Supporting Information for

Markovnikov selective hydroaminocarbonylation of alkenes over a porous monophoshine polymer supported palladium catalyst

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1. General Information

Chemicals and materials

All solvents and chemicals, unless otherwise noted, were obtained commercially and were used as received without further purification. All glassware was dried before using. Analytical thin layer chromatography (TLC) was performed using pre-coated Jiangyou silica gel HSGF254 (0.2mm ± 0.03mm). Flash chromatography was performed using silica gel 60, 0.063-0.2 mm, 200-300 mesh (Jiangyou, Yantai) with the indicated solvent system.

Instrumental measurements and physical characterization

Gas chromatography analysis was performed on Agilent 7890A GC equipped with a HP-5 capillary column and FID detector. GC-MS analysis was in general recorded on an Agilent 5977A MSD GC-MS. The contents of Pd in the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using Iris advantage Thermo Jarrel Ash device.

Fourier transform infrared (FT-IR) spectrum were recorded with a Bruker VERTEX 70FTIR spectrometer.

The liquid nuclear magnetic resonance spectra (NMR) were recorded on a Bruker AvanceTM III 400 MHz in deuterated chloroform unless otherwise noted. Data are reported in parts per million (ppm) as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dd = doublet of doublet and br = broad signal), coupling constant in Hz and integration.

Powder X-ray diffraction (PXRD) measurements were conducted were conducted by a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting CuKα1 radiation and a 6° position sensitive detector (PSD) (step size: 0.014°, step time: 25.05 s). The XRD patterns were scanned in the 2θ range of 0-80°.

Nitrogen adsorption-desorption isotherms were measured at 77 K using an American Quantachrome iQ_2 automated gas sorption analyzer. The samples were outgassed at 120 ℃ for 12 h before the measurements. Surface areas were calculated from the adsorption data using Langmuir and Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method.

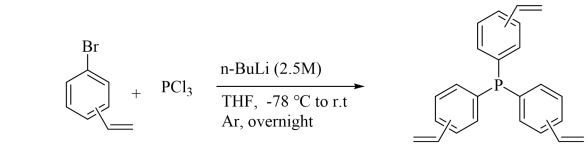
X-ray photoelectron spectroscopy (XPS) measurements were carried out by a VG ESCALAB 210 instrument equipped with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV Ar^+ ion gun. All spectra were recorded by using AlKa (1361 eV) radiation. The electron binding energy was referenced to the C1s peak at 284.8 eV.

The thermal properties of Pd/POL-*m*-3v-PPh_3 catalysts were evaluated using a METTLER TOLEDO simultaneous thermal analyzer over the temperature range from 30 to 800 °C under nitrogen atmosphere (20 mL/min) with a heating rate of 5 °C/min.

Field emission scanning electron microscopy (SEM) observations were performed on a Hitachi S-4800 microscope operated at an accelerating voltage of 5.0 kV.

High-resolution transmission electron microscope (HR-TEM) analysis was carried out on a Talos F200S operating at 200 kV.

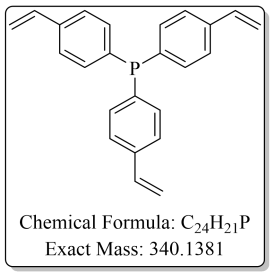
2. Synthetic procedures of the ligands



p or *m*-bromovinylbenzene

p-3vPPh$_3$ or *m*-3vPPh$_3$

Organic phosphine monomer was synthesized according to literature reports [1, 2].First of all, a solution of *n*-butyllithium in hexane (2.5 M, 12.6 ml, 31.5 mmol) was added dropwise over a period of 20 min to a solution of *p* or *m*-bromovinylbenzene (6.04 g, 33 mmol) in anhydrous tetrahydrofuran (40 ml) at -78 ℃ under argon atmosphere. The solution was stirred for 1 h and then phosphorus trichloride (1.37 g, 10 mmol) dissolved in anhydrous tetrahydrofuran (5 ml) was added dropwise over a period of 5 min. The mixture was continued to stir at -78 ℃ for 1 h and the system was recovered to room temperature, and allowed to react overnight. The reaction was quenched with 2M HCl solution. The mixture was extracted with ethyl acetate and water for 3 times, the combined organic phases were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using EtOAc–petroleum ether mixture as an eluent to afford the desired compound *p*-3vPPh$_3$ or *m*-3vPPh$_3$ as a white solid.

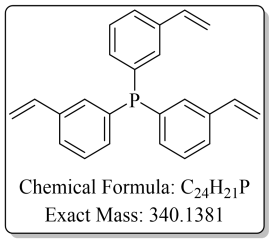


Tris(4-vinylphenyl)phosphane (*p*-3vPPh$_3$): white solid, 2.4 g, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.0 Hz, 6H), 7.27 (t, *J* = 7.7 Hz, 6H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 3H), 5.76 (d, *J* = 17.6 Hz, 3H), 5.26 (d, *J* = 10.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.09, 136.81, 136.70, 136.47, 134.09, 133.90, 126.47, 126.40, 114.82.

^{31}P NMR (162 MHz, $CDCl_3$) δ -6.85.



Tris(3-vinylphenyl)phosphane (*m*-3vPPh$_3$): white solid, 2.4 g, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 6H), 7.34 – 7.24 (m, 3H), 7.17 (t, *J* = 7.2 Hz, 3H), 6.64 (dd, *J* = 17.6, 10.9 Hz, 3H), 5.67 (d, *J* = 17.6 Hz, 3H), 5.21 (d, *J* = 11.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.80 (d, *J* = 7.7 Hz), 137.33 (d, *J* = 11.1 Hz), 136.59, 133.13 (d, *J* = 16.5 Hz), 132.01 (d, *J* = 23.0 Hz), 128.85 (d, *J* = 6.3 Hz), 126.63, 114.55.

^{31}P NMR (162 MHz, $CDCl_3$) δ -5.15.

3. Synthetic procedures of the porous organic polymer catalysts

Preparation of POL-*p*-3vPPh$_3$ or POL-*m*-3vPPh$_3$

Under an argon atmosphere, 0.6 g of *p*-3vPPh$_3$ (*m*-3vPPh$_3$) was dissolved in 6 ml of THF. Then, 15 mg of AIBN was added to the solution. The resulting mixture was transferred into an autoclave and stirred at room temperature for 30 minutes. Afterward, it was heated to 100 ℃ for 24 h without stirring. When the polymerization was complete, stop heating and allow to cool to room temperature. The resulting white solid was filtered, washed with THF (20 ml × 3), and dried under vacuum at 60 ℃ for 12 h. Finally, POL-*p*-3vPPh$_3$ was obtained.

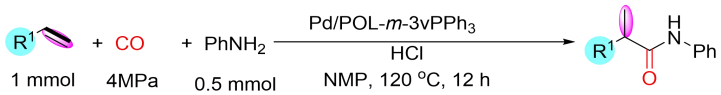
Preparation of Pd/POL-*p*-3vPPh$_3$ Or Pd/POL-*m*-3vPPh$_3$

Under argon atmosphere, 13 mg of Pd $(CH_3CN)_2Cl_2$ was dissolved in 10 mL of THF, followed by the addition of 200 mg of POL-*p*-3vPPh$_3$ or POL-*m*-3vPPh$_3$. After stirring for 24 h under argon atmosphere at room temperature, the resulted yellowish solid was filtered, washed with THF (20 ml×3), and dried under vacuum at 60 ℃ for 12 h, quantitative yield of the Pd/POL-*m*-3vPPh$_3$ was obtained 3.066 wt.% of Pd contents was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Preparation of Pd/POL-*m*-3vPPh$_3$-NaBH$_4$

The preparation of the Pd/POL-*m*-3vPPh$_3$-NaBH$_4$ has undergone some modifications according to previous literature[3]. Under argon atmosphere, 76 mg sodium borohydride was added to the mixture of methanol and ethanol (v: v=10:10), and then the mixture was added drop by drop to 100 mg Pd/POL-*m*-3vPPh$_3$, stirring at room temperature for 24 h. The solvent is removed by filtration, the black solid was filtered, washed with THF (10 ml×3) to obtain Pd/POL-*m*-3vPPh$_3$-NaBH$_4$ as black solid with yield of 83%.

4. General procedures for the hydroaminocarbonylation



As a typical hydroaminocarbonylation recipe, the as-prepared Pd/POL-*m*-3vPPh$_3$ catalyst (20 mg), styrene (104 mg, 1.0 mmol), aniline (47 mg, 0.5 mmol), HCl (0.06 mmol) and NMP (3 ml) were added into an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. GC yield was obtained by GC analysis using n-dodecane as the internal standard, isolated yield was obtained by flash column chromatography on silica gel using EtOAc–petroleum ether mixture as an eluent.

For recycling, the Pd/POL-*m*-3vPPh$_3$ catalyst was separated by centrifugation, washed with MeOH (8.0 ml×3), and dried under vacuum at 50 ℃ for 3 hours. The Pd contents of the used catalyst and filtrate after each run were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

5. Optimization of the reaction conditions

Comparison of activities of different palladium catalysts

First, five catalysts including $PdCl_2$, $PdCl_2$+PPh_3(P/Pd=2:1), Pd/ POL-*p*-3vpph$_3$, Pd/ POL-*m*-3vPPh$_3$, Pd/ POL-*m*-3VPPh$_3$-$NaBH_4$ were tested, and the dosage of Pd was 0.5 mg. The catalyst, styrene (104 mg, 1.0 mmol), aniline (47 mg, 0.5 mmol), HCl (0.6 mmol) and NMP (3 ml) were added into an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. GC yield was obtained by GC analysis using n-dodecane as the internal standard.

Screen of the reaction solvents

Five common solvents (THF, 1,4-Dioxane, CH_3CN, Toluene, NMP) were screened. Pd/POL-*m*-3vPPh$_3$ catalyst (20 mg), styrene (104 mg, 1.0 mmol), aniline (47 mg, 0.5 mmol), HCl (0.6 mmol) and solvent (3 ml) were added into an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. GC yield was obtained by GC analysis using n-dodecane as the internal standard.

Screen of acids

Different acids were screened. Pd/POL-*m*-3vPPh$_3$ catalyst (20 mg), styrene (104 mg, 1.0 mmol), aniline (47 mg, 0.5 mmol), acid (0.6 mmol) and NMP (3 ml) were added into an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. GC yield was obtained by GC analysis using n-dodecane as the internal standard.

Screen of the HCl dosage

The dosage of hydrochloric acid (X=0, 0.024, 0.06, 0.12, 0.6) was screened. Pd/POL-*m*-3vPPh$_3$ catalyst (20 mg), styrene (104 mg, 1.0 mmol), aniline (47 mg, 0.5 mmol), HCl (X mmol) and NMP (3 ml) were added into an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with

5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. GC yield was obtained by GC analysis using n-dodecane as the internal standard.

Screen of CO pressure

The CO pressure (X=0.5, 1, 2, 4) was screened. Pd/POL-*m*-3vPPh$_3$ catalyst (20 mg), styrene (104 mg, 1.0 mmol), aniline (47 mg, 0.5 mmol), HCl (0.06 mmol) and NMP (3 ml) were added into an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to X MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. GC yield was obtained by GC analysis using n-dodecane as the internal standard.

Screen of the reaction time

The reaction time (X=0.5, 1, 2, 3, 6, 9, 12) was screened. Pd/POL-*m*-3vPPh$_3$ catalyst (20 mg), styrene (104 mg, 1.0 mmol), aniline (47 mg, 0.5 mmol), HCl (0.06 mmol) and NMP (3 ml) were added into an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to X MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for X h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. GC yield was obtained by GC analysis using n-dodecane as the internal standard.

Table S1. Screen of the reaction temperature [a]

Entry	T (℃)	Yield (%)[b]	b/l[c]
1	60	trace	-
2	80	10	99:1
3	100	35	99:1
4	120	97	98:2

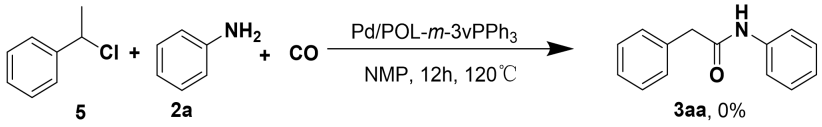
[a] Reaction conditions: Styrene (1.0 mmol), aniline (0.5 mmol), CO (4 MPa), Pd/POL-*m*-3vPPh$_3$ (20 mg), HCl (aq., 37wt.%, 0.12 equiv.), NMP (3 ml), 120 ℃， 12 h. [b] Determined by GC analysis using n-dodecane as the internal standard. [c] Determined by GC-MS of the crude products.

Table S2. Pd contents in the catalysts and the filtration after each cycle, and the corresponding reaction performance [a]

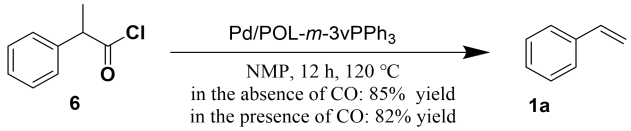
Entry	Recycling	Pd contents in the catalysts (wt.%)	Yield (%) [b]	b/l[c]
1	fresh	3.097	97	98:2
2	The 1st run	3.066	97	98:2
3	The 2nd run	2.917	97	98:2
4	The 3rd run	3.035	42	97:3

[a] Pd content was determined by ICP-AES. Reaction conditions: Styrene (1 mmol), aniline (0.5 mmol), CO (4 MPa), Pd/POL-*m*-3vPPh$_3$ (20 mg), HCl (aq., 37wt.%, 0.12 equiv.), NMP (3 ml), 120 °C, 12 h. [b] Determined by GC analysis using n-dodecane as the internal standard. [c] Determined by GC-MS of the crude products.

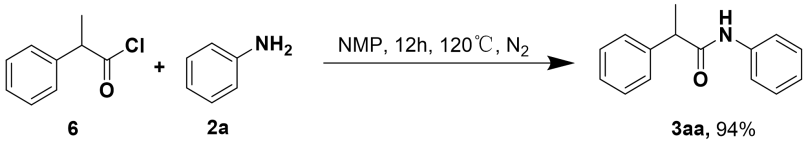
6. Controlled experiment



(1-chloroethyl)benzene **5** (1.0 mmol,), aniline (0.5 mmol), Pd/POL-*m*-3vPPh$_3$ (20 mg) and anhydrous NMP (3 ml) were added to an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with CO for three times, the pressure of CO was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to give the ratio of b/l of the products. No amide 3aa was observed.

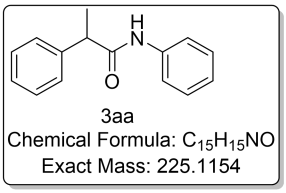


2-phenylpropanoyl chloride **6** (1.0 mmol), Pd/POL-*m*-3vPPh$_3$ (20 mg) and anhydrous NMP (3 ml) were added to an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with N_2 (CO) for three times, the pressure of N_2 (CO) was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to detected the products. The yield of styrene 1a was 85% (82%).



2-phenylpropanoyl chloride **6** (1.0 mmol,), aniline (0.5 mmol), Pd/POL-*m*-3vPPh$_3$ (20 mg) and anhydrous NMP (3 ml) were added to an 80 ml stainless-steel autoclave with a magnetic stir bar. After the autoclave was sealed and purged with N_2 for three times, the pressure of N_2 was adjusted to 4 MPa and the autoclave was put into a preheated reactor, then stirring at 120 °C for 12 h. After the reaction, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with ethyl acetate (6 ml), and the catalyst was removed from the system by centrifugation and analyzed by gas chromatography (Agilent 7890A GC equipped with a HP-5 capillary column with 5 wt.% phenyl groups and the FID detector) to detected the products. The yield of amide 3aa was 94%.

7. NMR data of the products

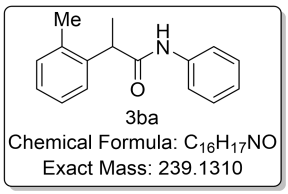


3aa
Chemical Formula: $C_{15}H_{15}NO$
Exact Mass: 225.1154

N,2-diphenylpropanamide[3]**:** white solid, 111 mg, 97% yield, 98% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.22 (m, 9H), 7.07 (dd, *J* = 18.3, 10.9 Hz, 2H), 3.71 (q, *J* = 7.1 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.41, 141.05, 137.97, 129.29, 129.04, 127.84, 127.71, 124.37, 119.81, 48.25, 18.69.

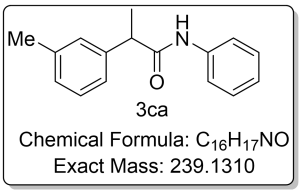


3ba
Chemical Formula: $C_{16}H_{17}NO$
Exact Mass: 239.1310

N-phenyl-2-(o-tolyl) propenamide: white solid, 99 mg, 84% yield, 98% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.2 Hz, 3H), 7.28 – 7.20 (m, 5H), δ 7.05 (t, *J* = 7.4 Hz, 2H), 3.93 (q, *J* = 7.2 Hz, 1H), 2.36 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.83, 138.92, 137.89, 136.51, 131.14, 128.98, 127.69, 127.09, 127.06, 124.36, 119.91, 44.71, 19.72, 17.77.

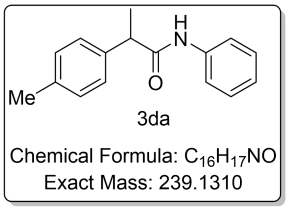


3ca
Chemical Formula: $C_{16}H_{17}NO$
Exact Mass: 239.1310

N-phenyl-2-(m-tolyl)propanamide: white solid, 102 mg, 88% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.27 – 7.18 (m, 3H), 7.17 – 7.00 (m, 4H), 3.68 (q, *J* = 7.1 Hz, 1H), 2.31 (s, 3H), 1.54 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.80, 140.98, 138.76, 138.07, 128.95, 128.89, 128.39, 128.28, 124.73, 124.23, 119.94, 47.87, 21.49, 18.62.

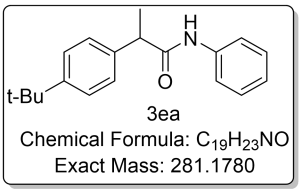


3da
Chemical Formula: $C_{16}H_{17}NO$
Exact Mass: 239.1310

N-phenyl-2-(p-tolyl) propenamide: white solid, 106 mg, 88% yield, 96% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 3H), 7.23 (dt, *J* = 8.2, 3.8 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.08 – 7.00 (m, 1H), 3.67 (q, *J* = 7.1 Hz, 1H), 2.33 (s, 3H), 1.55 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.87, 138.04, 137.99, 137.23, 129.82, 128.91, 127.63, 124.24, 119.90, 47.61, 21.13, 18.64.

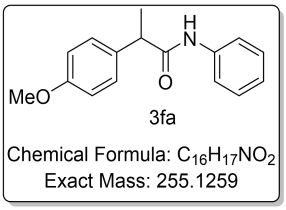


3ea
Chemical Formula: $C_{19}H_{23}NO$
Exact Mass: 281.1780

2-(4-(tert-butyl)phenyl)-N-phenylpropanamide: white solid, 128 mg, 89% yield, 98% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.22 (m, 5H), 7.04 (t, *J* = 7.4 Hz, 1H), 3.70 (q, *J* = 7.1 Hz, 1H), 1.57 (d, *J* = 7.1 Hz, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.80, 150.49, 138.07, 137.91, 128.96, 127.44, 126.09, 124.26, 119.89, 47.65, 34.60, 31.42, 18.64.

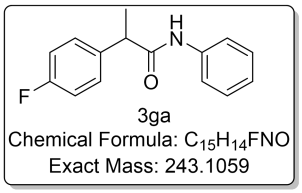


3fa
Chemical Formula: $C_{16}H_{17}NO_2$
Exact Mass: 255.1259

2-(4-methoxyphenyl)-N-phenylpropanamide: white solid, 119 mg, 92% yield, 98% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.30 – 7.12 (m, 4H), 7.12 – 6.92 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H), 3.66 (q, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.11, 158.89, 138.06, 133.02, 128.88, 128.74, 124.20, 119.92, 114.40, 55.30, 47.03, 18.70.

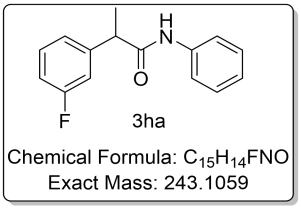


3ga
Chemical Formula: $C_{15}H_{14}FNO$
Exact Mass: 243.1059

2-(4-fluorophenyl)-N-phenylpropanamide: white solid, 108 mg, 94% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.18 (m, 4H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 8.7 Hz, 2H), 3.67 (q, *J* = 7.1 Hz, 1H), 1.50 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.85, δ 162.06 (d, $J_{C\text{-}F}$ = 245.8 Hz), 137.91, 136.80 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.17 (d, $J_{C\text{-}F}$ = 8.0 Hz) 128.92, 124.50, 120.28, 115.71 (d, $J_{C\text{-}F}$ = 21.3 Hz), 46.91, 18.80.

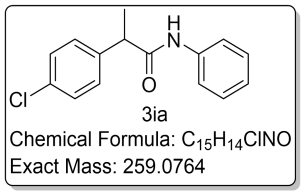


3ha
Chemical Formula: $C_{15}H_{14}FNO$
Exact Mass: 243.1059

2-(3-fluorophenyl)-N-phenylpropanamide[4]: white solid, 106 mg, 85% yield, 96% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.43 (d, *J* = 7.7 Hz, 2H), 7.33 – 7.22 (m, 3H), 7.16 – 7.04 (m, 3H), 6.97 (td, *J* = 8.4, 1.9 Hz, 1H), 3.69 (q, *J* = 7.1 Hz, 1H), 1.55 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.98, 163.16 (d, J_{C-F} = 246.8 Hz), 143.51 (d, J = 7.1 Hz), 137.81, 130.60 (d, J_{C-F} = 8.3 Hz), 129.03, 124.57, 123.39 (d, J_{C-F} = 2.9 Hz), 120.10, 115.01 (d, J = 36.6 Hz), 114.72 (d, J_{C-F}= 21.6 Hz), 47.73, 18.67.

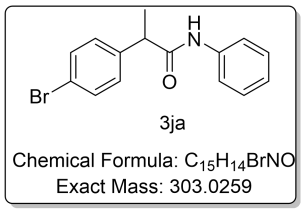


3ia
Chemical Formula: $C_{15}H_{14}ClNO$
Exact Mass: 259.0764

2-(4-chlorophenyl)-N-phenylpropanamide: white solid, 122 mg, 91% yield, 98% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.8 Hz, 2H), 7.35 – 7.21 (m, 7H), 7.08 (t, J = 7.4 Hz, 1H), 3.67 (q, J = 7.1 Hz, 1H), 1.56 (d, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.93, 139.53, 137.80, 133.52, 129.34, 129.12, 129.09, 124.59, 119.94, 47.60, 18.87.

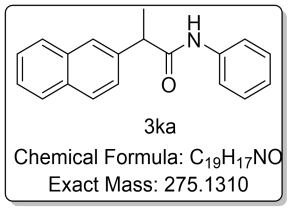


3ja
Chemical Formula: $C_{15}H_{14}BrNO$
Exact Mass: 303.0259

2-(4-bromophenyl)-N-phenylpropanamide: white solid, 130 mg, 80% yield, 92% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.34 – 7.22 (m, 4H), 7.16 (s,1 H), 7.08 (t, J = 7.3 Hz, 1H), 3.65 (d, J = 7.1 Hz, 1H), 1.56 (d, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.81, 140.05, 137.78, 132.30, 129.48, 129.10, 124.60, 121.61, 119.93, 47.69, 18.84.

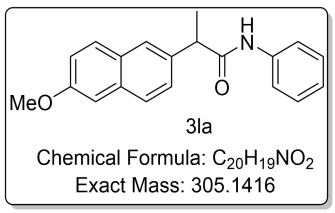


3ka
Chemical Formula: $C_{19}H_{17}NO$
Exact Mass: 275.1310

2-(naphthalen-2-yl)-N-phenylpropanamide[5]: white solid, 115 mg, 83% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 4H), 7.53 – 7.38 (m, 5H), 7.28 – 7.19 (m, 3H), 7.08 – 7.00 (m, 1H), 3.87 (q, J = 7.1 Hz, 1H), 1.67 (d, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 138.48, 137.93, 133.68, 132.83, 129.14, 129.01, 127.90, 127.85, 126.60, 126.25, 125.75, 124.39, 119.86, 48.32, 18.68.

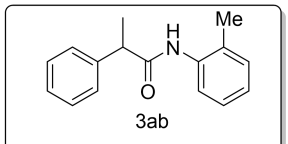


3la
Chemical Formula: $C_{20}H_{19}NO_2$
Exact Mass: 305.1416

2-(6-methoxynaphthalen-2-yl)-N-phenylpropanamide[5]: white solid, 140 mg, 87% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 11.5, 9.1 Hz, 3H), 7.41 (d, *J* = 8.5 Hz, 3H), 7.32 (s, 1H), 7.23 (dd, *J* = 9.5, 6.3 Hz, 2H), 7.18 – 7.09 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 3.90 (s, 3H), 3.83 (q, *J* = 7.1 Hz, 1H), 1.64 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 157.94, 137.98, 136.09, 133.97, 129.36, 129.11, 128.97, 127.91, 126.39, 126.25, 124.32, 119.85, 119.38, 105.78, 55.43, 48.07, 18.67.



3ab

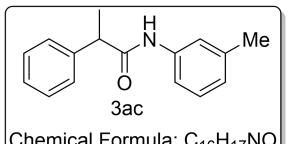
Chemical Formula: $C_{16}H_{17}NO$

Exact Mass: 239.1310

2-phenyl-N-(o-tolyl) propenamide[3]**:** white solid, 115 mg, 94% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.24 (m, 5H), 7.19 – 6.94 (m, 4H), 3.74 (q, *J* = 7.2 Hz, 1H), 1.86 (s, 3H), 1.59 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.49, 141.08, 135.70, 130.30, 129.12, 128.85, 127.80, 127.59, 126.60, 124.94, 122.63, 47.79, 18.08, 17.18.



3ac

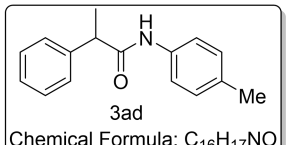
Chemical Formula: $C_{16}H_{17}NO$

Exact Mass: 239.1310

2-phenyl-N-(m-tolyl) propenamide[3]**:** white solid, 112 mg, 81% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.38 – 7.18 (m, 7H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 3.70 (q, *J* = 7.1 Hz, 1H), 2.22 (s, 3H), 1.54 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.80, 141.09, 138.74, 137.94, 128.96, 128.67, 127.63, 127.38, 125.04, 120.68, 117.12, 47.78, 21.40, 18.62.



3ad

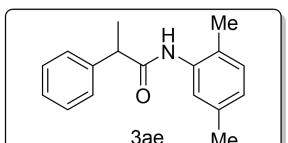
Chemical Formula: $C_{16}H_{17}NO$

Exact Mass: 239.1310

2-phenyl-N-(p-tolyl) propenamide[3]**:** white solid, 102 mg, 87% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.35 – 7.18 (m, 7H), 7.01 (d, *J* = 8.2 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 2.24 (s, 3H), 1.52 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.74, 141.15, 135.44, 133.83, 129.33, 128.94, 127.66, 127.35, 120.19, 47.70, 20.85, 18.62.



3ae

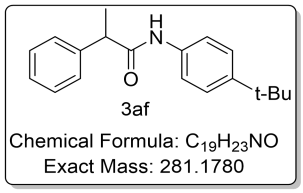
Chemical Formula: $C_{17}H_{19}NO$

Exact Mass: 253.1467

N-(2,5-dimethylphenyl)-2-phenylpropanamide: white solid, 105 mg, 80% yield, 98% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.45 – 7.24 (m, 5H), 6.94 (d, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 3.76 (q, *J* = 7.2 Hz, 1H), 2.27 (s, 3H), 1.83 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$**)** δ 172.42, 141.11, 136.51, 135.54, 130.14, 129.25, 127.90, 127.73, 125.61, 125.22, 122.86, 48.06, 21.17, 18.12, 16.76.



3af

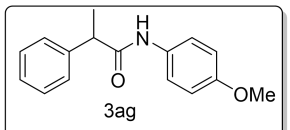
Chemical Formula: $C_{19}H_{23}NO$

Exact Mass: 281.1780

N-(4-(tert-butyl) phenyl)-2-phenylpropanamide: white solid, 126 mg, 86% yield, 97% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$**)** δ 7.46 (s, 1H), 7.39 – 7.30 (m, 6H), 7.29 – 7.21 (m, 3H), 3.71 (q, *J* = 7.1 Hz, 1H), 1.56 (d, *J* = 7.1 Hz, 3H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.51, 147.23, 141.18, 135.43, 129.08, 127.73, 127.48, 125.74, 119.69, 47.93, 34.38, 31.41, 18.67.



3ag

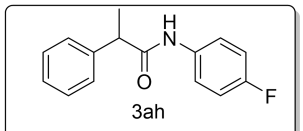
Chemical Formula: $C_{16}H_{17}NO_2$

Exact Mass: 255.1259

N-(4-methoxyphenyl)-2-phenylpropanamide: white solid, 117 mg, 91% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.14 (m, 8H), 6.78 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.69 (q, *J* = 7.1 Hz, 1H), 1.57 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.40, 156.45, 141.22, 131.11, 129.14, 127.78, 127.54, 121.81, 114.10, 55.54, 47.90, 18.72.



3ah

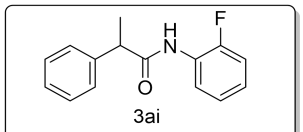
Chemical Formula: $C_{15}H_{14}FNO$

Exact Mass: 243.1059

N-(4-fluorophenyl)-2-phenylpropanamide[4]: white solid, 104 mg, 87% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.43 – 7.19 (m, 7H), 6.88 (t, *J* = 8.5 Hz, 2H), 3.69 (q, *J* = 6.8 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.95, 159.37 (d, $J_{C\text{-}F}$ = 243.5 Hz), 140.94, 133.97 (d, $J_{C\text{-}F}$ = 2.7 Hz), 129.03, 127.62, 127.52, 122.06 (d, $J_{C\text{-}F}$ = 7.8 Hz), 115.45 (d, $J_{C\text{-}F}$ = 22.4 Hz), 47.65, 18.59.



3ai

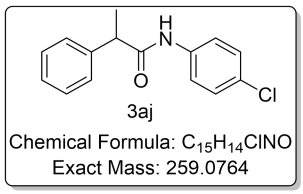
Chemical Formula: $C_{15}H_{14}FNO$

Exact Mass: 243.1059

N-(2-fluorophenyl)-2-phenylpropanamide[6]: white solid, 128mg, 95% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 31.2 Hz, 1H), 7.40 – 7.23 (m, 5H), 7.10 – 6.92 (m, 3H), 3.76 (q, *J* = 7.1 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.48, 152.47 (d, J_{C-F} = 243.2 Hz), 140.64, 129.16, 127.67, 126.39 (d, J_{C-F}= 10.0 Hz), 124.49 (d, J_{C-F} = 3.7 Hz), 124.32 (d, J_{C-F} = 7.7 Hz), 121.73, 114.71 (d, J_{C-F} = 19.2 Hz), ,48.13, 18.47.

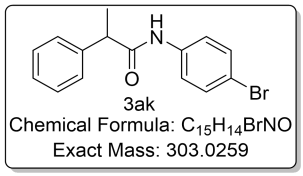


3aj
Chemical Formula: $C_{15}H_{14}ClNO$
Exact Mass: 259.0764

N-(4-chlorophenyl)-2-phenylpropanamide: white solid, 127 mg, 95% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.36 – 7.27 (m, 7H), 7.17 – 7.13 (m, 2H), 3.68 (q, *J* = 7.1 Hz, 1H), 1.53 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.00, 140.76, 136.49, 129.32, 129.10, 128.87, 127.62, 121.43,47.79, 18.58.

