Catalytic, Enantioselective 1,3-Dipolar Cycloadditions of Nitrile Imines with Alkylidine and Arylidine Oxindoles

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General Experimental Details

All air-sensitive procedures were conducted under inert atmosphere in a nitrogen-filled dry box or by standard Schlenk techniques. All reactions were performed under an atmosphere of nitrogen unless otherwise stated. All glassware for moisture sensitive reactions was dried at 140 °C in an oven. THF and CH_2Cl_2 were degassed by purging with argon for 45 minutes and dried

with a solvent purification system by passing through a one-meter column of activated alumina. Flash column chromatography was performed on Fisher brand silica gel 60 (230-400 mesh). Products of reactions were visualized on TLC plates under UV light or by staining with $KMnO_4$, phosphomolybdic acid, or ceric ammonium molybdate.

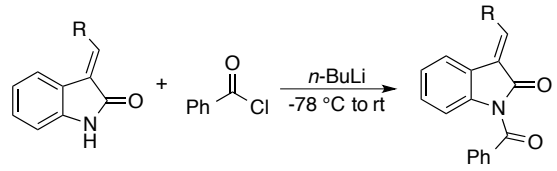
HRMS (ESI) analysis was performed at the Iowa State University Chemical Instrumentation Facility on an Agilent 6540 QTOF spectrometer. Optical rotations were measured on an Atago AP-300 automatic polarimeter. HPLC analyses were carried out on a Water Alliance HPLC system with an e2695 Separations Module and a 2489 (UV/Vis) dual wavelength detector. NMR spectra were acquired on Varian MR-400 and Bruker Avance III 600 spectrometers at the Iowa State University Chemical Instrumentation Facility. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to residual $CHCl_3$ in $CDCl_3$ (7.26 ppm for ^{1}H and 77.23 ppm for ^{13}C). ^{19}F NMR shifts are reported in ppm relative to trifluoroacetic acid as an external standard (F_3CCO_2H = -76.55 ppm).

Materials

Unless otherwise stated, reagents were purchased from Sigma-Aldrich and used without further purification. Methyleneindolinones **S1a-k** were synthesized according to literature procedures from oxindole and the appropriate aldehyde.[1] Methyleneindolinone **1d** was prepared according to a previously reported procedure.[1a] 4-Fluorophenylhydrazine and 4-trifluoromethylphenylhydrazine were purchased from AK Scientific. Hydrazones **S2a-g** were synthesized by stirring an equimolar mixture of the appropriate hydrazines and aldehydes in CH_2Cl_2 (0.33 M) in the presence of $MgSO_4$ until TLC analysis indicated consumption of the aldehyde. Filtration and concentration under reduced pressure afforded the hydrazone which was used without further purification or recrystallized from EtOH if necessary. Hydrazonoyl bromide **2a** was prepared according to a literature procedure from benzaldehyde phenylhydrazone.[2] Bisoxazoline ligand **L2** was prepared according to a previously reported procedure from (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol.[3] (1*R*,2*S*)-(+)-*cis*-1-Amino-2-indanol was purchased from Carbosynth. Magnesium bis(trifluoromethylsulfonyl)imide was purchased from Strem Chemicals and used without further purification. Magnesium perchloroate was purchased from Fisher Scientific and used without further purification. Powdered 4Å molecular sieves were purchased from Sigma-Aldrich and flame-dried under vacuum prior to use. *N*-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) were purchased from Sigma Aldrich and recrystallized from water before use.

1) a) Wang, G., Liu, X., Huang, T., Kuang, Y., Lin, L., Feng, X. *Org. Lett.* **2013,** *15*, 76-79. b) Zhang, W., Go, M. *Bioorg. Med. Chem.* **2009**, *17*, 2077-2090. c) Zhou, F. *Lett. Org. Chem* **2007**, *4*, 601-605.
2) Sibi, M. P., Stanley, L. M., Jasperse, C. P. *J. Am. Chem. Soc.* **2005**, *127*, 8276-8277.
3) Barnes, D. M.; Ji, J.; Fickes, M. G.; Fitzgerald, M. A.; King, S. A.; Morton, H. E.; Plagge, F. A.; Preskill, M.; Wagaw, S. H.; Wittenberger, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 13097-13105.

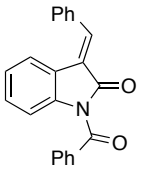
General Procedure for Synthesis of *N*-Acyl Methyleneindolinones 1a, 1e-n



S1a R = Ph
S1b R = 4-MeO-C_6H_4
S1c R = 4-Cl-C_6H_4
S1d R = 4-Br-C_6H_4
S1e R = 4-CF_3-C_6H_4
S1f R = 3-MeO-C_6H_4
S1g R = 3,4,5-MeO-C_6H_2
S1h R = 2-F-C_6H_4
S1i R = 2-Br-C_6H_4
S1j R = (*E*)-*t*-Bu
S1k R = (*Z*)-*t*-Bu

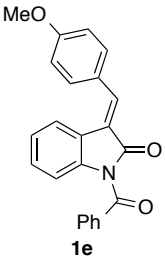
1a R = Ph
1e R = 4-MeO-C_6H_4
1f R = 4-Cl-C_6H_4
1g R = 4-Br-C_6H_4
1h R = 4-CF_3-C_6H_4
1i R = 3-MeO-C_6H_4
1j R = 3,4,5-MeO-C_6H_2
1k R = 2-F-C_6H_4
1l R = 2-Br-C_6H_4
1m R = (*E*)-*t*-Bu
1n R = (*Z*)-*t*-Bu

To a solution of the appropriate methyleneindolinone **S1** (1.0 equiv) in THF (0.1 M) at -78°C was added *n*-BuLi (1.05 equiv as a 2.5 M solution in hexanes). The reaction mixture was allowed to stir for 30 minutes before dropwise addition of benzoyl chloride (1.05 equiv). After addition of benzoyl chloride, the reaction was allowed to warm to room temperature until TLC analysis showed consumption of **S1**. After the reaction was judged to be complete by TLC analysis, the mixture was quenched with saturated ammonium chloride and extracted with ethyl acetate. The organic layer was separated and washed with water and brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting crude product was recrystallized from ethanol to give a mixture of *E*- and *Z*-methyleneindolinone isomers. Pure *E*-methyleneindolinones **1** isolated by fractional recrystallization from ethanol.



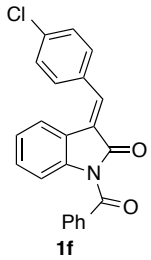
1a

(*E*)-1-Benzoyl-3-benzylideneindolin-2-one (1a): Prepared according to the general procedure from **S1a** (5.50 g, 24.9 mmol) to give **1a** (5.27 g, 16.2 mmol, 65%) as a yellow solid. m.p. = 153-154 °C **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 7.07 (dt, *J* = 7.8, 1.2 Hz 1H), 7.37 (dt, *J* = 1.2, 8.4 Hz 1H), 7.44-7.54 (m, 5H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.64-7.69 (m, 2H), 7.76 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.79-7.82 (m, 2H), 7.83 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 115.4, 122.3, 122.7, 124.5, 126.1, 128.3, 129.0, 129.4, 129.6, 130.3, 130.4, 133.0, 134.6, 134.7, 139.2, 140.7, 167.8, 169.6. **HRMS** (ESI) calcd. for $C_{22}H_{16}NO_2^+$ $[M+H]^+$ 326.1181, found 326.1178.



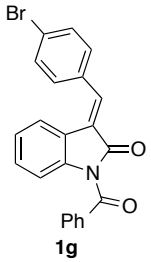
1e

(*E*)-1-Benzoyl-3-(4-methoxybenzylidene)indolin-2-one (1e): Prepared according to the general procedure from **S1b** (2.50 g, 9.95 mmol) to give **1e** (2.32 g, 6.27 mmol, 63%) as a yellow solid. m.p. = 160-162 °C **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.90 (s, 3H), 7.01 (d, *J* = 8.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.75-7.83 (m, 3H), 7.86-7.96 (m, 2H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 55.5, 114.3, 115.2, 122.2, 122.6, 123.9, 124.2, 126.8, 128.2, 129.5, 129.8, 131.6, 132.7, 134.7, 139.3, 140.2, 161.3, 168.0, 169.6. **HRMS** (ESI) calcd. for $C_{23}H_{18}NO_3^+$ $[M+H]^+$ 356.1287, found 356.1272.



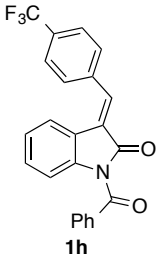
1f

(*E*)-1-Benzoyl-3-(4-chlorobenzylidene)indolin-2-one (1f): Prepared according to the general procedure from **S1c** (1.00 g, 7.82 mmol) to give **1f** (0.52 g, 2.9 mmol, 37%) as a yellow solid. m.p. = 203-205 °C **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.08 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.43-7.54 (m, 4H), 7.55-7.65 (m, 3H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.74 (s, 1H), 7.79 (d, *J* = 7.2 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 115.5, 122.1, 122.7, 124.6, 126.6, 128.4, 129.3, 129.7, 130.7, 130.8, 133.0, 133.1, 134.6, 136.2, 137.5, 140.8, 167.6, 169.6. **HRMS** (ESI) calcd. for $C_{22}H_{15}NO_2F^+$ $[M+H]^+$ 360.0791, found 360.0790.



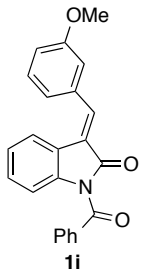
1g

(*E*)-1-Benzoyl-3-(4-bromobenzylidene)indolin-2-one (1g): Prepared according to the general procedure from **S1d** (2.00 g, 6.66 mmol) to give **1g** (1.28 g, 3.19 mmol, 48%) as yellow solid. m.p. = 182-186 °C **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.08 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.44-7.56 (m, 4H), 7.58-7.66 (m, 3H), 7.67-7.73 (m, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 115.6, 122.1, 122.7, 124.5, 124.6, 126.7, 128.4, 129.7, 130.7, 130.9, 132.3, 133.1, 133.5, 134.6, 137.5, 140.9, 167.6, 169.6. **HRMS** (ESI) calcd. for $C_{22}H_{15}NO_2Br^+$ $[M+H]^+$ 404.0286, found 404.0285.



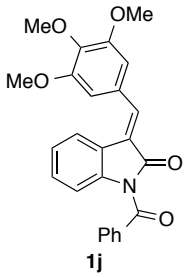
1h

(*E*)-1-Benzoyl-3-(4-(trifluoromethyl)benzylidene)indolin-2-one (1h): Prepared according to the general procedure from **S1e** (1.00 g, 3.46 mmol) to give **1h** (0.40 g, 1.0 mmol, 29%) as a yellow solid. m.p. = 175-177 °C **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 7.09 (t, *J* = 7.8 Hz, 1H) 7.41 (t, *J* = 7.8 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.58-7.66 (m, 2H), 7.74-7.83 (m, 7H), 7.93 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 115.7, 121.8, 122.9, 124.0 (q, *J* = 272.3 Hz), 124.7, 126.0 (q, *J* = 3.5 Hz) 128.0, 128.4, 129.5, 129.7, 131.1, 131.8 (q, *J* = 31.4 Hz), 133.2, 134.5, 136.5, 138.3, 141.1, 167.4, 169.5. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -63.5. **HRMS** (ESI) calcd. for $C_{23}H_{15}F_3NO_2^+$ $[M+H]^+$ 394.1055, found 394.1062.



1i

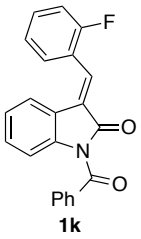
(*E*)-1-Benzoyl-3-(3-methoxybenzylidene)indolin-2-one (1i): Prepared according to the general procedure from **S1f** (5.00 g, 21.6 mmol) to give **1i** (4.09 g, 12.5 mmol, 58%) as a yellow solid. m.p. = 135-137 °C **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 3.85 (s, 3H), 7.01 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.08 (dt, *J* = 1.2, 12.0 Hz, 1H), 7.16 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.34-7.44 (m, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.77-7.82 (m, 4H), 7.92 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 55.6, 114.4, 115.4, 116.2, 121.8, 122.3, 123.0, 124.5, 126.4, 128.4, 129.6, 130.1, 130.4, 133.0, 134.7, 135.9, 139.0, 140.7, 160.0, 167.8, 169.6. **HRMS** (ESI) calcd. for $C_{23}H_{18}NO_3^+$ $[M+H]^+$ 356.1287, found 356.1283.



1j

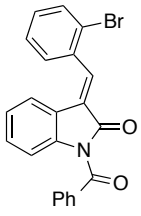
(*E*)-1-Benzoyl-3-(3,4,5-trimethoxybenzylidene)indolin-2-one (1j): Prepared according to the general procedure from **S1g** (7.50 g, 24.09 mmol) to give **1j** (2.67 g, 6.50 mmol, 27%) as a yellow solid. m.p. =191-192 °C **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 3.86 (s, 6H), 3.91 (s, 3H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.55 (s, 1H), 7.56-7.60 (m, 3H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.77-7.83 (m, 3H). **^{13}C NMR** ($CDCl_3$, 151 MHz,) δ 56.3, 61.0, 110.1, 114.7, 118.7, 123.5, 124.4, 125.5, 128.1, 128.9, 129.1, 129.6, 132.7, 134.6, 138.6, 139.2, 141.0, 152.7, 165.6, 169.8. **HRMS** (ESI) calcd. for

$C_{25}H_{22}NO_5^+$ $[M+H]^+$ 416.1498 found 416.1493.



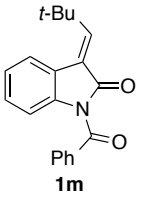
1k

(*E*)-1-Benzoyl-3-(2-fluorobenzylidene)indolin-2-one (1k): Prepared according to the general procedure from **S1h** (1.00 g, 4.18 mmol) to give **1k** (0.83 g, 2.4 mmol, 58%) as a yellow solid. m.p. = 209-211 °C **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 7.08 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.21 (t, *J* = 9.6 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.45-7.53 (m, 3H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.71 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.78-7.82 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 115.5, 116.5 (d, *J* = 21.1 Hz), 122.2, 122.8 (d, *J* = 14.7 Hz), 123.0, 124.4 (d, *J* = 3.6 Hz), 124.6, 128.0, 128.4, 129.7, 130.4, 130.8, 131.4, 132.2 (d, *J* = 8.4 Hz), 133.1, 134.7, 140.9, 160.7 (d, *J* = 252.5 Hz), 167.3, 169.6 **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -110.1 **HRMS** (ESI) calcd. for $C_{22}H_{15}NO_2F^+$ $[M+H]^+$ 344.1087, found 344.1087.



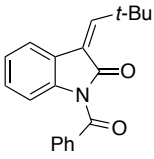
1l

(*E*)-1-Benzoyl-3-(2-bromobenzylidene)indolin-2-one (1l): Prepared according to the general procedure from **S1i** (1.20 g, 4.00 mmol) to give **1l** (0.70 g, 1.7 mmol, 43%) as a yellow solid. m.p. = 197-199 °C **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 7.03 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.30-7.45 (m, 4H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.62 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.72 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.78-7.82 (m, 3H), 7.92 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 115.5, 121.8, 122.8, 124.2, 124.4, 127.2, 127.4, 128.2, 129.4, 130.0, 130.6, 131.2, 132.8, 133.4, 134.5, 135.1, 137.2, 140.7, 167.1, 169.4. **HRMS** (ESI) calcd. for $C_{22}H_{15}NO_2Br^+$ $[M+H]^+$ 404.0286 found 404.0280.



1m

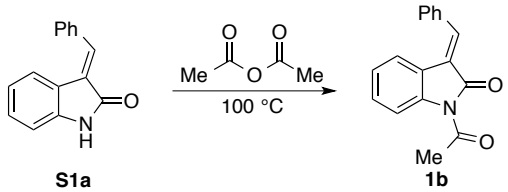
(*E*)-1-Benzoyl-3-(2,2-dimethylpropylidene)indolin-2-one (1m): Prepared according to a modified version of the general procedure from **S1j** (5.30 g, 26.3 mmol) to give **1m** (0.77 g, 2.63 mmol, 10%) as a light green oil. Compound **1m** was purified by flash column chromatography (98:2 hexanes:EtOAc) instead of purification by recrystallization. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.18 (s, 9H), 6.95-7.05 (m, 2H), 7.11 (t, *J* = 3.6 Hz, 1H), 7.22 (t, *J* = 4.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.51-7.57 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 28.9, 32.7, 114.9, 121.4, 124.1, 125.4, 126.1, 127.9, 129.0, 129.3, 132.5, 134.5, 140.4, 154.7, 167.8, 169.2. **HRMS** (ESI) calcd. for $C_{20}H_{20}NO_2^+$ $[M+H]^+$ 306.1494, found 306.1496.



1n

(*Z*)-1-Benzoyl-3-(2,2-dimethylpropylidene)indolin-2-one (1n): Prepared according to a modified version of the general procedure from **S1k** (5.30 g, 26.3 mmol) to give **1n** (0.21 g, 0.68 mmol, 3%) as a light green oil. Compound **1n** was purified by flash column chromatography (98:2 hexanes:EtOAc) instead of purification by recrystallization. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.36 (s, 9H), 7.07 (s, 1H) 7.16 (dt, *J* = 0.8, 7.6 Hz 1H), 7.31 (dt, *J* = 1.2, 8.0 Hz 1H), 7.41-7.50 (m, 3H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.72-7.78 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 29.3, 34.0, 114.9, 118.8, 124.4, 125.0, 125.9, 128.3, 129.0, 129.5, 132.8, 134.8, 138.8, 155.2, 165.0, 169.8. **HRMS** (ESI) calcd. for $C_{20}H_{20}NO_2^+$ $[M+H]^+$ 306.1494, found 306.1493.

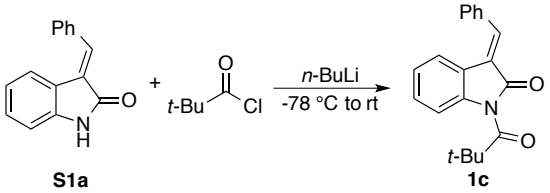
Synthesis of (*E*)-1-Acetyl-3-benzylideneindolin-2-one 1b



S1a **1b**

A suspension of (*E*)-3-benzylideneindolin-2-one **S1a** (13.5 g, 61 mmol) in acetic anhydride (300 mL) was heated to 100 ºC (bath temperature) with stirring overnight, during which time the suspension cleared to a deep red-brown solution. The mixture was cooled and poured into 1.4 L of H_2O. A yellow-orange product precipitated and was dissolved by shaking with 300 mL of 1:1 ^{t}BuOMe:Et_2O. The organic layer was separated, and the aqueous layer was extracted twice more with 300 mL of 1:1 ^{t}BuOMe:Et_2O. The combined organic extracts were washed with aqueous 2M NaOH (2 x 350 mL), H_2O (2 x 500 mL), and brine (1 x 300 mL), then dried over Na_2SO_4. Filtration and concentration under reduced pressure afforded a crude orange-red solid, which was recrystallized from EtOH (~125 mL), to afford the **1b** (11.2 g, 42.5 mmol, 70%) as yellow needles. m. p. = 123-124 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.77 (s, 3H), 7.04 (t, *J* = 7.6 Hz, 1H), 7.33 (dt, *J* = 0.8, 8.0 Hz, 1H), 7.42-7.53 (m, 3H), 7.61-7.67 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.89 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 27.1, 116.9, 122.1, 122.4, 124.7, 126.3, 129.0, 129.4, 130.3, 130.5, 134.6, 138.9, 140.5, 168.8, 171.1. **HRMS** (ESI) calcd. For $C_{17}H_{14}NO_2^+$ $[M+H]^+$ 264.1025, found 264.1023.

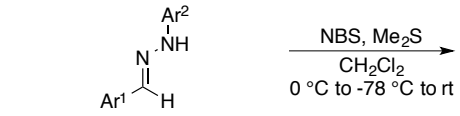
Synthesis of (*E*)-3-benzylidene-1-pivaloylindolin-2-one 1c



S1a **1c**

To a solution of **S1a** (0.50 g, 2.24 mmol) in THF (50 ml) at -78°C was added *n*-BuLi (1.10 equiv as a 2.5 M solution in hexanes). The reaction mixture was allowed to stir for 30 minutes before dropwise addition of pivaloyl chloride (1.05 equiv). After addition of pivaloyl chloride, the reaction was allowed to warm to room temperature until TLC analysis showed consumption of **S1a**. After the reaction was judged to be complete by TLC analysis, the mixture was quenched with saturated ammonium chloride and extracted with ethyl acetate. The organic layer was separated and washed with water and brine. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Crude mixture was purified by flash column chromatography to afford **1c** in 75% yield (0.512 g, 1.68 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.25 (s, 9H), 6.88 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.42-7.50 (m, 3H), 7.63-7.69 (m, 3H), 7.85 (s, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 27.3, 38.8, 110.5, 121.9, 122.2, 123.3, 127.7, 128.9, 129.6, 123.0, 130.1, 135.0, 138.1, 141.7, 170.8, 184.1. **HRMS** (ESI) calcd. For $C_{20}H_{20}NO_2^+$ $[M+H]^+$ 306.1489, found 306.1492.

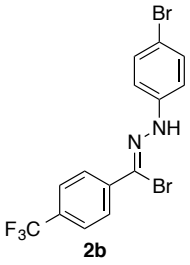
General Procedure for Synthesis of Hydrazonoyl Bromides 2b-g



S2a Ar^1 = Ph Ar^2 = Ph
S2b Ar^1 = 4-CF_3-C_6H_4, Ar^2 = Ph
S2c Ar^1 = 3-Br-C_6H_4, Ar^2 = Ph
S2d Ar^1 = 2-F-C_6H_4, Ar^2 = Ph
S2e Ar^1 = 2-Br-C_6H_4, Ar^2 = Ph
S2f Ar^1 = Ph, Ar^2 = 4-F-C_6H_4
S2g Ar^1 = Ph, Ar^2 = 4-CF_3-C_6H_4

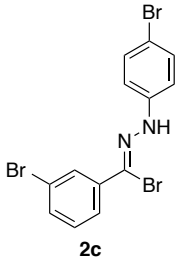
2a Ar^1 = Ph Ar^2 = 4-Br-C_6H_4
2b Ar^1 = 4-CF_3-C_6H_4, Ar^2 = 4-Br-C_6H_4
2c Ar^1 = 3-Br-C_6H_4, Ar^2 = 3-Br-C_6H_4
2d Ar^1 = 2-F-C_6H_4, Ar^2 = 3-Br-C_6H_4
2e Ar^1 = 2-Br-C_6H_4, Ar^2 = 3-Br-C_6H_4
2f Ar^1 = Ph, Ar^2 = 4-F-C_6H_4
2g Ar^1 = Ph, Ar^2 = 4-CF_3-C_6H_4

The following general procedure was adapted from the literature.[2] To a suspension of NBS (3 equiv) in dry CH_2Cl_2 [0.2M] at 0 ºC under N_2 was added Me_2S (6 equiv). After stirring for 15 min at 0 ºC, the mixture was cooled to -78 ºC for 10 min and a solution of the appropriate hydrazone **S2a-g** (1 equiv) in CH_2Cl_2 [0.5M] was added. The reaction was stirred at -78 ºC for 1 hr and then warmed to RT for 4 hr at which point the heterogeneous reaction mixture was filtered through a plug of silica gel, rinsing with 10 % EtOAc/hexanes, to remove the solid precipitates. The resulting solution was concentrated *in vacuo*, and the residue was purified by flash column chromatography on silica gel using 30% CH_2Cl_2/hexanes as eluent. This eluent system typically afforded better separation between the desired hydrazonoyl bromide and the hydrazone resulting from dehalogenation at the formyl position. Chromatography was performed as rapidly as possible due to the instability of the hydrazonoyl bromides on silica gel.



2b

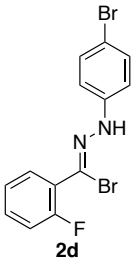
(*Z*)-*N*′-(4-bromophenyl)-4-(trifluoromethyl)benzohydrazonoyl bromide (2b): Prepared according to the general procedure from (*E*)-1-(4-bromophenyl)-2-(4-(trifluoromethyl)benzylidene)hydrazine **S2b** (1.50 g, 5.68 mmol) and the Corey-Kim complex of NBS (3.03 g, 17.0 mmol) and dimethyl sulfide (2.11 g, 2.50 mL, 34.08 mmol) as the brominating agent. After chromatography, the title compound **2b** was isolated as a pink solid in 29% yield (0.700 g, 1.66 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.07 (dd, *J* = 1.2, 7.8 Hz, 2H), 7.43 (dd, *J* = 1.2, 7.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 8.13 (s, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz): δ 114.2, 115.6, 118.6, 124.1 (q, *J* = 272.3 Hz), 125.6 (q, *J* = 3.8 Hz), 127.9, 131.3 (q, *J* = 32.5 Hz), 132.6, 138.9 (q, *J* = 1.4 Hz), 141.9. **^{19}F NMR** ($CDCl_3$, 565 MHz): δ -63.2. **HRMS** (ESI) calcd. for $C_{28}H_{17}Br_2F_6N_4^+$ [nitrile imine dimer + H]$^+$ 680.9719, found 680.9716.



2c

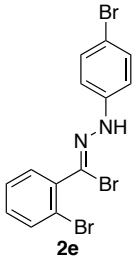
(*Z*)-3-bromo-*N*-(4-bromophenyl)benzohydrazonoyl bromide (2c): Prepared according to the general procedure from (*E*)-1-(3-bromobenzylidene)-2-(4-bromophenyl)hydrazine S**2c** (0.825 g, 3.00 mmol) and the Corey-Kim complex of NBS (1.60 g, 9.00 mmol) and dimethyl sulfide (1.12 g, 1.32 mL, 18.0 mmol) as the brominating agent. After chromatography, the title compound **2c** was isolated as a red/purple solid in 67% yield (0.900 g, 2.00 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.06 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 9.8, 7.8 Hz, 1H), 7.42 (d, *J* = 8.8 Hz), 7.49 (ddd, *J* = 9.0, 1.8, 1.2 Hz, 1H), 7.81 (ddd J = 7.8, 1.8, 1.2 Hz), 8.02 (t, *J* = 1.8 Hz, 1H), 8.05 (s, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz): δ 113.9, 115.5, 118.4, 122.8, 126.4, 130.1, 130.5, 132.5 (two coincident signals, as determined by HSQC),

137.6, 142.0. **HRMS** (ESI) calcd. for $C_{26}H_{17}Br_4N_4^+$ [nitrile imine dimer + H]$^+$ 700.8181, found 700.8170.



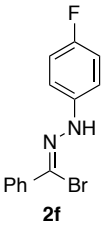
2d

(*Z*)-*N*′-(4-bromophenyl)-2-fluorobenzohydrazonoyl bromide (2e): Prepared according to the general procedure from (*E*)-1-(4-bromophenyl)-2-(2-fluorobenzylidene)hydrazine **S2e** (2.48 g, 11.58 mmol) and the Corey-Kim complex of NBS (6.18 g, 34.73 mmol) and dimethyl sulfide (4.31 g, 5.10 mL, 69.5 mmol) as the brominating agent. After chromatography, the title compound **2e** was isolated as a red solid in 28% yield (1.22 g, 3.30 mmol). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.03-7.08 (m, 2H), 7.13 (ddd, *J* = 10.2, 8.9, 1.2 Hz, 1H), 7.21 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.31-7.37 (m, 1H), 7.37-7.42 (m, 2H), 7.66 (dt, *J* = 1.8, 7.6 Hz, 1H), 8.07 (s, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 112.7 (d, *J* = 4.9 Hz), 113.7, 115.5, 116.7 (d, *J* = 22.3 Hz), 124.2 (d, *J* = 3.9 Hz), 124.6 (d, *J* = 10.4 Hz), 131.1 (d, *J* = 8.6 Hz), 131.5, 132.5, 142.1, 159.7 (d, *J* = 257.4 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -112.88. **HRMS** (ESI) calcd. for $C_{26}H_{17}Br_2F_2N_4^+$ [nitrile imine dimer + H]$^+$ 580.9783, found 580.9773.



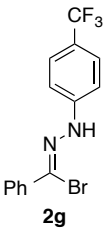
2e

(*Z*)-2-bromo-*N*′-(4-bromophenyl)benzohydrazonoyl bromide (2e): Prepared according to the general procedure from (*E*)-1-(2-bromobenzylidene)-2-(4-bromophenyl)hydrazine **S2e** (2.00 g, 7.27 mmol) and the Corey-Kim complex of NBS (3.88 g, 21.81 mmol) and dimethyl sulfide (2.70 g, 3.20 mL, 43.6 mmol) as the brominating agent. After chromatography, the title compound **2e** was isolated as a brown solid in 32% yield (1.00 g, 2.30 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.06 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.37-7.39 (m, 3H), 7.5 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz): δ 113.7, 115.5, 115.6, 122.6, 127.6, 130.9, 131.9, 132.4, 133.8, 137.8, 142.2. **HRMS** (ESI) for $C_{26}H_{17}Br_4N_4^+$ [nitrile imine dimer + H]$^+$ 700.8181, found 700.8169.



2f

(*Z*)-*N*′-(4-fluorophenyl)benzohydrazonoyl bromide (2f): Prepared according to the general procedure using (*E*)-1-benzylidene-2-(4-fluorophenyl)hydrazine (2.5 g, 11.67 mmol) and the Corey-Kim complex of NBS (6.23 g, 35.01 mmol) and dimethyl sulfide (4.35 g, 5.14 mL, 70.01 mmol) as the brominating agent. Upon chromatography, the title compound **X** was isolated as a red solid in 54% yield (1.84 g, 6.29 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 6.99-7.06 (m, 2H), 7.11-7.16 (m, 2H), 7.34-7.43 (m, 3H), 7.87-7.92 (m, 2H), 7.98 (s, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz): δ 114.9 (d, *J* = 7.7 Hz), 116.2 (d, *J* = 22.8 Hz), 119.7, 127.9, 128.6, 129.6, 135.9, 139.7 (d, *J* = 2.3 Hz), 158.1 (d, *J* = 239.2 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -123.5. **HRMS** (ESI) calcd. for $C_{26}H_{19}F_2N_4^+$ [nitrile imine dimer + H]$^+$ 425.1572, found 425.1569.

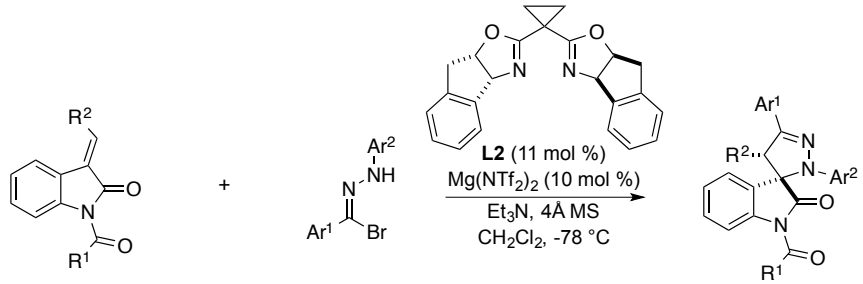


2g

(*Z*)-*N*′-(4-(trifluoromethyl)phenyl)benzohydrazonoyl bromide (2g): Prepared according to the general procedure from (*E*)-1-benzylidene-2-(4-(trifluoromethyl)phenyl)hydrazine **S2g** (0.700 g, 2.65 mmol) and the Corey-Kim complex of NBS (1.41 g, 7.95 mmol) and dimethyl sulfide (0.99 g, 1.17 mL, 15.9 mmol) as the brominating agent. After chromatography, the title compound **2g** was isolated as a red solid in 44% yield (0.400 g, 1.17 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 7.24 (d, *J* = 8.4 Hz, 2H), 7.38-7.46 (m, 3H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.86-7.96 (m, 2H), 8.20 (s, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz): δ 113.5, 121.7, 123.2 (q, *J* = 32.8

Hz), 124.7 (q, J = 270.9 Hz), 127.0 (q, J = 3.8 Hz), 128.1, 128.7, 130.1, 135.6, 145.8 (q, J = 1.2 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -62.0. **HRMS** (ESI) calcd. for $C_{28}H_{19}F_6N_4^+$ [nitrile imine dimer + H]$^+$ 525.1508, found 525.1508.

General Procedure for Synthesis of Spiro[pyrazolin-3,3′-oxindoles] 3a-t

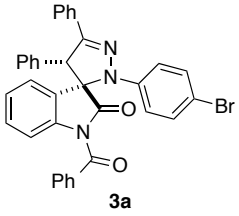


3a-t

1a R^1 = Ph, R^2 = Ph
1b R^1 = Me, R^2 = Ph
1c R^1 = *t*-Bu, R^2 = Ph
1d R^1 = O*t*-Bu, R^2 = Ph
1e R^1 = Ph, R^2 = 4-MeO-C_6H_4
1f R^1 = Ph, R^2 = 4-Cl-C_6H_4
1g R^1 = Ph, R^2 = 4-Br-C_6H_4
1h R^1 = Ph, R^2 = 4-CF_3-C_6H_4
1i R^1 = Ph, R^2 = 3-MeO-C_6H_4
1j R^1 = Ph, R^2 = 3,4,5-MeO-C_6H_2
1k R^1 = Ph, R^2 = 2-F-C_6H_4
1l R^1 = Ph, R^2 = 2-Br-C_6H_4
1m R^1 = Ph, R^2 = (*E*)-*t*-Bu
1n R^1 = Ph, R^2 = (*Z*)-*t*-Bu

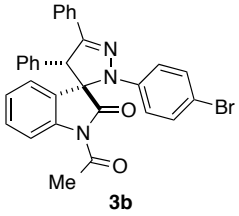
2a Ar^1 = Ph Ar^2 = 4-Br-C_6H_4
2b Ar^1 = 4-CF_3-C_6H_4, Ar^2 = 4-Br-C_6H_4
2c Ar^1 = 3-Br-C_6H_4, Ar^2 = 3-Br-C_6H_4
2d Ar^1 = 2-F-C_6H_4, Ar^2 = 3-Br-C_6H_4
2e Ar^1 = 2-Br-C_6H_4, Ar^2 = 3-Br-C_6H_4
2f Ar^1 = Ph, Ar^2 = 4-F-C_6H_4
2g Ar^1 = Ph, Ar^2 = 4-CF_3-C_6H_4

In a nitrogen-filled dry-box, $Mg(NTf_2)_2$ (11.7 mg, 0.0200 mmol, 0.100 equiv), **L2** (7.8 mg, 0.022 mmol, 0.11 equiv), the appropriate methyleneindolinone **1** (0.200 mmol, 1.00 equiv), and powdered 4Å molecular sieves (100 mg) were added to a 1-dram vial. The appropriate hydrazonoyl bromide **2** (0.240 mmol, 1.20 equiv) was added to a second 1-dram vial. Both vials were sealed with a PFTE/silicone-lined septum cap and removed from the dry-box. The mixture of $Mg(NTf_2)_2$, **L2**, methyleneindolinone **1**, and 4Å molecular sieves was suspended in CH_2Cl_2 (1 mL), allowed to stir for 15 minutes at room temperature, and cooled to -78 °C in a dry ice/acetone bath. Hydrazonoyl bromide **2** was dissolved in CH_2Cl_2 (1 mL) and added to the mixture of catalyst, dipolarophile and 4Å molecular sieves. The resulting mixture was allowed to stir for five minutes at -78 °C, then triethylamine (33 μL, 0.24 mmol) was added to initiate the cycloaddition reaction. The reaction mixture was allowed to stir for 4 h at -78 °C and monitored by TLC. Upon consumption of the methyleneindolinone **1**, the reaction mixture was filtered through a pad of silica (eluting with EtOAc). The crude reaction mixture was concentrated under reduced pressure. $CDCl_3$ (0.5-0.7 mL) was added to dissolve the crude reaction mixture, and the diastereomeric ratio was determined by ^{1}H NMR spectroscopy. The crude reaction mixture was purified by flash column silica gel chromatography (hexanes:EtOAc) to yield spiro[pyrazolin-3,3′-oxindoles] **3a-t**.



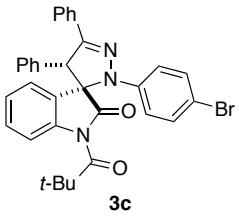
3a

(3S,4′S)-1-Benzoyl-2′-(4-bromophenyl)-4′,5′-diphenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3a) (Table 1, entry 5): Prepared according to the general procedure at half of the typical scale from **1a** (32.5 mg, 0.100 mmol) and **2a** (42.5 mg, 0.120 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3a** (58.5 mg, 0.98 mmol, 98%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.1 min (major); t_R 14.7 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 92% ee. $[\alpha]_D^{25}$ = -495.6° (c 0.46, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 5.10 (s, 1H), 6.44 (d, *J* = 7.2 Hz, 1H), 6.78-6.90 (m, 3H), 7.06 (bs, 2H), 7.18-7.42 (m, 13H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.60-7.72 (m, 2H), 7.77 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 63.1, 77.8, 114.9, 115.6, 119.6, 124.7, 125.0, 126.8, 127.2, 128.5, 128.6, 128.7, 129.2, 129.5, 129.6, 130.5, 131.1, 132.2, 133.5, 133.6, 134.0, 140.1, 144.3, 151.3, 169.3, 174.9. **HRMS** (ESI) calcd. for $C_{35}H_{25}N_3O_2Br^+$ $[M+H]^+$ 598.1130, found 598.1129.



3b

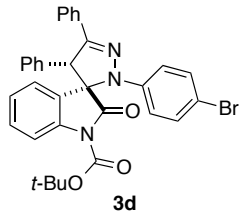
(3S,4′S)-1-Acetyl-2′-(4-bromophenyl)-4′,5′-diphenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3b) (Table 1, entry 9): Prepared according to the general procedure from **1b** (52.7 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3b** (81.3 mg, 0.152 mmol, 76%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.7 min (major); t_R 13.9 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 94% ee. $[\alpha]_D^{25}$ = -436.8° (c 0.55, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 2.76 (s, 3H), 5.19 (s, 1H), 6.51 (d, *J* = 7.2 Hz, 1H), 6.82-6.90 (m, 3H), 7.03 (bs, 2H), 7.22-7.42 (m, 9H), 7.73-7.81 (m, 2H), 8.32 (d, *J* = 7.8 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 26.8, 63.8, 77.2, 114.2, 116.8, 117.5, 124.2, 125.2, 126.0, 127.1, 128.6, 128.7, 129.0, 129.3, 129.4, 130.3, 131.3, 132.1, 133.8, 139.5, 143.3, 149.5, 170.7, 176.5. **HRMS** (ESI) calcd. for $C_{30}H_{23}BrN_3O_2^+$ $[M+H]^+$ 536.0974, found 536.0969.



3c

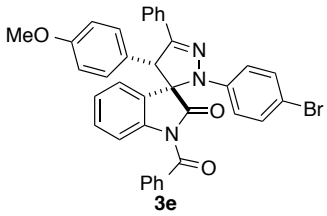
(3*S*,4′*S*)-2′-(4-bromophenyl)-4′,5′-diphenyl-1-pivaloyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3c) (Table 1, entry 10): Prepared according to the general procedure at half of the typical scale from **1c** (30.5 mg, 0.100 mmol) and **2a** (42.5 mg, 0.120 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3c** (56.0 mg, 0.97 mmol, 97%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.8 min (major); t_R 28.9 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 40% ee. $[\alpha]_D^{23}$ = -84.0° (c 0.88, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.24 (s, 9H), 5.16 (s, 1H), 6.35 (d, *J* = 7.2 Hz, 1H), 6.60 (t, *J* = 7.8 Hz, 1H), 6.77-6.82 (m, 2H), 6.96 (bs, 2H), 7.09 (t, *J* =7.8 Hz, 1H), 7.12-7.21 (m, 5H), 7.27-7.30 (m, 3H), 7.64-7.69 (m, 2H), 8.57 (s, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 27.2, 38.7, 62.9, 77.2, 110.7, 113.7, 117.2, 122.9, 125.4, 126.7, 127.1, 128.3, 128.6, 128.9, 129.2, 129.3, 129.9, 131.6, 132.0, 134.6, 134.0,

143.5, 149.8, 178.4, 184.1.**HRMS** (ESI) calcd. for $C_{28}H_{20}BrN_3O^+$ $[M-C_5H_9O]^+$ 494.0863, found 494.0861.



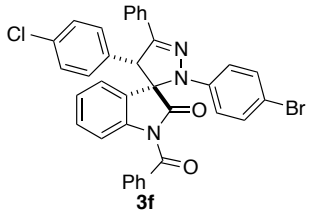
3d

***tert*-Butyl 2′-(4-bromophenyl)-2-oxo-4′,5′-diphenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazole]-1-carboxylate (3d) (Table 1, entry 11):** Prepared according to the general procedure from **1d** (64.3 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3d** (44.0 mg, 0.074 mmol, 37%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess of **3d** was determined to be 98% after cleavage of the Boc group to form **S3a**. $[\alpha]_D^{24}$ = -345.9 (c 0.37, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.64 (s, 9H), 5.13 (s, 1H), 6.38 (d, *J* = 3.6 Hz, 1H), 6.71 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 9.0 Hz, 2H), 6.92 (bs, 2H), 7.11-7.24 (m, 6H), 7.26-7.30 (m, 3H), 7.62-7.68 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 28.3, 63.6, 77.1, 85.4, 113.9, 115.4, 117.4, 123.9, 124.4, 126.1, 127.1, 128.4, 128.6, 128.9, 129.2, 129.4, 130.1, 131.4, 132.0, 134.2, 139.2, 143.2, 149.2, 149.3, 173.8. **HRMS** (ESI) calcd. for $C_{33}H_{29}N_3O_3Br^+$ $[M+H]^+$ 594.1392, found 594.1384.



3e

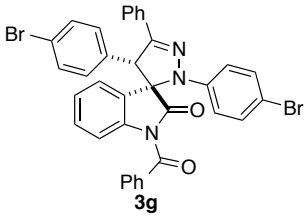
(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-4′-(4-methoxyphenyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3e) (Table 2, entry 1): Prepared according to the general procedure from **1e** (71.1 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3e** (102 mg, 0.162 mmol, 81%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 11.0 min (major); t_R 21.9 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{25}$ = -627.1° (c 0.47, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.67 (s, 3H), 4.95 (s, 1H), 6.41 (d, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 2H), 6.72-6.83 (m, 3H), 6.87 (bs, 2H), 7.14-7.29 (m, 10H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.49-7.60 (m, 2H), 7.68 (d, *J* = 8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 55.5, 62.4, 77.8, 114.5, 114.9, 115.6, 119.6, 124.8, 125.1, 126.0, 126.9, 127.2, 128.5, 128.6, 129.4, 129.5, 130.4, 130.8, 131.2, 132.2, 133.5, 133.6, 140.1, 144.3, 151.6, 159.8, 169.3, 174.9. **HRMS** (ESI) calcd. for $C_{36}H_{27}N_3O_3Br^+$ $[M+H]^+$ 628.1236, found 628.1225.



3f

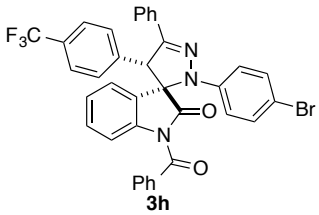
(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-4′-(4-chlorophenyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3f) (Table 2, entry 2): Prepared according to the general procedure from **1f** (72.0 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3f** (109 mg, 0.172 mmol, 86%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.4 min (major); t_R 16.5 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{24}$ = -396.1° (c 0.62, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 5.09 (s, 1H), 6.51 (d, *J* = 6.6 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.96 (dt, *J* = 0.6, 7.8 Hz, 1H), 7.01 (bs, 2H), 7.21-

7.39 (m, 13H), 7.57 (t, J = 7.8 Hz, 1H), 7.58-7.66 (m, 2H), 7.80 (d, J = 8.4 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 62.2, 77.7, 115.1, 115.9, 119.7, 124.4, 125.2, 126.7, 127.1, 128.5, 128.7, 129.4, 129.6, 129.7, 130.7, 130.8, 130.9, 132.2, 132.4, 133.4, 133.6, 134.7, 140.2, 144.1, 151.0, 169.2, 174.6. **HRMS** (ESI) calcd. for $C_{35}H_{24}N_3O_2BrCl^+$ $[M+H]^+$ 632.0740, found 632.0720.



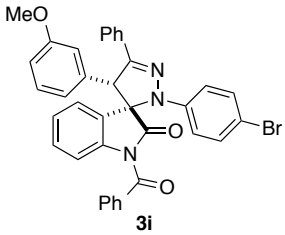
3g

(3S,4′S)-1-benzoyl-2′,4′-bis(4-bromophenyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3g) (Table 2, entry 3): Prepared according to the general procedure from **1g** (80.8 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3g** (85.3 mg, 0.126 mmol, 63%) as a yellow foam with a 90:10 diastereomeric ratio and a >95:5 regioisomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.0 min (major); t_R 17.2 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 94% ee. $[\alpha]_D^{26}$ = -506.8° (c 0.59, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 5.12 (s, 1H), 6.40 (dd, J = 7.8, 0.6 Hz, 1H), 6.68 (dt, J = 0.6, 7.2 Hz, 1H), 6.77-6.86 (m, 7H), 7.13 (dt, J = 1.2, 7.8 Hz, 2H), 7.16-7.19 (m, 2H), 7.27-7.31 (m, 6H) 7.59-7.64 (m, 3H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 62.2, 77.6, 115.1, 115.9, 119.7, 122.8, 124.3, 125.2, 126.7, 127.1, 128.5, 128.7, 129.6, 129.7, 130.7, 130.8, 131.2, 132.2, 132.4, 133.2, 133.4, 133.56, 140.7, 144.1, 151.0, 169.2, 174.5. **HRMS** (ESI) calcd. for $C_{35}H_{24}N_3O_2Br_2^+$ $[M+H]^+$ 676.0235, found 676.0204.



3h

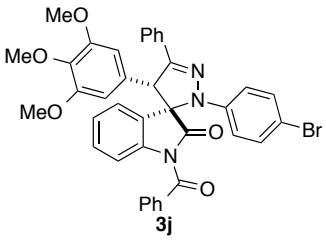
(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-5′-phenyl-4′-(4-(trifluoromethyl)phenyl)-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3h) (Table 2, entry 4): Prepared according to the general procedure from **1h** (78.7 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3h** (108 mg, 0.162 mmol, 81%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.4 min (major); t_R 15.3 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 80% ee. $[\alpha]_D^{24}$ = -433.4° (c 0.65, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.12 (s, 1H), 6.36 (d, J = 7.6 Hz, 1H), 6.80-6.90 (m, 3H), 7.17 (bs, 2H), 7.22-7.37 (m, 10H), 7.46-7.55 (m, 3H), 7.55-7.63 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 62.4, 77.8, 115.1, 116.1, 119.8, 124.0 (q, J = 272.25 Hz), 124.2, 125.1, 126.1 (q, J = 3.62 Hz), 126.5, 127.0, 128.5, 128.8, 129.6, 129.8, 130.1, 130.70, 130.74 (*q*, J=32.8 Hz), 130.9, 132.3, 133.4, 133.6, 138.3, 140.2, 144.0, 150.7, 169.2, 174.4. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -63.1. **HRMS** (ESI) calcd. for $C_{36}H_{24}F_3N_3O_2Br^+$ $[M+H]^+$ 666.1004, found 666.0973.



3i

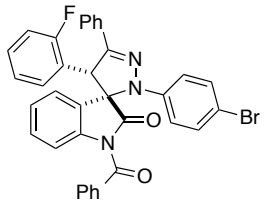
(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-4′-(3-methoxyphenyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3i) (Table 2, entry 5): Prepared according to the general procedure from **1i** (71.1 mg, 0.200 mmol) and **2a** (85.0 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3i** (113 mg, 0.180 mmol, 90%) as a yellow foam with a 90:10 diastereomeric ratio and a >95:5 regioisomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.2 min (major); t_R 19.9 min

(minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 94% ee. $[\alpha]_D^{26}$ = -497.4° (c 0.39, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 3.68 (s, 3H), 5.06 (s, 1H), 6.54 (d, *J* = 7.8 Hz, 1H), 6.62-6.73 (m, 1H), 6.78-6.83 (m, 1H), 6.84-6.93 (m, 3H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.24-7.39 (m, 11H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.62-7.70 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 55.5, 63.0, 77.8, 114.1, 114.9, 115.3, 115.6, 119.6, 121.9, 124.6, 125.0, 126.7, 127.1, 128.5, 128.6, 129.48, 129.53, 130.2, 130.5, 131.2, 132.2, 133.47, 133.53, 135.4, 140.1, 144.2, 151.3, 160.2, 169.3, 174.8. **HRMS** (ESI) calcd. for $C_{36}H_{27}N_3O_3Br^+$ $[M+H]^+$ 628.1236, found 628.1219.



