Supporting Information

Photocatalytic anti-Markovnikov hydroalkylation of 2-aryl enamides via 1,2-hydrogen atom transfer of amidyl radicals

Chengli Xiang, Lingli Liu, Changduo Pan,* Jin-Tao Yu*

Email: yujintao@cczu.edu.cn; panchangduo@jsut.edu.cn

Table of Contents

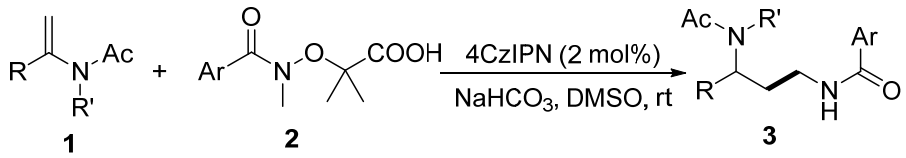
1.General Information

All chemicals used were used as purchased without further purification unless otherwise noted. ^{1}H NMR data were collected at ambient temperature on a 400 MHz NMR spectrometer and ^{13}C NMR on a 101 MHz NMR spectrometer. NMR are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0) as the internal standard. The coupling constants J are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). High-resolution mass spectra (HRMS) were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. Emission intensities were recorded using a FS5 spectrophotometer.

2. General Synthetic Procedures

All enamides **1**[1] and carboxylic acids **2**[2] were prepared according to the previous reports.

General procedure for the synthesis of compounds 3:



To an over-dried Schlenk tube equipped with a magnetic stir bar, enamide **1** (0.2 mmol, 1.0 equiv), carboxylic acid **2** (0.6 mmol, 3.0 equiv), 4CzIPN (2 mol%, 3.2 mg), $NaHCO_3$ (0.4 mmol) and DMSO (2 mL) was added. The tube was evacuated and backfilled with nitrogen (repeated for five times). Then, the solution was stirred at room temperature under 30 W 450-460 nm blue LEDs for 16 h. Then, H_2O was added into the reaction mixture and extracted by ethyl acetate (10 mL×2). The organic layers were dried over anhydrous Na_2SO_4 and condensed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired products **3**.

Figure S1. Photoreactor used in this work (30 W 450-460 nm blue LEDs, λmax = 454 nm).

1 mmol Scale Reaction for 3aa

To an over-dried Schlenk tube equipped with a magnetic stir bar, *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (251.1 mg, 1 mmol), 2-methyl-2-(*N*-methylbenzamidooxy)propanoic acid **2a** (711.3 mg, 3 mmol), 4CzIPN (2 mol%, 16 mg), $NaHCO_3$ (168 mg, 2 mmol) and DMSO (10 mL) was added. The tube was evacuated and backfilled with nitrogen (repeated for five times). The mixture was stirred at room temperature under 30 W 450-460 nm blue LEDs for 16 h. Then, the reaction mixture was washed with H_2O and extracted by ethyl acetate (10 mL×3). Then, the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 2:1) to obtain the product **3aa** (289.5 mg, 75% yield).

The Light Source and the Material of the Irradiation Vessel:

The photochemical reaction was carried out under visible light irradiation by a 30W 450-460 nm blue LED at room temperature. This blue LED was purchased from taobao (link: https://shop152143906.taobao.com/?spm=pc_detail.29232929/evo365560b447259.shop_block.dshopinfo.6cef7dd6EDPjwB). The blue LED's energy peak wavelength is 454 nm, the peak width at half-height is 17.0 nm, and irradiance@20 W is 38.51 mW/cm^2. The reaction vessel is a borosilicate glass tube. The distance between the tube and lamp is about 1.5 cm, and no filter is applied.

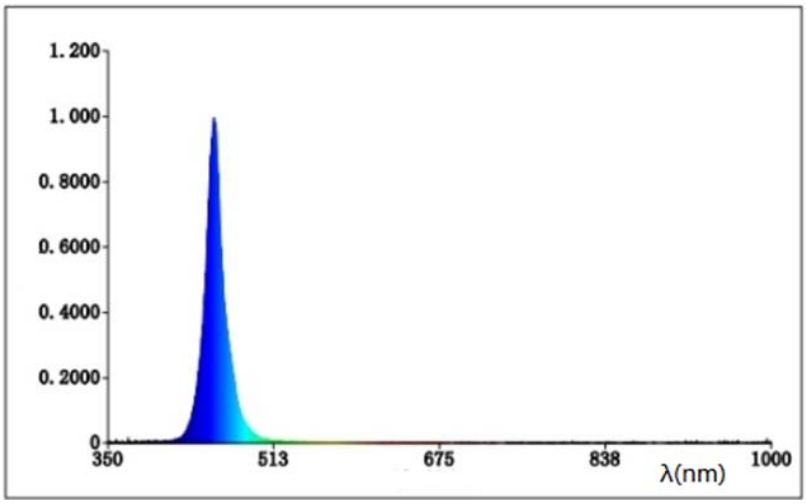
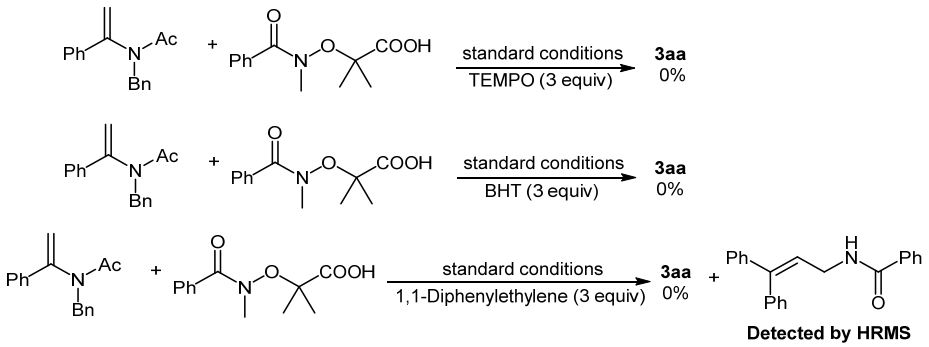


Figure S2. The spectral distribution of 30 W 450-460 nm blue LED

3.Mechanism Studies

3.1 Radical inhibiting and trapping experiments



The mixture of **1a** (0.1 mmol), **2a** (0.3 mmol), 4CzIPN (2 mol%), TMEPO (3 equiv) or BHT (3 equiv) or 1,1-diphenylethylene (3 equiv), and DMSO (1 mL) were added into Schlenk tube equipped with a teflon cap under N_2. The mixture was stirred at room temperature under 30 W 450-460 nm blue LEDs for 16 h. Then, the mixture was analyzed by HRMS.

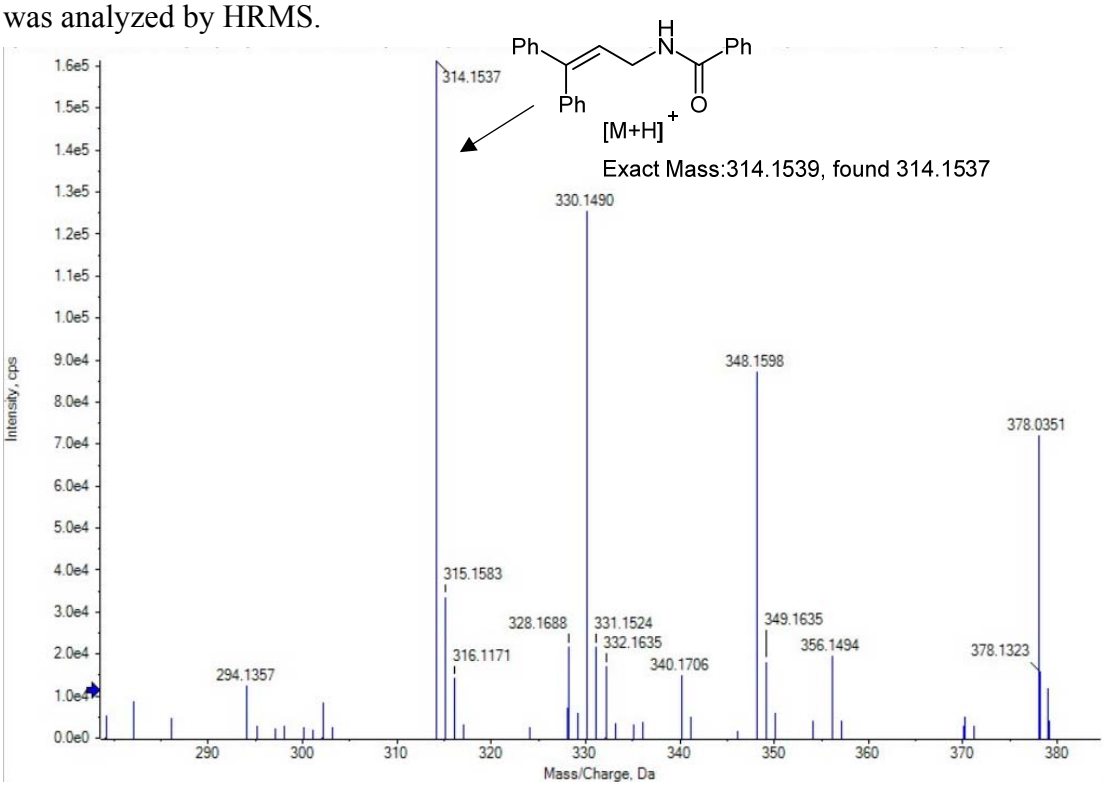
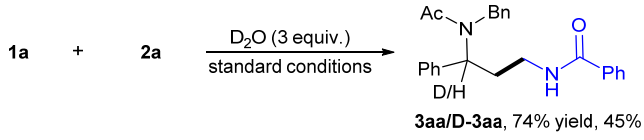


Figure S3. The HRMS spectrum for the radical-trapping experiment with 1,1-diphenylethylene

3.2 Deuterium labeling study



To an over-dried Schlenk tube equipped with a magnetic stir bar, *N*-benzyl-*N*-(1-phenylvinyl)acetamide **1a** (0.1 mmol, 25.1 mg), 2-methyl-2-(*N*-methylbenzamidooxy)propanoic acid **2a** (0.3 mmol, 71.1 mg), 4CzIPN (2 mol%, 1.6 mg), $NaHCO_3$ (0.2 mmol, 16.8 mg), D_2O (0.3 mmol, 60 mg), and DMSO (1 mL)

was added. The tube was evacuated and backfilled with nitrogen (repeated for five times). Then, the solution was stirred at room temperature under 30 W 450-460 nm blue LEDs for 16 h. Then, H_2O was added into the reaction mixture and extracted by ethyl acetate (10 mL×2). The organic layers were dried over anhydrous Na_2SO_4 and condensed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the products **3aa** and **D-3aa** in 74% yield (45% D). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.66-7.64 (m, 1H), 7.49-7.41 (m, 3H), 7.29-7.20 (m, 8H), 6.95-6.92 (m, 2H), 6.12-6.07 (m, 0.55H), 4.43 (d, J = 17.2 Hz, 1H), 4.16 (d, J = 17.2 Hz, 1H), 4.04-3.94 (m, 1H), 3.01-2.90 (m, 1H), 2.18 (s, 3H), 2.15-2.08 (m, 1H), 2.01-1.93 (m, 1H).

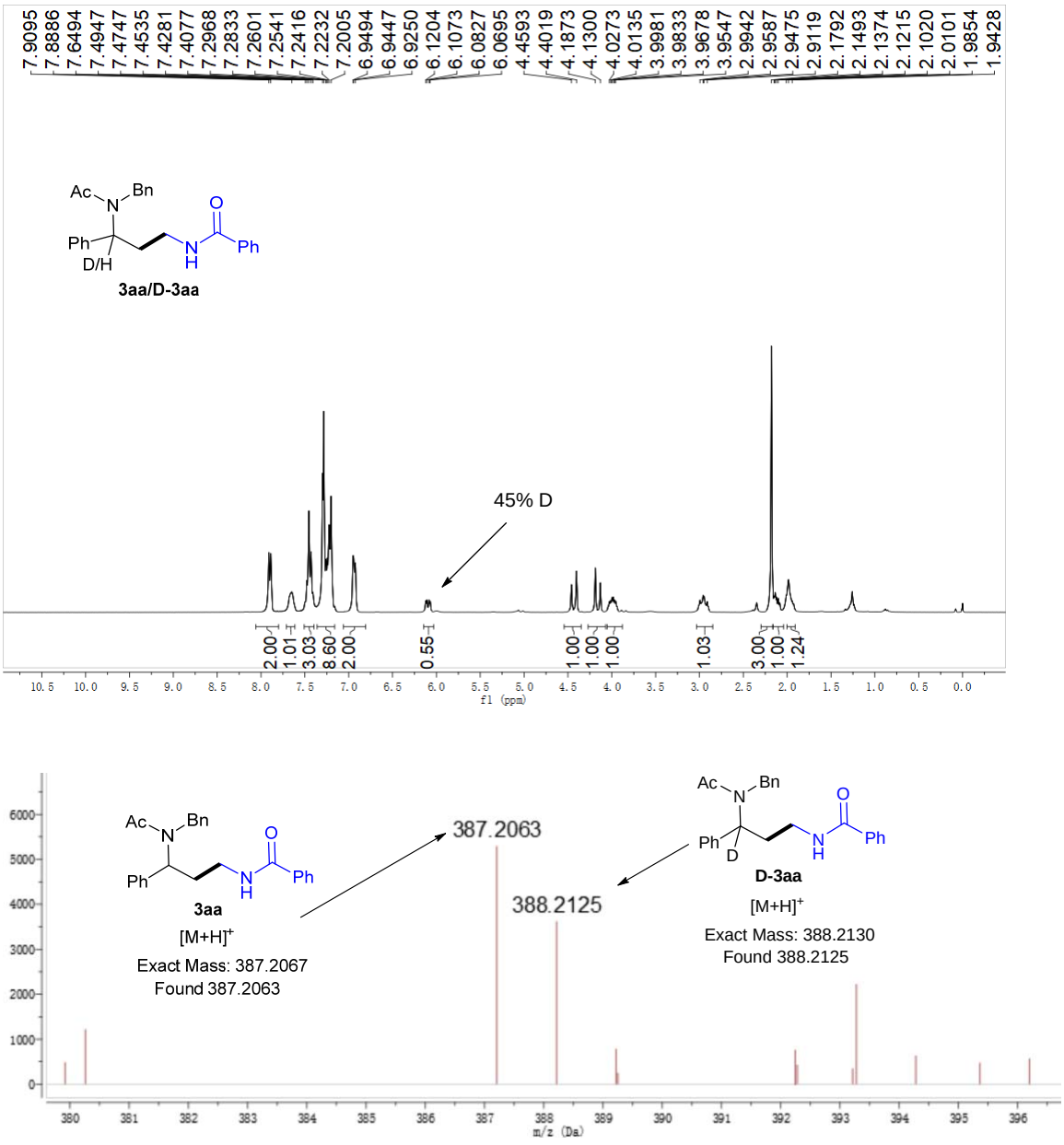


Figure S4. The ^{1}H NMR and HRMS spectrum of **3aa** and **D-3aa**

3.3 Fluorescence Quenching Experiments

Stern-Volmer fluorescence quenching experiments were carried out in DMSO at room temperature with newly prepared 4CzIPN solution and different concentrations of quencher at excitation wavelength of 378 nm. 4CzIPN was filled in DMSO (2.0 mL) into the helicoid quartz test tube, and the initial emission was collected. Compound **1a**, **2a** and **2a-Na** were used as a quencher, respectively to test their quenching effect on the excited 4CzIPN in DMSO at gradient concentrations. (Compound **2a-Na** was prepared via the reaction of compound **2a** with NaOH.)

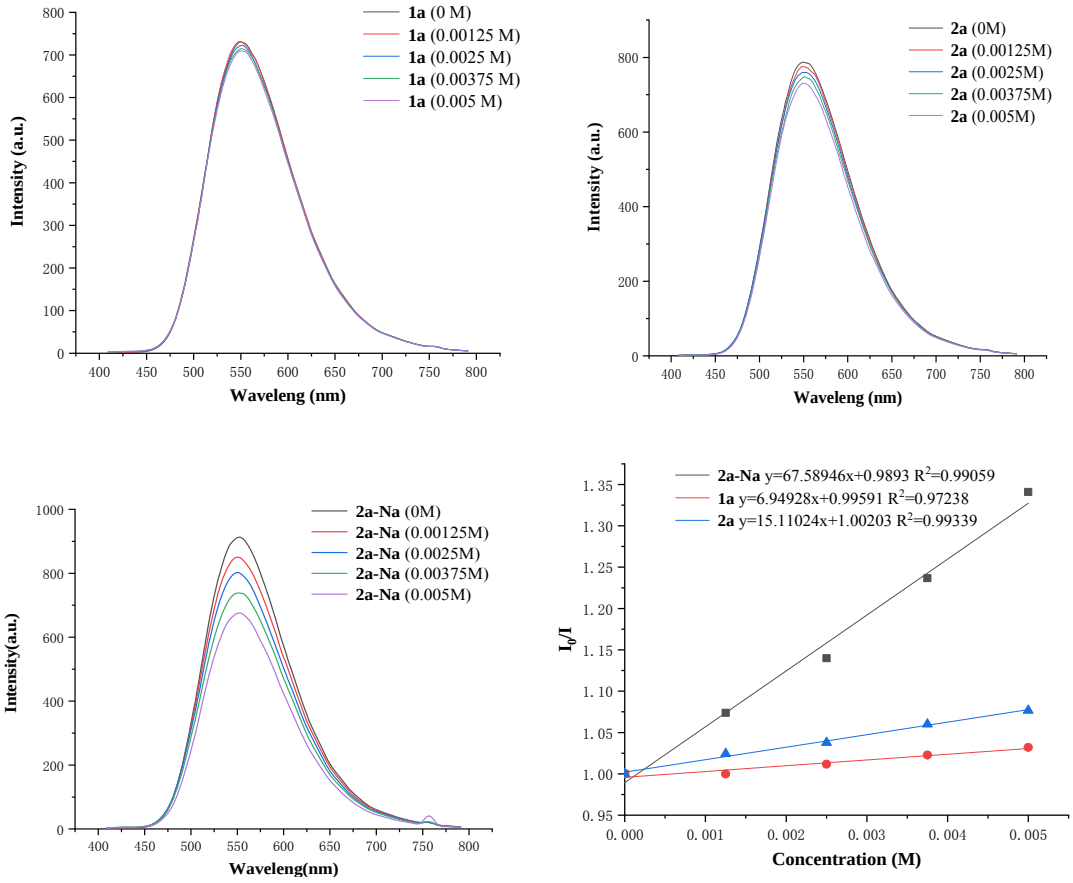
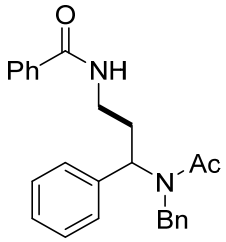


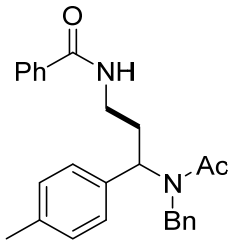
Figure S5. Fluorescence-quenching experiments and the Stern-Volmer plots.

4.Characterization Data for the Products

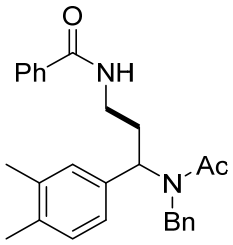


***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)benzamide** (**3aa**, 60.2 mg, 78% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.70-7.67 (m, 1H),

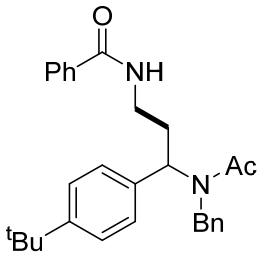
7.49-7.41 (m, 3H), 7.29-7.18 (m, 8H), 6.95-6.92 (m, 2H), 6.11-6.07 (m, 1H), 4.43 (d, J = 17.2 Hz, 1H), 4.16 (d, J = 17.2 Hz, 1H), 4.04-3.93 (m, 1H), 3.01-2.90 (m, 1H), 2.18 (s, 3H), 2.16-2.08 (m, 1H), 2.03-1.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.1, 138.5, 137.2, 134.4, 131.3, 128.68, 128.66, 128.6, 128.5, 128.1, 127.4, 127.1, 126.3, 54.1, 48.2, 36.1, 30.1, 22.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{26}N_2NaO_2$ 409.1886; Found 409.1865.



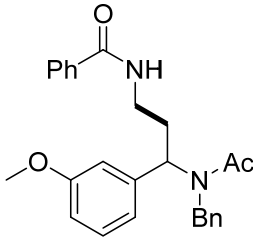
***N*-(3-(*N*-benzylacetamido)-3-(*p*-tolyl)propyl)benzamide** (**3ba**, 62.6 mg, 78% yield) colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 6.6 Hz, 2H), 7.69-7.66 (m, 1H), 7.49-7.40 (m, 3H), 7.24-7.16 (m, 5H), 7.09 (d, J = 7.9 Hz, 2H), 6.95 (d, J = 9.3 Hz, 2H), 6.06-6.02 (m, 1H), 4.41 (d, J = 17.2 Hz, 1H), 4.14 (d, J = 17.1 Hz, 1H), 4.00-3.92 (m, 1H), 2.99-2.91 (m, 1H), 2.29 (s, 3H), 2.17 (s, 3H), 2.12-2.07 (m, 1H), 1.97-1.89 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.1, 137.8, 137.4, 135.5, 134.4, 131.3, 129.3, 128.6, 128.5, 128.4, 127.4, 127.1, 126.4, 54.0, 48.2, 36.1, 30.3, 22.8, 21.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{29}N_2O_2$ 401.2224; Found 401.2224.



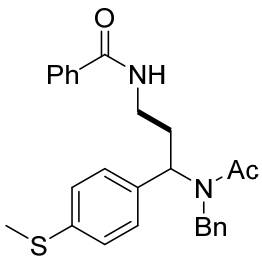
***N*-(3-(*N*-benzylacetamido)-3-(3,4-dimethylphenyl)propyl)benzamide** (**3ca**, 38.4 mg, 46% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 6.8 Hz, 2H), 7.62-7.55 (m, 1H), 7.40-7.31 (m, 3H), 7.16-7.11 (m, 3H), 6.97-6.87 (m, 5H), 5.95-5.91 (m, 1H), 4.31 (d, J = 17.0 Hz, 1H), 4.07 (d, J = 17.2 Hz, 1H), 3.91-3.83 (m, 1H), 2.91-2.82 (m, 1H), 2.14-2.07 (m, 9H), 2.06-1.95 (m, 1H), 1.88-1.80 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.11, 167.04, 137.47, 136.81, 136.39, 135.86, 134.47, 131.24, 130.23, 129.77, 128.56, 128.47, 127.32, 127.05, 126.41, 125.76, 54.03, 48.24, 36.17, 30.29, 22.84, 19.74, 19.39. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{30}N_2NaO_2$ 437.2199; Found 437.2196.



***N*-(3-(*N*-benzylacetamido)-3-(4-(tert-butyl)phenyl)propyl)benzamide** (**3da,** 43.8 mg, 49% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.3 Hz, 2H), 7.61-7.57 (m, 1H), 7.38-7.32 (m, 3H), 7.19 (d, J = 8.2 Hz, 2H), 7.13-7.09 (m, 5H), 6.82 (d, J = 6.8 Hz, 2H), 6.00-5.96 (m, 1H), 4.32 (d, J = 17.2 Hz, 1H), 4.12 (d, J = 17.2 Hz, 1H), 3.91-3.85 (m, 1H), 2.91-2.84 (m, 1H), 2.09 (s, 3H), 2.06-2.01 (m, 1H), 1.93-1.86 (m, 1H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 167.1, 151.1, 137.3, 135.4, 134.5, 131.3, 128.50, 128.49, 128.4, 127.3, 127.0, 126.4, 125.5, 53.6, 48.2, 36.2, 34.5, 31.3, 30.2, 22.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{34}N_2NaO_2$ 465.2512; Found 465.2505.

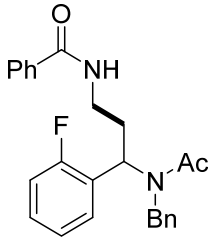


***N*-(3-(*N*-benzylacetamido)-3-(3-methoxyphenyl)propyl)benzamide** (**3ea**, 51.6 mg, 62% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.68-7.61 (m, 1H), 7.50-7.41 (m, 3H), 7.26-7.18 (m, 4H), 6.98-6.96 (m, 2H), 6.88 (dd, J = 7.7, 1.9 Hz, 1H), 6.81 (t, J = 2.1 Hz, 1H), 6.78-6.75 (m, 1H), 6.07-6.03 (m, 1H), 4.43 (d, J = 17.2 Hz, 1H), 4.16 (d, J = 17.2 Hz, 1H), 4.02-3.93 (m, 1H), 3.75 (s, 3H), 2.99-2.89 (m, 1H), 2.19 (s, 3H), 2.15-2.08 (m, 1H), 1.92-1.88 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.1, 159.7, 140.1, 137.3, 134.4, 131.3, 129.7, 128.6, 128.5, 127.4, 127.1, 126.4, 120.9, 114.6, 113.4, 55.3, 54.1, 48.3, 36.1, 30.2, 22.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{28}N_2NaO_3$ 439.1992; Found 439.1998.

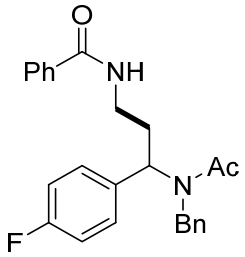


***N*-(3-(*N*-benzylacetamido)-3-(4-(methylthio)phenyl)propyl)benzamide** (**3fa**, 58.6

mg, 67% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.87 (m, 2H), 7.63-7.60 (m, 1H), 7.49-7.41 (m, 3H), 7.26-7.14 (m, 7H), 6.95 (d, J = 6.3 Hz, 2H), 6.05-6.01 (m, 1H), 4.41 (d, J = 17.1 Hz, 1H), 4.15 (d, J = 17.2 Hz, 1H), 4.00-3.93 (m, 1H), 2.98-2.90 (m, 1H), 2.44 (s, 3H), 2.19 (s, 3H), 2.13-2.06 (m, 1H), 1.96-1.88 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2 167.1 138.5, 137.2 135.2, 134.4 131.3, 129.1, 128.7 128.5, 127.5 127.0, 126.5, 126.4 53.8 48.2, 36.1 30.2, 22.8, 15.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{28}N_2NaO_2S$ 455.1764; Found 455.1760.

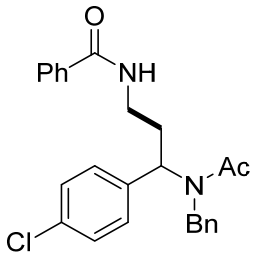


***N*-(3-(*N*-benzylacetamido)-3-(2-fluorophenyl)propyl)benzamide** (**3ga**, 51.6 mg, 64% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.85-7.82 (m, 1H), 7.50-7.42 (m, 3H), 7.30-7.26 (m, 1H), 7.22-7.14 (m, 4H), 7.05-7.01 (m, 1H), 6.97-6.88 (m, 3H), 6.29-6.25 (m, 1H), 4.40 (d, J = 17.3 Hz, 1H), 4.27 (d, J = 17.3 Hz, 1H), 4.11-4.02 (m, 1H), 3.00-2.90 (m, 1H), 2.19 (s, 3H), 2.10-2.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 167.1, 161.3 (d, $J_{C\text{-}F}$ = 247.0 Hz), 136.9, 134.3, 131.3, 130.0 (d, $J_{C\text{-}F}$ = 8.4 Hz), 129.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 128.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 127.3, 127.1, 125.9, 125.7, 125.6, 124.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 115.6 (d, $J_{C\text{-}F}$ = 21.8 Hz), 48.3 (d, $J_{C\text{-}F}$ = 2.8 Hz), 48.2, 35.7, 30.1, 22.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.39. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{25}N_2NaO_2$ 427.1792; Found 427.1786.

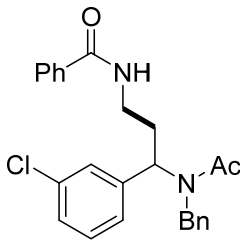


***N*-(3-(*N*-benzylacetamido)-3-(4-fluorophenyl)propyl)benzamide** (**3ha**, 45.4 mg, 56% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.1 Hz, 2H), 7.70-7.67 (m, 1H), 7.48-7.40 (m, 3H), 7.27-7.18 (m, 5H), 6.96-6.90 (m, 4H), 6.07-6.04 (m, 1H), 4.40 (d, J = 17.2 Hz, 1H), 4.19 (d, J = 17.3 Hz, 1H), 3.99-3.91 (m, 1H), 2.99-2.91 (m, 1H), 2.18 (s, 3H), 2.14-2.06 (m, 1H), 2.01-1.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 167.1, 162.2 (d, $J_{C\text{-}F}$ = 245.7 Hz), 137.0, 134. 4 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.3, 131.4, 130.4 (d, $J_{C\text{-}F}$ = 8.1 Hz), 128.7, 128.5, 127.5, 127.0, 126.2, 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 53.3, 48.0, 36.1, 30.4, 22.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.74. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}FN_2O_2$ 405.1973; Found

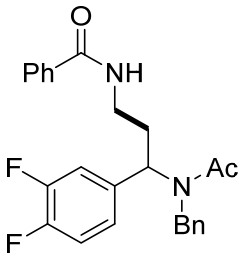
405.1969.



***N*-(3-(*N*-benzylacetamido)-3-(4-chlorophenyl)propyl)benzamide** (**3ia**, 74.8 mg, 89% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 6.9, 4.4 Hz, 2H), 7.61-7.57 (m, 1H), 7.47-7.39 (m, 3H), 7.24-7.19 (m, 7H), 6.94-6.91 (m, 2H), 6.04-6.00 (m, 1H), 4.39 (d, J = 17.3 Hz, 1H), 4.16 (d, J = 17.2 Hz, 1H), 3.96-3.88 (m, 1H), 2.99-2.91 (m, 1H), 2.18 (s, 3H), 2.14-2.05 (m, 1H), 1.98-1.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 167.1, 137.1, 137.0, 134.3, 133.6, 131.4, 130.0, 128.74, 128.70, 128.5, 127.5, 127.0, 126.3, 53.5, 48.2, 36.1, 30.2, 22.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}ClN_2O_2$ 421.1677; Found 421.1669.

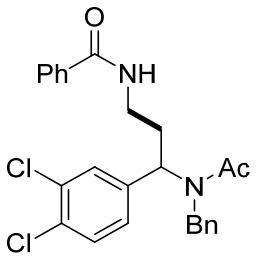


***N*-(3-(*N*-benzylacetamido)-3-(3-chlorophenyl)propyl)benzamide** (**3ja**, 63.2 mg, 76% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.65-7.60 (m, 1H), 7.50-7.41 (m, 3H), 7.27-7.15 (m, 7H), 6.96-6.94 (m, 2H), 6.06-6.02 (m, 1H), 4.41 (d, J = 17.2 Hz, 1H), 4.20 (d, J = 17.2 Hz, 1H), 3.99-3.93 (m, 1H), 2.98-2.90 (m, 1H), 2.21 (s, 3H), 2.15-2.04 (m, 1H), 2.00-1.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.1, 140.6, 136.8, 134.50 134.3, 131.4, 129.8, 129.0, 128.7, 128.5, 128.2, 127.5, 127.0, 126.7, 126.3, 53.6, 48.3, 36.0, 30.0, 22.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{25}ClN_2NaO_2$ 443.1497; Found 443.1502.

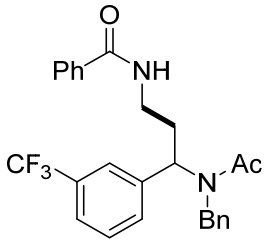


***N*-(3-(*N*-benzylacetamido)-3-(3,4-difluorophenyl)propyl)benzamide** (**3ka**, 74.2 mg, 88% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.4 Hz, 2H), 7.57-7.54 (m, 1H), 7.49-7.40 (m, 3H), 7.24-7.19 (m, 3H), 7.10-6.99 (m, 3H), 6.92 (d,

J = 7.0 Hz, 2H), 6.01-5.98 (m, 1H), 4.39 (d, J = 17.2 Hz, 1H), 4.22 (d, J = 17.3 Hz, 1H), 3.96-3.88 (m, 1H), 2.98-2.90 (m, 1H), 2.19 (s, 3H), 2.13-2.03 (m, 1H), 1.99-1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 167.2, 150.1 (dd, $J_{C\text{-}F}$ = 250.1, 12.7 Hz), 149.8 (dd, $J_{C\text{-}F}$ = 250.4, 12.5 Hz), 136.7, 135.7 (t, $J_{C\text{-}F}$ = 4.4 Hz), 134.2, 131.4, 128.7, 128.5, 127.6, 127.0, 126.2, 124.7 (dd, $J_{C\text{-}F}$ = 6.6, 3.6 Hz), 117.8 (d, $J_{C\text{-}F}$ = 17.5 Hz), 117.3 (d, $J_{C\text{-}F}$ = 17.3 Hz), 53.2, 48.2, 36.0, 30.2, 22.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -136.96 (d, J = 21.2 Hz, 1F), -138.29 (d, J = 21.4 Hz, 1F). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{25}N_2O_2$ 423.1879; Found 423.1877.

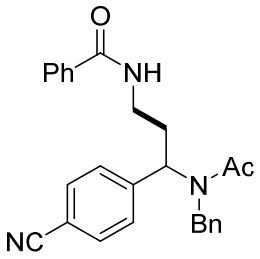


***N*-(3-(*N*-benzylacetamido)-3-(3,4-dichlorophenyl)propyl)benzamide** (**3la**, 64.8 mg, 71% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.85 (m, 2H), 7.52-7.41 (m, 4H), 7.33 (d, J = 2.1 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.26-7.19 (m, 3H), 7.11-7.08 (m, 1H), 6.96-6.93 (m, 2H), 6.01-5.97 (m, 1H), 4.39 (d, J = 17.3 Hz, 1H), 4.22 (d, J = 17.3 Hz, 1H), 3.98-3.90 (m, 1H), 2.98-2.89 (m, 1H), 2.22 (s, 3H), 2.14-2.06 (m, 1H), 1.96-1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 167.2, 138.9, 136.6, 134.2, 132.7, 132.1, 131.5, 130.8, 130.4, 128.7, 128.6, 127.8, 127.6, 127.0, 126.2, 53.2, 48.4, 36.0, 30.0, 22.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{24}Cl_2N_2NaO_2$ 477.1107; Found 477.1097.

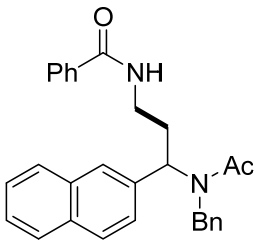


***N*-(3-(*N*-benzylacetamido)-3-(3-(trifluoromethyl)phenyl)propyl)benzamide** (**3ma**, 65.8 mg, 72% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.2 Hz, 2H), 7.64-7.61 (m, 1H), 7.50-7.40 (m, 6H), 7.33 (t, J = 7.7 Hz, 1H), 7.20-7.14 (m, 3H), 6.88 (d, J = 6.6 Hz, 2H), 6.13-6.10 (m, 1H), 4.39 (d, J = 17.2 Hz, 1H), 4.24 (d, J = 17.3 Hz, 1H), 4.01-3.94 (m, 1H), 3.00-2.92 (m, 1H), 2.22 (s, 3H), 2.16-2.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.2, 139.5, 136.5, 134.2, 131.9, 131.4, 130.9, 129.0, 128.6, 128.5, 127.5, 127.0, 126.6 (q, $J_{C\text{-}F}$ = 274.2 Hz), 126.1, 125.8 (q, $J_{C\text{-}F}$ = 2.7 Hz), 124.8 (q, $J_{C\text{-}F}$ = 3.5 Hz), 53.6, 48.2, 36.0, 29.9, 22.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.67. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{25}F_3N_2NaO_2S$ 477.1760;

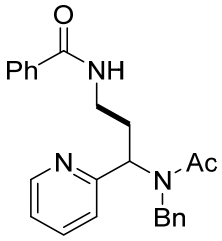
Found 477.1750.



