Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

tert-Butoxide Promoted One-Pot Azidation-Amindation of *para*-nitroanilines with aldehydes

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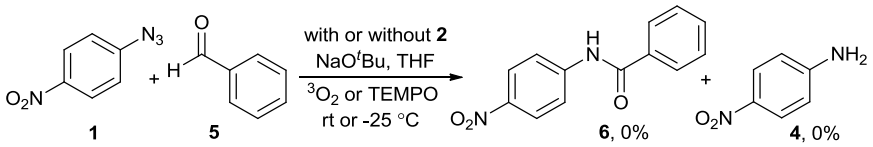
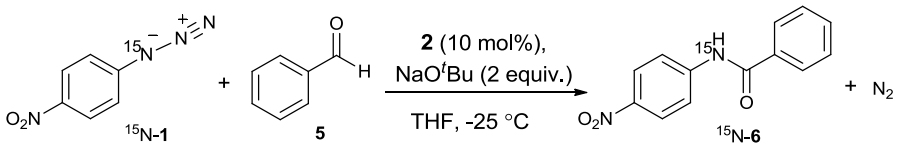
Schemes and Figures



Scheme S1 Evidence for an electron transfer process in the azido-amidation reaction of azide **1** as both $^3O_2$ and TEMPO radical shut down the reaction.



Scheme S2 Experiment carried out using ^{15}N-labelled *p*-nitroaniline ^{15}N-**1** showed retention of the labeled ^{15}N atom in the corresponding amide ^{15}N-**6**.

Materials and Methods

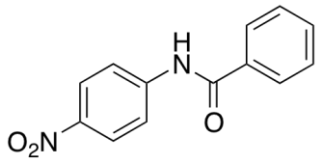
^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AV (III) 400, Bruker AV 400, Bruker DPX 400, AV 3500 (400MHz or 500 MHz (^{1}H), and 100 MHz or 125 MHz (^{13}C)) spectrometers. Chemical shifts are expressed in parts per million (ppm) and the spectra calibrated to residual solvent signals of DMSO (2.54 ppm (^{1}H) and 40.5 ppm (^{13}C)). Coupling constants are given in hertz (Hz) and the following notations indicate the multiplicity of the signals: s (singlet), d (doublet), brd (broad doublet), dd (double doublet), t (triplet), tt (triple triplet), q (quartet), m (multiplet). High Resolution Mass Spectra were recorded on a VG micron Autospec or Bruker microTOF. Fourier Transform Infrared Spectroscopy (FT-IR) spectra were obtained using a Perkin Elmer 1600 series or Bruker Tensor 27 spectrometer. Melting points were recorded using a STUART SMP3 apparatus and are uncorrected. Thin layer chromatography was carried out on Merck pre-coated silica gel plates (60F-254) and visualised using ultra violet light or $KMnO_4$ solution. THF was freshly distilled from sodium-benzophenone. Where necessary, reactions requiring anhydrous conditions were performed in dry solvents in flame dried or oven-dried apparatus under argon atmosphere.

Experimental Procedures

General procedure:

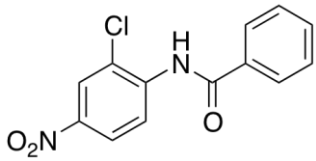
^{t}BuONO (0.53 mmol, 1.05 eq.) was added to a mixture of the aniline (0.50 mmol, 1.00 eq.) and $TMSN_3$ (0.53 mmol, 1.05 eq.) in THF (2 mL) at 0 ^{o}C. The mixture was stirred until deemed complete (TLC). Then, the solution was cooled to -25 ^{o}C at which temperature the aldehyde (0.75 mmol, 1.50 eq.), thiazolium salt **2** (0.05 mmol, 0.10 eq.) and NaO^{t}Bu (1.00 mmol, 2 eq.) were added sequentially. The resulting mixture was stirred until complete consumption of the azide (TLC). EtOAc (5 mL) and sat. $NaHSO_{3(aq)}$ (5 mL) were added and the layers separated. The organic layer was washed with $NaHSO_{3(aq)}$ (5 mL), 1 M $HCl_{(aq)}$ (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give the crude product. Purification of the crude residue by flash column chromatography on silica with [95:5:1-80:20:1 petrol:EtOAc:Et_3N] as eluent gave the corresponding amide.

***N*-(4-nitrophenyl)benzamide** (Table 2, Entry 1)



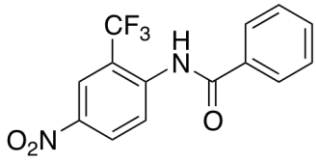
Yellow solid (0.139 g, 94 %); R_f (70:30 petrol-EtOAc) 0.3; mp 198-199 ˚C (lit.,[1] 199-201 ˚C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3431 (NH), 1692 (C=O), 1507 (NO_2), 1405, 1345, 1243, 1113; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.8 (s, 1H), 8.29–8.26 (m, 2H) 8.08–8.06 (m, 2H), 7.99–7.97 (m, 2H), 7.66–7.64 (m, 1H), 7.59–7.55 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5 (C), 145.7 (C), 142.7 (C), 134.2 (C), 132.4 (CH), 128.7 (CH), 128.1 (CH), 130.0 (CH), 120.9 (CH); ^{15}N NMR (100 MHz, DMSO-d_6) -248.5; HRMS ESI: calcd for $C_{13}H_{11}N_2O_3$ $[M+H]^+$, 243.0764; found, 243.0775; calcd for $C_{13}H_{10}NaN_2O_3$ $[M+Na]^+$, 265.0584; found 265.0588.

***N*-(3-chloro-4-nitrophenyl)benzamide** (Table 2, Entry 2)



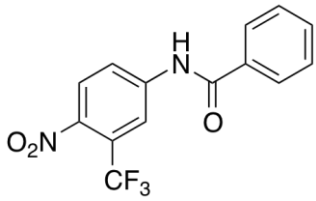
Yellow solid (0.117 g, 85%); R_f (70:30 petrol-EtOAc) 0.3; mp 160 ˚C (lit.,[2] 162-164 °C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3417 (NH), 1697 (C=O), 1511 (NO_2), 1398, 1345, 1253, 1121; ^1H NMR (400 MHz, DMSO-d_6) δ 10.3 (s, 1H), 8.42 (d, 1H, *J* = 2.6 Hz), 8.29 (dd, 1H, *J* = 8.9, 2.6 Hz), 8.26 (d, 1H, *J* = 8.9 Hz), 8.03–7.99 (m, 2H), 7.68–7.64 (m, 1H), 7.60–7.55 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5 (C), 145.0 (C), 141.3 (C), 133.4 (C), 132.4 (CH), 128.6 (CH), 128.1 (C), 127.9 (CH), 166.6 (CH), 124.9 (CH), 122.9 (CH); HRMS ESI: calcd for $C_{13}H_{10}ClN_2O_3$ $[M+H]^+$, 277.0374; found, 277.0373; calcd for $C_{13}H_9ClN_2NaO_3$ $[M+Na]^+$, 299.0194; found 299.0189.

***N*-(4-nitro-2-(trifluoromethyl)phenyl)benzamide** (Table 2, Entry 3)



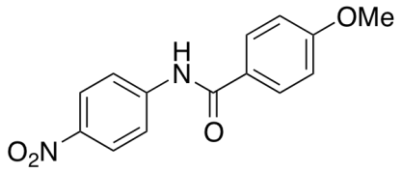
Yellow solid (0.119 g, 77%), R_f (70:30 petrol-EtOAc) 0.3; mp 158–161 ˚C; IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3414 (NH), 1707 (C=O), 1534 (NO_2), 1508 (NO_2), 1398, 1345, 1161, 1050; ^1H NMR (500 MHz, DMSO-d_6) δ 10.42 (s, 1H), 8.57 (dd, *J* = 8.8, 2.5 Hz, 1H), 8.52 (d, *J* = 2.5 Hz, 1H), 7.98–7.95 (m, 3H), 7.67–7.63 (m, 1H), 7.51–7.55 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.4 (C), 145.4 (C), 141.8 (C), 133.3 (C), 132.4 (CH), 131.8 (CH), 128.7 (CH), 128.0 (CH), 127.8 (CH), 126.3 (C, q, *J* = 33.1 Hz), 122.4 (CH); HRMS ESI: calcd for $C_{14}H_{10}F_3N_2O_3$ $[M+H]^+$, 311.0638; found, 311.0633; calcd for $C_{14}H_9F_3N_2NaO_3$ $[M+Na]^+$, 333.0457; found 333.0453.

***N*-(4-nitro-3-(trifluoromethyl)phenyl)benzamide** (Table 2, Entry 4)



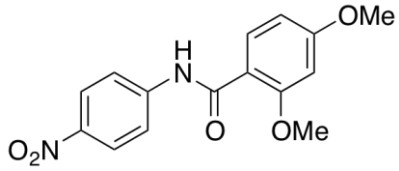
Yellow solid (0.130 g, 84%); R_f (70:30 petrol-EtOAc) 0.3; mp 129–131 ˚C (lit.,[3] 129 °C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3431 (NH), 1694 (C=O), 1520 (NO_2), 1415, 1322, 1250 (CF), 1163 (CF); ^1H NMR (500 MHz, DMSO-d_6) δ 11.0 (s, 1H), 8.49 (d, J = 2.2 Hz, 1H), 8.35 (dd, J = 9.0, 2.2 Hz, 1H), 8.26 (d, J = 9.0 Hz, 1H), 8.02–7.99 (m, 2H), 7.66–7.64 (m, 1H), 7.60–7.57 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) 170.0 (C), 144.4 (C), 142.1 (C), 134.2 (C), 133.0 (C), 129.7 (CH), 129.1 (CH), 128.4 (CH), 128.1 (CH), 123.7 (CH), 123.2 (C, q, J = 33.2 Hz), 118.8 (CH); HRMS ESI: calcd for $C_{14}H_9F_3N_2NaO_3$ $[M+Na]^+$, 333.0457; found 333.0450.

Methoxy-*N*-(4-nitrophenyl)benzamide (Table 2, Entry 5)



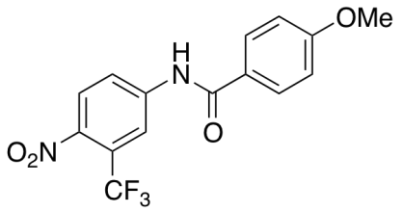
Yellow solid (0.124 g, 91 %); R_f (70:30 petrol-EtOAc) 0.3; mp 183-185 ˚C (lit.,[4] 184–185 °C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3435 (NH), 1685 (C=O), 1504 (NO_2), 1345, 1240, 1113, 1030; ^1H NMR (400 MHz, DMSO-d_6) δ 10.6 (s, 1H), 8.26–8.24 (m, 2H) 8.07–8.04 (m, 2H), 8.01–7.98 (m, 2H), 7.11–7.08 (m, 2H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9 (C), 162.8 (C), 146.2 (C), 142.7 (C), 130.4 (CH), 126.5 (C), 125.2 (CH), 120.1 (CH), 114.2 (CH), 55.9 (CH_3); HRMS ESI: calcd for $C_{14}H_{13}N_2O_4$ $[M+H]^+$, 273.0870; found, 273.0869; calcd for $C_{14}H_{12}NaN_2O_4$ $[M+Na]^+$, 295.0689; found 295.0689.

3,5-Dimethoxy-*N*-(4-nitrophenyl)benzamide (Table 2, Entry 6)



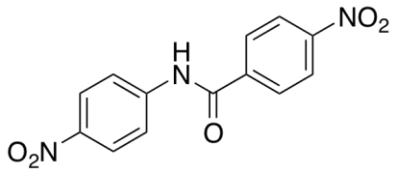
Yellow solid (0.119 g, 79%), R_f (70:30 petrol-EtOAc) 0.2; mp 198-199˚C; IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3356 (NH), 1674 (C=O), 1604, 1548 (NO_2), 1342, 1249, 1027; ^1H NMR (400 MHz, DMSO-d_6) δ 10.45 (s, 1H), 8.26–8.22 (m, 2H), 8.01-7.98 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 2.3 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.3 1H), 3.94 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5 (C), 163.4 (C), 158.5 (C), 145.2 (C), 142.2 (C), 132.0 (CH), 124.9 (CH), 119.4 (CH), 115.8 (C), 105.9 (CH), 95.6 (CH), 56.7 (CH_3), 56.1 (CH_3); HRMS ESI: calcd for $C_{15}H_{15}N_2O_5$ $[M+H]^+$, 303.0975; found, 303.0973; calcd for $C_{15}H_{14}N_2NaO_5$ $[M+Na]^+$, 325.0795; found 325.0792.

4-Methoxy-N-(4-nitro-3-(trifluoromethyl)phenyl)benzamide (Table 2, Entry 7)



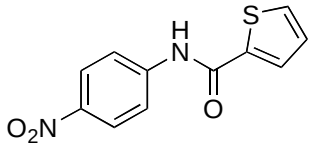
Yellow solid (0.138 g, 89%); R_f (70:30 petrol-EtOAc) 0.3; mp 110–113 ˚C (lit.,[3] 112–114 ^oC); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3436 (NH), 1686 (C=O), 1508 (NO_2), 1250 (CF), 1175 (CF), 1097, 1030; ^1H NMR (500 MHz, DMSO-d_6) δ 10.80 (s, 1H), 8.48 (d, *J* = 2.3 Hz, 1H), 8.35 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.02–7.99 (m, 2H), 7.12–7.10 (m, 2H), 3.32 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.7 (C), 162.7 (C), 144.3 (C), 141.4 (C), 130.1 (CH), 127.7 (CH), 125.6 (C), 123.0 (CH), 122.5 (C, q, *J* = 33.2 Hz), 121.1 (C), 118.2 (CH), 133.9 (CH), 55.6 (CH_3); HRMS ESI: calcd for $C_{15}H_{12}F_3N_2O_4$ $[M+H]^+$, 341.0744; found, 341.0743; calcd for $C_{15}H_{11}F_3N_2NaO_4$ $[M+Na]^+$, 363.0563; found 363.0568.

4-Nitro-*N*-(4-nitrophenyl) benzamide (Table 2, Entry 8)



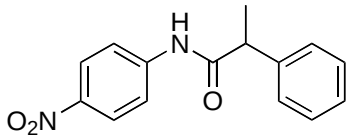
Yellow solid (0.052 g, 38%), R_f (70:30 petrol-EtOAc) 0.2; mp 266-270 ˚C (lit.,[5] 267-269 ^{o}C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3693 (NH), 1600 (C=O), 1530 (NO_2), 1511 (NO_2), 1346, 1241, 1113; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.11 (s, 1H), 8.42–8.41 (m, 2H), 8.39–8.38 (m, 2H), 8.23–8.22 (m, 2H), 8.09–8.05 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) 165.2 (C), 149.0 (C), 145.5 (C), 143.3 (C), 140,4 (C), 130.0 (CH), 125.4 (CH), 124.1 (CH), 120.6 (CH); HRMS ESI: calcd for $C_{13}H_{10}N_3O_5$ $[M+H]^+$, 288.2351; found, 288.9213; calcd for $C_{13}H_9N_3NaO_5$ $[M+Na]^+$, 310.2169; found 310.0425.

***N*-(4-nitrophenyl)thiophene-2-carboxamide** (Table 2, Entry 9)



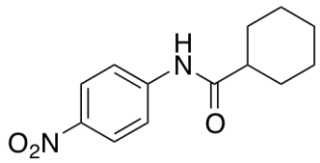
Yellow solid (0.102 g, 82%), R_f (70:30 petrol:EtOAc) 0.3; mp 221-223 ˚C (lit.,[6] 222-224 ^{o}C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3430 (NH), 1673 (amide), 1600, 1506 (NO_2), 1344, 1245, 1113; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.75 (s, 1H), 8.29–8.25 (m, 2H), 8.10 (dd, J = 3.8, 1.1 Hz, 1H), 8.04–8.00 (m, 2H), 7.95 (dd, J = 5.0, 1.1 Hz, 1H), 7.27 (dd, J = 5.0, 3.8 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.5 (C), 145.2 (C), 142.5 (C), 139.1 (C), 133.1 (CH), 130.3 (CH), 128.3 (CH), 124.9 (CH), 119.8 (CH); HRMS ESI: calcd for $C_{11}H_9N_2O_3S$ $[M+H]^+$, 249.0328; found, 249.0315; calcd for $C_{11}H_8N_2NaO_3S$ $[M+Na]^+$, 271.0148; found 271.0140.

