

## *Supporting Information*

# Palladium-Catalyzed Asymmetric Decarboxylative [4+2] Dipolar Cycloaddition of 4-Vinyl-1,3-Dioxan-2-ones with $\alpha,\beta$ -Disubstituted Nitroalkenes Enabled by Benzylic Substituted *P,N*-Ligand

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## 1. General Methods

The reactions were carried out in flame-dried glassware under a dry argon atmosphere with standard vacuum-line techniques. All solvents were purified and dried by using standard methods prior to use. Commercially available reagents were used without further purification. For reactions that require heating, the heat source is oil bath. NMR spectra were recorded on 400 MHz Varian-400, 400M Agilent-400 or 300 MHz Bruker AM-300 NMR spectrometers. Chemical shifts of <sup>1</sup>H NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or unresolved), coupling constants (Hz), and integration. Chemical shifts of <sup>13</sup>C NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl<sub>3</sub>: δ 77.1 ppm). Infrared spectra were recorded from thin films of pure samples. Mass and HRMS spectra were measured in EI or ESI mode and the mass analyzer type used for the HRMS was TOF. Thin layer chromatography was performed on pre-coated glassback plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. Enantiomer ratios were determined by chiral HPLC analysis in comparison with authentic racemic materials. The nitroalkenes **2**<sup>1</sup> and compound **1** (4-vinyl-1,3-dioxan-2-one)<sup>2</sup> were prepared according to literature procedures. The ligand **L10** and **L11**<sup>3</sup> were prepared according to the method reported previously from our laboratories.

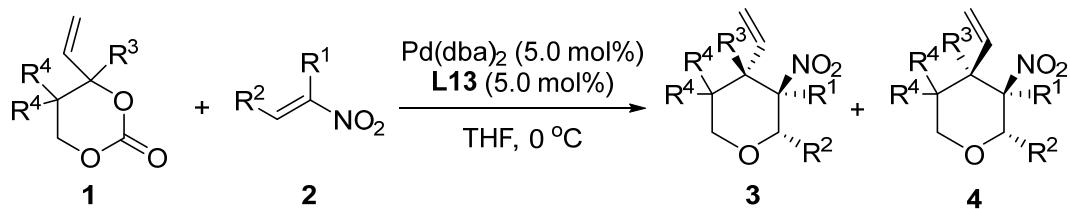
## 2. Optimization of reaction conditions for Pd-catalyzed [4+2]-cycloaddition of 4-vinyl-1,3-dioxan-2-one **1a** with nitroalkene **2a**<sup>a</sup>

		 1a + (E)-2a → 3a + 4a					
entry	[Pd]	solvent	T/°C	yield/% <sup>b</sup>	dr/% <sup>c</sup>	ee/% <sup>d</sup>	
1	Pd <sub>2</sub> dba <sub>3</sub> ·CHCl <sub>3</sub>	THF	25	83	11/1	94	
2	Pd <sub>2</sub> dba <sub>3</sub>	THF	25	83	12/1	94	

3	Pd(dba) <sub>2</sub>	THF	25	88	12/1	95
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	THF	25	33	7/1	92
5	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	THF	25	trace	--	--
6	[Pd(C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub>	THF	25	NR	--	--
7	Pd(OAc) <sub>2</sub>	THF	25	NR	--	--
8	Pd(dba) <sub>2</sub>	Et <sub>2</sub> O	25	92	14/1	92
9	Pd(dba) <sub>2</sub>	dioxane	25	68	10/1	93
10	Pd(dba) <sub>2</sub>	<i>t</i> -BuOMe	25	96	14/1	92
11	Pd(dba) <sub>2</sub>	tuolene	25	40	12/1	90
12	Pd(dba) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	8	11/1	88
13	Pd(dba) <sub>2</sub>	DMSO	25	12	6/1	83
14 <sup>e</sup>	Pd(dba) <sub>2</sub>	THF	0	92	17/1	96
15 <sup>e</sup>	Pd(dba) <sub>2</sub>	THF	-10	67	20/1	95
16 <sup>e</sup>	Pd(dba) <sub>2</sub>	THF	-20	64	20/1	94

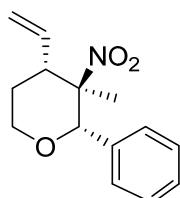
<sup>a</sup>Molar ratio of [Pd]/(*S,S*)-L13/2a/1a = 10.0/10.0/200/100, 25 °C, 12 h. <sup>b</sup>Isolated yield of 3a and 4a. <sup>c</sup>dr (3a/4a ratio) determined by <sup>1</sup>H NMR. <sup>d</sup>ee of 3a determined by chiral HPLC. <sup>e</sup>Molar ratio of Pddba<sub>2</sub>/(*S,S*)-L13/2a/1a = 5.0/5.0/150/100, 4 days.

### 3. General experimental procedure for Table 2 and characterization of products



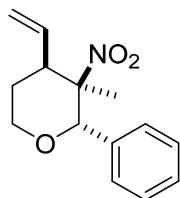
To a flame dried sealing tube was added Pddba<sub>2</sub> (0.005 mmol, 2.9 mg), **L13** (0.005 mmol, 2.2 mg), freshly distilled anhydrous THF (2.0 mL). The resulting mixture was allowed to stir for 30 mins. Then, compound **1** (0.15 mmol) and nitroalkene **2** (0.1 mmol) were added subsequently. The resulting reaction mixture was stirred at 0 °C for 4 days (monitored by TLC). After the volatiles were removed in vacuo, the ratio of two diastereoisomers was determined by <sup>1</sup>H NMR. Then the resulting residue was purified by flash chromatography on silica gel with petroleum ether and ethyl acetate as eluent to give diastereomers **3** and **4**.

**(2S,3R,4R)-3-methyl-3-nitro-2-phenyl-4-vinyltetrahydro-2H-pyran (3a)**



White solid; mp: 68.1-68.5 °C; yield: 92%; 23 mg; dr: 17/1; ee (major isomer): 96%; HPLC (Chiralcel AD-H, 4.6 mm × 250 mm, Hexane/i-Propanol = 99/1, 0.7 ml/min, 214 nm), t<sub>major</sub> = 12.7 min, t<sub>minor</sub> = 9.6 min; [α]<sub>D</sub><sup>25</sup> = -18.07 (c 1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.26 (m, 3H), 7.16 (dd, *J* = 6.6, 2.6 Hz, 2H), 5.70 – 5.46 (m, 1H), 5.20 – 5.05 (m, 2H), 4.96 (s, 1H), 4.31 – 4.17 (m, 1H), 3.82 (td, *J* = 12.0, 3.7 Hz, 1H), 3.48 – 3.26 (m, 1H), 1.83 (m, 2H), 1.30 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.6, 134.5, 128.4, 128.1, 126.7, 118.6, 93.7, 83.9, 68.3, 48.4, 27.8, 10.6; IR (film) 3186, 2957, 2922, 2860, 1641, 1529, 1446, 1388, 1351, 1252, 1212, 1097, 1028, 990, 928, 898, 864, 705 cm<sup>-1</sup>; MS (ESI) *m/z*: 270.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>14</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 265.1547, found: 265.1547.

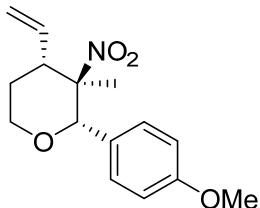
**3-methyl-3-nitro-2-phenyl-4-vinyltetrahydro-2H-pyran (4a)**



Sample of **4a** for characterization was obtained using **L5** as the ligand according to general experimental procedure. yield: 18%; 22 mg. Colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.34 – 7.24 (m, 3H), 6.33 (dt, *J* = 16.7, 10.0 Hz, 1H), 5.36 (s, 1H), 5.22 – 5.09 (m, 2H), 4.12 – 3.90 (m, 2H), 2.85 – 2.72 (m, 1H), 2.42 – 2.21 (m, 1H), 1.79 (ddd, *J* = 14.1, 5.1, 2.8 Hz, 1H), 1.63 (s, 3H); <sup>13</sup>C NMR

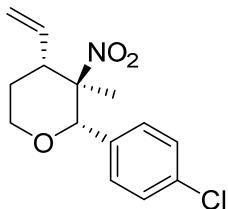
(101 MHz, CDCl<sub>3</sub>) δ 136.5, 134.2, 128.4, 128.2, 127.9, 118.8, 91.9, 77.4, 64.3, 49.3, 28.3, 19.0; IR (film) 3110, 2965, 2919, 2868, 1643, 1527, 1451, 1383, 1349, 1237, 1207, 1096, 1033, 990, 932, 902, 858, 803, 699, 577 cm<sup>-1</sup>; MS (EI) *m/z*: 200.0 (M-HNO<sub>2</sub>)<sup>+</sup>; HRMS (EI) calcd for C<sub>14</sub>H<sub>17</sub>NO<sub>3</sub> (M)<sup>+</sup>: 247.1208, found: 247.1210.

**(2*S*,3*R*,4*R*)-2-(4-methoxyphenyl)-3-methyl-3-nitro-4-vinyltetrahydro-2*H*-pyran (3b)**



Colorless oil; yield: 68%; 19 mg; dr: 7/1; ee (major isomer): 97%; HPLC (Chiralcel AD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 98/2, 1.0 ml/min, 214 nm), t<sub>major</sub> = 27.7 min, t<sub>minor</sub> = 15.1 min; [α]<sub>D</sub><sup>25</sup> = -20.47 (*c* 1.10, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.09 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.71 – 5.52 (m, 1H), 5.20 – 5.06 (m, 2H), 4.91 (s, 1H), 4.33 – 4.09 (m, 1H), 3.89 – 3.72 (m, 4H), 3.43 – 3.32 (m, 1H), 1.92 – 1.70 (m, 2H), 1.31 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.6, 134.6, 128.0, 127.7, 118.6, 113.5, 93.9, 83.8, 68.4, 55.2, 48.4, 27.9, 10.6; IR (film) 3080, 3003, 2954, 1640, 1612, 1584, 1512, 1459, 1440, 1388, 1247, 1177, 1098, 1030, 993, 929, 830, 797, 772, 699, 592 cm<sup>-1</sup>; MS (EI) *m/z*: 277.0 (M)<sup>+</sup>; HRMS (EI) calc for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> (M)<sup>+</sup>: 277.1314, found: 277.1312.

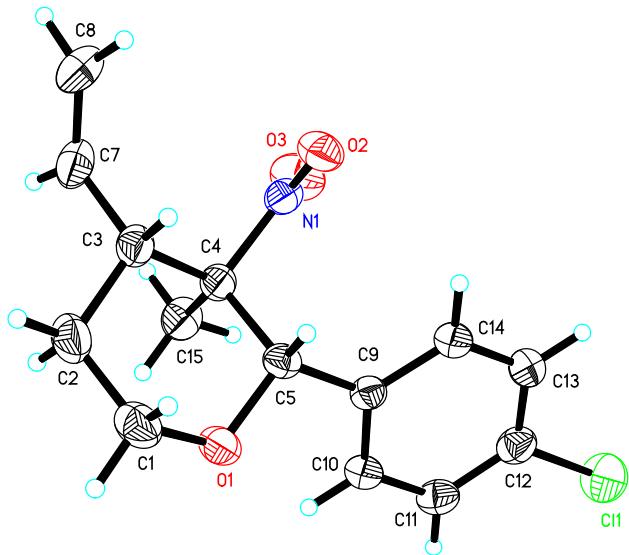
**(2*S*,3*R*,4*R*)-2-(4-chlorophenyl)-3-methyl-3-nitro-4-vinyltetrahydro-2*H*-pyran (3c)**



White solid; mp: 67.1–69.8 °C; yield: 99%; 28 mg; dr: 16/1; ee (major isomer): 97%; HPLC (Chiralcel AD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 98/2, 1.0 ml/min, 214 nm), t<sub>major</sub> = 8.5 min, t<sub>minor</sub> = 6.5 min; [α]<sub>D</sub><sup>25</sup> = -20.93 (*c* 1.30, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 5.68 – 5.49 (m, 1H), 5.14 (dd, *J* = 13.5, 10.0 Hz, 2H), 4.94 (s, 1H), 4.27 (m, 1H), 3.83 (td, *J* = 11.5, 4.5 Hz, 1H), 3.37 (m, 1H), 1.89 – 1.77 (m, 2H), 1.28 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 134.4, 134.3, 134.2, 128.4, 128.1, 118.9, 93.6, 83.3, 68.4, 48.4, 27.8, 10.6;

IR (film) 3074, 3002, 2956, 2921, 2874, 2850, 1636, 1598, 1534, 1491, 1436, 1388, 1352, 1249, 1132, 1090, 1046, 989, 901, 851, 826, 796, 744, 695, 661, 574 cm<sup>-1</sup>; MS (EI) *m/z*: 281.0 (M)<sup>+</sup>; HRMS (EI) calc for C<sub>14</sub>H<sub>16</sub>NO<sub>3</sub>Cl (M)<sup>+</sup>: 281.0819, found: 281.0812.

Crystals of **3c** were grown by slow evaporation of petroleum ether/ethyl acetate solution of **3c** at 0 °C. Data were obtained at 296 K on a Bruker D8 Venture diffractometer with graphite-monochromated Mo K $\alpha$  radiation.



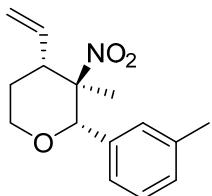
**Figure S1.** Molecular structure of **3c** with thermal ellipsoids at 50% probability.

Crystal data and structure refinement for mo\_d8v18368\_0m.

Identification code	mo_d8v18368_0m
Empirical formula	C <sub>14</sub> H <sub>16</sub> Cl N O <sub>3</sub>
Formula weight	281.73
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 7.9200(4) Å b = 10.7145(5) Å
	= 90°. = 90°.

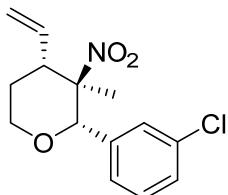
	c = 16.7252(10) Å	= 90°.
Volume	1419.28(13) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.318 Mg/m <sup>3</sup>	
Absorption coefficient	0.272 mm <sup>-1</sup>	
F(000)	592	
Crystal size	0.200 x 0.170 x 0.140 mm <sup>3</sup>	
Theta range for data collection	2.435 to 25.986°.	
Index ranges	-9<=h<=9, -13<=k<=13, -17<=l<=20	
Reflections collected	7946	
Independent reflections	2773 [R(int) = 0.0332]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6386	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2773 / 0 / 182	
Goodness-of-fit on F <sup>2</sup>	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0713	
R indices (all data)	R1 = 0.0385, wR2 = 0.0756	
Absolute structure parameter	-0.02(3)	
Extinction coefficient	0.097(10)	
Largest diff. peak and hole	0.101 and -0.145 e.Å <sup>-3</sup>	

**(2*S*,3*R*,4*R*)-3-methyl-3-nitro-2-(*m*-tolyl)-4-vinyltetrahydro-2*H*-pyran (3d)**



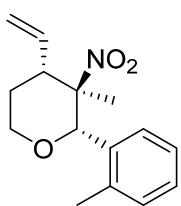
Colorless oil; yield: 92%; 24 mg; dr: 13/1; ee (major isomer): 94%; HPLC (DAICEL IC-3, 3.0 mm × 150 mm, Carbon dioxide/Methanol = 98/2, 0.8 ml/min, 214 nm), t<sub>major</sub> = 3.8 min, t<sub>minor</sub> = 3.5 min; [α]<sub>D</sub><sup>25</sup> = -16.02 (c 1.05, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.07 (m, 4H), 5.70 – 5.49 (m, 1H), 5.14 (m, 2H), 4.92 (s, 1H), 4.27 (dd, J = 12.0, 4.0 Hz, 1H), 3.82 (td, J = 12.0, 4.0 Hz, 1H), 3.45 – 3.31 (m, 1H), 2.31 (s, 3H), 1.92 – 1.74 (m, 2H), 1.32 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.8, 135.6, 134.6, 129.2, 128.1, 127.4, 124.0, 118.6, 93.7, 84.1, 68.4, 48.5, 27.9, 21.5, 10.7; IR (film) 3078, 3007, 2955, 2924, 2857, 1639, 1605, 1534, 1446, 1386, 1350, 1255, 1217, 1164, 1100, 995, 873, 782, 698, 661, 505 cm<sup>-1</sup>; MS (ESI) m/z: 284.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>15</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 279.1714, found: 279.1703.

**(2*S*,3*R*,4*R*)-2-(3-chlorophenyl)-3-methyl-3-nitro-4-vinyltetrahydro-2*H*-pyran (3e)**



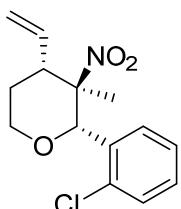
Colorless oil; yield: 75%; 21 mg; dr: 7/1; ee (major isomer): 91%; HPLC (Chiralcel OD-H, 4.6 mm × 250 mm, Hexane/i-Propanol = 98/2, 0.6 ml/min, 214 nm), t<sub>major</sub> = 13.4 min, t<sub>minor</sub> = 11.8 min; [α]<sub>D</sub><sup>25</sup> = -27.97 (c 1.10, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 – 7.18 (m, 3H), 6.98 (d, J = 7.5 Hz, 1H), 5.67 – 5.50 (m, 1H), 5.15 (dd, J = 13.7, 10.5 Hz, 2H), 4.95 (s, 1H), 4.31 – 4.22 (m, 1H), 3.82 (td, J = 11.6, 4.5 Hz, 1H), 3.36 (dd, J = 11.0, 6.3 Hz, 1H), 1.93 – 1.79 (m, 2H), 1.30 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.7, 134.3, 134.2, 129.5, 128.7, 126.9, 125.0, 118.9, 93.5, 83.2, 68.4, 48.4, 27.8, 10.6; IR (film) 3079, 2950, 2859, 1641, 1573, 1534, 1470, 1432, 1388, 1351, 1251, 1208, 1104, 994, 932, 892, 861, 784, 739, 659, 578 cm<sup>-1</sup>; MS (EI) m/z: 234.0 (M-HNO<sub>2</sub>)<sup>+</sup>; HRMS (EI) calc for C<sub>14</sub>H<sub>16</sub>OCl(M-NO<sub>2</sub>)<sup>+</sup>: 235.0890, found: 235.0893.

**(2S,3R,4R)-3-methyl-3-nitro-2-(*o*-tolyl)-4-vinyltetrahydro-2*H*-pyran (3f)**



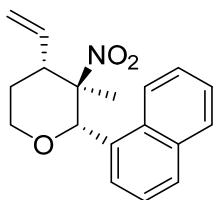
Colorless oil; yield: 69%; 18 mg; dr: 6/1; ee (major isomer): 85%; HPLC (DAICEL IC-3, 3.0 mm × 150 mm, Carbon dioxide/Ethanol = 99/1, 1.0 ml/min, 214 nm), t<sub>major</sub> = 7.4 min, t<sub>minor</sub> = 6.4 min; [α]<sub>D</sub><sup>25</sup> = -6.43 (c 1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.30 (m, 1H), 7.17 (m, 2H), 7.13 – 7.06 (m, 1H), 5.70 – 5.49 (m, 1H), 5.22 – 5.03 (m, 3H), 4.31 – 4.16 (m, 1H), 3.84 (td, *J* = 12.0, 4.0 Hz, 1H), 3.62 – 3.48 (m, 1H), 2.23 (s, 3H), 1.94 – 1.81 (m, 2H), 1.51 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.2, 134.8, 133.9, 130.8, 128.5, 128.4, 125.3, 118.7, 92.8, 80.9, 68.7, 48.0, 28.0, 19.5, 11.5; IR (film) 3075, 2926, 2856, 1640, 1534, 1451, 1383, 1350, 1292, 1217, 1095, 1033, 989, 864, 762, 700, 662, 577 cm<sup>-1</sup>; MS (ESI) *m/z*: 284.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>15</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 279.1714, found: 279.1703.

**(2S,3R,4R)-2-(2-chlorophenyl)-3-methyl-3-nitro-4-vinyltetrahydro-2*H*-pyran (3g)**



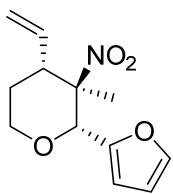
Colorless oil; yield: 64%; 18 mg; dr: 11/1; (major isomer) ee: 83%; HPLC (Chiralcel AD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 98/2, 0.6 ml/min, 214 nm), t<sub>major</sub> = 12.4 min, t<sub>minor</sub> = 11.5 min; [α]<sub>D</sub><sup>25</sup> = 15.55 (c 1.20, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.35 – 7.20 (m, 3H), 5.72 – 5.55 (m, 1H), 5.34 (s, 1H), 5.22 – 5.11 (m, 2H), 4.32 – 4.16 (m, 1H), 3.85 (m, 1H), 3.64 (dd, *J* = 16.5, 7.2 Hz, 1H), 1.88 (m, 2H), 1.49 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 134.7, 133.6, 133.34, 130.0, 129.7, 129.6, 126.2, 118.9, 92.0, 79.9, 68.7, 46.9, 28.0, 11.6; IR (film) 3077, 2954, 2858, 1639, 1536, 1468, 1439, 1384, 1348, 1284, 1252, 1207, 1097, 1040, 990, 929, 864, 802, 752, 704, 663, 627, 575, 466 cm<sup>-1</sup>; MS (ESI) *m/z*: 304.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>14</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>Cl (M+NH<sub>4</sub>)<sup>+</sup>: 299.1157, found: 299.1157.

**(2S,3R,4R)-3-methyl-2-(naphthalen-1-yl)-3-nitro-4-vinyltetrahydro-2H-pyran (3h)**



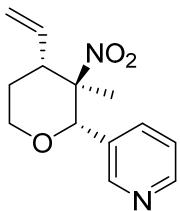
Brown oil; yield: 47%; 14 mg; dr: 7/1; ee (major isomer): 73%; HPLC (Chiralcel OD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 99/1, 1.0 ml/min, 214 nm), t<sub>major</sub> = 24.3 min, t<sub>minor</sub> = 46.6 min; [α]<sub>D</sub><sup>25</sup> = 48.68 (*c* 1.30, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.48 (m, 4H), 5.72 – 5.51 (m, 2H), 5.22 – 5.12 (m, 2H), 4.34 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.93 (td, *J* = 12.0, 4.0 Hz, 1H), 3.66 (dt, *J* = 12.0, 6.0 Hz, 1H), 1.95 (m, 2H), 1.51 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 134.7, 133.6, 131.6, 131.1, 129.5, 128.7, 126.8, 126.2, 125.6, 124.6, 123.2, 118.8, 93.5, 81.5, 68.9, 48.2, 28.1, 11.9; IR (film) 3052, 3012, 2953, 2927, 2857, 1638, 1597, 1535, 1446, 1386, 1344, 1216, 1168, 1097, 986, 928, 859, 750, 700, 664, 551 cm<sup>-1</sup>; MS (ESI) *m/z*: 320.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 315.1703, found: 315.1702.

**(2*R*,3*R*,4*R*)-2-(furan-2-yl)-3-methyl-3-nitro-4-vinyltetrahydro-2*H*-pyran (3i)**



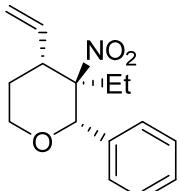
Brown oil; yield: 38%; 9 mg; dr: 13/1; ee (major isomer): 85%; HPLC (Chiralcel OD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 98/2, 1.0 ml/min, 214 nm), t<sub>major</sub> = 12.2 min, t<sub>minor</sub> = 17.3 min; [α]<sub>D</sub><sup>25</sup> = -24.00 (*c* 1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (s, 1H), 6.28 (m, 2H), 5.70 – 5.52 (m, 1H), 5.22 – 5.02 (m, 3H), 4.25 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.82 (td, *J* = 12.0, 4.0 Hz, 1H), 3.30 – 3.16 (m, 1H), 1.94 – 1.72 (m, 2H), 1.44 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.9, 142.8, 134.0, 119.0, 110.2, 108.8, 92.7, 79.0, 68.6, 48.3, 27.8, 11.3; IR (film) 2929, 2860, 1639, 1537, 1447, 1389, 1348, 1253, 1219, 1146, 1101, 990, 929, 891, 808, 741, 654, 595, 569 cm<sup>-1</sup>; MS (ESI) *m/z*: 260.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>12</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 255.1339, found: 255.1342.

**3-((2*S*,3*R*,4*R*)-3-methyl-3-nitro-4-vinyltetrahydro-2*H*-pyran-2-yl)pyridine (3j)**



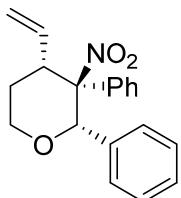
White solid; mp: 70.9–71.4 °C; yield: 60%; 15 mg; dr: 12/1; ee (major isomer): 98%; HPLC (Chiralcel AD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 90/10, 1.0 ml/min, 214 nm),  $t_{\text{major}} = 34.3$  min,  $t_{\text{minor}} = 18.2$  min;  $[\alpha]_D^{25} = -25.95$  (*c* 0.50, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.56 (d, *J* = 4.8 Hz, 1H), 8.46 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.15 (m, 1H), 5.61 (ddd, *J* = 17.5, 10.4, 7.5 Hz, 1H), 5.25 – 5.09 (m, 2H), 5.01 (s, 1H), 4.36 – 4.23 (m, 1H), 3.84 (td, *J* = 11.7, 4.5 Hz, 1H), 3.45 – 3.32 (m, 1H), 1.95 – 1.78 (m, 2H), 1.32 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.9, 148.3, 134.5, 134.1, 131.4, 123.1, 119.1, 93.3, 82.1, 68.5, 48.4, 27.7, 10.5; IR (film) 2923, 2859, 2085, 1736, 1636, 1581, 1535, 1431, 1387, 1355, 1256, 1166, 1094, 1018, 932, 866, 798, 705, 615, 573 cm<sup>-1</sup>; MS (EI) *m/z*: 201.0 (M–HNO<sub>2</sub>)<sup>+</sup>; HRMS (EI) calc for C<sub>13</sub>H<sub>16</sub>NO (M–NO<sub>2</sub>)<sup>+</sup>: 202.1232, found: 202.1235.

**(2*S*,3*R*,4*R*)-3-ethyl-3-nitro-2-phenyl-4-vinyltetrahydro-2*H*-pyran (3k)**



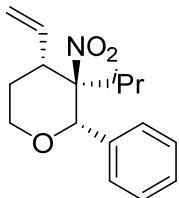
Colorless oil; yield: 77%; 20 mg; dr: 17/1; ee (major isomer): 97%; HPLC (Chiralcel OJ-3, 3.0 mm × 150 mm, Carbon dioxide/*i*-Propanol = 95/5, 0.8 ml/min, 214 nm),  $t_{\text{major}} = 5.7$  min,  $t_{\text{minor}} = 6.8$  min;  $[\alpha]_D^{25} = -4.10$  (*c* 1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.27 (m, 3H), 7.17 (m, 2H), 5.79 (m, 1H), 5.12 (m, 2H), 4.90 (s, 1H), 4.32 (dd, *J* = 12.0, 4.9 Hz, 1H), 3.84 (td, *J* = 12.0, 3.4 Hz, 1H), 3.60 – 3.50 (m, 1H), 1.97 (m, 4H), 0.95 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.0, 135.9, 128.4, 128.1, 126.7, 117.2, 96.2, 85.6, 68.6, 48.7, 27.7, 20.3, 10.0; IR (film) 3077, 2939, 2858, 1638, 1532, 1455, 1347, 1253, 1213, 1168, 1106, 1025, 991, 922, 813, 756, 706, 667, 568 cm<sup>-1</sup>; MS (ESI) *m/z*: 284.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>15</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 279.1703, found: 279.1703.

**(2S,3S,4R)-3-nitro-2,3-diphenyl-4-vinyltetrahydro-2H-pyran (3l)**



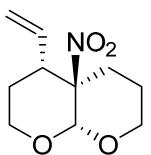
White solid; mp: 108.3–109.3 °C; yield: 96%; 30 mg; dr: 8/1; ee (major isomer): 96%; HPLC (Chiralcel OJ-3, 3.0 mm × 150 mm, Carbon dioxide/*i*-Propanol = 90/10, 1.0 mL/min, 214 nm),  $t_{\text{major}} = 3.8$  min,  $t_{\text{minor}} = 3.3$  min;  $[\alpha]_D^{25} = 33.46$  (*c* 1.30, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (m, 2H), 7.25 (m, 3H), 7.19 (m, 5H), 5.52 – 5.36 (m, 1H), 5.22 – 5.07 (m, 3H), 4.40 (dd, *J* = 12.0, 5.0 Hz, 1H), 3.97 (td, *J* = 12.0, 2.8 Hz, 1H), 3.83 (ddd, *J* = 12.3, 7.8, 4.3 Hz, 1H), 1.94 (m, 1H), 1.79 (d, *J* = 14.1 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.8, 135.4, 131.0, 128.4, 128.0, 127.7, 126.6, 118.7, 99.8, 87.0, 68.9, 49.4, 28.9; IR (film) 3065, 3030, 2959, 2929, 2858, 1638, 1536, 1497, 1447, 1362, 1330, 1251, 1216, 1158, 1103, 1001, 924, 789, 754, 703, 630, 598 cm<sup>-1</sup>; MS (ESI) *m/z*: 332.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 327.1703, found: 327.1703.

**(2S,3R,4R)-3-isopropyl-3-nitro-2-phenyl-4-vinyltetrahydro-2H-pyran (3m)**



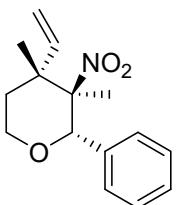
Colorless oil; 24 mg; yield: 87%; dr: 5/1; ee (major isomer): 93%; HPLC (Chiralcel OD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 99/1, 0.7 mL/min, 214 nm), Major diastereomer:  $t_{\text{major}} = 9.8$  min,  $t_{\text{minor}} = 10.9$  min;  $[\alpha]_D^{25} = 20.77$  (*c* 1.07, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 – 7.24 (m, 5H), 5.95 (ddd, *J* = 17.3, 10.4, 7.1 Hz, 1H), 5.14 (dd, *J* = 20.2, 13.8 Hz, 2H), 4.92 (s, 1H), 4.30 (dd, *J* = 11.4, 5.0 Hz, 1H), 3.81 (td, *J* = 11.9, 3.2 Hz, 1H), 3.76 – 3.66 (m, 1H), 2.65 – 2.50 (m, 1H), 2.28 (dd, *J* = 13.2, 5.4 Hz, 1H), 1.87 (d, *J* = 13.9 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.9, 136.8, 128.3, 127.9, 127.4, 116.5, 99.4, 86.5, 68.0, 48.0, 30.0, 28.0, 21.5, 20.5; IR (film) 3077, 2927, 2857, 1637, 1532, 1458, 1363, 1254, 1197, 1108, 1025, 997, 921, 863, 794, 766, 701, 668, 570 cm<sup>-1</sup>; MS (ESI) *m/z*: 298.1 (M+Na)<sup>+</sup>; HRMS (ESI) calcd for C<sub>16</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 293.1871, found: 293.1860.

**(4*R*,4*aR*,8*aR*)-4*a*-nitro-4-vinyloctahydropyrano[2,3-*b*]pyran (3n)**



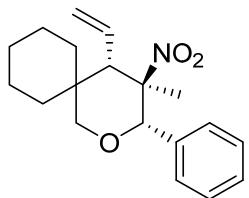
White solid; **mp:** 85.5–86.3 °C; yield: 60%; 13 mg; dr: 12/1; ee (major isomer): 96%; HPLC (Chiralcel OD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 99/1, 1.0 ml/min, 214 nm), *t*<sub>major</sub> = 20.1 min, *t*<sub>minor</sub> = 26.3 min; [α]<sub>D</sub><sup>25</sup> = -11.25 (*c* 0.50, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.66 – 5.52 (m, 1H), 5.28 (s, 1H), 5.09 (m, 2H), 4.18 (ddd, *J* = 11.8, 4.9, 1.2 Hz, 1H), 4.06 – 3.92 (m, 1H), 3.76 (td, *J* = 12.3, 2.8 Hz, 1H), 3.65 (dd, *J* = 11.1, 5.5 Hz, 1H), 2.91 (ddd, *J* = 12.3, 7.8, 4.9 Hz, 1H), 2.43 – 2.27 (m, 1H), 2.13 – 2.01 (m, 1H), 1.92 (m, 1H), 1.78 (m, 1H), 1.67 (m, 1H), 1.54 (d, *J* = 11.1 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 132.9, 119.0, 97.3, 89.6, 65.7, 60.2, 48.6, 27.7, 20.3, 19.9; IR (film) 3082, 2936, 2861, 1641, 1536, 1440, 1352, 1250, 1128, 1078, 1021, 992, 925, 892, 792, 757, 680, 616, 529 cm<sup>-1</sup>; MS (ESI) *m/z*: 236.1 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>10</sub>H<sub>19</sub>N<sub>2</sub>O<sub>4</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 231.1339, found: 231.1339.

**(2*S*,3*R*,4*R*)-3,4-dimethyl-3-nitro-2-phenyl-4-vinyltetrahydro-2*H*-pyran (3o)**



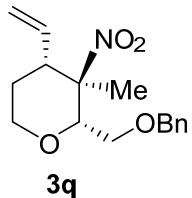
Colorless oil; yield: 42%; 11 mg; dr > 20/1; ee (major isomer): 91%; HPLC (Chiralcel OJ-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 99/1, 0.7 ml/min, 214 nm), *t*<sub>major</sub> = 15.7 min, *t*<sub>minor</sub> = 25.2 min; [α]<sub>D</sub><sup>25</sup> = -13.31 (*c* 0.50, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.21 (m, 5H), 5.83 (dd, *J* = 16.0, 9.0 Hz, 1H), 5.49 (s, 1H), 5.17 (d, *J* = 8.0 Hz, 1H), 5.06 (d, *J* = 20.0 Hz, 1H), 4.18 – 3.94 (m, 2H), 2.21 (td, *J* = 12.0, 4.0 Hz, 1H), 1.61 – 1.54 (m, 1H), 1.47 (s, 3H), 1.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.7, 136.5, 128.5, 128.2, 127.9, 114.3, 93.8, 77.5, 64.2, 42.6, 33.1, 22.0, 14.9; IR (film) 3085, 2922, 2862, 1636, 1530, 1449, 1381, 1346, 1252, 1109, 1006, 975, 923, 870, 824, 778, 745, 708, 630, 551 cm<sup>-1</sup>; MS (ESI) *m/z*: 279.1 (M+NH<sub>4</sub>)<sup>+</sup>; HRMS (ESI) calc for C<sub>15</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 279.1714, found: 279.1703.

**(3S,4R,5S)-4-methyl-4-nitro-3-phenyl-5-vinyl-2-oxaspiro[5.5]undecane (3p)**



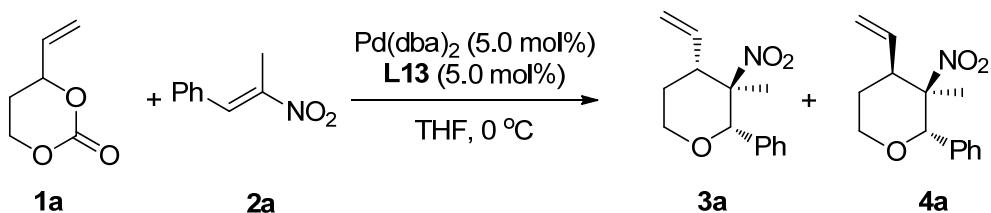
Colorless oil; yield: 44%; 14 mg; dr: 6/1; ee (major isomer): 92%; HPLC (Chiralcel OJ-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 99/1, 1.0 ml/min, 214 nm), t<sub>major</sub> = 8.3 min, t<sub>minor</sub> = 13.3 min; [α]<sub>D</sub><sup>25</sup> = -29.58 (*c* 0.93, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (m, 3H), 7.20 – 7.12 (m, 2H), 5.80 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.23 (d, *J* = 10.0 Hz, 1H), 5.08 (m, 2H), 4.57 (d, *J* = 12.0 Hz, 1H), 3.40 (d, *J* = 12.0 Hz, 1H), 2.94 (d, *J* = 10.0 Hz, 1H), 2.06 (d, *J* = 12.6 Hz, 1H), 1.67 (m, 2H), 1.61 – 1.49 (m, 3H), 1.39 – 1.19 (m, 6H), 1.09 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.1, 130.5, 128.3, 128.2, 126.5, 122.4, 95.0, 85.0, 75.3, 60.0, 37.1, 35.3, 27.2, 25.7, 22.0, 21.6, 14.5; IR (film) 3073, 2959, 2924, 2859, 1645, 1631, 1603, 1533, 1494, 1450, 1388, 1347, 1259, 1171, 1127, 1074, 976, 926, 861, 798, 743, 704, 650, 630, 565 cm<sup>-1</sup>; MS (ESI) *m/z*: 338.2 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>19</sub>H<sub>29</sub>N<sub>2</sub>O<sub>3</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 333.2173, found: 333.2171.

**(2*R*,3*R*,4*R*)-2-((benzyloxy)methyl)-3-methyl-4-nitro-4-vinyltetrahydro-2*H*-pyran (3q)**



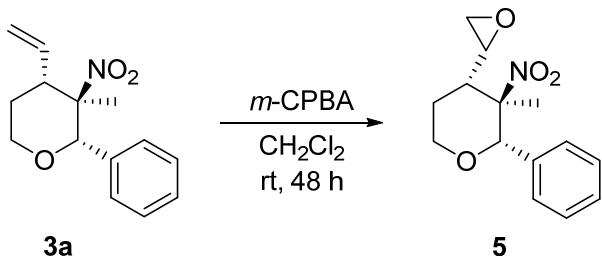
Brown oil; yield: 24%; 7 mg; dr: 3/1; (major isomer) ee: 83%; HPLC (Chiralcel OD-H, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 99/1, 1.0 mL/min, 214nm), t<sub>major</sub> = 19.1 min, t<sub>minor</sub> = 21.1 min; [α]<sub>D</sub><sup>25</sup> = 37.86 (*c* 0.40, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.20 (m, 5H), 5.63 – 5.51 (m, 1H), 5.12 (m, 2H), 4.48 (q, *J* = 12.0 Hz, 2H), 4.26 – 4.05 (m, 2H), 3.76 – 3.61 (m, 1H), 3.50 (m, 1H), 3.31 (m, 1H), 3.15 – 3.04 (m, 1H), 1.78 – 1.66 (m, 2H), 1.43 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.4, 134.0, 128.4, 127.7, 127.6, 118.9, 90.7, 80.4, 73.5, 68.6, 67.9, 48.7, 27.9, 10.8; IR (film) 3030, 2924, 2857, 1641, 1536, 1496, 1453, 1390, 1372, 1220, 1169, 1108, 1026, 995, 866, 799, 735, 659, 620, 589 cm<sup>-1</sup>; MS (ESI) *m/z*: 309.0 (M+NH<sub>4</sub>)<sup>+</sup>; HRMS (ESI) calcd for C<sub>16</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> (M+NH<sub>4</sub>)<sup>+</sup>: 309.1809, found: 309.1811.

#### 4. Pd-catalyzed asymmetric [4+2]-cycloaddition reaction of 4-vinyl-1,3-dioxan-2-one **1a** and nitroalkene **2a** at 1 mmol scale



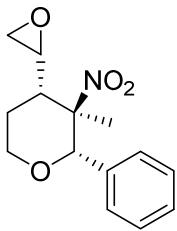
To a flame dried sealing tube was added Pddba<sub>2</sub> (0.05 mmol, 29 mg), **L13** (0.05 mmol, 22 mg), freshly distilled anhydrous THF (20 mL). The resulting mixture was allowed to stir for 30 mins. Then, compound **1a** (1.5 mmol, 192 mg) and nitroalkene **2a** (1 mmol, 163 mg) were added subsequently. The resulting reaction mixture was stirred at 0 °C for 4 days (monitored by TLC). After the volatiles were removed in vacuo, the ratio of diastereoisomers **3a** and **4a** was determined by <sup>1</sup>H NMR. Then the resulting residue was purified by flash chromatography on silica gel with petroleum ether and ethyl acetate as eluent to give diastereomers **3a** and **4a** (0.225 g, yield: 91%, dr = 10/1, ee: 93%).

#### 5. The preparation of compound **5**



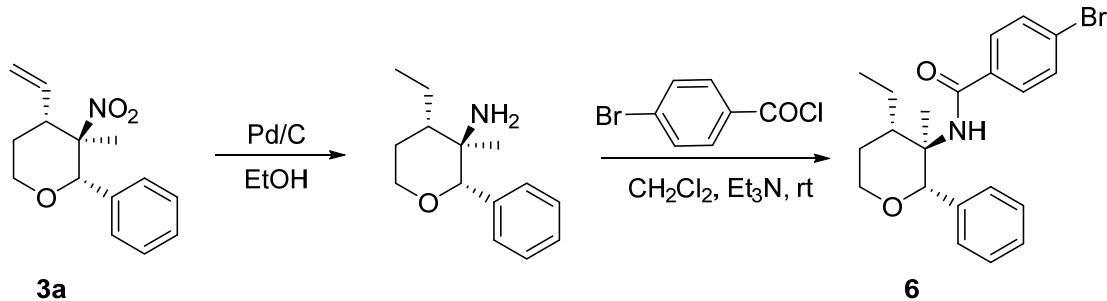
To a solution of optically active **3a** (ee: 96%, 0.08 mol, 20 mg) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was added *m*-CPBA (0.25 mmol, 42 mg, 3 equiv) in one portion at ambient temperature. The reaction mixture was stirred for 24 h. The reaction mixture was added saturated aqueous Na<sub>2</sub>SO<sub>3</sub> (1.0 mL) at 0 °C and stirred for 30 min. The reaction mixture was neutralized with saturated aqueous NaHCO<sub>3</sub> (2 mL) and extracted with Et<sub>2</sub>O. The combined organic layers were washed with brine (10 mL) and dried over anhydrous MgSO<sub>4</sub>. The volatiles were removed in vacuo. Flash chromatography on silica gel, using diethyl ether-hexanes (1:20) as eluent, provided an epoxide **5** (12 mg, 57% yield) as a colorless oil.

**(2S,3R,4S)-3-methyl-3-nitro-4-(oxiran-2-yl)-2-phenyltetrahydro-2H-pyran (5)**



White solid; mp: 131.8–132.2 °C, yield: 57%; 12 mg; ee: 94%; HPLC (Chiralcel AD-H, 4.6 mm × 250 mm, Hexane/i-Propanol = 99/1, 0.7 ml/min, 214 nm), Major diastereomer:  $t_{\text{major}} = 28.4$  min,  $t_{\text{minor}} = 19.5$  min;  $[\alpha]_D^{25} = -6.12$  ( $c$  0.80, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (m, 3H), 7.15 (m, 2H), 4.89 (s, 1H), 4.30 (m, 1H), 3.79 (dd,  $J = 9.0, 4.0$  Hz, 1H), 2.83 – 2.72 (m, 1H), 2.72 – 2.63 (m, 1H), 2.63 – 2.47 (m, 2H), 2.04 – 1.83 (m, 2H), 1.47 (s, 3H); <sup>13</sup>C NMR (101 MHz, CHCl<sub>3</sub>) δ 135.1, 128.7, 128.3, 126.9, 92.5, 84.1, 68.3, 51.0, 47.0, 45.3, 25.7, 11.6; IR (film) 3004, 2975, 2877, 1642, 1605, 1533, 1451, 1392, 1353, 1289, 1248, 1172, 1136, 1099, 1027, 995, 915, 894, 847, 759, 696, 620, 549 cm<sup>-1</sup>; MS (ESI) *m/z*: 216.0 (M–HNO<sub>2</sub>)<sup>+</sup>; HRMS (ESI) calc for C<sub>14</sub>H<sub>18</sub>NO<sub>4</sub> (M+H)<sup>+</sup>: 264.1230, found: 264.1231.

## 6. The preparation of compound 6

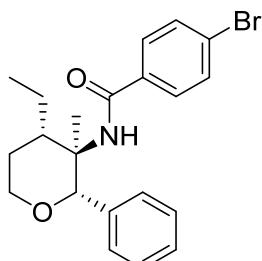


The optically active **3a** (ee: 96%, 0.065 mmol, 16 mg) was dissolved in EtOH (5 mL). Then 10 wt% Pd/C (20 mol%, 14 mg) was added subsequently. The resulting solution was allowed to stir for 4 hours at room temperature under H<sub>2</sub> balloon. The reaction mixture was filtered through celite and washed with EtOH. After concentrated in vacuo, the resulting crude product was used for the next step without further purification.

The 5 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added to above crude product. The resulting mixture was then put under a positive pressure of N<sub>2</sub> and chilled to 0 °C. Once chilled, dry triethylamine (1.2 equiv) and benzoyl chloride (1.2 equiv, 0.078 mmol, 17 mg) were added, and the reaction mixture was stirred at 0 °C for 30 minutes. The ice bath was then removed and the reaction mixture was stirred at room temperature for over night

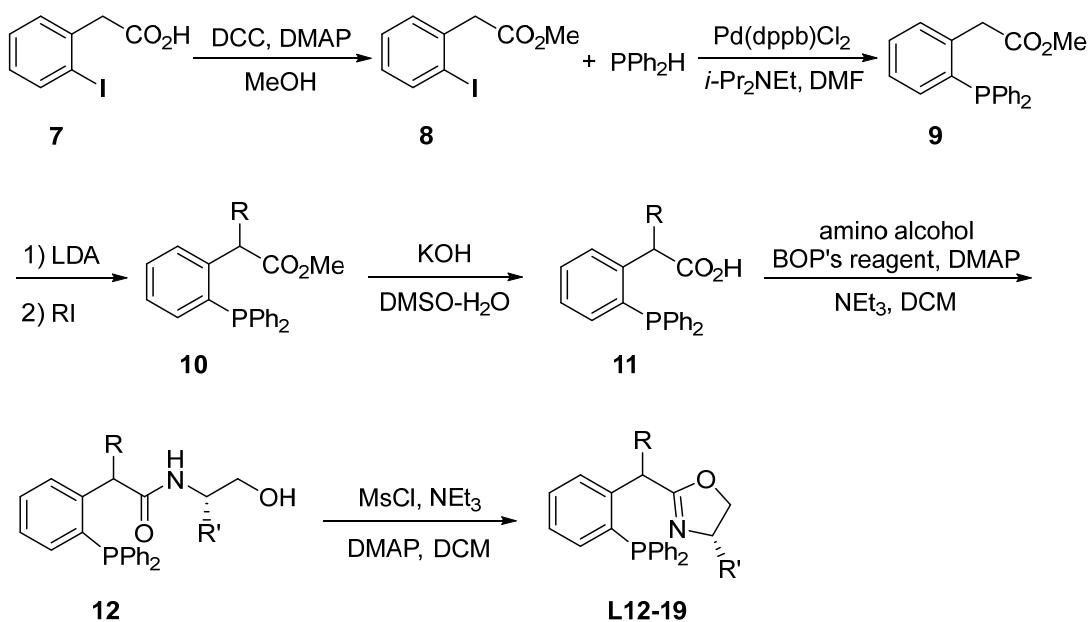
(monitored by TLC). The solvent was removed under reduced pressure. The crude product was purified by preparative TLC to give product **6** (yield for two steps).

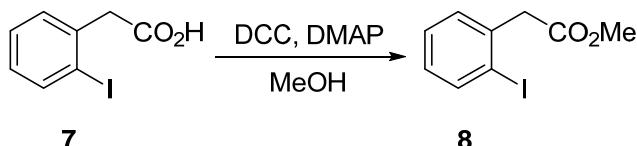
**4-bromo-N-((2*S*,3*R*,4*S*)-4-ethyl-3-methyl-2-phenyltetrahydro-2*H*-pyran-3-yl)benzamide (6)**



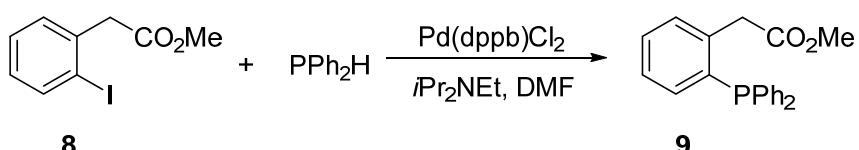
White solid; mp: 63.5–64.7 °C, yield: 73%; 19 mg; ee: 96%; HPLC (Chiralcel IA, 4.6 mm × 250 mm, Hexane/*i*-Propanol = 98/2, 0.7 ml/min, 214 nm), Major diastereomer:  $t_{\text{major}} = 14.3$  min,  $t_{\text{minor}} = 19.6$  min;  $[\alpha]_D^{25} = -99.09$  (*c* 1.40, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (m, 4H), 7.32 – 7.17 (m, 5H), 5.43 (s, 1H), 5.30 (s, 1H), 4.17 (dd, *J* = 12.0, 4.0 Hz, 1H), 3.89 – 3.63 (m, 1H), 3.23 – 3.08 (m, 1H), 1.87 (d, *J* = 12.0 Hz, 1H), 1.71 – 1.49 (m, 2H), 1.18 – 1.06 (m, 1H), 1.04 (s, 3H), 0.95 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.5, 138.6, 134.6, 131.8, 128.3, 127.6, 127.5, 127.3, 125.9, 81.0, 68.9, 60.3, 40.8, 28.5, 22.7, 14.7, 12.0; IR (film) 3391, 3269, 3182, 3062, 2919, 2849, 1629, 1587, 1544, 1482, 1450, 1374, 1310, 1195, 1139, 1029, 989, 883, 789, 703, 681, 587 cm<sup>-1</sup>; MS (ESI) *m/z*: 424.0 (M+Na)<sup>+</sup>; HRMS (ESI) calc for C<sub>21</sub>H<sub>25</sub>NO<sub>2</sub>Br (M+H)<sup>+</sup>: 402.1063, found: 402.1064.

## 7. The preparation of ligands L12-19

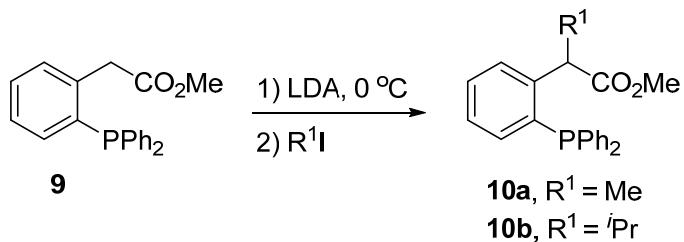




At 0 °C, **7** (5.24 g, 20.0 mmol), DCC (5.0 g, 24.0 mmol), and DMAP (150 mg) were mixed in MeOH (80 mL). The mixture was stirred at room temperature until the reaction was completed as monitored by TLC. The reaction mixture was filtered through a silica gel pad and washed with CH<sub>2</sub>Cl<sub>2</sub>. After removal of the solvent, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **8**<sup>4</sup> as a white solid (5.4 g, 98% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.23–7.18 (m, 2H), 6.90–6.85 (m, 1H), 3.72 (s, 2H), 3.63 (s, 3H).

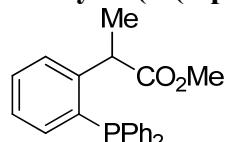


The flask is equipped with a reflux condenser with a two-tap Schlenk adapter connected to a bubbler and an argon/vacuum manifold. 20.0 mmol (5.6 g) of methyl 2-(2-iodophenyl)acetate **8**, 40 mL DMF, 13.2 mL *i*Pr<sub>2</sub>NEt, 1.0 mmol (5 mol%, 0.175 g) of PdCl<sub>2</sub> and 1.2 mmol (6 mol%, 0.51 g) of dppb are filled into an appropriate nitrogen-flushed 100-mL flask. 24.0 mmol (4.4 ml) of Ph<sub>2</sub>PH were added with a syringe under a counter flow of argon. To remove oxygen from the system, liquid nitrogen frozen-vacuum deoxygenation-unfreeze was cycled three times. After the Schlenk was filled with argon. The reaction mixture was stirred at 130 °C for 40 h, subsequent cooling (down to 40 °C). The complex was washed with distilled water (2 × 15 mL) and Et<sub>2</sub>O (3 × 15 mL). The organic phase was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to provide the product **9**<sup>3</sup> (Colorless oil, 6.0 g, 90% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.20 (m, 12H), 7.19 – 7.11 (m, 1H), 6.93 (d, *J* = 3.5 Hz, 1H), 3.96 (s, 2H), 3.40 (d, *J* = 2.3 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.5, 138.9 (d, *J*<sub>PC</sub> = 27 Hz), 136.5 (d, *J*<sub>PC</sub> = 13 Hz), 136.1 (d, *J*<sub>PC</sub> = 10 Hz), 133.9, 133.7, 130.5 (d, *J*<sub>PC</sub> = 5 Hz), 129.1, 128.6, 128.4, 128.3, 127.4, 51.6, 39.7 (d, *J*<sub>PC</sub> = 23 Hz); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ -15.4.



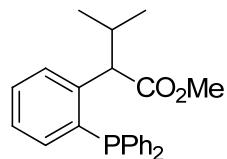
Anhydrous THF 10 mL and LDA 4.5 mmol (1.5 equiv) were added to a round-bottom flask precooled to -78 °C under argon atmosphere. The aliphatic acid **9** (3.0 mmol, 1.0 g, 1.0 equiv) was added slowly and the resulting mixture was allowed to stir for 1 h. After the addition of CH<sub>3</sub>I (or <sup>i</sup>PrI) 4.5 mmol (1.5 equiv), the mixture was warmed to ambient temperature for overnight. 10% HCl solution was added until pH of reaction mixture was 7. The aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to provide the product **10**.

**methyl 2-(2-(diphenylphosphino)phenyl)propanoate (10a)**



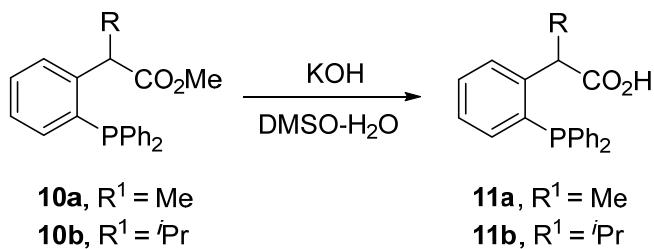
colorless viscous oil, yield: 60%, 0.63 g. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34-7.24 (m, 12H), 7.17-7.14 (m, 1H), 6.92 (dd, *J* = 7.6 Hz, 3.2 Hz, 1H), 4.72-4.65 (m, 1H), 3.43 (s, 3H), 1.36 (d, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.0, 145.7 (d, *J<sub>PC</sub>* = 26 Hz), 136.6 (d, *J<sub>PC</sub>* = 9 Hz), 136.3 (d, *J<sub>PC</sub>* = 10 Hz), 135.6 (d, *J<sub>PC</sub>* = 13 Hz), 134.0 (d, *J<sub>PC</sub>* = 6 Hz), 133.9, 133.8 (d, *J<sub>PC</sub>* = 12 Hz), 129.5, 128.8, 128.62, 128.60 (d, *J<sub>PC</sub>* = 7 Hz), 128.4 (d, *J<sub>PC</sub>* = 7 Hz), 127.2, 127.1, 51.8, 42.4 (d, *J<sub>PC</sub>* = 26 Hz), 18.9; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -16.2; IR (film): 3054, 2950, 1736, 1586, 1469, 1434, 1376, 1331, 1205, 1171, 1091, 1027, 967, 859, 802, 775, 745, 697 cm<sup>-1</sup>; MS (EI) *m/z* (%): 348 (M<sup>+</sup>, 3.82), 349 (0.90), 333 (100), 317 (5.53), 305 (52.27), 290 (17.45); HRMS calcd for C<sub>22</sub>H<sub>21</sub>O<sub>2</sub>P (M<sup>+</sup>): 348.1279, found 348.1275.

**methyl 2-(2-(diphenylphosphino)phenyl)-3-methylbutanoate (10b)**



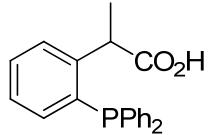
colorless viscous oil, yield: 93%, 1.05 g. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.60 (q, *J* = 4.4 Hz, 1H), 7.36-7.19 (m, 11H), 7.14(t, *J* = 8.0 Hz, 1H), 6.97 (q, *J* = 8.0 Hz, 1H),

4.48 (t,  $J = 10.4$  Hz, 1H), 3.31 (s, 3H), 1.37-1.23 (m, 1H), 1.04 (d,  $J = 7.0$  Hz, 3H), 0.68 (d,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.6, 143.7 (d,  $J_{\text{PC}} = 26$  Hz), 137.0 (d,  $J_{\text{PC}} = 10$  Hz), 136.7 (d,  $J_{\text{PC}} = 10$  Hz), 134.3, 134.0, 133.8, 133.6, 129.5, 128.6, 128.5, 128.4, 128.2 (d,  $J_{\text{PC}} = 7$  Hz), 127.6 (d,  $J_{\text{PC}} = 5$  Hz), 127.1, 55.1 (d,  $J_{\text{PC}} = 26$  Hz), 51.3, 32.7, 21.4, 20.0;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -17.3; IR (film): 3054, 2960, 2872, 1732, 1586, 1467, 1433, 1387, 1368, 1328, 1287, 1232, 1200, 1160, 1132, 1091, 1069, 1014, 904, 744, 696  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 376 ( $\text{M}^+$ , 5.77), 361 (100), 333 (73.59), 330 (1.45), 317 (23.45), 301 (5.55), 261 (11.03), 183 (22.94); HRMS calcd for  $\text{C}_{24}\text{H}_{25}\text{O}_2\text{P}$   $\text{M}^+$ : 376.1592, found 376.1598.



A solution of phenylacetate (5.0 mmol) in DMSO (37 ml) was treated with solution of sodiumhydroxide (0.74 g, 18.5 mmol) in water (9 ml) at ambient temperature. To remove oxygen from the system, liquid nitrogen frozen-vacuum deoxygenation-unfreeze was cycled three times. After the Schlenk was filled with argon, the reaction mixture was stirred at 140 °C for 2 h. The mixture was cooled to ambient temperature. The residue was diluted with water (40 ml) and the mixture was acidified to pH = 4 using dilute hydrochloric acid and extracted with EA (3 x 30 ml). Combined organic extracts were washed with brine (40 mL) and dried over anhydrous sodium sulfate. The volatiles were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to give 2-phenylacetic acid **11**.

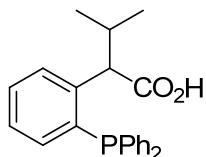
#### **2-(2-(diphenylphosphino)phenyl)propanoic acid (11a)**



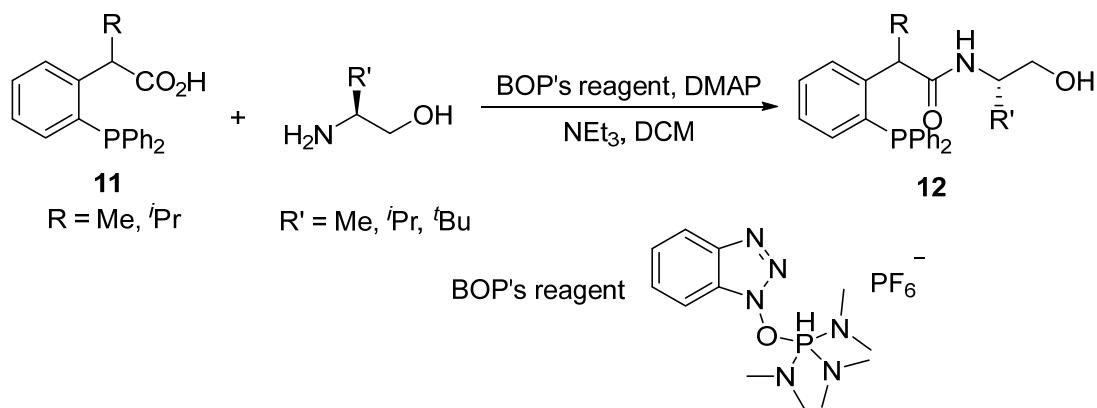
colorless viscous oil, yield: 88%, 1.47 g.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.20 (br, 1H), 7.38-7.22 (m, 12H), 7.17-7.31 (m, 1H), 6.94-6.91 (m, 1H), 471-4.64 (m, 1H), 1.36 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101MHz,  $\text{CDCl}_3$ )  $\delta$  180.4, 145.2 (d,  $J_{\text{PC}} = 26$  Hz), 136.4 (d,  $J_{\text{PC}} = 9$  Hz), 136.2 (d,  $J_{\text{PC}} = 10$  Hz), 135.7 (d,  $J_{\text{PC}} = 12$  Hz), 134.1, 134.0, 133.8 (d,  $J_{\text{PC}} = 20$  Hz), 129.4, 128.8, 128.7, 128.5 (d,  $J_{\text{PC}} = 7$  Hz), 128.4 (d,  $J_{\text{PC}} = 7$  Hz), 127.4, 127.2 (d,  $J_{\text{PC}} = 4$  Hz), 42.6 (d,  $J_{\text{PC}} = 26$  Hz), 18.7;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -16.0; IR (film): 3055, 2978, 1702, 737, 694  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 334 ( $\text{M}^+$ , 18.84),

319 (45.22), 289 (24.57), 207 (19.02), 183 (36.49), 165 (35.30), 133 (55.69); HRMS (EI) calculated for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>P [M<sup>+</sup>]: 334.1123, found: 334.1121.

**2-(2-(diphenylphosphino)phenyl)-3-methylbutanoic acid (11b)**

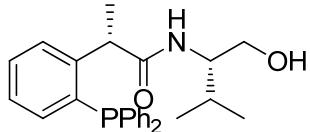


colorless viscous oil, yield: 94%, 1.70 g. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.68 (br, 1H), 7.58-7.55 (m, 1H), 7.35-7.21 (m, 11H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 11.2 Hz, 1H), 4.49 (t, *J* = 10.4 Hz, 1H), 2.40-2.31 (m, 1H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.60 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 180.0, 143.3 (d, *J*<sub>PC</sub> = 26 Hz), 137.3 (d, *J*<sub>PC</sub> = 12 Hz), 136.7 (d, *J*<sub>PC</sub> = 8 Hz), 136.6, 134.5 (d, *J*<sub>PC</sub> = 7 Hz), 133.9 (d, *J*<sub>PC</sub> = 21 Hz), 133.5 (d, *J*<sub>PC</sub> = 9 Hz), 129.4, 128.6, 128.4 (d, *J*<sub>PC</sub> = 4 Hz), 128.39, 128.30 (d, *J*<sub>PC</sub> = 7 Hz), 127.6 (d, *J*<sub>PC</sub> = 4 Hz), 127.3, 55.2 (d, *J*<sub>PC</sub> = 26 Hz), 32.3, 21.3, 20.0; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ -17.4; IR (film): 3054, 2962, 1701, 1434, 740, 694 cm<sup>-1</sup>; MS (EI) *m/z* (%): 362 (M<sup>+</sup>, 11.29), 347 (9.23), 319 (100), 301 (6.26), 287 (4.61), 261 (3.75), 187 (35.42), 165 (29.62), 133 (7.34); HRMS (EI) calculated for C<sub>23</sub>H<sub>23</sub>O<sub>2</sub>P [M<sup>+</sup>], 362.1436, found: 362.1444.

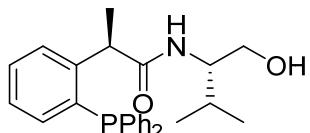


To a solution of 2-phenylacetic acid **11** (0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) were added L-valinal or L-Alaninol or L-tert-leucinol (0.6 mmol), BOP's reagent (243 mg, 0.55 mmol), Et<sub>3</sub>N (0.21 mL), and DMAP (10 mg). The reaction mixture was stirred overnight at room temperature. After completion of the reaction (monitored by TLC), water (10 mL) was added and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to give **12**. The two

diastereoisomers can be separated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100/1-3/1), in which *S,S* isomer with larger R<sub>f</sub> value and *R,S* isomer with lower R<sub>f</sub> value.

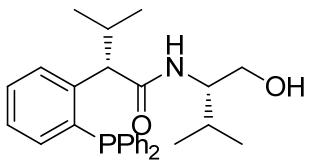


**12a**, colorless viscous oil, reaction scale: 0.5 mmol, yield: 36%, 0.075 g,  $[\alpha]_D^{25} = +77.8$  (0.9, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.53-7.50 (m, 1H), 7.39-7.23 (m, 11H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.87-6.84 (m, 1H), 5.50 (d, *J* = 6.8 Hz, 1H), 4.43-4.37 (m, 1H), 3.49-3.43 (m, 2H), 3.37-3.33 (m, 1H), 2.40 (brs, 1H), 1.72-1.63 (m, 1H), 1.40 (d, *J* = 7.2 Hz, 3H), 0.85 (d, *J* = 7.2 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  175.0, 146.2 (d, *J<sub>PC</sub>* = 25 Hz), 136.1, 135.6 (d, *J<sub>PC</sub>* = 9 Hz), 134.7, 134.2 (d, *J<sub>PC</sub>* = 19 Hz), 133.7, 133.5 (d, *J<sub>PC</sub>* = 8 Hz), 129.9, 129.3, 129.0, 128.9 (d, *J<sub>PC</sub>* = 8 Hz), 128.7 (d, *J<sub>PC</sub>* = 7 Hz), 127.4, 127.1 (d, *J<sub>PC</sub>* = 4 Hz), 63.9, 57.7, 43.5 (d, *J<sub>PC</sub>* = 23 Hz), 28.6, 19.4, 18.6, 18.4; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -15.2; IR (film): 3406, 3055, 2961, 2872, 1658 1586, 1511, 1467, 1435, 1370, 1223, 1168, 1119, 1071, 1027, 998, 915, 744, 697 cm<sup>-1</sup>; MS (EI) *m/z* (%): 401 ((M-18)<sup>+</sup>, 3.61), 388 (10.46), 376 (1.15), 359 (0.66), 332 (22.28), 317 (20.53), 306 (100), 290 (10.72); HRMS calcd for C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub>P (M<sup>+</sup>): 419.2014, found 419.2025.

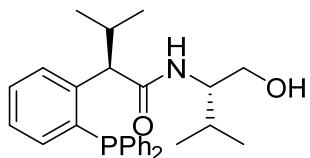


**12b**, colorless viscous oil, reaction scale: 0.5 mmol, yield: 39%, 0.082 g,  $[\alpha]_D^{25} = -137.8$  (0.75, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52-7.49 (m, 1H), 7.37-7.23 (m, 11H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.87-6.84 (m, 1H), 5.67 (d, *J* = 6.8 Hz, 1H), 4.43-4.36 (m, 1H), 3.65-3.54 (m, 2H); 3.47-3.42 (m, 1H), 3.27 (br, 1H), 1.70-1.62 (m, 1H), 1.36 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H), 0.64 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  174.6, 146.1 (d, *J<sub>PC</sub>* = 24 Hz), 135.7 (d, *J<sub>PC</sub>* = 8 Hz), 135.4 (d, *J<sub>PC</sub>* = 8 Hz), 134.5 (d, *J<sub>PC</sub>* = 10 Hz), 134.1 (d, *J<sub>PC</sub>* = 20 Hz), 133.5 (d, *J<sub>PC</sub>* = 19 Hz), 133.1, 129.6, 129.2, 128.8 (d, *J<sub>PC</sub>* = 7 Hz), 128.7, 128.5 (d, *J<sub>PC</sub>* = 7 Hz), 127.2, 127.0, 63.5, 56.8, 43.3 (d, *J<sub>PC</sub>* = 23 Hz), 28.8, 19.3, 18.1, 17.9; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -15.2; IR (film): 3406, 3055, 2961, 1658 1586, 1511, 1467, 1435, 1370, 1265, 1223, 1168, 1119, 1071, 1027, 998, 915, 741, 696 cm<sup>-1</sup>; MS (EI) *m/z* (%): 419 (M<sup>+</sup>, 0.27),

401 (3.60), 388 (11.23), 376 (1.40), 359 (0.64), 332 (23.94), 317 (23.42), 306 (100), 290 (8.87); HRMS calcd for C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub>P (M<sup>+</sup>): 419.2014, found 419.2017.

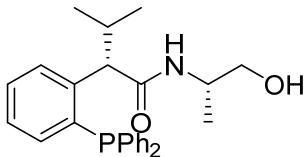


**12c**, colorless viscous oil, reaction scale: 5.0 mmol, yield: 29%, 0.65 g,  $[\alpha]_D^{25} = -67.6$  (2.5, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.67-7.63 (m, 1H), 7.32-7.25 (m, 11H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.92-6.88 (m, 1H), 5.90 (dd, *J* = 8.4 Hz, 3.0 Hz, 1H), 4.05 (dd, *J* = 10.5 Hz, 8.4 Hz, 1H), 3.62-3.54 (m, 1H), 3.30 (s, 2H), 2.75 (s, 1H), 2.56-2.49 (m, 1H), 1.83-1.72 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.77 (d, *J* = 6.6 Hz, 3H), 0.54 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 174.1, 144.3 (d, *J*<sub>PC</sub> = 25 Hz), 135.9 (d, *J*<sub>PC</sub> = 8 Hz), 135.6 (d, *J*<sub>PC</sub> = 8 Hz), 135.2 (d, *J*<sub>PC</sub> = 8 Hz), 133.9, 133.7 (d, *J*<sub>PC</sub> = 11 Hz), 133.5, 129.7, 128.9, 128.8 (d, *J*<sub>PC</sub> = 9 Hz), 128.6, 128.4 (d, *J*<sub>PC</sub> = 7 Hz), 127.3 (d, *J*<sub>PC</sub> = 5 Hz), 126.9, 63.3, 57.1 (d, *J*<sub>PC</sub> = 24 Hz), 56.8, 31.2, 28.1, 21.5, 19.51, 19.5, 18.2; <sup>31</sup>P-NMR (120 MHz, CDCl<sub>3</sub>) δ -16.3; IR (film): 3406, 2958, 2925, 1656, 1514, 1465, 1435, 1368, 1070, 745, 697 cm<sup>-1</sup>; MS (EI) *m/z* (%): 447 (M<sup>+</sup>, 0.71), 446 (0.62), 432 (2.00), 416 (18.06), 404 (10.18), 360 (33.17), 345 (23.93), 334 (100), 319 (97.18), 317 (32.75); HRMS calcd for C<sub>28</sub>H<sub>34</sub>NO<sub>2</sub>P (M<sup>+</sup>): 447.2324, found 447.2325.

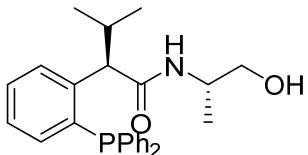


**12d**, colorless viscous oil, reaction scale: 5 mmol, yield: 68%, 1.53 g,  $[\alpha]_D^{25} = +7.6$  (0.7, CHCl<sub>3</sub>); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.54 (dd, *J* = 7.8 Hz, 4.8 Hz, 1H), 7.23-7.13 (m, 11H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.85-6.81 (m, 1H), 6.04 (d, *J* = 4.8 Hz, 1H), 3.93 (dd, *J* = 10.2 Hz, 8.7 Hz, 1H), 3.55-3.40 (m, 4H), 2.43 (br, 1H), 1.63-1.53 (m, 1H), 0.90 (d, *J* = 6.3 Hz, 3H), 0.68 (d, *J* = 6.9 Hz, 3H), 0.60 (d, *J* = 6.9 Hz, 3H), 0.31 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 174.3, 144.3 (d, *J*<sub>PC</sub> = 25 Hz), 135.8 (d, *J*<sub>PC</sub> = 8 Hz), 135.4 (d, *J*<sub>PC</sub> = 7 Hz), 135.3 (d, *J*<sub>PC</sub> = 8 Hz), 134.2, 133.9 (d, *J*<sub>PC</sub> = 11 Hz), 133.5, 129.6, 129.0, 128.7 (d, *J*<sub>PC</sub> = 8 Hz), 128.5 (d, *J*<sub>PC</sub> = 7 Hz), 128.4, 127.4 (d, *J*<sub>PC</sub> = 5 Hz), 126.8, 63.7, 57.0, 56.9 (d, *J*<sub>PC</sub> = 23 Hz), 31.1, 28.8, 21.4, 19.4, 19.2, 18.3 (2C); <sup>31</sup>P NMR (120 MHz, CDCl<sub>3</sub>) δ -15.8; IR (film): 3406, 2957, 2924, 1659, 1510, 1465, 1436, 1168, 1117, 745, 696 cm<sup>-1</sup>; MS (EI) *m/z* (%): 447 (M<sup>+</sup>, 0.77), 446 (0.73), 432 (2.32), 416 (16.72), 404 (10.24), 334 (97.98), 332 (2.10), 317 (32.23),

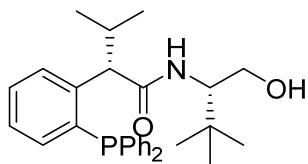
305 (1.61), 291 (11.00); HRMS calcd for C<sub>28</sub>H<sub>34</sub>NO<sub>2</sub>P (M<sup>+</sup>): 447.2324, found 447.2331.



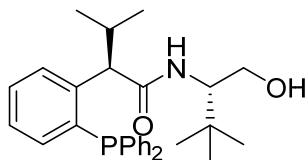
**12e**, colorless viscous oil, reaction scale: 3 mmol, yield: 42%, 0.53 g, [α]<sub>D</sub><sup>25</sup> = -61.6 (1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68-7.65 (m, 1H), 7.36-7.23 (m, 11H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 6.4 Hz, 4.4 Hz, 1H), 5.59 (d, *J* = 6.8 Hz, 1H), 4.06-4.01 (m, 1H), 3.83 (brs, 1H), 3.21-3.14 (m, 2H), 2.86 (brs, 1H), 2.50 (brs, 1H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.61 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 173.8, 144.3 (d, *J*<sub>PC</sub> = 26 Hz), 136.2 (d, *J*<sub>PC</sub> = 9 Hz), 135.8 (d, *J*<sub>PC</sub> = 8 Hz), 135.4 (d, *J*<sub>PC</sub> = 8 Hz), 133.9 (d, *J*<sub>PC</sub> = 15 Hz), 133.8, 133.6 (d, *J*<sub>PC</sub> = 1 Hz), 129.7, 129.0, 128.8, 128.7, 128.5, 127.4 (d, *J*<sub>PC</sub> = 5 Hz), 126.9, 66.4, 56.8 (d, *J*<sub>PC</sub> = 24 Hz), 47.5, 31.8, 21.4, 19.6, 16.8; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ -17.4; IR (film): 3404, 3053, 2974, 1655, 1512, 1434, 745, 696 cm<sup>-1</sup>; MS (EI) *m/z* (%): 419 (M<sup>+</sup>, 0.78), 401 (13.66), 388 (9.06), 376 (15.46), 360 (48.29), 334 (84.76), 319 (100), 301 (12.96), 287 (11.03); HRMS calcd for C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub>P (M<sup>+</sup>): 419.2014, found 419.2019.



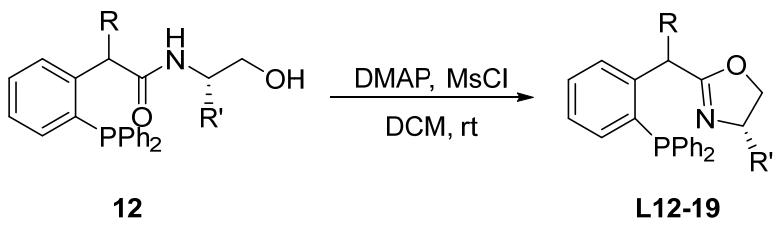
**12f**, colorless viscous oil, reaction scale: 3 mmol, yield: 38%, 0.48 g, [α]<sub>D</sub><sup>25</sup> = +52.6 (1.3, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (dd, *J* = 7.2 Hz, 4.4 Hz, 1H), 7.40-7.37 (m, 7H), 7.30-7.27 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 1H), 6.95 (dd, *J* = 7.6 Hz, 3.2 Hz, 1H), 5.81 (d, *J* = 4.8 Hz, 1H), 4.10-4.05 (m, 1H), 3.85 (brs, 1H), 3.54-3.50 (m, 2H), 3.45-3.41 (m, 1H), 2.55 (brs, 1H), 1.07 (d, *J* = 6.4 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H), 0.62 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 174.1, 144.1 (d, *J*<sub>PC</sub> = 24 Hz), 136.0 (d, *J*<sub>PC</sub> = 29 Hz), 135.6 (d, *J*<sub>PC</sub> = 32 Hz), 133.9, 133.8 (d, *J*<sub>PC</sub> = 10 Hz), 133.7, 133.6, 129.7, 128.9, 128.8 (d, *J*<sub>PC</sub> = 7 Hz), 128.7, 128.5 (d, *J*<sub>PC</sub> = 6 Hz), 127.5 (d, *J*<sub>PC</sub> = 4 Hz), 126.9, 67.2, 56.8 (d, *J*<sub>PC</sub> = 24 Hz), 47.9, 31.7, 21.4, 19.7, 16.3; <sup>31</sup>P-NMR (162 MHz, CDCl<sub>3</sub>): δ -17.5; IR (film): 3406, 3003, 2820, 1657, 1510, 1216, 743, 696 cm<sup>-1</sup>; MS (EI) *m/z* (%): 419 (M<sup>+</sup>, 0.83), 401 (15.04), 388 (5.98), 376 (15.15), 360 (46.51), 334 (80.31), 319 (100), 301 (12.99), 287 (9.92); HRMS calcd for C<sub>26</sub>H<sub>30</sub>NO<sub>2</sub>P (M<sup>+</sup>): 419.2014, found 419.2012.



**12g**, colorless viscous oil, reaction scale: 4.0 mmol, yield: 23%, 0.43 g,  $[\alpha]_D^{25} = 37.8$  (0.9,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.63 (m, 1H), 7.20-7.60 (m, 11H), 7.14 (t,  $J = 8.0$  Hz, 1H), 6.85-6.94 (m, 1H), 5.87 (d,  $J = 8.0$  Hz, 1H), 4.11-4.00 (m, 1H), 3.70 (brs, 1H), 3.56 (d,  $J = 8.0$  Hz, 1H), 3.13-3.02 (m, 1H), 2.54 (s, 1H), 1.79 (s, 1H), 1.01 (d,  $J = 8.0$  Hz, 3H), 0.85 (s, 9H), 0.55 (d,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.9, 144.5 (d,  $J_{\text{PC}} = 25$  Hz), 135.9 (d,  $J_{\text{PC}} = 8$  Hz), 135.7 (d,  $J_{\text{PC}} = 8$  Hz), 135.1 (d,  $J_{\text{PC}} = 7$  Hz), 133.9 (d,  $J_{\text{PC}} = 13$  Hz), 133.8, 133.6, 130.0, 129.1 (d,  $J_{\text{PC}} = 5$  Hz), 128.9 (d,  $J_{\text{PC}} = 7$  Hz), 128.6 (d,  $J_{\text{PC}} = 7$  Hz), 127.5 (d,  $J_{\text{PC}} = 4$  Hz), 127.1, 63.2, 59.8, 57.4 (d,  $J_{\text{PC}} = 24$  Hz), 33.0, 31.3, 26.9, 21.7, 19.6;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -17.4; IR (film): 3407, 3055, 2959, 1662, 1508, 1466, 1215, 1167, 744, 695  $\text{cm}^{-1}$ ; MS (ESI)  $m/z$ : 462.0 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{37}\text{NO}_2\text{P}$  ( $\text{M}+\text{H}$ ) $^+$ : 462.2551, found: 462.2555.