***N*-(3-(*N*-benzylacetamido)-3-(4-cyanophenyl)propyl)benzamide** (**3na**, 59.2 mg, 72% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.0 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.49-7.37 (m, 6H), 7.24-7.19 (m, 3H), 6.91-6.89 (m, 2H), 6.09-6.05 (m, 1H), 4.40 (d, J = 17.3 Hz, 1H), 4.23 (d, J = 17.3 Hz, 1H), 3.98-3.90 (m, 1H), 3.01-2.93 (m, 1H), 2.22 (s, 3H), 2.19-2.11 (m, 1H), 2.07-2.01 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.2, 144.0, 136.5, 134.1, 132.3, 131.5, 129.4, 128.7, 128.6, 127.7, 127.0, 126.2, 118.4, 111.8, 53.7, 48.4, 36.1, 29.8, 22.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}N_3O_2$ 412.2020; Found 412.2017.

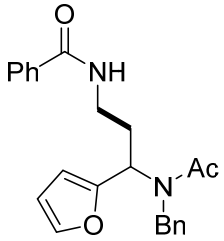


***N*-(3-(*N*-benzylacetamido)-3-(naphthalen-2-yl)propyl)benzamide** (**3oa**, 60.2 mg, 69% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.80-7.72 (m, 5H), 7.50-7.36 (m, 6H), 7.22-7.16 (m, 3H), 6.98-6.95 (m, 2H), 6.26-6.22 (m, 1H), 4.44 (d, J = 17.1 Hz, 1H), 4.13 (d, J = 17.1 Hz, 1H), 4.07-4.00 (m, 1H), 3.06-2.98 (m, 1H), 2.33-2.26 (m, 1H), 2.23 (s, 3H), 2.08-2.03 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 167.1, 137.3, 136.1, 134.4, 133.1, 132.9, 131.3, 128.7, 128.53, 128.50, 128.0, 127.6, 127.5, 127.2, 127.1, 126.8, 126.4, 126.3, 54.3, 48.4, 36.1, 30.2, 22.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{29}N_2O_2$ 437.2224; Found 437.2223.

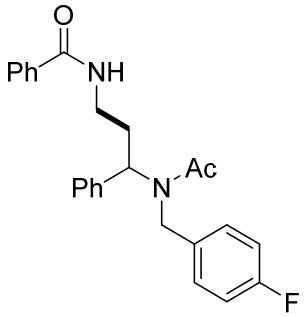


***N*-(3-(*N*-benzylacetamido)-3-(pyridin-2-yl)propyl)benzamide** (**3pa**, 51.8 mg, 67% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 3.9 Hz, 1H), 7.90-7.87 (m, 2H), 7.55-7.49 (m, 2H), 7.48-7.41 (m, 3H), 7.30 (d, J = 7.8 Hz, 1H), 7.19-7.11 (m,

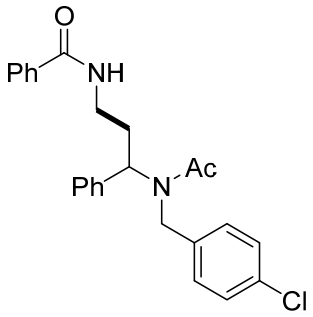
3H), 7.06-7.03 (m, 1H), 6.85 (d, J = 6.4 Hz, 2H), 6.11-6.07 (m, 1H), 4.75 (d, J = 17.4 Hz, 1H), 4.45 (d, J = 17.4 Hz, 1H), 4.03-3.95 (m, 1H), 3.03-2.95 (m, 1H), 2.33-2.23 (m, 2H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 167.0, 157.5, 149.1, 137.3, 136.5, 134.5, 131.3, 128.5, 128.4, 127.1, 126.9, 125.8, 124.8, 122.9, 55.48, 47.8, 36.3, 30.1, 22.5. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{25}N_3NaO_2$ 410.1839; Found 410.1843.



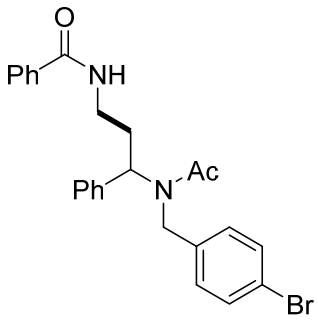
***N*-(3-(*N*-benzylacetamido)-3-(furan-2-yl)propyl)benzamide** (**3qa**, 49.4 mg, 63% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 7.76-7.73 (m, 1H), 7.41 (d, J = 8.6 Hz, 2H), 7.30-7.18 (m, 7H), 6.94 (d, J = 6.7 Hz, 2H), 6.09-6.05 (m, 1H), 4.43 (d, J = 17.1 Hz, 1H), 4.14 (d, J = 17.2 Hz, 1H), 4.04-3.97 (m, 1H), 2.95-2.87 (m, 1H), 2.20 (s, 3H), 2.16-2.10 (m, 1H), 1.98-1.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 165.9, 138.4, 137.5, 137.1, 132.8, 128.7, 128.69, 128.67, 128.65, 128.5, 128.2, 127.5, 126.4, 54.1, 48.2, 36.0, 30.0, 22.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_3$ 377.1860; Found 377.1863.



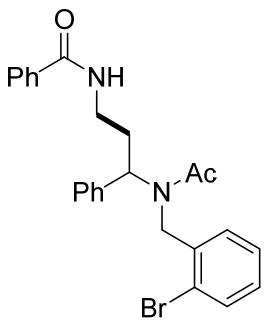
***N*-(3-(*N*-(4-fluorobenzyl)acetamido)-3-phenylpropyl)benzamide** (**3ra**, 54.2 mg, 68% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 6.8 Hz, 2H), 7.64-7.62 (m, 1H), 7.50-7.41 (m, 3H), 7.29-7.21 (m, 5H), 6.91-6.83 (m, 4H), 6.11-6.07 (m, 1H), 4.39 (d, J = 17.1 Hz, 1H), 4.18 (d, J = 17.1 Hz, 1H), 4.03-3.95 (m, 1H), 2.98-2.89 (m, 1H), 2.20-2.10 (m, 4H), 2.04-1.96 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 167.1, 163.1, 160.6, 138.4, 134.4, 132.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 131.3, 128.7, 128.5, 128.2, 127.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 127.0, 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 54.1, 47.4, 36.1, 30.2, 22.7. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.94. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}FN_2O_2$ 405.1973; Found 405.1972.



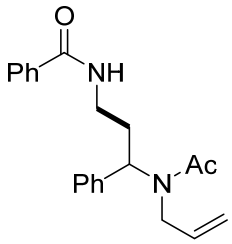
***N*-(3-(*N*-(4-chlorobenzyl)acetamido)-3-phenylpropyl)benzamide** (**3sa**, 58.0 mg, 69% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.62-7.59 (m, 1H), 7.48-7.41 (m, 3H), 7.29-7.21 (m, 5H), 7.18-7.15 (m, 2H), 6.81 (d, J = 8.3 Hz, 2H), 6.11-6.07 (m, 1H), 4.39 (d, J = 17.3 Hz, 1H), 4.19 (d, J = 17.4 Hz, 1H), 4.03-3.95 (m, 1H), 2.99-2.90 (m, 1H), 2.19-2.14 (m, 1H), 2.13 (s, 3H), 2.04-1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 167.1, 138.3, 135.7, 134.4, 133.1, 131.4, 128.7, 128.6, 128.5, 128.2, 127.6, 127.0, 54.1, 47.4, 36.2, 30.2, 22.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{26}ClN_2NaO_2$ 443.1497; Found 443.1498.



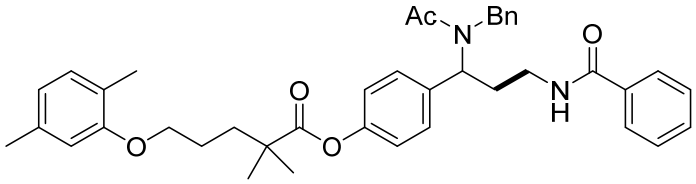
***N*-(3-(*N*-(4-bromobenzyl)acetamido)-3-phenylpropyl)benzamide** (**3ta**, 70.4 mg, 76% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 6.8 Hz, 2H), 7.62-7.59 (m, 1H), 7.48-7.41 (m, 3H), 7.32-7.20 (m, 7H), 6.75 (d, J = 8.2 Hz, 2H), 6.11-6.07 (m, 1H), 4.36 (d, J = 17.4 Hz, 1H), 4.17 (d, J = 17.4 Hz, 1H), 4.02-3.94 (m, 1H), 2.99-2.91 (m, 1H), 2.19-2.14 (m, 1H), 2.12 (s, 3H), 2.04-1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 167.1, 138.3, 136.3, 134.3, 131.7, 131.4, 128.7, 128.6, 128.5, 128.2, 127.9, 127.0, 121.1, 54.1, 47.5, 36.2, 30.2, 22.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{25}BrN_2NaO_2$ 487.0992; Found 487.0983.



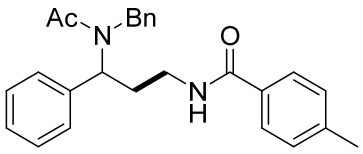
***N*-(3-(*N*-(2-bromobenzyl)acetamido)-3-phenylpropyl)benzamide** (**3ua**, 58.0 mg, 62% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.60-7.57 (m, 1H), 7.48-7.38 (m, 4H), 7.29-7.27 (m, 2H), 7.20-7.16 (m, 2H), 7.13-7.09 (m, 1H), 7.06-7.02 (m, 1H), 7.00-6.95 (m, 1H), 6.77-6.75 (m, 1H), 6.09 (t, J = 7.7 Hz, 1H), 4.46-4.36 (m, 2H), 4.08-4.00 (m, 1H), 3.05-2.97 (m, 1H), 2.21-2.15 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.1, 137.7, 135.3, 134.4, 132.6, 131.4, 128.8, 128.6, 128.5, 128.2, 127.3, 127.1, 127.0, 121.9, 54.2, 48.1, 36.2, 30.4, 22.3. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{25}BrN_2NaO_2$ 487.0992; Found 487.0989.



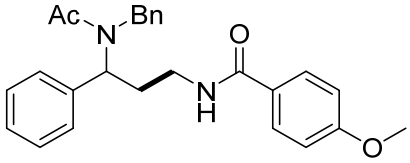
***N*-(3-(*N*-allylacetamido)-3-phenylpropyl)benzamide** (**3va**, 45.4 mg, 67% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.90 (m, 2H), 7.78-7.75 (m, 1H), 7.49-7.41 (m, 3H), 7.35-7.27 (m, 5H), 6.06-6.02 (m, 1H), 5.41-5.31 (m, 1H), 5.05-4.98 (m, 2H), 4.22-4.14 (m, 1H), 3.71-3.65 (m, 1H), 3.61-3.54 (m, 1H), 2.90-2.81 (m, 1H), 2.28-2.22 (m, 1H), 2.21 (s, 3H), 2.14-2.06 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 167.0, 138.8, 134.3, 134.0, 131.3, 128.7, 128.5, 128.3, 128.0, 127.1, 117.8, 53.3, 47.2, 35.8, 29.5, 22.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}N_2O_2$ 337.1911; Found 337.1903.



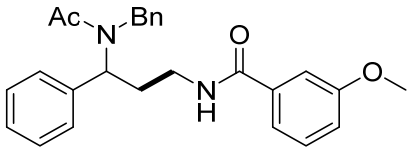
4-(3-Benzamido-1-(*N*-benzylacetamido)propyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**3wa**, 72.0 mg, 57% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.63-7.60 (m, 1H), 7.50-7.37 (m, 5H), 7.28-7.17 (m, 5H), 7.00-6.98 (m, 3H), 6.67-6.62 (m, 2H), 6.09-6.06 (m, 1H), 4.43 (d, J = 17.2 Hz, 1H), 4.12 (d, J = 17.0 Hz, 1H), 3.99-3.93 (m, 3H), 2.99-2.90 (m, 1H), 2.30 (s, 3H), 2.20 (s, 3H), 2.17-2.16 (m, 3H), 2.13-2.07 (m, 1H), 1.96-1.83 (m, 6H), 1.36 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 173.2, 167.1, 156.8, 150.7, 137.2, 136.5, 136.1, 134.4, 131.3, 130.4, 129.6, 128.8, 128.5, 127.6, 127.1, 126.4, 123.6, 121.8, 120.7, 111.9, 67.7, 53.7, 48.3, 42.5, 37.1, 36.1, 30.3, 25.3, 25.2, 22.9, 21.5, 15.9. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{40}H_{46}N_2NaO_5$ 657.3299; Found 657.3304.



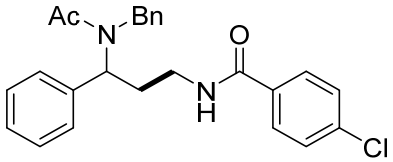
***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-4-methylbenzamide** (**3ab**, 58.2 mg, 73% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.64-7.61 (m, 1H), 7.29-7.18 (m, 10H), 6.93 (d, J = 6.8 Hz, 2H), 6.10-6.07 (m, 1H), 4.42 (d, J = 17.1 Hz, 1H), 4.16 (d, J = 17.2 Hz, 1H), 4.01-3.93 (m, 1H), 2.98-2.90 (m, 1H), 2.37 (s, 3H), 2.17 (s, 3H), 2.14-2.08 (m, 1H), 1.99-1.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 167.0, 141.6, 138.6, 137.2, 131.6, 129.2, 128.7, 128.64, 128.62, 128.1, 127.4, 127.1, 126.3, 54.1, 48.2, 36.0, 30.2, 22.8, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{29}N_2O_2$ 401.2224; Found 401.2227.



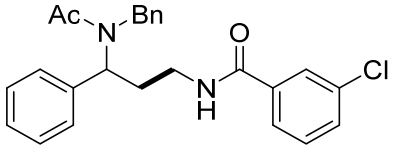
***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-4-methoxybenzamide** (**3ac**, 48.4 mg, 58% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.9 Hz, 2H), 7.61-7.56 (m, 1H), 7.29-7.25 (m, 4H), 7.24-7.18 (m, 4H), 6.93 (d, J = 8.7 Hz, 4H), 6.11-6.07 (m, 1H), 4.42 (d, J = 17.2 Hz, 1H), 4.15 (d, J = 17.2 Hz, 1H), 4.02-3.94 (m, 1H), 3.83 (s, 3H), 2.96-2.88 (m, 1H), 2.17 (s, 3H), 2.15-2.07 (m, 1H), 2.00-1.94 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 166.6, 162.0, 138.6, 137.2, 128.8, 128.7, 128.64, 128.61, 128.1, 127.4, 126.8, 126.3, 113.7, 55.4, 54.1, 48.2, 36.0, 30.1, 22.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{29}N_2O_3$ 417.2173; Found 417.2167.



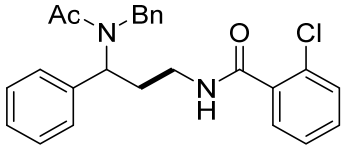
***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-3-methoxybenzamide** (**3ad**, 61.2 mg, 73% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 1H), 7.49-7.43 (m, 2H), 7.34 (d, J = 8.0 Hz, 1H), 7.29-7.26 (m, 4H), 7.24-7.18 (m, 4H), 7.03-7.00 (m, 1H), 6.94-6.92 (m, 2H), 6.10-6.07 (m, 1H), 4.43 (d, J = 17.2 Hz, 1H), 4.16 (d, J = 17.2 Hz, 1H), 4.00-3.92 (m, 1H), 3.84 (s, 3H), 3.00-2.92 (m, 1H), 2.17 (s, 3H), 2.14-2.09 (m, 1H), 2.01-1.93 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 166.9, 159.8, 138.6, 137.2, 135.9, 129.5, 128.7, 128.64, 128.61, 128.0, 127.4, 126.3, 118.9, 117.8, 112.2, 55.4, 54.1, 48.2, 36.2, 30.1, 22.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{29}N_2O_3$ 417.2173; Found 417.2177.



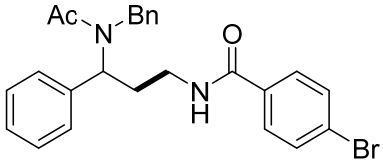
***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-4-chlorobenzamide** (**3ae**, 53.6 mg, 64% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 7.76-7.73 (m, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.30-7.18 (m, 8H), 6.94 (d, J = 6.2 Hz, 2H), 6.09-6.05 (m, 1H), 4.43 (d, J = 17.2 Hz, 1H), 4.14 (d, J = 17.2 Hz, 1H), 4.04-3.96 (m, 1H), 2.94-2.86 (m, 1H), 2.20 (s, 3H), 2.16-2.08 (m, 1H), 1.98-1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 165.9, 138.4, 137.5, 137.1, 132.8, 128.7, 128.69, 128.67, 128.65, 128.5, 128.2, 127.5, 126.4, 54.1, 48.2, 36.0, 30.0, 22.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{25}ClN_2NaO_2$ 443.1497; Found 443.1501.



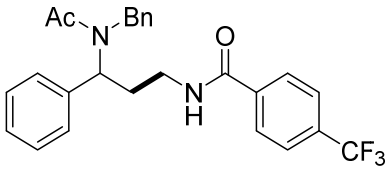
***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-3-chlorobenzamide** (**3af**, 52.2 mg, 62% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, J = 1.9 Hz, 1H), 7.77-7.72 (m, 2H), 7.45-7.42 (m, 1H), 7.38 (d, J = 7.8 Hz, 1H), 7.32-7.27 (m, 4H), 7.26-7.17 (m, 4H), 6.95-6.92 (m, 2H), 6.08-6.04 (m, 1H), 4.43 (d, J = 17.1 Hz, 1H), 4.15 (d, J = 17.2 Hz, 1H), 3.99-3.93 (m, 1H), 2.98-2.89 (m, 1H), 2.19 (s, 3H), 2.16-2.08 (m, 1H), 1.97-1.93 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 165.7, 138.4, 137.1, 136.2, 134.7, 131.3, 129.8, 128.69, 128.67, 128.65, 128.2, 127.7, 127.5, 126.3, 124.9, 54.1, 48.2, 36.2, 30.1, 22.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}ClN_2O_2$ 421.1677; Found 421.1676.



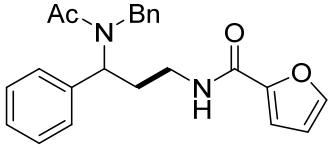
***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-2-chlorobenzamide** (**3ag**, 44.6 mg, 53% yield) , colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 1H), 7.38-7.36 (m, 2H), 7.33-7.26 (m, 6H), 7.22-7.17 (m, 3H), 7.14-7.11 (m, 1H), 6.93 (d, J = 6.5 Hz, 2H), 6.11-6.07 (m, 1H), 4.42 (d, J = 17.3 Hz, 1H), 4.19 (d, J = 17.3 Hz, 1H), 3.90-3.81 (m, 1H), 3.09-3.00 (m, 1H), 2.24-2.17 (m, 1H), 2.12 (s, 3H), 2.04-1.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 166.8, 138.6, 137.4, 135.7, 131.0, 130.8, 130.2, 129.6, 128.7, 128.6, 128.1, 127.3, 127.0, 126.3, 54.2, 48.2, 36.6, 30.4, 22.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{26}ClN_2O_2$ 421.1677; Found 421.1680.



***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-4-bromobenzamide** (**3ah**, 51.8 mg, 56% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 3H), 7.55 (d, J = 8.3 Hz, 2H), 7.31-7.17 (m, 8H) , 6.93 (d, J = 6.5 Hz, 2H), 6.08-6.04 (m, 1H), 4.42 (d, J = 17.2 Hz, 1H), 4.13 (d, J = 17.1 Hz, 1H), 4.02-3.94 (m, 1H), 2.94-2.86 (m, 1H), 2.19 (s, 3H), 2.11-2.07 (m, 1H), 1.98-1.89 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 166.0, 138.4, 137.1, 133.3, 131.7, 128.8, 128.7, 128.6, 128.2, 127.5, 126.4, 126.0, 54.1, 48.2, 36.0, 30.0, 22.8. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{25}BrN_2NaO_2$ 487.0992; Found 487.0988.

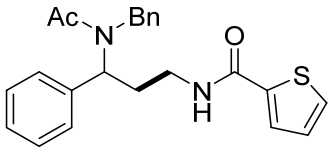


***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)-4-(trifluoromethyl)benzamide** (**3ai**, 30.0 mg, 33% yield) , colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.0 Hz, 2H), 7.96-7.92 (m, 1H), 7.70 (d, J = 7.9 Hz, 2H), 7.33-7.20 (m, 8H), 6.95 (d, J = 7.0 Hz, 2H), 6.07 (d, J = 12.4 Hz, 1H), 4.44 (d, J = 17.1 Hz, 1H), 4.14 (d, J = 17.0 Hz, 1H), 4.06-3.98 (m, 1H), 2.93 (t, J = 12.7 Hz, 1H), 2.21 (s, 3H), 2.16-2.09 (m, 1H), 1.99-1.92 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 165.7, 138.3, 137.7, 137.1, 132.9 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.7, 128.6, 128.2, 127.6, 127.5, 126.4, 126.3 (q, $J_{C\text{-}F}$ = 276.5 Hz), 125.5 (q, $J_{C\text{-}F}$ = 3.6 Hz), 54.1, 48.2, 36.1, 30.0, 22.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.86. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}F_3N_2O_2$ 455.1941; Found 455.1938.



***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)furan-2-carboxamide** (**3aj**, 51.4 mg, 67% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.47 (m, 1H), 7.40-7.36 (m, 1H), 7.29-7.26 (m, 4H), 7.25-7.18 (m, 4H), 7.07 (d, J = 3.5 Hz, 1H), 6.93 (d, J = 6.7 Hz, 2H), 6.46-6.45 (m, 1H), 6.08-6.05 (m, 1H), 4.42 (d, J = 17.2 Hz, 1H), 4.16 (d, J = 17.3 Hz, 1H), 3.88-3.80 (m, 1H), 3.04-2.96 (m, 1H), 2.16 (s, 3H), 2.13-2.02 (m, 1H), 2.02-1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 158.5, 148.1, 144.1, 138.6, 137.3, 128.7, 128.63, 128.61, 128.0, 127.4, 126.3, 113.8, 111.8, 54.1, 48.2,

35.6, 30.4, 22.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_3$ 377.1860; Found 377.1859.



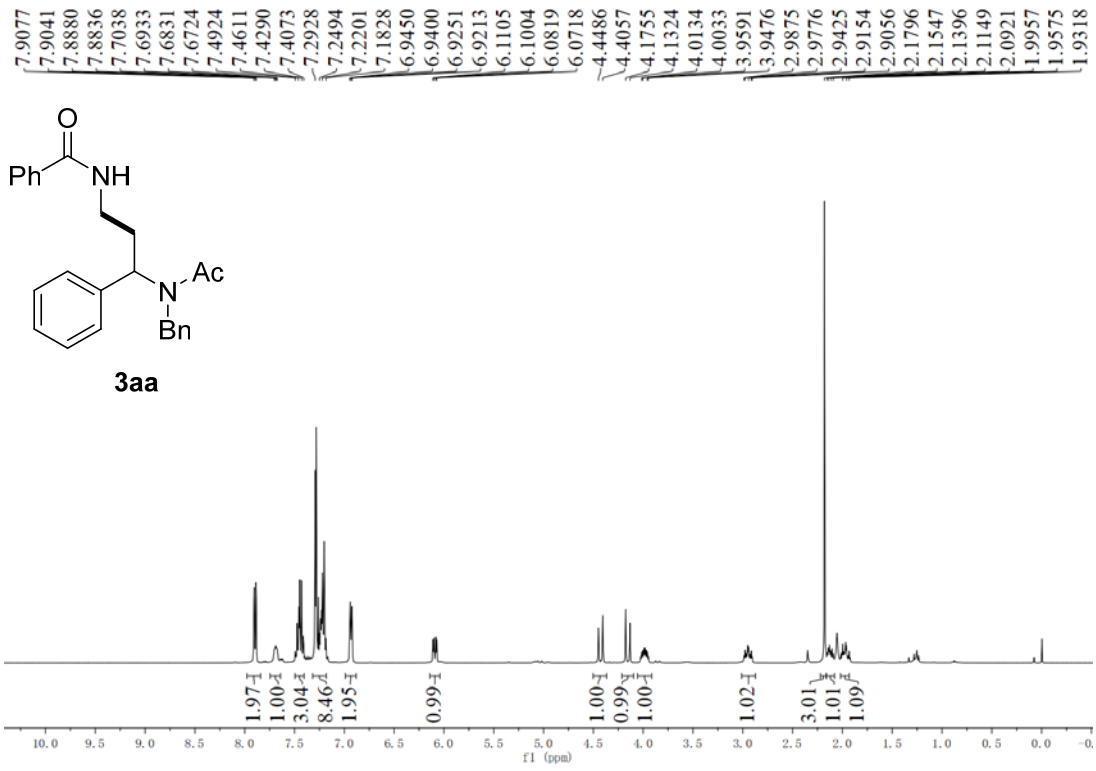
***N*-(3-(*N*-benzylacetamido)-3-phenylpropyl)thiophene-2-carboxamide** (**3ak**, 27.0 mg, 34% yield), colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 3.6 Hz, 1H), 7.59-7.56 (m, 1H), 7.44 (d, J = 5.0 Hz, 1H), 7.29-7.19 (m, 8H), 7.07 (t, J = 4.6 Hz, 1H), 6.93 (d, J = 6.4 Hz, 2H), 6.10-6.06 (m, 1H), 4.43 (d, J = 17.1 Hz, 1H), 4.14 (d, J = 17.2 Hz, 1H), 3.98-3.90 (m, 1H), 2.96-2.88 (m, 1H), 2.19 (s, 3H), 2.16-2.07 (m, 1H), 1.99-1.90 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 161.8, 139.6, 138.5, 137.2, 129.9, 128.7, 128.6, 128.1, 127.9, 127.7, 127.4, 126.3, 54.1, 48.2, 36.0, 30.1, 22.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{25}N_2O_2S$ 393.1631; Found 393.1626.

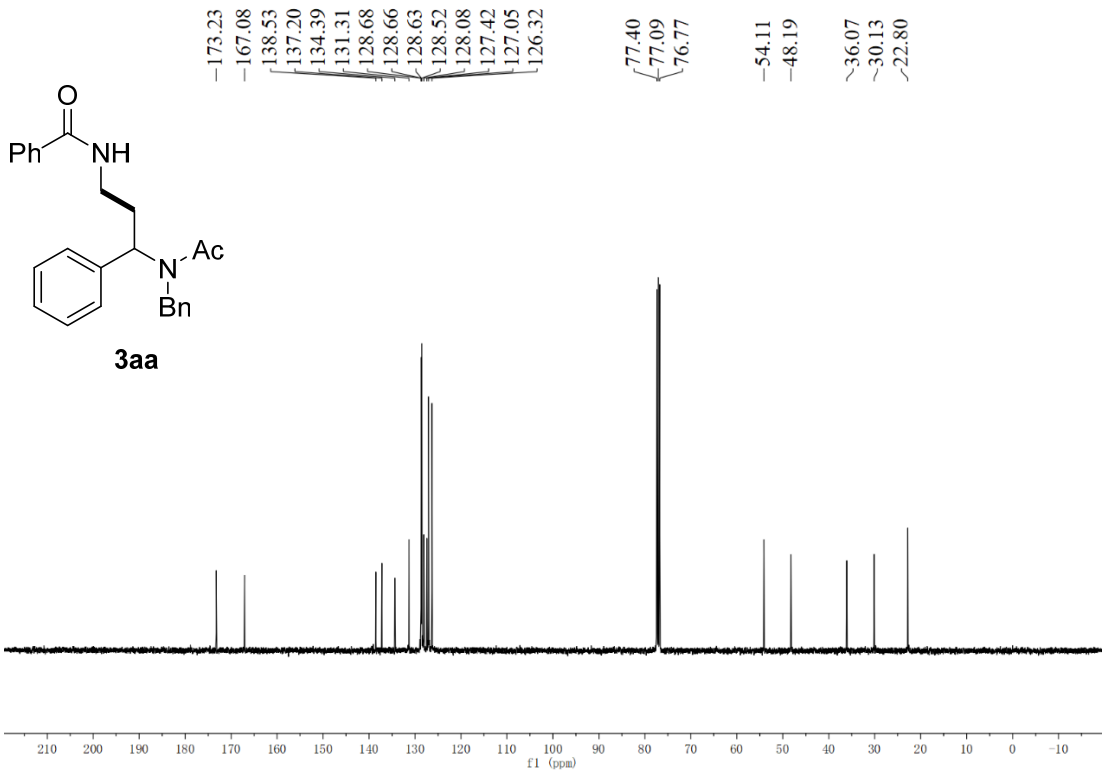
5. References

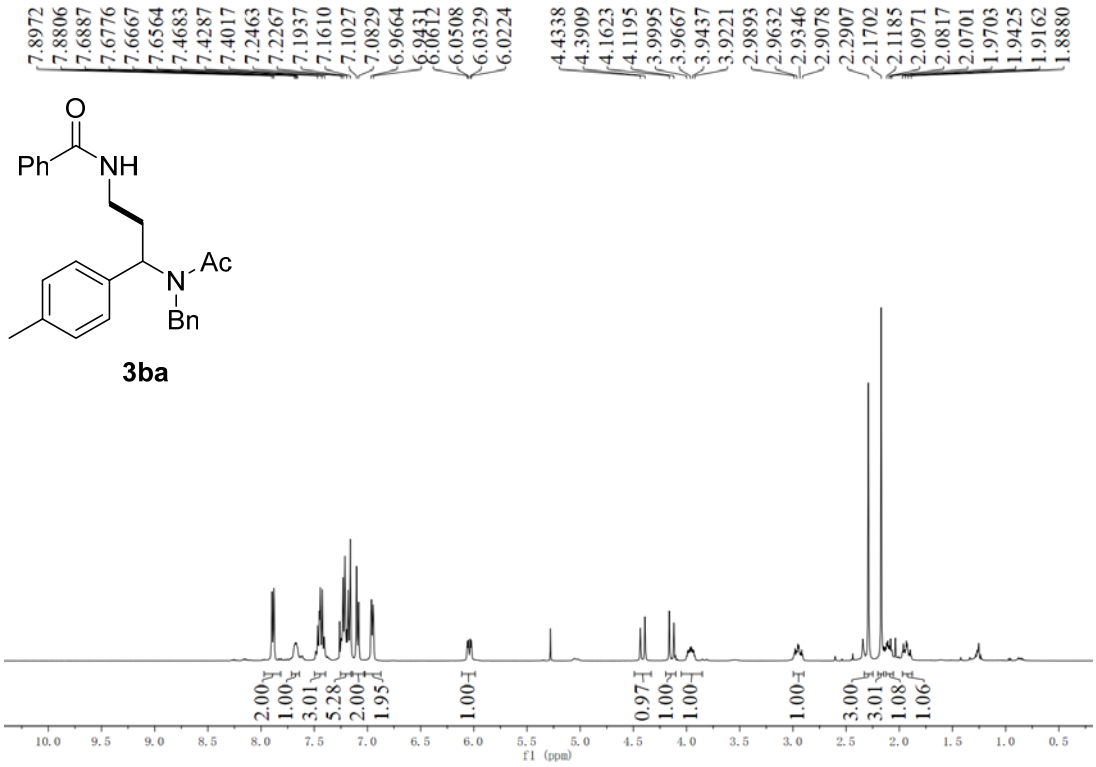
1. H. Liu, Y. Wu, L. Liu, J.-T. Yu and C. Pan, Photocatalytic chemo-, regio- & stereoselective olefinic β-C–H decarboxylative alkylation of enamides with diacyl peroxides, *Chem. Commun*., 2023, **59**, 8556-8559.

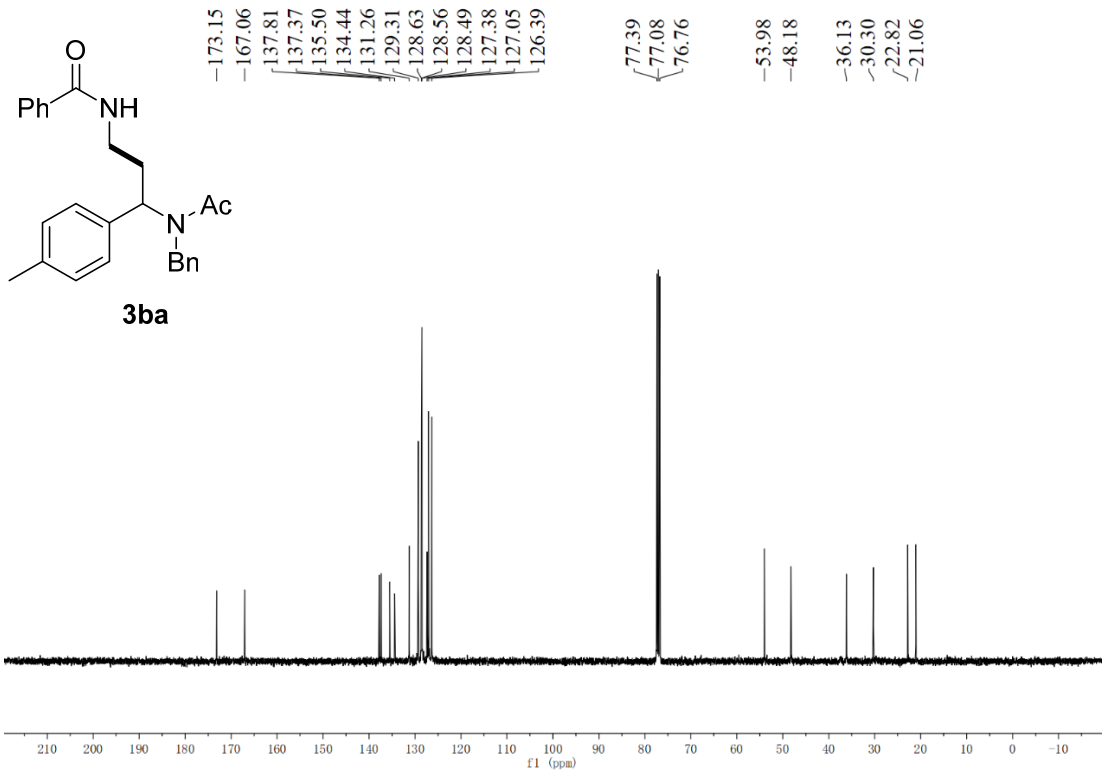
2. J. H. Kim, A. Ruffoni, Y. S. Al-Faiyz, N. S. Sheikh and D. Leonori, Divergent Strain-Release Amino-Functionalization of [1.1.1]Propellane with Electrophilic Nitrogen-Radicals, *Angew. Chem. Int. Ed.,* 2020, **59**, 8225-8231.

