Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information for

$Cu(OTf)_2$-catalyzed Ritter reaction: Efficient synthesis of amides from nitriles and halohydrocarbons in water

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General information:

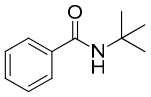
Melting points are recorded with a micro melting point apparatus and uncorrected. NMR spectra were recorded with a 400 MHz spectrometer for ^{1}H NMR, 100 MHz for ^{13}C NMR. Chemical shifts δ are given in ppm relative to tetramethylsilane in $CDCl_3$ or to the residual proton signals of the deuterated solvent DMSO-d_6 for ^{1}H and ^{13}C NMR. High resolution mass spectra were taken with a 3000 mass spectrometer, using Bruker micro OTOF system. For column chromatography 200-300 mesh silica gel (GF254) was used as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). All reagents and solvents were purchased from commercial sources and purified commonly before used.

Typical experimental procedure for the reaction of nitriles and halohydrocarbon

A mixture of nitrile (0.5 mmol), halohydrocarbon (0.75 mmol), Copper(II) trifluoromethanesulfonate (5%×0.5 mmol) and 200 μL water was placed in a round bottom flask. Then the reaction mixture was heated at 100 ^{o}C for the given time. After completion of the reaction monitored by thin layer chromatography (TLC), and then extracted with ethyl acetate (3×10 mL). The organic layers were collected, combined, washed with water (3×10 mL), dried over anhydrous Na_2SO_4, and concentrated under vacuum. The resulted residue was purified by column chromatography over silica gel using ethyl acetate and petroleum ether as the eluent, to give the target product.

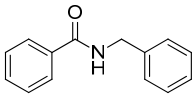
Characterization of compounds

N-(tert-butyl)benzamide (3g):



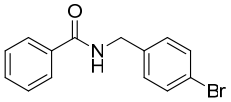
White powder. M.p. 119-121 ^{o}C; ν_{max}(KBr)/cm^{-1} 3324 (NH), 1637 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.48-7.38 (m, 3H), 5.96 (br s, 1H), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 135.9, 131.0, 128.4, 126.7, 51.6, 28.9. NMR data corresponded with data reported by Akamanchi.[1]

N-benzylbenzamide[2] (3a):



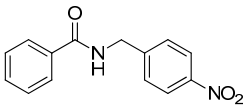
White powder. M.p. 96-97 ^{o}C; ν_{max}(KBr)/cm^{-1} 3325 (NH), 1641 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* =7.6 Hz, 2H), 6.86 (br s, 1H), 4.60 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.5, 138.3, 134.4, 131.5, 128.7, 128.5, 127.8, 127.5, 127.0, 44.0.

N-(4-bromobenzyl)benzamide[2] (3b):



White powder. M.p. 139-141 ^{o}C; ν_{max}(KBr)/cm^{-1} 3305 (NH), 1638 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.45-7.39 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.72 (br s, 1H), 4.55 (d, *J* = 6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 167.5, 137.3, 134.1, 131.8, 131.8, 129.5, 128.6, 127.0, 121.4, 43.4.

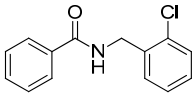
N-(4-nitrobenzyl)benzamide (3d):



White powder. M.p. 157-158 ^{o}C; ν_{max}(KBr)/cm^{-1} 3421 (NH), 1637 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.56-7.43 (m, 5H), 6.80 (br s, 1H), 4.73 (d, *J* = 6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.6, 147.2, 145.9, 133.7, 132.0, 128.7, 128.2, 127.0, 124.0, 43.3.

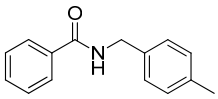
NMR data corresponded with data reported by Mazal.[2]

N-(2-chlorobenzyl)benzamide (3e):



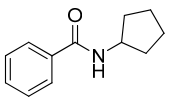
White powder. M.p. 113-114 °C; ν_{max}(KBr)/cm^{-1} 3289 (NH), 1631 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.39-7.33 (m, 4H), 7.20 (t, *J* = 4 Hz, 2H), 7.08 (br s, 1H), 4.66 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.6, 135.6, 134.2, 133.5, 131.6, 129.9, 129.5, 128.9, 128.5, 127.1, 41.9; HRMS: calcd for$C_{14}H_{13}ClNO$ $[M+H]^+$ 246.0680, found 246.0682.

N-(4-methylbenzyl)benzamide (3c):



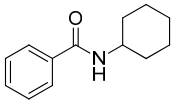
White powder. M.p. 129-130 °C; ν_{max}(KBr)/cm^{-1} 3307 (NH), 1634 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H),7.15 (d, *J* = 8.8 Hz, 2H), 6.82 (br s, 1H), 4.57 (d, *J* = 5.6 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 137.2, 135.3, 134.4, 131.5, 129.4, 129.1, 128.6, 128.5, 127,9, 127.1, 43.8, 39.0, 21.2, 19.4. NMR data corresponded with data reported by Darbeau.[3]

N-cyclopentylbenzamide (3h):



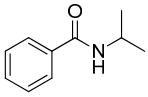
White powder. M.p. 143-144 °C; ν_{max}(KBr)/cm^{-1} 3297 (NH), 1628 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 6.21 (br s, 1H), 4.43-4.34 (m, 1H), 2.10-2.06 (m, 2H), 1.75-1.59 (m, 4H), 1.52-1.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.2, 134.9, 131.2, 128.4, 126.8, 51.7, 33.2, 23.8; HRMS: calcd for $C_{12}H_{16}NO$ $[M+H]^+$ 190.1226, found 190.1226.

N-cyclohexylbenzamide[4] (3i):



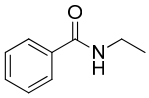
White powder. M.p. 139-140 °C; ν_{max}(KBr)/cm^{-1} 3242 (NH), 1628 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 5.98 (br s, 1H), 4.02-3.93 (m, 1H), 2.04-2.01 (m, 2H), 1.77-1.64 (m, 4H), 1.48-1.38 (m, 2H), 1.28-1.19 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.6, 135.0, 131.2, 128.5, 126.8, 48.7, 33.2, 25.6, 24.9.

N-isopropylbenzamide (3j):



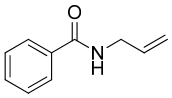
White powder. M.p. 89-90 °C; ν_{max}(KBr)/cm^{-1} 3299 (NH), 1633 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 5.97 (br s, 1H), 4.33-4.24 (m, 1H), 1.26 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.7, 134.9, 131.2, 128.5, 126.8, 41.9, 22.9. NMR data corresponded with data reported by Hanson.[5]

N-ethylbenzamide (3k):



White powder. M.p. 67-69 °C; ν_{max}(KBr)/cm^{-1} 3319 (NH), 1637 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 6.8 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 6.27 (br s, 1H), 3.52-3.45 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.5, 134.8, 131.3, 128.5, 126.8, 34.9, 14.9; HRMS: calcd for $C_9H_{13}NO$ $[M+H]^+$ 150.0913, found 150.0907.

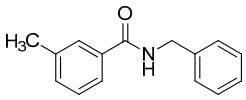
N-allylbenzamide (3f):



White oil. ν_{max}/cm^{-1} 3315 (NH), 1640 (C=O);^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 6.26 (br s, 1H), 5.99-5.89 (m, 1H), 5.27 (dd, J_1 = 17 Hz, J_2 = 1.4 Hz, 1H), 5.19 (dd, J_1 = 10.2 Hz, J_2 = 1.2 Hz, 1H), 4.10 (t, *J* = 5.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100

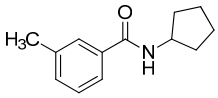
MHz): δ 167.3, 134.4, 134.1, 131.5, 128.6, 126.9, 116.7, 42.4. NMR data corresponded with data reported by Fisher.[6]

N-benzyl-3-methylbenzamide (3o):



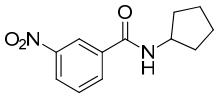
White powder. M.p. 97-98 ^{o}C; ν_{max}(KBr)/cm^{-1} 3324 (NH), 1637 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63 (s, 1H), 7.57 (d, *J* = 6.8 Hz, 1H), 7.32-7.24 (m, 7H), 7.01 (s, 1H), 4.58 (d, *J* = 5.6 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.8, 138.4, 138.3, 134.3, 132.2, 128.7, 128.4, 127.9, 127.8, 127.4, 124.1, 44.0, 21.4; HRMS: calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1224, found 226.1226.

N-(cyclopentylmethyl)-3-methylbenzamide (3r):



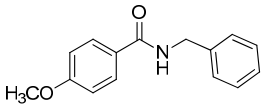
White powder. M.p.107-108 ^{o}C; ν_{max}(KBr)/cm^{-1} 3246 (NH), 1629 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (s, 1H), 7.51 (t, *J* = 3.6 Hz, 1H), 7.25 (d, *J* = 4.8 Hz, 2H), 6.34 (br d, *J* = 5.6 Hz, 1H), 4.40-4.31 (m, 1H), 2.34 (s, 3H), 2.07-2.00 (m, 2H), 1.73-1.55 (m, 4H), 1.51-1.43 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.4, 138.2, 134.8, 131.9, 128.2, 127.6, 123.8, 51.6, 33.1, 23.8, 21.3; HRMS: calcd for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1383, found 204.1376.

N-cyclopentyl-3-nitrobenzamide (3n):



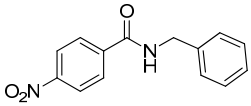
White powder. M.p. 146-147^{o}C; ν_{max}(KBr)/cm^{-1} 3292 (NH), 1637 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.54 (s, 1H), 8.30 (dd, J_1 = 8.2 Hz, J_2 = 1.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8 Hz, 1H), 6.53 (br d, *J* = 6.4 Hz, 1H), 4.43-4.35 (m, 1H), 2.13-2.05 (m, 2H), 1.78-1.60 (m, 4H), 1.57-1.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.8, 148.0, 136.4, 133.3, 129.8, 125.8, 121.7, 52.1, 33.0, 23.8; HRMS: calcd for $C_{12}H_{15}N_2O_3$ $[M+H]^+$ 235.1077, found 235.1074.

N-benzyl-4-methoxybenzamide (3l):



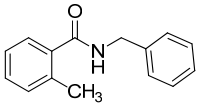
White powder. M.p. 110-112°C; ν_{max}(KBr)/cm^{-1} 3269 (NH), 1633 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.35-7.29 (m, 5H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.50 (br s, 1H), 4.62 (d, *J* = 5.6 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9, 162.2, 133.4, 128.8, 128.7, 127.9, 127.5, 126.6, 113.7, 55.4, 44.0. NMR data corresponded with data reported by Tamaddon.[7]

N-benzyl-4-nitrobenzamide[8] (3m):



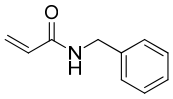
White powder. M.p. 144-146 °C; ν_{max}(KBr)/cm^{-1} 3281 (NH), 1633 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.39-7.30 (m, 4H), 7.18 (t, *J* = 6.8 Hz, 1H), 6.69 (br s, 1H), 4.65 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.3, 149.56, 139.9, 137.4, 128.9, 128.2, 128.0, 123.8, 44.4.

N-benzyl-2-methylbenzamide (3s):



White powder. M.p. 98-99 °C; ν_{max}(KBr)/cm^{-1} 3280 (NH), 1629 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.15 (m, 9H), 6.28 (br s, 1H), 4.57 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.0, 138.2, 136.1, 131.0, 129.9, 128.8, 127.8, 127.6, 126.7, 125.7, 43.8, 19.9; HRMS: calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1226, found 226.1224.

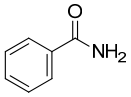
N-benzylacrylamide (3q):



White powder. M.p. 59-60 °C; ν_{max}(KBr)/cm^{-1} 3289 (NH), 1639 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.28 (m, 5H), 6.31 (d, *J* = 16 Hz, 1H), 6.15-6.08 (m, 1H), 6.06 (br s, 1H), 5.65 (dd, J_1 = 10.2 Hz, J_2 = 1.2 Hz, 1H), 4.50 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.8, 165.6, 137.9, 130.6, 128.7,

127.8, 127.8, 127.5, 126.8, 43.7, 39.5, 27.7. NMR data corresponded with data reported by Tamaddon.[7]

Benzamide[9]:



White powder. M.p. 112-114 ^{o}C; ν_{max}(KBr)/cm^{-1} 3370 (NH), 3176 (NH), 1660 (C=O); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 6.14 (br s, 1H), 5.92 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.0, 128.6, 127.3.

References:

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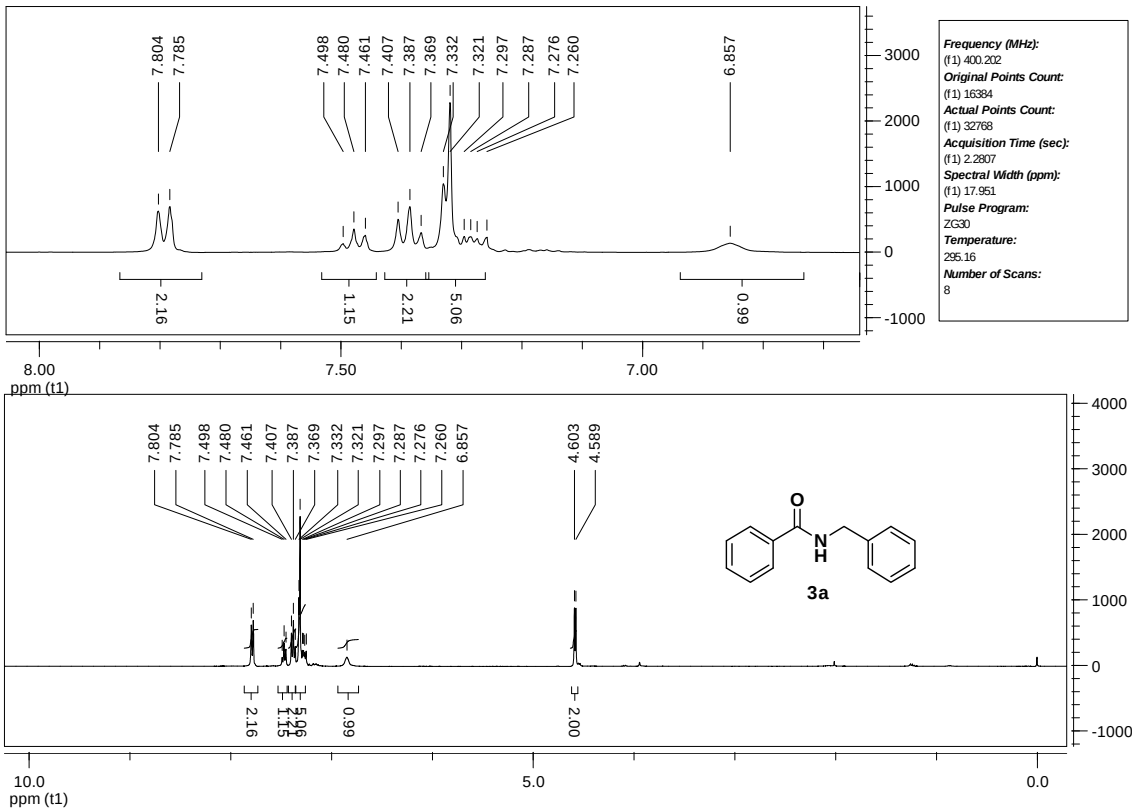
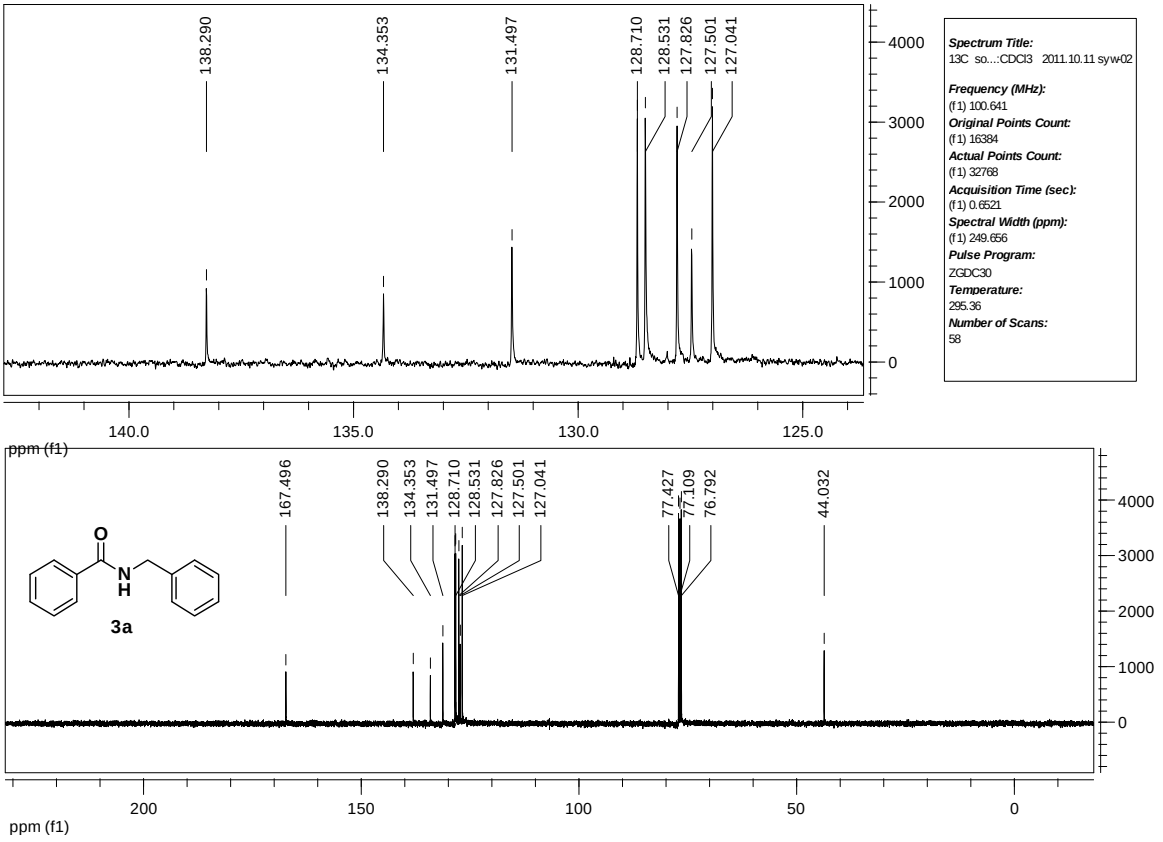
Copies of ^{1}H and ^{13}C NMR spectra

