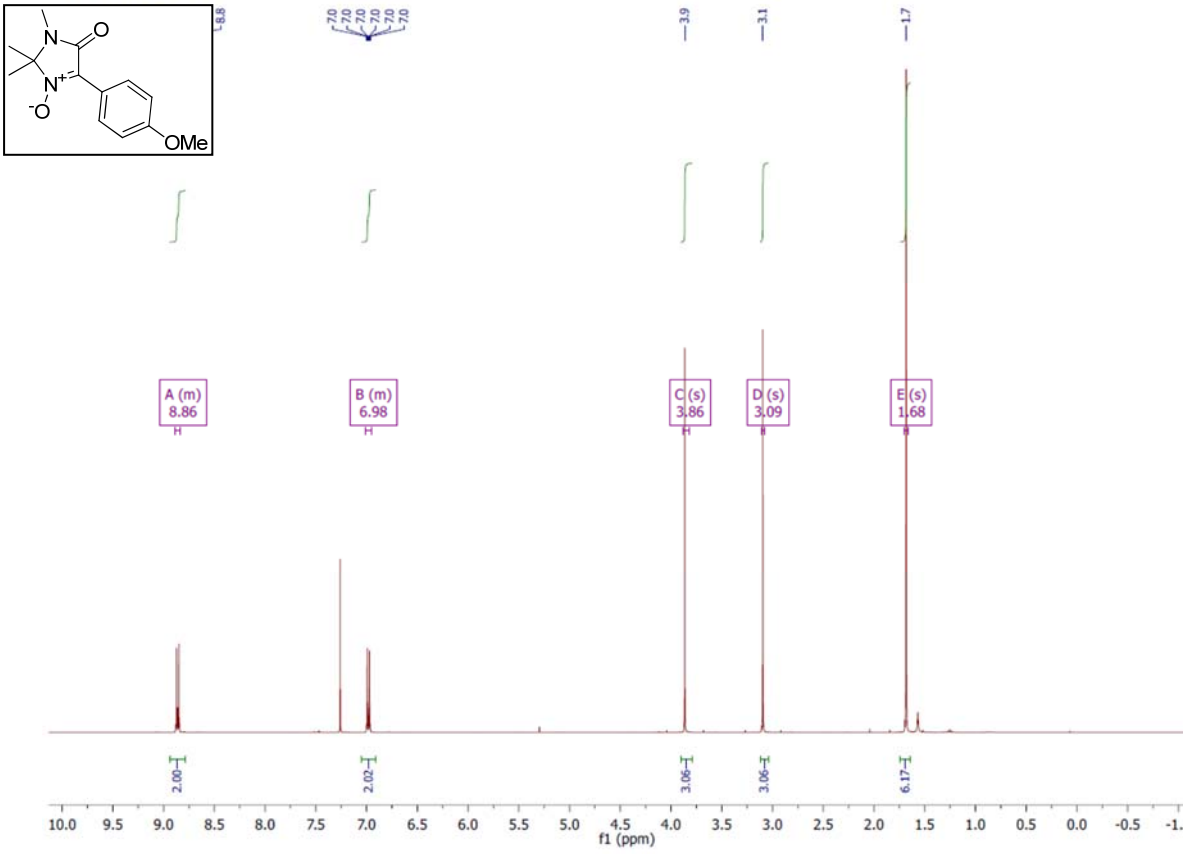


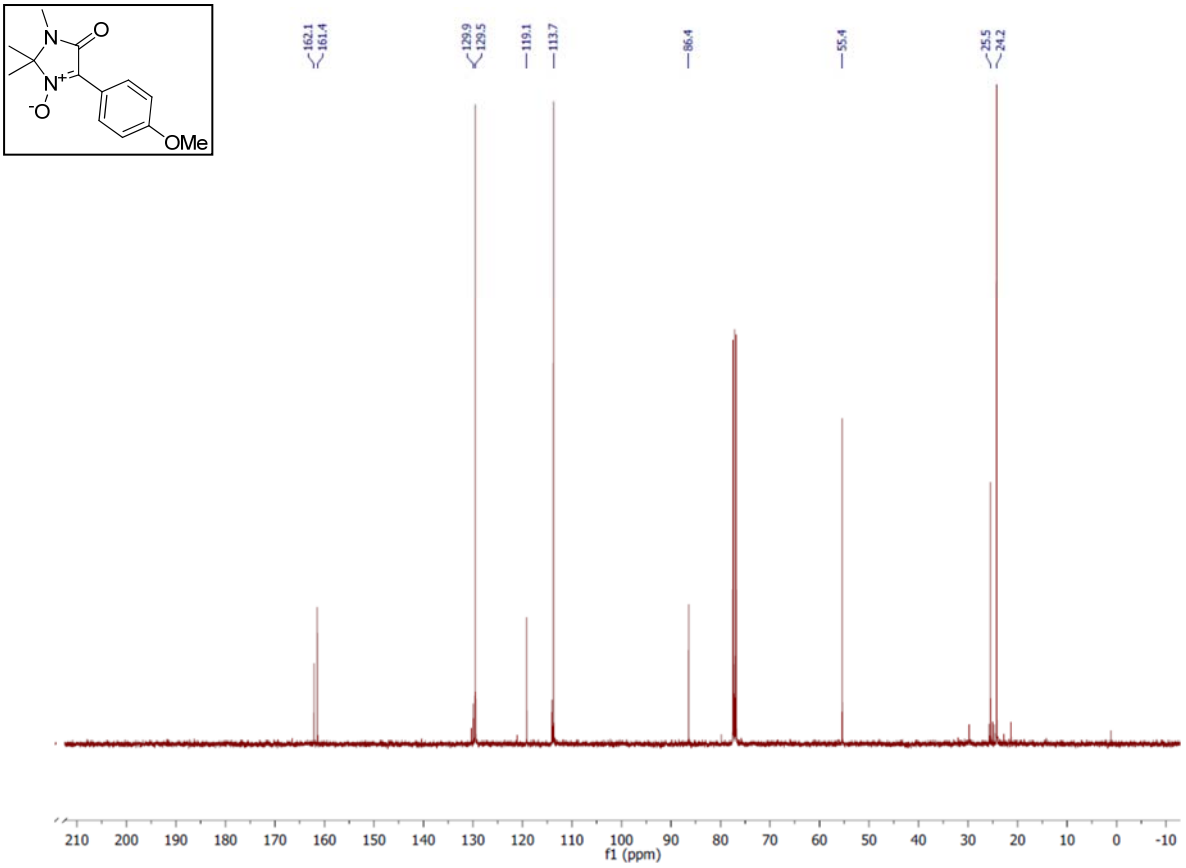




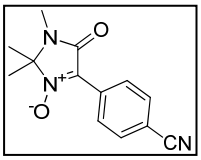


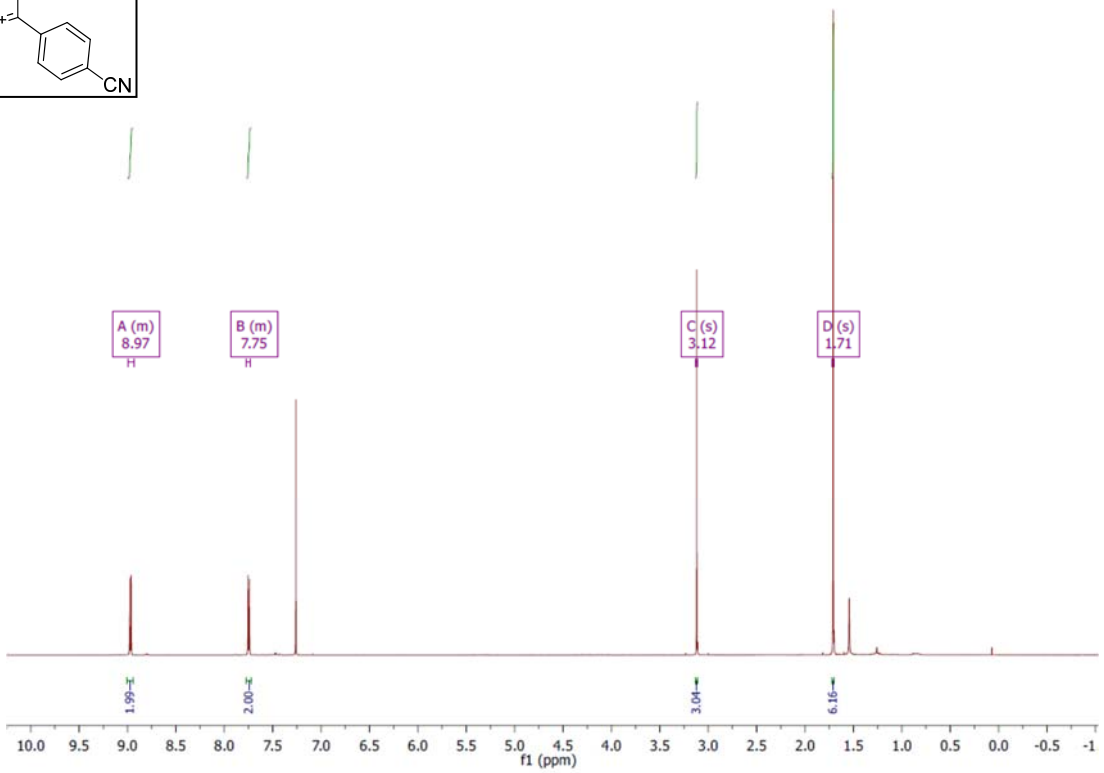
4-(4-Methoxyphenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazole 3-oxide

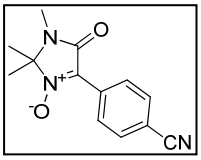




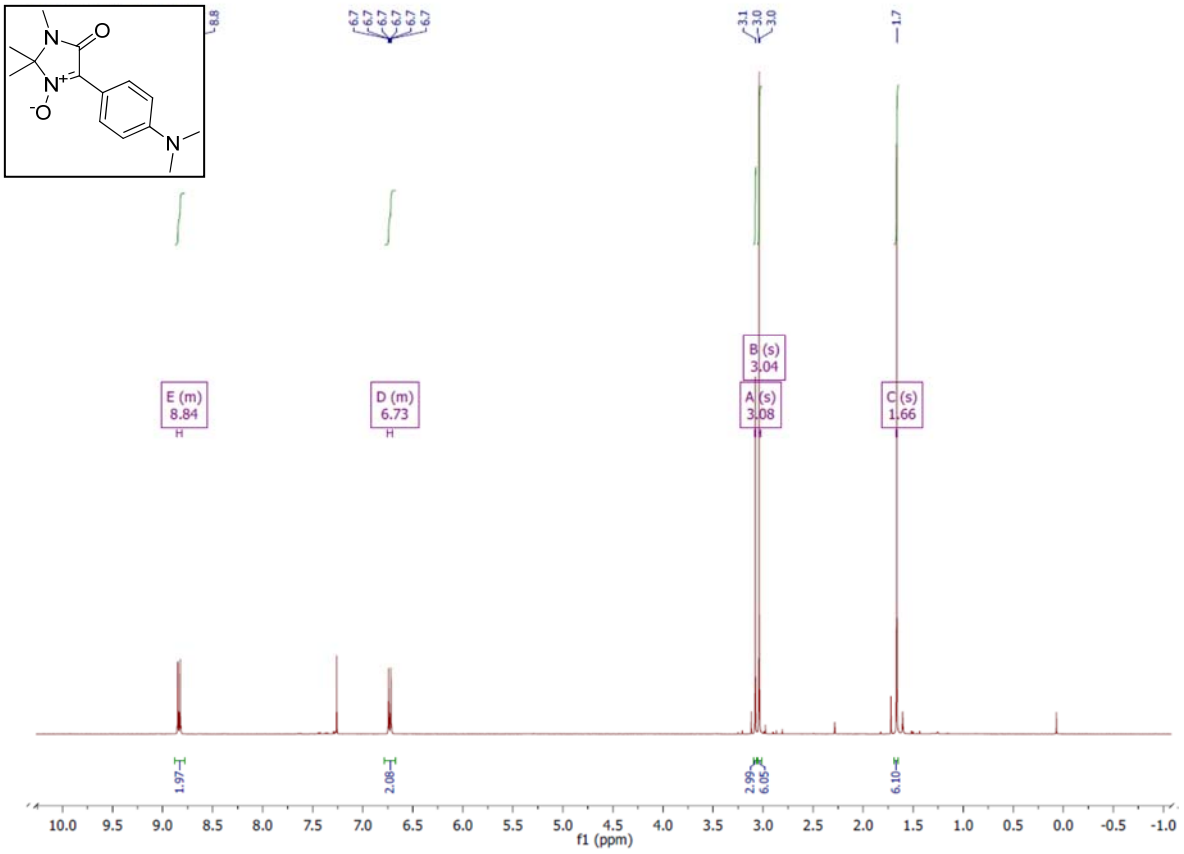
4-(4-Cyanophenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazole 3-oxide

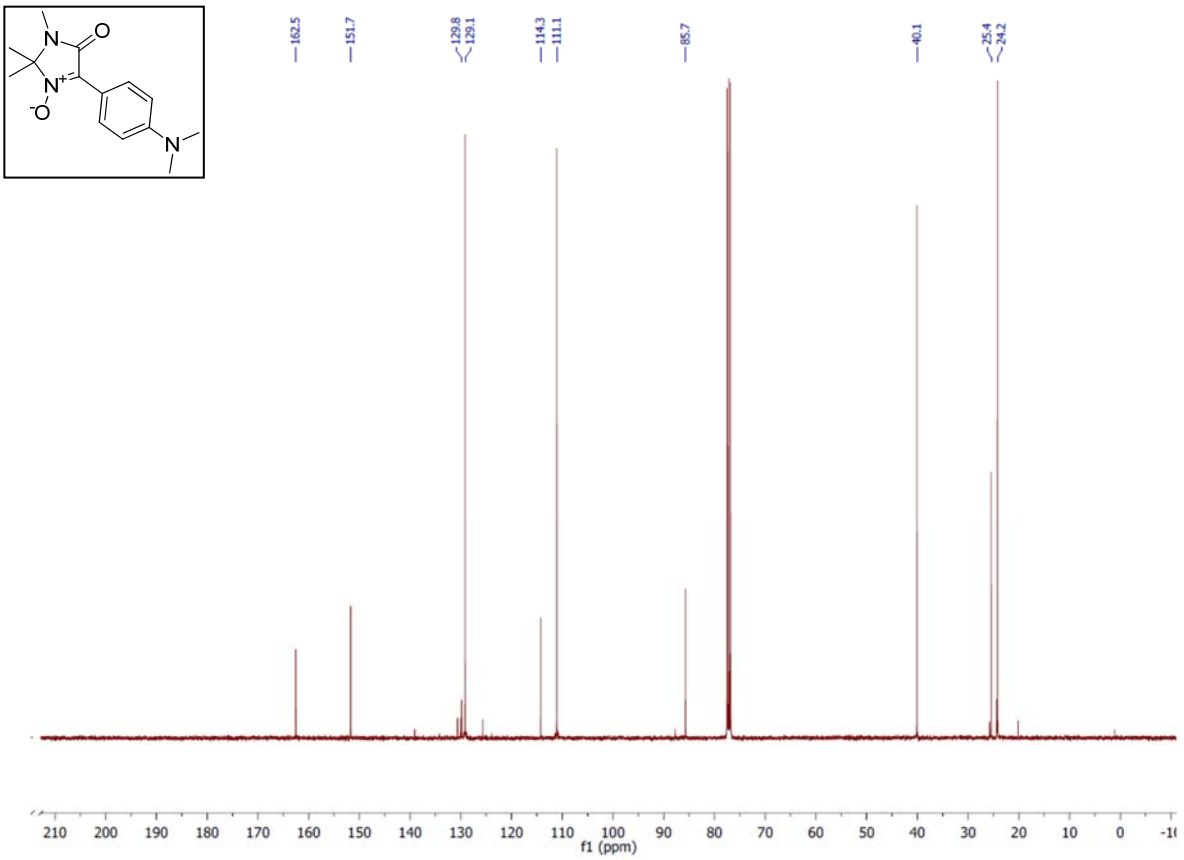




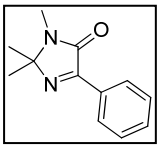


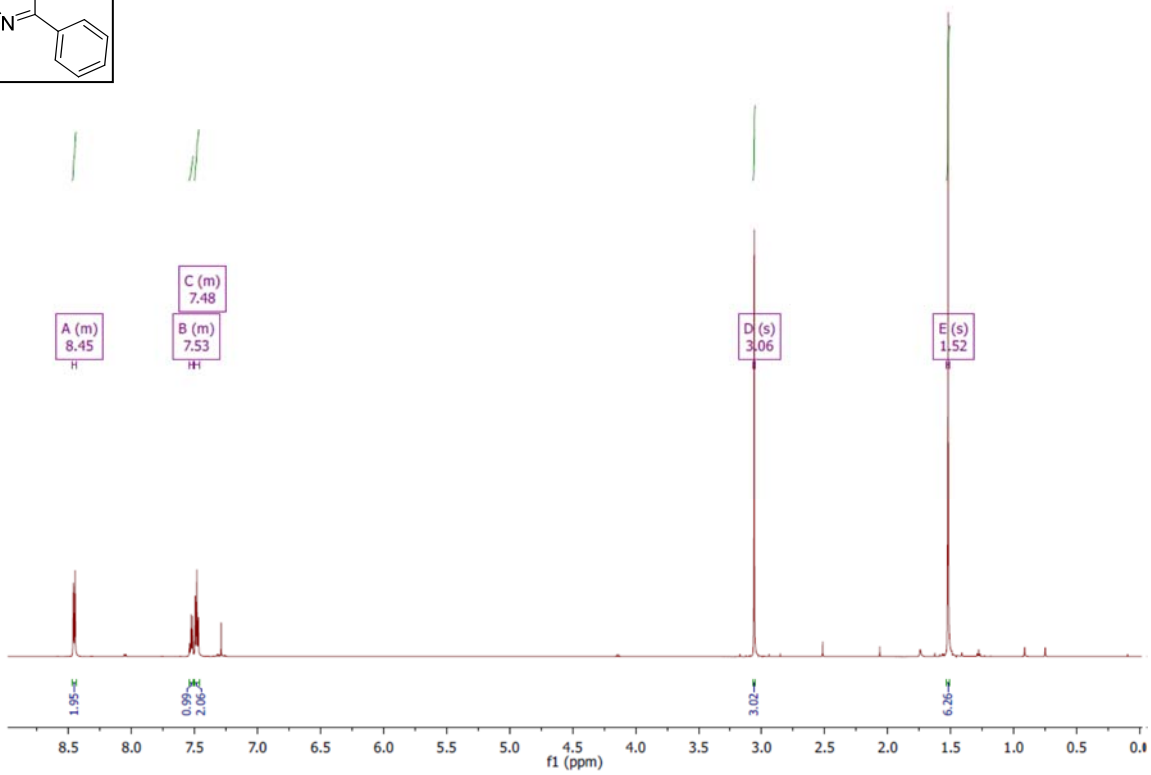
4-(4-(Dimethylamino)phenyl)-1,2,2-trimethyl-5-oxo-2,5-dihydro-1*H*-imidazol-3-oxide

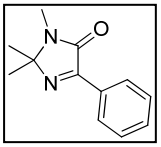




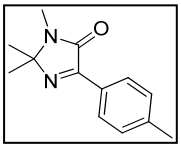
1,2,2-Trimethyl-4-phenyl-1*H*-imidazol-5(2*H*)-one (1a)

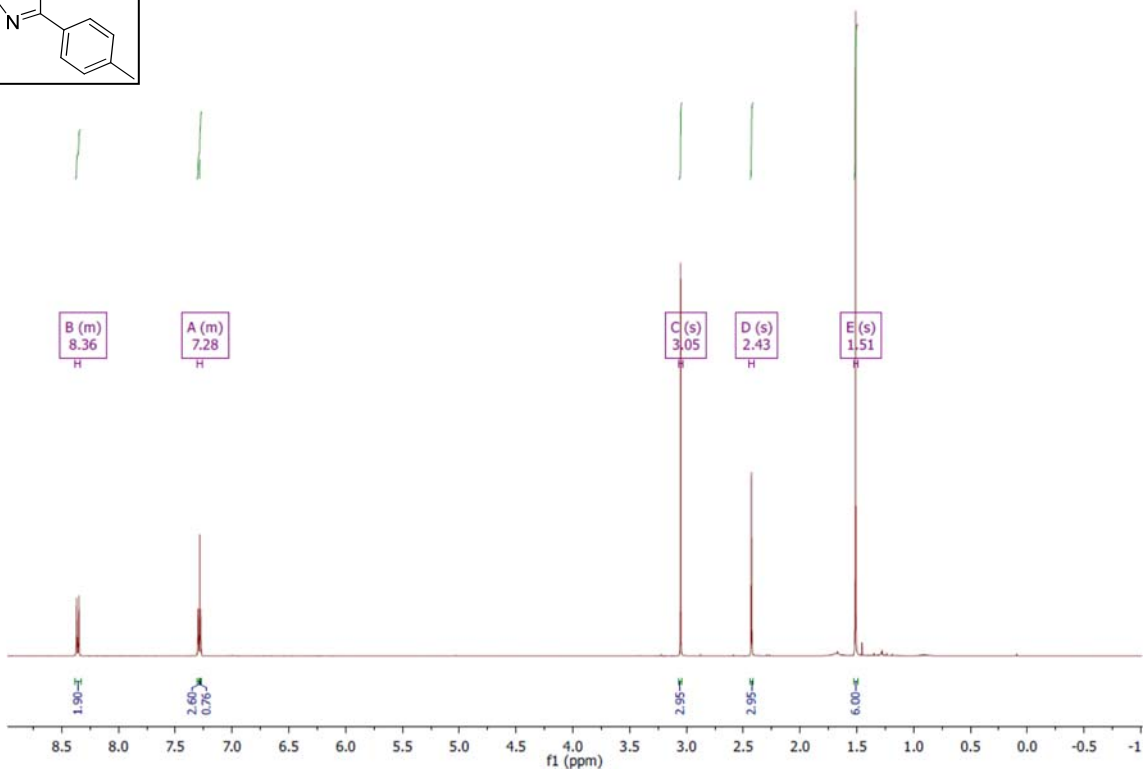


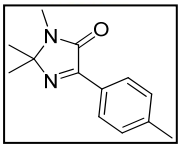




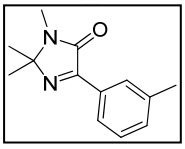
1,2,2-Trimethyl-4-(*p*-tolyl)-1*H*-imidazol-5(2*H*)-one (1b)

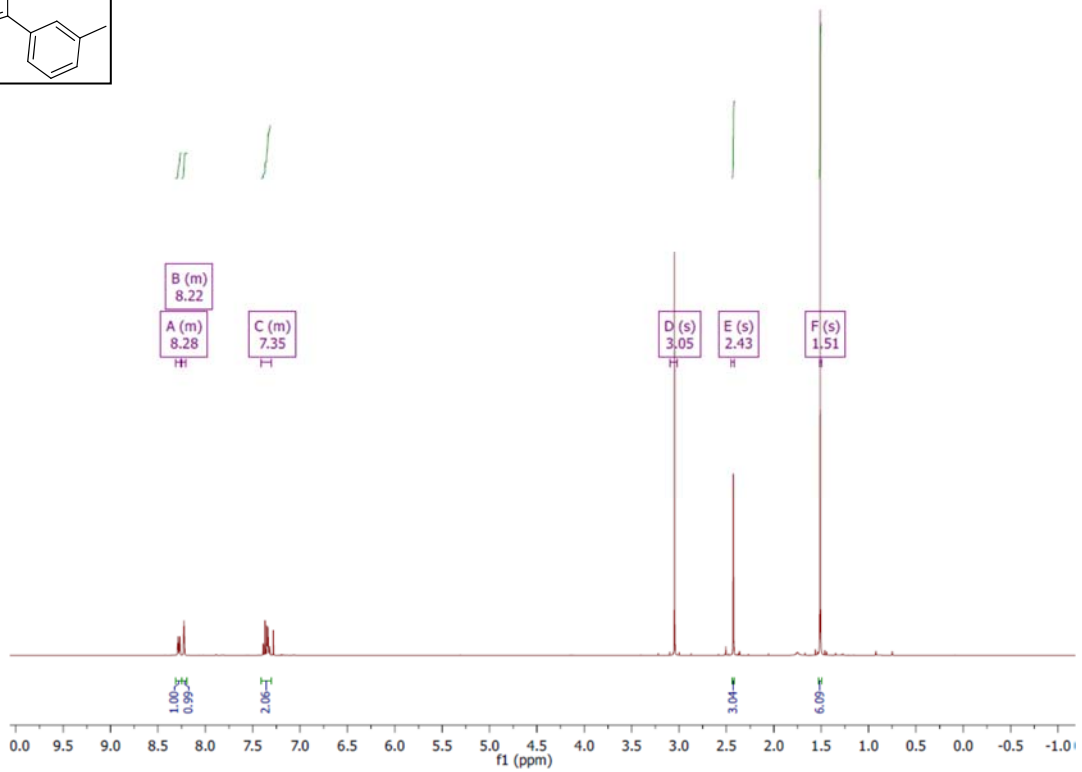


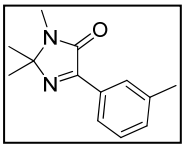




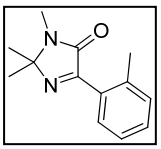
1,2,2-Trimethyl-4-(*m*-tolyl)-1*H*-imidazol-5(2*H*)-one (1c)

