Enantioselective Dearomative [3+2] Cycloadditions of Indoles with Azomethine Ylides Derived from Alanine Imino Esters

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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) or Silacycle Siala-P silica gel or on a Teledyne Isco CombiFlash Rf automated chromatography system with RediSep Rf Gold normal-phase silica columns. Products of reactions were visualized on TLC plates under UV light.

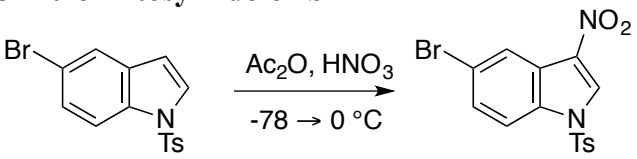
HRMS (ESI) analysis was performed at the Iowa State University Chemical Instrumentation Facility on an Agilent 6540 QTOF spectrometer. Optical rotations were measured on an Atago AP-300 automatic polarimeter. HPLC analyses were carried out on a Water Alliance HPLC system with an e2695 Separations Module 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

Benzaldehyde, 4-chlorobenzaldehyde, 4-methylbenzaldehyde, 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, 2-methoxybenzaldehyde, and 2-chlorobenzaldehyde were purchased from Sigma-Aldrich and used without further purification. 4-Trifluoromethylbenzaldehyde, 4-bromobenzaldehyde, 3-bromobenzaldehyde, and 2-fluorobenzaldehyde were purchased from Oakwood Chemical Company and used without further purification. DL-Alanine was purchased from AK Scientific and used without further purification. DL-alanine methyl ester hydrochloride was prepared by bubbling HCl gas through a methanolic solution of DL-alanine followed by removal of the volatiles under reduced pressure to furnish the amine hydrochloride. DL-Alanine isopropyl ester hydrochloride was prepared by bubbling HCl gas through a solution of DL-alanine in isopropanol followed by removal of the volatiles under reduced pressure to furnish the required amine hydrochloride. Tosyl chloride and indole were purchased from Sigma-Aldrich and used without further purification. 5-bromoindole was purchased from Frontier Scientific and used without further purification. 5-Bromo-*N*-tosylindole was prepared according to a literature procedure.[1] 3-Nitro-*N*-tosylindole **1a** was prepared according to a literature procedure.[2]

$Cu(OTf)_2$, *rac*-BINAP, (*R*)-BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthalene), (*R*)-segphos ((*R*)-(+)-5,5′-Bis(diphenylphosphino)-4,4′ -bi-1,3-benzodioxole), and (*R*)-difluorphos ((*R*)-(-)-5,5'-Bis(diphenylphosphino)-2,2,2′,2′-tetrafluoro-4,4′-bi-1,3-benzodioxole) were purchased from Strem Chemicals and used without further purification.

Synthesis of 5-Bromo-3-nitro-*N*-tosylindole 1b[3]



1b

5-Bromo-*N*-tosylindole (2.30 g, 6.57 mmol, 1.00 equiv) was added to a round bottom flask and suspended in 32 ml of acetic anhydride. A solution of 1.3 mL of 70% nitric acid and 13 mL of acetic anhydride was added dropwise over 30 minutes to the suspension of 5-bromo-3-nitroindole at -78 °C. The solution was warmed to 0 °C and maintained at this temperature for 4 h. The reaction was quenched with water and extracted with dichloromethane (3x). The combined organic layer was washed with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield crude 5-bromo-3-nitro-*N*-tosylindole **1b**. Crude **1b** was recrystallized from 1:1 hexane:dichloromethane to yield 5-bromo-3-nitro-*N*-tosylindole **1b** (1.35 g, 3.41 mmol, 52%). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 2.41 (s, 3H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.57 (dd, *J* = 9.0, 1.4 Hz, 1H), 7.83-7.90 (m, 3H), 8.40 (d, *J* = 1.4 Hz, 1H), 8.54

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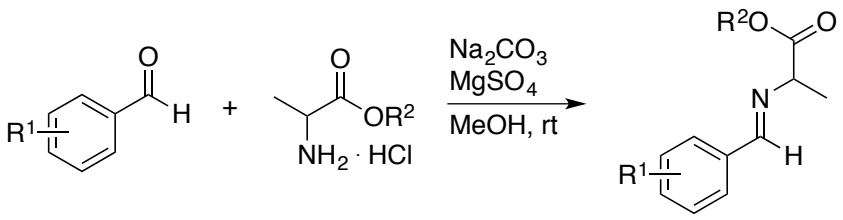
3) a) Awata, A.; Arai, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 10462. b) Zhao, J.-Q.; Zhou, M.-Q.; Wu, Z.-J.; Wang, Z.-H.; Yue, D.-F.; Xu, X.-Y.; Zhang, X.-M.; Yuan, W.-C. *Org. Lett.* **2015**, *17*, 2238. c) Zhao, J.-Q.; Wu, Z.-J.; Zhou, M.-Q.; Xu, X.-Y.; Zhang, X.-M.; Yuan, W.-C. *Org. Lett.* **2015**, *17*, 5020.

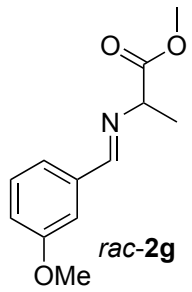
(s, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 22.0, 115.3, 120.1, 123.5, 124.2, 127.66, 127.67, 128.8, 130.2, 130.9, 132.5, 133.8, 147.3.

General Procedure for Synthesis of Imino Esters *rac*-2a-l



rac-**2a**: R^1 = H, R^2 = Me
rac-**2b**: R^1 = 4-CF_3, R^2 = Me
rac-**2c**: R^1 = 4-Cl, R^2 = Me
rac-**2d**: R^1 = 4-Br, R^2 = Me
rac-**2e**: R^1 = 4-Me, R^2 = Me
rac-**2f**: R^1 = 4-MeO, R^2 = Me
rac-**2g**: R^1 = 3-MeO, R^2 = Me
rac-**2h**: R^1 = 3-Br, R^2 = Me
rac-**2i**: R^1 = 2-MeO, R^2 = Me
rac-**2j**: R^1 = 2-F, R^2 = Me
rac-**2k**: R^1 = 2-Cl, R^2 = Me
rac-**2l**: R^1 = H, R^2 = *i*-Pr

To a suspension of DL-alanine methyl ester hydrochloride or DL-alanine isopropyl ester hydrochloride (1.2 equiv), sodium carbonate (1.5 equiv), and a small amount of magnesium sulfate in methanol (0.36 M solution with respect to the amine hydrochloride) was added the appropriate aldehyde (1 equiv). The reaction mixture was stirred for 12 h at room temperature. The reaction mixture was then filtered through celite into a separatory funnel. The mixture was extracted into diethyl ether. The ether layer was washed with water (2x) and brine (2x). The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to afford imino esters *rac*-**2a**-**2l**, which were used without further purification. NMR spectra match reported NMR data for known imino esters **2a**,[4] **2b**,[5] **2c**,[4] **2d**,[5] **2e**,[5] **2f**,[5] **2i**,[6] **2j**,[5] **2k**,[7] and **2l**.[7,8]



rac-**2g**

Methyl (*E*)-2-((3-methoxybenzylidene)amino)propanoate (*rac*-2g): Prepared according to the general procedure from DL-alanine methyl ester hydrochloride (1.00 g, 7.17 mmol) and 3-methoxybenzaldehyde (0.72 mL, 5.9 mmol) to yield *rac*-**2g** as a yellow oil in 87% yield (1.13 g, 5.12 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.52 (d, *J* = 6.8 Hz, 3H), 3.72 (s, 3H), 3.81 (s, 3H), 4.14 (q, *J* = 6.8 Hz, 1H), 6.97 (d, *J* = 7.8 Hz, 1H), 7.24-7.33 (m, 2H), 7.37 (s, 1H), 8.26 (s, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 19.4, 52.1, 55.3, 67.9, 111.9, 117.9, 121.8, 129.5, 137.2, 159.9, 162.9, 172.9. **HRMS** (ESI) calcd. for $C_{12}H_{16}NO_3^+$ $[M+H]^+$ 222.1125, found 222.1130.

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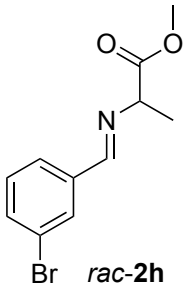
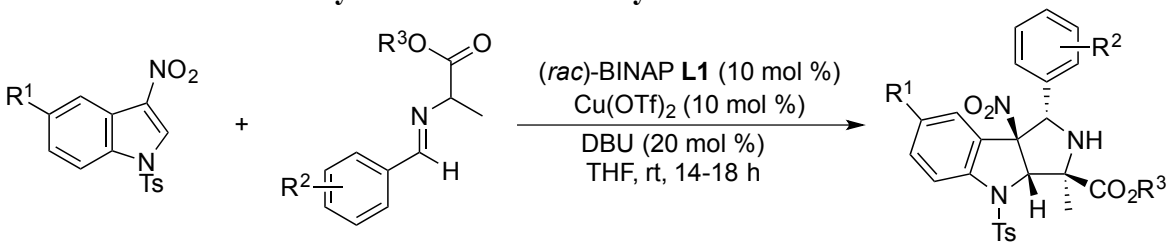


rac-**2h**

Methyl (*E*)-2-((3-bromobenzylidene)amino)propanoate (*rac*-2h): Prepared according to the general procedure from DL-alanine methyl ester hydrochloride (1.00 g, 7.17 mmol) and 3-bromobenzaldehyde (0.70 mL, 6.0 mmol) to yield *rac*-**2h** as a yellow oil in 91% yield (1.46 g, 5.40 mmol). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.56 (d, *J* = 6.8 Hz, 3H), 3.78 (s, 3H), 4.20 (q, *J* = 6.8 Hz, 1H), 7.31 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 8.00 (s, 1H), 8.28 (s, 1H). **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 19.6, 52.5, 68.0, 123.1, 127.5, 130.3, 131.1, 134.2, 137.8, 161.6, 172.9. **HRMS** (ESI) calcd. for $C_{11}H_{13}BrNO_2^+$ $[M+H]^+$ 270.0124, found 270.0126.

General Procedure for Synthesis of Racemic Pyrroloindolines *exo′*-3a-m



1a: R^1 = H
1b: R^1 = Br

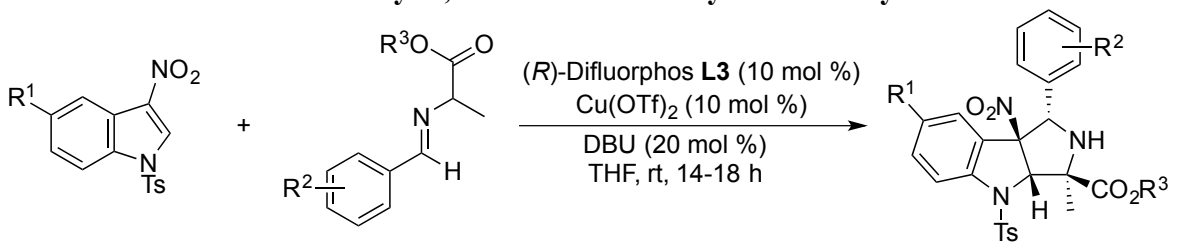
rac-**2a**: R^2 = H, R^3 = Me
rac-**2b**: R^2 = 4-CF_3, R^3 = Me
rac-**2c**: R^2 = 4-Cl, R^3 = Me
rac-**2d**: R^2 = 4-Br, R^3 = Me
rac-**2e**: R^2 = 4-Me, R^3 = Me
rac-**2f**: R^2 = 4-MeO, R^3 = Me
rac-**2g**: R^2 = 3-MeO, R^3 = Me
rac-**2h**: R^2 = 3-Br, R^3 = Me
rac-**2i**: R^2 = 2-OMe, R^3 = Me
rac-**2j**: R^2 = 2-F, R^3 = Me
rac-**2k**: R^2 = 2-Cl, R^3 = Me
rac-**2l**: R^2 = H, R^3 = *i*-Pr

exo′-**3a**: R^1 = H, R^2 = H, R^3 = Me
exo′-**3b**: R^1 = H, R^2 = 4-CF_3, R^3 = Me
exo′-**3c**: R^1 = H, R^2 = 4-Cl, R^3 = Me
exo′-**3d**: R^1 = H, R^2 = 4-Br, R^3 = Me
exo′-**3e**: R^1 = H, R^2 = 4-Me, R^3 = Me
exo′-**3f**: R^1 = H, R^2 = 4-MeO, R^3 = Me
exo′-**3g**: R^1 = H, R^2 = 3-MeO, R^3 = Me
exo′-**3h**: R^1 = H, R^2 = 3-Br, R^3 = Me
exo′-**3i**: R^1 = H, R^2 = 2-OMe, R^3 = Me
exo′-**3j**: R^1 = H, R^2 = 2-F, R^3 = Me
exo′-**3k**: R^1 = H, R^2 = 2-Cl, R^3 = Me
exo′-**3l**: R^1 = H, R^2 = H, R^3 = *i*-Pr
exo′-**3m**: R^1 = Br, R^2 = H, R^3 = Me

In a nitrogen-filled dry-box, $Cu(OTf)_2$ (7.2 mg, 0.020 mmol, 0.10 equiv), (*rac*)-BINAP (12.5 mg, 0.0200 mmol, 0.100 equiv), and the appropriate indole **1a** or **1b** (0.200 mmol, 1.00 equiv) were added to a 1-dram vial. In a second 1-dram vial, a 0.48 M solution of the appropriate imino ester *rac*-**2a**-**2l** in THF was prepared. Both vials were sealed with a PTFE/silicone-lined septum cap and removed from the dry-box. The mixture of $Cu(OTf)_2$, (*rac*)-BINAP, and the indole was suspended in THF (0.5 mL) and allowed to stir for 1 h at room temperature. DBU (40 μL of a 1 M solution in THF, 0.040 mmol, 0.20 equiv) and the appropriate imino ester (0.50 mL of a 0.48M solution in THF, 0.24 mmol, 1.2 equiv) were then added to the vial containing the mixture of Lewis acid and dipolarophile. The reaction mixture was allowed to stir overnight at room temperature and was monitored by TLC. Once the reaction was judged to be complete, the reaction mixture was filtered through a pad of silica (eluting with EtOAc). The crude reaction mixture was then concentrated under reduced pressure. $CDCl_3$ (2 ml) was added to dissolve the crude reaction mixture, and the diastereomeric ratio was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard. The crude reaction mixture was purified by flash

column silica gel chromatography (hexanes:EtOAc) to yield racemic pyrroloindolines *exo′*-**3a-m**.

General Procedure for Catalytic, Enantioselective Synthesis of Pyrroloindolines *exo′*-3a-m

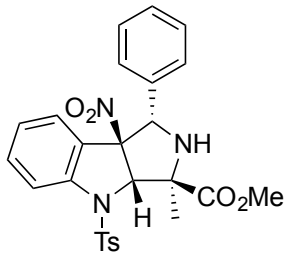


1a: R^1 = H
1b: R^1 = Br

rac-**2a**: R^2 = H, R^3 = Me
rac-**2b**: R^2 = 4-CF_3, R^3 = Me
rac-**2c**: R^2 = 4-Cl, R^3 = Me
rac-**2d**: R^2 = 4-Br, R^3 = Me
rac-**2e**: R^2 = 4-Me, R^3 = Me
rac-**2f**: R^2 = 4-MeO, R^3 = Me
rac-**2g**: R^2 = 3-MeO, R^3 = Me
rac-**2h**: R^2 = 3-Br, R^3 = Me
rac-**2i**: R^2 = 2-OMe, R^3 = Me
rac-**2j**: R^2 = 2-F, R^3 = Me
rac-**2k**: R^2 = 2-Cl, R^3 = Me
rac-**2l**: R^2 = H, R^3 = *i*-Pr

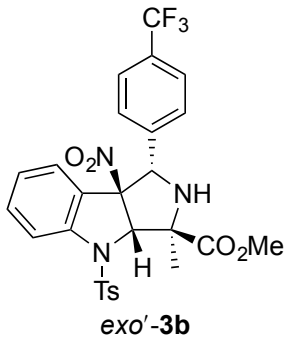
exo′-**3a**: R^1 = H, R^2 = H, R^3 = Me
exo′-**3b**: R^1 = H, R^2 = 4-CF_3, R^3 = Me
exo′-**3c**: R^1 = H, R^2 = 4-Cl, R^3 = Me
exo′-**3d**: R^1 = H, R^2 = 4-Br, R^3 = Me
exo′-**3e**: R^1 = H, R^2 = 4-Me, R^3 = Me
exo′-**3f**: R^1 = H, R^2 = 4-MeO, R^3 = Me
exo′-**3g**: R^1 = H, R^2 = 3-MeO, R^3 = Me
exo′-**3h**: R^1 = H, R^2 = 3-Br, R^3 = Me
exo′-**3i**: R^1 = H, R^2 = 2-OMe, R^3 = Me
exo′-**3j**: R^1 = H, R^2 = 2-F, R^3 = Me
exo′-**3k**: R^1 = H, R^2 = 2-Cl, R^3 = Me
exo′-**3l**: R^1 = H, R^2 = H, R^3 = *i*-Pr
exo′-**3m**: R^1 = Br, R^2 = H, R^3 = Me

In a nitrogen-filled dry-box, $Cu(OTf)_2$ (7.2 mg, 0.020 mmol, 0.10 equiv), *R*-difluorphos (15.3 mg, 0.0200 mmol, 0.100 equiv), and the appropriate indole **1a** or **1b** (0.200 mmol, 1.00 equiv) were added to a 1-dram vial. In a second 1-dram vial, a 0.48 M solution of the appropriate imino ester *rac*-**2a**-**2l** in THF was prepared. Both vials were sealed with a PTFE/silicone-lined septum cap and removed from the dry-box. The mixture of $Cu(OTf)_2$, *R*-difluorphos, and the indole was suspended in THF (0.5 mL) and allowed to stir for 1 h at room temperature. DBU (40 μL of a 1 M solution in THF, 0.040 mmol, 0.20 equiv) and the appropriate imino ester (0.50 mL of a 0.48M solution in THF, 0.24 mmol, 1.2 equiv) were then added to the vial containing the mixture of Lewis acid and dipolarophile. The reaction mixture was allowed to stir overnight at room temperature and was monitored by TLC. Once the reaction was judged to be complete, the reaction mixture was filtered through a pad of silica (eluting with EtOAc). The crude reaction mixture was then concentrated under reduced pressure. $CDCl_3$ (2 ml) was added to dissolve the crude reaction mixture, and the diastereomeric ratio was determined by ^{1}H NMR spectroscopy using dibromomethane as the internal standard. The crude reaction mixture was purified by flash column silica gel chromatography (hexanes:EtOAc) to yield pyrroloindolines *exo′*-**3a**-**m**.



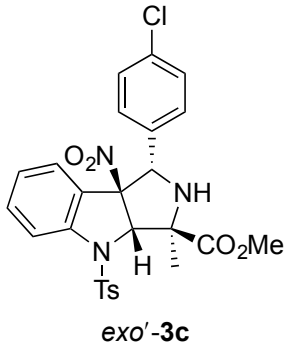
exo′-**3a**

Methyl (1*S*,3*R*,3a*S*,8b*S*)-3-methyl-8b-nitro-1-phenyl-4-tosyl 1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3a): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2a** (45.9 mg, 0.240 mmol) to yield a 93:3:4 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield *exo′*-**3a** (76.0 mg, 0.150 mmol, 75%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.9 min (major); t_R 11.5 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 89% ee. $[\alpha]_D^{24}$ = -55.8° (c 0.50, $CHCl_3$).**^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.73 (s, 3H), 2.31 (s, 3H), 2.45-2.91 (br s, 1H), 3.96 (s, 3H), 4.76 (s, 1H), 5.82 (dd, *J* = 7.8, 0.8 Hz, 1H), 5.88 (s, 1H), 6.72 (ddd, *J* = 8.4, 7.8, 0.8 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.22 (appt, *J* = 7.6 Hz, 2H), 7.29-7.38 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H) , 7.77 (d, *J* = 8.4 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 21.8, 22.2, 53.6, 69.0, 69.1, 74.5, 101.5, 117.0, 124.1, 124.4, 127.7, 128.2, 128.7, 129.0, 129.3, 129.88, 131.6, 132.8, 135.2, 144.7, 145.1, 175.8. **HRMS** (ESI) calcd. for $C_{26}H_{26}N_3O_6S$+ [M+H]+ 508.1537, found 508.1538.



exo′-**3b**

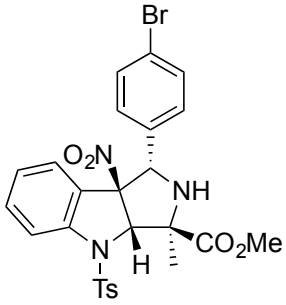
Methyl (1*S*,3*R*,3a*S*,8b*S*)-3-methyl-8b-nitro-4-tosyl-1-(4-(trifluoromethyl)phenyl)-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3b): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2b** (62.2 mg, 0.240 mmol) to yield a >98:1:1 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3b** (96.0 mg, 0.167 mmol, 83%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.3 min (major); t_R 34.1 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 81% ee. $[\alpha]_D^{25}$ = -69.3° (c 0.55, $CHCl_3$).**^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.75 (s, 1H), 2.31 (s, 3H), 2.48-2.94 (br s, 1H), 3.96 (s, 3H), 4.81 (s, 1H), 5.82 (d, *J* = 8.0 Hz, 1H), 5.89 (s, 1H), 6.73 (dd, 8.2, 7.6 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 6.6 Hz, 2H), 7.36 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.43-7.54 (m, 4H), 7.79 (d, *J* = 8.2 Hz, 1H). **^{13}C NMR** ^{13}C NMR ($CDCl_3$, 151 MHz) δ 21.7, 22.0, 53.6, 68.2, 68.9, 74.2, 101.2, 117.0, 124.06 (q, *J* = 272.3 Hz), 124.07, 124.1, 124.9 (q, *J* = 3.7 Hz), 127.8, 128.1, 129.4, 129.8, 131.4 (q, *J* = 32.5 Hz), 131.9, 132.6, 139.5, 144.7, 145.2, 175.5. **^{19}F NMR** ($CDCl_3$, 565 MHz) δ -63.27. **HRMS** (ESI) calcd. for $C_{27}H_{25}F_3N_3O_6S$+ [M+H]+ 576.1411, found 576.1415.



exo′-**3c**

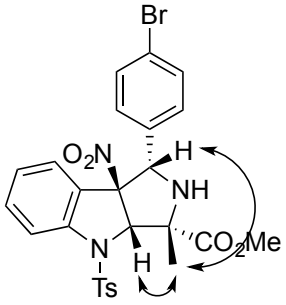
Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(4-chlorophenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3c): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2c** (54.2 mg, 0.240 mmol) to yield a 78:5:17 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3c** (76.0 mg, 0.140 mmol, 70%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC

analysis (254 nm, 25 °C) t_R 7.1 min (major); t_R 25.8 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 88% ee. $[\alpha]_D^{23}$ = -39.5° (c 0.51, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 2.30 (s, 3H), 2.62-2.73 (br s, 1H), 3.95 (s, 3H), 4.71 (d, *J* = 3.5 Hz, 1H) 5.87 (d, *J* = 1.2 Hz, 1H), 5.91 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.77 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H) 7.20 (d, *J* = 8.0 Hz, 2H), 7.36 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 21.8, 22.1, 53.6, 68.2, 68.9, 74.2, 101.2, 117.0, 124.2, 127.8, 128.3, 128.5, 129.9 (2C), 130.2, 131.8, 132.7, 133.8, 135.1, 144.7, 145.2, 175.7. **HRMS** (ESI) calcd. for $C_{26}H_{25}ClN_3O_6S$+ [M+H]+ 542.1147, found 542.1152.



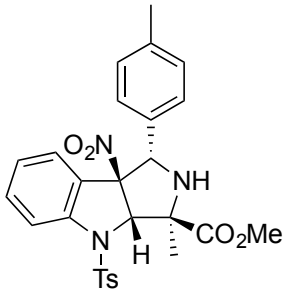
exo′-**3d**

Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(4-bromophenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3d): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2d** (64.8 mg, 0.240 mmol) to yield a 95:4:1 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3d** (92.0 mg, 0.157 mmol, 78%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.7 min (major); t_R 31.4 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 90% ee. $[\alpha]_D^{23}$ = -252.1° (c 0.48, $CHCl_3$). **^{1}H NMR** ($(CD_3)_2CO$, 400 MHz) δ 1.70 (s, 3H), 2.32 (s, 3H), 3.47-3.57 (br s, 1H), 3.89 (s, 3H), 4.86 (d, *J* = 3.6 Hz, 1H), 5.89-6.01 (m, 2H), 6.83 (ddd, *J* = 8.2, 7.4, 0.7 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.40-7.49 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H) **^{13}C NMR** ($(CD_3)_2CO$, 101 MHz) δ 21.4, 21.9, 53.4, 68.6, 69.2, 75.2, 102.0, 117.2, 123.2, 124.7, 125.4, 128.6, 128.8, 130.6, 131.6, 131.7, 132.6, 133.8, 136.1, 145.5, 146.0, 175.5. **HRMS** (ESI) calcd. for $C_{26}H_{25}BrN_3O_6S$+ [M+H]+ 586.0642, found 586.0643.



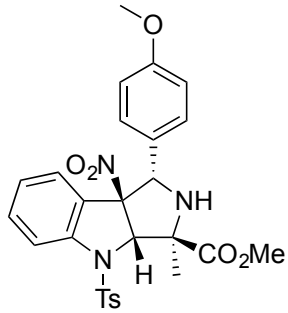
exo-**3d**

Methyl (1*R*,3*R*,3a*S*,8b*S*)-1-(4-bromophenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo*-3d): An analytical sample of *exo*-**3d** was isolated from the reaction of **1a** and **2d**. The relative stereochemistry was assigned by NOE analysis. **^{1}H NMR** ($(CD_3)_2CO$, 400 MHz) δ 1.87 (s, 3H), 2.29 (s, 3H), 3.32 (d, *J* = 12.0 Hz, 1H), 3.87 (s, 3H), 5.23 (d, *J* = 12.0 Hz, 1H), 5.39 (s, 1H), 5.96 (dd, *J* = 7.9, 0.6 Hz, 1H), 6.93 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H). **HRMS** (ESI) calcd. for $C_{26}H_{25}BrN_3O_6S$+ [M+H]+ 586.0642, found 586.0655.



