Electronic Supplementary Information

Direct condensation of functionalized sp^3 carbons with formanilides for enamine synthesis using *in situ* generated HMDS amide catalyst

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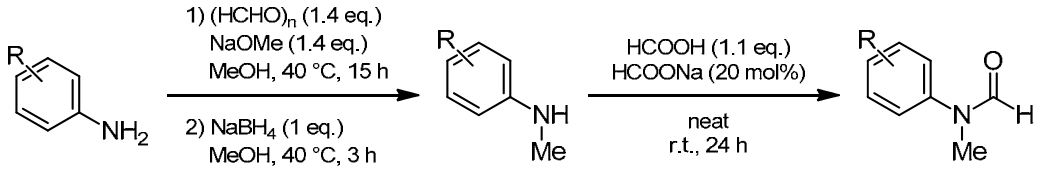
General Comments.

Unless otherwise noted, reactions were carried out under an argon atmosphere using dry solvents. Melting points (mp) were determined with a Yazawa micro melting point apparatus and uncorrected. Infrared (IR) data were recorded on Shimadzu software. The spectra were acquired in 32 scans per spectrum at a resolution of four, and absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). NMR data were recorded on either a JEOL AL400 spectrometer (395.75 MHz for ^{1}H, 99.50 MHz for ^{13}C) or a JEOL ECA600 spectrometer (600.172 MHz for ^{1}H, 150.907 for ^{13}C). Chemical shifts are expressed in δ (parts per million, ppm) values, and coupling constants (*J*) are expressed in herts (Hz). ^{1}H NMR spectra were referenced to a tetramethylsilane (TMS) as an internal standard or to a solvent signal ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were referenced to a solvent signal ($CDCl_3$: 77.0 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dt = double triplet. Low and high resolution mass spectra (LRMS and HRMS) were obtained from Mass Spectrometry Resource, Graduate School of Pharmaceutical Sciences, Tohoku University, on a JEOL JMS-DX303 and JMS-700 spectrometer respectively. Elemental analyses (*Anal.*) were performed on Yanaco CHN CORDER MT-6 at Central Analytical Center, Graduate School of Pharmaceutical Sciences, Tohoku University.

Materials.

Unless otherwise noted, commercially available materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used after appropriate purification (distillation and recrystallization). Flash column chromatography was performed with Kanto silica gel 60 N (spherical, neutral, 40–50 μm). Reactions were monitored by thin-layer chromatography on precoated plates of silica gel (Merck Silica gel 60 F254).

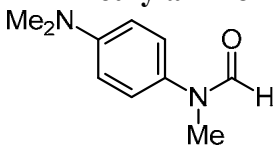
General procedure for the synthesis of *N*-methylformanilides (2c, 2f, 2g, 2h, 2i)[1]



To a solution of anilines (10 mmol) and sodium methoxide (14 mmol, 2.8 g) in MeOH (25 mL) was added paraformaldehyde (14 mmol, 443 mg). The reaction mixture was warmed to 40 °C and stirred for 15 h. $NaBH_4$ (10 mmol, 411 mg) was added to the reaction mixture and the reaction was stirred at 40 °C for 3 h. Quenched with sat. $NaHCO_3$ aq., the reaction mixture was extracted with diethyl ether. The organic layers were collected, washed with brine, dried over $MgSO_4$ and concentrated under a reduced presser. Purification by column chromatography on silica gel afforded *N*-methylanilines.

To a mixture of *N*-methylanilines (10 mmol) and formic acid (11 mmol, 419 μL) was added sodium formate (2 mmol, 139 mg). The reaction mixture was stirred at room temperature for 24 h. After the reaction was complete, EtOAc was added to the reaction mixture, and sodium formate was removed by filteration. The organic layers were washed with brine and sat. $NaHCO_3$ aq., dried over Na_2SO_4 and concentrated under a reduced presser. Purification by column chromatography on silica gel afforded *N*-methylformanilides (**2c, 2f, 2g, 2h, 2i**).

4'-Dimethylamino-*N*-methylformanilide (2c)



Colorless needles (recrystallized from hexane/EtOAc, mp 105–106 °C).

IR (neat): 2889, 1658, 1521, 1343, 1232, 979, 818 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 2.96 (s, 6H), 3.25 (s, 3H), 6.71 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 8.30 (s, 1H).

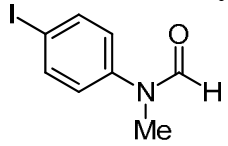
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 32.71, 40.50, 112.77, 124.60, 131.33, 149.34,

162.46.

LRMS (EI) m/z: 178 (M^+).

HRMS: Calcd. for $C_{10}H_{14}N_2O$: 178.1106, found: 178.1092.

4'-Iodo-*N*-methylformanilide (2g)



Yellow crystal (recrystallized from hexane/chloroform, mp 91–94 °C).

IR (neat): 1665, 1486, 1330, 1108, 1006, 814, 710 cm^{-1}.

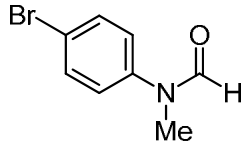
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 3.29 (s, 3H), 6.92–6.95 (m, 2H), 7.72–7.74 (m, 2H), 8.47 (s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 31.83, 90.46, 123.89, 138.66, 138.68, 161.83.

LRMS (EI) m/z: 261 (M^+).

HRMS: Calcd. for C_8H_8INO: 260.9651, found: 260.9640.

4'-Bromo-*N*-methylformanilide (2h)



White solid (recrystallized from petroleum ether/EtOAc, mp 71–72 °C).

IR (neat): 2904, 1669, 1489, 1332, 1112, 1010, 980, 845, 814, 712 cm^{-1}.

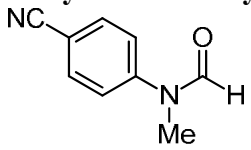
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 3.30 (s, 3H), 7.06 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 8.46 (s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 31.95, 119.69, 123.75, 132.05, 132.71, 161.88.

LRMS (EI) m/z: 213 (M^+).

HRMS: Calcd. for $C_8H_8{}^{79}BrNO$: 212.9789, found: 212.9789.

4'-Cyano-*N*-methylformanilide (2i)



Colorless crystal (recrystallized from petroleum ether/EtOAc, mp 105–106 °C).

IR (neat): 2223, 1669, 1603, 1507, 1341, 1316, 1261, 1113, 972, 854, 827 cm^{-1}.

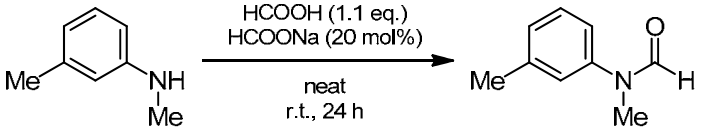
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 3.36 (s, 3H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H), 8.67 (s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 31.18, 109.19, 118.08, 120.95, 133.64, 145.75, 161.45.

LRMS (EI) m/z: 160 (M^+).

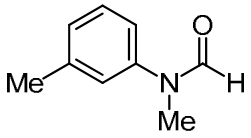
HRMS: Calcd. for $C_9H_8N_2O$: 160.0637, found: 160.0624.

Synthesis of 2e [1]



To a mixture of *N*-methyl-*m*-toluidine (10 mmol, 1.3 mL) and formic acid (11 mmol, 419 μL) was added sodium formate (2 mmol, 139 mg). The reaction mixture was stirred at room temperature for 24 h. After the reaction was complete, EtOAc was added to the reaction mixture, and sodium formate was removed by filteration. The organic layers were washed with brine and sat. $NaHCO_3$ aq., dried over Na_2SO_4 and concentrated under a reduced presser. Purification by column chromatography on silica gel afforded **4e**.

***N*,3'-Dimethylformanilide (2e)**



Colorless liquid.

IR (neat): 2917, 1671, 1607, 1588, 1494, 1334, 1116, 780 cm^{-1}.

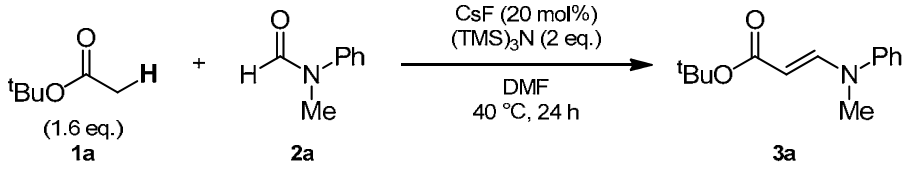
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 2.38 (s, 3H), 3.30 (s, 3H), 6.96–6.98 (m, 2H), 7.09 (d, J = 7.3 Hz, 1H), 7.29 (dd, J = 7.8 Hz, 1H), 8.46 (s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 21.18, 31.79, 119.20, 122.83, 126.92, 129.17, 139.43, 141.94, 162.07.

LRMS (EI) m/z: 149 (M^+).

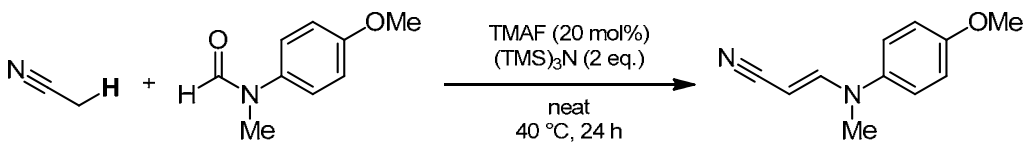
HRMS: Calcd. for $C_9H_{11}NO$: 149.0841, found: 149.0843.

Typical procedure for the deprotonative functionalization of *tert*-butylacetate catalyzed by CsF (Table 1, entry 4).



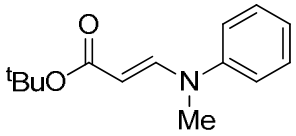
A solution of $(TMS)_3N$ (0.4 mmol, 96 mg) and CsF (0.04 mmol, 6.1 mg) in DMF (0.2 mL) was added *tert*-butyl acetate (0.32 mmol, 44 μL) and *N*-methylformanilide (0.2 mmol, 27 mg) by a syringe over 3 minutes. The reaction mixture was warmed to 40 °C and stirred for 24 h. Quenched with sat. NH_4Cl aq., the reaction mixture was extracted with ethyl acetate (10 mL x 3). The organic layers were collected, washed with brine, dried over $MgSO_4$ and concentrated under a reduced presser. Purification by column chromatography on silica gel afforded the compound.

Typical procedure for the deprotonative functionalization of acetonitrile catalyzed by TMAF (Table 3, entry 2).



A mixture of acetonitrile (0.2 mL), $(TMS)_3N$ (0.4 mmol, 96 mg) and TMAF (0.04 mmol, 3.8 mg) was added 4'-methoxy-*N*-methylformanilide (0.2 mmol, 34 mg) by a syringe over 3 minutes. The reaction mixture was warmed to 50 °C and stirred for 24 h. Quenched with sat. NH_4Cl aq., the reaction mixture was extracted with ethyl acetate (10 mL x 3). The organic layers were collected, washed with brine, dried over $MgSO_4$ and concentrated under a reduced presser. Purification by column chromatography on silica gel afforded the compound.

(*E*)-*tert*-Butyl {3-[methyl(phenyl)amino]}acrylate (3a)



Pale yellow oil (35.4 mg, 76%).

IR (neat): 2975, 1688, 1617, 1587, 1500, 1262, 1145, 1111, 976, 800, 755 cm^{-1}.

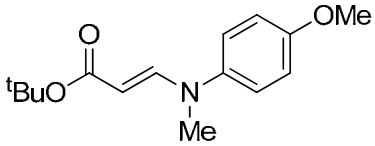
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.50 (s, 9H), 3.22 (s, 3H), 4.90 (d, *J* = 13.2 Hz, 2H), 7.09–7.13 (m, 3H), 7.31–7.36 (m, 2H), 7.88 (d, *J* = 13.2 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 28.47, 36.40, 78.77, 92.32, 119.57, 123.82, 129.36, 146.68, 147.71, 168.75.

LRMS (EI) *m/z*: 233 (M^+).

HRMS: Calcd. for $C_{14}H_{19}NO_2$: 233.1416, found: 280.1402.

(*E*)-*tert*-Butyl 3-{[*N*-(4-methoxyphenyl)-*N*-(methyl)amino]}acrylate (3b)



Pale yellow oil (42.6 mg, 81%).

IR (neat): 2975, 1684, 1599, 1511, 1242, 1144, 1111, 1034, 979, 798 cm^{-1}.

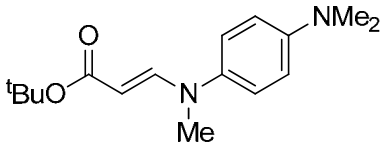
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.49 (s, 9H), 3.18 (s, 3H), 3.80 (s, 3H), 4.79 (d, *J* = 13.2 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 13.7 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 28.45, 30.84, 55.46, 78.51, 90.86, 114.50, 121.81, 140.34, 148.68, 156.49, 168.91.

LRMS (EI) *m/z*: 263 (M^+).

HRMS: Calcd. for $C_{15}H_{21}NO_3$: 263.1521, found: 263.1519.

(*E*)-*tert*-Butyl 3-[*N*-(4-dimethylamino)-*N*-(methyl)amino]acrylate (3c)



Pale yellow oil (40.8 mg, 74%).

IR (neat): 2977, 1684, 1598, 1520, 1265, 1114, 1008, 980, 810, 794 cm^{-1}.

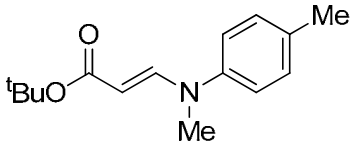
^{1}H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.48 (s, 9H), 2.93 (s, 6H), 3.16 (s, 3H), 4.74 (d, *J* = 13.2 Hz, 1H), 6.69 (d, *J* = 9.3 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 13.2 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 28.52, 30.87, 37.71, 40.81, 78.34, 89.90, 113.20, 122.00, 148.00, 149.16, 169.13.

LRMS (EI) *m/z*: 276 (M^+).

HRMS: Calcd. for $C_{16}H_{24}N_2O_2$: 276.1838, found: 276.1844.

(*E*)-*tert*-Butyl 3-[*N*-(methyl)-*N*-(*p*-tolyl)amino]acrylate (3d)



Pale yellow oil (40.5 mg, 82%).

IR (neat): 2975, 1689, 1621, 1597, 1514, 1364, 1334, 1254, 1144, 1109, 1005, 978, 800 cm^{-1}.

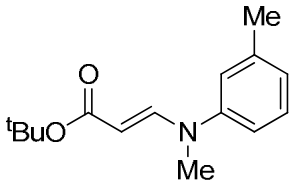
^{1}H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.49 (s, 9H), 2.32 (s, 3H), 3.19 (s, 3H), 4.84 (d, *J* = 13.2 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.83 (d, *J* = 13.2 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 20.60, 28.46, 36.65, 78.60, 91.53, 119.73, 129.85, 133.58, 144.36, 148.03, 168.83.

LRMS (EI) *m/z*: 247 (M^+).

HRMS: Calcd. for $C_{15}H_{21}NO_2$: 247.1572, found: 247.1571.

(*E*)-*tert*-Butyl 3-[*N*-(methyl)-*N*-(*m*-tolyl)amino]acrylate (3e)



Pale yellow oil (41.5 mg, 84%).

IR (neat): 2975, 1690, 1619, 1598, 1581, 1496, 1364, 1275, 1141, 1113, 1017, 975, 801, 778 cm^{-1}.

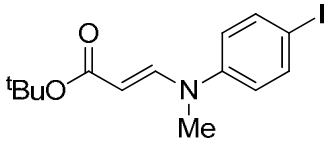
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.50 (s, 9H), 2.35 (s, 3H), 3.20 (s, 3H), 4.88 (d, *J* = 13.6 Hz, 1H), 6.90-6.94 (m, 3H), 7.19-7.23 (m, 1H), 7.87 (d, *J* = 13.6 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 21.43, 28.47, 36.39, 78.70, 91.95, 116.61, 120.31, 124.64, 129.12, 139.33, 146.66, 147.81, 168.83.

LRMS (EI) *m/z*: 247 (M^+).

HRMS: Calcd. for $C_{15}H_{21}NO_2$: 247.1572, found: 247.1583.

(*E*)-*tert*-Butyl 3-[*N*-(4-iodophenyl)-*N*-(methyl)amino]acrylate (3g)



Red needles (31.6 mg, 44%; recrystallized from hexane, mp 104–105 °C).

IR (neat): 2972, 1689, 1614, 1576, 1492, 1366, 1274, 1257, 1153, 1125, 969, 917, 813 cm^{-1}.

