Palladium-catalyzed oxidation of β-C(sp^3)-H bond of primary alkylamines through a rare four-membered palladacycle intermediate

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Supporting Information

Table of Contents

1. Methods and Materials 2

2. Synthesis of tert-Butyl Alkylamine Derivatives 3

3. H/D Exchange Experiments 7

4. Investigation of Effect of the Ligand 7

5. Synthesis of Salicyladehyde Imines 8

6. Acetoxylation of the β-C-H Bond: 15

7. Removal and Recovery of the Directing Group 22

8. Mechanistic Investigation 23

9. Crystallographic Information 26

10. Computational Details 30

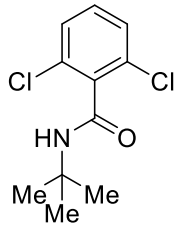
11. NMR Spectrum 49

12. References 97

1. *Methods and Materials*

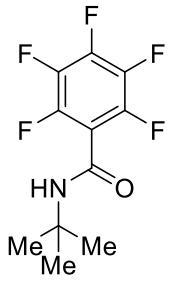
All air-sensitive manipulations were conducted in an N_2-filled glove-box. All solvents and reagents were used as received unless otherwise noted. Reaction temperatures refer to temperatures of an aluminum heating block, which were controlled by an electronic temperature modulator. All catalytic reactions were set up in an N_2-filled dry box with oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars. Purification by column chromatography was performed using a Teledyne Isco CombiFlash® R_f system with Redi*Sep* R_f Gold™ columns or manually loaded columns. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVQ-400, AV-500, and AV-600 spectrometers with ^{13}C operating frequencies of 100 MHz, 125 MHz, and 150 MHz, respectively. ^{19}F NMR spectra were recorded on a Bruker AVQ-400 spectrometer with a ^{19}F operating frequency of 376 MHz. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal ($CDCl_3$: 7.26 ppm for ^{1}H NMR and 77.2 ppm for ^{13}C NMR). High-resolution mass spectral data were obtained from the QB3/Chemistry Mass Spectrometry Facility at the University of California Berkeley and the Lawrence-Berkeley National Laboratory Catalysis Center.

2. *Synthesis of tert-Butyl Alkylamine Derivatives*



_N_-(tert-butyl)-2,6-dichlorobenzamide (1a-4)

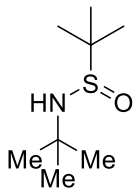
To a solution of *tert*-butyl amine (0.73 g, 10 mmol) and Et_3N (1.3 g, 13 mmol) in DCM (10 mL) was added 2,6-dichlorobenzoyl chloride (2.4 g, 12 mmol) dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 8-12 h. The mixture was diluted with DCM (50 mL), washed with an aqueous solution of HCl (2.0 M, 10 mL), water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1a-4** as a white solid (1.9 g, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, J = 8.2 Hz, 2H), 7.21 (t, J = 8.2 Hz, 1H), 5.50 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 136.7, 132.1, 130.2, 127.9, 52.5, 28.6; **HRMS** (ESI+) calcd for $C_{11}H_{14}Cl_2NO$ $[M+H]^+$ 246.0447, found 246.0449.



_N_-(tert-butyl)-2,3,4,5,6-pentafluorobenzamide (1a-5)

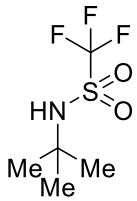
To a solution of *tert*-butyl amine (0.88 g, 12 mmol) and Et_3N (1.2 g, 12 mmol) in DCM (10 mL) was added pentafluorobenzoyl chloride (2.3 g, 10 mmol) dropwise at 0 °C. The reaction mixture was warmed to room temperature and stirred for 8-12 h. The mixture was diluted with DCM (50 mL), washed with an aqueous solution of HCl (2.0 M, 10 mL), water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1a-5** as a white solid (1.5 g, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (brs, 1H), 1.46 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.3, 143.8 (d br, J = 251.5 Hz), 141.9 (d br, J = 259.4 Hz), 137.5 (d br, J = 256.0 Hz), 112.7 (s, br), 53.2, 28.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -141.6 (dd, J = 21.6, 6.6 Hz,

2H), -152.09 (t, J = 20.7 Hz, 1H), -160.3–160.6 (m, 2H); **HRMS** (ESI+) calcd for $C_{11}H_{11}F_5NO$ $[M+H]^+$ 268.0755, found 268.0758.



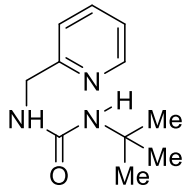
***N*-(tert-butyl)-2-methylpropane-2-sulfinamide (1a-7)**

To a solution of *tert*-butyl amine (0.88 g, 12 mmol), Et_3N (1.2 g, 12 mmol), and catalytic amount of DMAP in DCM (10 mL) was added *tert*-butylsulfinyl chloride (1.4 g, 10 mmol) dropwise at room temperate. The reaction mixture was warmed to room temperature and stirred for 8-12 h. The mixture was diluted with DCM (50 mL), washed with aqueous solution of HCl (2.0 M, 10 mL), water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→70:30) to give compound **1a-7** as a white solid (0.82 g, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.98 (brs, 1H), 1.28 (s, 9H), 1.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 55.2, 53.2, 31.1, 22.5; **HRMS** (ESI+) calcd for $C_8H_{20}NOS$ $[M+H]^+$ 178.1260, found 178.1260.



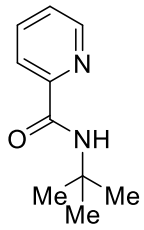
***N*-(tert-butyl)-1,1,1-trifluoromethanesulfinamide (1a-8)**

To a solution of *tert*-butyl amine (0.88 g, 12 mmol) and Et_3N (1.2 g, 12 mmol) in DCM (10 mL) was added trifluoromethanesulfonic anhydride (2.8 g, 10 mmol) dropwise at -78 ^{o}C. The reaction mixture was warmed to room temperature and stirred for 8-12 h. The mixture was diluted with DCM (50 mL), washed with an aqueous solution of HCl (2.0 M, 10 mL), water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→70:30) to give compound **1a-8** as a white solid (1.7 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.75 (brs, 1H), 1.43 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 119.2 (q, J = 320.9 Hz), 58.1, 30.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ -77.9; **HRMS** (ESI+) calcd for $C_5H_9F_3NO_2S$ $[M-H]^-$ 204.0312, found 204.0314.



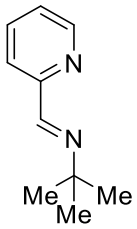
1-(*tert*-Butyl)-3-(pyridin-2-ylmethyl)urea (1a-12)

To a solution of *tert*-butyl isocyanate (0.99 g, 10 mmol) and 2-picolyl amine (1.1 g, 10 mmol) in DCM (10 mL) was added *N,N*-diisopropylethylamine (2.6 g, 20 mmol) dropwise at room temperature. The reaction mixture was stirred at room temperature overnight. The mixture was diluted with DCM (50 mL), washed with water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→50:50) to give compound **1a-12** as a white solid (1.2 g, 59%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.50 (d, J = 4.9 Hz, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.17 (t, J = 7.8 Hz, 1H), 5.50 (s, 1H), 4.71 (s, 1H), 4.45 (s, 2H), 1.33 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.0, 157.5, 148.7, 136.7, 122.1, 122.0, 50.4, 45.4, 29.5; **HRMS** (ESI+) calcd for $C_{11}H_{18}N_3O$ $[M+H]^+$ 208.1444, found 208.1446.



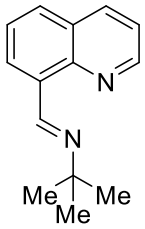
***N*-(*tert*-butyl)picolinamide (1a-13)**

To a solution of *tert*-butyl amine (2.1 g, 30 mmol) and magnesium dibromide (1.8 g, 12 mmol) in MeCN (10 mL) was added methyl pyridine-2-carboxylate (1.4 g, 10 mmol). The reaction mixture was stirred at room temperature overnight. The mixture was diluted with DCM (50 mL), washed with water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→50:50) to give compound **1a-13** as a white solid (1.0 g, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (d, J = 4.7 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 8.00 (s, 1H), 7.83 (t, J = 7.8 Hz, 1H), 7.39 (dd, J = 7.6, 4.8 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.4, 150.8, 147.7, 137.3, 125.8, 121.6, 50.8, 28.7; **HRMS** (ESI+) calcd for $C_{10}H_{15}N_2O$ $[M+H]^+$ 179.1179, found 179.1180.



***N-tert*-butyl-1-(pyridin-2-yl)methanimine (1a-14)**

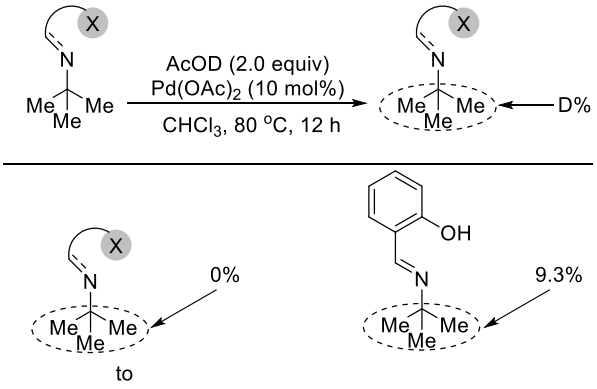
To a 20-mL vial were added 2-pyridinecarboxaldehyde (0.54 g, 5.0 mmol), *tert*-butylamine (0.36 g, 5.0 mmol), and water (1 mL). The reaction mixture was stirred overnight at room temperature, diluted with DCM (20 mL), and washed with brine (10 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give compound **1a-14** as a yellow oil (0.71 g, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.63 (d, J = 6.9 Hz, 1H), 8.37 (s, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.73 (t, J = 6.8 Hz, 1H), 7.38–7.26 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.4, 155.5, 149.2, 136.5, 124.4, 120.9, 57.8, 29.6; **HRMS** (ESI+) calcd for $C_{10}H_{15}N_2$ $[M+H]^+$ 163.1230, found 163.1223.



***N-tert*-butyl-1-(quinolin-8-yl)methanimine (1a-15)**

To a 20-mL vial were added 8-quinolinecarboxaldehyde (0.80 g, 5.0 mmol), tert-butylamine (5 mL), and 4Å molecular sieves. The reaction mixture was stirred overnight at room temperature and then filtered through a short pad of Celite, eluting with EA (10 mL). The filtrate was concentrated in *vacuo* to give compound **1a-15** as a yellow oil (0.75 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.97 (dd, J = 4.2, 1.8 Hz, 1H), 8.43 (dd, J = 7.2, 1.5 Hz, 1H), 8.17 (dd, J = 8.3, 1.8 Hz, 1H), 7.87 (dd, J = 8.1, 1.5 Hz, 1H), 7.60 (ddd, J = 8.0, 7.2, 0.6 Hz, 1H), 7.43 (dd, J = 8.3, 4.1 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.4, 149.9, 146.9, 136.2, 134.2, 129.8, 128.2, 127.2, 126.6, 121.1, 58.0, 30.0; **HRMS** (ESI+) calcd for $C_{14}H_{17}N_2$ $[M+H]^+$ 213.1386, found 213.1395.

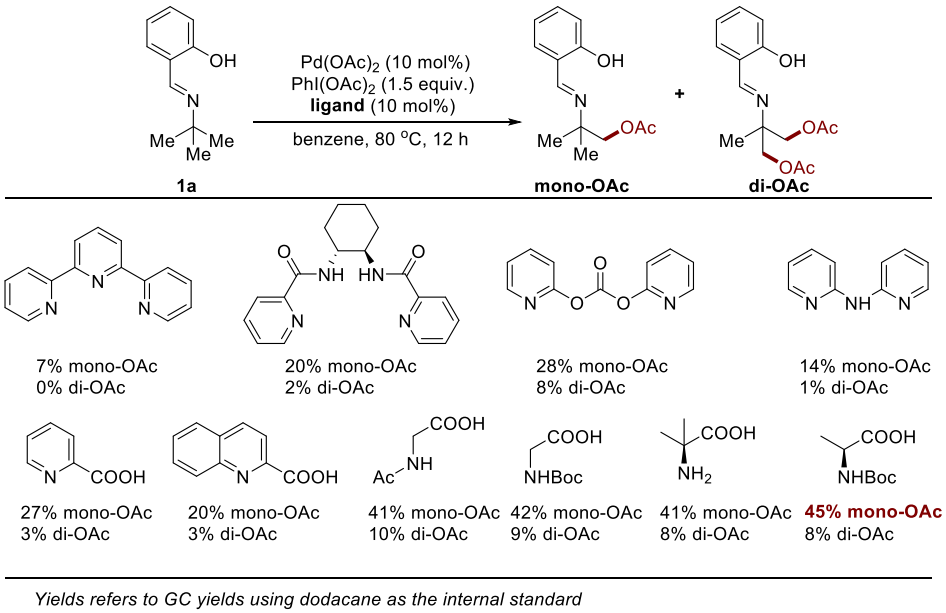
3. *H/D Exchange Experiments*



Procedure for the H/D exchange experiment: In a 4-mL screw-top vial, compound **1a-n** (**n**=**1-16**) (0.10 mmol) was added to a solution of $Pd(OAc)_2$ (2.2 mg, 10 mmol%) and AcOD (12 mg, 0.20 mmol) in $CHCl_3$ (1.0 mL). The vial was capped, and the reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the crude reaction mixture was analyzed by ^2H NMR spectroscopy using $CDCl_3$ as internal standard. No deuterium incorporation was observed for compounds **1a-1** to **1a-15**. For compound **1a-16**, 9.3% of the hydrogen atoms in the *tert*-butyl group were deuteriated.

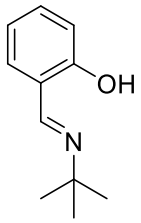
4. *Investigation of Effect of the Ligand*

In a 4-mL screw-top vial, compound **1a** (0.10 mmol) was added to a solution of $Pd(OAc)_2$ (2.2 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and ligand (10 mol%) in benzene (1.0 mL). The vial was capped, and the reaction mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the crude reaction mixture was analyzed by GC using dodecane as internal standard.



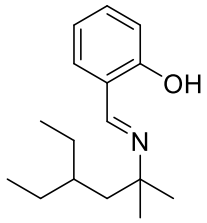
Yields refers to GC yields using dodecane as the internal standard

5. *Synthesis of Salicyladehyde Imines*



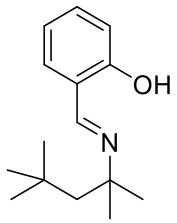
2-((*tert*-butylimino)methyl)phenol (1a) (General Procedure A):

To a solution of salicylaldehyde (1.22 g, 10.0 mmol) in DCM (5 mL) was added *tert*-butyl amine (0.767 g, 10.5 mmol) in one-portion. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with DCM (50 mL) and washed with brine. The organic layer was dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* to give compound **1a** as a yellow oil (1.70 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.39 (s, 1H), 8.36 (s, 1H), 7.35–7.25 (m, 2H), 6.97 (dd, J = 8.4, 1.2 Hz, 1H), 6.87 (td, J = 7.5, 1.1 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.1, 159.6, 132.0, 131.3, 118.8, 118.1, 117.3, 56.9, 29.6; **HRMS** (ESI+) calcd for $C_{11}H_{16}NO$ $[M+H]^+$ 178.1226, found 178.1220.



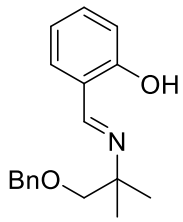
(E)-2-(((4-ethyl-2-methylhexan-2-yl)imino)methyl)phenol (1b)

Following General Procedure A, 4-ethyl-2-methylhexan-2-amine (0.28 g, 2.0 mmol) and salicylaldehyde (0.29 g, 2.4 mmol) were allowed to react. The reaction mixture was stirred for 2 h, diluted with DCM (30 mL), and washed with brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→90:10) to give compound **1b** as a yellow oil (0.28 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.39 (s, 1H), 8.33 (s, 1H), 7.29 (ddd, J = 10.6, 7.5, 1.5 Hz, 2H), 6.97 (d, J = 8.3 Hz, 1H), 6.87 (td, J = 7.5, 1.1 Hz, 1H), 1.57 (d, J = 4.0 Hz, 2H), 1.33 (s, 6H), 1.41–1.26 (m, 5H), 0.83 (t, J = 7.1 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 159.7, 132.0, 131.3, 118.8, 118.0, 117.3, 60.0, 47.1, 36.4, 27.6, 27.2, 10.8; **HRMS** (ESI+) calcd for $C_{16}H_{26}NO$ $[M+H]^+$ 248.2009, found 248.2018.



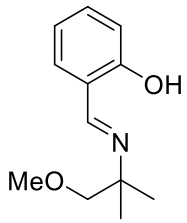
2-(((2,4,4-trimethylpentan-2-yl)imino)methyl)phenol (1c)

Following General Procedure A, salicylaldehyde (0.61 g, 5.0 mmol) and 2,4,4-trimethylpentan-2-amine (0.65 g, 5.0 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→90:10) to give compound **1c** as a yellow oil (1.0 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.52 (s, 1H), 8.34 (s, 1H), 7.42–7.24 (m, 2H), 6.96 (d, J = 8.3 Hz, 1H), 6.87 (td, J = 7.4, 1.1 Hz, 1H), 1.75 (s, 2H), 1.40 (s, 6H), 0.98 (s, 9H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.2, 159.5, 132.0, 131.3, 118.9, 118.0, 117.4, 60.6, 56.3, 32.0, 31.7, 29.5; **HRMS** (ESI+) calcd for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1852, found 234.1855.



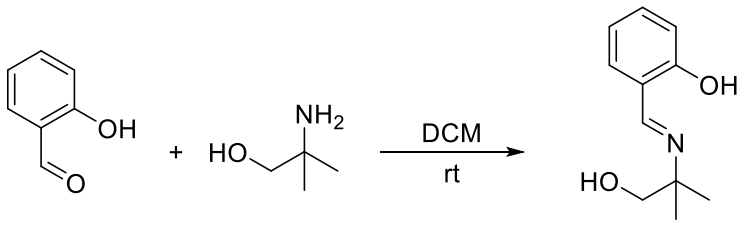
(E)-2-(((1-(benzyloxy)-2-methylpropan-2-yl)imino)methyl)phenol (1d)

To a solution of 1-(benzyloxy)-2-methylpropan-2-amine (0.18 g, 1.0 mmol) and 4Å molecular sieves (0.3 g) in DCM (5 mL) was added salicylaldehyde (0.12 g, 1.0 mmol) in one-portion. The reaction mixture was stirred for 2 h and filtered through a short pad of Celite, rinsing with DCM (10 mL). The filtrate was concentrated in *vacuo* to give compound **1d** as a yellow oil (0.24 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.19 (s, 1H), 8.40 (s, 1H), 7.39–7.21 (m, 7H), 6.95 (d, J = 8.4 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 4.54 (s, 2H), 3.46 (d, J = 1.2 Hz, 2H), 1.35 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.9, 161.8, 138.3, 132.1, 131.5, 128.4, 127.6, 127.5, 118.9, 118.2, 117.3, 77.8, 73.4, 60.0, 24.5; **HRMS** (ESI+) calcd for $C_{18}H_{22}NO_2$ $[M+H]^+$ 284.1645, found 284.1654.



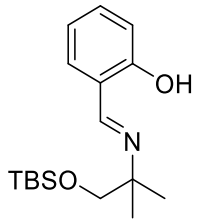
(E)-2-(((1-methoxy-2-methylpropan-2-yl)imino)methyl)phenol (1e)

Following General Procedure A, 1-methoxy-2-methylpropan-2-amine (0.25 g, 2.5 mmol) and salicylaldehyde (0.36 g, 3.0 mmol) were allowed to react. The reaction mixture was stirred for 2 h, diluted with DCM (30 mL), and washed with brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→90:10) to give compound **1e** as a yellow oil (0.49 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.20 (s, 1H), 8.40 (s, 1H), 7.35–7.26 (m, 2H), 6.96 (dd, J = 8.2, 1.2 Hz, 1H), 6.88 (td, J = 7.6, 1.2 Hz, 1H), 3.40 (s, 2H), 3.38 (s, 3H), 1.35 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.9, 161.6, 132.1, 131.5, 118.9, 118.2, 117.2, 80.7, 59.9, 59.5, 24.4; **HRMS** (ESI+) calcd for $C_{12}H_{18}NO_2$ $[M+H]^+$ 208.1332, found 208.1339.



2-(((1-hydroxy-2-methylpropan-2-yl)imino)methyl)phenol

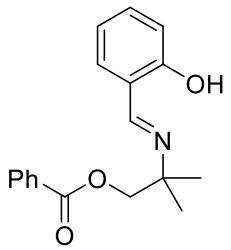
To a solution of 2-methyl-2-amino-1-propanol (1.78 g, 20.0 mmol) in DCM (10 mL) was added salicylaldehyde (2.44 g, 20.0 mmol) in one-portion. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with DCM (50 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* to give the hydroxyl imine as a yellow solid (3.74 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.87 (brs, 1H), 8.40 (s, 1H), 7.35–7.25 (m, 2H), 6.94 (dd, J = 8.3, 1.1 Hz, 1H), 6.88 (td, J = 7.5, 1.1 Hz, 1H), 3.61 (s, 2H), 1.61 (brs, 1H), 1.33 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 161.6, 132.4, 131.6, 118.8, 118.4, 117.2, 71.2, 61.0, 23.6; **HRMS** (ESI+) calcd for $C_{11}H_{16}NO_2$ $[M+H]^+$ 194.1176, found 194.1178.



2-(((1-((tert-butyldimethylsilyl)oxy)-2-methylpropan-2-yl)imino)methyl)phenol (1f)

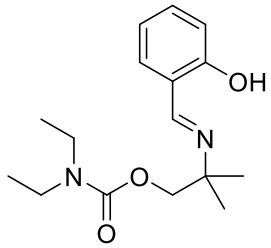
To a solution of 2-(((1-hydroxy-2-methylpropan-2-yl)imino)methyl)phenol (0.58 g, 3.0 mmol) and TBSCl (0.45 g, 3.0 mmol) in DCM (15 mL) was added imidazole (0.25 g, 3.6 mmol). The reaction mixture was stirred at room temperature overnight, diluted with DCM (30 mL), washed with water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash column

chromatography on silica gel (hexane : EA 100:0→90:10) to give compound **1f** as a yellow oil (0.59 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.21 (s, 1H), 8.37 (s, 1H), 7.32–7.26 (m, 1H), 7.24 (dd, J = 7.6, 1.7 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 6.84 (td, J = 7.5, 1.1 Hz, 1H), 3.52 (s, 2H), 1.29 (s, 6H), 0.86 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 162.1, 161.9, 132.0, 131.4, 118.9, 118.1, 117.3, 70.5, 60.7, 25.8, 23.9, 18.2, -5.6; **HRMS** (ESI+) calcd for $C_{17}H_{30}NO_2Si$ $[M+H]^+$ 308.2040, found 308.2069.



2-((2-hydroxybenzylidene)amino)-2-methylpropyl benzoate (1g)

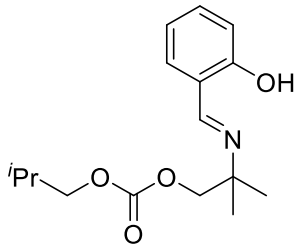
To a solution of 2-(((1-hydroxy-2-methylpropan-2-yl)imino)methyl)phenol (0.38 g, 2.0 mmol) and benzoic ahnydride (0.45 g, 2.0 mmol) in DCM (5 mL) was added DMAP (0.26 g, 2.1 mmol) at room temperature. The reaction mixture was stirred overnight, diluted with DCM (30 mL), washed with water (20 mL) and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→90:10) to give compound **1g** as a yellow oil (0.48 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.76 (s, 1H), 8.49 (s, 1H), 8.05 (dd, J = 8.4, 1.4 Hz, 2H), 7.76–7.54 (m, 1H), 7.46 (dd, J = 8.4, 7.2 Hz, 2H), 7.41–7.30 (m, 2H), 6.99 (dd, J = 8.4, 1.2 Hz, 1H), 6.91 (td, J = 7.6, 1.2 Hz, 1H), 4.39 (s, 2H), 1.47 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 161.9, 161.3, 133.1, 132.3, 131.6, 130.0, 129.6, 128.5, 118.9, 118.5, 117.2, 71.6, 59.4, 24.4; **HRMS** (ESI+) calcd for $C_{18}H_{20}NO_3$ $[M+H]^+$ 298.1438, found 298.1438.



2-((2-hydroxybenzylidene)amino)-2-methylpropyl diethylcarbamate (1h)

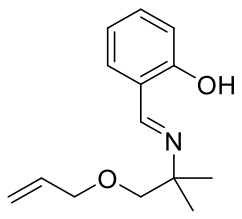
To a solution of 2-(((1-hydroxy-2-methylpropan-2-yl)imino)methyl)phenol (0.38 g, 2.0 mmol) and *N,N*-diisopropylethylamine (0.29 g, 2.2 mmol) in DCM (5 mL) were added diethylcarbamic chloride (0.30 g, 2.2 mmol) and DMAP (0.26 g, 2.1 mmol). The reaction mixture was stirred at 50 °C overnight. The mixture was diluted with DCM (30 mL), washed with water (20 mL), and then brine (10 mL). The organic layer was dried over Na_2SO_4 and filtered. The filtrate was

concentrated in *vacuo*, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→60:40) to give compound **1h** as a yellow oil (0.14 g, 24%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.82 (s, 1H), 8.41 (s, 1H), 7.40–7.21 (m, 2H), 6.97 (dd, J = 8.2, 1.1 Hz, 1H), 6.89 (td, J = 7.4, 1.1 Hz, 1H), 4.13 (s, 2H), 3.33-3.27 (m, 4H), 1.39 (s, 6H), 1.15-1.08 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.5, 161.4, 155.6, 132.2, 131.4, 118.9, 118.4, 117.2, 71.8, 59.4, 41.9, 41.3, 24.4, 14.1, 13.5; **HRMS** (ESI+) calcd for $C_{16}H_{25}N_2O_3$ $[M+H]^+$ 293.1860, found 293.1866.



2-((2-hydroxybenzylidene)amino)-2-methylpropyl isobutyl carbonate (1l)

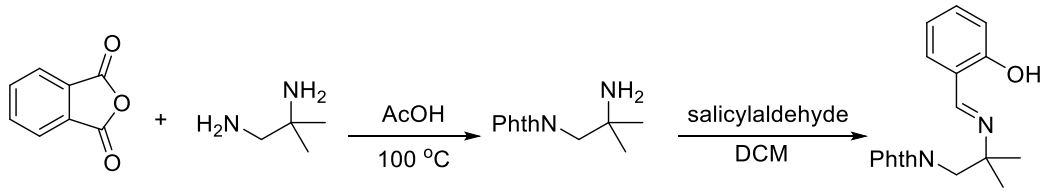
To a solution of 2-(((1-hydroxy-2-methylpropan-2-yl)imino)methyl)phenol (0.38 g, 2.0 mmol) in THF (5 mL) was added NaH (0.16 g, 60%, 4.4 mmol) in portions under N_2 at 0 °C. The reaction mixture was stirred for 1 h, followed by addition of isobutyl chloroformate (0.22 g, 1.6 mmol). The reaction was allowed to react at room temperature for 8 h and quenched with water (5 mL). The mixture was extracted with EA (10 mL*3). The combined organic layers were washed with water (10 mL) and then brine (10 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1l** (0.31 g, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.59 (s, 1H), 8.42 (s, 1H), 7.56–7.24 (m, 2H), 6.97 (dd, J = 8.3, 1.1 Hz, 1H), 6.90 (td, J = 7.5, 1.1 Hz, 1H), 4.19 (s, 2H), 3.92 (d, J = 6.8 Hz, 2H), 1.98 (dh, J = 13.5, 6.7 Hz, 1H), 1.39 (s, 6H), 0.94 (d, J = 6.7 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.1, 161.2, 155.3, 132.3, 131.6, 118.8, 118.5, 117.1, 74.3, 74.3, 59.3, 27.7, 24.1, 18.9; **HRMS** (ESI+) calcd for $C_{16}H_{24}NO_4$ $[M+H]^+$ 294.1700, found 294.1709.



2-(((1-(allyloxy)-2-methylpropan-2-yl)imino)methyl)phenol (1j)

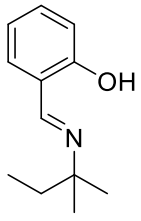
To a solution of 2-(((1-hydroxy-2-methylpropan-2-yl)imino)methyl)phenol (0.38 g, 2.0 mmol) in THF (5 mL) was added NaH (0.16 g, 60%, 4.4 mmol) in portions under N_2 at 0 °C. After the

reaction mixture was stirred for 1 h, allyl bromide (0.24 g, 2.0 mmol) was added. The reaction was stirred at room temperature for 8 h and quenched with water (5 mL). The mixture was extracted with EA (10 mL*3), and the combined organic layers were washed with water (10 mL) and then brine (10 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in *vacuo*, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→90:10) to give compound **1j** (0.25 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.20 (s, 1H), 8.42 (s, 1H), 7.44–7.20 (m, 2H), 6.96 (dd, J = 8.3, 1.2 Hz, 1H), 6.88 (td, J = 7.5, 1.1 Hz, 1H), 5.89 (ddt, J = 17.3, 10.7, 5.4 Hz, 1H), 5.27 (dq, J = 17.2, 1.7 Hz, 1H), 5.18 (dq, J = 10.5, 1.5 Hz, 1H), 4.01 (d, J = 5.5 Hz, 2H), 3.45 (s, 2H), 1.36 (s, 6H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 161.9, 161.7, 134.7, 132.1, 131.5, 118.9, 118.2, 117.2, 116.8, 77.9, 72.4, 60.0, 24.5; **HRMS** (ESI+) calcd for $C_{14}H_{20}NO_2$ $[M+H]^+$ 234.1489, found 234.1484.



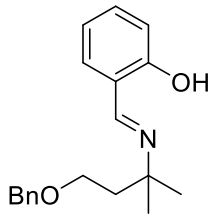
2-(2-((2-hydroxybenzylidene)amino)-2-methylpropyl)isoindoline-1,3-dione (1k)

To a solution of phthalic anhydride (0.45 g, 3.0 mmol) in AcOH (2 mL) was added 2-methyl-1,2-propanediamine (0.26 g, 3.0 mmol). The reaction mixture was stirred at 100 °C for 8 h, and the volatile materials were evaporated in vacuo. The residue was dissolved in DCM (50 mL), followed by addition of salicylaldehyde (0.44 g, 3.6 mmol), and the resulting mixture was allowed to react at room temperature for 8 h. After remove of the solvent, the crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→70:30) to give compound **1k** as a light-yellow solid (0.42 g, 44% over 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.35 (s, 1H), 8.39 (s, 1H), 7.88 (dd, J = 5.4, 3.2 Hz, 2H), 7.73 (dd, J = 5.4, 3.2 Hz, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.00 (d, J = 8.2 Hz, 1H), 6.87 (t, J = 7.8 Hz, 1H), 3.91 (s, 2H), 1.41 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 161.8, 161.0, 134.0, 132.2, 131.9, 131.6, 123.5, 118.9, 118.4, 117.2, 61.1, 48.6, 25.8; **HRMS** (ESI+) calcd for $C_{19}H_{19}N_2O_3$ $[M+H]^+$ 323.1390, found 323.1399.



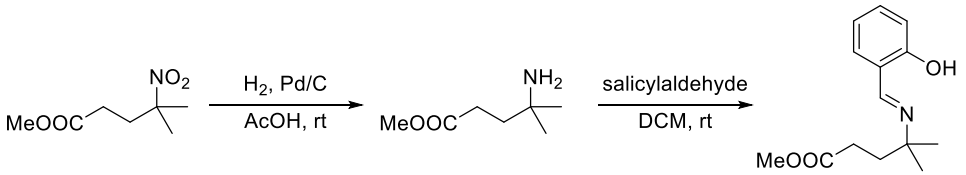
2-((tert-pentylimino)methyl)phenol (1l)

To a solution of 2-methyl-2-butanamine (0.91 g, 11 mmol) in DCM (10 mL) was added salicylaldehyde (1.2 g, 10 mmol) in one-portion. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with DCM (50 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* to give compound **1l** as a yellow oil (1.7 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.49 (s, 1H), 8.33 (s, 1H), 7.37–7.14 (m, 2H), 6.96 (dd, J = 8.2, 1.2 Hz, 1H), 6.87 (td, J = 7.4, 1.2 Hz, 1H), 1.67 (q, J = 7.5 Hz, 2H), 1.32 (s, 6H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.3, 160.1, 132.0, 131.3, 118.8, 118.0, 117.4, 59.5, 35.9, 26.6, 8.5; **HRMS** (ESI+) calcd for $C_{12}H_{18}NO$ $[M+H]^+$ 192.1383, found 192.1387.



2-(((4-(benzyloxy)-2-methylbutan-2-yl)imino)methyl)phenol (1m)

To a solution of 4-(benzyloxy)-2-methylbutan-2-amine (0.19 g, 1.0 mmol) in DCM (5 mL) was added salicylaldehyde (0.15 g, 1.2 mmol) in one-portion. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with DCM (20 mL) and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo,* and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→90:10) to give compound **1m** as a yellow oil (0.16 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 14.06 (s, 1H), 8.25 (s, 1H), 7.48–7.13 (m, 7H), 6.87 (dd, J = 8.4, 1.2 Hz, 1H), 6.79 (td, J = 7.4, 1.2 Hz, 1H), 4.39 (s, 2H), 3.50 (t, J = 6.9 Hz, 2H), 1.91 (t, J = 6.9 Hz, 2H), 1.27 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.8, 160.4, 138.4, 132.1, 131.4, 128.4, 127.6, 127.5, 118.8, 118.2, 117.2, 73.1, 66.9, 58.7, 42.6, 27.6; **HRMS** (ESI+) calcd for $C_{19}H_{24}NO_2$ $[M+H]^+$ 198.1802, found 198.1811.

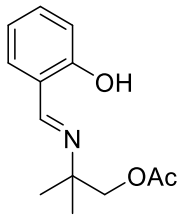


Methyl-4-((2-hydroxybenzylidene)amino)-4-methylpentanoate (1n)

To a solution of methyl 4-methyl-4-nitropentanoate (0.35 g, 2.0 mmol) in AcOH (5 mL) was added Pd/C (0.20 g, 10 wt. %). H_2 was bubbled through the reaction mixture for 20 min. The reaction mixture was stirred under H_2 for 8 h and filtered through a short pad of Celite, rinsing with with EA (10 mL). The filtrate was concentrated in *vacuo*, and the residue was dissolved in DCM (5 mL), followed by addition salicylaldehyde (0.24 g, 2.0 mmol). The reaction mixture

was stirred at room temperature for 2h. The mixture was diluted with DCM (30 mL), washed with brine (10 mL), dried over N_2SO_4, and filtered. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1n** (0.18 g, 36%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.90 (s, 1H), 8.32 (s, 1H), 7.42–7.22 (m, 2H), 6.94 (dd, J = 8.4, 1.0 Hz, 1H), 6.87 (td, J = 7.6, 1.0 Hz, 1H), 3.63 (s, 3H), 2.90–2.22 (m, 2H), 2.28–1.86 (m, 2H), 1.32 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 161.5, 160.8, 132.2, 131.5, 118.8, 118.4, 117.1, 58.8, 51.7, 38.1, 29.4, 26.9; **HRMS** (ESI+) calcd for $C_{14}H_{20}NO_3$ $[M+H]^+$ 250.1438, found 250.1437.

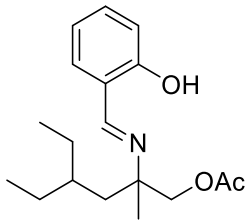
6. *Palladium-Catalyzed Acetoxylation of β-C-H Bond*



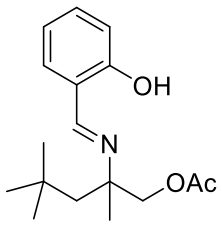
General Procedure B: In an N_2-filled glove-box, $Pd(OAc)_2$ (2.2 mg, 10 mol%), *N*-Boc-Ala (1.9 mg, 10 mol%), and $PhI(OAc)_2$ (48 mg, 1.5 equiv) were weighted into a 4-mL screw-top vial, followed by addition of benzene (1.0 mL) and imine **1a** (17.7 mg, 0.100 mmol). The vial was capped with a Teflon-lined screw cap and stirred at 80 °C. The reaction mixture was stirred for 6 hour and cooled to room temperature. The volatile materials were removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give the products (**mono-2a**: 8.9 mg, 37% and **di-2a**:3.2 mg, 11%). Product **mono-2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.71 (s, 1H), 8.40 (s, 1H), 7.39–7.27 (m, 2H), 6.98 (dd, J = 8.4, 1.0 Hz, 1H), 6.91 (td, J = 7.5, 1.1 Hz, 1H), 4.13 (s, 2H), 2.09 (s, 3H), 1.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 161.7, 161.3, 132.3, 131.6, 118.9, 118.5, 117.2, 71.3, 59.1, 24.2, 20.8; **HRMS** (ESI+) calcd for $C_{13}H_{18}NO_3$ $[M+H]^+$ 236.1281, found 236.1280. Product **di-2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.27 (s, 1H), 8.44 (s, 1H), 7.38–7.27 (m, 2H), 7.30 (dd, J = 7.7, 1.4 Hz, 2H), 6.96 (d, J = 8.6 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 4.25 (d, J = 11.2 Hz, 2H), 4.18 (d, J = 11.2 Hz, 2H), 2.08 (s, 6H), 1.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 163.7, 161.1, 132.8, 131.9, 118.7, 118.7, 117.2, 67.2, 61.2, 20.8, 18.7; **HRMS** (ESI+) calcd for $C_{15}H_{20}NO_5$ $[M+H]^+$ 294.1336, found 294.1343.

1.0 mmol-scale reaction: $Pd(OAc)_2$ (22 mg, 10 mol%), N-Boc-Ala (19 mg, 10 mol%), and $PhI(OAc)_2$ (480 mg, 1.5 equiv) were weighted into a 20-mL screw-top vial. To this vial were added benzene (10 mL) and **1a** (177 mg, 1.00 mmol). The reaction mixture was stirred at 80 °C for 6 h. The volatile materials were removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give the

products (**mono-2a**: 75.1 mg, 32% and **di-2a**: 22.4 mg, 8%). NMR data matched with those reported above.

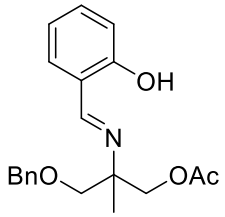


Following General Procedure B, the reaction was allowed to react with $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1b** (24.7 mg, 0.100 mmol). The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give the products (**mono-2b**: 11.0 mg, 36% and **di-2b**: 5.1 mg, 14%). Product **mono-2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.74 (s, 1H), 8.35 (s, 1H), 7.35–7.26 (m, 2H), 6.95 (d, J = 8.4 Hz, 1H), 6.88 (td, J = 7.4, 1.2 Hz, 1H), 4.13 (d, J = 11.0 Hz, 1H), 4.10 (d, J = 11.0 Hz, 1H), 2.05 (s, 3H), 1.66 (dd, J = 14.4, 3.6 Hz, 1H), 1.60–1.52 (m, 2H), 1.33 (s, 3H), 1.35–1.23 (m, 4H), 0.82 (t, J = 7.2 Hz, 3H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 161.9, 161.4, 132.3, 131.6, 118.8, 118.4, 117.2, 70.5, 62.1, 42.3, 35.7, 27.2, 26.9, 20.9, 20.5, 10.8, 10.6; **HRMS** (ESI+) calcd for $C_{18}H_{28}NO_3$ $[M+H]^+$ 306.2064, found 306.2073. Product **di-2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.27 (s, 1H), 8.45 (s, 1H), 7.36 (ddd, J = 8.4, 7.4, 1.6 Hz, 1H), 7.30 (dd, J = 7.4, 1.6 Hz, 1H), 6.99 (dd, J = 8.4, 1.2 Hz, 1H), 6.93 (td, J = 7.6, 1.2 Hz, 1H), 4.35 (d, J = 11.4 Hz, 2H), 4.28 (d, J = 11.4 Hz, 2H), 2.10 (s, 6H), 1.70 (d, J = 5.2 Hz, 2H), 1.45–1.36 (m, 1H), 1.36–1.30 (m, 4H), 0.83 (t, J = 7.4 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 163.6, 161.1, 132.7, 131.9, 118.7, 118.6, 117.2, 65.1, 63.5, 37.6, 35.2, 26.9, 20.8, 10.5; **HRMS** (ESI+) calcd for $C_{20}H_{30}NO_5$ $[M+H]^+$ 364.2118, found 364.2117.

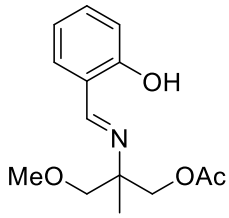


Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), *N*-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1c** (23.3 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give the products (**mono-2c**: 5.8 mg, 20% and **di-2c**: 5.8 mg, 17%). Product **mono-2c** ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.92 (s, 1H), 8.40 (s, 1H), 7.41–7.29 (m, 2H), 7.00 (d, J = 8.4 Hz, 1H), 6.93 (t, J = 7.4 Hz, 1H), 4.14 (s, 2H), 2.10 (s, 3H), 1.88 (d, J = 14.6 Hz, 1H), 1.70 (d, J = 14.6 Hz, 1H), 1.48 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 161.8, 161.4,

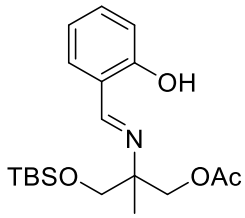
132.3, 131.6, 118.9, 118.4, 117.2, 71.3, 62.7, 51.6, 31.8, 31.8, 21.5, 20.9; **HRMS** (ESI+) calcd for $C_{17}H_{26}NO_3$ $[M+H]^+$ 292.1907, found 292.1908. Product **di-2c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.36 (s, 1H), 8.48 (s, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.32 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.96 (t, J = 7.4 Hz, 1H), 4.43 (d, J = 11.2 Hz, 2H), 4.33 (d, J = 11.2 Hz, 2H), 2.12 (s, 6H), 1.84 (s, 2H), 1.02 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 163.6, 161.1, 132.8, 131.9, 118.7, 118.7, 117.2, 65.6, 64.1, 47.2, 31.9, 31.6, 20.8; **HRMS** (ESI+) calcd for $C_{19}H_{28}NO_5$ $[M+H]^+$ 350.1962, found 350.1970.



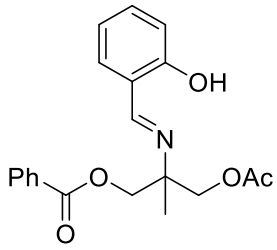
Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1d** (28.3 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1d** (5.1 mg, 18%) and product **2d** (12.2 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.65 (s, 1H), 8.46 (s, 1H), 7.56–7.17 (m, 7H), 6.96 (dd, J = 8.4, 1.2 Hz, 1H), 6.89 (td, J = 7.4, 1.2 Hz, 1H), 4.54 (s, 2H), 4.27 (d, J = 10.8 Hz, 1H), 4.24 (d, J = 10.8 Hz, 1H), 3.61 (d, J = 9.2 Hz, 1H), 3.49 (d, J = 9.2 Hz, 1H), 2.05 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 170.8, 163.5, 161.3, 137.9, 132.5, 131.8, 128.4, 127.7, 127.6, 118.9, 118.5, 117.2, 73.7, 73.5, 67.8, 62.1, 20.8, 19.1; **HRMS** (ESI+) calcd for $C_{20}H_{24}NO_4$ $[M+H]^+$ 342.1700, found 342.1705.



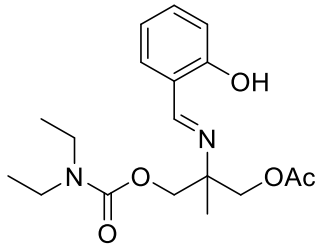
Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1e** (20.7 mg, 0.100 mmol). The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1e** (4.3 mg) and product **2e** (10.3 mg, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.66 (s, 1H), 8.47 (s, 1H), 7.41–7.29 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 6.91 (td, J = 7.4, 1.2 Hz, 1H), 4.26 (d, J = 11.2 Hz, 1H), 4.24 (d, J = 11.2 Hz, 1H), 3.54 (d, J = 9.4 Hz, 1H), 3.44 (d, J = 9.4 Hz, 1H), 3.38 (s, 3H), 2.10 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 163.5, 161.3, 132.4, 131.8, 118.9, 118.5, 117.2, 76.6, 67.8, 62.1, 59.5, 20.8, 18.8; **HRMS** (ESI+) calcd for $C_{14}H_{20}NO_4$ $[M+H]^+$ 266.1387, found 266.1395.



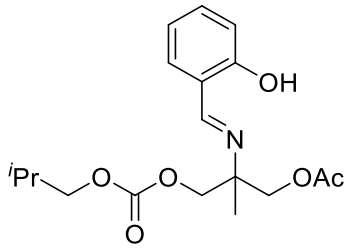
Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), *N*-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1f** (30.7 mg, 0.100 mmol) were allowed to react. The reaction was stirred at 80 °C for 3 h. After cooling to room temperature, the reaction vial was taken into the glove-box, and $PhI(OAc)_2$ (22 mg, 0.75 mmol) was added. The vial was capped, and the reaction mixture was stirred at 80 °C for 7 h. After volatile materials were removed, the crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give **1f** (5.2 mg) and product **2f** (10.1 mg, 28%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.65 (s, 1H), 8.47 (s, 1H), 7.39–7.30 (m, 1H), 7.31–7.26 (m, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.90 (td, J = 7.4, 1.2 Hz, 1H), 4.26 (d, J = 11.2 Hz, 1H), 4.23 (d, J = 11.2 Hz, 1H), 3.75 (d, J = 9.8 Hz, 1H), 3.60 (d, J = 9.8 Hz, 1H), 2.10 (s, 3H), 1.34 (s, 3H), 0.90 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 163.5, 161.4, 132.5, 131.7, 118.8, 118.5, 117.2, 67.4, 66.9, 62.8, 25.8, 20.8, 18.4, 18.2, -5.6; **HRMS** (ESI+) calcd for $C_{19}H_{32}NO_4Si$ $[M+H]^+$ 366.2095, found 366.2096.



Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1g** (29.7 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give product **2g** (9.6 mg, 27%). ^{1}H NMR (600 MHz, C_6D_6) δ 13.58 (s, 1H), 8.17–8.05 (m, 3H), 8.10 (s, 1H), 7.11–6.97 (m, 5H), 6.90 (dd, J = 7.7, 1.6 Hz, 1H), 6.66 (td, J = 7.4, 1.2 Hz, 1H), 4.26 (s, 2H), 4.14 (d, J = 11.2 Hz, 1H), 4.06 (d, J = 11.2 Hz, 1H), 1.57 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 169.4, 165.6, 163.6, 161.9, 132.9, 132.8, 131.9, 130.1, 129.6, 128.4, 119.0, 118.4, 117.5, 67.3, 66.9, 61.4, 19.8, 18.2; **HRMS** (ESI+) calcd for $C_{20}H_{22}NO_5$ $[M+H]^+$ 356.1496, found 356.1492.

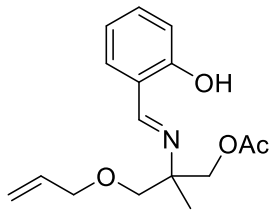


Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1h** (29.2 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→50:50) to give compound **1h** (4.4 mg, 15%), product **mono-2h** (12 mg, 35%), and product **di-2h** (2.4 mg, 6%). Product **mono-2h**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.31 (s, 1H), 8.45 (s, 1H), 7.32 (ddd, J = 8.2, 7.3, 1.7 Hz, 1H), 7.30–7.24 (m, 1H), 6.95 (dd, J = 8.3, 1.0 Hz, 1H), 6.89 (td, J = 7.5, 1.1 Hz, 1H), 4.26 (d, J = 9.8 Hz, 1H), 4.24 (d, J = 9.8 Hz, 1H), 4.21 (d, J = 6.2 Hz, 1H), 4.19 (d, J = 6.2 Hz, 1H), 3.38–3.14 (m, 4H), 2.08 (s, 3H), 1.38 (s, 3H), 1.14–1.04 (m, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 163.6, 161.2, 155.3, 132.7, 131.8, 118.8, 118.6, 117.2, 67.8, 67.5, 61.6, 42.1, 41.4, 20.8, 19.0, 14.1, 13.4; **HRMS** (ESI+) calcd for $C_{18}H_{27}N_2O_5$ $[M+H]^+$ 351.1914, found 351.1917. Product **di-2h**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.96 (s, 1H), 8.51 (s, 1H), 7.35 (ddd, J = 8.3, 7.3, 1.7 Hz, 1H), 7.28 (dd, J = 7.7, 1.7 Hz, 1H), 6.97 (dd, J = 8.4, 1.0 Hz, 1H), 6.91 (td, J = 7.5, 1.1 Hz, 1H), 4.39 (s, 2H), 4.37 (d, J = 3.8 Hz, 4H), 3.36–3.16 (m, 4H), 2.08 (s, 6H), 1.16–0.97 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 165.3, 161.1, 154.9, 133.1, 132.1, 118.8, 118.6, 117.3, 64.0, 63.7, 63.5, 42.3, 41.5, 20.8, 14.1, 13.3; **HRMS** (ESI+) calcd for $C_{20}H_{29}N_2O_7$ $[M+H]^+$ 409.1969, found 409.1966.

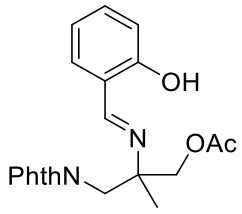


Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1i** (27.9 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1i** (5.3 mg, 19%) and product **2i** (14.6 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.14 (s, 1H), 8.45 (s, 1H), 7.42–7.26 (m, 2H), 6.95 (dd, J = 8.2, 1.2 Hz, 1H), 6.89 (td, J = 7.4, 1.2 Hz, 1H), 4.32 (d, J = 10.8 Hz, 1H), 4.27 (d, J = 9.6 Hz, 1H), 4.24 (d, J = 9.6 Hz, 1H), 4.20 (d, J = 11.2 Hz, 1H), 3.91 (d, J = 6.8 Hz, 2H), 2.08 (s, 3H), 1.95 (dp, J = 13.4, 6.6 Hz, 1H), 1.39 (s, 3H), 0.92 (d, J = 6.6 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 164.0, 161.1, 155.1,

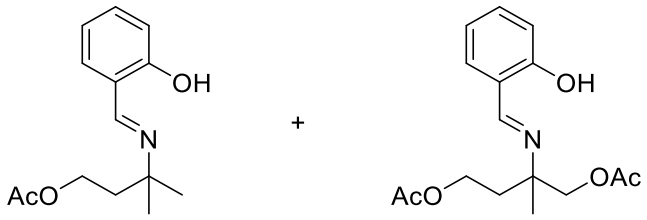
132.8, 132.0, 118.7, 118.7, 117.2, 74.4, 70.4, 67.2, 61.4, 27.7, 20.8, 18.9, 18.6; **HRMS** (ESI+) calcd for $C_{16}H_{26}NO_6$ $[M+H]^+$ 352.1755, found 352.1756.



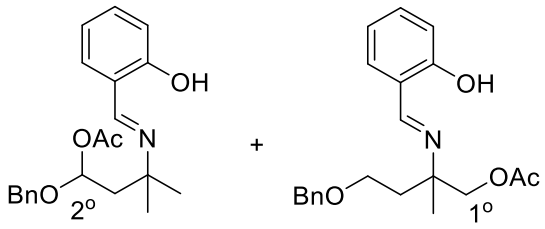
Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1j** (23.3 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give compound **1j** (2.6 mg, 11%) and product **2j** (14.6 mg, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.63 (s, 1H), 8.46 (s, 1H), 7.35–7.25 (m, 2H), 6.95 (dd, J = 8.4, 1.0 Hz, 1H), 6.88 (td, J = 7.4, 1.0 Hz, 1H), 5.85 (ddt, J = 17.2, 10.8, 5.6 Hz, 1H), 5.25 (dq, J = 17.2, 1.8 Hz, 1H), 5.17 (dq, J = 10.4, 1.4 Hz, 1H), 4.25 (d, J = 11.2 Hz, 1H), 4.22 (d, J = 11.2 Hz, 1H), 3.99 (t, J = 1.6 Hz, 1H), 3.98 (t, J = 1.6 Hz, 1H), 3.57 (d, J = 9.4 Hz, 1H), 3.46 (d, J = 9.4 Hz, 1H), 2.07 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 163.5, 161.3, 134.4, 132.4, 131.8, 118.9, 118.5, 117.2, 117.1, 73.9, 72.5, 67.8, 62.1, 20.8, 18.9; **HRMS** (ESI+) calcd for $C_{16}H_{22}NO_4$ $[M+H]^+$ 292.1543, found 292.1545.



Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (48 mg, 1.5 equiv), and **1k** (32.2 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→60:40) to give product **2k** (11.4 mg, 30%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.02 (s, 1H), 8.48 (s, 1H), 7.88 (dd, J = 5.4, 3.2 Hz, 2H), 7.75 (dd, J = 5.4, 3.2 Hz, 2H), 7.34 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 8.8 Hz, 1H), 6.99 (d, J = 8.8 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 4.27 (d, J = 11.4 Hz, 1H), 4.18 (d, J = 11.4 Hz, 1H), 4.02 (d, J = 13.8 Hz, 1H), 4.01 (d, J = 13.8 Hz, 1H), 2.10 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 168.4, 163.9, 161.0, 134.2, 132.7, 132.0, 131.8, 123.6, 118.8, 118.6, 117.3, 68.4, 62.8, 44.9, 20.8, 19.7; **HRMS** (ESI+) calcd for $C_{21}H_{21}N_2O_5$ $[M+H]^+$ 381.1445, found 381.1440.

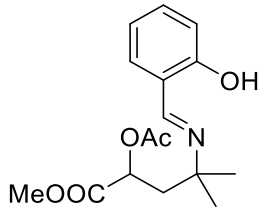


Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (71 mg, 2.5 equiv), and **1l** (19.1 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give product **mono-2l** (13.9 mg, 56%) and product **di-2l** (4.0 mg, 13%). Product **mono-2l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.87 (s, 1H), 8.34 (s, 1H), 7.35–7.24 (m, 2H), 6.94 (dd, J = 8.4, 1.2 Hz, 1H), 6.87 (td, J = 7.4, 1.1 Hz, 1H), 4.15 (t, J = 7.0 Hz, 2H), 1.99 (t, J = 7.0 Hz, 2H), 1.99 (s, 3H), 1.35 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 161.4, 160.6, 132.2, 131.5, 118.8, 118.4, 117.1, 61.1, 58.5, 41.6, 27.3, 20.9; **HRMS** (ESI+) calcd for $C_{14}H_{20}NO_3$ $[M+H]^+$ 250.1438, found 250.1434. Product **di-2l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.39 (s, 1H), 8.39 (s, 1H), 7.32 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H), 7.29 (dd, J = 7.6, 1.6 Hz, 1H), 6.96 (dd, J = 8.4, 1.2 Hz, 1H), 6.90 (td, J = 7.6, 1.2 Hz, 1H), 4.28–4.12 (m, 3H), 4.11 (d, J = 11.2 Hz, 1H), 2.14–2.05 (m, 1H), 2.07 (s, 3H), 2.05–1.95 (m, 1H), 1.99 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.7, 162.8, 161.1, 132.6, 131.8, 118.7, 118.7, 117.2, 70.0, 60.7, 60.2, 37.0, 20.9, 20.8, 20.6; **HRMS** (ESI+) calcd for $C_{16}H_{22}NO_5$ $[M+H]^+$ 308.1492, found 308.1491.



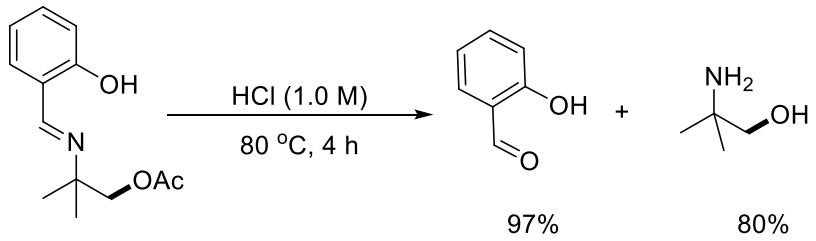
Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (71 mg, 2.5 equiv), and **1m** (29.7 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give product **2^0-2m** (8.5 mg, 24%) and product **1^0-2m** (8.9 mg, 25%). Product **2^0-2m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.86 (s, 1H), 8.29 (s, 1H), 7.38–7.25 (m, 6H), 7.24 (dd, J = 7.6, 1.6 Hz, 1H), 6.98 (dd, J = 8.4, 1.2 Hz, 1H), 6.88 (td, J = 7.4, 1.2 Hz, 1H), 6.09 (t, J = 5.2 Hz, 1H), 4.67 (d, J = 11.8 Hz, 1H), 4.56 (d, J = 11.8 Hz, 1H), 2.16 (d, J = 5.2 Hz, 2H), 1.98 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 161.4, 160.5, 137.0, 132.1, 131.5, 128.4, 127.9, 127.8, 118.9, 118.3, 117.2, 96.0, 71.1, 58.0, 47.3, 28.5, 27.0, 21.0; **HRMS** (ESI+) calcd for $C_{21}H_{26}NO_4[M+H]^+$ 356.1856, found 356.1861. Product **1^0-2m**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.65 (s, 1H), 8.38 (s, 1H), 7.55–7.17 (m, 7H), 6.98 (dd, J = 8.4, 1.2 Hz, 1H), 6.91 (td, J = 7.6, 1.2 Hz, 1H), 4.49 (d, J = 11.5 Hz, 1H), 4.46 (d, J = 11.5 Hz, 1H), 4.19 (d, J =

11.5 Hz, 1H), 4.16 (d, J = 11.5 Hz, 1H), 3.63–3.52 (m, 2H), 2.10–1.97 (m, 2H), 2.07 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 162.5, 161.3, 138.1, 132.4, 131.7, 128.4, 127.6, 127.6, 118.8, 118.5, 117.2, 73.2, 70.2, 66.0, 60.9, 38.1, 21.0, 20.8; **HRMS** (ESI+) calcd for $C_{21}H_{26}NO_4[M+H]^+$ 356.1856, found 356.1866.