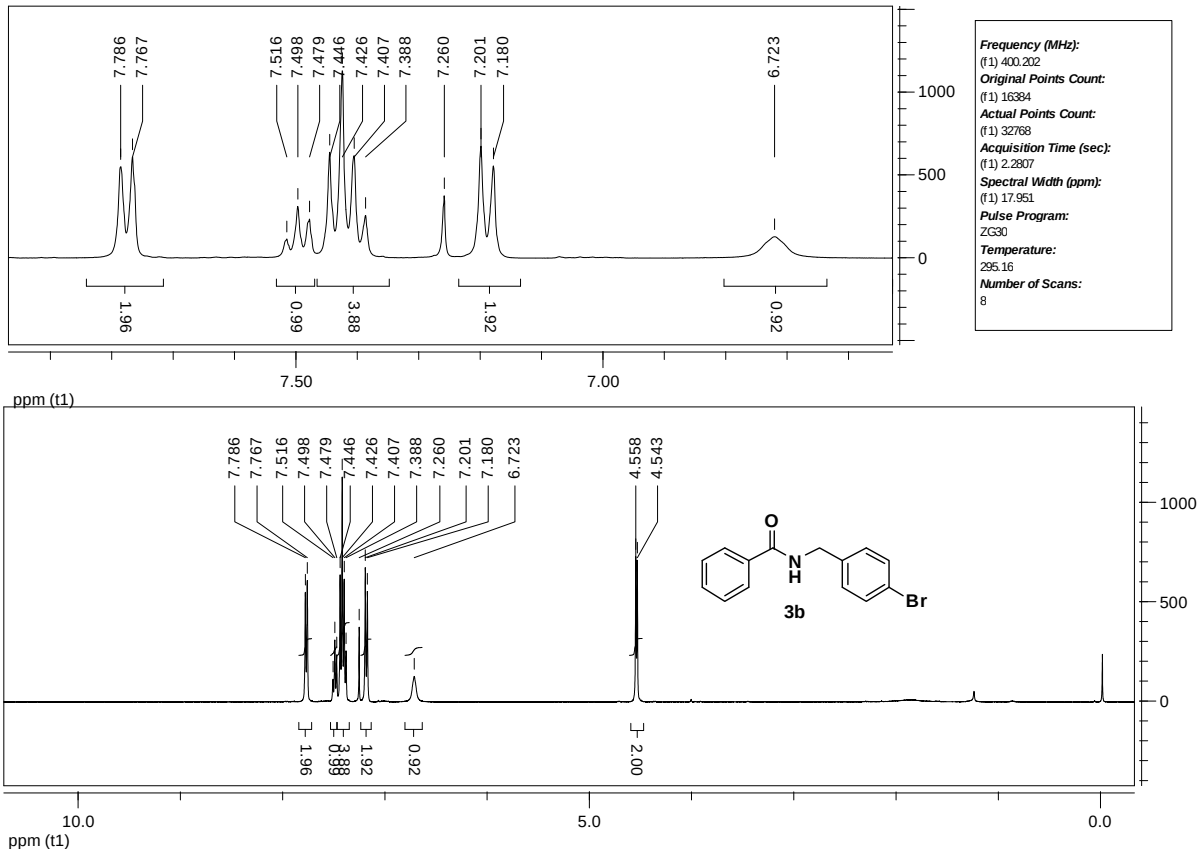
^{1}H NMR Spectrum for 3a



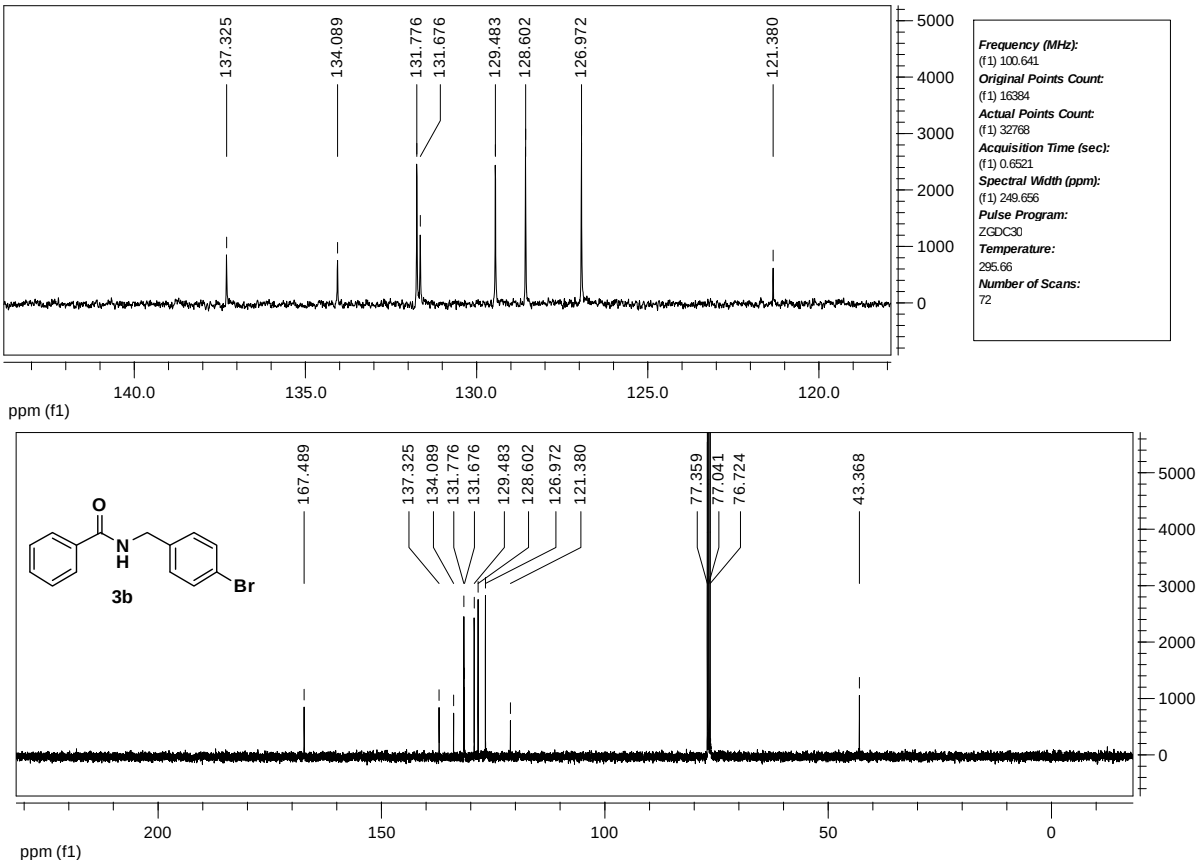
^{13}C NMR Spectrum for 3a



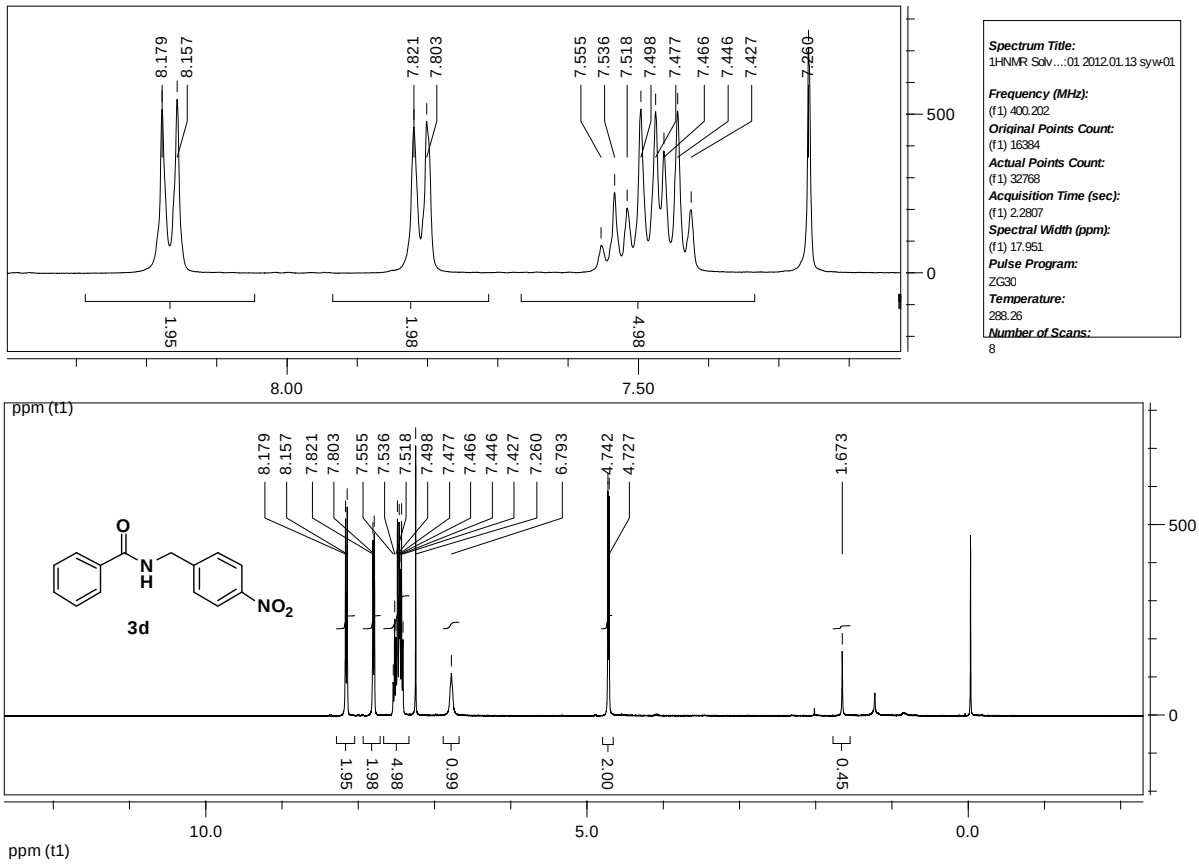
^{1}H NMR Spectrum for 3b



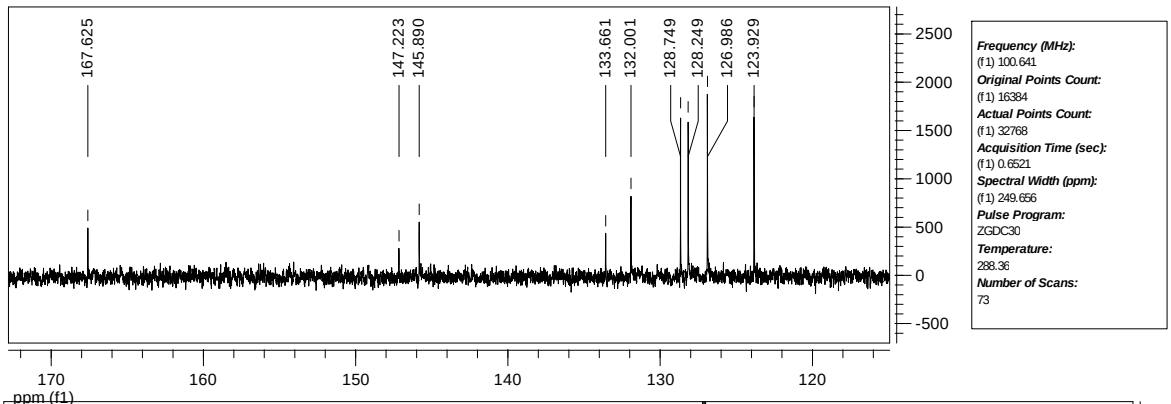
^{13}C NMR Spectrum for 3b

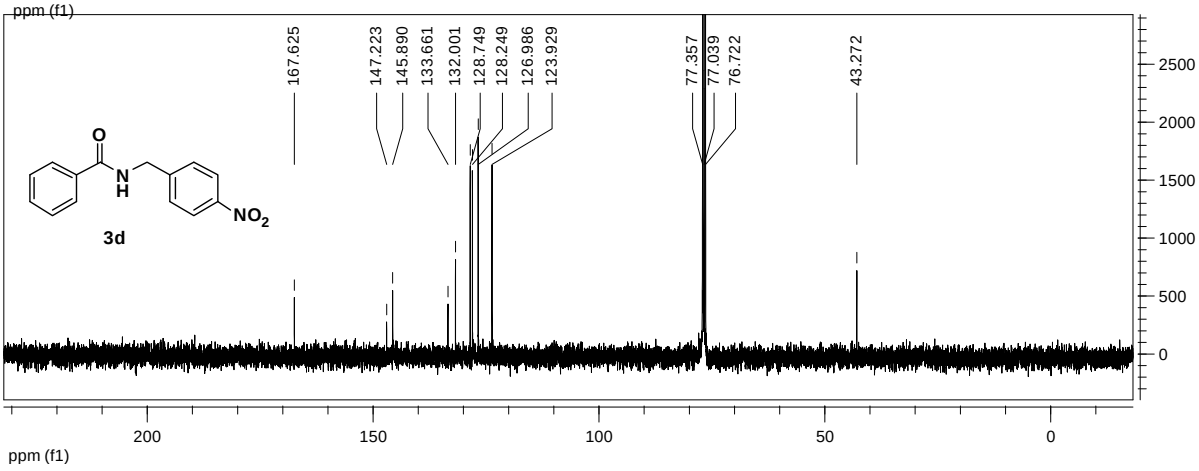


^{1}H NMR Spectrum for 3d

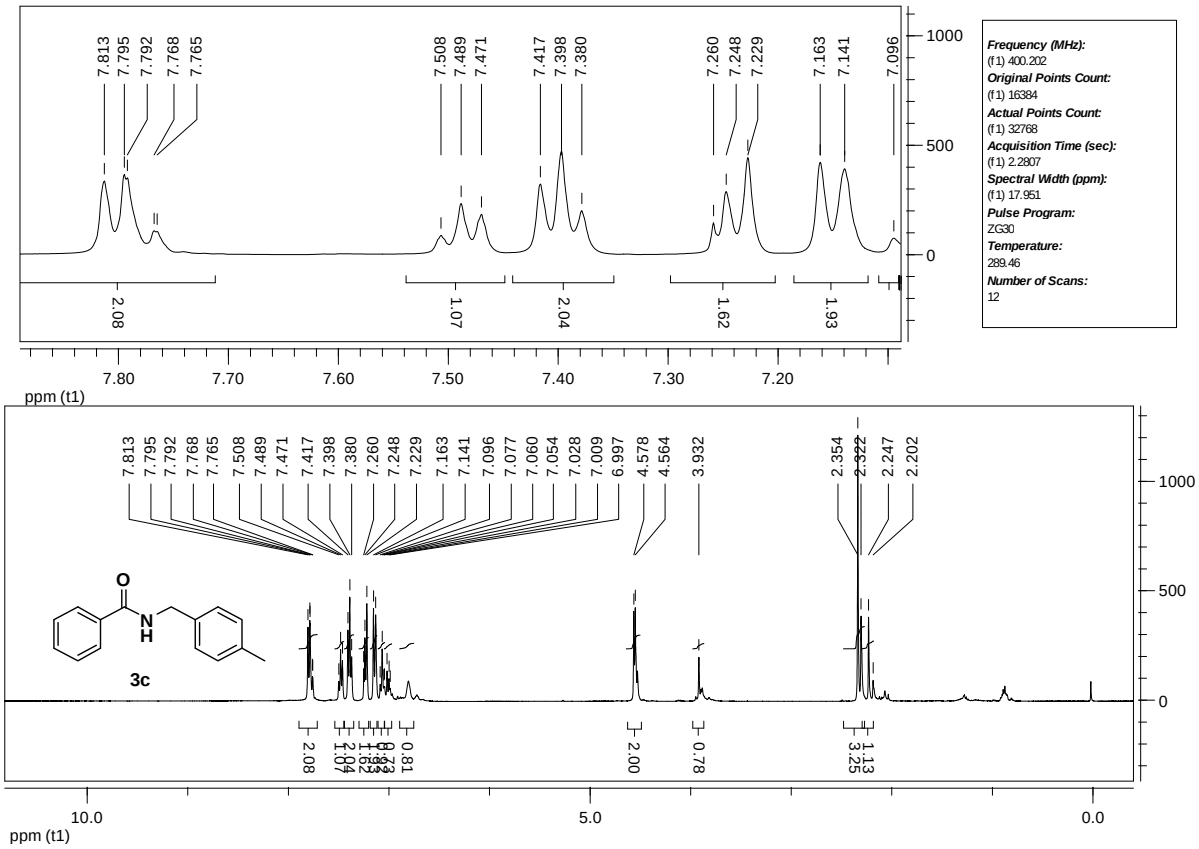