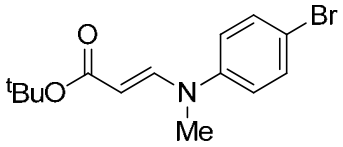
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.49 (s, 9H), 3.19 (s, 3H), 4.93 (d, *J* = 13.7 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 9.3 Hz, 2H), 7.81 (d, *J* = 13.6 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 28.43, 36.14, 79.01, 86.82, 93.57, 121.17, 138.24, 146.28, 146.72, 168.43.

LRMS (EI) *m/z*: 359 (M^+).

HRMS: Calcd. for $C_{14}H_{18}INO_2$: 359.0382, found: 359.0386.

(*E*)-*tert*-Butyl 3-[*N*-(4-bromophenyl)-*N*-(methyl)amino]acrylate (3h)



Pale yellow oil (29.2 mg, 47%).

IR (neat): 2974, 1688, 1615, 1581, 1494, 1274, 1258, 1153, 1125, 1005, 813 cm^{-1}.

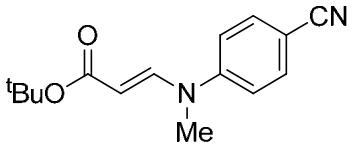
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.50 (s, 9H), 3.19 (s, 3H), 4.92 (d, *J* = 13.2 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 13.2 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 28.43, 36.31, 79.00, 93.39, 116.54, 120.93, 132.32, 145.66, 146.95, 168.47.

LRMS (EI) *m/z*: 311 (M^+).

HRMS: Calcd. for $C_{14}H_{18}{}^{79}BrNO_2$: 311.0528, found: 311.0502.

(*E*)-*tert*-Butyl 3-[*N*-(4-cyanophenyl)-*N*-(methyl)amino]acrylate (3i)



Colorless crystal (recrystallized from hexane/EtOAc, mp 147–148 °C).

IR (neat): 2977, 2222, 1693, 1623, 1587, 1511, 1277, 1263, 1153, 1114, 983, 847, 808 cm^{-1}.

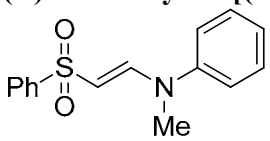
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 1.51 (s, 9H), 3.25 (s, 3H), 5.10 (d, *J* = 13.6 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 13.2 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 28.38, 35.45, 79.58, 96.58, 105.91, 118.14, 118.74, 135.60, 145.04, 149.42, 167.89.

LRMS (EI) *m/z*: 258 (M^+).

HRMS: Calcd. for $C_{15}H_{18}N_2O_2$: 258.1368, found: 258.1354.

(*E*)-*N*-Methyl-*N*-[(2-phenylsulfonyl)vinyl]aniline (4b)



White solid (48.0 mg, 88%; recrystallized from hexane/EtOAc, mp 89–90 °C).

IR (neat): 3080, 1609, 1584, 1498, 1285, 1136, 1083, 884, 760, 726 cm^{-1}.

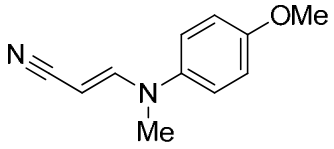
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 3.21 (s, 3H), 5.31 (d, J = 13.2 Hz, 1H), 7.13-7.19 (m, 3H), 7.36-7.40 (m, 2H), 7.47-7.53 (m, 3H), 7.84 (d, J = 12.7 Hz, 1H), 7.86-7.91 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 37.26, 98.70, 120.31, 125.02, 126.43, 128.92, 129.57, 131.94, 144.22, 145.97, 147.09.

LRMS (EI) *m/z*: 273 (M^+).

HRMS: Calcd. for $C_{15}H_{15}NO_2S$: 273.0823, found: 273.0816.

(*E*)-3-[*N*-(4-Methoxyphenyl)-*N*-(methyl)amino]acrylonitrile (4c)



Orange oil (27.4 mg, 73%).

IR (neat): 2929, 2197, 1616, 1509, 1344, 1244, 1131, 1032, 829, 737 cm^{-1}.

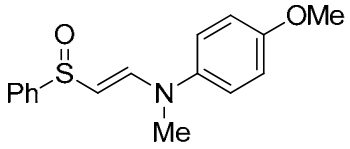
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 3.16 (s, 3H), 3.81 (s, 3H), 4.05 (d, J = 13.7 Hz, 1H), 6.89 (d, J = 9.3 Hz, 2H), 7.02 (d, J = 9.3 Hz, 2H), 7.29 (d, J = 13.6 Hz, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 37.26, 98.70, 120.31, 125.02, 126.43, 128.92, 129.57, 131.94, 144.22, 145.97, 147.09.

LRMS (EI) *m/z*: 188 (M^+).

HRMS: Calcd. for $C_{11}H_{12}N_2O$: 188.0950, found: 188.0963.

(*E*)-4-Methoxy-*N*-methyl-*N*-[(2-phenylsulfinyl)vinyl]aniline (4d)



White solid (53.4 mg, 93%; recrystallized from hexane/EtOAc, mp 132–133 °C).

IR (neat): 3042, 3009, 2934, 2843, 1597, 1517, 1349, 1294, 1247, 1129, 1015, 945, 834 cm^{-1}.

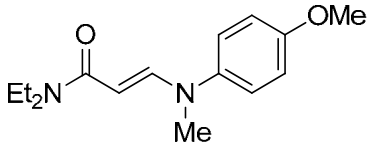
^1H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 3.16 (s, 3H), 3.81 (s, 3H), 5.37 (d, *J* = 13.2 Hz, 1H), 6.90 (d, *J* = 9.3 Hz, 2H), 7.07 (d, *J* = 9.3 Hz, 2H), 7.42-7.50 (m, 4H), 7.68 (d, *J* = 6.8 Hz, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 37.59, 55.55, 104.56, 114.74, 122.11, 124.52, 128.80, 129.72, 139.90, 146.83, 147.30, 156.88.

LRMS (EI) *m/z*: 287 (M^+).

HRMS: Calcd. for $C_{16}H_{17}NO_2S$: 287.0980, found: 287.0987.

(*E*)-*N*,*N*-Diethyl-3-[*N*-(4-methoxyphenyl)-*N*-(methyl)amino]acrylamide (4e)



Orange oil.

IR (neat): 2971, 1635, 1511, 1263, 1241, 1120, 1034, 828, 779 cm^{-1}.

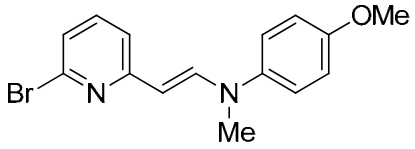
^1H NMR (600 MHz, $CDCl_3$/TMS) σ (ppm): 1.18 (s, 6H), 3.21 (s, 3H), 3.41 (br, 4H), 3.79 (s, 3H), 5.13 (d, *J* = 12.1 Hz, 1H), 6.86 (d, *J* = 9.2 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 12.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) σ (ppm): 13.65-14.49, 37.41, 40.74-41.97, 55.50, 89.16, 114.45, 121.55, 140.74, 147.95, 156.13, 167.84.

LRMS (EI) *m/z*: 262 (M^+).

HRMS: Calcd. for $C_{15}H_{22}N_2O_2$: 262.1681, found: 262.1678.

(*E*)-*N*-[2-(6-Bromopyridine-2-yl)vinyl]-4-methoxy-*N*-methylaniline (4g)



Brown oil (33.1mg, 52%).

IR (neat): 2953, 2931, 2903, 2834, 1625, 1572, 1507, 1435, 1240, 1155, 1111, 1034, 978, 910 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$/TMS) σ (ppm): 3.26 (s, 3H), 3.80 (s, 3H), 5.44 (d, *J* = 13.2 Hz, 1H), 6.87-6.89 (m, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 7.06-7.08 (m, 2H), 7.24-7.28 (m, 1H), 7.85 (d, *J* = 13.7 Hz, 1H).

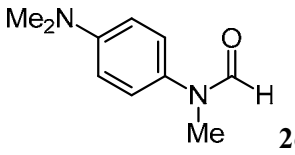
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) σ (ppm): 30.89, 37.16, 55.55, 99.22, 114.54, 117.50, 121.53 (or 121.38), 138.18, 140.83, 141.05, 141.62, 155.89, 159.69.

LRMS (EI) *m/z*: 318 (M^+).

HRMS: Calcd. for $C_{15}H_{15}{}^{79}BrN_2O$: 318.0368, found: 318.0369.

Reference.

1. B. Goutam and L. Sujay, *Tetrahedron Lett*., 2010, **51**, 2319–2322.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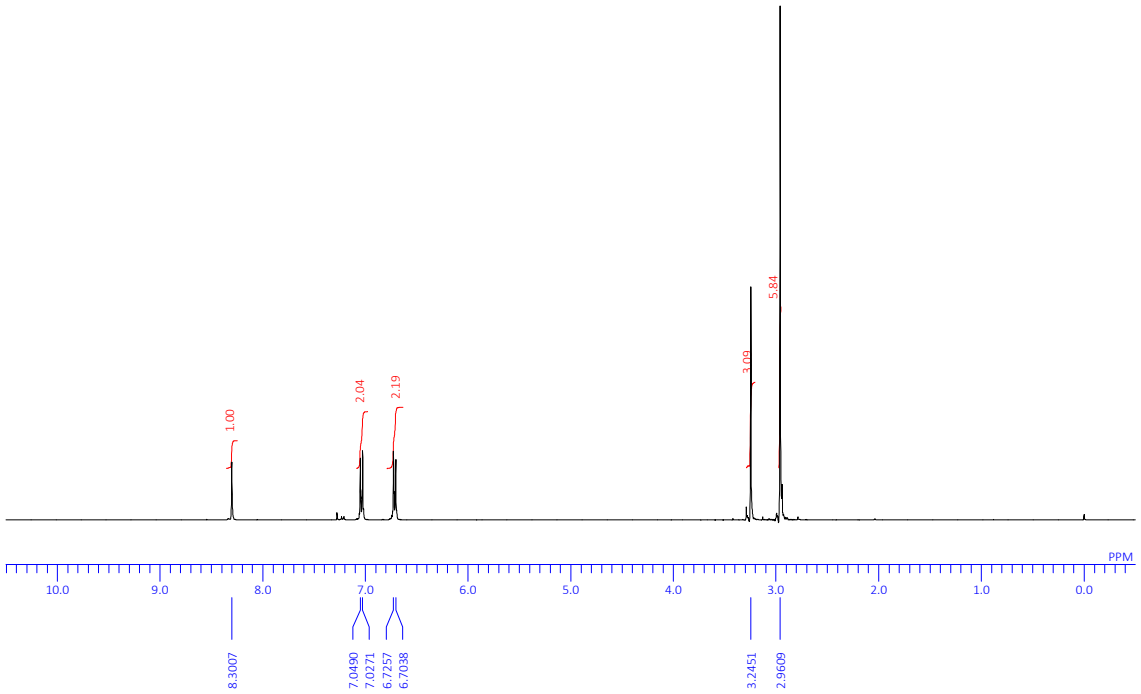
O
N
H
Me

2c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6.7257
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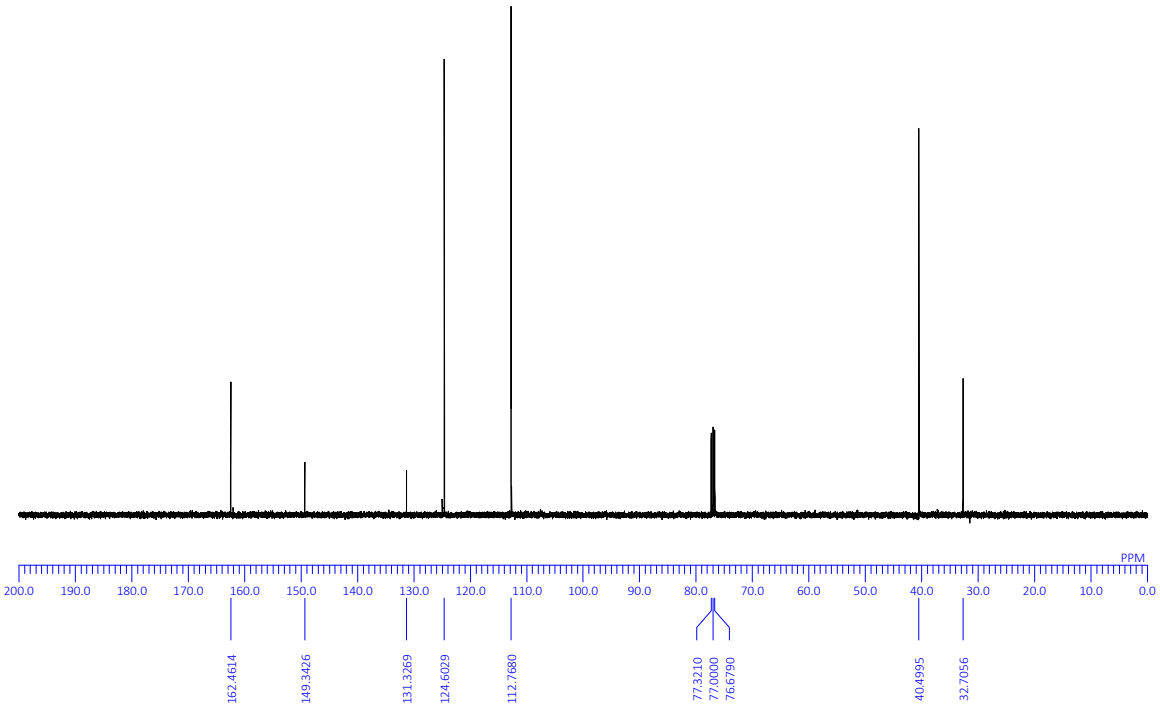
3.2451
2.9609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60.0
50.0
40.0
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20.0
10.0
0.0
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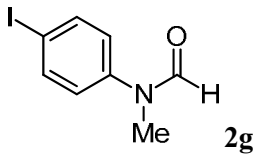
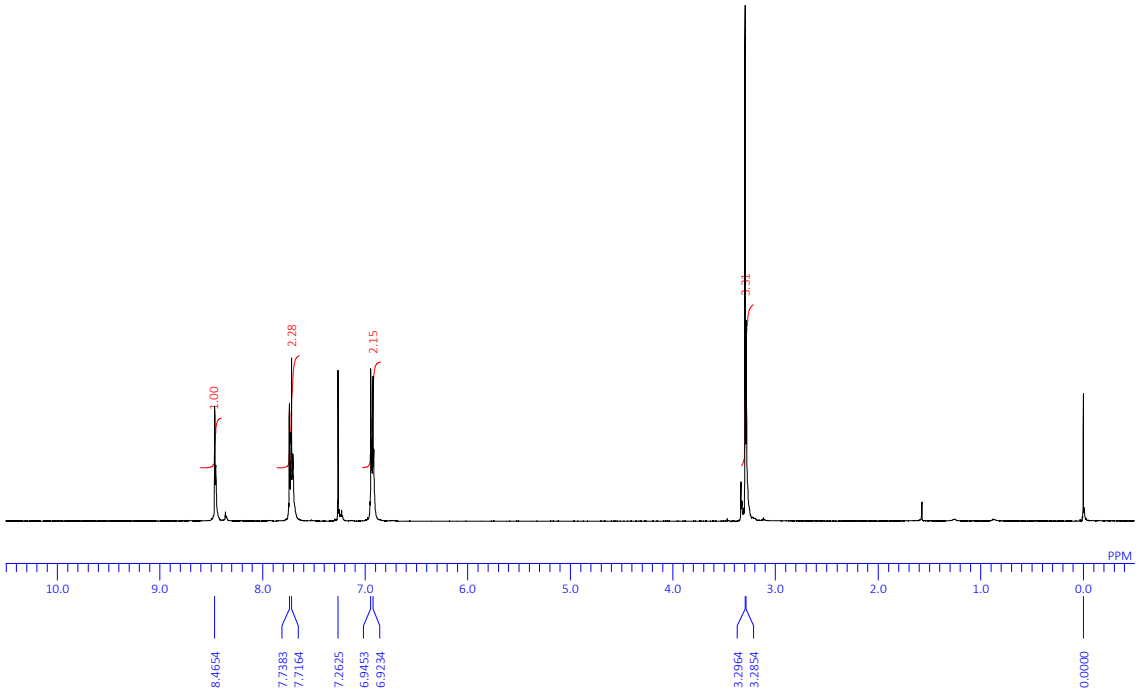
40.4995
32.7056