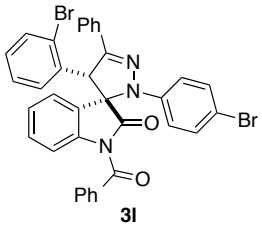
3j

(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-5′-phenyl-4′-(3,4,5-trimethoxyphenyl)-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3j) (Table 2, entry 6): Prepared according to the general procedure from **1j** (83.0 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (80:20 hexanes:EtOAc) to yield **3j** (125 mg, 0.182 mmol, 91%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.7 min (major); t_R 37.6 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 61% ee. $[\alpha]_D^{26}$ = -22.2 (c 0.63, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 3.56 (s, 6H), 3.89 (s, 3H), 5.28 (s, 1H), 6.14 (s, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 7.21-7.34 (m, 8H), 7.40-7.49 (m, 2H), 7.52-7.62 (m, 3H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.89 (d, J = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 56.2, 61.1, 68.3, 78.7, 107.3, 113.8, 116.3, 116.8, 123.8, 126.5, 127.0, 128.1, 128.6, 129.2, 129.6, 130.2, 130.6, 131.1, 132.2, 133.1, 133.3, 138.4, 139.9, 143.2, 147.6, 153.5, 168.7, 171.6. **HRMS** (ESI) calcd. for $C_{38}H_{31}N_3O_5Br^+$ $[M+H]^+$ 688.1447, found 688.1440.



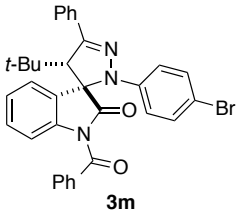
3k

(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-4′-(2-fluorophenyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3k) (Table 2, entry 8): Prepared according to the general procedure from **1k** (68.7 mg, 0.200 mmol) and **2a** (85.0 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3k** (104 mg, 0.168 mmol, 84%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.1 min (major); t_R 12.4 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 92% ee. $[\alpha]_D^{24}$ = -323.0° (c 0.52, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 5.55 (s, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 6.78-6.91 (m, 4H), 7.08 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.20-7.26 (m, 1H), 7.28-7.37 (m, 6H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.62-7.69 (m, 2H), 7.84 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 55.4, 115.2, 115.8 (d, *J* = 21.9 Hz), 118.7, 121.8 (d, *J* = 15.1 Hz), 124.5, 124.61, 124.62, 124.8, 126.1, 126.9, 128.5, 128.7, 129.46, 129.56, 130.5, 130.6, 130.9, 132.2, 133.4, 133.7, 140.4, 143.7, 149.1, 160.7 (d, *J* = 248.1Hz), 169.0, 174.9. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -116.5. **HRMS** (ESI) calcd. for $C_{35}H_{24}N_3O_2BrF^+$ $[M+H]^+$ 616.1036, found 616.1030.



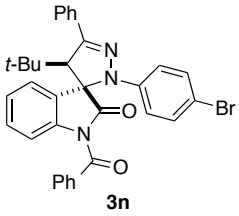
3l

(3S,4′S)-1-benzoyl-4′-(2-bromophenyl)-2′-(4-bromophenyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3l) (Table 2, entry 9): Prepared according to the general procedure from **1l** (80.8 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3l** (58.3 mg, 0.086 mmol, 43%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.3 min (major); t_R 13.0 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 0% ee. **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 5.56 (s, 1H), 6.24 (d, J = 11.4 Hz, 1H), 6.66-6.79 (m, 3H), 6.96-7.06 (m, 1H), 7.09-7.21 (m, 8H), 7.22-7.35 (m, 6H), 7.42 (t, J = 10.8 Hz, 1H), 7.45-7.51 (m, 2H), 7.71 (d, J = 12 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 61.4, 77.4, 115.2, 115.6, 119.4, 124.5, 124.8, 126.1, 126.4, 127.0, 128.1, 128.5, 128.8, 129.57, 129.61, 130.2, 130.6, 130.8, 131.0, 132.2, 133.3, 133.4, 133.6, 133.8, 141.1, 144.0, 150.5, 169.0, 174.6. **HRMS** (ESI) calcd. for $C_{35}H_{24}N_3O_2Br_2^+$ $[M+H]^+$ 676.0235, found 676.0228.



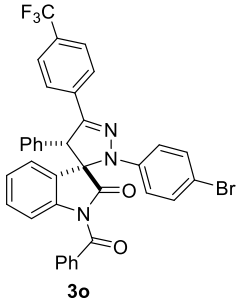
3m

(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-4′-(tert-butyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3m) (Table 2, entry 10): Prepared according to the general procedure from **1m** (61.1 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3m** (81.0 mg, 0.140 mmol, 70%) as a tan foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.8 min (major); t_R 39.5 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 99% ee. $[\alpha]_D^{25}$ = -258.6 (c 0.52, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 0.87 (s, 9H), 4.17 (s, 1H), 6.76 (d, J = 9 Hz, 2H), 7.19-7.26 (m, 3H), 7.36-7.43 (m, 3H), 7.43-7.50 (m, 3H), 7.51-7.57 (m, 2H), 7.57-7.64 (m, 3H), 7.67 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 29.9, 34.8, 70.8, 78.2, 114.9, 115.7, 119.1, 125.0, 125.2, 128.2, 128.4, 128.5, 128.6, 129.1, 129.7, 130.9, 131.9, 133.6, 133.7, 135.2, 140.5, 143.6, 153.9, 169.2, 176.5. **HRMS** (ESI) calcd. for $C_{33}H_{29}N_3O_2Br^+$ $[M+H]^+$ 578.1443, found 578.1440.



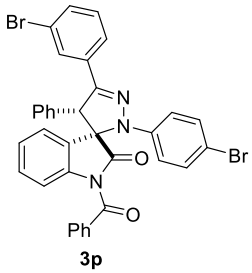
3n

(3S,4′R)-1-benzoyl-2′-(4-bromophenyl)-4′-(tert-butyl)-5′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3n) (Equation 1): Prepared according to the general procedure from **1n** (61.1 mg, 0.200 mmol) and **2a** (85.0 mg, 0.240 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **3n** (74.0 mg, 0.128 mmol, 64%) as a tan foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.5 min (minor); t_R 13.8 min (major) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 66% ee. $[\alpha]_D^{26}$ = -194.4 (c 0.36, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 0.97 (s, 9H), 4.01 (s, 1H), 6.86 (d, J = 9.0 Hz, 2H), 7.24 (t, J = 7.8 Hz, 1H), 7.30 (d, J = 9.0 Hz, 2H), 7.35-7.52 (m, 9H), 7.55-7.64 (m, 3H), 7.70 (d, J = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 29.7, 35.0, 73.2, 78.3, 115.4, 115.6, 120.0, 123.4, 126.2, 128.1, 128.5, 128.6, 129.1, 129.7, 130.4, 131.0, 132.0, 133.5, 133.9, 135.2, 138.8, 143.5, 153.6, 169.4, 172.7. **HRMS** (ESI) calcd. for $C_{33}H_{29}N_3O_2Br^+$ $[M+H]^+$ 578.1443, found 578.1444.



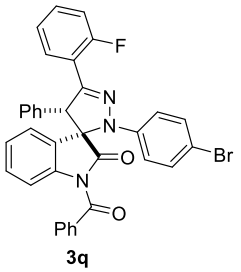
3o

(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-4′-phenyl-5′-(4-(trifluoromethyl)phenyl)-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3o) (Table 3, entry 1): Prepared according to the general procedure from **1a** (65 mg, 0.20 mmol) and **2b** (101 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **3o** (114 mg, 0.172 mmol, 86%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 8.22 min (major); t_R 20.84 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 94% ee. $[\alpha]_D^{25}$= -370.5 (c 0.50, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 5.11 (s, 1H), 6.45 (dd, *J* = 1.2, 7.8, Hz, 1H), 6.82-6.90 (m, 3H), 6.95-7.10 (br s, 2H), 7.23-7.30 (br s, 2H), 7.31-7.35 (m, 5H), 7.37 (t, *J* = 8.4 Hz, 2H), 7.49-7.53 (m, 3H), 7.55 (t, 7.2 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.77 (d, *J* = 7.2 Hz, 1H). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -63.2. **HRMS** (ESI) Exact mass calcd. for $C_{36}H_{24}BrF_3N_3O_2^+$ $[M+H]^+$ 666.0999, found: 666.0996. This material was contaminated by traces of the starting alkylidene oxindole; to separate them, the *N*-benzoyl group was cleaved as described below.



3p

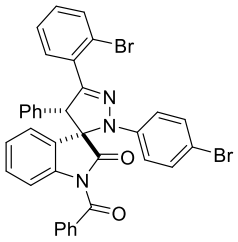
(3S,4′S)-1-benzoyl-5′-(3-bromophenyl)-2′-(4-bromophenyl)-4′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3p) (Table 3, entry 2): Prepared according to the general procedure from **1a** (65 mg, 0.20 mmol) and **2c** (104 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **3p** (98.0 mg, 0.145 mmol, 72%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.81 min (major); t_R 10.90 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 84% ee. $[\alpha]_D^{25}$= -420.0 (c 0.50, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 5.04 (s, 1H), 6.42 (dd, *J* = 1.2, 7.8 Hz, 1H), 6.81-6.88 (m, 3H)), 6.95-7.08 (br s, 1H), 7.10 (t, *J* = 7.8 Hz, 1H), 7.24-7.28 (br s, 3H), 7.29-7.34 (m, 5H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.40 (dt, *J* = 1.2, 7.8 Hz, 2H), 7.54 (tt, *J* = 1.2, 7.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.93 (t, *J* = 1.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 62.7, 77.9, 115.0, 115.9, 119.6, 122.9, 124.3, 125.0, 125.6, 126.7, 128.5, 128.9, 129.3, 129.5, 129.8, 130.1 (two coincident resonances, as determined by HSQC), 130.6, 132.2, 132.3, 133.2, 133.47, 133.52, 133.54, 140.2, 143.8, 149.8, 169.2, 174.7. **HRMS** (ESI) Exact mass calcd. for $C_{35}H_{24}Br_2N_3O_2^+$ $[M+H]^+$ 676.0230, found 676.0254.



3q

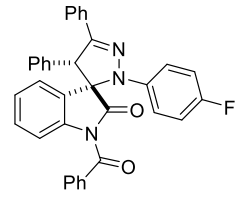
(3S,4′S)-1-benzoyl-2′-(4-bromophenyl)-5′-(2-fluorophenyl)-4′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3q) (Table 3, entry 3): Prepared according to the general procedure from **1a** (65 mg, 0.20 mmol) and **2e** (89 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **3q** (111 mg, 0.180 mmol, 90%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.51 min (major); t_R 11.07 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 90% ee. $[\alpha]_D^{25}$= -539.3 (c 0.51, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.27 (d,

J = 2 Hz, 1H), 6.40 (d, *J* = 8 Hz, 1H), 6.78-6.85 (m, 3H), 6.90 (dd, *J* = 8.4, 11.6 Hz, 1H), 6.98-7.03 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.16-7.25 (m, 4H), 7.25-7.38 (m, 7H), 7.51 (dt, *J* = 0.8, 7.2 Hz, 1H), 7.75 (d, *J* = 8 Hz, 1H), 8.00 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 64.4 (d, *J* = 6.5 Hz), 77.5 (d, *J* = 4.8 Hz), 114.9, 115.7, 116.6 (d, *J* = 22.5 Hz), 119.4 (d, *J* = 11.0 Hz), 119.5, 124.4, 124.4 (d, *J* = 8.5 Hz), 125.0, 126.6, 128.48, 128.51, 128.9, 129.45, 129.49, 129.54, 130.5, 131.2 (d, *J* = 8.6 Hz), 132.2, 133.47, 133.53, 133.9, 140.1, 144.0, 148.2 (d, *J* = 3.8 Hz), 160.4 (d, *J* = 254.7 Hz), 169.2, 174.7. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -112.88. **HRMS** (ESI) Exact mass calcd. for $C_{35}H_{24}BrFN_3O_2^+$ $[M+H]^+$ 616.1030; found: 616.1028.



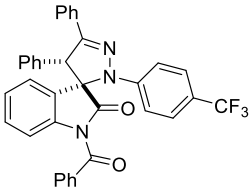
3r

(3S,4′S)-1-benzoyl-5-(2-bromophenyl)-2′-(4-bromophenyl)-4′-phenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3r) (Table 3, entry 4): Prepared according to the general procedure from **1a** (65 mg, 0.20 mmol) and **2e** (104 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **3r** (110 mg, 0.162 mmol, 81%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.38 min (major); t_R 20.16 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 62% ee. $[\alpha]_D^{25}$= -247.0 (c 0.51, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 5.70 (s, 1H), 6.61 (dd, *J* = 1.2, 7.8 Hz, 1H), 6.83-6.88 (m, 3H), 7.02-7.05 (m, 2H), 7.13 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.18-7.22 (m, 3H), 7.23-7.27 (m, 2H), 7.28-7.31 (m, 2H), 7.40 (t, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 1.8, 7.8 Hz, 2H), 7.55-7.59 (m, 2H), 7.60 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz): δ 64.8, 77.9, 114.9, 115.5, 119.1, 122.0, 124.3, 124.9, 126.5, 127.5, 128.5, 128.6, 128.9, 129.7, 129.8, 130.39, 130.44, 131.6, 132.0, 132.2, 133.2, 133.5, 133.6, 134.6, 139.9, 143.7, 150.5, 169.1, 174.8. **HRMS** (ESI) Exact mass calcd. for $C_{35}H_{24}Br_2N_3O_2$ $[M+H]^+$ 676.0230, found 676.0225.



3s

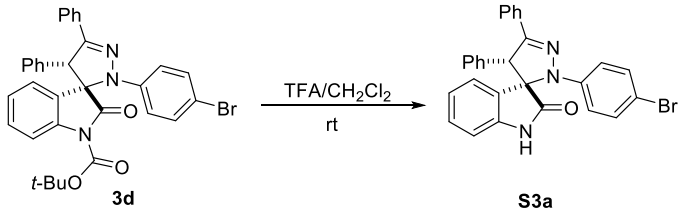
(3S,4′S)-1-benzoyl-2′-(4-fluorophenyl)-4′,5′-diphenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3s) (Table 3, entry 5): Prepared according to the general procedure from **1a** (65 mg, 0.20 mmol) and **2f** (70 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **3s** (89.0 mg, 0.166 mmol, 83%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.05 min (major); t_R 10.70 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 91% ee. $[\alpha]_D^{24}$= -617.0 (c 0.56, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.09 (s, 1H), 6.45 (dd, J = 8, 0.8 Hz, 1H), 6.87 (dt, J = 0.8, 7.6 Hz 1H), 6.92-6.97 (m, 4H), 7.10 (bs, 2H), 7.21 (dd, J = 8, 1.2 Hz, 2H), 7.24-7.30 (m, 6H), 7.31-7.37 (m, 3H), 7.52 (t, J = 7.6 Hz, 1H), 7.62-7.69 (m, 2H), 7.76 (d, J = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHZ) δ 62.6, 78.4, 114.8, 115.7, 115.9, 120.8 (d, J = 7.9 Hz) 124.8, 124.9, 126.9, 127.1, 128.4, 128.6, 129.2, 129.4, 129.5, 129.7, 130.4, 131.2, 133.4, 133.6, 134.1, 140.4, 141.5 (d, J = 2.4 Hz) 151.7, 159.5 (d, J = 243.9 Hz) 169.3, 174.8. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -120.1. **HRMS** (ESI) Exact mass calcd. for $C_{35}H_{25}FN_3O_2$ $[M+H]^+$ 538.1925, found 538.1925.



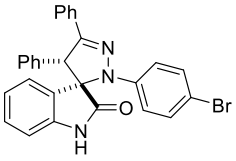
3t

(3S,4′S)-1-benzoyl-4′,5′-diphenyl-2′-(4-(trifluoromethyl)phenyl)-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (3t) (Table 3, entry 6): Prepared according to the general procedure from **1a** (65 mg, 0.20 mmol) and **2g** (82 mg, 0.24 mmol). The crude reaction mixture was purified by flash column chromatography (95:5 hexanes:EtOAc) to give **3t** (103 mg, 0.174 mmol, 87%) as a yellow foam with >95:5 diastereomeric and regioisomeric ratios. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.18 min (major); t_R 8.61 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 90:10, 1.0 mL/min] to be 90% ee. $[\alpha]_D^{24}$= -450.9 (c 0.51, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz): δ 5.16 (s, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.95-7.05 (br m, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 7.24-7.35 (m, 9H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.44-7.47 (m, 4H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.58-7.73 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 63.6, 77.2, 115.2, 115.9, 123.7 (q, *J* = 32.6 Hz), 124.5, 124.6 (q, *J* = 270.9), 125.1, 126.6, 126.6 (q, *J* = 3.5 Hz), 127.3, 128.5, 128.7, 128.7, 129.2, 129.5, 129.6, 129.7, 130.5, 131.0, 133.5, 133.6, 134.0, 139.8, 147.5, 151.1, 169.1, 174.9. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -62.19. **HRMS** (ESI) Exact mass calcd. for $C_{36}H_{25}F_3N_3O_2^+$ $[M+H]^+$ 588.1893, found 588.1898.

Synthesis of S3a from 3d



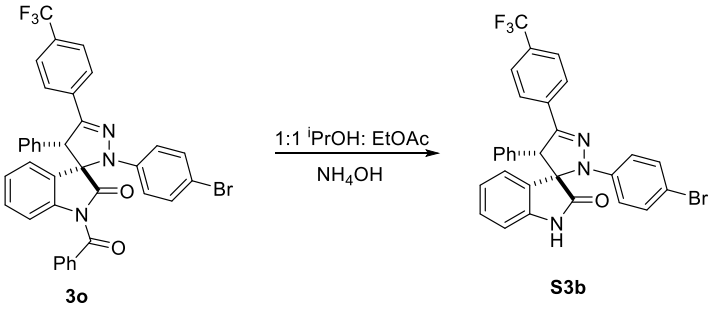
3d **S3a**

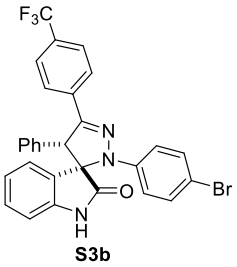


S3a

(3S,4′S)-2′-(4-bromophenyl)-4′,5′-diphenyl-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (S3a). **A** 1:1 mixture of CH_2Cl_2:trifluoroacetic acid (1 ml) was added to compound **3d** (44 mg, 0.074 mmol) under an atmosphere of nitrogen, and the mixture was stirred at room temperature until TLC showed complete consumption of **3d**. The volatiles were evaporated under reduced pressure to yield **S3a** (34 mg, 0.069 mmol, 92%) as a tan powder. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.6 min (major); t_R 28.3 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{24}$= -141.1 (c 0.68, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.17 (s, 1H), 6.34 (d, J = 7.2 Hz, 1H), 6.60 (t, J = 7.6 Hz, 1H), 6.72-6.83 (m, 3H), 6.91-7.02 (m, 2H), 7.08 (dt, J = 0.8 Hz, 7.8 Hz 1H), 7.12-7.20 (m, 5H), 7.27-7.31 (m, 3H), 7.63-7.70 (m, 2H), 8.61 (s, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 62.9, 77.4, 110.8, 113.6, 117.0, 122.9, 125.3, 126.7, 127.1, 128.3, 128.6, 128.9, 129.2, 129.3, 129.9, 131.5, 132.0, 134.6, 139.9, 143.4, 149.7, 178.5. **HRMS** (ESI) Exact mass calcd. for $C_{28}H_{21}BrN_3O^+$ $[M+H]^+$ 494.0868, found 494.0868.

Synthesis of S3b from 3o

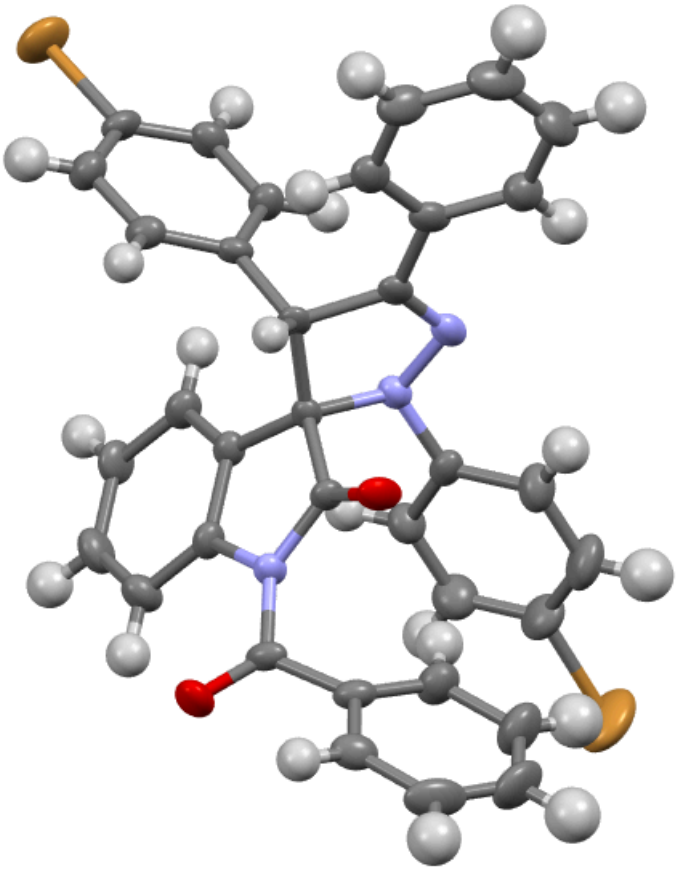




3S,4′S)-2′-(4-bromophenyl)-4′-phenyl-5′-(4-(trifluoromethyl)phenyl)-2′,4′-dihydrospiro[indoline-3,3′-pyrazol]-2-one (S3b): To a solution of **3o** (121 mg, 0.181 mmol) in 1:1 ^{i}PrOH:EtOAc (4 mL) was added ammonium hydroxide (0.03 mL). The reaction mixture was stirred at room temperature until TLC analysis indicated complete consumption of **3o**, at which point brine (3 mL) was added and the layers were separated. The aqueous layer was extracted with EtOAc (2 x 2mL), and the combined organic extracts were passed through a glass Pasteur pipette packed with ~2 cm of silica gel. The resulting solution was concentrated under reduced pressure to yield the crude **3o**. The crude product was purified by flash column chromatography (80:20 hexanes:EtOAc) to afford **3o** (48 mg, 0.085 mmol, 73%) as a yellow. HPLC analysis confirmed that no racemization had occurred during the cleavage reaction, although ~5% of a minor diastereomer had formed. HPLC analysis (254 nm, 25 °C) t_R 5.64 min (major); t_R 12.5 min (minor) [Chiracel AD-H (0.46 cm x 25cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 92% ee. $[\alpha]_D^{25}$= -273.5 (c 0.49, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 5.17 (s, 1H), 6.34 (d, *J* = 8.4 Hz, 1H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.94 (br s, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.13-7.23 (m, 5H), 7.53 (d, *J* = 8.4Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 8.74 (br s, 1H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 62.6, 77.3, 110.9, 114.2, 117.1, 123.0, 123.7 (q, *J* = 273.5 Hz), 124.9, 125.6 (q, *J* = 3.5 Hz), 126.7, 127.1, 128.6, 129.1, 129.2, 130.1, 130.5 (q, *J* = 32.4 Hz), 132.1, 134.1, 135.0 (q, *J* = 1.1 Hz), 139.9, 142.9, 148.1, 178.2. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -63.2 **HRMS** (ESI) Exact mass calcd. for $C_{29}H_{19}BrF_3N_3O_2$ $[M+H]^+$ 562.0736, found 562.0737.

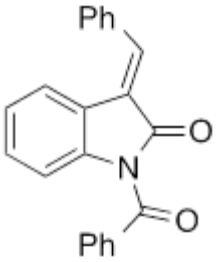
Absolute Stereochemistry and Structure of 3g

Supplementary X-ray diffraction data and structure refinement for **3g** is contained in CCDC 958182. These data can be accessed free of charge from the Cambridge Crystallographic Data Center at www.ccdc.cam.ac.uk/data_request/cif.



7.932 7.919 7.834 7.813 7.811 7.799 7.792 7.766 7.765 7.753 7.752 7.669 7.666 7.655 7.654 7.631 7.629 7.627 7.617 7.606 7.604 7.602 7.517 7.514 7.510 7.504 7.499 7.496 7.491 7.488 7.486 7.480 7.478 7.475 7.470 7.466 7.460 7.454 7.386 7.385 7.373 7.373 7.360 7.358 7.083 7.081 7.070 7.068 7.057 7.055

Parameter	Value
Solvent	CDCl3
Temperature	297.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	83
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2012-12-13T11:02:15
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



1a

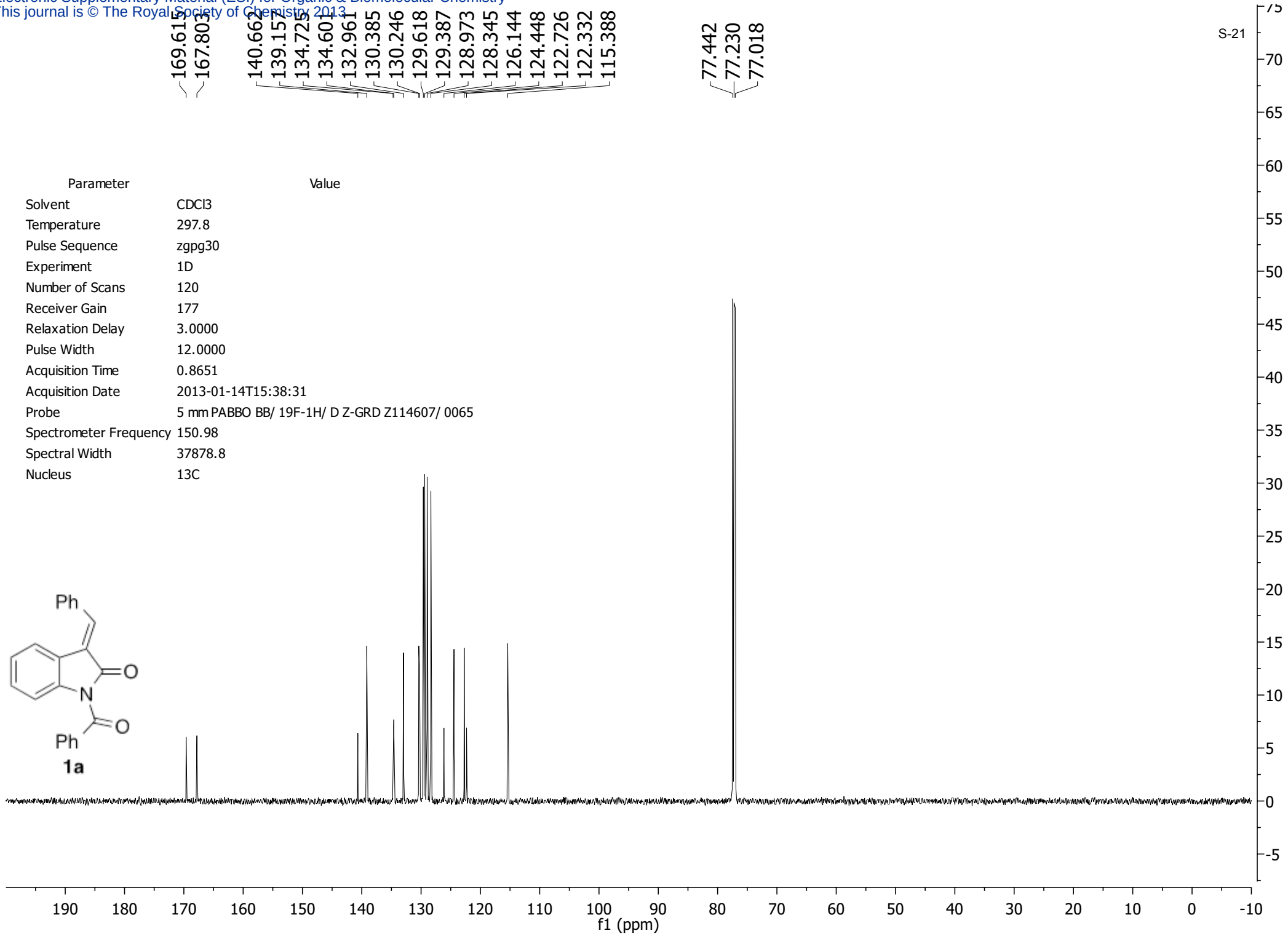
0.97 0.95 1.95 1.01 2.00 1.03 5.00 1.03 1.00

f1 (ppm)

169.615
167.803
140.662
139.157
134.725
134.601
132.961
130.385
130.246
129.618
129.387
128.973
128.345
126.144
124.448
122.726
122.332
115.388
77.442
77.230
77.018

Parameter	Value
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	120
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-14T15:38:31
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

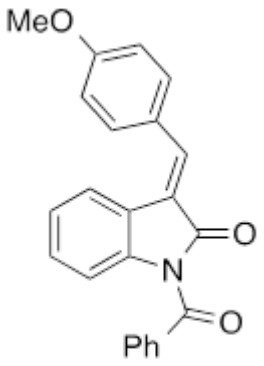
1a



KPL_95_10152012
new experiment

7.941 7.921 7.901 7.882 7.805 7.787 7.783 7.773 7.681 7.659 7.624 7.605 7.587 7.512 7.492 7.473 7.380 7.362 7.343 7.260 7.118 7.099 7.080 7.018 6.997 3.899

Parameter	Value
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2012-10-15T13:04:03
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



1e

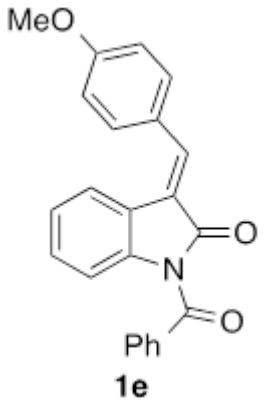
1.91 2.83 2.11 1.02 1.97 1.03 0.99 2.05

3.00

f1 (ppm)

169.729
168.110
161.473
140.340
139.449
134.851
132.873
131.751
129.900
129.604
128.313
126.912
124.363
124.070
122.721
122.316
115.331
114.409
77.442
77.230
77.018
55.645

Parameter	Value
Solvent	CDCl3
Temperature	297.8
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	106
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-14T15:48:25
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



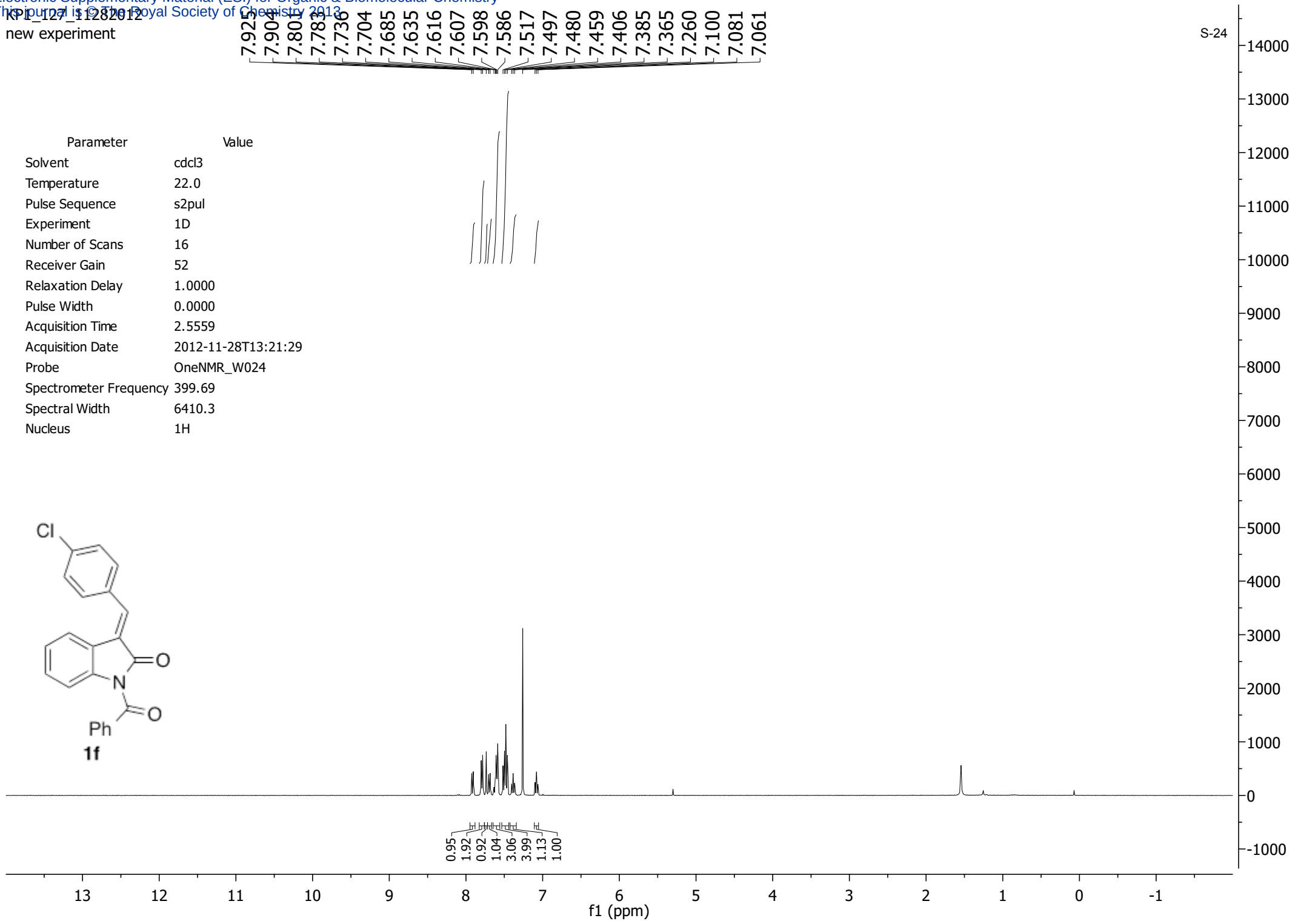
1e

f1 (ppm)

KPL_127_11282012
new experiment

Parameter	Value
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	52
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2012-11-28T13:21:29
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

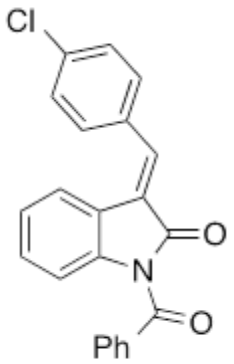
1f



KPL_127_11272012carbon1
new experiment

169.559
167.627
140.815
137.457
136.172
134.604
133.080
130.747
129.648
129.344
128.392
126.645
124.555
122.695
122.050
115.532
77.548
77.230
76.913

Parameter	Value
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2012-11-27T10:25:02
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



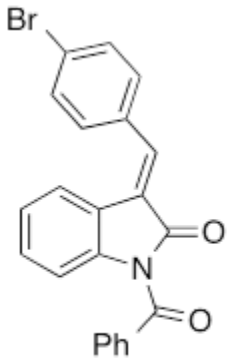
1f

f1 (ppm)

KPL_99_1092012
new experiment

7.924 7.904 7.802 7.783 7.709 7.683 7.640 7.619 7.599 7.535 7.516 7.498 7.479 7.407 7.387 7.368 7.260 7.100 7.080 7.062

Parameter	Value
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	38
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2012-10-09T11:15:26
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



1g

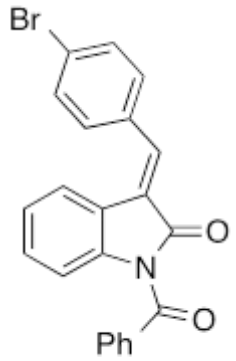
0.96 1.90 1.90 2.94 4.08 1.05 1.00

f1 (ppm)

TG2_41_1142013carbon1.1r

169.561 167.634 140.856 137.464 134.623 133.512 133.097 132.326 130.926 130.740 129.663 128.410 126.730 124.498 122.738 122.064 115.566 77.441 77.230 77.018

Parameter	Value
Solvent	CDCl3
Temperature	297.4
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	320
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-14T11:24:31
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



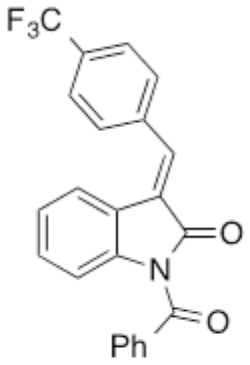
1g

f1 (ppm)

KPT_71_1092012_crop1
new experiment

7.928 7.908 7.811 7.793 7.790 7.784 7.753 7.646 7.627 7.606 7.586 7.526 7.506 7.487 7.420 7.401 7.380 7.260 7.096 7.077 7.057

Parameter	Value
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2012-10-09T11:09:35
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



1h

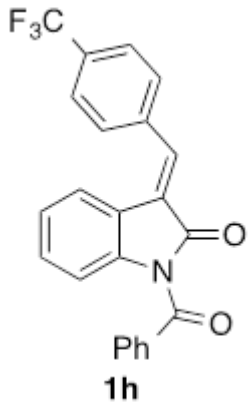
0.93 6.60 1.98 1.97 1.04 1.00

f1 (ppm)

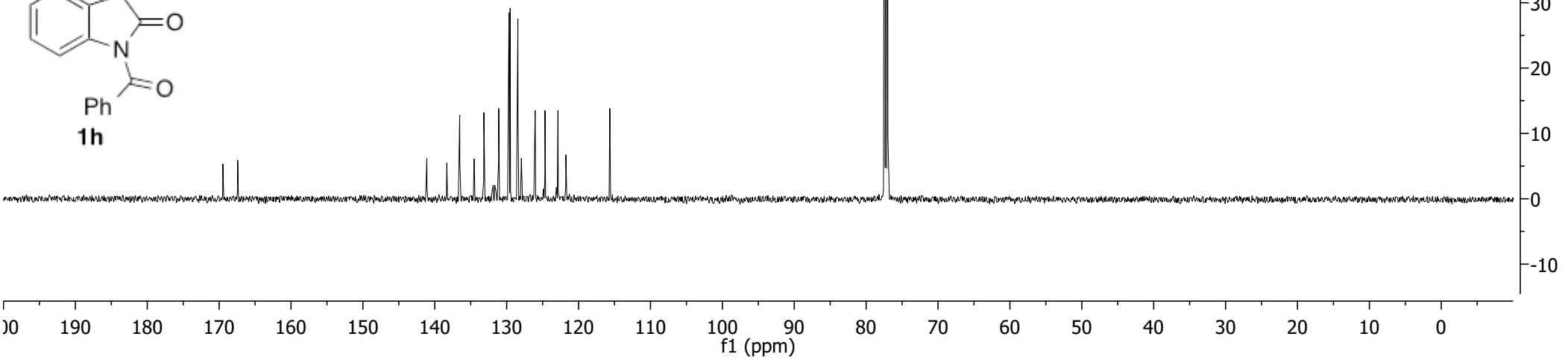
crystal crop 2

169.477 167.415 141.106 138.321 136.534 134.532 133.174 132.073 131.874 131.656 131.439 131.108 129.683 129.522 128.439 127.956 126.698 126.060 126.037 124.891 124.667 123.088 122.868 121.766 121.283

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	308
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-21T12:37:35
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

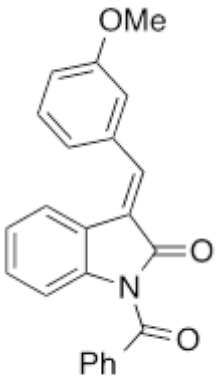


1h



7.926 7.912 7.806 7.796 7.796 7.783 7.626 7.613 7.601 7.513 7.500 7.487 7.426 7.407 7.394 7.382 7.369 7.357 7.356 7.260 7.248 7.235 7.162 7.090 7.088 7.077 7.076 7.064 7.063 7.015 7.011 7.001 6.997 3.851

Parameter	Value
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	88
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-01-30T15:45:55
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



1i

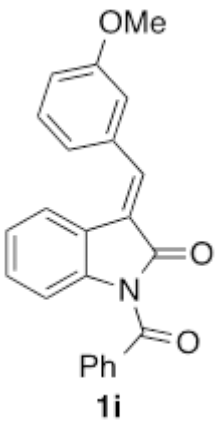
1.01 3.92 1.03 2.06 2.12 1.03 1.01 1.05 1.01

3.00

f1 (ppm)

169.638
167.825
159.959
140.733
139.027
135.895
134.739
132.998
130.424
130.121
129.644
128.376
126.346
124.471
123.007
122.327
121.763
116.169
115.414
114.360
77.441
77.230
77.018
55.603

Parameter	Value
Solvent	CDCl3
Temperature	298.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	189
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-30T16:12:33
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

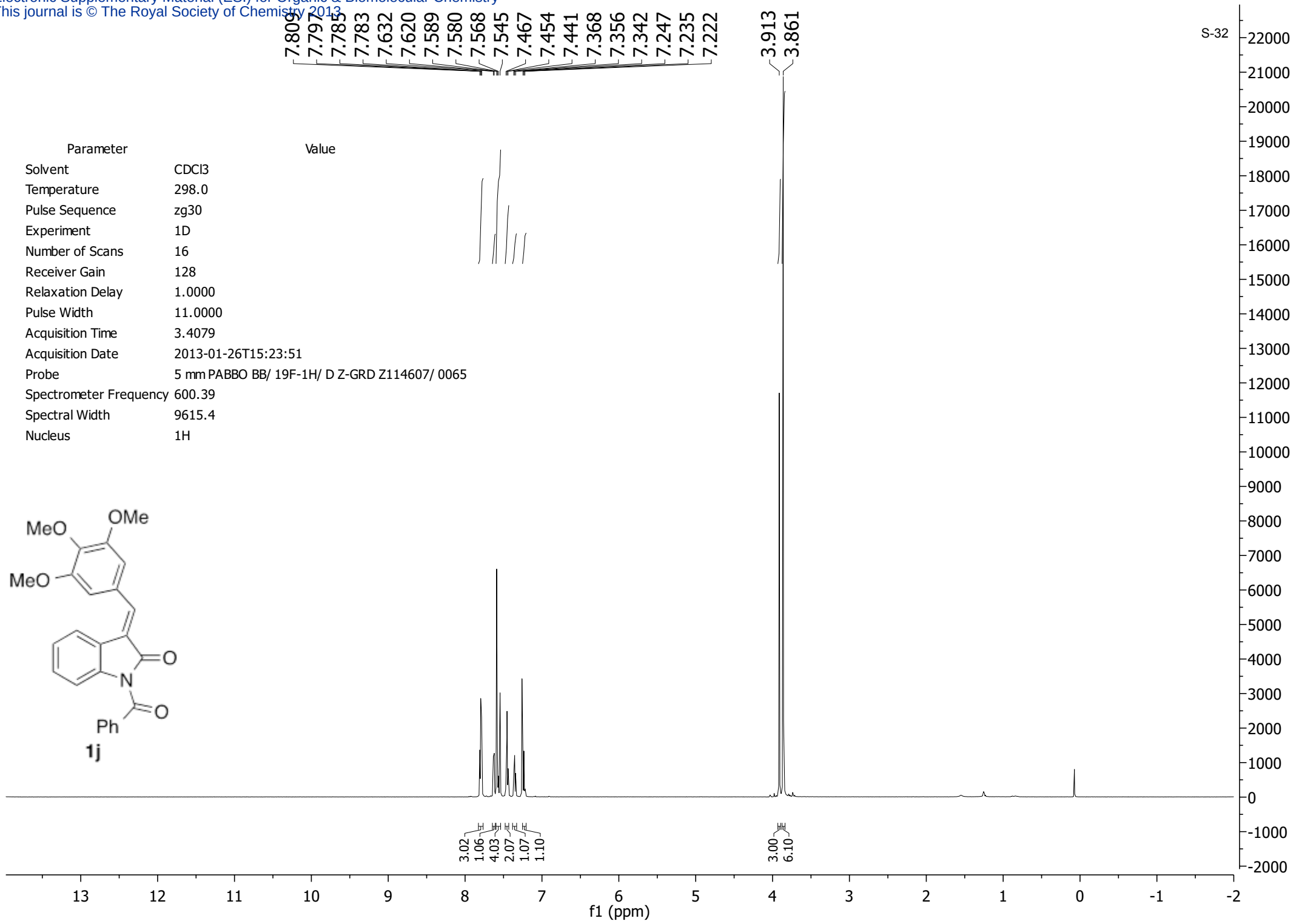


1i

f1 (ppm)

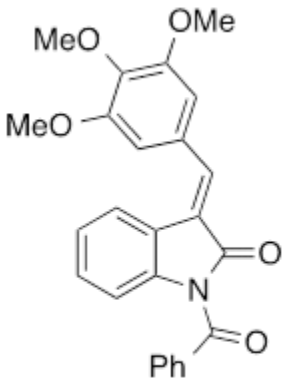
Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-01-26T15:23:51
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

1j



169.952
165.781
152.886
141.229
139.348
138.830
134.762
132.906
129.805
129.259
129.063
128.297
125.679
124.562
123.708
118.890
114.902
110.257
77.441
77.230
77.018
61.208
56.472

Parameter	Value
Solvent	CDCl3
Temperature	298.6
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	350
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-26T15:37:17
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



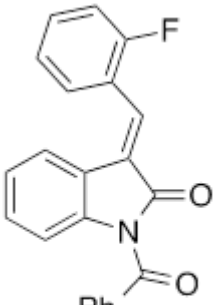
1j

f1 (ppm)

Carbon

7.826 7.816 7.809 7.807 7.796 7.793 7.718 7.716 7.705 7.704 7.693 7.691 7.629 7.617 7.604 7.563 7.550 7.516 7.503 7.490 7.482 7.478 7.476 7.469 7.466 7.462 7.456 7.453 7.399 7.398 7.385 7.373 7.371 7.277 7.264 7.252 7.226 7.210 7.195 7.090 7.089 7.078 7.076 7.065 7.063

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2012-10-23T11:32:30
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



1k

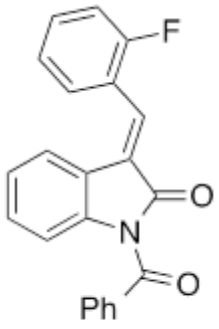
0.95 2.75 0.98 0.97 0.98 2.98 1.01 1.53 1.02 1.00

f1 (ppm)

carbon

169.092
167.317
161.557
159.885
140.923
134.676
133.053
132.260
132.204
131.353
131.333
130.748
130.354
130.338
129.660
128.392
127.946
124.606
124.400
123.034
123.024
122.812
122.715
122.161
116.585
116.445
115.483
77.441
77.230
77.019

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2012-10-23T11:40:53
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

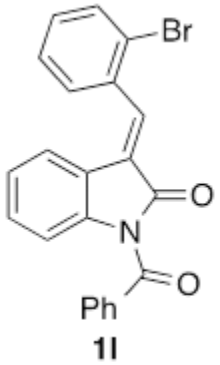


1k

f1 (ppm)

Recrystallized

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-01-22T15:32:48
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



1l

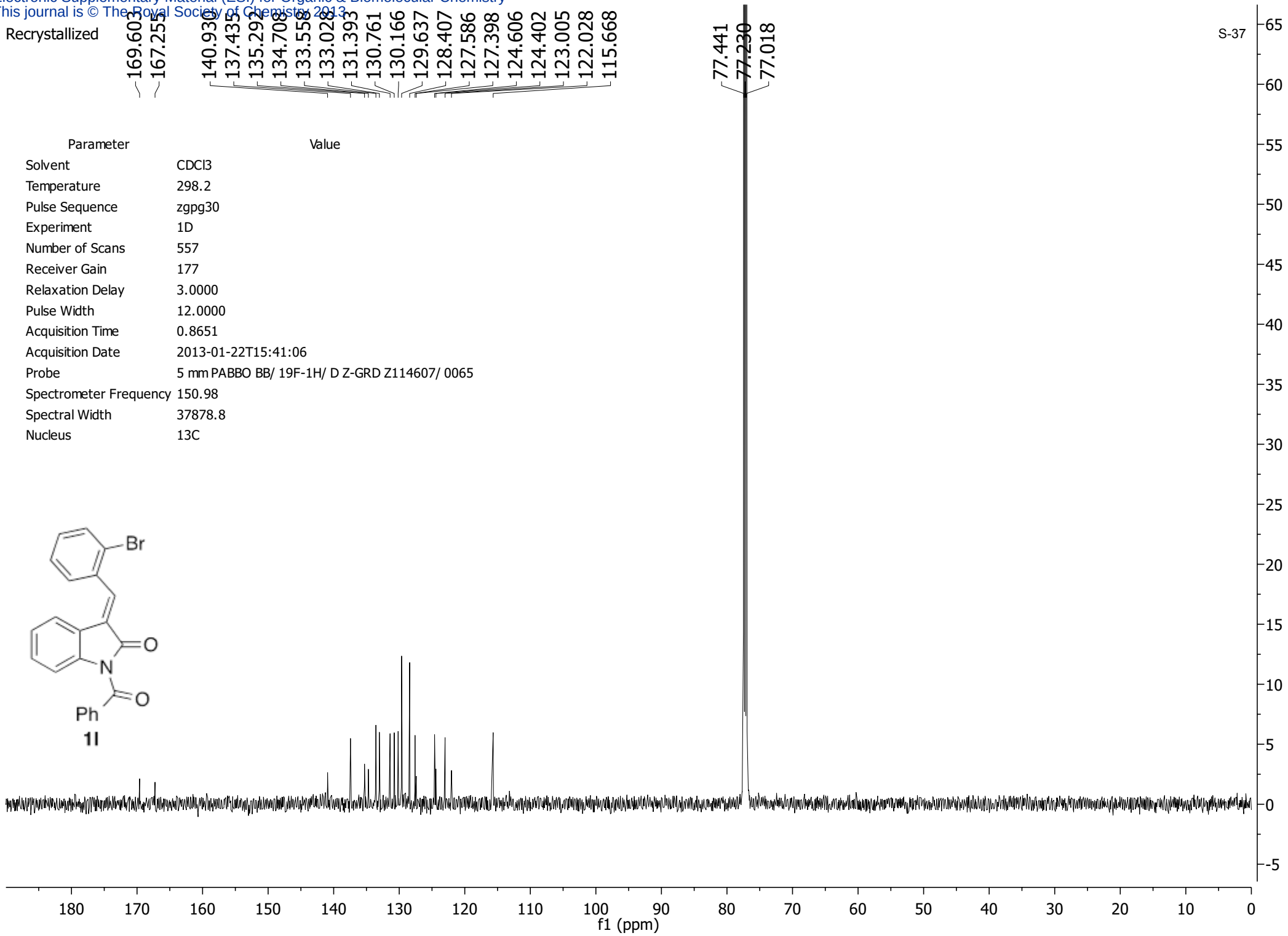
f1 (ppm)