^{13}C NMR Spectrum for 3d

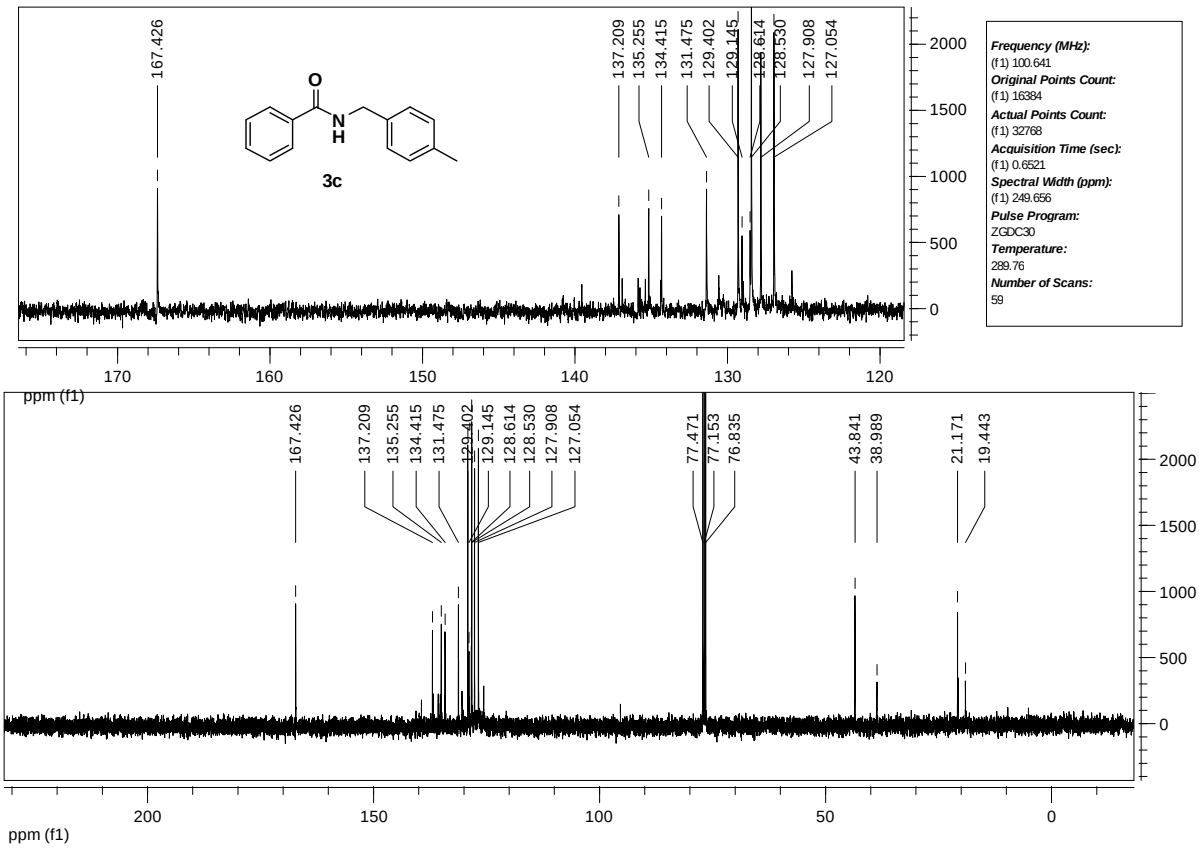




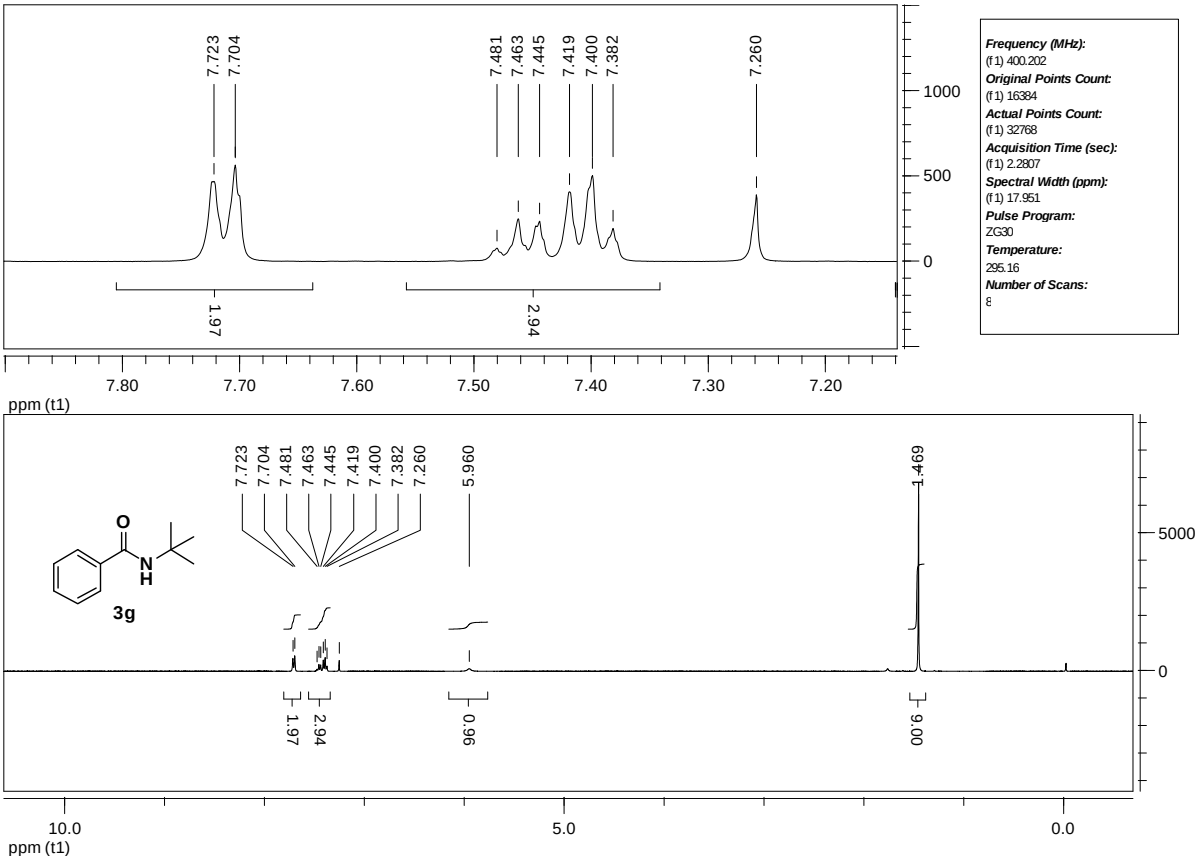
^{1}H NMR Spectrum for 3c



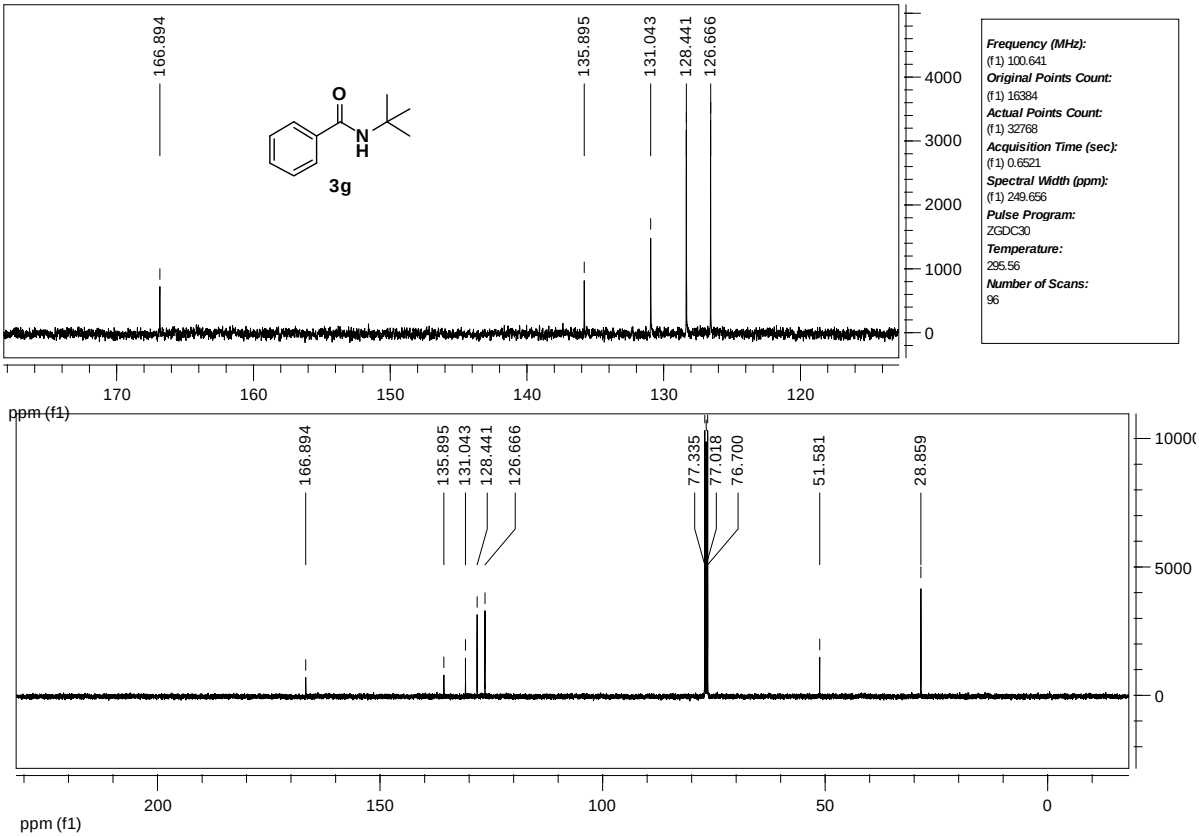
^{13}C NMR Spectrum for 3c



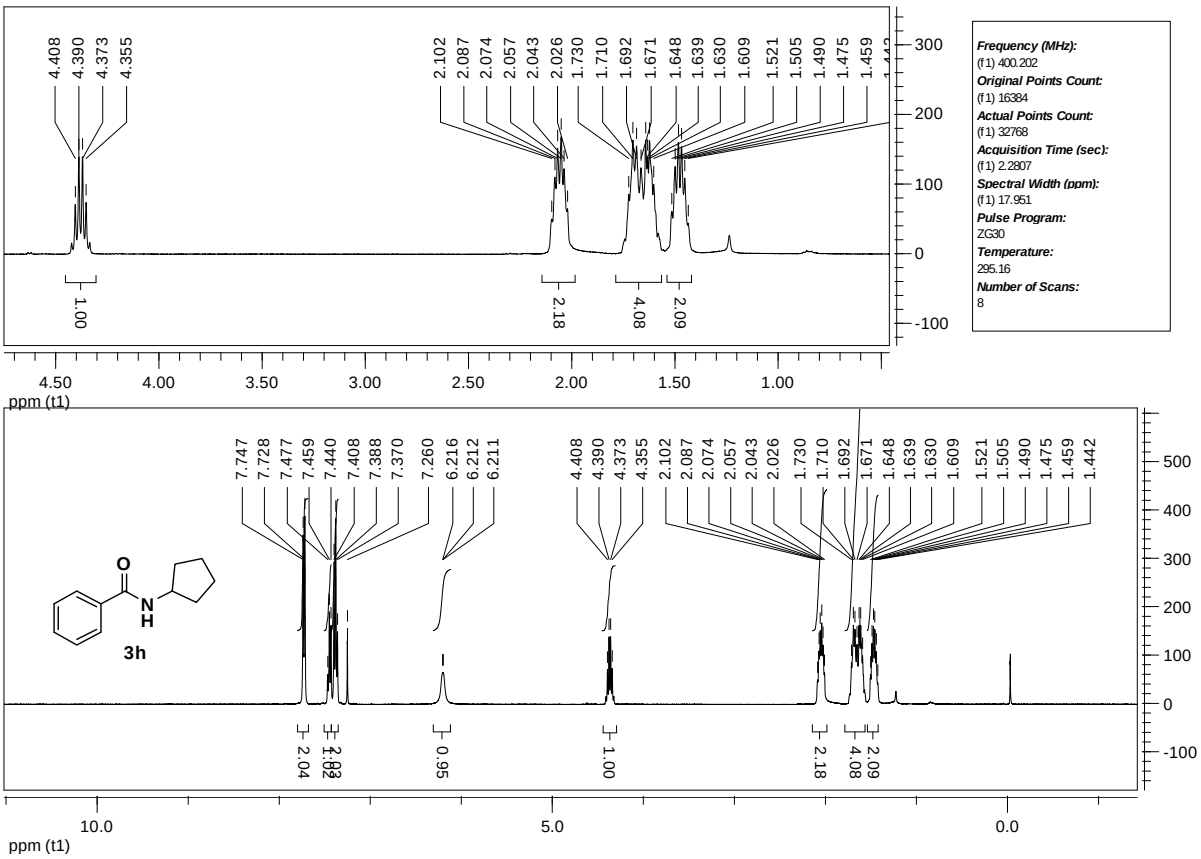
^{1}H NMR Spectrum for 3g



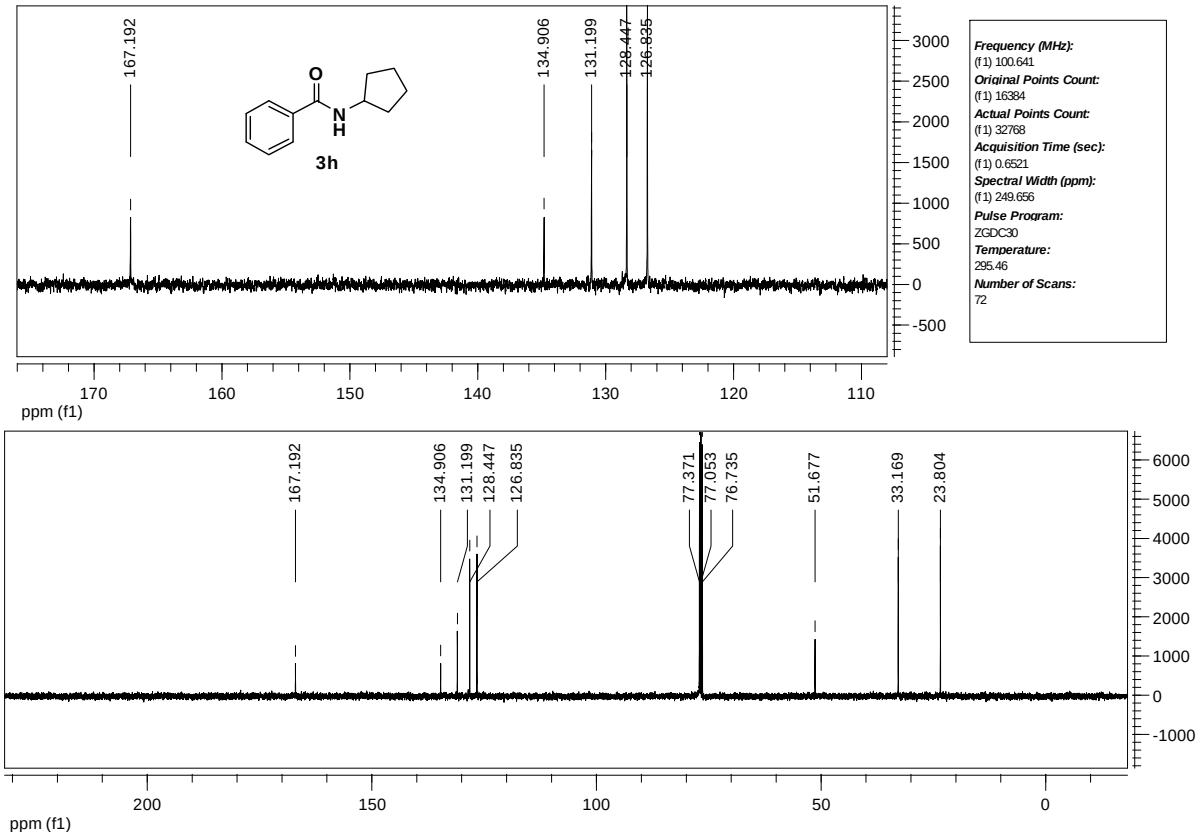
^{13}C NMR Spectrum for 3g