I
O
N
H
Me

2g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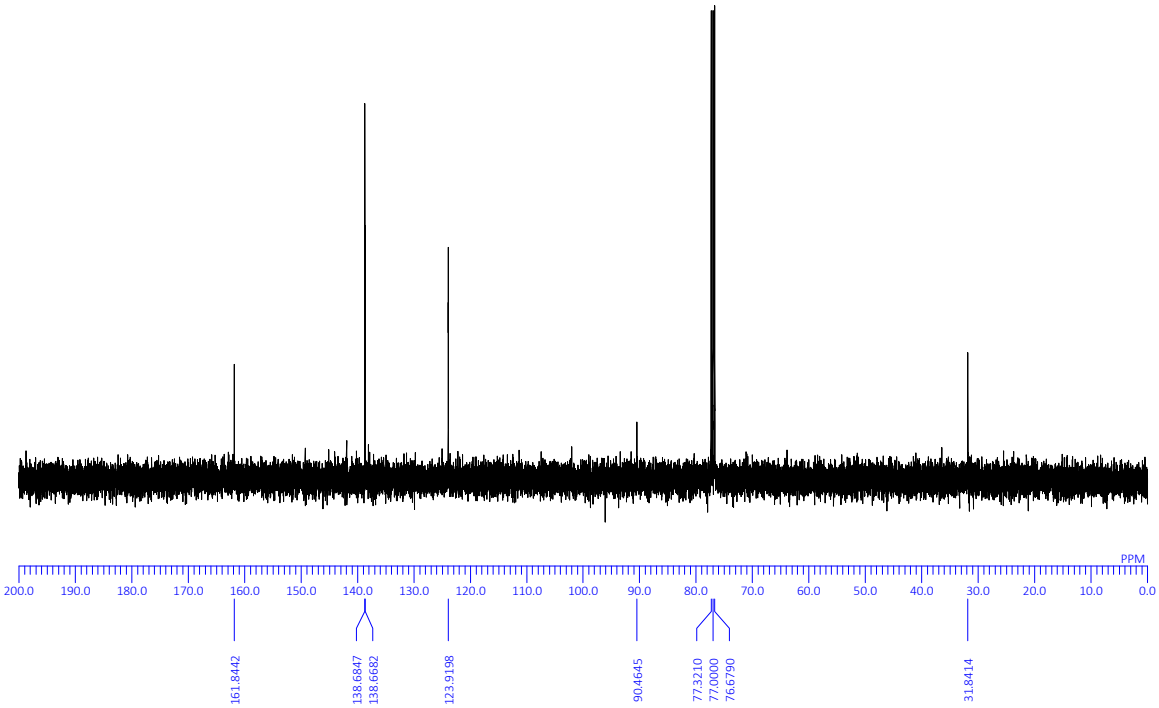
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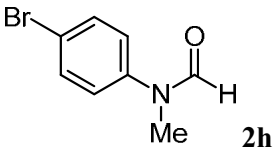
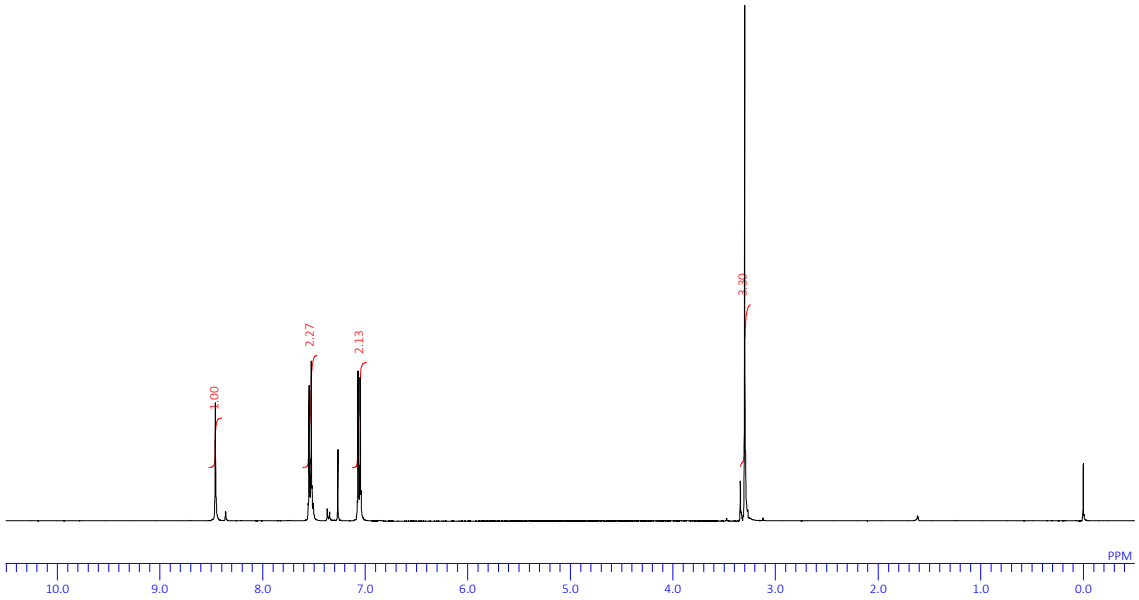

Br
O
N
H
Me

2h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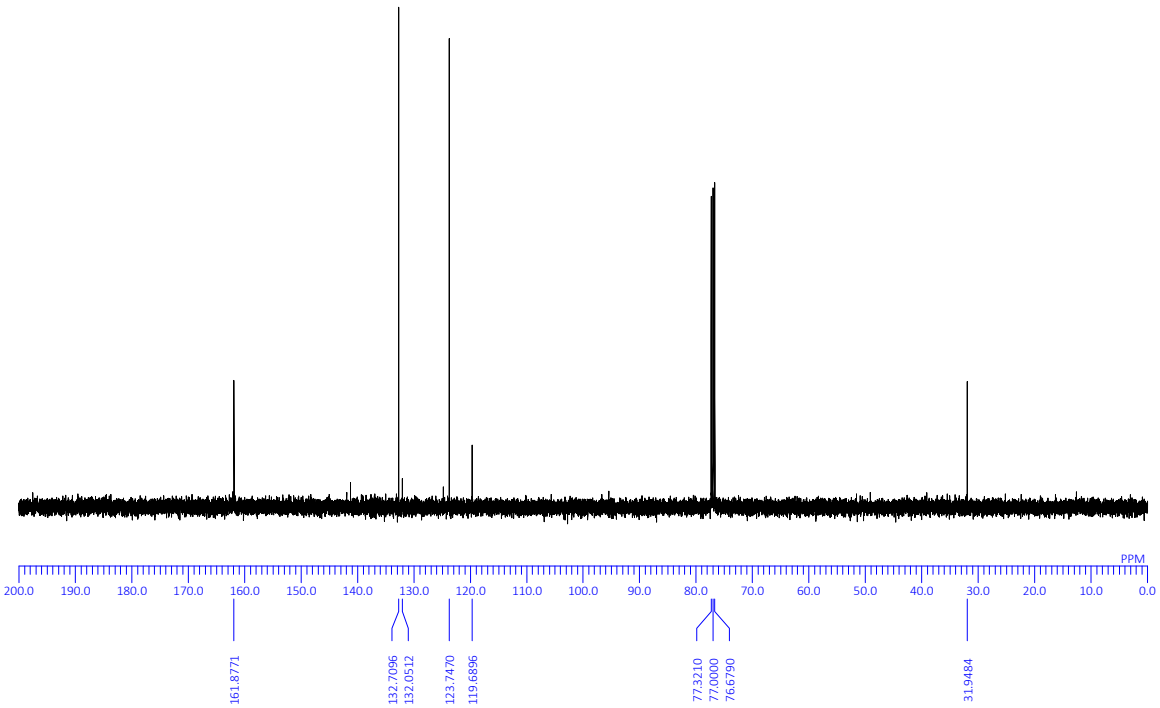
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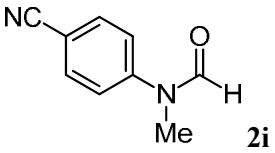
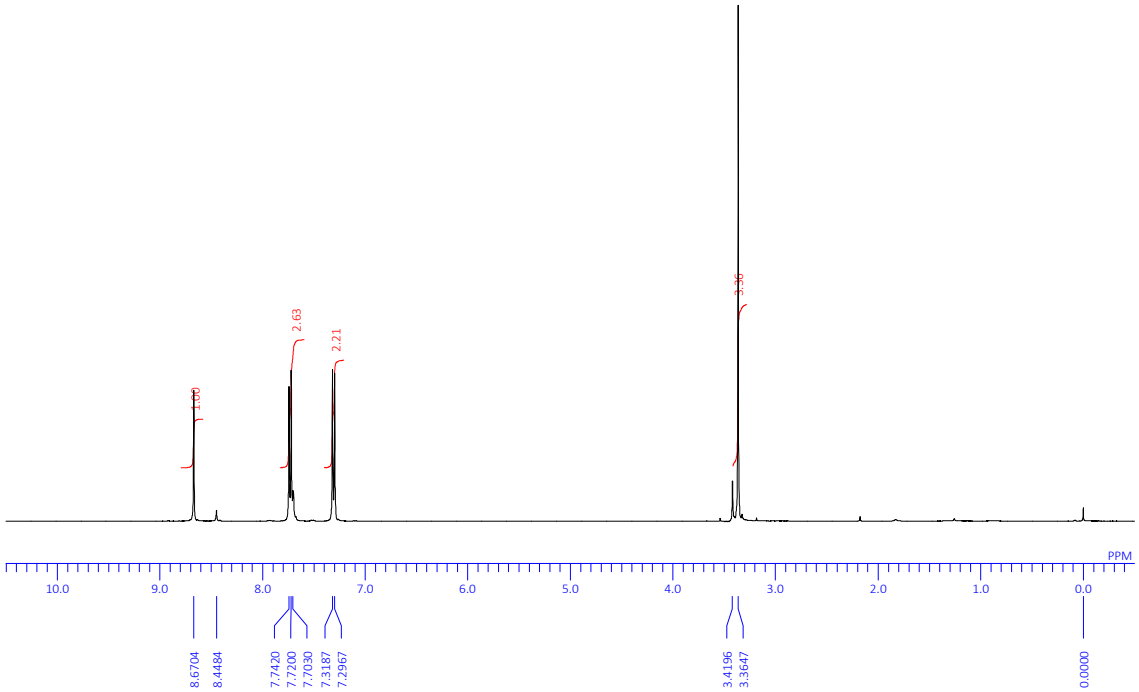
31.9484


NC
O
N
H
Me

2i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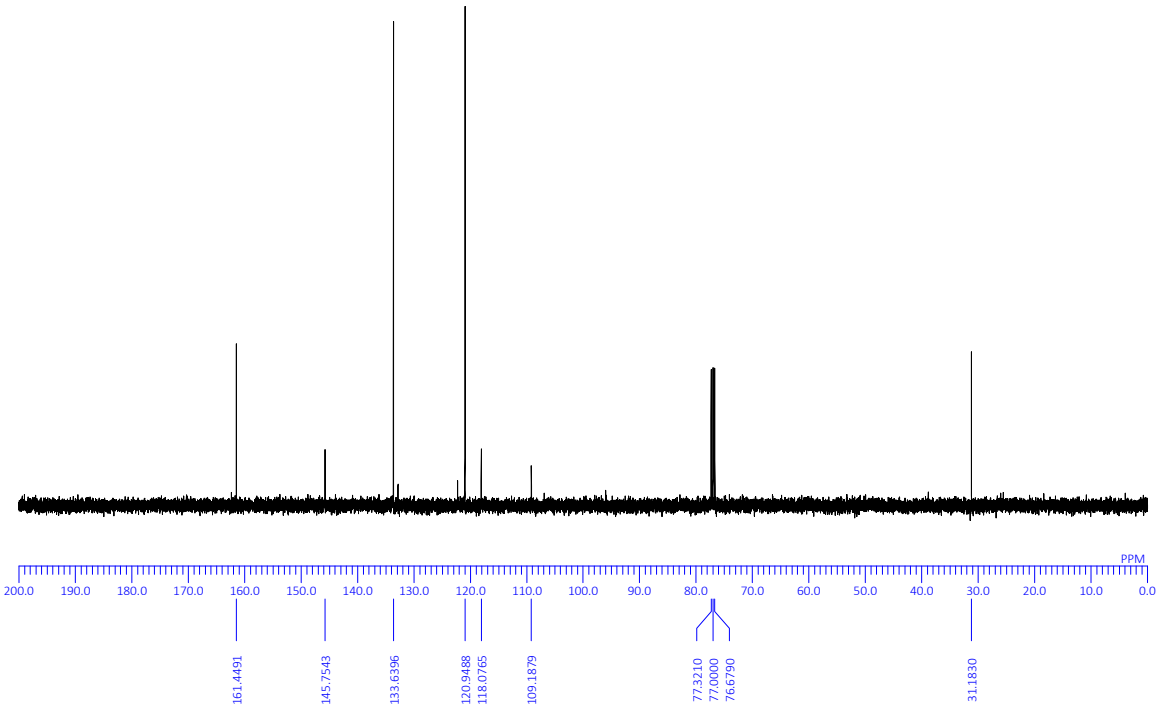
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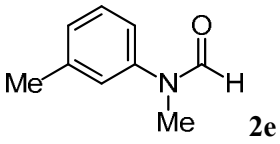
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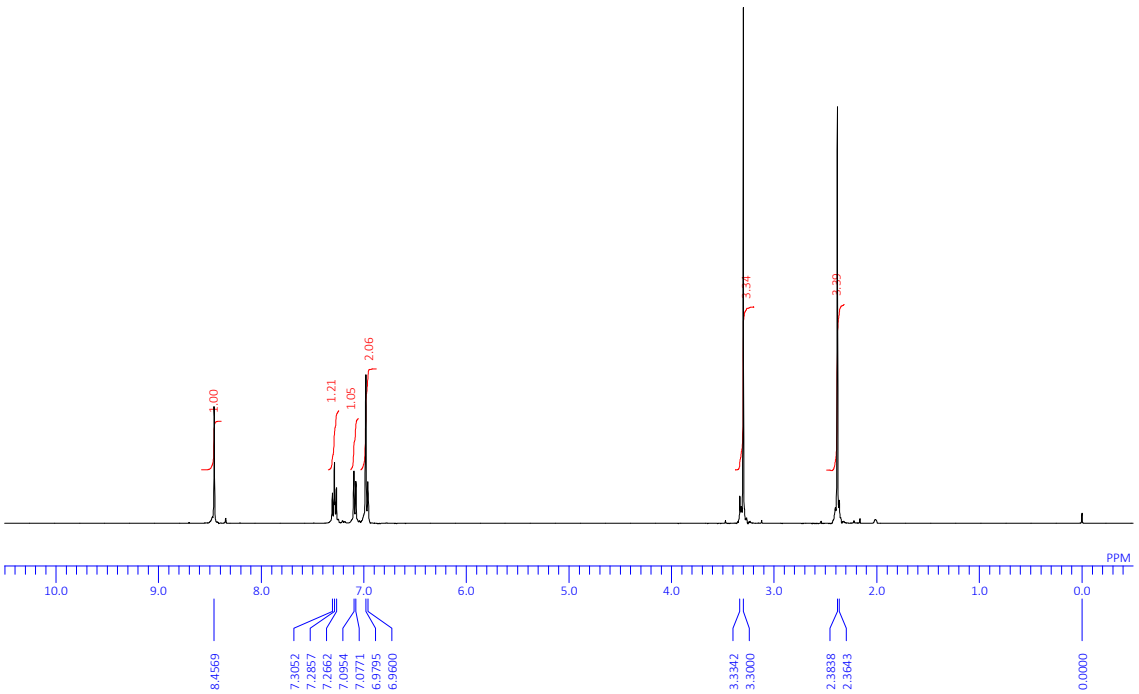
N
O
H
Me