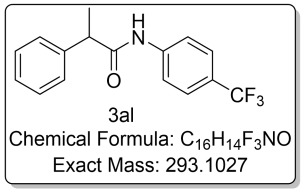


3ak
Chemical Formula: $C_{15}H_{14}BrNO$
Exact Mass: 303.0259

N-(4-bromophenyl)-2-phenylpropanamide: white solid, 92 mg, 86% yield, 99%, branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.40 – 7.25 (m, 9H), 3.68 (q, *J* = 7.1 Hz, 1H), 1.55 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.77, 140.75, 137.01, 131.87, 129.20, 127.68, 121.62, 116.94, 47.97, 18.63.

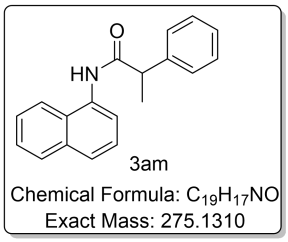


3al
Chemical Formula: $C_{16}H_{14}F_3NO$
Exact Mass: 293.1027

2-phenyl-N-(4-(trifluoromethyl)phenyl) propenamide: white solid, 138 mg, 95% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.49 (dd, *J* = 30.5, 8.3 Hz, 4H), 7.40 – 7.22 (m,5H), 3.73 (q, *J* = 6.8 Hz, 1H), 1.57 (d, *J* = 6.7 Hz, 3H).

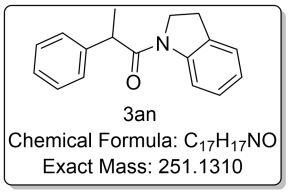
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.21, 141.01, 140.58, 129.24, 127.79, 127.65, 126.12 (q, J_{C-F} = 3.7 Hz), 125.65 (d, J_{C-F} = 43.6 Hz) 122.78, 119.67, 48.05, 18.59.



N-(naphthalen-1-yl)-2-phenylpropanamid ： white solid, 107 mg, 95% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.66 (dd, *J* = 17.3, 7.7 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.18 (m, 9H), 3.75 (q, *J* = 7.0 Hz, 1H), 1.50 (d, *J* = 7.1 Hz, 3H).

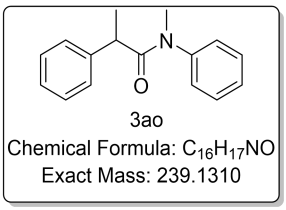
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.33, 141.24, 133.92, 132.31, 129.00, 128.42, 127.77, 127.43, 125.99, 125.74, 125.67, 125.43, 121.04, 120.78, 47.44, 18.30.



1-(indolin-1-yl)-2-phenylpropan-1-one[7]：white solid, 107 mg, 80% yield, 97% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.25 – 7.14 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.97 (td, *J* = 7.4, 0.8 Hz, 1H), 4.05 (td, *J* = 10.4, 6.5 Hz, 1H), 3.84 (q, *J* = 6.8 Hz, 1H), 3.73 (td, *J* = 10.4, 6.6 Hz, 1H), 3.18 – 3.00 (m, 1H), 3.00 – 2.88 (m, 1H), 1.52 (d, *J* = 6.9 Hz, 3H).

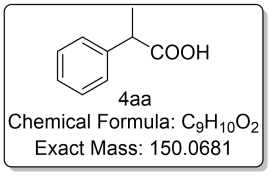
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.99, 143.36, 141.13, 131.16, 129.00, 127.55, 127.49, 127.03, 124.50, 123.68, 117.22, 47.68, 46.26, 28.01, 20.56.



N-methyl-N,2-diphenylpropanamide[4]: colorless oily liquid, 98 mg, 77% yield, 91% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 3H), 7.23 – 7.14 (m, 3H), 7.07 – 6.95 (m, 4H), 3.64 (q, *J* = 6.9 Hz, 1H), 3.23 (s, 3H), 1.39 (d, *J* = 6.9 Hz, 3H).

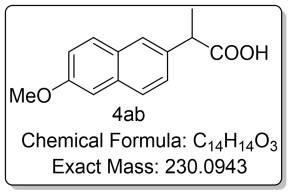
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.05, 143.82, 141.97, 129.57, 128.38, 127.85, 127.56, 126.63, 43.12, 37.74, 20.35.



2-phenylpropanoic acid: Colorless liquid，64 mg, 81% yield, 99% branched selectivity.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 7.37 – 7.24 (m, 5H), 3.73 (q, *J* = 7.2 Hz, 1H), 1.51 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.09, 139.89, 128.81, 127.73, 127.52, 45.52, 18.21.



4ab

Chemical Formula: $C_{14}H_{14}O_3$

Exact Mass: 230.0943

2-(6-methoxynaphthalen-2-yl)propanoic acid: white solid, 97 mg, 84% yield, 99% branched selectivity.

1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 9.2 Hz, 3H), 7.45 (dd, J = 8.5, 1.7 Hz, 1H), 7.21 – 7.12 (m, 2H), 4.23 – 3.64 (m, 4H), 1.63 (d, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 180.99, 157.84, 135.00, 133.96, 129.44, 129.03, 127.37, 126.33, 126.28, 119.17, 105.73, 55.43, 45.41, 18.24.

8. Catalyst characterization

Experimental PXRD profiles

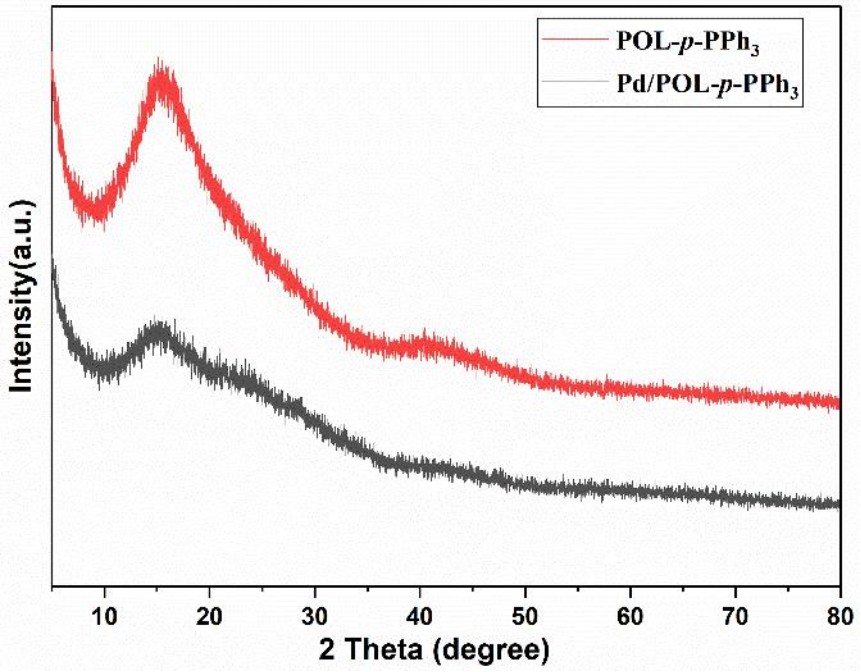


Fig. S1 PXRD profiles of POL-*p*-3vPPh$_3$, Pd/POL-*p*-3vPPh$_3$

In-stiu DRIFTS spectra

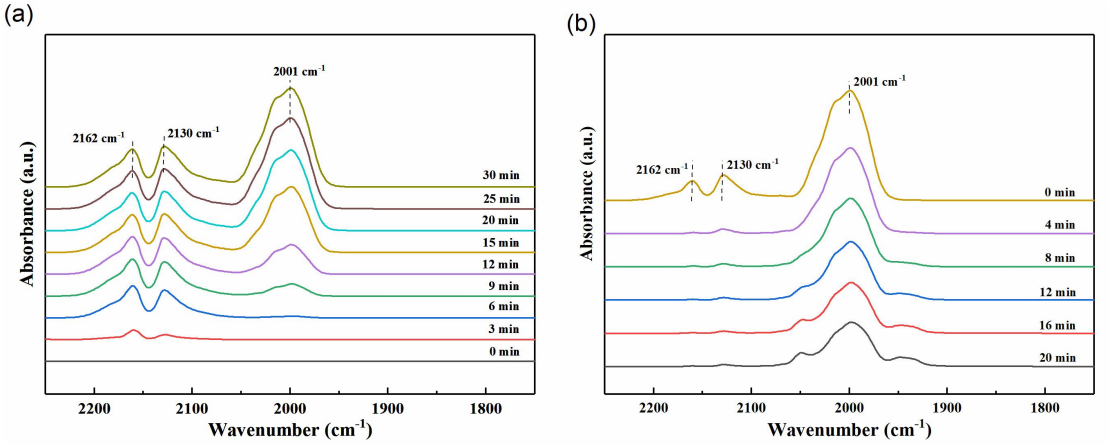


Fig. S2 In stiu DRIFTS spectra using CO probe. (a) after exposure to CO and (b) Ar purging at 303 K.

Scanning electron micrographs

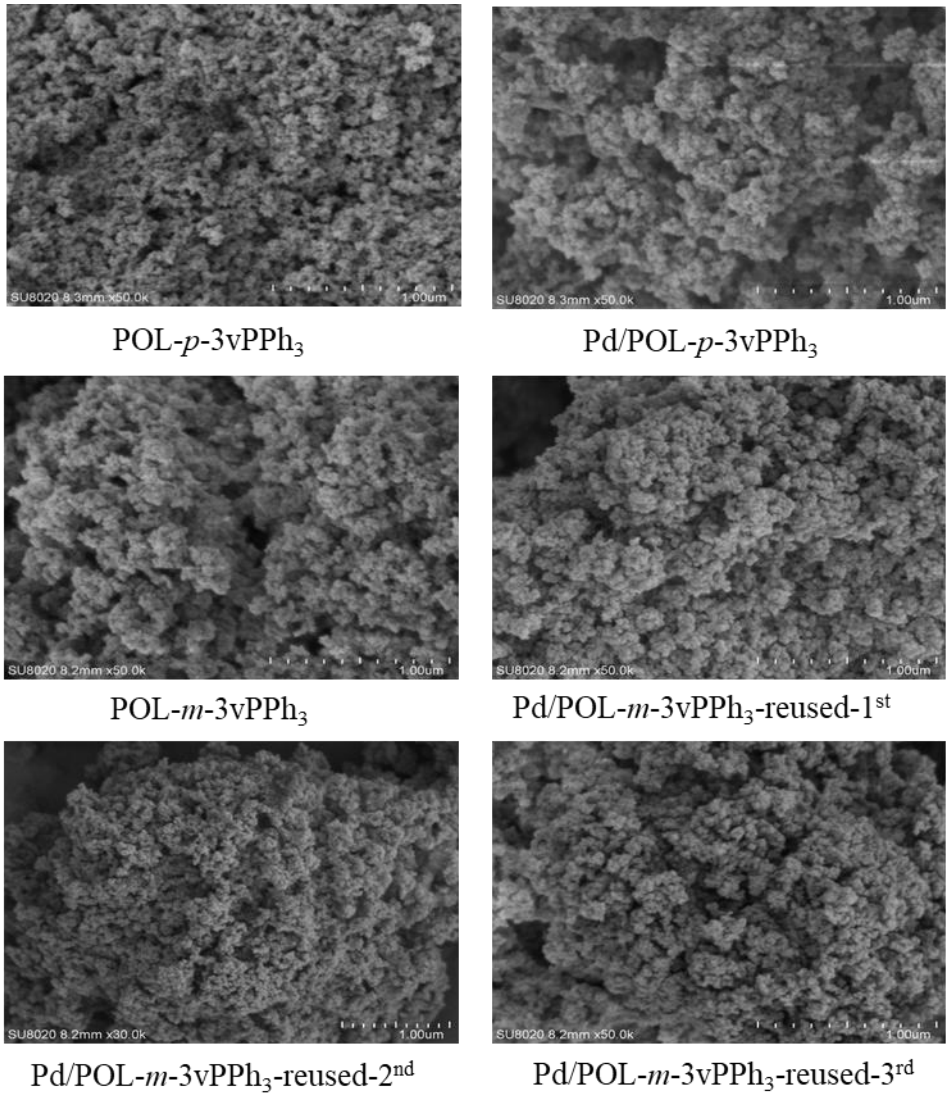


Fig. S3 SEM images of the POL-*p*-3vPPh$_3$, Pd/POL-*p*-3vPPh$_3$, POL-*m*-3vPPh$_3$, Pd/POL-*m*-3vPPh$_3$-reused-1st, Pd/POL-*m*-3vPPh$_3$-reused-2nd and Pd/POL-*m*-3vPPh$_3$-reused-3rd.

Transmission electron micrographs

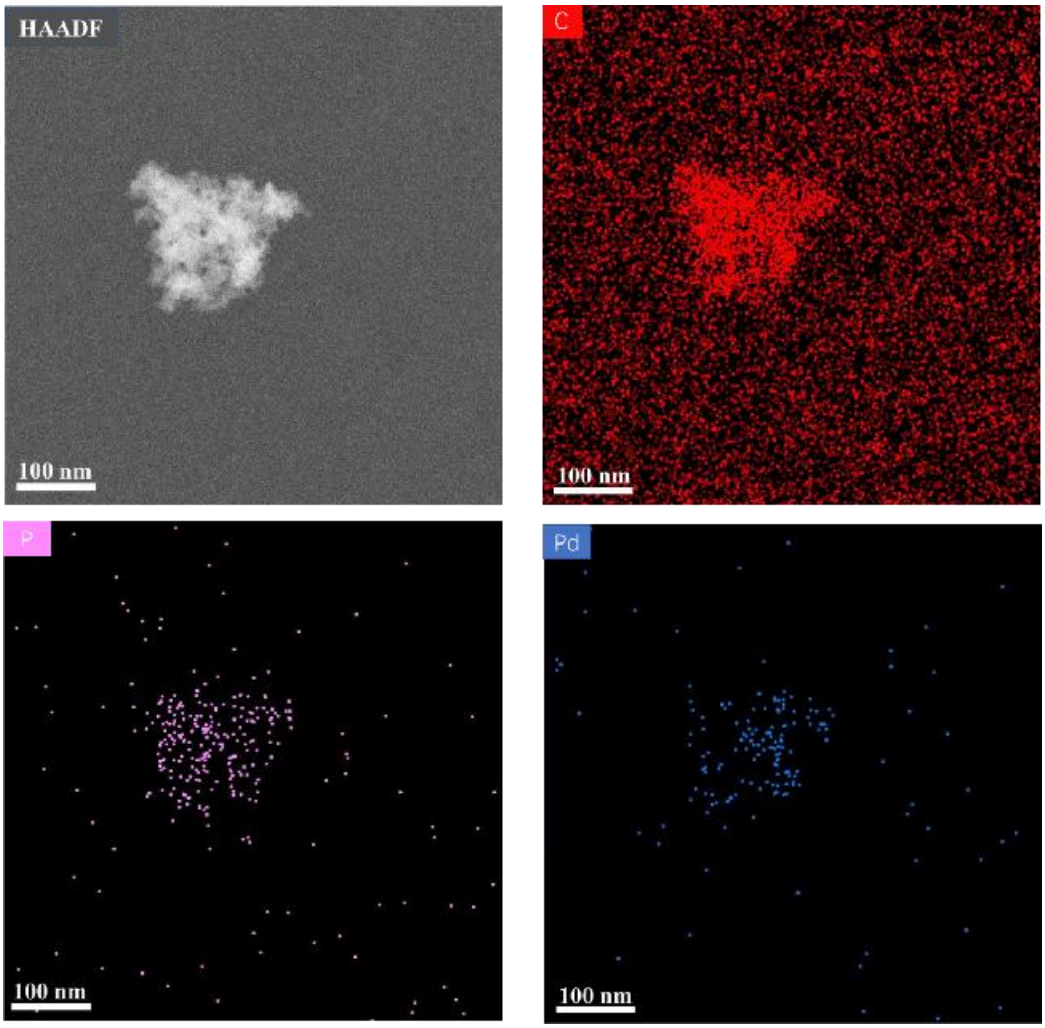


Fig. S4 TEM images of the Pd/POL-*m*-3v-PPh_3

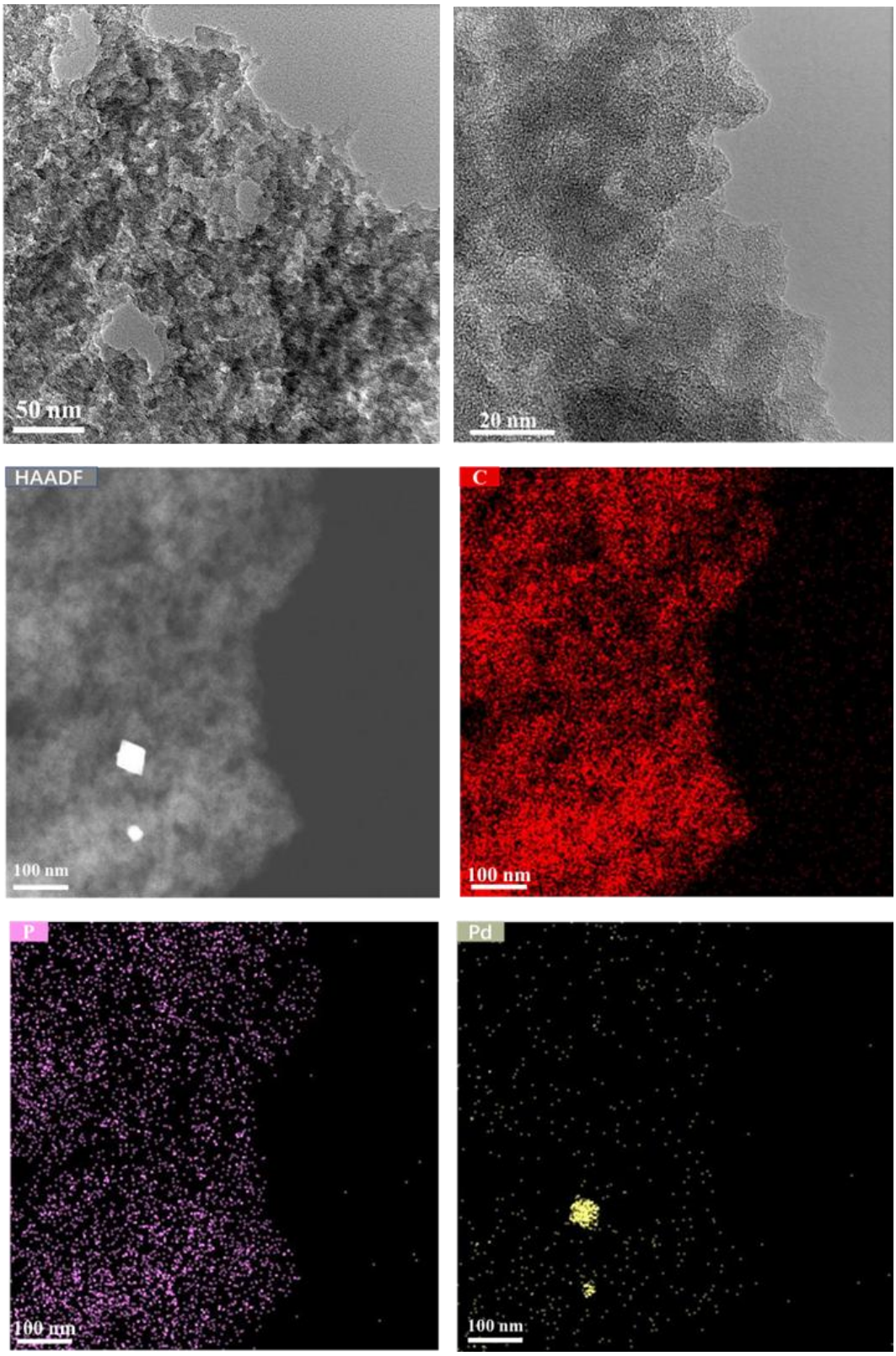


Fig. S5 TEM images of the Pd/POL-*m*-3v-PPh_3-reused-3rd

N_2 adsorption-desorption analysis

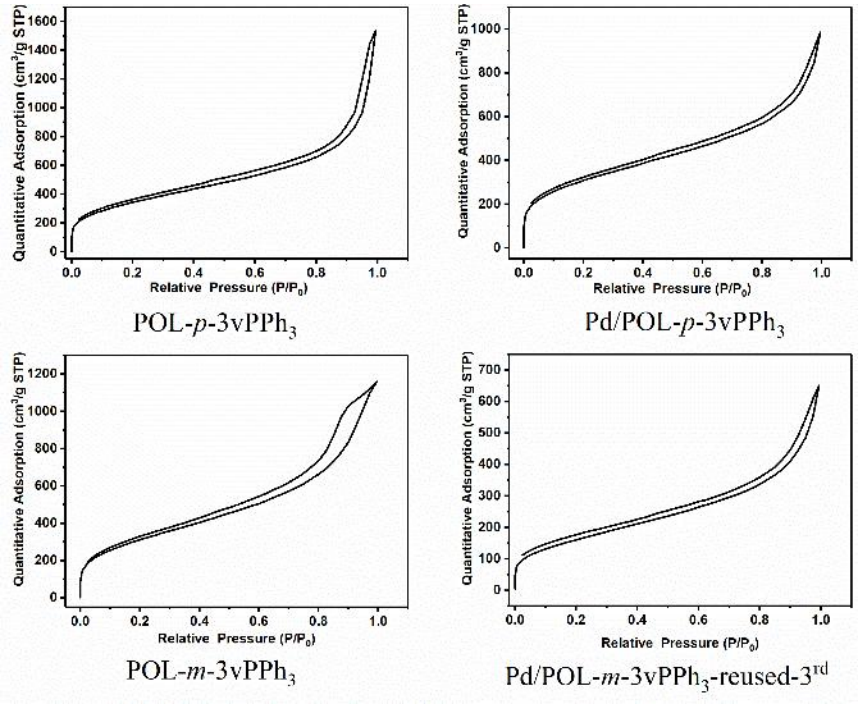


Fig. S6 N_2 adsorption-desorption isotherm of POL-*p*-3vPPh$_3$, Pd/POL-*p*-3vPPh$_3$, POL-*m*-3vPPh$_3$, and Pd/POL-*m*-3vPPh$_3$-3rd.

.

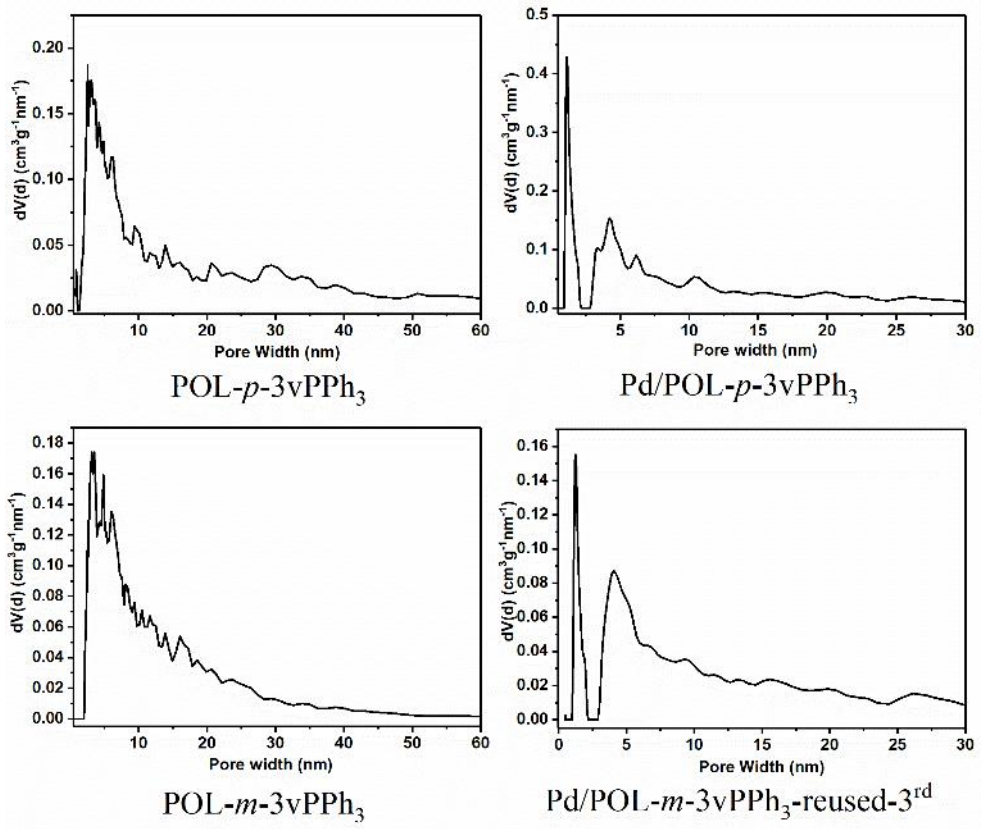


Fig. S7 Pore size distribution of POL-*p*-3vPPh$_3$, Pd/POL-*p*-3vPPh$_3$, POL-*m*-3vPPh$_3$ and Pd/POL-*m*-3vPPh$_3$-reused-3rd.

Table S3. The physical properties of the POPs catalysts.

Entry	Catalyst	SA (m^2/g) [a]	APW (nm)[a]	PV (cm^3/g) [a]
1	POL-*p*-3vPPh$_3$	1235	2.58	2.38
2	Pd/POL-*p*-3vPPh$_3$	1100	1.14	1.52
3	POL-*m*-3vPPh$_3$	1119	3.18	1.80
4	Pd/POL-*m*-3vPPh$_3$	1022	1.24	1.62
5	Pd/POL-*m*-3vPPh$_3$-reused-3rd	577	1.25	1.01

[a] Determined by an IQ$_2$ automated gas sorption analyzer. SA: BET surface area; APW: average pore width; PV: pore volume.

Table S4. Comparison of the reaction performance of Pd/POL-*m*-3vPPh$_3$ reported in this work with other heterogeneous catalysts.

Alkene/Amine	Cat.	CO(MPa)	T (°C)	Yield (%)	Amide (b/l)	Ref.
Styrene/Aniline (1:0.5)	Pd/POL-*m*-3vPPh$_3$	4	120	97	98:2	This Work
Styrene/Aniline (4:1)	Pd-610	4	130	89	71:29	6
Phenylacetylene/*p*-toluidine (1.5:1)	Pd/DVB-0.2-PAM-Naph	4	120	69	-	8
Styrene/Aniline (0.5:0.6)	Pd@POC	4	110	97	77:1	3

We summarized the precedent heterogeneous catalysts for the hydroaminocarbonylation of aromatic alkenes with branched selectivity in Table S4, suggesting that Pd/POL-*m*-3vPPh$_3$ catalyst exhibited superior activity and branched selectivity.

TGA analysis

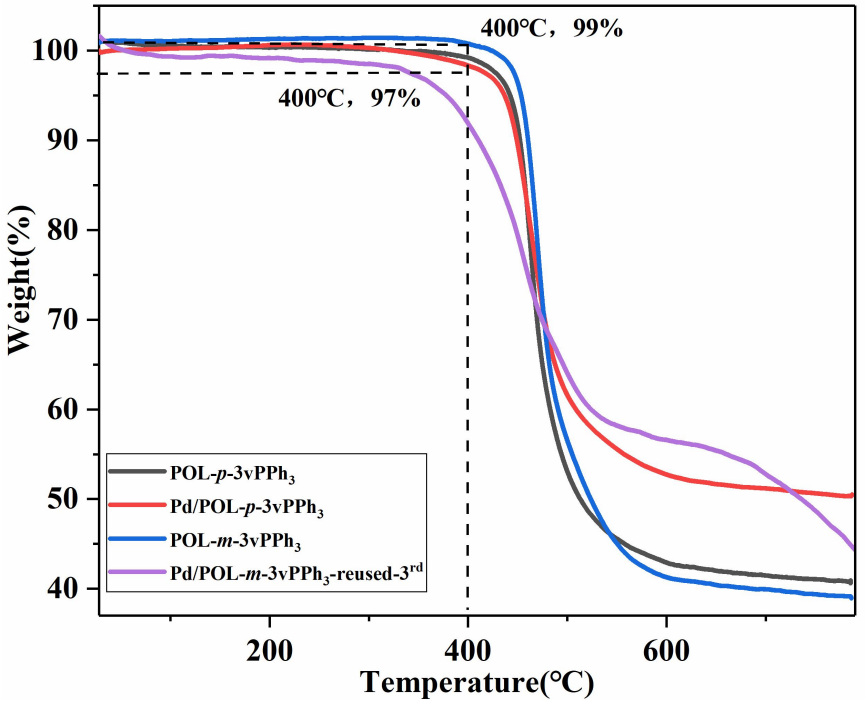


Fig. S8 TG curve of the POL-*p*-3vPPh$_3$, Pd/POL-*p*-3vPPh$_3$, POL-*m*-3vPPh$_3$ and Pd/POL-*m*-3vPPh$_3$-reused-3rd.

X-ray photoelectron spectroscopy analysis

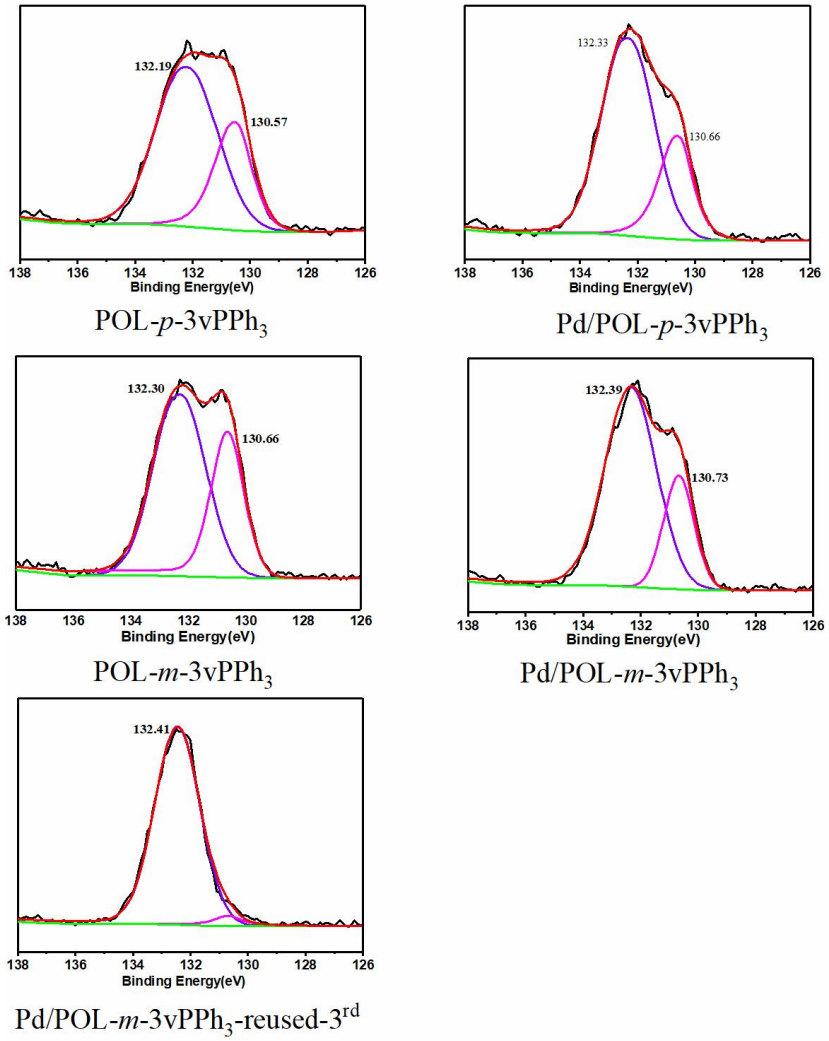


Fig. S9 P 2p XPS analysis of POL-*p*-3vPPh$_3$, Pd/POL-*p*-3vPPh$_3$, POL-*m*-3vPPh$_3$, Pd/POL-*m*-3vPPh$_3$, Pd/POL-*m*-3vPPh$_3$-reused-3rd.