Following General Procedure B, $Pd(OAc)_2$ (2.2 mg, 10 mol%), N-Boc-Ala (1.9 mg, 10 mol%), $PhI(OAc)_2$ (71 mg, 2.5 equiv), and **1n** (24.9 mg, 0.100 mmol) were allowed to react. The crude product was purified by flash column chromatography on silica gel (hexane : EA 100:0→80:20) to give **1n** (5.5 mg, 22%) and product **2n** (12.6 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.63 (s, 1H), 8.32 (s, 1H), 7.35–7.22 (m, 2H), 6.94 (dd, J = 8.4, 1.0 Hz, 1H), 6.87 (td, J = 7.4, 1.2 Hz, 1H), 5.13 (dd, J = 8.4, 3.4 Hz, 1H), 3.70 (s, 3H), 2.36–2.13 (m, 2H), 2.01 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 170.4, 161.2, 160.9, 132.3, 131.6, 118.8, 118.5, 117.1, 69.7, 58.7, 52.5, 44.0, 27.7, 26.9, 20.5; **HRMS** (ESI+) calcd for $C_{16}H_{22}NO_5$ $[M+H]^+$ 308.1492, found 308.1498.

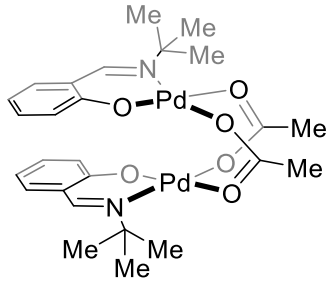
7. *Removal and Recovery of the Directing Group*



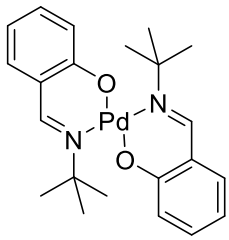
To an aqueous solution of HCl (1.0 M, 1.0 mL) was added **mono-2a** (47 mg, 0.20 mmol), and the resulting reaction mixture was stirred at 80 °C for 4 h. After cooling to room temperature, the mixture was diluted with water (1.0 mL) and extracted with hexane (5 mL*5). The combined organic layers were dried over Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* to give salicylaldehyde (23.5 mg, 96%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 9.90 (s, 1H), 7.59–7.50 (m, 2H), 7.09–6.97 (m, 2H).[1] To obtain the amino alcohol, the acidic aqueous layer was basified with NaOH (3.0 M) to reach a pH of 14, followed by addition of NaCl (0.6 g). The resulting solution was extracted with DCM (20 mL*5), and the combined organic layers were dried over Na_2SO_4. After filtration, the filtrate was concentrated in *vacuo* to give 2-methyl-2-amino propanol (14.1%, 80%) as a colorless oil. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 3.28 (s, 2H), 1.88 (brs, 3H), 1.10 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 71.7, 50.6, 27.3. These NRM data matched with those reported in literature.[1]

8. *Mechanistic Investigation*

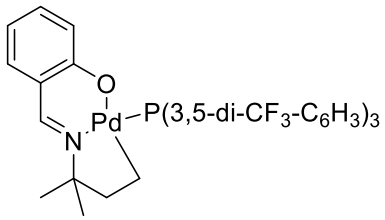


Modifications were made to procedures reported for the synthesis of similar palladium complexes.[2] In a 20 mL vial were added compound **1a** (177 mg, 1.00 mmol) and $Pd(OAc)_2$ (224 mmol, 1.0 mmol), followed by $CHCl_3$ (5 mL). The vial was capped, and the reaction mixture was stirred at 80 °C for 6 h. After cooling to room temperature, the volatile materials were evaporated *in vacuo* to give the crude product as a yellow solid. The crude product was rinsed with hexane. Product **4** was obtained as a pale-yellow solid (269 mg, 39%). Crystals suitable for X-ray crystallography were obtained by recrystallizing the product from pentane at –20 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.14 (ddd, J = 8.5, 6.9, 1.8 Hz, 2H), 6.75 (d, J = 8.5 Hz, 2H), 6.70 (dd, J = 7.8, 1.8 Hz, 2H), 6.48 (ddd, J = 7.9, 6.9, 1.2 Hz, 2H), 6.41 (s, 2H), 2.00 (s, 6H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.3 (2H), 162.1 (2H), 157.9 (2H), 135.5 (2H), 134.2 (2H), 122.9 (2H), 118.9 (2H), 114.7 (2H), 64.4 (2H), 30.7 (2H), 24.1 (2H); **HRMS** (ESI+) calcd for $C_{26}H_{34}N_2O_6Pd_2$ $[M]^+$ 684.0485, found 684.0485.

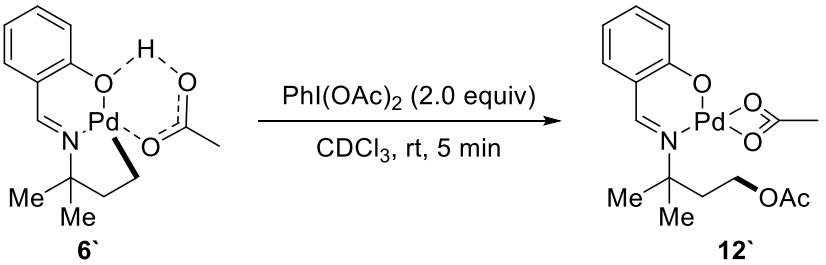


Modifications were made to procedures reported for the synthesis of similar palladium complexes.[3] In a 20 mL vial was added compound **1a** (177 mg, 1.00 mmol), $Pd(OAc)_2$ (224 mmol, 1.0 mmol), and Na_2CO_3 (106 mg, 1.00 mmol), followed by $CHCl_3$ (3 mL). The vial was capped, and the reaction mixture was stirred at 80 °C for 4 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of silica gel, and the filtrate was concentrated under reduced pressure to give the product **6** as a yellowish red solid (210 mg, 46%). Crystals suitable for X-ray crystallography were obtained by vial-in-vial diffusion of hexane into an acetone solution of the product at –20 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (s, 2H), 7.18–7.08 (m, 4H), 6.78 (dd, J = 8.2, 1.0 Hz, 2H), 6.56 (ddd, J = 7.9, 7.0, 1.1 Hz, 2H),

1.70 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0 (2H), 159.7 (2H), 134.2 (2H), 133.5 (2H), 125.6 (2H), 119.8 (2H), 115.4 (2H), 63.2 (2H), 31.6 (18H); **HRMS** (ESI+) calcd for $C_{22}H_{29}N_2O_2Pd$ $[M+H]^+$ 459.1258, found 459.1272.



Modifications were made to procedures reported for the synthesis of similar palladium complexes.[2,4] To a solution of compound **1l** (48 mg, 0.25 mmol) in $CHCl_3$ (5 mL) was added $Pd(OAc)_2$ (62 mg, 0.28 mmol) in one-portion. The resulting mixture was stirred under nitrogen at 80 ^oC for 2 h. After the reaction mixture was cooled to room temperature, tris[3,5-bis(trifulуromethyl)phenyl]phosphine (0.20 g, 0.30 mmol) was added. The mixture was heated at 80 ^oC for 1 h. The reaction mixture was cooled to room temperature, filtered through a short pad of Celite, and rinsed with ethyl acetate (5 mL). The eluent was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give compound **7** as a light-yellow solid (0.21 g, 86%). Crystals suitable for X-ray crystallography were obtained by vial-in-vial diffusion of pentane into a methanol solution of the title complex. ^{1}H NMR (600 MHz, C_6D_6) δ 8.36 (d, J = 10.3 Hz, 6H), 7.79 (d, J = 15.1 Hz, 1H), 7.61 (s, 3H), 7.37 (t, J = 7.7 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 7.04 (d, J = 7.9 Hz, 1H), 6.58 (t, J = 7.3 Hz, 1H), 1.48 (q, J = 6.2 Hz, 2H), 1.38 (t, J = 6.4 Hz, 2H), 0.98 (s, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 166.7, 159.2, 135.8, 135.1, 133.7 (dd, J = 13.3, 3.7 Hz), 133.4 (d, J = 41.4 Hz), 132.6 (qd, J = 33.9, 9.9 Hz), 125.0 (brs, 1H), 122.7, 122.6 (q, J = 273.5 Hz), 119.8, 114.1, 70.1, 48.2, 27.2 (d, J = 6.9 Hz), 25.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4; **HRMS** (ESI+) calcd for $C_{10}H_{22}N$ $[M+H]^+$ 944.0416, found 966.0410.



To a solution of compound **1l** (96 mg, 0.50 mmol) in $CDCl_3$ (5 mL) was added $Pd(OAc)_2$ (112 mg, 0.500 mmol) in one-portion. The resulting mixture was stirred under nitrogen at 80 ^oC for 3 h to give complex **6'**. The freshly prepared solution of **6'** (0.5 mL) was added to an NMR tube charged with $PhI(OAc)_2$ (32 mg, 0.10 mmol). After shaking to ensure that the $PhI(OAc)_2$

had dissolved completely, ^{1}H NMR spectroscopy was conducted. Analysis of the ^{1}H NMR spectrum showed that all of the complex **6'** was consumed, and complex **12'** formed in 46% yield.

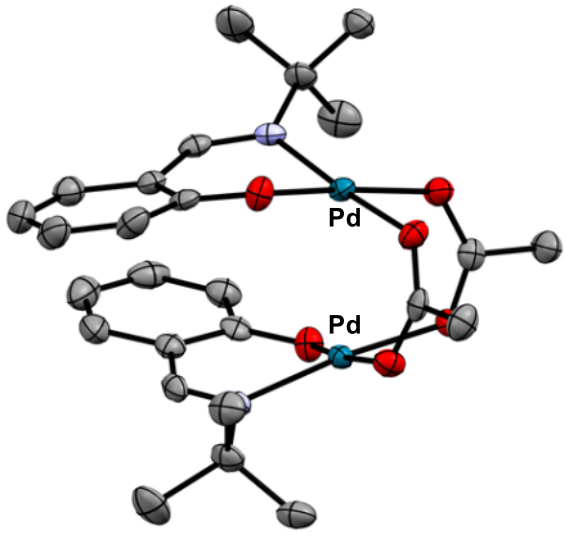


Figure S1. Solid-state structure of complex **4** determined by single crystal X-ray diffraction. The thermal ellipsoids were set to 75% probability. All hydrogen atoms were omitted for clarity.

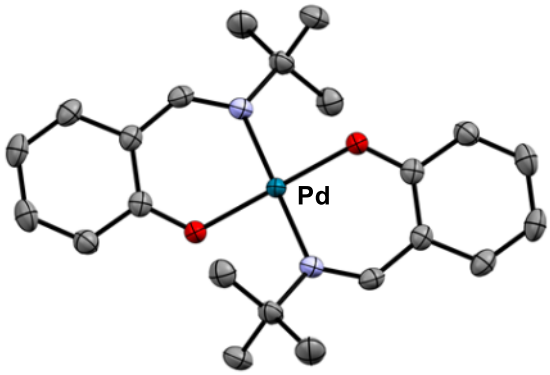


Figure S2. Solid-state structure of complex **6** determined by single crystal X-ray diffraction. The thermal ellipsoids were set to 75% probability. All hydrogen atoms were omitted for clarity.

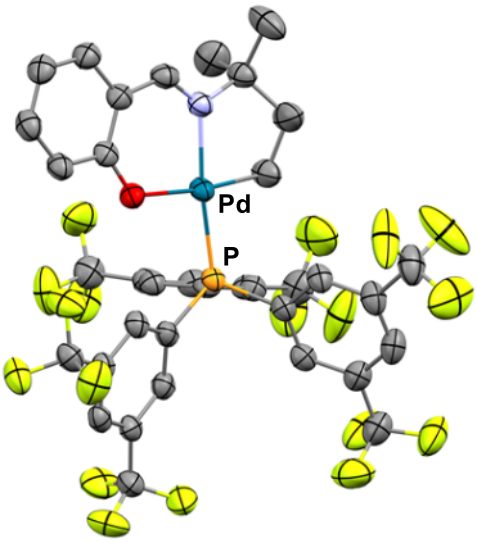


Figure S3. Solid-state structure of complex **7** determined by single crystal X-ray diffraction. The thermal ellipsoids were set to 75% probability. All hydrogen atoms were omitted for clarity.

9. Crystallographic Information

Complex 4

A yellow block 0.17 x 0.15 x 0.09 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 50 mm and exposure time was 1.00 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 26.370° in θ. A total of 28226 reflections were collected covering the indices -12<=h<=12, -14<=k<=14, -15<=l<=15. 5546 reflections were founded to be symmetry independent, with an R_{int} of 0.0793. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P -1 (No. 2). The data were integrated using the CrysAlis^{Pro} 1.171.39.46e software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table S1. Crystal data and structure refinement for complex **4**

Empirical formula	$C_{26}H_{34}N_2O_6Pd_2$
Formula weight	683.35
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n

Unit cell dimensions	a = 8.9433(3) Å	α = 90°.
	b = 34.4853(9) Å	β = 113.354(4)°.
	c = 9.5969(3) Å	γ = 90°.
Volume	2717.31(16) $Å^3$	
Z	4	
Density (calculated)	1.670 Mg/m^3	
Absorption coefficient	1.365 mm^{-1}	
F(000)	1376	
Crystal size	0.190 x 0.160 x 0.080 mm^3	
Theta range for data collection	2.889 to 26.371°.	
Index ranges	-11<=h<=10, -43<=k<=43, -11<=l<=11	
Reflections collected	28988	
Independent reflections	5538 [R(int) = 0.0435]	
Completeness to theta = 26.371°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85298	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5538 / 0 / 333	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0237, wR2 = 0.0505	
R indices (all data)	R1 = 0.0291, wR2 = 0.0520	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.459 and -0.450 e.$Å^{-3}$	

Complex 6

An orange block 0.24 x 0.18 x 0.11 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 50 mm and exposure time was 0.75 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 26.372° in θ. A total of 36629 reflections were collected covering the indices -23<=h<=23, -9<=k<=9, -18<=l<=18. 2058 reflections were founded to be symmetry independent, with an R_{int} of 0.0523. Indexing and unit cell refinement indicated a C-centered, monoclinic lattice. The space group was found to be C 2/c (No. 15). The data were integrated using the $CrysAlis^{Pro}$ 1.171.39.46e software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-

2014.

Table S2. Crystal data and structure refinement for complex **5**.

Empirical formula	$C_{22}H_{28}N_2O_2Pd$	
Formula weight	458.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 19.1646(4) Å	α = 90°.
	b = 7.69380(10) Å	β= 108.664(2)°.
	c = 14.4178(3) Å	γ = 90°.
Volume	2014.09(7) $Å^3$	
Z	4	
Density (calculated)	1.513 Mg/m^3	
Absorption coefficient	0.940 mm^{-1}	
F(000)	944	
Crystal size	0.240 x 0.180 x 0.110 mm^3	
Theta range for data collection	2.875 to 26.372°.	
Index ranges	-23<=h<=23, -9<=k<=9, -18<=l<=18	
Reflections collected	36629	
Independent reflections	2058 [R(int) = 0.0523]	
Completeness to theta = 26.372°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.77574	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2058 / 0 / 127	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0170, wR2 = 0.0436	
R indices (all data)	R1 = 0.0181, wR2 = 0.0442	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.397 and -0.233 e.$Å^{-3}$	

Complex 7

A yellow block 0.40 x 0.24 x 0.16 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 50 mm and exposure time was 0.50 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 26.372° in θ. A total of 39516 reflections were collected covering the indices -12<=h<=12, -15<=k<=15, -19<=l<=19. 7869 reflections were founded to be symmetry independent, with an R_{int} of 0.0510. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P -1 (No. 2). The data were integrated using the CrysAlis^{Pro} 1.171.39.46e

software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Table S3. Crystal data and structure refinement for complex **7**.

Empirical formula	$C_{37}H_{28}F_{18}NO_2PPd$	
Formula weight	997.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.9613(3) Å	α = 89.843(3)°.
	b = 12.3262(4) Å	β = 88.801(2)°.
	c = 15.8096(5) Å	γ = 82.682(2)°.
Volume	1924.95(11) $Å^3$	
Z	2	
Density (calculated)	1.722 Mg/m^3	
Absorption coefficient	0.647 mm^{-1}	
F(000)	992	
Crystal size	0.400 x 0.240 x 0.160 mm^3	
Theta range for data collection	2.775 to 26.372°.	
Index ranges	-12<=h<=12, -15<=k<=15, -19<=l<=19	
Reflections collected	39516	
Independent reflections	7869 [R(int) = 0.0510]	
Completeness to theta = 26.372°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.60221	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7869 / 36 / 576	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0967	
R indices (all data)	R1 = 0.0418, wR2 = 0.0998	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.391 and -0.946 e.$Å^{-3}$	

10. Computational Details

Computational Methods

All calculations were performed with the Gaussian 16 program package.[5]

Geometry optimizations for all reported structures were performed with the dispersion-corrected B3LYP-D3 functional with a mixed basis set of LANL2DZ (for Pd and I) and 6-31G(d) (for other atoms).[6] Frequency calculations were performed on all optimized structures to ensure that each local minimum lacked imaginary frequencies and that each transition state contained exactly one imaginary frequency. Internal reaction coordinate (IRC) calculations were performed to confirm that all calculated transition states can reach the reactants and products. Bulk solvent effects were incorporated for geometry optimizations using the SMD model[7] with benzene as the solvent.

Single point energies of all reported structures were calculated using the dispersion-corrected M06-D3 functional with a mixed basis set of SDD (for Pd and I) and 6-311+G(d,p) (for other atoms).[6] Bulk solvent effects were incorporated for all single point calculations using the SMD model[7] with benzene as the solvent. The reported Gibbs free energies were corrected using the quasi-harmonic model[8] with a cut-off frequency of 100 cm^{-1} at T = 353.15 K.

Optimized Structures of Key Intermediates 10/10' and 5/5'

Figure S4. Optimized structures of hydrogen-bonding-stabilized palladacycles **4**/**4'** and unstabilized intermediates **10**/**10'**. Color code: Pd (cyan), O (red), N (blue), C (grey), H (white).

Energy Data for All Reported Structures

Structure	E (Hartree)	ZPE (Hartree)	H (Hartree)	qh-G (Hartree)	Imaginary frequency (cm^{-1})
HOAc	-229.037175	0.062077	-228.969658	-229.009406	-
OAc^-	-228.522617	0.048532	-228.4687531	-228.507934	-
$PhI(OAc)_2$	-699.698051	0.193468	-699.486604	-699.560274	-
PhI	-242.908794	0.090401	-242.811572	-242.857425	-
4	-1827.474566	0.569452	-1826.865578	-1826.987000	-
4'	-1906.060332	0.627027	-1905.391006	-1905.518919	-
9	-913.708093	0.283486	-913.4049648	-913.481441	-
9'	-953.000964	0.312426	-952.6675623	-952.747042	-
TS(9-10)	-913.667035	0.277314	-913.3706246	-913.445655	-1329.51
TS(9'-10')	-952.968233	0.306895	-952.6412872	-952.718487	-1361.47
10	-913.682589	0.282044	-913.3808394	-913.457429	-
10'	-952.992337	0.311677	-952.6600811	-952.738509	-
5	-913.704023	0.281608	-913.4028054	-913.479418	-
5'	-953.014911	0.311596	-952.6829869	-952.761072	-

11	-1370.5279	0.386912	-1370.110988	-1370.212001	-
11'	-1409.84037	0.416871	-1409.392919	-1409.494656	-
12	-1141.461655	0.322508	-1141.114710	-1141.202249	-
12'	-1180.770744	0.352525	-1180.392990	-1180.482400	-
TS(12-8)	-1141.441293	0.321389	-1141.095714	-1141.182765	-272.76
TS(12'-8')	-1180.745252	0.351072	-1180.369147	-1180.457940	-370.89
8	-1141.538386	0.326682	-1141.187712	-1141.274862	-
8'	-1180.835408	0.356493	-1180.454112	-1180.542680	-

Table S4. Electronic energies (E), zero-point energy corrections (ZPE), enthalpies (H), quasi-harmonic Gibbs free energies calculated at T = 353.15 K (qh-G), and imaginary frequencies of all reported structures.

Cartesian Coordinates (Å) of Optimized Structures

HOAc

C	-1.39502800	-0.10885100	-0.00000100
C	0.09233200	0.12473200	-0.00000100
O	0.64624600	1.20283100	0.00000000
O	0.77529200	-1.04630400	0.00000000
H	-1.91746000	0.84846200	-0.00006400
H	-1.68144900	-0.69054500	0.88296600
H	-1.68143500	-0.69066500	-0.88289200
H	1.72421800	-0.81475100	0.00000600

OAc^- anion

C	-1.35069900	-0.05833900	0.00002500
H	-1.73089000	-1.08734000	0.00332400
H	-1.74766300	0.46970600	0.87892300
H	-1.74750100	0.46386900	-0.88244300
C	0.21434800	0.00144700	0.00002600
O	0.69229400	1.16579100	0.00000000
O	0.81322600	-1.10390100	-0.00001400

$PhI(OAc)_2$

C	-0.00000300	-1.52583300	0.00000100
C	0.92202800	-2.19237600	0.80043200
C	0.91560100	-3.58972100	0.79078600
C	-0.00000900	-4.28653200	-0.00000100
C	-0.91561600	-3.58971600	-0.79078800
C	-0.92203600	-2.19237000	-0.80043100
H	1.63910100	-1.64599900	1.40049800
H	1.62901500	-4.12780300	1.40851400
H	-0.00001200	-5.37286900	-0.00000200

H	-1.62903200	-4.12779300	-1.40851700
H	-1.63910700	-1.64599000	-1.40049700
I	0.00000200	0.62914000	0.00000300
O	2.18607900	0.30531400	-0.11538000
C	2.78601900	1.47755400	-0.12803000
C	4.29703900	1.37183800	-0.18652700
O	2.18185500	2.54696200	-0.09498900
O	-2.18607800	0.30532200	0.11538400
C	-2.78601200	1.47756400	0.12803300
C	-4.29703400	1.37185500	0.18650200
O	-2.18184400	2.54697000	0.09499800
H	4.66394700	0.82684000	0.68986000
H	4.73828800	2.36978600	-0.21389100
H	4.59596500	0.80631700	-1.07526100
H	-4.59598100	0.80618800	1.07513600
H	-4.66393400	0.82700800	-0.68998300
H	-4.73827400	2.36980300	0.21401800

PhI

C	3.36375300	-0.00000100	0.00000000
C	2.66362200	1.20788200	0.00000000
C	1.26583600	1.21688800	0.00000000
C	0.58423500	0.00000100	0.00000000
C	1.26583400	-1.21688700	0.00000000
C	2.66362000	-1.20788300	0.00000000
H	4.45018300	-0.00000200	0.00000000
H	3.20112200	2.15241000	0.00000000
H	0.72410900	2.15655400	0.00000000
H	0.72410400	-2.15655100	0.00000000
H	3.20111900	-2.15241200	0.00000000
I	-1.56871800	0.00000000	0.00000000

4

C	-0.08475300	3.56121100	1.69925000
C	-0.41175000	2.18313900	1.72608500
C	0.43285800	1.27436500	2.43479000
C	1.54787300	1.81770800	3.13171900
C	1.84661800	3.16647400	3.07010300
C	1.03704400	4.05708000	2.33574200
H	-0.74252900	4.23420000	1.15468400
H	2.16548300	1.12703800	3.69698900
H	2.71878900	3.54210800	3.60023000
H	1.27536200	5.11544900	2.29478300
C	-3.61422500	0.43292300	0.61066700
C	-4.44635000	1.69451000	0.91707500
H	-4.20243100	2.53654000	0.26029900
H	-5.50155200	1.45796300	0.74744300
H	-4.33712900	2.01239300	1.96039200

C	-3.72366000	0.12442400	-0.88973600
H	-3.12113600	-0.74016900	-1.16166500
H	-4.76926400	-0.08274200	-1.14665400
H	-3.38639100	0.98205000	-1.47786300
C	-4.17065700	-0.71802300	1.46935500
H	-4.02390400	-0.50709900	2.53492700
H	-5.24604500	-0.82129600	1.28507700
H	-3.69468700	-1.66862800	1.22792100
N	-2.15722500	0.60173700	0.97566100
O	0.23068100	-0.01226900	2.51695000
C	-1.67687100	1.79128600	1.15930100
H	-2.31484500	2.63425400	0.90469600
Pd	-0.90008200	-1.01736000	1.20936800
O	-0.33705200	-2.65020700	-1.60060000
O	-1.95147500	-2.30618600	-0.03783600
C	-1.44785200	-2.89145300	-1.04841700
C	-2.30245000	-3.96715100	-1.68528700
H	-2.90426500	-3.50378500	-2.47700100
H	-1.67280600	-4.73409400	-2.14249700
H	-2.97722200	-4.41158100	-0.95043200
C	0.08483900	3.56127100	-1.69930200
C	0.41176200	2.18317900	-1.72609300
C	-0.43292000	1.27442400	-2.43473400
C	-1.54793700	1.81780500	-3.13164000
C	-1.84660600	3.16658800	-3.07006600
C	-1.03695400	4.05717800	-2.33577000
H	0.74268100	4.23424800	-1.15479800
H	-2.16559800	1.12714500	-3.69686700
H	-2.71878000	3.54224900	-3.60016900
H	-1.27520400	5.11556500	-2.29485700
C	3.61418900	0.43293000	-0.61061500
C	4.44630000	1.69453200	-0.91698200
H	4.20240800	2.53652000	-0.26014200
H	5.50150800	1.45796700	-0.74740800
H	4.33703500	2.01248500	-1.96027400
C	3.72364300	0.12439200	0.88977900
H	3.12112100	-0.74020400	1.16169500
H	4.76924600	-0.08278800	1.14668200
H	3.38638300	0.98200100	1.47793900
C	4.17064000	-0.71798000	-1.46934500
H	4.02386100	-0.50702500	-2.53490800
H	5.24603400	-0.82123300	-1.28509200
H	3.69469400	-1.66859900	-1.22792800
N	2.15718700	0.60173500	-0.97559800
O	-0.23077800	-0.01220600	-2.51691200
C	1.67686800	1.79129100	-1.15929800
H	2.31487200	2.63424800	-0.90472300
Pd	0.90002700	-1.01738200	-1.20942900
O	1.95145600	-2.30620400	0.03770500
O	0.33700800	-2.65026300	1.60042300
C	1.44792600	-2.89132900	1.04842900
C	2.30284700	-3.96662100	1.68555200
H	1.67347500	-4.73282500	2.14436300
H	2.97655900	-4.41215200	0.95037500
H	2.90585800	-3.50258000	2.47594800

4’

C	-0.48718000	-3.57336500	-1.63456500
C	-0.82057300	-2.19792000	-1.57658300
C	-0.18856900	-1.28344600	-2.47374700
C	0.71818200	-1.81876100	-3.43036800
C	1.03347600	-3.16518900	-3.44728100
C	0.44253600	-4.06114400	-2.53317800
H	-0.98194000	-4.25083600	-0.94280300
H	1.16758500	-1.12396400	-4.13277100
H	1.74657200	-3.53471100	-4.18057400
H	0.69192100	-5.11753300	-2.55441600
C	-3.65540700	-0.47598600	0.30935900
C	-4.50559700	-1.76273900	0.26274700
H	-4.08582200	-2.56179900	0.88369700
H	-5.49626500	-1.53238100	0.66798000
H	-4.64049800	-2.14483400	-0.75390500
C	-3.38133200	-0.14057100	1.78376900
H	-2.76928400	0.75382100	1.88079700
H	-4.33116300	0.02623000	2.30548100
H	-2.86267600	-0.97113800	2.26928400
C	-4.43965700	0.67451800	-0.37477800
H	-5.37963600	0.78865600	0.18114800
H	-3.88711000	1.60608100	-0.23657400
N	-2.33461500	-0.63072300	-0.40754000
O	-0.41559000	0.00151500	-2.50026300
C	-1.90809900	-1.81559200	-0.71231100
H	-2.45948600	-2.66387700	-0.31437500
Pd	-1.17799700	0.99742300	-0.94212800
O	-1.88007200	2.28256700	0.53268300
O	0.08090100	2.63404700	1.62711000
C	-1.13482400	2.87225300	1.37802700
C	-1.80187400	3.94932400	2.20728100
H	-1.06769600	4.68412700	2.54506900
H	-2.59876800	4.43468700	1.63913500
H	-2.24660200	3.47586000	3.09148300
C	-4.74777600	0.47079900	-1.86161600
H	-5.40737200	-0.38689800	-2.03628100
H	-5.24968100	1.35786900	-2.26525400
H	-3.83184000	0.31779000	-2.44328600
C	0.48748700	-3.57355300	1.63430900
C	0.82073200	-2.19806800	1.57641600
C	0.18861600	-1.28371200	2.47362400
C	-0.71807000	-1.81919700	3.43021800
C	-1.03322100	-3.16565700	3.44704100
C	-0.44218700	-4.06149100	2.53287900
H	0.98233500	-4.25092500	0.94251200
H	-1.16753500	-1.12449600	4.13267600
H	-1.74627400	-3.53530500	4.18031400
H	-0.69146200	-5.11790600	2.55404700
C	3.65544200	-0.47574500	-0.30934800
C	4.50573300	-1.76243800	-0.26286500

H	4.08601400	-2.56147100	-0.88388900
H	5.49637900	-1.53196300	-0.66808500
H	4.64068000	-2.14462300	0.75374700
C	3.38135500	-0.14021900	-1.78373100
H	2.76932500	0.75419400	-1.88068300
H	4.33118300	0.02660700	-2.30543900
H	2.86268000	-0.97074200	-2.26930300
C	4.43960200	0.67474900	0.37490800
H	5.37959900	0.78898500	-0.18097000
H	3.88701000	1.60629100	0.23675800
N	2.33465200	-0.63064400	0.40751700
O	0.41548300	0.00126900	2.50022000
C	1.90825000	-1.81557300	0.71220400
H	2.45974600	-2.66378300	0.31425800
Pd	1.17785200	0.99739700	0.94219300
O	-0.08102300	2.63417500	-1.62685200
O	1.87996300	2.28269800	-0.53242700
C	1.13472600	2.87232500	-1.37784300
C	1.80185100	3.94921000	-2.20727100
H	2.24595800	3.47562400	-3.09172500
H	1.06781900	4.68433200	-2.54468500
H	2.59920600	4.43419300	-1.63945700
C	4.74766300	0.47092800	1.86174500
H	5.40729000	-0.38675200	2.03637700
H	5.24950800	1.35799000	2.26547700
H	3.83170500	0.31783300	2.44335700

9

C	3.83750400	0.65386500	0.00633400
C	2.47240600	0.26279200	0.00310600
C	2.14668200	-1.12831100	-0.00008200
C	3.21682500	-2.06414600	0.00031700
C	4.53300000	-1.64445400	0.00350300
C	4.85991700	-0.27234900	0.00654700
H	4.06963700	1.71705300	0.00867800
H	2.95758300	-3.11817900	-0.00211500
H	5.32708700	-2.38735700	0.00360800
H	5.89707700	0.04776400	0.00899100
C	-0.64675100	2.48800100	0.00049800
C	0.18894000	3.78133200	0.00478700
H	0.82002100	3.87442800	-0.88622000
H	-0.50100800	4.63071000	0.00460900
H	0.81572700	3.87123100	0.89915600
C	-1.51017900	2.47309100	-1.27503000
H	-2.17739700	1.61018600	-1.30454700
H	-2.12611900	3.37881700	-1.31092100
H	-0.87198000	2.45544800	-2.16595300
C	-1.51693900	2.46916100	1.27135000
H	-0.88353300	2.44864300	2.16563300
H	-2.13298000	3.37482900	1.30681400
H	-2.18445900	1.60629500	1.29442000
N	0.19797700	1.23805400	0.00070100

O	0.93203900	-1.60556300	-0.00346500
C	1.49340000	1.31367500	0.00309400
H	1.93351600	2.30732300	0.00537600
Pd	-0.75353000	-0.56923700	-0.00479000
O	-2.09402600	-2.22446100	-0.01262100
O	-2.84565000	-0.16857000	-0.00870100
C	-3.08689500	-1.42796000	-0.00888000
C	-4.49749100	-1.93179100	0.02485800
H	-5.13421500	-1.30755600	-0.60861300
H	-4.53848400	-2.97386100	-0.30015300
H	-4.87535200	-1.86594300	1.05255700

9'

C	-3.85427400	0.64387000	0.10970400
C	-2.50009900	0.21720200	0.09874000
C	-2.21016800	-1.17498600	-0.03708200
C	-3.30330100	-2.07627800	-0.15341000
C	-4.60809600	-1.62253500	-0.13788100
C	-4.89974700	-0.24893800	-0.00567400
H	-4.05921100	1.70761800	0.21239100
H	-3.07087100	-3.13162600	-0.25557200
H	-5.42058000	-2.33938700	-0.22979700
H	-5.92810400	0.09828500	0.00490500
C	0.67155000	2.34591100	0.37489900
C	-0.13479200	3.65078600	0.51923300
H	-0.74799700	3.65513100	1.42734000
H	0.57526600	4.47944700	0.60185800
H	-0.77934900	3.85885900	-0.34001700
C	1.52181200	2.17684000	1.64898500
H	2.16616900	1.29772700	1.59596000
H	2.16064500	3.05699100	1.78391500
H	0.87406400	2.08451700	2.52830600
C	1.58317000	2.43261500	-0.87932400
H	2.18986000	3.34093600	-0.76967400
H	2.28136900	1.59239500	-0.86769000
N	-0.20210400	1.12514300	0.24316200
O	-1.00820300	-1.68284100	-0.06322700
C	-1.49483800	1.23541200	0.22436100
H	-1.90893800	2.23629900	0.31334500
Pd	0.70295900	-0.69920600	0.07223300
O	1.99023400	-2.38777900	-0.07937000
O	2.80900800	-0.37047800	0.14734800
C	3.00882100	-1.62957400	0.01351800
C	4.40209300	-2.17518800	-0.06295900
H	5.05914100	-1.62550600	0.61682400
H	4.40822500	-3.24106500	0.17643800
H	4.78157900	-2.04087800	-1.08345700
C	0.84669700	2.45860200	-2.22163600
H	0.17889300	3.32236000	-2.31851300
H	1.56847200	2.51030200	-3.04489700
H	0.24867100	1.55142900	-2.36336100

TS(9-10)

C	3.98111000	0.43706700	0.10564500
C	2.58183100	0.20028100	0.04073100
C	2.09485500	-1.15889700	-0.00869600
C	3.07427000	-2.19422800	0.01338000
C	4.42552700	-1.92013000	0.07511400
C	4.89849300	-0.59131700	0.12207300
H	4.32351200	1.46923000	0.14253800
H	2.70773500	-3.21551900	-0.02227200
H	5.13452900	-2.74470100	0.08809600
H	5.96304400	-0.38462700	0.17102600
C	-0.55011000	2.41862000	0.00508800
C	-0.63487200	2.96142600	1.43902100
H	0.32528300	3.38866600	1.74970600
H	-1.39644900	3.74669600	1.49861300
H	-0.90196300	2.16255000	2.13896400
C	-0.20662100	3.52964500	-0.99115900
H	-0.06939300	3.11841300	-1.99699500
H	-1.02366100	4.25880600	-1.02337300
H	0.70826700	4.06137400	-0.70413200
C	-1.86327700	1.66983400	-0.39048300
H	-2.71400800	2.19430600	0.06388100
H	-2.01572900	1.67736100	-1.47456900
N	0.43725100	1.32026600	-0.03372700
O	0.84614600	-1.53929300	-0.06983200
C	1.72610600	1.35278800	0.03897900
H	2.20637100	2.33182000	0.10812600
Pd	-0.70092300	-0.24810200	-0.13037300
C	-3.28087200	-1.44636600	0.09308400
C	-4.35587500	-2.50350600	0.16035000
H	-4.71822400	-2.57689200	1.19206200
H	-5.20350300	-2.20511300	-0.46470100
H	-3.97290000	-3.47342500	-0.16102700
O	-3.61899600	-0.24051000	0.32892900
H	-2.56024500	0.54191100	0.10545900
O	-2.09644000	-1.80911300	-0.18371500

TS(9'-10')

C	-3.96376300	0.01748800	-0.35294600
C	-2.56212500	-0.07892600	-0.13790400
C	-1.97755500	-1.36404400	0.12405800
C	-2.85282200	-2.48915100	0.14900000
C	-4.20893100	-2.35368200	-0.06732600
C	-4.78430800	-1.08966800	-0.32310400
H	-4.38838400	1.00072500	-0.54614300
H	-2.40533600	-3.45805700	0.34811100
H	-4.84277600	-3.23708400	-0.03951000
H	-5.85229000	-0.99332900	-0.49213100
C	0.04758800	2.70073300	-0.04485500

C	-0.65508600	3.64436200	-1.03628600
H	-1.66525000	3.92267400	-0.71855100
H	-0.07896000	4.57223400	-1.11598100
H	-0.71312200	3.19119100	-2.03204100
C	-0.09665300	3.23727000	1.39150000
H	0.37648800	2.57036100	2.11859700
H	0.36302400	4.22847600	1.47661700
H	-1.15553700	3.32489700	1.65968900
C	1.52607200	2.56784000	-0.44912900
H	1.57900900	2.38937100	-1.53064500
H	2.01430900	3.53457500	-0.26479100
N	-0.53038500	1.31548500	-0.06637800
O	-0.71589500	-1.58087400	0.35018900
C	-1.81190900	1.14137000	-0.18334300
H	-2.41695700	2.03544100	-0.33635700
Pd	0.75885800	-0.21025900	0.22386800
O	2.07083500	-1.83191800	0.44063400
O	3.45735400	-0.66692100	-0.87307100
C	3.12801000	-1.72951400	-0.25214100
C	4.03673900	-2.92873700	-0.35986500
H	5.07245800	-2.62598100	-0.17914900
H	3.73978100	-3.70949300	0.34208100
H	3.98004900	-3.32092200	-1.38199100
C	2.26645300	1.44677900	0.28064900
H	2.63427700	0.27164400	-0.40321100
H	3.34690400	1.57541800	0.11913200
H	2.16894200	1.49637400	1.37111700

10

C	-3.82683700	-0.44545300	0.10104400
C	-2.41814900	-0.28360600	0.01312600
C	-1.57555000	-1.45907700	-0.13549500
C	-2.25363600	-2.71826400	-0.17521900
C	-3.62575500	-2.82745200	-0.08418300
C	-4.43729500	-1.68138400	0.05559100
H	-4.43632400	0.45030800	0.20926000
H	-1.62844100	-3.59985600	-0.28792200
H	-4.08668300	-3.81237200	-0.12239600
H	-5.51709600	-1.77115800	0.12555200
C	-0.08279800	2.79316100	0.11162200
C	-0.54434800	3.65689200	-1.06509500
H	-1.61908200	3.86893800	-1.01030800
H	-0.00608400	4.61145100	-1.05757200
H	-0.33945900	3.15057600	-2.01480200
C	-0.39607900	3.45484900	1.45603500
H	-0.08825400	2.80555100	2.28320200
H	0.14808200	4.40261100	1.53787400
H	-1.46739000	3.66512400	1.56134300
C	1.39825600	2.33050700	-0.01206500
H	1.89894100	2.68233000	-0.91895600
H	2.00275100	2.54130900	0.87536000
N	-0.69824200	1.44351700	0.04003000

O	-0.28219100	-1.46681800	-0.23717000
C	-1.93396200	1.06999400	0.08636500
H	-2.68900000	1.85446800	0.19577600
Pd	0.88484600	0.34206300	-0.15154700
C	3.19305500	-1.69237900	0.07140600
C	2.38381600	-2.52753700	1.02509900
H	2.79630500	-3.52961300	1.17426800
H	2.35048900	-2.00642100	1.98955500
H	1.35646500	-2.58719200	0.65145400
O	4.41145100	-2.11547100	-0.28305600
H	4.61116600	-2.96857600	0.14002200
O	2.82249900	-0.62002200	-0.39604300

10’

C	-3.70030900	-1.00462400	-0.16474900
C	-2.32466900	-0.67576800	-0.02262700
C	-1.36588900	-1.73583600	0.19763900
C	-1.88522600	-3.06760200	0.25213300
C	-3.22936200	-3.34133900	0.10706100
C	-4.16201800	-2.30311000	-0.10533200
H	-4.40687600	-0.19257900	-0.32848100
H	-1.16566900	-3.86377400	0.42320900
H	-3.57405300	-4.37209000	0.15961100
H	-5.21943000	-2.52233400	-0.21822700
C	-0.72481100	2.81254600	-0.10137400
C	-1.80466400	3.48460100	-0.96330900
H	-2.79919900	3.45323400	-0.50505700
H	-1.54779900	4.54095700	-1.09647000
H	-1.86120000	3.02074400	-1.95467000
C	-0.81646300	3.31647200	1.35009000
H	-0.06684300	2.83447100	1.98460300
H	-0.65971900	4.40092100	1.38583000
H	-1.80492600	3.09700800	1.76990600
C	0.66983300	3.07191900	-0.70088900
H	0.61800300	2.86711400	-1.77852100
H	0.91565500	4.13929500	-0.59079000
N	-0.84735300	1.31208700	-0.06508200
O	-0.09314100	-1.56397700	0.35219700
C	-2.00458200	0.72490400	-0.10958200
H	-2.87466200	1.37146700	-0.23371000
Pd	0.88367300	0.32796300	0.15276500
C	3.22504100	-1.62290200	-0.11651300
C	2.48625500	-2.35837500	-1.19947500
H	2.99017800	-3.27213100	-1.52693500
H	1.48324500	-2.58337900	-0.82185100
H	2.36507500	-1.68249000	-2.05321900
C	1.72706300	2.16873700	-0.06177600
H	2.63277900	2.09427300	-0.67598900
H	2.01878600	2.50640100	0.94153900
O	4.40731900	-2.09106300	0.29651600
H	4.64181600	-2.89978400	-0.19085500
O	2.81783900	-0.59820300	0.42262200

5

C	-3.73595900	-0.69520400	-0.00013900
C	-2.34262800	-0.42767300	0.00002300
C	-1.42073600	-1.54239200	0.00014400
C	-1.98111900	-2.84821100	0.00012700
C	-3.34723900	-3.06189000	-0.00004200
C	-4.24615500	-1.97888000	-0.00018900
H	-4.41970000	0.15171800	-0.00024200
H	-1.28592600	-3.68309200	0.00025500
H	-3.72743900	-4.08082300	-0.00006800
H	-5.31846100	-2.14846400	-0.00032900
C	-0.26553300	2.84471000	-0.00008400
C	-0.71635400	3.57516400	-1.26726800
H	-1.80506100	3.70515500	-1.29018500
H	-0.25247200	4.56715800	-1.30564100
H	-0.41471600	3.01650000	-2.16009800
C	-0.71628500	3.57540300	1.26699400
H	-0.41460200	3.01690300	2.15991000
H	-0.25240800	4.56740800	1.30516800
H	-1.80499400	3.70539000	1.28994400
C	1.25190400	2.49421600	-0.00009900
H	1.78131100	2.81460100	-0.90202000
H	1.78130100	2.81465100	0.90181300
N	-0.77057100	1.44512700	0.00005800
O	-0.11573200	-1.42750800	0.00042100
C	-1.96970700	0.97073800	0.00000800
H	-2.79337600	1.69070900	-0.00006900
Pd	0.90065400	0.46630900	0.00012400
C	3.06456900	-1.69401000	-0.00018700
C	4.46826700	-2.23159200	-0.00019700
H	4.61763200	-2.86209800	0.88309700
H	4.61742000	-2.86315800	-0.88272900
H	5.18869000	-1.41295700	-0.00066500
O	2.14291300	-2.62639800	-0.00027500
H	1.19177800	-2.25640400	-0.00006700
O	2.84991500	-0.47004400	0.00001400

5'

C	-3.49733900	-1.51769600	-0.10481400
C	-2.18295100	-0.99128300	-0.01431900
C	-1.07861200	-1.90660400	0.08340100
C	-1.36911600	-3.29648000	0.06693500
C	-2.66599600	-3.76749700	-0.02968700
C	-3.75182300	-2.87584800	-0.11494400
H	-4.32711400	-0.81663900	-0.17074300
H	-0.52919100	-3.98186300	0.13959700
H	-2.84518000	-4.84017200	-0.03697300

H	-4.76924800	-3.24751300	-0.18764800
C	-1.13856900	2.71143900	0.02131000
C	-2.38548900	3.24959000	-0.69560100
H	-3.31365800	3.04113100	-0.15238900
H	-2.30389700	4.33829700	-0.78147200
H	-2.46915000	2.83472000	-1.70650200
C	-1.15856300	3.12640000	1.50338800
H	-0.28834000	2.73372000	2.03747800
H	-1.15773400	4.21913900	1.58950600
H	-2.05893700	2.74222100	1.99639600
C	0.13867600	3.20481900	-0.68603800
H	0.01514400	3.03696600	-1.76389300
H	0.23169900	4.29175400	-0.54048100
N	-1.03287700	1.20917100	-0.01891100
O	0.16414700	-1.51781300	0.20048600
C	-2.08453600	0.45238700	-0.02853200
H	-3.05175200	0.95628400	-0.05909000
Pd	0.84799500	0.50602700	0.00151300
C	3.29370300	-1.32490800	-0.01896300
C	4.76544900	-1.62690900	-0.07090500
H	4.98067100	-2.24597500	-0.94861700
H	5.34291000	-0.70284200	-0.11493700
H	5.05010000	-2.20466900	0.81527600
C	1.37895500	2.45493300	-0.19323200
H	2.21875200	2.53301200	-0.89316000
H	1.71456800	2.79611600	0.79480000
O	2.53199500	-2.38679700	0.02560000
H	1.53104600	-2.15222600	0.08176600
O	2.88747500	-0.14875800	-0.01910300

11

C	-3.99138600	-0.82647500	-0.43534300
C	-2.61008500	-0.51038900	-0.29967600
C	-1.63433300	-1.58194400	-0.34509400
C	-2.13770700	-2.90386600	-0.51788900
C	-3.48698000	-3.16205000	-0.64268000
C	-4.43719200	-2.11833400	-0.60373100
H	-4.70904300	-0.00907800	-0.40090300
H	-1.40624200	-3.70560100	-0.54908300
H	-3.82146700	-4.18854900	-0.77328000
H	-5.49679700	-2.33111600	-0.70354300
C	-0.71697900	2.83078100	0.26434100
C	-1.04511100	3.68876300	-0.96003100
H	-2.12894500	3.79666600	-1.08264200
H	-0.61430400	4.68840600	-0.83390400
H	-0.62743700	3.22978400	-1.85994000
C	-1.32198200	3.38462100	1.55662500
H	-1.09536200	2.71582300	2.39121200
H	-0.89898700	4.37379000	1.76480600
H	-2.40924700	3.49012500	1.46675100
C	0.80648500	2.55005700	0.39783100
H	1.42918800	2.91100200	-0.41792300

H	1.23006000	2.68932400	1.39017900
N	-1.15248500	1.42929000	0.04724000
O	-0.35036300	-1.42045100	-0.25028900
C	-2.30749000	0.88017900	-0.12046200
H	-3.15812500	1.56723700	-0.11933200
Pd	0.56079100	0.52133100	0.11986400
C	2.86391300	-1.39593500	0.09591900
C	4.32384200	-1.74026500	0.07272200
H	4.49637900	-2.69968300	0.56697300
H	4.63022100	-1.83394800	-0.97614900
H	4.90991300	-0.95106000	0.54598100
O	2.07251300	-2.40595800	-0.08015700
H	1.10166600	-2.14606600	-0.10471200
O	2.52658300	-0.20151100	0.25762700
C	1.23416800	0.15812900	-2.74156800
C	1.05451200	0.67543400	-4.16602000
H	1.61358800	0.04507200	-4.86104200
H	-0.00888900	0.65748500	-4.43069400
H	1.39687700	1.71266200	-4.24341900
O	1.82070900	-0.88527500	-2.49418600
O	0.67506000	0.97727100	-1.87639400
C	0.53304800	-0.58965200	2.85028500
C	0.11514900	-0.40534100	4.30603300
H	-0.97307200	-0.29057200	4.36543300
H	0.42371400	-1.27440100	4.89113800
H	0.56605100	0.50261900	4.72029700
O	1.05394400	-1.61636600	2.44142400
O	0.24780700	0.48498500	2.14470100

11’

C	3.83348100	0.50094700	1.24629700
C	2.45906700	0.28097100	0.95714700
C	1.53137700	1.37184800	1.09683300
C	2.05672200	2.63663300	1.47609600
C	3.40271400	2.81239600	1.73160900
C	4.31094800	1.73828400	1.62444200
H	4.52240600	-0.33613600	1.15112700
H	1.35420600	3.45958000	1.56526100
H	3.76510400	3.79559300	2.02242000
H	5.36623000	1.88478400	1.83200400
C	0.85077400	-2.93903900	-0.44018800
C	2.18526100	-3.55654500	-0.88281000
H	2.85209600	-3.76405400	-0.03933200
H	1.98074600	-4.51403000	-1.37287300
H	2.70569200	-2.91114300	-1.59884400
C	0.23010000	-3.77471700	0.69227800
H	-0.70633700	-3.33976100	1.04268100
H	0.05019800	-4.79699800	0.34028900
H	0.91798000	-3.82013800	1.54417700
C	-0.08784300	-2.81998000	-1.66087200
H	0.47318900	-2.38137500	-2.49111900
H	-0.40755600	-3.82670700	-1.96532200

N	1.01133800	-1.52455500	0.04815800
O	0.24825400	1.23435400	0.93632400
C	2.11718000	-1.04618400	0.52244200
H	2.94365500	-1.75508000	0.57744200
Pd	-0.58591600	-0.35669800	-0.30709900
C	-2.52181300	1.91384100	-0.46234300
C	-3.85924900	2.49734600	-0.80930100
H	-3.78005100	3.57753700	-0.95287700
H	-4.26740300	2.01678100	-1.70009000
H	-4.53113000	2.30678400	0.03615000
C	-1.30402900	-1.96134800	-1.37619900
H	-1.76749000	-1.52559500	-2.26113100
H	-2.03878700	-2.39398700	-0.69739000
O	-1.75976500	2.67430800	0.24753600
H	-0.88398500	2.22026700	0.50439800
O	-2.25722600	0.75438100	-0.86551600
C	0.57417000	1.36592100	-2.39486300
C	1.44151700	1.45312100	-3.64670400
H	2.46109700	1.13107600	-3.40546700
H	1.06006000	0.78770900	-4.42789300
H	1.46261100	2.48312000	-4.00930500
O	0.12552500	2.35702300	-1.83759300
O	0.41341400	0.11264800	-2.02588800
C	-2.28364300	-0.53865000	2.13254000
C	-2.62297600	-1.37408000	3.36438400
H	-3.38219800	-0.86256700	3.96020200
H	-2.98564900	-2.36396000	3.06781300
H	-1.72008200	-1.52034600	3.96790300
O	-2.75021800	0.57753400	1.95627900
O	-1.45178300	-1.18974500	1.34817200

12

C	3.89840300	-0.77414200	-0.57133000
C	2.54612400	-0.35829700	-0.38417500
C	2.26106600	0.79382200	0.46350000
C	3.39907500	1.43601800	1.05446700
C	4.68530200	0.99516900	0.84540300
C	4.95408600	-0.12589500	0.02246000
H	4.08469100	-1.63693200	-1.20807500
H	3.19273600	2.29416800	1.68684800
H	5.51108200	1.51800100	1.32291900
H	5.97371800	-0.46288600	-0.13536100
C	-0.84100600	-1.73538600	-1.66264600
C	-0.79490400	-1.65455200	-3.19072500
H	0.08999800	-2.16902700	-3.58276900
H	-1.68471700	-2.13549200	-3.61170900
H	-0.76856200	-0.61175400	-3.52263100
C	-0.83292600	-3.17988800	-1.15579900
H	-0.81860600	-3.19603500	-0.06264900
H	-1.73129500	-3.69865800	-1.50799100
H	0.04372700	-3.72201100	-1.52805500
C	-2.00427100	-0.90438300	-1.05743800

H	-2.53367200	-0.25795100	-1.75665800
H	-2.65284300	-1.41157100	-0.34896200
N	0.27553500	-0.96357900	-1.06664600
O	1.09813000	1.28524800	0.71464900
C	1.56163100	-1.12466700	-1.07111400
H	1.92237100	-1.94946600	-1.69160600
Pd	-0.71671800	0.31804300	0.00773000
C	-1.61513700	-1.30198900	2.22267200
O	-2.75618100	-0.92467900	2.00216200
O	-0.54994200	-1.04894000	1.48068700
C	-1.72597800	2.53999000	-0.46835900
O	-1.94378400	1.96794900	0.64438900
O	-1.04242400	1.89782800	-1.35021500
C	-1.23657600	-2.14581300	3.43304200
H	-0.63241200	-3.00790500	3.13350200
H	-0.63276000	-1.54129300	4.11901300
H	-2.14350400	-2.47916200	3.94213000
C	-2.20545400	3.92845400	-0.75065600
H	-1.40530000	4.63292600	-0.49258100
H	-2.43479100	4.04363100	-1.81338100
H	-3.08256900	4.15659800	-0.14022900

12’

C	3.78449100	0.72737200	0.75242300
C	2.45001900	0.25971000	0.56333300
C	2.23004000	-1.05427900	-0.01289800
C	3.40272600	-1.80909500	-0.34592400
C	4.67105600	-1.31064600	-0.15590900
C	4.87989800	-0.02398500	0.39886500
H	3.92590200	1.71456500	1.18852700
H	3.24026500	-2.79447900	-0.77215300
H	5.52958100	-1.91665600	-0.43727600
H	5.88586300	0.35605100	0.54659500
C	-0.81405800	2.07342200	1.48771600
C	-0.40106800	2.51471000	2.90081000
H	0.52567800	3.09765300	2.90336400
H	-1.18671500	3.15249400	3.31982400
H	-0.27183300	1.64792600	3.55746600
C	-0.80527800	3.26492500	0.51592200
H	-1.13041400	2.97416500	-0.48586400
H	-1.47847200	4.04735300	0.88418900
H	0.20146300	3.69113800	0.44080600
C	-2.19438100	1.39031300	1.54129400
H	-2.21690800	0.69983900	2.39207600
H	-2.96660100	2.15308300	1.71835100
N	0.12039700	1.01186200	0.97148000
O	1.07936500	-1.58391800	-0.21748400
C	1.41713200	1.12517100	1.02573300
H	1.77430600	2.02585200	1.52833300
Pd	-0.76160000	-0.42739600	-0.09850800
C	-2.50531800	0.63927000	0.26207700
H	-3.28820100	-0.11316500	0.36577500

H	-2.63268900	1.23959400	-0.63443900
C	-0.68853600	1.26894900	-2.59277000
O	-1.82782000	1.70982400	-2.50281800
O	-0.05025300	0.50716300	-1.73330300
C	-1.91262300	-2.56277200	0.41402700
O	-1.83562700	-2.13904600	-0.78537700
O	-1.47424000	-1.79458100	1.34436400
C	0.20712300	1.56464100	-3.79228900
H	1.16950500	1.96515800	-3.45847300
H	0.40698900	0.63527100	-4.33629700
H	-0.29102800	2.27901200	-4.45128900
C	-2.45708200	-3.91720200	0.73454100
H	-1.62631700	-4.63357100	0.73615100
H	-2.91636800	-3.91840500	1.72641200
H	-3.17941700	-4.22425000	-0.02584600

TS(12-8)

C	4.28957900	-0.74276800	0.37653600
C	2.92235400	-0.43413900	0.15948200
C	2.50511100	0.94145200	0.07149600
C	3.51091300	1.93604000	0.23203800
C	4.82734600	1.59698400	0.47396400
C	5.23392500	0.24692500	0.55059500
H	4.58266500	-1.78991100	0.41360500
H	3.19719700	2.97257500	0.15980500
H	5.56381400	2.38677700	0.60100100
H	6.27368400	-0.00509100	0.73372100
C	-0.21334300	-2.36006400	-0.70572500
C	0.39273900	-3.12702200	-1.91305600
H	1.11655300	-3.86761800	-1.55533300
H	-0.39474600	-3.67006700	-2.44503300
H	0.88948700	-2.44588900	-2.61032700
C	-0.77595900	-3.34532800	0.32962900
H	-1.19389300	-2.80528100	1.18030400
H	-1.55632100	-3.96624000	-0.12358800
H	0.02721200	-3.99928300	0.68431400
C	-1.26004100	-1.47573700	-1.32339400
H	-0.98258900	-0.66465500	-1.99202200
H	-2.23942800	-1.90108600	-1.48004000
N	0.72273300	-1.42204500	-0.05580200
O	1.29433900	1.35366600	-0.19844800
C	2.01363100	-1.50797300	-0.11318600
H	2.45454900	-2.45551200	-0.42947100
Pd	-0.34662500	0.27334800	0.27274900
C	-3.02182500	-0.57804100	0.94679100
O	-3.29767500	-0.57818800	-0.26325600
O	-1.82853500	-0.56706000	1.43628500
C	-1.85335300	2.31176000	-0.89298300
O	-1.47167200	1.95881600	0.30975400
O	-1.55798100	1.73331300	-1.94022800
C	-4.12780800	-0.57831600	1.98947200
H	-4.25892300	0.45164400	2.34145300

H	-5.06530700	-0.92861900	1.55333600
H	-3.84899800	-1.19375600	2.84887500
C	-2.75141800	3.54062200	-0.87993500
H	-2.29666500	4.34403300	-0.29138800
H	-2.93449400	3.88239700	-1.90122000
H	-3.70708500	3.28514400	-0.40702600

TS(12'-8')

C	4.24950100	0.61373800	-0.49459300
C	2.89152700	0.35847400	-0.18337000
C	2.46522100	-0.98198400	0.09546100
C	3.44615400	-2.00774100	0.03057700
C	4.75854400	-1.72617100	-0.30322200
C	5.17623100	-0.40744600	-0.57568500
H	4.55479400	1.64192000	-0.67936400
H	3.12224400	-3.02014100	0.25091500
H	5.47931000	-2.53893700	-0.35407200
H	6.20957400	-0.19856600	-0.83433400
C	-0.06553300	2.67079300	0.42774700
C	0.78091500	3.72758300	1.16315600
H	1.52083700	4.19745700	0.50765000
H	0.11922500	4.52505100	1.51695900
H	1.29617000	3.30178300	2.03205000
C	-0.65310700	3.30816700	-0.84523700
H	-1.26168500	2.59403400	-1.40015600
H	-1.26813000	4.17604300	-0.58035500
H	0.15988900	3.65015700	-1.49536900
C	-1.21302700	2.21021800	1.39502900
H	-1.04652000	2.66464600	2.39334600
H	-2.17630300	2.60083500	1.05908300
N	0.71734600	1.46605000	0.02498900
O	1.25369100	-1.31017100	0.46699800
C	2.01228300	1.48331000	-0.00608600
H	2.51804300	2.43626900	0.14774400
Pd	-0.32293000	-0.31018500	-0.30821300
C	-1.34832400	0.78218300	1.76014000
H	-0.47326500	0.18594800	1.99437100
H	-2.21569600	0.49620800	2.33383300
C	-3.01990000	0.44778700	-0.77221700
O	-3.16299100	0.30609100	0.46203900
O	-1.89296400	0.49144500	-1.37861600
C	-1.67509000	-2.63483100	0.59278100
O	-1.28681800	-2.07696100	-0.52652600
O	-1.56695600	-2.15622200	1.72102000
C	-4.24552500	0.57683400	-1.65663100
H	-4.40173400	-0.38124700	-2.16587400
H	-5.12992800	0.81536900	-1.06285700
H	-4.08143500	1.33968300	-2.42319400
C	-2.30594400	-4.00316400	0.35991800
H	-2.68525800	-4.40681900	1.30144800
H	-3.12229600	-3.92541800	-0.36637600
H	-1.55972100	-4.68809500	-0.05851700