2e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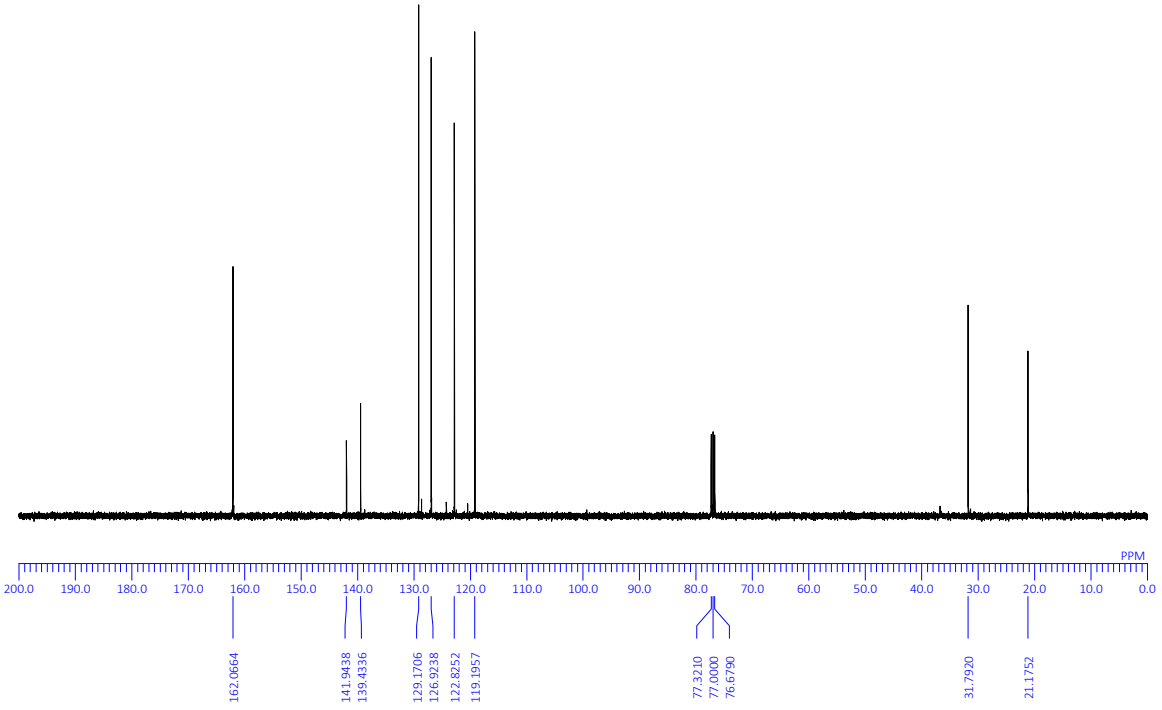
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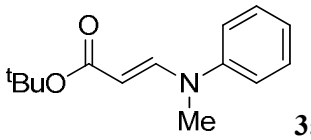
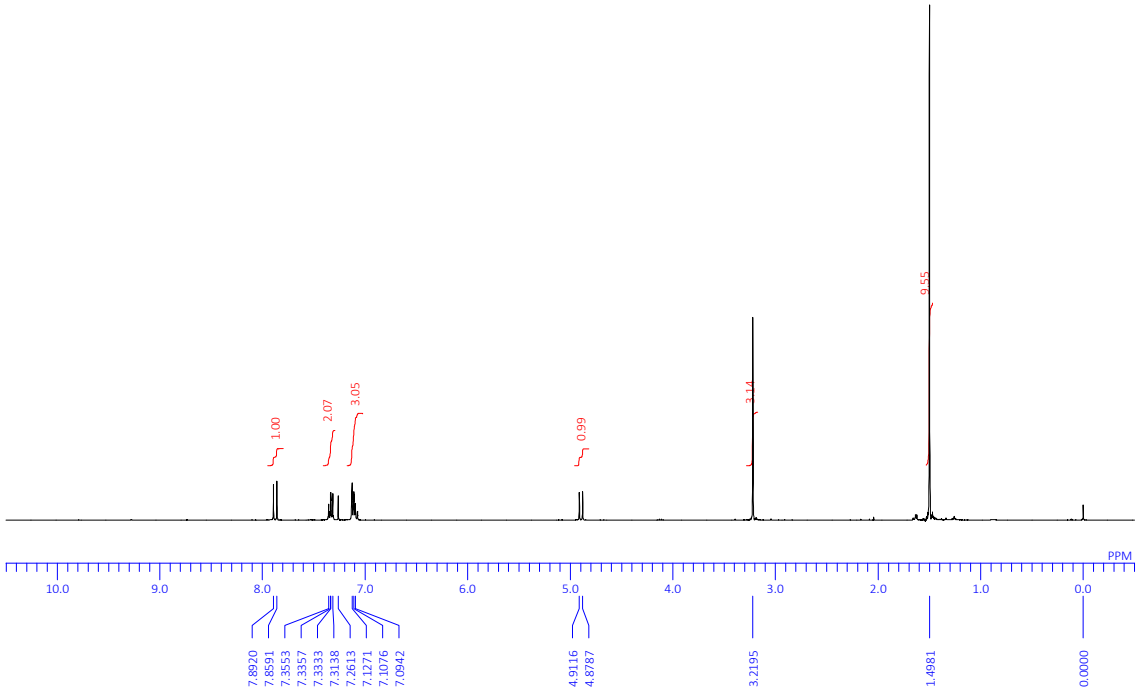

O
tBuO
N
Me

3a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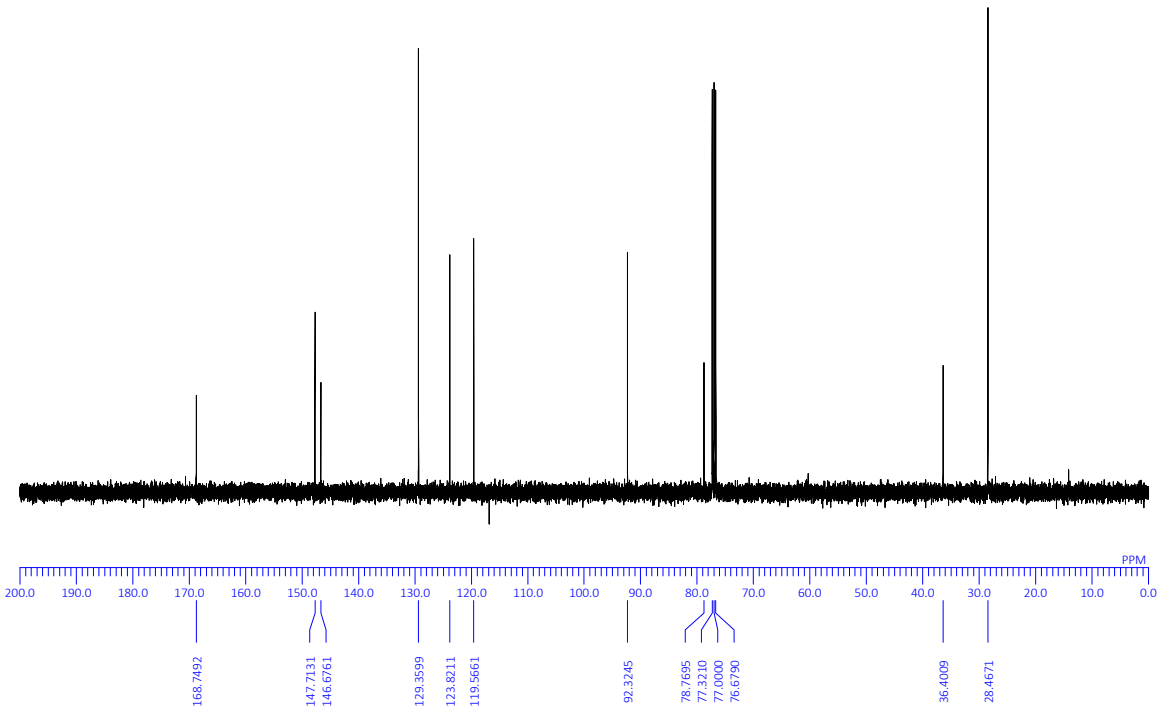
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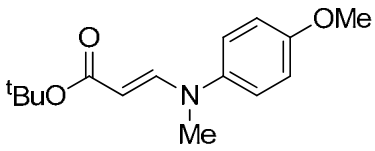
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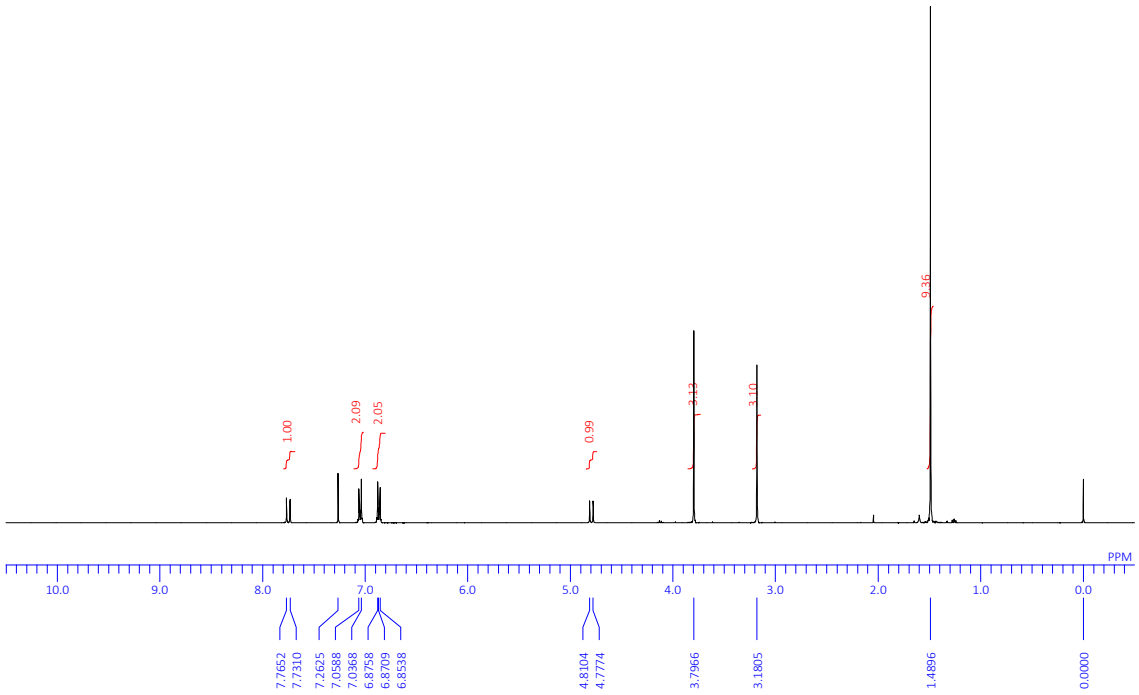
OMe
tBuO
N
Me

3b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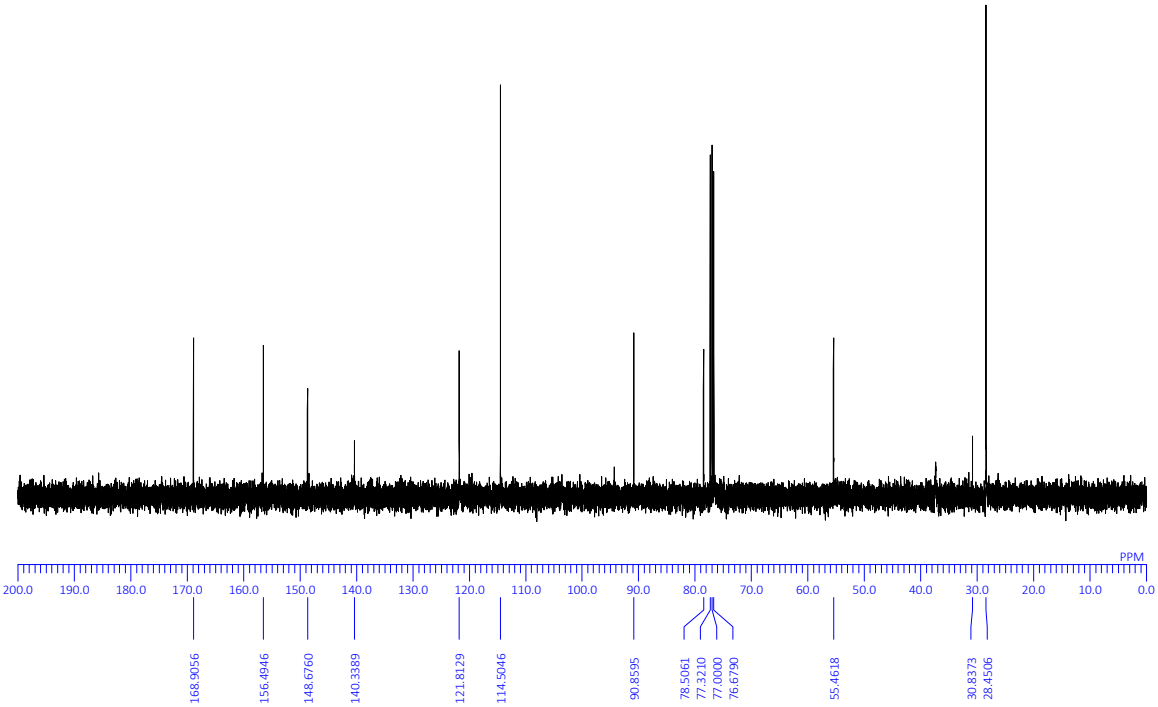
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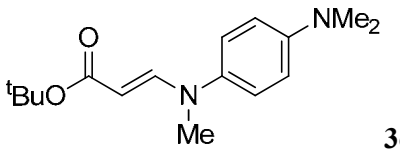
O
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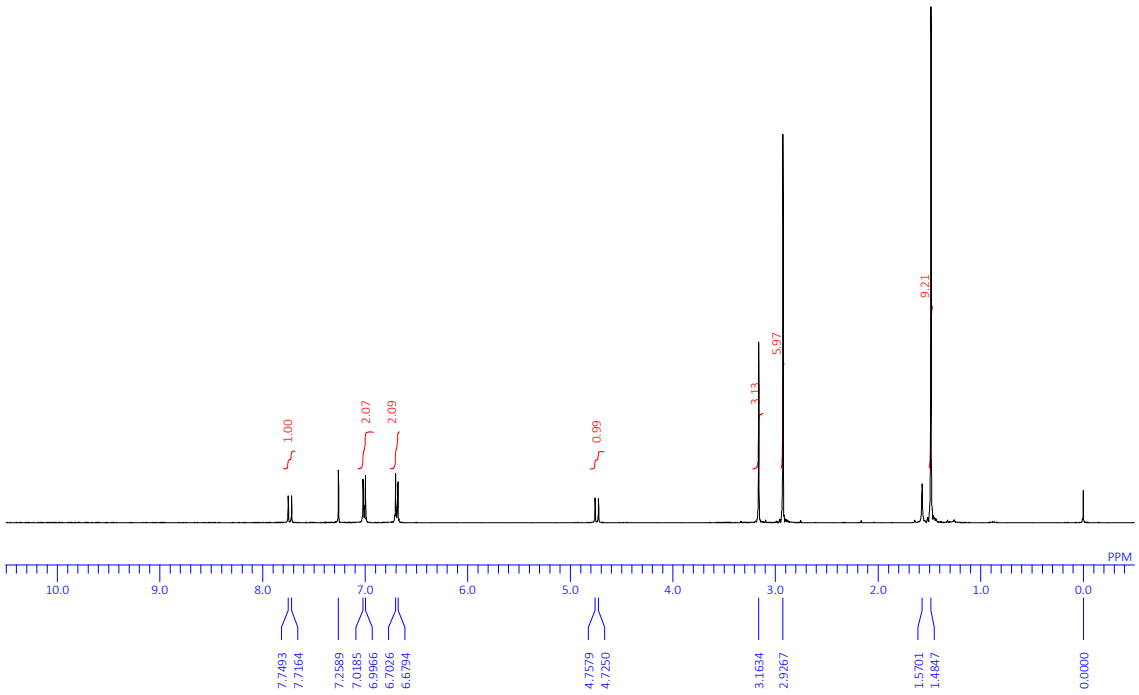
tBuO
N
Me