***N*-(4-nitrophenyl)-2-phenylpropanamide** (Table 2, Entry 10)



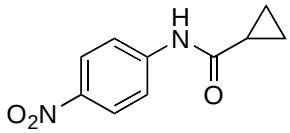
Yellow solid (0.127 g, 94%), R_f (70:30 petrol:EtOAc) 0.3; mp 168–169 ˚C; IR (FTIR, $CHCl_3$) ν_{max} cm $^{-1}$: 3401 (NH), 1702 (C=O), 1599, 1533 (NO_2), 1506 (NO_2), 1344, 1249, 1177, 1114; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.65 (s, 1H), 8.22–8.18 (m, 2H), 7.86–7.82 (m, 2H), 7.40–7.32 (m, 4H), 7.26–7.22 (m, 1H), 3.89 (q, *J* =7.0 Hz, 1H), 1.43 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2 (C), 145.3 (C), 142.1 (C), 141.2 (C), 128.5 (CH), 127.3 (CH), 126.9 (CH), 124.9 (CH), 118.9 (CH), 46.2 (CH), 18.6 (CH_3); HRMS ESI: calcd for $C_{15}H_{15}N_2O_3$ $[M+H]^+$, 271.1077; found, 271.1070; calcd for $C_{15}H_{14}N_2NaO_3$ $[M+Na]^+$, 293.0897; found 293.0901.

***N*-(4-nitrophenyl)cyclohexanecarboxamide** (Table 2, Entry 11)



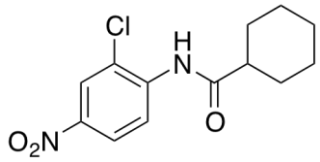
Colourless solid (0.109 g, 88%); R_f (70:30 petrol-EtOAc) 0.4; mp 160–163 ˚C (lit.,[7] 162-163 ^{o}C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3429 (NH), 1702 (C=O)), 1505 (NO_2), 1345, 1246, 1163, 1114; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.4 (s, 1H), 8.21–8.17 (m, 2H), 7.86–7.83 (m, 2H), 2.83 (tt, *J* = 11.5, 3.5 Hz, 1H), 1.84–1.81 (m, 2H), 1.78– 1.74 (m, 2H), 1.66–1.64 (m, 1H), 1.45–1.16 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.2 (C), 145.7 (C), 141.9 (C), 124.9 (CH), 118.6 (CH), 44.9 (CH), 28.9 (CH_2), 25.3 (CH_2), 25.1 (CH_2); HRMS ESI: calcd for $C_{13}H_{16}NaN_2O_3$ $[M+Na]^+$, 271.1053; found 271.1055.

***N*-(4-nitrophenyl)cyclopropanecarboxamide** (Table 2, Entry 12)[9]



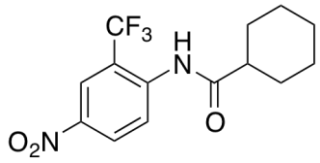
Yellow solid (0.102 g, 78%), R_f (70:30 petrol:EtOAc) 0.4; mp 145-147 ˚C (lit.,[8] 183-185 ^{o}C); IR (FTIR, $CHCl_3$) ν_{max} cm $^{-1}$: 3430 (NH), 1701 (C=O), 1507 (NO_2), 1343 (NO_2), 1159, 1035, 953, 853; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.81 (s, 1H), 8.22–8.18 (m, 2H), 7.85–7.81 (m, 2H), 2.50 (app quintet, J = 1.8 Hz, 1H), 0.88–0.86 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.7 (C), 144.4 (C), 141.9 (C), 125.0 (CH), 118.6 (CH), 14.8 (CH), 7.9 (CH_2); HRMS ESI: calcd for $C_{10}H_{10}N_2NaO_3$ $[M+Na]^+$, 229.0584; found, 229.0581.

***N*-(2-chloro-4-nitrophenyl)cyclohexanecarboxamide** (Table 2, Entry 13)



Colourless solid (0.130 g, 92%); R_f (70:30 petrol-EtOAc) 0.4; mp 156-158 ˚C; IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3692 (NH), 1619 (C=O), 1524 (NO_2), 1443, 1241, 1025, 930; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.69 (s, 1H), 8.34–8.34 (m, 1H), 8.19–8.19 (m, 2H), 2.64 (tt, J = 11.4, 3.4 Hz, 1H), 1.86–1.83 (m, 2H), 1.76–1.74 (m, 2H), 1.67 – 1.64 (m, 1H), 1.45–1.16 (m, 5H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.2 (C), 143.1 (C), 141.3 (C), 124.9 (CH), 124.8 (C), 124.1 (CH), 123.0 (CH), 44.1 (CH), 29.1 (CH_2), 25.3 (CH_2), 25.1 (CH_2); HRMS ESI: calcd for $C_{13}H_{16}ClN_2O_3$ $[M+H]^+$, 283.0844; found, 283.0834; calcd for $C_{13}H_{15}ClN_2NaO_3$ $[M+Na]^+$, 305.0663; found 305.0653.

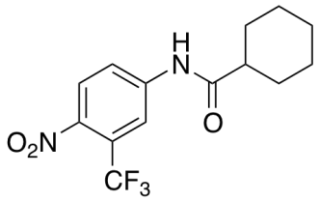
***N*-(4-nitro-2-(trifluoromethyl)phenyl)cyclohexanecarboxamide** (Table 2, Entry 14)



Colourless solid (0.131 g, 83%): R_f (70:30 petrol-EtOAc) 0.4; mp 142-145 ˚C; IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3428 (NH), 1706 (C=O), 1517 (NO_2), 1320, 1275 (CF), 1163 (CF), 1077; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.72 (s, 1H), 8.49 (dd, J = 8.9, 2.6 Hz, 1H), 8.44

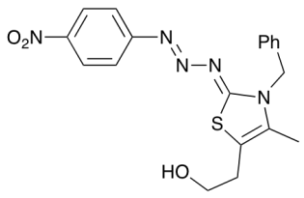
(d, *J* = 2.6 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 2.55 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.85–1.82 (m, 2H), 1.78–1.74 (m, 2H), 1.66–1.62 (m, 1H), 1.44–1.16 (m, 5H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 175.2 (C), 144.2 (C), 141.6 (C), 130.1 (CH), 127.8 (CH), 123.5 (C, q, *J* = 31.3 Hz), 122.2 (CH), 121.4 (C), 43.8 (CH), 28.9 (CH_2), 25.4 (CH_2), 25.1 (CH_2); HRMS ESI: calcd for $C_{14}H_{16}F_3N_2O_3$ $[M+H]^+$, 317.1108; found, 317.1094; calcd for $C_{14}H_{15}F_3N_2NaO_3$ $[M+Na]^+$, 339.0927; found 339.0914.

***N*-(4-nitro-3-(trifluoromethyl)phenyl)cyclohexanecarboxamide** (Table 2, Entry 15)



Colourless solid (0.138 g, 87%); R_f (70:30 petrol-EtOAc) 0.4; mp 128-130 °C (lit.,[3] 129-131 °C); IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3415 (NH), 1706 (C=O), 1517 (NO_2), 1380, 1225 (CF), 1142 (CF), 1068; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.62 (s, 1H), 8.29 (d, *J* = 2.2 Hz, 1H), 8.17 (d, *J* = 8.9 Hz, 1H), 8.04 (dd, *J* = 8.9, 2.2 Hz, 1H), 2.36 (tt, *J* = 11.4, 3.4 Hz, 2H), 1.85–1.82 (m, 2H), 1.77-173 (m, 2H), 1.66–1.63 (m, 1H), 1.45–1.15 (m, 5H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 175.6 (C), 144.2 (C), 141.1 (C), 127.8 (CH), 122.9 (C, q, *J* = 31.3 Hz), 122.0 (CH), 121.0 (C), 117.1 (CH), 45.1 (CH), 28.9 (CH_2), 25.3 (CH_2), 25.1 (CH_2); HRMS ESI: calcd for $C_{14}H_{16}F_3N_2O_3$ $[M+H]^+$, 317.1108; found, 317.1095; calcd for $C_{14}H_{15}F_3N_2NaO_3$ $[M+Na]^+$, 339.0927; found 339.0919.

2-((*Z*)-3-benzyl-4-methyl-2-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydrothiazol-5-yl) ethanol (7)



1-azido-4-nitrobenzene **1** (50.0 mg, 0.305 mmol) and the thiazolium salt **2** (82.0 mg, 0.305 mmol) were dissolved in THF (1 mL) and the corresponding mixture was cooled to -78 °C. NaH (30.5 mg, 60% w/w mineral oil, 0.761 mmol) was added to the

mixture in one portion. The reaction mixture was allowed to warm to room temperature, at which point a bright red colour appeared. The reaction was stirred at room temperature until complete (TLC, 5 h). The reaction mixture was then poured onto saturated ammonium chloride solution (5 mL) and the products extracted with ethyl acetate (3 x 5 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered and the solvents removed *in vacuo*. The resulting residue was finally subjected to flash column chromatography (eluting with ethyl acetate) to deliver the product as a bright red solid (98.0 mg, 81%), R_f (EtOAc) 0.2; IR (FTIR, $CHCl_3$) ν_{max} cm^{-1}: 3108 (OH), 1520 (NO_2), 1428 (N=N), 1327, 1134, 1106; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (d, J = 8.9 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.41-7.37 (m, 2H), 7.33-7.30 (m, 1H), 7.26-7.24 (m, 2H), 5.42 (s, 2H), 4.93 (t, J = 5.7 Hz, 1H), 3.59 (app q, J = 5.7 Hz, 2H), 2.76 (t, J = 5.7 Hz, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.8 (C), 155.6 (C), 145.4 (C), 135.8 (C), 133.1 (C), 128.9 (CH), 127.7 (CH), 126.5 (CH), 125.0 (CH), 121.7 (CH), 116.5 (C), 60.5 (CH_2), 48.6 (CH_2), 29.7 (CH_2), 11.2 (CH_3); HRMS ESI: calcd for $C_{19}H_{20}N_5O_3S$ $[M+H]^+$, 398.1281; found, 398.1291; calcd for $C_{19}H_{19}N_5NaO_3S$ $[M+Na]^+$, 420.1101; found, 420.1122.

References

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[4] T. J. Broxton, C. J. Carolane and L. W. Deady, *Aust. J. Chem.,* **28**, 1975, 451-454.

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[8] Y. -H. Yang and M. Shi, *J. Org. Chem.*, **70**, 2005, 8645-8648.

NMR spectra

2-((*Z*)-3-benzyl-4-methyl-2-((*E*)-(4-nitrophenyl)triaz-2-en-1-ylidene)-2,3-dihydrothiazol-5-yl) ethanol (SI1)

12/10/2012 14:32:40
UserID j_bur SampleID jb1254 SupervisorID moses Lab Phone No. 13540 Slot Number 35

Acquisition Time (sec)	3.9846	***Comment***	UserID j_bur SampleID jb1254 SupervisorID moses Lab Phone No. 13540 Slot Number 35				
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Frequency (MHz)	400.07	***Nucleus***	1H	***Number of Transients***	16	***Origin***	av3400
Original Points Count	32768	***Owner***	nmruser	***Points Count***	65536	***Pulse Sequence***	zg30
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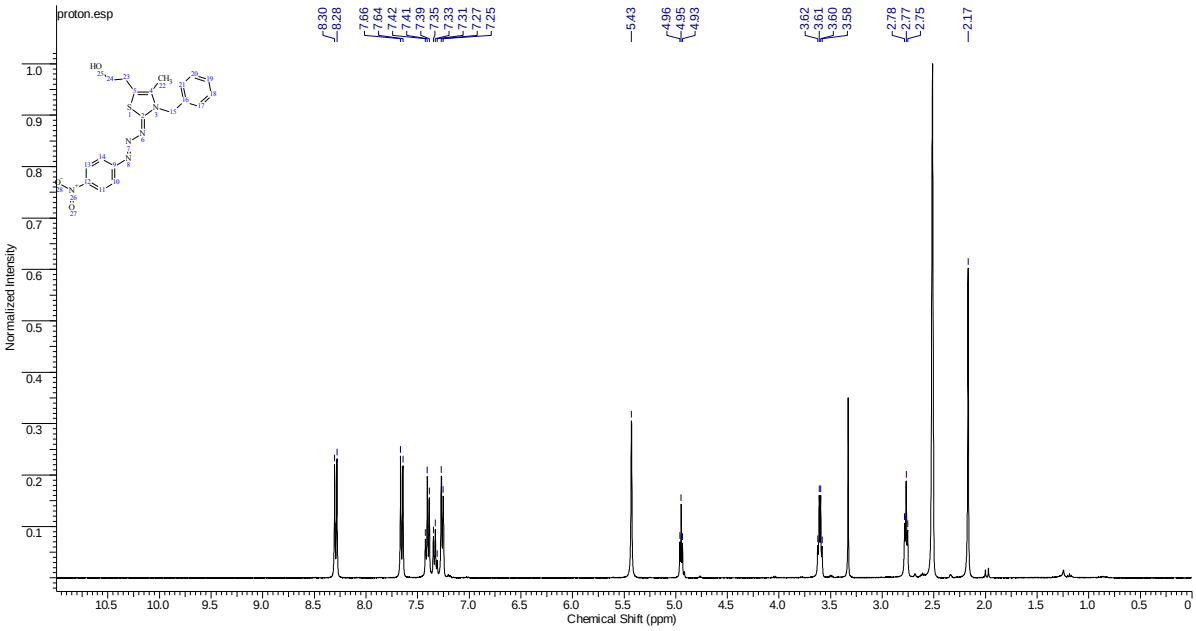
Spectrum Type	STANDARD	***Sweep Width (Hz)***	8223.56	***Temperature (degree C)***	25.000		



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Formula $C_{19}H_{18}N_6O_2S$	***FW***	397.4509	

Acquisition Time (sec)	0.6832	***Comment***	UserID j_bur SampleID jb1254 SupervisorID moses Lab Phone No. 13540 Slot Number 12				
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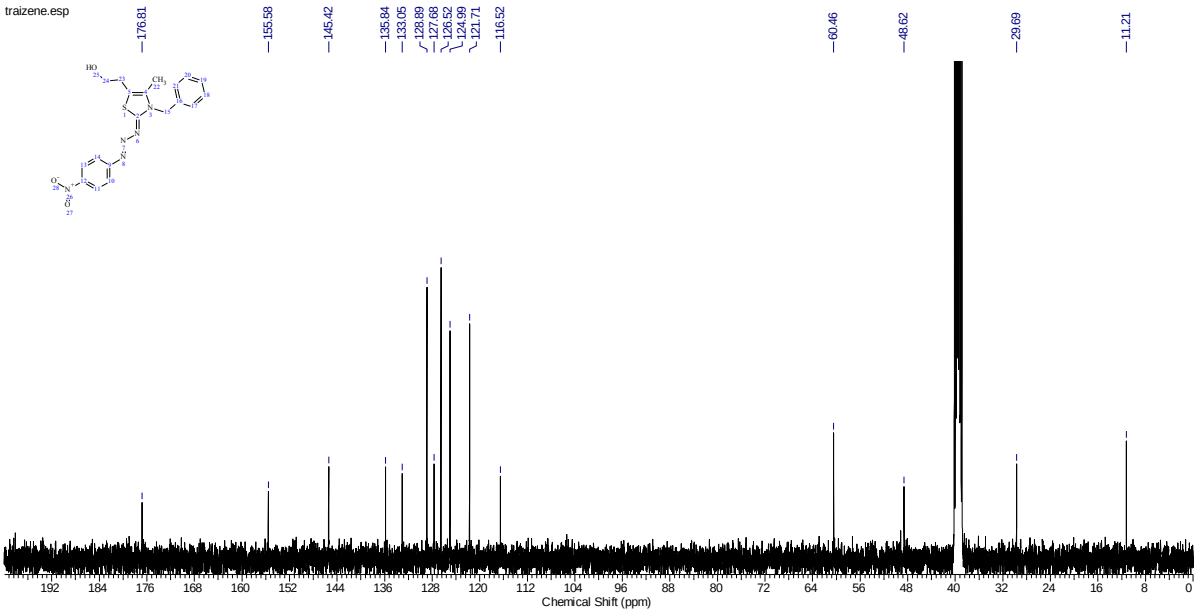
Receiver Gain	18390.40	***SW(cyclical) (Hz)***	23980.81	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	11017.3057
Spectrum Type	STANDARD	***Sweep Width (Hz)***	23980.08	***Temperature (degree C)***	25.160		



\\128.243.125.107\Public\Moses Group Work\James Burnley\azide reduction paper\NMR SI\triazene\traizene.esp

***N*-(4-nitrophenyl)benzamide** (Table 2, Entry 1)

Formula $C_{13}H_{10}N_2O_3$	***FW*** 242.2301						
Acquisition Time (sec)	3.9846	***Comment***	Slot No. 48 Sample ID gc3-48-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
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File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC3-48-1\1\PDATA\1\1R					***Frequency (MHz)***	400.20
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Owner	nmruser	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	645.10
SW(cyclical) (Hz)	8223.68	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	2465.0803	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8223.56	***Temperature (degree C)***	25.000				