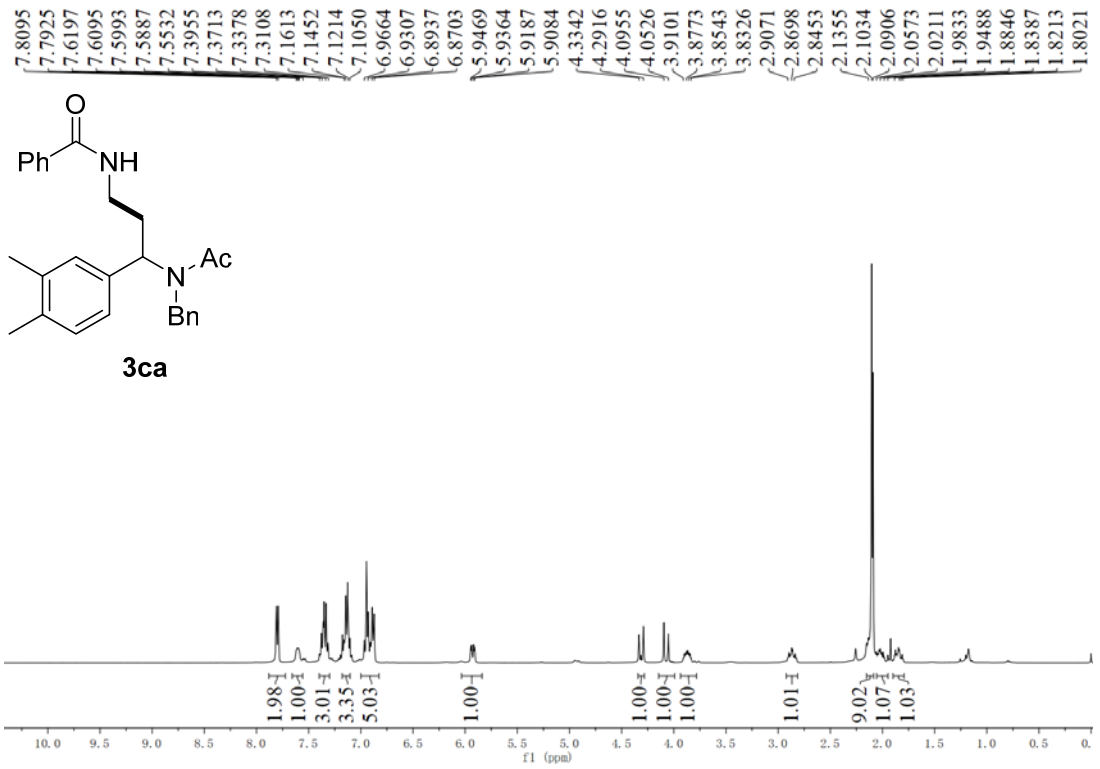
6.Copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR Spectra



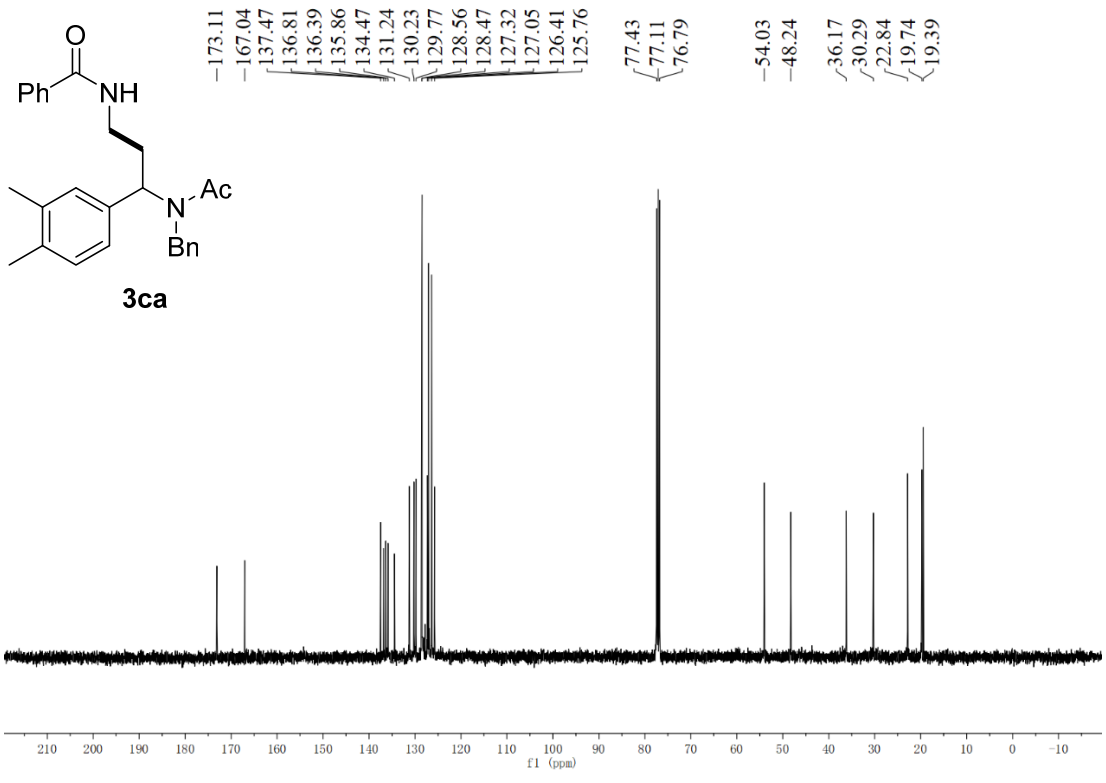



7.8972
7.8806
7.6887
7.6776
7.6667
7.6564
7.4683
7.4287
7.4017
7.2463
7.2267
7.1937
7.1610
7.1027
7.0829
6.9664
6.9431
6.0612
6.0508
6.0329
6.0224
4.4338
4.3909
4.1623
4.1195
3.9995
3.9667
3.9437
3.9221
2.9893
2.9632
2.9346
2.9078
2.2907
2.1702
2.1185
2.0971
2.0817
2.0701
1.9703
1.9425
1.9162
1.8880
O
Ph
NH
N
Ac
Bn
3ba
2.00
1.00
3.01
5.28
2.00
1.95
1.00
0.97
1.00
1.00
1.00
3.00
3.01
1.08
1.06
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
f1 (ppm)

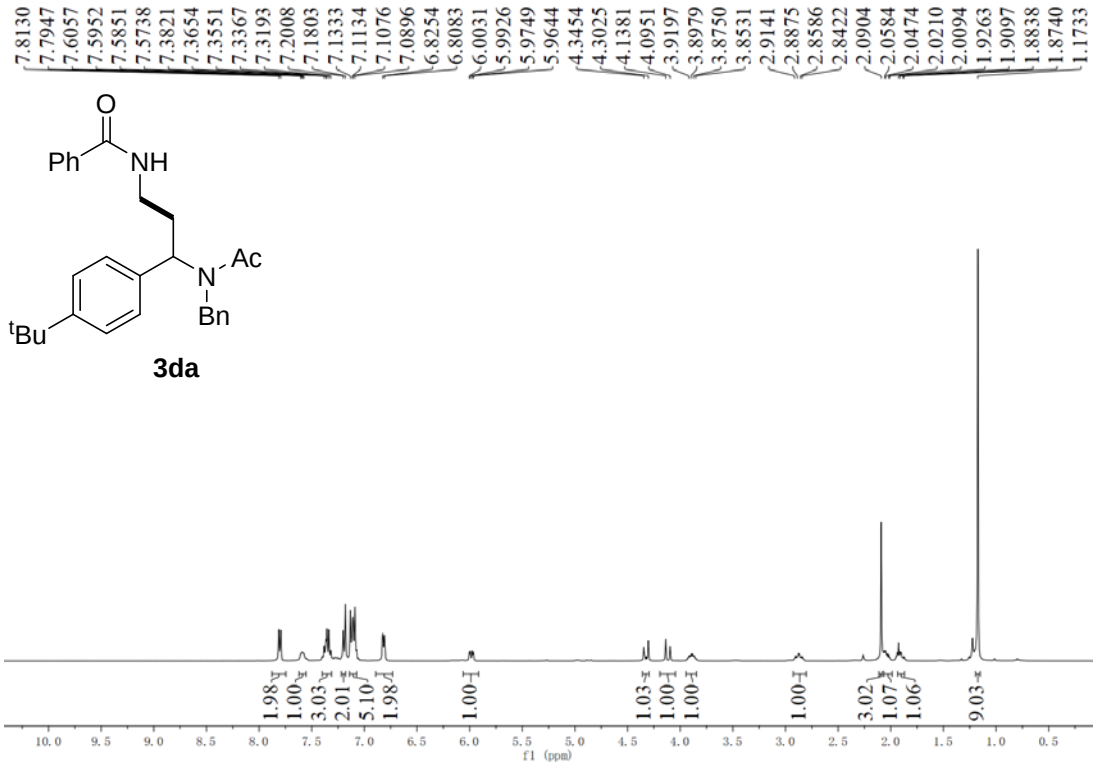

173.15
167.06
137.81
137.37
135.50
134.44
131.26
129.31
128.63
128.56
128.49
127.38
127.05
126.39
77.39
77.08
76.76
53.98
48.18
36.13
30.30
22.82
21.06
O
Ph
NH
N
Ac
Bn
3ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

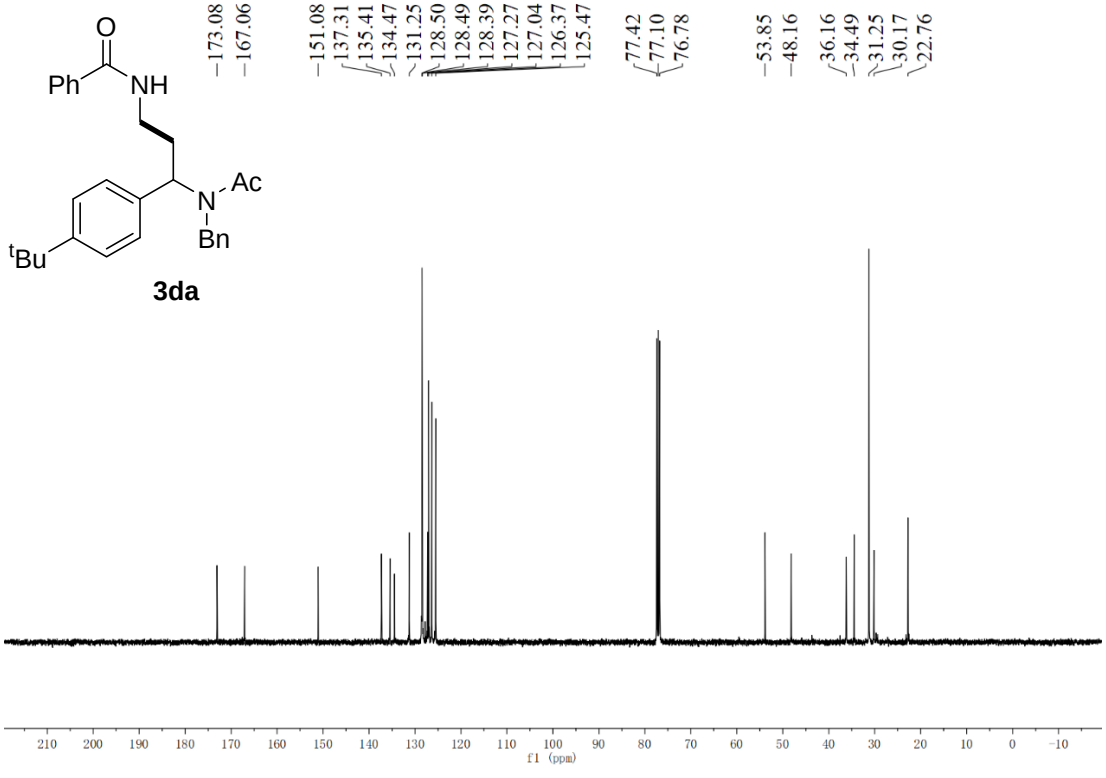

7.8095
7.7925
7.6197
7.6095
7.5993
7.5887
7.5532
7.3955
7.3713
7.3378
7.3108
7.1613
7.1452
7.1214
7.1050
6.9664
6.9307
6.8937
6.8703
5.9469
5.9364
5.9187
5.9084
4.3342
4.2916
4.0955
4.0526
3.9101
3.8773
3.8543
3.8326
2.9071
2.8698
2.8453
2.1355
2.1034
2.0906
2.0573
2.0211
1.9833
1.9488
1.8846
1.8387
1.8213
1.8021
O
Ph
NH
N
Ac
Bn
1.98
1.00
3.01
3.35
5.03
1.00
1.00
1.00
1.00
1.01
9.02
1.07
1.03
f1 (ppm)

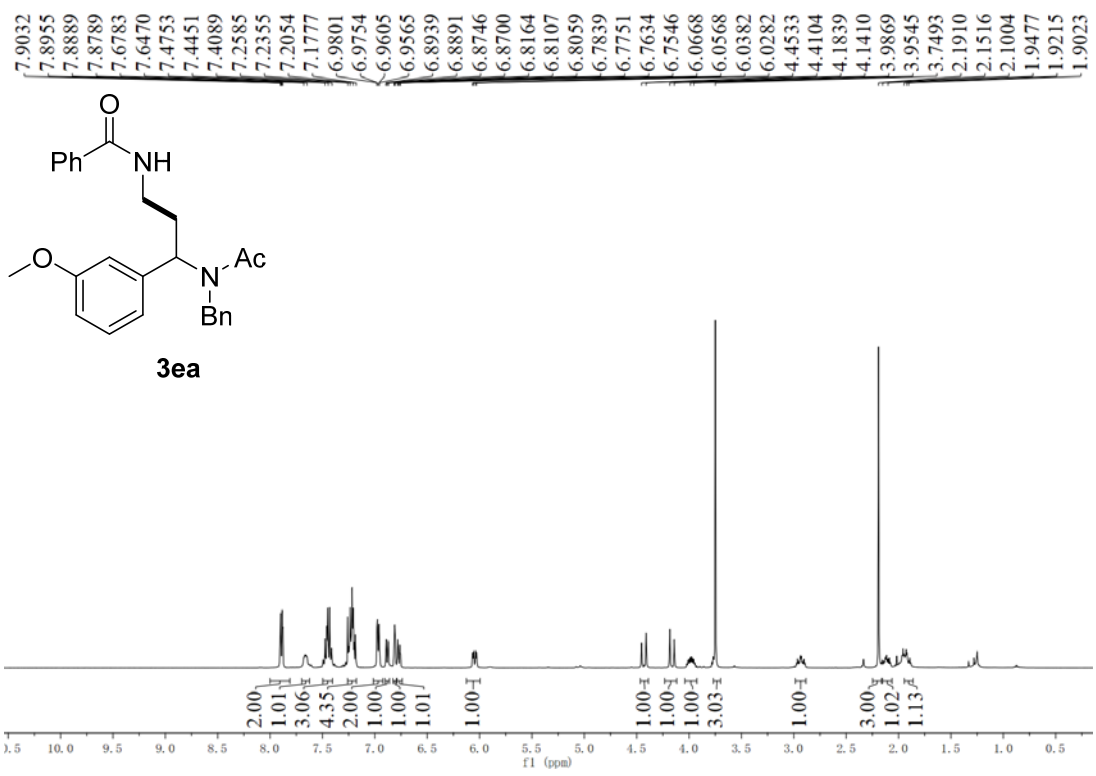
3ca

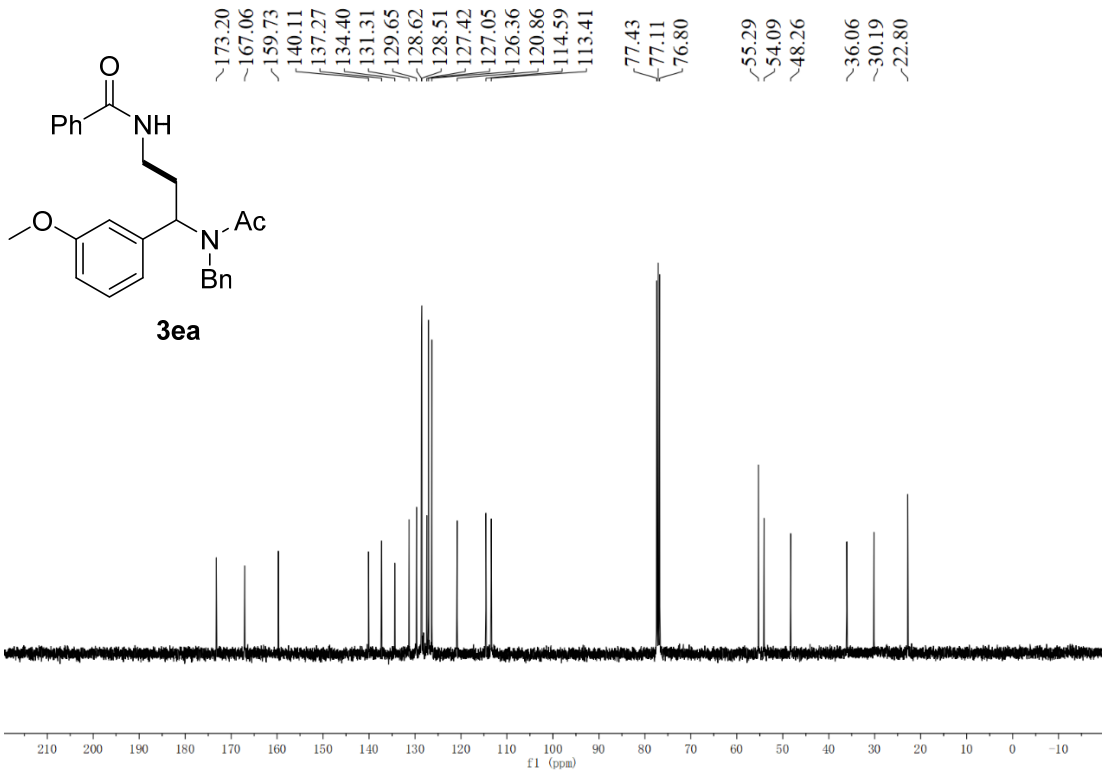

173.11
167.04
137.47
136.81
136.39
135.86
134.47
131.24
130.23
129.77
128.56
128.47
127.32
127.05
126.41
125.76
77.43
77.11
76.79
54.03
48.24
36.17
30.29
22.84
19.74
19.39
O
Ph
NH
N
Ac
Bn
f1 (ppm)

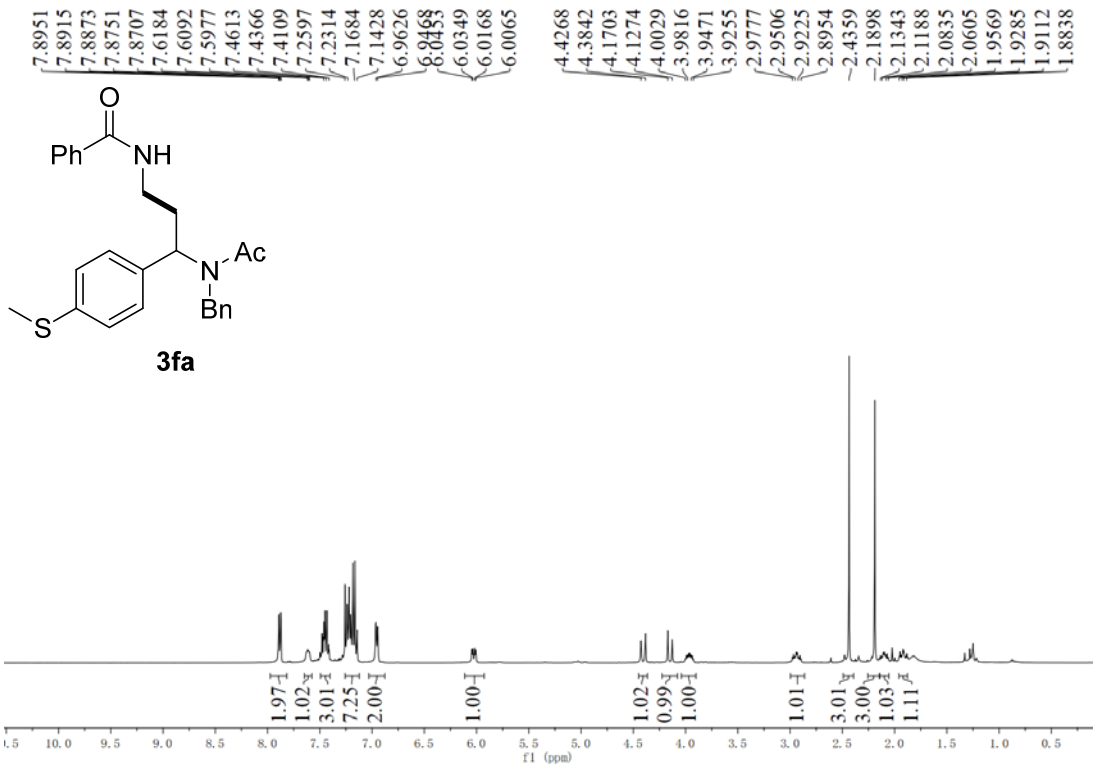
3ca

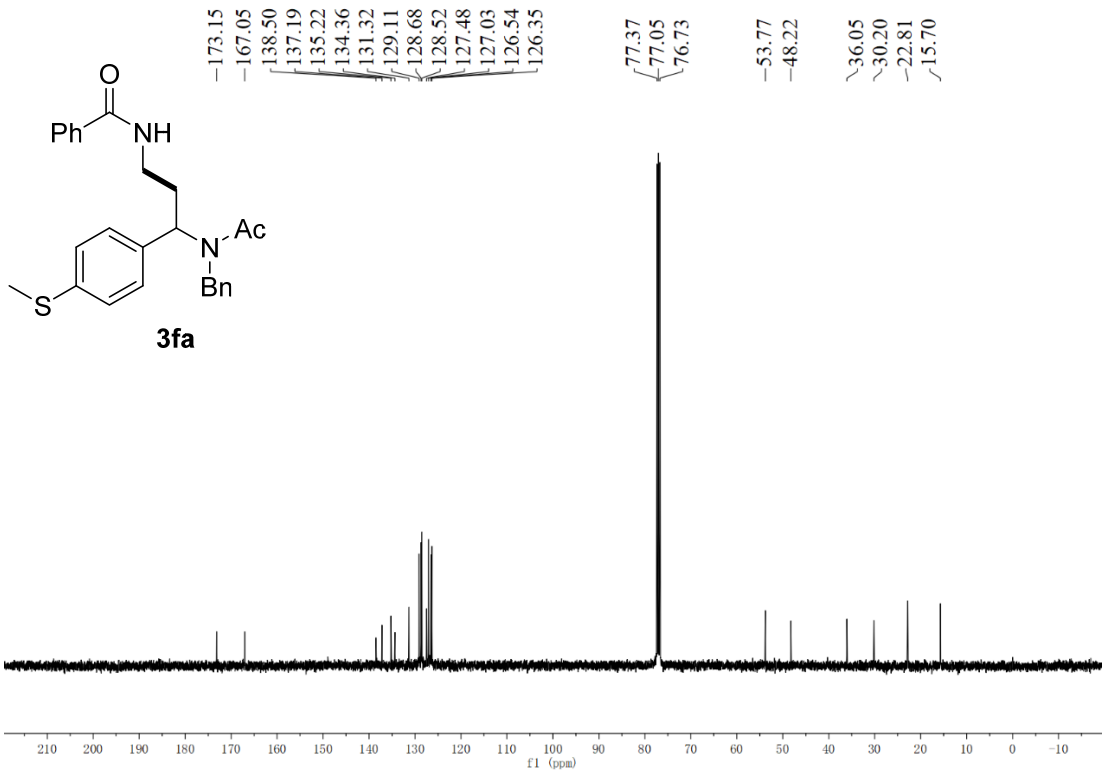

7.8130
7.7947
7.6057
7.5952
7.5851
7.5738
7.3821
7.3654
7.3551
7.3367
7.3193
7.2008
7.1803
7.1333
7.1134
7.1076
7.0896
6.8254
6.8083
6.0031
5.9926
5.9749
5.9644
4.3454
4.3025
4.1381
4.0951
3.9197
3.8979
3.8750
3.8531
2.9141
2.8875
2.8586
2.8422
2.0904
2.0584
2.0474
2.0210
2.0094
1.9263
1.9097
1.8838
1.8740
1.1733
O
Ph
NH
Ac
N
Bn
tBu
3da
1.98
1.00
3.03
2.01
5.10
1.98
1.00
1.03
1.00
1.00
1.00
3.02
1.07
1.06
9.03
f1 (ppm)

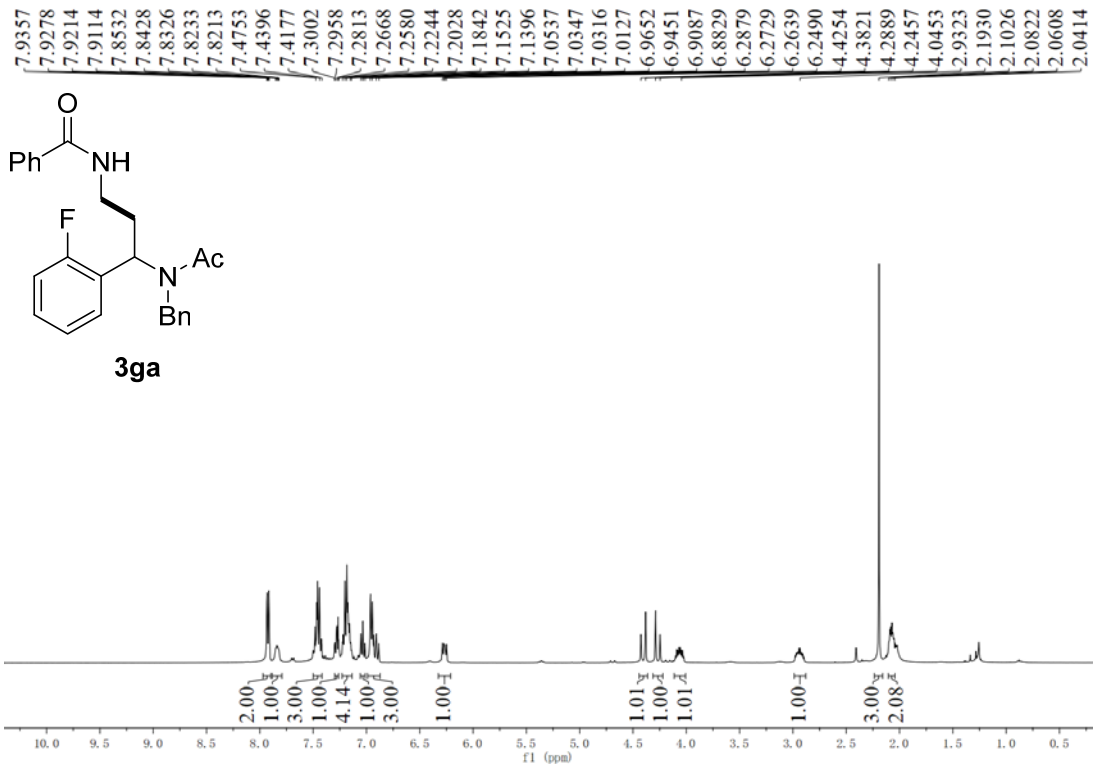

173.08
167.06
151.08
137.31
135.41
134.47
131.25
128.50
128.49
128.39
127.27
127.04
126.37
125.47
77.42
77.10
76.78
53.85
48.16
36.16
34.49
31.25
30.17
22.76
O
Ph
NH
Ac
N
Bn
tBu
3da
f1 (ppm)

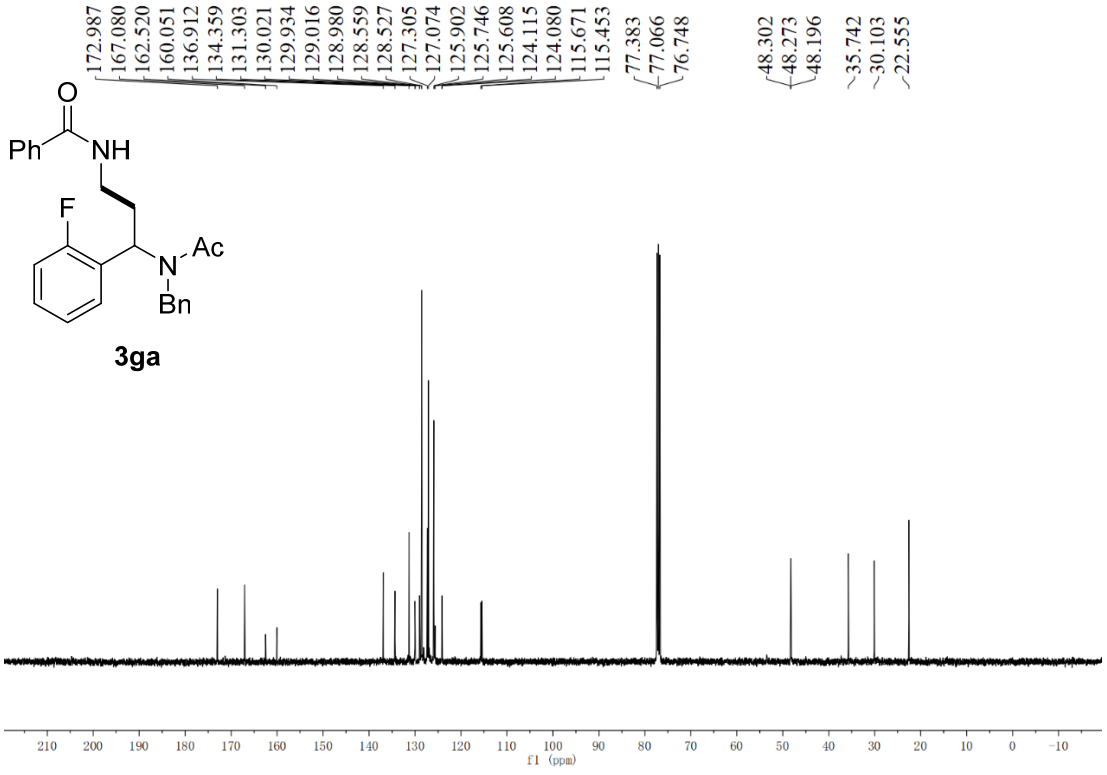

7.9032
7.8955
7.8889
7.8789
7.6783
7.6470
7.4753
7.4451
7.4089
7.2585
7.2355
7.2054
7.1777
6.9801
6.9754
6.9605
6.9565
6.8939
6.8891
6.8746
6.8700
6.8164
6.8107
6.8059
6.7839
6.7751
6.7634
6.7546
6.0668
6.0568
6.0382
6.0282
4.4533
4.4104
4.1839
4.1410
3.9869
3.9545
3.7493
2.1910
2.1516
2.1004
1.9477
1.9215
1.9023
Ph
NH
O
N
Ac
Bn
O
3ea
2.00
1.01
3.06
4.35
2.00
1.00
1.00
1.01
1.00
1.00
1.00
1.00
3.03
1.00
3.00
1.02
1.13
f1 (ppm)

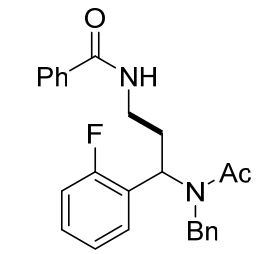

173.20
167.06
159.73
140.11
137.27
134.40
131.31
129.65
128.62
128.51
127.42
127.05
126.36
120.86
114.59
113.41
77.43
77.11
76.80
55.29
54.09
48.26
36.06
30.19
22.80
Ph
NH
O
N
Ac
Bn
O
3ea
f1 (ppm)


7.8951
7.8915
7.8873
7.8751
7.8707
7.6184
7.6092
7.5977
7.4613
7.4366
7.4109
7.2597
7.2314
7.1684
7.1428
6.9626
6.0468
6.0453
6.0349
6.0168
6.0065
4.4268
4.3842
4.1703
4.1274
4.0029
3.9816
3.9471
3.9255
2.9777
2.9506
2.9225
2.8954
2.4359
2.1898
2.1343
2.1188
2.0835
2.0605
1.9569
1.9285
1.9112
1.8838
O
Ph
NH
N
Ac
Bn
S
3fa
1.97
1.02
3.01
7.25
2.00
1.00
1.02
0.99
1.00
1.01
3.01
3.00
1.03
1.11
f1 (ppm)


173.15
167.05
138.50
137.19
135.22
134.36
131.32
129.11
128.68
128.52
127.48
127.03
126.54
126.35
77.37
77.05
76.73
53.77
48.22
36.05
30.20
22.81
15.70
O
Ph
NH
N
Ac
Bn
S
3fa
f1 (ppm)

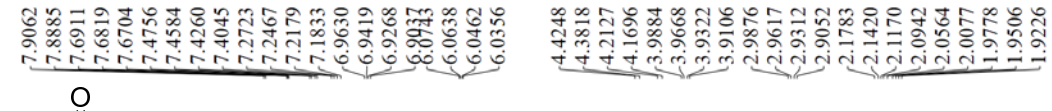

7.9357
7.9278
7.9214
7.9114
7.8532
7.8428
7.8326
7.8233
7.8213
7.4753
7.4396
7.4177
7.3002
7.2958
7.2813
7.2668
7.2580
7.2244
7.2028
7.1842
7.1525
7.1396
7.0537
7.0347
7.0316
7.0127
6.9652
6.9451
6.9087
6.8829
6.2879
6.2729
6.2639
6.2490
4.4254
4.3821
4.2889
4.2457
4.0453
2.9323
2.1930
2.1026
2.0822
2.0608
2.0414
O
Ph
NH
F
Ac
N
Bn
3ga
2.00
1.00
3.00
1.00
4.14
1.00
3.00
1.00
1.01
1.00
1.01
1.00
3.00
2.08
f1 (ppm)

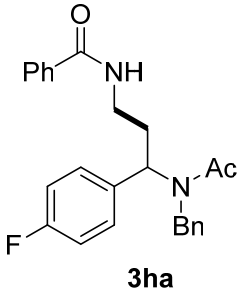

172.987
167.080
162.520
160.051
136.912
134.359
131.303
130.021
129.934
129.016
128.980
128.559
128.527
127.305
127.074
125.902
125.746
125.608
124.115
124.080
115.671
115.453
77.383
77.066
76.748
48.302
48.273
48.196
35.742
30.103
22.555
O
Ph
NH
F
Ac
N
Bn
3ga
f1 (ppm)