Recrystallized

169.603 167.255 140.930 137.435 135.292 134.708 133.556 133.028 131.393 130.761 130.166 129.637 128.407 127.586 127.398 124.606 124.402 123.005 122.028 115.668 77.441 77.230 77.018

Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	557
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-22T15:41:06
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

1l

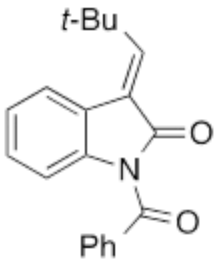


TG2_109_rack2_3_18_21520113
STANDARD 1H OBSERVE - profile

7.723, 7.703, 7.611, 7.591, 7.551, 7.533, 7.343, 7.324, 7.306, 7.231, 7.211, 7.193, 7.124, 7.105, 7.087, 7.010, 6.994, 6.977, 6.975

1.180

Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-02-15T10:45:02
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



1m

0.96, 1.01, 1.93, 1.03, 2.02, 1.04, 2.02

9.00

2500
2000
1500
1000
500
0

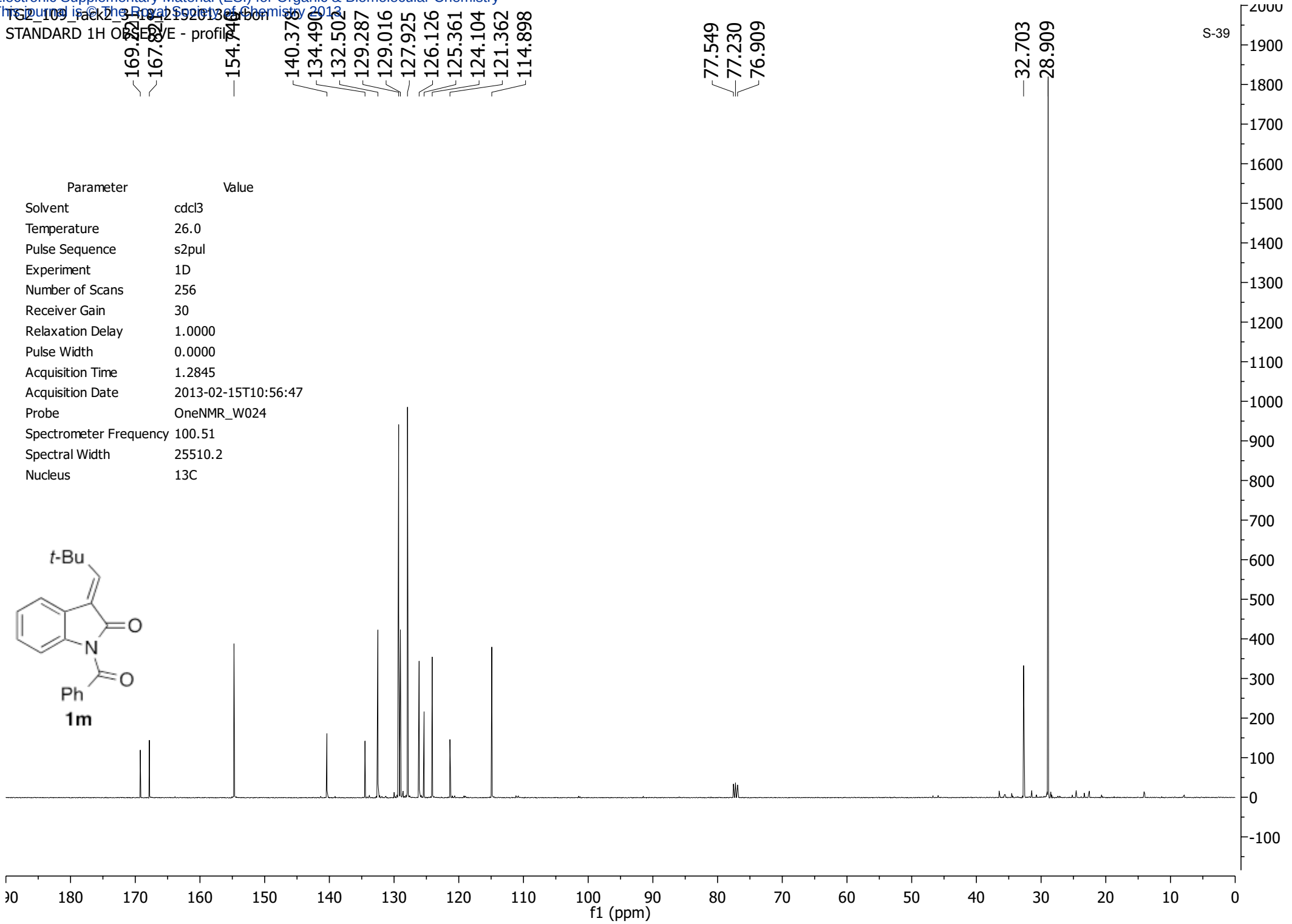
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2

f1 (ppm)

TG2_109_rack2_3_18_12152013 carbon
STANDARD 1H OBSERVE - profile

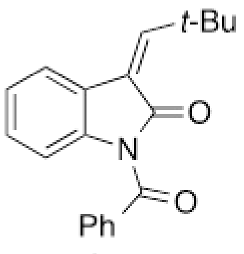
Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-02-15T10:56:47
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

1m

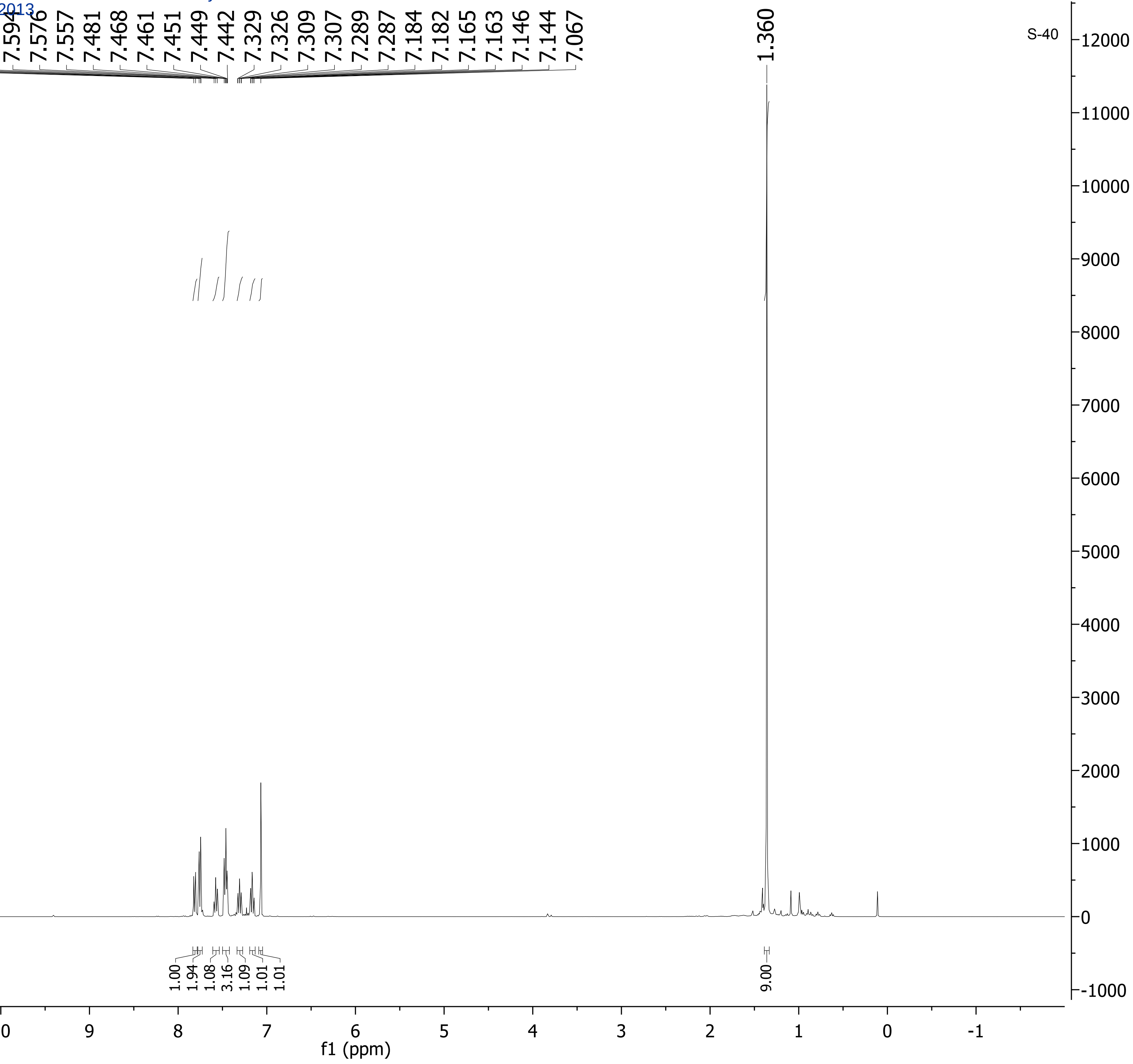


TG2_109_frac56_85_215201...
STANDARD 1H OBSERVE - profile

Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	18
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-02-15T10:28:59
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

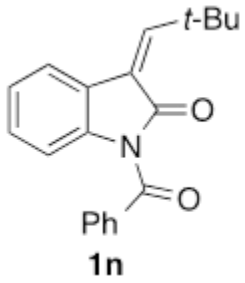


1n



TG2_109_frac56_85_21320 13carbon
STANDARD 1H OBSERVE profile

Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-02-15T10:41:01
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



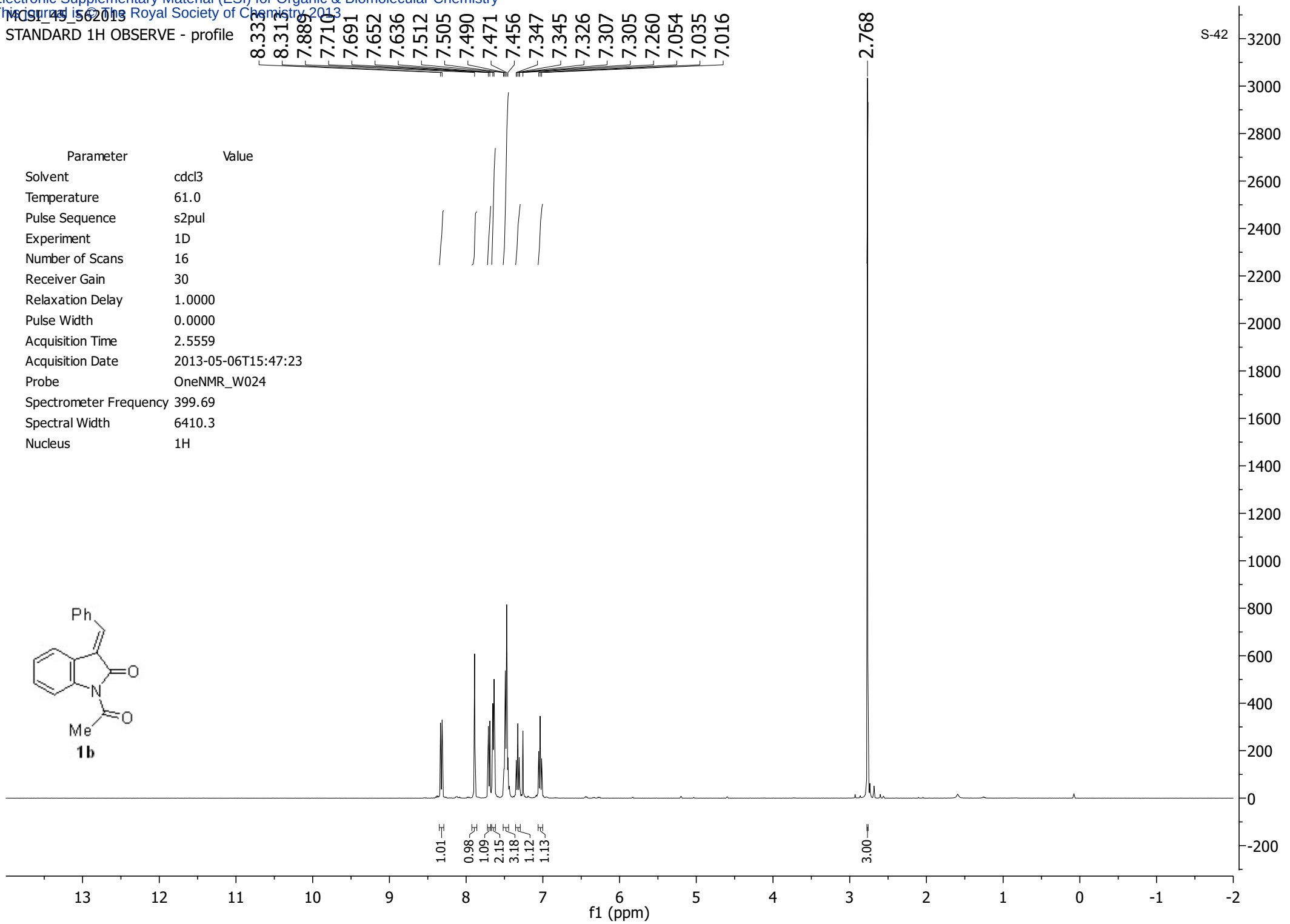
1n

f1 (ppm)

MCSI_45_562015
STANDARD 1H OBSERVE - profile

Parameter	Value
Solvent	cdcl3
Temperature	61.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-05-06T15:47:23
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

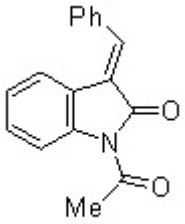
1b



MCSI_45_56201scarbon 1
STANDARD 1H OBSERVE profile

171.609 168.807 140.461 138.896 134.603 130.468 130.251 129.387 128.997 126.262 124.674 122.351 122.058 116.937 77.548 77.230 76.912 27.139

Parameter	Value
Solvent	cdcl3
Temperature	61.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	480
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-05-06T15:48:38
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

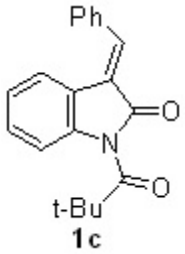


1b

f1 (ppm)

7.852 7.678 7.677 7.675 7.674 7.667 7.665 7.664 7.662 7.651 7.638 7.496 7.493 7.491 7.488 7.482 7.481 7.479 7.477 7.469 7.467 7.453 7.451 7.448 7.440 7.434 7.428 7.426 7.233 7.220 7.208 6.928 6.915 6.891 6.878 6.865 1.252

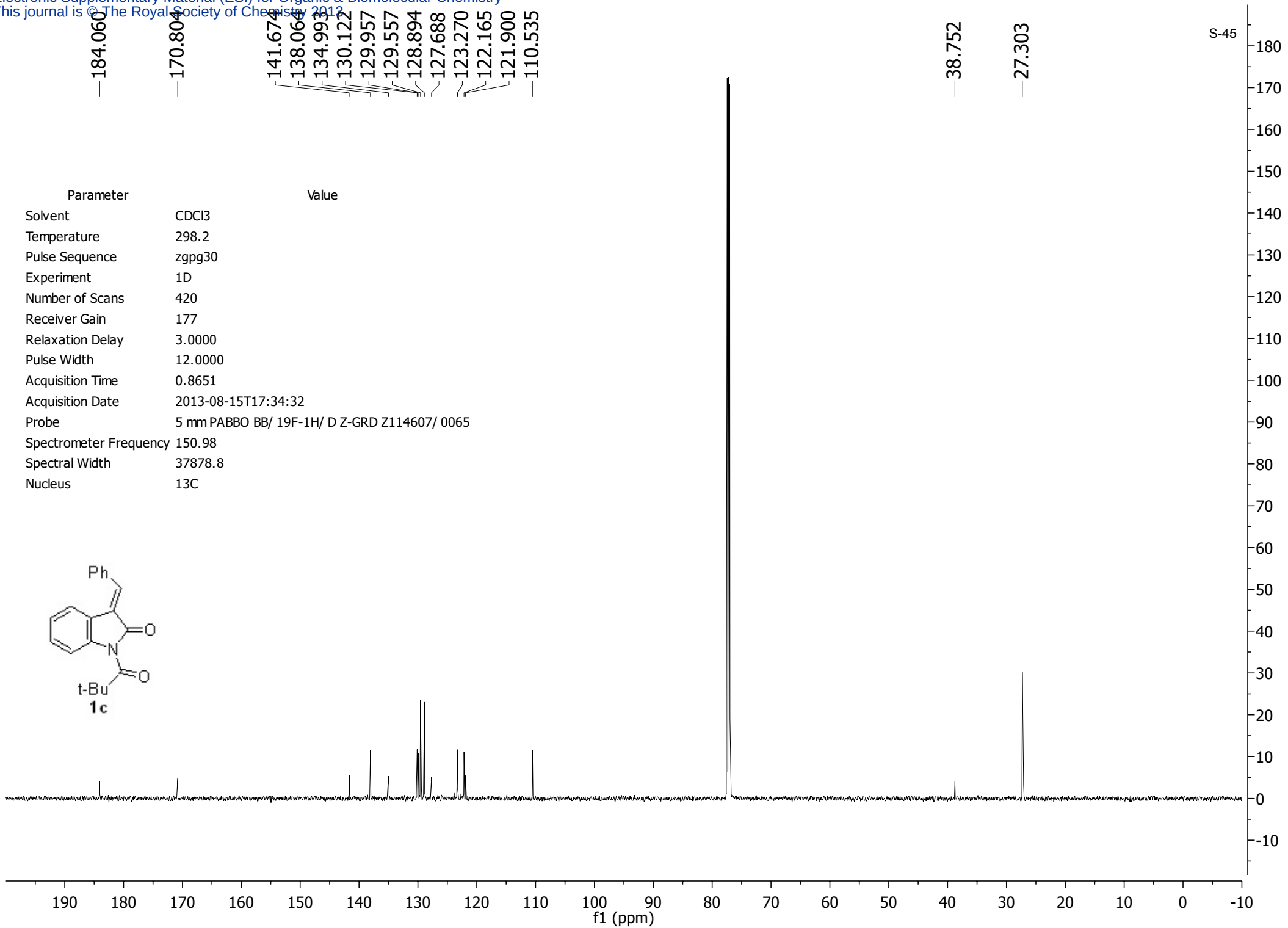
Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-08-15T16:49:06
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



1c

1.05 3.40 3.51 1.13 1.04 1.08 7.24

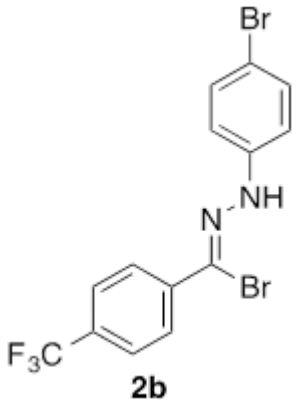
f1 (ppm)



MCS_LS_I_117char.1.fid
MCS I-117char, 1H

8.122 7.995 7.982 7.651 7.638 7.432 7.418 7.082 7.067

Parameter	Value
Solvent	CDCl3
Temperature	298.7
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-05T09:43:00
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



2b

1.00 1.97 2.01 1.96 1.98

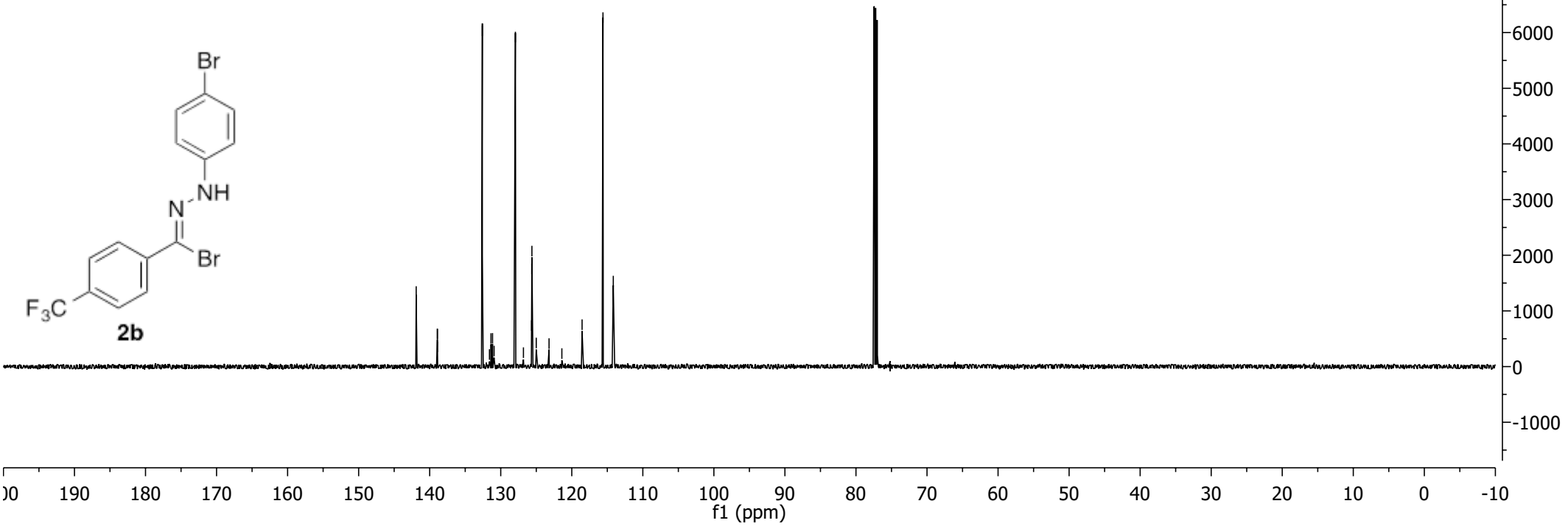
f1 (ppm)

MCS_LS_I_117char.3.fid
MCS I-117char, 13C

141.906 138.927 138.913 138.905 132.594 131.582 131.371 131.155 130.938 127.937 126.805 125.663 125.638 125.613 125.587 125.002 123.200 121.397 118.551 115.609 114.158

Parameter	Value
Solvent	CDCl3
Temperature	299.4
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	780
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-04-05T10:38:13
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

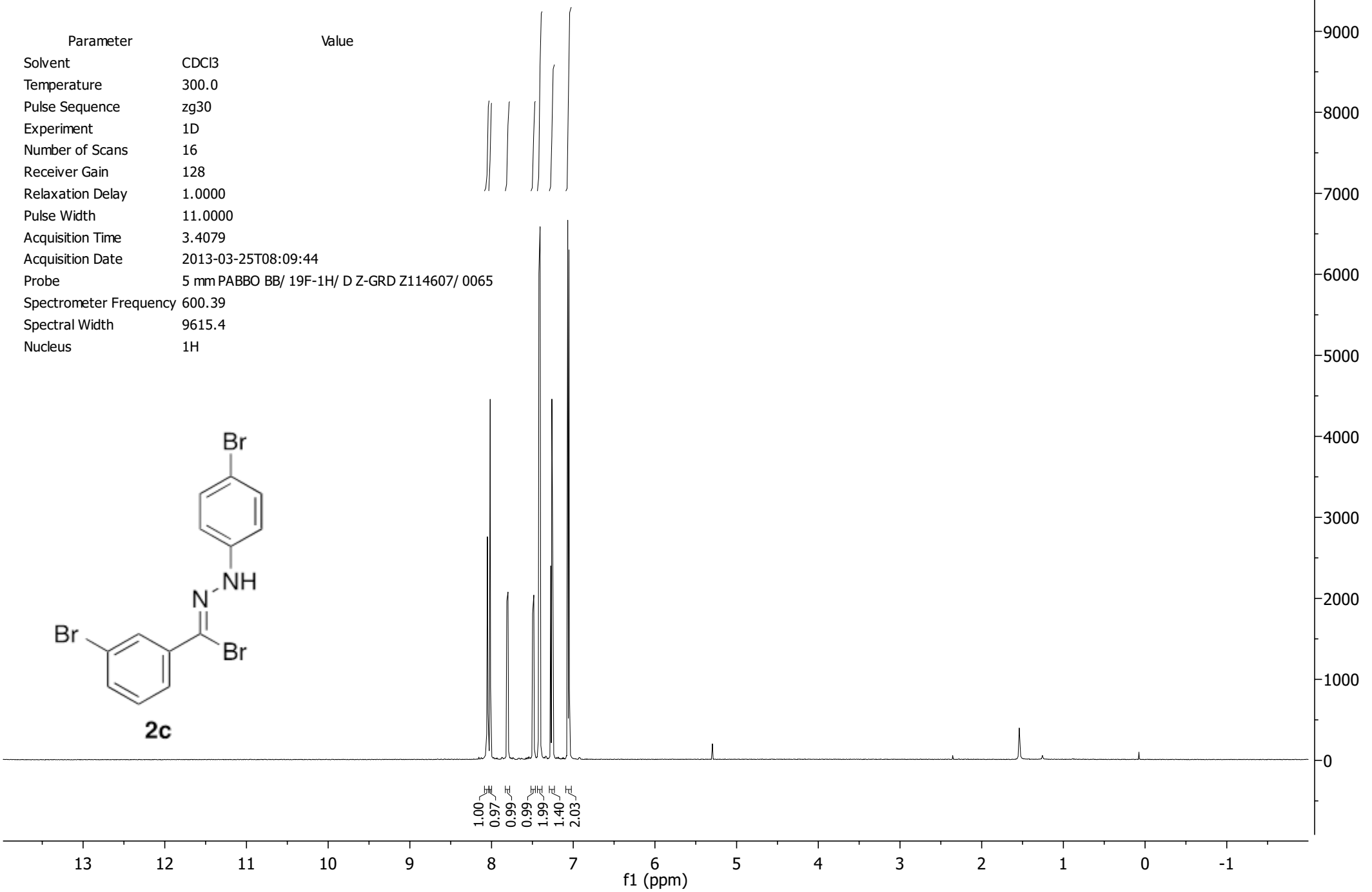
2b



MCS_LS_I_82.10.fid
MCS I-82, DCM solvent

Parameter	Value
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-03-25T08:09:44
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

2c

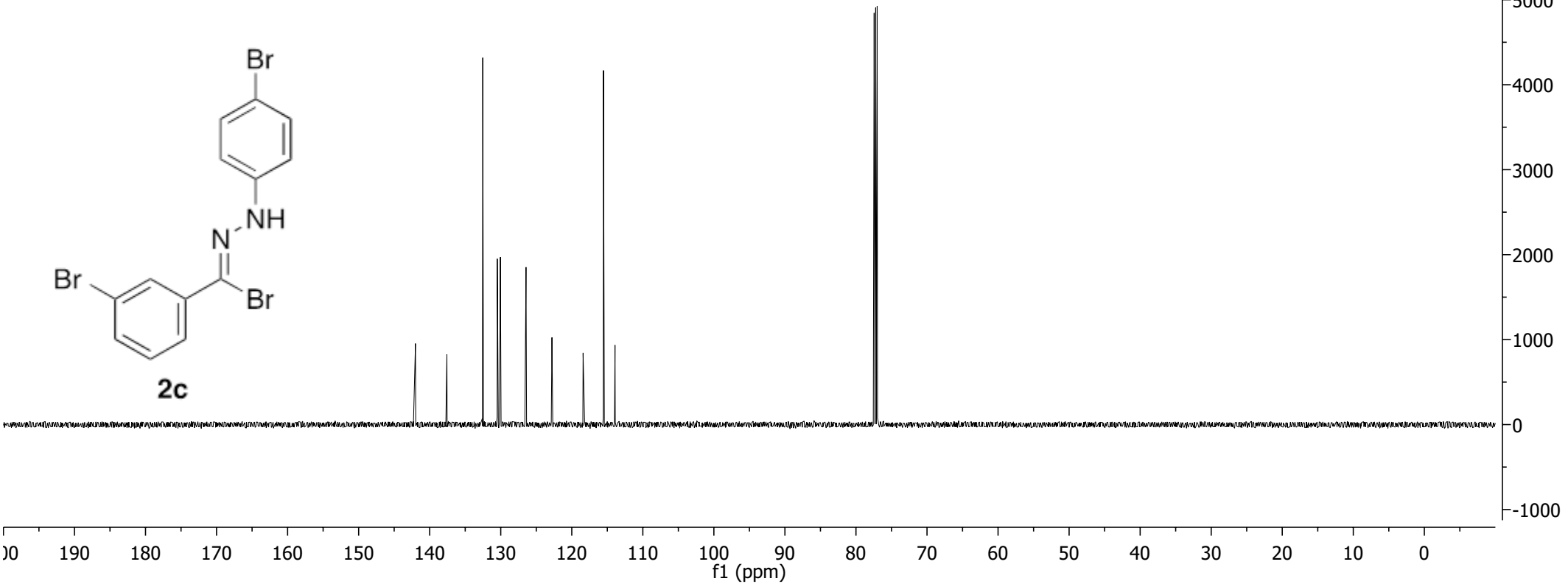


MCS_LS_I_82cnar.2.nd
MCS I-82 pdt 13C

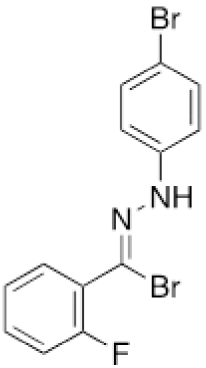
142.002
137.576
132.532
130.488
130.050
126.440
122.793
118.409
115.542
113.915

Parameter	Value
Solvent	CDCl3
Temperature	299.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	631
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-04-02T11:52:49
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

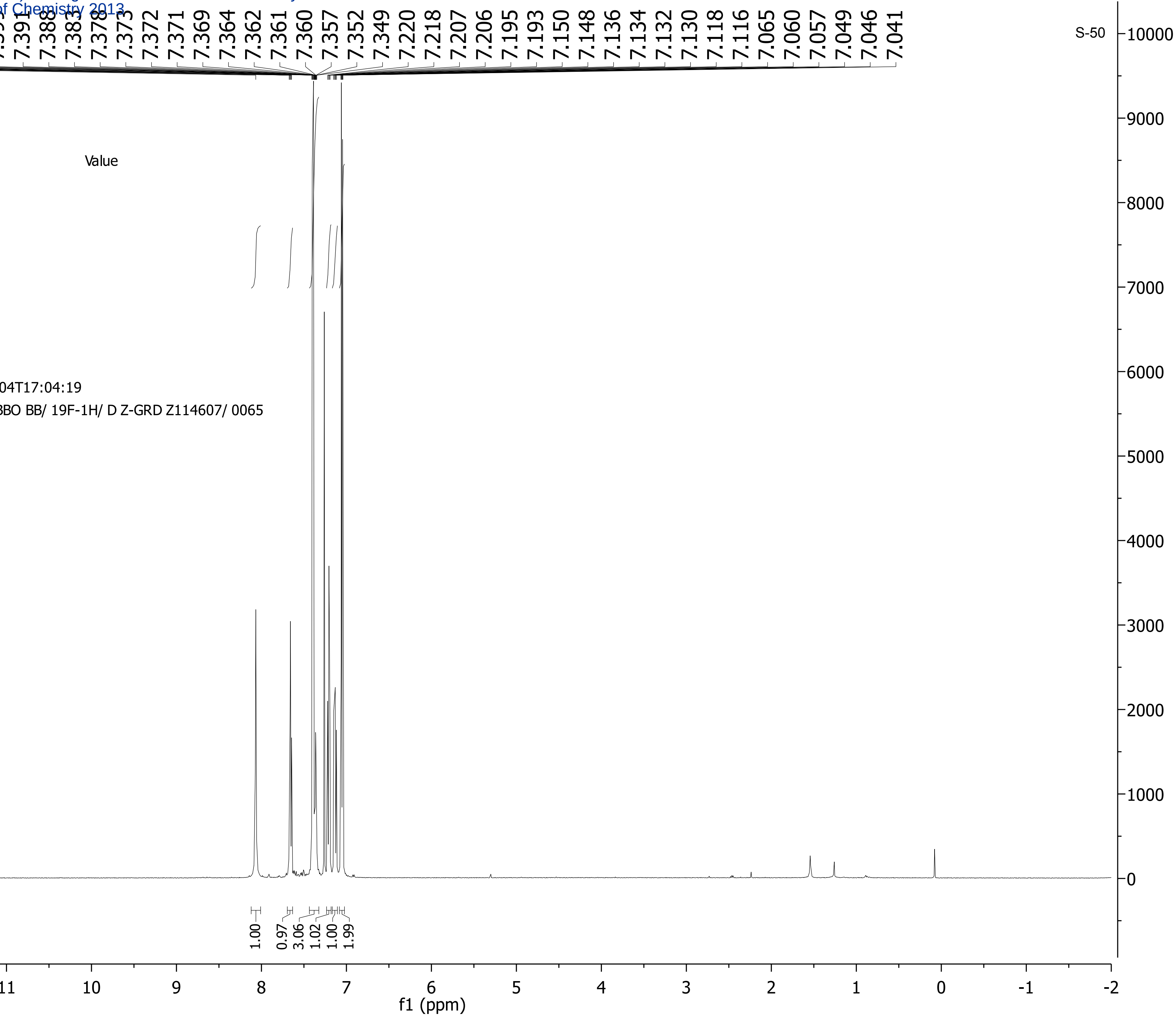
2c



Parameter	Value
Solvent	CDCl3
Temperature	297.6
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-01-04T17:04:19
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



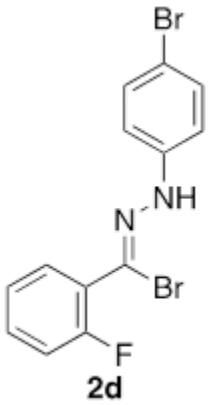
2d



CARBON_01
MCS I-94A pdt; 13C

160.947
158.398
142.138
132.457
131.462
131.450
131.158
131.073
124.657
124.553
124.235
124.196
116.782
116.563
115.504
113.727
112.698
112.647

Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	512
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-02-12T16:28:46
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



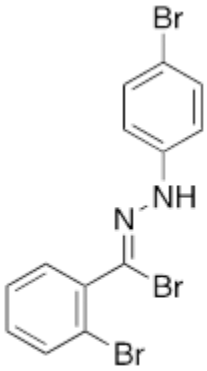
2d

f1 (ppm)

MCS_LS_I_124char.1.fid
MCS I-124 pdt 1H

7.991 7.663 7.649 7.527 7.514 7.392 7.379 7.260 7.245 7.062 7.048

Parameter	Value
Solvent	CDCl3
Temperature	298.8
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-02T16:06:49
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



2e

1.00 1.06 1.07 3.17 1.62 2.13

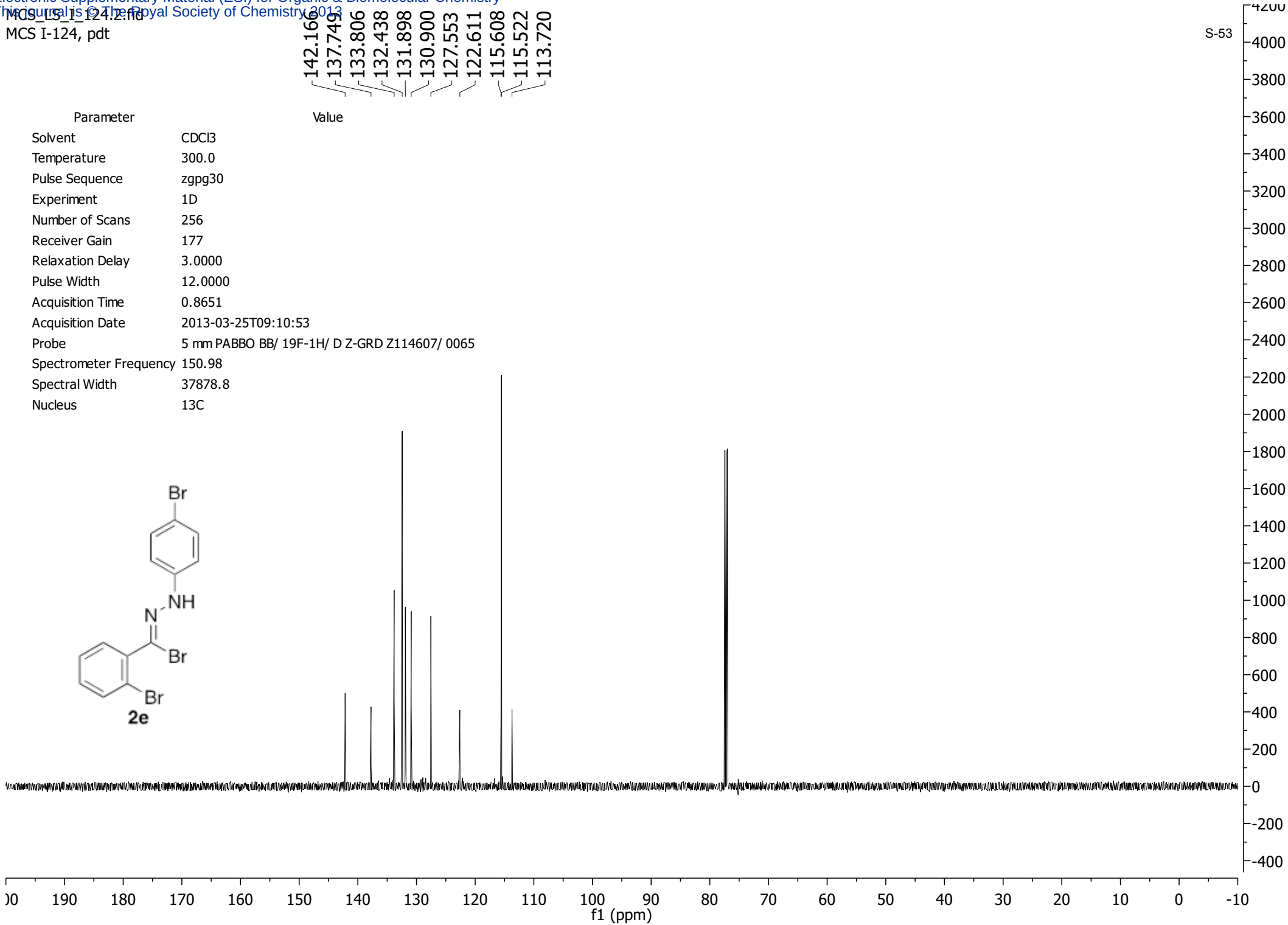
f1 (ppm)

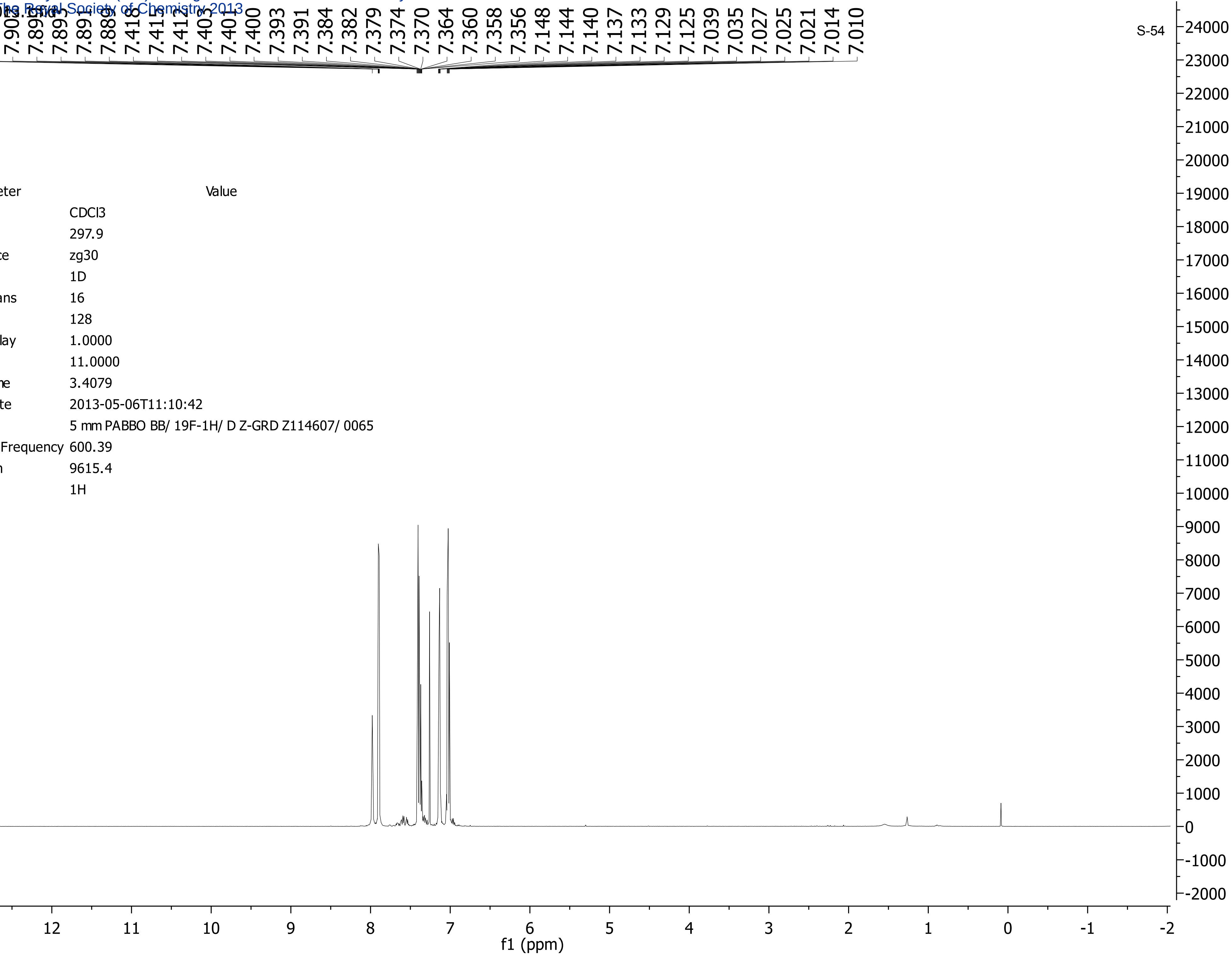
MCS_LS_I_124.2.fid
MCS I-124, pdt

142.166
137.749
133.806
132.438
131.898
130.900
127.553
122.611
115.608
115.522
113.720

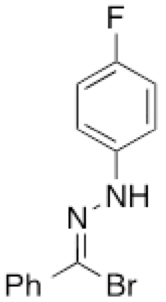
Parameter	Value
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	256
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-03-25T09:10:53
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

2e





Parameter	Value
Solvent	CDCl3
Temperature	297.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-05-06T11:10:42
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

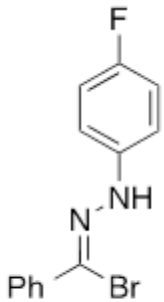


2f

TG2_189_562013.2.fid
carbon

158.924
157.339
139.668
135.864
129.588
128.632
127.846
119.714
116.316
116.165
114.941
114.891

Parameter	Value
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	273
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-05-06T11:14:08
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



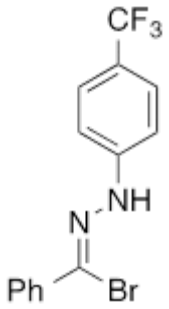
2f

f1 (ppm)

MCS_LS_I_101.1.fid
MCS I-101 pdt

8.200 7.925 7.922 7.911 7.909 7.568 7.553 7.426 7.416 7.413 7.410 7.244 7.230

Parameter	Value
Solvent	CDCl3
Temperature	298.5
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	88
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-02-11T22:01:36
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

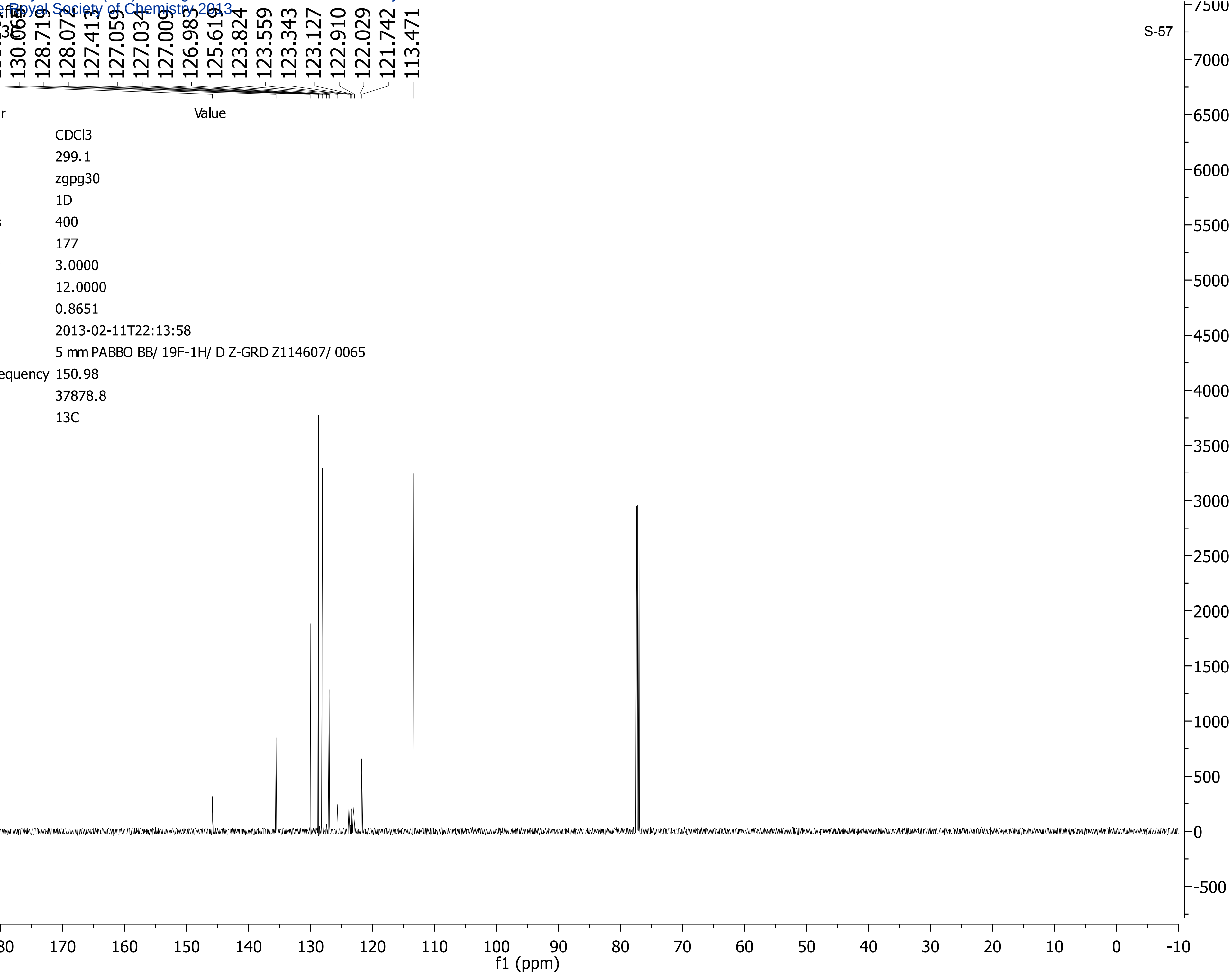


2g

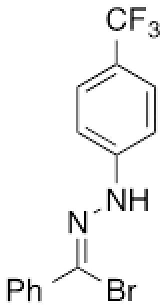
1.00 1.97 2.05 3.02 2.04

f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



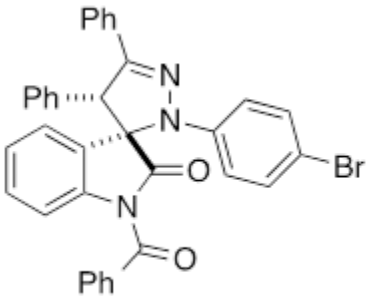
Parameter	Value
Solvent	CDCl3
Temperature	299.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	400
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-02-11T22:13:58
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