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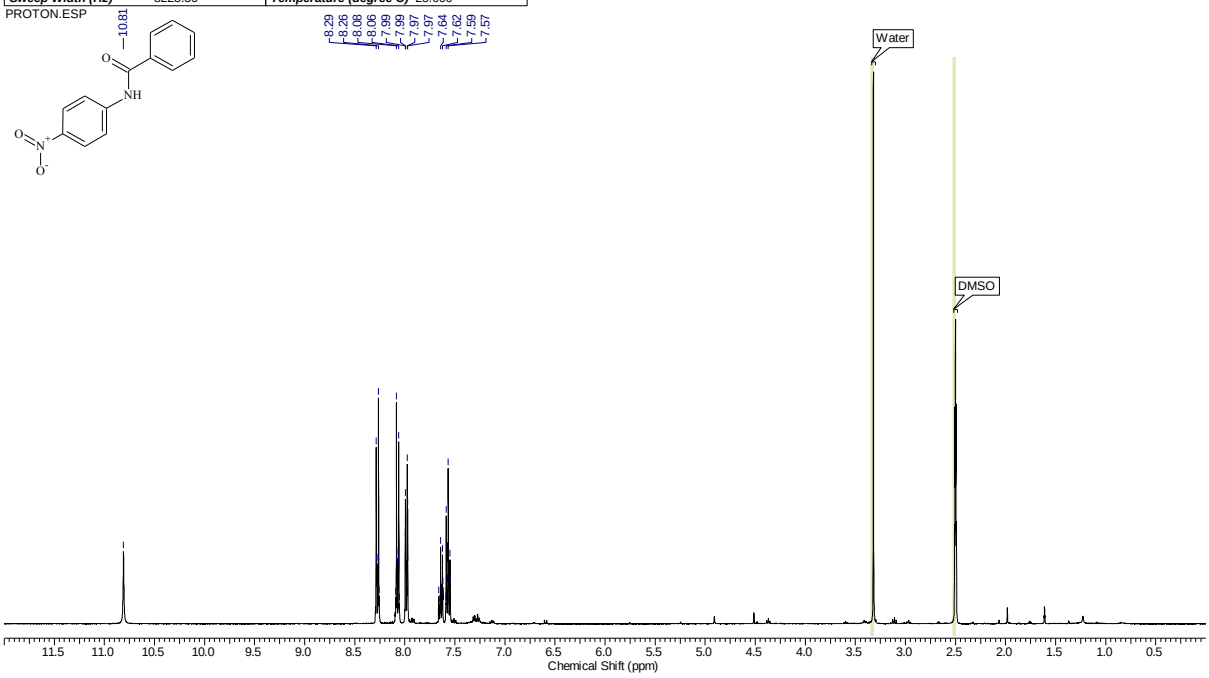

Formula $C_{13}H_{10}N_2O_3$	***FW*** 242.2301						
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Date	31 Mar 2012 19:16:32			***Date Stamp***	31 Mar 2012 19:16:32		
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Owner	nmruser	***Points Count***	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	9195.20
SW(cyclical) (Hz)	25125.63	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	11039.0381	***Spectrum Type***	STANDARD
Sweep Width (Hz)	25124.86	***Temperature (degree C)***	25.000				

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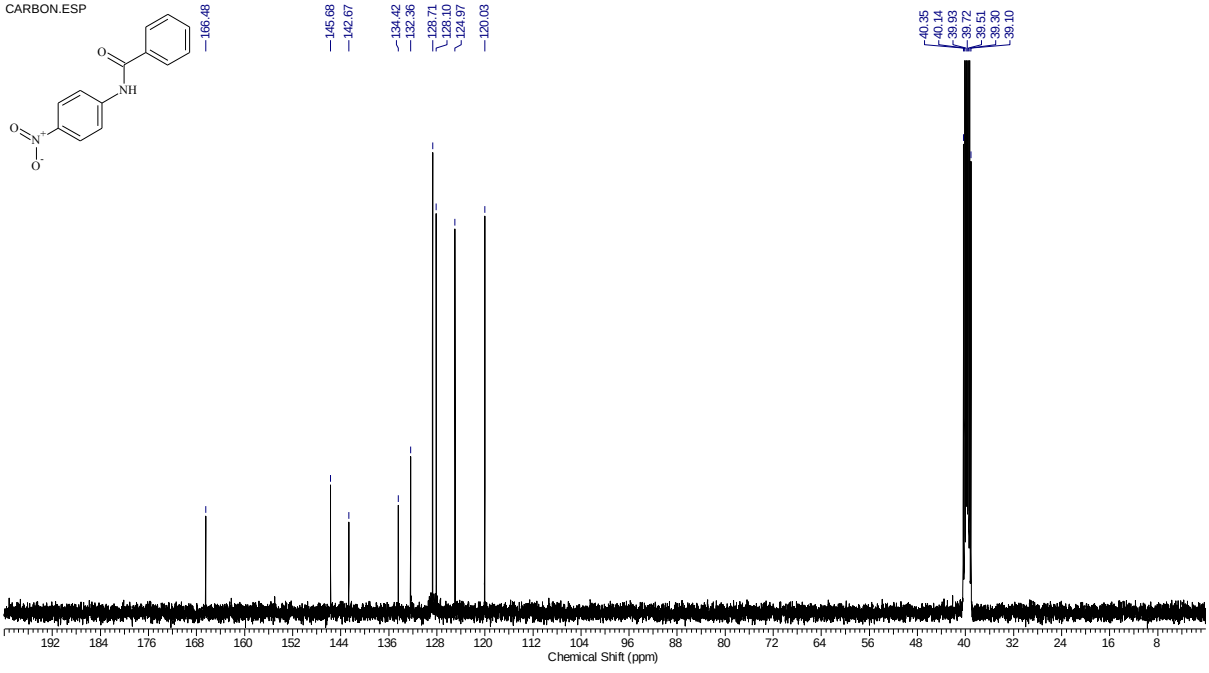
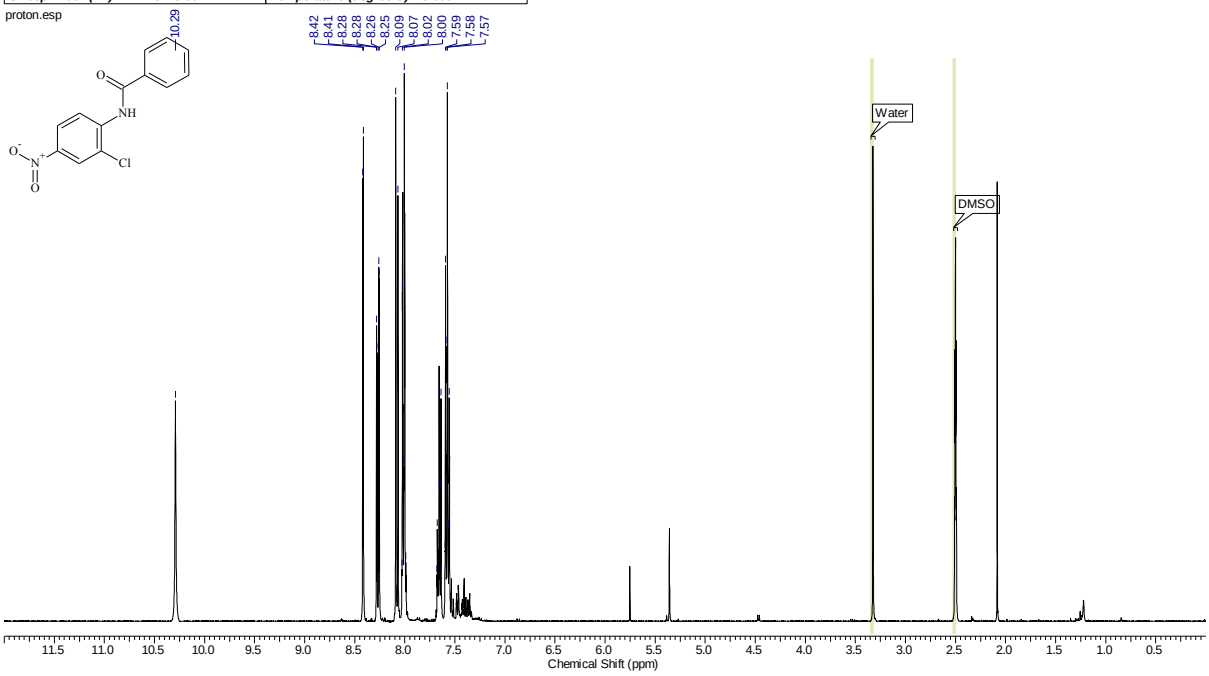
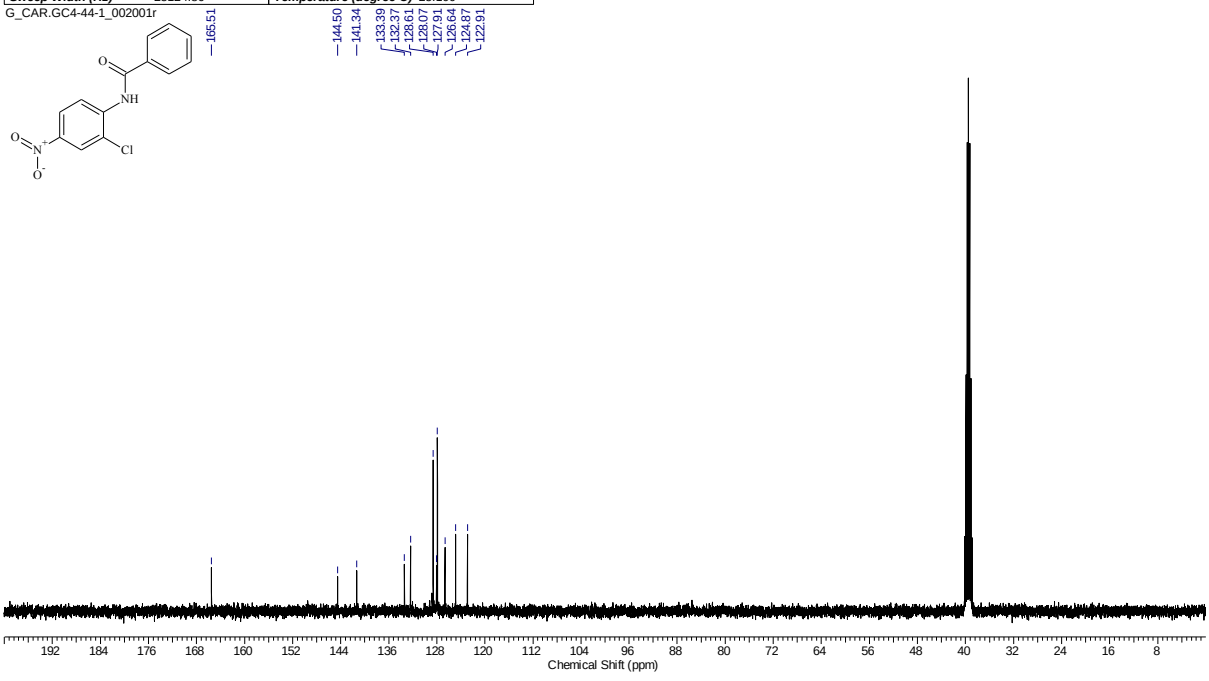


***N*-(3-chloro-4-nitrophenyl)benzamide** (Table 2, Entry 2)

Formula $C_{13}H_9ClN_2O_3$	***FW*** 276.6752						
Acquisition Time (sec)	3.9846	***Comment***	Slot No. 24 Sample ID gc4-44-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	30 Mar 2012 09:34:08			***Date Stamp***	30 Mar 2012 09:34:08		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-44-1\1\PDATA\1\1R					***Frequency (MHz)***	400.20
Nucleus	1H	***Number of Transients***	16	***Origin***	dpx400	***Original Points Count***	32768
Owner	nmruser	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	456.10
SW(cyclical) (Hz)	8223.68	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	2465.0803	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8223.56	***Temperature (degree C)***	25.000				

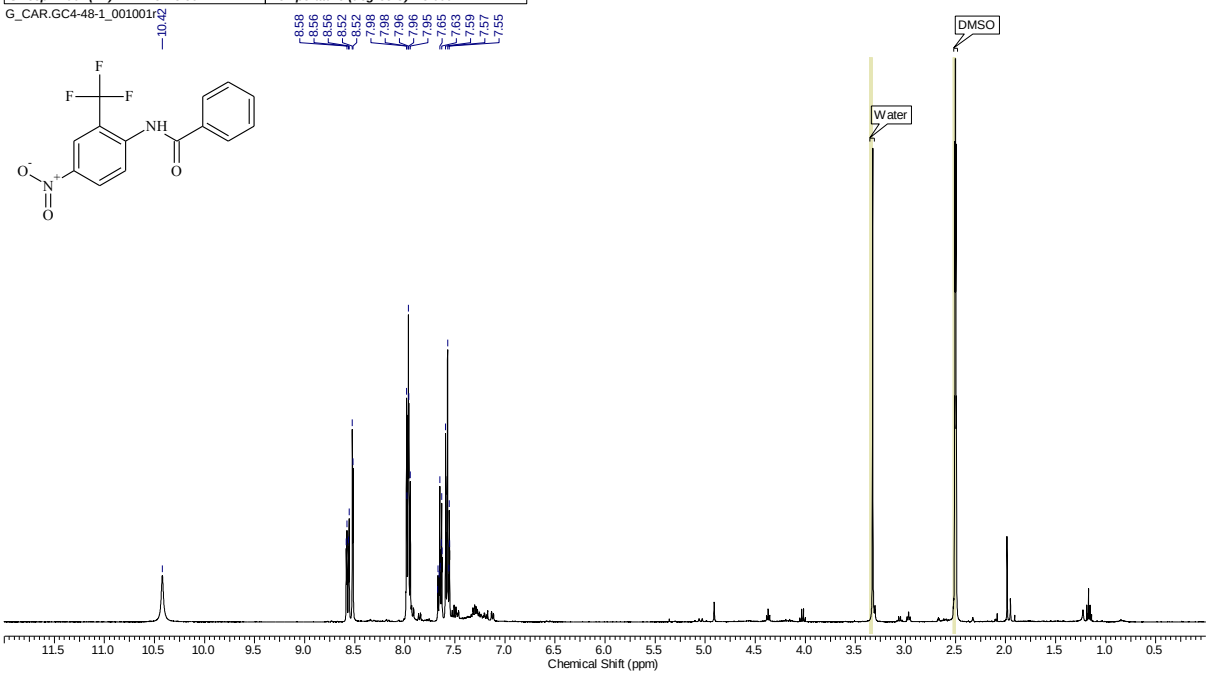


Formula $C_{13}H_9ClN_2O_3$	***FW*** 276.6752						
Acquisition Time (sec)	0.6521	***Comment***	Slot No. 24 Sample ID gc4-44-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	30 Mar 2012 09:40:32			***Date Stamp***	30 Mar 2012 09:40:32		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-44-1\2\PDATA\1\1R					***Frequency (MHz)***	100.63
Nucleus	13C	***Number of Transients***	128	***Origin***	dpx400	***Original Points Count***	16384
Owner	nmruser	***Points Count***	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	4597.60
SW(cyclical) (Hz)	25125.63	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	11017.5684	***Spectrum Type***	STANDARD
Sweep Width (Hz)	25124.86	***Temperature (degree C)***	25.100				



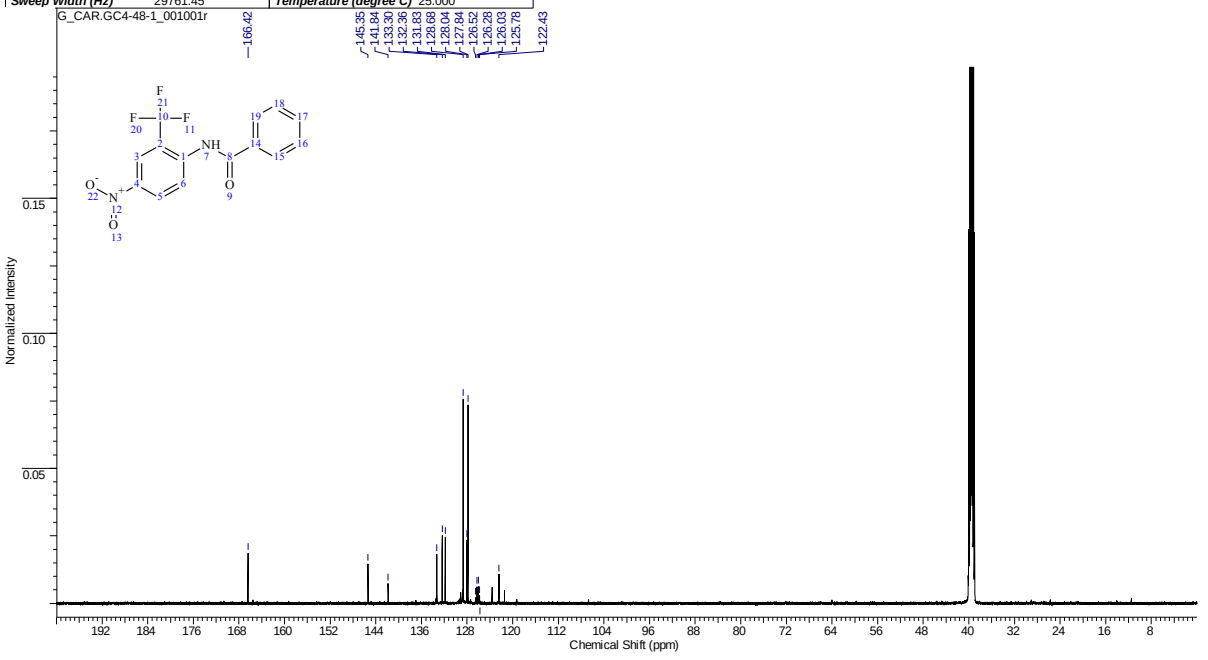
N-(4-nitro-2-(trifluoromethyl)phenyl)benzamide (Table 2, Entry 3)

