Rhodium-Catalyzed, Enantioselective Hydroacylation of *ortho*-Allylbenzaldehydes

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Supporting Information

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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 nitrogen unless otherwise stated. All glassware for moisture sensitive reactions was dried in an oven at 140 °C for at least two hours before use. THF was 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. Anhydrous 1,4-dioxane and DMF were purchased from Aldrich and used as received. Flash column chromatography was performed on SiliFlash® P60 silica gel (40-63μm, 60Å) using hexanes, hexanes/ethyl acetate, hexanes/diethyl ether, or pentane/diethyl ether mixtures. Products were visualized on TLC by UV light or by staining with $KMnO_4$, ceric ammonium molybdate (CAM), vanillin or *o*-anisaldehyde.

HRMS (ESI) analysis was performed at the Iowa State University Chemical Instrumentation Facility on an Agilent 6540 QTOF spectrometer. HPLC analyses were carried out on a Waters Alliance HPLC system with an e2695 separations module and a 2489 dual wavelength detector. Optical rotations were measured on an Atago AP-300 automatic polarimeter using a 0.5 dm cell. The absolute configuration of compound **2a** was assigned as *R* based on comparison of the optical rotation with the literature value,[1,2] and the absolute configuration of compounds **2b**-**2n** were assigned by analogy. NMR spectra were acquired on Varian MR-400 and Bruker Avance III 600 spectrometers at the Iowa State University Chemical Instrumentation Facility. Chemical shifts are reported in ppm relative to residual solvent peaks ($CDCl_3$ = 7.26 ppm for ^1H and 77.16 ppm for ^{13}C) or an external standard (CF_3CO_2H:$CDCl_3$ = -77.56 ppm for ^{19}F). Coupling constants are reported in hertz.

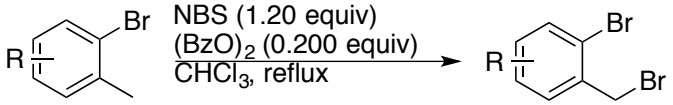
Materials

2-Bromobenzaldehyde, 2-bromobenzylbromide, 2-bromo-5-fluorotoluene, 2-bromo-5-fluorotoluene, 2-bromo-4-fluorotoluene, 2-bromo-5-chlorotoluene, 4-bromo-3-methylanisole, and 2,2'-bipyridine were purchased from AK Scientific and used without further purification. Ethylene glycol, benzoyl peroxide, α-bromostyrene, δ-valerolactone, 2,3-dibromopropene, pyridium chlorochromate (PCC), methyltriphenylphosphonium bromide, 6-bromopiperonal, 5-oxo-5-phenylvaleric acid, 1,5-cyclooctadiene, ethylmagnesium bromide (3.0 M in diethyl ether), vinylmagnesium bromide (1.0 M in THF), 1-propenylmagnesium bromide (0.5 M in THF), methyllithium (1.6 M in diethyl ether), diisobutylaluminum hydride (1.0 M in hexanes) and copper iodide were purchased from Sigma-Aldrich and used as received. *n*-Butyllithium solution (2.5 M in hexanes) was purchased from Sigma-Aldrich and titrated with recrystallized diphenylacetic acid. 2-Bromopropene was purchased from GFS Chemicals and used without further purification. *N*-bromosuccinimide (NBS) was purchased from Sigma-Aldrich and purified by recrystallization from H_2O before use. 2-Bromopent-1-ene was prepared according to a literature procedure[3] from 2,3-dibromopropene and ethylmagnesium bromide. 5-Bromo-6-(1,3-dioxolan-2-yl)benzo[*d*][1,3]dioxole was prepared according to a literature procedure[4,5] from 6-bromopiperonal and ethylene glycol. 5-Phenylhex-5-enal

(**5**) was prepared according to literature procedures from 5-oxo-5-phenylvaleric acid.[6] 2-(2-Bromoallyl)benzaldehyde was prepared according to a literature procedure from 2-bromobenzaldehyde, ethylene glycol and 2,3-dibromopropene.[7]

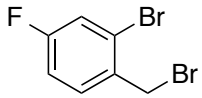
$[Rh(COD)Cl]_2$, $[Rh(COD)_2]BF_4$, *rac*-BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthalene), (*R*)-BINAP ((*R)*-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene), (*R*)-MeO-BIPHEP ((*R*)-2,2′-bis(diphenylphosphino)-1,1′-biphenyl), (*R*)-DTBM-MeO-BIPHEP ((*R*)-2,2′-bis(di(3,5-di-*t*-butyl-4-methoxyphenyl)phosphino)-6,6′-dimethoxy-1,1′-biphenyl), (R)-SEGPHOS ((*R*)-2,2′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole), (*R*)-DTBM-SEGPHOS ((*R*)-2,2′-bis(di(3,5-di-*t*-butyl-4-methoxyphenyl)phosphino)-4,4′-bi-1,3-benzodioxole) and silver tetrafluoroborate were purchased from Strem Chemicals and used without further purification. NaBARF (Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) was prepared according to a literature procedure.[8] $[Rh(COD)_2]BARF$ was prepared according to a literature procedure from $[Rh(COD)Cl]_2$, 1,5-cyclooctadiene and NaBARF.[9]

General Procedure A: Synthesis of *ortho*-Bromobenzylbromide S2b-S2e



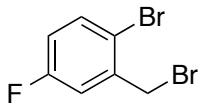
S2b-S2e

To a solution of the appropriate *ortho*-bromotoluene derivative in $CHCl_3$ was added NBS (1.20 equiv) and $(PhCO_2)_2$ (0.200 equiv). The reaction mixture was heated to reflux under N_2 for 6-24 h. The solution was cooled to room temperature and quenched by the addition of sat. $NaHCO_3$ solution. The organic layer was washed with $NaHCO_3$ (3x) and brine, then dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography or recrystallization to yield the appropriate *ortho*-bromobenzylbromide **S2b-S2e**.



S2b

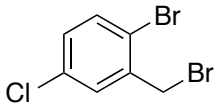
2-Bromo-1-(bromomethyl)-4-fluorobenzene[10,11] (S2b): Prepared according to general procedure A from 2-bromo-4-fluorotoluene (5.10 g, 27.0 mmol), NBS (5.77 g, 32.4 mmol) and $Ph(CO_2)_2$ (1.31 g, 5.40 mmol) under reflux for 6 h. The crude product was purified by flash column chromatography (95:5 Hex:EtOAc) to yield **S2b** (2.99 g, 11.14 mmol, 46%) as a white amorphous solid. m.p. = 50–51 °C (lit = 51–52 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.58 (s, 2H), 7.03 (ddd, *J* = 8.4, 8.0, 2.4 Hz, 1H), 7.33 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.44 (dd, *J* = 8.4, 5.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 32.6, 115.4 (d, *J* = 21.0 Hz), 120.8 (d, *J* = 24.2 Hz), 124.9 (d, *J* = 10.0 Hz), 132.4 (d, *J* = 8.8 Hz), 133.3 (d, *J* = 3.4 Hz), 162.3 (d, *J* = 251.6 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ -111.4 (m, 1F).



S2c

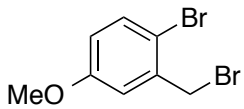
1-Bromo-2-(bromomethyl)-4-fluorobenzene[12] (S2c): Prepared according to general procedure A from 2-bromo-5-fluorotoluene (5.10 g, 27.0 mmol), NBS (5.77 g, 32.4 mmol) and $Ph(CO_2)_2$ (1.31 g, 5.40 mmol) under reflux for 24 h. The crude product was purified by flash column chromatography (95:5 Hex:EtOAc) to yield **S2c** (2.36 g, 8.91

mmol, 33%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.54 (s, 2H), 6.91 (ddd, *J* = 8.8, 8.8, 3.2 Hz, 1H), 7.20 (dd, *J* = 8.8, 3.2 Hz, 1H), 7.53 (dd, *J* = 8.8, 5.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.5, 47.3 (d, *J* = 22.0 Hz), 48.1 (d, *J* = 23.0 Hz), 48.5 (d, *J* = 3.2 Hz), 64.5 (d, *J* = 7.8 Hz), 68.8 (d, *J* = 7.6 Hz), 91.8 (d, *J* = 246.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ -114.5 (m, 1F).



S2d

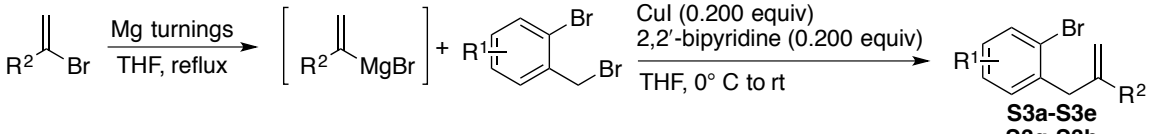
1-Bromo-2-(bromomethyl)-4-chlorobenzene[10] (S2d): Prepared according to general procedure A from 2-bromo-5-chlorotoluene (5.55 g, 27.0 mmol), NBS (5.77 g, 32.4 mmol) and $Ph(CO_2)_2$ (1.31 g, 5.40 mmol) under reflux for 18 h. The crude product was purified by flash column chromatography (95:5 Hex:EtOAc) to yield **S2d** (2.74 g, 9.65 mmol, 36%) as a pale orange amorphous solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.53 (s, 2H), 7.15 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 32.3, 122.2, 130.1, 131.0, 133.7, 134.3, 138.6.



S2e

1-Bromo-2-(bromomethyl)-4-methoxybenzene[13] (S2e): Prepared according to general procedure A from 4-bromo-3-methylanisole (8.04 g, 40.0 mmol), NBS (8.54 g, 48.0 mmol) and $Ph(CO_2)_2$ (1.94 g, 8.00 mmol) under reflux for 24 h. The crude product was purified by recrystallization from hexanes to yield **S2e** (3.44 g, 12.3 mmol, 31%) as a white crystalline solid. m.p = 92-93 °C (lit = 92-93 °C) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.80 (s, 3H), 4.56 (s, 2H), 6.74 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.99 (d, *J* = 3.0 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 33.6, 55.7, 114.8, 116.2, 116.7, 134.0, 137.9, 159.3.

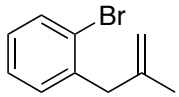
General Procedure B: Synthesis of S3a-S3e, **S3g-S3h, S3o, and S7**



S3a-S3e
S3g-S3h
S3o, S7

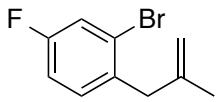
To an oven-dried schlenk flask equipped with a stir bar and under nitrogen atmosphere was added Mg turnings (2.20-3.50 equiv), a few crystals of I_2 and anhydrous THF (4-50 mL). In a separate oven-dried round bottom flask, a solution of the appropriate vinyl bromide (1.67-2.50 equiv) in anhydrous THF (4-10 mL) was prepared. An initial volume of 1 mL of the vinyl bromide solution was added to the Mg suspension and the mixture was heated gently with a heat gun to initiate formation of the Grignard reagent. The remaining vinyl bromide solution was added slowly, keeping the solution of Grignard reagent at reflux. The reaction mixture was refluxed for an additional 2-4 hours and cooled to room temperature. To an oven-dried 100 mL round bottom flask was added the appropriate 2-bromobenzylbromide (1.00 equiv), CuI (0.200 equiv), 2,2′-bipyridine (0.200 equiv) and dry THF (10 mL), and the mixture was cooled to 0 °C. The solution of Grignard reagent was slowly transferred to this mixture via cannula. The combined reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched by the addition of sat. NH_4Cl solution and extracted with Et_2O

(3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography to yield the appropriate *ortho*-allylbromobenzene derivative **S3a**-**S3e**, **S3g**-**S3h**, **S3o, S7**. As noted with each compound, HRMS values for **S3b**-**S3e** were found after loss of a -C_3H_5 unit.



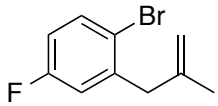
S3a

1-Bromo-2-(2-methylallyl)benzene[14] **(S3a):** Prepared according to general procedure B from 2-bromopropene (2.42 g, 20.0 mmol) and 2-bromobenzylbromide (2.99 g, 12.0 mmol). The crude product was purified by flash column chromatography (100% hexanes) to yield **S3a** (1.78 g, 8.42 mmol, 70%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.76 (s, 3H), 3.46 (s, 2H), 4.59 (s, 1H), 4.86 (s, 1H), 7.05-7.10 (m, 1H), 7.18-7.29 (m, 2H), 7.55 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.6, 44.0, 112.5, 125.3, 127.3, 127.9, 131.0, 132.9, 139.2, 143.5.



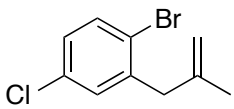
S3b

2-Bromo-4-fluoro-1-(2-methylallyl)benzene (S3b): Prepared according to general procedure B from 2-bromopropene (1.09 g, 9.00 mmol) and **S2b (**1.45 g, 5.40 mmol). The crude product was purified by flash column chromatography (98:2 Hex:EtOAc) to yield **S3b** (0.794 g, 3.47 mmol, 64%) as a yellow oil containing 5% 1-fluoro-4-(2-methylallyl)benzene. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.74 (s, 3H), 3.42 (s, 2H), 4.57 (s, 1H), 4.86 (s, 1H), 6.98 (ddd, J = 8.4, 8.4, 2.8 Hz, 1H), 7.19 (dd, J = 8.4, 6.0 Hz, 1H), 7.30 (dd, J = 8.4, 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.5, 43.2, 112.7, 114.5 (d, J = 20.4 Hz), 119.9 (d, J = 24.0 Hz), 124.9 (d, J = 9.2 Hz), 131.6 (d, J = 8.0 Hz), 135.1 (d, J = 3.4 Hz), 143.4, 161.0 (d, J = 247.4 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ -115.7 (m, 1F). HRMS (ESI) calcd. for $C_{10}H_{10}BrF$ ($M+H^+$-C_3H_5) 186.9558, found 186.9551.



S3c

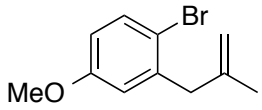
1-Bromo-4-fluoro-2-(2-methylallyl)benzene (S3c): Prepared according to general procedure B from 2-bromopropene (1.09 g, 9.00 mmol) and **S2c** (1.45 g, 5.40 mmol, 0.600 equiv). The crude product was purified by flash column chromatography (98:2 Hex:EtOAc) to yield **S3c** (0.425 g, 1.86 mmol, 34%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.76 (s, 3H), 3.43 (s, 2H), 4.64 (s, 1H), 4.90 (s, 1H), 6.83 (ddd, J = 9.6, 8.8, 3.2 Hz, 1H), 6.97 (dd, J = 9.6, 3.2 Hz, 1H), 7.50 (dd, J = 8.8, 5.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.6, 44.1, 113.2, 115.1 (d, J = 22.4 Hz), 117.6 (d, J = 22.8 Hz), 119.2 (d, J = 3.0 Hz), 133.9 (d, J = 7.8 Hz), 141.4 (d, J = 7.6 Hz), 142.9, 162.1 (d, J = 245.2 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): δ -116.0 (m, 1F). HRMS (ESI) calcd. for C_7H_5BrF ($M+H^+$-C_3H_5) 186.9558, found 186.9549.



S3d

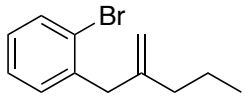
1-Bromo-4-chloro-2-(2-methylallyl)benzene (S3d): Prepared according to general procedure B from 2-bromopropene (2.42 g, 20.0 mmol) and **S2d** (2.28 g, 8.00 mmol). The crude product was purified by flash column chromatography (100% hexanes) to yield **S3d** (1.25 g, 5.10 mmol, 64%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.75 (s, 3H), 3.41 (s, 2H), 4.62 (s, 1H), 4.89 (s, 1H), 7.06 (dd, J = 8.4, 2.8 Hz, 1H), 7.21 (d, J = 2.8 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.9, 43.8,

113.1, 127.4, 127.9, 130.6, 133.3, 133.8, 140.9, 142.7. HRMS (ESI) calcd. for $C_{10}H_{10}BrCl$ ($M+H^+-C_3H_5$) 202.9263, found 202.9260.



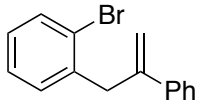
S3e

1-Bromo-4-methoxy-2-(2-methylallyl)benzene (S3e): Prepared according to general procedure B from 2-bromopropene (2.06 g, 17.0 mmol) and **S2e** (2.86 g, 10.2 mmol). The crude product was purified by flash column chromatography (100% hexanes) to yield **S3e** (1.55 g, 6.41 mmol, 63%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.78 (s, 3H), 3.43 (s, 2H), 3.78 (s, 3H), 4.65 (s, 1H), 4.89 (s, 1H), 6.66 (dd, J = 8.8, 3.0 Hz, 1H), 6.81 (d, J = 3.0 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.6, 44.2, 55.4, 112.6, 113.6, 115.7, 116.5, 133.3, 140.2, 143.4, 159.0. HRMS (ESI) calcd. for $C_{11}H_{13}BrO$ ($M+H^+-C_3H_5$) 198.9759, found 198.9753.



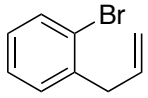
S3g

1-Bromo-2-(2-methylenepentyl)benzene (S3g): Prepared according to general procedure B from 2-bromopent-1-ene (2.09 g, 14.0 mmol) and 2-bromobenzylbromide (2.10 g, 8.40 mmol). The crude product was purified by flash column chromatography (100% hexanes) to yield **S3g** (0.681 g, 2.85 mmol, 34%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94 (t, J = 7.6, 3H), 1.54 (m, 2H), 2.05 (t, J = 7.6 Hz, 2H), 3.47 (s, 2H), 4.58 (s, 1H), 4.88 (s, 1H), 7.03-7.09 (m, 1H), 7.20-7.26 (m, 2H), 7.55 (dd, J = 7.2, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.0, 21.0, 38.4, 42.4, 111.6, 125.3, 127.3, 127.8, 131.1, 132.9, 139.4, 147.4. HRMS (ESI) calcd. for $C_{12}H_{15}Br$ ($M+H^+-C_5H_9$) 168.9653, found 168.9645.



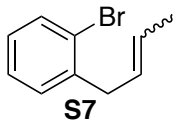
S3h

1-Bromo-2-(2-phenylallyl)benzene (S3h): Prepared according to general procedure B from α-bromostyrene (3.66 g, 20.0 mmol) and 2-bromobenzylbromide (2.99 g, 12.0 mmol). The crude product was purified by flash column chromatography (100% hexanes) to yield **S3h** (1.70 g, 6.23 mmol, 52%) as a pale yellow oil which contained 10% of prop-2-ene-1,2-diyldibenzene. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.93 (s, 2H), 4.86 (s, 1H), 5.52 (s, 1H), 7.07 (ddd, J = 8.0, 2.4, 1.6 Hz, 1H), 7.18-7.34 (m, 5H), 7.47 (m, 2H), 7.56 (dd, J = 8.0, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 41.5, 114.8, 125.3, 126.1, 127.5, 127.8, 128.0, 128.5, 131.1, 132.9, 139.1, 140.8, 145.6. HRMS (ESI) calcd. for $C_{15}H_{13}Br$ ($M+H^+-C_8H_7$) 168.9653, found 168.9647.



S3o

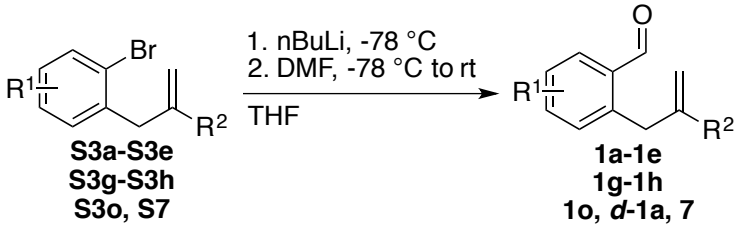
1-Allyl-2-bromobenzene[14,15] **(S3o):** Prepared according to a modified version of general procedure B from vinylmagnesium bromide (12.0 mL of a 1.00 M solution, 12.00 mmol) and 2-bromobenzylbromide (1.80 g, 7.20 mmol). The crude product was purified by flash column chromatography (100% hexanes) to yield **S3o** (0.880 g, 4.46 mmol, 37%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.52 (d, J = 6.4 Hz, 2H), 5.05-5.14 (m, 2H), 5.98 (ddt, J = 16.8, 10.0, 6.4 Hz, 1H), 7.05 – 7.11 (m, 1H), 7.15-7.32 (m, 2H), 7.55 (dd, J = 8.4, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.3, 116.7, 124.7, 127.6, 128.0, 130.6, 132.9, 135.7, 139.6.



S7

1-Bromo-2-(but-2-en-1-yl)benzene[16] (S7): Prepared according to a modified version of general procedure B from 1-propenylmagnesium bromide (24.0 mL of a 0.5 M solution, 12.00 mmol) and 2-bromobenzylbromide (1.80 g, 7.20 mmol). The crude product was purified by flash column chromatography (100% hexanes) to yield **S7** as a mixture of isomers (*E:Z* = 1.6:1.0) (1.38 g, 6.53 mmol, 54%) as a colorless oil. Spectral data is consistent with previous reports.[16]

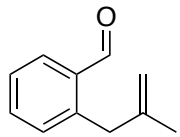
General Procedure C: Synthesis of *ortho*-Allylbenzaldehydes 1a-1e, **1g-h**, **1o, *d*-1a, 7**



S3a-S3e
S3g-S3h
S3o, S7

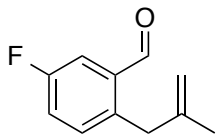
1a-1e
1g-1h
1o, *d*-1a, 7

To a solution of the appropriate *ortho*-allylbromobenzene derivative **S3a-S3e, S3g-S3h**, **S3o** and **S7** (1.00 equiv) in THF at -78 °C was added *n*-BuLi (1.00-1.10 equiv of 1.10-1.80M solutions in hexanes), dropwise. This solution was kept at -78 °C for 1 hour, warmed to room temperature for 30 minutes, and then cooled back to -78 °C for 10 minutes before DMF (1.50-3.00 equiv) was added dropwise. The solution was allowed to warm to room temperature overnight before it was quenched by the addition of a sat. NH_4Cl solution. The reaction mixture was extracted with Et_2O (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexanes:EtOAc) to yield the appropriate *ortho*-allylbenzaldehyde **1a-1e**, **1g-h, 1o, *d*-1a**, and **7**.



1a

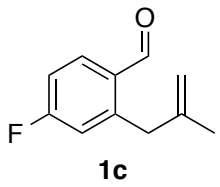
2-(2-Methylallyl)benzaldehyde[14,15] (1a): Prepared according to general procedure C from **S3a** (1.27 g, 6.00 mmol), *n*-BuLi (5.08 mL of a 1.30 M solution in hexanes, 1.10 equiv) and DMF (1.34 mL, 3.00 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1a** (0.779 g, 4.86 mmol, 81%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.78 (s, 3H), 3.73 (s, 2H), 4.45 (s, 1H), 4.84 (s, 1H), 7.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.40 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.53 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.25 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.1, 40.3, 112.6, 127.1, 130.7, 131.8, 134.0, 134.4, 142.2, 145.4, 192.2.



1b

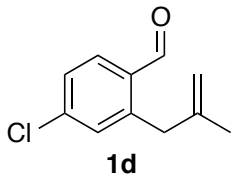
5-Fluoro-2-(2-methylallyl)benzaldehyde (1b): Prepared according to general procedure C from **S3b** (0.401 g, 1.75 mmol), *n*-BuLi (1.41 mL of a 1.30 M solution in hexanes, 1.05 equiv) and DMF (0.20 mL, 1.50 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1b** (0.093 g, 0.522 mmol, 30%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.78 (s, 3H), 3.68 (s, 2H), 4.44 (s, 1H), 4.86 (s, 1H), 7.20-7.28 (m, 2H), 7.57 (dd, *J* = 8.8, 1.2 Hz, 1H), 10.2 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.9, 39.5, 112.9,

115.8 (d, J = 35.7), 121.0 (d, J = 21.6 Hz), 133.5 (d, J = 7.0 Hz), 135.8 (d, J = 6.0 Hz), 137.9 (d, J = 3.2 Hz), 145.2, 161.8 (d, J = 246.0), 190.5. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -115.9 (m, 1F). HRMS (ESI) calcd. for $C_{11}H_{11}FO$ ($M+H^+$) 179.0867, found 179.0860.



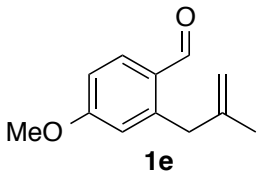
1c

4-Fluoro-2-(2-methylallyl)benzaldehyde (1c): Prepared according to general procedure C from **S3c** (0.401 g, 1.75 mmol), *n*-BuLi (1.41 mL of a 1.30 M solution in hexanes, 1.05 equiv) and DMF (0.20 mL, 1.50 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1c** (0.164 g, 0.92 mmol, 53%) as a yellow oil.^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.78 (s, 3H), 3.73 (s, 2H), 4.50 (s, 1H), 4.88 (s, 1H), 6.99 (dd, J = 9.6, 2.8 Hz, 1H), 7.07 (ddd, J = 9.6, 8.4, 2.8 Hz, 1H), 7.89 (dd, J = 8.4, 6.0 Hz, 1H), 10.17 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.9, 40.1, 113.2, 114.4 (d, J = 22.0 Hz), 118.4 (d, J = 22.0 Hz), 131.0 (d, J = 2.6 Hz), 133.6 (d, J = 10.0 Hz), 144.4, 145.6 (d, J = 9.0 Hz), 166.0 (d, J = 255.0 Hz), 190.4. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -104.9 (m, 1F). HRMS (ESI) calcd. for $C_{11}H_{11}FO$ ($M+H^+$) 179.0867, found 179.0863.



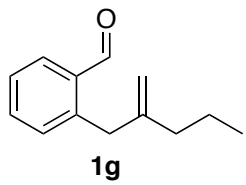
1d

4-Chloro-2-(2-methylallyl)benzaldehyde (1d): Prepared according to general procedure C from **S3d** (0.908 g, 3.70 mmol), *n*-BuLi (3.13 mL of a 1.30 M solution in hexanes, 1.10 equiv) and DMF (0.86 mL, 3.00 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1d** (0.219 g, 1.12 mmol, 30%) as a yellow oil.^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.78 (s, 3H), 3.70 (s, 2H), 4.48 (s, 1H), 4.88 (s, 1H), 7.28 (d, J = 2.0 Hz, 1H), 7.37 (dd, J = 8.2, 2.0 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 10.18 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.0, 40.0, 113.3, 127.5, 131.6, 132.0, 132.8, 140.3, 144.0, 144.5, 190.8. HRMS (ESI) calcd. for $C_{11}H_{11}ClO$ ($M+H^+$) 195.0571, found 195.0568.



1e

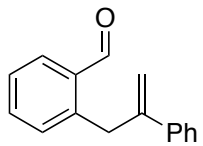
4-Methoxy-2-(2-methylallyl)benzaldehyde (1e): Prepared according to general procedure C from **S3e** (1.09 g, 4.50 mmol), *n*-BuLi (3.46 mL of a 1.30 M solution in hexanes, 1.00 equiv) and DMF (0.520 mL, 1.50 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1e** (0.703 g, 3.70 mmol, 82%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.70 (s, 3H), 3.64 (s, 2H), 3.79 (s, 3H), 4.44 (s, 1H), 4.77 (s, 1H), 6.70 (d, J = 2.4 Hz, 1H), 6.80 (dd, J = 8.8, 2.4 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 10.01 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.9, 40.4, 55.5, 112.1, 112.5, 116.8, 128.0, 133.5, 144.7, 144.9, 163.6, 190.6. HRMS (ESI) calcd. for $C_{12}H_{14}O_2$ ($M+H^+$) 191.1067, found 191.1065.



1g

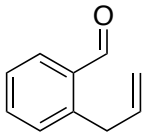
2-(2-Methylenepentyl)benzaldehyde (1g): Prepared according to general procedure C from **S3g** (0.957 g, 4.00 mmol), *n*-BuLi (2.33 mL of a 1.80 M solution in hexanes, 1.05 equiv) and DMF (0.93 mL, 3.00 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1g** (0.296 g, 1.57 mmol, 39%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (t, J = 7.6 Hz, 3H), 1.41 – 1.53 (m, 2H), 2.01 (t, J = 7.2 Hz, 2H), 3.68 (s, 2H), 4.36 (s, 1H),

4.80 (s, 1H), 7.22 (dd, J = 7.6, 1.0 Hz, 1H), 7.33 (ddd, J = 7.6, 7.6, 1.0 Hz, 1H), 7.46 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.82 (dd, J = 7.6, 1.2 Hz, 1H), 10.18 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.8, 20.9, 38.7, 38.7, 111.7, 126.9, 130.4, 131.8, 133.8, 134.4, 142.2, 149.3, 192.0. HRMS (ESI) calcd. for $C_{13}H_{16}O$ ($M+H^+$) 189.1274, found 189.1271.



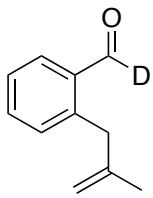
1h

2-(2-Phenylallyl)benzaldehyde[7,17] (1h): Prepared according to general procedure C from **S3h** (1.09 g, 4.00 mmol), *n*-BuLi (2.33 mL of a 1.80 M solution in hexanes, 1.05 equiv) and DMF (0.93 mL, 3.00 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1h** (0.332 g, 1.49 mmol, 37%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.18 (s, 2H), 4.66 (d, J = 1.2 Hz, 1H), 5.41 (d, J = 1.2 Hz, 1H), 7.16-7.34 (m, 5H), 7.40-7.44 (m, 3H), 7.80 (dd, J = 6.4, 1.2 Hz, 1H), 10.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.6, 114.9, 126.0, 127.0, 127.8, 128.4, 131.5, 131.6, 133.9, 134.2, 140.9, 141.7, 147.5, 192.3. HRMS (ESI) calcd. for $C_{16}H_{14}O$ ($M+Na^+$) 245.0937, found 245.0935.



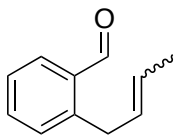
1o

2-Allylbenzaldehyde[14,15] (1o): Prepared according to general procedure C from **S3o** (0.788 g, 4.00 mmol), *n*-BuLi (4.00 mL of a 1.10 M solution in hexanes, 1.10 equiv) and DMF (0.93 mL, 3.00 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1o** (0.344 g, 2.36 mmol, 59%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.82 (d, J = 6.4 Hz, 2H), 4.98 (dd, J = 17.2, 1.8 Hz, 1H), 5.09 (dd, J = 10.2, 1.8 Hz, 1H), 6.05 (ddt, J = 17.2, 10.2, 6.4, 1H), 7.30 (dd, J = 7.6, 0.8 Hz, 1H), 7.40 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.55 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.85 (dd, J = 7.6, 0.8 Hz 1H), 10.26 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.5, 116.4, 126.9, 131.6, 131.6, 133.8, 133.9, 136.9, 142.2, 192.3.



***d*-1a**

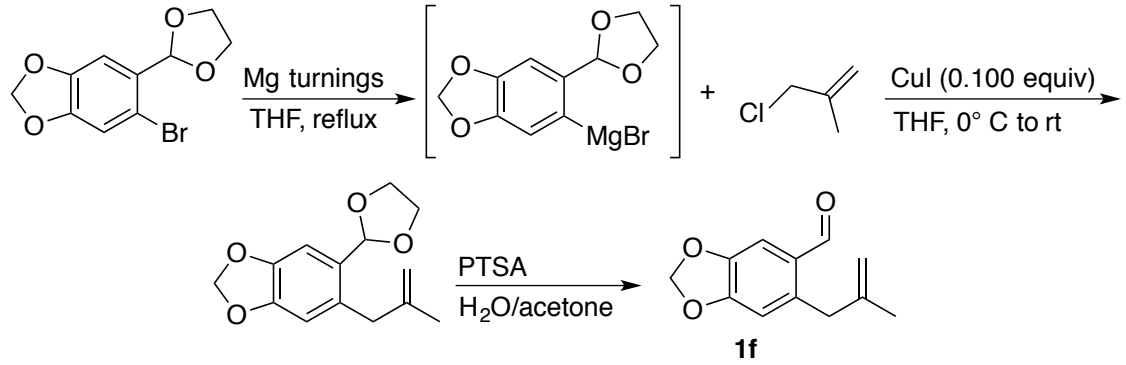
***d*$_1$-2-(2-Methylallyl)benzaldehyde (*d*-1a):** Prepared according to a modified version of general procedure C from **S3a** (0.866 g, 4.10 mmol), *n*-BuLi (1.87 mL of a 2.30 M solution in hexanes, 1.05 equiv) and DMF-d_7 (0.957 mL, 3.00 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield ***d*-1a** (0.414 g, 2.57 mmol, 63%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.78 (s, 3H), 3.72 (s, 2H), 4.45 (s, 1H), 4.84 (s, 1H), 7.28 (dd, J = 7.6, 0.8 Hz, 1H), 7.39 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.53 (ddd, J = 8.0, 7.6, 0.8 Hz, 1H), 7.87 (dd, 8.0, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.0, 40.3, 112.6, 127.1, 130.6, 131.7, 134.0, 134.3 (t, J = 3.0 Hz), 142.2, 145.4, 191.9 (t, J = 26.4 Hz). HRMS (ESI) calcd. for $C_{11}H_{11}DO$ ($M+H^+$) 162.1024, found 162.1021.

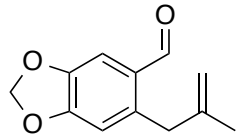


7

2-(But-2-en-1-yl)benzaldehyde[18] (7): Prepared according to general procedure C from **S7** (1.37 g, 6.50 mmol), *n*-BuLi (2.83 mL of a 2.30 M solution in hexanes, 1.00 equiv) and DMF (1.50 mL, 3.00 equiv). The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **7** (0.797 g, 4.97 mmol, 76%) as a yellow oil (*E:Z* = 1.3:1). Spectral data is consistent with previous reports.[18]

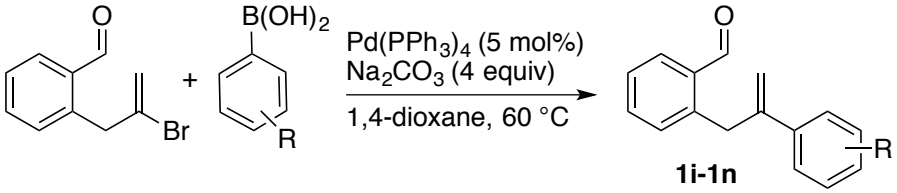
Synthesis of 6-(2-Methylallyl)benzo[*d*][1,3]dioxole-5-carbaldehyde 1f



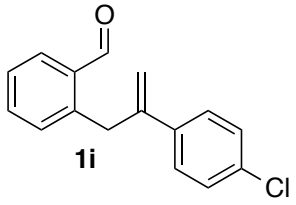


6-(2-Methylallyl)benzo[*d*][1,3]dioxole-5-carbaldehyde (1f): To an oven-dried schlenk flask equipped with a stir bar and under nitrogen atmosphere was added Mg turnings (0.182 g, 7.50 mmol, 1.50 equiv), a few crystals of I_2 and anhydrous THF (20 mL). In a separate oven-dried round bottom flask, a solution of 5-bromo-6-(1,3-dioxolan-2-yl)benzo[*d*][1,3]dioxole (1.37 g, 5.00 mmol, 1.00 equiv) in anhydrous THF (8 mL) was prepared. An initial volume of 1 mL of the solution of 5-bromo-6-(1,3-dioxolan-2-yl)benzo[*d*][1,3]dioxole was added to the Mg suspension via syringe and the mixture was heated gently with a heat gun to initiate the formation of the Grignard reagent. The remaining solution of 5-Bromo-6-(1,3-dioxolan-2-yl)benzo[*d*][1,3]dioxole was added slowly while keeping the solution of the Grignard reagent at reflux. The reaction mixture was refluxed for an additional 2 hours and cooled to room temperature. To an oven-dried 100 mL round bottom flask was added 3-chloro-2-methylprop-1-ene (0.734 mL, 7.50 mmol, 1.50 equiv), CuI (0.143 g, 0.750 mmol, 0.100 equiv) and dry THF (10 mL), and the mixture was cooled to 0 °C. The solution of the Grignard reagent was slowly transferred to this mixture via cannula. The combined reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched by the addition of sat. NH_4Cl solution and extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was refluxed for 2 h following the addition of 20 mL H_2O, 20 mL acetone and PTSA (150 mg). Upon cooling to room temperature, the product was extracted with CH_2Cl_2 (3x), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1f** (0.209 g, 1.02 mmol, 20%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.76 (s, 3H), 3.63 (s, 2H), 4.52 (s, 1H), 4.86 (s, 1H), 6.03 (s, 2H), 6.71 (s, 1H), 7.35 (s, 1H), 10.1 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.8, 40.0, 102.0, 108.0, 111.1, 112.9, 129.1, 139.8, 145.2, 147.2, 152.6, 189.6. HRMS (ESI) calcd. for $C_{12}H_{12}O_3$ ($M+H^+$) 205.0859, found 205.0859.