2g

7.777 7.763 7.653 7.647 7.642 7.553 7.540 7.528 7.373 7.360 7.347 7.331 7.325 7.308 7.294 7.277 7.274 7.266 7.260 7.059 6.865 6.850 6.844 6.831 6.442 6.430 5.094

Parameter	Value
Solvent	CDCl3
Temperature	297.4
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	88
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-01-17T19:17:08
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



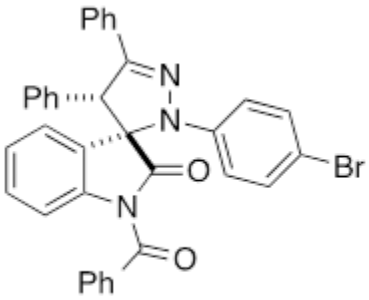
3a

1.08 2.22 1.10 13.43 1.90 3.25 1.04 1.00

f1 (ppm)

174.850 169.282 151.340 144.252 140.126 134.039 133.552 133.488 132.179 131.144 130.468 129.553 129.494 129.164 128.665 128.644 128.499 127.154 126.759 124.994 124.689 119.569 115.618 114.919 77.828 77.442 77.230 77.019 63.057

Parameter	Value
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	509
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-17T19:30:35
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



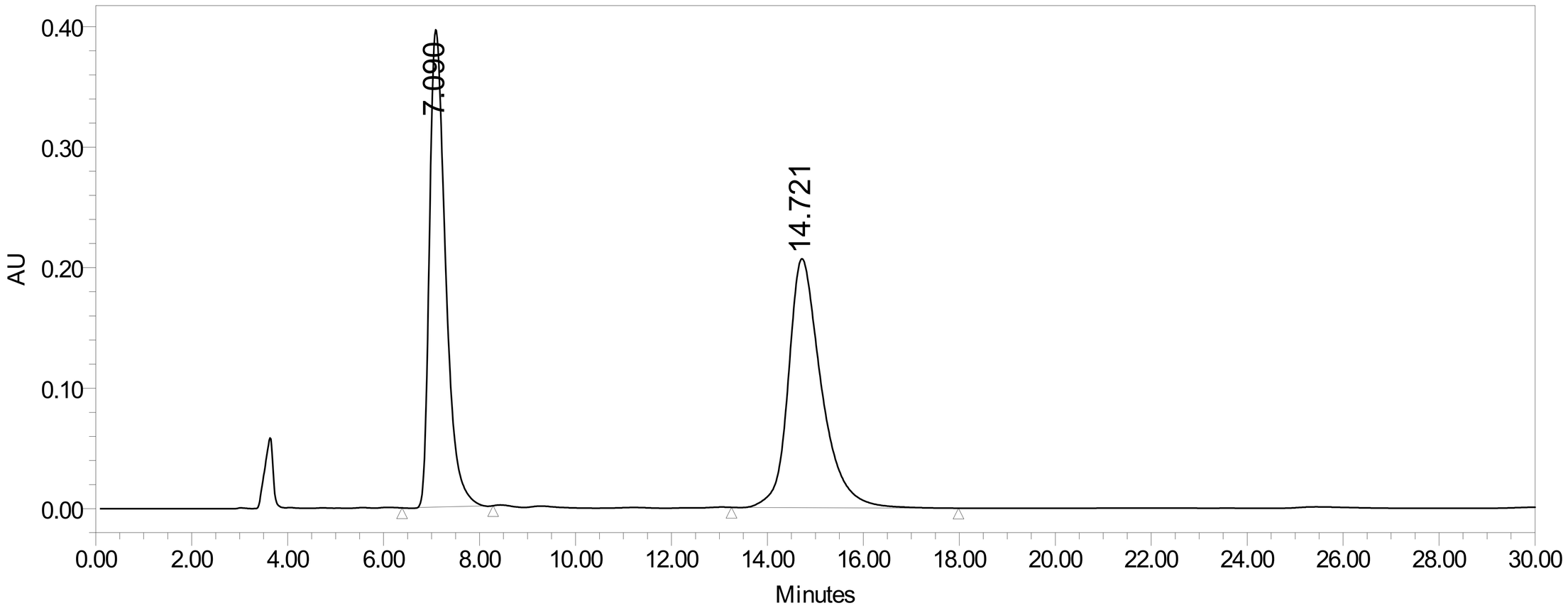
3a

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	LS_X_36A_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02292013
Vial:	29	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/1/2013 5:37:45 PM CST		
Date Processed:	3/7/2013 7:16:00 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8497; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

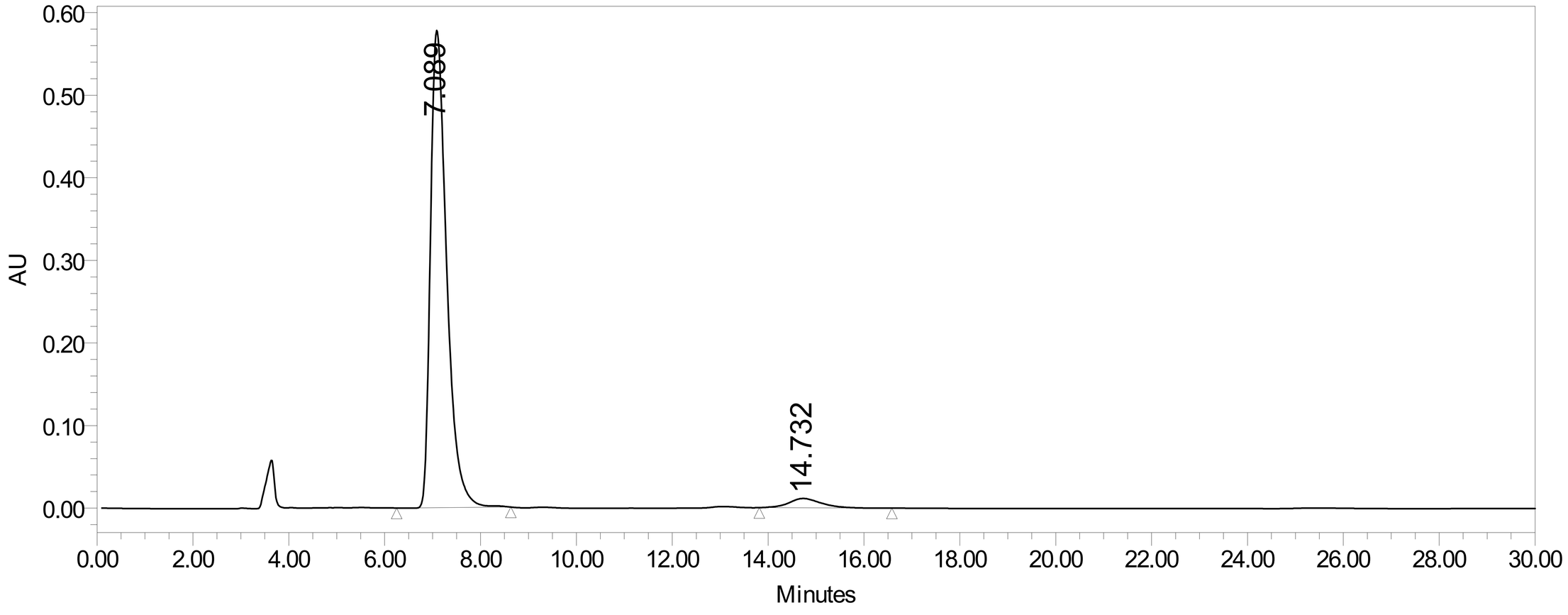
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.090	9238211	48.38	396610
2	W2489 ChA 254nm	14.721	9856572	51.62	206525

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	LS_X_38A_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02292013
Vial:	30	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/1/2013 6:08:25 PM CST		
Date Processed:	3/7/2013 7:17:39 PM CST		



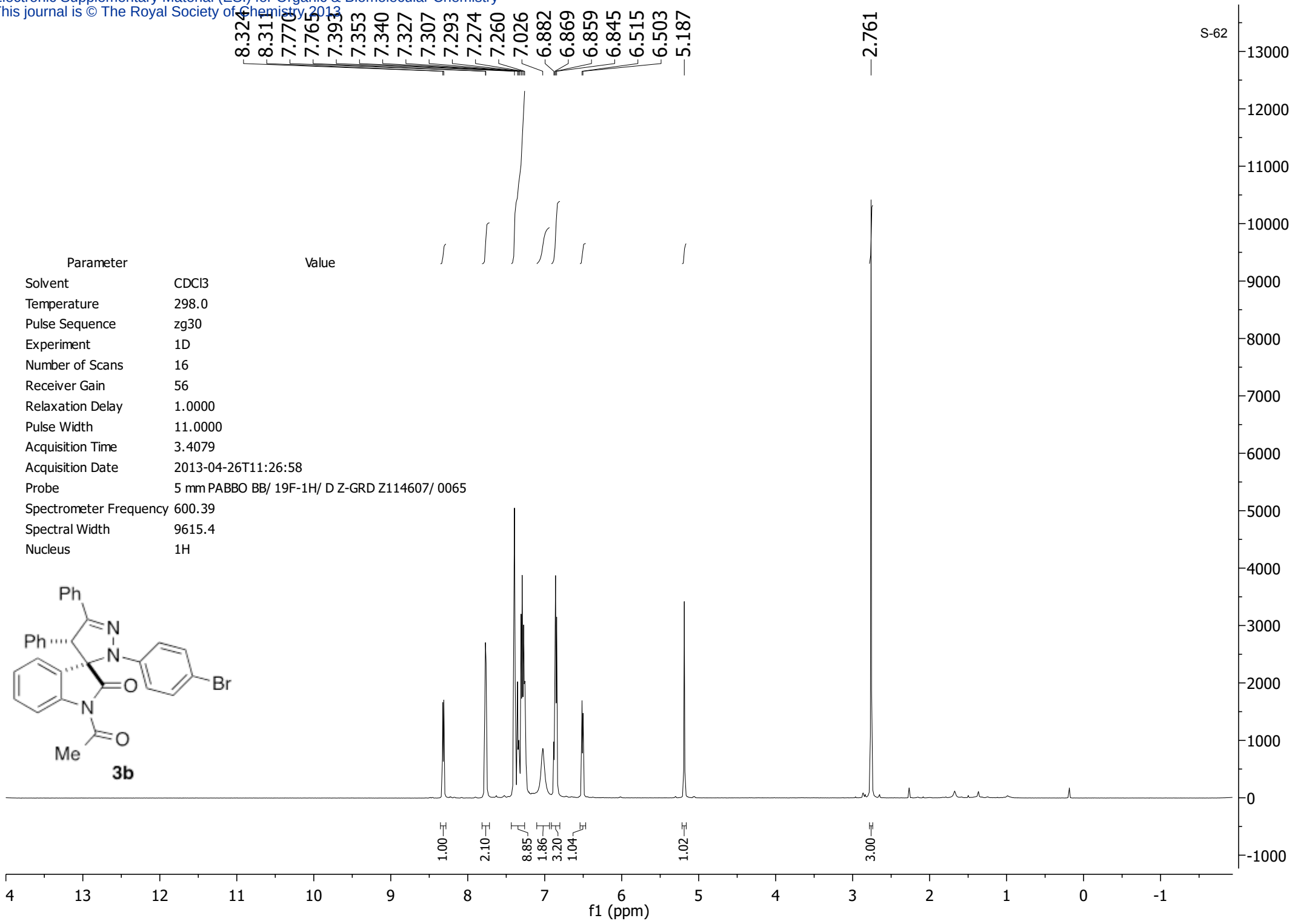
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8499; Processing Method: TG

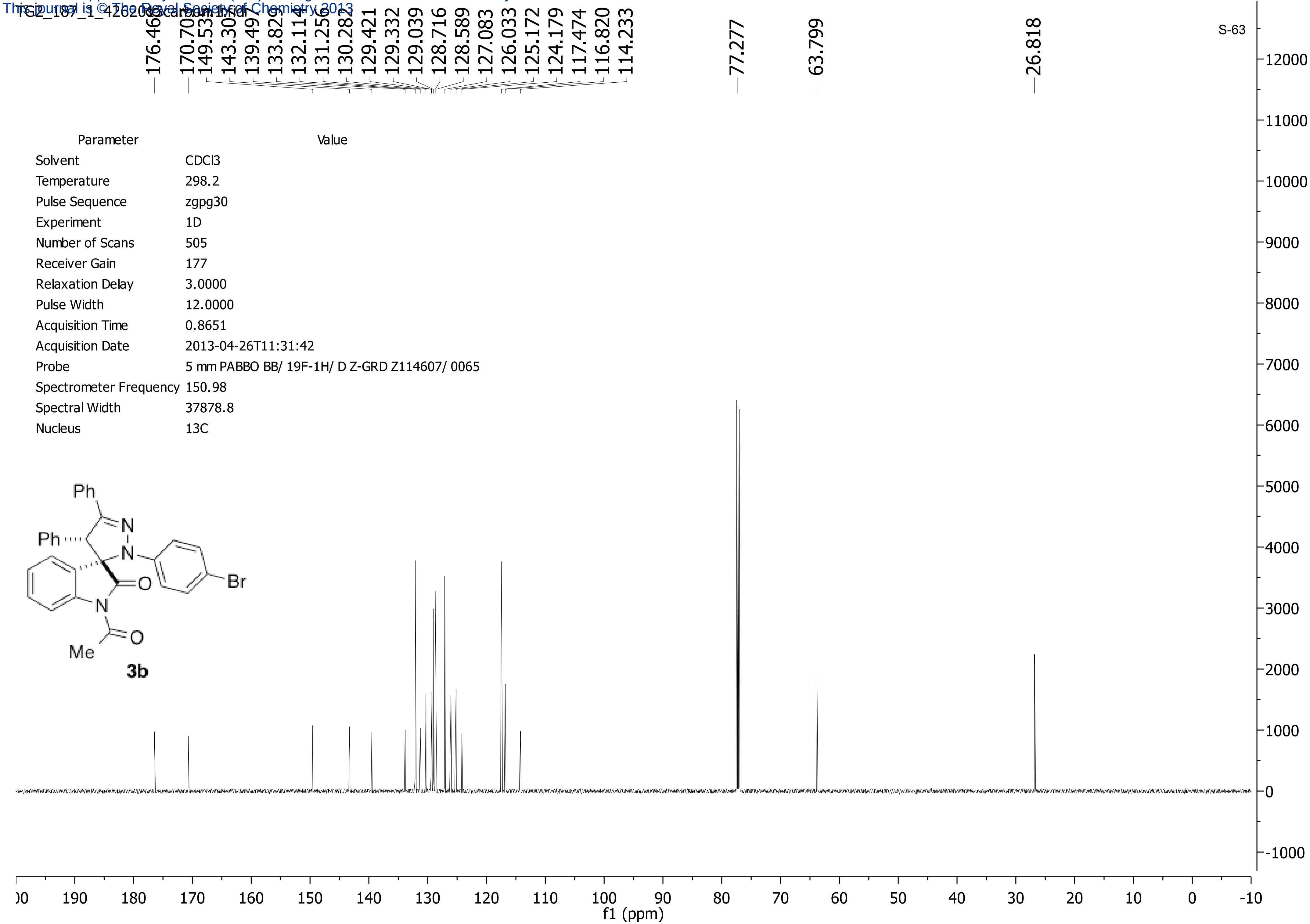
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.089	13601917	96.22	578428
2	W2489 ChA 254nm	14.732	534804	3.78	11342

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	56
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-26T11:26:58
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

3b





Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	505
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-04-26T11:31:42
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

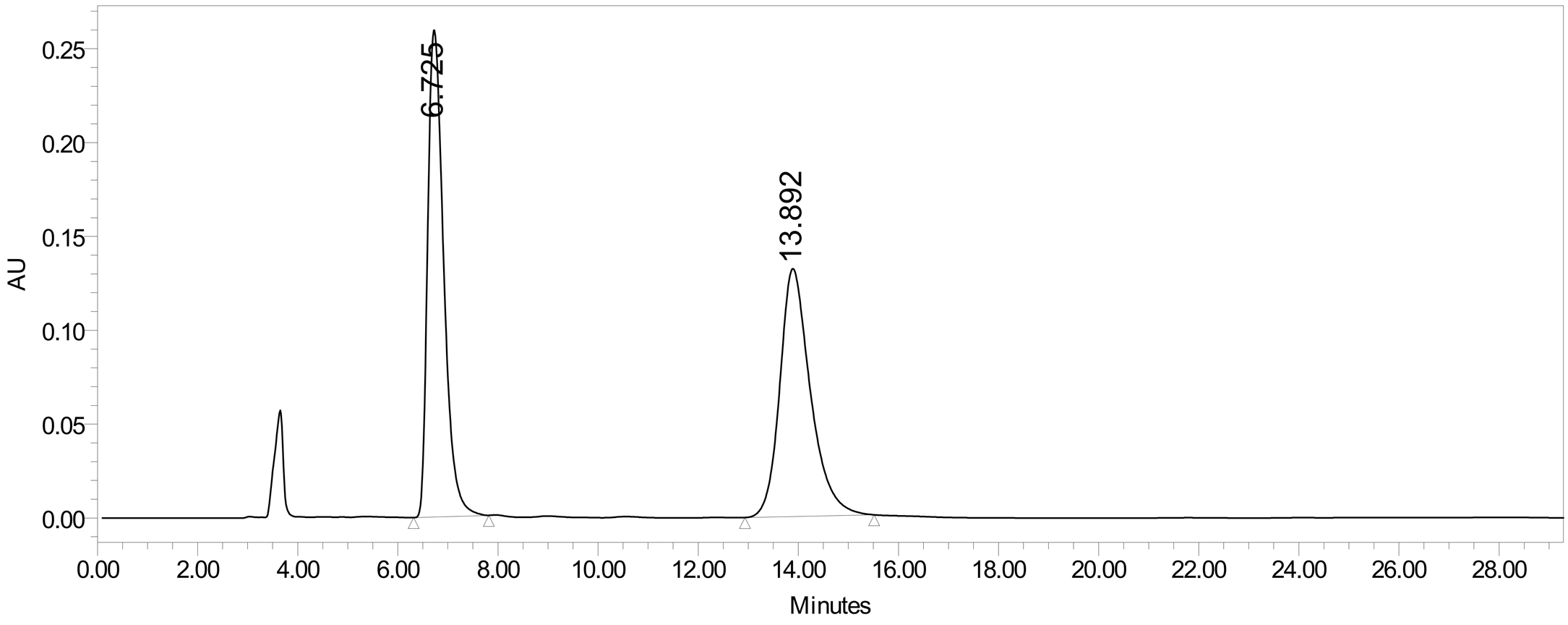
3b

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_187_2_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_187_4262013
Vial:	7	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	nacetylparentracemic
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	4/26/2013 1:49:59 PM CDT		
Date Processed:	5/4/2013 6:01:40 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2214; Processing Method: nacetylparentracemic

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.725	5773154	50.72	259821
2	W2489 ChA 254nm	13.892	5610170	49.28	132092

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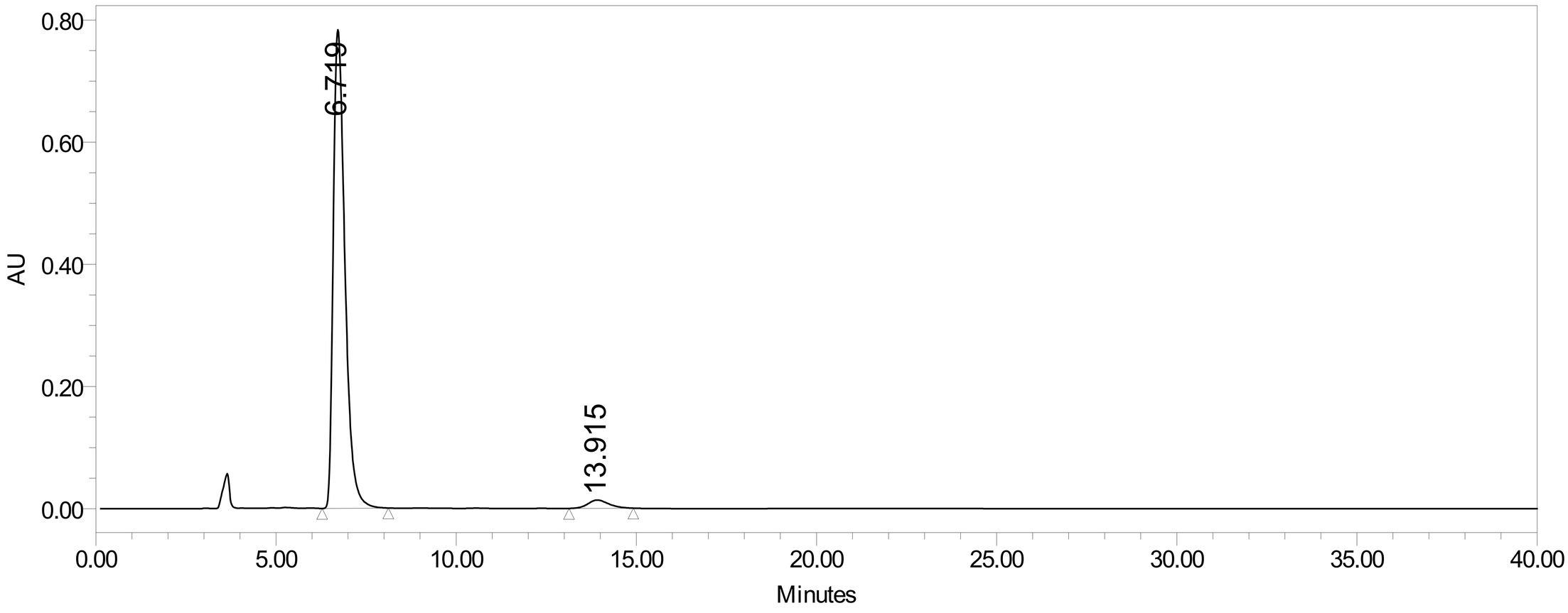
Injection Summary Report

SAMPLE INFORMATION

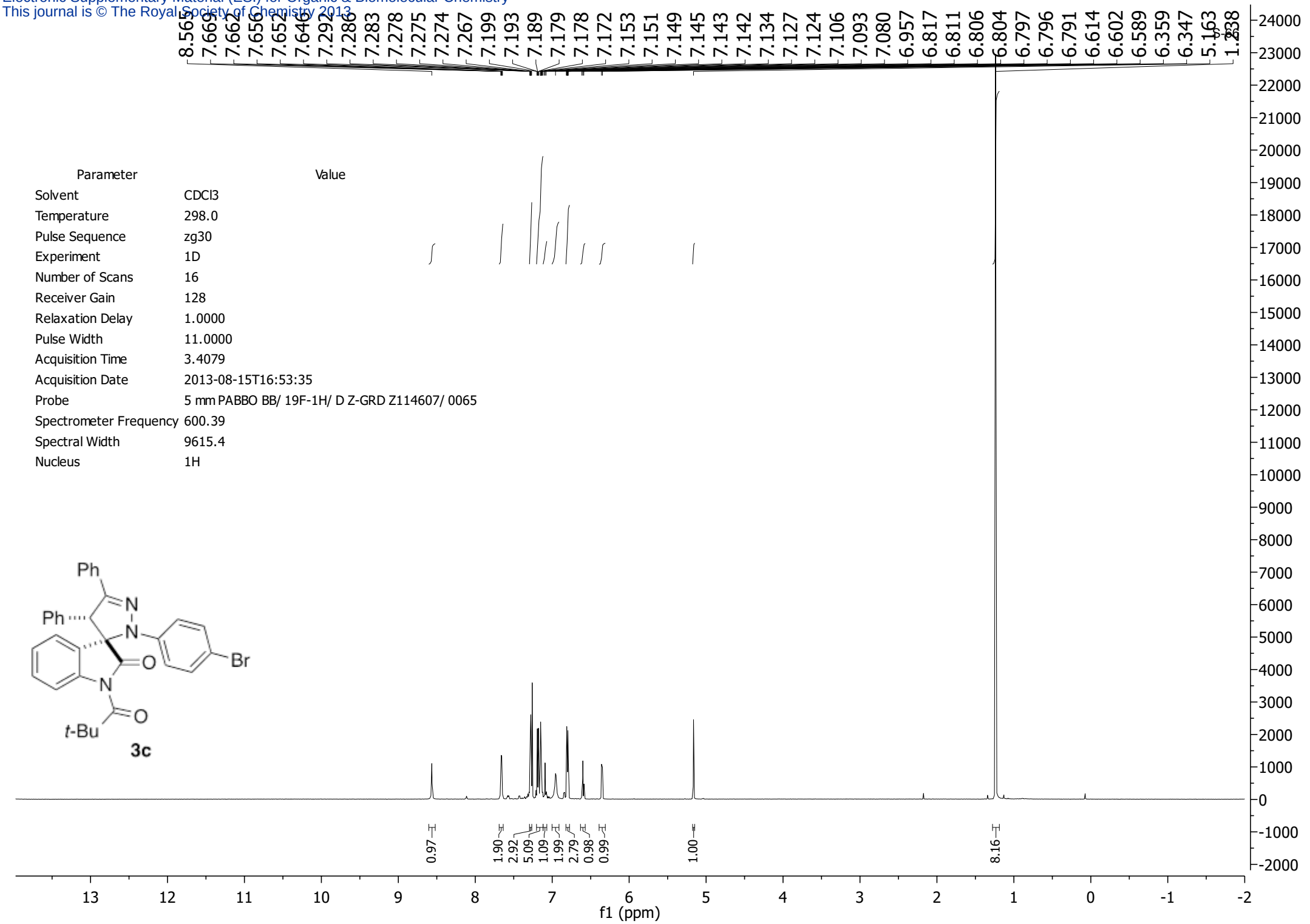
Sample Name:	TG2_187_1_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_187_4262013
Vial:	9	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	Nacetylparentenantioenriched
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	4/26/2013 2:20:10 PM CDT		
Date Processed:	5/4/2013 6:06:41 PM CDT		

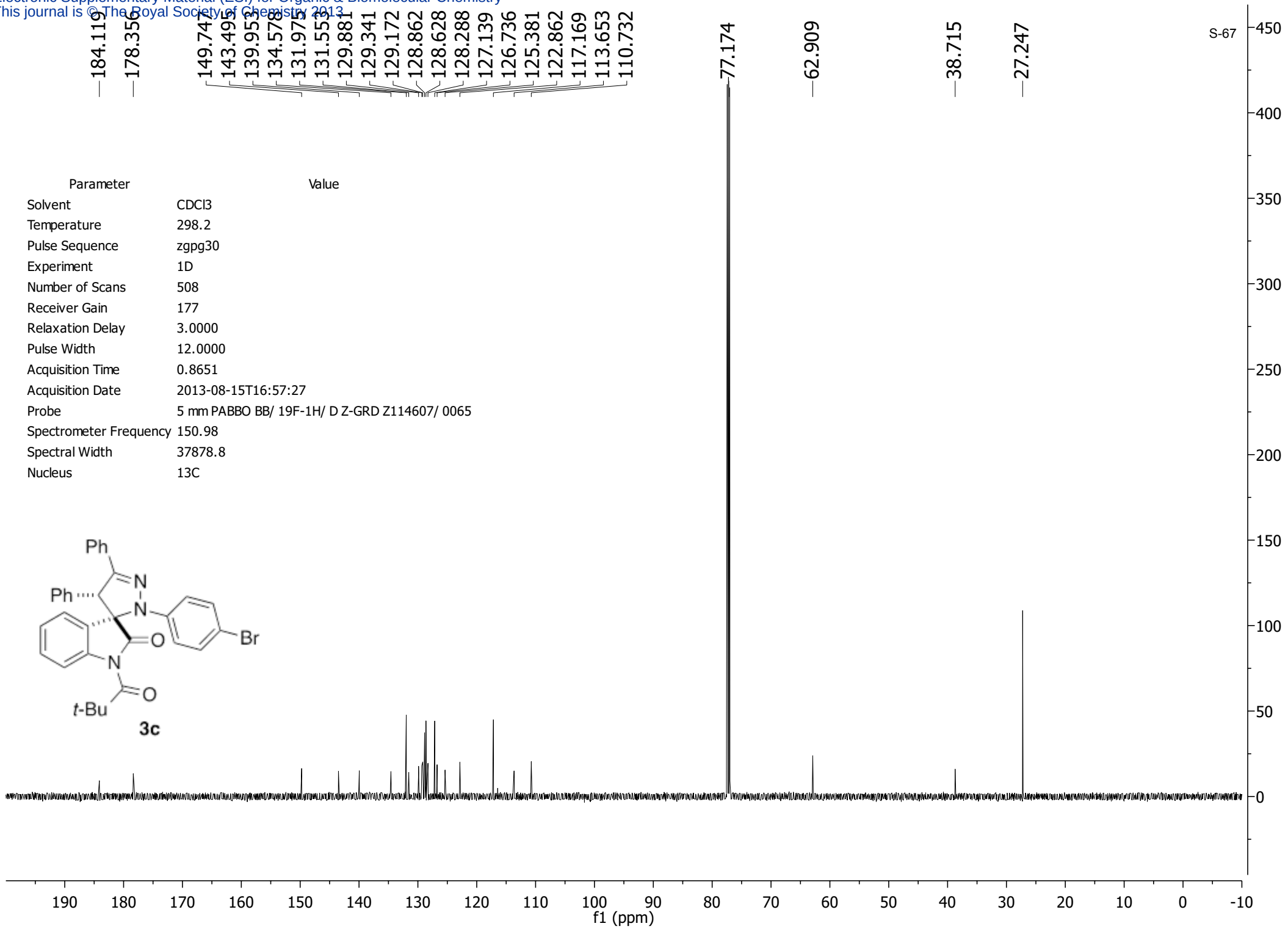


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2216; Processing Method: Nacetylparentenantioenriched

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.719	17609044	96.98	783651
2	W2489 ChA 254nm	13.915	548362	3.02	13593





Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	508
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-08-15T16:57:27
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

3c

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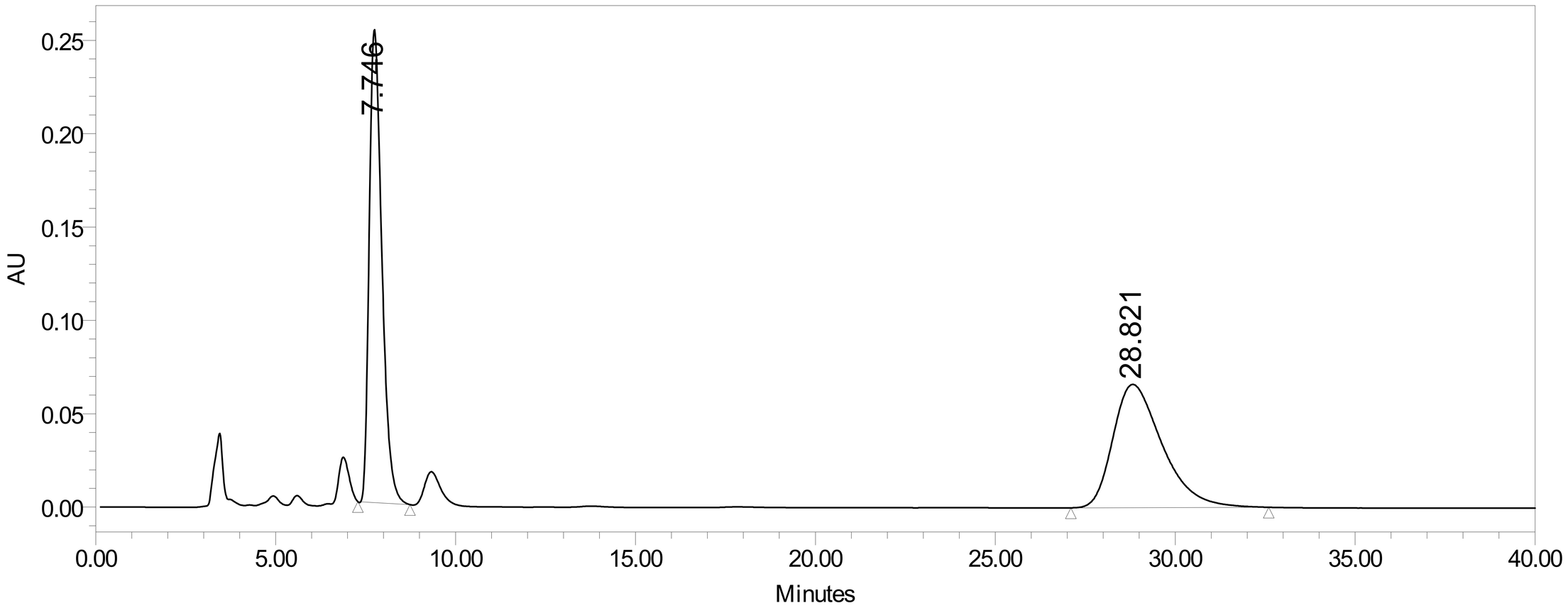
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	LSX_41A_ADH20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	LSX41_8172013
Vial:	6	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	8/17/2013 2:25:50 PM CDT		
Date Processed:	8/22/2013 10:41:20 AM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5901; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.746	6187955	49.64	253341
2	W2489 ChA 254nm	28.821	6278613	50.36	66005

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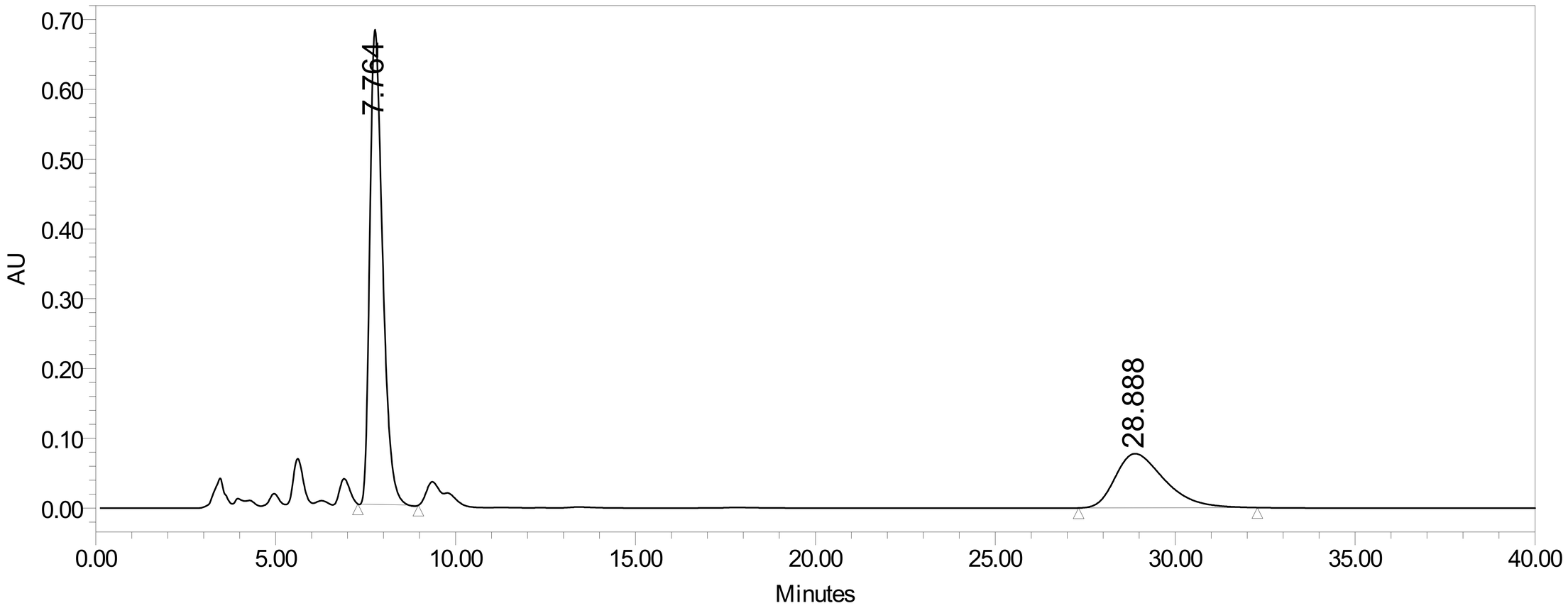
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	LSX_41B_ADH20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	LSX41_8172013
Vial:	7	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	8/17/2013 3:06:31 PM CDT		
Date Processed:	8/22/2013 10:42:43 AM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5903; Processing Method: tony1

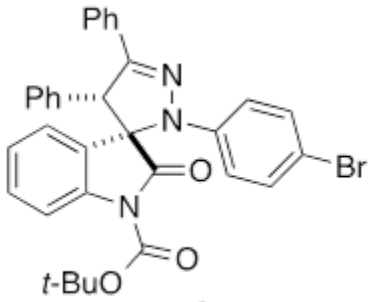
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.764	16811535	69.49	680341
2	W2489 ChA 254nm	28.888	7379807	30.51	77646

TG2_185_1_1_522013.1.fid

7.880 7.866 7.661 7.655 7.649 7.645 7.282 7.277 7.272 7.263 7.233 7.231 7.219 7.203 7.188 7.172 7.161 7.148 6.926 6.769 6.754 6.726 6.725 6.713 6.701 6.388 6.376 1.638

Parameter	Value
Solvent	CDCl3
Temperature	297.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	83
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-05-02T19:37:30
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



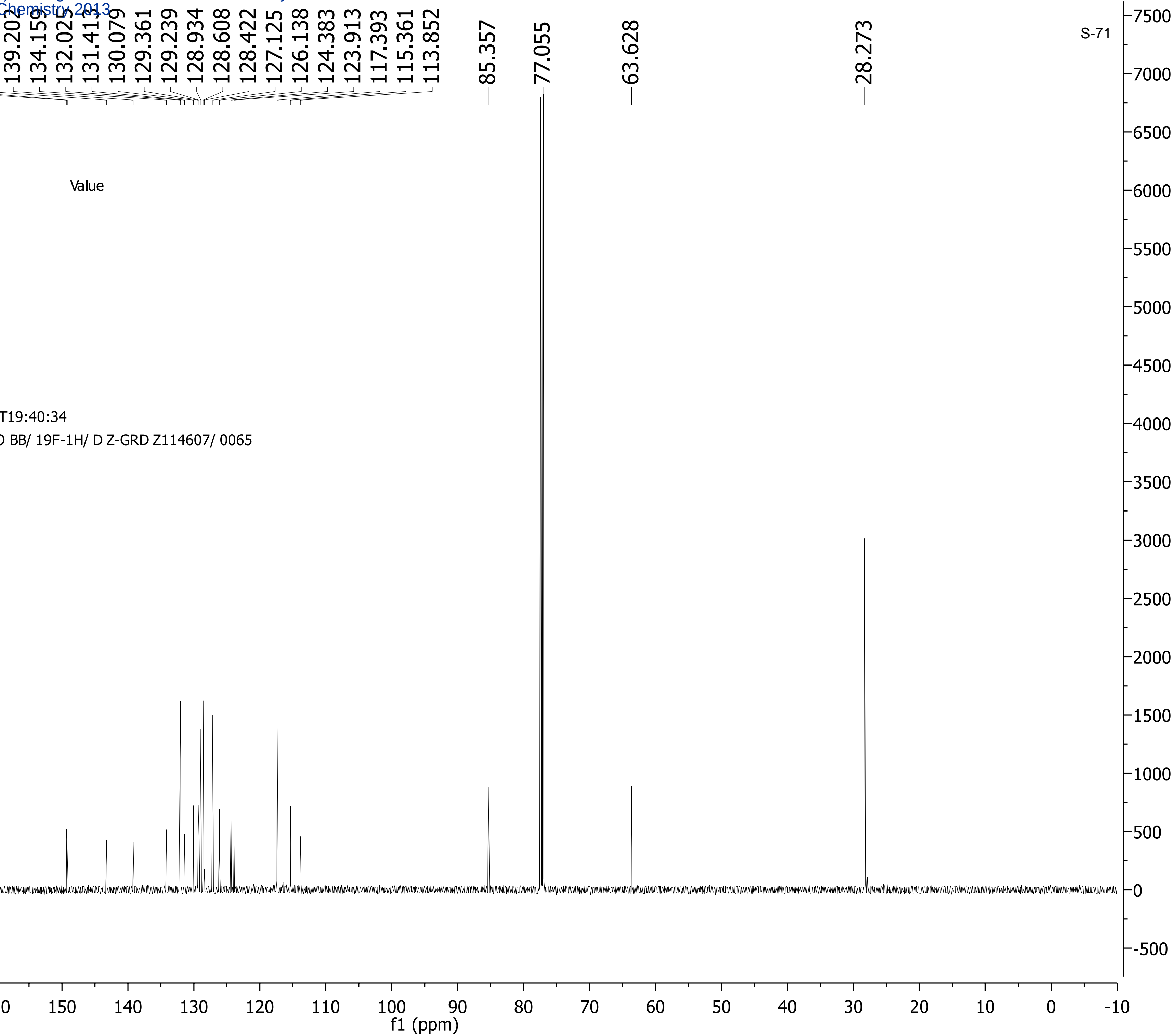
3d

0.97 2.00 3.86 6.17 1.91 1.92 0.99 0.97 1.00 9.10

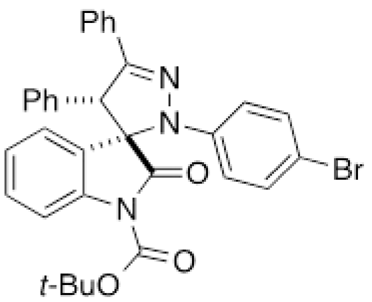
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

carbon



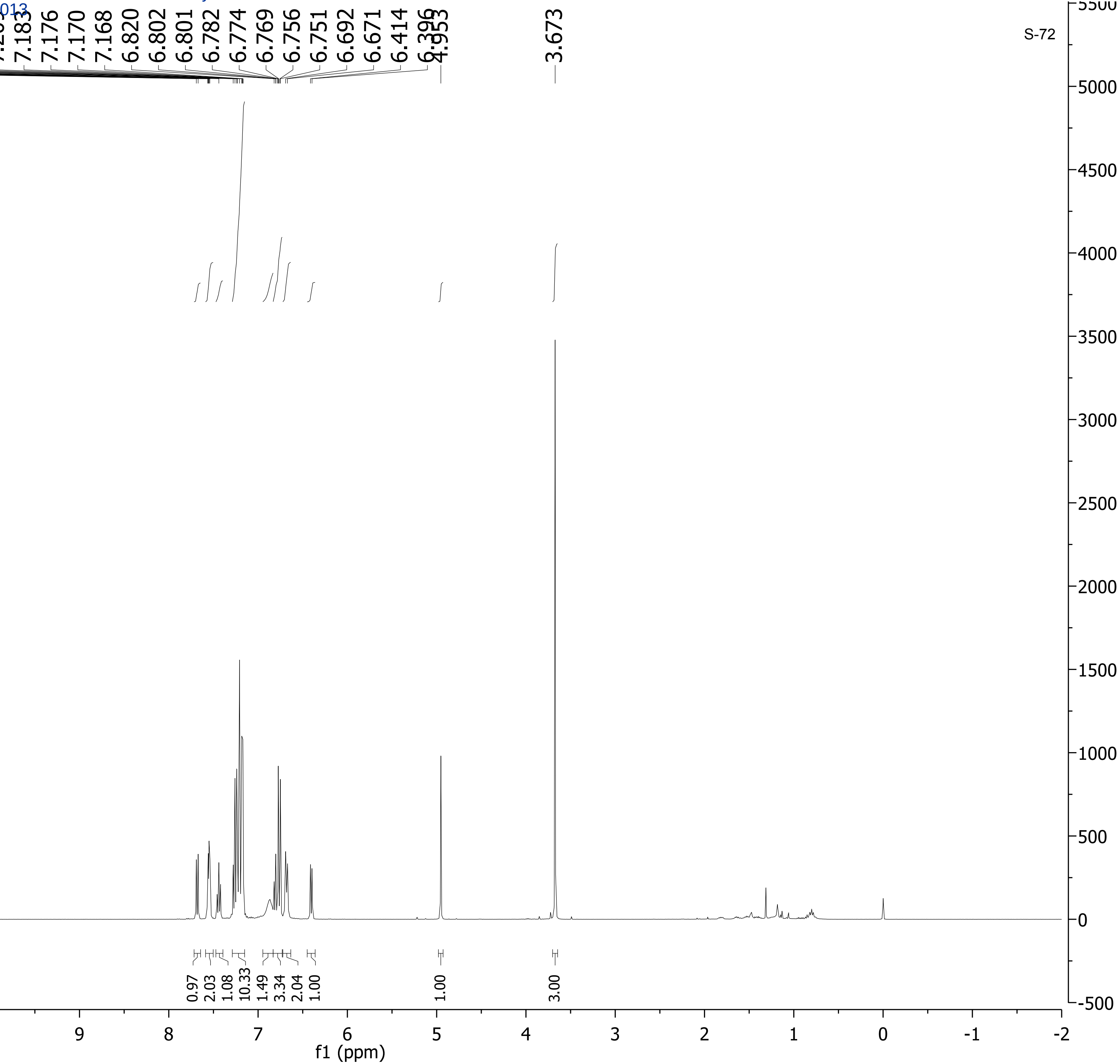
Parameter	Value
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	565
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-05-02T19:40:34
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

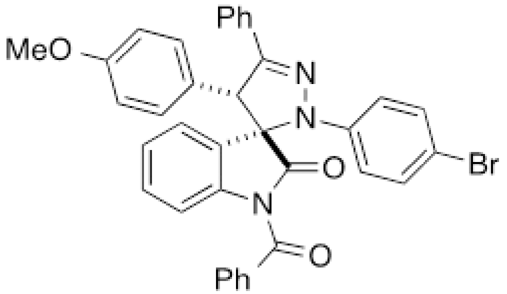


3d

STANDARD 1H OBSERVE - profile

Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-02-28T20:24:33
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H





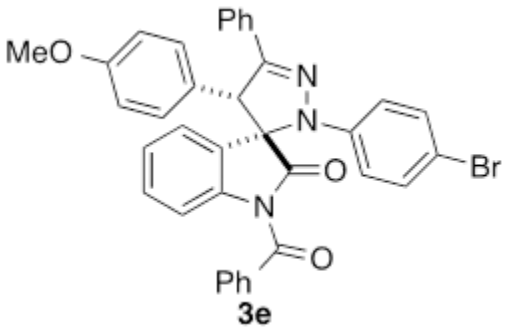
3e

TG2_131_2282013mod1_09carbon

STANDARD 1H OBSERVE_2profile

174.88 169.29 159.752 151.640 144.332 140.117 133.564 133.449 132.154 131.196 130.766 130.417 129.535 129.443 128.608 128.473 127.152 126.897 125.950 125.068 124.808 119.550 115.549 114.891 114.491 77.839 77.547 77.230 76.912 62.435 55.447

Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	618
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-02-28T20:35:57
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



3e

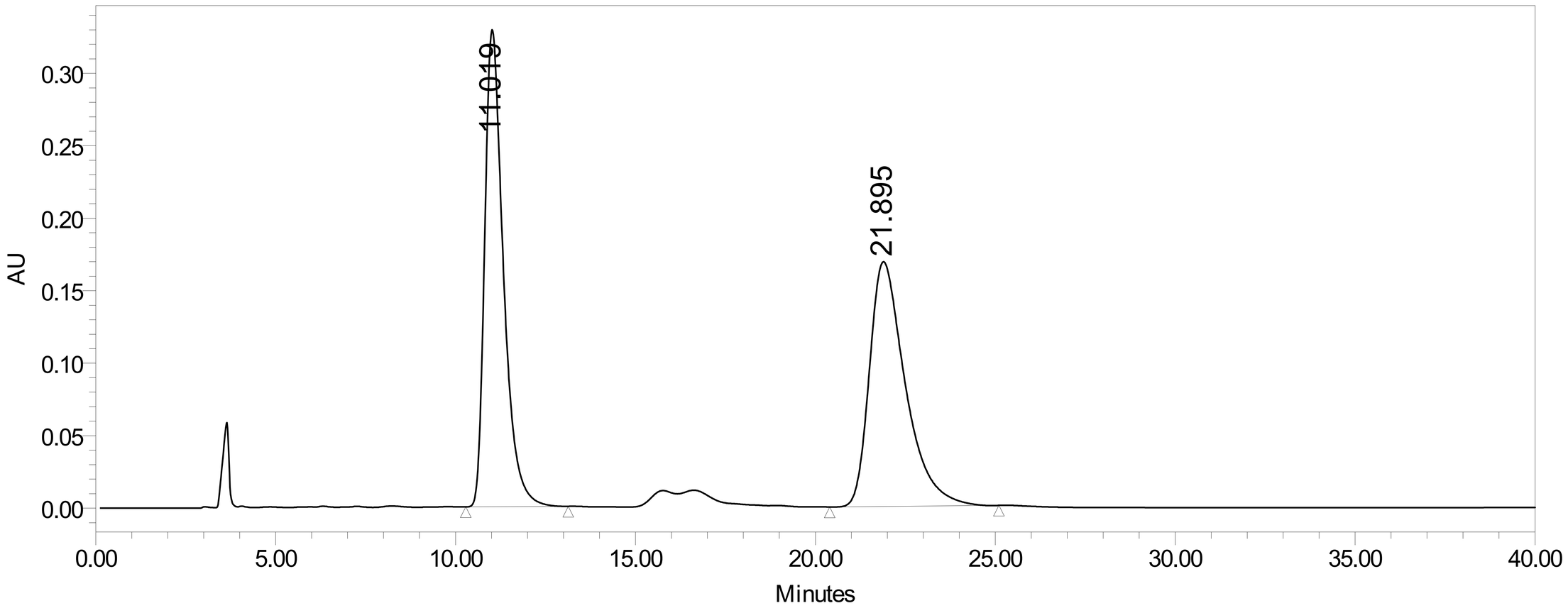
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG1_129_2_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02292013
Vial:	13	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/1/2013 4:16:12 PM CST		
Date Processed:	3/7/2013 7:21:17 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8501; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.019	11873910	50.35	329186
2	W2489 ChA 254nm	21.895	11706775	49.65	168855