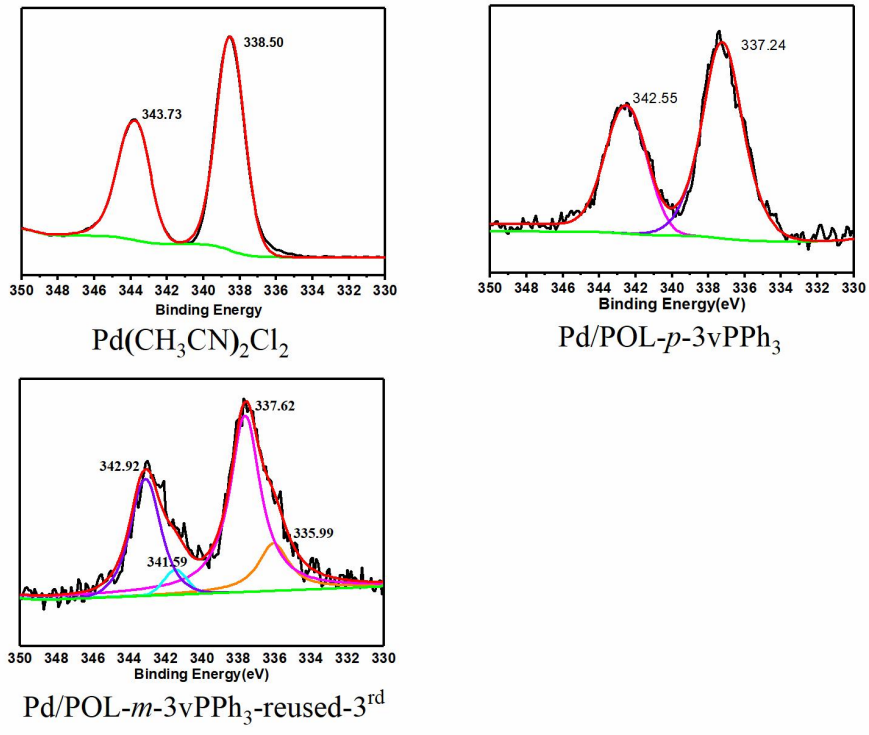


Fig. S10 Pd 3d XPS analysis of $Pd(CH_3CN)_2Cl_2$, Pd/POL-*p*-3vPPh_3, Pd/POL-*m*-3vPPh_3-reused-3[rd].

9. Reaction mechanism

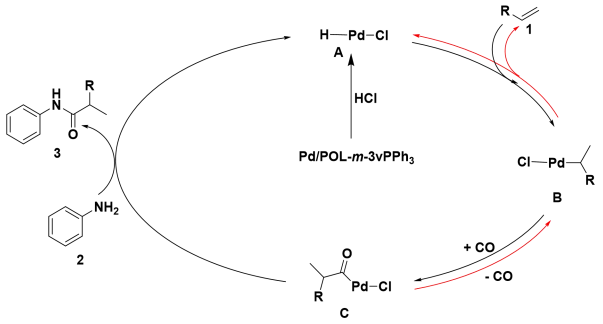
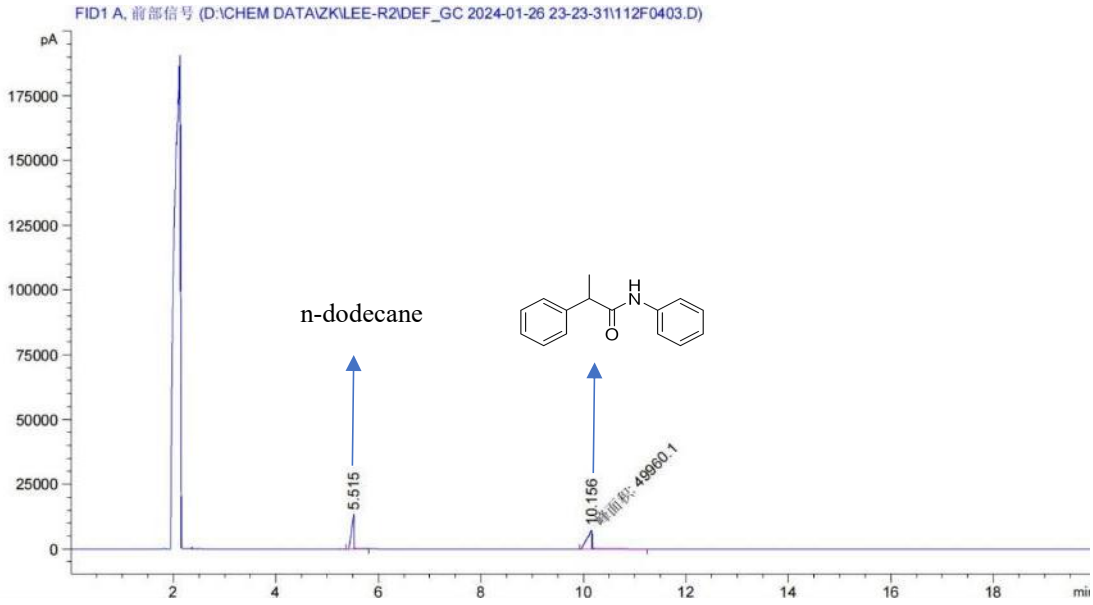


Fig. S11 Proposed reaction mechanism

10. Copies of quantitative GC and NMR spectra

Quantitative GC spectra of styrene hydroaminocarbonylation



Peak No.	Ret. time	Area	Area%
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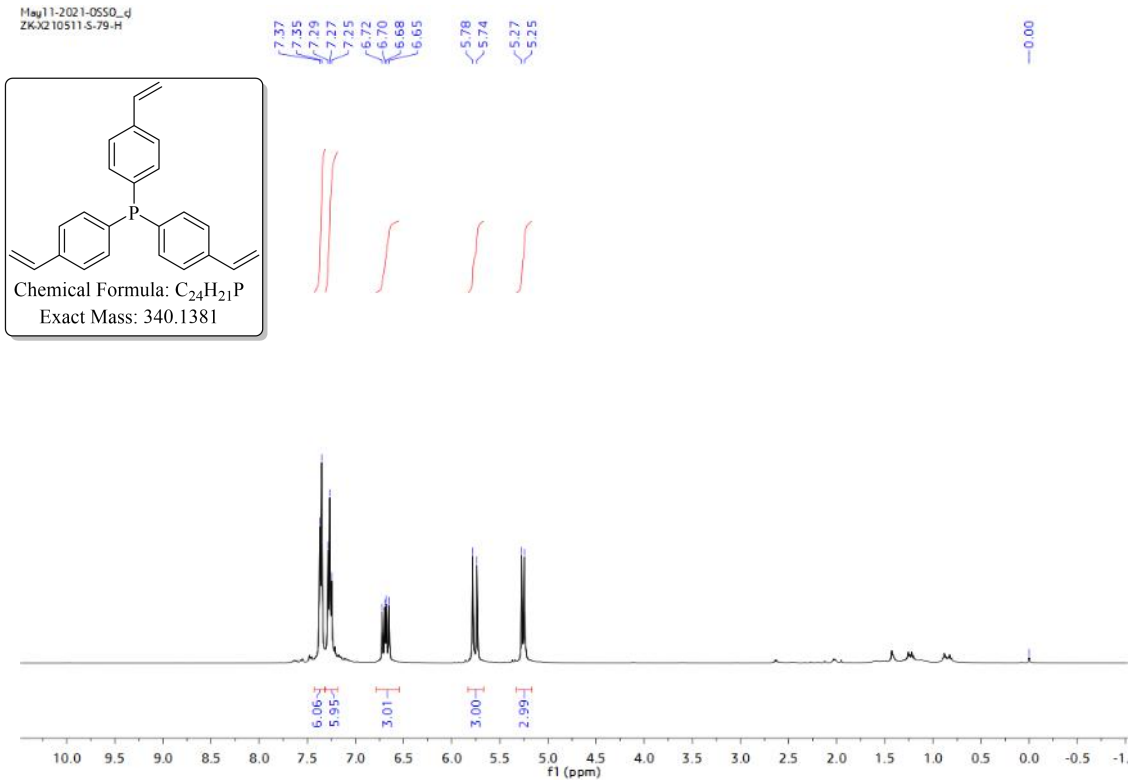
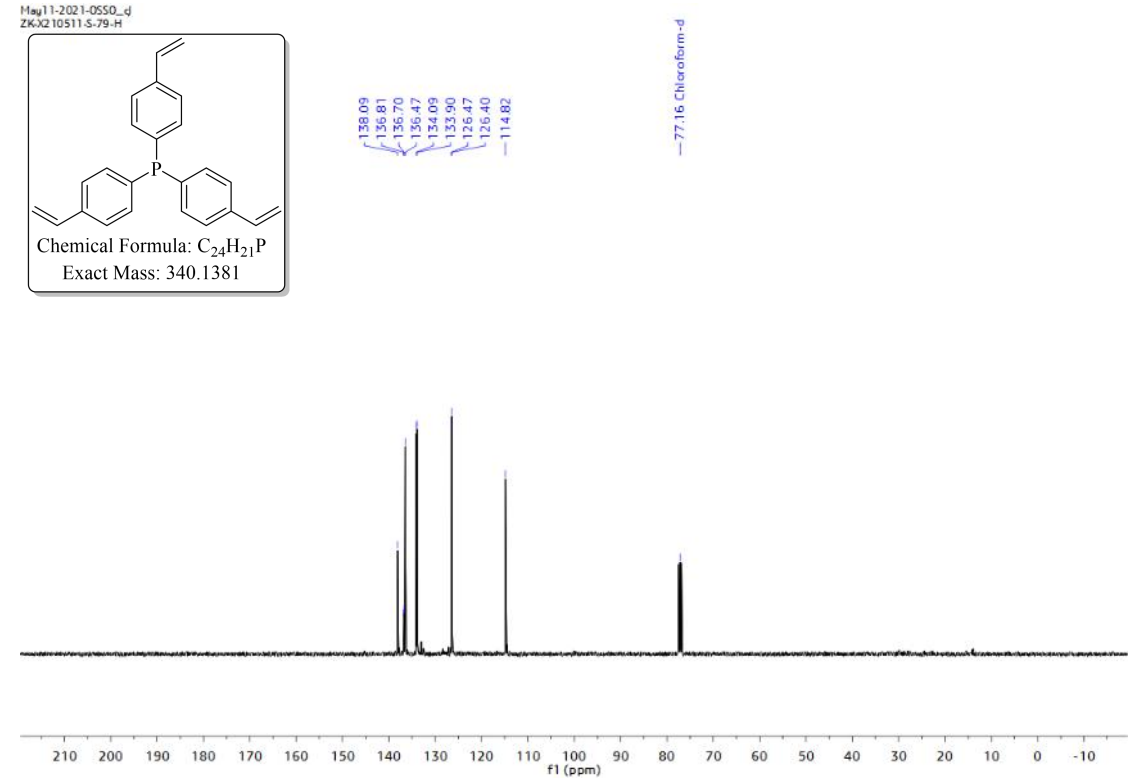
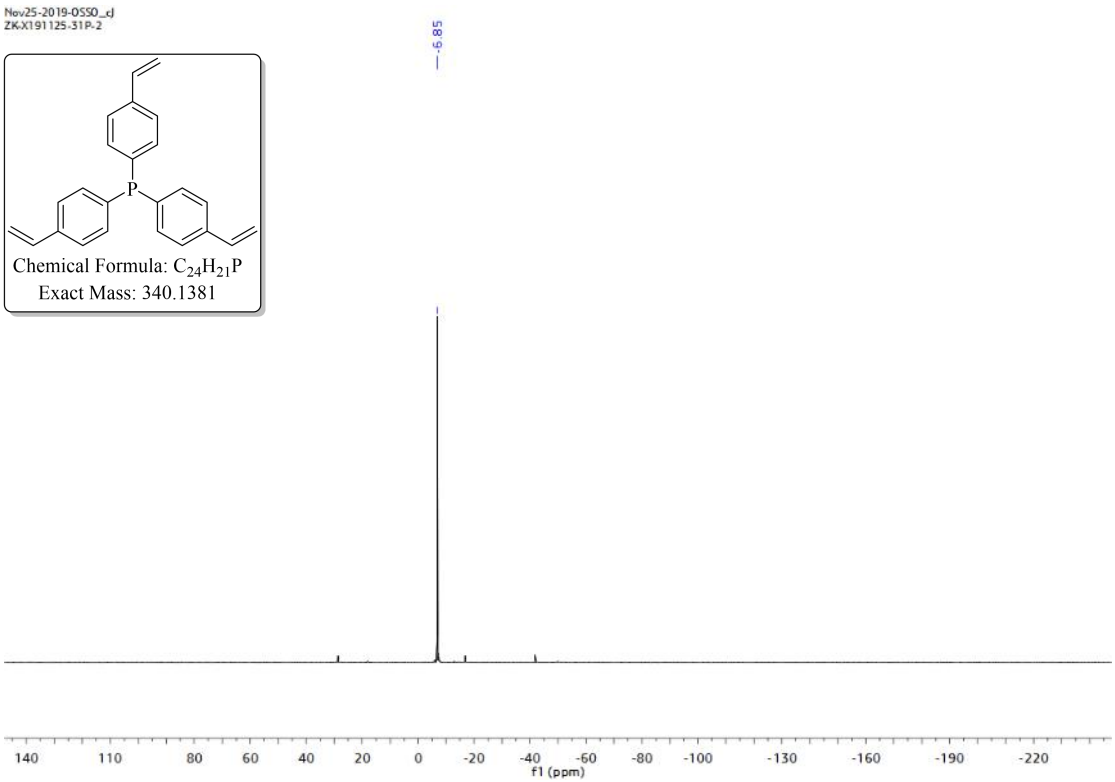
2	10.156	49960	52.3711
Total		95396	100

NMR spectra of the ligands



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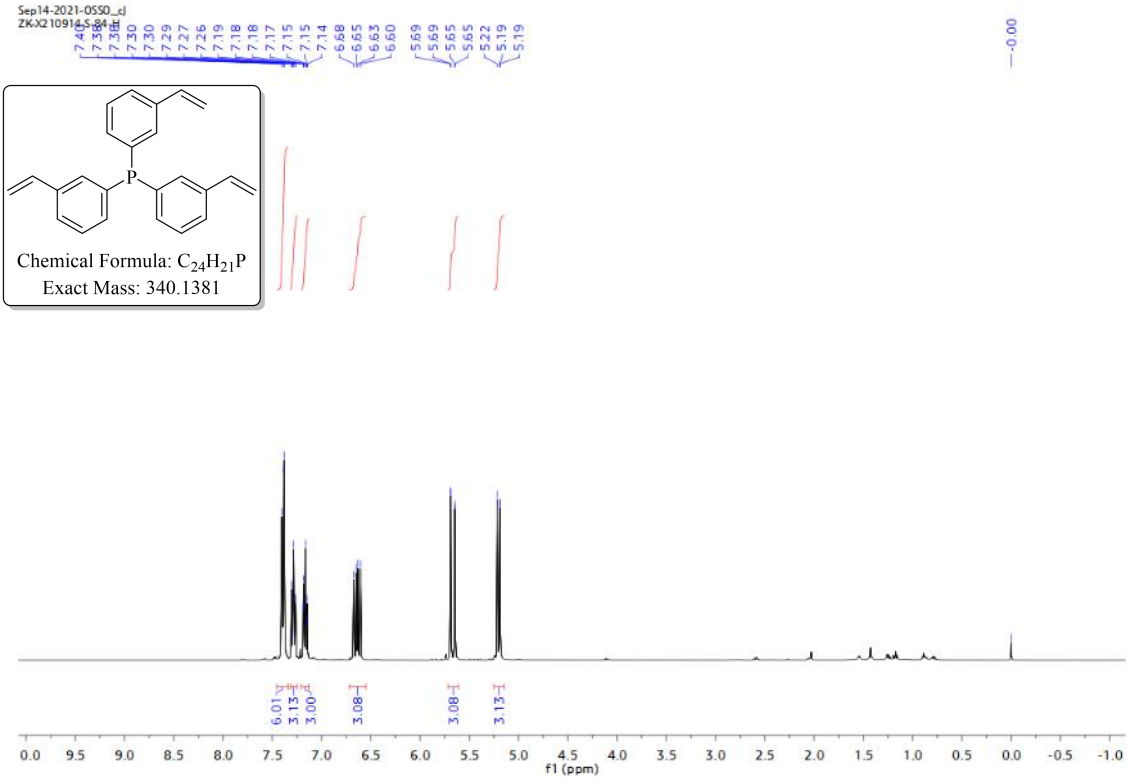
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-0.00
Chemical Formula: C24H21P
Exact Mass: 340.1381
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0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
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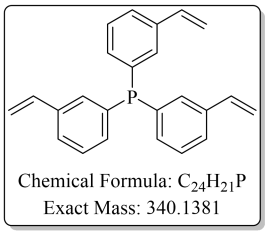

Chemical Formula: $C_{24}H_{21}P$
Exact Mass: 340.1381

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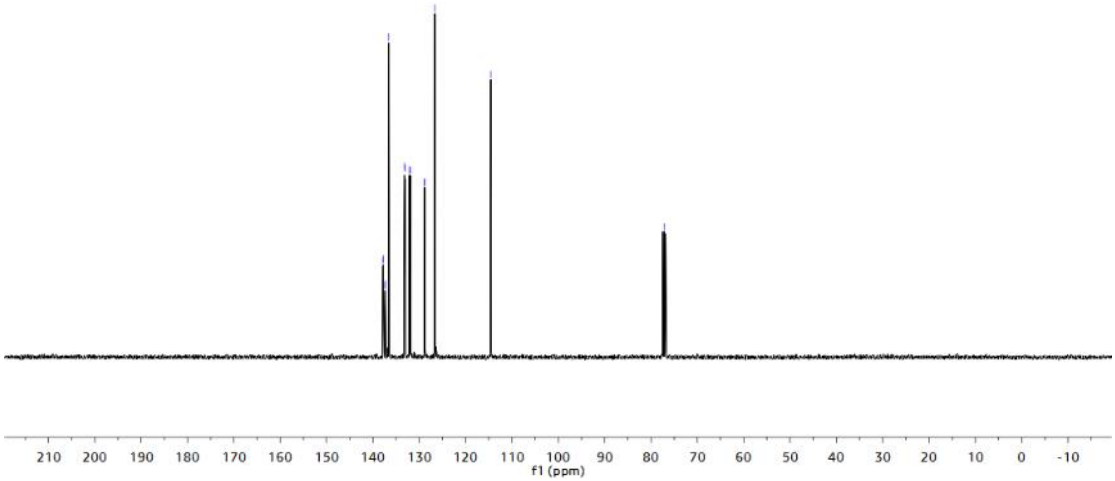
114.55

77.16 Chloroform-d



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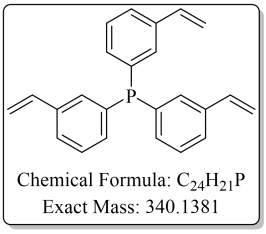

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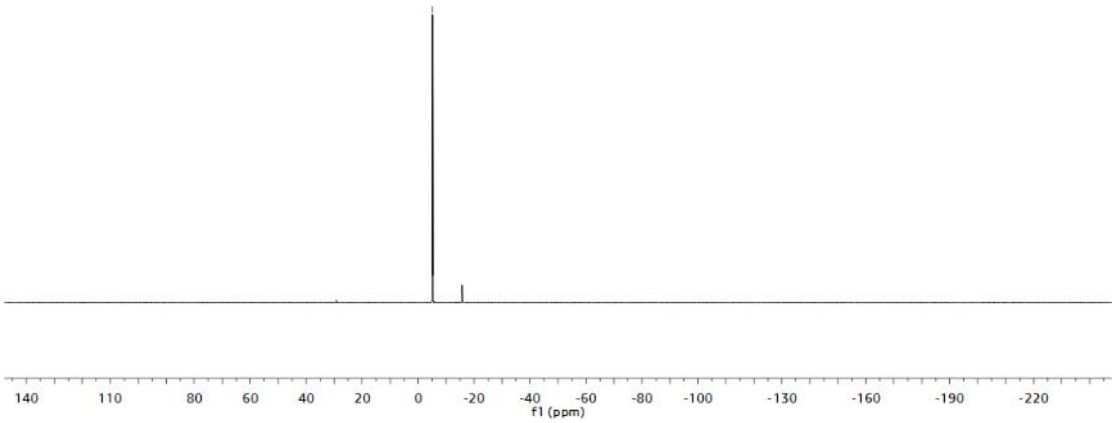
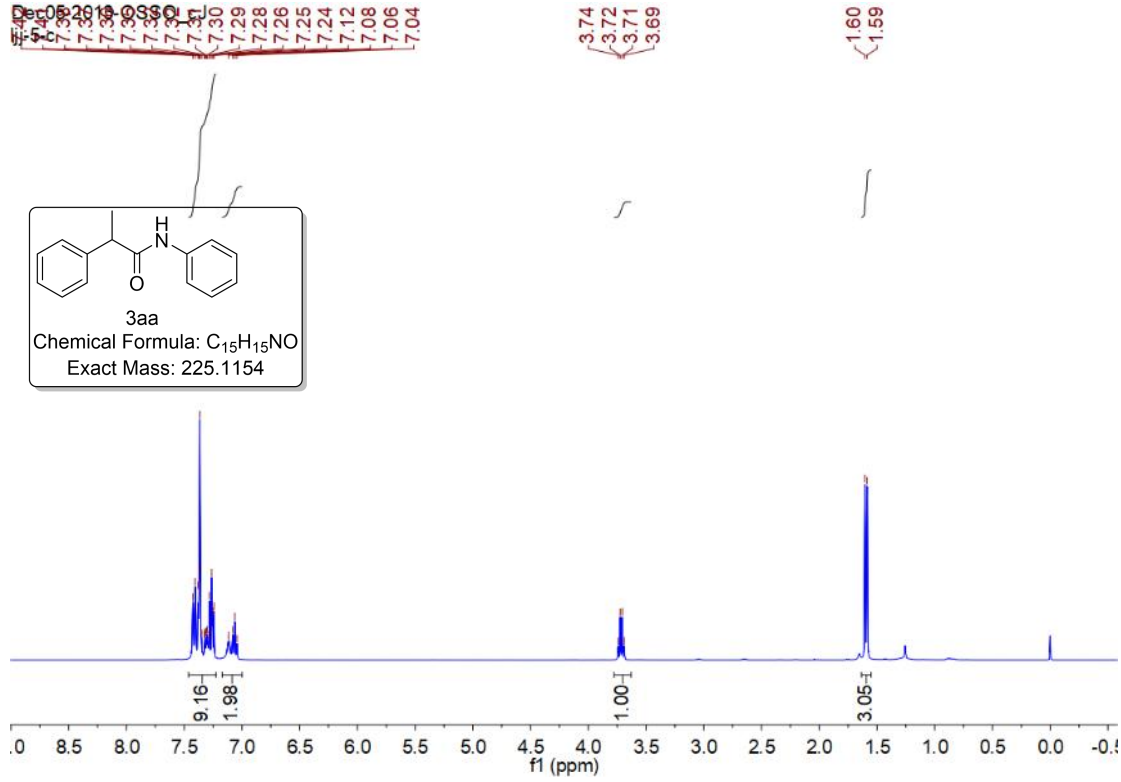
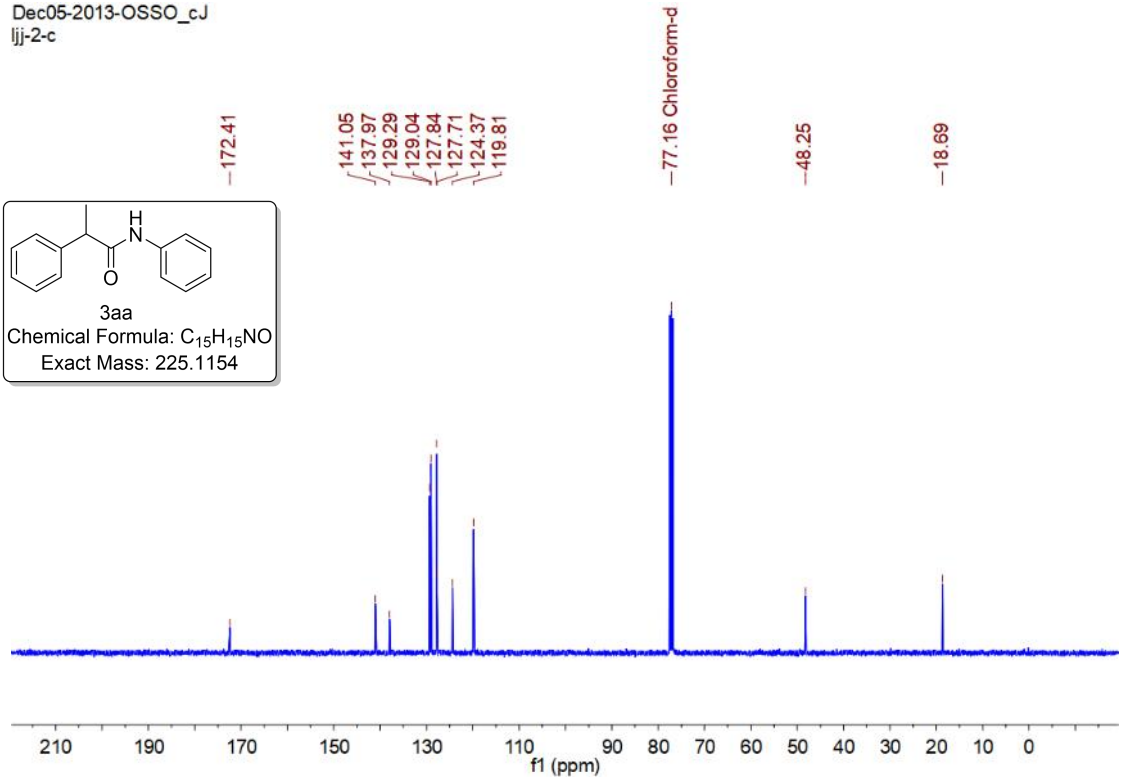
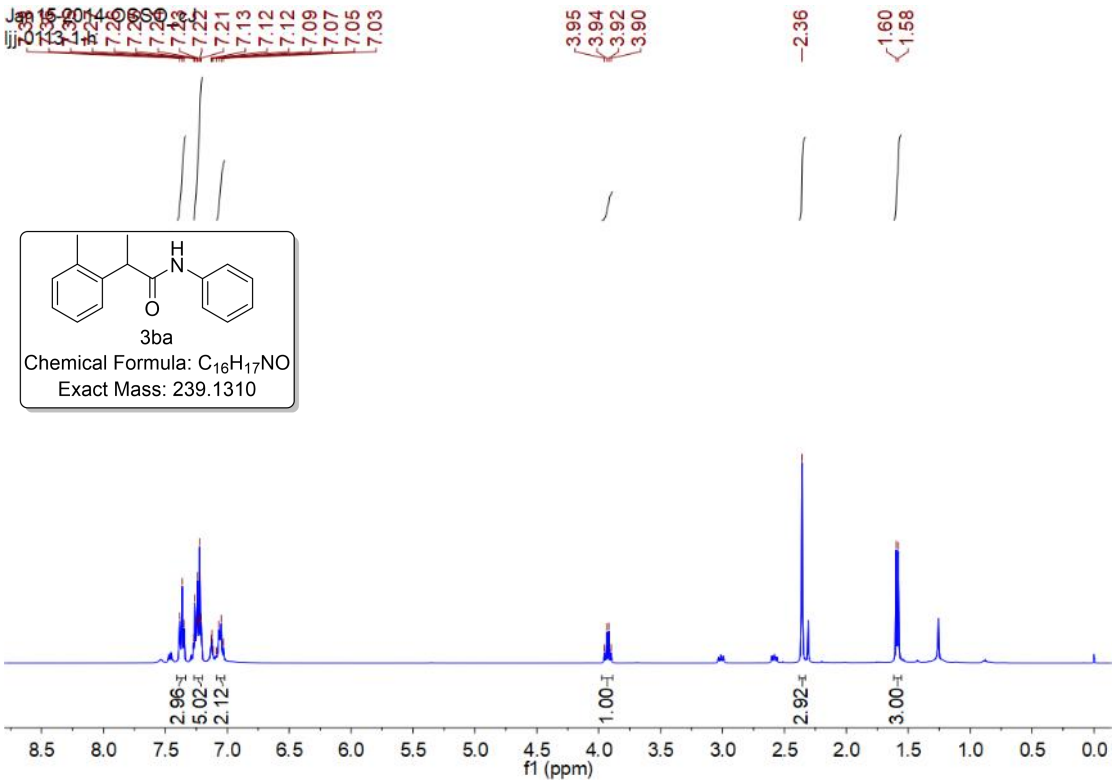