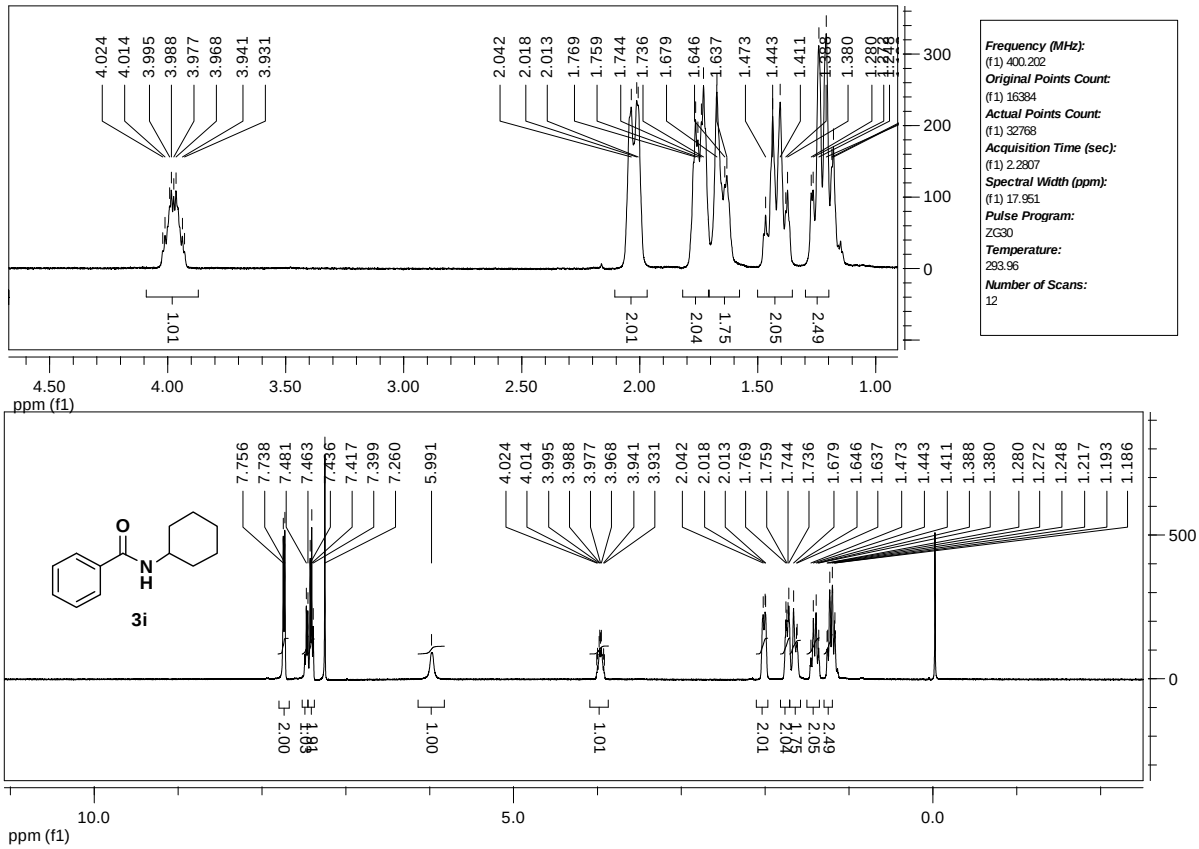
^{1}H NMR Spectrum for 3h



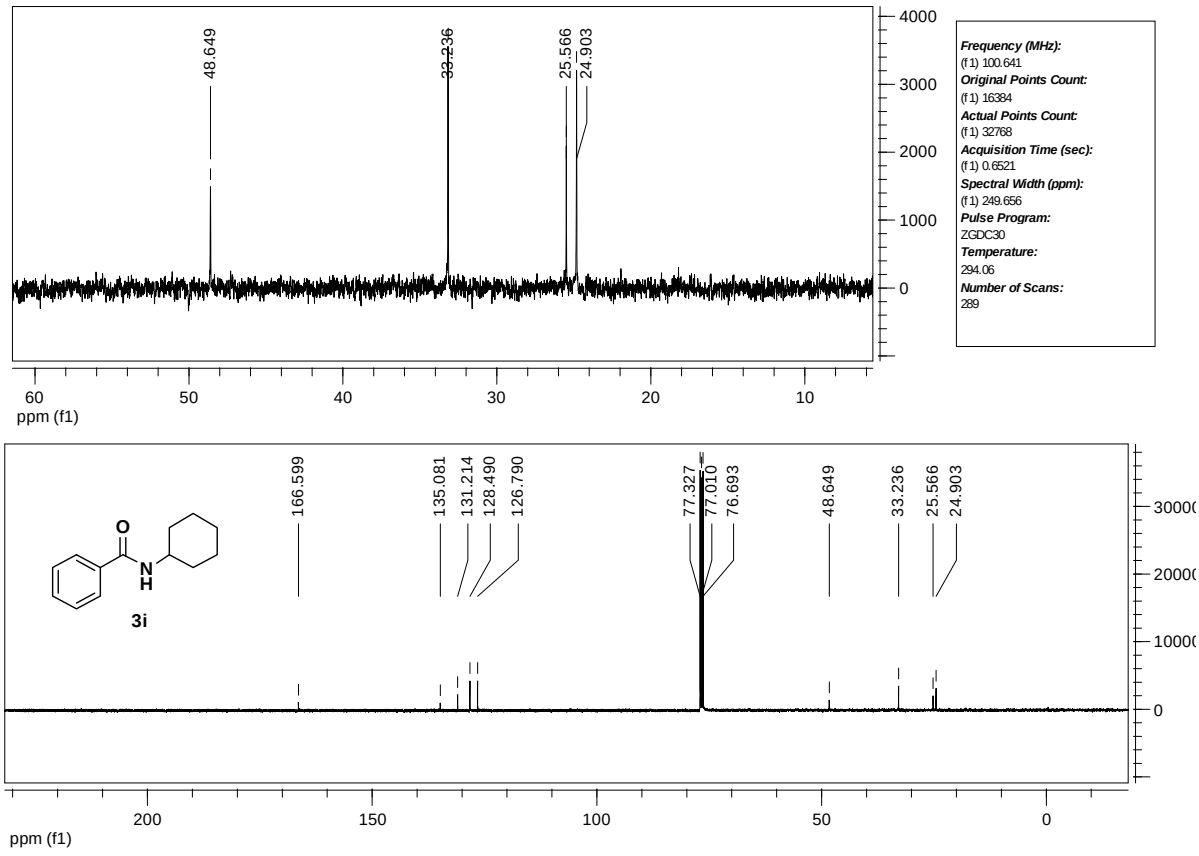
^{13}C NMR Spectrum for 3h



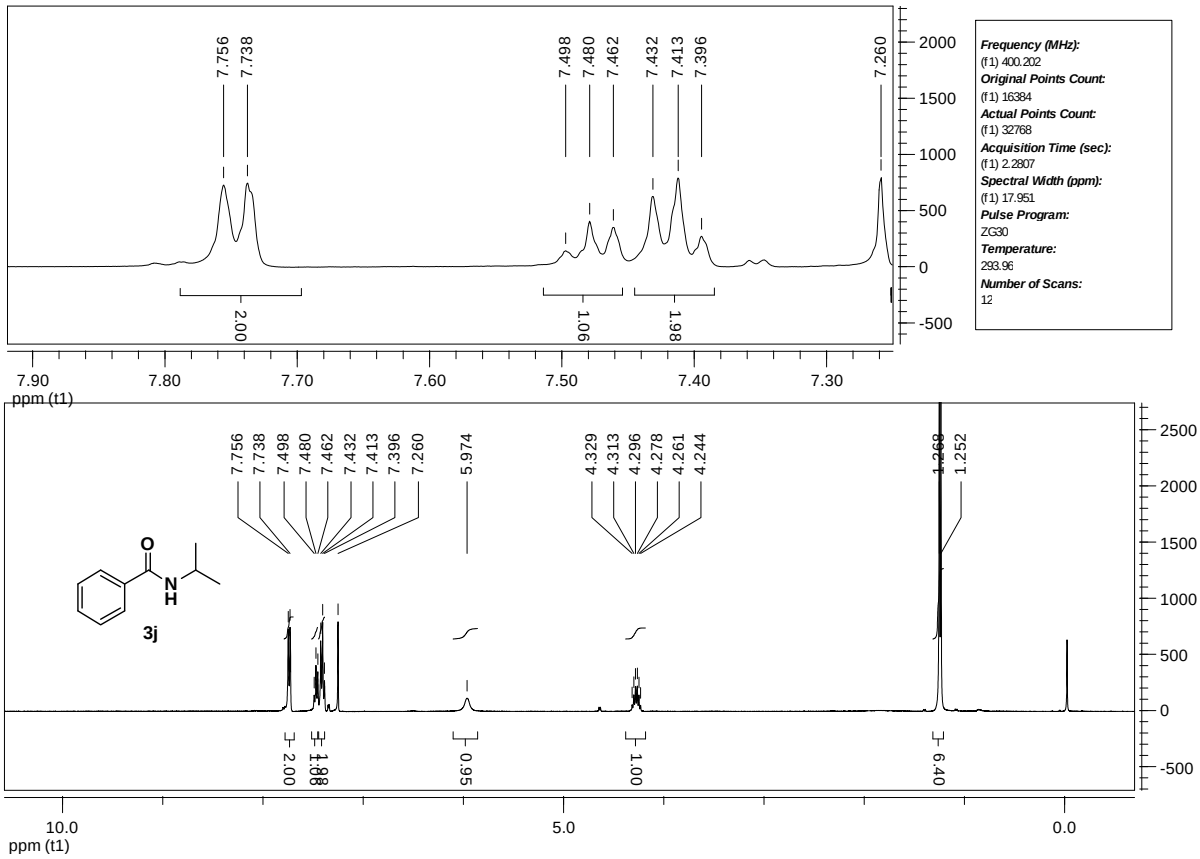
^{1}H NMR Spectrum for 3i



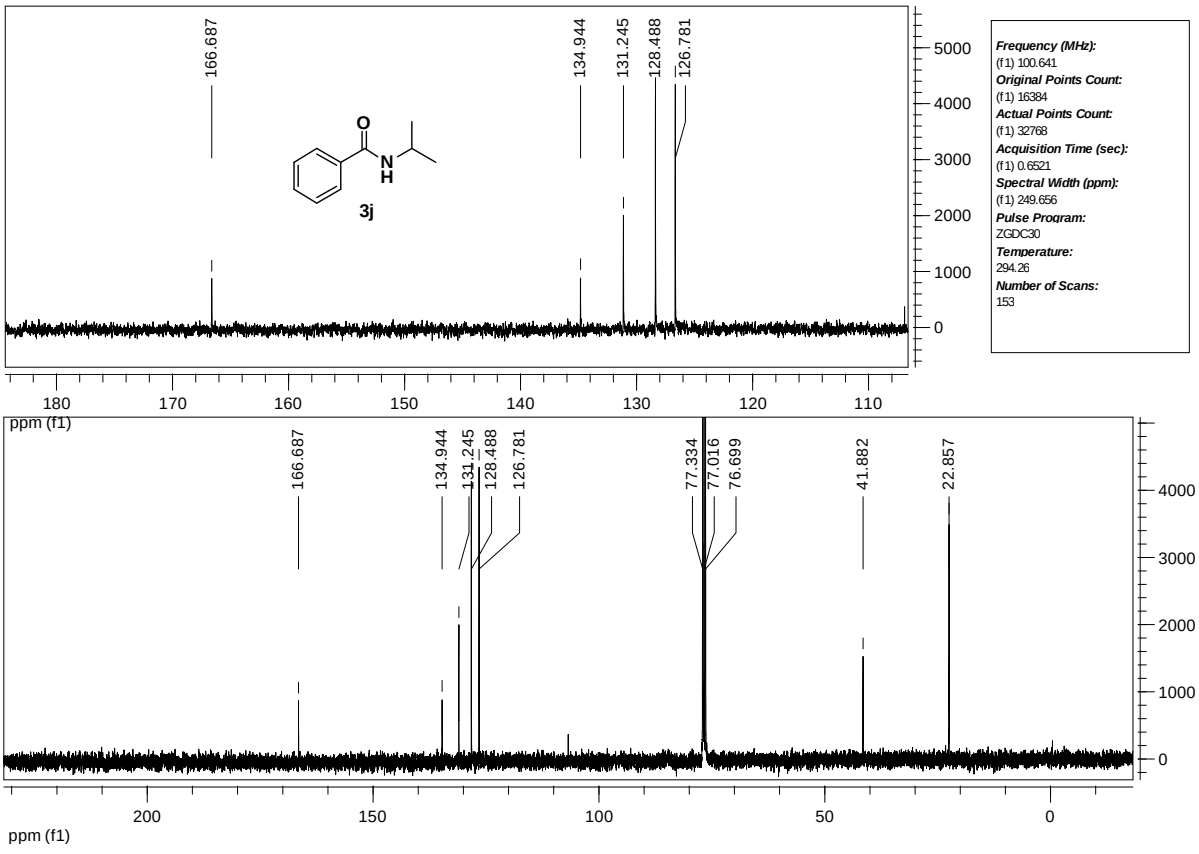
^{13}C NMR Spectrum for 3i



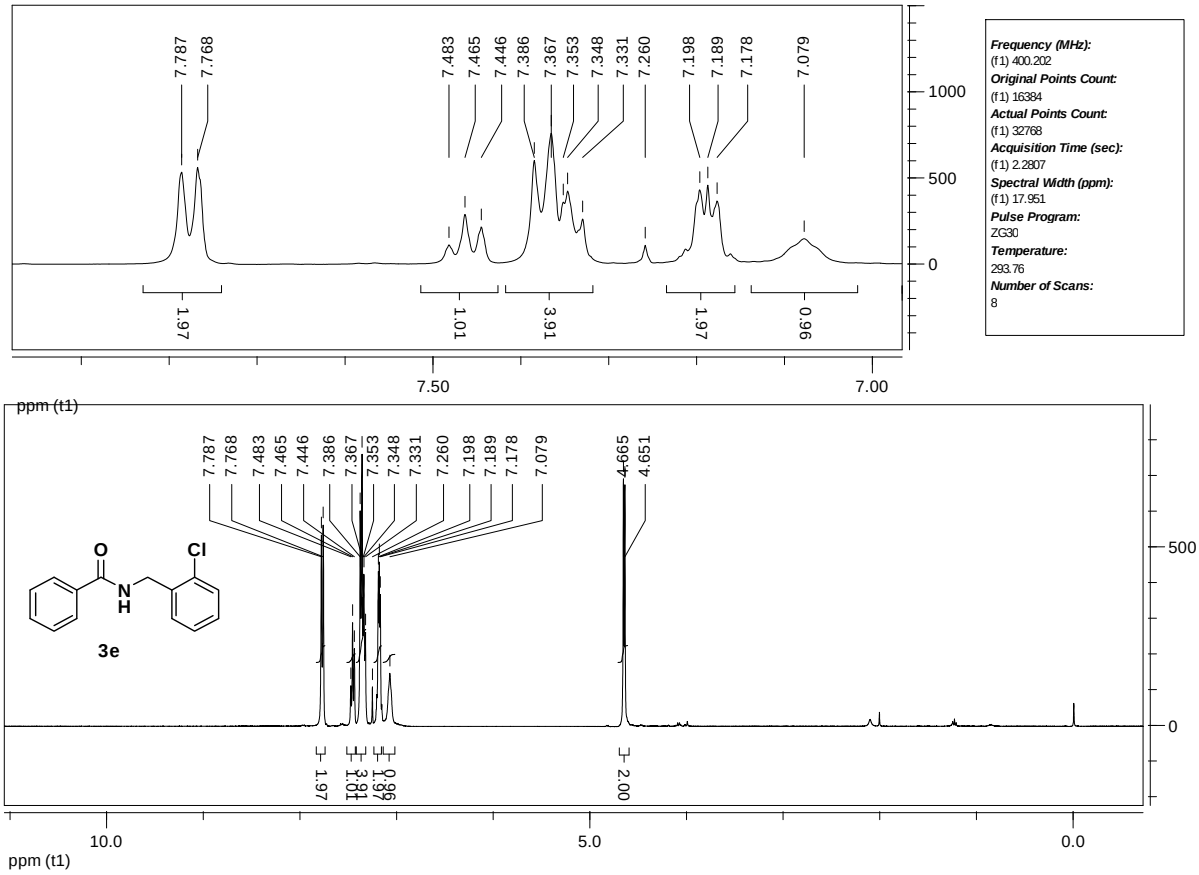
^{1}H NMR Spectrum for 3j