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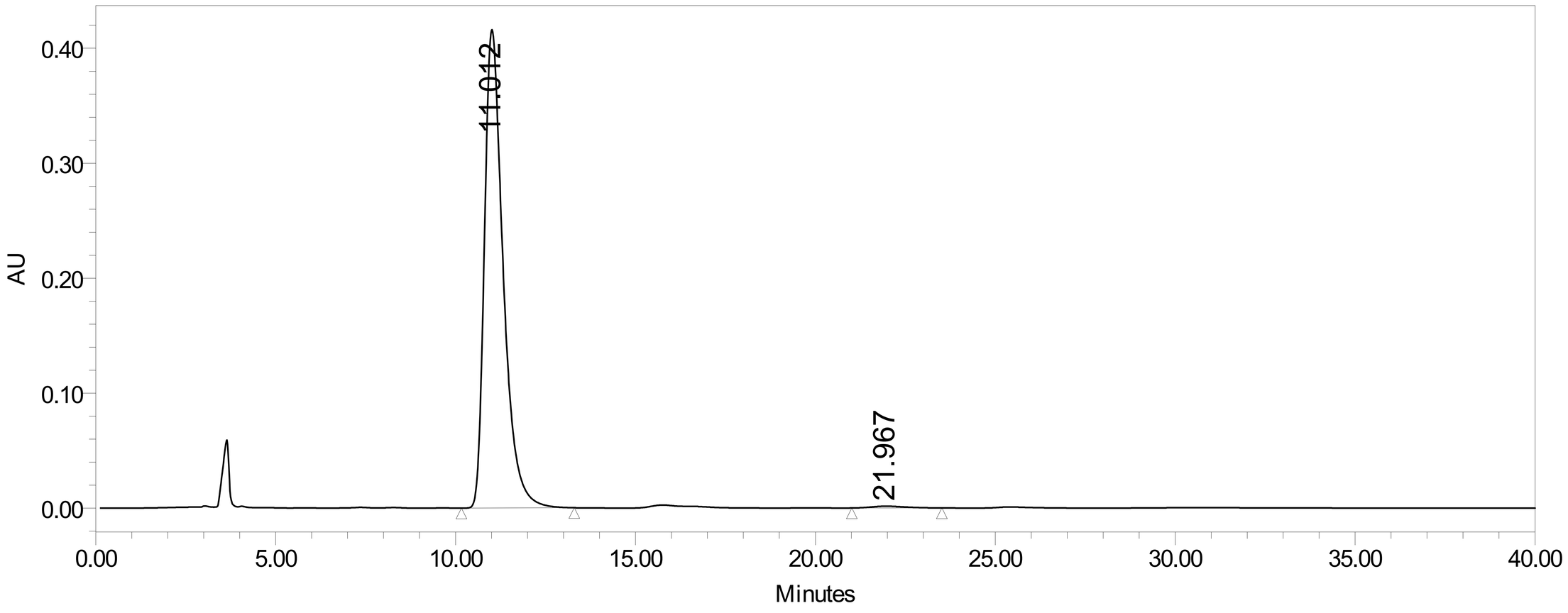
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_131_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02292013
Vial:	14	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/1/2013 4:56:55 PM CST		
Date Processed:	3/7/2013 7:23:32 PM CST		



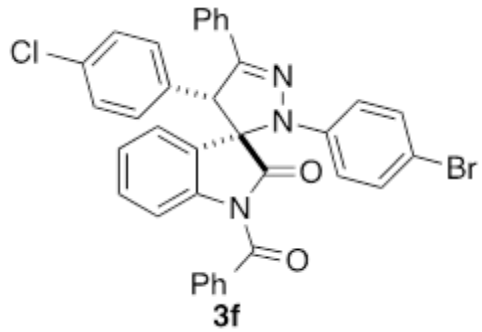
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8503; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.012	15062188	99.34	416183
2	W2489 ChA 254nm	21.967	100670	0.66	1572

7.812 7.798 7.652 7.649 7.641 7.636 7.572 7.399 7.386 7.373 7.364 7.349 7.321 7.318 7.312 7.298 7.276 7.263 6.973 6.972 6.960 6.959 6.947 6.946 6.887 6.872 6.517 6.506 5.090

Parameter	Value
Solvent	CDCl3
Temperature	297.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	75
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-01-05T15:31:16
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



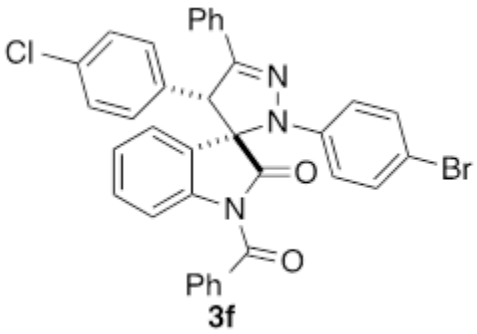
3f

1.02 2.32 1.12 14.09 1.66 1.28 2.13 1.04 1.00

f1 (ppm)

174.581 169.221 151.040 144.112 140.192 134.660 133.577 133.423 132.666 132.227 130.960 130.837 130.730 129.681 129.570 129.421 128.737 128.515 127.085 126.681 125.223 124.385 119.722 115.902 115.080 77.702 77.442 77.230 77.018 62.223

Parameter	Value
Solvent	CDCl3
Temperature	297.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	260
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-05T15:42:17
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



3f

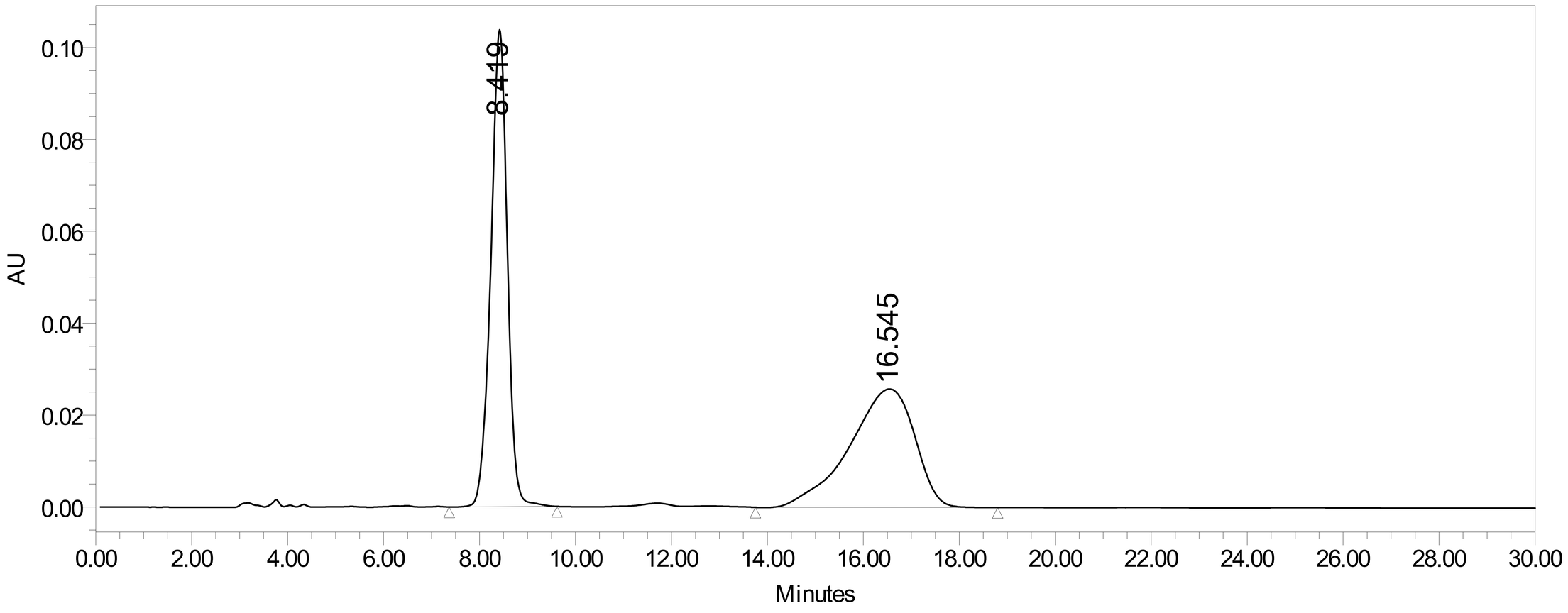
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG1_241_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG1_241_12202012
Vial:	5	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	um
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/20/2012 12:19:03 PM CST		
Date Processed:	3/7/2013 6:46:45 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8489; Processing Method: um

Processed Channel Descr.: W2489 ChA 254nm

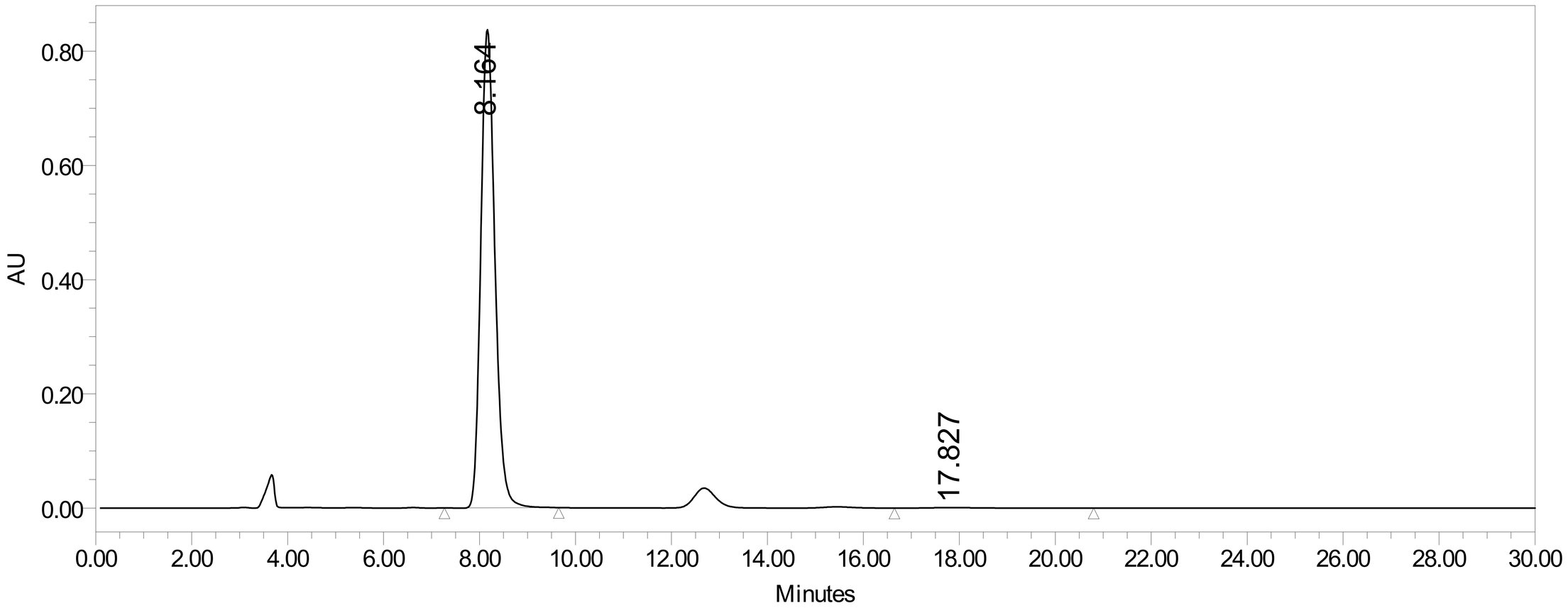
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.419	2478532	50.46	103826
2	W2489 ChA 254nm	16.545	2432960	49.54	25763

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_81_1_10%IPA1mpmADH	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_81_1192013
Vial:	12	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/19/2013 4:54:59 PM CST		
Date Processed:	3/7/2013 7:12:47 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8495; Processing Method: TG

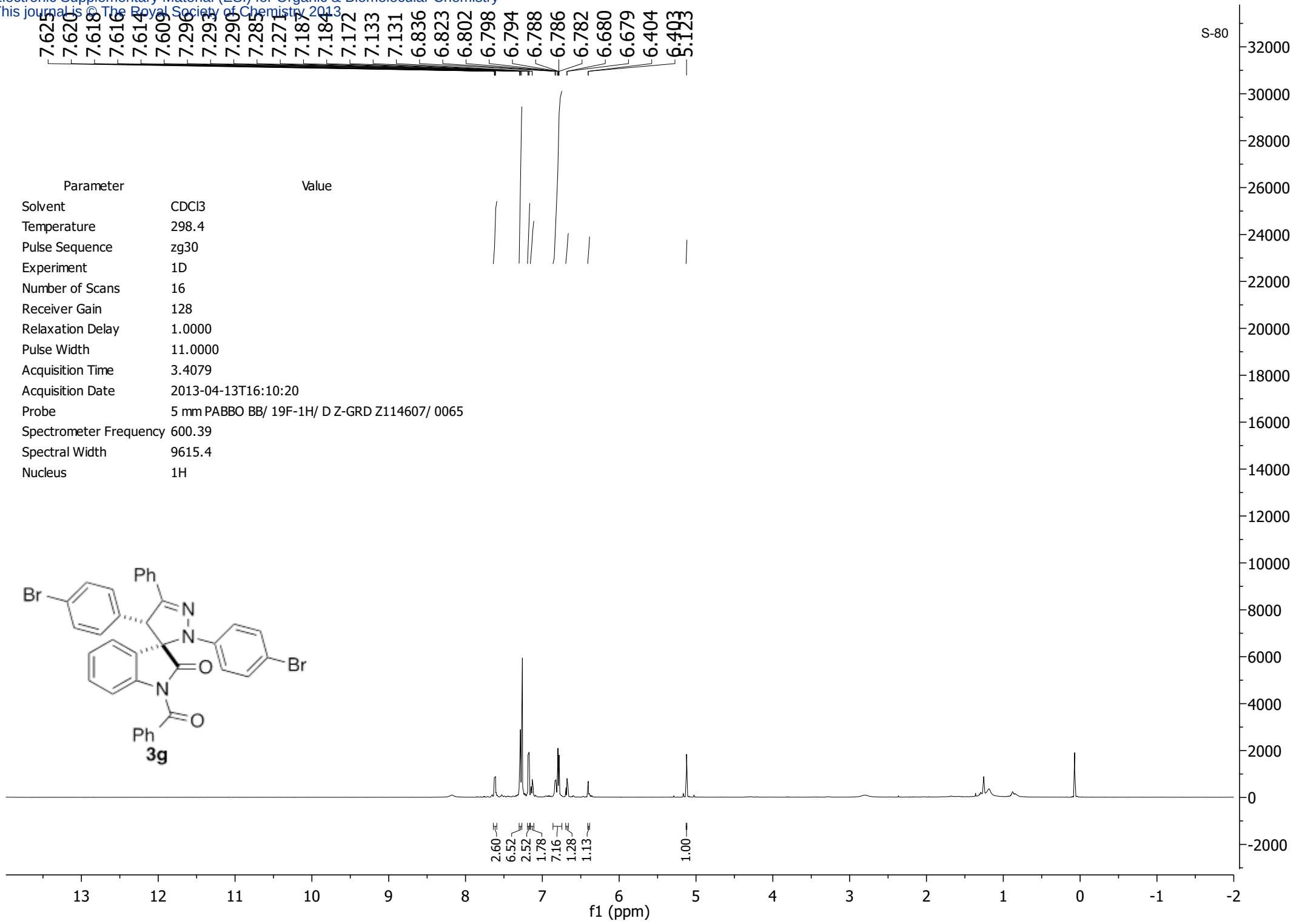
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.164	17129073	99.70	837479
2	W2489 ChA 254nm	17.827	51014	0.30	835

7.625 7.620 7.618 7.616 7.614 7.609 7.296 7.293 7.290 7.285 7.271 7.187 7.184 7.172 7.133 7.131 6.836 6.823 6.802 6.798 6.794 6.788 6.786 6.782 6.680 6.679 6.404 6.403 5.123

Parameter	Value
Solvent	CDCl3
Temperature	298.4
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-13T16:10:20
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

3g

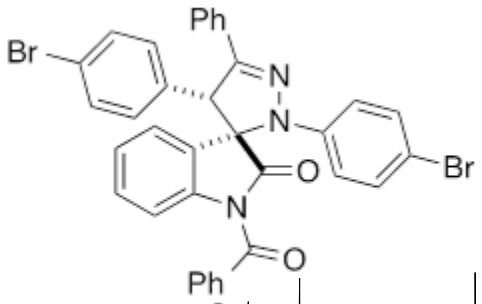


TG1_227_4_1 1 carbon

Automated Probe tuning parameter

174.521 169.099 150.899 144.088 140.461 133.669 133.376 133.148 132.355 132.210 131.253 130.773 130.731 129.678 129.549 128.728 128.496 127.058 126.654 125.231 124.322 122.791 119.732 115.914 115.057 77.610 77.548 77.230 76.912 62.223

Parameter	Value
Solvent	cdcl3
Temperature	22.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2012-11-01T16:17:55
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



3g

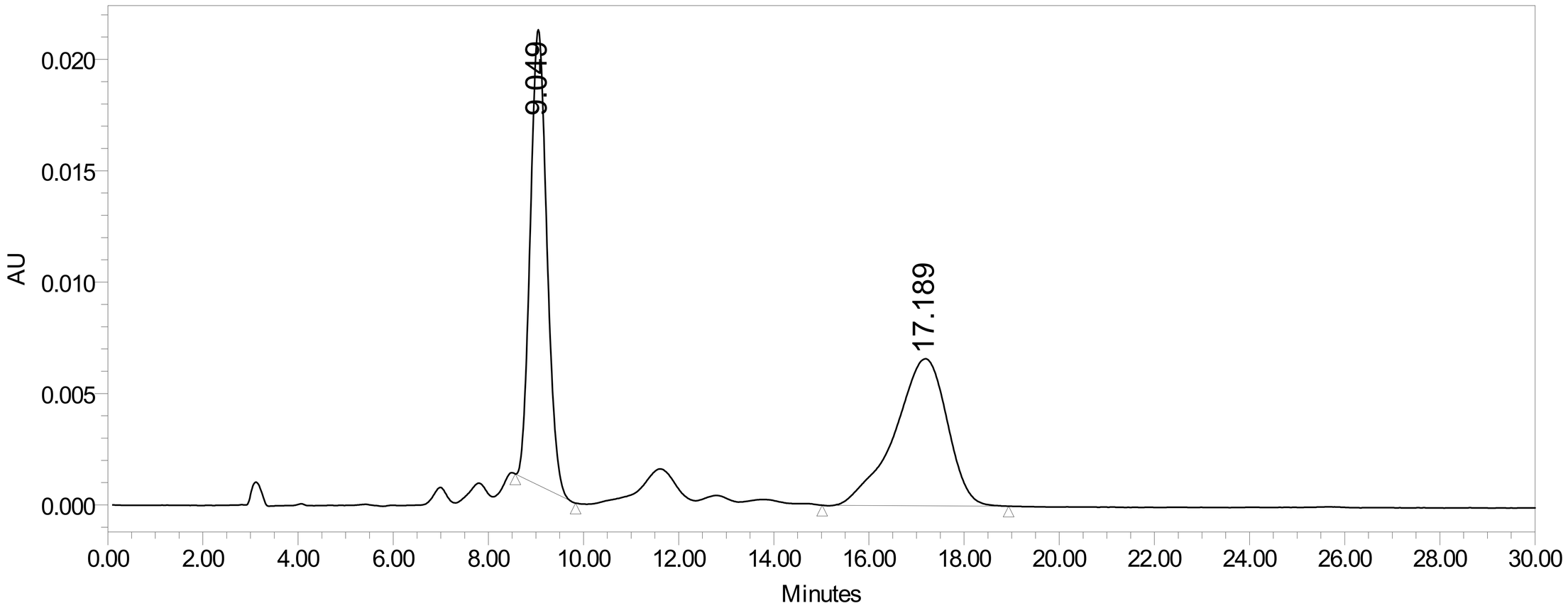
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG1_229_4_ADH1mpm10%IPA	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG_10302012
Vial:	30	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	10/30/2012 3:53:18 PM CDT		
Date Processed:	3/7/2013 7:54:48 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8537; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

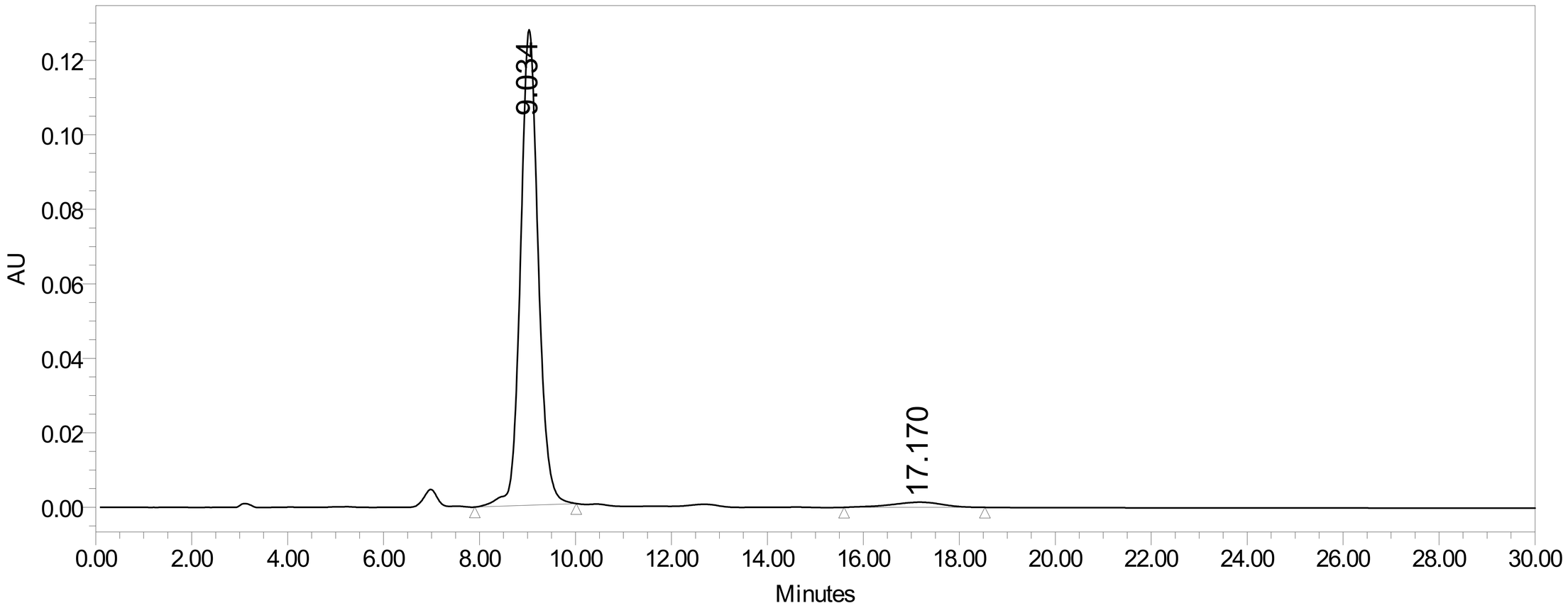
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.049	495886	49.45	20438
2	W2489 ChA 254nm	17.189	506903	50.55	6598

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG1_227_4_ADH1mpm10%IPA	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG_10302012
Vial:	28	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	10/30/2012 2:41:57 PM CDT		
Date Processed:	3/7/2013 7:56:39 PM CST		



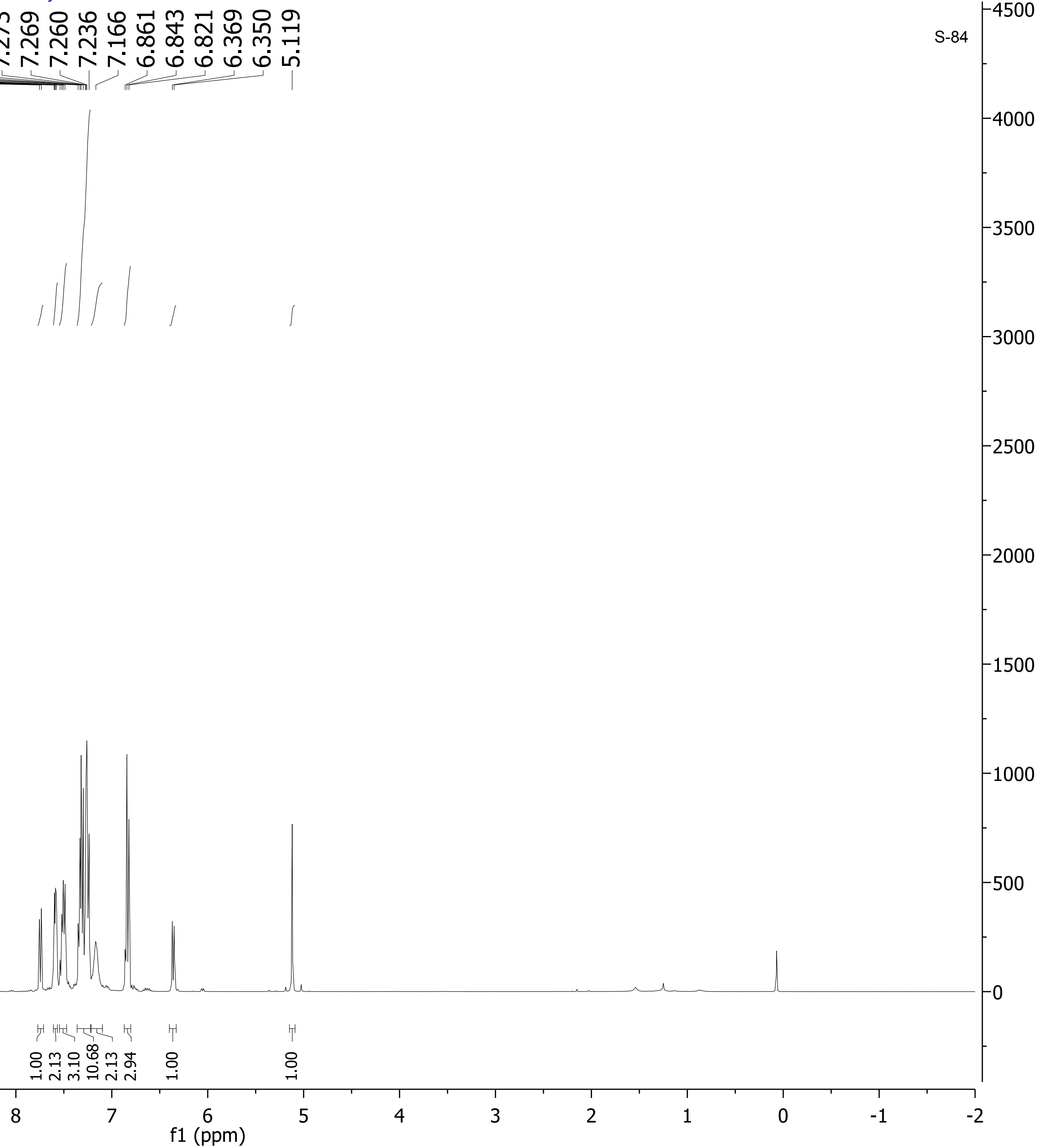
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8539; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

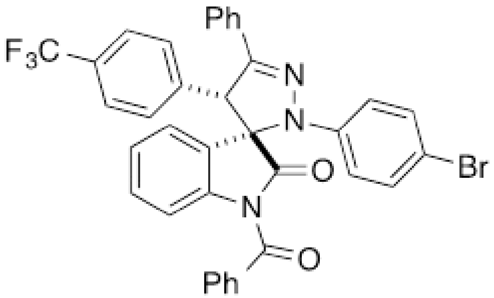
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.034	3275898	96.99	127675
2	W2489 ChA 254nm	17.170	101787	3.01	1391

TG1_237_2_22122013

STANDARD 1H OBSERVE - profile



Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-02-21T17:31:45
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

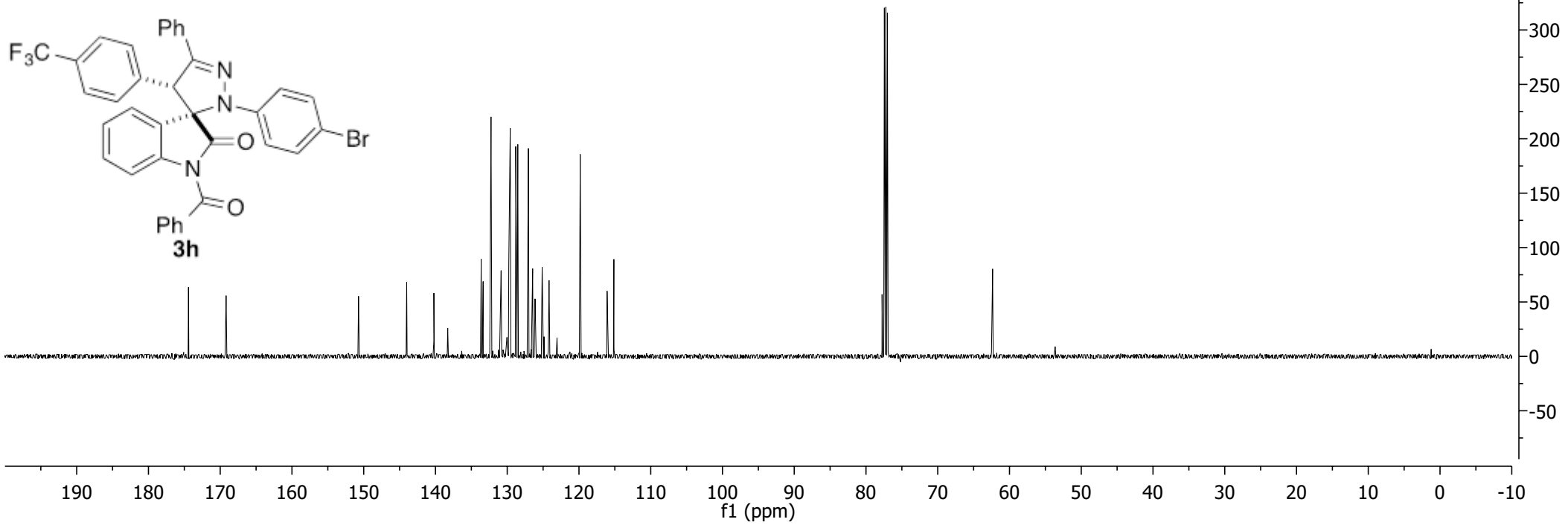


3h

174.426 169.171 150.722 144.010 140.219 138.281 133.628 133.354 132.256 131.234 131.018 130.852 130.801 130.700 130.584 130.059 129.782 129.582 128.810 128.526 127.047 126.666 126.454 126.164 126.140 126.116 126.092 124.862 124.279 124.169 123.059 119.827 116.078 115.136 77.761 77.441 77.230 77.018 62.353

Parameter	Value
Solvent	CDCl3
Temperature	298.3
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	461
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-04T16:23:58
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

3h

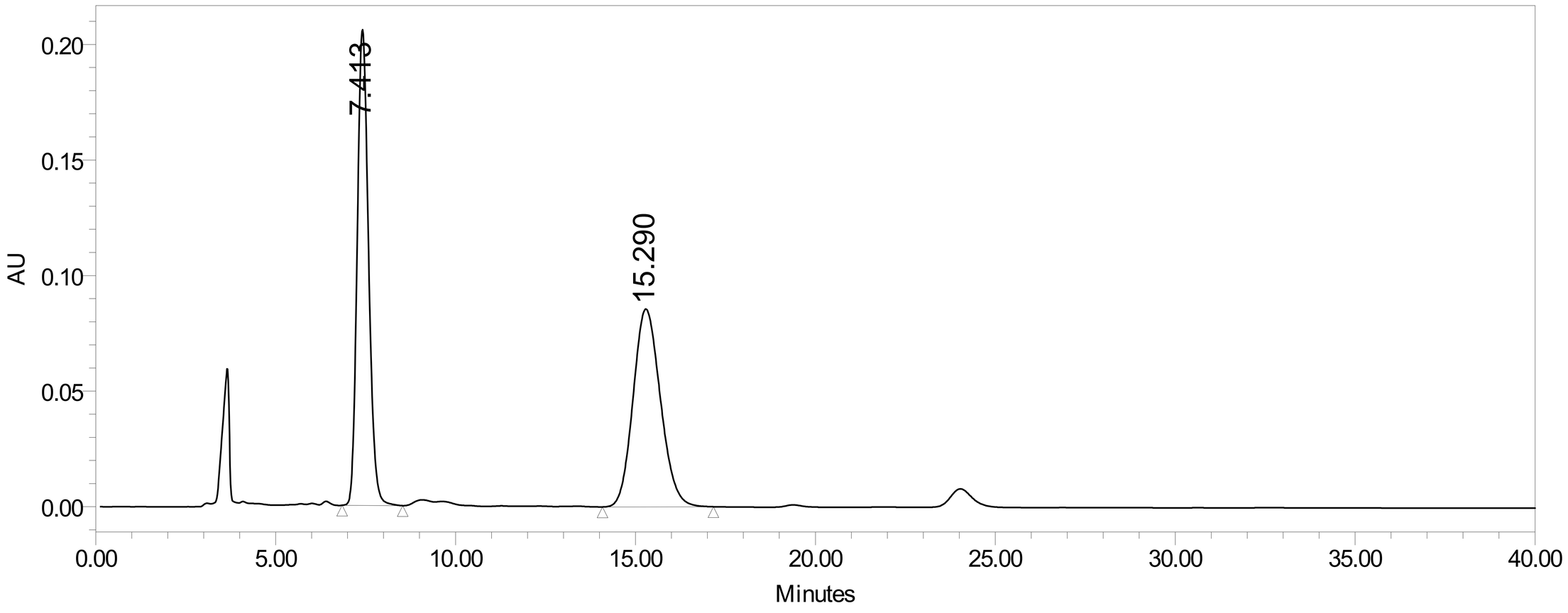


Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_87_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_87_1302013
Vial:	46	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/30/2013 7:23:41 PM CST		
Date Processed:	3/7/2013 7:32:44 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8509; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

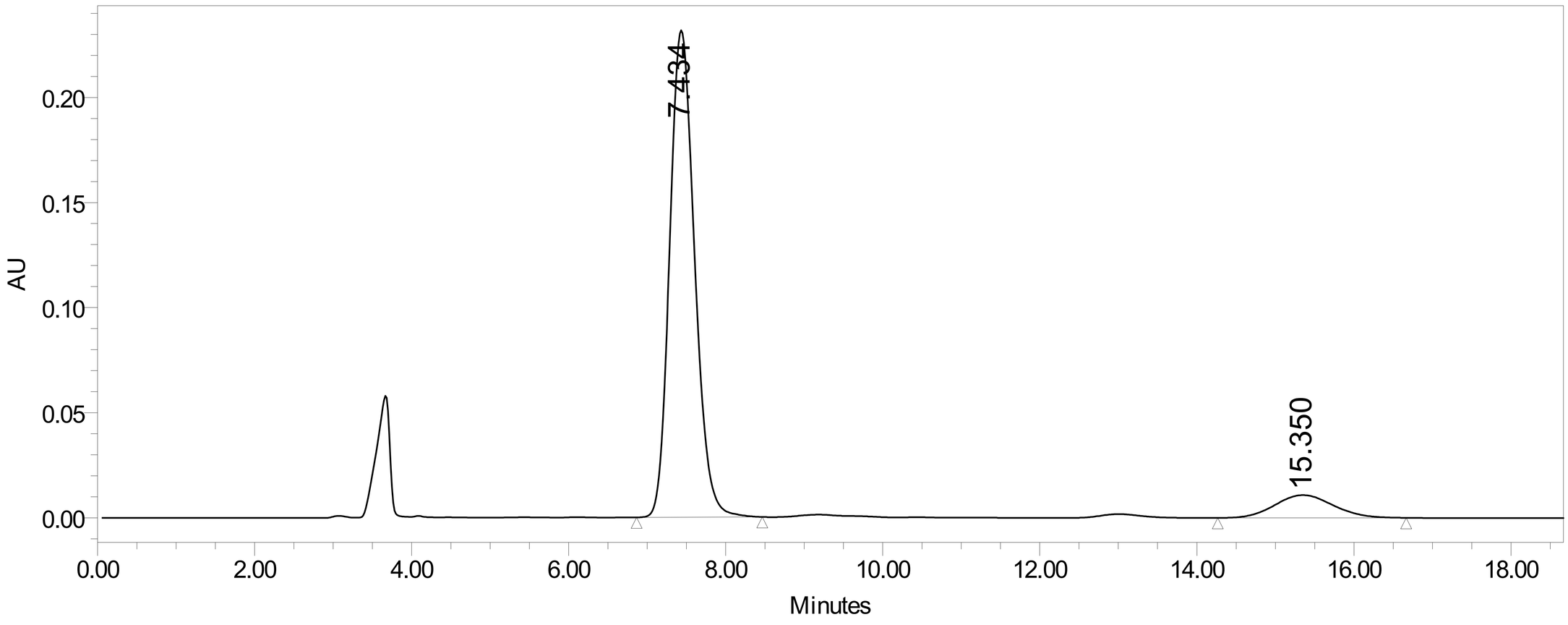
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.413	4514938	49.97	205873
2	W2489 ChA 254nm	15.290	4519993	50.03	85592

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_87_1_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_87_1302013
Vial:	47	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/30/2013 8:04:23 PM CST		
Date Processed:	3/7/2013 7:34:27 PM CST		

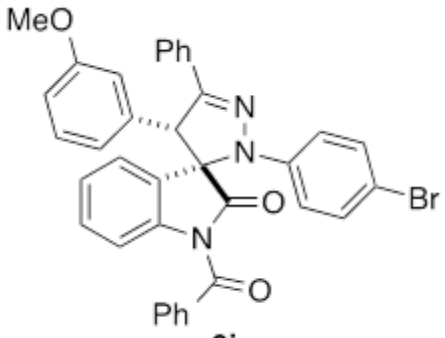


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8511; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.434	5092253	90.07	231704
2	W2489 ChA 254nm	15.350	561503	9.93	10829

Parameter	Value
Solvent	CDCl3
Temperature	298.5
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	61
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-02-17T18:49:15
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

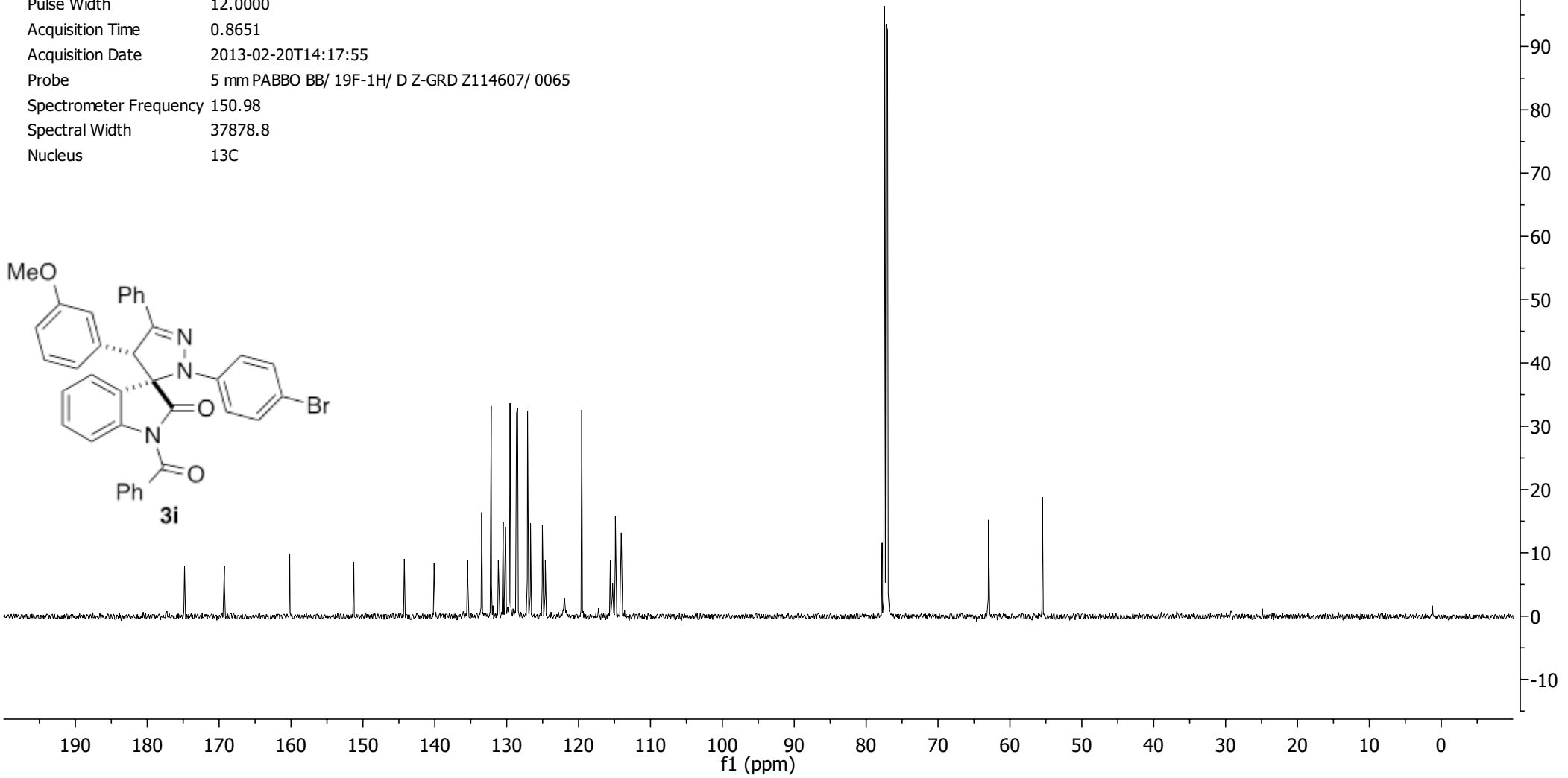


3i

174.811 169.267 160.182 151.269 144.237 140.095 135.444 133.526 133.473 132.153 131.165 130.485 130.147 129.533 129.478 128.627 128.479 127.098 126.683 125.036 124.628 121.979 119.561 115.586 115.267 114.880 114.061 77.780 77.442 77.230 77.019 62.983 55.478

Parameter	Value
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	264
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-02-20T14:17:55
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

3i

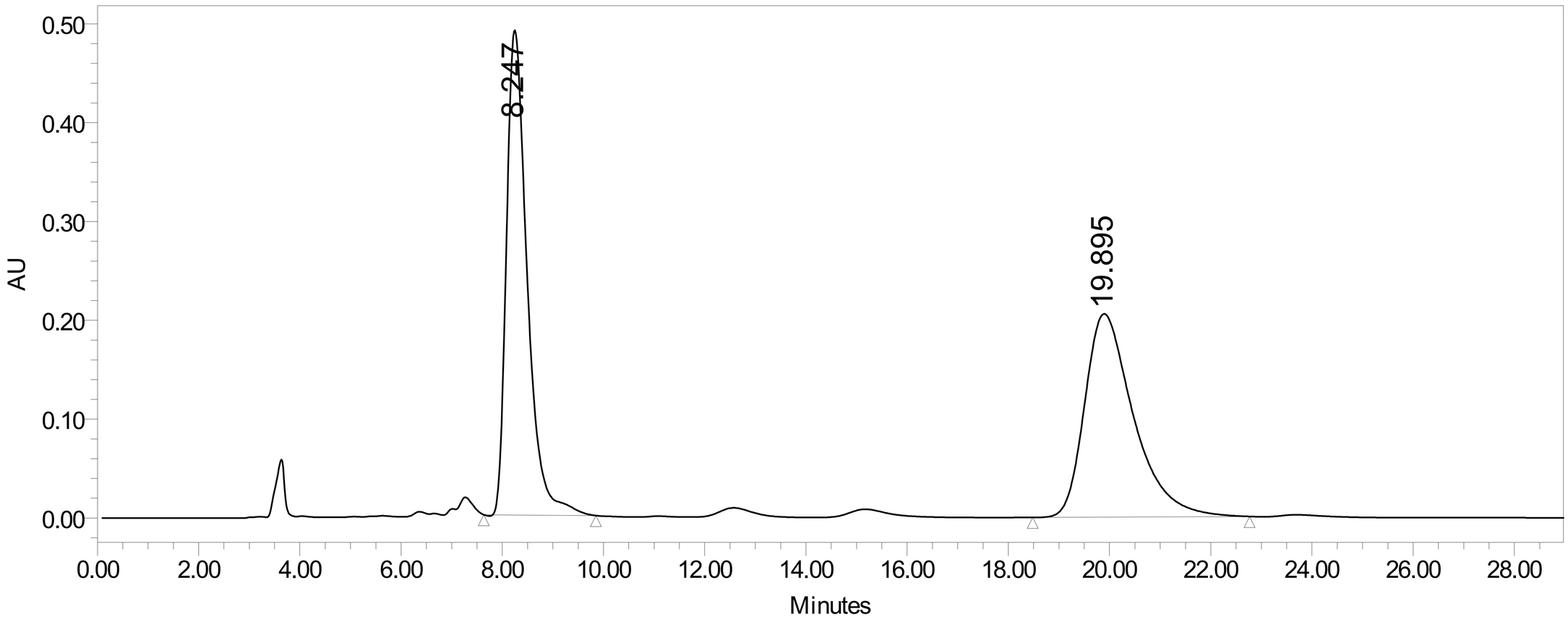


Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_119_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02162013
Vial:	13	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/16/2013 9:23:24 PM CST		
Date Processed:	3/7/2013 7:51:04 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8533; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.247	13983960	50.35	490581
2	W2489 ChA 254nm	19.895	13790823	49.65	205799

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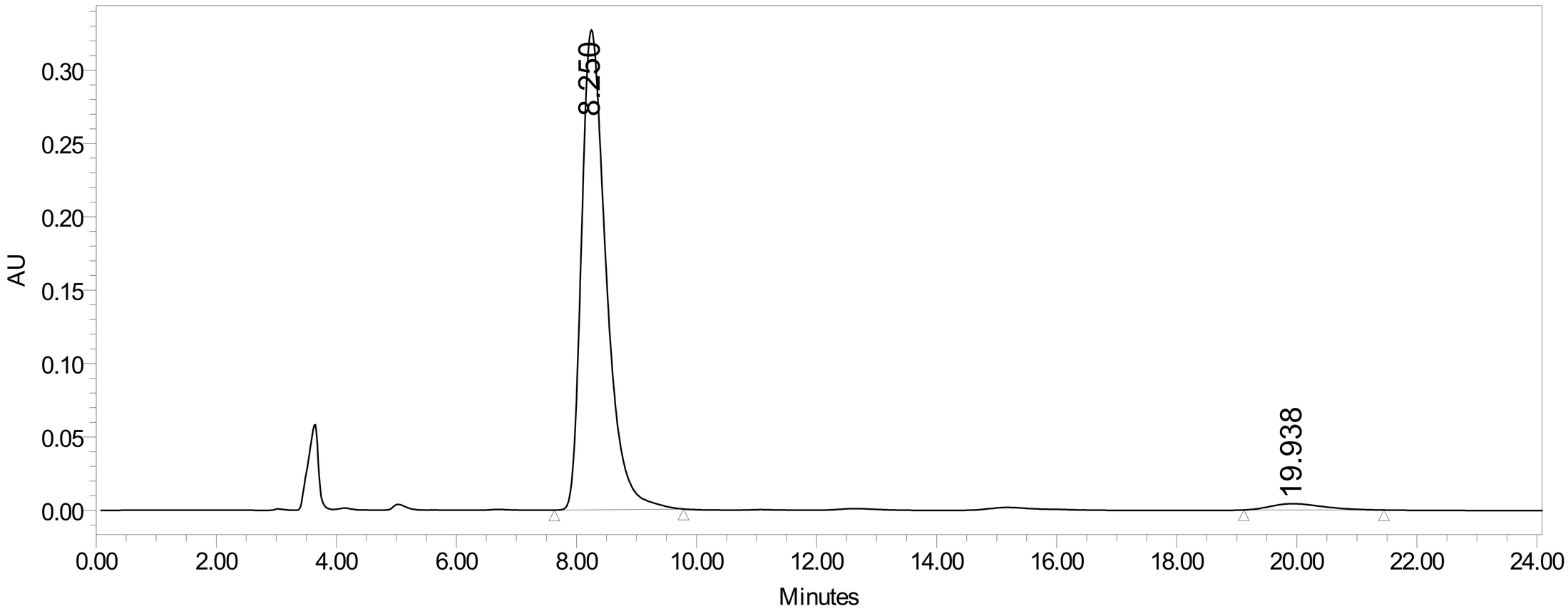
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_119_1_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02162013
Vial:	14	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/16/2013 9:52:58 PM CST		
Date Processed:	3/7/2013 7:52:26 PM CST		