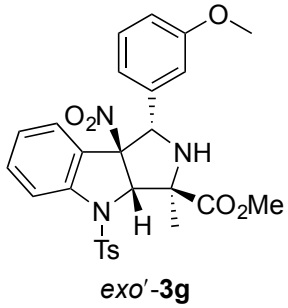
exo′-**3e**

Methyl (1*S*,3*R*,3a*S*,8b*S*)-3-methyl-8b-nitro-1-(p-tolyl)-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3e): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2e** (49.3 mg, 0.240 mmol) to yield a 90:7:3 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3e** (79.0 mg, 0.151 mmol, 76%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.6 min (major); t_R 22.4 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 91% ee. $[\alpha]_D^{25}$ = -312.5° (c 0.51, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 2.30 (s, 3H), 2.33 (s, 3H), 2.55-2.78 (br s, 1H), 3.95 (s, 3H), 4.72 (s, 1H), 5.83-5.94 (m, 2H), 6.75 (dd, *J* = 8.2, 7.8 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.34 (appt, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 21.4, 21.8, 22.2, 53.6, 68.9, 69.0, 74.4, 101.4, 116.9, 124.1, 124.4, 127.7, 128.5, 128.8, 129.1, 129.9, 131.6, 132.0, 132.8, 139.1, 144.6, 145.1, 175.9. **HRMS** (ESI) calcd. for $C_{27}H_{28}N_3O_6S$+ [M+H]+ 522.1693, found 522.1695.



exo′-**3f**

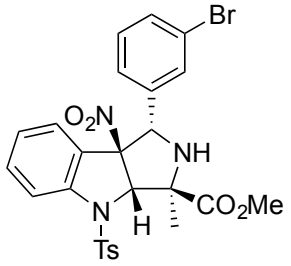
Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(4-methoxyphenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3f): Prepared according to the general procedure from **1a** (64.4 mg, 0.204 mmol) and **2f** (53.1 mg, 0.240 mmol) to yield a 95:4:1 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 70:30 hexanes:EtOAc) to yield *exo′*-**3f** (78.0 mg, 0.145 mmol, 71%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.2 min (major); t_R 37.6 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 96% ee. $[\alpha]_D^{25}$ = -141.2° (c 0.51, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 2.30 (s, 3H), 2.59-2.73 (bs, 1H), 3.79 (s, 3H), 3.95 (s, 3H), 4.69 (s, 1H), 5.88 (s, 1H), 5.93 (d, *J* = 7.8 Hz, 1H), 6.69-6.82 (m, 3H), 6.91 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 21.8, 22.2, 53.6, 55.5, 68.79, 68.84, 74.3, 101.4, 113.4, 116.9, 124.1, 124.4, 127.1, 127.7, 129.1, 129.86, 129.90, 131.6, 132.7, 144.6, 145.1, 160.3, 175.9 **HRMS** (ESI) calcd. for $C_{27}H_{28}N_3O_7S$+ [M+H]+ 538.1642, found 538.1642.



exo′-**3g**

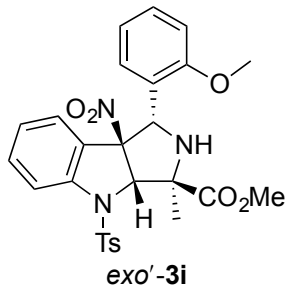
Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(3-methoxyphenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3g): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2g** (53.1 mg, 0.240 mmol) to yield a 89:8:3 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 70:30 hexanes:EtOAc) to yield *exo′*-**3g** (77.0 mg, 0.143 mmol, 72%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.7 min (major); t_R 12.7 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0

mL/min] to be 89% ee. $[\alpha]_D^{25}$ = -69.1° (c 0.55, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.73 (s, 3H), 2.30 (s, 3H), 2.41-2.93 (bs, 1H), 3.63 (s, 3H), 3.96 (s, 3H), 4.76 (s, 1H), 5.86 (s, 1H), 5.91 (d, *J* = 7.6 Hz, 1H), 6.51 (s, 1H), 6.62 (d, *J* = 6.4 Hz, 1H), 6.75 (dd, *J* = 8.2, 7.8 Hz, 1H), 6.86 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.14 (dd, *J* = 8.2, 6.4 Hz, 1H), 7.34 (ddd, *J* = 7.8, 7.6, 0.8 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 21.7, 22.1, 53.5, 55.4, 68.92, 68.99, 74.5, 101.4, 113.5, 115.5, 116.9, 120.96, 120.99, 124.0, 124.3, 127.7, 129.0, 129.2, 129.8, 131.6, 132.7, 144.6, 145.1, 159.4, 175.8. **HRMS** (ESI) calcd. for $C_{27}H_{28}N_3O_7S$+ [M+H]+ 538.1642, found 538.1646.



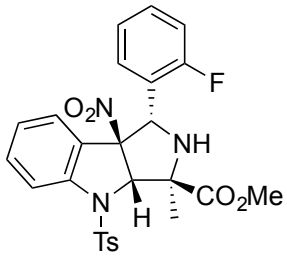
exo′-**3h**

Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(3-bromophenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3h): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2h** (64.8 mg, 0.240 mmol) to yield a 69:8:23 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3h** (47.0 mg, 0.080 mmol, 40%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.6 min (major); t_R 12.3 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 80% ee. $[\alpha]_D^{24}$ = -846.2° (c 0.56, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.73 (s, 3H), 2.31 (s, 3H), 2.64-2.74 (br s, 1H), 3.95 (s, 3H), 4.72(s, 1H), 5.82-5.92 (m, 2H), 6.79 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.98 (d, *J* = 6.6 Hz, 1H), 7.06-7.17 (m, 4H), 7.37 (dd, *J* = 8.0, 7.6 Hz, 1H), 7.42-7.50 (m, 3H), 7.79 (d, *J* = 8.0 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 21.8, 22.1, 53.7, 68.2, 69.0, 74.2, 101.3, 117.1, 122.3, 124.10, 124.11, 127.6, 127.8, 128.5, 129.7, 129.9, 131.85, 131.91, 132.4, 132.6, 137.7, 144.7, 145.2, 175.6. **HRMS** (ESI) calcd. for $C_{26}H_{25}BrN_3O_6S$+ [M+H]+ 586.0642, found 586.0646.



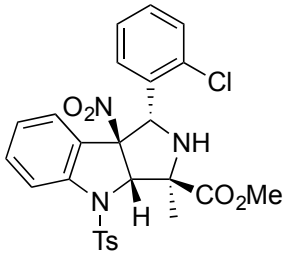
exo′-**3i**

Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(2-methoxyphenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate(*exo′*-3i): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2i** (53.1 mg, 0.240 mmol) to yield a 74:7:19 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3i** (42.0 mg, 0.078 mmol, 39%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 7.0 min (major); t_R 16.5 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 82% ee. $[\alpha]_D^{25}$ = +42.4° (c 0.24, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.71 (s, 3H), 2.30 (s, 3H), 2.55-2.81 (br s, 1H), 3.60 (s, 3H), 4.00 (s, 3H), 5.24 (s, 1H), 5.76 (s, 1H), 5.93 (d, *J* = 8.0 Hz, 1H), 6.72-6.78 (m, 2H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.20-7.43 (m, 4H), 7.76 (d, *J* = 8.0 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 21.8, 22.4, 53.6, 54.9, 64.3, 69.1, 76.1, 100.4, 109.8, 117.3, 120.4, 123.9, 124.2, 124.4, 127.4, 128.6, 129.5, 129.8, 129.9, 131.2, 132.5, 144.6, 145.1, 157.5, 176.1. **HRMS** (ESI) calcd. for $C_{27}H_{28}N_3O_7S$+ [M+H]+ 538.1642, found 538.1646.



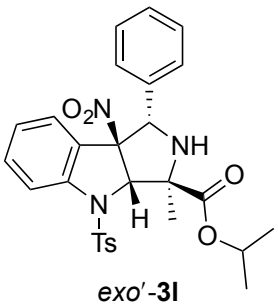
exo′-**3j**

Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(2-fluorophenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3j): Prepared according to the general procedure from **1a** (64.8 mg, 0.205 mmol) and **2j** (50.2 mg, 0.240 mmol) to yield a 67:5:27 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3j** (55.0 mg, 0.104 mmol, 51%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.9 min (major); t_R 15.3 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 87% ee. $[\alpha]_D^{25}$ = -24.3° (c 0.41, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.71 (s, 3H), 2.29 (s, 3H), 2.43-2.94 (br s, 1H), 3.98 (s, 3H) 5.14 (s, 1H), 5.85 (s, 1H), 6.01 (d, *J* = 7.8 Hz, 1H), 6.78 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.88-6.98 (m, 2H), 7.02 (appt, *J* = 9.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.27-7.43 (m, 4H), 7.78 (d, *J* = 8.0 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 21.7, 22.3, 53.7, 62.9, 69.1, 74.9, 100.6, 115.3 (d, *J* = 21.4 Hz), 117.2, 122.5 (d, *J* = 12.2 Hz), 123.8 (d, *J* = 3.3 Hz), 123.9, 124.3, 127.5, 129.2, 129.88, 129.92 (d, *J* = 3.5 Hz), 130.6 (d, *J* = 8.5 Hz) 131.6, 132.4, 144.7, 145.2, 161.1 (d, *J* = 248.1 Hz), 175.7. **^{19}F NMR** ($CDCl_3$, 565 MHz) δ -117.22. **HRMS** (ESI) calcd. for $C_{26}H_{25}FN_3O_6S$+ [M+H]+ 526.1443, found 526.1455.



exo′-**3k**

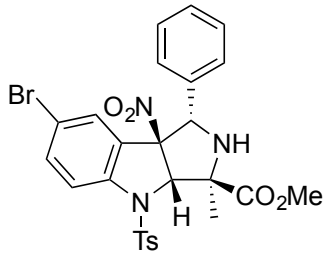
Methyl (1*S*,3*R*,3a*S*,8b*S*)-1-(2-chlorophenyl)-3-methyl-8b-nitro-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3k): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2k** (54.2 mg, 0.240 mmol) to yield a 88:8:4 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3k** (92.0 mg, 0.170 mmol, 85%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 5.4 min (major); t_R 7.5 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 79% ee. $[\alpha]_D^{25}$ = -35.3° (c 0.62, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.72 (s, 3H), 2.30 (s, 3H), 2.59-2.82 (br s, 1H), 4.02 (s, 3H), 5.35 (s, 1H), 5.78 (s, 1H), 6.03 (d, *J* = 7.8 Hz, 1H), 6.78 (dd, *J* = 8.0, 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.00 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.22 (ddd, *J* = 8.0, 7.6, 1.4 Hz, 1H), 7.32-7.41 (m, 4H), 7.79 (d, *J* = 8.0 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 21.7, 22.4, 53.7, 65.5, 68.9, 75.4, 100.3, 117.3, 123.8, 124.1, 126.3, 127.5, 129.6, 129.9, 130.0, 130.1, 131.0, 131.6, 132.2, 133.3, 134.5, 144.7, 145.3, 175.9. **HRMS** (ESI) calcd. for $C_{26}H_{25}ClN_3O_6S$+ [M+H]+ 542.1147, found 542.1152.



exo′-**3l**

Isopropyl (1*S*,3*R*,3a*S*,8b*S*)-3-methyl-8b-nitro-1-phenyl-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3l): Prepared according to the general procedure from **1a** (63.2 mg, 0.200 mmol) and **2l** (52.6 mg, 0.240 mmol) to yield a 93:7 mixture of *exo′*:*exo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3l** (76.0 mg, 0.142 mmol, 71%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 4.6 min (major); t_R 6.7 min (minor) [Chiracel AD-H (0.46 cm x 25

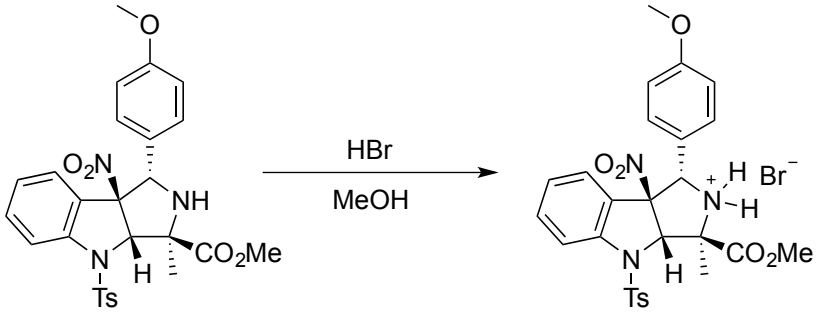
cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 94% ee. $[\alpha]_D^{25}$ = -45.3° (c 0.53, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.41 (d, *J* = 6.0 Hz, 3H), 1.46 (d, *J* = 6.0 Hz, 3H), 1.71 (s, 3H), 2.31 (s, 3H), 2.43-3.12 (br s, 1H), 4.76 (s, 1H), 5.24 (septet, *J* = 6.0 Hz, 1H), 5.74-5.93 (m, 2H), 6.73 (dd, *J* = 8.2, 7.6 Hz, 1H), 7.00 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.22 (appt, *J* = 7.2 Hz, 2H), 7.29-7.38 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 21.7, 21.95, 22.04, 22.1, 68.9, 69.3, 70.3, 74.4, 101.6, 117.1, 124.1, 124.4, 127.7, 128.2, 128.7, 129.0, 129.3, 129.8, 131.6, 132.6, 135.4, 144.8, 145.1, 174.9. **HRMS** (ESI) calcd. for $C_{28}H_{30}N_3O_6S$+ [M+H]+ 536.1850, found 536.1851.



exo′-**3m**

Methyl (1*S*,3*R*,3a*S*,8b*S*)-7-bromo-3-methyl-8b-nitro-1-phenyl-4-tosyl-1,2,3,3a,4,8b-hexahydropyrrolo[3,4-b]indole-3-carboxylate (*exo′*-3m): Prepared according to the general procedure from **1b** (79.0 mg, 0.200 mmol) and **2a** (45.9 mg, 0.240 mmol) to yield a >98:1:1 mixture of *exo′*:*exo*:*endo* diastereomers. The mixture was purified by flash column chromatography (100:0 to 80:20 hexanes:EtOAc) to yield *exo′*-**3m** (93.0 mg, 0.159 mmol, 79%) as a white foam with >95:5 diastereomeric ratio. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 6.1 min (major); t_R 8.4 min (minor) [Chiracel AD-H (0.46 cm x 25 cm)(from Daicel Chemical Ind., Ltd.) hexane/i-PrOH, 80:20, 1.0 mL/min] to be 91% ee. $[\alpha]_D^{25}$ = -312.5° (c 0.51, $CHCl_3$). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 1.71 (s, 3H), 2.33 (s, 3H), 2.69-2.77 (br s, 1H), 3.96 (s, 3H), 4.73 (d, *J* = 3.4 Hz, 1H), 5.80 (d, *J* = 2.0 Hz, 1H), 5.86 (d, *J* = 1.2 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 7.6, 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.42-7.47 (m, 3H), 7.64 (d, *J* = 8.7 Hz, 1H) **^{13}C NMR** ($CDCl_3$, 151 MHz) δ 21.8, 22.1, 53.6, 69.1, 69.3, 74.7, 100.9, 116.9, 118.3, 126.1, 127.6, 128.3, 128.5, 129.7, 130.1, 132.2, 132.4, 134.5, 134.7, 143.7, 145.5, 175.6. **HRMS** (ESI) calcd. for $C_{26}H_{25}BrN_3O_6S$+ [M+H]+ 586.0642, found 586.0641.

Synthesis of 3f·HBr



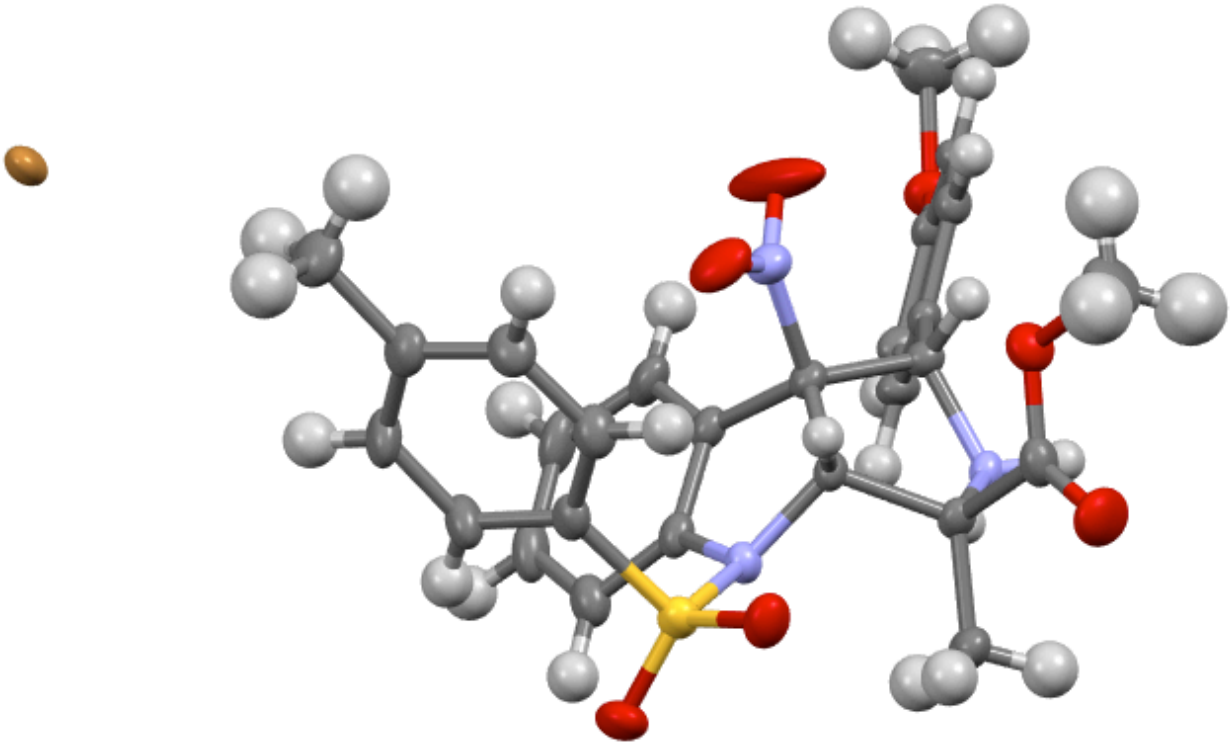
3f **3f**·HBr

Compound **3f** (153.0 mg, 0.284 mmol, 86% ee) was added to a 20 mL scintillation vial and dissolved in 6 mL of methanol. To this solution were added 6 drops of concentrated HBr. The vial was capped and the reaction was stirred overnight at room temperature. The volatiles were evaporated under reduced pressure to yield **3f**·HBr (175.0 mg, 0.283 mmol, >99%). $[\alpha]_D^{25}$ = -30.7° (c 0.52, $CHCl_3$). A single crystal of this compound was grown from hexane:dichloromethane. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.24 (s, 3H), 2.29 (s, 3H), 3.76 (s, 3H), 4.03 (s, 3H), 5.54-5.61 (m, 2H), 5.89 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.88 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.29-7.40 (m, 4H), 7.47 (dd, *J* = 7.6, 7.4 Hz, 1H), 7.83

(d, J = 8.0 Hz, 1H), 7.87-8.17 (br s, 2H). **^{13}C NMR** ($CDCl_3$, 101 MHz) δ 19.2, 21.7, 54.9, 55.4, 68.9, 71.8, 74.2, 77.4, 99.7, 114.0, 118.9, 120.8, 125.3, 127.6, 129.5, 130.0, 131.2, 132.0, 133.5, 144.9, 145.7, 161.0, 169.8. **HRMS** (ESI) calcd. for $C_{27}H_{28}N_3O_7S^+$ [M+] 538.1642, found 538.1644.

Absolute Stereochemistry and Structure of 3f·HBr

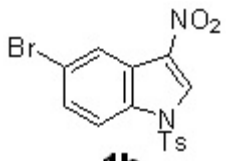
The absolute configuration of *exo′*-**3f**·HBr was determined to be (1*S*,3*R*,3a*S*,8b*S*) by X-ray crystallographic analysis. Supplementary X-ray diffraction data and structure refinement for *exo′*-**3f**·HBr contained in CCDC 1434459. These data can be accessed free of charge from the Cambridge Crystallographic Data Center at https://summary.ccdc.cam.ac.uk/structure-summary-form.



8.535 8.403 8.400 7.886 7.871 7.863 7.849 7.575 7.572 7.560 7.557 7.351 7.337 7.260

2.410

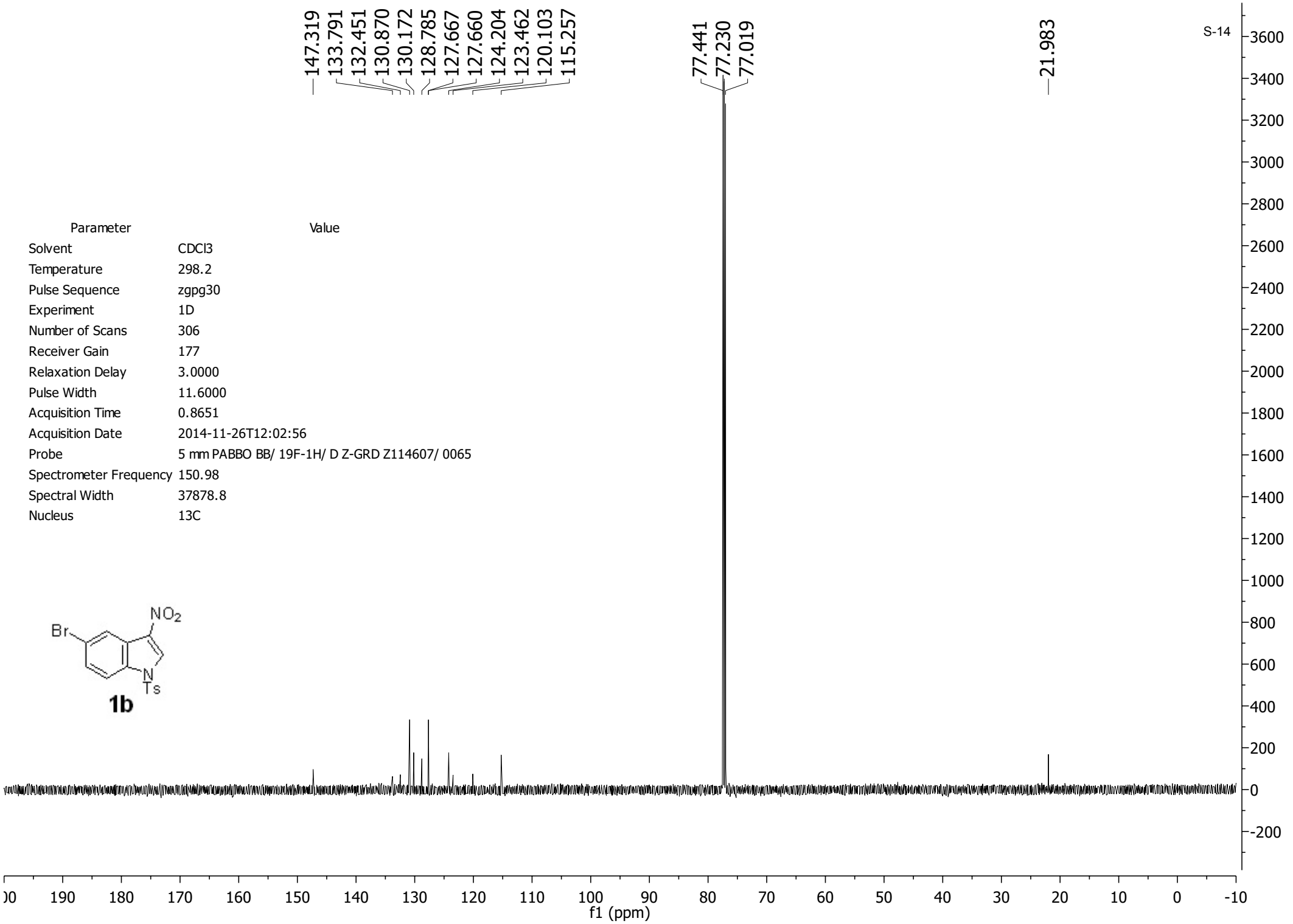
Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2014-11-26T11:59:52
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