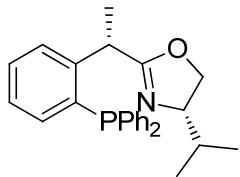


**12h**, colorless viscous oil, reaction scale: 4.0 mmol, yield: 43%, 0.8 g,  $[\alpha]_D^{25} = -71.6$  (1.07,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.56 (m, 1H), 7.30-7.54 (m, 9H), 7.24 – 7.16 (m, 2H), 7.13 (t,  $J = 8.0$  Hz, 1H), 6.92 (dd,  $J = 8.0, 4.0$  Hz, 1H), 6.43 (d,  $J = 4.0$  Hz, 1H), 3.98 (dd,  $J = 12.0, 8.0$  Hz, 1H), 3.86 (d,  $J = 12.0$  Hz, 1H), 3.75 (td,  $J = 8.0, 4.0$  Hz, 1H), 3.52 (t,  $J = 8.0$  Hz, 1H), 2.70 (s, 1H), 2.50-2.54 (m, 1H), 0.96 (d,  $J = 8.0$  Hz, 3H), 0.82 (s, 9H), 0.24 (d,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.0, 144.2 (d,  $J_{\text{PC}} = 24$  Hz), 135.7 (d,  $J_{\text{PC}} = 8$  Hz), 135.3 (d,  $J_{\text{PC}} = 8$  Hz), 135.1 (d,  $J_{\text{PC}} = 6$  Hz), 134.6 (d,  $J_{\text{PC}} = 20$  Hz), 133.7, 133.5 (d,  $J_{\text{PC}} = 11$  Hz), 129.7, 129.4, 128.7 (d,  $J_{\text{PC}} = 5$  Hz), 128.65 (d,  $J_{\text{PC}} = 3$  Hz), 128.6, 127.5 (d,  $J_{\text{PC}} = 5$  Hz), 127.0, 63.6, 60.1, 57.2 (d,  $J_{\text{PC}} = 23$  Hz), 33.5, 30.7, 26.8, 21.6, 19.4;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -16.4; IR (film): 3387, 3003, 2870, 1661, 1512, 1214, 743, 695  $\text{cm}^{-1}$ ; MS (ESI)  $m/z$ : 462.0 ( $\text{M}+\text{H}$ ) $^+$ ; HRMS (ESI) calcd for  $\text{C}_{29}\text{H}_{37}\text{NO}_2\text{P}$  ( $\text{M}+\text{H}$ ) $^+$ : 462.2556, found: 462.2553.

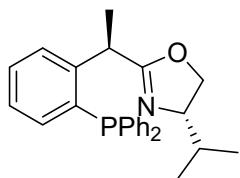


(*S,S*)-**L12**: R = Me, R' = *i*Pr; (*R,S*)-**L16**: R = Me, R' = *i*Pr;  
 (*S,S*)-**L13**: R = *i*Pr, R' = *i*Pr; (*R,S*)-**L17**: R = *i*Pr, R' = *i*Pr;  
 (*S,S*)-**L14**: R = *i*Pr, R' = Me; (*R,S*)-**L18**: R = *i*Pr, R' = Me;  
 (*S,S*)-**L15**: R = *i*Pr, R' = *t*Bu; (*R,S*)-**L19**: R = *i*Pr, R' = *t*Bu.

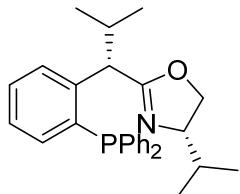
MsCl (32  $\mu$ L) was added dropwise into a solution of **12** (0.35 mmol), Et<sub>3</sub>N (0.24 ml), and DMAP (50 mg) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with H<sub>2</sub>O (10 mL). The resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL  $\times$  3). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to give **L12-19** as colorless oil.



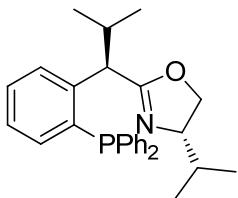
(*S,S*)-**L12**, colorless viscous oil, yield: 51%, 0.07 g,  $[\alpha]_D^{25} = -0.5$  (0.95, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (dd, *J* = 7.8 Hz, 4.6 Hz, 1H), 7.35-7.22 (m, 11H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.91 (dd, *J* = 7.8 Hz, 4.2 Hz, 1H), 4.69-4.62 (m, 1H), 4.02-3.96 (m, 1H), 3.89-3.84 (m, 2H), 1.75-1.70 (m, 1H), 1.36 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.1, 146.9 (d, *J*<sub>PC</sub> = 26 Hz), 136.7 (d, *J*<sub>PC</sub> = 9 Hz), 135.3 (d, *J*<sub>PC</sub> = 12 Hz), 134.1 (d, *J*<sub>PC</sub> = 20 Hz), 134.0, 133.8 (d, *J*<sub>PC</sub> = 20 Hz), 129.4, 128.8, 128.5 (d, *J*<sub>PC</sub> = 7 Hz), 128.4, 128.3 (d, *J*<sub>PC</sub> = 7 Hz), 128.2, 127.1, 127.0, 71.6, 69.6, 36.6 (d, *J*<sub>PC</sub> = 25 Hz), 32.3, 20.0, 18.8, 17.6; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -16.2; IR (film): 3053, 2958, 1662, 1434, 744, 696 cm<sup>-1</sup>; MS (EI) *m/z* (%): 401 (M<sup>+</sup>, 5.65), 386 (4.52), 358 (8.51), 330 (100), 324 (17.88), 315 (9.32), 288 (56.95), 256 (36.24); HRMS calcd for C<sub>26</sub>H<sub>28</sub>NOP M<sup>+</sup>: 401.1908, found 401.1907.



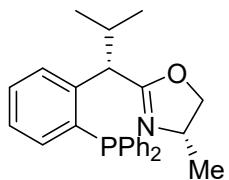
**(R,S)-L16**, colorless viscous oil, yield: 47%, 0.07 g,  $[\alpha]_D^{25} = -92.5$  (0.55,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (dd,  $J = 8.0$  Hz, 4.4 Hz, 1H), 7.35-7.25 (m, 11H), 7.14 (t,  $J = 7.4$  Hz, 1H), 6.91 (dd,  $J = 7.8$  Hz, 4.2 Hz, 1H), 4.70-4.62 (m, 1H), 4.06 (td,  $J = 6.8$  Hz, 1.6 Hz, 1H), 3.86-3.78 (m, 2H), 1.81-1.74 (m, 1H), 1.35 (d,  $J = 7.2$  Hz, 3H), 0.93 (d,  $J = 6.8$  Hz, 3H), 0.84 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.2, 146.9 (d,  $J_{\text{PC}} = 26$  Hz), 136.7 (d,  $J_{\text{PC}} = 10$  Hz), 136.6 (d,  $J_{\text{PC}} = 9$  Hz), 135.4 (d,  $J_{\text{PC}} = 11$  Hz), 134.2, 134.0, 133.9 (d,  $J_{\text{PC}} = 8$  Hz), 133.7, 129.4, 128.8, 128.5 (d,  $J_{\text{PC}} = 9$  Hz), 128.3 (d,  $J_{\text{PC}} = 6$  Hz), 127.0, 126.9, 71.6, 69.5, 36.6 (d,  $J_{\text{PC}} = 27$  Hz), 32.3, 19.9, 19.0, 17.7;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -16.2; IR (film): 3054, 2959, 1662, 1434, 743, 697  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 401 ( $M^+$ , 5.66), 386 (4.69), 358 (8.35), 330 (100), 324 (17.74), 315 (9.72), 288 (58.26), 256 (36.84); HRMS calcd for  $\text{C}_{26}\text{H}_{28}\text{NOP}$   $M^+$ : 401.1908, found 401.1911.



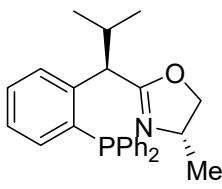
**(S,S)-L13**, colorless viscous oil, reaction scale: 1.5 mmol, 0.45 g, yield: 72%,  $[\alpha]_D^{25} = +16.4$  (0.7,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (dd,  $J = 7.5$ , 4.5 Hz, 1H), 7.37 – 7.19 (m, 11H), 7.12 (t,  $J = 7.4$  Hz, 1H), 7.00 (dd,  $J = 7.4$ , 3.3 Hz, 1H), 4.56 (t,  $J = 10.4$  Hz, 1H), 3.90 (d,  $J = 11.2$  Hz, 1H), 3.83 – 3.73 (m, 2H), 2.46 – 2.33 (m, 1H), 1.62 (dd,  $J = 12.6$ , 6.5 Hz, 1H), 1.09 (d,  $J = 6.8$  Hz, 3H), 0.80 (d,  $J = 6.8$  Hz, 3H), 0.76 (d,  $J = 6.7$  Hz, 3H), 0.64 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 145.5 (d,  $J_{\text{PC}} = 27$  Hz), 137.2 (d,  $J_{\text{PC}} = 11$  Hz), 137.1 (d,  $J_{\text{PC}} = 11$  Hz), 136.6 (d,  $J_{\text{PC}} = 11$  Hz), 134.5, 133.8 (d,  $J_{\text{PC}} = 20$  Hz), 133.5 (d,  $J_{\text{PC}} = 20$  Hz), 129.2, 128.4, 128.3 (d,  $J_{\text{PC}} = 6$  Hz), 128.2 (d,  $J_{\text{PC}} = 2$  Hz), 128.1, 127.8 (d,  $J_{\text{PC}} = 5$  Hz), 126.8, 71.6, 69.1, 49.2 (d,  $J_{\text{PC}} = 26$  Hz), 32.5, 32.4, 21.4, 20.5, 18.7, 17.9;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -18.3; IR (film): 3054, 2961, 1658, 1468, 990, 743, 695  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 429 ( $M^+$ , 4.76), 414 (13.59), 386 (79.41), 359 (56.49), 358 (21.97), 344 (100), 316 (19.87), 301 (23.12), 284 (35.36); HRMS calcd for  $\text{C}_{28}\text{H}_{32}\text{NOP}$  ( $M^+$ ): 429.2222, found 429.2223.



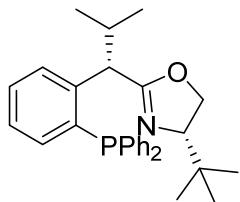
**(R,S)-L17**, colorless viscous oil, reaction scale: 3.4 mmol, 0.83 g, yield: 57%,  $[\alpha]_D^{25} = -83.4$  (0.45,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68–7.65 (m, 1H), 7.34–7.19 (m, 11H), 7.14–7.10 (m, 1H), 7.01–6.98 (m, 1H), 4.53 (t,  $J = 6.0$  Hz, 1H), 3.98 (dd,  $J = 9.2$  Hz, 8.4 Hz, 1H), 3.75 (dt,  $J = 8.0$  Hz, 6.0 Hz, 1H), 3.65 (t,  $J = 8.0$  Hz, 1H), 2.44–2.38 (m, 1H), 1.76–1.67 (m, 1H), 1.07 (d,  $J = 6.8$  Hz, 3H), 0.83 (d,  $J = 6.8$  Hz, 3H), 0.73 (d,  $J = 6.8$  Hz, 3H), 0.64 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.8, 145.4 (d,  $J_{\text{PC}} = 26$  Hz), 137.2 (d,  $J_{\text{PC}} = 10$  Hz), 137.1 (d,  $J_{\text{PC}} = 11$  Hz), 136.7 (d,  $J_{\text{PC}} = 12$  Hz), 134.4 (d,  $J_{\text{PC}} = 1$  Hz), 133.9 (d,  $J_{\text{PC}} = 20$  Hz), 133.5 (d,  $J_{\text{PC}} = 18$  Hz), 129.1, 128.4, 128.3 (d,  $J_{\text{PC}} = 7$  Hz), 128.1, 128.08, 128.04 (d,  $J_{\text{PC}} = 2$  Hz), 126.8, 71.6, 68.9, 49.0 (d,  $J_{\text{PC}} = 26$  Hz), 32.4, 32.0, 21.4, 20.4, 18.9, 17.5;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -18.2; IR (film): 3054, 2958, 1660, 1467, 1434, 991, 743, 695  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 429 ( $M^+$ , 4.86), 430 (2.05), 386 (69.20), 359 (54.78), 344 (100), 316 (21.08), 301 (26.26), 284 (34.35); HRMS calcd for  $\text{C}_{28}\text{H}_{32}\text{NOP}$   $M^+$ : 429.2222, found 429.2219.



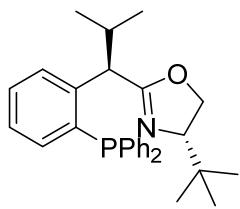
**(S,S)-L14**, colorless viscous oil, reaction scale: 1.3 mmol, 0.32 g, yield: 62%,  $[\alpha]_D^{25} = +2.8$  (1.4,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 7.6, 4.4$  Hz, 1H), 7.39 – 7.20 (m, 11H), 7.12 (t,  $J = 7.3$  Hz, 1H), 6.98 (dd,  $J = 7.2, 3.4$  Hz, 1H), 4.49 (t,  $J = 10.3$  Hz, 1H), 4.00 (dt,  $J = 9.2, 6.7$  Hz, 1H), 3.94 – 3.85 (m, 1H), 3.56 (t,  $J = 7.5$  Hz, 1H), 2.47 – 2.34 (m, 1H), 1.09 (t,  $J = 6.7$  Hz, 6H), 0.67 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 145.1 (d,  $J_{\text{PC}} = 26$  Hz), 137.0 (d,  $J_{\text{PC}} = 11$  Hz), 136.9 (d,  $J_{\text{PC}} = 10$  Hz), 136.6 (d,  $J_{\text{PC}} = 11$  Hz), 134.3, 133.8 (d,  $J_{\text{PC}} = 20$  Hz), 133.5 (d,  $J_{\text{PC}} = 19$  Hz), 133.4, 129.3, 128.4, 128.3 (d,  $J_{\text{PC}} = 6$  Hz), 128.13 (d,  $J_{\text{PC}} = 1$  Hz), 128.10, 127.8 (d,  $J_{\text{PC}} = 5$  Hz), 126.8, 73.0, 61.1, 48.8 (d,  $J_{\text{PC}} = 26$  Hz), 32.6, 21.3, 21.2, 20.5;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -18.2; IR (film): 3054, 2961, 1658, 1468, 1434, 990, 743, 695  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 401 ( $M^+$ , 5.41), 386 (4.57), 358 (98.53), 344 (100), 316 (14.26), 301 (16.70), 345 (26.20), 284 (25.64); HRMS calcd for  $\text{C}_{26}\text{H}_{28}\text{NOP}$   $M^+$ : 401.1909, found 401.1904.



**(R,S)-L18**, colorless viscous oil, reaction scale: 1.1 mmol, 0.25 g, yield: 55%,  $[\alpha]_D^{25} = -8.5$  (0.65, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.60 (dd, *J* = 7.8, 4.6 Hz, 1H), 7.37 – 7.18 (m, 11H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.00 (dd, *J* = 7.4, 3.2 Hz, 1H), 4.51 (t, *J* = 10.2 Hz, 1H), 4.16 – 4.07 (m, 1H), 3.99 (dd, *J* = 11.3, 4.4 Hz, 1H), 3.49 (t, *J* = 7.6 Hz, 1H), 2.46 – 2.31 (m, 1H), 1.14 (d, *J* = 6.5 Hz, 3H), 1.07 (d, *J* = 6.5 Hz, 3H), 0.60 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.6, 145.2 (d, *J*<sub>PC</sub> = 27 Hz), 137.3 (d, *J*<sub>PC</sub> = 11 Hz), 137.0 (d, *J*<sub>PC</sub> = 11 Hz), 136.9 (d, *J*<sub>PC</sub> = 12 Hz), 134.5, 134.0 (d, *J*<sub>PC</sub> = 20 Hz), 133.5 (d, *J*<sub>PC</sub> = 19 Hz), 129.3, 128.5, 128.4 (d, *J*<sub>PC</sub> = 6 Hz), 128.2, 128.1 (d, *J*<sub>PC</sub> = 2 Hz), 127.8 (d, *J*<sub>PC</sub> = 5 Hz), 126.8, 73.3, 61.2, 48.9 (d, *J*<sub>PC</sub> = 26 Hz), 32.3, 21.4, 20.5; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  -18.4; IR (film): 3054, 2961, 1658, 1467, 1434, 988, 743, 696 cm<sup>-1</sup>; MS (EI) *m/z* (%): 401 (M<sup>+</sup>, 4.91), 386 (5.12), 358 (91.30), 344 (100), 316 (15.51), 301 (16.63), 345 (25.91), 284 (29.15); HRMS calcd for C<sub>26</sub>H<sub>28</sub>NOP M<sup>+</sup>: 401.1909, found 401.1916.



**(S,S)-L15**, colorless viscous oil, reaction scale: 0.93 mmol, 0.2 g, yield: 48%,  $[\alpha]_D^{25} = 25.1$  (1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.36 – 7.22 (m, 11H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.60 (t, *J* = 12.0 Hz, 1H), 3.97 – 3.89 (m, 2H), 3.74 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.44 – 2.29 (m, 1H), 1.09 (d, *J* = 8.0 Hz, 3H), 0.73 (s, 9H), 0.64 (d, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.5, 145.8 (d, *J*<sub>PC</sub> = 26 Hz), 137.4 (d, *J*<sub>PC</sub> = 11 Hz), 137.2 (d, *J*<sub>PC</sub> = 11 Hz), 136.6 (d, *J*<sub>PC</sub> = 12 Hz), 134.7, 133.9, 133.7 (d, *J*<sub>PC</sub> = 1 Hz), 133.5, 129.2, 128.4, 128.3, 128.2 (d, *J*<sub>PC</sub> = 2 Hz), 127.8 (d, *J*<sub>PC</sub> = 5 Hz), 126.8, 75.3, 68.0, 49.3 (d, *J*<sub>PC</sub> = 26 Hz), 33.9, 32.5, 25.7, 21.4, 20.5; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -18.4; IR (film): 3054, 2957, 1660, 1466, 1433, 980, 743, 694 cm<sup>-1</sup>; MS (ESI) *m/z*: 461.0 (M+NH<sub>4</sub>)<sup>+</sup>; HRMS (ESI) calcd for C<sub>29</sub>H<sub>35</sub>NOP (M+H)<sup>+</sup>: 444.2451, found 444.2458.



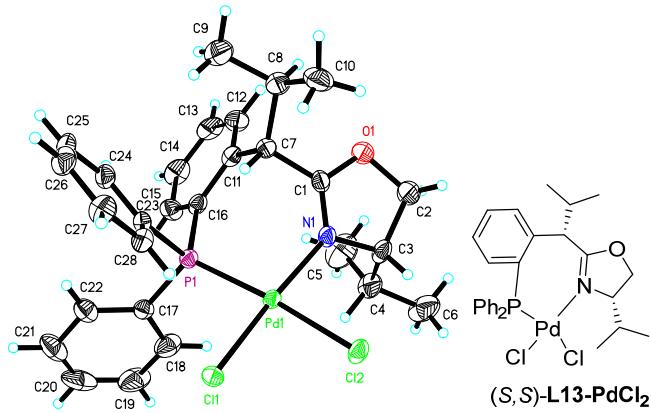
**(R,S)-L19**, colorless viscous oil, reaction scale: 1.7 mmol, 0.36 g, yield: 48%,  $[\alpha]_D^{25} = -44.8$  (0.94, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.71 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.37 – 7.24 (m, 9H), 7.23 – 7.18 (m, 2H), 7.11 (td, *J* = 8.0, 4.0 Hz, 1H), 6.98 (ddd, *J* = 8.0, 4.0, 1.2 Hz, 1H), 4.51 (t, *J* = 12.0 Hz, 1H), 3.93 (dd, *J* = 12.0, 8.0 Hz, 1H), 3.71 (t, *J* = 8.0 Hz, 1H), 3.62 (dd, *J* = 12.0, 8.0 Hz, 1H), 2.49 – 2.34 (m, 1H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.75 (s, 9H), 0.68 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.9, 145.5 (d, *J*<sub>PC</sub> = 27 Hz), 137.3 (d, *J*<sub>PC</sub> = 11 Hz), 137.2 (d, *J*<sub>PC</sub> = 10 Hz), 136.6 (d, *J*<sub>PC</sub> = 12 Hz), 134.3, 134.0, 133.7 (d, *J*<sub>PC</sub> = 11 Hz), 133.5, 129.1, 128.4 (d, *J*<sub>PC</sub> = 3 Hz), 128.3, 128.1, 128.0, 126.7, 75.5, 67.8, 49.0 (d, *J*<sub>PC</sub> = 26 Hz), 33.7, 32.7, 25.9, 21.4, 20.5; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  -18.1; IR (film): 3054, 2956, 1661, 1466, 1433, 988, 743, 694 cm<sup>-1</sup>; MS (ESI) *m/z*: 461.0(M+NH<sub>4</sub>)<sup>+</sup>; HRMS (ESI) calcd for C<sub>29</sub>H<sub>35</sub>NOP (M+H)<sup>+</sup>: 444.2451, found 444.2449.

## 8. Single-crystal X-ray diffraction data of (S,S)-L13-PdCl<sub>2</sub> and (R,S)-L17-PdCl<sub>2</sub>

Single crystal preparation:

To a flame dried sealing tube was added PdCl<sub>2</sub> (18 mg, 0.1 mmol), (S,S)-L13 or (R,S)-L17 (43 mg, 0.1 mmol), freshly distilled anhydrous THF (2.0 mL). The resulting mixture was stirred overnight at room temperature. The solution was filtered. After removal of solvent under reduced pressure, the resulting yellow solid was dissolve in chloroform/*n*-hexane. The slow evaporation at 0 °C resulted in the formation of single crystal suitable for X-ray analysis.

Data of (S,S)-L13-PdCl<sub>2</sub> and (R,S)-L17-PdCl<sub>2</sub> were obtained at 193 K on a Bruker D8 Venture diffractometer with graphite-monochromated Mo K $\alpha$  radiation.

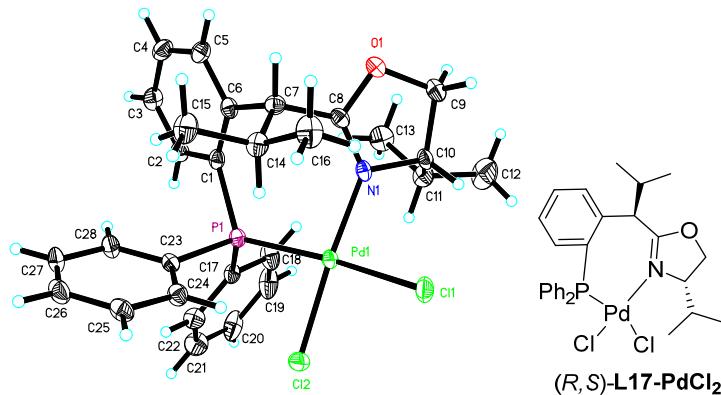


**Figure S2.** Molecular structure of complex  $(S,S)$ -L13- $\text{PdCl}_2$  with thermal ellipsoids at 50% probability.

Crystal data and structure refinement for mo\_d8v19810\_0m.

Identification code	mo_d8v19810_0m	
Empirical formula	C <sub>29</sub> H <sub>33</sub> Cl <sub>5</sub> N O P Pd	
Formula weight	726.18	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 15.9680(10) Å	= 90°.
	b = 10.9454(7) Å	=
	c = 23.6451(16) Å	= 90°.
Volume	3907.4(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.234 Mg/m <sup>3</sup>	
Absorption coefficient	0.877 mm <sup>-1</sup>	
F(000)	1472	
Crystal size	0.190 x 0.130 x 0.100 mm <sup>3</sup>	
Theta range for data collection	1.822 to 25.499°.	
Index ranges	-18<=h<=19, -13<=k<=13, -28<=l<=28	
Reflections collected	45243	
Independent reflections	14495 [R(int) = 0.0422]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5711	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	14495 / 1 / 694	

Goodness-of-fit on F <sup>2</sup>	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1000
R indices (all data)	R1 = 0.0473, wR2 = 0.1051
Absolute structure parameter	0.014(14)
Extinction coefficient	0.0023(3)
Largest diff. peak and hole	0.772 and -0.389 e. $\text{\AA}^{-3}$



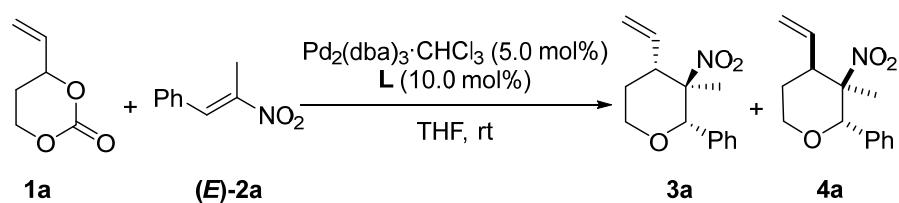
**Figure S3.** Molecular structure of complex  $(R,S)\text{-L17-PdCl}_2$  with thermal ellipsoids at 50% probability.

Crystal data and structure refinement for mo\_d8v19540\_0m.

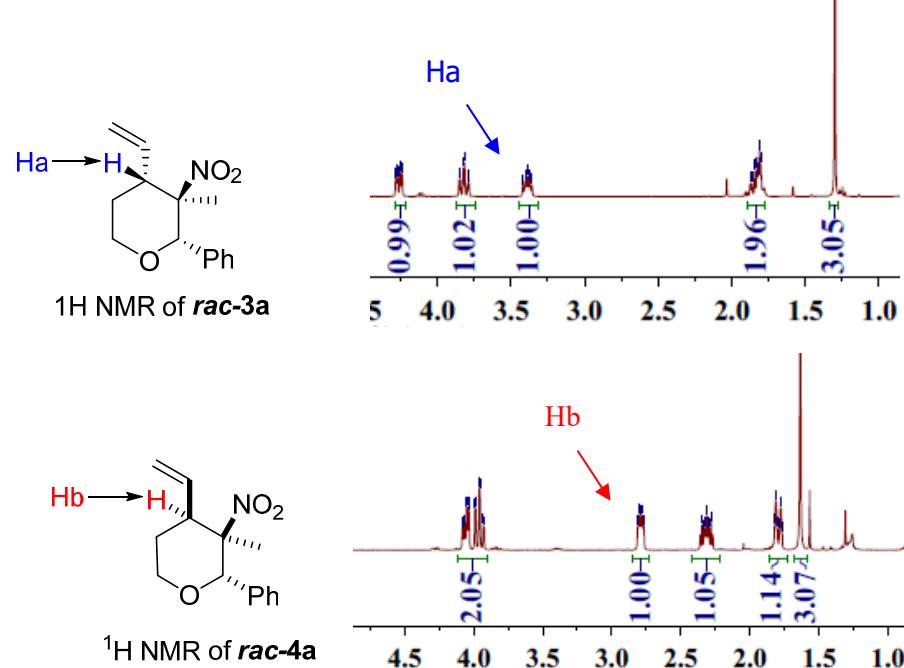
Identification code	mo_d8v19540_0m
Empirical formula	C <sub>28</sub> H <sub>33</sub> Cl <sub>2</sub> N O <sub>1.50</sub> P Pd
Formula weight	615.82
Temperature	193(2) K
Wavelength	0.71073 $\text{\AA}$
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	$a = 10.1792(14) \text{ \AA}$ $= 90^\circ$ . $b = 14.3643(18) \text{ \AA}$ $= 90^\circ$ . $c = 19.208(2) \text{ \AA}$ $= 90^\circ$ .
Volume	2808.5(6) $\text{\AA}^3$
Z	4
Density (calculated)	1.456 Mg/m <sup>3</sup>
Absorption coefficient	0.931 mm <sup>-1</sup>
F(000)	1260
Crystal size	0.160 x 0.140 x 0.100 mm <sup>3</sup>
Theta range for data collection	2.672 to 25.999°.
Index ranges	-12 <= h <= 12, -17 <= k <= 17, -23 <= l <= 22

Reflections collected	21548
Independent reflections	5520 [ $R(\text{int}) = 0.0505$ ]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.4711
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	5520 / 6 / 324
Goodness-of-fit on $F^2$	1.081
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0311$ , $wR_2 = 0.0718$
R indices (all data)	$R_1 = 0.0364$ , $wR_2 = 0.0758$
Absolute structure parameter	0.022(14)
Extinction coefficient	0.0040(6)
Largest diff. peak and hole	0.488 and -0.661 e. $\text{\AA}^{-3}$

**9. The diastereomers and enantiomers analysis of products of Pd-catalyzed [4+2]-cycloaddition of 4-vinyl-1,3-dioxan-2-one 1a and nitroalkene 2a with chiral benzylic substituted  $P,N$ -ligands**

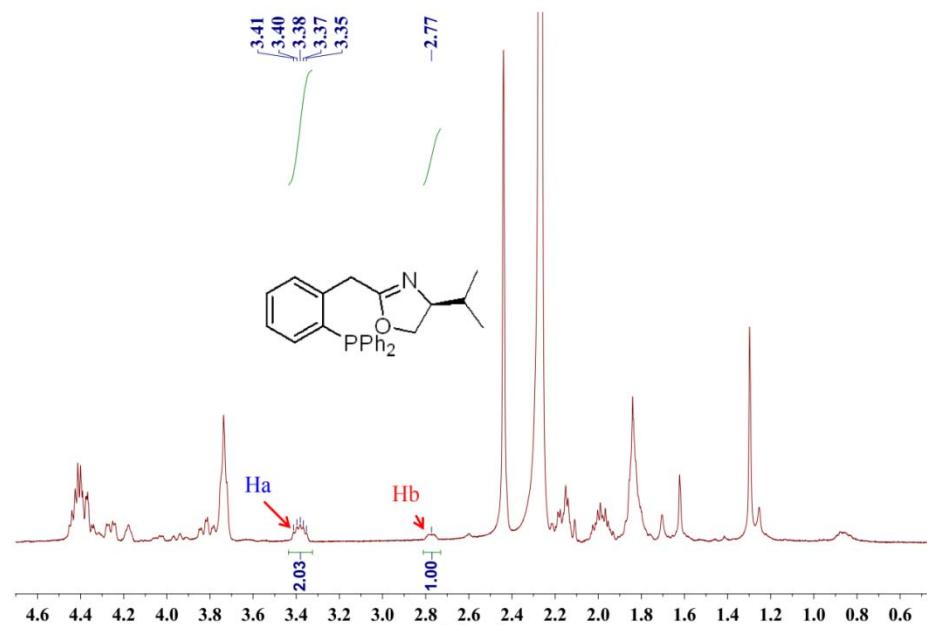


**a) diastereomers analysis**

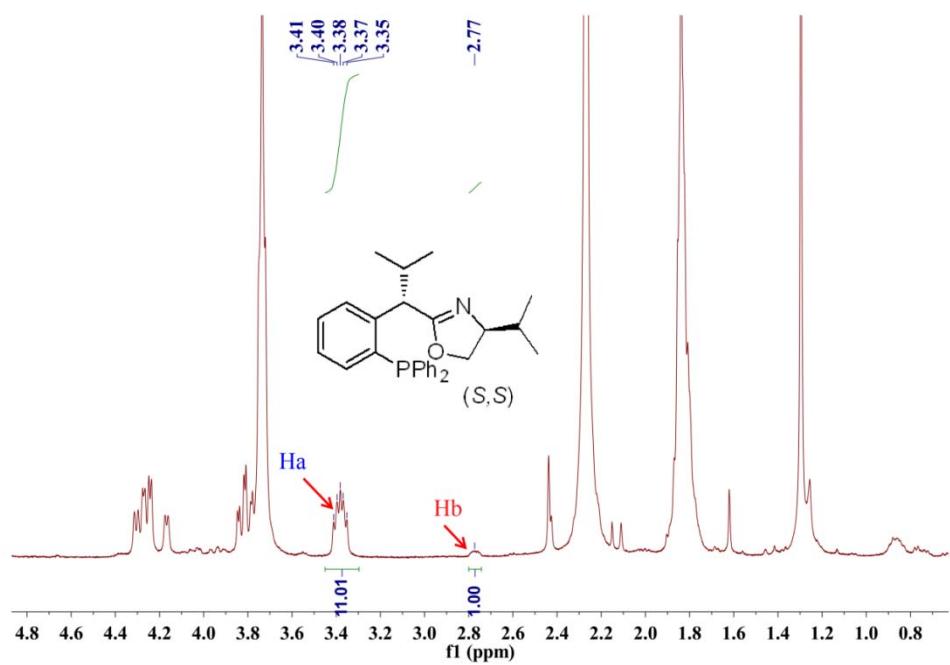


The  $^1\text{H}$  NMR spectra of crude product indicated diastereomer **3a** are the main isomer of the reaction with different chiral benzylic substituted  $P,N$ -ligands as shown below.

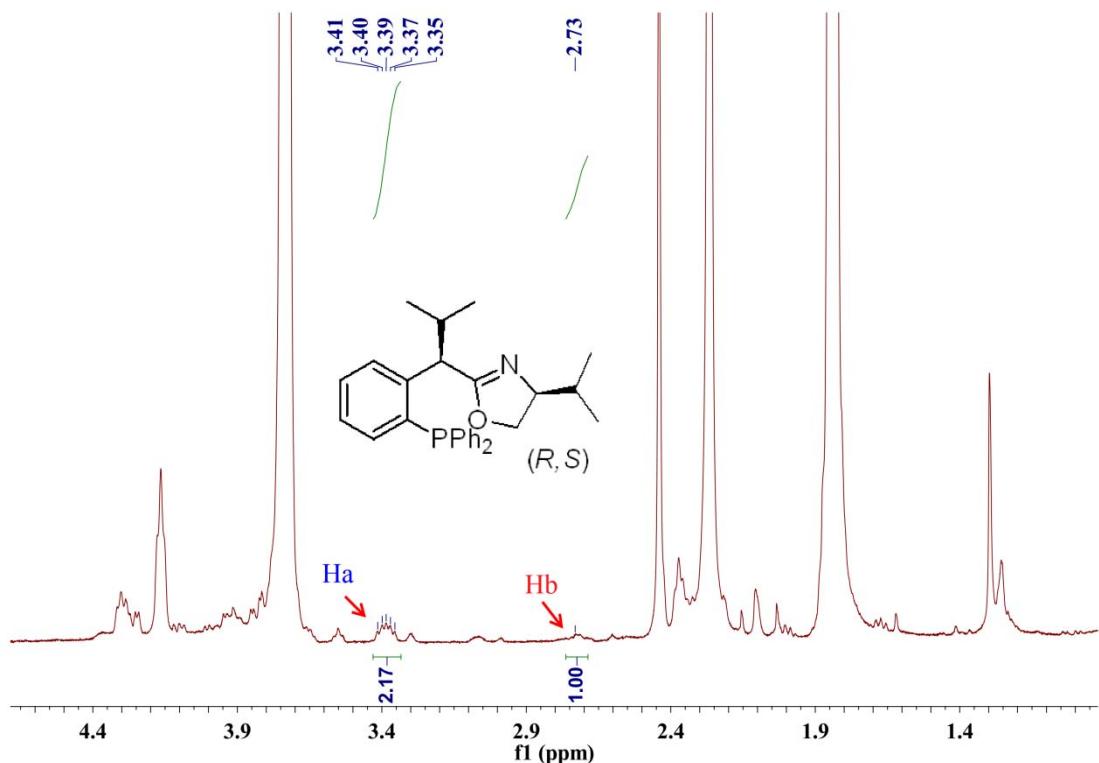
**L10**



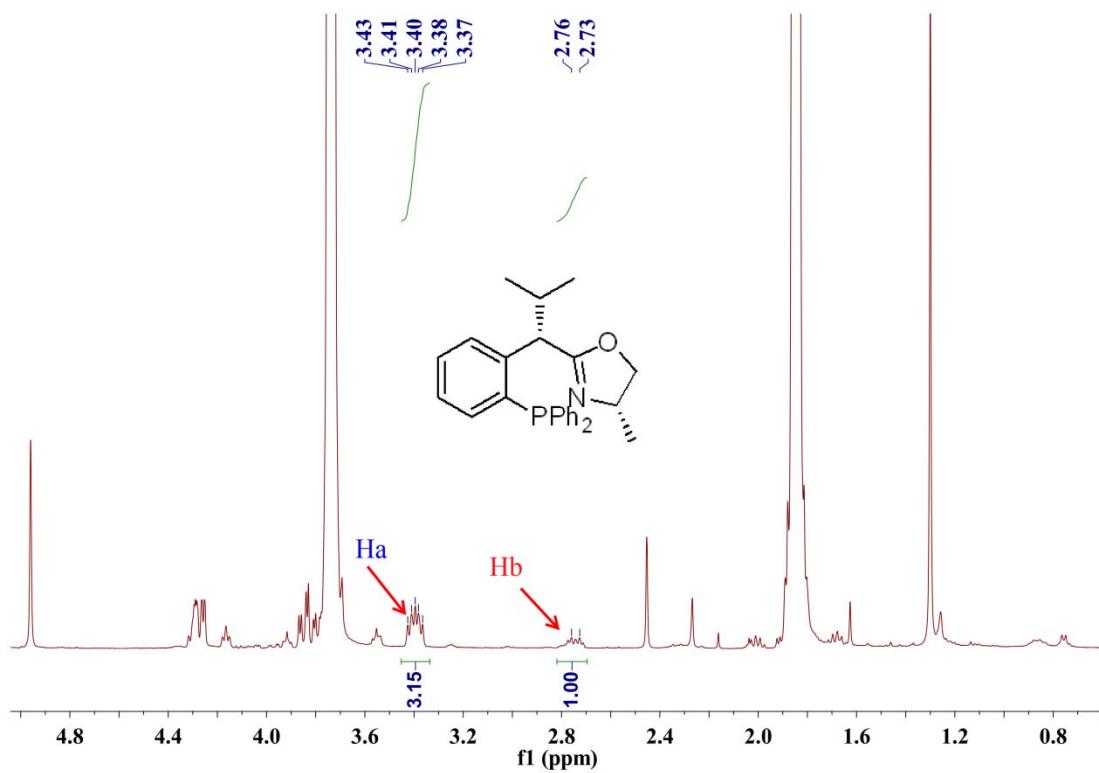
**(S,S)-L13**



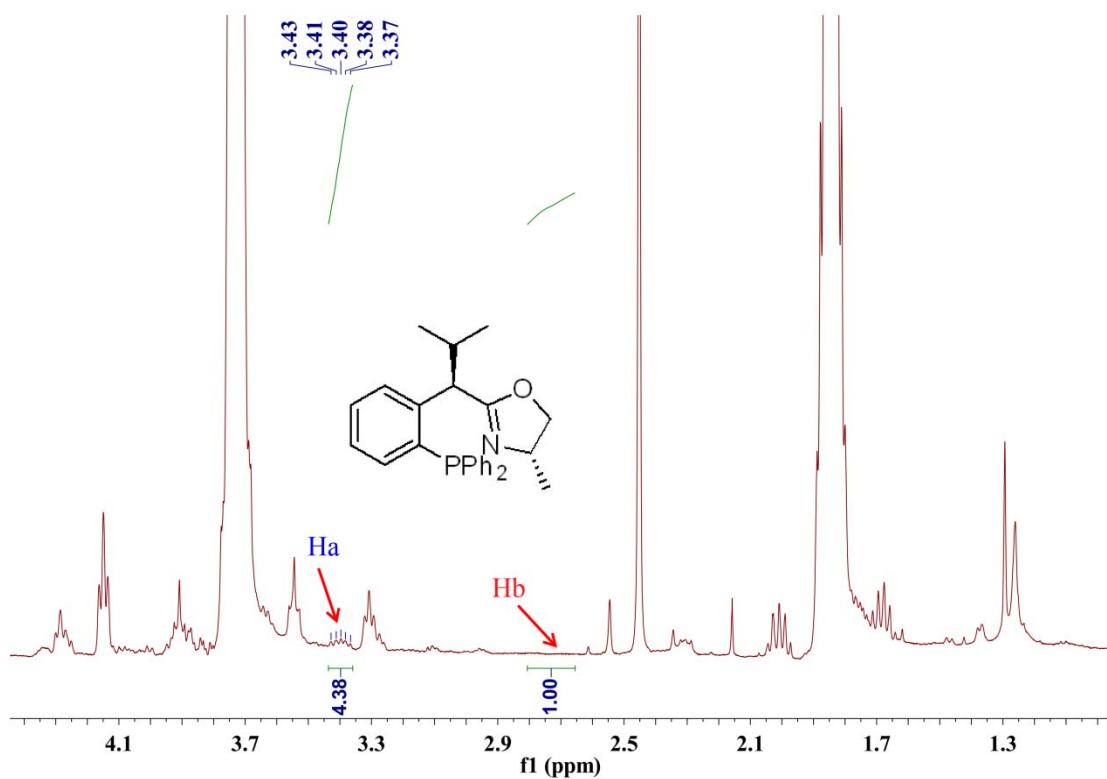
(*R,S*)-L17



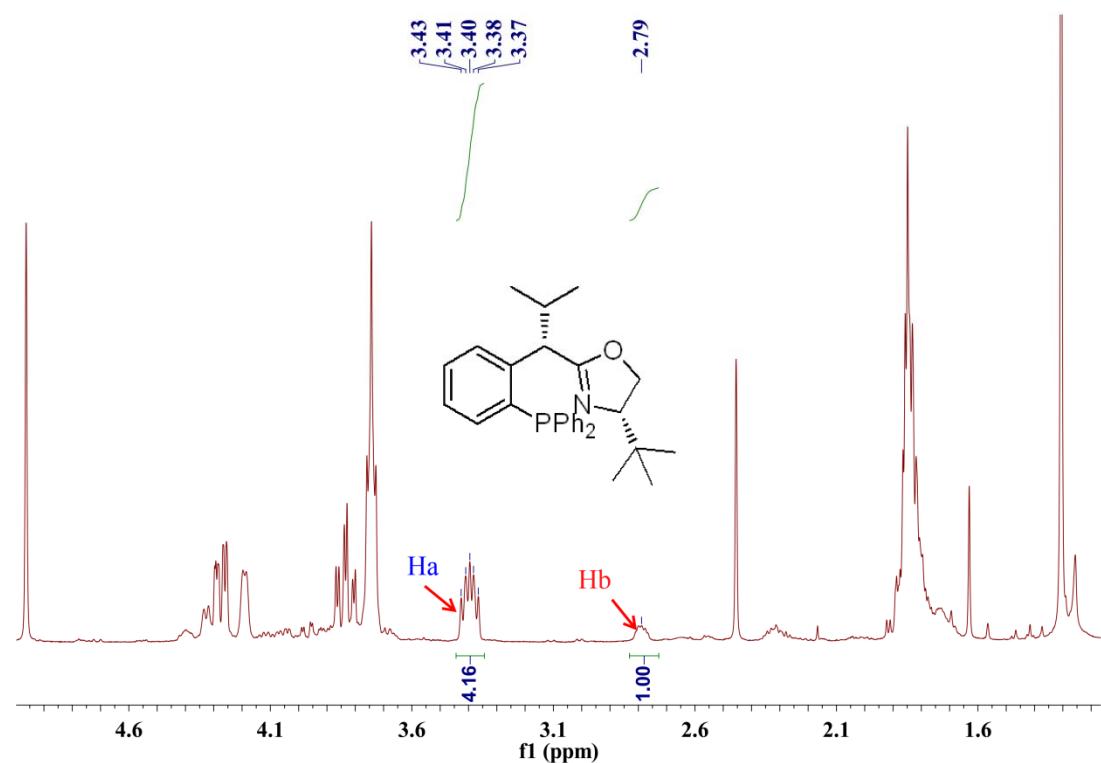
(*S,S*)-L14



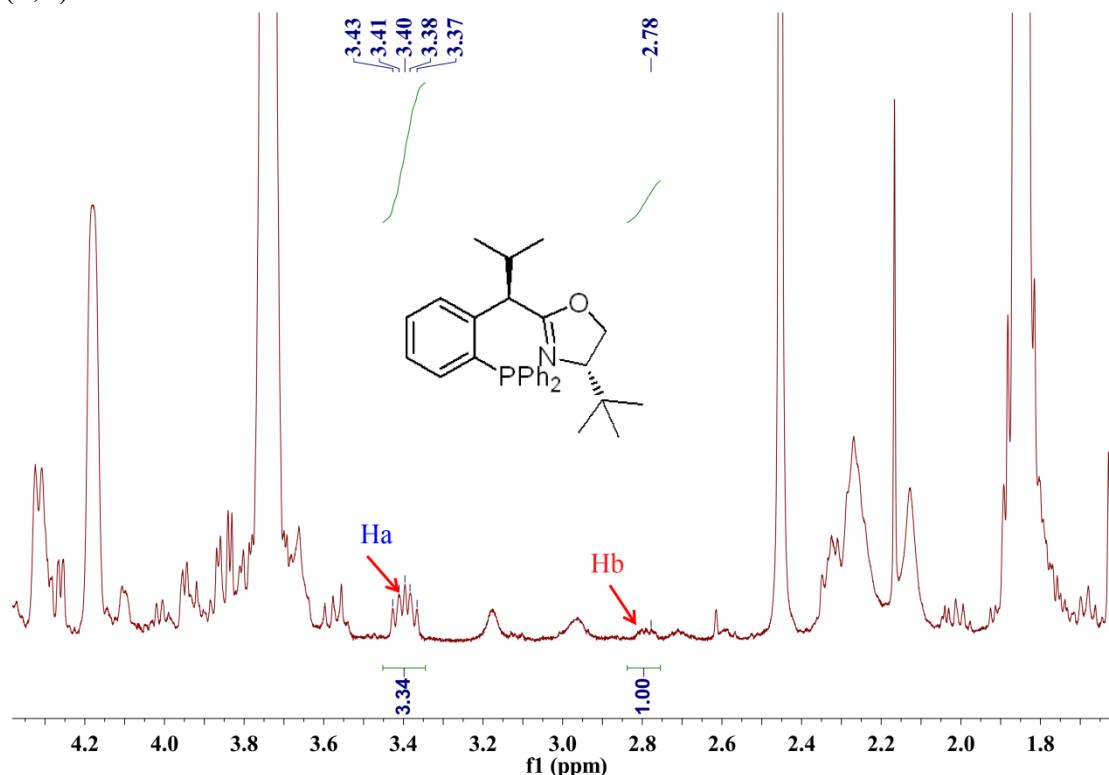
(*R,S*)-L18



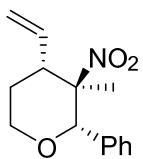
(*S,S*)-L15



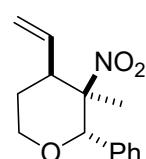
**(R,S)-L19**



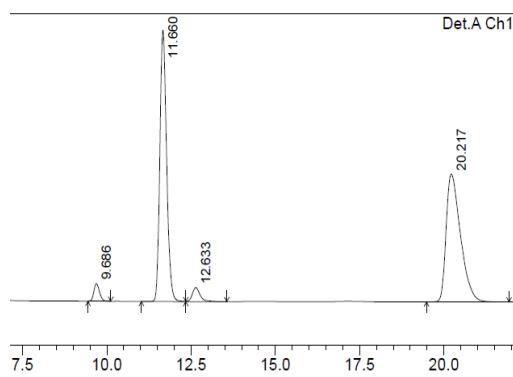
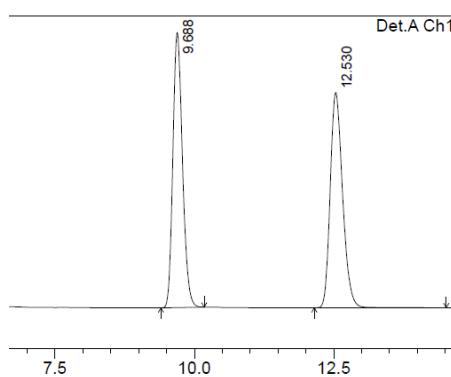
**b) enantiomers analysis**



HPLC spectrum  
of *rac*-3a

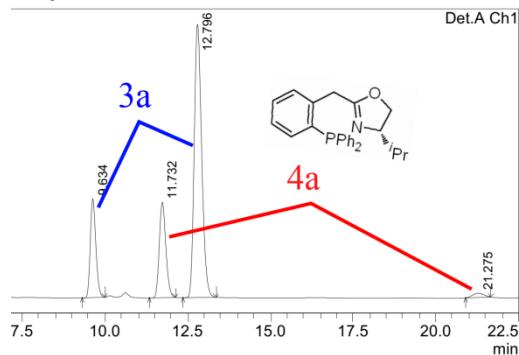


HPLC spectrum of *rac*-4a  
containing small amount of *rac*-3a



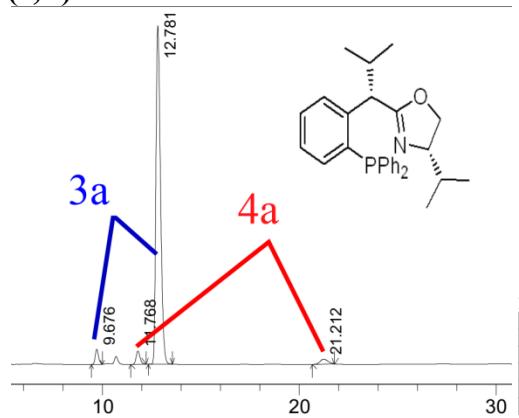
The above two HPLC spectra indicated two peaks at 9.68 and 12.53 min correspond to *rac*-3a, while two peaks at 11.66 and 20.21 min correspond to *rac*-4a.

HPLC spectrum of products **3a** and **4a** of the reaction with different chiral benzylic substituted *P,N*-ligands as shown below

**L10**

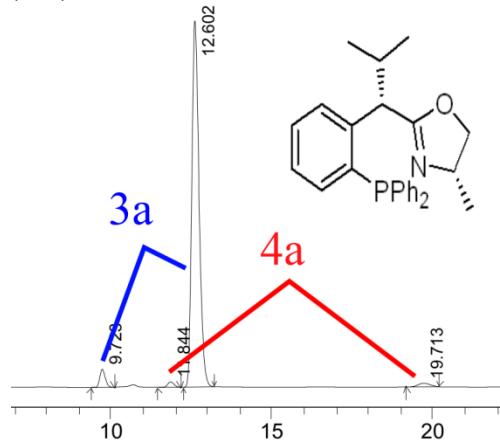
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.634	1300457	112257	16.704	20.951
2	11.732	1499184	108384	19.256	20.228
3	12.796	4870779	310380	62.563	57.926
4	21.275	114948	4796	1.476	0.895
Total		7785368	535818	100.000	100.000

**(S,S)-L13**

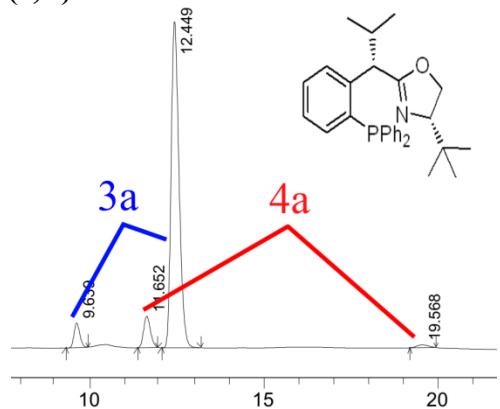
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.676	465904	38681	3.068	4.112
2	11.768	456856	33242	3.008	3.533
3	12.781	13918350	856397	91.638	91.032
4	21.212	347241	12447	2.286	1.323
Total		15188350	940767	100.000	100.000

**(S,S)-L14**

Detector A Ch1 214nm

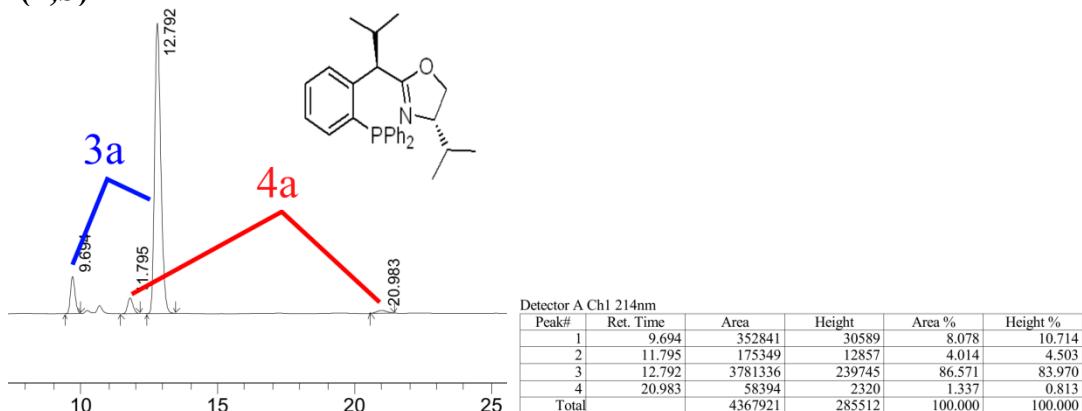
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.723	237526	20458	3.453	4.614
2	11.844	83508	6196	1.214	1.398
3	12.602	6448163	412579	93.743	93.058
4	19.713	109343	4124	1.590	0.930
Total		6878541	443357	100.000	100.000

**(S,S)-L15**

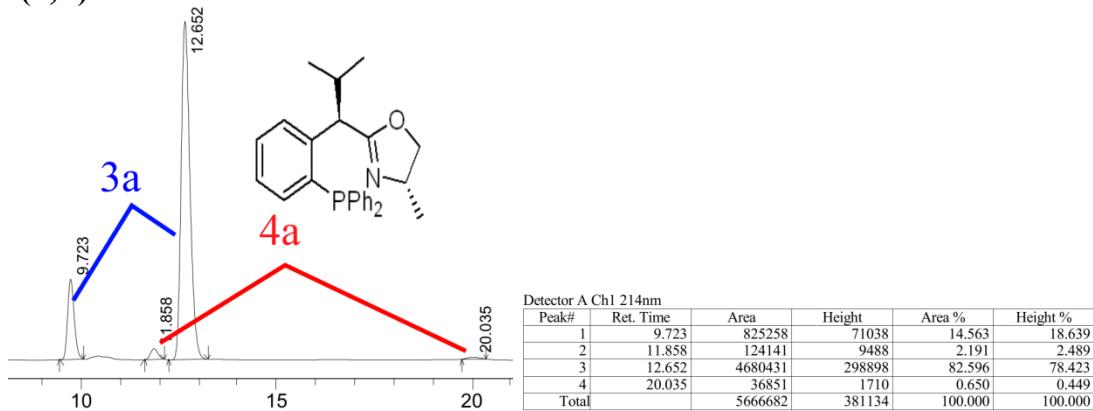
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.639	642299	55862	4.791	6.395
2	11.652	977477	71385	7.292	8.172
3	12.449	11636780	739953	86.809	84.705
4	19.568	148525	6370	1.108	0.729
Total		13405080	873569	100.000	100.000

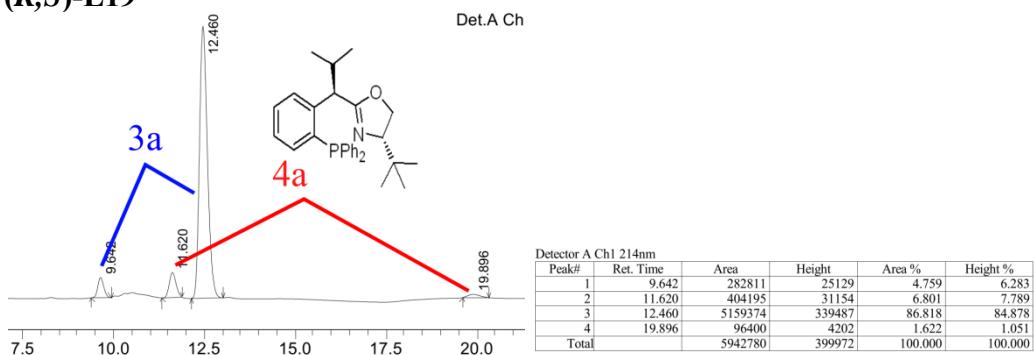
**(R,S)-L17**



**(R,S)-L18**



**(R,S)-L19**

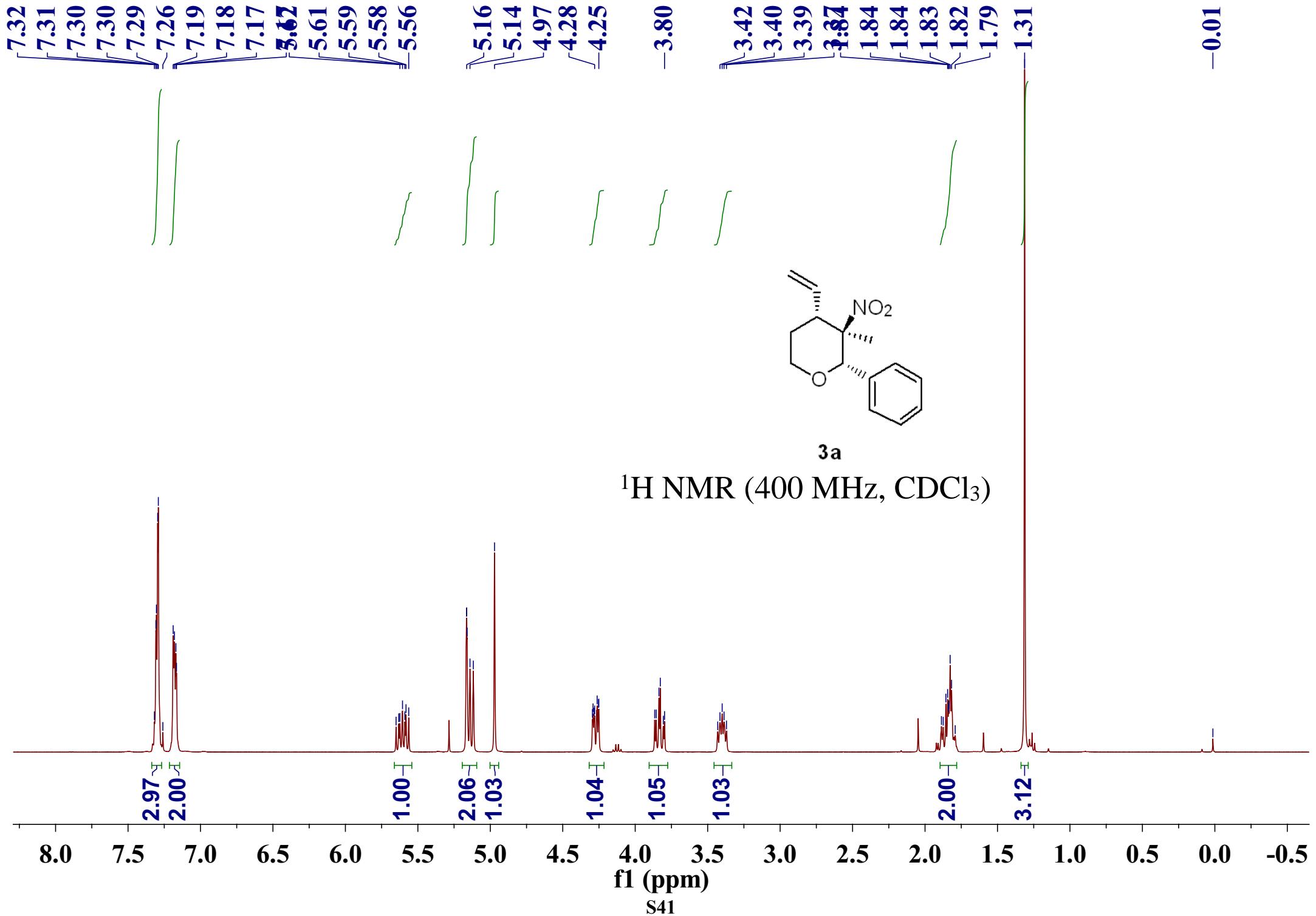


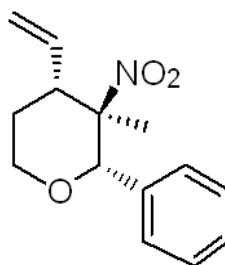
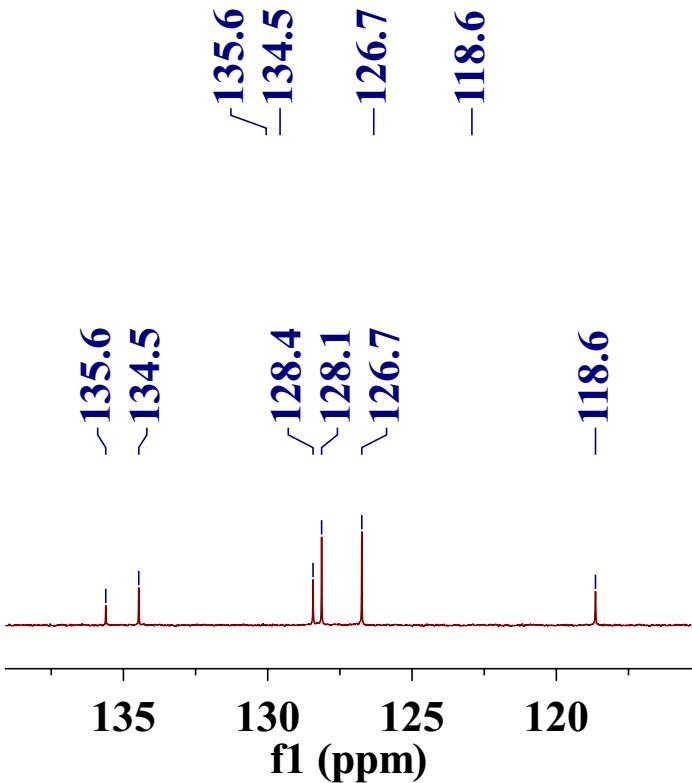
The above HPLC spectra of **3a** (major diastereomer) and **4a** (minor diastereomer) show that main peak is at ca. 12.6 min for the major diastereoisomer **3a**. It indicates that major enantiomer of **3a** obtained with these chiral benzylic substituted *P,N*-ligands is the same, that is, the product **3a** obtained by chiral benzylic substituted (*S,S*)- or (*R,S*)-*P,N*-ligands has the same absolute configuration.

## 10. References

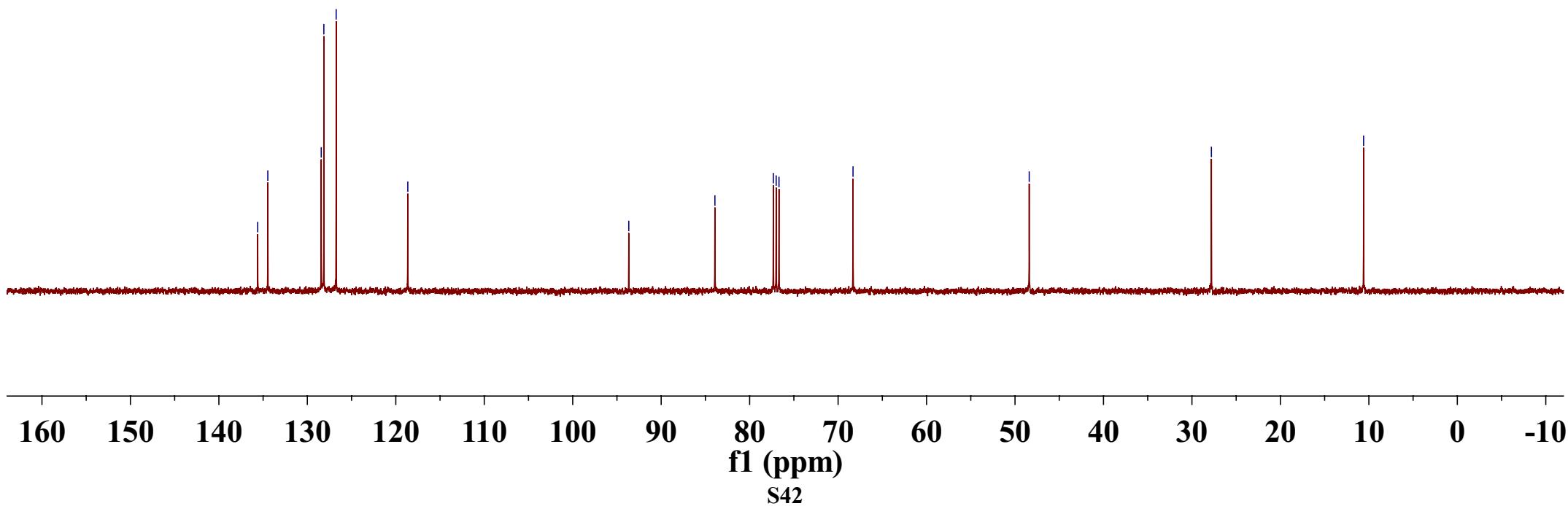
- (1) (a) Black, P. J.; Cami-Kobeci, G.; Edwards, M. G.; Slatford, P. A.; Whittlesey, M. K.; Williams, J. M. *Org. Biomol. Chem.* **2006**, *4*, 116–125. (b) Dharuman, S.;

- Gupta, P.; Kancharla, P. K.; Vankar, Y. D.; *J. Org. Chem.* **2013**, *78*, 8442–8450. (c)  
Anderson, J. C.; Blake, A. J.; Mills, M.; Ratcliffe, P. D. *Org. Lett.* **2008**, *10*,  
4141–4143. (d) Andrey, O.; Vidonne, A.; Alexakis, A. *Tetrahedron Lett.* **2003**, *44*,  
7901–7904. (e) Clark, A. H.; McCorvy, J. D.; Watts, V. J.; Nichols, D. E. *Bioorg.  
Med. Chem.* **2011**, *19*, 5420–5431.
- (2) Bando, T.; Tanaka, S.; Fugami, K.; Yoshida, Z.-I.; Tamaru, Y. *Bull. Chem. Soc.  
Jpn.* **1992**, *65*, 97–110.
- (3) Wu, W.-Q.; Peng, Q.; Dong, D.-X.; Hou, X.-L.; Wu, Y.-D. *J. Am. Chem. Soc.*  
**2008**, *130*, 9717–9725.
- (4) Tummatorn, J.; Dudley, G. B. *Org. Lett.* **2011**, *13*, 1572–1575.



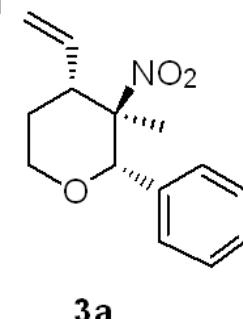


**3a**

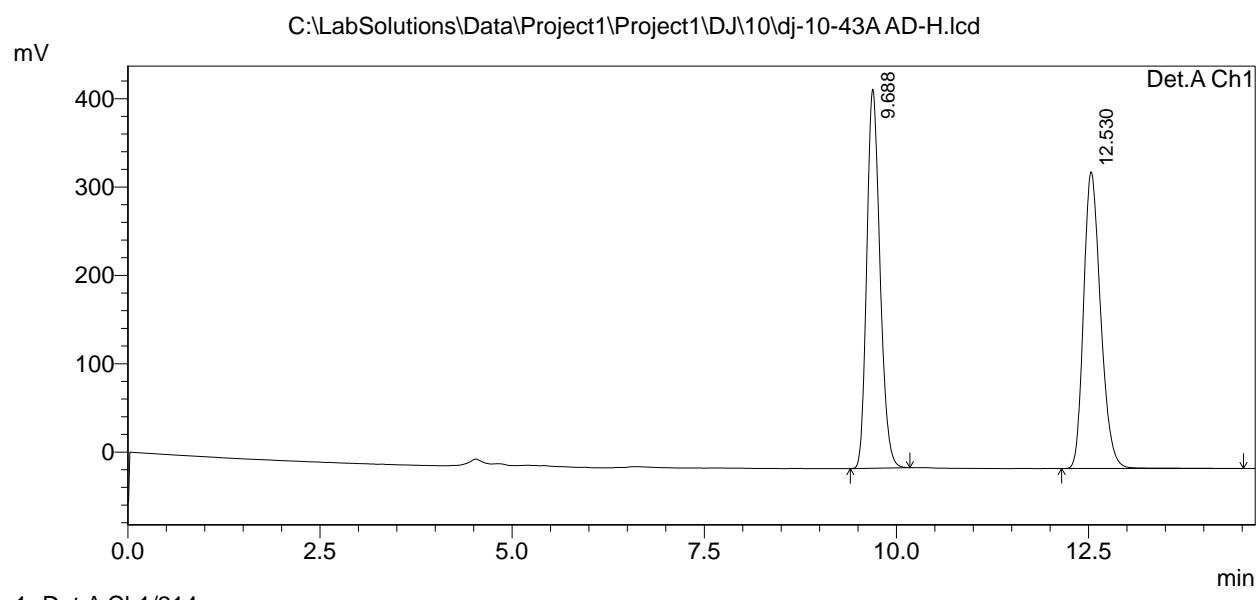


# ==== Shimadzu LCsolution Analysis Report ====

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 Vail # :  
 Injection Volume : 2 uL  
 Data File Name : dj-10-43A AD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2017-11-23 15:28:49  
 Data Processed : 2017-11-23 15:43:30



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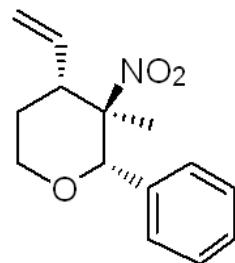
PeakTable

Detector A Ch1 214nm

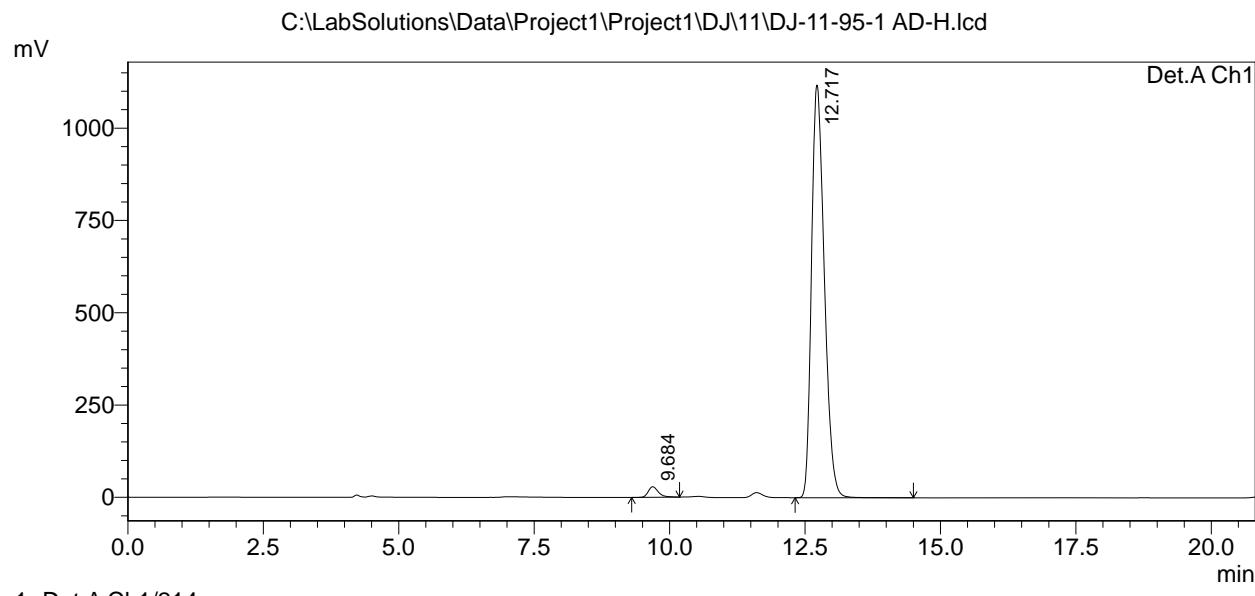
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.688	5133923	429134	49.748	56.096
2	12.530	5185891	335862	50.252	43.904
Total		10319814	764996	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

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 Sample Name : DJ-11-95-1 AD-H  
 Sample ID : AD-H,99/1,0.7,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-95-1 AD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-5-21 16:16:47  
 Data Processed : 2018-5-21 16:37:37

**3a**

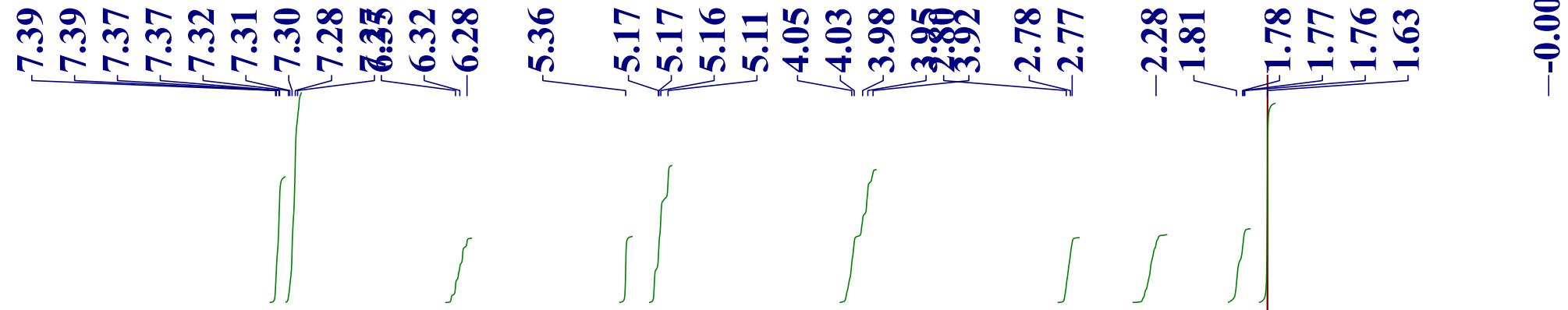
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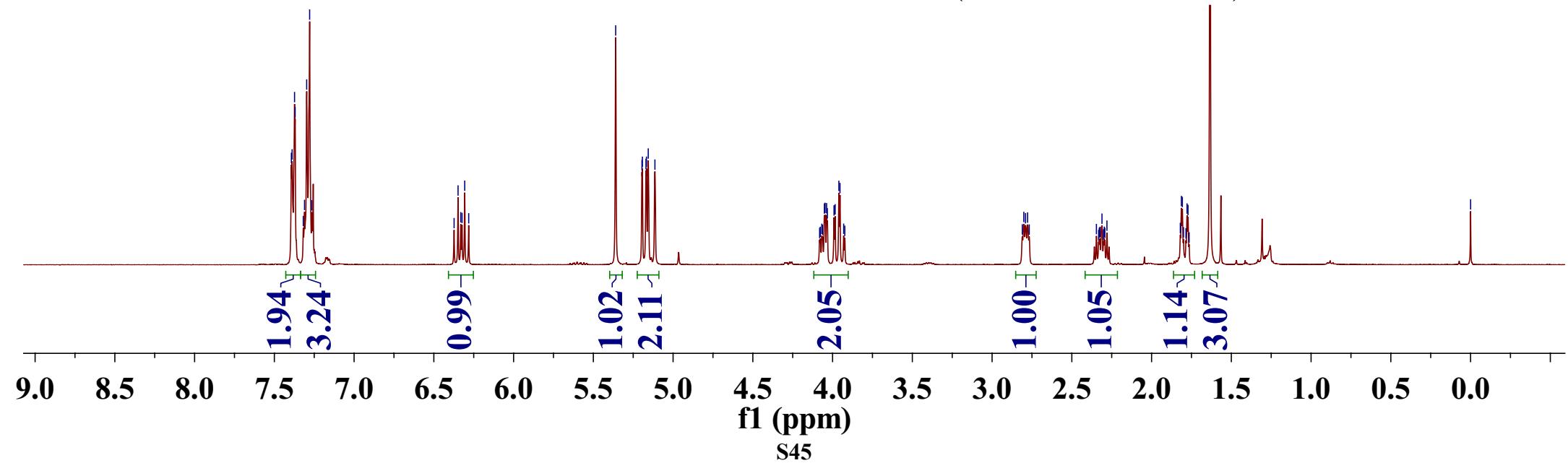
PeakTable

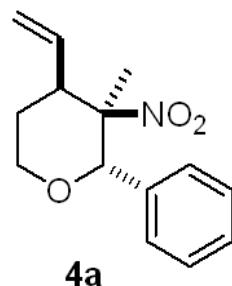
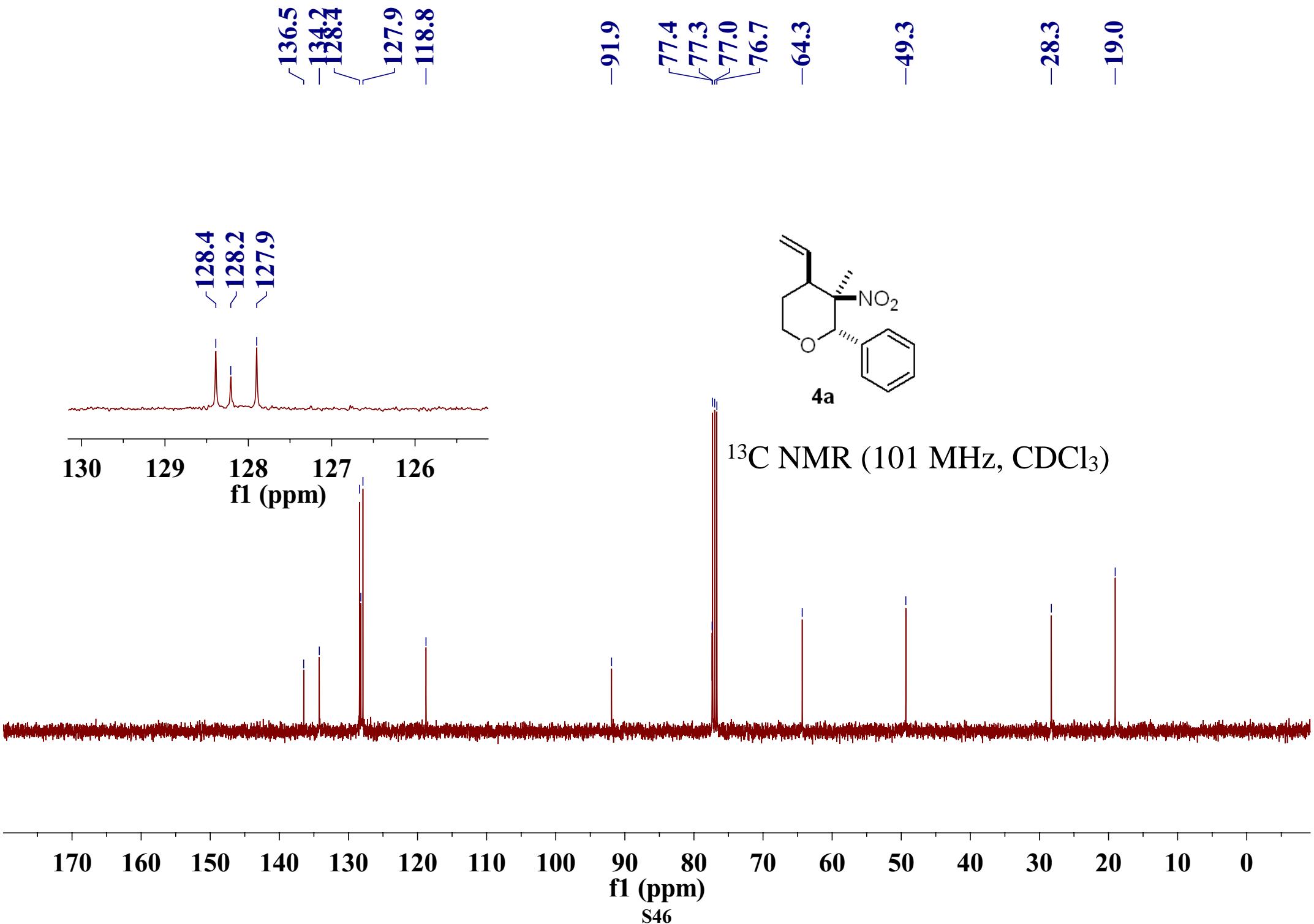
Detector A Ch1 214nm