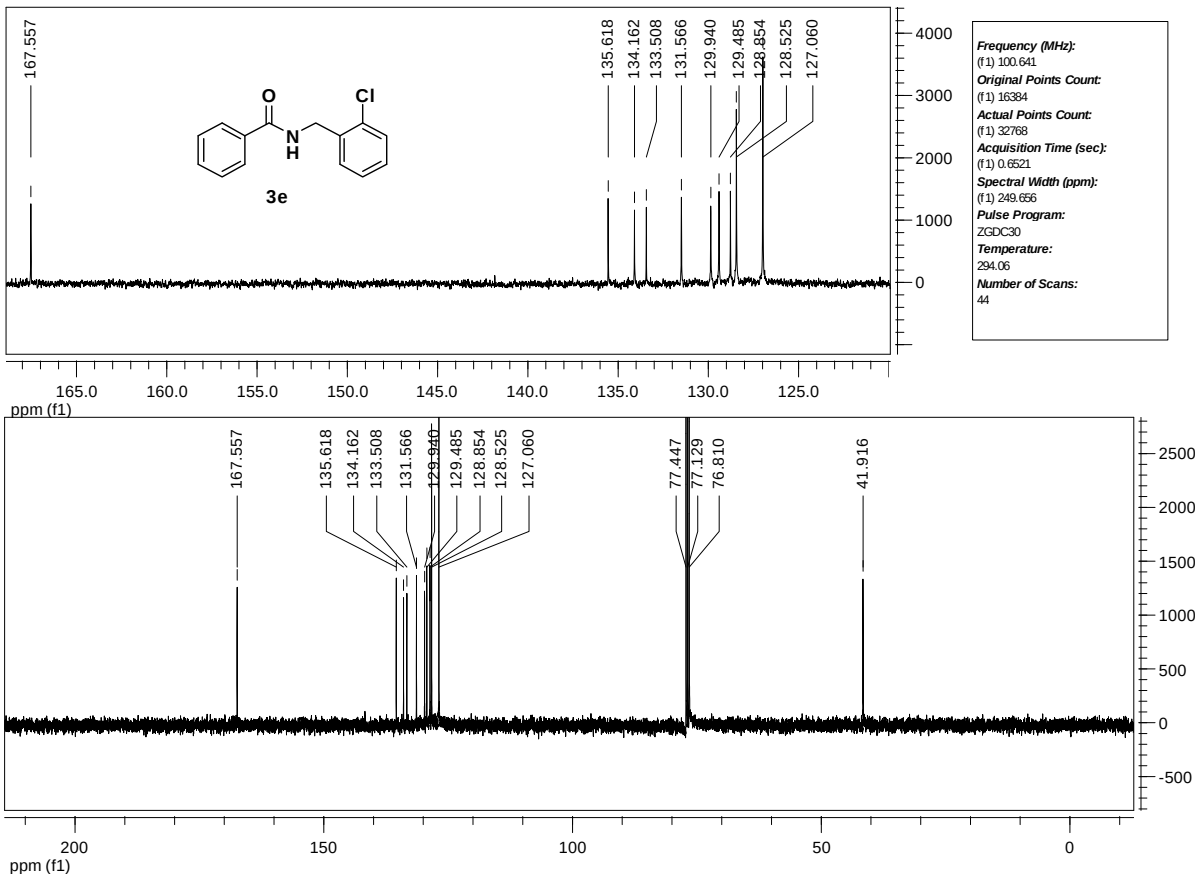
^{13}C NMR Spectrum for 3j



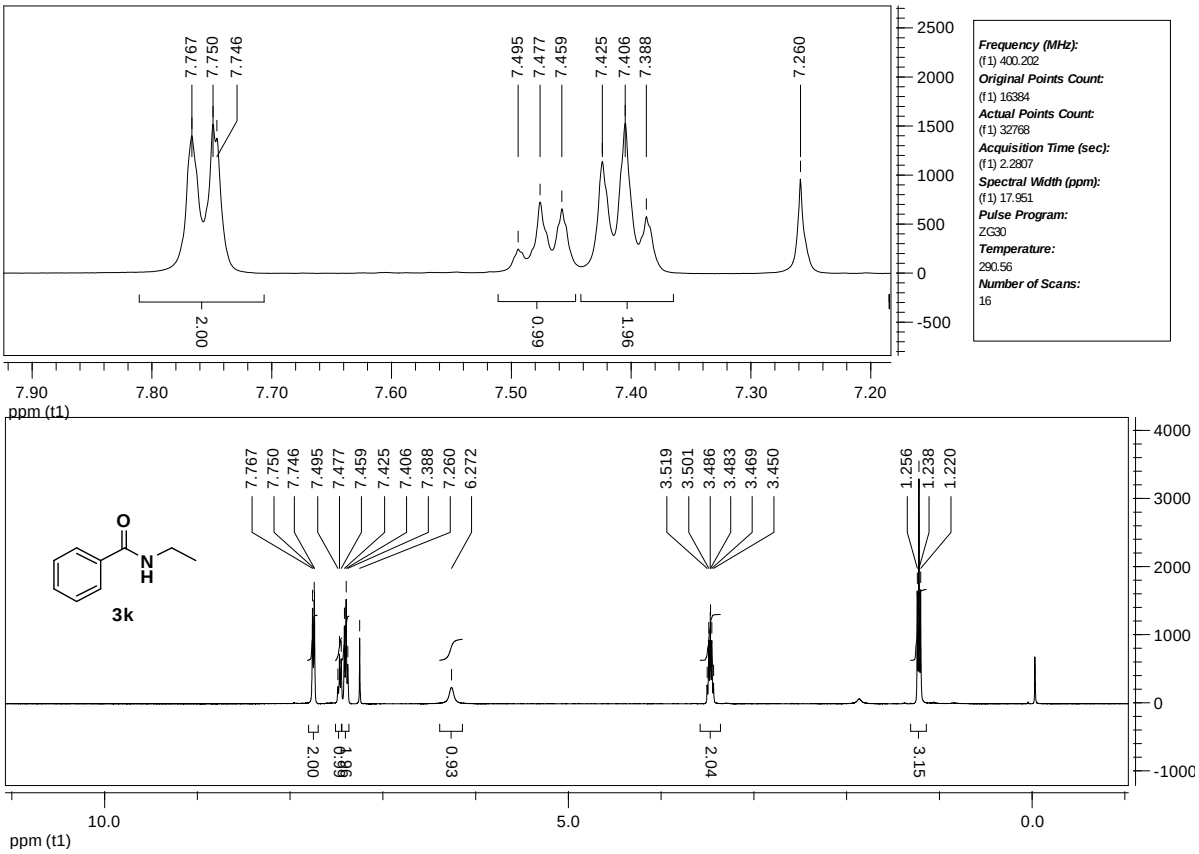
^{1}H NMR Spectrum for 3e



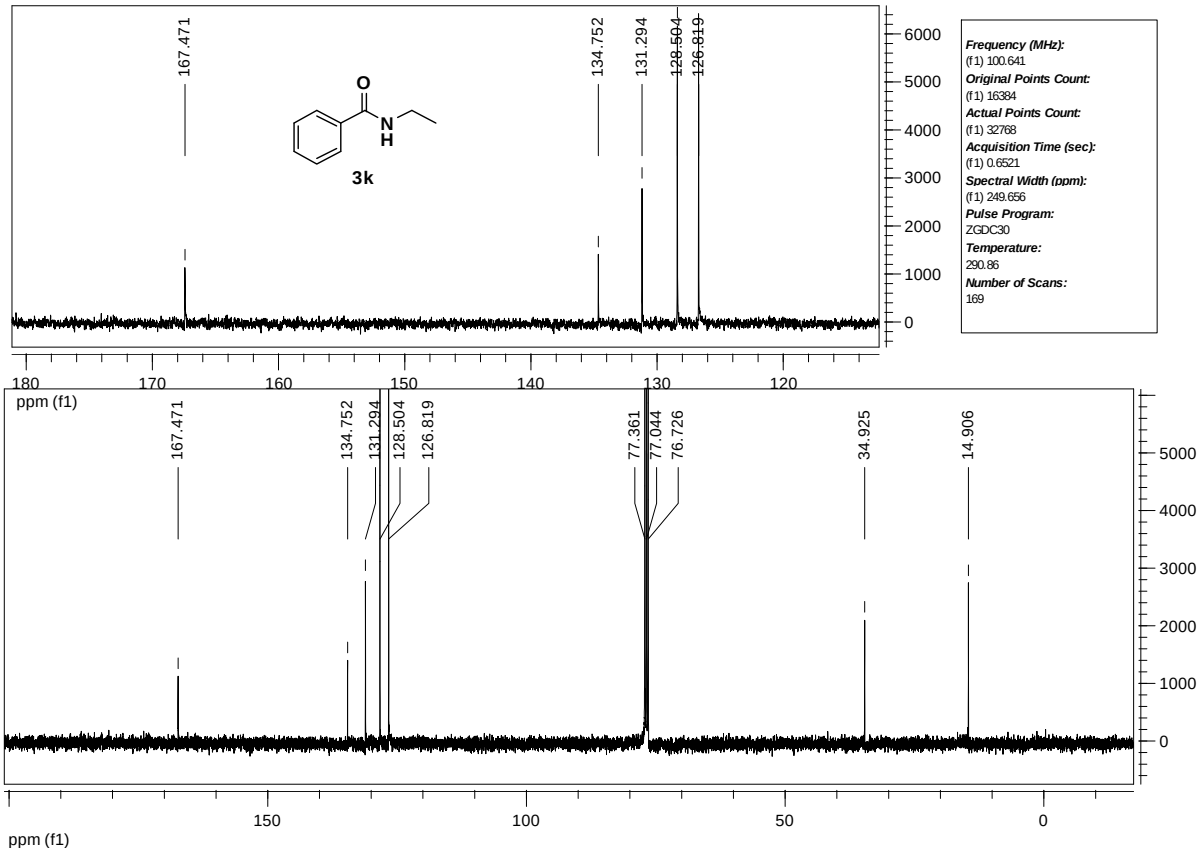
^{13}C NMR Spectrum for 3e



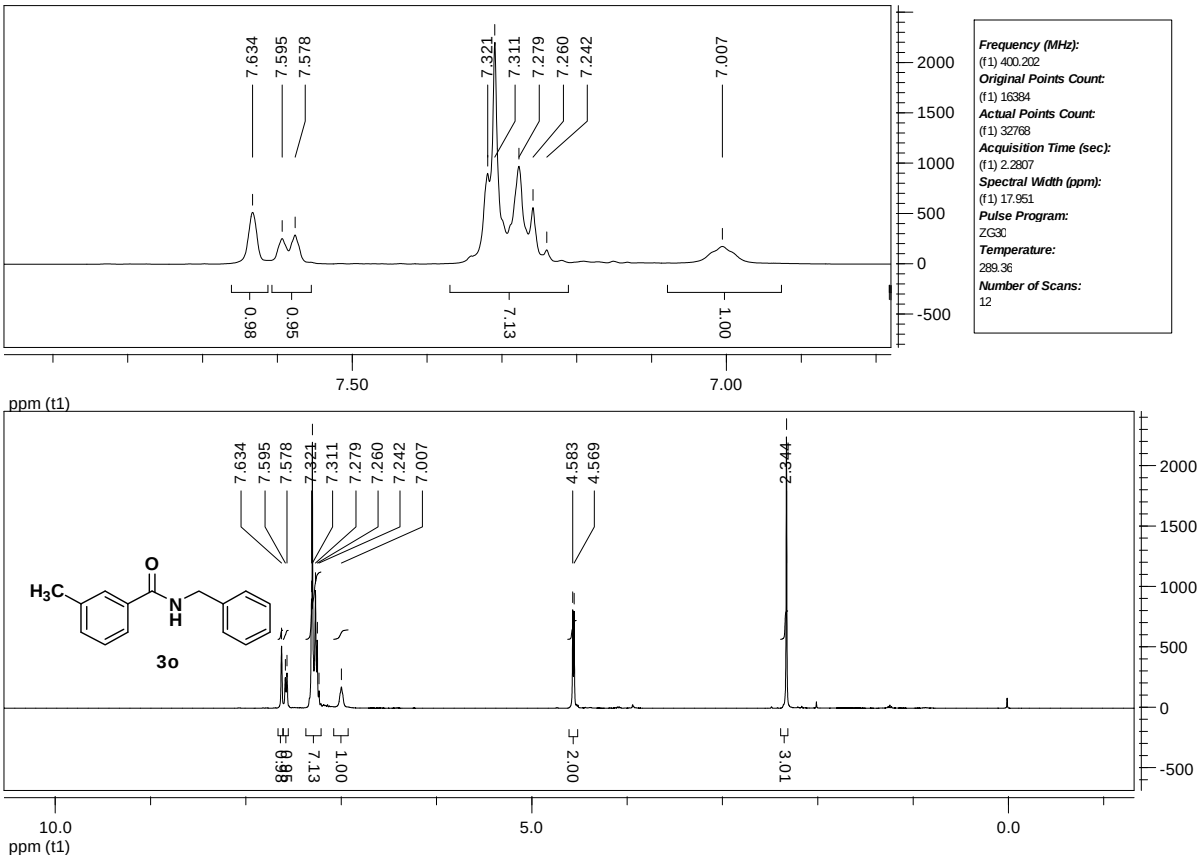
^{1}H NMR Spectrum for 3k



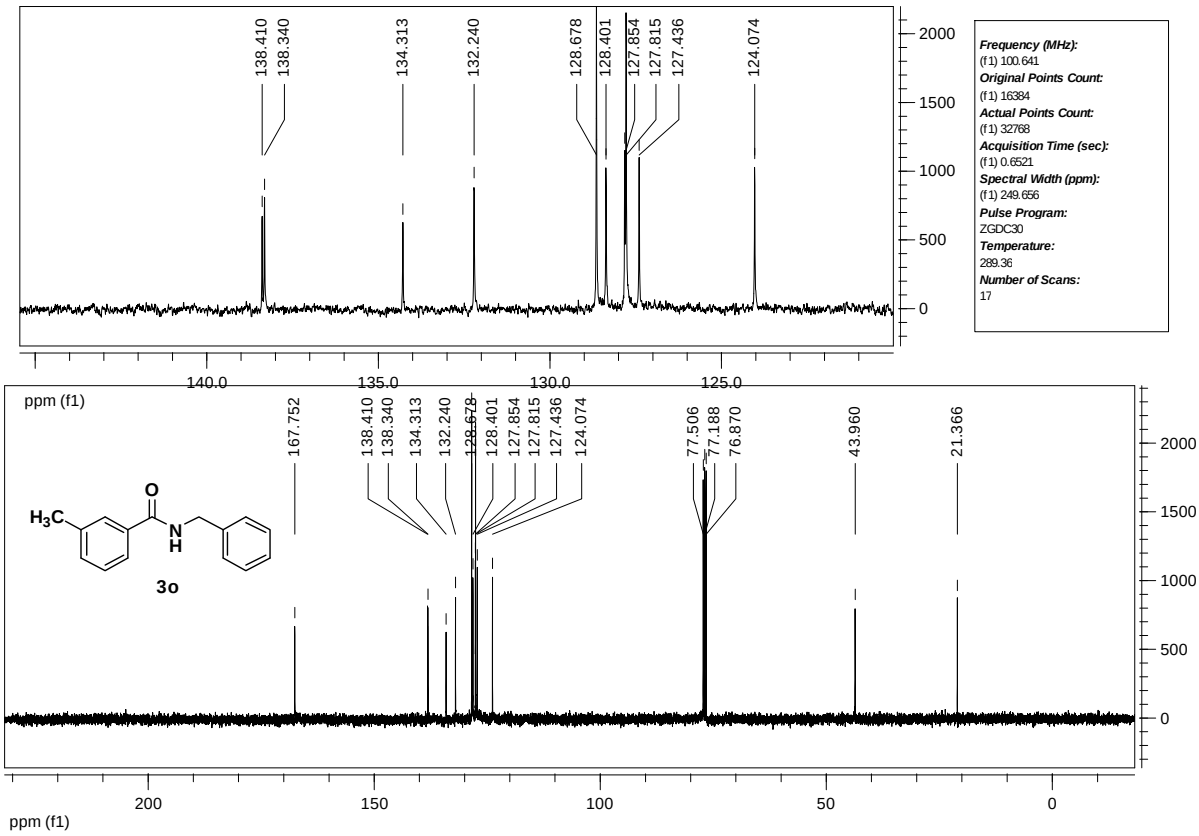
^{13}C NMR Spectrum for 3k



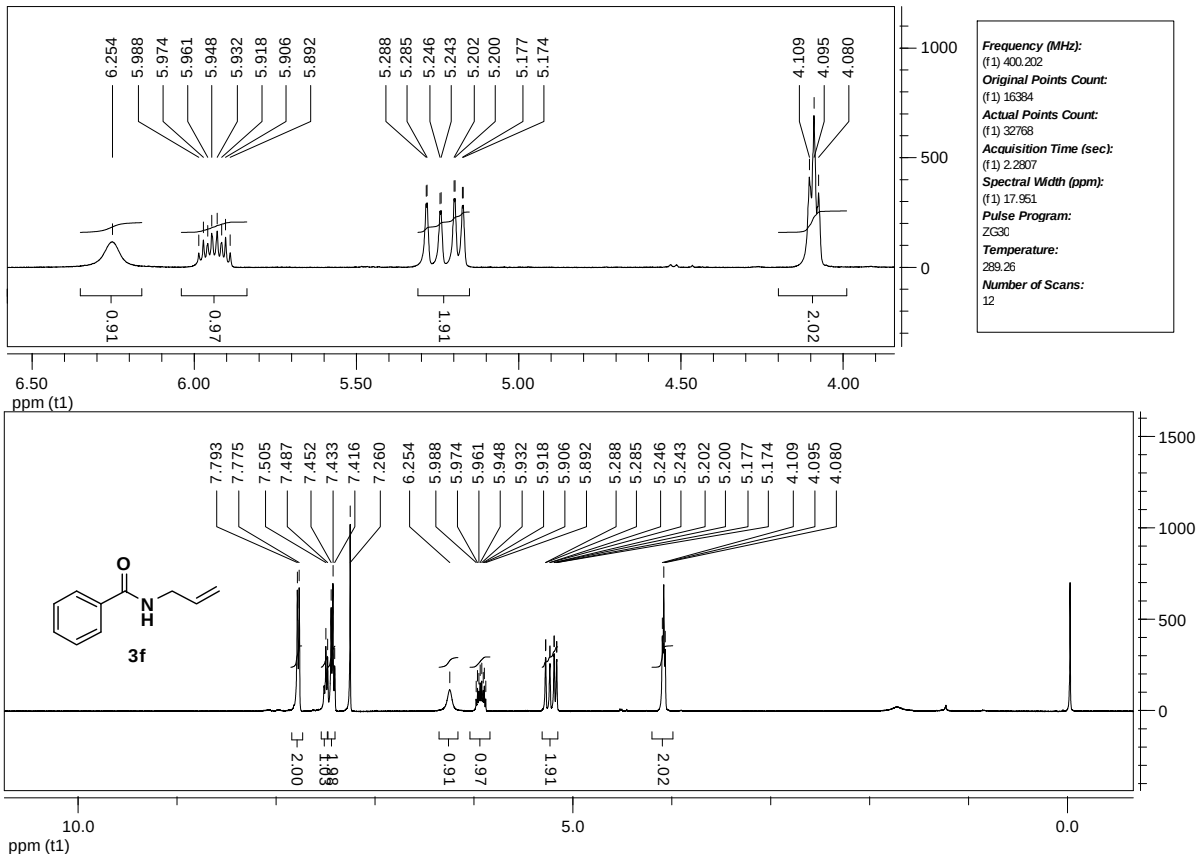