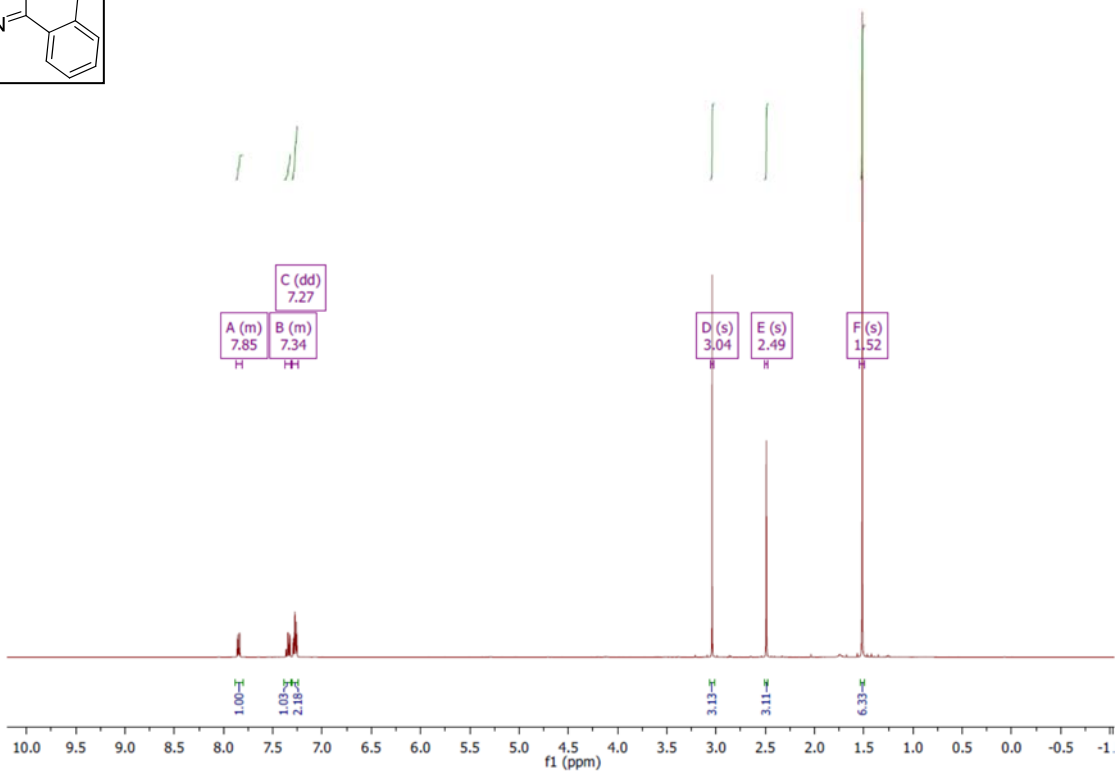


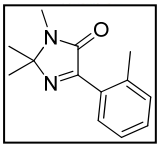




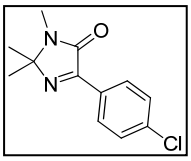
1,2,2-Trimethyl-4-(*o*-tolyl)-1*H*-imidazol-5(2*H*)-one (1d)

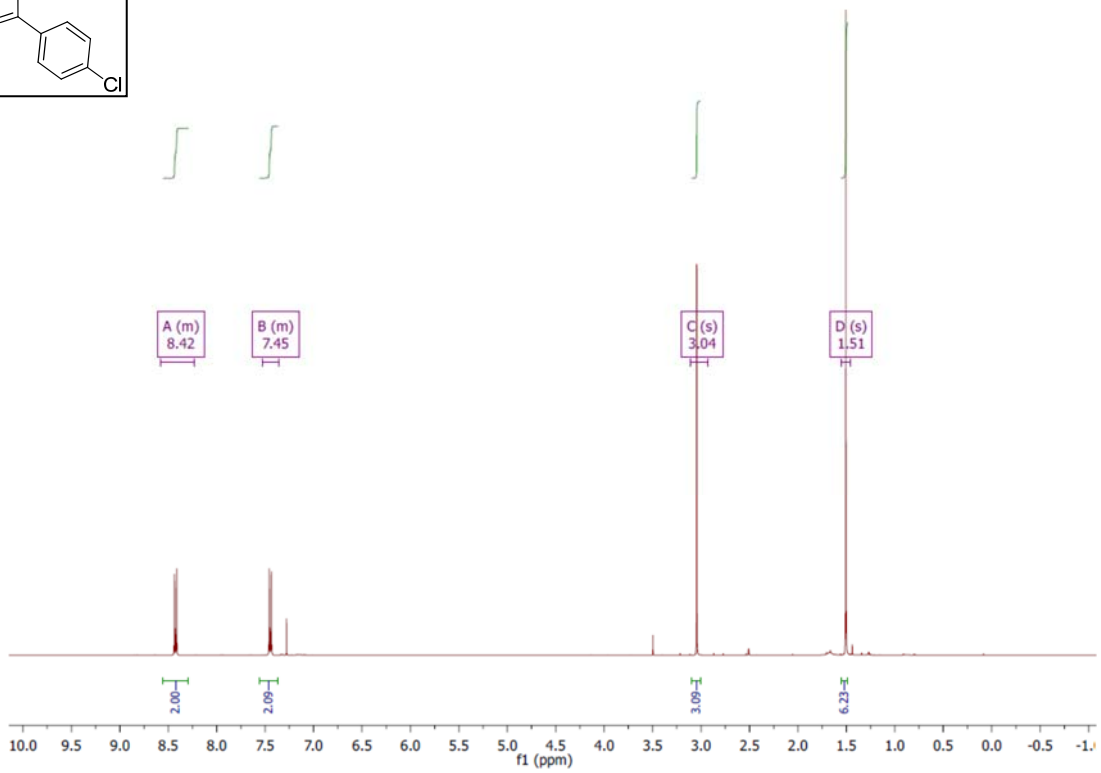


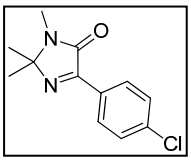




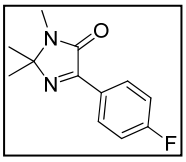
4-(4-Chlorophenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1e)

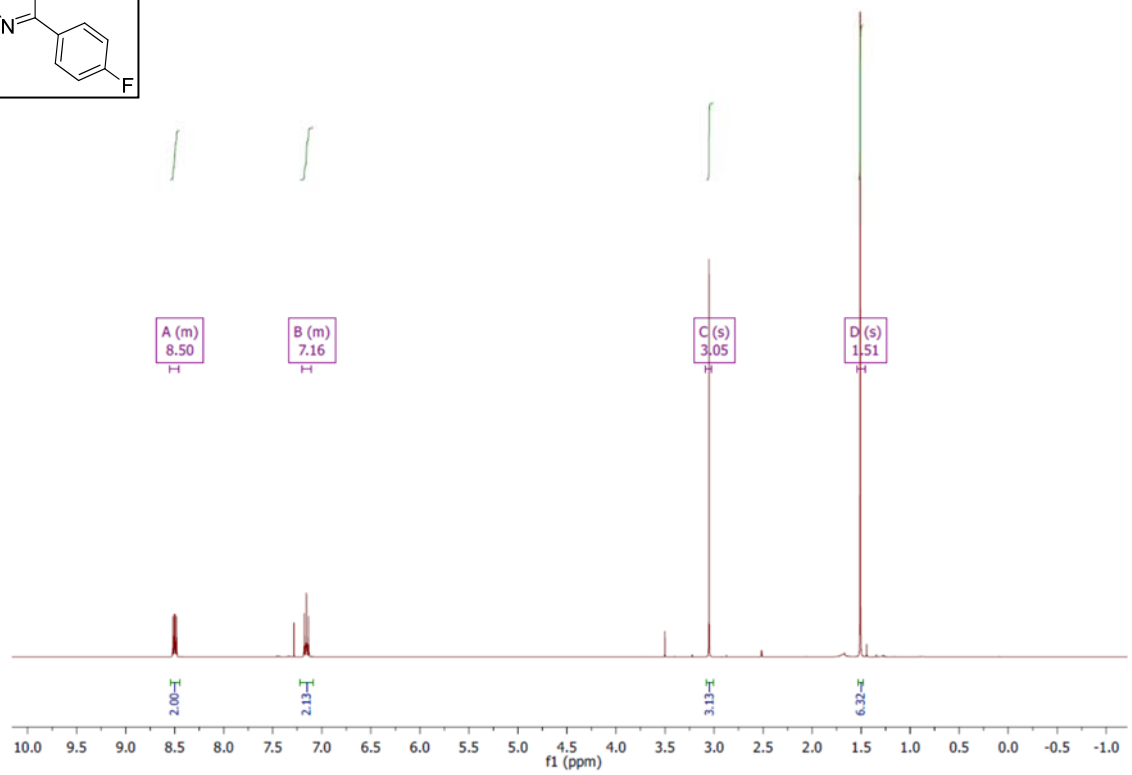


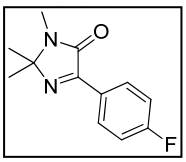


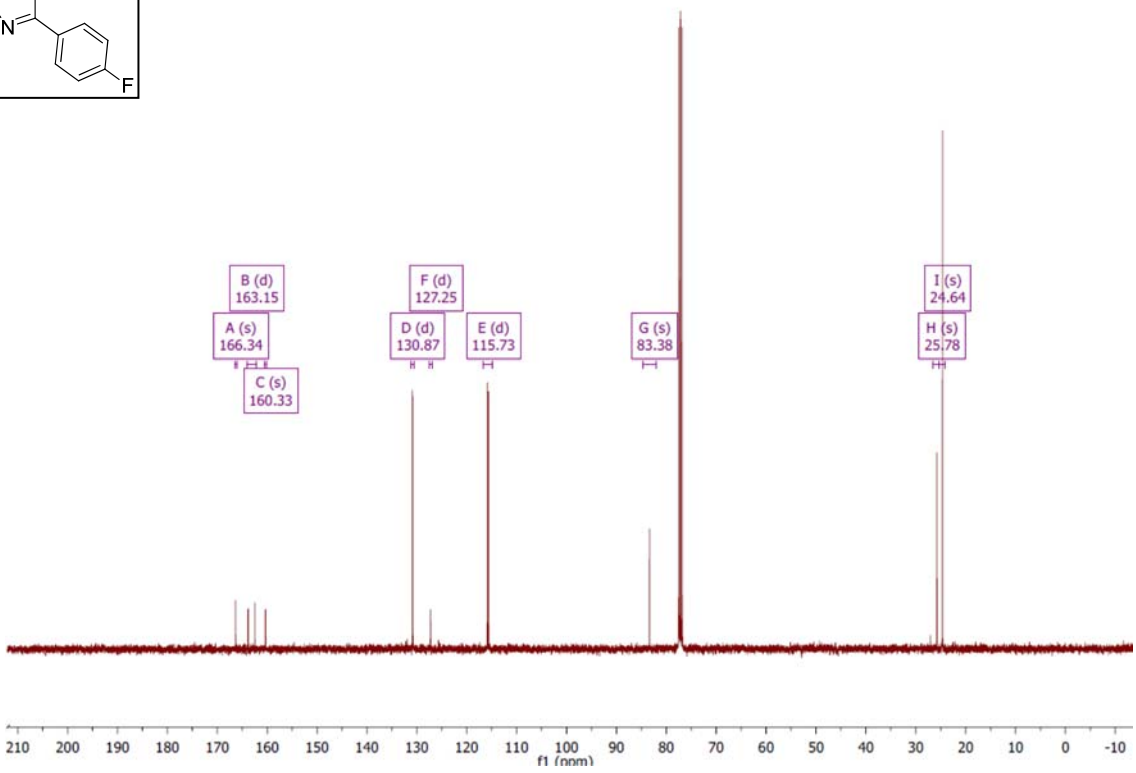


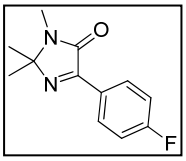
4-(4-Fluorophenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1f)

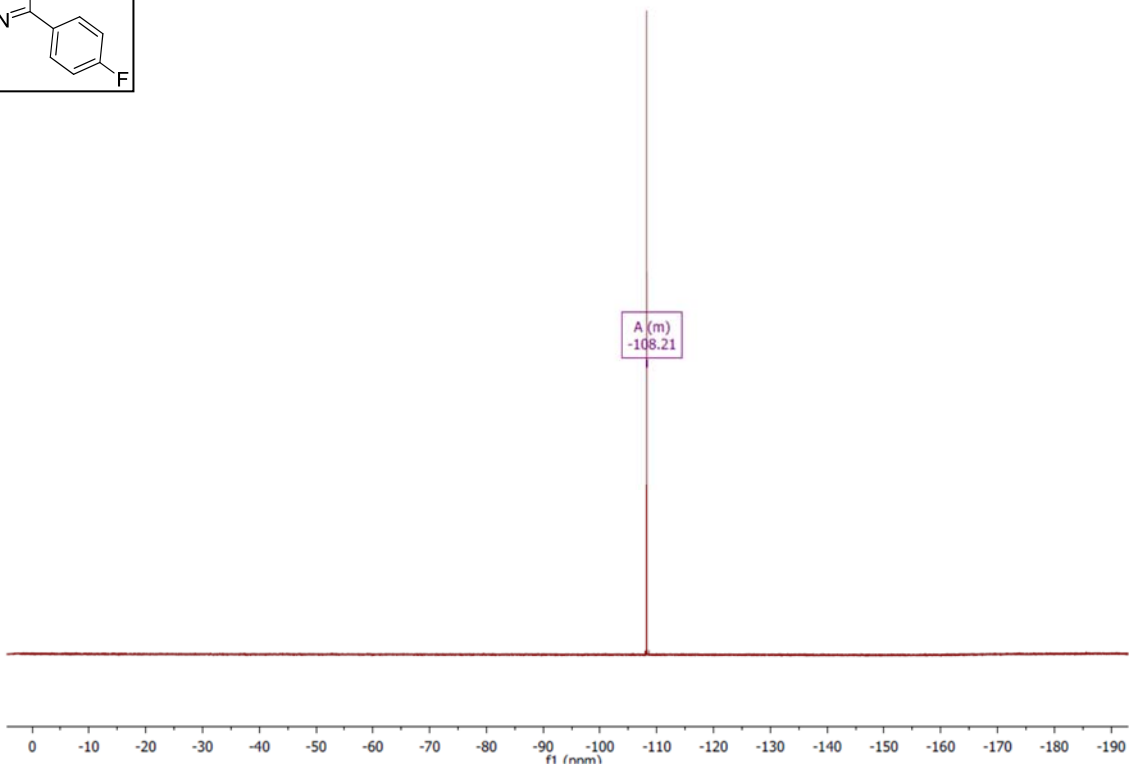









N
O
N
F


A (m)
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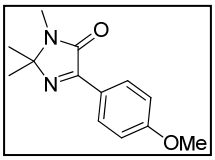
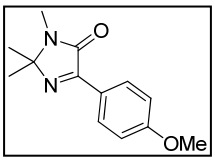
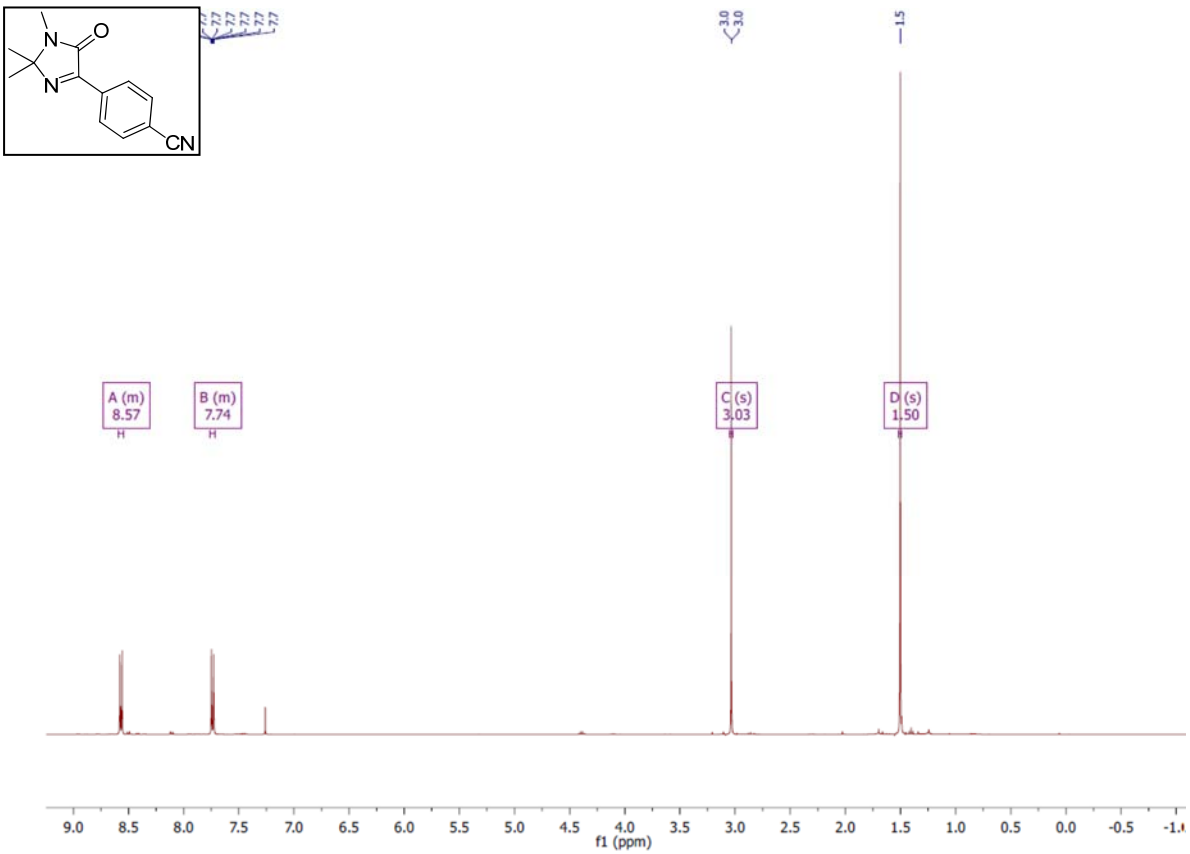
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

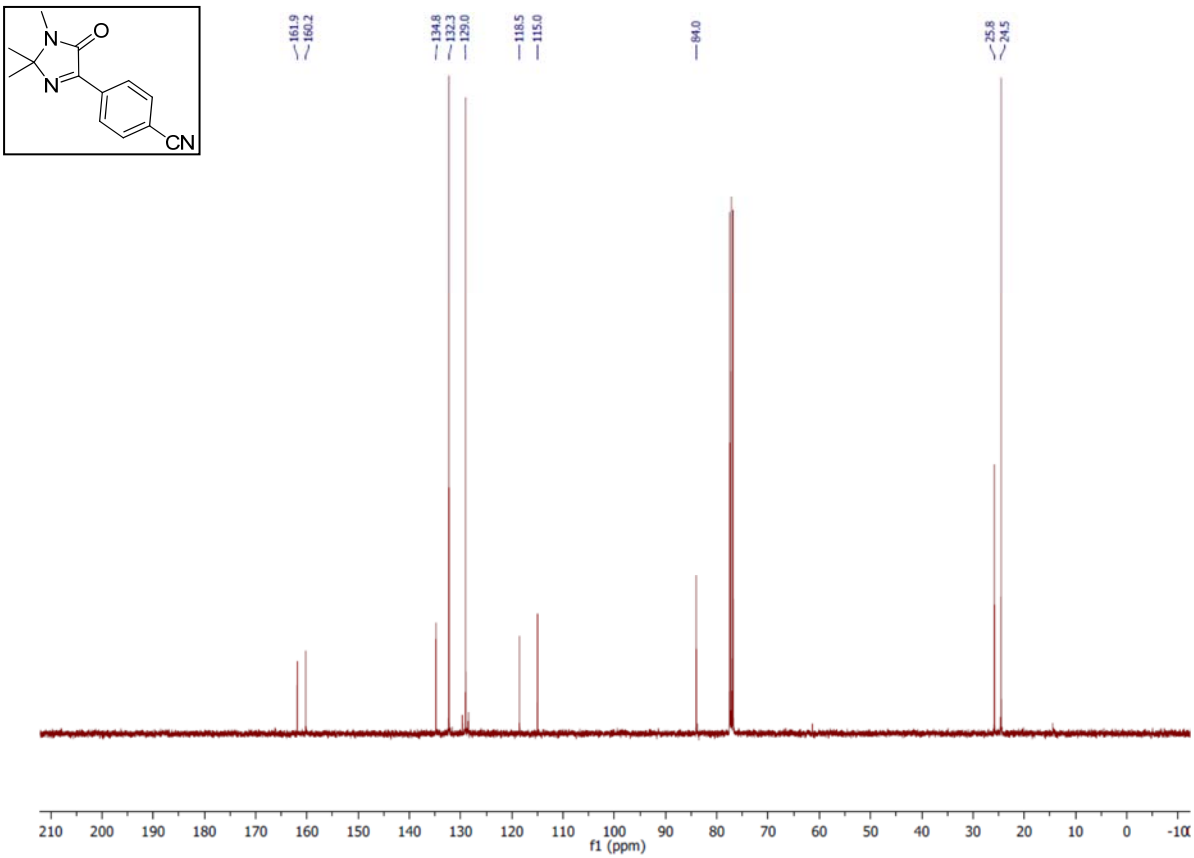
4-(4-Methoxyphenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1g)