8

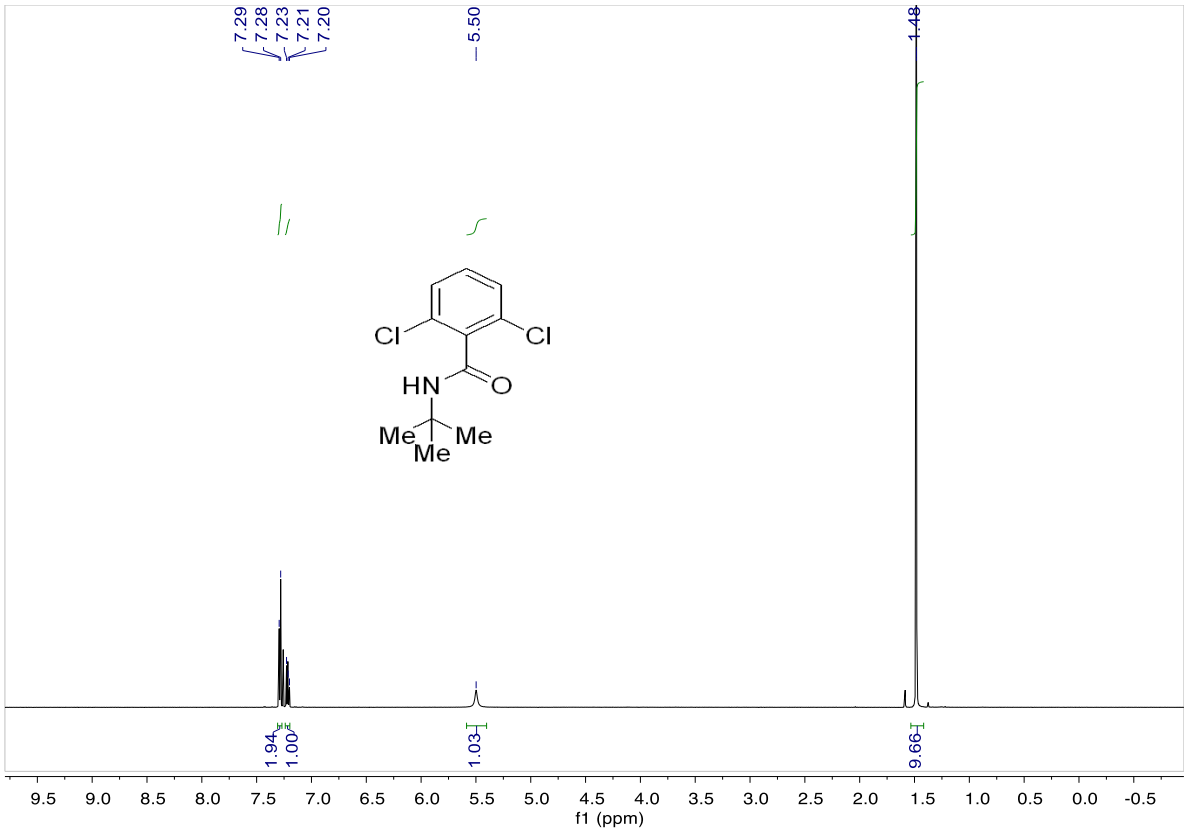
C	-3.87338700	0.37778900	-0.45616900
C	-2.51730800	-0.04536800	-0.41911500
C	-2.21522800	-1.38315200	-0.01163100
C	-3.30154400	-2.23445300	0.33384100
C	-4.60620700	-1.78486100	0.28649200
C	-4.90868800	-0.46468900	-0.11039600
H	-4.08708600	1.39793700	-0.76867500
H	-3.06133100	-3.24781700	0.63963700
H	-5.41150900	-2.46198300	0.56108800
H	-5.93765900	-0.12081900	-0.14430200
C	0.62161800	1.95613500	-1.26974100
C	1.54359500	1.51652300	-2.42048200
H	0.93844700	1.21970400	-3.28385100
H	2.18374700	2.35306900	-2.72242600
H	2.18516500	0.68083500	-2.13935600
C	-0.18629200	3.18222100	-1.73337200
H	-0.79999900	3.60547300	-0.93316900
H	0.52024900	3.95678700	-2.04758900
H	-0.82109100	2.94799600	-2.59453600
C	1.46336800	2.35493300	-0.03805100
H	2.11221000	1.54526100	0.29258500
H	2.07008700	3.23197900	-0.28095400
N	-0.23423200	0.79347800	-0.85980600
O	-1.01428500	-1.88220700	0.06668300
C	-1.52628200	0.91581400	-0.80947200
H	-1.94713900	1.87435700	-1.10082100
Pd	0.69147100	-0.92594300	-0.25737900
C	0.46606100	1.93143000	2.10591400
O	0.57749000	2.74992600	1.02877200
O	1.15971000	0.95710200	2.30216400
C	3.01003900	-1.72258600	0.11967100
O	2.01108600	-2.48083800	0.33770600
O	2.78302100	-0.55285000	-0.35427700
C	-0.65586600	2.39165800	3.00094000
H	-0.53847800	1.95174300	3.99270000
H	-0.69008000	3.48273800	3.06541300
H	-1.60623600	2.04838400	2.57354100
C	4.40731800	-2.15696400	0.43879000
H	5.10976500	-1.73488000	-0.28517000
H	4.67451800	-1.77996300	1.43383400
H	4.47499900	-3.24742500	0.44842700

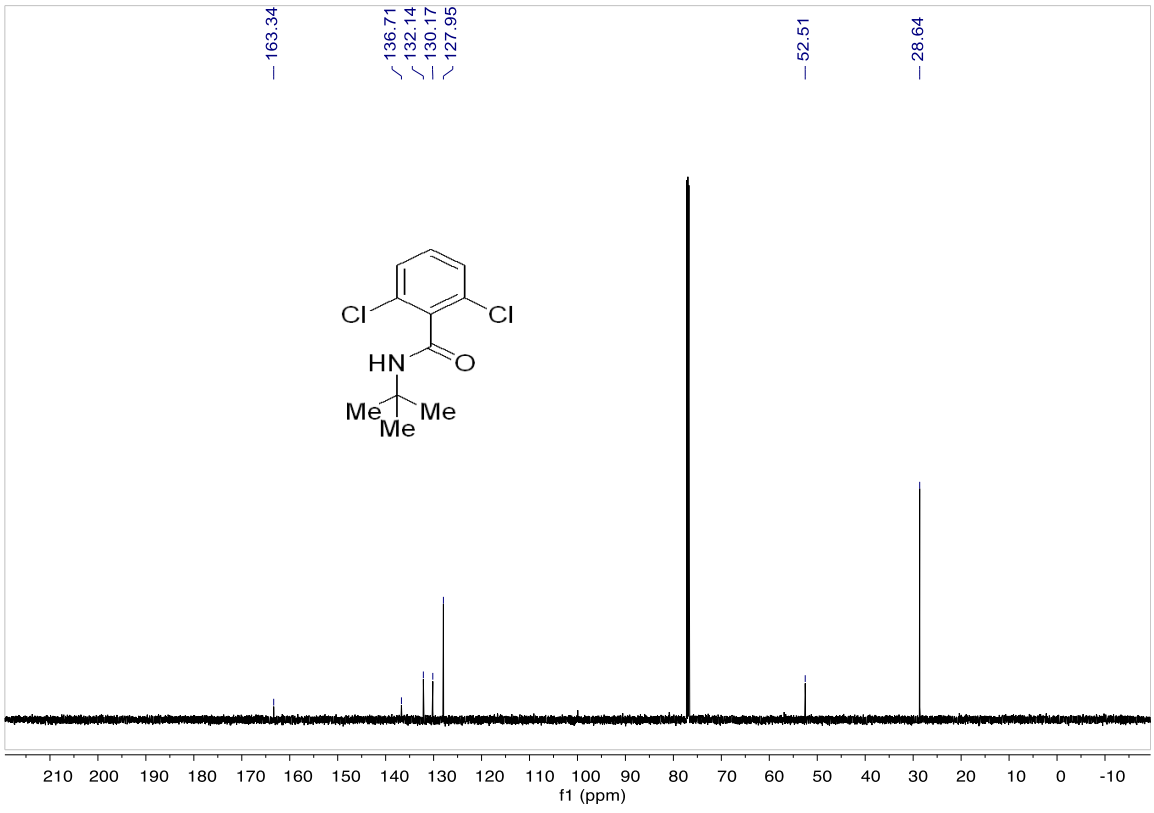
8'

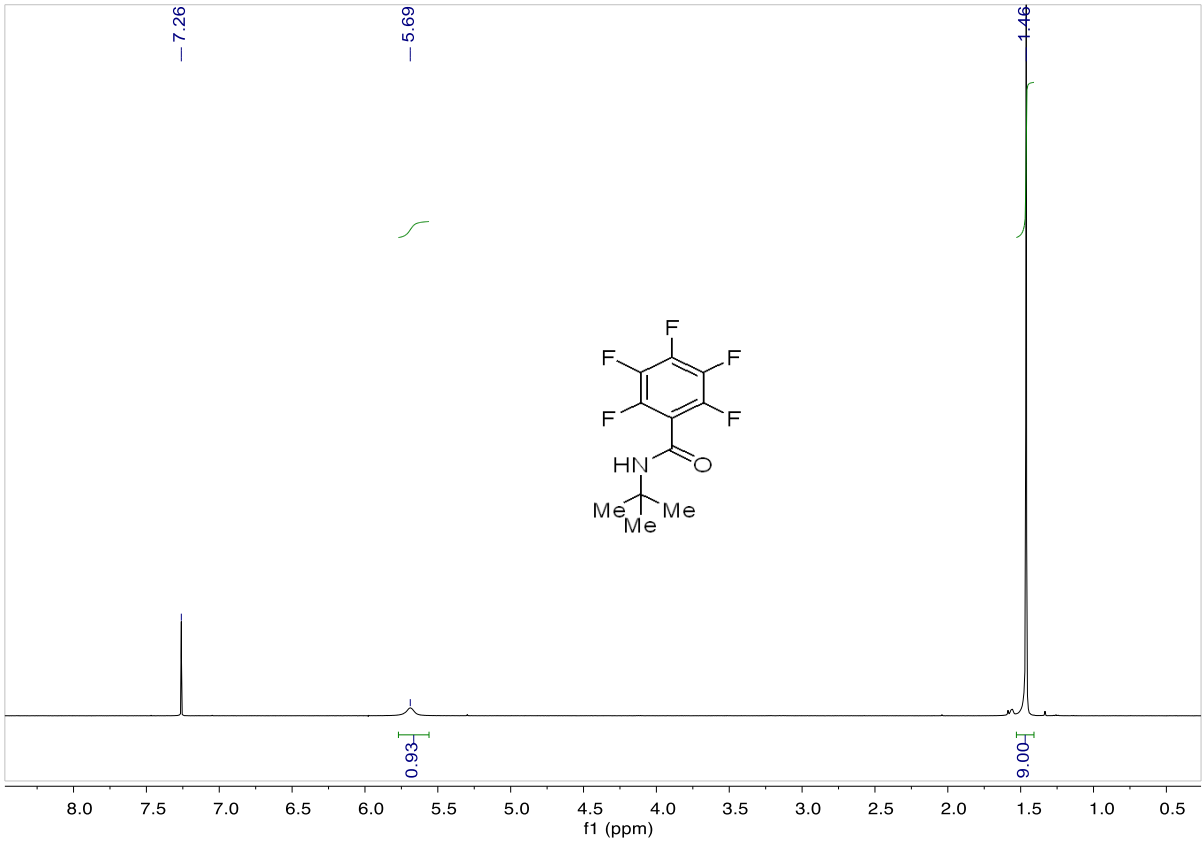
C	3.89585800	0.60713500	0.59636100
C	2.55268300	0.15505700	0.51775500
C	2.29637800	-1.20128700	0.15255600

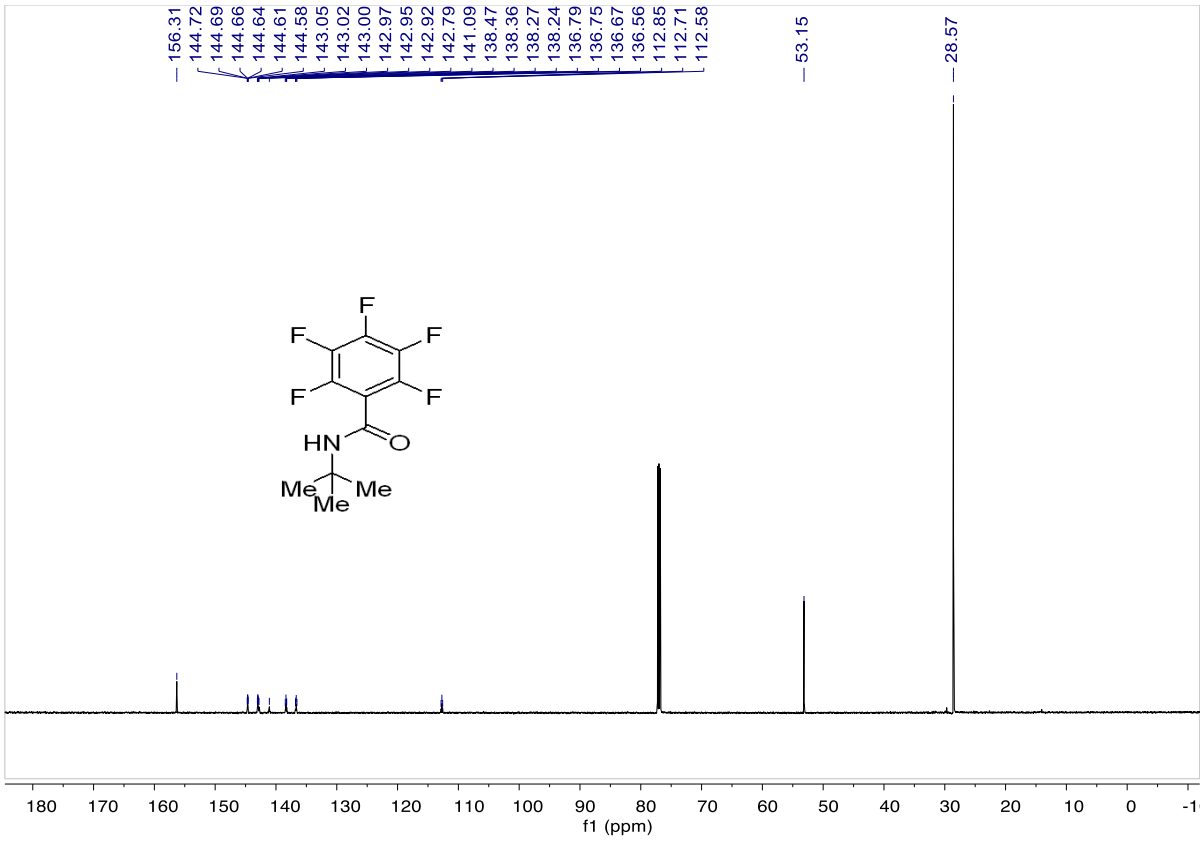
C	3.40900600	-2.04252000	-0.11691000
C	4.70335100	-1.56675600	-0.02635900
C	4.96230300	-0.22855300	0.33408000
H	4.07569700	1.64453700	0.87083000
H	3.20076700	-3.07065000	-0.39589400
H	5.53211100	-2.23804000	-0.23821600
H	5.98194500	0.13743700	0.40196900
C	-0.66952700	2.14341400	1.08170800
C	-1.45413200	1.82365900	2.37075600
H	-0.75779000	1.63436900	3.19544200
H	-2.08437100	2.67802900	2.64199500
H	-2.09798600	0.95121300	2.24994800
C	0.09523200	3.46010600	1.31090900
H	0.73372700	3.74397500	0.46905300
H	-0.63874900	4.26028800	1.45008200
H	0.71014300	3.42049700	2.21665300
C	-1.65593700	2.30400300	-0.10492800
H	-2.20458900	1.37418200	-0.25919400
H	-2.39776900	3.05819400	0.18961000
N	0.23582000	0.97090000	0.80629100
O	1.10451900	-1.72460700	0.03086900
C	1.52279300	1.12061300	0.78734200
H	1.91197800	2.11485000	0.98993900
Pd	-0.62555500	-0.84624400	0.44349800
C	-1.07028300	2.76284500	-1.43870000
H	-1.87508600	2.84031700	-2.17567100
H	-0.57504500	3.73309200	-1.36042000
C	-0.46138500	0.75348300	-2.57086800
O	-0.04387100	1.88310600	-1.95388900
O	-1.63173800	0.46438600	-2.72150800
C	-2.90052000	-1.83435100	0.37413700
O	-1.86865000	-2.53530900	0.11674700
O	-2.72290600	-0.61113900	0.71438300
C	0.70029500	-0.09421700	-3.02224200
H	0.82195300	-0.92113300	-2.31346400
H	0.47190600	-0.52200600	-4.00211800
H	1.63136600	0.47497600	-3.06072600
C	-4.28196800	-2.39796300	0.25052900
H	-4.93278000	-1.97464700	1.02070900
H	-4.68859100	-2.12039400	-0.72980300
H	-4.25779500	-3.48769200	0.32474000

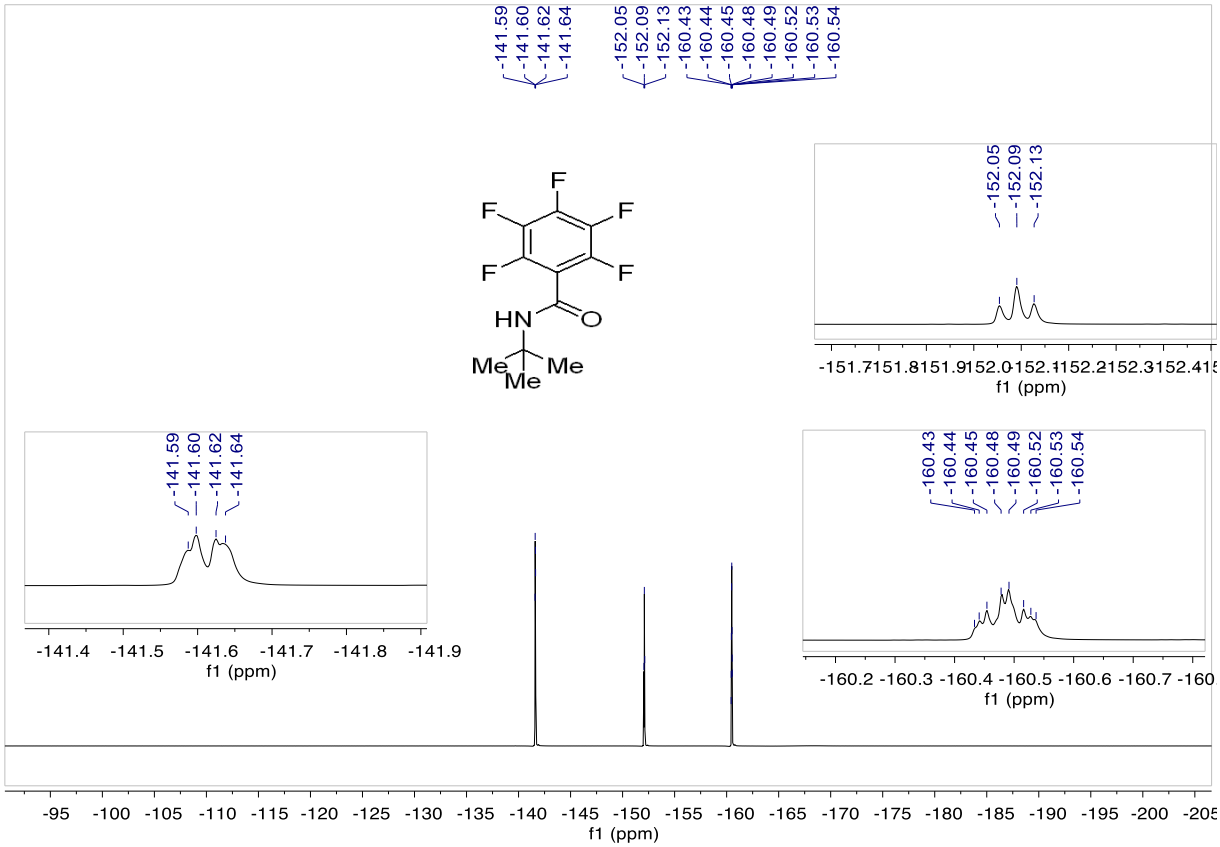
11. NMR Spectrum

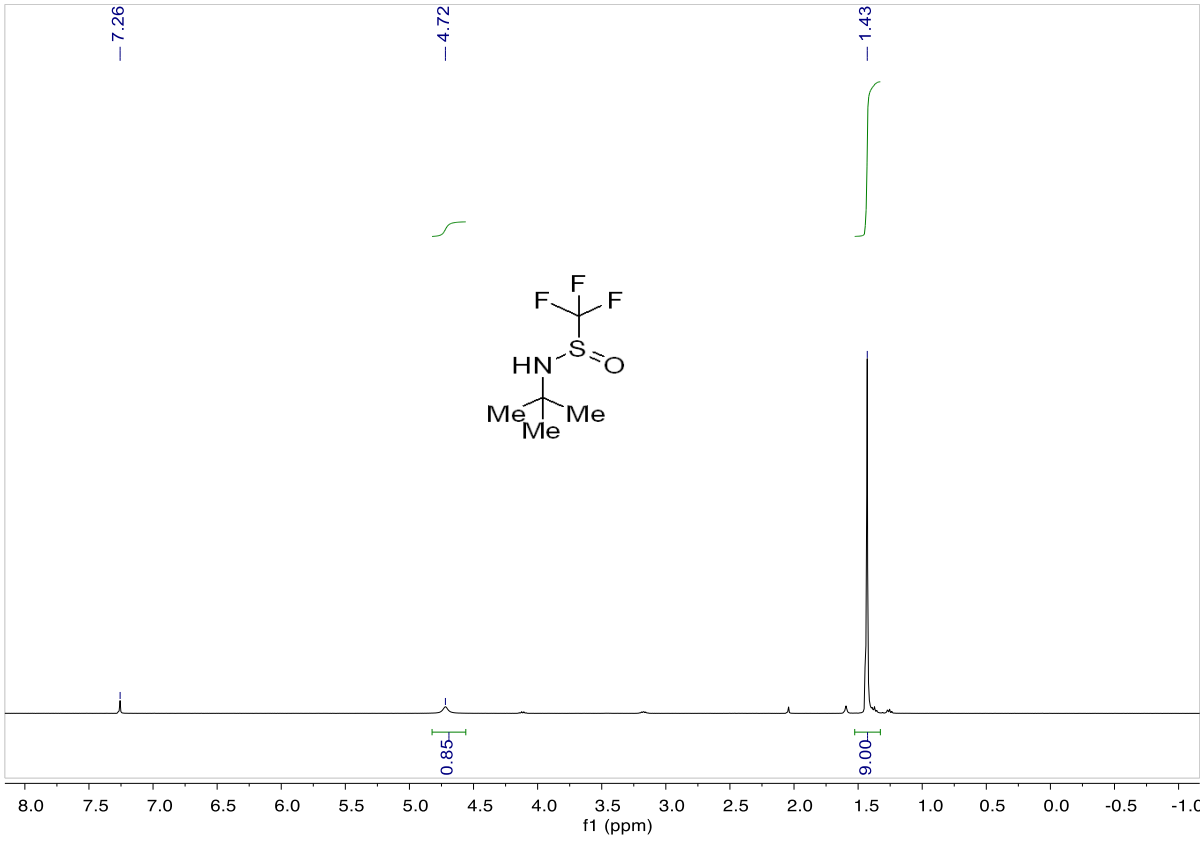


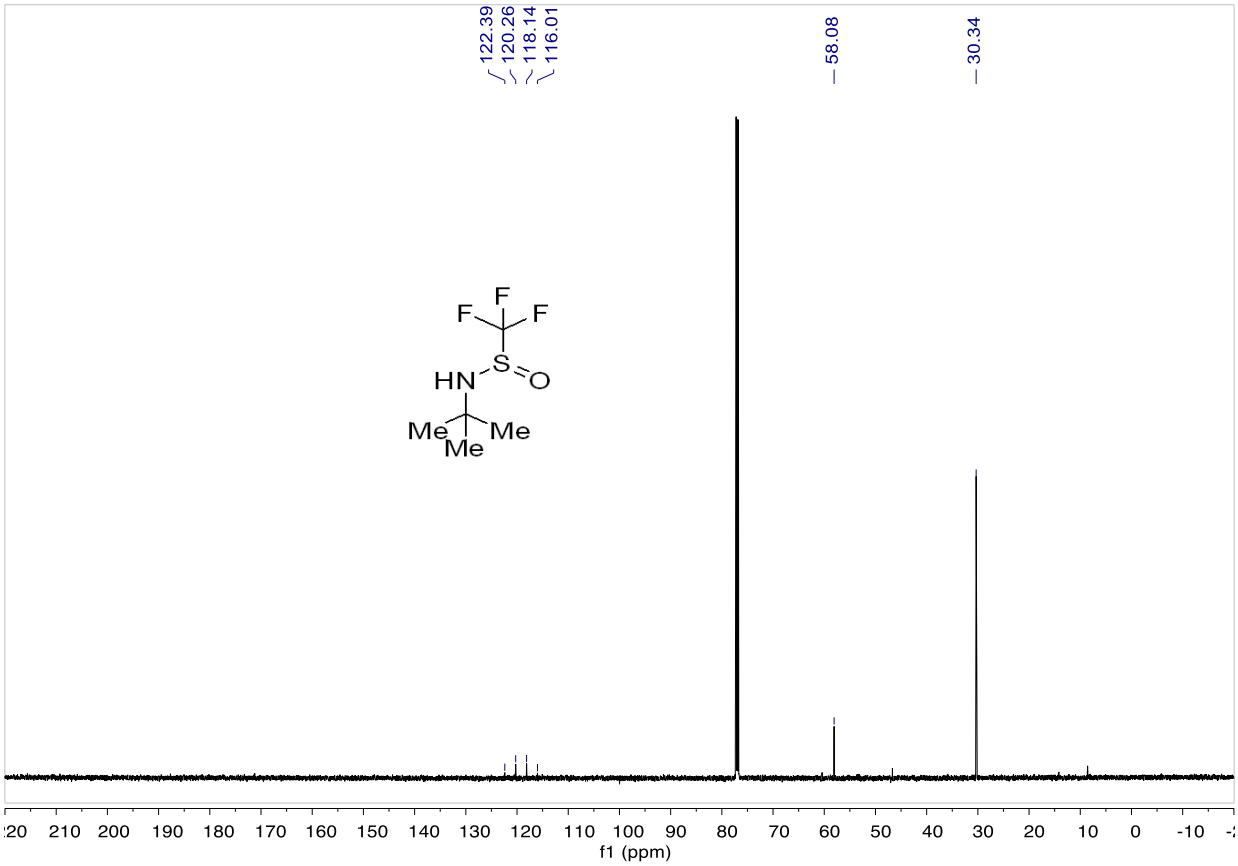


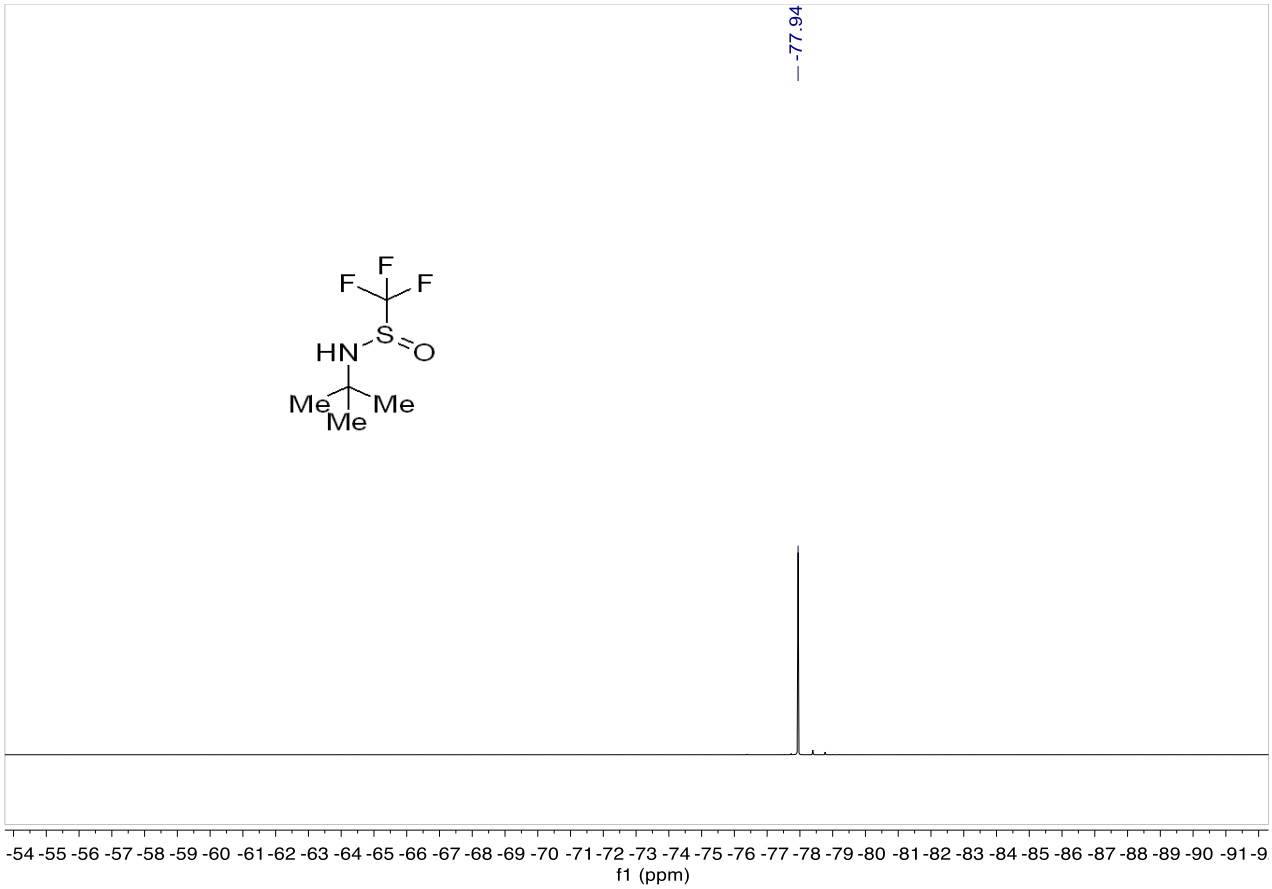

7.26
5.69
1.46
F
F
F
F
F
HN
O
Me
Me
Me
0.93
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

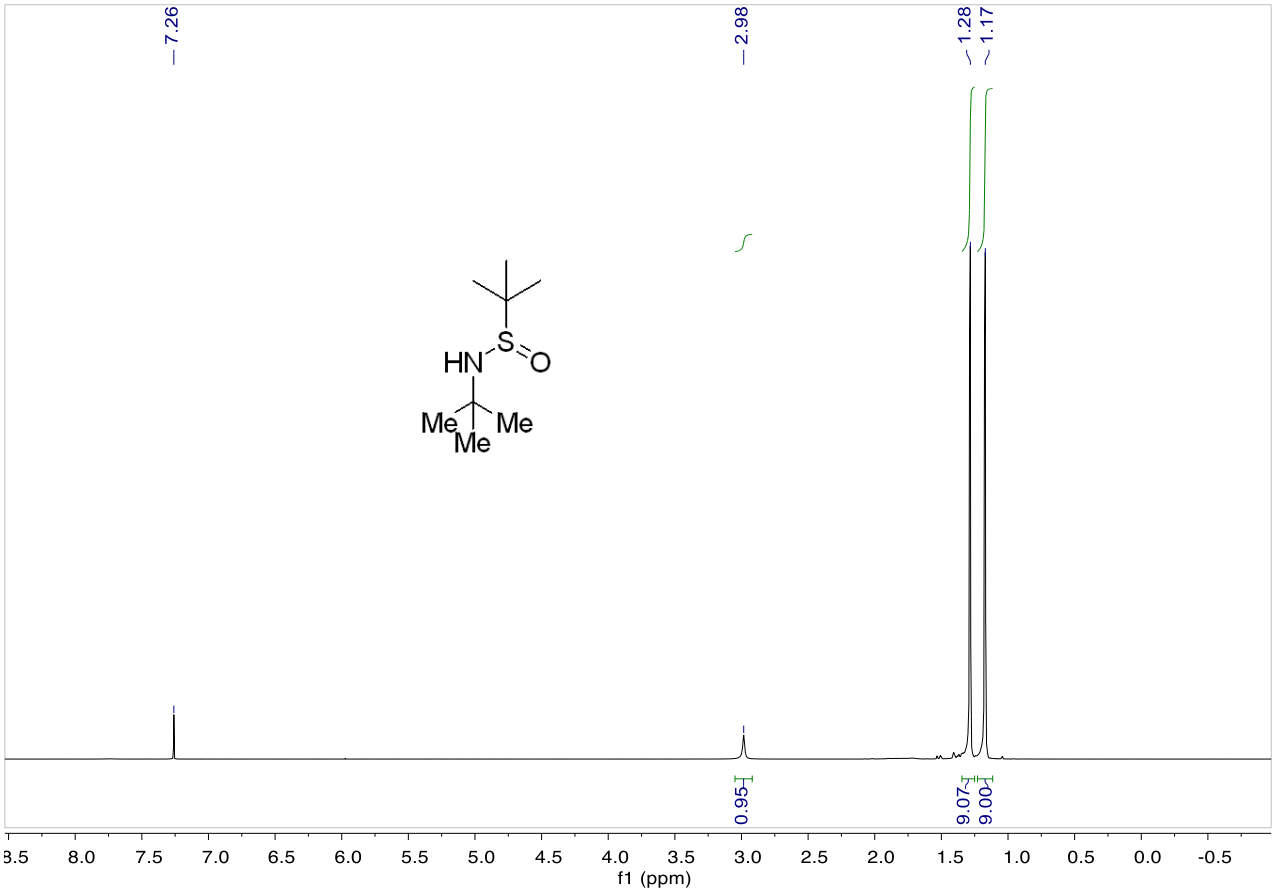

156.31
144.72
144.69
144.66
144.64
144.61
144.58
143.05
143.02
143.00
142.97
142.95
142.92
142.79
141.09
138.47
138.36
138.27
138.24
136.79
136.75
136.67
136.56
112.85
112.71
112.58
53.15
28.57
F
F
F
F
F
HN
O
Me
Me
Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

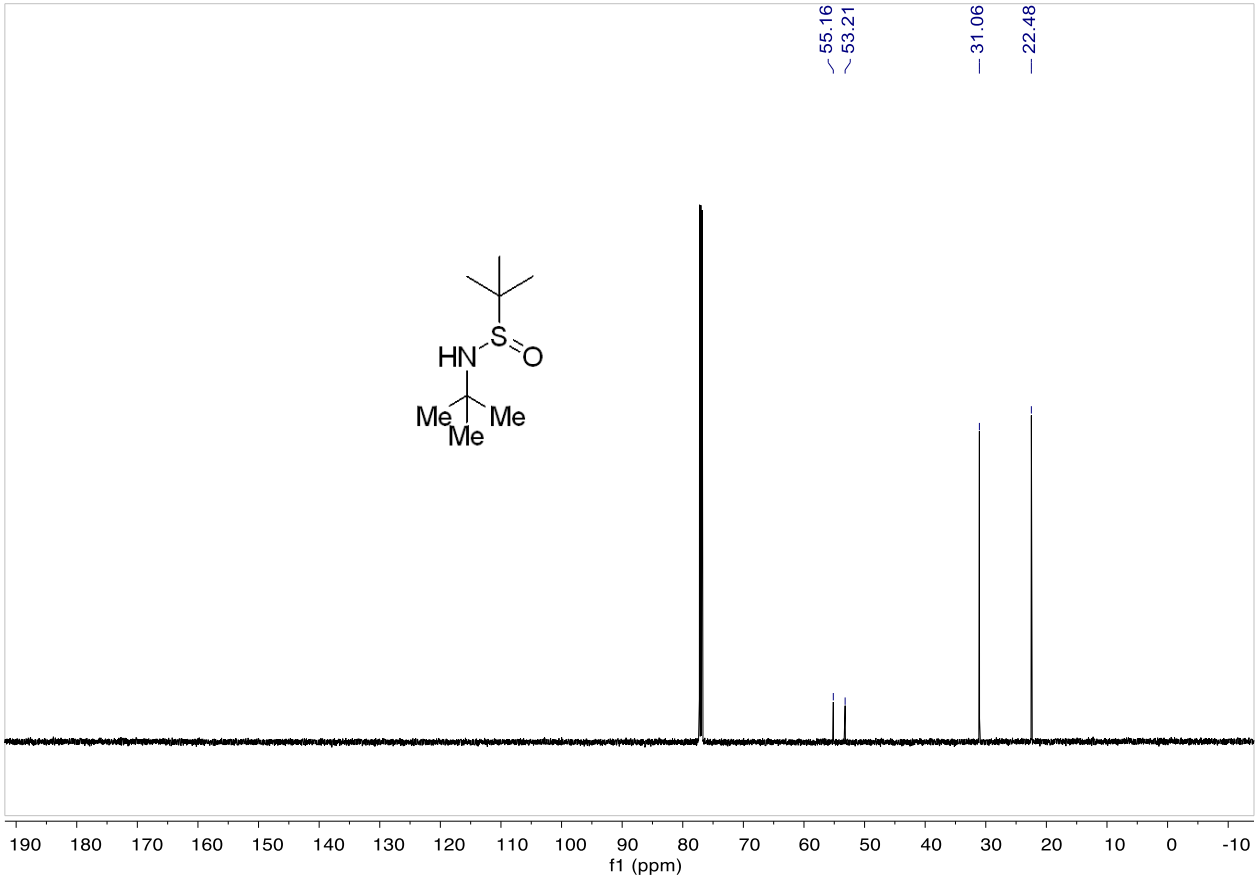

-141.59
-141.60
-141.62
-141.64
-152.05
-152.09
-152.13
-160.43
-160.44
-160.45
-160.48
-160.49
-160.52
-160.53
-160.54
F
F
F
F
F
HN
O
Me
Me
Me
-152.05
-152.09
-152.13
-151.7 -151.8 -151.9 -152.0 -152.1 -152.2 -152.3 -152.4
f1 (ppm)
-141.59
-141.60
-141.62
-141.64
-141.4 -141.5 -141.6 -141.7 -141.8 -141.9
f1 (ppm)
-160.43
-160.44
-160.45
-160.48
-160.49
-160.52
-160.53
-160.54
-160.2 -160.3 -160.4 -160.5 -160.6 -160.7 -160
f1 (ppm)
-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205
f1 (ppm)

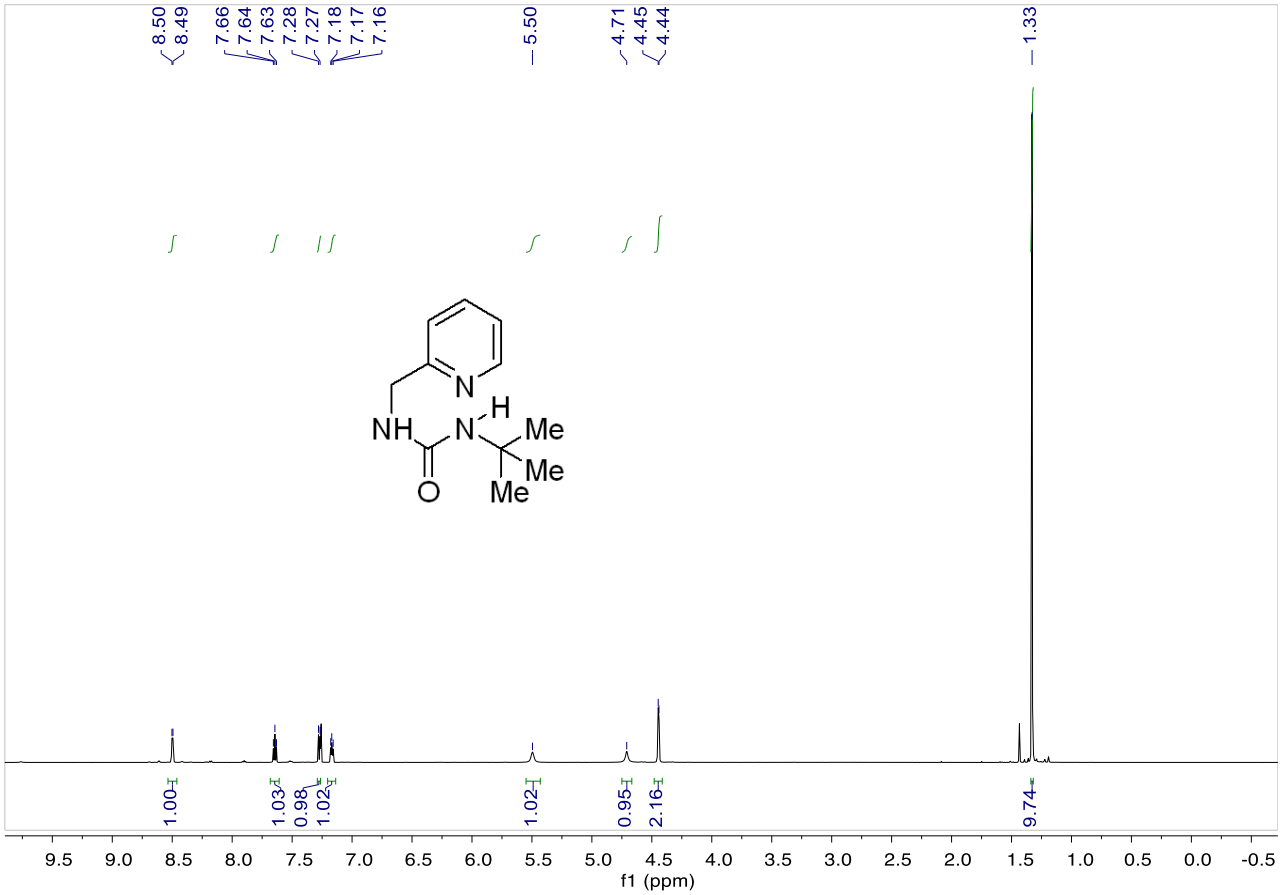

7.26
4.72
1.43
F
F
F
S
HN
O
Me
Me
Me
0.85
9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

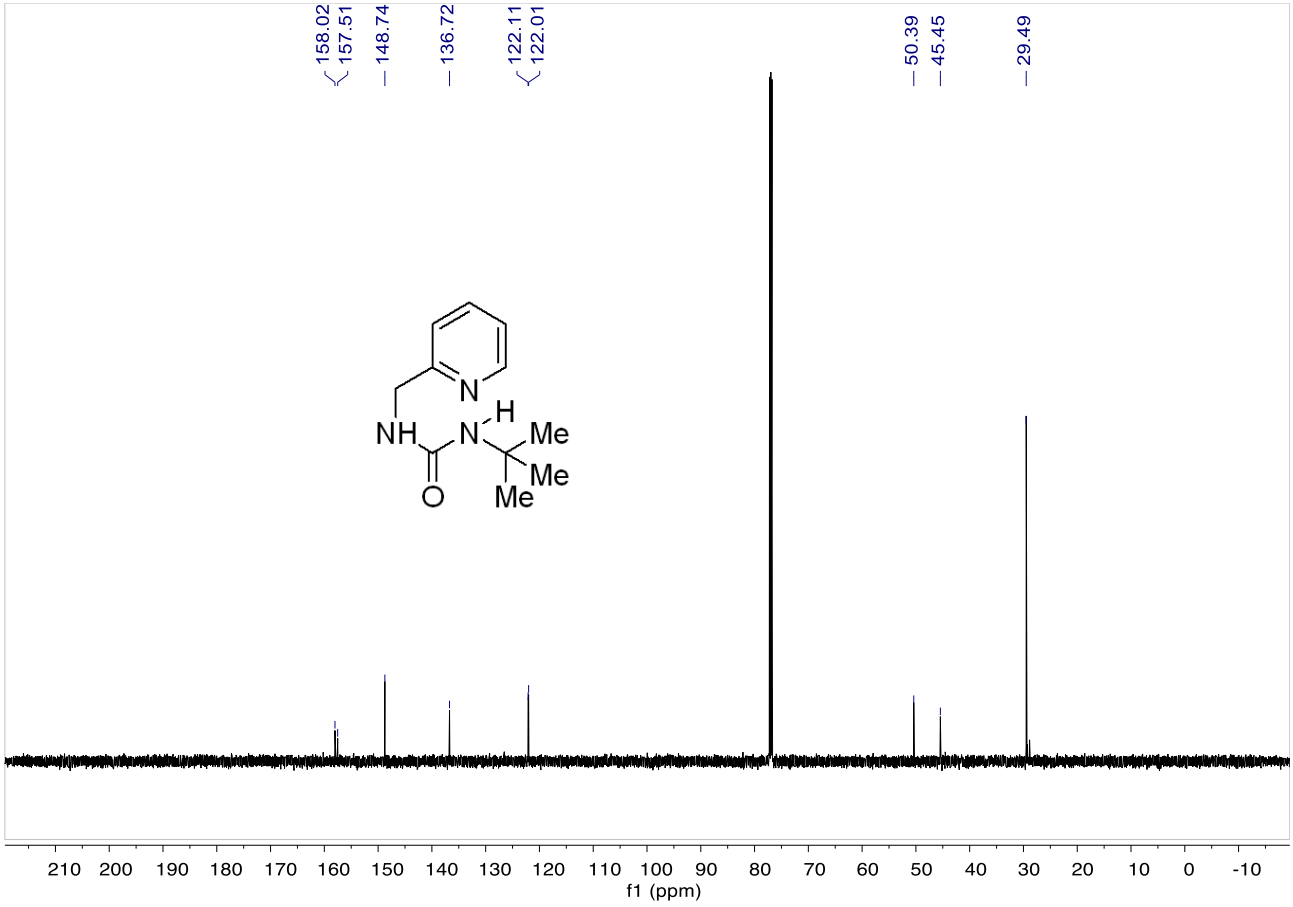

122.39
120.26
118.14
116.01
58.08
30.34
F
F
F
S
O
HN
Me
Me
Me
f1 (ppm)

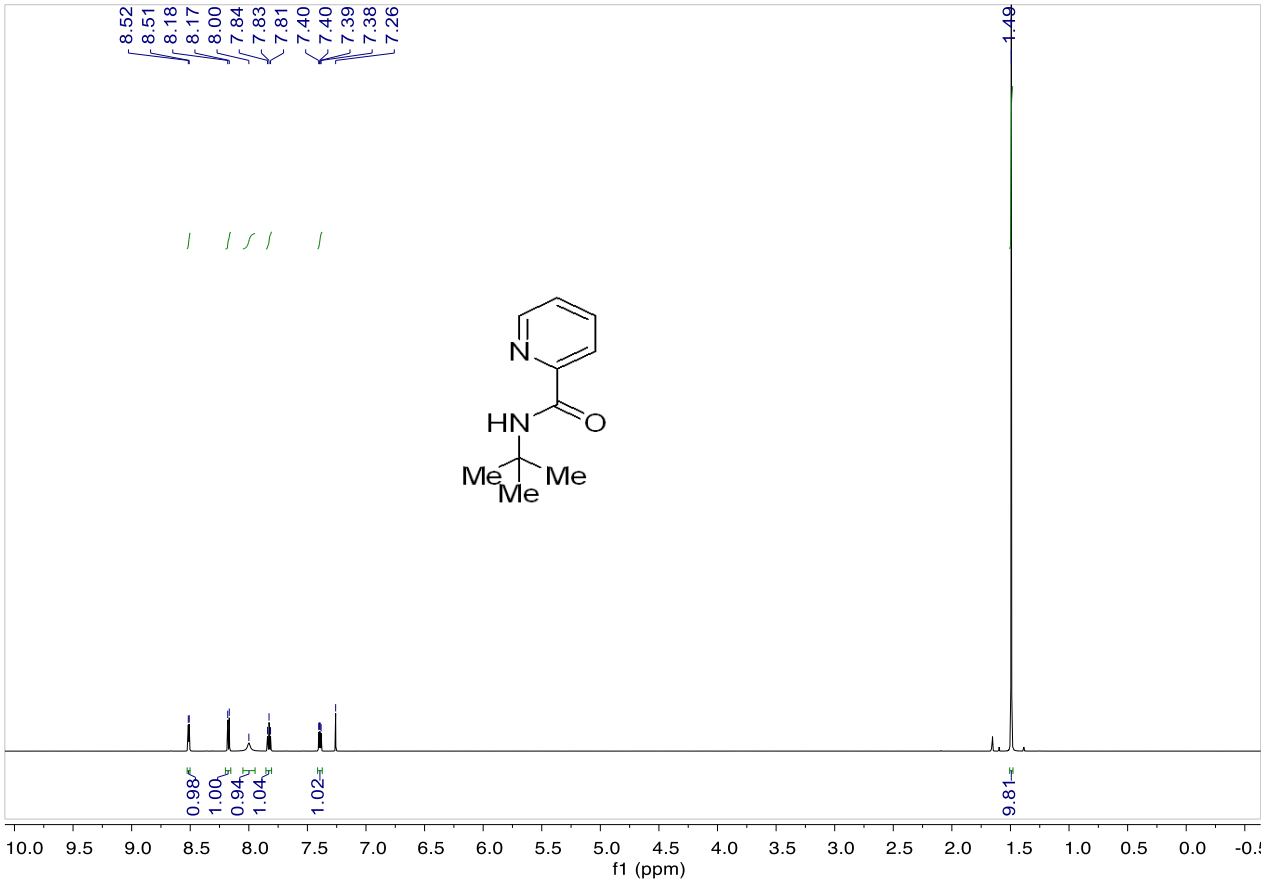

-77.94
F
F
F
S
O
HN
Me
Me
Me
f1 (ppm)

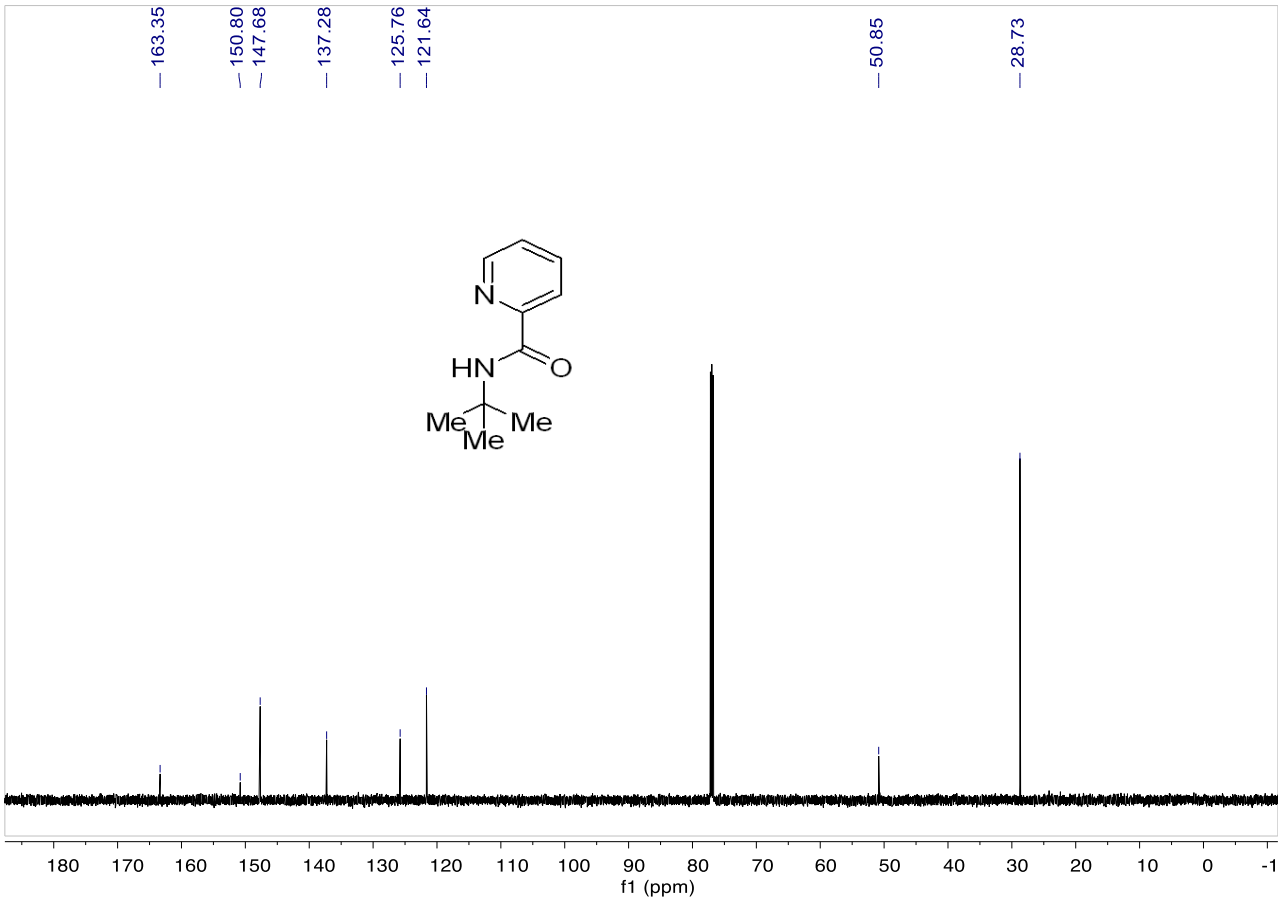

7.26
2.98
1.28
1.17
HN
S
O
Me
Me
Me
0.95
9.07
9.00
f1 (ppm)


55.16
53.21
31.06
22.48
HN
S
O
Me
Me
Me
f1 (ppm)


8.50
8.49
7.66
7.64
7.63
7.28
7.27
7.18
7.17
7.16
5.50
4.71
4.45
4.44
1.33
N
NH
N
H
Me
Me
Me
O
1.00
1.03
0.98
1.02
1.02
0.95
2.16
9.74
f1 (ppm)


158.02
157.51
148.74
136.72
122.11
122.01
50.39
45.45
29.49
N
NH
N
H
Me
Me
Me
O
f1 (ppm)


8.52
8.51
8.18
8.17
8.00
7.84
7.83
7.81
7.40
7.40
7.39
7.38
7.26
1.49
N
HN
O
Me
Me
Me
0.98
1.00
0.94
1.04
1.02
9.81
f1 (ppm)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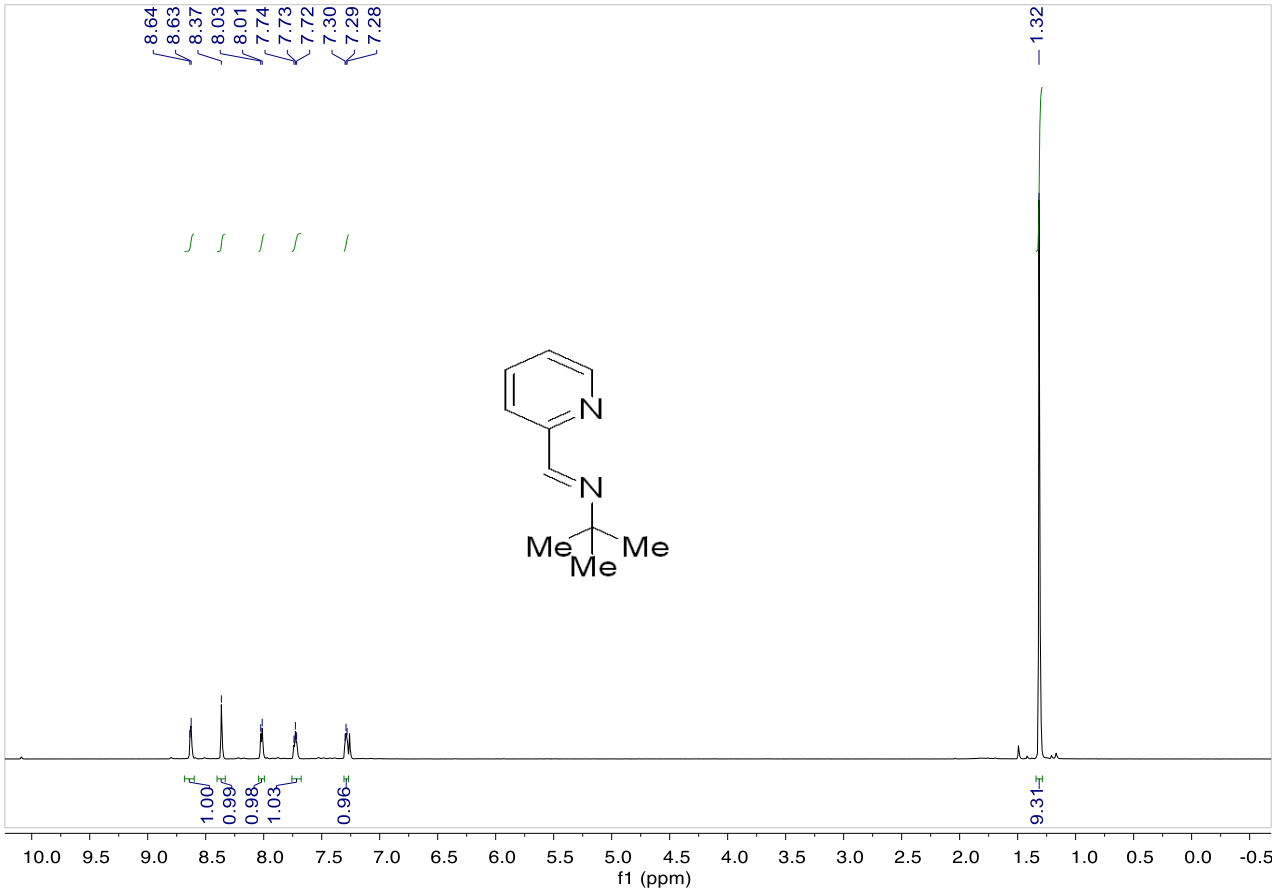
121.64
50.85
28.73
N
HN
O
Me
Me
Me
f1 (ppm)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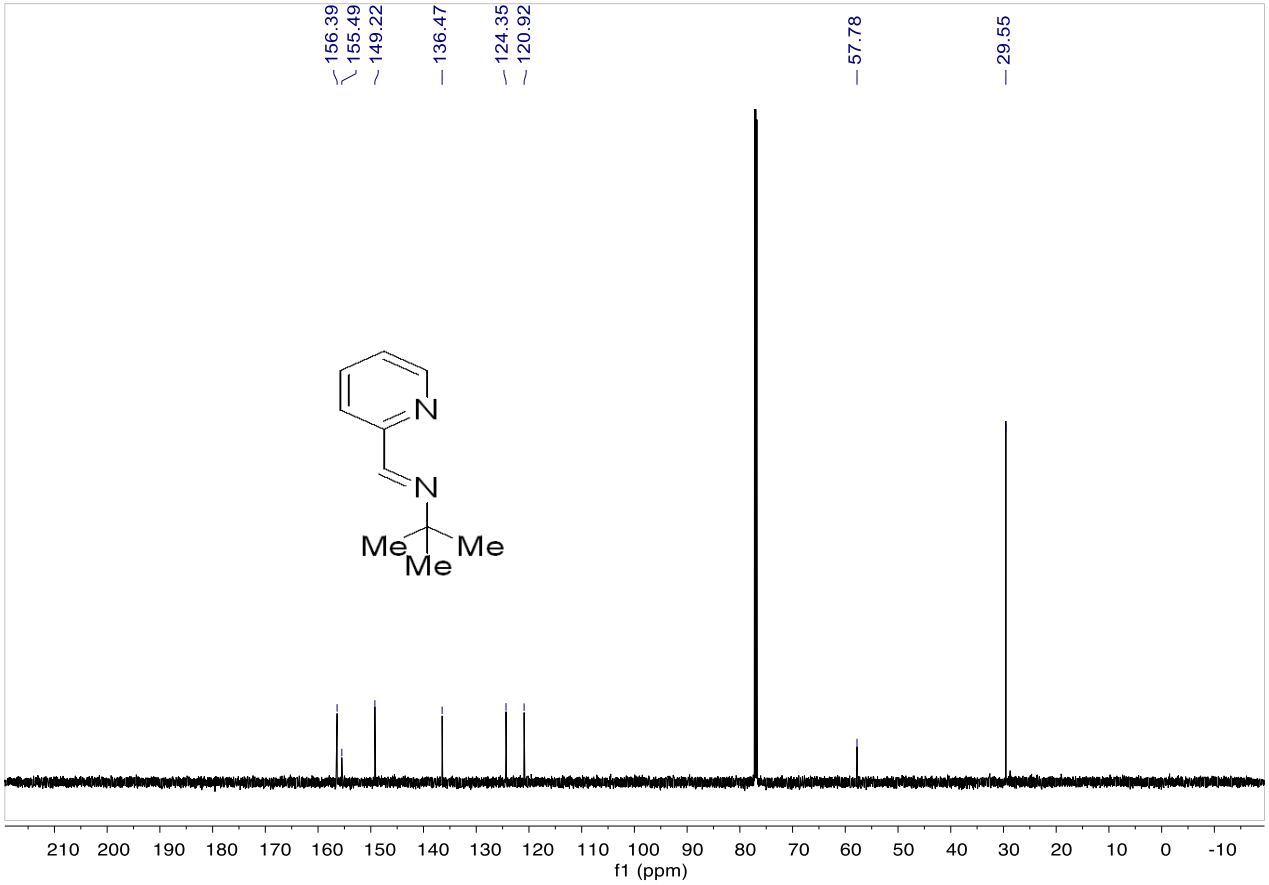
8.63
8.37
8.03
8.01
7.74
7.73
7.72
7.30
7.29
7.28
1.32
N
N
Me
Me
Me
1.00
0.99
0.98
1.03
0.96
9.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