3c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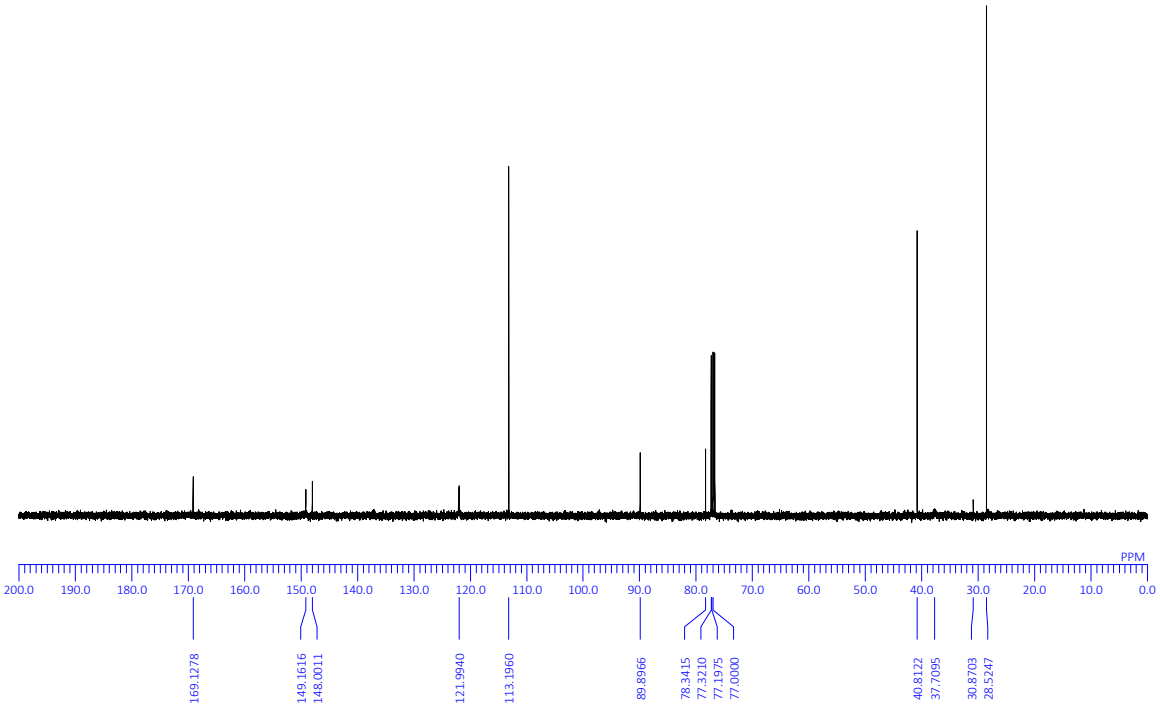
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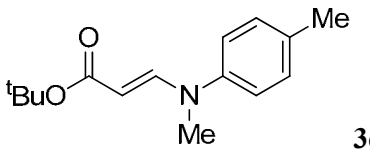
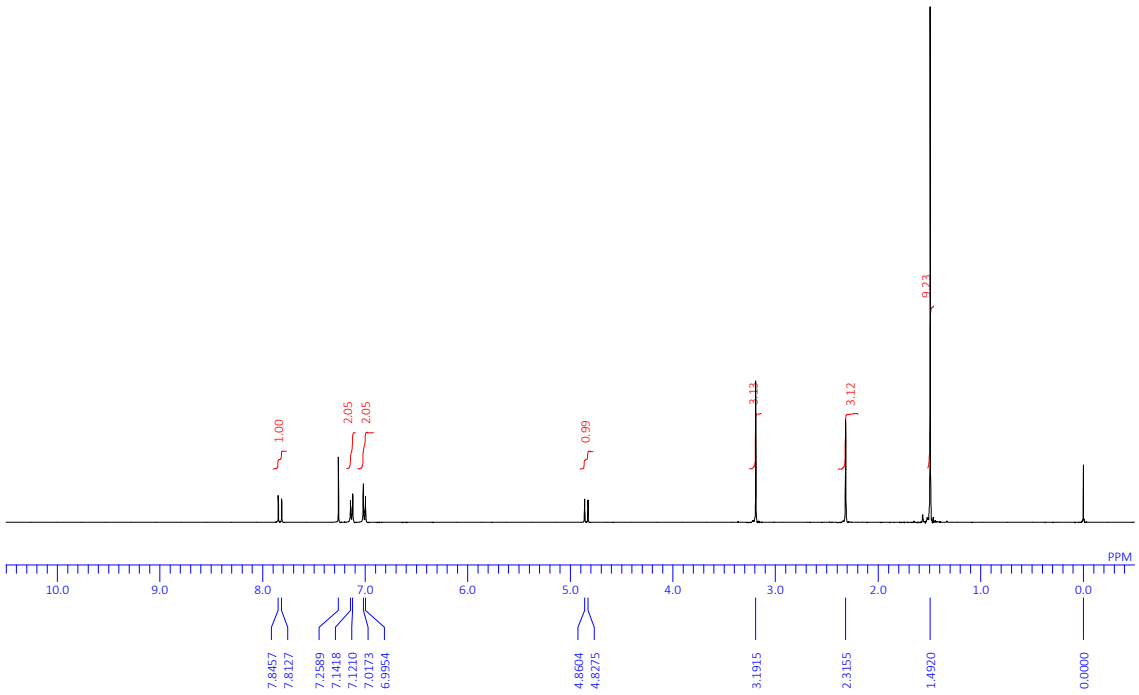

O
tBuO
N
Me
Me

3d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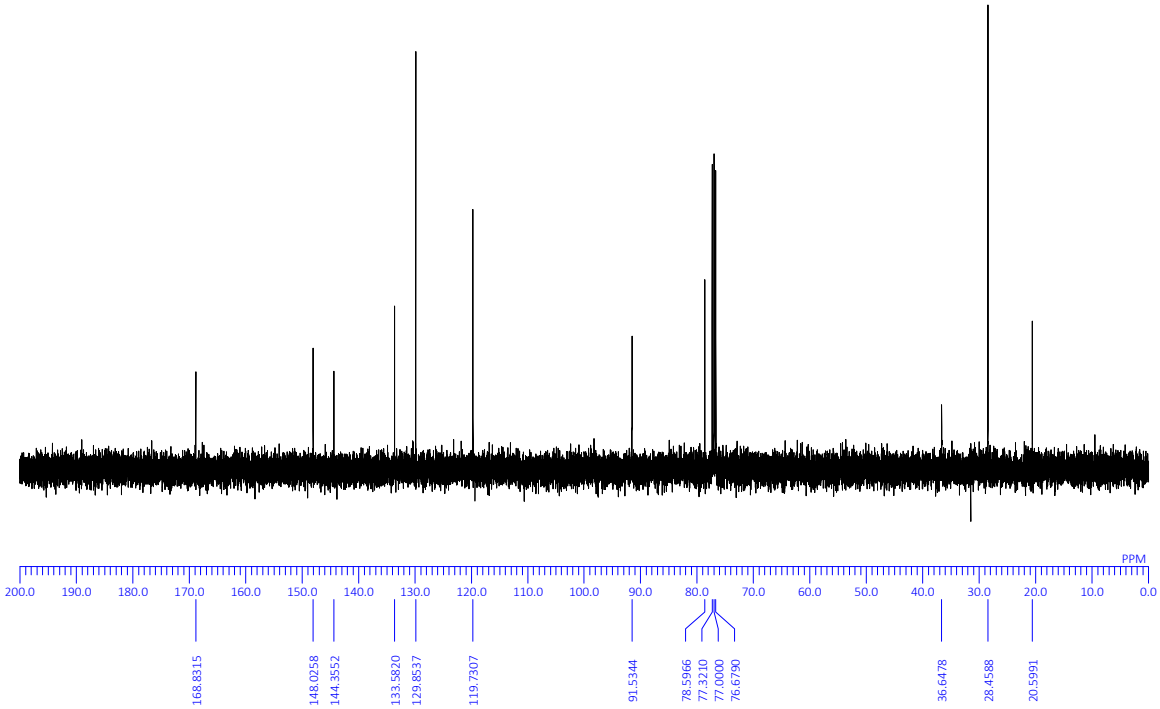
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20.0
10.0
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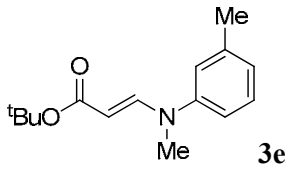
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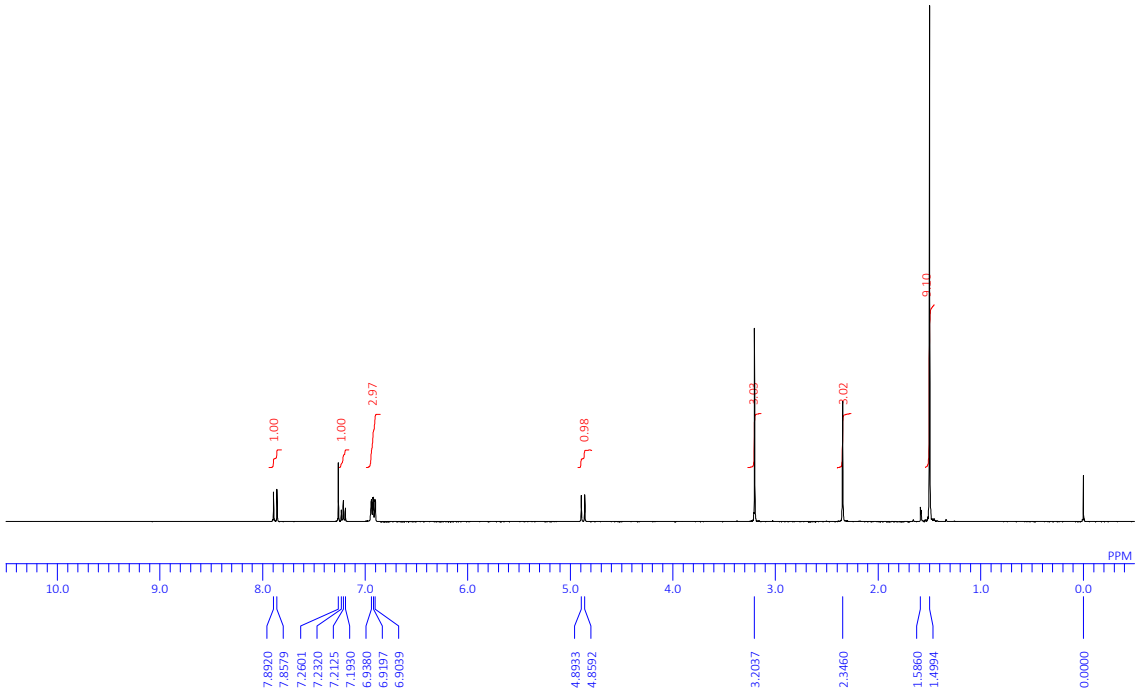
N
Me

3e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7.2320
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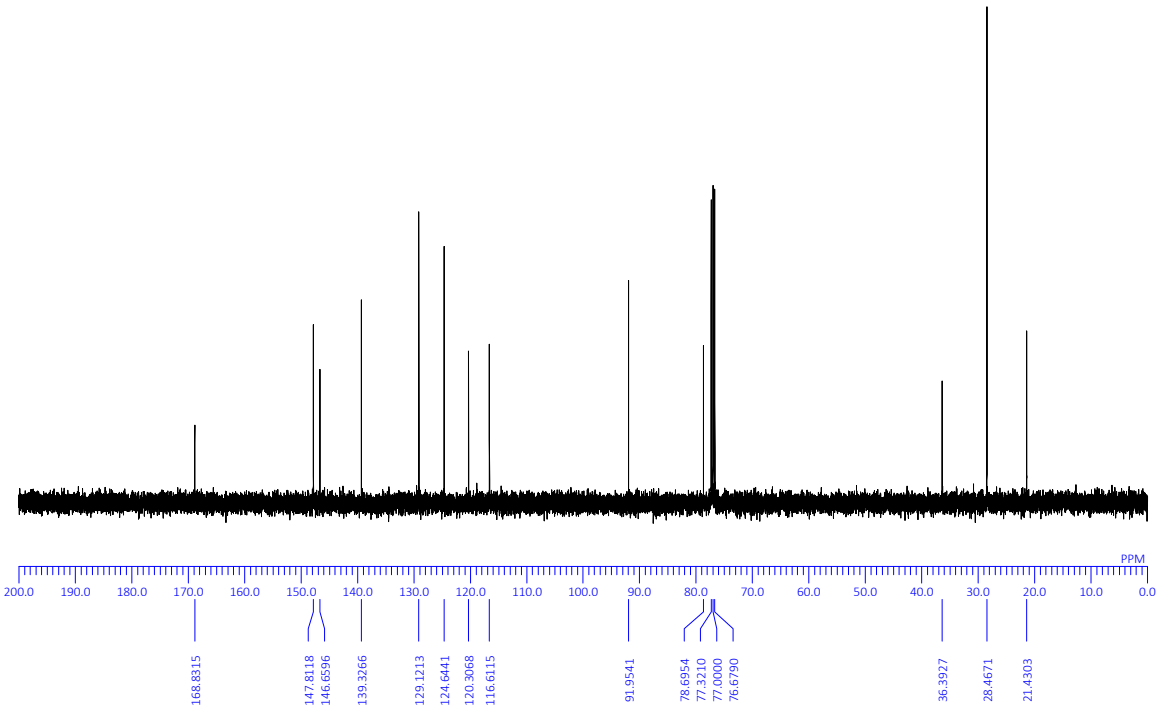
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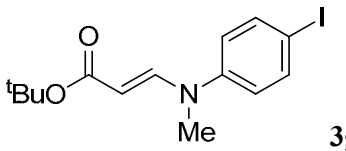
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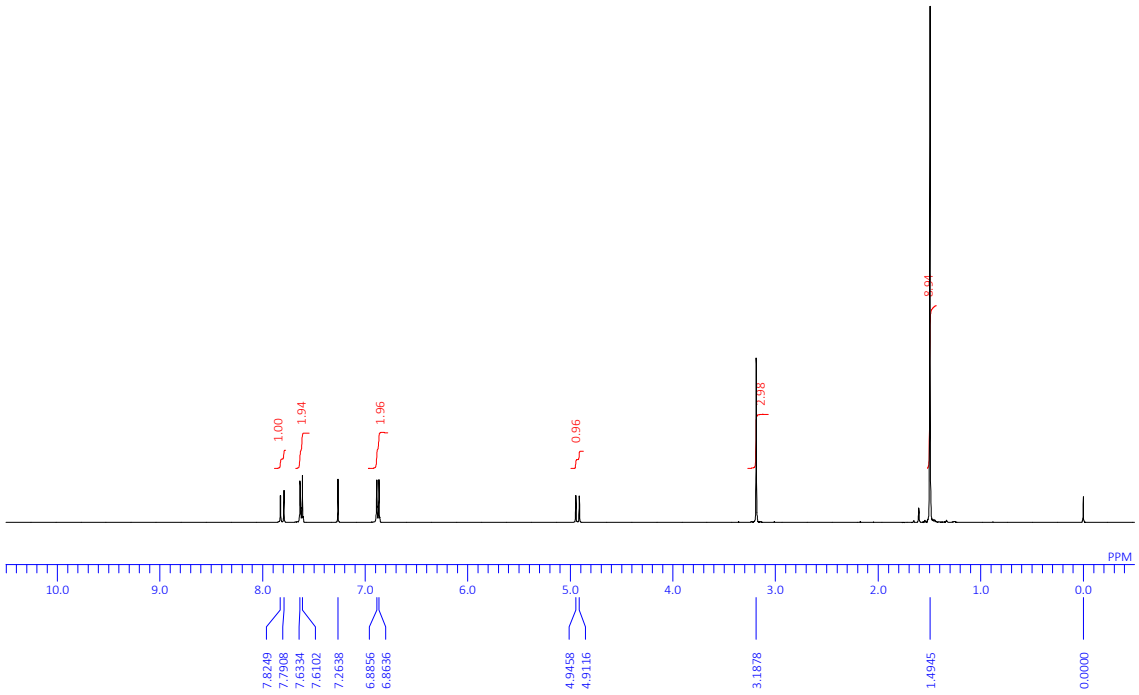
N
Me
I