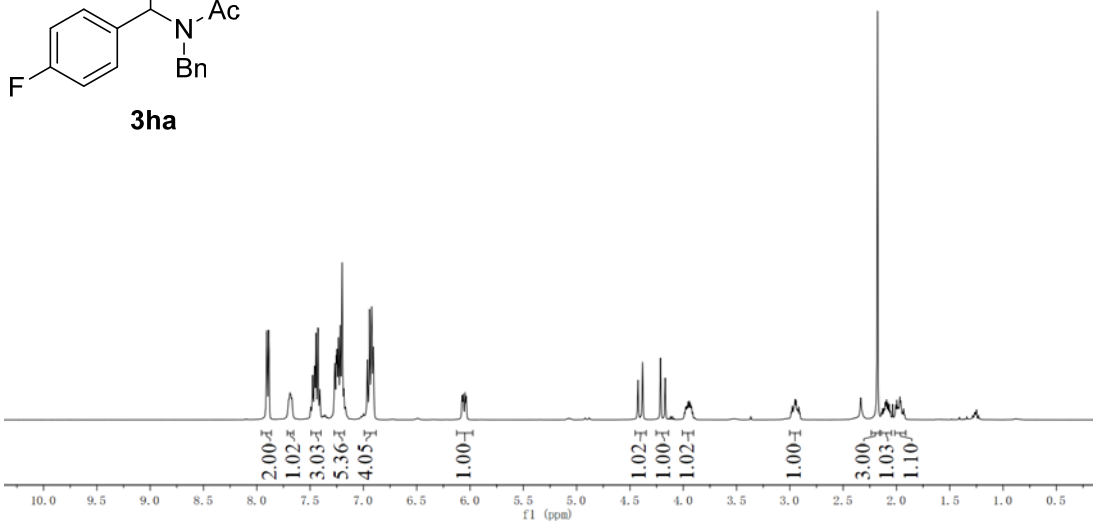
3ga

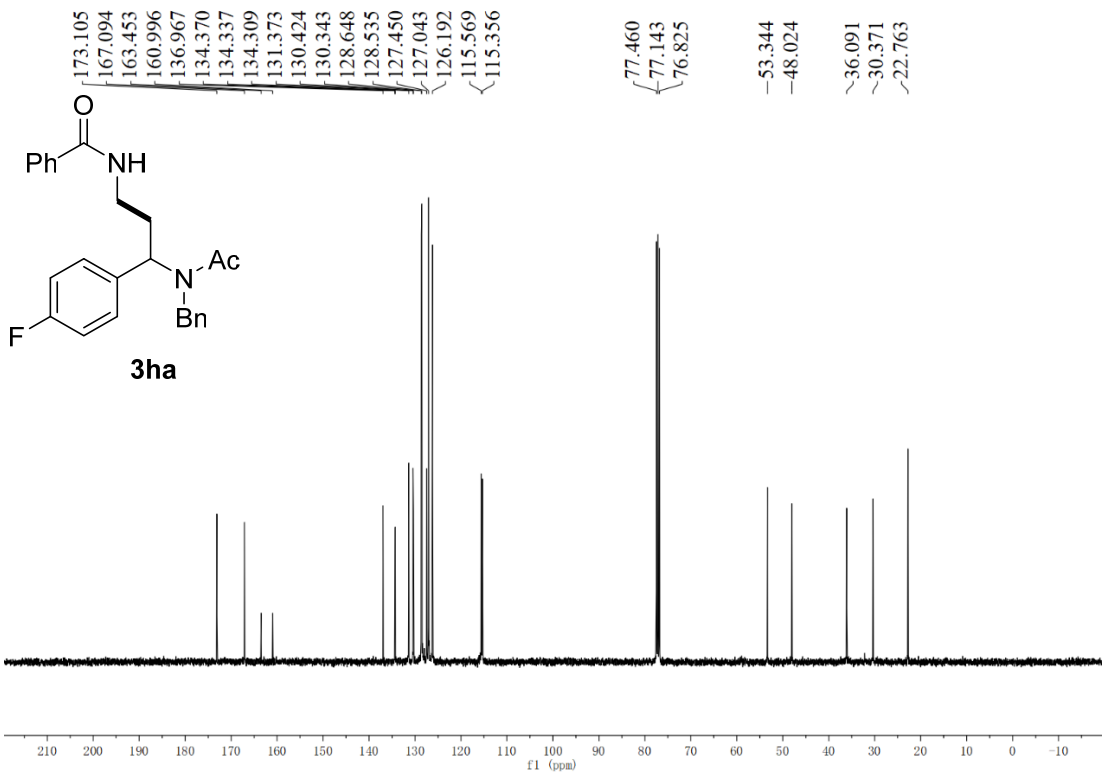
^{19}F NMR (282 M, $CDCl_3$)

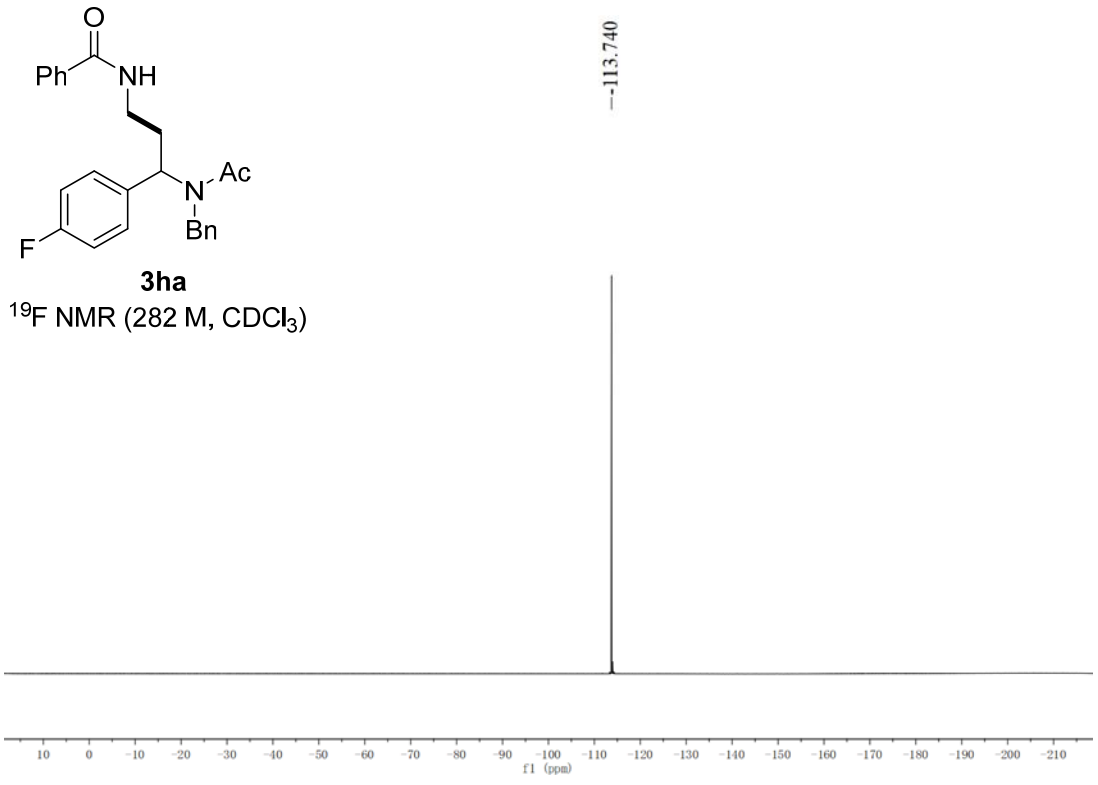


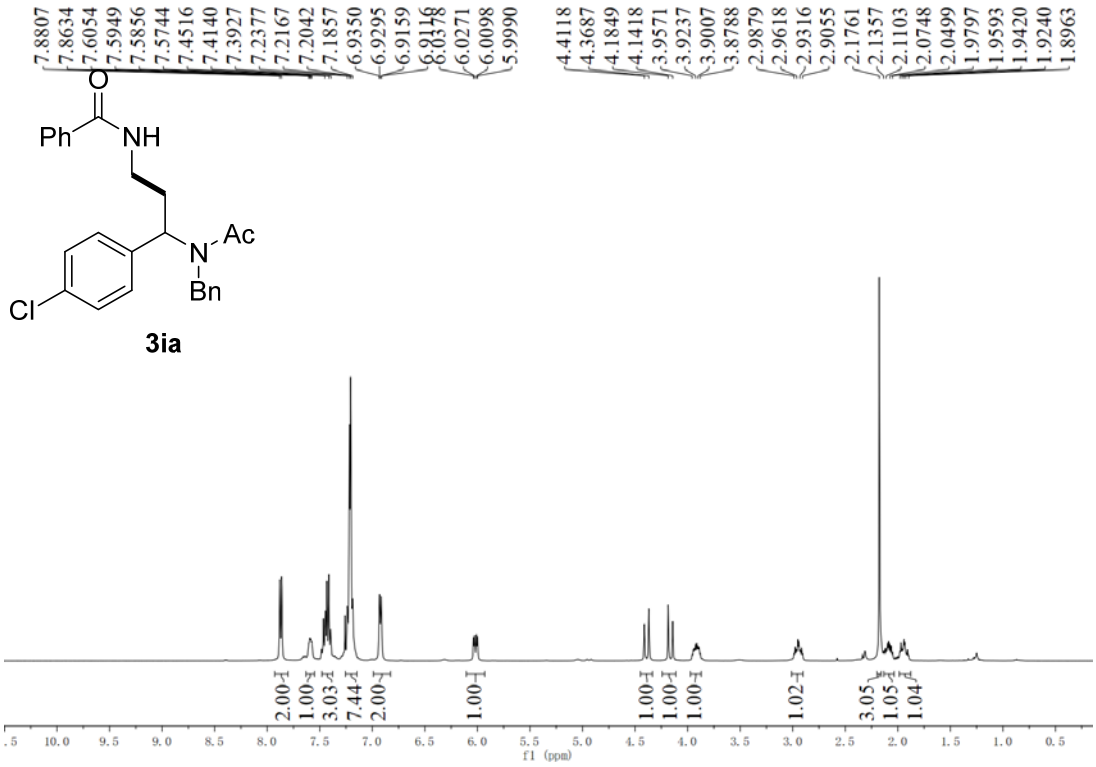


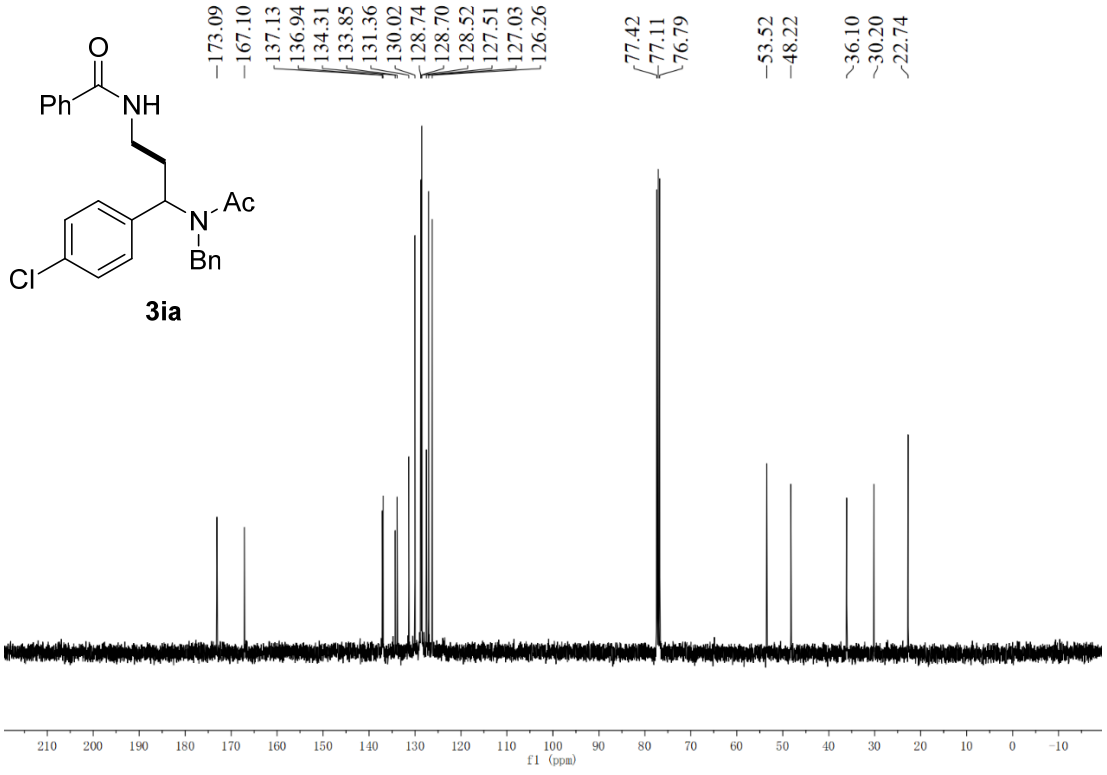
3ha

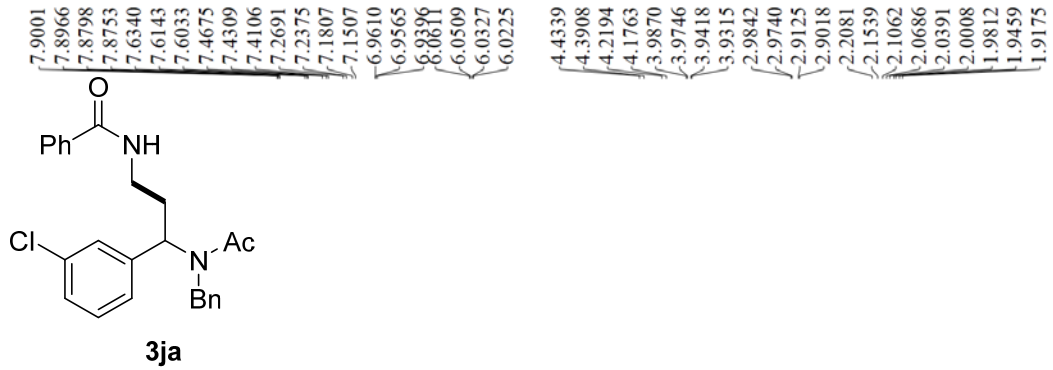



173.105
167.094
163.453
160.996
136.967
134.370
134.337
134.309
131.373
130.424
130.343
128.648
128.535
127.450
127.043
126.192
115.569
115.356
77.460
77.143
76.825
53.344
48.024
36.091
30.371
22.763
O
Ph
NH
N
Ac
Bn
F
3ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

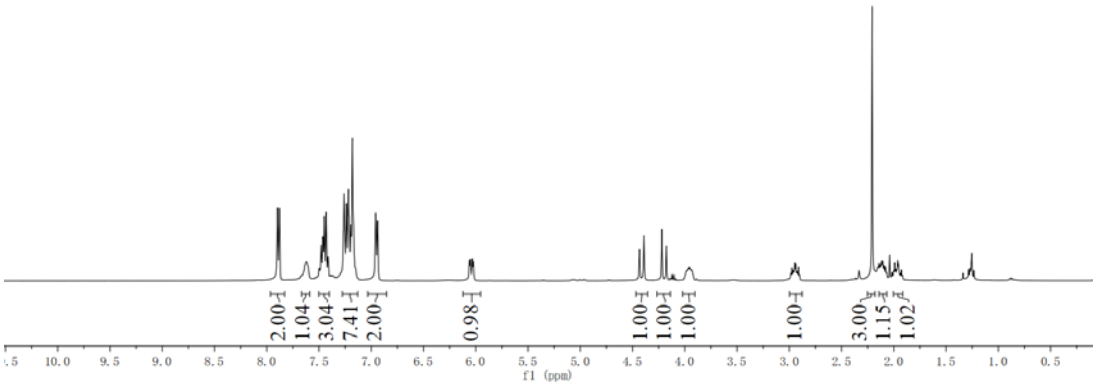

O
Ph
NH
N
Ac
Bn
F
3ha
19F NMR (282 M, CDCl3)
-113.740
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

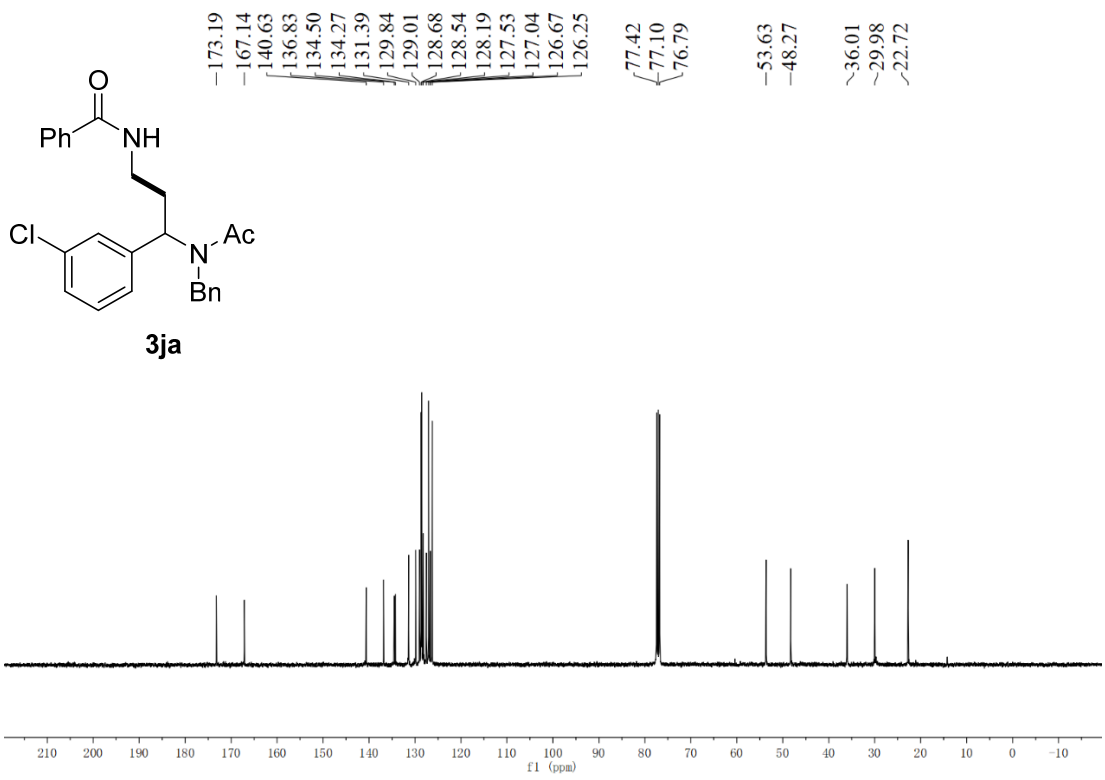

7.8807
7.8634
7.6054
7.5949
7.5856
7.5744
7.4516
7.4140
7.3927
7.2377
7.2167
7.2042
7.1857
6.9350
6.9295
6.9159
6.0271
6.0098
5.9990
4.4118
4.3687
4.1849
4.1418
3.9571
3.9237
3.9007
3.8788
2.9879
2.9618
2.9316
2.9055
2.1761
2.1357
2.1103
2.0748
2.0499
1.9797
1.9593
1.9420
1.9240
1.8963
O
Ph
NH
Ac
N
Bn
Cl
3ia
2.00
1.00
3.03
7.44
2.00
1.00
1.00
1.00
1.00
1.02
3.05
1.05
1.04
f1 (ppm)


173.09
167.10
137.13
136.94
134.31
133.85
131.36
130.02
128.74
128.70
128.52
127.51
127.03
126.26
77.42
77.11
76.79
53.52
48.22
36.10
30.20
22.74
O
Ph
NH
Ac
N
Bn
Cl
3ia
f1 (ppm)

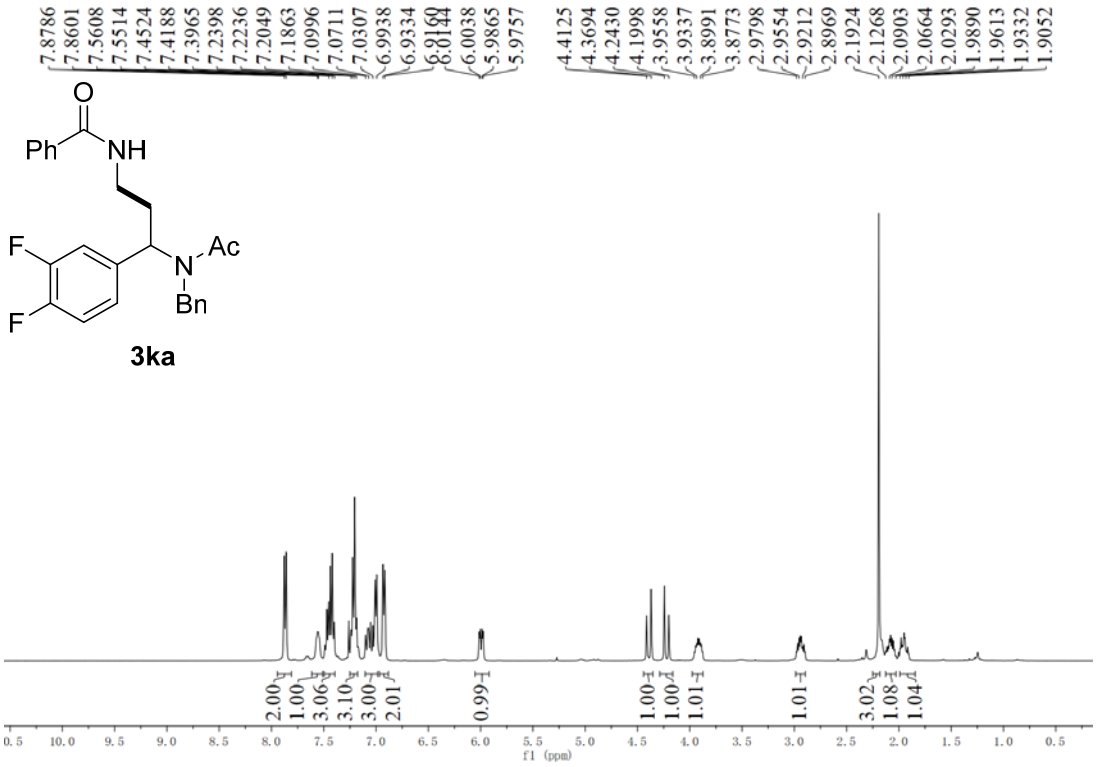

7.9001
7.8966
7.8798
7.8753
7.6340
7.6143
7.6033
7.4675
7.4309
7.4106
7.2691
7.2375
7.1807
7.1507
6.9610
6.9565
6.9396
6.8811
6.0509
6.0327
6.0225
4.4339
4.3908
4.2194
4.1763
3.9870
3.9746
3.9418
3.9315
2.9842
2.9740
2.9125
2.9018
2.2081
2.1539
2.1062
2.0686
2.0391
2.0008
1.9812
1.9459
1.9175
O
Ph
NH
Cl
N
Ac
Bn

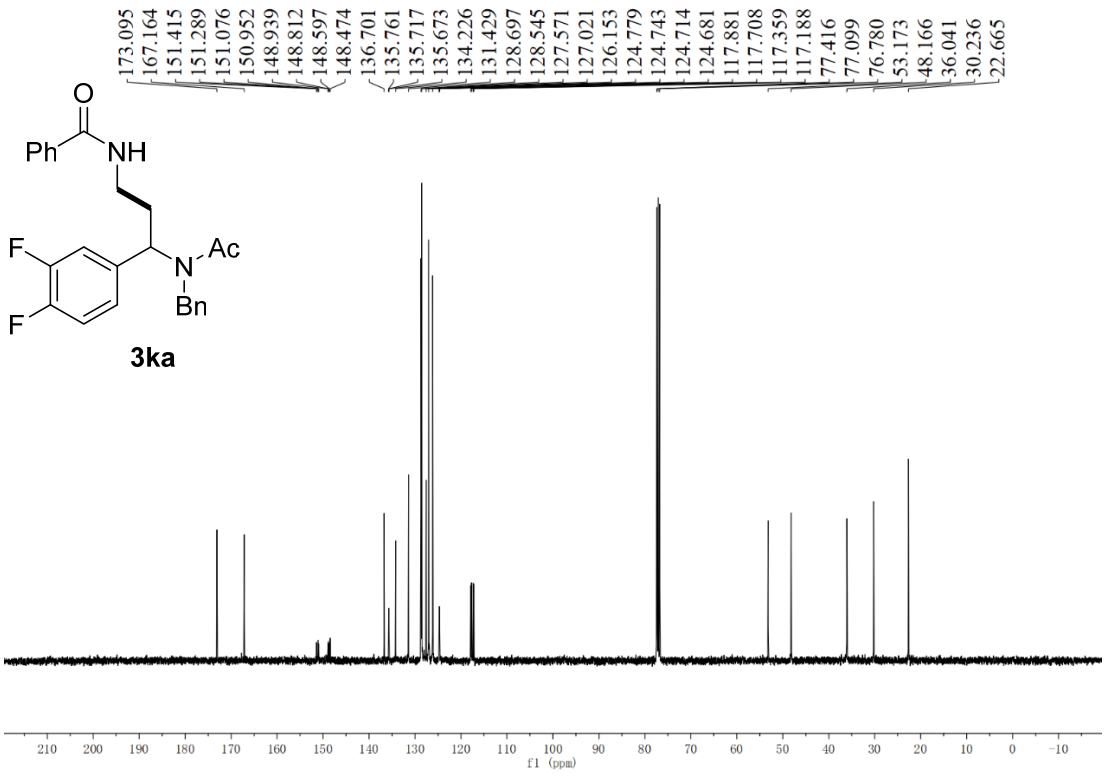
3ja

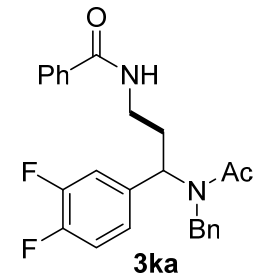

2.00
1.04
3.04
7.41
2.00
0.98
1.00
1.00
1.00
1.00
3.00
1.15
1.02
f1 (ppm)


173.19
167.14
140.63
136.83
134.50
134.27
131.39
129.84
129.01
128.68
128.54
128.19
127.53
127.04
126.67
126.25
77.42
77.10
76.79
53.63
48.27
36.01
29.98
22.72
O
Ph
NH
Cl
N
Ac
Bn
f1 (ppm)

3ja

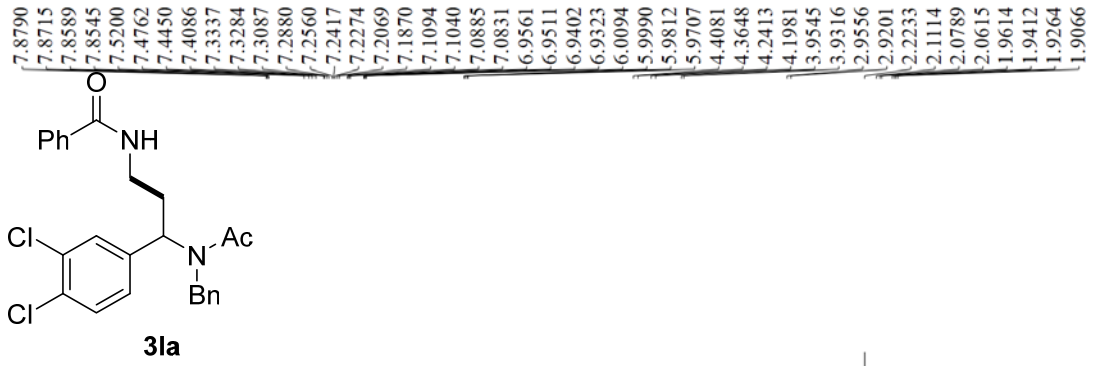

7.8786
7.8601
7.5608
7.5514
7.4524
7.4188
7.3965
7.2398
7.2236
7.2049
7.1863
7.0996
7.0711
7.0307
6.9938
6.9334
6.0038
5.9865
5.9757
4.4125
4.3694
4.2430
4.1998
3.9558
3.9337
3.8991
3.8773
2.9798
2.9554
2.9212
2.8969
2.1924
2.1268
2.0903
2.0664
2.0293
1.9890
1.9613
1.9332
1.9052
O
Ph
NH
F
F
N
Ac
Bn
3ka
2.00
1.00
3.06
3.10
3.00
2.01
0.99
1.00
1.00
1.01
1.01
3.02
1.08
1.04
f1 (ppm)


173.095
167.164
151.415
151.289
151.076
150.952
148.939
148.812
148.597
148.474
136.701
135.761
135.717
135.673
134.226
131.429
128.697
128.545
127.571
127.021
126.153
124.779
124.743
124.714
124.681
117.881
117.708
117.359
117.188
77.416
77.099
76.780
53.173
48.166
36.041
30.236
22.665
O
Ph
NH
F
F
N
Ac
Bn
3ka
f1 (ppm)

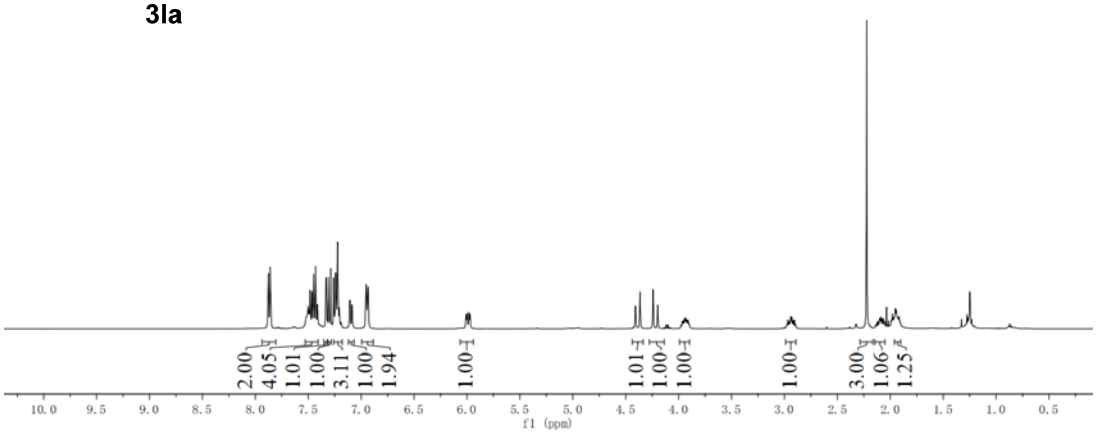


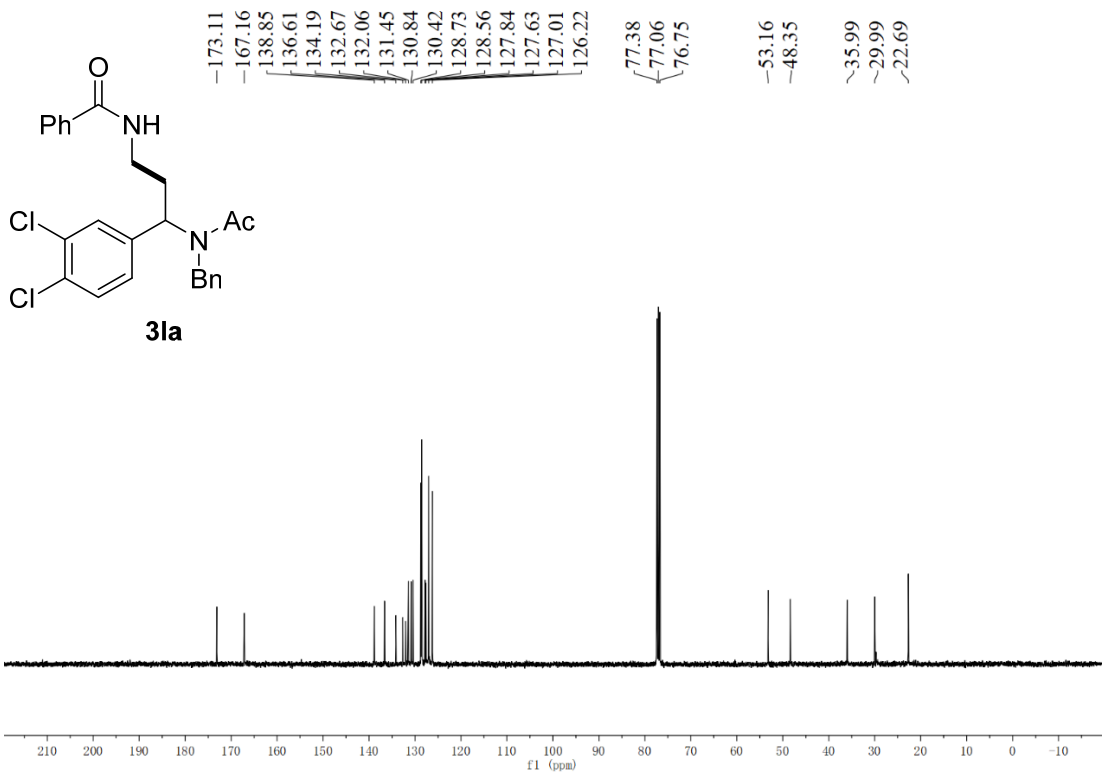
3ka

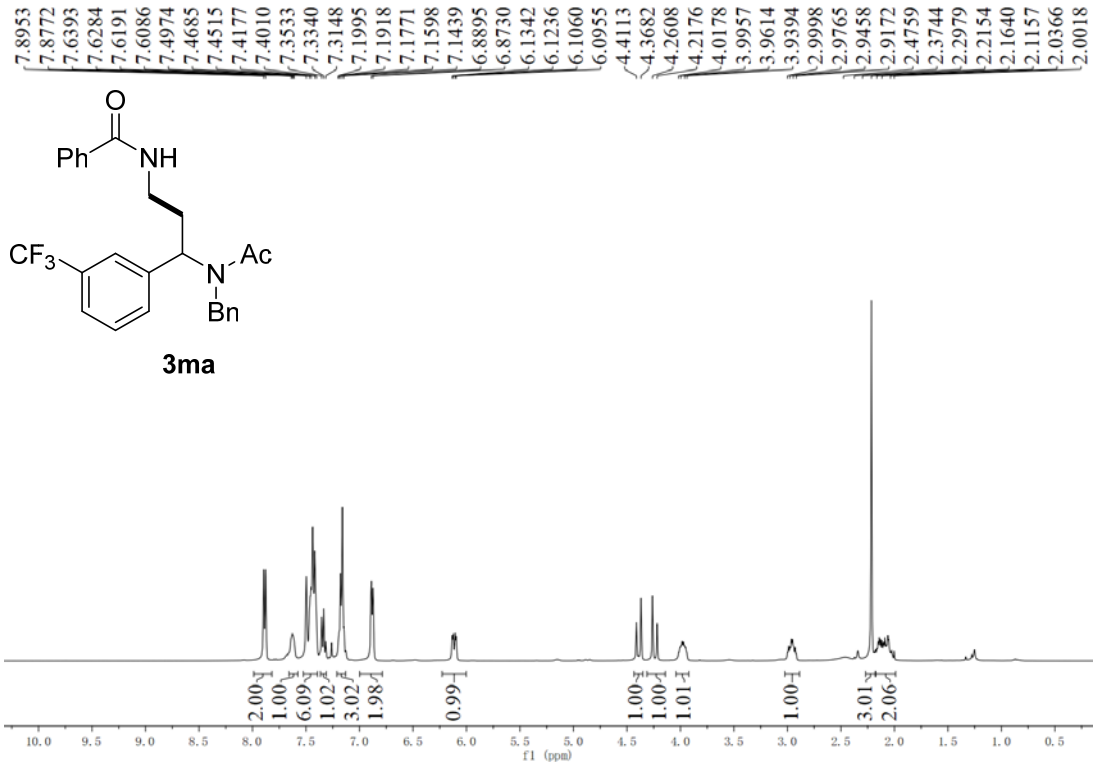
^{19}F NMR (282 M, $CDCl_3$)