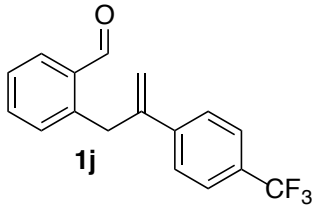
General Procedure D: Synthesis of *ortho*-Allylbenzaldehydes 1i-1n



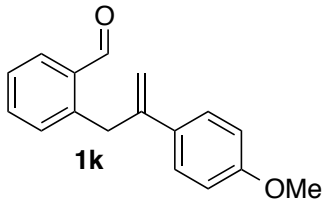
Compounds **1i-1n** were prepared according to a procedure reported by Glorius *et al*.[7] To an oven dried Schlenk flask was added $Pd(PPh_3)_4$ (0.050-0.100 mmol, 0.05 equiv), the appropriate arylboronic acid (1.20-3.00 mmol, 1.50 equiv), 1.6-4.0 mL of a 2M solution of aqueous Na_2CO_3, 2-(2-bromoallyl)benzaldehyde (0.800-2.00 mmol, 1.00 equiv) and 4-10 mL of 1,4-dioxane. The flask was evacuated and backfilled with nitrogen three times and stirred for 16 hours at 60 °C. The reaction was quenched with 10 mL of water and extracted with 20 mL EtOAc (3x). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography (Hex:EtOAc) to yield *ortho*-allylbenzaldehydes **1i-1n**.



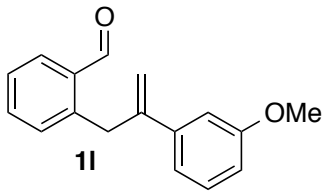
2-(2-(4-Chlorophenyl)allyl)benzaldehyde (1i): Prepared according to general procedure D from $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, 0.05 equiv), 4-chlorophenylboronic acid (469 mg, 3.00 mmol, 1.50 equiv), 4 mL of a 2M aqueous Na_2CO_3 solution, 2-(2-bromoallyl)benzaldehyde (450 mg, 2.00 mmol, 1.00 equiv) and 10 mL 1,4-dioxane. The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1i** (0.378 g, 1.47 mmol, 74%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.23 (s, 2H), 4.75 (s, 1H), 5.44 (s, 1H), 7.27-7.31 (m, 3H), 7.38-7.45 (m, 3H), 7.52 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.84 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.2 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.8, 115.4, 127.3, 127.5, 128.6, 131.6, 132.5, 133.6, 134.0, 134.2, 139.4, 141.4, 146.4, 192.6. HRMS (ESI) calcd. for $C_{16}H_{13}ClO$ ($M+H^+$) 257.0728, found 257.0723.



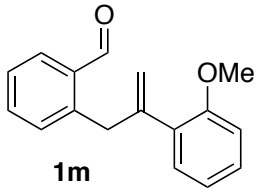
2-(2-(4-(Trifluoromethyl)phenyl)allyl)benzaldehyde[7] (1j): Prepared according to general procedure D from $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, 0.05 equiv), 4-(trifluoromethyl)phenylboronic acid (570 mg, 3.00 mmol, 1.50 equiv), 4 mL of a 2M aqueous Na_2CO_3 solution, 2-(2-bromoallyl)benzaldehyde (450 mg, 2.00 mmol, 1.00 equiv) and 10 mL 1,4-dioxane. The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1j** (0.432 g, 1.49 mmol, 74%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.26 (s, 2H), 4.83 (s, 1H), 5.50 (s, 1H), 7.31 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.40 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 7.53 (ddd, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.58 (s, 4H), 7.87 (dd, *J* = 7.6, 1.2 Hz, 1H), 10.2 (s, 1H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.8, 116.6, 124.3 (q, *J* = 270.5 Hz), 125.5 (q, *J* = 3.8 Hz), 126.5, 127.4, 129.8 (q, *J* = 32.4 Hz), 131.7, 133.0, 134.0, 134.2, 141.0, 144.6 (q, *J* = 1.4 Hz), 146.5, 192.7.^{19}F NMR ($CDCl_3$, 376 MHz): δ -62.5 (s, 1F). HRMS (ESI) calcd. for $C_{17}H_{13}F_3O$ ($M+H^+$) 291.0991, found 291.0995.



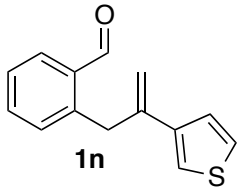
2-(2-(4-Methoxyphenyl)allyl)benzaldehyde[7] (1k): Prepared according to general procedure D from $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, 0.05 equiv), 4-methoxyphenylboronic acid (456 mg, 3.00 mmol, 1.50 equiv), 4 mL of a 2M aqueous Na_2CO_3 solution, 2-(2-bromoallyl)benzaldehyde (450 mg, 2.00 mmol, 1.00 equiv) and 10 mL 1,4-dioxane. The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1k** (0.324 g, 1.28 mmol, 64%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.81 (s, 3H), 4.22 (s, 2H), 4.64 (s, 1H), 5.41 (s, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.32 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.37 – 7.44 (m, 3H), 7.51 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.2 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.8, 55.4, 113.6, 113.8, 127.1, 127.2, 131.5, 131.6, 133.3, 134.0, 134.2, 142.0, 146.7, 159.4, 192.5. HRMS (ESI) calcd. for $C_{17}H_{16}O_2$ ($M+H^+$) 253.1223, found 253.1228.



2-(2-(3-Methoxyphenyl)allyl)benzaldehyde (1l): Prepared according to general procedure D from $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, 0.05 equiv), 3-methoxyphenylboronic acid (456 mg, 3.00 mmol, 1.50 equiv), 4 mL of a 2M aqueous Na_2CO_3 solution, 2-(2-bromoallyl)benzaldehyde (450 mg, 2.00 mmol, 1.00 equiv) and 10 mL 1,4-dioxane. The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1l** (0.278 g, 1.10 mmol, 55%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.84 (s, 3H), 4.26 (s, 2H), 4.76 (s, 1H), 5.50 (s, 1H), 6.86 (ddd, *J* = 8.0, 2.4, 0.8 Hz, 1H), 7.03 (dd, *J* = 2.4, 2.4 Hz, 1H), 7.10 (ddd, *J* = 8.0, 1.2, 0.8 Hz, 1H), 7.28 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.35 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.44 (ddd, *J* = 8.0, 7.6, 0.8 Hz, 1H), 7.55 (ddd, *J* = 8.0, 7.6, 1.6 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.3 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.8, 55.4, 112.1, 113.1, 115.3, 118.6, 127.2, 129.5, 131.6, 131.7, 134.0, 134.2, 141.8, 142.5, 147.5, 159.7, 192.5. HRMS (ESI) calcd. for $C_{17}H_{16}O_2$ ($M+H^+$) 253.1223, found 253.1229.



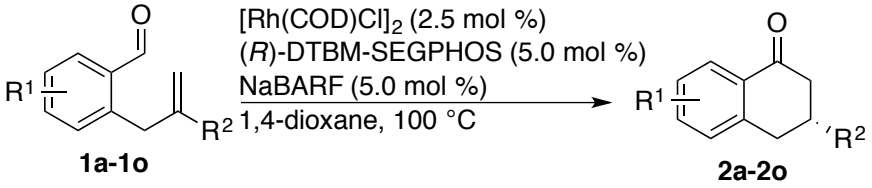
2-(2-(2-Methoxyphenyl)allyl)benzaldehyde (1m): Prepared according to general procedure D from $Pd(PPh_3)_4$ (116 mg, 0.100 mmol, 0.05 equiv), 2-methoxyphenylboronic acid (456 mg, 3.00 mmol, 1.50 equiv), 4 mL of a 2M aqueous Na_2CO_3 solution, 2-(2-bromoallyl)benzaldehyde (450 mg, 2.00 mmol, 1.00 equiv) and 10 mL 1,4-dioxane. The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1m** (0.272 g, 1.08 mmol, 54%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.86 (s, 3H), 4.17 (s, 2H), 4.81 (q, *J* = 1.6 Hz, 1H), 5.12 (q, *J* = 1.6 Hz, 1H), 6.84-6.92 (m, 2H), 7.08 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.23 – 7.32 (m, 2H), 7.34 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.50 (ddd, *J* = 7.6, 7.2, 1.6 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.3 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 38.5, 55.5, 110.7, 116.6, 120.8, 127.1, 128.96, 129.03, 130.2, 131.6, 132.0, 133.9, 134.5, 142.5, 148.9, 156.5, 192.4. HRMS (ESI) calcd. for $C_{17}H_{16}O_2$ ($M+Na^+$) 275.1043, found 275.1046.



1n

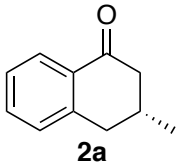
2-(2-(Thiophen-3-yl)allyl)benzaldehyde (1n): Prepared according to a modified version of general procedure D from $Pd(PPh_3)_4$ (46.0 mg, 0.050 mmol, 0.063 equiv), 3-thienylboronic acid (154 mg, 1.20 mmol, 1.50 equiv), 1.6 mL of a 2M aqueous Na_2CO_3 solution, 2-(2-bromoallyl)benzaldehyde (180 mg, 0.800 mmol, 1.00 equiv) and 4 mL 1,4-dioxane. The crude product was purified by flash column chromatography (90:10 Hex:EtOAc) to yield **1n** (94.2 mg, 0.413 mmol, 52%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.19 (s, 2H), 4.63 (s, 1H), 5.51 (s, 1H), 7.22-7.27 (m, 3H), 7.31 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.40 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.50 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.86 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.2 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.6, 113.8, 120.9, 125.7, 125.8, 127.2, 131.60, 131.63, 134.0, 134.3, 141.5, 142.0, 142.3, 192.5. HRMS (ESI) calcd. for $C_{14}H_{12}OS$ ($M+H^+$) 229.0682, found 229.0685.

General Procedure E: Hydroacylation of *ortho*-Allylbenzaldehydes 2a-2o



1a-1o **2a-2o**

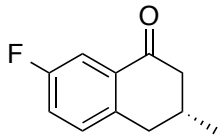
In a nitrogen-filled dry box, the appropriate *ortho*-allylbenzaldehyde **1a-1o** (0.200 mmol, 1.00 equiv), $[Rh(COD)Cl]_2$ (2.5 mg, 0.0050 mmol, 0.025 equiv), (*R*)-DTBM-SEGPHOS (11.8 mg, 0.010 mmol, 0.050 equiv), NaBARF (8.9 mg, 0.010 mmol, 0.050 equiv), and anhydrous 1,4-dioxane (1 mL) were added to a 1-dram vial. The vial was sealed with a PFTE/silicone-lined septum cap and removed from the dry box. The reaction mixture was heated to 100 °C and allowed to stir at this temperature until the reaction was judged to be complete by TLC analysis. The mixture was cooled to rt, filtered through a pad of silica gel (eluting with EtOAc), and concentrated under reduced pressure. $CDCl_3$ (0.7 mL) was added to dissolve the crude mixture along with CH_2Br_2 (7.0 μL, 0.100 mmol) as an internal standard. Conversion and hydroacylation/alkene isomerization ratio were determined by ^{1}H NMR spectroscopy of the crude reaction mixture. The crude reaction mixture was purified by flash column silica gel chromatography (hexanes:EtOAc or hexanes:Et_2O) to yield **2a-2o**. Enantiomeric excess was determined by chiral HPLC analysis.



2a

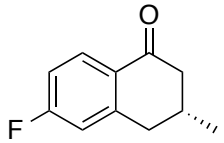
(*R*)-3-Methyl-3,4-dihydronaphthalen-1(2*H*)-one[1,16,18] (2a): Prepared according to general procedure E from **1a** (32.0 mg, 0.200 mmol) (reaction time = 12 h). The crude product (hydroacylation:isomerization = 10.7:1) was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **2a** (27.1 mg, 0.169 mmol, 85%) as a colorless oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 20.9 min (major); t_R 22.1 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 93:7, 0.3 mL/min] to be 98% ee. Lit:[1,2] $[\alpha]_D^{25}$ = -32.2° (c 6.10, EtOH), found $[\alpha]_D^{25}$= -36.7° (c 0.98, EtOH), $[\alpha]_D^{25}$ = -32.9° (c 0.85, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.14 (d, *J* =

6.0 Hz, 3H), 2.27-2.34 (m, 2H), 2.65-2.75 (m, 2H), 2.97 (dd, *J* = 16.4, 3.2 Hz, 1H), 7.24 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.30 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.47 (ddd, *J* = 8.0, 7.6, 0.8 Hz, 1H), 8.02 (dd, *J* = 8.0, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.5, 30.6, 38.2, 47.3, 126.7, 127.1, 129.0, 132.3, 133.6, 143.9, 198.7.



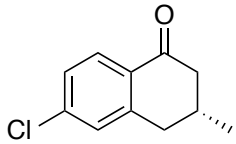
2b

(*R*)-7-Fluoro-3-methyl-3,4-dihydronaphthalen-1(2*H*)-one (2b): Prepared according to general procedure E from **1b** (35.6 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = 9:1) was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **2b** (21.3 mg, 0.120 mmol, 60%) as a yellow oil that solidified on standing. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 31.5 min (major); t_R 32.8 min (minor) [Chiracel AS-H+OJ-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 99:1, 0.5 mL/min] to be 98% ee. $[\alpha]_D^{25}$= -32.4° (c 0.68, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.15 (d, *J* = 6.4 Hz, 3H), 2.25-2.39 (m, 2H), 2.64 (dd, *J* = 16.4, 9.2 Hz, 1H), 2.74 (dd, *J* = 13.2, 2.0 Hz, 1H), 2.96 (dd, *J* = 16.4, 3.2 Hz, 1H), 7.18 (ddd, *J* = 9.2, 8.4, 2.8 Hz, 1H), 7.23 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.68 (dd, *J* = 9.2, 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 30.7, 37.4, 46.9, 113.0 (d, *J* = 22.0, Hz), 120.9 (d, *J* = 22.0 Hz), 130.7 (d, *J* = 7.0 Hz), 133.9 (d, *J* = 6.0 Hz), 139.6 (d, *J* = 3.0 Hz), 161.7 (d, *J* = 244.6 Hz), 197.6. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -116.2 (m, 1F). HRMS (ESI) calcd. for $C_{11}H_{11}FO$ ($M+H^+$) 179.0867, found 179.0863.



2c

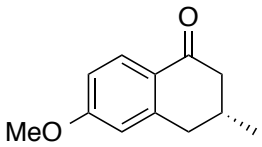
(*R*)-6-Fluoro-3-methyl-3,4-dihydronaphthalen-1(2*H*)-one (2c): Prepared according to general procedure E from **1c** (35.6 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **2c** (31.6 mg, 0.177 mmol, 88%) as a yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 12.0 min (major); t_R 15.0 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 99:1, 0.5 mL/min] to be 98% ee. $[\alpha]_D^{25}$= -16.4° (c 1.46, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.14 (d, *J* = 6.4 Hz, 3H), 2.23-2.39 (m, 2H), 2.67 (dd, *J* = 16.0, 10.0 Hz, 1H), 2.72 (dd, *J* = 9.6, 1.6 Hz, 1H), 2.95 (dd, *J* = 16.0, 3.6 Hz, 1H), 6.91 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.97 (ddd, *J* = 9.2, 8.8, 2.4, 1H), 8.04 (dd, *J* = 8.8, 6.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 30.5, 38.2, 47.0, 114.4 (d, *J* = 22.2), 115.2 (d, *J* = 21.2 Hz), 129.0 (d, *J* = 2.8 Hz), 130.2 (d, *J* = 10.0 Hz), 146.5 (d, *J* = 9.0 Hz), 165.9 (d, *J* = 254.4 Hz), 197.1. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -105.8 (m, 1F). HRMS (ESI) calcd. for $C_{11}H_{11}FO$ ($M+H^+$) 179.0867, found 179.0865.



2d

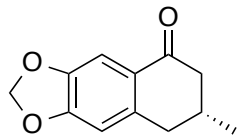
(*R*)-6-Chloro-3-methyl-3,4-dihydronaphthalen-1(2*H*)-one (2d): Prepared according to general procedure E from **1d** (38.9 mg, 0.200 mmol) using 10 mol% catalyst loading (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (90:10 hexanes: EtOAc) to yield **2d** (35.4 mg, 0.182 mmol, 91%) as a yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 14.0 min (major); t_R 15.6

min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 95:5, 0.5 mL/min] to be 97% ee. $[\alpha]_D^{25}$= -68.3° (c 0.82, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.14 (d, *J* = 6.0 Hz, 3H), 2.26-2.39 (m, 2H), 2.67 (dd, *J* = 16.8, 10.4 Hz, 1H), 2.73 (dd, *J* = 13.2, 2.0 Hz, 1H), 2.95 (dd, *J* = 16.8, 3.6 Hz, 1H), 7.25 (d, *J* = 0.8 Hz, 1H), 7.27 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 30.5, 37.9, 47.0, 127.3, 128.81, 128.80, 130.8, 139.8, 145.4, 197.4. HRMS (ESI) calcd. for $C_{11}H_{11}ClO$ ($M+H^+$) 195.0571, found 195.0566.



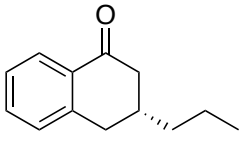
2e

(*R*)-6-Methoxy-3-methyl-3,4-dihydronaphthalen-1(2*H*)-one (2e): Prepared according to general procedure E from **1e** (38.1 mg, 0.200 mmol) (reaction time = 12 h). The crude product (hydroacylation:isomerization = 19:1) was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **2e** (32.0 mg, 0.168 mmol, 84%) as a white amorphous solid. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 23.5 min (major); t_R 25.8 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 0.5 mL/min] to be 99% ee. $[\alpha]_D^{25}$ = -49.4° (c 0.77, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (d, *J* = 6.4 Hz, 3H), 2.19-2.34 (m, 2H), 2.60-2.70 (m, 2H), 2.92 (dd, J = 16.4, 3.6 Hz, 1H), 3.84 (s, 3H), 6.68 (d, *J* = 2.4 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.5, 30.7, 38.6, 47.0, 55.5, 112.8, 113.1, 126.0, 129.5, 145.4, 163.7, 197.4. HRMS (ESI) calcd. for $C_{12}H_{14}O_2$ ($M+H^+$) 191.1067, found 191.1063.



2f

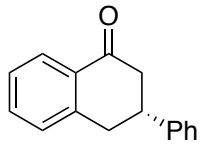
(*R*)-7-Methyl-7,8-dihydronaphtho[2,3-*d*][1,3]dioxol-5(6*H*)-one (2f): Prepared according to general procedure E from **1f** (40.8 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = 9.8:1) was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **2f** (35.0 mg, 0.171 mmol, 85%) as a colorless oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 26.0 min (major); t_R 28.4 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 0.5 mL/min] to be 99% ee. $[\alpha]_D^{25}$= -61.3° (c 1.24, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (d, *J* = 6.0 Hz, 3H), 2.18-2.35 (m, 2H), 2.59 (dd, *J* = 16.0, 10.4 Hz, 1H), 2.67 (dd, *J* = 12.8, 1.6 Hz, 1H), 2.87 (dd, *J* = 16.0, 3.6, 1H), 6.00 (s, 2H), 6.65 (s, 1H), 7.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 30.8, 38.4, 46.8, 101.7, 106.2, 108.1, 127.1, 140.8, 147.0, 152.2, 196.9. HRMS (ESI) calcd. for $C_{12}H_{12}O_3$ ($M+H^+$) 205.0859, found 205.0853.



2g

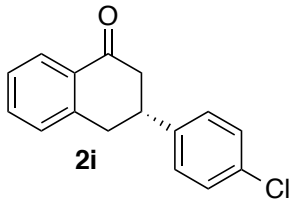
(*R*)-3-Propyl-3,4-dihydronaphthalen-1(2*H*)-one[19] (2g): Prepared according to general procedure E from **1g** (37.7 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (90:10 hexanes:Et_2O) to yield **2g** (33.3 mg, 0.177 mmol, 89%) as a yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 11.3 min (major); t_R 12.5 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 95:5,

0.5 mL/min] to be 96% ee. $[\alpha]_D^{25}$ = -28.1° (c 1.21, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88-0.96 (m, 3H), 1.35-1.48 (m, 4H), 2.16-2.25 (m, 1H), 2.31 (dd, *J* = 16.8, 12.0 Hz, 1H), 2.69 (dd, *J* = 16.4, 10.4 Hz, 1H), 2.77 (ddd, *J* = 16.8, 3.2, 1.6 Hz, 1H), 2.96-3.05 (m, 1H), 7.24 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.30 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.46 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 8.01 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 19.8, 35.2, 36.3, 38.1, 45.6, 126.7, 127.1, 129.0, 132.6, 133.6, 144.0, 198.9. HRMS (ESI) calcd. for $C_{13}H_{16}O$ ($M+H^+$) 189.1274, found 189.1270.



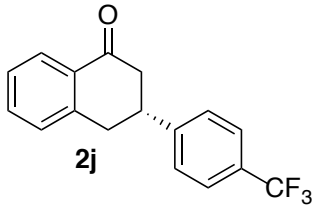
2h

(*R*)-3-Phenyl-3,4-dihydronaphthalen-1(2*H*)-one[17] (2h): Prepared according to general procedure E from **1h** (44.5 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **2h** (37.0 mg, 0.166 mmol, 83%) as a pale brown oil which contained 4% of 2-(2-phenylprop-1-en-1-yl)benzaldehyde **3h** (*E*:*Z* = 1:1). The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 10.3 min (major); t_R 22.9 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 0.5 mL/min] to be 97% ee. $[\alpha]_D^{25}$ = -5.71° (c 1.40, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.82 (dd, *J* = 16.4, 12.8 Hz, 1H), 2.93-2.99 (ddd, *J* = 16.4, 4.0, 1.6 Hz, 1H), 3.12-3.27 (m, 2H), 3.40-3.49 (m, 1H), 7.40-7.42 (m, 7H), 7.50 (ddd, *J* = 8.0, 7.6, 1.2 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.8, 41.2, 46.1, 126.8, 127.0, 127.1, 127.3, 128.9, 129.0, 132.2, 133.9, 143.4, 143.5, 197.9. HRMS (ESI) calcd. for $C_{16}H_{14}O$ ($M+Na^+$) 245.0937, found 245.0934.



2i

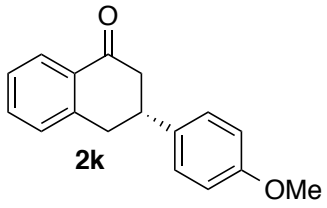
(*R*)-3-(4-Chlorophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2i): Prepared according to general procedure E from **1i** (51.3 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **2i** (38.0 mg, 0.148 mmol, 74%) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 31.9 min (major); t_R 42.9 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 95:5, 0.5 mL/min] to be 98% ee. $[\alpha]_D^{25}$ = -4.21° (c 1.9, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.79 (dd, *J* = 16.4, 12.8 Hz, 1H), 2.93 (ddd, *J* = 16.8, 4.4, 1.2 Hz, 1H), 3.10-3.24 (m, 2H), 3.36-3.49 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.52 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 8.07 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.7, 40.6, 46.0, 127.2, 127.4, 128.2, 128.97, 129.04, 132.1, 132.8, 134.0, 142.0, 143.1, 197.5. HRMS (ESI) calcd. for $C_{16}H_{13}ClO$ ($M+H^+$) 257.0728, found 257.0731.



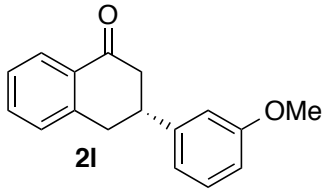
2j

(*R*)-3-(4-(Trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2j): Prepared according to general procedure E from **1j** (58.1 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **2j** (45.6 mg, 0.157 mmol, 79%) as a

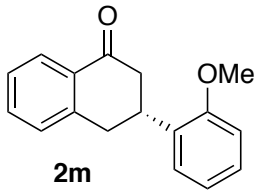
yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 9.75 min (major); t_R 13.5 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 1.0 mL/min] to be 96% ee. $[\alpha]_D^{25}$ = -2.89° (c 2.09, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.85 (dd, *J* = 16.8, 12.8 Hz, 1H), 2.98 (ddd, *J* = 16.8, 4.0, 1.6 Hz, 1H), 3.14-3.29 (m, 2H), 3.46-3.60 (m, 1H), 7.29 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.37 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.53 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 8.09 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.4, 41.0, 45.7, 125.9 (q, *J* = 3.7 Hz), 126.9 (q, *J* = 270.4 Hz), 127.26, 127.30, 127.4, 129.0, 129.4 (q, *J* = 32.4 Hz), 132.1, 134.1, 142.9, 147.4, 197.1. ^{19}F NMR ($CDCl_3$, 376 MHz): δ -63.46 (s, 1F). HRMS (ESI) calcd. for $C_{17}H_{13}F_3O$ ($M+H^+$) 291.0991, found 291.0995.



(*R*)-3-(4-Methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2k): Prepared according to general procedure E from **1k** (50.5 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **2k** (40.4 mg, 0.160 mmol, 80%) as a pale yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 20.5 min (major); t_R 29.5 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{25}$ = -7.14° (c 1.12, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.80 (dd, *J* = 16.4, 12.8 Hz, 1H), 2.95 (ddd, *J* = 16.4, 4.4, 1.2 Hz, 1H), 3.11-3.23 (m, 2H), 3.36-3.47 (m, 1H), 3.81 (s, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.35 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.51 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 8.08 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 38.1, 40.4, 46.3, 55.4, 114.2, 127.0, 127.3, 127.8, 129.0, 132.2, 133.9, 135.7, 143.6, 158.6, 198.1. HRMS (ESI) calcd. for $C_{17}H_{16}O_2$ ($M+H^+$) 253.1223, found 253.1231.

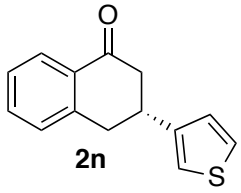


(*R*)-3-(3-Methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2l): Prepared according to general procedure E from **1l** (50.5 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **2l** (36.2 mg, 0.143 mmol, 72%) as a yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 13.8 min (major); t_R 16.9 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{25}$ = -10.5° (c 1.72, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.79 (dd, *J* = 16.4, 13.2 Hz, 1H), 2.94 (ddd, *J* = 16.4, 4.0, 1.6 Hz, 1H), 3.09-3.24 (m, 2H), 3.35-3.46 (m, 1H), 3.79 (s, 3H), 6.76-6.84 (m, 2H), 6.87 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.22-7.29 (m, 2H), 7.32 (ddd, *J* = 8.0, 7.6, 0.8 Hz, 1H), 7.48 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 8.05 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 37.7, 41.2, 46.1, 55.3, 112.0, 113.0, 119.1, 127.1, 127.3, 129.0, 130.0, 132.2, 134.0, 143.5, 145.2, 160.0, 197.9. HRMS (ESI) calcd. for $C_{17}H_{16}O_2$ ($M+H^+$) 253.1223, found 253.1227.



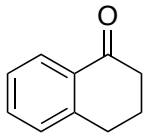
2m

(*R*)-3-(2-Methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-one (2m): Prepared according to general procedure E from **1m** (50.5 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = 18:1) was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **2m** (35.4 mg, 0.140 mmol, 70%) as a yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 21.4 min (major); t_R 27.6 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 0.5 mL/min] to be 97% ee. $[\alpha]_D^{25}$ = -6.02° (c 1.66, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.89 (dd, *J* = 16.4, 12.4 Hz, 1H), 2.97 (ddd, *J* = 16.4, 4.0, 1.6 Hz, 1H), 3.17 (ddd, *J* = 16.4, 2.8, 0.8 Hz, 1H), 3.27 (dd, *J* = 12.4, 0.8 Hz, 1H), 3.80-3.93 (m, 4H), 6.94 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.00 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.24-7.34 (m, 3H), 7.37 (ddd, *J* = 7.6, 7.2, 0.8 Hz, 1H), 7.53 (ddd, *J* = 7.6, 7.2, 1.2 Hz, 1H), 8.12 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.1, 36.0, 44.8, 55.4, 110.7, 120.8, 126.79, 126.83, 127.3, 128.0, 129.0, 131.6, 132.3, 133.7, 144.3, 157.1, 198.7. HRMS (ESI) calcd. for $C_{17}H_{16}O_2$ ($M+H^+$) 253.1223, found 253.1225.



2n

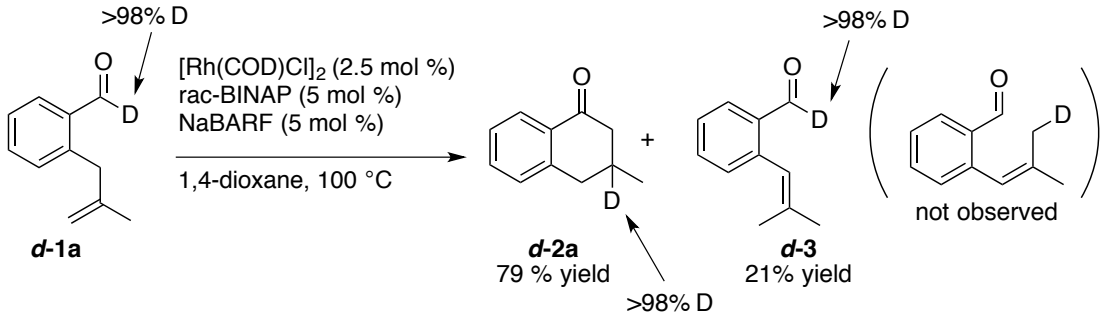
(*R*)-3-(Thiophen-3-yl)-3,4-dihydronaphthalen-1(2*H*)-one (2n): Prepared according to general procedure E from **1n** (45.7 mg, 0.200 mmol) (reaction time = 24 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield **2n** (22.6 mg, 0.099 mmol, 49%) as a yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 13.5 min (major); t_R 17.3 min (minor) [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 90:10, 1.0 mL/min] to be 98% ee. $[\alpha]_D^{25}$ = -17.6° (c 1.02, $CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.80 (dd, *J* = 16.4, 12.4 Hz, 1H), 3.05 (ddd, *J* = 16.4, 3.6, 1.6 Hz, 1H), 3.17 (dd, *J* = 16.4, 10.8 Hz, 1H), 3.28 (ddd, *J* = 16.4, 2.8, 1.6 Hz, 1H), 3.52-3.62 (m, 1H), 7.07 (m, 2H), 7.26-7.40 (m, 3H), 7.51 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 8.07 (dd, *J* = 7.6, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 36.4, 37.2, 45.8, 120.0, 126.2, 126.4, 127.0, 127.2, 128.9, 132.1, 133.8, 143.1, 144.5, 197.6. HRMS (ESI) calcd. for $C_{14}H_{12}OS$ ($M+H^+$) 229.0682, found 229.0685.

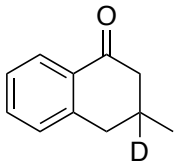


2o

3,4-Dihydronaphthalen-1(2*H*)-one[20] (2o): Prepared according to general procedure E from **1o** (29.2 mg, 0.200 mmol) (reaction time = 10 h). The crude product (hydroacylation:isomerization = >20:1) was purified by flash column chromatography (90:10 hexanes:Et_2O) to yield **2o** (21.2 mg, 0.145 mmol, 73%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.14 (m, 2H), 2.66 (t, *J* = 6.4 Hz, 2H), 2.97 (t, *J* = 6.0 Hz, 2H), 7.25 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 7.31 (ddd, *J* = 8.0, 7.6, 0.8 Hz, 1H), 7.47 (ddd, *J* = 8.0, 7.6, 1.0 Hz, 1H), 8.03 (dd, *J* = 8.0, 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.4, 29.8, 39.3, 126.8, 127.3, 128.9, 132.7, 133.5, 144.6, 198.5.

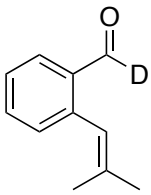
Rh-catalyzed Hydroacylation of *d*-1a





***d*-2a**

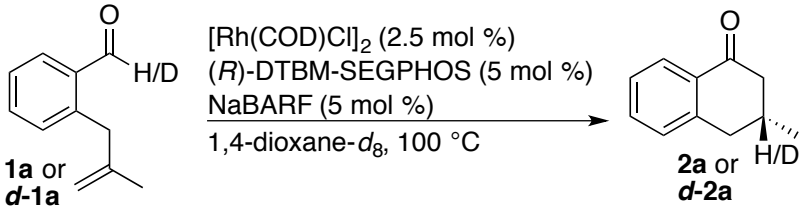
3-Methyl-3,4-dihydronaphthalen-1(2*H*)-one-3-*d* (*d*-2a): Prepared according to a modified version of general procedure D using *rac*-Binap from ***d*-1a** (32.2 mg, 0.200 mmol) (reaction time = 16 h). The crude product was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield ***d*-2a** (25.2 mg, 0.156 mmol, 79%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.13 (s, 3H), 2.30 (d, J = 16.8 Hz, 1H), 2.68 (d, J = 16.4 Hz, 1H), 2.72 (d, J = 16.8 Hz, 1H), 2.96 (d, J = 16.4, 1H), 7.24 (dd, J = 7.6, 0.8 Hz, 1H), 7.30 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.47 (ddd, J = 7.6, 7.2, 0.8 Hz, 1H), 8.01 (dd, J = 7.2, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 30.2 (t, J = 19.4 Hz), 38.0, 47.2, 126.7, 127.1, 129.0, 132.3, 133.6, 143.9, 198.8. HRMS (ESI) calcd. for $C_{11}H_{11}DO$ ($M+H^+$) 162.1024, found 162.1020.



***d*-3**

***d*$_1$-2-(2-Methylprop-1-en-1-yl)benzaldehyde (*d*-3):** Prepared according to a modified version of general procedure D using *rac*-Binap from ***d*-1a** (32.2 mg, 0.200 mmol) (reaction time = 16 h). The crude product was purified by flash column chromatography (95:5 hexanes:EtOAc) to yield ***d*-3** (5.9 mg, 0.037 mmol, 19%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.65 (s, 3H), 1.96 (s, 3H), 6.58 (s, 1H), 7.23 (dd, J = 7.6, 0.8 Hz, 1H), 7.36 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.54 (ddd, J = 7.6, 7.6, 0.8 Hz, 1H), 7.89 (dd, J = 7.6, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.6, 26.2, 121.3, 126.9, 128.1, 130.9, 133.7, 133.8 (t, J = 3.7 Hz), 139.5, 142.4, 192.6 (t, J = 26.6). HRMS (ESI) calcd. for $C_{11}H_{11}DO$ ($M+H^+$) 162.1024, found 162.1023.

Kinetic Isotope Effect for 1a Versus *d*-1a



The kinetic isotope effect was determined by measuring the initial rate constants for two independent experiments for the hydroacylation of **1a** and ***d*-1a**. The reactions were

monitored by ^{1}H NMR spectroscopy (T = 373K) using 1,3,5-trimethoxybenzene as an internal standard. Reaction mixtures were prepared as follows: In a nitrogen-filled dry box, **1a** or ***d*-1a** (16.0 mg, 0.100 mmol, 1.00 equiv), $[Rh(COD)Cl]_2$ (1.23 mg, 0.0025 mmol, 0.025 equiv), (*R*)-DTBM-SEGPHOS (5.90 mg, 0.005 mmol, 0.050 equiv), NaBARF (4.43 mg, 0.005 mmol, 0.050 equiv), 1,3,5-trimethoxybenzene (5.61 mg, 0.033 mmol, 0.333 equiv), and anhydrous 1,4-dioxane-d_8 (0.5 mL) were added to a 1-dram vial. The vial was agitated to dissolve all solids and the solution was transferred to a dry J-Young NMR tube, sealed and immediately subjected to ^{1}H NMR analysis (T = 373K). Data points were collected every 3 minutes and the initial rate constants were determined from the first 5% of the reaction data. The following initial rate constants were measured based on the slope of the first order kinetics plots (Figure S1 and Figure S2): $k_H = (1.826 \pm 0.10) \times 10^{-4}$ sec^{-1}; $k_D = (1.535 \pm 0.06) \times 10^{-4}$ sec^{-1}. The KIE was found to be 1.19 based on the initial rate constants k_H and k_D. Figure S3 and Figure S4 show [**1a**] and [***d*-1a**] vs time through the 3rd half-life of the reaction and support first order dependence on **1a** and ***d*-1a** for the overall reaction.