156.39
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136.47
124.35
120.92
57.78
29.55
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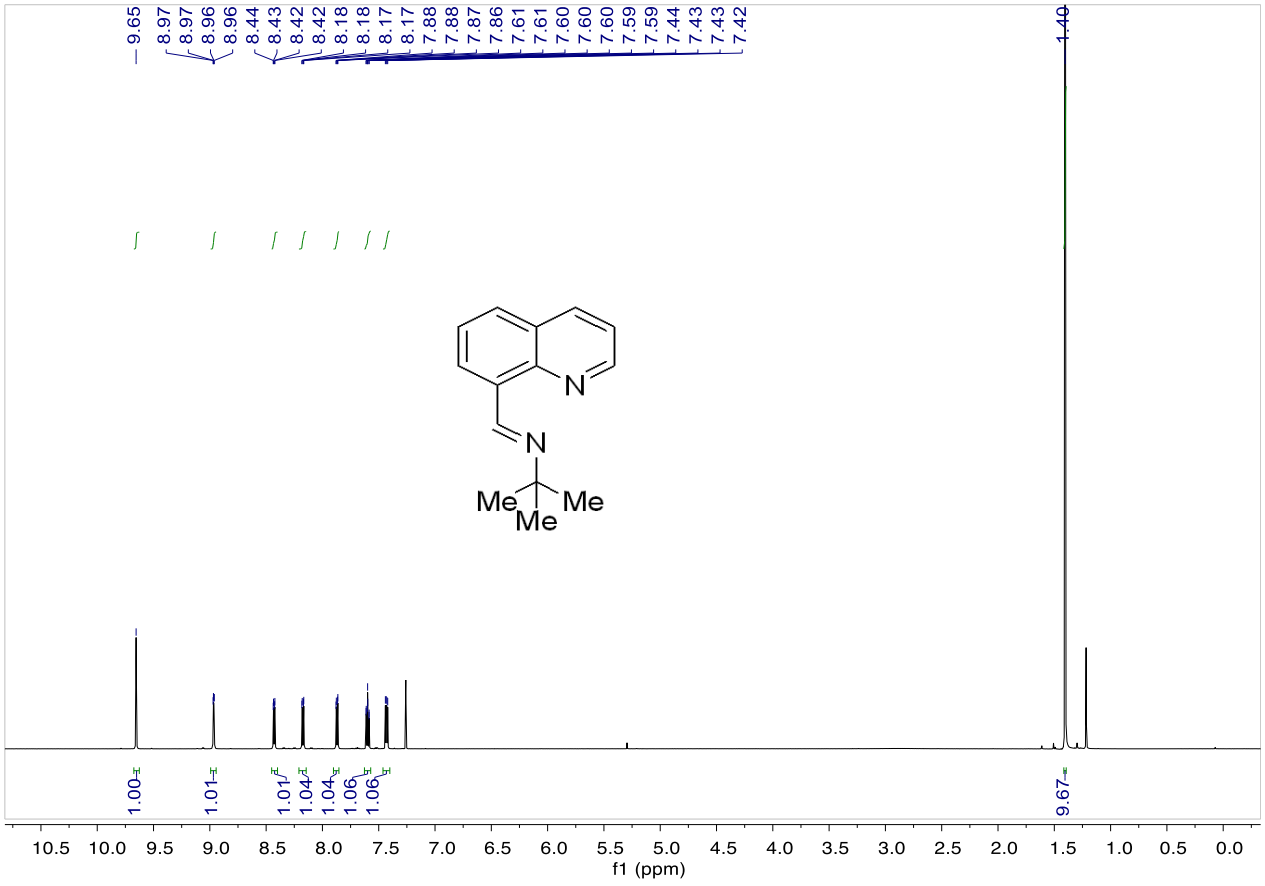
N
Me
Me
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.97
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8.96
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8.43
8.42
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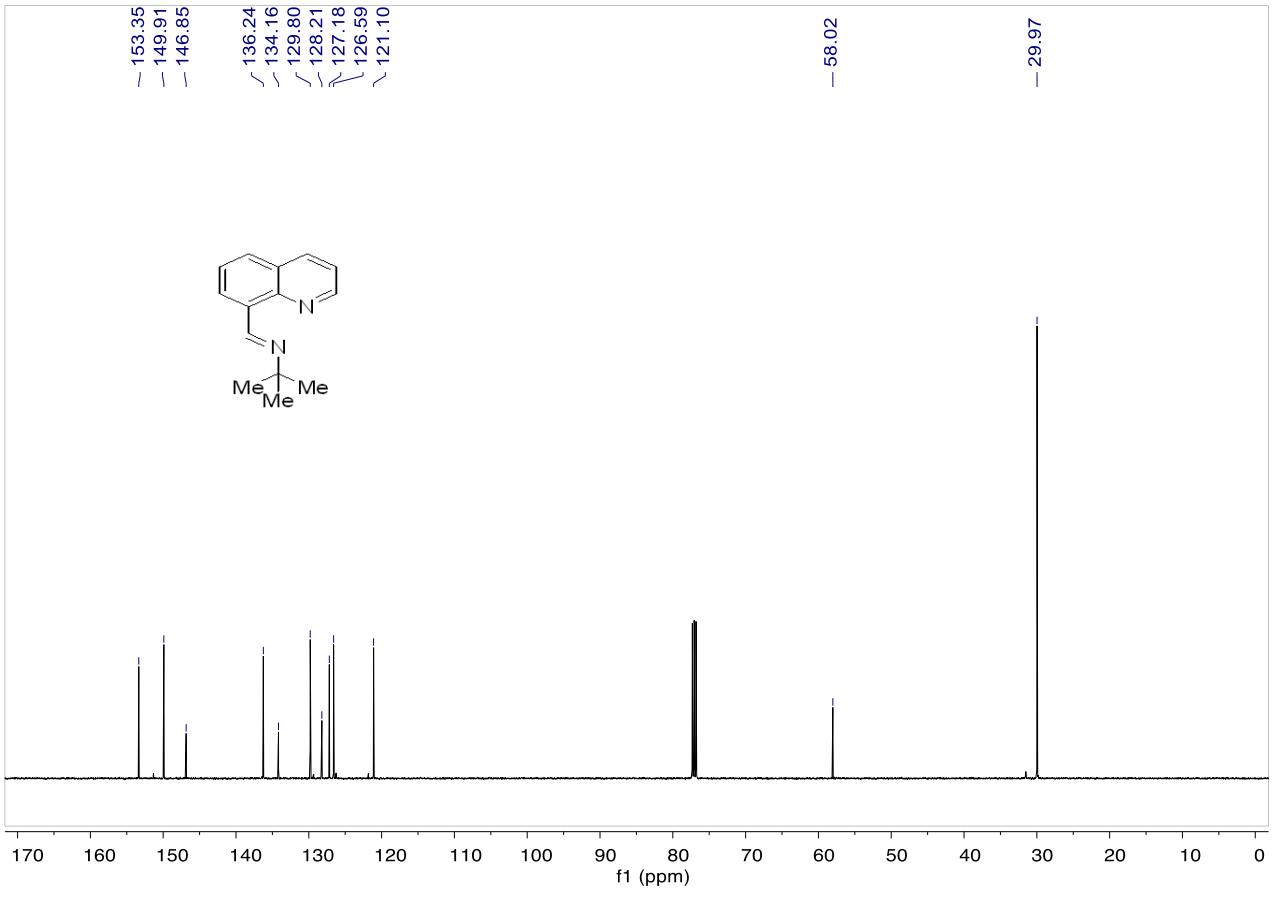
8.18
8.18
8.17
8.17
7.88
7.88
7.87
7.86
7.61
7.61
7.60
7.60
7.60
7.59
7.59
7.44
7.43
7.43
7.42
1.40
N
N
Me
Me
Me
1.00
1.01
1.01
1.04
1.04
1.06
1.06
9.67
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.35
149.91
146.85
136.24
134.16
129.80
128.21
127.18
126.59
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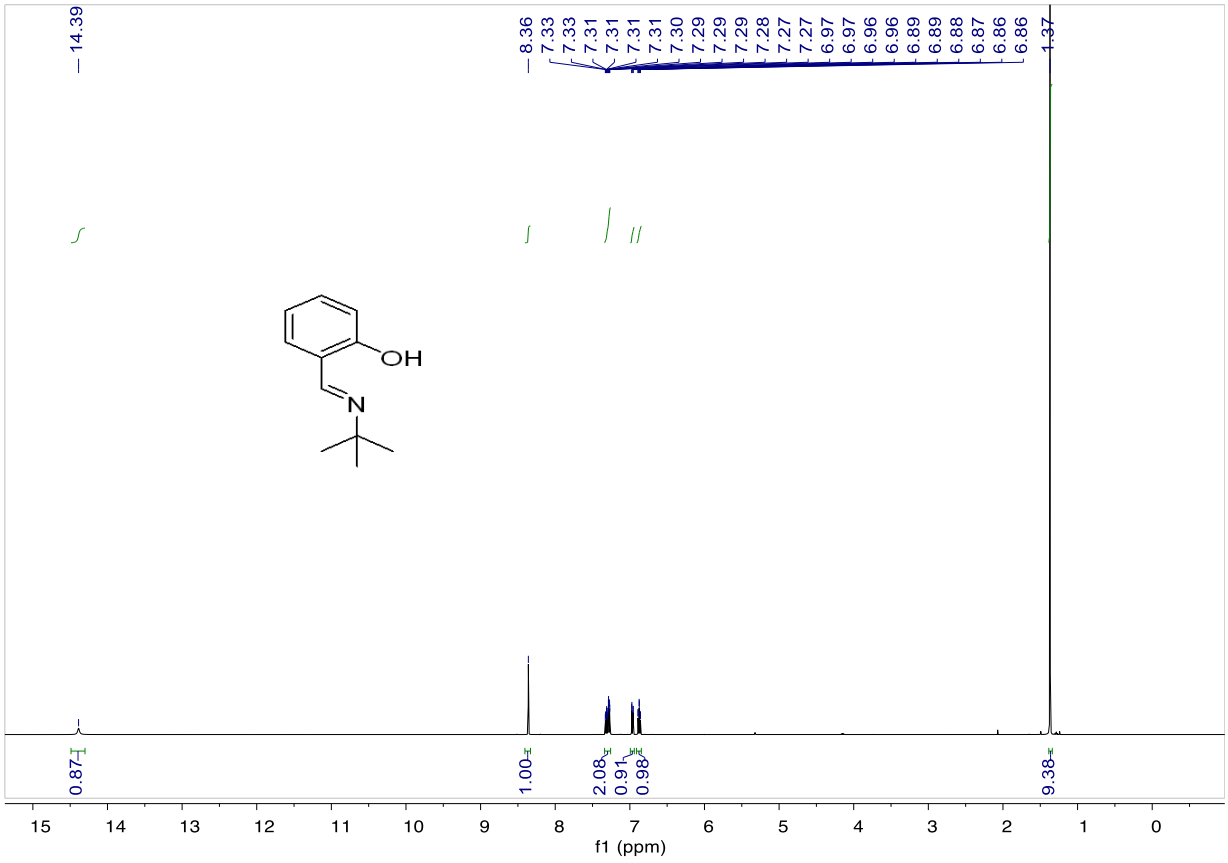
29.97
N
N
Me
Me
Me
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.31
7.31
7.30
7.29
7.29
7.29
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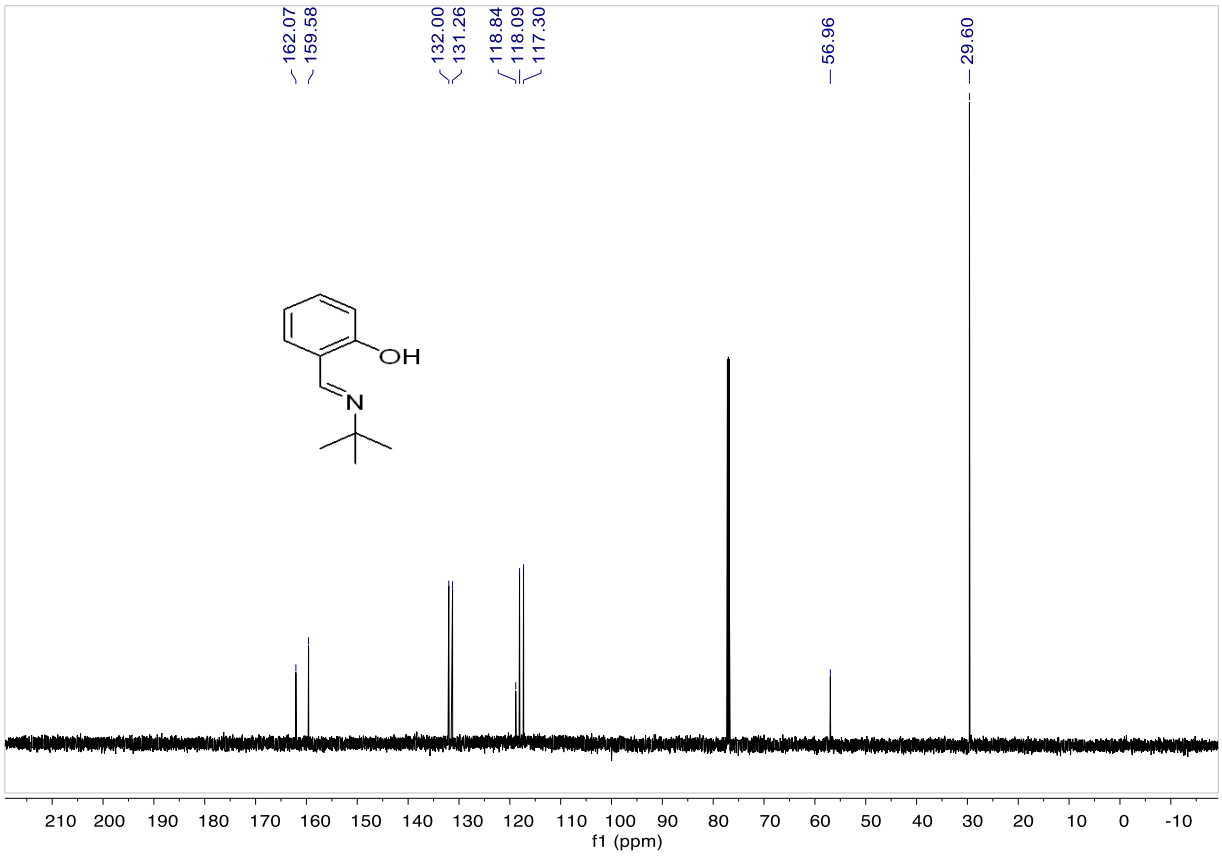
7.27
7.27
6.97
6.97
6.96
6.96
6.89
6.89
6.88
6.87
6.86
6.86
1.37
OH
N
0.87
1.00
2.08
0.91
0.98
9.38
f1 (ppm)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118.09
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56.96
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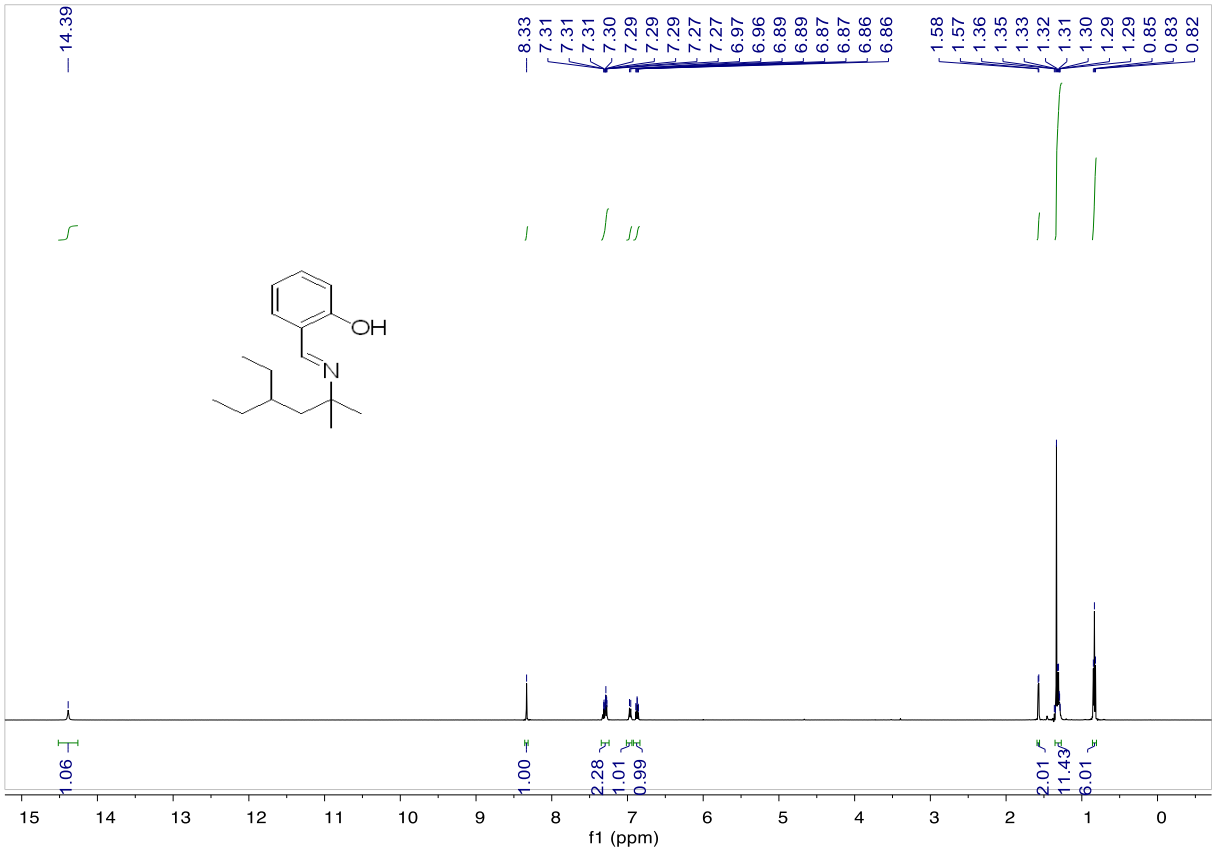
OH
N
f1 (ppm)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6.89
6.89
6.87
6.87
6.86
6.86
1.58
1.57
1.36
1.35
1.33
1.32
1.31
1.30
1.29
1.29
0.85
0.83
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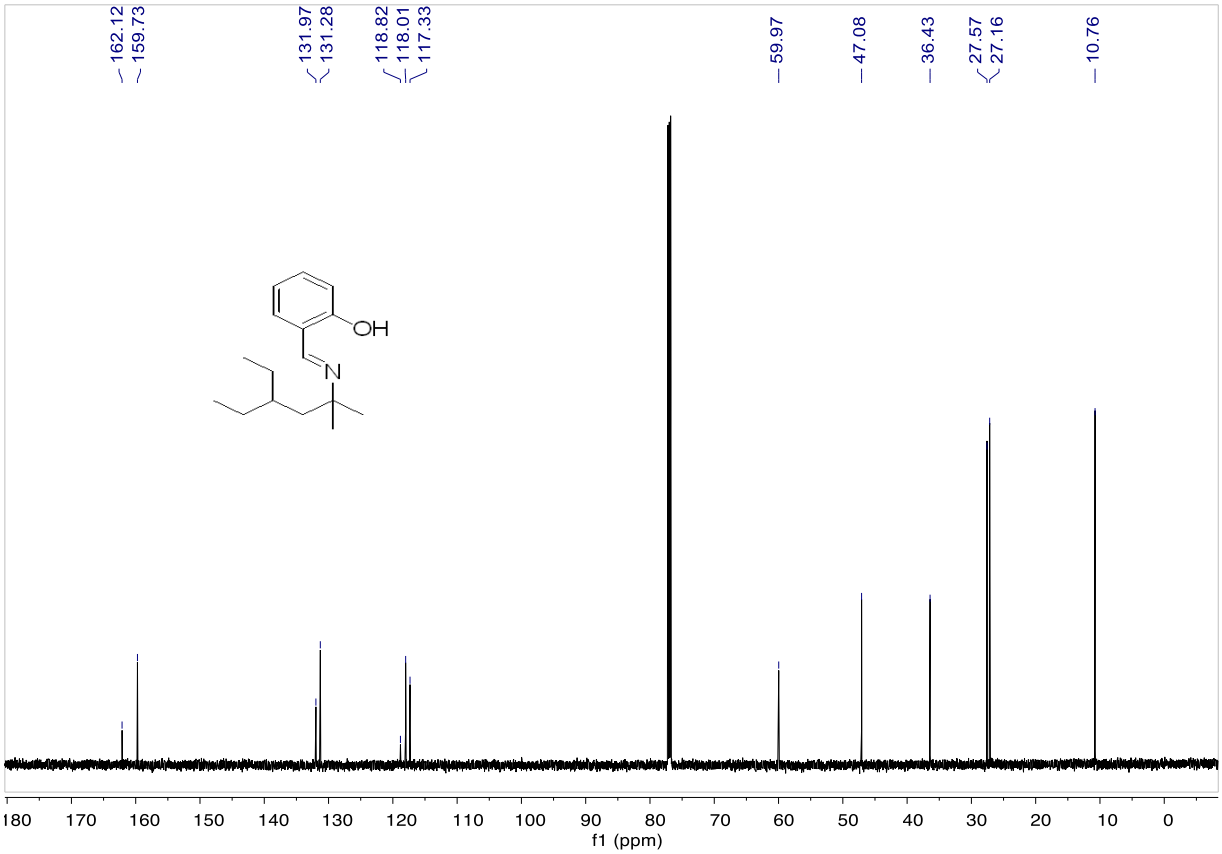
N
1.06
1.00
2.28
1.01
0.99
2.01
11.43
6.01
f1 (ppm)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59.97
47.08
36.43
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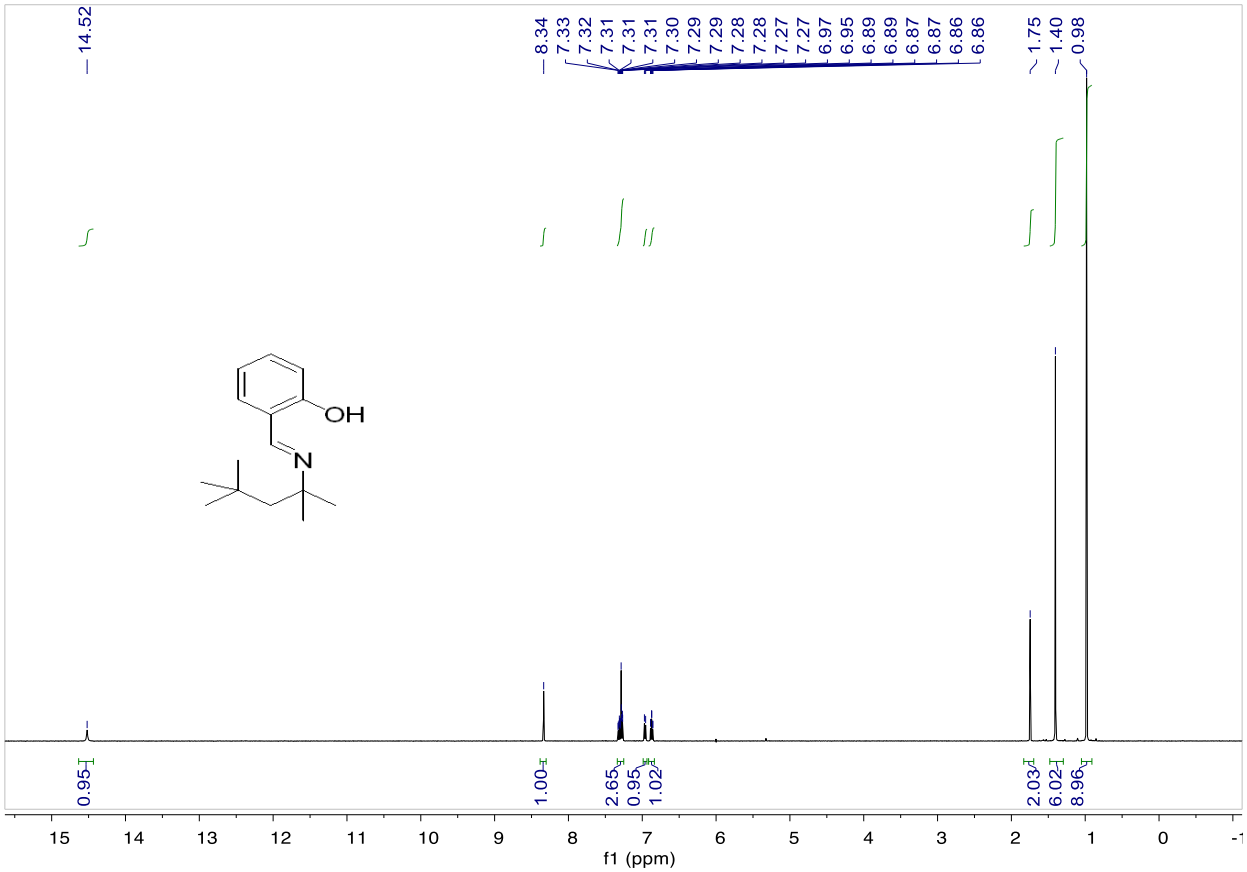
27.16
10.76
OH
N
f1 (ppm)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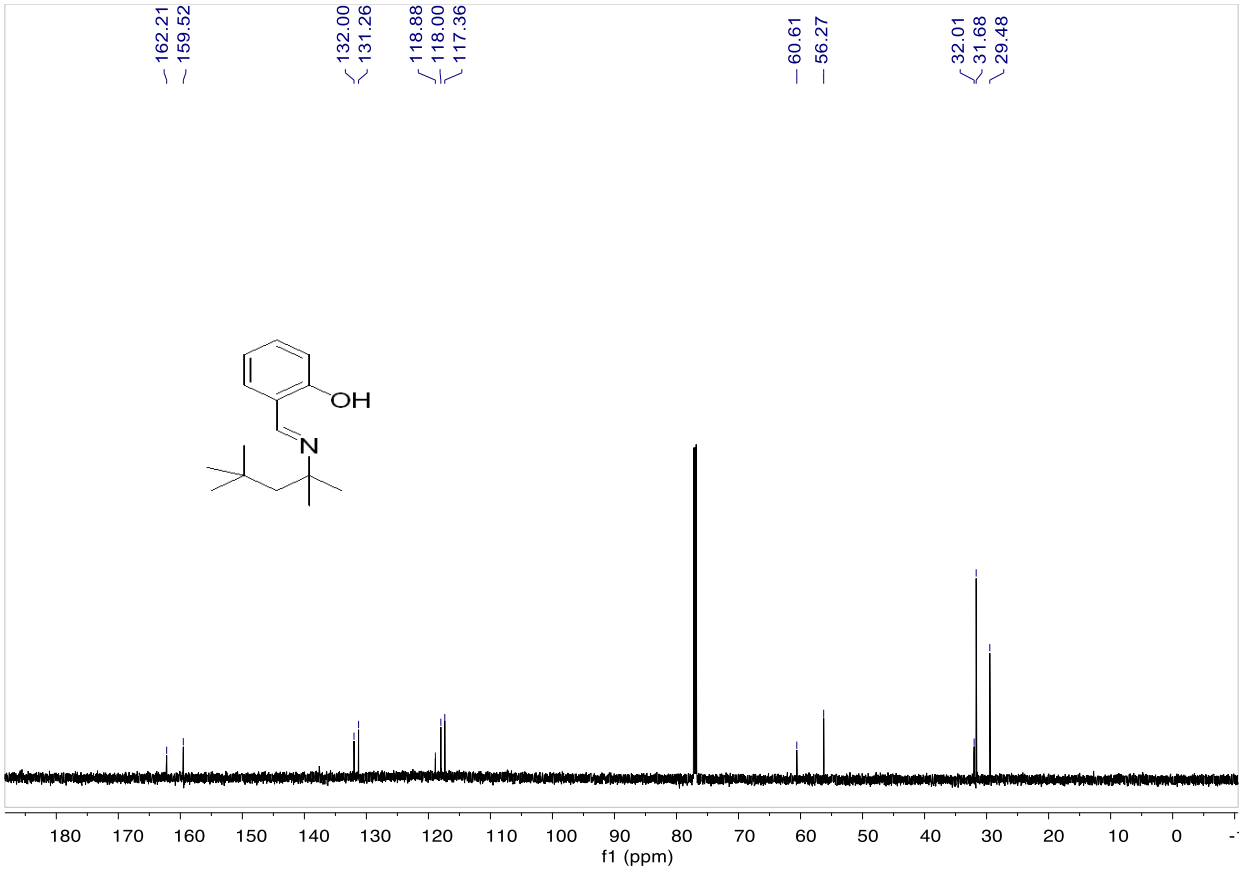
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
6.97
6.95
6.89
6.89
6.87
6.87
6.86
6.86
1.75
1.40
0.98
OH
N
0.95
1.00
2.65
0.95
1.02
2.03
6.02
8.96
f1 (ppm)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118.00
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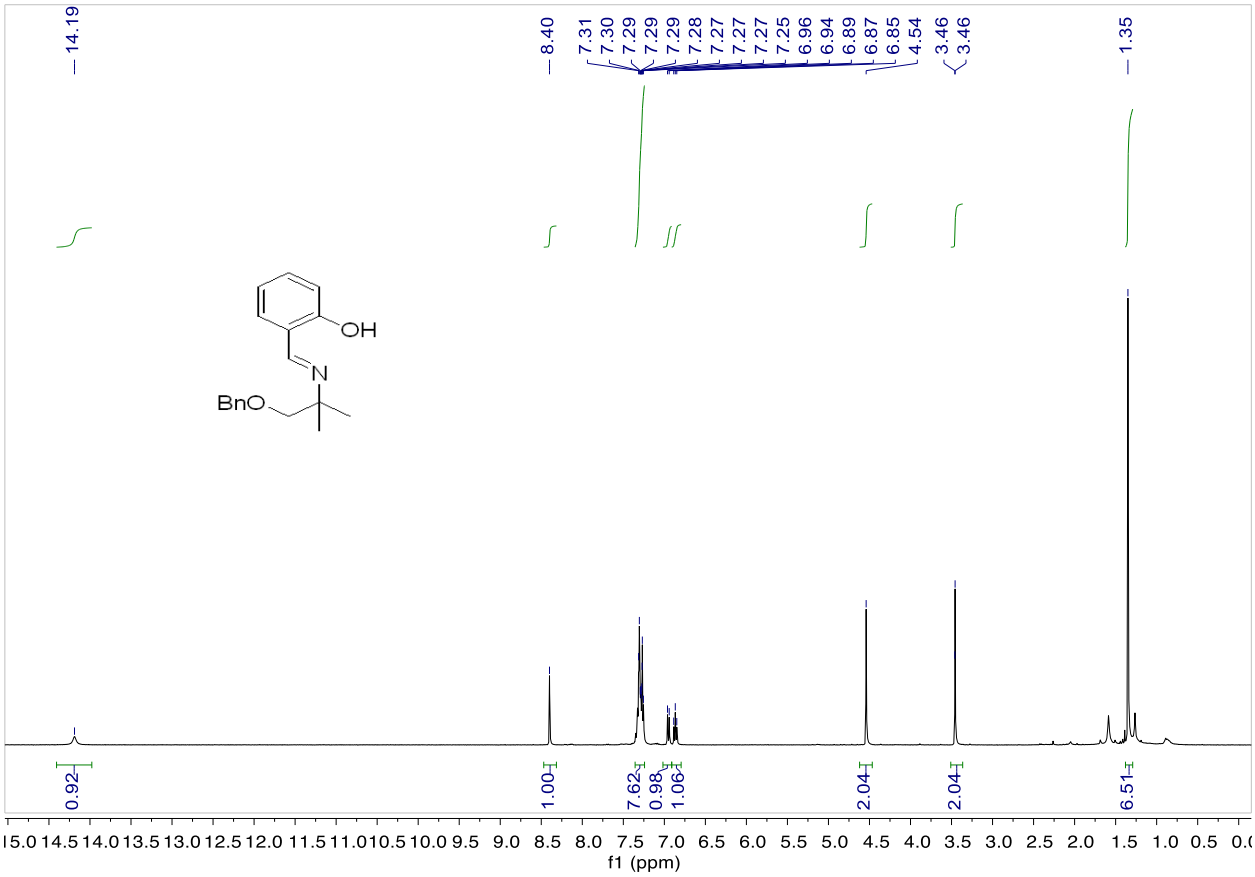
56.27
32.01
31.68
29.48
OH
N
f1 (ppm)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7.30
7.29
7.29
7.29
7.28
7.27
7.27
7.27
7.25
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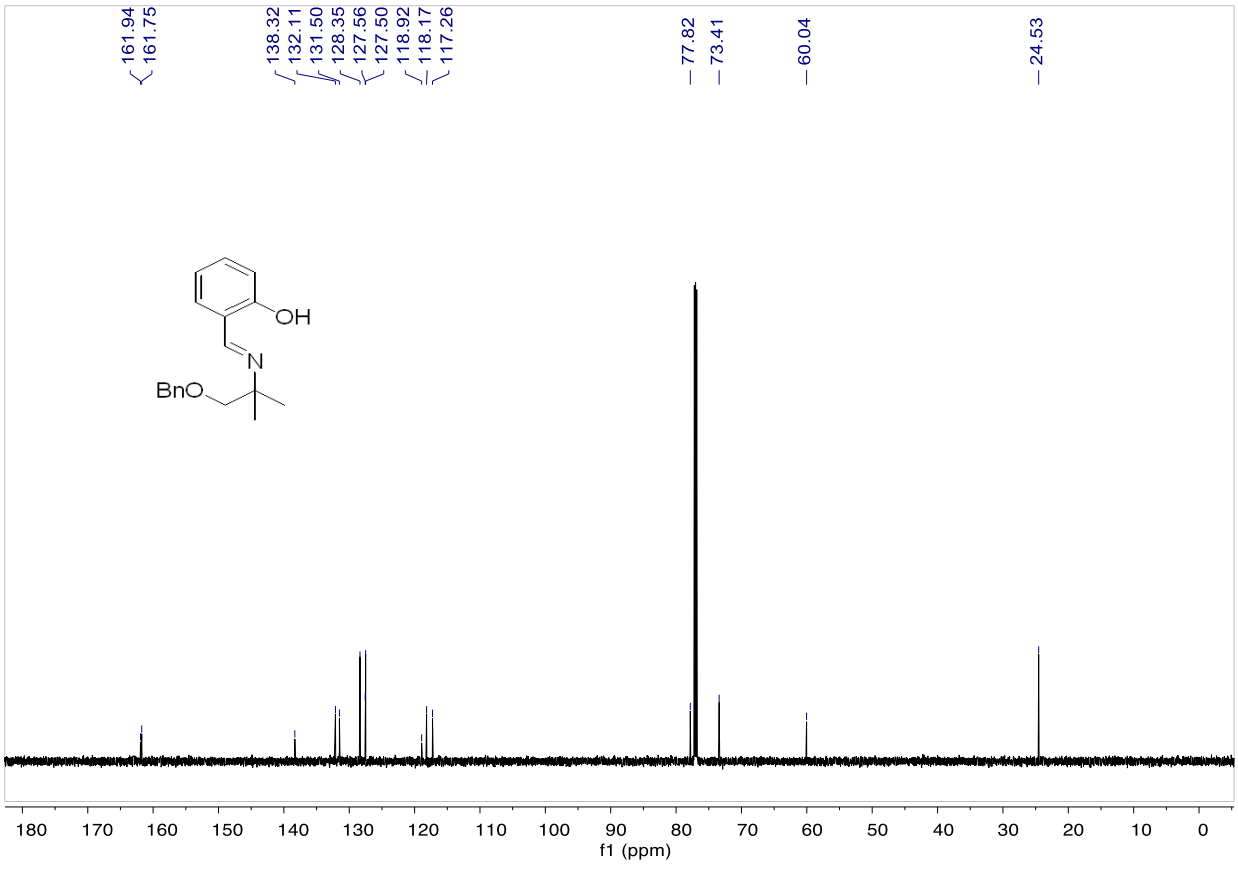
6.94
6.89
6.87
6.85
4.54
3.46
3.46
1.35
OH
N
BnO
0.92
1.00
7.62
0.98
1.06
2.04
2.04
6.51
f1 (ppm)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161.75
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128.35
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118.17
117.26
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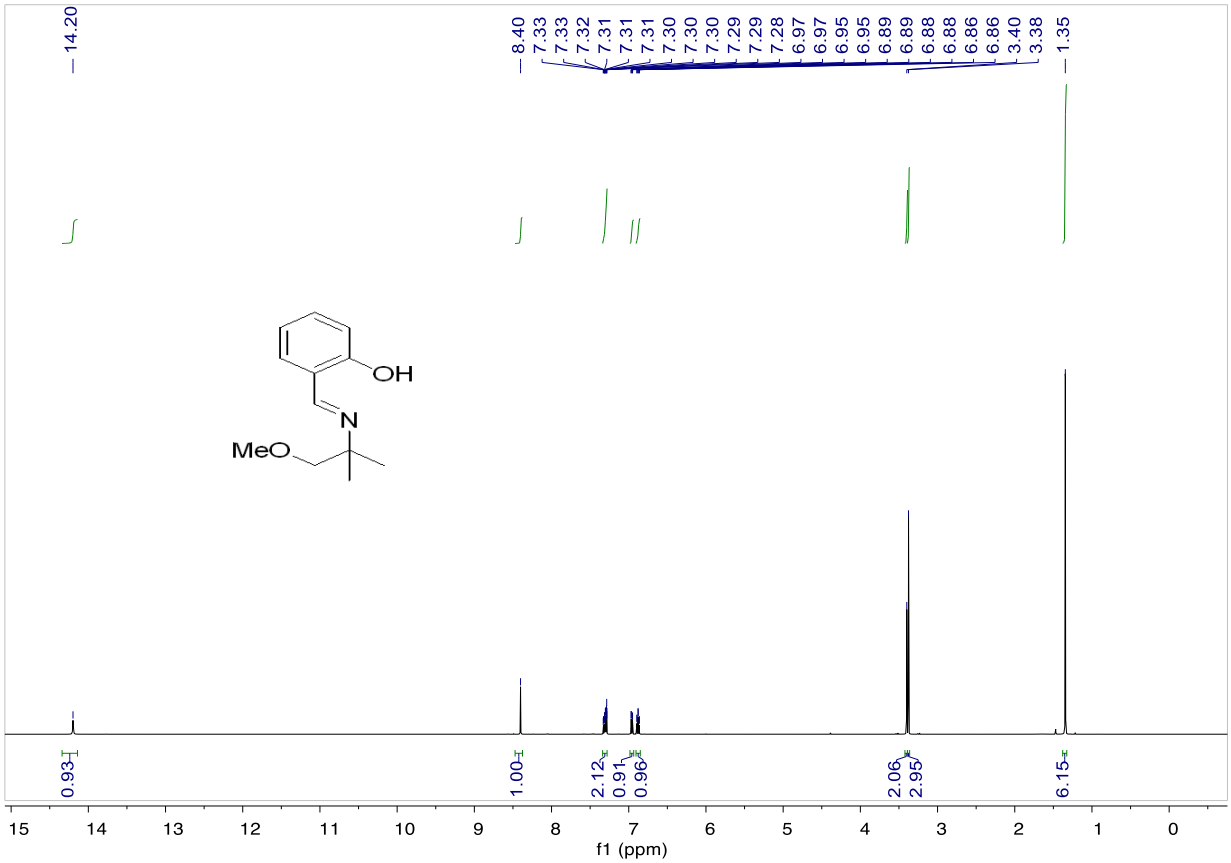
73.41
60.04
24.53
OH
N
BnO
f1 (ppm)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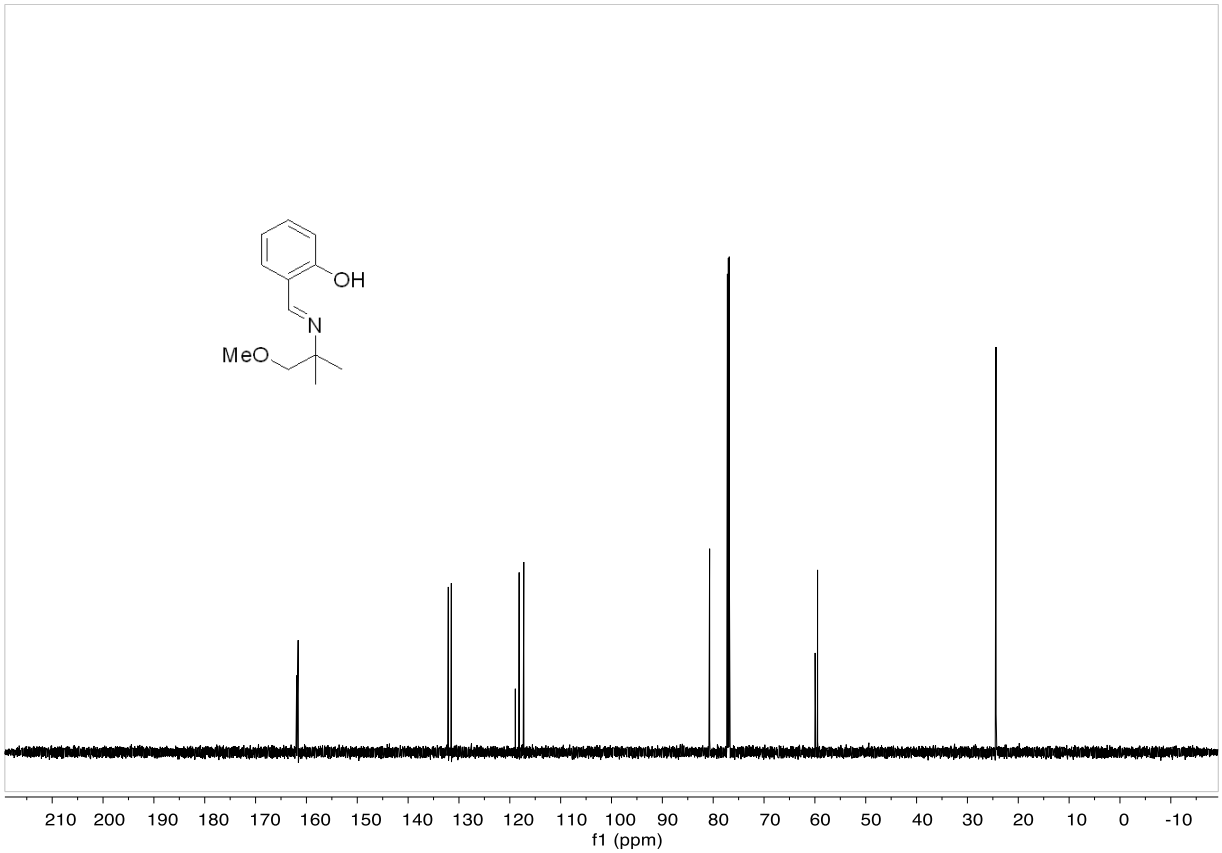
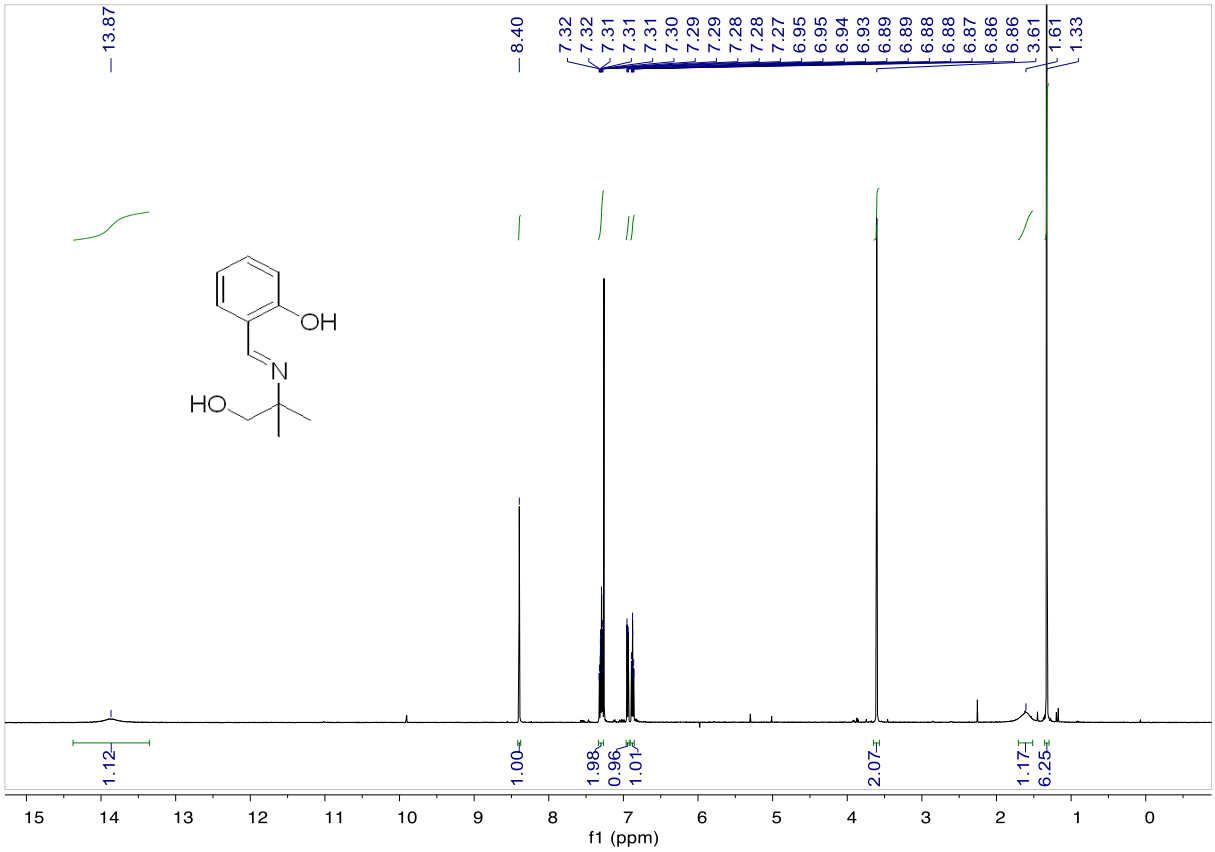
7.30
7.30
7.29
7.29
7.28
6.97
6.97
6.95
6.95
6.89
6.89
6.88
6.88
6.86
6.86
3.40
3.38
1.35
OH
N
MeO
0.93
1.00
2.12
0.91
0.96
2.06
2.95
6.15
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