1b

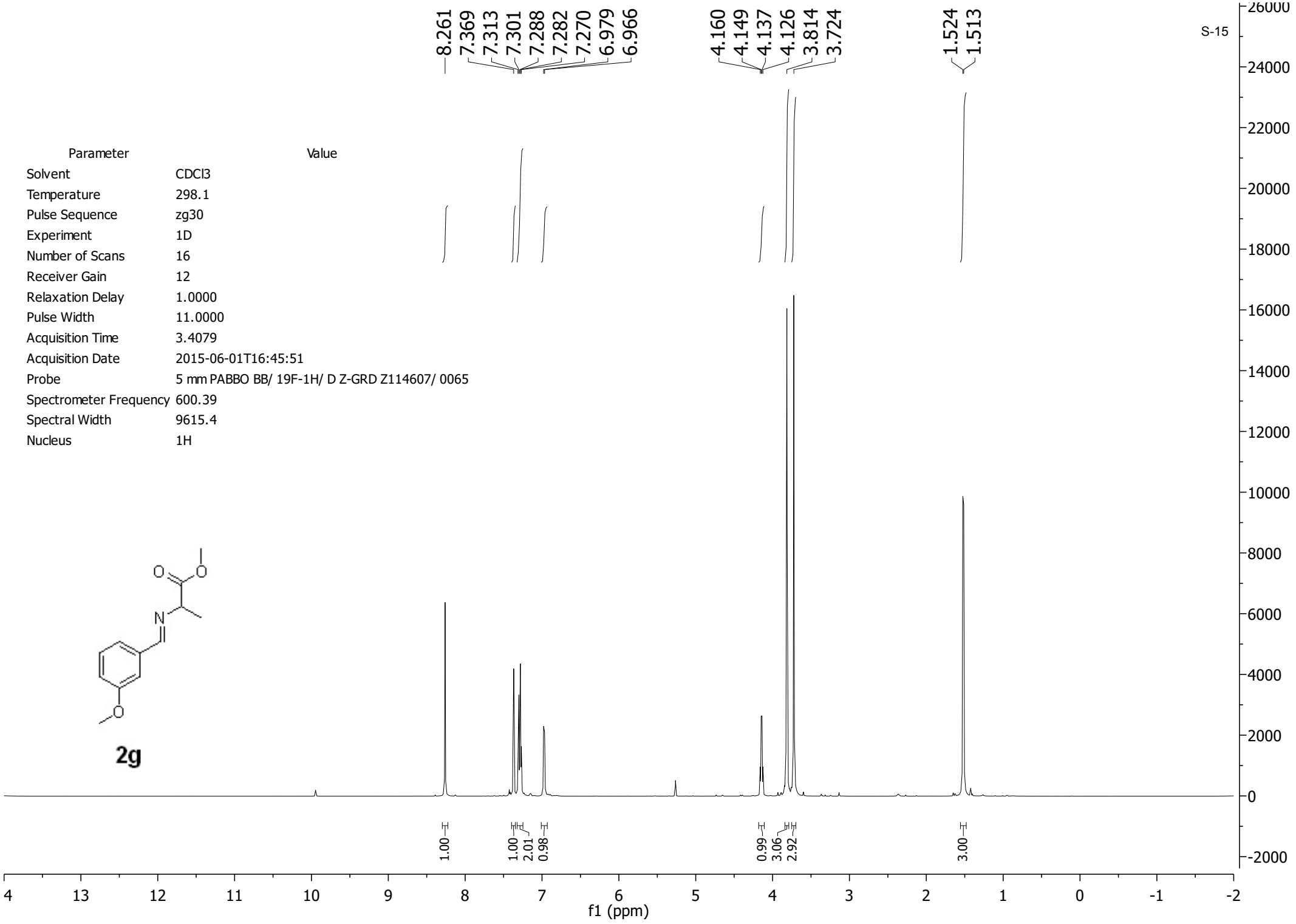
0.94 0.95 3.14 1.07 2.04 3.00

f1 (ppm)



Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	306
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	11.6000
Acquisition Time	0.8651
Acquisition Date	2014-11-26T12:02:56
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C

1b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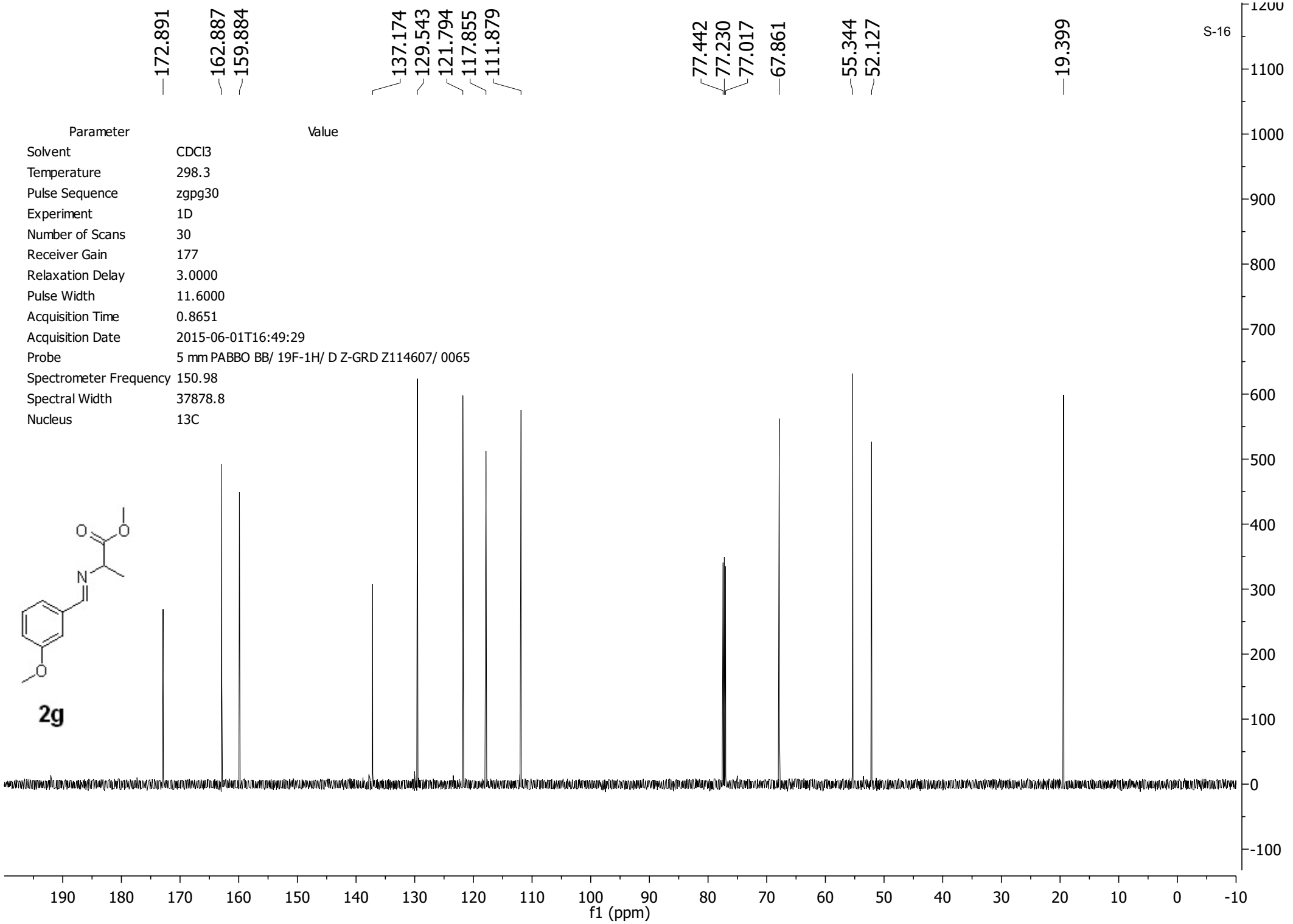
7.313
7.301
7.288
7.282
7.270
6.979
6.966
4.160
4.149
4.137
4.126
3.814
3.724
1.524
1.513
Parameter Value
Solvent CDCl3
Temperature 298.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 12
Relaxation Delay 1.0000
Pulse Width 11.0000
Acquisition Time 3.4079
Acquisition Date 2015-06-01T16:45:51
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
1.00
2.01
0.98
0.99
3.06
2.92
3.00
f1 (ppm)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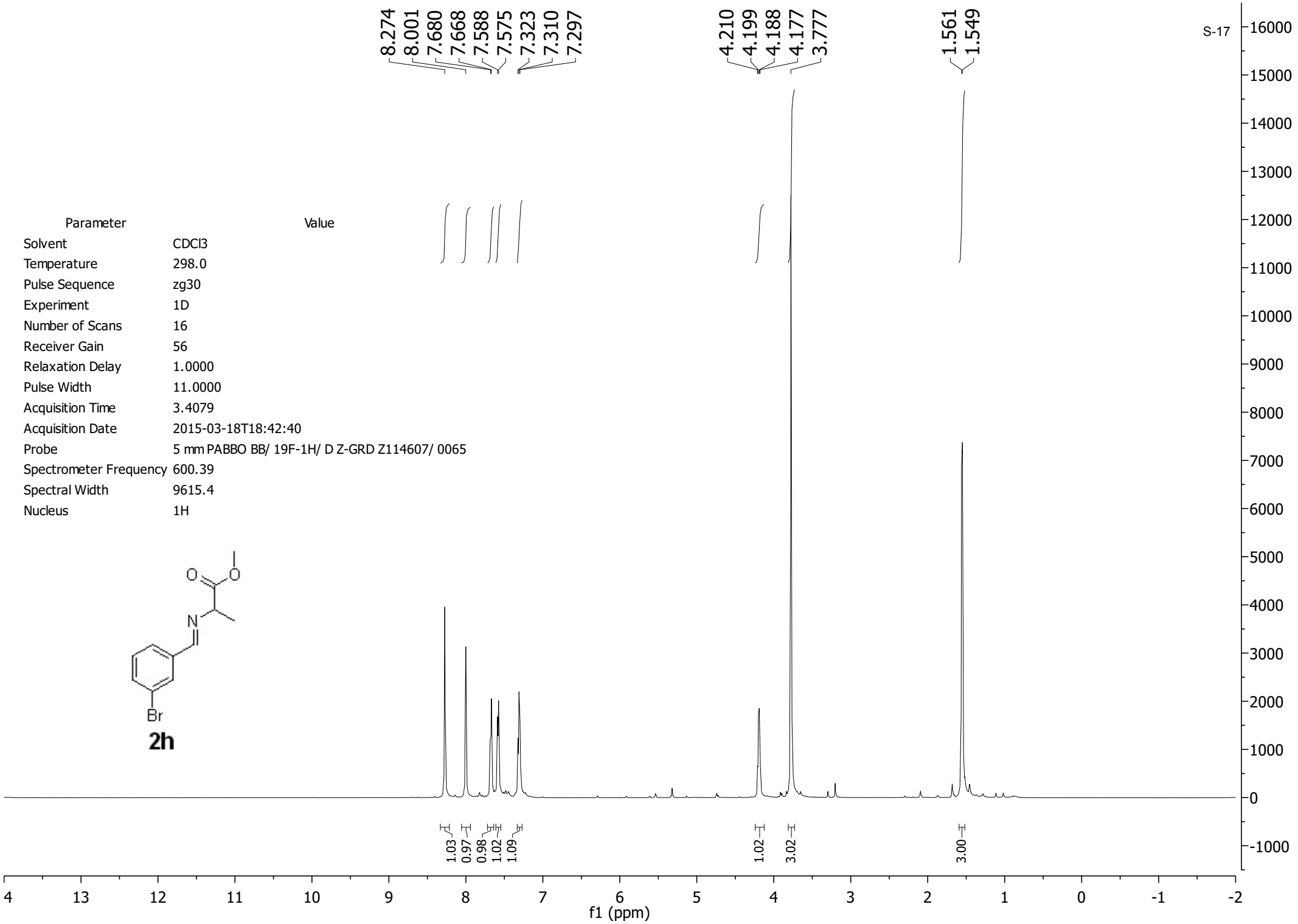
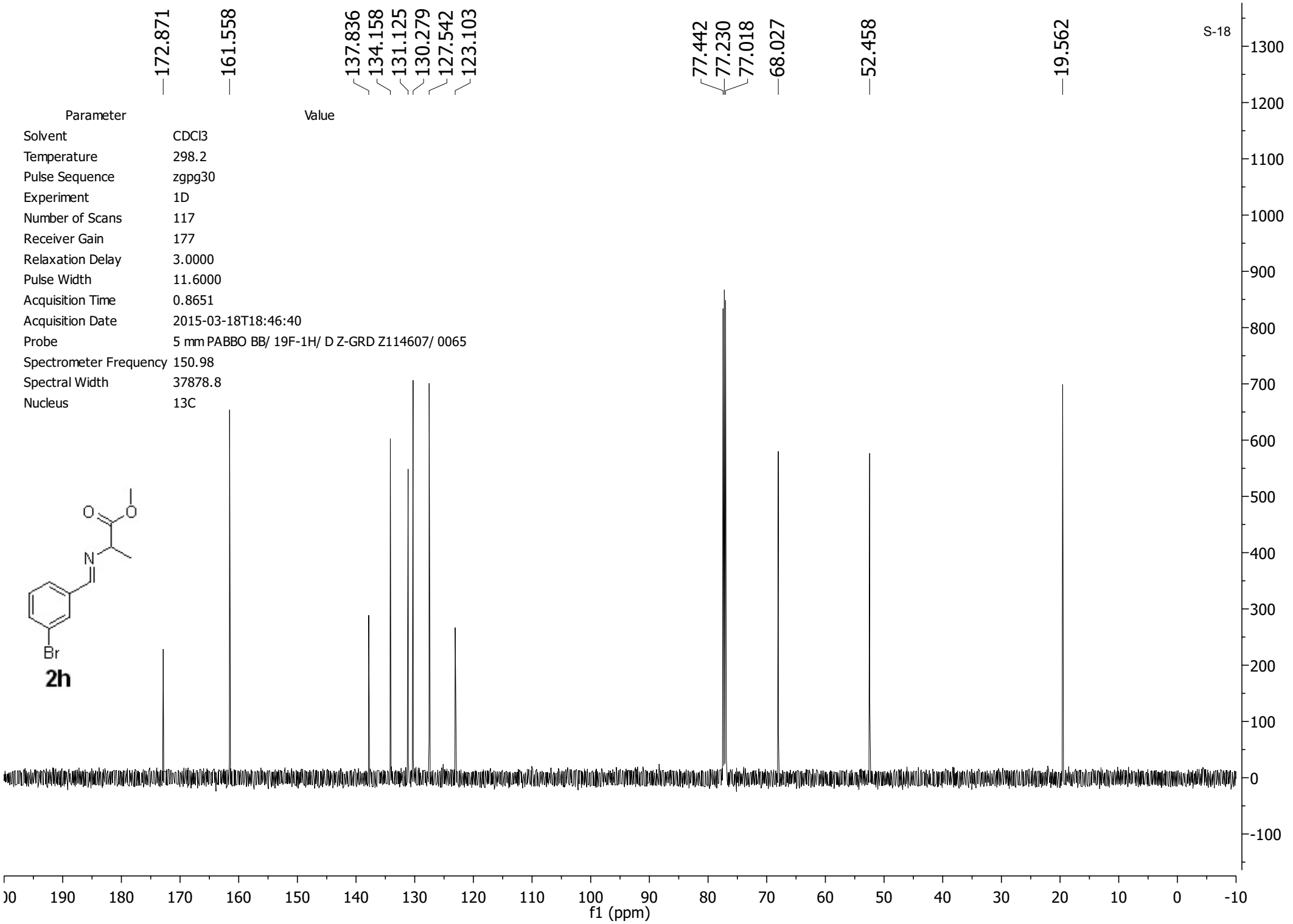
137.174
129.543
121.794
117.855
111.879
77.442
77.230
77.017
67.861
55.344
52.127
19.399
Parameter Value
Solvent CDCl3
Temperature 298.3
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 30
Receiver Gain 177
Relaxation Delay 3.0000
Pulse Width 11.6000
Acquisition Time 0.8651
Acquisition Date 2015-06-01T16:49:29
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency 150.98
Spectral Width 37878.8
Nucleus 13C
2g
f1 (ppm)



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	2015-03-18T18:42:40
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

2h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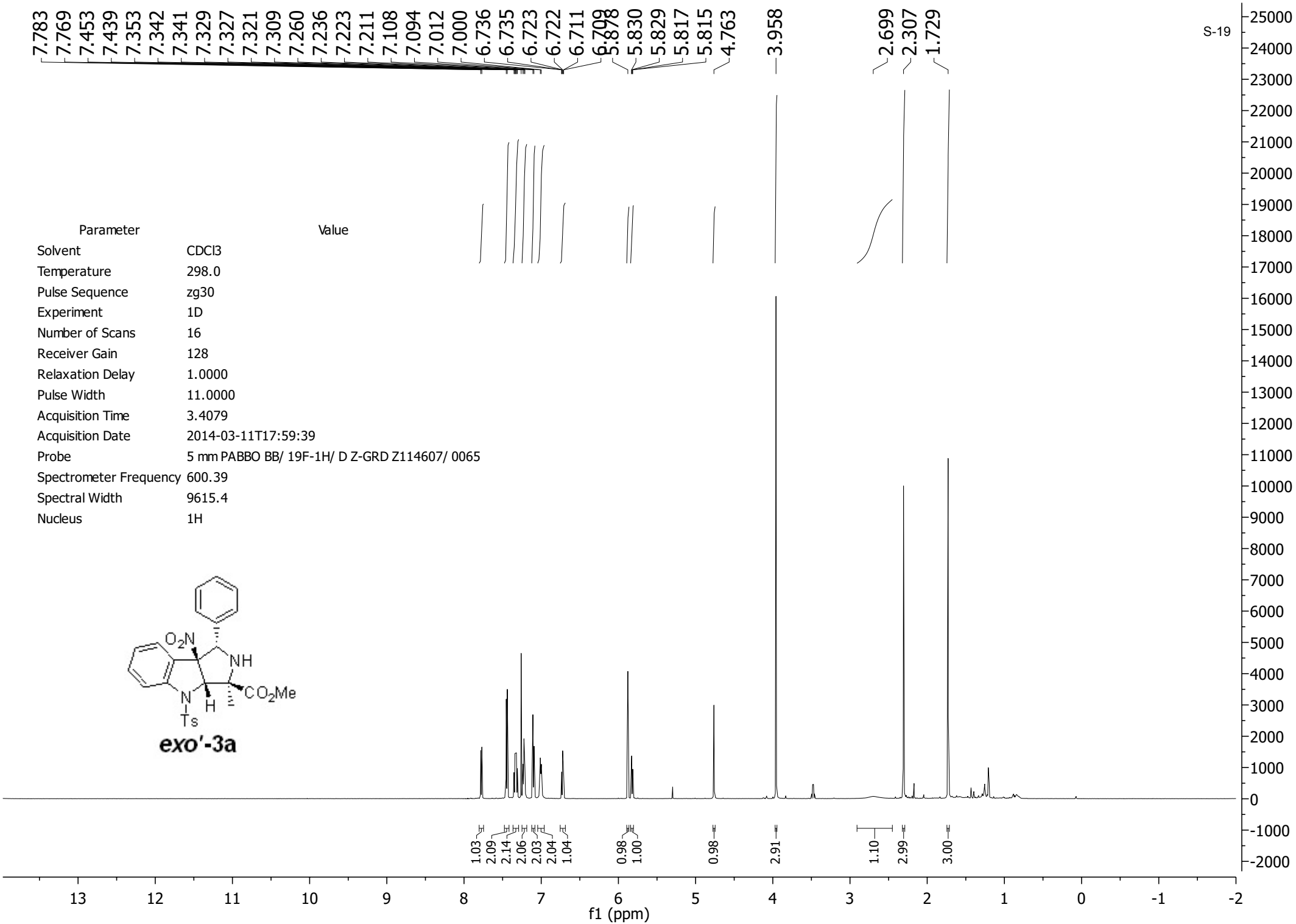
134.158
131.125
130.279
127.542
123.103
77.442
77.230
77.018
68.027
52.458
19.562
Parameter Value
Solvent CDCl3
Temperature 298.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 117
Receiver Gain 177
Relaxation Delay 3.0000
Pulse Width 11.6000
Acquisition Time 0.8651
Acquisition Date 2015-03-18T18:46:40
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency 150.98
Spectral Width 37878.8
Nucleus 13C
O
O
N
Br
2h
f1 (ppm)

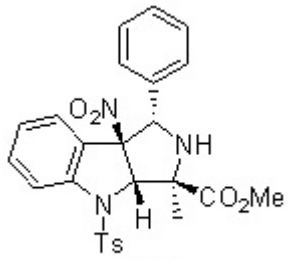


Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	128
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2014-03-11T17:59:39
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

***exo'*-3a**

175.843
145.144
144.692
135.224
132.748
131.625
129.882
129.313
128.967
128.692
128.177
127.725
124.376
124.080
116.957
101.468
77.441
77.230
77.018
74.484
69.097
68.972
53.600
22.215
21.772

Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	290
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	12.0000
Acquisition Time	0.8651
Acquisition Date	2014-03-11T18:03:17
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



***exo'*-3a**

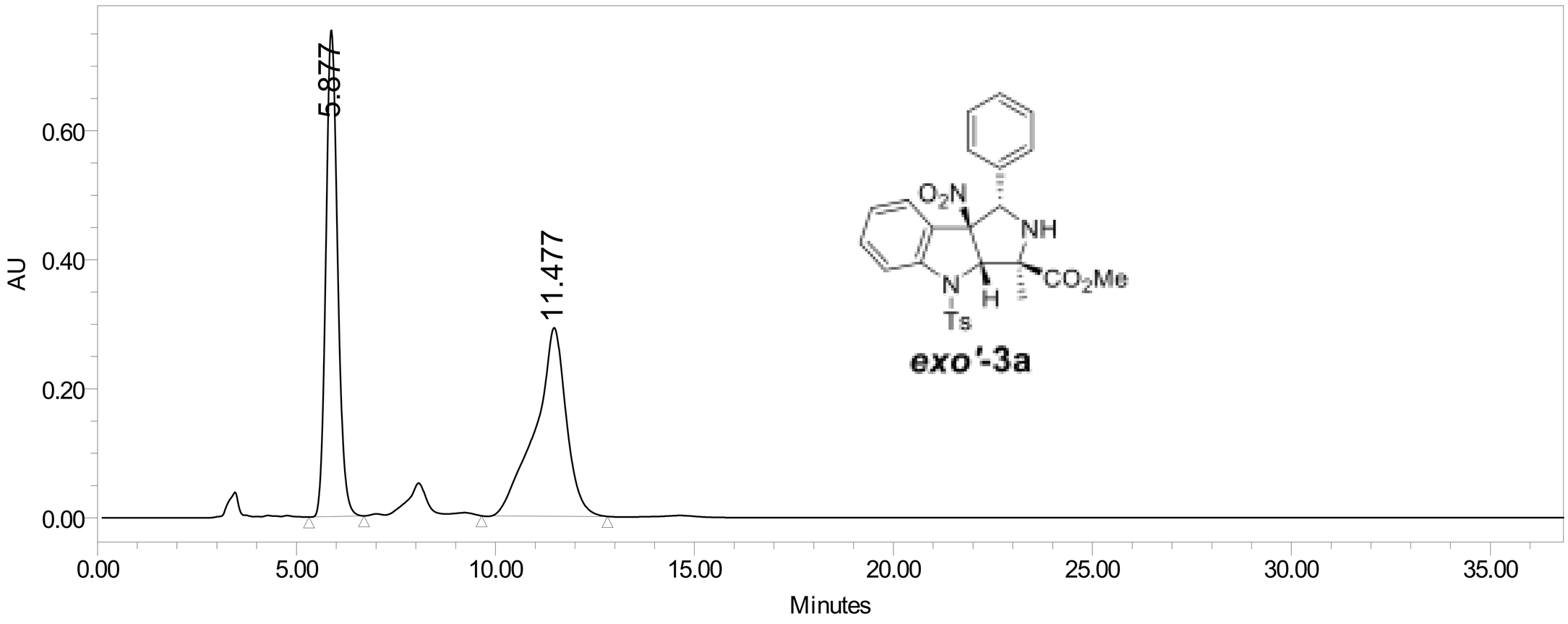
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Songchen Xu racemic
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:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/18/2014 9:13:40 PM CDT		
Date Processed:	10/6/2015 3:11:18 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17259; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

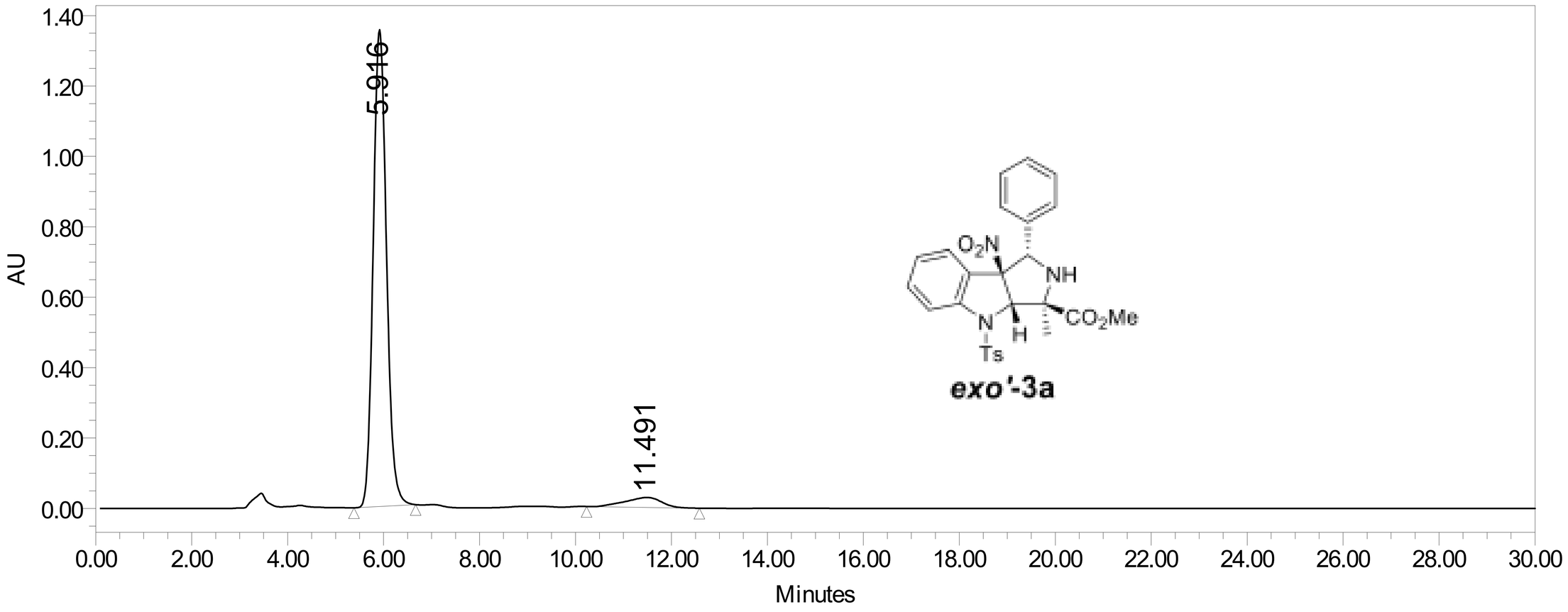
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.877	15533538	49.38	754676
2	W2489 ChA 254nm	11.477	15923396	50.62	292109