3g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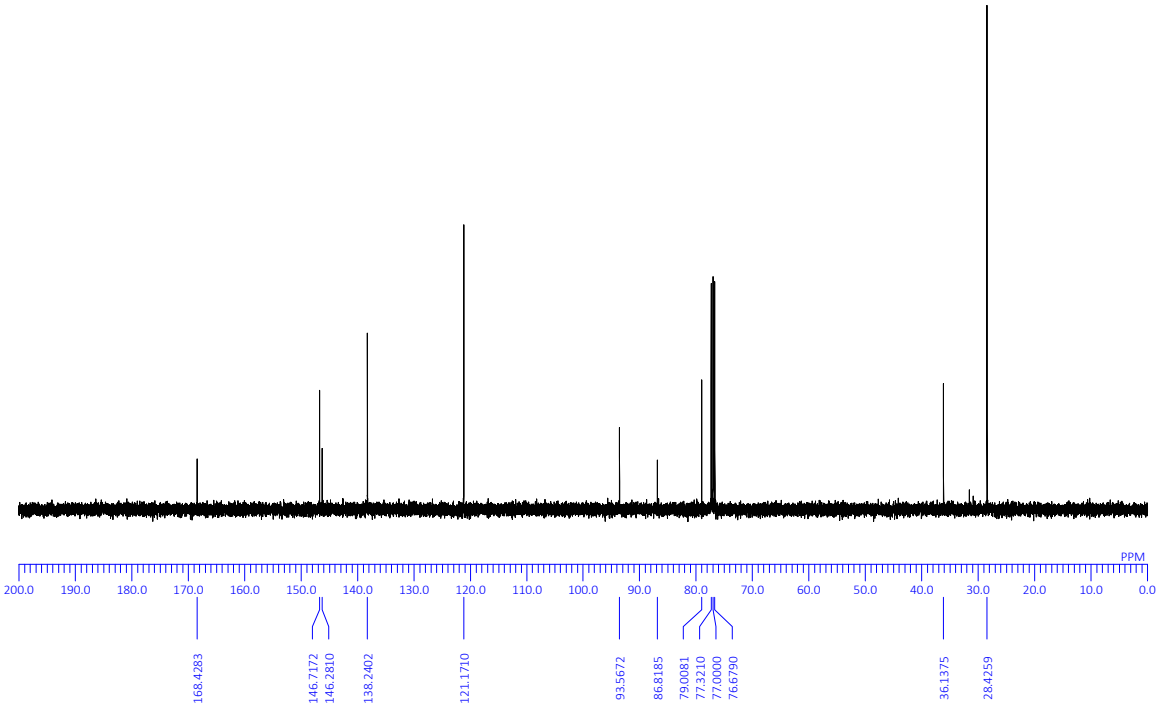
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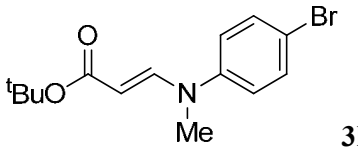
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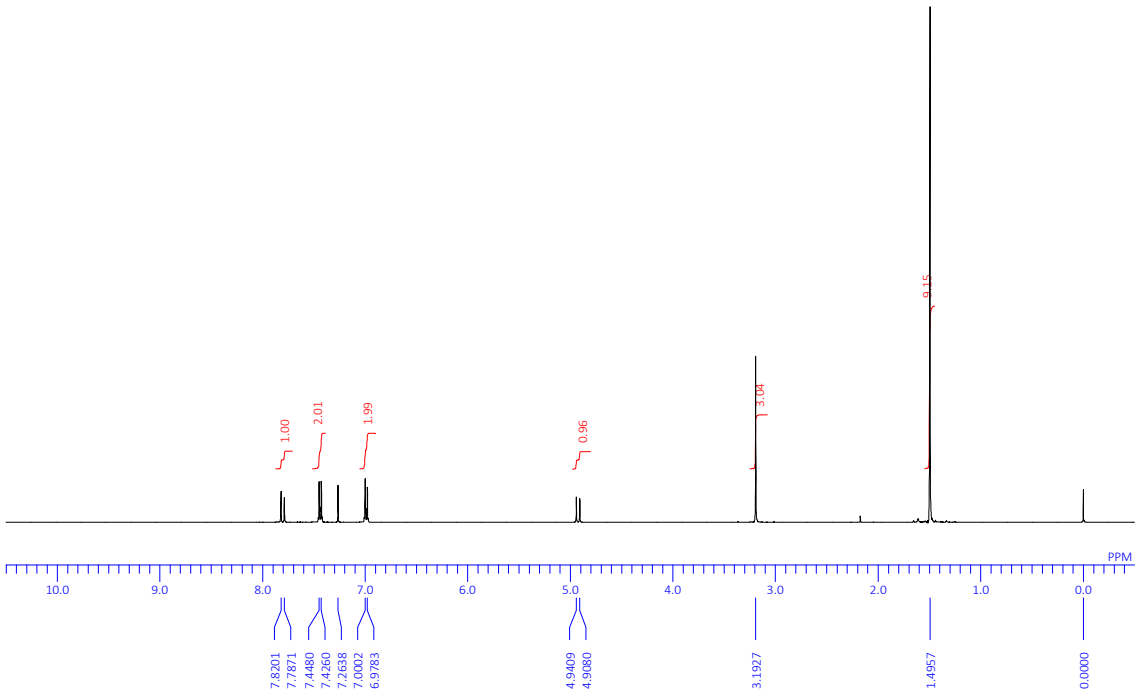
Br

3h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1.4957
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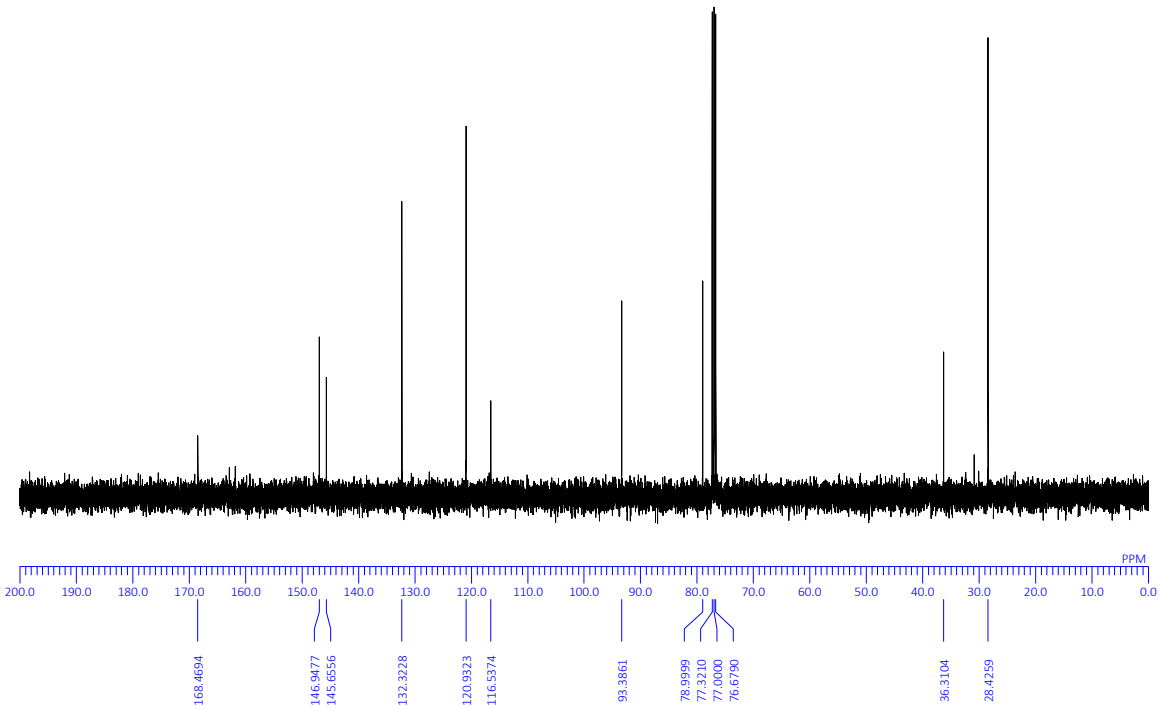
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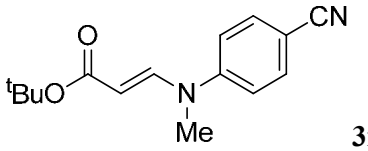
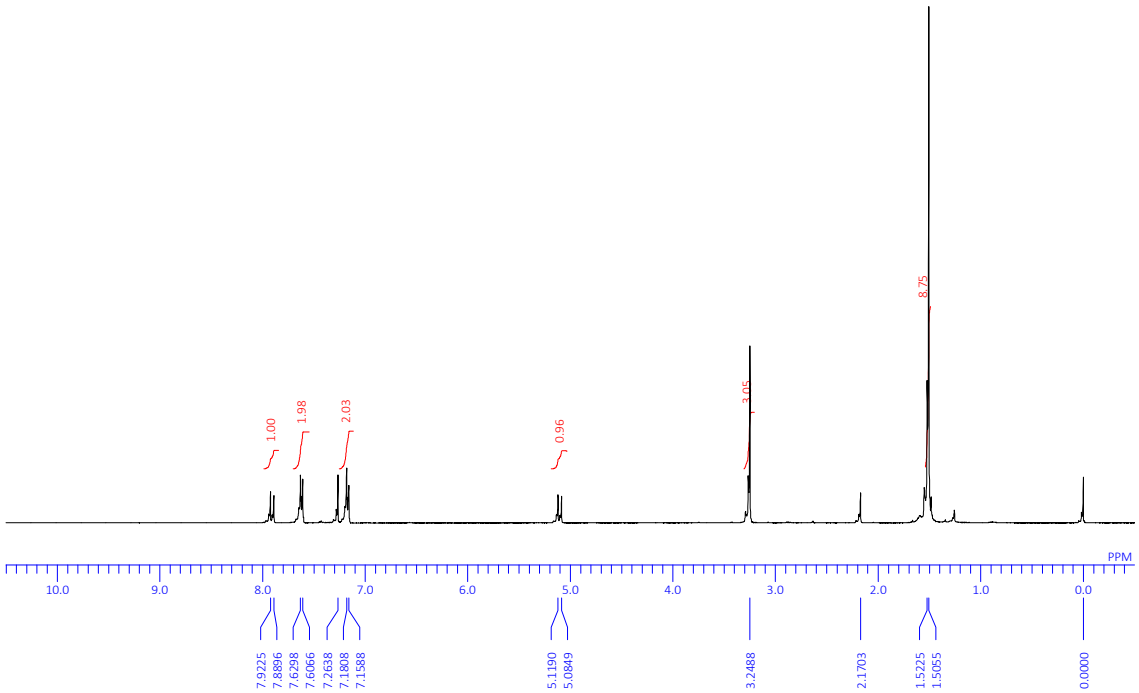

O
CN
tBuO
N
Me

3i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4.0
3.0
2.0
1.0
0.0
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7.6298
7.6066
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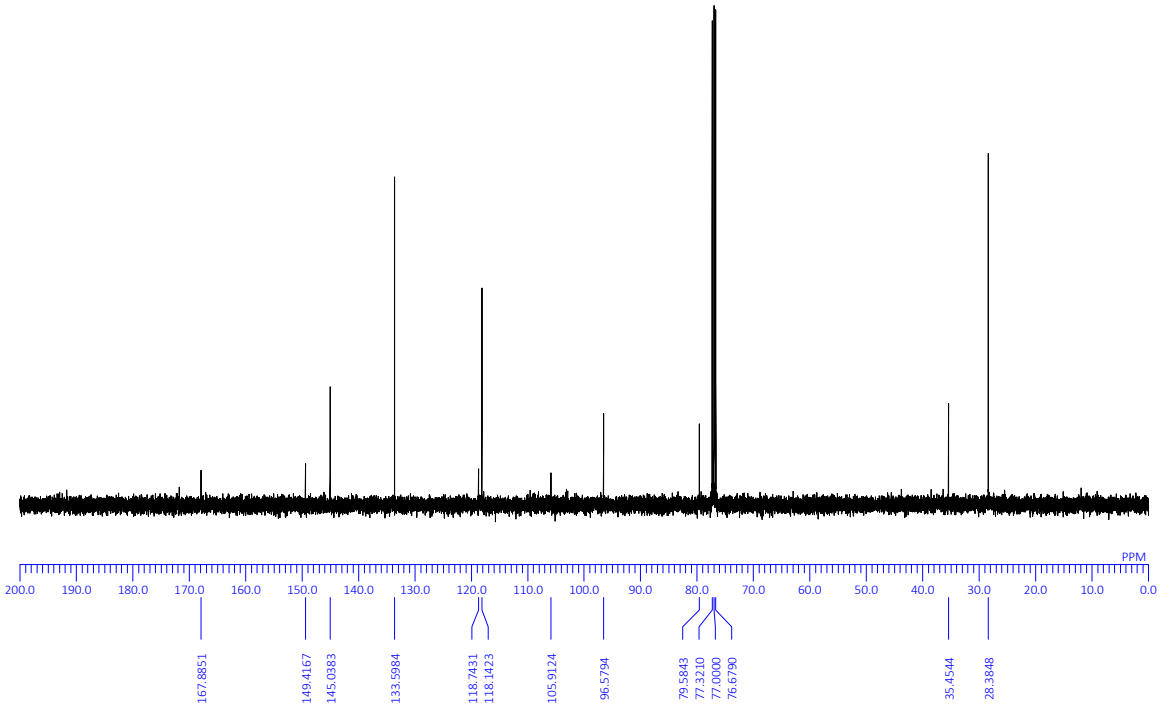
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110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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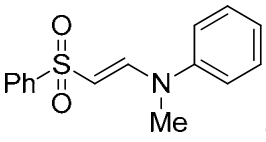
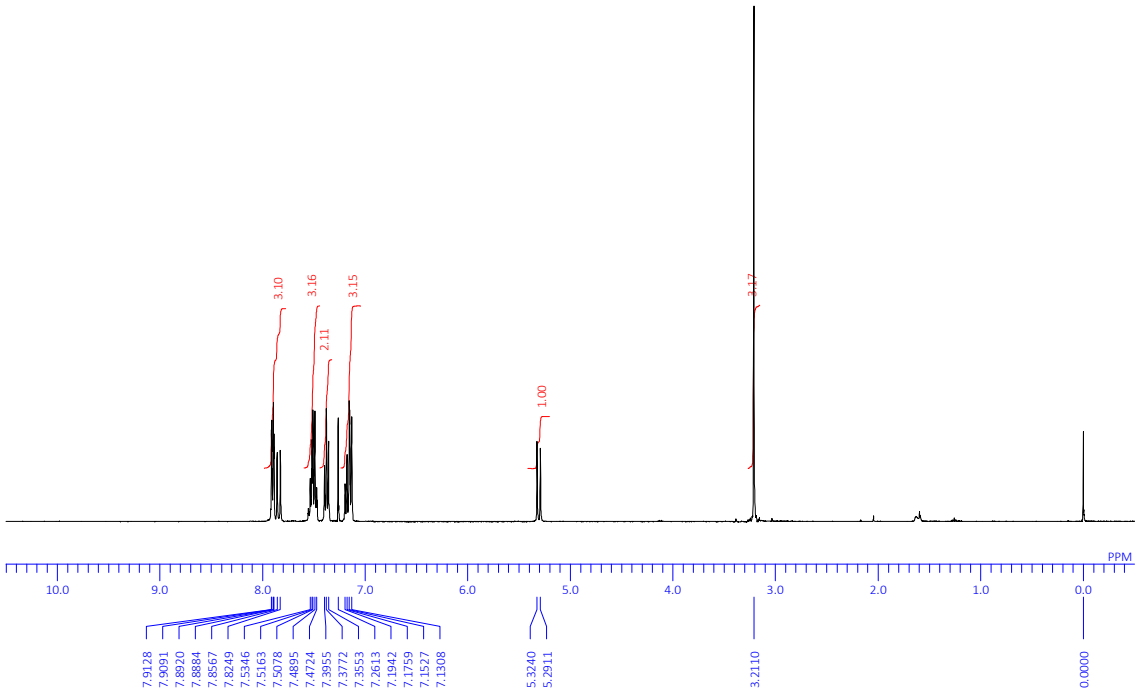
76.6790
35.4544
28.3848