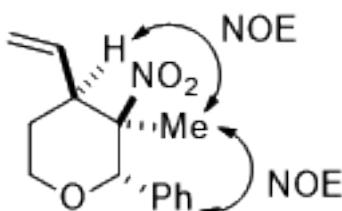
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.684	376140	28786	2.001	2.511
2	12.717	18424180	1117641	97.999	97.489
Total		18800320	1146426	100.000	100.000



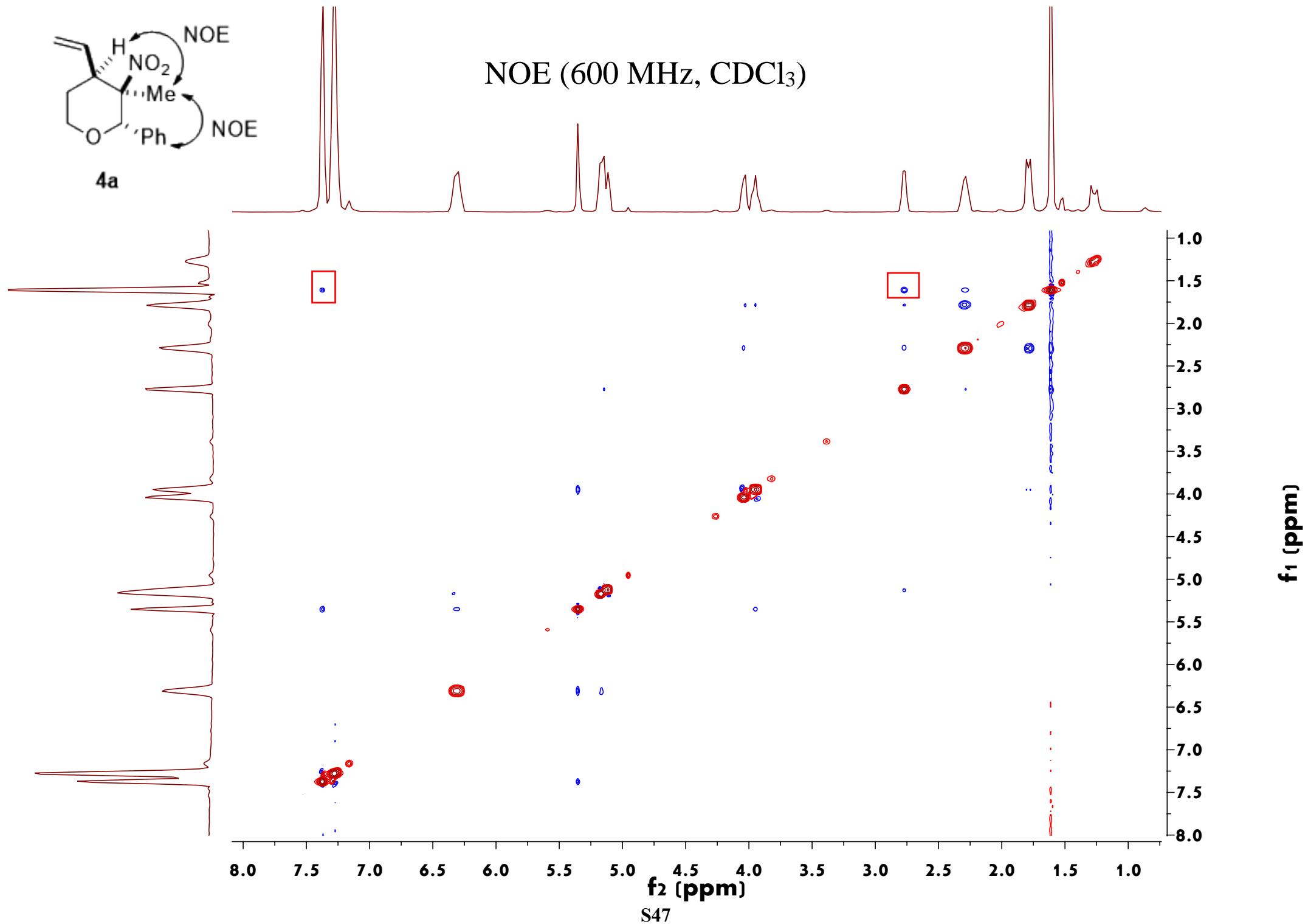
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



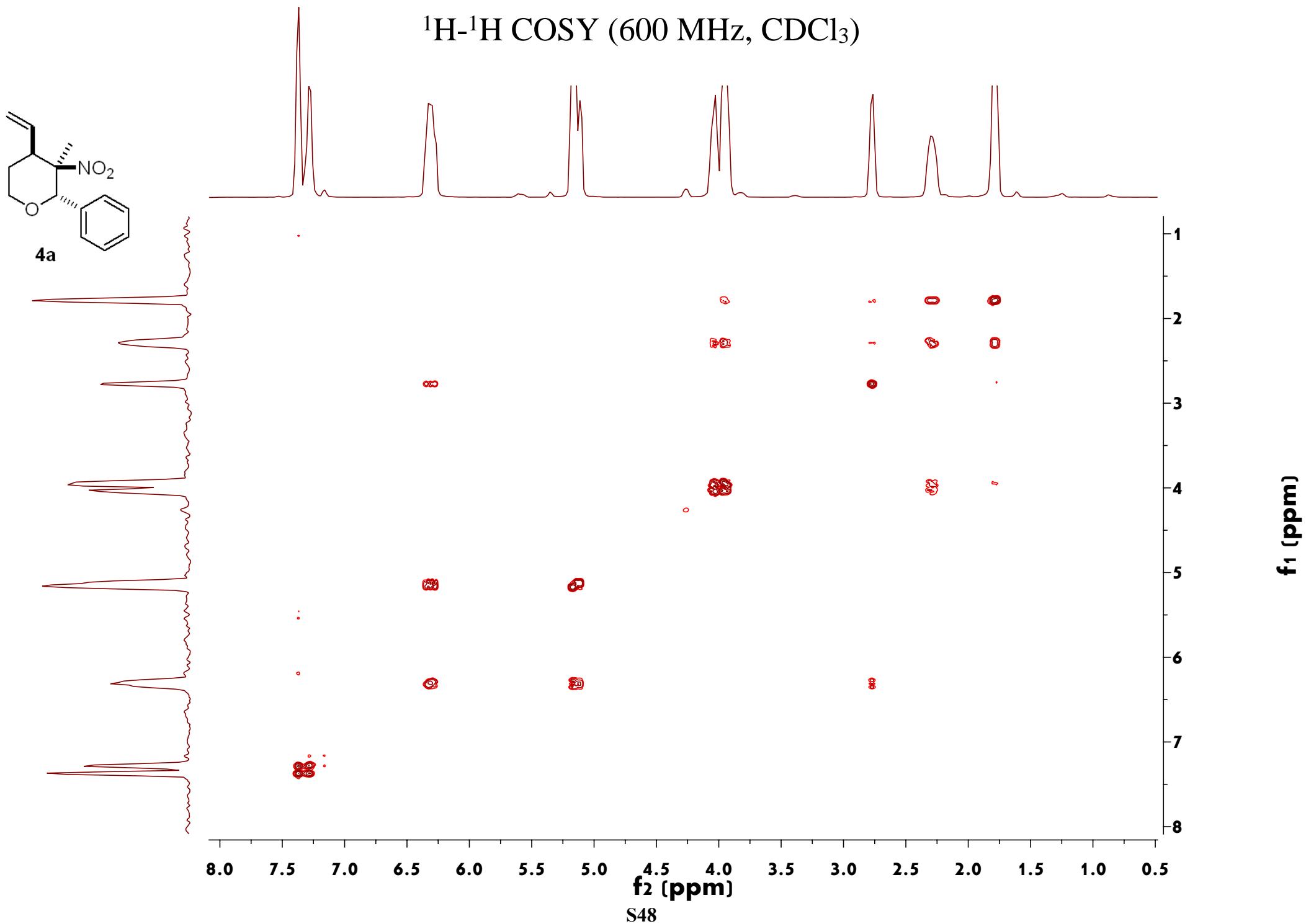


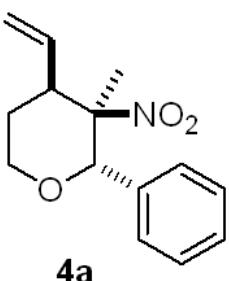


NOE (600 MHz,  $\text{CDCl}_3$ )

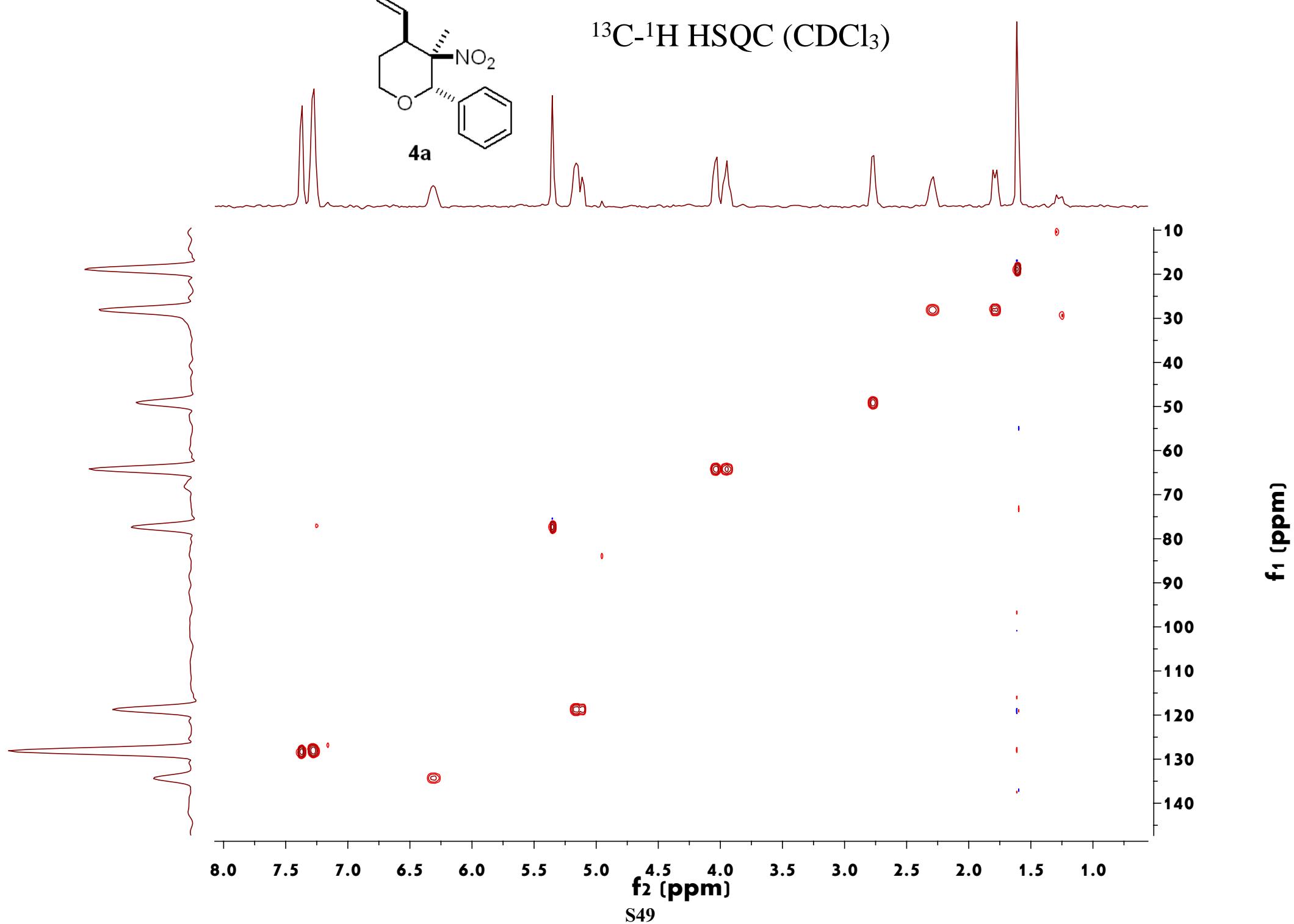


$^1\text{H}$ - $^1\text{H}$  COSY (600 MHz,  $\text{CDCl}_3$ )





$^{13}\text{C}$ - $^1\text{H}$  HSQC ( $\text{CDCl}_3$ )



-0.00

7.26  
7.10  
7.08  
6.83  
6.81

5.62  
5.58  
5.55

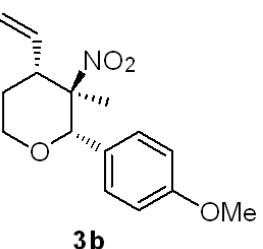
5.15  
5.13  
4.91  
4.27  
4.24

3.77

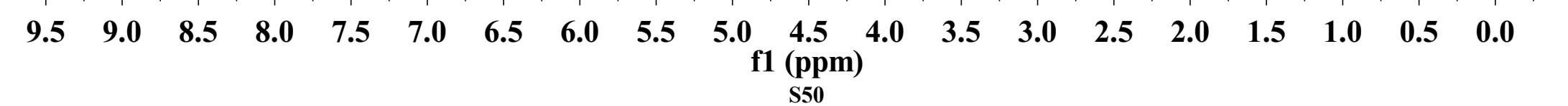
3.38  
3.35

1.88

1.85  
1.83  
1.82  
1.81  
-1.31



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



-159.5

-134.6

128.0

127.7

-118.6

-113.5

-93.9

-83.8

-76.7

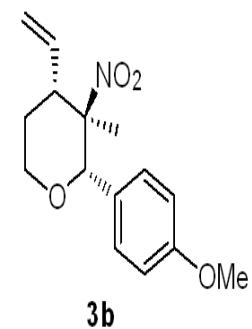
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-55.2

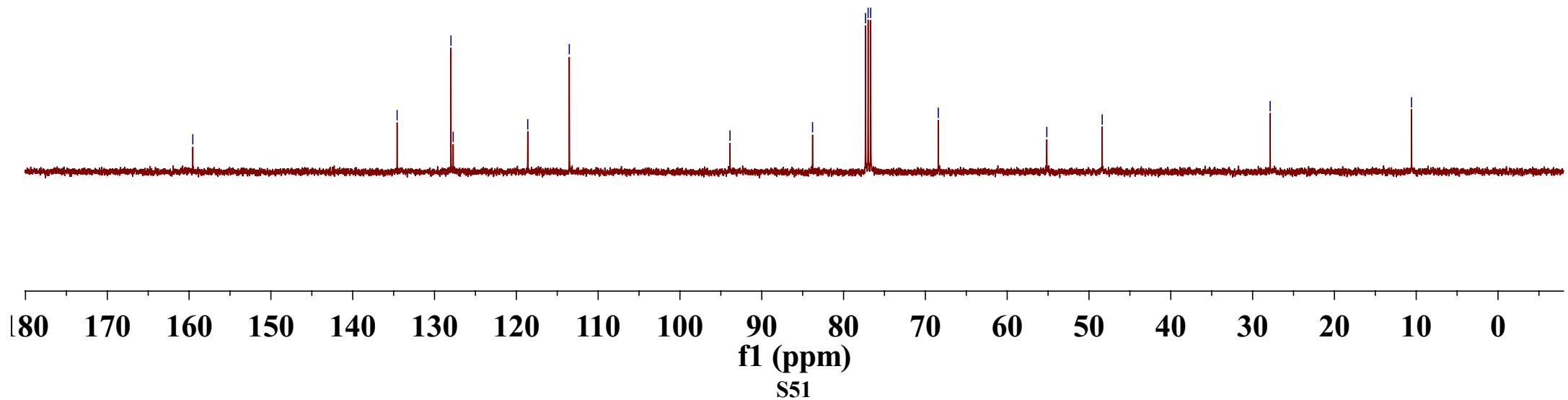
-48.4

-27.9

-10.6

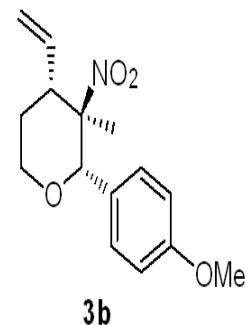


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

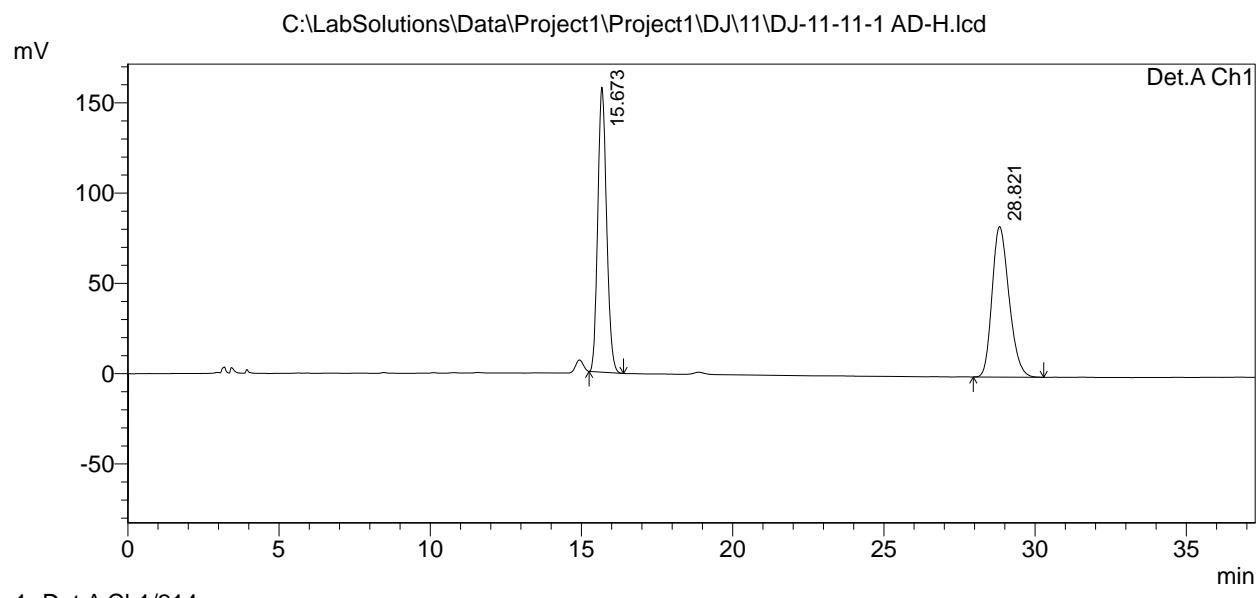


# ==== Shimadzu LCsolution Analysis Report ====

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 Sample ID : AD-H,98/2,1.0,214  
 Vail # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-11-1 AD-H.lcd  
 Method File Name : 123.lcm  
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 Report File Name : Default.lcr  
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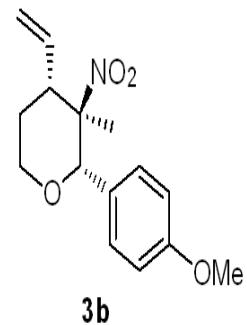
PeakTable

Detector A Ch1 214nm

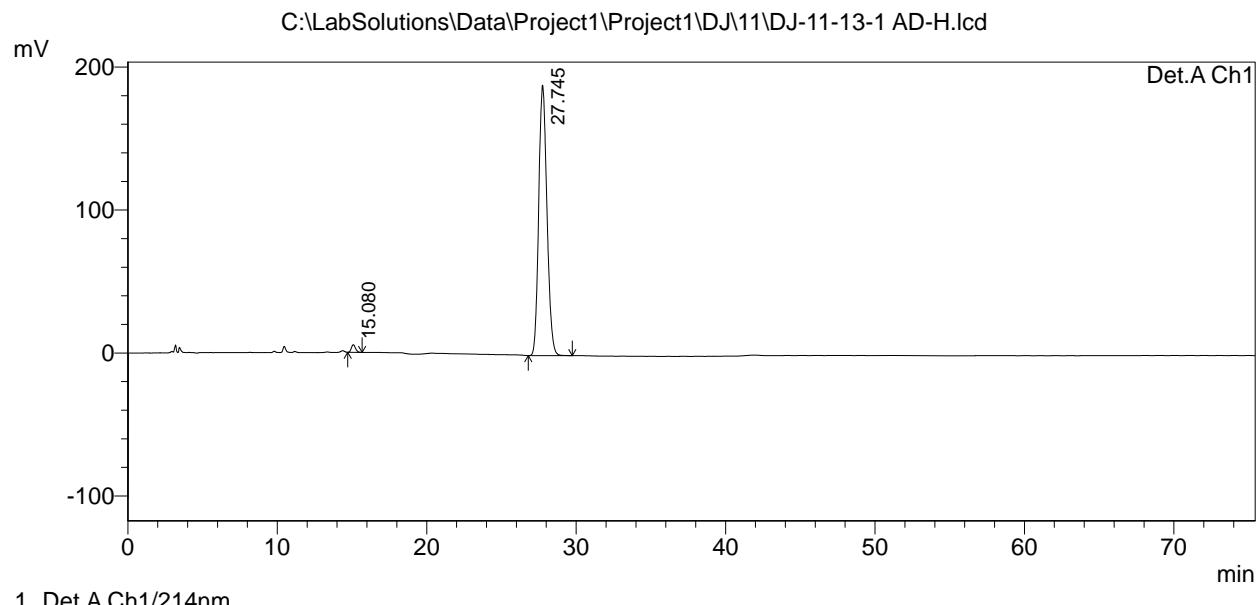
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.673	3207516	157889	49.683	65.438
2	28.821	3248402	83392	50.317	34.562
Total		6455918	241281	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

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 Sample ID : AD-H,98/2,1,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-13-1 AD-H.lcd  
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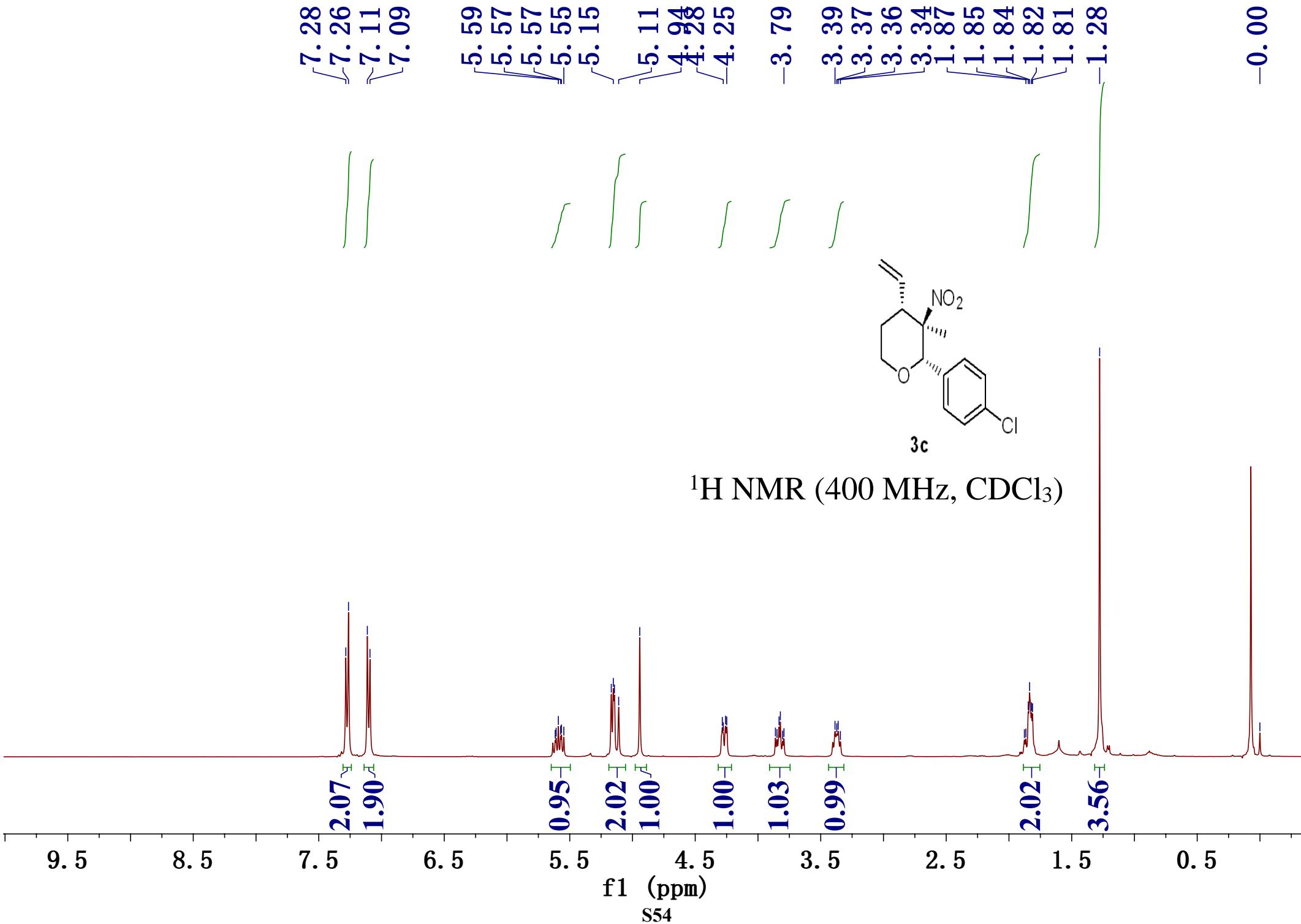
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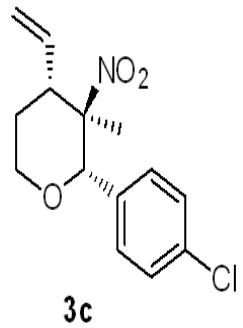
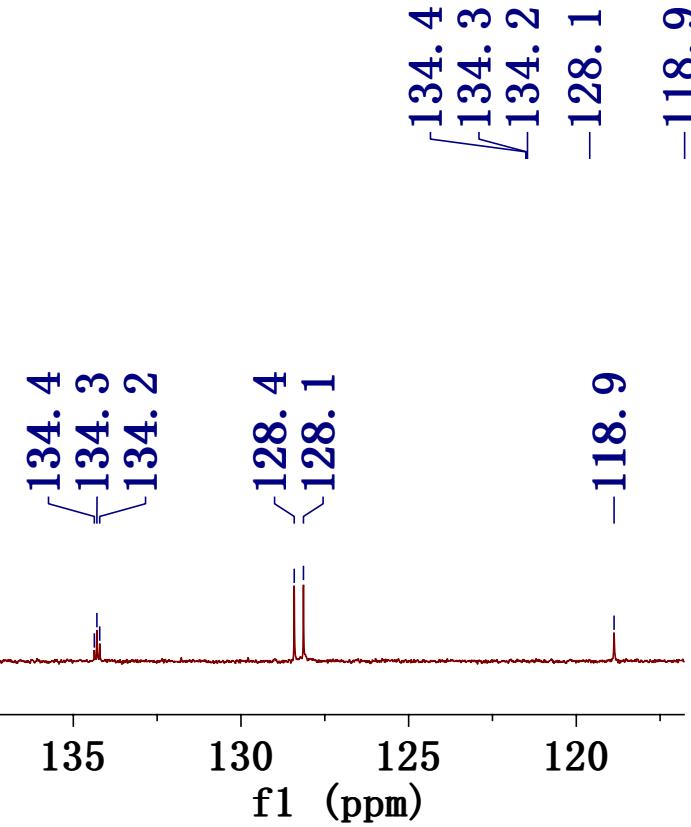


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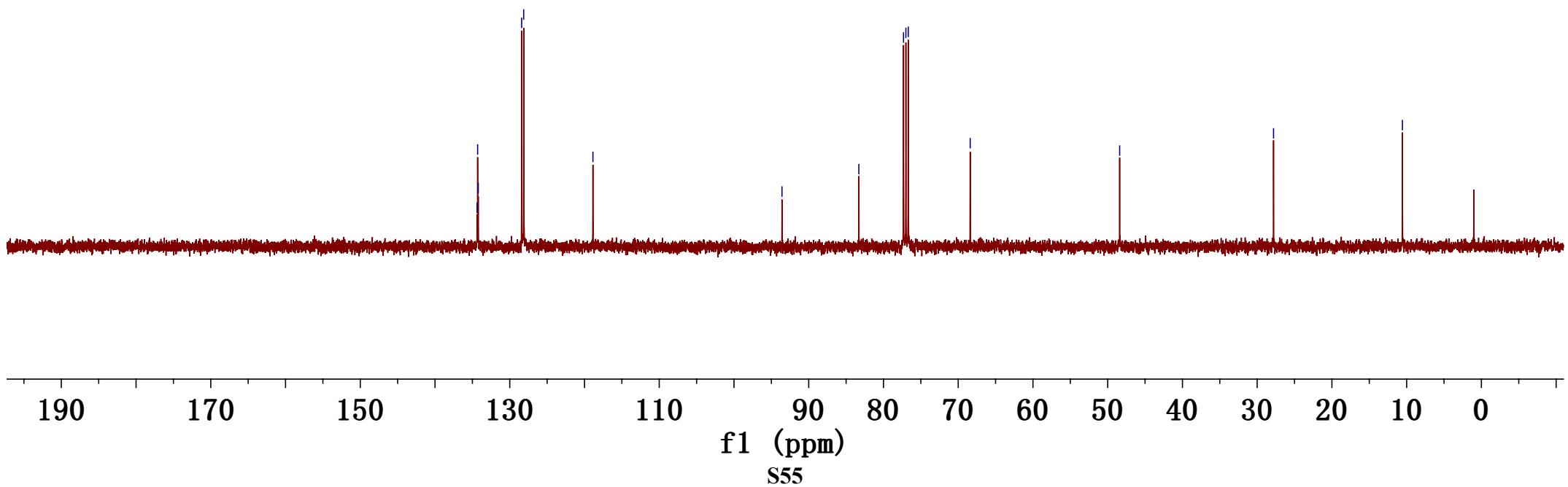
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.080	103929	5360	1.409	2.755
2	27.745	7272689	189222	98.591	97.245
Total		7376618	194582	100.000	100.000



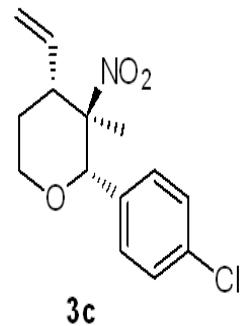


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

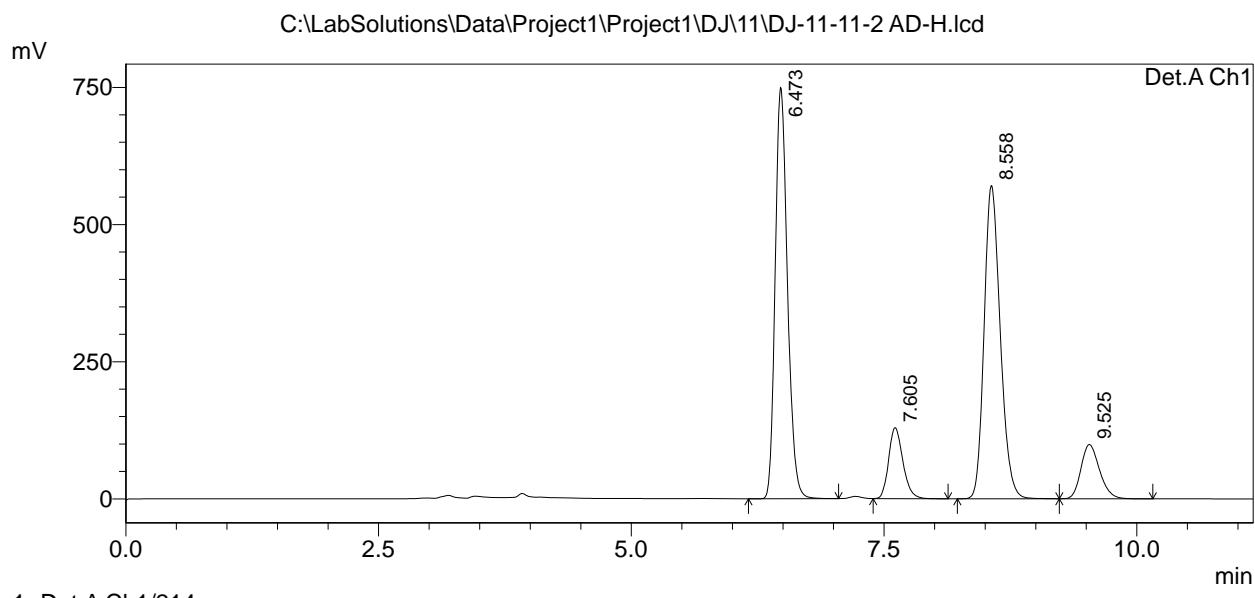


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-11-2 AD-H  
 Sample ID : AD-H,98/2,1.0,214  
 Vail # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-11-2 AD-H.lcd  
 Method File Name : 123.lcm  
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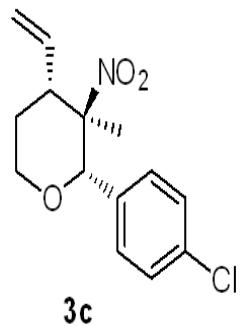
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Detector A Ch1 214nm

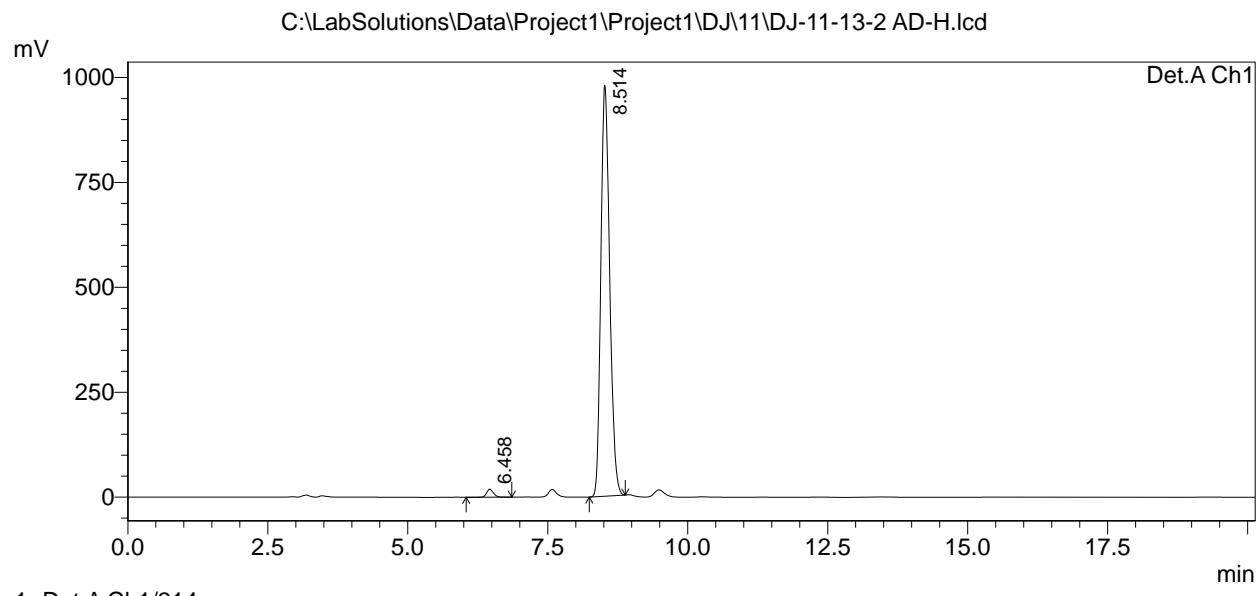
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.473	6306456	750269	41.525	48.412
2	7.605	1271687	129513	8.374	8.357
3	8.558	6339878	570940	41.746	36.841
4	9.525	1268952	99035	8.356	6.390
Total		15186972	1549758	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
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 Sample ID : AD-H,98/2,1,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
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 Data Processed : 2018-2-4 18:39:53



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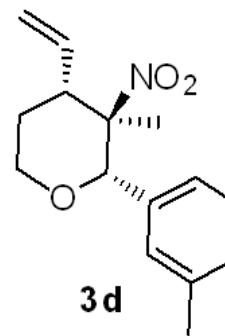
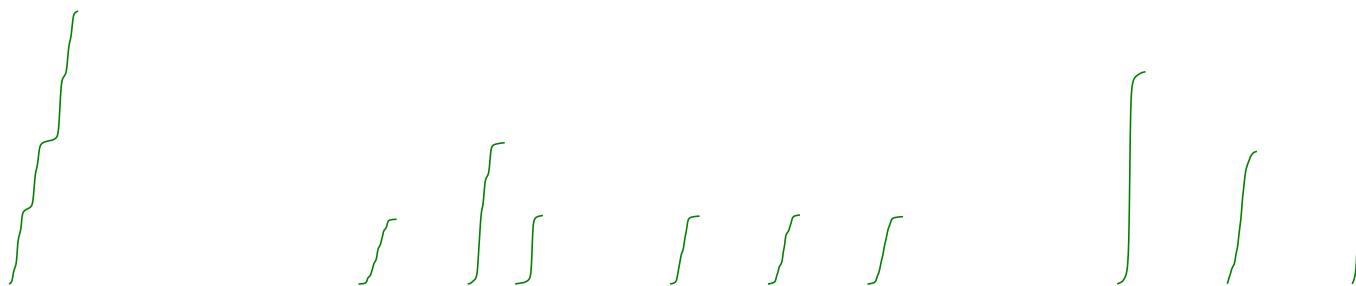


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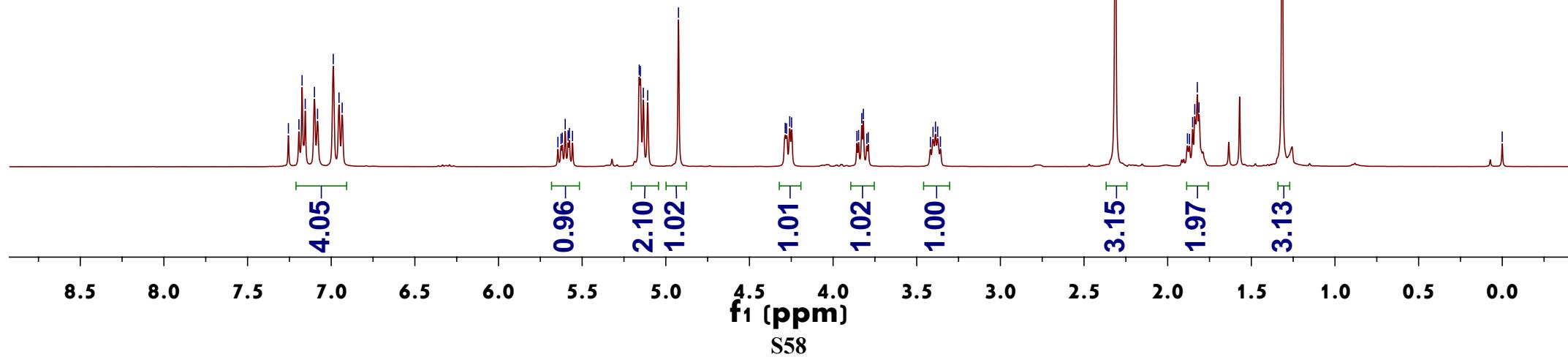
Detector A Ch1 214nm

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2	8.514	10739464	979682	98.499	98.076
Total		10903170	998901	100.000	100.000

7.26  
7.19  
7.17  
7.16  
7.10  
7.08  
6.99  
6.95  
6.93  
5.62  
5.58  
5.56  
5.16  
5.11  
4.92  
4.28  
4.25  
-3.79  
-3.39  
-3.37  
-3.36  
-2.31  
-1.85  
-1.81  
-1.32  
-0.00



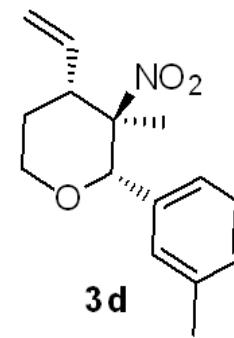
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



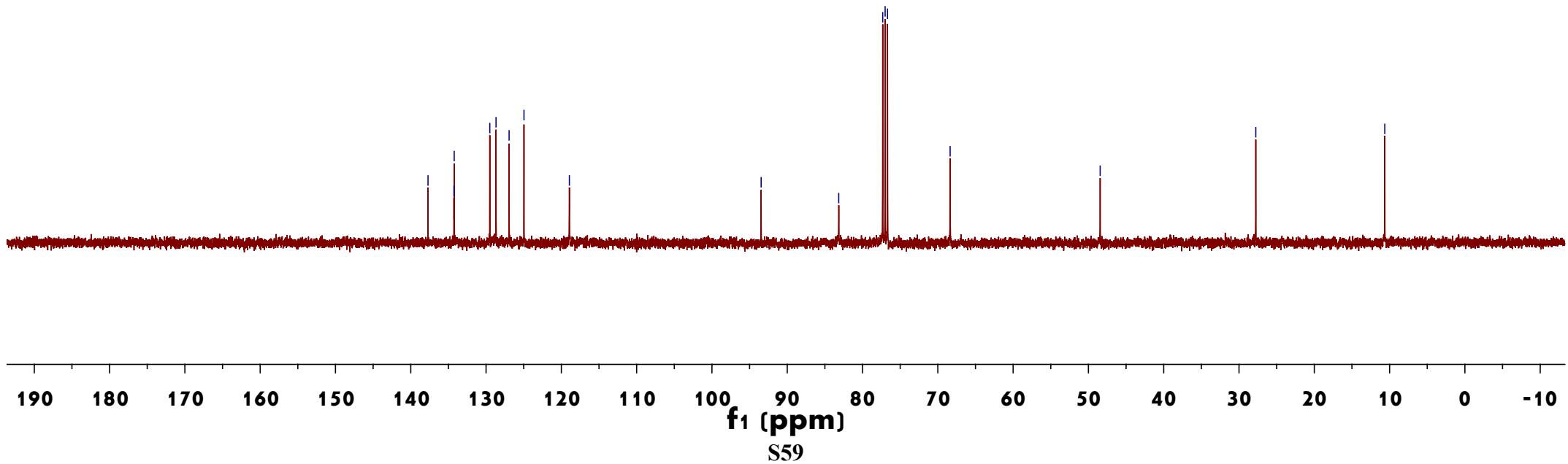
137.71  
134.27  
134.23  
129.50  
128.68  
126.94  
124.96  
-118.93

-93.47  
-83.16  
-76.68  
-68.37

-48.44  
-27.77  
-10.64

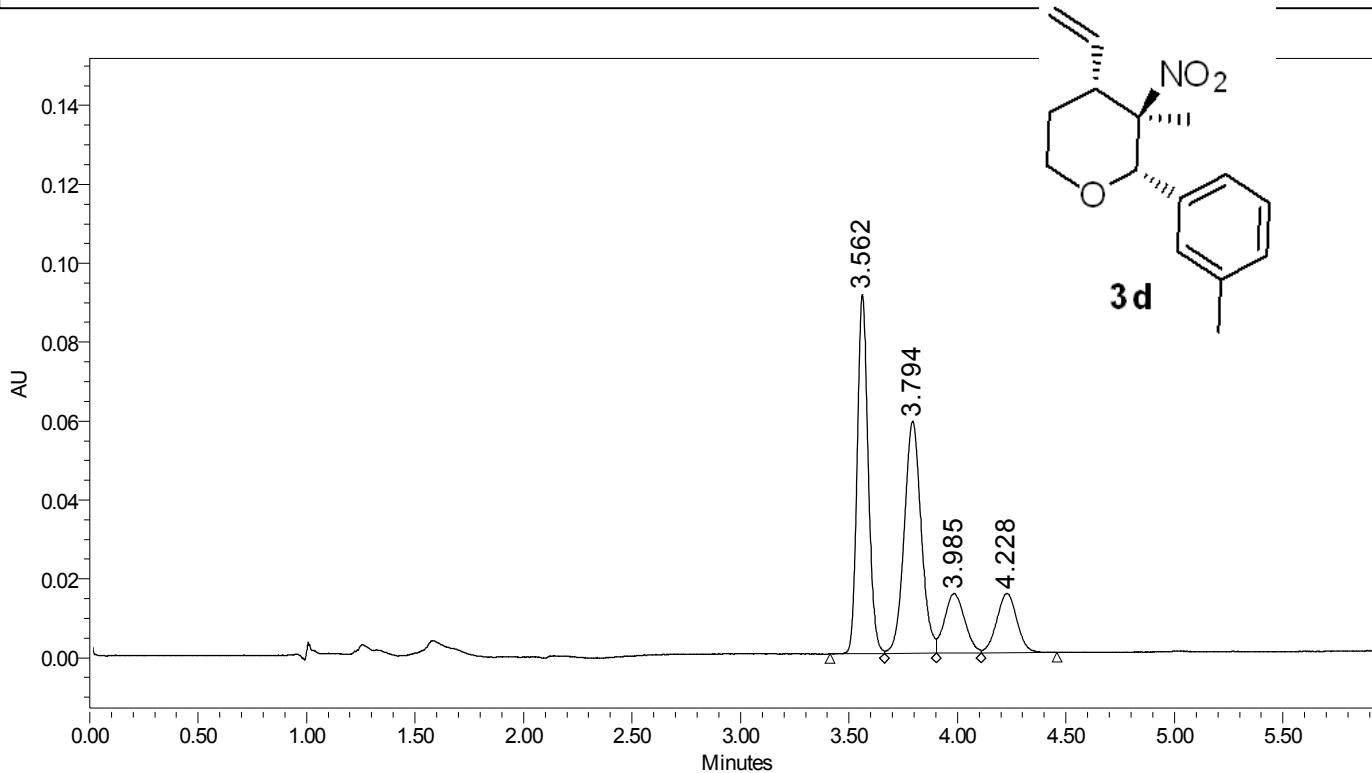


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



## SAMPLE INFORMATION

Sample Name: DJ-11-89-2-rac      Acquired By: System  
Sample Type: Unknown      Sample Set Name:  
Vial: 1:a,1      Acq. Method Set: test  
Injection #: 1      Processing Method: TEST  
Injection Volume: 0.30 ul      Channel Name: PDA Ch1 214nm@4.8nm  
Run Time: 60.0 Minutes      Proc. Chnl. Descr.: PDA Ch1 214nm@4.8nm  
  
Date Acquired: 5/25/2018 1:55:16 PM CST  
Date Processed: 5/25/2018 2:13:04 PM CST



	RT	Peak Type	Height	Width (sec)	Area	% Area
1	3.562	Unknown	91015	15.100	322668	38.35
2	3.794	Unknown	58801	14.250	322146	38.28
3	3.985	Unknown	15124	12.400	98303	11.68
4	4.228	Unknown	15055	21.000	98338	11.69

Reported by User: System

Report Method: Default Individual Report

Report Method ID 1982

Page: 1 of 1

Project Name: TEST

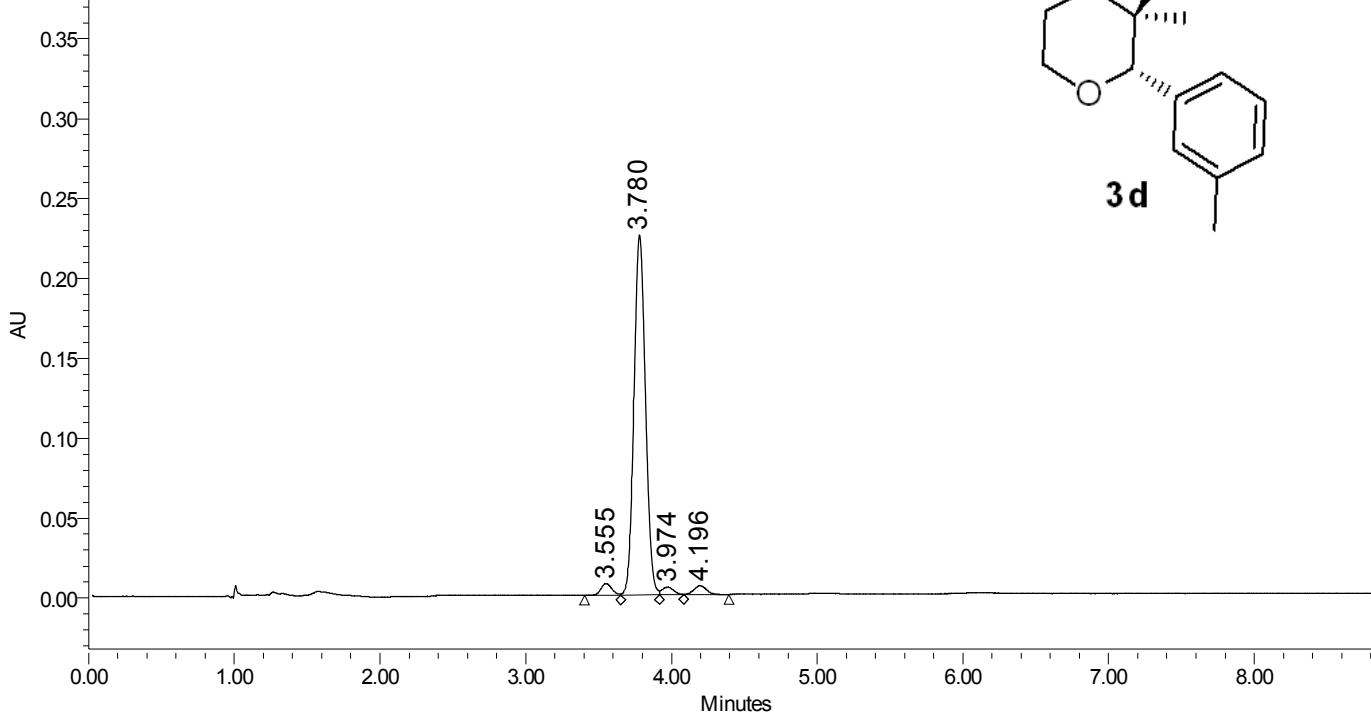
Date Printed:

5/25/2018

2:14:50 PM PRC

## SAMPLE INFORMATION

Sample Name: DJ-11-89-1 Acquired By: System  
Sample Type: Unknown Sample Set Name:  
Vial: 1:a,2 Acq. Method Set: test  
Injection #: 1 Processing Method TEST  
Injection Volume: 0.30 ul Channel Name: PDA Ch1 214nm@4.8nm  
Run Time: 60.0 Minutes Proc. Chnl. Descr.: PDA Ch1 214nm@4.8nm  
  
Date Acquired: 5/25/2018 2:03:13 PM CST  
Date Processed: 5/25/2018 2:13:48 PM CST



	RT	Peak Type	Height	Width (sec)	Area	% Area
1	3.555	Unknown	7178	14.700	36078	2.70
2	3.780	Unknown	225087	16.000	1242158	92.86
3	3.974	Unknown	4815	10.050	26496	1.98
4	4.196	Unknown	5530	18.550	33006	2.47

Reported by User: System

Report Method: Default Individual Report

Report Method ID 1982

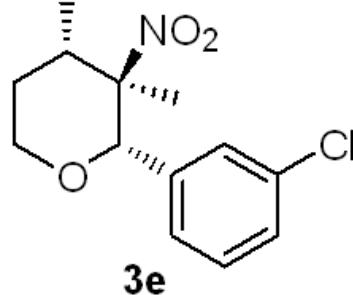
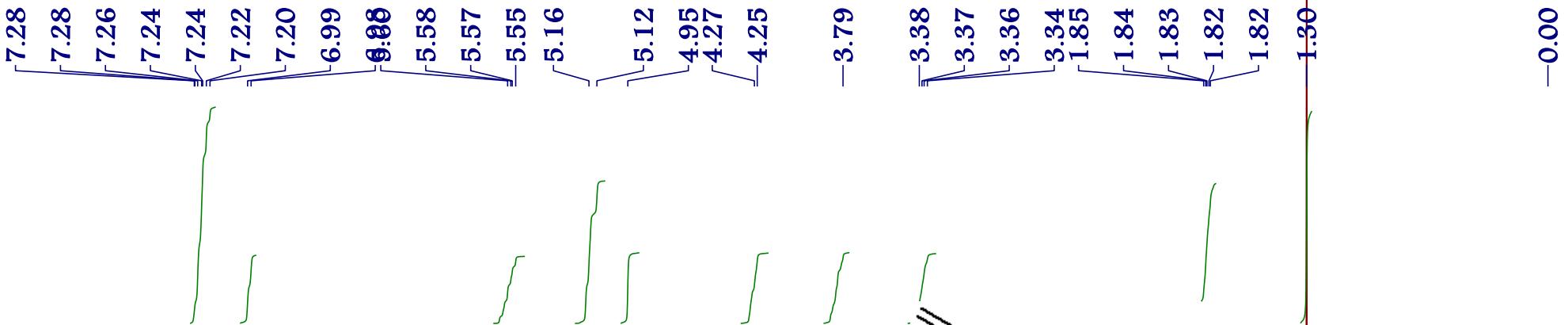
Page: 1 of 1

Project Name: TEST

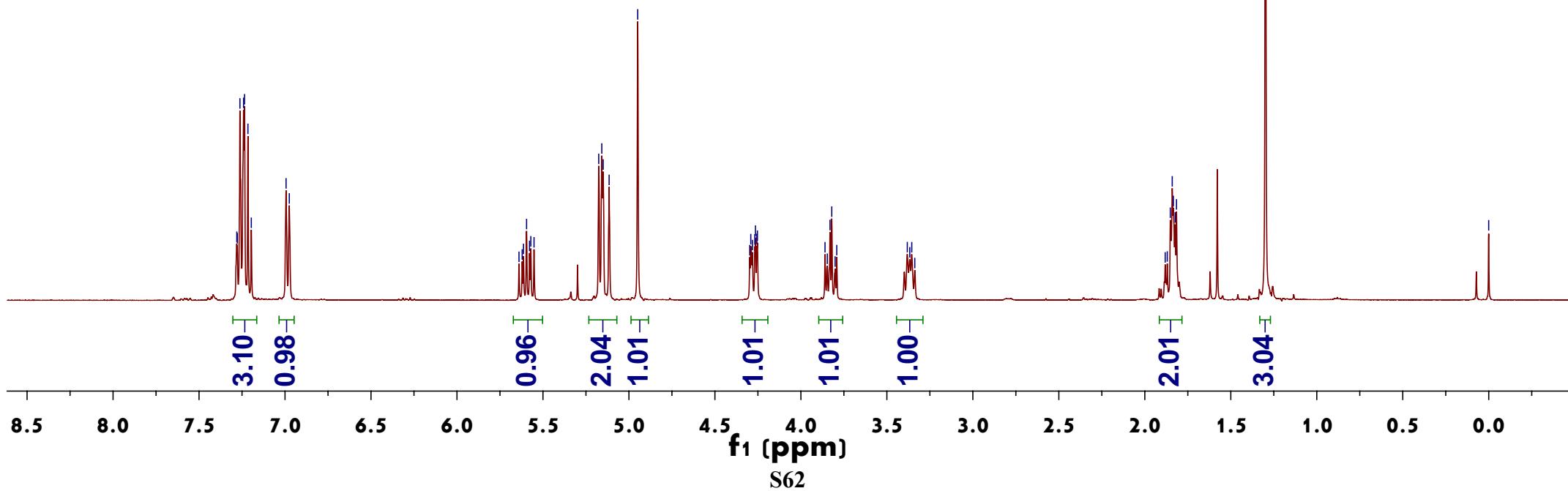
Date Printed:

5/25/2018

2:14:25 PM PRC



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



137.71  
134.27  
134.23  
129.50  
128.68  
126.94  
124.96  
-118.93

-93.47

-83.16

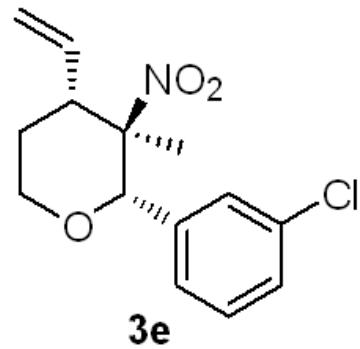
-76.68

-68.37

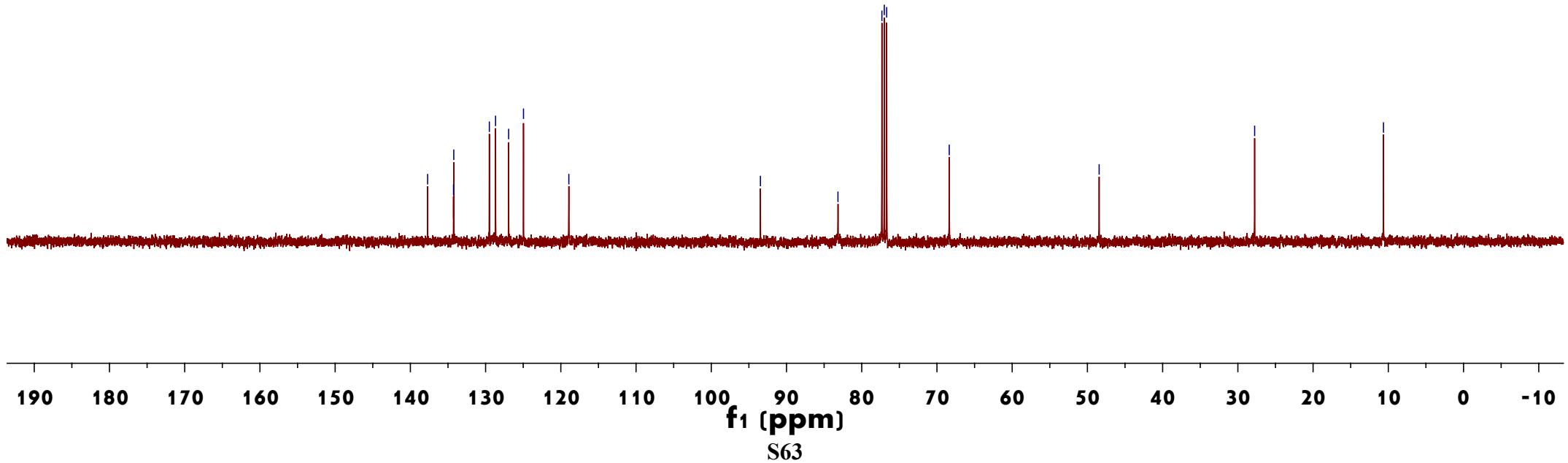
-48.44

-27.77

-10.64

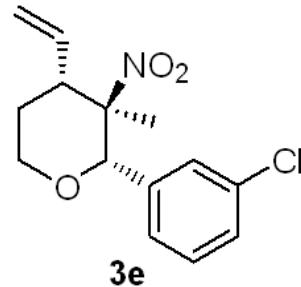


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

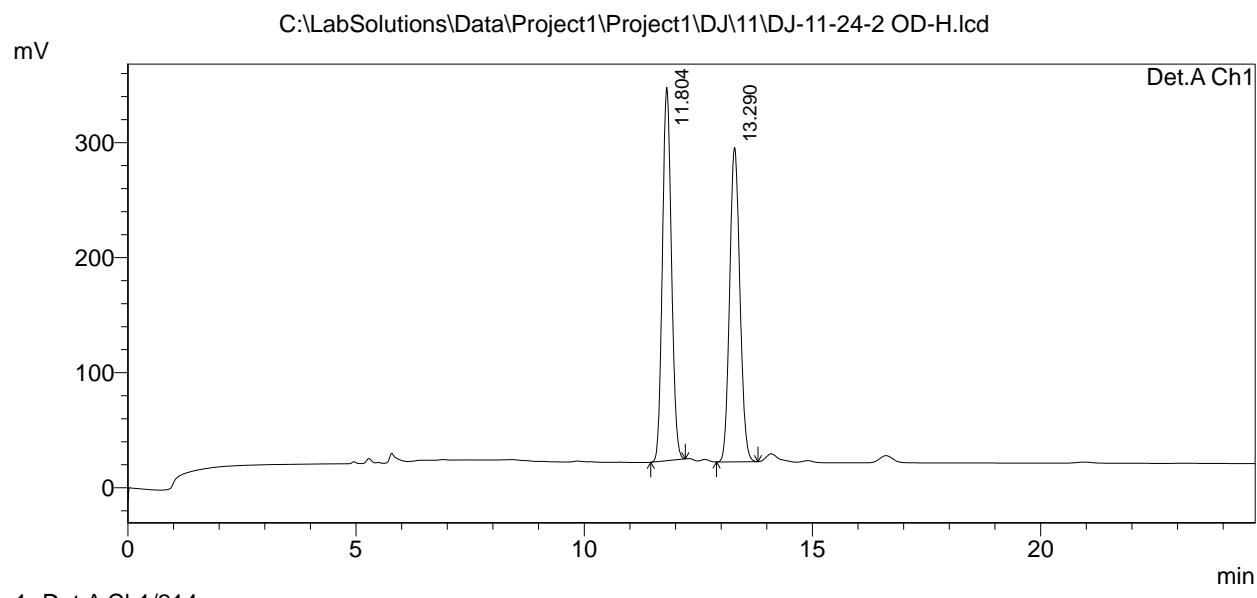


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-24-2 OD-H  
 Sample ID : OD-H,98/2,0.6,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-24-2 OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-15 14:37:22  
 Data Processed : 2018-3-15 15:02:05



## <Chromatogram>



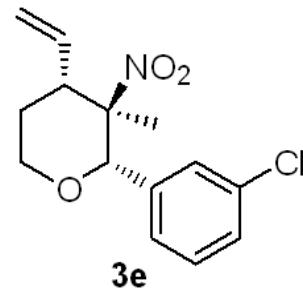
PeakTable

Detector A Ch1 214nm

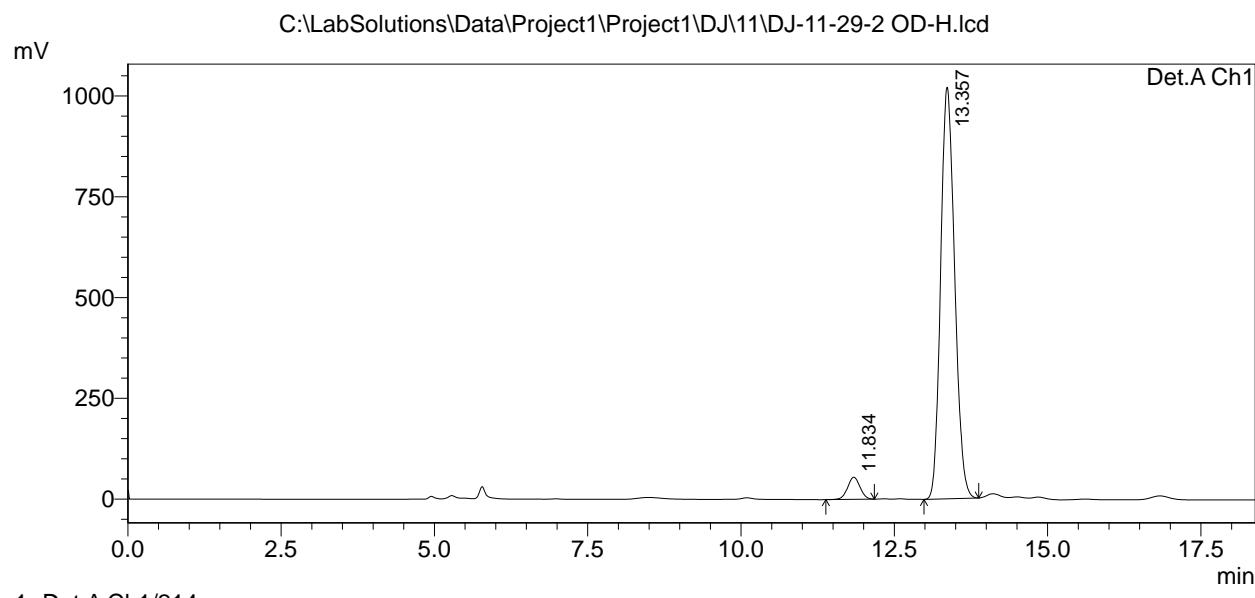
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.804	4454299	324747	51.026	54.305
2	13.290	4275165	273263	48.974	45.695
Total		8729464	598010	100.000	100.000

==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-29-2 OD-H  
 Sample ID : OD-H,98/2,0.6,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-29-2 OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-15 15:04:32  
 Data Processed : 2018-3-15 15:22:56



**<Chromatogram>**

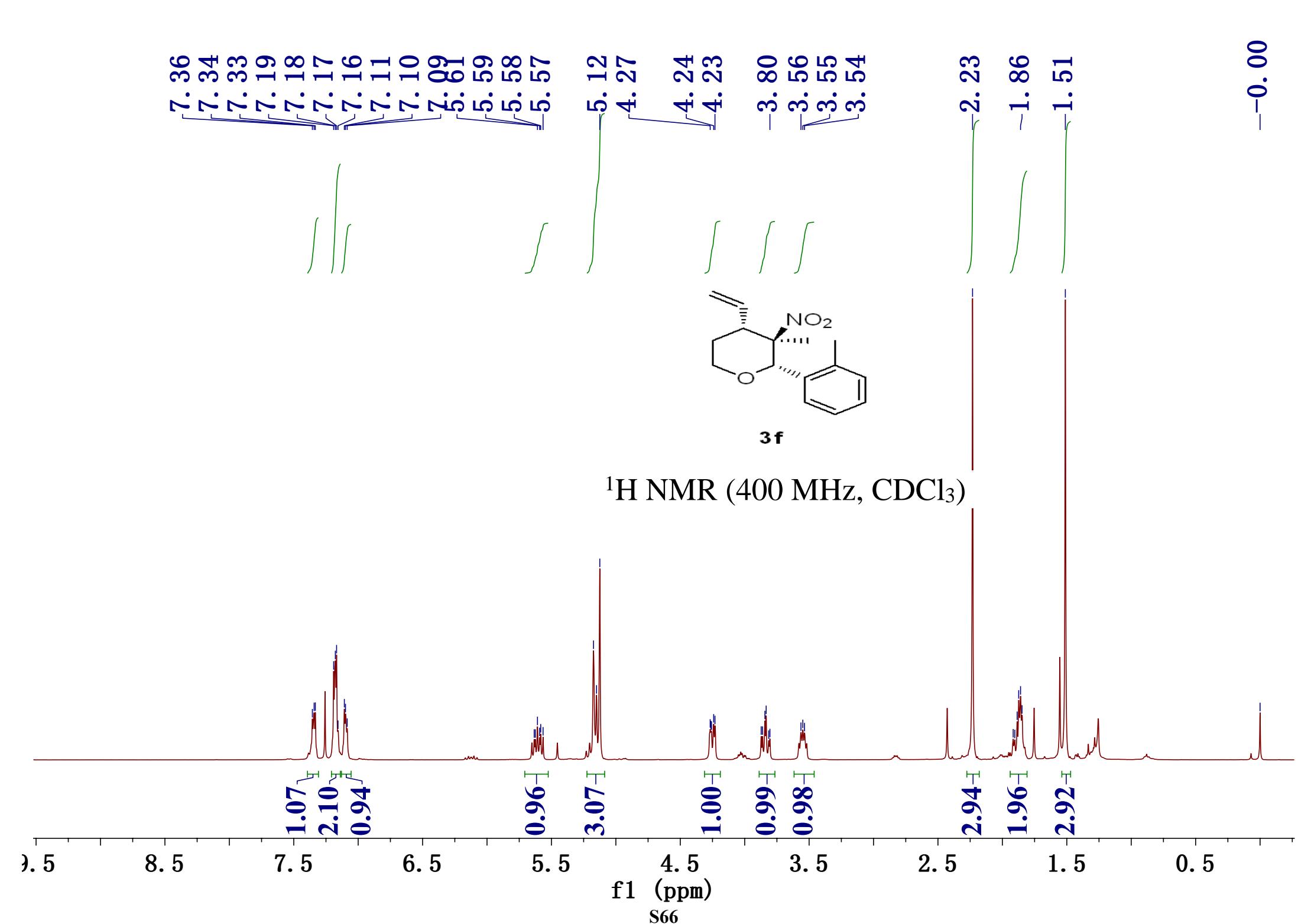


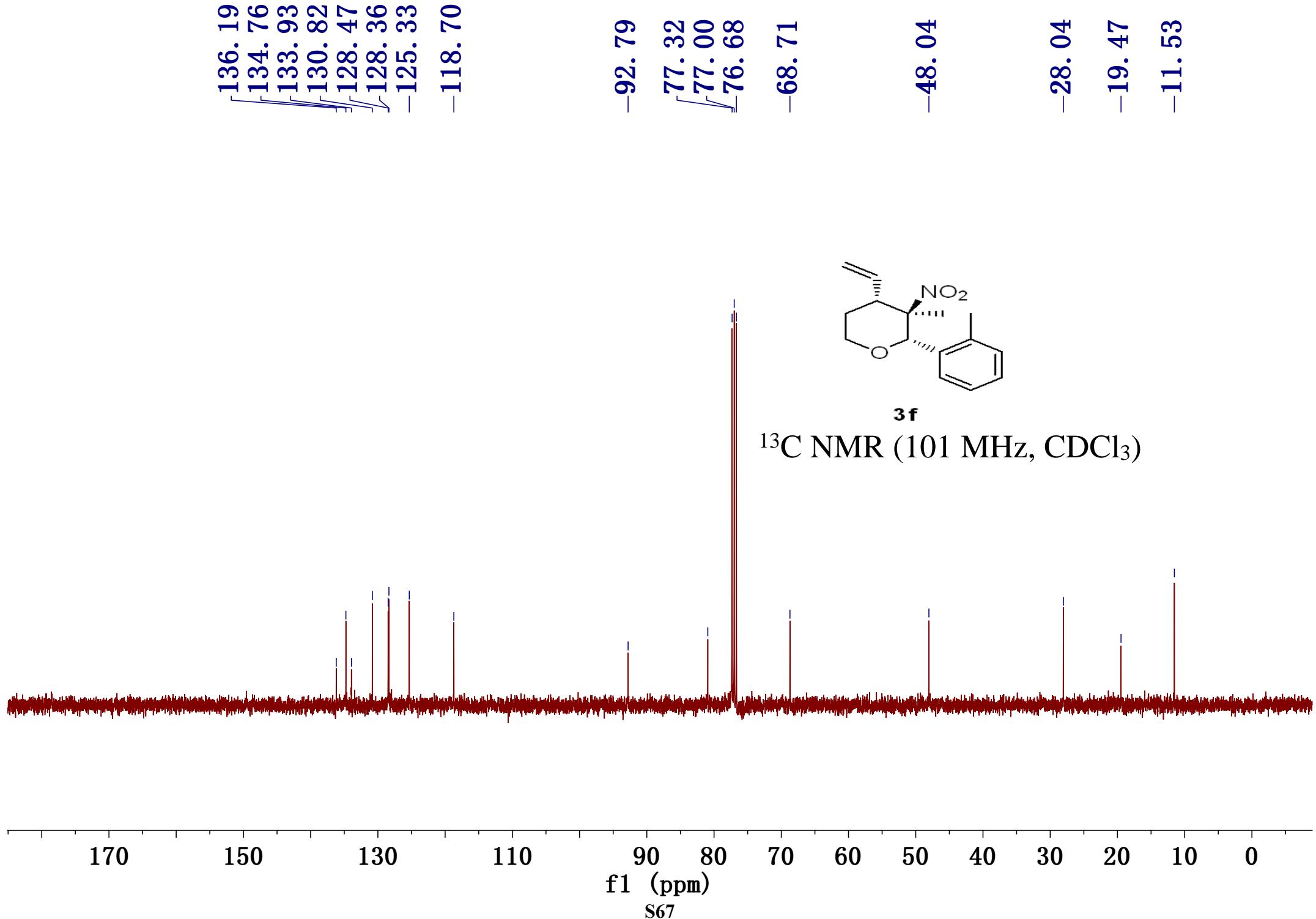
1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

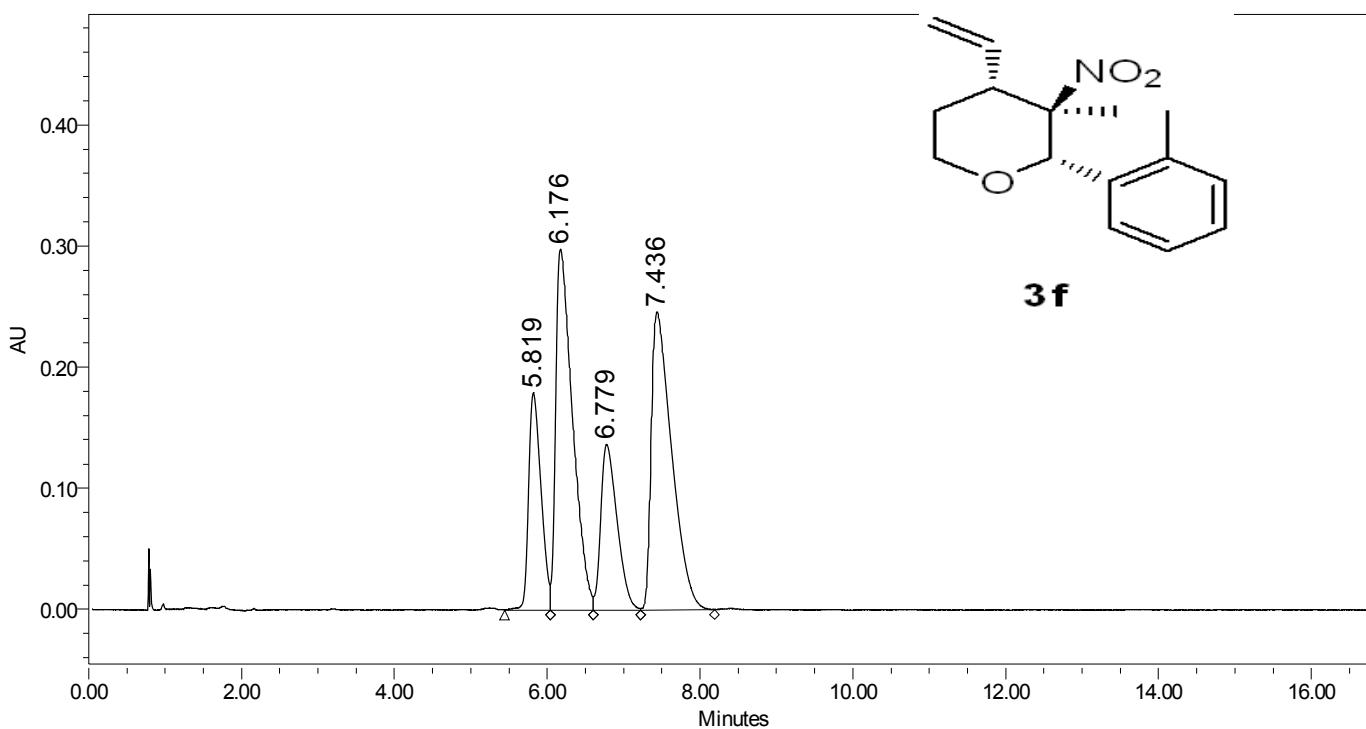
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.834	774146	54897	4.550	5.101
2	13.357	16239824	1021279	95.450	94.899
Total		17013970	1076176	100.000	100.000





## SAMPLE INFORMATION

Sample Name: dj-11-88-1-rac-ic-3-99-1-etho Acquired By: System  
Sample Type: Unknown Sample Set Name:  
Vial: 1:E,3 Acq. Method Set: test  
Injection #: 1 Processing Method TEST  
Injection Volume: 2.00 ul Channel Name: PDA Ch1 220nm@4.8nm  
Run Time: 60.0 Minutes Proc. Chnl. Descr.: PDA Ch1 220nm@4.8nm  
  
Date Acquired: 6/7/2018 2:49:47 PM CST  
Date Processed: 6/7/2018 3:07:45 PM CST



	RT	Peak Type	Height	Width (sec)	Area	% Area
1	5.819	Unknown	179257	35.800	2036704	15.45
2	6.176	Unknown	298107	33.750	4547212	34.50
3	6.779	Unknown	136585	37.200	2046938	15.53
4	7.436	Unknown	246122	57.950	4547849	34.51

Reported by User: System

Report Method: Default Individual Report

Report Method ID 3056

Page: 1 of 1

Project Name: TEST

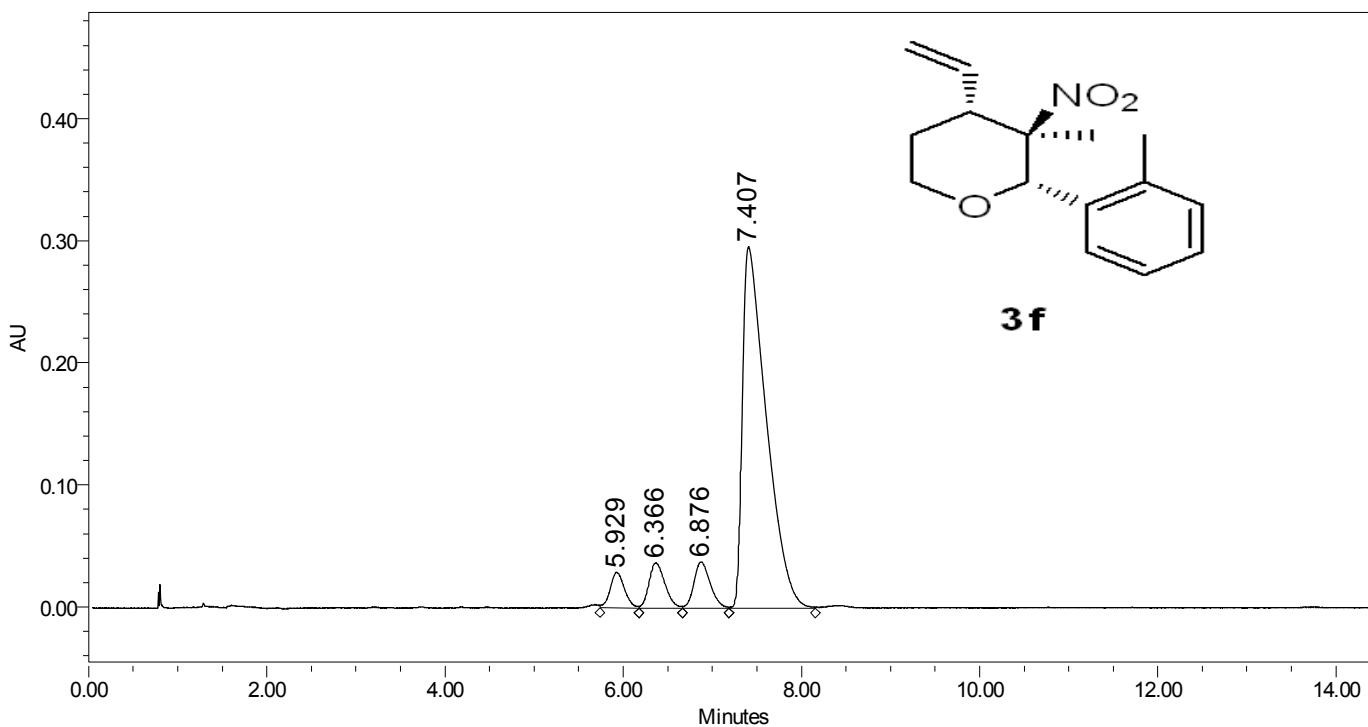
Date Printed:

6/7/2018

3:10:49 PM PRC

## SAMPLE INFORMATION

Sample Name: dj-12-1-2 Acquired By: System  
Sample Type: Unknown Sample Set Name:  
Vial: 1:E,4 Acq. Method Set: test  
Injection #: 1 Processing Method TEST  
Injection Volume: 1.00 ul Channel Name: PDA Ch1 220nm@4.8nm  
Run Time: 60.0 Minutes Proc. Chnl. Descr.: PDA Ch1 220nm@4.8nm  
  
Date Acquired: 6/7/2018 2:33:14 PM CST  
Date Processed: 6/7/2018 3:07:29 PM CST



	RT	Peak Type	Height	Width (sec)	Area	% Area
1	5.929	Unknown	29065	26.200	324252	4.79
2	6.366	Unknown	36930	29.550	452754	6.68
3	6.876	Unknown	37571	31.250	474498	7.01
4	7.407	Unknown	295699	58.150	5521413	81.52

Reported by User: System

Report Method: Default Individual Report

Report Method ID 3056

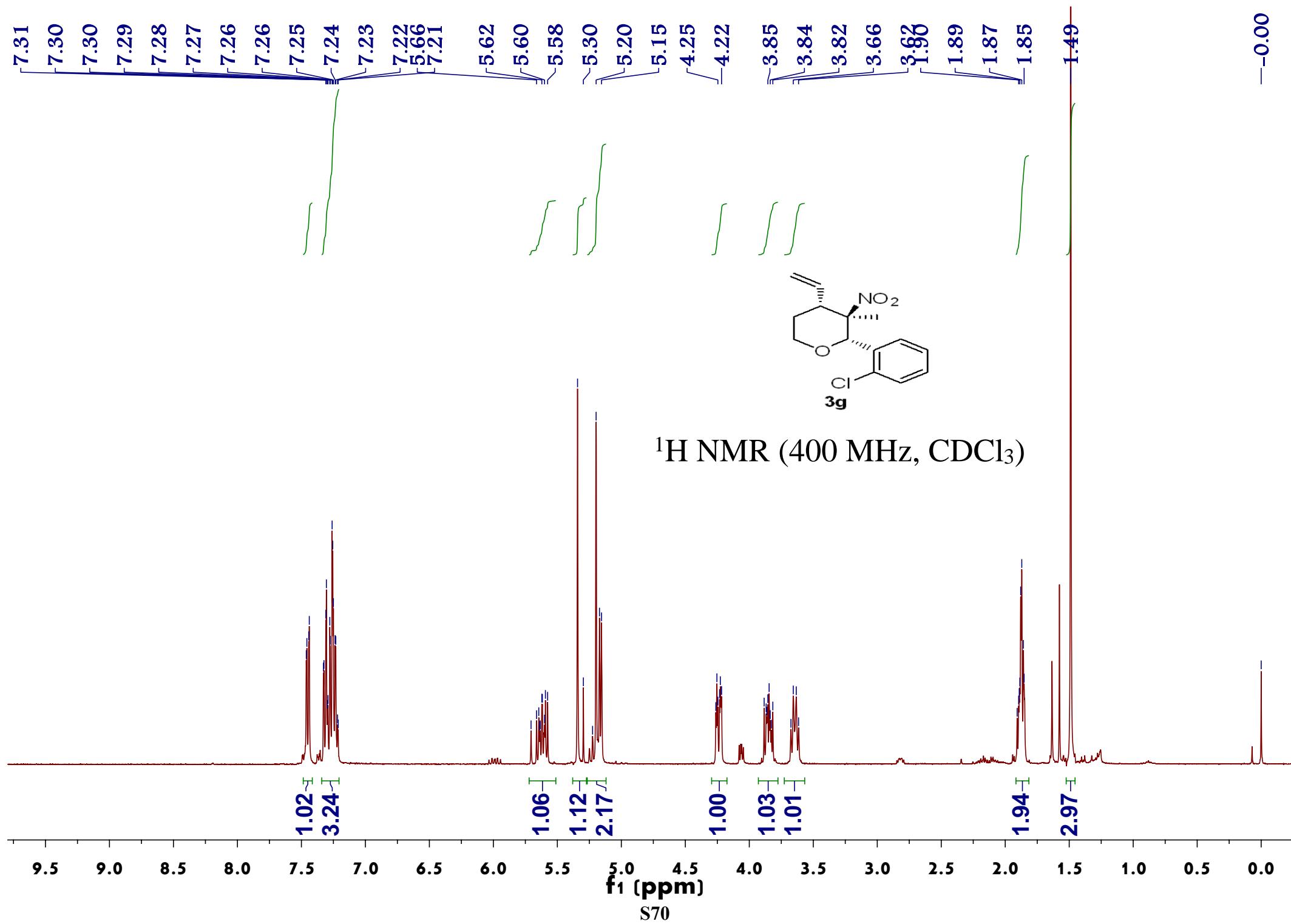
Page: 1 of 1

Project Name: TEST

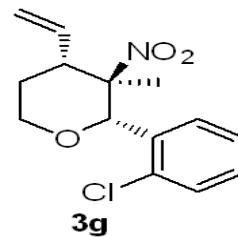
Date Printed:

6/7/2018

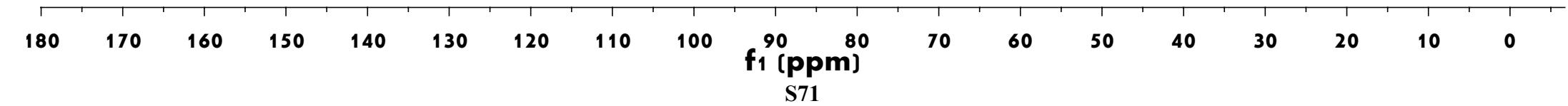
3:11:10 PM PRC



134.68  
133.64  
133.35  
130.02  
129.71  
129.59  
-126.22  
-118.86  
-92.00  
77.32  
76.68  
-68.67  
-46.92  
-27.95  
-11.64

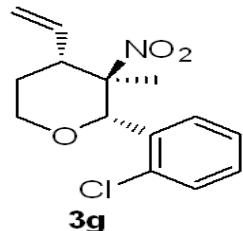


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

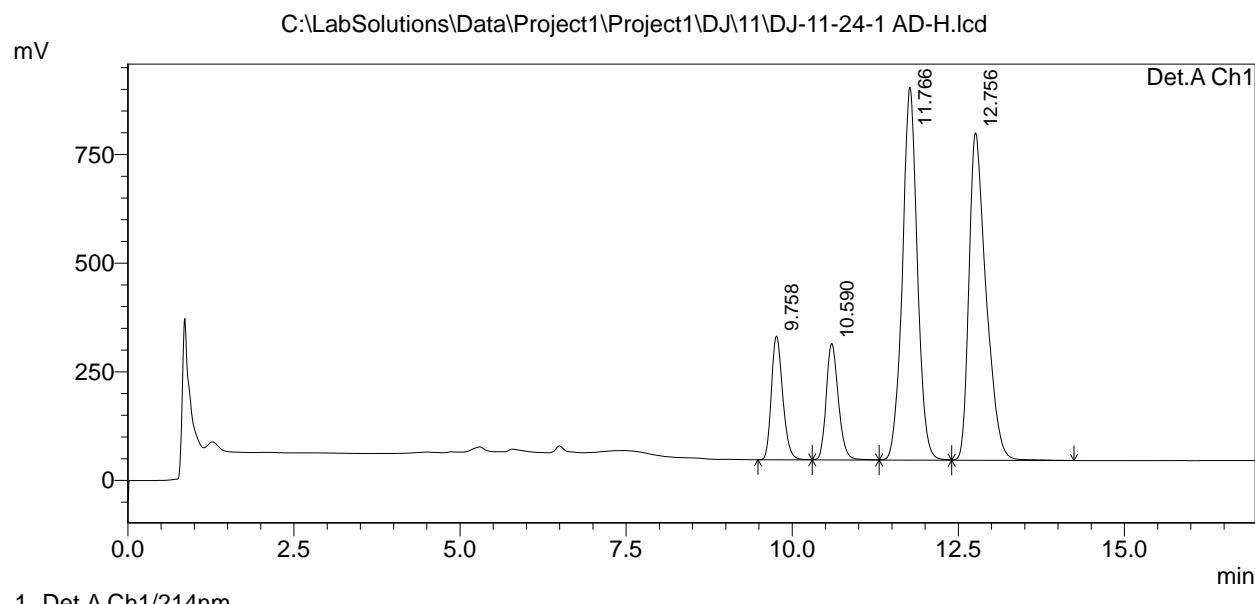


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-24-1 AD-H  
 Sample ID : AD-H,98/2,0.6,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-24-1 AD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-8 13:46:57  
 Data Processed : 2018-3-8 14:03:55



## <Chromatogram>



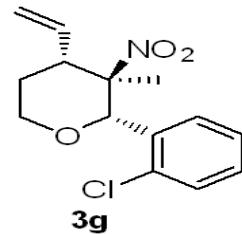
PeakTable

Detector A Ch1 214nm

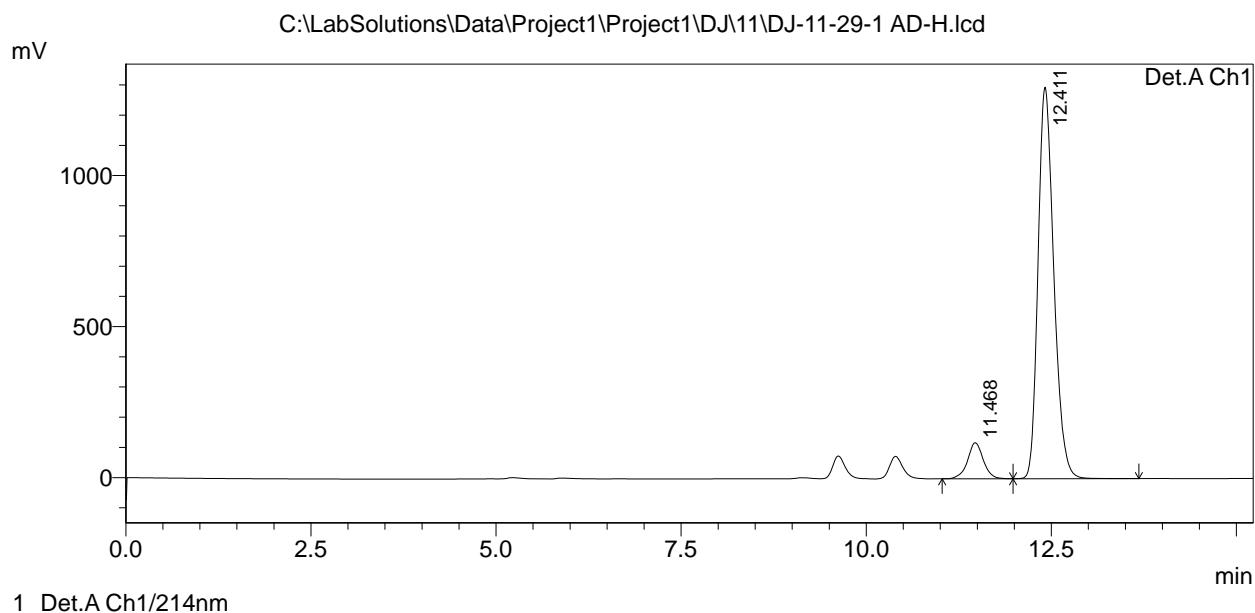
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.758	3385340	284646	10.032	13.147
2	10.590	3417584	268337	10.128	12.393
3	11.766	13429514	858428	39.798	39.648
4	12.756	13511761	753737	40.042	34.812
Total		33744199	2165148	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-29-1 AD-H  
 Sample ID : AD-H,98/2,0.6,214  
 Vail # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-29-1 AD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-14 20:13:44  
 Data Processed : 2018-3-14 20:28:58



## <Chromatogram>



PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.468	1766614	119458	8.434	8.437
2	12.411	19178962	1296428	91.566	91.563
Total		20945576	1415886	100.000	100.000

--0.00

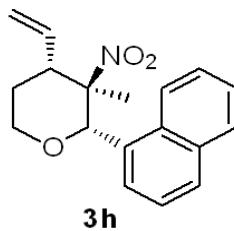
-1.51

1.89  
1.92  
1.93  
1.95  
3.33  
3.66  
3.69  
3.91  
5.16  
5.20  
5.35  
4.32

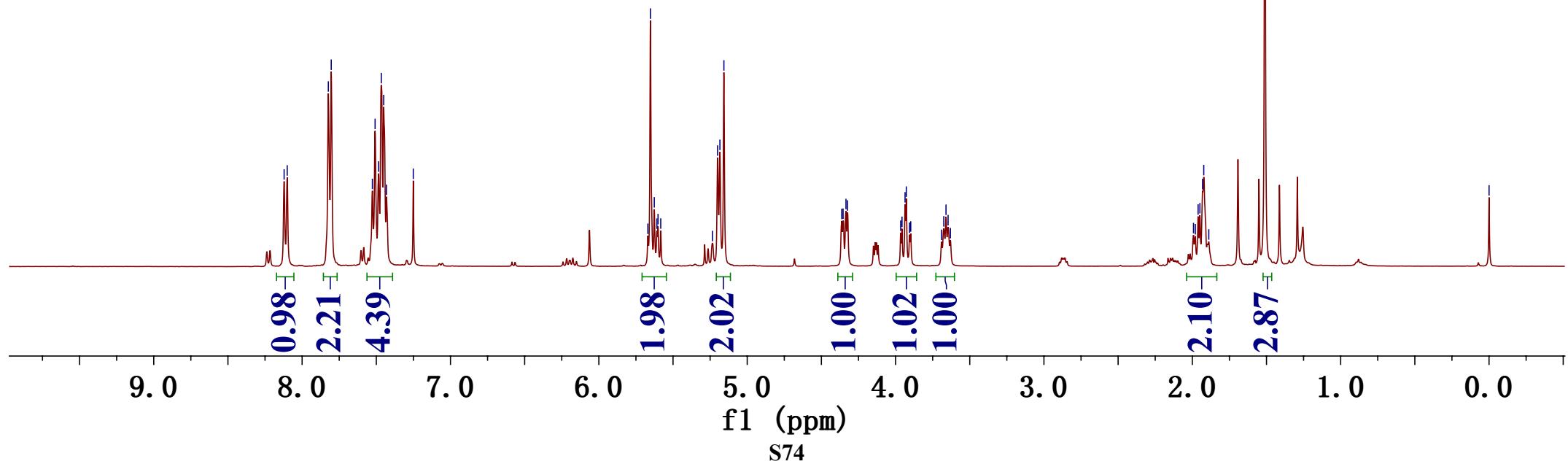
3.94  
5.61  
5.60  
5.58

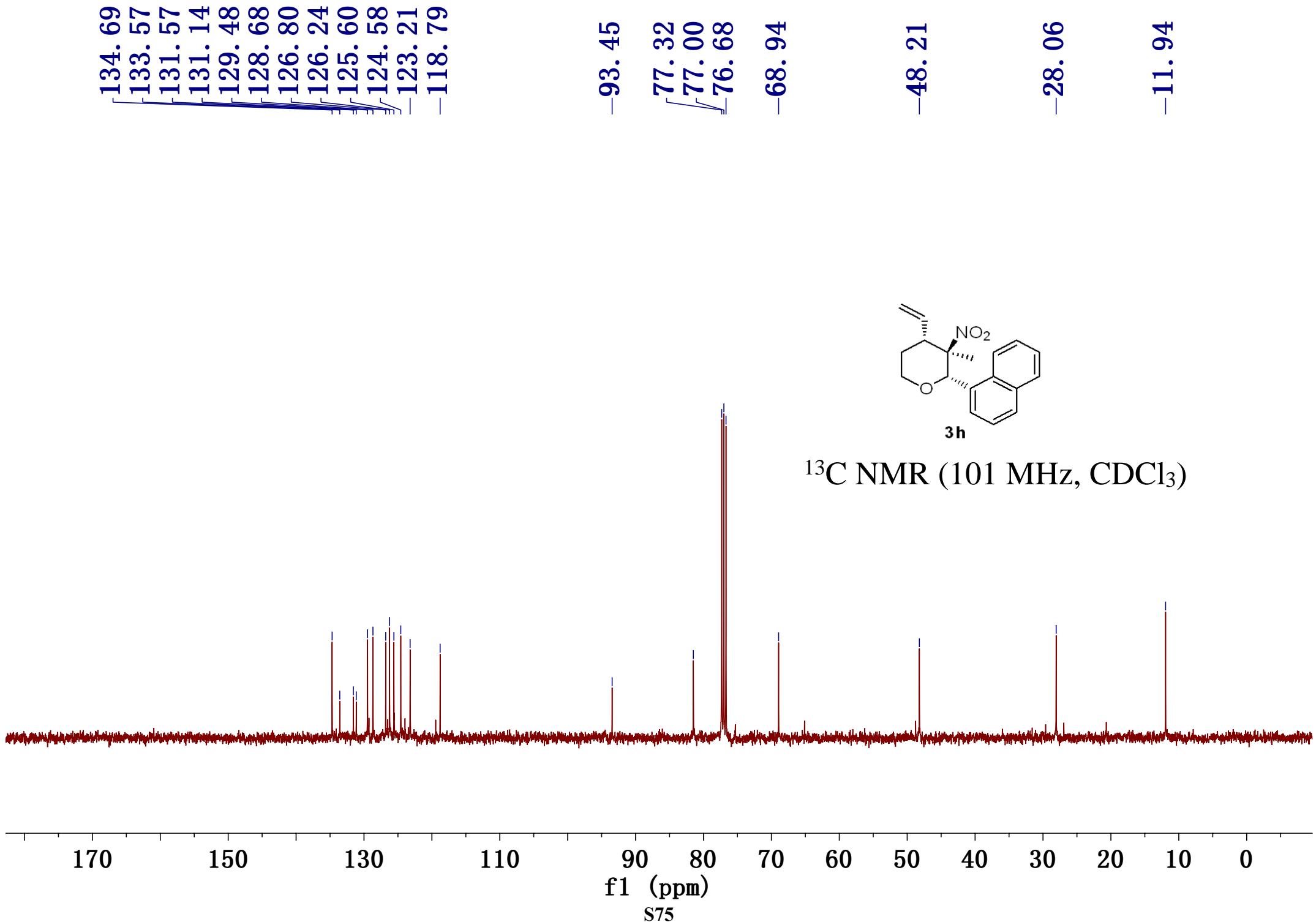
7.47  
7.45  
7.43  
7.65

8.12  
8.10  
7.59  
7.51



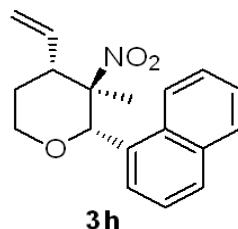
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



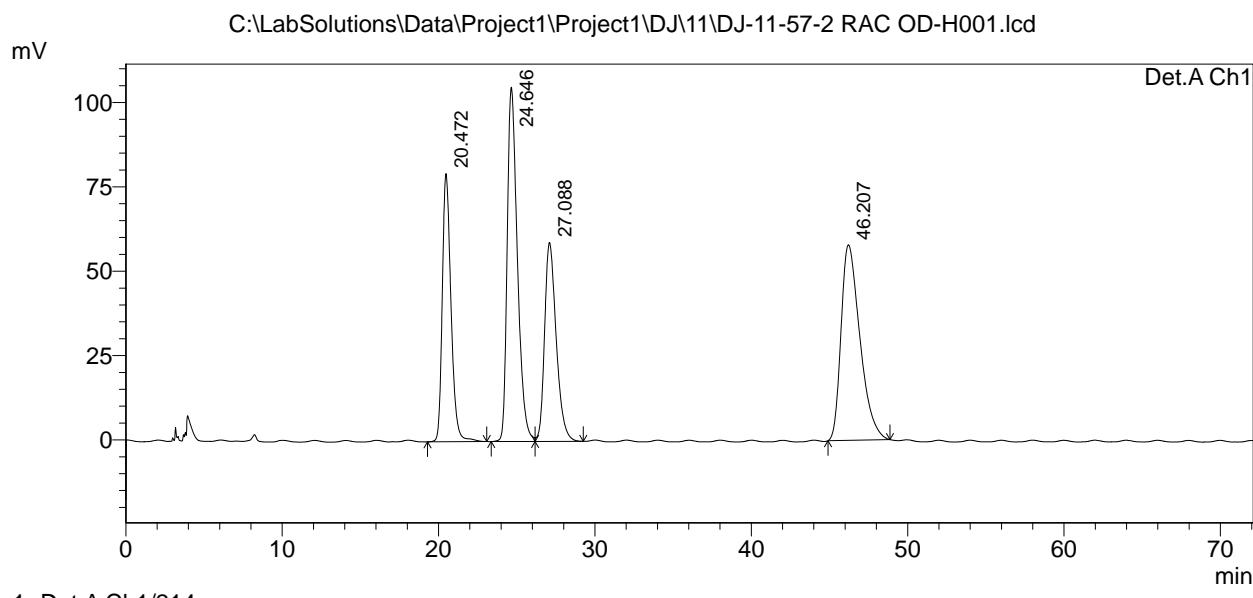


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-57-2 RAC OD-H  
 Sample ID : OD-H,99/1,1,214  
 Vail # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-57-2 RAC OD-H001.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-4-12 17:39:49  
 Data Processed : 2018-4-12 18:51:55



## <Chromatogram>



Detector A Ch1 214nm

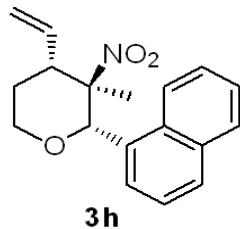
PeakTable

Detector A Ch1 214nm

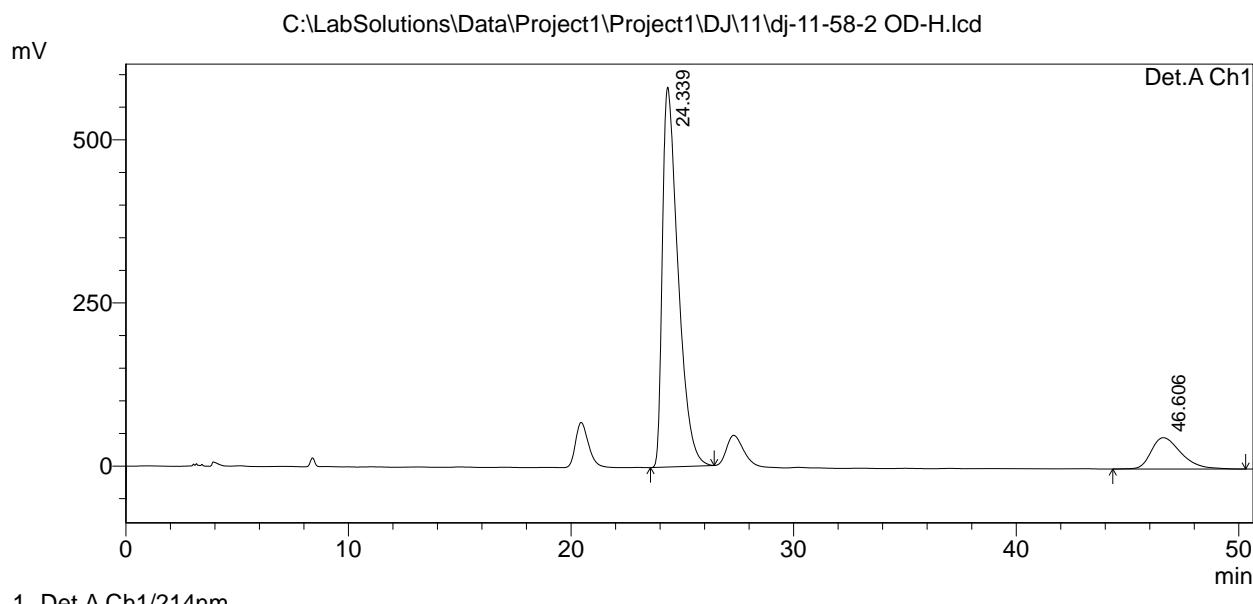
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.472	3077531	79486	19.574	26.368
2	24.646	4751166	105031	30.219	34.842
3	27.088	3049937	59003	19.398	19.573
4	46.207	4844010	57929	30.809	19.217
Total		15722645	301448	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : dj-11-58-2 OD-H  
 Sample ID : OD-H,99/1,1,214  
 Vail # :  
 Injection Volume : 2 uL  
 Data File Name : dj-11-58-2 OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-4-18 8:43:57  
 Data Processed : 2018-4-18 9:34:37



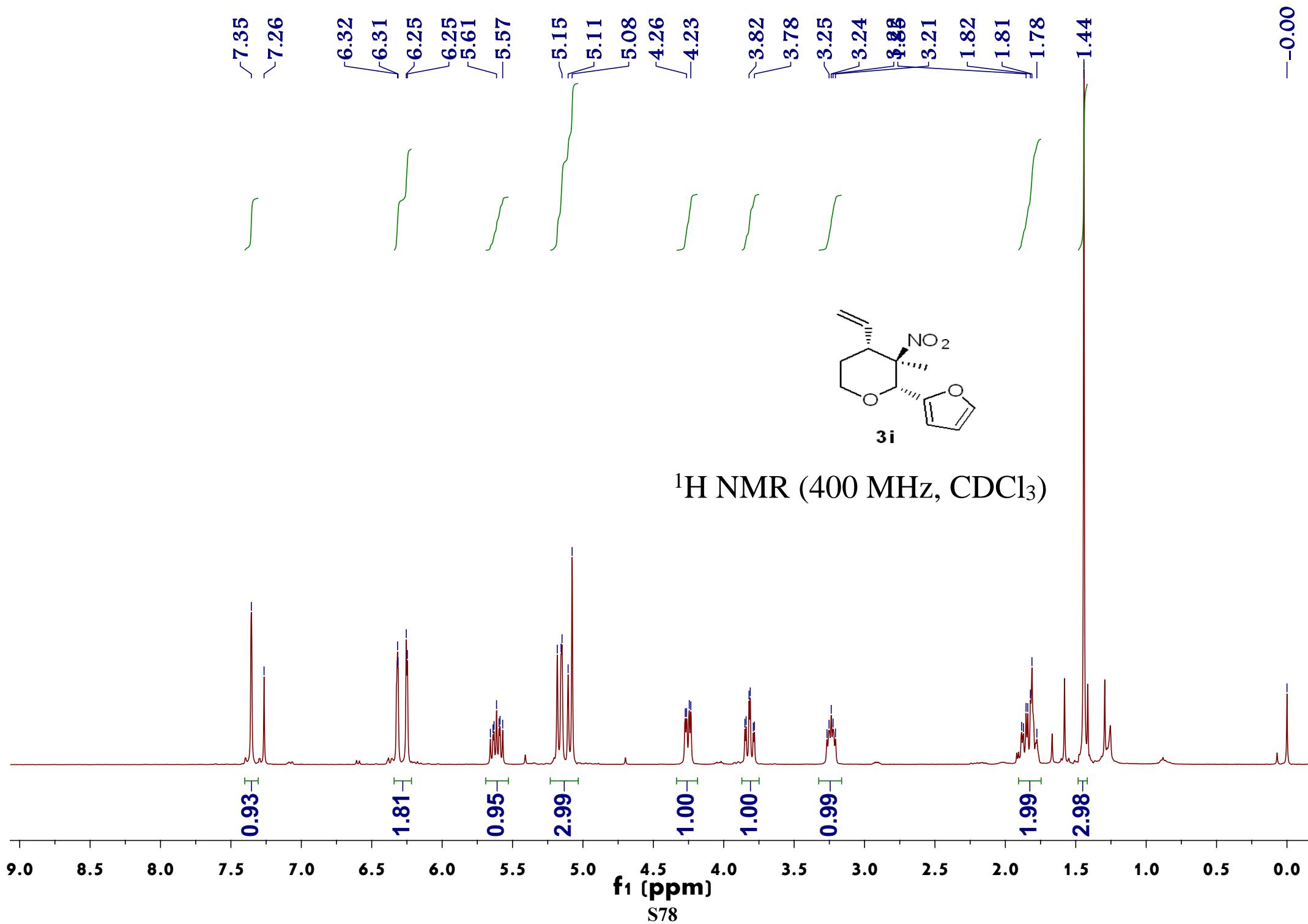
## <Chromatogram>



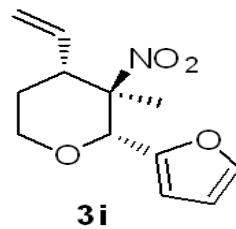
PeakTable

Detector A Ch1 214nm

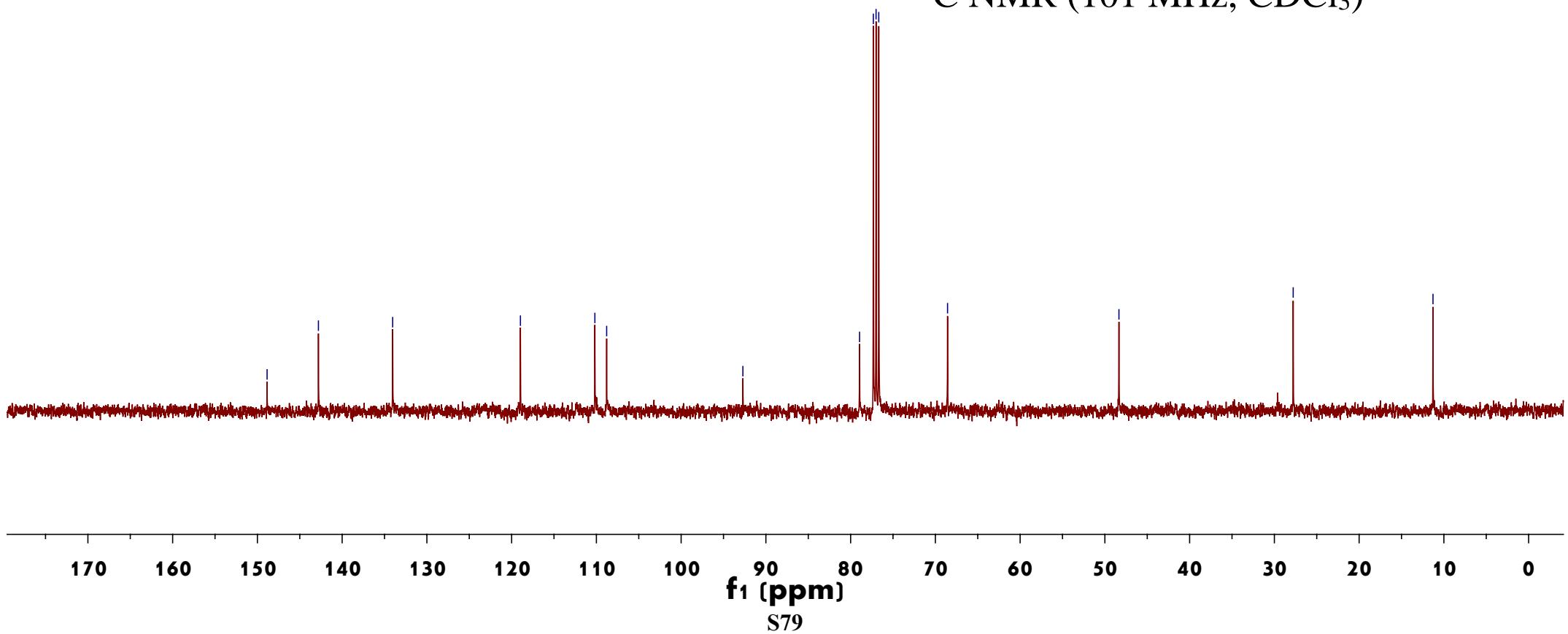
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.339	28557230	582345	86.379	92.376
2	46.606	4502987	48066	13.621	7.624
Total		33060218	630411	100.000	100.000



—148.86  
—142.80  
—134.04  
—118.96  
—110.18  
—108.79  
—92.71  
—77.32  
—76.68  
—68.56  
—48.34  
—27.78  
—11.28

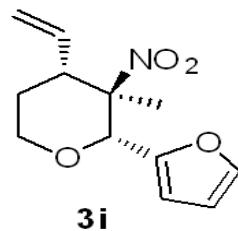


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

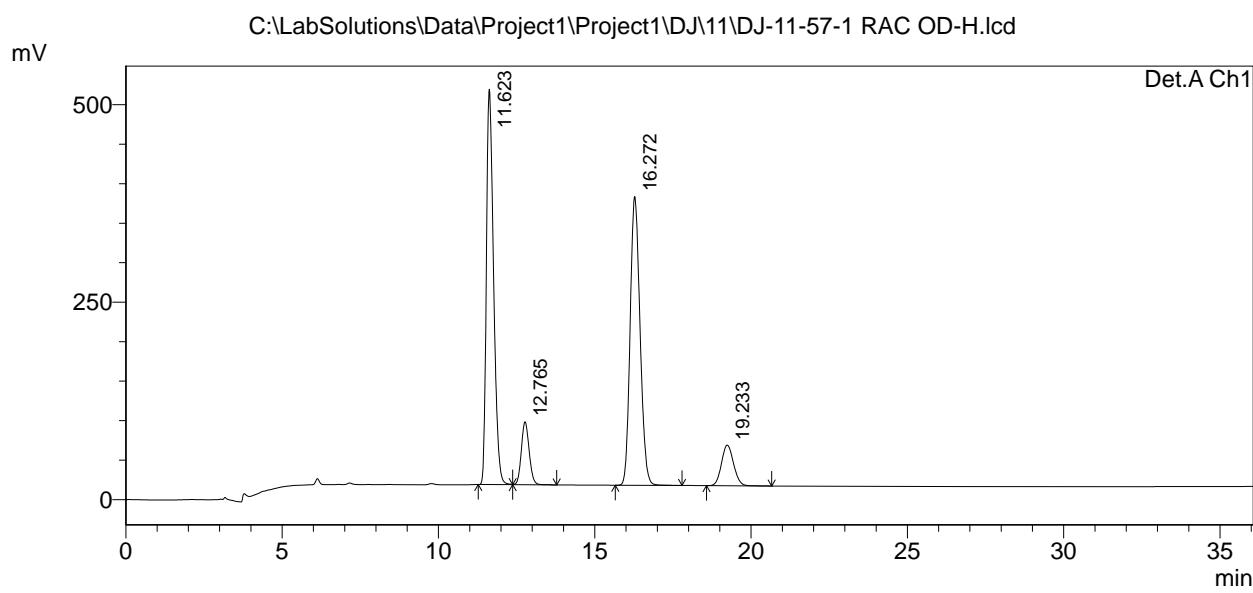


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-57-1 RAC OD-H  
 Sample ID : OD-H,98/2,1,214  
 Vail # :  
 Injection Volume : 2 uL  
 Data File Name : DJ-11-57-1 RAC OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-4-12 16:16:23  
 Data Processed : 2018-4-12 16:52:26



## <Chromatogram>



1 Det.A Ch1/214nm

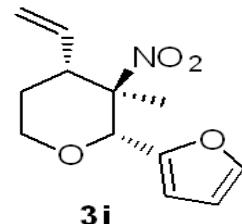
PeakTable

Detector A Ch1 214nm

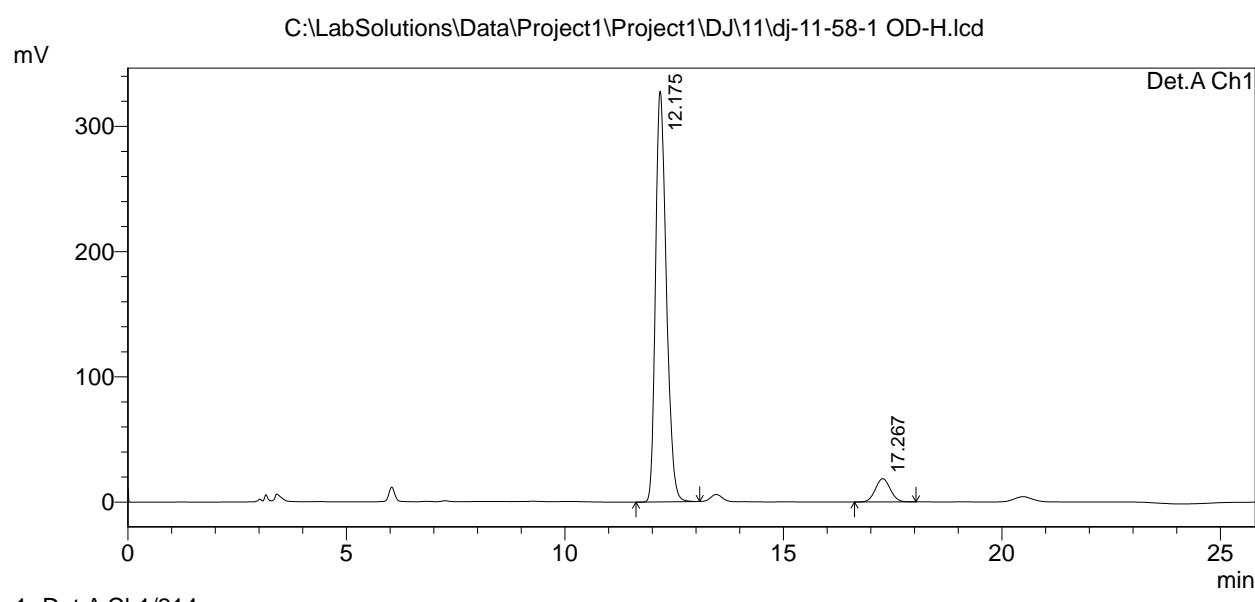
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.623	8002730	500779	42.511	50.188
2	12.765	1387548	79814	7.371	7.999
3	16.272	8050299	365698	42.764	36.650
4	19.233	1384516	51515	7.355	5.163
Total		18825094	997807	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : dj-11-58-1 OD-H  
 Sample ID : OD-H,98/2,1,214  
 Vial # :  
 Injection Volume : 2 uL  
 Data File Name : dj-11-58-1 OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-4-18 9:44:20  
 Data Processed : 2018-4-18 10:10:08



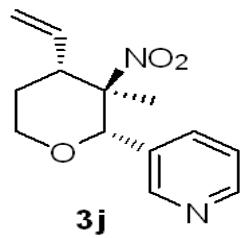
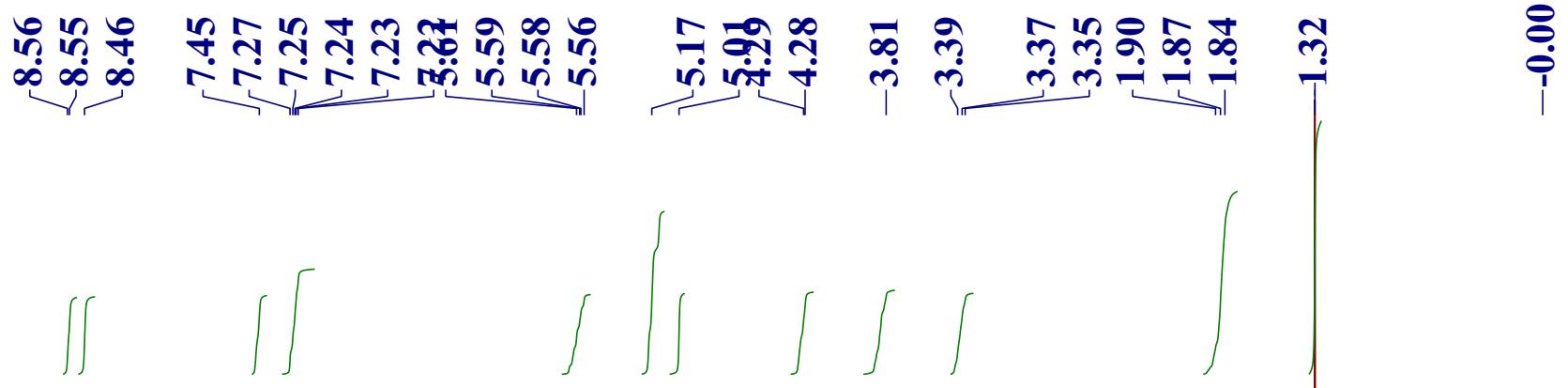
## <Chromatogram>



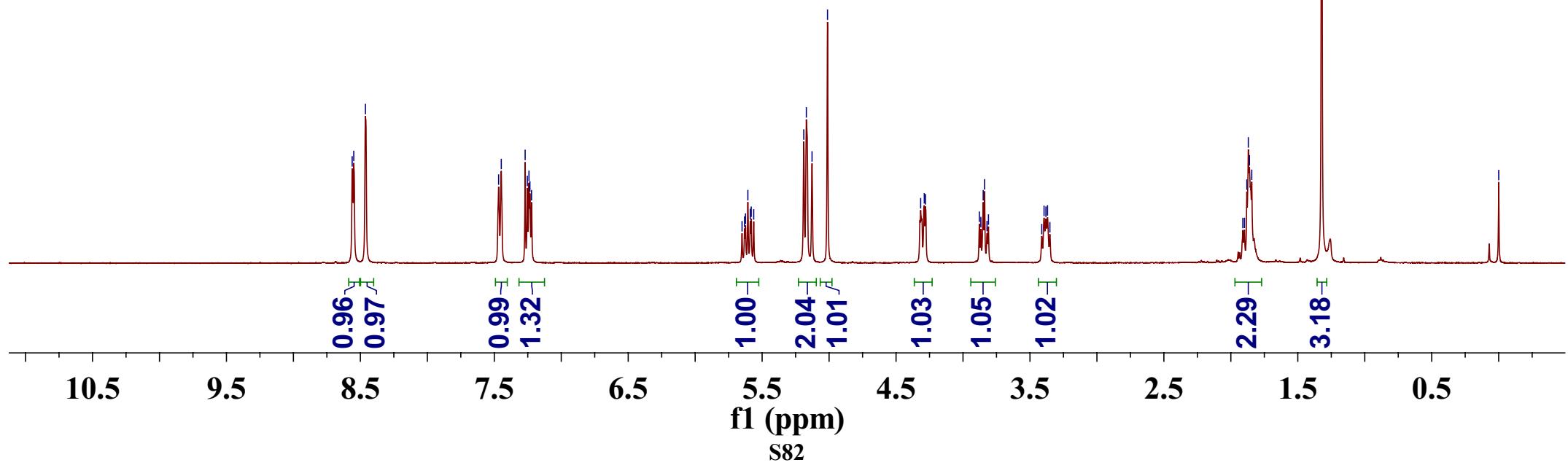
PeakTable

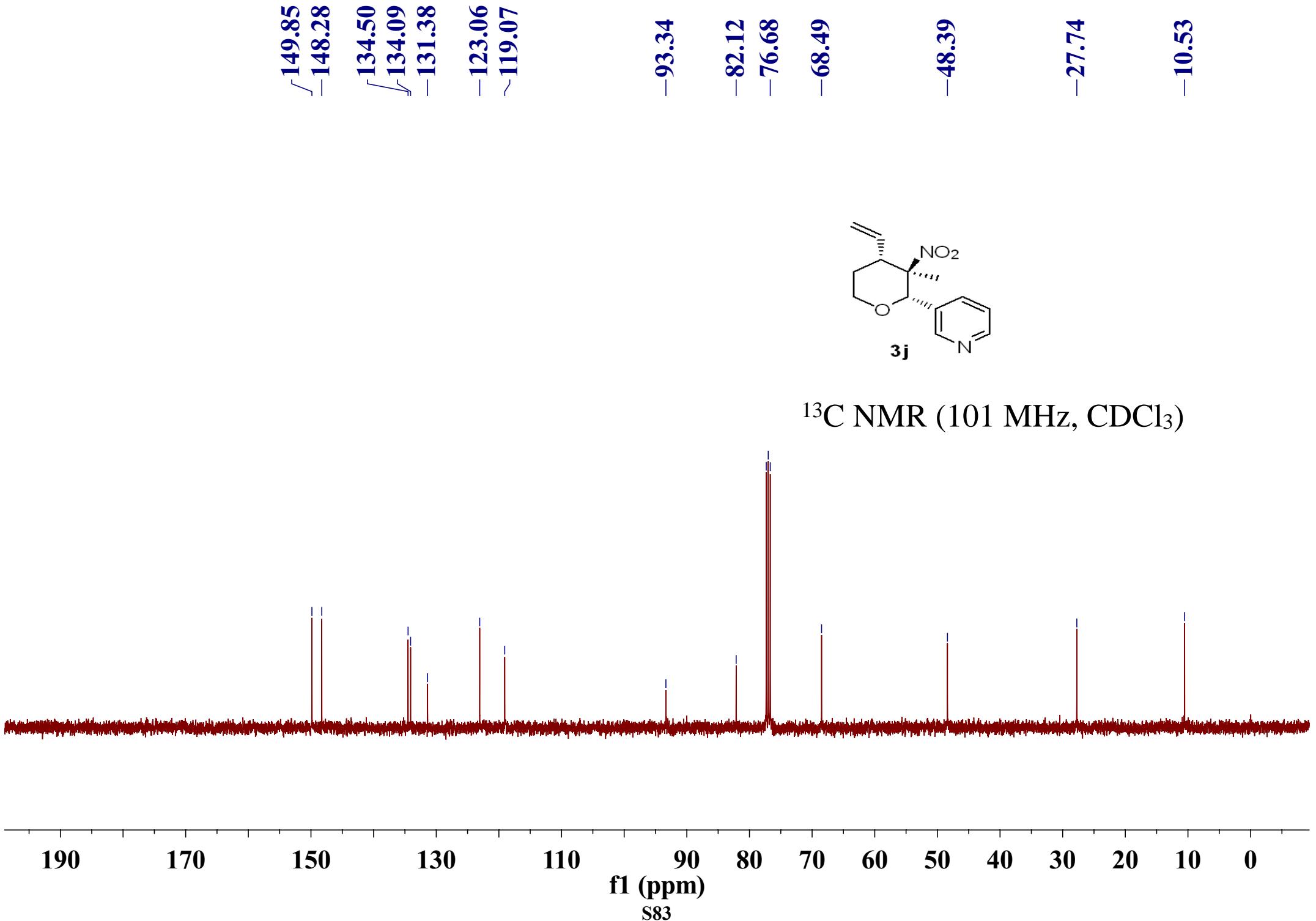
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.175	5637223	327911	92.739	94.634
2	17.267	441359	18594	7.261	5.366
Total		6078582	346505	100.000	100.000



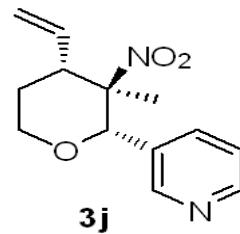
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



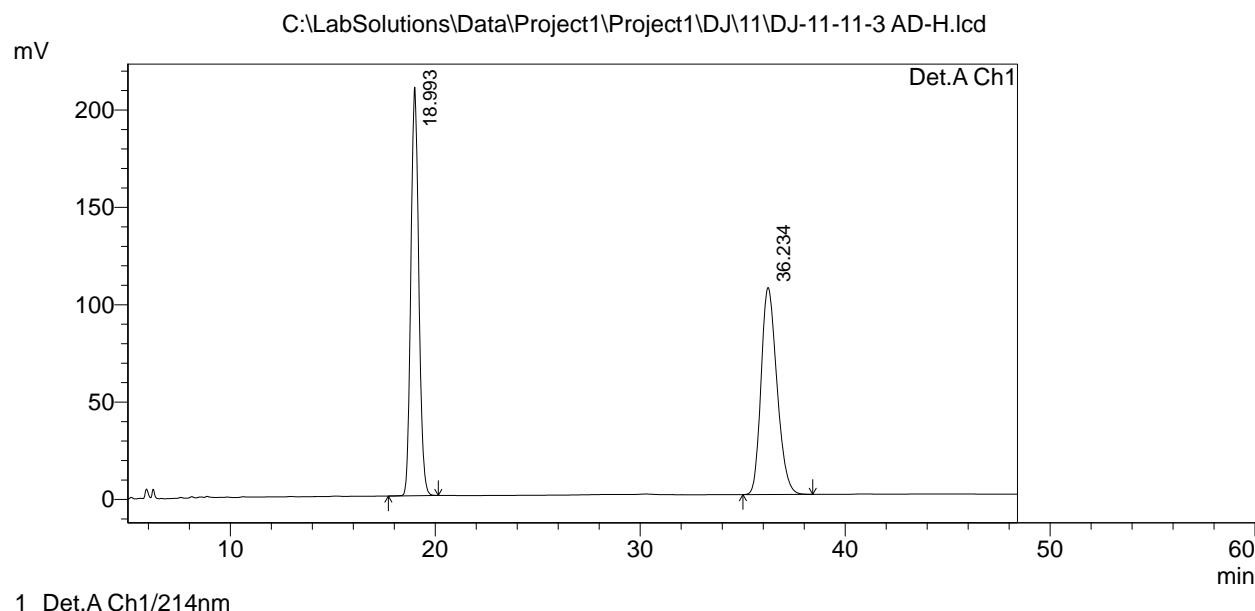


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-11-3 AD-H  
 Sample ID : AD-H,90/10,1.0,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-11-3 AD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-1-31 11:56:57  
 Data Processed : 2018-1-31 12:45:23



## <Chromatogram>



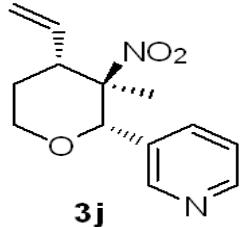
PeakTable

Detector A Ch1 214nm

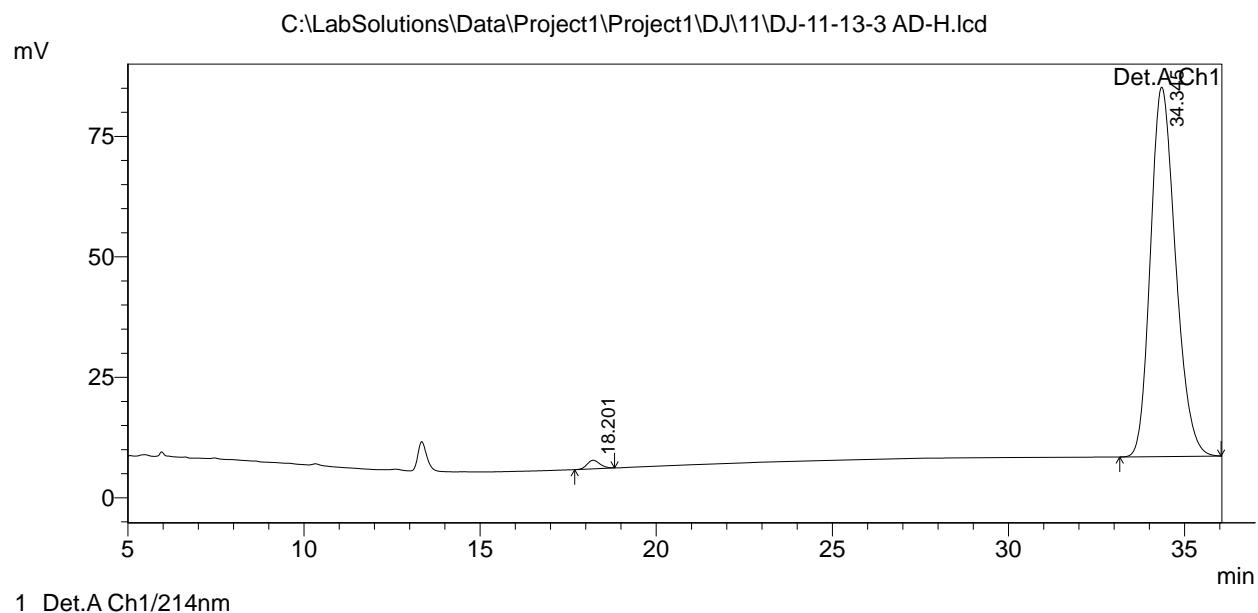
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.993	5658368	209832	49.795	66.385
2	36.234	5705044	106253	50.205	33.615
Total		11363412	316086	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-13-3 AD-H  
 Sample ID : AD-H,90/10,1,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-13-3 AD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-2-4 18:49:26  
 Data Processed : 2018-2-4 19:25:30

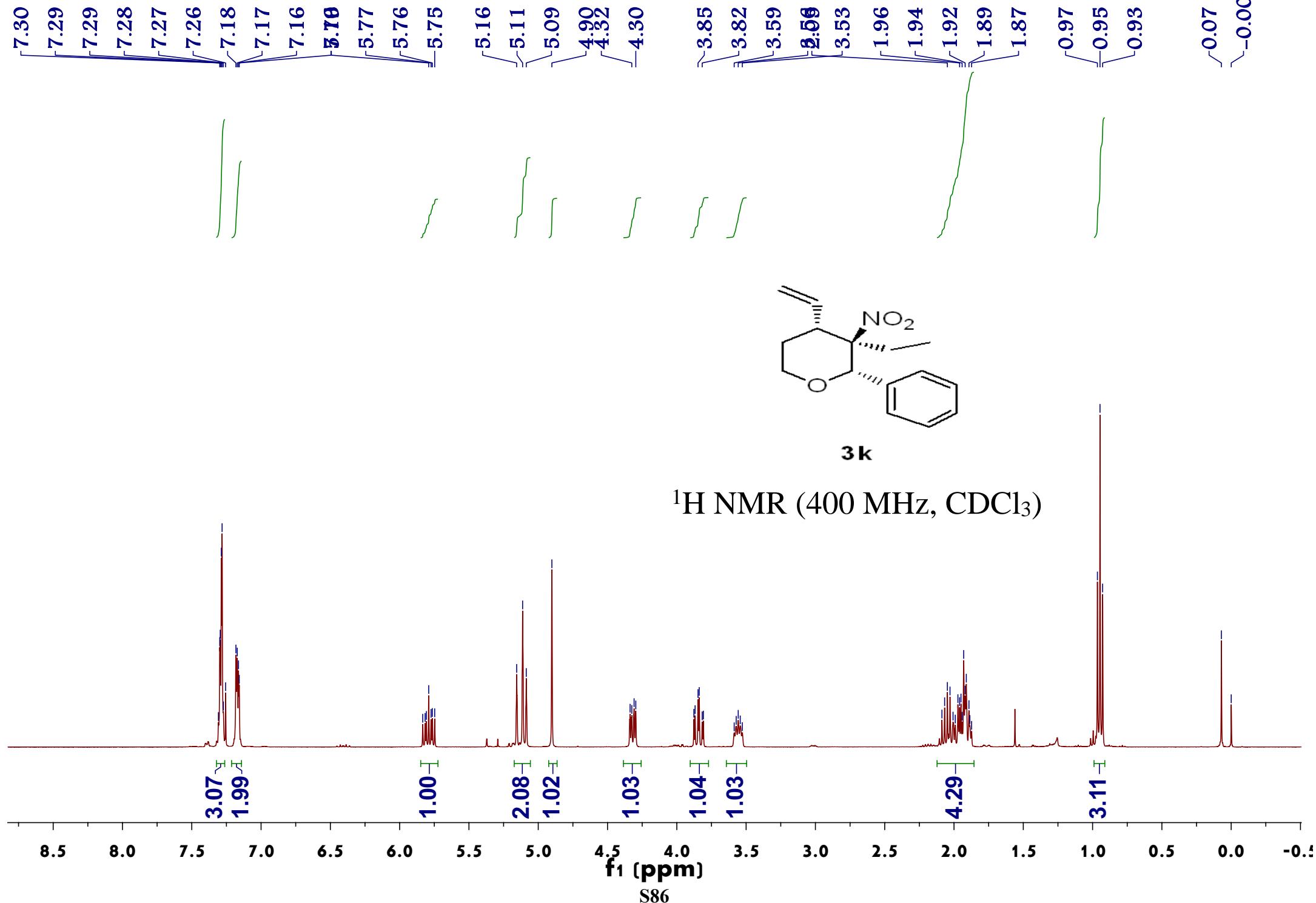


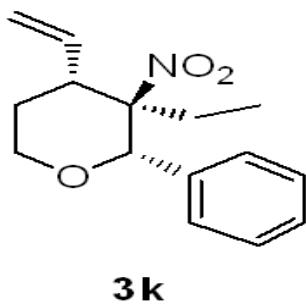
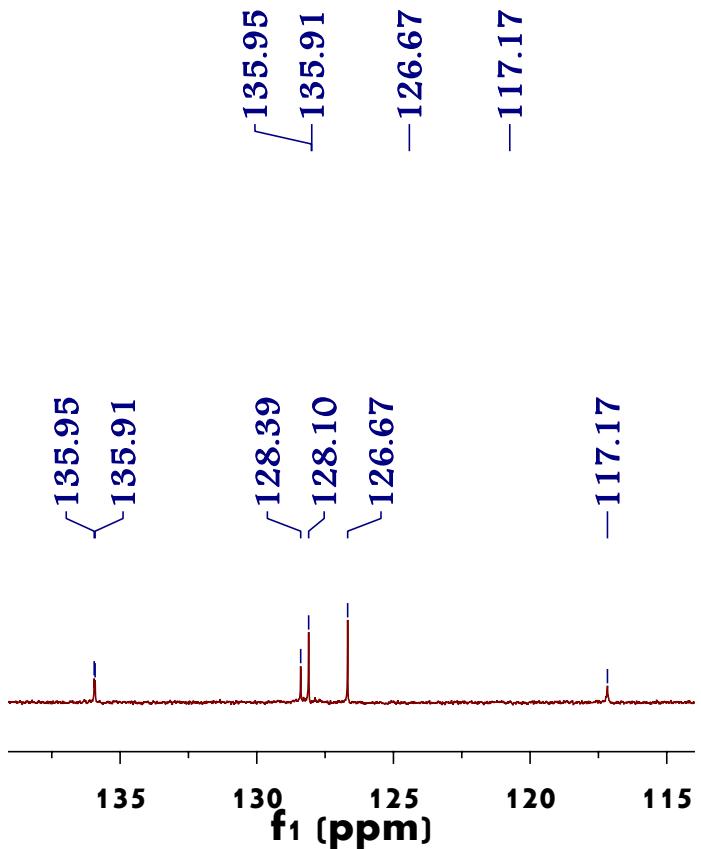
## <Chromatogram>



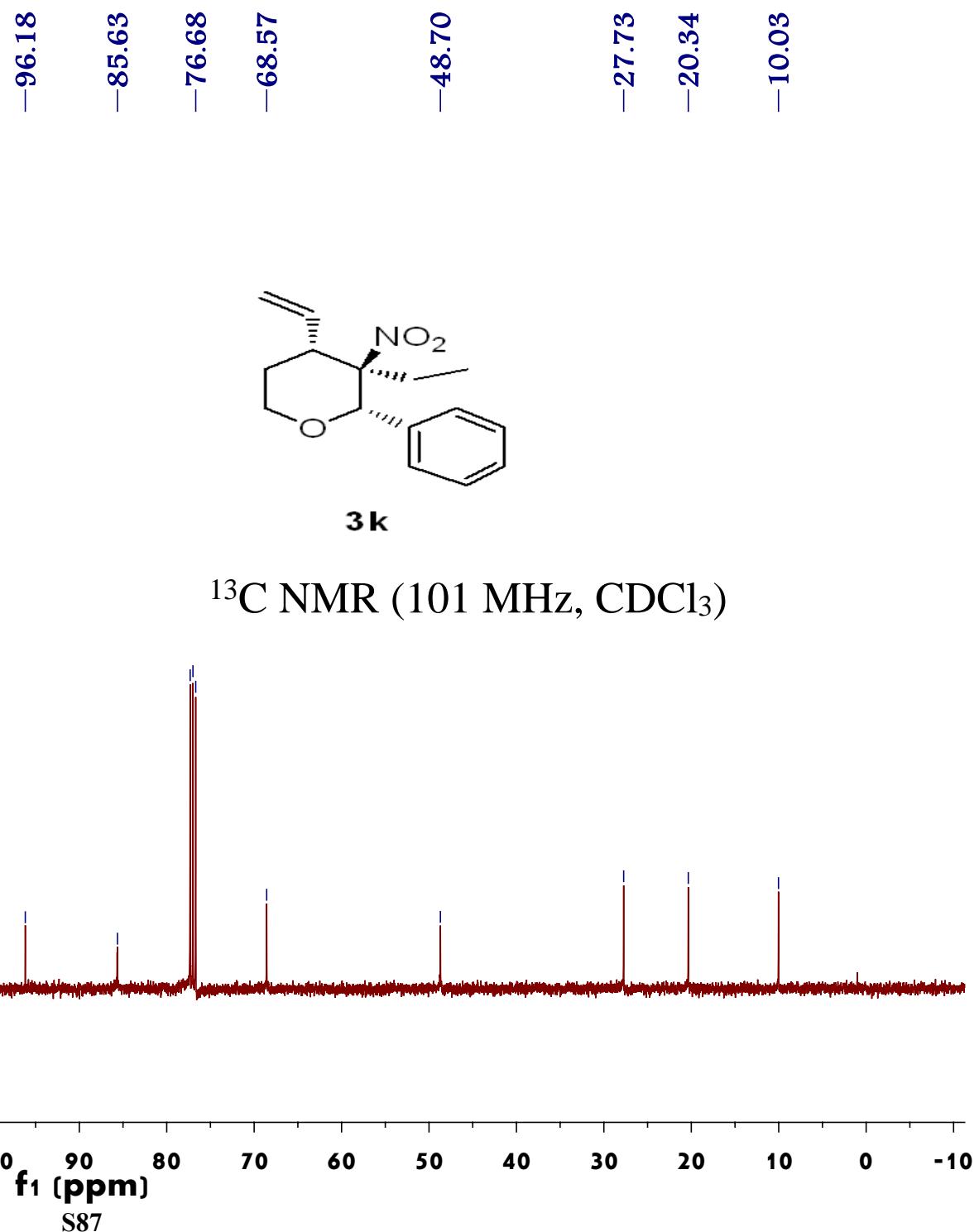
PeakTable

Detector A Ch1 214nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.201	45077	1782	1.173	2.271
2	34.345	3796484	76686	98.827	97.729
Total		3841561	78468	100.000	100.000



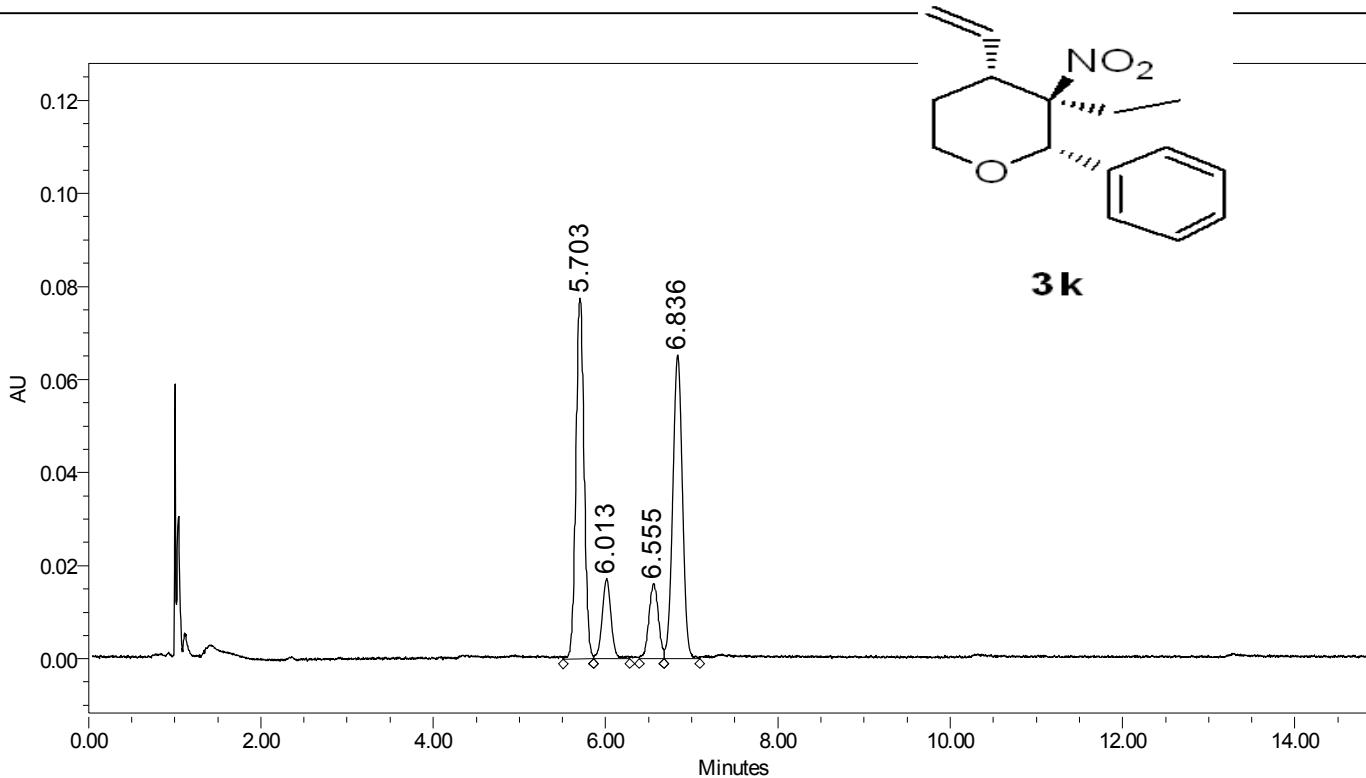


**3k**



## SAMPLE INFORMATION

Sample Name: DJ-11-32-1-RAC-OJ-3-95-5-0.8      Acquired By: System  
Sample Type: Unknown      Sample Set Name:  
Vial: 1:f,4      Acq. Method Set: test  
Injection #: 6      Processing Method: TEST  
Injection Volume: 1.00 ul      Channel Name: PDA Ch1 214nm@4.8nm  
Run Time: 15.0 Minutes      Proc. Chnl. Descr.: PDA Ch1 214nm@4.8nm  
  
Date Acquired: 3/22/2018 1:00:05 PM CST  
Date Processed: 3/22/2018 2:51:07 PM CST



	RT	Area	% Area	Height
1	5.703	508122	40.17	77512
2	6.013	125141	9.89	17242
3	6.555	121565	9.61	16093
4	6.836	509999	40.32	65266

Reported by User: System

Report Method: Default Individual Report

Report Method ID 1271

Page: 1 of 1

Project Name: TEST

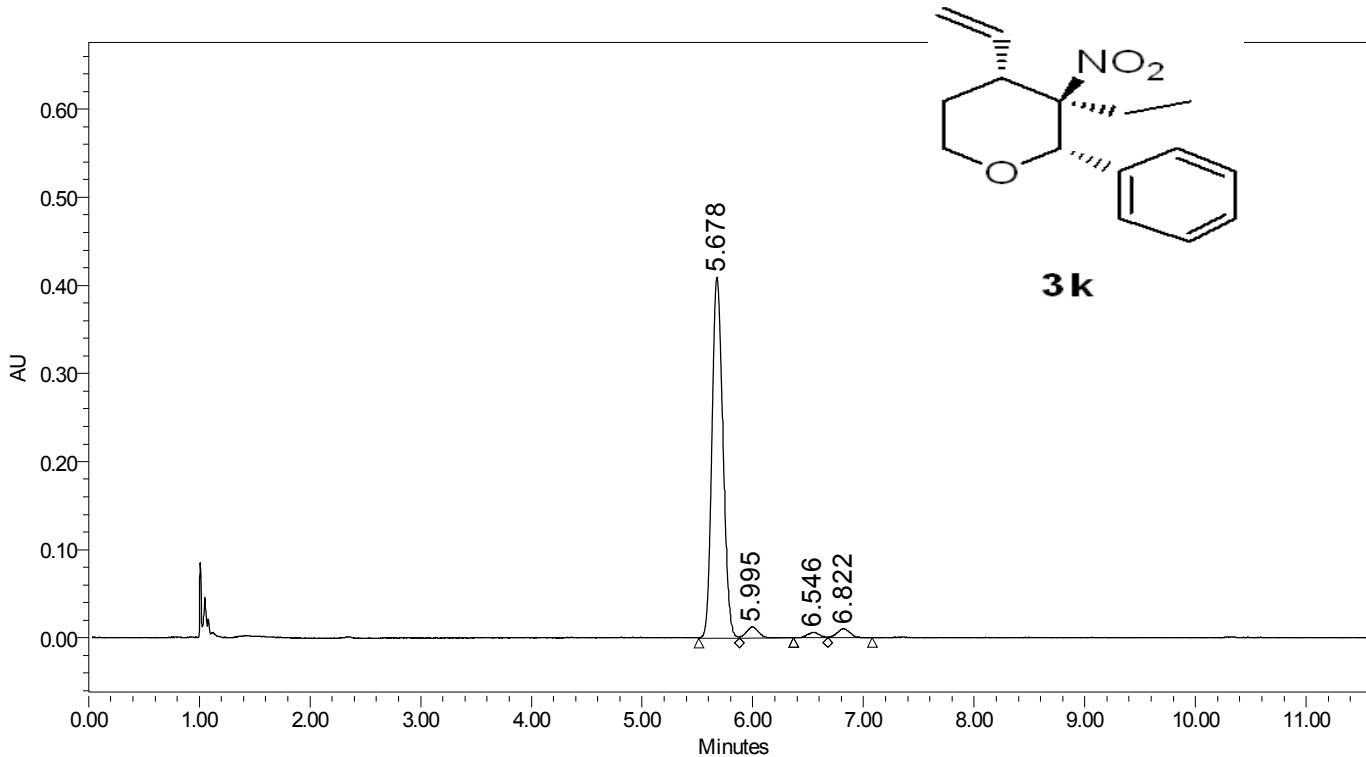
Date Printed:

3/22/2018

3:16:46 PM PRC

## SAMPLE INFORMATION

Sample Name: DJ-11-34-1 Acquired By: System  
Sample Type: Unknown Sample Set Name:  
Vial: 1:f,5 Acq. Method Set: test  
Injection #: 1 Processing Method TEST  
Injection Volume: 2.00 ul Channel Name: PDA Ch1 214nm@4.8nm  
Run Time: 15.0 Minutes Proc. Chnl. Descr.: PDA Ch1 214nm@4.8nm  
  
Date Acquired: 3/22/2018 1:16:24 PM CST  
Date Processed: 3/22/2018 2:51:25 PM CST



	RT	Area	% Area	Height
1	5.678	2826815	92.42	409372
2	5.995	96050	3.14	12528
3	6.546	49951	1.63	6262
4	6.822	85702	2.80	10279

Reported by User: System

Report Method: Default Individual Report

Report Method ID 1271

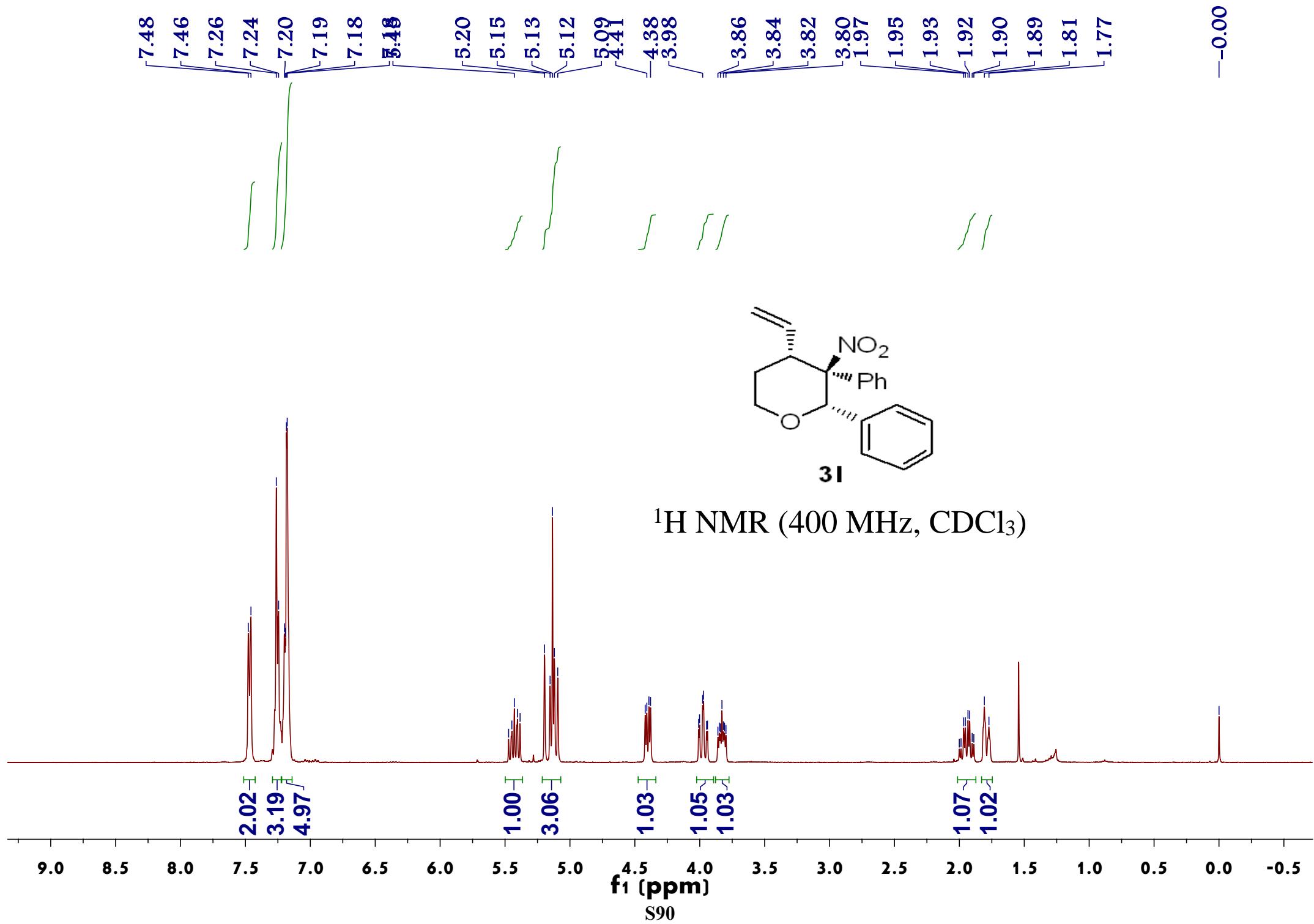
Page: 1 of 1

Project Name: TEST

Date Printed:

3/22/2018

3:16:02 PM PRC



135.77  
135.44  
130.97  
128.43  
128.04  
127.71  
126.62

-118.67

-99.78

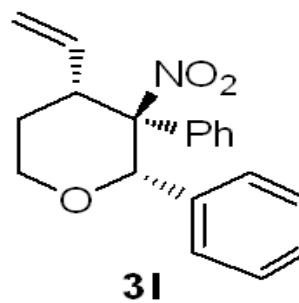
-87.04

-76.68

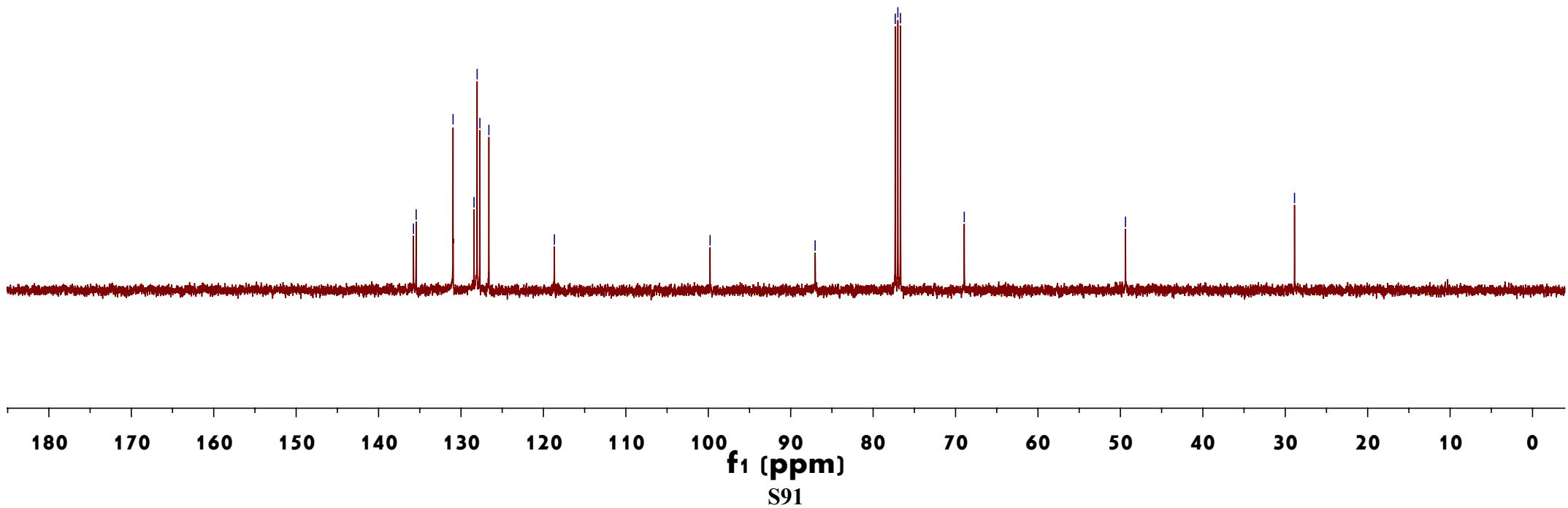
-68.94

-49.38

-28.87

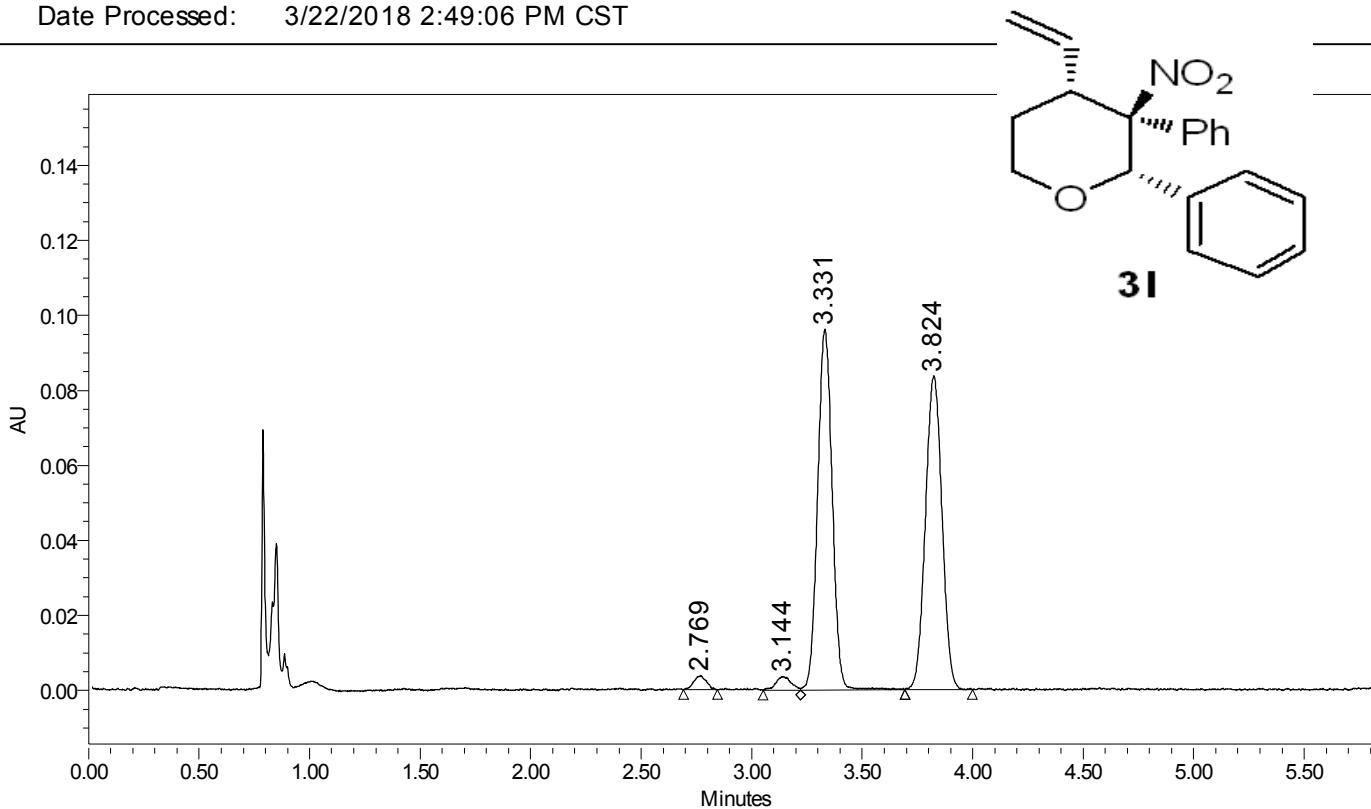


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



## SAMPLE INFORMATION

Sample Name: DJ-11-32-2-RAC-OJ-9-1-1      Acquired By: System  
Sample Type: Unknown      Sample Set Name:  
Vial: 1:f,6      Acq. Method Set: test  
Injection #: 1      Processing Method: TEST  
Injection Volume: 3.00 ul      Channel Name: PDA Ch1 214nm@4.8nm  
Run Time: 15.0 Minutes      Proc. Chnl. Descr.: PDA Ch1 214nm@4.8nm  
  