NMR spectra of the products



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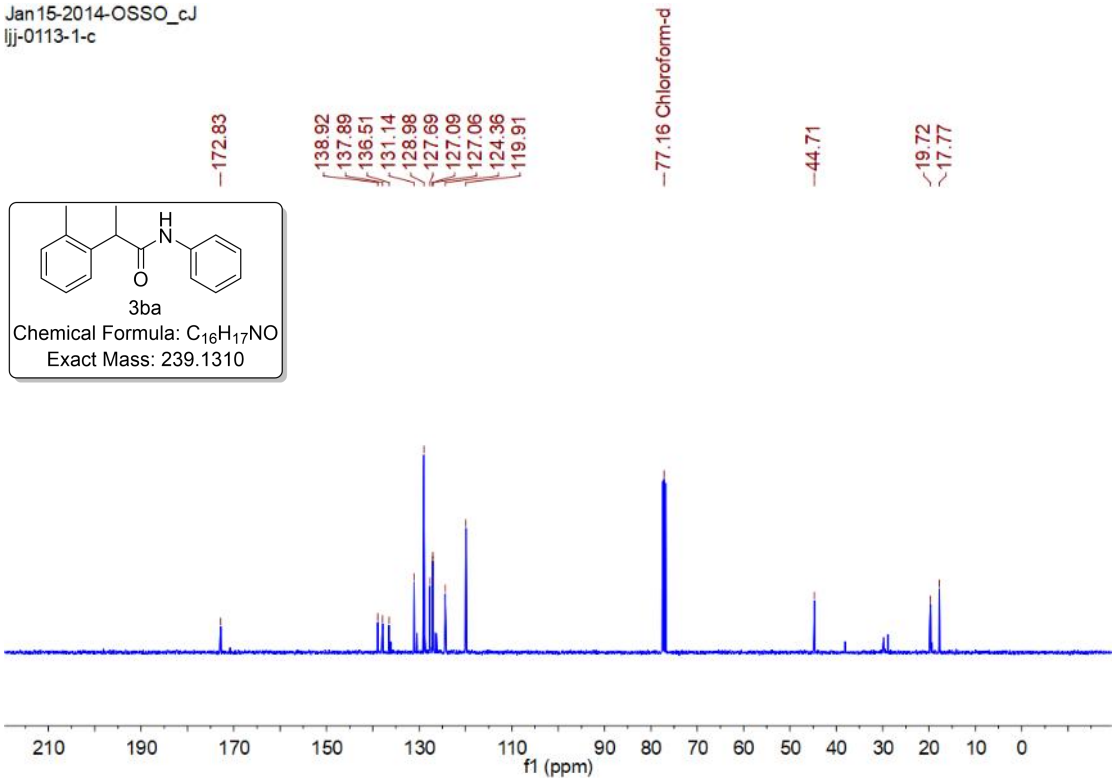
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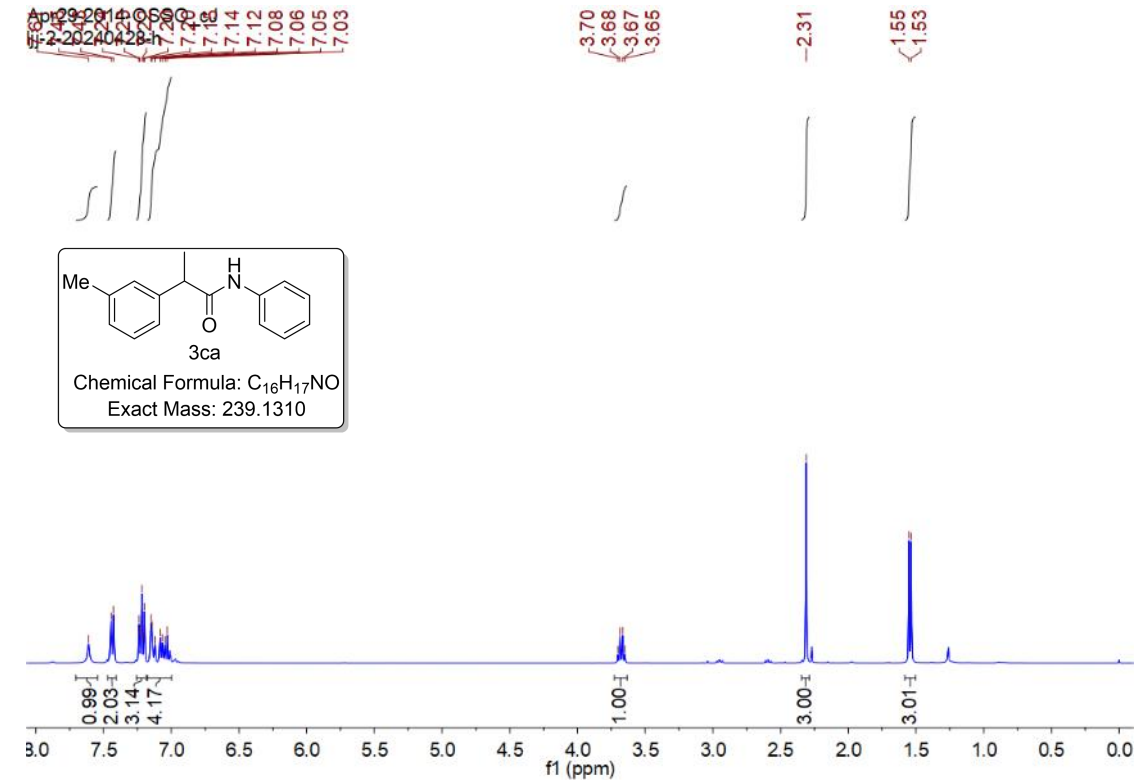
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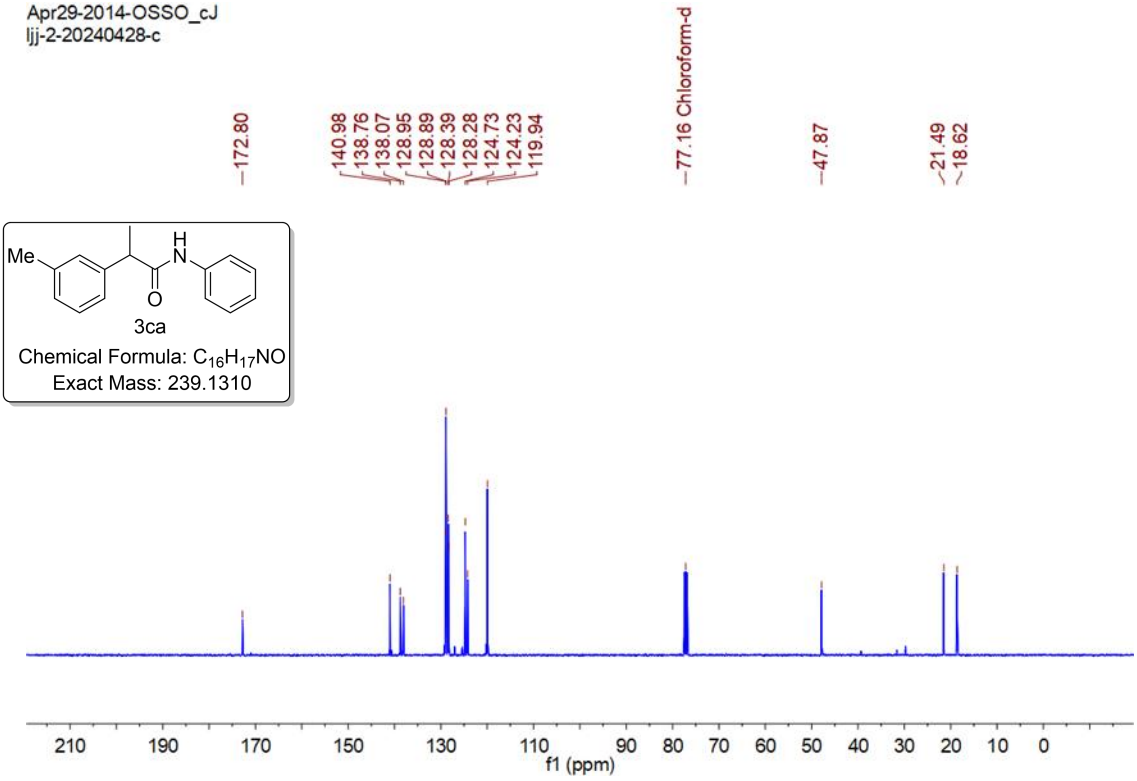
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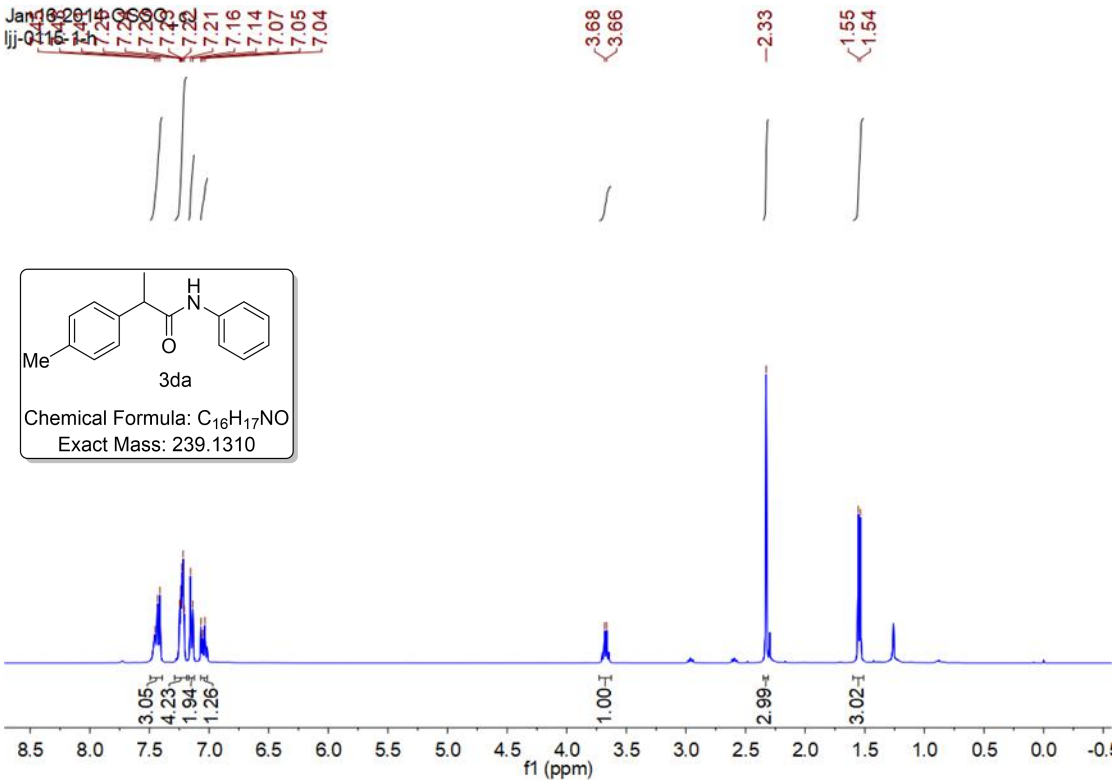
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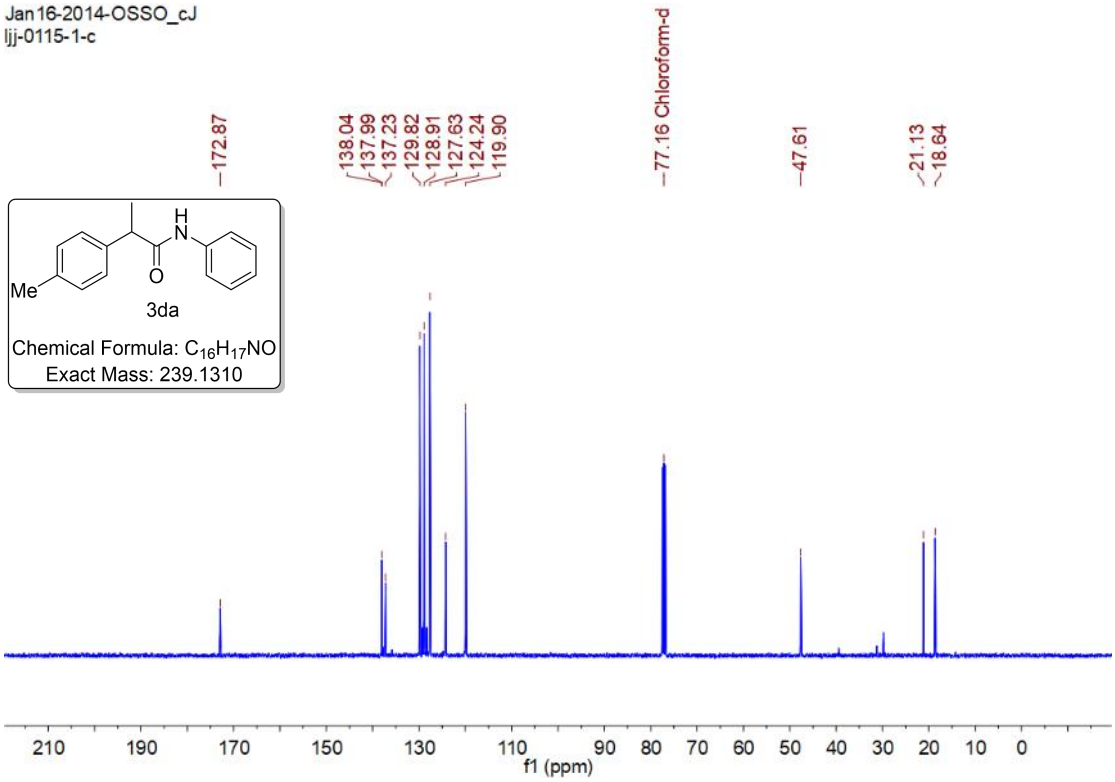
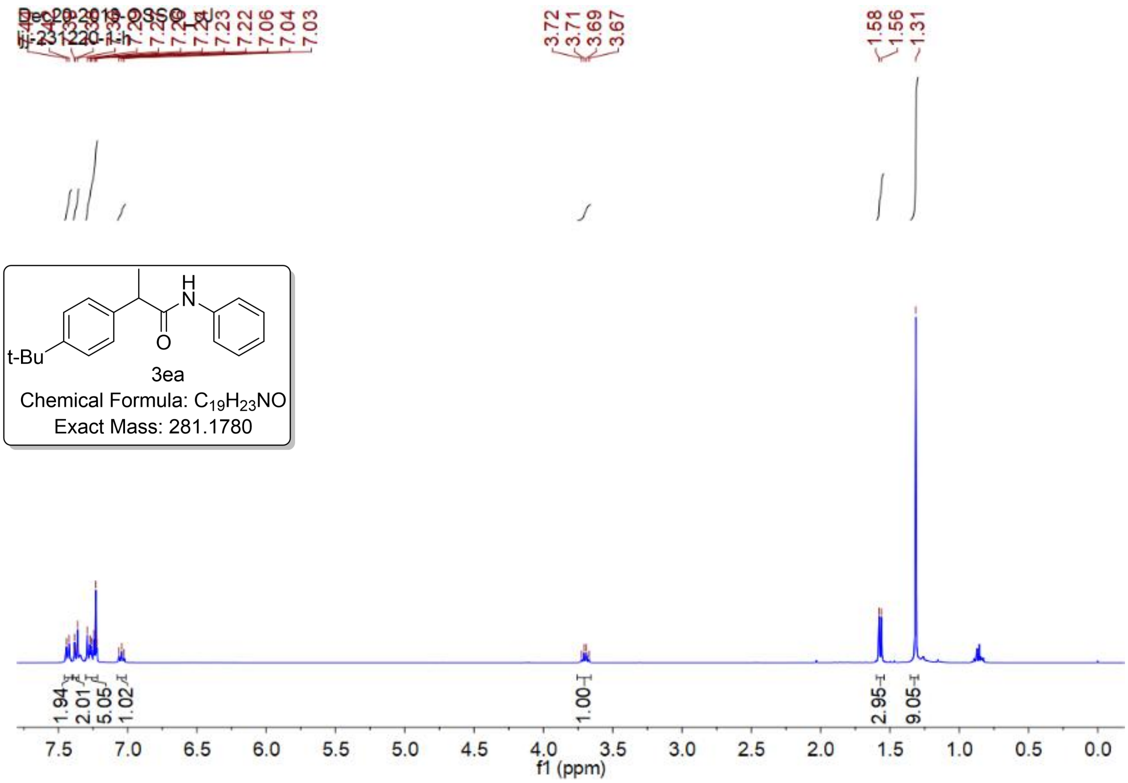
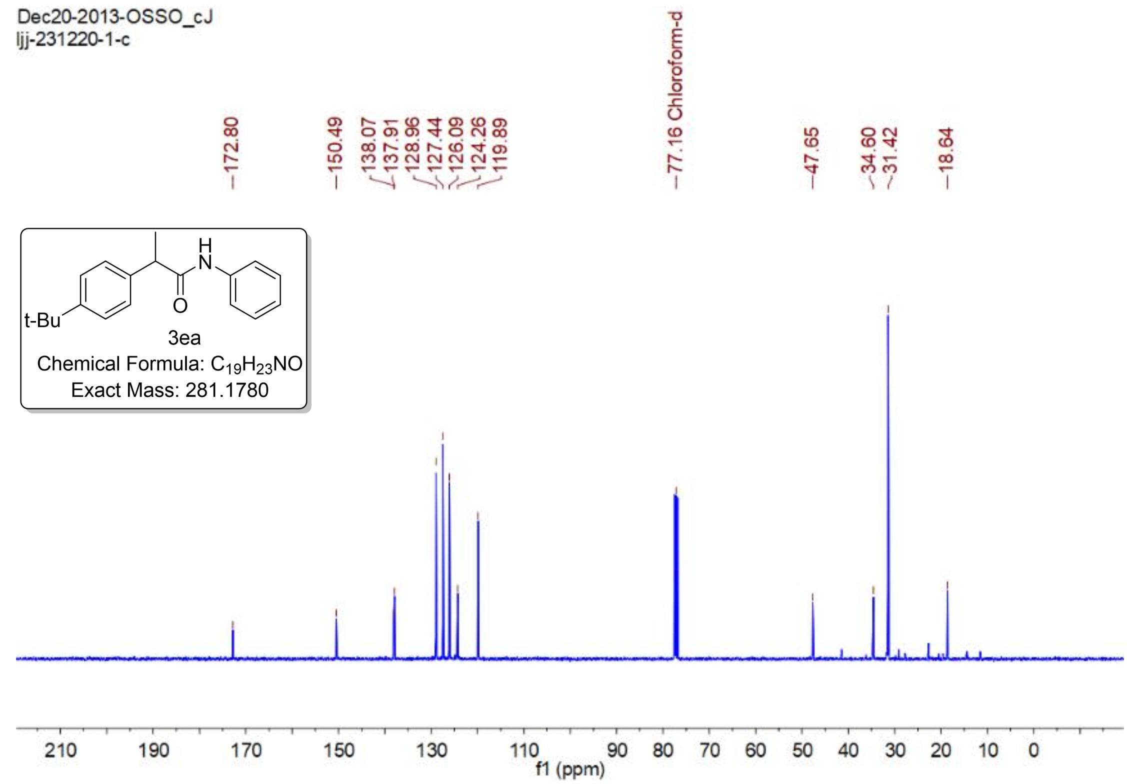
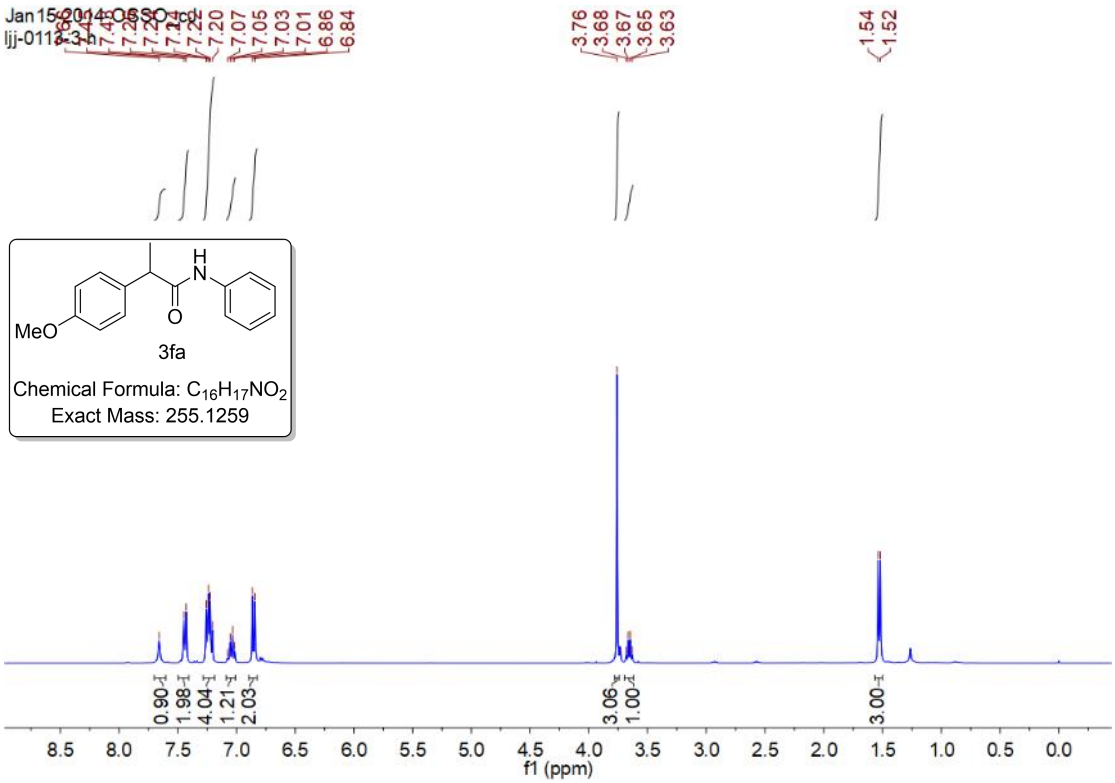
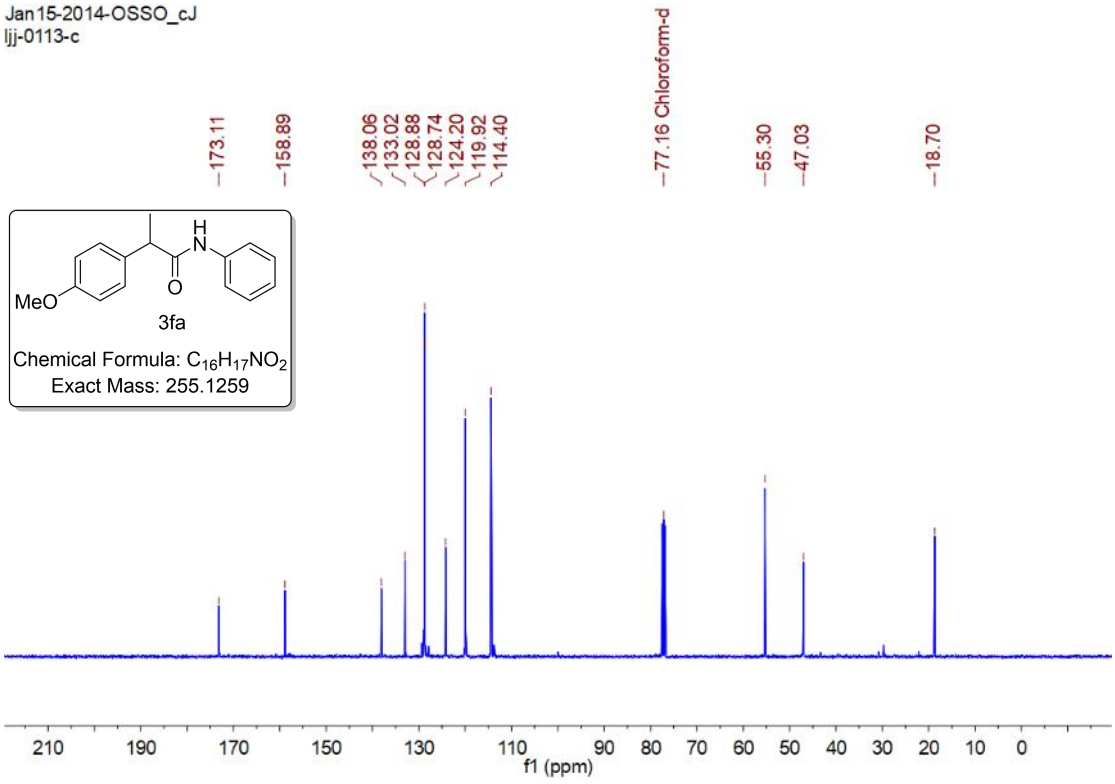
f1 (ppm)

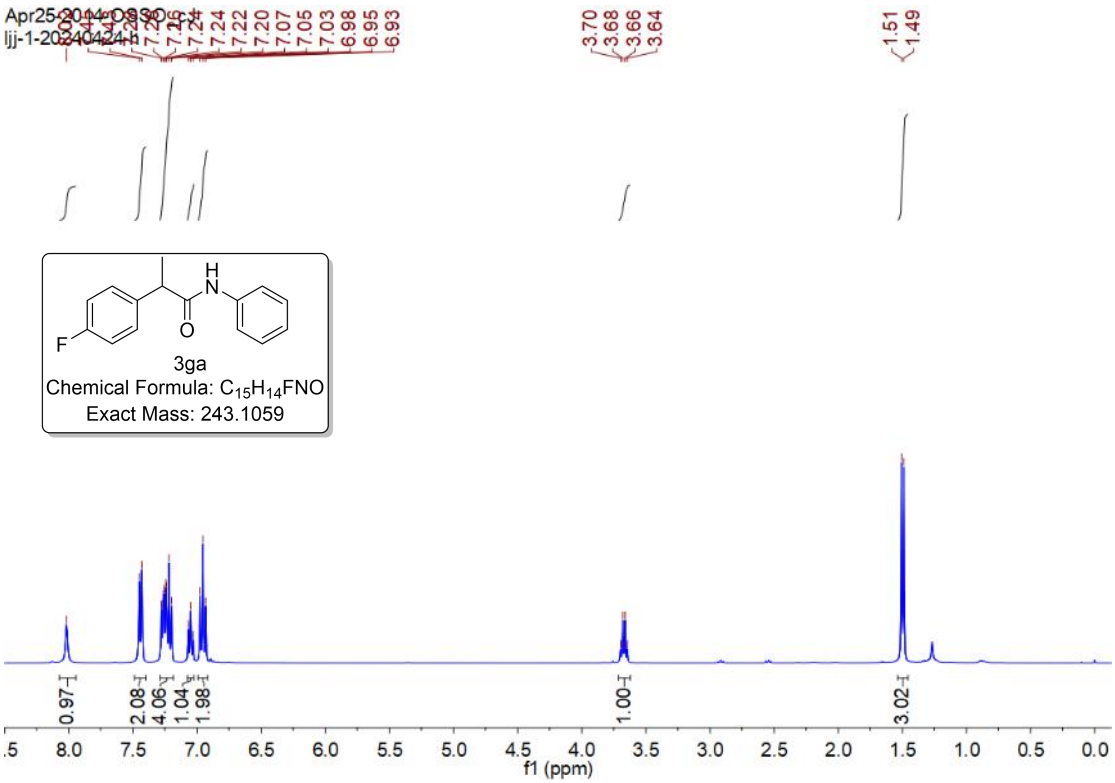

Jan16-2014-OSSO_cJ
ljj-0115-1-c
172.87
138.04
137.99
137.23
129.82
128.91
127.63
124.24
119.90
77.16 Chloroform-d
47.61
21.13
18.64
H
N
O
Me
3da
Chemical Formula: C16H17NO
Exact Mass: 239.1310
f1 (ppm)

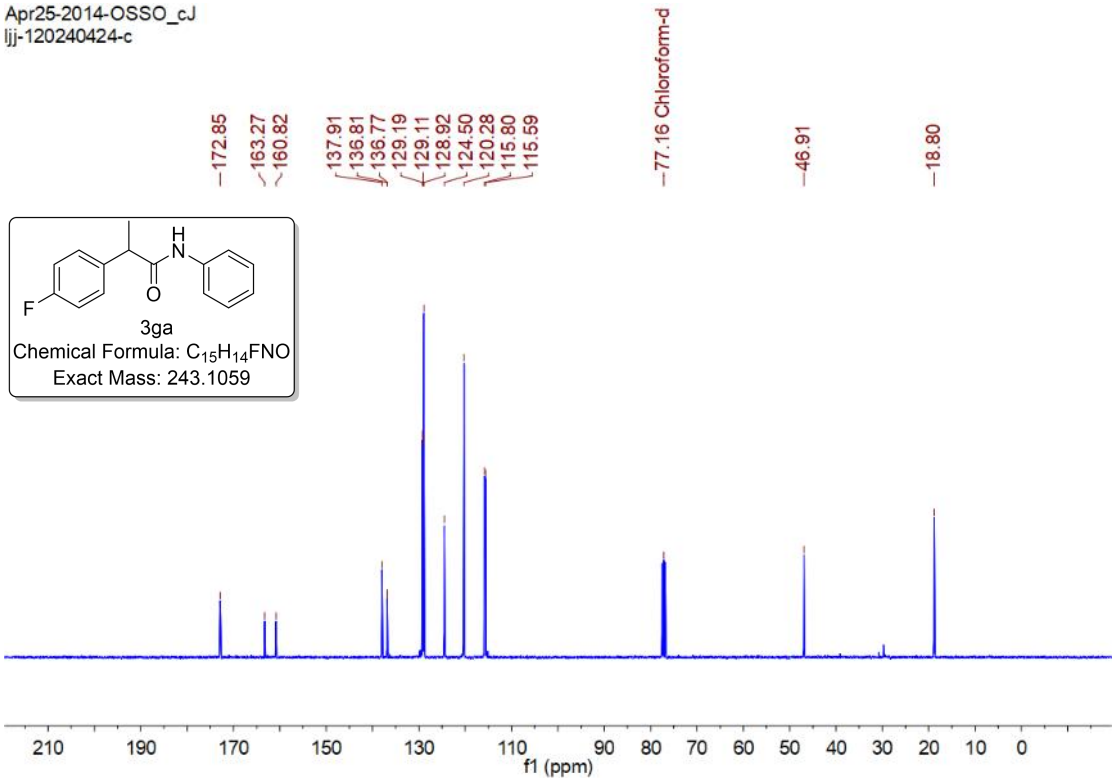

Dec20-2013-OSSO_cJ
ljj-231220-1-h
7.23
7.22
7.06
7.04
7.03
3.72
3.71
3.69
3.67
1.58
1.56
1.31
t-Bu
H
N
O
3ea
Chemical Formula: $C_{19}H_{23}NO$
Exact Mass: 281.1780
1.94
2.01
5.05
1.02
1.00
2.95
9.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

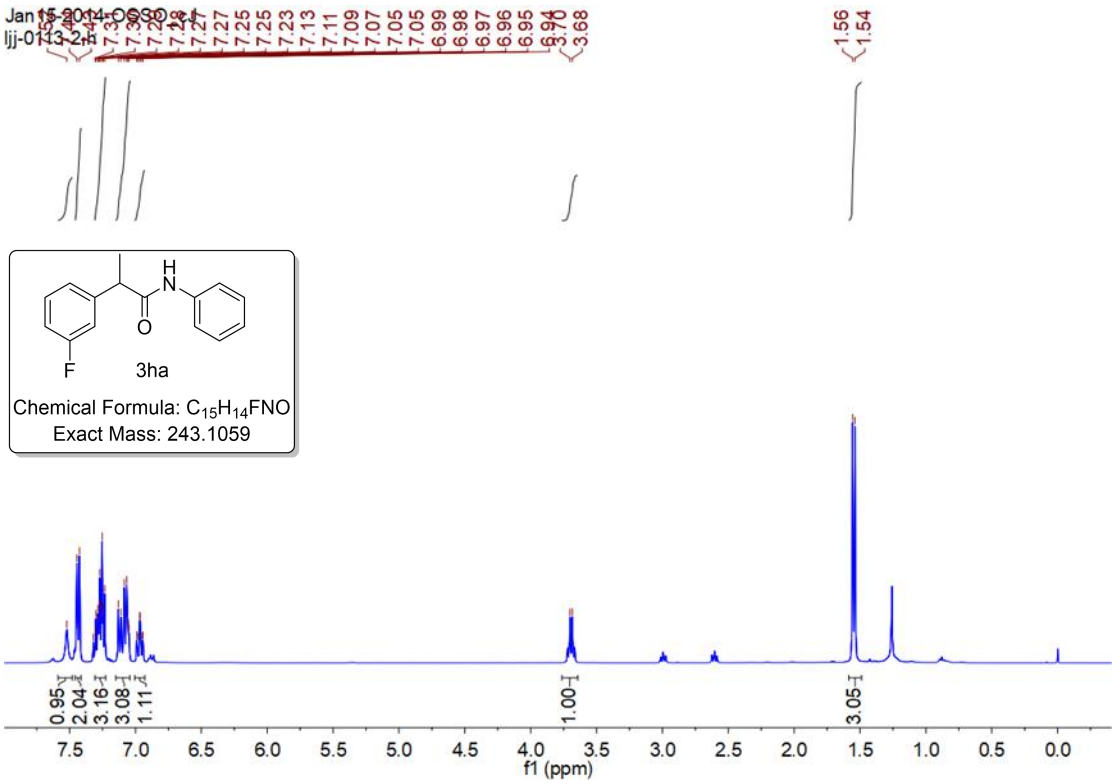

Dec20-2013-OSSO_cJ
ljj-231220-1-c
172.80
150.49
138.07
137.91
128.96
127.44
126.09
124.26
119.89
77.16 Chloroform-d
47.65
34.60
31.42
18.64
t-Bu
H
N
O
3ea
Chemical Formula: $C_{19}H_{23}NO$
Exact Mass: 281.1780
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