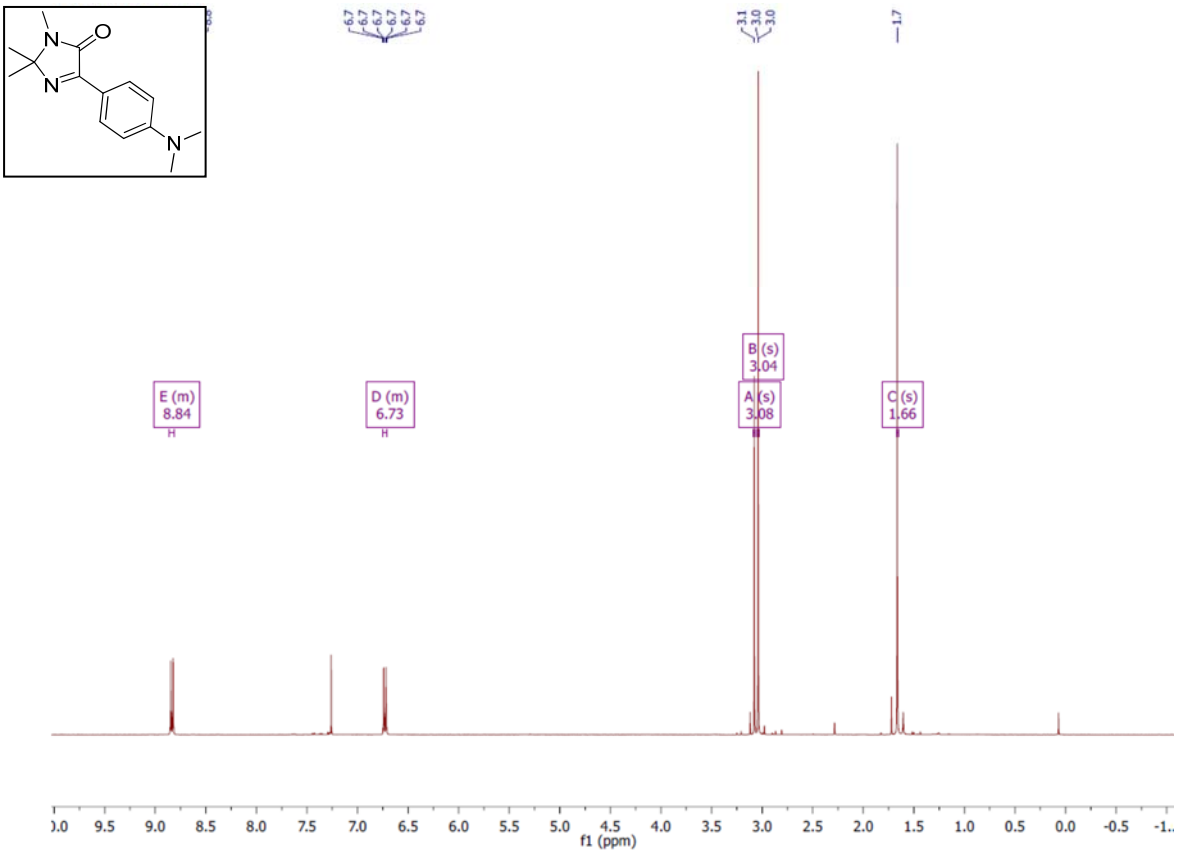


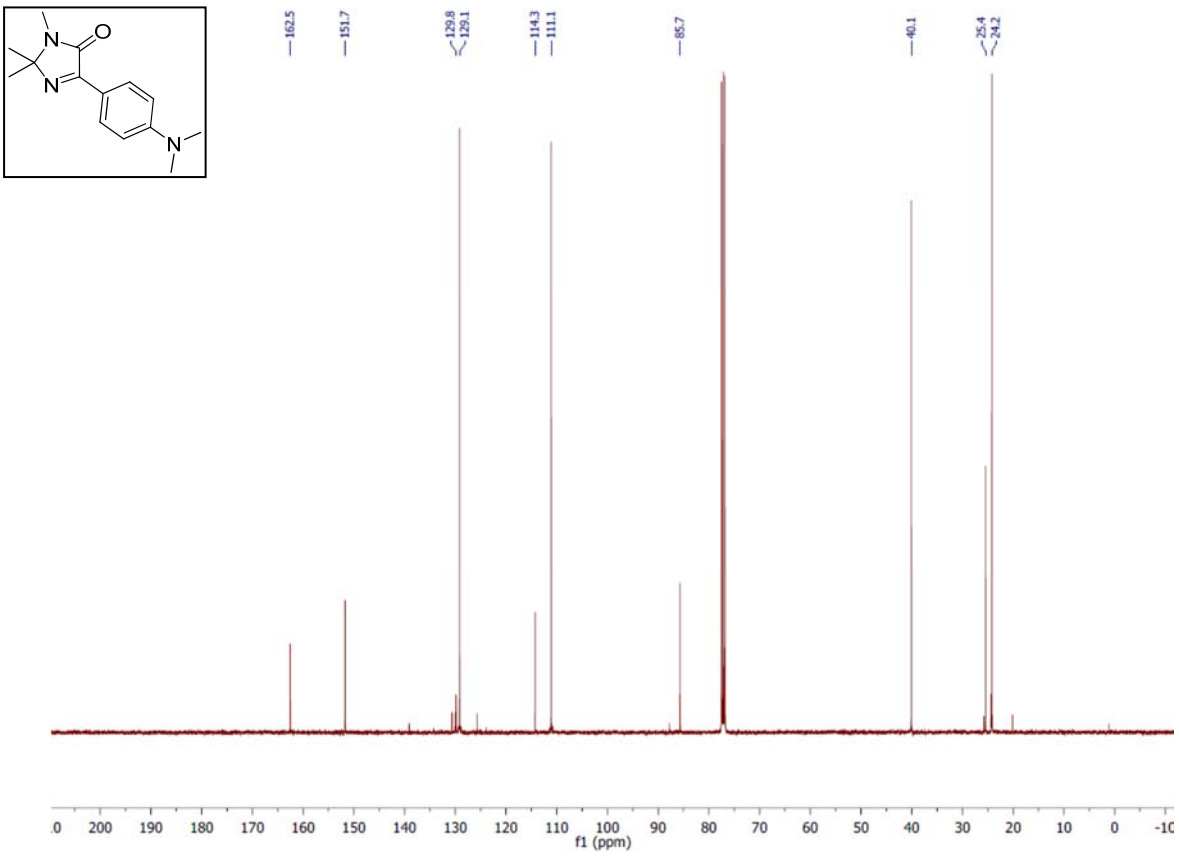
4-(1,2,2-Trimethyl-5-oxo-2,5-dihydro-1*H*-imidazol-4-yl)benzonitrile (1h)



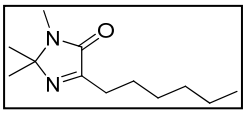


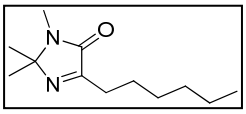
4-(4-(Dimethylamino)phenyl)-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1i)



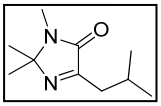


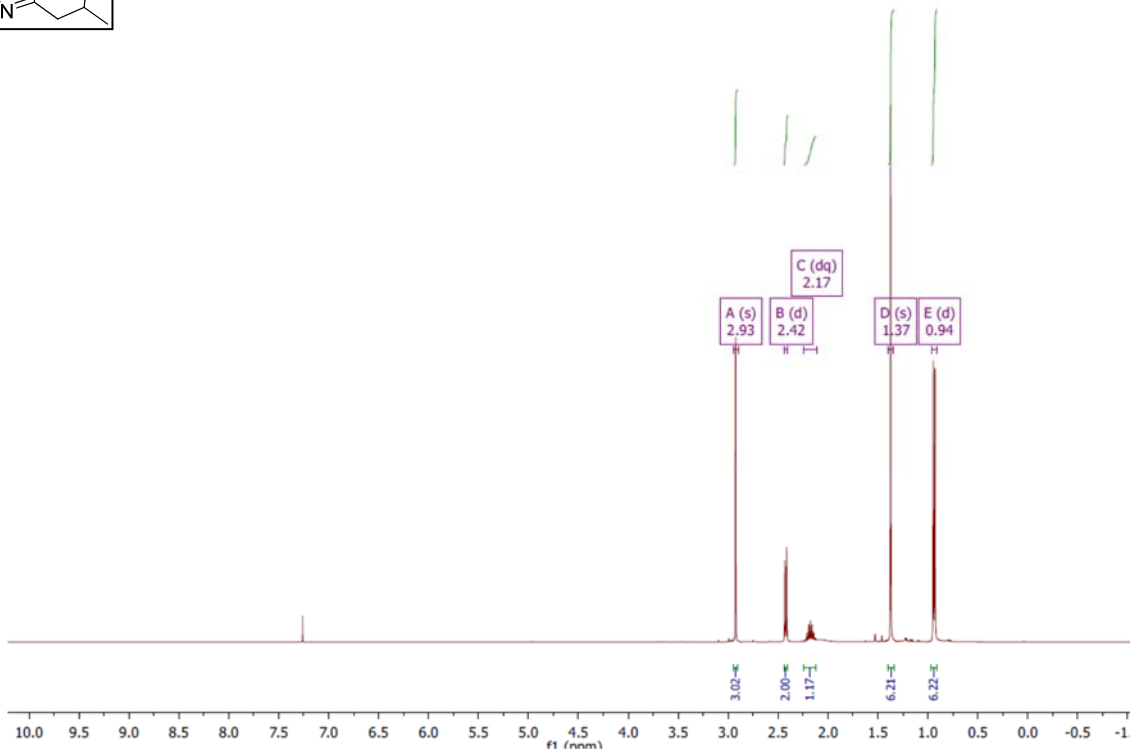
4-Hexyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1j)

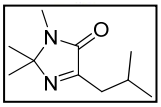




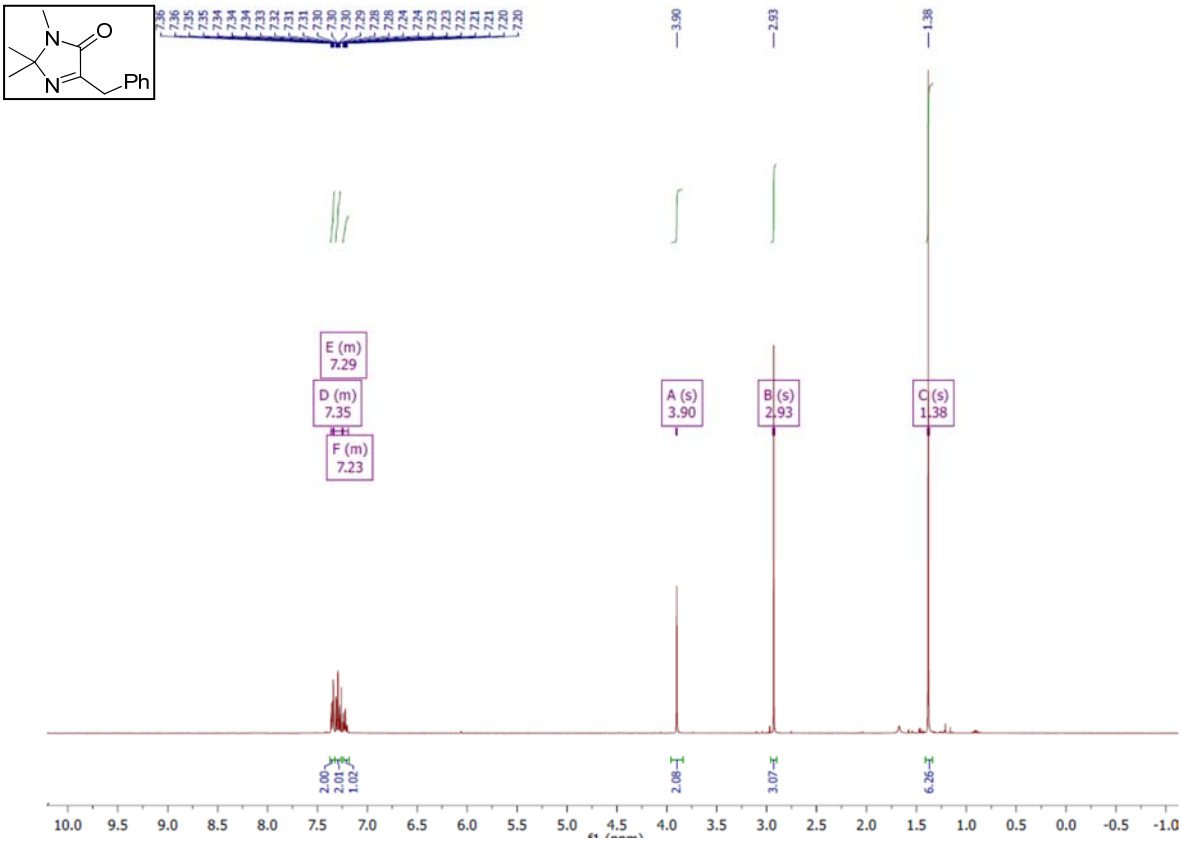
4-Isobutyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1k)

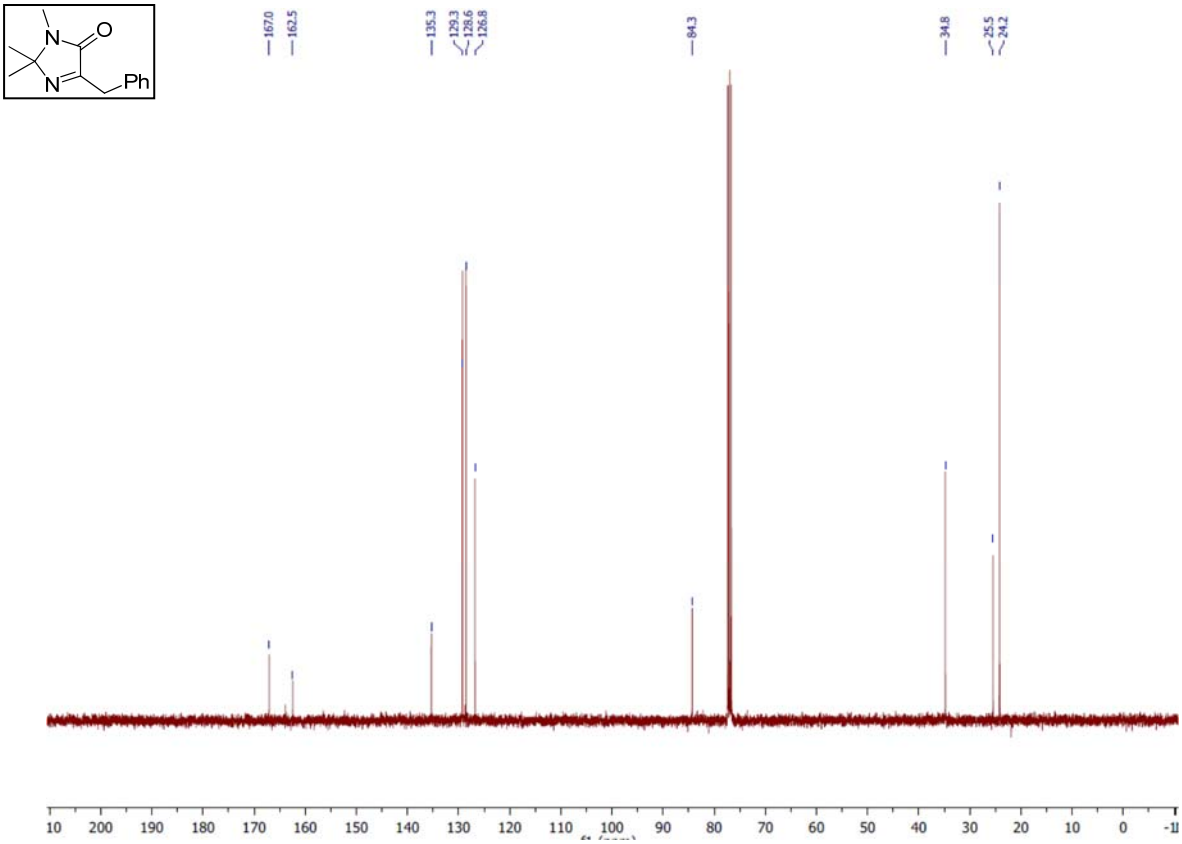




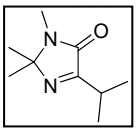


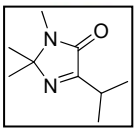
4-Benzyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1l)



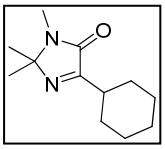


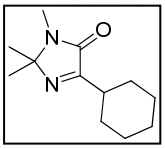
4-Isopropyl-1,2,2-trimethyl-1H-imidazol-5(2H)-one (1m)



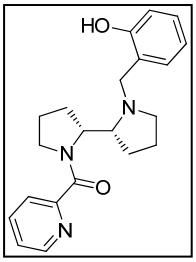


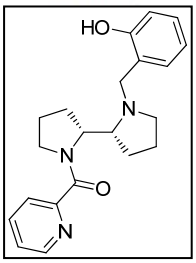
4-Cyclohexyl-1,2,2-trimethyl-1*H*-imidazol-5(2*H*)-one (1n)

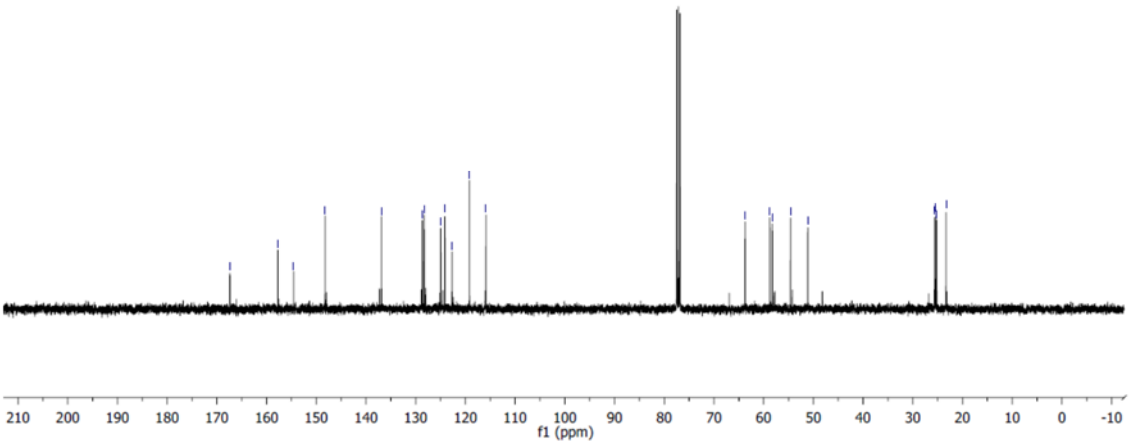




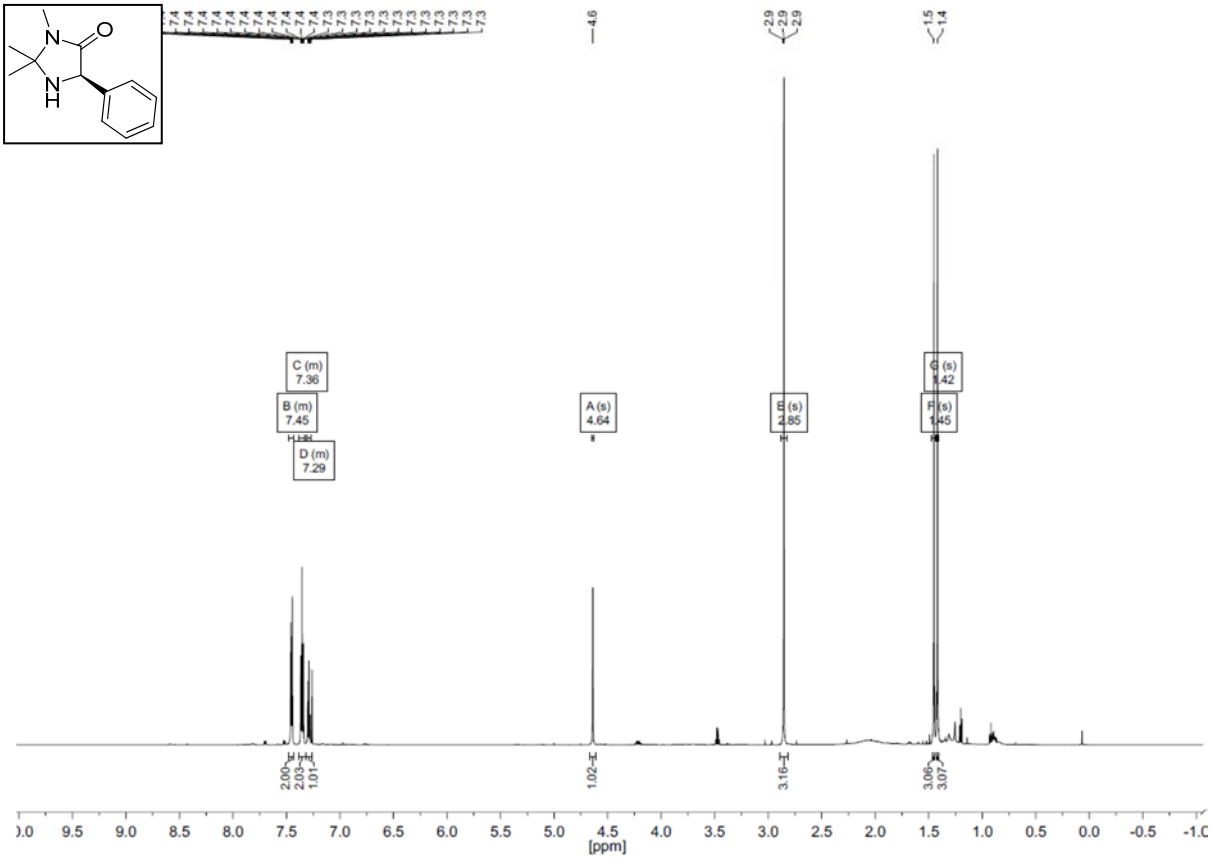
((2*R*,2'*R*)-1'-(2-hydroxybenzyl)-[2,2'-bipyrrolidin]-1-yl)(pyridin-2-yl)methanon (Catalyst E)

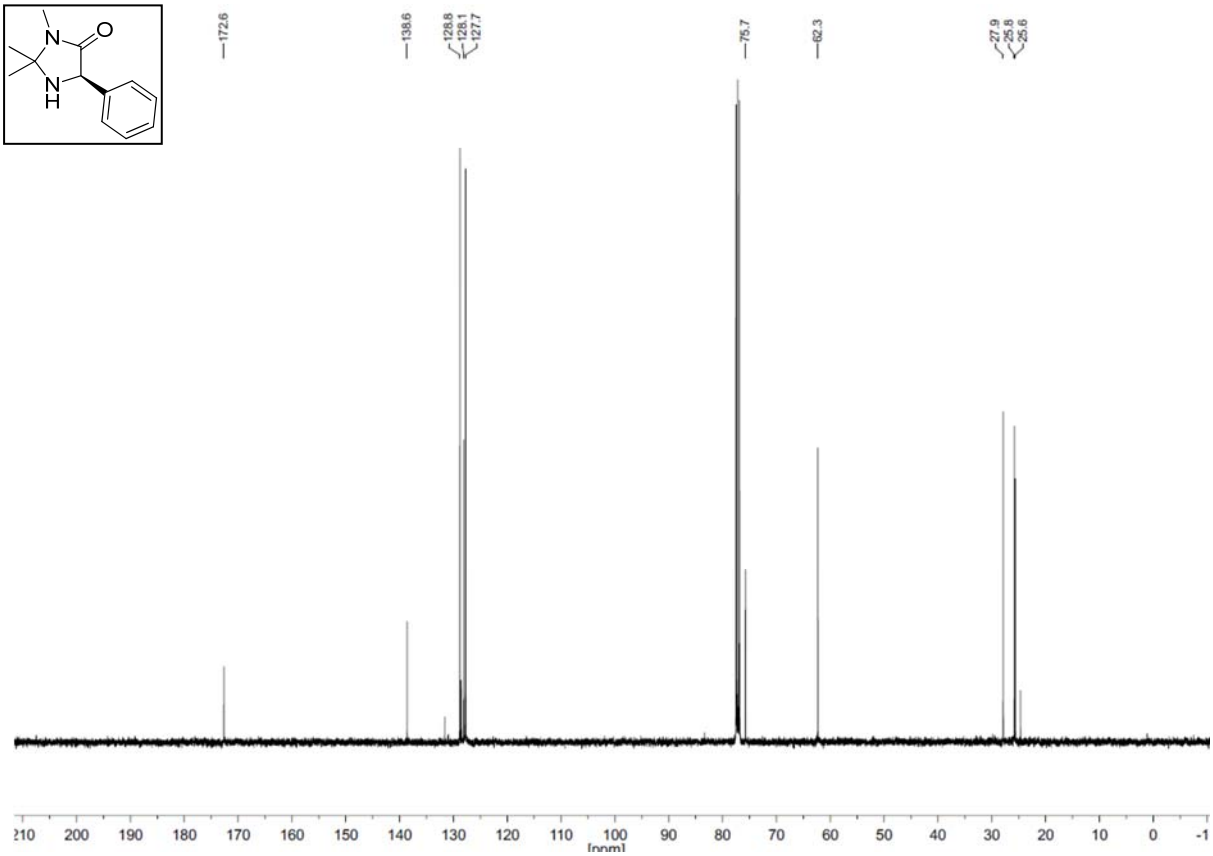




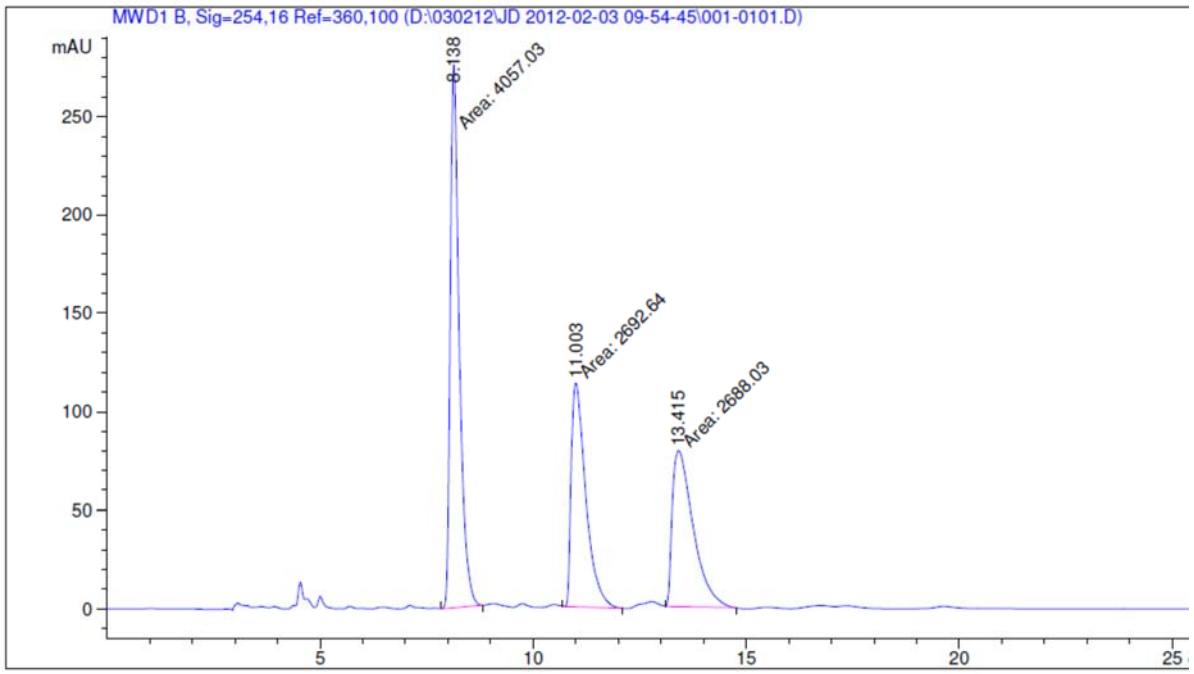


(*R*)-2,2,3-Trimethyl-5-phenylimidazolidin-4-on (2a)