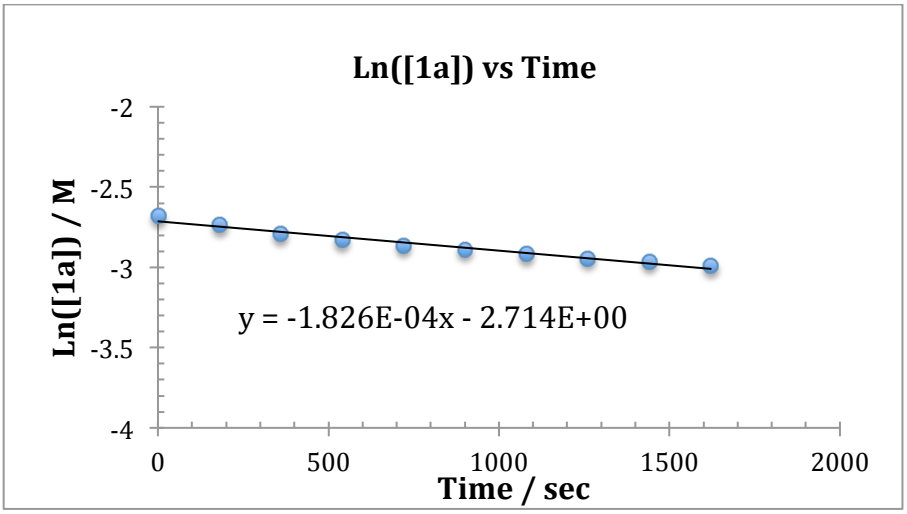


Figure S1: Plot of ln([**1a**]) with time for the first 5% of total reaction time.

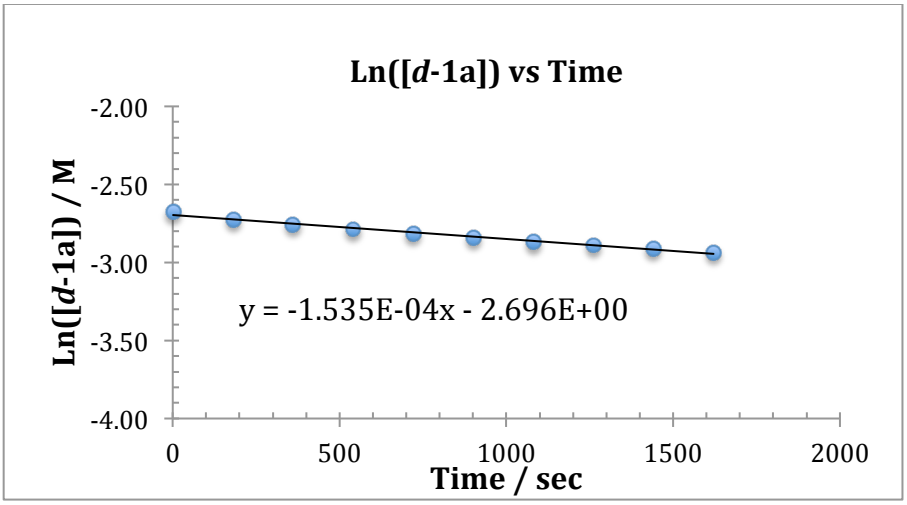


Figure S2: Plot of ln([***d*-1a**]) with time for the first 5% of total reaction time.

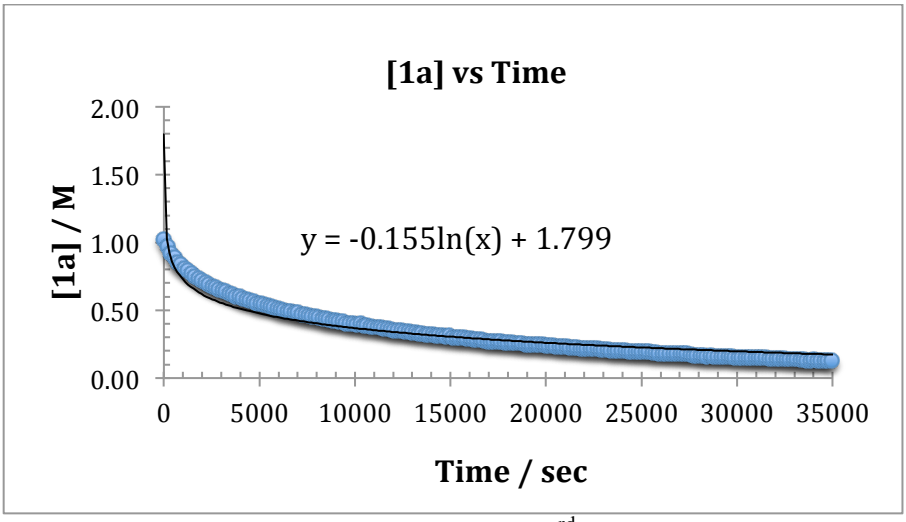


Figure S3: Plot of [**1a**] vs time through 3rd half-life of the reaction.

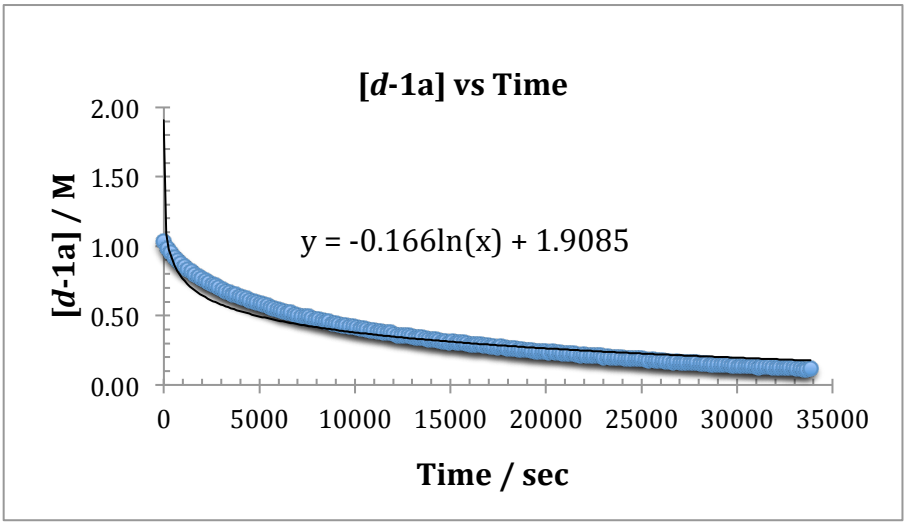
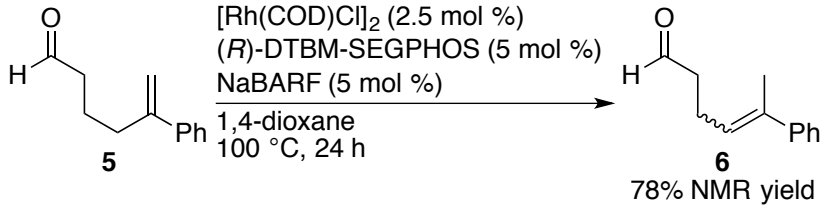


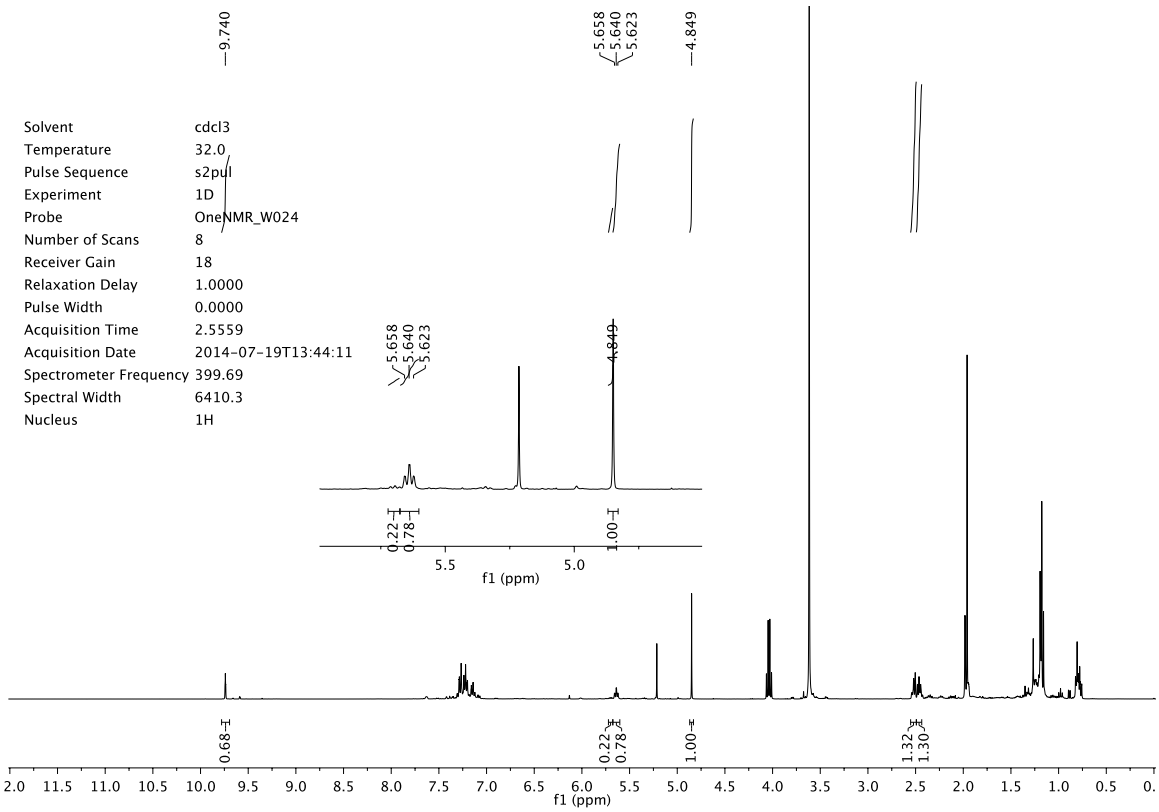
Figure S4: Plot of [***d*-1a**] vs time through 3rd half-life of the reaction.

Rh-Catalyzed Hydroacylation of 5-Phenylhex-5-enal 5

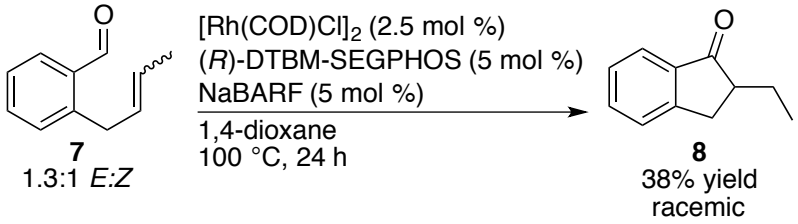


In a nitrogen-filled dry box, 5-phenylhex-5-enal **5** (0.200 mmol, 1.00 equiv), $[Rh(COD)Cl]_2$ (2.5 mg, 0.0050 mmol, 0.025 equiv), (*R*)-DTBM-SEGPHOS (11.8 mg, 0.010 mmol, 0.050 equiv), NaBARF (8.9 mg, 0.010 mmol, 0.050 equiv), and anhydrous 1,4-dioxane (1 mL) were added to a 1-dram vial. The vial was sealed with a

PFTE/silicone-lined septum cap and removed from the dry box. The reaction mixture was heated to 100 °C and allowed to stir at this temperature until the reaction was judged to be complete by TLC analysis. The mixture was cooled to rt, filtered through a pad of silica gel (eluting with EtOAc), and concentrated under reduced pressure. $CDCl_3$ (0.7 mL) was added to dissolve the crude mixture along with CH_2Br_2 (7.0 μL, 0.100 mmol) as an internal standard. Compound **6** was not isolated. The ^1H NMR spectrum of the crude reaction mixture is shown below, integrated relative to the CH_2Br_2 standard.



Rh-Catalyzed Hydroacylation of 7



In a nitrogen-filled dry box, 2-(but-2-en-1-yl)benzaldehyde **7** (0.200 mmol, 1.00 equiv), $[Rh(COD)Cl]_2$ (2.5 mg, 0.0050 mmol, 0.025 equiv), (*R*)-DTBM-SEGPHOS (11.8 mg, 0.010 mmol, 0.050 equiv), NaBARF (8.9 mg, 0.010 mmol, 0.050 equiv), and anhydrous 1,4-dioxane (1 mL) were added to a 1-dram vial. The vial was sealed with a PFTE/silicone-lined septum cap and removed from the dry box. The reaction mixture was heated to 100 °C and allowed to stir at this temperature until the reaction was judged to be complete by TLC analysis. The mixture was cooled to rt, filtered through a pad of

silica gel (eluting with EtOAc), and concentrated under reduced pressure. $CDCl_3$ (0.7 mL) was added to dissolve the crude mixture along with CH_2Br_2 (7.0 μL, 0.100 mmol) as an internal standard. The crude product was purified by flash column chromatography (90:10 hexanes:EtOAc) to yield **8** (12.3 mg, 0.077 mmol, 38%) as a light yellow oil. The enantiomeric excess was determined by HPLC analysis (254 nm, 25 °C) t_R 15.3 min; t_R 19.7 min [Chiracel AS-H (0.46cm x 25cm) (from Daicel Chemical Ind., Ltd.) hexane/^{i}PrOH, 95:5, 0.5 mL/min] to be 0% ee. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.01 (t, *J* = 7.2 Hz, 1H), 1.47 – 1.58 (m, 1H), 1.91-2.04 (m, 1H), 2.57 – 2.67 (m, 1H), 2.83 (dd, *J* = 17.2, 4.0 Hz, 1H), 3.32 (dd, *J* = 17.2, 8.0 Hz, 1H), 7.36 (ddd, *J* = 7.6, 7.6, 0.8 Hz, 1H), 7.46 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.58 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.75 (dd, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.8, 24.6, 32.5, 48.9, 124.0, 126.7, 127.4, 134.8, 137.1, 154.0, 209.2. Spectral data for **8** is consistent with previous reports.[17,21]

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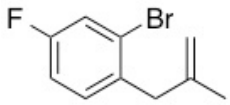
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



S3b

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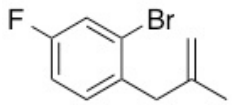
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



S3b

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131.510
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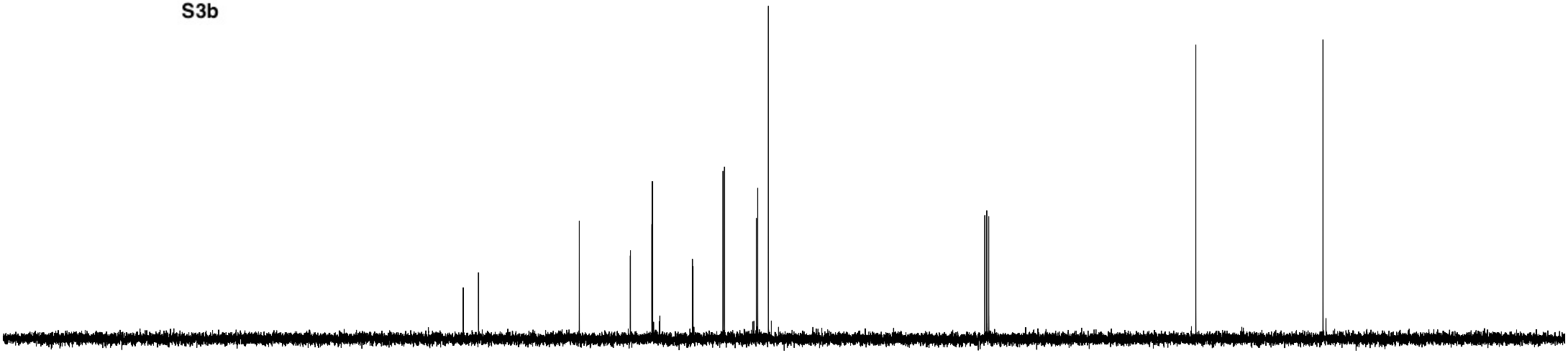
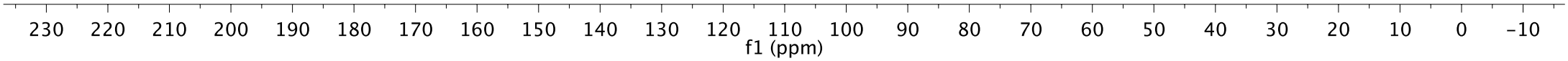
22.518





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Spectral Width	89285.7
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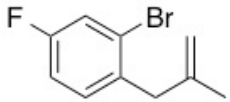
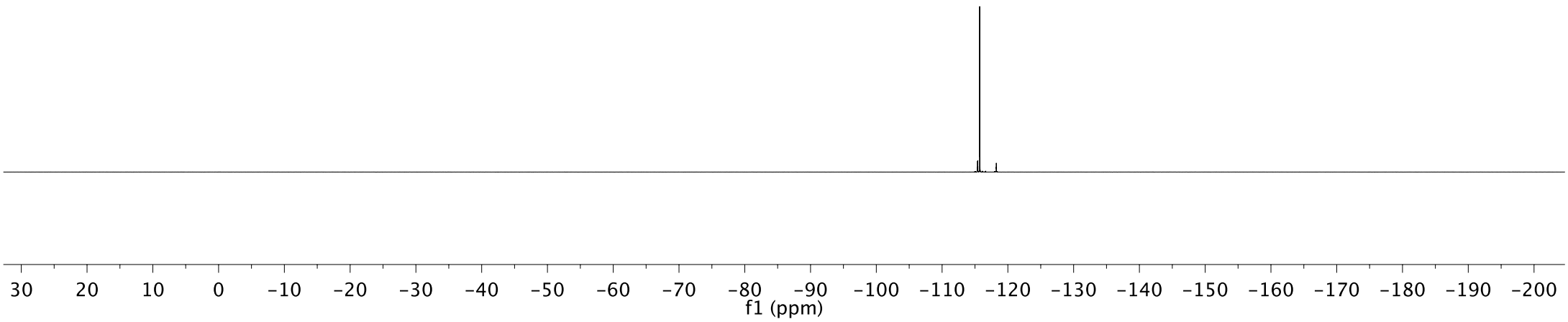


S3b



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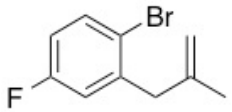

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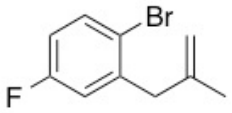
Nucleus	13C



S3c

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141.475
141.400
133.947
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119.270
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117.803
117.576
115.227
115.003
113.198
44.139
22.578

Solvent	cdcl3
Temperature	32.0
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Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
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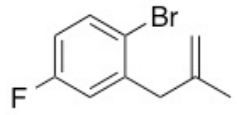
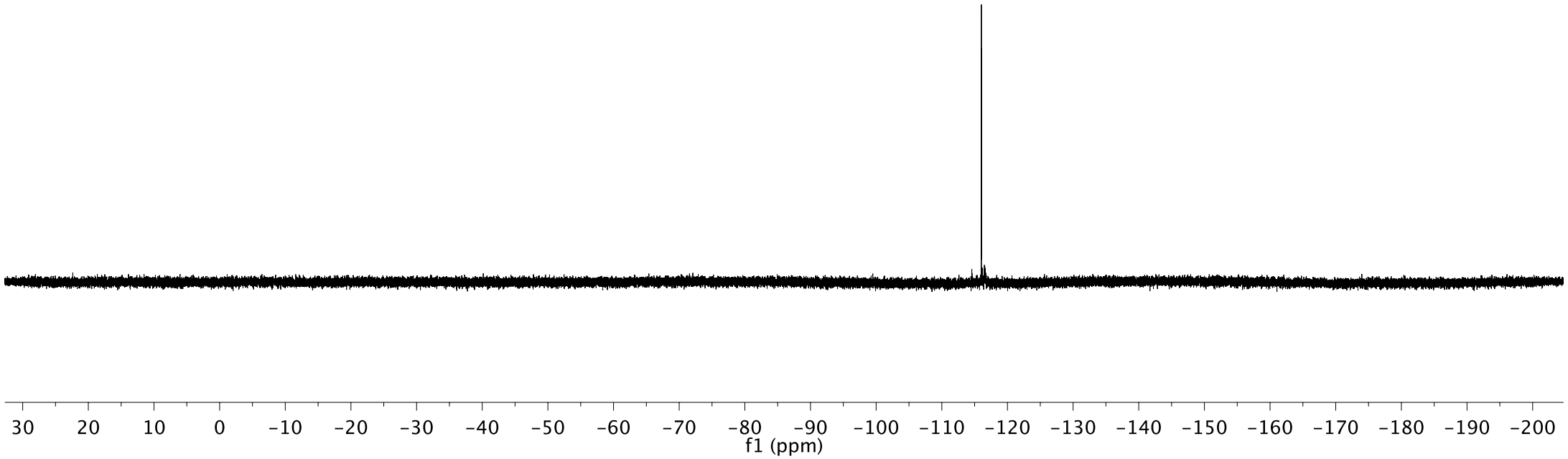
Acquisition Time	0.7340
Spectrometer Frequency	376.05
Spectral Width	89285.7
Nucleus	19F



S3c



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Experiment	1D
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Number of Scans	16
Receiver Gain	60
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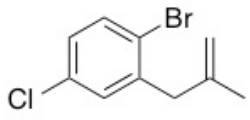
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



S3d

Solvent	cdcl3
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Experiment	1D
Probe	OneNMR_W024
Number of Scans	48
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

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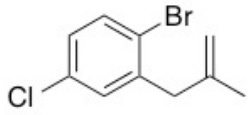
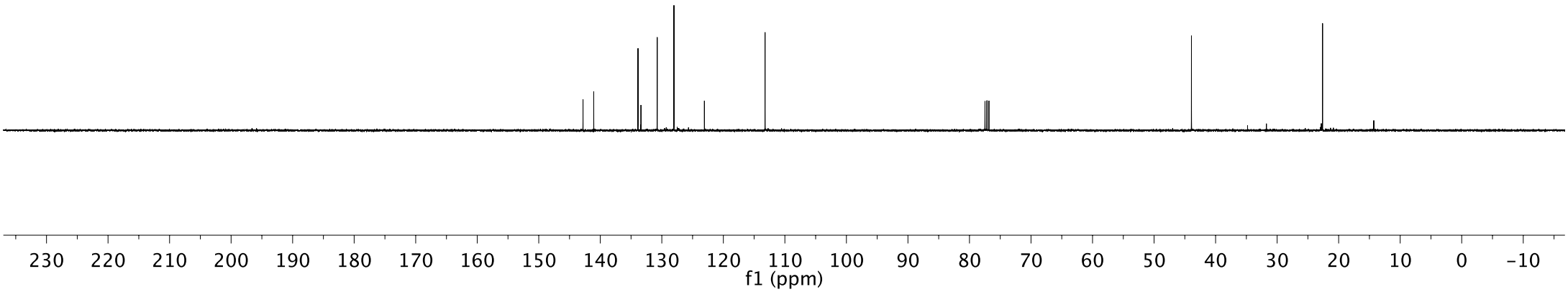
133.871
133.389
130.749
128.029
123.080
113.221
77.160
43.924
22.616



S3d



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Number of Scans	16
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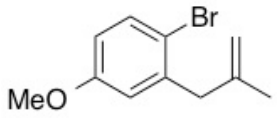
Spectral Width	6410.3
Nucleus	1H



S3e

Solvent	cdcl3
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Experiment	1D
Probe	OneNMR_W024
Number of Scans	48
Receiver Gain	30
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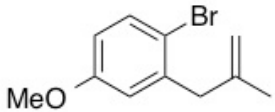
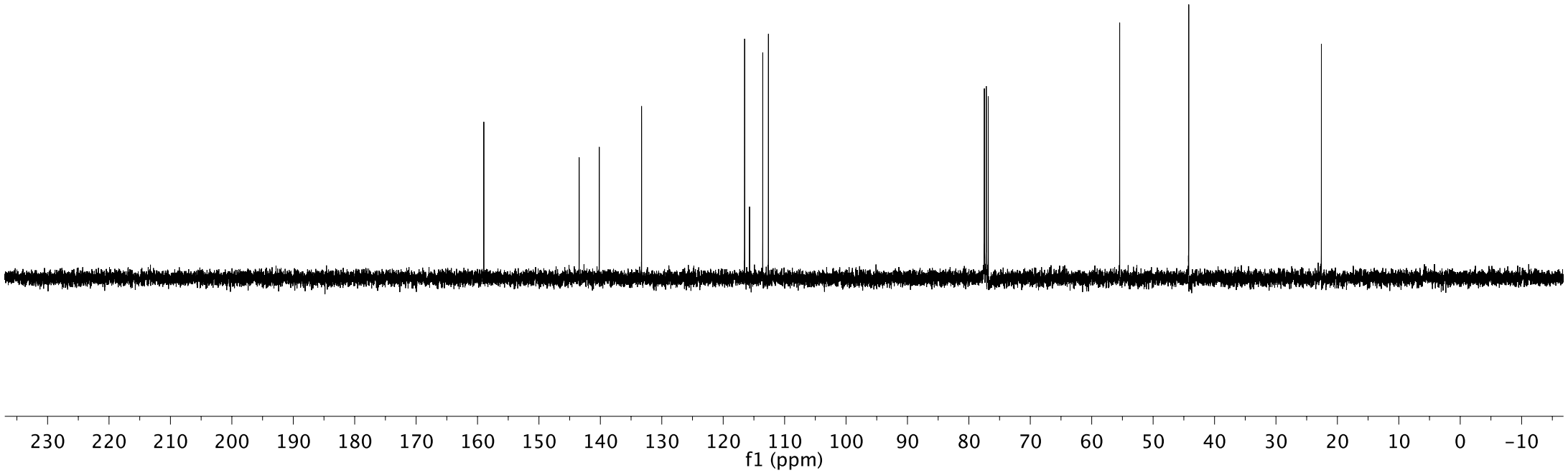
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



S3e



Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	6
Relaxation Delay	1.0000
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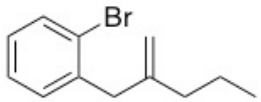
Spectral Width	6410.3
Nucleus	1H



S3g

Solvent	cdcl3
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Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	64
Receiver Gain	30
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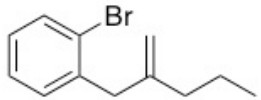
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



S3g

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111.589
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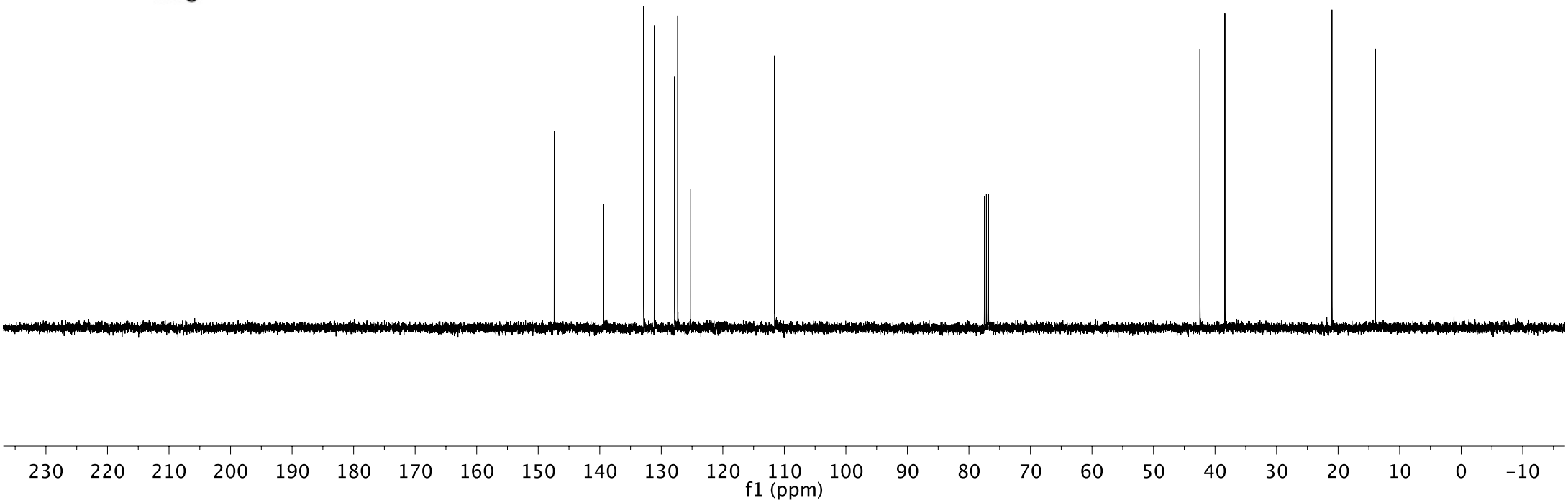
38.405
21.003
13.956



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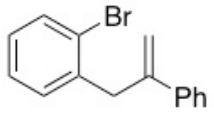
Spectral Width	6410.3
Nucleus	1H

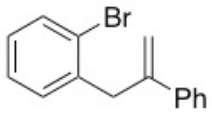


S3h

145.590
140.818
139.069
132.892
131.054
128.481
128.054
127.755
127.524
126.144
125.254
114.819

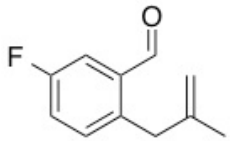
41.539

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



S3h

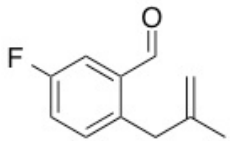
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



1b

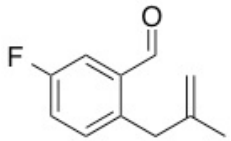
190.497
162.988
160.527
145.192
137.980
137.948
135.863
135.804
133.532
133.462
121.085
120.870
115.866
115.648
112.870
39.487
22.874

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	192
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



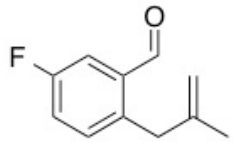
1b

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

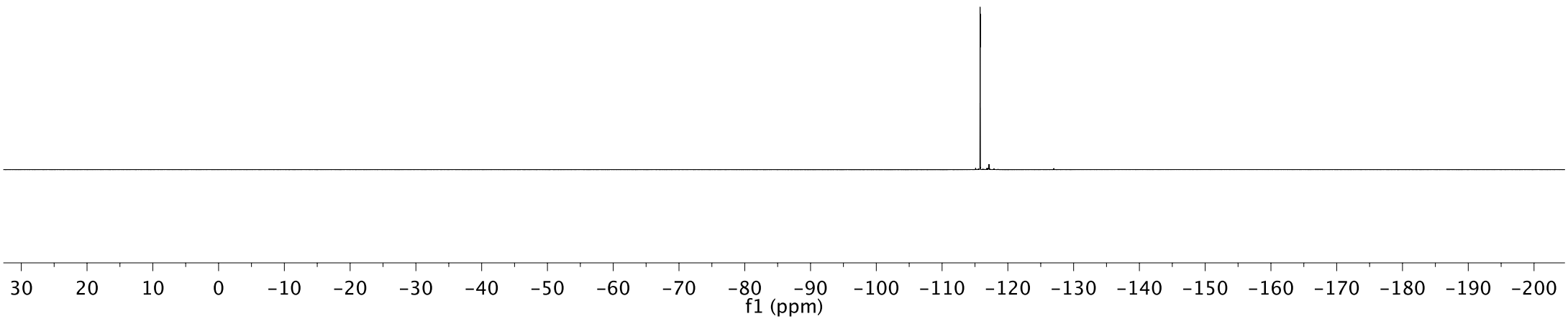


1b

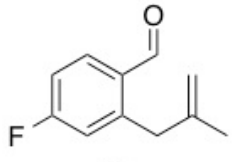
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	48
Relaxation Delay	1.0000
Pulse Width	2.3667
Acquisition Time	0.7340
Spectrometer Frequency	376.05
Spectral Width	89285.7
Nucleus	19F



1b



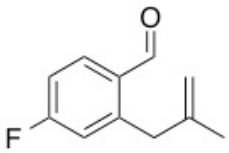
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



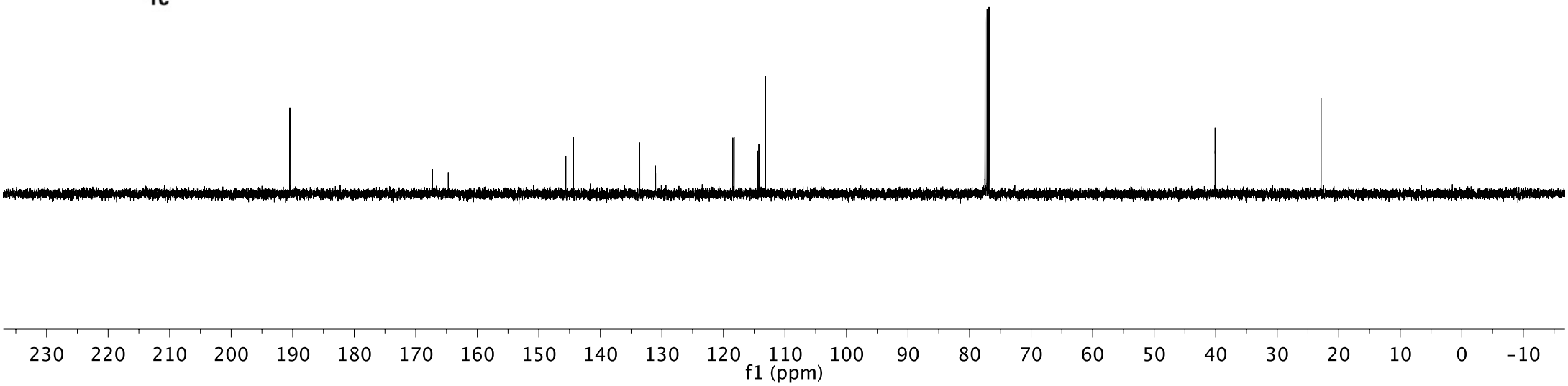
1c

190.464
167.266
164.716
145.698
145.609
144.385
133.696
133.596
131.040
131.014
118.470
118.254
114.459
114.242
113.180
40.102
22.870

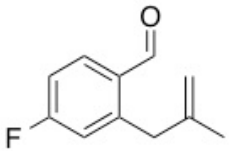
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



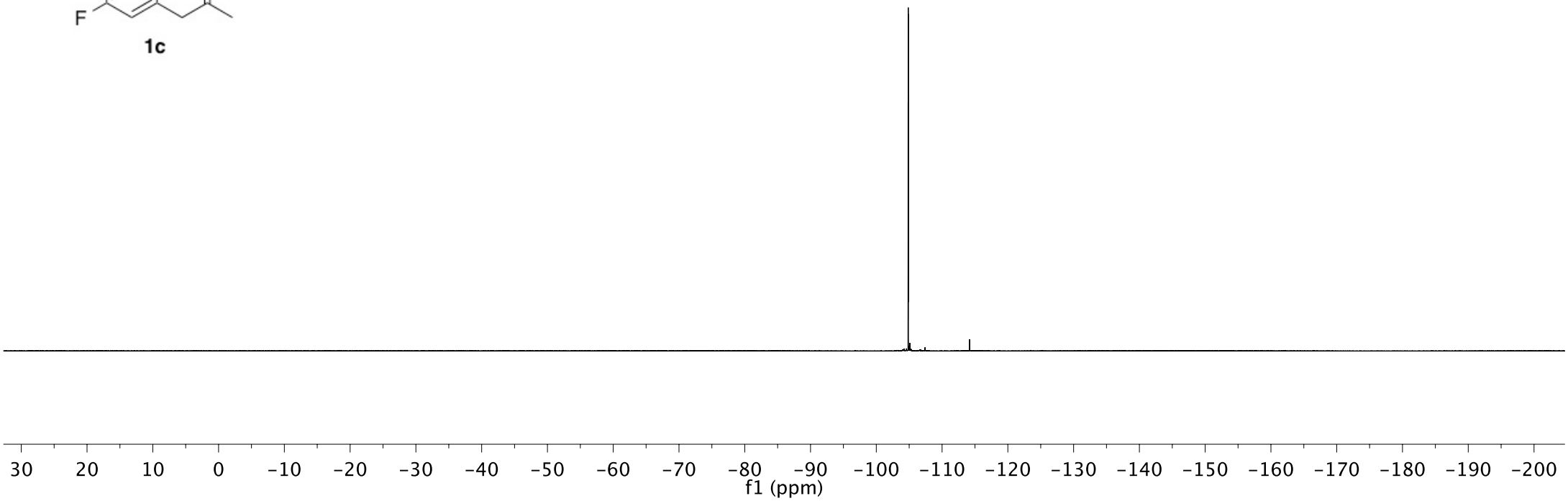
1c



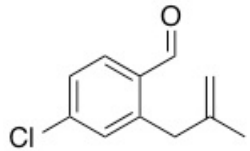
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	52
Relaxation Delay	1.0000
Pulse Width	2.3667
Acquisition Time	0.7340
Spectrometer Frequency	376.05
Spectral Width	89285.7
Nucleus	19F