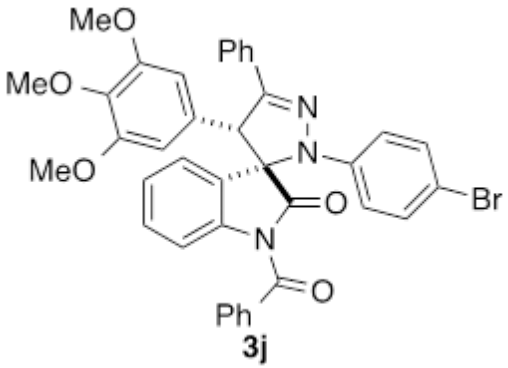
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8535; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.250	9336902	97.28	327146
2	W2489 ChA 254nm	19.938	260911	2.72	4307

7.895 7.881 7.706 7.688 7.588 7.575 7.562 7.474 7.462 7.446 7.433 7.420 7.319 7.312 7.284 7.273 7.264 7.250 6.943 6.930 6.853 6.839 6.142 5.275 3.887 3.555

Parameter	Value
Solvent	CDCl3
Temperature	297.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-03-12T15:34:46
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



3j

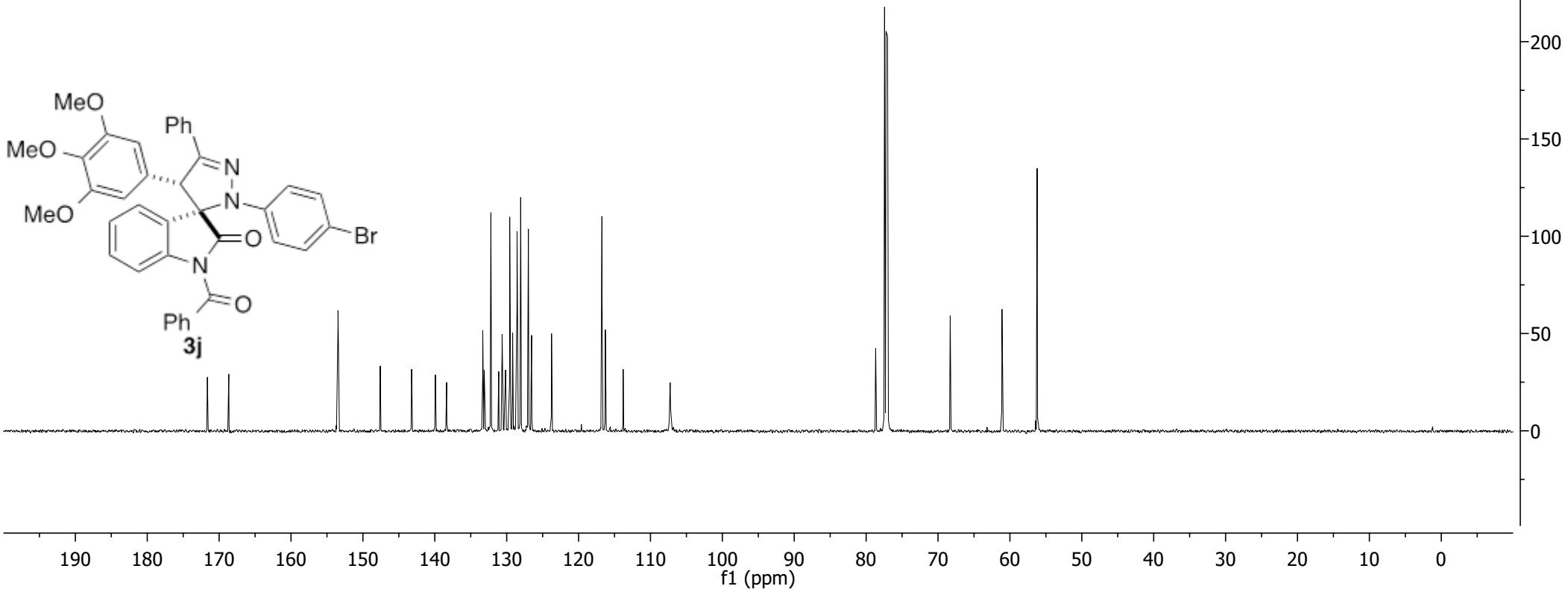
1.00 1.10 3.12 2.15 7.92 2.10 2.04 2.00 1.00 3.00 6.03

f1 (ppm)

171.634 168.654 153.462 147.590 143.227 139.919 138.353 133.327 133.123 132.197 131.106 130.636 130.159 129.578 129.172 128.557 128.055 126.984 126.535 123.759 116.751 116.276 113.795 107.260 78.678 68.305 61.105 56.212

Parameter	Value
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	656
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-01-28T11:16:06
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

3j

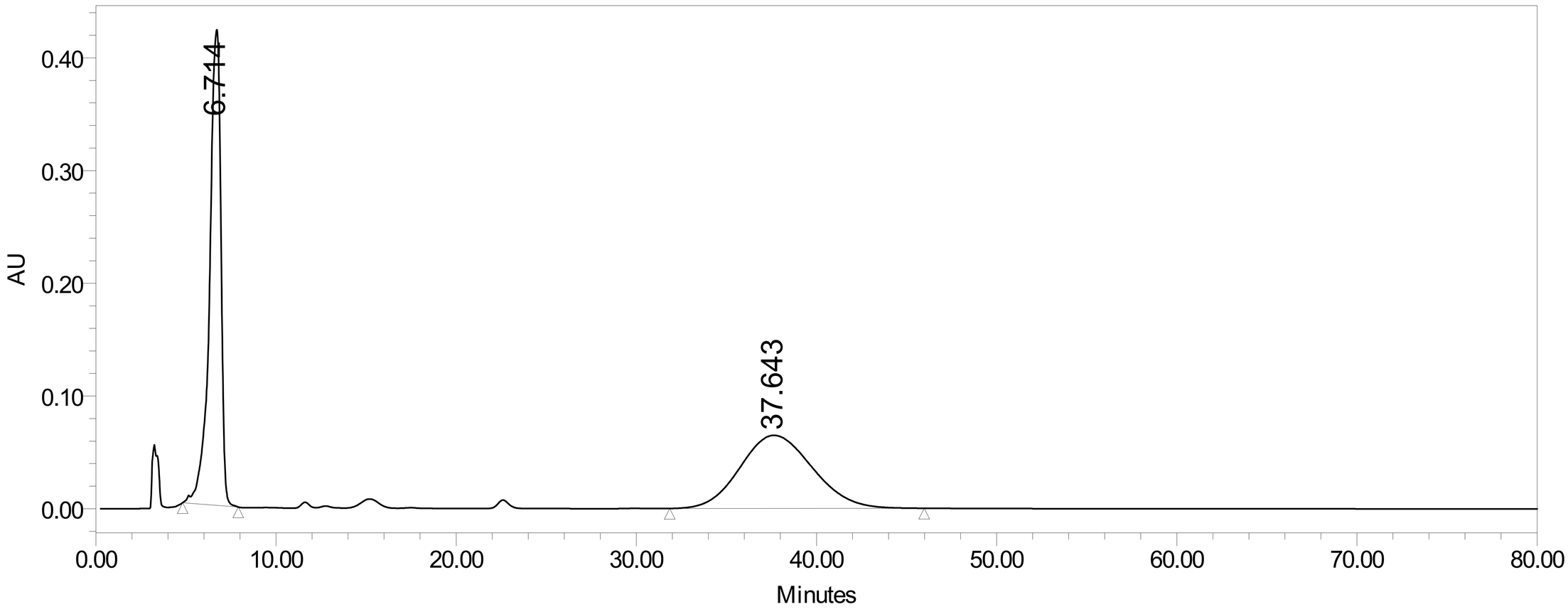


Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_101_3_20%IPA60min	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_101_1282013
Vial:	116	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	20.00 ul	Channel Name:	W2489 ChA
Run Time:	80.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/28/2013 1:55:52 PM CST		
Date Processed:	3/7/2013 7:36:17 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8513; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

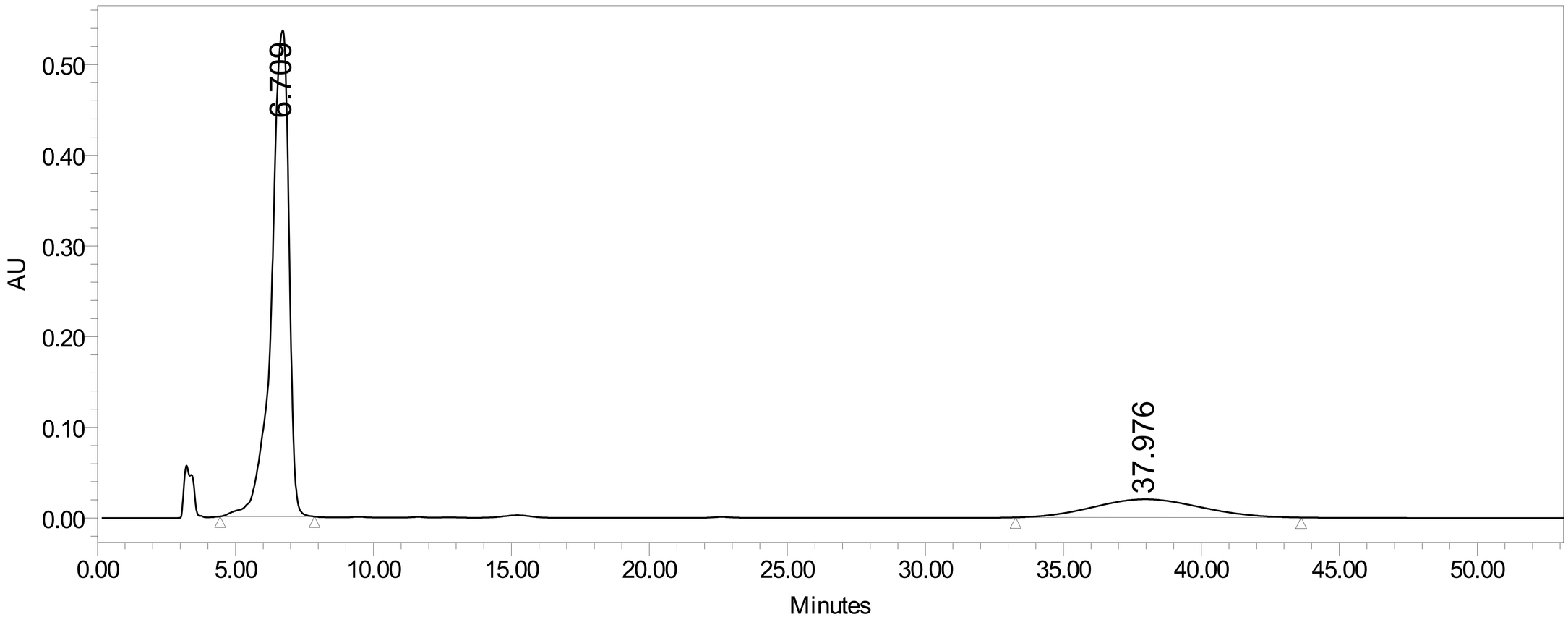
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.714	18460260	50.44	422106
2	W2489 ChA 254nm	37.643	18140270	49.56	64862

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_101_1_20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_101_1282013
Vial:	117	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	20.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/28/2013 5:25:19 PM CST		
Date Processed:	3/7/2013 7:38:04 PM CST		



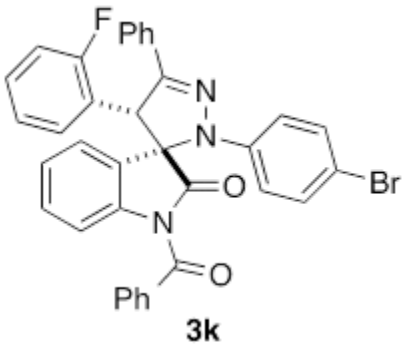
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8515; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.709	23668298	81.36	536325
2	W2489 ChA 254nm	37.976	5421155	18.64	20071

7.839 7.825 7.647 7.642 7.637 7.547 7.535 7.456 7.444 7.403 7.390 7.377 7.335 7.322 7.306 7.301 7.296 7.281 7.224 7.170 7.072 6.863 6.847 6.827 6.812 6.442 6.429 5.547

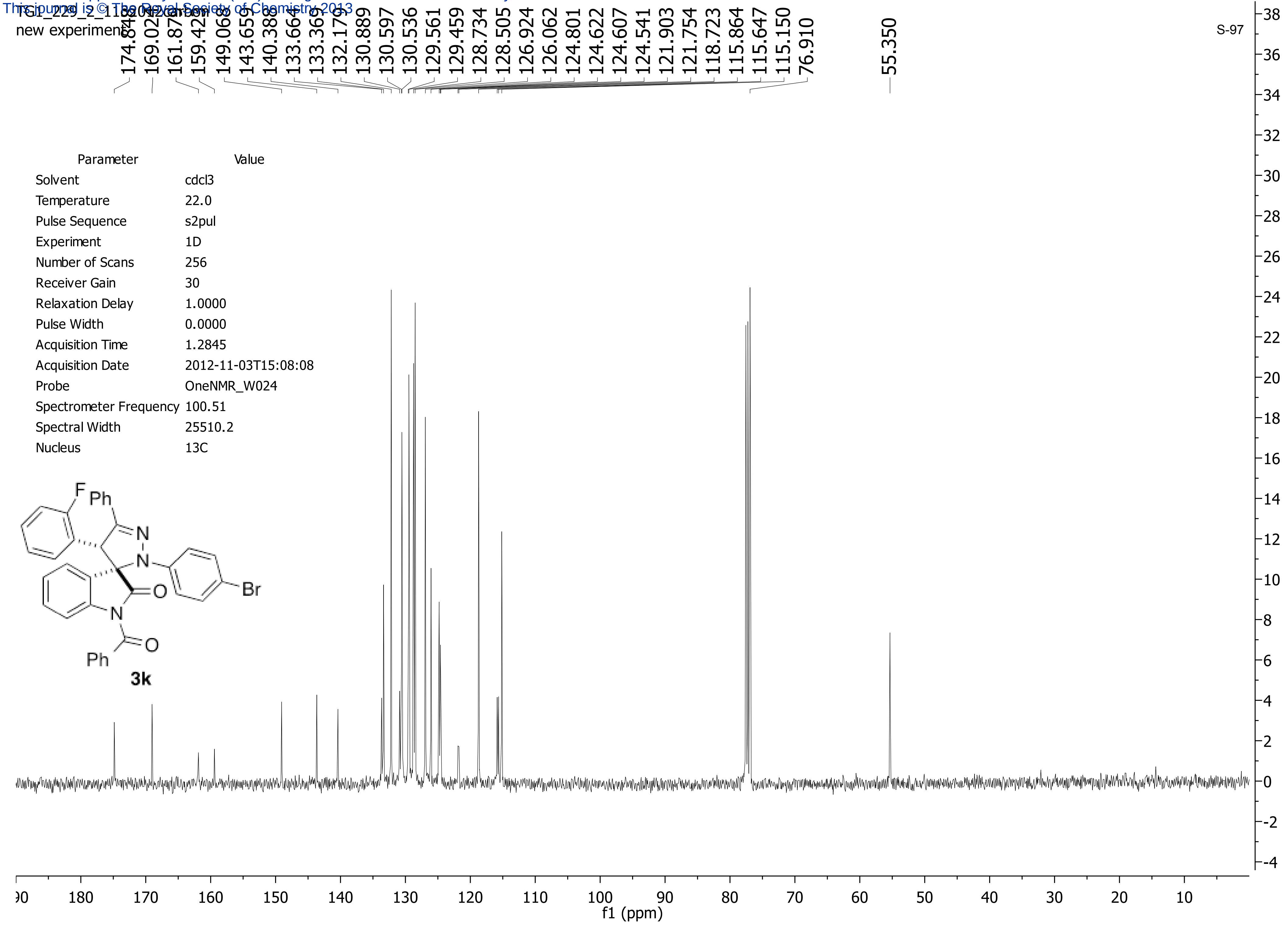
Parameter	Value
Solvent	CDCl3
Temperature	296.9
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	68
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-01-05T14:42:07
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



3k

1.00 2.16 1.17 2.11 2.22 6.56 1.27 1.20 1.12 4.27 1.00 1.00

f1 (ppm)

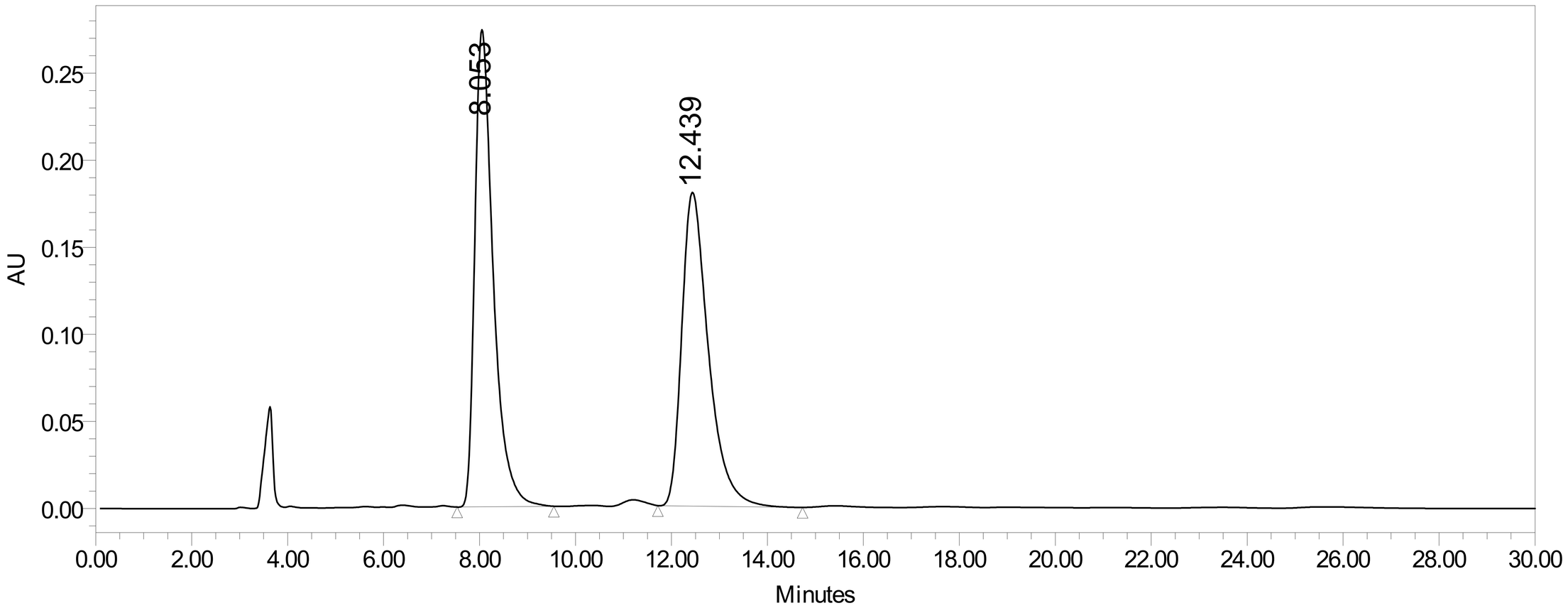

new experiment
174.84
169.02
161.87
159.42
149.06
143.65
140.38
133.66
133.36
132.17
130.889
130.597
130.536
129.561
129.459
128.734
128.505
126.924
126.062
124.801
124.622
124.607
124.541
121.903
121.754
118.723
115.864
115.647
115.150
76.910
55.350
Parameter Value
Solvent cdcl3
Temperature 22.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 256
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.2845
Acquisition Date 2012-11-03T15:08:08
Probe OneNMR_W024
Spectrometer Frequency 100.51
Spectral Width 25510.2
Nucleus 13C
F
Ph
N
N
Br
O
N
O
Ph
3k
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG1_229_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02292013
Vial:	31	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/1/2013 6:39:07 PM CST		
Date Processed:	3/7/2013 7:27:39 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8505; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

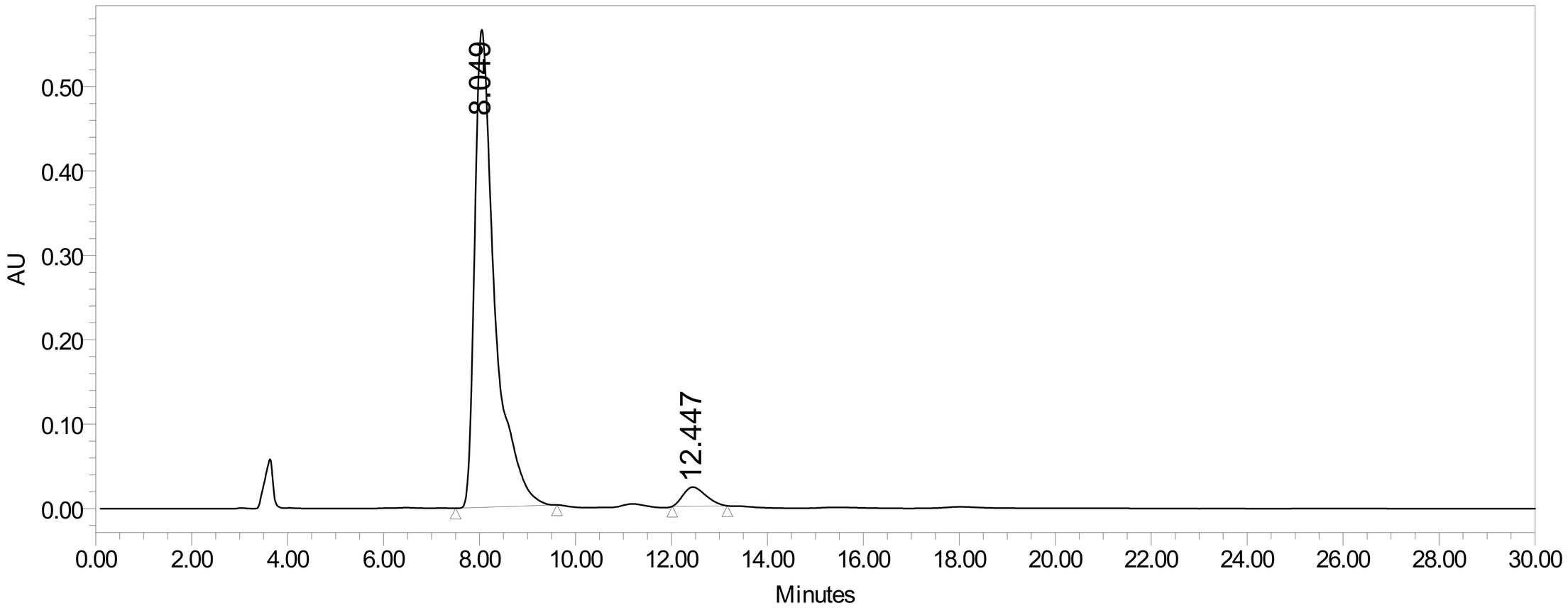
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.053	7305093	51.25	274041
2	W2489 ChA 254nm	12.439	6949348	48.75	180160

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG1_229_1_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02292013
Vial:	32	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/1/2013 7:10:01 PM CST		
Date Processed:	3/7/2013 7:30:22 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8507; Processing Method: TG

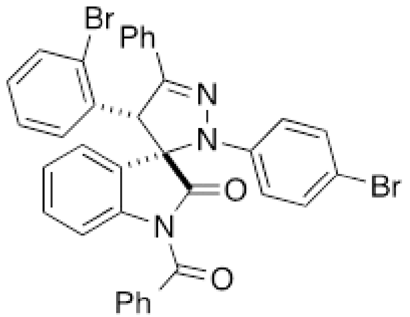
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.049	16403549	95.70	565978
2	W2489 ChA 254nm	12.447	736438	4.30	22480

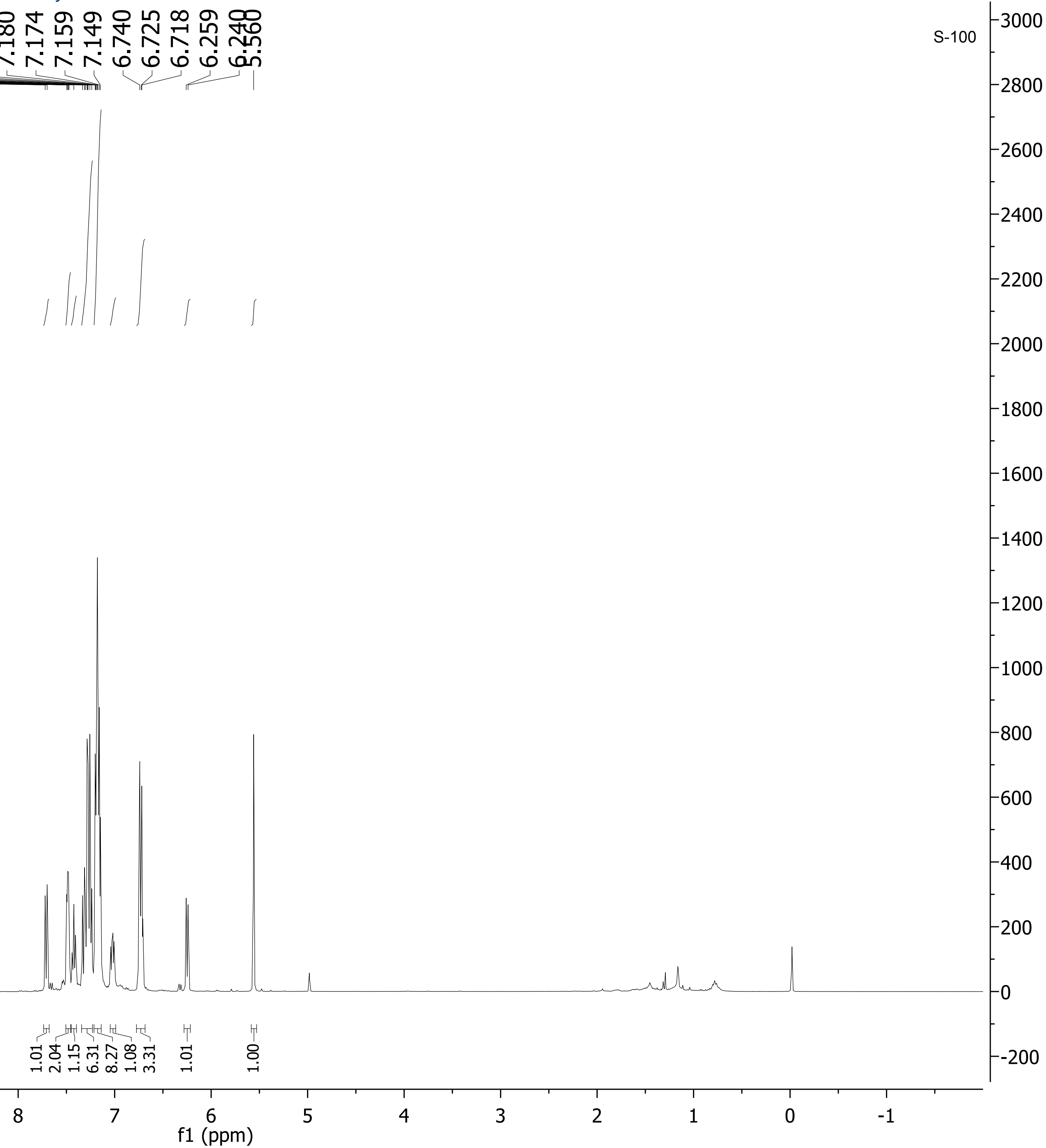
STANDARD 1H OBSERVE - profile

S-100

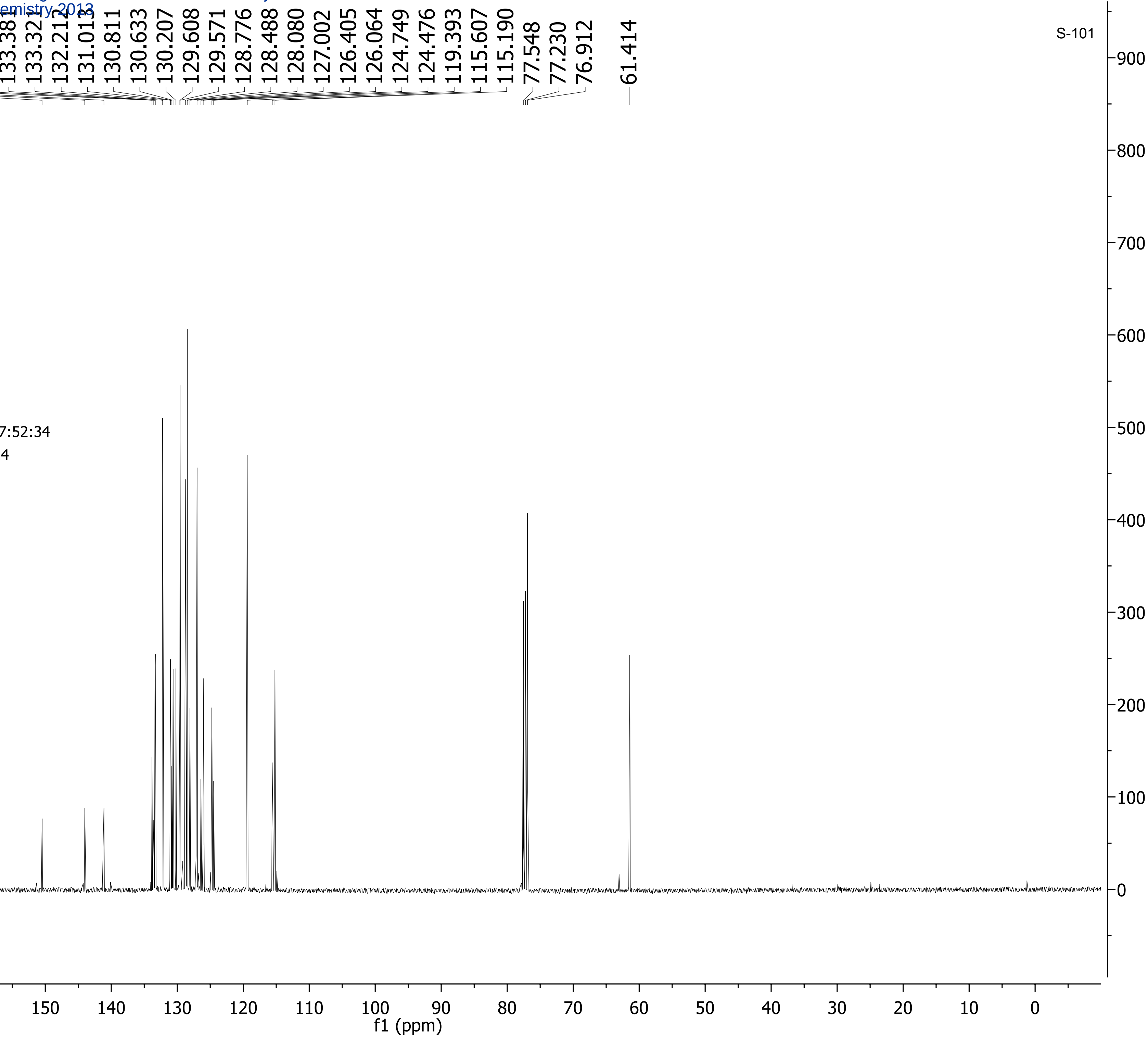
Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-02-21T17:36:30
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



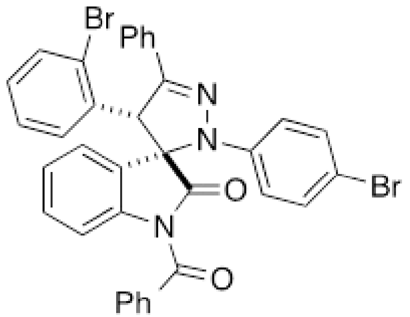
3l



TG2_91_2_2212013carbon
STANDARD 1H OBSERVE - profile



Parameter	Value
Solvent	cdcl3
Temperature	26.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	2238
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-02-21T17:52:34
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



3l

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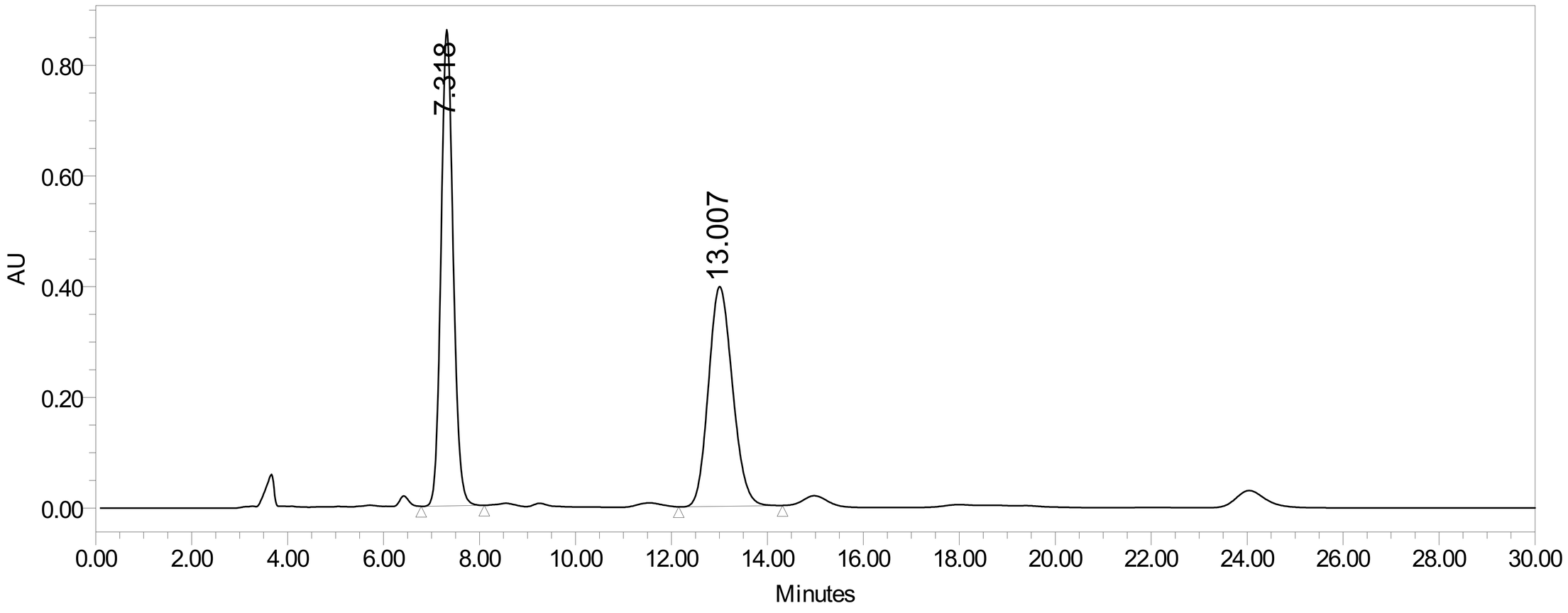
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_91_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	AVI_FEB_13_2013
Vial:	117	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/13/2013 7:44:24 PM CST		
Date Processed:	3/7/2013 7:44:39 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8521; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.318	15183491	52.35	860664
2	W2489 ChA 254nm	13.007	13821955	47.65	396984

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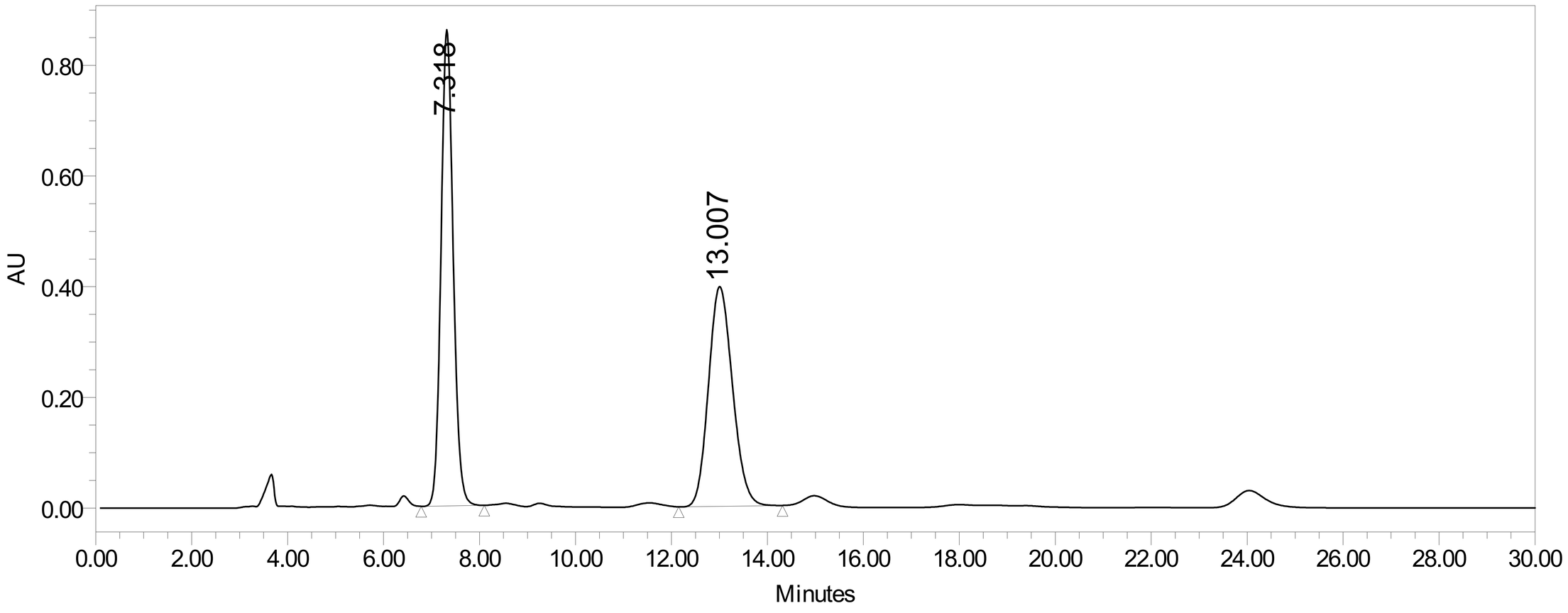
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_91_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	AVI_FEB_13_2013
Vial:	117	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/13/2013 7:44:24 PM CST		
Date Processed:	3/7/2013 7:44:39 PM CST		



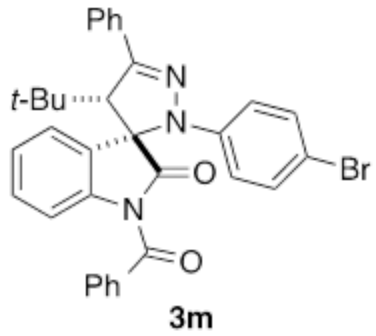
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8521; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.318	15183491	52.35	860664
2	W2489 ChA 254nm	13.007	13821955	47.65	396984

7.821 7.808 7.677 7.664 7.620 7.607 7.599 7.586 7.550 7.546 7.537 7.479 7.468 7.456 7.443 7.408 7.398 7.271 7.252 7.239 7.234 7.219 6.769 6.754 4.167 0.870

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	56
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-02-20T18:54:03
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



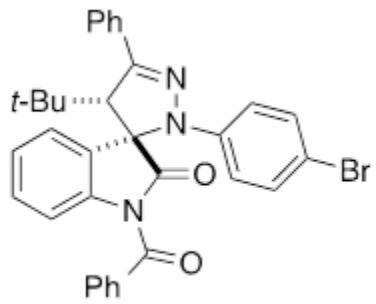
3m

0.97 1.02 2.95 2.03 3.01 2.94 2.92 1.94 0.98 9.00

f1 (ppm)

176.459 169.181 153.927 143.607 140.451 135.149 133.651 133.572 131.890 130.911 129.728 129.086 128.559 128.533 128.442 128.211 125.242 125.013 119.093 115.730 114.850 78.242 77.441 77.230 77.018 70.801 34.817 29.875

Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	522
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-02-20T18:57:18
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



3m

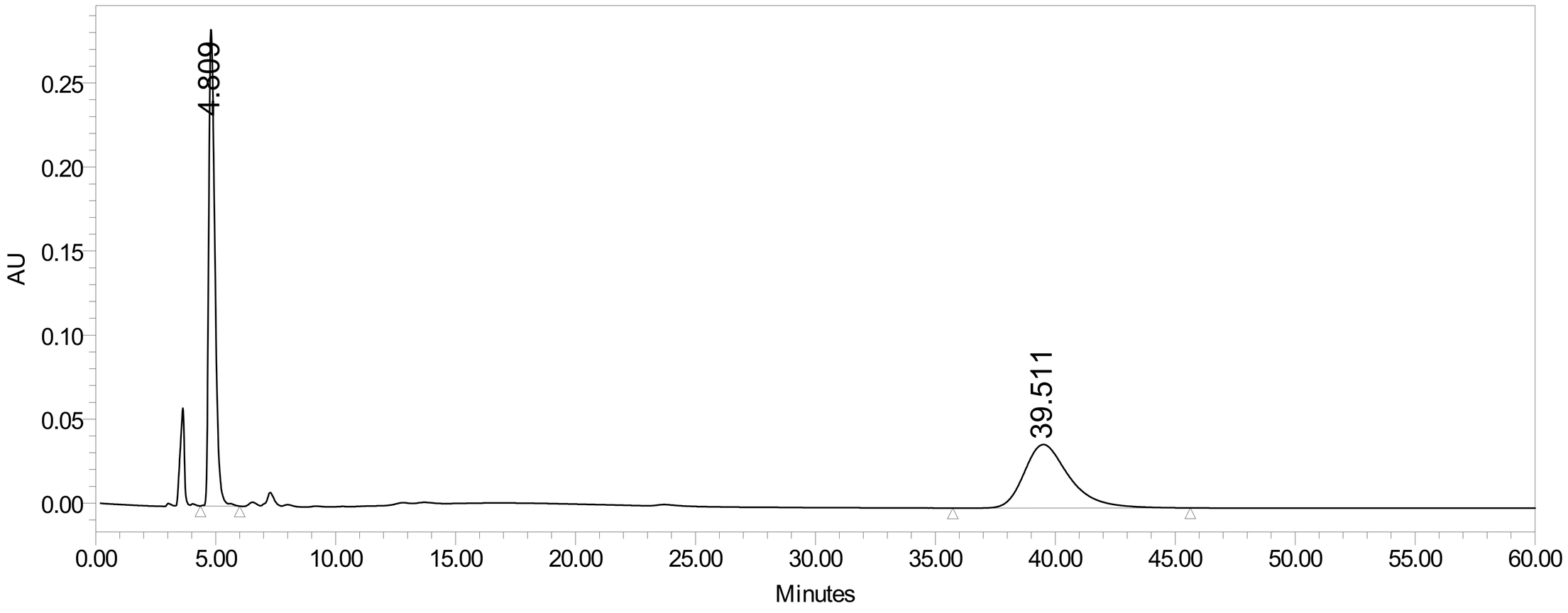
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_125_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02202913
Vial:	13	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/20/2013 5:29:48 PM CST		
Date Processed:	3/7/2013 7:39:49 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8517; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.809	5086172	50.72	284316
2	W2489 ChA 254nm	39.511	4942214	49.28	37760

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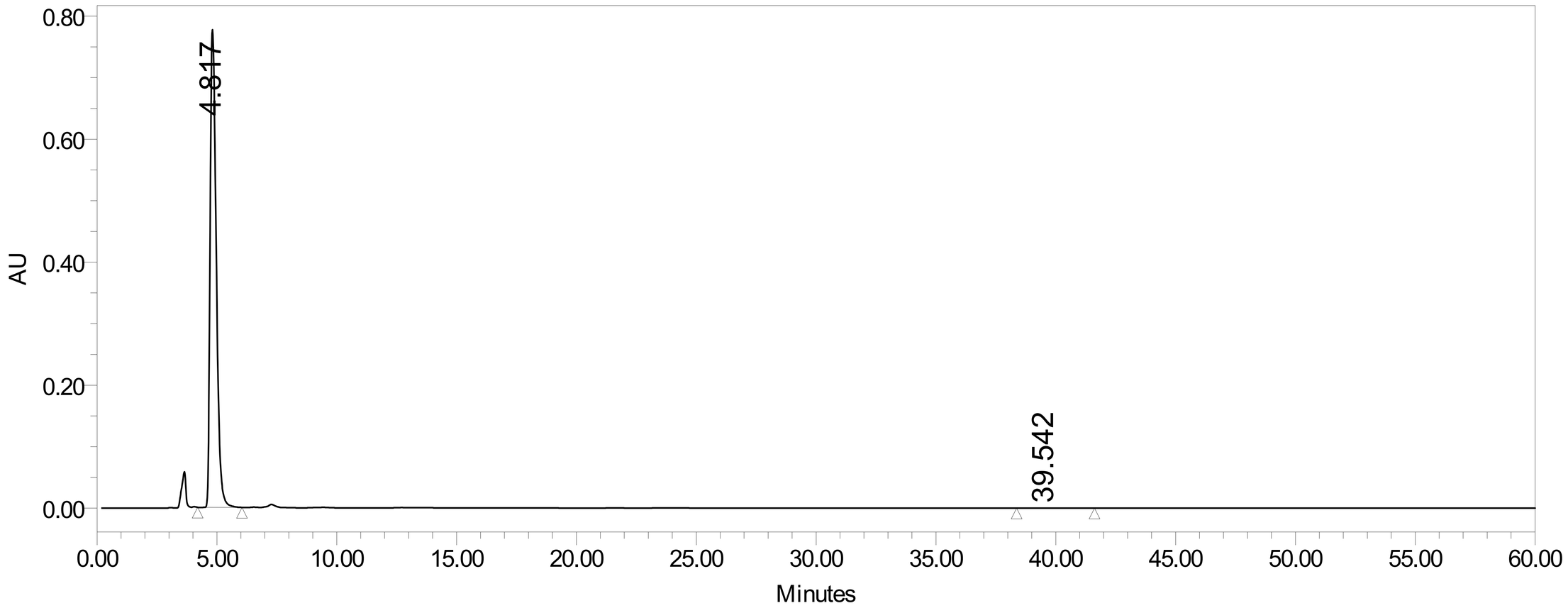
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_125_1_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02202913
Vial:	14	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/20/2013 6:30:42 PM CST		
Date Processed:	3/7/2013 7:41:35 PM CST		



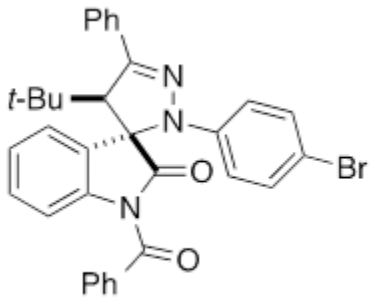
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8519; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.817	13825745	99.96	776884
2	W2489 ChA 254nm	39.542	5592	0.04	63

7.711 7.697 7.622 7.610 7.594 7.591 7.580 7.510 7.498 7.475 7.463 7.456 7.444 7.432 7.420 7.309 7.294 7.274 7.253 7.241 7.228 6.868 6.853 4.009 0.970

Parameter	Value
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	61
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-02-25T15:18:33
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



3n

1.00 2.94 9.33 1.96 1.29 1.95 0.96 9.00

f1 (ppm)

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138.782
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133.854
133.544
131.978
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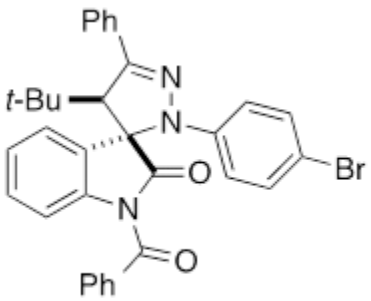
130.346
129.658
129.089
128.610
128.534
128.091
126.170
123.428
120.006
115.586
115.443
78.273
77.442
77.230
77.019
73.173
34.985
29.672

Parameter	Value
Solvent	CDCl3
Temperature	298.7
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	258
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-02-25T15:24:33
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