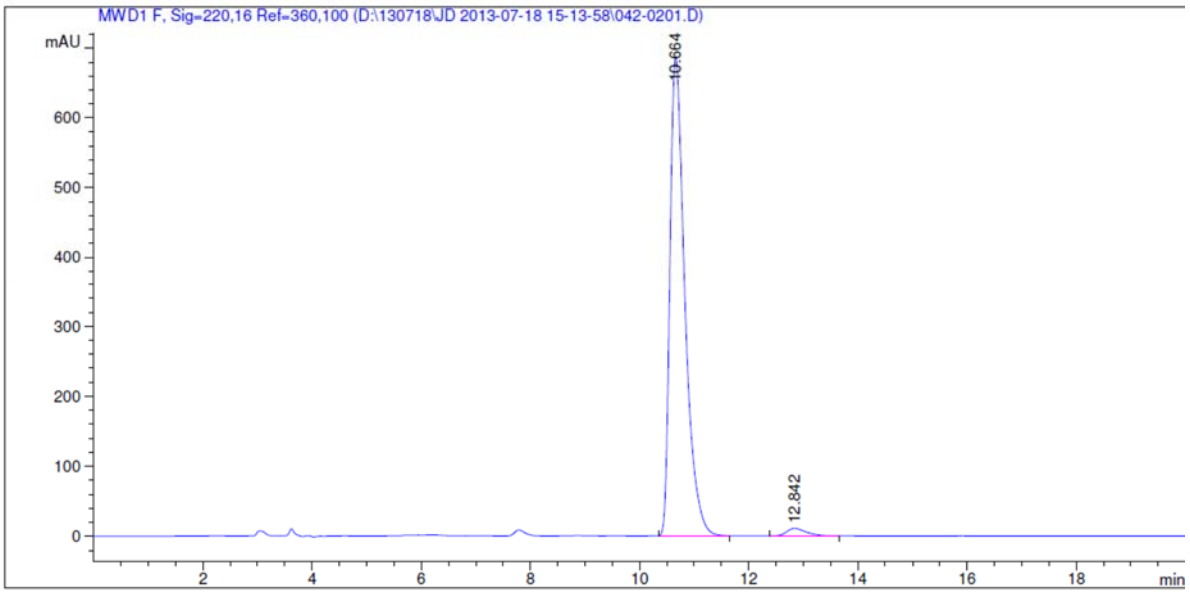
Method Info : Heptan:Ethanol 90 : 10 Flow: 1ml/ min Det:254nm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.138	MM	0.2439	4057.02783	277.26544	42.9875
2	11.003	MM	0.3945	2692.63745	113.75210	28.5307
3	13.415	MM	0.5688	2688.03418	78.76353	28.4819

0.1 mmol-Scale

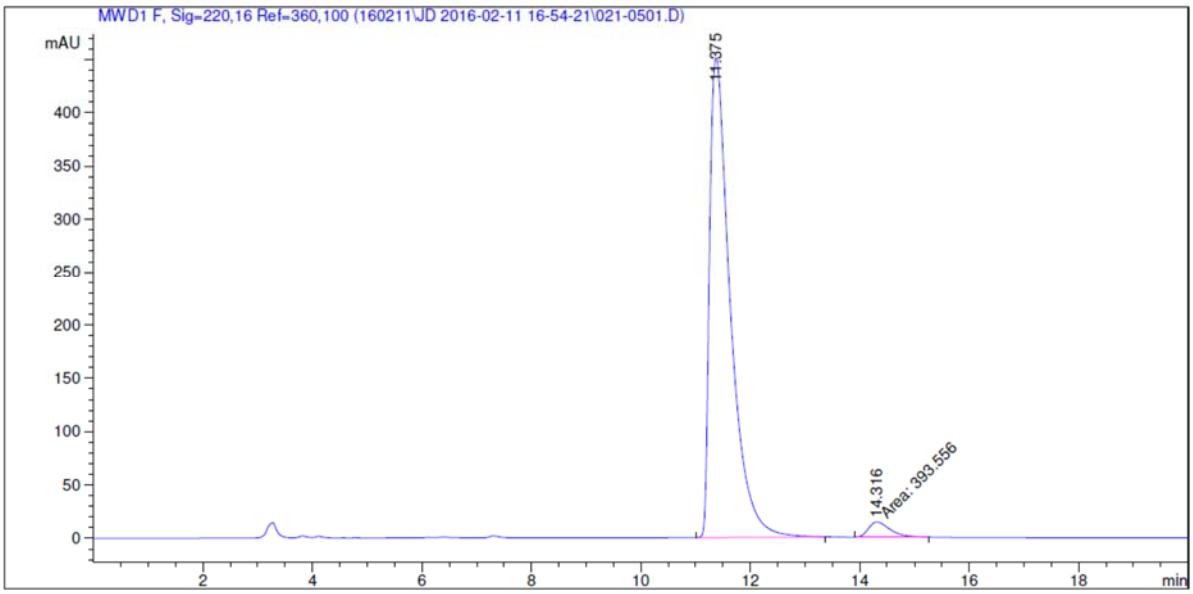
Method Info : Heptan:EtOH 90:10 Flow: 1.0 ml/ min Det: 220 nm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.664	BB	0.2855	1.30277e4	686.26837	97.9068
2	12.842	BB	0.3872	278.53149	10.86046	2.0932

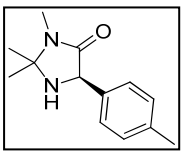
1.0 mmol-Scale

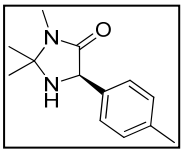
Method Info : Heptan: IPA 90:10 Flow 1.0 ml/min Det:220 nm



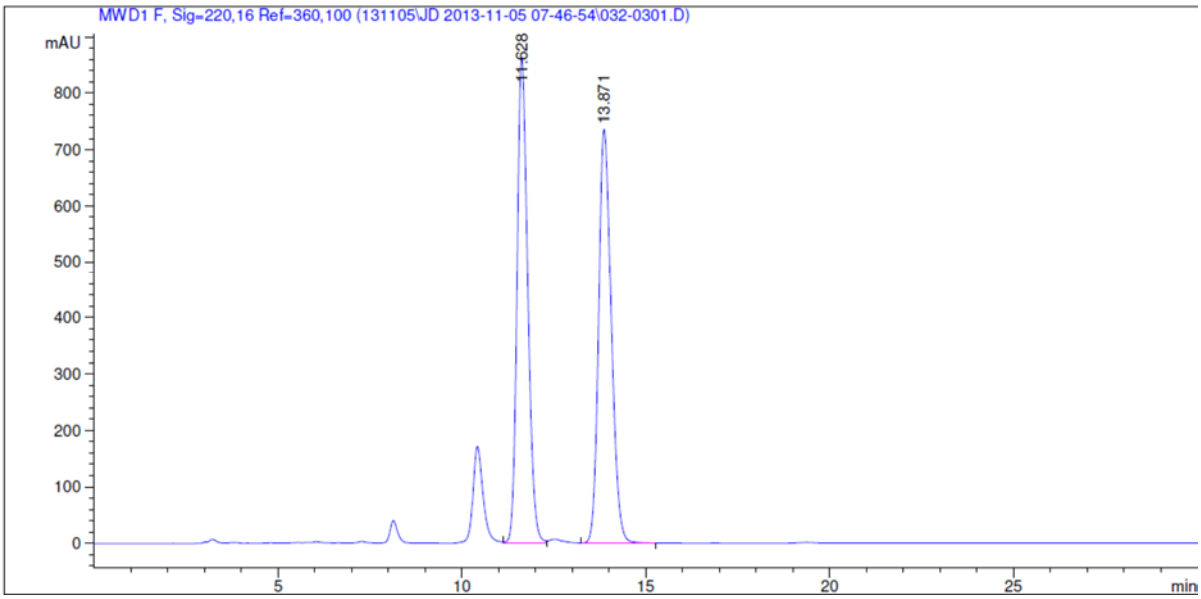
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.375	BB	0.3958	1.18155e4	450.81653	96.7765
2	14.316	MM	0.4601	393.55557	14.25506	3.2235

(*R*)-2,2,3-Trimethyl-5-(*p*-tolyl)imidazolidin-4-on (2b)



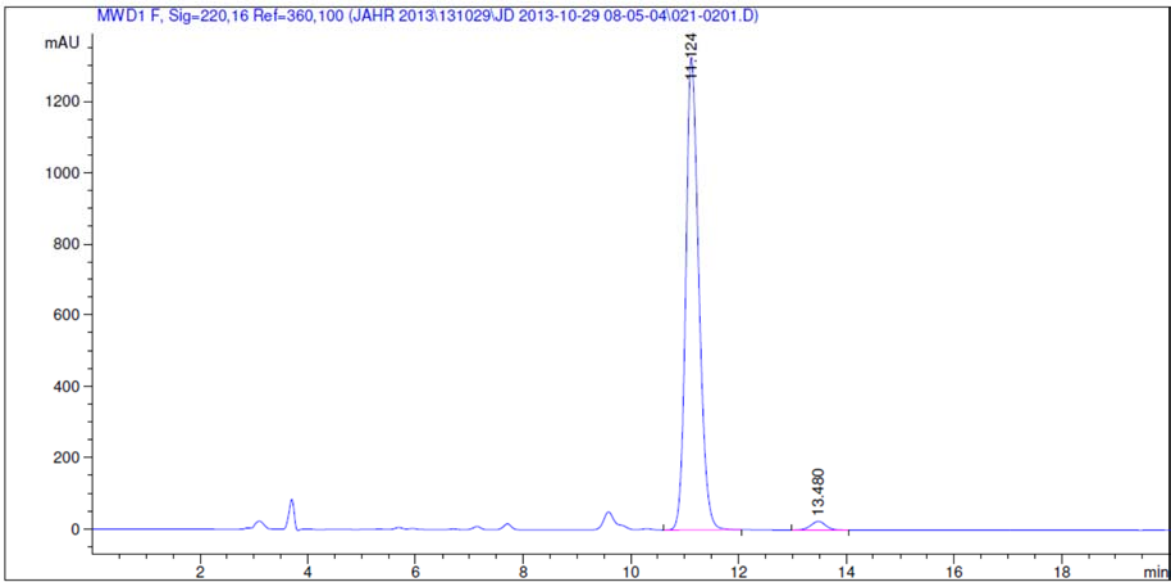


Method Info : Heptan : Ethanol 90:10 Flow 1.0 Det:220m



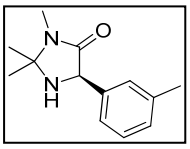
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.628	VV	0.3126	1.74897e4	862.54590	49.9609
2	13.871	VB	0.3656	1.75171e4	736.06885	50.0391

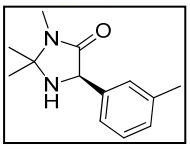
Method Info : Heptan 90:10 Flow 1.0 220 nm 20 min



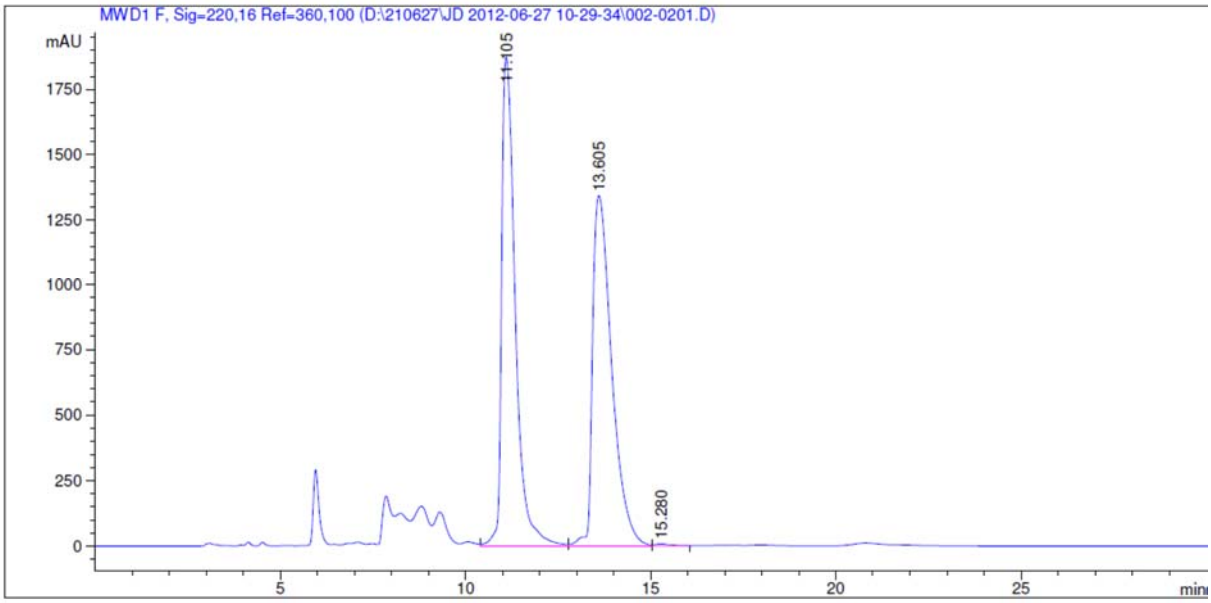
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.124	VB	0.2539	2.22762e4	1326.91541	97.9379
2	13.480	BB	0.2952	469.02802	24.30052	2.0621

(*R*)-2,2,3-Trimethyl-5-(*m*-tolyl)imidazolidin-4-on (2c)



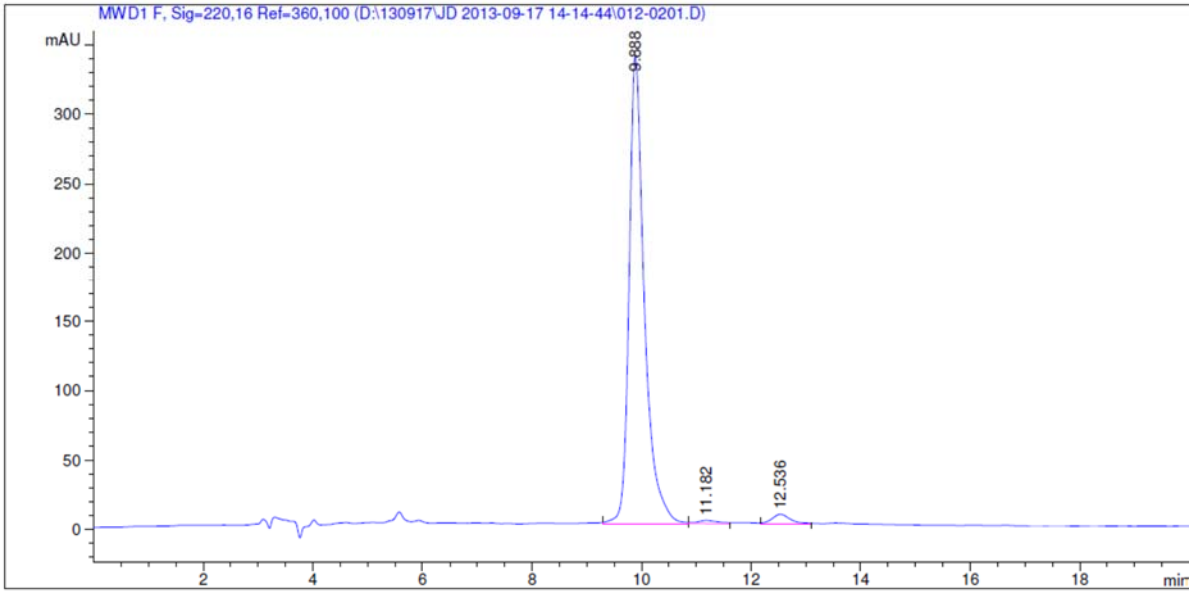


Method Info : Heptan:Ethanol 90:10 Flow: 1 ml/ min Det: 220 nm



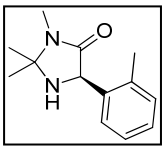
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.105	VV	0.3935	4.76814e4	1870.01672	49.5836
2	13.605	VV	0.5558	4.82680e4	1341.36841	50.1937
3	15.280	VB	0.4161	214.13055	7.61512	0.2227

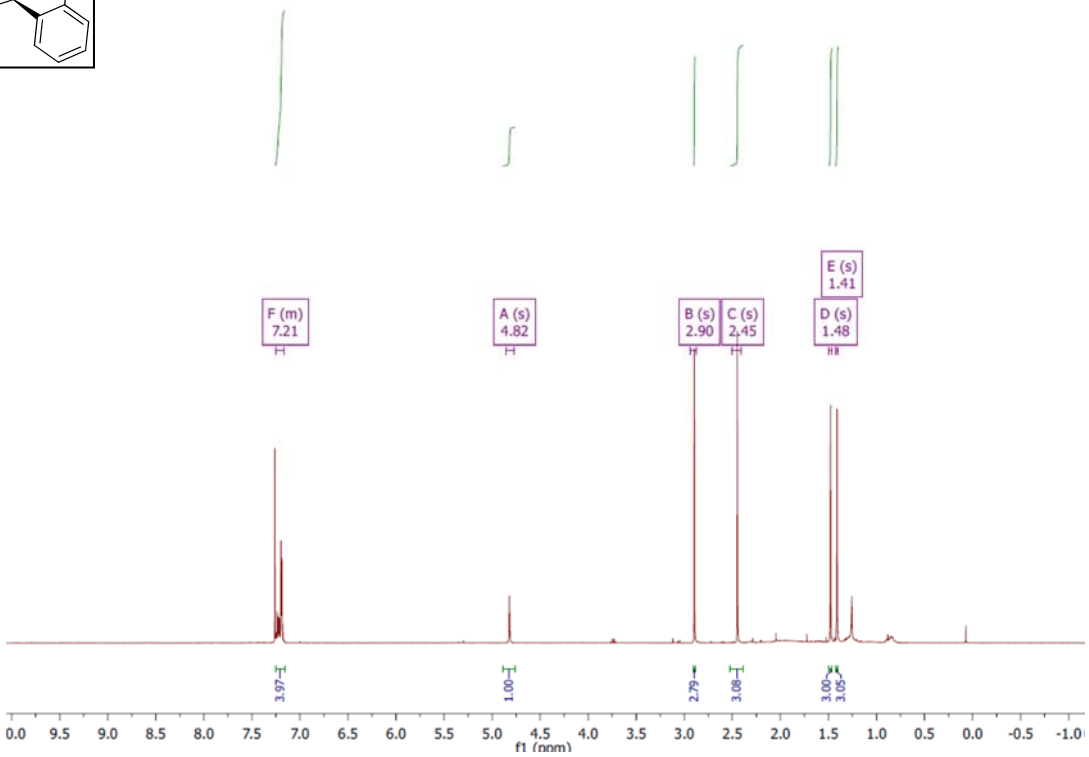
Method Info : Heptan Ethanol 90:10 Flow: 1 ml/ min Det: 220 20grad C

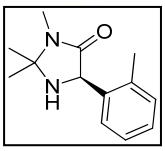


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.888	BB	0.2902	6549.67090	337.86987	96.7819
2	11.182	BB	0.3820	62.21537	2.28245	0.9193
3	12.536	BB	0.3478	155.56520	6.77717	2.2987

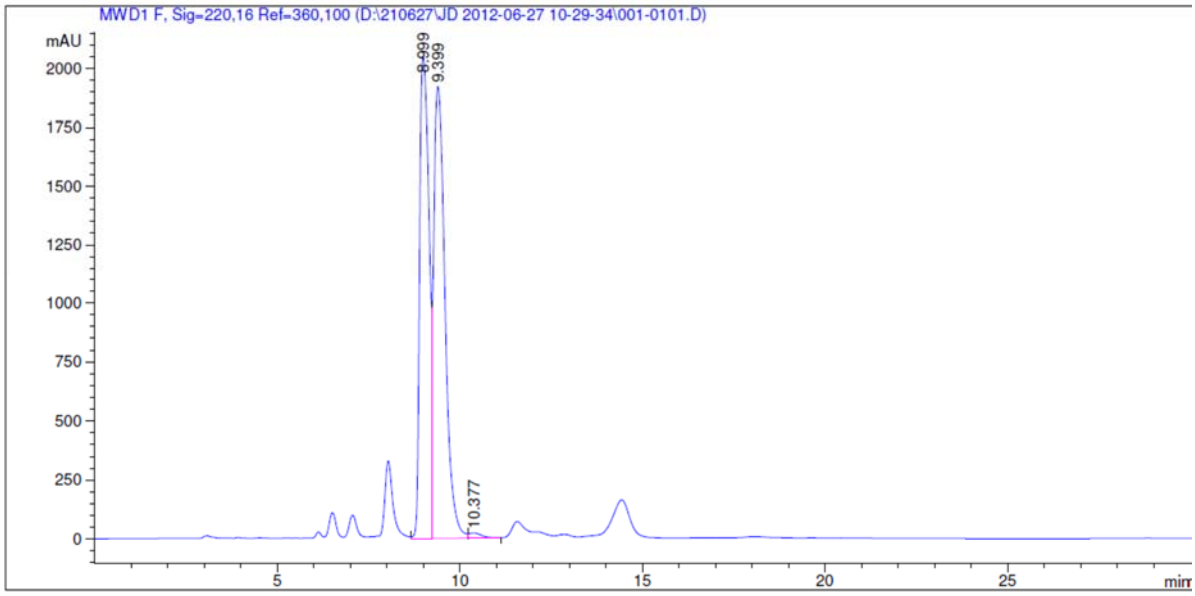
(*R*)-2,2,3-Trimethyl-5-(*o*-tolyl)imidazolidin-4-on (2d)





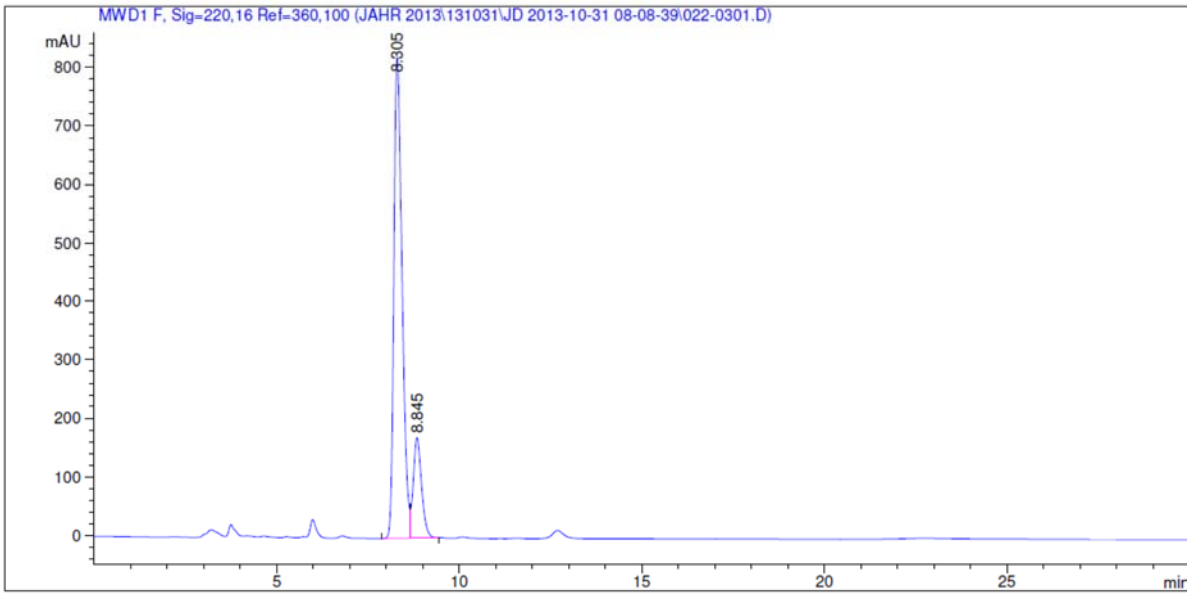


Method Info : Heptan:Ethanol 90:10 Flow: 1 ml/ min Det: 220 nm



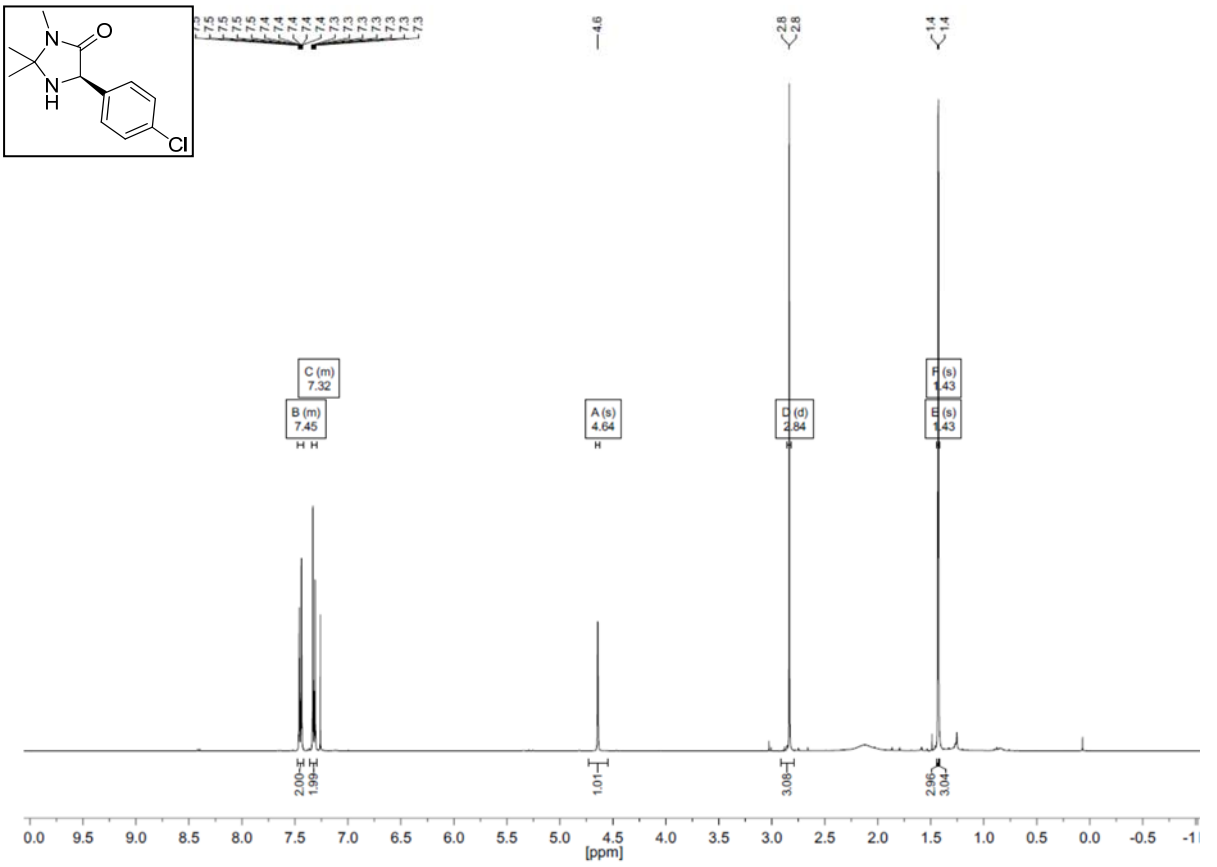
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.999	VV	0.2871	3.62846e4	2043.74023	46.5347
2	9.399	VV	0.3301	4.10889e4	1916.50024	52.6963
3	10.377	VV	0.3969	599.60529	22.07314	0.7690