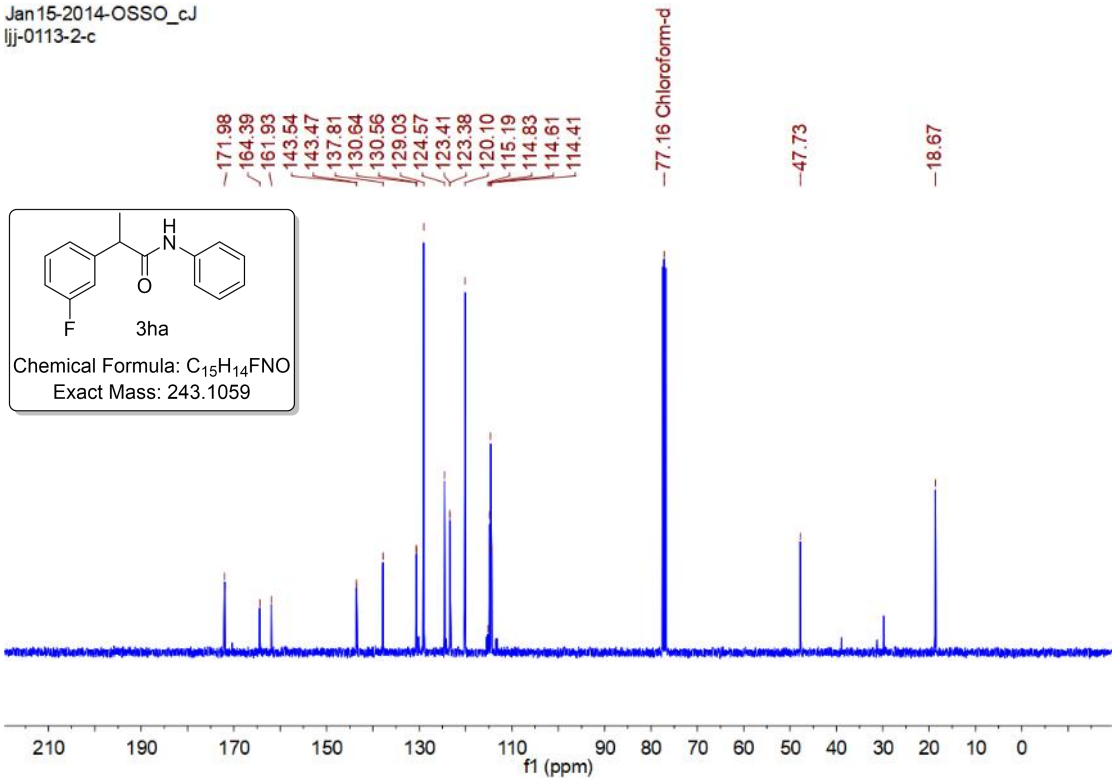

Jan15-2014-OSSO_cJ
ljj-0113-3-h
7.48
7.24
7.22
7.20
7.07
7.05
7.03
7.01
6.86
6.84
3.76
3.68
3.67
3.65
3.63
1.54
1.52
MeO
3fa
Chemical Formula: C16H17NO2
Exact Mass: 255.1259
0.90
1.98
4.04
1.21
2.03
3.06
1.00
3.00
f1 (ppm)

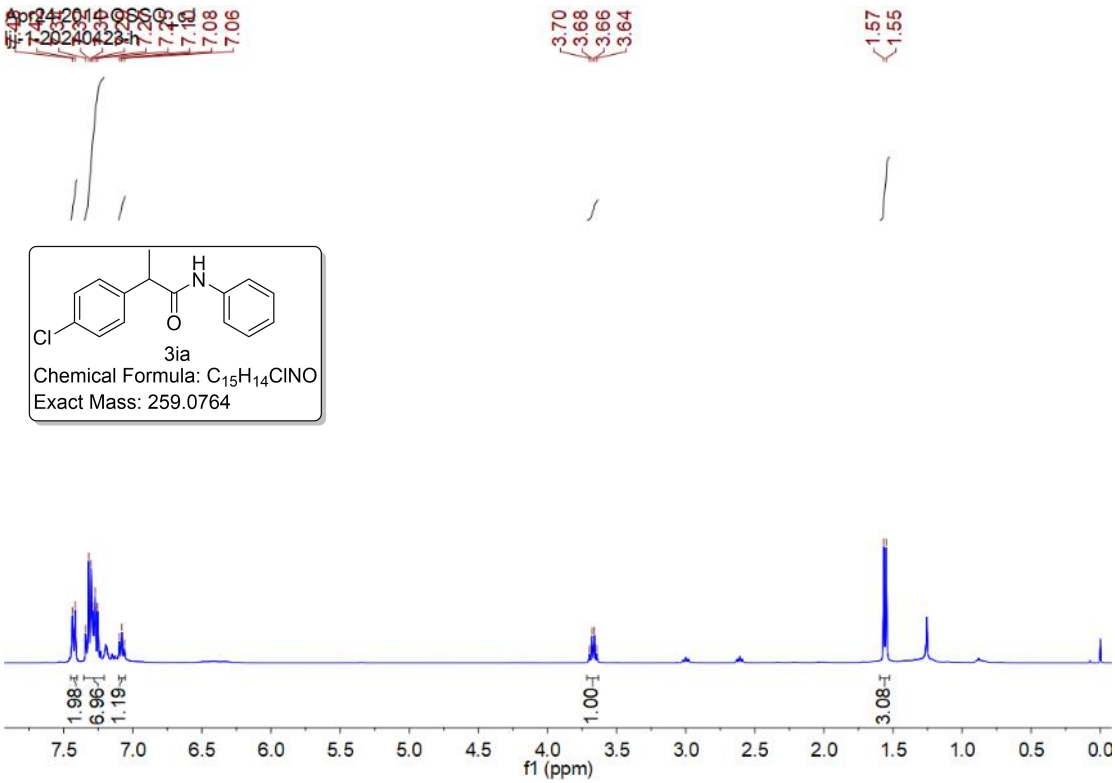

Jan15-2014-OSSO_cJ
ljj-0113-c
173.11
158.89
138.06
133.02
128.88
128.74
124.20
119.92
114.40
77.16 Chloroform-d
55.30
47.03
18.70
MeO
3fa
Chemical Formula: C16H17NO2
Exact Mass: 255.1259
f1 (ppm)

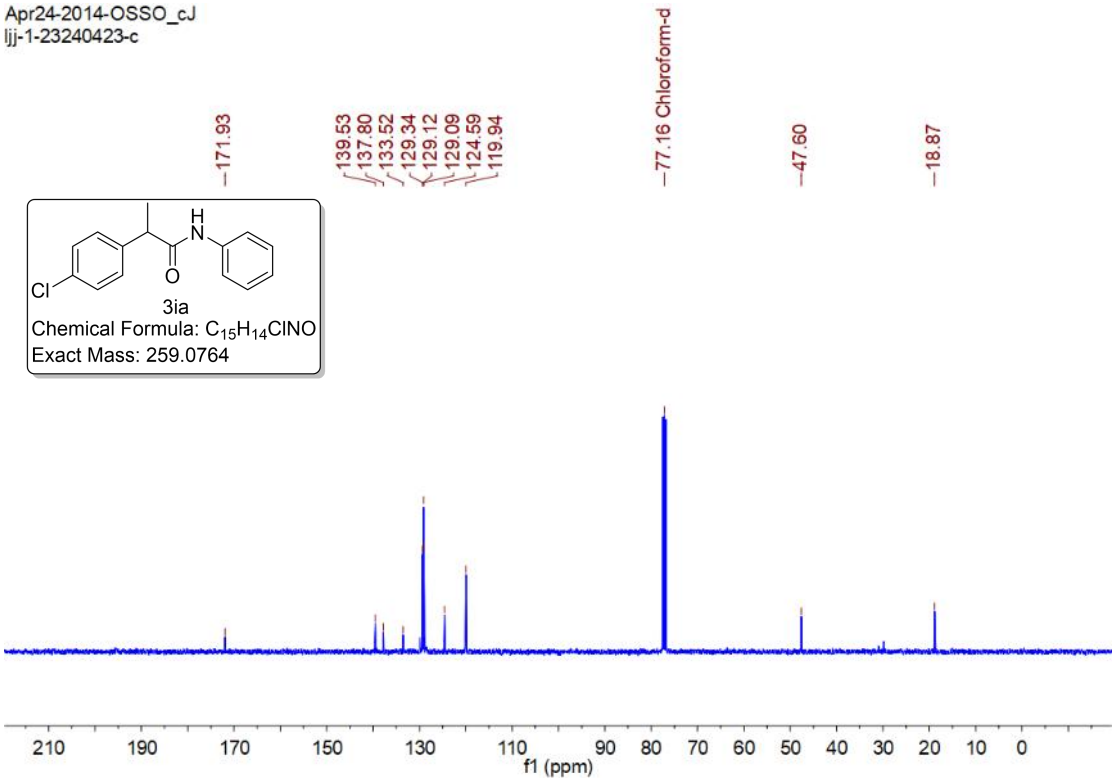

Apr25-2014-OSSO
ljj-1-20240424-h
8.14
8.12
7.46
7.24
7.22
7.20
7.07
7.05
7.03
6.98
6.95
6.93
3.70
3.68
3.66
3.64
1.51
1.49
F
H
N
O
3ga
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
0.97
2.08
4.06
1.04
1.98
1.00
3.02
f1 (ppm)

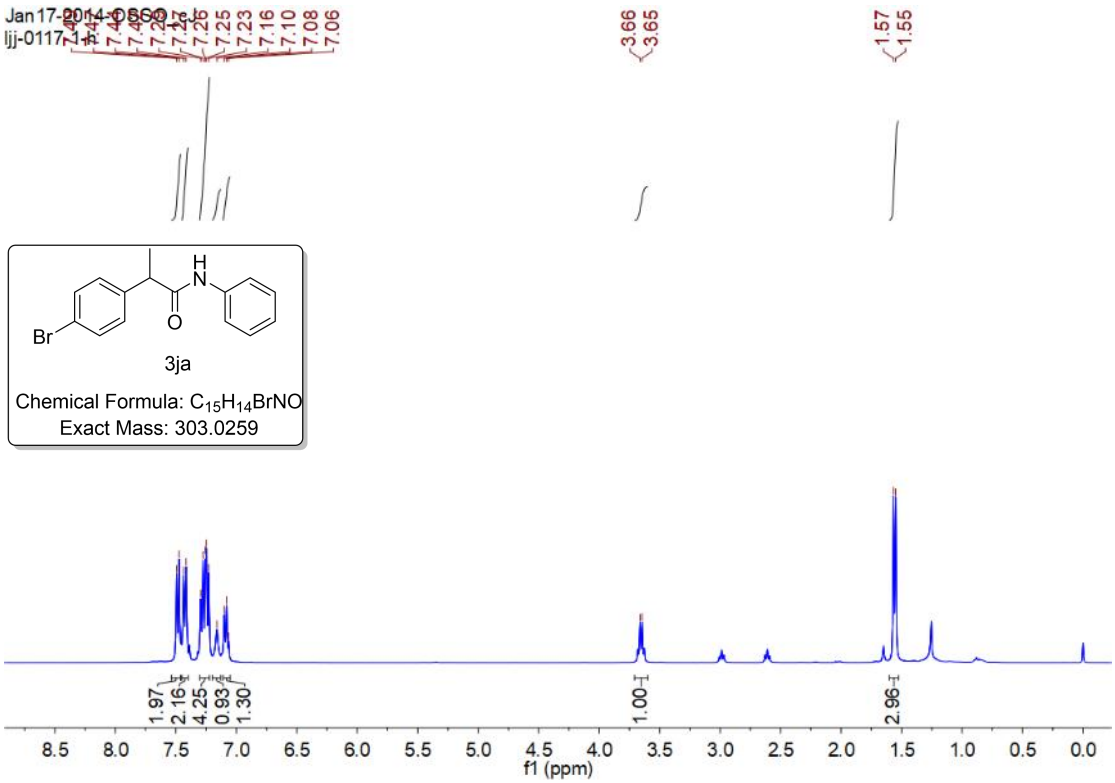

Apr25-2014-OSSO_cJ
ljj-120240424-c
172.85
163.27
160.82
137.91
136.81
136.77
129.19
129.11
128.92
124.50
120.28
115.80
115.59
77.16 Chloroform-d
46.91
18.80
F
H
N
O
3ga
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
f1 (ppm)

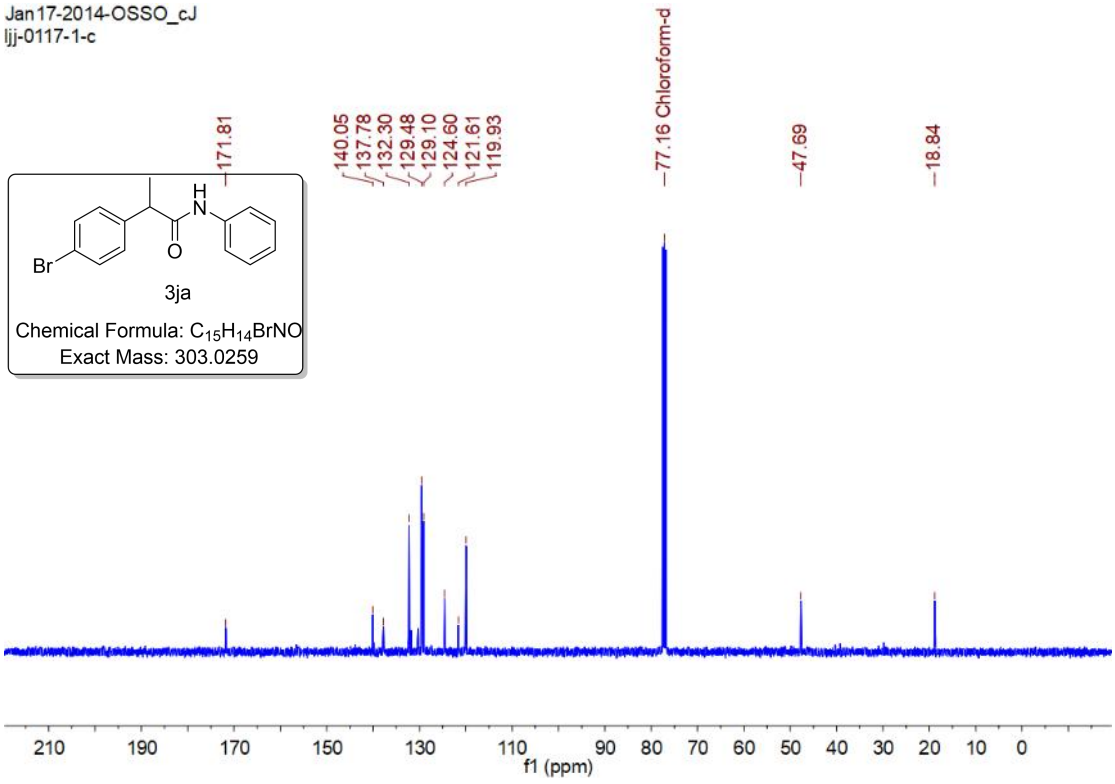

Jan15-2014-OSSO_cJ
ljj-0113-2-h
7.44
7.43
7.34
7.33
7.28
7.27
7.27
7.25
7.25
7.23
7.13
7.11
7.09
7.07
7.05
7.05
6.99
6.98
6.97
6.96
6.95
6.94
3.70
3.68
1.56
1.54
H
N
O
F
3ha
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
0.95
2.04
3.16
3.08
1.11
1.00
3.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

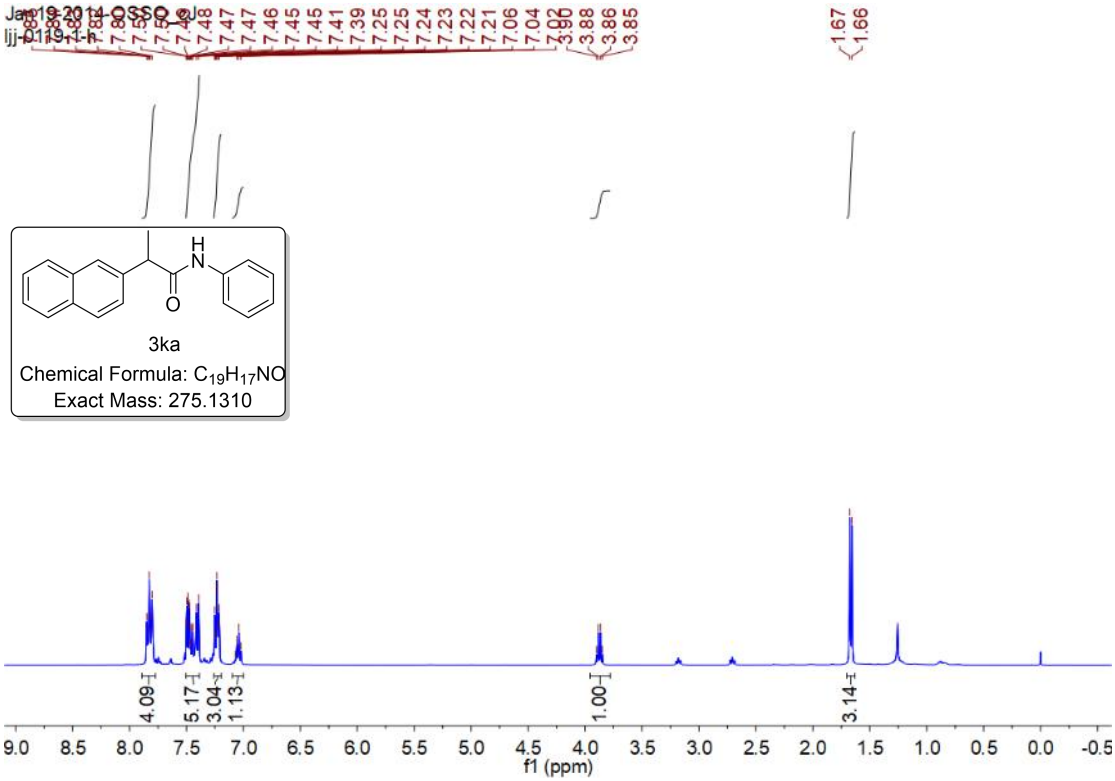

Jan15-2014-OSSO_cJ
ljj-0113-2-c
171.98
164.39
161.93
143.54
143.47
137.81
130.64
130.56
129.03
124.57
123.41
123.38
120.10
115.19
114.83
114.61
114.41
77.16 Chloroform-d
47.73
18.67
H
N
O
F
3ha
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

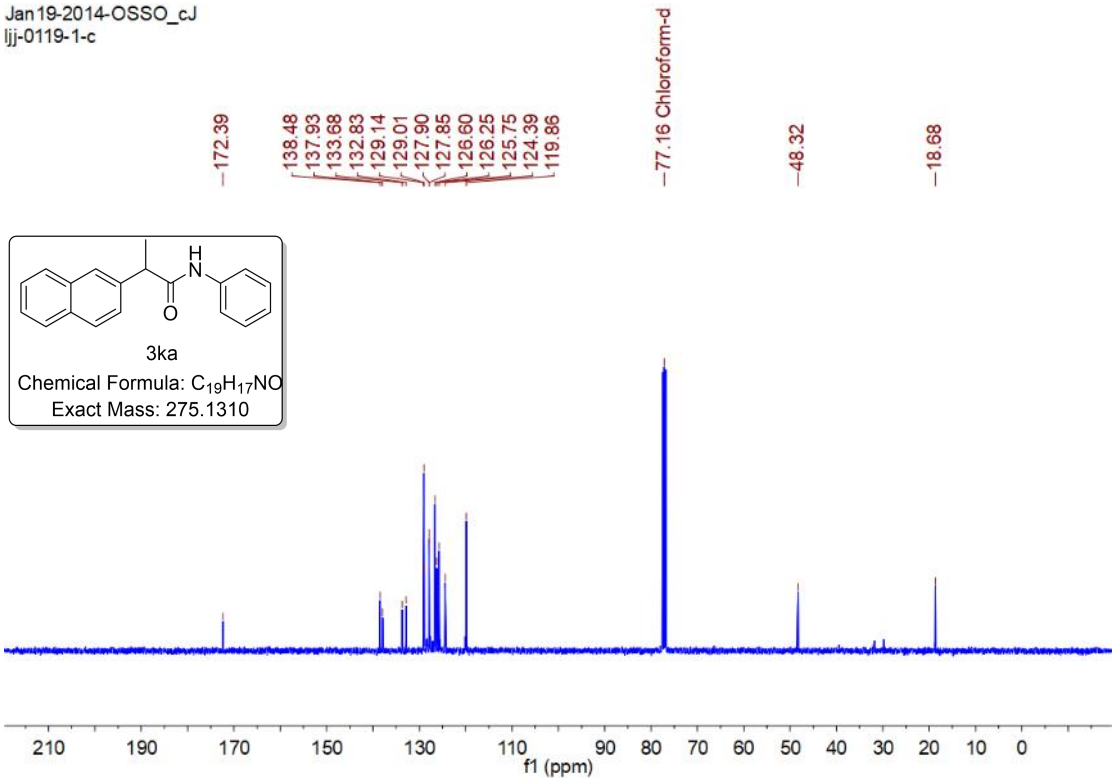

Apr24-2014-OSSO
ljj-1-20240423-h
7.08
7.06
3.70
3.68
3.66
3.64
1.57
1.55
3ia
Chemical Formula: C15H14ClNO
Exact Mass: 259.0764
1.98
6.96
1.19
1.00
3.08
f1 (ppm)

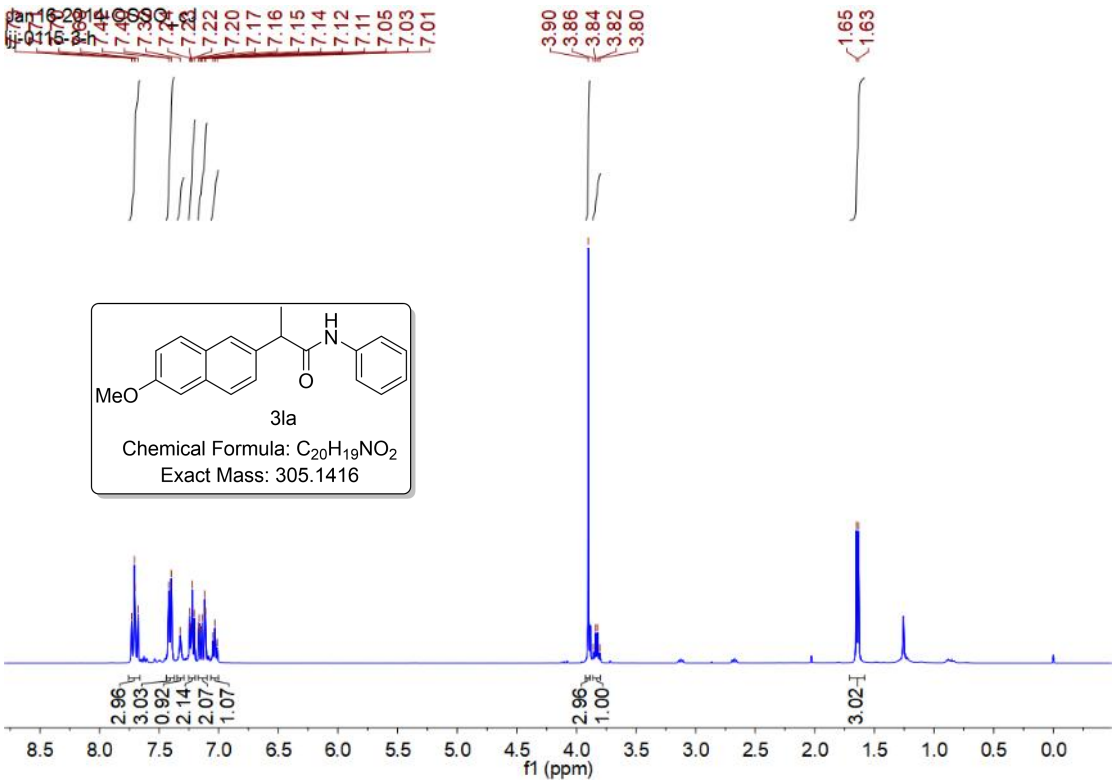

Apr24-2014-OSSO_cJ
ljj-1-23240423-c
171.93
139.53
137.80
133.52
129.34
129.12
129.09
124.59
119.94
77.16 Chloroform-d
47.60
18.87
3ia
Chemical Formula: C15H14ClNO
Exact Mass: 259.0764
f1 (ppm)

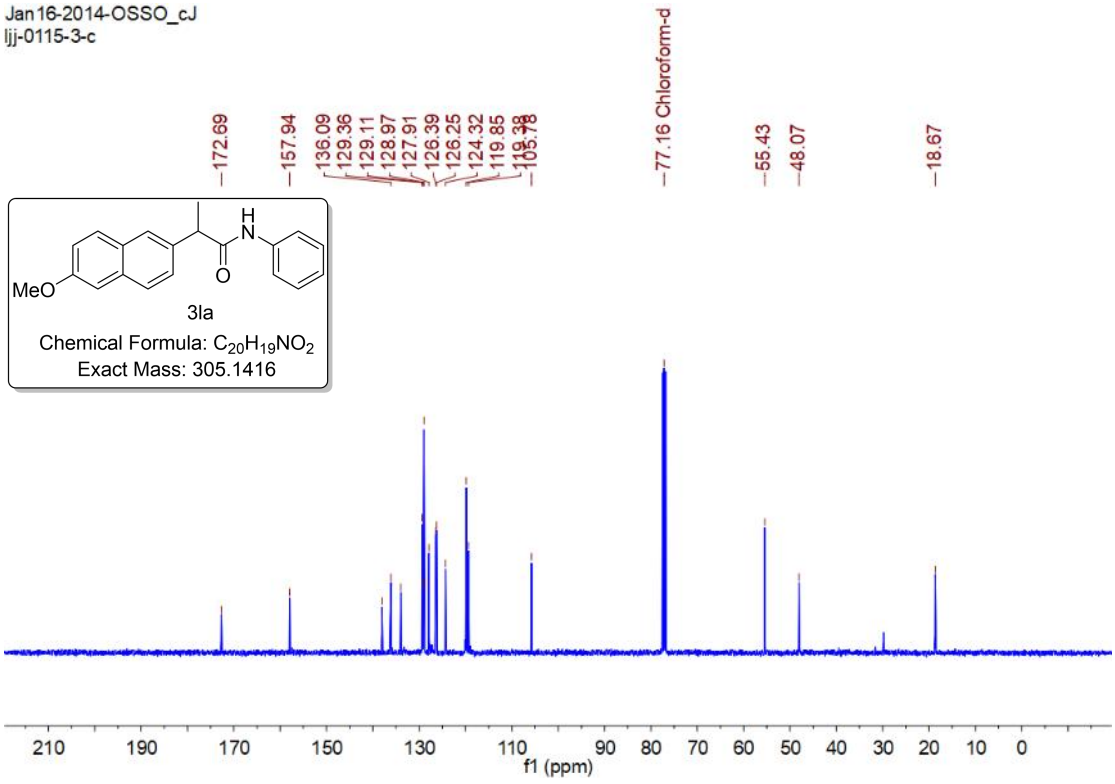

Jan17-2014-OSSO_cJ
ljj-0117-1-h
7.44
7.43
7.42
7.41
7.26
7.25
7.23
7.16
7.10
7.08
7.06
3.66
3.65
1.57
1.55
Br
H
N
O
3ja
Chemical Formula: C15H14BrNO
Exact Mass: 303.0259
1.97
2.16
4.25
0.93
1.30
1.00
2.96
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

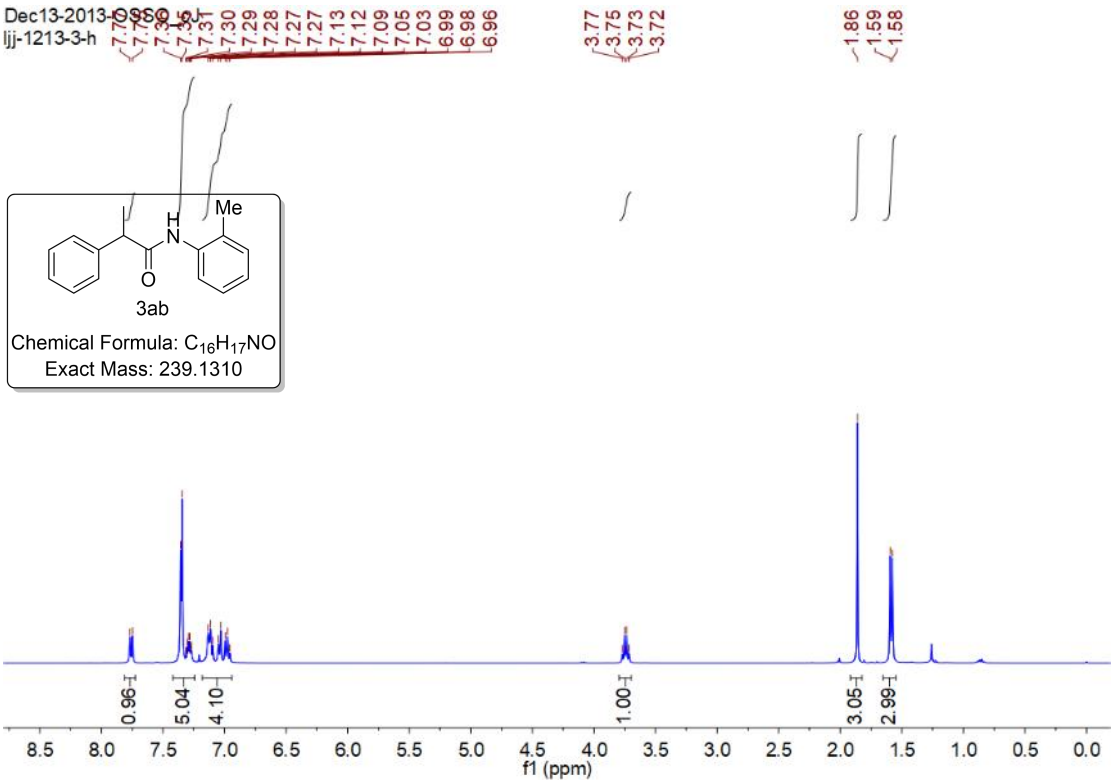

Jan17-2014-OSSO_cJ
ljj-0117-1-c
171.81
140.05
137.78
132.30
129.48
129.10
124.60
121.61
119.93
77.16 Chloroform-d
47.69
18.84
Br
H
N
O
3ja
Chemical Formula: C15H14BrNO
Exact Mass: 303.0259
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

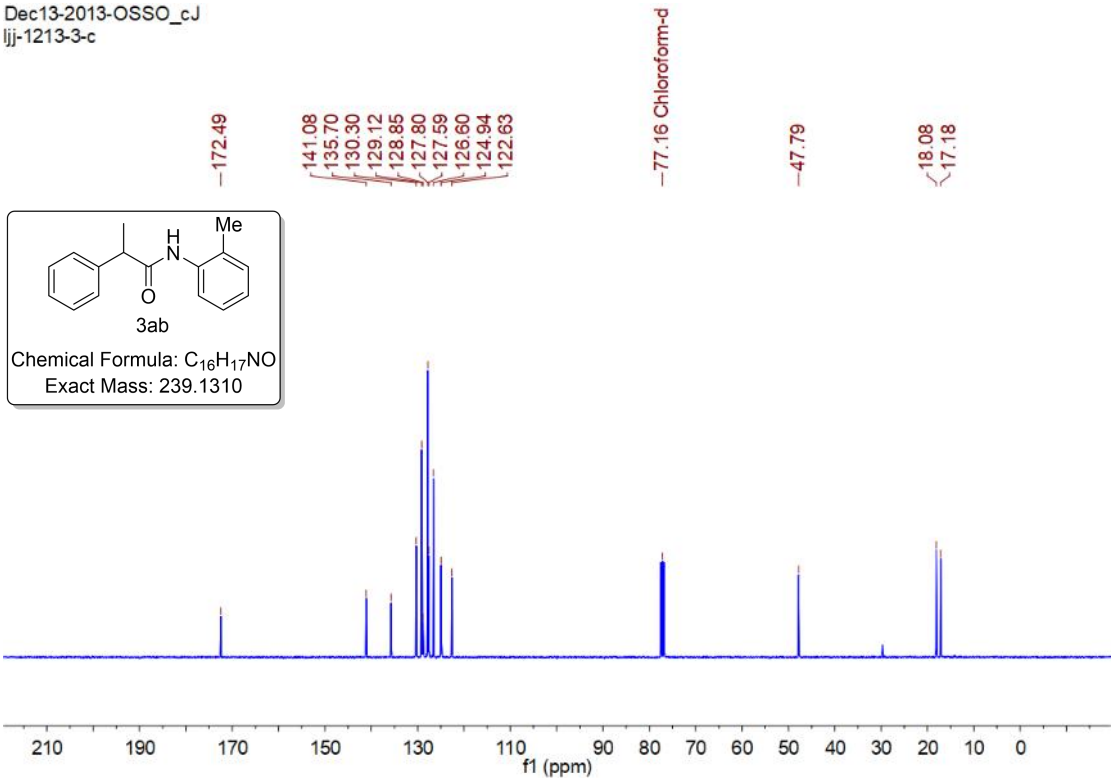

Jan19-2014-OSSO_cJ
ljj-0119-1-h
7.82
7.80
7.55
7.54
7.48
7.47
7.47
7.46
7.45
7.45
7.41
7.39
7.25
7.25
7.24
7.23
7.22
7.21
7.06
7.04
7.02
3.90
3.88
3.86
3.85
1.67
1.66
H
N
O
3ka
Chemical Formula: C19H17NO
Exact Mass: 275.1310
4.09
5.17
3.04
1.13
1.00
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