^{1}H NMR Spectrum for 3o



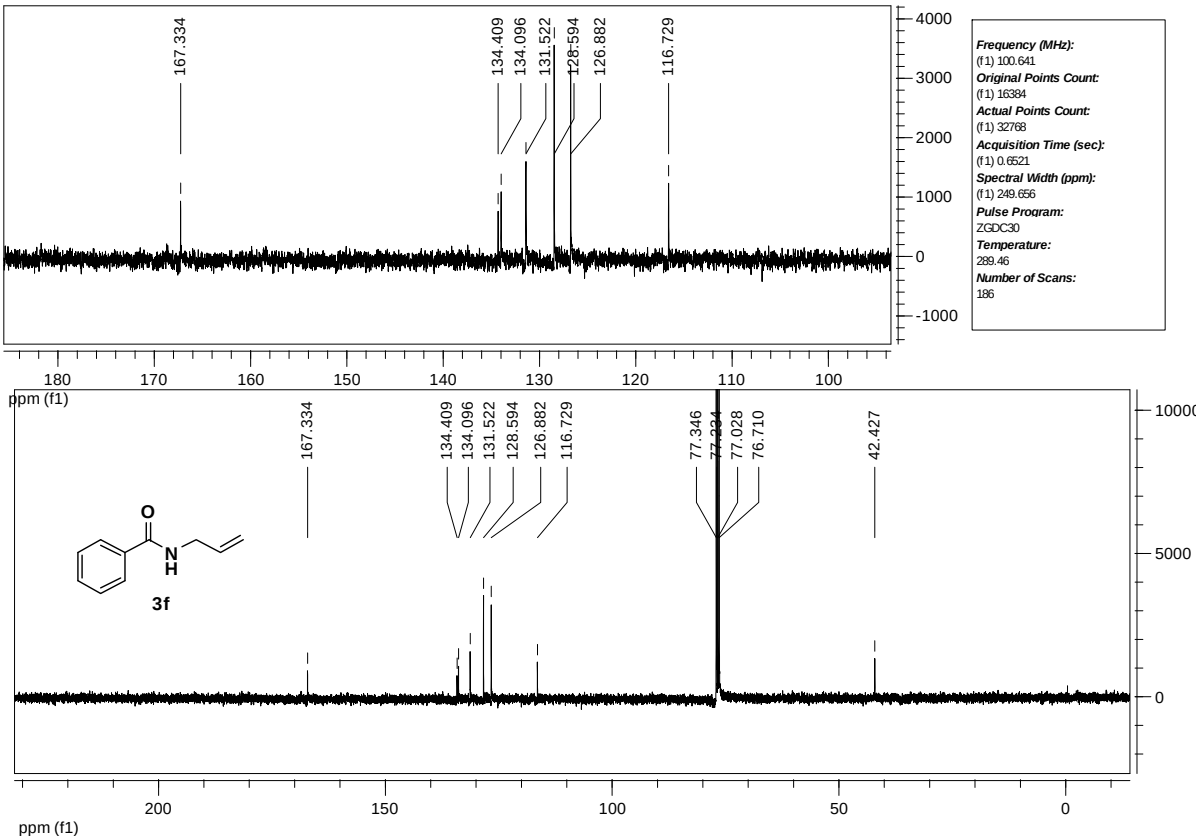
^{13}C NMR Spectrum for 3o



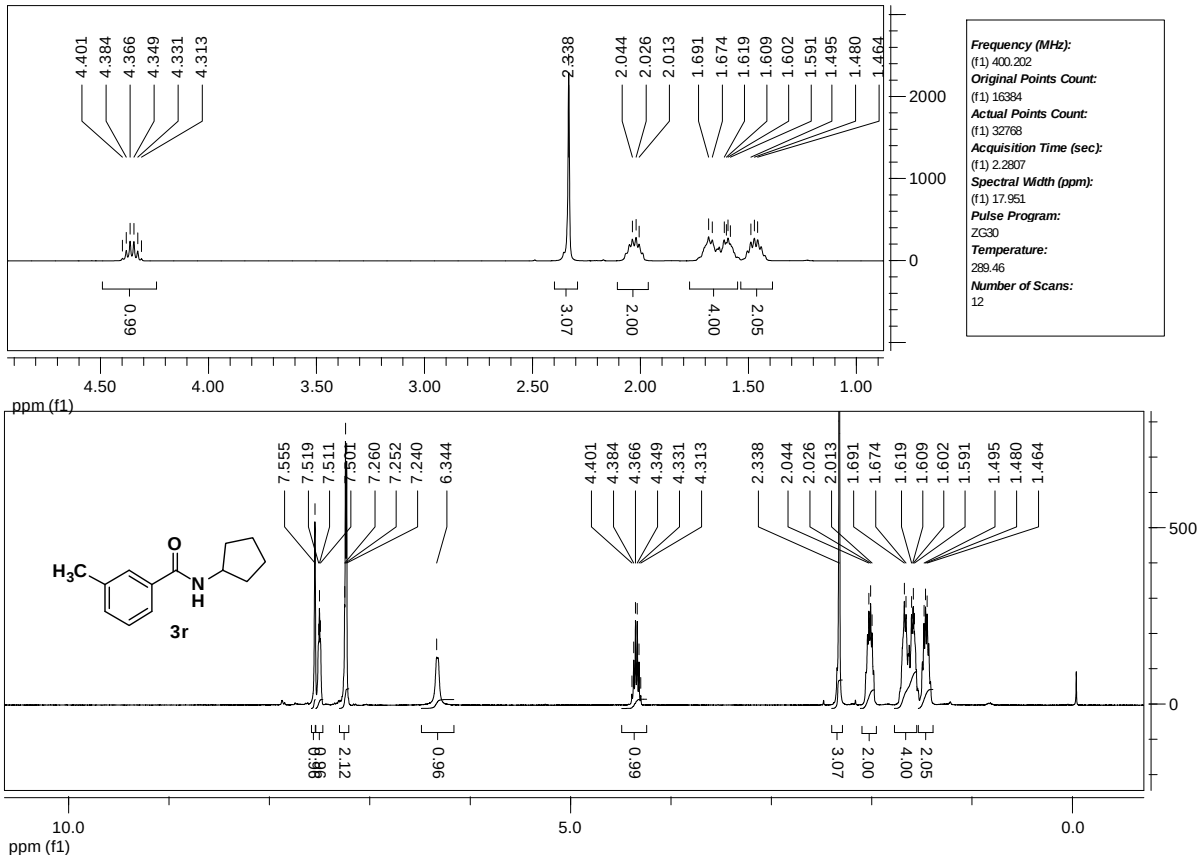
^{1}H NMR Spectrum for 3f



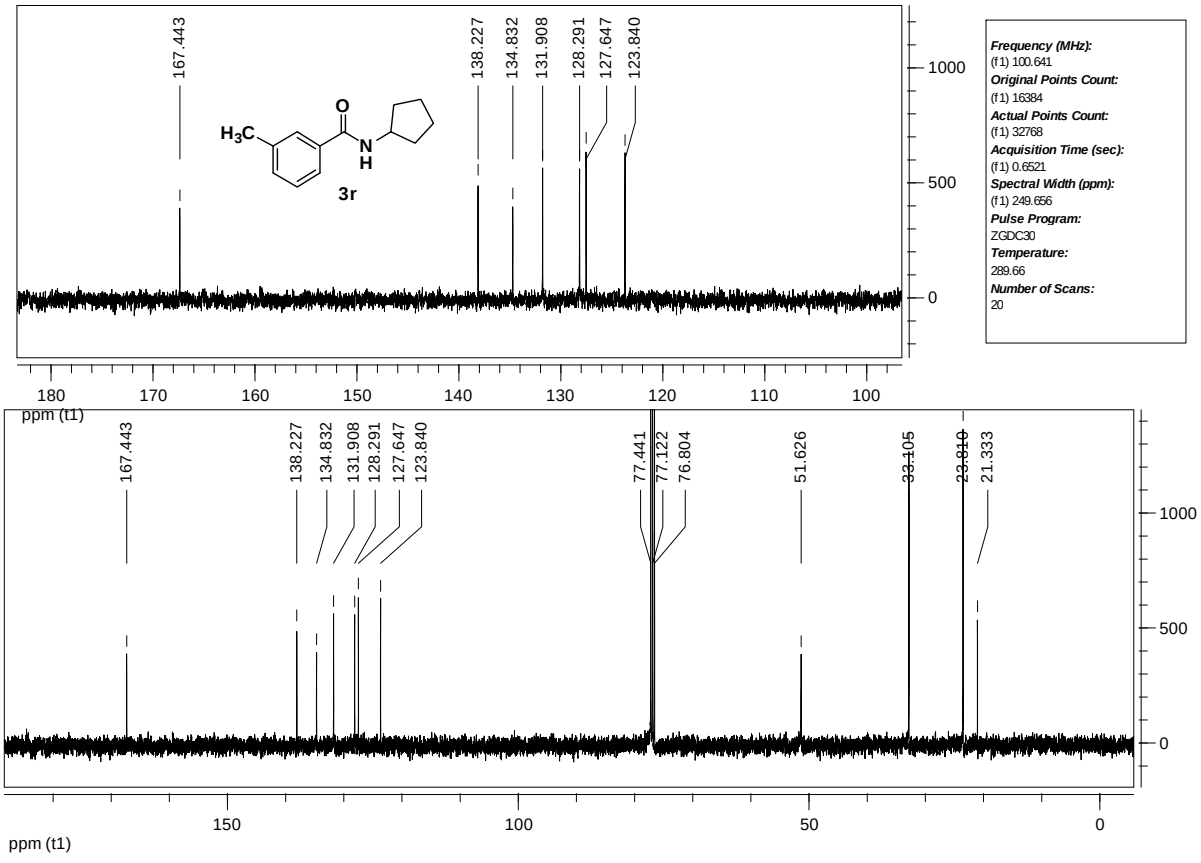
^{13}C NMR Spectrum for 3f



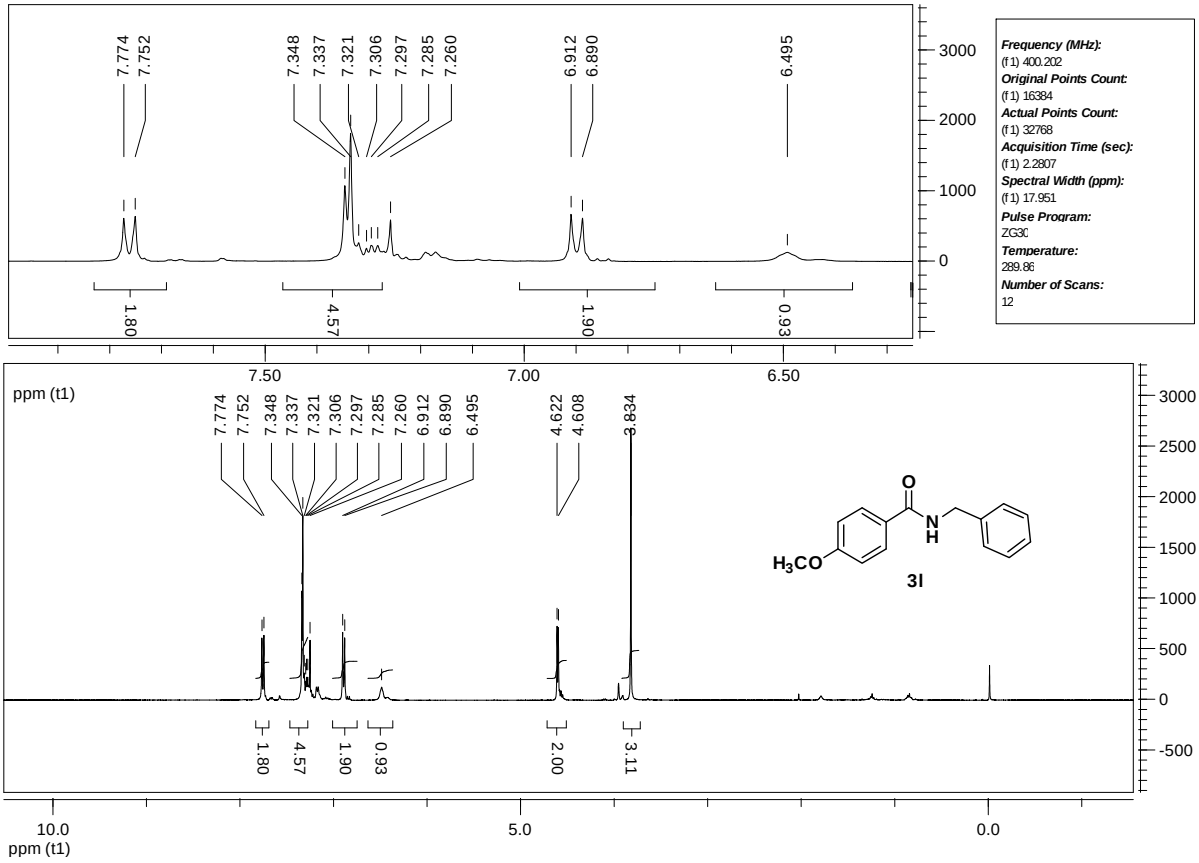
^{1}H NMR Spectrum for 3r



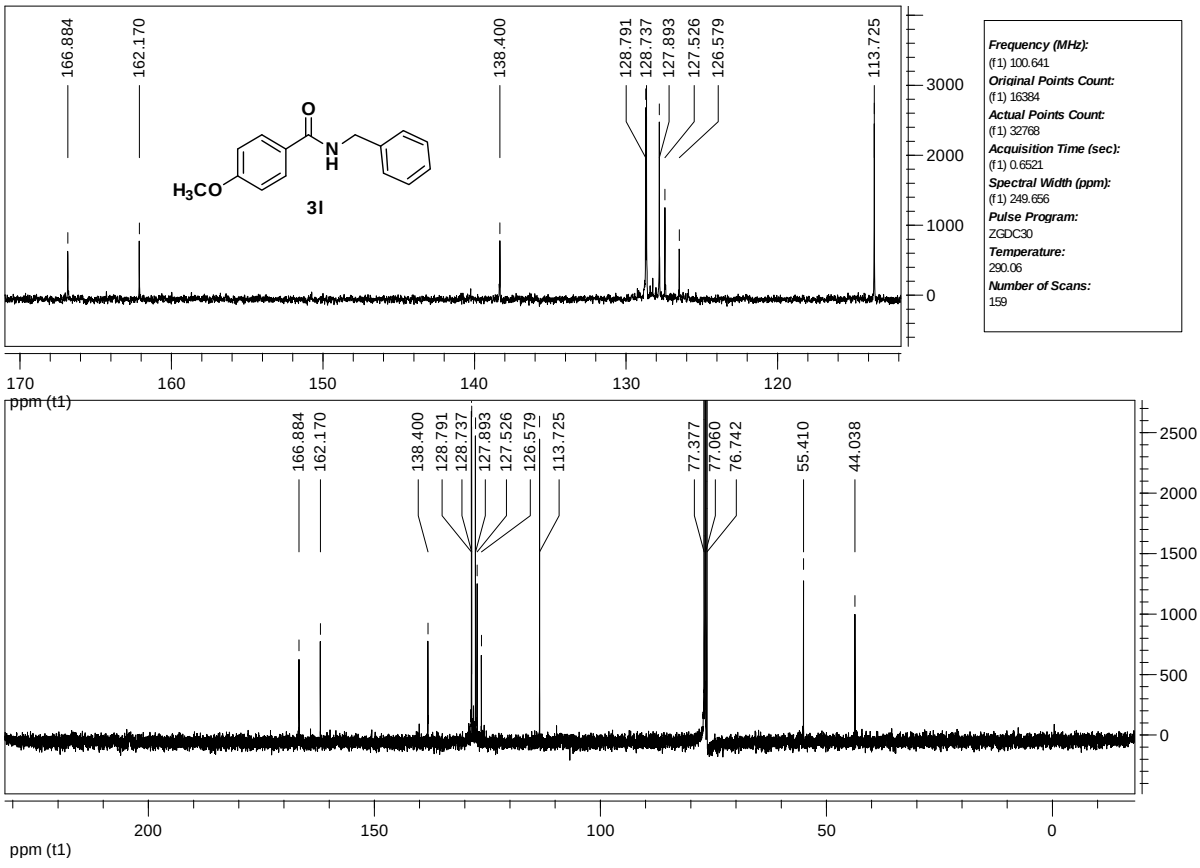
^{13}C NMR Spectrum for 3r