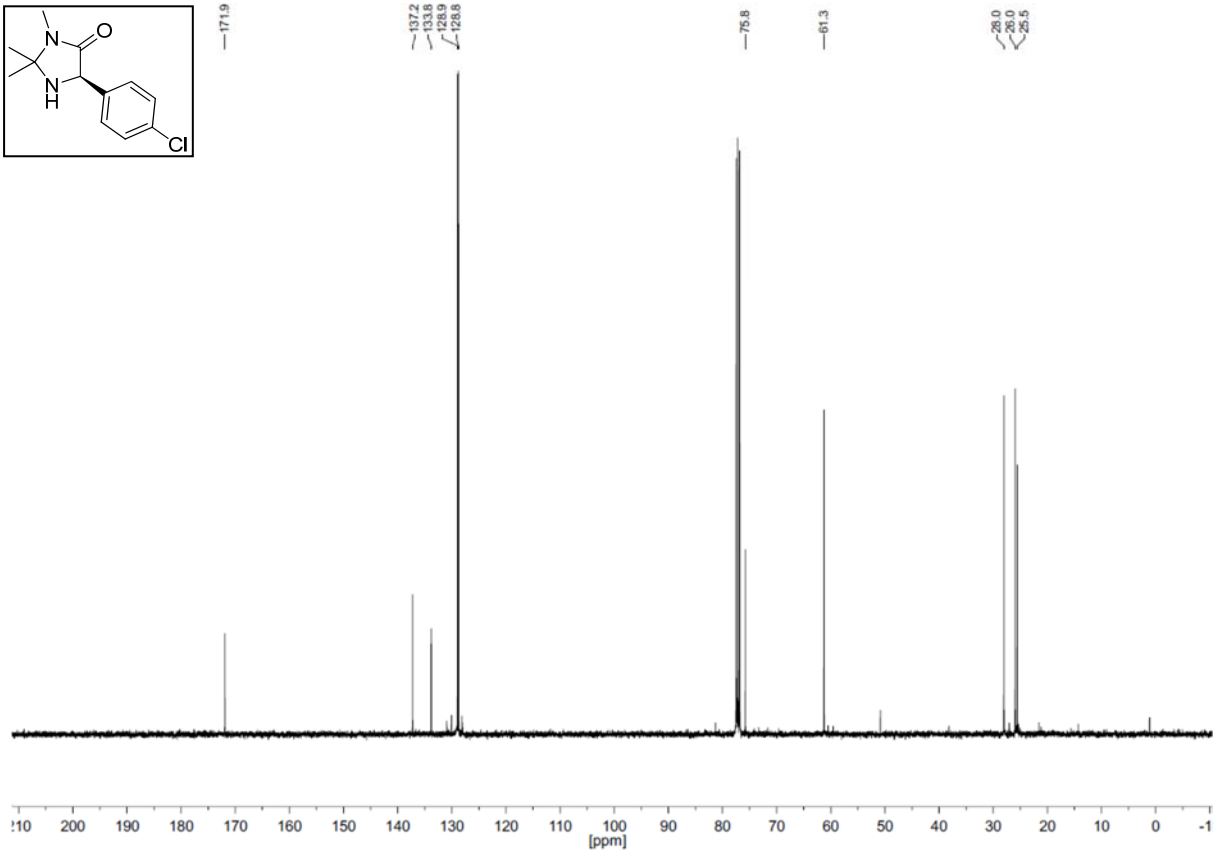
Method Info : Heptan > Ethanol 90:10 Flow 1.0 220 nm



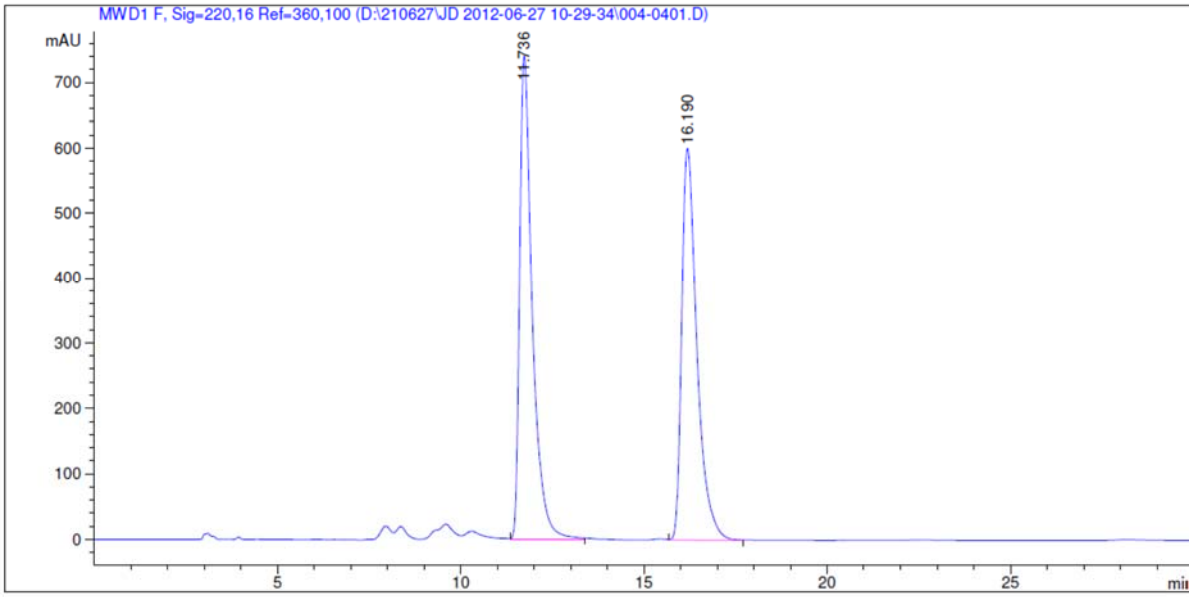
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.305	BV	0.2356	1.26622e4	822.40967	82.1112
2	8.845	VB	0.2415	2758.57886	171.60883	17.8888

(*R*)-5-(4-Chlorophenyl)-2,2,3-trimethylimidazolidin-4-on (2e)



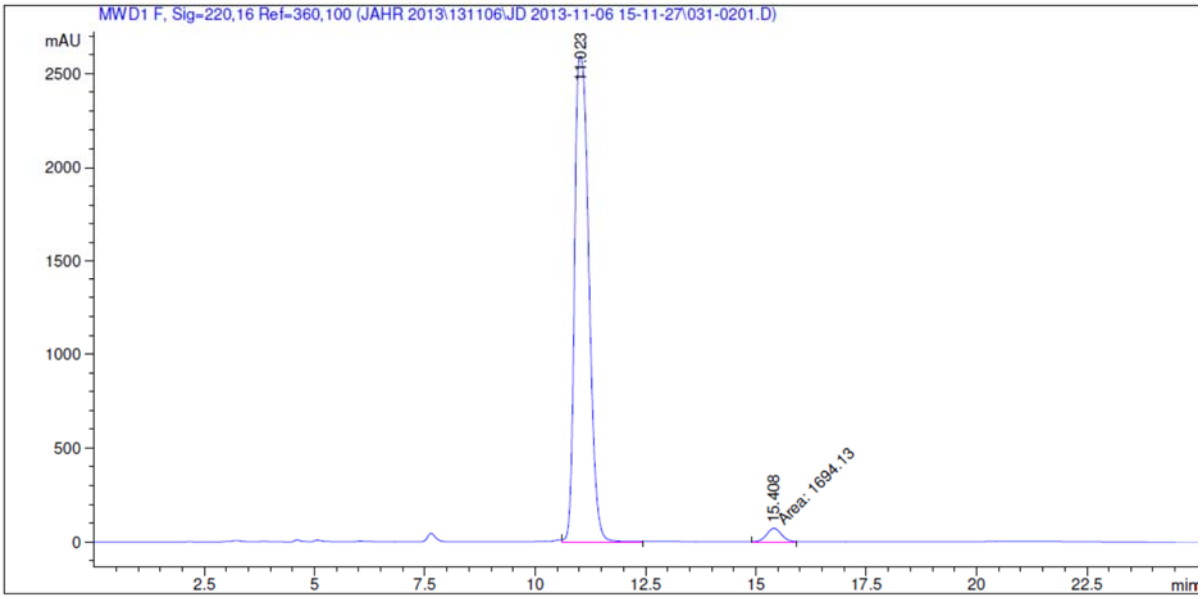


Method Info : Heptan:Ethanol 90:10 Flow: 1 ml/ min Det: 220 nm



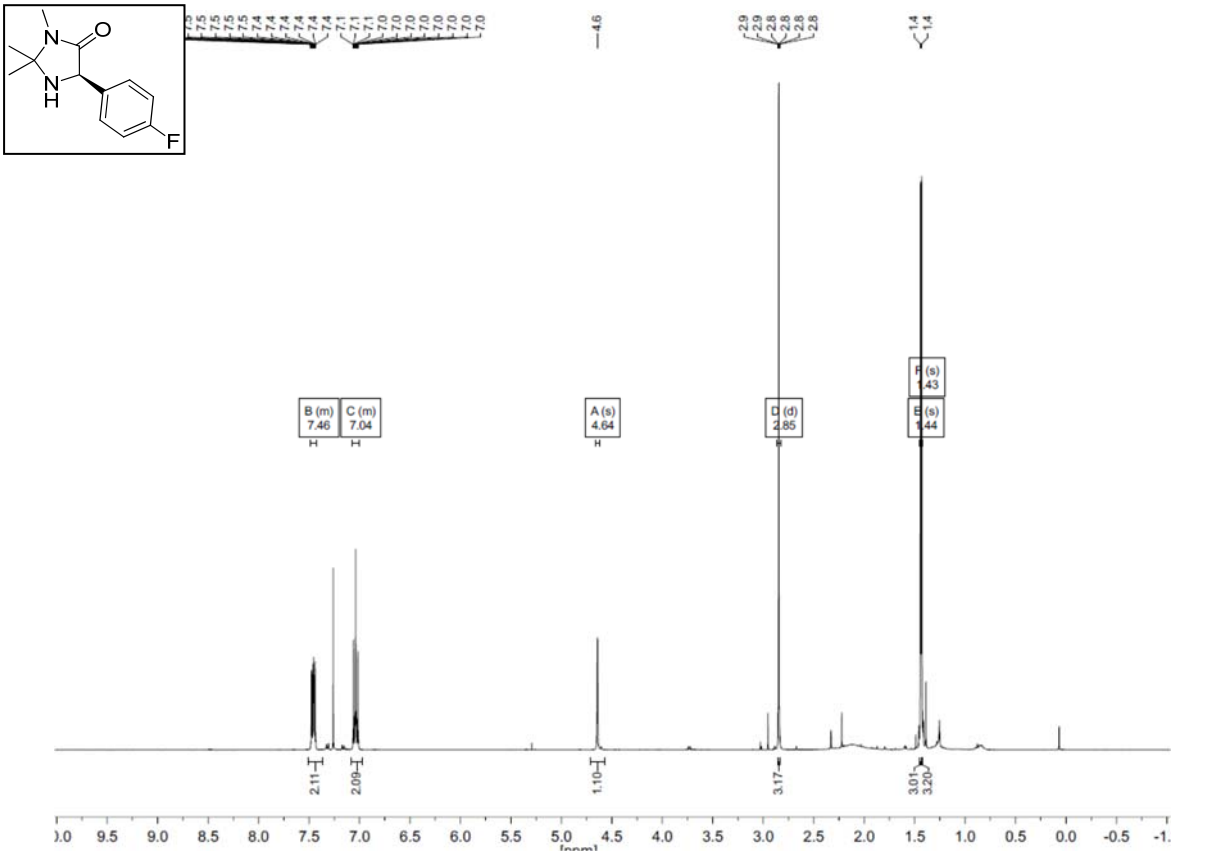
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.736	BB	0.3625	1.78943e4	739.02167	50.7560
2	16.190	VB	0.4415	1.73612e4	600.21735	49.2440

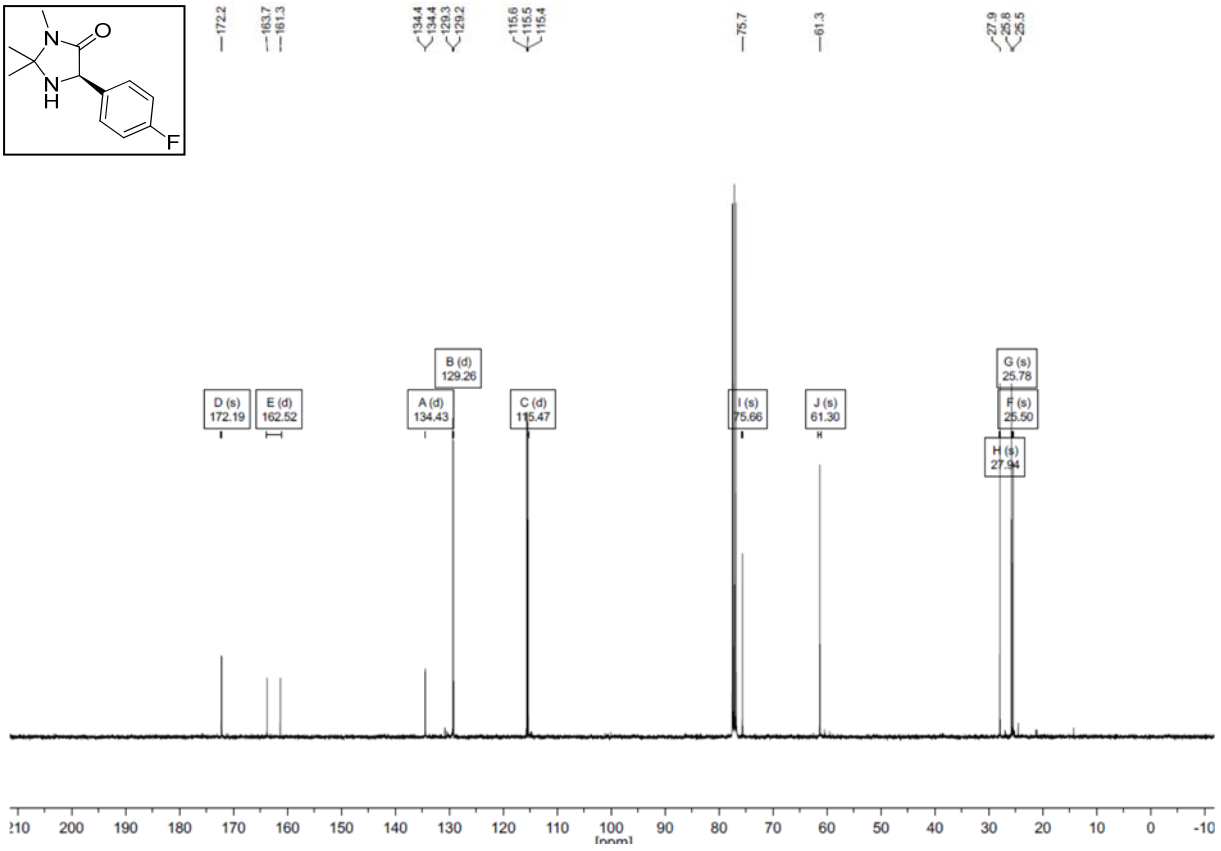
Method Info : Heptan : Ethanol 90.10 Flow 1.0 Det:220nm



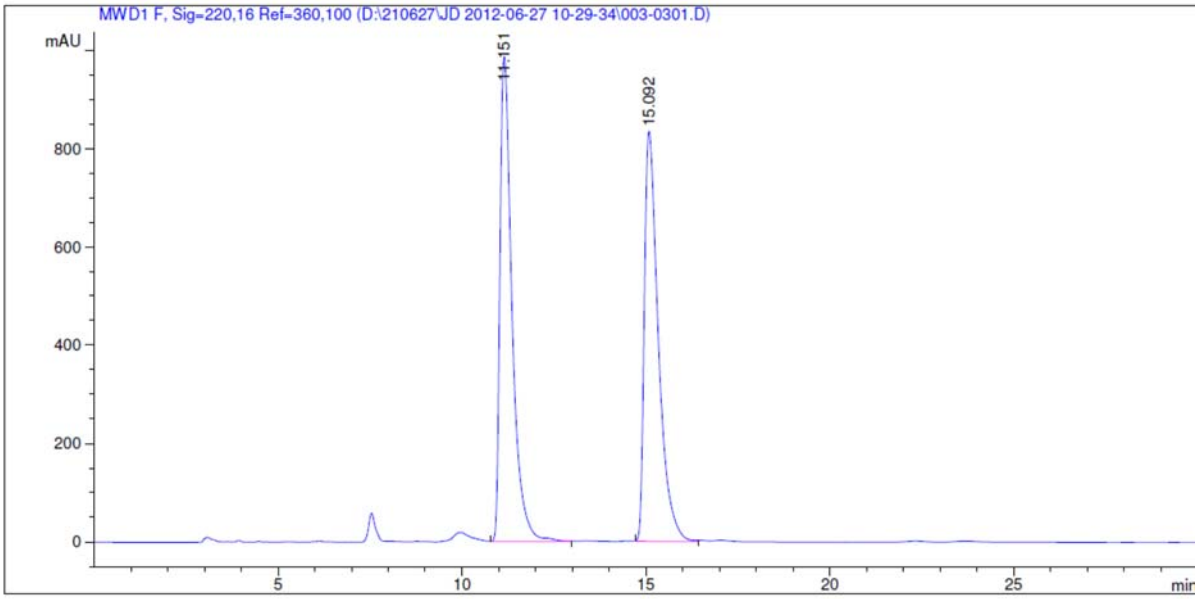
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.023	VB	0.3542	5.82602e4	2592.61914	97.1743
2	15.408	MM	0.3917	1694.13379	72.08499	2.8257

(*R*)-5-(4-Fluorophenyl)-2,2,3-trimethylimidazolidin-4-on (2f)



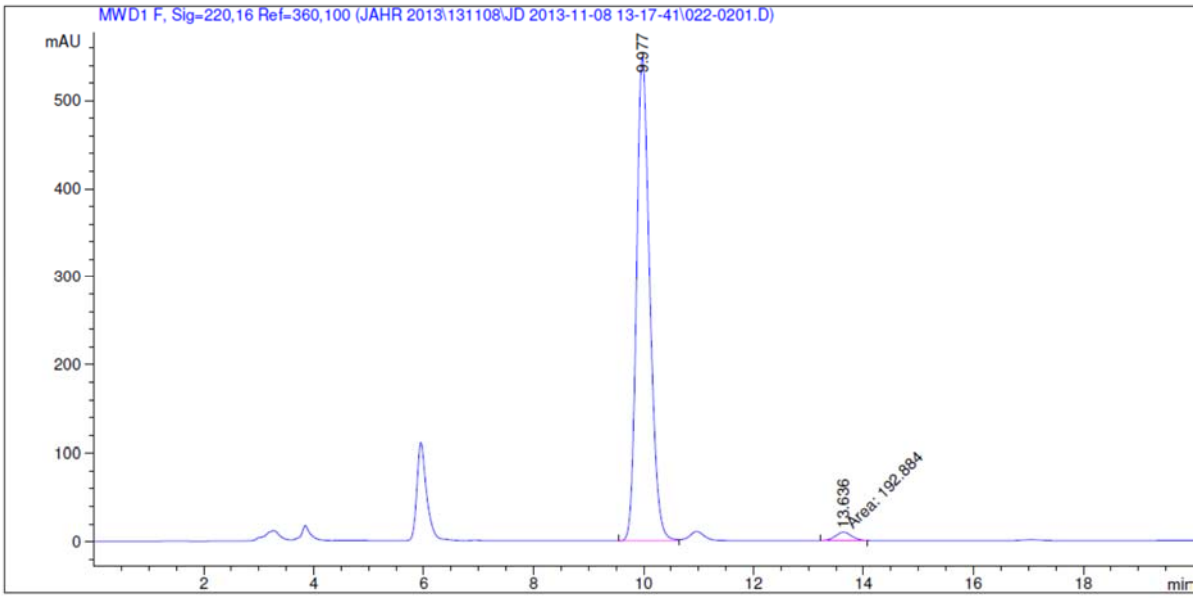


Method Info : Heptan:Ethanol 90:10 Flow: 1 ml/ min Det: 220 nm



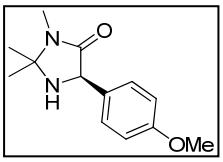
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.151	VB	0.3485	2.26327e4	983.48114	50.5601
2	15.092	BB	0.3976	2.21313e4	834.04163	49.4399

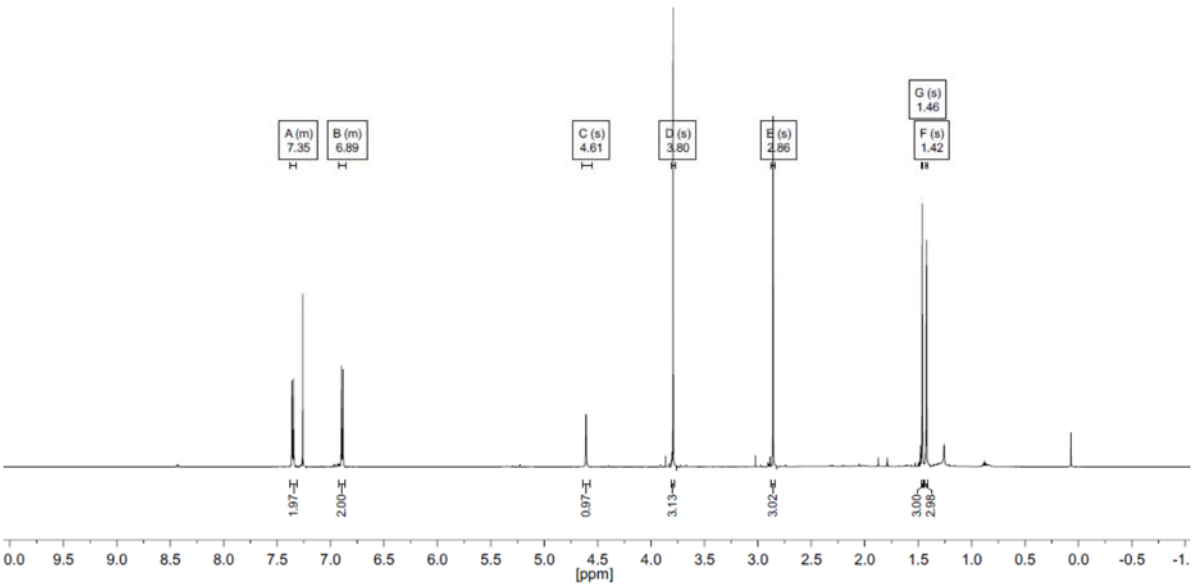
Method Info : Heptan : Ethanol 90.10 Flow 1.0 Det:220nm