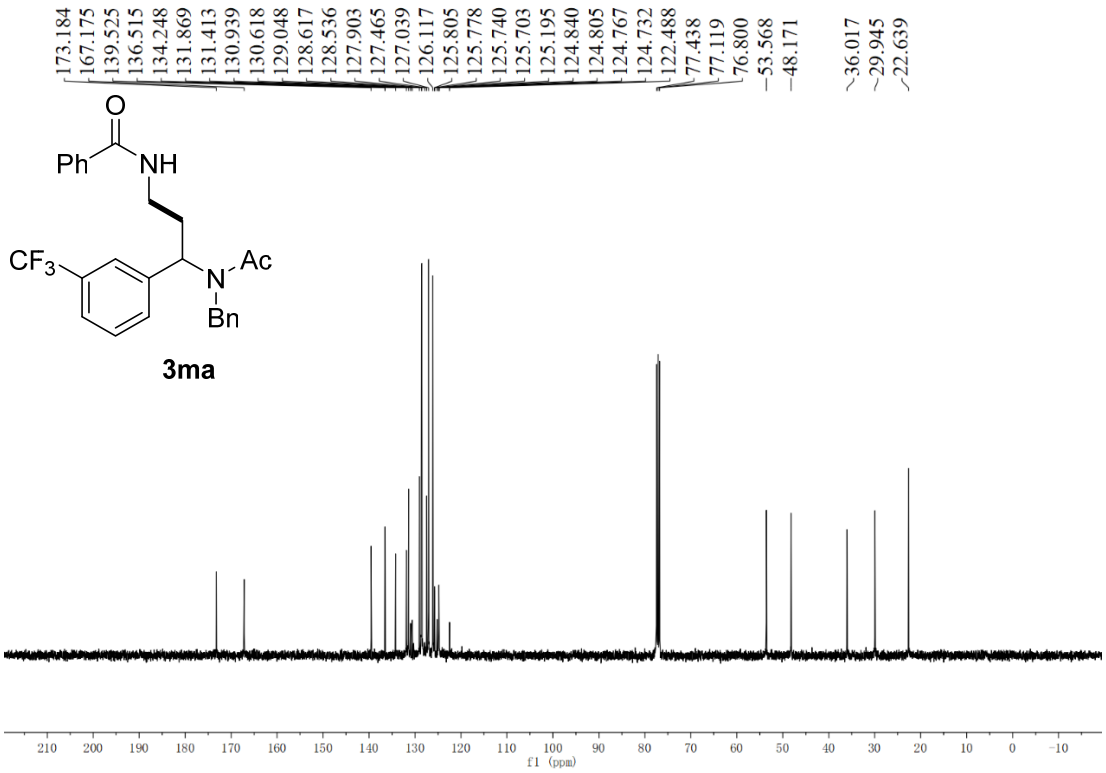


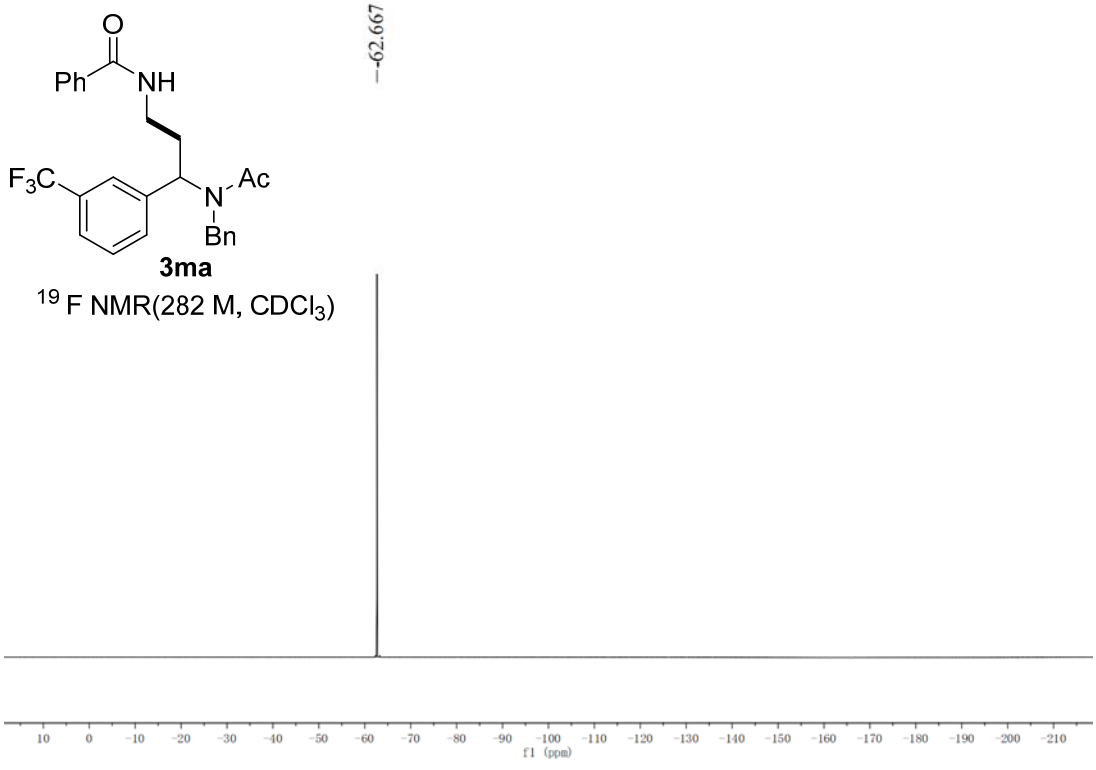
3la

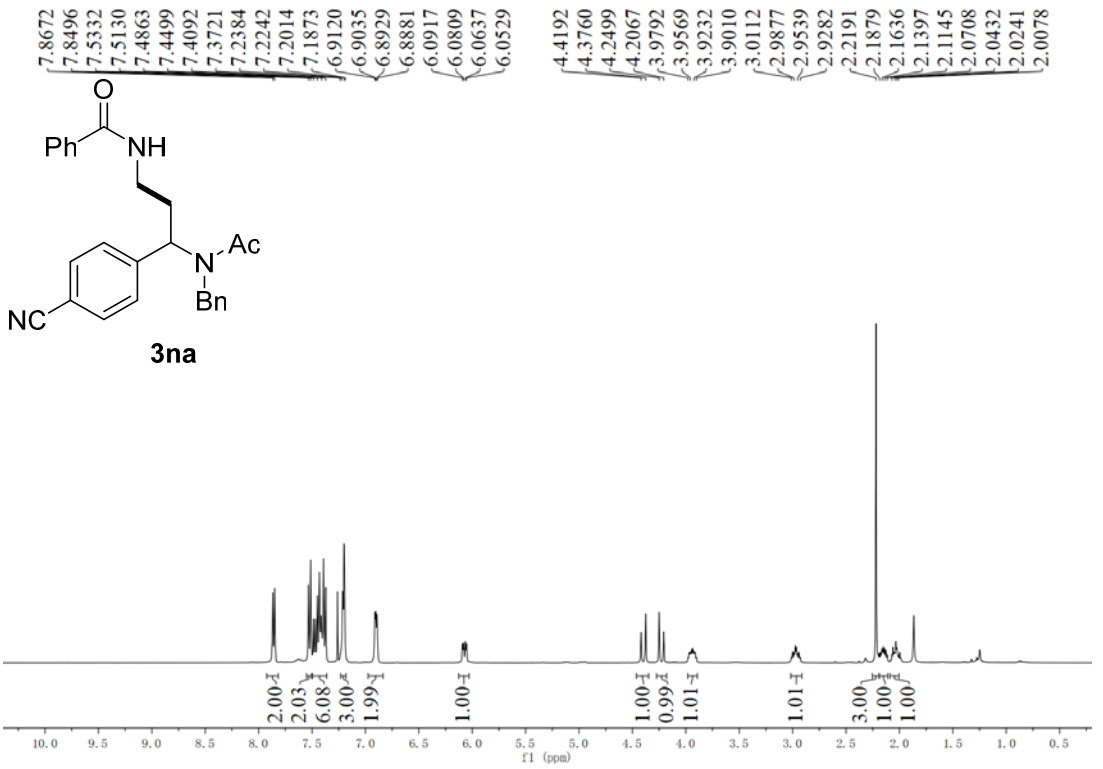


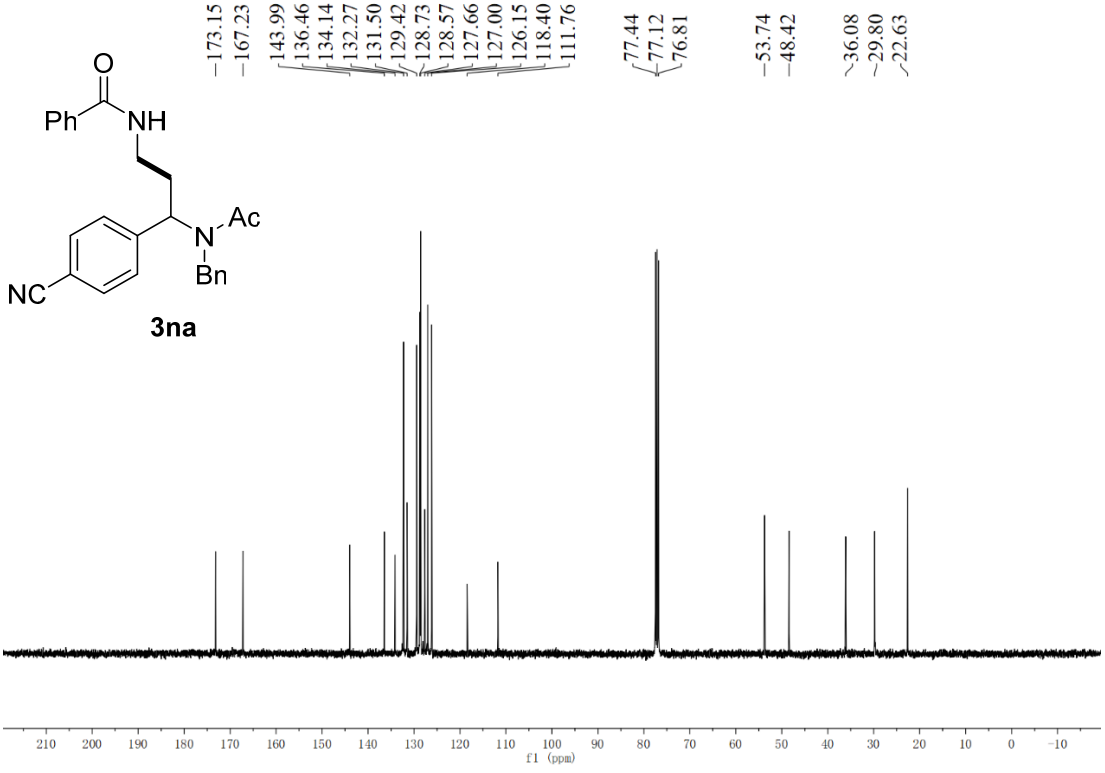

173.11
167.16
138.85
136.61
134.19
132.67
132.06
131.45
130.84
130.42
128.73
128.56
127.84
127.63
127.01
126.22
77.38
77.06
76.75
53.16
48.35
35.99
29.99
22.69
O
Ph
NH
Cl
Cl
N
Ac
Bn
3la
f1 (ppm)

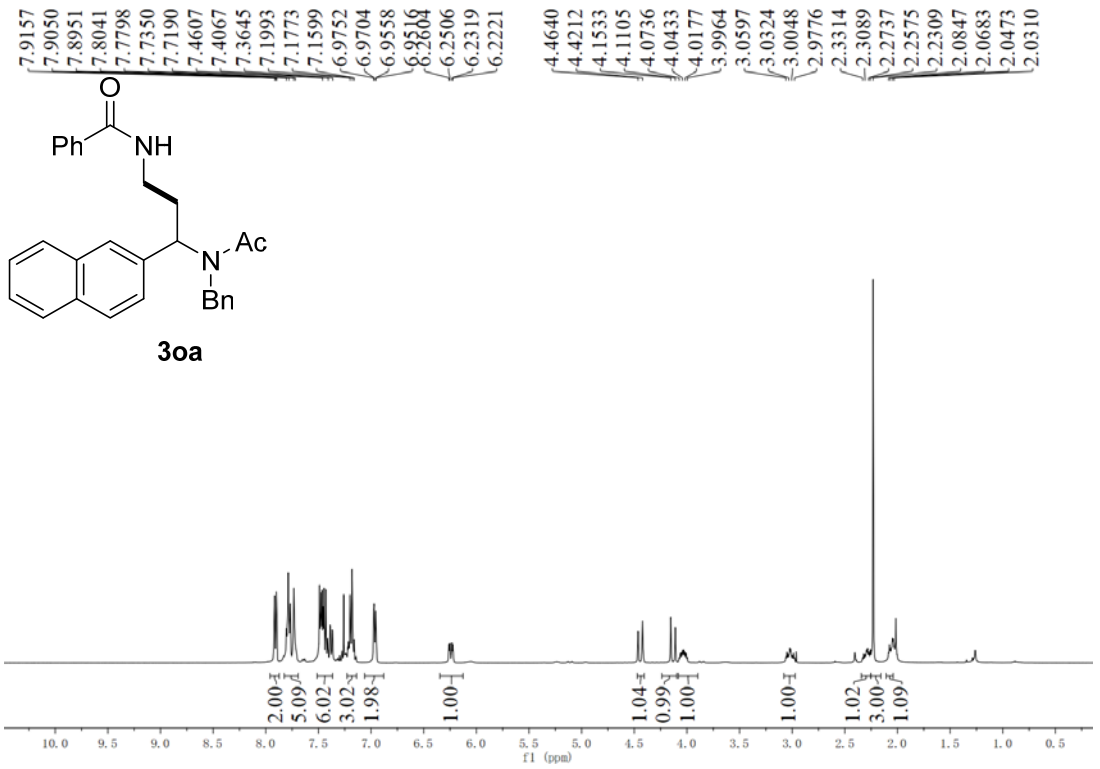

7.8953
7.8772
7.6393
7.6284
7.6191
7.6086
7.4974
7.4685
7.4515
7.4177
7.4010
7.3533
7.3340
7.3148
7.1995
7.1918
7.1771
7.1598
7.1439
6.8895
6.8730
6.1342
6.1236
6.1060
6.0955
4.4113
4.3682
4.2608
4.2176
4.0178
3.9957
3.9614
3.9394
2.9998
2.9765
2.9458
2.9172
2.4759
2.3744
2.2979
2.2154
2.1640
2.1157
2.0366
2.0018
O
Ph
NH
CF3
N
Ac
Bn
3ma
2.00
1.00
6.09
1.02
3.02
1.98
0.99
1.00
1.00
1.01
1.00
3.01
2.06
f1 (ppm)


173.184
167.175
139.525
136.515
134.248
131.869
131.413
130.939
130.618
129.048
128.617
128.536
127.903
127.465
127.039
126.117
125.805
125.778
125.740
125.703
125.195
124.840
124.805
124.767
124.732
122.488
77.438
77.119
76.800
53.568
48.171
36.017
29.945
22.639
O
Ph
NH
CF3
N
Ac
Bn
3ma
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)

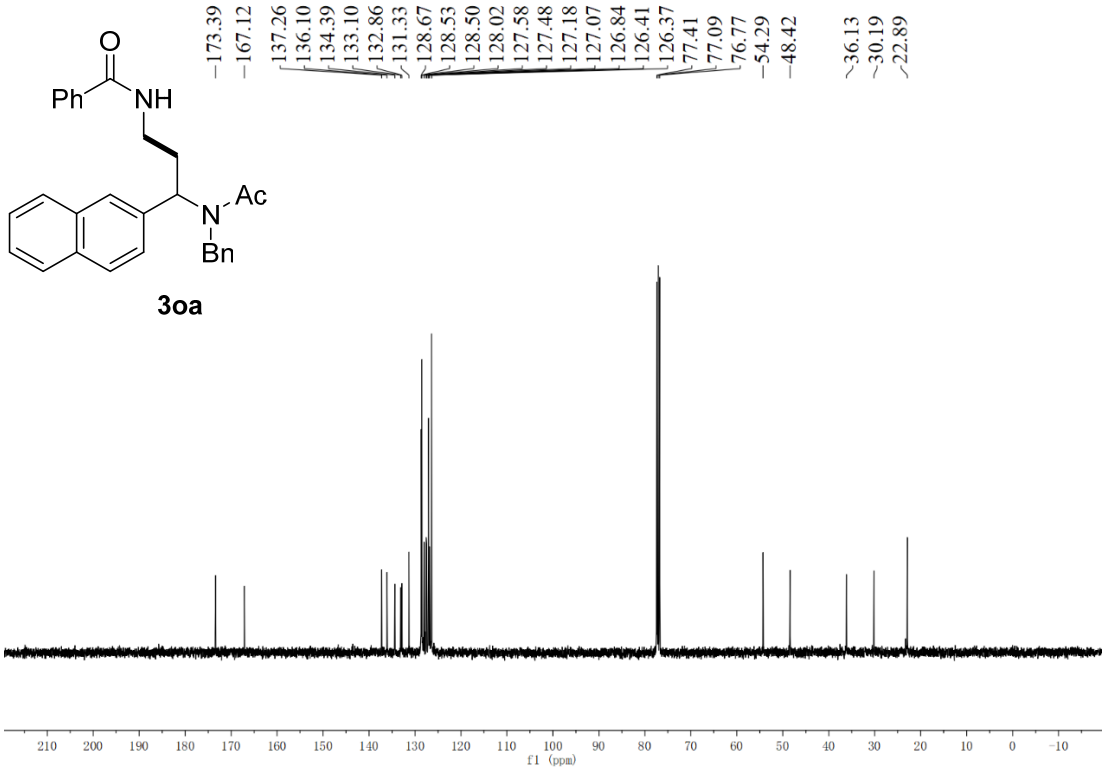

-62.667
O
Ph
NH
F3C
N
Ac
Bn
3ma
19 F NMR(282 M, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.8672
7.8496
7.5332
7.5130
7.4863
7.4499
7.4092
7.3721
7.2384
7.2242
7.2014
7.1873
6.9120
6.9035
6.8929
6.8881
6.0917
6.0809
6.0637
6.0529
4.4192
4.3760
4.2499
4.2067
3.9792
3.9569
3.9232
3.9010
3.0112
2.9877
2.9539
2.9282
2.2191
2.1879
2.1636
2.1397
2.1145
2.0708
2.0432
2.0241
2.0078
Ph
NH
O
N
Ac
Bn
NC
3na
2.00
2.03
6.08
3.00
1.99
1.00
1.00
0.99
1.01
1.01
3.00
1.00
1.00
f1 (ppm)

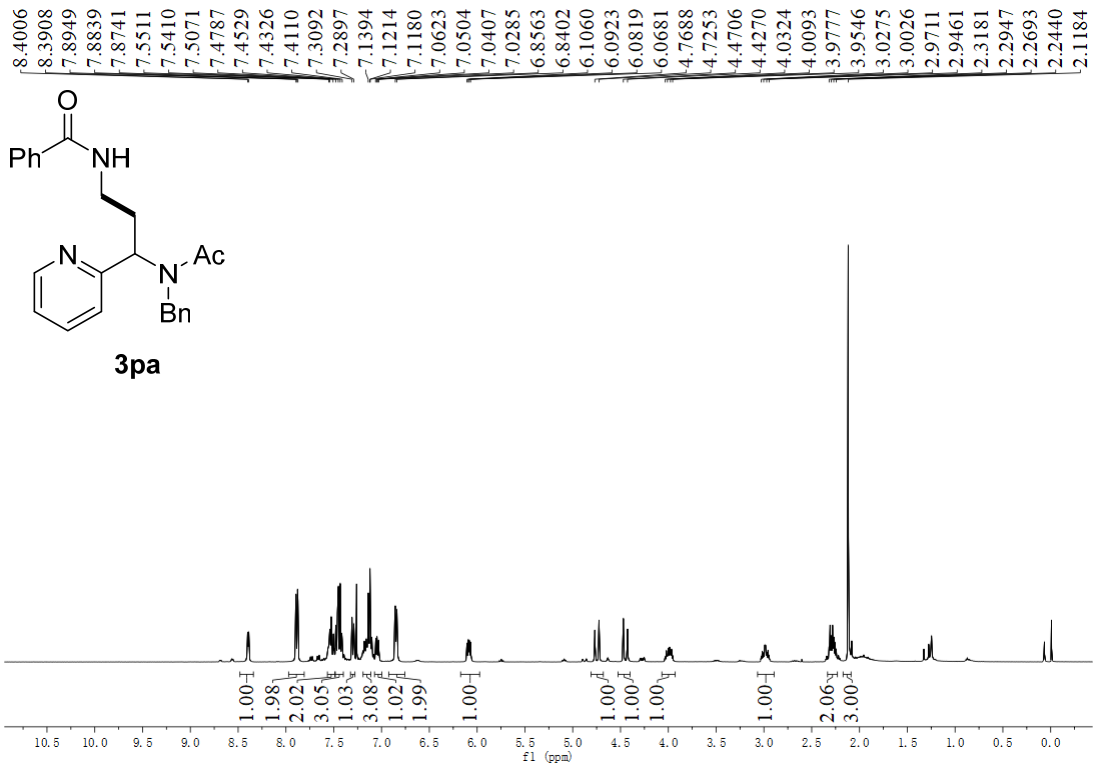

173.15
167.23
143.99
136.46
134.14
132.27
131.50
129.42
128.73
128.57
127.66
127.00
126.15
118.40
111.76
77.44
77.12
76.81
53.74
48.42
36.08
29.80
22.63
Ph
NH
O
N
Ac
Bn
NC
3na
f1 (ppm)


7.9157
7.9050
7.8951
7.8041
7.7798
7.7350
7.7190
7.4607
7.4067
7.3645
7.1993
7.1773
7.1599
6.9752
6.9704
6.9558
6.9516
6.2604
6.2506
6.2319
6.2221
4.4640
4.4212
4.1533
4.1105
4.0736
4.0433
4.0177
3.9964
3.0597
3.0324
3.0048
2.9776
2.3314
2.3089
2.2737
2.2575
2.2309
2.0847
2.0683
2.0473
2.0310
O
Ph
NH
Ac
N
Bn
2.00
5.09
6.02
3.02
1.98
1.00
1.04
0.99
1.00
1.00
1.02
3.00
1.09
f1 (ppm)

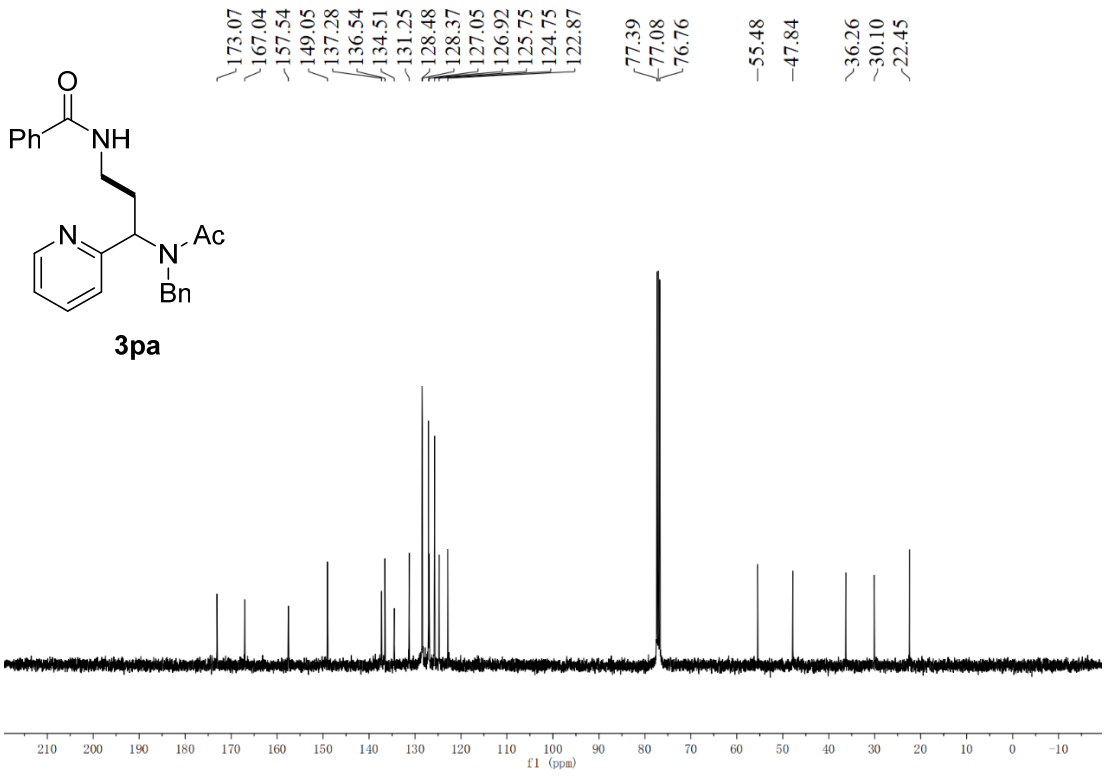
3oa


173.39
167.12
137.26
136.10
134.39
133.10
132.86
131.33
128.67
128.53
128.50
128.02
127.58
127.48
127.18
127.07
126.84
126.41
126.37
77.41
77.09
76.77
54.29
48.42
36.13
30.19
22.89
O
Ph
NH
Ac
N
Bn
f1 (ppm)

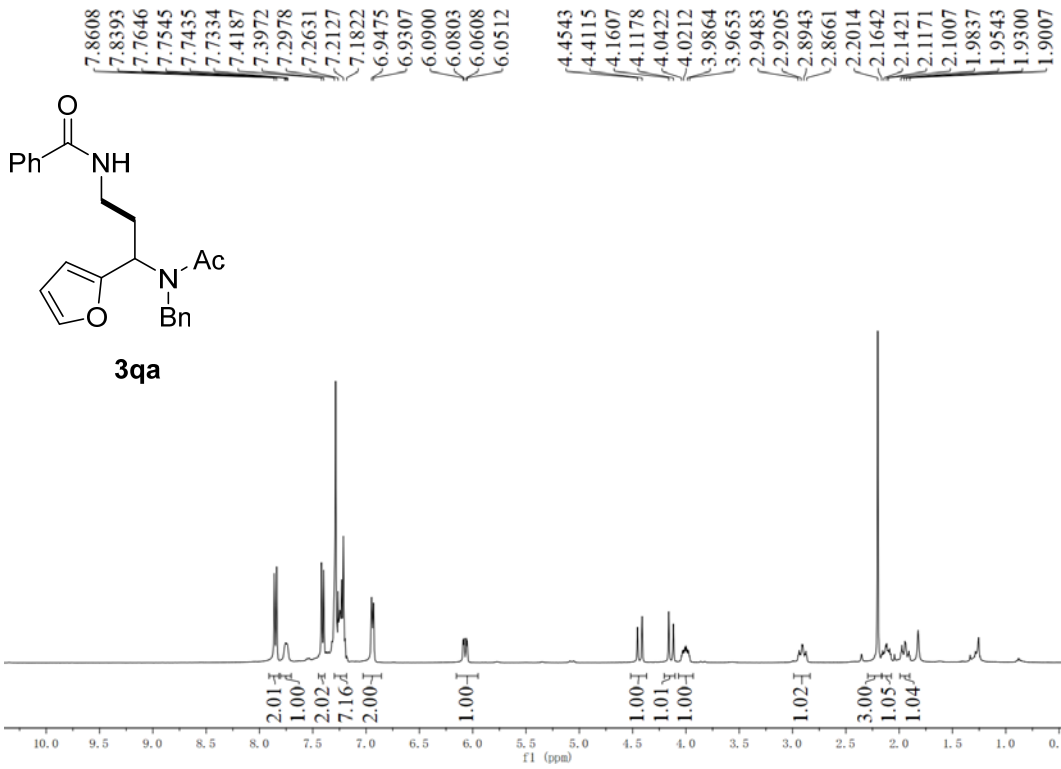
3oa

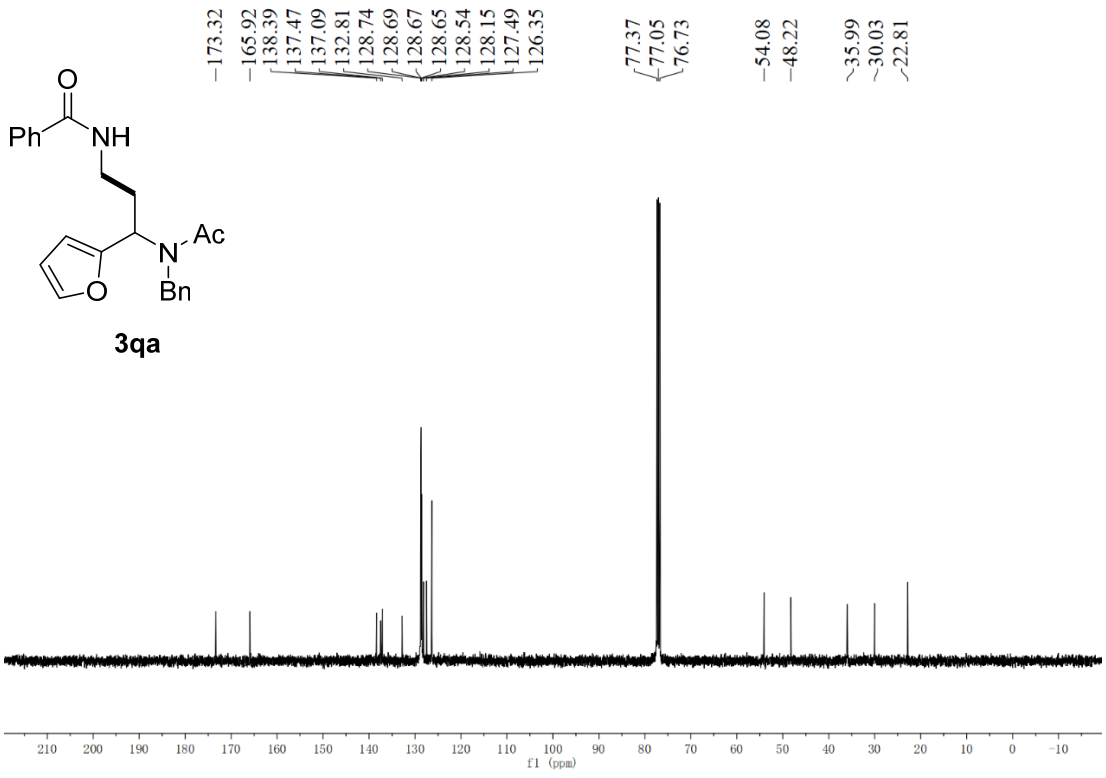

8.4006
8.3908
7.8949
7.8839
7.8741
7.5511
7.5410
7.5071
7.4787
7.4529
7.4326
7.4110
7.3092
7.2897
7.1394
7.1214
7.1180
7.0623
7.0504
7.0407
7.0285
6.8563
6.8402
6.1060
6.0923
6.0819
6.0681
4.7688
4.7253
4.4706
4.4270
4.0324
4.0093
3.9777
3.9546
3.0275
3.0026
2.9711
2.9461
2.3181
2.2947
2.2693
2.2440
2.1184
Ph
NH
N
N
Ac
Bn
1.00
1.98
2.02
3.05
1.03
3.08
1.02
1.99
1.00
1.00
1.00
1.00
1.00
2.06
3.00
f1 (ppm)

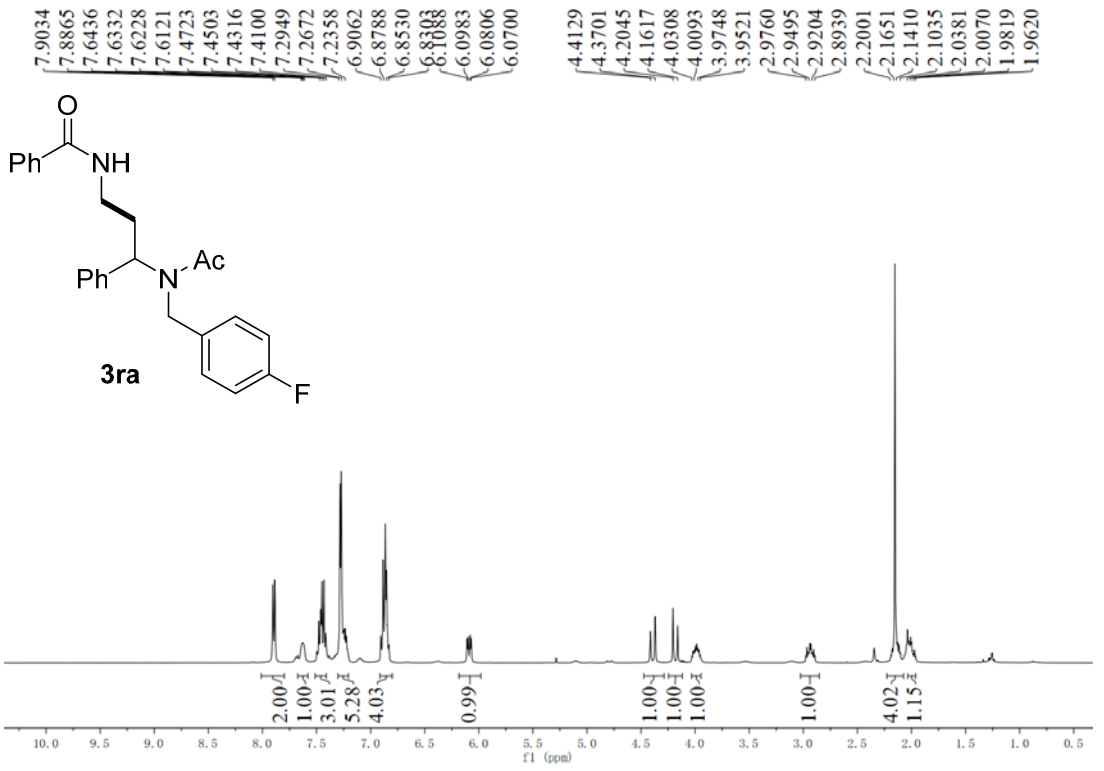
3pa

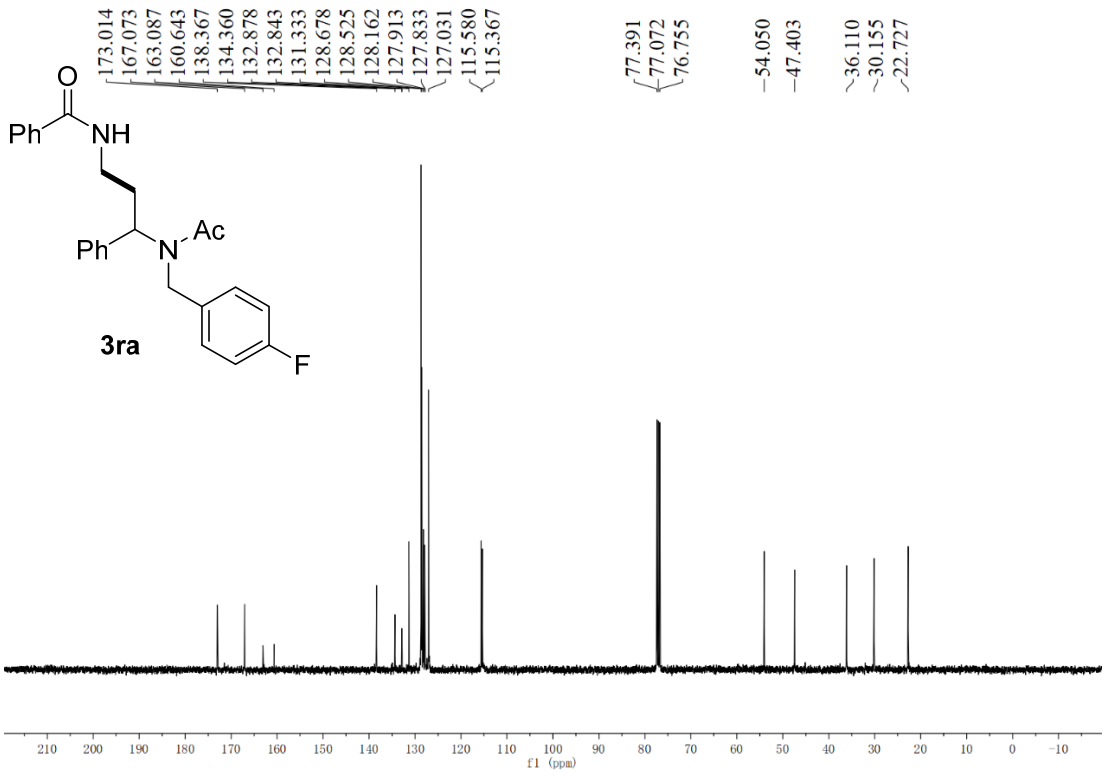

173.07
167.04
157.54
149.05
137.28
136.54
134.51
131.25
128.48
128.37
127.05
126.92
125.75
124.75
122.87
77.39
77.08
76.76
55.48
47.84
36.26
30.10
22.45
Ph
NH
N
N
Ac
Bn
f1 (ppm)