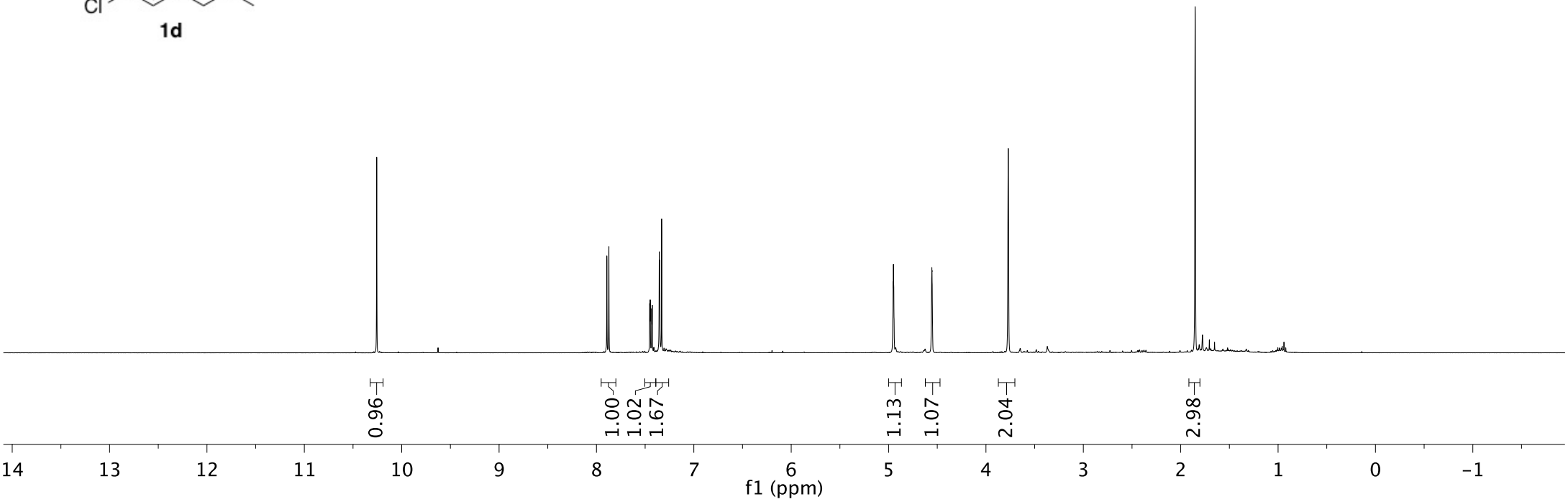
1c



Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

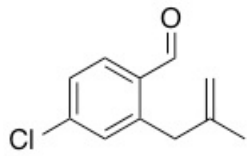


1d



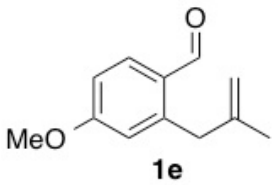
190.845
144.519
143.955
140.315
132.825
132.046
131.632
127.504
113.261
39.990
22.994

Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	288
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

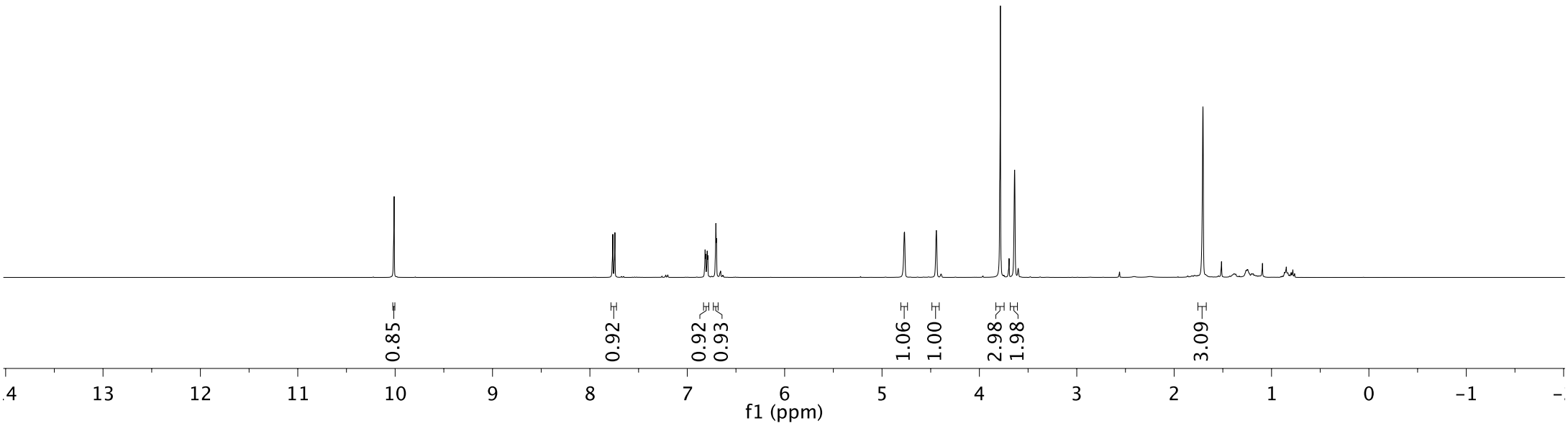


1d

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	0
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

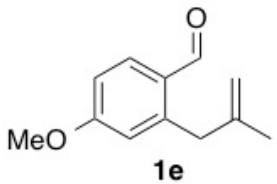


1e

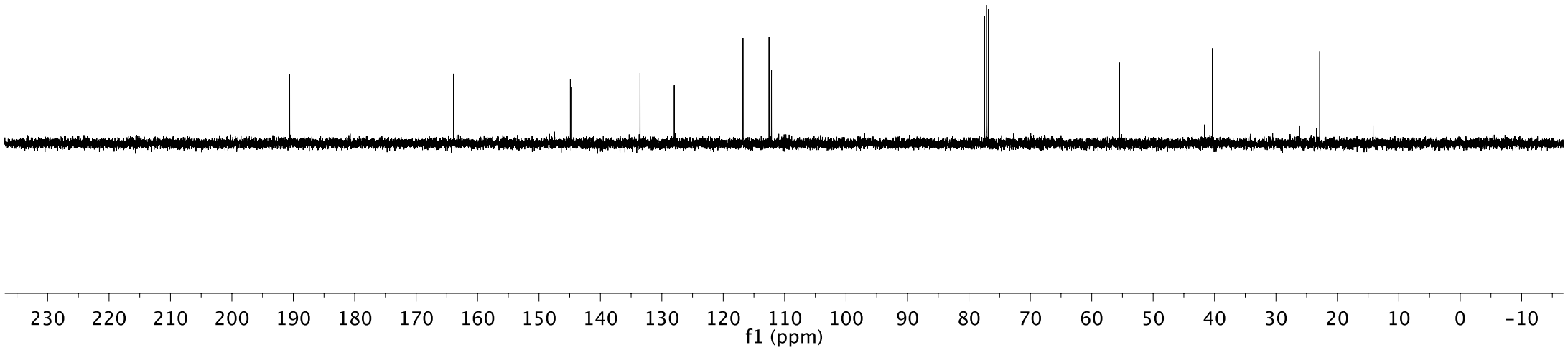


190.591
163.883
144.891
144.714
133.549
127.975
116.784
112.540
112.147
55.490
40.361
22.873

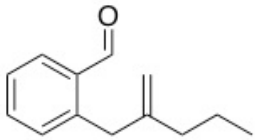
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	48
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



1e



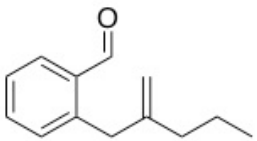
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	18
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



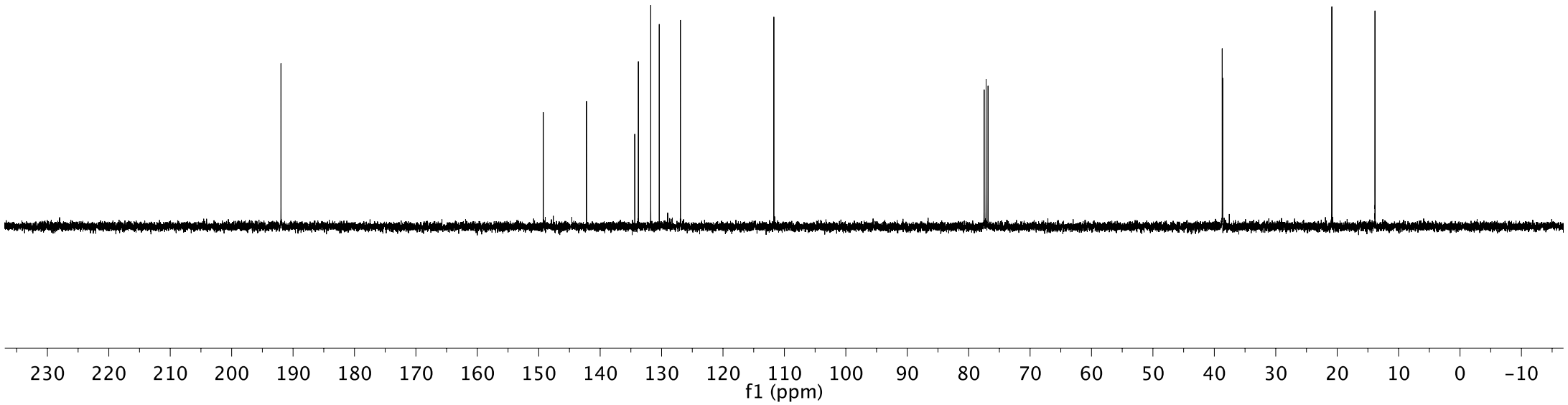
1g

191.968
149.260
142.228
134.365
133.777
131.764
130.378
126.931
111.720
38.718
38.652
20.867
13.843

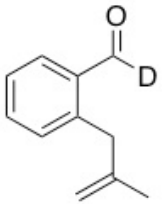
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



1g



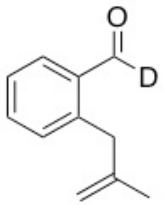
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



***d*-1a**

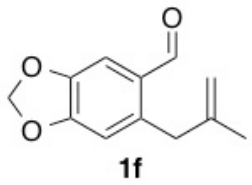
192.157
191.893
191.626
145.357
142.222
134.350
134.320
134.285
133.949
131.731
130.617
127.094
112.612
40.314
23.035

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

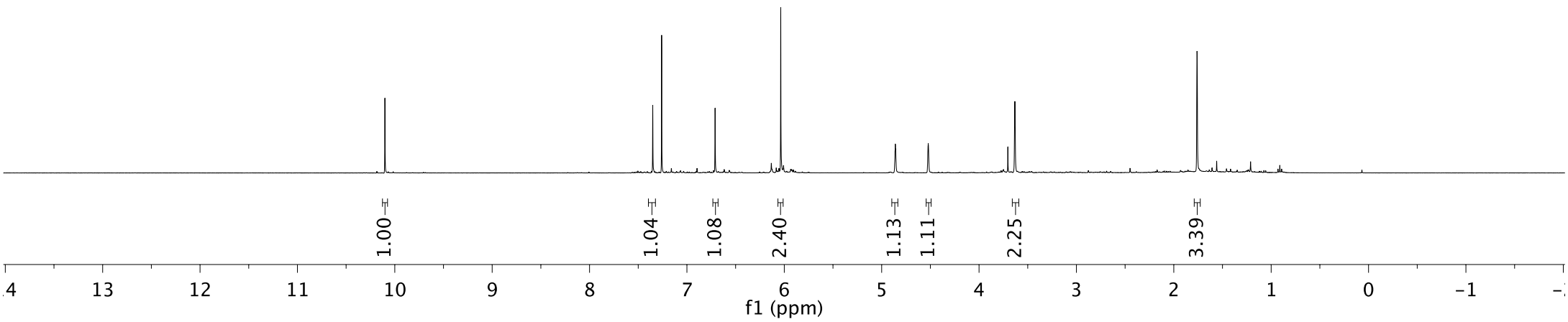


***d*-1a**

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	32
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

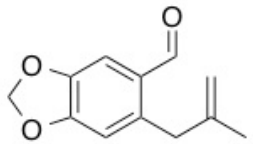


1f

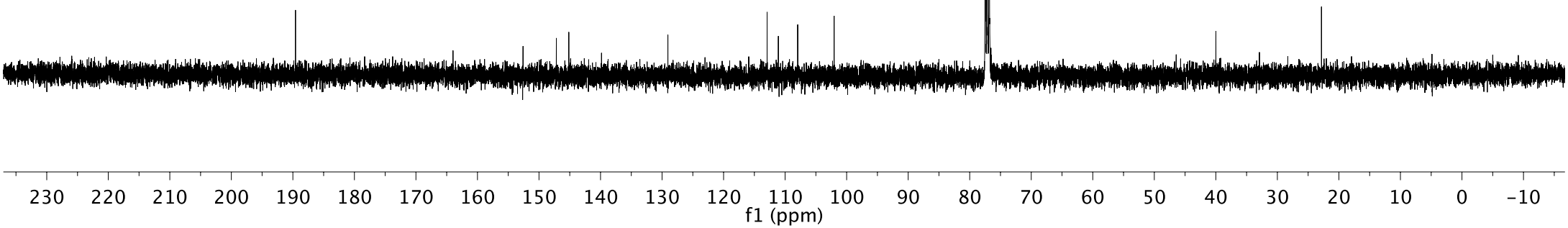


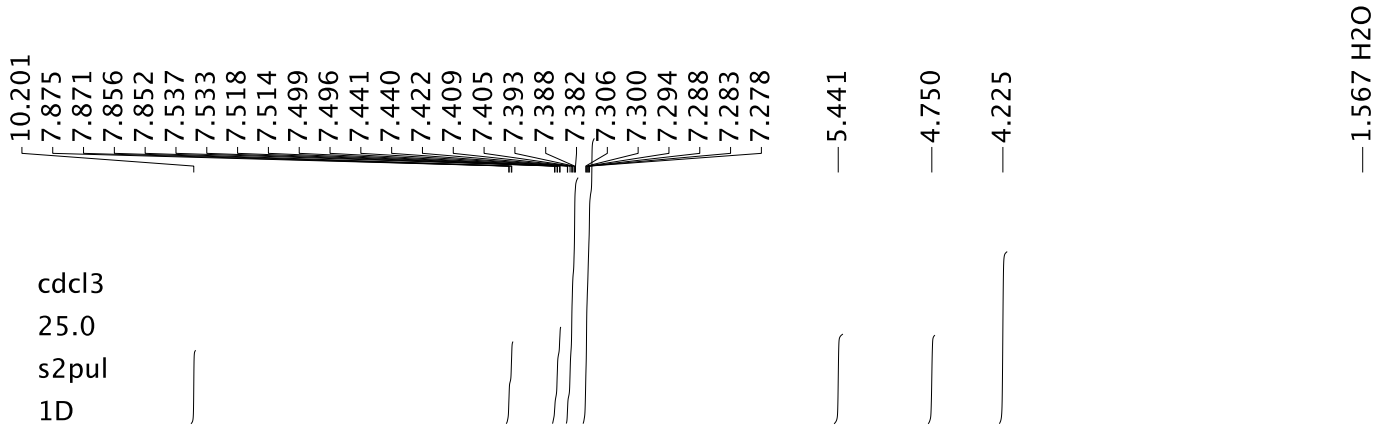
189.574
152.592
147.177
145.154
139.837
129.052
112.926
111.101
107.952
102.036
39.991
22.832

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	5000
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

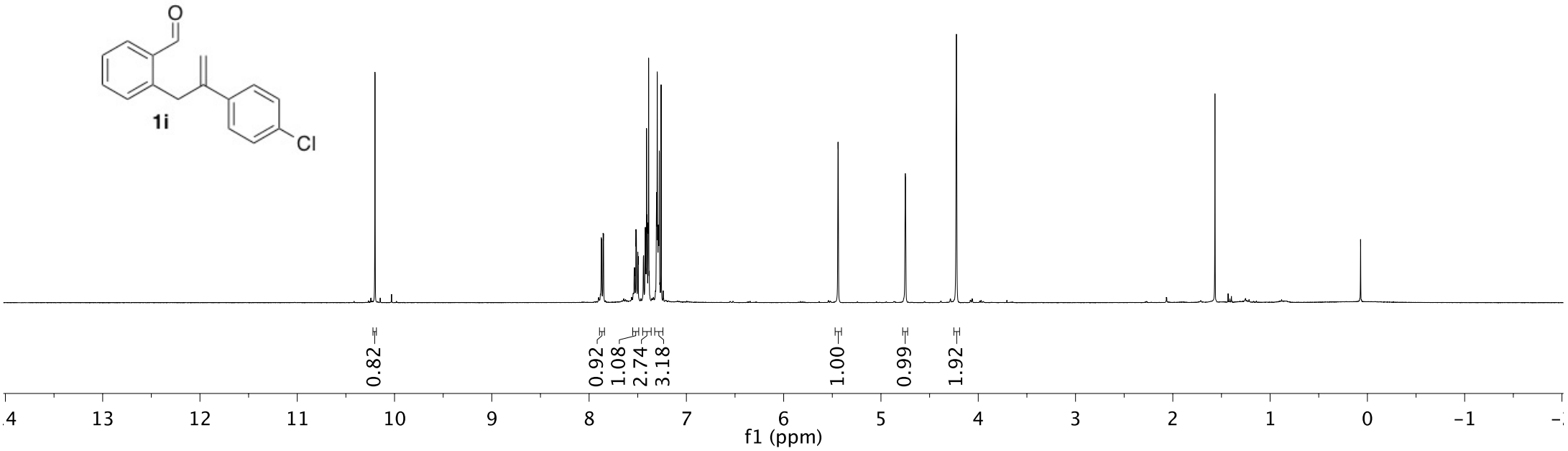


1f



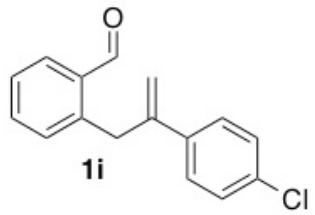


Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	42
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H

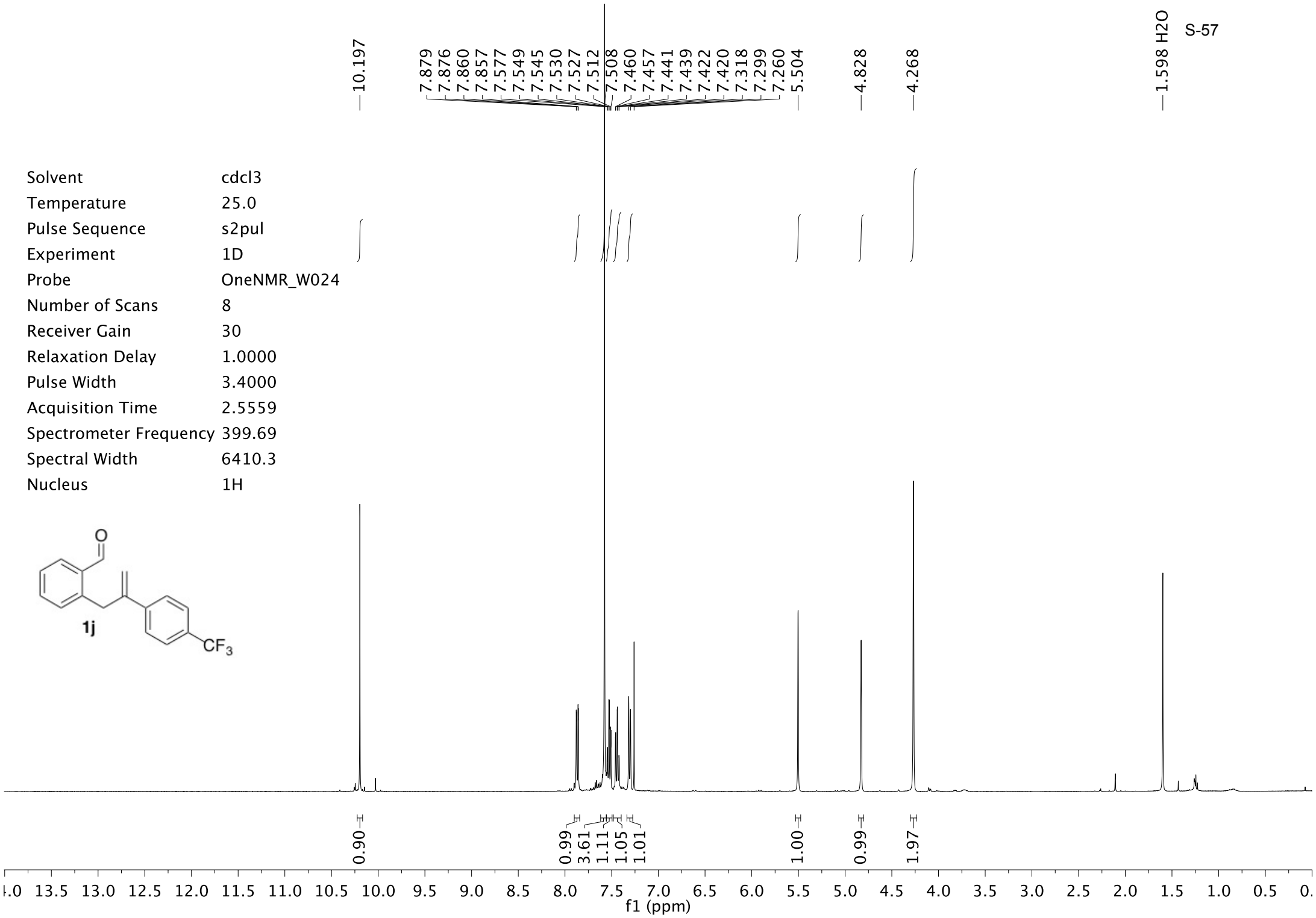


192.608
146.408
141.365
139.401
134.186
133.992
133.628
132.465
131.653
128.645
127.455
127.284
115.388
77.160
37.770

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	80
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

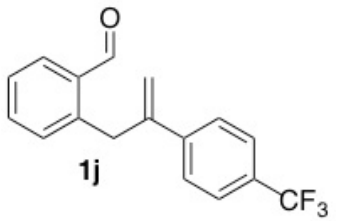


1i


10.197
7.879
7.876
7.860
7.857
7.577
7.549
7.545
7.530
7.527
7.512
7.508
7.460
7.457
7.441
7.439
7.422
7.420
7.318
7.299
7.260
5.504
4.828
4.268
1.598 H2O
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
1j
CF3
0.90
0.99
3.61
1.11
1.05
1.01
1.00
0.99
1.97
f1 (ppm)

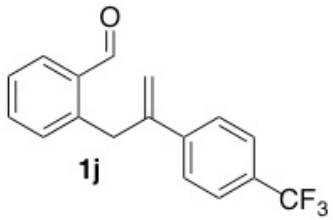
192.674
146.512
144.621
144.607
141.042
134.188
134.018
132.965
131.703
130.278
129.945
129.620
129.302
128.328
127.392
126.483
125.630
125.544
125.506
125.468
125.429
122.925
120.218
116.648
77.160
37.783

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	544
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



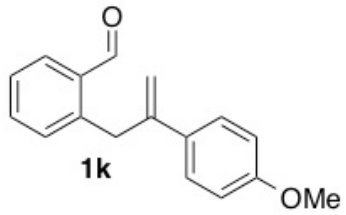
1j

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	54
Relaxation Delay	1.0000
Pulse Width	3.4333
Acquisition Time	0.7340
Spectrometer Frequency	376.05
Spectral Width	89285.7
Nucleus	19F



1j

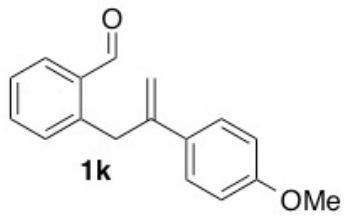
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



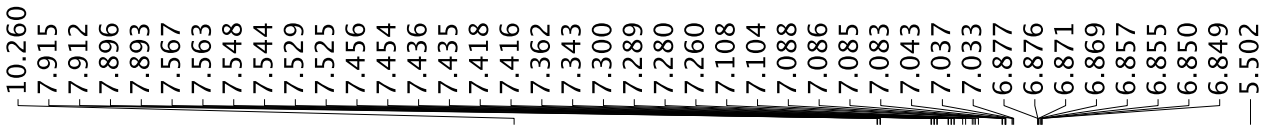
1k

192.520
159.393
146.731
142.053
134.245
133.991
133.347
131.636
131.503
127.189
127.120
113.837
113.559
77.160
55.421
37.784

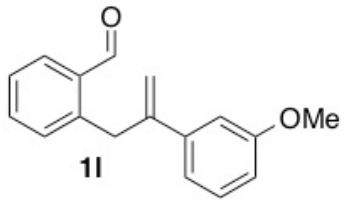
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



1k



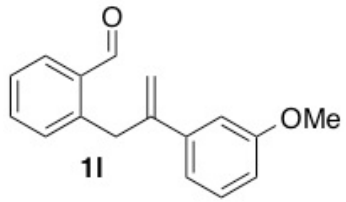
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



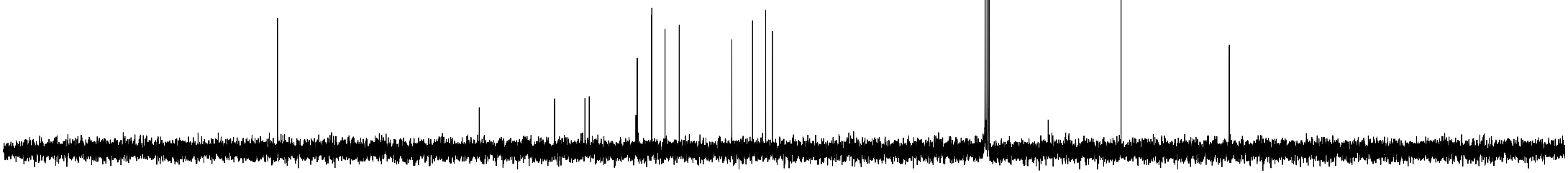
1l

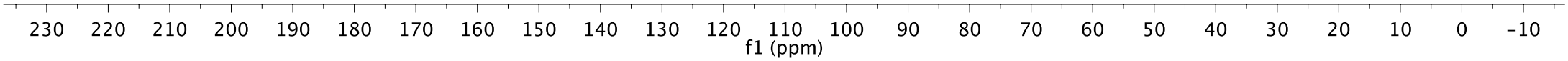
192.488
159.693
147.457
142.515
141.818
134.237
134.020
131.710
131.648
129.502
127.195
118.646
115.275
113.144
112.060
77.160
55.388
37.801

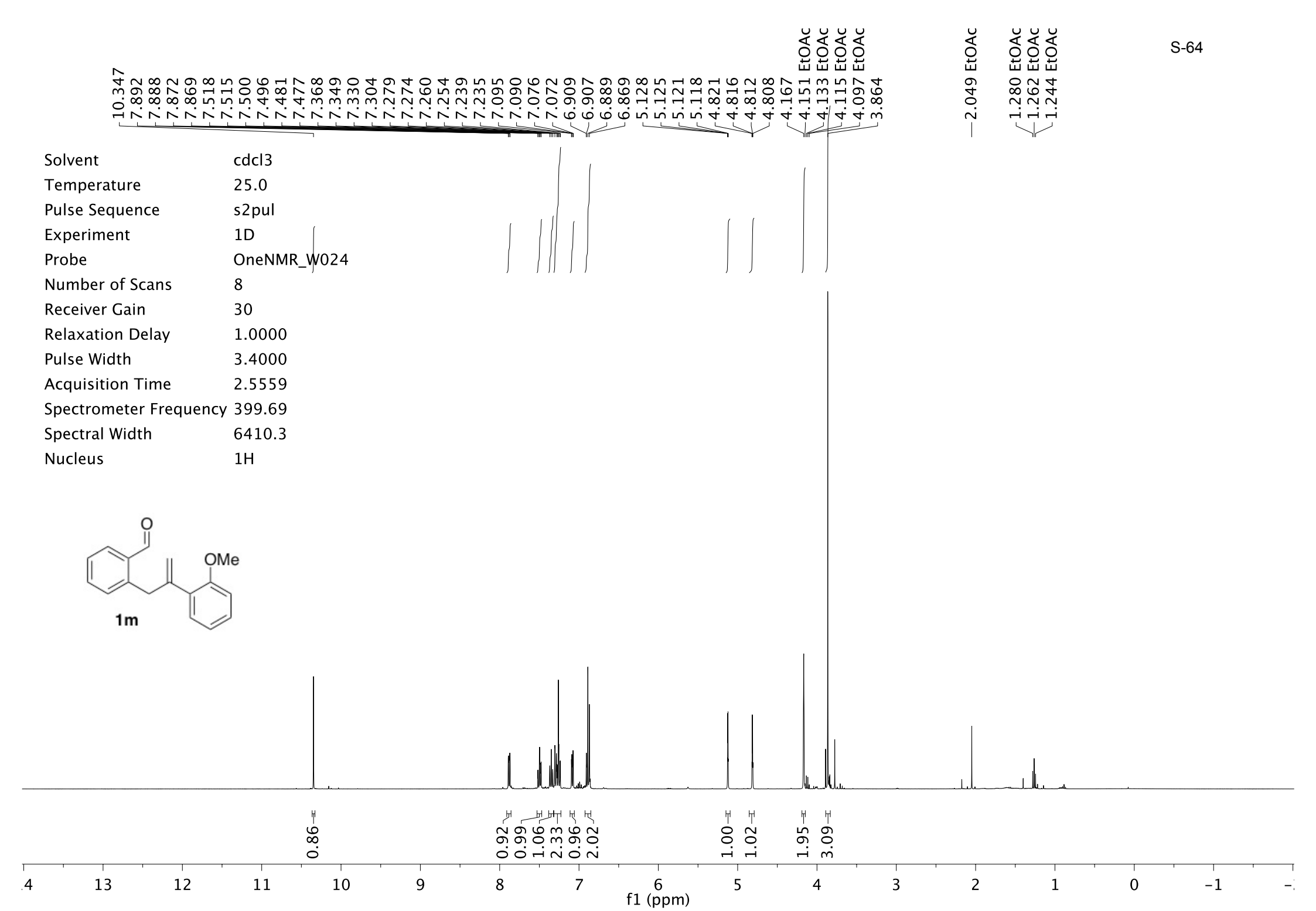
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



1l

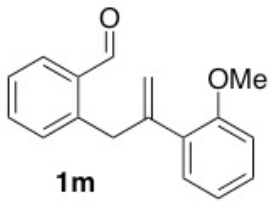




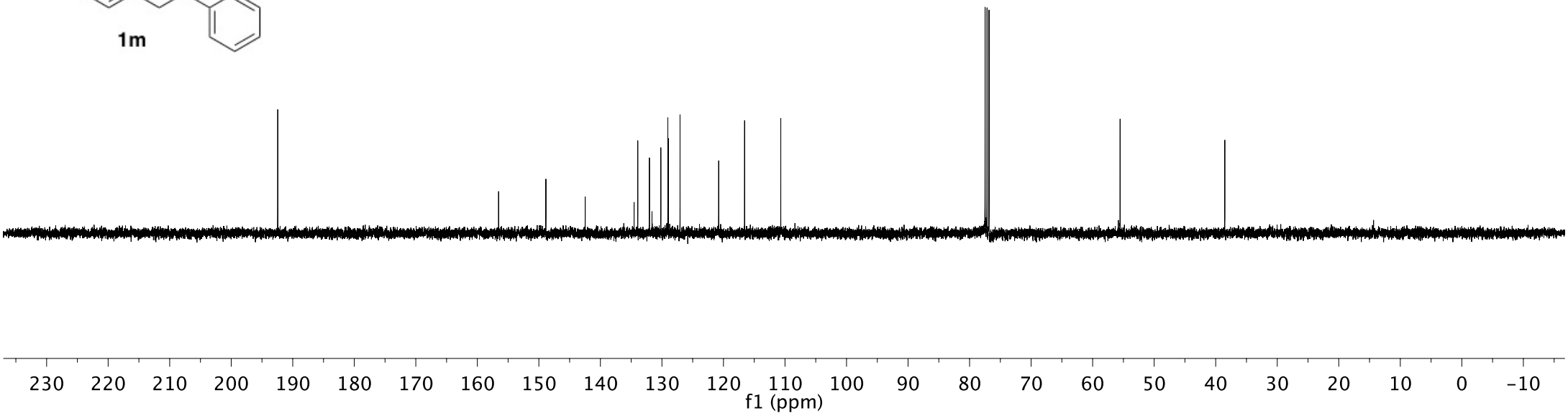

10.347
7.892
7.888
7.872
7.869
7.518
7.515
7.500
7.496
7.481
7.477
7.368
7.349
7.330
7.304
7.279
7.274
7.260
7.254
7.239
7.235
7.095
7.090
7.076
7.072
6.909
6.907
6.889
6.869
5.128
5.125
5.121
5.118
4.821
4.816
4.812
4.808
4.167
4.151 EtOAc
4.133 EtOAc
4.115 EtOAc
4.097 EtOAc
3.864
2.049 EtOAc
1.280 EtOAc
1.262 EtOAc
1.244 EtOAc
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
OMe
1m
0.86
0.92
0.99
1.06
2.33
0.96
2.02
1.00
1.02
1.95
3.09
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

192.434
156.542
148.860
142.469
134.524
133.925
132.034
131.614
130.175
129.039
128.960
127.056
120.771
116.562
110.683
77.160
55.537
38.522

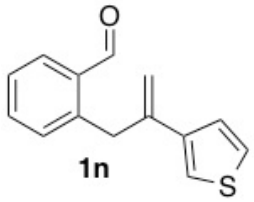
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



1m



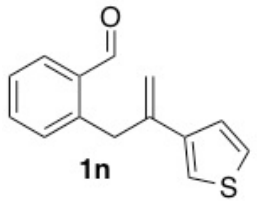
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



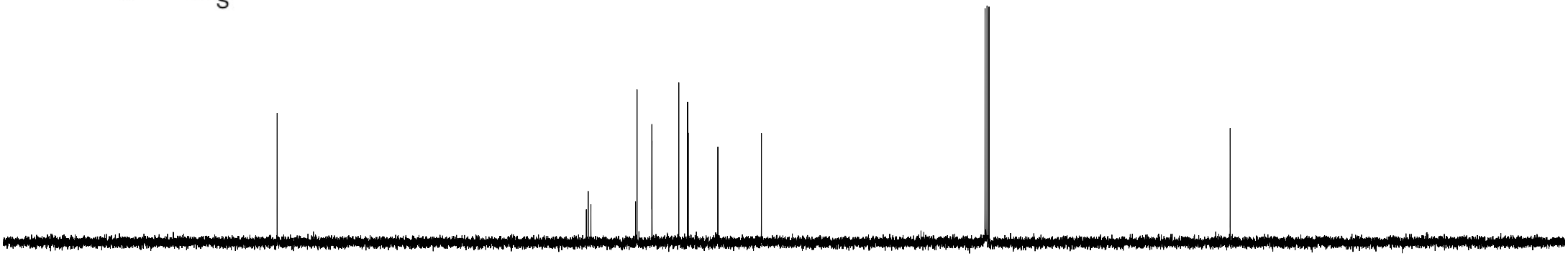
1n

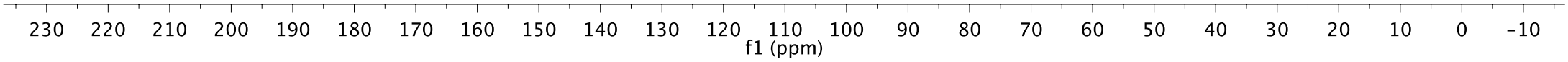
192.531
142.280
141.977
141.537
134.286
134.038
131.630
131.601
127.253
125.821
125.721
120.904
113.826
77.160
37.646

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

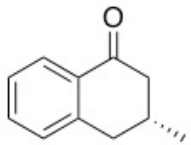


1n





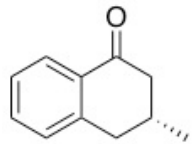
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2a

198.678
143.932
133.631
132.337
128.961
127.132
126.745
47.319
38.185
30.642
21.529

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2014-07-07T16:30:51
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2a