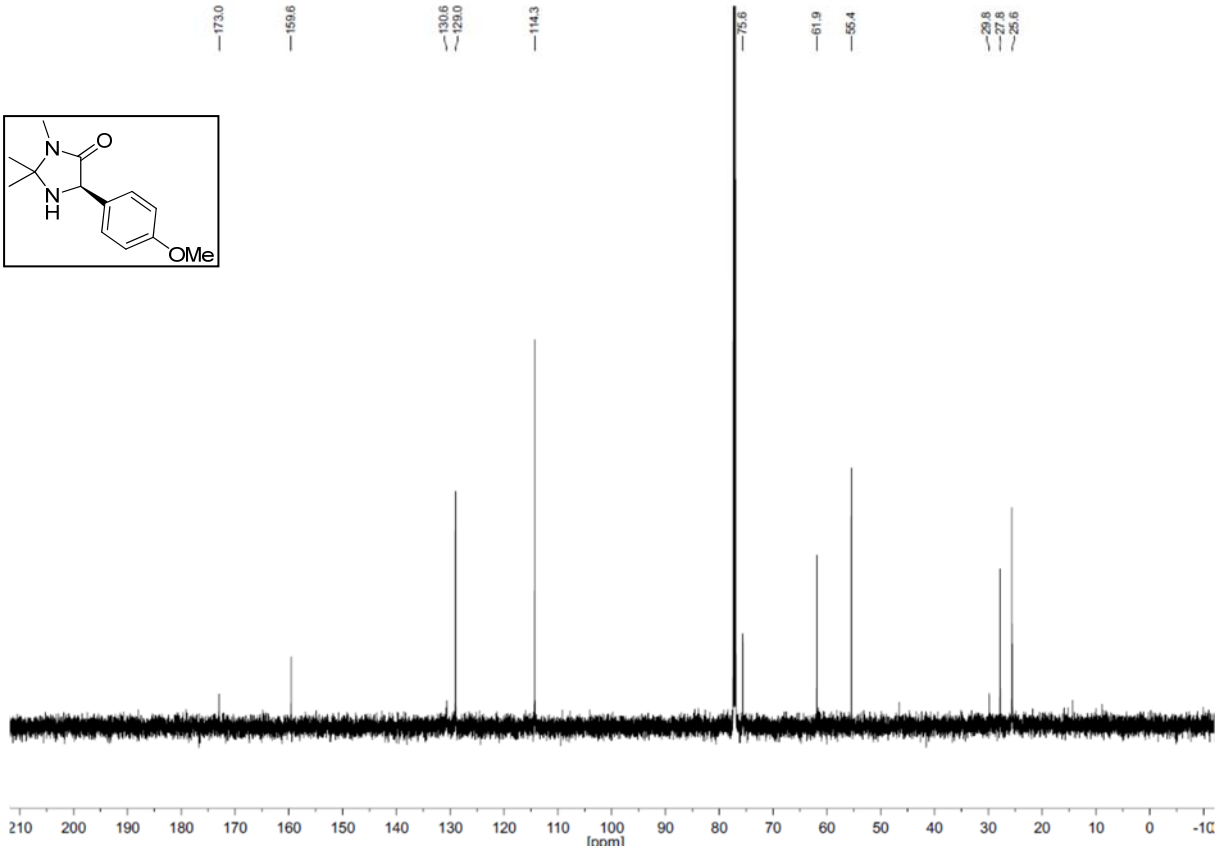


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.977	BV	0.2575	9192.52246	548.67303	97.9449
2	13.636	MM	0.3402	192.88368	9.45086	2.0551

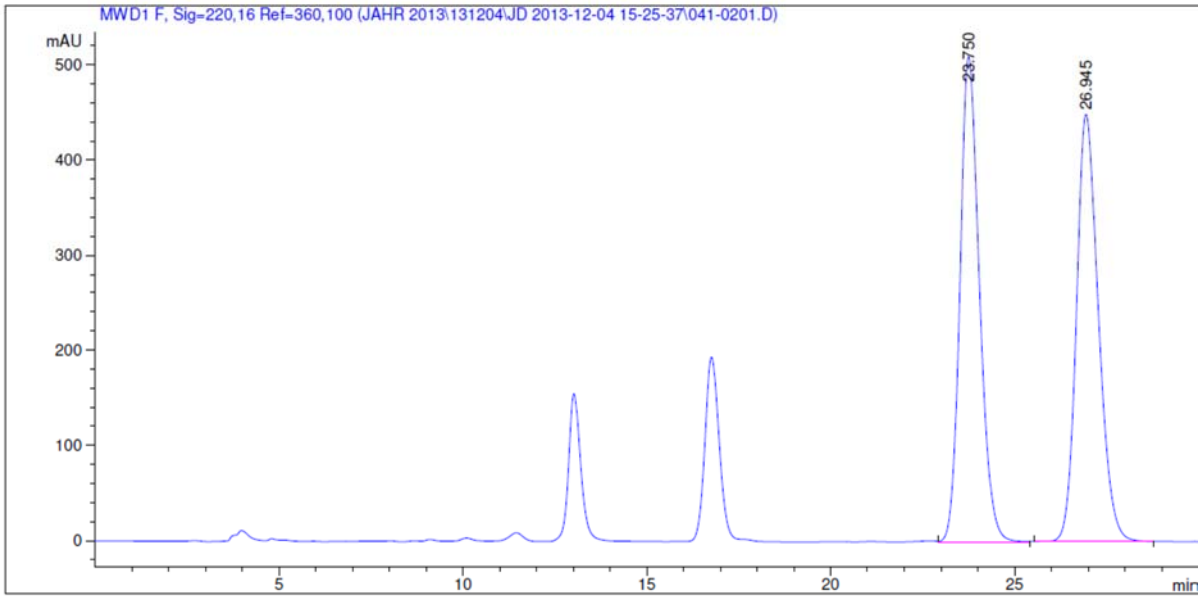
(*R*)-5-(4-Methoxyphenyl)-2,2,3-trimethylimidazolidin-4-on (2g)





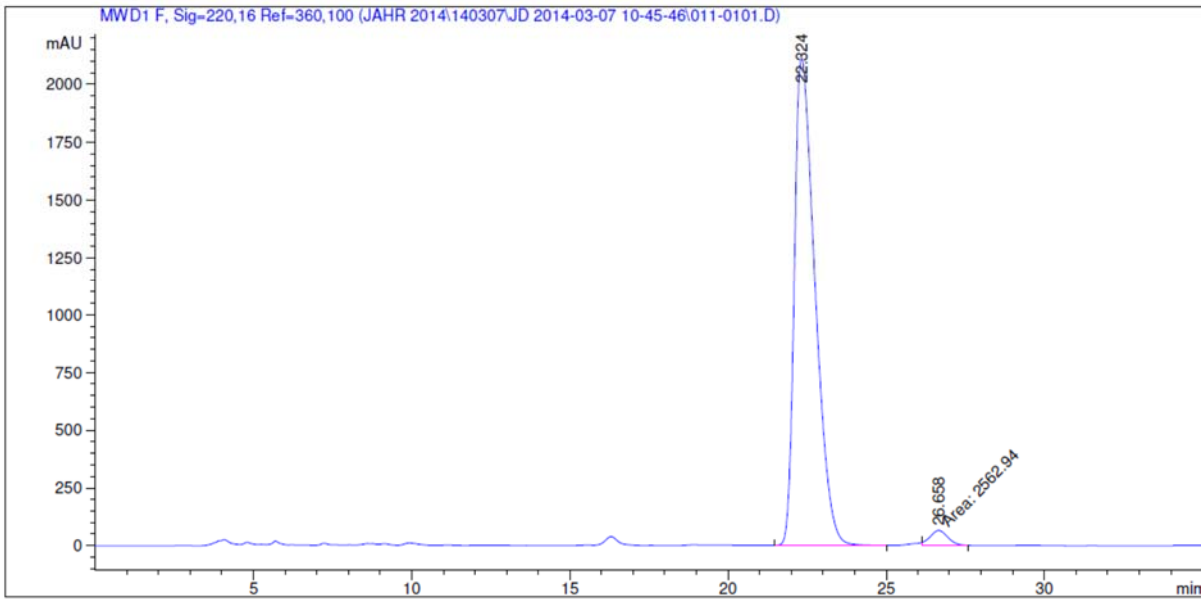


Method Info : Heptan : Ethanol 90 :10 Flow 0.8 ml/min Det:220 nm



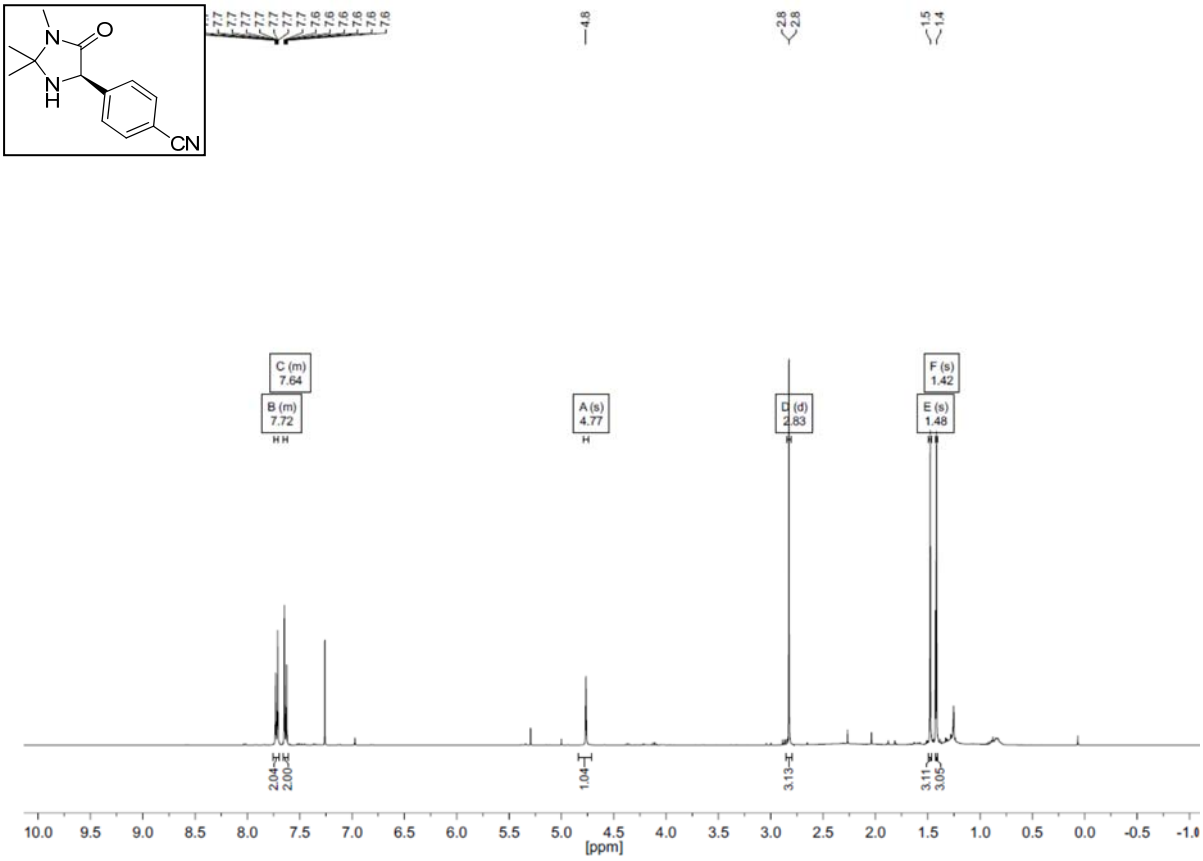
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.750	VB	0.5601	1.86990e4	509.56418	50.0827
2	26.945	BB	0.6324	1.86372e4	448.89322	49.9173

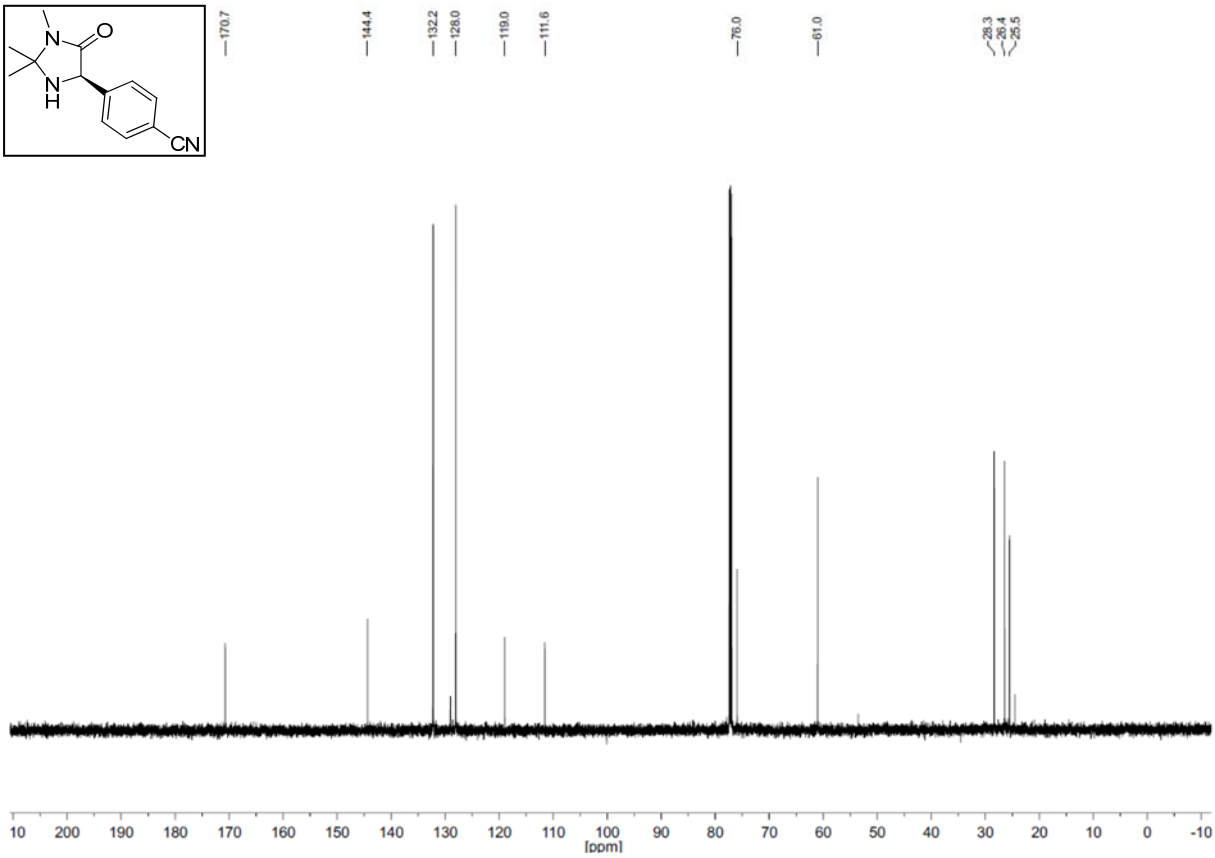
Method Info : Heptan : Ethanol 90:10 Flow 0.8 ml/min Det:220 nm



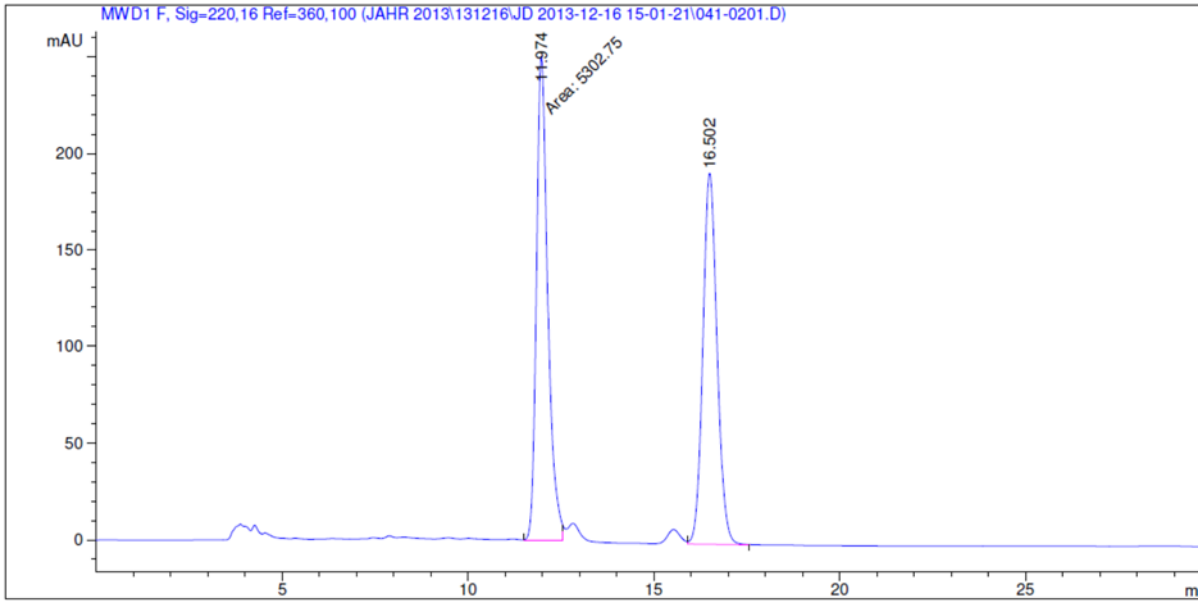
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.324	BB	0.6883	9.55641e4	2110.53174	97.3881
2	26.658	MM	0.6568	2562.94019	65.03365	2.6119

(*R*)-4-(1,2,2-Trimethyl-5-oxoimidazolidin-4-yl)benzonitril (2h)



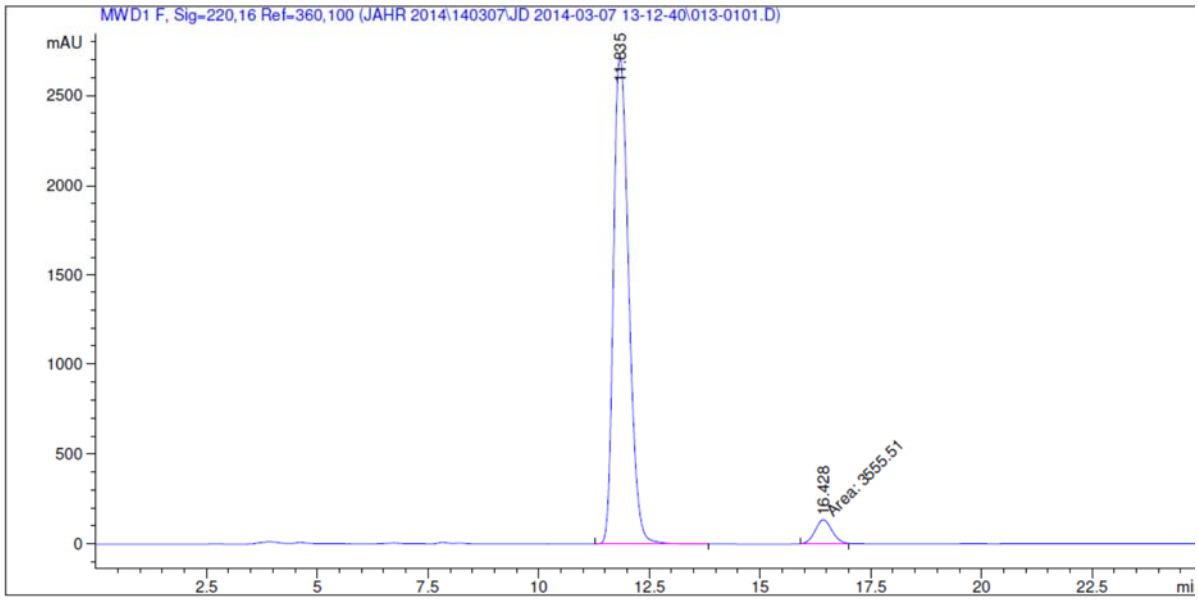


Method Info : Heptan : Ethanol 80 : 20 Flow 0.8 ml/min Det:220 nm



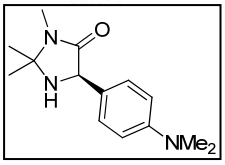
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.974	MM	0.3527	5302.75146	250.55412	50.9158
2	16.502	VB	0.4083	5111.99658	192.22241	49.0842

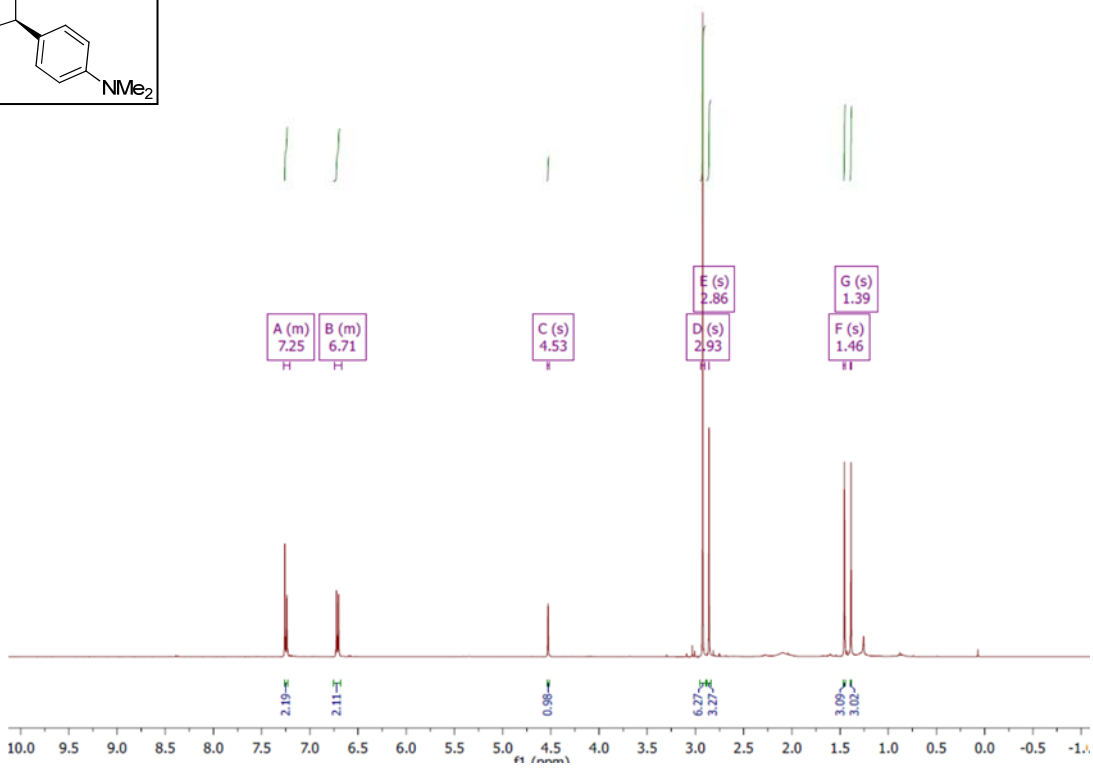
Method Info : Heptan : Ethanol 80:20 Flow 0.8 ml/min Det:220 nm

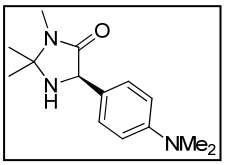


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.835	VB	0.3734	6.49581e4	2711.93457	94.8105
2	16.428	MM	0.4435	3555.50513	133.60098	5.1895

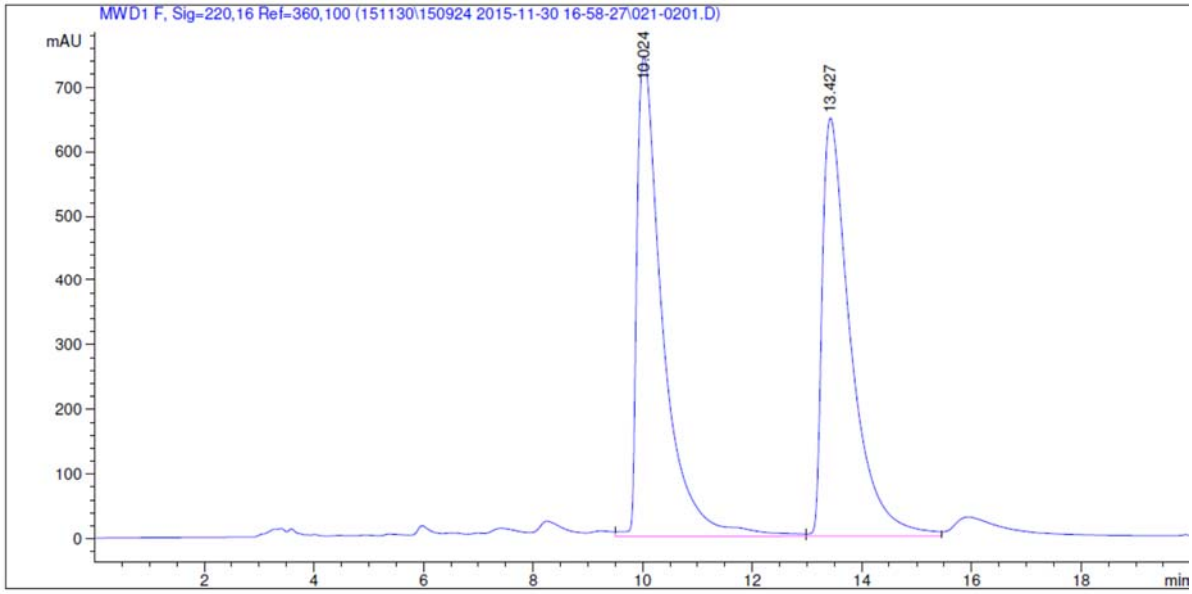
(*R*)-5-(4-(Dimethylamino)phenyl)-2,2,3-trimethylimidazolidin-4-on (2i)