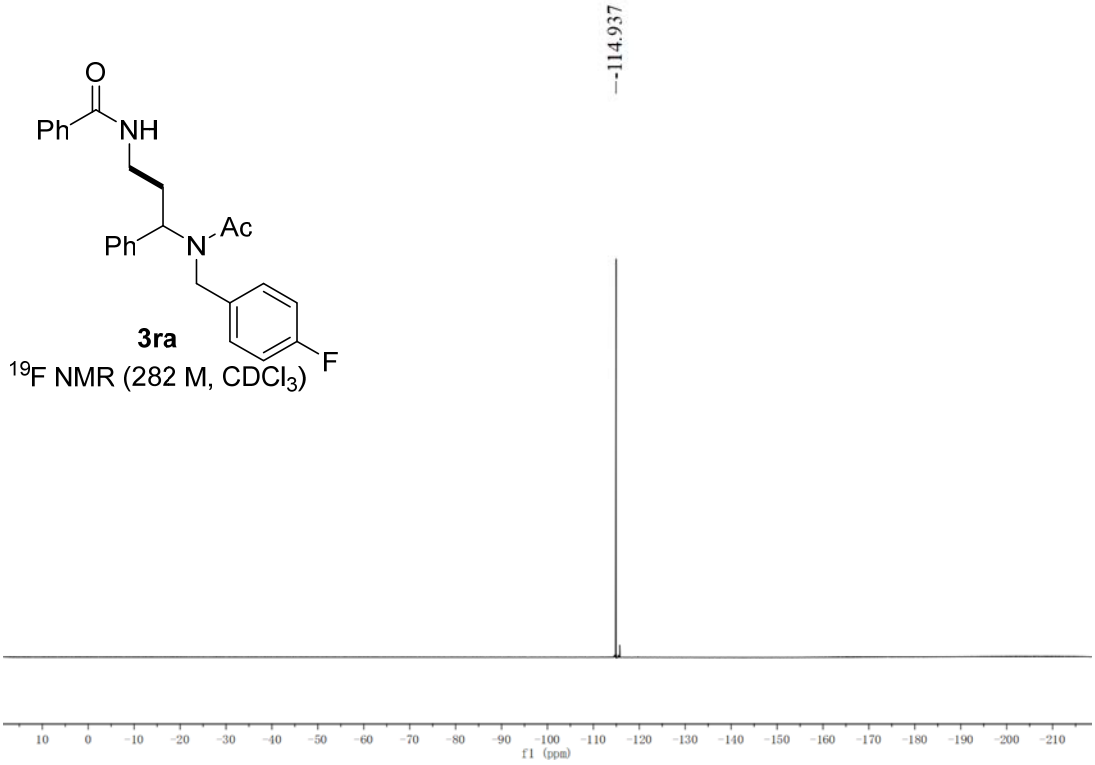
3pa

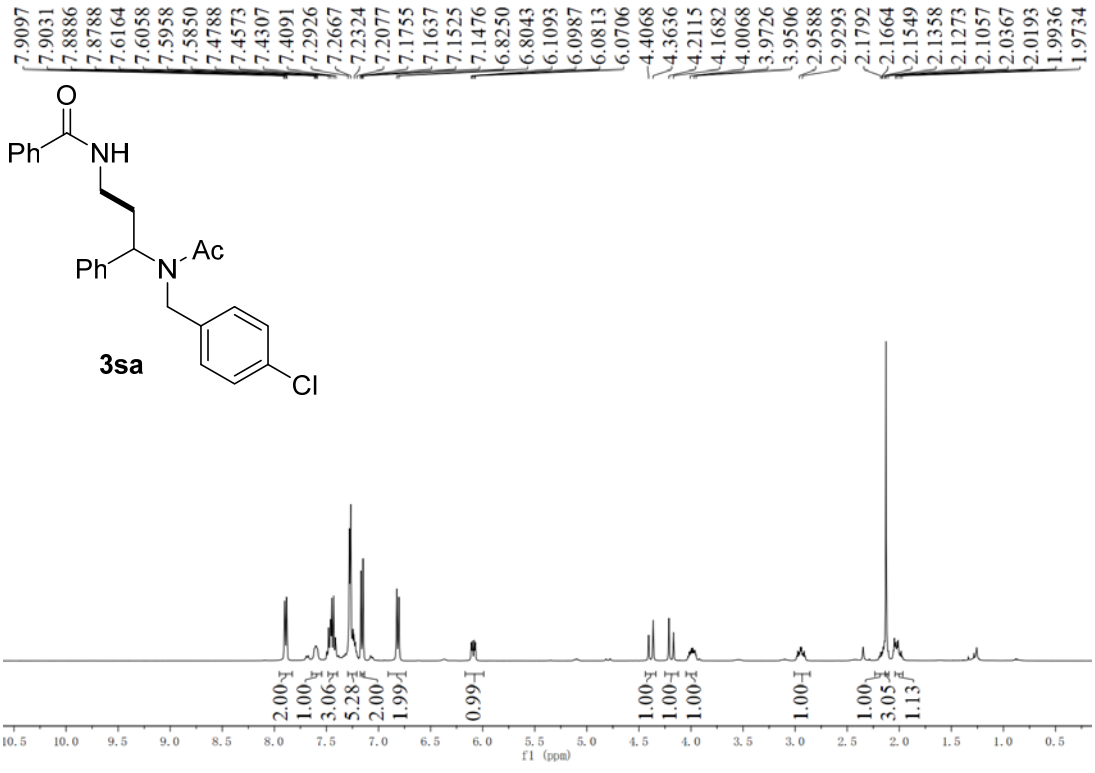

7.8608
7.8393
7.7646
7.7545
7.7435
7.7334
7.4187
7.3972
7.2978
7.2631
7.2127
7.1822
6.9475
6.9307
6.0900
6.0803
6.0608
6.0512
4.4543
4.4115
4.1607
4.1178
4.0422
4.0212
3.9864
3.9653
2.9483
2.9205
2.8943
2.8661
2.2014
2.1642
2.1421
2.1171
2.1007
1.9837
1.9543
1.9300
1.9007
Ph
NH
O
N
Ac
Bn
O
3qa
2.01
1.00
2.02
7.16
2.00
1.00
1.00
1.01
1.00
1.02
3.00
1.05
1.04
f1 (ppm)

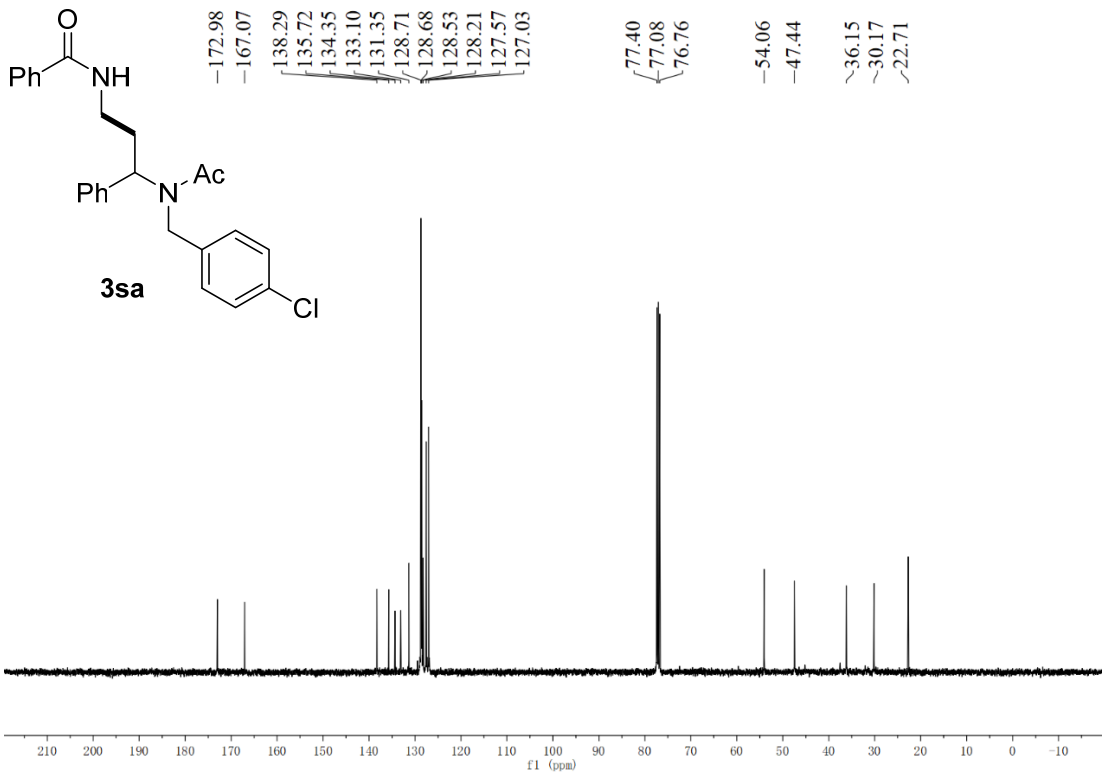

173.32
165.92
138.39
137.47
137.09
132.81
128.74
128.69
128.67
128.65
128.54
128.15
127.49
126.35
77.37
77.05
76.73
54.08
48.22
35.99
30.03
22.81
Ph
NH
O
N
Ac
Bn
O
3qa
f1 (ppm)

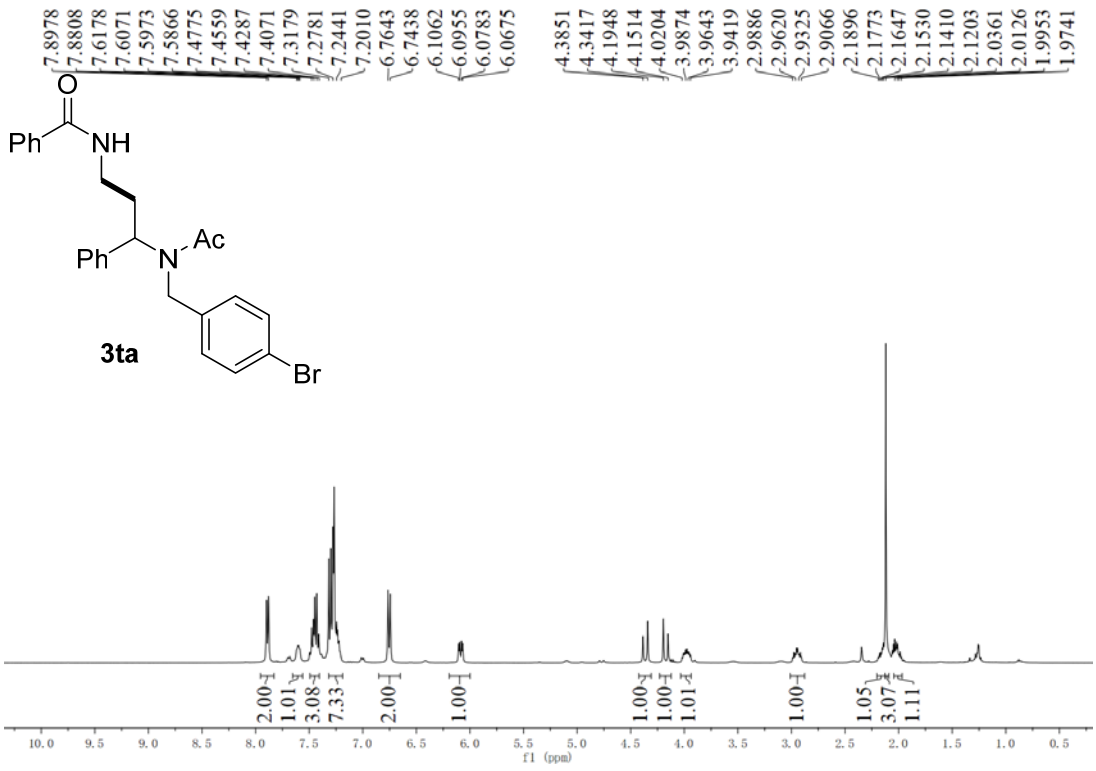

7.9034
7.8865
7.6436
7.6332
7.6228
7.6121
7.4723
7.4503
7.4316
7.4100
7.2949
7.2672
7.2358
6.9062
6.8788
6.8530
6.8303
6.1088
6.0983
6.0806
6.0700
4.4129
4.3701
4.2045
4.1617
4.0308
4.0093
3.9748
3.9521
2.9760
2.9495
2.9204
2.8939
2.2001
2.1651
2.1410
2.1035
2.0381
2.0070
1.9819
1.9620
O
Ph
NH
Ph
N
Ac
F
3ra
2.00
1.00
3.01
5.28
4.03
0.99
1.00
1.00
1.00
1.00
4.02
1.15
f1 (ppm)

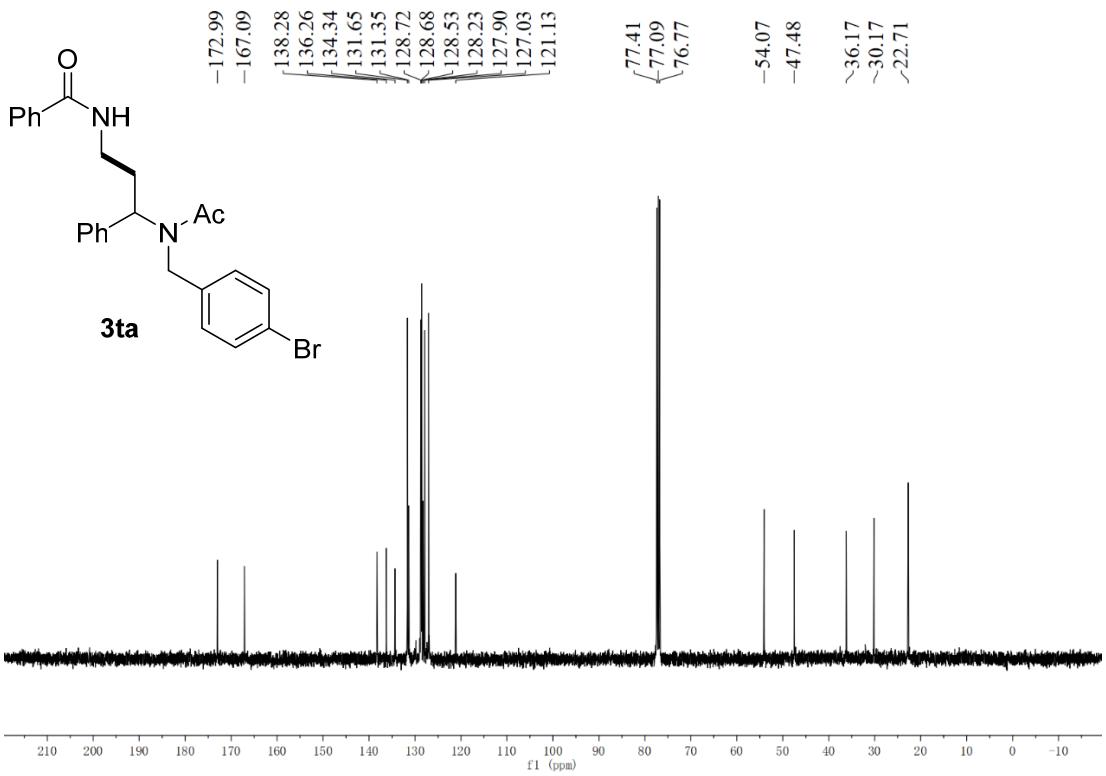

173.014
167.073
163.087
160.643
138.367
134.360
132.878
132.843
131.333
128.678
128.525
128.162
127.913
127.833
127.031
115.580
115.367
77.391
77.072
76.755
54.050
47.403
36.110
30.155
22.727
O
Ph
NH
Ph
N
Ac
F
3ra
f1 (ppm)

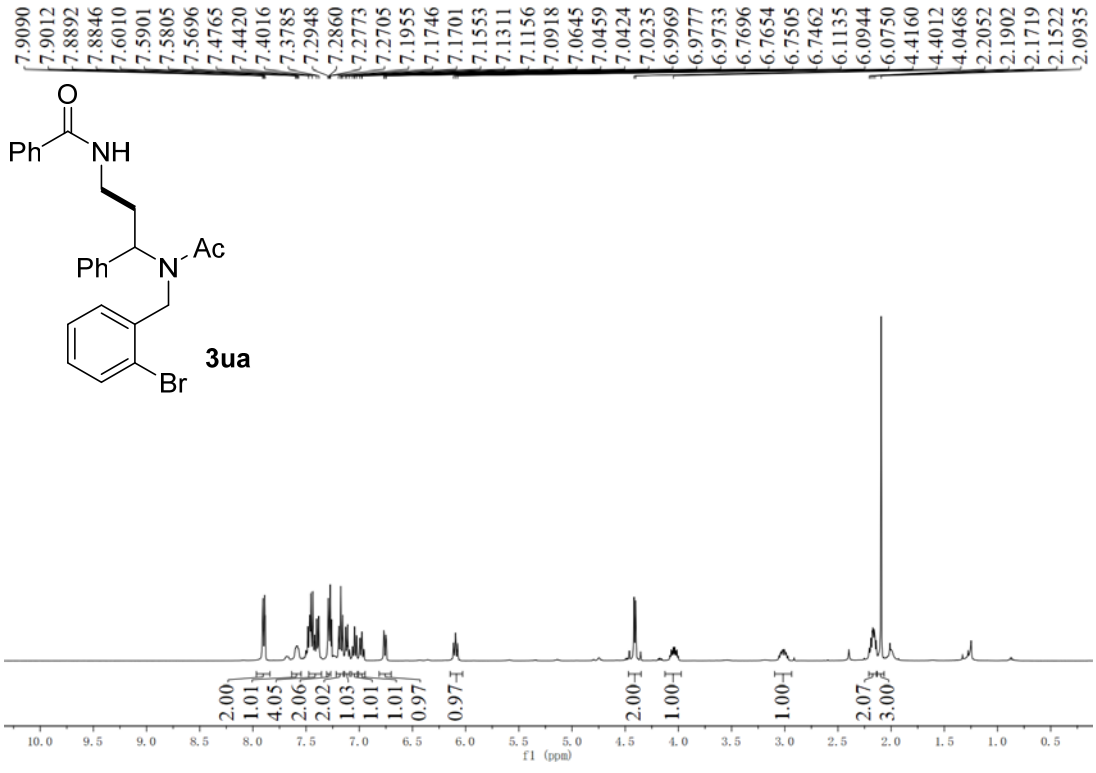

O
Ph
NH
Ph
N
Ac
F
3ra
^{19}F NMR (282 M, CDCl$_3$)
-114.937
f1 (ppm)

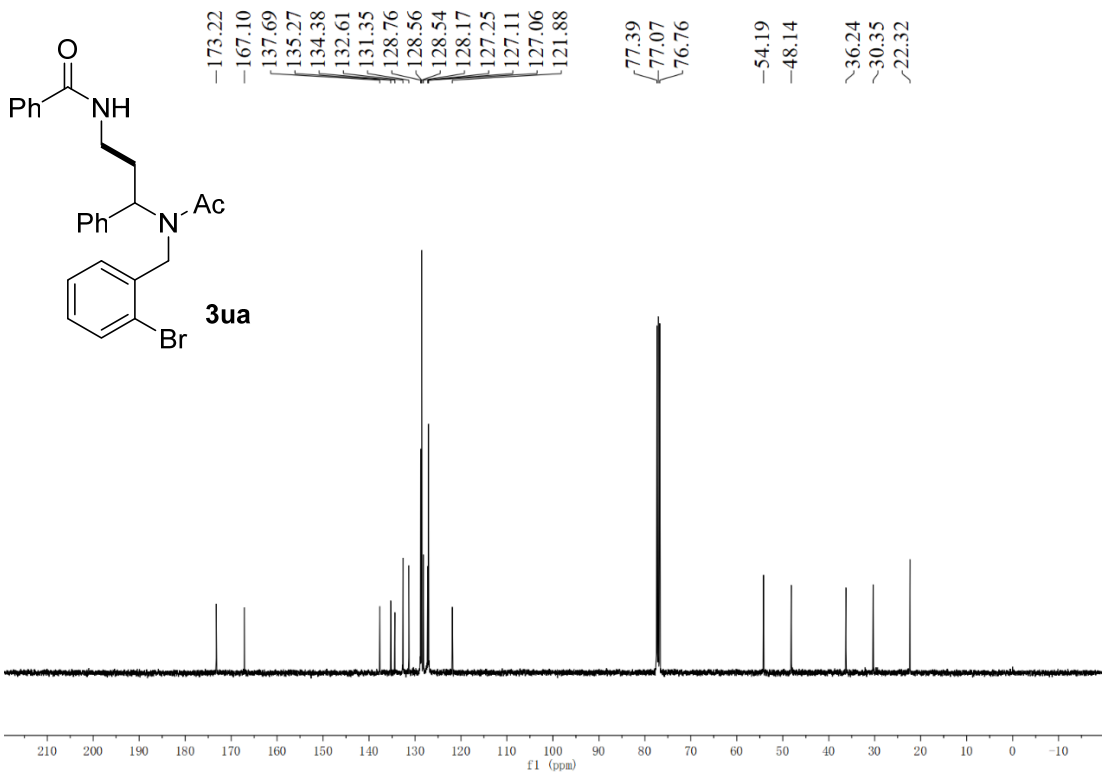

7.9097
7.9031
7.8886
7.8788
7.6164
7.6058
7.5958
7.5850
7.4788
7.4573
7.4307
7.4091
7.2926
7.2667
7.2324
7.2077
7.1755
7.1637
7.1525
7.1476
6.8250
6.8043
6.1093
6.0987
6.0813
6.0706
4.4068
4.3636
4.2115
4.1682
4.0068
3.9726
3.9506
2.9588
2.9293
2.1792
2.1664
2.1549
2.1358
2.1273
2.1057
2.0367
2.0193
1.9936
1.9734
O
Ph
NH
Ph
N
Ac
Cl
3sa
2.00
1.00
3.06
5.28
2.00
1.99
0.99
1.00
1.00
1.00
1.00
1.00
3.05
1.13
f1 (ppm)

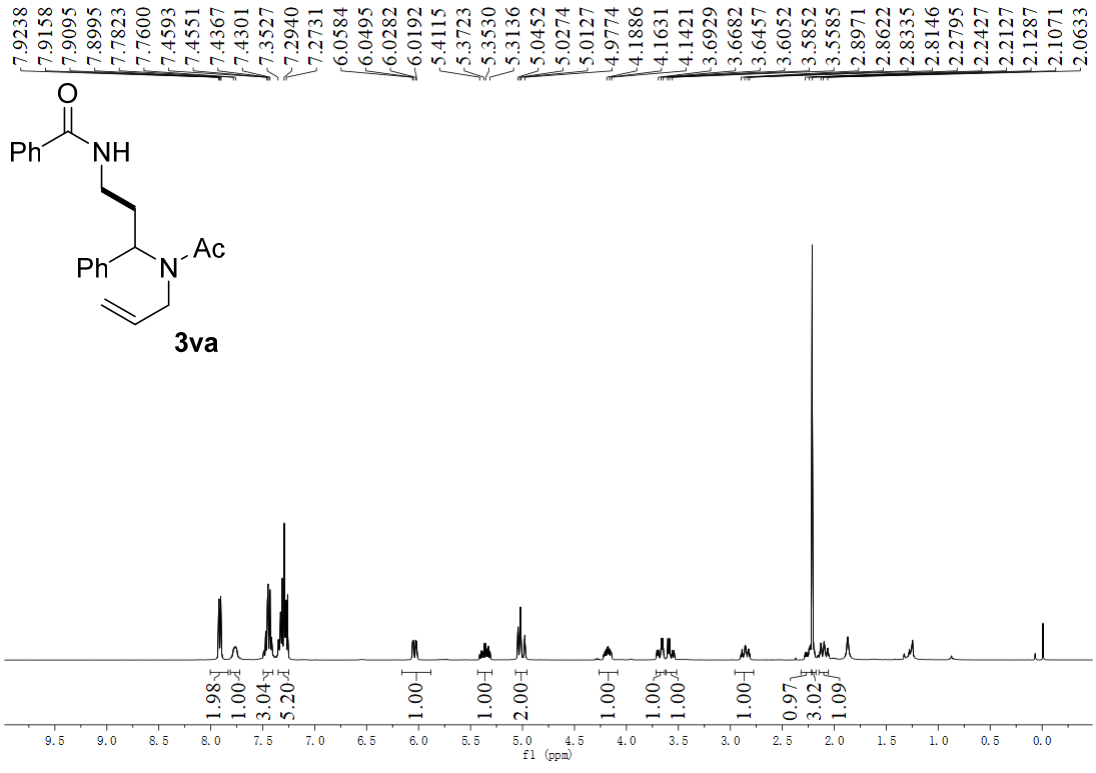

O
Ph
NH
Ph
N
Ac
Cl
3sa
172.98
167.07
138.29
135.72
134.35
133.10
131.35
128.71
128.68
128.53
128.21
127.57
127.03
77.40
77.08
76.76
54.06
47.44
36.15
30.17
22.71
f1 (ppm)

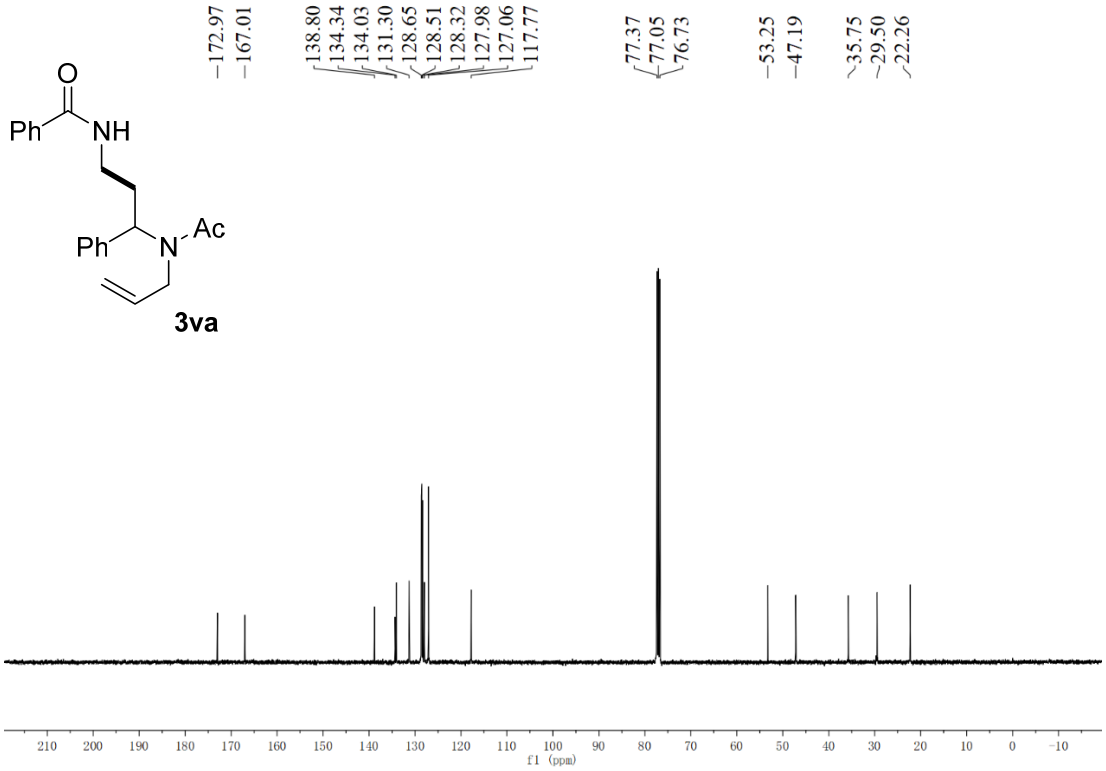

7.8978
7.8808
7.6178
7.6071
7.5973
7.5866
7.4775
7.4559
7.4287
7.4071
7.3179
7.2781
7.2441
7.2010
6.7643
6.7438
6.1062
6.0955
6.0783
6.0675
4.3851
4.3417
4.1948
4.1514
4.0204
3.9874
3.9643
3.9419
2.9886
2.9620
2.9325
2.9066
2.1896
2.1773
2.1647
2.1530
2.1410
2.1203
2.0361
2.0126
1.9953
1.9741
O
Ph
NH
Ph
N
Ac
Br
3ta
2.00
1.01
3.08
7.33
2.00
1.00
1.00
1.00
1.01
1.00
1.05
3.07
1.11
f1 (ppm)

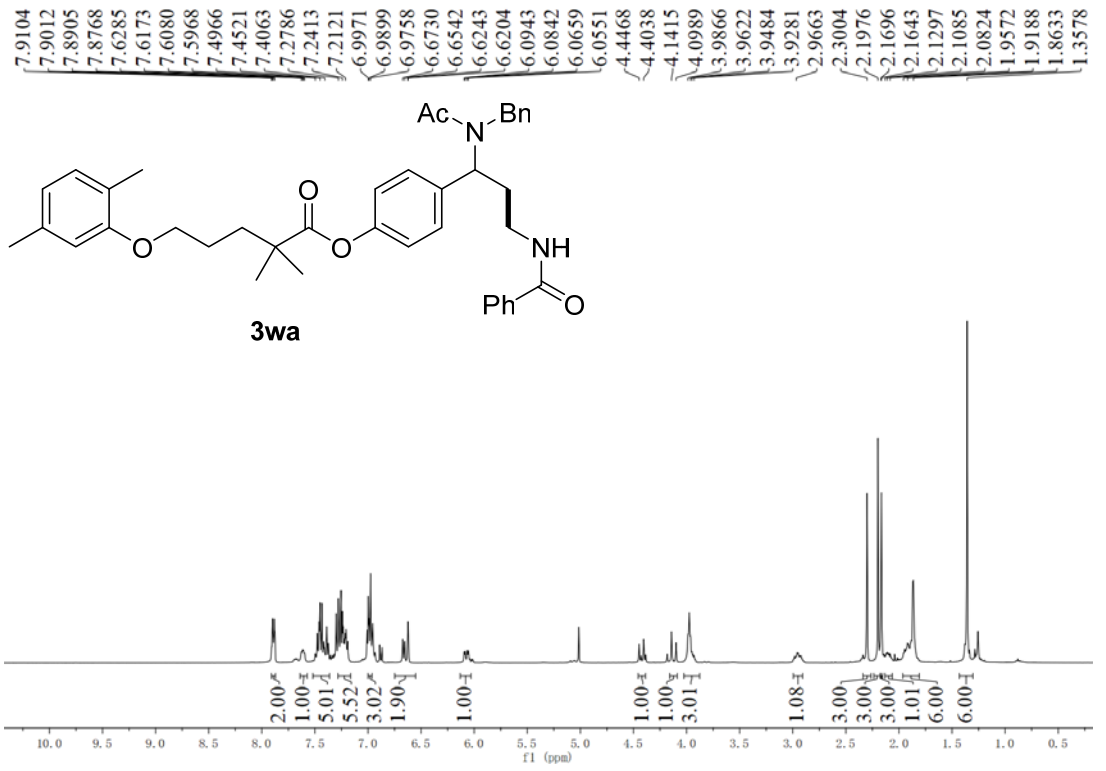

172.99
167.09
138.28
136.26
134.34
131.65
131.35
128.72
128.68
128.53
128.23
127.90
127.03
121.13
77.41
77.09
76.77
54.07
47.48
36.17
30.17
22.71
O
Ph
NH
Ph
N
Ac
Br
3ta
f1 (ppm)

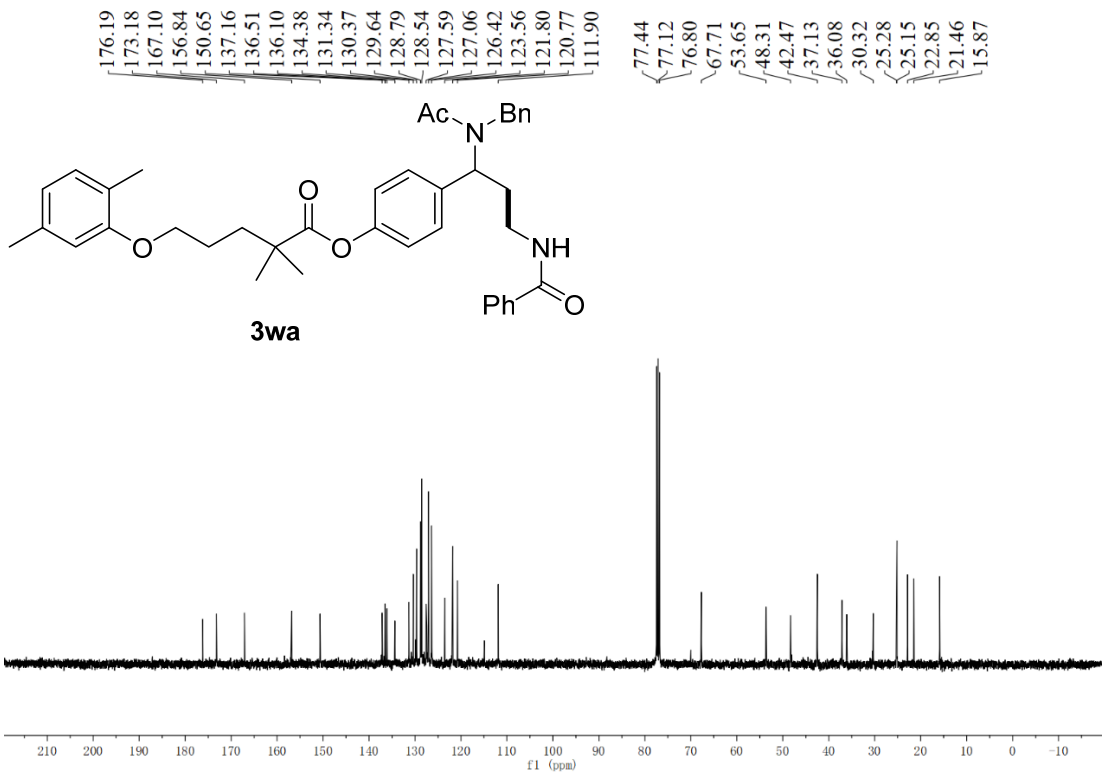

7.9090
7.9012
7.8892
7.8846
7.6010
7.5901
7.5805
7.5696
7.4765
7.4420
7.4016
7.3785
7.2948
7.2860
7.2773
7.2705
7.1955
7.1746
7.1701
7.1553
7.1311
7.1156
7.0918
7.0645
7.0459
7.0424
7.0235
6.9969
6.9777
6.9733
6.7696
6.7654
6.7505
6.7462
6.1135
6.0944
6.0750
4.4160
4.4012
4.0468
2.2052
2.1902
2.1719
2.1522
2.0935
O
Ph
NH
Ph
N
Ac
Br
3ua
2.00
1.01
4.05
2.06
2.02
1.03
1.01
1.01
0.97
0.97
2.00
1.00
1.00
2.07
3.00
f1 (ppm)