OH
N
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.31
7.30
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7.29
7.28
7.28
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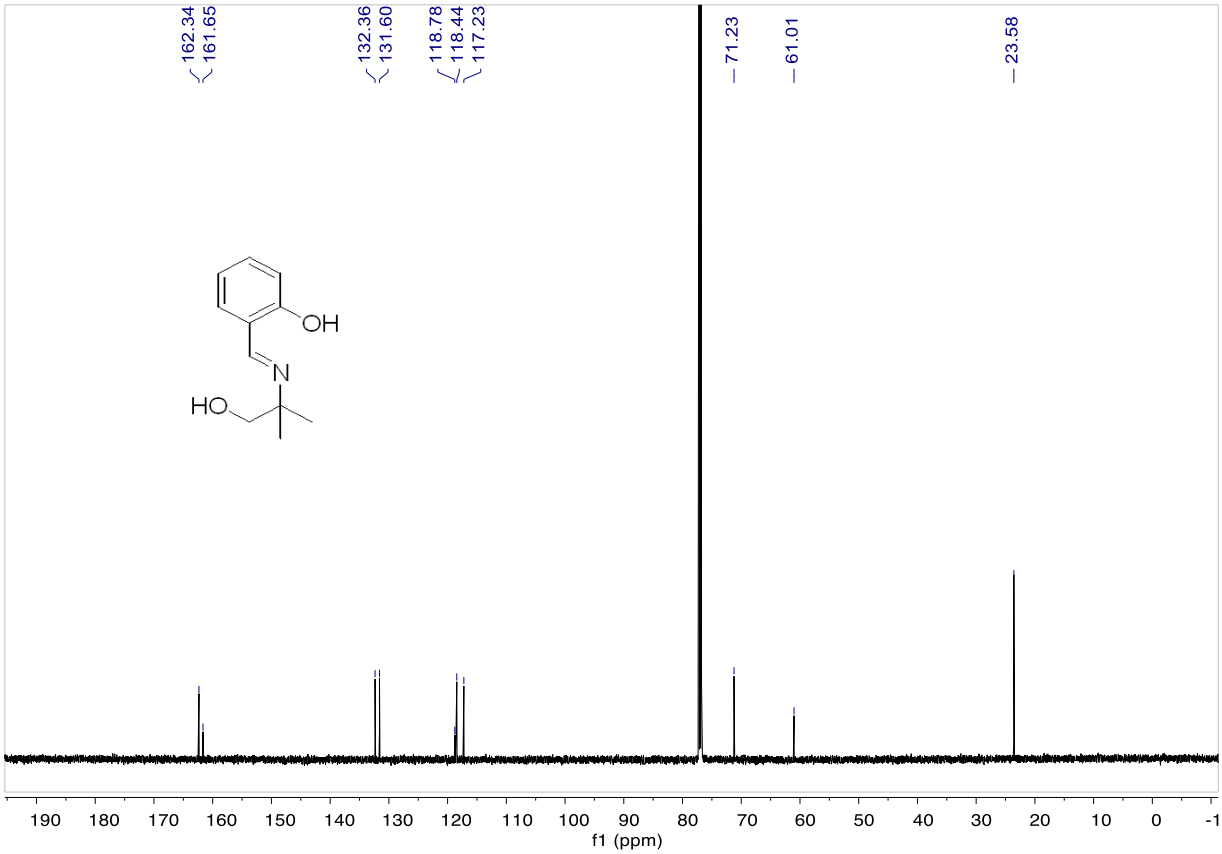
6.95
6.95
6.94
6.93
6.89
6.89
6.88
6.88
6.87
6.86
6.86
3.61
1.61
1.33
OH
N
HO
1.12
1.00
1.98
0.96
1.01
2.07
1.17
6.25
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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23.58
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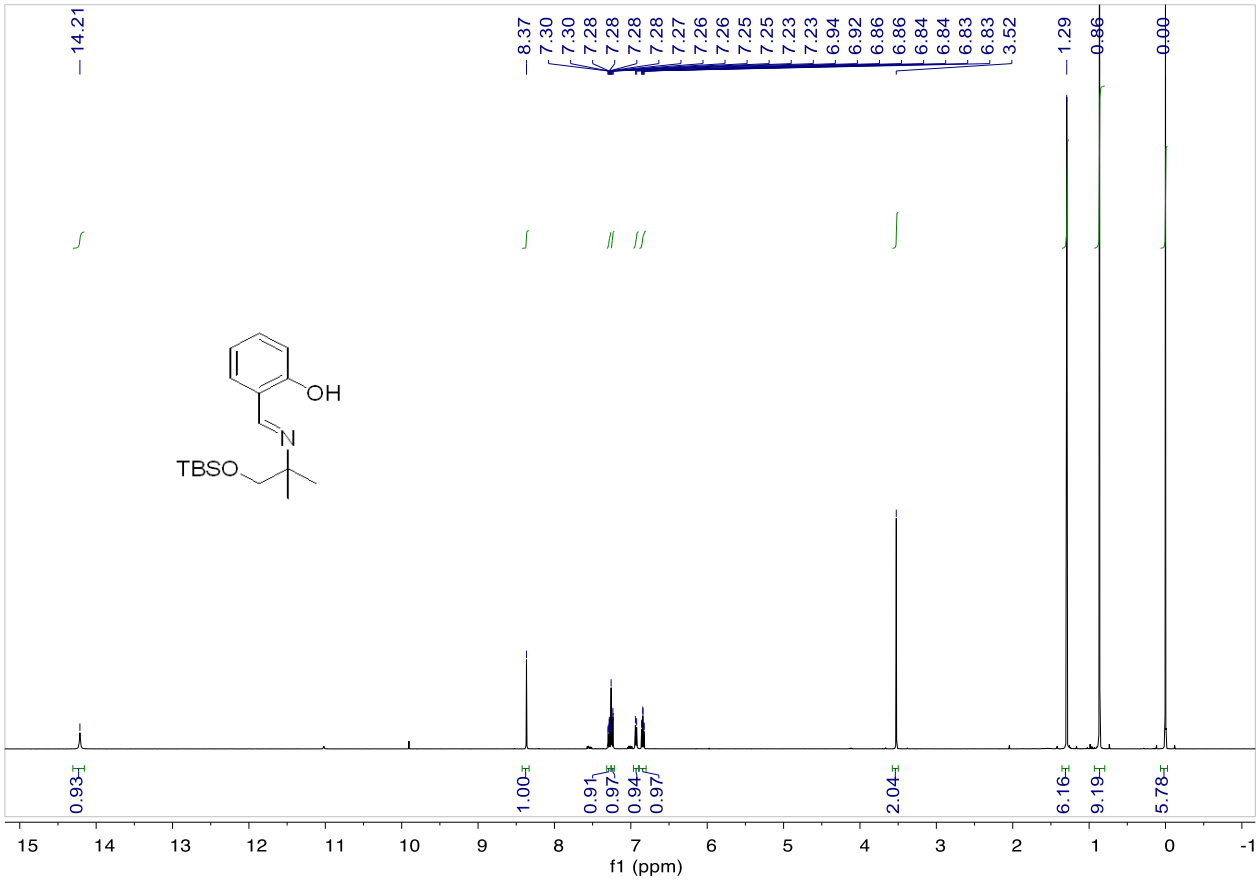
N
HO
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)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7.28
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7.28
7.27
7.26
7.26
7.25
7.25
7.23
7.23
6.94
6.92
6.86
6.86
6.84
6.84
6.83
6.83
3.52
1.29
0.86
0.00
OH
N
TBSO
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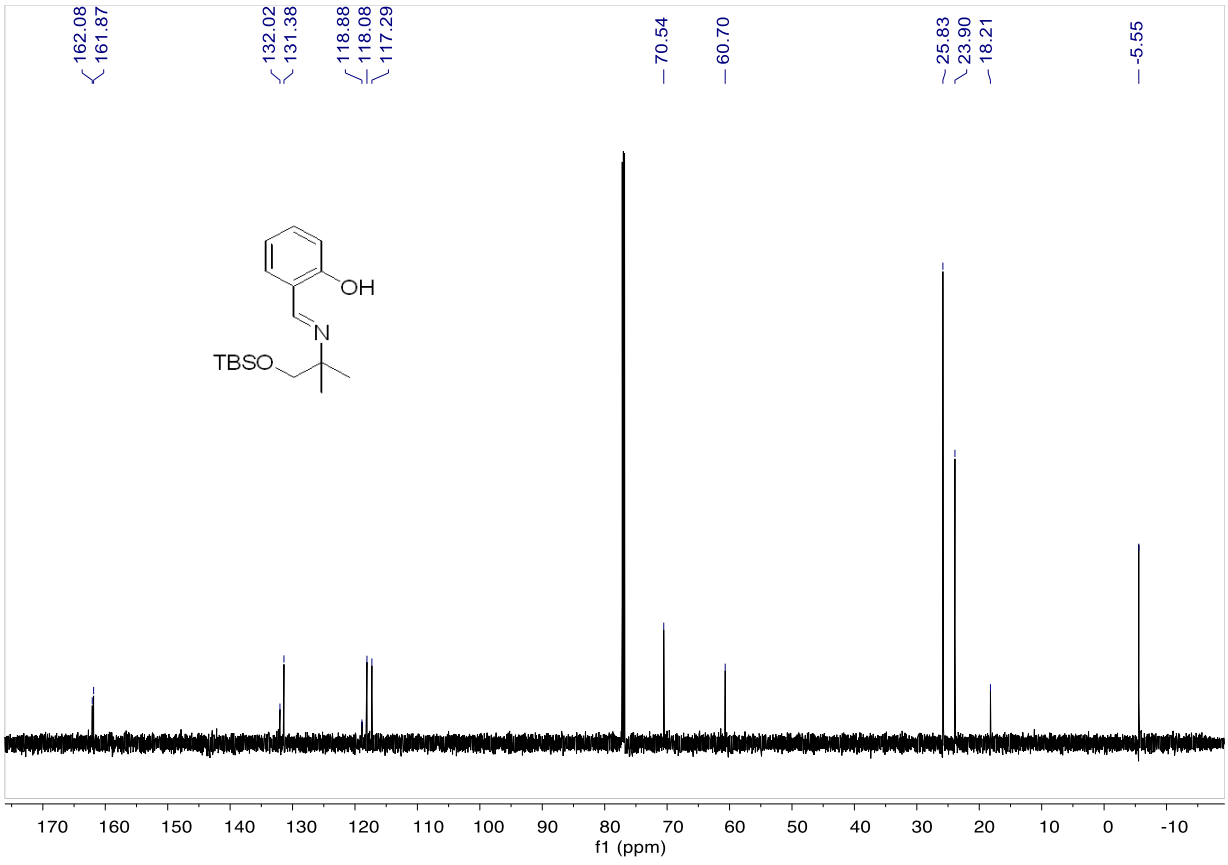
0.91
0.97
0.94
0.97
2.04
6.16
9.19
5.78
f1 (ppm)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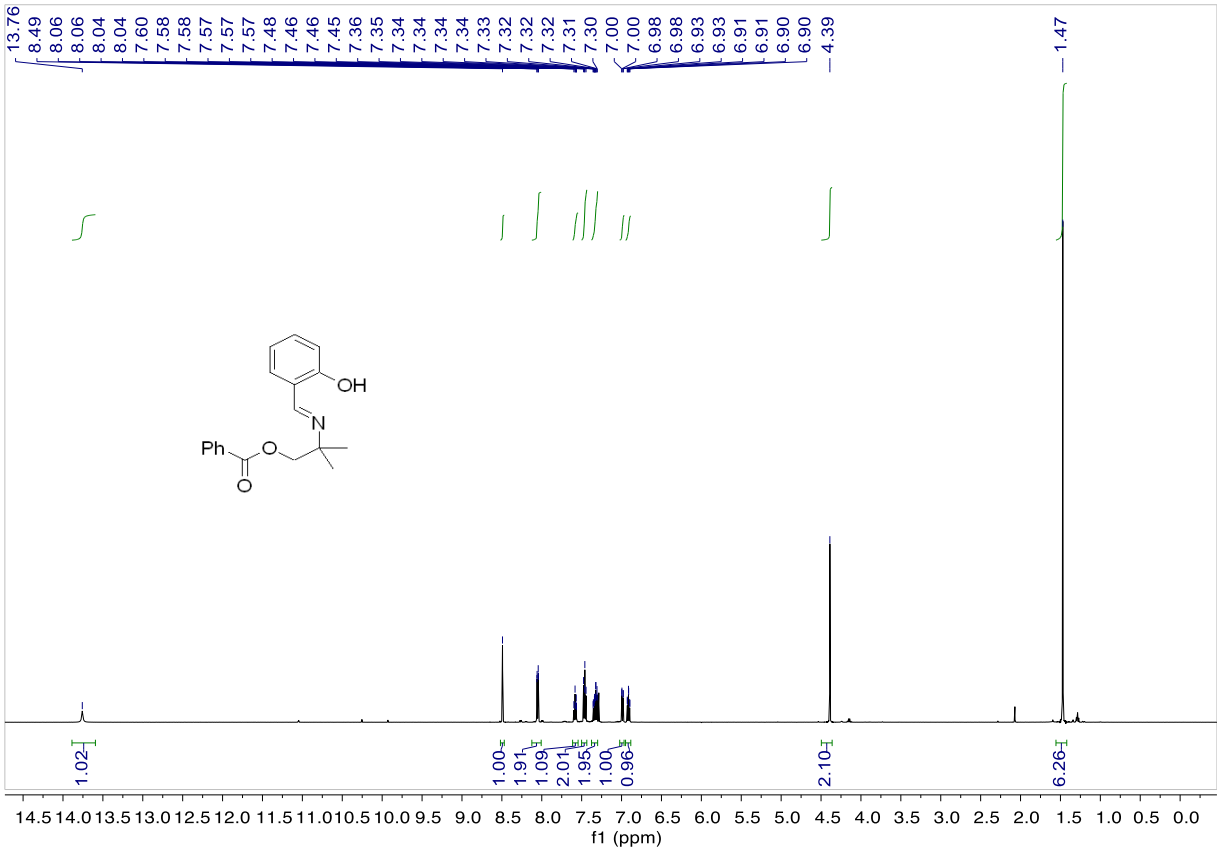
25.83
23.90
18.21
-5.55
OH
N
TBSO
f1 (ppm)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7.46
7.45
7.36
7.35
7.34
7.34
7.34
7.34
7.33
7.32
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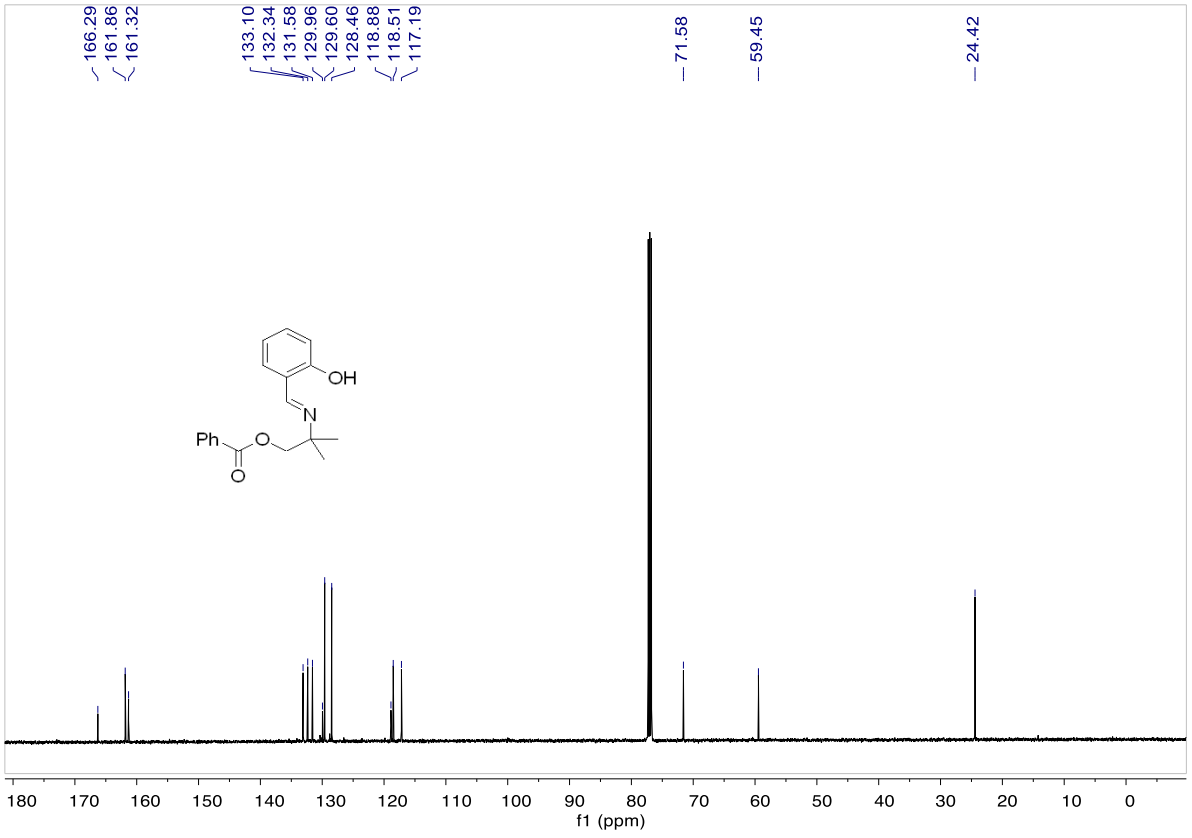
7.32
7.31
7.30
7.00
7.00
6.98
6.98
6.93
6.93
6.91
6.91
6.90
6.90
4.39
1.47
OH
N
Ph
O
O
1.02
1.00
1.91
1.09
2.01
1.95
1.00
0.96
2.10
6.26
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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118.51
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59.45
24.42
OH
N
Ph
O
O
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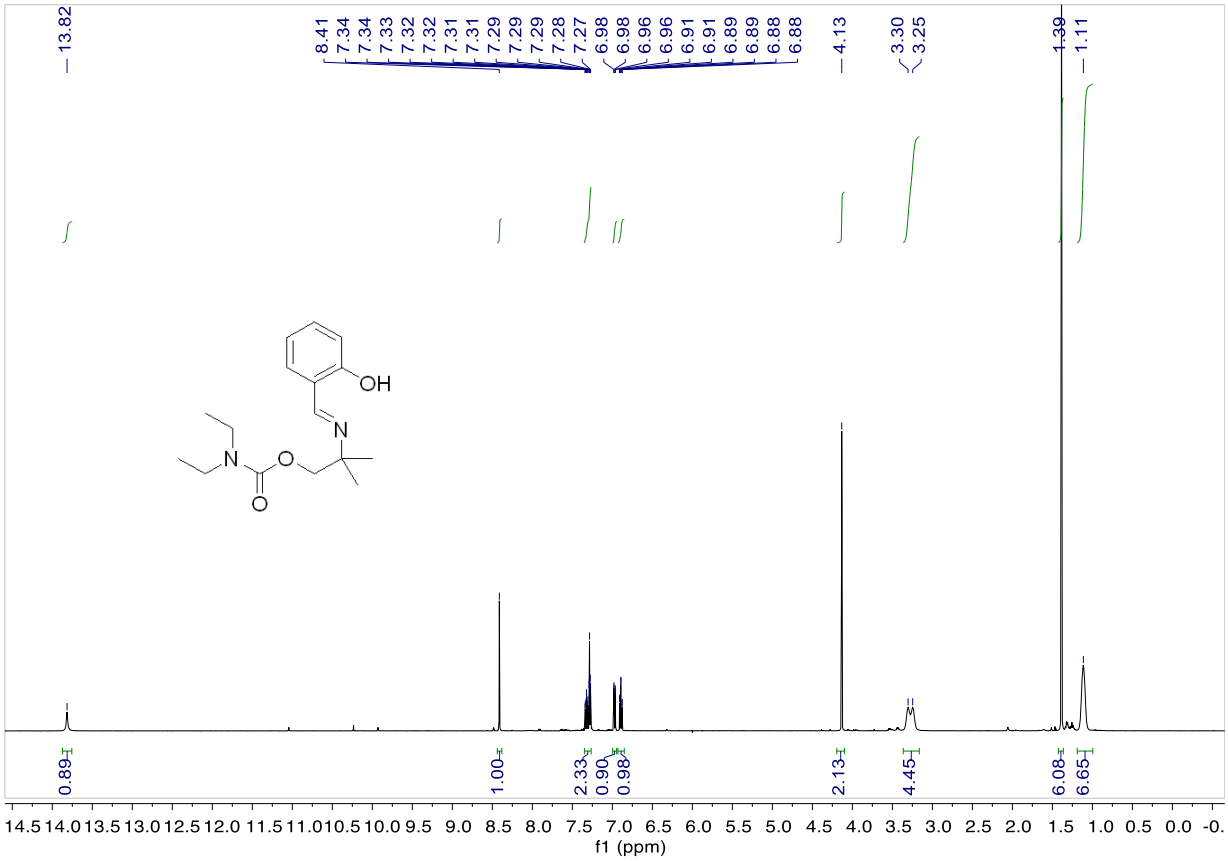
f1 (ppm)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7.29
7.28
7.27
6.98
6.98
6.96
6.96
6.91
6.91
6.89
6.89
6.88
6.88
4.13
3.30
3.25
1.39
1.11
OH
N
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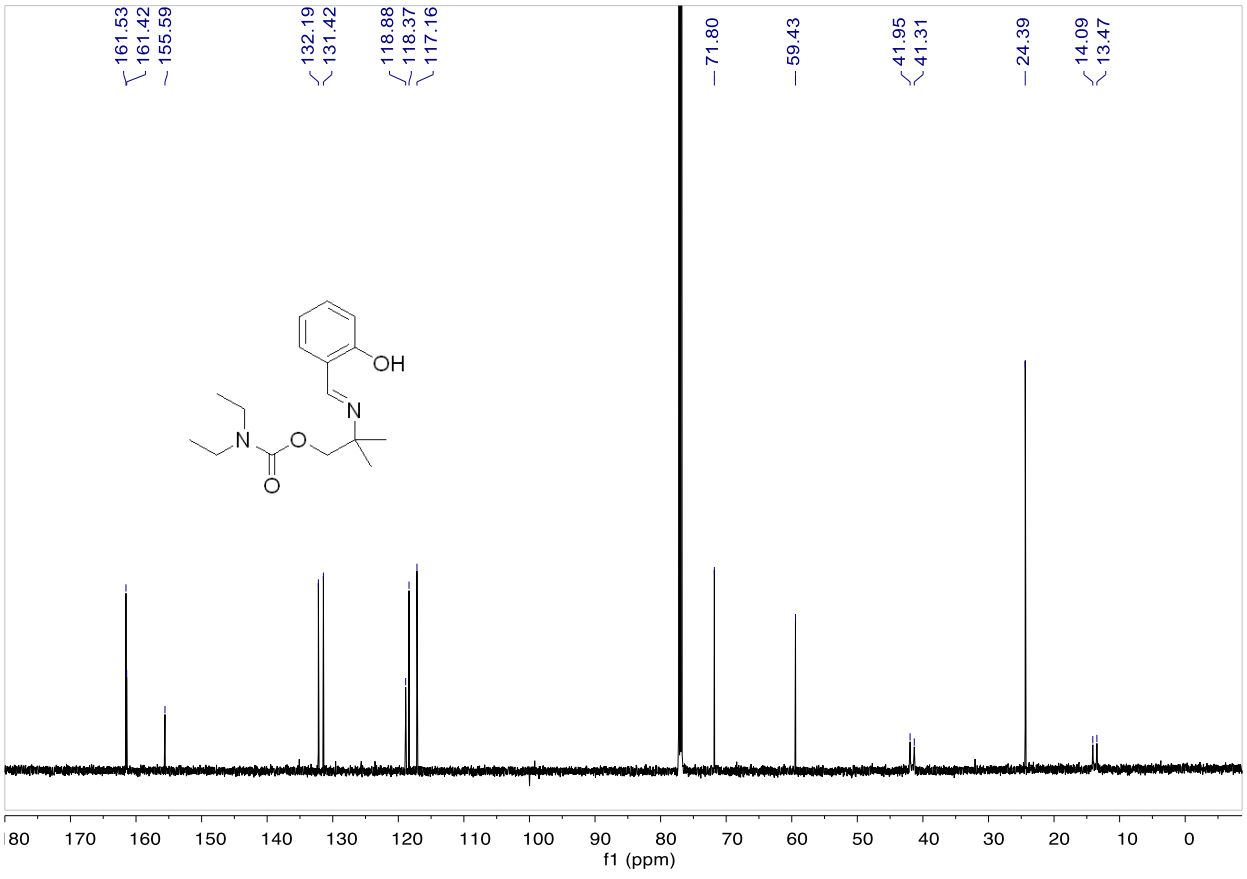
1.00
2.33
0.90
0.98
2.13
4.45
6.08
6.65
f1 (ppm)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OH
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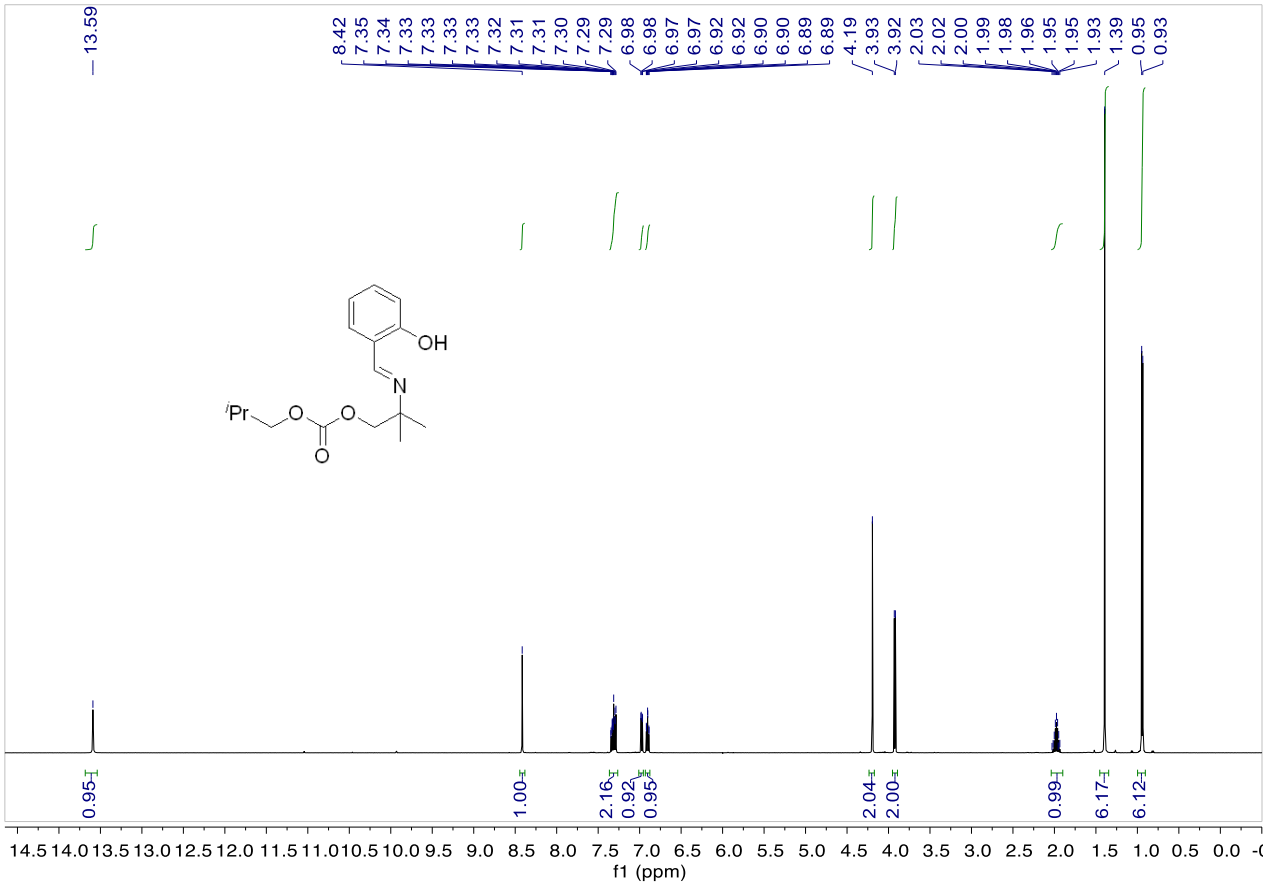
N
O
O
f1 (ppm)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6.97
6.97
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6.90
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3.92
2.03
2.02
2.00
1.99
1.98
1.96
1.95
1.95
1.93
1.39
0.95
0.93
OH
N
iPr
O
O
O
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0.92
0.95
2.04
2.00
0.99
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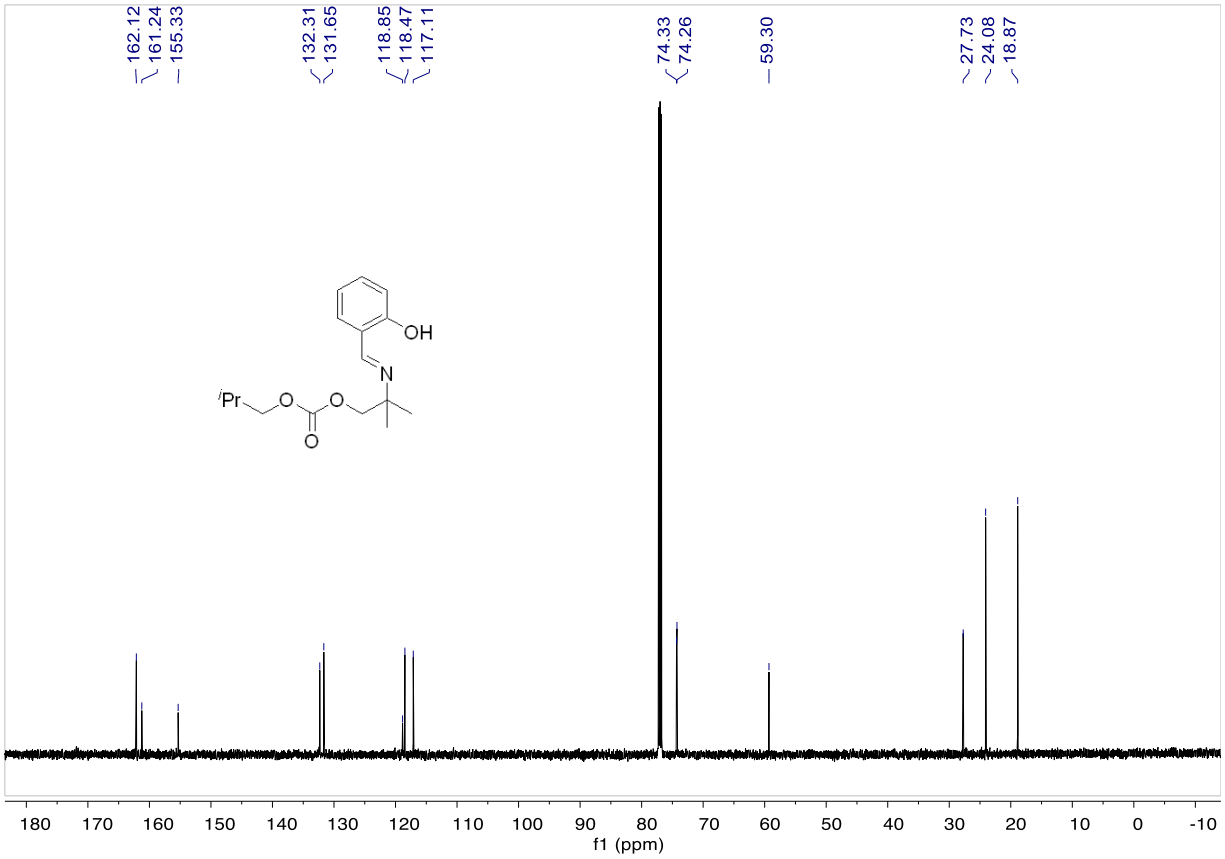
6.12
f1 (ppm)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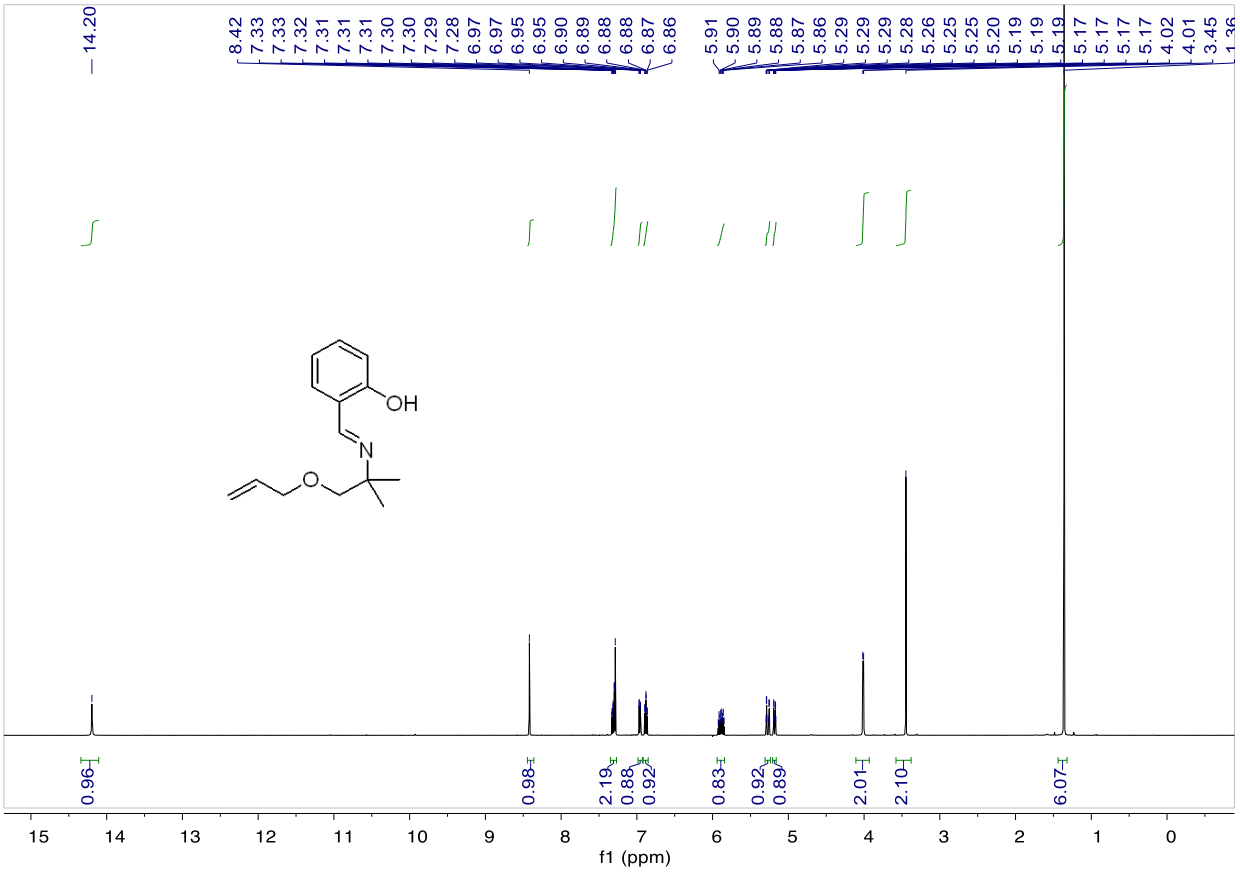
N
iPr
O
O
O
f1 (ppm)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5.88
5.87
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5.29
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5.29
5.28
5.26
5.25
5.25
5.20
5.19
5.19
5.19
5.17
5.17
5.17
5.17
4.02
4.01
3.45
OH
N
O
0.96
0.98
2.19
0.88
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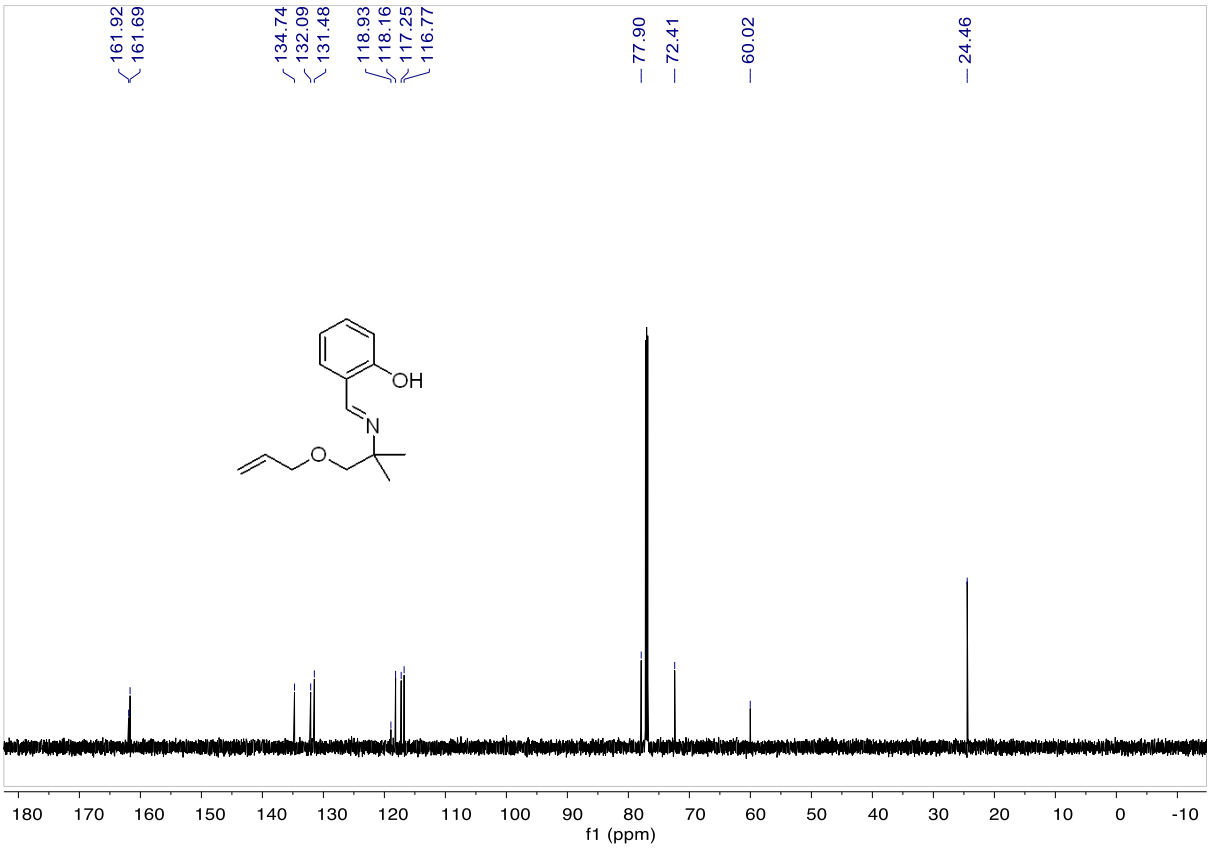
0.92
0.89
2.01
2.10
6.07
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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118.93
118.16
117.25
116.77
77.90
72.41
60.02
24.46
OH
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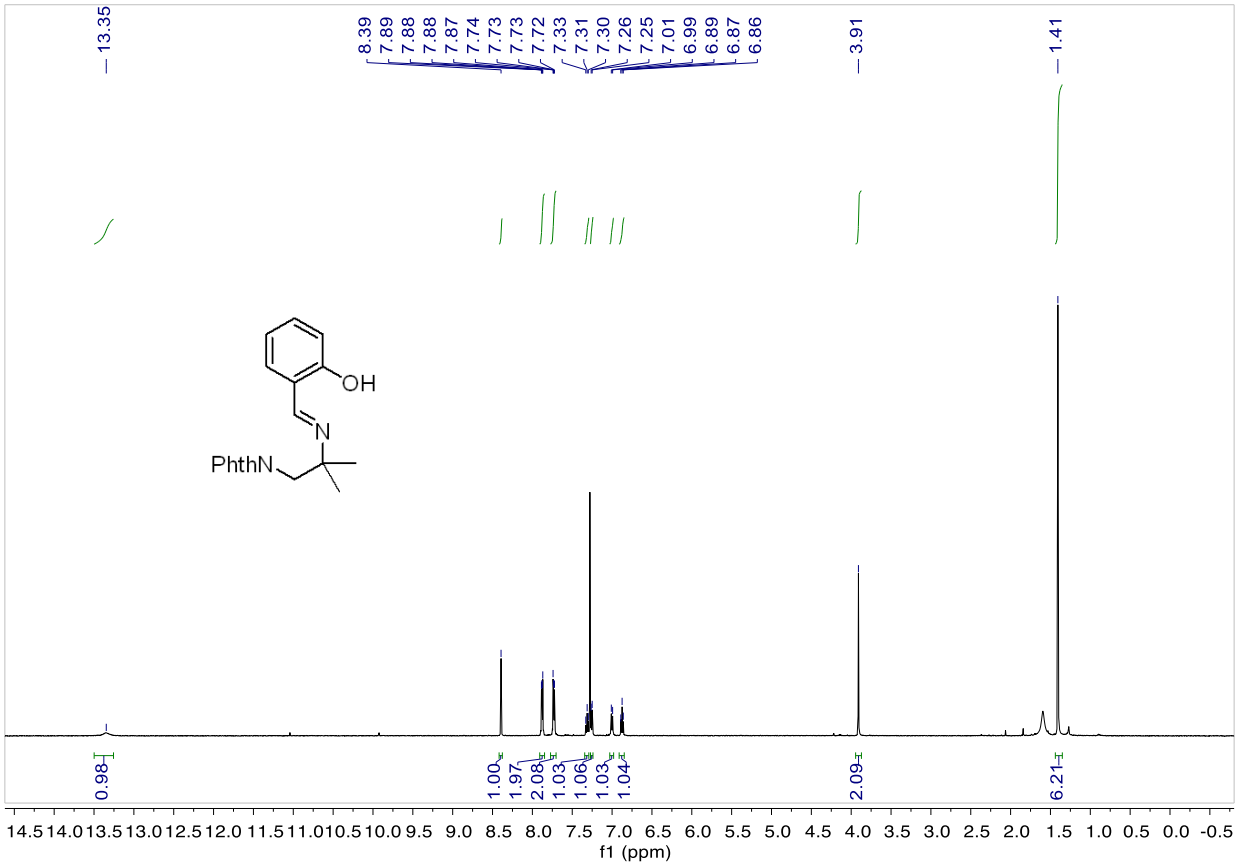
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.72
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7.31
7.30
7.26
7.25
7.01
6.99
6.89
6.87
6.86
3.91
1.41
OH
N
PhthN
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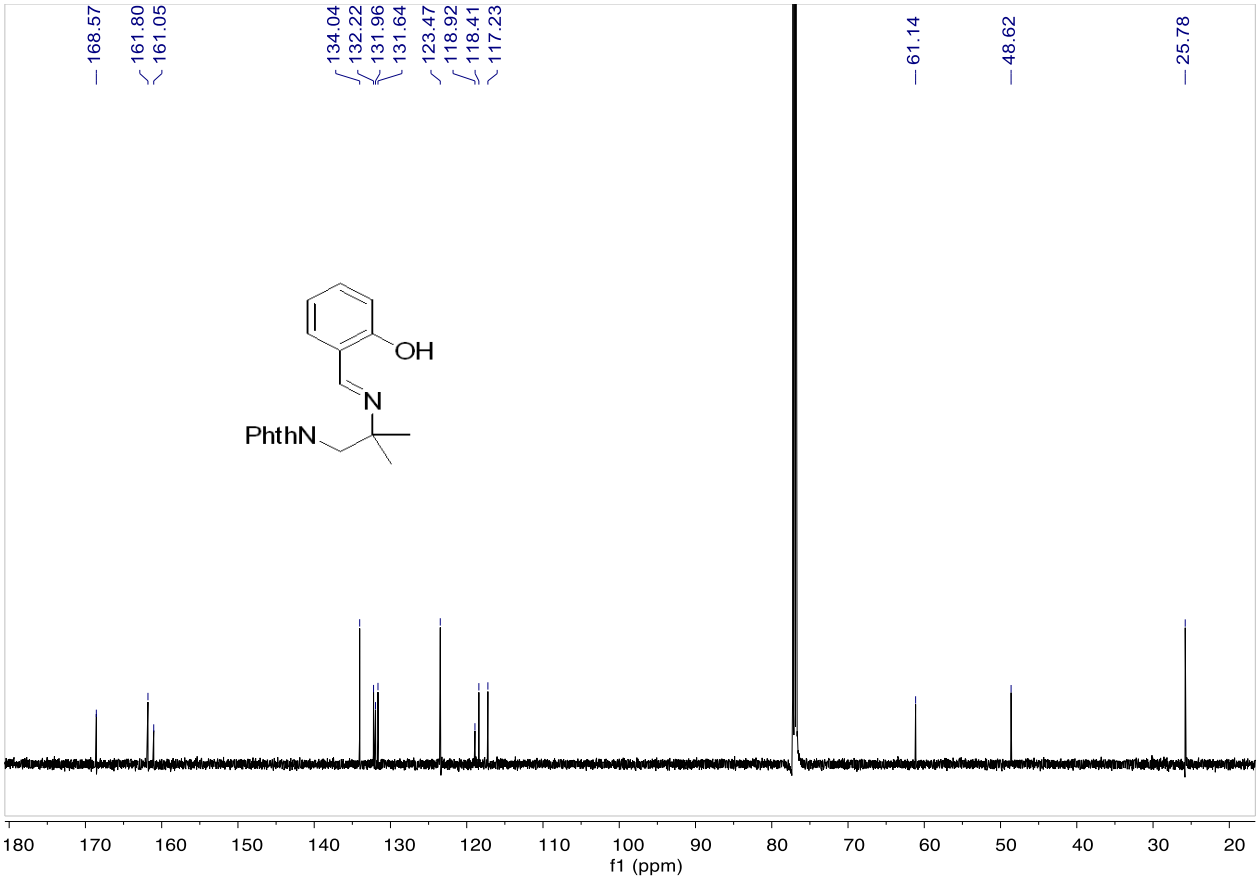
1.97
2.08
1.03
1.06
1.03
1.04
2.09
6.21
f1 (ppm)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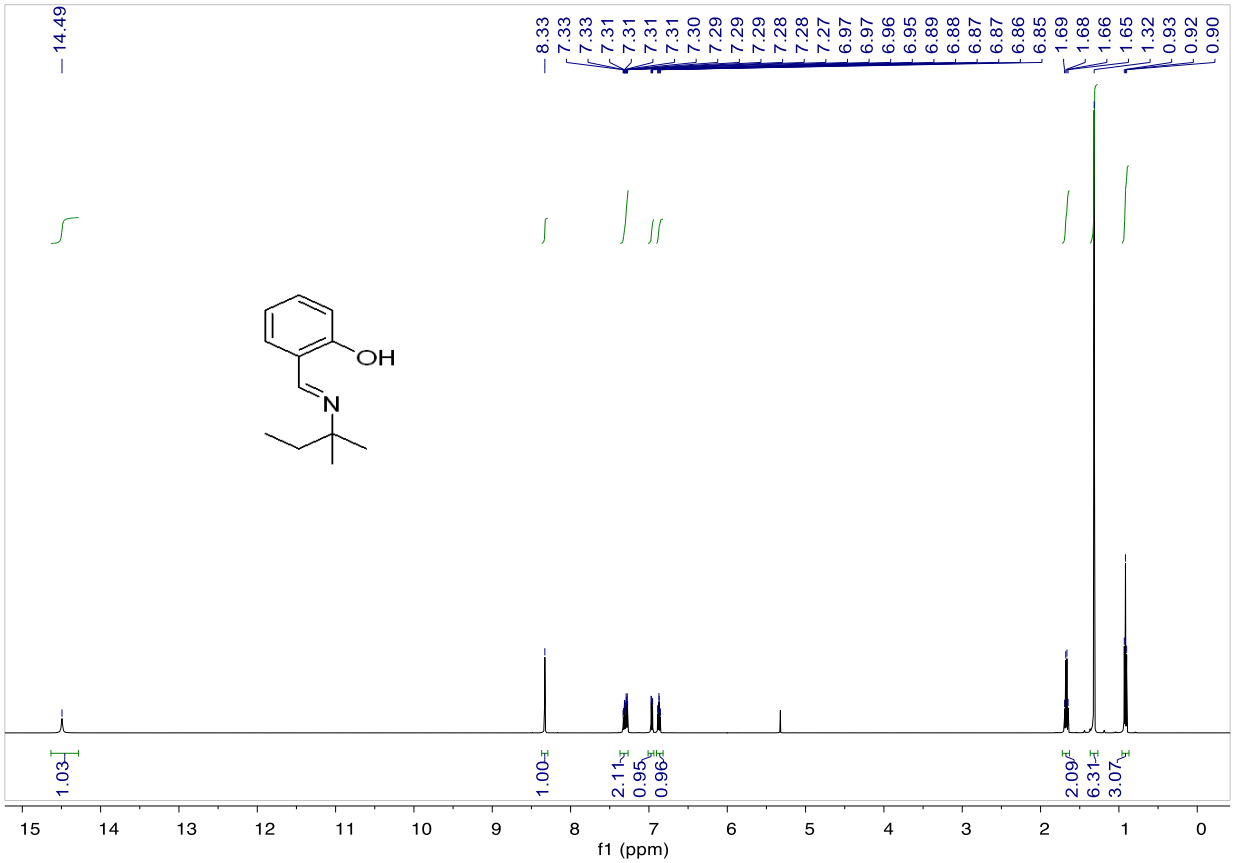
123.47
118.92
118.41
117.23
61.14
48.62
25.78
OH
N
PhthN
f1 (ppm)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7.33
7.31
7.31
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7.31
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7.29
7.29
7.29
7.28
7.28
7.27
6.97
6.96
6.95
6.89
6.88
6.87
6.87
6.86
6.85
1.69
1.68
1.66
1.65
1.32
0.93
0.92
0.90
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N
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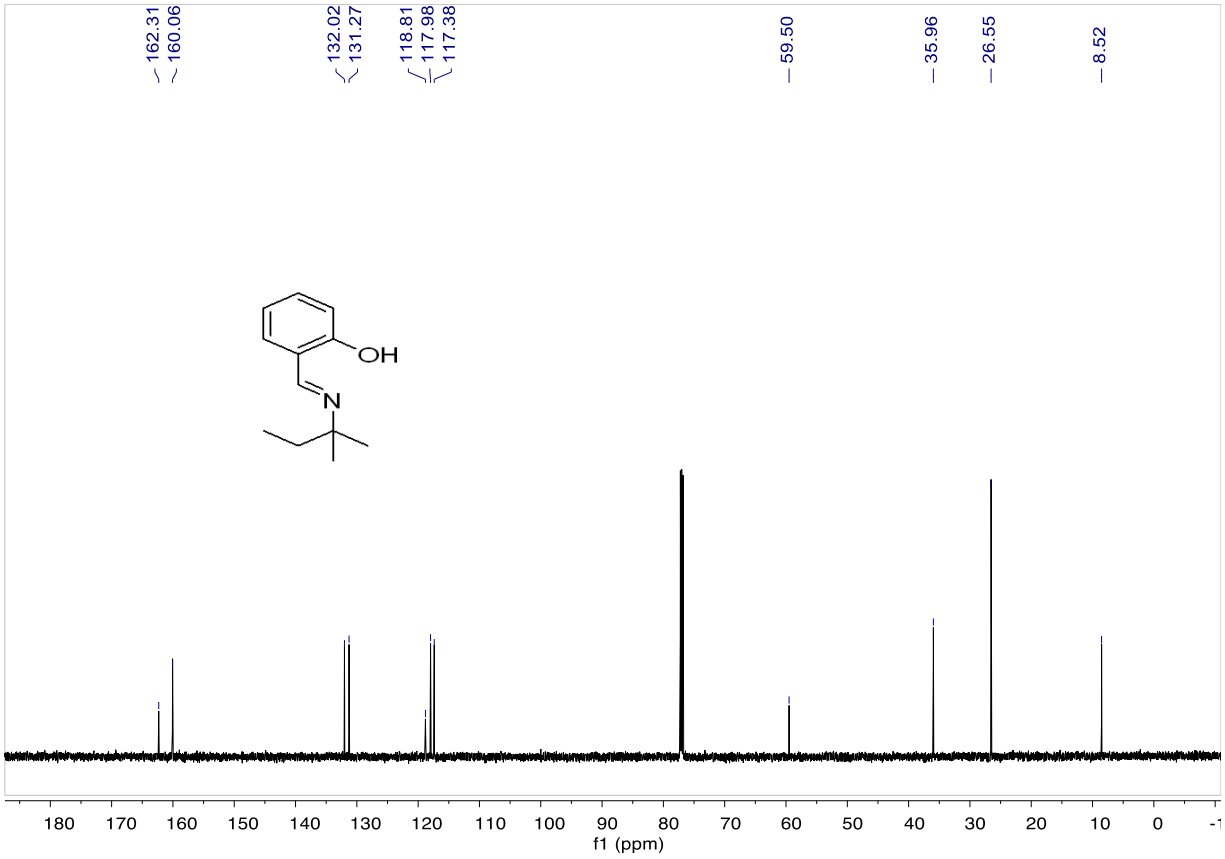
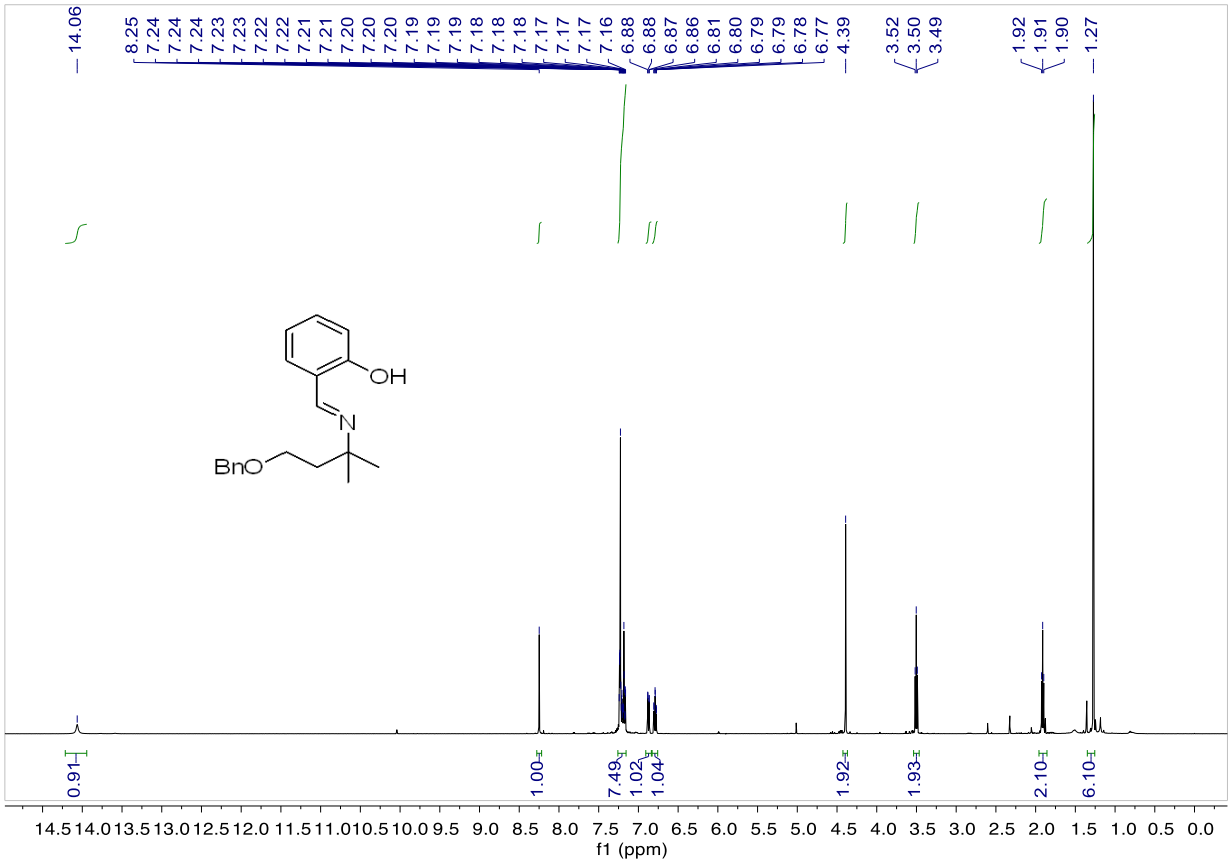
1.00
2.11
0.95
0.96
2.09
6.31
3.07
f1 (ppm)