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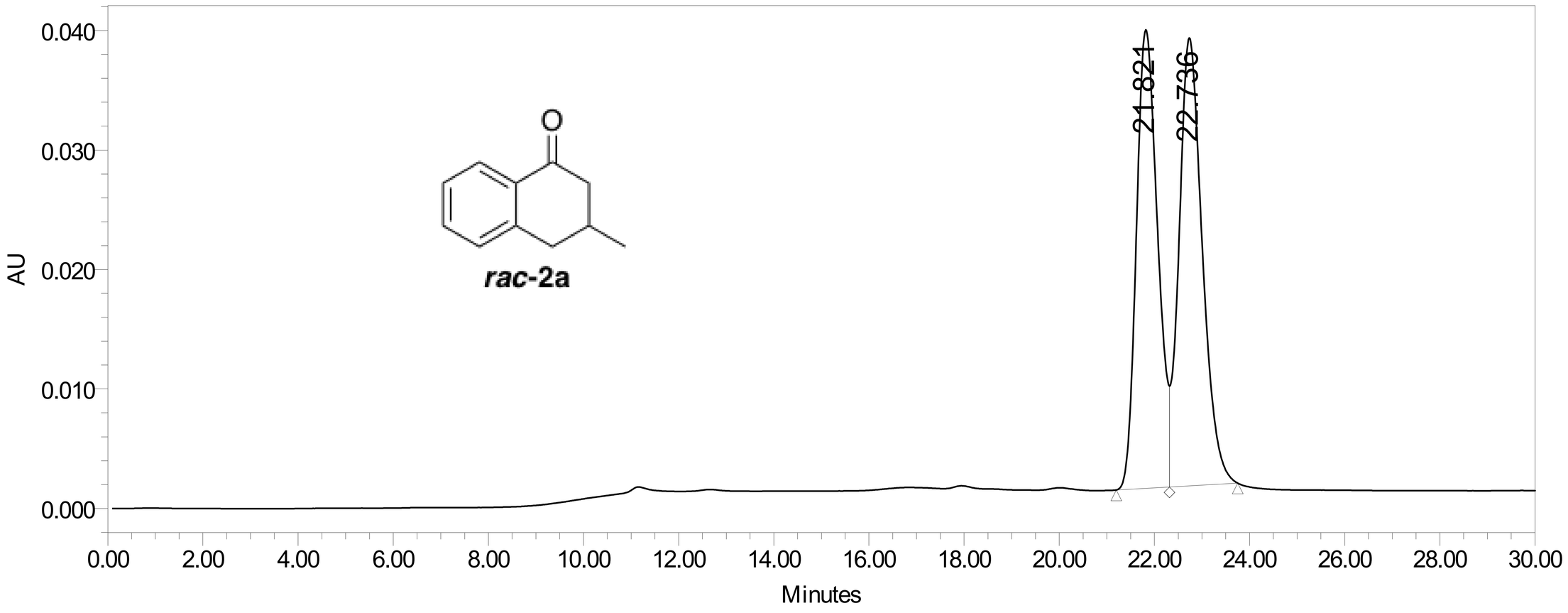
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten062015
Vial:	47	Acq. Method Set:	2_ASH 93_7 0pt3mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/20/2015 11:26:45 AM CDT		
Date Processed:	6/21/2015 2:33:25 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14442; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	21.821	1185883	48.10	38391
2	W2489 ChA 254nm	22.736	1279445	51.90	37493

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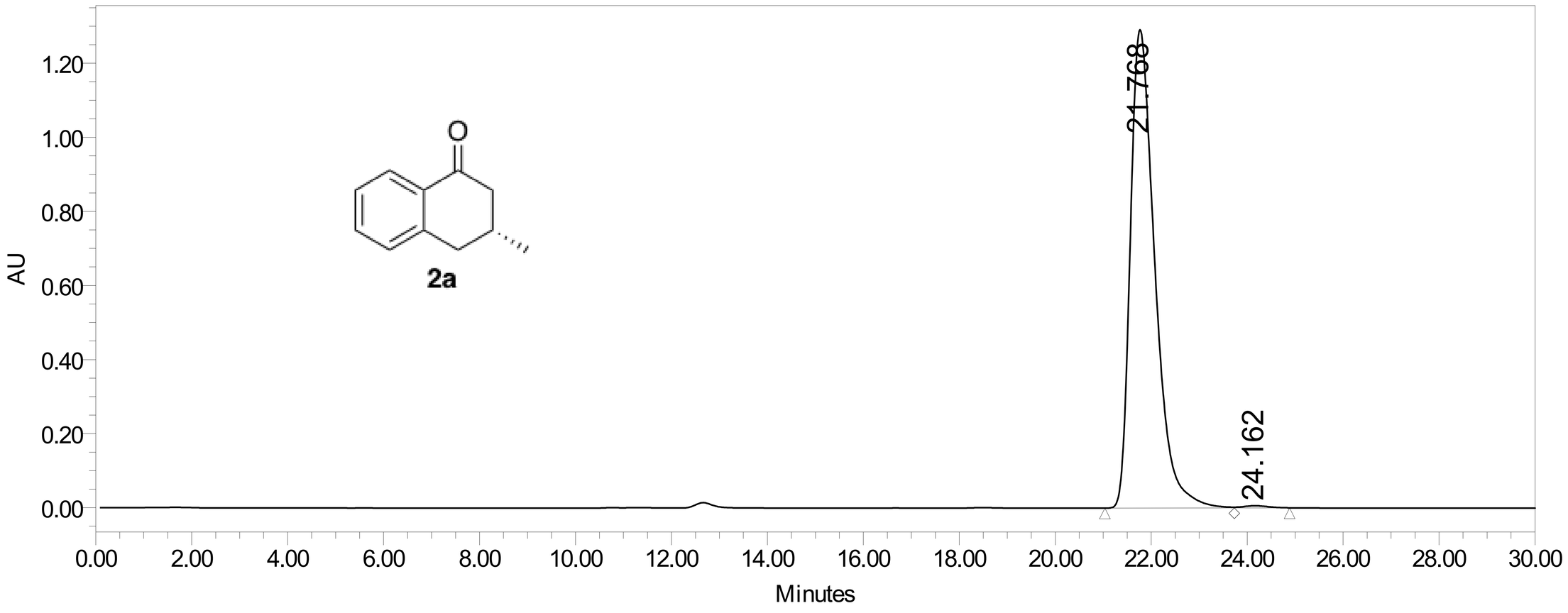
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	KJ_3-9_ASH_93to7_0pt3mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten061715
Vial:	29	Acq. Method Set:	2_ASH 93_7 0pt3mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/17/2015 10:04:06 PM CDT		
Date Processed:	6/19/2015 10:37:12 AM CDT		

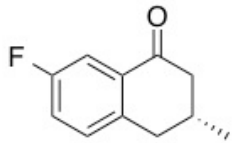


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14312; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	21.768	45896516	99.54	1291571
2	W2489 ChA 254nm	24.162	211794	0.46	5955

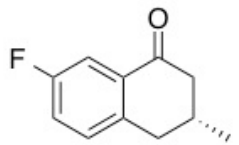
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2b

197.592
162.885
160.438
139.595
139.564
133.918
133.858
130.774
130.703
121.016
120.797
113.104
112.959
46.860
37.416
30.677
21.412

Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

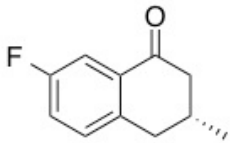


2b

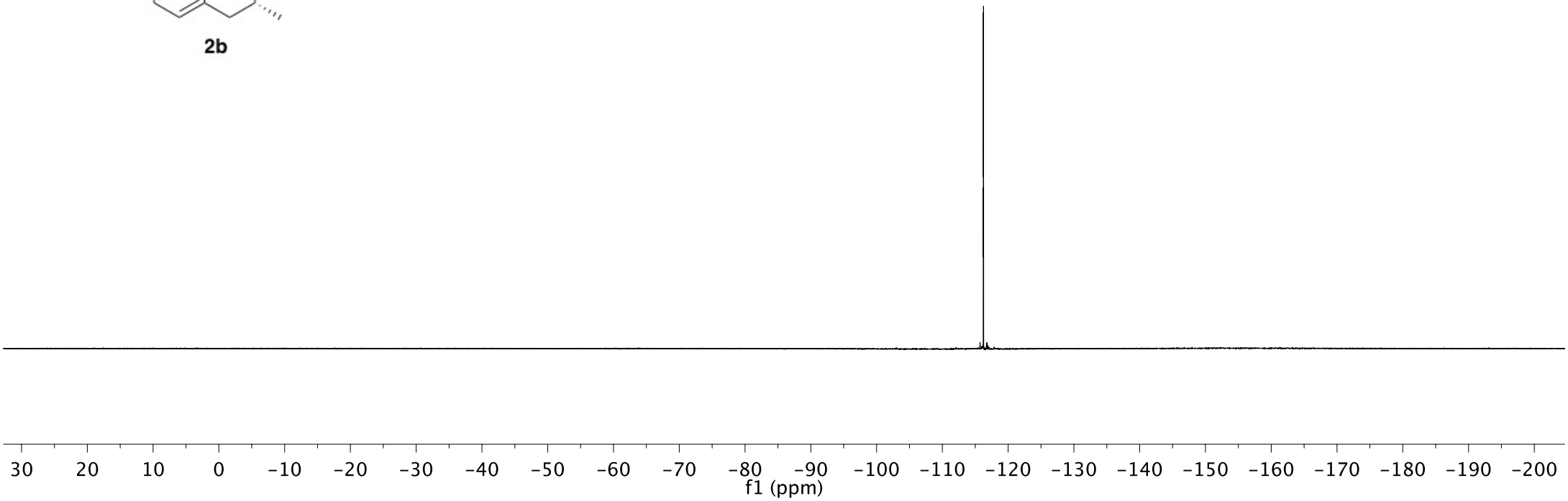
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	2.3667
Acquisition Time	0.7340
Spectrometer Frequency	376.05
Spectral Width	89285.7
Nucleus	19F



2b



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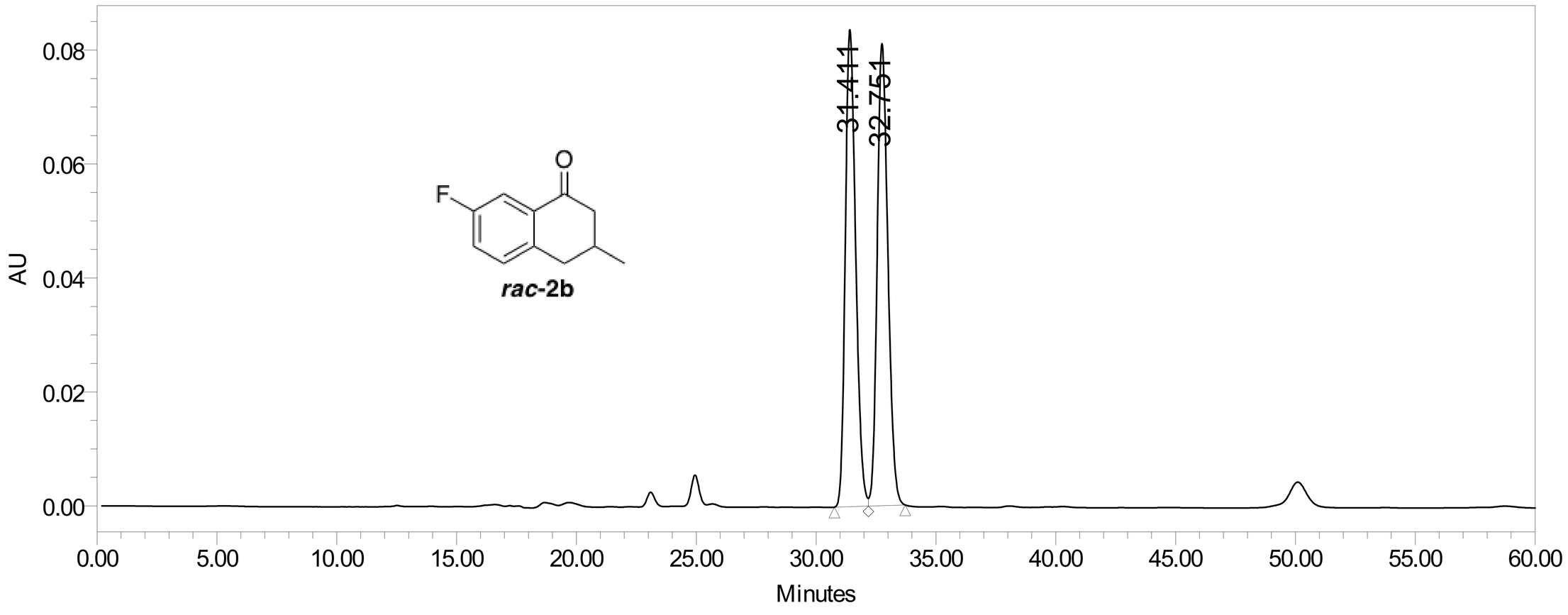
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten063014
Vial:	60	Acq. Method Set:	2_ASH 99_1 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/30/2014 5:58:33 PM CDT		
Date Processed:	2/21/2015 1:04:29 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9605; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	31.411	2515190	49.96	83759
2	W2489 ChA 254nm	32.751	2519187	50.04	81077

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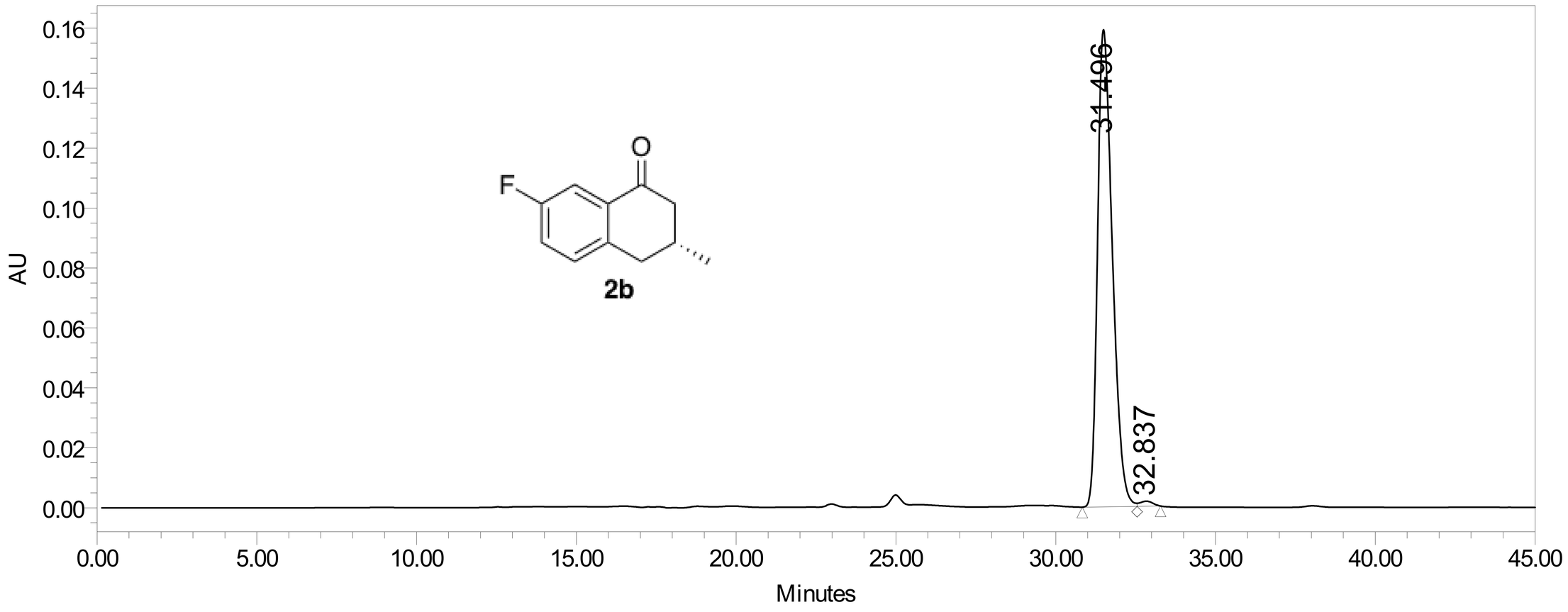
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten063014
Vial:	61	Acq. Method Set:	2_ASH 99_1 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	45.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/30/2014 6:59:15 PM CDT		
Date Processed:	2/21/2015 1:05:44 PM CST		

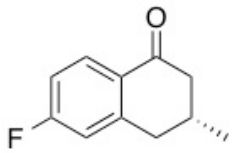


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9609; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	31.496	5122456	99.10	159233
2	W2489 ChA 254nm	32.837	46753	0.90	1681

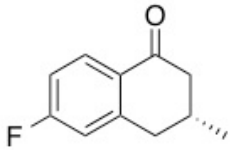
Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2c

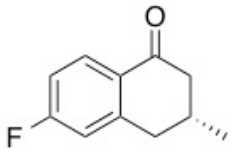
197.103
167.175
164.634
146.998
146.906
130.253
130.153
129.004
128.975
115.351
115.138
114.507
114.289
46.985
38.216
30.539
21.399

Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	144
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

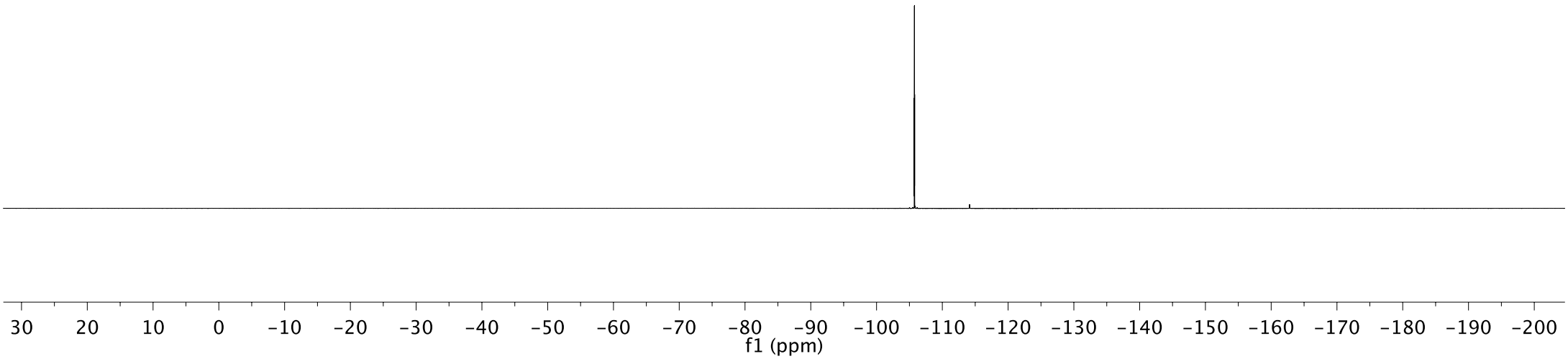


2c

Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	56
Relaxation Delay	1.0000
Pulse Width	2.3667
Acquisition Time	0.7340
Spectrometer Frequency	376.05
Spectral Width	89285.7
Nucleus	19F



2c



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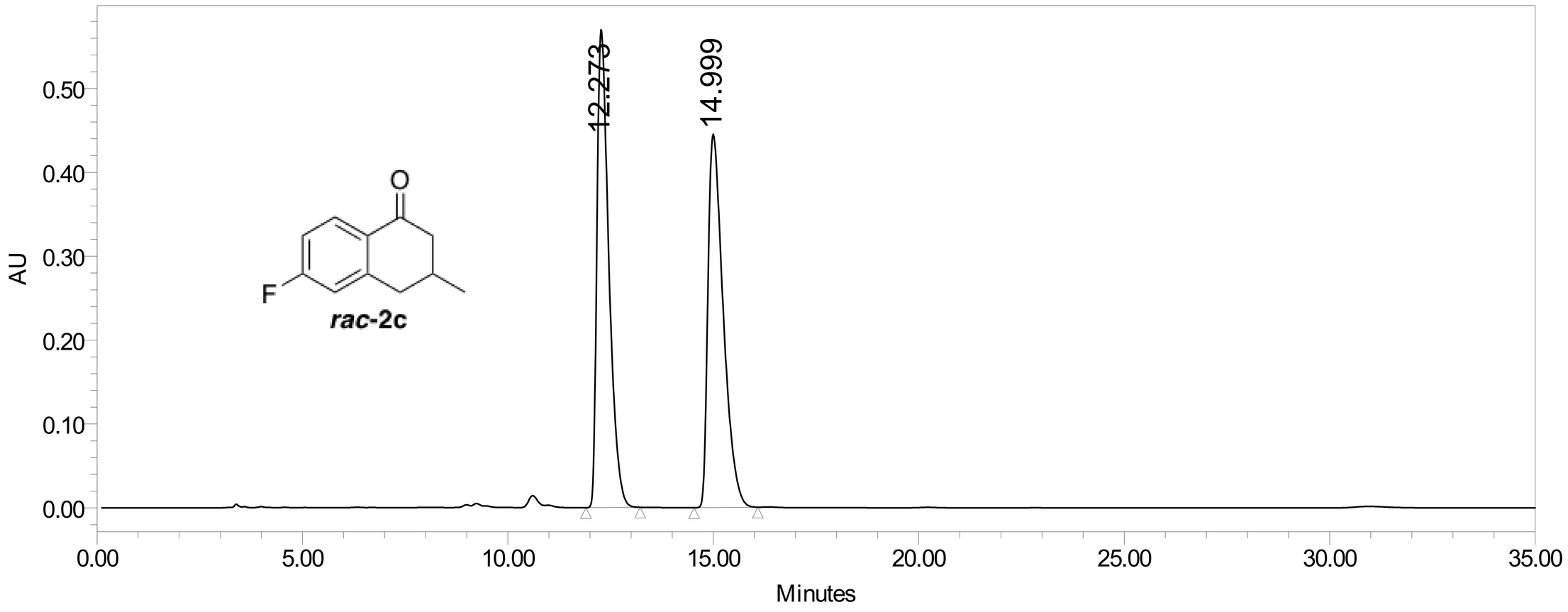
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten041114
Vial:	32	Acq. Method Set:	2_ASH 99_1 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	4/11/2014 12:59:37 PM CDT		
Date Processed:	2/21/2015 1:00:24 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9597; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	12.273	11451026	49.81	570531
2	W2489 ChA 254nm	14.999	11536079	50.19	445099

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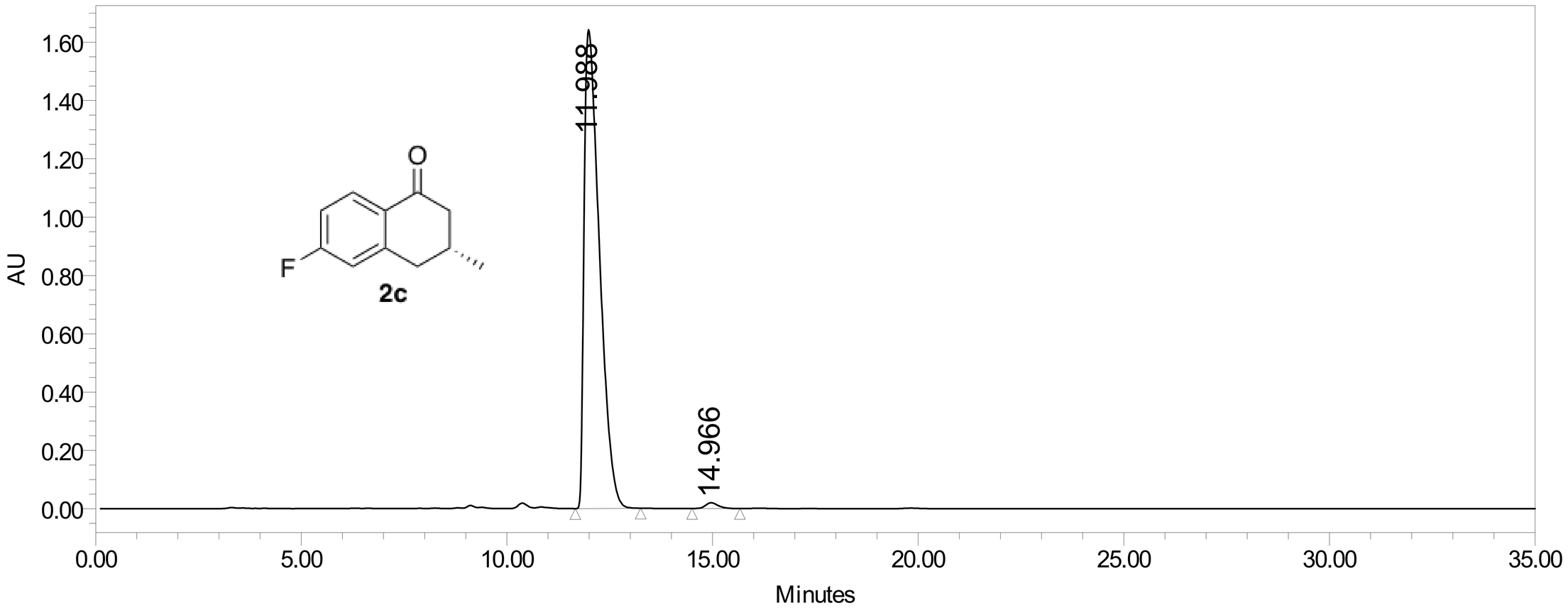
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten041114
Vial:	33	Acq. Method Set:	2_ASH 99_1 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	4/11/2014 3:21:53 PM CDT		
Date Processed:	2/21/2015 1:02:14 PM CST		

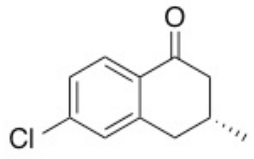


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9601; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.988	42582120	99.01	1643307
2	W2489 ChA 254nm	14.966	425038	0.99	19811

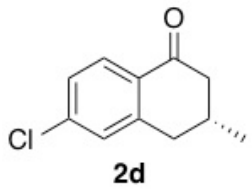
Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2d

197.418
145.446
139.838
130.775
128.816
128.795
127.267
77.160
47.026
37.893
30.461
21.374

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	192
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2d

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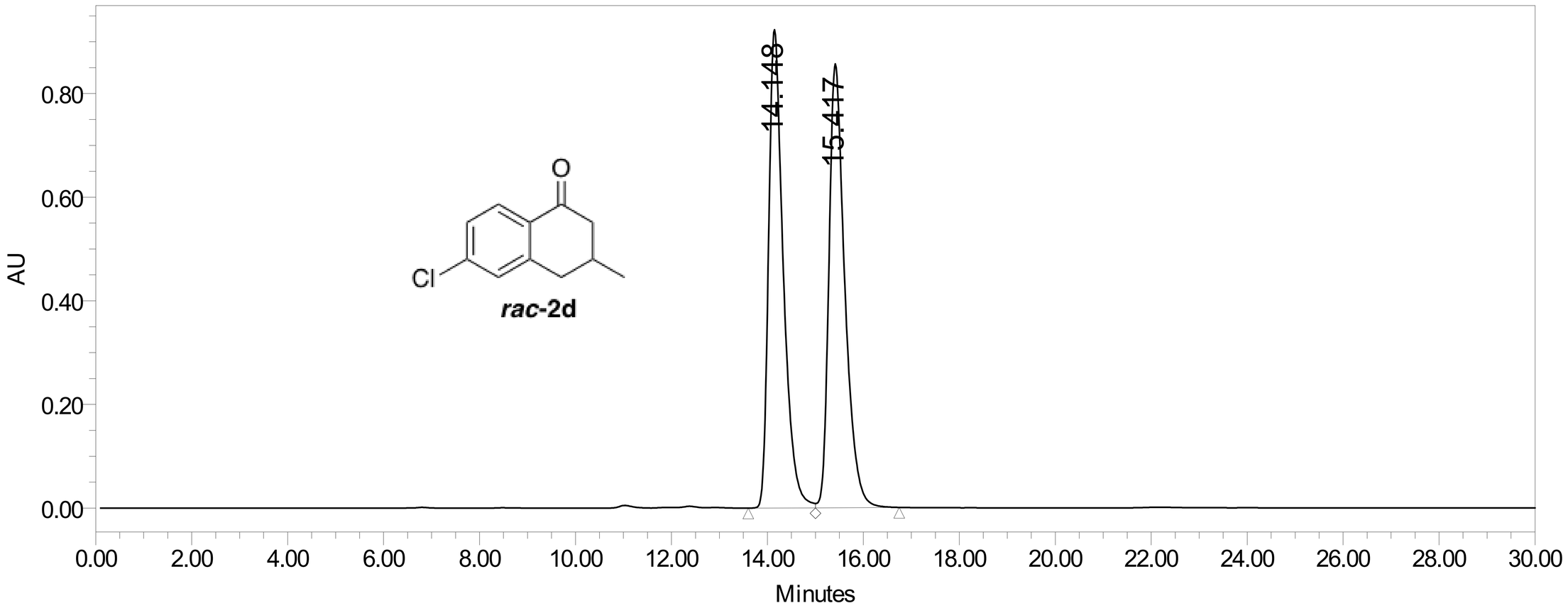
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten061715
Vial:	30	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/17/2015 10:54:57 PM CDT		
Date Processed:	6/19/2015 10:34:40 AM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14315; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.148	19663926	49.94	923242
2	W2489 ChA 254nm	15.417	19710581	50.06	856544

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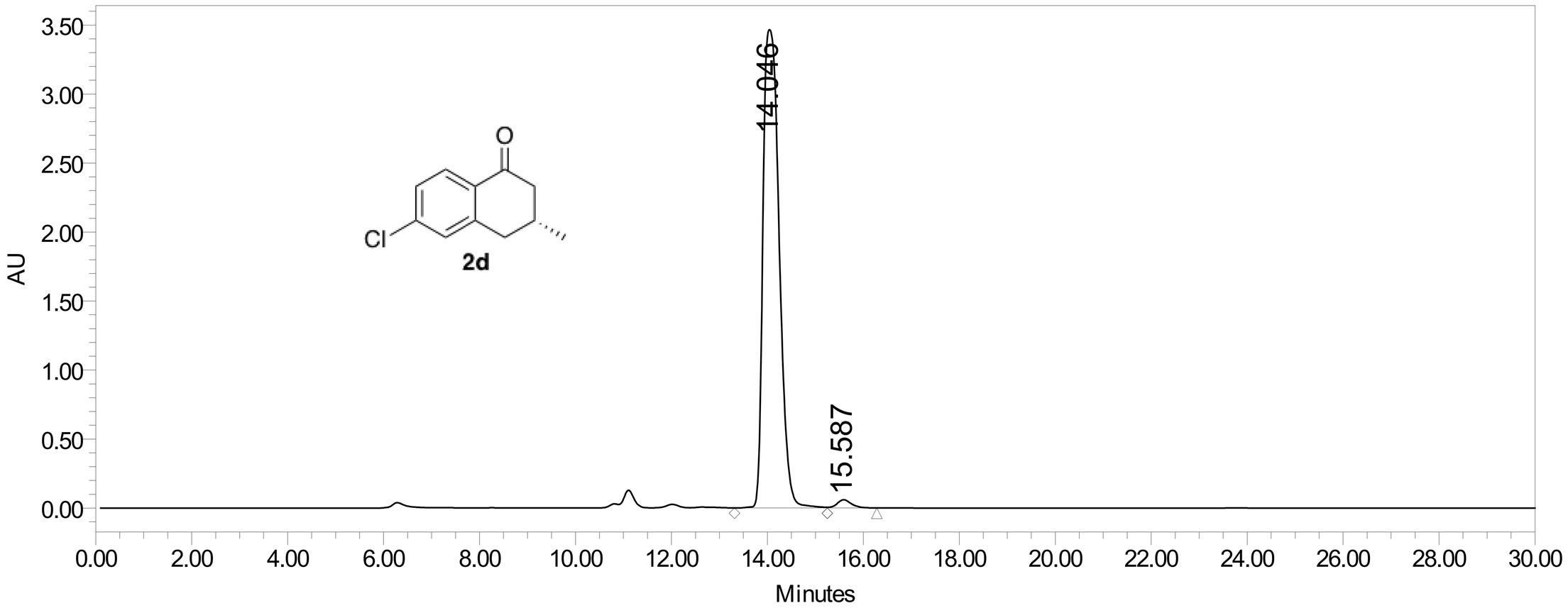
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	KJ_3-13_ASH_95to5_0pt5mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten040314
Vial:	43	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	4/3/2014 1:21:45 PM CDT		
Date Processed:	2/21/2015 1:10:32 PM CST		

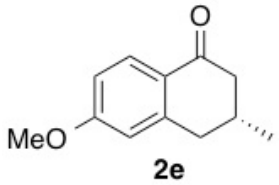


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9617; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	14.046	81228623	98.52	3466481
2	W2489 ChA 254nm	15.587	1219193	1.48	59136

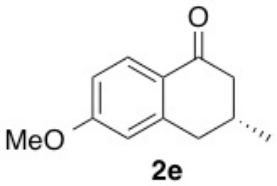
Solvent	cdcl3
Temperature	35.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2e

197.406
163.747
146.397
129.538
126.010
113.063
112.834
55.527
47.061
38.554
30.657
21.489

Solvent	cdcl3
Temperature	35.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2e

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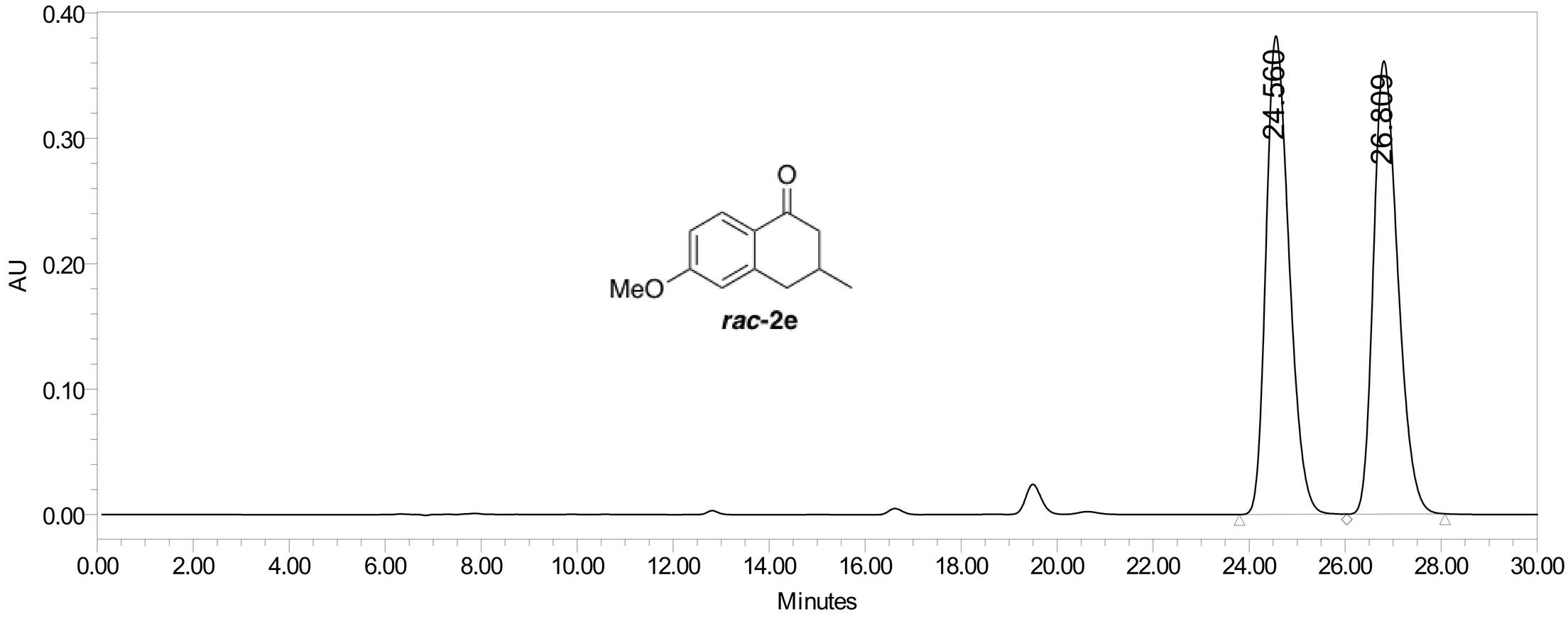
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten030214
Vial:	10	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/2/2014 1:52:41 PM CST		
Date Processed:	2/21/2015 1:12:16 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 12009; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	24.560	12736029	50.08	381616
2	W2489 ChA 254nm	26.809	12693572	49.92	361517