Date Acquired: 3/22/2018 2:30:13 PM CST  
Date Processed: 3/22/2018 2:49:06 PM CST



	RT	Area	% Area	Height
1	2.769	15104	1.67	3729
2	3.144	17000	1.88	3596
3	3.331	439329	48.58	96119
4	3.824	432990	47.87	83596

Reported by User: System

Report Method: Default Individual Report

Report Method ID 1271

Page: 1 of 1

Project Name: TEST

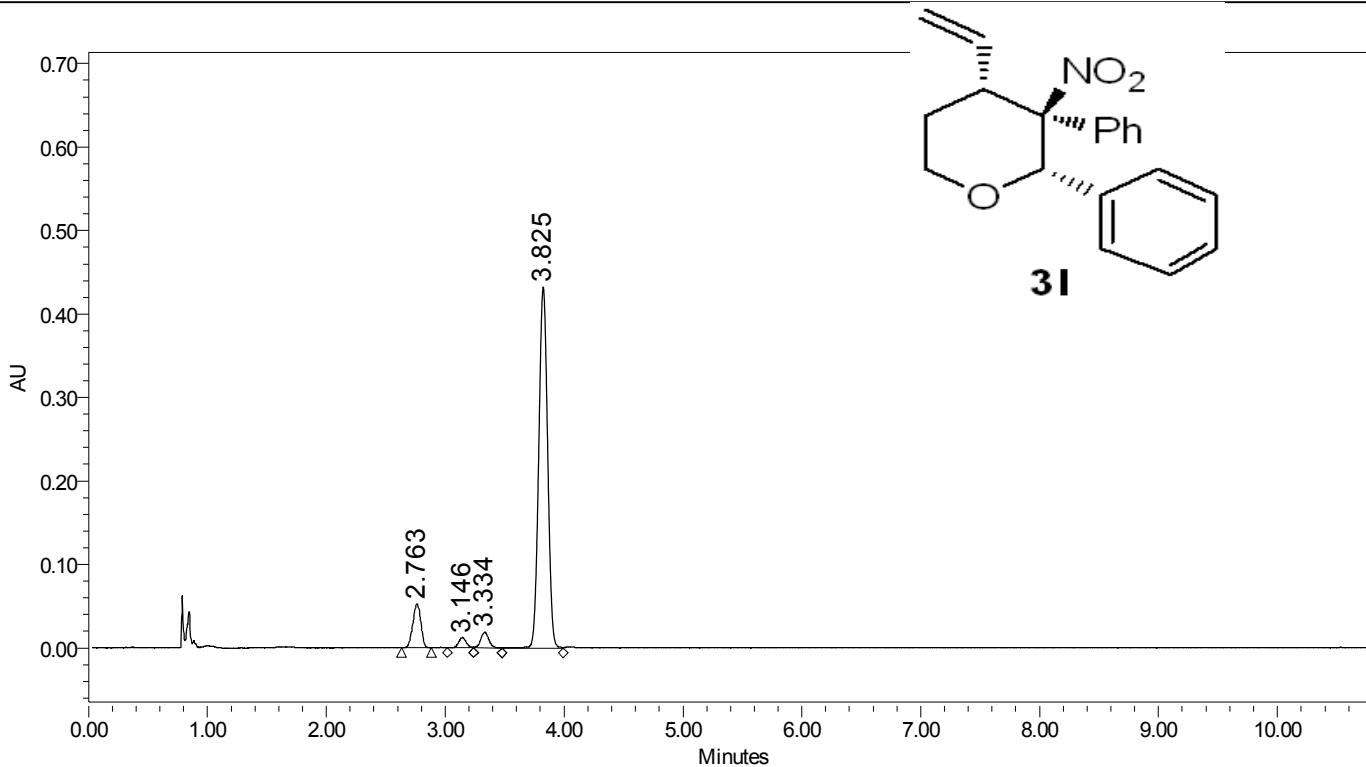
Date Printed:

3/22/2018

3:17:30 PM PRC

## SAMPLE INFORMATION

Sample Name: DJ-11-34-2      Acquired By: System  
Sample Type: Unknown      Sample Set Name:  
Vial: 1:f,7      Acq. Method Set: test  
Injection #: 1      Processing Method: TEST  
Injection Volume: 3.00 ul      Channel Name: PDA Ch1 214nm@4.8nm  
Run Time: 15.0 Minutes      Proc. Chnl. Descr.: PDA Ch1 214nm@4.8nm  
  
Date Acquired: 3/22/2018 2:37:21 PM CST  
Date Processed: 3/22/2018 2:48:44 PM CST



	RT	Area	% Area	Height
1	2.763	242823	9.21	52569
2	3.146	54446	2.07	12323
3	3.334	89289	3.39	18987
4	3.825	2248964	85.33	432142

Reported by User: System

Report Method: Default Individual Report

Report Method ID 1271

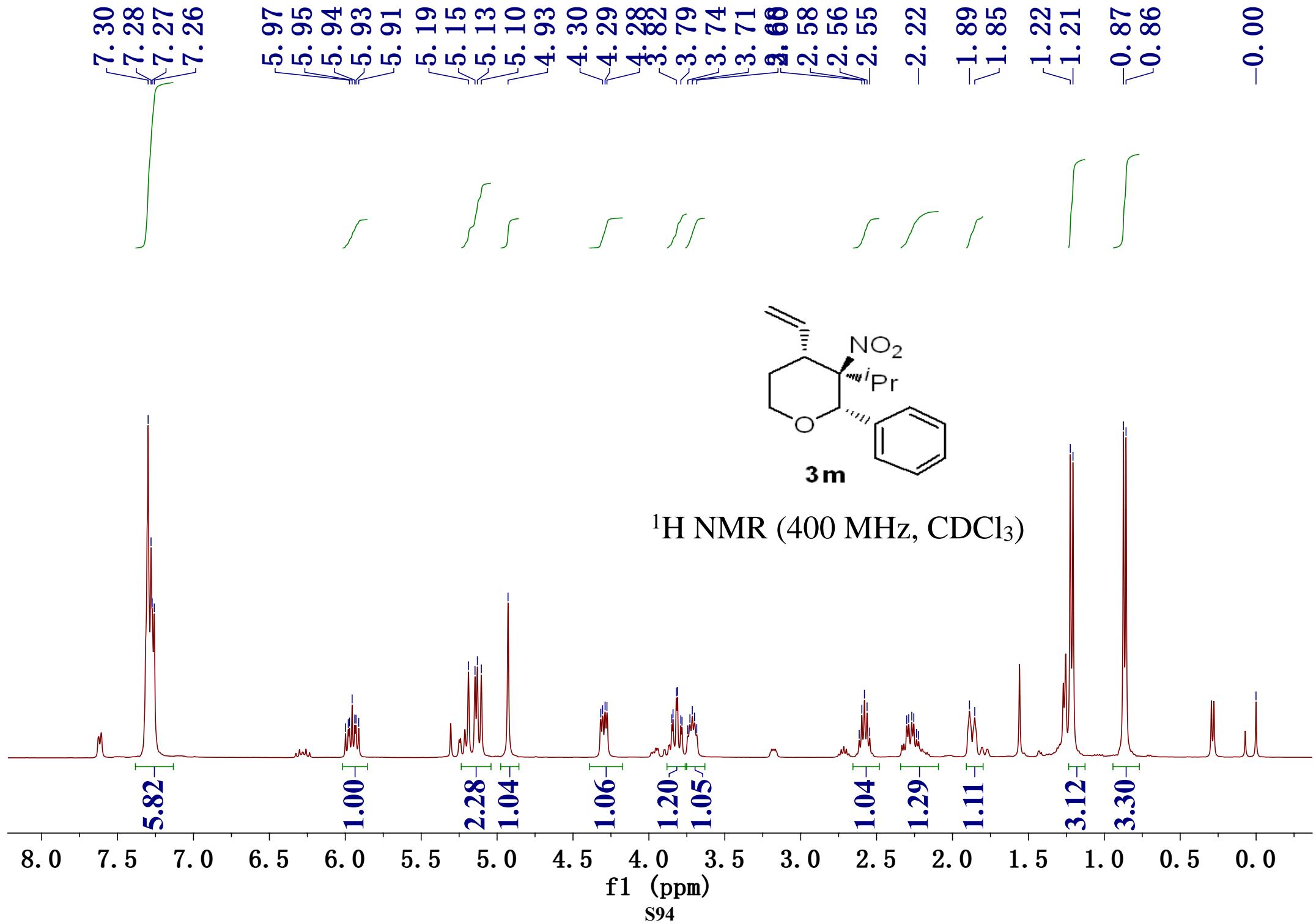
Page: 1 of 1

Project Name: TEST

Date Printed:

3/22/2018

3:17:54 PM PRC



136.94  
136.86

127.94  
127.40

-116.50

-99.46

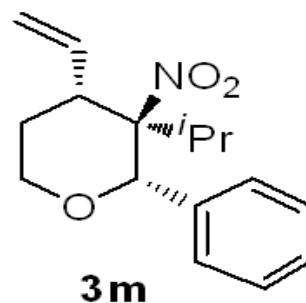
-86.55  
77.00  
76.68

-68.06  
-63.23

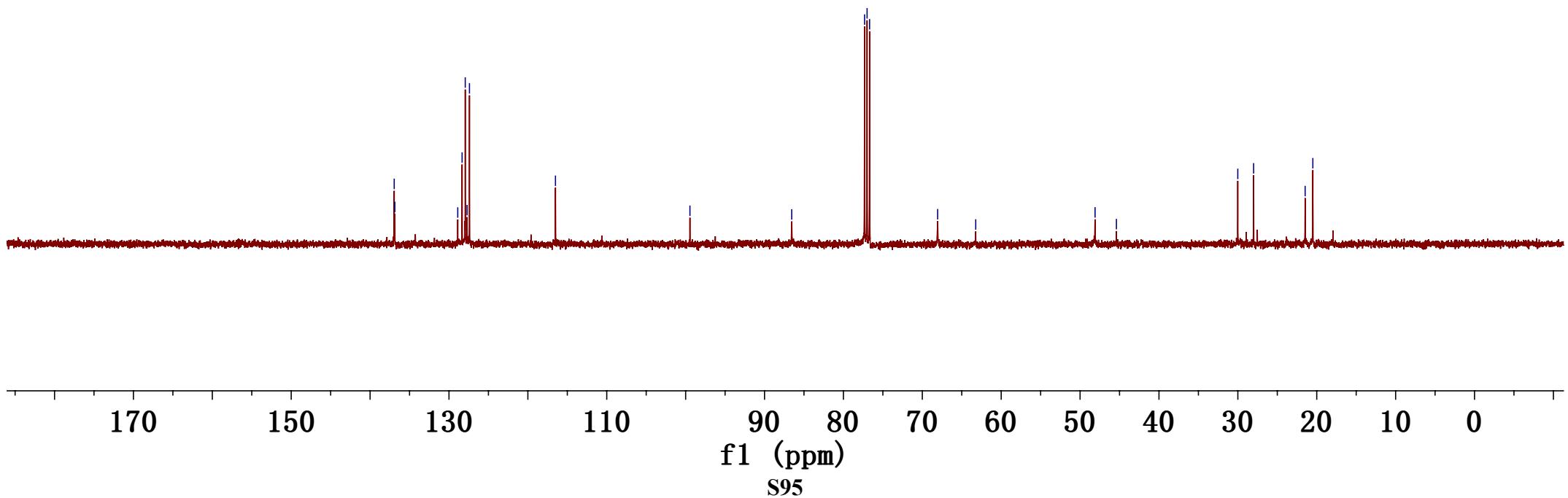
-48.10  
-45.40

30.01  
28.00

-21.47  
-20.49



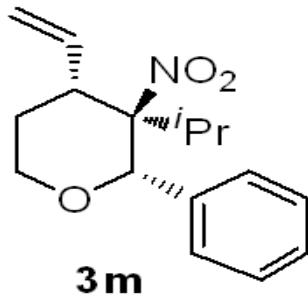
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



# ==== Shimadzu LCsolution Analysis Report ====

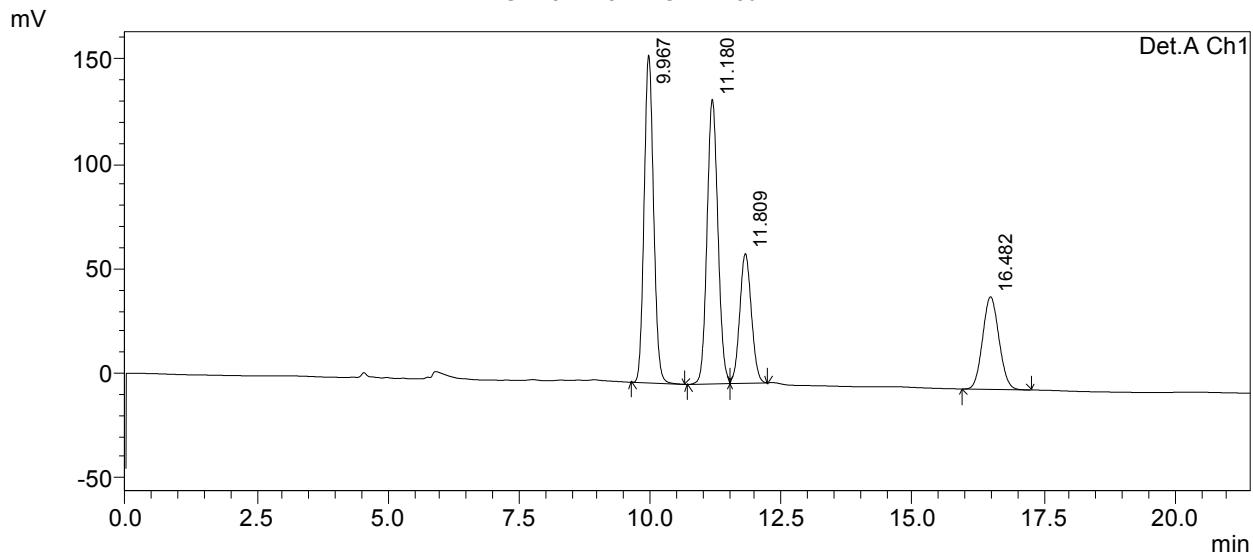
G:\DJ-14-34-1 OD-H.lcd

Acquired by : Admin  
 Sample Name : DJ-14-34-1 OD-H  
 Sample ID : OD-H,99/1,0.7,214  
 Vial # :  
 Injection Volume : 1 uL  
 Data File Name : DJ-14-34-1 OD-H.lcd  
 Method File Name : 1.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2019-3-18 20:11:39  
 Data Processed : 2019-3-18 20:33:06



## <Chromatogram>

G:\DJ-14-34-1 OD-H.lcd



PeakTable

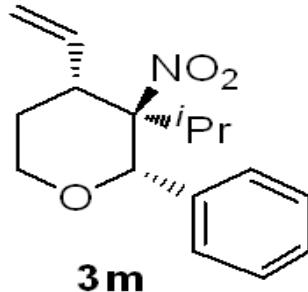
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.967	1964831	156464	33.645	39.274
2	11.180	1959191	135855	33.548	34.101
3	11.809	955296	61898	16.358	15.537
4	16.482	960582	44170	16.449	11.087
Total		5839901	398387	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

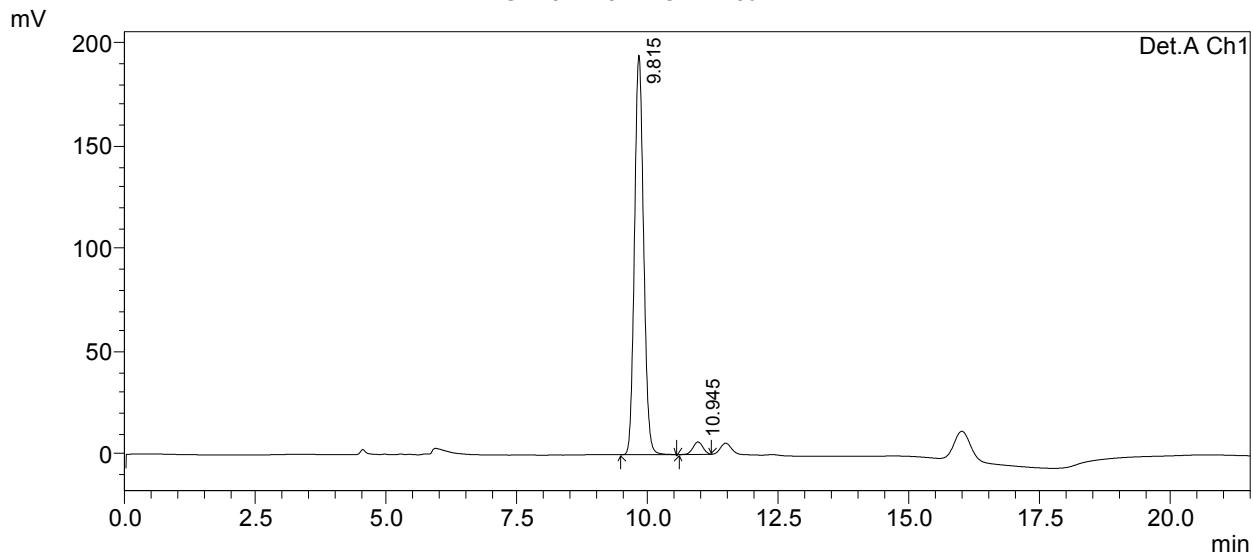
G:\DJ-14-34-2 OD-H.lcd

Acquired by : Admin  
 Sample Name : DJ-14-34-2 OD-H  
 Sample ID : OD-H,99/1,0.7,214  
 Vail # :  
 Injection Volume : 1 uL  
 Data File Name : DJ-14-34-2 OD-H.lcd  
 Method File Name : 1.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2019-3-18 20:34:27  
 Data Processed : 2019-3-18 20:55:58



## <Chromatogram>

G:\DJ-14-34-2 OD-H.lcd



1 Det.A Ch1/214nm

PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.815	2357774	194539	96.723	96.986
2	10.945	79883	6046	3.277	3.014
Total		2437657	200585	100.000	100.000

-7.27

5.60  
5.58  
5.57  
5.55

5.13  
5.09

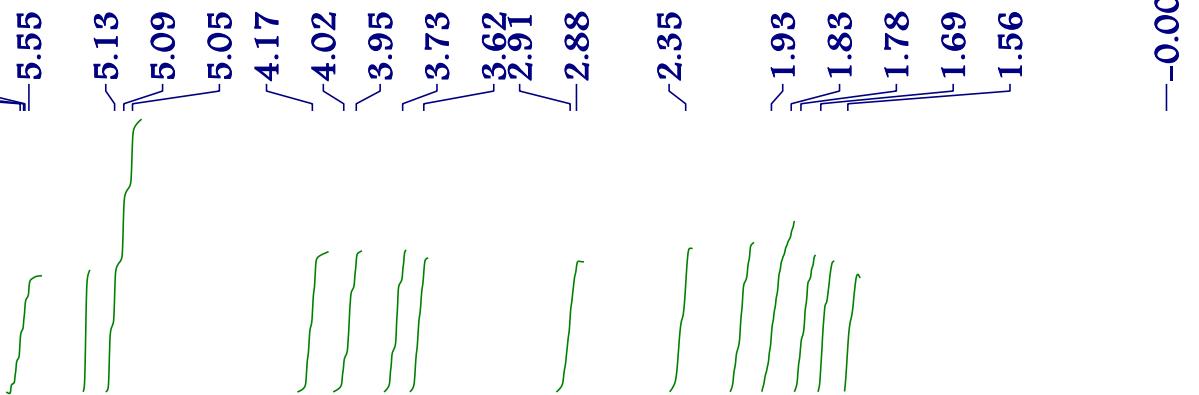
5.05  
4.17  
4.02

3.95  
3.73  
3.62  
2.91  
2.88

2.35

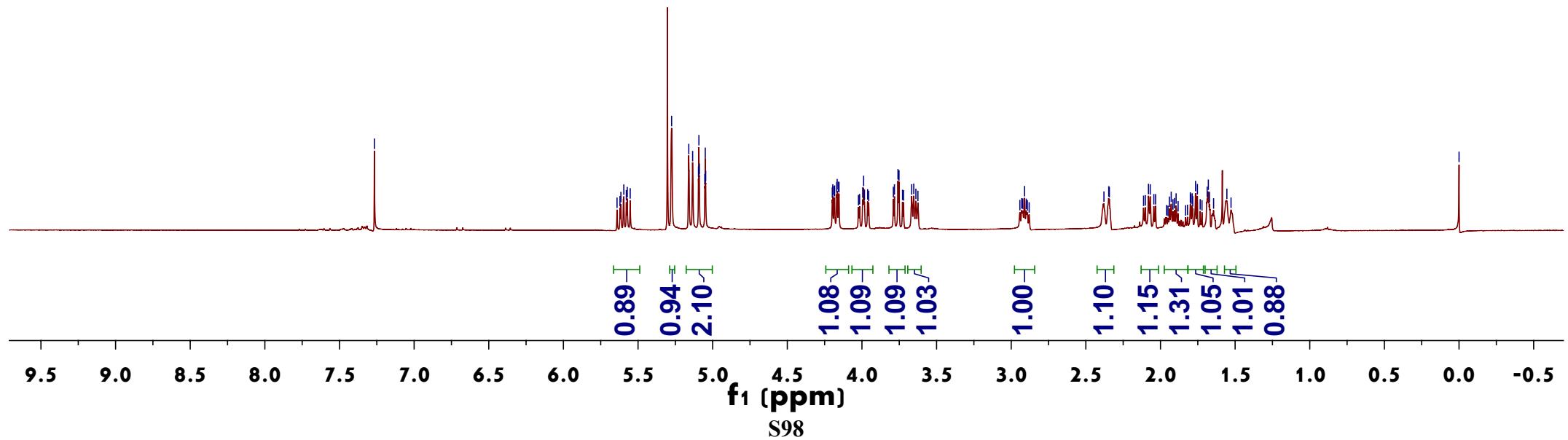
1.93  
1.83  
1.78  
1.69  
1.56

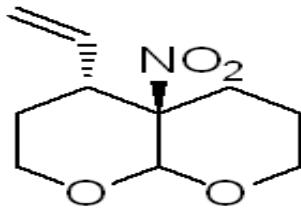
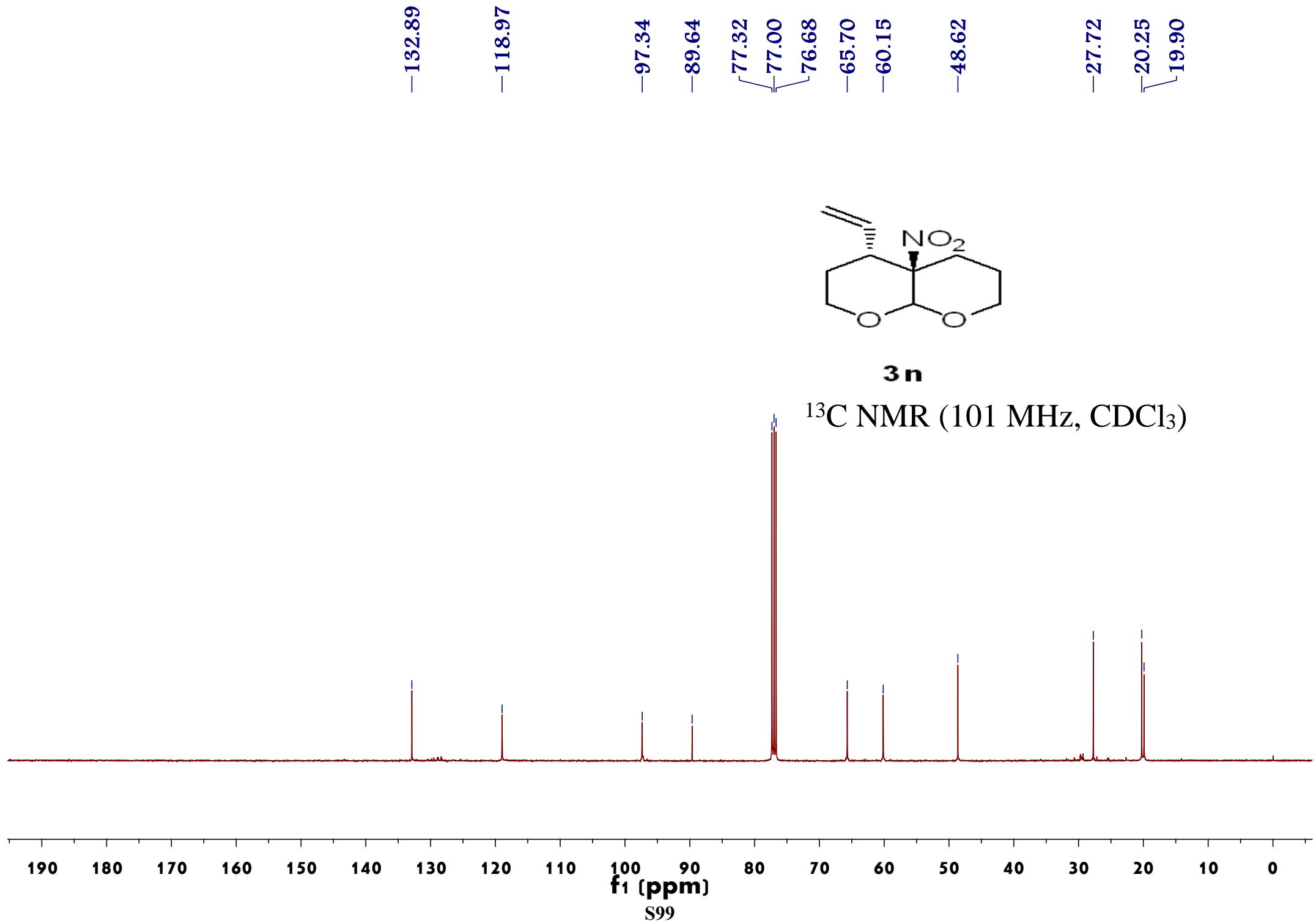
-0.00



**3n**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



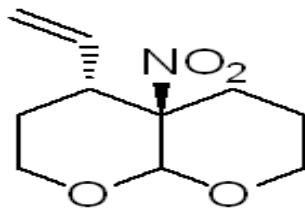


3 n

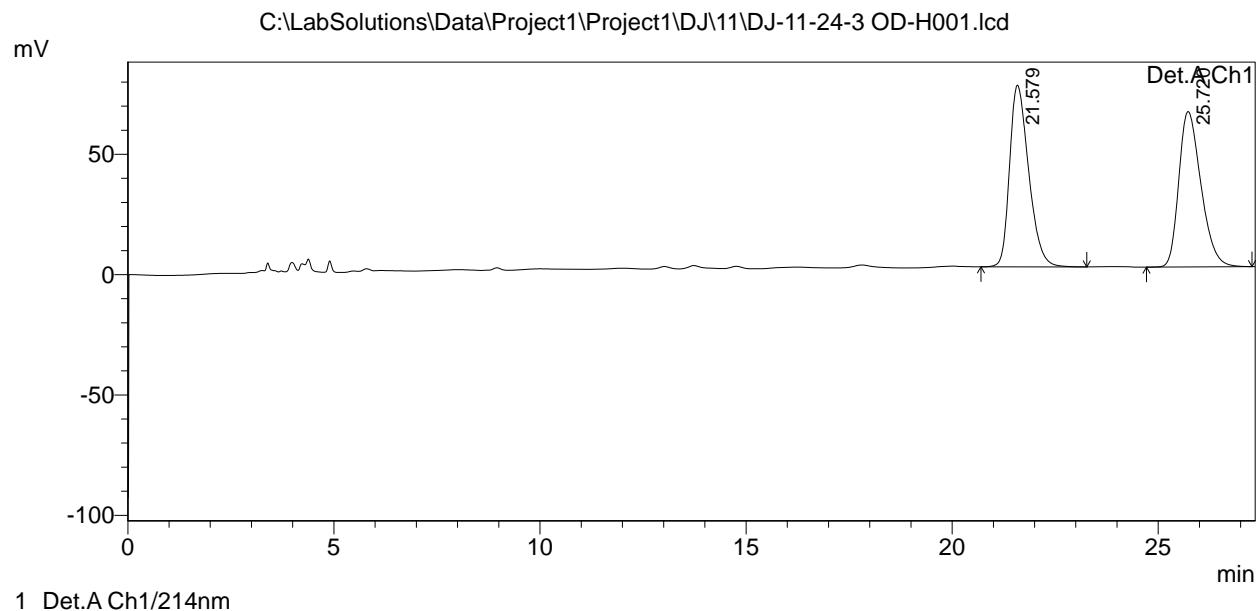
### <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-24-3 OD-H  
 Sample ID : OD-H,99/1,1.0,214  
 Vail # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-24-3 OD-H001.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-20 19:38:03  
 Data Processed : 2018-3-20 20:05:34

**3n**

## <Chromatogram>



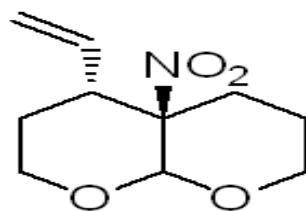
PeakTable

Detector A Ch1 214nm

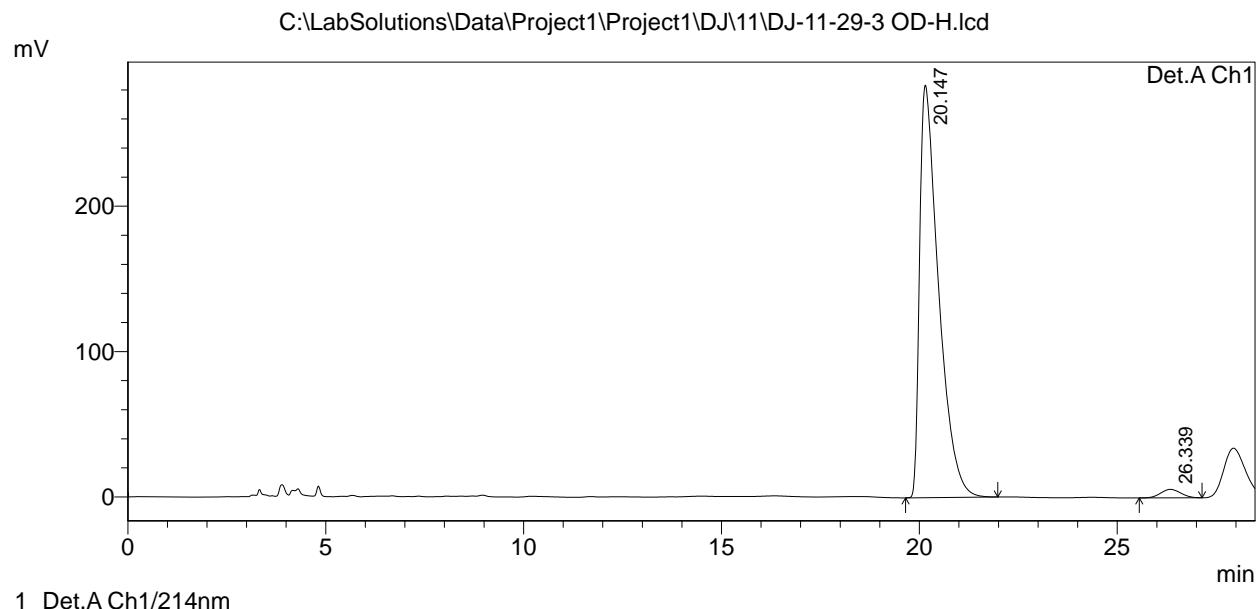
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.579	2440542	75543	50.333	53.918
2	25.720	2408208	64564	49.667	46.082
Total		4848750	140107	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-29-3 OD-H  
 Sample ID : OD-H,99/1,1.0,214  
 Vial # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : DJ-11-29-3 OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-20 20:07:29  
 Data Processed : 2018-3-20 20:35:58

**3n**

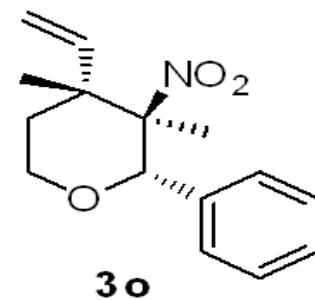
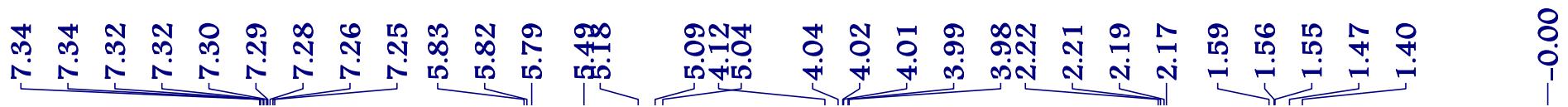
## <Chromatogram>



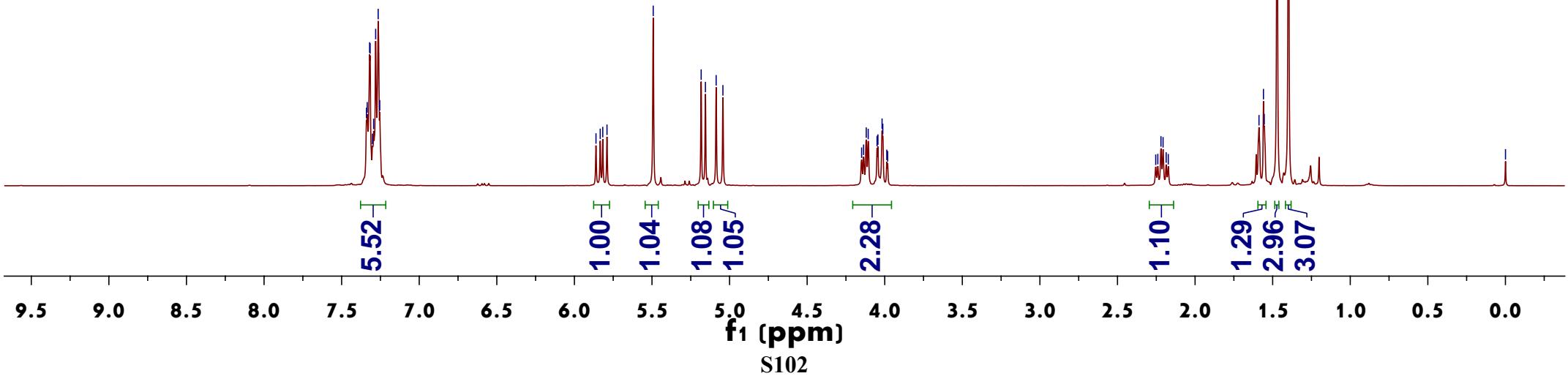
PeakTable

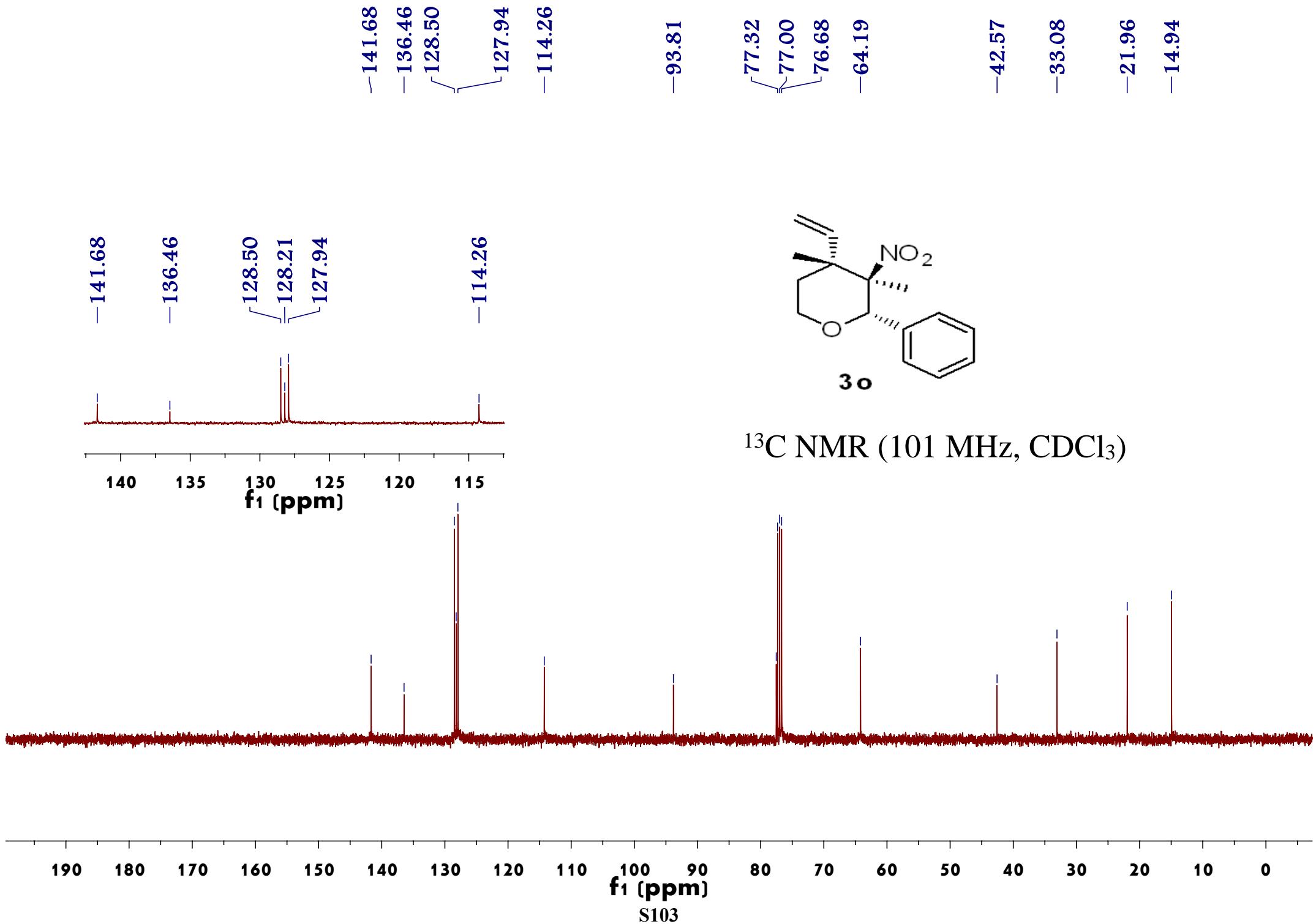
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.147	9450948	283823	97.848	97.973
2	26.339	207858	5873	2.152	2.027
Total		9658806	289696	100.000	100.000



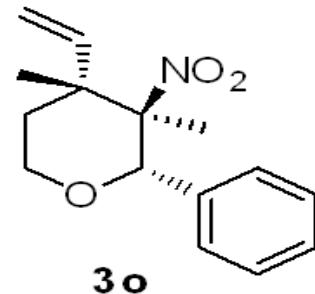
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



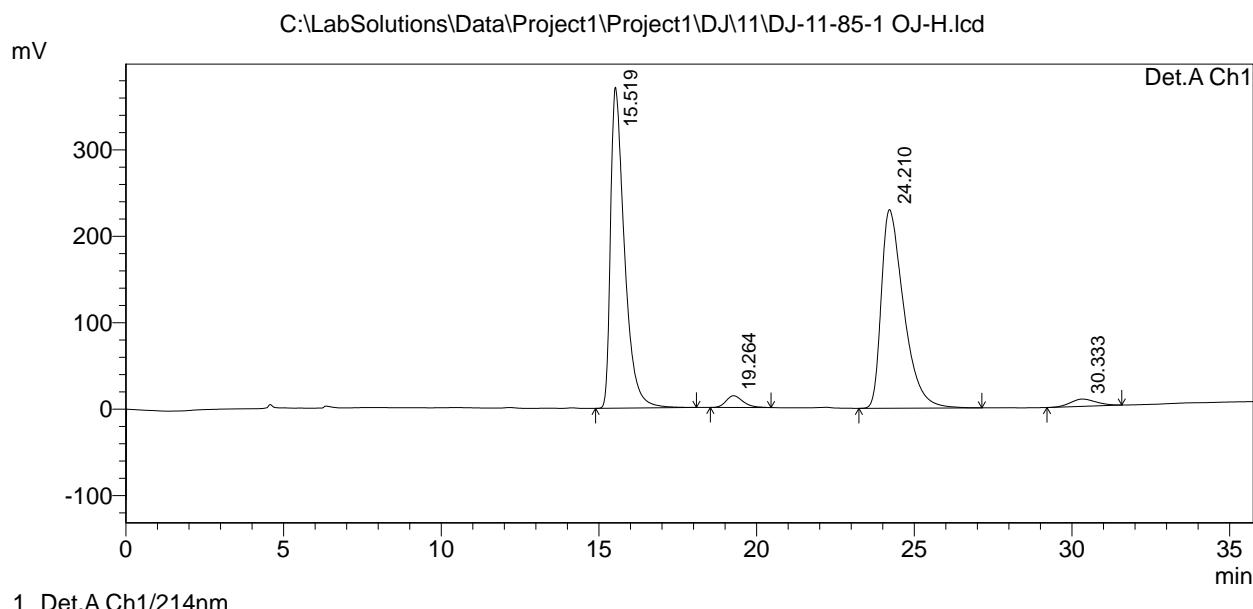


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : DJ-11-85-1 OJ-H  
 Sample ID : OJ-H,99/1,0.7,214  
 Vail # :  
 Injection Volume : 2 uL  
 Data File Name : DJ-11-85-1 OJ-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-5-21 15:21:28  
 Data Processed : 2018-5-21 15:57:13



## <Chromatogram>

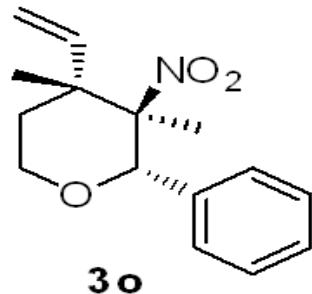


PeakTable

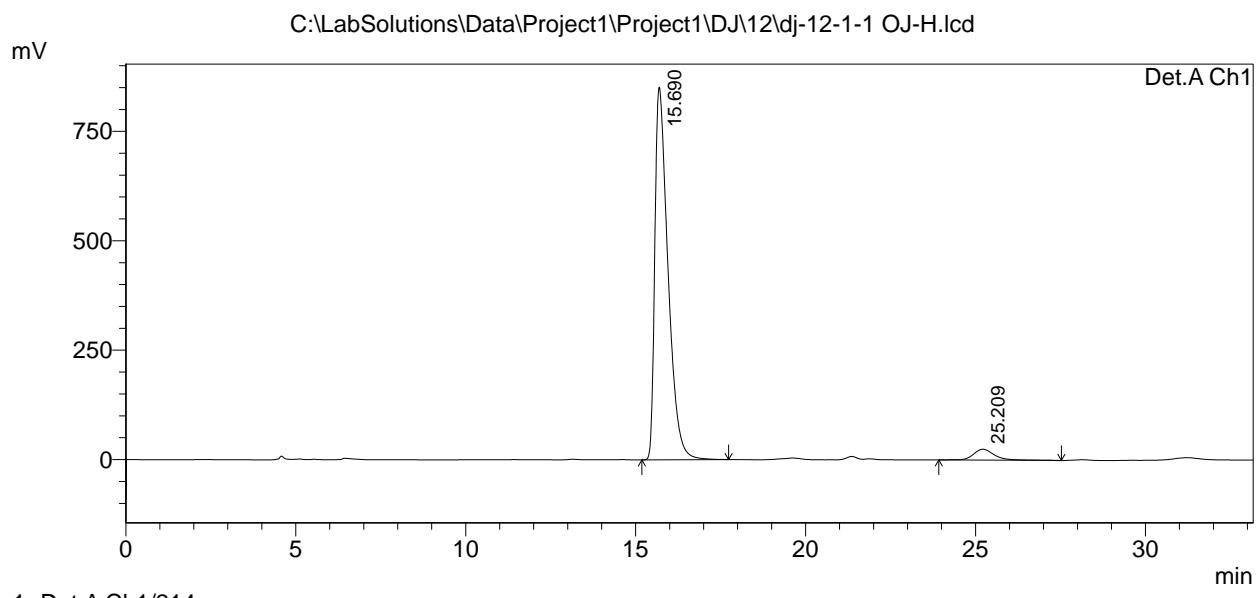
Detector A Ch1 214nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.519	11406877	371447	47.943	59.594
2	19.264	509881	13609	2.143	2.183
3	24.210	11402414	229830	47.924	36.873
4	30.333	473567	8408	1.990	1.349
Total		23792738	623294	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : dj-12-1-1 OJ-H  
 Sample ID : OJ-H,99/1,0.7,214  
 Vail # :  
 Injection Volume : 2  $\mu$ L  
 Data File Name : dj-12-1-1 OJ-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-6-5 9:45:35  
 Data Processed : 2018-6-5 10:18:46



## <Chromatogram>

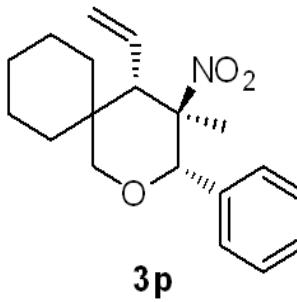
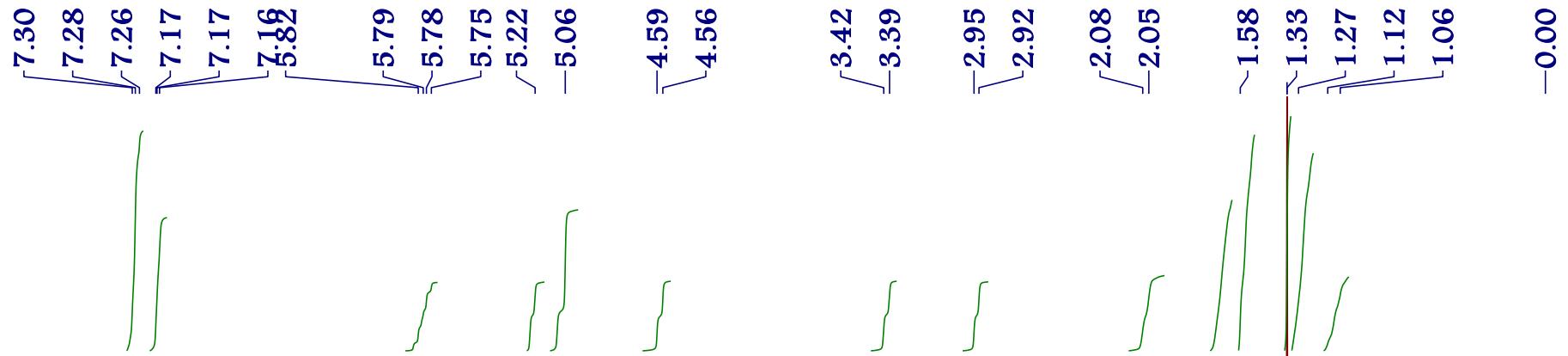


1 Det.A Ch1/214nm

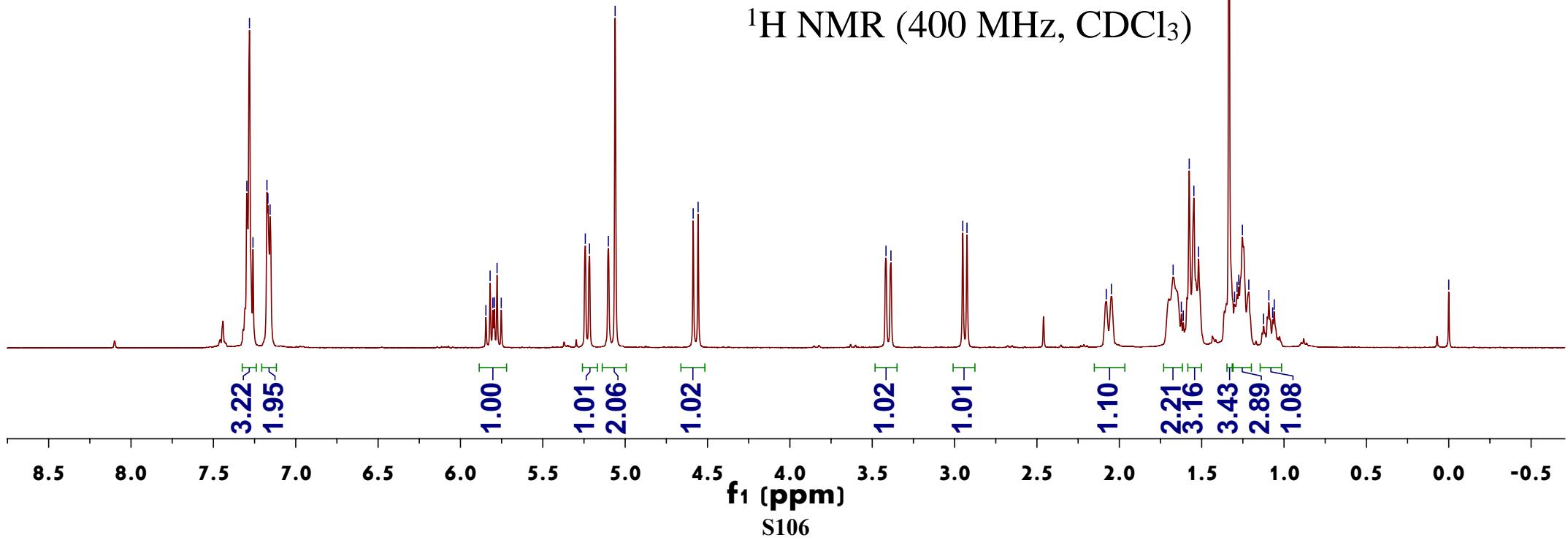
PeakTable

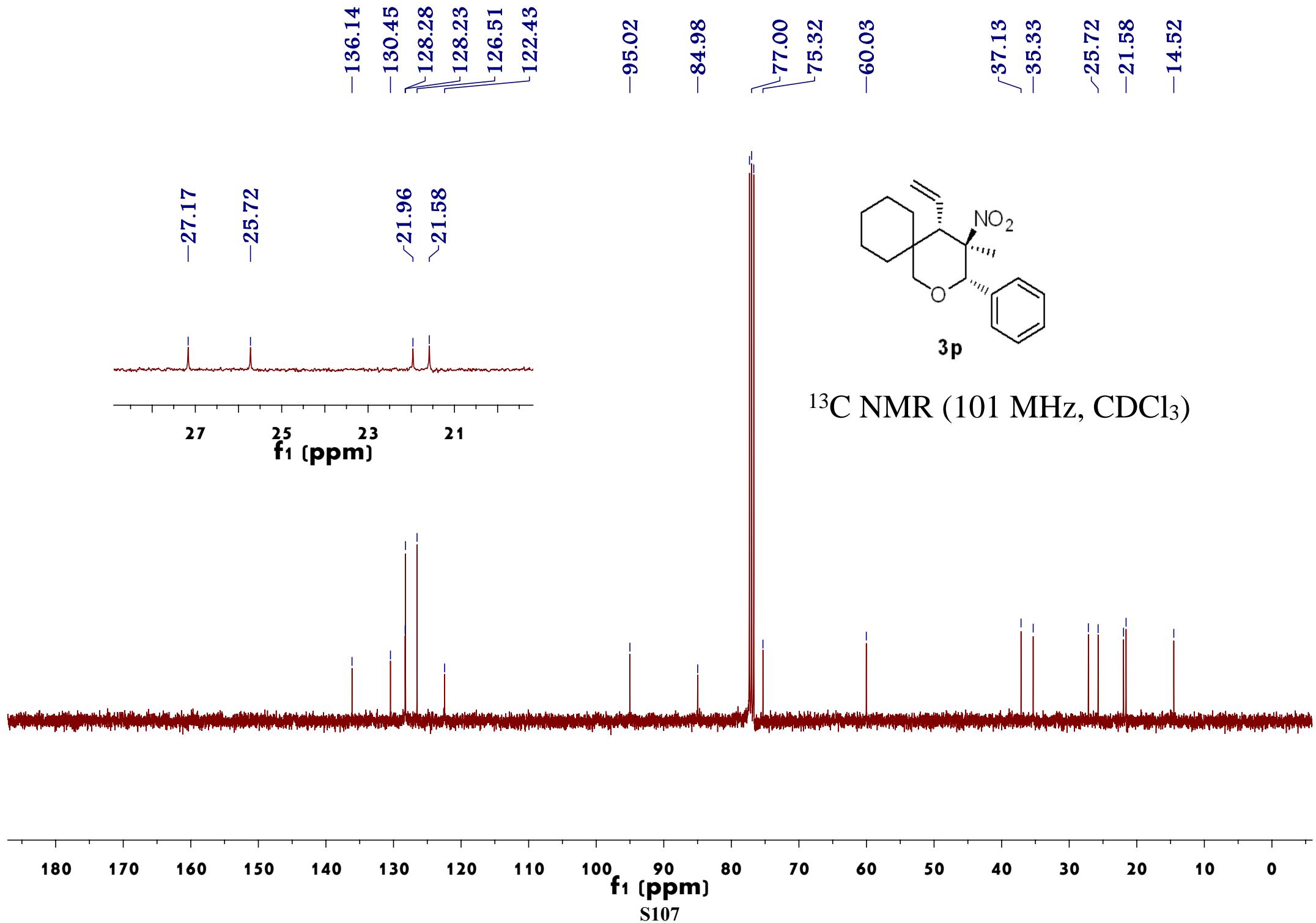
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.690	22868596	851624	95.524	97.160
2	25.209	1071605	24892	4.476	2.840
Total		23940201	876516	100.000	100.000



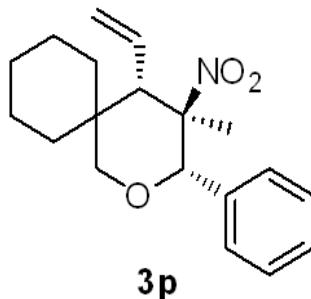
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



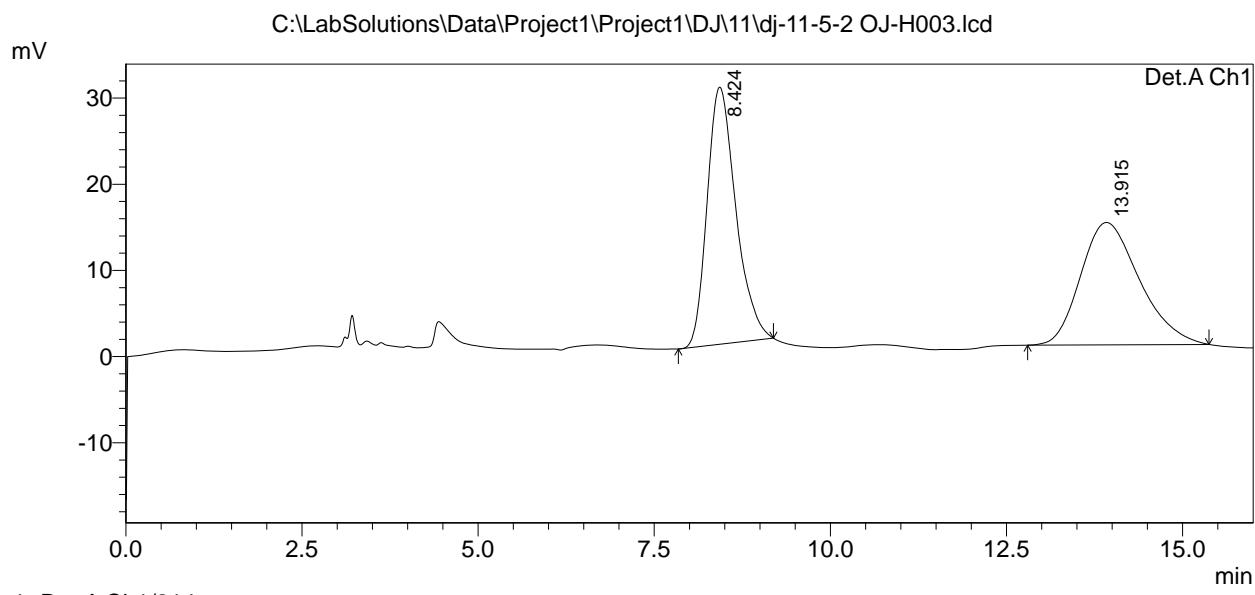


# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : dj-11-5-2 OJ-H  
 Sample ID : OJ-H,99/1,1,214  
 Vail # :  
 Injection Volume : 2 uL  
 Data File Name : dj-11-5-2 OJ-H003.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-13 16:57:30  
 Data Processed : 2018-3-13 17:55:04



## <Chromatogram>



1 Det.A Ch1/214nm

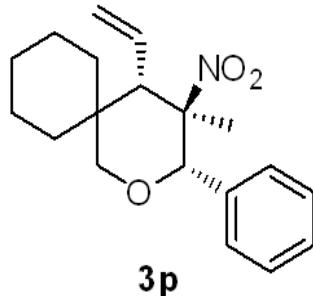
PeakTable

Detector A Ch1 214nm

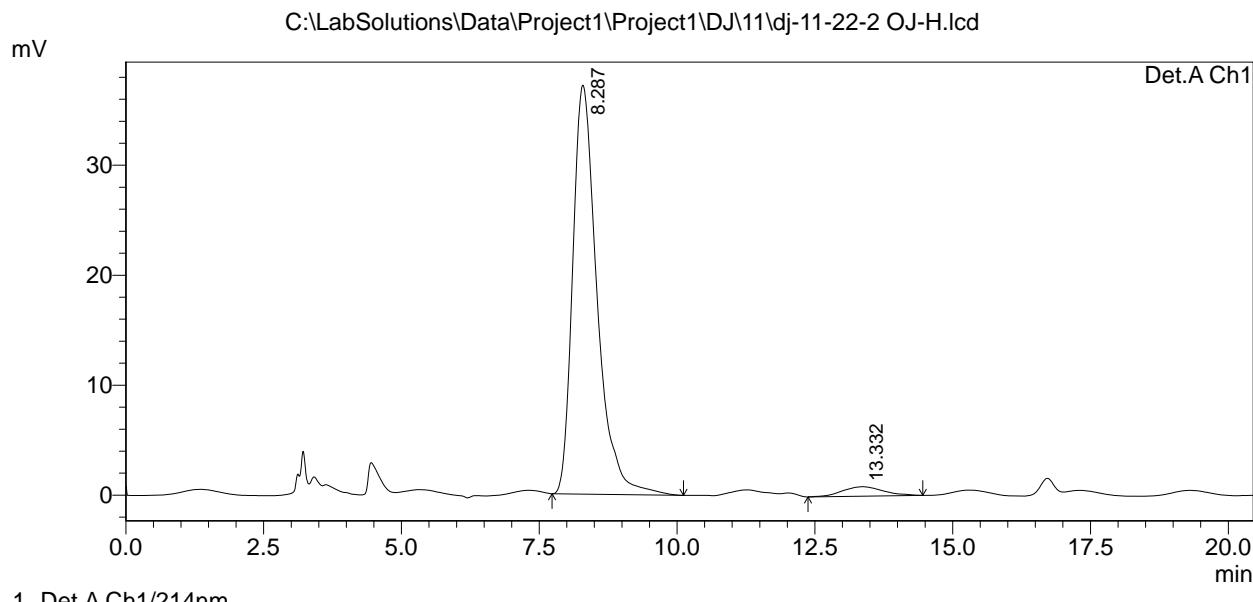
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.424	846146	29850	50.600	67.750
2	13.915	826069	14209	49.400	32.250
Total		1672216	44060	100.000	100.000

# ==== Shimadzu LCsolution Analysis Report ====

Acquired by : Admin  
 Sample Name : dj-11-22-2 OJ-H  
 Sample ID : OJ-H,99/1,1,214  
 Vail # :  
 Injection Volume : 2 uL  
 Data File Name : dj-11-22-2 OJ-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-3-13 17:28:45  
 Data Processed : 2018-3-13 17:49:14



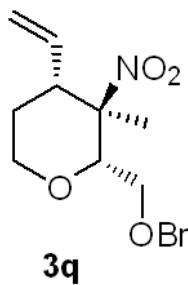
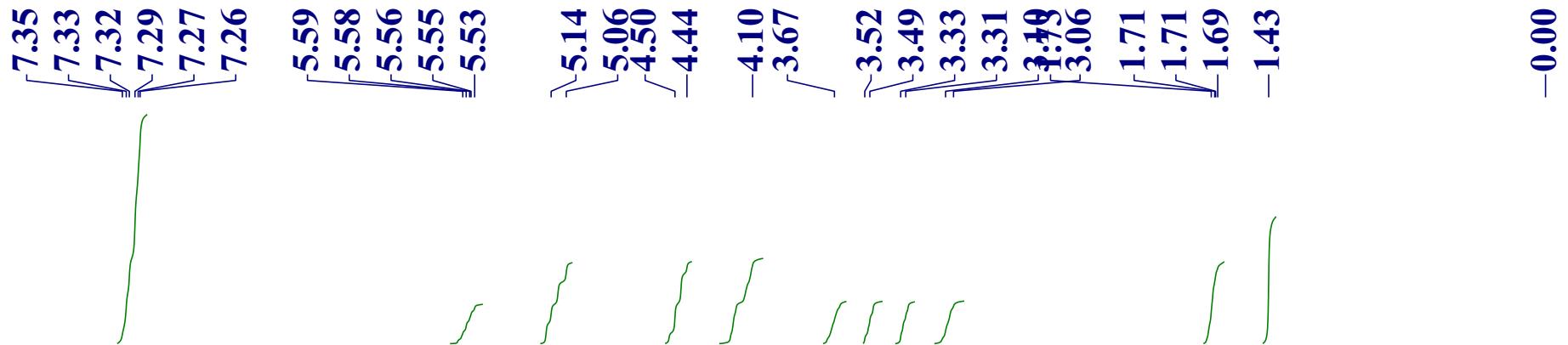
## <Chromatogram>



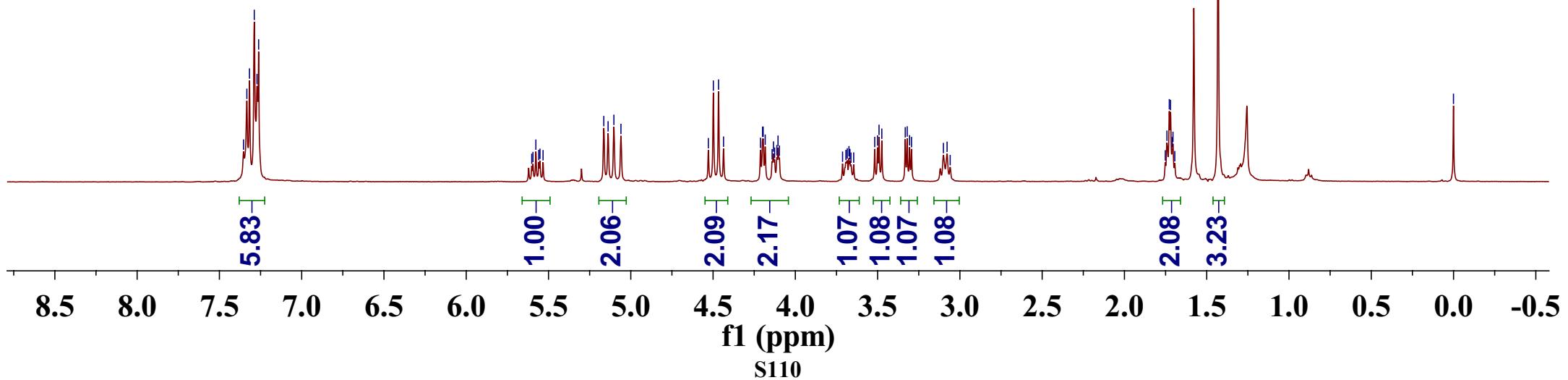
PeakTable

Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.287	1144944	37197	96.224	97.724
2	13.332	44931	866	3.776	2.276
Total		1189875	38063	100.000	100.000



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



-137.41  
-133.98  
-128.39  
127.64  
-118.89

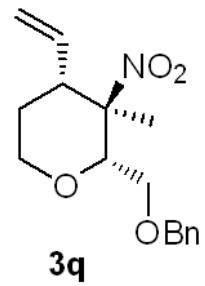
-90.75

77.00  
76.68  
-73.52  
-68.61  
67.87

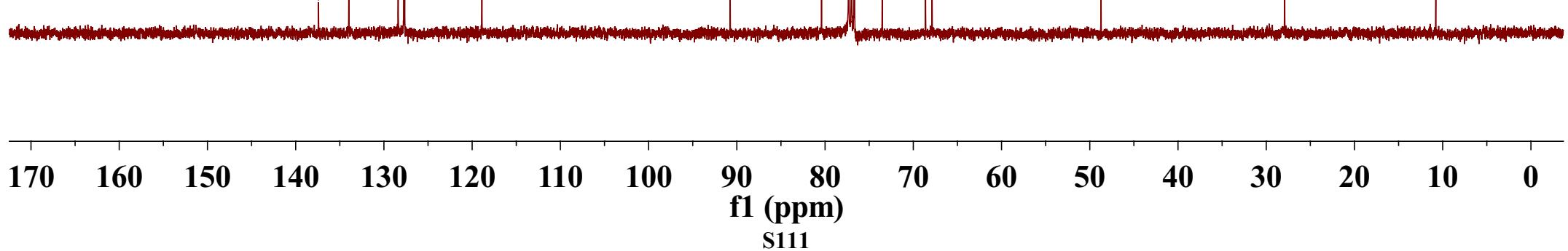
-48.72

-27.91

-10.78



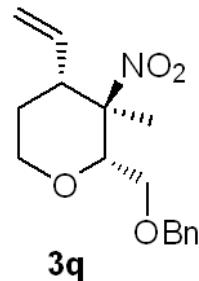
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



# ==== Shimadzu LCsolution Analysis Report ====

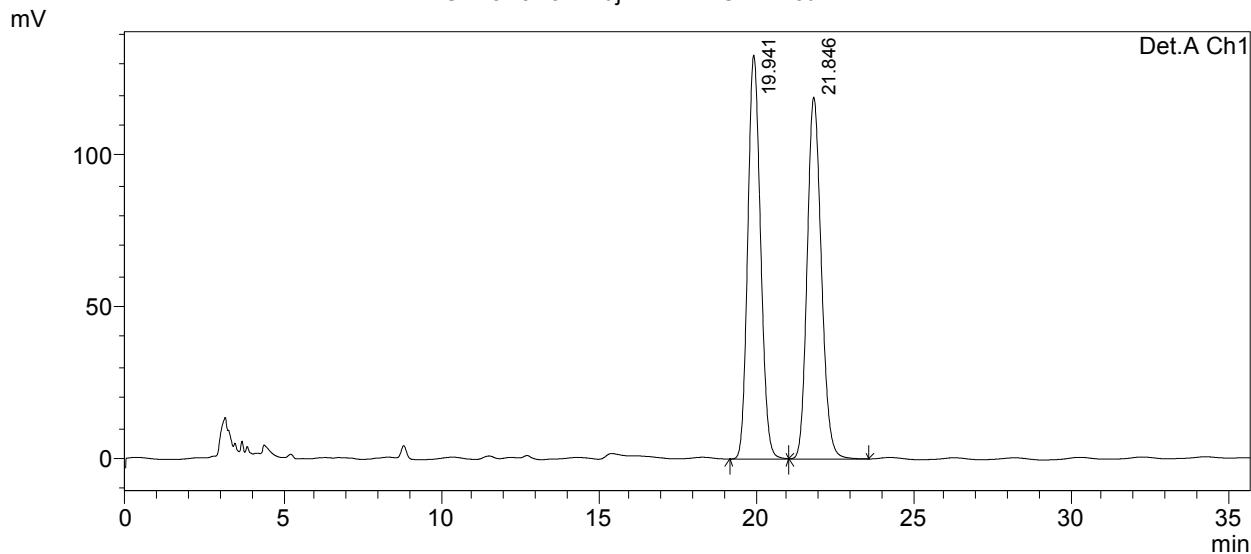
G:\DJDJDJ\12\dj-12-22-1 OD-H.lcd

Acquired by : Admin  
 Sample Name : dj-12-22-1 OD-H  
 Sample ID : OD-H,99/1,1.0,214  
 Vail # :  
 Injection Volume : 2 uL  
 Data File Name : dj-12-22-1 OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-6-20 9:03:28  
 Data Processed : 2018-6-20 9:39:10



## <Chromatogram>

G:\DJDJDJ\12\dj-12-22-1 OD-H.lcd



1 Det.A Ch1/214nm

PeakTable

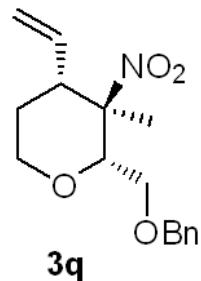
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.941	3759550	133368	50.072	52.740
2	21.846	3748743	119512	49.928	47.260
Total		7508292	252880	100.000	100.000

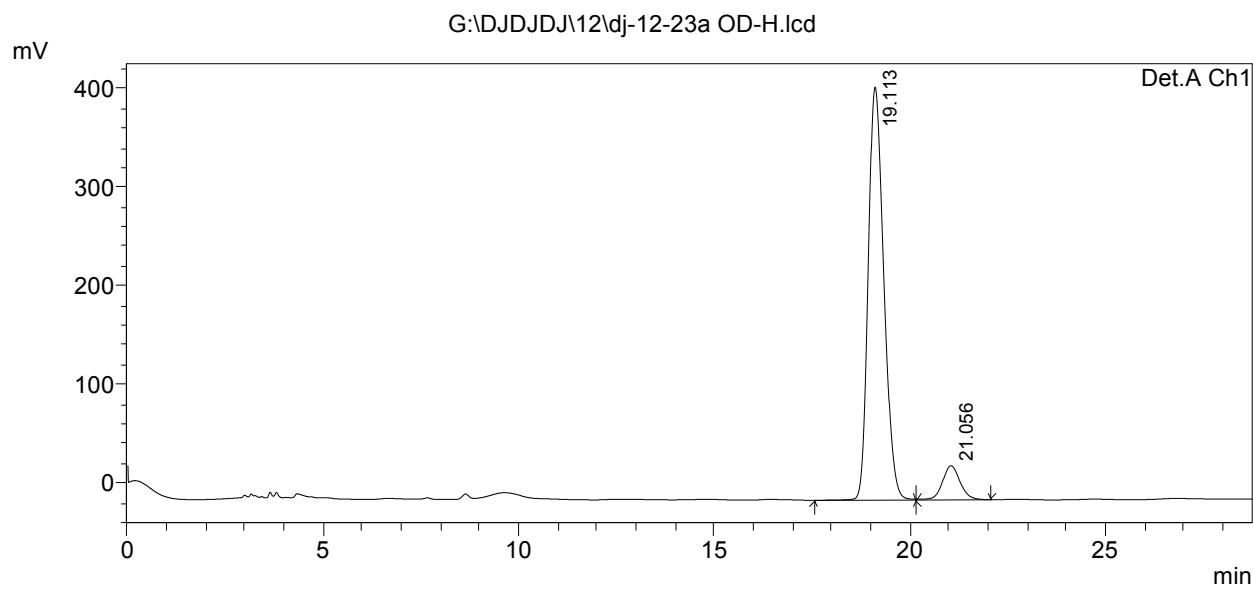
# ==== Shimadzu LCsolution Analysis Report ====

G:\DJDJDJ\12\dj-12-23a OD-H.lcd

Acquired by : Admin  
 Sample Name : dj-12-23a OD-H  
 Sample ID : OD-H,99/1,1.0,214  
 Vial # :  
 Injection Volume : 2 uL  
 Data File Name : dj-12-23a OD-H.lcd  
 Method File Name : 123.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-6-20 10:18:52  
 Data Processed : 2018-6-20 10:47:38



## <Chromatogram>



PeakTable

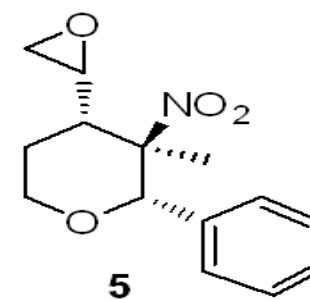
Detector A Ch1 214nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.113	11601040	419007	91.361	92.349
2	21.056	1097005	34714	8.639	7.651
Total		12698045	453721	100.000	100.000

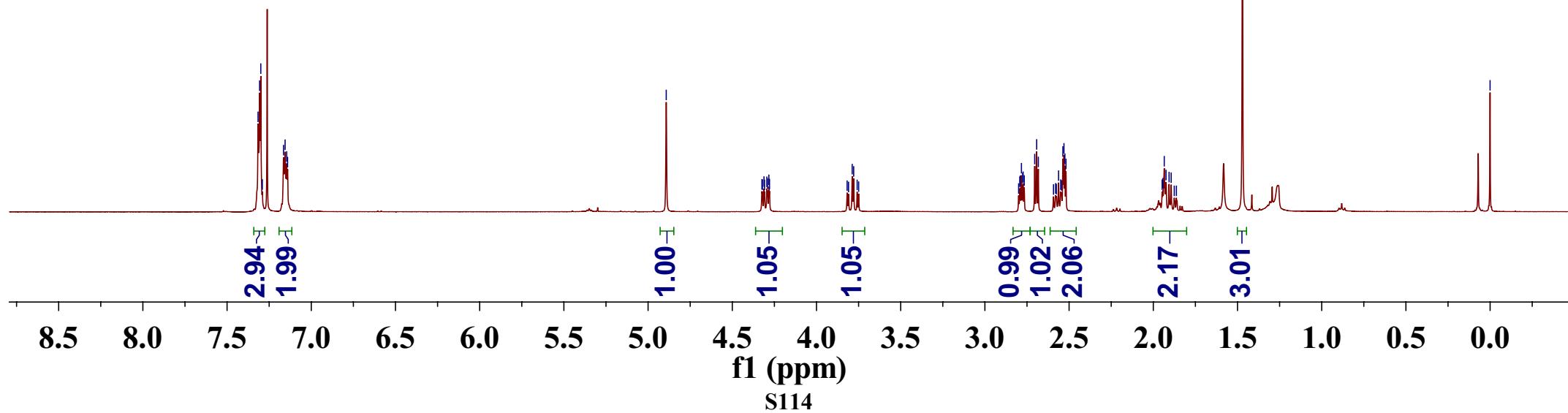
7.32  
7.31  
7.30  
7.29  
7.16  
7.16  
7.15  
7.14