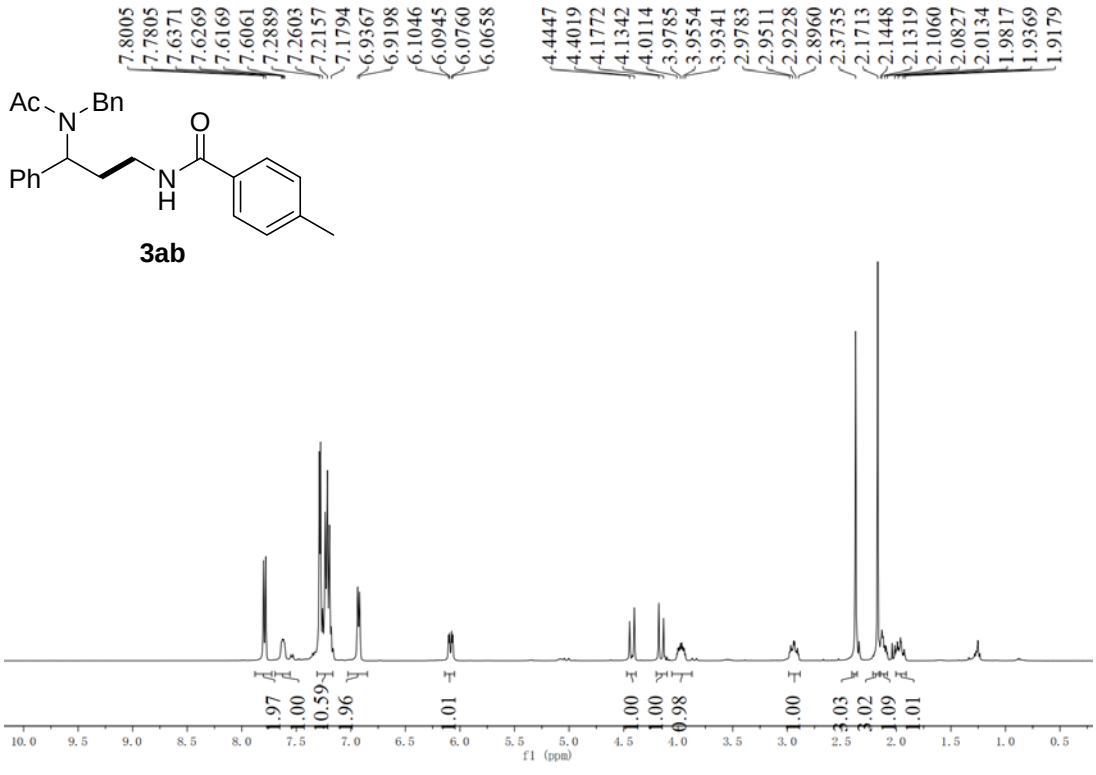

173.22
167.10
137.69
135.27
134.38
132.61
131.35
128.76
128.56
128.54
128.17
127.25
127.11
127.06
121.88
77.39
77.07
76.76
54.19
48.14
36.24
30.35
22.32
O
Ph
NH
Ph
N
Ac
Br
3ua
f1 (ppm)

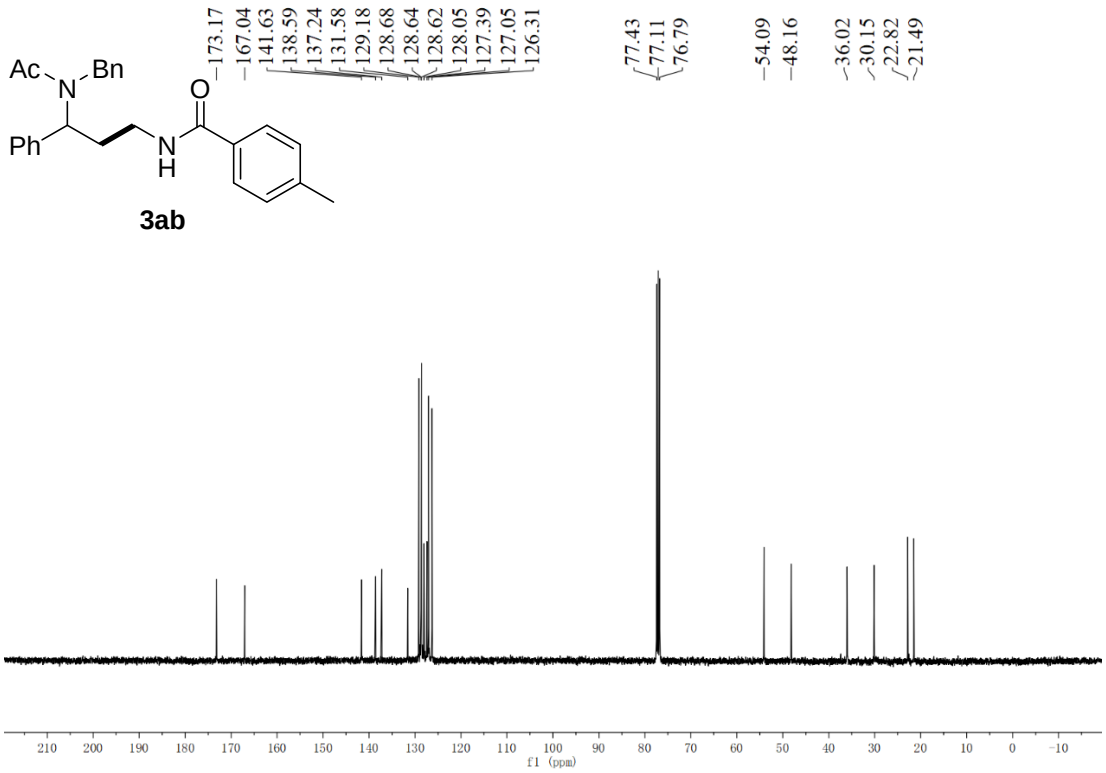

7.9238
7.9158
7.9095
7.8995
7.7823
7.7600
7.4593
7.4551
7.4367
7.4301
7.3527
7.2940
7.2731
6.0584
6.0495
6.0282
6.0192
5.4115
5.3723
5.3530
5.3136
5.0452
5.0274
5.0127
4.9774
4.1886
4.1631
4.1421
3.6929
3.6682
3.6457
3.6052
3.5852
3.5585
2.8971
2.8622
2.8335
2.8146
2.2795
2.2427
2.2127
2.1287
2.1071
2.0633
O
Ph
NH
Ph
N
Ac
3va
1.98
1.00
3.04
5.20
1.00
1.00
2.00
1.00
1.00
1.00
1.00
0.97
3.02
1.09
f1 (ppm)


172.97
167.01
138.80
134.34
134.03
131.30
128.65
128.51
128.32
127.98
127.06
117.77
77.37
77.05
76.73
53.25
47.19
35.75
29.50
22.26
O
Ph
NH
Ph
N
Ac
3va
f1 (ppm)

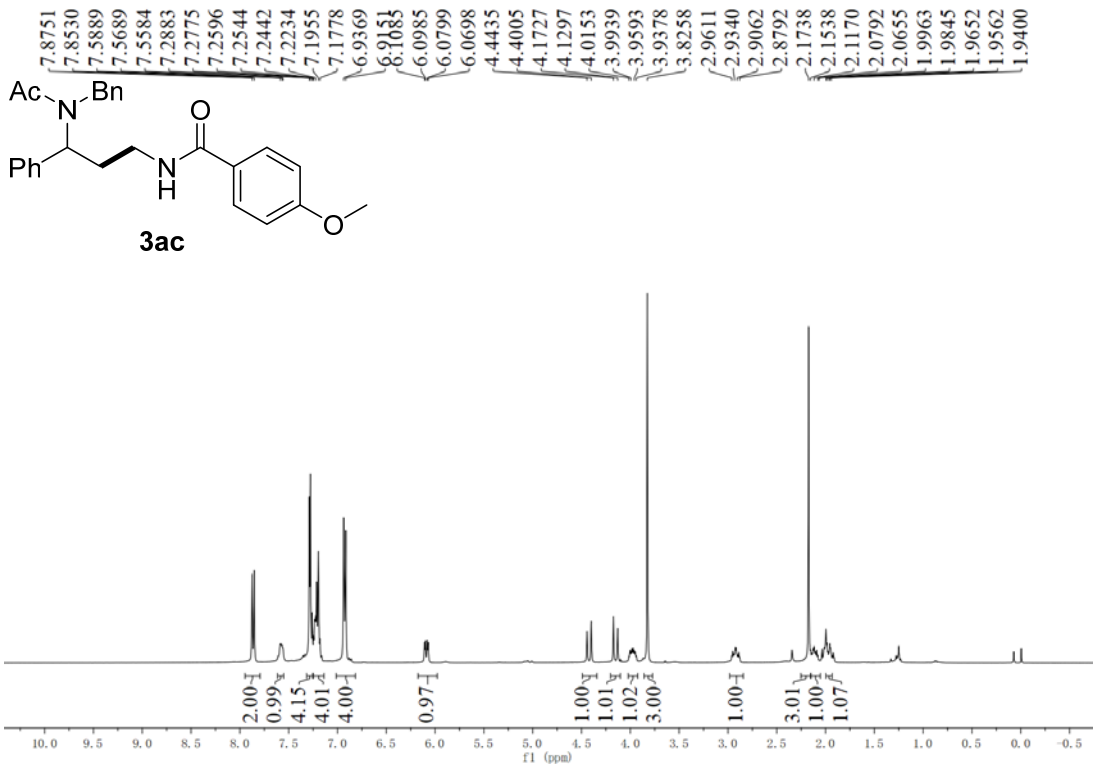

7.9104
7.9012
7.8905
7.8768
7.6285
7.6173
7.6080
7.5968
7.4966
7.4521
7.4063
7.2786
7.2413
7.2121
6.9971
6.9899
6.9758
6.6730
6.6542
6.6243
6.6204
6.0943
6.0842
6.0659
6.0551
4.4468
4.4038
4.1415
4.0989
3.9866
3.9622
3.9484
3.9281
2.9663
2.3004
2.1976
2.1696
2.1643
2.1297
2.1085
2.0824
1.9572
1.9188
1.8633
1.3578
Ac
N
Bn
O
O
O
NH
Ph
O
3wa
2.00
1.00
5.01
5.52
3.02
1.90
1.00
1.00
1.00
3.01
1.08
3.00
3.00
3.00
1.01
6.00
6.00
f1 (ppm)


176.19
173.18
167.10
156.84
150.65
137.16
136.51
136.10
134.38
131.34
130.37
129.64
128.79
128.54
127.59
127.06
126.42
123.56
121.80
120.77
111.90
77.44
77.12
76.80
67.71
53.65
48.31
42.47
37.13
36.08
30.32
25.28
25.15
22.85
21.46
15.87
Ac
N
Bn
O
O
O
NH
Ph
O
3wa
f1 (ppm)

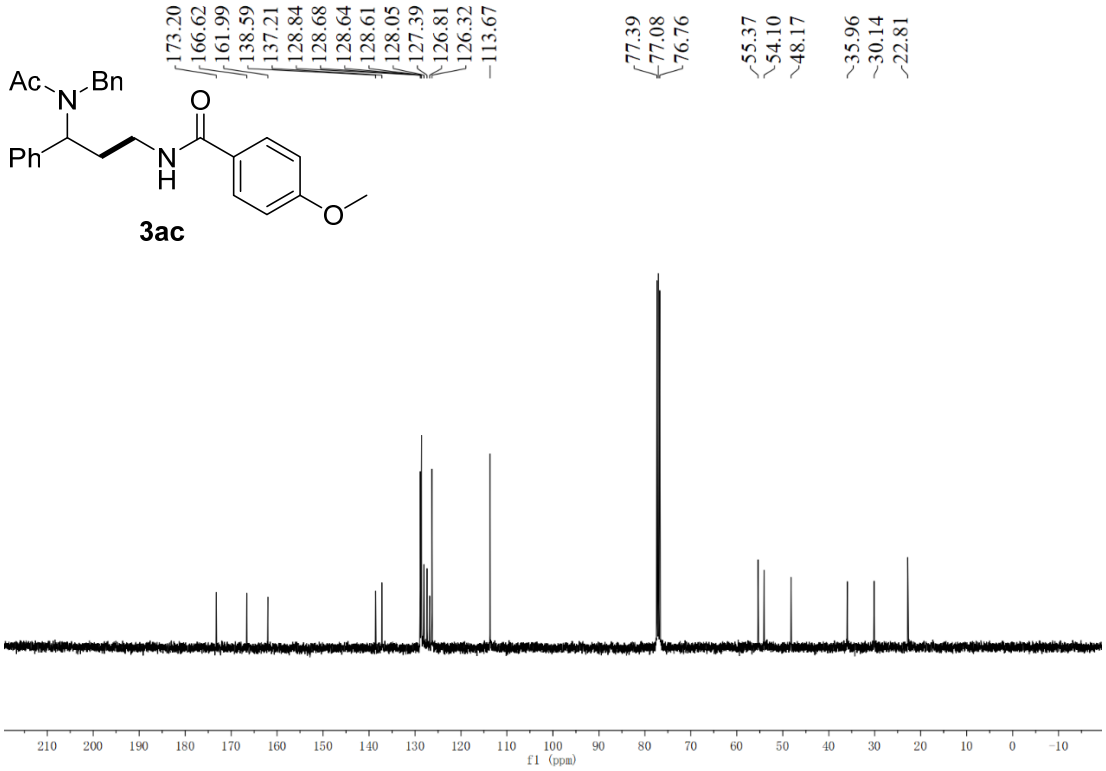

7.8005
7.7805
7.6371
7.6269
7.6169
7.6061
7.2889
7.2603
7.2157
7.1794
6.9367
6.9198
6.1046
6.0945
6.0760
6.0658
4.4447
4.4019
4.1772
4.1342
4.0114
3.9785
3.9554
3.9341
2.9783
2.9511
2.9228
2.8960
2.3735
2.1713
2.1448
2.1319
2.1060
2.0827
2.0134
1.9817
1.9369
1.9179
Ac
N
Bn
Ph
N
H
O
3ab
1.97
1.00
10.59
1.96
1.01
1.00
1.00
0.98
1.00
3.03
3.02
1.09
1.01
f1 (ppm)

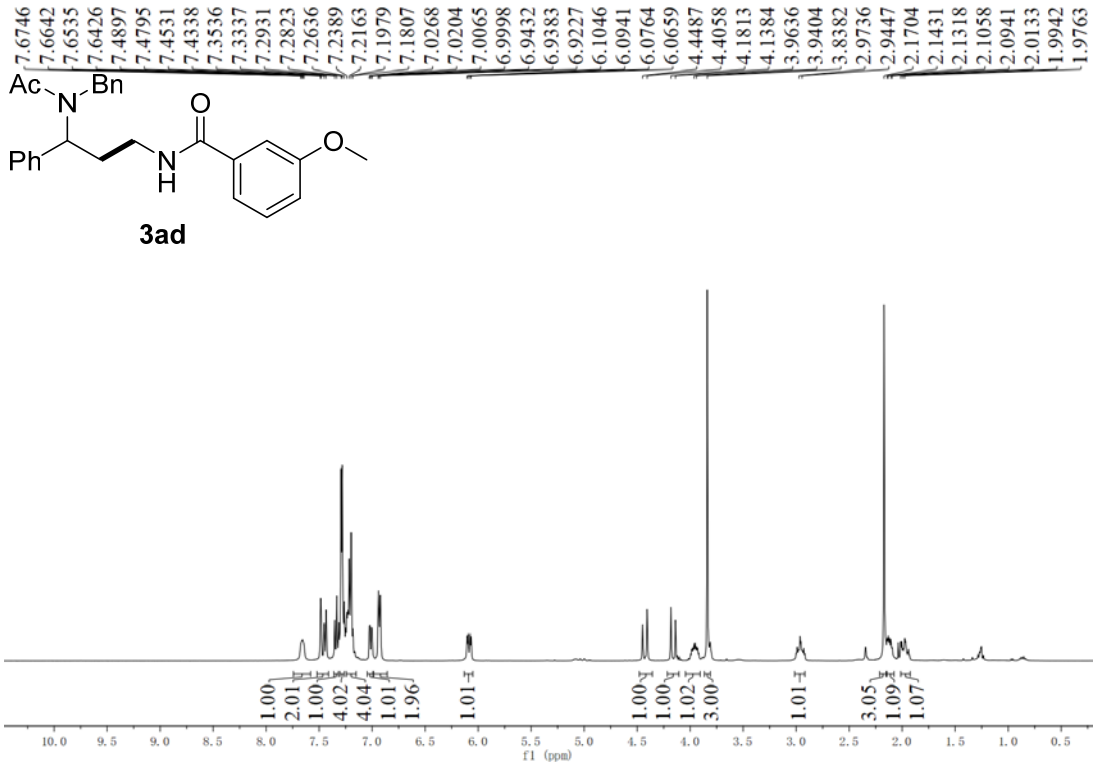

173.17
167.04
141.63
138.59
137.24
131.58
129.18
128.68
128.64
128.62
128.05
127.39
127.05
126.31
77.43
77.11
76.79
54.09
48.16
36.02
30.15
22.82
21.49
Ac
N
Bn
Ph
O
N
H
f1 (ppm)

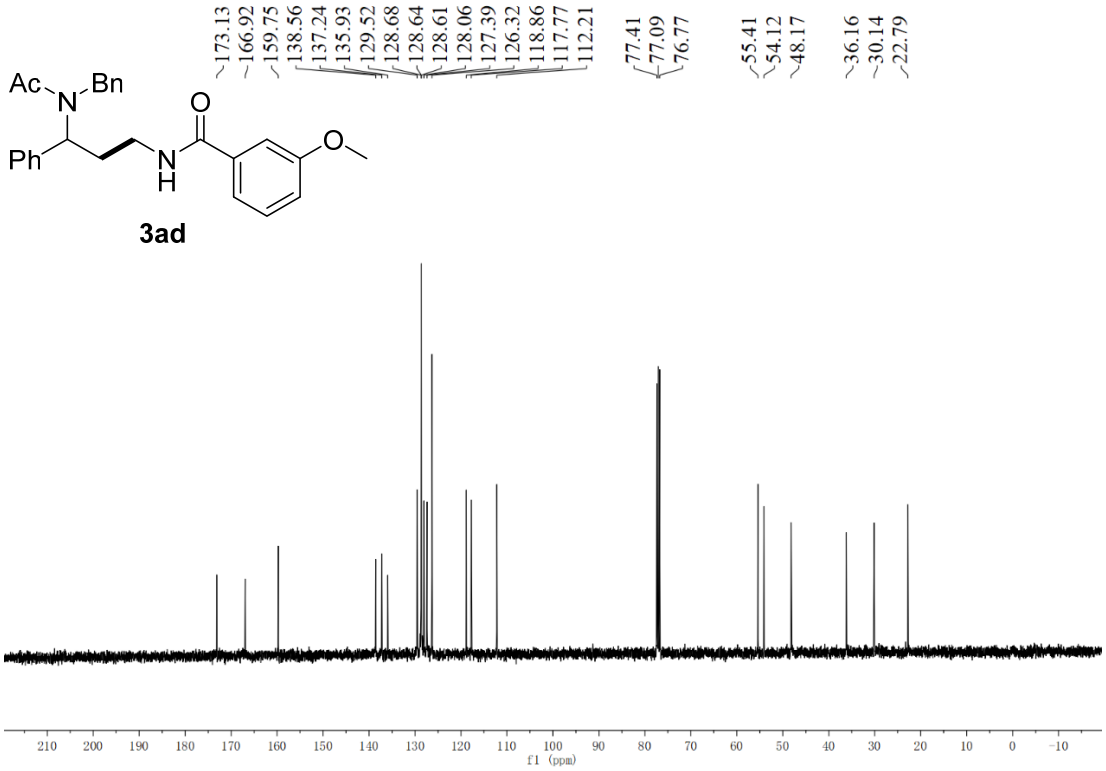
3ab


7.8751
7.8530
7.5889
7.5689
7.5584
7.2883
7.2775
7.2596
7.2544
7.2442
7.2234
7.1955
7.1778
6.9369
6.9151
6.1085
6.0985
6.0799
6.0698
4.4435
4.4005
4.1727
4.1297
4.0153
3.9939
3.9593
3.9378
3.8258
2.9611
2.9340
2.9062
2.8792
2.1738
2.1538
2.1170
2.0792
2.0655
1.9963
1.9845
1.9652
1.9562
1.9400
Ac
N
Bn
Ph
O
N
H
O
2.00
0.99
4.15
4.01
4.00
0.97
1.00
1.01
1.02
3.00
1.00
3.01
1.00
1.07
f1 (ppm)

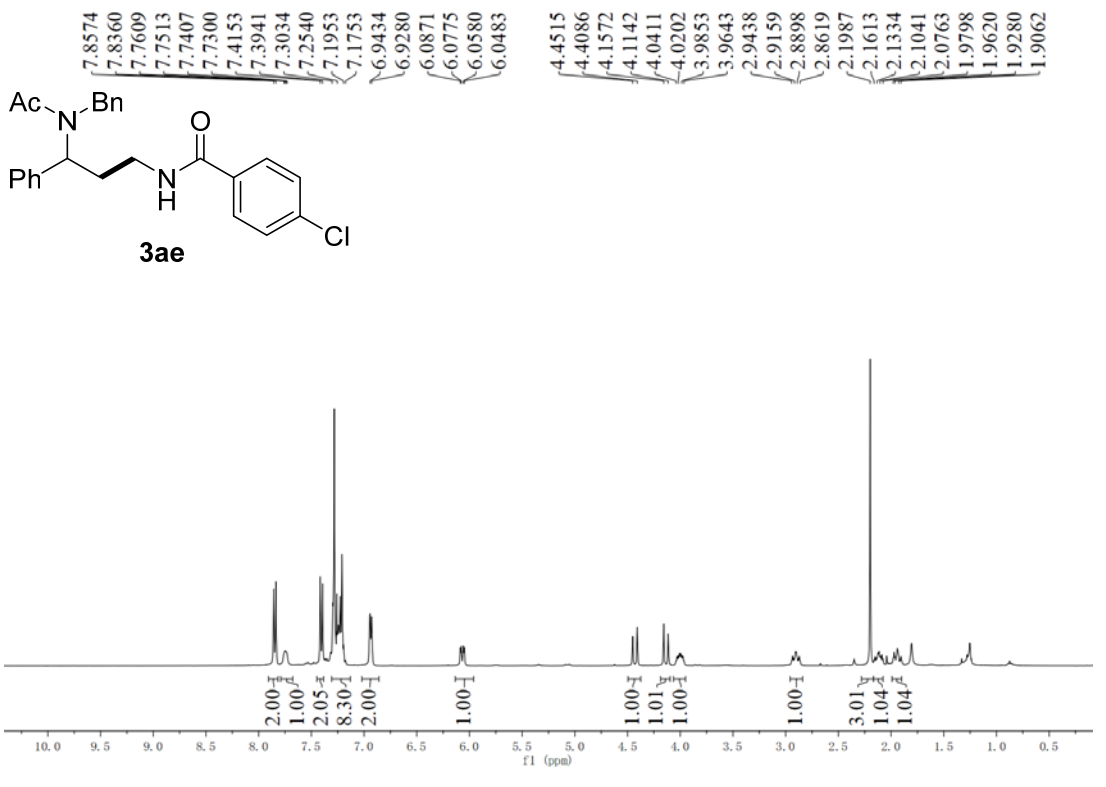
3ac


173.20
166.62
161.99
138.59
137.21
128.84
128.68
128.64
128.61
128.05
127.39
126.81
126.32
113.67
77.39
77.08
76.76
55.37
54.10
48.17
35.96
30.14
22.81
Ac
N
Bn
Ph
O
N
H
O
3ac
f1 (ppm)

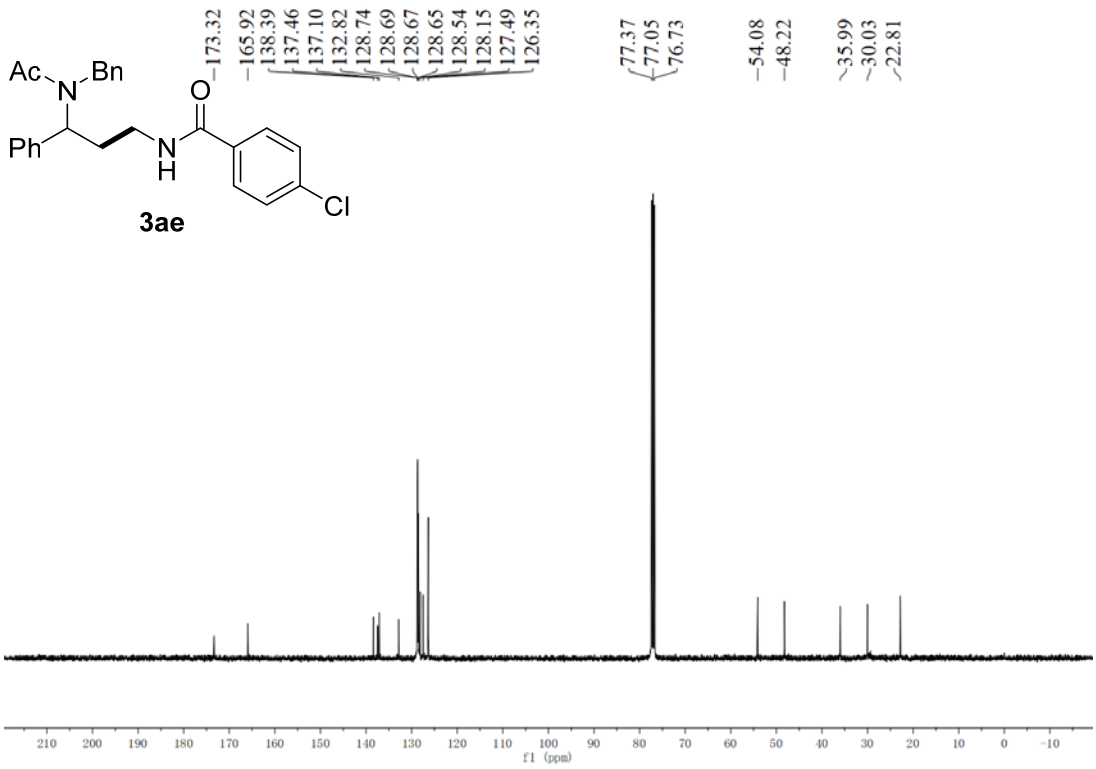

7.6746
7.6642
7.6535
7.6426
7.4897
7.4795
7.4531
7.4338
7.3536
7.3337
7.2931
7.2823
7.2636
7.2389
7.2163
7.1979
7.1807
7.0268
7.0204
7.0065
6.9998
6.9432
6.9383
6.9227
6.1046
6.0941
6.0764
6.0659
4.4487
4.4058
4.1813
4.1384
3.9636
3.9404
3.8382
2.9736
2.9447
2.1704
2.1431
2.1318
2.1058
2.0941
2.0133
1.9942
1.9763
Ac
N
Bn
Ph
O
N
H
O
3ad
1.00
2.01
1.00
4.02
4.04
1.01
1.96
1.01
1.00
1.00
1.02
3.00
1.01
3.05
1.09
1.07
f1 (ppm)

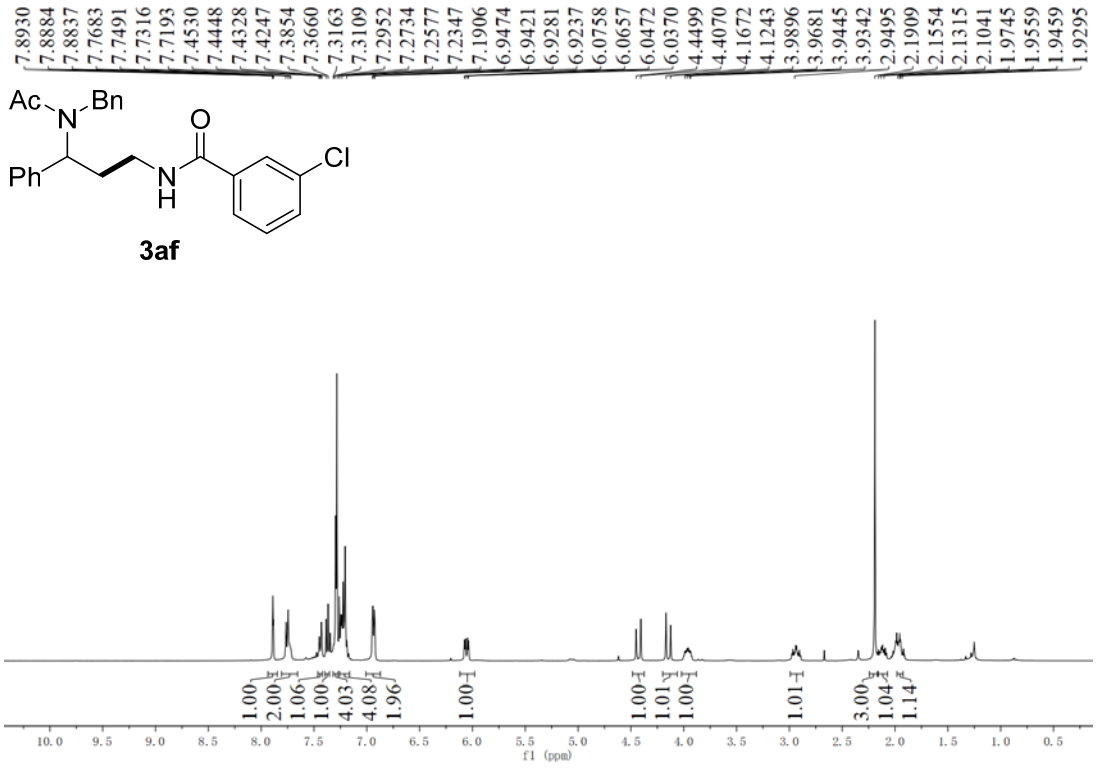

173.13
166.92
159.75
138.56
137.24
135.93
129.52
128.68
128.64
128.61
128.06
127.39
126.32
118.86
117.77
112.21
77.41
77.09
76.77
55.41
54.12
48.17
36.16
30.14
22.79
Ac
N
Bn
Ph
O
N
H
O
f1 (ppm)

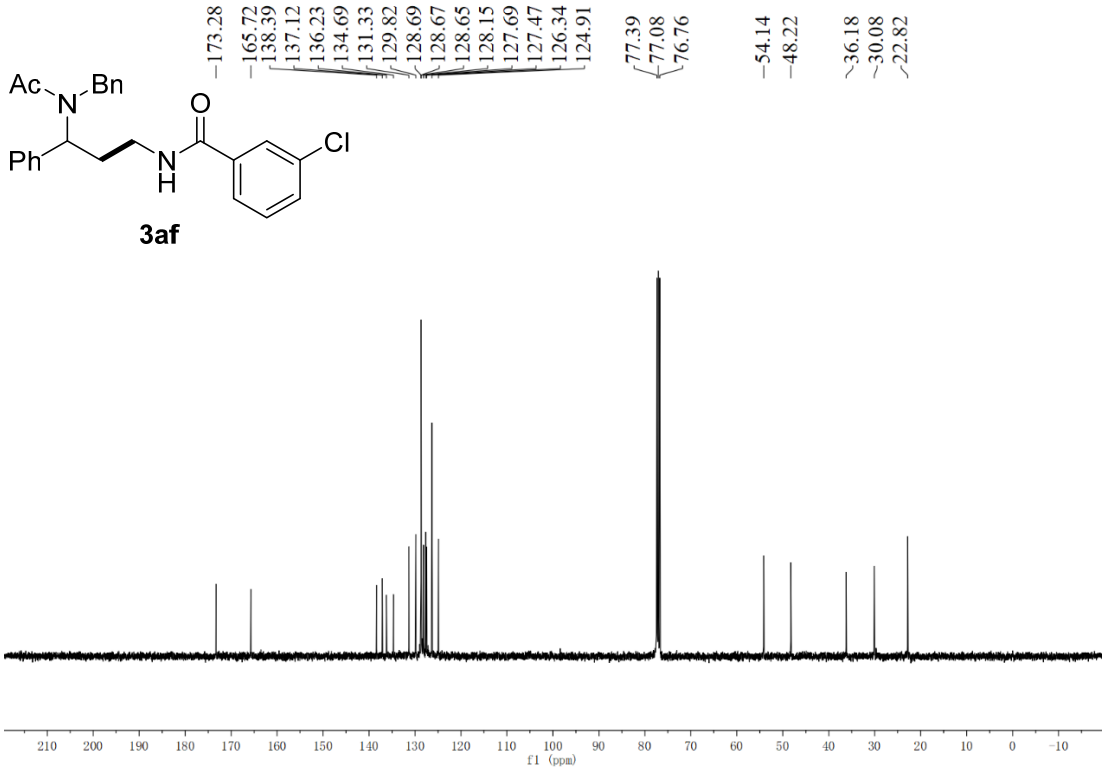
3ad


7.8574
7.8360
7.7609
7.7513
7.7407
7.7300
7.4153
7.3941
7.3034
7.2540
7.1953
7.1753
6.9434
6.9280
6.0871
6.0775
6.0580
6.0483
4.4515
4.4086
4.1572
4.1142
4.0411
4.0202
3.9853
3.9643
2.9438
2.9159
2.8898
2.8619
2.1987
2.1613
2.1334
2.1041
2.0763
1.9798
1.9620
1.9280
1.9062
Ac
N
Bn
Ph
O
N
H
Cl
2.00
1.00
2.05
8.30
2.00
1.00
1.00
1.01
1.00
1.00
3.01
1.04
1.04
f1 (ppm)