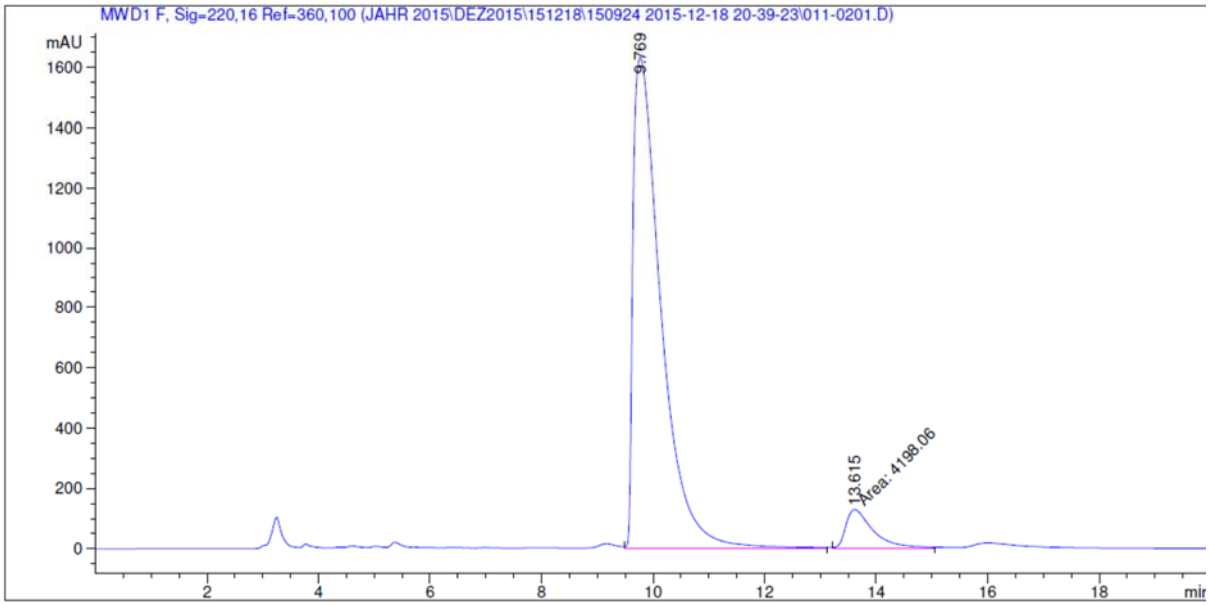


Method Info : Heptan:IPrOH 80 :20 Flow 1.0ml/min Det:220 nm



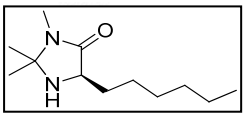
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.024	VV	0.4774	2.42279e4	744.94092	50.9321
2	13.427	VV	0.5299	2.33411e4	648.54761	49.0679

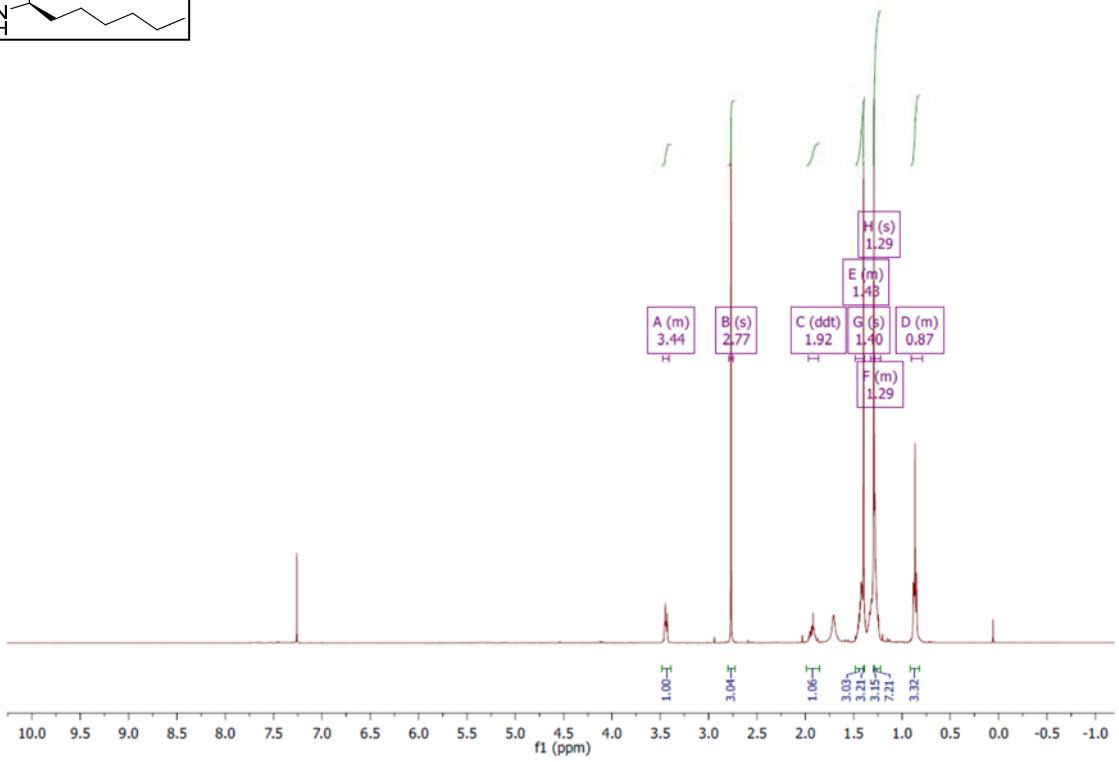
Method Info : Heptan:IPrOH 80 :20 Flow 1.0ml/min Det:220 nm

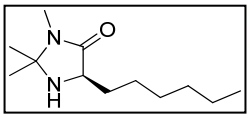


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.769	VB	0.5283	5.67906e4	1630.67224	93.1167
2	13.615	MM	0.5543	4198.06152	126.22135	6.8833

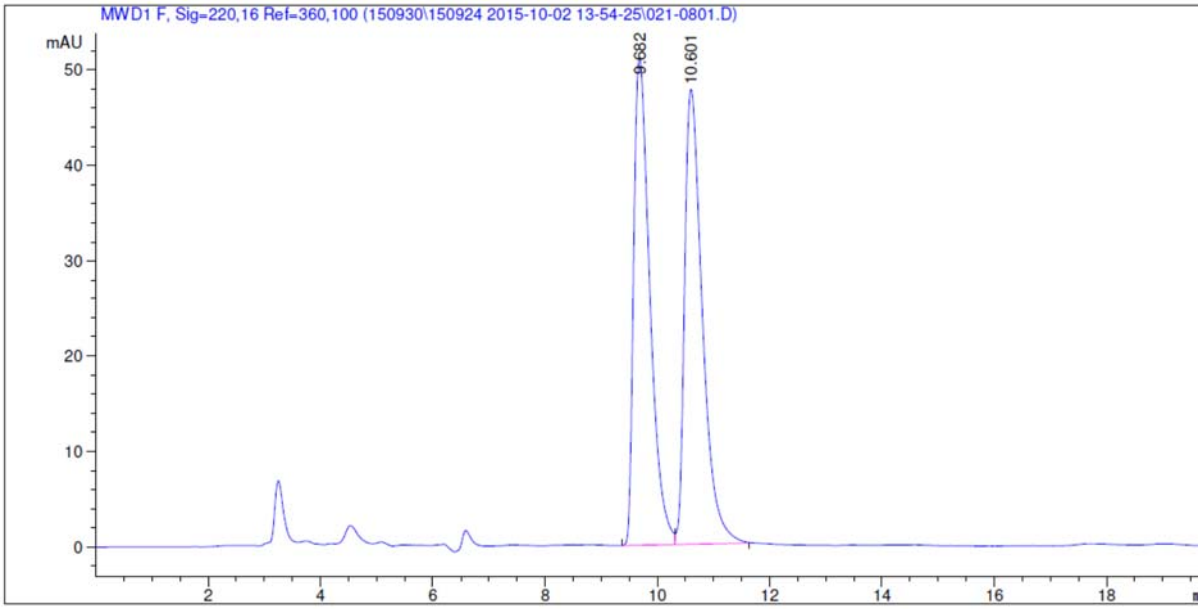
(*R*)-5-Hexyl-2,2,3-trimethylimidazolidin-4-on (2j)





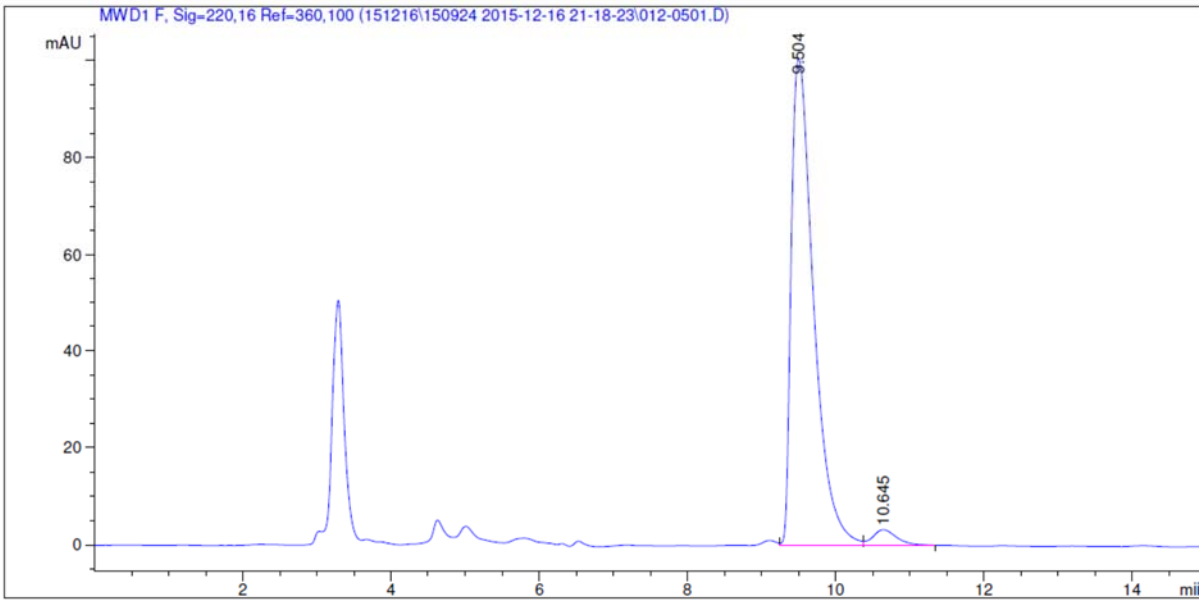


Method Info : Heptan: IPA 95:5 Flow 1.0 ml/min Det:220 nm



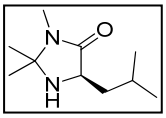
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.682	BV	0.3101	1025.40076	51.09300	49.4250
2	10.601	VB	0.3366	1049.25940	47.70996	50.5750

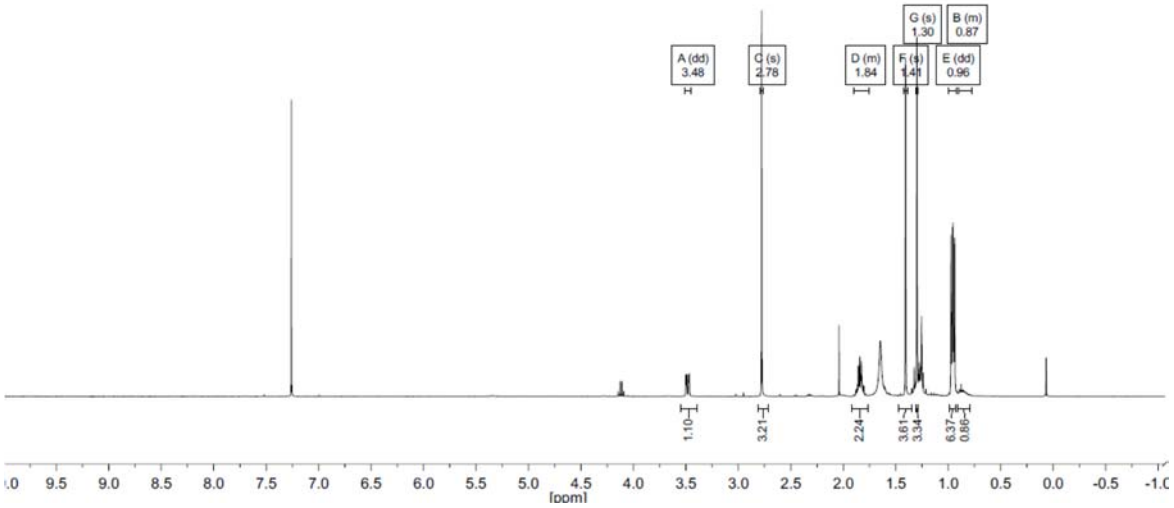
Method Info : Heptan: IPA 95:5 Flow 1.0 ml/min Det:220 nm

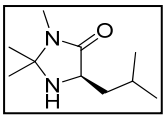


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.504	VV	0.3174	2097.85620	100.56700	96.5662
2	10.645	VB	0.3322	74.59801	3.26944	3.4338

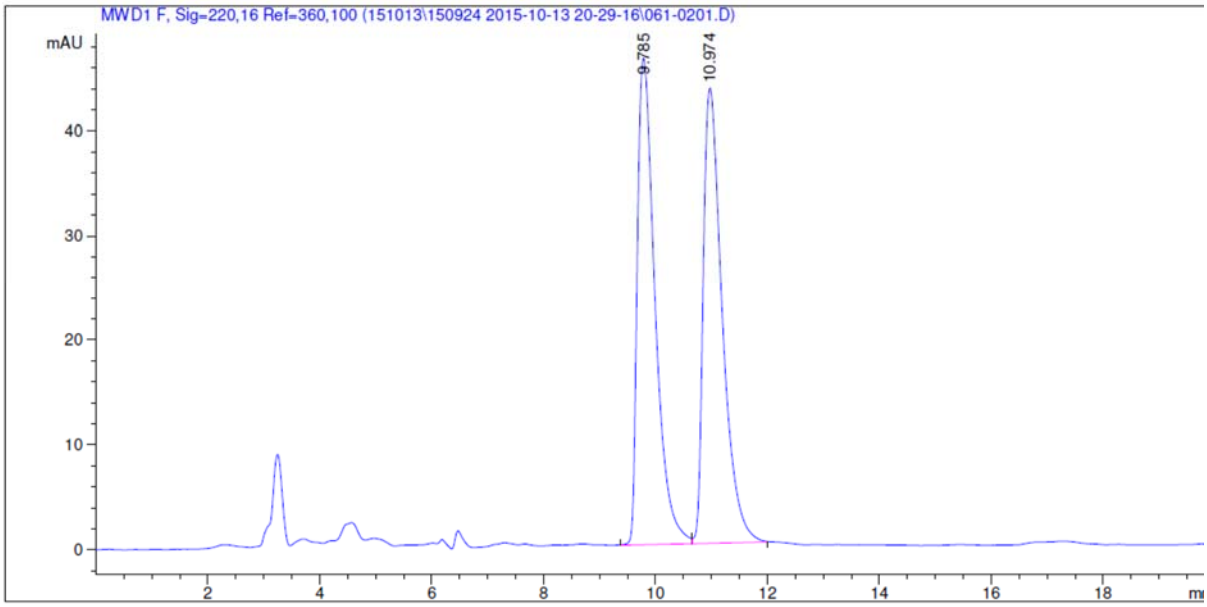
(*R*)-5-Isobutyl-2,2,3-trimethylimidazolidin-4-one (2k)





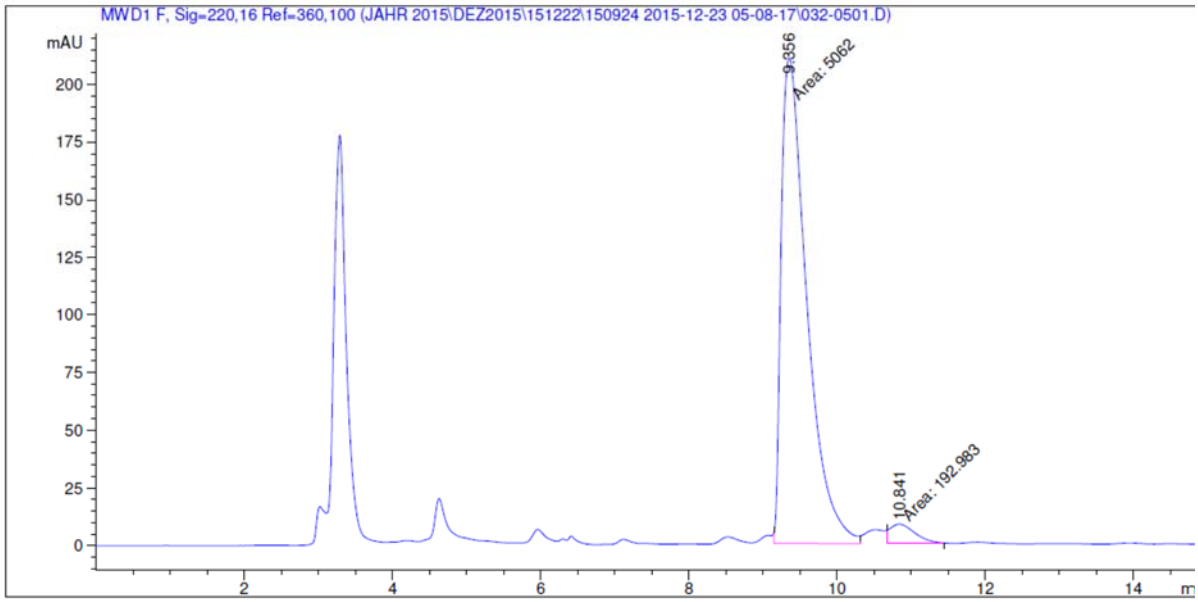


Method Info : Heptan: IPA 95:5 Flow 1.0 ml/min Det:220 nm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.785	BV	0.3359	1019.29236	46.46140	49.8553
2	10.974	VB	0.3613	1025.20972	43.45367	50.1447

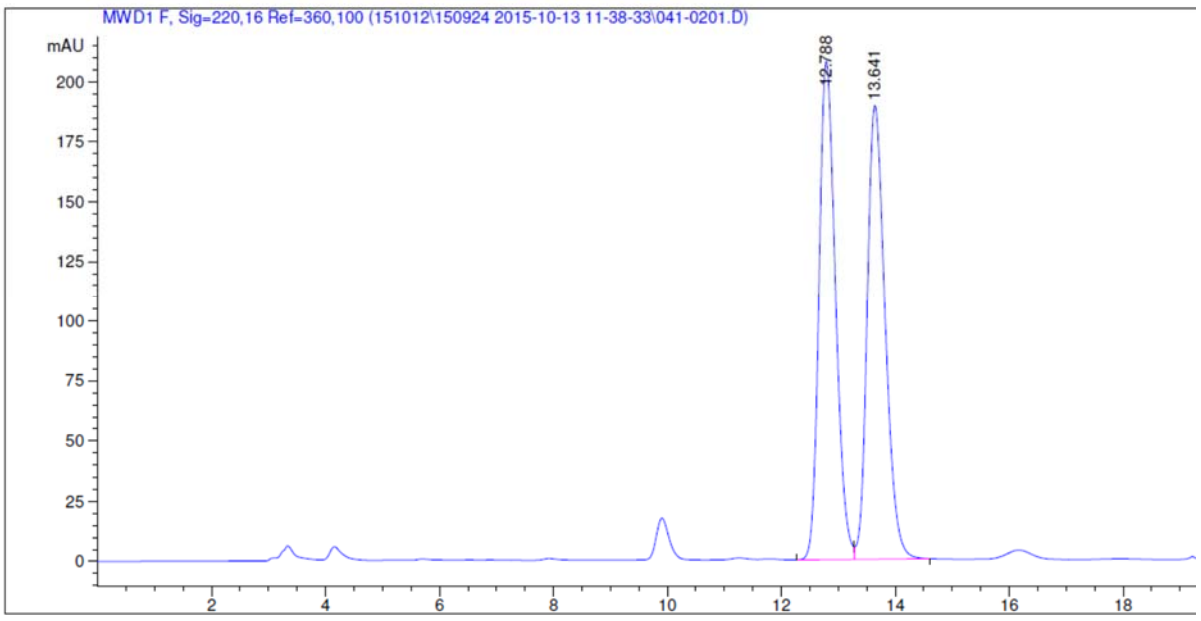
Method Info : Heptan: IPA 95:5 Flow 1.0 ml/min Det:220 nm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.356	MM	0.4009	5061.99561	210.44225	96.3276
2	10.841	MM	0.3907	192.98280	8.23239	3.6724

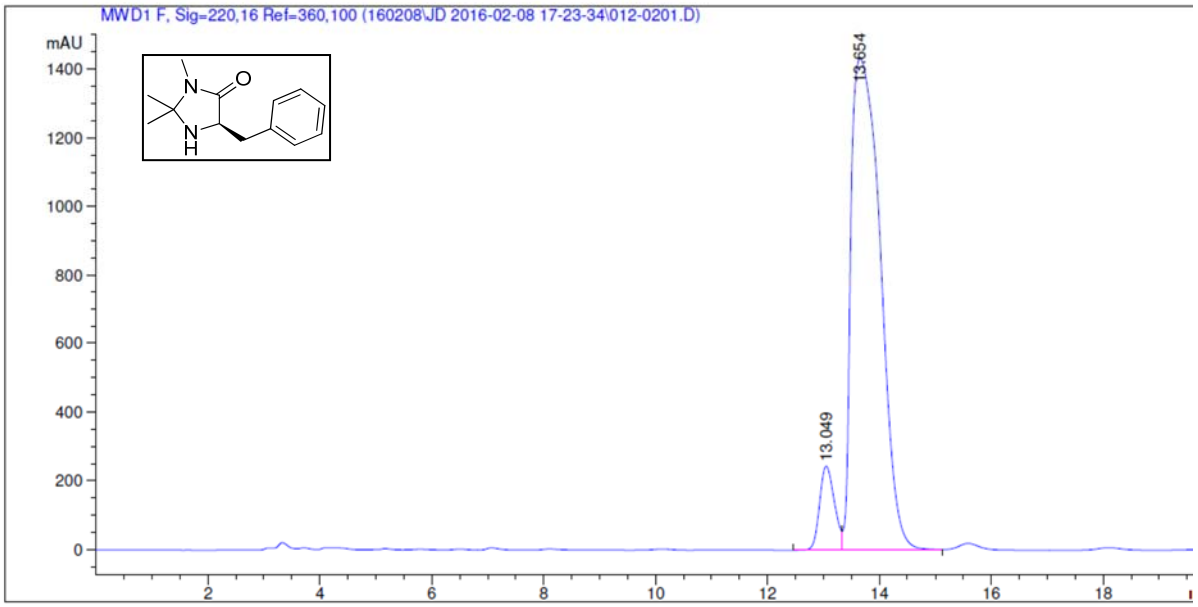
(*R*)-5-Benzyl-2,2,3-trimethylimidazolidin-4-on (2l)