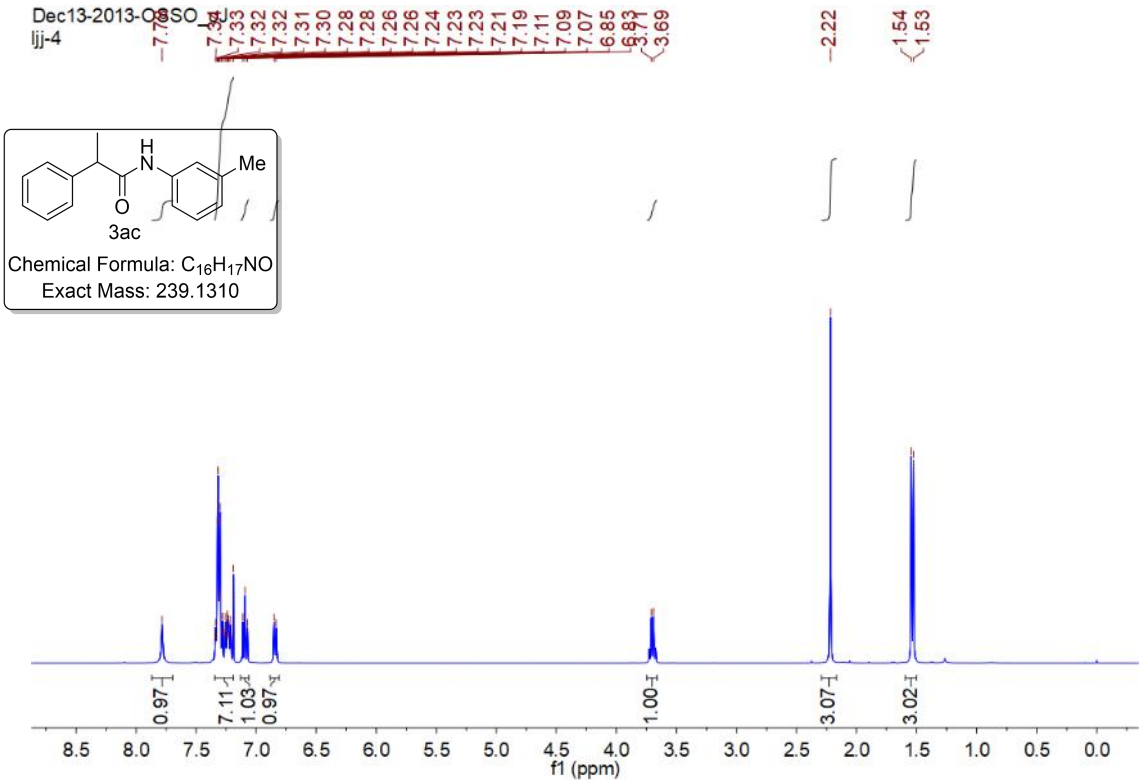

Jan19-2014-OSSO_cJ
ljj-0119-1-c
172.39
138.48
137.93
133.68
132.83
129.14
129.01
127.90
127.85
126.60
126.25
125.75
124.39
119.86
77.16 Chloroform-d
48.32
18.68
H
N
O
3ka
Chemical Formula: C19H17NO
Exact Mass: 275.1310
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

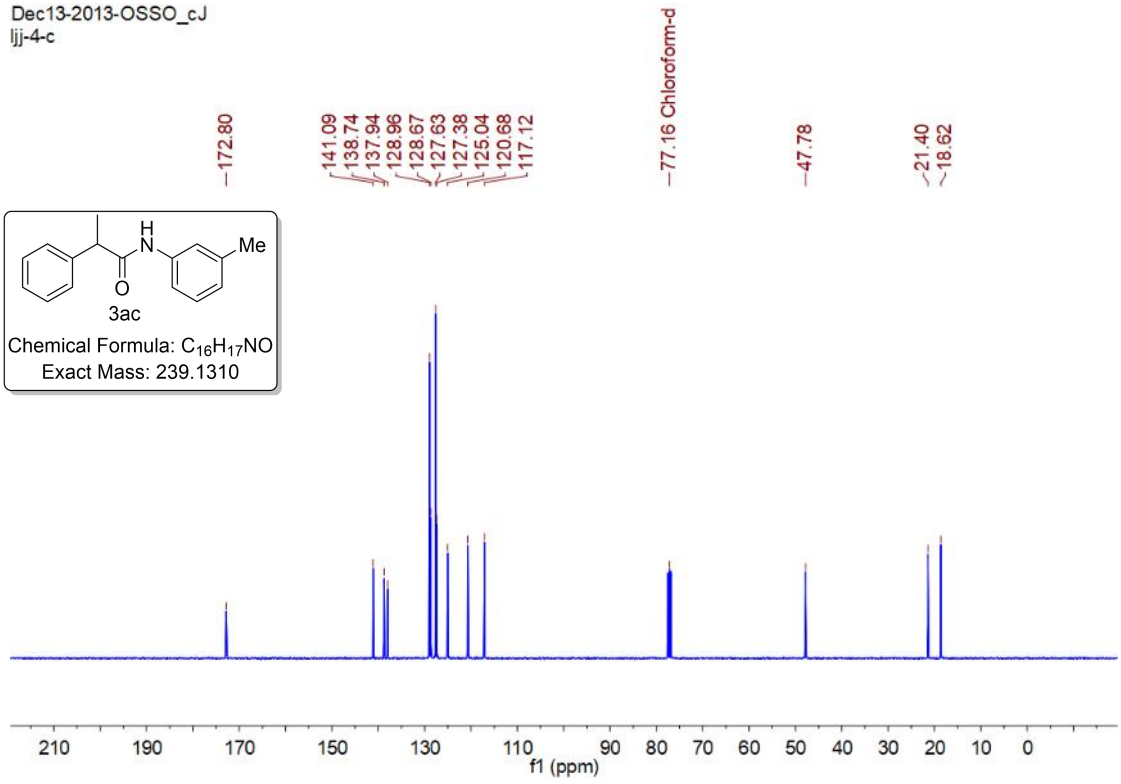

Jan16-2014-OSSO_cJ
ljj-0115-3-h
7.71
7.69
7.48
7.46
7.34
7.24
7.23
7.22
7.20
7.17
7.16
7.15
7.14
7.12
7.11
7.05
7.03
7.01
3.90
3.86
3.84
3.82
3.80
1.65
1.63
H
N
O
MeO
3la
Chemical Formula: C20H19NO2
Exact Mass: 305.1416
2.96
3.03
0.92
2.14
2.07
1.07
2.96
1.00
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

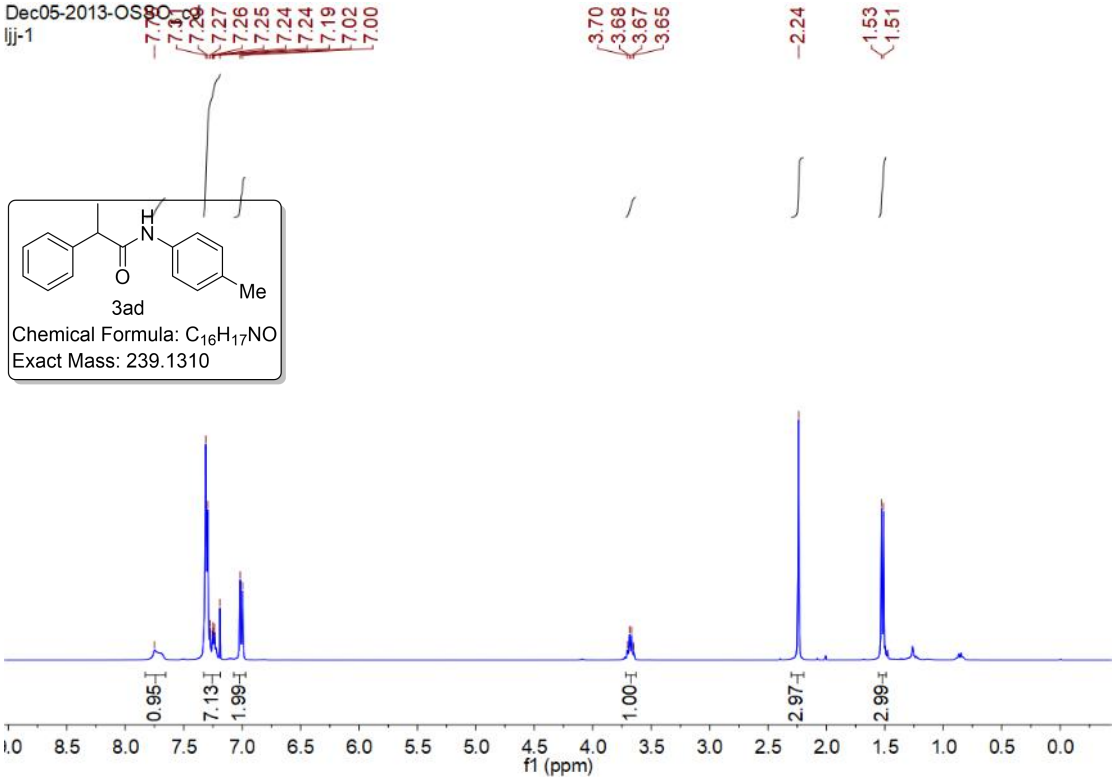

Jan16-2014-OSSO_cJ
ljj-0115-3-c
172.69
157.94
136.09
129.36
129.11
128.97
127.91
126.39
126.25
124.32
119.85
77.16 Chloroform-d
55.43
48.07
18.67
H
N
O
MeO
3la
Chemical Formula: C20H19NO2
Exact Mass: 305.1416
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

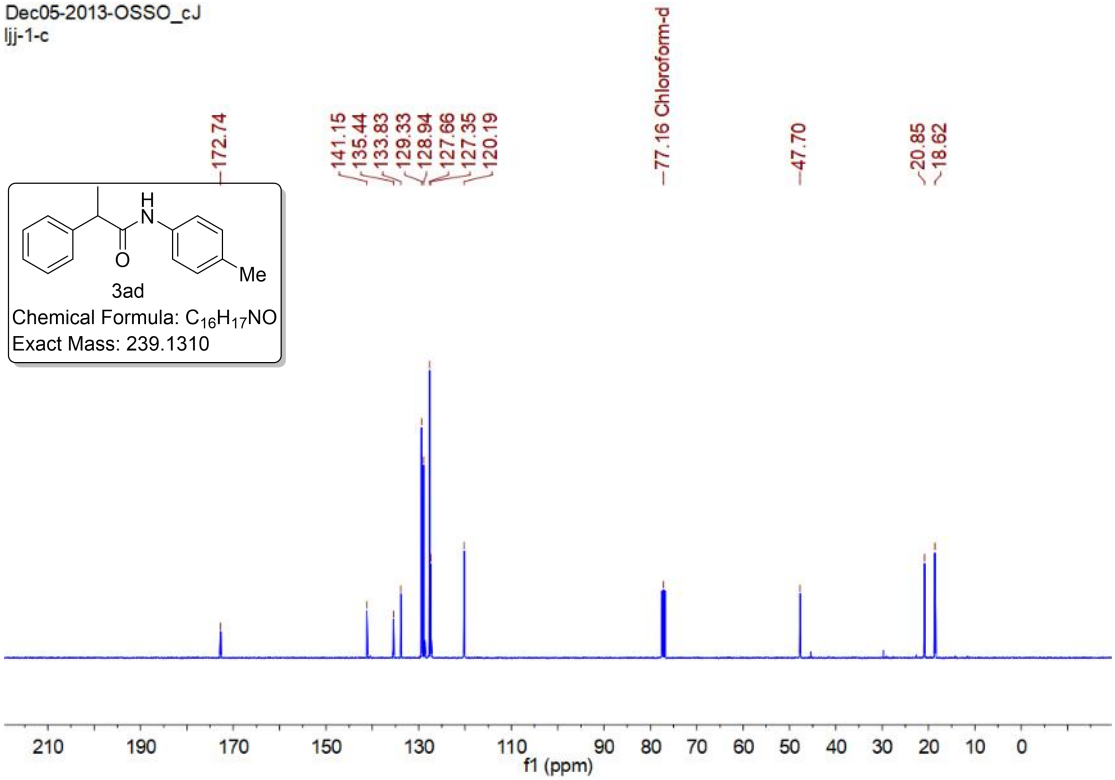

Dec13-2013-OSSO_cJ
ljj-1213-3-h
7.77
7.75
7.37
7.31
7.30
7.29
7.28
7.27
7.27
7.13
7.12
7.09
7.05
7.03
6.99
6.98
6.96
3.77
3.75
3.73
3.72
1.86
1.59
1.58
Me
H
N
O
3ab
Chemical Formula: C16H17NO
Exact Mass: 239.1310
0.96
5.04
4.10
1.00
3.05
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

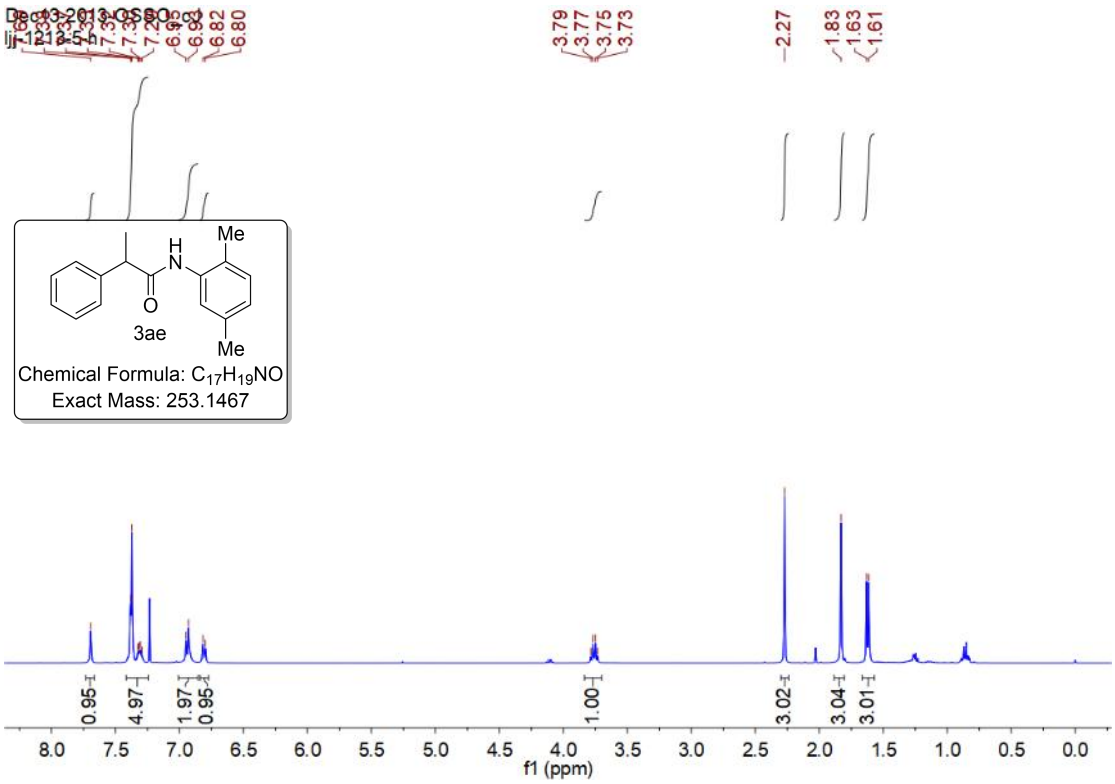

Dec13-2013-OSSO_cJ
ljj-1213-3-c
172.49
141.08
135.70
130.30
129.12
128.85
127.80
127.59
126.60
124.94
122.63
77.16 Chloroform-d
47.79
18.08
17.18
Me
H
N
O
3ab
Chemical Formula: C16H17NO
Exact Mass: 239.1310
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

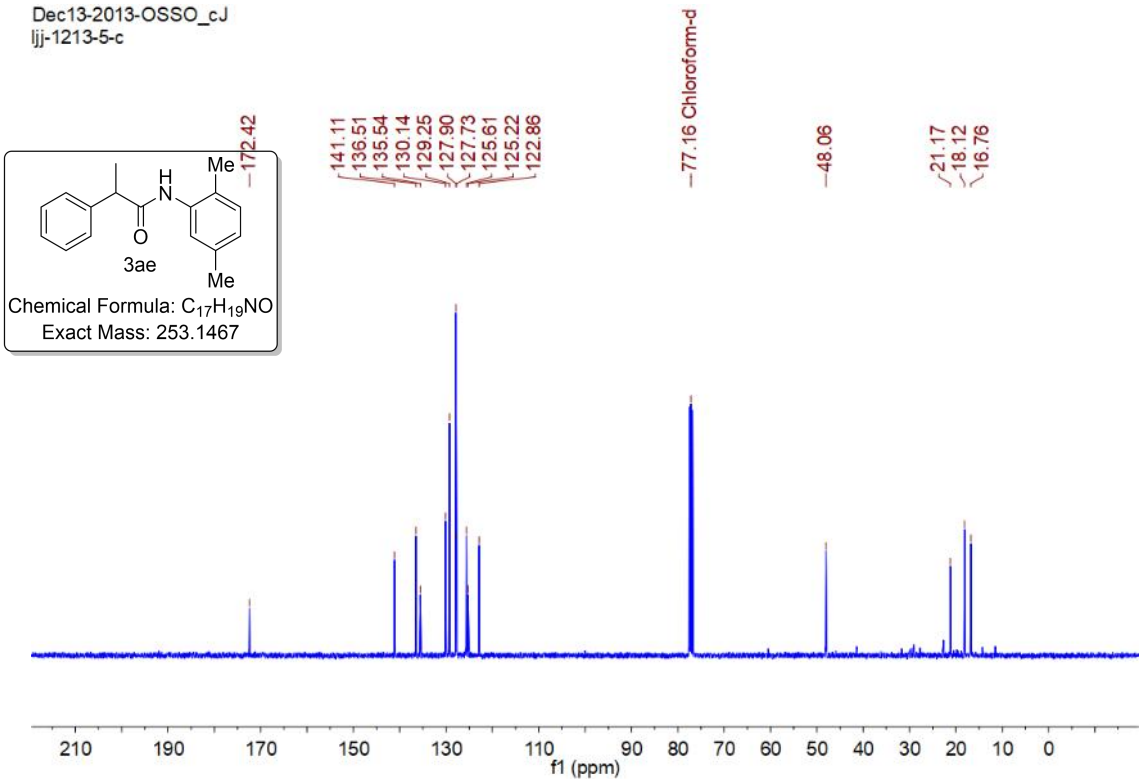

Dec13-2013-OSSO_cJ
ljj-4
7.34
7.33
7.32
7.32
7.31
7.30
7.28
7.28
7.26
7.26
7.24
7.23
7.23
7.21
7.19
7.11
7.09
7.07
6.85
6.83
3.71
3.69
2.22
1.54
1.53
H
N
O
Me
3ac
Chemical Formula: C16H17NO
Exact Mass: 239.1310
0.97
7.11
1.03
0.97
1.00
3.07
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

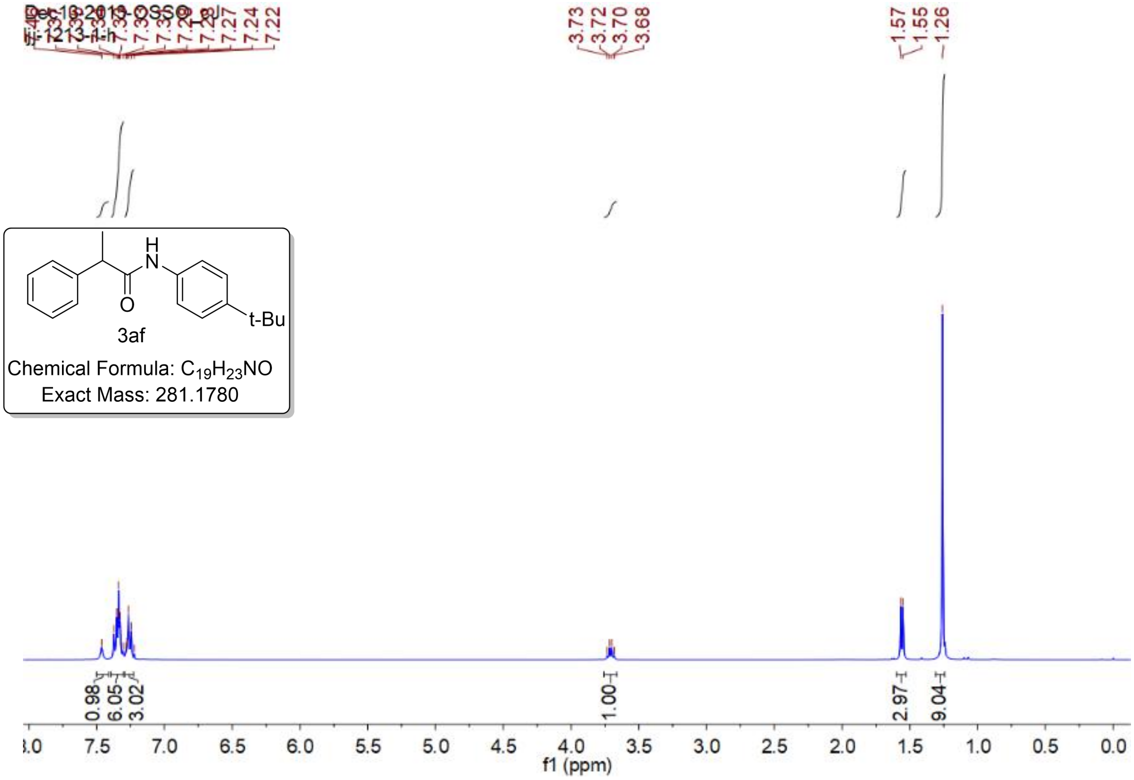

Dec13-2013-OSSO_cJ
ljj-4-c
172.80
141.09
138.74
137.94
128.96
128.67
127.63
127.38
125.04
120.68
117.12
77.16 Chloroform-d
47.78
21.40
18.62
H
N
O
Me
3ac
Chemical Formula: C16H17NO
Exact Mass: 239.1310
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

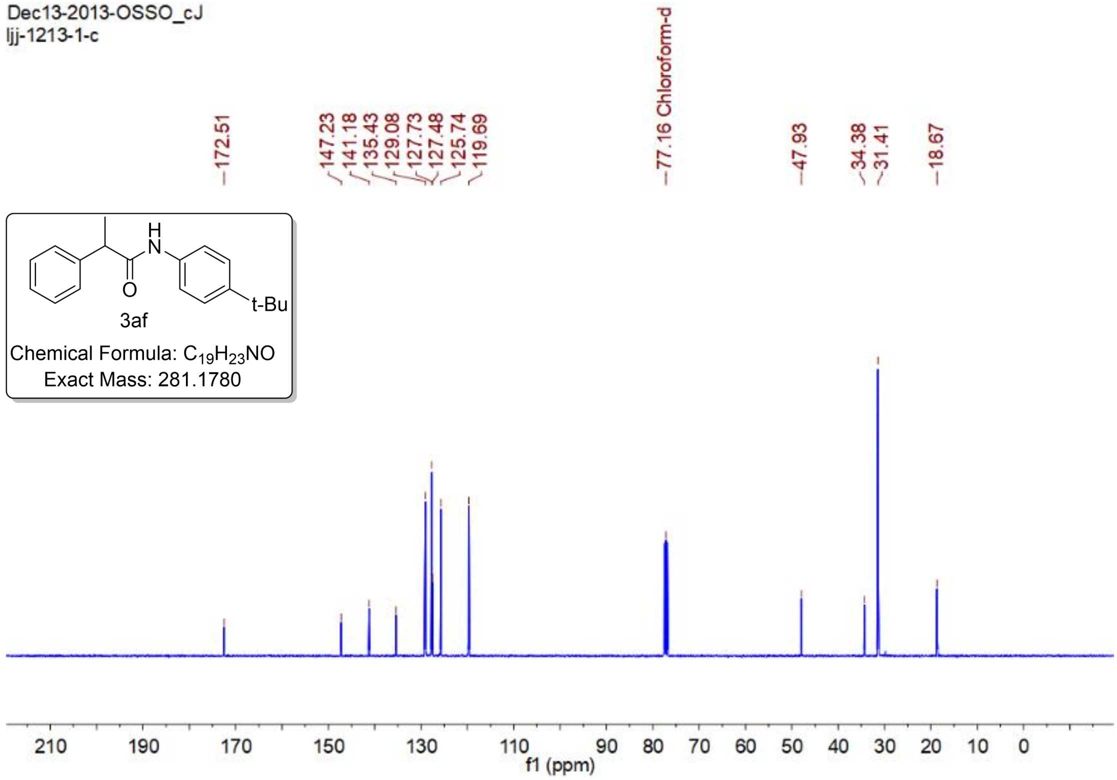

Dec05-2013-OSSO_cJ
ljj-1
7.31
7.29
7.27
7.26
7.25
7.24
7.24
7.19
7.02
7.00
3.70
3.68
3.67
3.65
2.24
1.53
1.51
3ad
Chemical Formula: C16H17NO
Exact Mass: 239.1310
0.95
7.13
1.99
1.00
2.97
2.99
f1 (ppm)

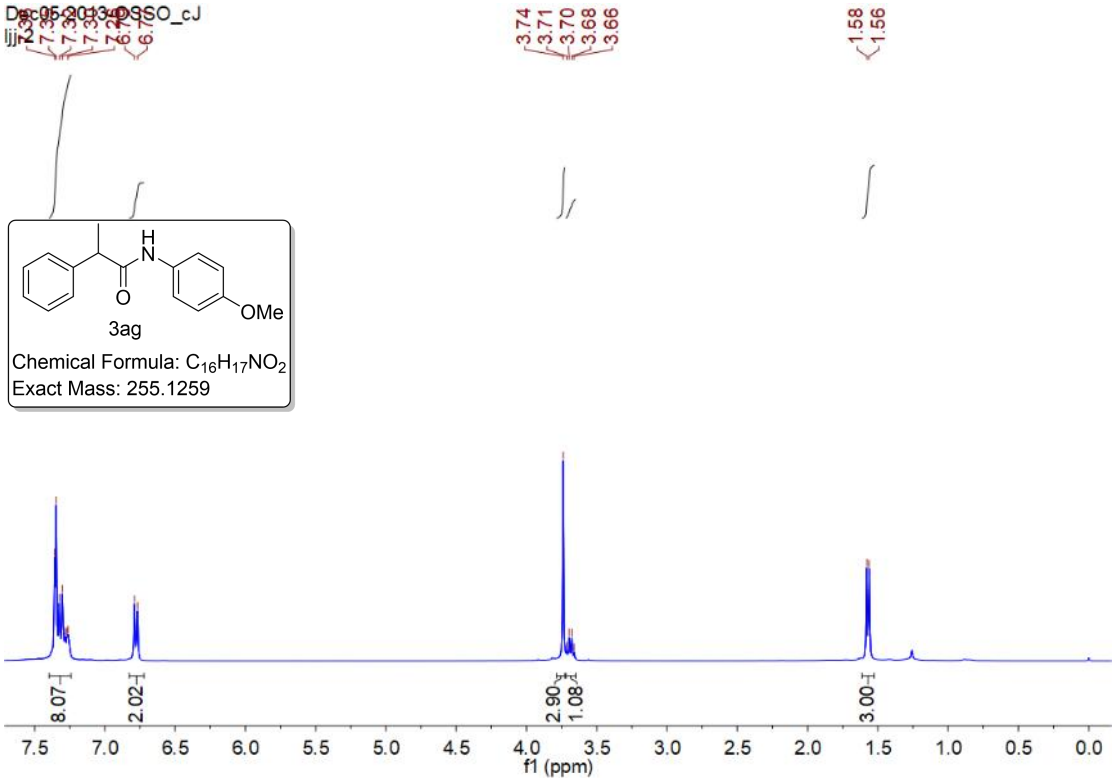

Dec05-2013-OSSO_cJ
ljj-1-c
172.74
141.15
135.44
133.83
129.33
128.94
127.66
127.35
120.19
77.16 Chloroform-d
47.70
20.85
18.62
3ad
Chemical Formula: C16H17NO
Exact Mass: 239.1310
f1 (ppm)

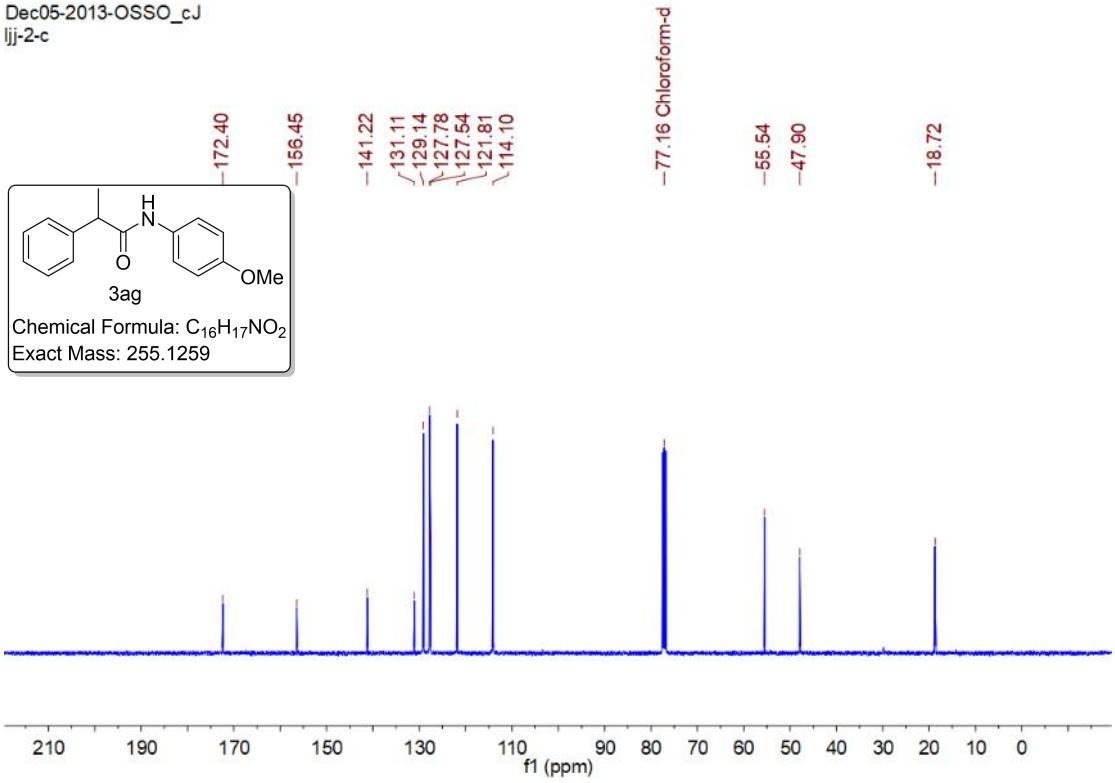

3ae
Chemical Formula: C17H19NO
Exact Mass: 253.1467
f1 (ppm)