O
S
O
Ph
N
Me

4b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3.17
PPM
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.8920
7.8884
7.8567
7.8249
7.5346
7.5163
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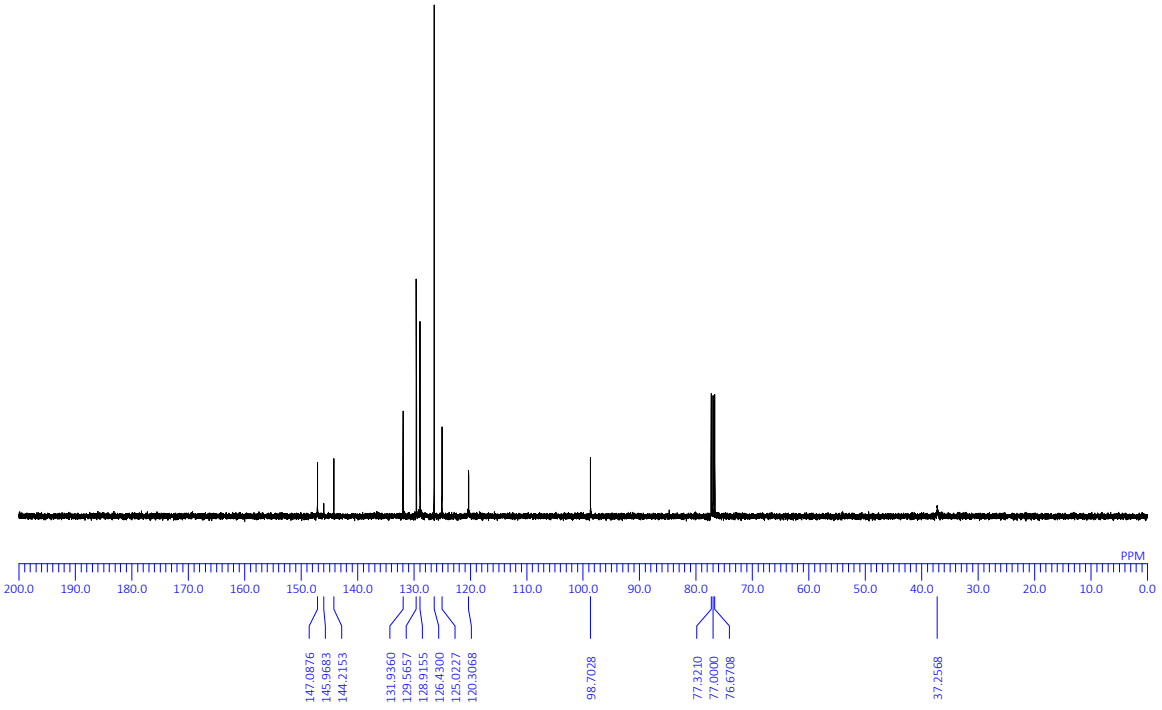
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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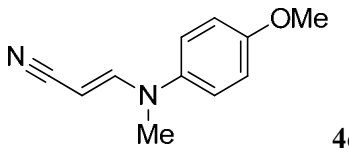
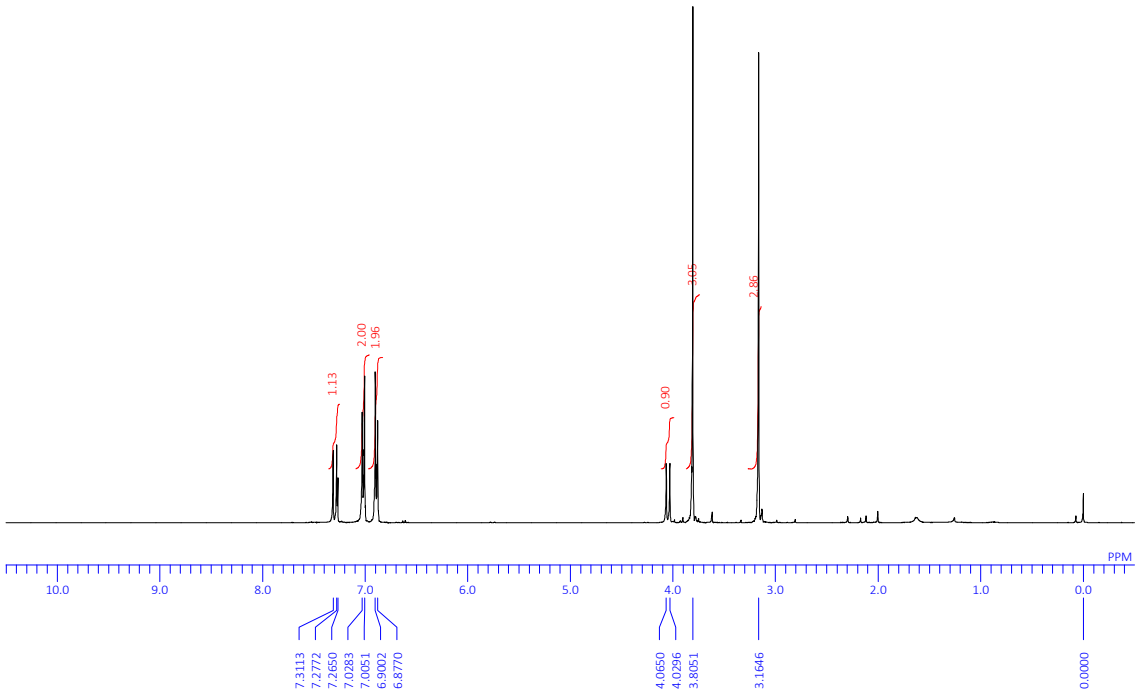
77.0000
76.6708
37.2568


N
OMe
N
Me

4c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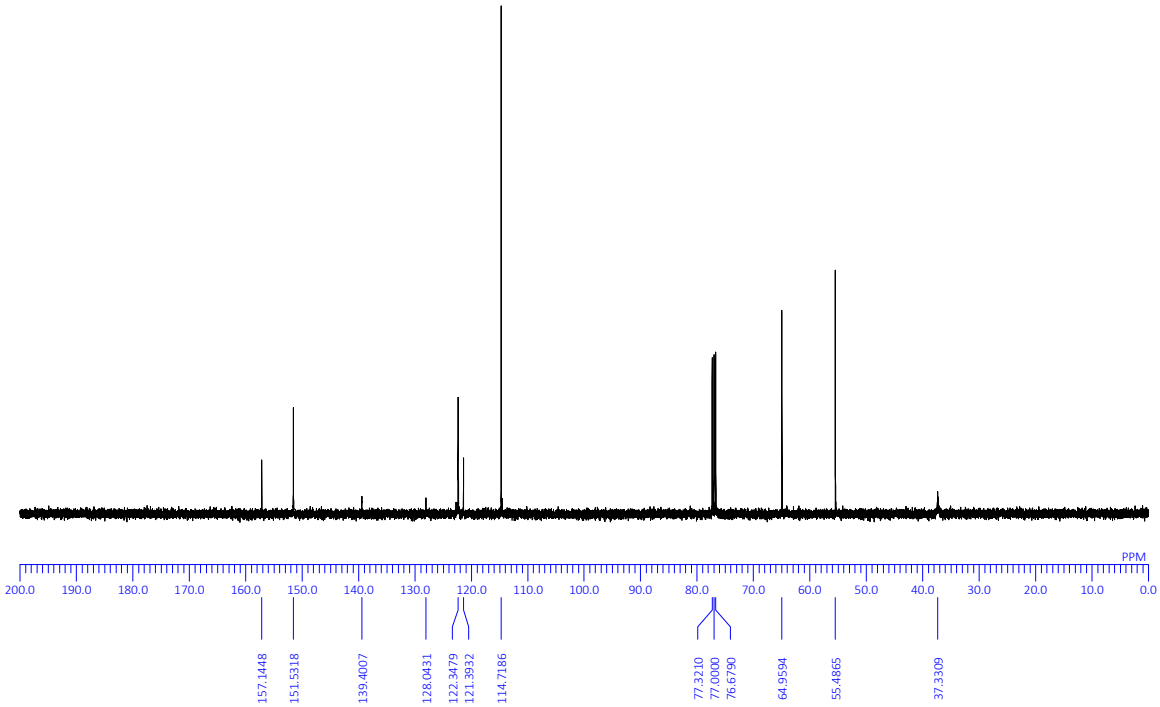
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80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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151.5318
139.4007
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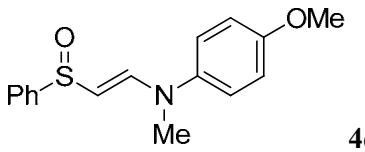
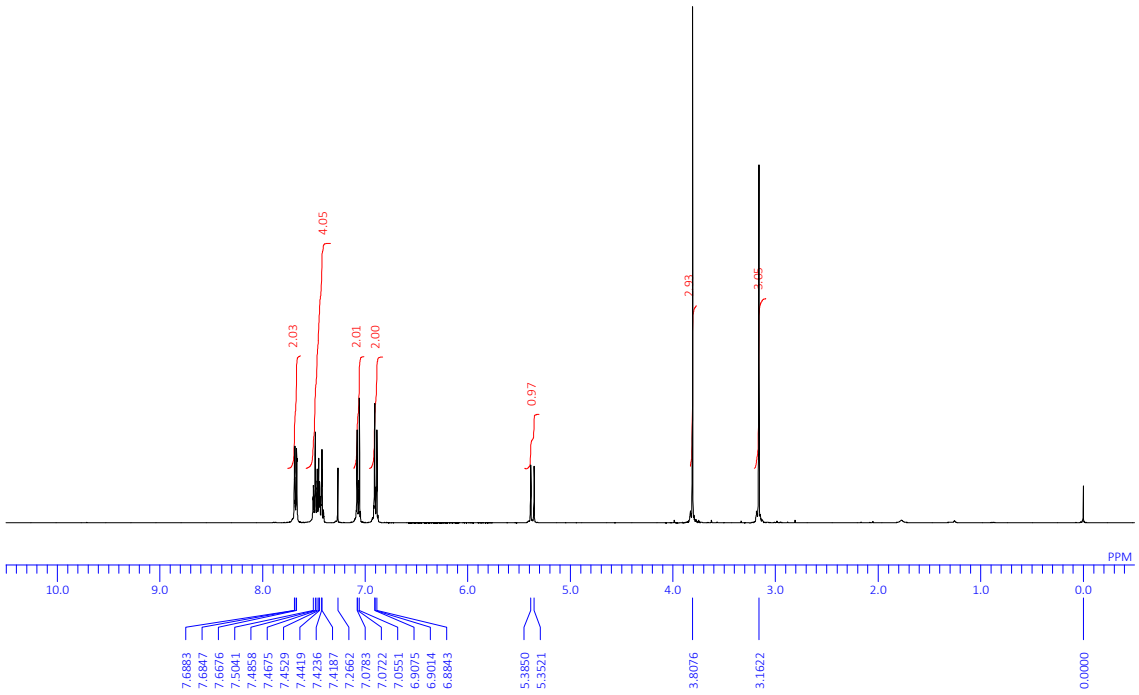
55.4865
37.3309


OMe
O
Ph
S
N
Me

4d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3.0
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7.4236
7.4187
7.2662
7.0783
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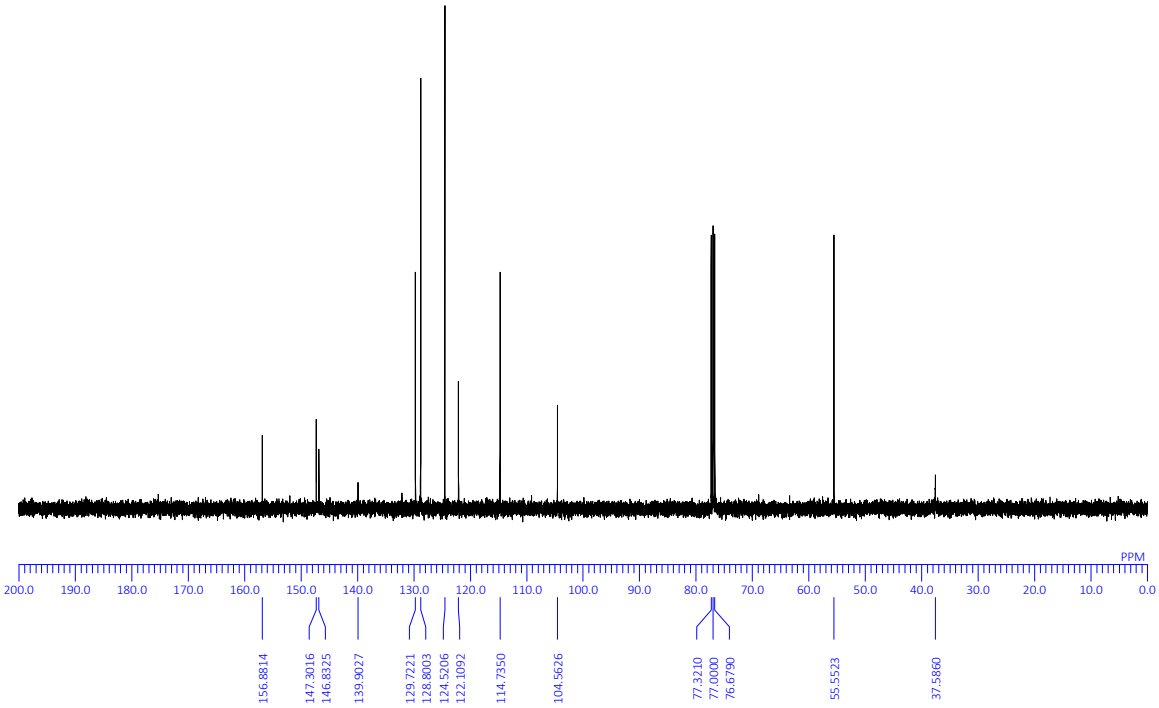
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90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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147.3016
146.8325
139.9027
129.7221
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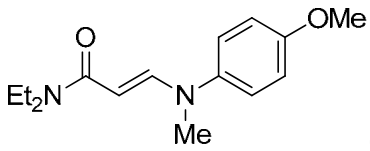
76.6790
55.5523
37.5860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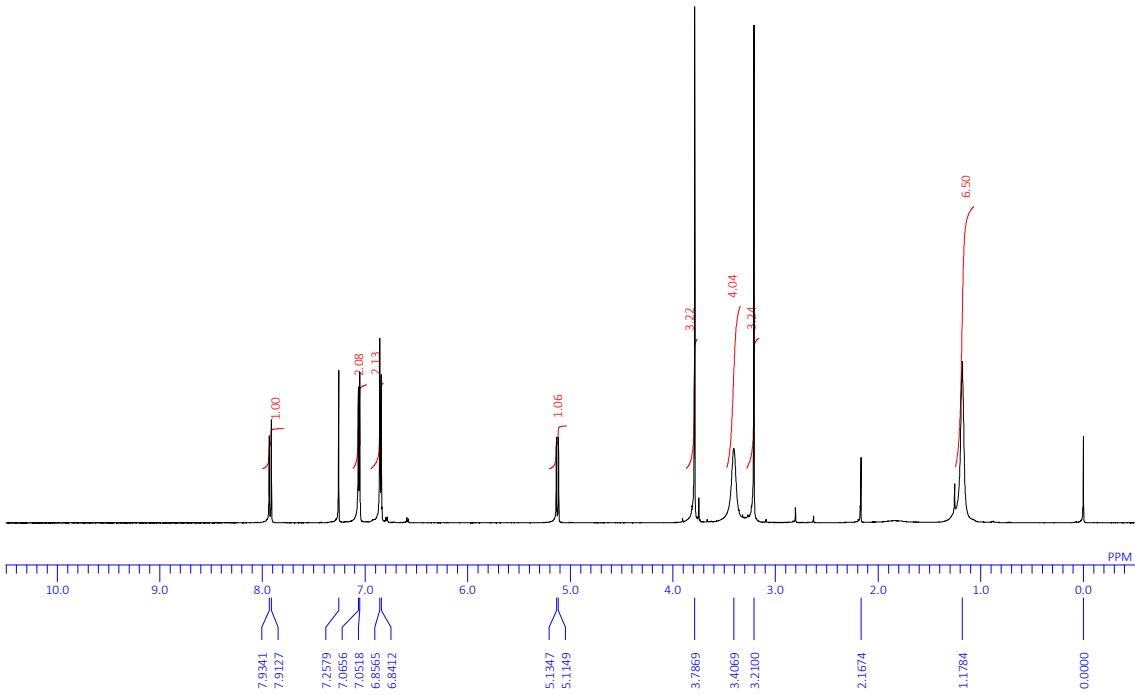
OMe
Et2N
N
Me

4e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3.0
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7.0656
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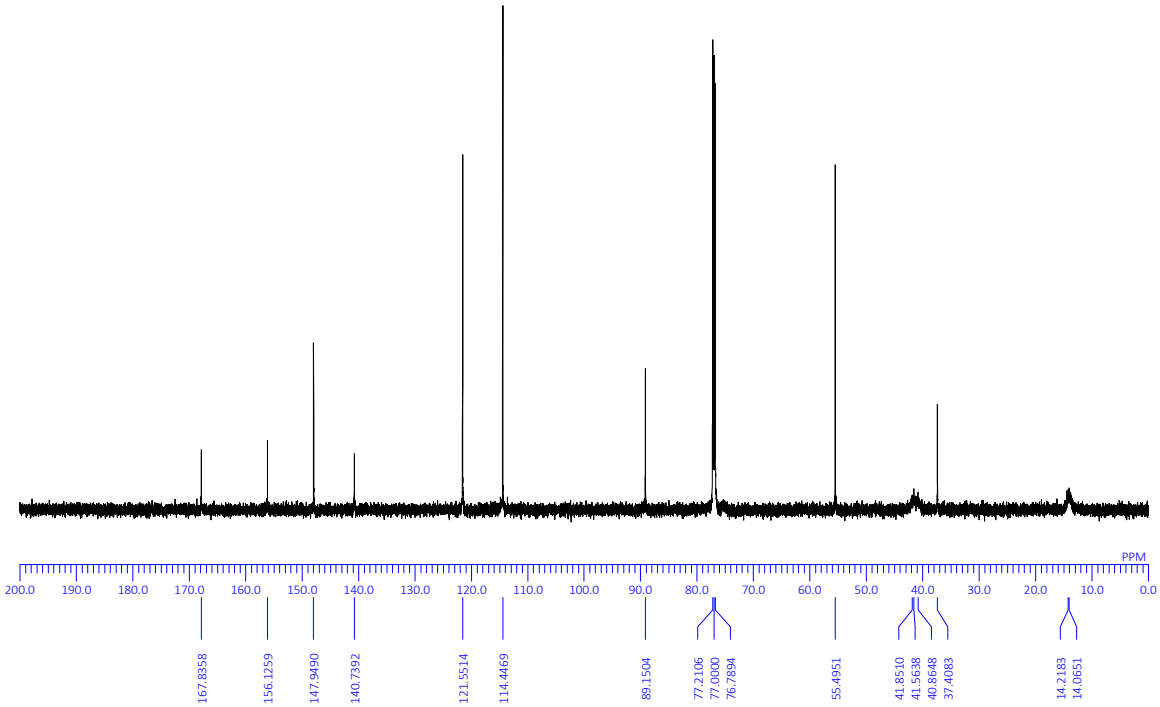
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80.0
70.0
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30.0
20.0
10.0
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167.8358
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147.9490
140.7392
121.5514
114.4469
89.1504
77.2106
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55.4951
41.8510
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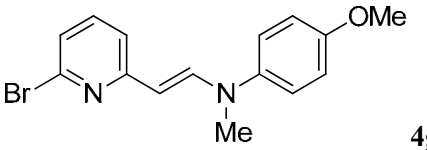
40.8648
37.4083
14.2183
14.0651