162.31
160.06
132.02
131.27
118.81
117.98
117.38
59.50
35.96
26.55
8.52
OH
N
f1 (ppm)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8.25
7.24
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.18
7.17
7.17
7.17
7.16
6.88
6.88
6.87
6.86
6.81
6.80
6.79
6.79
6.78
6.77
4.39
3.52
3.50
3.49
1.92
1.91
1.90
1.27
OH
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BnO
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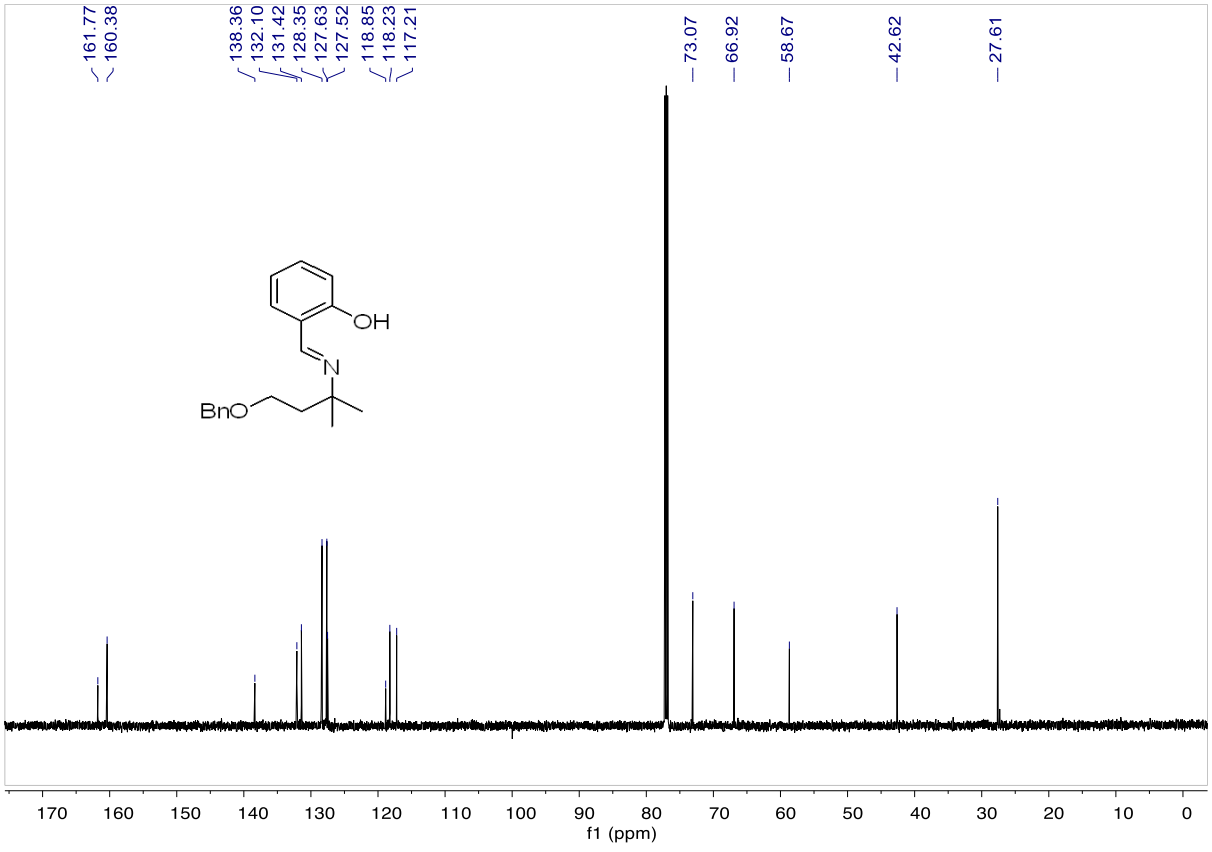
1.02
1.04
1.92
1.93
2.10
6.10
f1 (ppm)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131.42
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127.63
127.52
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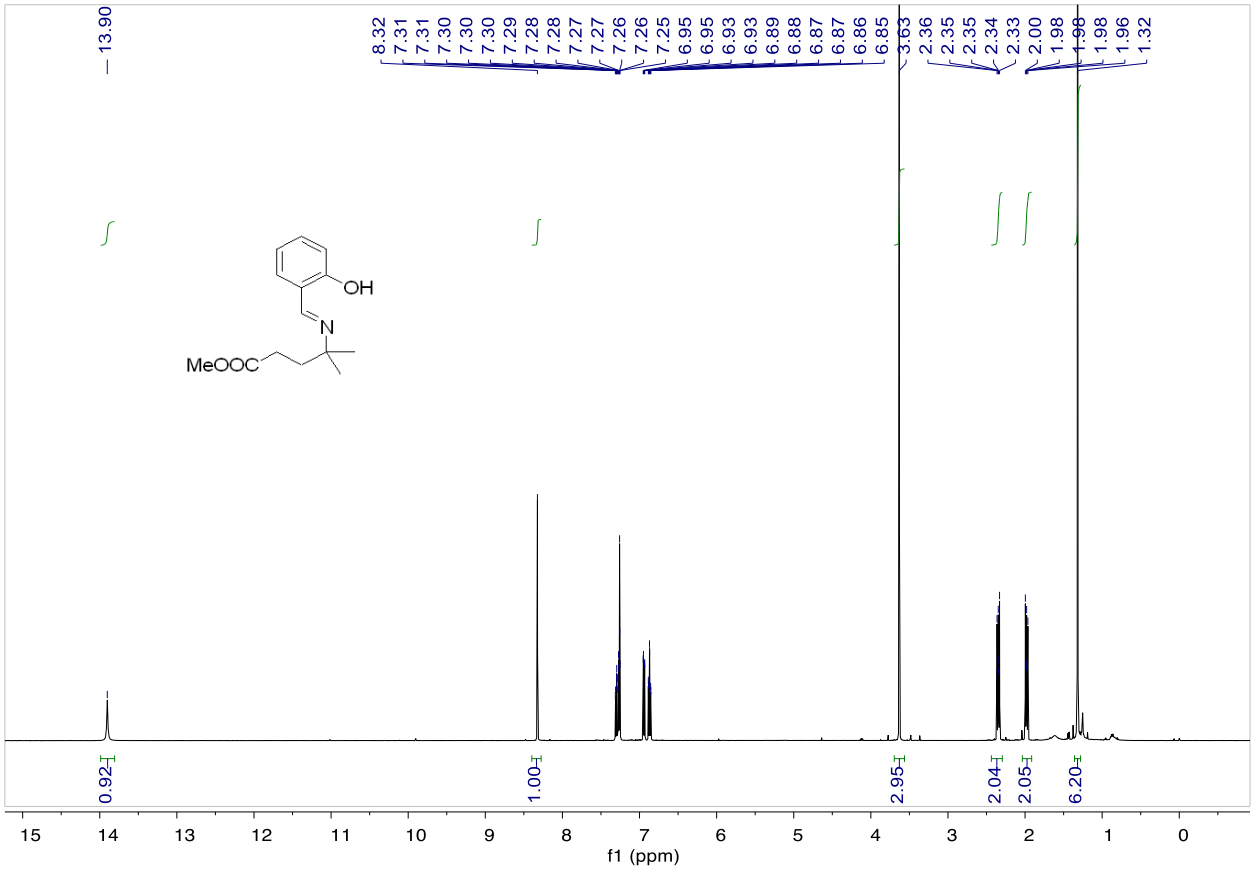
117.21
73.07
66.92
58.67
42.62
27.61
OH
N
BnO
f1 (ppm)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8.32
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7.31
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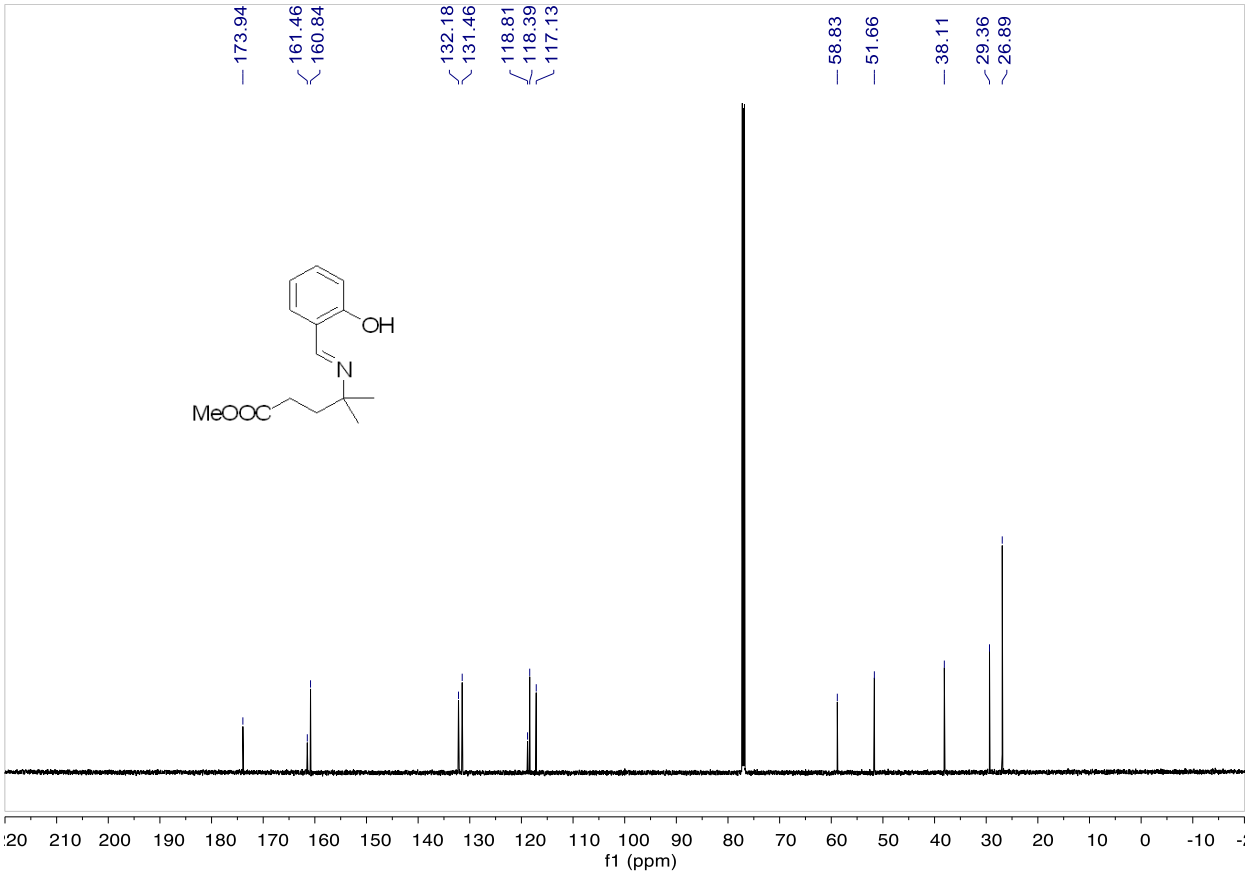
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
6.95
6.95
6.93
6.93
6.89
6.88
6.87
6.87
6.86
6.85
3.63
2.36
2.35
2.35
2.34
2.33
2.00
1.98
1.98
1.98
1.96
1.32
OH
N
MeOOC
0.92
1.00
2.95
2.04
2.05
6.20
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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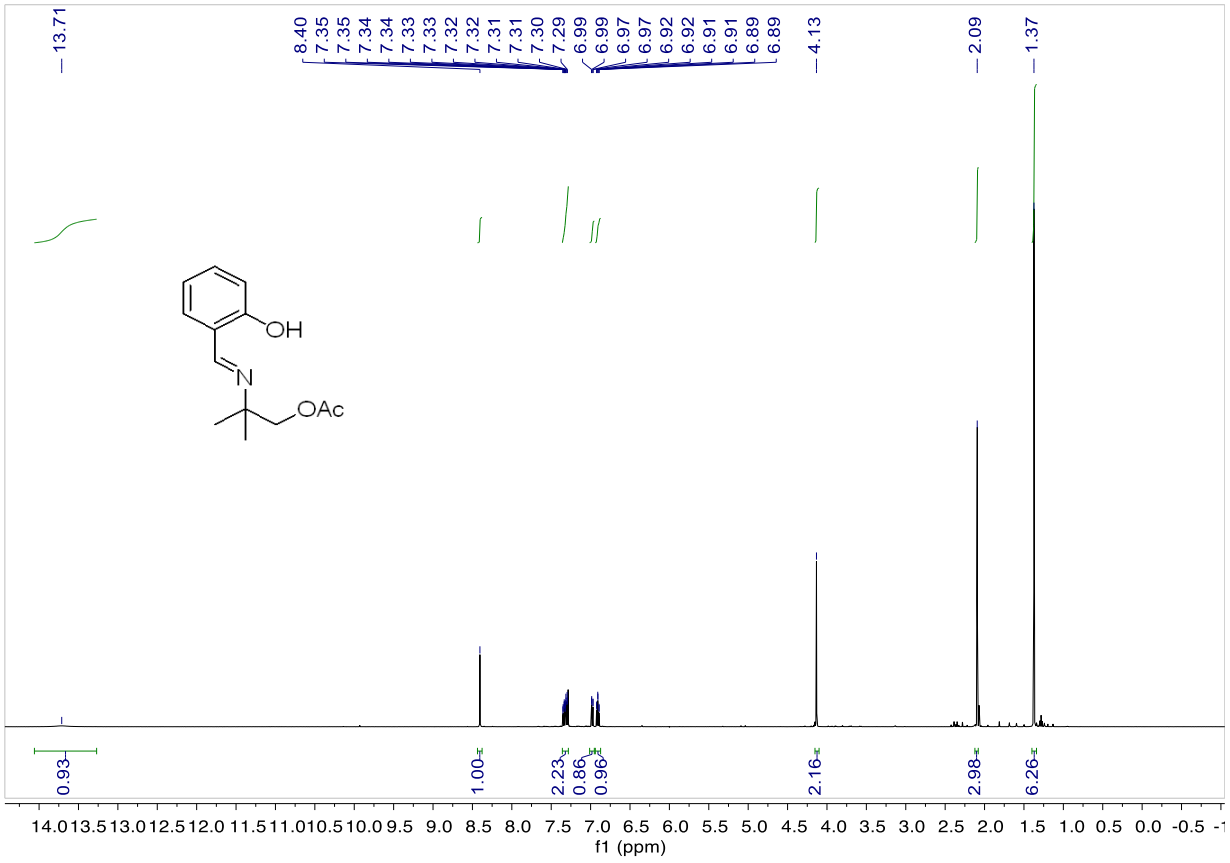
161.46
160.84
132.18
131.46
118.81
118.39
117.13
58.83
51.66
38.11
29.36
26.89
OH
N
MeOOC
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.29
6.99
6.99
6.97
6.97
6.92
6.92
6.91
6.91
6.89
6.89
4.13
2.09
1.37
OH
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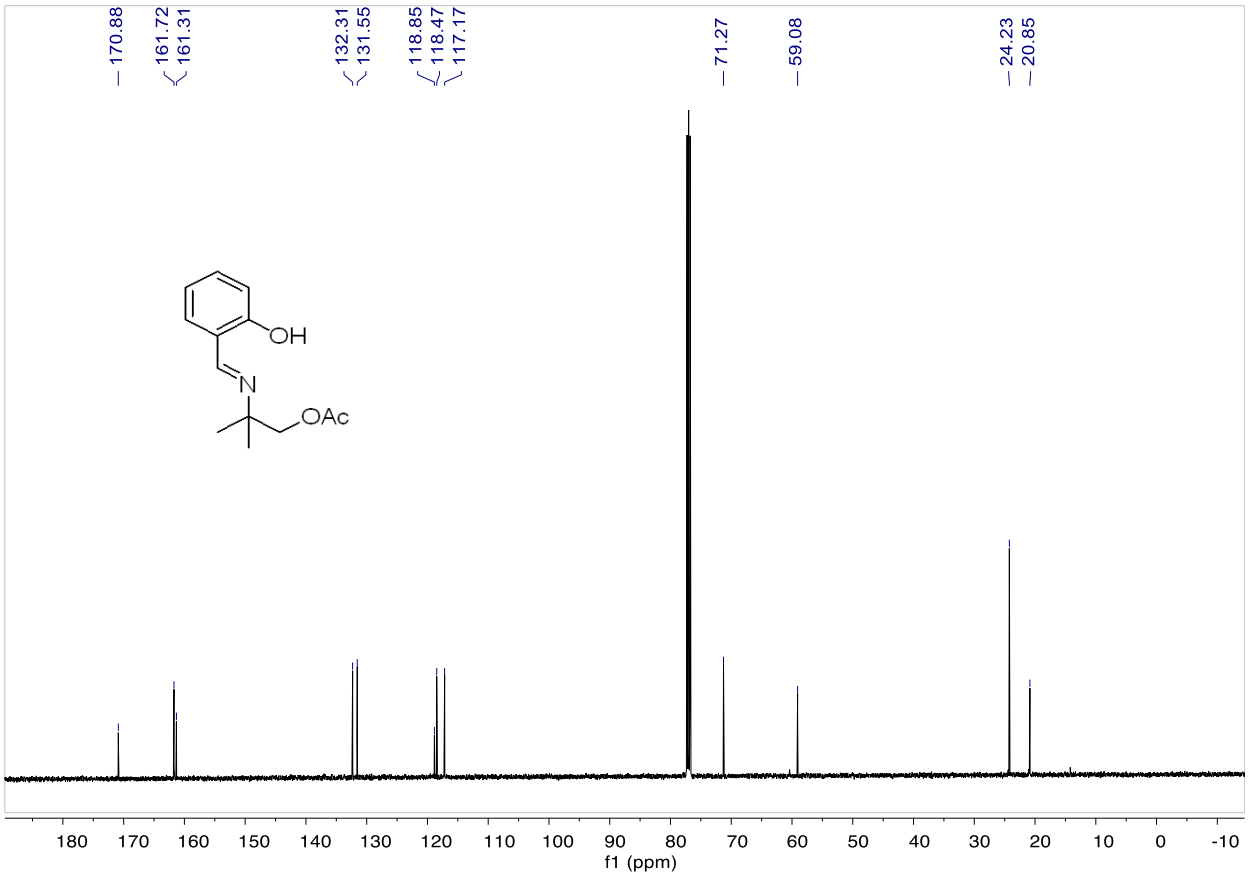
OAc
0.93
1.00
2.23
0.86
0.96
2.16
2.98
6.26
f1 (ppm)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161.72
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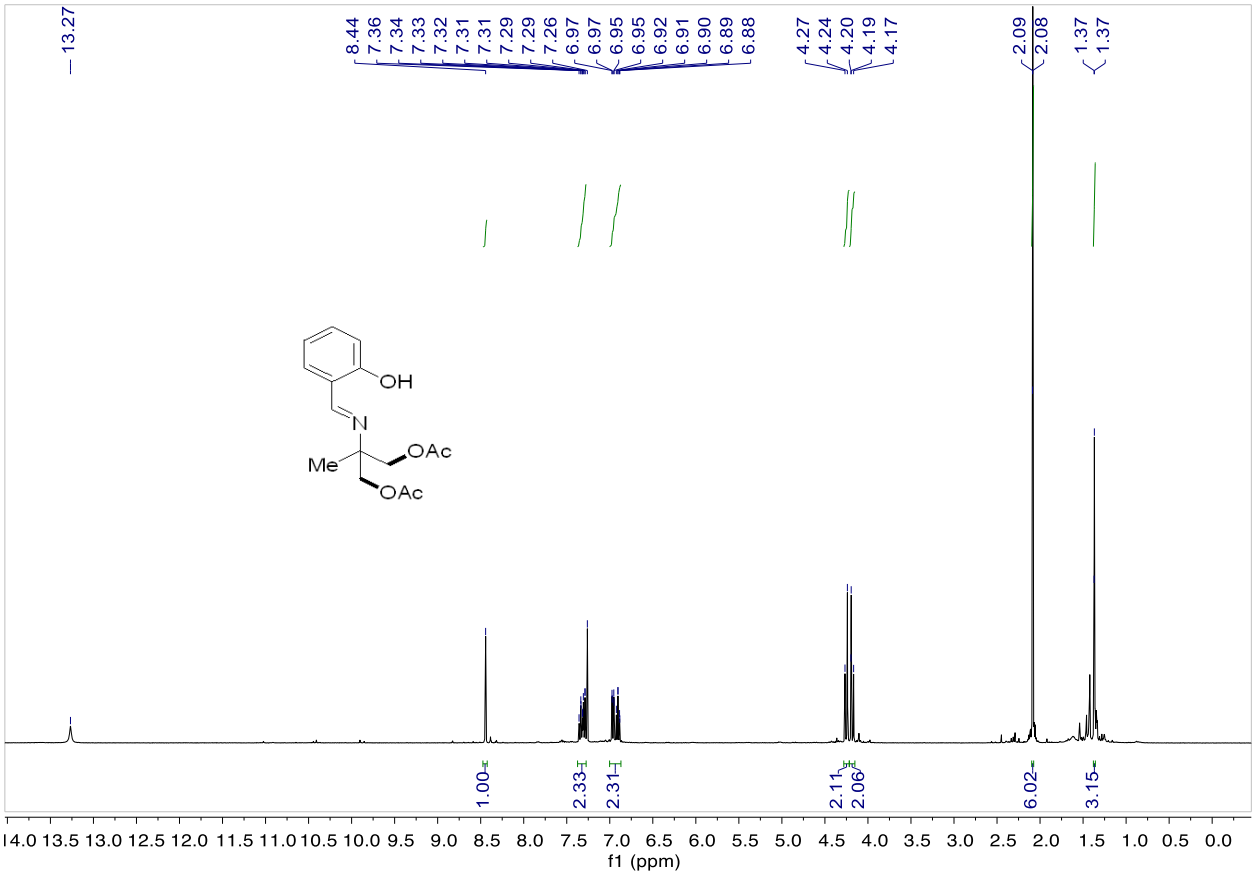
118.47
117.17
71.27
59.08
24.23
20.85
OH
N
OAc
f1 (ppm)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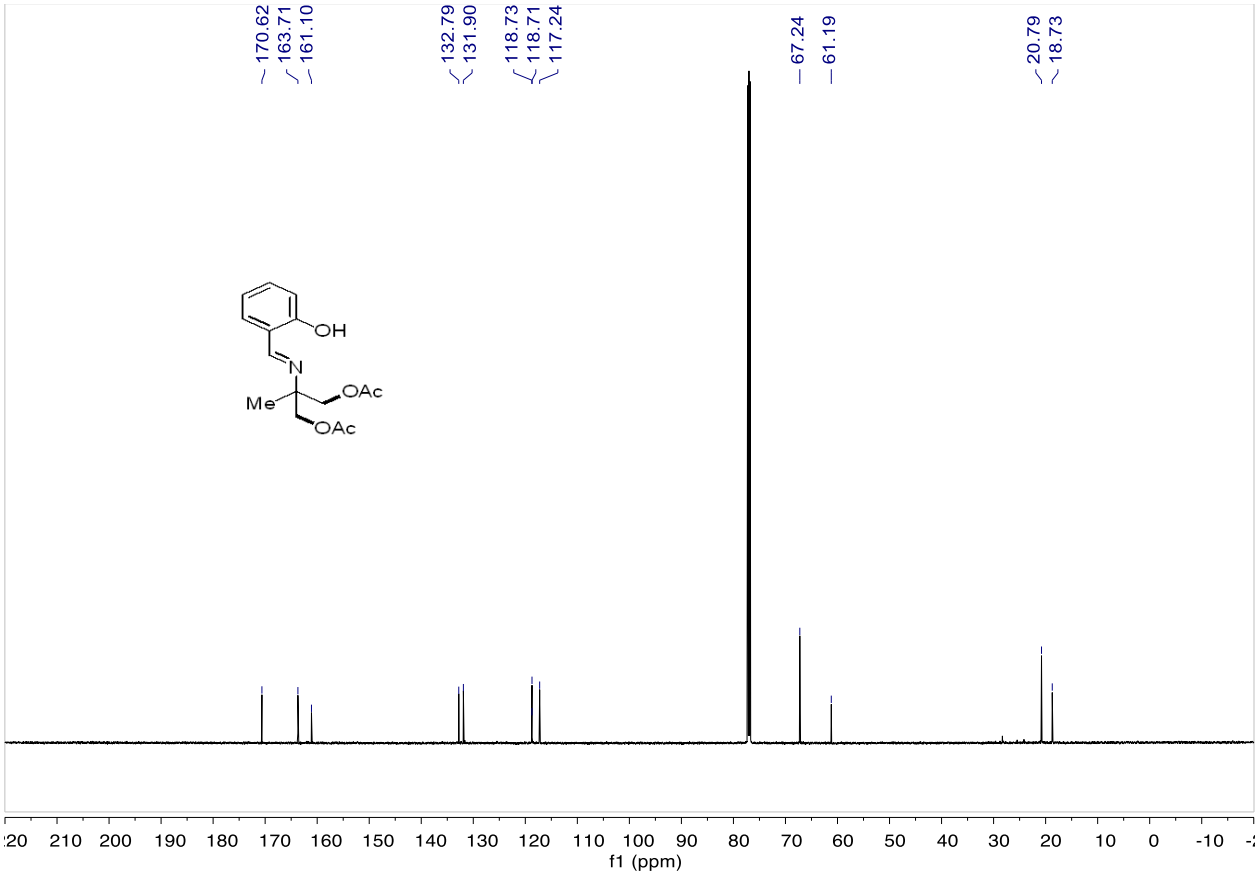
7.31
7.31
7.29
7.29
7.26
6.97
6.97
6.95
6.95
6.92
6.91
6.90
6.89
6.88
4.27
4.24
4.20
4.19
4.17
2.09
2.08
1.37
1.37
OH
N
OAc
Me
OAc
1.00
2.33
2.31
2.11
2.06
6.02
3.15
f1 (ppm)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131.90
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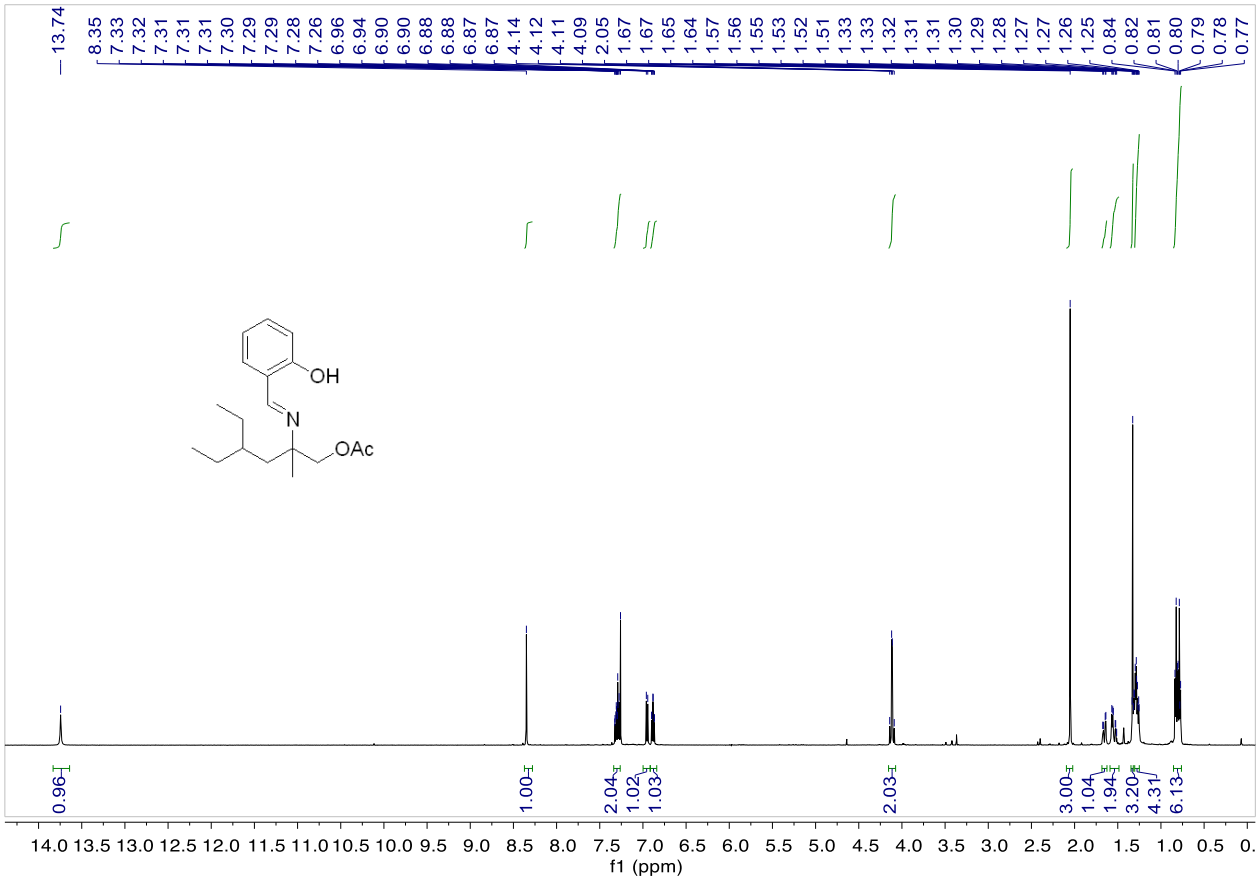
117.24
67.24
61.19
20.79
18.73
OH
N
OAc
Me
OAc
f1 (ppm)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7.31
7.30
7.29
7.29
7.28
7.26
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6.90
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6.88
6.87
6.87
4.14
4.12
4.11
4.09
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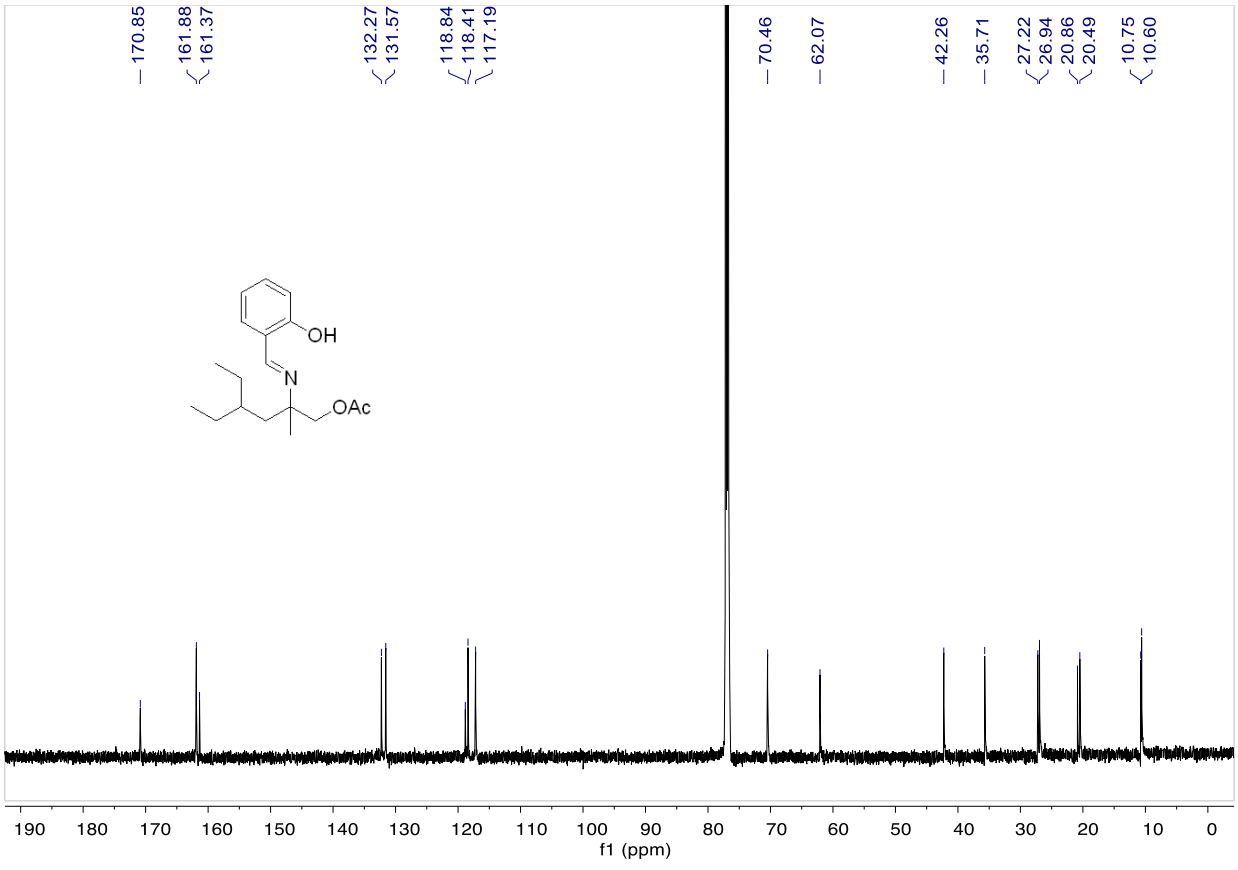
1.57
1.56
1.55
1.53
1.52
1.51
1.33
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.27
1.27
1.26
1.25
0.84
0.82
0.81
0.80
0.79
0.78
0.77
OH
N
OAc
0.96
1.00
2.04
1.02
1.03
2.03
3.00
1.04
1.94
3.20
4.31
6.13
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)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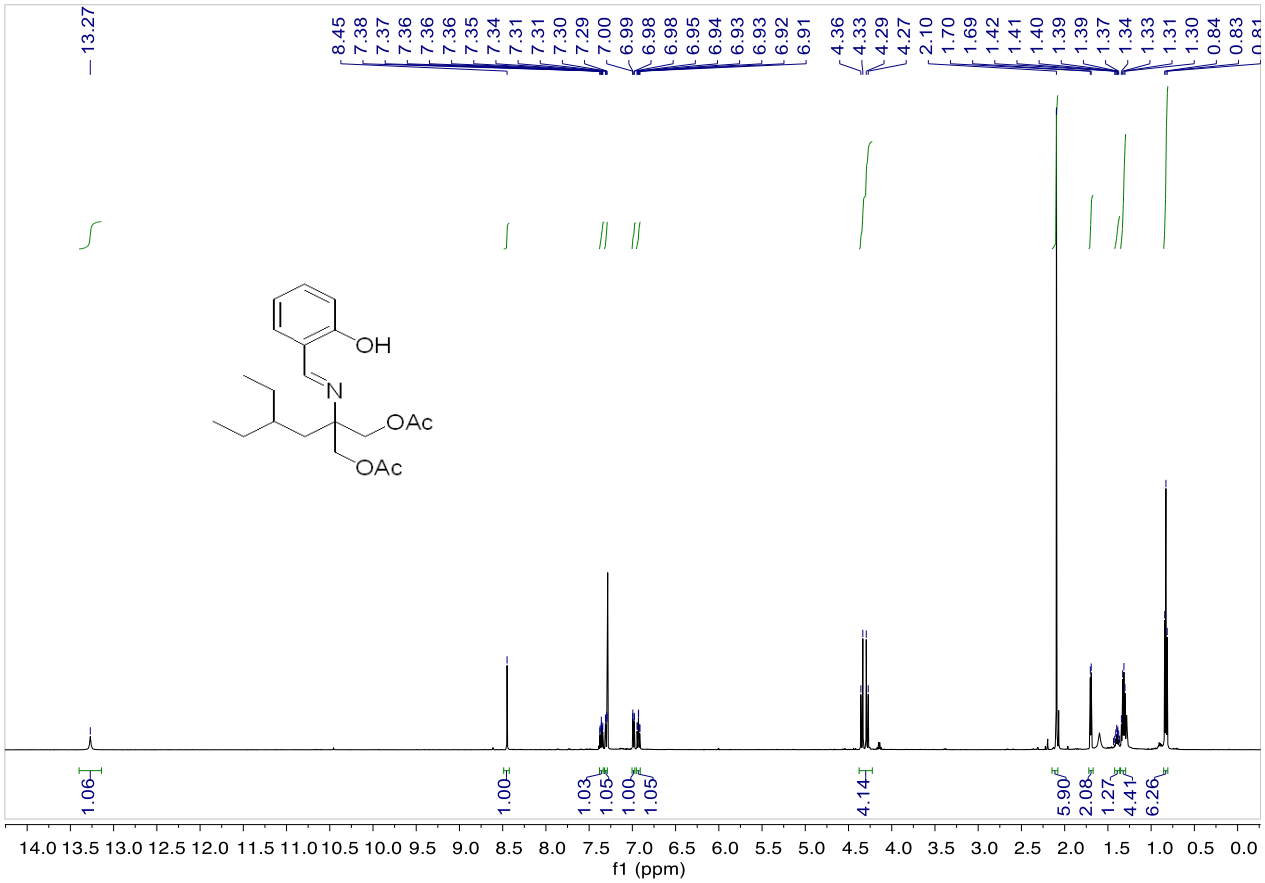
70.46
62.07
42.26
35.71
27.22
26.94
20.86
20.49
10.75
10.60
OH
N
OAc
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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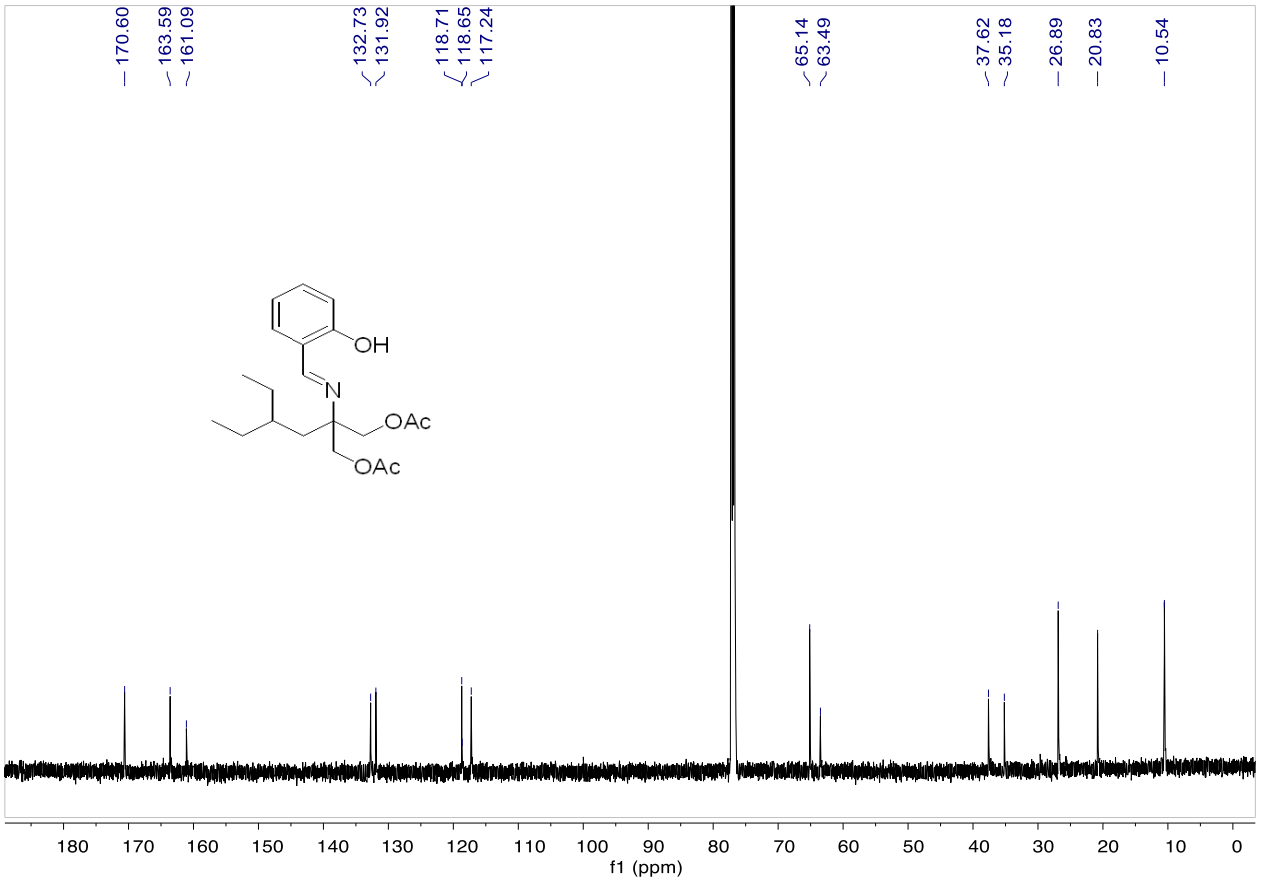
7.31
7.31
7.30
7.29
7.00
6.99
6.98
6.98
6.95
6.94
6.93
6.93
6.92
6.91
4.36
4.33
4.29
4.27
2.10
1.70
1.69
1.42
1.41
1.40
1.39
1.39
1.37
1.34
1.33
1.31
1.30
0.84
0.83
OH
N
OAc
OAc
1.06
1.00
1.03
1.05
1.00
1.05
4.14
5.90
2.08
1.27
4.41
6.26
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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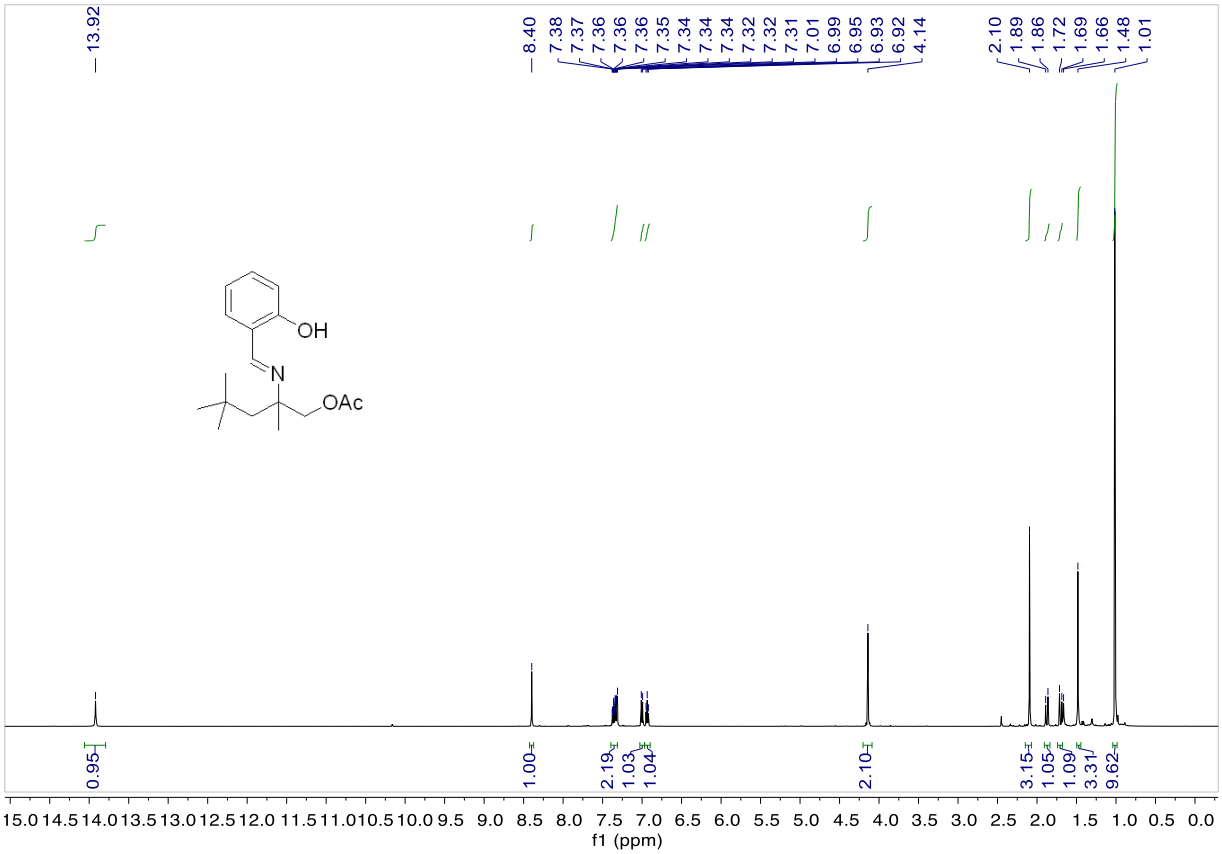
118.65
117.24
65.14
63.49
37.62
35.18
26.89
20.83
10.54
OH
N
OAc
OAc
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.36
7.36
7.35
7.34
7.34
7.34
7.32
7.32
7.31
7.01
6.99
6.95
6.93
6.92
4.14
2.10
1.89
1.86
1.72
1.69
1.66
1.48
1.01
OH
N
OAc
0.95
1.00
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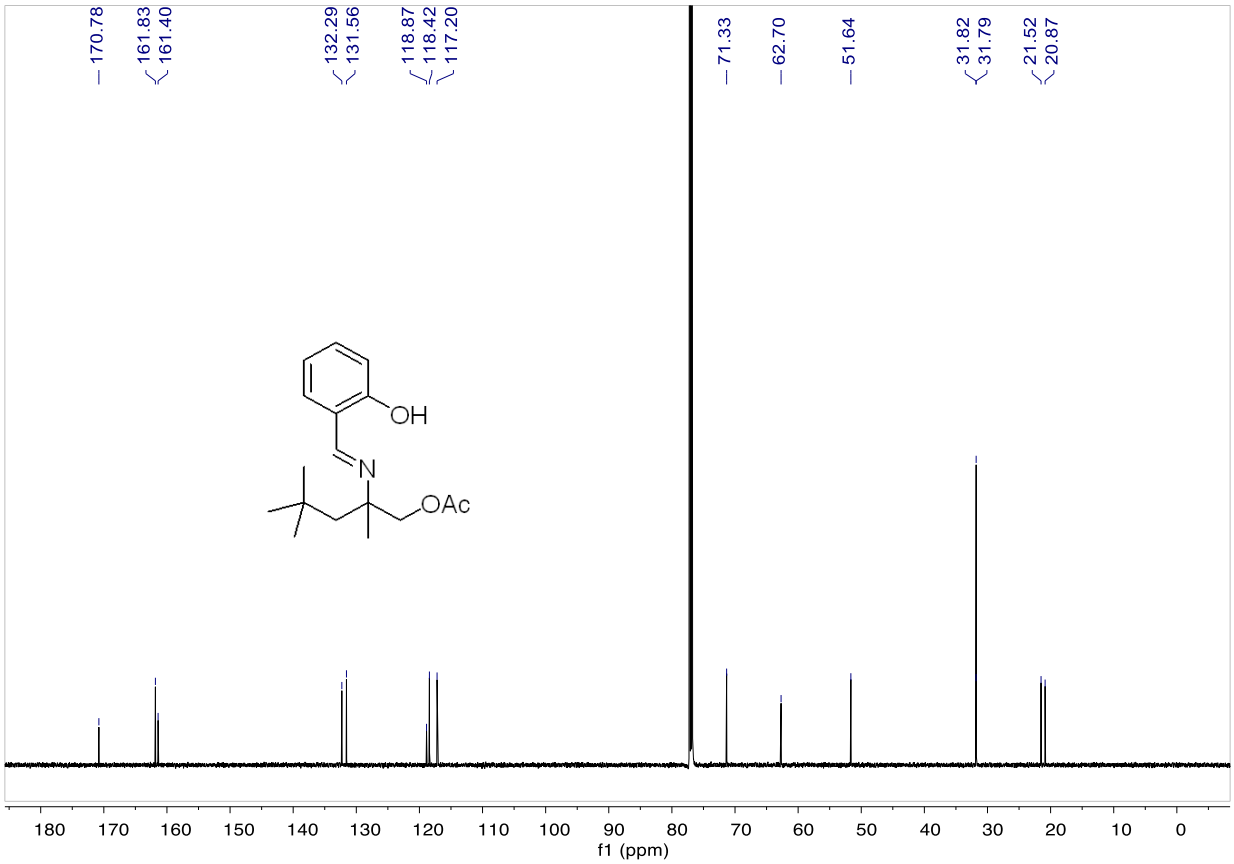
1.03
1.04
2.10
3.15
1.05
1.09
3.31
9.62
f1 (ppm)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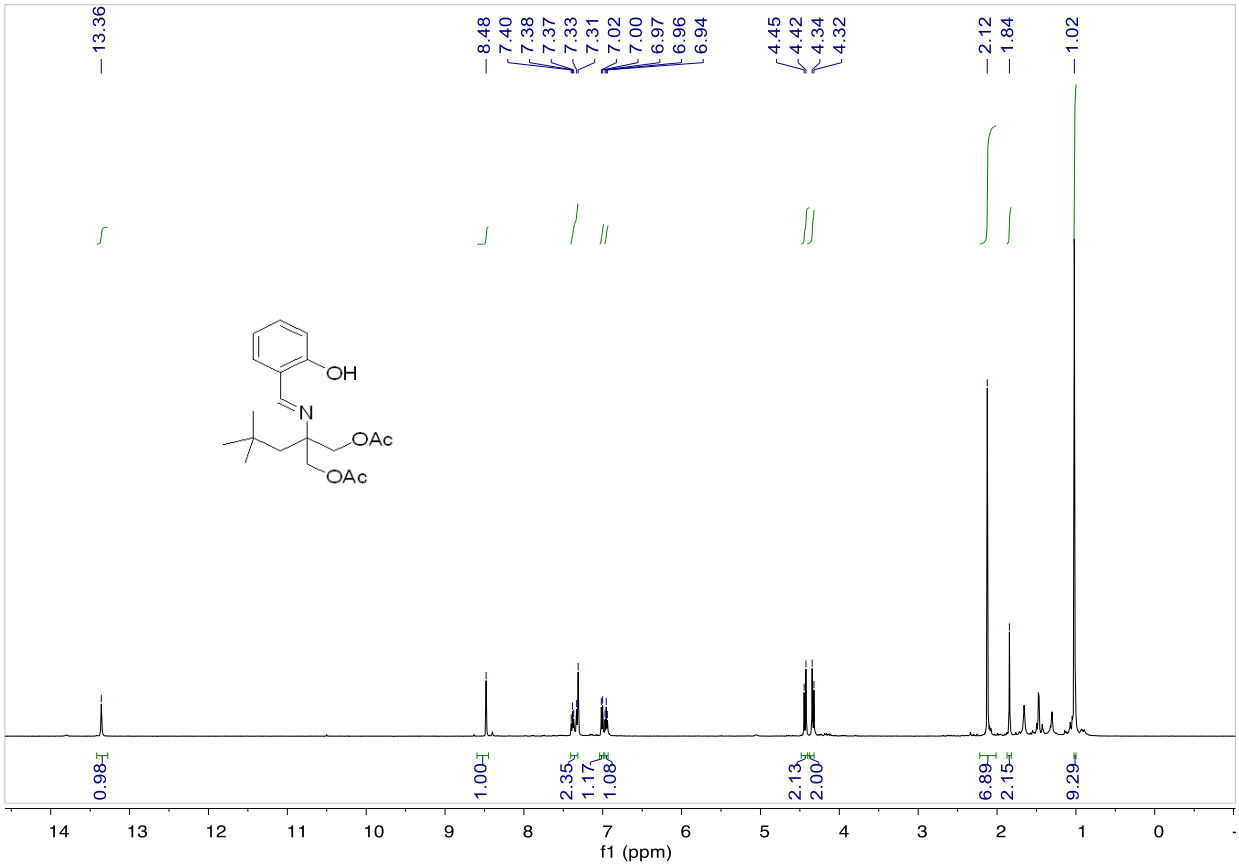
71.33
62.70
51.64
31.82
31.79
21.52
20.87
OH
N
OAc
f1 (ppm)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7.38
7.37