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_230_582015
Vial:	73	Acq. Method Set:	1_ADH 80_20 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:	5/8/2015 1:30:47 PM CDT		
Date Processed:	10/6/2015 3:13:28 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17261; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
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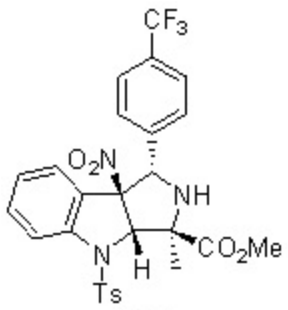
2	W2489 ChA 254nm	11.491	1492663	5.43	28312

7.796 7.782 7.490 7.475 7.461 7.369 7.356 7.343 7.260 7.179 7.169 7.117 7.104 6.741 6.728 6.715 5.894 5.825 5.812 4.805 3.956 2.725 2.305 1.748

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	50
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2015-10-13T15:27:42
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



***exo'*-3b**

1.00 4.01 1.05 1.93 2.05 1.01 0.99 1.00 1.00 2.95 0.99 3.00 3.00

f1 (ppm)

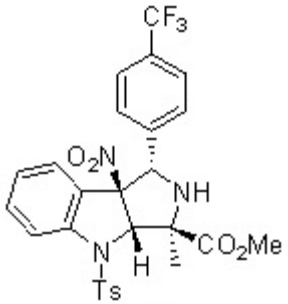
175.522
145.200
144.692
139.529
132.610
131.880
131.686
131.471
131.256
131.041
129.842
129.400
128.129
127.759
126.760
124.957
124.933
124.908
124.108
124.067
123.154
121.351
117.002
101.230

77.442
77.230
77.018
74.177
68.933
68.186

53.581

22.025
21.672

Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	570
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	11.6000
Acquisition Time	0.8651
Acquisition Date	2015-06-18T11:17:03
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



***exo'*-3b**

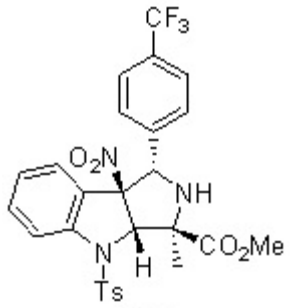
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

-63.274

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgfhigqn
Experiment	1D
Number of Scans	1
Receiver Gain	177
Relaxation Delay	5.0000
Pulse Width	14.0000
Acquisition Time	0.3408
Acquisition Date	2015-06-18T11:59:00
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	564.89
Spectral Width	96153.8
Nucleus	19F



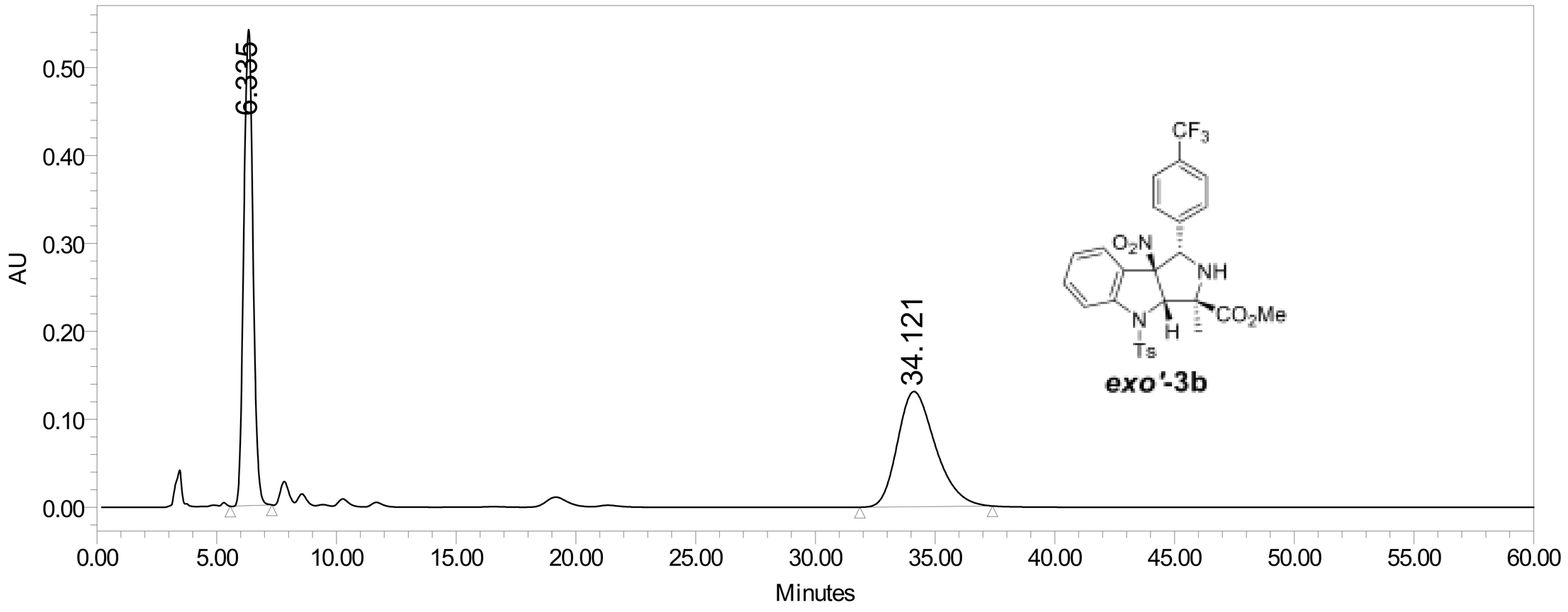
***exo'*-3b**

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG3_126_1_ADH20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_126_852014
Vial:	35	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:	8/5/2014 2:51:02 PM CDT		
Date Processed:	10/6/2015 2:14:52 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17221; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

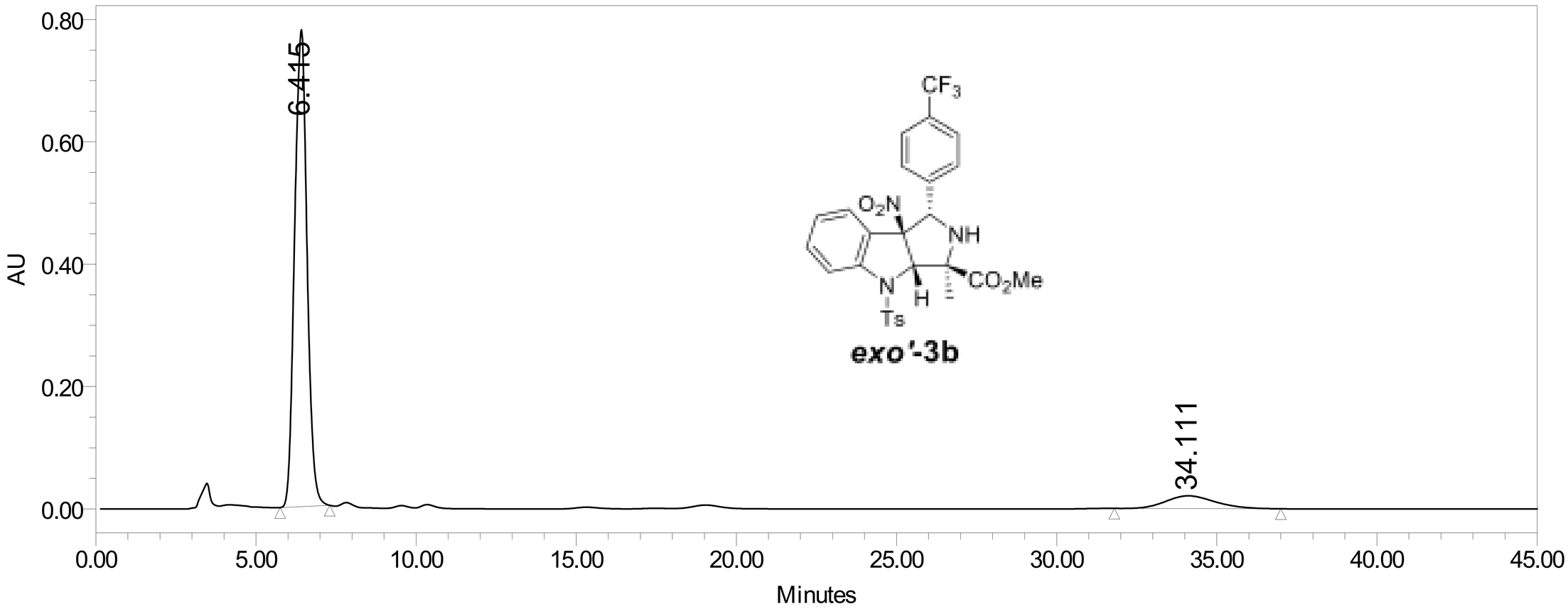
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.335	14536758	50.20	541297
2	W2489 ChA 254nm	34.121	14419045	49.80	130974

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG3_212_1_ADH20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_212_3192015
Vial:	37	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	45.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/19/2015 5:33:26 PM CDT		
Date Processed:	10/6/2015 2:27:07 PM CDT		



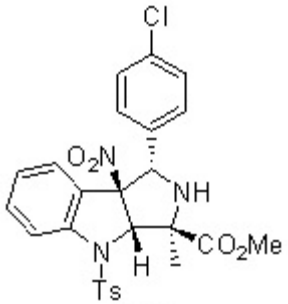
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17223; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.415	21025201	90.38	779475
2	W2489 ChA 254nm	34.111	2236930	9.62	20834

7.789 7.769 7.469 7.448 7.378 7.375 7.357 7.339 7.336 7.260 7.211 7.190 7.115 7.095 6.974 6.955 6.791 6.789 6.772 6.771 6.753 6.751 5.920 5.918 5.900 5.899 5.878 5.875 4.716 4.708 3.950 2.683 2.303 1.724

Parameter	Value
Solvent	cdcl3
Temperature	25.0
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	2015-10-23T13:47:46
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



***exo'*-3c**

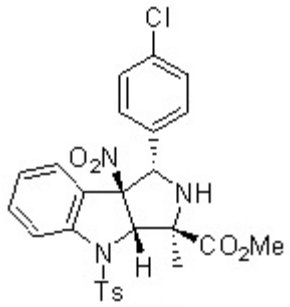
CH_2Cl_2

1.02 2.02 1.07 1.96 2.01 1.96 1.11 1.00 0.97 1.04 1.06 2.93 3.00

f1 (ppm)

175.674
145.184
144.666
135.122
133.842
132.646
131.797
130.229
129.872
128.539
128.319
127.755
124.169
116.972
101.206
77.548
77.230
76.912
74.169
68.871
68.240
53.634
22.126
21.761

Parameter	Value
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	816
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2014-11-01T15:39:43
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



***exo'*-3c**

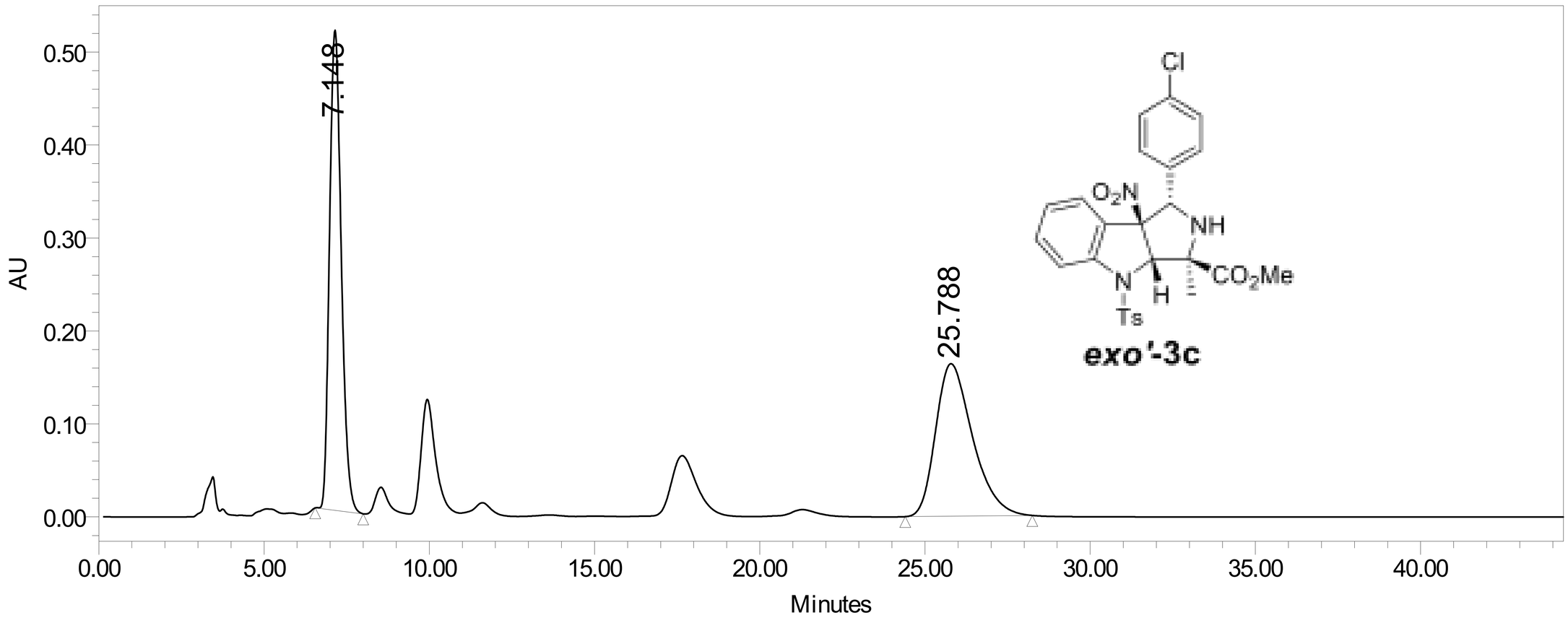
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_127_882014
Vial:	60	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:	8/8/2014 10:27:27 AM CDT		
Date Processed:	10/6/2015 2:28:59 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17225; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

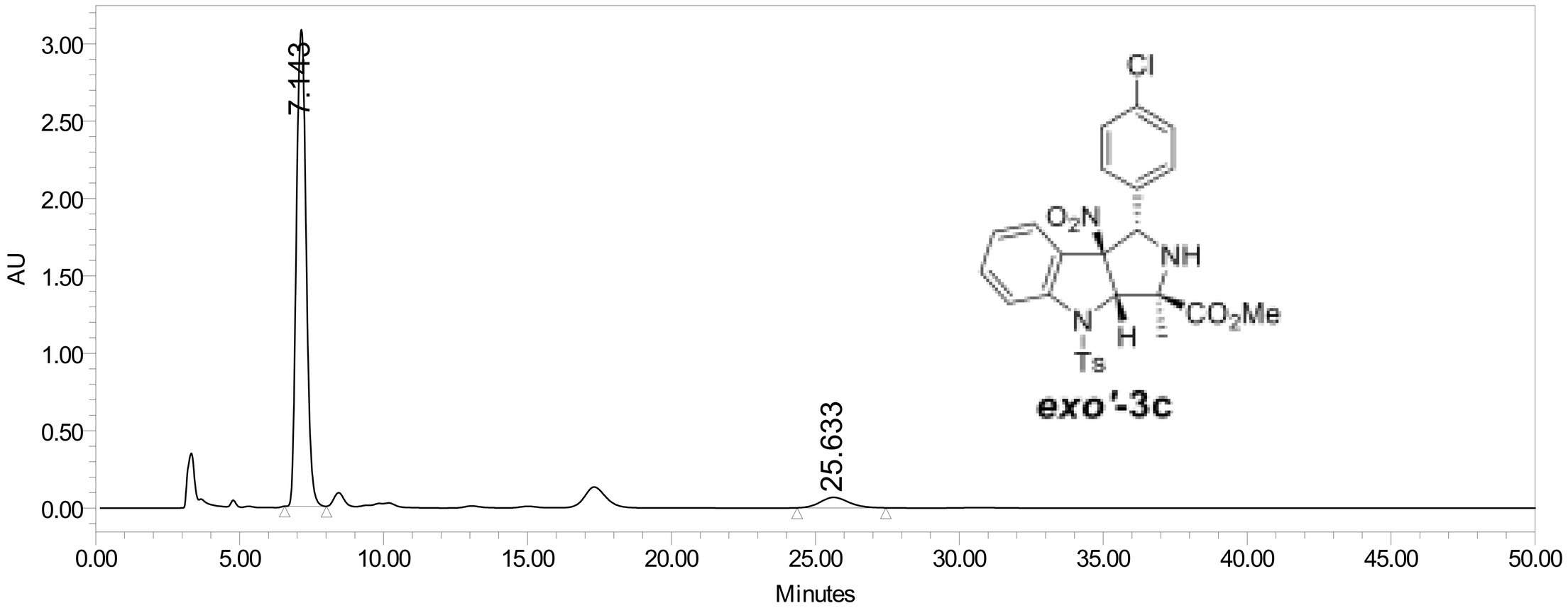
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.148	12755718	50.07	516519
2	W2489 ChA 254nm	25.788	12720762	49.93	164060

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_164_1132014
Vial:	3	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	11/3/2014 4:40:25 PM CST		
Date Processed:	10/6/2015 2:31:12 PM CDT		

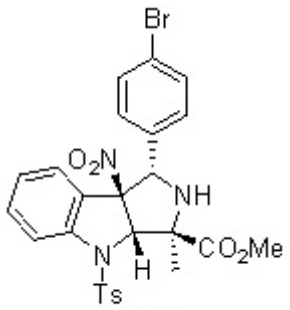


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17227; Processing Method: Tony1

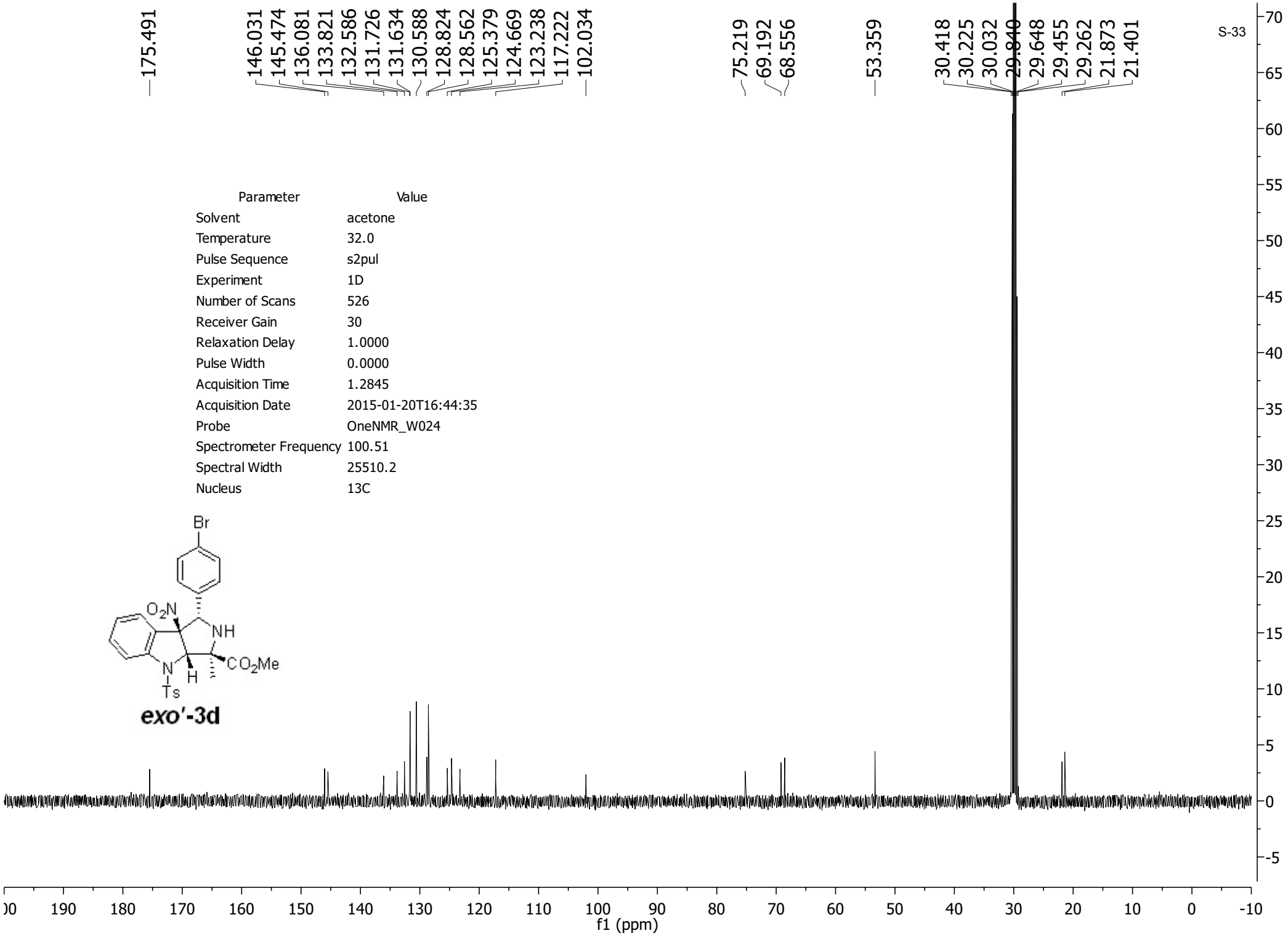
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.143	72571841	93.96	3081543
2	W2489 ChA 254nm	25.633	4663451	6.04	67528

Parameter	Value
Solvent	acetone
Temperature	32.0
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	2015-01-20T16:34:00
Probe	OneNMR_W024
Spectrometer Frequency	399.70
Spectral Width	6410.3
Nucleus	1H



***exo'*-3d**

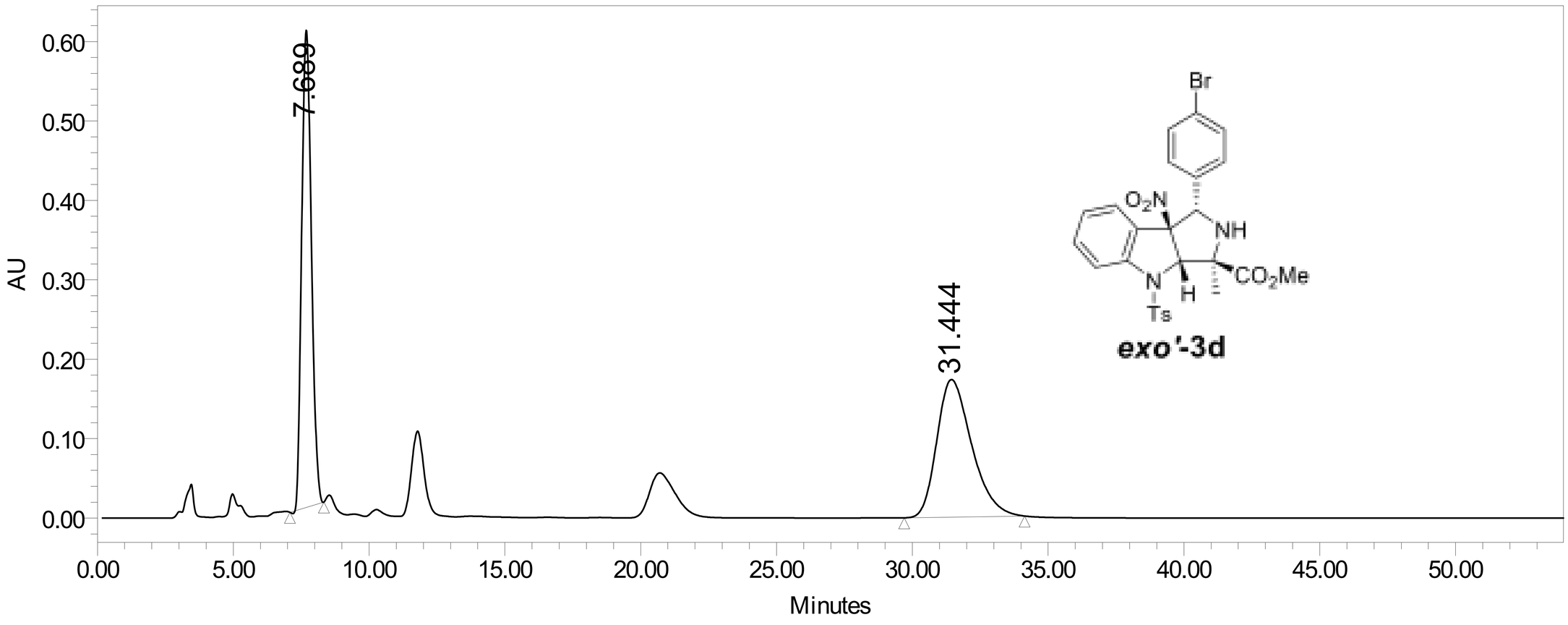

175.491
146.031
145.474
136.081
133.821
132.586
131.726
131.634
130.588
128.824
128.562
125.379
124.669
123.238
117.222
102.034
75.219
69.192
68.556
53.359
30.418
30.225
30.032
29.840
29.648
29.455
29.262
21.873
21.401
Parameter Value
Solvent acetone
Temperature 32.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 526
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.2845
Acquisition Date 2015-01-20T16:44:35
Probe OneNMR_W024
Spectrometer Frequency 100.51
Spectral Width 25510.2
Nucleus 13C
Br
O2N
NH
CO2Me
N
H
Ts
exo'-3d
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG3_128_1_1_20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_128_872014
Vial:	40	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:	8/7/2014 3:43:06 PM CDT		
Date Processed:	10/6/2015 2:32:31 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17229; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