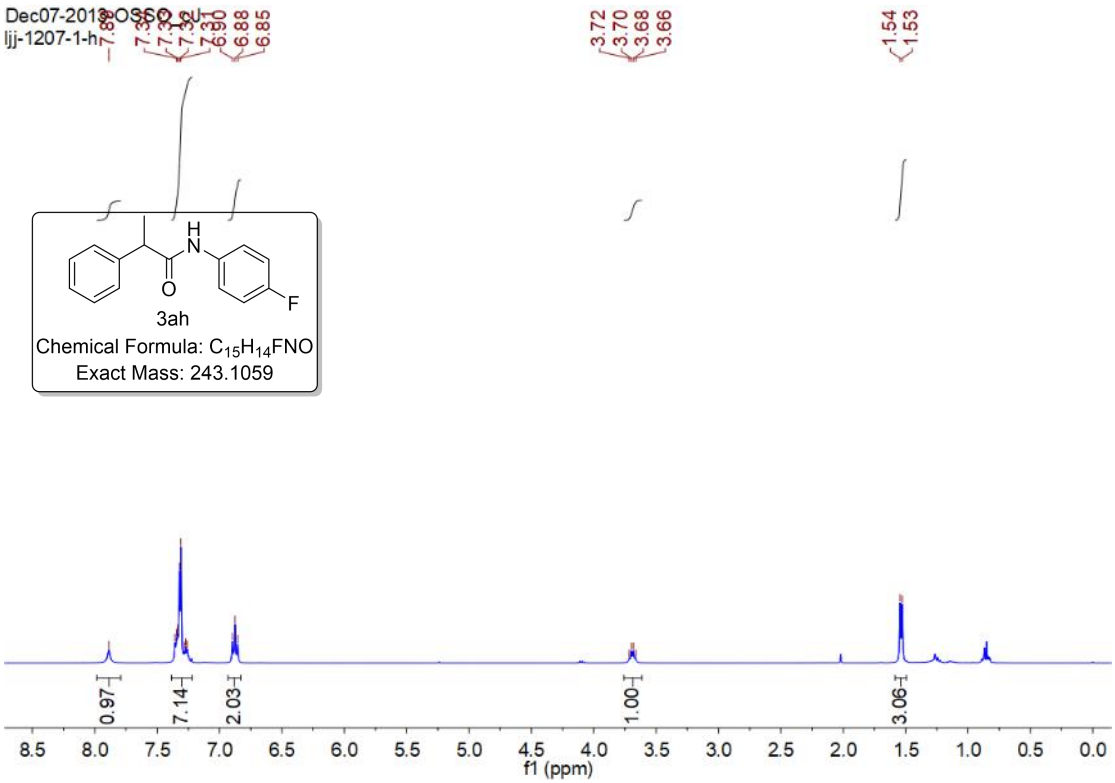

Dec13-2013-OSSO_cJ
ljj-1213-5-c
3ae
Chemical Formula: C17H19NO
Exact Mass: 253.1467
f1 (ppm)

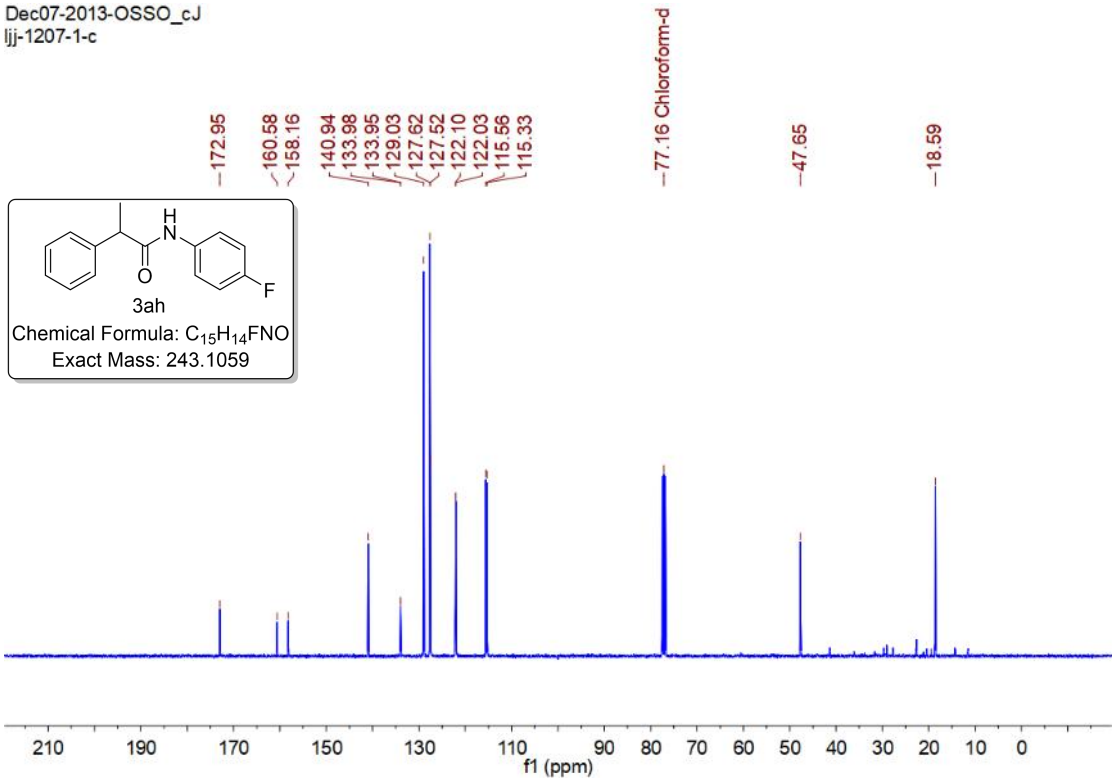

7.27
7.24
7.22
3.73
3.72
3.70
3.68
1.57
1.55
1.26
3af
Chemical Formula: $C_{19}H_{23}NO$
Exact Mass: 281.1780
0.98
6.05
3.02
1.00
2.97
9.04
f1 (ppm)

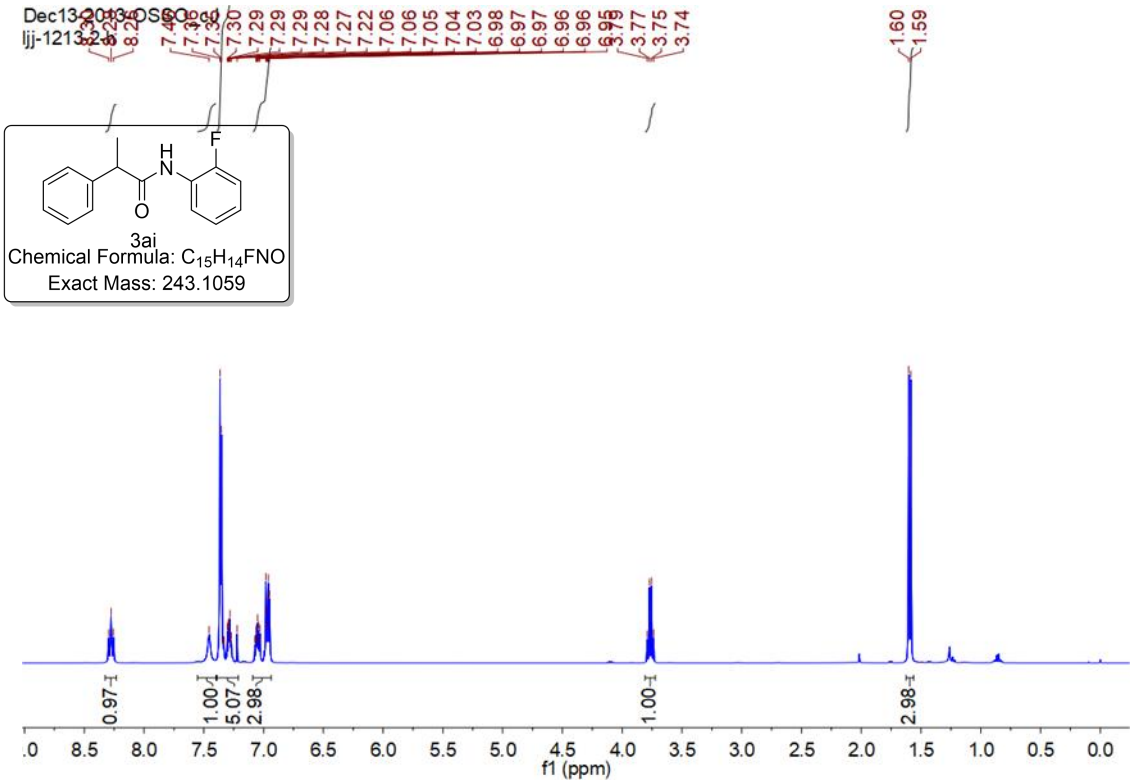

Dec13-2013-OSSO_cJ
ljj-1213-1-c
172.51
147.23
141.18
135.43
129.08
127.73
127.48
125.74
119.69
77.16 Chloroform-d
47.93
34.38
31.41
18.67
3af
Chemical Formula: $C_{19}H_{23}NO$
Exact Mass: 281.1780
f1 (ppm)

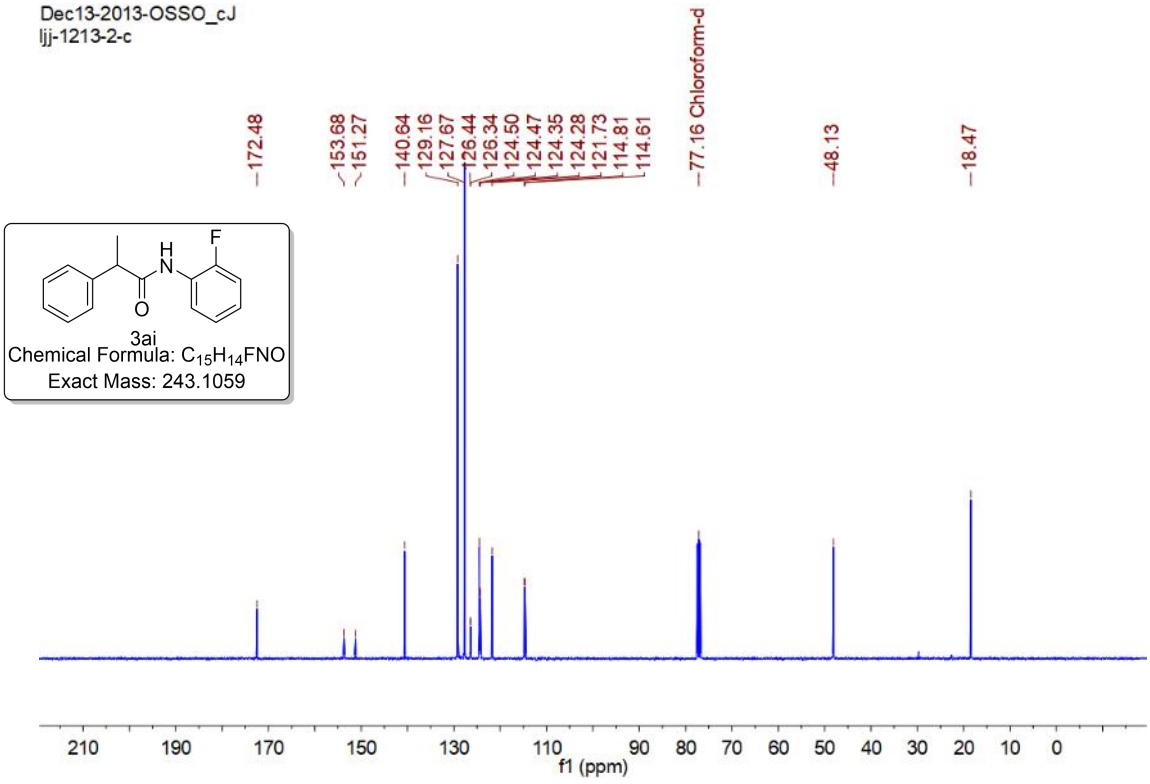

3.74
3.71
3.70
3.68
3.66
1.58
1.56
3ag
Chemical Formula: C16H17NO2
Exact Mass: 255.1259
8.07
2.02
2.90
1.08
3.00
f1 (ppm)

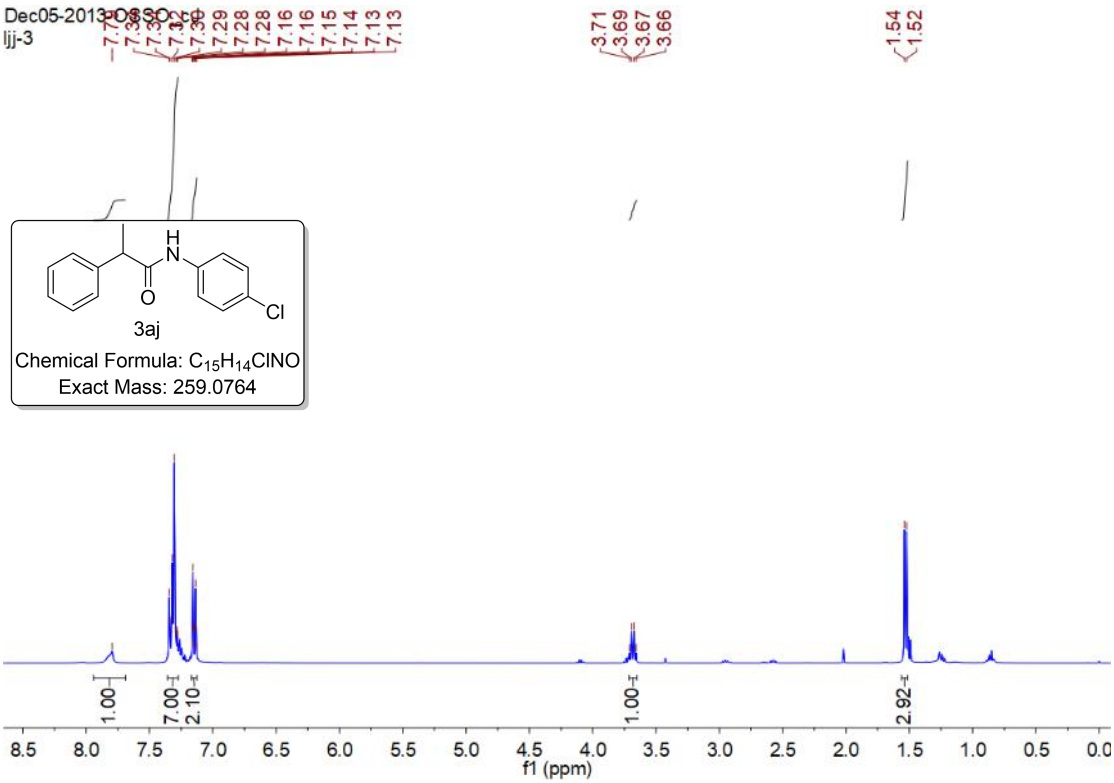

Dec05-2013-OSSO_cJ
ljj-2-c
172.40
156.45
141.22
131.11
129.14
127.78
127.54
121.81
114.10
77.16 Chloroform-d
55.54
47.90
18.72
3ag
Chemical Formula: C16H17NO2
Exact Mass: 255.1259
f1 (ppm)

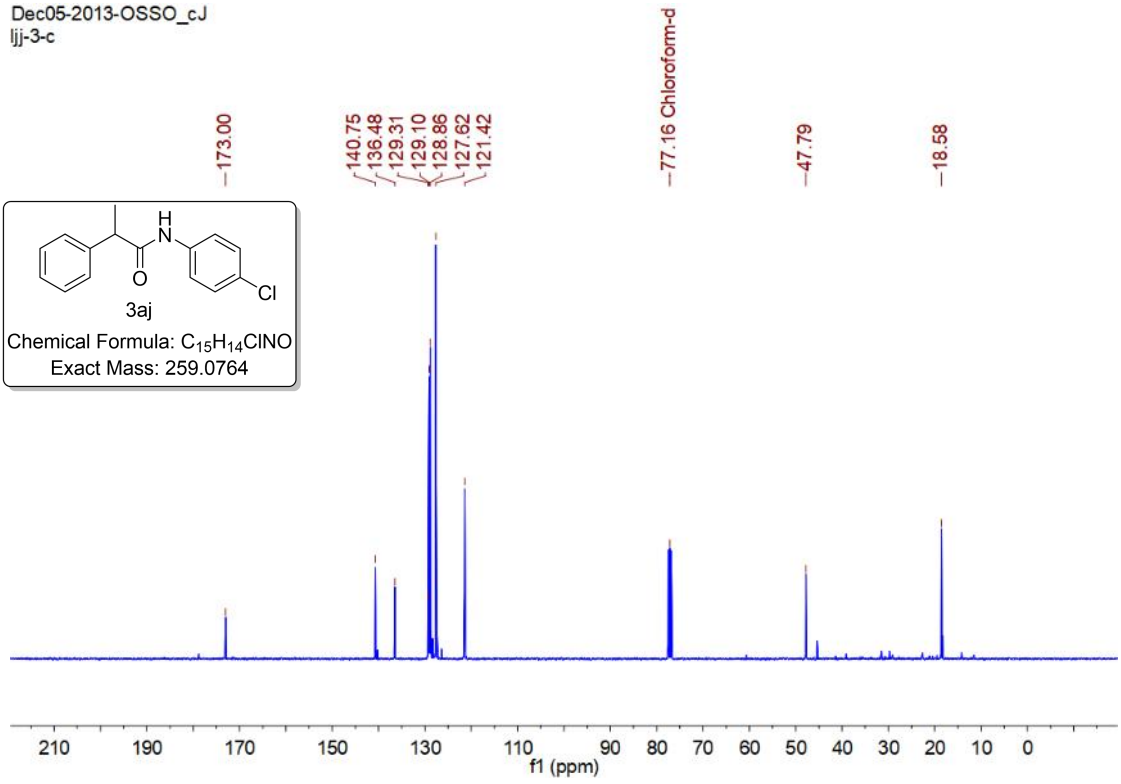

Dec07-2013-OSSO_cJ
ljj-1207-1-h
7.89
7.33
7.32
7.31
6.90
6.88
6.85
3.72
3.70
3.68
3.66
1.54
1.53
H
N
O
F
3ah
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
0.97
7.14
2.03
1.00
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

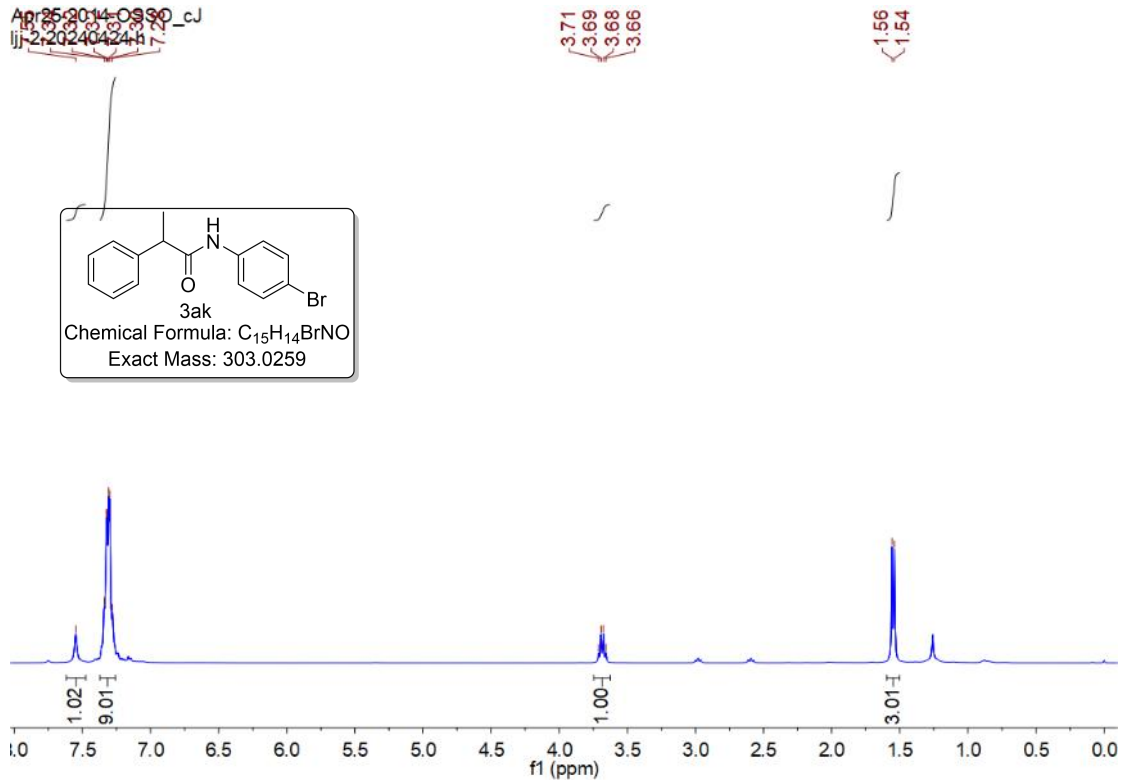

Dec07-2013-OSSO_cJ
ljj-1207-1-c
172.95
160.58
158.16
140.94
133.98
133.95
129.03
127.62
127.52
122.10
122.03
115.56
115.33
77.16 Chloroform-d
47.65
18.59
H
N
O
F
3ah
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

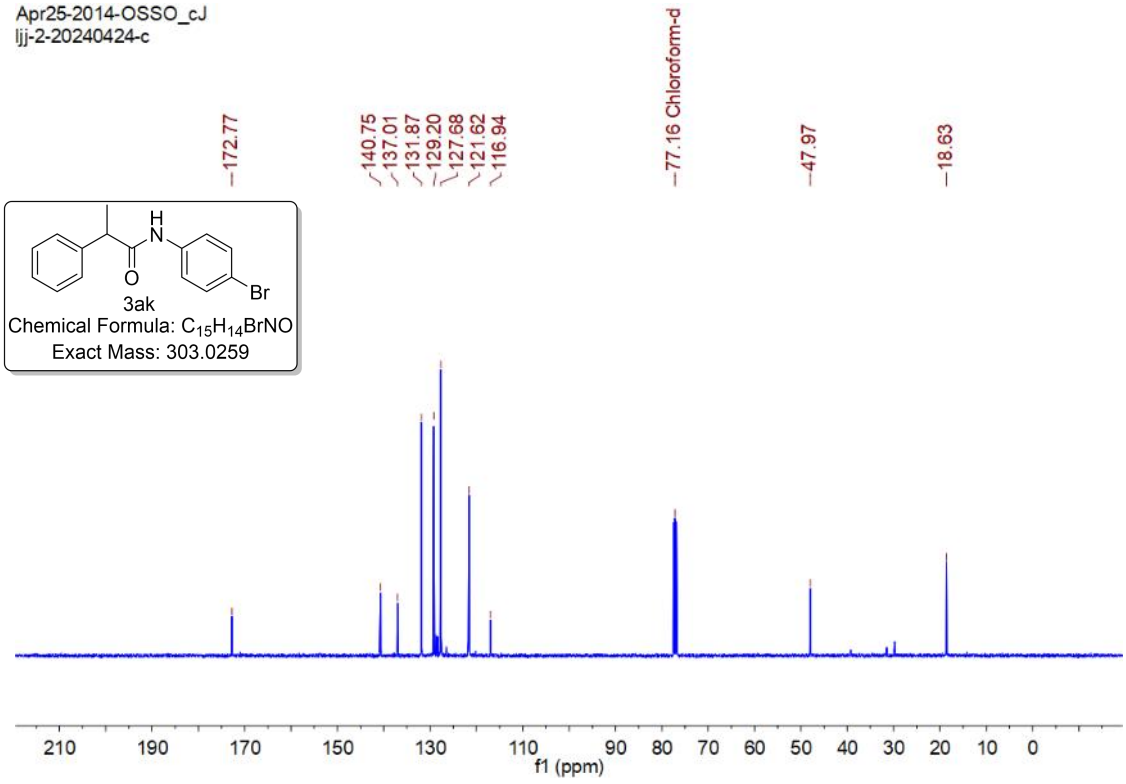

Dec13-2013-OSSO_cJ
ljj-1213-2-b
3ai
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
f1 (ppm)

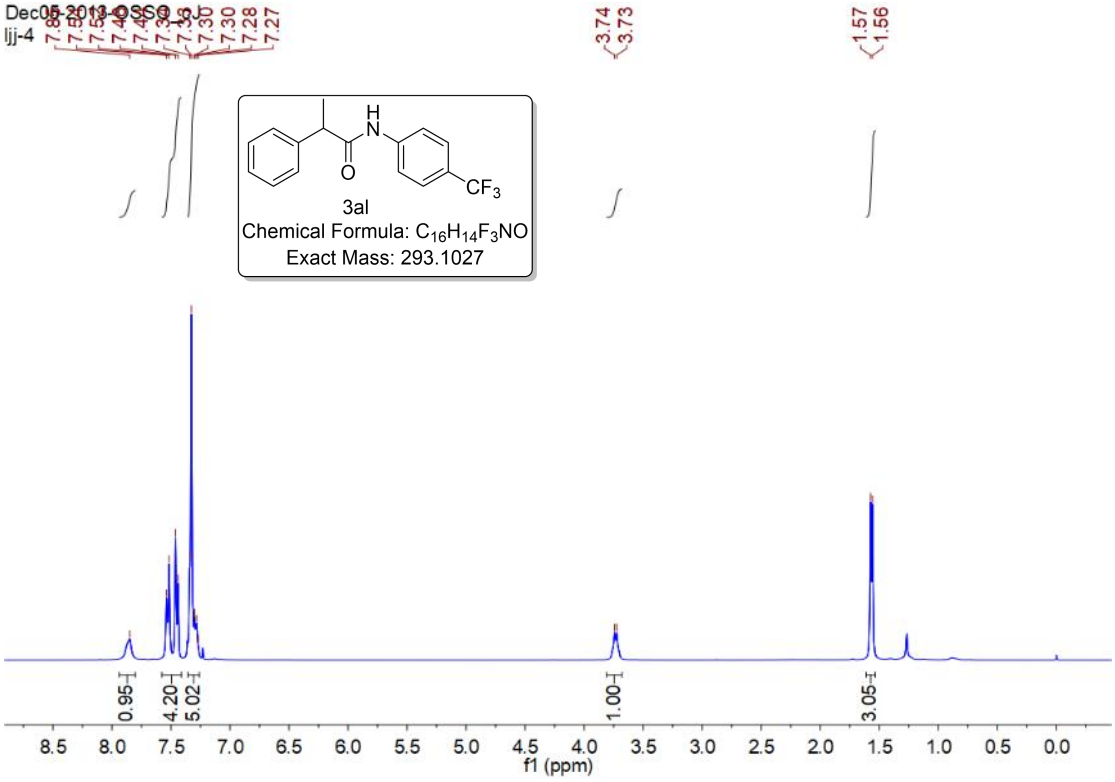

Dec13-2013-OSSO_cJ
ljj-1213-2-c
Chloroform-d
3ai
Chemical Formula: C15H14FNO
Exact Mass: 243.1059
f1 (ppm)

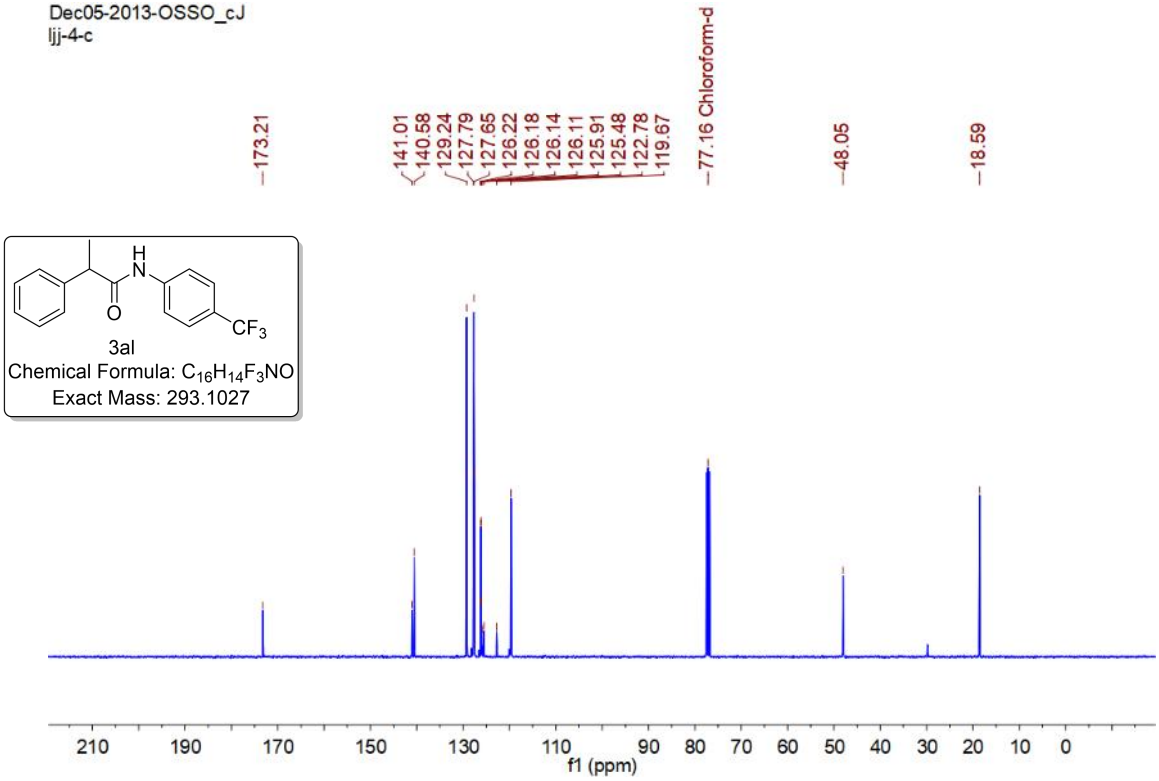

Dec05-2013-OSSO_cJ
ljj-3
7.54
7.53
7.42
7.36
7.29
7.28
7.28
7.16
7.16
7.15
7.14
7.13
7.13
3.71
3.69
3.67
3.66
1.54
1.52
3aj
Chemical Formula: C15H14ClNO
Exact Mass: 259.0764
1.00
7.00
2.10
1.00
2.92
f1 (ppm)