Formula $C_{14}H_9F_3N_2O_3$	**FW**	310.2281					
Acquisition Time (sec)	3.9846	**Comment**	Slot No. 39 Sample ID gc4-48-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	05 Apr 2012 05:50:08			**Date Stamp**	05 Apr 2012 05:50:08		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-48-1\1\PDATA\1\1R					**Frequency (MHz)**	400.20
Nucleus	1H	**Number of Transients**	16	**Origin**	dpx400	**Original Points Count**	32768
Owner	nmruser	**Points Count**	65536	**Pulse Sequence**	zg30	**Receiver Gain**	287.40
SW(cyclical) (Hz)	8223.68	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	2465.2061	**Spectrum Type**	STANDARD
Sweep Width (Hz)	8223.56	**Temperature (degree C)**	25.000				



01/06/2012 16:41:09

Formula $C_{14}H_9F_3N_2O_3$	**FW**	310.2281					
Acquisition Time (sec)	1.1010	**Comment**	UserID g_car SampleID gc4-48-1 SupervisorID moses Lab Phone No. 13540 Slot 1				
Date	22 May 2012 10:46:40			**Date Stamp**	22 May 2012 10:46:40		
File Name	\\brukav3500\nmr_data\G_CAR\NMR\G_CAR.GC4-48-1\1\PDATA\1\1R					**Frequency (MHz)**	125.76
Nucleus	13C	**Number of Transients**	320	**Origin**	av3500	**Original Points Count**	32768
Owner	service	**Points Count**	65536	**Pulse Sequence**	zgpg30	**Receiver Gain**	2050.00
SW(cyclical) (Hz)	29761.90	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	13777.2344	**Spectrum Type**	STANDARD
Sweep Width (Hz)	29761.45	**Temperature (degree C)**	25.000				



N-(4-nitro-3-(trifluoromethyl)phenyl)benzamide (Table 2, Entry 4)

Formula $C_{14}H_9F_3N_2O_3$	**FW**	310.2281	

Acquisition Time (sec)	3.9846	**Comment**	Slot No. 52 Sample ID gc4_28_2 SupervisorID moses Lab Phone No. 13540 UserID g_car				
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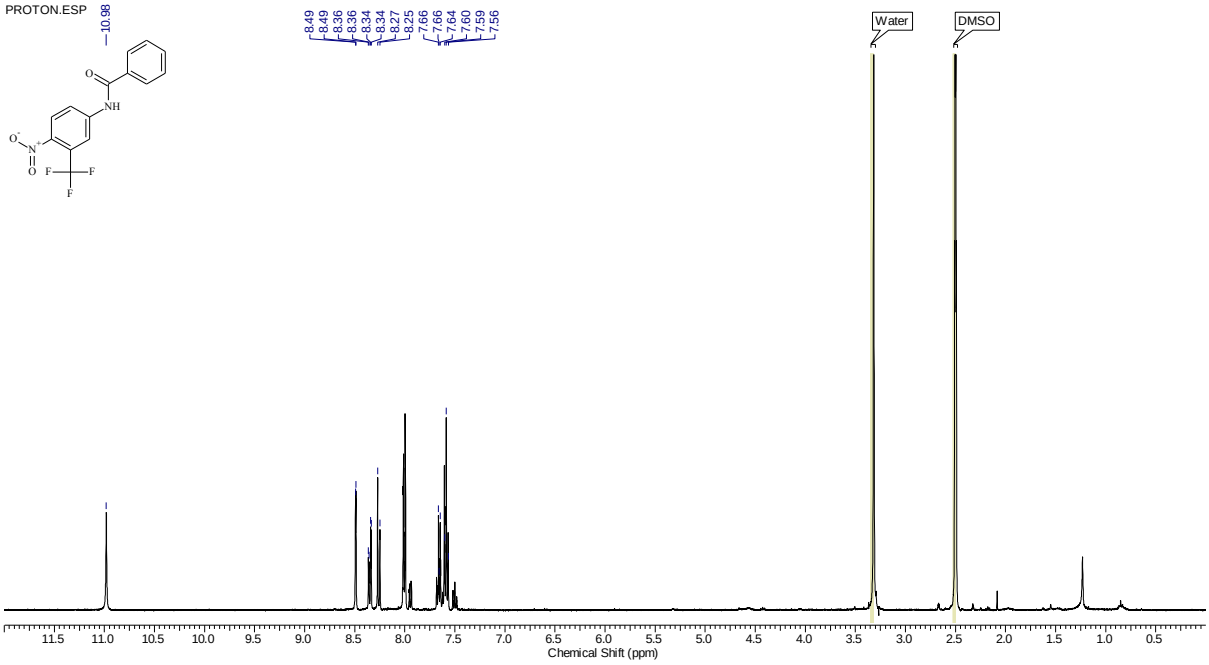
Nucleus	1H	**Number of Transients**	16	**Origin**	dpx400	**Original Points Count**	32768
Owner	nmruser	**Points Count**	65536	**Pulse Sequence**	zg30	**Receiver Gain**	912.30
SW(cyclical) (Hz)	8223.68	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	2465.0803	**Spectrum Type**	STANDARD
Sweep Width (Hz)	8223.56	**Temperature (degree C)**	25.000				



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Formula $C_{14}H_9F_3N_2O_3$	**FW**	310.2281	

Acquisition Time (sec)	1.1010	**Comment**	UserID g_car SampleID gc4-41-1 SupervisorID moses Lab Phone No. 13540 Slot 1				
Date	15 May 2012 13:28:48			**Date Stamp**	15 May 2012 13:28:48		
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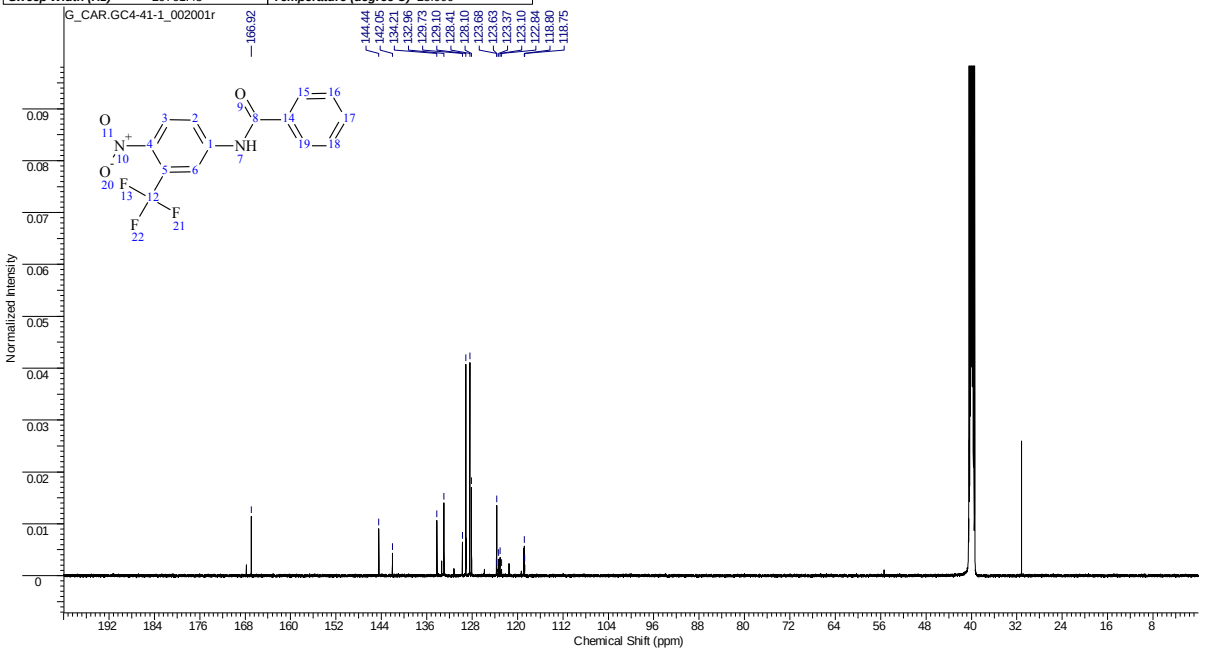
Nucleus	13C	**Number of Transients**	1024	**Origin**	av3500	**Original Points Count**	32768
Owner	service	**Points Count**	65536	**Pulse Sequence**	zgpg30	**Receiver Gain**	2050.00
SW(cyclical) (Hz)	29761.90	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	13833.3623	**Spectrum Type**	STANDARD
Sweep Width (Hz)	29761.45	**Temperature (degree C)**	25.000				



Methoxy-*N*-(4-nitrophenyl)benzamide (Table 2, Entry 5)

Formula $C_{14}H_{12}N_2O_4$	***FW*** 272.2561		
Acquisition Time (sec) 3.9846	***Comment*** Slot No. 39 Sample ID gc4-39-1 SupervisorID moses Lab Phone No. 13540 UserID g_car		
Date 28 Mar 2012 15:11:12		***Date Stamp*** 28 Mar 2012 15:11:12	
File Name \\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-39-1\2\PDATA\1\1R			***Frequency (MHz)*** 400.20
Nucleus 1H	***Number of Transients*** 16	***Origin*** dpx400	***Original Points Count*** 32768
Owner nmruser	***Points Count*** 65536	***Pulse Sequence*** zg30	***Receiver Gain*** 645.10
SW(cyclical) (Hz) 8223.68	***Solvent*** DMSO-d6	***Spectrum Offset (Hz)*** 2465.0803	***Spectrum Type*** STANDARD
Sweep Width (Hz) 8223.56	***Temperature (degree C)*** 25.000		

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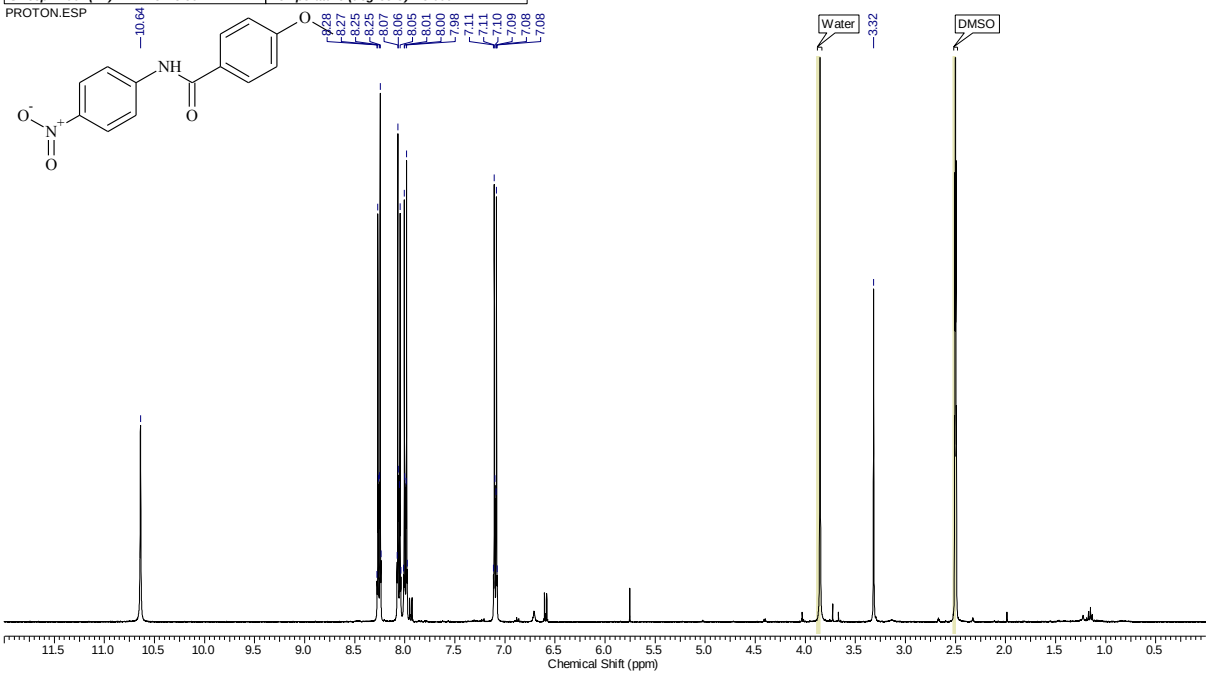

Formula $C_{14}H_{12}N_2O_4$	***FW*** 272.2561		
Acquisition Time (sec) 0.6521	***Comment*** Slot No. 39 Sample ID gc4-39-1 SupervisorID moses Lab Phone No. 13540 UserID g_car		
Date 28 Mar 2012 15:41:04		***Date Stamp*** 28 Mar 2012 15:41:04	
File Name \\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-39-1\3\PDATA\1\1R			***Frequency (MHz)*** 100.63
Nucleus 13C	***Number of Transients*** 128	***Origin*** dpx400	***Original Points Count*** 16384
Owner nmruser	***Points Count*** 32768	***Pulse Sequence*** zgpg30	***Receiver Gain*** 18390.40
SW(cyclical) (Hz) 25125.63	***Solvent*** DMSO-d6	***Spectrum Offset (Hz)*** 11060.5078	***Spectrum Type*** STANDARD
Sweep Width (Hz) 25124.86	***Temperature (degree C)*** 25.100		

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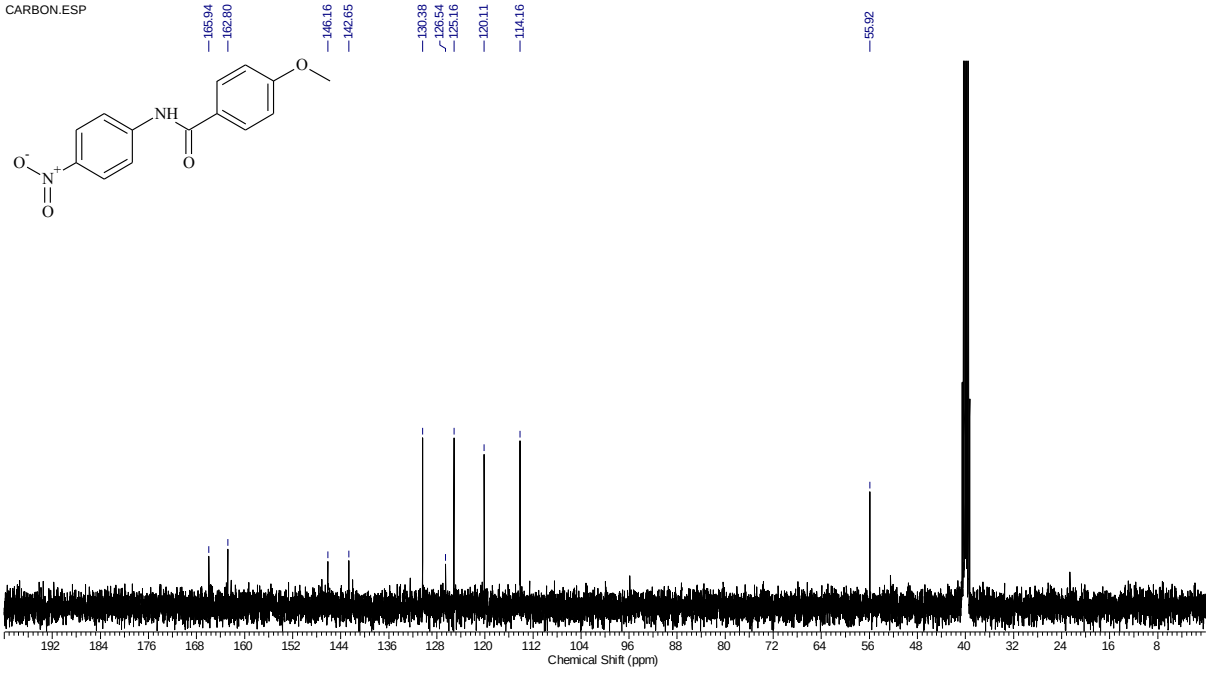
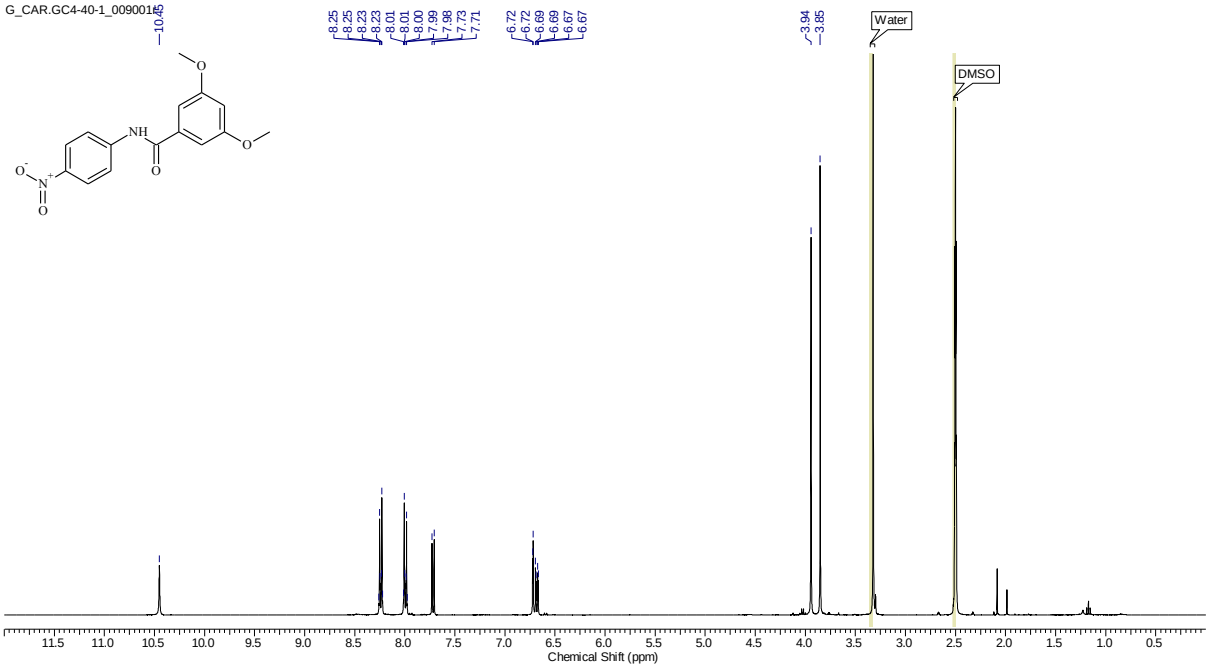