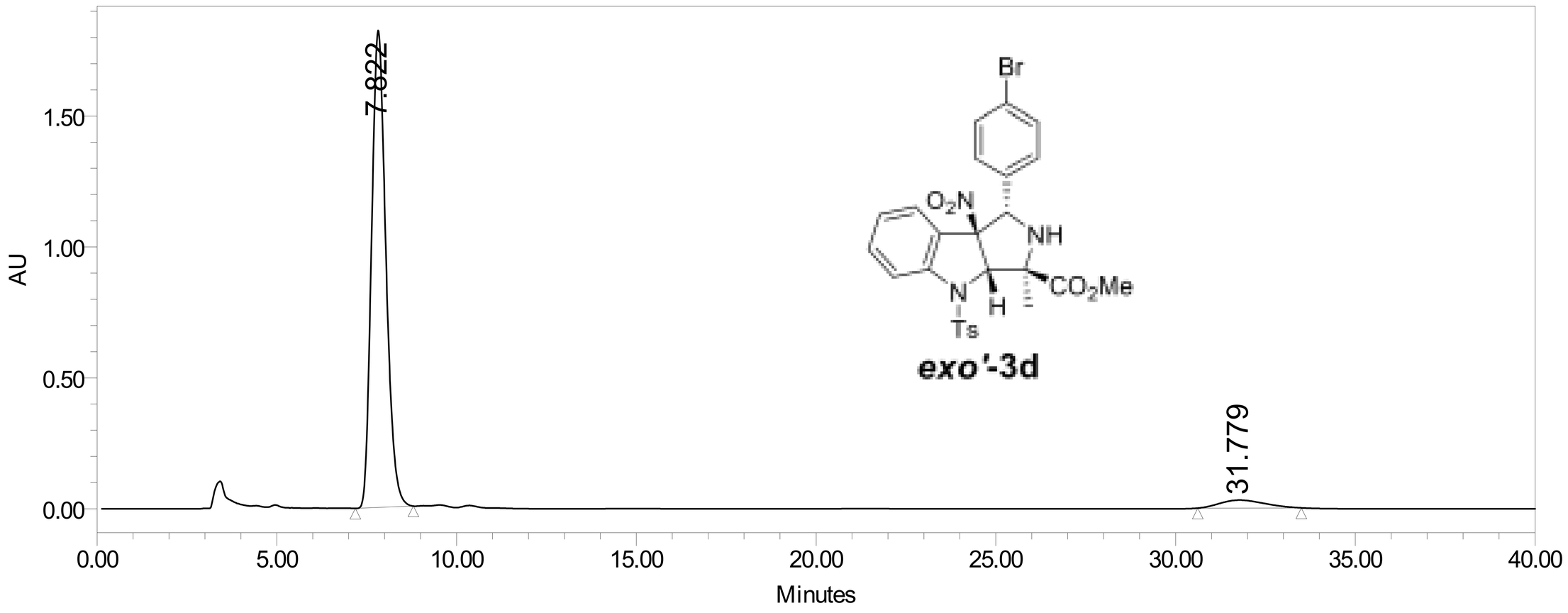
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.689	14898663	49.12	601164
2	W2489 ChA 254nm	31.444	15431396	50.88	173210

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

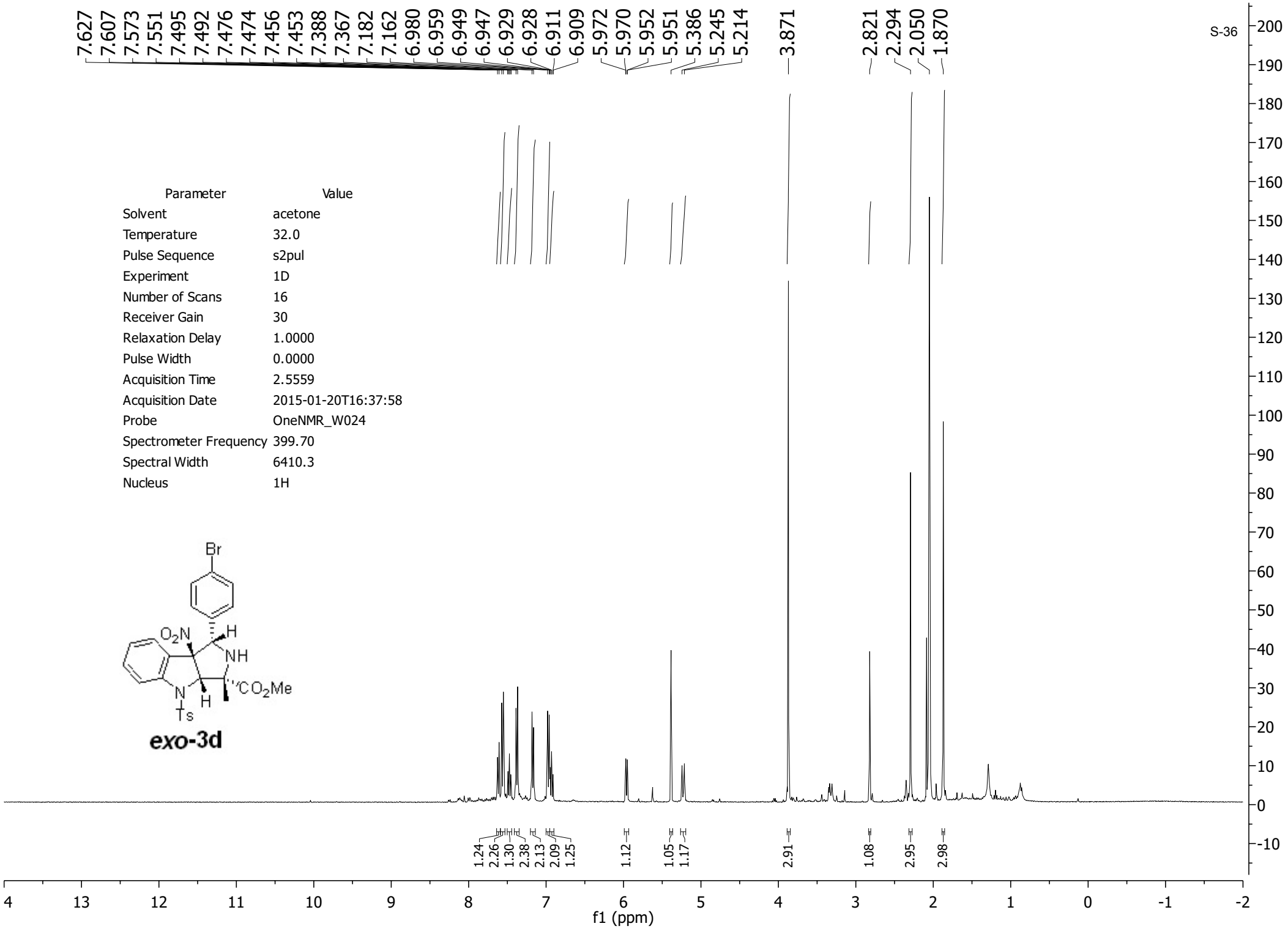
Sample Name:	TG3_180_4_1_20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	STWP1_T1
Vial:	45	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/20/2015 2:35:27 PM CST		
Date Processed:	10/6/2015 2:34:53 PM CDT		



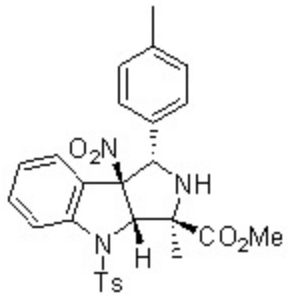
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17231; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.822	50546760	95.11	1823029
2	W2489 ChA 254nm	31.779	2601108	4.89	30283


7.627
7.607
7.573
7.551
7.495
7.492
7.476
7.474
7.456
7.453
7.388
7.367
7.182
7.162
6.980
6.959
6.949
6.947
6.929
6.928
6.911
6.909
5.972
5.970
5.952
5.951
5.386
5.245
5.214
3.871
2.821
2.294
2.050
1.870
Parameter Value
Solvent acetone
Temperature 32.0
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 2015-01-20T16:37:58
Probe OneNMR_W024
Spectrometer Frequency 399.70
Spectral Width 6410.3
Nucleus 1H
Br
O2N
H
NH
CO2Me
N
H
Ts
exo-3d
1.24
2.26
1.30
2.38
2.13
2.09
1.25
1.12
1.05
1.17
2.91
1.08
2.95
2.98
f1 (ppm)

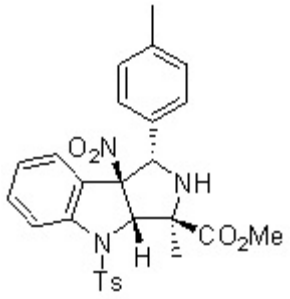
Parameter	Value
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2015-01-22T13:17:17
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



***exo'*-3e**

175.848
145.093
144.638
139.126
132.756
132.031
131.552
129.856
129.124
128.823
128.535
127.687
124.395
124.061
116.870
101.380
77.548
77.230
76.912
74.420
69.005
68.899
53.557
22.192
21.749
21.432

Parameter	Value
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1004
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2015-01-22T13:18:29
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



***exo'*-3e**

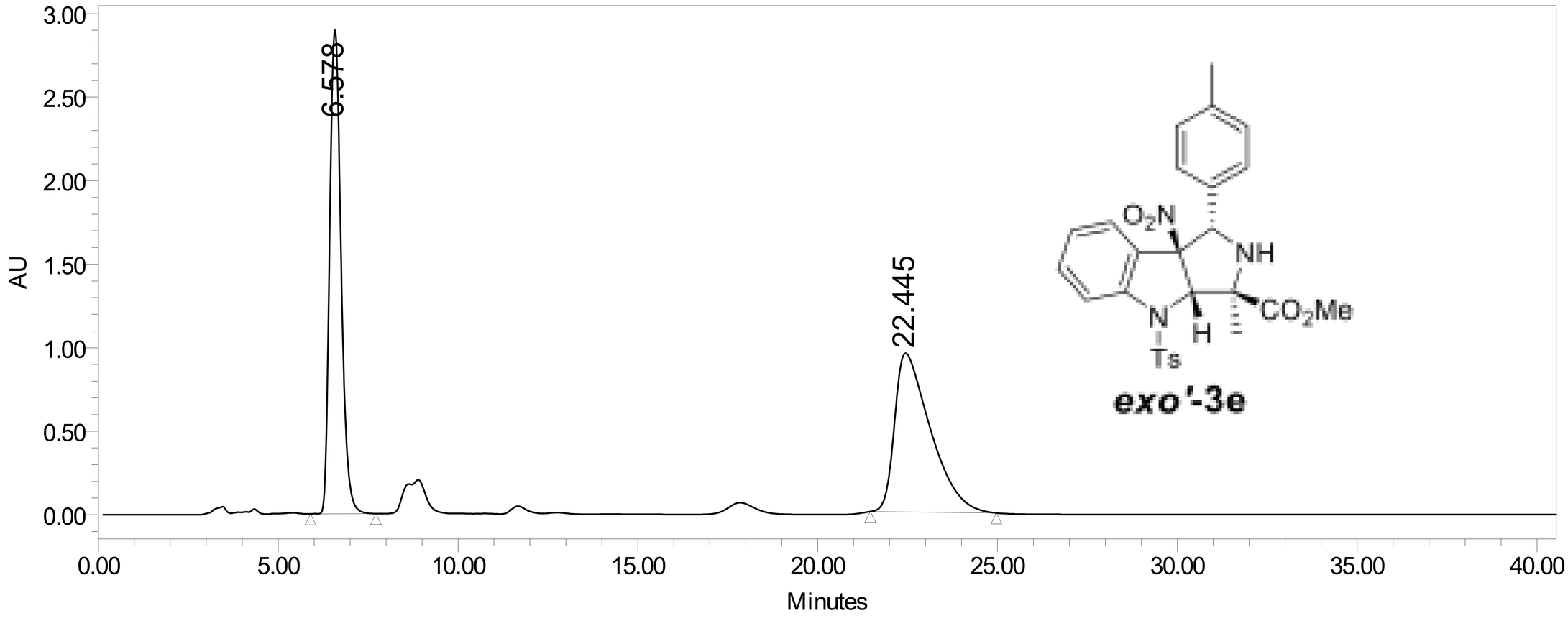
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_157_1092014
Vial:	80	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:	10/9/2014 7:21:46 PM CDT		
Date Processed:	10/6/2015 2:51:16 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17241; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

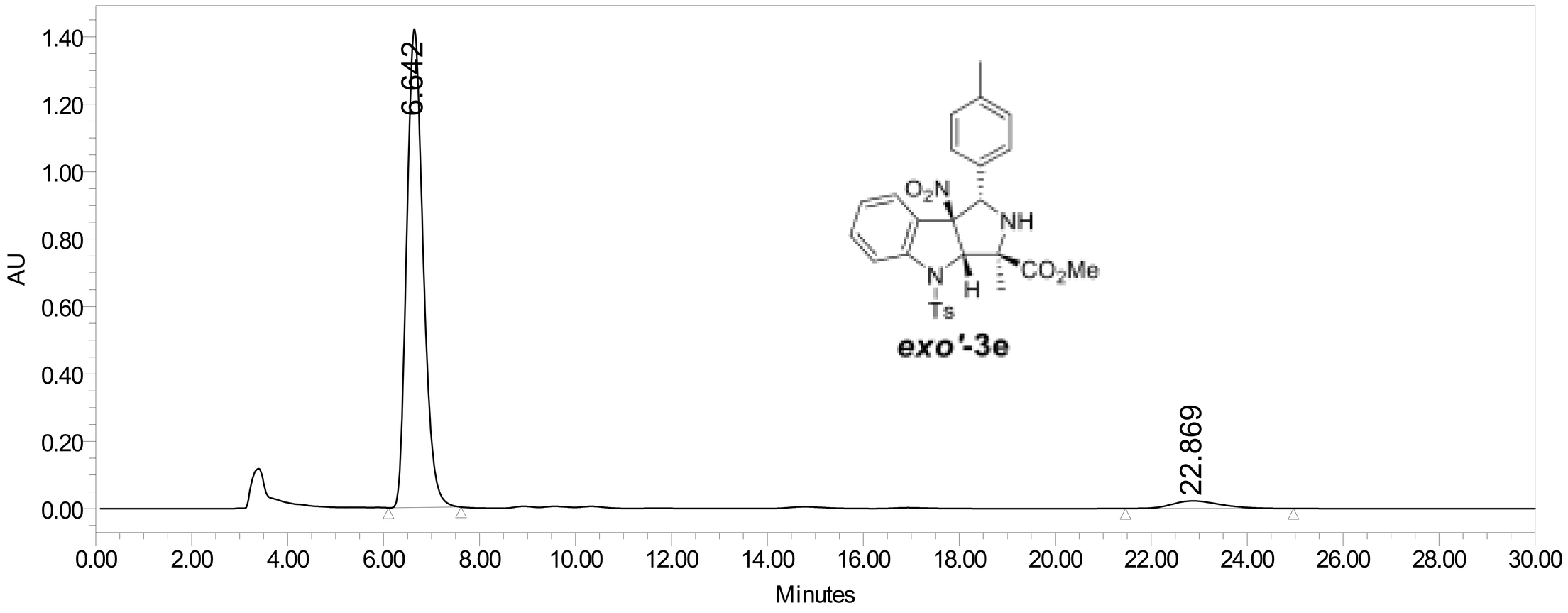
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.578	63883311	49.21	2897730
2	W2489 ChA 254nm	22.445	65933575	50.79	950704

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG3_180_2_1_20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	STWP1_T1
Vial:	43	Acq. Method Set:	1_ADH 80_20 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:	1/20/2015 1:44:11 PM CST		
Date Processed:	10/6/2015 2:52:49 PM CDT		

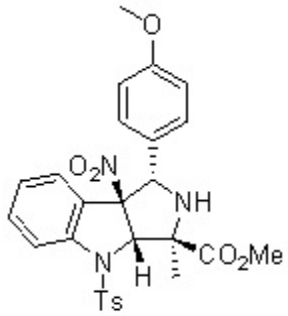


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17243; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.642	33899269	95.64	1419418
2	W2489 ChA 254nm	22.869	1545143	4.36	22335

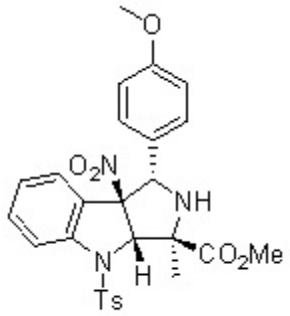
Parameter	Value
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	2.5559
Acquisition Date	2014-11-01T14:53:34
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



***exo'*-3f**

175.862
160.342
145.101
144.627
132.740
131.573
129.896
129.861
129.121
127.713
127.100
124.435
124.080
116.874
113.438
101.407
77.548
77.230
76.912
74.277
68.836
68.789
55.480
53.574
22.197
21.767

Parameter	Value
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	728
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2014-11-01T15:10:01
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



***exo'*-3f**

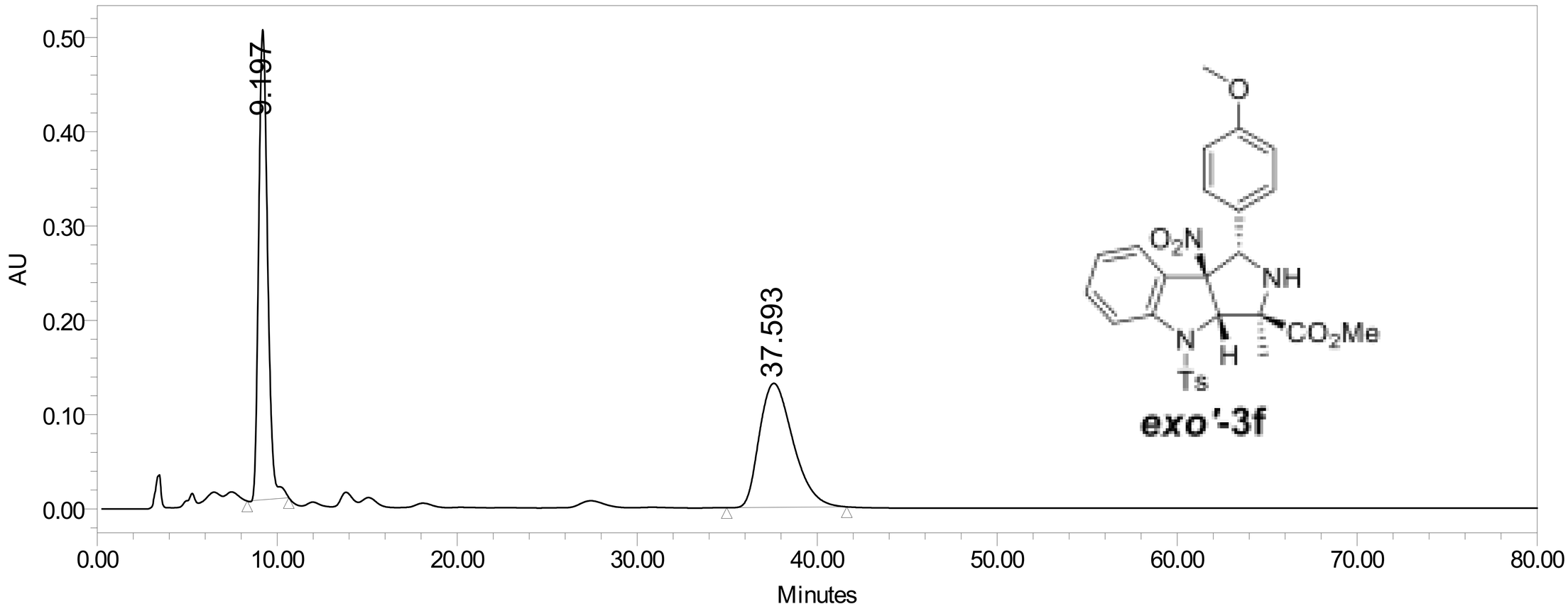
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten081114
Vial:	70	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	80.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	8/11/2014 7:28:23 PM CDT		
Date Processed:	10/6/2015 2:36:20 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17233; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

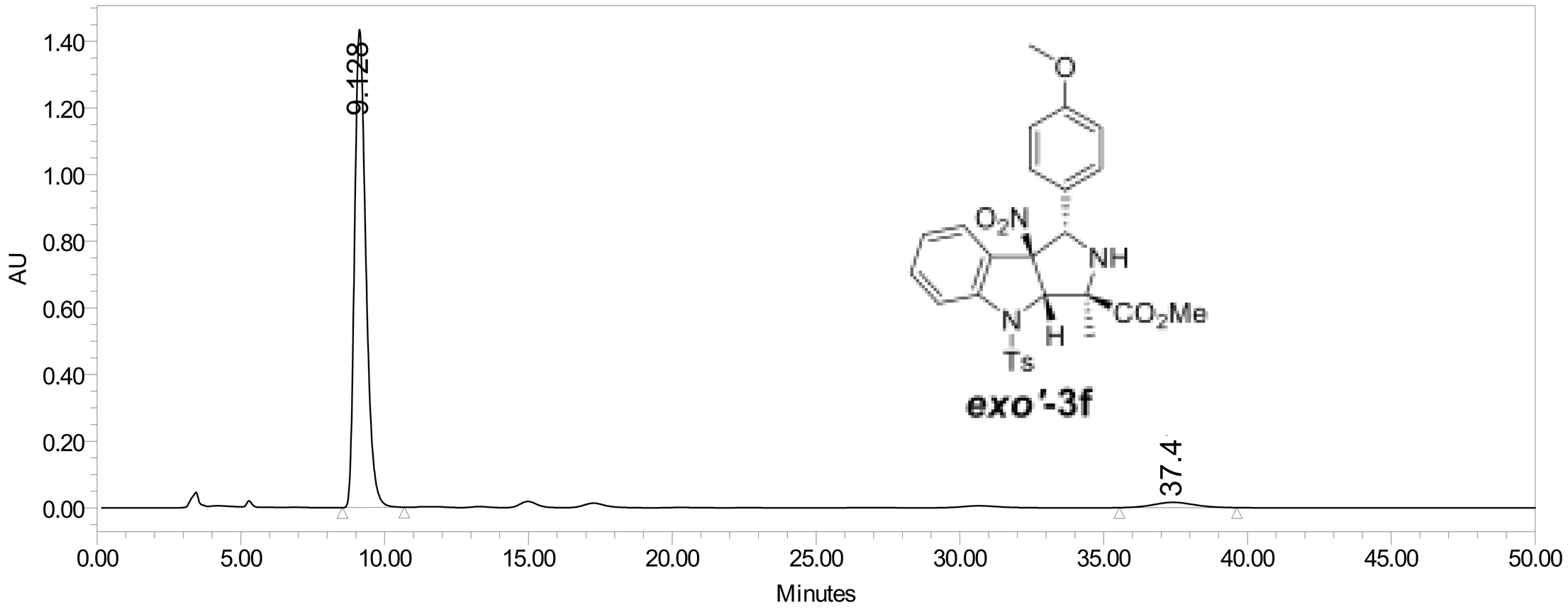
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.197	17237134	50.19	498541
2	W2489 ChA 254nm	37.593	17105436	49.81	131481

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_164_1132014
Vial:	2	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	11/3/2014 3:49:29 PM CST		
Date Processed:	10/6/2015 2:40:30 PM CDT		

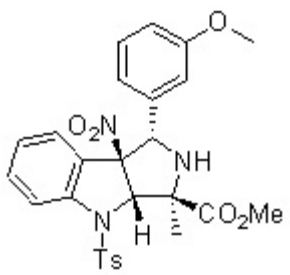


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17235; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.128	39198856	96.12	1434506
2	W2489 ChA 254nm	37.416	1582554	3.88	15935

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	2015-03-03T17:49:36
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



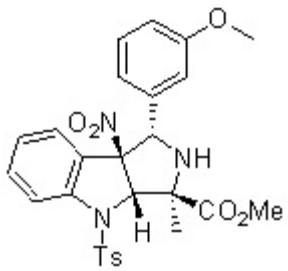
***exo'*-3g**

acetone

f1 (ppm)

175.768
159.398
145.103
144.631
132.677
131.572
129.833
129.152
128.966
127.665
124.333
124.042
120.986
120.964
116.934
115.446
113.487
101.390
77.441
77.230
77.018
74.483
68.988
68.916
55.386
53.543
22.144
21.712

Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	163
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	11.6000
Acquisition Time	0.8651
Acquisition Date	2015-10-17T15:59:44
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



***exo'*-3g**

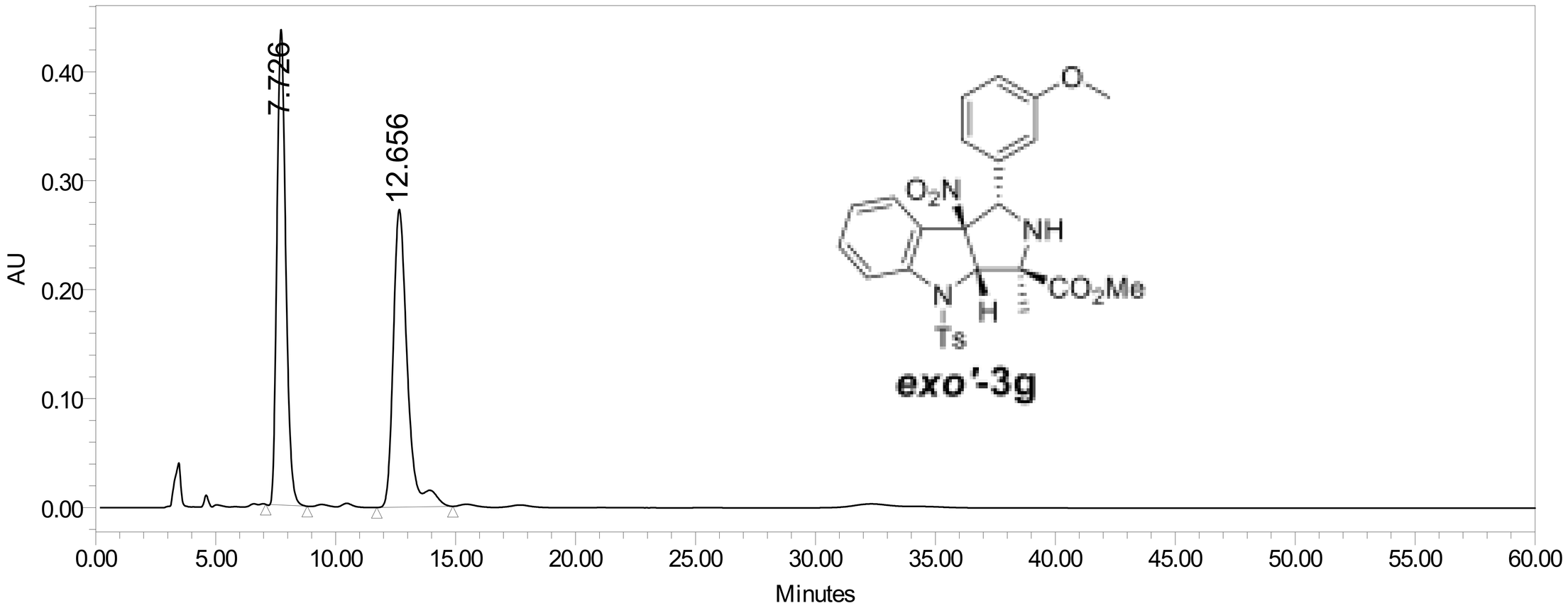
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_197_342015
Vial:	33	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:	3/4/2015 7:48:17 PM CST		
Date Processed:	10/6/2015 3:15:11 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17263; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.726	1119584	50.05	436658
2	W2489 ChA 254nm	12.656	1117191	49.95	273289