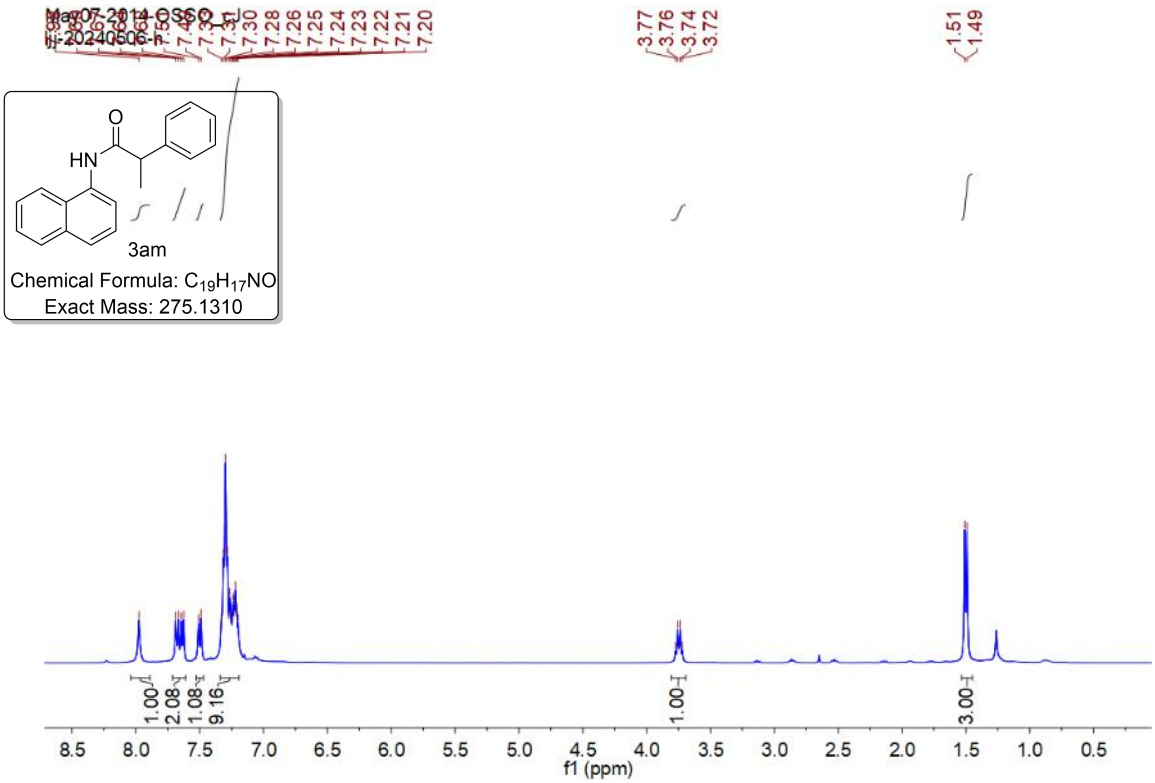

Dec05-2013-OSSO_cJ
ljj-3-c
173.00
140.75
136.48
129.31
129.10
128.86
127.62
121.42
77.16 Chloroform-d
47.79
18.58
3aj
Chemical Formula: C15H14ClNO
Exact Mass: 259.0764
f1 (ppm)

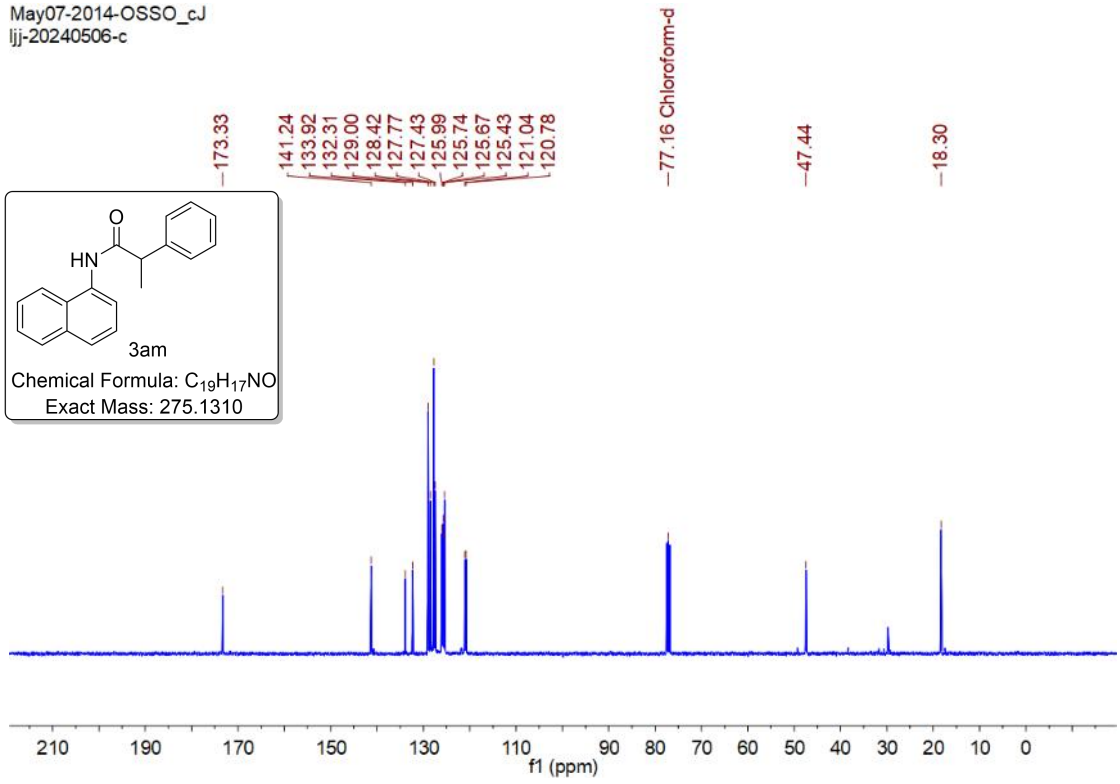

Apr25-2014-OSSO_cJ
ljj-2-20240424-h
3.71
3.69
3.68
3.66
1.56
1.54
3ak
Chemical Formula: C15H14BrNO
Exact Mass: 303.0259
1.02
9.01
1.00
3.01
f1 (ppm)

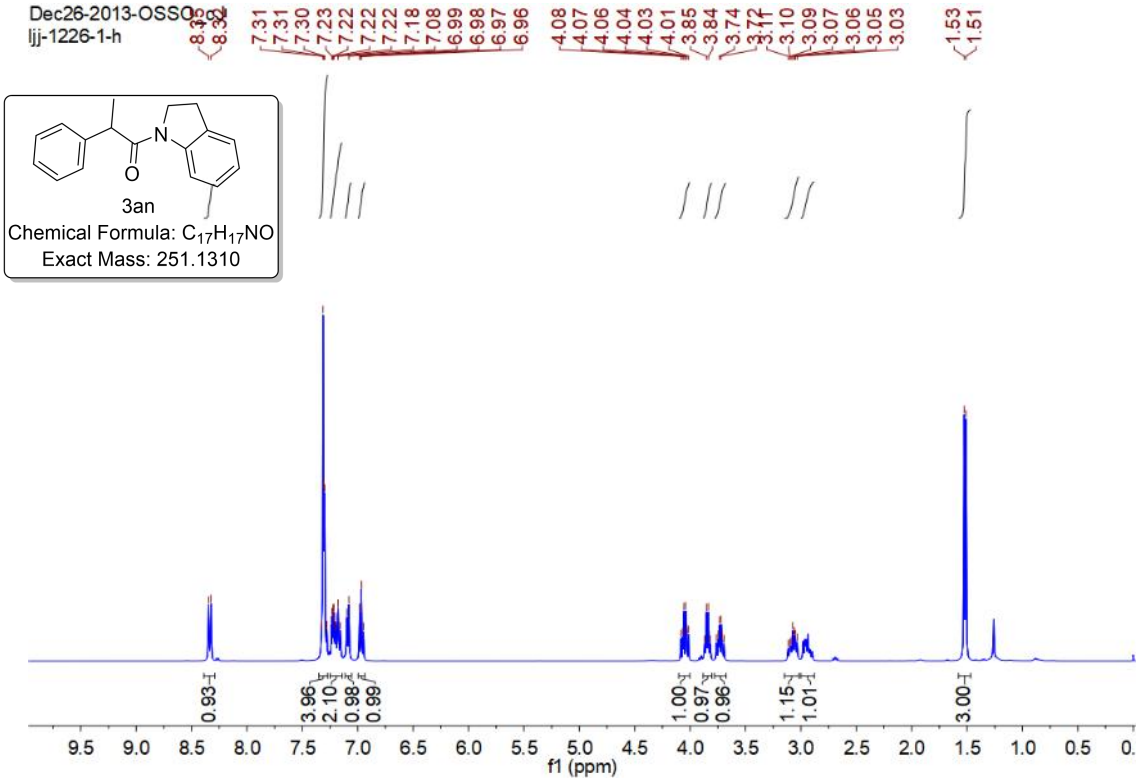

Apr25-2014-OSSO_cJ
ljj-2-20240424-c
172.77
140.75
137.01
131.87
129.20
127.68
121.62
116.94
77.16 Chloroform-d
47.97
18.63
3ak
Chemical Formula: C15H14BrNO
Exact Mass: 303.0259
f1 (ppm)

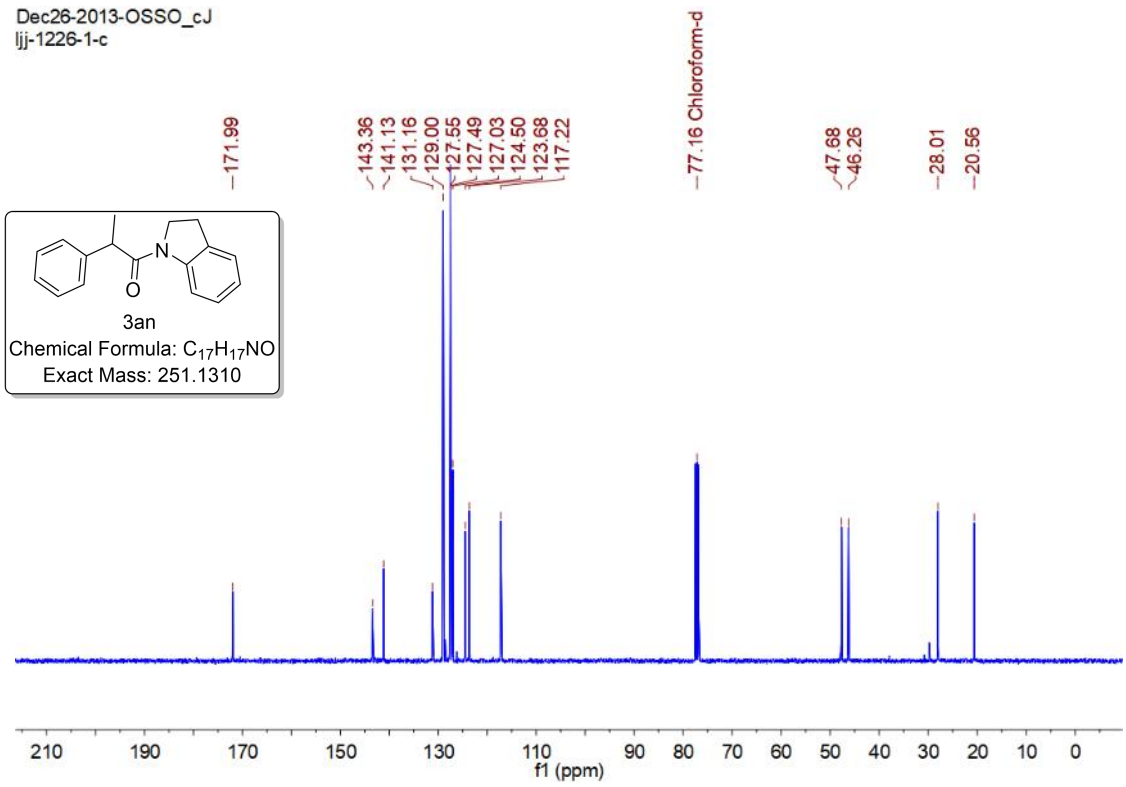

Dec05-2013-OSSO
ljj-4
7.30
7.28
7.27
3.74
3.73
1.57
1.56
3al
Chemical Formula: C16H14F3NO
Exact Mass: 293.1027
0.95
4.20
5.02
1.00
3.05
f1 (ppm)

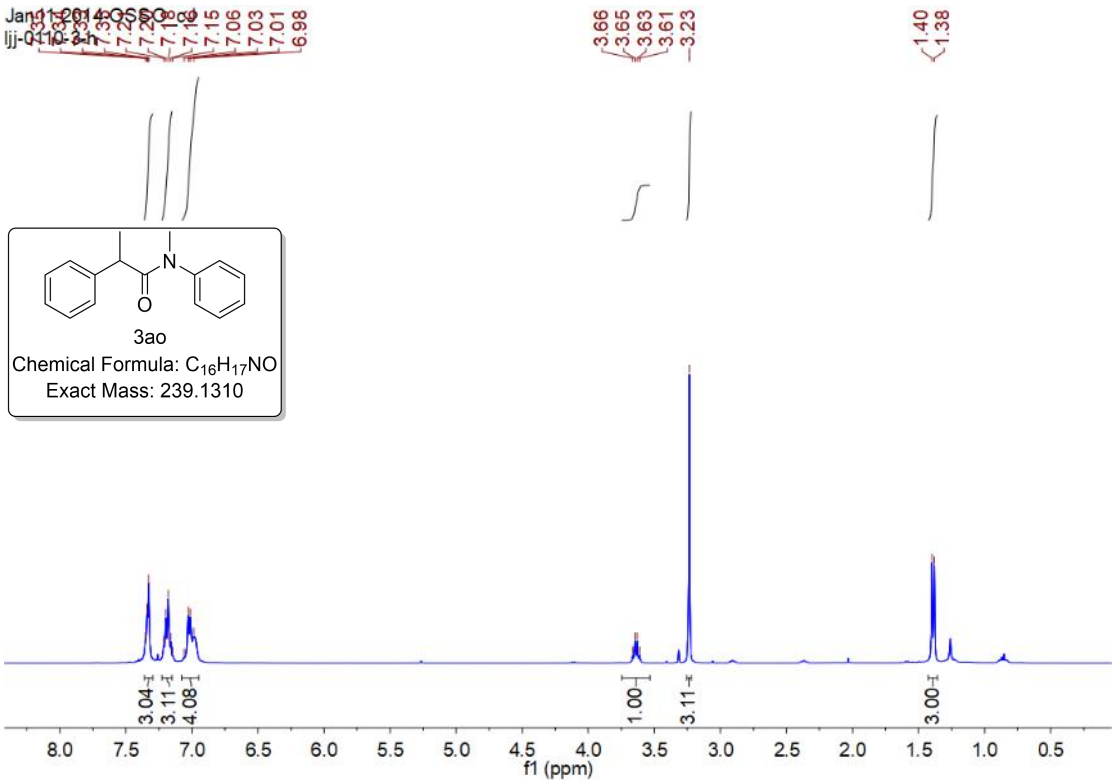

Dec05-2013-OSSO_cJ
ljj-4-c
173.21
141.01
140.58
129.24
127.79
127.65
126.22
126.18
126.14
126.11
125.91
125.48
122.78
119.67
77.16 Chloroform-d
48.05
18.59
3al
Chemical Formula: C16H14F3NO
Exact Mass: 293.1027
f1 (ppm)

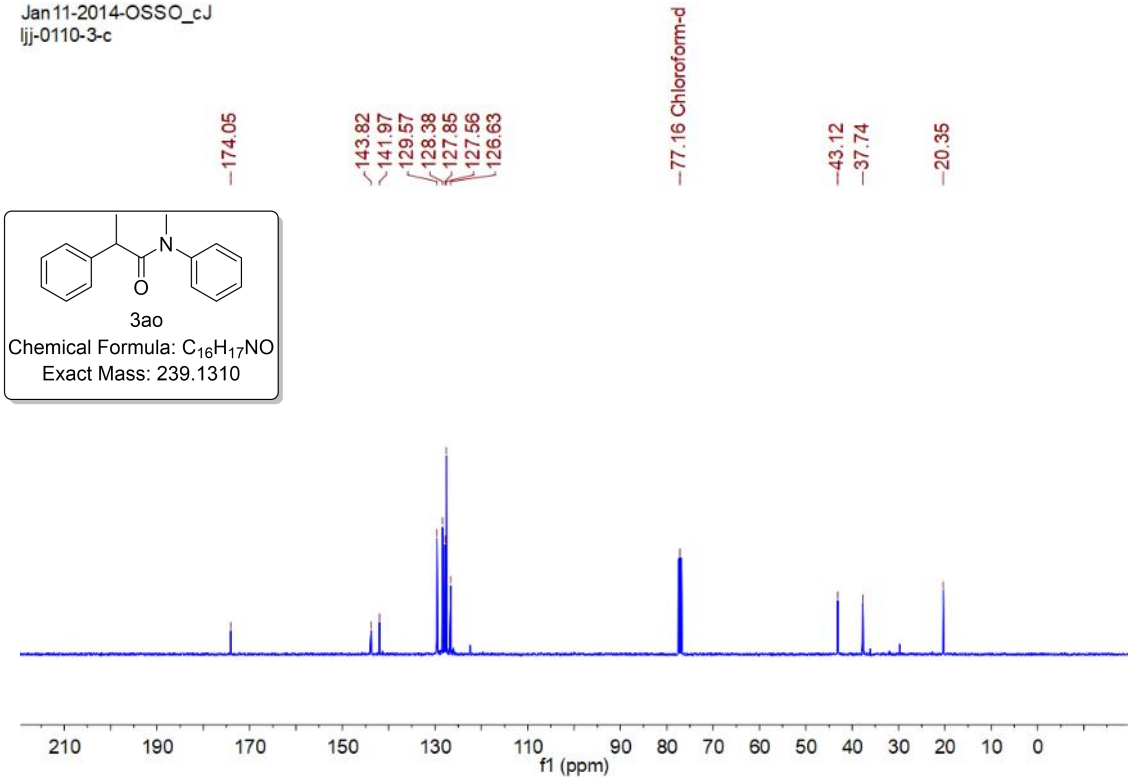

May07-2014-OSSO
ljj-20240506-h
7.31
7.30
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.20
3.77
3.76
3.74
3.72
1.51
1.49
O
HN
3am
Chemical Formula: C19H17NO
Exact Mass: 275.1310
1.00
2.08
1.08
9.16
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

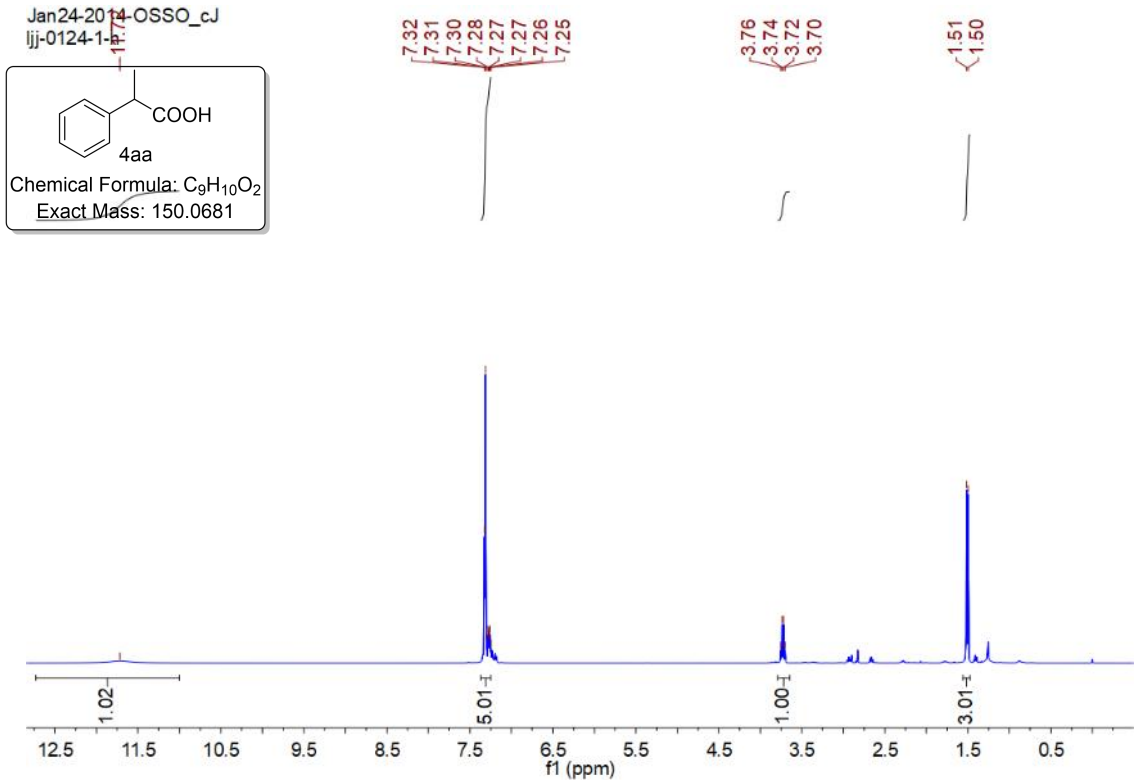

May07-2014-OSSO_cJ
ljj-20240506-c
173.33
141.24
133.92
132.31
129.00
128.42
127.77
127.43
125.99
125.74
125.67
125.43
121.04
120.78
77.16 Chloroform-d
47.44
18.30
O
HN
3am
Chemical Formula: C19H17NO
Exact Mass: 275.1310
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

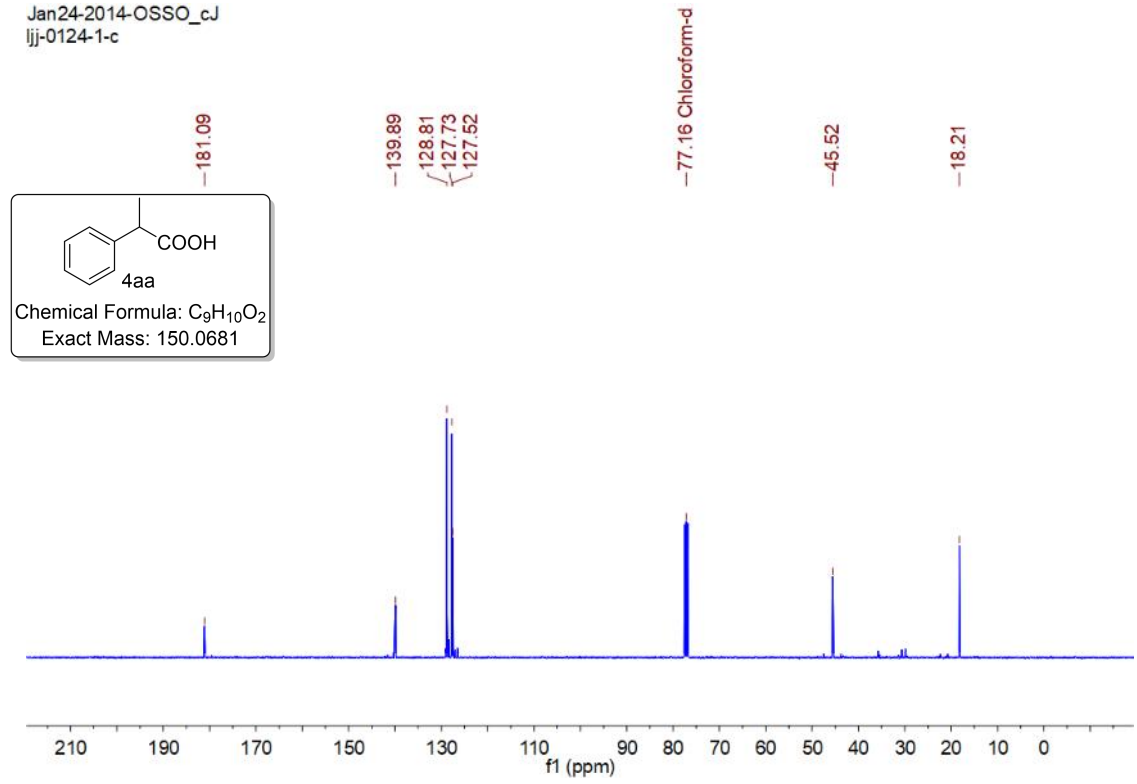

Dec26-2013-OSSO
ljj-1226-1-h
8.35
8.32
7.31
7.31
7.30
7.23
7.22
7.22
7.22
7.18
7.08
6.99
6.98
6.97
6.96
4.08
4.07
4.06
4.04
4.03
4.01
3.85
3.84
3.74
3.72
3.11
3.10
3.09
3.07
3.06
3.05
3.03
1.53
1.51
3an
Chemical Formula: C17H17NO
Exact Mass: 251.1310
0.93
3.96
2.10
0.98
0.99
1.00
0.97
0.96
1.15
1.01
3.00
f1 (ppm)

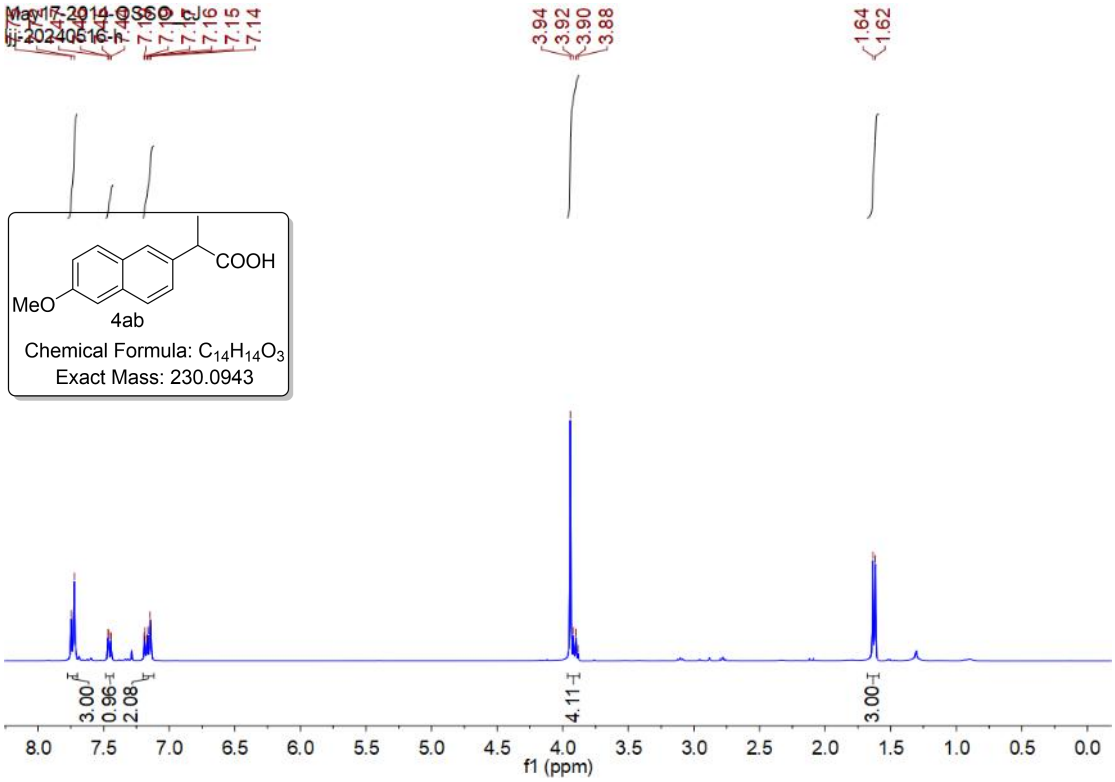

Dec26-2013-OSSO_cJ
ljj-1226-1-c
171.99
143.36
141.13
131.16
129.00
127.55
127.49
127.03
124.50
123.68
117.22
77.16 Chloroform-d
47.68
46.26
28.01
20.56
3an
Chemical Formula: C17H17NO
Exact Mass: 251.1310
f1 (ppm)

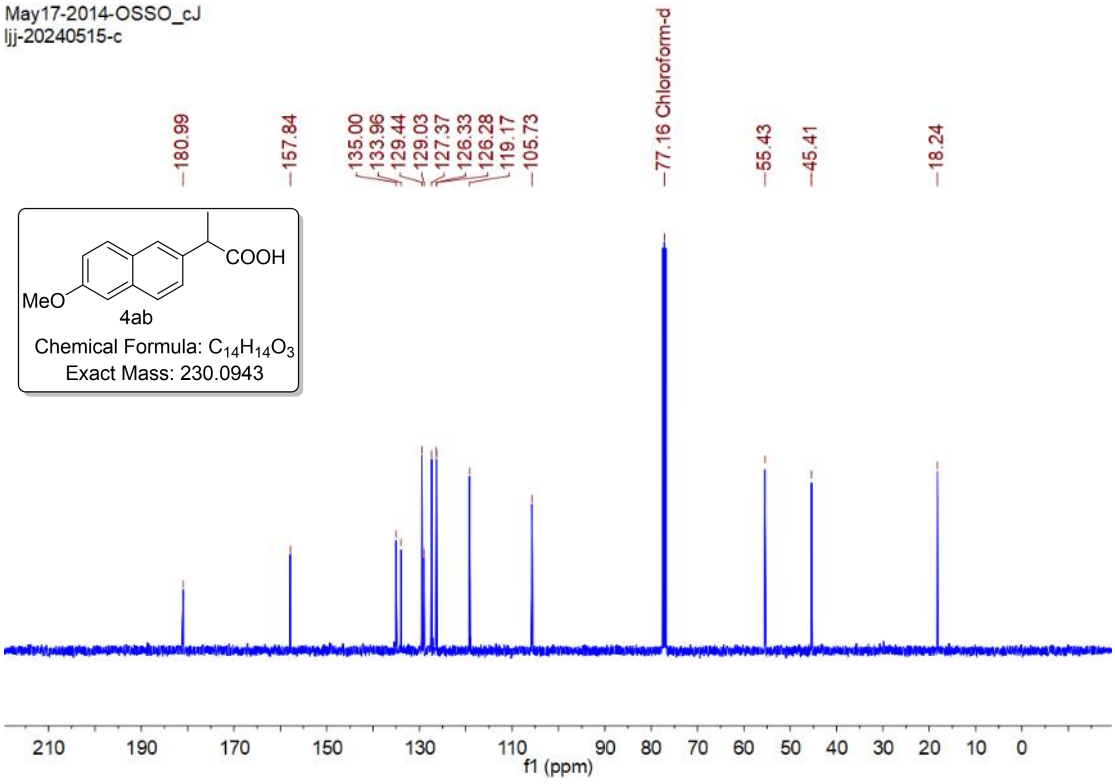

Jan11-2014-OSSO_cJ
ljj-0110-3-h
7.36
7.21
7.19
7.16
7.15
7.06
7.03
7.01
6.98
3.66
3.65
3.63
3.61
3.23
1.40
1.38
3ao
Chemical Formula: C16H17NO
Exact Mass: 239.1310
3.04
3.11
4.08
1.00
3.11
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Jan11-2014-OSSO_cJ
ljj-0110-3-c
174.05
143.82
141.97
129.57
128.38
127.85
127.56
126.63
77.16 Chloroform-d
43.12
37.74
20.35
3ao
Chemical Formula: C16H17NO
Exact Mass: 239.1310
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Jan24-2014-OSSO_cJ
ljj-0124-1-H
COOH
4aa
Chemical Formula: C9H10O2
Exact Mass: 150.0681
7.32
7.31
7.30
7.28
7.27
7.27
7.26
7.25
3.76
3.74
3.72
3.70
1.51
1.50
1.02
5.01
1.00
3.01
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


Jan24-2014-OSSO_cJ
ljj-0124-1-c
181.09
139.89
128.81
127.73
127.52
77.16 Chloroform-d
45.52
18.21
COOH
4aa
Chemical Formula: C9H10O2
Exact Mass: 150.0681
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


May17-2014-OSSO_cJ
ljj-20240516-h
7.17
7.16
7.15
7.14
3.94
3.92
3.90
3.88
1.64
1.62
COOH
MeO
4ab
Chemical Formula: C14H14O3
Exact Mass: 230.0943
3.00
0.96
2.08
4.11
3.00
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
f1 (ppm)


May17-2014-OSSO_cJ
ljj-20240515-c
180.99
157.84
135.00
133.96
129.44
129.03
127.37
126.33
126.28
119.17
105.73
77.16 Chloroform-d
55.43
45.41
18.24
COOH
MeO
4ab
Chemical Formula: C14H14O3
Exact Mass: 230.0943
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

11. References

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