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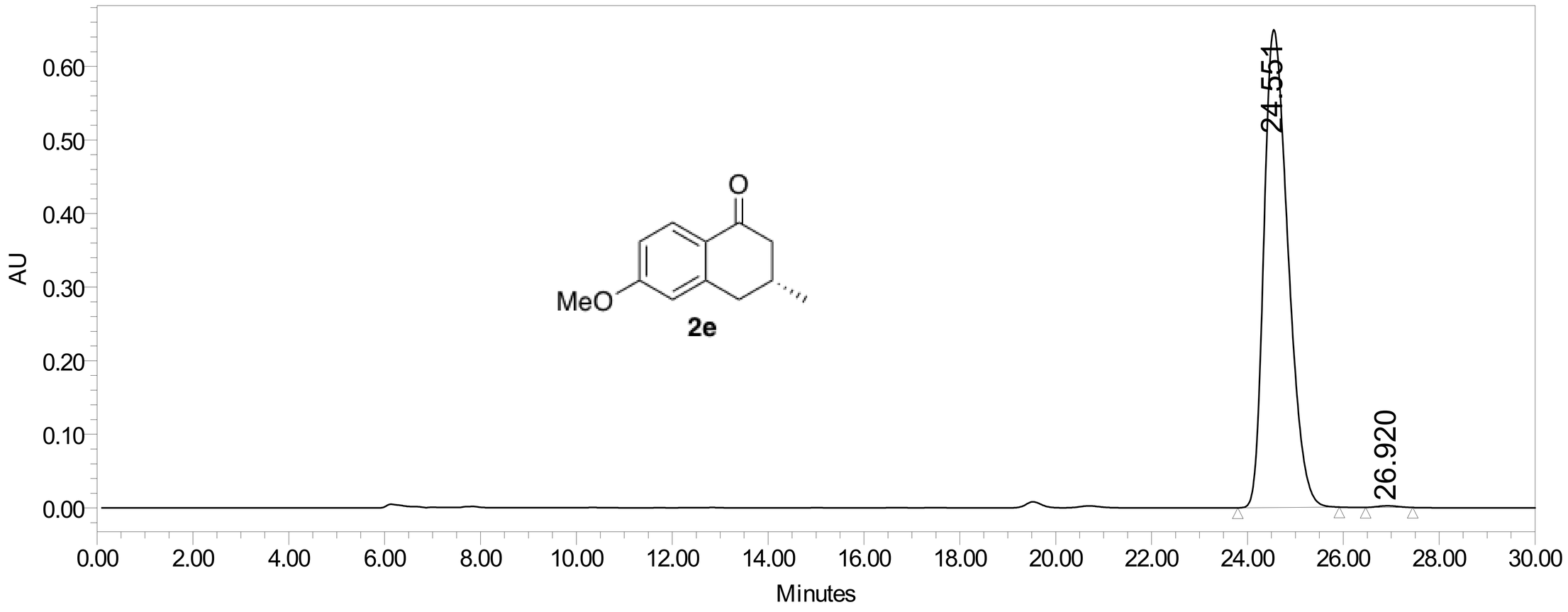
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten030214
Vial:	11	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	3/2/2014 4:45:32 PM CST		
Date Processed:	2/21/2015 1:14:01 PM CST		

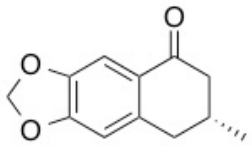


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 12013; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	24.551	22700698	99.70	649522
2	W2489 ChA 254nm	26.920	67931	0.30	2313

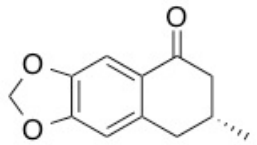
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2f

196.918
152.226
147.022
140.849
127.132
108.112
106.182
101.708
77.160
46.797
38.440
30.820
21.393

Solvent	cdcl3
Temperature	50.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2f

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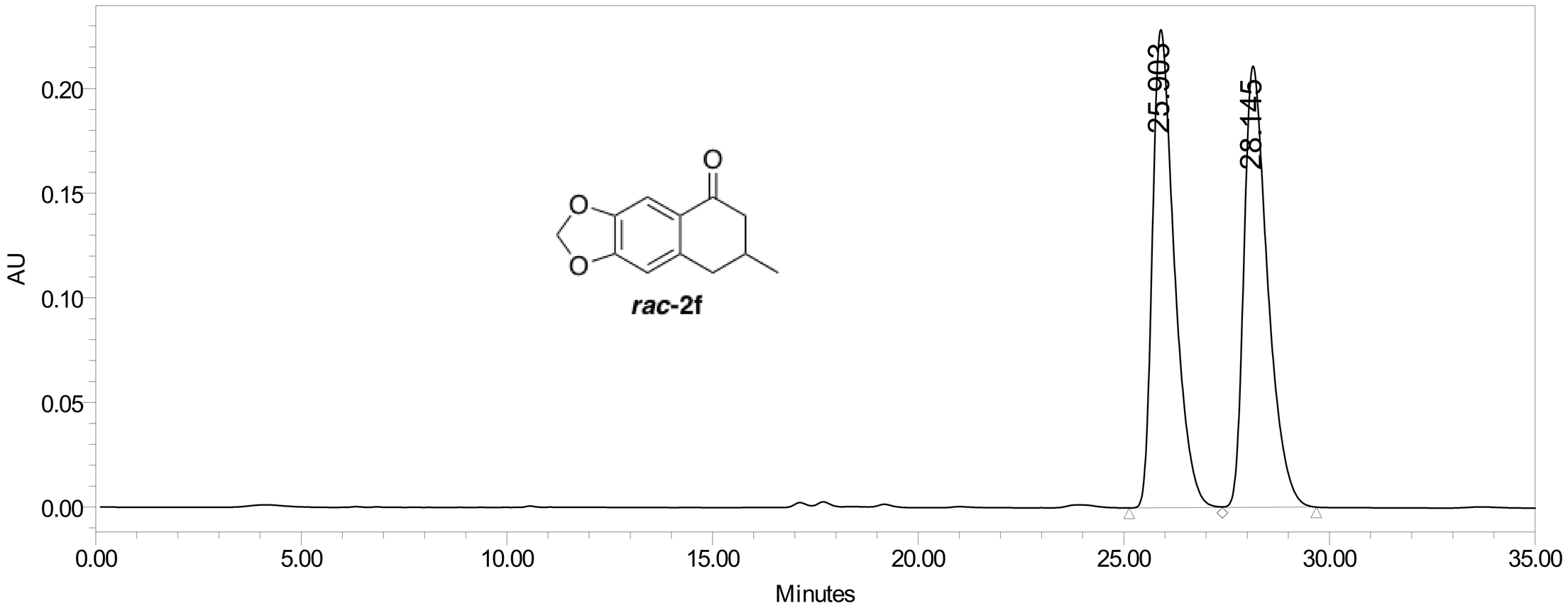
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten041014
Vial:	46	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	4/10/2014 3:22:01 PM CDT		
Date Processed:	2/21/2015 12:57:26 PM CST		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9589; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	25.903	8478221	49.98	228572
2	W2489 ChA 254nm	28.145	8484176	50.02	210932

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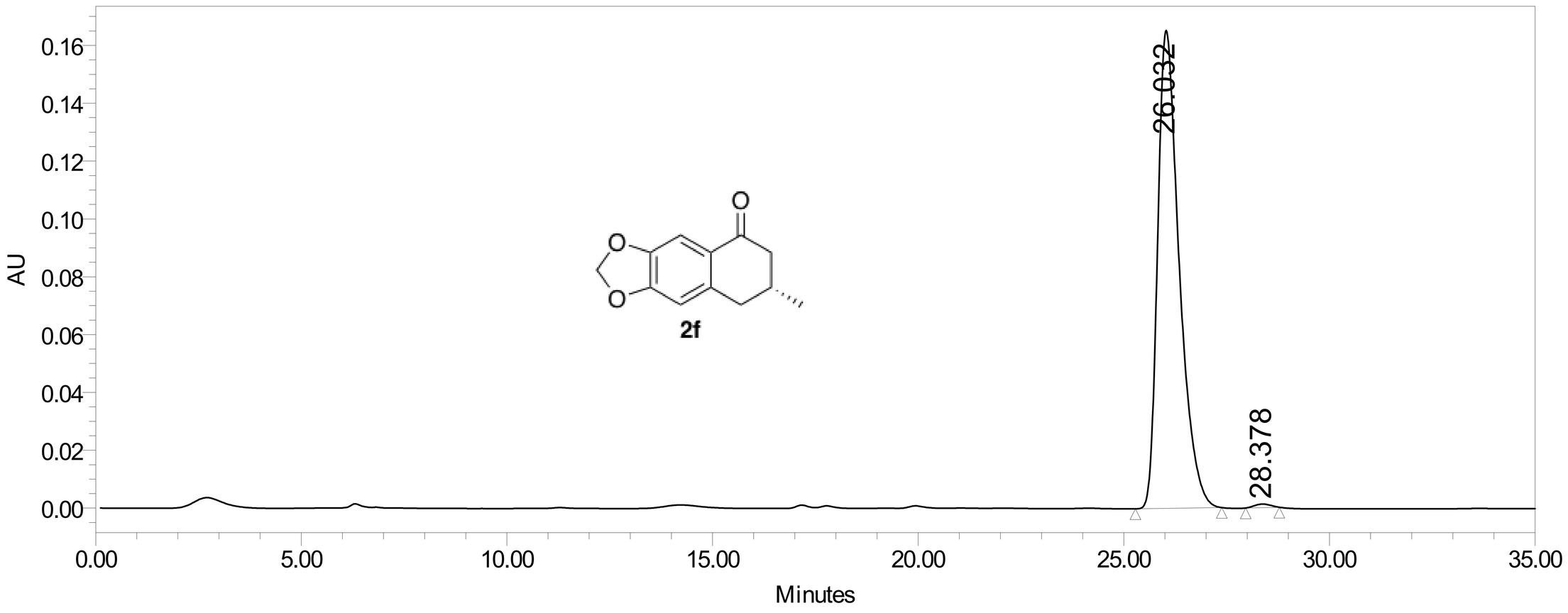
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten041014
Vial:	47	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	35.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	4/10/2014 3:57:41 PM CDT		
Date Processed:	2/21/2015 12:58:37 PM CST		

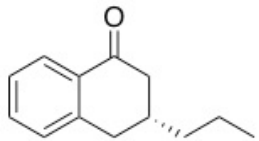


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9593; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	26.032	6022679	99.46	165338
2	W2489 ChA 254nm	28.378	32779	0.54	1226

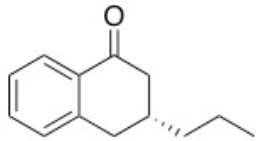
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2g

198.850
143.969
133.631
132.560
129.035
127.092
126.724
45.588
38.137
36.317
35.211
19.827
14.235

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	128
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	2.7500
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2g

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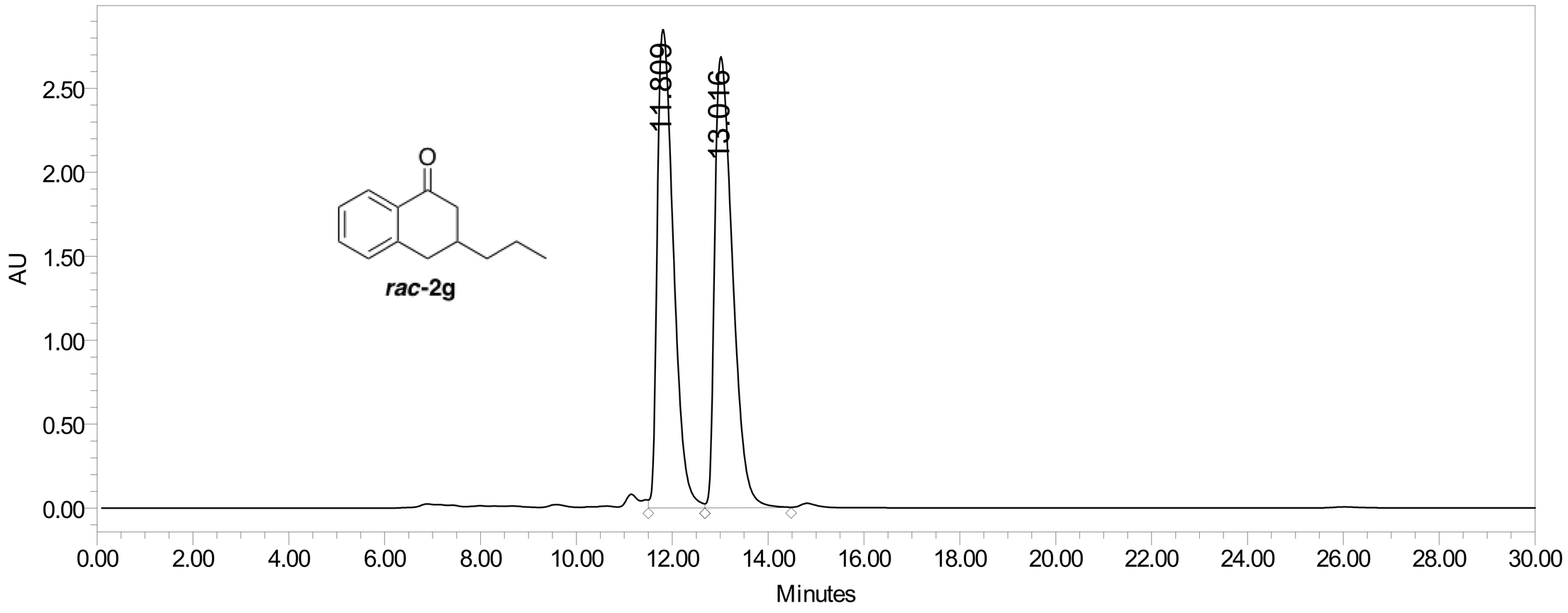
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten061815
Vial:	48	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/18/2015 2:41:53 PM CDT		
Date Processed:	6/19/2015 10:35:02 AM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14318; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.809	66987865	49.02	2852474
2	W2489 ChA 254nm	13.016	69663363	50.98	2685986

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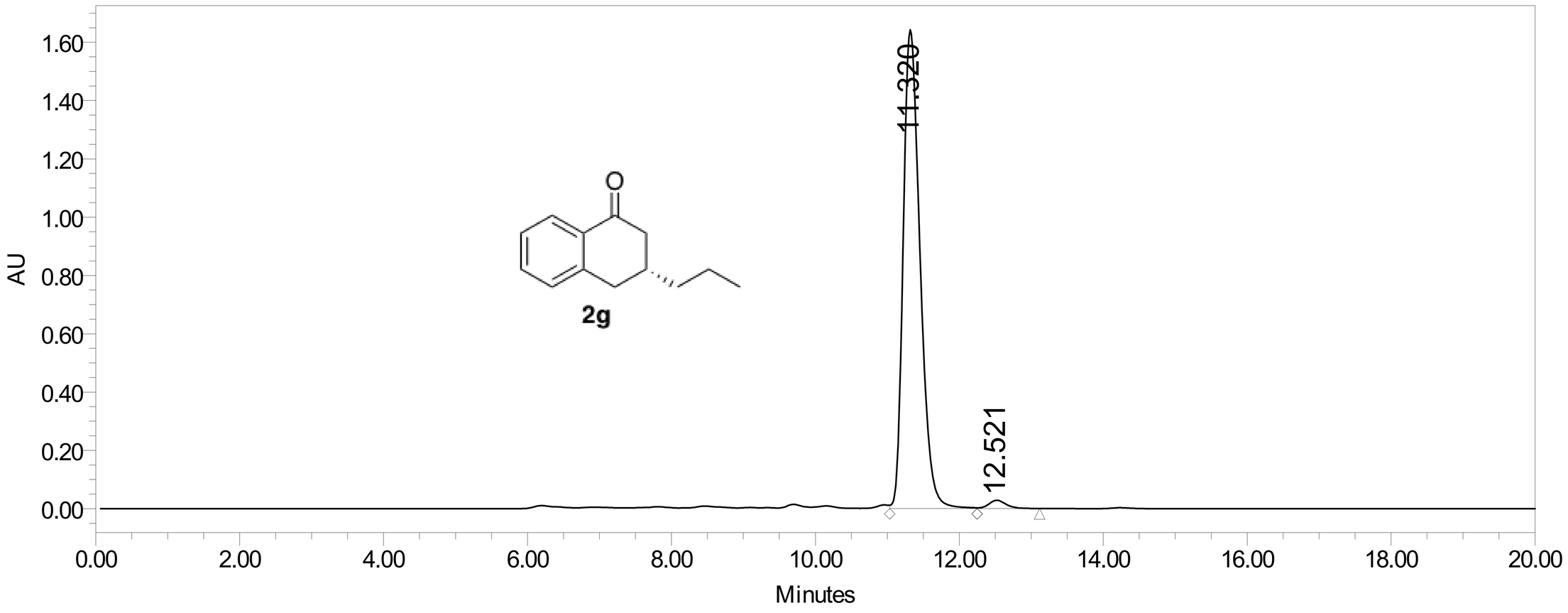
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten061714
Vial:	36	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/17/2014 4:02:50 PM CDT		
Date Processed:	2/21/2015 1:24:21 PM CST		

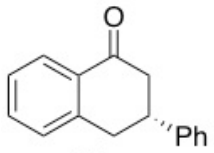


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 9633; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	11.320	26708347	98.26	1643306
2	W2489 ChA 254nm	12.521	473365	1.74	28263

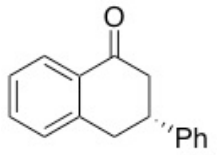
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



2h

197.881
143.549
143.495
133.905
132.230
128.976
128.914
127.334
127.107
127.067
126.808
46.094
41.246
37.820

Solvent	cdcl3
Temperature	32.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	144
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.2845
Acquisition Date	2014-07-09T20:51:46
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2h

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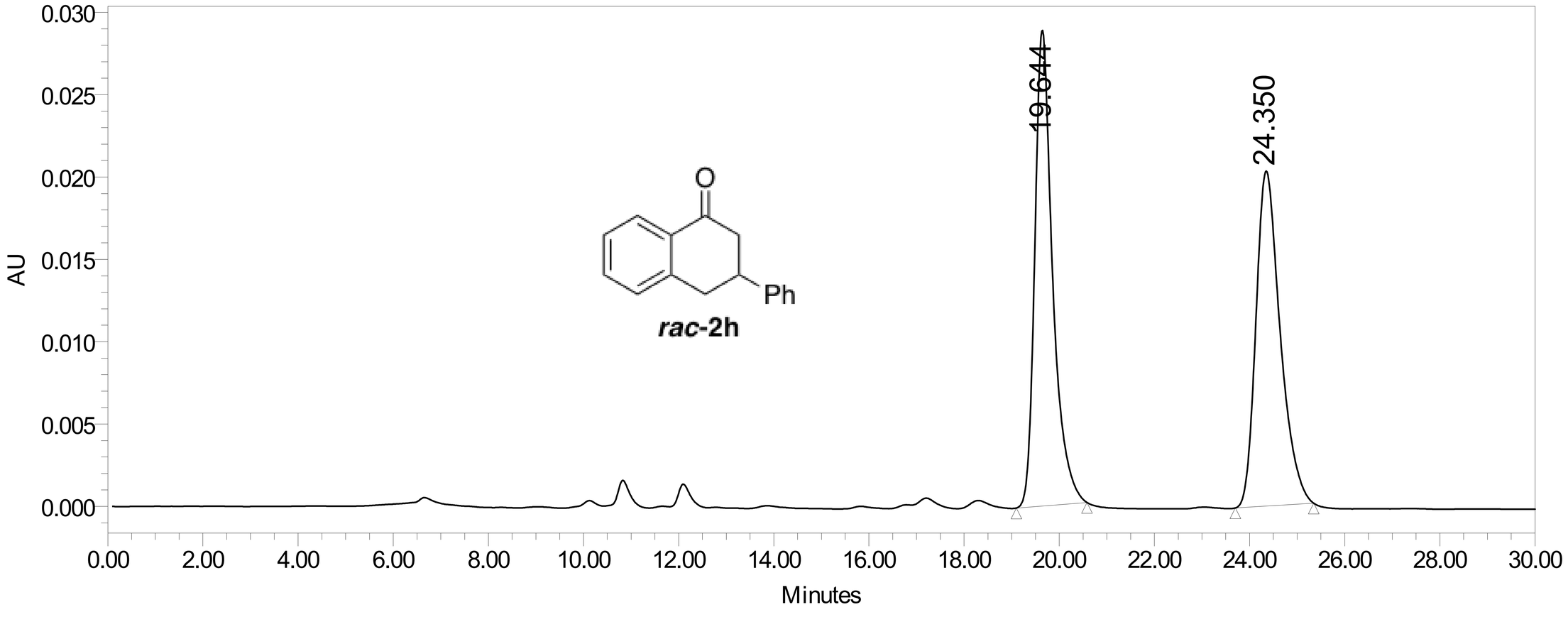
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten062115_2
Vial:	27	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/21/2015 5:55:30 PM CDT		
Date Processed:	6/21/2015 6:32:05 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14461; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	19.644	750285	51.04	28900
2	W2489 ChA 254nm	24.350	719677	48.96	20352

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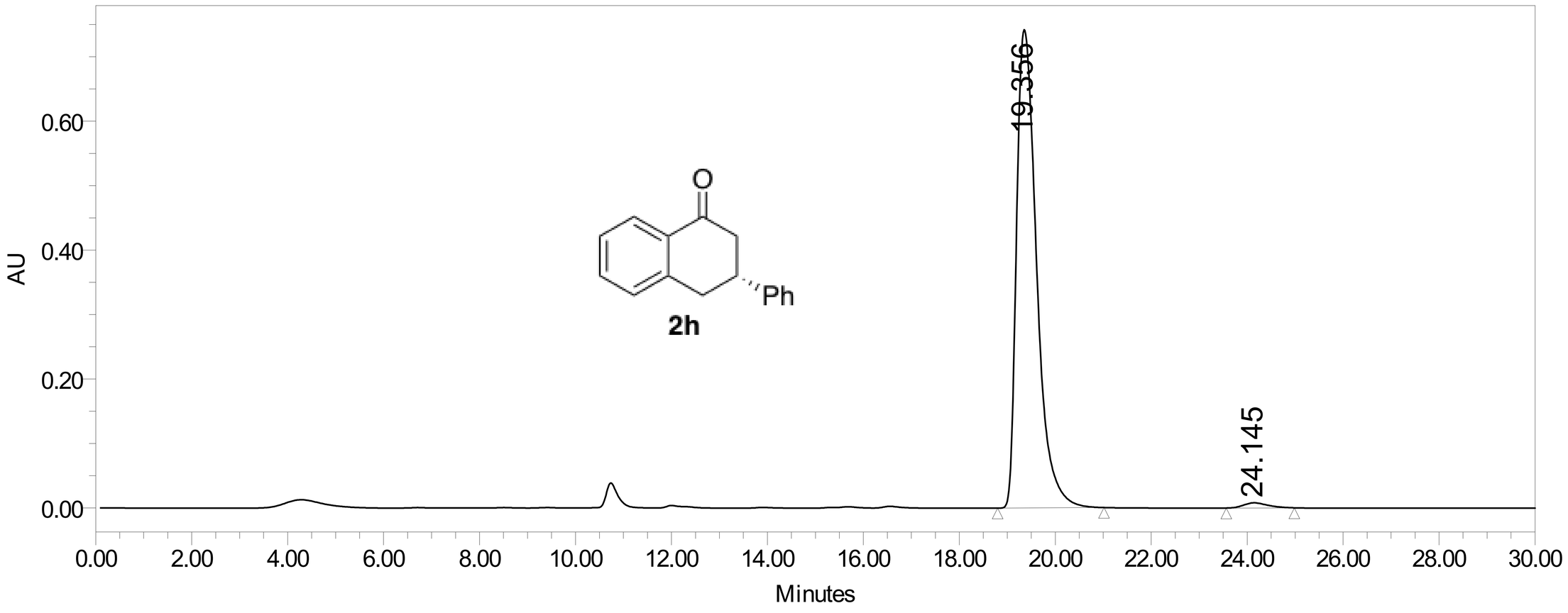
Injection Summary Report

SAMPLE INFORMATION

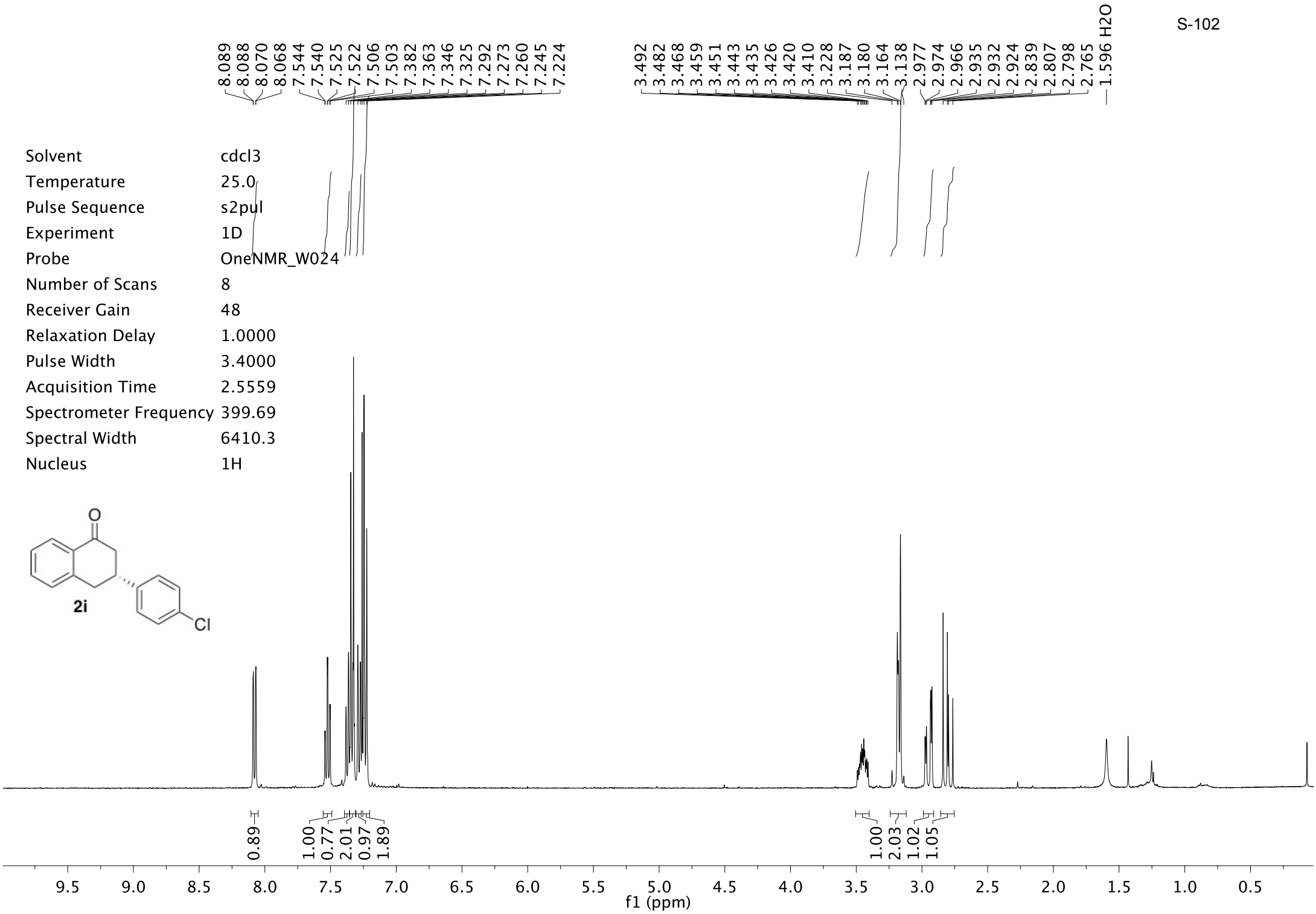
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten061715
Vial:	32	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	6/18/2015 12:16:25 AM CDT		
Date Processed:	6/19/2015 10:35:34 AM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14324; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	19.356	21466144	98.73	742651
2	W2489 ChA 254nm	24.145	276414	1.27	7934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8.088
8.070
8.068
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7.540
7.525
7.522
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7.503
7.382
7.363
7.346
7.325
7.292
7.273
7.260
7.245
7.224
3.492
3.482
3.468
3.459
3.451
3.443
3.435
3.426
3.420
3.410
3.228
3.187
3.180
3.164
3.138
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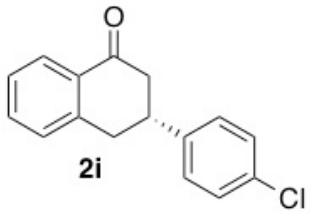
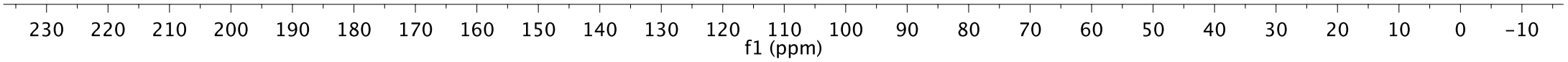
2.974
2.966
2.935
2.932
2.924
2.839
2.807
2.798
2.765
1.596 H2O
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 48
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
2i
Cl
0.89
1.00
0.77
2.01
0.97
1.89
1.00
2.03
1.02
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

197.485
143.114
141.963
134.036
132.804
132.136
129.048
128.971
128.203
127.390
127.212
77.160
45.957
40.638
37.669

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	80
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2i

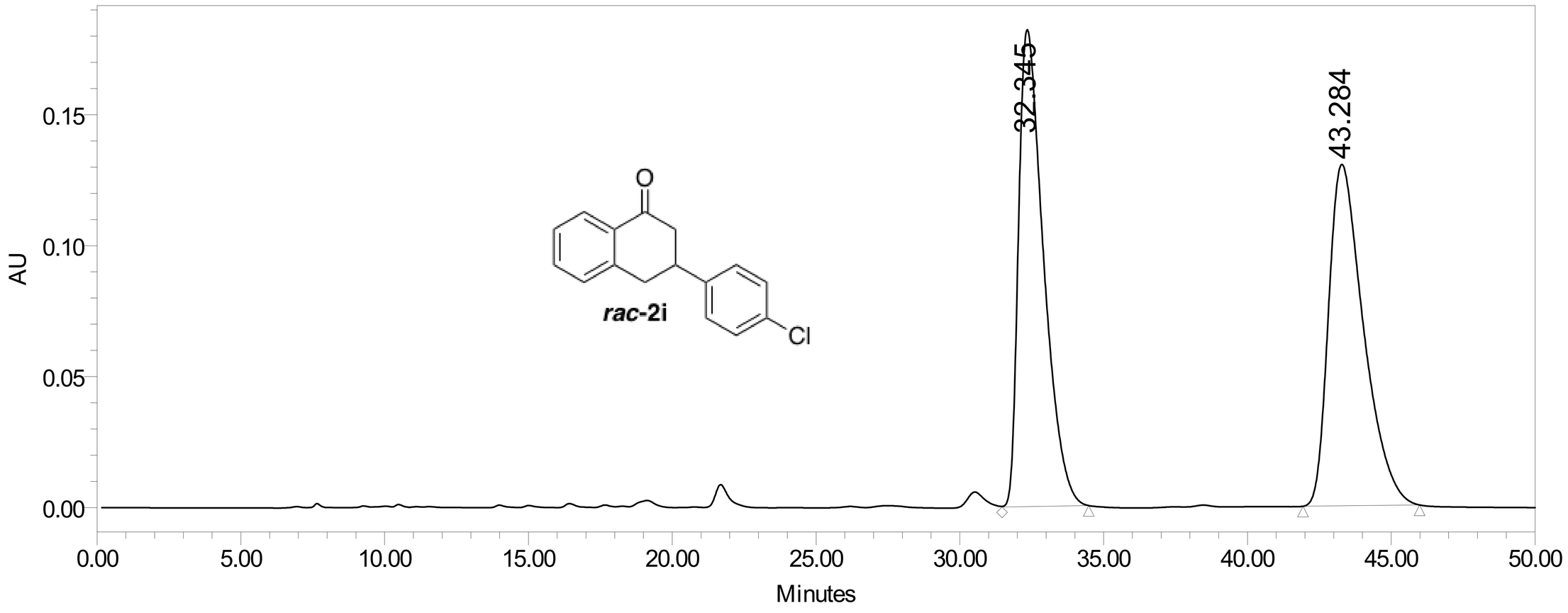


Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070115
Vial:	34	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/1/2015 8:05:43 PM CDT		
Date Processed:	7/10/2015 4:22:36 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14895; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	32.345	10991017	49.93	182112
2	W2489 ChA 254nm	43.284	11023203	50.07	130356

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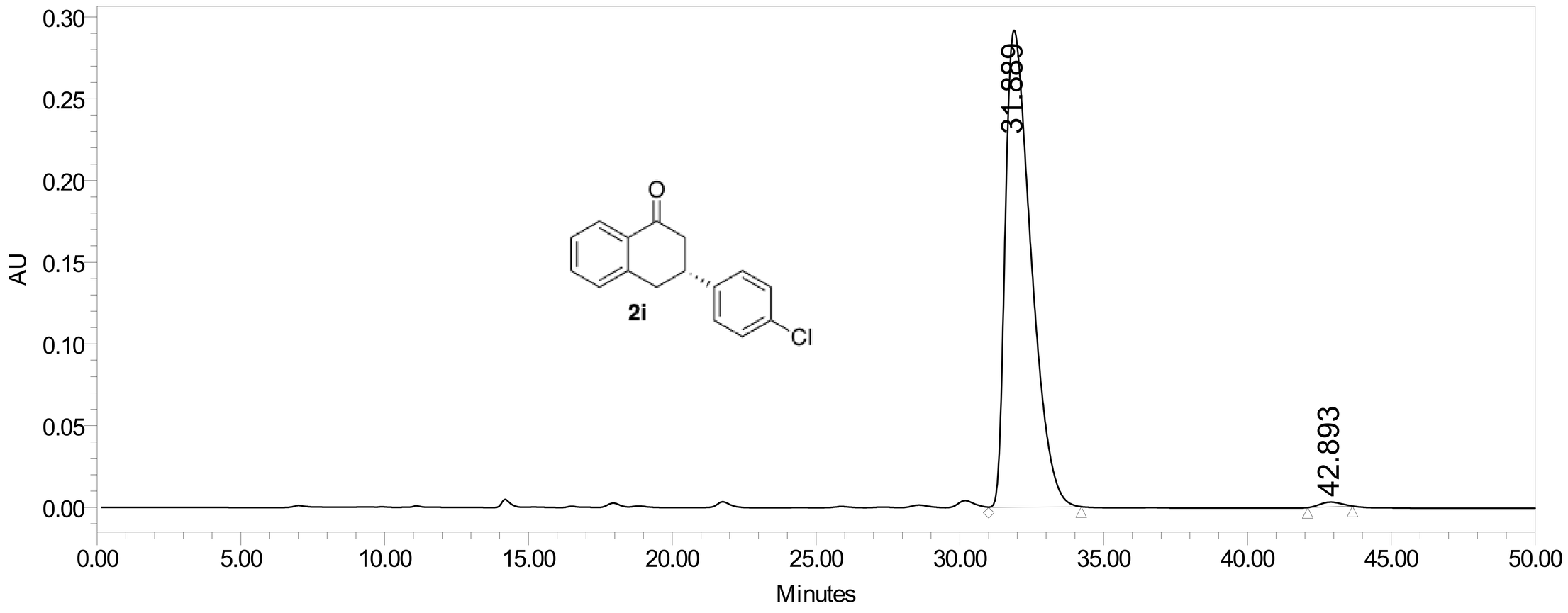
Injection Summary Report

SAMPLE INFORMATION

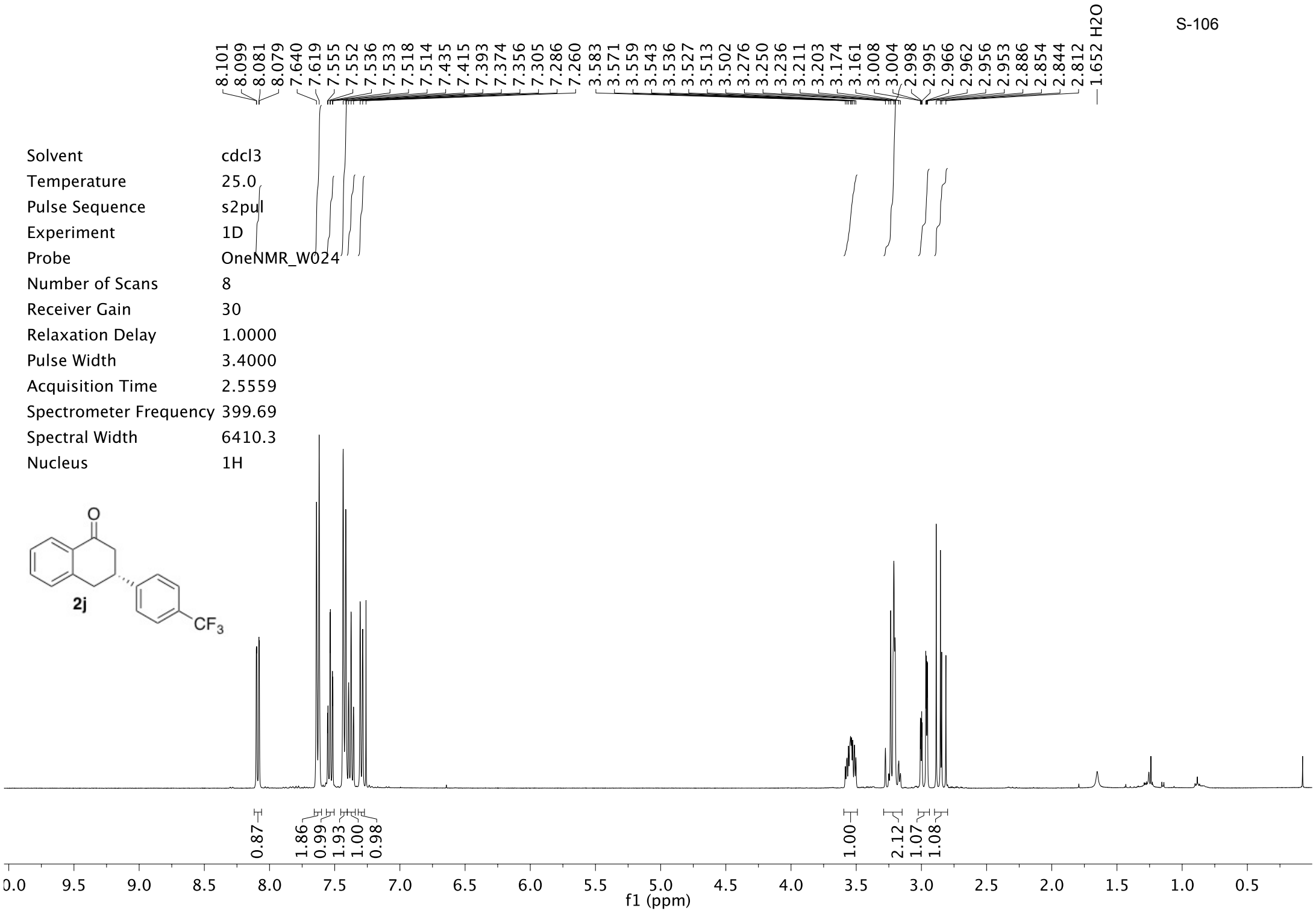
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten071015
Vial:	35	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	50.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/10/2015 4:36:39 PM CDT		
Date Processed:	7/13/2015 9:57:31 AM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14956; Processing Method: Kirsten