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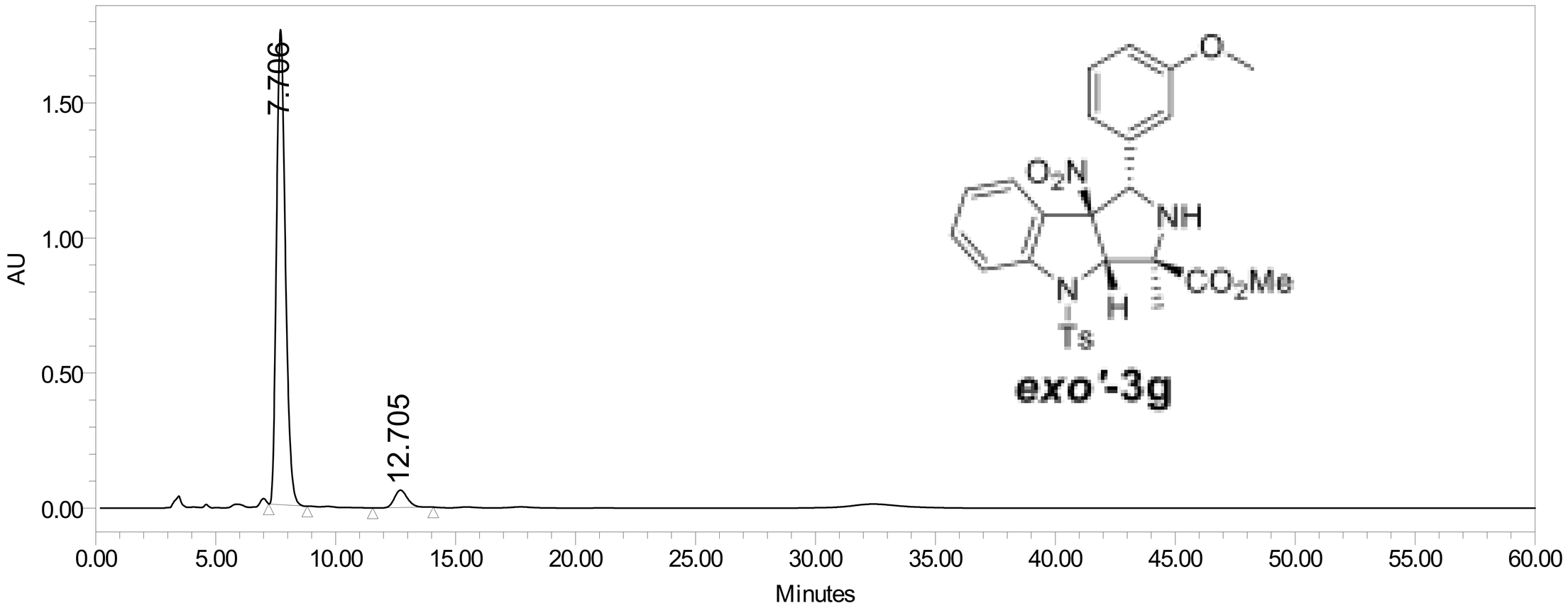
Injection Summary Report

SAMPLE INFORMATION

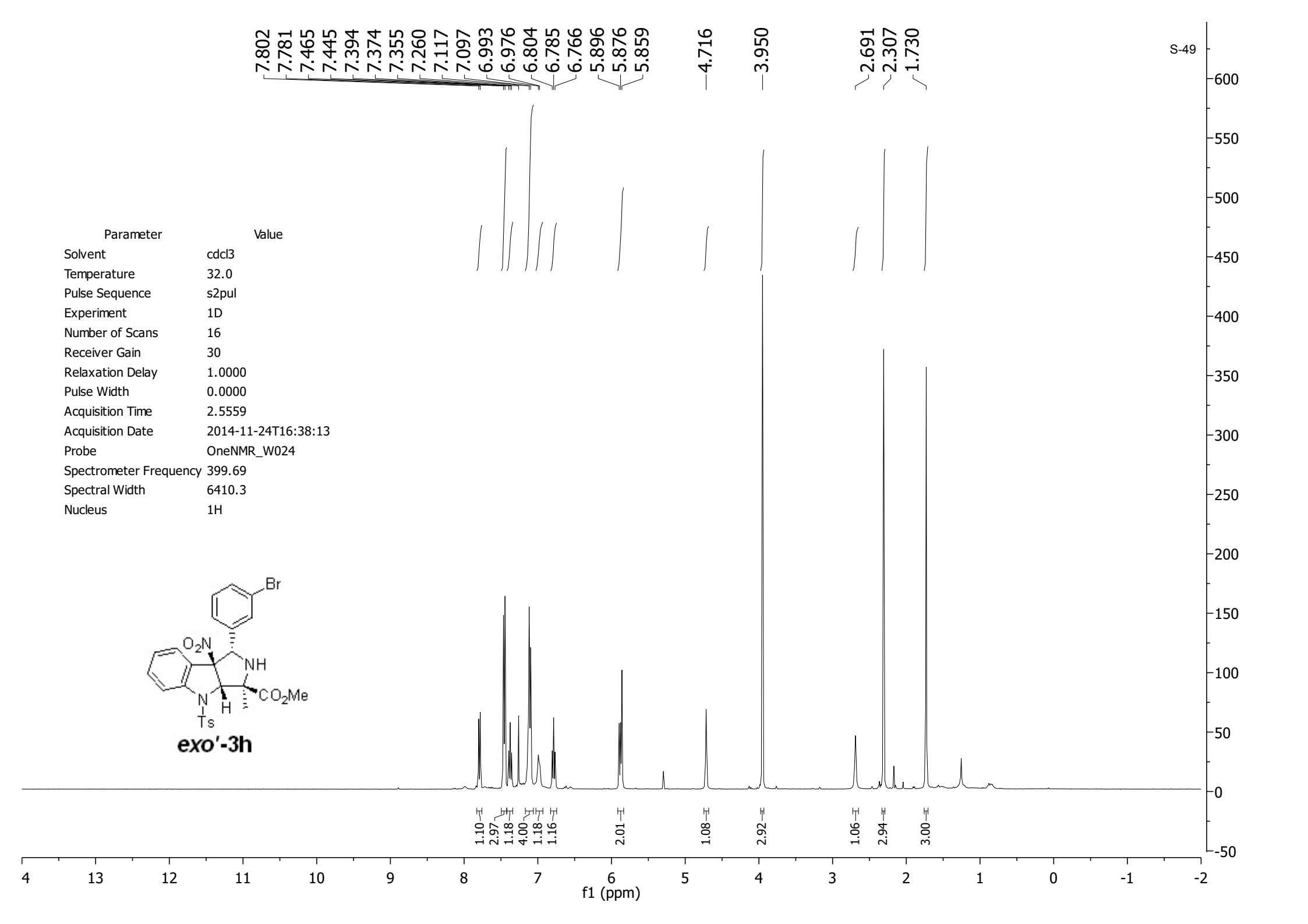
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_197_342015
Vial:	34	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/4/2015 8:48:56 PM CST		
Date Processed:	10/6/2015 3:17:26 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17265; Processing Method: Tony1

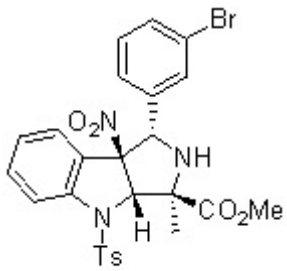
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.706	45121470	94.87	1759162
2	W2489 ChA 254nm	12.705	2442324	5.13	64443


7.802
7.781
7.465
7.445
7.394
7.374
7.355
7.260
7.117
7.097
6.993
6.976
6.804
6.785
6.766
5.896
5.876
5.859
4.716
3.950
2.691
2.307
1.730
Parameter Value
Solvent cdcl3
Temperature 32.0
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 2014-11-24T16:38:13
Probe OneNMR_W024
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
Br
O2N
NH
CO2Me
N
H
Ts
exo'-3h
1.10
2.97
1.18
4.00
1.18
1.16
2.01
1.08
2.92
1.06
2.94
3.00
f1 (ppm)

175.641
145.200
144.666
137.718
132.630
132.383
131.913
131.854
129.881
129.661
128.529
127.764
127.607
124.109
124.099
122.312
117.112
101.259
77.548
77.230
76.912
74.213
68.934
68.234
53.660
22.113
21.777

Parameter	Value
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	826
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2014-11-24T16:57:55
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



***exo'*-3h**

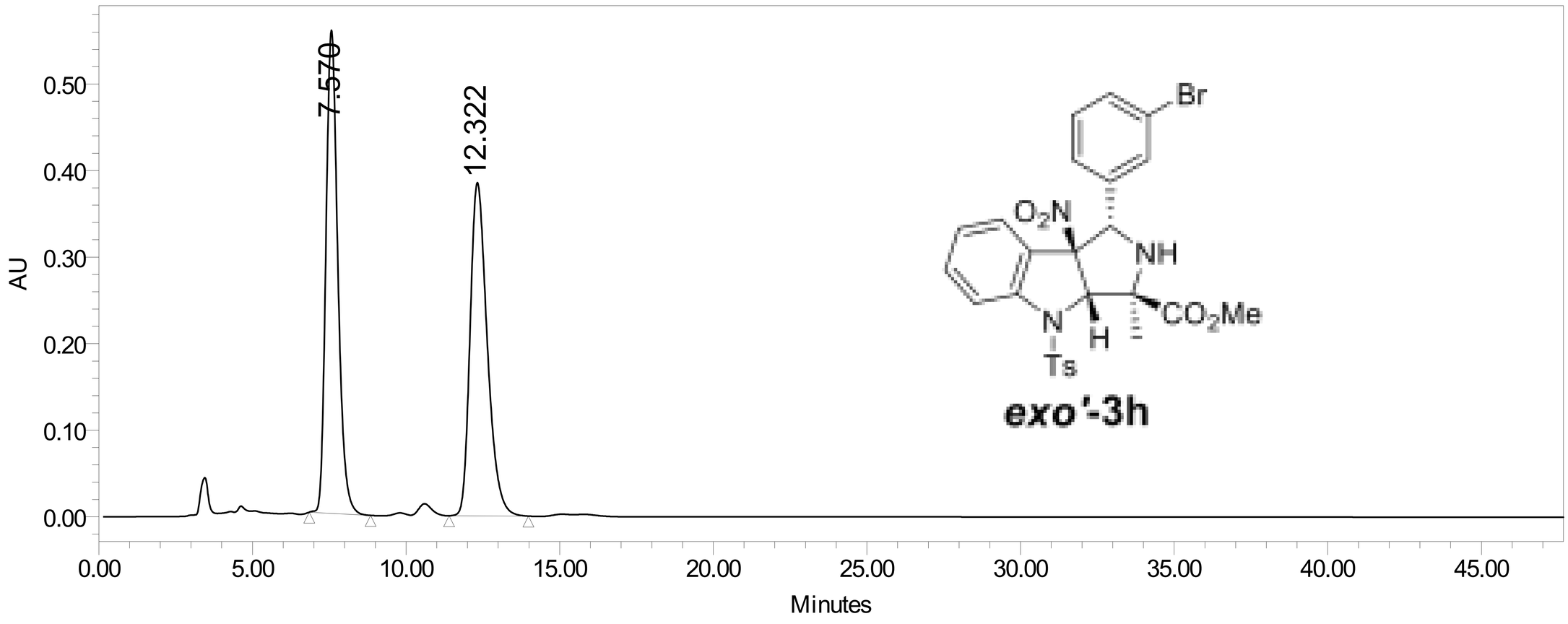
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_166_11252014
Vial:	54	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:	11/25/2014 5:11:32 PM CST		
Date Processed:	10/6/2015 2:54:10 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17245; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.570	14970987	49.99	558288
2	W2489 ChA 254nm	12.322	14975098	50.01	385086

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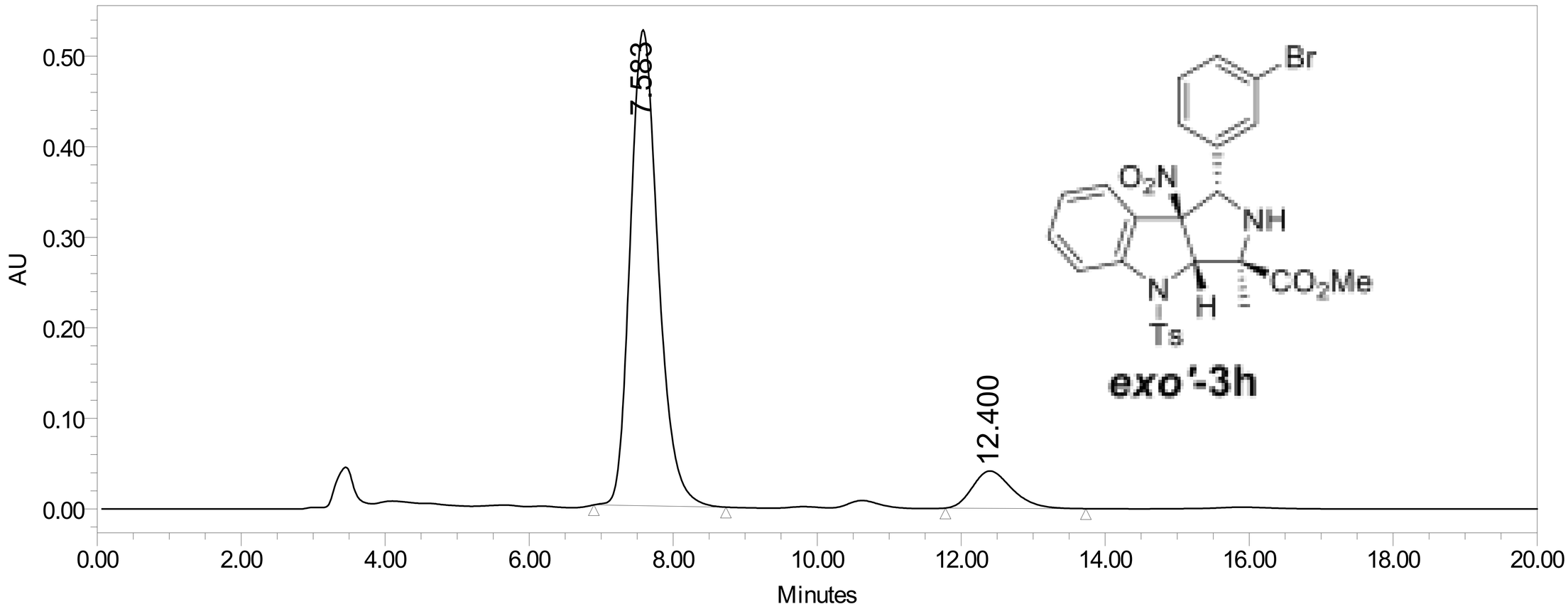
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_166_11252014
Vial:	57	Acq. Method Set:	1_ADH 80_20 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:	11/25/2014 6:00:06 PM CST		
Date Processed:	10/6/2015 2:55:28 PM CDT		



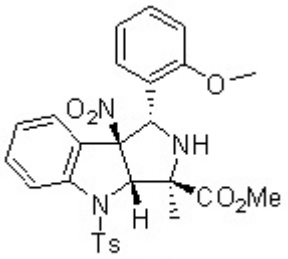
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17247; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.583	14198734	90.06	525694
2	W2489 ChA 254nm	12.400	1567983	9.94	41085

7.773 7.759 7.365 7.352 7.339 7.326 7.313 7.277 7.263 7.253 7.083 7.069 6.926 6.913 6.811 6.797 6.770 6.766 6.758 6.745 5.936 5.923 5.764 5.239 3.998 3.599 2.693 2.304 1.710

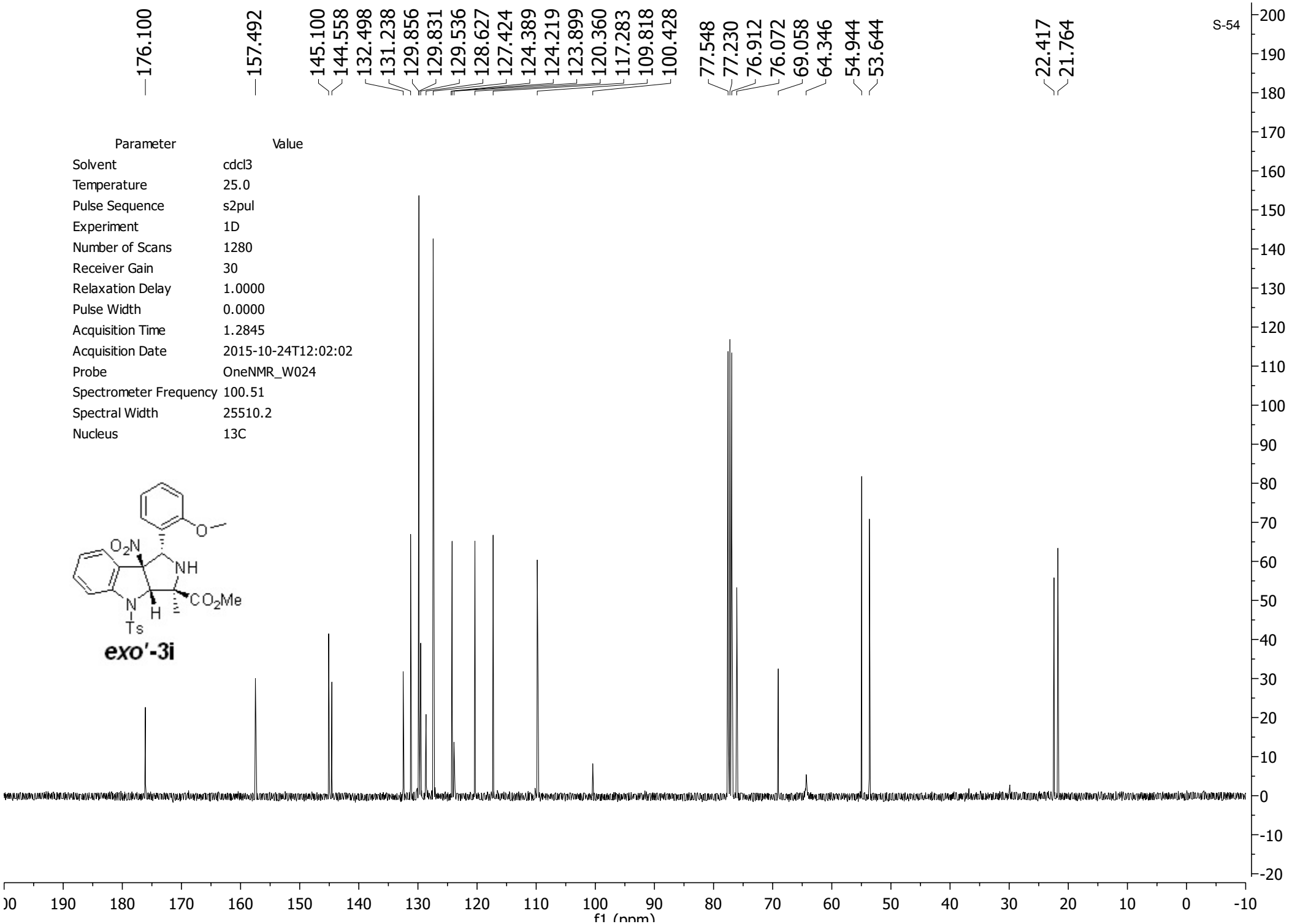
Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	75
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2014-12-12T20:17:55
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H



***exo'*-3i**

1.08 4.98 2.02 1.03 1.08 2.06 1.05 1.05 1.05 3.05 3.02 1.07 3.00 3.06

f1 (ppm)


176.100
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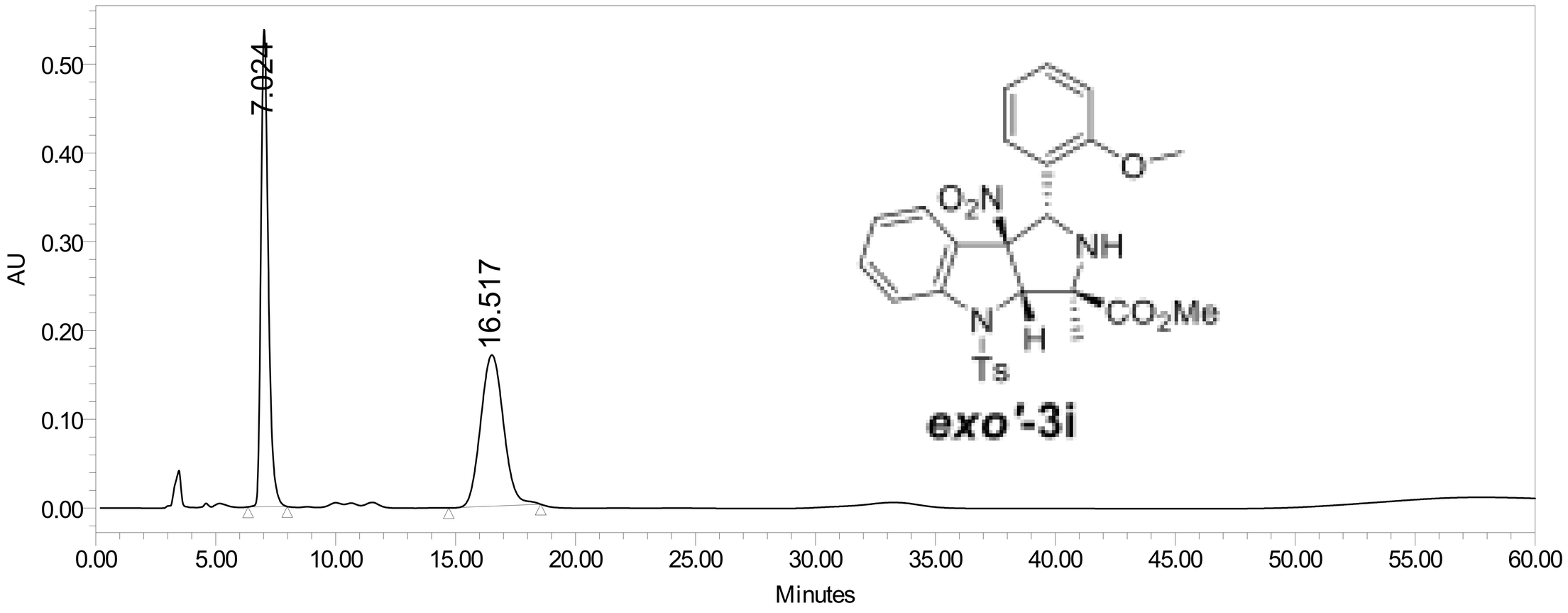
145.100
144.558
132.498
131.238
129.856
129.831
129.536
128.627
127.424
124.389
124.219
123.899
120.360
117.283
109.818
100.428
77.548
77.230
76.912
76.072
69.058
64.346
54.944
53.644
22.417
21.764
Parameter Value
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 1280
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 1.2845
Acquisition Date 2015-10-24T12:02:02
Probe OneNMR_W024
Spectrometer Frequency 100.51
Spectral Width 25510.2
Nucleus 13C
O
O2N
NH
N
H
CO2Me
Ts
exo'-3i
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_173_12132014
Vial:	14	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:	12/13/2014 3:14:48 PM CST		
Date Processed:	10/6/2015 3:05:27 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17255; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.024	11425964	50.38	537899
2	W2489 ChA 254nm	16.517	11255494	49.62	170233