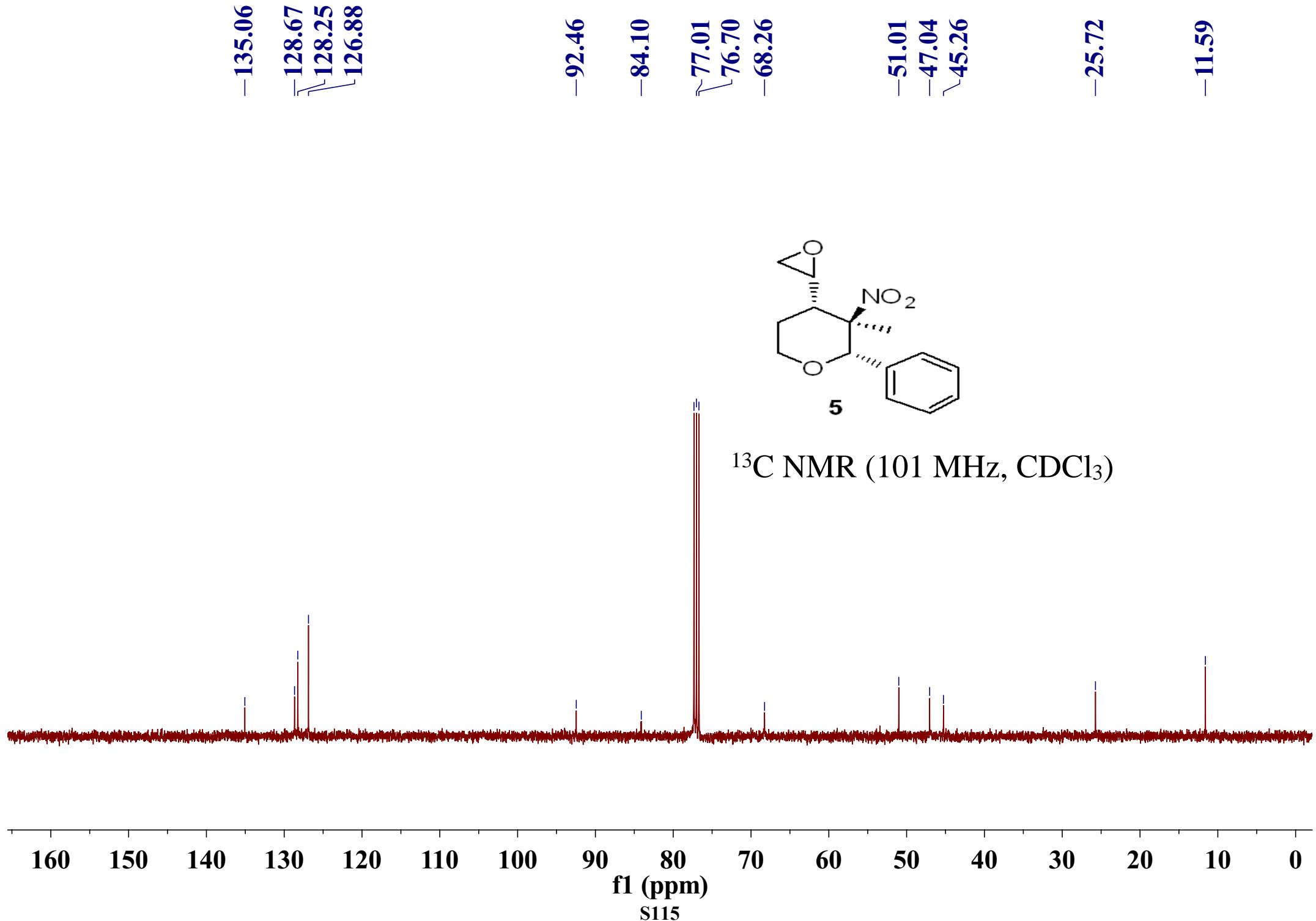
-4.89  
4.32  
4.29  
4.28  
3.79  
3.78  
3.76  
3.75  
3.75  
2.78  
2.70  
2.58  
2.55  
2.52  
1.92  
1.86  
-1.47

-0.00



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

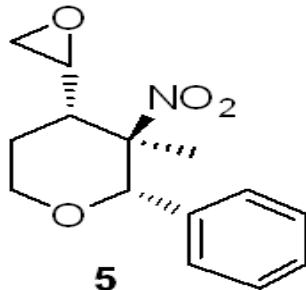




# ==== Shimadzu LCsolution Analysis Report ====

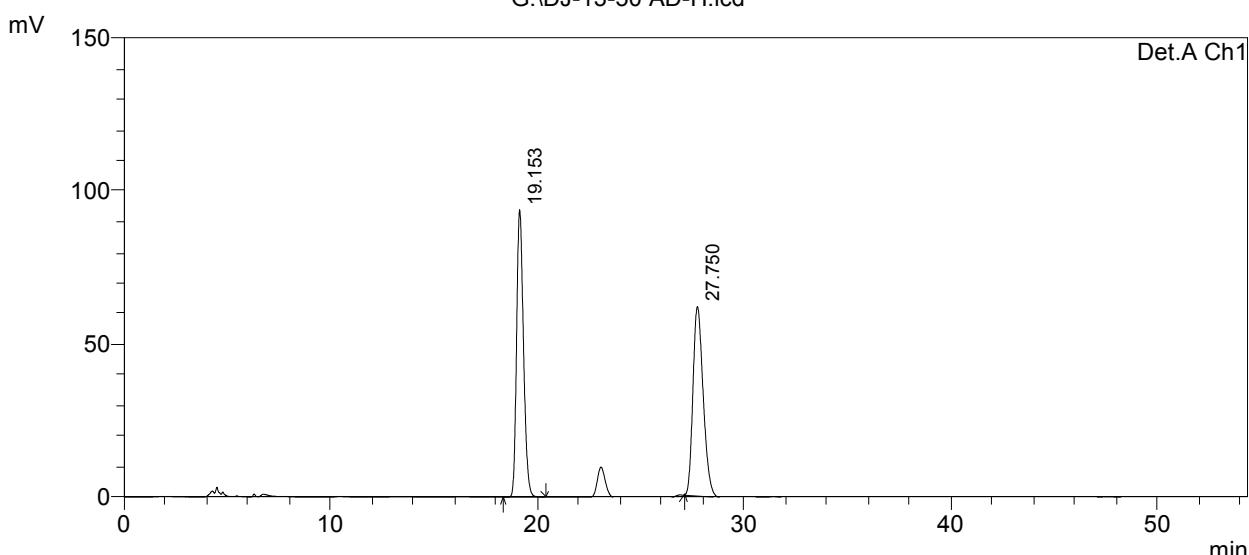
G:\DJ-13-50 AD-H.lcd

Acquired by : Admin  
 Sample Name : DJ-13-50 AD-H  
 Sample ID : AD-H,99/1,0.7,215  
 Vial # :  
 Injection Volume : 1 uL  
 Data File Name : DJ-13-50 AD-H.lcd  
 Method File Name : 1.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-11-23 14:23:51  
 Data Processed : 2018-11-23 15:18:15



## <Chromatogram>

G:\DJ-13-50 AD-H.lcd



1 Det.A Ch1/215nm

PeakTable

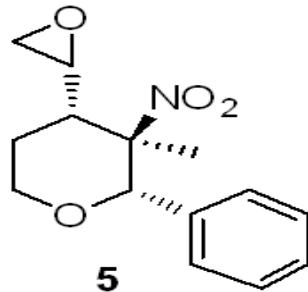
Detector A Ch1 215nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.153	2177040	93981	50.446	60.260
2	27.750	2138538	61978	49.554	39.740
Total		4315578	155958	100.000	100.000

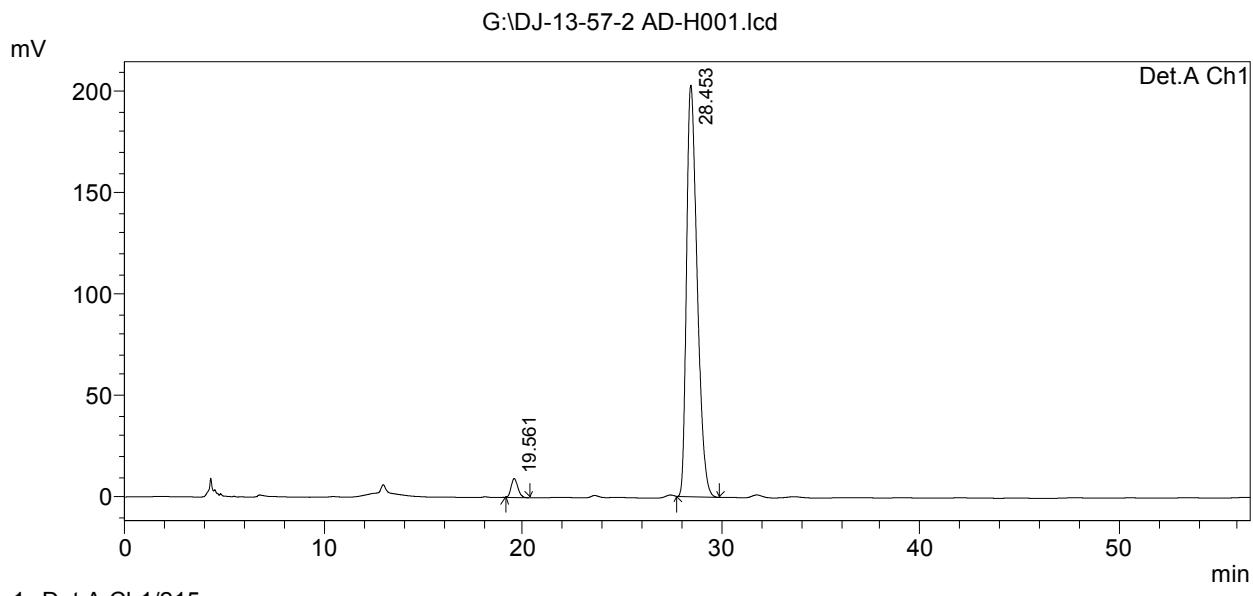
# ==== Shimadzu LCsolution Analysis Report ====

G:\DJ-13-57-2 AD-H001.lcd

Acquired by : Admin  
 Sample Name : DJ-13-57-2 AD-H  
 Sample ID : AD-H,99/1,0.7,215  
 Vial # :  
 Injection Volume : 1 uL  
 Data File Name : DJ-13-57-2 AD-H001.lcd  
 Method File Name : 1.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-11-23 15:27:02  
 Data Processed : 2018-11-23 16:23:39



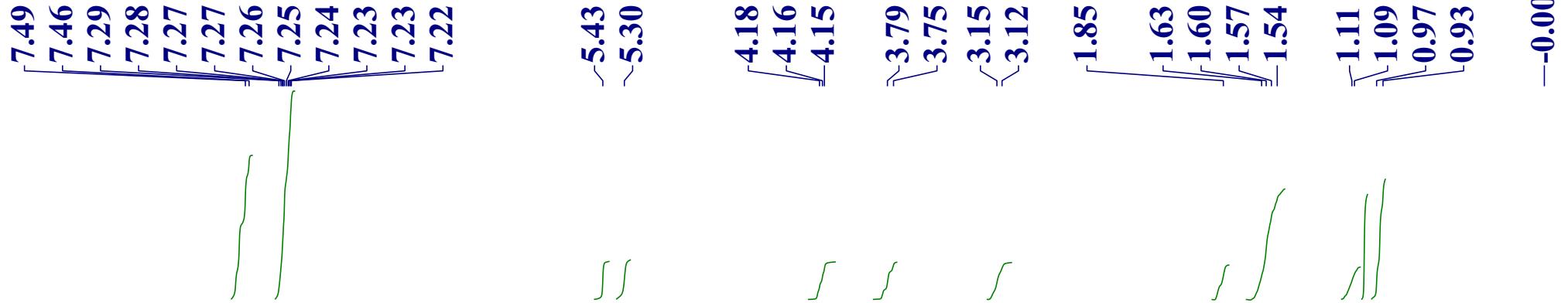
## <Chromatogram>



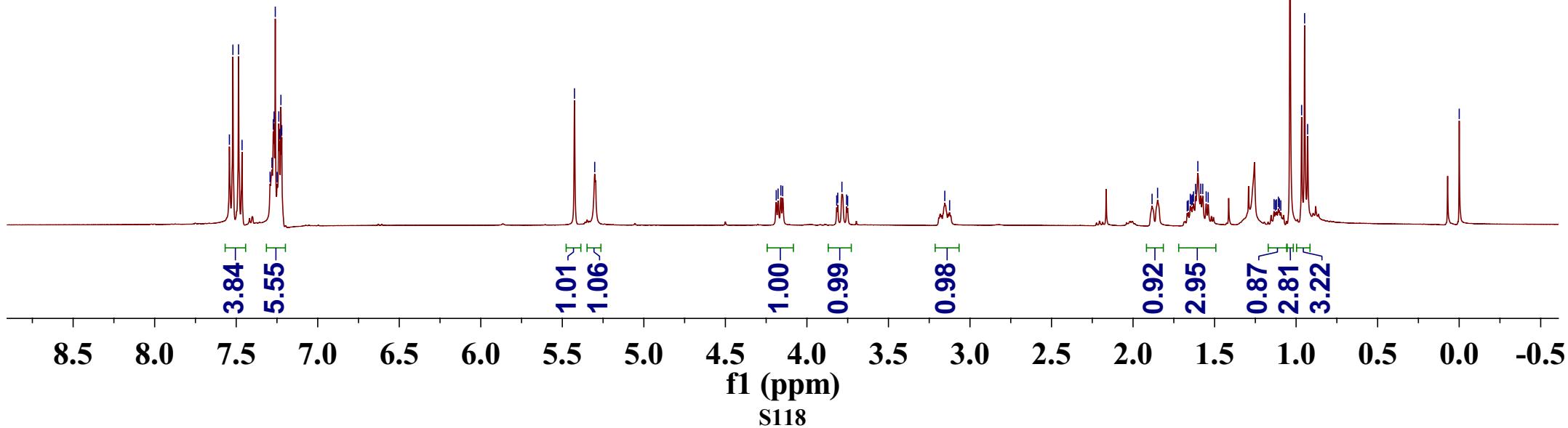
PeakTable

Detector A Ch1 215nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.561	219267	9407	2.819	4.424
2	28.453	7558468	203243	97.181	95.576
Total		7777735	212650	100.000	100.000



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

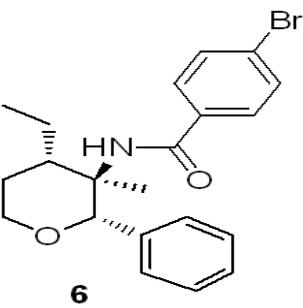


-166.49

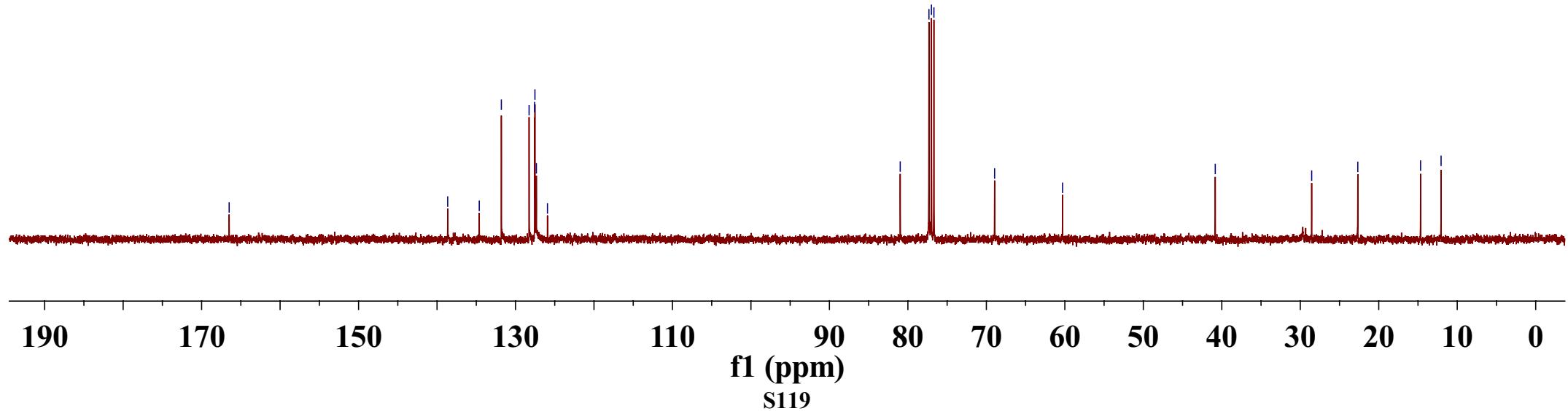
138.64  
134.62  
131.80  
128.27  
127.57  
127.52  
127.34  
125.93

80.98  
77.32  
77.00  
76.68  
-68.95  
-60.29  
-40.83

-28.54  
-22.67  
-14.67  
-12.06



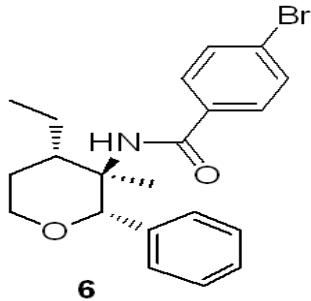
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



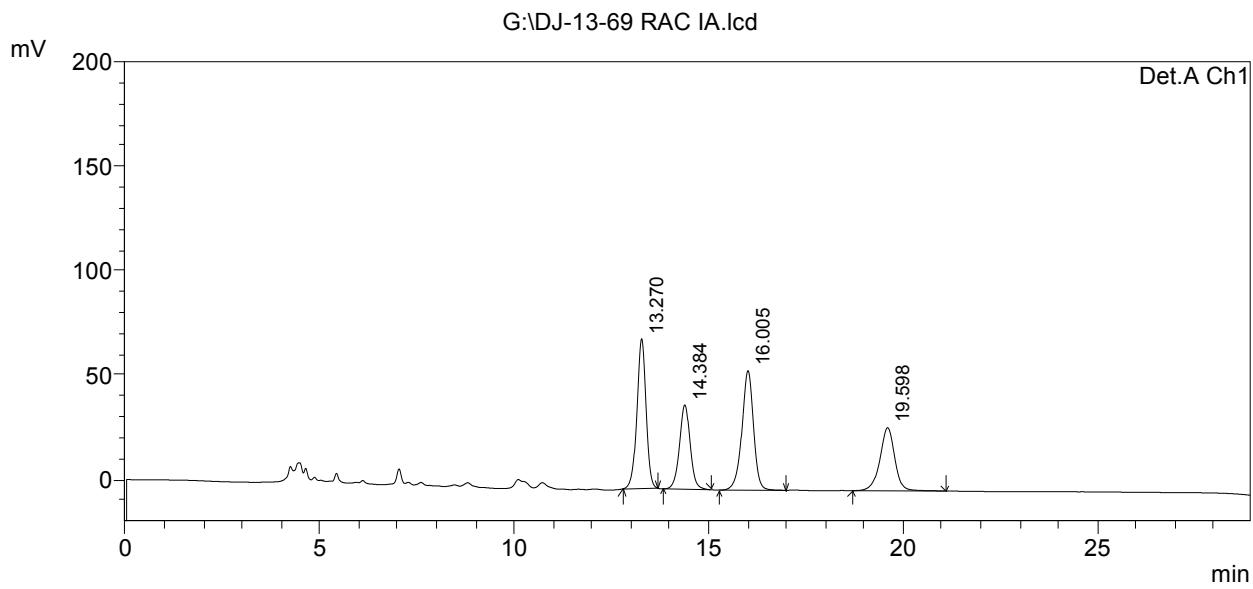
# ==== Shimadzu LCsolution Analysis Report ====

G:\DJ-13-69 RAC IA.lcd

Acquired by : Admin  
 Sample Name : DJ-13-69 RAC IA  
 Sample ID : IA,92/8,0.7,215  
 Vial # :  
 Injection Volume : 1 uL  
 Data File Name : DJ-13-69 RAC IA.lcd  
 Method File Name : 1.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-11-23 8:59:00  
 Data Processed : 2018-11-23 9:27:56



## <Chromatogram>



PeakTable

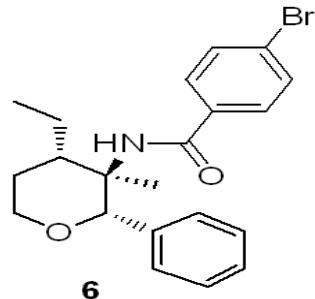
Detector A Ch1 215nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.270	1179381	71868	29.827	35.952
2	14.384	771561	40443	19.513	20.231
3	16.005	1193993	57328	30.197	28.678
4	19.598	809112	30263	20.463	15.139
Total		3954047	199902	100.000	100.000

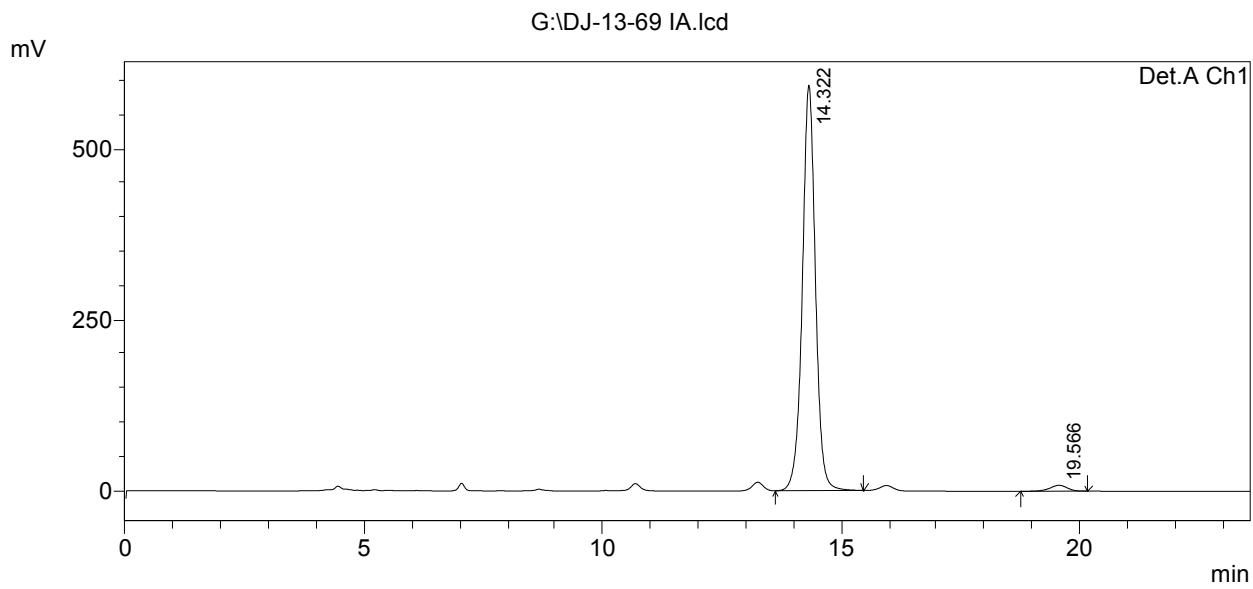
# ==== Shimadzu LCsolution Analysis Report ====

G:\DJ-13-69 IA.lcd

Acquired by : Admin  
 Sample Name : DJ-13-69 IA  
 Sample ID : IA.92/8.0.7.215  
 Vial # :  
 Injection Volume : 1 uL  
 Data File Name : DJ-13-69 IA.lcd  
 Method File Name : 1.lcm  
 Batch File Name :  
 Report File Name : Default.lcr  
 Data Acquired : 2018-11-23 9:29:57  
 Data Processed : 2018-11-23 13:46:34



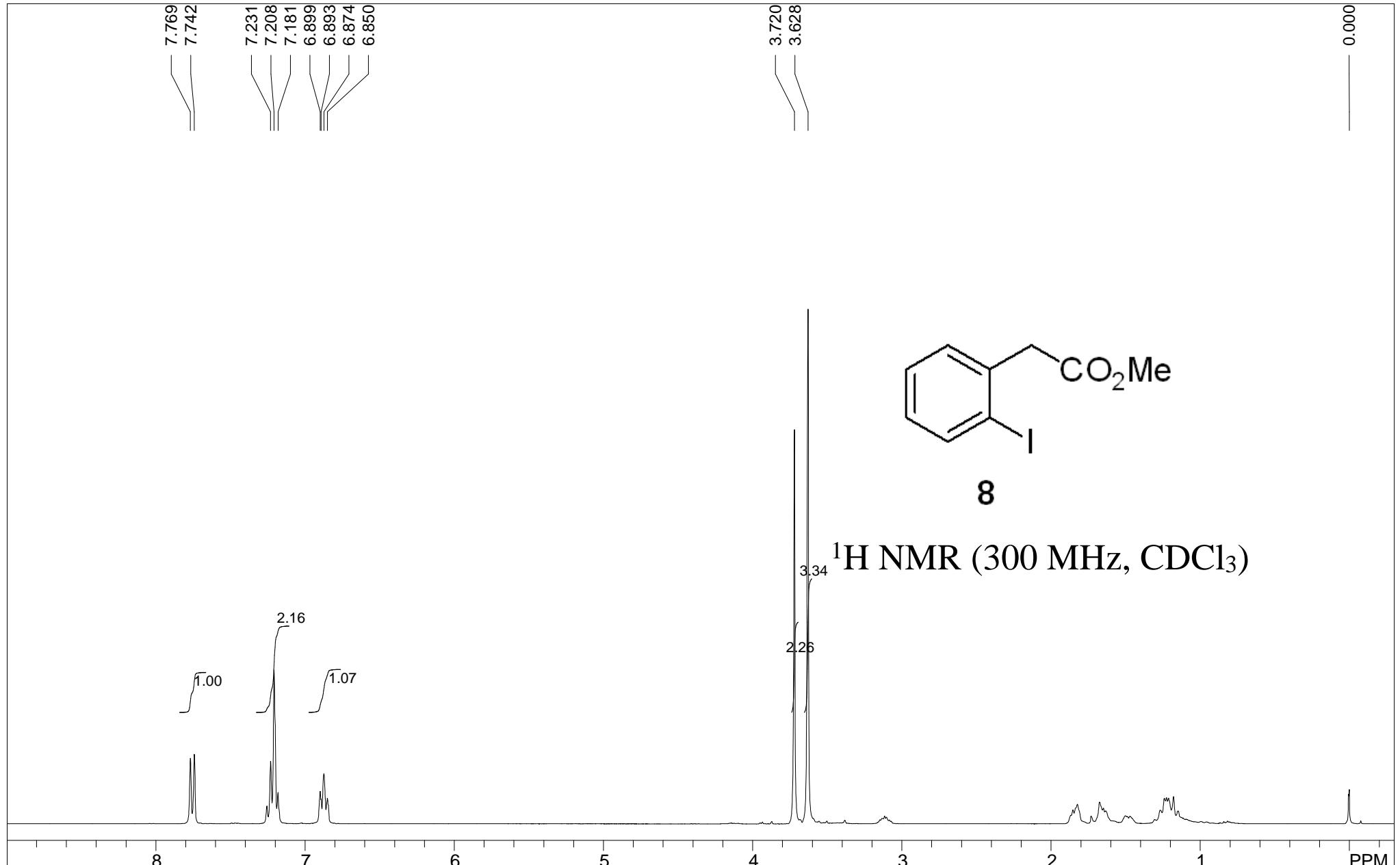
## <Chromatogram>



PeakTable

Detector A Ch1 215nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.322	11307993	592435	98.071	98.563
2	19.566	222430	8638	1.929	1.437
Total		11530423	601073	100.000	100.000



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F1: 300.029

F2: 75.449

SW1: 5495

EX: s2pul

PW: 4.2 us

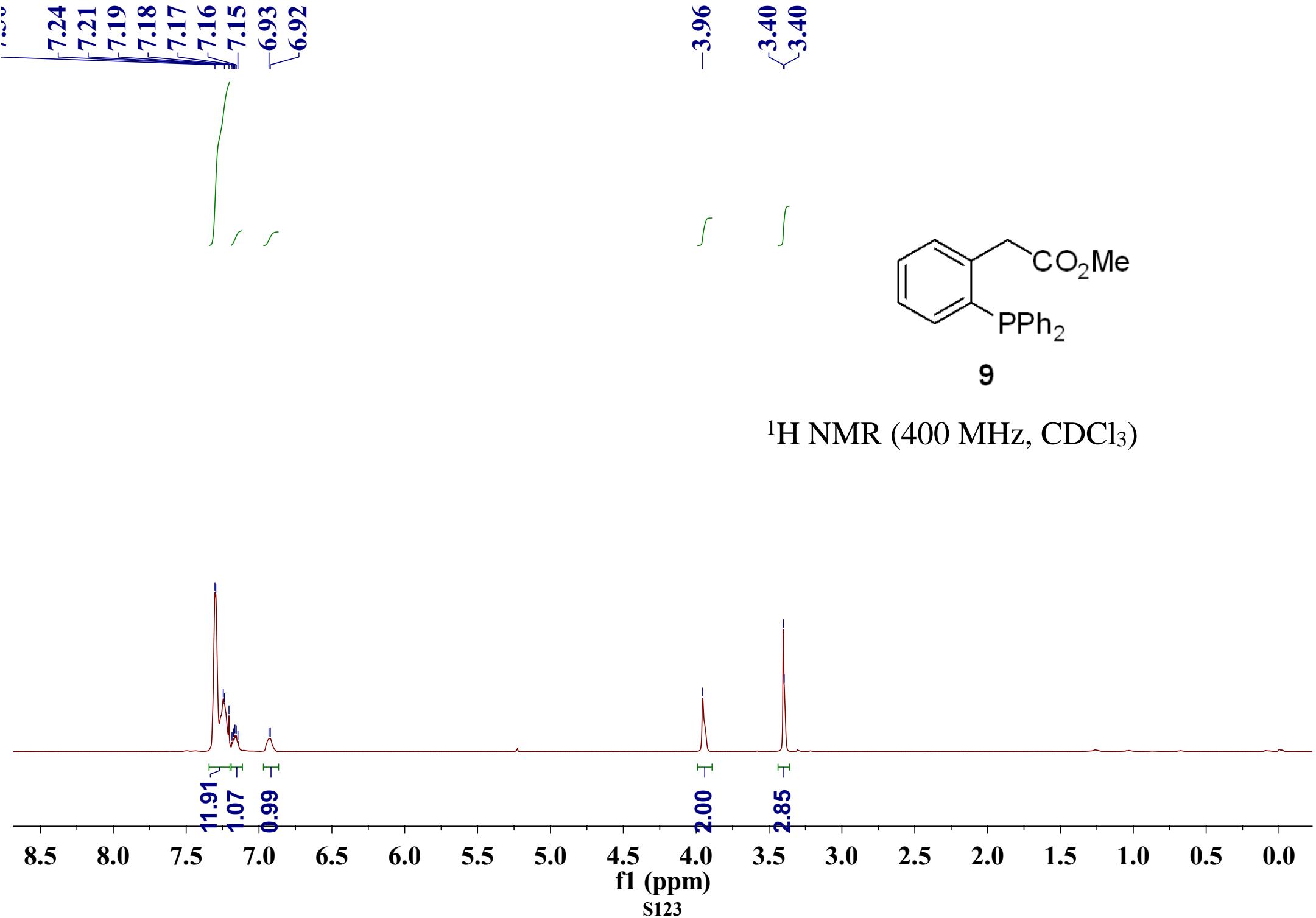
PD: 1.0 sec

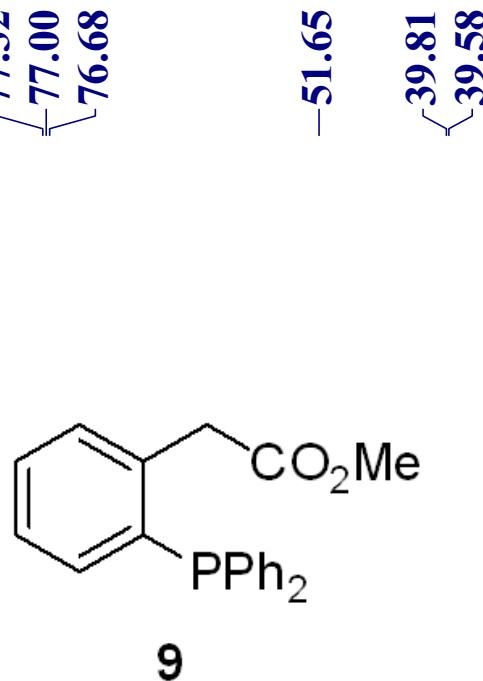
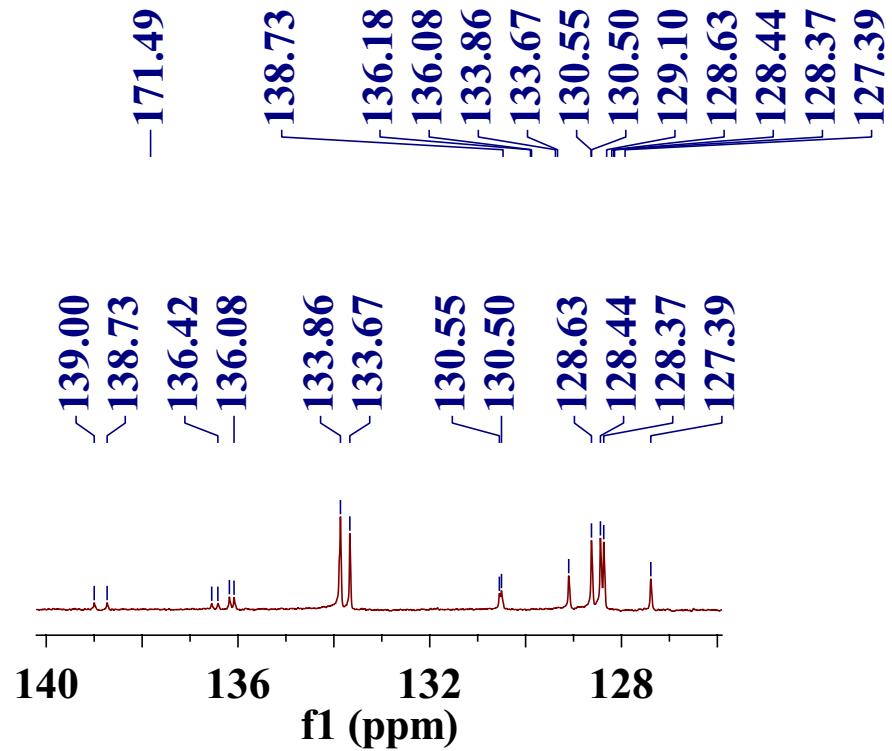
NA: 12

OF1: 2091.3  
PTS1d: 11118 , 16384

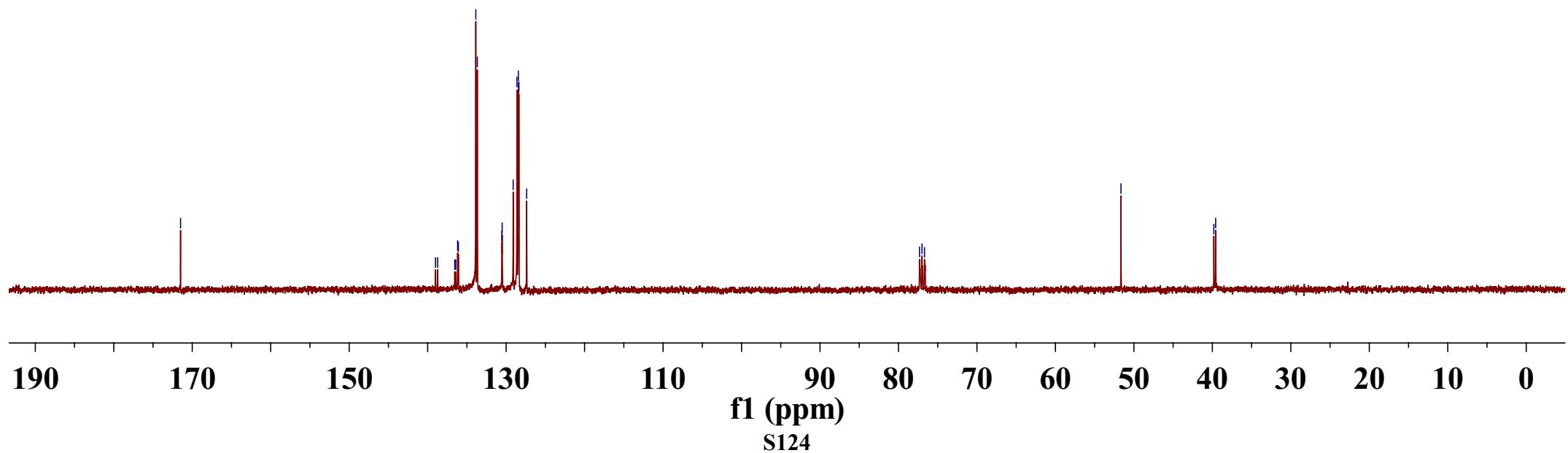
Nuts - \$hyd-18-17-H.fid

USER: -- DATE: May 20 2011

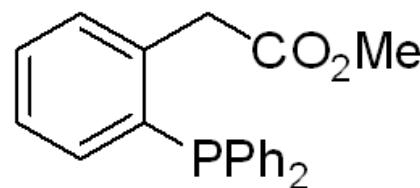




<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

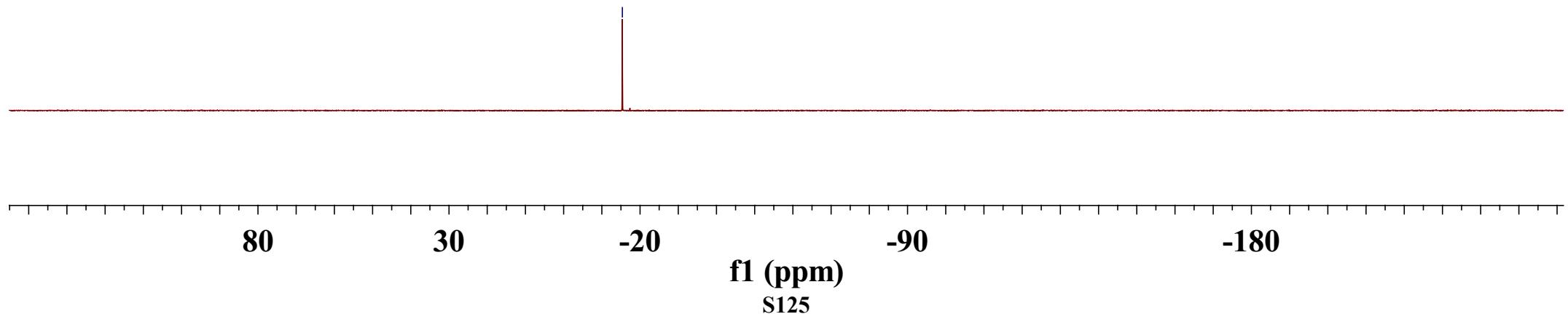


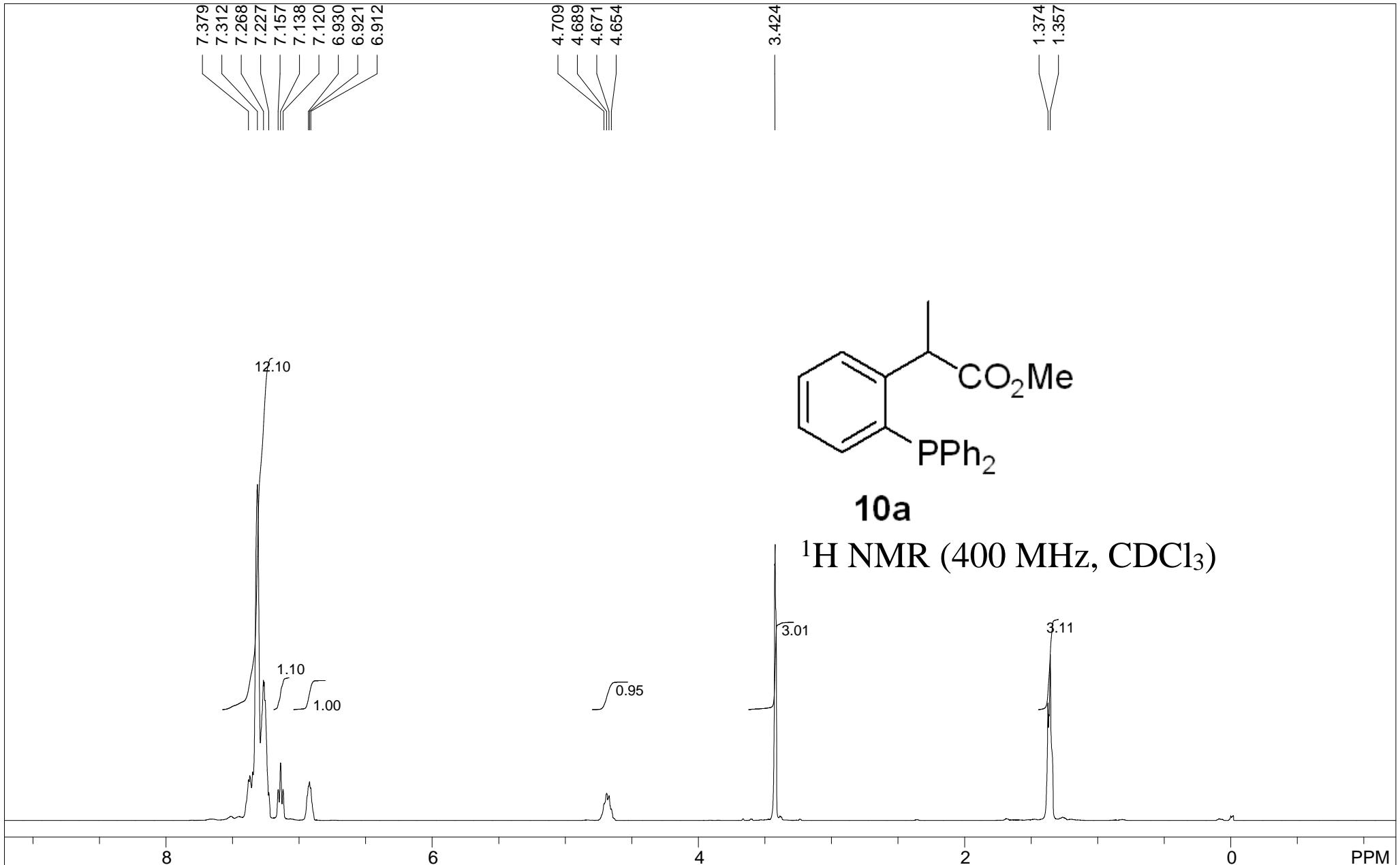
-15.37



**9**

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)





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F1: 400.032

F2: 100.597

SW1: 7225

EX: s2pul

PW: 10.3 usec

PD: 1.0 sec

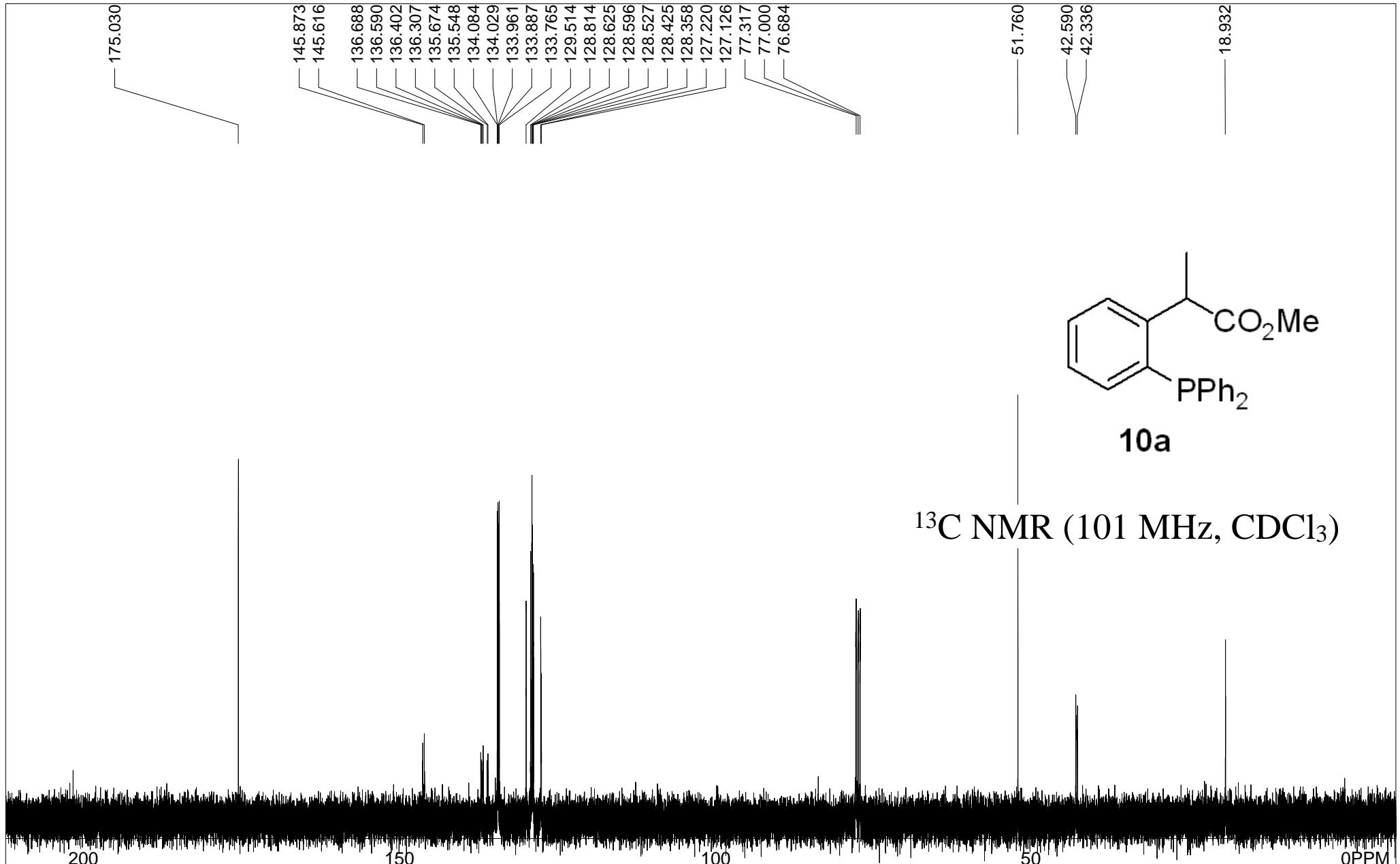
OF1: 2793.5

NA: 16

LB: 0.0

USER: -- DATE: Mar 20 2012

Nuts - \$hyd-12-96-H.fid



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F1: 100.598

F2: 400.031

SW1: 24510

EX: s2pul

OF1: 10558.9

PW: 7.3 usec

PD: 1.0 sec

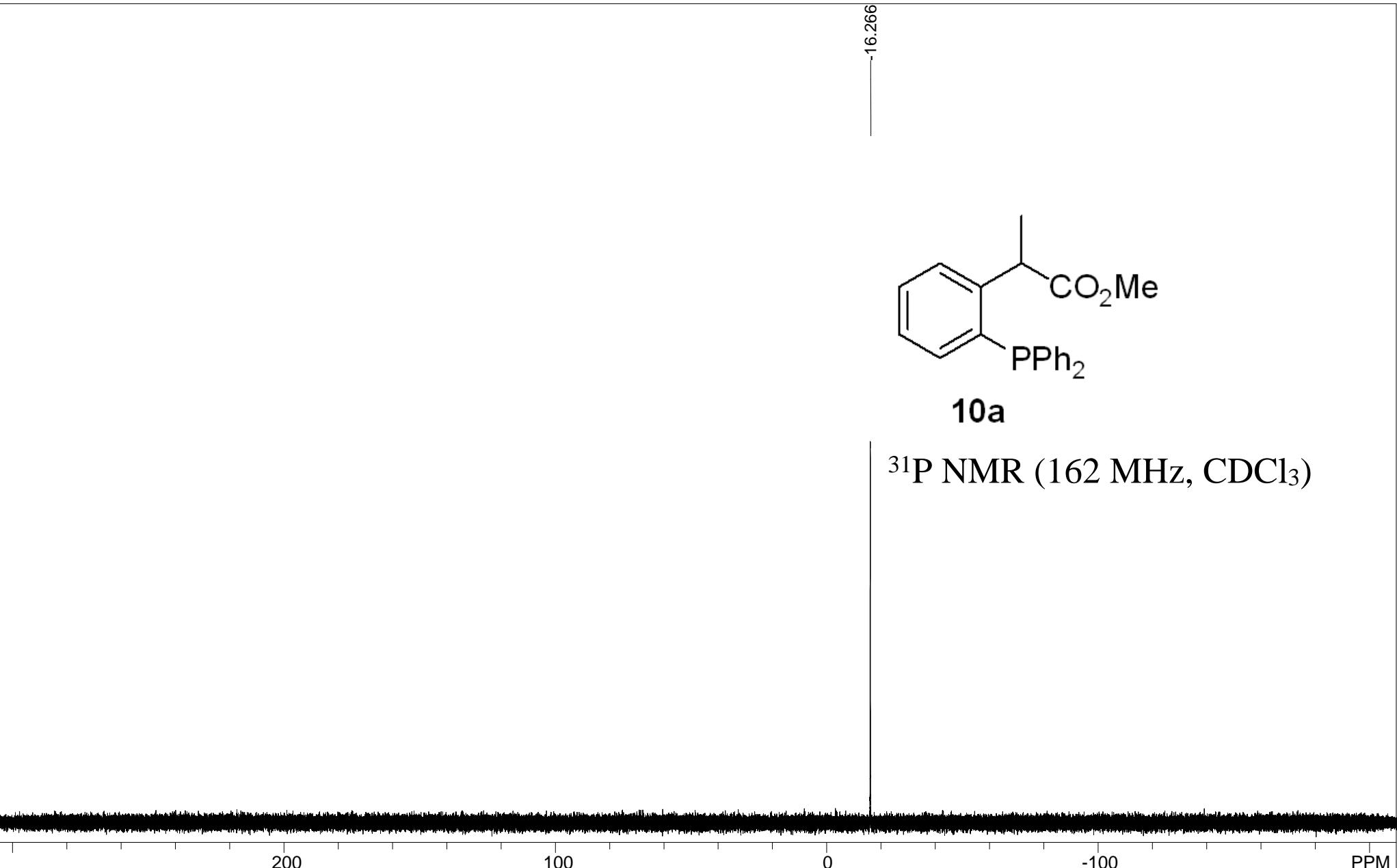
NA: 156

LB: 0.0

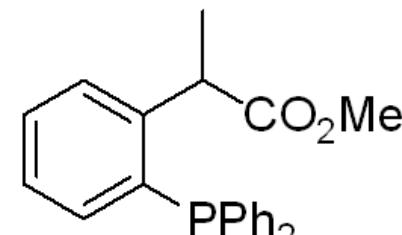
USER: -- DATE: Mar 20 2012

PTS1d: 65536

Nuts - \$hyd-12-96-C.fid



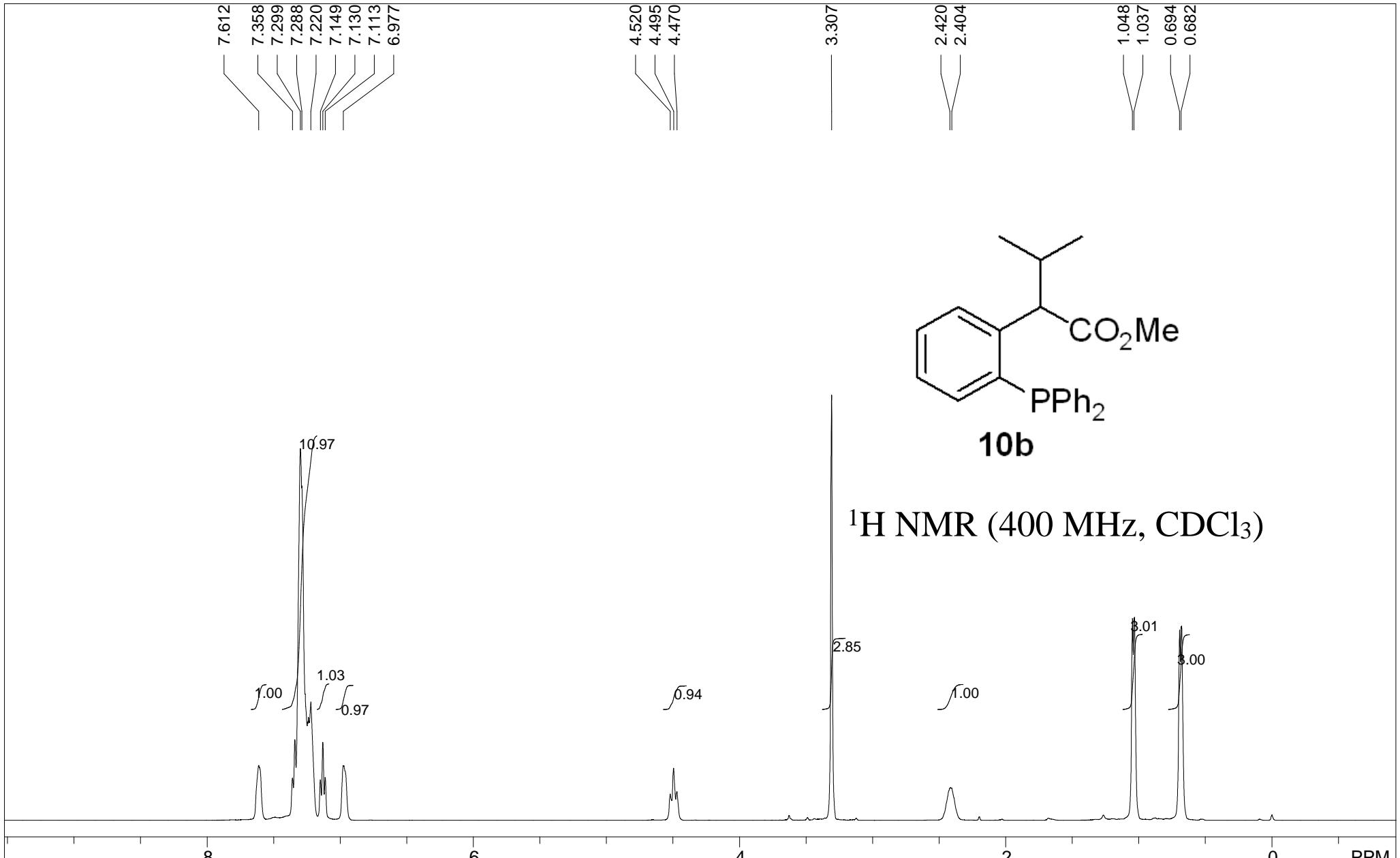
-16.266



**10a**

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)

:blank line							USER: -- DATE: Mar 20 2012
F1: 161.942	F2: 400.031	SW1: 83333		OF1: 7691.9		PTS1d: 131072	
EX: s2pul		PW: 5.0 usec	PD: 1.0 sec	NA: 40	LB: 0.0		Nuts - \$hyd-12-96-P.fid



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F1: 400.031

F2: 100.597

SW1: 7022

EX: s2pul

OF1: 2691.9

PTS1d: 32768

Nuts - \$hyd-22-43-H.fid

PW: 10.3 usec

PD: 1.0 sec

NA: 16

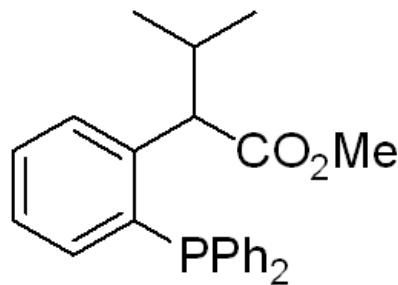
LB: 0.0

174.458

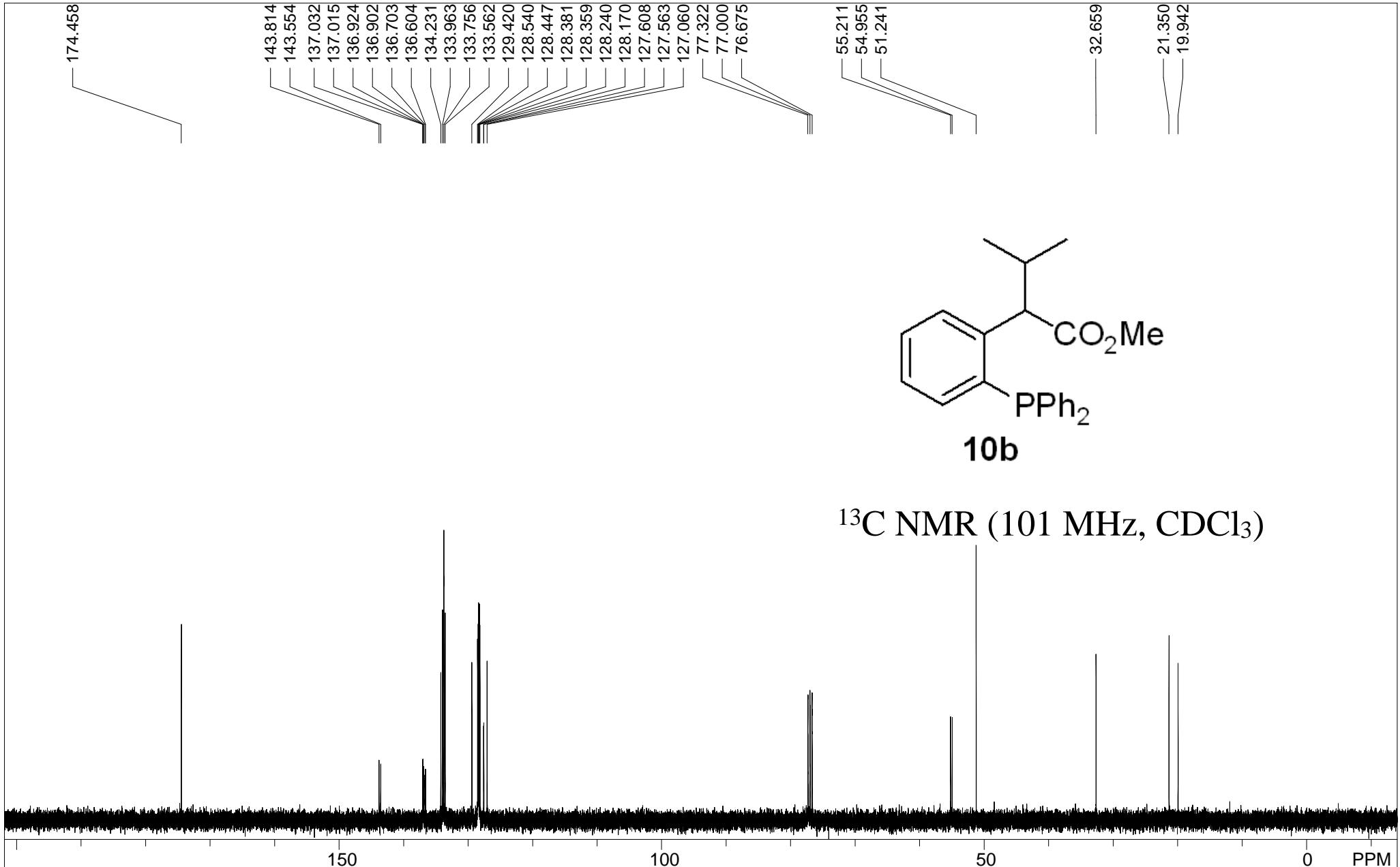
143.814  
143.554  
137.032  
137.015  
136.924  
136.902  
136.703  
136.604  
134.231  
133.963  
133.756  
133.562  
129.420  
128.540  
128.447  
128.381  
128.359  
128.240  
128.170  
127.608  
127.563  
127.060  
77.322  
77.000  
76.675

55.211  
54.955  
51.241

32.659  
21.350  
19.942



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



Std carbon;blank line

USER: -- DATE: Mar 22 2012

F1: 100.598

F2: 400.031

SW1: 24510

OF1: 10551.7

PTS1d: 65536

EX: s2pul

PW: 7.3 usec

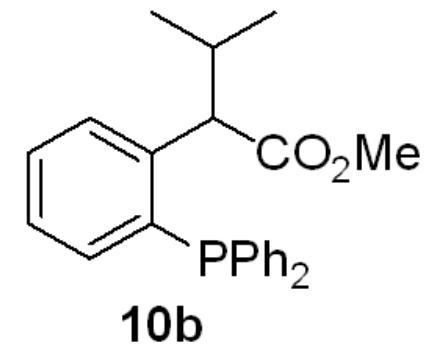
PD: 1.0 sec

NA: 136

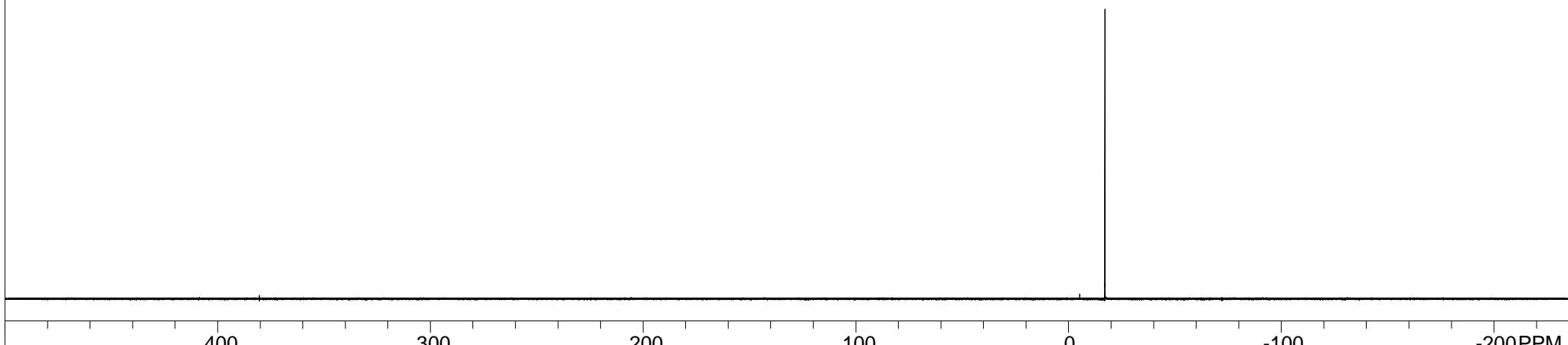
LB: 0.0

Nuts - \$hyd-22-43-C.fid

-17.274



$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )



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F1: 161.956

F2: 400.031

SW1: 119048

EX: s2pul

PW: 5.0 usec

PD: 1.0 sec

OF1: 21456.3

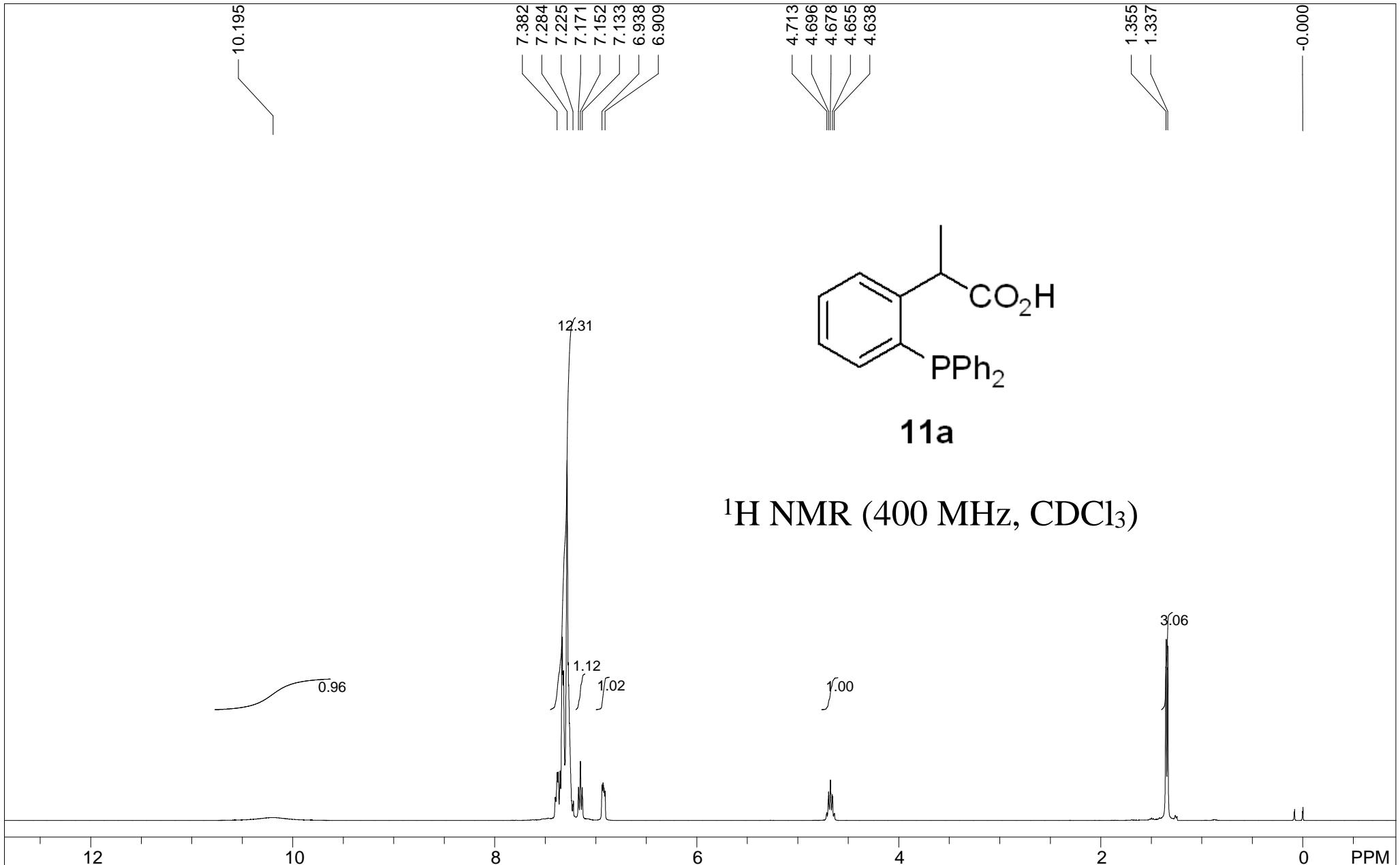
NA: 24

LB: 0.0

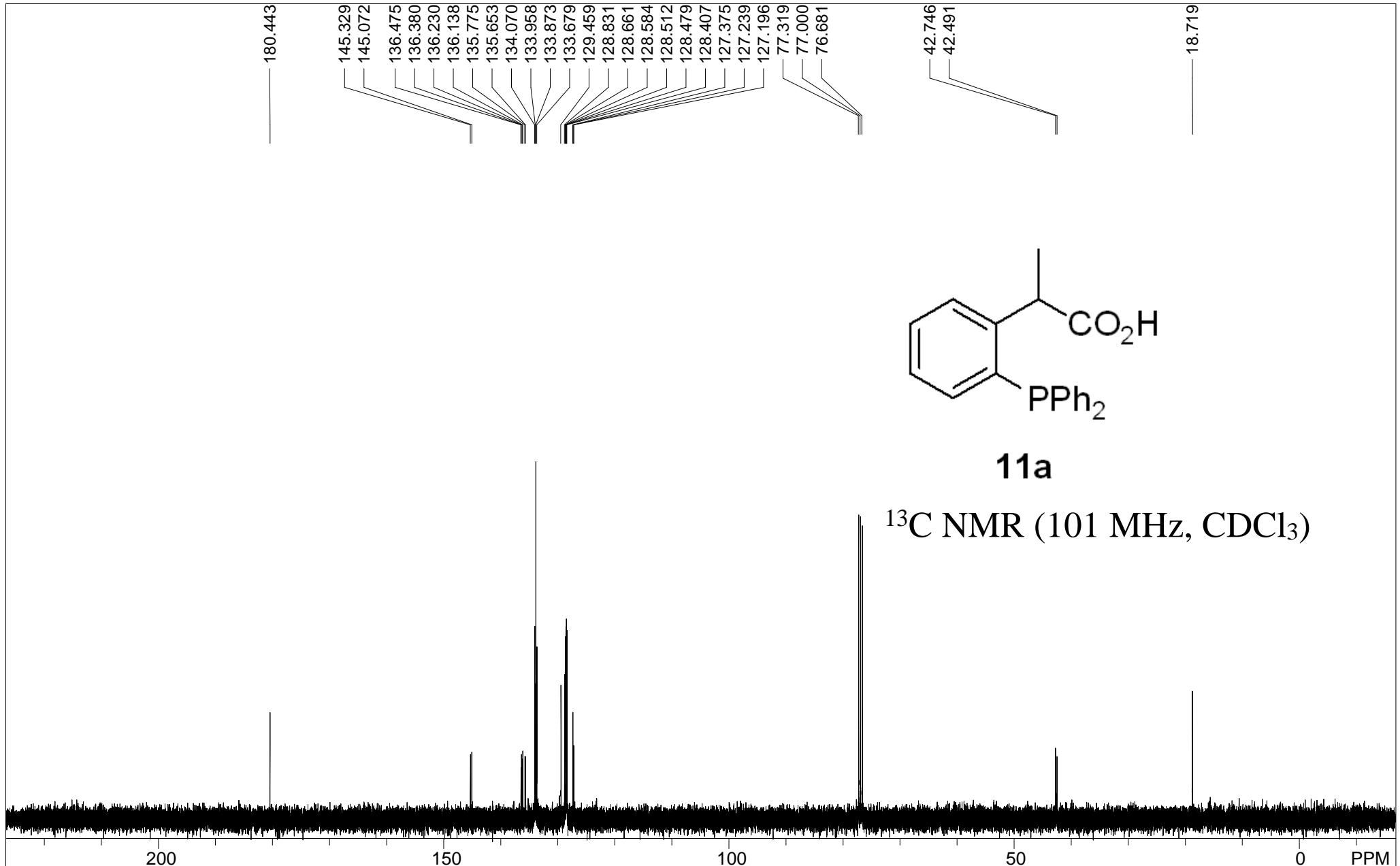
USER: -- DATE: Mar 22 2012

PTS1d: 131072

Nuts - \$hyd-22-43-P.fid



:blank line	:blank line						USER: -- DATE: Mar 20 2012
F1: 400.032	F2: 100.597	SW1: 7225		OF1: 2793.2		PTS1d: 32768	
EX: s2pul		PW: 10.3 usec	PD: 1.0 sec	NA: 20	LB: 0.0		Nuts - \$hjq-1-33-H.fid



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F1: 100.598

200

180.443

145.329  
145.072  
136.475  
136.380  
136.230  
136.138  
135.775  
135.653  
134.070  
133.958  
133.873  
133.679  
129.459  
128.831  
128.661  
128.584  
128.512  
128.479  
128.407  
127.375  
127.239  
127.196  
77.319  
77.000  
76.681

42.746  
42.491

18.719

USER: -- DATE: Mar 20 2012

EX: s2pul

150

SW1: 24510

100

OF1: 10555.9

50

PTS1d: 65536

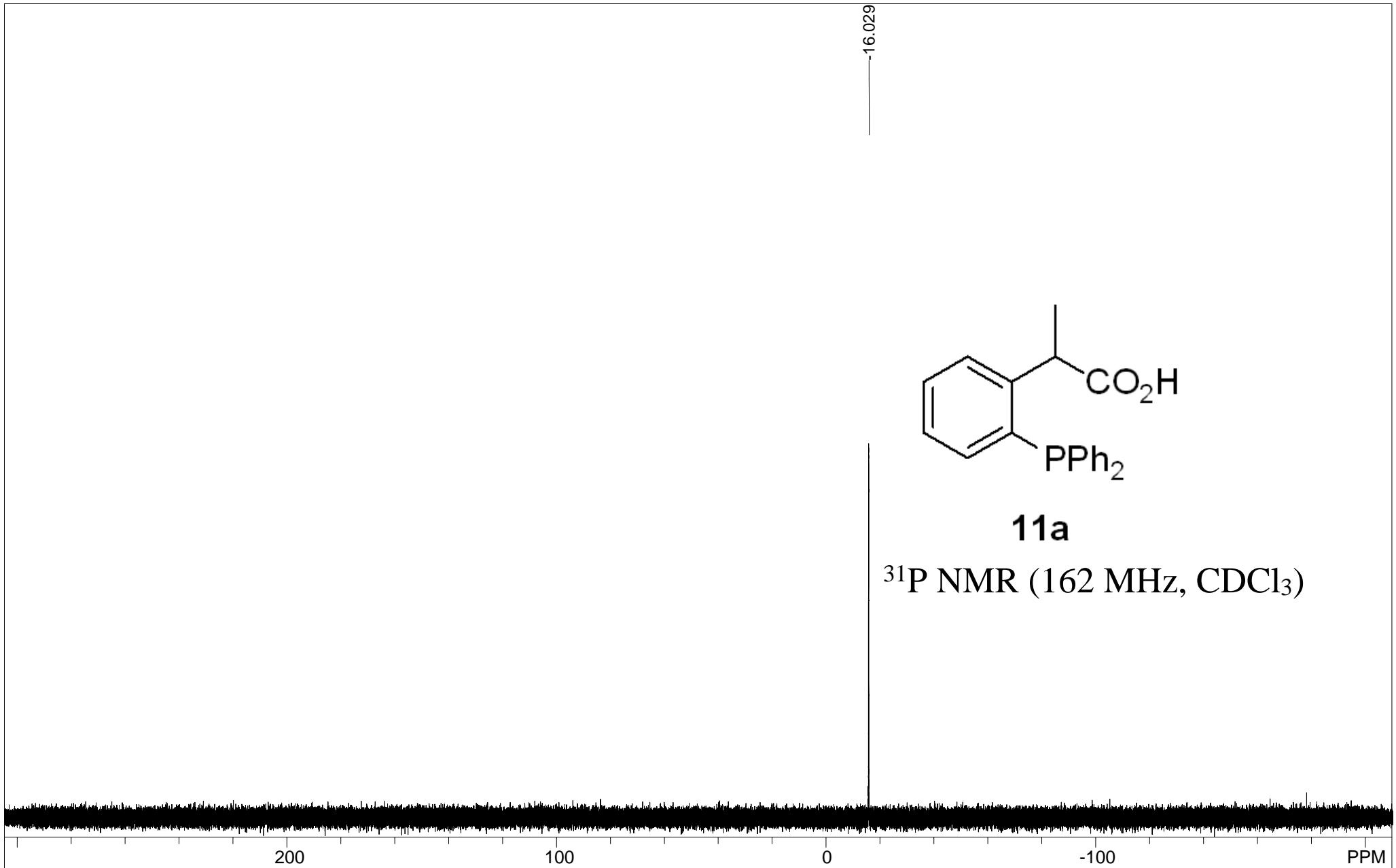
Nuts - \$hjq-1-33-C.fid

PW: 7.3 usec

PD: 1.0 sec

NA: 84

LB: 0.0



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F1: 161.942

F2: 400.031

SW1: 83333

100

OF1: 7691.9

USER: -- DATE: Mar 20 2012

EX: s2pul

PW: 5.0 usec

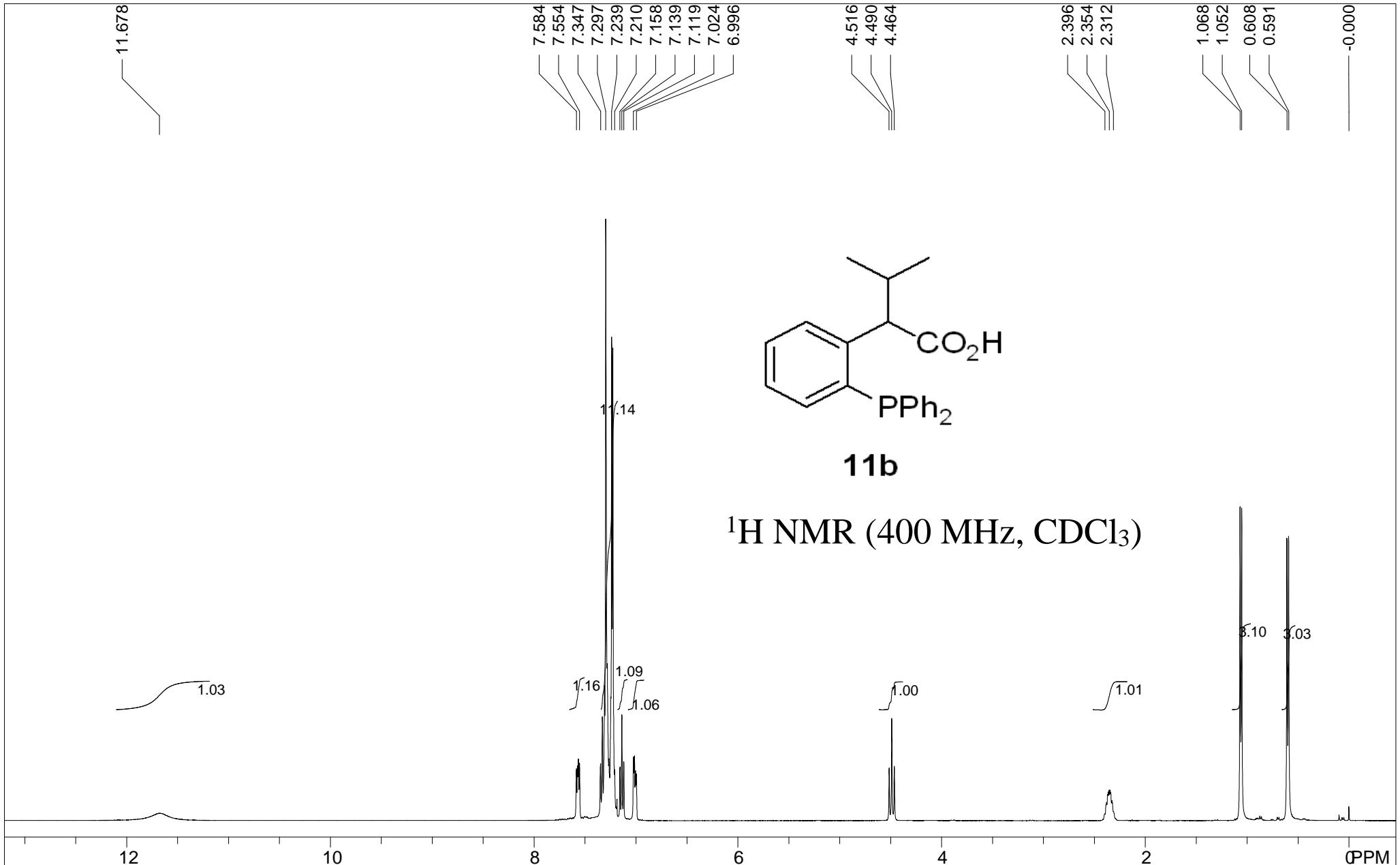
PD: 1.0 sec

NA: 24

LB: 0.0

PTS1d: 131072

Nuts - \$hjq-1-33-P.fid



:blank line

F1: 400.032

F2: 100.597

SW1: 8803

EX: s2pul

PW: 4.4 usec

PD: 1.0 sec

OF1: 3578.5

NA: 12

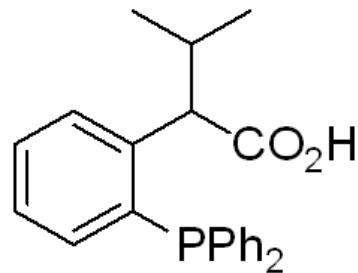
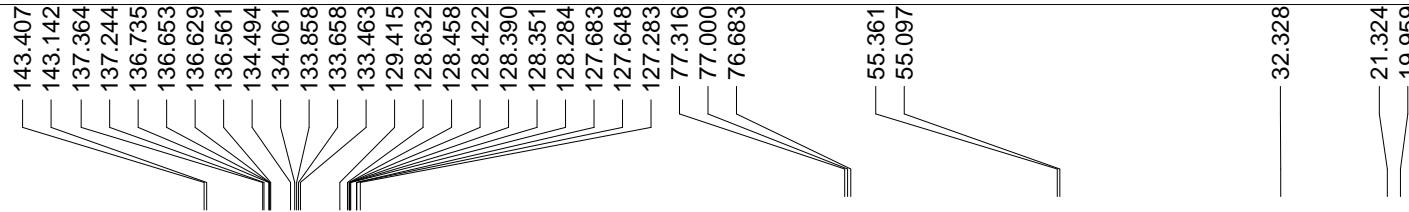
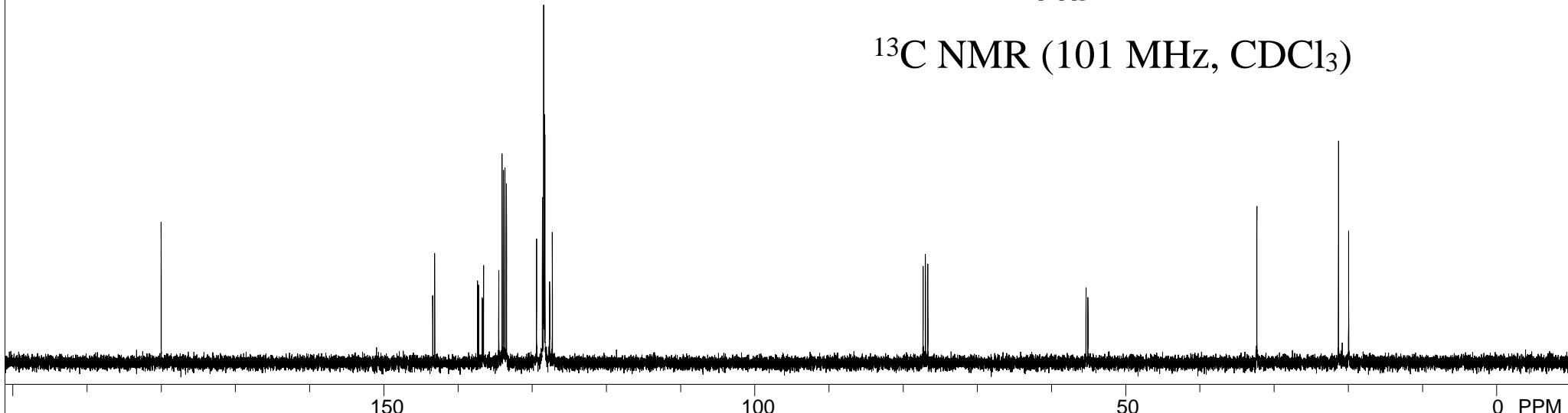
LB: 0.0