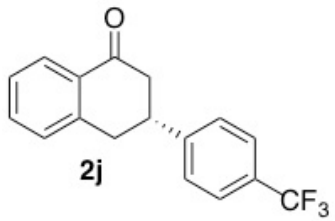
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	31.889	18154060	99.21	291806
2	W2489 ChA 254nm	42.893	143928	0.79	2873


8.101
8.099
8.081
8.079
7.640
7.619
7.555
7.552
7.536
7.533
7.518
7.514
7.435
7.415
7.393
7.374
7.356
7.305
7.286
7.260
3.583
3.571
3.559
3.543
3.536
3.527
3.513
3.502
3.276
3.250
3.236
3.211
3.203
3.174
3.161
3.008
3.004
2.998
2.995
2.966
2.962
2.956
2.953
2.886
2.854
2.844
2.812
1.652 H2O
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
2j
CF3
0.87
1.86
0.99
1.93
1.00
0.98
1.00
2.12
1.07
1.08
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

197.148
147.401
142.879
134.104
132.091
129.920
129.596
129.272
128.973
127.418
127.296
127.257
125.955
125.917
125.880
125.845
125.568
122.864
77.160
45.670
41.029
37.394

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	192
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



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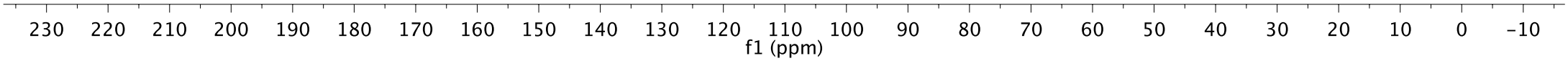
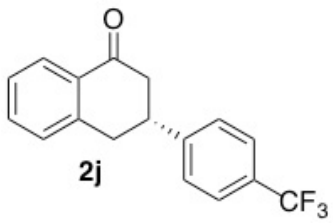


-63.460

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	16
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	3.4333
Acquisition Time	0.7340
Spectrometer Frequency	376.05
Spectral Width	89285.7
Nucleus	19F



2j

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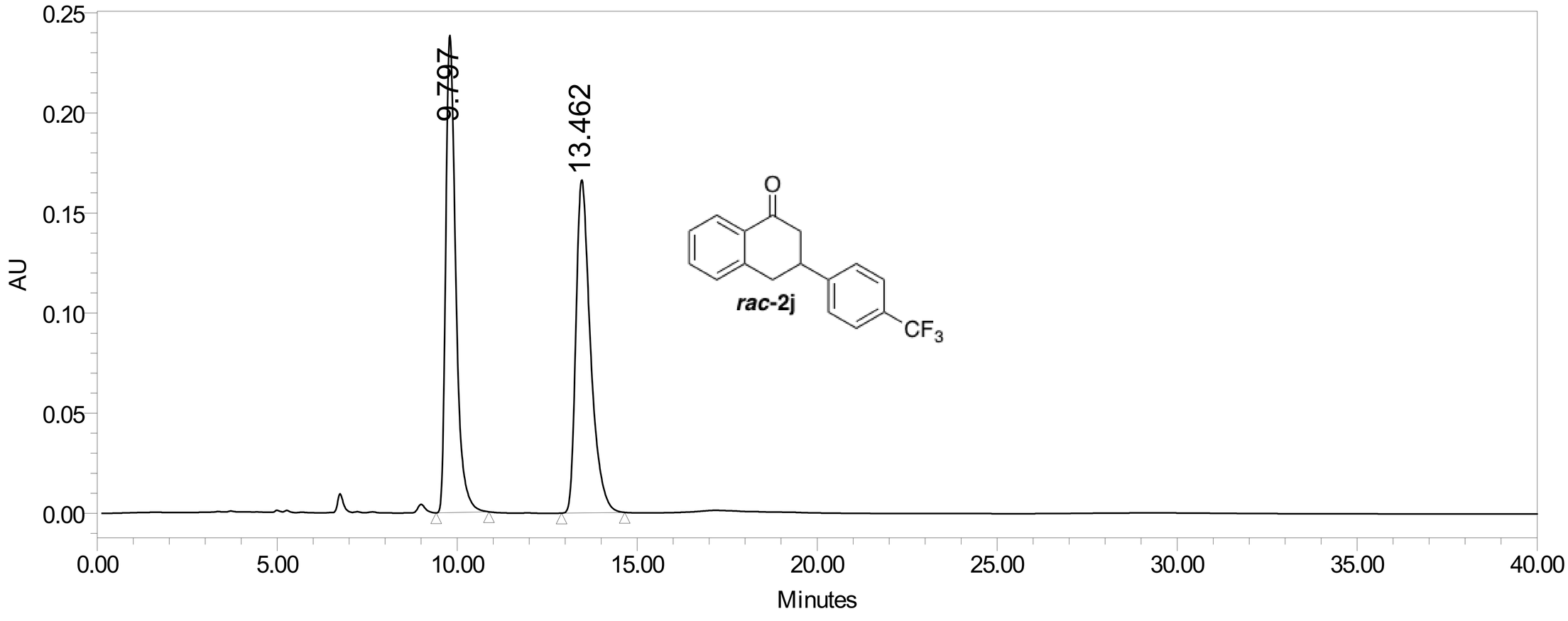
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	KJ_4-229A_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070215
Vial:	32	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/2/2015 9:53:45 AM CDT		
Date Processed:	7/10/2015 4:19:56 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14889; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.797	4630886	49.79	238447
2	W2489 ChA 254nm	13.462	4669868	50.21	166335

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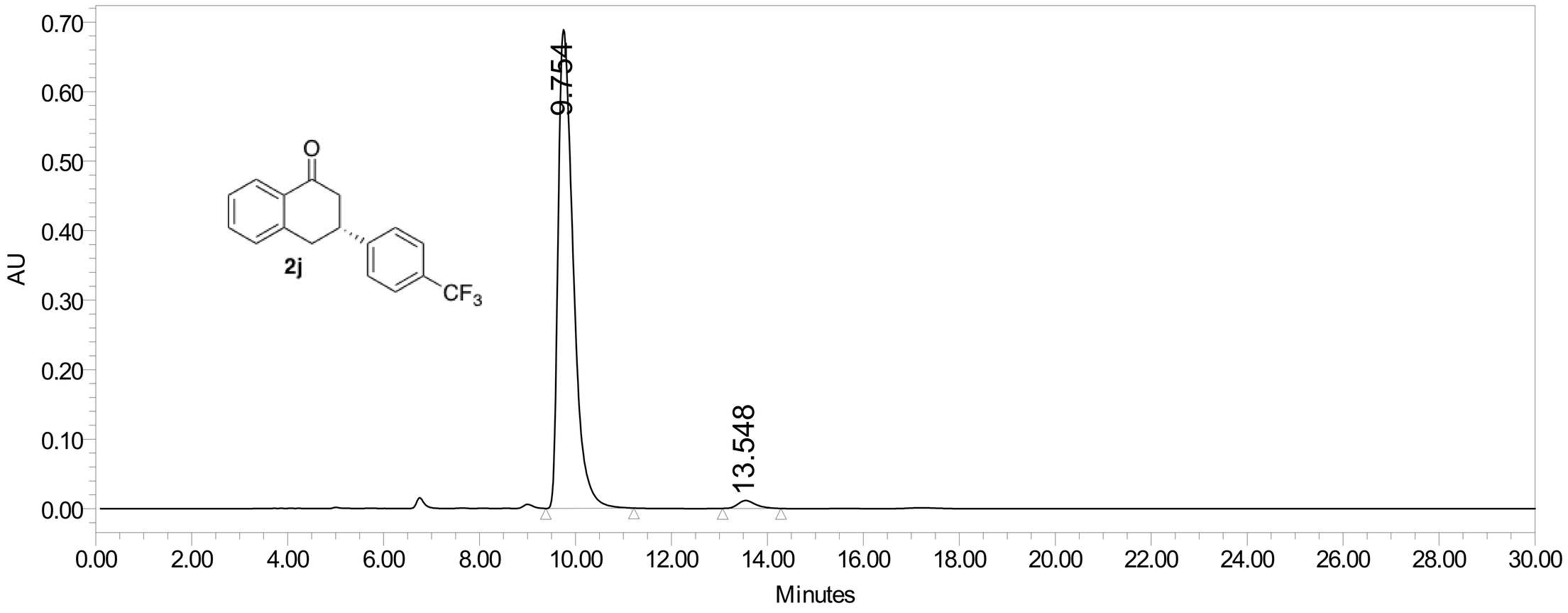
Injection Summary Report

SAMPLE INFORMATION

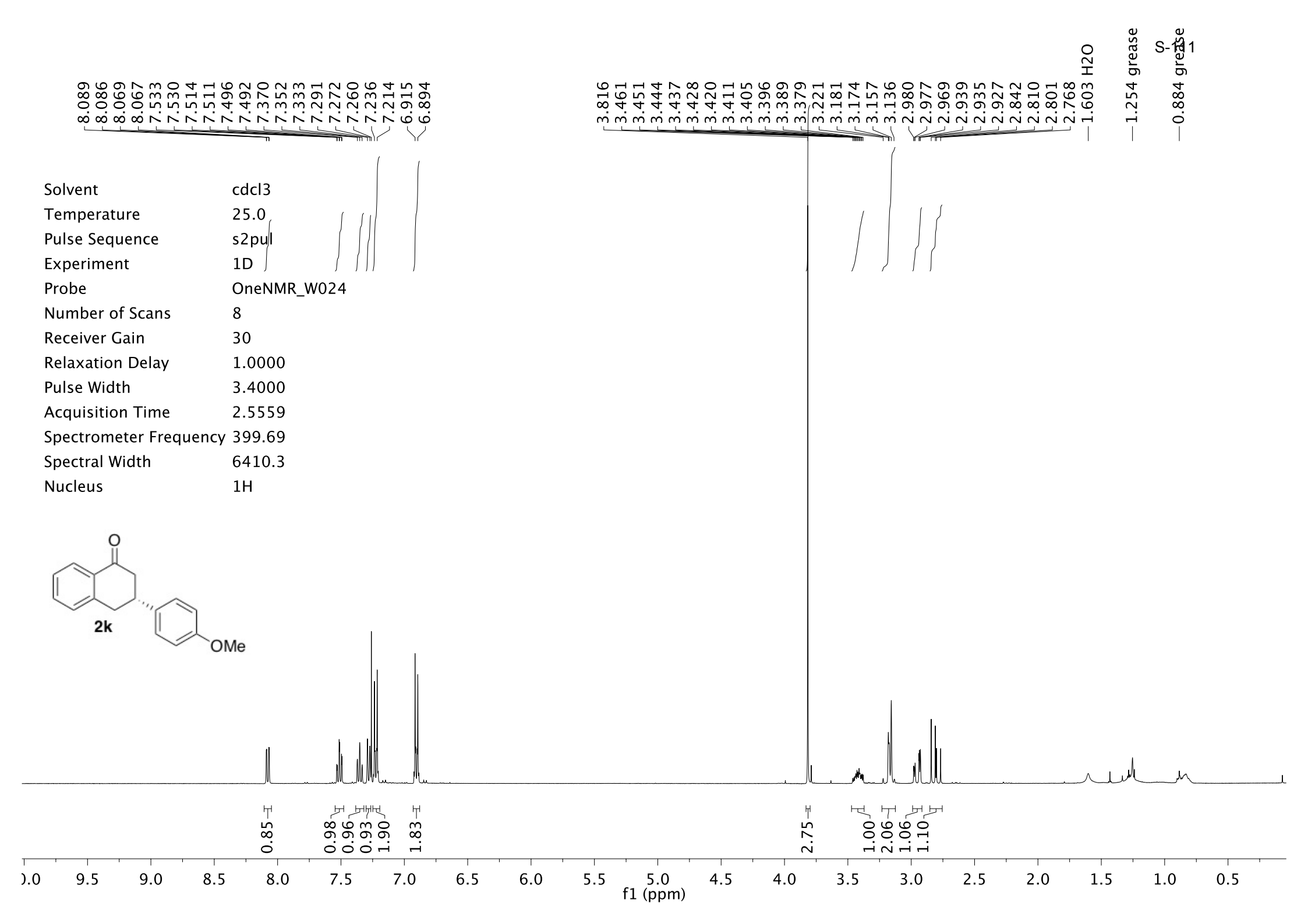
Sample Name:	KJ_4-229B_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070215
Vial:	33	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/2/2015 4:48:23 PM CDT		
Date Processed:	7/10/2015 4:21:02 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14892; Processing Method: Kirsten

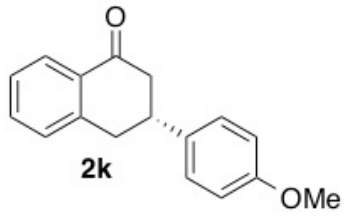
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	9.754	15091053	98.10	688907
2	W2489 ChA 254nm	13.548	292306	1.90	11363

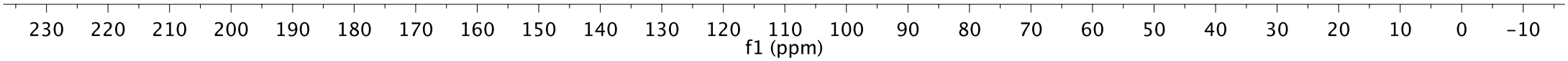

8.089
8.086
8.069
8.067
7.533
7.530
7.514
7.511
7.496
7.492
7.370
7.352
7.333
7.291
7.272
7.260
7.236
7.214
6.915
6.894
3.816
3.461
3.451
3.444
3.437
3.428
3.420
3.411
3.405
3.396
3.389
3.379
3.221
3.181
3.174
3.157
3.136
2.980
2.977
2.969
2.939
2.935
2.927
2.842
2.810
2.801
2.768
1.603 H2O
1.254 grease
0.884 grease
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
2k
OMe
0.85
0.98
0.96
0.93
1.90
1.83
2.75
1.00
2.06
1.06
1.10
f1 (ppm)

198.101
158.574
143.596
135.749
133.891
132.217
128.980
127.756
127.300
127.027
114.218
77.160
55.430
46.377
40.451
38.090

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	64
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2k



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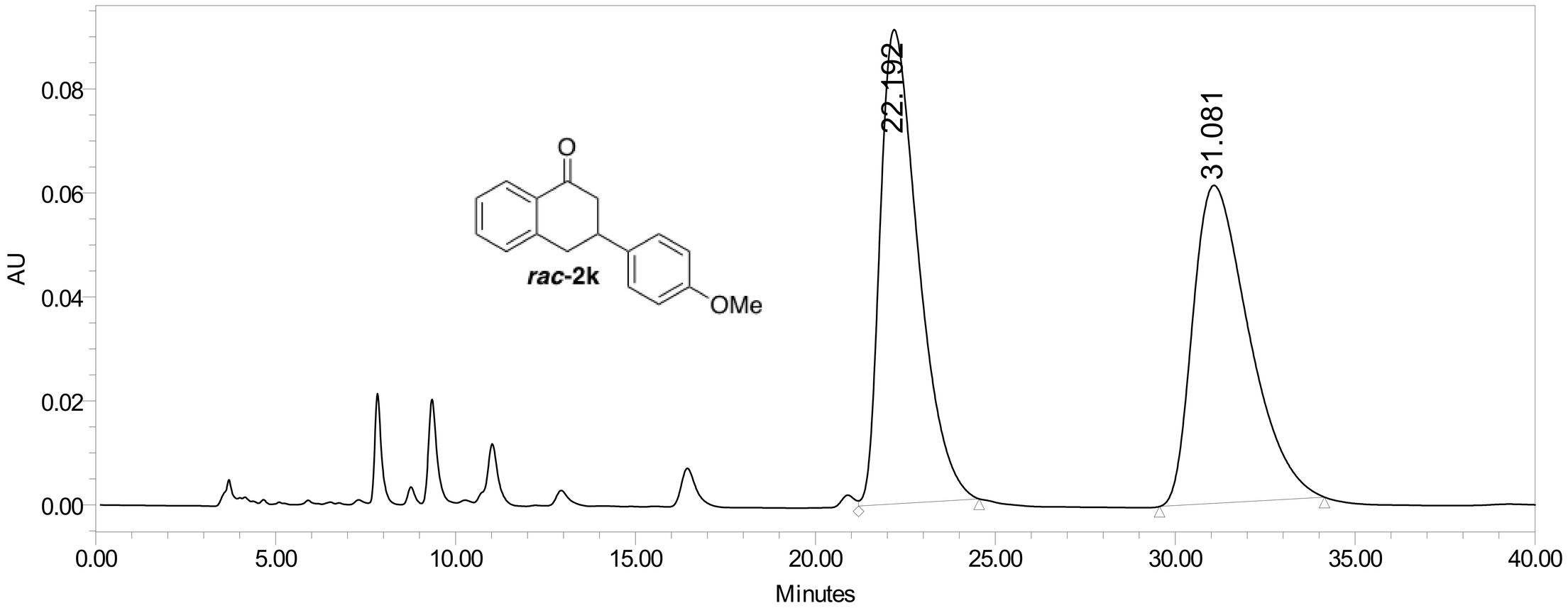
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	KJ_4-228A_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	KLV_7_27_2015
Vial:	30	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/27/2015 11:26:39 AM CDT		
Date Processed:	7/27/2015 1:19:30 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 15663; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	22.192	6732284	50.43	91183
2	W2489 ChA 254nm	31.081	6617876	49.57	61143

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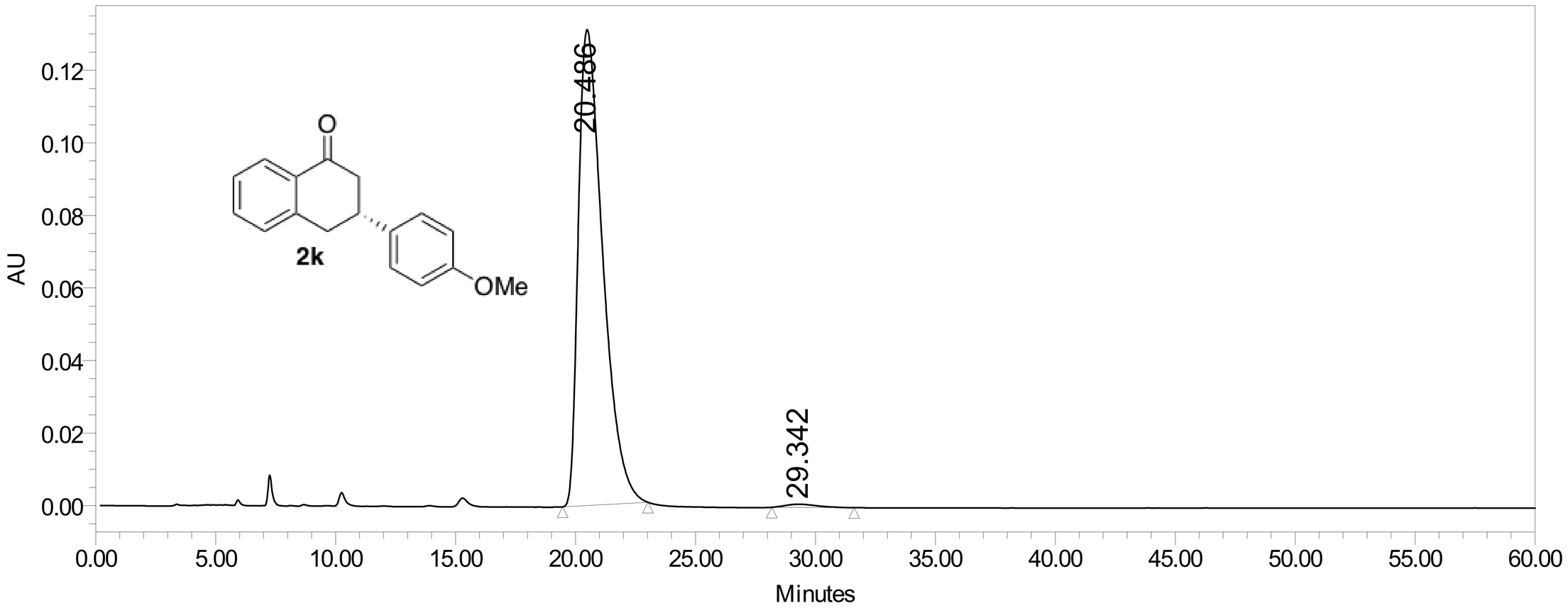
Injection Summary Report

SAMPLE INFORMATION

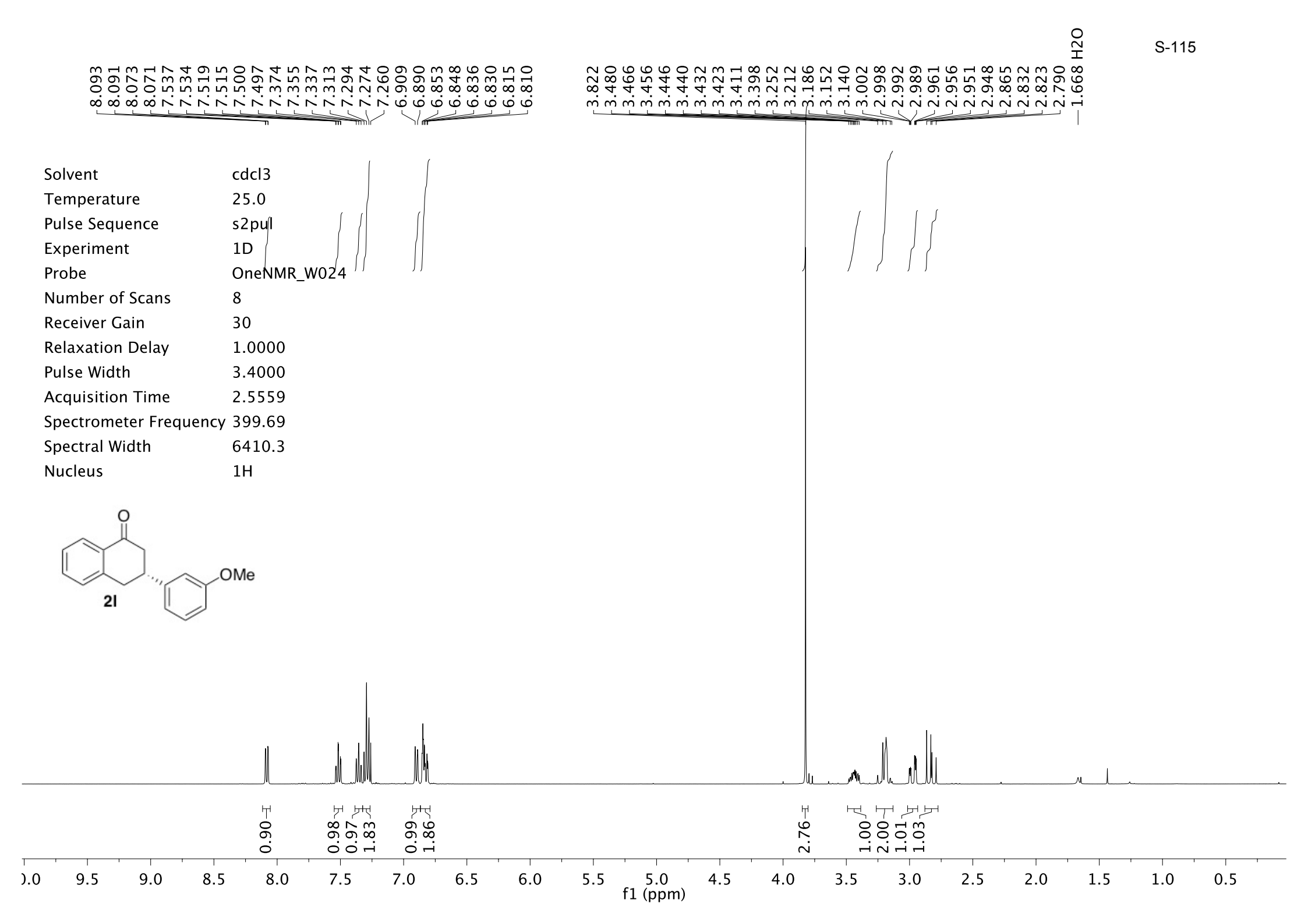
Sample Name:	KJ_4-243_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070715
Vial:	32	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/7/2015 5:18:48 PM CDT		
Date Processed:	7/10/2015 4:13:54 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14883; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	20.486	9320252	99.14	131220
2	W2489 ChA 254nm	29.342	80716	0.86	880


8.093
8.091
8.073
8.071
7.537
7.534
7.519
7.515
7.500
7.497
7.374
7.355
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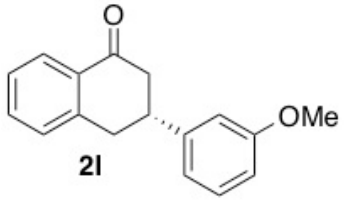
7.313
7.294
7.274
7.260
6.909
6.890
6.853
6.848
6.836
6.830
6.815
6.810
3.822
3.480
3.466
3.456
3.446
3.440
3.432
3.423
3.411
3.398
3.252
3.212
3.186
3.152
3.140
3.002
2.998
2.992
2.989
2.961
2.956
2.951
2.948
2.865
2.832
2.823
2.790
1.668 H2O
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
OMe
2l
0.90
0.98
0.97
1.83
0.99
1.86
2.76
1.00
2.00
1.01
1.03
f1 (ppm)

197.897
159.952
145.197
143.462
133.920
132.168
129.918
128.971
127.307
127.059
119.099
112.962
111.991
77.160
55.336
46.057
41.233
37.716

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	48
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2l

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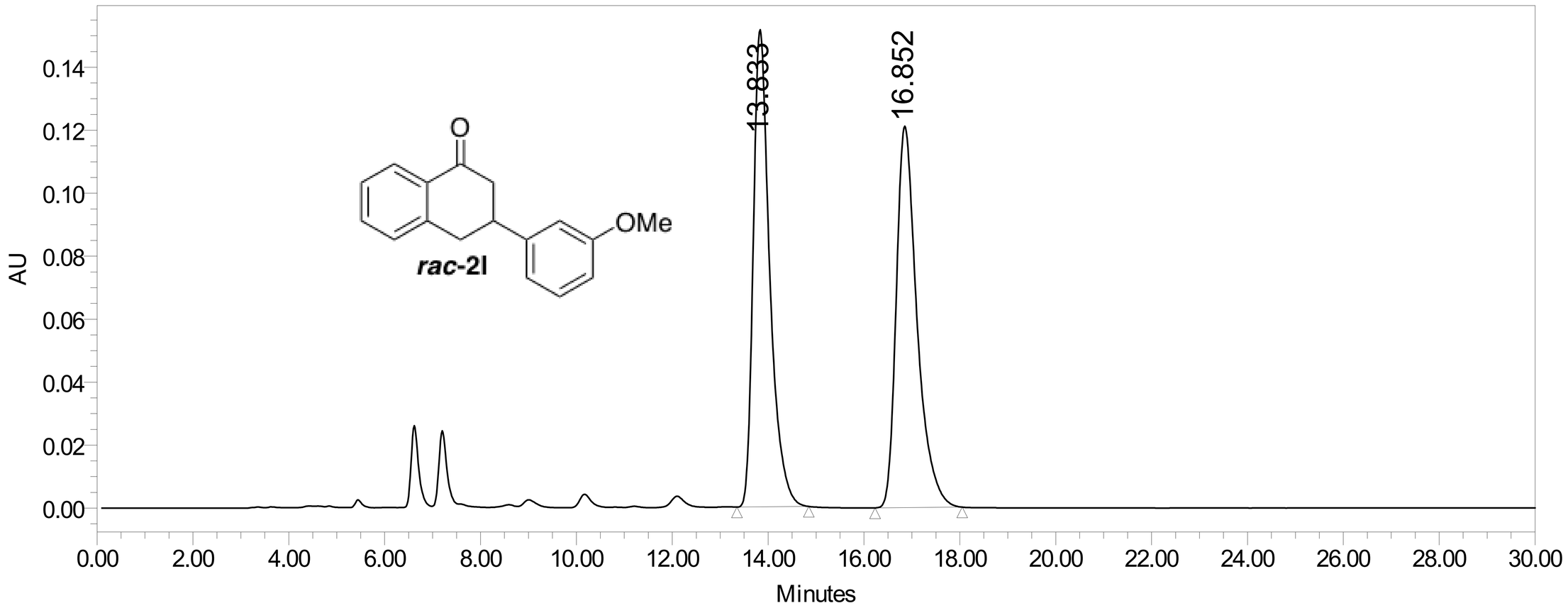
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	KJ_4-238A_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070615
Vial:	36	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/6/2015 5:31:32 PM CDT		
Date Processed:	7/27/2015 1:59:10 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 15681; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

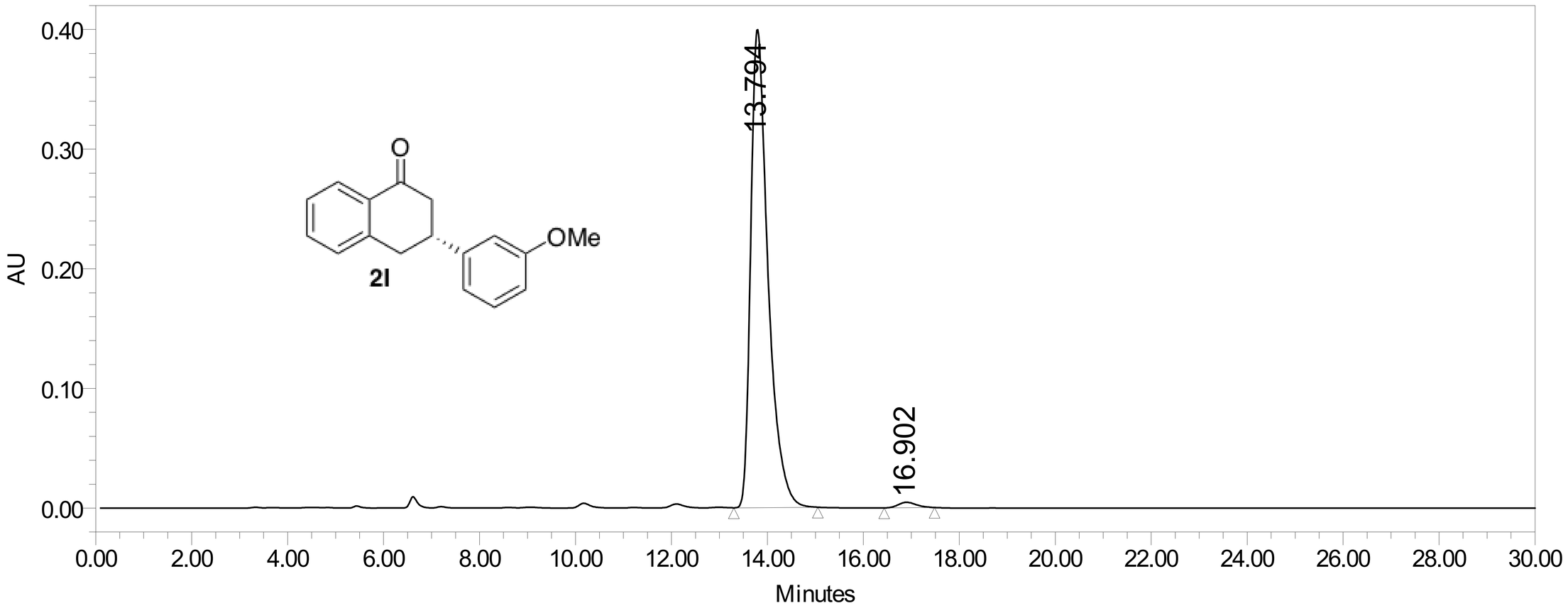
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.833	3618172	49.86	151549
2	W2489 ChA 254nm	16.852	3638227	50.14	121160

Empower™ 3 SOFTWARE

Injection Summary Report

SAMPLE INFORMATION

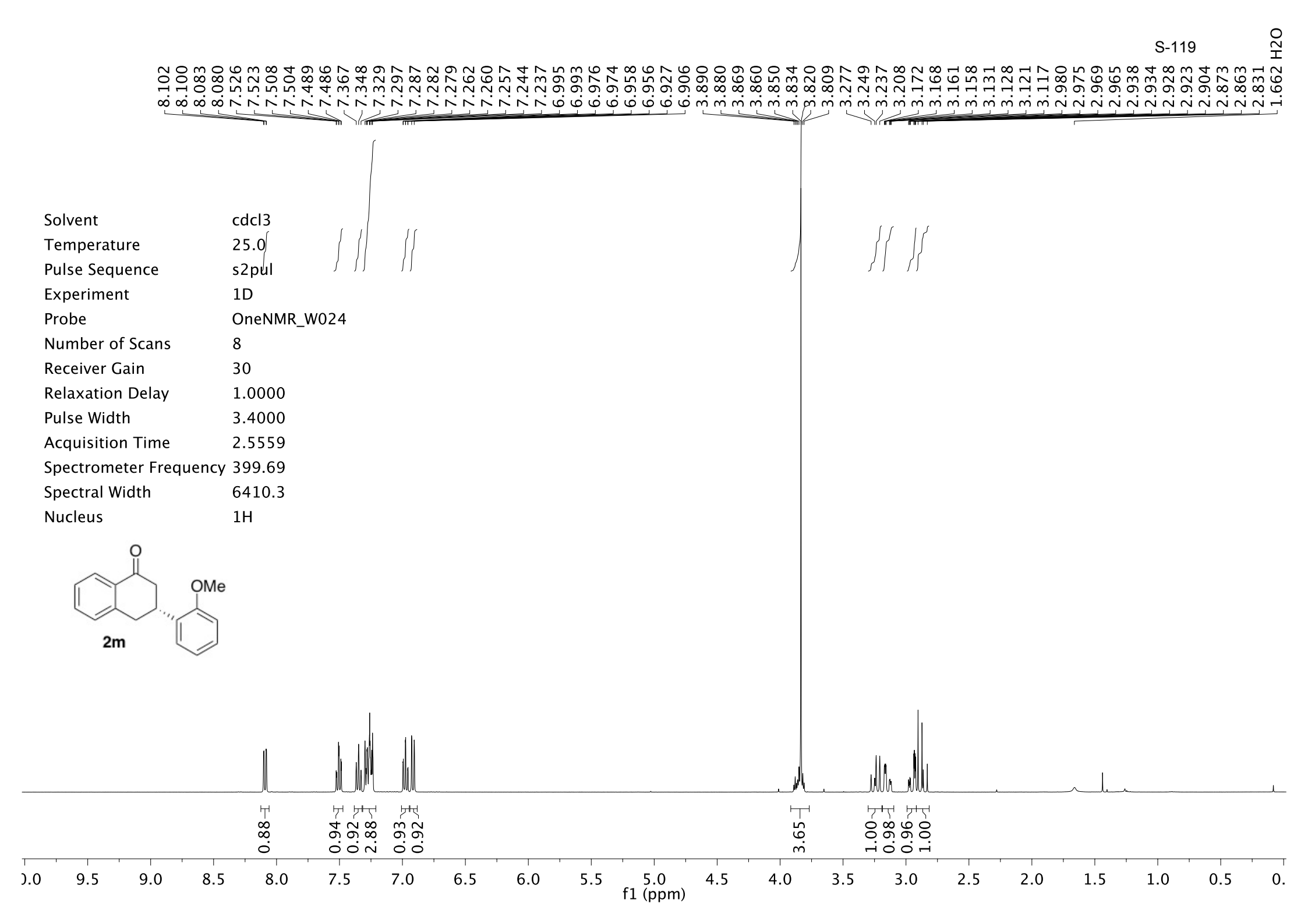
Sample Name:	KJ_4-238B_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070615
Vial:	37	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/6/2015 6:02:13 PM CDT		
Date Processed:	7/27/2015 1:59:50 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 15684; Processing Method: Kirsten