3,5-Dimethoxy-*N*-(4-nitrophenyl)benzamide (Table 2, Entry 6)

Formula $C_{15}H_{14}N_2O_5$	***FW*** 302.2821		

Acquisition Time (sec)	3.9846	***Comment***	Slot No. 40 Sample ID gc4-40-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	05 Apr 2012 11:29:20			***Date Stamp***	05 Apr 2012 11:29:20		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-40-1\9\PDATA\1\1R					***Frequency (MHz)***	400.20
Nucleus	1H	***Number of Transients***	16	***Origin***	dpx400	***Original Points Count***	32768
Owner	nmruser	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	322.50
SW(cyclical) (Hz)	8223.68	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	2465.2061	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8223.56	***Temperature (degree C)***	25.000				

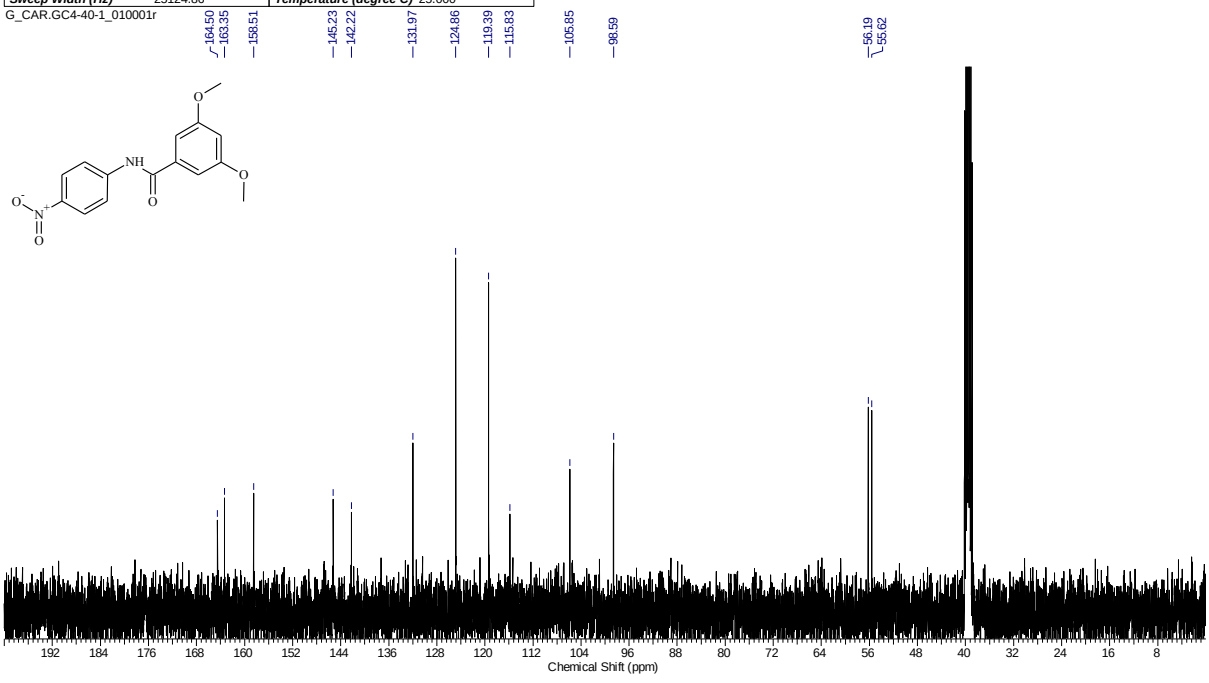
G_CAR.GC4-40-1_009001r



Formula $C_{15}H_{14}N_2O_5$	***FW*** 302.2821		

Acquisition Time (sec)	0.6521	***Comment***	Slot No. 40 Sample ID gc4-40-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	05 Apr 2012 11:33:36			***Date Stamp***	05 Apr 2012 11:33:36		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-40-1\10\PDATA\1\1R					***Frequency (MHz)***	100.63
Nucleus	13C	***Number of Transients***	128	***Origin***	dpx400	***Original Points Count***	16384
Owner	nmruser	***Points Count***	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	5792.60
SW(cyclical) (Hz)	25125.63	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	11018.3350	***Spectrum Type***	STANDARD
Sweep Width (Hz)	25124.86	***Temperature (degree C)***	25.000				

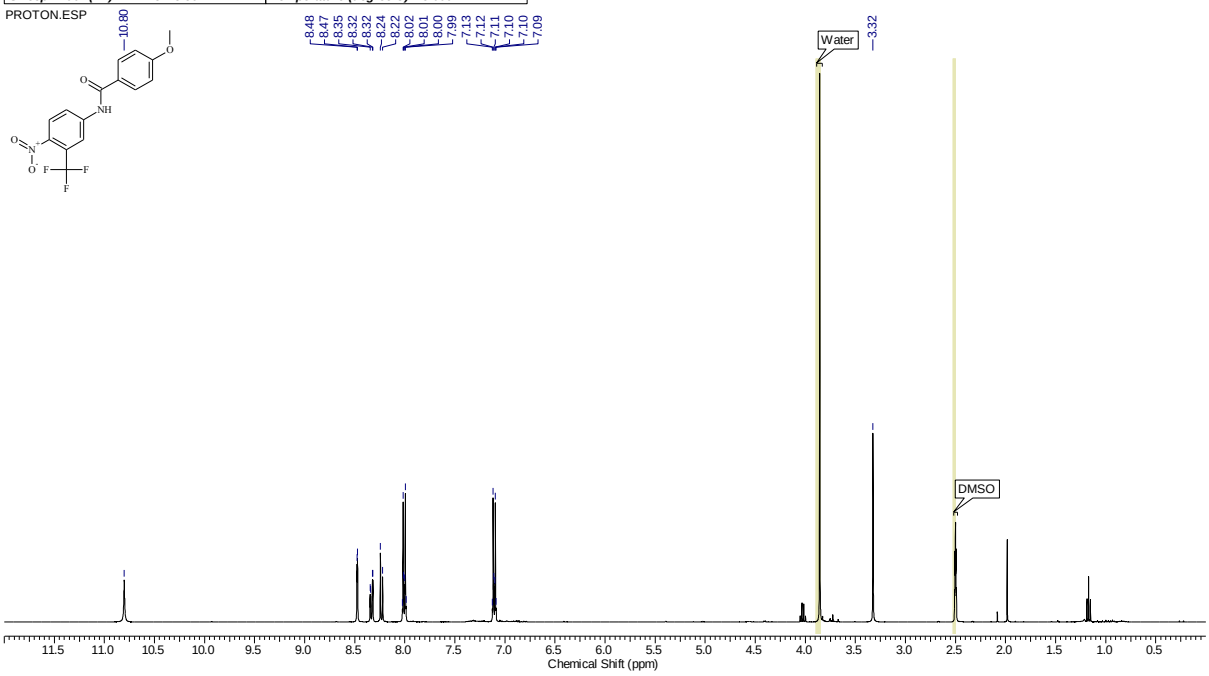
G_CAR.GC4-40-1_010001r



4-Methoxy-N-(4-nitro-3-(trifluoromethyl)phenyl)benzamide (Table 2, Entry 7)

Formula $C_{15}H_{11}F_3N_2O_4$		***FW*** 340.2540	

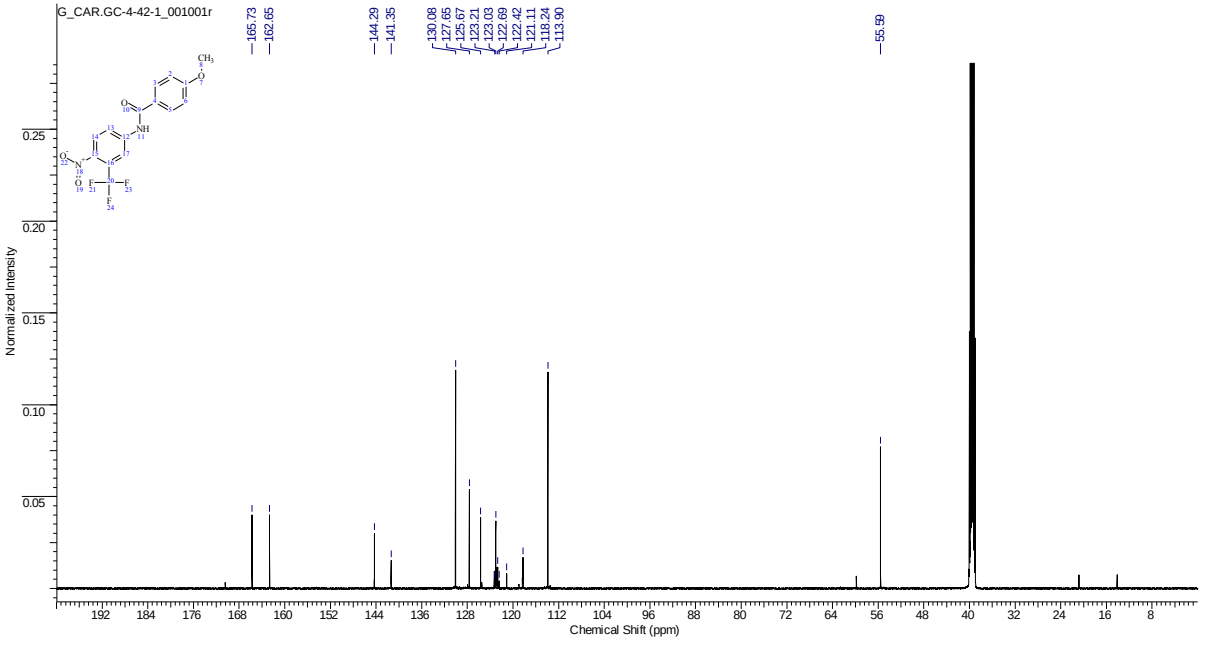
Acquisition Time (sec)	3.9846	***Comment***	Slot No. 22 Sample ID gc4-42-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	30 Mar 2012 09:17:04			***Date Stamp***	30 Mar 2012 09:17:04		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-42-1\5\PDATA\1\1R					***Frequency (MHz)***	400.20
Nucleus	1H	***Number of Transients***	16	***Origin***	dpx400	***Original Points Count***	32768
Owner	nmruser	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	456.10
SW(cyclical) (Hz)	8223.68	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	2465.0803	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8223.56	***Temperature (degree C)***	25.000				



01/06/2012 15:31:23

Formula $C_{15}H_{11}F_3N_2O_4$		***FW*** 340.2540	

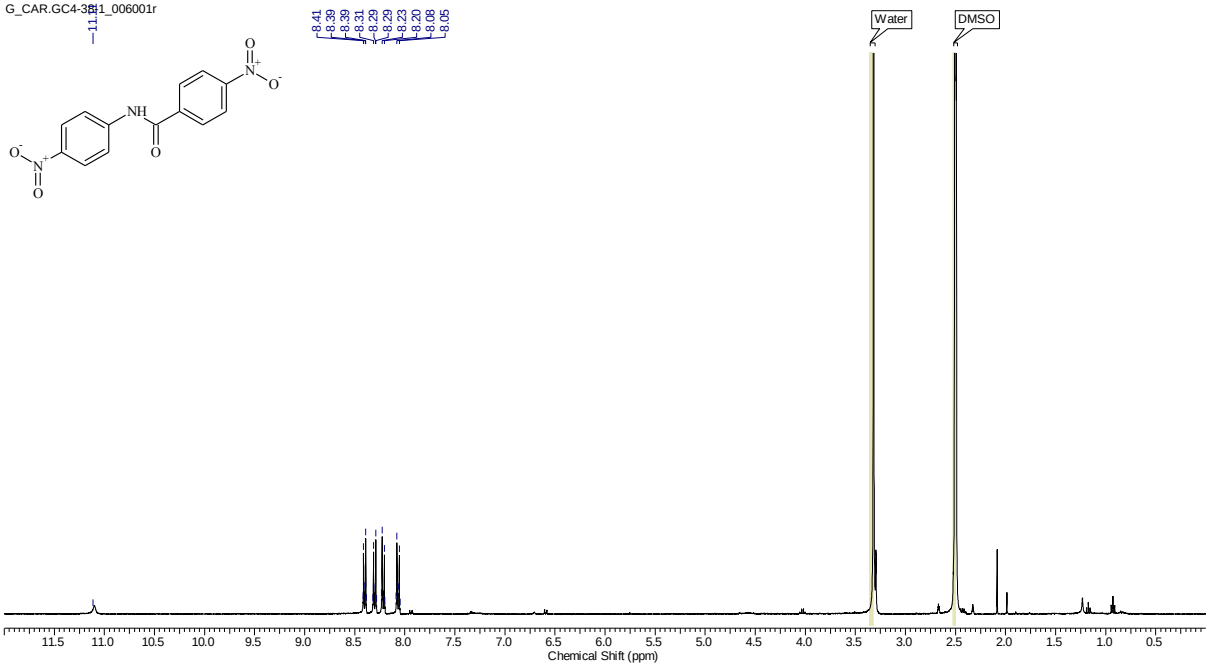
Acquisition Time (sec)	1.1010	***Comment***	UserID g_car SampleID gc-4-42-1 SupervisorID moses Lab Phone No. 13540 Slot 3				
Date	21 May 2012 16:38:40			***Date Stamp***	21 May 2012 16:38:40		
File Name	\\brukav3500\nmr_data\G_CAR\NMR\G_CAR.GC-4-42-1\1\PDATA\1\1R					***Frequency (MHz)***	125.76
Nucleus	13C	***Number of Transients***	512	***Origin***	av3500	***Original Points Count***	32768
Owner	service	***Points Count***	65536	***Pulse Sequence***	zgpg30	***Receiver Gain***	2050.00
SW(cyclical) (Hz)	29761.90	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	13780.8672	***Spectrum Type***	STANDARD
Sweep Width (Hz)	29761.45	***Temperature (degree C)***	25.000				



4-Nitro-*N*-(4-nitrophenyl) benzamide (Table 2, Entry 8)