PTS1d: 32768

Nuts - \$hyd-16-76-H.fid

USER: -- DATE: Mar 12 2011

180.011

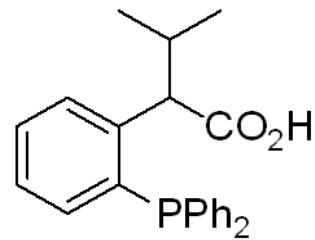
**11b**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

zf-15-9-C13-r;blank line

USER: -- DATE: Mar 12 2011

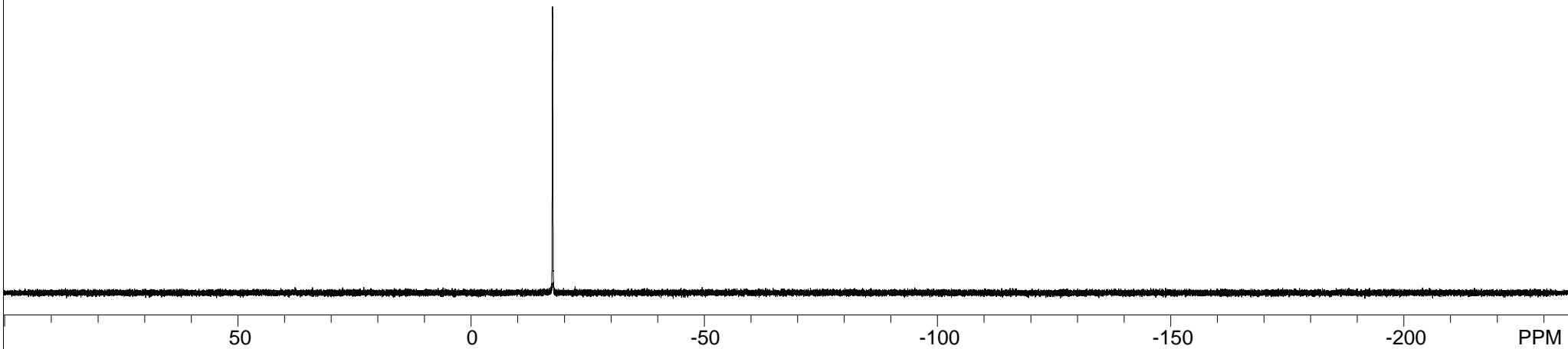
F1: 100.598	F2: 400.031	SW1: 24510		OF1: 10550.2		PTS1d: 32768	
EX: s2pul		PW: 7.3 usec	PD: 1.0 sec	NA: 32	LB: 0.0		Nuts - \$hyd-16-76-C.fid

17.425



**11b**

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )



R-f-1007193

F1: 161.924

EX: s2pul

F2: 400.031

PW: 5.0 usec

PD: 1.0 sec

SW1: 54348

NA: 12

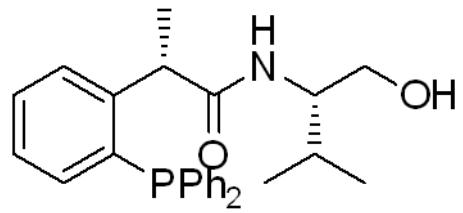
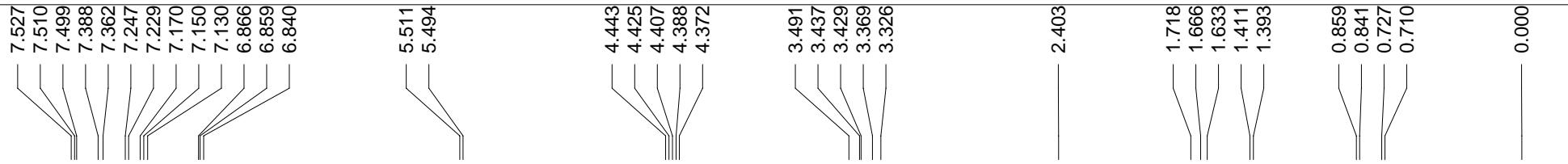
OF1: -10930.6

LB: 0.0

PTS1d: 65536

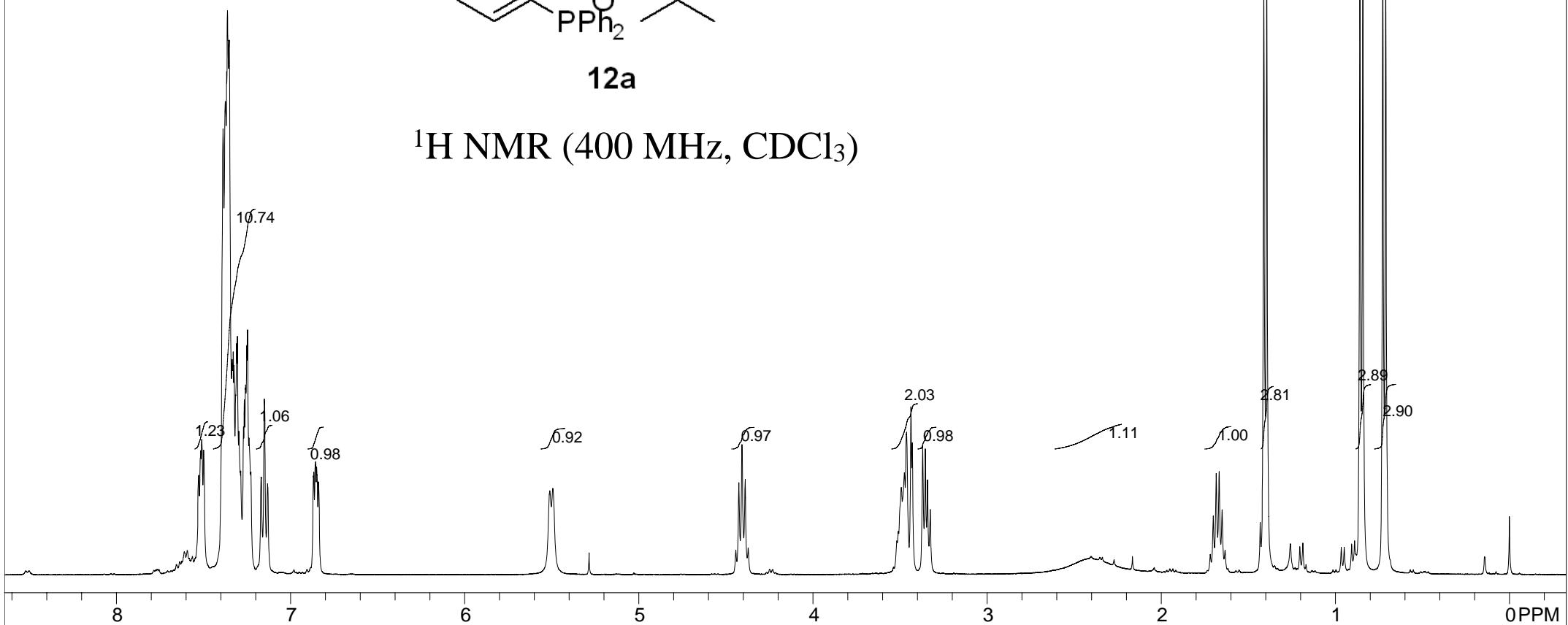
Nuts - \$hyd-16-76-P.fid

USER: -- DATE: Mar 12 2011



**12a**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



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F1: 400.037

F2: 100.598

SW1: 6410

OF1: 2801.0

PTS1d: 32768

EX: s2pul

PW: 4.4 usec

PD: 2.0 sec

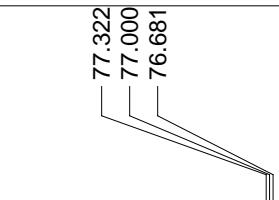
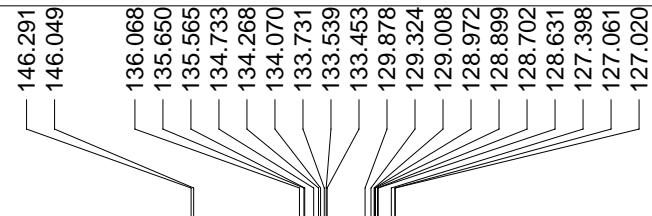
NA: 24

LB: 0.0

USER: -- DATE: Sep 14 2009

Nuts - \$hyd-8-52-a-H.fid

175.030

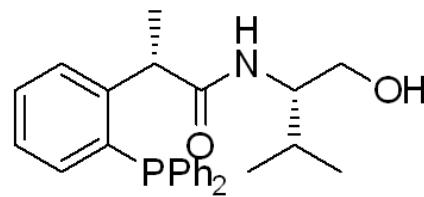
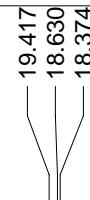
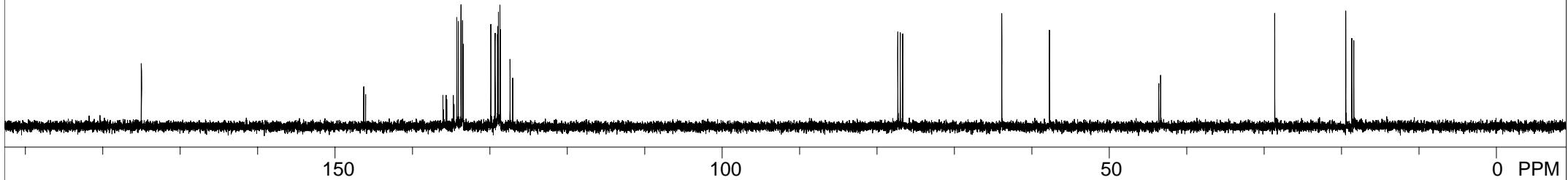


63.886

57.724



28.600

**12a** $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

hyd-8-52-a-C-400M

F1: 100.600 F2: 400.037

SW1: 25000 PW: 7.3 usec

EX: s2pul PD: 1.0 sec

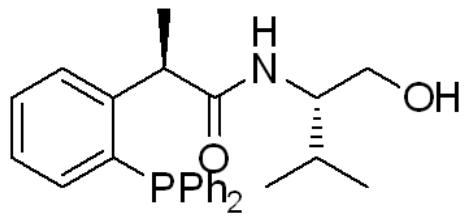
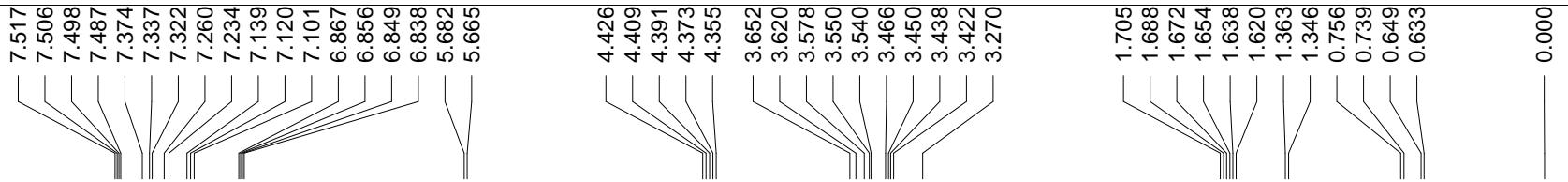
OF1: 10808.6

NA: 140 LB: 0.0

PTS1d: 32768

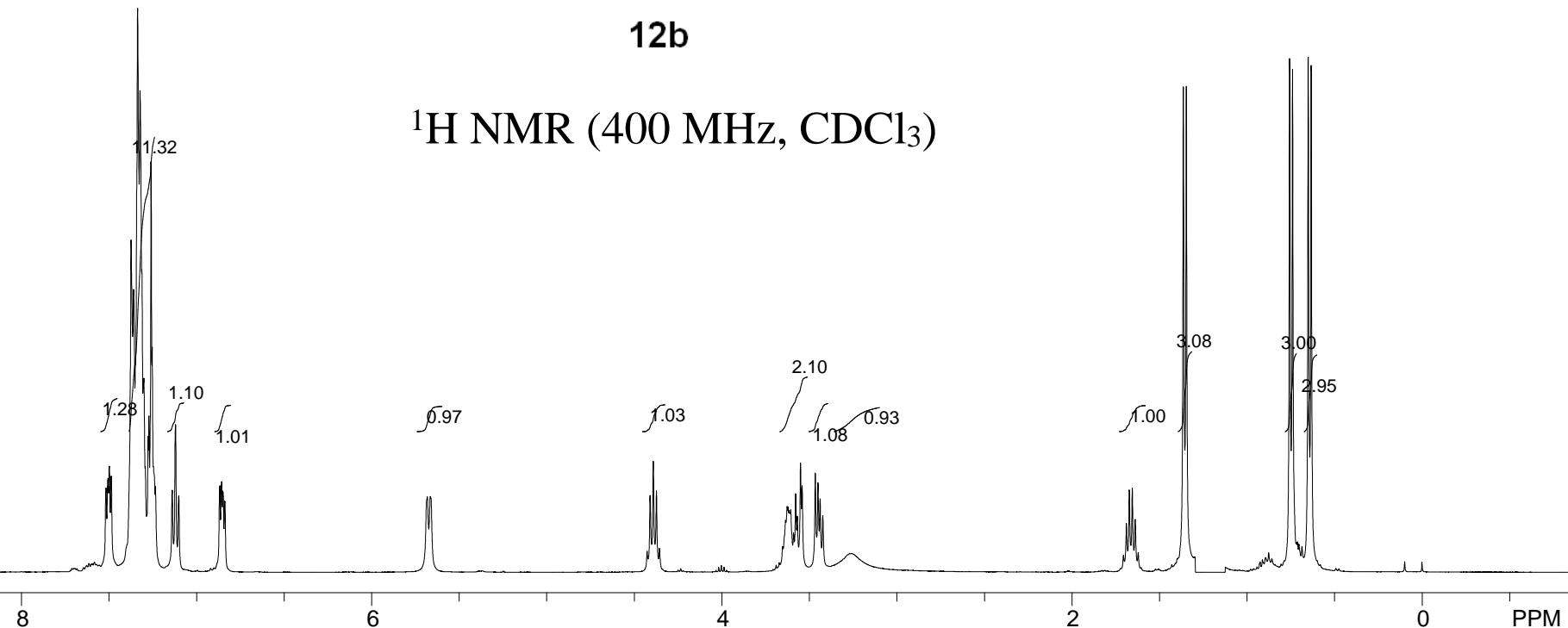
Nuts - \$hyd-8-52-a-C.fid

USER: -- DATE: Sep 14 2009



**12b**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



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F1: 400.031

F2: 100.597

SW1: 7022

EX: s2pul

PW: 10.3 usec

PD: 1.0 sec

OF1: 2708.3

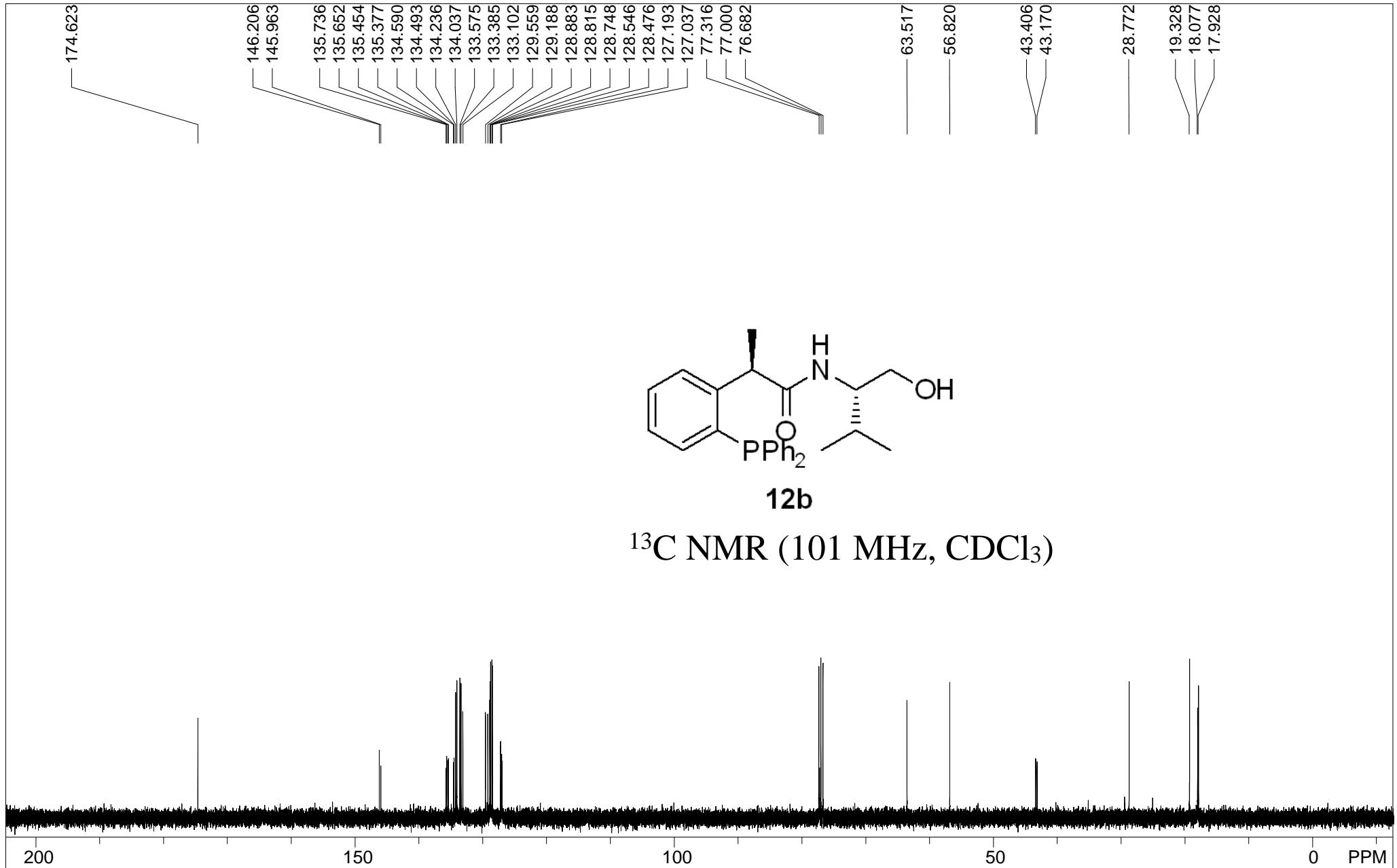
NA: 16

LB: 0.0

PTS1d: 32768

USER: -- DATE: Mar 22 2012

Nuts - \$hyd-22-44-B-H.fid



**12b**

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

Std carbon;blank line

USER: -- DATE: Mar 22 2012

F1: 100.598

F2: 400.031

SW1: 24510

OF1: 10543.9

PTS1d: 65536

EX: s2pul

PW: 7.3 usec

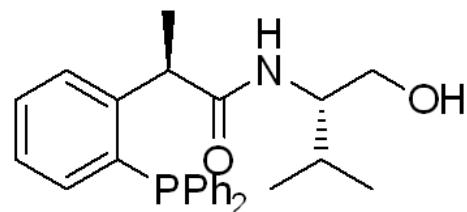
PD: 1.0 sec

NA: 48

LB: 0.0

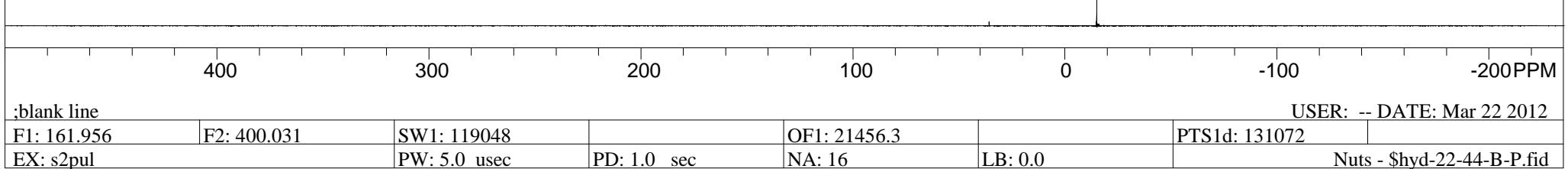
Nuts - \$hyd-22-44-B-C.fid

15.227



**12b**

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )



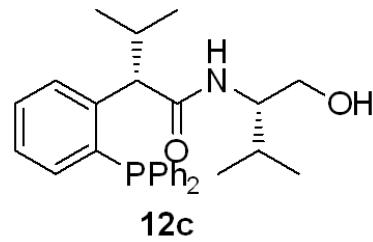
7.673  
7.632  
7.329  
7.279  
7.245  
7.115  
7.090  
7.065  
6.918  
6.904  
6.896  
6.882

5.913  
5.903  
5.885  
5.875

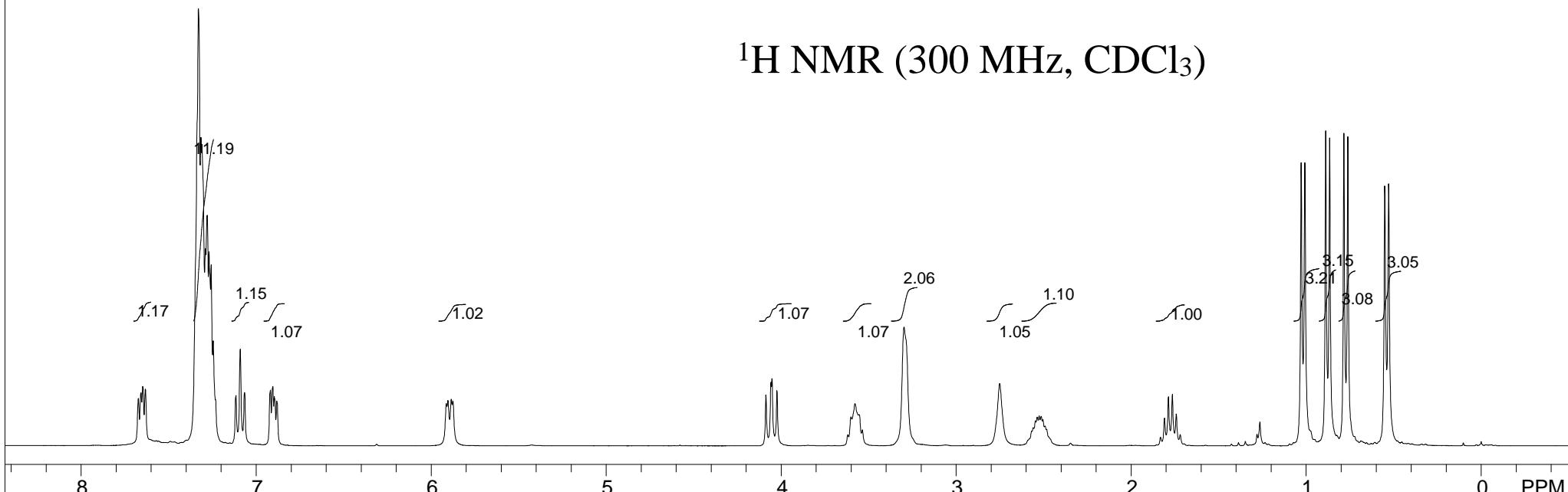
4.087  
4.058  
4.052  
4.024  
4.024  
3.619  
3.578  
3.536  
3.298

2.751  
2.559  
2.537  
2.491  
1.831  
1.765  
1.719

1.028  
1.006  
0.888  
0.865  
0.783  
0.761  
0.551  
0.529



<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



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F1: 300.029

F2: 300.028

SW1: 5005

5

OF1: 2035.8

2

PTS1d: 16384

USER: -- DATE: Mar 15 2011  
Nuts - \$hyd-16-81-1-H.fid

EX: s2pul

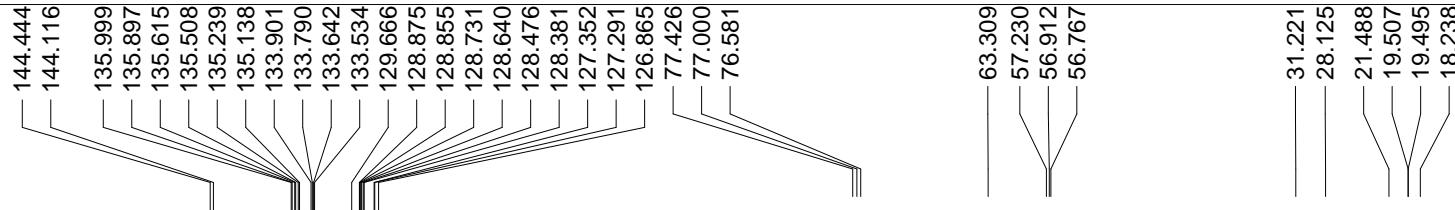
PW: 4.2 usec

PD: 1.0 sec

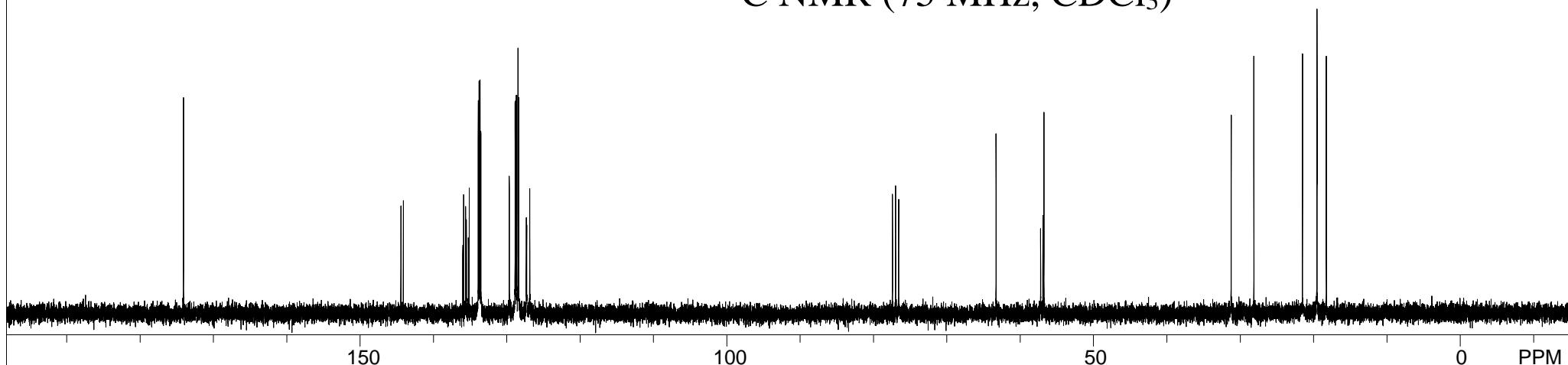
NA: 16

LB: 0.0

174.082



<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)



021201

USER: -- DATE: Mar 15 2011

F1: 75.450

F2: 300.028

SW1: 18797

OF1: 7735.5

PTS1d: 32768

EX: s2pul

PW: 4.6 usec

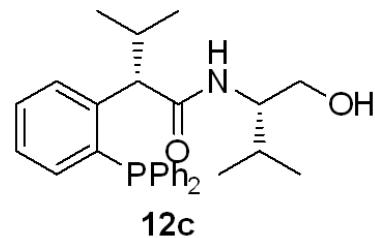
PD: 1.0 sec

NA: 60

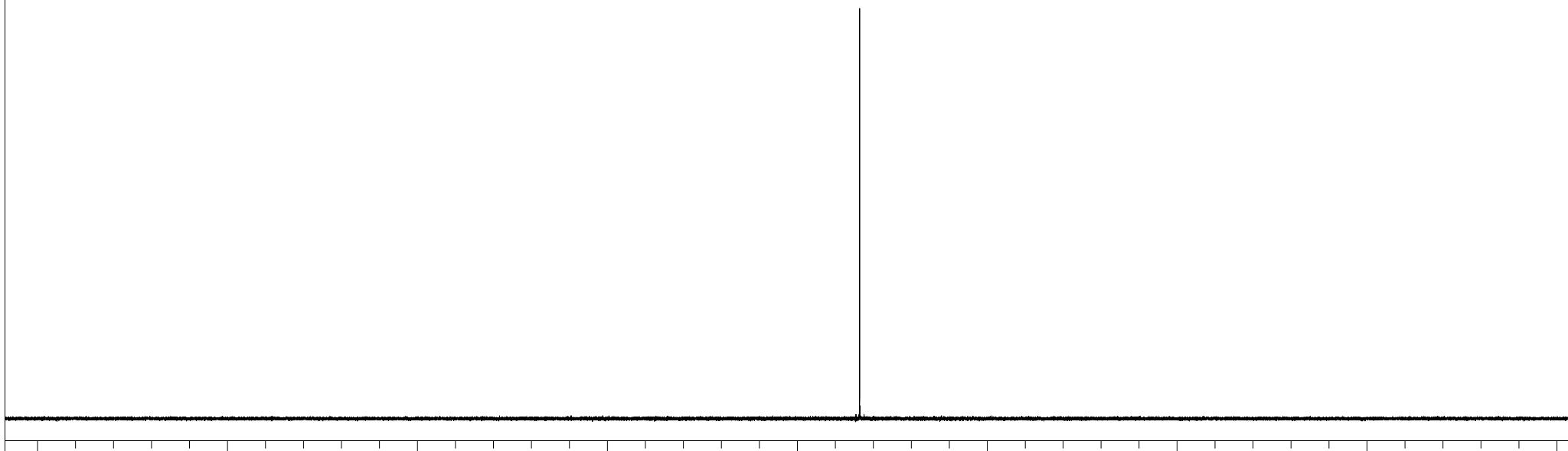
LB: 0.0

Nuts - \$hyd-16-81-1-C.fid

-16.313

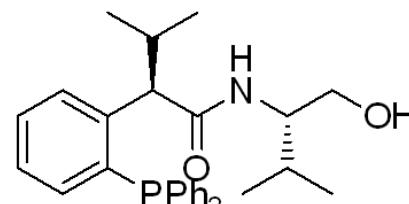
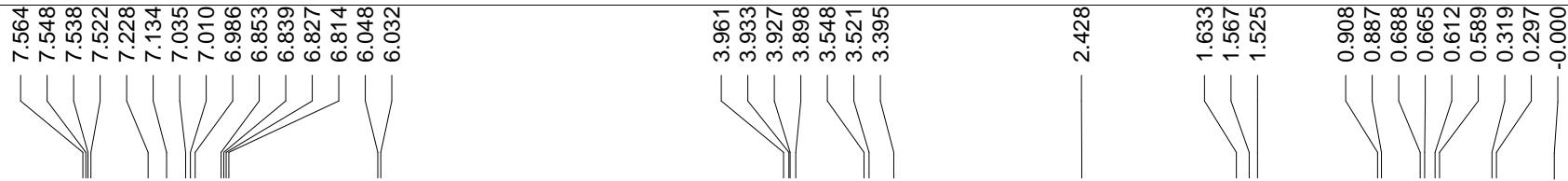


$^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ )



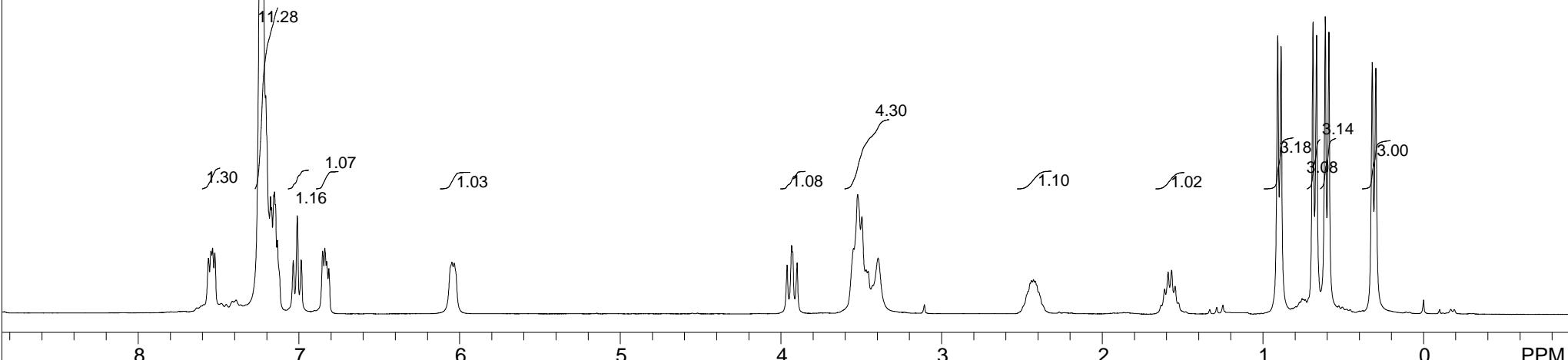
P-31 STANDARD PARAMETERS PHOSPHATE REGION

F1: 121.453	F2: 300.028	SW1: 50000		OF1: 338.4		PTS1d: 65536	USER: -- DATE: Mar 15 2011
EX: s2pul		PW: 3.9 usec	PD: 1.0 sec	NA: 16	LB: 0.0		Nuts - \$hyd-16-81-1-P.fid



**12d**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



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F1: 300.029

F2: 300.028

SW1: 5005

PD: 1.0 sec

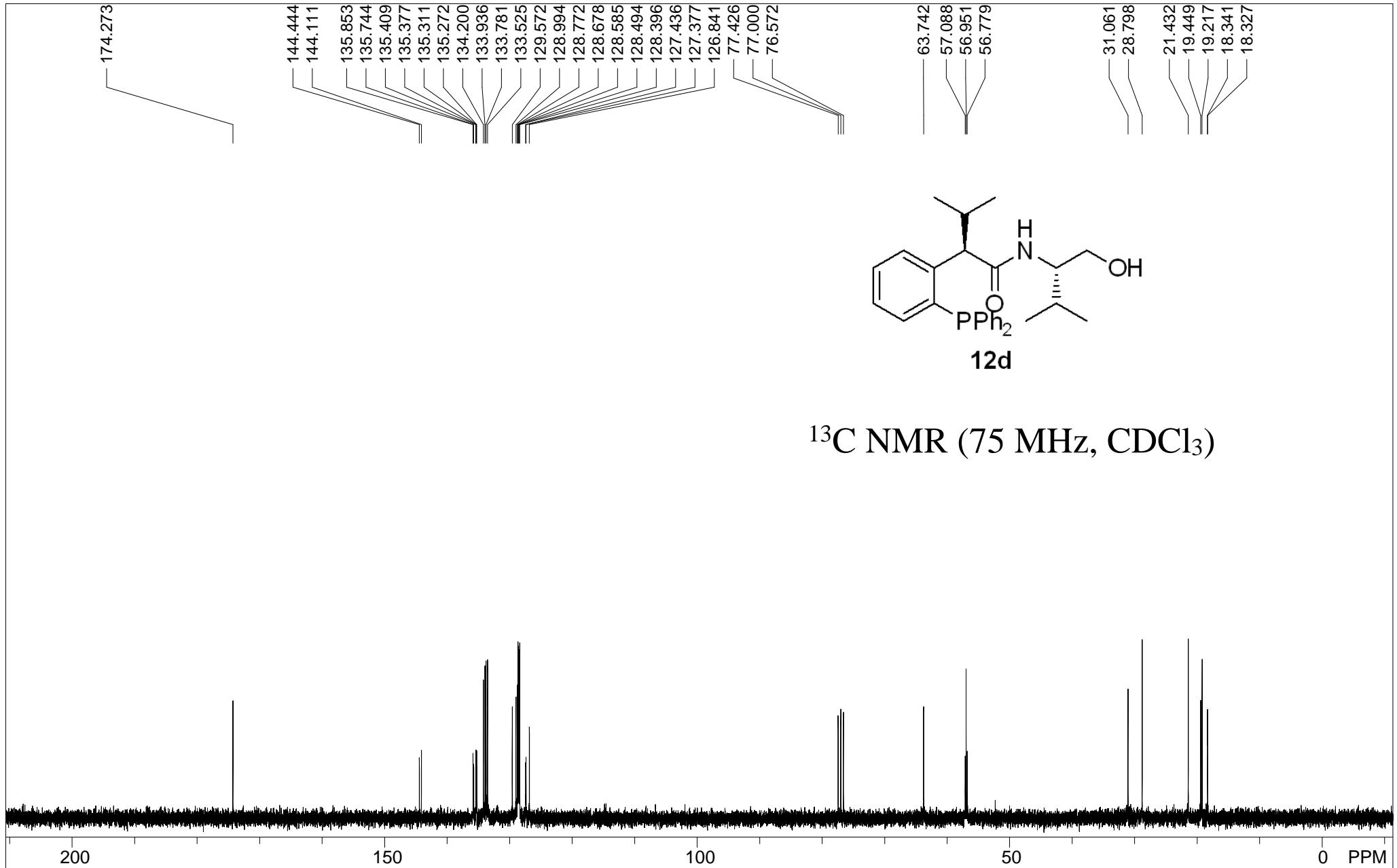
OF1: 2007.3

NA: 16

PTS1d: 16384

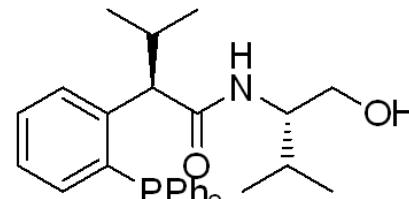
Nuts - \$hyd-16-81-2-H.fid

USER: -- DATE: Mar 15 2011



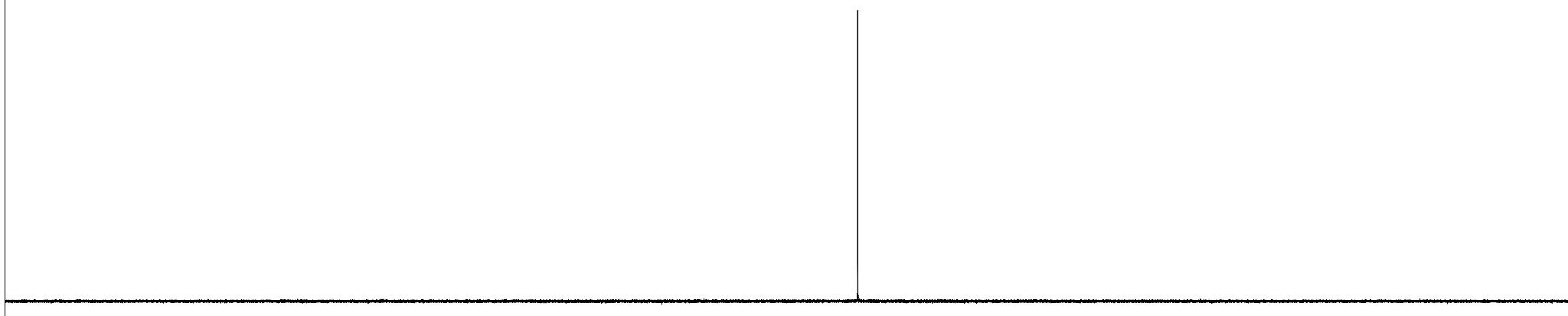
021201						USER: -- DATE: Mar 15 2011
F1: 75.450	F2: 300.028	SW1: 18797		OF1: 7738.1	PTS1d: 32768	
EX: s2pul		PW: 4.6 usec	PD: 1.0 sec	NA: 72	LB: 0.0	Nuts - \$hyd-16-81-2-C.fid

-15.818



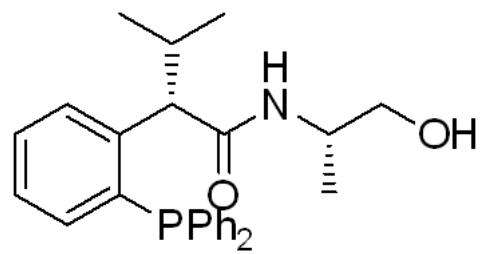
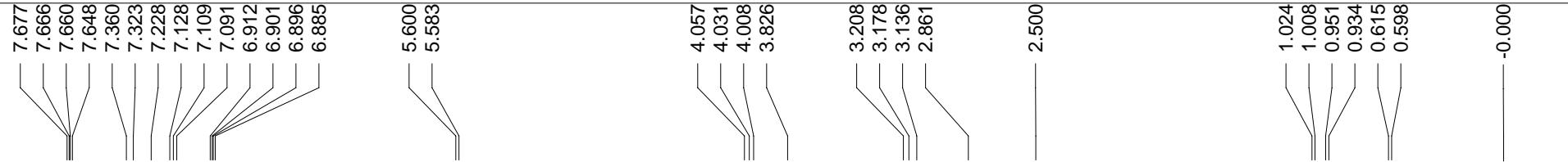
**12d**

<sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>)



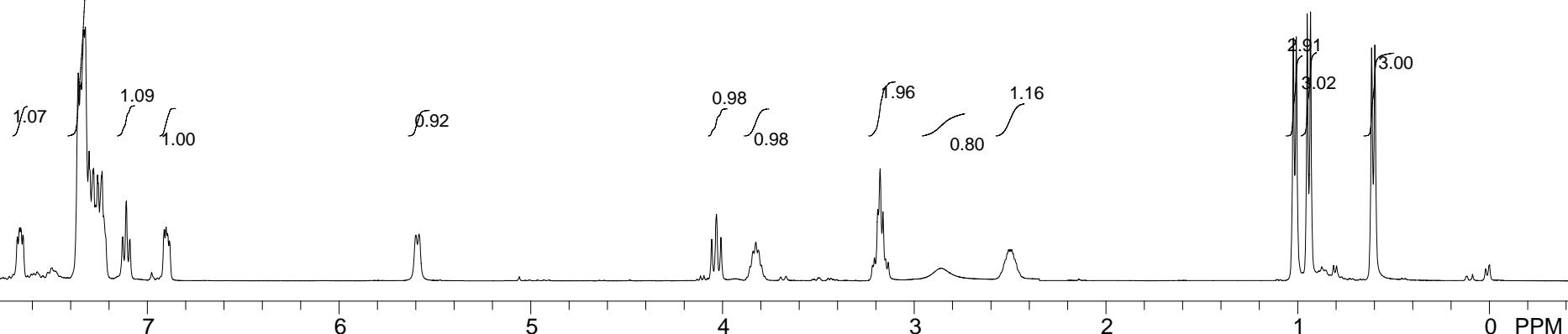
P-31 STANDARD PARAMETERS PHOSPHATE REGION

F1: 121.453	F2: 300.028	SW1: 50000		OF1: 338.4		PTS1d: 65536	USER: -- DATE: Mar 15 2011
EX: s2pul		PW: 3.9 usec	PD: 1.0 sec	NA: 12	LB: 0.0		Nuts - \$hyd-16-81-2-P.fid



**12e**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> )



0811

USER: -- DATE: Aug 13 2009

F1: 400.037

F2: 100.598

SW1: 6410

OF1: 2400.1

PTS1d: 32768

EX: s2pul

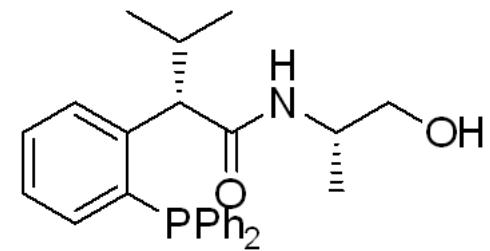
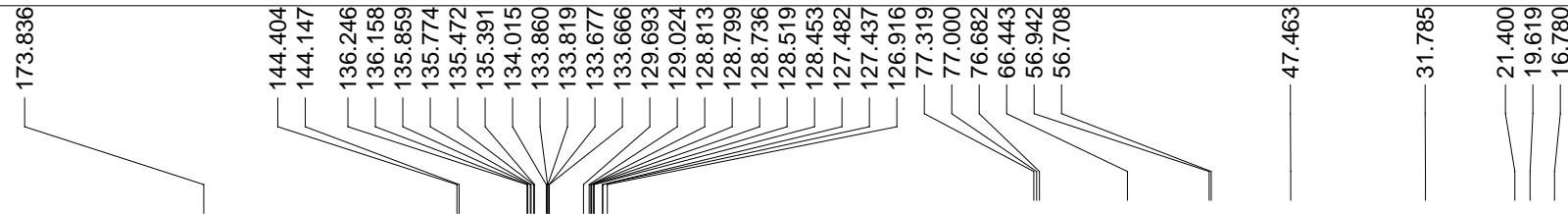
PW: 4.4 usec

PD: 1.0 sec

NA: 10

LB: 0.0

Nuts - \$hyd-7-33-1-H.fid



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

200 150 100 50 0 PPM

whm-19-13-C

USER: -- DATE: Aug 13 2009

F1: 100.599 F2: 400.037

SW1: 24510

OF1: 10548.1

PTS1d: 32768

EX: s2pul

PW: 7.3 usec

PD: 1.0 sec

NA: 36

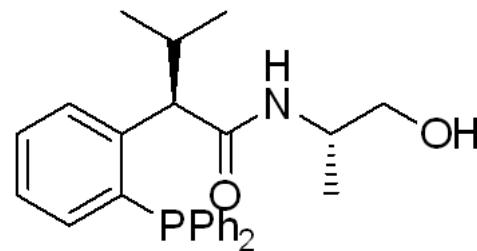
LB: 0.0

Nuts - \$hyd-7-33-1-C.fid

7.721  
7.710  
7.703  
7.692  
7.398  
7.373  
7.302  
7.283  
7.272  
7.181  
7.162  
7.142  
6.965  
6.957  
6.946  
6.938  
5.803  
5.791

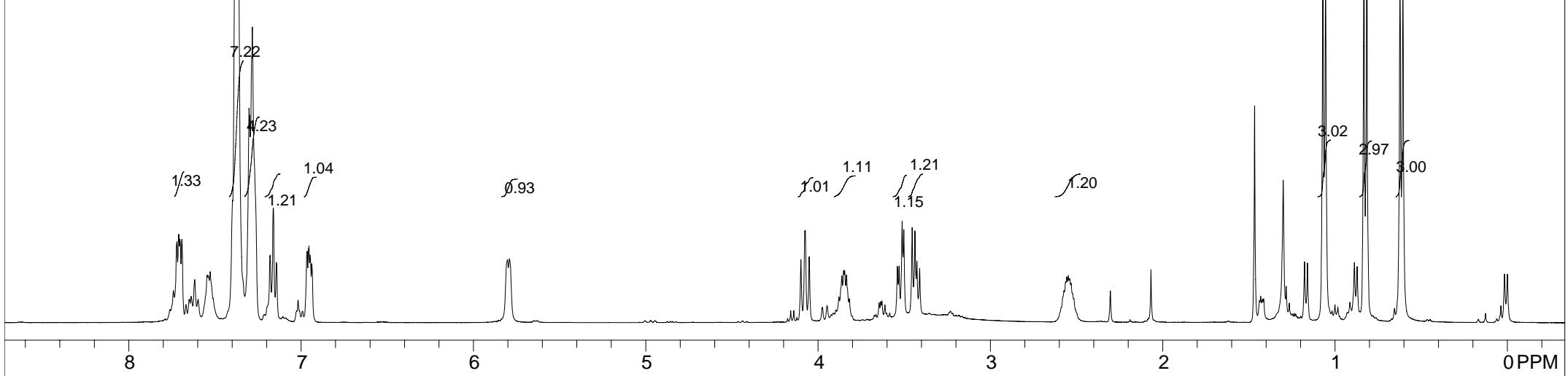
4.100  
4.077  
4.051  
3.879  
3.846  
3.819  
3.540  
3.529  
3.512  
3.502  
3.454  
3.438  
3.427  
3.410  
2.548

1.071  
1.055  
0.833  
0.816  
0.623  
0.606  
-0.000



**12f**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



0811

F1: 400.037

F2: 100.598

SW1: 6410

OF1: 2416.3

PTS1d: 32768

EX: s2pul

PW: 4.4 usec

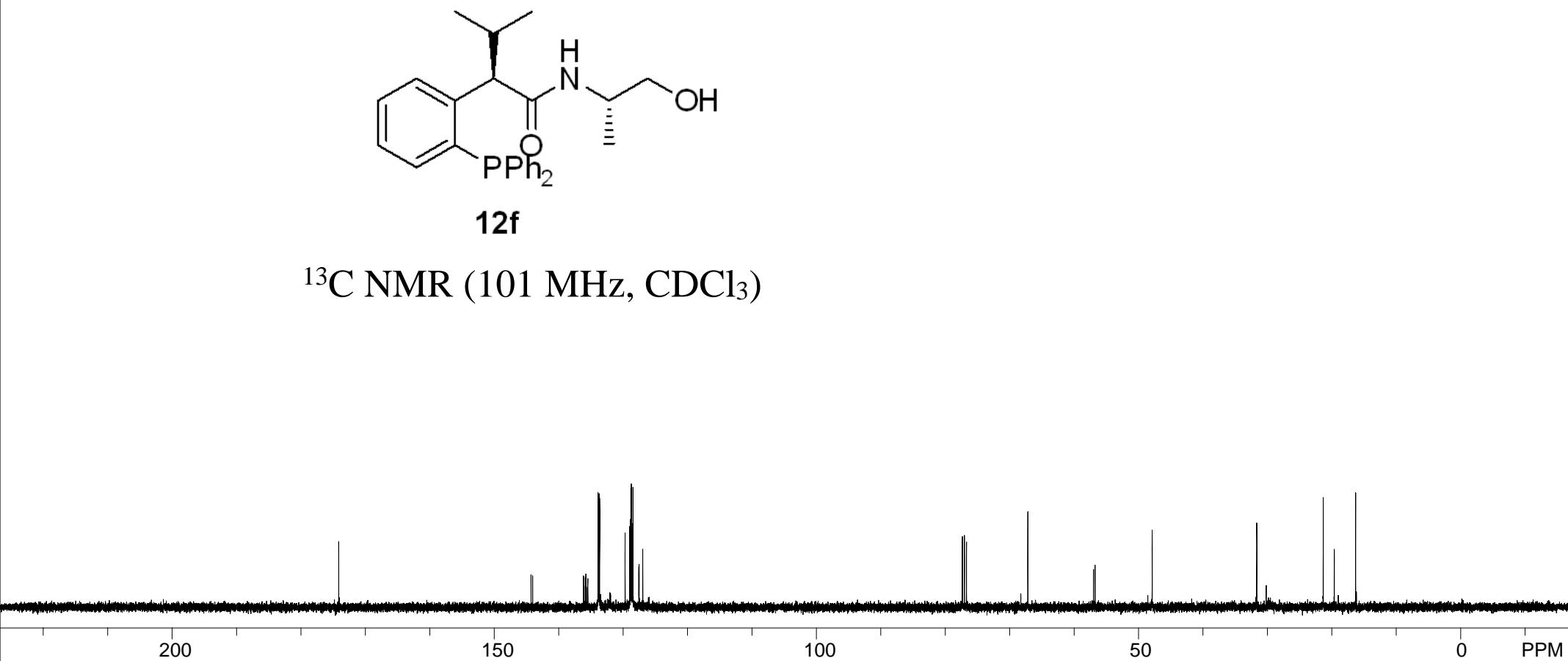
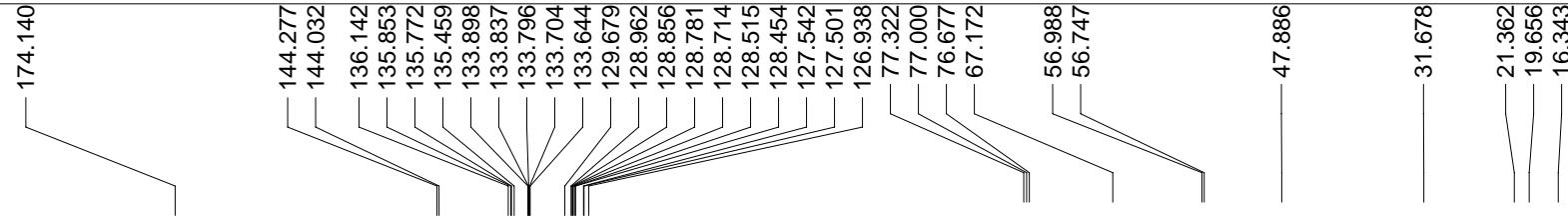
PD: 1.0 sec

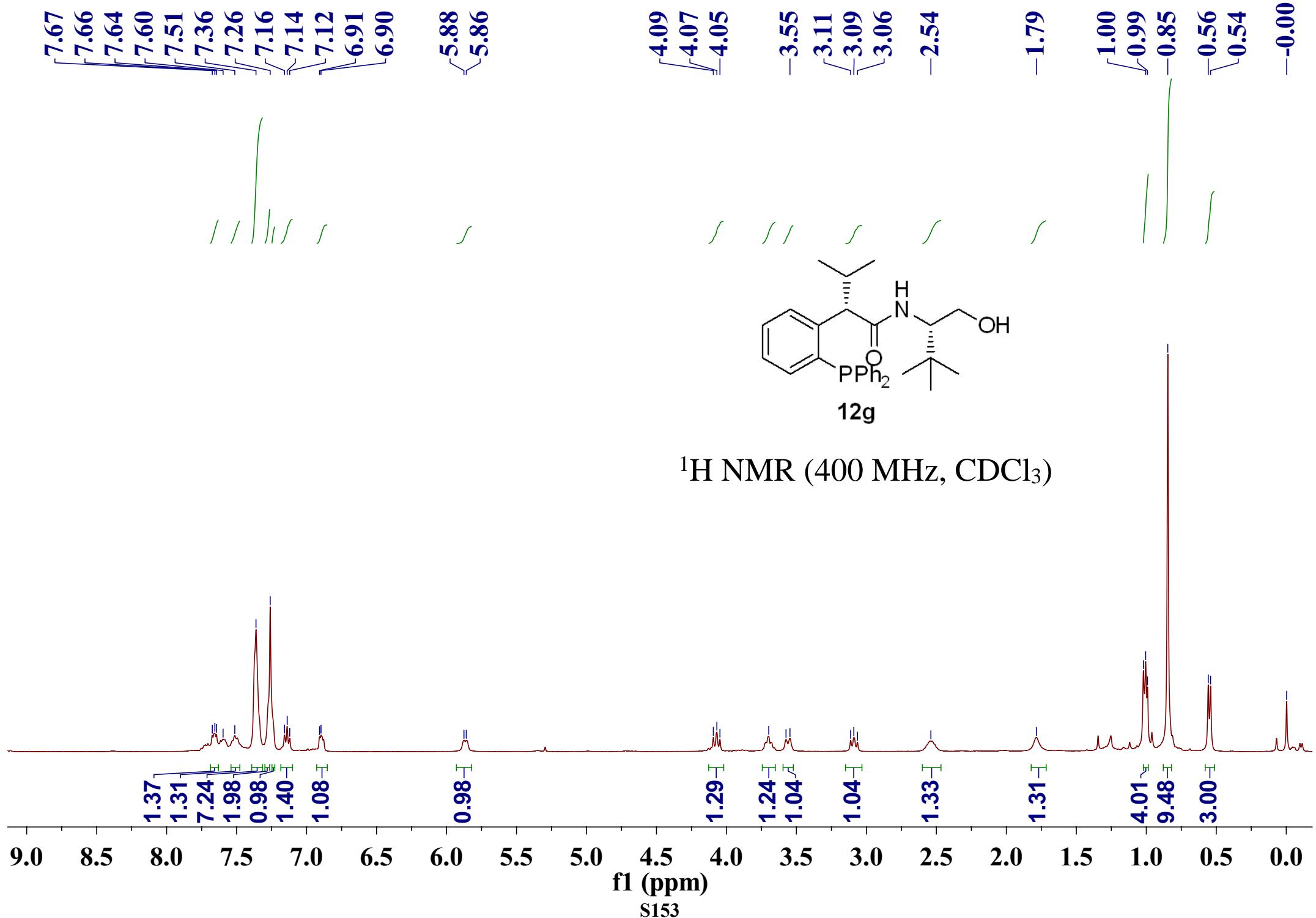
NA: 18

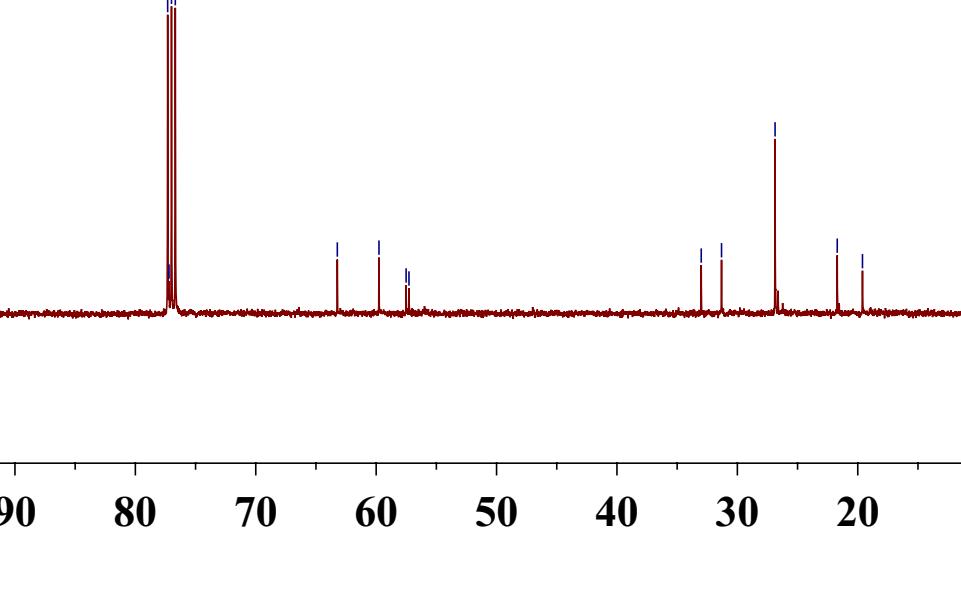
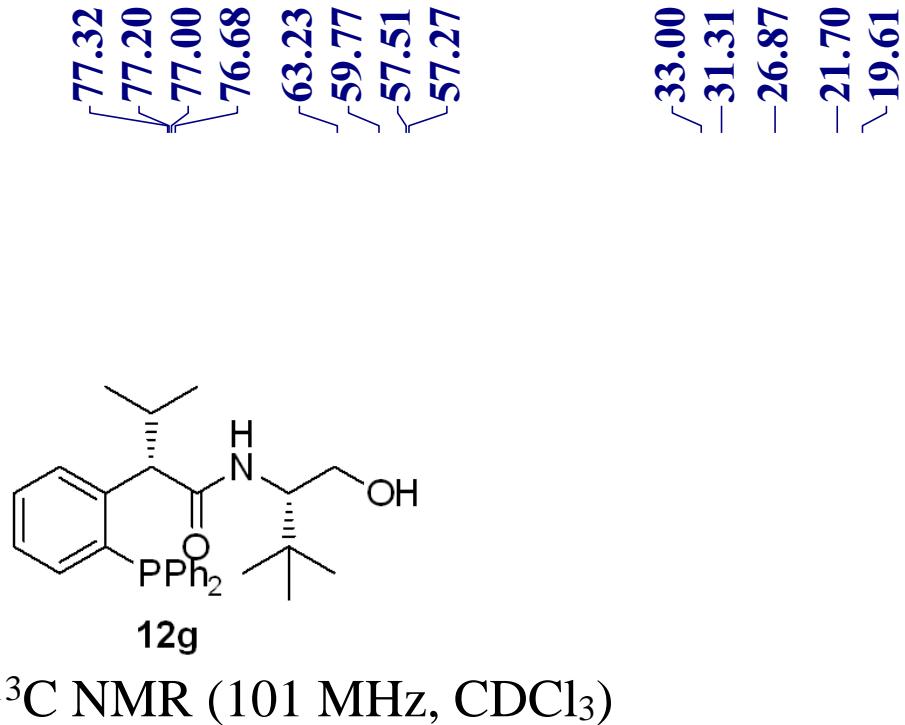
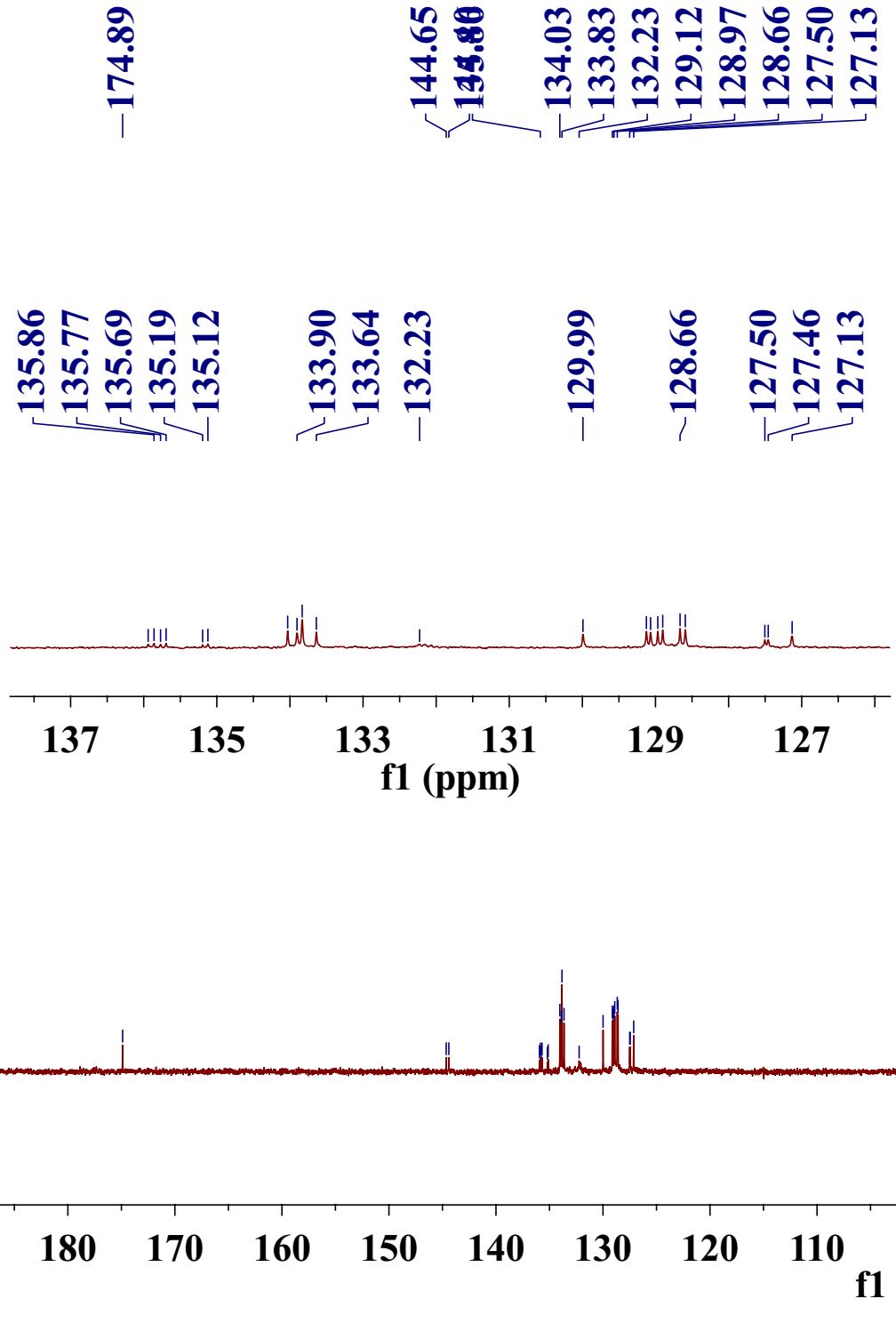
LB: 0.0

USER: -- DATE: Aug 13 2009

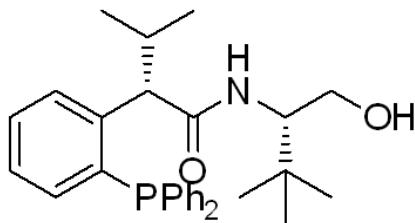
Nuts - \$hyd-7-33-2-H.fid





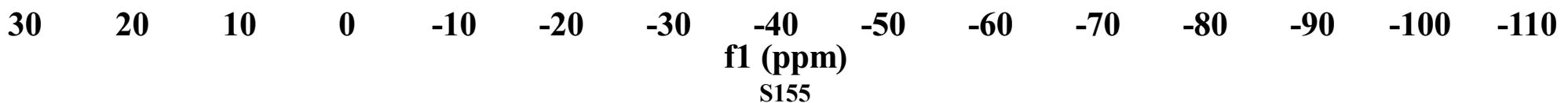


-17.40



12g

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )



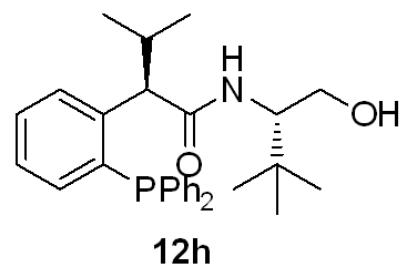
7.44  
7.33  
7.21  
7.15  
6.93  
6.91

6.44  
6.43

3.98  
3.77  
3.76  
3.75  
3.73  
3.73  
3.54  
3.52  
3.49

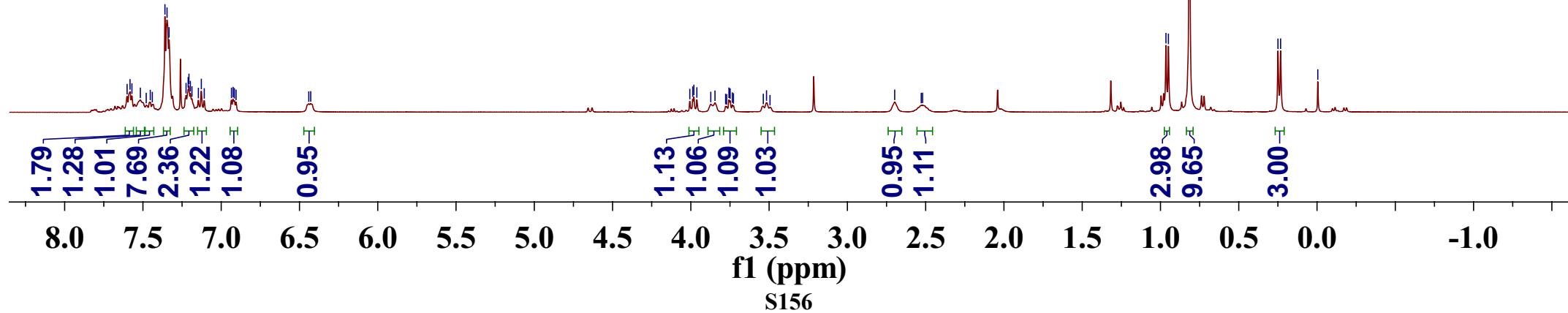
2.70  
2.53  
2.52

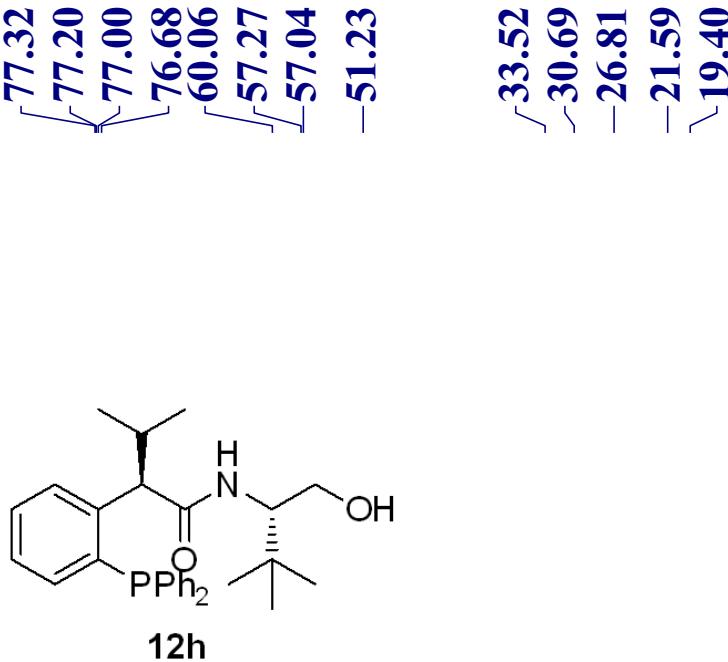
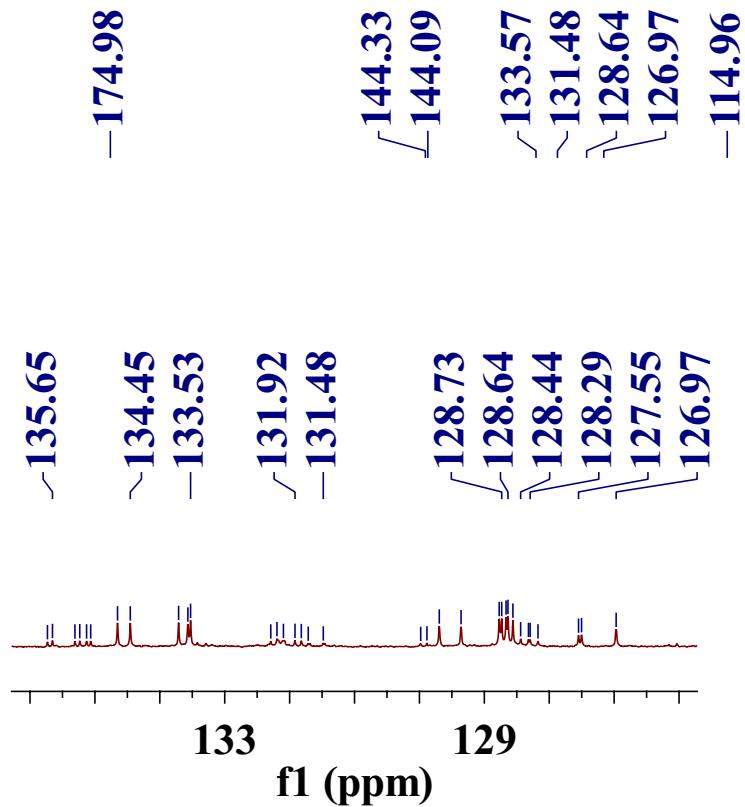
0.97  
0.95  
-0.82  
0.25  
0.23  
-0.00



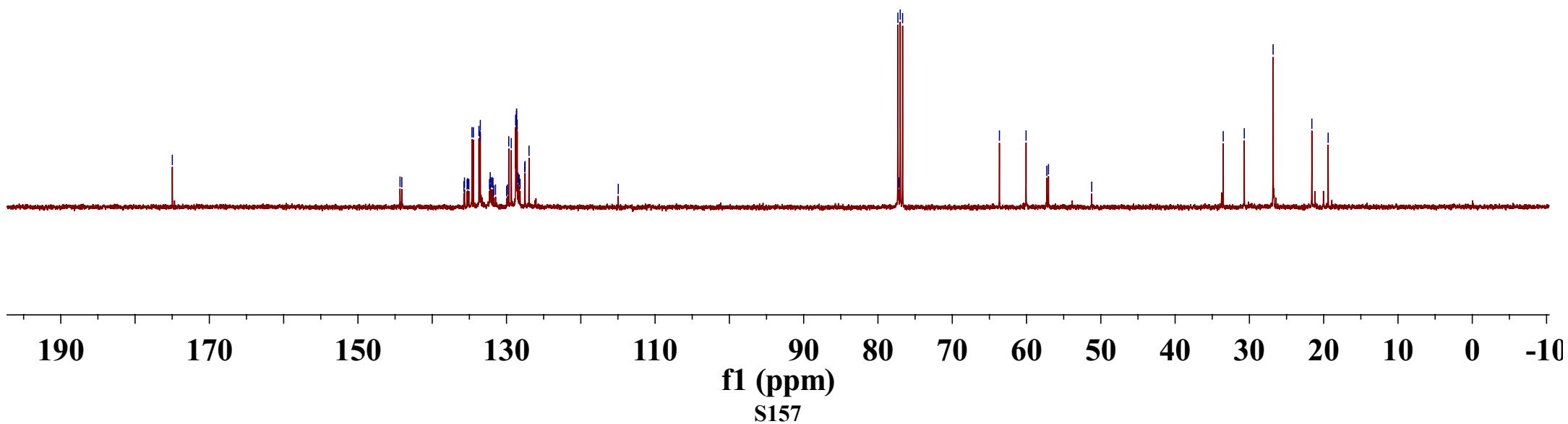
**12h**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

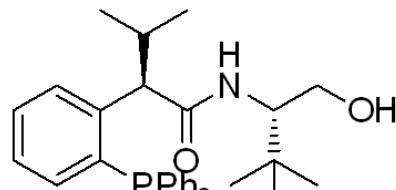




<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

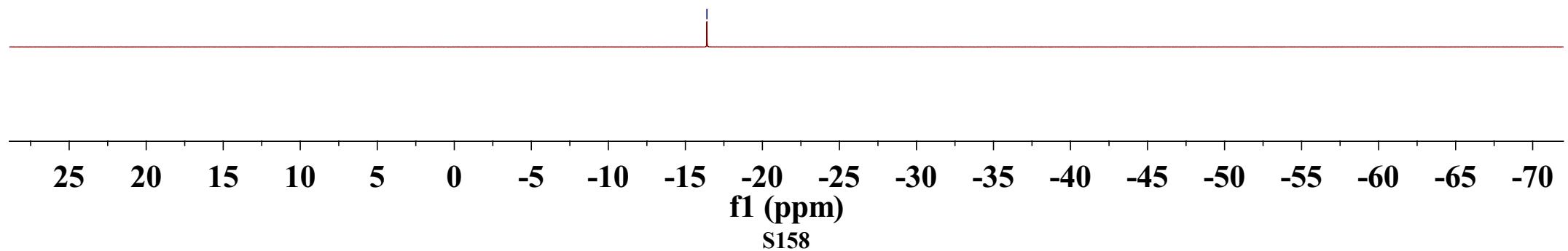


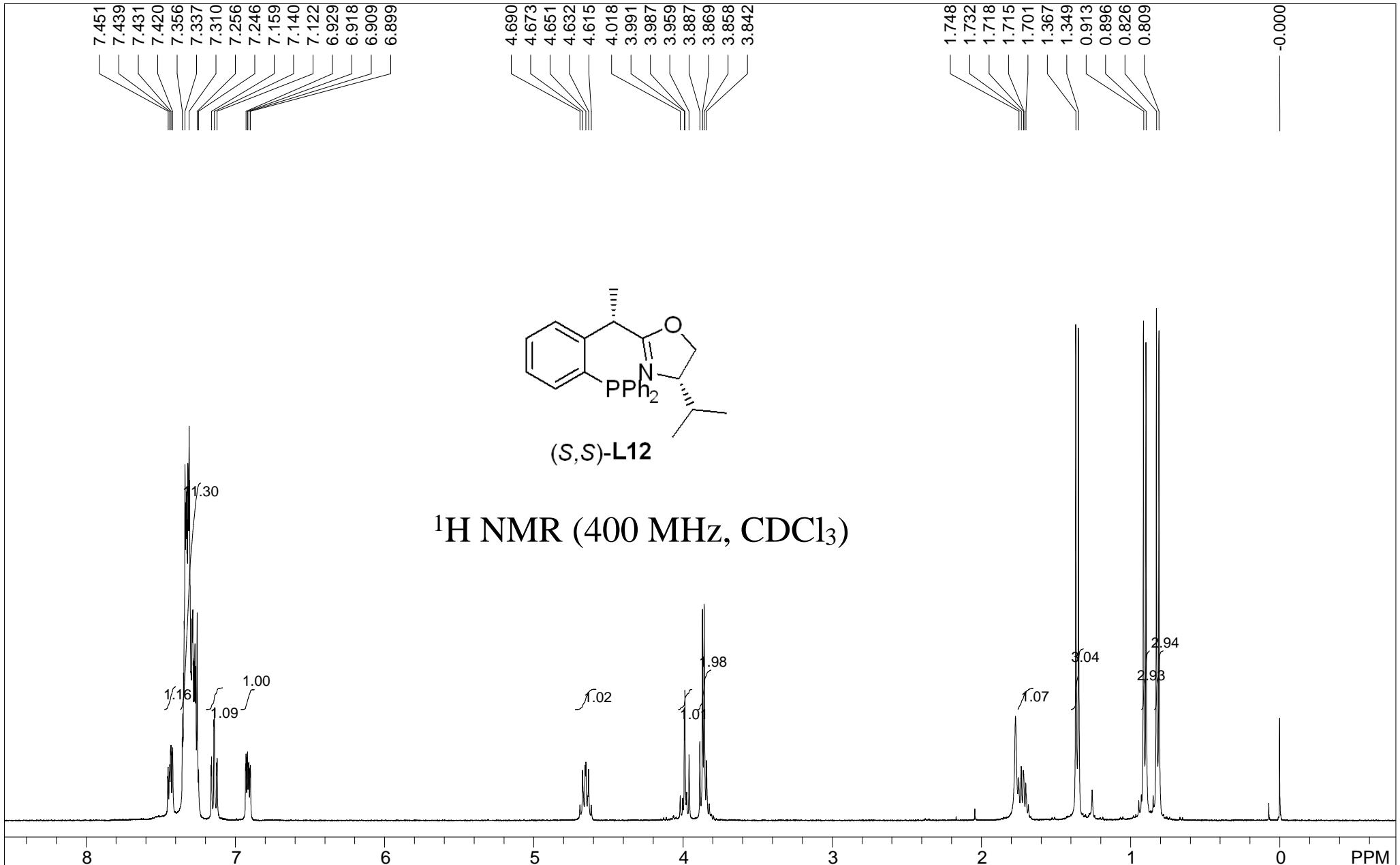
-16.40



**12h**

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)