3n

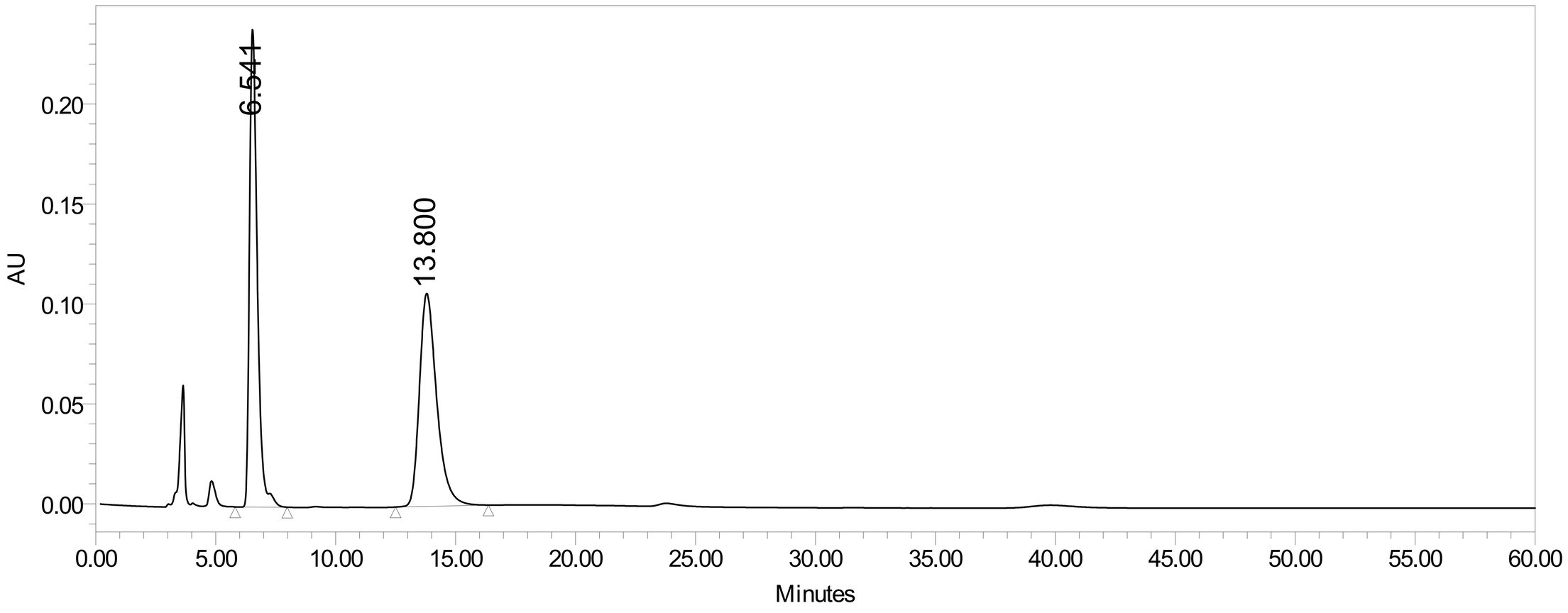
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_129_3_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02252013
Vial:	115	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/25/2013 2:27:03 PM CST		
Date Processed:	3/7/2013 7:47:32 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8525; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.541	5411159	50.40	239105
2	W2489 ChA 254nm	13.800	5326047	49.60	106489

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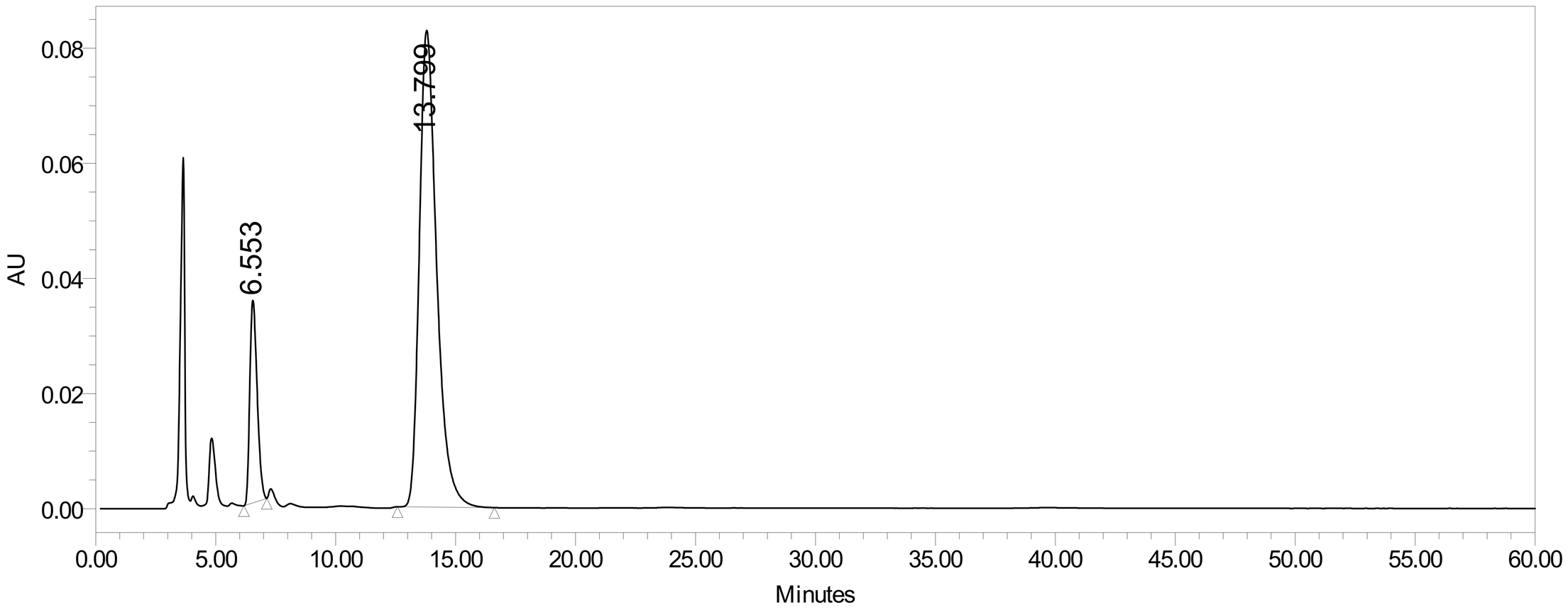
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_129_1_ADH10%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	adu02252013
Vial:	116	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/25/2013 3:28:00 PM CST		
Date Processed:	3/7/2013 7:48:47 PM CST		

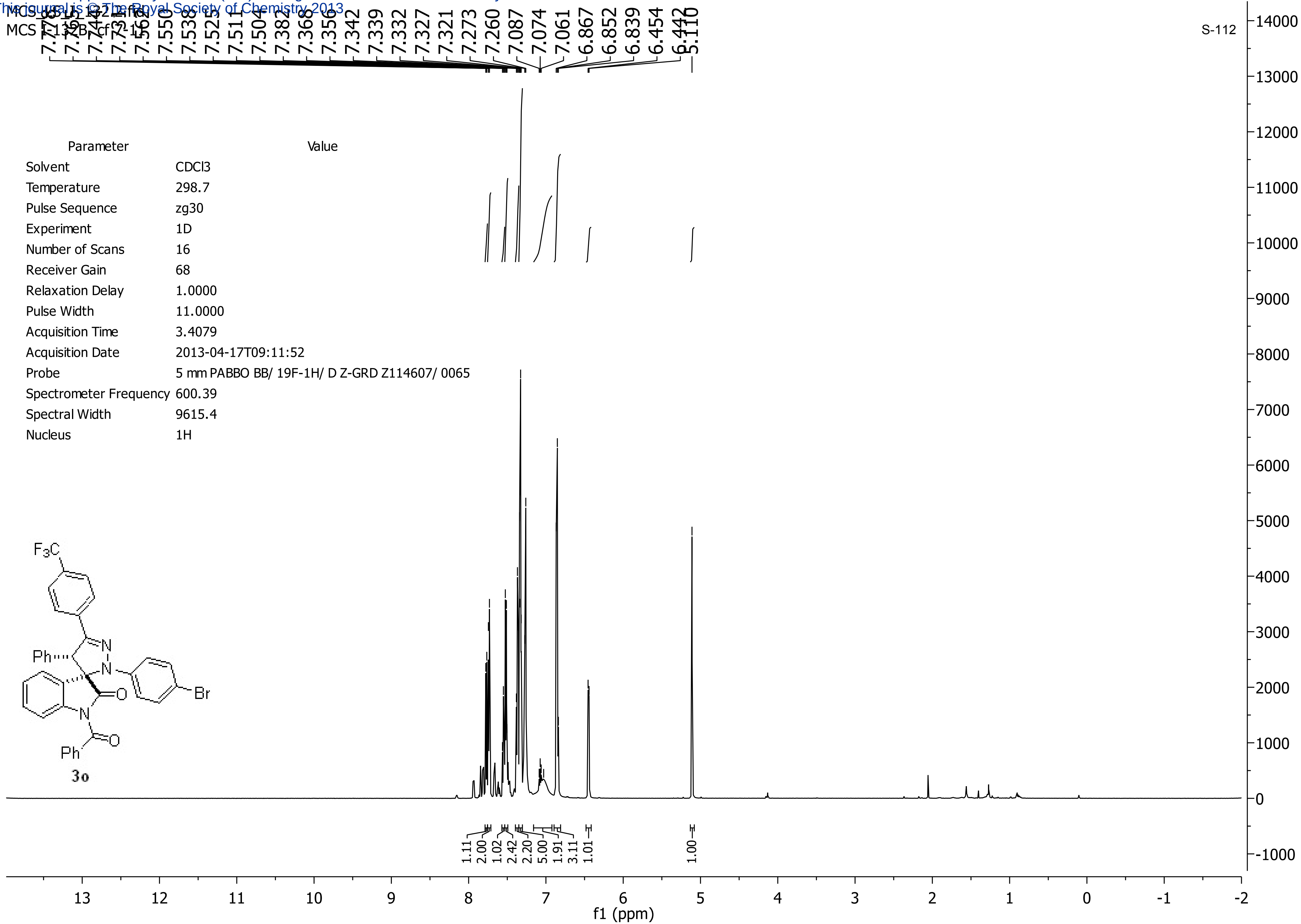


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 8531; Processing Method: TG

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.553	750552	15.30	35199
2	W2489 ChA 254nm	13.799	4154203	84.70	82792

Parameter	Value
Solvent	CDCl3
Temperature	298.7
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	68
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-17T09:11:52
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



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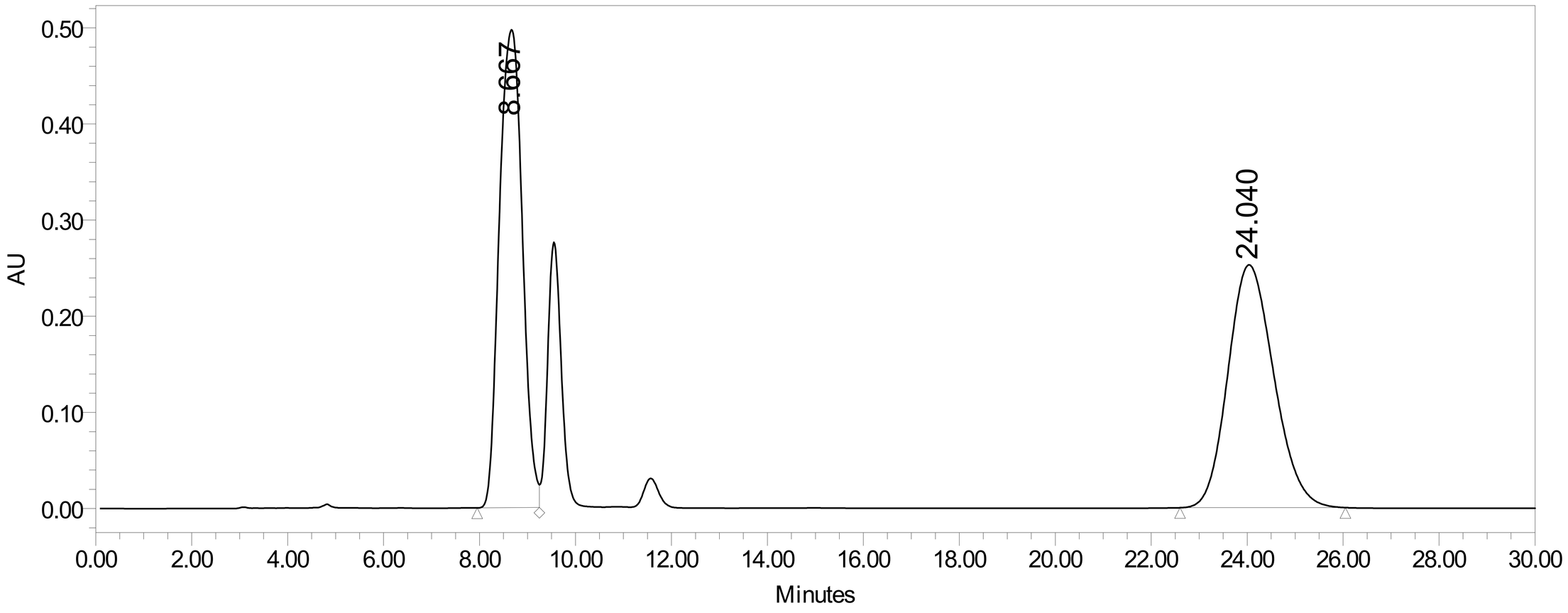
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS-I-68rac_ADH9010_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	46	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	11/8/2012 6:41:06 PM CST		
Date Processed:	8/21/2013 4:11:01 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5786; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.667	16603116	49.73	497172
2	W2489 ChA 254nm	24.040	16782690	50.27	252580

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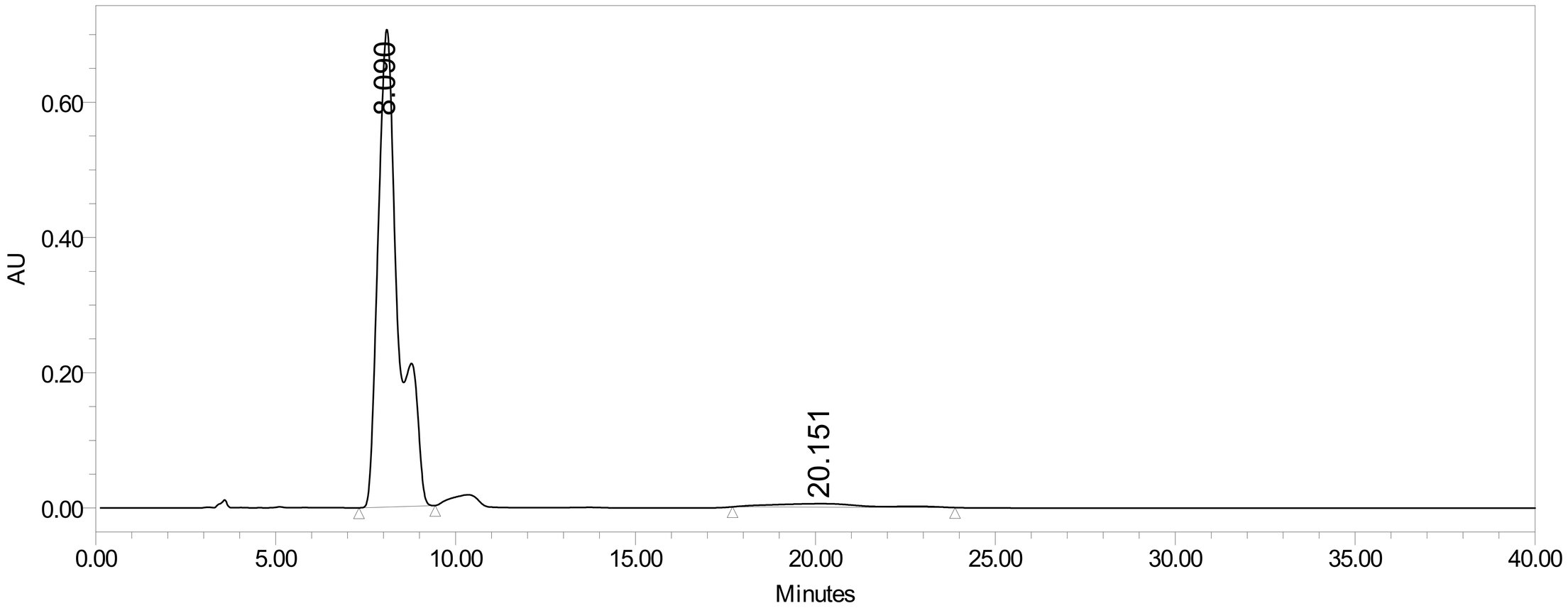
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS_I_80A_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	102	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/13/2012 2:24:59 PM CST		
Date Processed:	8/21/2013 4:36:16 PM CDT		

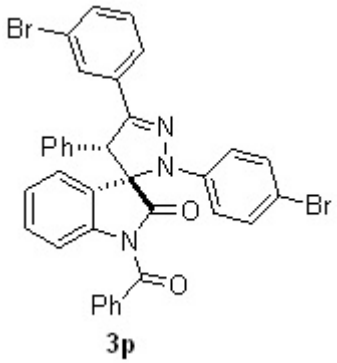


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5859; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	8.090	28270670	96.74	706380
2	W2489 ChA 254nm	20.151	952453	3.26	5135

Parameter	Value
Solvent	CDCl3
Temperature	298.8
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	75
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-17T09:08:03
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



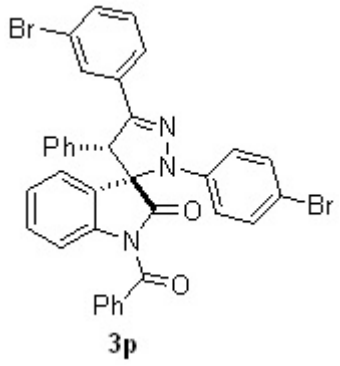
3p

f1 (ppm)

MCS_LS_I_132.4.fid
MCS I-132A, 13C

174.681 169.173 149.844 143.833 140.145 133.535 133.524 133.467 133.238 132.292 132.220 130.592 130.143 129.757 129.544 129.271 128.865 128.509 126.720 125.641 125.028 124.335 122.888 119.583 115.913 114.983 77.929 62.717

Parameter	Value
Solvent	CDCl3
Temperature	299.5
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	685
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-04-17T10:08:13
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



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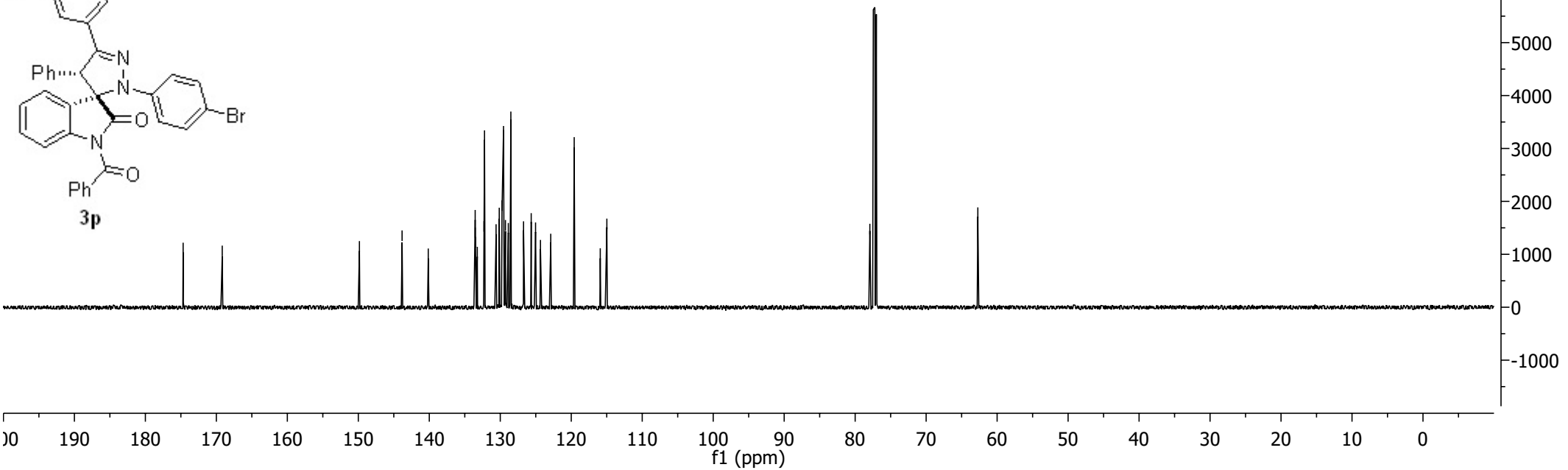
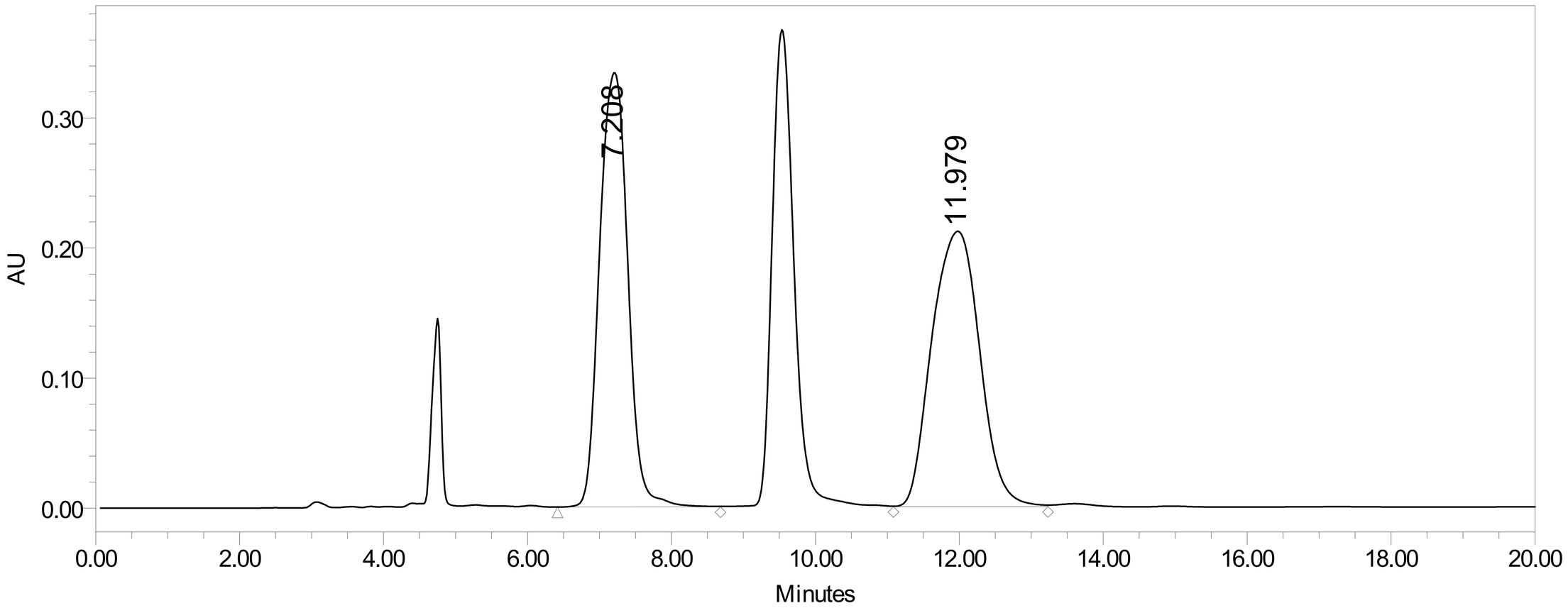


Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS_I_64rac_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	25	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	MCS_3Br_rac_smnotpicked
Injection Volume:	10.00 ul	Channel Name:	W2489 ChB
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChB 220nm
Date Acquired:	10/19/2012 1:09:32 PM CDT		
Date Processed:	8/21/2013 3:57:08 PM CDT		



Channel: W2489 ChB; Processed Channel: W2489 ChB 220nm; Result Id: 5757; Processing Method: MCS_3Br_rac_smnotpicked

Processed Channel Descr.: W2489 ChB 220nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChB 220nm	7.208	9097256	48.23	334215
2	W2489 ChB 220nm	11.979	9764628	51.77	211781

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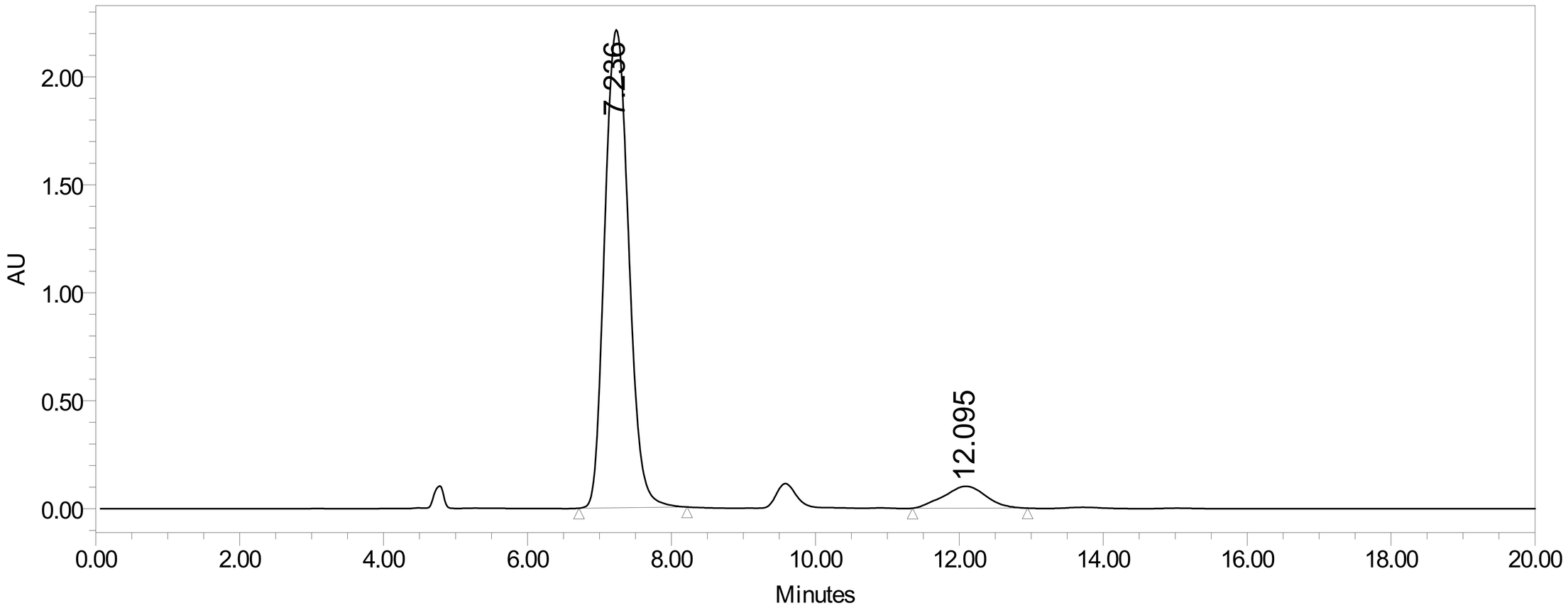
Injection Summary Report

SAMPLE INFORMATION

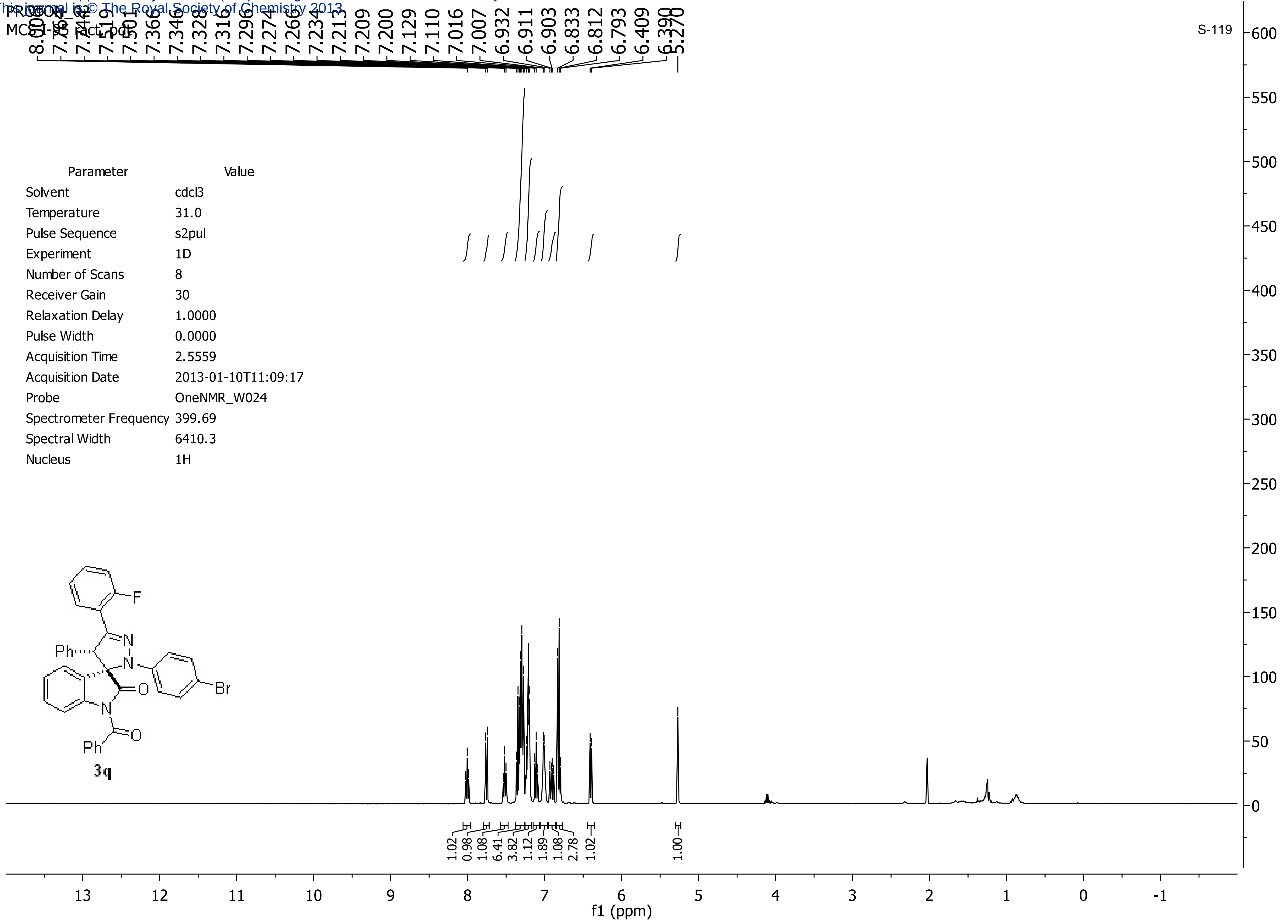
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	27	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	10/19/2012 1:50:50 PM CDT		
Date Processed:	8/21/2013 4:03:20 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5775; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.236	51289783	92.50	2214011
2	W2489 ChA 254nm	12.095	4157557	7.50	101536



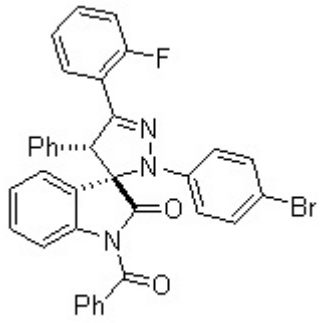
3q

Parameter	Value
Solvent	cdcl3
Temperature	31.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-01-10T11:09:17
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

CARBON_01
MCS I-99 pdt; 2-F dipole,13C

174.529 169.208 161.692 159.171 148.232 143.966 140.096 133.845 133.525 133.465 132.172 131.238 131.153 130.456 129.541 129.485 129.453 128.932 128.509 128.479 126.640 124.948 124.509 124.476 124.424 119.524 119.420 119.310 116.755 116.533 115.739 114.929 77.482 77.433 64.416 64.352

Parameter	Value
Solvent	cdcl3
Temperature	31.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-01-29T16:45:40
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



3q

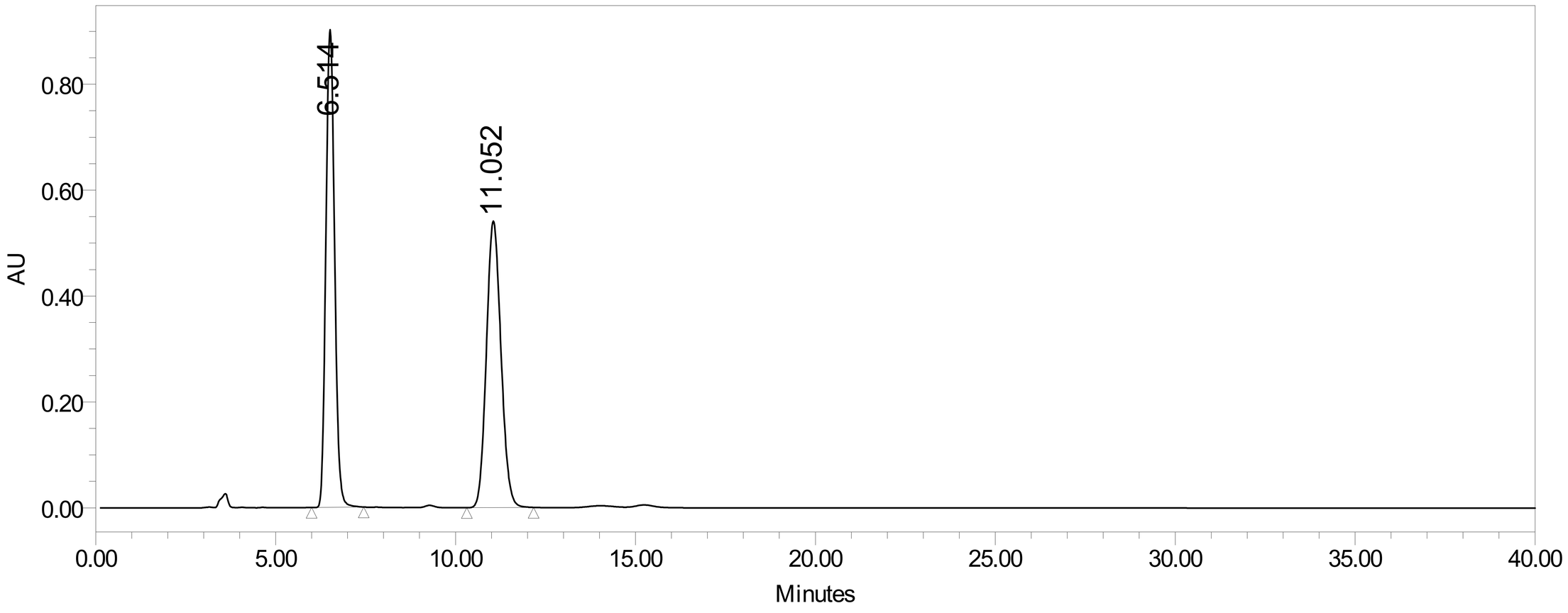
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS_I-95rac_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	76	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony3
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/15/2013 2:41:15 PM CST		
Date Processed:	8/21/2013 4:51:20 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5885; Processing Method: tony3

Processed Channel Descr.: W2489 ChA 254nm

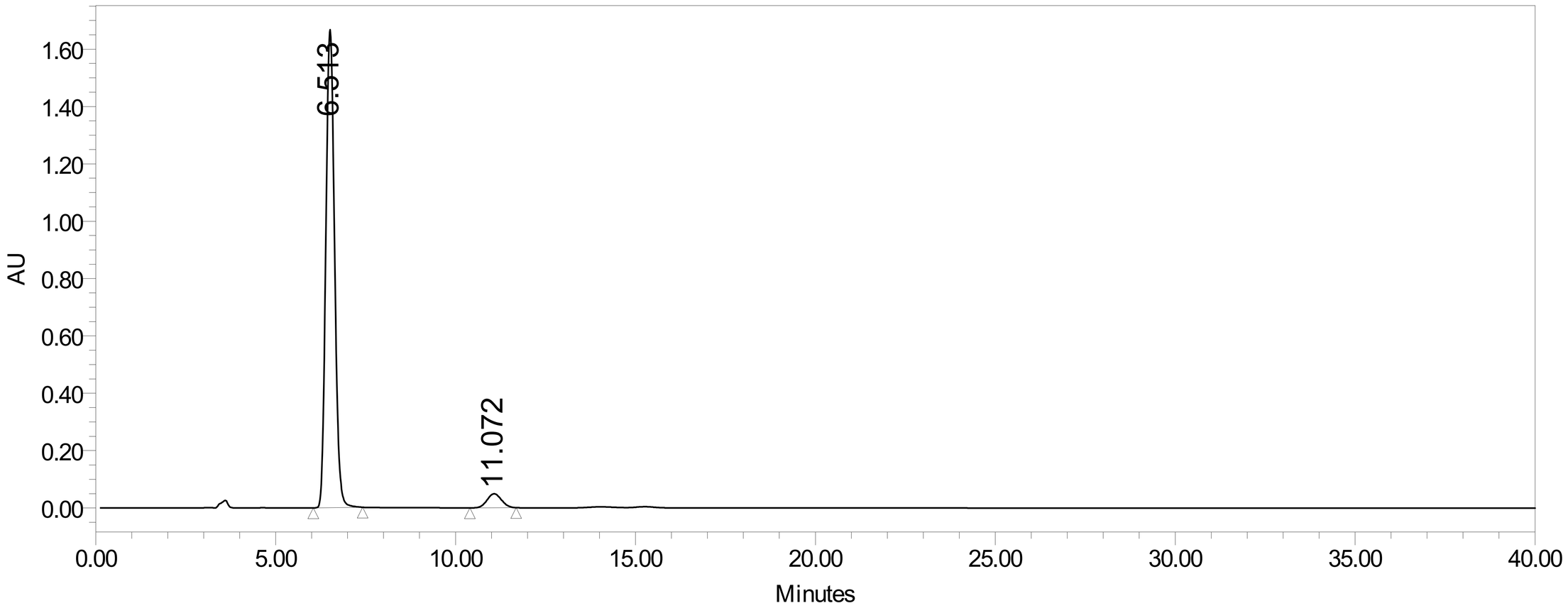
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.514	15201390	49.95	902448
2	W2489 ChA 254nm	11.052	15232146	50.05	541131

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

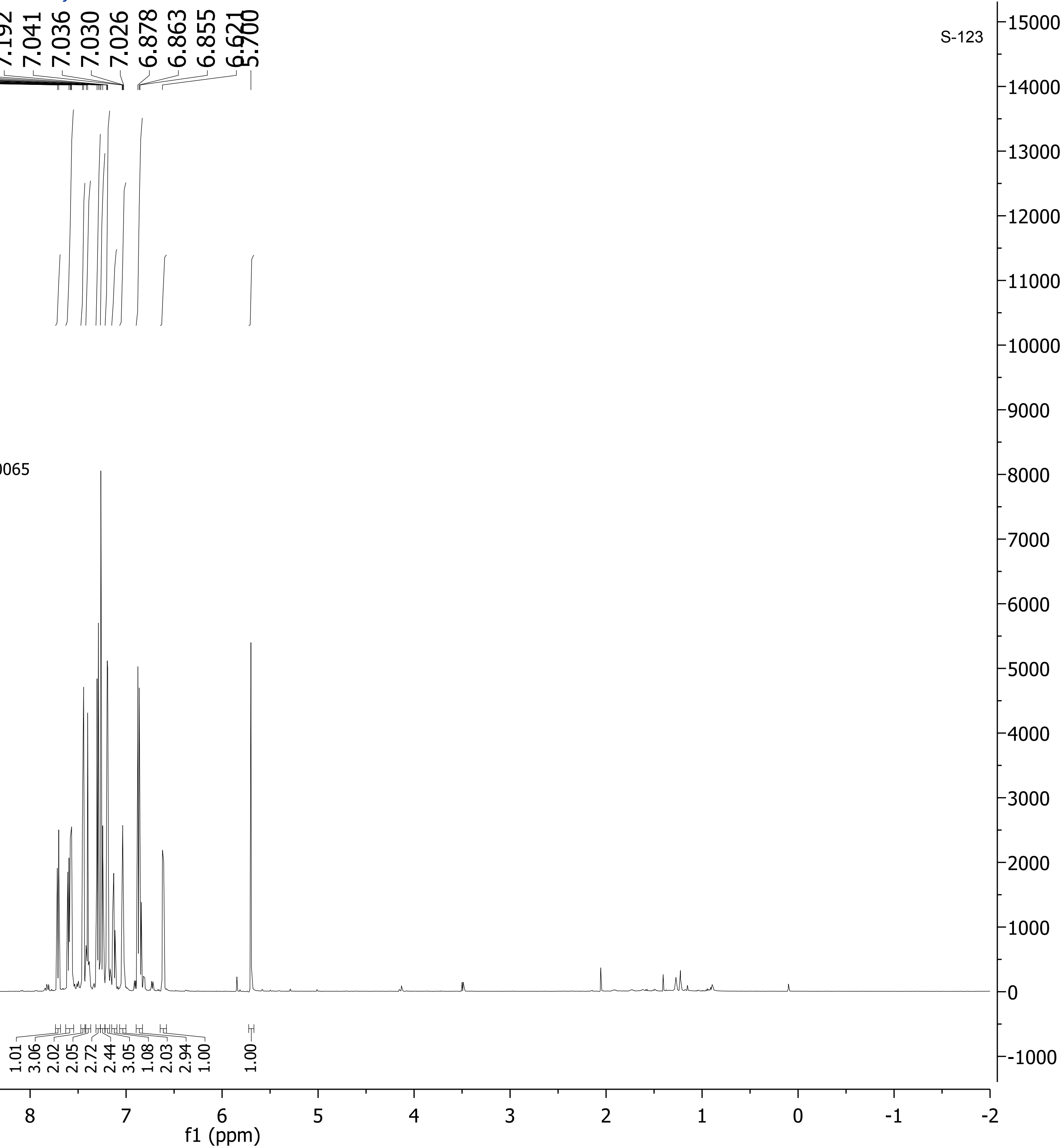
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	77	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony4
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/15/2013 3:21:53 PM CST		
Date Processed:	8/21/2013 4:52:14 PM CDT		



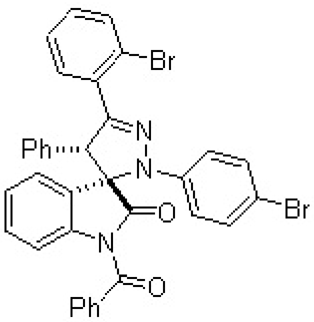
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5887; Processing Method: tony4

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.513	28140315	95.39	1667749
2	W2489 ChA 254nm	11.072	1361350	4.61	48984

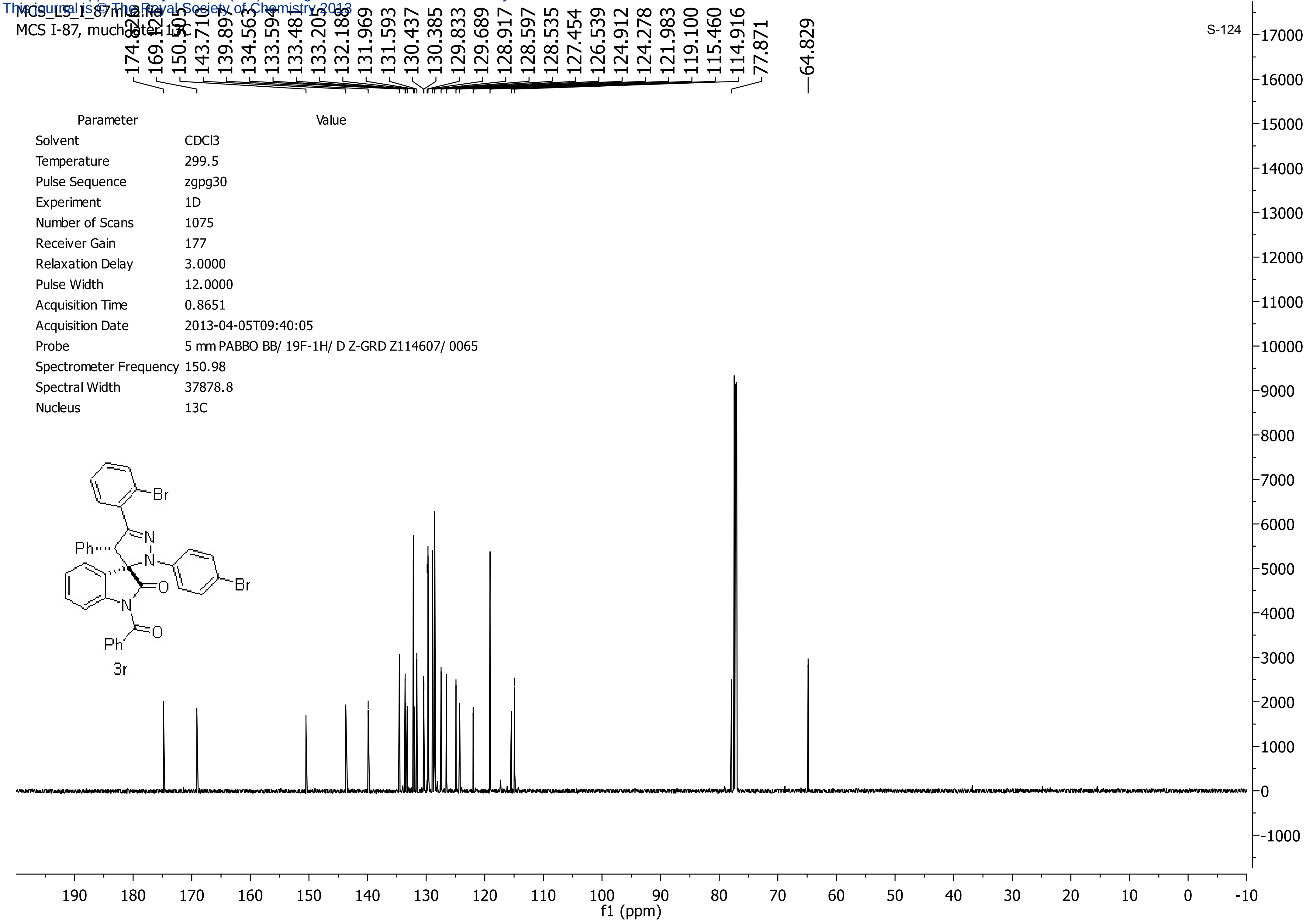


Parameter	Value
Solvent	CDCl3
Temperature	298.6
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	68
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-05T08:27:24
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



3r

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



Parameter	Value
Solvent	CDCl3
Temperature	299.5
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1075
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-04-05T09:40:05
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

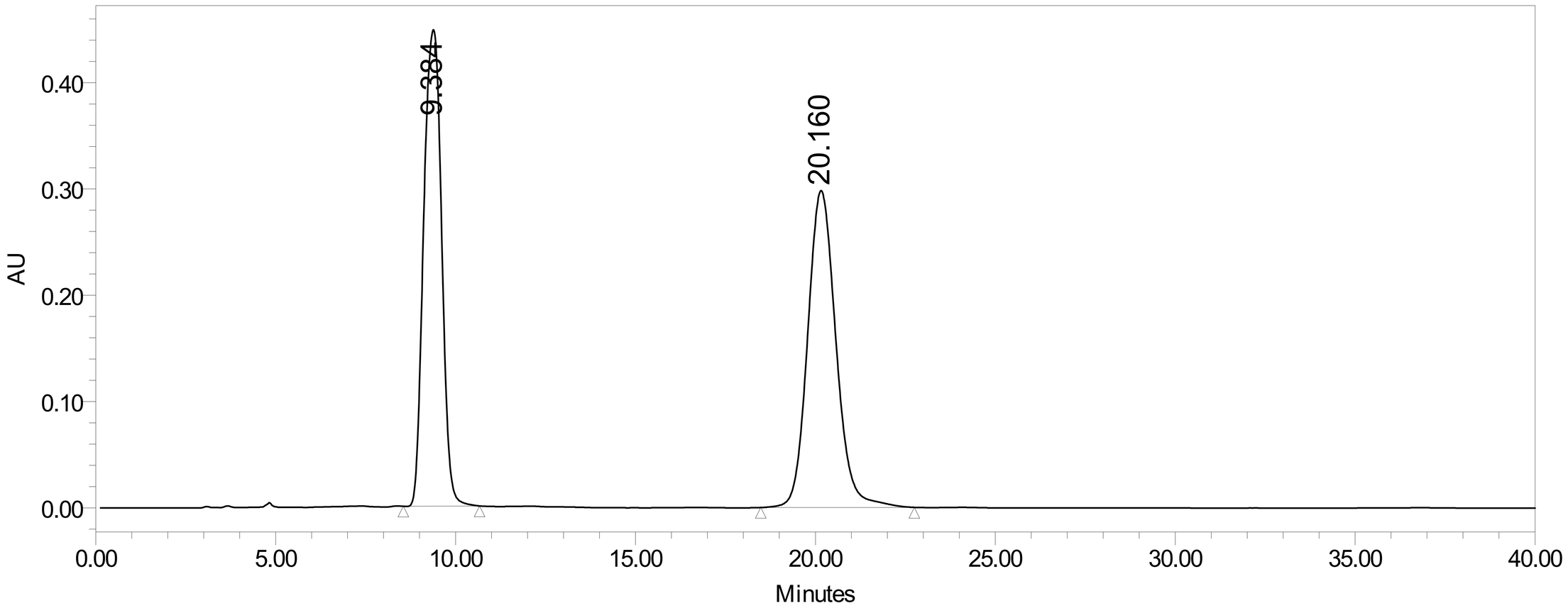
3r

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS-I-70rac_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	97	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	11/14/2012 6:56:43 PM CST		
Date Processed:	8/21/2013 4:17:23 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5813; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