7.33
7.31
7.02
7.00
6.97
6.96
6.94
4.45
4.42
4.34
4.32
2.12
1.84
1.02
OH
N
OAc
OAc
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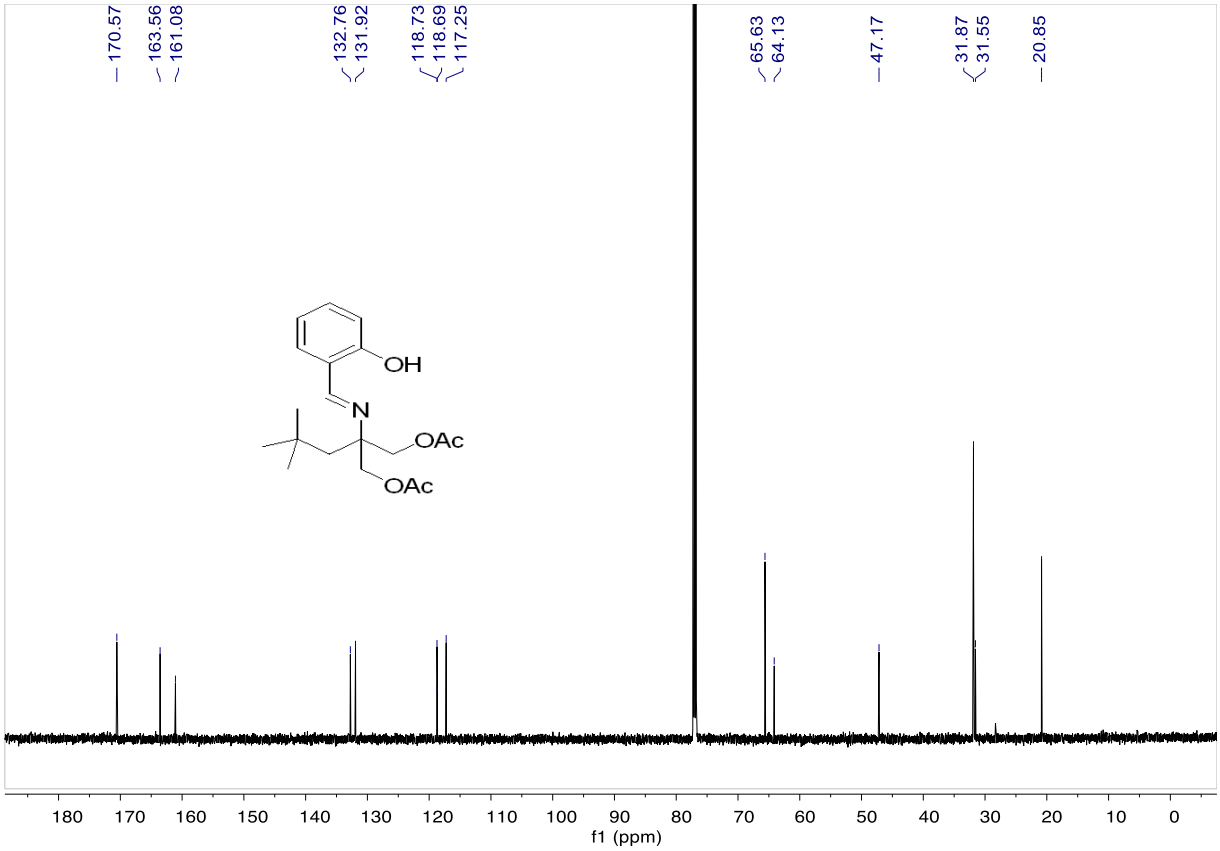
1.00
2.35
1.17
1.08
2.13
2.00
6.89
2.15
9.29
f1 (ppm)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20.85
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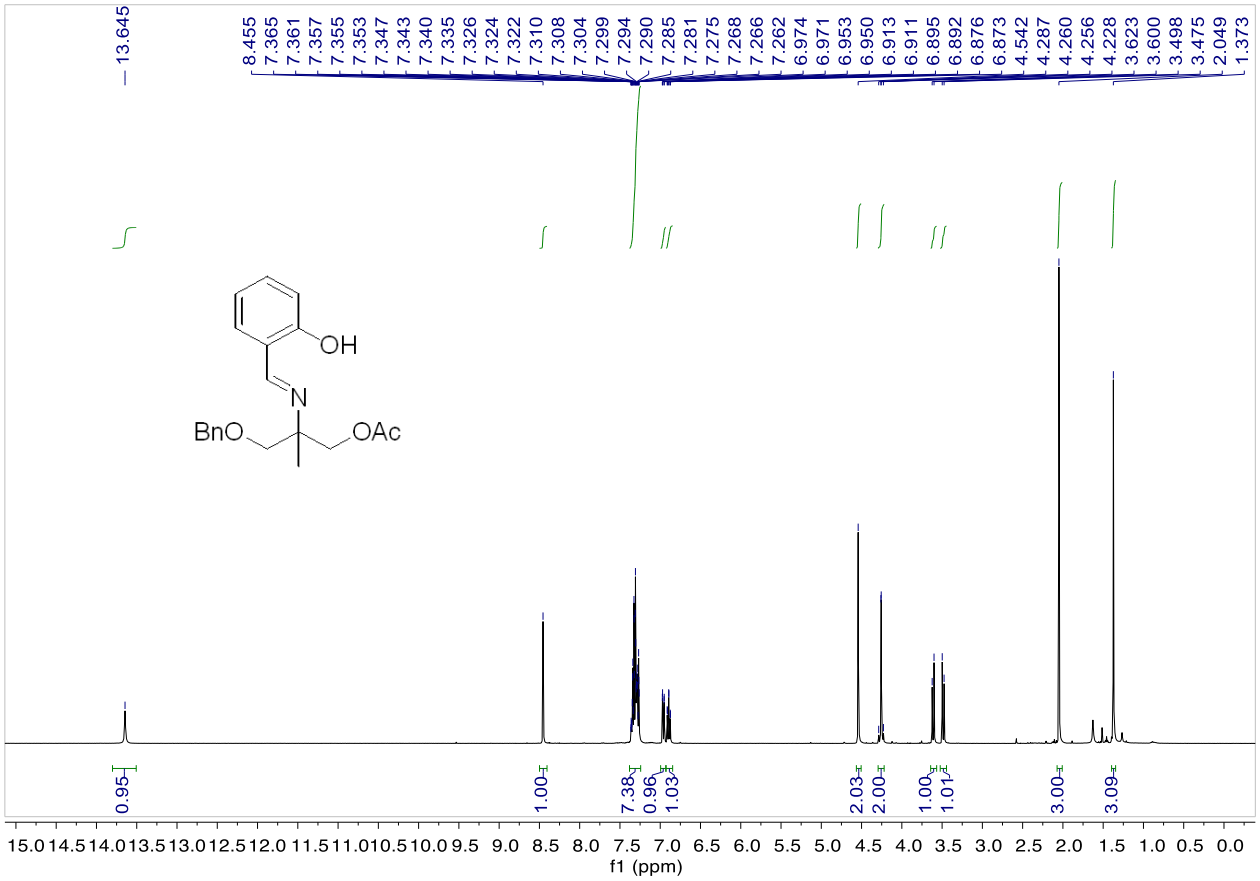
OAc
OAc
f1 (ppm)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7.322
7.310
7.308
7.304
7.299
7.294
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7.281
7.275
7.268
7.266
7.262
6.974
6.971
6.953
6.950
6.913
6.911
6.895
6.892
6.876
6.873
4.542
4.287
4.260
4.256
4.228
3.623
3.600
3.498
3.475
2.049
1.373
OH
N
BnO
OAc
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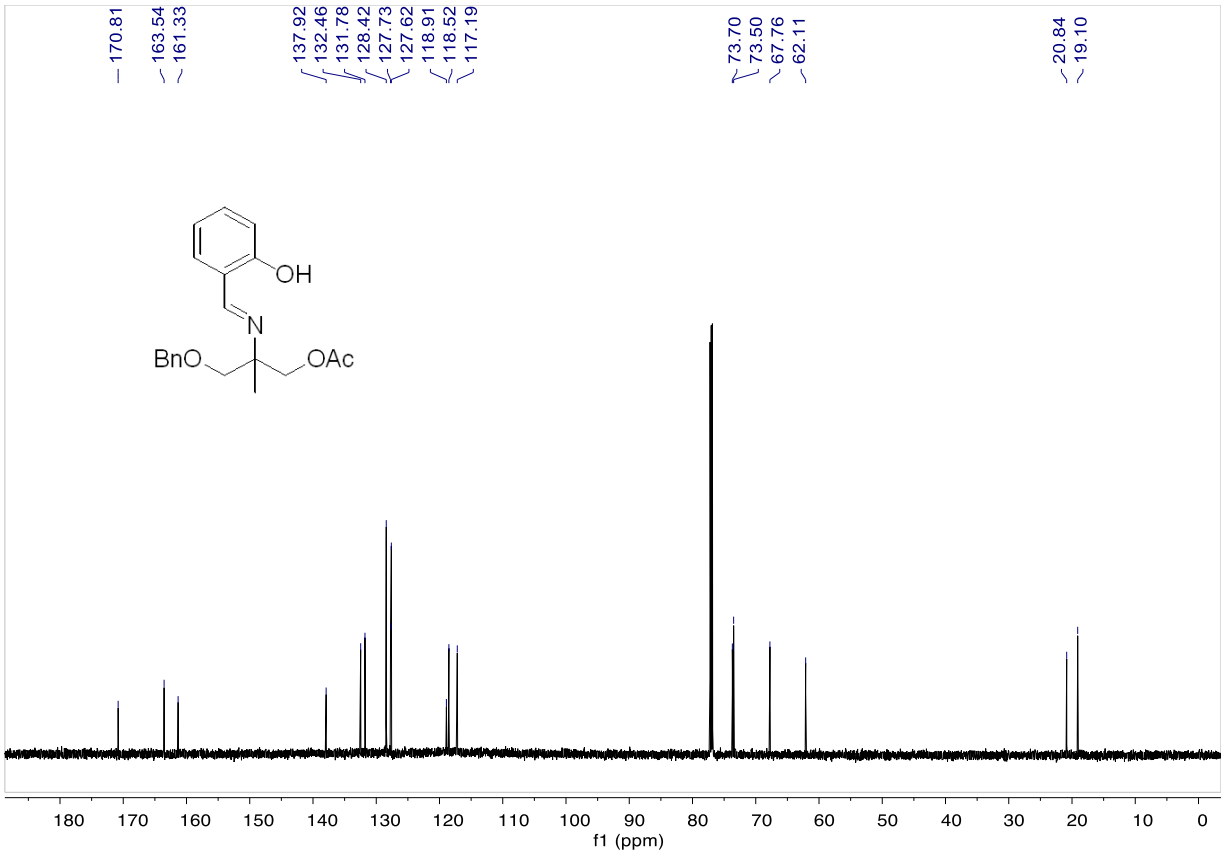
1.03
2.03
2.00
1.00
1.01
3.00
3.09
f1 (ppm)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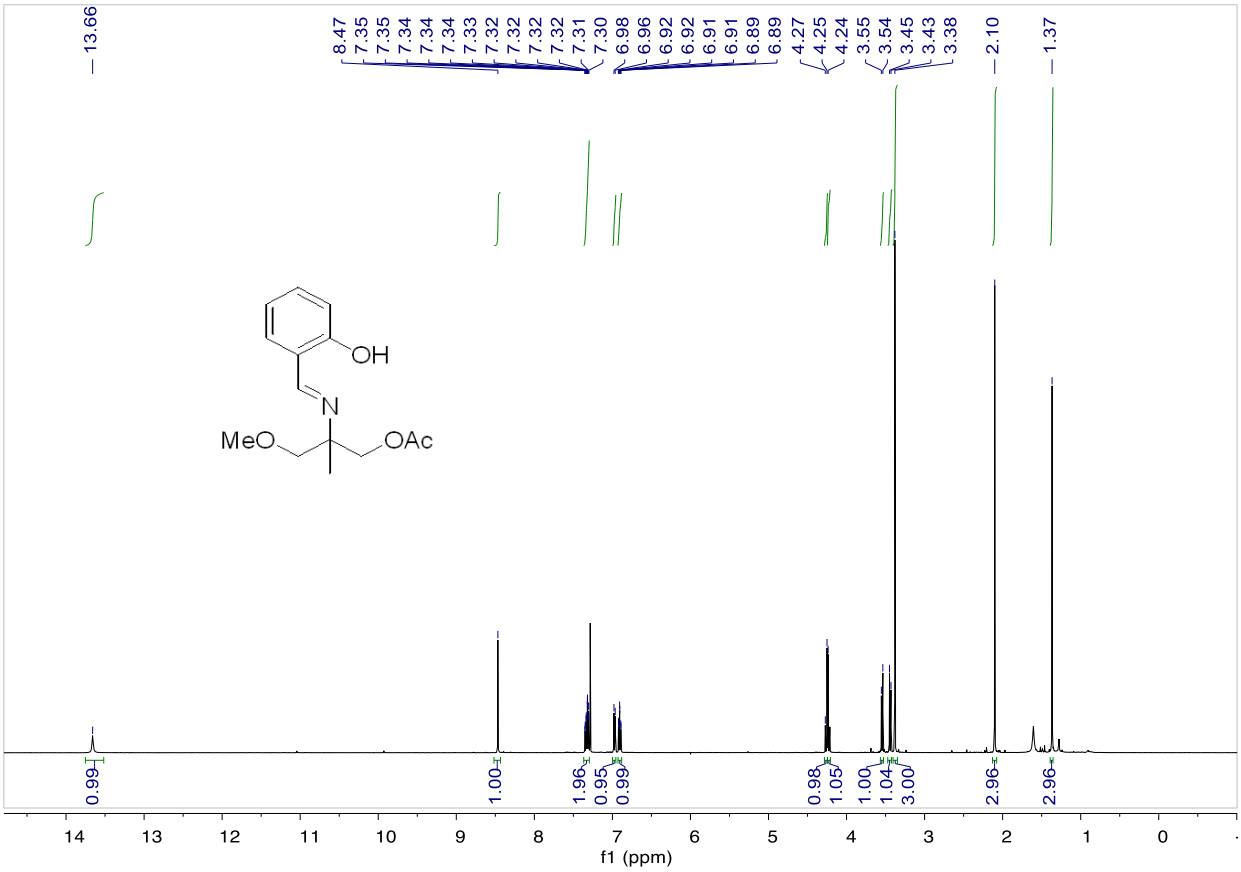
73.50
67.76
62.11
20.84
19.10
OH
N
BnO
OAc
f1 (ppm)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7.33
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7.32
7.32
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7.30
6.98
6.96
6.92
6.92
6.91
6.91
6.89
6.89
4.27
4.25
4.24
3.55
3.54
3.45
3.43
3.38
2.10
1.37
OH
N
MeO
OAc
0.99
1.00
1.96
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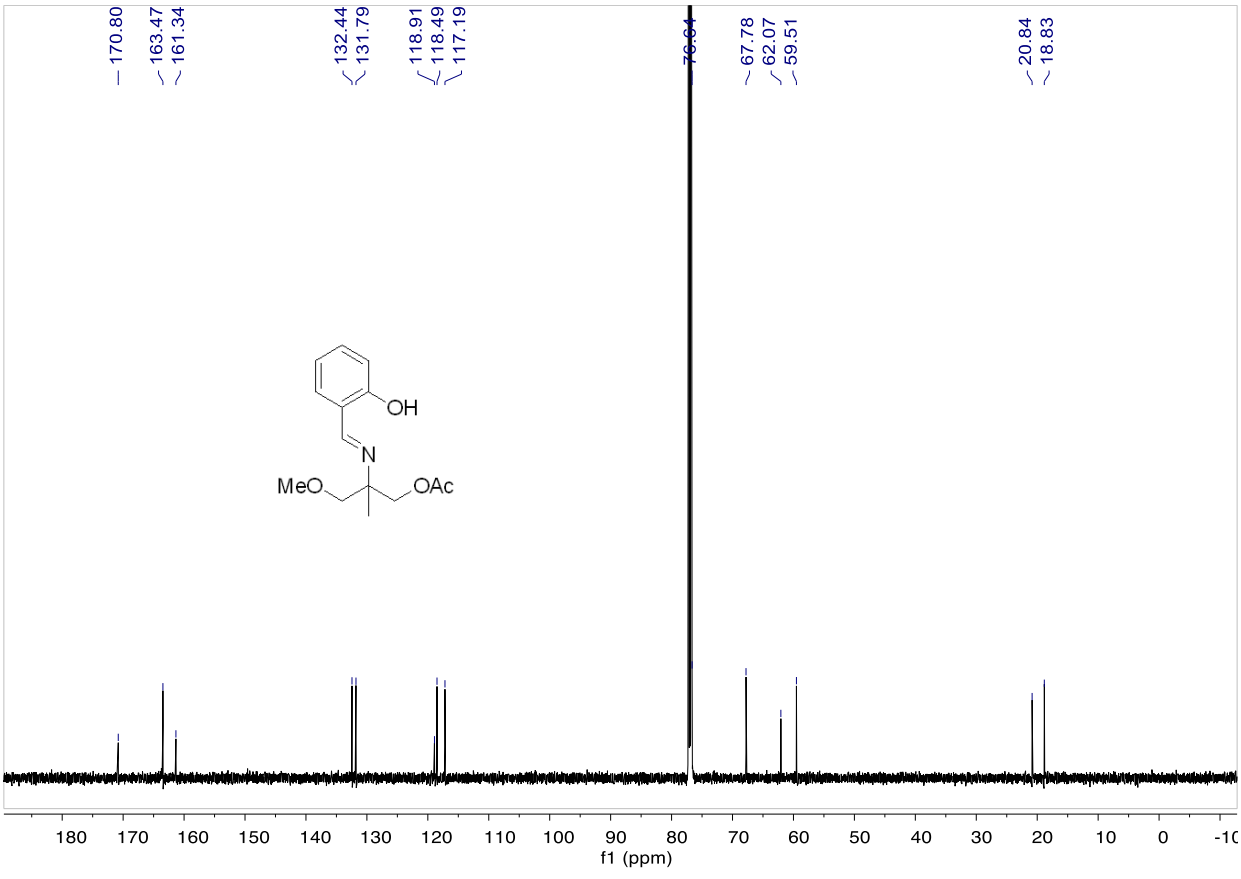
0.99
0.98
1.05
1.00
1.04
3.00
2.96
2.96
f1 (ppm)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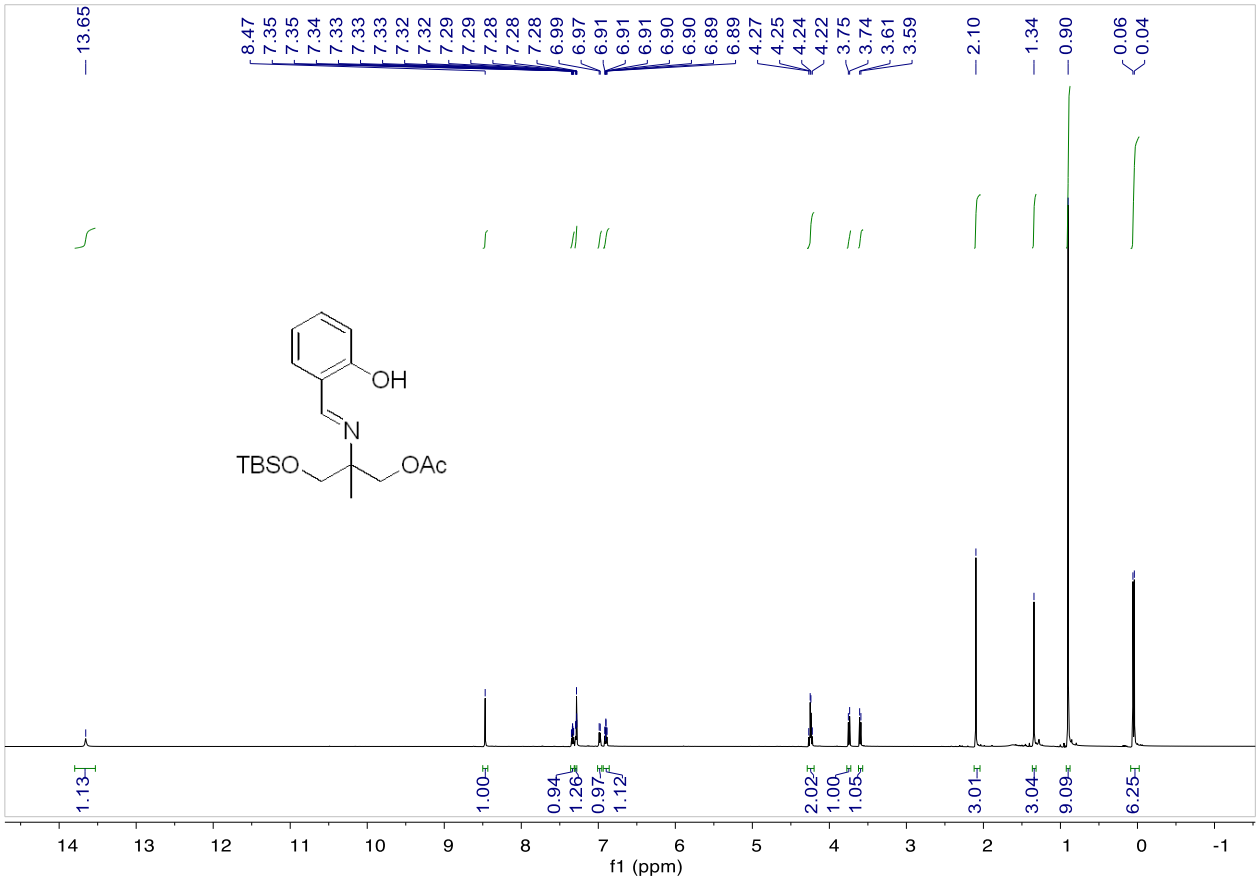
59.51
20.84
18.83
OH
N
MeO
OAc
f1 (ppm)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7.33
7.33
7.33
7.32
7.32
7.29
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7.28
7.28
6.99
6.97
6.91
6.91
6.91
6.90
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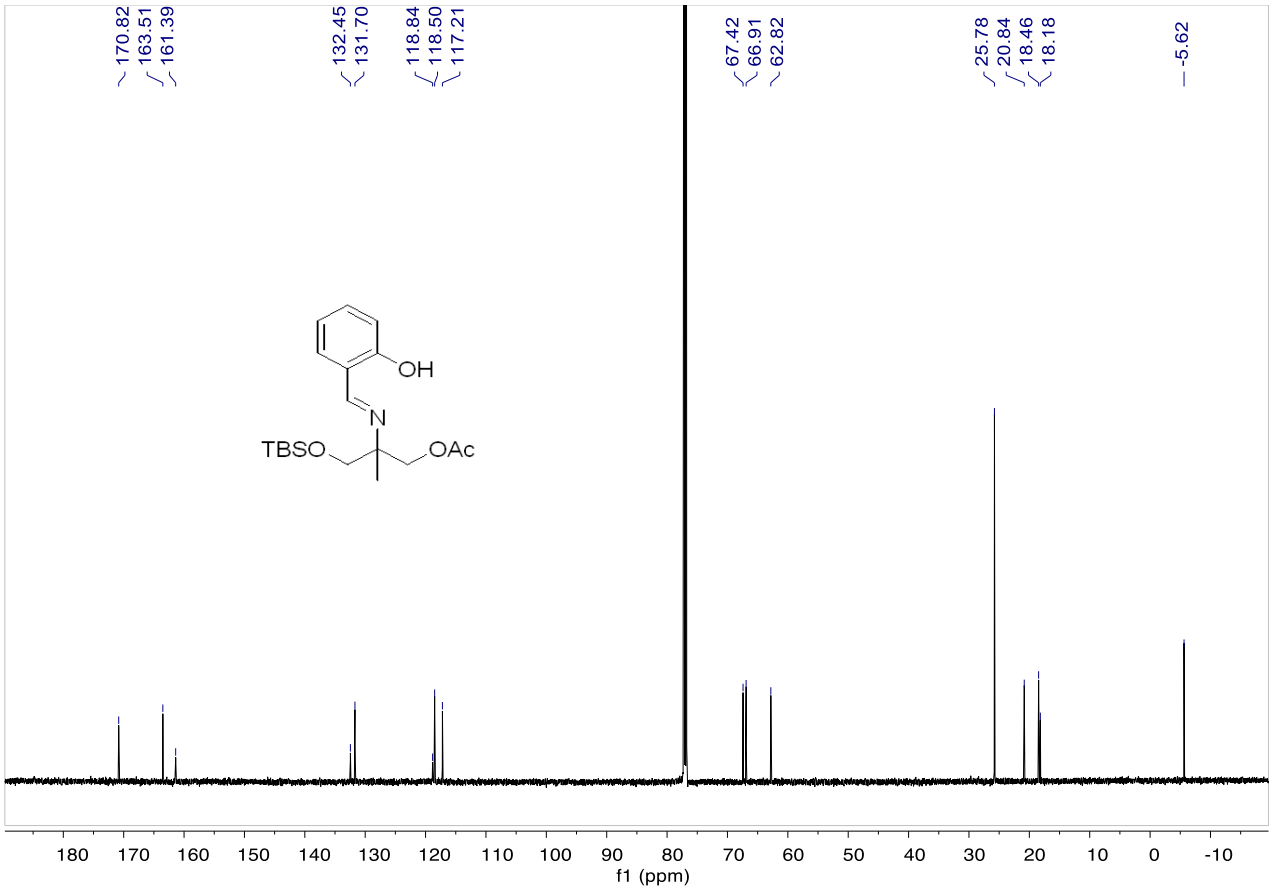
6.89
6.89
4.27
4.25
4.24
4.22
3.75
3.74
3.61
3.59
2.10
1.34
0.90
0.06
0.04
OH
N
TBSO
OAc
1.13
1.00
0.94
1.26
0.97
1.12
2.02
1.00
1.05
3.01
3.04
9.09
6.25
f1 (ppm)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117.21
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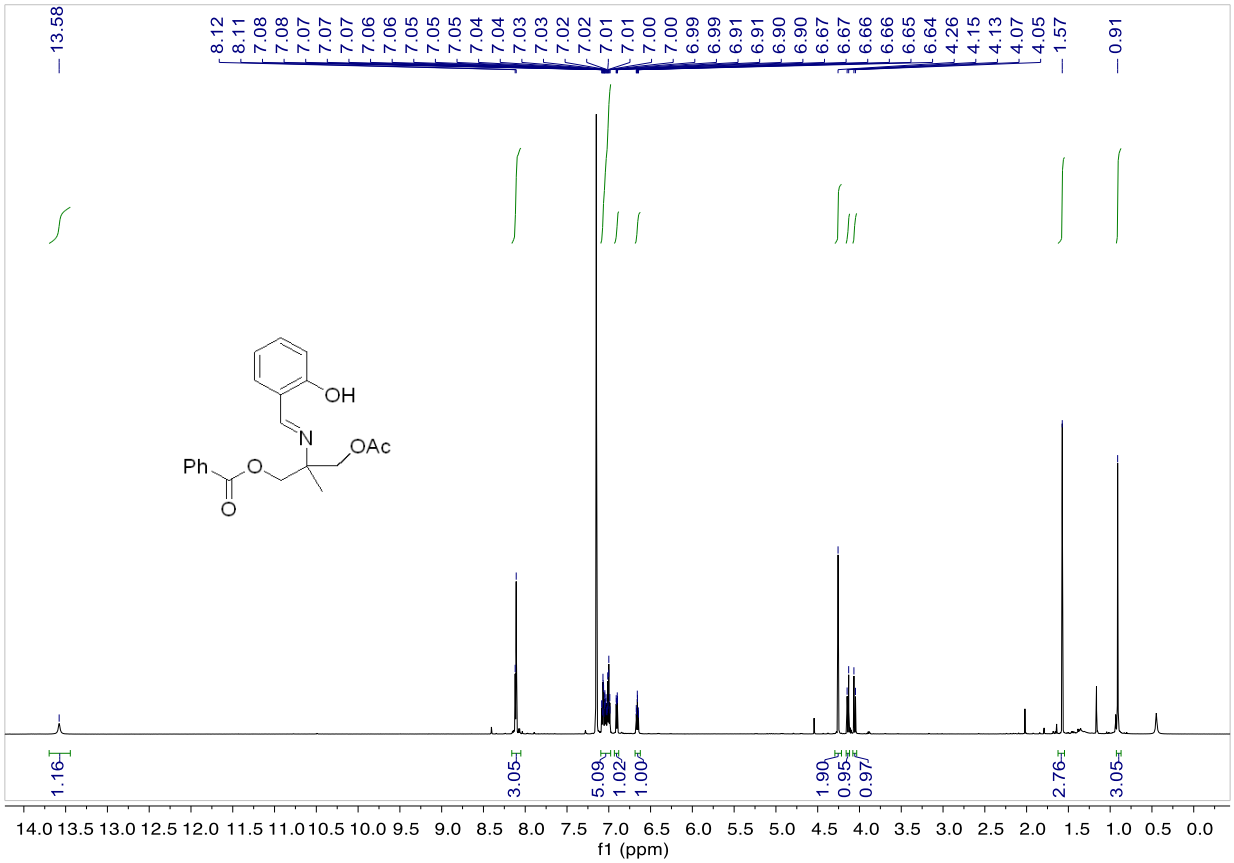
25.78
20.84
18.46
18.18
-5.62
OH
N
TBSO
OAc
f1 (ppm)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7.08
7.07
7.07
7.07
7.06
7.06
7.05
7.05
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7.04
7.04
7.03
7.03
7.02
7.02
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7.01
7.00
7.00
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6.99
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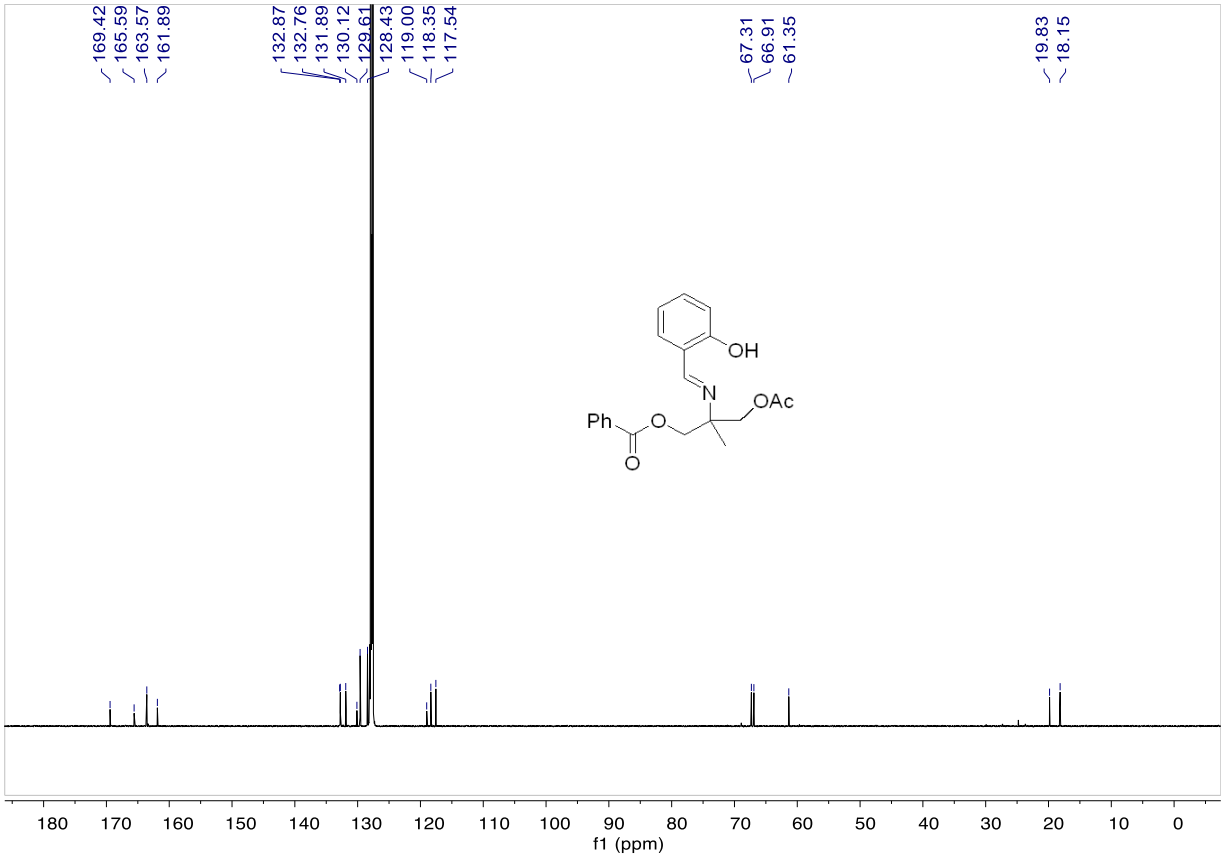
6.91
6.90
6.90
6.67
6.67
6.66
6.66
6.65
6.64
4.26
4.15
4.13
4.07
4.05
1.57
0.91
OH
N
OAc
Ph
O
O
1.16
3.05
5.09
1.02
1.00
1.90
0.95
0.97
2.76
3.05
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.43
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118.35
117.54
67.31
66.91
61.35
19.83
18.15
OH
N
OAc
Ph
O
O
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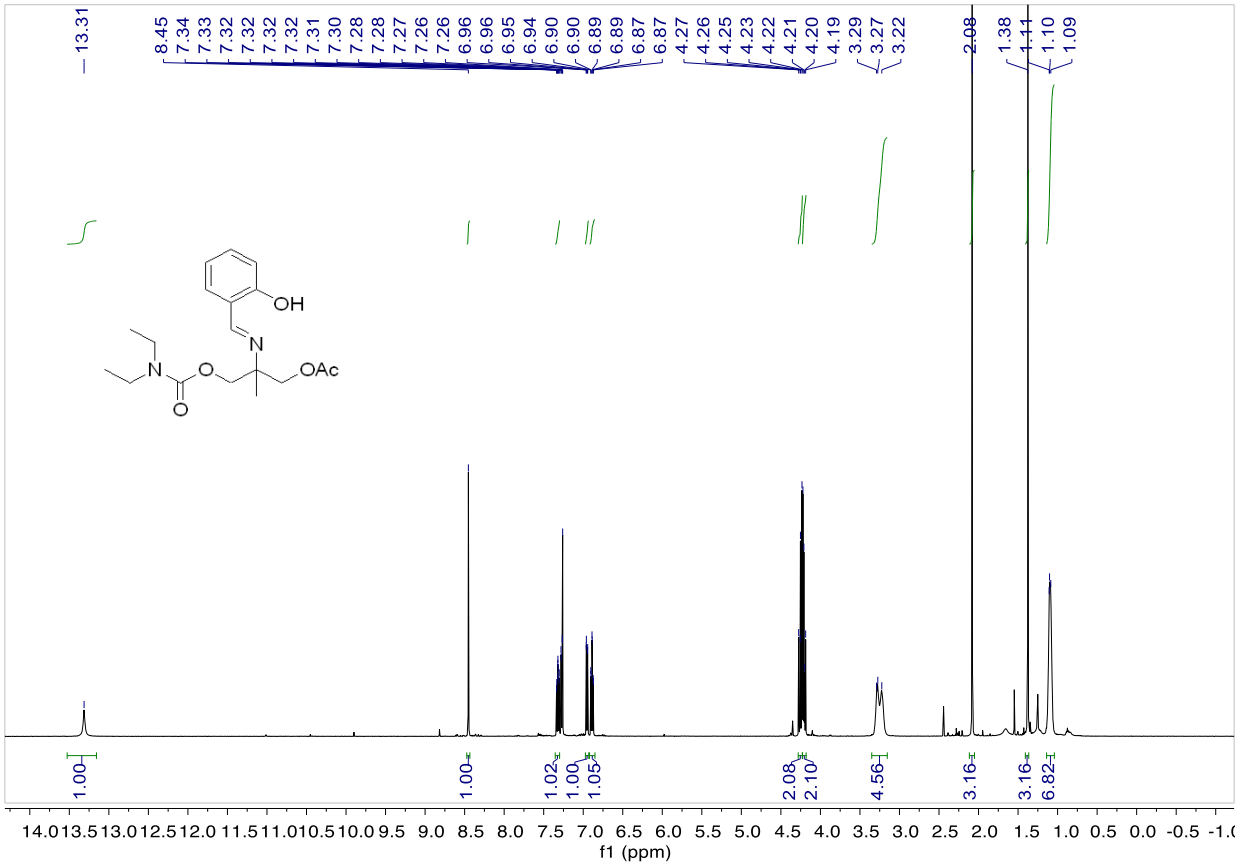
f1 (ppm)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7.28
7.27
7.26
7.26
6.96
6.96
6.95
6.94
6.90
6.90
6.89
6.89
6.87
6.87
4.27
4.26
4.25
4.23
4.22
4.21
4.20
4.19
3.29
3.27
3.22
2.08
1.38
1.11
1.10
1.09
OH
N
N
O
O
OAc
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1.05
2.08
2.10
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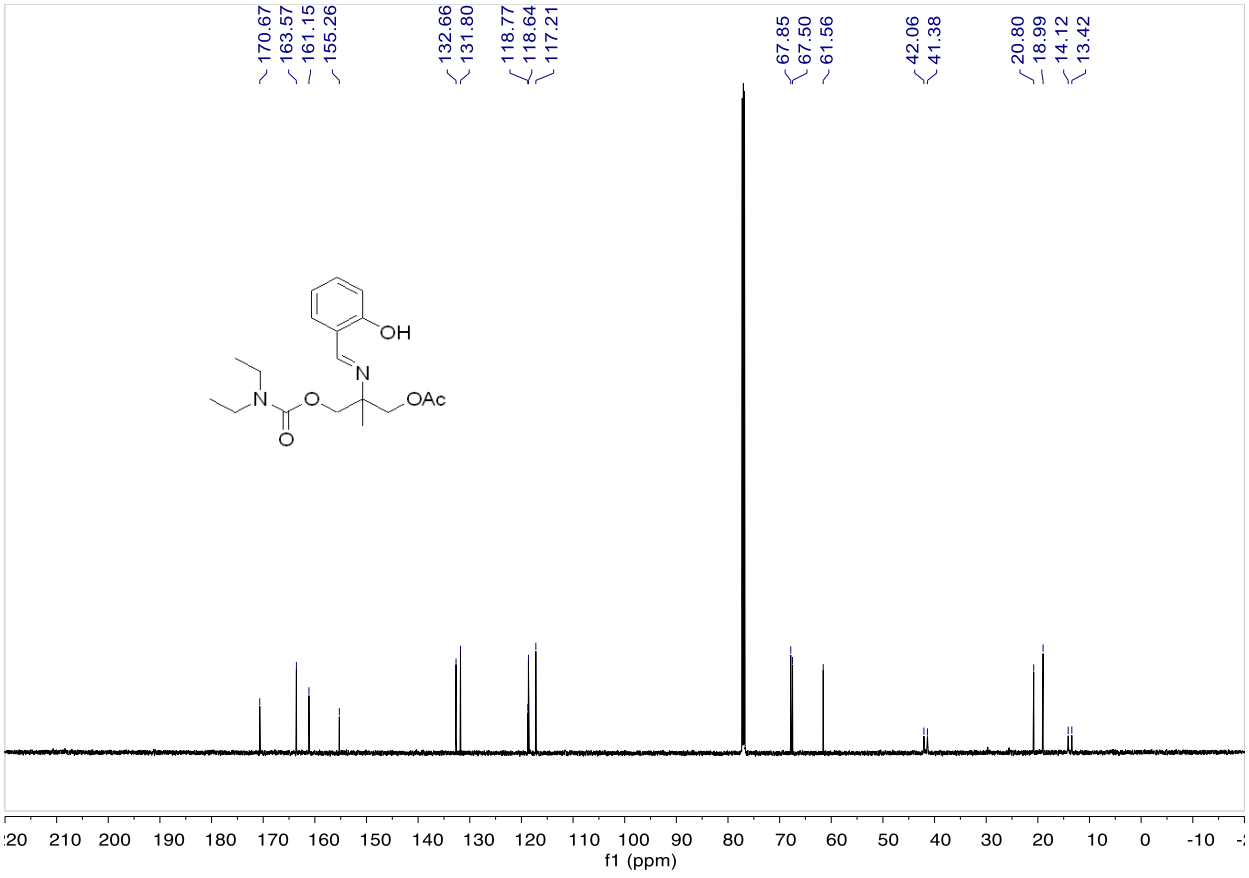
3.16
6.82
f1 (ppm)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67.50
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14.12
13.42
OH
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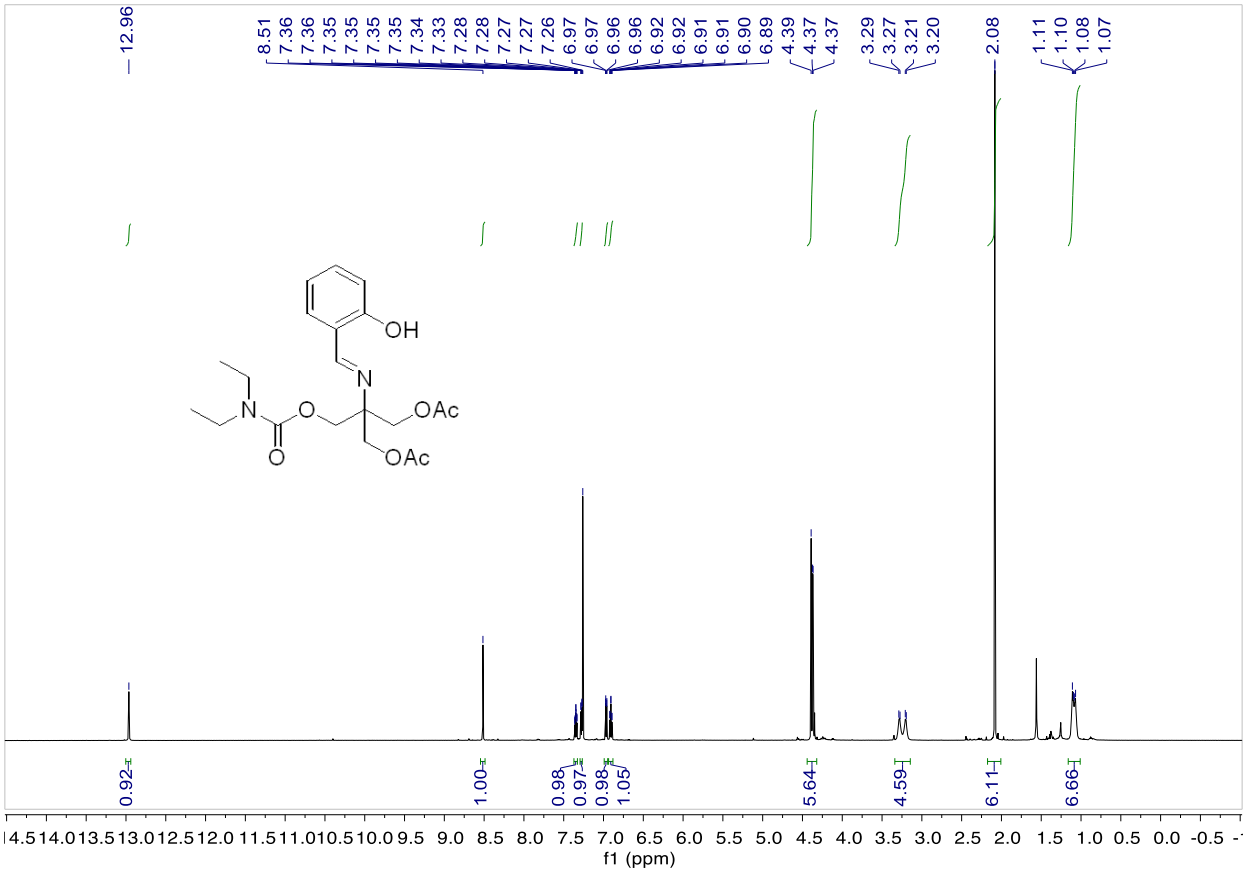
N
O
O
OAc
f1 (ppm)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7.27
7.27
7.26
6.97
6.96
6.96
6.92
6.92
6.91
6.91
6.90
6.89
4.39
4.37
4.37
3.29
3.27
3.21
3.20
2.08
1.11
1.10
1.08
1.07
OH
N
N
O
O
OAc
OAc
O
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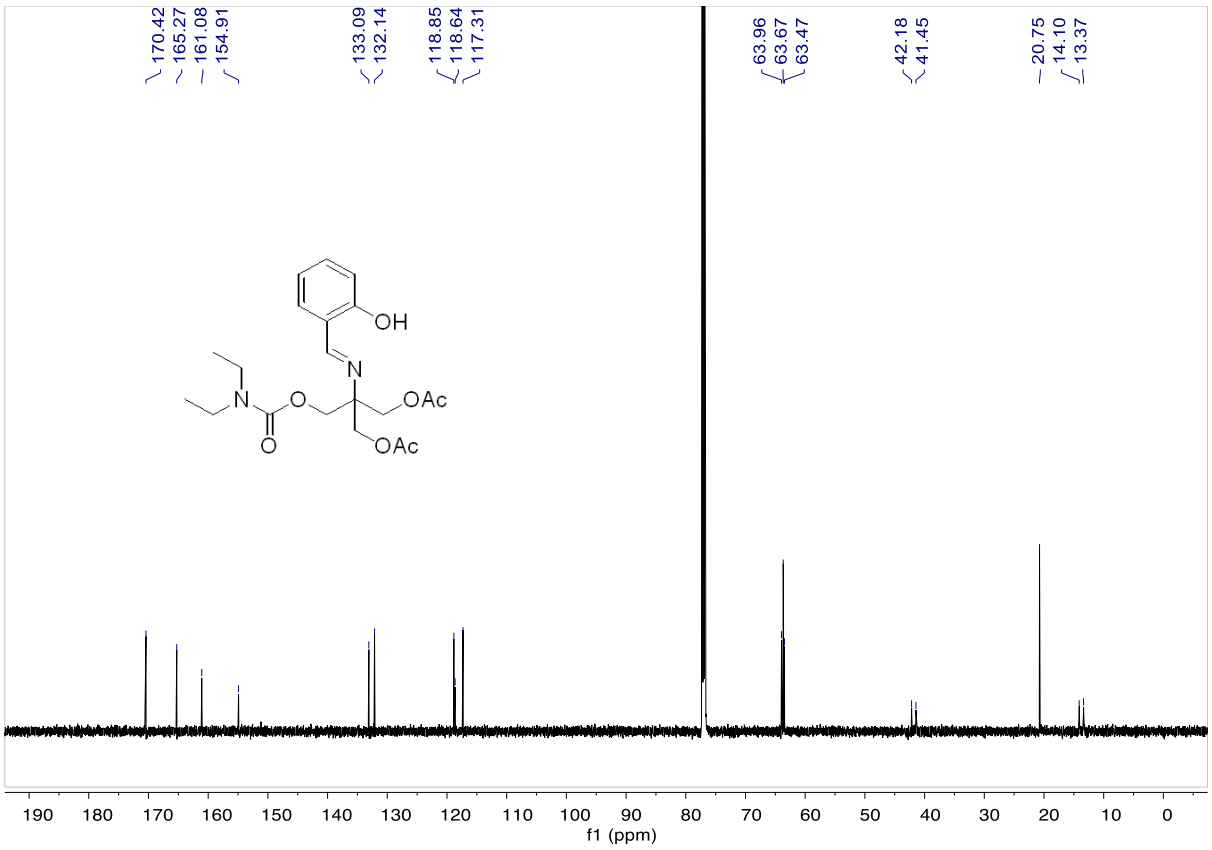
0.98
0.97
0.98
1.05
5.64
4.59
6.11
6.66
f1 (ppm)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117.31
63.96
63.67
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20.75
14.10
13.37
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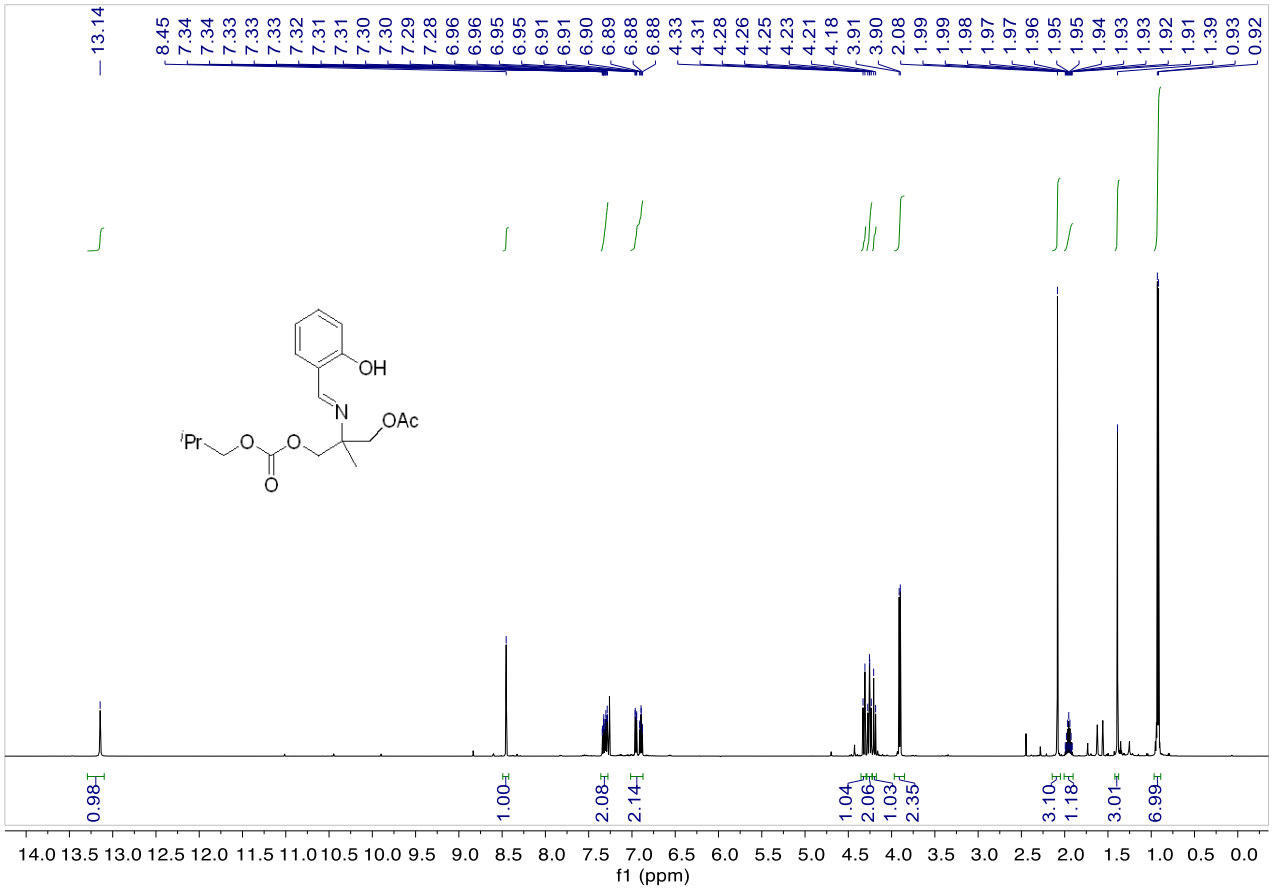
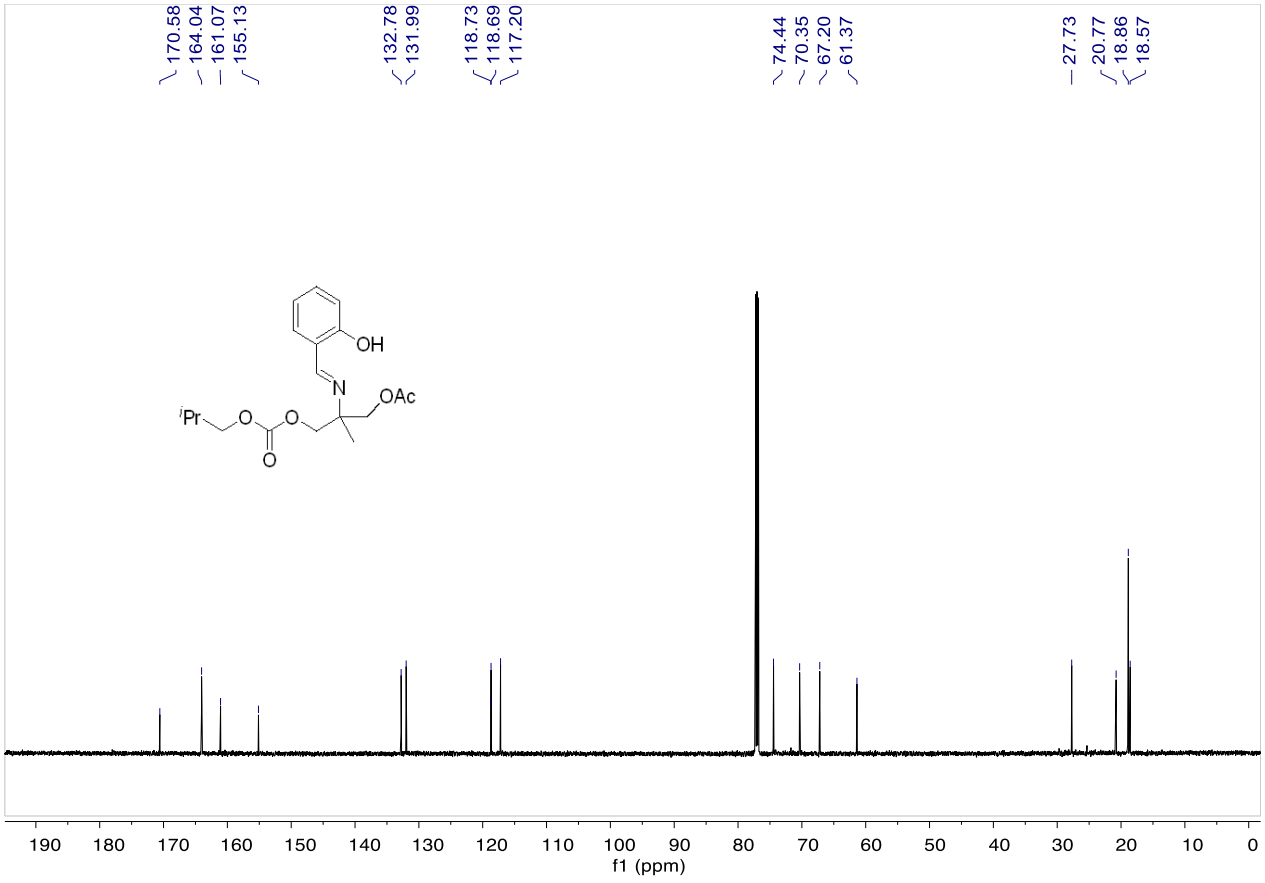
O
O
OAc
OAc
O
f1 (ppm)