Method Info : Heptan: EtOH 95:5 Flow 1.0 ml/min Det:220 nm



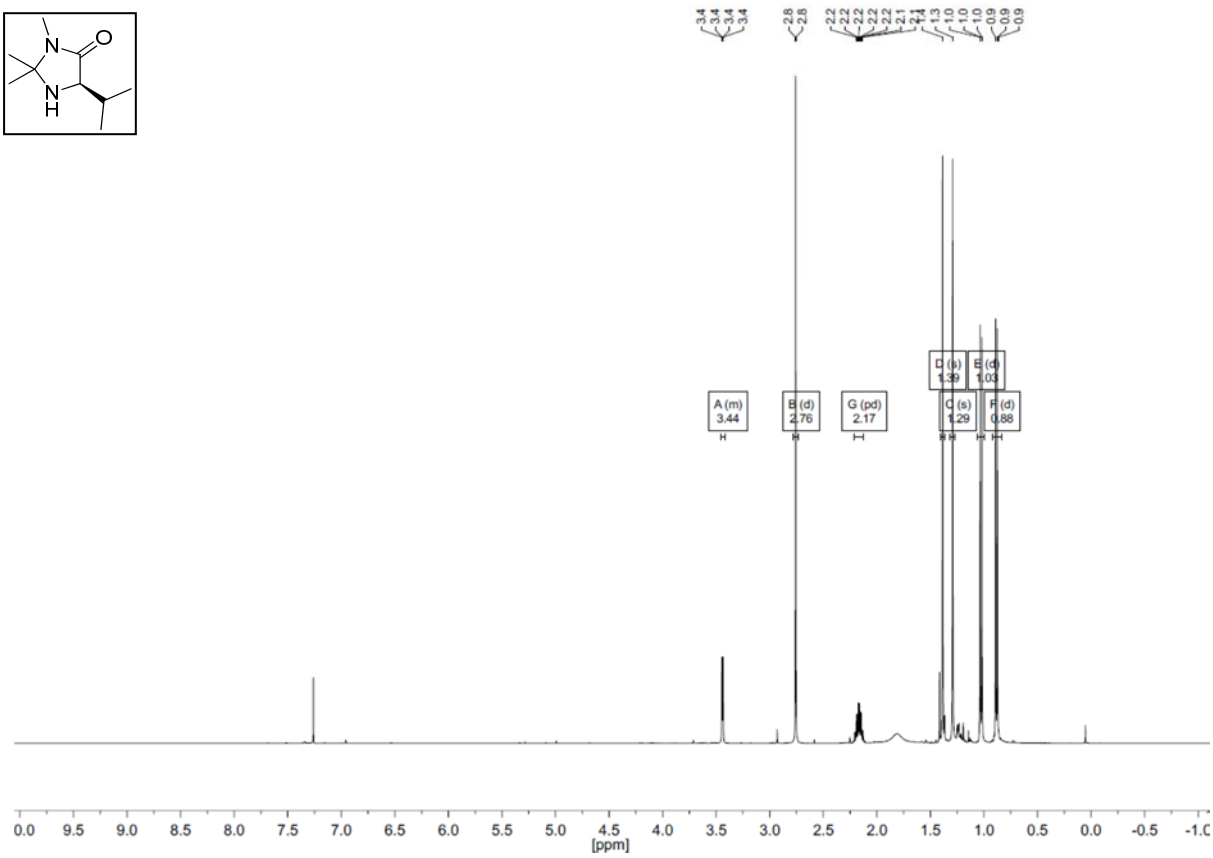
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.788	BV	0.3103	4171.21338	207.72289	50.2534
2	13.641	VB	0.3387	4129.14551	189.17377	49.7466

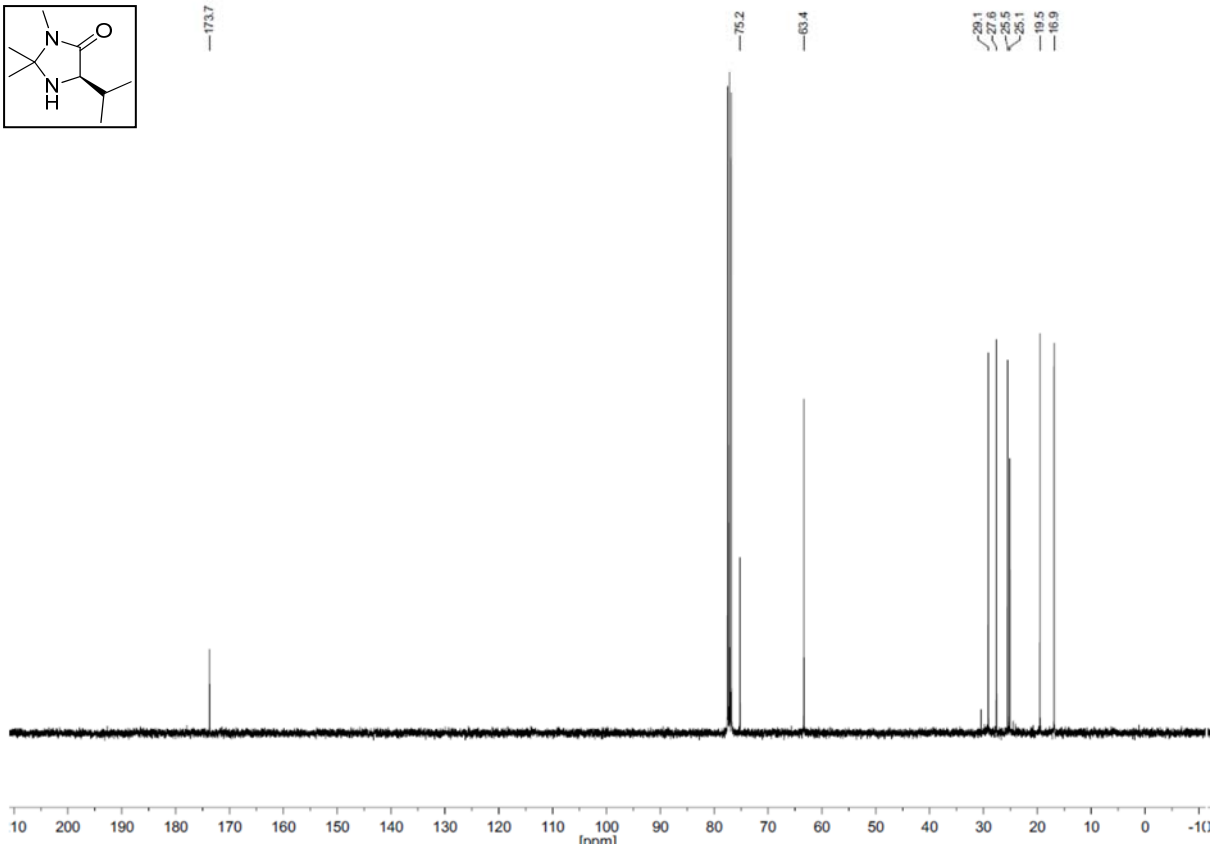
Method Info : Heptan: EtOH 95:5 Flow 1.0 ml/min Det:220 nm



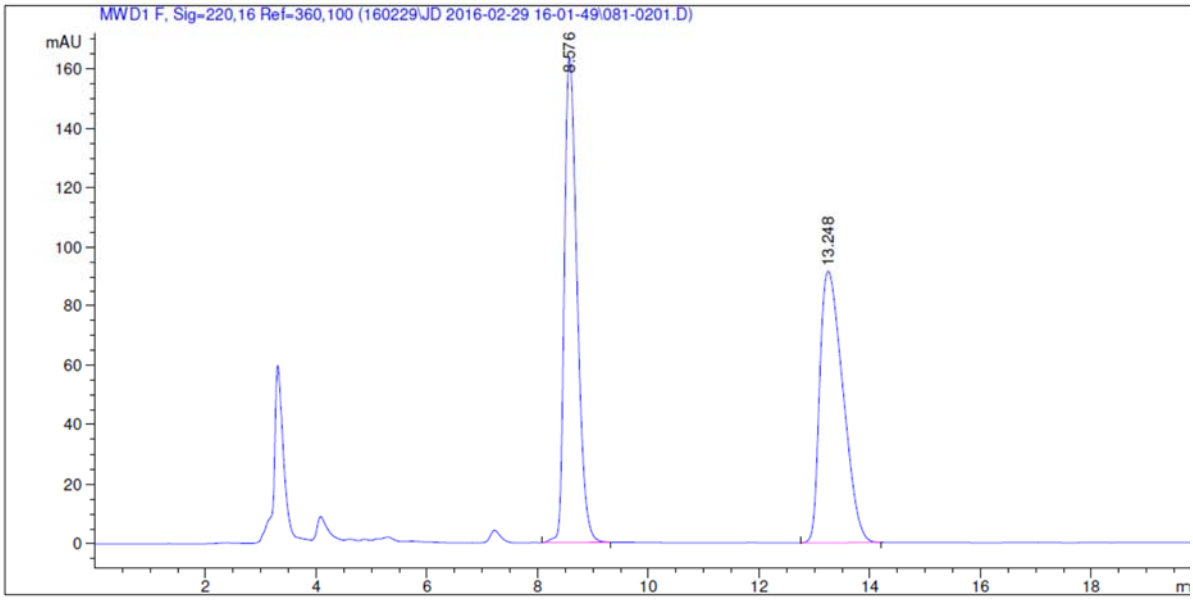
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.049	BV	0.2893	4497.08301	243.64632	7.9874
2	13.654	VV	0.5977	5.18050e4	1433.31750	92.0126

(*R*)-5-Isopropyl-2,2,3-trimethylimidazolidin-4-one (2m)



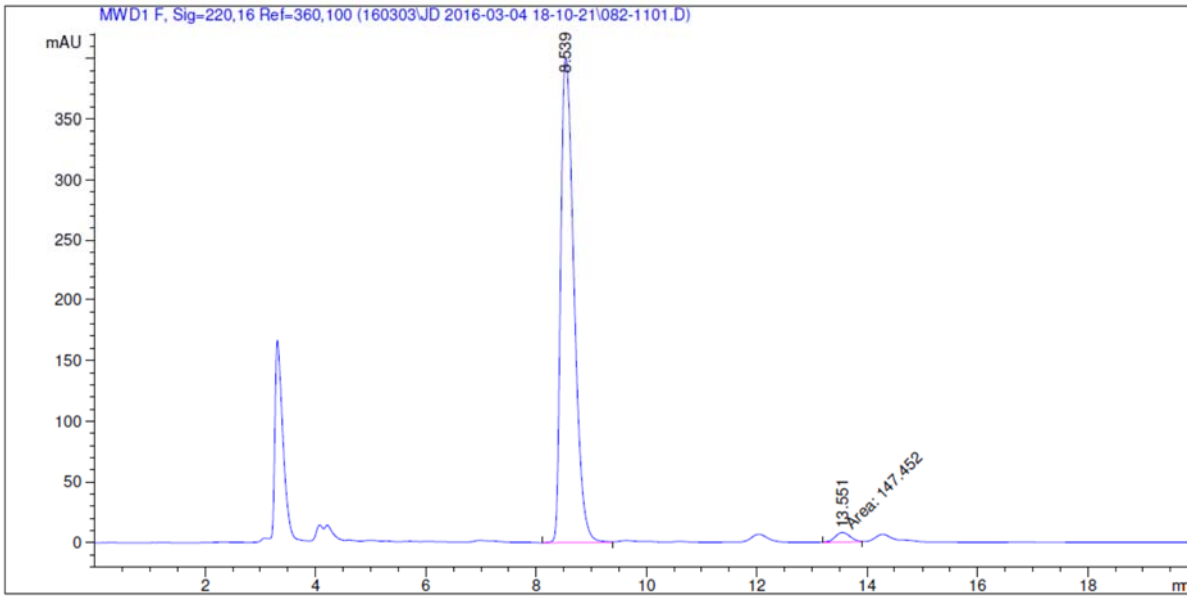


Method Info : Heptan: EtOH 95:5 Flow 1.0 ml/min Det:220 nm



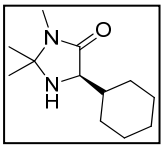
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.576	BB	0.2479	2607.18408	163.61948	49.6081
2	13.248	BB	0.4612	2648.37378	91.63389	50.3919

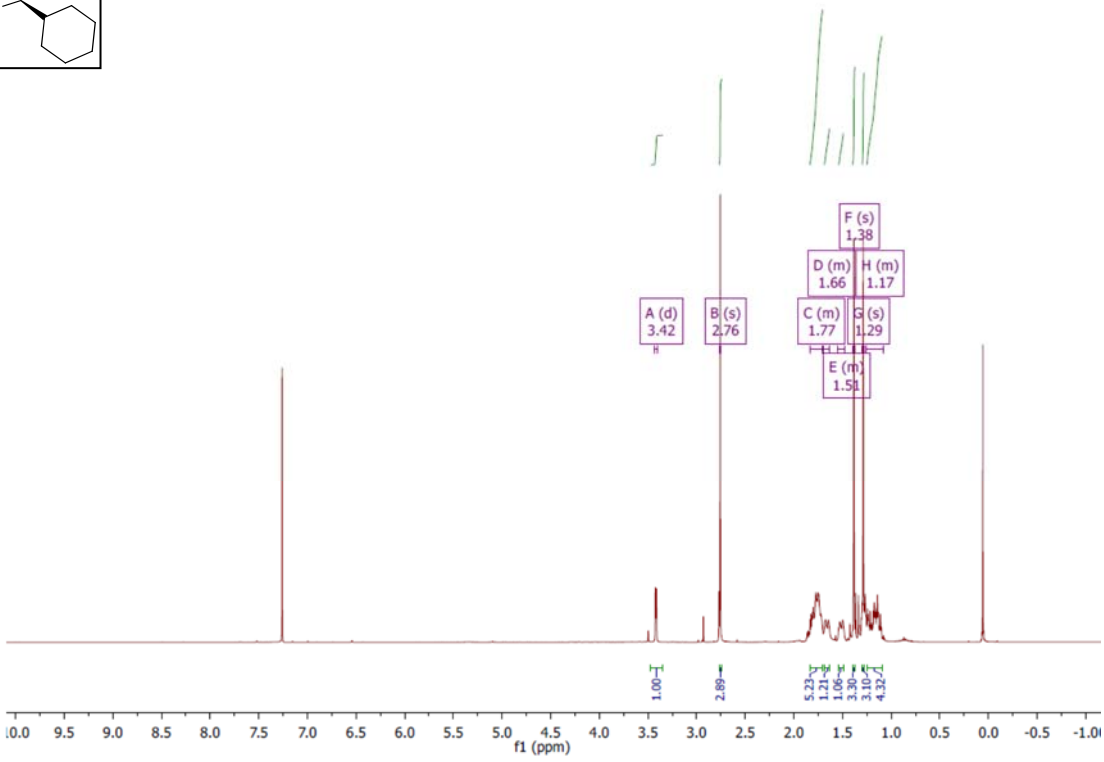
Method Info : Heptan: EtOH 95:5 Flow 1.0 ml/min Det:220 nm

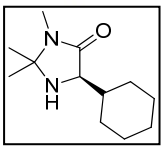


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.539	BB	0.2619	6666.01709	401.01962	97.8359
2	13.551	MM	0.3156	147.45221	7.78751	2.1641

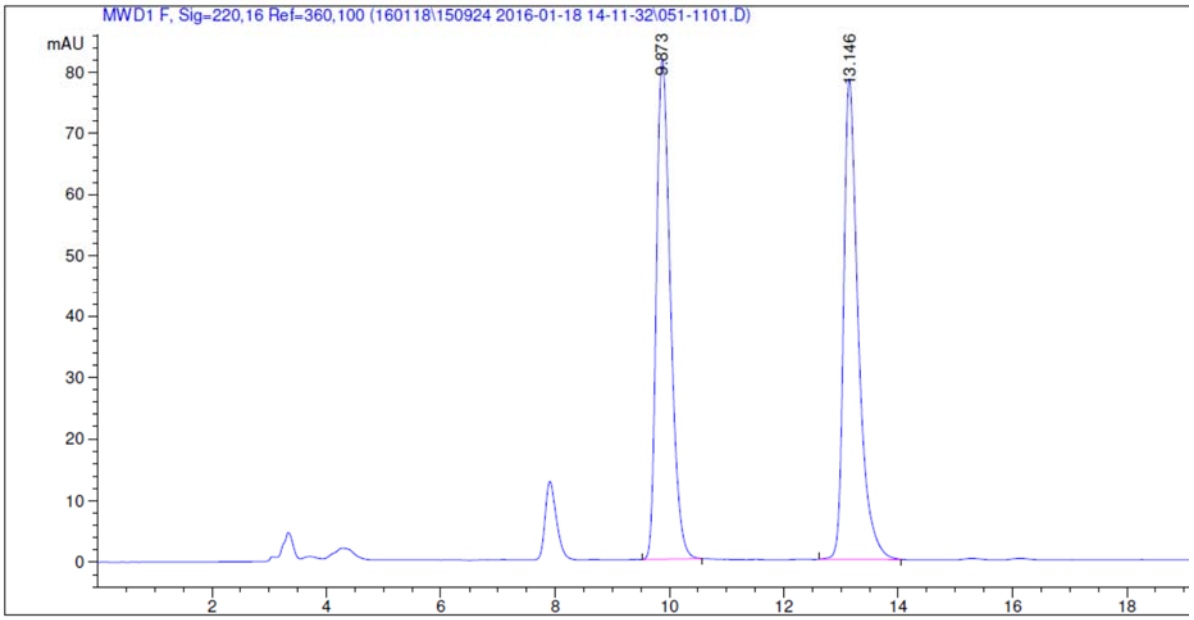
(*R*)-5-Cyclohexyl-2,2,3-trimethylimidazolidin-4-one (2n)





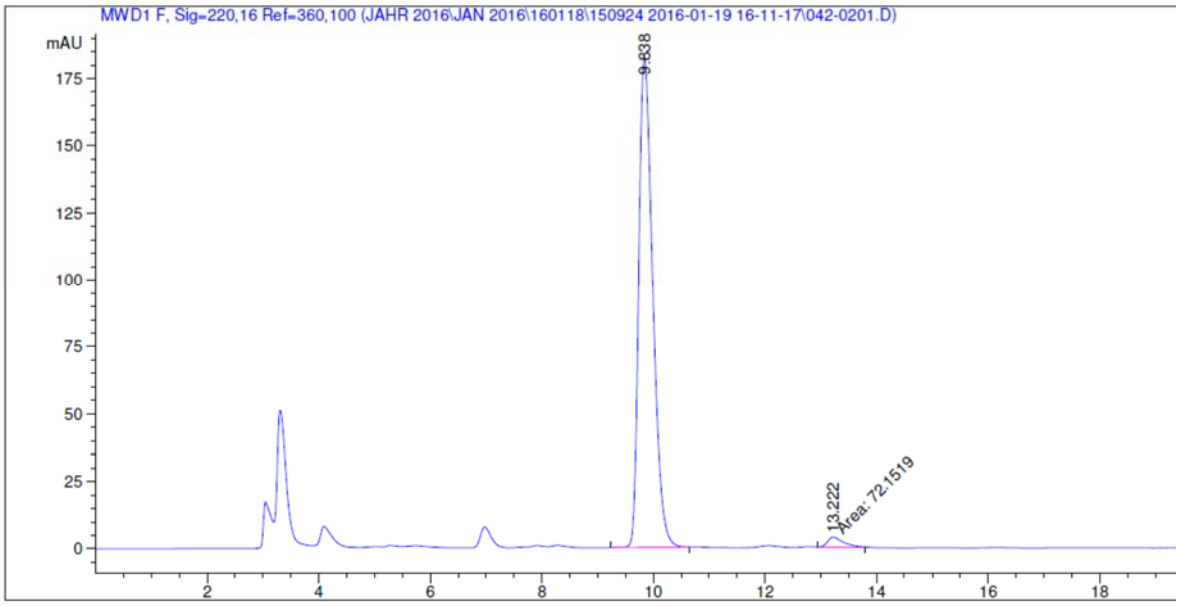


Method Info : Heptan: EtOH 95:5 Flow 1.0 ml/min Det:220 nm



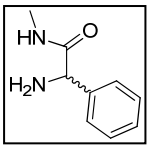
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.873	BB	0.2644	1387.90833	81.61398	49.9104
2	13.146	BB	0.2651	1392.88904	78.45223	50.0896

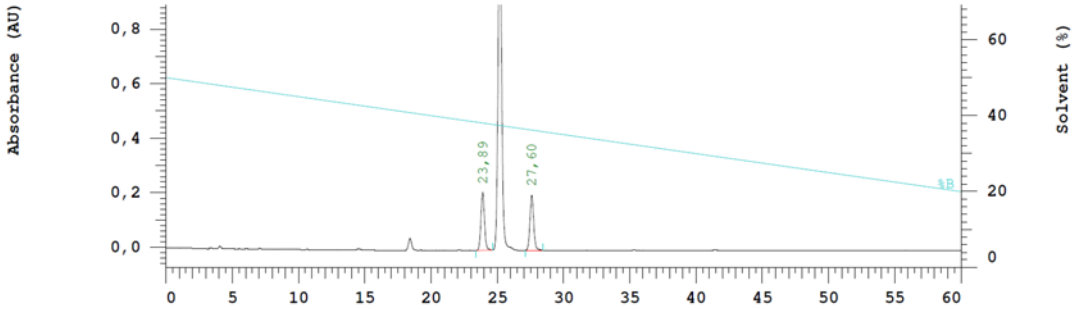
Method Info : Heptan: EtOH 95:5 Flow 1.0 ml/min Det:220 nm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.838	BB	0.2734	3173.86938	182.06596	97.7772
2	13.222	MM	0.3241	72.15190	3.71061	2.2228

D-Phenylglycine methyl amide (5)

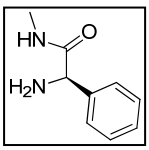


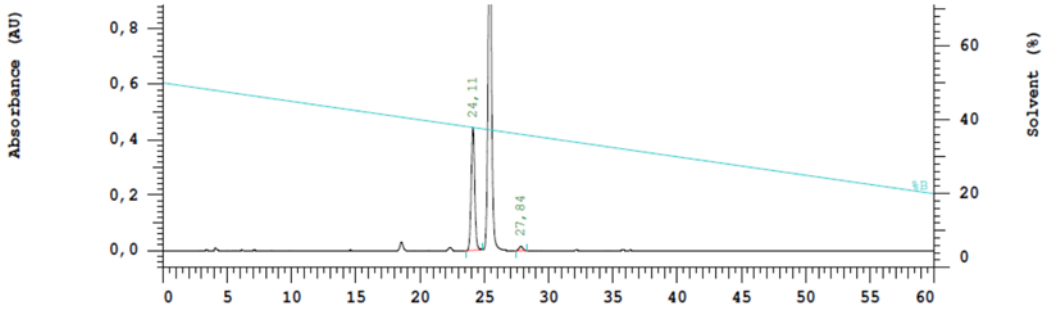


Time (min)	%ACN	%0.1%	%Wasse	%Metha	Flow (ml/min)
0,0	50,0	50,0	0,0	0,0	0,600
60,0	80,0	20,0	0,0	0,0	0,600

No.	RT	Area	Conc 1
1	23,89	1986919	50,079
2	27,60	1980653	49,921

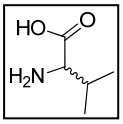
The unpicked peak at the retention time of 25.5 minutes belongs to the derivatisation reagent.[6]

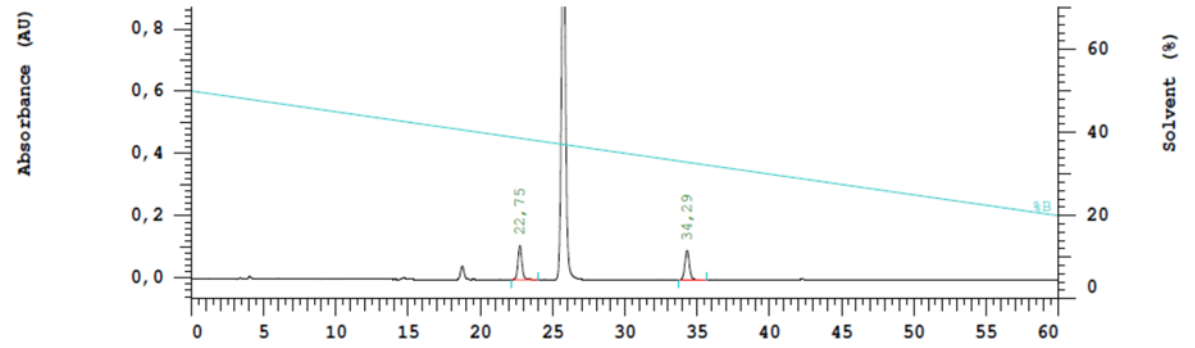




No.	RT	Area	Conc 1
1	24,11	4205374	96,515
2	27,84	151862	3,485

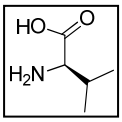
D-Valine (4)

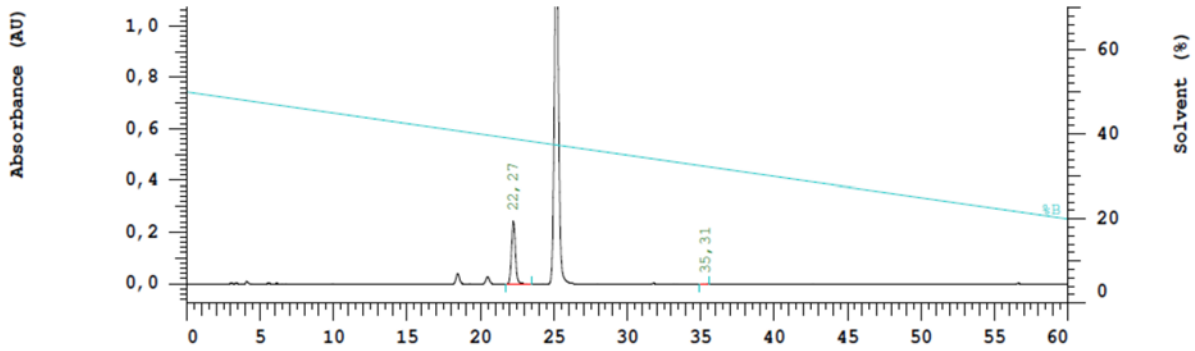




Time (min)	%ACN	%0.1%	%Wasse	%Metha	Flow (ml/min)
0,0	50,0	50,0	0,0	0,0	0,600
60,0	80,0	20,0	0,0	0,0	0,600

No.	RT	Area	Conc 1
1	22,75	1047977	50,621
2	34,29	1022262	49,379





No.	RT	Area	Conc 1
1	22,27	2237918	99,362
2	35,31	14363	0,638