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F1: 400.037

F2: 100.598

SW1: 6410

OF1: 2799.0

PTS1d: 32768

EX: s2pul

PW: 4.4 usec

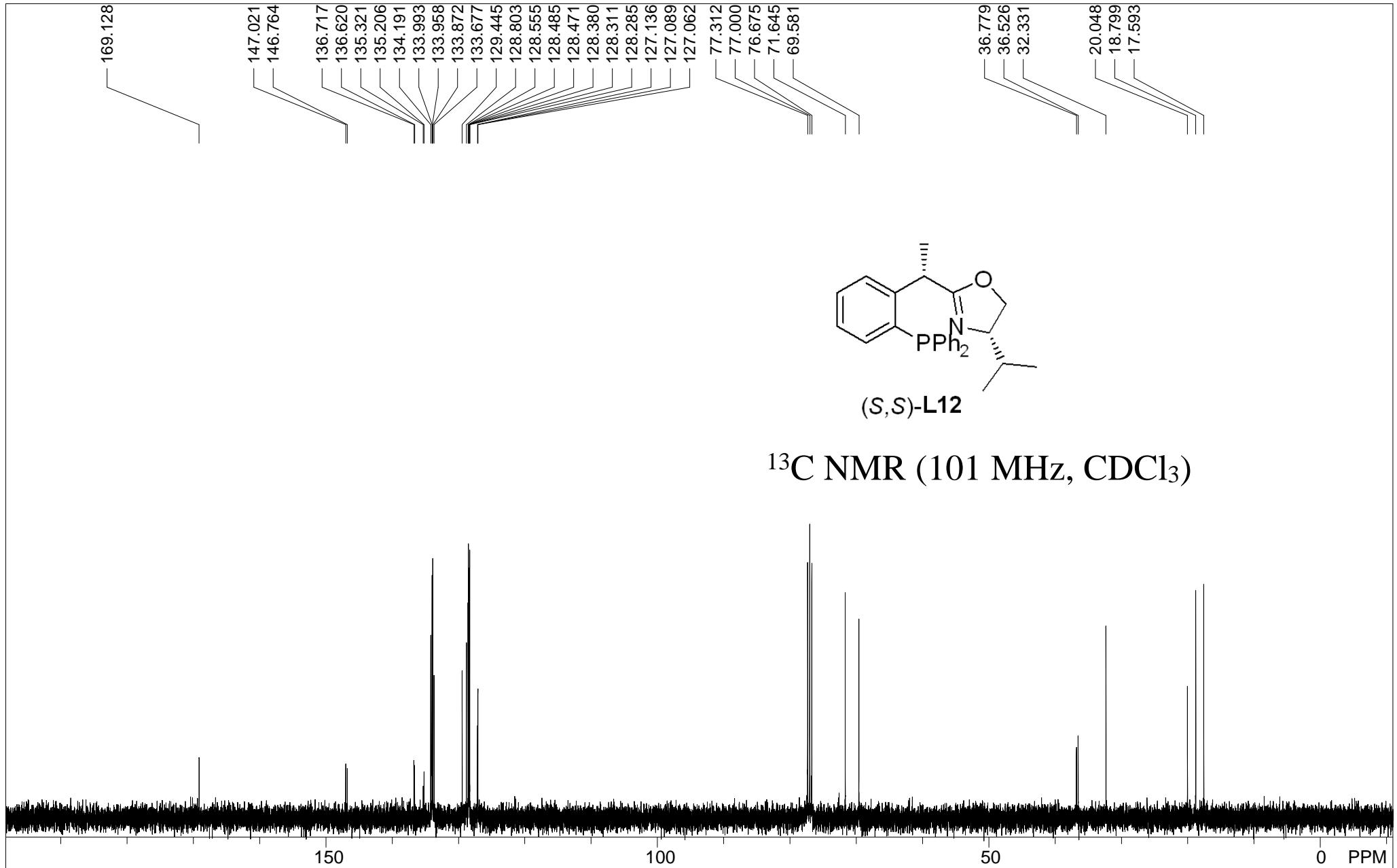
PD: 1.0 sec

NA: 12

LB: 0.0

Nuts - \$hyd-8-64-H.fid

USER: -- DATE: Sep 14 2009



hyd-8-64-C-400M

F1: 100.600 F2: 400.037

SW1: 25000

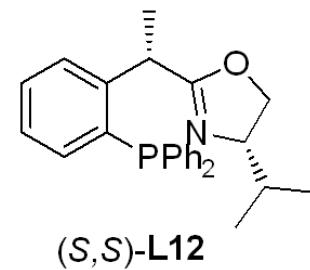
EX: s2pul

PW: 7.3 usec PD: 1.0 sec OF1: 10811.3 NA: 258 LB: 0.0 PTS1d: 32768

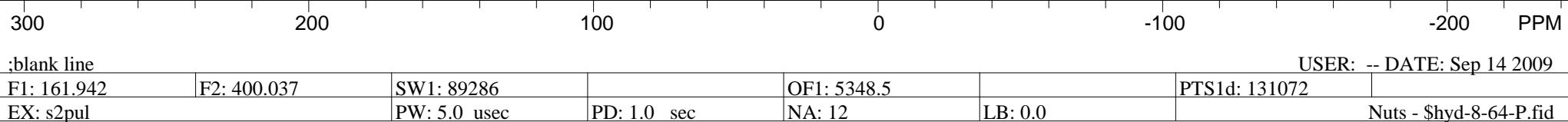
USER: -- DATE: Sep 14 2009

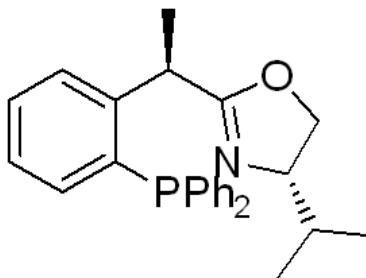
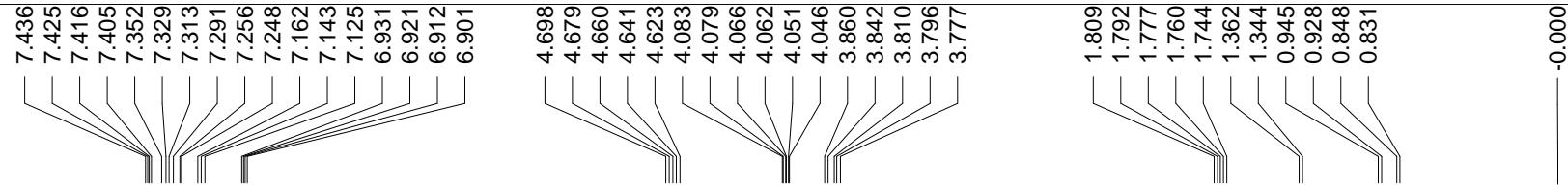
Nuts - \$hyd-8-64-C.fid

-16.242



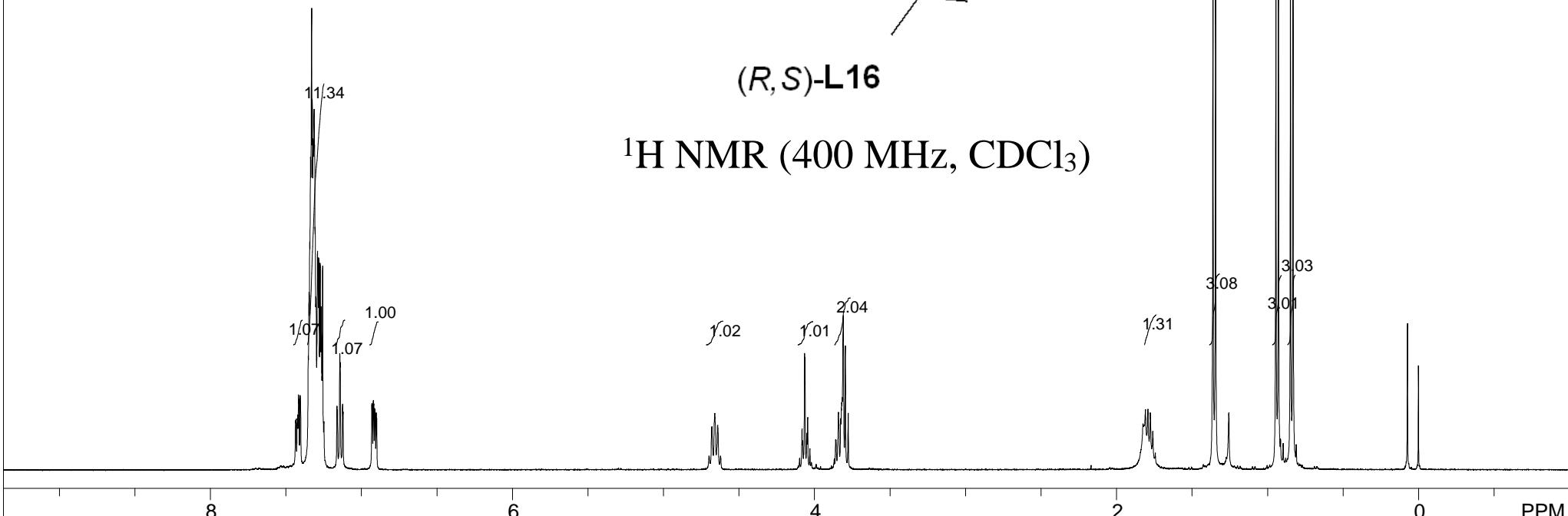
<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)





$(R,S)$ -L16

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



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F1: 400.037

F2: 100.598

SW1: 6410

EX: s2pul

PW: 4.4 usec

PD: 1.0 sec

NA: 16

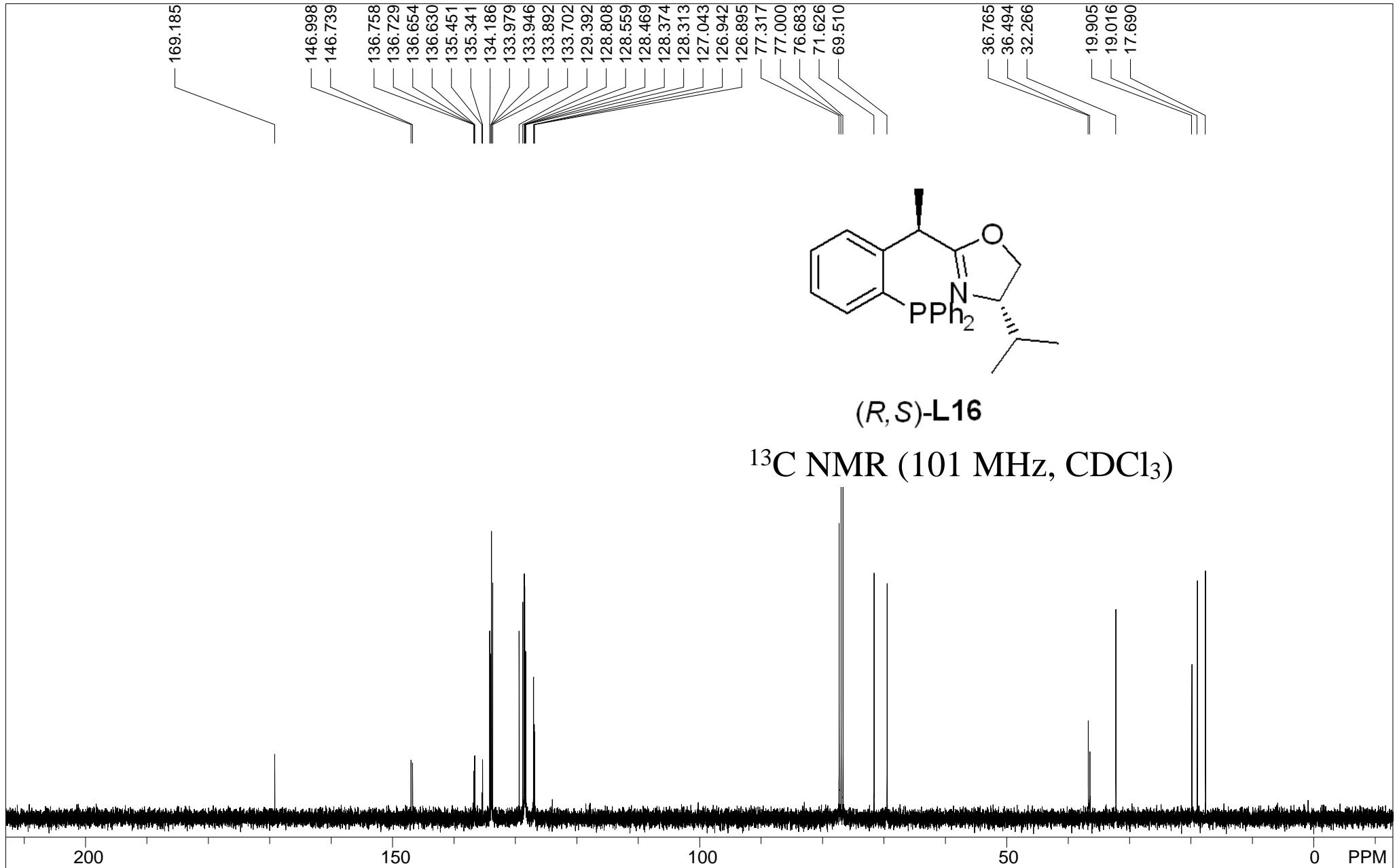
OF1: 2799.7

LB: 0.0

PTS1d: 32768

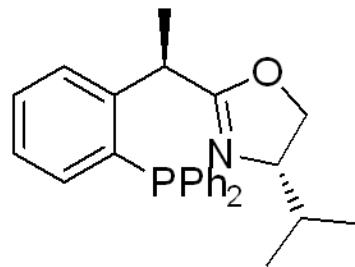
USER: -- DATE: Sep 14 2009

Nuts - \$hyd-8-65-H.fid



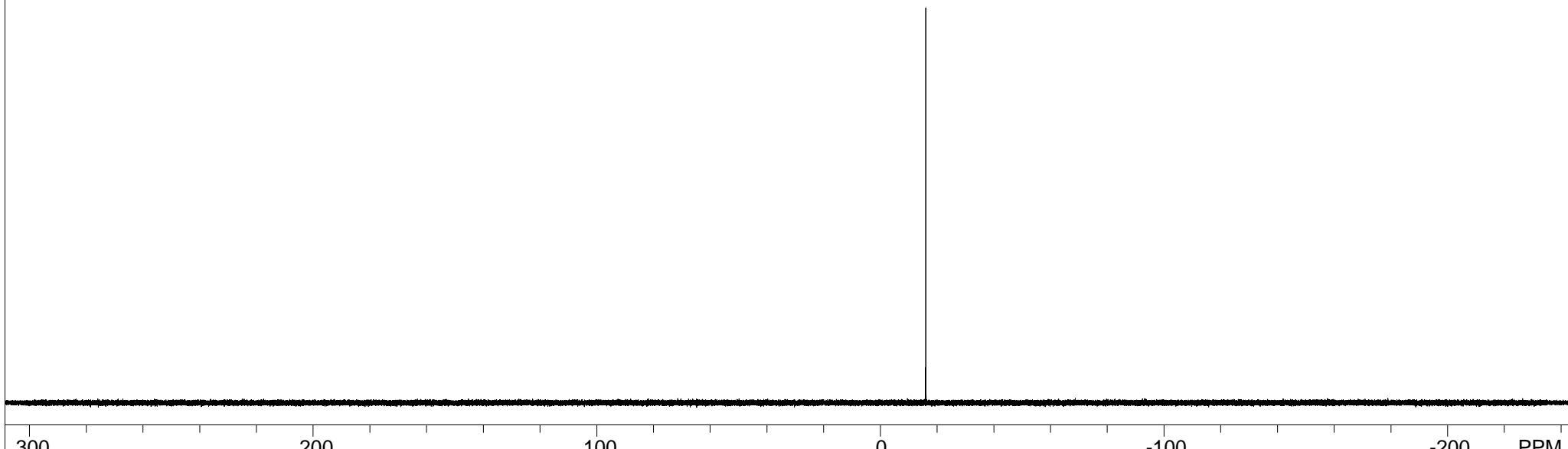
hyd-8-65-C-400M						USER: -- DATE: Sep 14 2009
F1: 100.600	F2: 400.037	SW1: 25000		OF1: 10811.8		PTS1d: 32768
EX: s2pul		PW: 7.3 usec	PD: 1.0 sec	NA: 622	LB: 0.0	Nuts - \$hyd-8-65-C.fid

-16.197



(*R,S*)-L16

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )



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F1: 161.942

EX: s2pul F2: 400.037

SW1: 89286

PW: 5.0 usec

PD: 1.0 sec

NA: 8

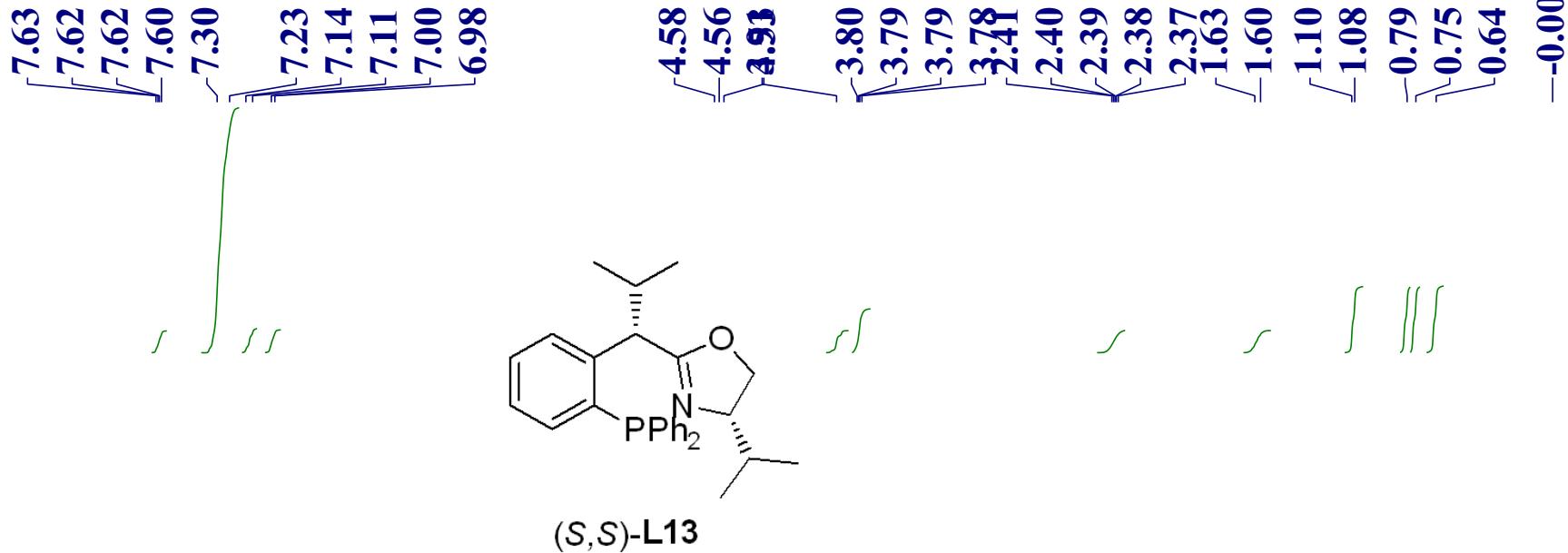
OF1: 5348.5

LB: 0.0

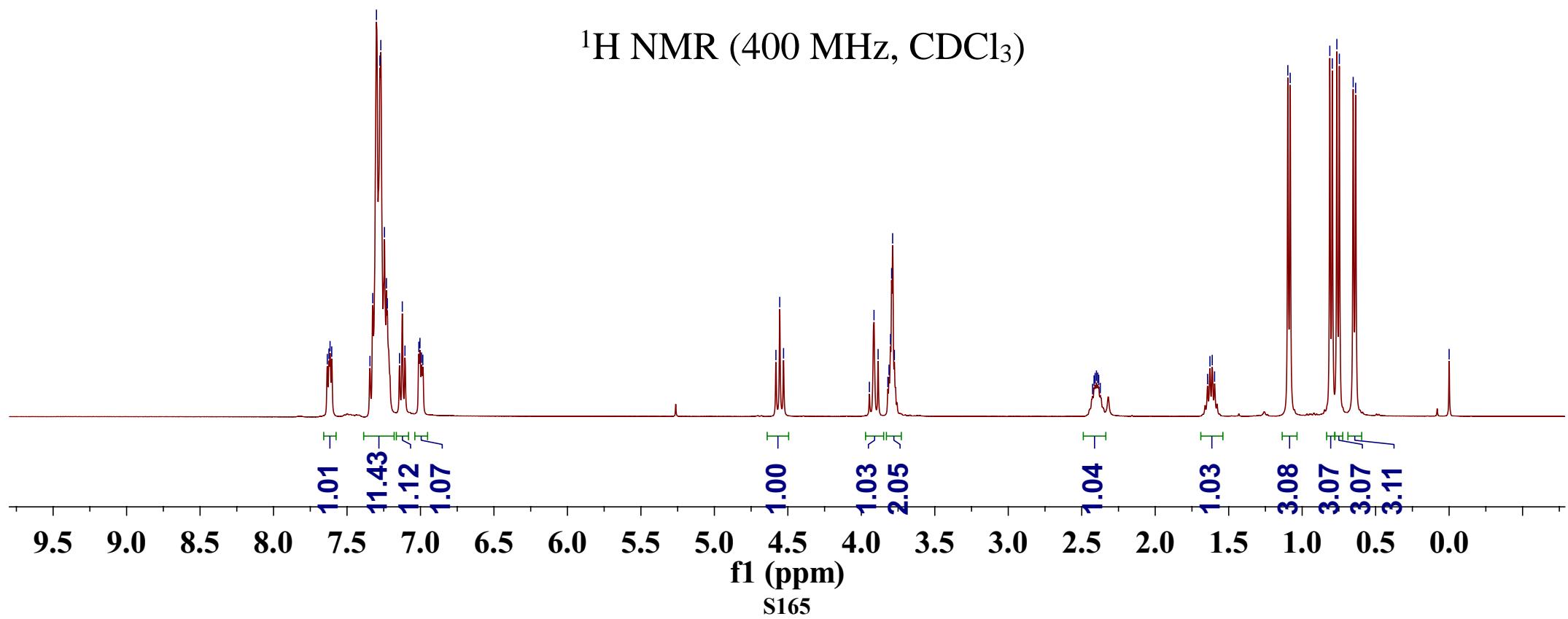
USER: -- DATE: Sep 14 2009

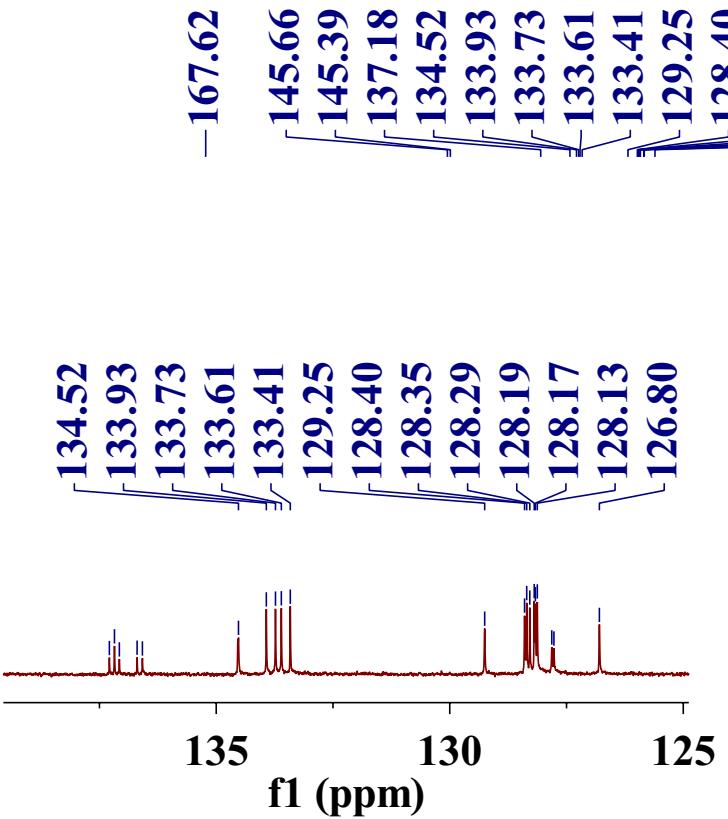
PTS1d: 131072

Nuts - \$hyd-8-65-P.fid



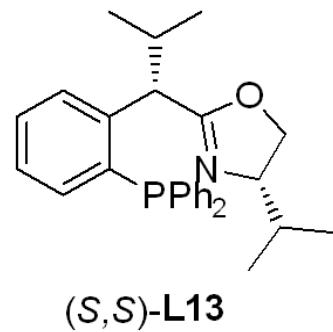
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





135      130      125  
f1 (ppm)

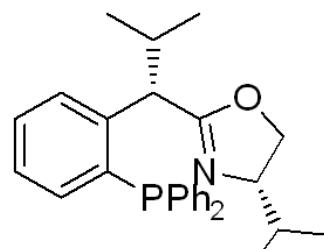
190    180    170    160    150    140    130    120    110    100    90    80    70    60    50    40    30    20    10    0  
f1 (ppm)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

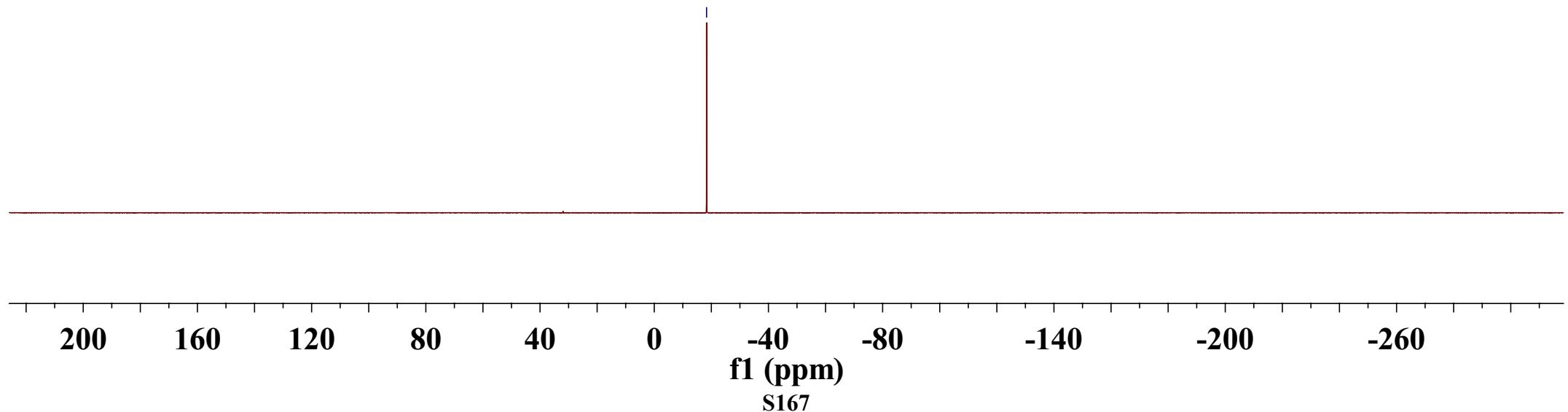
49.29  
49.03  
32.48  
32.45  
21.37  
20.49  
18.73  
17.89

-18.33



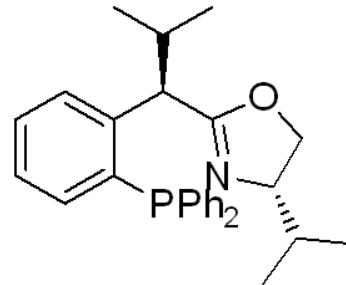
(*S,S*)-L13

<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)



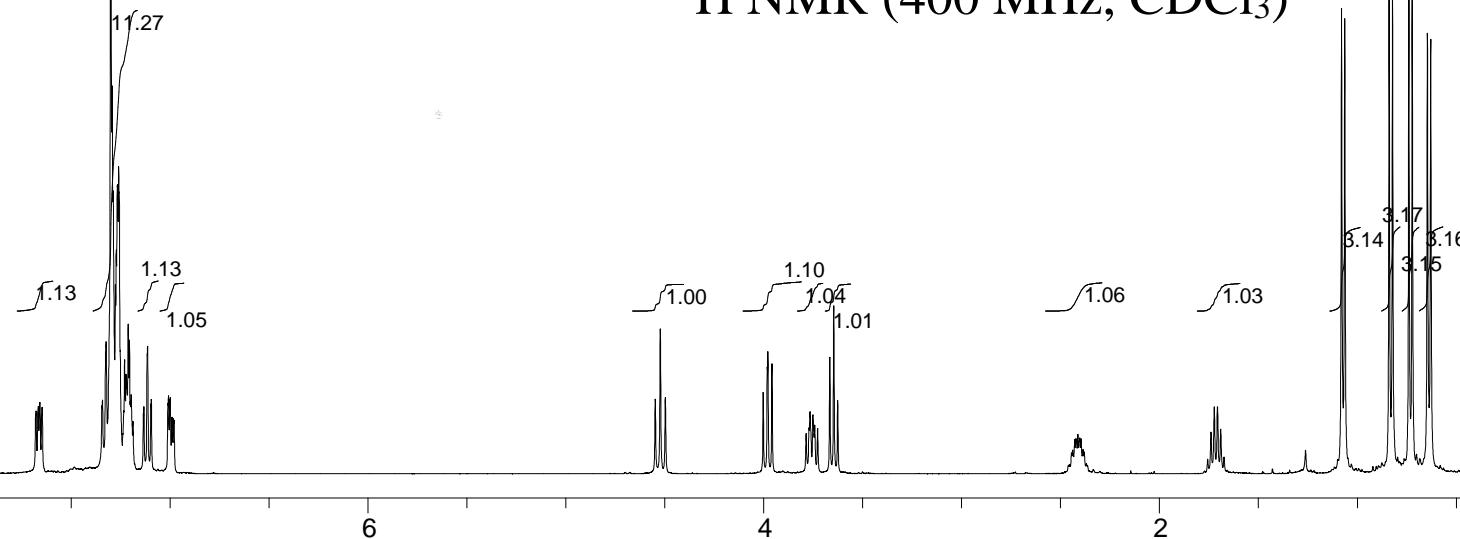
7.677  
7.666  
7.658  
7.647  
7.345  
7.300  
7.293  
7.260  
7.239  
7.188  
7.135  
7.113  
7.095  
7.011  
6.979

4.548  
4.523  
4.497  
4.003  
3.982  
3.979  
3.958  
3.785  
3.770  
3.766  
3.751  
3.742  
3.728  
3.666  
3.646  
3.626  
2.445  
2.412  
2.380  
1.756  
1.722  
1.674  
1.079  
1.063  
0.839  
0.822  
0.739  
0.722  
0.646  
0.629  
0.000



(*R,S*)-L17

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



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F1: 400.037

F2: 100.598

SW1: 6410

EX: s2pul

PW: 4.7 usec

PD: 1.0 sec

NA: 8

OF1: 2391.2

LB: 0.0

PTS1d: 32768

Nuts - \$hyd-11-69-H.fid

USER: -- DATE: Mar 23 2010

167.834

145.569

145.306

137.305

137.200

137.192

137.081

136.741

136.625

134.379

134.362

134.002

133.806

133.599

133.411

129.118

128.432

128.354

128.286

128.122

128.087

128.082

128.054

128.034

126.756

77.324

77.000

76.686

71.626

68.658

49.126

48.868

32.445

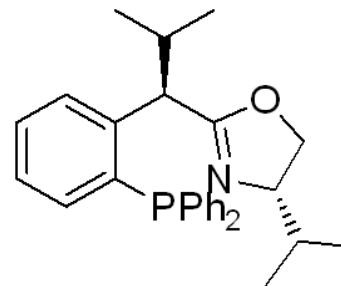
32.024

21.360

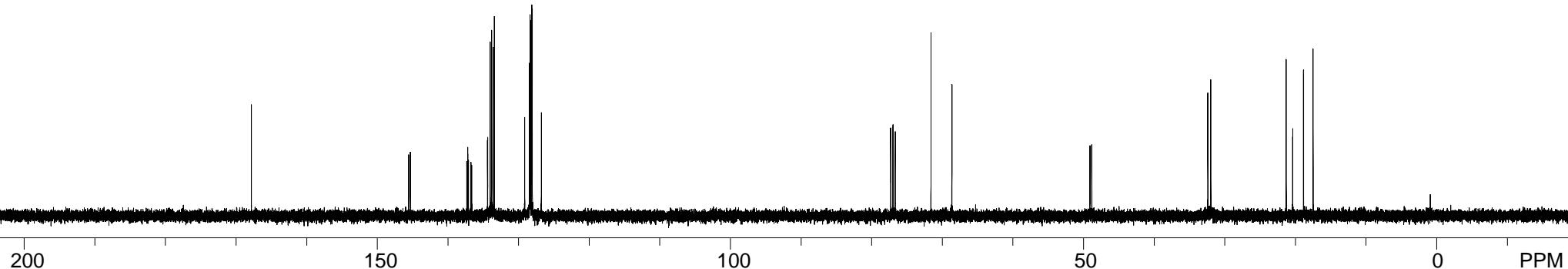
20.436

18.901

17.553



(R,S)-L17

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

hyd-11-69-C-400M

USER: -- DATE: Mar 23 2010

F1: 100.599

F2: 400.037

SW1: 26042

OF1: 10299.8

PTS1d: 65536

EX: s2pul

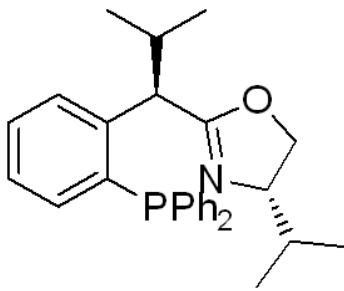
PW: 7.4 usec

PD: 1.0 sec

NA: 48

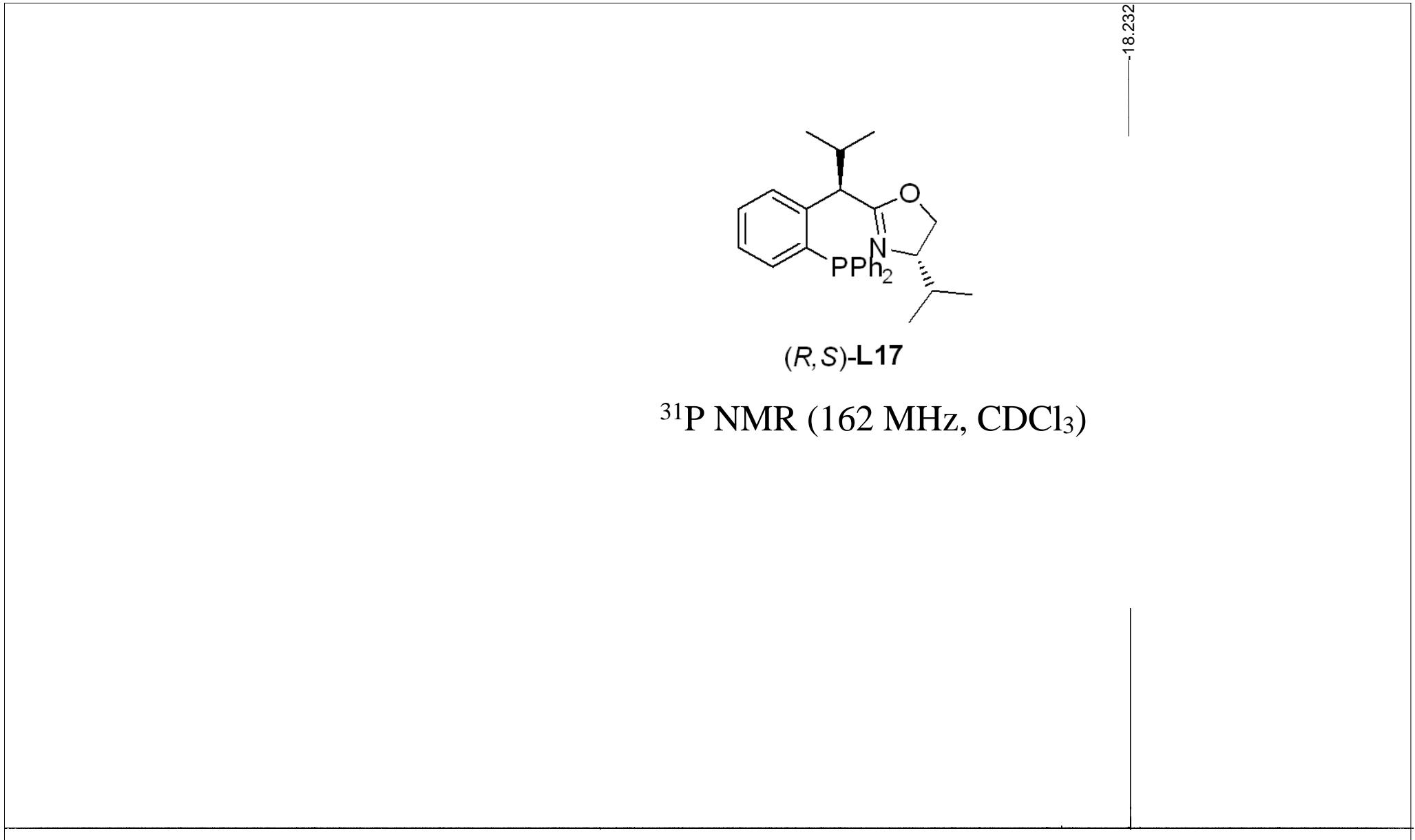
LB: 0.0

Nuts - \$hyd-11-69-C.fid



(*R,S*)-L17

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )



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F1: 161.984

F2: 400.037

SW1: 166667

400

200

0

PPM

USER: -- DATE: Mar 23 2010

EX: s2pul

PW: 5.3 usec

PD: 1.0 sec

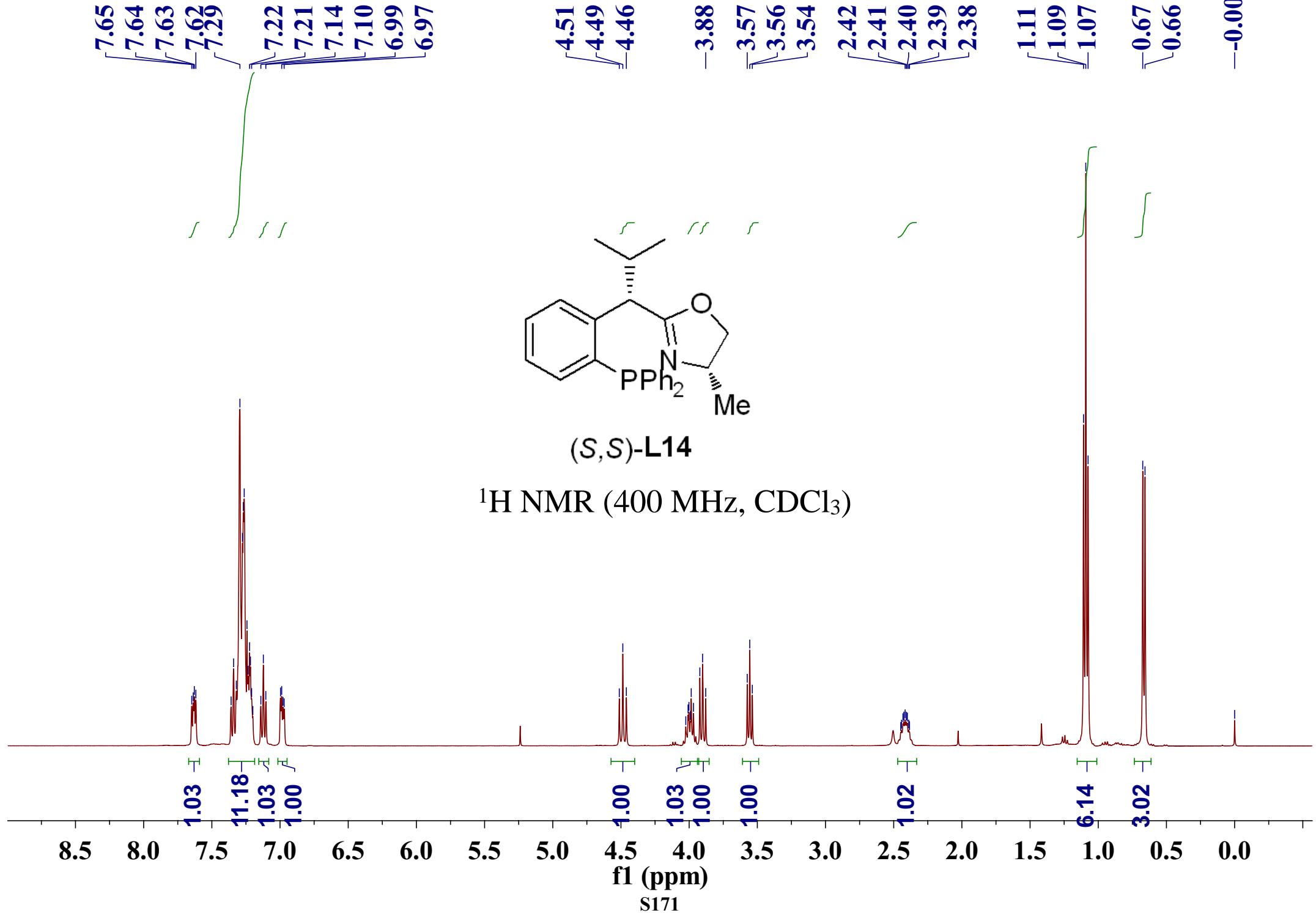
NA: 4

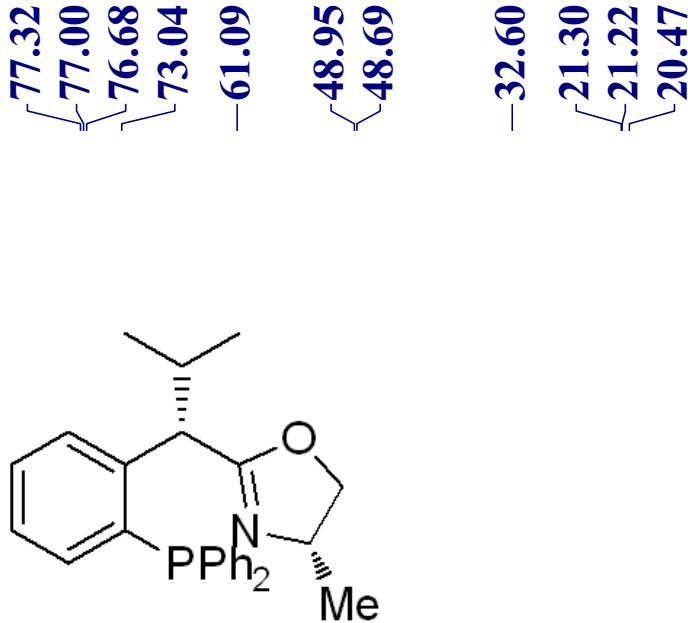
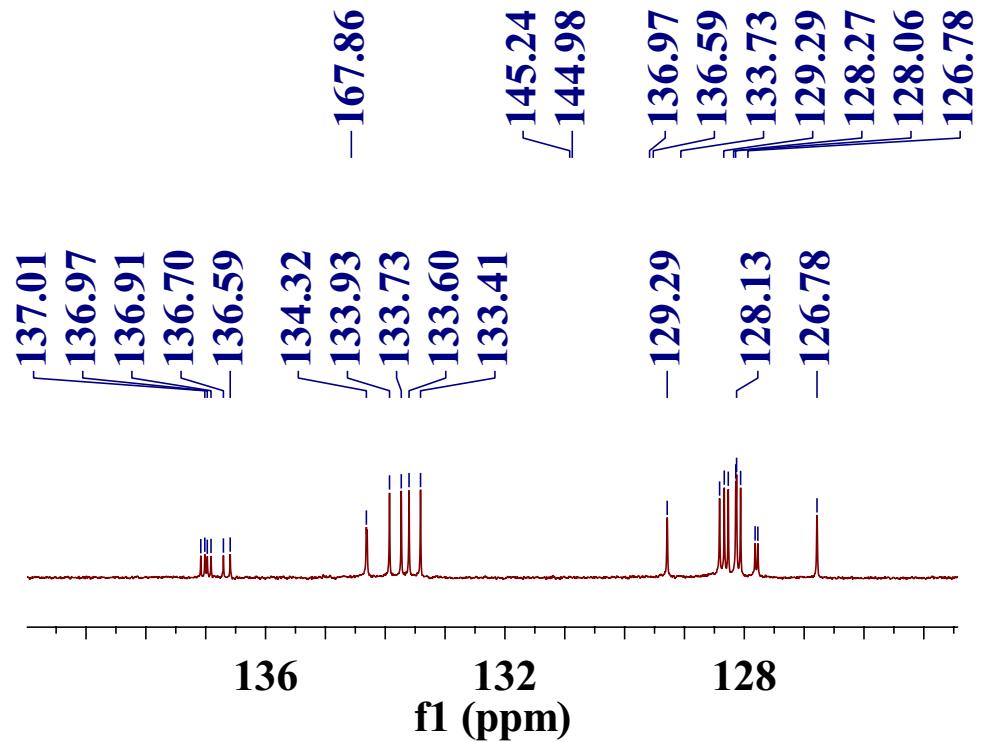
OF1: 46961.7

PTS1d: 262144

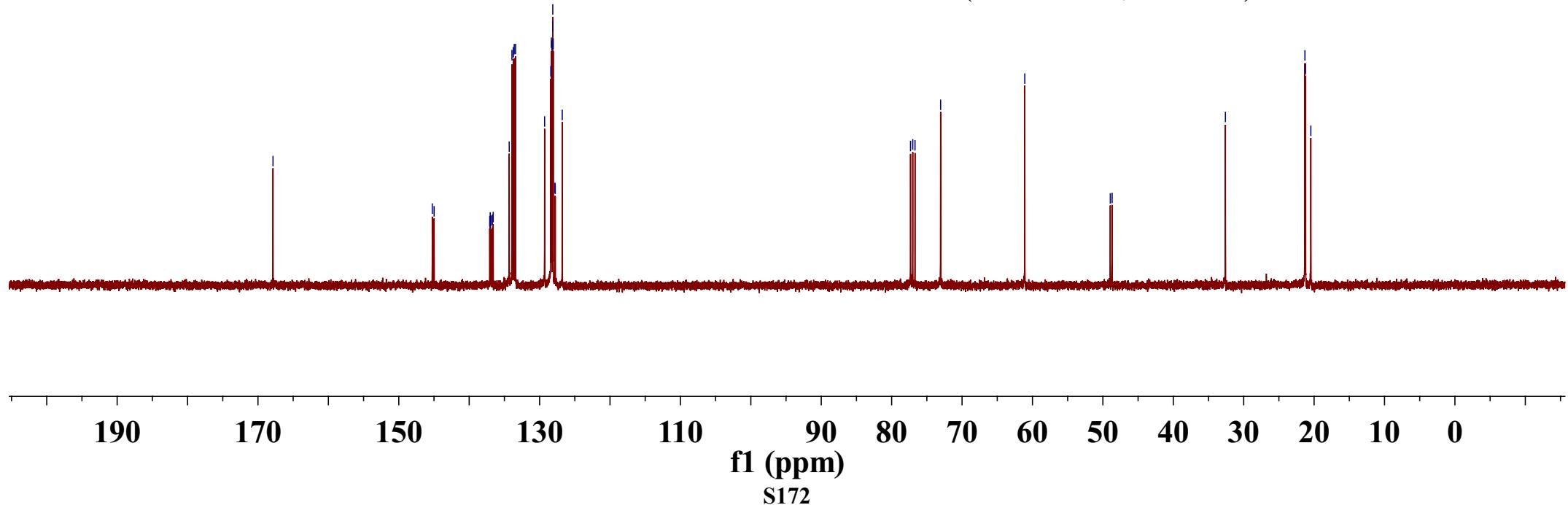
LB: 0.0

Nuts - \$hyd-11-69-P.fid

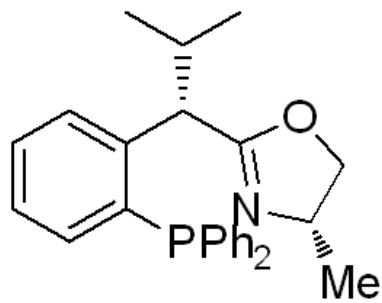




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

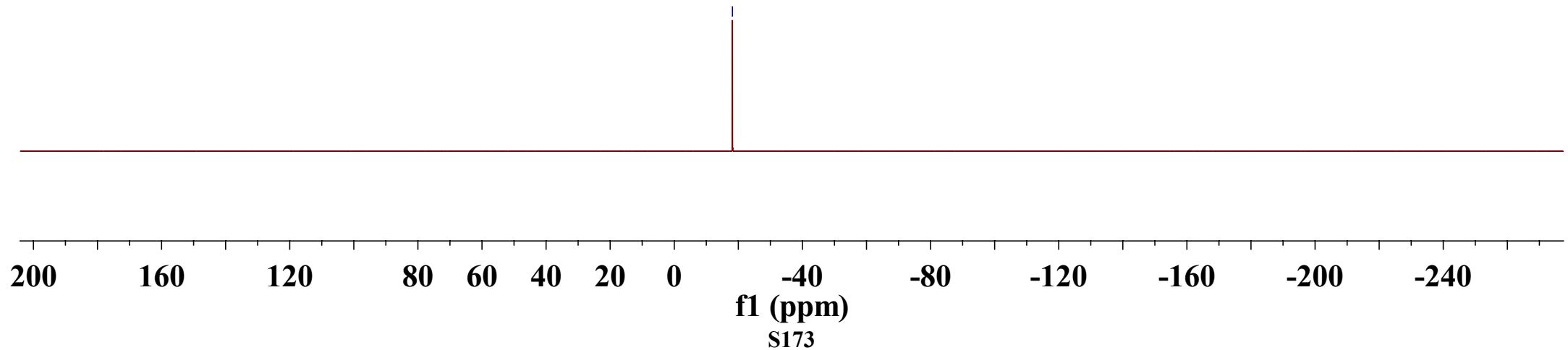


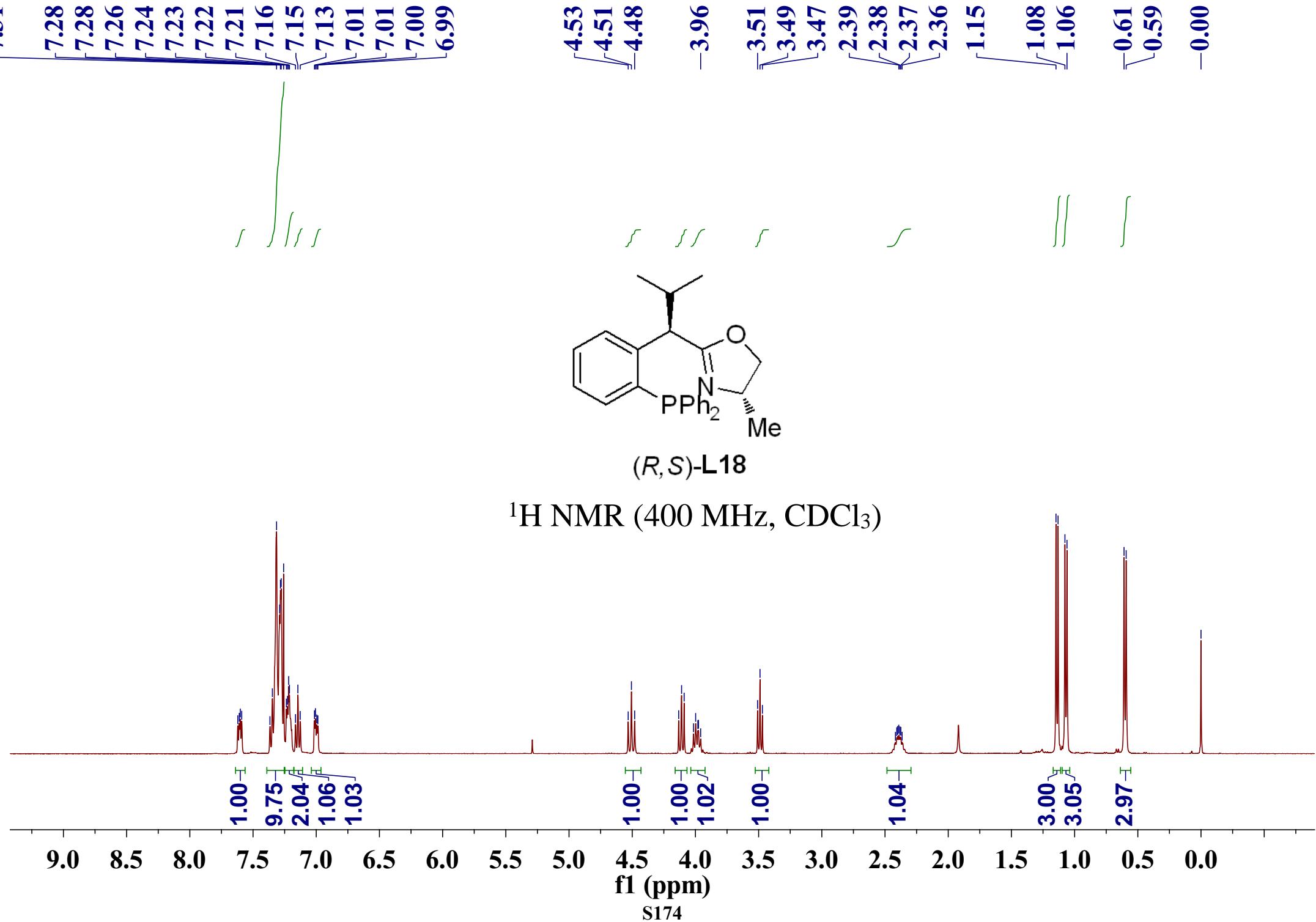
-18.16

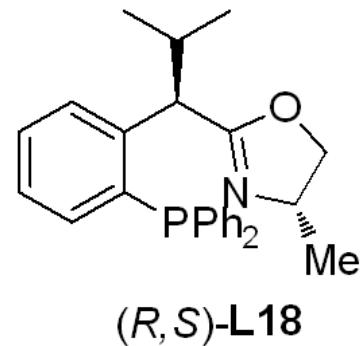
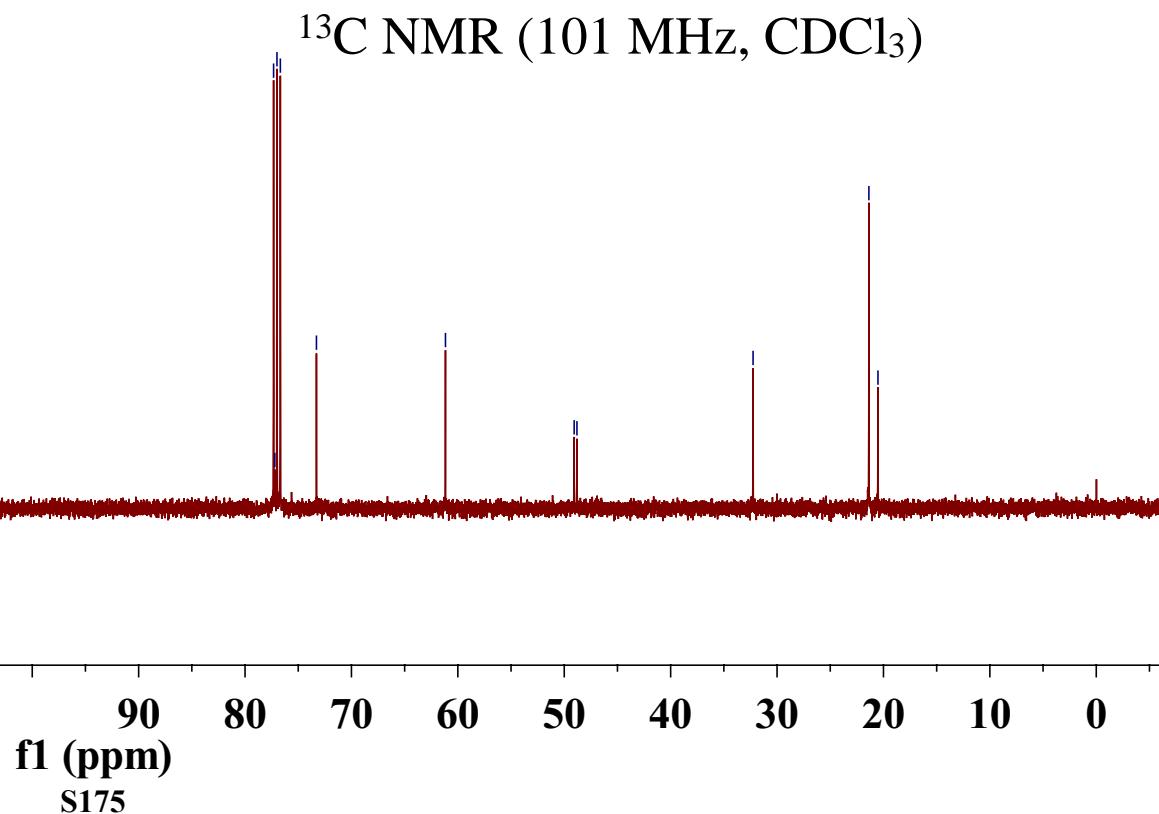
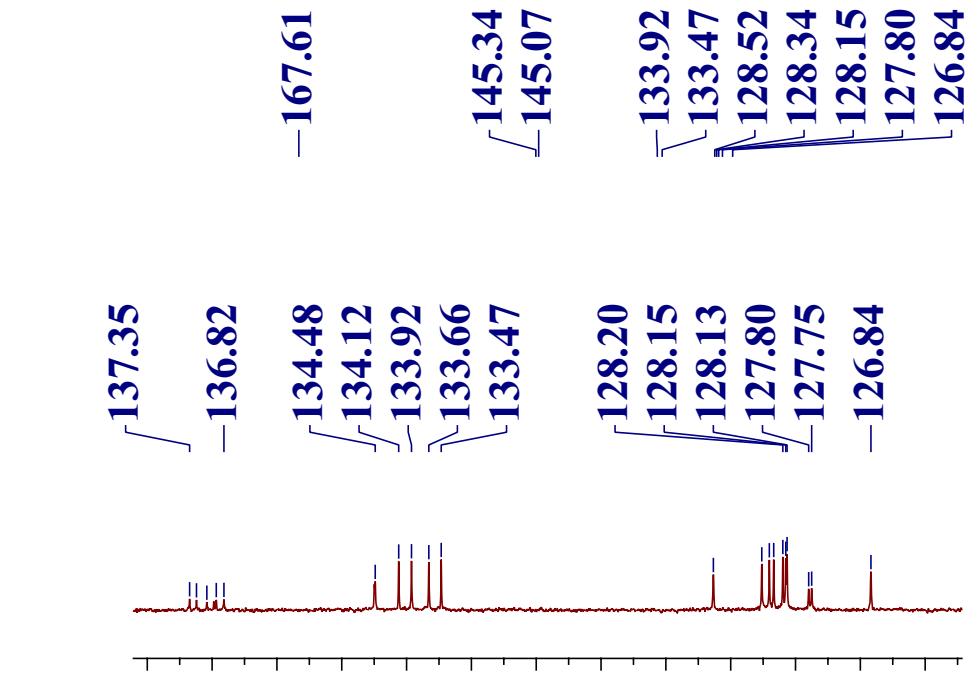


(*S,S*)-L14

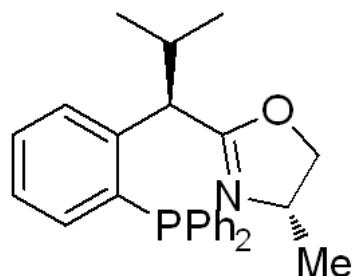
$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )







-18.38



(*R,S*)-L18

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )

240

200

160

120

80

40

0

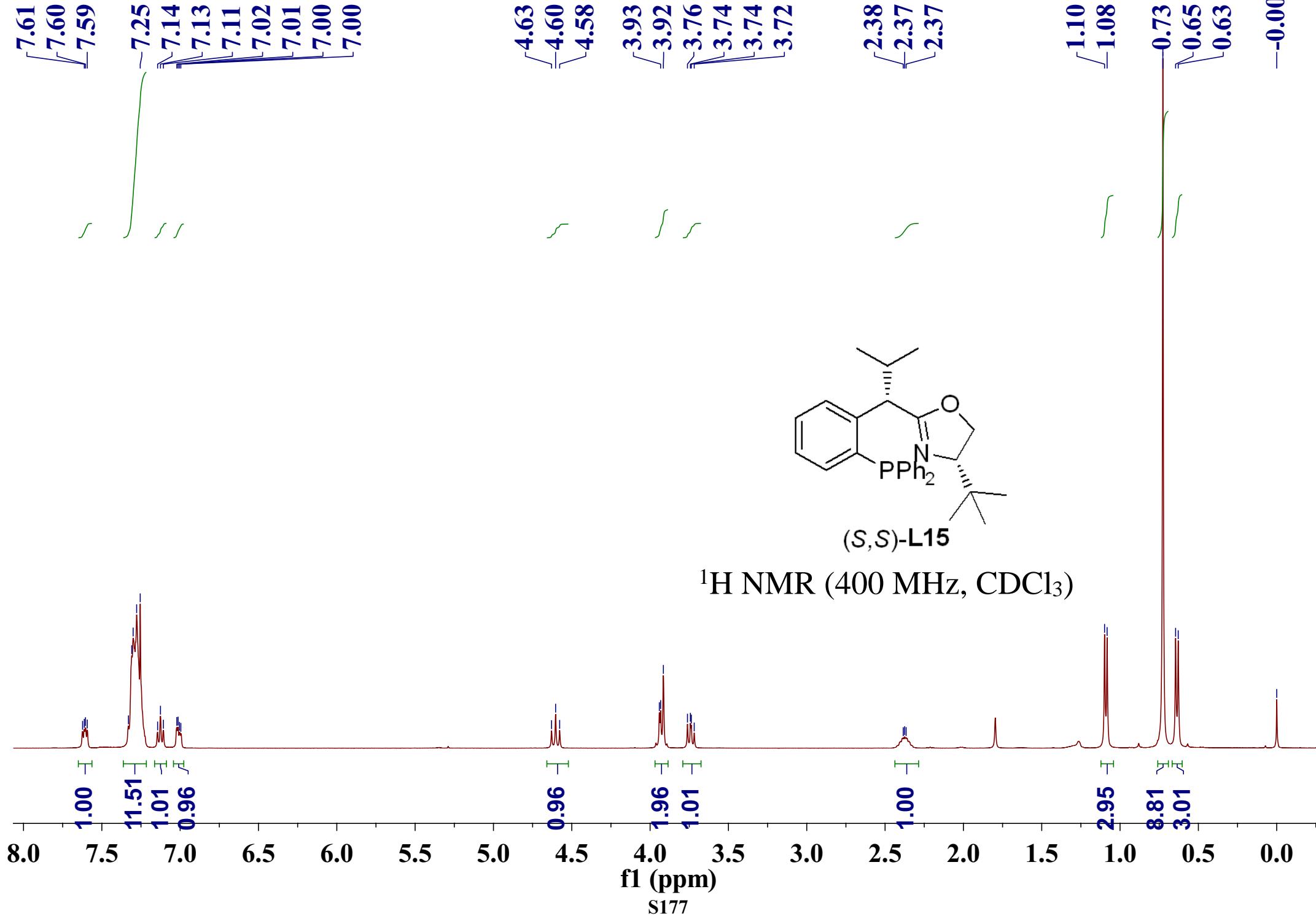
-40

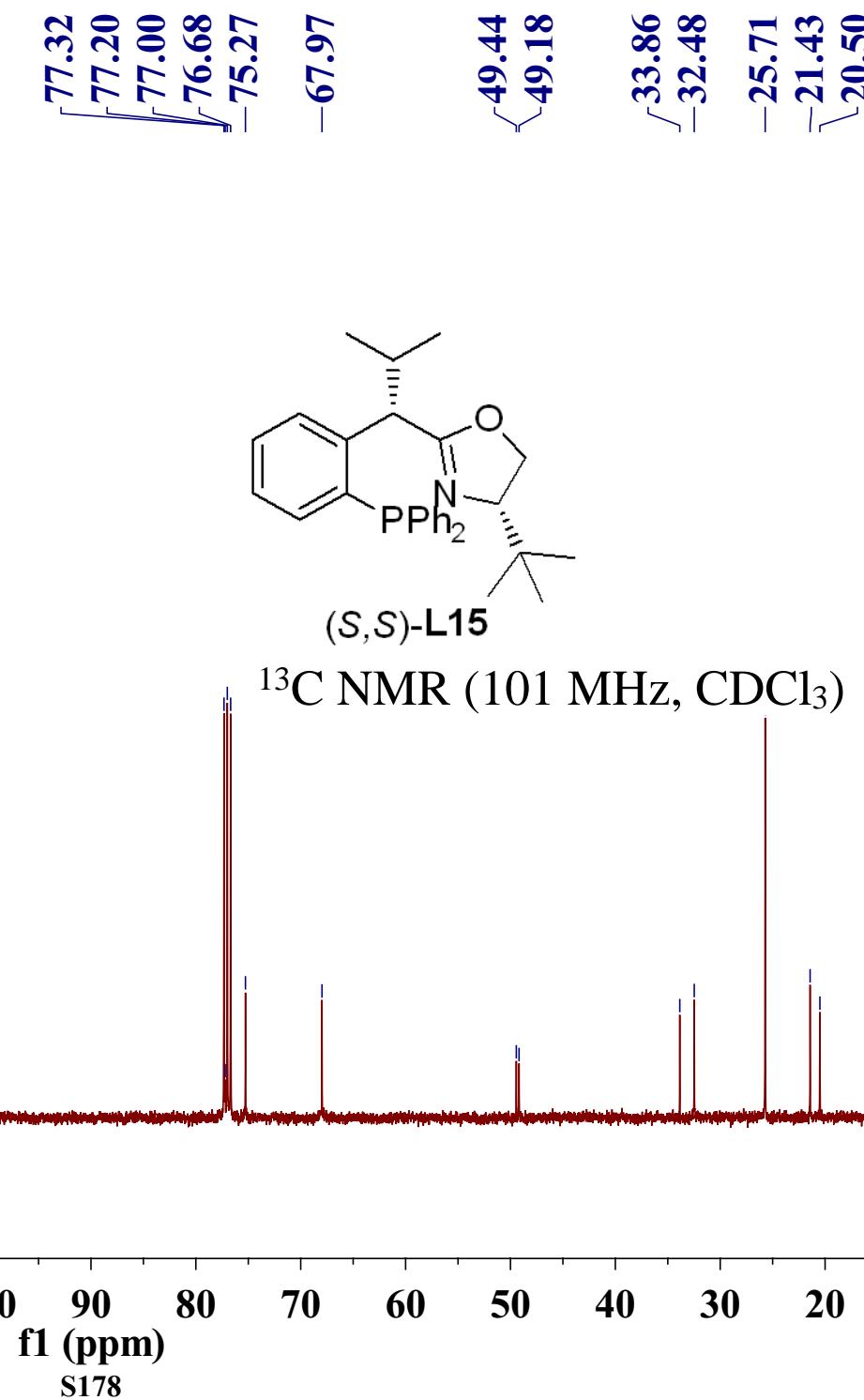
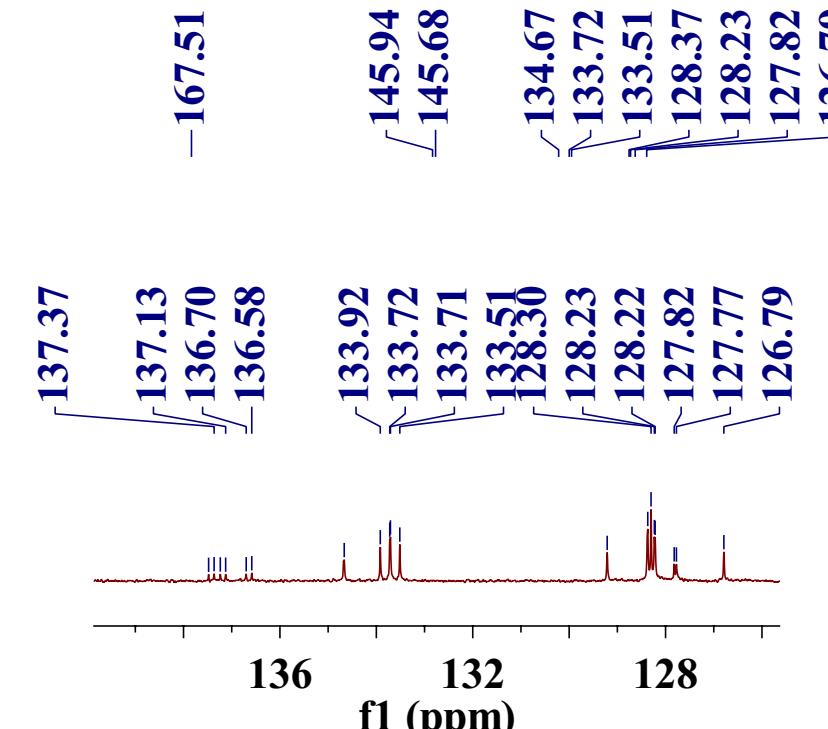
-80

-140

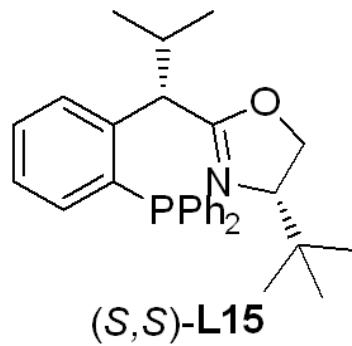
-200

f1 (ppm)  
S176

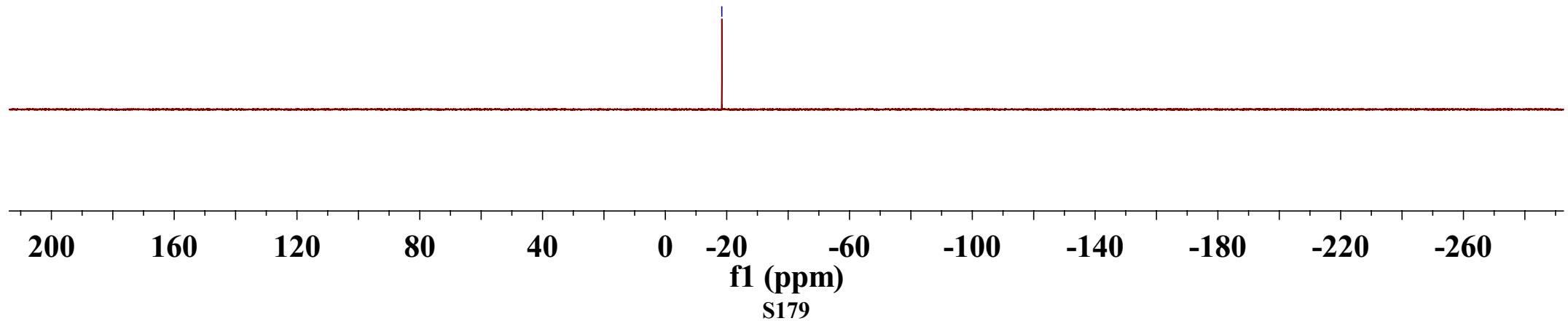




-18.40



<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)



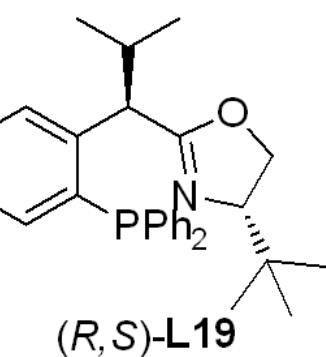
7.72  
7.71  
7.70  
7.69

7.32  
7.28  
7.23  
7.20  
7.13  
7.09  
6.99  
6.97

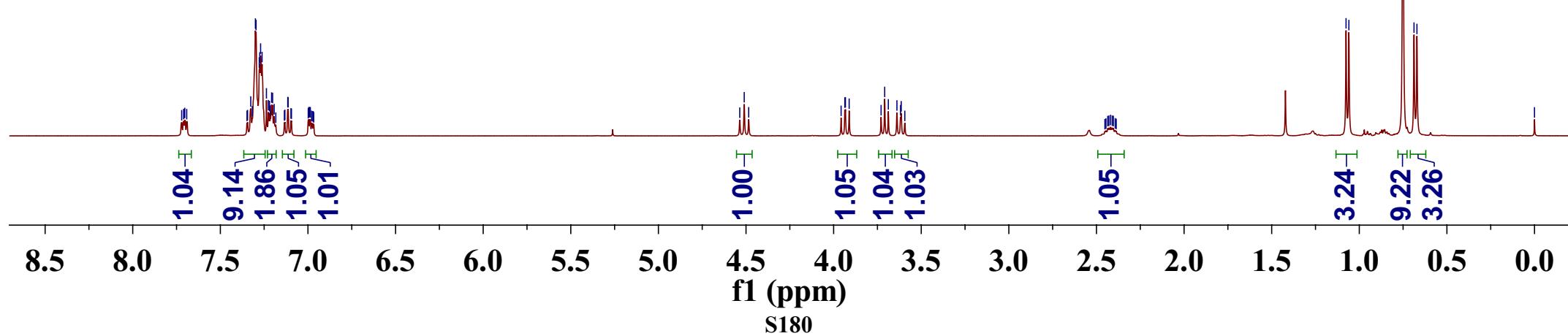
4.54  
4.51  
4.48  
3.71  
3.69  
3.64  
3.62  
3.61  
3.59  
2.43  
2.42  
2.41  
2.40  
2.39  
2.39

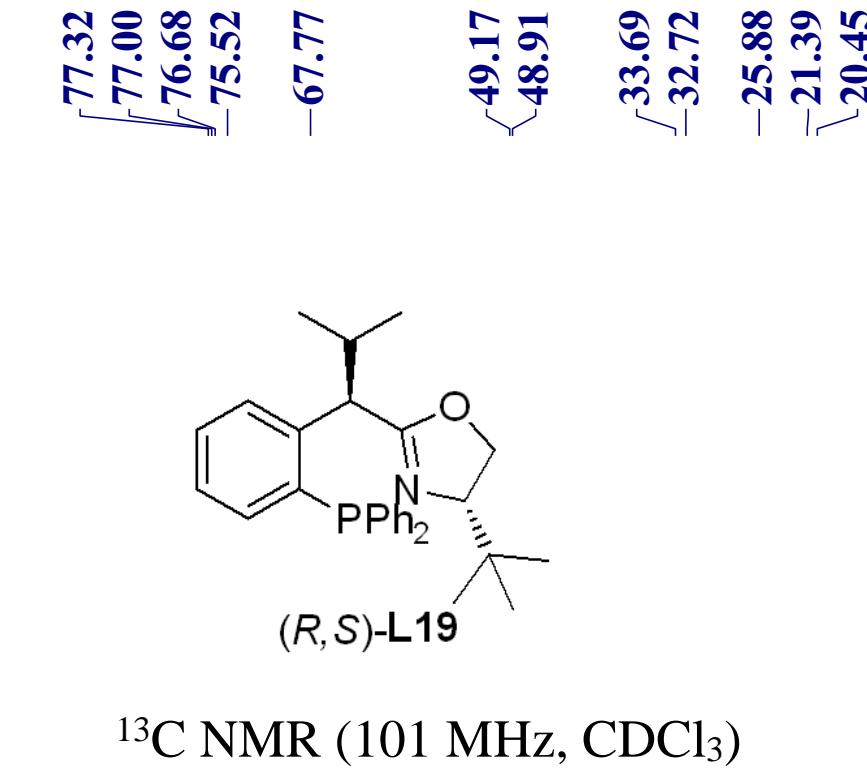
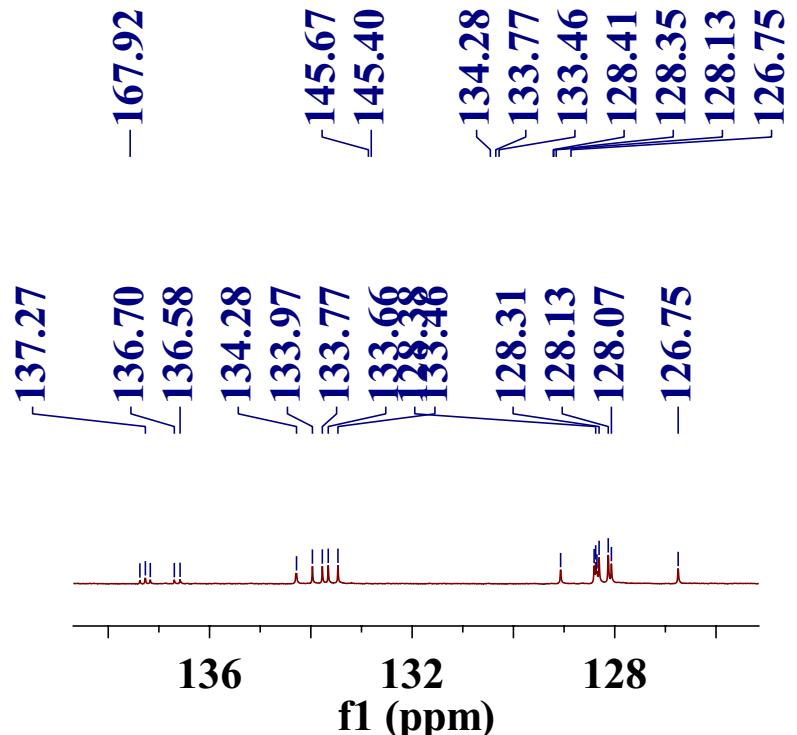
1.08  
1.06  
0.75  
0.69  
0.67  
-0.00

ʃ ʃ ʃ ʃ

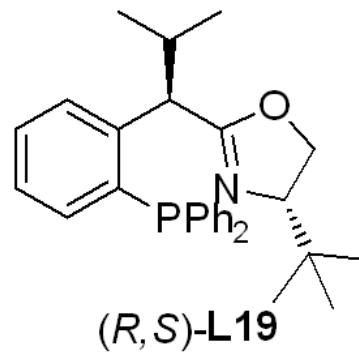


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





-18.09



<sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)