OMe
Br
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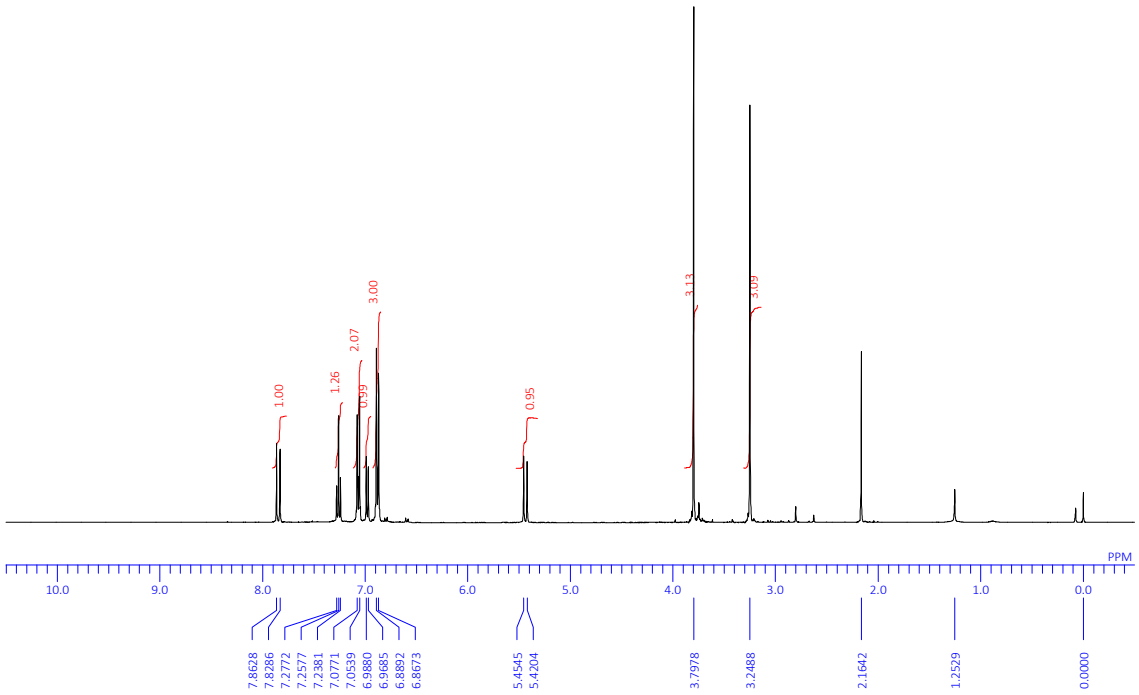
N
Me

4g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3.0
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0.0
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7.2772
7.2577
7.2381
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7.0539
6.9880
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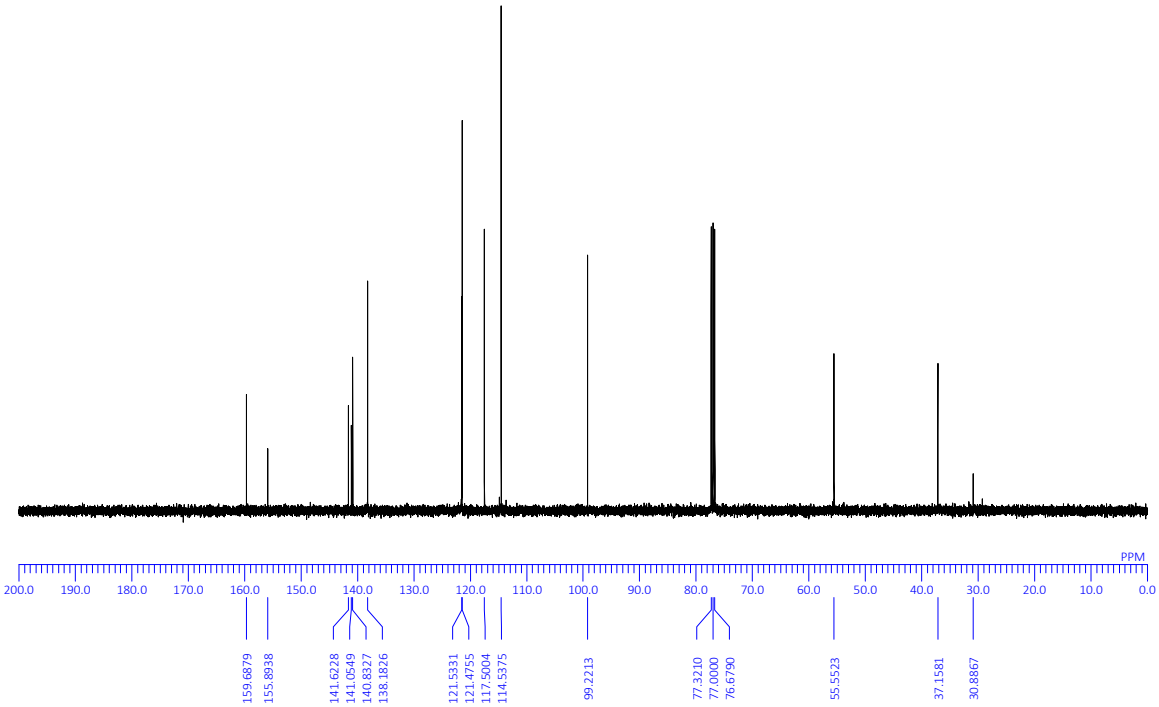
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40.0
30.0
20.0
10.0
0.0
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155.8938
141.6228
141.0549
140.8327
138.1826
121.5331
121.4755
117.5004
114.5375
99.2213
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37.1581
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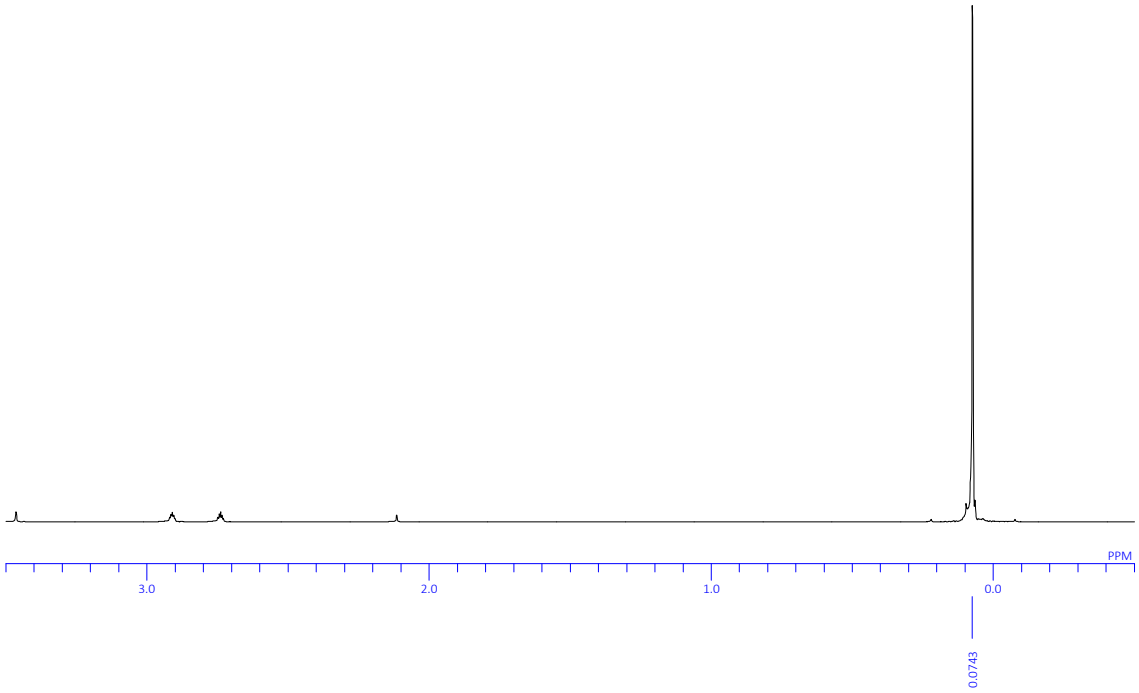
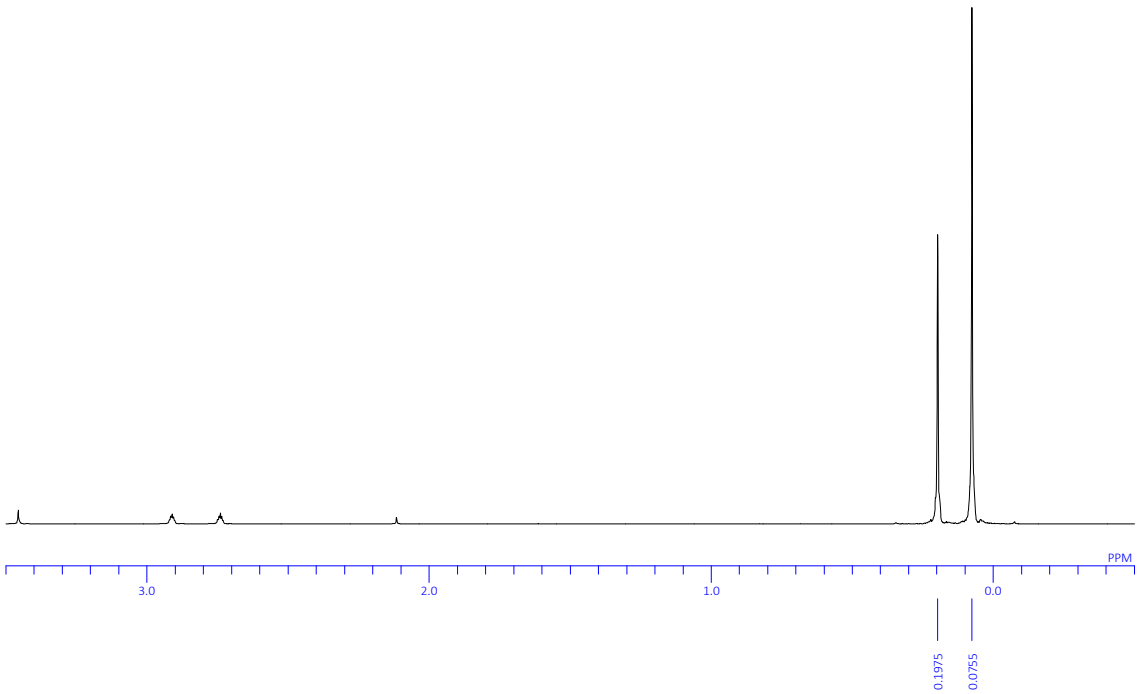
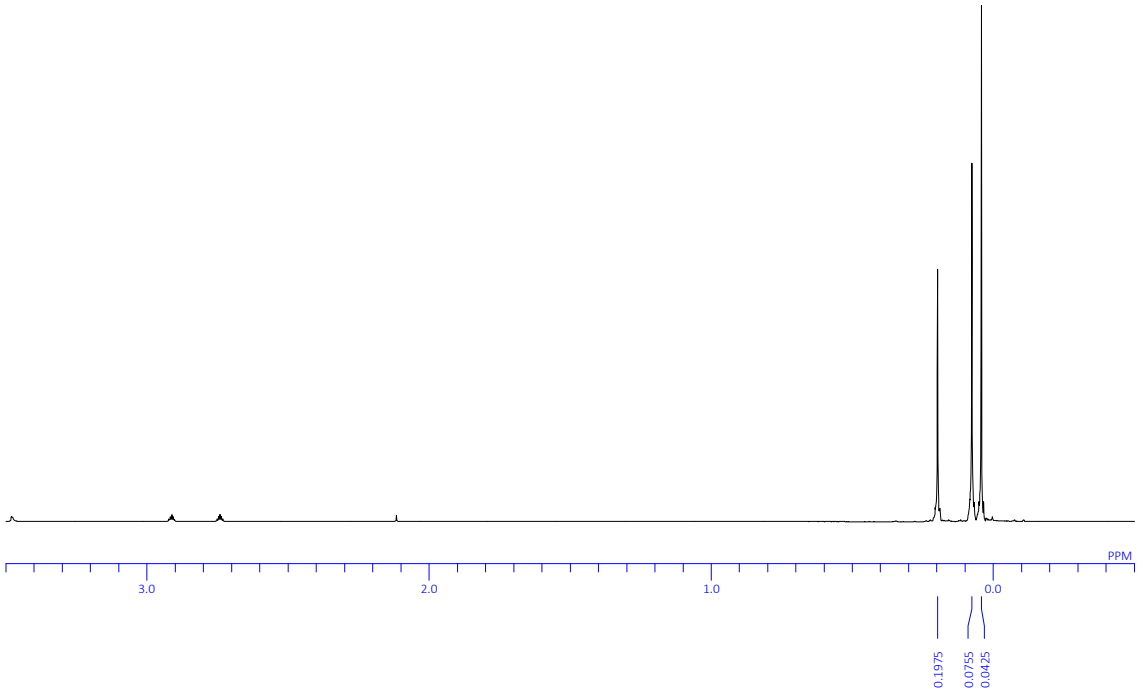
^{1}H NMR spectra of $(TMS)_2O$ (DMF-d7)



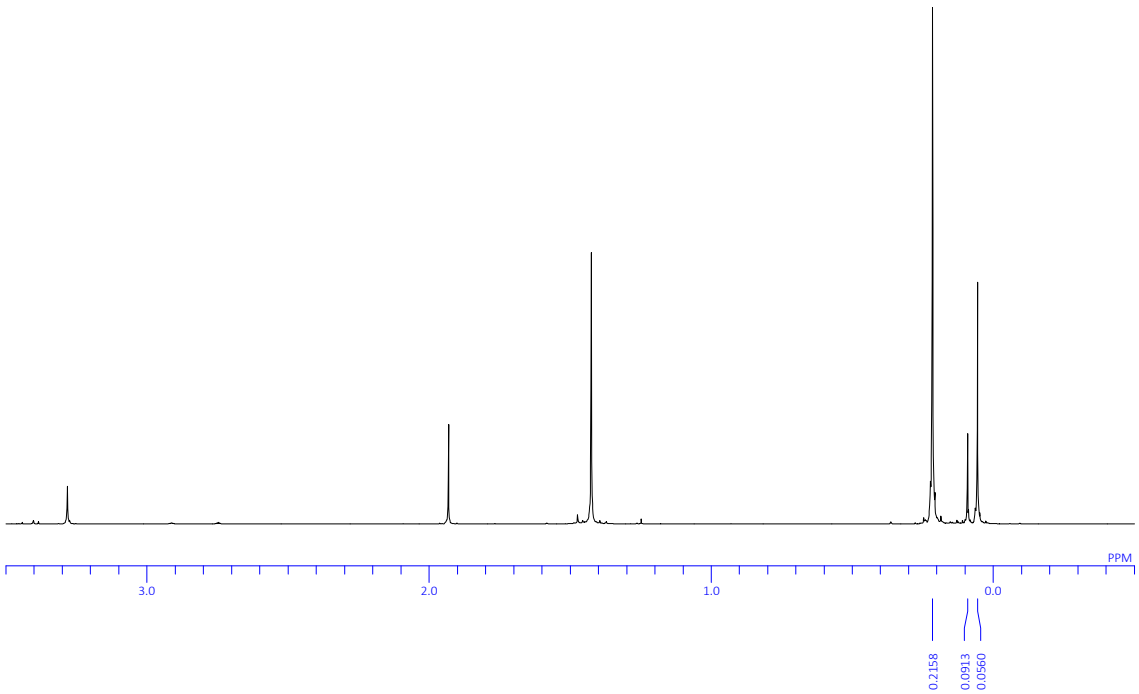
^{1}H NMR spectra of $(TMS)_2O$ + $(TMS)_3N$ (DMF-d7)



^{1}H NMR spectra of $(TMS)_2O$ + $(TMS)_3N$ + TMSOH (DMF-d7)



^{1}H NMR spectra of the reaction mixture (DMF-d7)



^{1}H NMR spectra comparison between the reference (top) and the reaction mixture (bottom) showing the formation of silanol and disiloxane.