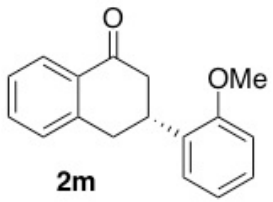
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.794	10000726	98.81	399821
2	W2489 ChA 254nm	16.902	120478	1.19	4569

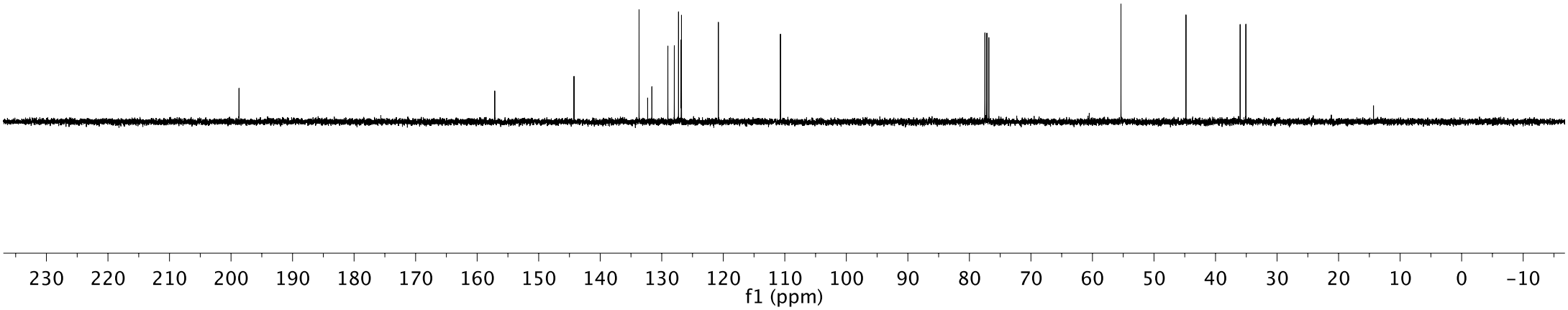

8.102
8.100
8.083
8.080
7.526
7.523
7.508
7.504
7.489
7.486
7.367
7.348
7.329
7.297
7.287
7.282
7.279
7.262
7.260
7.257
7.244
7.237
6.995
6.993
6.976
6.974
6.958
6.956
6.927
6.906
3.890
3.880
3.869
3.860
3.850
3.834
3.820
3.809
3.277
3.249
3.237
3.208
3.172
3.168
3.161
3.158
3.131
3.128
3.121
3.117
2.980
2.975
2.969
2.965
2.938
2.934
2.928
2.923
2.904
2.873
2.863
2.831
1.662 H2O
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 30
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
OMe
2m
0.88
0.94
0.92
2.88
0.93
0.92
3.65
1.00
0.98
0.96
1.00
f1 (ppm)

198.702
157.140
144.260
133.687
132.291
131.603
129.004
127.959
127.274
126.835
126.793
120.798
110.705
77.160
55.367
44.803
35.996
35.067

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	48
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2m



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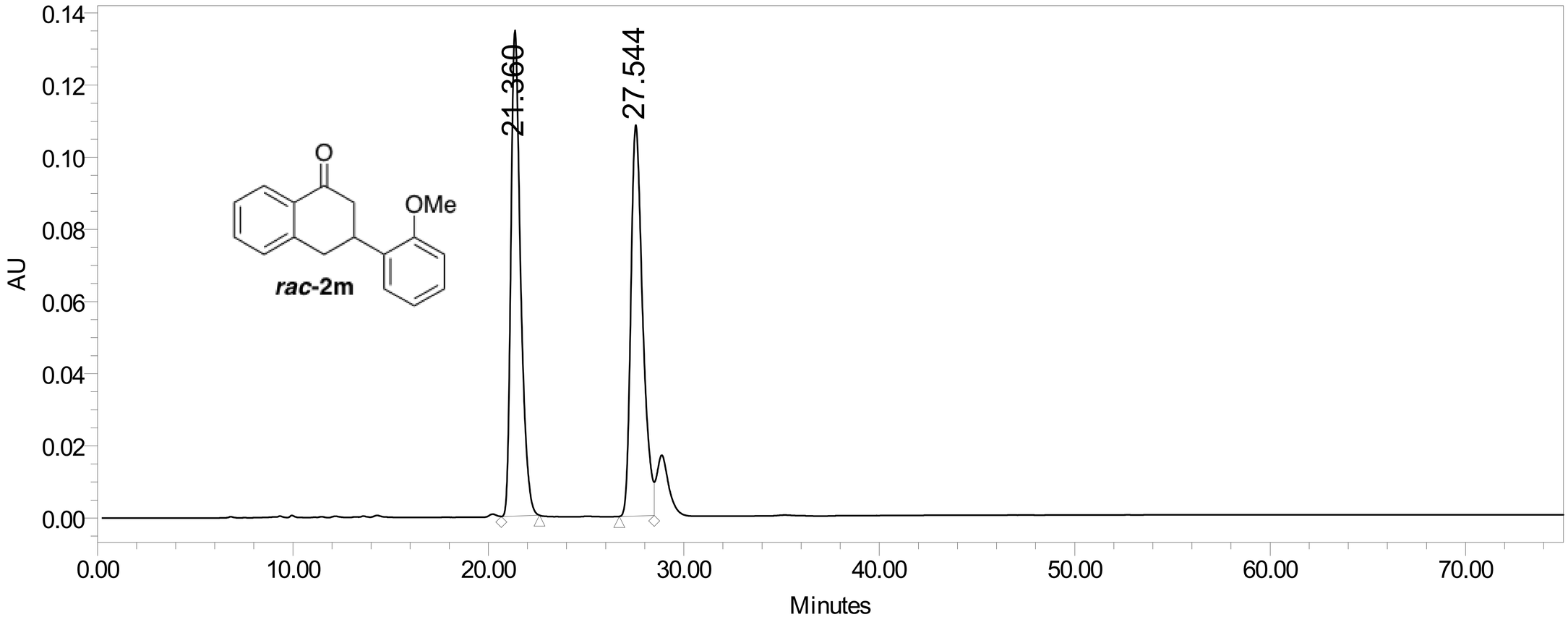
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070615
Vial:	38	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	75.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/6/2015 12:37:53 PM CDT		
Date Processed:	7/10/2015 4:25:29 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14904; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	21.360	4616216	50.33	134752
2	W2489 ChA 254nm	27.544	4554823	49.67	108377

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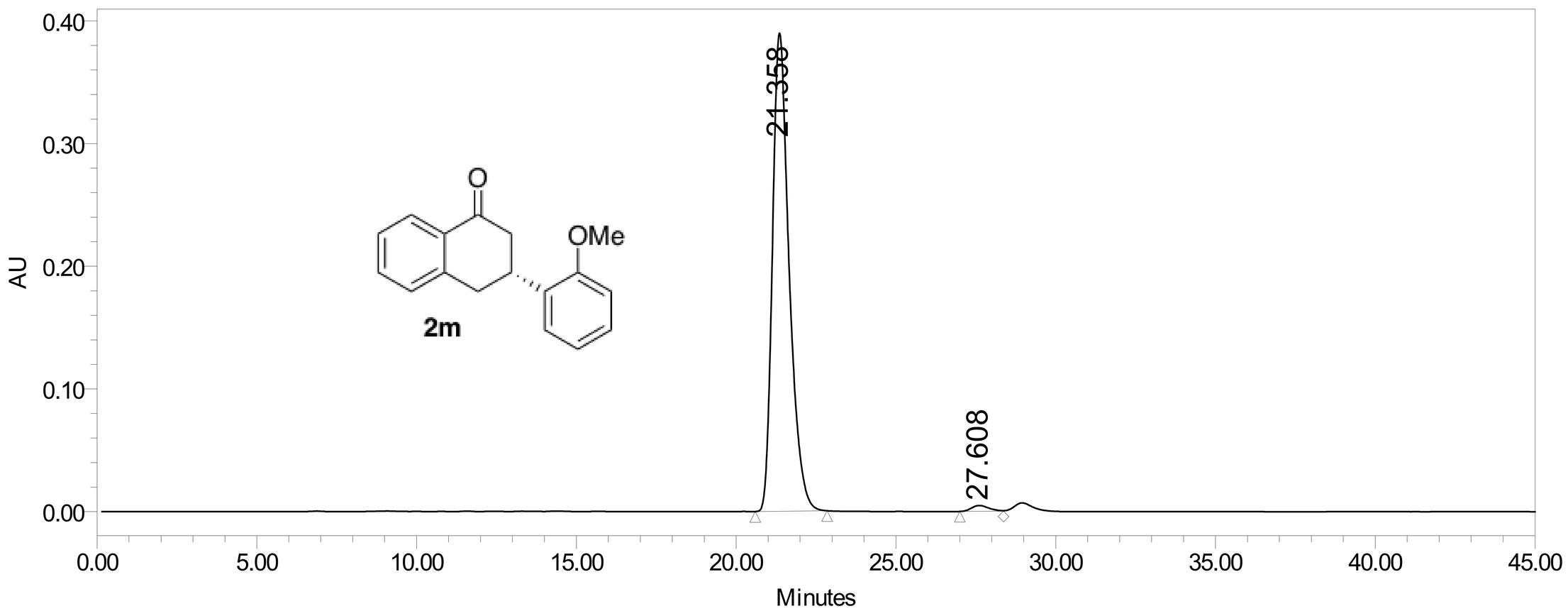
Injection Summary Report

SAMPLE INFORMATION

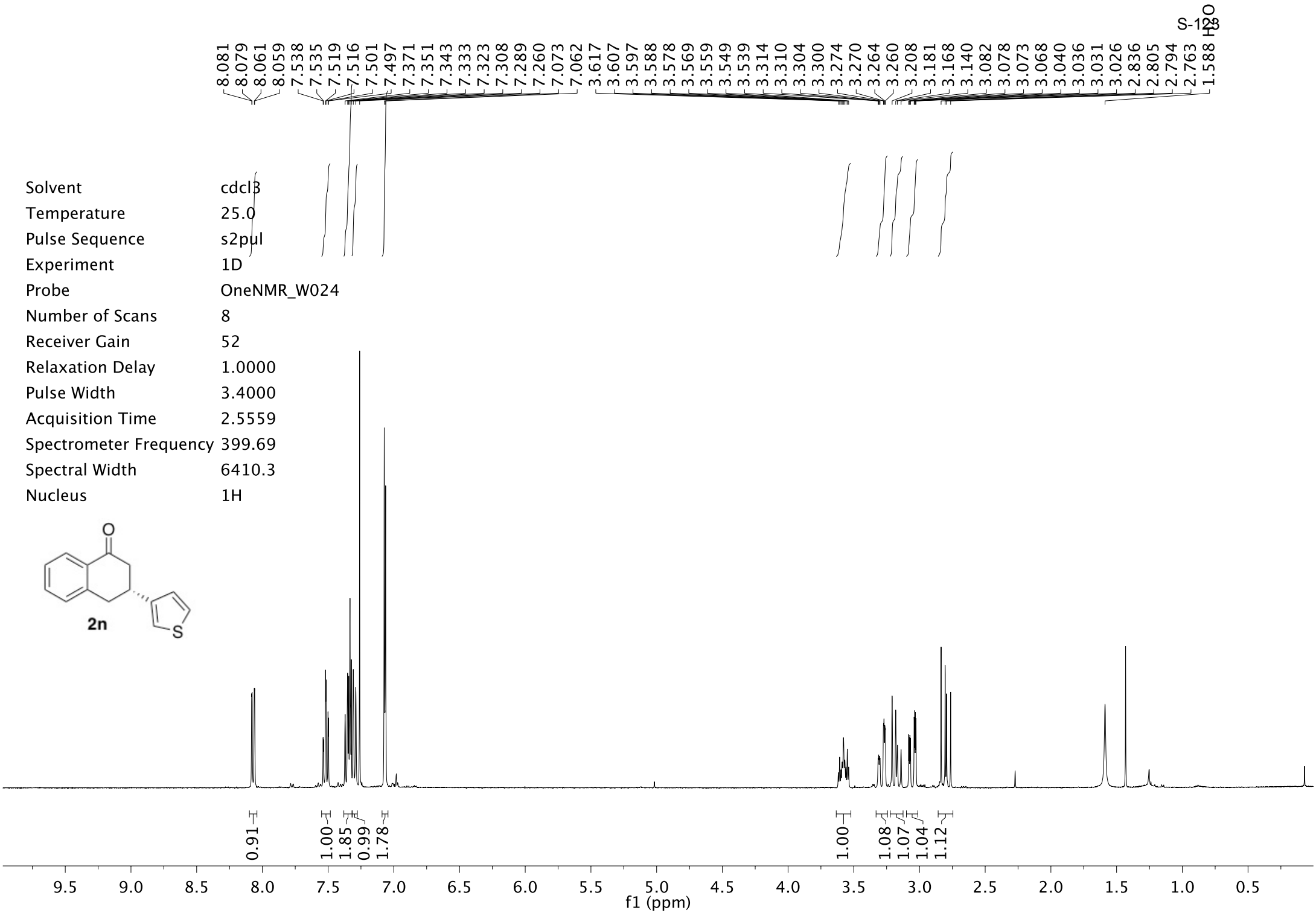
Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070615
Vial:	39	Acq. Method Set:	2_ASH 90_10 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	45.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/6/2015 2:39:15 PM CDT		
Date Processed:	7/10/2015 4:26:14 PM CDT		



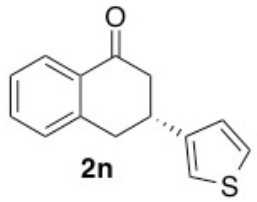
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14907; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

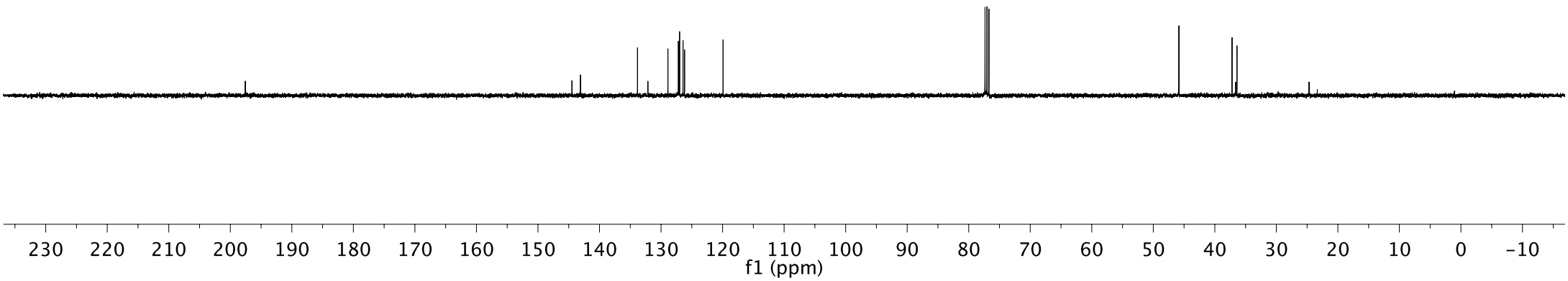
	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	21.358	14134269	98.72	389960
2	W2489 ChA 254nm	27.608	183694	1.28	4789


S-123
H2O
8.081
8.079
8.061
8.059
7.538
7.535
7.519
7.516
7.501
7.497
7.371
7.351
7.343
7.333
7.323
7.308
7.289
7.260
7.073
7.062
3.617
3.607
3.597
3.588
3.578
3.569
3.559
3.549
3.539
3.314
3.310
3.304
3.300
3.274
3.270
3.264
3.260
3.208
3.181
3.168
3.140
3.082
3.078
3.073
3.068
3.040
3.036
3.031
3.026
2.836
2.805
2.794
2.763
1.588
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 52
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
S
2n
0.91
1.00
1.85
0.99
1.78
1.00
1.08
1.07
1.04
1.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	144
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2n



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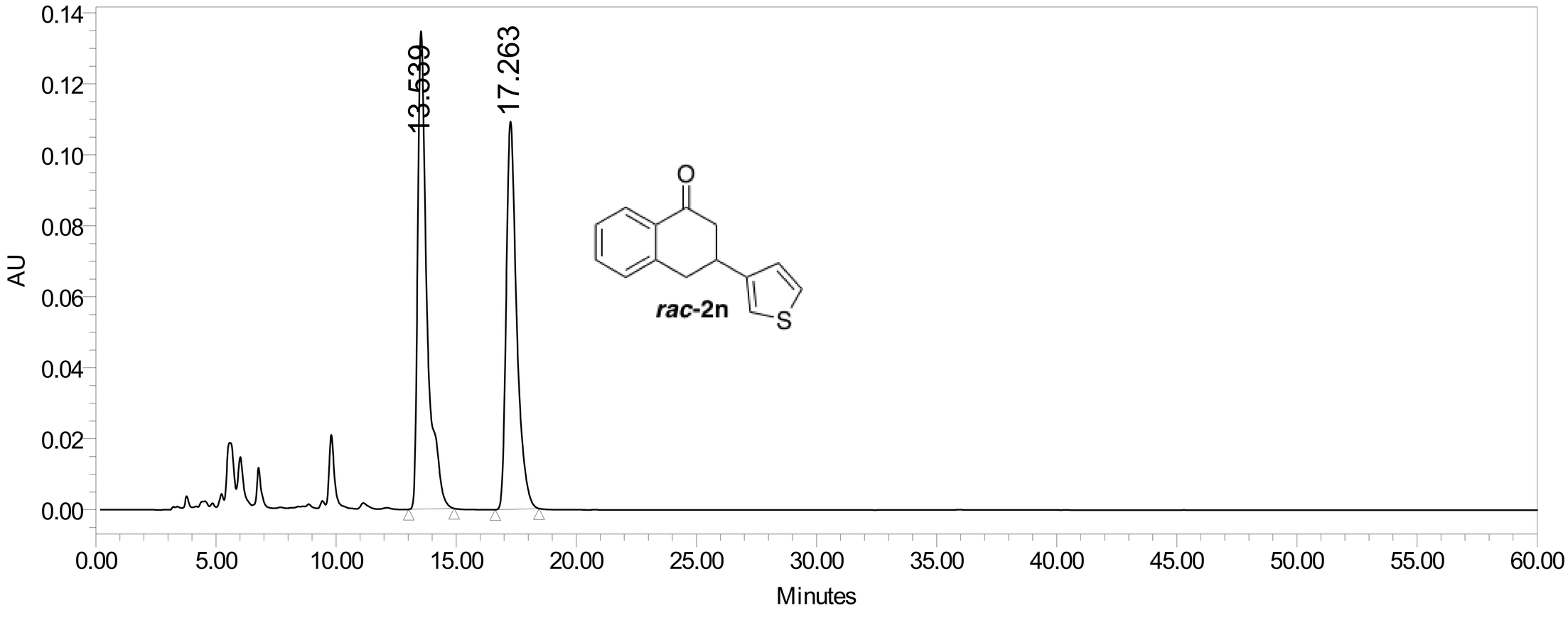
Injection Summary Report

SAMPLE INFORMATION

Sample Name:	KJ_4-242A_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070715
Vial:	30	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/7/2015 6:19:30 PM CDT		
Date Processed:	7/10/2015 4:28:12 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14910; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.539	3640247	52.39	134781
2	W2489 ChA 254nm	17.263	3308568	47.61	109292

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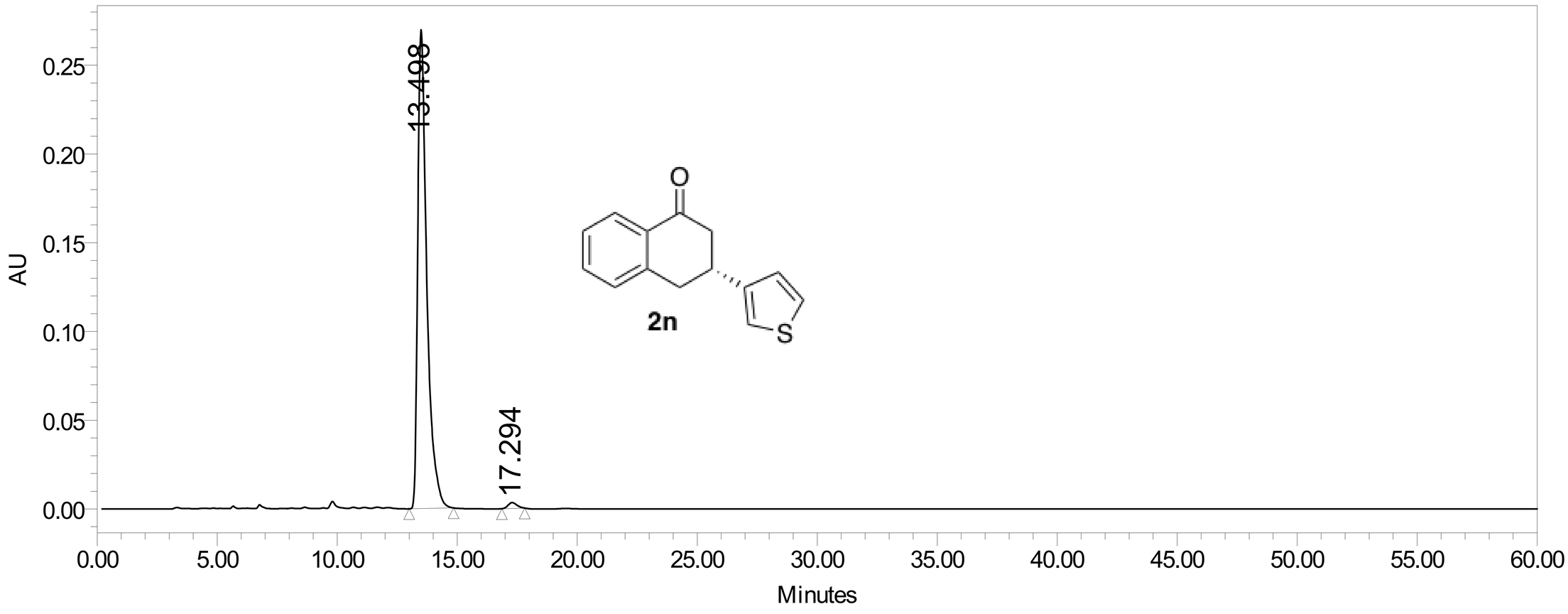
Injection Summary Report

SAMPLE INFORMATION

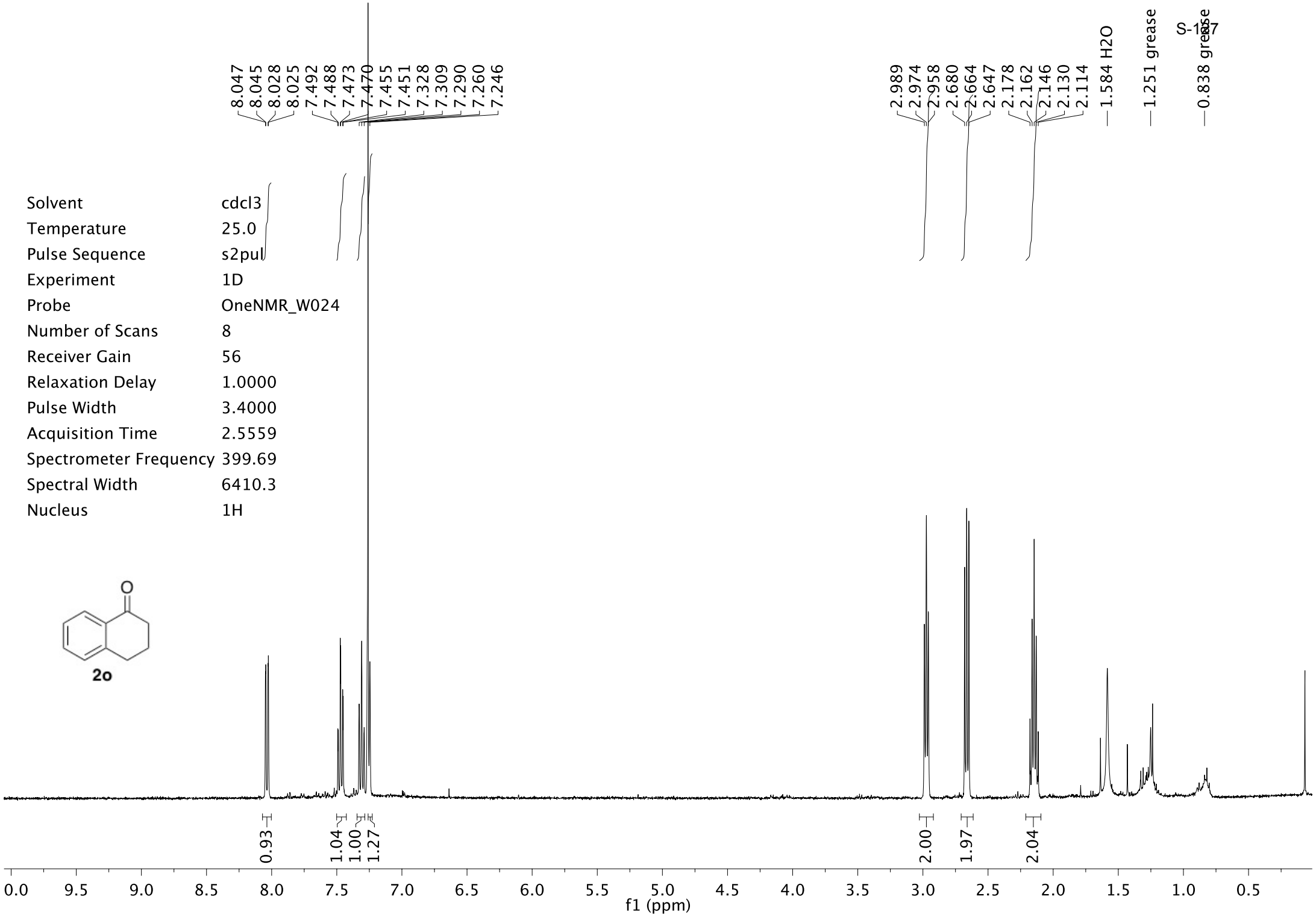
Sample Name:	KJ_4-242B_ASH_90to10_1mpm	Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten070715
Vial:	31	Acq. Method Set:	2_ASH 90_10 1mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	60.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/7/2015 7:20:08 PM CDT		
Date Processed:	7/10/2015 4:28:57 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 14913; Processing Method: Kirsten

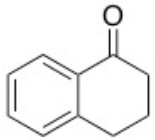
Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	13.498	7070963	98.82	269876
2	W2489 ChA 254nm	17.294	84125	1.18	3305


8.047
8.045
8.028
8.025
7.492
7.488
7.473
7.470
7.455
7.451
7.328
7.309
7.290
7.260
7.246
2.989
2.974
2.958
2.680
2.664
2.647
2.178
2.162
2.146
2.130
2.114
1.584 H2O
1.251 grease
0.838 grease
Solvent cdcl3
Temperature 25.0
Pulse Sequence s2pul
Experiment 1D
Probe OneNMR_W024
Number of Scans 8
Receiver Gain 56
Relaxation Delay 1.0000
Pulse Width 3.4000
Acquisition Time 2.5559
Spectrometer Frequency 399.69
Spectral Width 6410.3
Nucleus 1H
O
2o
0.93
1.04
1.00
1.27
2.00
1.97
2.04
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

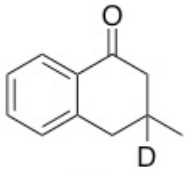
198.613
144.635
133.542
132.716
128.905
127.301
126.760
77.160
39.312
29.843
23.421

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	160
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



2o

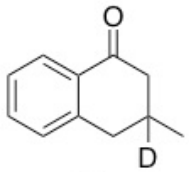
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	32
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



***d*-2a**

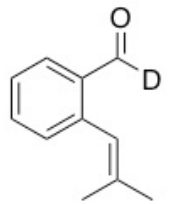
198.799
143.945
133.646
132.282
128.961
127.106
126.728
47.183
38.039
30.361
30.167
29.971
21.402

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



***d*-2a**

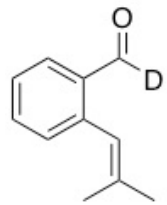
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



***d*-3**

192.907
192.641
192.371
142.383
139.455
133.807
133.770
133.716
130.876
128.131
126.945
121.291
60.569 EtOAc
26.211
21.217 EtOAc
19.555
14.344 EtOAc

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	5312
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C

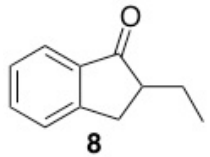


***d*-3**

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

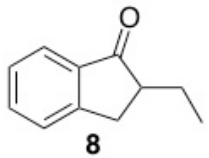
Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	8
Receiver Gain	44
Relaxation Delay	1.0000
Pulse Width	3.4000
Acquisition Time	2.5559
Spectrometer Frequency	399.69
Spectral Width	6410.3
Nucleus	1H



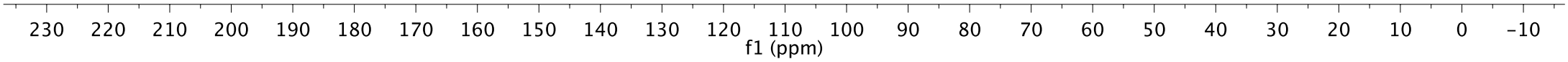
8

209.199
154.003
137.087
134.779
127.445
126.693
123.990
77.160
48.907
32.480
24.632
11.790

Solvent	cdcl3
Temperature	25.0
Pulse Sequence	s2pul
Experiment	1D
Probe	OneNMR_W024
Number of Scans	256
Receiver Gain	30
Relaxation Delay	1.0000
Pulse Width	3.2000
Acquisition Time	1.2845
Spectrometer Frequency	100.51
Spectral Width	25510.2
Nucleus	13C



8



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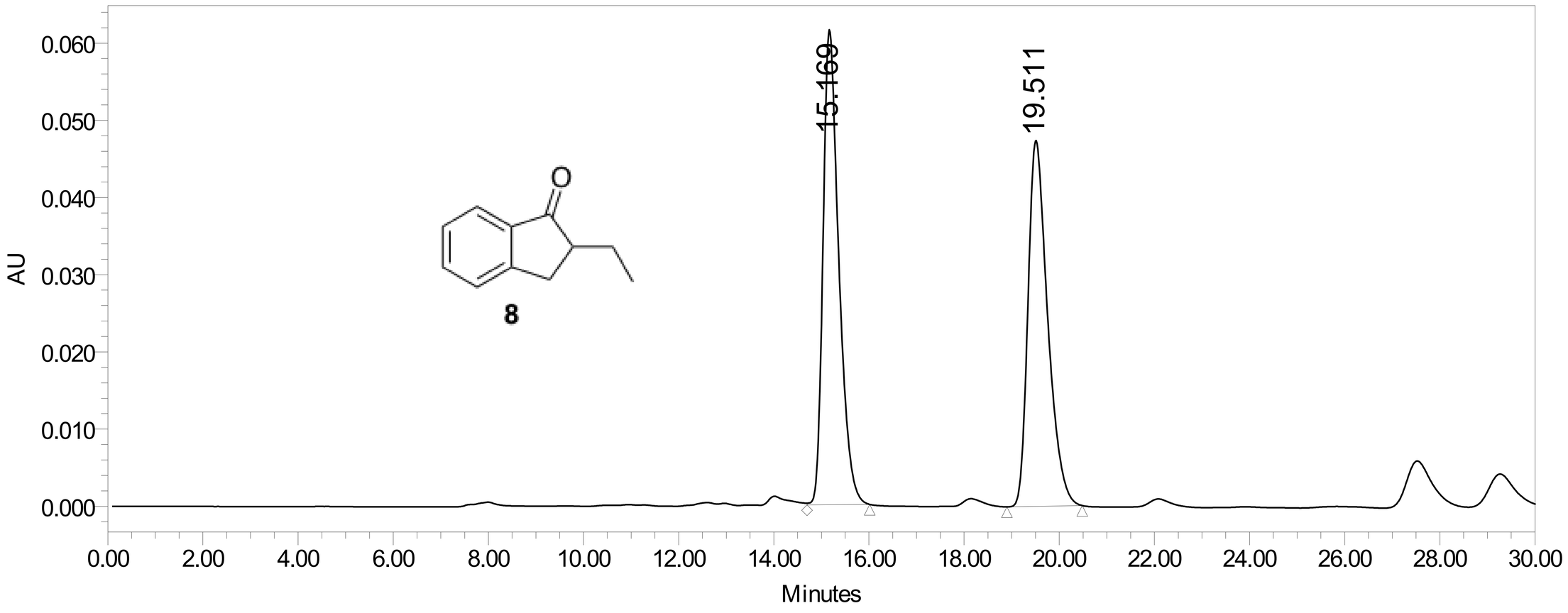
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten072415
Vial:	82	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/24/2015 9:58:11 AM CDT		
Date Processed:	7/27/2015 1:56:22 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 15675; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.169	1417000	51.00	61542
2	W2489 ChA 254nm	19.511	1361451	49.00	47406

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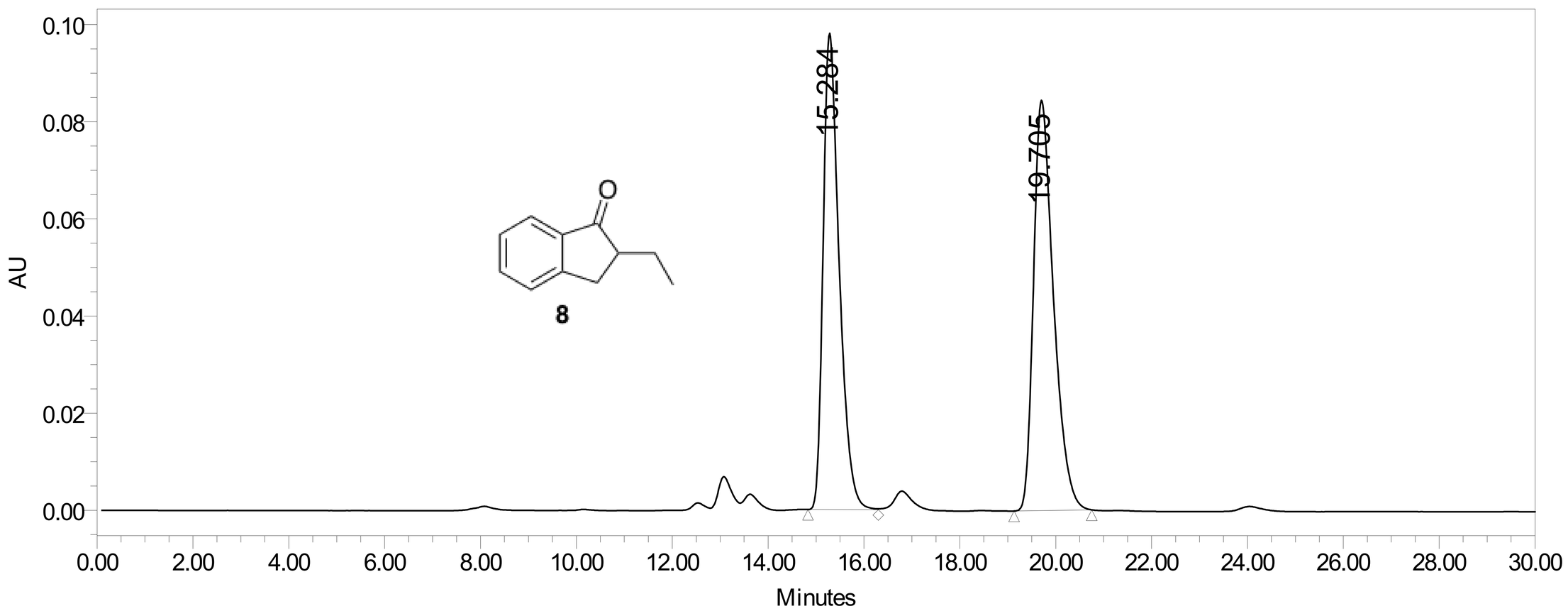
Injection Summary Report

SAMPLE INFORMATION

Sample Name:		Acquired By:	System
Sample Type:	Unknown	Sample Set Name	Kirsten072415
Vial:	83	Acq. Method Set:	2_ASH 95_5 0pt5mpm
Injection #:	1	Processing Method	Kirsten
Injection Volume:	10.00 ul	Channel Name:	W2489 ChA
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	W2489 ChA 254nm
Date Acquired:	7/24/2015 9:27:18 AM CDT		
Date Processed:	7/27/2015 1:57:17 PM CDT		



Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 15678; Processing Method: Kirsten

Processed Channel Descr.: W2489 ChA 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	W2489 ChA 254nm	15.284	2278848	48.18	98104
2	W2489 ChA 254nm	19.705	2450860	51.82	84537