Formula $C_{13}H_9N_3O_5$	***FW***	287.2277	

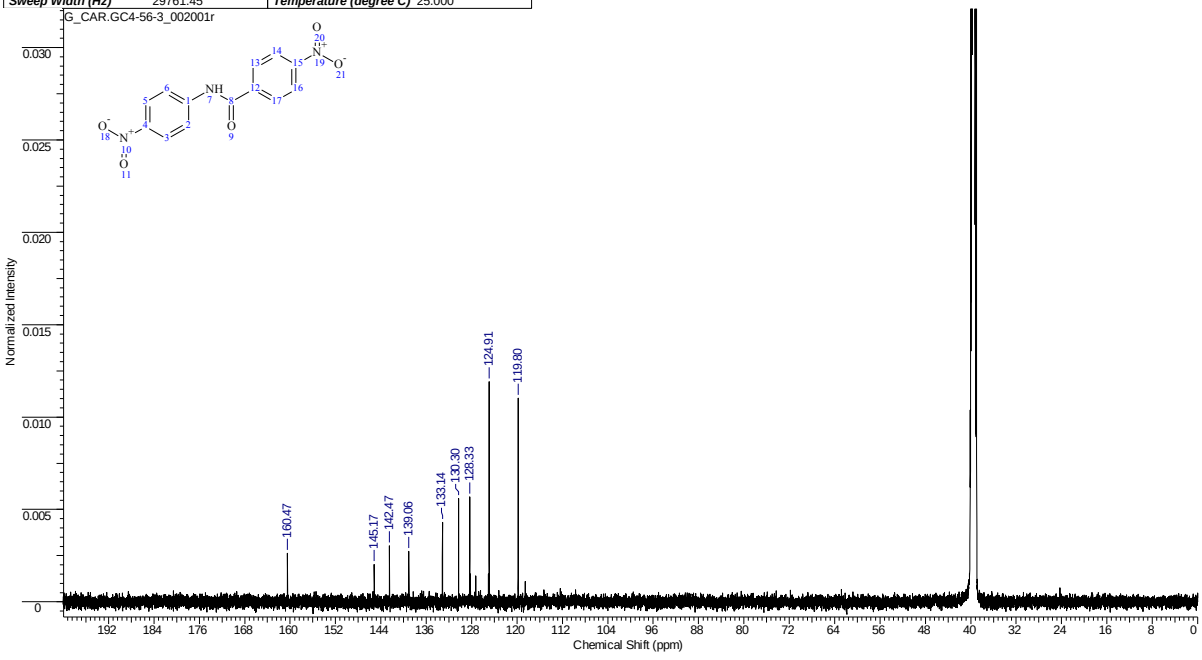
Acquisition Time (sec)	3.9846	***Comment***	Slot No. 38 Sample ID gc4-38-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	05 Apr 2012 11:12:16			***Date Stamp***	05 Apr 2012 11:12:16		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-38-1\6\PDATA\1\1R					***Frequency (MHz)***	400.20
Nucleus	1H	***Number of Transients***	16	***Origin***	dpx400	***Original Points Count***	32768
Owner	nmruser	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	645.10
SW(cyclical) (Hz)	8223.68	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	2465.2061	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8223.56	***Temperature (degree C)***	25.000				



25/05/2012 15:37:33

Formula $C_{13}H_9N_3O_5$	***FW***	287.2277	

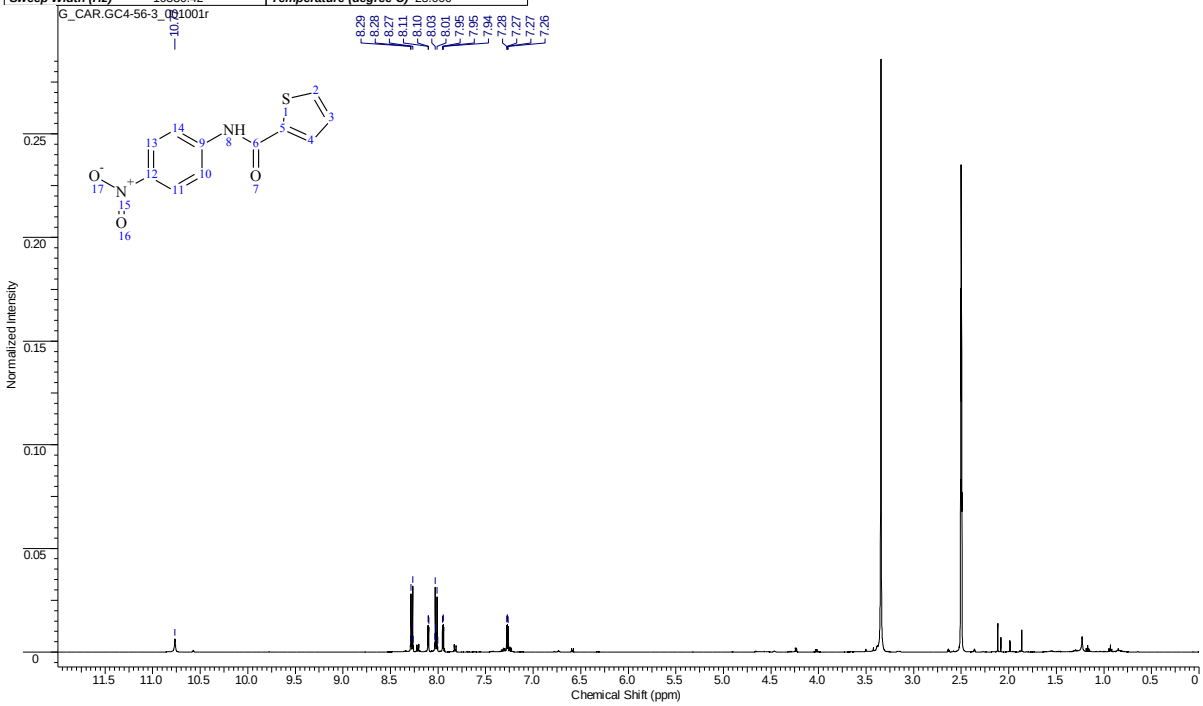
Acquisition Time (sec)	1.1010	***Comment***	UserID g_car SampleID gc4-56-3 SupervisorID moses Lab Phone No. 13540 Slot 1				
Date	16 May 2012 10:53:04			***Date Stamp***	16 May 2012 10:53:04		
File Name	\\brukav3500\nmr_data\G_CAR\NMR\G_CAR.GC4-56-3\2\PDATA\1\1R					***Frequency (MHz)***	125.76
Nucleus	13C	***Number of Transients***	400	***Origin***	av3500	***Original Points Count***	32768
Owner	service	***Points Count***	65536	***Pulse Sequence***	zgpg30	***Receiver Gain***	2050.00
SW(cyclical) (Hz)	29761.90	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	13777.2344	***Spectrum Type***	STANDARD
Sweep Width (Hz)	29761.45	***Temperature (degree C)***	25.000				



***N*-(4-nitrophenyl)thiophene-2-carboxamide** (Table 2, Entry 9)

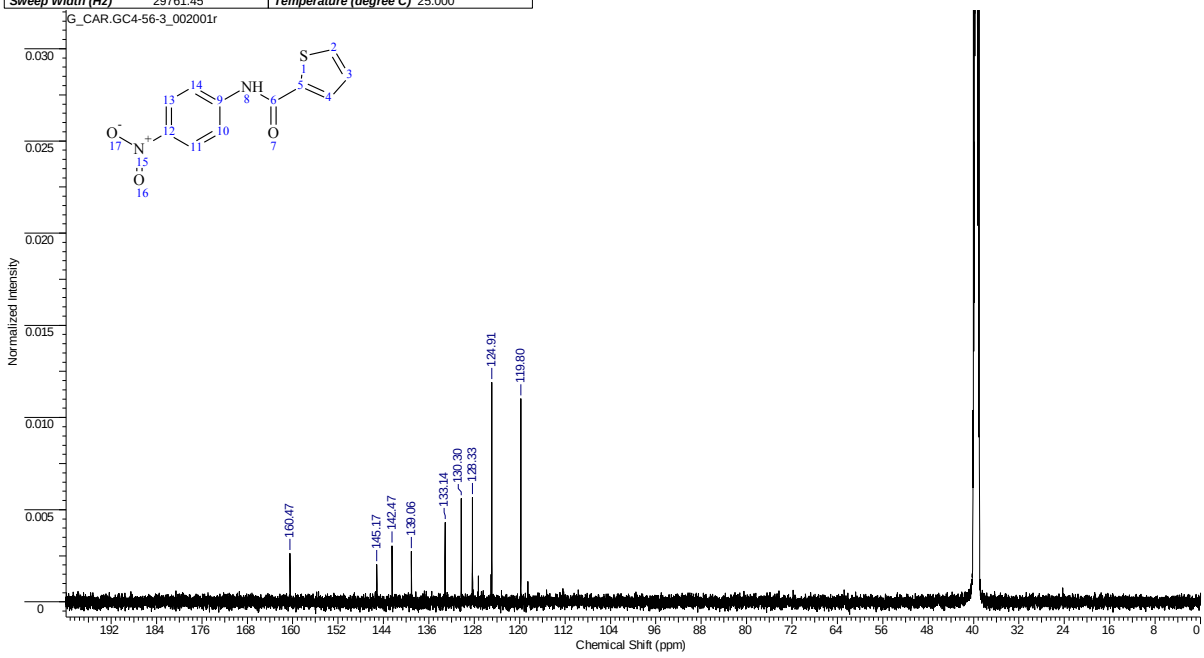
25/05/2012 15:53:16

Formula $C_{11}H_8N_2O_3S$	***FW*** 248.2578						
Acquisition Time (sec)	3.1719	***Comment***	UserID g_car SampleID gc4-56-3 SupervisorID moses Lab Phone No. 13540 Slot 1				
Date	16 May 2012 09:57:36			***Date Stamp***	16 May 2012 09:57:36		
File Name	\\brukav3500\nmr_data\G_CAR\NMR\G_CAR.GC4-56-3\1\PDATA\1\1R					***Frequency (MHz)***	500.13
Nucleus	1H	***Number of Transients***	16	***Origin***	av3500	***Original Points Count***	32768
Owner	service	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	575.00
SW(cyclical) (Hz)	10330.58	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	3083.0349	***Spectrum Type***	STANDARD
Sweep Width (Hz)	10330.42	***Temperature (degree C)***	25.000				



25/05/2012 15:34:00

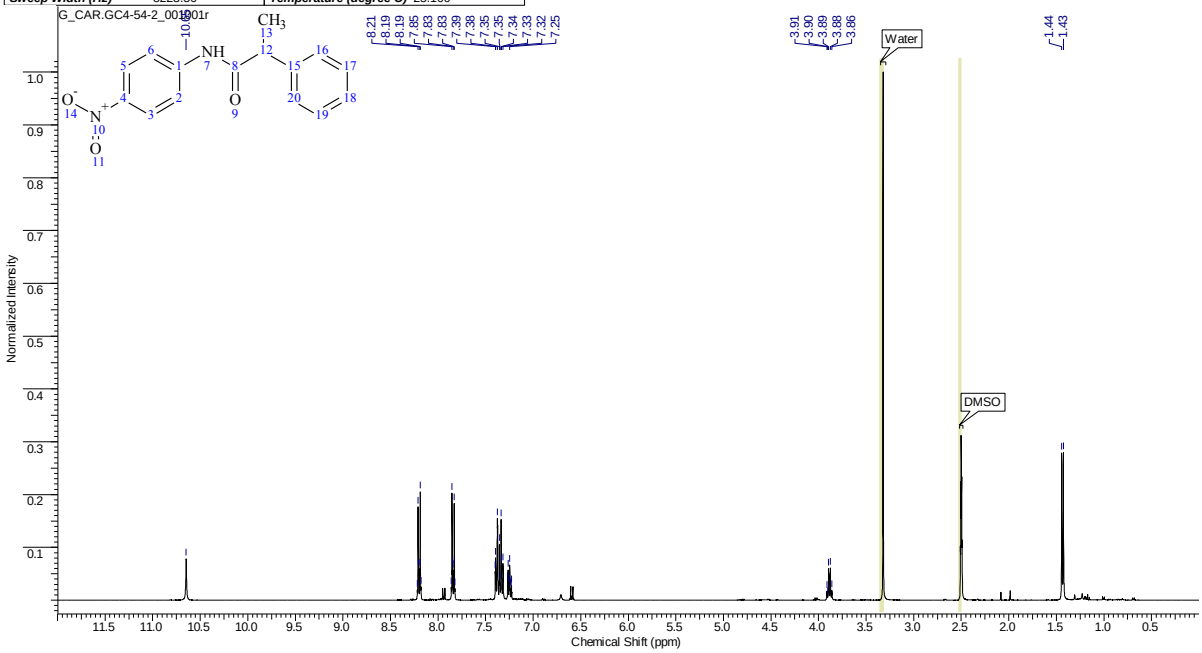
Formula $C_{11}H_8N_2O_3S$	***FW*** 248.2578						
Acquisition Time (sec)	1.1010	***Comment***	UserID g_car SampleID gc4-56-3 SupervisorID moses Lab Phone No. 13540 Slot 1				
Date	16 May 2012 10:53:04			***Date Stamp***	16 May 2012 10:53:04		
File Name	\\brukav3500\nmr_data\G_CAR\NMR\G_CAR.GC4-56-3\2\PDATA\1\1R					***Frequency (MHz)***	125.76
Nucleus	13C	***Number of Transients***	400	***Origin***	av3500	***Original Points Count***	32768
Owner	service	***Points Count***	65536	***Pulse Sequence***	zgpg30	***Receiver Gain***	2050.00
SW(cyclical) (Hz)	29761.90	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	13777.2344	***Spectrum Type***	STANDARD
Sweep Width (Hz)	29761.45	***Temperature (degree C)***	25.000				



***N*-(4-nitrophenyl)-2-phenylpropanamide** (Table 2, Entry 10)

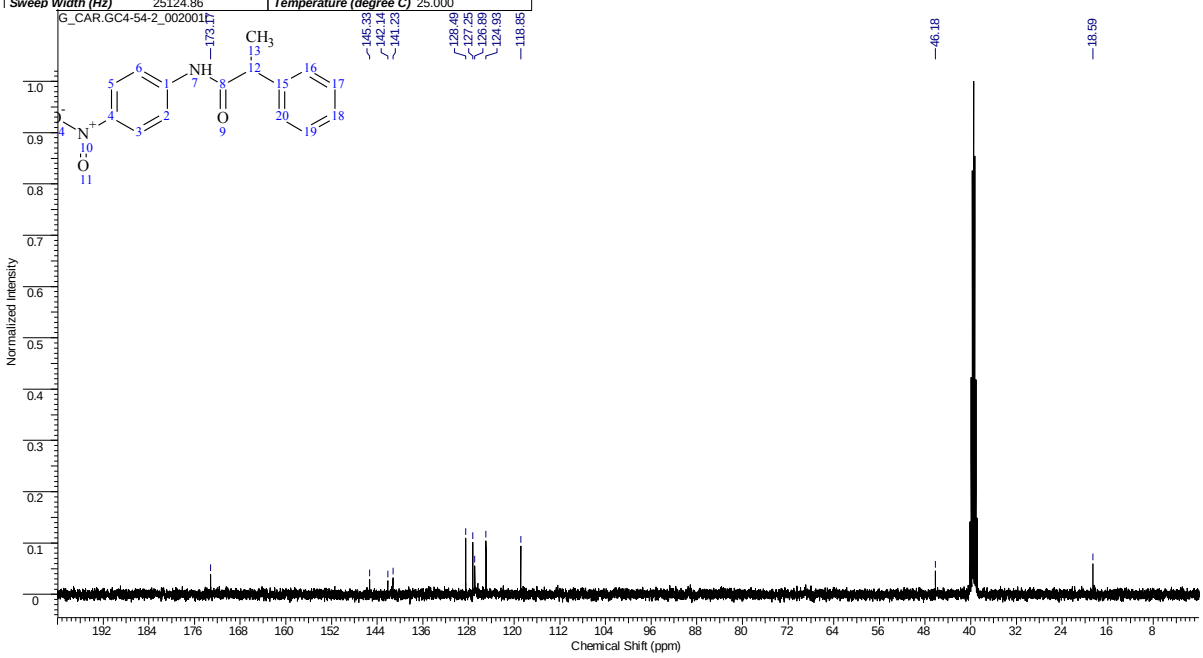
01/06/2012 14:39:47

Formula $C_{15}H_{14}N_2O_3$	***FW*** 270.2833		
Acquisition Time (sec) 3.9846	***Comment*** Slot No. 54 Sample ID gc4-54-2 SupervisorID moses Lab Phone No. 13540 UserID g_car		
Date 11 May 2012 10:33:52	***Date Stamp*** 11 May 2012 10:33:52		
File Name \\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-54-2\1\PDATA\1\1R			***Frequency (MHz)*** 400.20
Nucleus 1H	***Number of Transients*** 16	***Origin*** dpx400	***Original Points Count*** 32768
Owner nmruser	***Points Count*** 65536	***Pulse Sequence*** zg30	***Receiver Gain*** 574.70
SW(cyclical) (Hz) 8223.68	***Solvent*** DMSO-d6	***Spectrum Offset (Hz)*** 2465.0803	***Spectrum Type*** STANDARD
Sweep Width (Hz) 8223.56	***Temperature (degree C)*** 25.100		