13.14
8.45 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.28 6.96 6.95 6.95 6.91 6.91 6.90 6.89 6.88 6.88
4.33 4.31 4.28 4.26 4.25 4.23 4.21 4.18 3.91 3.90 2.08 1.99 1.99 1.98 1.97 1.97 1.96 1.95 1.95 1.94 1.93 1.93 1.92 1.91 1.39 0.93 0.92
OH
N
OAc
iPr
O
O
O
0.98 1.00 2.08 2.14 1.04 2.06 1.03 2.35 3.10 1.18 3.01 6.99
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.78 131.99
118.73 118.69 117.20
74.44 70.35 67.20 61.37
27.73 20.77 18.86 18.57
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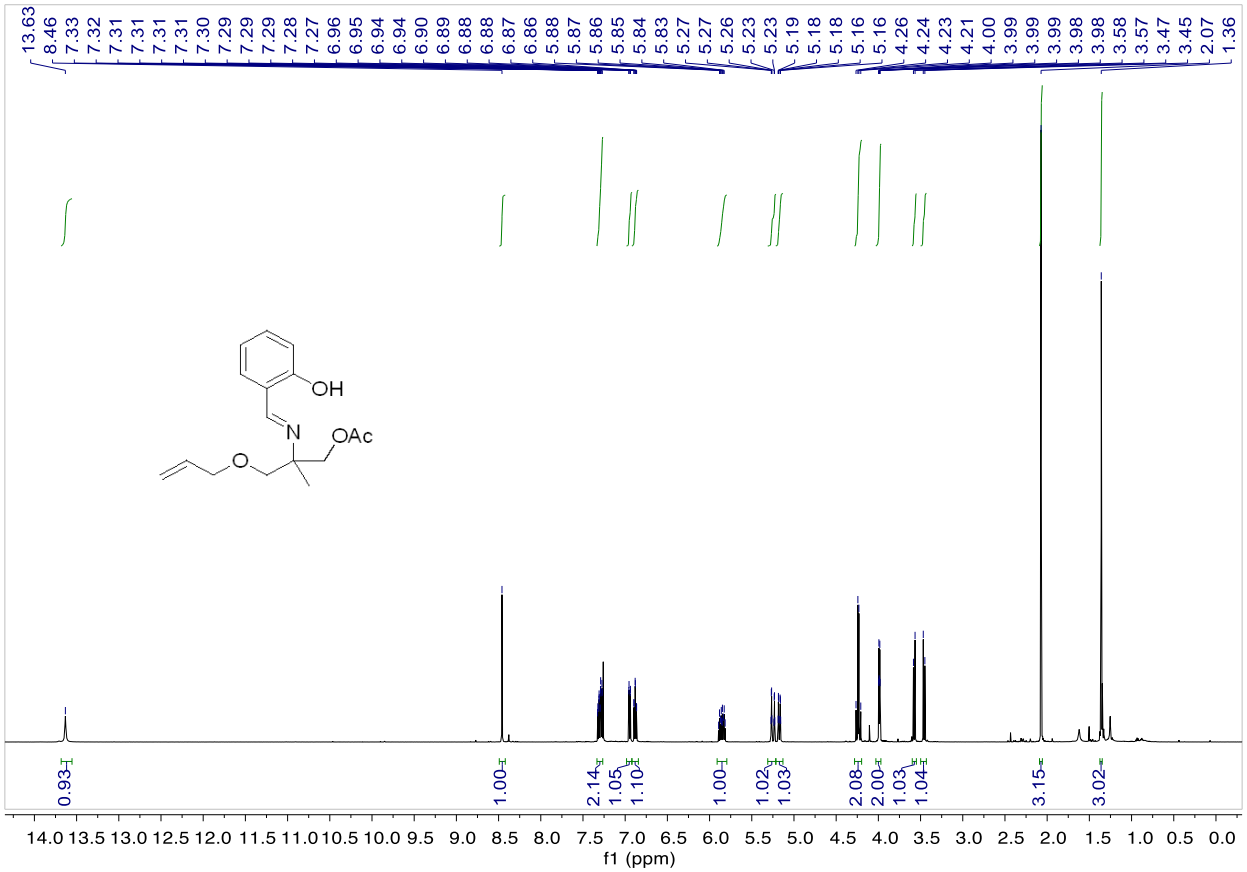
N
OAc
iPr
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.31
7.30
7.29
7.29
7.29
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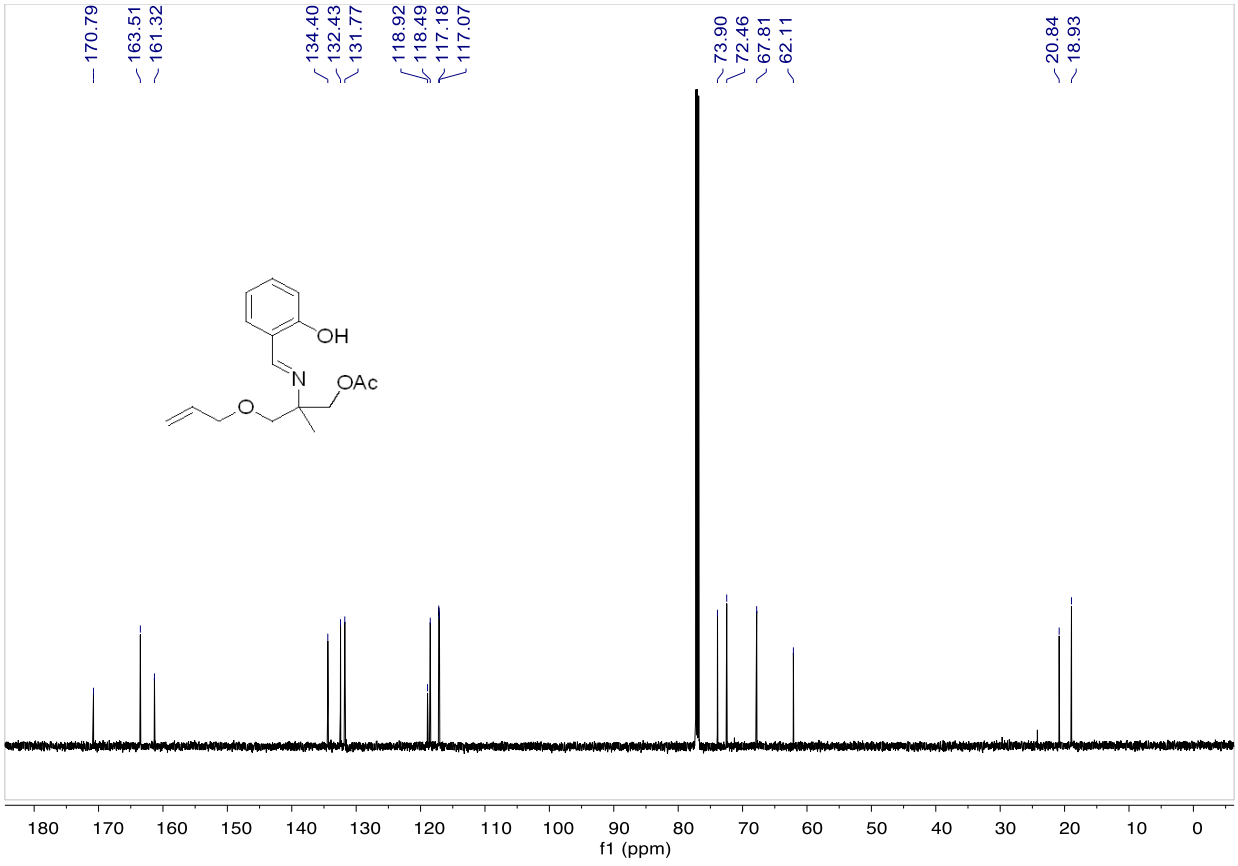
7.27
6.96
6.95
6.94
6.94
6.90
6.89
6.88
6.88
6.87
6.86
5.88
5.87
5.86
5.85
5.84
5.83
5.27
5.27
5.26
5.23
5.23
5.19
5.18
5.18
5.16
5.16
4.26
4.24
4.23
4.21
4.00
3.99
3.99
3.99
3.98
3.98
3.58
3.57
3.47
3.45
2.07
1.36
OH
N
OAc
O
0.93
1.00
2.14
1.05
1.10
1.00
1.02
1.03
2.08
2.00
1.03
1.04
3.15
3.02
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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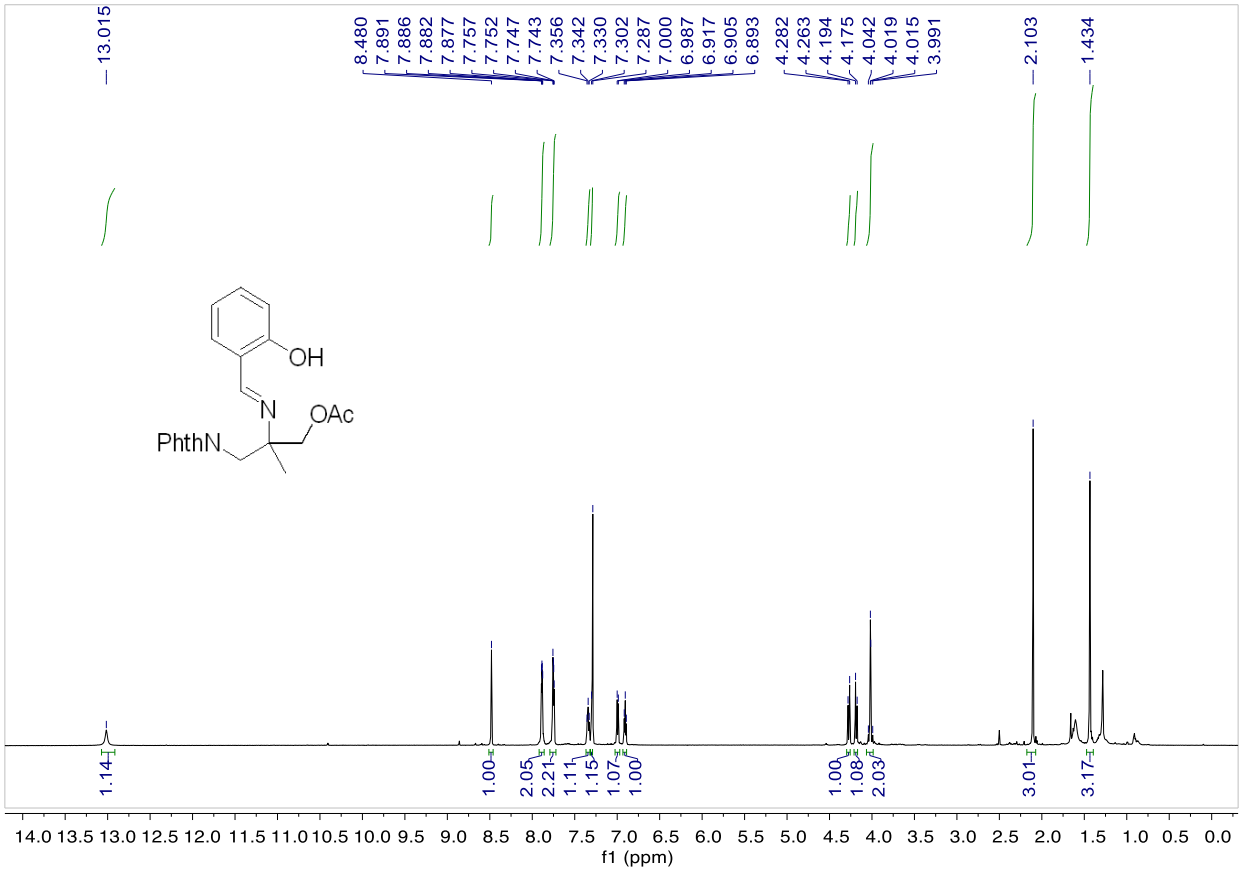
131.77
118.92
118.49
117.18
117.07
73.90
72.46
67.81
62.11
20.84
18.93
OH
N
OAc
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.752
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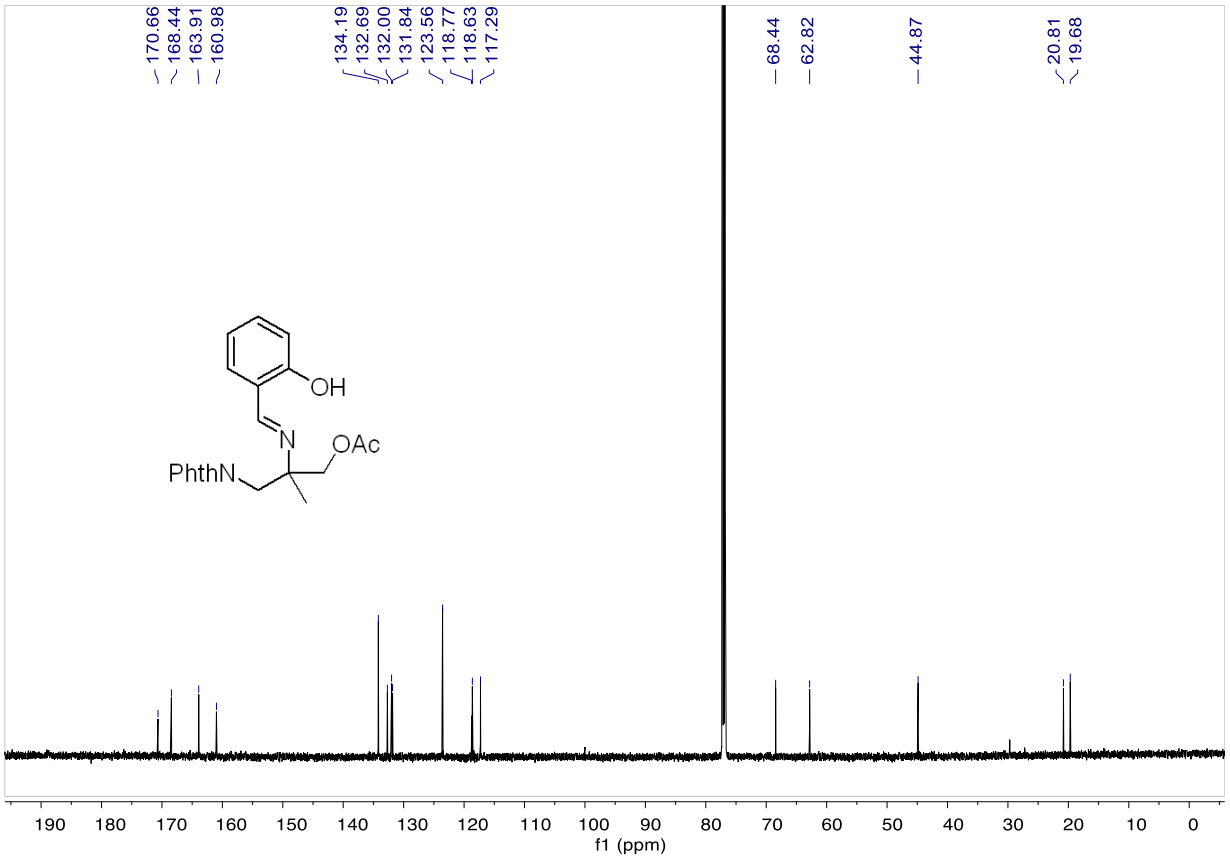
7.342
7.330
7.302
7.287
7.000
6.987
6.917
6.905
6.893
4.282
4.263
4.194
4.175
4.042
4.019
4.015
3.991
2.103
1.434
OH
N
OAc
PhthN
1.14
1.00
2.05
2.21
1.11
1.15
1.07
1.00
1.00
1.08
2.03
3.01
3.17
f1 (ppm)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132.69
132.00
131.84
123.56
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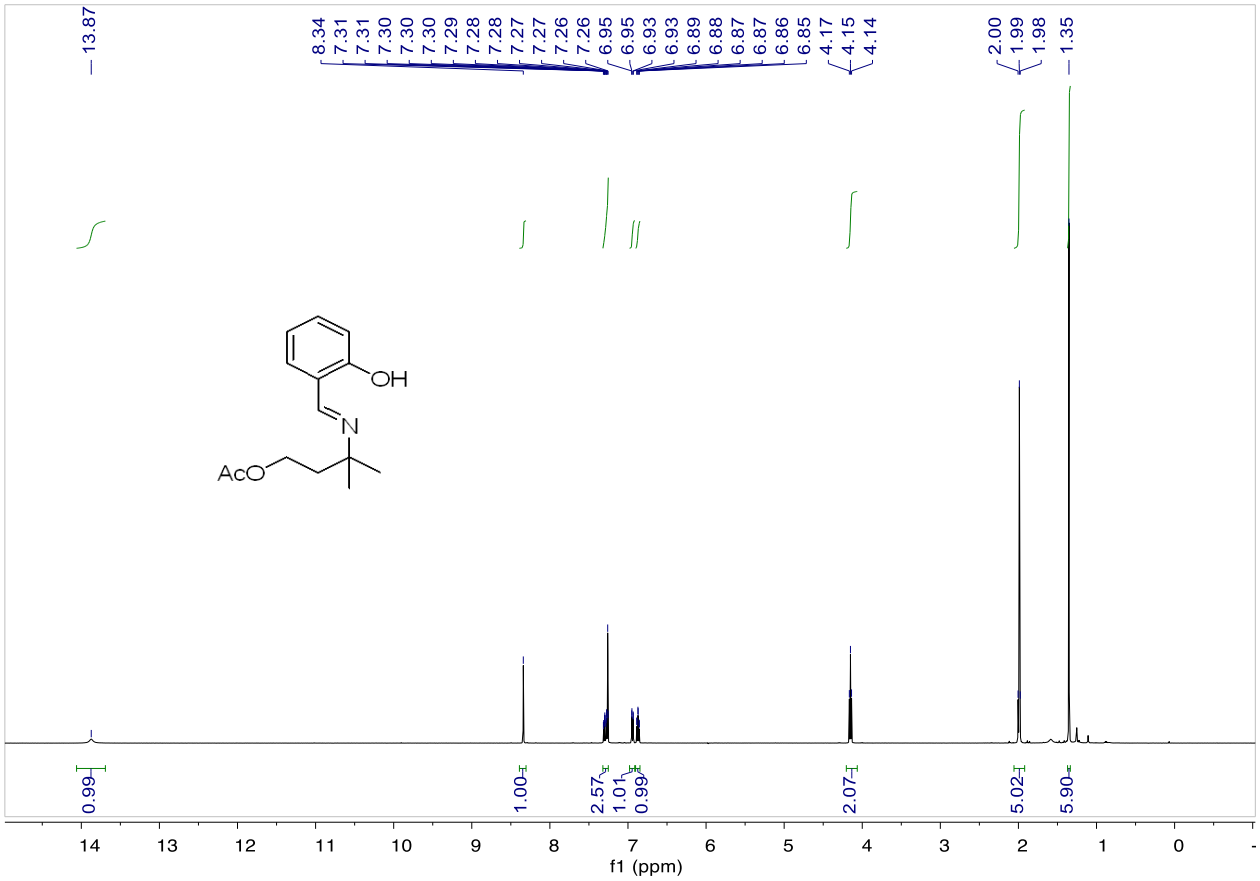
68.44
62.82
44.87
20.81
19.68
OH
N
OAc
PhthN
f1 (ppm)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7.29
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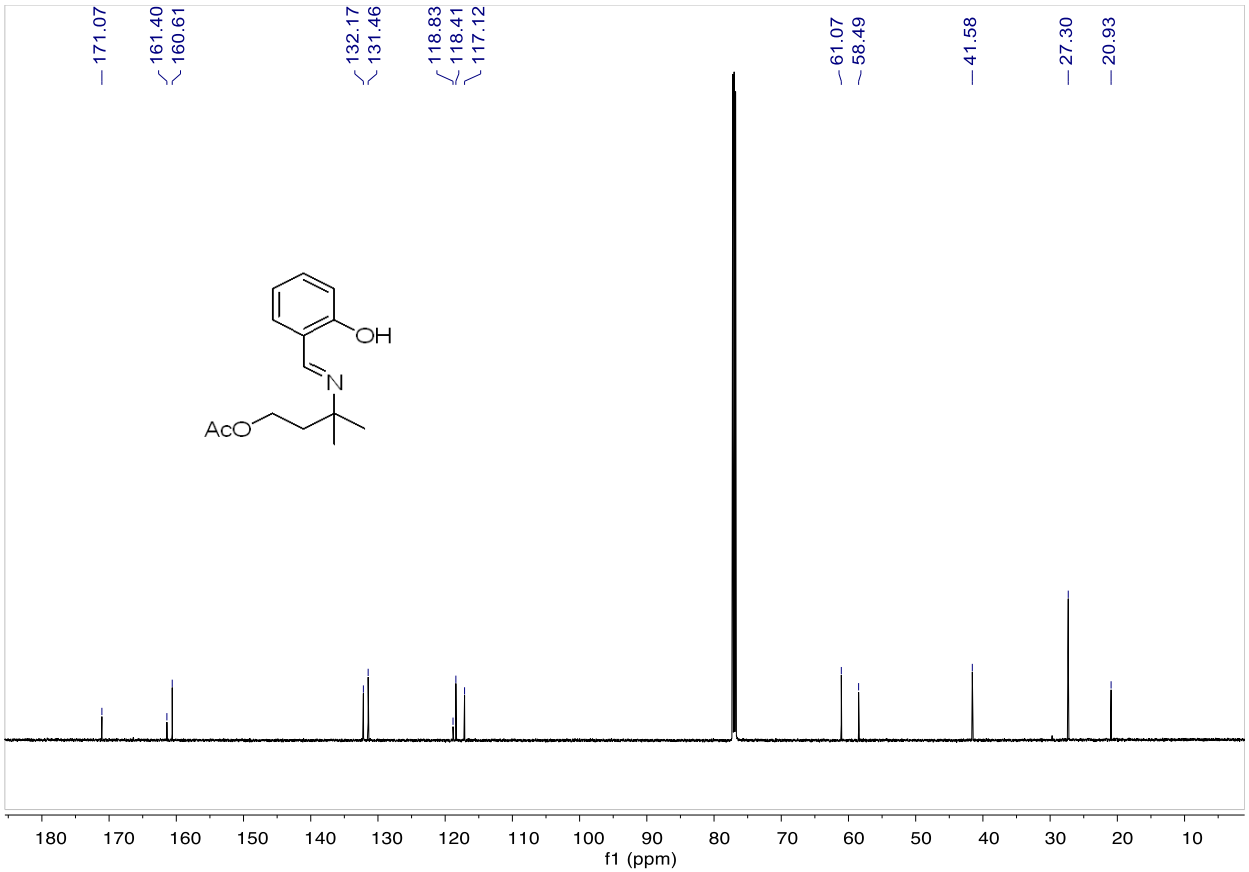
7.28
7.27
7.27
7.26
7.26
6.95
6.95
6.93
6.93
6.89
6.88
6.87
6.87
6.86
6.85
4.17
4.15
4.14
2.00
1.99
1.98
1.35
OH
N
AcO
0.99
1.00
2.57
1.01
0.99
2.07
5.02
5.90
f1 (ppm)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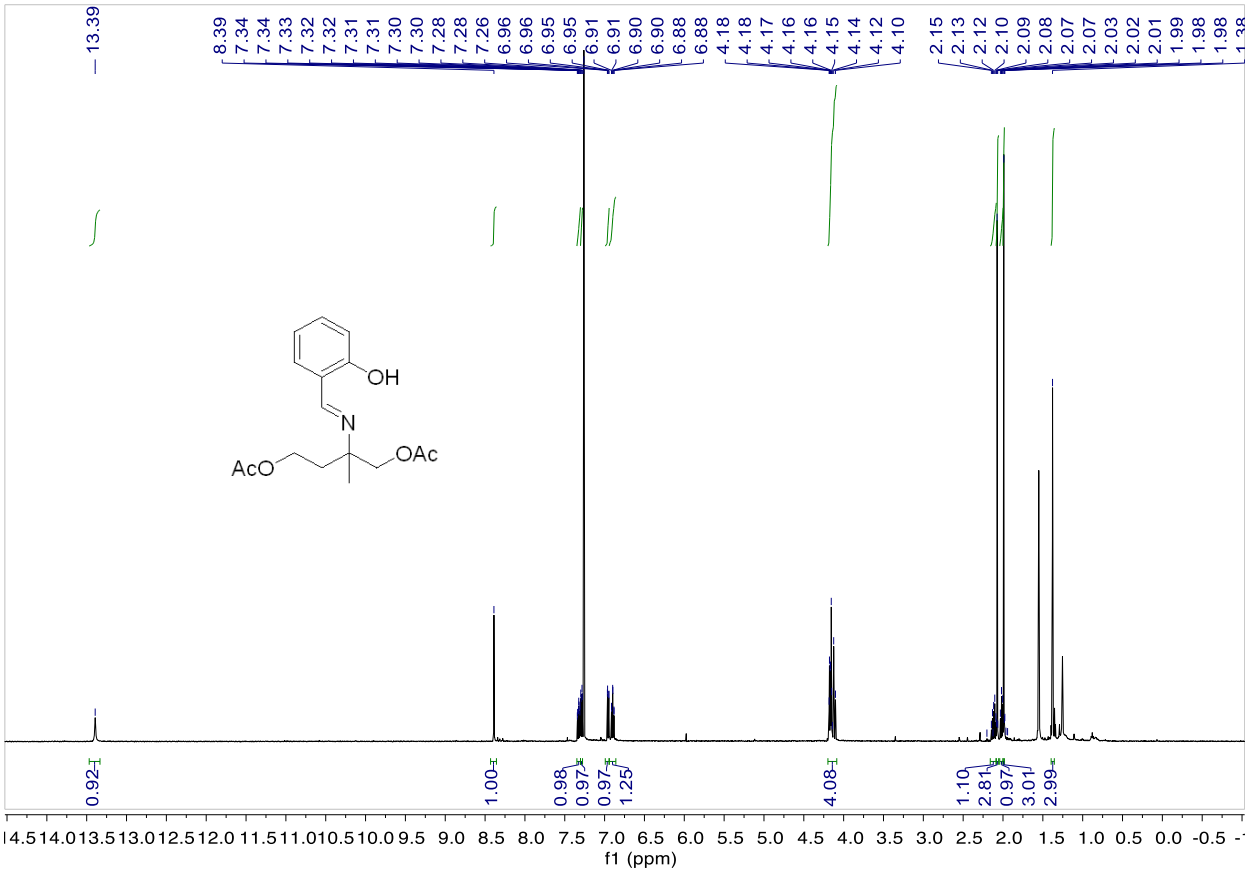
117.12
61.07
58.49
41.58
27.30
20.93
OH
N
AcO
f1 (ppm)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7.31
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7.30
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6.95
6.91
6.91
6.90
6.90
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6.88
4.18
4.18
4.17
4.16
4.16
4.15
4.14
4.12
4.10
2.15
2.13
2.12
2.10
2.09
2.08
2.07
2.07
2.03
2.02
2.01
1.99
1.98
1.98
OH
N
AcO
OAc
0.92
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0.97
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4.08
1.10
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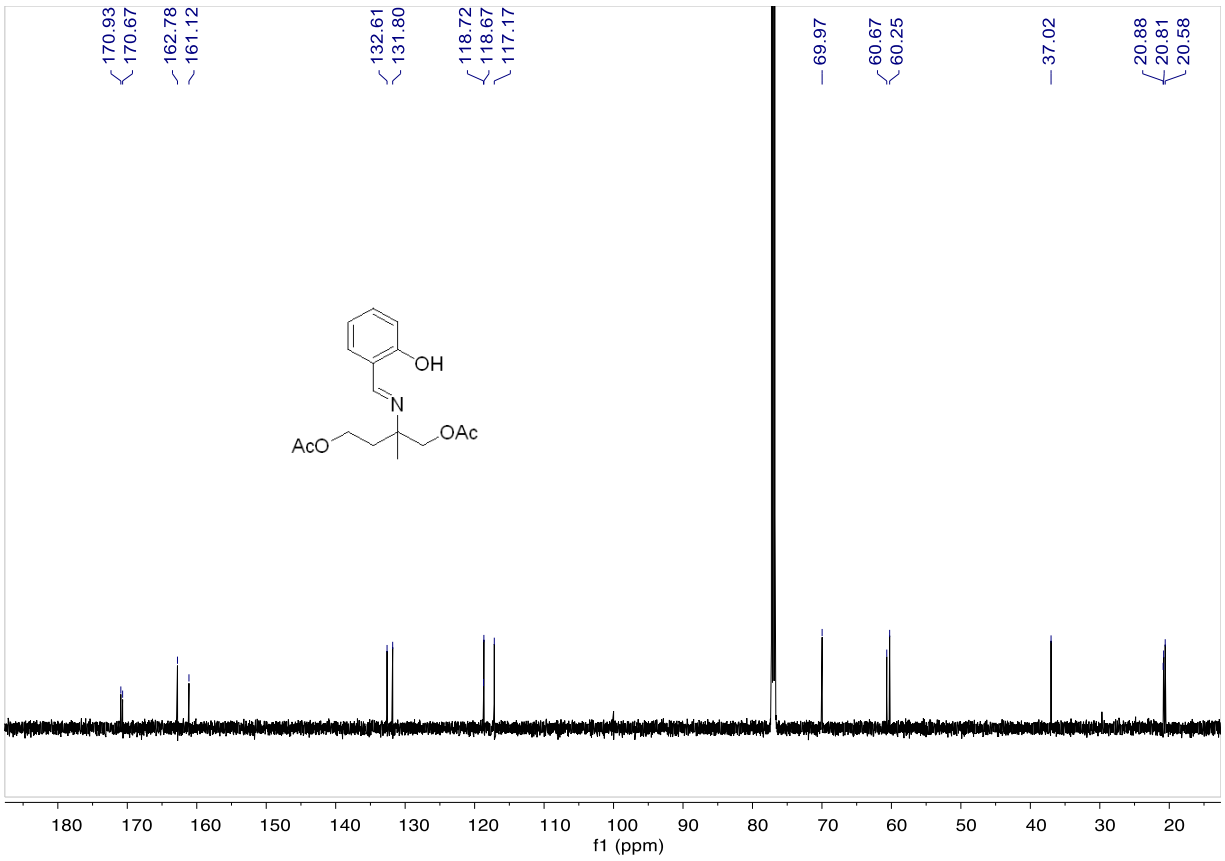
0.97
3.01
2.99
f1 (ppm)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37.02
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20.81
20.58
OH
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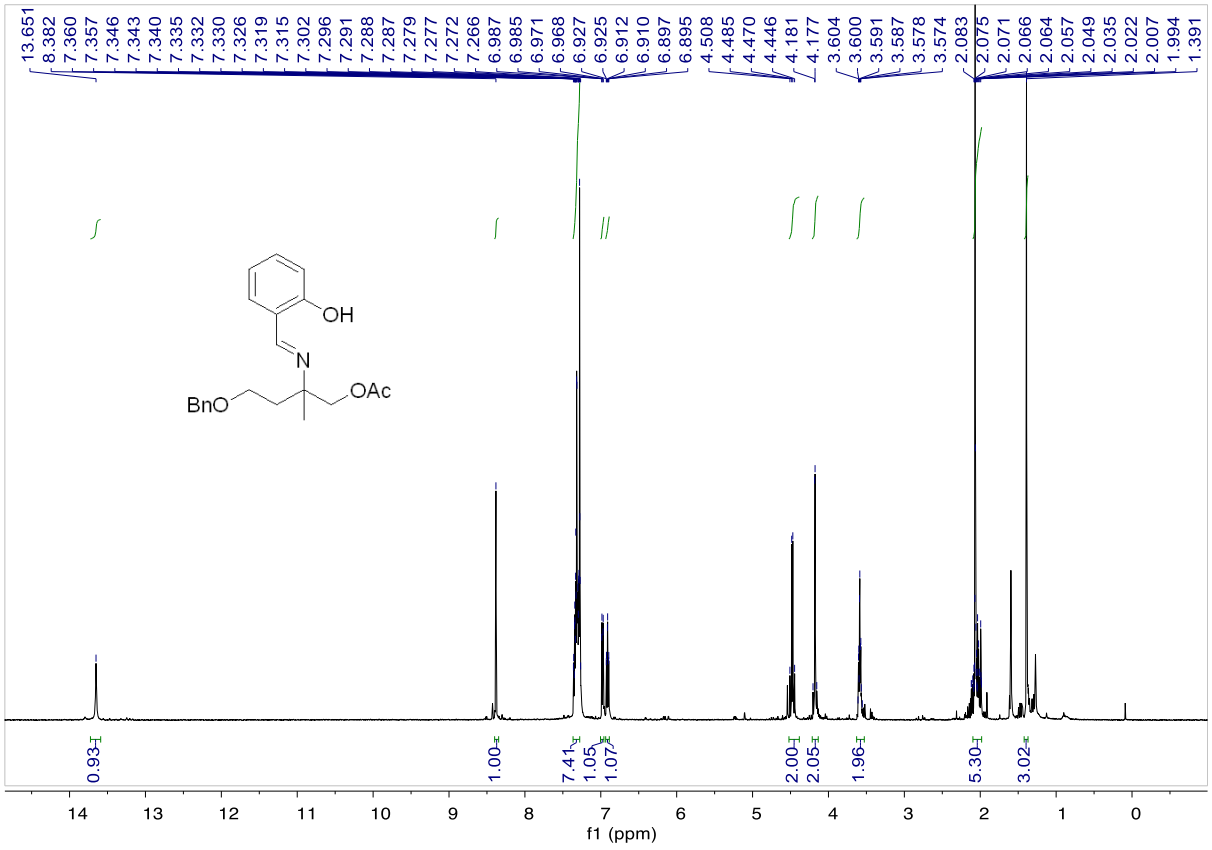
AcO
OAc
f1 (ppm)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7.272
7.266
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6.985
6.971
6.968
6.927
6.925
6.912
6.910
6.897
6.895
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4.470
4.446
4.181
4.177
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3.600
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3.587
3.578
3.574
2.083
2.075
2.071
2.066
2.064
2.057
2.049
2.035
2.022
2.007
1.994
1.391
OH
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BnO
OAc
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1.05
1.07
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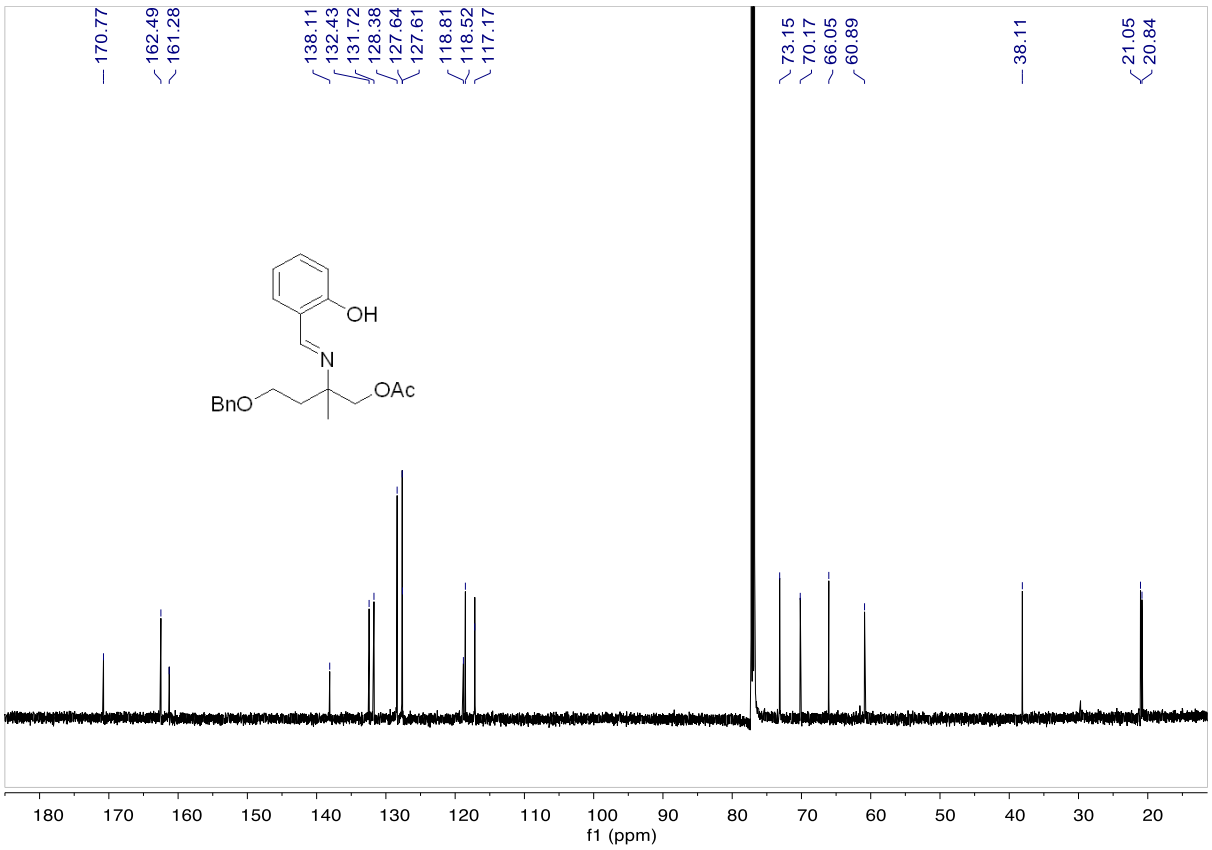
3.02
f1 (ppm)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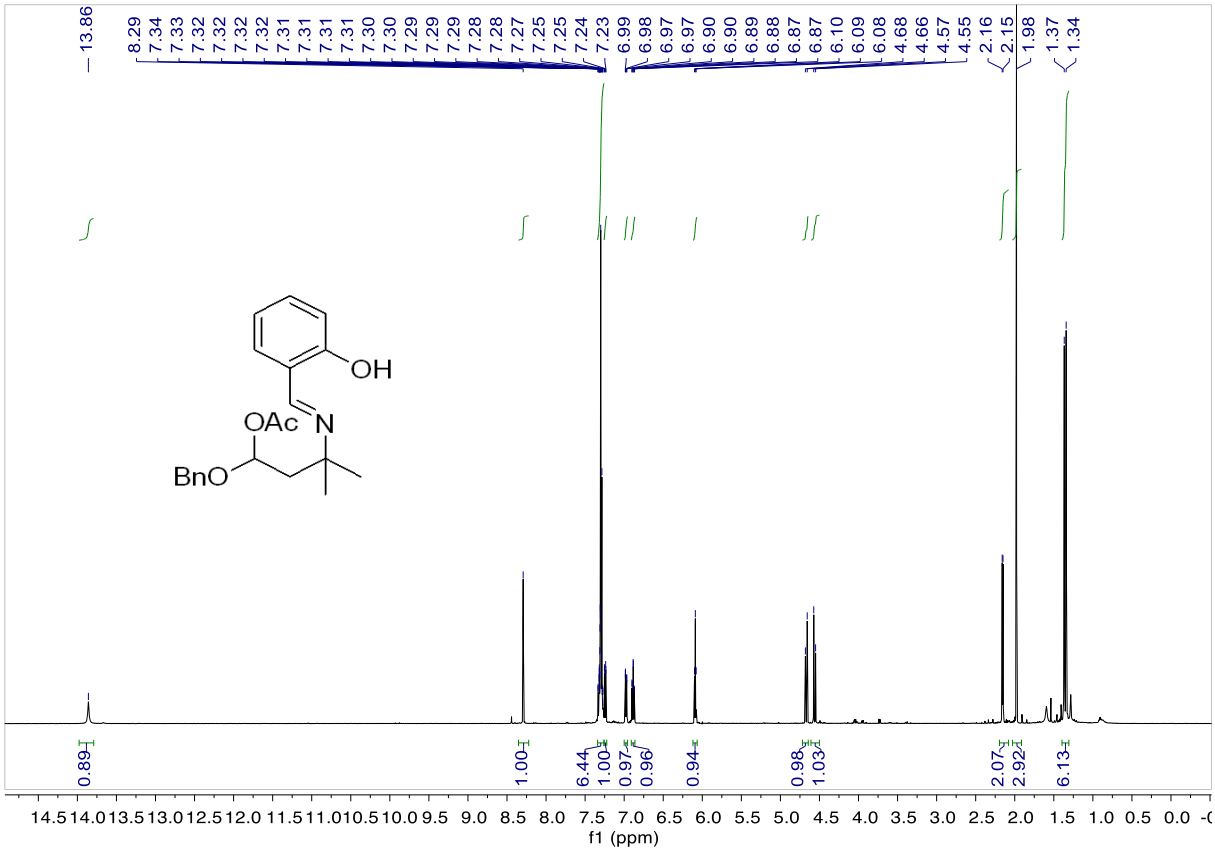
66.05
60.89
38.11
21.05
20.84
OH
N
BnO
OAc
f1 (ppm)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6.88
6.87
6.87
6.10
6.09
6.08
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4.66
4.57
4.55
2.16
2.15
1.98
1.37
1.34
OH
OAc
N
BnO
0.89
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6.44
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0.96
0.94
0.98
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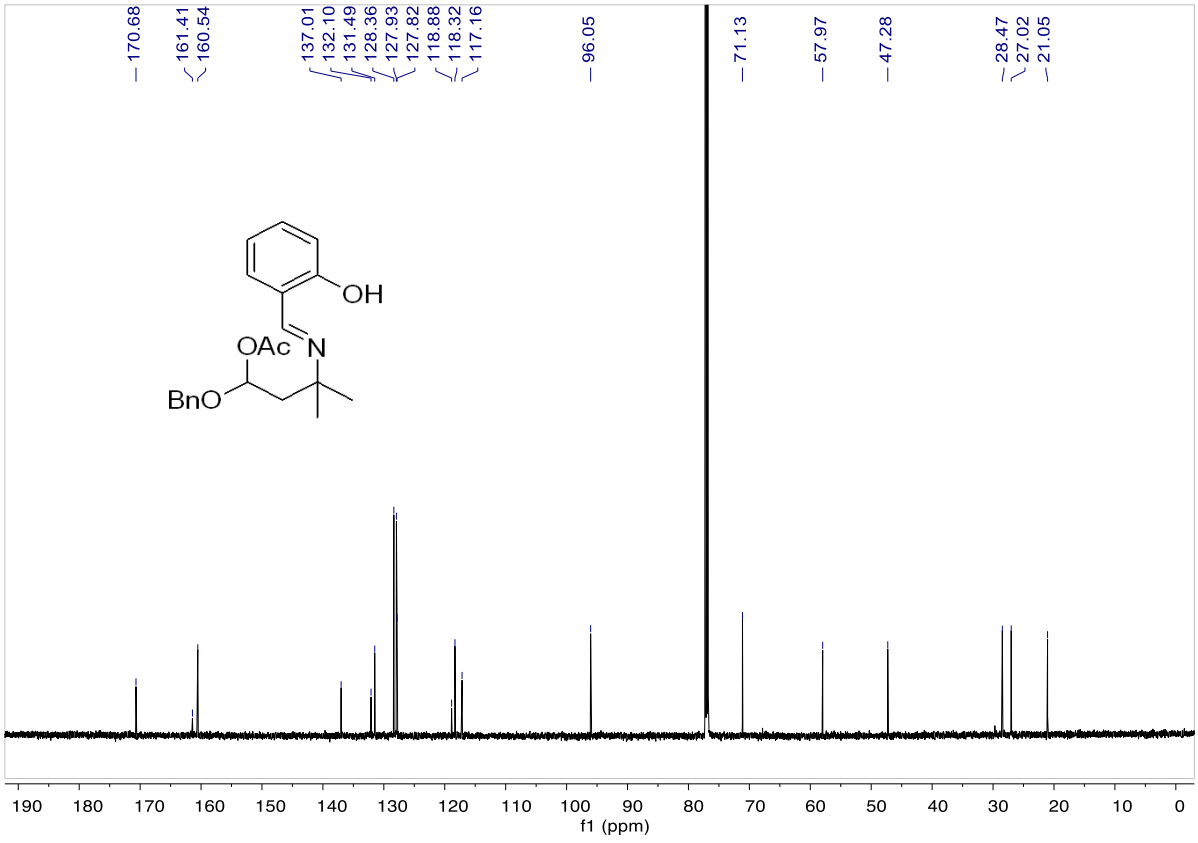
2.07
2.92
6.13
f1 (ppm)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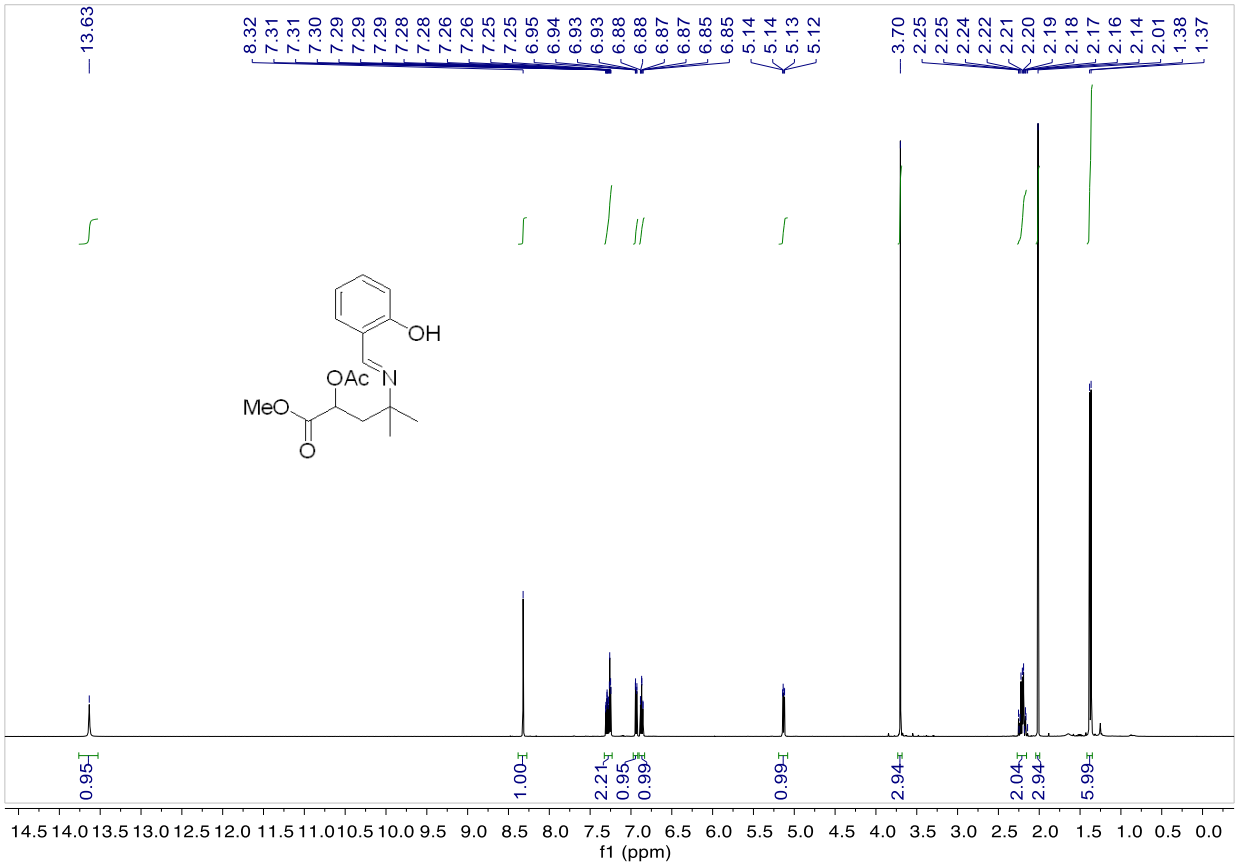
127.82
118.88
118.32
117.16
96.05
71.13
57.97
47.28
28.47
27.02
21.05
OH
OAc
N
BnO
f1 (ppm)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7.25
6.95
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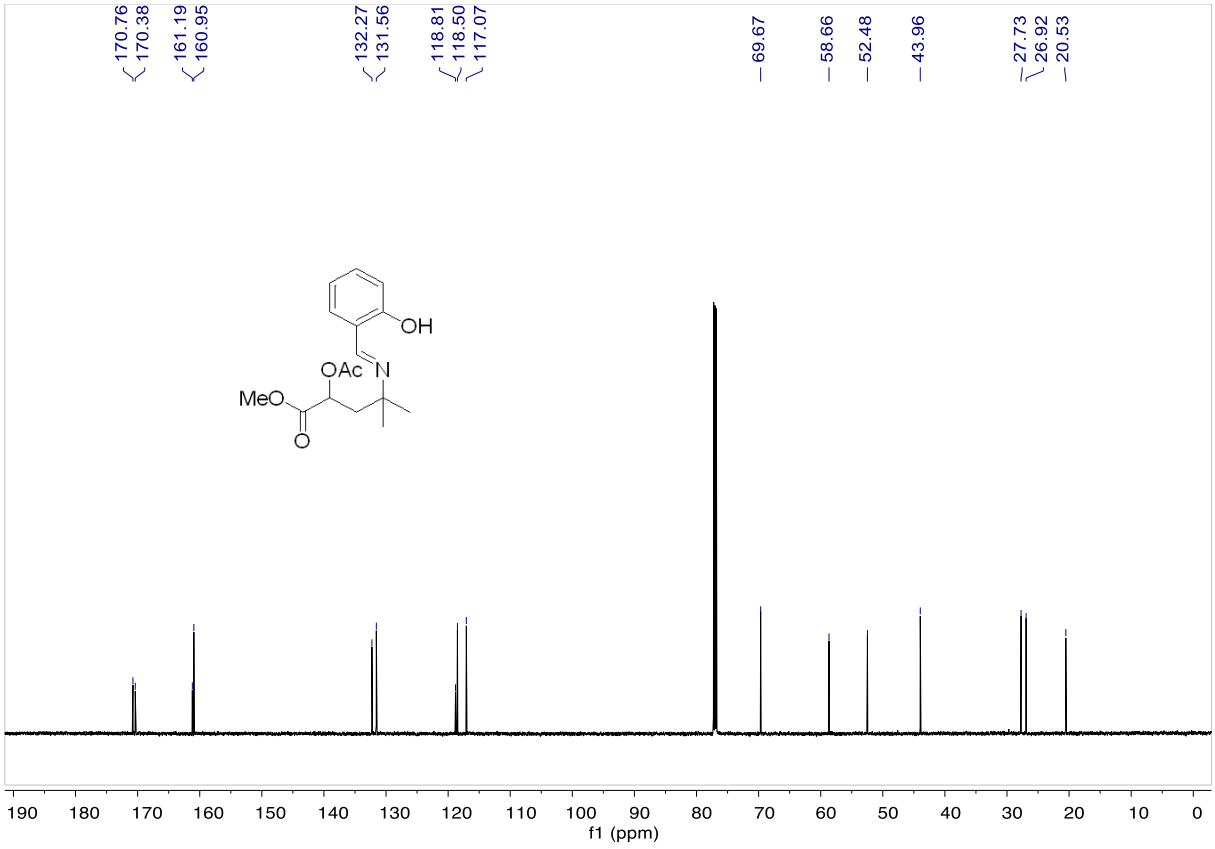
6.93
6.93
6.88
6.88
6.87
6.87
6.85
6.85
5.14
5.14
5.13
5.12
3.70
2.25
2.25
2.24
2.22
2.21
2.20
2.19
2.18
2.17
2.16
2.14
2.01
1.38
1.37
OH
OAc
N
MeO
O
0.95
1.00
2.21
0.95
0.99
0.99
2.94
2.04
2.94
5.99
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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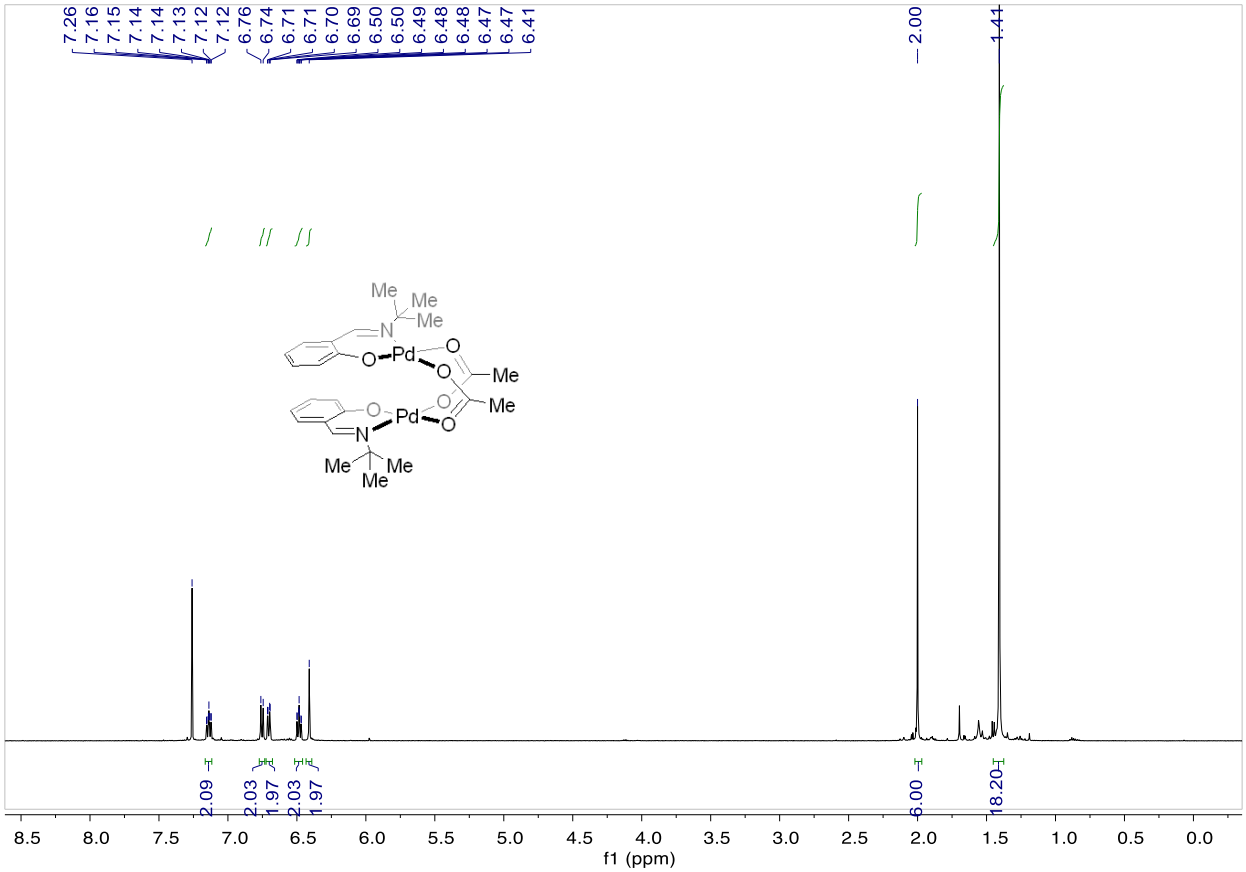
69.67
58.66
52.48
43.96
27.73
26.92
20.53
OH
OAc
N
MeO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.70
6.69
6.50
6.50
6.49
6.48
6.48
6.47
6.47
6.41
2.00
1.44
Me
Me
Me
N
O
Pd
O
O
Me
O
Pd
O
O
Me
N
Me
Me
Me
2.09
2.03
1.97
2.03
1.97
6.00
18.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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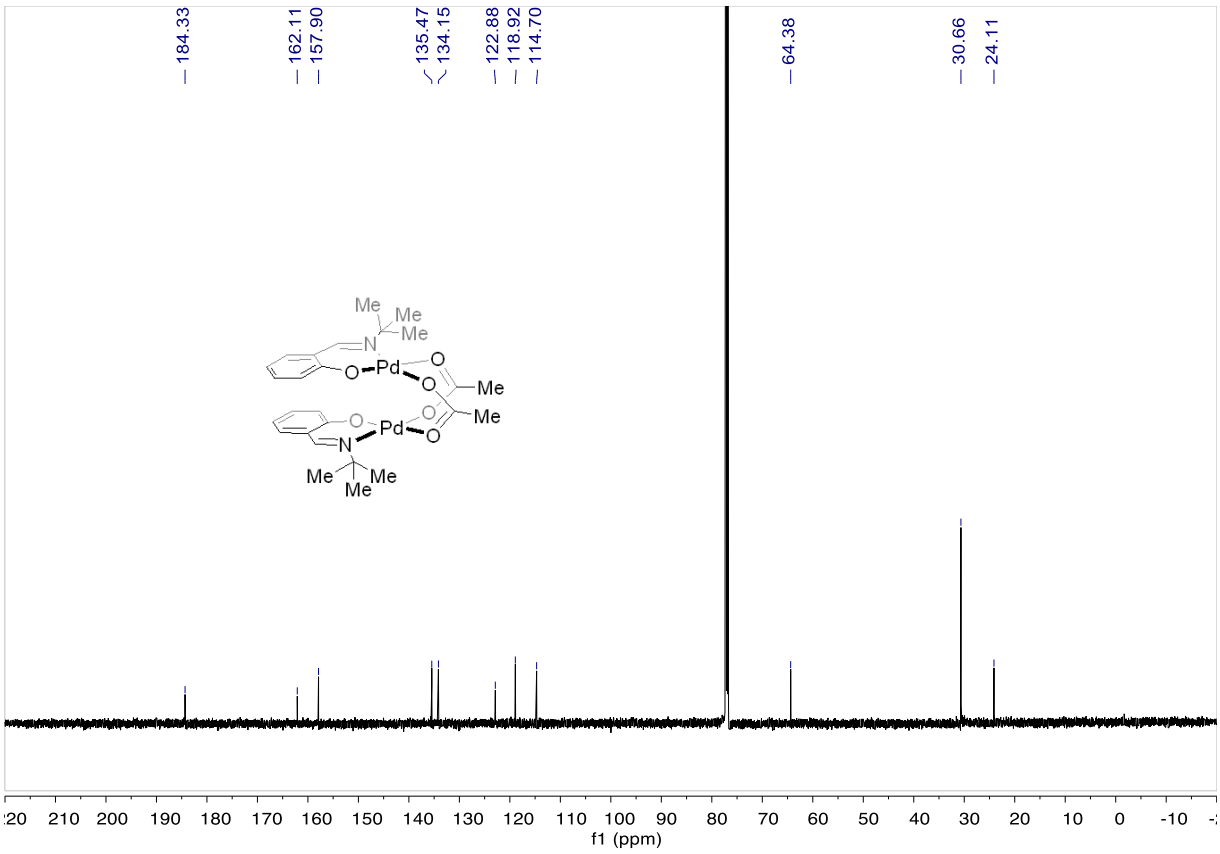
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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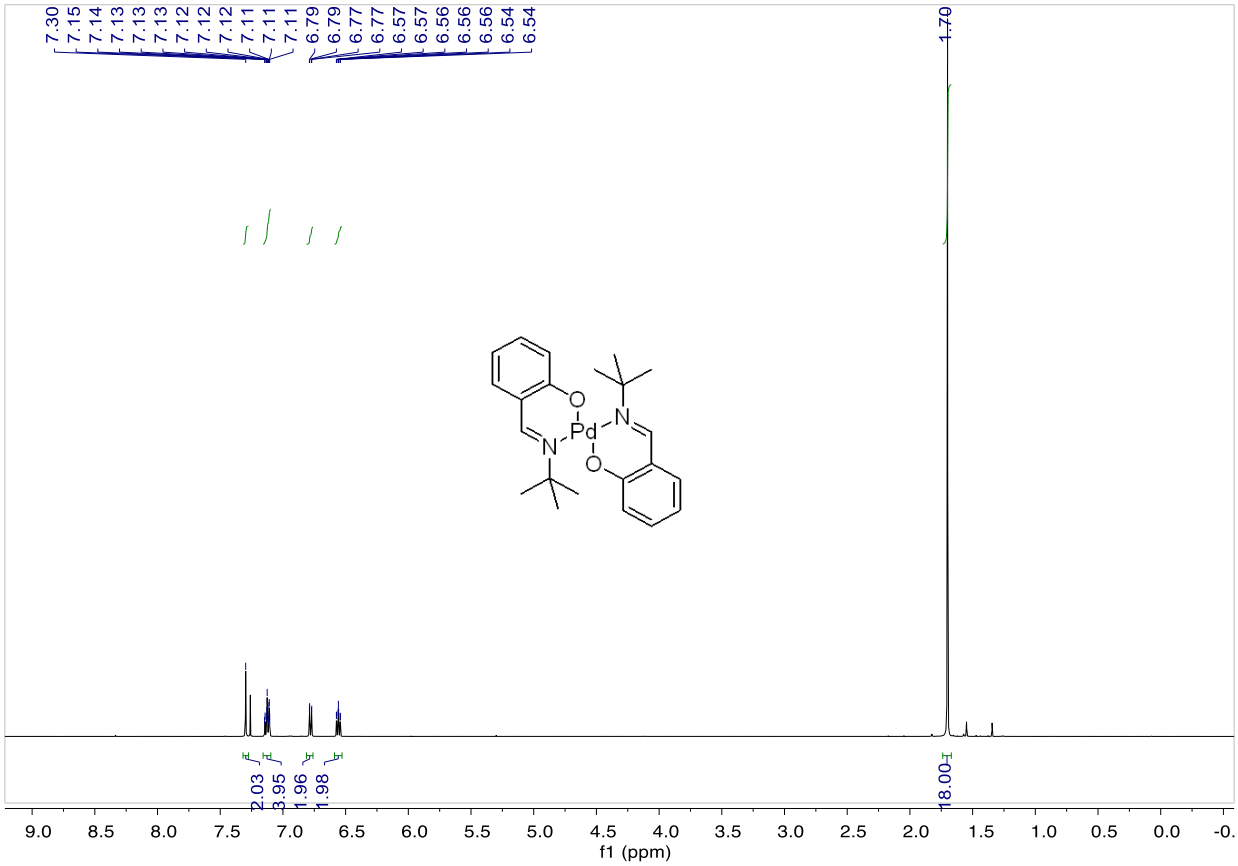
134.15
122.88
118.92
114.70
64.38
30.66
24.11
Me
Me
Me
N
O
Pd
O
O
Me
O
Pd
O
O
Me
N
Me
Me
Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.54
6.54
1.70
O
Pd
N
N
O
2.03
3.95
1.96
1.98
18.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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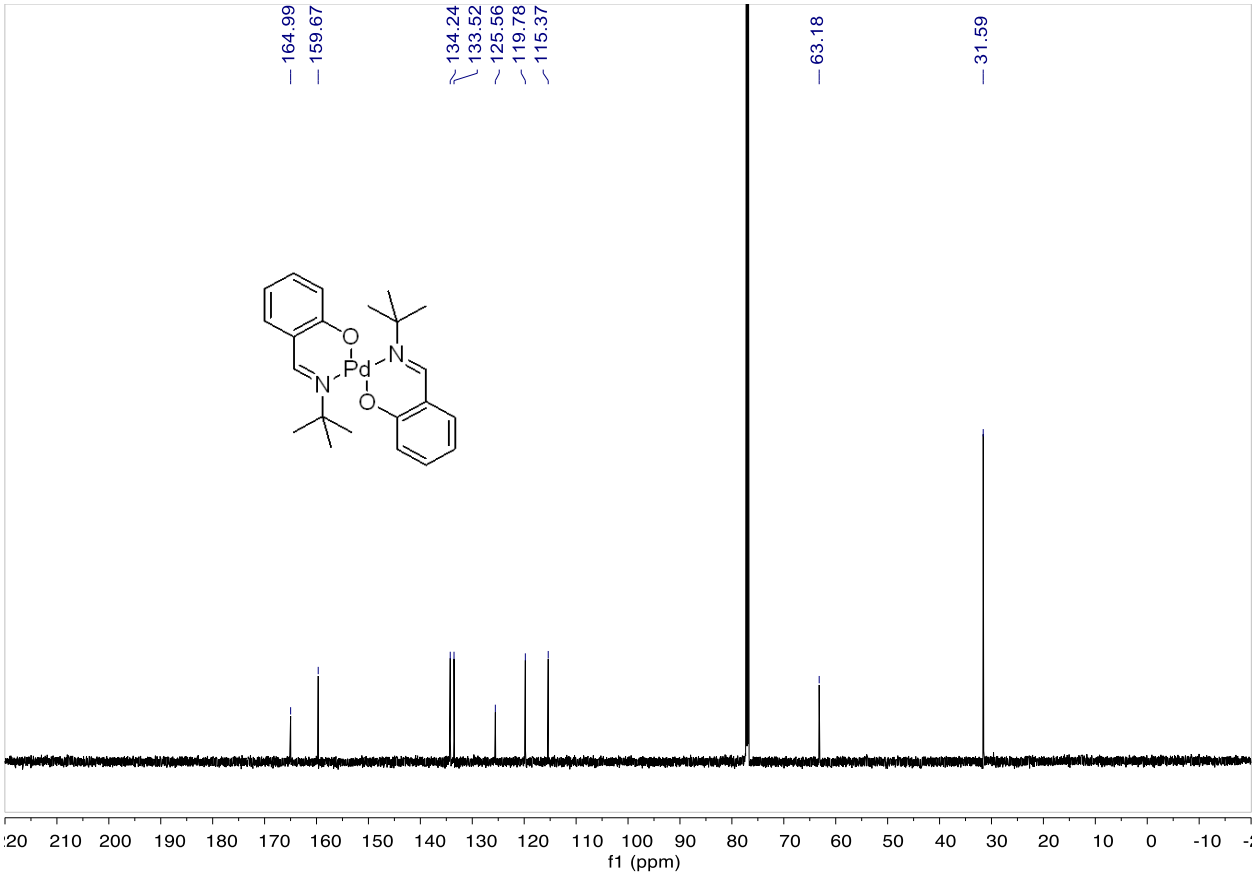
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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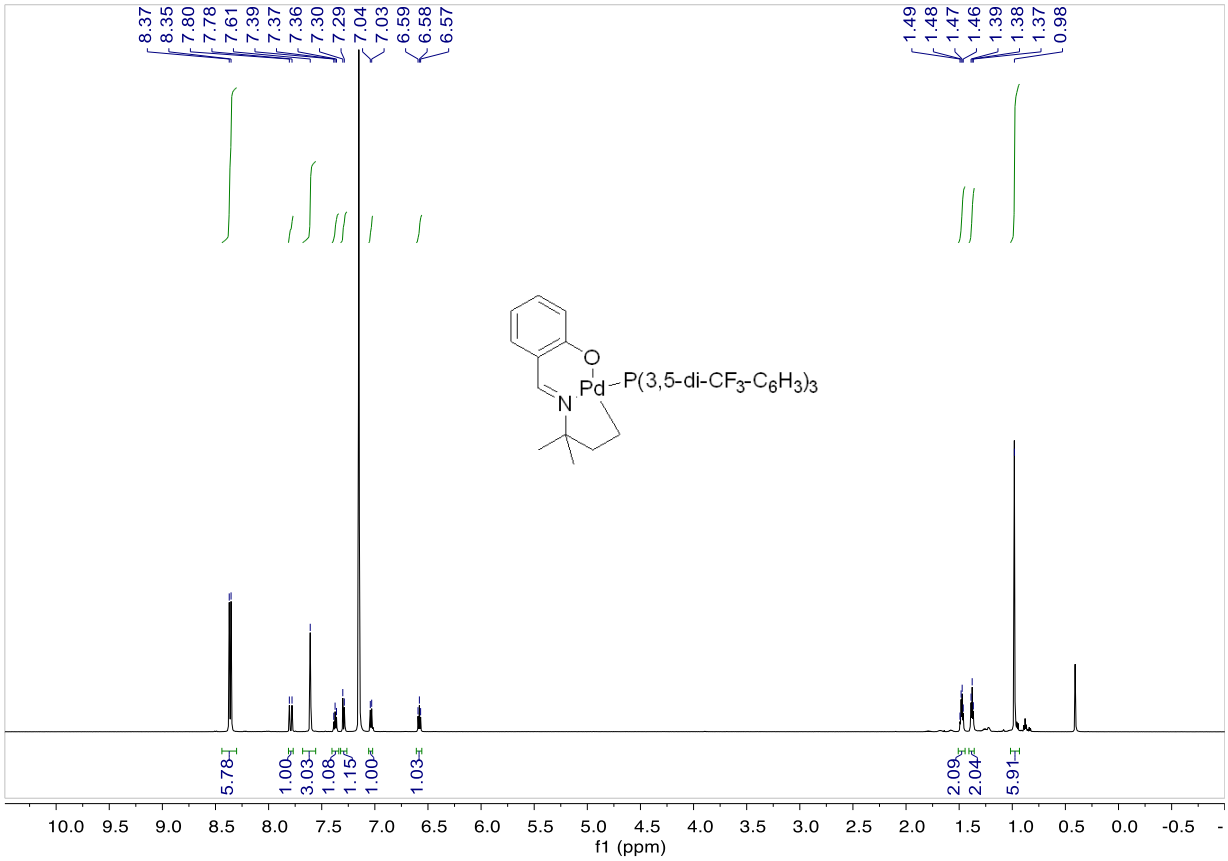
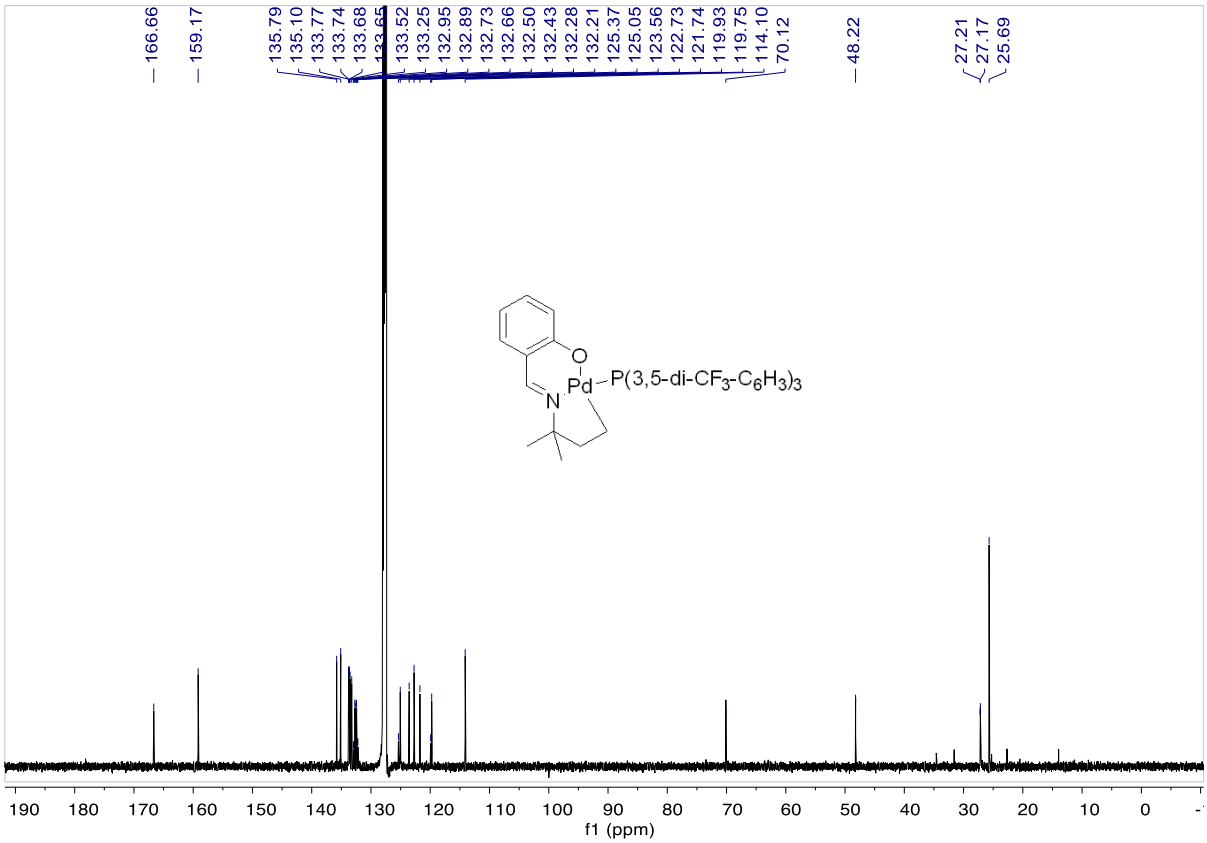
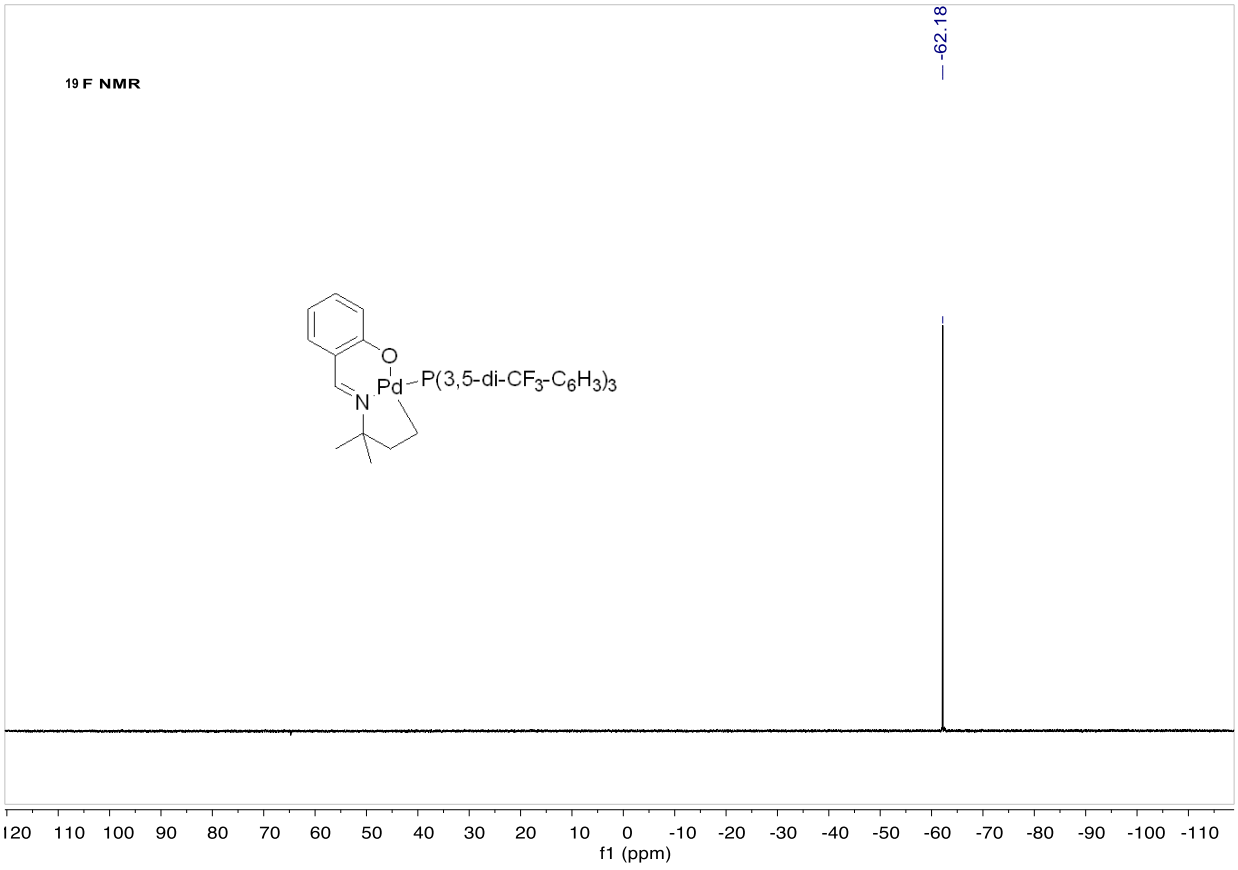
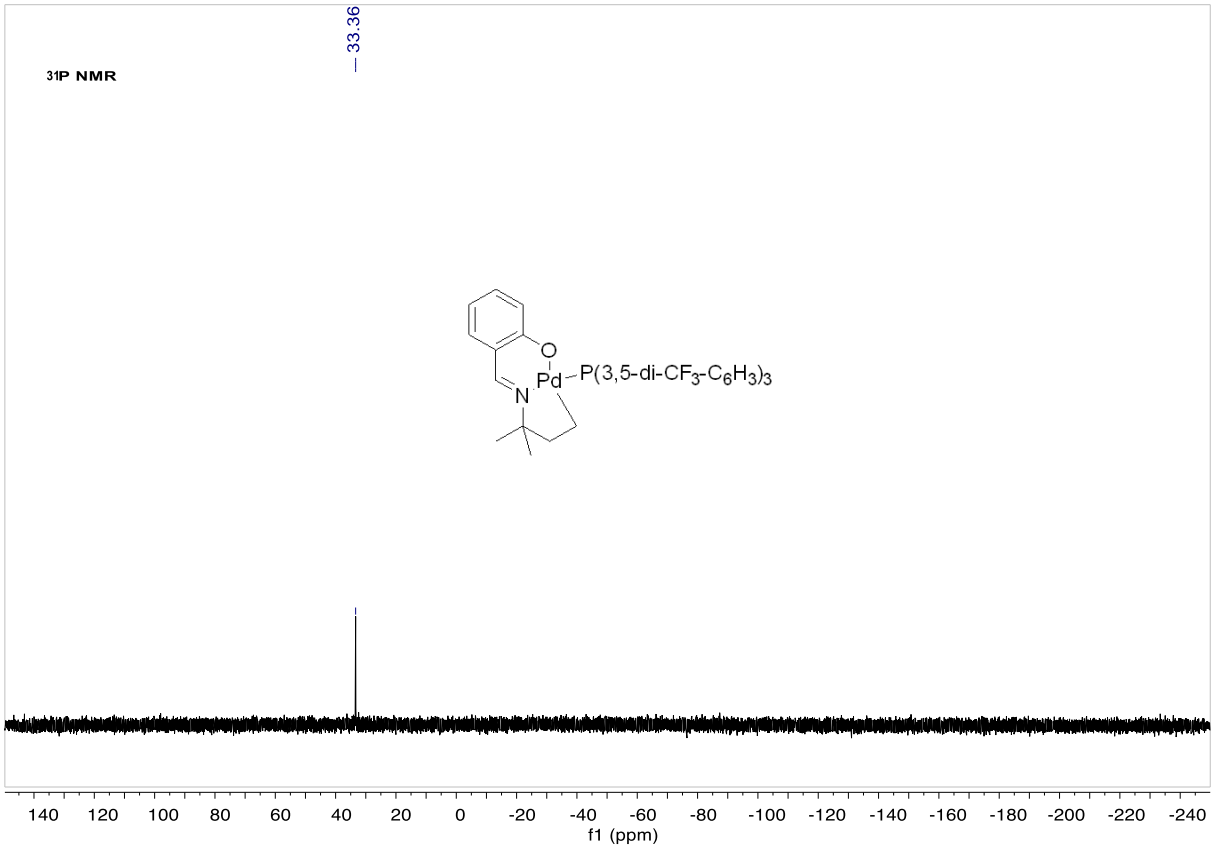
115.37
63.18
31.59
O
Pd
N
N
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.37
8.35
7.80
7.78
7.61
7.39
7.37
7.36
7.30
7.29
7.04
7.03
6.59
6.58
6.57
1.49
1.48
1.47
1.46
1.39
1.38
1.37
0.98
O
Pd
P(3,5-di-CF3-C6H3)3
N
5.78
1.00
3.03
1.08
1.15
1.00
1.03
2.09
2.04
5.91
f1 (ppm)


166.66
159.17
135.79
135.10
133.77
133.74
133.68
133.65
133.52
133.25
132.95
132.89
132.73
132.66
132.50
132.43
132.28
132.21
125.37
125.05
123.56
122.73
121.74
119.93
119.75
114.10
70.12
48.22
27.21
27.17
25.69
O
Pd
P(3,5-di-CF3-C6H3)3
N
f1 (ppm)


19F NMR
-62.18
O
Pd
P(3,5-di-CF3-C6H3)3
N
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110
f1 (ppm)


31P NMR
33.36
O
Pd
P(3,5-di-CF3-C6H3)3
N
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

12. References

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