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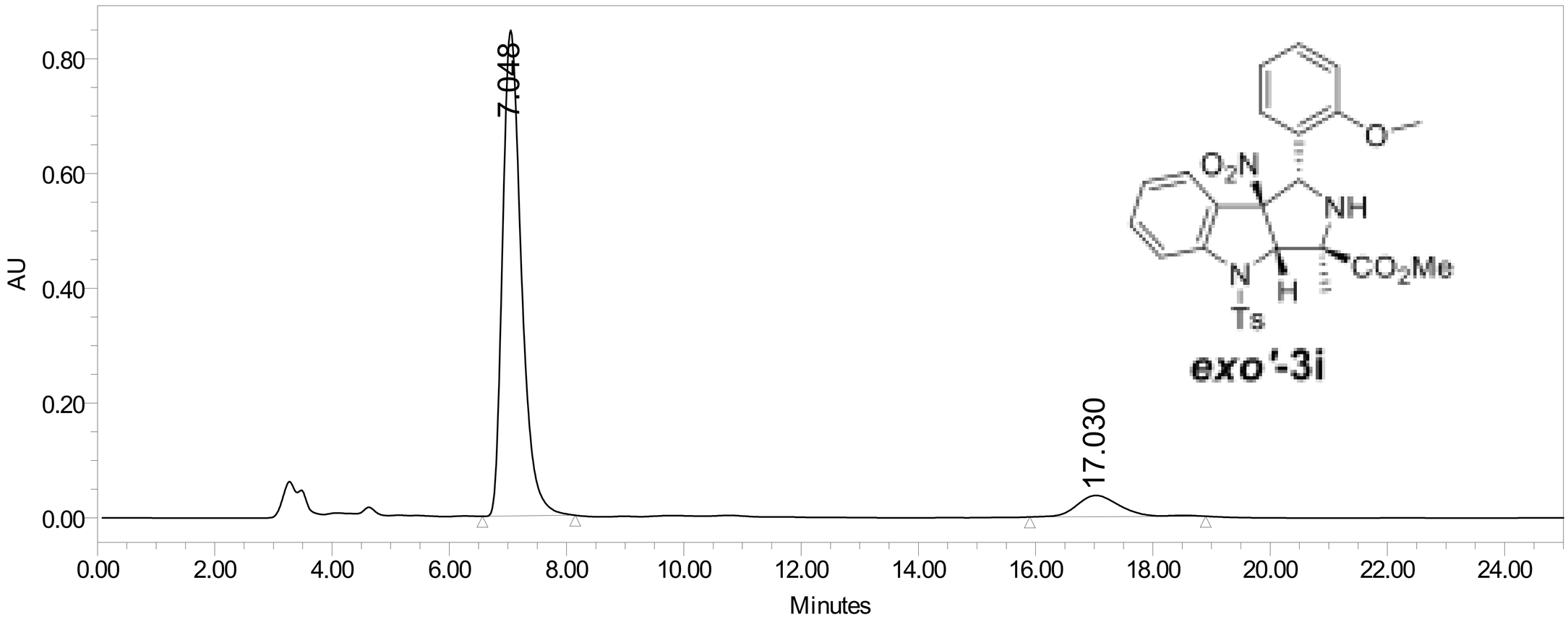
Injection Summary Report

SAMPLE INFORMATION

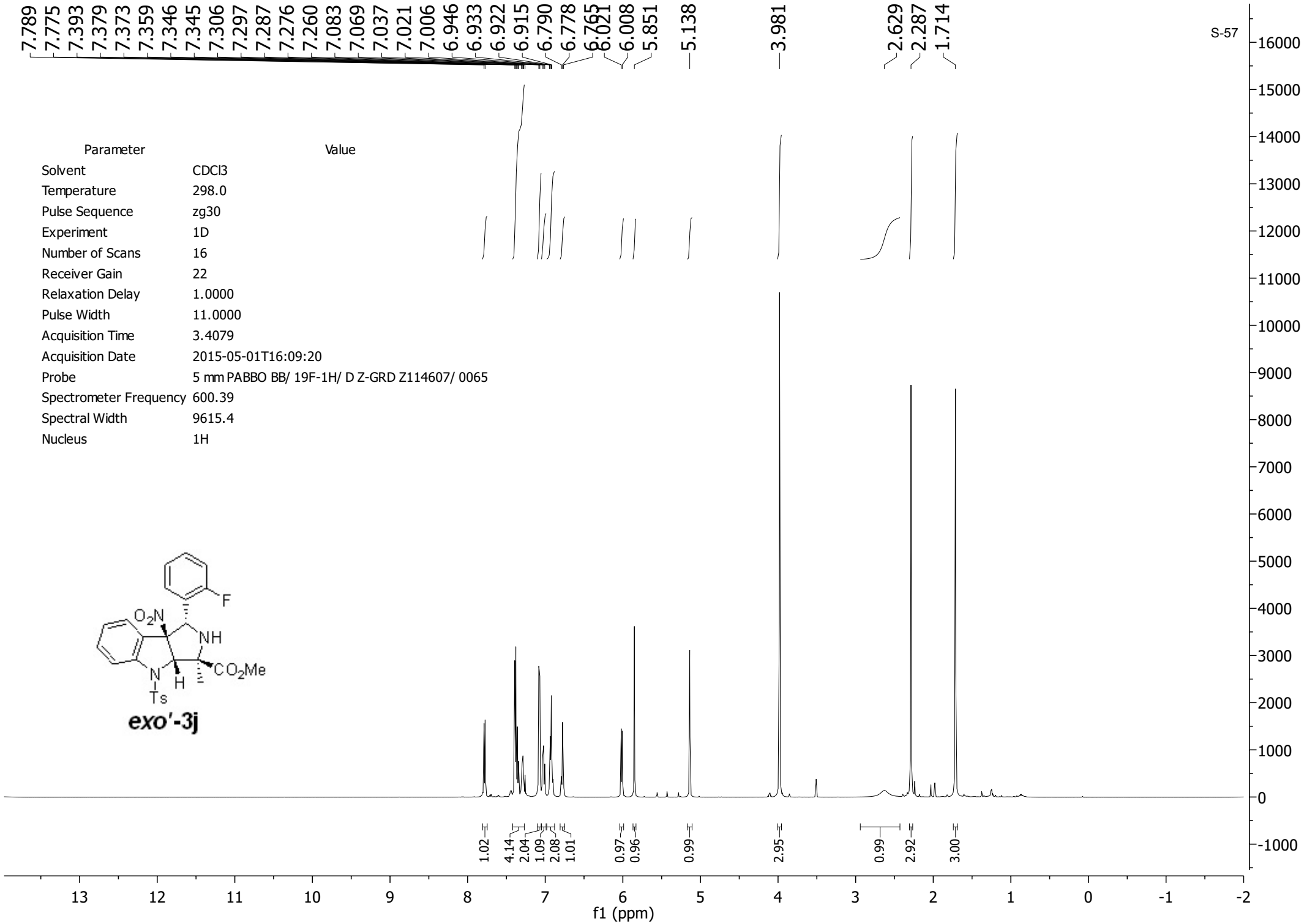
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_173_12162014
Vial:	57	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	12/16/2014 7:40:56 PM CST		
Date Processed:	10/6/2015 3:08:10 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17257; Processing Method: Tony1

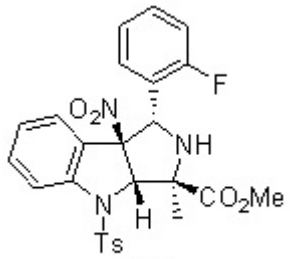
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	7.048	18853160	90.89	846762
2	W2489 ChA 254nm	17.030	1890322	9.11	37062


7.789
7.775
7.393
7.379
7.373
7.359
7.346
7.345
7.306
7.297
7.287
7.276
7.260
7.083
7.069
7.037
7.021
7.006
6.946
6.933
6.922
6.915
6.790
6.778
6.765
6.021
6.008
5.851
5.138
3.981
2.629
2.287
1.714
Parameter Value
Solvent CDCl3
Temperature 298.0
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 22
Relaxation Delay 1.0000
Pulse Width 11.0000
Acquisition Time 3.4079
Acquisition Date 2015-05-01T16:09:20
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency 600.39
Spectral Width 9615.4
Nucleus 1H
F
O2N
NH
N
H
CO2Me
Ts
exo'-3j
1.02
4.14
2.04
1.09
2.08
1.01
0.97
0.96
0.99
2.95
0.99
2.92
3.00
f1 (ppm)

175.729
161.963
160.320
145.220
144.675
132.434
131.643
130.663
130.607
129.934
129.911
129.876
129.216
127.490
124.259
123.934
123.845
123.823
122.549
122.468
117.238
115.363
115.221
100.596
77.442
77.230
77.018
74.932
69.086
62.861
53.693
22.282
21.689

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	11.6000
Acquisition Time	0.8651
Acquisition Date	2015-05-01T16:12:33
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



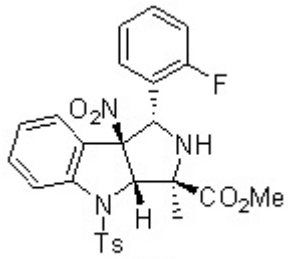
***exo'*-3j**

14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

Parameter	Value
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgfhigqn
Experiment	1D
Number of Scans	1
Receiver Gain	177
Relaxation Delay	5.0000
Pulse Width	14.0000
Acquisition Time	0.3408
Acquisition Date	2015-10-13T14:30:52
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	564.89
Spectral Width	96153.8
Nucleus	19F



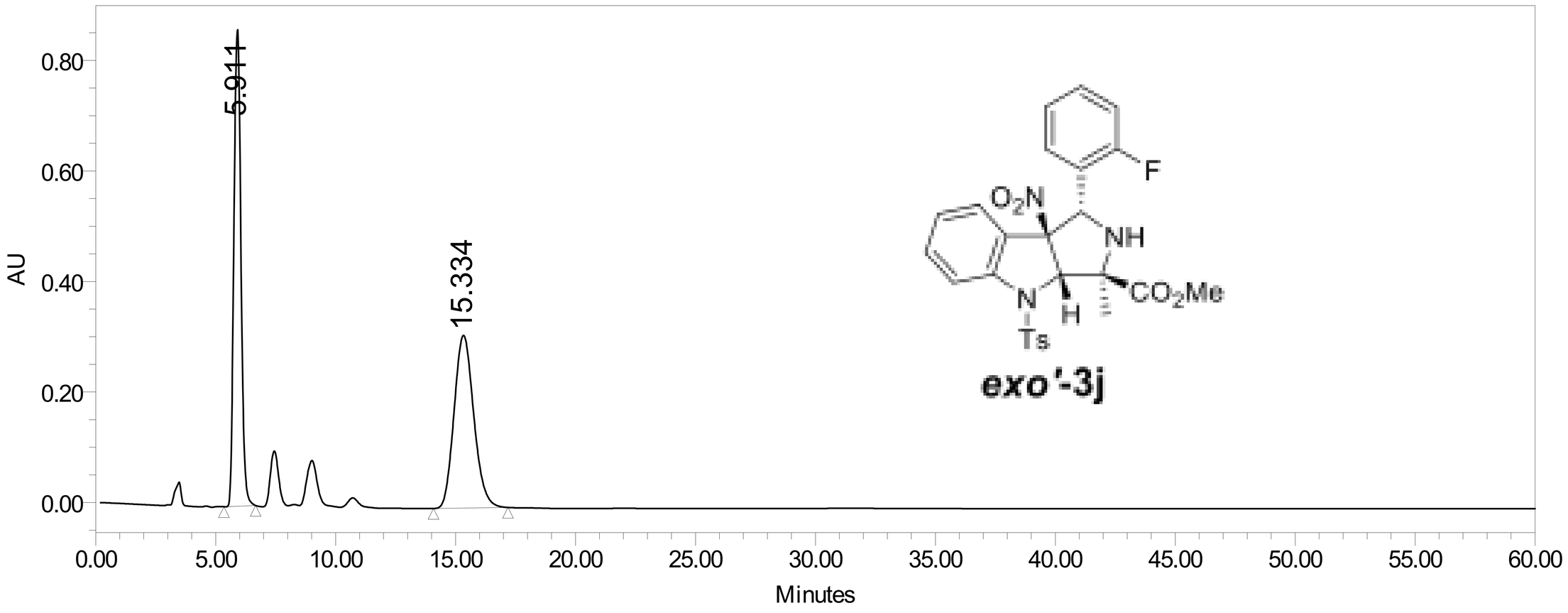
***exo'*-3j**

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_173_12132014
Vial:	15	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:	12/13/2014 4:15:28 PM CST		
Date Processed:	10/6/2015 2:56:33 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17249; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.911	17560448	49.59	863049
2	W2489 ChA 254nm	15.334	17852281	50.41	312459

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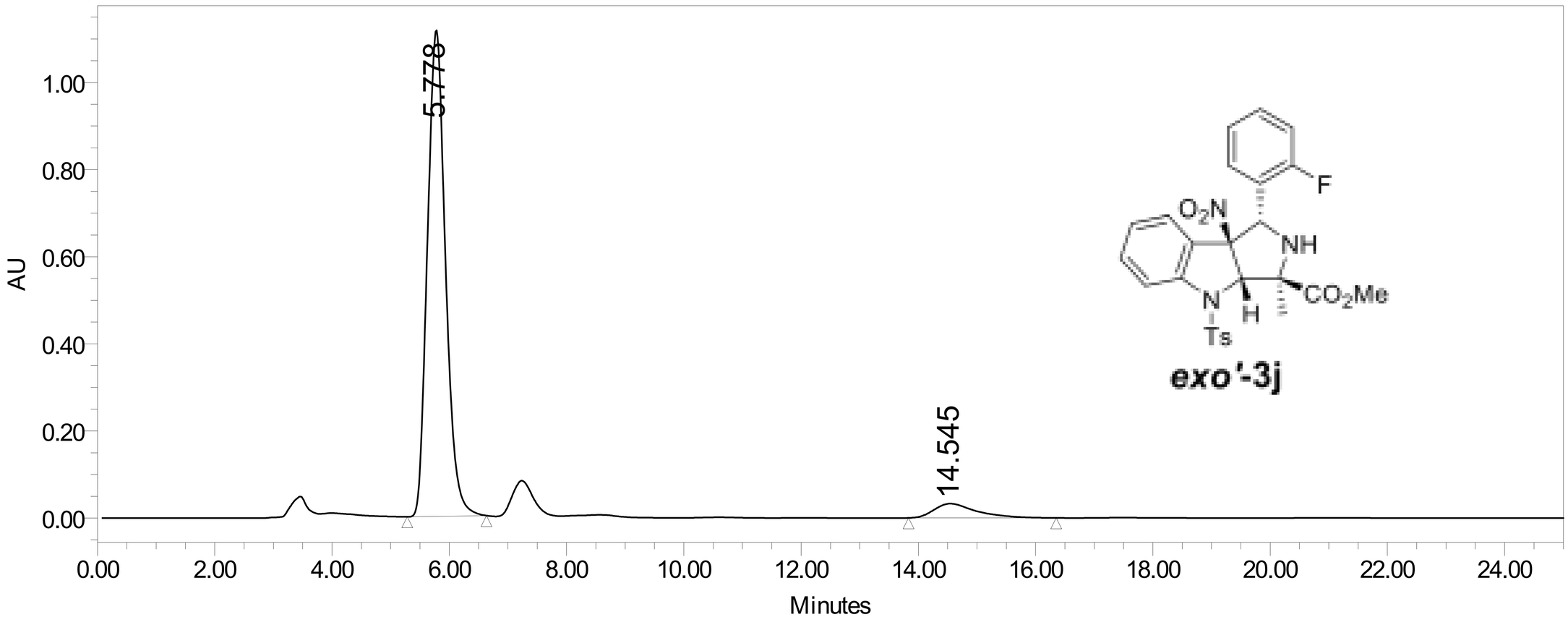
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG3_180_1_1_20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	STWP1_T1
Vial:	42	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	25.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	1/20/2015 1:18:34 PM CST		
Date Processed:	10/6/2015 2:58:46 PM CDT		



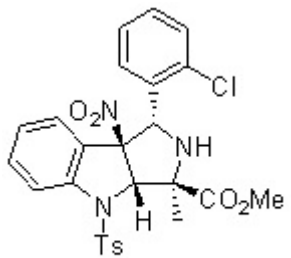
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17251; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.778	23881359	93.58	1116923
2	W2489 ChA 254nm	14.545	1638958	6.42	32804

7.798 7.778 7.383 7.382 7.362 7.341 7.260 7.244 7.241 7.225 7.206 7.202 7.084 7.064 7.015 6.996 6.978 6.898 6.878 6.802 6.783 6.764 6.037 6.018 5.775 5.354 4.020 2.704 2.295 1.724

Parameter	Value
Solvent	cdcl3
Temperature	32.0
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	2015-01-21T16:43:56
Probe	OneNMR_W024
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



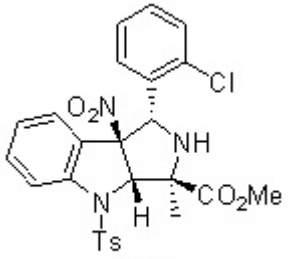
***exo'*-3k**

1.02 3.84 1.20 2.02 1.10 1.03 1.06 0.99 0.97 0.99 2.92 1.16 2.95 3.00

f1 (ppm)

175.872
145.250
144.704
134.462
133.338
132.240
131.548
130.971
130.118
129.966
129.869
129.578
127.466
126.276
124.133
123.776
117.325
100.299
77.442
77.230
77.019
75.352
68.850
65.523
53.715
22.385
21.705

Parameter	Value
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	127
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	11.6000
Acquisition Time	0.8651
Acquisition Date	2015-10-13T16:07:28
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



***exo'*-3k**

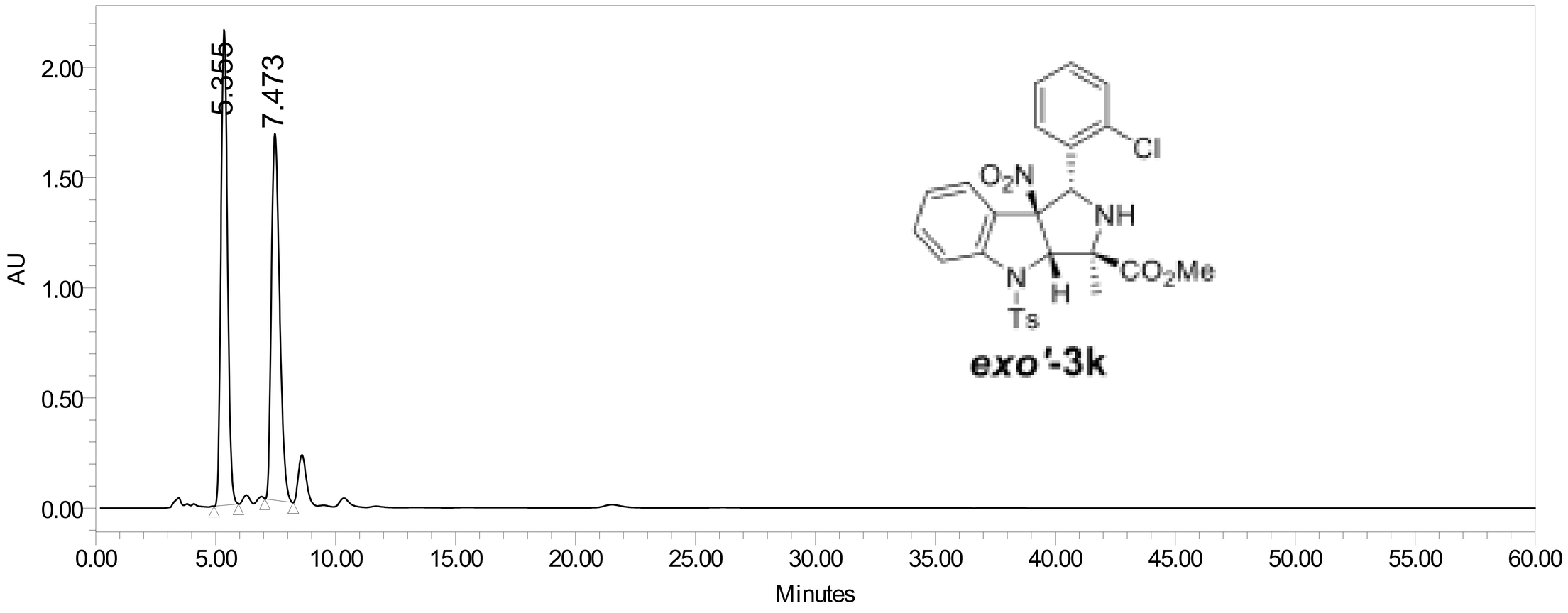
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_157_1092014
Vial:	78	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:	10/9/2014 5:36:46 PM CDT		
Date Processed:	10/6/2015 2:41:57 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17237; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.355	40744085	50.56	2160537
2	W2489 ChA 254nm	7.473	39841956	49.44	1664069

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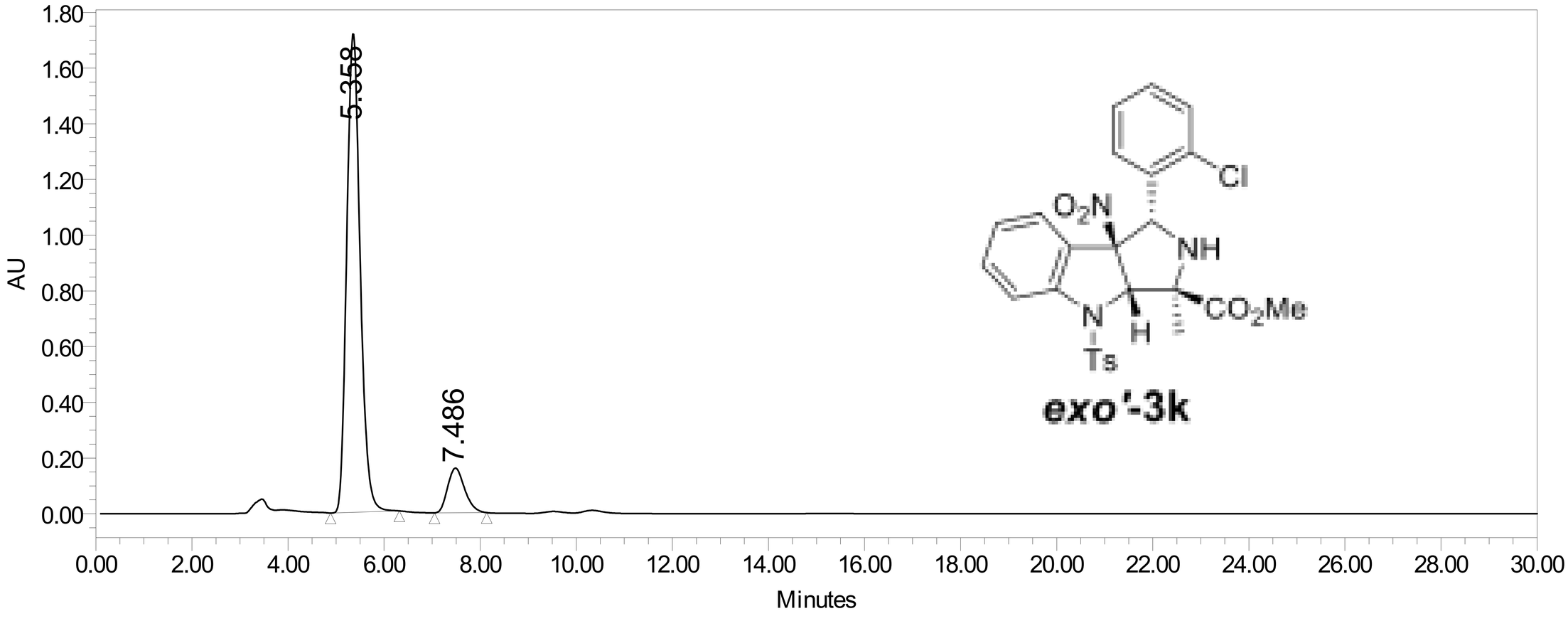
Injection Summary Report

SAMPLE INFORMATION

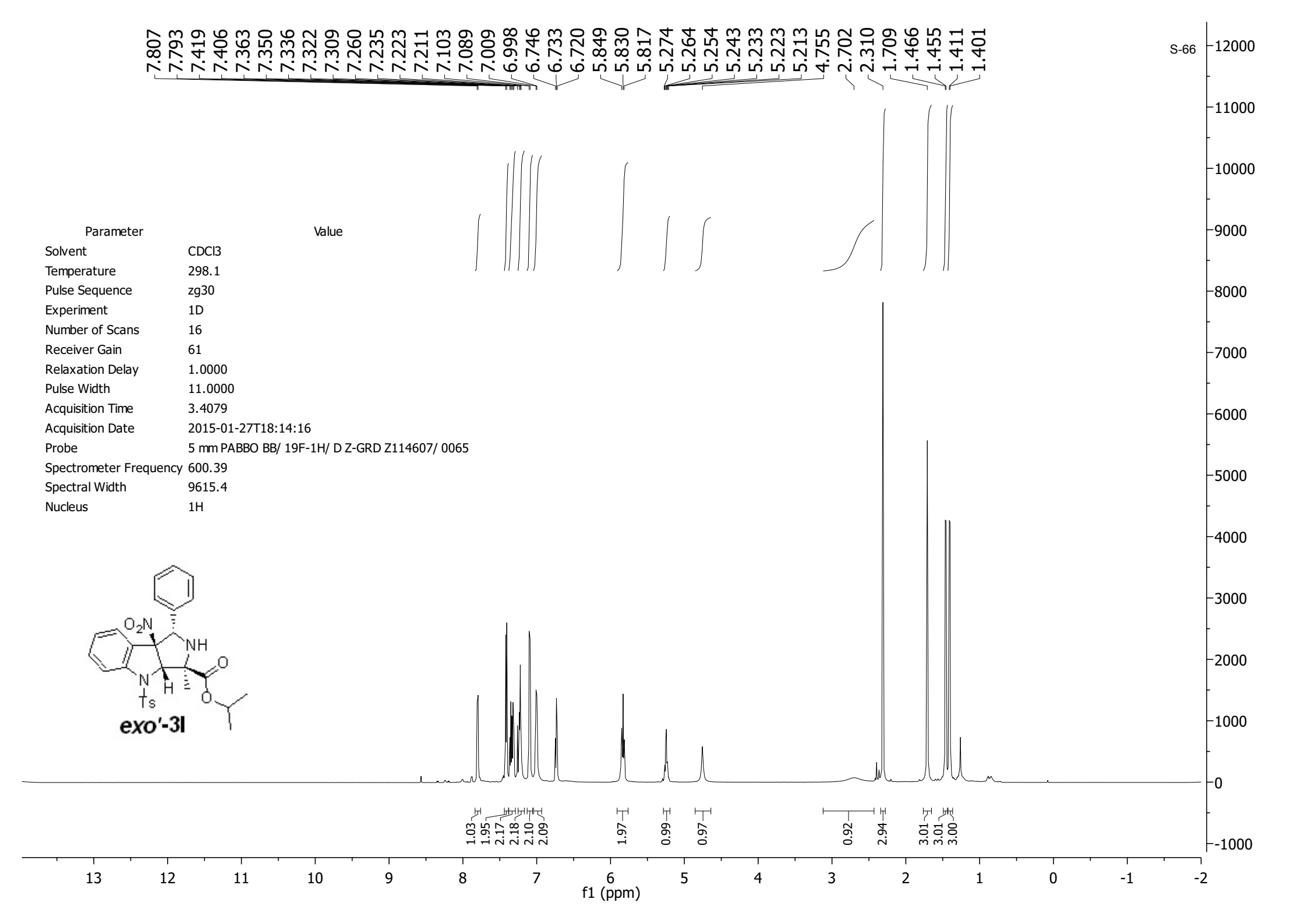
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_212_3192015
Vial:	39	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/19/2015 7:04:47 PM CDT		
Date Processed:	10/6/2015 2:49:23 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17239; Processing Method: Tony1