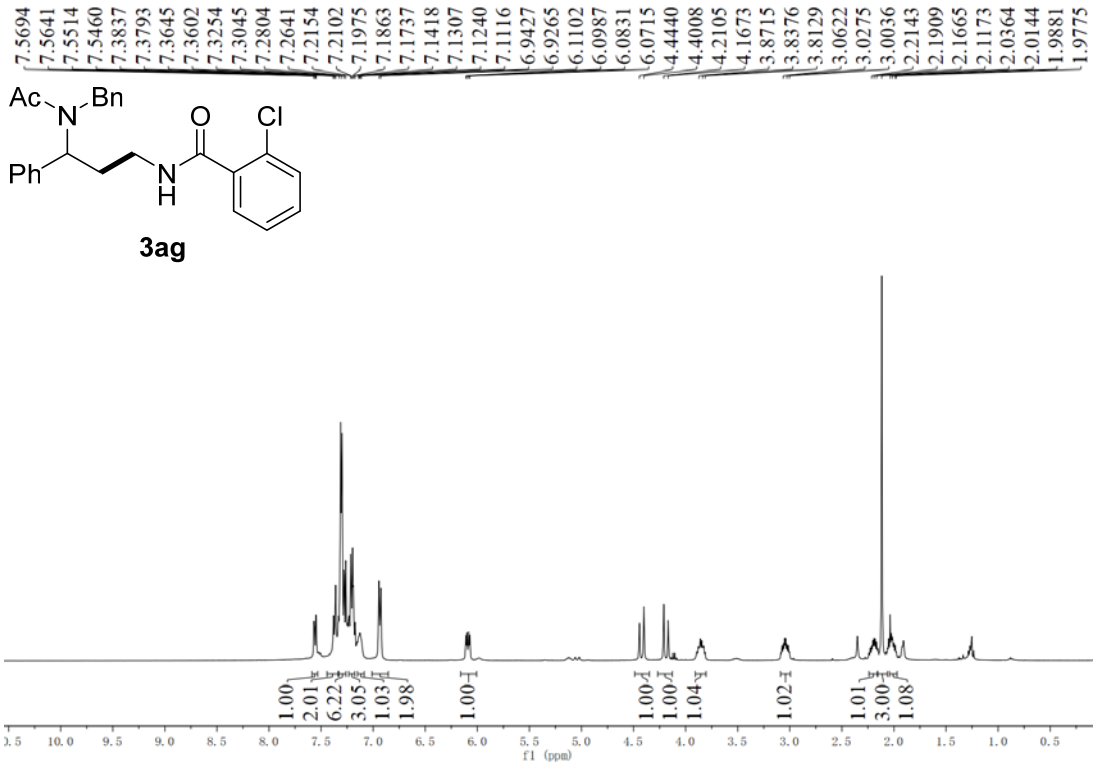
3ae


173.32
165.92
138.39
137.46
137.10
132.82
128.74
128.69
128.67
128.65
128.54
128.15
127.49
126.35
77.37
77.05
76.73
54.08
48.22
35.99
30.03
22.81
Ac
N
Bn
Ph
O
N
H
Cl
3ae
f1 (ppm)

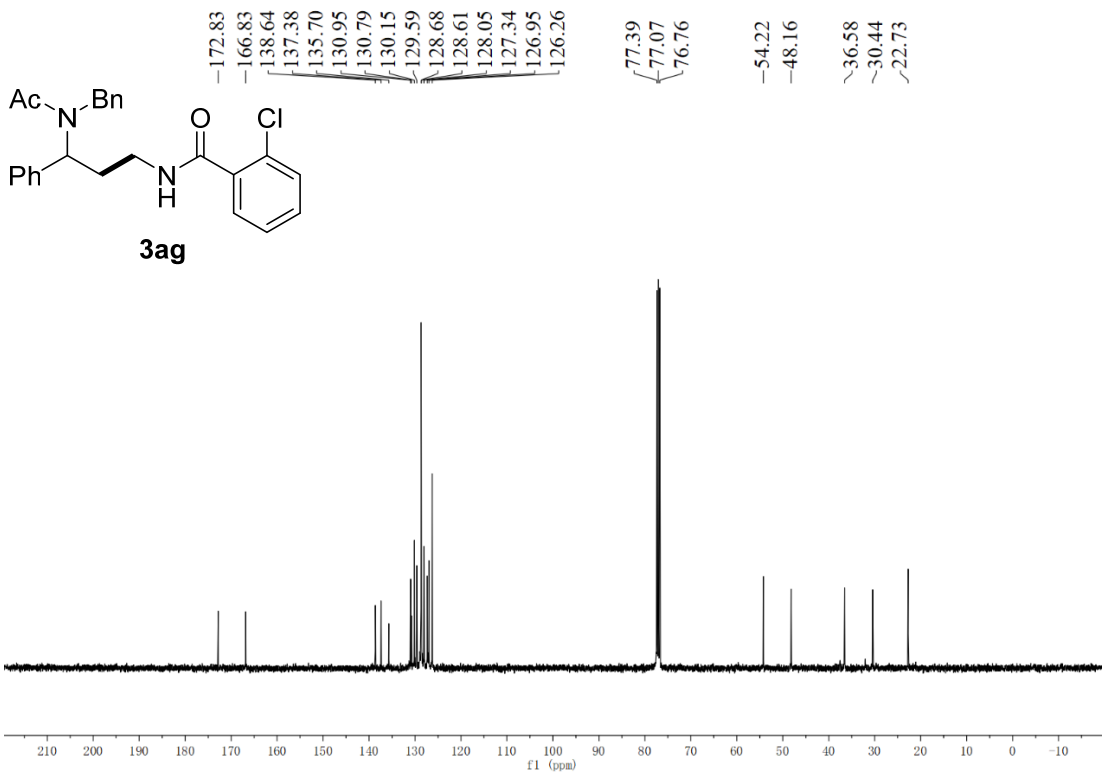

7.8930
7.8884
7.8837
7.7683
7.7491
7.7316
7.7193
7.4530
7.4448
7.4328
7.4247
7.3854
7.3660
7.3163
7.3109
7.2952
7.2734
7.2577
7.2347
7.1906
6.9474
6.9421
6.9281
6.9237
6.0758
6.0657
6.0472
6.0370
4.4499
4.4070
4.1672
4.1243
3.9896
3.9681
3.9445
3.9342
2.9495
2.1909
2.1554
2.1315
2.1041
1.9745
1.9559
1.9459
1.9295
Ac
N
Bn
Ph
O
N
H
Cl
3af
1.00
2.00
1.06
1.00
4.03
4.08
1.96
1.00
1.00
1.01
1.00
1.01
3.00
1.04
1.14
f1 (ppm)

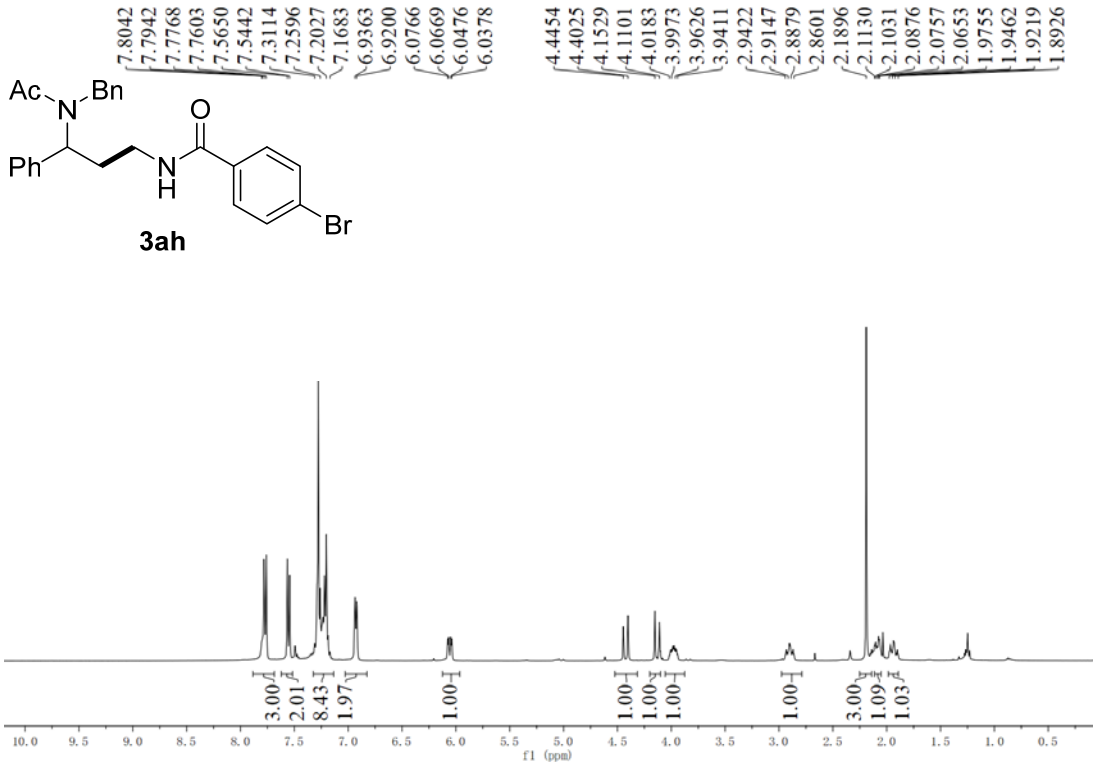

173.28
165.72
138.39
137.12
136.23
134.69
131.33
129.82
128.69
128.67
128.65
128.15
127.69
127.47
126.34
124.91
77.39
77.08
76.76
54.14
48.22
36.18
30.08
22.82
Ac
N
Bn
Ph
O
N
H
Cl
f1 (ppm)

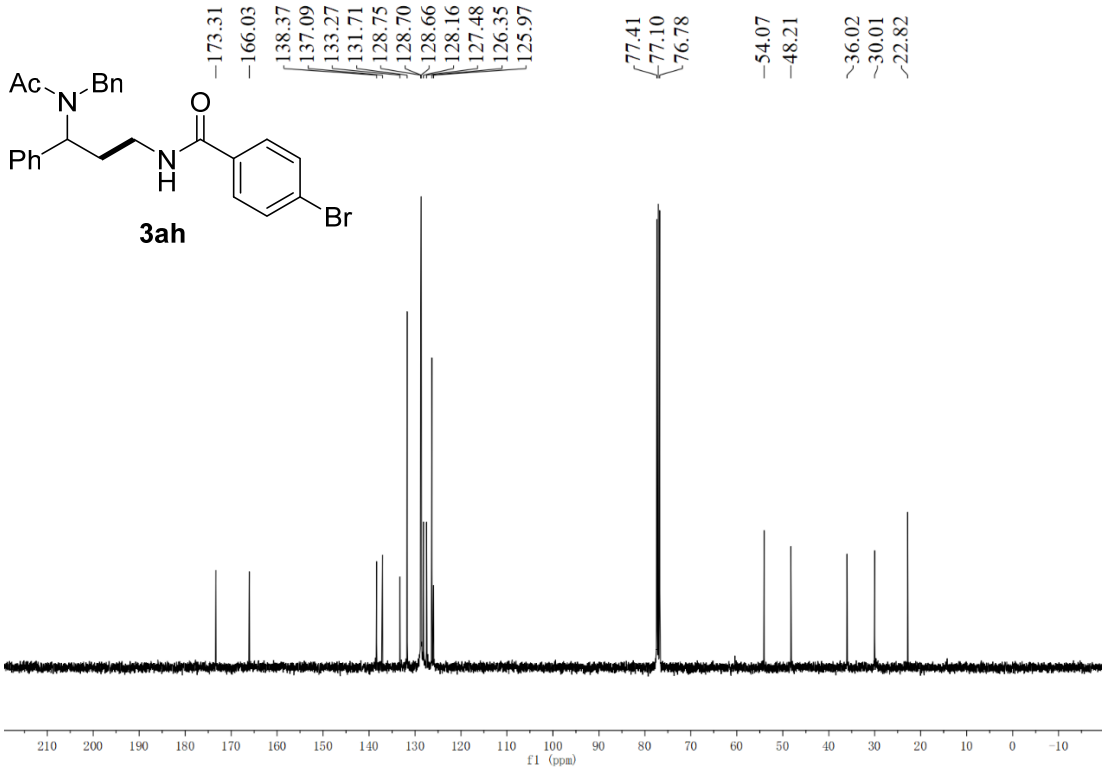
3af

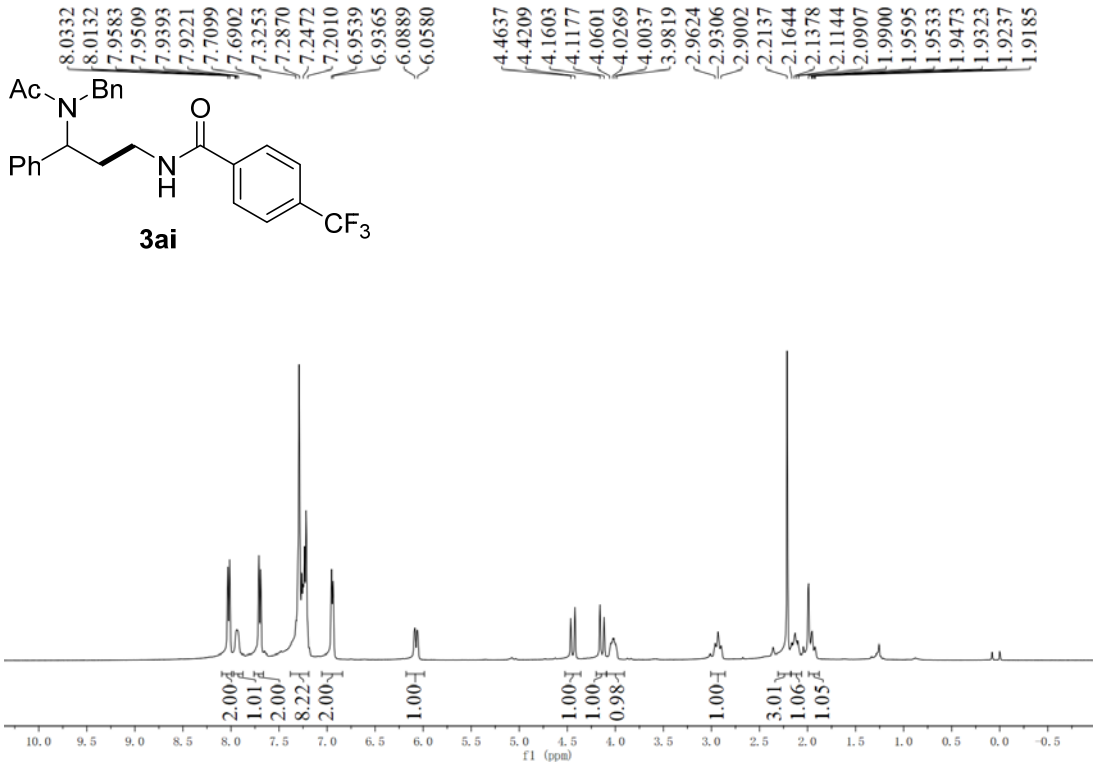

7.5694
7.5641
7.5514
7.5460
7.3837
7.3793
7.3645
7.3602
7.3254
7.3045
7.2804
7.2641
7.2154
7.2102
7.1975
7.1863
7.1737
7.1418
7.1307
7.1240
7.1116
6.9427
6.9265
6.1102
6.0987
6.0831
6.0715
4.4440
4.4008
4.2105
4.1673
3.8715
3.8376
3.8129
3.0622
3.0275
3.0036
2.2143
2.1909
2.1665
2.1173
2.0364
2.0144
1.9881
1.9775
Ac
N
Bn
Ph
O
N
H
Cl
1.00
2.01
6.22
3.05
1.03
1.98
1.00
1.00
1.00
1.04
1.02
1.01
3.00
1.08
f1 (ppm)

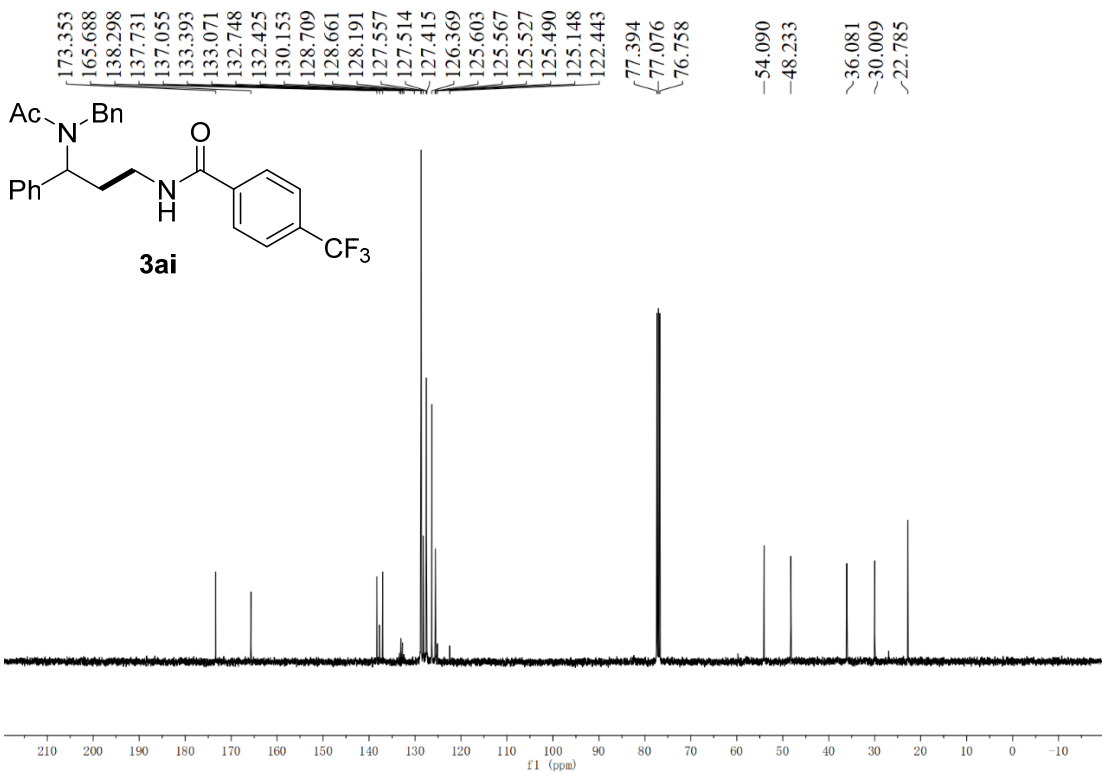
3ag

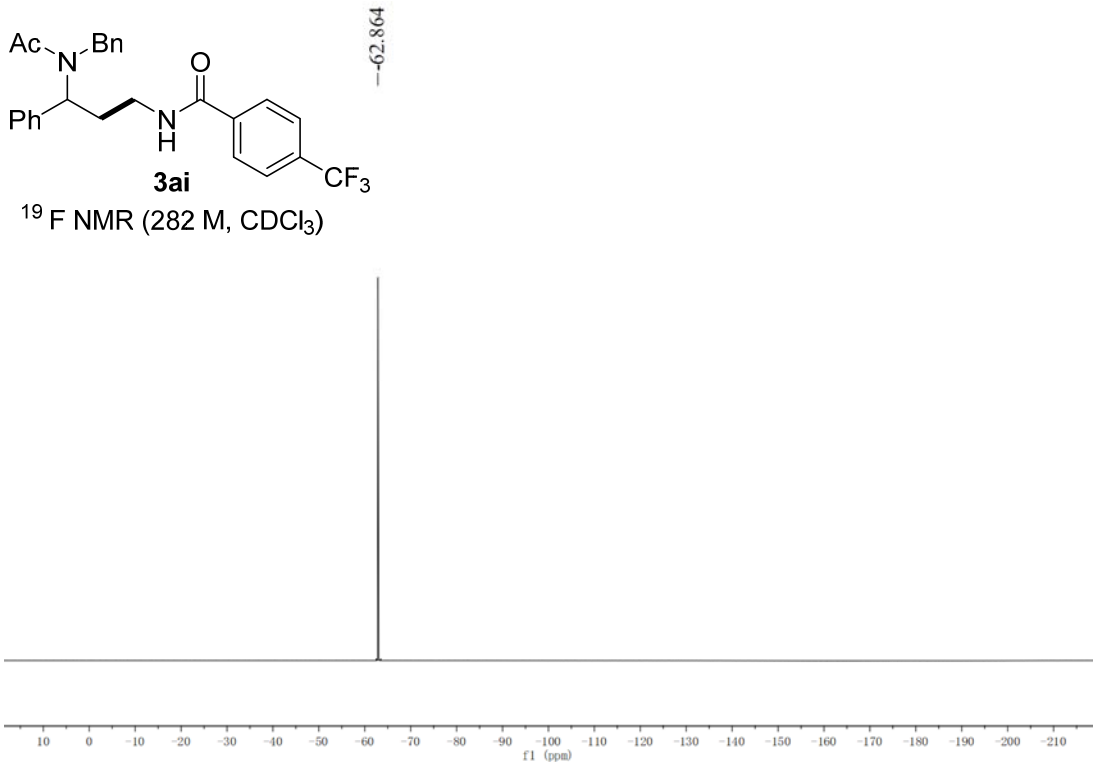

172.83
166.83
138.64
137.38
135.70
130.95
130.79
130.15
129.59
128.68
128.61
128.05
127.34
126.95
126.26
77.39
77.07
76.76
54.22
48.16
36.58
30.44
22.73
Ac
N
Bn
Ph
O
N
H
Cl
3ag
f1 (ppm)

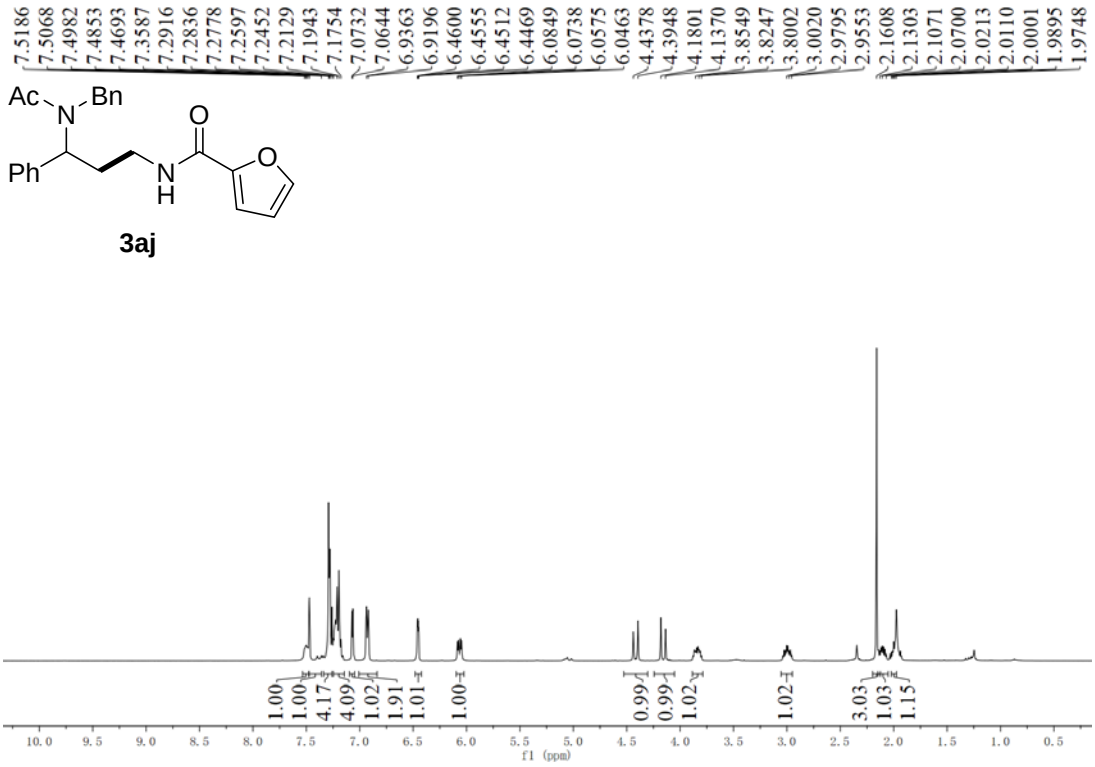

7.8042
7.7942
7.7768
7.7603
7.5650
7.5442
7.3114
7.2596
7.2027
7.1683
6.9363
6.9200
6.0766
6.0669
6.0476
6.0378
4.4454
4.4025
4.1529
4.1101
4.0183
3.9973
3.9626
3.9411
2.9422
2.9147
2.8879
2.8601
2.1896
2.1130
2.1031
2.0876
2.0757
2.0653
1.9755
1.9462
1.9219
1.8926
Ac
N
Bn
Ph
O
N
H
Br
3ah
3.00
2.01
8.43
1.97
1.00
1.00
1.00
1.00
1.00
3.00
1.09
1.03
f1 (ppm)

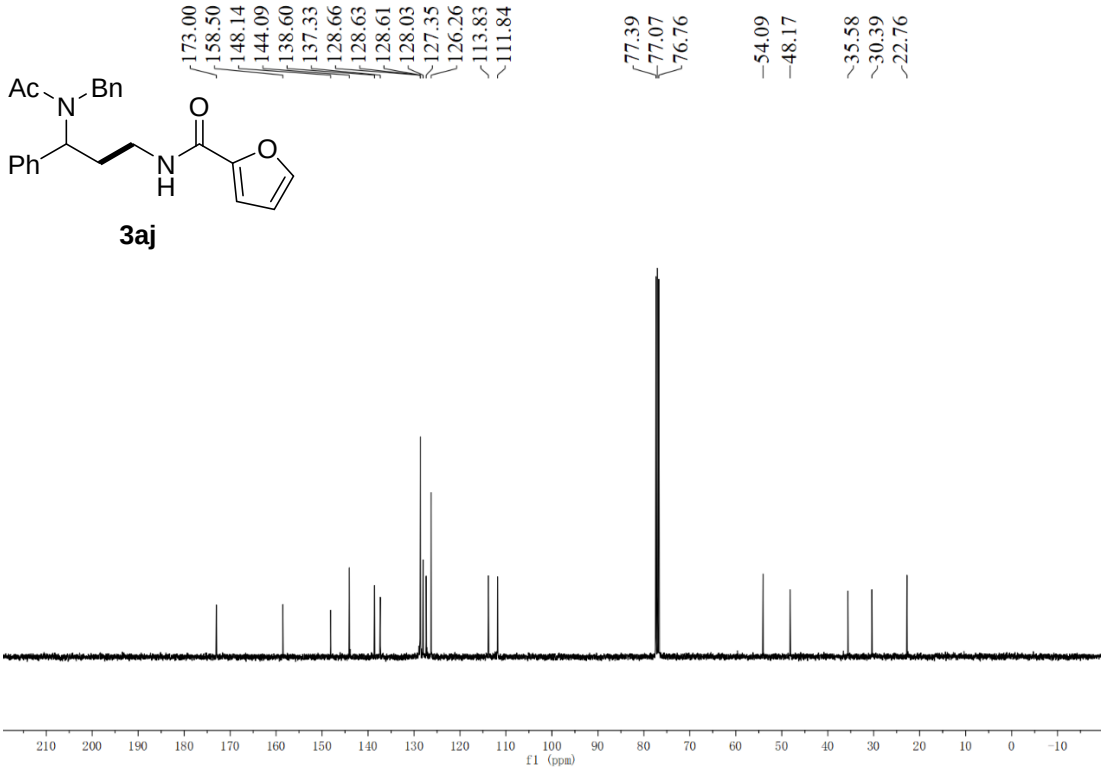

173.31
166.03
138.37
137.09
133.27
131.71
128.75
128.70
128.66
128.16
127.48
126.35
125.97
77.41
77.10
76.78
54.07
48.21
36.02
30.01
22.82
Ac
N
Bn
Ph
O
N
H
Br
3ah
f1 (ppm)

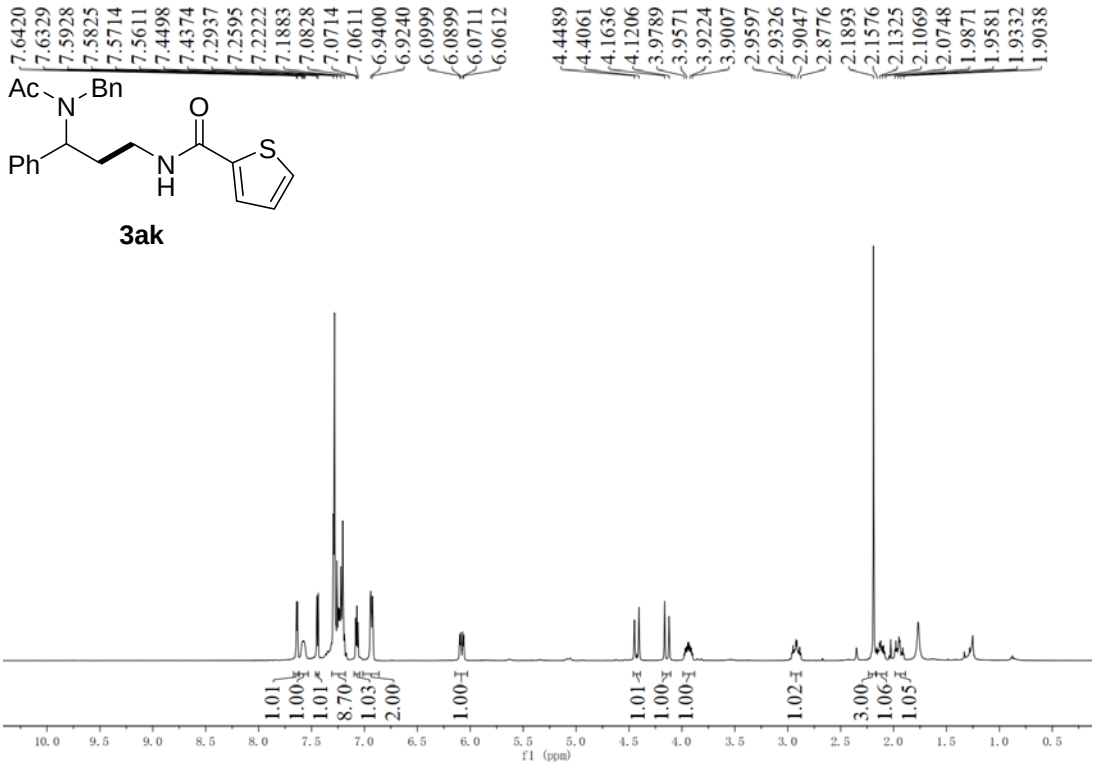

8.0332
8.0132
7.9583
7.9509
7.9393
7.9221
7.7099
7.6902
7.3253
7.2870
7.2472
7.2010
6.9539
6.9365
6.0889
6.0580
4.4637
4.4209
4.1603
4.1177
4.0601
4.0269
4.0037
3.9819
2.9624
2.9306
2.9002
2.2137
2.1644
2.1378
2.1144
2.0907
1.9900
1.9595
1.9533
1.9473
1.9323
1.9237
1.9185
Ac
N
Bn
Ph
O
N
H
CF3
3ai
2.00
1.01
2.00
8.22
2.00
1.00
1.00
1.00
0.98
1.00
3.01
1.06
1.05
f1 (ppm)


173.353
165.688
138.298
137.731
137.055
133.393
133.071
132.748
132.425
130.153
128.709
128.661
128.191
127.557
127.514
127.415
126.369
125.603
125.567
125.527
125.490
125.148
122.443
77.394
77.076
76.758
54.090
48.233
36.081
30.009
22.785
Ac
N
Bn
Ph
O
N
H
CF3
3ai
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)

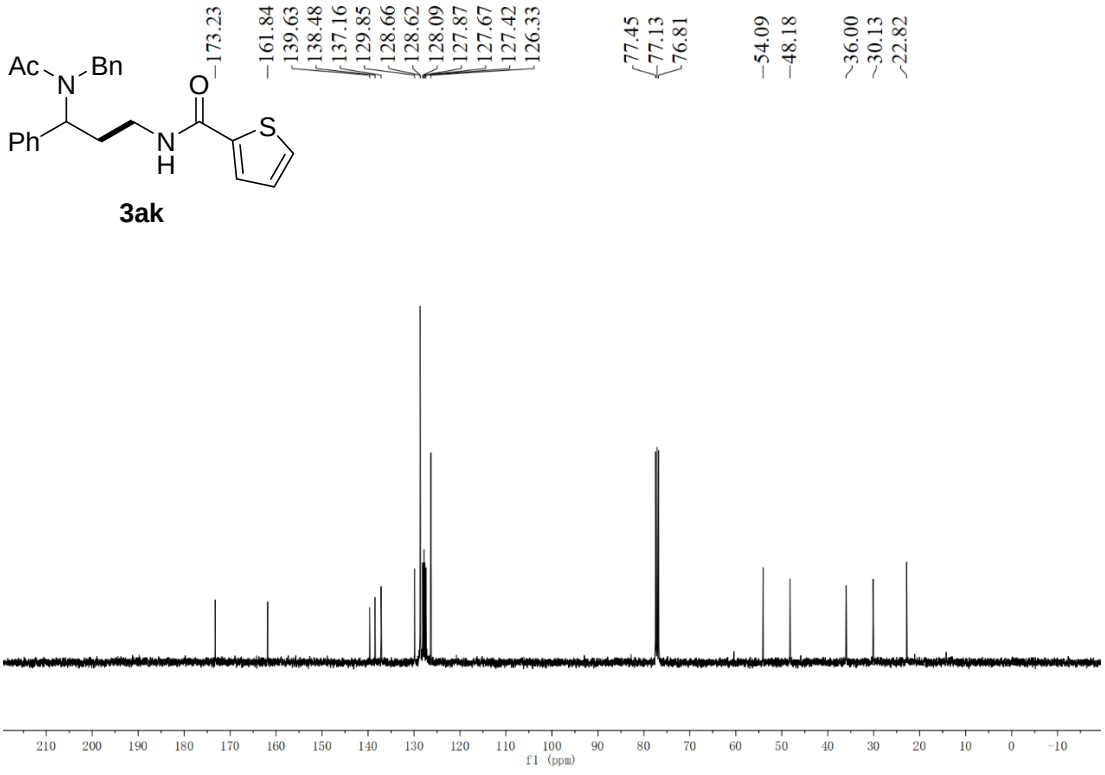

-62.864
Ac
N
Bn
Ph
O
N
H
CF3
3ai
19 F NMR (282 M, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.5186
7.5068
7.4982
7.4853
7.4693
7.3587
7.2916
7.2836
7.2778
7.2597
7.2452
7.2129
7.1943
7.1754
7.0732
7.0644
6.9363
6.9196
6.4600
6.4555
6.4512
6.4469
6.0849
6.0738
6.0575
6.0463
4.4378
4.3948
4.1801
4.1370
3.8549
3.8247
3.8002
3.0020
2.9795
2.9553
2.1608
2.1303
2.1071
2.0700
2.0213
2.0110
2.0001
1.9895
1.9748
Ac
N
Bn
Ph
O
N
H
O
3aj
1.00
1.00
4.17
4.09
1.02
1.91
1.01
1.00
0.99
0.99
1.02
1.02
3.03
1.03
1.15
f1 (ppm)


173.00
158.50
148.14
144.09
138.60
137.33
128.66
128.63
128.61
128.03
127.35
126.26
113.83
111.84
77.39
77.07
76.76
54.09
48.17
35.58
30.39
22.76
Ac
N
Bn
Ph
O
N
H
O
3aj
f1 (ppm)


7.6420
7.6329
7.5928
7.5825
7.5714
7.5611
7.4498
7.4374
7.2937
7.2595
7.2222
7.1883
7.0828
7.0714
7.0611
6.9400
6.9240
6.0999
6.0899
6.0711
6.0612
4.4489
4.4061
4.1636
4.1206
3.9789
3.9571
3.9224
3.9007
2.9597
2.9326
2.9047
2.8776
2.1893
2.1576
2.1325
2.1069
2.0748
1.9871
1.9581
1.9332
1.9038
Ac
N
Bn
Ph
N
H
O
S
1.01
1.00
1.01
8.70
1.03
2.00
1.00
1.01
1.00
1.00
1.02
3.00
1.06
1.05
f1 (ppm)

3ak


173.23
161.84
139.63
138.48
137.16
129.85
128.66
128.62
128.09
127.87
127.67
127.42
126.33
77.45
77.13
76.81
54.09
48.18
36.00
30.13
22.82
Ac
N
Bn
Ph
N
H
O
S
f1 (ppm)

3ak