01/06/2012 14:43:27

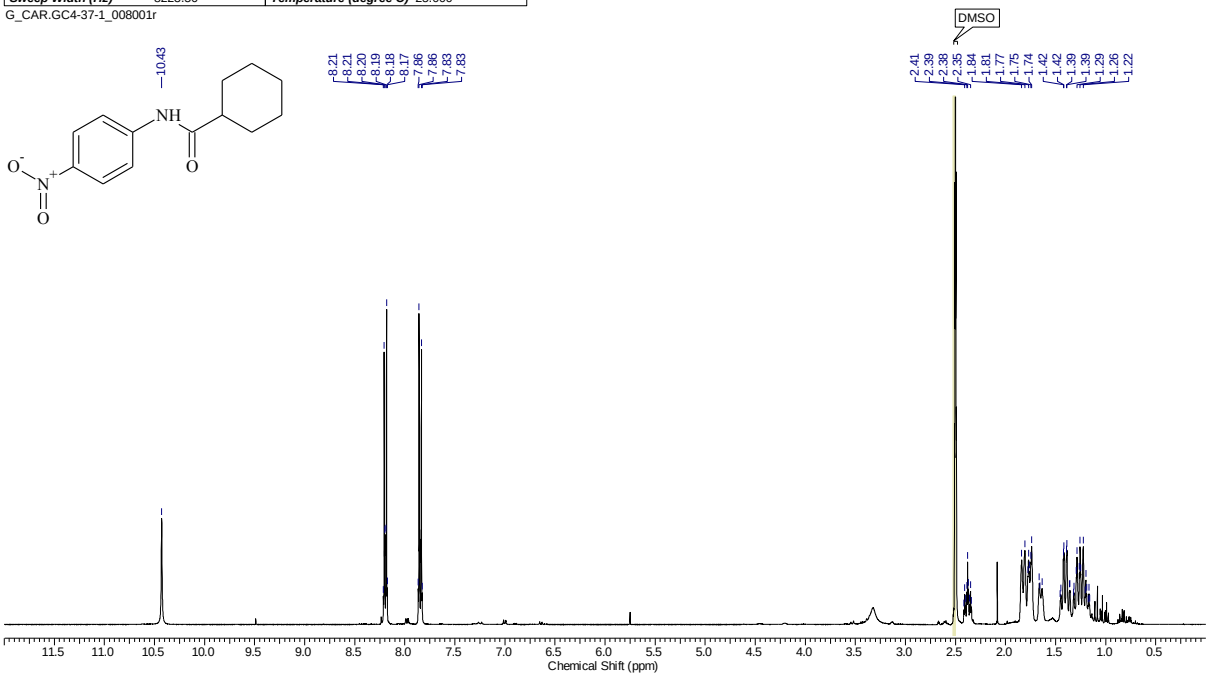
Formula $C_{15}H_{14}N_2O_3$	***FW*** 270.2833		
Acquisition Time (sec) 0.6521	***Comment*** Slot No. 54 Sample ID gc4-54-2 SupervisorID moses Lab Phone No. 13540 UserID g_car		
Date 11 May 2012 11:18:40	***Date Stamp*** 11 May 2012 11:18:40		
File Name \\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-54-2\2\PDATA\1\1R			***Frequency (MHz)*** 100.63
Nucleus 13C	***Number of Transients*** 128	***Origin*** dpx400	***Original Points Count*** 16384
Owner nmruser	***Points Count*** 32768	***Pulse Sequence*** zgpg30	***Receiver Gain*** 10321.30
SW(cyclical) (Hz) 25125.63	***Solvent*** DMSO-d6	***Spectrum Offset (Hz)*** 11018.3350	***Spectrum Type*** STANDARD
Sweep Width (Hz) 25124.86	***Temperature (degree C)*** 25.000		



N-(4-nitrophenyl)cyclohexanecarboxamide (Table 2, Entry 11)

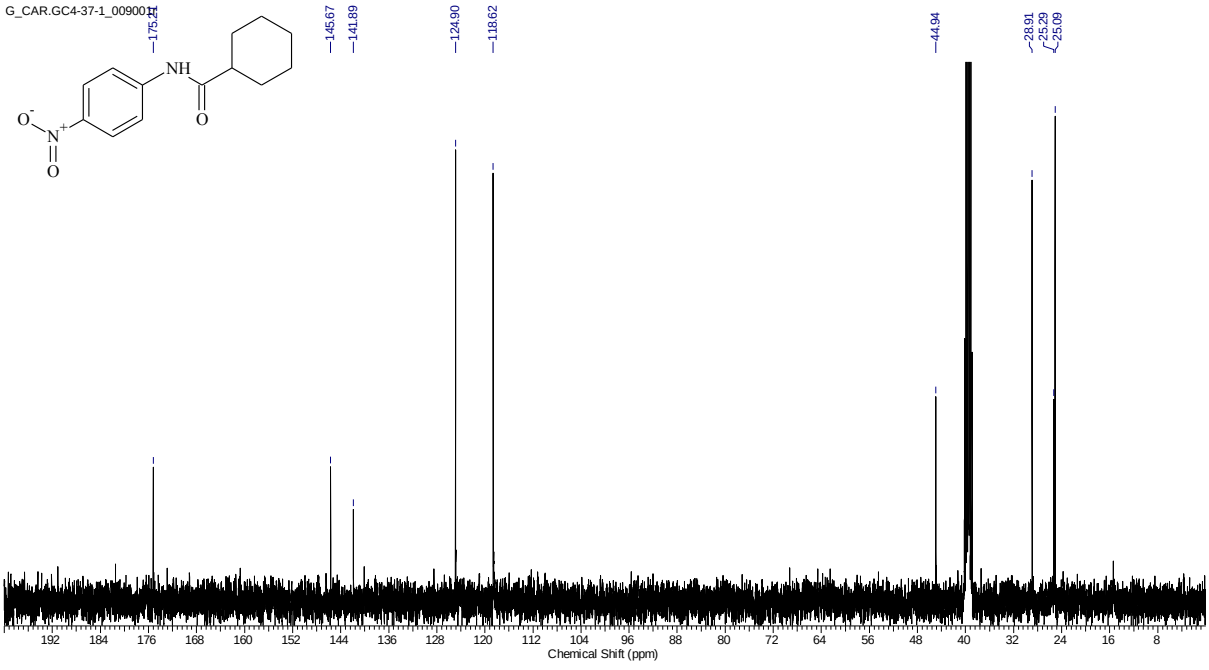
Formula $C_{13}H_{16}N_2O_3$	**FW**	248.2777					
Acquisition Time (sec)	3.9846	**Comment**	Slot No. 37 Sample ID gc4-37-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	05 Apr 2012 05:16:00			**Date Stamp**	05 Apr 2012 05:16:00		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-37-1\8\PDATA\1\1R					**Frequency (MHz)**	400.20
Nucleus	1H	**Number of Transients**	16	**Origin**	dpx400	**Original Points Count**	32768
Owner	nmruser	**Points Count**	65536	**Pulse Sequence**	zg30	**Receiver Gain**	256.00
SW(cyclical) (Hz)	8223.68	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	2465.2061	**Spectrum Type**	STANDARD
Sweep Width (Hz)	8223.56	**Temperature (degree C)**	25.000				

G_CAR.GC4-37-1_008001r



Formula $C_{13}H_{16}N_2O_3$	**FW**	248.2777					
Acquisition Time (sec)	0.6521	**Comment**	Slot No. 37 Sample ID gc4-37-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	05 Apr 2012 05:22:24			**Date Stamp**	05 Apr 2012 05:22:24		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-37-1\9\PDATA\1\1R					**Frequency (MHz)**	100.63
Nucleus	13C	**Number of Transients**	128	**Origin**	dpx400	**Original Points Count**	16384
Owner	nmruser	**Points Count**	32768	**Pulse Sequence**	zgpg30	**Receiver Gain**	20642.50
SW(cyclical) (Hz)	25125.63	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	11018.3350	**Spectrum Type**	STANDARD
Sweep Width (Hz)	25124.86	**Temperature (degree C)**	25.000				

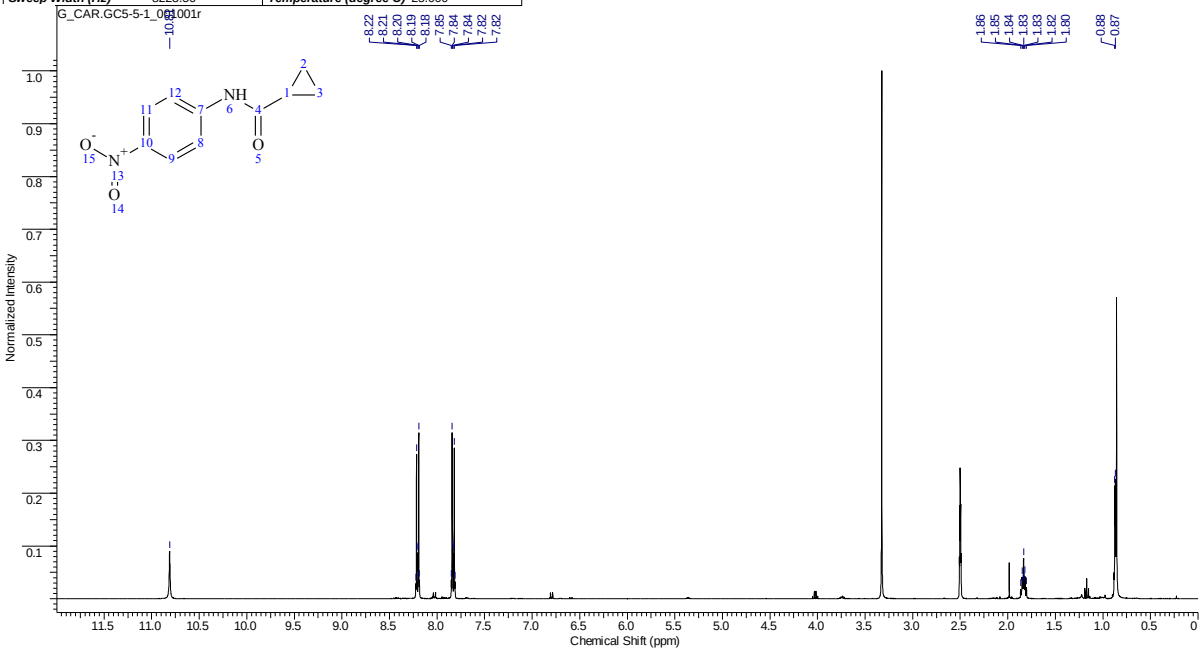
G_CAR.GC4-37-1_009001r



***N*-(4-nitrophenyl)cyclopropanecarboxamide** (Table 2, Entry 12)

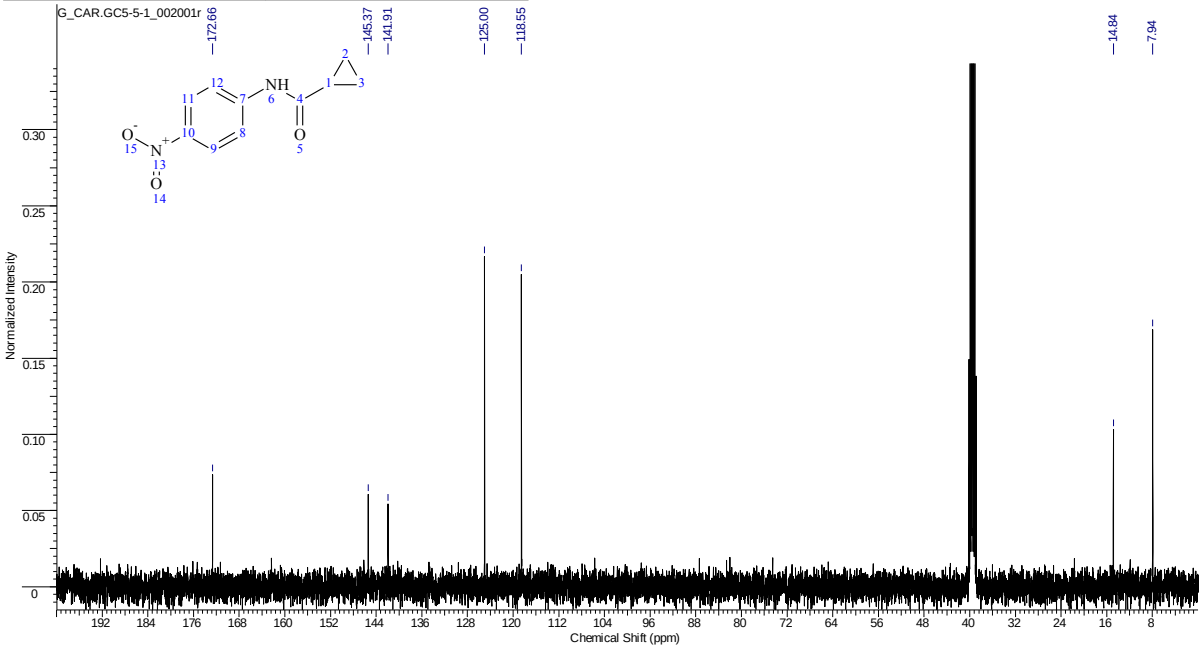
25/05/2012 16:02:26

Formula $C_{10}H_{10}N_2O_3$	***FW*** 206.1980						
Acquisition Time (sec)	3.9846	***Comment***	Slot No. 21 Sample ID gc5-5-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	01 May 2012 18:04:00			***Date Stamp***	01 May 2012 18:04:00		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC5-5-1\1\PDATA\1\1R					***Frequency (MHz)***	400.20
Nucleus	1H	***Number of Transients***	16	***Origin***	dpx400	***Original Points Count***	32768
Owner	nmruser	***Points Count***	65536	***Pulse Sequence***	zg30	***Receiver Gain***	456.10
SW(cyclical) (Hz)	8223.68	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	2465.2061	***Spectrum Type***	STANDARD
Sweep Width (Hz)	8223.56	***Temperature (degree C)***	25.000				



25/05/2012 16:09:08

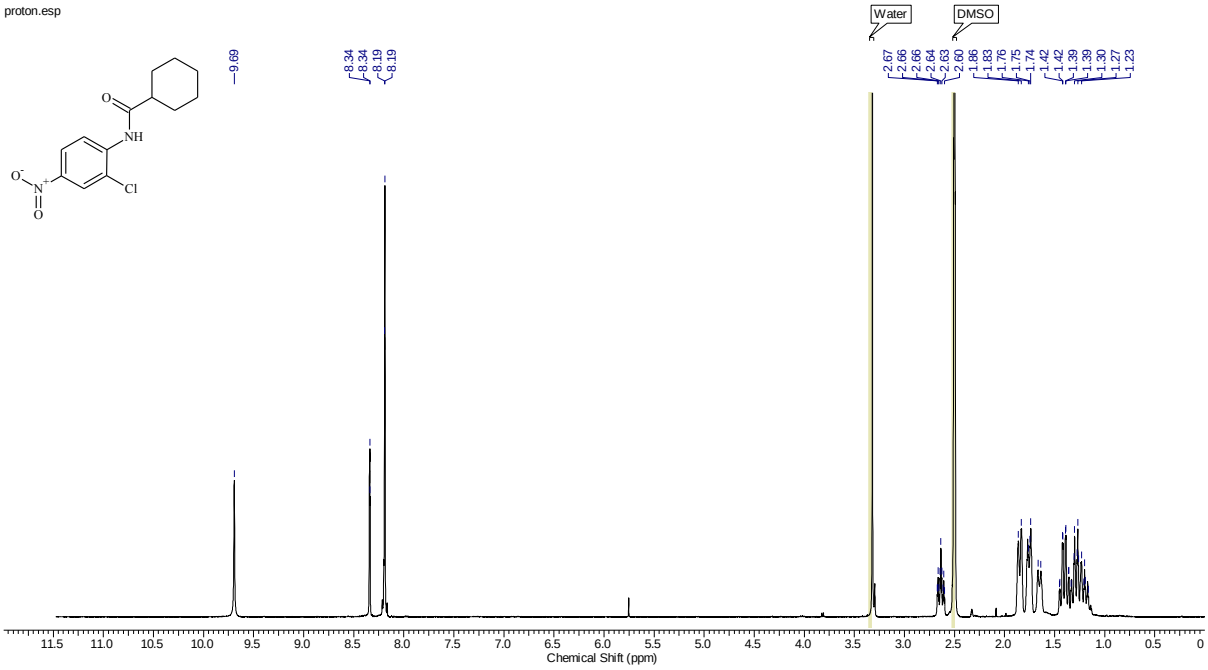
Formula $C_{10}H_{10}N_2O_3$	***FW*** 206.1980						
Acquisition Time (sec)	0.6521	***Comment***	Slot No. 21 Sample ID gc5-5-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	01 May 2012 18:33:52			***Date Stamp***	01 May 2012 18:33:52		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC5-5-1\2\PDATA\1\1R					***Frequency (MHz)***	100.63
Nucleus	13C	***Number of Transients***	128	***Origin***	dpx400	***Original Points Count***	16384
Owner	nmruser	***Points Count***	32768	***Pulse Sequence***	zgpg30	***Receiver Gain***	5160.60
SW(cyclical) (Hz)	25125.63	***Solvent***	DMSO-d6	***Spectrum Offset (Hz)***	11019.1025	***Spectrum Type***	STANDARD
Sweep Width (Hz)	25124.86	***Temperature (degree C)***	25.000				