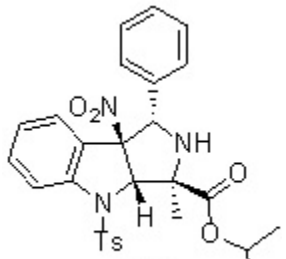
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	5.358	33314590	89.39	1720279
2	W2489 ChA 254nm	7.486	3956302	10.61	160403


7.807
7.793
7.419
7.406
7.363
7.350
7.336
7.322
7.309
7.260
7.235
7.223
7.211
7.103
7.089
7.009
6.998
6.746
6.733
6.720
5.849
5.830
5.817
5.274
5.264
5.254
5.243
5.233
5.223
5.213
4.755
2.702
2.310
1.709
1.466
1.455
1.411
1.401
S-66
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 2015-01-27T18:14:16
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency 600.39
Spectral Width 9615.4
Nucleus 1H
O2N
NH
O
N
H
Ts
exo'-3l
1.03
1.95
2.17
2.18
2.10
2.09
1.97
0.99
0.97
0.92
2.94
3.01
3.01
3.00
f1 (ppm)

174.781
145.116
144.834
135.371
132.641
131.589
129.844
129.269
129.045
128.651
128.151
127.646
124.349
124.081
117.124
101.615
77.441
77.230
77.018
74.430
70.269
69.251
68.888
22.066
22.043
21.945
21.744

Parameter	Value
Solvent	CDCl3
Temperature	298.3
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	734
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	11.6000
Acquisition Time	0.8651
Acquisition Date	2015-01-27T18:18:06
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



***exo*'-3l**

9000
8000
7000
6000
5000
4000
3000
2000
1000
0

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

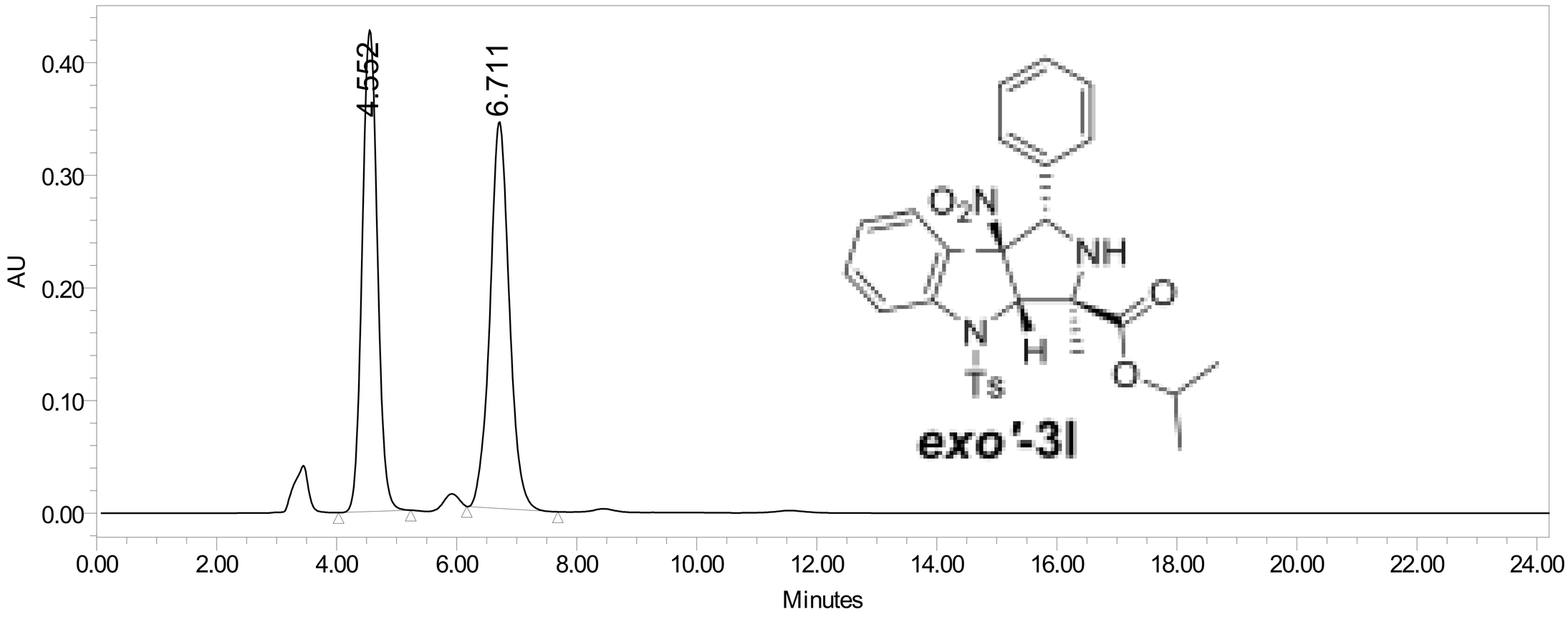
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_104_722014
Vial:	44	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:	7/2/2014 12:15:10 PM CDT		
Date Processed:	10/6/2015 3:19:11 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17267; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.552	7516517	49.38	427709
2	W2489 ChA 254nm	6.711	7706498	50.62	343362

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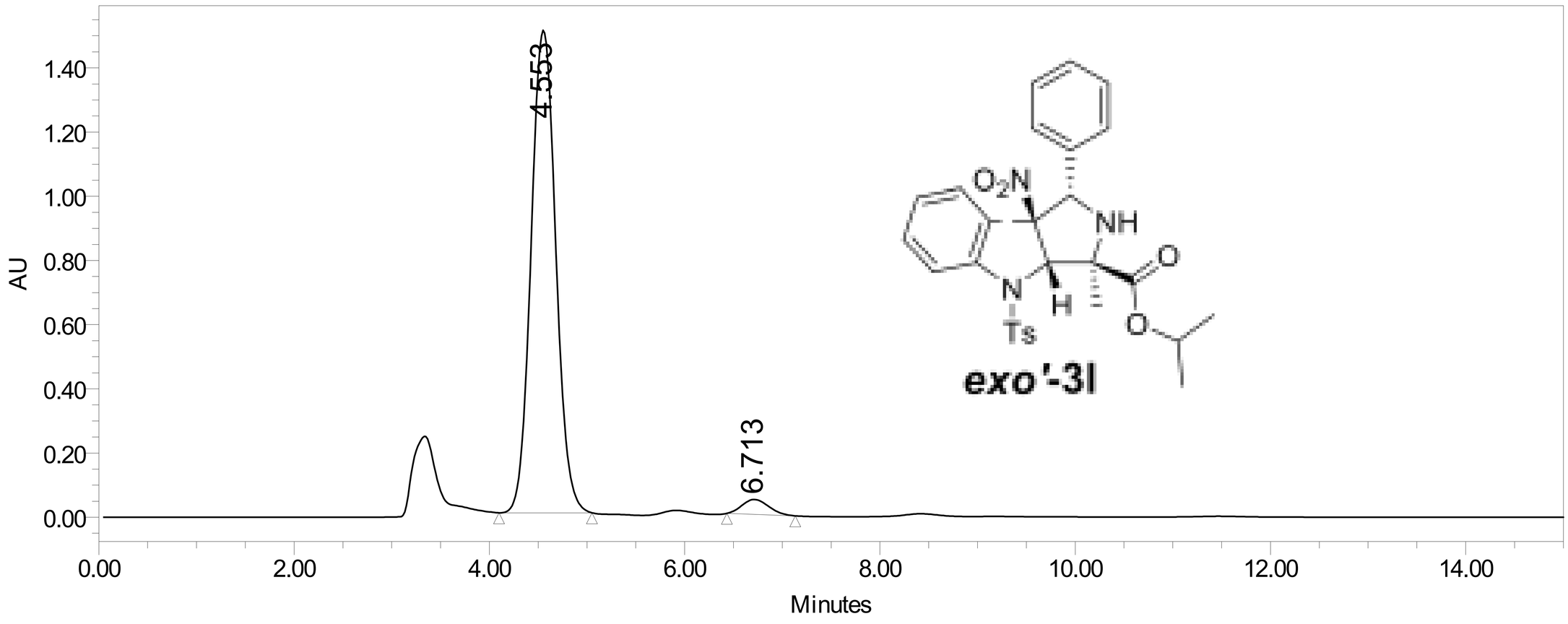
Injection Summary Report

SAMPLE INFORMATION

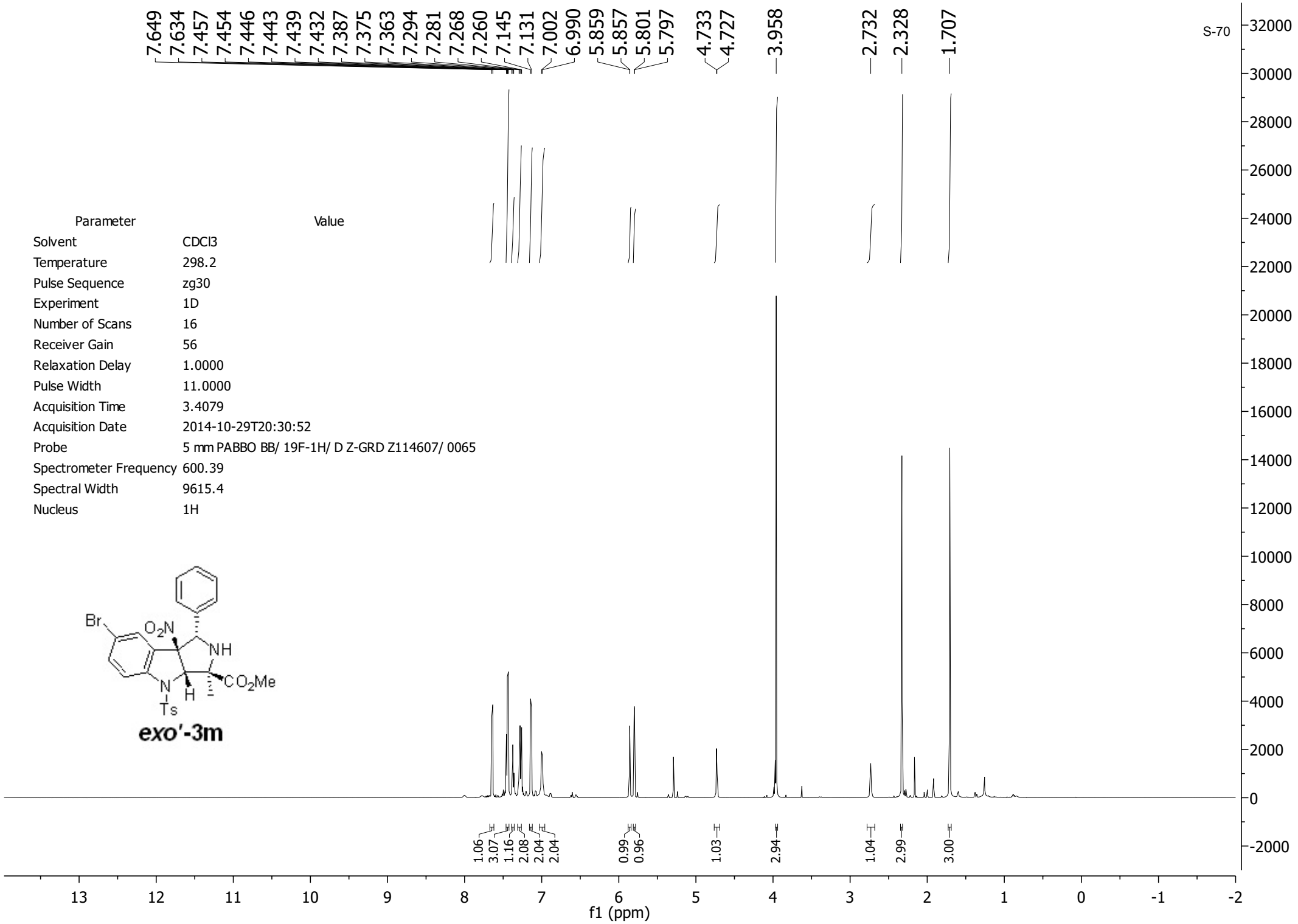
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_104_732014
Vial:	12	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	15.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/3/2014 1:43:31 PM CDT		
Date Processed:	10/6/2015 3:20:51 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17269; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	4.553	26395158	96.78	1503828
2	W2489 ChA 254nm	6.713	877874	3.22	46367

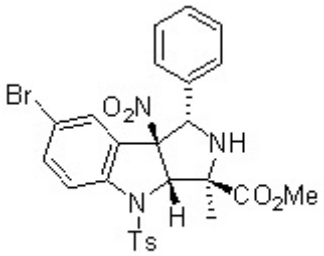


Parameter	Value
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	56
Relaxation Delay	1.0000
Pulse Width	11.0000
Acquisition Time	3.4079
Acquisition Date	2014-10-29T20:30:52
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	600.39
Spectral Width	9615.4
Nucleus	1H

***exo'*-3m**

175.594
145.451
143.693
134.728
134.490
132.441
132.181
130.071
129.692
128.459
128.319
127.644
126.120
118.273
116.861
100.878
77.442
77.230
77.019
74.705
69.255
69.046
53.640
22.133
21.775

Parameter	Value
Solvent	CDCl3
Temperature	298.3
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	180
Receiver Gain	177
Relaxation Delay	3.0000
Pulse Width	11.6000
Acquisition Time	0.8651
Acquisition Date	2014-10-29T20:34:05
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z114607/ 0065
Spectrometer Frequency	150.98
Spectral Width	37878.8
Nucleus	13C



***exo'*-3m**

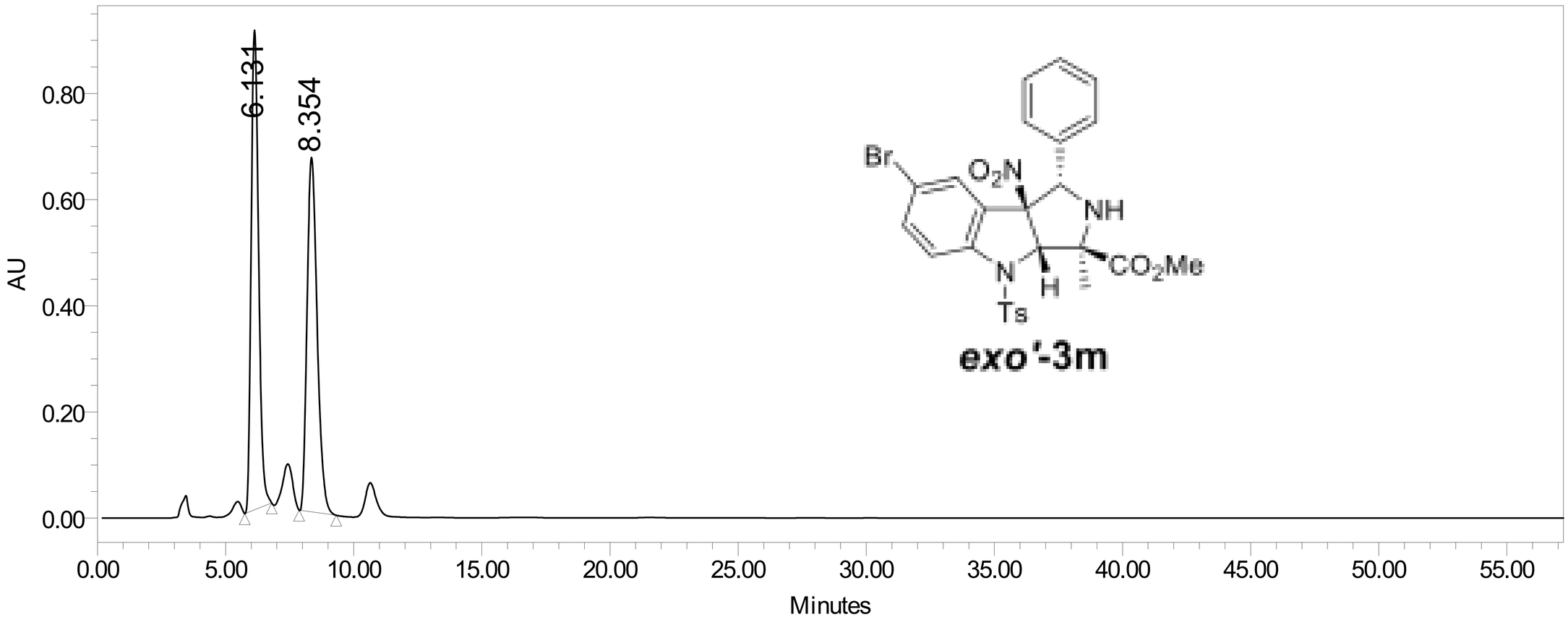
f1 (ppm)

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:	TG3_153_4_ADH20%IPA1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_153_9242014
Vial:	67	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:	9/24/2014 12:42:12 PM CDT		
Date Processed:	10/6/2015 3:22:12 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17271; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

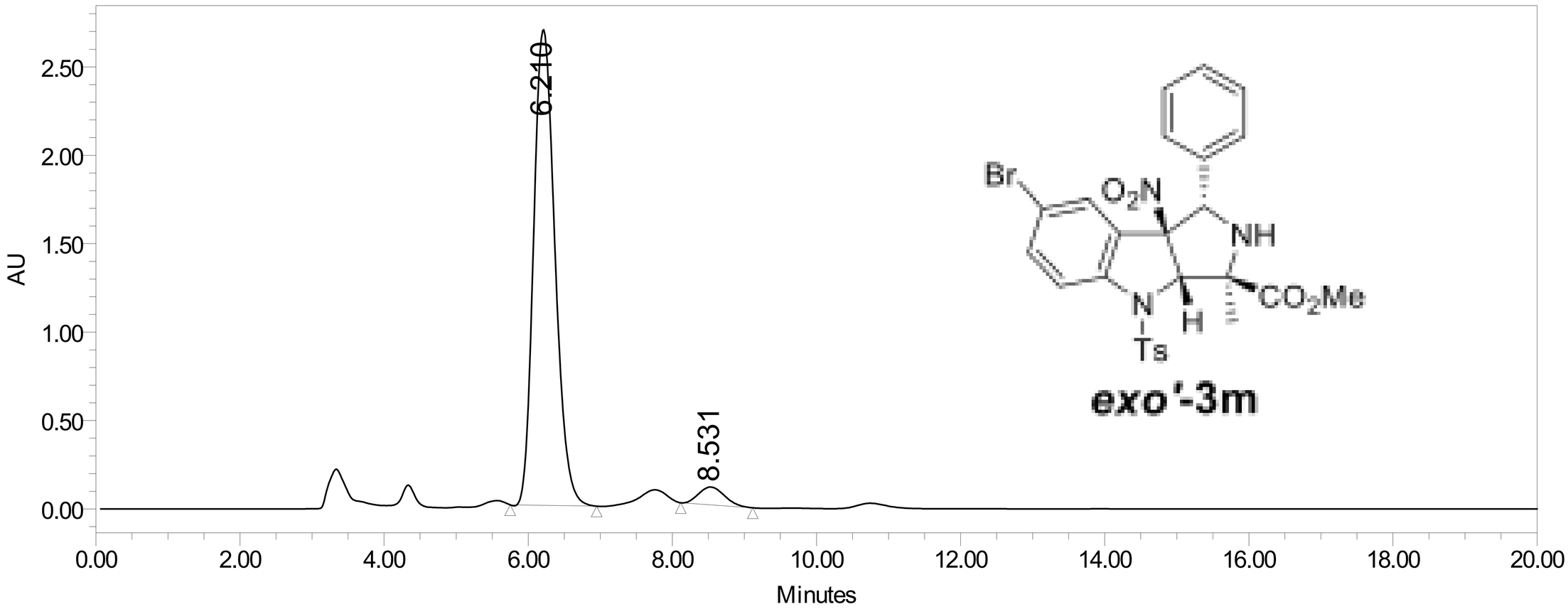
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.131	18240548	49.89	903684
2	W2489 ChA 254nm	8.354	18324443	50.11	667732

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

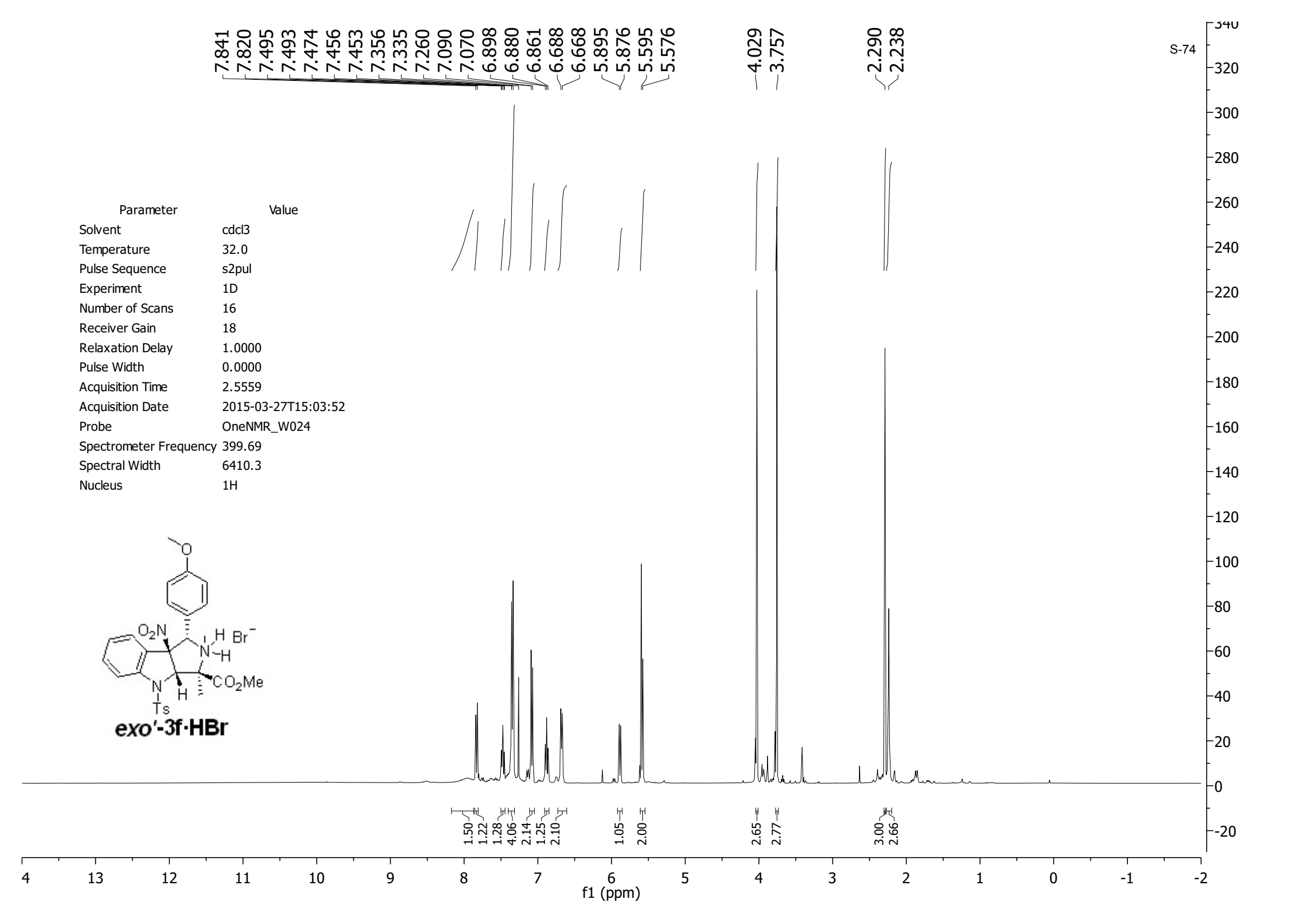
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	TG3_185_1_272015
Vial:	1	Acq. Method Set:	1_ADH 80_20 1mpm
Injection #:	1	Processing Method	Tony1
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	2/7/2015 4:03:11 PM CST		
Date Processed:	10/6/2015 3:23:34 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 17273; Processing Method: Tony1

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	6.210	55205963	95.64	2692804
2	W2489 ChA 254nm	8.531	2514957	4.36	101081


7.841
7.820
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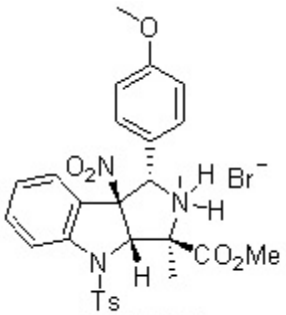
7.493
7.474
7.456
7.453
7.356
7.335
7.260
7.090
7.070
6.898
6.880
6.861
6.688
6.668
5.895
5.876
5.595
5.576
4.029
3.757
2.290
2.238
Parameter Value
Solvent cdcl3
Temperature 32.0
Pulse Sequence s2pul
Experiment 1D
Number of Scans 16
Receiver Gain 18
Relaxation Delay 1.0000
Pulse Width 0.0000
Acquisition Time 2.5559
Acquisition Date 2015-03-27T15:03:52
Probe OneNMR_W024
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
O2N
H Br−
N
H
CO2Me
N
H
Ts
exo'-3f·HBr
1.50
1.22
1.28
4.06
2.14
1.25
2.10
1.05
2.00
2.65
2.77
3.00
2.66
f1 (ppm)

169.789
161.002
145.685
144.902
133.475
131.966
131.190
130.015
129.459
127.546
125.318
120.764
118.855
114.041
99.731
77.548
77.435
77.230
76.912
74.214
71.805
68.881
55.409
54.920
21.715
19.208

Parameter	Value
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1006
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2015-04-06T15:07:13
Probe	OneNMR_W024
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



***exo*'-3f·HBr**

f1 (ppm)