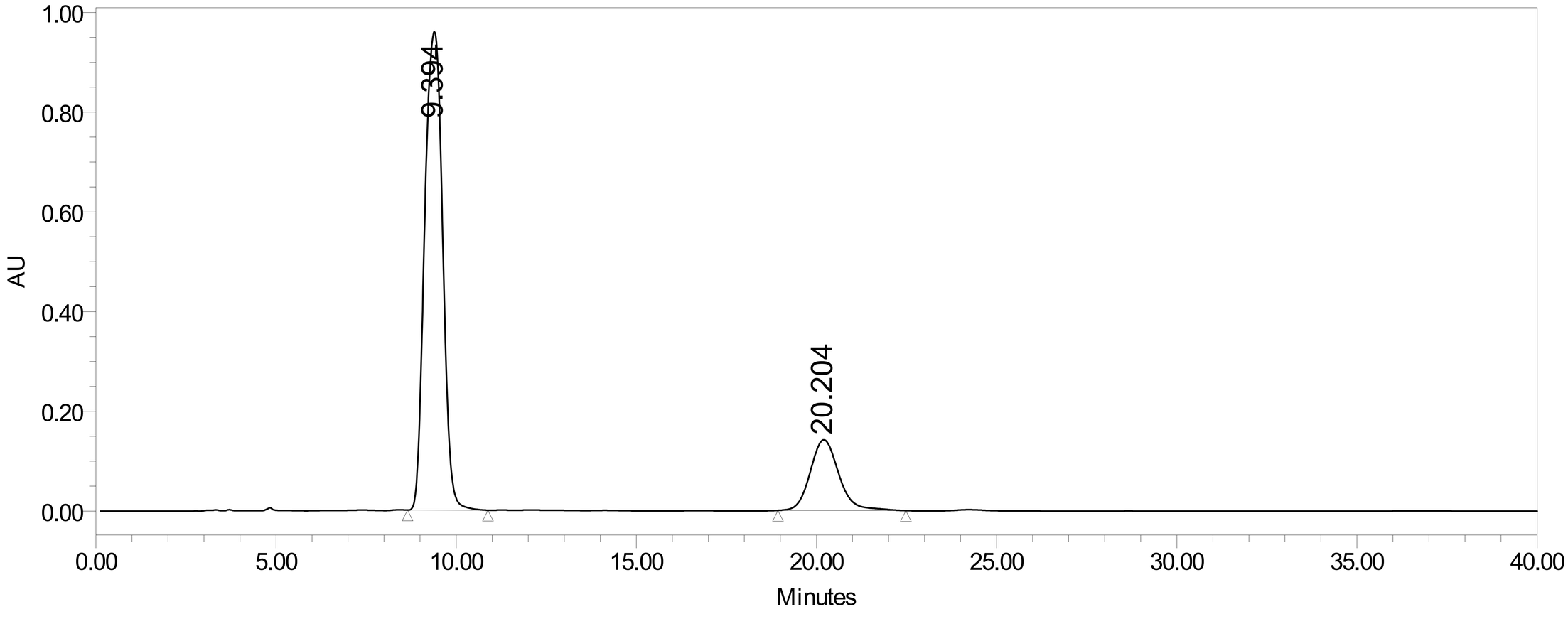
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.384	15480963	48.74	448319
2	W2489 ChA 254nm	20.160	16282143	51.26	298171

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS-I-70AT1_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	98	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	11/14/2012 7:37:23 PM CST		
Date Processed:	8/21/2013 4:18:04 PM CDT		



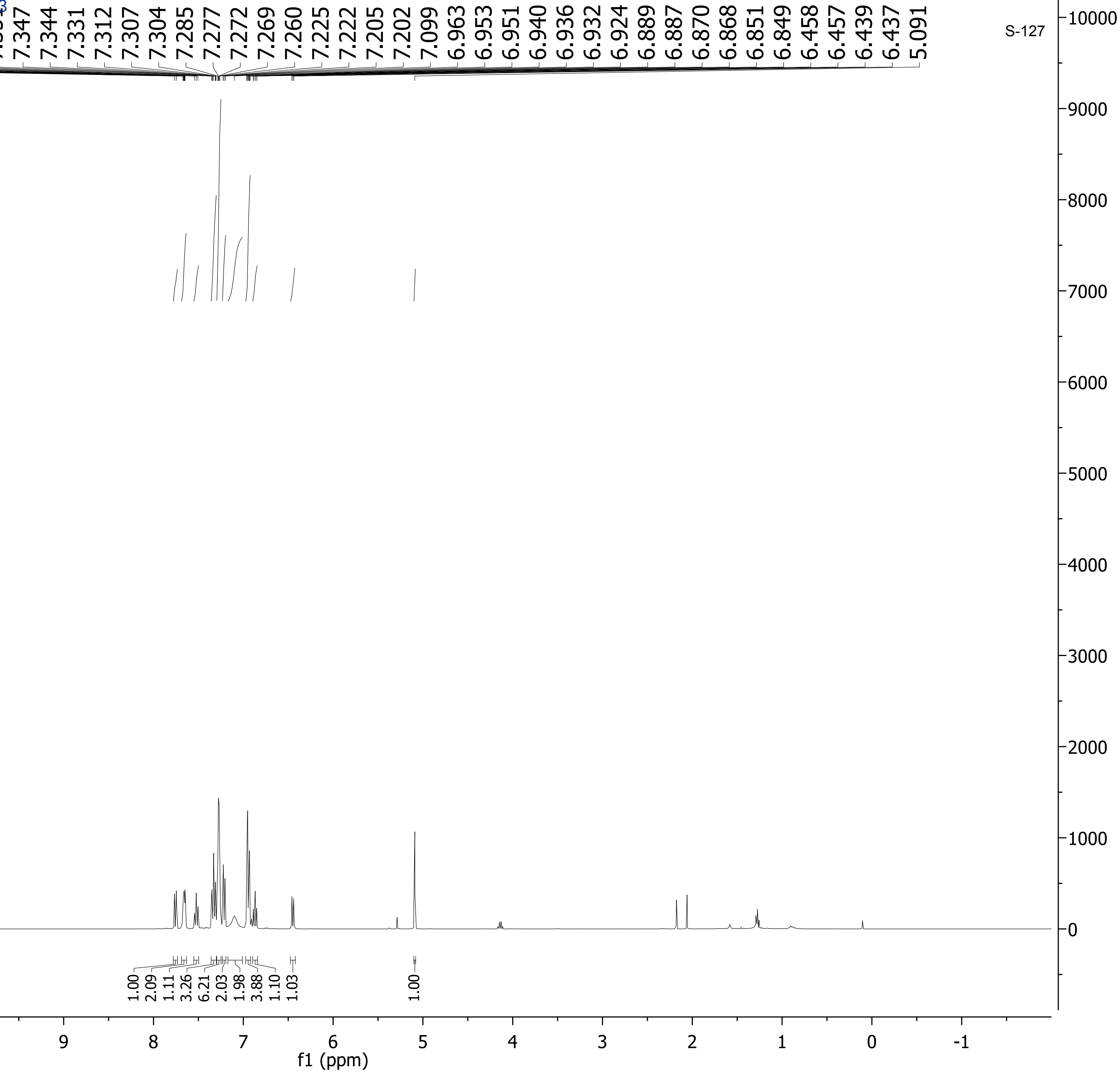
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5815; Processing Method: tony1

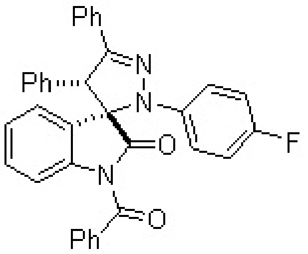
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.394	33179976	80.91	959528
2	W2489 ChA 254nm	20.204	7828448	19.09	141761

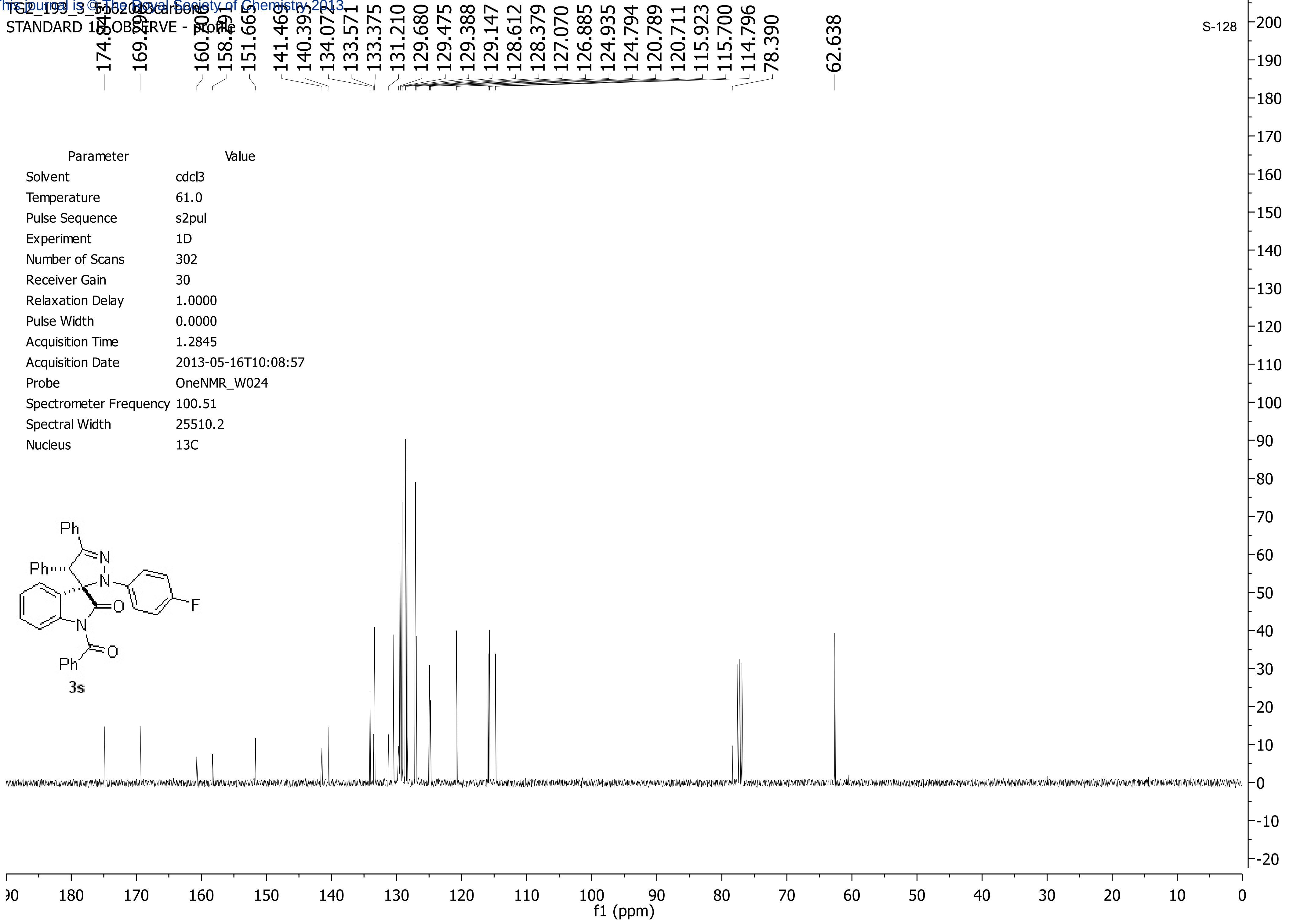
STANDARD 1H OBSERVE - profile

Parameter	Value
Solvent	cdcl3
Temperature	61.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-05-16T10:06:53
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H





3s



Parameter	Value
Solvent	cdcl3
Temperature	61.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	302
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-05-16T10:08:57
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

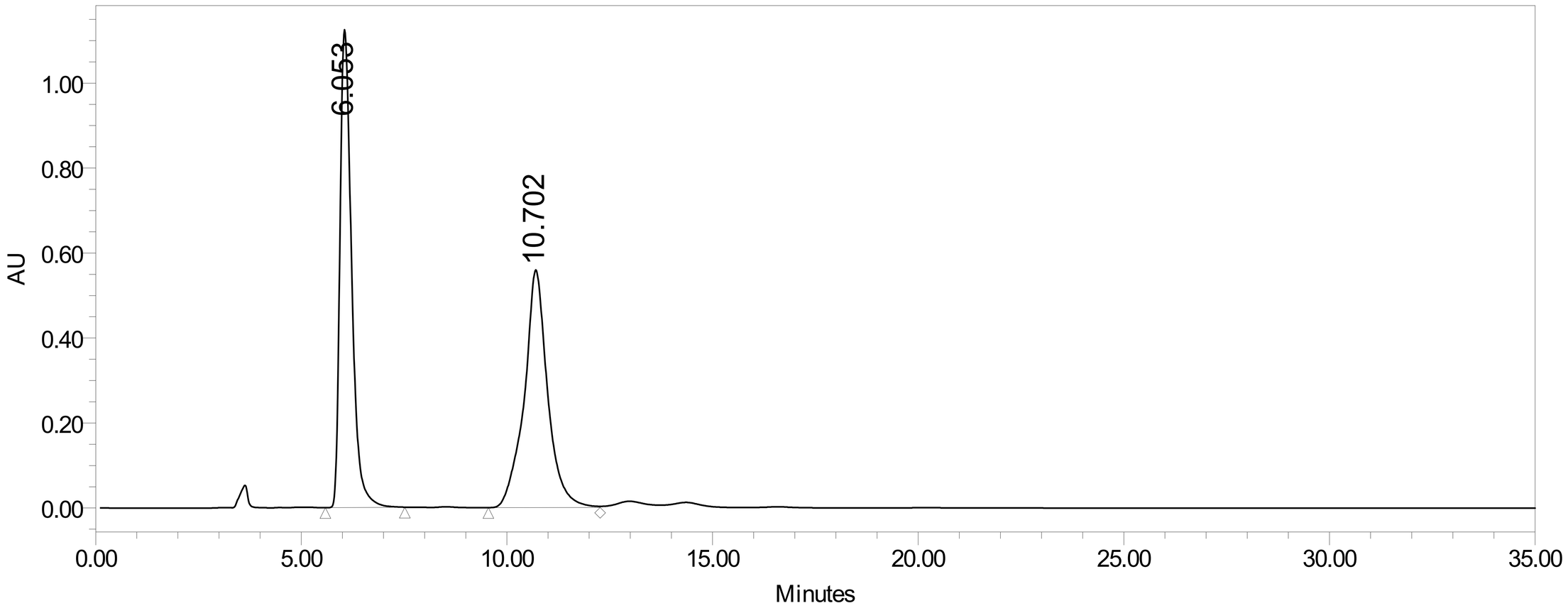
3s

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_191_2_ADH1mpm10%IPA	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_191_592013
Vial:	13	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	TG2_191r
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	5/9/2013 11:46:56 AM CDT		
Date Processed:	5/18/2013 7:18:46 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2959; Processing Method: TG2_191r

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.053	22161812	50.08	1125230
2	W2489 ChA 254nm	10.702	22090040	49.92	559224

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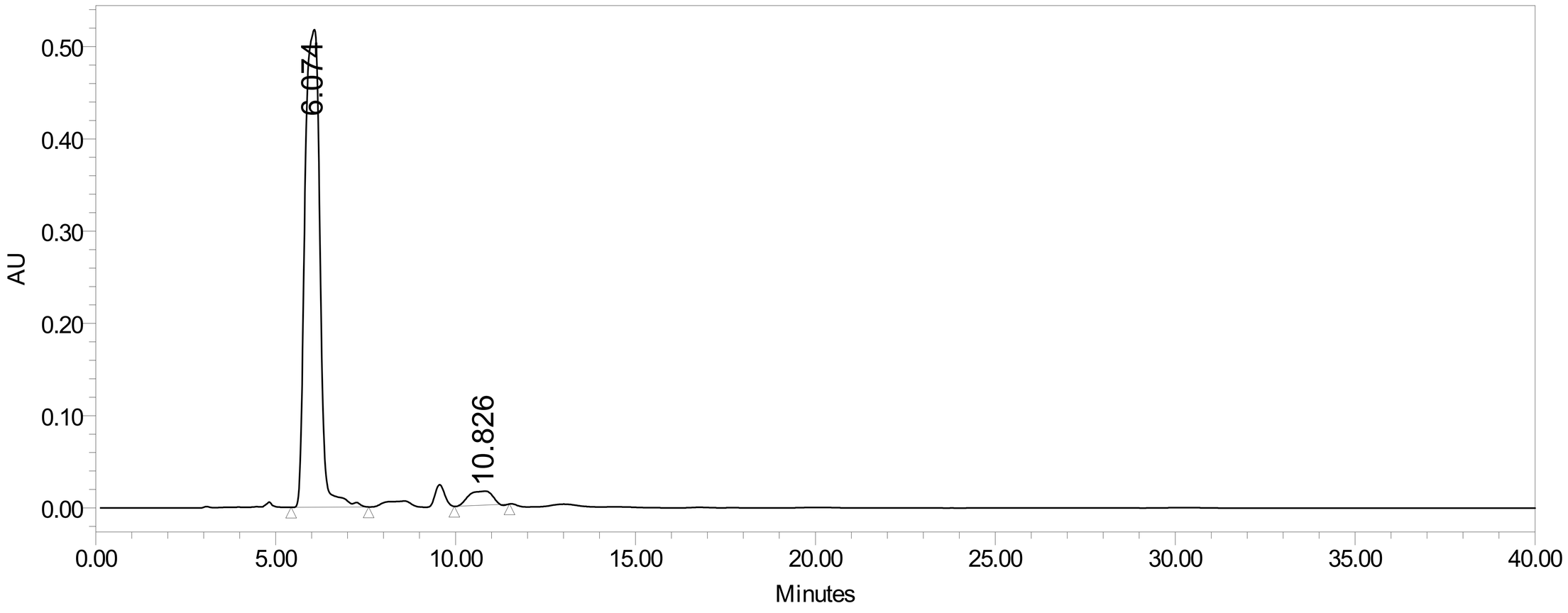
Injection Summary Report

SAMPLE INFORMATION

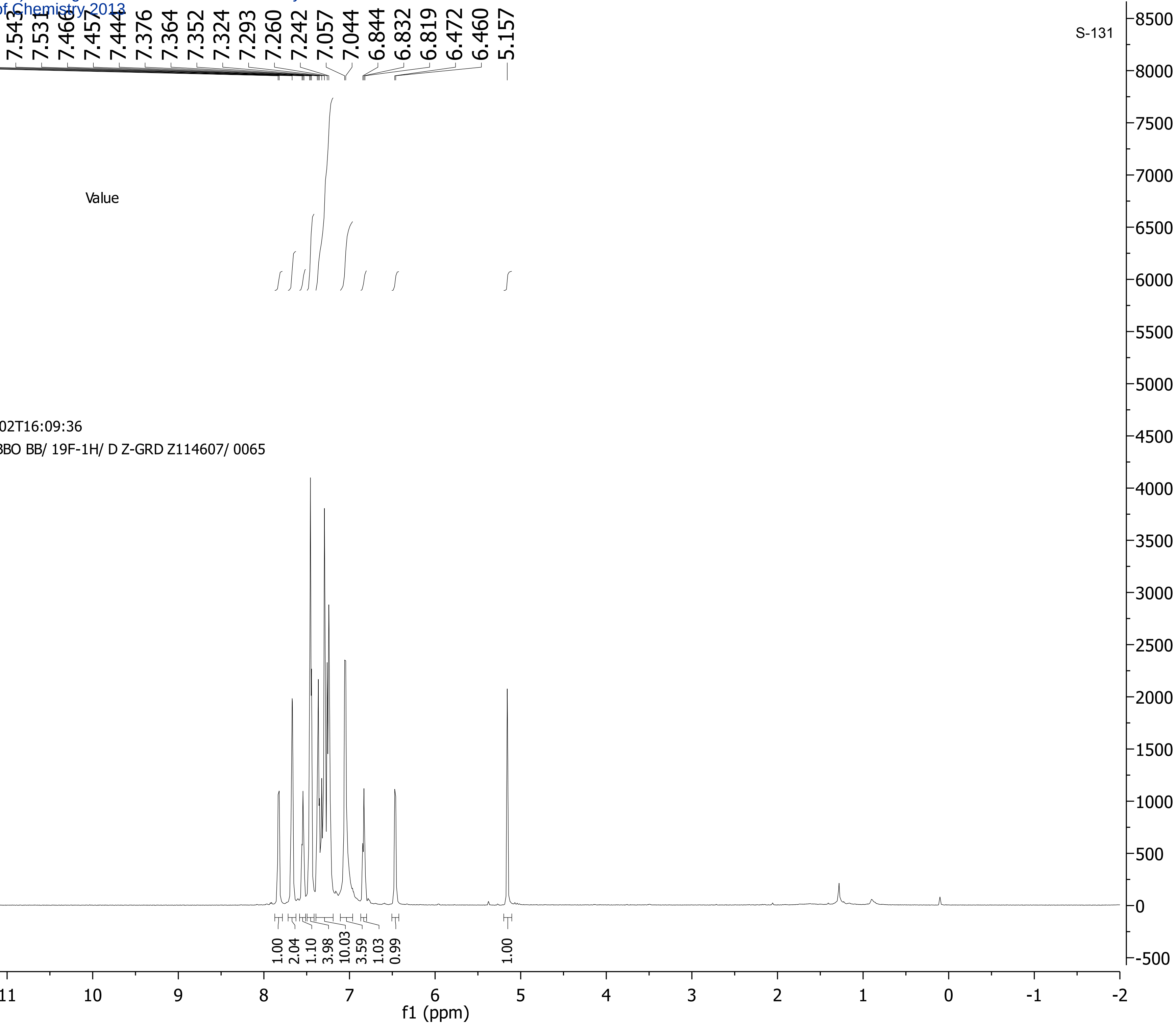
Sample Name:	MCS-I-71AT1_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	100	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	11/14/2012 8:58:40 PM CST		
Date Processed:	8/21/2013 4:23:40 PM CDT		



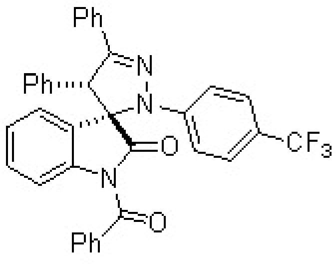
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5829; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.074	14934852	95.47	518185
2	W2489 ChA 254nm	10.826	708273	4.53	15056



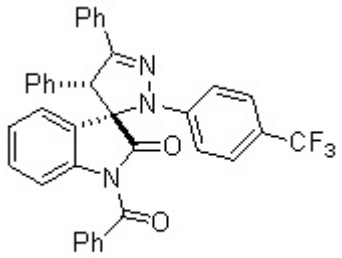
Parameter	Value
Solvent	CDCl3
Temperature	298.8
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	75
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2013-04-02T16:09:36
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



3t

174.92 169.11 151.05 147.44 139.80 133.94 133.56 133.49 131.00 130.51 129.67 129.58 129.18 128.73 128.69 128.50 127.27 126.62 126.60 126.54 125.51 125.07 124.49 124.01 123.79 123.72 123.58 123.36 115.92 115.23 77.23 63.63

Parameter	Value
Solvent	CDCl3
Temperature	299.7
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	1530
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2013-04-02T17:51:57
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



3t

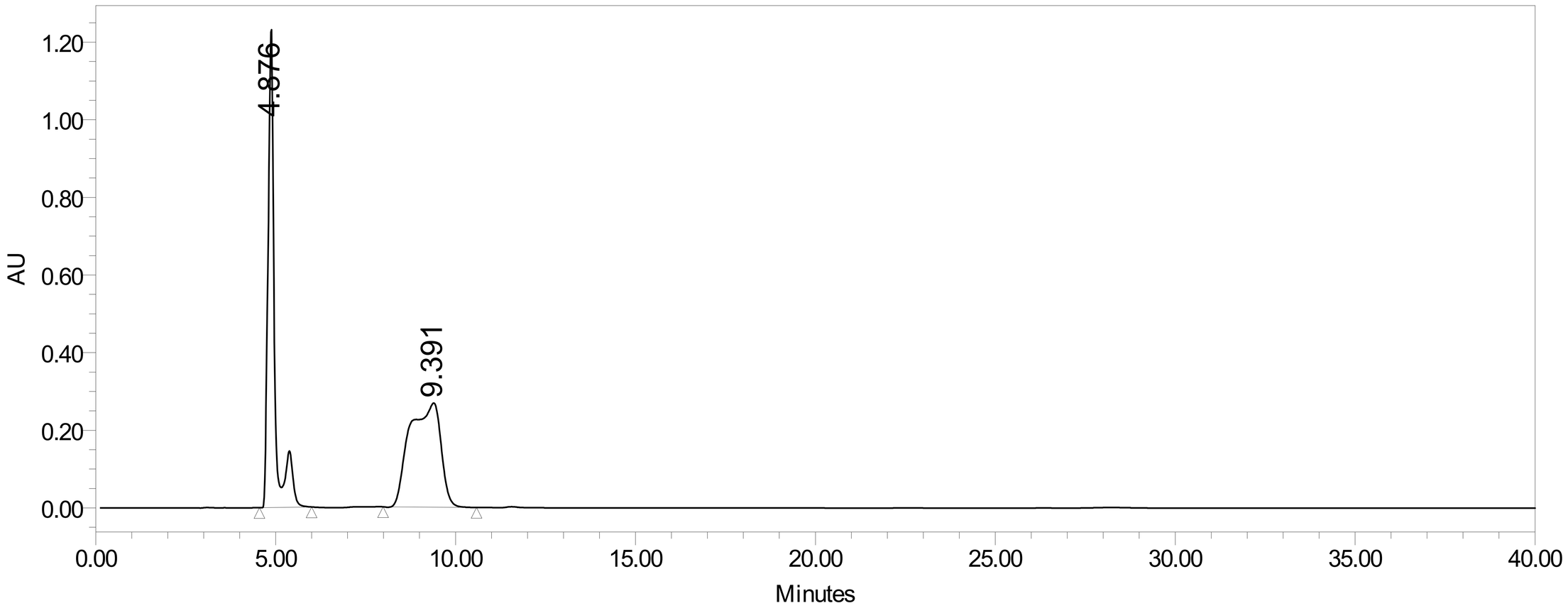
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS_I-75rac_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	5	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/7/2012 1:58:46 PM CST		
Date Processed:	8/21/2013 4:26:02 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5845; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

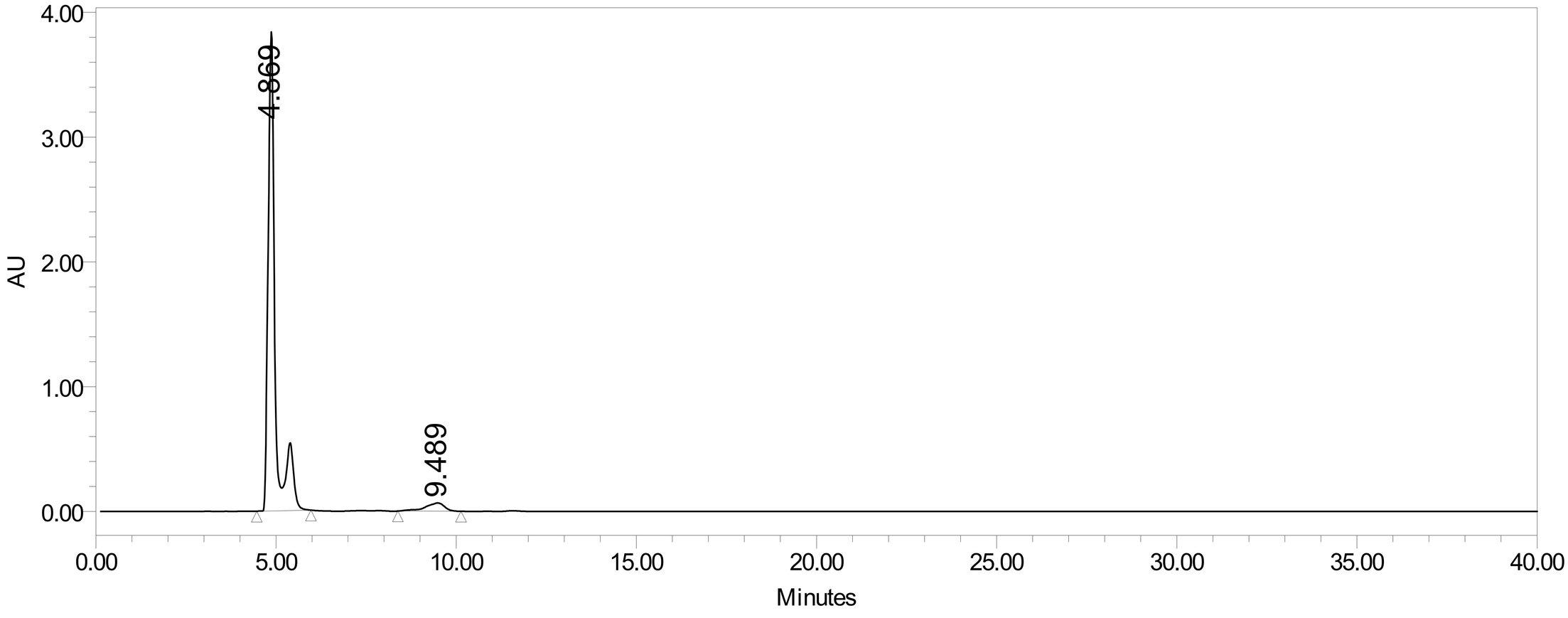
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.876	15653704	49.27	1237997
2	W2489 ChA 254nm	9.391	16117858	50.73	268507

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS_I-75AT1_9010ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	6	Acq. Method Set:	1_ADH 90_10 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/7/2012 2:39:27 PM CST		
Date Processed:	8/21/2013 4:26:44 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5847; Processing Method: tony1

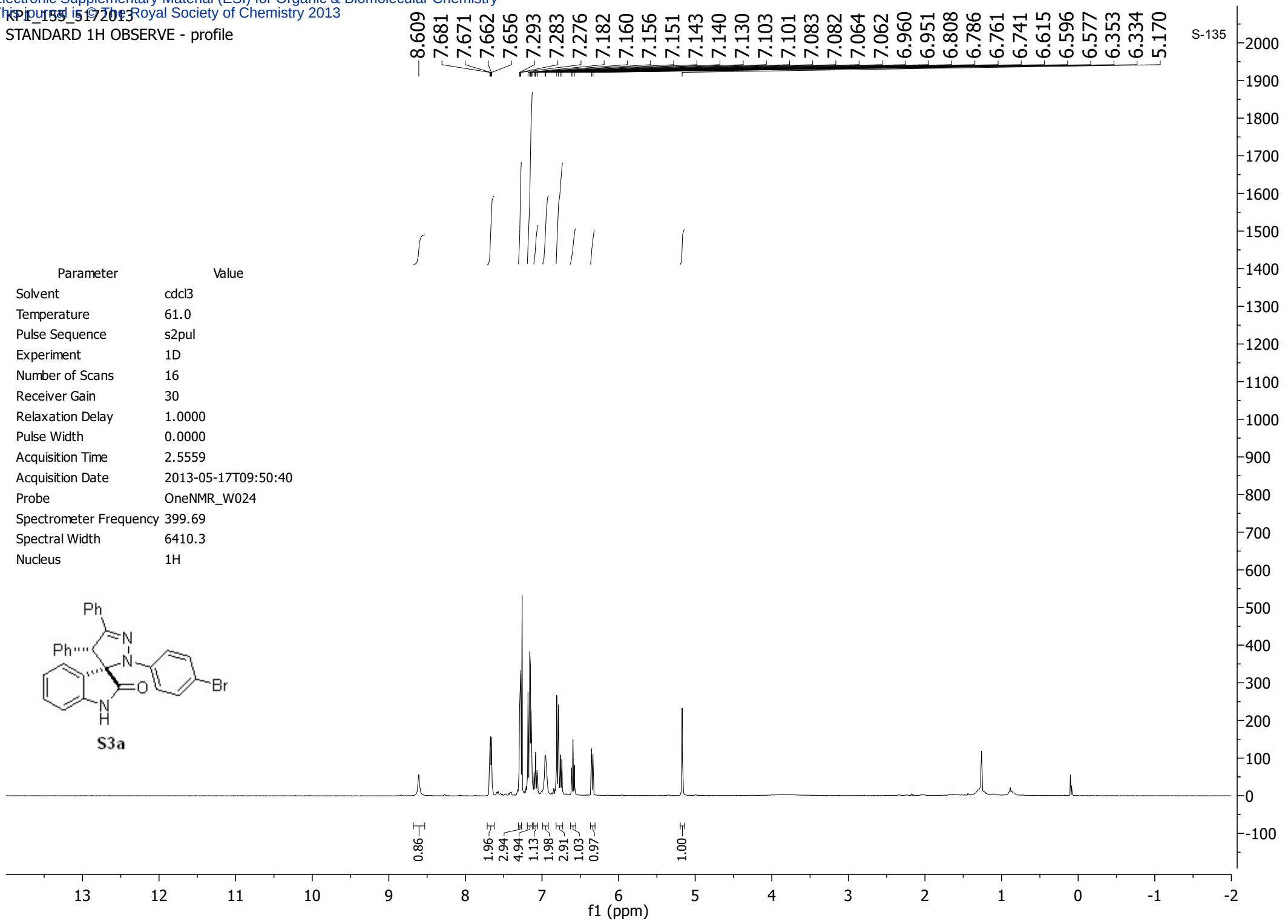
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.869	52152677	95.48	3840733
2	W2489 ChA 254nm	9.489	2468808	4.52	66349

KPL_155_5172013
STANDARD 1H OBSERVE - profile

Parameter	Value
Solvent	cdcl3
Temperature	61.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-05-17T09:50:40
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

S3a

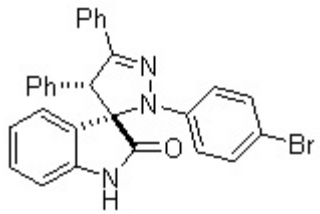


KPL_155_carbon_5172013

STANDARD 1H OBSERVE - proton

178.455 149.716 143.432 139.871 134.562 131.977 131.531 129.908 129.310 129.178 128.856 128.633 128.288 127.127 126.662 125.318 122.873 117.026 113.621 110.811 77.430 62.881

Parameter	Value
Solvent	cdcl3
Temperature	61.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	548
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-05-17T09:53:10
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



S3a

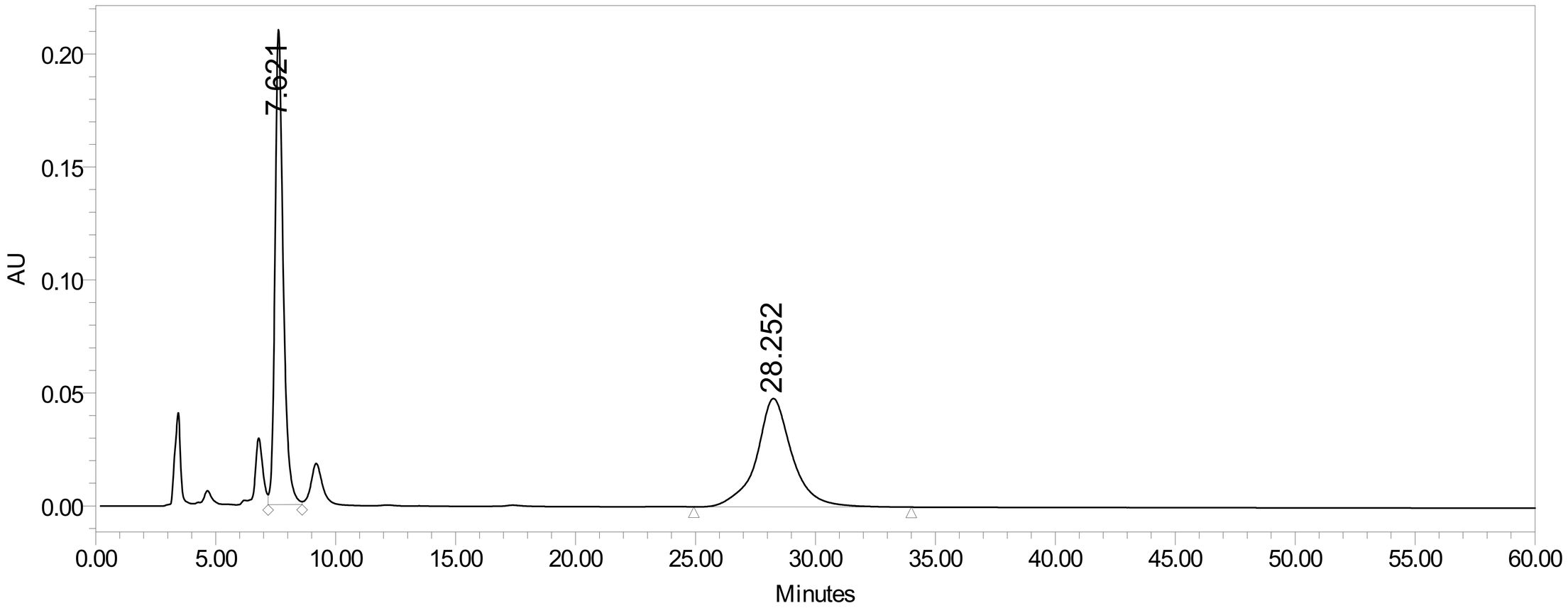
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG2_193_ADH1mpm20%IPA	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_193_5102013
Vial:	42	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	TG2_193
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	5/10/2013 4:41:18 PM CDT		
Date Processed:	5/18/2013 7:05:06 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2951; Processing Method: TG2_193

Processed Channel Descr.: W2489 ChA 254nm

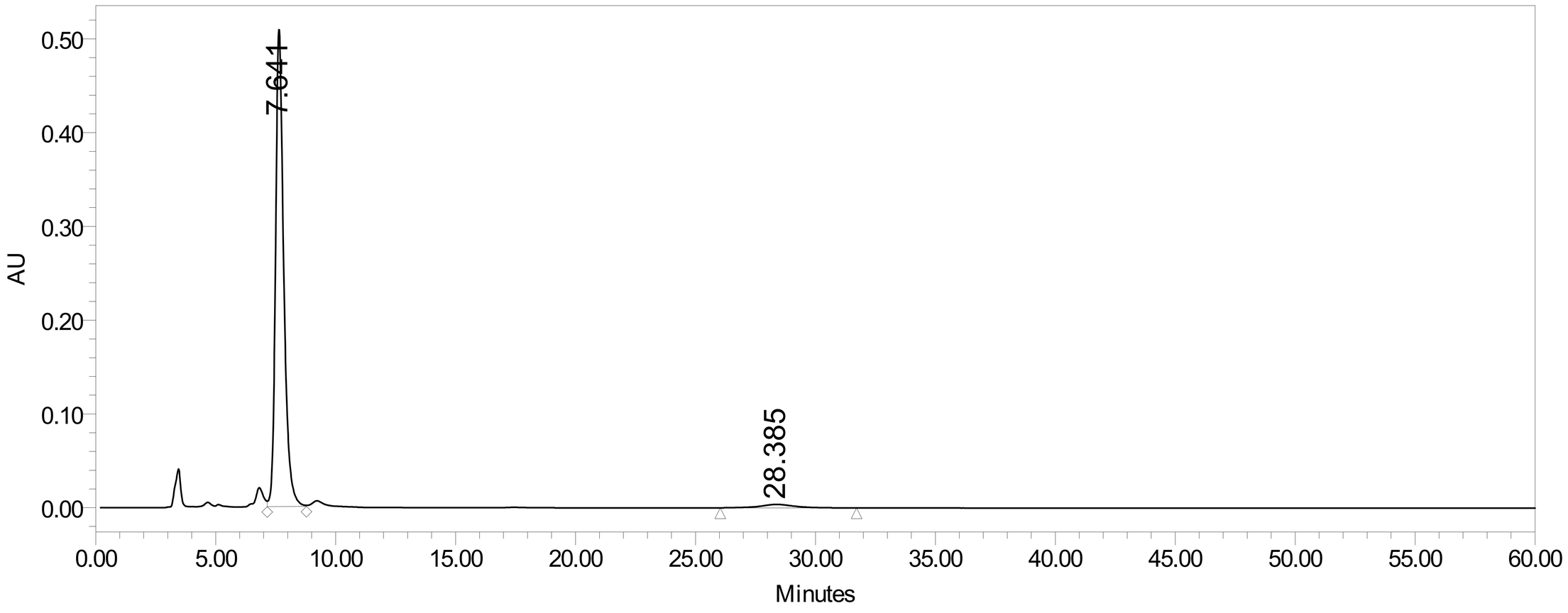
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.621	4982468	50.04	210299
2	W2489 ChA 254nm	28.252	4974088	49.96	47976

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	KP1_155_ADH1mpm20%IPA	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG2_193_5102013
Vial:	43	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	KP1_155
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	5/10/2013 5:42:11 PM CDT		
Date Processed:	5/18/2013 7:10:37 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2955; Processing Method: KP1_155

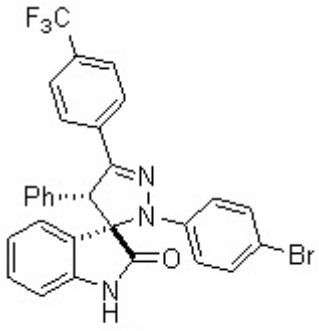
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.641	12052383	97.07	509415
2	W2489 ChA 254nm	28.385	364356	2.93	3682

PROTON_01
MCS I-137

8.758 7.772 7.751 7.543 7.524 7.261 7.201 7.178 7.173 7.161 7.102 7.083 7.063 6.943 6.818 6.795 6.758 6.739 6.619 6.600 6.581 6.352 6.334 5.174

Parameter	Value
Solvent	cdcl3
Temperature	90.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2013-04-24T18:17:33
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



S3b

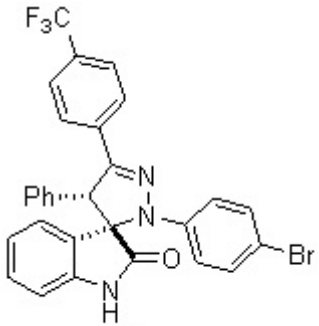
1.14 2.15 2.09 5.05 1.17 2.11 2.14 1.10 1.17 1.09 1.00

f1 (ppm)

CARBON-13

178.177 148.017 142.861 139.939 134.990 134.978 134.064 132.082 131.011 130.688 130.365 130.104 130.041 129.203 129.047 128.586 127.105 126.658 125.666 125.629 125.591 125.551 124.883 122.953 117.099 114.154 110.934 77.303 62.572

Parameter	Value
Solvent	cdcl3
Temperature	90.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	3200
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2013-04-24T19:02:33
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



S3b

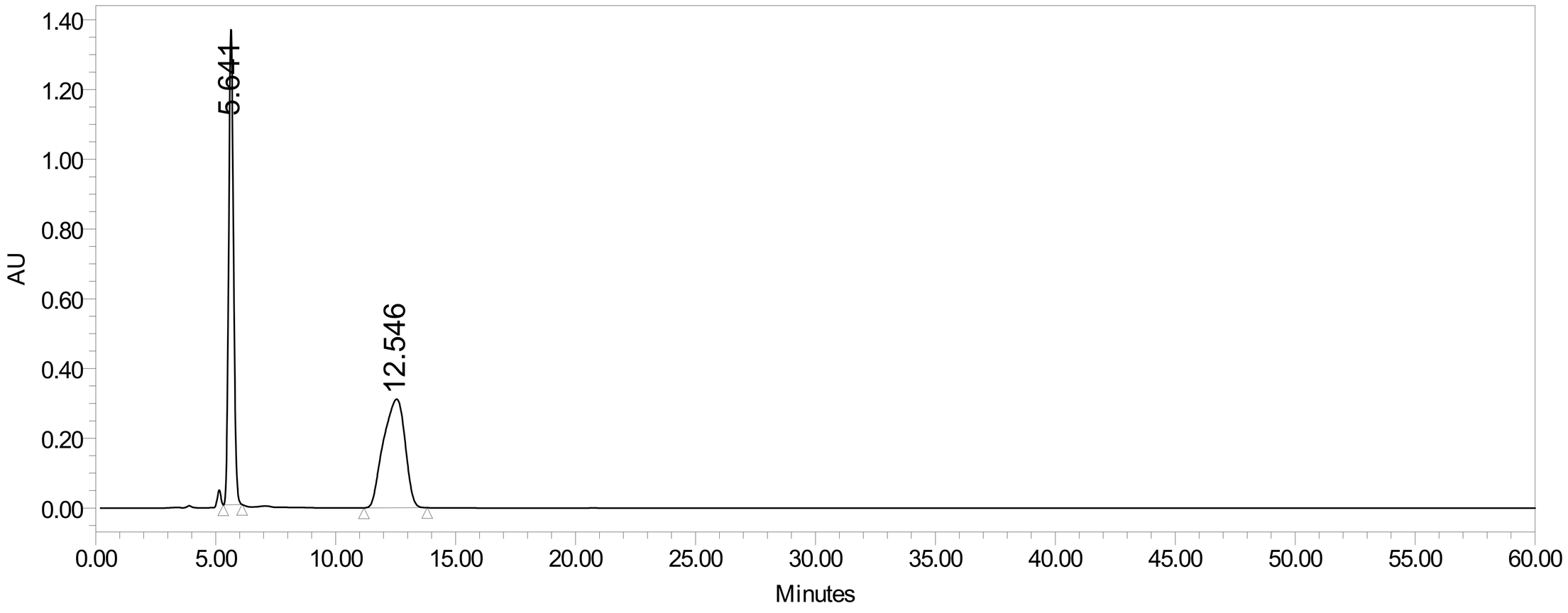
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS_I_83_8020ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	104	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/13/2012 5:38:20 PM CST		
Date Processed:	8/21/2013 4:42:19 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5866; Processing Method: tony1

Processed Channel Descr.: W2489 ChA 254nm

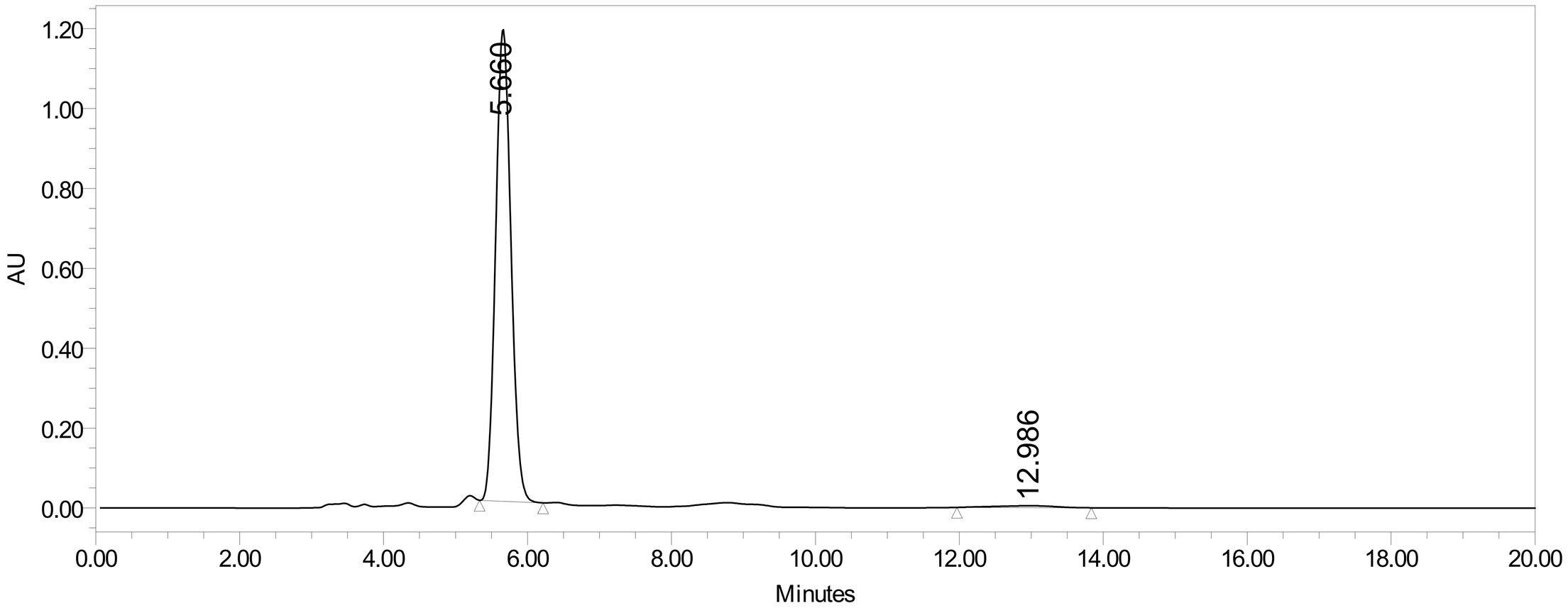
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.641	19070394	49.35	1367022
2	W2489 ChA 254nm	12.546	19570794	50.65	311655

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	MCS_I_81A_8020ADH1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	
Vial:	101	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	tony2
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/14/2012 10:13:04 AM CST		
Date Processed:	8/21/2013 4:45:51 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 5873; Processing Method: tony2

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.660	17431782	98.46	1183082
2	W2489 ChA 254nm	12.986	272007	1.54	4706