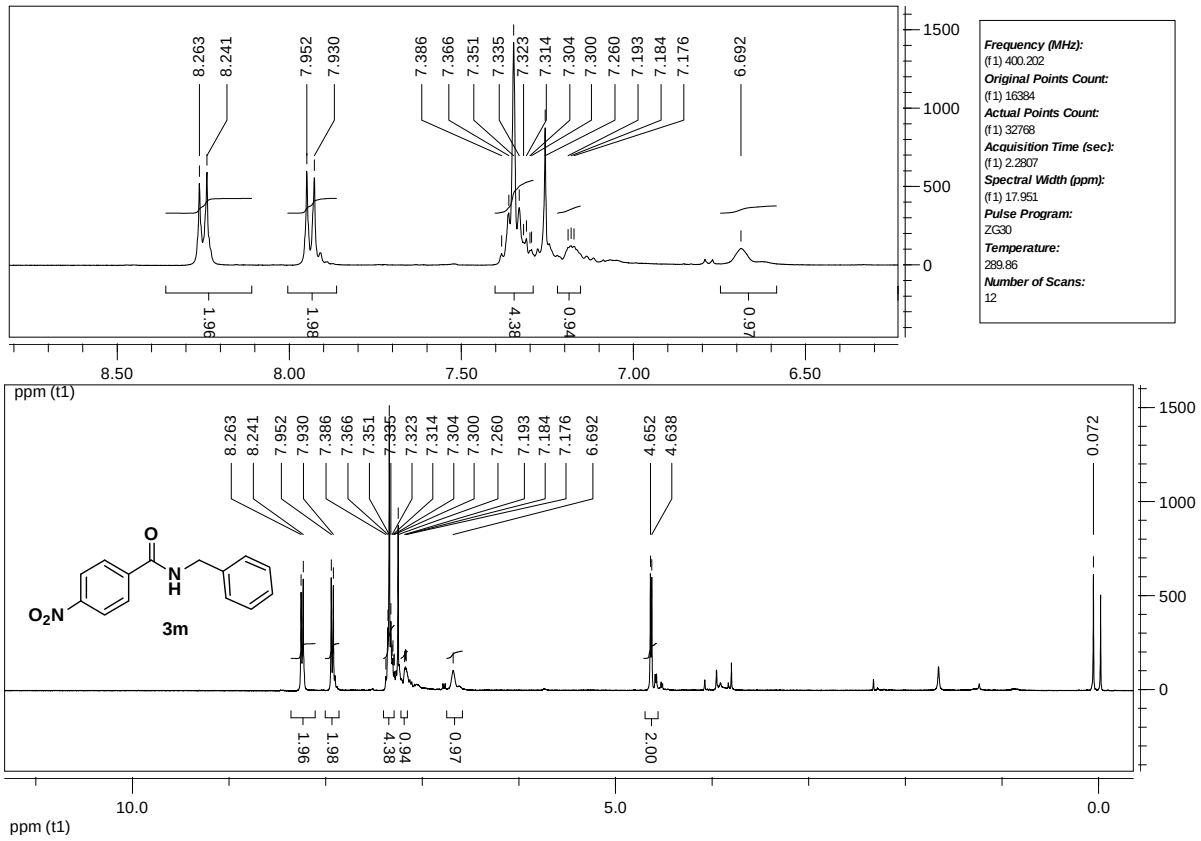
^{1}H NMR Spectrum for 3l



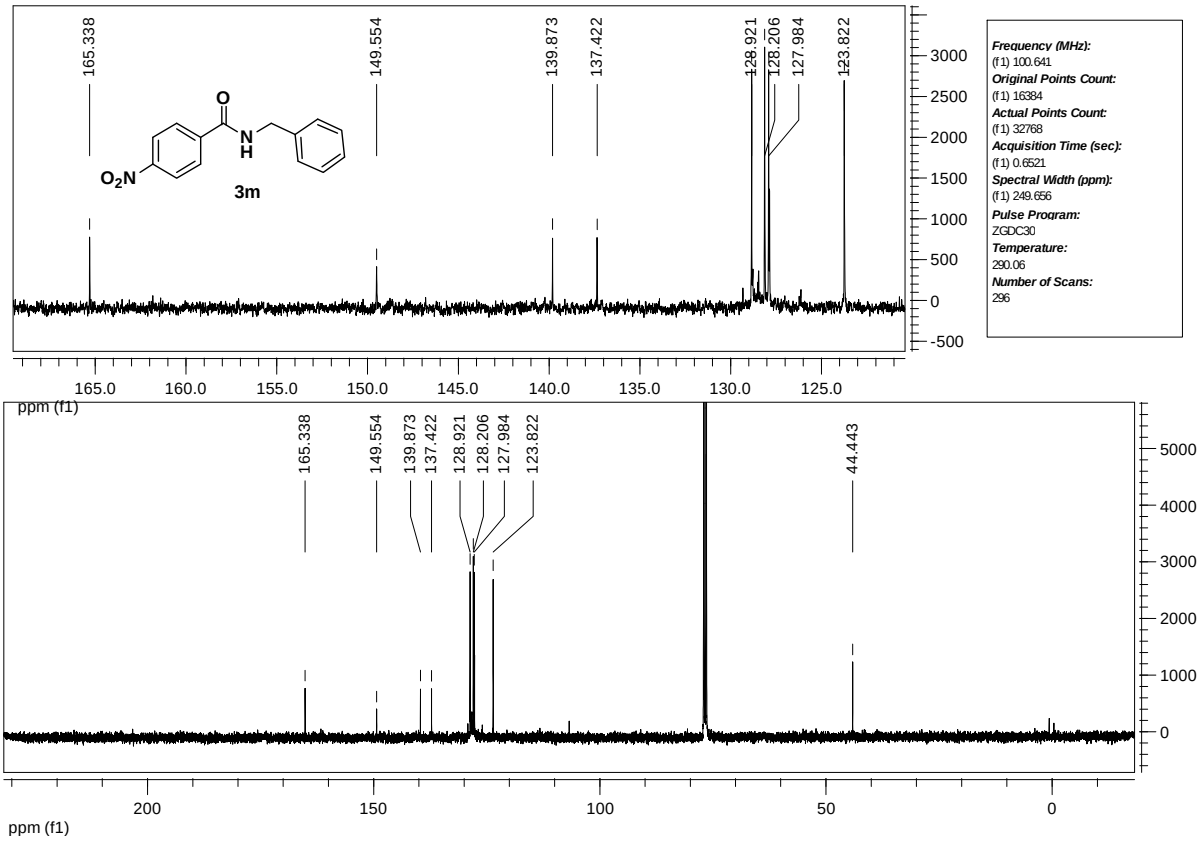
^{13}C NMR Spectrum for 3l



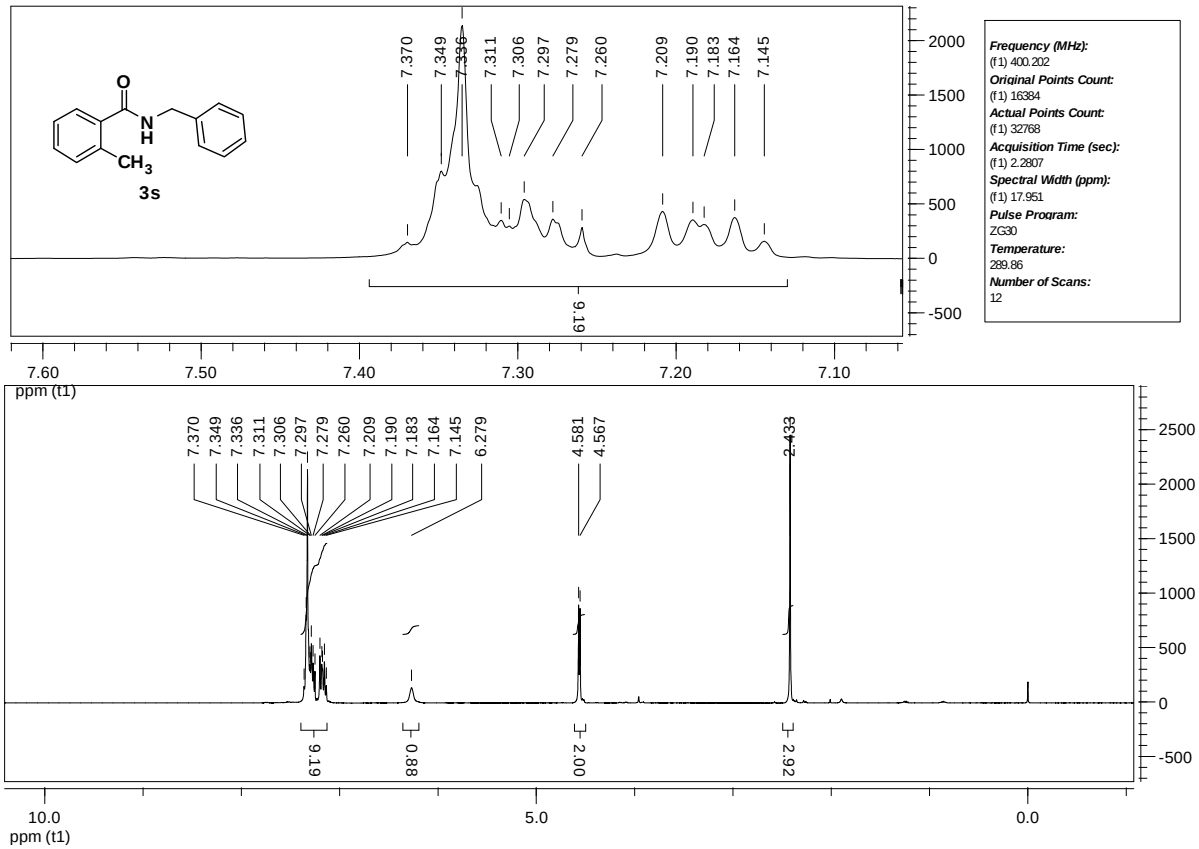
^{1}H NMR Spectrum for 3m



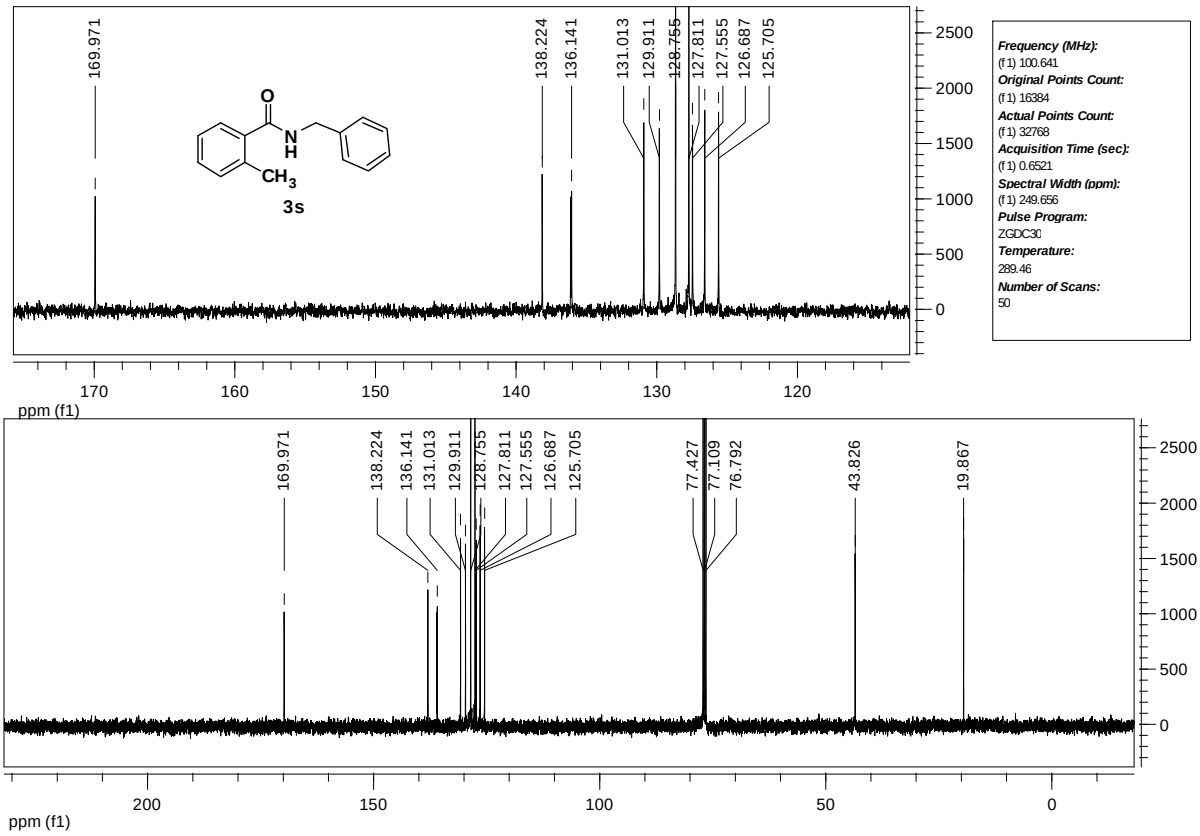
^{13}C NMR Spectrum for 3m



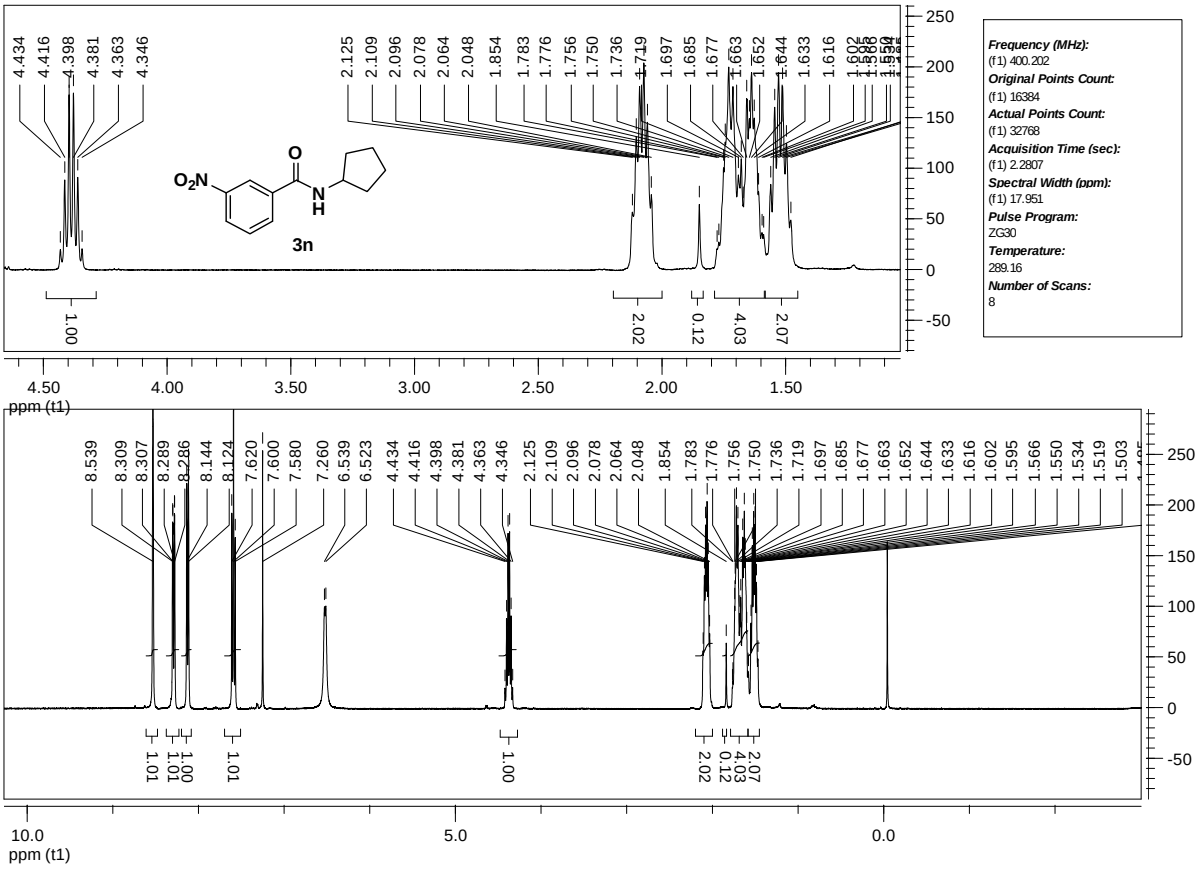
^{1}H NMR Spectrum for 3s