N-(2-chloro-4-nitrophenyl)cyclohexanecarboxamide (Table 2, Entry 13)

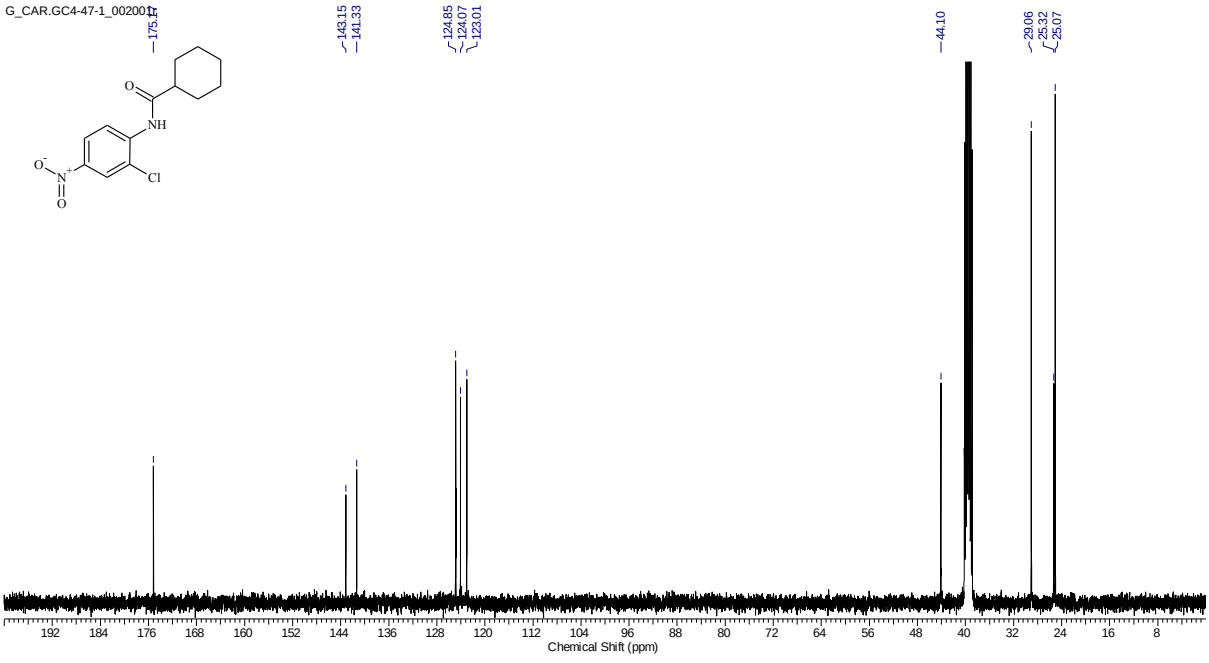
Formula $C_{13}H_{15}ClN_2O_3$		**FW** 282.7228	
Acquisition Time (sec)	3.4210	**Comment**	UserID g_car SampleID gc4-47-1 SupervisorID moses Lab Phone No. 13540 Slot Number 47
Date	04 Apr 2012 04:54:40	**Date Stamp**	04 Apr 2012 04:54:40
File Name	\\brukav400\nmr_data\G_CAR\NMR\G_CAR.GC4-47-1\1\PDATA\1\1R		**Frequency (MHz)** 400.13
Nucleus	1H	**Number of Transients** 16	**Origin** av400 **Original Points Count** 16384
Owner	nmruser	**Points Count** 32768	**Pulse Sequence** zg30 **Receiver Gain** 181.00
SW(cyclical) (Hz)	4789.27	**Solvent** DMSO-d6	**Spectrum Offset (Hz)** 2197.4238 **Spectrum Type** STANDARD
Sweep Width (Hz)	4789.13	**Temperature (degree C)** 25.160	

proton.esp



Formula $C_{13}H_{15}ClN_2O_3$		**FW** 282.7228	
Acquisition Time (sec)	0.6832	**Comment**	UserID g_car SampleID gc4-47-1 SupervisorID moses Lab Phone No. 13540 Slot Number 47
Date	04 Apr 2012 05:54:24	**Date Stamp**	04 Apr 2012 05:54:24
File Name	\\brukav400\nmr_data\G_CAR\NMR\G_CAR.GC4-47-1\2\PDATA\1\1R		**Frequency (MHz)** 100.61
Nucleus	13C	**Number of Transients** 2048	**Origin** av400 **Original Points Count** 16384
Owner	nmruser	**Points Count** 32768	**Pulse Sequence** zgpg30 **Receiver Gain** 11585.20
SW(cyclical) (Hz)	23980.81	**Solvent** DMSO-d6	**Spectrum Offset (Hz)** 11017.3057 **Spectrum Type** STANDARD
Sweep Width (Hz)	23980.08	**Temperature (degree C)** 25.160	

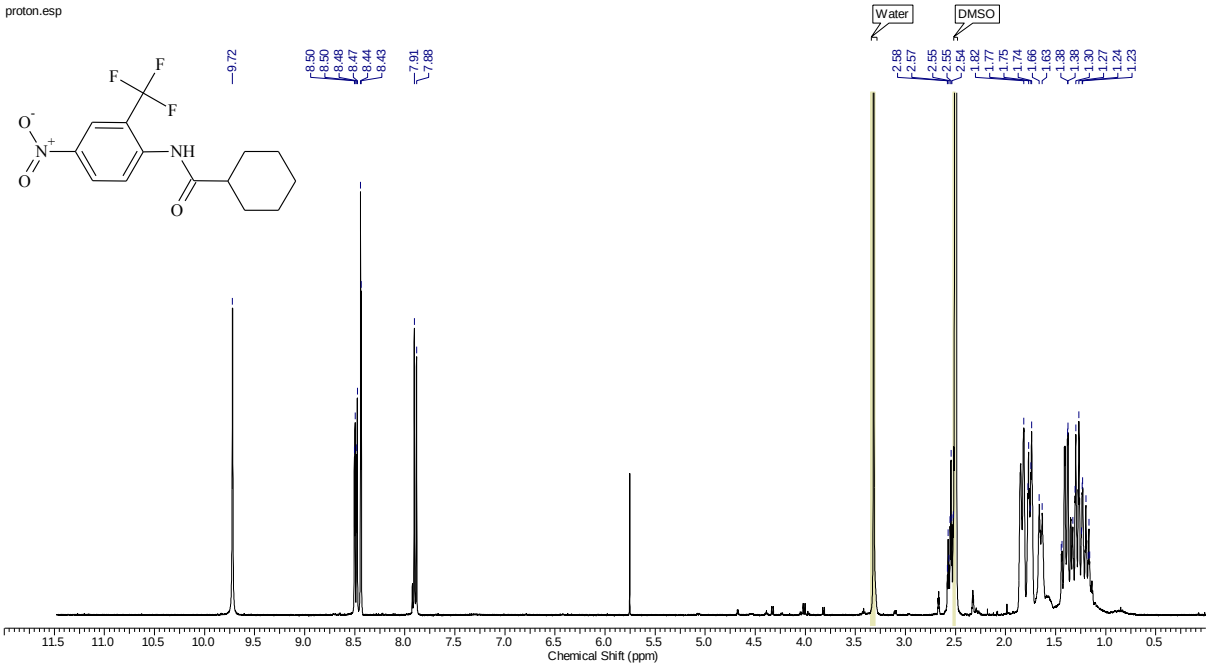
G_CAR.GC4-47-1_002001



N-(4-nitro-2-(trifluoromethyl)phenyl)cyclohexanecarboxamide (Table 2, Entry 14)

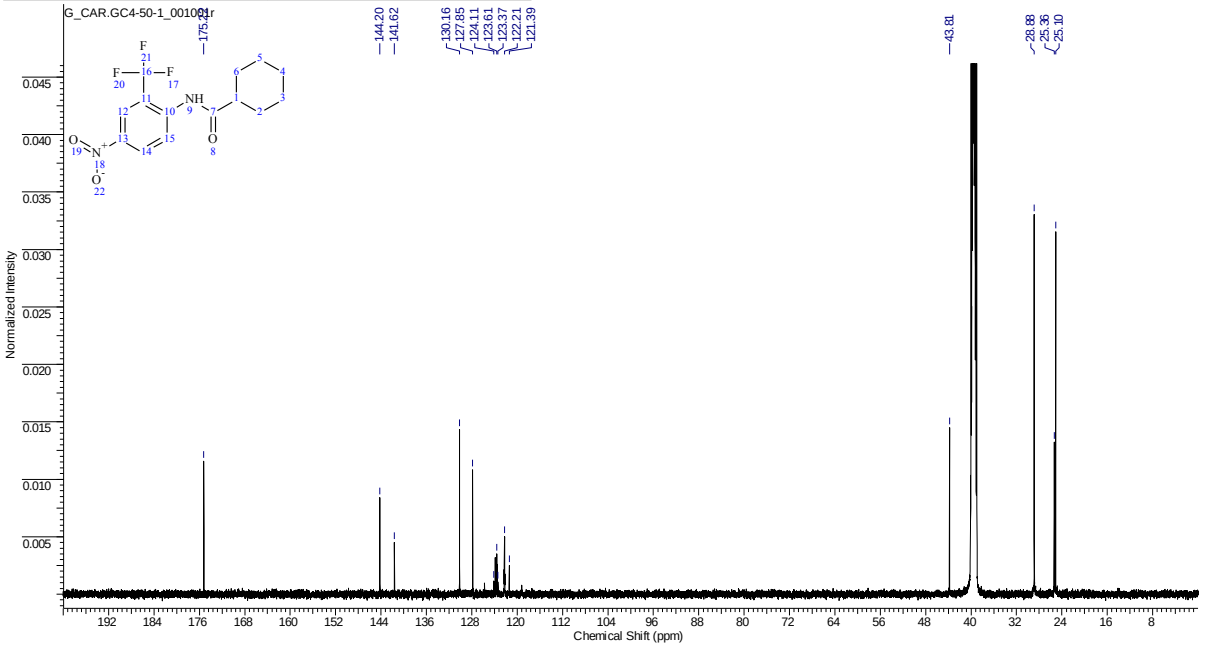
Formula $C_{14}H_{15}F_3N_2O_3$		**FW** 316.2757	
Acquisition Time (sec) 3.4210	**Comment** UserID g_car SampleID gc4-50-1 SupervisorID moses Lab Phone No. 13540 Slot Number 50		
Date 04 Apr 2012 07:09:04		**Date Stamp** 04 Apr 2012 07:09:04	
File Name \\brukav400\nmr_data\G_CAR\NMR\G_CAR.GC4-50-1\1\PDATA\1\1R			**Frequency (MHz)** 400.13
Nucleus 1H	**Number of Transients** 16	**Origin** av400	**Original Points Count** 16384
Owner nmruser	**Points Count** 32768	**Pulse Sequence** zg30	**Receiver Gain** 181.00
SW(cyclical) (Hz) 4789.27	**Solvent** DMSO-d6	**Spectrum Offset (Hz)** 2197.2776	**Spectrum Type** STANDARD
Sweep Width (Hz) 4789.13	**Temperature (degree C)** 25.160		

proton.esp



01/06/2012 15:56:58

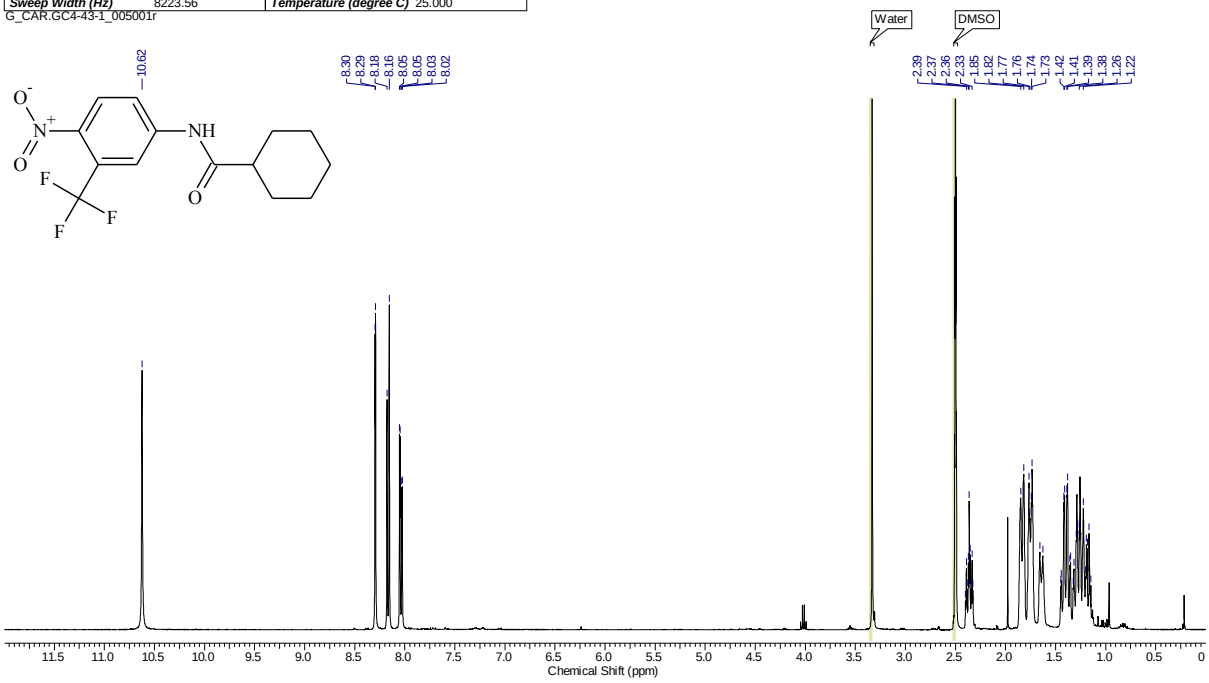
Formula $C_{14}H_{15}F_3N_2O_3$		**FW** 316.2757	
Acquisition Time (sec) 1.1010	**Comment** UserID g_car SampleID gc4-50-1 SupervisorID moses Lab Phone No. 13540 Slot 2		
Date 22 May 2012 12:18:24		**Date Stamp** 22 May 2012 12:18:24	
File Name \\brukav3500\nmr_data\G_CAR\NMR\G_CAR.GC4-50-1\1\PDATA\1\1R			**Frequency (MHz)** 125.76
Nucleus 13C	**Number of Transients** 512	**Origin** av3500	**Original Points Count** 32768
Owner service	**Points Count** 65536	**Pulse Sequence** zgpg30	**Receiver Gain** 2050.00
SW(cyclical) (Hz) 29761.90	**Solvent** DMSO-d6	**Spectrum Offset (Hz)** 13777.2344	**Spectrum Type** STANDARD
Sweep Width (Hz) 29761.45	**Temperature (degree C)** 25.000		



N-(4-nitro-3-(trifluoromethyl)phenyl)cyclohexanecarboxamide (Table 2, Entry 15)

Formula $C_{14}H_{15}F_3N_2O_3$		**FW**	316.2757				
Acquisition Time (sec)	3.9846	**Comment**	Slot No. 43 Sample ID gc4-43-1 SupervisorID moses Lab Phone No. 13540 UserID g_car				
Date	05 Apr 2012 14:17:52			**Date Stamp**	05 Apr 2012 14:17:52		
File Name	\\brukdpx400\nmr_data\G_CAR\NMR\G_CAR.GC4-43-1\5\PDATA\1\1R					**Frequency (MHz)**	400.20
Nucleus	1H	**Number of Transients**	16	**Origin**	dpx400	**Original Points Count**	32768
Owner	nmruser	**Points Count**	65536	**Pulse Sequence**	zg30	**Receiver Gain**	181.00
SW(cyclical) (Hz)	8223.68	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	2465.0808	**Spectrum Type**	STANDARD
Sweep Width (Hz)	8223.56	**Temperature (degree C)**	25.000				

G_CAR.GC4-43-1_005001r



01/06/2012 16:10:47

Formula $C_{14}H_{15}F_3N_2O_3$		**FW**	316.2757				
Acquisition Time (sec)	1.1010	**Comment**	UserID g_car SampleID gc-4-43-1 SupervisorID moses Lab Phone No. 13540 Slot 2				
Date	21 May 2012 14:54:08			**Date Stamp**	21 May 2012 14:54:08		
File Name	\\brukav3500\nmr_data\G_CAR\NMR\G_CAR.GC-4-43-1\1\PDATA\1\1R					**Frequency (MHz)**	125.76
Nucleus	13C	**Number of Transients**	512	**Origin**	av3500	**Original Points Count**	32768
Owner	service	**Points Count**	65536	**Pulse Sequence**	zgpg30	**Receiver Gain**	1030.00
SW(cyclical) (Hz)	29761.90	**Solvent**	DMSO-d6	**Spectrum Offset (Hz)**	13780.8672	**Spectrum Type**	STANDARD
Sweep Width (Hz)	29761.45	**Temperature (degree C)**	25.000