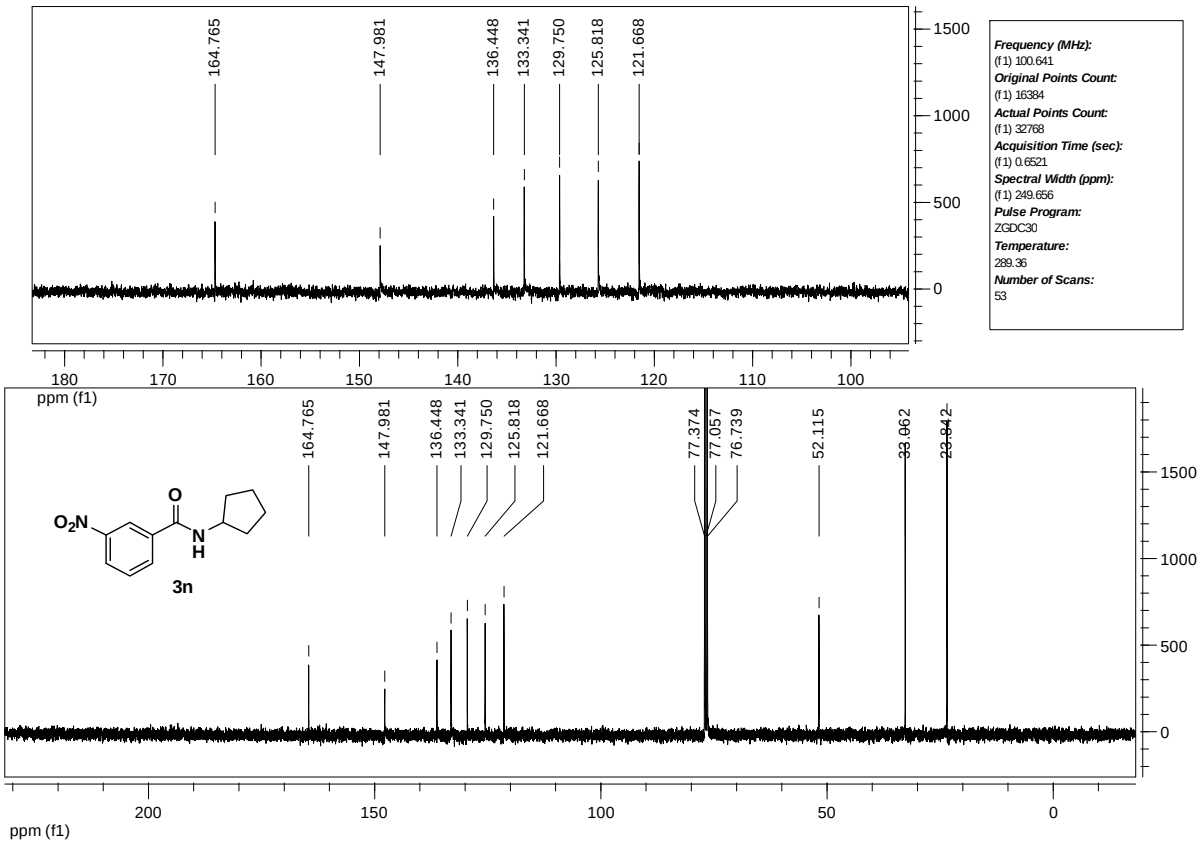
^{13}C NMR Spectrum for 3s



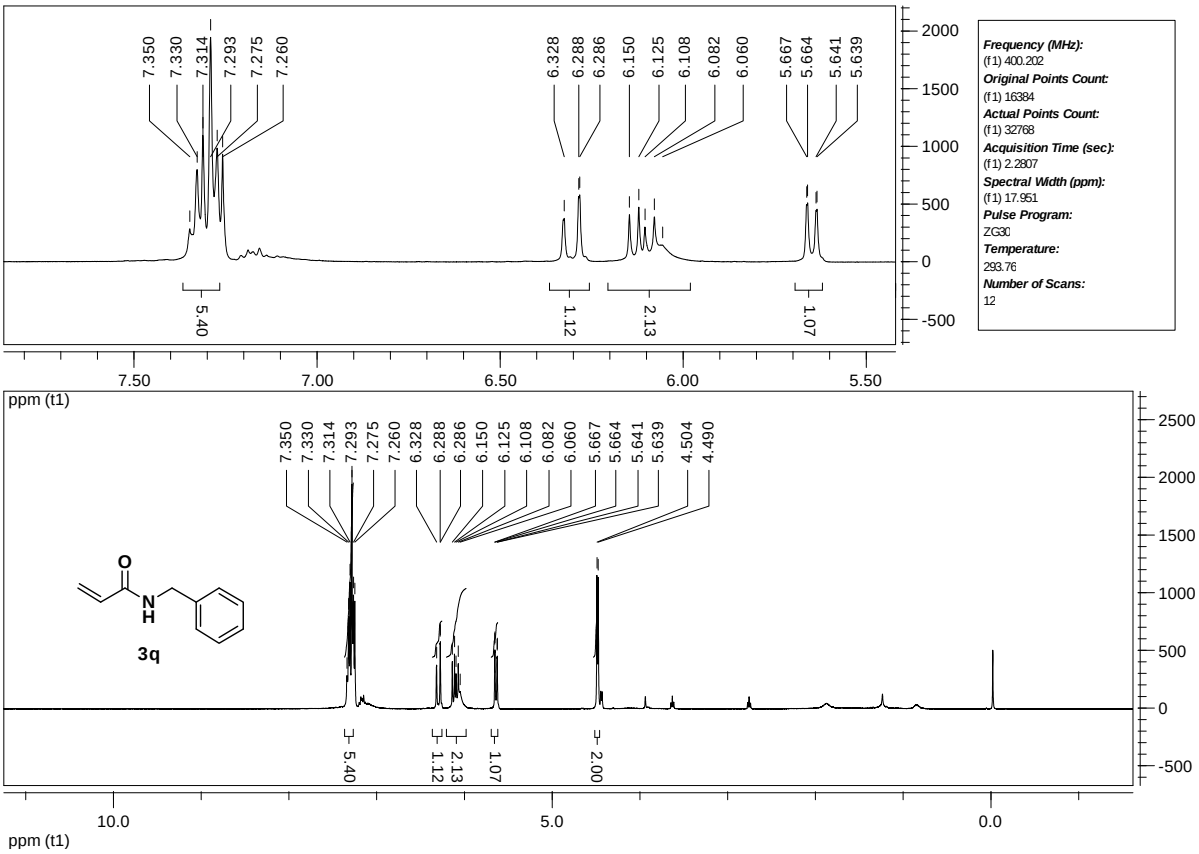
^{1}H NMR Spectrum for 3n



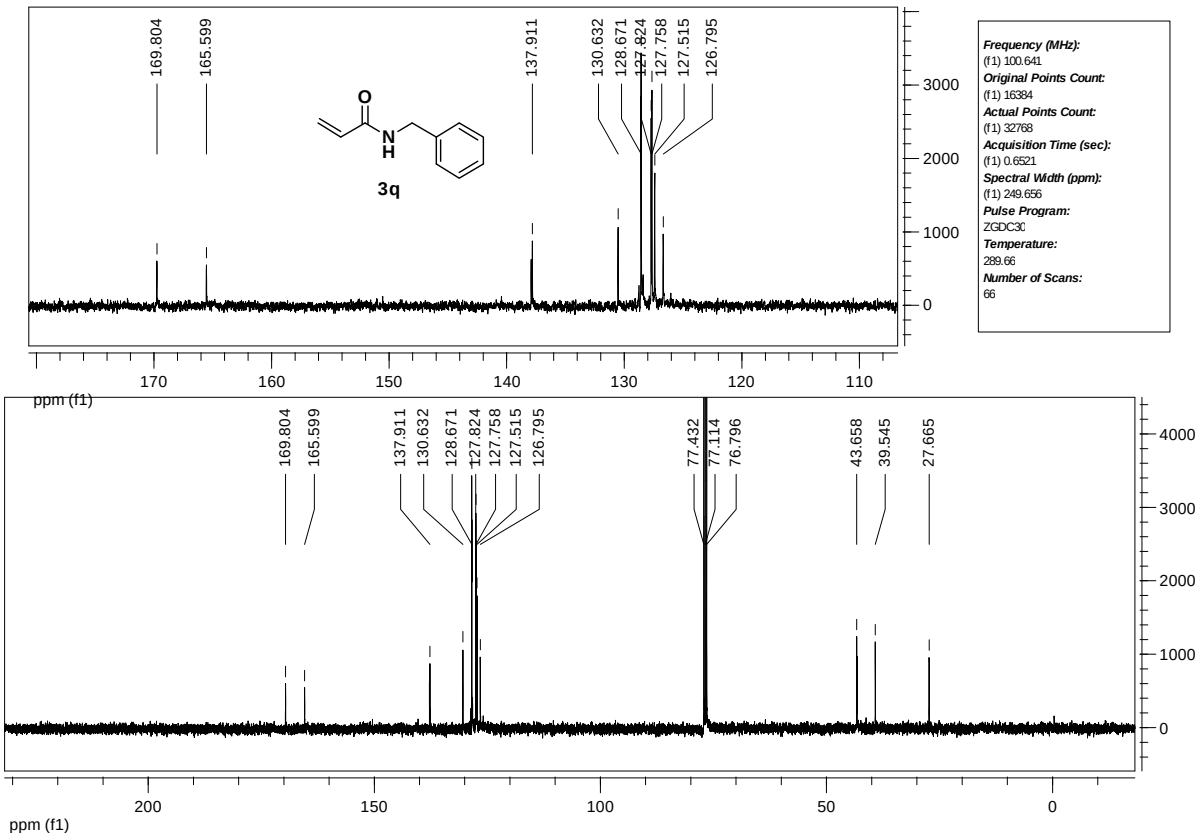
^{13}C NMR Spectrum for 3n



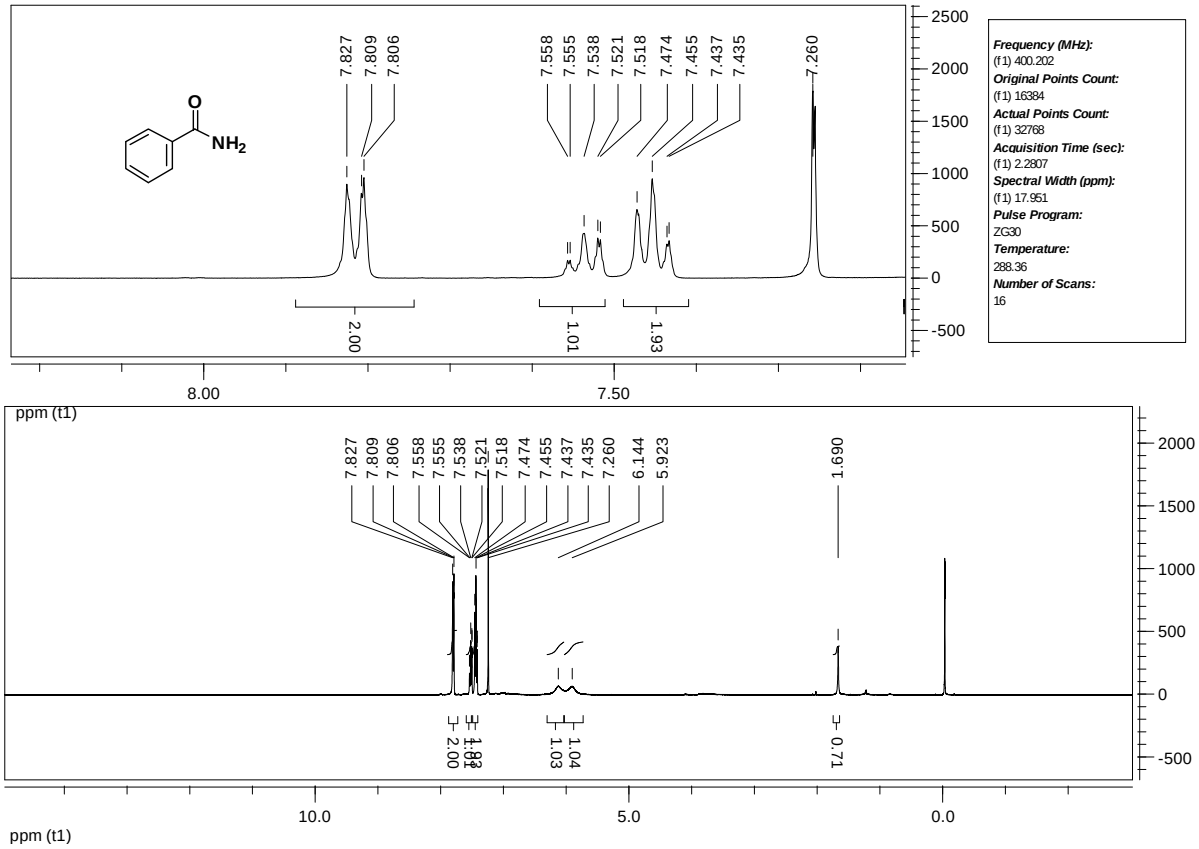
^{1}H NMR Spectrum for 3q



^{13}C NMR Spectrum for 3q



^{1}H NMR Spectrum for benzamide:



^{13}C NMR Spectrum for benzamide: