Supporting Information

Diverse Secondary C(sp^3)−H bond functionalization *via* Site-Selective Trifluoroacetoxylation of Aliphatic Amines

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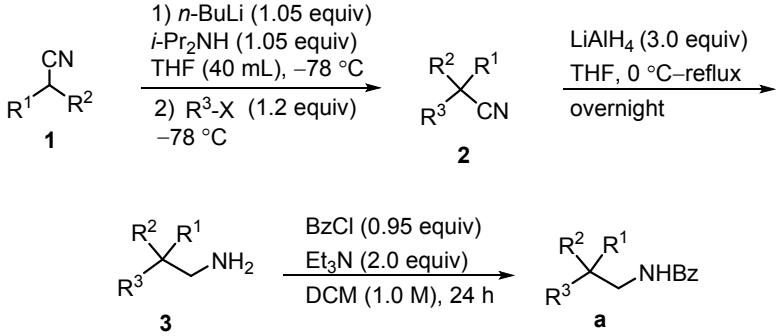
Instrumentation and Chemical

NMR spectra were recorded on Bruker 400 and 600 M spectrometers, operating at 400 and 600 MHz for ^{1}H NMR and 100 and 150 MHz for ^{13}C NMR spectrophotometer using $CDCl_3$ and TMS as the internal standard. Chemical shift values for ^{1}H and ^{13}C are referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C; Chemical shifts are reported in δ ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz) and integration. Column chromatography was performed on silica gel 200-300 mesh. High-resolution mass spectra (HRMS) were recorded on electron-spray ionization (ESI) technique.

All reactions were carried out under nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard noteprocedures unless otherwise noted. CuI was purchased from Energy Chemical Reagent Co., Ltd., $PhI(OTFA)_2$ was purchased from Beijing Innochem Science & Technology Co., Ltd. Tetrabuylammonium bromide (TBAB) was purchased from Tokyo Chemical Industry Co., Ltd. DCM was freshly distilled over CaH_2 under N_2.

General Procedure: Preparation of aliphatic amides

Procedure A



n-BuLi in hexane (2.5 M, 20 mmol, 1.05 equiv) was added dropwise to a solution of *i*-

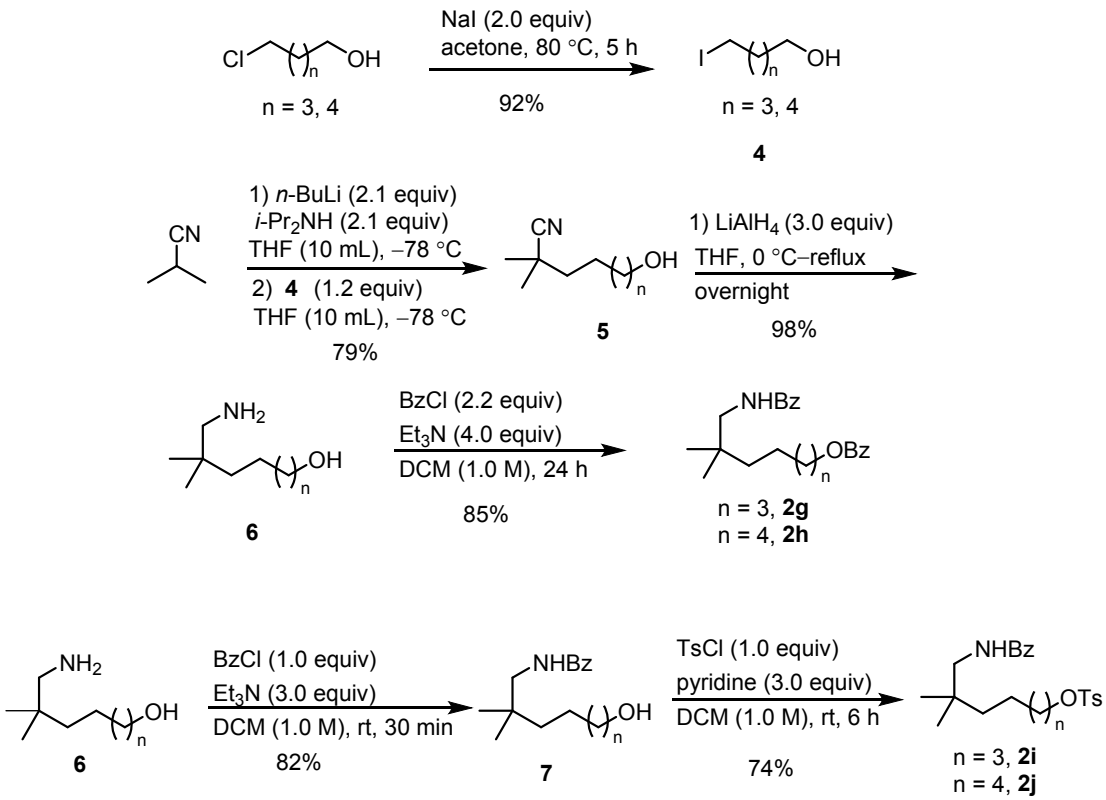
Pr_2NH (3.5 mL, 21.0 mmol, 1.05 equiv) in THF (40 mL) at –78 ºC and stirred for 0.5 h. Then alkyl nitrile **1** (20 mmol, 1.0 equiv) was added dropwise to the resulting LDA solution at –78 ºC and stirred at this temperature for 1 h. Alkyl halide (30 mmol, 1.5 equiv) was then added dropwise to the solution at –78 ºC. After the addition, the mixture was warmed to room temperature and stirred overnight. After down, the mixture was quenched with saturated aqueous NH_4Cl, and extracted with EtOAc (20 mL × 3). Combined extracts were washed with water, brine solution and dried with anhydrous Na_2SO_4. Solvent was evaporated in Rota-evaporator. The residue was purified by silica gel chromatography (2%–10% EtOAc/petroleum ether) to provide corresponding nitrile **2**.

$LiAlH_4$ (2.28 g, 60 mmol, 3.0 equiv) was slowly added to the solution of crude nitrile in THF (30 mL) at room temperature. Then the mixture was heated to 88 ºC for 24 hours. After that, the reaction was cooled down, the $Na_2SO_4 \cdot 10H_2O$ was added slowly until the mixture was clear to quench the reaction, filtered, solid was washed with Et_2O, the combined ether solution was concentrated in vacuo to give the desired amide **3**.

To a solution of amine **3** (10 mmol, 1.0 equiv) in dichloromethane (20 mL) was added triethylamine (2.78 mL, 20 mmol, 2.0 equiv) at 0 ºC. Benzoyl chloride (1.34 g, 9.5 mmol, 0.95 equiv) was added dropwise. Then the mixture was stirring overnight at room temperature. Then the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried with anhydrous Na_2SO_4. Evaporation and column chromatography on silica gel (ethyl acetate/hexane = 1:100–1:5 as eluent) afforded corresponding amides **a** as white solid. Aliphatic amide substrates ***PG* 2**-***PG* 6**, ***PG* 8**-***PG* 13**, **2a**-**2f**, **2k**-**2u**, **2ag** were prepared according to the procedure A.

***PG* 7** can be found in reference 1.

Procedure B



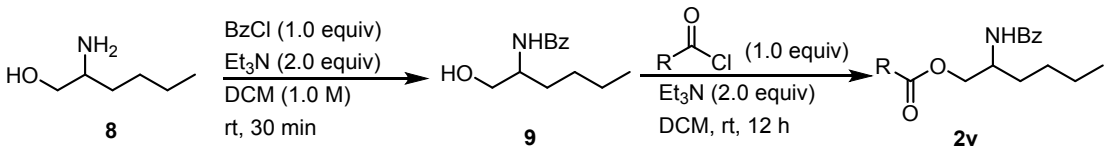
To a solution of 5-chloropentan-1-ol (20 mmol, 1.0 equiv) in acetone (20 mL) was added NaI (40 mmol, 2.0 equiv). Then the mixture was reflux for 5 hours until the 5-chloropentan-1-ol was consumed. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:20:0.5 as eluent) afforded corresponding **4** as colorless oil.

Follow procedure A to give the aliphatic amides **2g** and **2h.**

To a solution of amino alcohol **6** (10 mmol, 1.0 equiv) in dichloromethane (10 mL) was added triethylamine (4.17 mL, 30 mmol, 3.0 equiv) at room temperature. Benzoyl chloride (1.34 g, 9.5 mmol, 0.95 equiv) was added dropwise under the same temperature. Then the mixture was stirring for 30 min at room temperature (detected by TLC). After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:2:1 as eluent) afforded amino protected compound **7** as white solid. Compound 7 (10 mmol, 1.0 equiv) was dissolved in the DCM (10 mL), pyridine (2.41 mL, 30 mmol,

3.0 equiv) was added dropwise at 0 ºC, then Tosyl Chloride (10 mmol, 1.0 equiv) was added portion wise. The mixture was stiring for 24 h. After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:10:0.5 as eluent) to give the desired product **2i** and **2j**.

Procedure C:

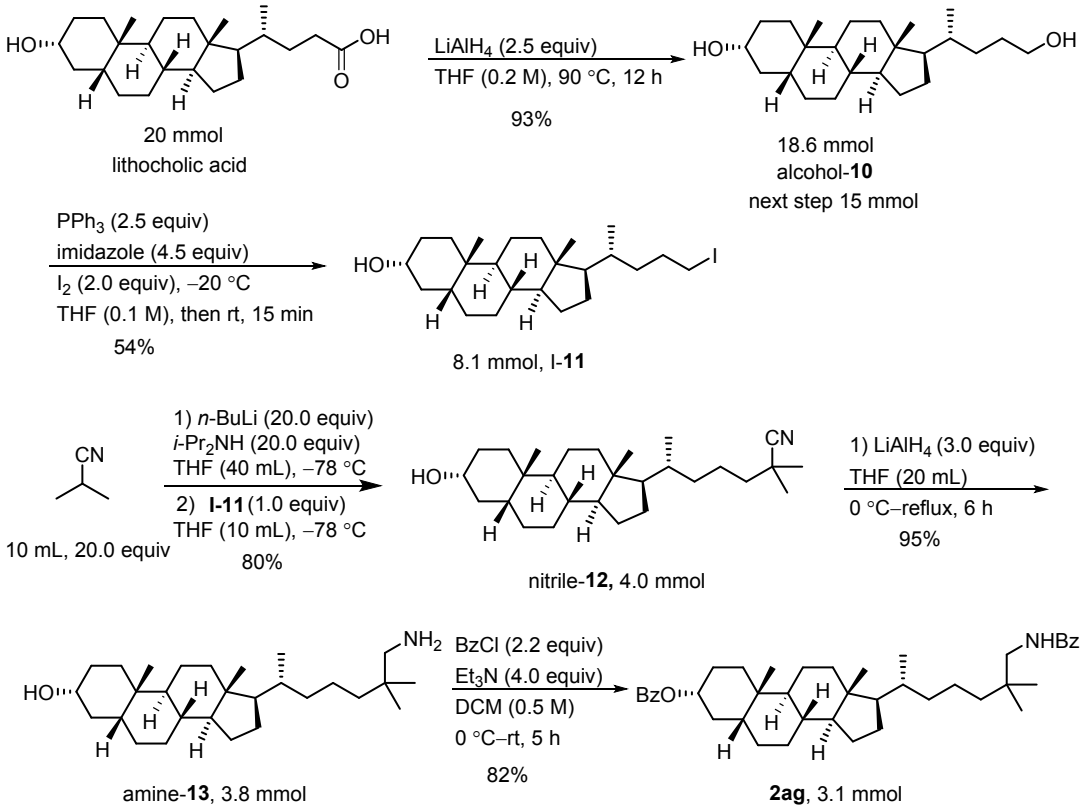


The amino alcohol **8** (20 mmol, 1.0 equiv) was dissolved in DCM (20 mL), Et_3N (5.6 mL, 40 mmol, 2.0 equiv) was added dropwise, then BzCl was added at room temperature, the reaction mixture was stiring for 30 min. After that, the mixture was quenched by water (20 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (20 mL × 2). The combined organic phase was washed with brine (30 mL), and then dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:20:0.5 as eluent) afforded amino protected compound **9** as white solid. Compound **9** was followed the same procedure as above to give **2v** as a white solid.

2w-2y, 2z, 2aa were prepared as the above procedure C.

2ab[2], **2ac**[2], **2ad**[2], **2af** [3] were synthesized according to previous reported procedure.

Preparation of **2ak**:



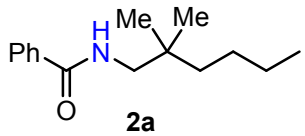
Lithocholic acid (7.53 g, 20 mmol, 1.0 equiv) was dissolved in THF (100 mL), $LiAlH_4$ (1.9 g, 50 mmol, 2.5 equiv) was added portion wise under 0 ºC, then the mixture was refluxing for 12 h. After that, the reaction was cooled down, the $Na_2SO_4 \cdot 10H_2O$ was added slowly until the mixture was clear to quench the reaction, filtered, solid was washed with Et_2O, the combined ether solution was concentrated in vacuo to give the alcohol-**10**.

PPh_3 (9.83 g, 37.5 mmol, 2.5 equiv) and 1*H*-imidazole (4.6 g, 67.5 mmol, 4.5 equiv) were successively added to a soln. of alcohol-**10** (5.43 g, 15 mmol, 1.0 equiv) in THF (150 mL). The mixture was cooled to −20 ºC and I_2 (7.61 g, 30 mmol, 2.0 equiv) was added in three portions each 5 min. After 15 min, the mixture was removed from the cooling bath and stirred for 30 min at rt. The reaction was quenched by slow addition of sat. $NaHCO_3$ soln. (15 mL) and sat. $Na_2S_2O_3$ soln. (15 mL). The aq. Layer was extracted with EtOAc (25 mL × 3), the combined organic layer dried over Na_2SO_4. Evaporation and column chromatography on silica gel (EA/PE/DCM = 1:8:0.5 as eluent) afforded I-**11**.

Then followed the procedure A afforded the product **2ag**.

Characterization Data for amides

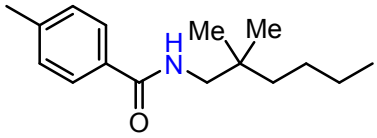
***N*-(2,2-dimethylhexyl)benzamide (2a, *PG* 1)**



2a

White solid. mp: 71.8–73.0 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 2H), 6.09 (br s, 1H), 3.30 (d, J = 6.0 Hz, 2H), 1.24–1.30 (m, 6H), 0.95 (s, 6H), 0.91 (t, J = 6.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.59, 135.01, 131.09, 128.37, 126.74, 49.47, 39.72, 34.38, 26.00, 24.91, 23.42, 13.99. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{23}NNaO$, 256.1672; found, 256.1675. **IR** (KBr, cm^{-1}): ν 3414, 1637, 1400, 1118, 617.

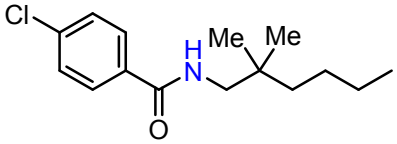
***N*-(2,2-dimethylhexyl)-4-methylbenzamide (*PG* 2)**



***PG* 2**

White solid. mp: 68.2–68.6 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.66 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 6.13 (br s, 1H), 3.28 (d, J = 6.3 Hz, 2H), 2.39 (s, 3H), 1.21–1.34 (m, 6H), 0.93 (s, 6H), 0.90 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.52, 141.61, 132.17, 129.17, 126.74, 49.44, 39.76, 34.39, 26.08, 25.00, 23.51, 21.39, 14.10. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{25}NNaO$, 270.1828; found, 270.1821. **IR** (KBr, cm^{-1}): ν 3474, 3415, 2957, 2925, 1639, 1397, 838.

***N*-(2,2-dimethylhexyl)-4-chlorobenzamide (*PG* 3)**

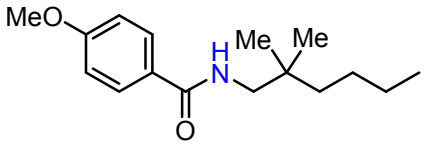


***PG* 3**

White solid. mp: 89.5–90.0 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz,

2H), 7.39 (d, J = 8.4 Hz, 2H), 6.25 (br s, 1H), 3.26 (d, J = 6.3 Hz, 2H), 1.21–1.34 (m, 6H), 0.93 (s, 6H), 0.90 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.60, 137.39, 133.36, 128.71, 128.23, 49.61, 39.75, 34.42, 26.05, 24.96, 23.48, 14.08. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}ClNNaO$, 290.1282; found, 290.1275. **IR** (KBr, cm^{-1}): ν 3476, 3415, 2961, 2926, 1789, 1637, 1597, 1484, 823.

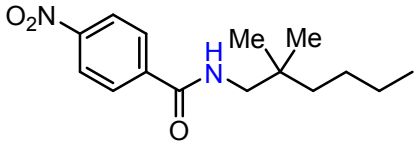
***N*-(2,2-dimethylhexyl)-4-methoxybenzamide (*PG* 4)**



***PG* 4**

White solid. mp: 86.0–87.3 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.01 (br s, 1H), 3.86 (s, 3H), 3.28 (d, J = 6.3 Hz, 2H), 1.23–1.33 (m, 6H), 0.94 (s, 6H), 0.91 (t, J = 6.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.07, 161.89, 128.51, 127.25, 113.60, 55.29, 49.42, 39.74, 34.38, 26.04, 24.95, 23.47, 14.06. **HRMS–ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{16}H_{26}NO_2$, 264.1958; found, 264.1960. **IR** (KBr, cm^{-1}): ν 3415, 1637, 1399, 1251, 1173, 614.

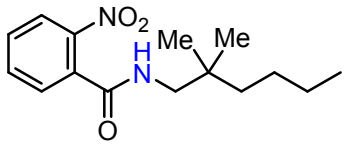
***N*-(2,2-dimethylhexyl)-4-nitrobenzamide (*PG* 5)**



***PG* 5**

White solid. mp: 73.1–74.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.4 Hz, 2H), 6.12 (br s, 1H), 3.32 (d, J = 6.1 Hz, 2H), 1.26–1.34 (m, 6H), 0.96 (s, 6H), 0.92 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.72, 149.33, 140.64, 128.00, 123.73, 49.88, 39.74, 34.48, 26.04, 24.95, 23.45, 14.06. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}N_2NaO_3$, 301.1523; found, 301.1515. **IR** (KBr, cm^{-1}): ν 3475, 3415, 2927, 1640, 1399, 1108, 866.

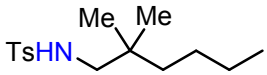
***N*-(2,2-dimethylhexyl)-2-nitrobenzamide (*PG* 6)**



***PG* 6**

White solid. mp: 72.3–73.4 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.53 (d, J = 7.5 Hz, 1H), 5.78 (br s, 1H), 3.32 (d, J = 6.3 Hz, 2H), 1.22–1.35 (m, 6H), 0.97 (s, 6H), 0.92 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.65, 146.31, 133.58, 133.13, 130.27, 128.67, 124.39, 49.79, 39.67, 34.31, 26.01, 24.89, 23.44, 14.07. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}N_2NaO_3$, 301.1523; found, 301.1515. **IR** (KBr, cm^{-1}): ν 3416, 1638, 1399, 1119, 616.

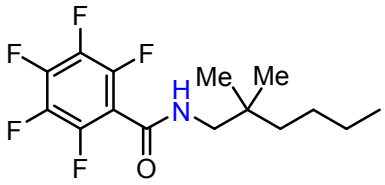
***N*-(2,2-dimethylhexyl)-4-methylbenzenesulfonamide (*PG* 7)**



***PG* 7**

White solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.30 (t, J = 6.9 Hz, 1H), 2.68 (d, J = 6.9 Hz, 2H), 2.43 (s, 3H), 1.19–1.25 (m, 2H), 1.09–1.17 (m, 4H), 0.84 (t, J = 7.2 Hz, 3H), 0.82 (s, 6H).

***N*-(2,2-dimethylhexyl)-2,3,4,5,6-pentafluorobenzamide (*PG* 8)**

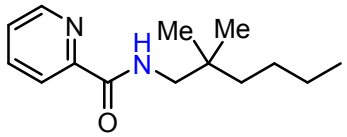


***PG* 8**

Yellow solid. mp: 31.9–33.4 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.86 (br s, 1H), 3.30 (d, J = 6.3 Hz, 2H), 1.22–1.33 (m, 6H), 0.94 (s, 6H), 0.91 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.43, 49.87, 39.55, 34.30, 26.01, 24.85, 23.44, 14.01. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{18}F_5NNaO$, 346.1201; found, 346.1192.

IR (KBr, cm^{-1}): ν 3474, 3415, 1620, 1399, 1115, 618.

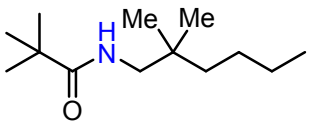
***N*-(2,2-dimethylhexyl)picolinamide (*PG* 9)**



***PG* 9**

Yellow oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.56 (d, J = 4.2 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.17 (br s, 1H), 7.85 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 6.3 Hz, 1H), 3.30 (d, J = 6.6 Hz, 2H), 1.23–1.37 (m, 6H), 0.96 (s, 6H), 0.91 (t, J = 6.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.09, 149.79, 147.82, 137.12, 125.83, 122.01, 49.02, 39.55, 34.31, 25.94, 24.81, 23.33, 13.94. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{22}N_2NaO$, 257.1624; found, 257.1624. **IR** (KBr, cm^{-1}): ν 3397, 3060, 2929, 2866, 1680, 1529, 1388, 1293, 624.

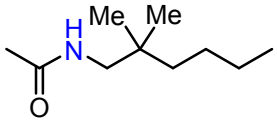
***tert*-butyl (2,2-dimethylhexyl)carbamate (*PG* 10)**



***PG* 10**

White solid. mp: 72.3–73.4 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.63 (br s, 1H), 3.07 (d, J = 6.0 Hz, 2H), 1.26–1.32 (m, 4H), 1.21 (s, 9H), 1.17–1.18 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H), 0.86 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.20, 48.74, 39.69, 38.83, 34.20, 27.63, 27.05, 26.01, 24.96, 23.48, 14.05. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{13}H_{27}NNaO$, 236.1985; found, 236.1985. **IR** (KBr, cm^{-1}): ν 3416, 2961, 1638, 1220, 1184, 702.

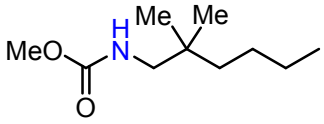
***N*-(2,2-dimethylhexyl)acetamide (*PG* 11)**



***PG* 11**

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.62 (br s, 1H), 3.07 (d, J = 6.3 Hz, 2H), 2.01 (s, 3H), 1.17–1.30 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H), 0.86 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.11, 49.22, 39.62, 33.95, 26.01, 24.85, 23.48, 23.40, 14.06. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{10}H_{21}NNaO$, 194.1515; found, 194.1513. **IR** (KBr, cm^{-1}): ν 3414, 2960, 2630, 1655, 1556, 1466, 605.

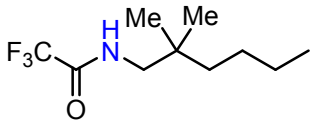
methyl (2,2-dimethylhexyl)carbamate (*PG* 12)



***PG* 12**

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.65 (s, 1H), 3.67 (s, 3H), 3.00 (d, J = 6.4 Hz, 2H), 1.24–1.29 (m, 2H), 1.16–1.24 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H), 0.85 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.33, 52.02, 51.01, 39.43, 34.16, 26.02, 24.74, 23.51, 14.08. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{10}H_{21}NNaO_2$, 210.1465; found, 210.1462. **IR** (KBr, cm^{-1}): ν 3416, 2956, 1638, 1399, 1122, 615.

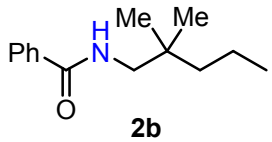
***N*-(2,2-dimethylhexyl)-2,2,2-trifluoroacetamide (*PG* 13)**



***PG* 13**

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.40 (br s, 1H), 3.19 (d, J = 6.3 Hz, 2H), 1.20–1.36 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H), 0.90 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.42 (q, J = 42.0 Hz), 115.99 (q, J = 285.0 Hz), 49.50, 39.49, 34.29, 25.95, 24.67, 23.37, 13.96. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{10}H_{18}F_3NNaO$, 248.1233; found, 248.1230. **IR** (KBr, cm^{-1}): ν 3414, 2963, 2934, 1706, 1621, 1592, 1121, 1167, 723.

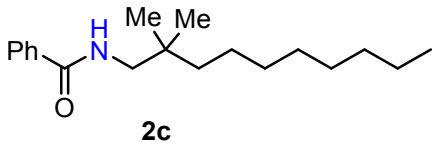
***N*-(2,2-dimethylpentyl)benzamide (2b)**



2b

White solid. mp: 70.1–70.4 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0, 8.0 Hz, 2H), 6.11 (s, 1H), 3.30 (d, J = 8.0 Hz, 2H), 1.30–1.37 (m, 2H), 1.21–1.28 (m, 2H), 0.95 (s, 6H), 0.91 (t, J = 8.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.62, 135.05, 131.24, 128.52, 126.76, 49.55, 42.50, 34.52, 25.00, 17.10, 14.94. **HRMS–ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{14}H_{22}NO$, 220.1696; found, 220.1699. **IR** (KBr, cm^{-1}): ν 3475, 3414, 1638, 1399, 1119, 618.

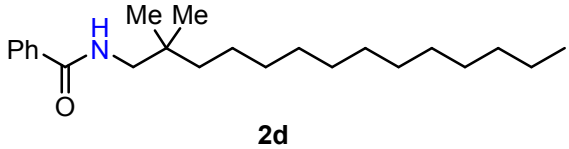
***N*-(2,2-dimethyldecyl)benzamide (2c)**



2c

White solid. mp: 55.8–56.1 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.45 (dd, J = 6.0, 6.0 Hz, 2H), 6.09 (br s, 1H), 3.30 (d, J = 6.0 Hz, 2H), 1.22–1.35 (m, 14H), 0.94 (s, 6H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.62, 135.07, 131.25, 128.53, 126.76, 49.53, 40.08, 34.43, 31.85, 30.48, 29.57, 29.28, 25.01, 23.86, 22.63, 14.09. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{31}NNaO$,312.2298; found, 312.2296. **IR** (KBr, cm^{-1}): ν 3475, 3415, 1638, 1399, 1119, 617.

***N*-(2,2-dimethyltetradecyl)benzamide (2d)**

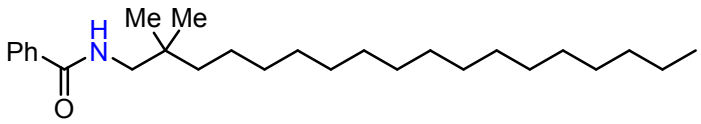


2d

White solid. mp: 58.2–59.0 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 2H), 6.09 (br s, 1H), 3.30 (d, J = 6.0 Hz, 2H), 1.22–1.30 (m, 22H), 0.94 (s, 6H), 0.88 (t, J = 6.0 Hz, 3H). **^{13}C NMR**

(150 MHz, $CDCl_3$) δ 167.63, 135.09, 131.22, 128.51, 126.77, 49.55, 40.11, 34.44, 31.87, 30.49, 29.63, 29.62, 29.61, 29.30, 25.01, 23.87, 22.64, 14.07. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{39}NNaO$, 368.2924; found, 368.2927. **IR** (KBr, cm^{-1}): ν 3550, 3476, 3414, 2959, 2921, 1639, 1537, 1121, 802, 639.

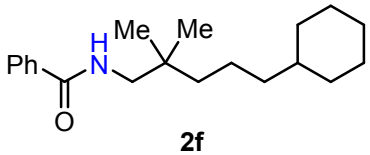
***N*-(2,2-dimethyloctadecyl)benzamide (2e)**



2e

White solid. mp: 71.1–71.8 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.8, 7.2 Hz, 2H), 6.08 (br s, 1H), 3.30 (d, J = 6.3 Hz, 2H), 1.21–1.33 (m, 30H), 0.94 (s, 6H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.61, 135.14, 131.25, 128.55, 126.77, 49.57, 40.13, 34.45, 31.90, 30.51, 29.67, 29.66, 29.63, 29.33, 25.04, 23.89, 22.66, 14.09. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{27}H_{47}NNaO$, 424.3550; found, 424.3552. **IR** (KBr, cm^{-1}): ν 3475, 3415, 2920, 1638, 1399, 1119, 616.

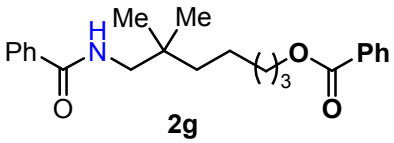
***N*-(5-cyclohexyl-2,2-dimethylpentyl)benzamide (2f)**



2f

White solid. mp: 112.4–113.0 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.5, 7.2 Hz, 2H), 6.09 (br s, 1H), 3.29 (d, J = 6.3 Hz, 2H), 1.59–1.72 (m, 5H), 1.27–1.33 (m, 2H), 1.19–1.25 (m, 5H), 1.11–1.17 (m, , 3H), 0.94 (s, 6H), 0.83–0.88 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.59, 135.08, 131.21, 128.50, 126.74, 49.55, 45.71, 40.36, 38.25, 37.52, 34.47, 33.36, 26.65, 26.34, 25.00, 21.00, 8.55. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{31}NNaO$, 324.2298; found, 324.2297. **IR** (KBr, cm^{-1}): ν 3475, 3414, 2923, 2848, 1639, 1551, 1304, 1106, 705.

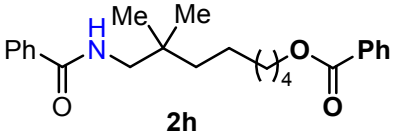
7-benzamido-6,6-dimethylheptyl benzoate (**2g**)



2g

White solid. mp: 57.6–58.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, J = 6.0 Hz, 2H), 7.76 (d, J = 6.0 Hz, 2H), 7.55 (t, J = 6.0 Hz, 1H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 4H), 6.12 (br s, 1H), 4.32 (t, J = 6.0 Hz, 2H), 3.31 (d, J = 6.0 Hz, 2H), 1.76–1.81 (m, 2H), 1.35–1.46 (m, 4H), 1.28–1.31 (m, 2H), 0.95 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.61, 166.54, 134.96, 132.69, 131.13, 130.32, 129.38, 128.40, 128.19, 126.75, 64.85, 49.40, 39.81, 34.49, 28.59, 26.75, 24.90, 23.50. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{29}NNaO_3$, 390.2040; found, 390.2035. **IR** (KBr, cm^{-1}): ν 3417, 1721, 1634, 1396, 1113, 710, 617.

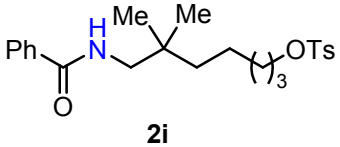
8-benzamido-7,7-dimethyloctyl benzoate (**2h**)



2h

White solid. mp: 56.2–56.4 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.43 (dd, J = 8.0, 8.0 Hz, 4H), 6.08 (br s, 1H), 4.31 (t, J = 6.0 Hz, 2H), 3.30 (d, J = 8.0 Hz, 2H), 1.73–1.80 (m, 2H), 1.43–1.56 (m, 2H), 1.24–1.39 (m, 6H), 0.95(s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.62, 166.60, 135.02, 132.73, 131.21, 130.40, 129.44, 128.48, 128.24, 126.74, 64.96, 49.48, 39.95, 34.46, 30.05, 28.62, 25.95, 24.97, 23.75. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{31}NNaO_3$,404.2196; found, 404.2191. **IR** (KBr, cm^{-1}): ν 3474, 3415, 1637, 1399, 1111, 616.

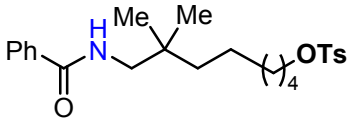
7-benzamido-6,6-dimethylheptyl 4-methylbenzenesulfonate (**2i**)



2i

White solid. mp: 58.3–59.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 (d, J = 6.0 Hz, 2H), 7.76 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.6 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 2H), 7.33 (d, J = 6.0 Hz, 2H), 6.11 (br s, 1H), 4.02 (t, J = 6.0 Hz, 2H), 3.27 (d, J = 6.0 Hz, 2H), 2.44 (s, 3H), 1.63–1.68(m, 2H), 1.21–1.31 (m, 6H), 0.92 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.60, 144.61, 134.90, 133.03, 131.23, 129.75, 128.48, 127.74, 126.75, 70.50, 49.31, 39.65, 34.46, 28.65, 26.05, 24.91, 23.16, 21.53. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{31}NNaO_4S$, 440.1866; found, 440.1860. **IR** (KBr, cm^{-1}): ν 3475, 3415, 1636, 1400, 1171, 618.

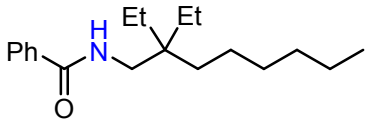
8-benzamido-7,7-dimethyloctyl 4-methylbenzenesulfonate (**2j**)



2j

White solid. mp: 67.8–69.3 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 6.09 (br s, 1H), 4.01 (t, J = 6.3 Hz, 2H), 3.28 (d, J = 6.3 Hz, 2H), 2.45 (s, 3H), 1.64 (quint, J = 6.6 Hz, 2H), 1.30–1.35 (m, 2H), 1.19–1.29 (m, 6H), 0.93 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.47, 144.46, 134.69, 132.67, 130.93, 129.57, 128.16, 127.49, 126.66, 70.44, 49.19, 39.57, 34.37, 29.42, 28.42, 24.98, 24.70, 23.36, 21.32. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{33}NNaO_4S$, 454.2023; found, 454.2020. **IR** (KBr, cm^{-1}): ν 3475, 3415, 3255, 2923, 1639, 1560, 1467, 1357, 1176, 954, 813, 662.

***N*-(2,2-diethyloctyl)benzamide** (**2k**)

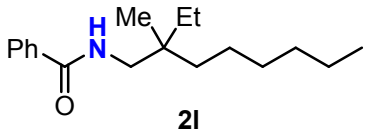


2k

White solid. mp: 46.8–47.6 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 2H), 5.95 (br s, 1H), 3.32 (d, J = 6.0 Hz, 2H), 1.22–1.32 (m, 14H), 0.88 (t, J = 6.0 Hz, 3H), 0.85 (t, J = 6.0 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 167.40, 135.08, 131.07, 128.39, 126.67, 43.78, 38.63, 34.06, 31.70, 30.09, 26.78, 22.75, 22.55, 13.94, 7.42. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{31}NNaO$, 312.2298; found, 312.2308. **IR** (KBr, cm^{-1}): ν 3550, 3475, 3414, 2926, 1636, 1301, 1174, 619.

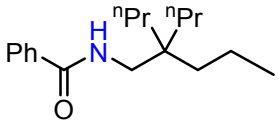
***N*-(2-ethyl-2-methyloctyl)benzamide (2l)**



2l

White solid. mp: 57.6–58.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.44 (dd, J = 7.2, 7.2 Hz, 2H), 6.02 (br s, 1H), 3.32 (d, J = 6.0 Hz, 2H), 1.22–1.38 (m, 12H), 0.90 (s, 3H), 0.89–0.85 (m, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.60, 135.00, 131.14, 128.42, 126.72, 46.99, 37.02, 36.56, 31.74, 30.11, 29.65, 23.26, 22.57, 22.56, 13.99, 7.86. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{29}NNaO$, 298.2141; found, 298.2149. **IR** (KBr, cm^{-1}): ν 3752, 3550, 3475, 2926, 1639, 1550, 1383, 704.

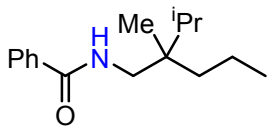
***N*-(2,2-dipropylpentyl)benzamide (2m)**



2m

White solid. mp: 104.2–104.8 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, J = 6.0 Hz, 2H), 7.51 (t, J = 6.0 Hz, 1H), 7.45 (dd, J = 6.0, 6.0 Hz, 2H), 5.96 (br s, 1H), 3.32 (d, J = 6.0 Hz, 2H), 1.26–1.30 (m, 6H), 1.21–1.23 (m, 6H), 0.90 (t, J = 6.0 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.51, 135.18, 131.19, 128.54, 126.71, 44.86, 38.91, 37.85, 16.29, 14.97. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{29}NNaO$, 298.2141; found, 298.2149. **IR** (KBr, cm^{-1}): ν 3754, 3652, 3476, 2928, 1637, 1557, 1171, 698.

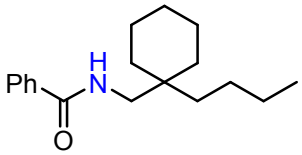
***N*-(2-isopropyl-2-methylpentyl)benzamide (2n)**



2n

White solid. **mp**: 63.2–64.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.5, 7.2 Hz, 2H), 6.01 (br s, 1H), 3.39 (dd, J = 13.8, 6.0 Hz, 2H), 1.67 (sept, J = 6.6 Hz, 1H), 1.24–1.32 (m, 4H), 0.92 (d, J = 6.6 Hz, 6H), 0.91 (s, 3H), 0.86 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.56, 135.14, 131.23, 128.55, 126.72, 45.29, 38.65, 38.37, 32.80, 19.47, 17.25, 17.17, 16.68, 15.09. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{25}NNaO$, 270.1828; found, 270.1828. **IR** (KBr, cm^{-1}): ν 3551, 3476, 2960, 1634, 1317, 1183, 710, 619.

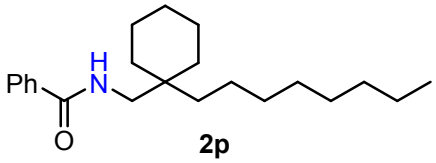
***N*-((1-butylcyclohexyl)methyl)benzamide (2o)**



2o

White solid. mp: 91.5–93.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.8, 7.2 Hz, 2H), 6.01 (br s, 1H), 3.38 (d, J = 6.0 Hz, 2H), 1.50–1.57 (m, 2H), 1.40–1.48 (m, 4H), 1.26–1.39 (m, 10H), 0.92 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.58, 135.17, 131.19, 128.52, 126.74, 45.80, 36.32, 35.55, 33.75, 26.22, 25.11, 23.57, 21.44, 14.06. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{27}NNaO$, 296.1985; found, 296.1984. **IR** (KBr, cm^{-1}): ν 3751, 3474, 2930, 1642, 1546, 1303, 699, 613.

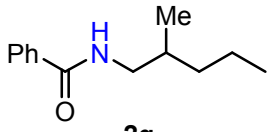
***N*-((1-octylcyclohexyl)methyl)benzamide (2p)**



2p

White solid. mp: 62.5–62.9 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (t, J = 6.0, 6.0 Hz, 2H), 6.01 (br s, 1H), 3.38 (d, J = 6.0 Hz, 2H), 1.38–1.53 (m, 7H), 1.33–1.37 (m, 4H), 1.21–1.31 (m, 13H), 0.87 (t, J = 6.0 Hz, 3H). **^{13}C NMR** (150MHz, $CDCl_3$) δ 167.53, 135.10, 131.12, 128.44, 126.73, 45.80, 36.33, 35.79, 33.68, 31.82, 30.52, 29.50, 29.25, 26.18, 22.82, 22.57, 21.41, 14.02. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{35}NNaO$, 352.2611; found, 352.2613. **IR** (KBr, cm^{-1}): ν 3474, 3415, 2926, 1637, 1549, 1301, 700, 613.

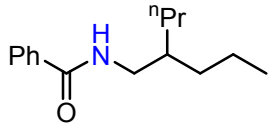
***N*-(2-methylpentyl)benzamide (2q)**



2q

Colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.2, 7.5 Hz, 2H), 6.14 (br s, 1H), 3.41 (ddd, J = 13.2, 7.2, 6.0 Hz, 1H), 3.27 (ddd, J = 13.2, 7.2, 6.0 Hz, 1H), 1.73–1.81 (m, 1H), 1.38–1.46 (m, 2H), 1.29–1.37 (m, 1H), 1.15–1.22 (m, 1H), 0.97 (d, J = 6.6 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.62, 134.72, 131.00, 128.22, 126.81, 45.90, 36.56, 32.97, 19.85, 17.44, 14.13. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{13}H_{19}NNaO$,228.1359; found, 228.1351. **IR** (KBr, cm^{-1}): ν 3317, 2961, 1643, 1543, 1300, 702.

***N*-(2-propylpentyl)benzamide (2r)**

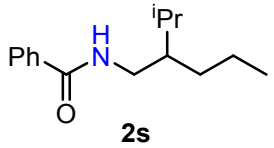


2r

White solid. mp: 63.7–64.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 2H), 6.05 (br s, 1H), 3.41 (t, J = 6.0 Hz, 2H), 1.65 (sept, J = 6.0 Hz, 1H), 1.34–1.41 (m, 4H), 1.30–1.33 (m, 4H), 0.92 (t, J = 6.0 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.57, 134.89, 131.16,

128.43, 126.77, 43.24, 37.54, 34.16, 19.74, 14.37. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{23}NNaO$, 256.1672; found, 256.1676. **IR** (KBr, cm^{-1}): ν 3752, 3551, 3476, 2956, 2925, 1631, 1540, 1301, 695.

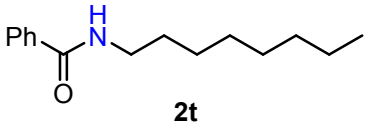
***N*-(2-isopropylpentyl)benzamide (2s)**



2s

White solid. mp: 69.6–71.3 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.44 (dd, J = 6.0, 6.0 Hz, 2H), 6.03 (s, 1H), 3.38–3.47 (m, 2H), 1.75–1.81(m, 1H), 1.44–1.50 (m, 1H), 1.32–1.44 (m, 3H), 1.18–1.25 (m, 1H), 0.95 (d, J = 6.0, 3H), 0.94 (d, J = 6.0, 3H), 0.92 (t, J = 6.0, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.49, 134.96, 131.20, 128.49, 126.76, 43.90, 41.14, 31.16, 28.61, 20.82, 19.42, 19.06, 14.42. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{23}NNaO$, 256.1672; found, 256.1675. **IR** (KBr, cm^{-1}): ν 3474, 3415, 1633, 1549, 1315, 1122, 705, 617.

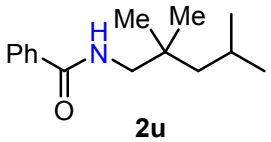
***N*-octylbenzamide (2t)**



2t

White solid. mp: 41.6–42.0 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.43 (dd, J = 7.5, 7.5 Hz, 2H), 6.13 (br s, 1H), 3.43–3.47 (m, 2H), 1.58–1.66 (m, 2H), 1.27–1.40 (m, 10H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.49, 134.73, 131.00, 128.23, 126.83, 40.01, 31.65, 29.52, 29.17, 29.07, 26.90, 22.48, 13.93. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{23}NNaO$, 256.1672; found, 256.1672. **IR** (KBr, cm^{-1}): ν 3474, 3415, 2921, 1631, 1532, 1121, 615.

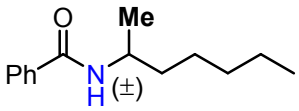
***N*-(2,2,4-trimethylpentyl)benzamide (2u)**



2u

White solid. mp: 58.0–58.5 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.5, 7.2 Hz, 2H), 6.11 (br s, 1H), 3.31 (d, J = 6.3 Hz, 2H), 1.75 (sept, J = 6.0 Hz, 1H), 1.23 (d, J = 5.4 Hz, 2H), 0.98 (s, 6H), 0.95 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.59, 135.01, 131.24, 128.52, 126.75, 50.04, 48.85, 35.17, 25.44, 23.98. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{23}NNaO$, 256.1672; found, 256.1665. **IR** (KBr, cm^{-1}): ν 3474, 3415, 2958, 1638, 1398, 1178, 614.

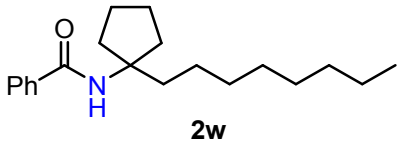
***N*-(2-heptanyl)benzamide (2v)**



2v

White solid. mp: 64.7–65.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.49 (t, J = 8.0 Hz, 1H), 7.42 (dd, J = 8.0, 8.0 Hz, 2H), 5.86 (d, J = 8.0 Hz, 1H), 4.14–4.24 (m, 1H), 1.50–1.57 (m, 2H), 1.27–1.40 (m, 6H), 1.23 (d, J = 8.0 Hz, 3H), 0.88 (t, J = 6.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.77, 135.07, 131.15, 128.44, 126.77, 45.73, 36.98, 31.67, 25.73, 22.52, 20.98, 13.96. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{21}NNaO$, 242.1515; found, 242.1518. **IR** (KBr, cm^{-1}): ν 3415, 2923, 1633, 1457, 1162, 889, 698.

***N*-(1-octylcyclopentyl)benzamide (2w)**

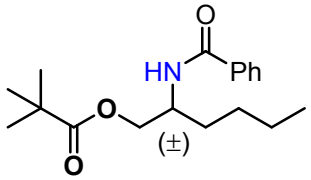


2w

White solid. mp: 89.1–89.7 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 1H), 7.42 (dd, J = 8.0, 8.0 Hz, 2H), 5.84 (br s, 1H), 2.05–2.11 (m, 2H), 1.90–1.94 (m, 2H), 1.68–1.77 (m, 6H), 1.24–1.29 (m, 12H), 0.86 (t, J = 6.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.89, 135.92, 131.02, 128.46, 126.65,

65.19, 38.12, 37.35, 31.82, 29.97, 29.60, 29.26, 25.10, 23.75, 22.62, 14.06. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{31}NNaO$, 324.2298; found, 324.2288. **IR** (KBr, cm^{-1}): ν 3416, 2924, 1636, 1400, 1119, 617.

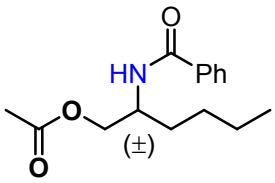
(±)2-benzamidohexyl pivalate (**2x**)



2x

White solid. mp: 71.8–73.3 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.2, 7.5 Hz, 2H), 6.21 (d, J = 7.5 Hz, 1H), 4.40–4.46 (m, 1H), 4.32 (dd, J = 11.4, 6.3 Hz, 1H), 4.12 (dd, J = 11.4, 4.2 Hz, 1H), 1.53–1.64 (m, 2H), 1.33–1.42 (m, 4H), 1.19 (s, 9H), 0.90 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.72, 167.01, 134.40, 131.30, 128.41, 126.77, 65.58, 49.01, 38.77, 31.25, 27.82, 27.03, 22.41, 13.81. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{27}NNaO_3$, 328.1883; found, 328.1887. **IR** (KBr, cm^{-1}): ν 3417, 2925, 1637, 1400, 1173, 614.

(±) *2*-benzamidohexyl acetate (**2y**)

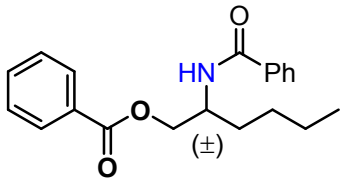


2y

White solid. mp: 63.7–64.3 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 1H), 7.44 (dd, J = 8.0, 8.0 Hz, 2H), 6.20 (d, J = 8.0 Hz, 1H), 4.36–4.44 (m, 1H), 4.30 (dd, J = 12.0, 4.0 Hz, 1H), 4.14 (dd, J = 12.0, 4.0 Hz, 1H), 2.08 (s, 3H), 1.52–1.66 (m, 2H), 1.32–1.43 (m, 4H), 0.91 (t, J = 8.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.25, 167.14, 134.47, 131.37, 128.45, 126.85, 65.93, 48.95, 31.27, 27.94, 22.44, 20.75, 13.84. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for

$C_{15}H_{21}NNaO_3$, 286.1414; found, 286.1418. **IR** (KBr, cm^{-1}): ν 3415, 2926, 1732, 1637, 1399, 1121, 695, 616.

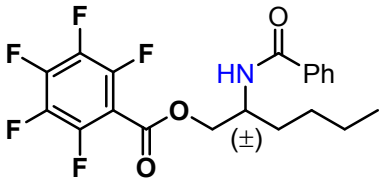
(±)2-benzamidohexyl benzoate (2z)



2z

White solid. mp: 117.0–118.0 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.8, 7.2 Hz, 2H), 7.42 (dd, J = 7.8, 7.5 Hz, 2H), 6.32 (d, J = 7.2 Hz, 1H), 4.53–4.57 (m, 1H), 4.52 (dd, J = 11.1, 6.0 Hz, 1H), 4.43 (dd, J = 11.1, 3.3 Hz, 1H), 1.71–1.76 (m, 1H), 1.64–1.69 (m, 1H), 1.42–1.50 (m, 2H), 1.33–1.41 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.23, 166.90, 134.59, 133.20, 131.47, 129.81, 129.66, 128.59, 128.47, 126.87, 66.51, 49.28, 31.55, 28.07, 22.56, 13.93. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{23}NNaO_3$, 348.1570; found, 348.1576. **IR** (KBr, cm^{-1}): ν 3416, 2956, 1719, 1635, 1399, 1127, 706, 615.

(±)2-benzamidohexyl 2,3,4,5,6-pentafluorobenzoate (2aa)

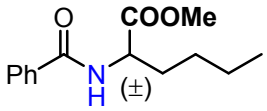


2aa

White solid. mp: 96.0–97.6 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 6.15 (d, J = 7.8 Hz, 1H), 4.57 (dd, J = 10.5, 4.2 Hz, 1H), 4.49–4.54 (m, 2H), 1.62–1.73 (m, 2H), 1.34–1.45 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.20, 158.90, 134.12, 131.42, 128.37, 126.79, 67.89, 48.42, 31.04, 27.94, 22.35, 13.74. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{18}F_5NNaO_3$, 438.1099; found, 438.1089. **IR** (KBr, cm^{-1}): ν

3475, 3415, 1734, 1639, 1531, 1396, 1106, 696.

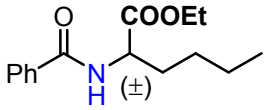
(±)-methyl 2-benzamidohexanoate (2ab)



2ab

White solid. mp: 69.5–71.3 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 7.5, 7.5 Hz, 2H), 6.65 (d, J = 7.2 Hz, 1H), 4.84 (dd, J = 13.2, 7.2 Hz, 1H), 3.79 (s, 3H), 1.95–1.99 (m, 1H), 1.76–1.82 (m, 1H), 1.30–1.41 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.06, 166.95, 133.65, 131.37, 128.20, 126.91, 52.39, 52.06, 31.79, 27.29, 22.05, 13.61. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{14}H_{19}NNaO_3$, 272.1257; found, 272.1252. **IR** (KBr, cm^{-1}): ν 3415, 2954, 1752, 1634, 1363, 1157, 720, 633.

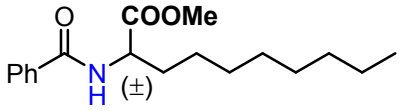
(±)-ethyl 2-benzamidohexanoate (2ac)



2ac

White solid. mp: 79.4–81.1 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.8, 7.5 Hz, 2H), 6.68 (d, J = 7.2 Hz, 1H), 4.82 (dt, J = 13.2, 7.2 Hz, 1H), 4.25 (dq, J = 7.2, 1.8 Hz, 2H), 1.95–2.00 (m, 1H), 1.76–1.82 (m, 1H), 1.30–1.44 (m, 4H), 1.31 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.68, 166.92, 133.95, 131.47, 128.37, 126.95, 61.27, 52.51, 32.15, 27.25, 22.19, 14.04, 13.71. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{21}NNaO_3$, 286.1414; found, 286.1410. **IR** (KBr, cm^{-1}): ν 3415, 2924, 1745, 1637, 1399, 1161, 715, 618.

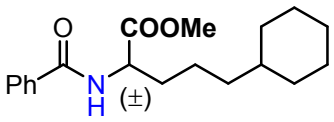
(±)-methyl 2-benzamidodecanoate (2ad)



2ad

White solid. mp: 49.7–50.8 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 6.0 Hz, 2H), 7.50 (t, J = 6.0 Hz, 1H), 7.42 (t, J = 6.0 Hz, 2H), 6.77 (br s, 1H), 4.82 (dt, J = 9.0, 6.0 Hz, 1H), 3.77 (s, 3H), 1.92–1.97 (m, 1H), 1.75–1.80 (m, 1H), 1.20–1.41 (m, 12H), 0.87 (t, J = 6.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.22, 166.95, 133.97, 131.60, 128.48, 127.01, 52.54, 52.29, 32.52, 31.71, 29.25, 29.15, 29.08, 25.21, 22.54, 13.99. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{27}NNaO_3$, 328.1883; found, 328.1889. **IR** (KBr, cm^{-1}): ν 3289, 2923, 1745,1642, 1213, 703.

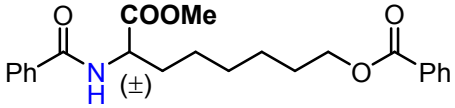
(±)-methyl 2-benzamido-5-cyclohexylpentanoate (2ae)



2ae

White solid. mp: 61.4–63.2 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.2, 7.5 Hz, 2H), 6.65 (d, J = 7.5 Hz, 1H), 4.83 (td, J = 7.5, 5.7 Hz, 1H), 3.78 (s, 3H), 1.90–1.96 (m, 1H), 1.73–1.79 (m, 1H), 1.61–1.68(m, 5H), 1.38–1.45 (m, 1H), 1.30–1.37 (m, 1H), 1.09–1.24 (m, 6H), 0.80–0.90 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.30, 166.99, 134.04, 131.71, 128.60, 127.04, 52.59, 52.41, 37.40, 36.98, 33.31, 33.24, 32.97, 26.62, 26.32, 22.52. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{19}H_{27}NNaO_3$, 340.1883; found, 340.1881. **IR** (KBr, cm^{-1}): ν 3416, 2922, 1749, 1637, 1400, 1169, 614.

7-benzamido-8-methoxy-8-oxooctyl benzoate (2af)

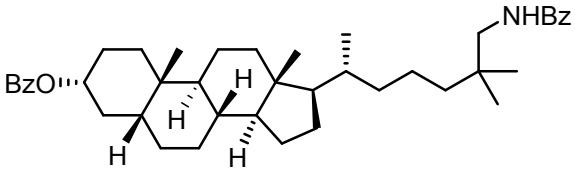


2af

White solid. mp: 61.9–62.8 ºC; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz,

2H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.42–7.46 (m, 4H), 6.67 (t, *J* = 6.9 Hz, 1H), 4.85 (dd, *J* = 13.2, 6.5 Hz, 1H), 4.30 (t, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 1.95–2.02 (m, 1H), 1.71–1.84 (m, 3H), 1.33–1.44 (m, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.05, 166.96, 166.49, 133.77, 132.69, 131.56, 130.25, 129.35, 128.39, 128.18, 126.95, 64.75, 52.39, 52.28, 32.30, 28.70, 28.43, 25.67, 25.08. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{27}NNaO_5$, 420.1781; found, 420.1780. **IR** (KBr, cm^{-1}): ν 3416, 2924, 1636, 1400, 1118, 617.

17-(-7-benzamido-6,6-dimethyl-2-heptanyl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl benzoate (2ag)



2ag

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.6 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 6.10 (t, *J* = 5.7 Hz, 1H), 4.95–5.00 (m, 1H), 3.30 (d, *J* = 6.3 Hz, 2H), 1.98 (t, *J* = 11.1 Hz, 2H), 1.86–1.88 (m, 2H), 1.77–1.83 (m, 2H), 1.67-1.69 (m, 1H), 1.51–1.57 (m, 3H), 1.32–1.48 (m, 8H), 1.16–1.29 (m, 8H), 1.08–1.13 (m, 4H), 0.96 (s, 3H), 0.95 (s, 6H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.65 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.62, 166.13, 135.11, 132.66, 131.31, 130.90, 129.50, 128.59, 128.23, 126.77, 74.99, 56.49, 56.26, 49.63, 42.69, 41.94, 40.65, 40.47, 40.15, 36.75, 35.79, 35.73, 35.06, 34.62, 34.51, 32.33, 28.33, 27.04, 26.74, 26.34, 25.11, 25.05, 24.19, 23.36, 20.87, 20.26, 18.68, 12.04. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{42}H_{59}N_2NaO_3$, 648.4387; found, 648.4377. **IR** (KBr, cm^{-1}): ν 3750, 3474, 2924, 1637, 1460, 1399, 615.

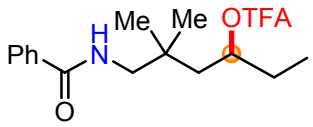
Procedures for Site-Selective Oxidation Trifluoroacetoxylation of Aliphatic Amines

Procedure A: To an oven-dried 25 mL Schlenk tube, **2a** (23.3 mg, 0.10 mmol, 1.0 equiv), TBAB (16.2 mg, 0.05 mmol, 50 mol%), Br_2 (6.0 μL, 0.12 mmol, 1.2 equiv), 1.0 mL DCM were added sequentially. The reaction mixture was stirred at room temperature for 15 min. After that, CuI (3.8 mg, 0.02 mmol, 20 mol%), $PhI(OTFA)_2$ (95.0 mg, 0.22 mmol, 2.2 equiv) were added, the tube was sealed and placed in a 100 ℃ parallel synthesizer and stirred for 5 h. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. Flash Silica gel column purification (EtOAc/petroleum ether/DCM = 1:25:0.5 as eluent) of the crude product provided **3a** (21.4 mg, 0.08mmol) in 72% isolated yield.

Procedure B: Changed: AgOAc (3.3 mg, 0.02 mmol, 20mol%). Other process is the same as the **Procedure A**.

Characterization Data for Product

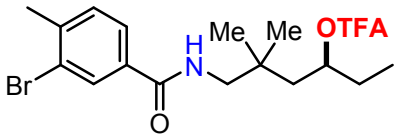
6-benzamido-5,5-dimethylhexan-3-yl 2,2,2-trifluoroacetate (3a)



3a

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 6.0 Hz, 2H), 7.52 (t, J = 9.0 Hz, 1H), 7.46 (dd, J = 6.0, 9.0 Hz, 2H), 6.29 (br s, 1H), 5.19–5.23 (m, 1H), 3.53 (dd, J = 12.0, 6.0 Hz, 1H), 3.10 (dd, J = 12.0, 6.0 Hz, 1H), 1.81 (dd, J = 12.0 , 9.0 Hz, 1H), 1.71 (td, J = 9.0, 6.0 Hz, 2H), 1.56 (dd, J = 12.0, 1.8 Hz, 1H), 0.98 (s, 6H), 0.92 (t, J = 9.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.68, 157.24 (q, J = 42.0 Hz) 134.64, 131.52, 128.65, 126.77, 114.55 (q, J = 285.0 Hz), 78.35, 49.33, 42.31, 34.54, 28.66, 25.34, 25.19, 9.06. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{22}F_3NNaO_3$, 368.1444; found, 368.1442. **IR** (KBr, cm^{-1}): ν 3415, 1679, 1544, 1205, 800, 716.

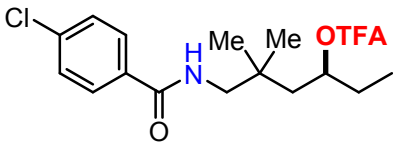
5,5-dimethyl-6-(4-methylbenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-*PG* 2)



***3-PG* 2**

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 6.22 (s, 1H), 5.18-5.21 (m, 1H), 3.52 (dd, J = 13.8, 7.8 Hz, 1H), 3.08 (dd, J = 13.8, 5.4 Hz, 1H), 2.45 (s, 3H), 1.79 (dd, J = 15.3, 8.4 Hz, 1H), 1.66–1.75 (m, 2H), 1.55 (dd, J = 15.3, 1.8 Hz, 1H), 0.98 (s, 6H), 0.93 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.14, 157.27 (q, J = 42.0 Hz), 141.74, 133.81, 130.89, 130.87, 125.52, 125.15, 114.54 (q, J = 285.0 Hz), 78.37, 49.32, 42.31, 34.57, 28.65, 25.42, 25.22, 22.99, 9.09. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{23}BrF_3NNaO_3$, 460.0706; found, 460.0700. **IR** (KBr, cm^{-1}): ν 3415, 1637, 1400, 1172, 617.

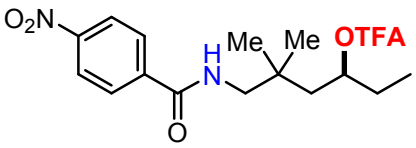
6-(4-chlorobenzamido)-5,5-dimethylhexan-3-yl 2,2,2-trifluoroacetate (3-*PG* 3)



***3-PG* 3**

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.27 (br s, 1H), 5.16–5.23 (m, 1H), 3.52 (dd, J = 13.8, 7.8 Hz, 1H), 3.09 (dd, J = 13.8, 5.4 Hz, 1H), 1.80 (dd, J = 15.4, 8.4 Hz, 1H), 1.67–1.75 (m, 2H), 1.55 (d, J = 15.4 Hz, 1H), 0.98 (s, 6H), 0.93 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.62, 157.27 (q, 42.0 Hz), 137.78, 132.96, 128.90, 128.22, 114.55, 78.38, 49.32, 42.37, 34.54, 28.65, 25.48, 25.21, 9.07. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{21}F_3NClNaO_3$, 402.1054; found, 402.1041. **IR** (KBr, cm^{-1}): ν 3415, 1637, 1400, 1120, 617.

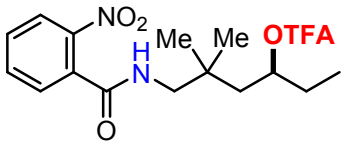
5,5-dimethyl-6-(4-nitrobenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-*PG* 5)



***3-PG* 5**

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.30 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 6.46 (br s, 1H), 5.15–5.23 (m, 1H), 3.57 (dd, J = 13.8, 7.8 Hz, 1H), 3.13 (dd, J = 13.8, 5.4 Hz, 1H), 1.82 (dd, J = 15.3, 8.1 Hz, 1H), 1.69–1.78 (m, 2H), 1.58 (dd, J = 15.4, 2.1 Hz, 1H), 1.00 (s, 6H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 165.73, 157.31 (q, J = 42.0 Hz), 149.60, 140.16, 128.01, 123.87, 114.53 (q, J = 285.0 Hz), 78.41, 49.44, 42.43, 34.57, 28.64, 25.64, 25.20, 9.07. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{21}F_3N_2NaO_5$, 413.1295; found, 413.1282. **IR** (KBr, cm^{-1}): ν 3416, 1638, 1400, 1172, 615, 481.

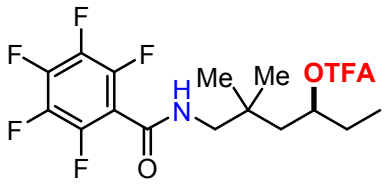
5,5-dimethyl-6-(2-nitrobenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-*PG* 6)



***3-PG* 6**

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.8 Hz, 1H), 7.50 (d, J = 7.5 Hz, 1H), 6.03 (br s, 1H), 5.21–5.24 (m, 1H), 3.49–3.52 (m, 1H), 3.09 (dd, J = 13.8, 5.7 Hz, 1H), 1.83 (dd, J = 15.6, 8.7 Hz, 1H), 1.69–1.77 (m, 2H), 1.66 (d, J = 15.3 Hz, 1H), 1.01 (s, 3H), 0.98 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.63, 157.23 (q, J = 42.0 Hz), 146.61, 133.62, 133.03, 130.53, 128.64, 124.56, 114.58 (q, J = 285.0 Hz), 78.49, 49.89, 42.16, 34.53, 28.65, 25.26, 25.21, 8.98. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{21}F_3N_2NaO_5$, 413.1295; found, 413.129. **IR** (KBr, cm^{-1}): ν 3415, 1638, 1400, 1120, 616, 480.

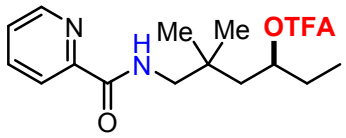
5,5-dimethyl-6-(perfluorobenzamido)hexan-3-yl 2,2,2-trifluoroacetate (3-*PG* 8)



***3-PG* 8**

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.15 (br s, 1H), 5.16–5.20 (m, 1H), 3.52 (dd, J = 13.8, 7.8 Hz, 1H), 3.10 (dd, J = 13.8, 5.4 Hz, 1H), 1.79 (dd, J = 15.3, 8.4 Hz, 1H), 1.66–1.76 (m, 2H), 1.57 (d, J = 15.3 Hz, 1H), 0.98 (d, J = 8.4 Hz, 6H), 0.93 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.64, 157.25 (q, J = 42.0 Hz), 114.51 (q, J = 285.0 Hz), 78.17, 49.65, 42.14, 34.43, 28.62, 25.29, 24.99, 8.97. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{17}F_8NNaO_7$, 458.0973; found, 458.0960. **IR** (KBr, cm^{-1}): ν 3416, 1639, 1511, 1399, 1118, 616, 482.

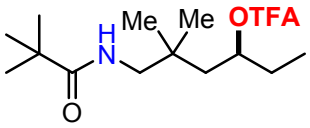
5,5-dimethyl-6-(picolinamido)hexan-3-yl 2,2,2-trifluoroacetate (3-*PG* 9)



***3-PG* 9**

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.57 (d, J = 4.5 Hz, 1H), 8.23 (br s, 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.86 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 6.9, 5.4 Hz, 1H), 5.21–5.25 (m, 1H), 3.44 (dd, J = 13.5, 7.5 Hz, 1H), 3.19 (dd, J = 13.5, 6.0 Hz, 1H), 1.81 (dd, J = 15.3, 8.7 Hz, 1H), 1.65–1.76 (m, 2H), 1.58 (d, J = 13.2 Hz, 1H), 0.99 (d, J = 3.6 Hz, 6H), 0.91 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 164.47, 149.78, 148.07, 137.38, 126.18, 122.31, 78.12, 49.37, 42.39, 34.53, 28.70, 25.20, 24.96, 9.03 ($OCOCF_3$ is difficult to detect). **HRMS–ESI (m/z)**: $[M+Na]^+$ calcd. for $C_{16}H_{21}F_3N_2NaO_3$, 369.1396; found, 369.1389. **IR** (KBr, cm^{-1}): ν 3415, 2960, 1621, 1533, 1399, 1170, 619, 480.

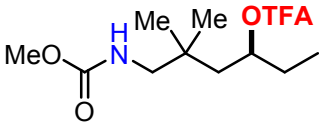
5,5-dimethyl-6-pivalamidohexan-3-yl 2,2,2-trifluoroacetate (*3-PG-10*)



***3-PG* 10**

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.76 (br s, 1H), 5.15–5.18 (m, 1H), 3.32 (dd, J = 13.8, 7.8 Hz, 1H), 2.85 (dd, J = 13.8, 5.4 Hz, 1H), 1.64 –1.73 (m, 3H), 1.46 (dd, J = 15.3, 2.1 Hz, 1H), 1.21 (s, 9H), 0.91 (t, J = 7.8 Hz, 3H), 0.90 (s, 3H), 0.89 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.38, 157.19 (q, J = 42.0 Hz), 114.59 (q, 285.0 Hz), 78.34, 48.57, 42.24, 38.88, 34.38, 28.62, 27.62, 25.31, 25.14, 8.99. **HRMS–ESI** (m/z): $[M+Na]^+$ calcd. for $C_{15}H_{26}F_3NNaO_3$, 348.1757; found, 348.1762. **IR** (KBr, cm^{-1}): ν 3415, 2962, 1778, 1541, 1165, 702.

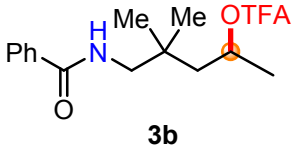
6-((methoxycarbonyl)amino)-5,5-dimethylhexan-3-yl-2,2,2-trifluoroacetate (3-*PG* 12)



***3-PG* 12**

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.12–5.15 (m, 1H), 4.75 (br s, 1H), 3.67 (s, 3H), 3.12 (dd, J = 13.8, 7.5 Hz, 1H), 2.90 (dd, J = 13.8, 5.7 Hz, 1H), 1.73 (dd, J = 15.5, 8.7 Hz, 1H), 1.64–1.68 (m, 2H), 1.48 (d, J = 15.3 Hz, 1H), 0.91 (t, J = 11.1 Hz, 3H), 0.90 (s, 3H), 0.86 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 157.36, 157.18 (q, J = 42.0 Hz,), 114.58 (q, J = 285.0 Hz), 78.13, 52.18, 51.15, 42.08, 34.18, 28.68, 24.94, 24.83, 8.98. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{12}H_{20}F_3NNaO_4$, 322.1237; found, 322.1243. **IR** (KBr, cm^{-1}): ν 3753, 3416, 2926, 1622, 1400, 1172, 615, 472.

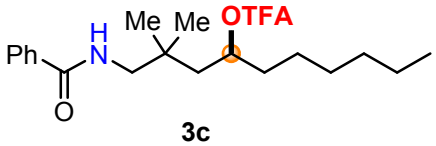
5-benzamido-4,4-dimethylpentan-2-yl 2,2,2-trifluoroacetate (3b)



3b

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 6.33 (br s, 1H), 5.28–5.33 (m, 1H), 3.54 (dd, J = 13.8, 7.8 Hz, 1H), 3.09 (dd, J = 13.8, 5.7 Hz, 1H), 1.87 (dd, J = 15.3, 8.4 Hz, 1H), 1.52 (dd, J = 15.3, 2.7 Hz, 1H), 1.38 (d, J = 6.0 Hz, 3H), 0.99 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.68, 157.00 (q, J = 42.0 Hz), 134.61, 131.52, 128.63, 126.77, 114.46 (q, J = 285.0 Hz), 74.24, 49.27, 44.50, 34.63, 25.41, 25.26, 21.61. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3NNaO_3$, 354.1287; found, 354.1282. **IR** (KBr, cm^{-1}): ν 3415, 2960, 1638, 1399, 1173, 616.

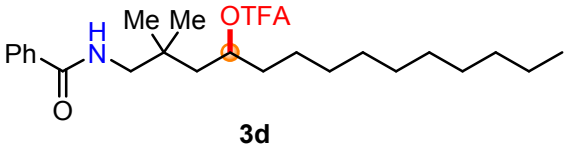
1-benzamido-2,2-dimethyldecan-4-yl 2,2,2-trifluoroacetate (3c)



3c

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 6.31 (br s, 1H), 5.22–5.26 (m, 1H), 3.51 (dd, J = 13.8, 7.5 Hz, 1H), 3.10 (dd, J = 13.8, 5.7 Hz, 1H), 1.80 (dd, J = 15.4, 8.4 Hz, 1H), 1.61–1.68 (m, 2H), 1.57 (dd, J = 15.4, 2.4 Hz, 1H), 1.21–1.33 (m, 8H), 0.98 (d, J = 1.8 Hz, 6H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.69, 157.16 (q, J = 42.0 Hz), 134.63, 131.43, 128.55, 126.78, 114.52 (q, J = 285.0 Hz) 77.40, 49.38, 42.77, 35.66, 34.56, 31.49, 28.83, 25.27, 25.14, 24.68, 22.41, 13.92. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{30}F_3NNaO_3$, 424.2070; found, 424.2066. **IR** (KBr, cm^{-1}): ν 3416, 2960, 1680, 1538, 1465, 1167, 711.

1-benzamido-2,2-dimethyltetradecan-4-yl 2,2,2-trifluoroacetate (3d)

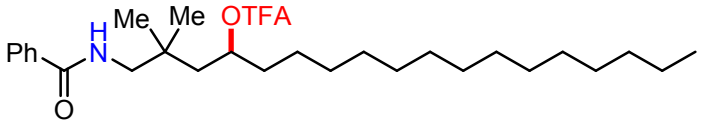


3d

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.5, 7.2 Hz, 2H), 6.29 (br s, 1H), 5.22–5.26 (m, 1H), 3.51 (dd, J = 13.8, 7.5 Hz, 1H), 3.10 (dd, J = 13.8, 5.4 Hz, 1H), 1.80 (dd, J = 15.4, 8.4 Hz,

1H), 1.58–1.73 (m, 2H), 1.57 (dd, J = 15.4, 1.8 Hz, 1H), 1.14–1.34 (m, 16H), 0.98 (s, 6H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.67, 157.22 (q, J = 42.0 Hz), 134.68, 131.50, 128.63, 126.79, 114.57 (q, J = 285.0 Hz), 77.45, 49.40, 42.84, 35.71, 34.59, 31.86, 29.52, 29.44, 29.35, 29.26, 29.22, 25.40, 25.19, 24.78, 22.65, 14.07. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{38}F_3NNaO_3$, 480.2696; found, 480.2691. **IR** (KBr, cm^{-1}): ν 3415, 2926, 1638, 1400, 1172, 617.

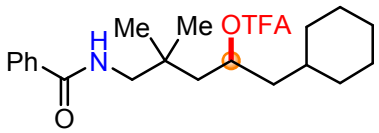
1-benzamido-2,2-dimethyloctadecan-4-yl 2,2,2-trifluoroacetate (3e)



3e

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 7.2, 7.2 Hz, 2H), 6.25 (br s, 1H), 5.22–5.26 (m, 1H), 3.53 (dd, J = 13.8, 7.5 Hz, 1H), 3.10 (dd, J = 13.8, 5.4 Hz, 1H), 1.81 (dd, J = 15.4, 8.4 Hz, 1H), 1.60–1.71 (m, 2H), 1.57 (dd, J = 15.0, 2.4 Hz, 1H), 1.20–1.34 (m, 24H), 0.98 (s, 3H), 0.97 (s, 3H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.66, 157.24 (q, J = 42.0 Hz), 134.70, 131.53, 128.67, 126.80, 114.59 (q, J = 285.0 Hz), 77.47, 49.40, 42.85, 35.74, 34.61, 31.93, 29.69, 29.68, 29.66, 29.64, 29.60, 29.48, 29.39, 29.36, 29.26, 25.46, 25.22, 24.82, 22.70, 14.12. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{29}H_{46}F_3NNaO_3$, 536.3322; found, 536.3321. **IR** (KBr, cm^{-1}): ν 3416, 1636, 1400, 1119, 616.

(5-benzamido-1-cyclohexyl-4,4-dimethylpentan-2-yl 2,2,2-trifluoroacetate (3f)

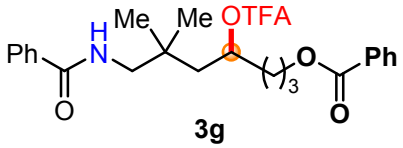


3f

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 7.8, 7.2 Hz, 2H), 6.31 (br s, 1H), 5.30–5.36 (m, 1H), 3.52 (dd, J = 13.8, 7.5 Hz, 1H), 3.12 (dd, J = 13.8, 5.4 Hz, 1H), 1.76–1.80 (m, 2H), 1.62–

1.69 (m, 5H), 1.56–1.61 (m, 2H), 1.43–1.49 (m, 1H), 1.12–1.22 (m, 5H), 0.99 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.64, 157.22 (q, J = 42.0 Hz), 134.64, 131.52, 128.64, 126.79, 114.53 (q, J = 285.0 Hz), 75.62, 49.37, 43.48, 43.31, 34.66, 34.00, 33.29, 33.02, 26.27, 26.03, 25.97, 25.57, 25.21. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{30}F_3NNaO_3$, 436.2070; found, 436.2084. **IR** (KBr, cm^{-1}): ν 3415, 2925, 1638, 1400, 1120, 616.

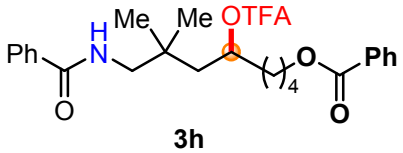
7-benzamido-6,6-dimethyl-4-(2,2,2-trifluoroacetoxy)heptyl benzoate (3g)



3g

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.43 (dd, J = 7.2, 7.5 Hz, 4H), 6.32 (br s, 1H), 5.35–5.40 (m, 1H), 4.29–4.38 (m, 2H), 3.55 (dd, J = 13.8, 7.5 Hz, 1H), 3.11 (dd, J = 13.8, 5.4 Hz, 1H), 1.75–1.87 (m, 5H), 1.60 (dd, J = 15.4, 2.4 Hz, 1H), 0.99 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.70, 166.51, 157.26 (q, J = 42.0 Hz), 134.61, 133.00, 131.53, 130.07, 129.55, 128.65, 128.38, 126.79, 114.53 (q, J = 285.0 Hz), 76.70, 64.00, 49.28, 42.72, 34.67, 32.36, 25.41, 25.26, 24.21. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{28}F_3NNaO_5$, 502.1812; found, 502.1808. **IR** (KBr, cm^{-1}): ν 3416, 1636, 1400, 1120, 616.

8-benzamido-7,7-dimethyl-5-(2,2,2-trifluoroacetoxy)octyl benzoate (3h)

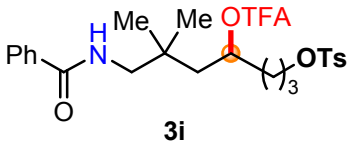


3h

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.42–7.45 (m, 4H), 6.27 (br s, 1H), 5.28–5.32 (m, 1H), 4.31 (t, J = 6.3 Hz, 2H), 3.54 (dd, J = 13.8, 7.8 Hz, 1H), 3.10 (dd, J = 13.8, 5.4 Hz, 1H), 1.73–1.84 (m, 5H), 1.58 (dd, J = 15.4, 2.1 Hz, 1H), 1.45–1.52 (m, 2H), 0.98 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.70, 166.58,

157.23 (q, J = 42.0 Hz), 134.57, 132.92, 131.56, 130.23, 129.51, 128.66, 128.34, 126.78, 114.53 (q, J = 285.0 Hz), 64.34, 49.35, 42.81, 35.39, 34.62, 28.34, 25.30, 21.38. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{30}F_3NNaO_5$, 516.1968; found: 516.1964. **IR** (KBr, cm^{-1}): ν 3418, 1637, 1400, 1120, 615.

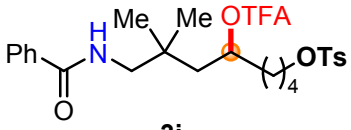
1-benzamido-2,2-dimethyl-7-(tosyloxy)heptan-4-yl 2,2,2-trifluoroacetate(3i)



3i

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 2H), 7.76 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 7.5 Hz, 2H), 7.46 (dd, J = 7.5, 7.5 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 6.27 (br s, 1H), 5.25–5.29 (m, 1H), 4.00–4.08 (m, 2H), 3.50 (dd, J = 13.8, 7.5 Hz, 1H), 3.10 (dd, J = 13.8, 5.7 Hz, 1H), 2.45 (s, 3H), 1.77 (dd, J = 15.4, 8.4 Hz, 1H), 1.64–1.73 (m, 4H), 1.53 (dd, J = 15.3, 2.4 Hz, 1H), 0.96 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.73, 157.20 (q, J = 42.0 Hz), 144.96, 134.51, 132.85, 131.58, 129.91, 128.68, 127.86, 126.81, 114.44 (q, J = 285.0 Hz), 76.19, 69.45, 49.23, 42.66, 34.66, 31.84, 25.42, 25.16, 24.31, 21.62. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{30}F_3NNaO_6S$, 552.1638; found, 552.1633. **IR** (KBr, cm^{-1}): ν 3417, 1637, 1400, 1120, 615.

1-benzamido-2,2-dimethyl-8-(tosyloxy)octan-4-yl 2,2,2-trifluoroacetate (3j)

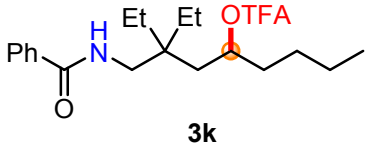


3j

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 4H), 7.52 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 8.1, 7.5 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.28 (br s, 1H), 5.20–5.24 (m, 1H), 4.00 (t, J = 6.3 Hz, 2H), 3.53 (dd, J = 13.8, 7.8 Hz, 1H), 3.07 (dd, J = 13.8, 5.4 Hz, 1H), 2.45 (s, 3H), 1.77 (dd, J = 15.3, 8.7 Hz, 1H), 1.62–1.66 (m, 4H), 1.53 (d, J = 15.3 Hz, 1H), 1.31–1.38 (m, 2H), 0.96 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.72, 157.19 (q, J = 42.0 Hz), 144.85, 134.59, 132.97, 131.60, 129.89,

128.70, 127.87, 126.82, 114.51 (q, J = 285.0 Hz), 76.78, 69.88, 49.34, 42.65, 34.99, 34.64, 28.40, 25.38, 25.23, 21.64, 20.77. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{32}F_3NNaO_6S$, 566.1795; found: 566.1793. **IR** (KBr, cm^{-1}): ν 3417, 1636, 1400, 1119, 616.

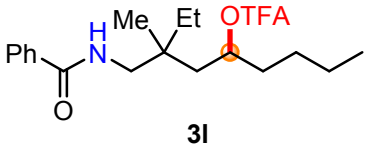
3-(benzamidomethyl)-3-ethylnonan-5-yl 2,2,2-trifluoroacetate (3k)



3k

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 6.18 (br s, 1H), 5.26–5.29 (m, 1H), 3.69 (dd, J = 14.4, 8.4 Hz, 1H), 2.97 (dd, J = 14.4, 4.8 Hz, 1H), 1.78 (dd, J = 16.2, 9.0 Hz, 1H), 1.65–1.70 (m, 2H), 1.60 (d, J = 18.9 Hz, 1H), 1.23–1.37 (m, 8H), 0.87–0.91 (m, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.45, 156.63 (q, J = 42.0 Hz), 134.67, 131.47, 128.63, 126.74, 114.55 (q, J = 285,0 Hz), 77.16, 43.73, 39.22, 37.58, 35.56, 26.92, 26.64, 22.39, 13.83, 7.43, 7.38. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{30}F_3NO_3Na$, 424.2070; found: 424.2064. **IR** (KBr, cm^{-1}): ν 3751, 3415, 2927, 1640, 1400, 1126, 704, 614.

3-(benzamidomethyl)-3-methylnonan-5-yl -2,2,2-trifluoroacetate (3l)

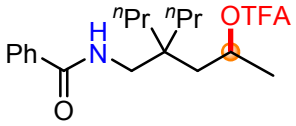


3l

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 1/2×4H, 1/2×4H), 7.51 (t, J = 6.9 Hz, 1/2×2H, 1/2×2H), 7.45 (dd, J = 8.1, 6.9 Hz, 1/2×4H, 1/2×4H), 6.22 (br s, 1/2×2H, 1/2×2H), 5.21–5.29 (m, 1/2×2H, 1/2×2H), 3.60 (t, J = 6.9 Hz, 1H), 3.58 (t, J = 6.9 Hz, 1H), 3.09 (t, J = 4.8 Hz, 1H), 3.06 (t, J = 4.8 Hz, 1H), 1.82 (dd, J = 15.6, 8.4 Hz, 1H), 1.78 (dd, J = 15.6, 8.4 Hz, 1H), 1.63–1.67 (m, 1/2×4H, 1/2×4H), 1.61 (dd, J = 15.6, 2.4 Hz, 1H), 1.55 (dd, J = 15.6, 2.4 Hz, 1H), 1.27–1.38 (m, 1/2×12H, 1/2×12H), 0.93 (s, 3H), 0.91 (s, 3H), 0.91 (t, J = 7.2 Hz, 3H), 0.90 (t, J

= 7.2 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.60, 167.57, 157.24 (q, J = 42.0 Hz), 157.15 (q, J = 42.0 Hz), 134.70, 134.68, 131.50, 131.49, 128.65, 128.64, 126.77, 126.75, 114.57 (q, J = 285.0 Hz), 114.55 (q, J = 285.0 Hz), 77.29, 77.26, 46.86, 46.84, 40.46, 39.98, 37.02, 36.89, 35.52, 35.48, 30.40, 30.17, 26.94, 26.90, 22.68, 22.44, 22.36, 13.83, 7.90, 7.88. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{28}F_3NNaO_3$, 410.1913; found, 410.1913. **IR** (KBr, cm^{-1}): ν 3417, 1638, 1400, 1122, 616.

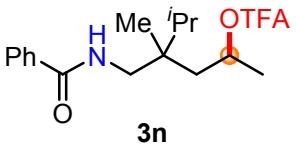
4-(benzamidomethyl)-4-propylheptan-2-yl 2,2,2-trifluoroacetate (3m)



3m

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.46 (dd, J = 7.5, 7.2 Hz, 2H), 6.19 (br s, 1H), 5.29–5.34 (m, 1H), 3.71 (dd, J = 14.1, 8.1 Hz, 1H), 2.97 (dd, J = 14.1, 4.8 Hz, 1H), 1.85 (dd, J = 15.8, 8.7 Hz, 1H), 1.53 (dd, J = 15.9, 2.1 Hz, 1H), 1.38 (d, J = 6.3 Hz, 3H), 1.13–1.35 (m, 9H), 0.92 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.48, 156.97 (q, J = 42.0 Hz), 134.74, 131.46, 128.65, 126.72, 114.46 (q, J = 285.0 Hz) 74.09, 44.63, 40.49, 39.35, 37.67, 37.43, 21.72, 16.28, 14.76, 14.72. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{28}F_3NNaO_3$, 410.1913; found, 410.1903. **IR** (KBr, cm^{-1}): ν 3417, 1636, 1400, 1120, 616.

4-(benzamidomethyl)-4,5-dimethylhexan-2-yl 2,2,2-trifluoroacetate (3n)

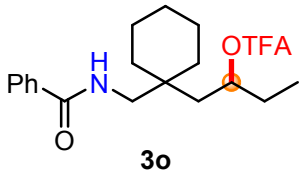


3n

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (t, J = 6.9 Hz, 1/2×4H, 1/2×4H), 7.51 (t, J = 7.8 Hz, 1/2×2H, 1/2×2H), 7.46 (dd, J = 6.9, 7.8 Hz , 1/2×4H, 1/2×4H), 6.22 (br s, 1/2×2H, 1/2×2H), 5.31–5.37 (m, 1/2×2H, 1/2×2H), 3.85 (dd, J = 14.1, 8.4

Hz, 1H), 3.73 (dd, J = 14.1, 8.1 Hz, 1H), 3.10 (dd, J = 14.1, 4.8 Hz, 1H), 2.97 (dd, J = 14.1, 4.8 Hz, 1H), 1.93 (dd, J = 15.6, 9.0 Hz, 1H), 1.86 (dd, J = 15.6, 8.4 Hz, 1H), 1.67 (dd, J = 16.2, 3.0 Hz, 1H), 1.63–1.69 (sept, J = 6.6 Hz, 1/2×2H, 1/2×2H), 1.54 (d, J = 16.2 Hz, 1H), 1.39 (d, J = 6.6 Hz, 3H), 1.38 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H), 0.92 (d, J = 6.9 Hz, 3H), 0.91 (d, J = 6.9 Hz, 3H), 0.91 (s, 3H), 0.85 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.60, 167.54, 157.01 (q, J = 42.0 Hz), 156.86 (q, J = 42.0 Hz), 134.68, 134.67, 131.49, 131.47, 128.66, 128.62, 126.76, 126.70, 114.49 (q, J = 285.0 Hz), 114.45 (q, J = 285.0 Hz), 74.27, 74.21, 45.48, 45.18, 41.21, 40.44, 39.27, 38.90, 33.17, 32.84, 21.82, 21.69, 19.42, 18.74, 17.32, 17.30, 17.20, 17.15. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{18}H_{24}F_3NNaO_3$, 382.1600; Found: 382.1579. **IR** (KBr, cm^{-1}): ν 3415, 2964, 1779, 1649, 1381, 1200, 715.

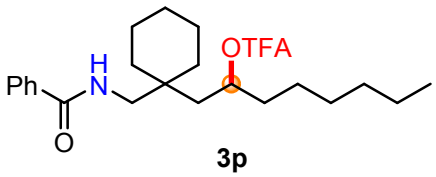
1-(1-(benzamidomethyl)cyclohexyl)butan-2-yl 2,2,2-trifluoroacetate (3o)



3o

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 6.32 (br s, 1H), 5.25–5.29 (m, 1H), 3.92 (dd, J = 14.1, 8.7 Hz, 1H), 2.93 (dd, J = 14.1, 4.5 Hz, 1H), 1.85 (dd, J = 15.8, 8.1 Hz, 1H), 1.65–1.78 (m, 2H), 1.58–1.65 (m, 1H), 1.61 (dd, J = 15.8, 3.6 Hz, 1H), 1.51–1.58 (m, 1H), 1.42–1.51 (m, 4H), 1.25–1.41 (m, 4H), 0.94 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.57, 157.21 (q, J = 42.0 Hz), 134.64, 131.44, 128.60, 126.75, 114.57 (q, J = 285.0 Hz), 78.32, 36.69, 34.12, 34.00, 28.73, 25.97, 21.40, 21.24, 9.09. **HRMS–ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{20}H_{27}F_3NO_3$, 386.1938; found, 386.1943. **IR** (KBr, cm^{-1}): ν 3415, 2930, 1777, 1642, 1398, 1172, 710.

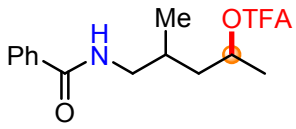
1-(1-(benzamidomethyl)cyclohexyl)octan-2-yl 2,2,2-trifluoroacetate (3p)



3p

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.5, 7.5 Hz, 2H), 6.31 (br s, 1H), 5.25–5.32 (m, 1H), 3.92 (dd, J = 14.1, 8.7 Hz, 1H), 2.93 (dd, J = 14.1, 4.5 Hz, 1H), 1.85 (dd, J = 15.7, 8.1 Hz, 1H), 1.61–1.73 (m, 3H), 1.51–1.58 (m, 1H), 1.20–1.51 (m, 17H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.51, 157.20 (q, J = 42.0 Hz), 134.64, 131.45, 128.61, 126.77, 114.56 (q, J = 285.0 Hz), 77.42, 36.74, 35.77, 34.13, 34.10, 31.56, 28.92, 25.99, 24.81, 22.46, 21.42, 21.26, 14.00. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{24}H_{34}F_3NNaO_3$, 464.2383; found, 464.2380. **IR** (KBr, cm^{-1}): ν 3414, 2925, 1641, 1400, 1128, 699.

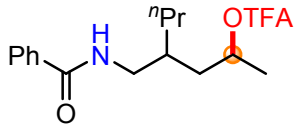
5-benzamido-4-methylpentan-2-yl 2,2,2-trifluoroacetate (3q)



3q

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5Hz, 2H), 7.51 (d, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.5, 7.1 Hz, 2H), 6.28 (br s, 1H), 5.24–5.30 (m, 1H), 3.39–3.44 (m, 1H), 3.33–3.38 (m, 1H), 1.85–1.91 (m, 1H), 1.65–1.72 (m, 2H), 1.37 (d, J = 6.3 Hz, 3H), 1.02 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.73, 157.13 (q, J = 42.0 Hz), 134.51, 131.53, 128.63, 126.80, 114.53 (q, J = 285.0 Hz), 75.11, 45.40, 40.02, 30.55, 19.77, 17.94. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{18}F_3NNaO_3$, 340.1131; found, 340.1122. **IR** (KBr, cm^{-1}): ν 3415, 2959, 1640, 1380, 1150, 803, 700.

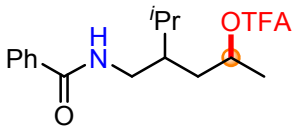
4-(benzamidomethyl)heptan-2-yl 2,2,2-trifluoroacetate (3r)



3r

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.44 (dd, J = 7.2, 7.2 Hz, 2H), 6.23 (br s, 1H), 5.29–5.35 (m, 1H), 3.56–3.60 (m, 1H), 3.29–3.34 (m, 1H), 1.76–1.80 (m, 1H), 1.67–1.74 (m, 1H), 1.55–1.62 (m, 1H), 1.38–1.43 (m, 3H), 1.37 (d, J = 12.0 Hz, 3H), 1.28–1.32 (m, 1H), 0.92 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.77, 157.23 (q, J = 42.0 Hz), 134.54, 131.51, 128.63, 126.78, 114.56 (q, J = 285.0 Hz), 75.15, 42.99, 38.04, 34.91, 34.56, 20.15, 19.69, 14.14. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{22}F_3NNaO_3$, 368.1444; Found: 368.1441. **IR** (KBr, cm^{-1}): ν 3415, 2961, 1780, 1639, 1399, 1170, 703, 616.

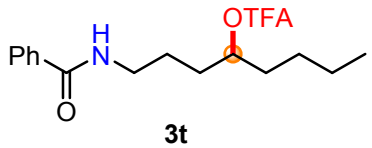
4-(benzamidomethyl)-5-methylhexan-2-yl 2,2,2-trifluoroacetate (3s)



3s

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.8, 7.5 Hz, 2H), 6.16 (br s, 1H), 5.27–5.33 (m, 1H), 3.52–3.58 (m, 1H), 3.39–3.45 (m, 1H), 1.83 (sept, J = 7.8 Hz, 1H), 1.77–1.80 (m, 1H), 1.52 (d, J = 3.6 Hz, 1H), 1.50 (d, J = 3.6 Hz, 1H), 1.38 (d, J = 6.3 Hz, 3H), 0.96 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.66, 157.40 (q, J = 42.0 Hz), 134.51, 131.51, 128.64, 126.79, 114.59 (q, J = 285.0 Hz) 75.51, 41.53, 40.87, 35.41, 29.10, 20.32, 19.63, 18.46. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{22}F_3NNaO_3$, 368.1444; found, 368.1443. **IR** (KBr, cm^{-1}): ν 3415, 1622, 1400, 1122, 616.

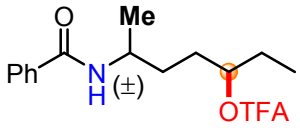
1-benzamidooctan-4-yl 2,2,2-trifluoroacetate (3t)



3t

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 6.18 (br s, 1H), 5.08–5.14 (m, 1H), 3.44–3.53 (m, 2H), 1.73–1.79 (m, 2H), 1.60–1.72 (m, 4H), 1.27–1.36 (m, 4H), 0.90 (t, J = 6.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.58, 157.41 (q, J = 42.0 Hz), 134.49, 131.51, 128.61, 126.81, 114.63 (q, J = 285.0 Hz), 79.50, 39.51, 33.35, 31.11, 27.09, 25.49, 22.32, 13.82. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{22}F_3NNaO_3$, 368.1444; found, 368.1442. **IR** (KBr, cm^{-1}): ν 3415, 2960, 1465, 1174, 618.

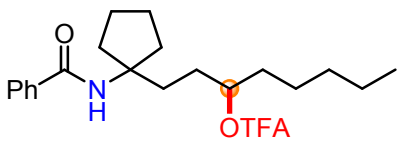
6-benzamidoheptan-3-yl 2,2,2-trifluoroacetate (3v)



3v

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, J = 6.6 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.44 (dd, J = 7.5, 6.6 Hz, 2H), 5.87 (d, J = 8.4 Hz, 1H), 5.04–5.09 (m, 1H), 4.22–4.28 (m, 1H), 1.75–1.78 (m, 2H), 1.68–1.73 (m, 2H), 1.53–1.61 (m, 2H), 1.26 (d, J = 6.6 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.97, 157.38 (q, J = 42.0 Hz), 134.67, 131.45, 128.58, 126.77, 114.69 (q, J = 285.0 Hz), 80.70, 45.15, 32.70, 29.91, 26.71, 21.19, 9.23. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{20}F_3NNaO_3$, 354.1287; found, 354.1294. **IR** (KBr, cm^{-1}): ν 3416, 1637, 1400, 1172, 616.

(1-benzamidocyclopentyl)octan-3-yl 2,2,2-trifluoroacetate (3w)

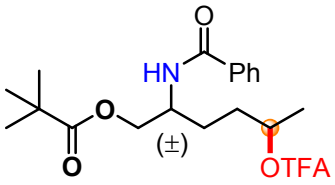


3w

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, J = 7.2 Hz, 2H), 7.50 (t, J =

7.5 Hz, 1H), 7.43 (dd, J = 7.2, 7.5 Hz, 2H), 5.81 (br s, 1H), 5.04 (quint, J = 6.0 Hz, 1H), 2.08–2.14 (m, 2H), 2.01–2.03 (m, 1H), 1.89–1.94 (m, 1H), 1.62–1.75 (m, 10H), 1.23–1.33 (m, 6H), 0.85 (t, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.00, 157.28 (q, J = 42.0 Hz), 135.52, 131.30, 128.59, 126.65, 114.65 (q, J = 285.0), 80.12, 64.69, 38.33, 38.24, 33.19, 32.16, 31.35, 29.31, 24.59, 23.56, 22.38, 13.86. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{30}F_3NNaO_3$, 436.2070; found, 430.2064. **IR** (KBr, cm^{-1}): ν 3415, 1637, 1400, 1175, 618.

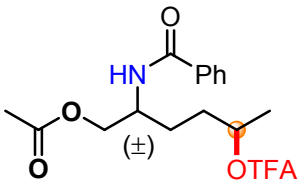
2-benzamido-5-(2,2,2-trifluoroacetoxy)hexyl pivalate (3x)



3x

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 7.5 Hz, 2H), 6.35 (d, J = 8.7 Hz, 1H), 5.15–5.20 (m, 1H), 4.45–4.51 (m, 1H), 4.34 (dd, J = 11.7, 6.3 Hz, 1H), 4.12 (dd, J = 11.7, 3.6 Hz, 1H), 1.75–1.87 (m, 2H), 1.59–1.65 (m, 2H), 1.37 (d, J = 6.3 Hz, 3H), 1.19 (s, 9H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 178.97, 167.13, 157.09 (q, J = 42.0 Hz), 134.01, 131.73, 128.68, 126.83, 114.51 (q, J = 285.0 Hz), 75.93, 65.61, 48.78, 38.93, 31.78, 27.54, 27.09, 19.59. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{26}F_3NNaO_5$, 440.1655; found, 440.1662. **IR** (KBr, cm^{-1}): ν 3416, 1638, 1400, 1168, 617.

6-acetoxy-5-benzamidohexan-2-yl 2,2,2-trifluoroacetate (3y)

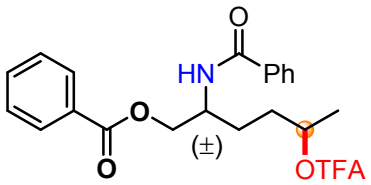


3y

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 6.9 Hz, 1H), 7.46 (dd, J = 7.5, 6.9 Hz, 2H), 6.34 (d, J = 9.0 Hz, 1H), 5.15–5.20 (m,

1H), 4.39–4.50 (m, 1H), 4.32 (dd, J = 11.5, 5.4 Hz, 1H), 4.10–4.17 (m, 1H), 2.09 (s, 3H), 1.89–1.95 (m, 1H), 1.81–1.86 (m, 1H), 1.74–1.79 (m, 1H), 1.63–1.67 (m, 1H), 1.37 (d, J = 6.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.40, 167.23, 157.10 (q, J = 42.0 Hz), 134.05, 131.76, 128.69, 126.88, 114.53 (q, J = 285.0 Hz), 75.89, 65.87, 48.54, 31.78, 27.45, 20.75, 19.58. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{20}F_3NNaO_5$, 398.1186; found, 398.1192. **IR** (KBr, cm^{-1}): ν 3415, 1638, 1398, 1171, 616.

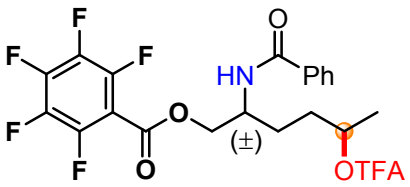
2-benzamido-5-(2,2,2-trifluoroacetoxy)hexyl benzoate (3z)



3z

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.1 Hz, 1H), 7.51 (t, J = 6.9 Hz, 1H), 7.45 (dd, J = 7.5, 7.1 Hz, 4H), 6.45 (d, J = 8.4 Hz, 1H), 5.17–5.22 (m, 1H), 4.57–4.63 (m, 1H), 4.53 (dt, J = 11.4, 6.0 Hz, 1H), 4.43–4.47 (m, 1H), 1.96–2.00 (m, 1H), 1.81–1.86 (m, 1H), 1.75–1.80 (m, 2H), 1.38 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.34, 166.93, 157.12 (q, J = 42.0 Hz), 134.09, 133.42, 131.73, 129.65, 129.45, 128.68, 128.53, 126.89, 114.53 (q, J = 285.0 Hz), 75.92, 66.38, 48.80, 31.84, 27.59, 19.60. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{22}F_3NNaO_5$, 460.1342; found, 460.1333. **IR** (KBr, cm^{-1}): ν 3417, 1636, 1400, 1119, 615.

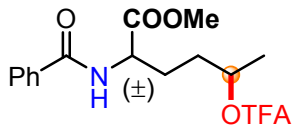
2-benzamido-5-(2,2,2-trifluoroacetoxy)hexyl-2,3,4,5,6-pentafluorobenzoate (3aa)



3aa

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.46 (dd, J = 7.5, 7.3 Hz, 2H), 6.29 (d, J = 8.2 Hz, 1H), 4.58 (dd, J = 10.8, 3.6 Hz, 1H), 4.52–4.56 (m, 1H), 4.50 (dd, J = 10.2, 3.0 Hz, 1H), 4.16 (dd, J = 12.7, 6.4 Hz, 1H), 1.88–2.02 (m, 3H), 1.72–1.82 (m, 1H), 1.72 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.13, 133.95, 131.83, 128.70, 126.88, 67.99, 53.39, 50.91, 48.40, 37.46, 29.95, 26.37. ($OCOCF_3$ is difficult to detect). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{17}F_8NNaO_5$, 550.0871; Found: 550.0860. **IR** (KBr, cm^{-1}): ν 3417, 1638, 1400, 1118, 616.

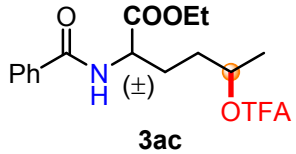
methyl-2-benzamido-5-(2,2,2-trifluoroacetoxy)hexanoate (3ab)



3ab

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.47 (dd, J = 7.5, 7.2 Hz, 2H), 6.75 (d, J = 6.9 Hz, 1H), 5.13–5.18 (m, 1H), 4.86–4.89 (m, 1H), 3.81 (s, 3H), 2.03–2.11 (m, 1H), 1.71–1.84 (m, 3H), 1.36 (d, J = 6.3 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.62, 167.10, 157.05 (q, J = 42.0 Hz) 133.62, 131.96, 128.68, 127.03, 114.50 (q, J = 285.0 Hz), 75.66, 52.77, 51.86, 31.21, 28.63, 19.56. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{16}H_{18}F_3NNaO_5$, 384.1029; found: 384.1029. **IR** (KBr, cm^{-1}): ν 3415, 1620, 1400, 1121, 617.

(±)-ethyl-2-benzamido-5-(2,2,2-trifluoroacetoxy)hexanoate (3ac)

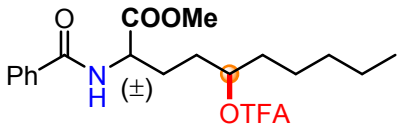


3ac

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.47 (dd, J = 7.2, 7.2 Hz, 2H), 6.74 (d, J = 7.5 Hz, 1H), 4.79–4.87 (m, 1H), 4.26 (q, J = 7.2 Hz, 2H), 4.10–4.18 (m, 1H), 2.20–2.28 (m, 1H), 1.83–1.99 (m,

3H), 1.71 (d, J = 6.6 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.15, 167.09, 157.04 (q, J = 42.0 Hz), 133.68, 131.92, 128.67, 127.02, 114.50 (q, J = 285.0 Hz), 75.68, 61.97, 51.87, 31.14, 28.62, 19.58, 14.08. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{17}H_{20}F_3NNaO_5$, 398.1186; found, 398.1183. **IR** (KBr, cm^{-1}): ν 3416, 1637, 1400, 1172, 616.

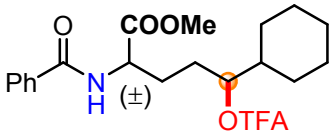
methyl-2-benzamido-5-(2,2,2-trifluoroacetoxy)decanoate (3ad)



3ad

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 6.9 Hz, 2/5×2 H, 3/5×2 H), 7.53 (t, J = 7.2 Hz, 2/5×1 H, 3/5×1 H), 7.45 (dd, J = 7.2, 6.9 Hz, 2/5×2 H, 3/5×2H), 6.68–6.78 (m, 2/5×1H, 3/5×1H), 5.08–5.14(m, 2/5×1H), 4.81–4.89 (m, 2/5×1H, 3/5×1H), 3.98–4.05 (m, 3/5×1H), 3.79 (s, 2/5×3 H, 3/5×3H), 2.24–2.29 (m, 2/5×1H), 1.99–2.07 (m, 3/5×1H), 1.25–2.00 (m, 2/5×11H, 3/5×11H), 0.88 (t, J = 6.0 Hz, 2/5×3H, 3/5×3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.64, 172.56, 167.10, 167.06, 133.65, 133.63, 131.95 (C×2), 128.68 (C×2), 127.03 (C×2), 79.17, 79.06, 52.76, 52.74, 52.17, 51.88, 33.61, 33.32, 31.32, 31.29, 29.51, 29.45, 28.59, 28.18, 24.56, 24.53, 22.35 (C×2), 13.86 (C×2). ($OCOCF_3$ is difficult to detect). **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{20}H_{26}F_3NNaO_3$, 440.1655; found, 440.1662. **IR** (KBr, cm^{-1}): ν 3416, 1636, 1400, 1119, 616.

methyl-2-benzamido-5-cyclohexyl-5-(2,2,2-trifluoroacetoxy)pentanoate (3ae)

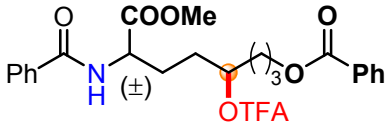


3ae

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2/5×2 H, 3/5×2

H), 7.54 (t, J = 6.9 Hz, 2/5×1 H, 3/5×1 H), 7.46 (dd, J = 8.1, 6.9 Hz, 2/5×2 H, 3/5×2H), 6.70 (d, J = 7.2 Hz, 3/5×1H), 6.68 (d, J = 7.2 Hz, 2/5×1H), 4.86–4.89 (m, 2/5×1H), 4.81–4.86 (m, 3/5×1H), 3.97–4.00 (m, 2/5×1H), 3.92–3.96 (m, 3/5×1H), 3.80 (s, 2/5×3 H, 3/5×3H), 2.28–2.33 (m, 3/5×1H), 2.05–2.16 (m, 2/5×1H), 1.64–2.01 (m, 2/5×7H, 3/5×7H), 1.47–1.55 (m, 3/5×1H, 2/5×1H), 1.18–1.28 (m, 3/5×6H), 1.10–1.17 (m, 2/5×6H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 172.88, 172.82, 167.15, 167.06, 133.78, 133.76, 131.87(2×C), 128.66, 128.65, 127.05 (C×2), 64.65, 64.57, 52.68, 52.63, 52.19, 51.83, 44.65, 44.30, 32.08, 31.87, 31.52, 31.33, 30.88, 30.83, 29.40, 29.30, 26.16 (C×2), 26.07 (C×2), 25.95 (C×2) ($OCOCF_3$ is difficult to detect). **^{1}HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{21}H_{26}F_3NNaO_5$, 452.1655; found, 452.1646. **IR** (KBr, cm^{-1}): ν 3415, 1621, 1400, 1120, 617.

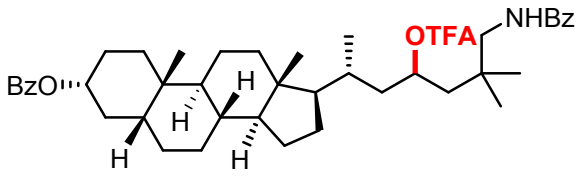
7-benzamido-8-methoxy-8-oxo-4-(2,2,2-trifluoroacetoxy)octyl benzoate (3af)



3af

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2 H), 7.80 (d, J = 7.8 Hz, 2 H), 7.56 (t, J = 7.2 Hz, 2H), 7.45 (dd, J = 7.2, 7.8 Hz, 4H), 6.75 (d, J = 7.8 Hz, 1H), 5.23 (br s, 1H), 4.88–4.90 (m, 1H), 4.30–4.38 (m, 2H), 3.80 (s, 3H), 2.28–2.34 (m, 1H), 1.74–2.09 (m, 7H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.55, 167.13, 166.46, 157.27 (q, J = 42.0 Hz), 133.59, 133.01, 131.96, 130.04, 129.54, 128.68, 128.38, 127.03, 114.56 (q, J = 285.0 Hz), 78.36, 63.98, 52.79, 51.78, 30.40, 29.55, 28.60, 24.38. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{26}NF_3NaO_7$, 532.1554; found, 532.1553. **IR** (KBr, cm^{-1}): ν 3415, 1722, 1534, 1277, 714.

(3R,5R,8R,9S,10S,13R,14S,17R)-17-((2R,4R)-7-benzamido-6,6-dimethyl-4-(2,2,2-trifluoroacetoxy)heptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (3ag)

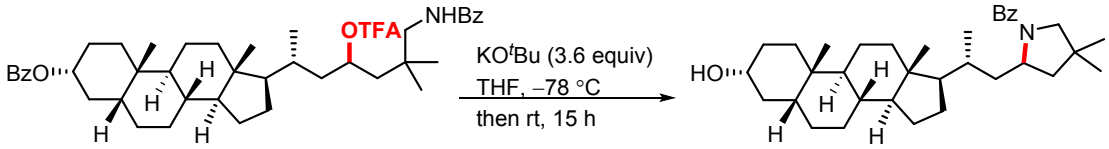


3ag

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 7.43 (dd, J = 7.2, 7.5 Hz, 2H), 6.35 (t, J = 6.4 Hz, 1H), 5.40 (br s, 1H), 4.92–5.03 (m, 1H), 3.52 (dd, J = 13.7, 7.6 Hz, 1H), 3.14 (dd, J = 13.7, 5.6 Hz, 1H), 1.95-1.98 (m, 2H), 1.79-1.92 (m, 6H), 1.66-1.69 (m, 1H), 1.52–1.57 (m, 4H), 1.36-1.49 (m, 4H), 1.26-1.32 (m, 3H), 1.20-1.22 (m, 2H), 1.14-1.17 (m, 2H), 1.04-1.11 (m, 4H), 0.99 (s, 6H), 0.98 (s, 3H), 0.96 (s, 3H), 0.62 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.64, 166.12, 157.47 (q, J = 42.0 Hz), 134.62, 132.66, 131.52, 130.93, 129.50, 128.64, 128.24, 126.81, 114.59 (q, J = 285.0 Hz), 75.48, 74.99, 56.47, 56.30, 49.48, 44.31, 43.15, 42.81, 41.94, 40.45, 40.06, 35.76, 35.06, 34.75, 34.63, 32.50, 32.36, 28.37, 27.02, 26.76, 26.31, 25.50, 25.36, 24.12, 23.35, 20.82, 18.86, 11.80. **HRMS–ESI** (m/z): $[M+Na]^+$ calcd. for $C_{44}H_{58}F_3NNaO_5$, 760.4159; found, 760.4153. **IR** (KBr, cm^{-1}): ν 3416, 1636, 1400, 1120, 616.

Late-stage functionalization of steroids compounds:

Preparation of 4ag:

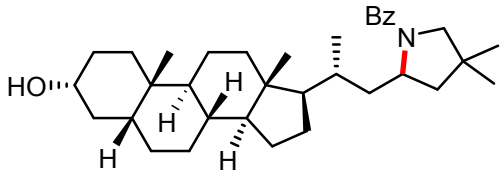


3ag **4ag**

Procedure: KO^{t}Bu (13 mg, 0.12 mmol, 3.6 equiv) was added to an oven-dried vial and then THF (0.2 mL) was added under agron atmosphere. The mixture was cooled to −78 ºC. Five minutes later, a solution of **3ag** (23.9 mg, 0.032 mmol, 1.0 equiv) in THF (0.4 mL) was slowly added and stiring for another 30 min at that temperature. Then, the reaction was allowed to warm to room temperature and stired for 5 hours. The reaction was diluted with water, extracted with EtOAc and washed with brine.

The combined solvent was dried with Na_2SO_4 and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 5:1:0.5 as eluent) to give the title product **4ag**.

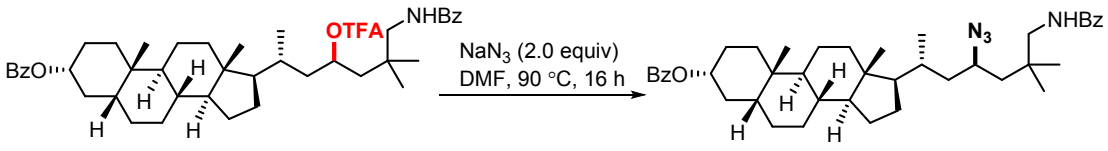
((2R)-2-((2R)-2-((3R,5R,8R,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)propyl)-4,4-dimethylpyrrolidin-1-yl)(phenyl)methanone (4ag)



4ag

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, J = 7.5 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.44 (dd, J = 7.5, 7.2 Hz, 2H), 7.30 (t, J = 6.0 Hz, 1H), 3.91–3.97 (m, 1H), 3.59–3.67 (m, 1H), 3.51 (dd, J = 13.5, 6.3 Hz, 1H), 3.31 (dd, J = 13.5, 6.9 Hz, 1H), 2.16 (d, J = 5.1 Hz, 1H), 1.99–2.01 (m, 1H), 1.77–1.88 (m, 4H), 1.63–1.70 (m, 1H), 1.48–1.62 (m, 4H), 1.36–1.45 (m, 6H), 1.17–1.30 (m, 6H), 1.04–1.11 (m, 5H), 1.02 (s, 3H), 0.98 (d, J = 8.7 Hz, 3H), 0.97 (s, 3H), 0.92 (s, 3H), 0.69 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.45, 135.05, 131.17, 128.49, 126.90, 71.86, 66.18, 56.85, 56.56, 48.80, 47.84, 46.10, 42.86, 42.07, 40.42, 40.25, 36.44, 35.83, 35.32, 34.80, 34.56, 32.49, 30.54, 29.69 (grease), 28.61, 28.57, 27.18, 26.40, 24.86, 24.19, 23.36, 20.82, 18.54, 12.13. **HRMS–ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{35}H_{53}NHO_2$, 520.4149; found, 520.4149. **IR** (KBr, cm^{-1}): ν 3752, 3415, 1623, 1400, 1120, 615.

Preparation of 5ag:

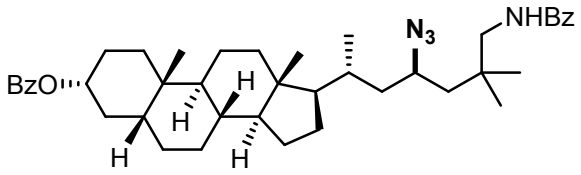


3ag **5ag**

Procedure: 3ag (23.5 mg, 0.032 mmol, 1.0 equiv), NaN_3 (4.2 mg, 0.064 mmol, 2.0 equiv), DMF (0.15 mL), were added to an oven-dried vial, and the mixture was heated at 90 ºC for 6 hours. The reaction was diluted with water, extracted with

EtOAc and washed with brine. The combined solvent was dried with anhydrous Na_2SO_4 and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 10:1:0.5 as eluent) to give the title product **5ag**.

(3R,5R,8R,10S,13R,14S,17R)-17-((2R,4R)-4-azido-7-benzamido-6,6-dimethylheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (5ag)

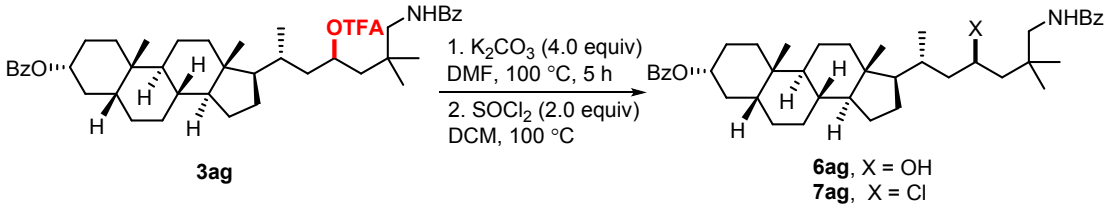


5ag

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, J = 8.1 Hz, 1/2×4H, 1/2×4H), 7.78 (d, J = 7.2 Hz, 1/2×4H, 1/2×4H), 7.55 (t, J = 7.5 Hz, 1/2×2H, 1/2×2H), 7.51 (t, J = 6.6 Hz, 1/2×2H, 1/2×2H), 7.45 (dd, J = 8.1, 7.2 Hz, 1/2×4H, 1/2×4H), 7.43 (dd, J = 7.2, 6.6 Hz, 1/2×4H, 1/2×4H), 6.64 (t, J = 6.0 Hz, 1H), 6.45 (t, J = 6.1 Hz, 1H), 4.94–5.01 (m, 1/2×2H, 1/2×2H), 3.59 (dd, J = 13.7, 7.8 Hz, 1H), 3.52 (dd, J = 13.5, 7.5 Hz, 1H), 3.40–3.54 (m, 1/2×2H, 1/2×2H), 3.23 (dd, J = 13.8, 5.7 Hz, 1H), 3.17 (dd, J = 13.8, 5.1 Hz, 1H), 1.92–2.00 (m, 1/2×4H, 1/2×4H), 1.75–1.93 (m, 1/2×10H, 1/2×10H), 1.61–1.69 (m, 1/2×6H, 1/2×6H), 1.49–1.55 (m, 1/2×4H, 1/2×4H), 1.36–1.47 (m, 1/2×14H, 1/2×14H), 1.25–1.31 (m, 1/2×7H, 1/2×7H), 1.07–1.13 (m, 1/2×11H, 1/2×11H), 1.06 (s, 3H), 1.03 (s, 3H), 1.02 (s, 3H), 1.00 (s, 3H), 0.99 (s, 3H), 0.97 (d, J = 6.6 Hz, 3H), 0.96 (s, 6H), 0.70 (s, 3H), 0.66 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.49, 167.37, 166.13, 134.87, 134.81, 132.68, 132.66, 131.42, 131.37, 130.94, 130.92, 129.51, 128.63, 128.61, 128.24, 126.81, 75.00, 74.97, 57.24, 56.76, 56.51, 56.48, 56.46, 49.18, 48.45, 44.84, 43.14, 42.99, 42.86, 41.95, 41.94, 41.59, 40.48, 40.45, 40.19, 40.16, 35.80, 35.79, 35.07, 34.81, 34.73, 34.65, 33.53, 33.30, 32.36, 28.60, 28.45, 27.03, 26.85, 26.77, 26.33, 26.31, 26.16, 25.23, 25.13, 24.19, 24.14, 23.37, 20.86, 18.76, 18.53, 12.05, 12.04. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{42}H_{58}N_4NaO_3$, 689.4401; found, 689.4400. **IR** (KBr, cm^{-1}): ν 3418, 1637, 1400,

1118, 614.

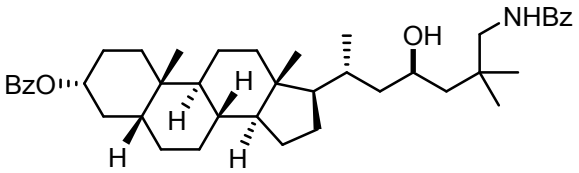
Preparation of 6ag and 7ag:



Procedure: 3ag (23.5 mg, 0.032 mmol, 1.0 equiv), K_2CO_3 (28 mg, 0.2 mmol, 4.0 equiv), DMF (0.1 mL) were added to an oven-dried vial, and the mixture was heated at 100 ℃ for 5 hours. The reaction was diluted with water, extracted with EtOAc and washed with brine. The combined solvent was dried with Na_2SO_4 and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 5:1:0.5 as eluent) to give the title product **6ag**.

To a solution of **6ag** (10.8 mg, 0.02 mmol, 1.0 equiv) in DCM (0.1 mL) was added $SOCl_2$ (0.04 mmol, 2.0 equiv) at room temperature then the vial was sealed with a cap and heated at 100 ℃ for 1.5 hours. The vial was allowed to cool to room temperature. The solvent was then removed in vacuo and the residue was further purified with flash column chromatography (PE: EtOAc: DCM = 5:1:0.5) to give the titled compound **7ag.**

(3R,5R,8R,10S,13R,14S,17R)-17-((2R,4R)-7-benzamido-4-hydroxy-6,6-dimethylheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (6ag)

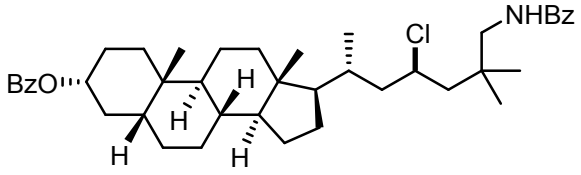


6ag

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, J = 7.2 Hz, 2H), 7.80 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.43 (dd, J = 7.2, 7.5 Hz, 2H), 7.42 (dd, J = 7.2, 7.2 Hz, 2H), 7.29 (t, J = 6.3 Hz, 1H), 4.95–5.00 (m, 1H), 3.93–3.96 (m, 1H), 3.52 (dd, J = 13.5, 6.3 Hz, 1H), 3.31 (dd, J = 13.5, 6.9 Hz, 1H),

2.15 (d, J = 4.5 Hz, 1H), 2.01–2.03 (m, 1H), 1.97 (q, J = 12.0 Hz, 1H), 1.79–1.91 (m, 4H), 1.66–1.71 (m, 1H), 1.50–1.60 (m, 6H), 1.39–1.47 (m, 4H), 1.26–1.31 (m, 3H), 1.18–1.23 (m, 3H), 1.06–1.15 (m, 5H), 1.02 (s, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.98 (s, 3H), 0.97 (s, 3H), 0.71 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.45, 166.14, 135.03, 132.67, 131.18, 130.93, 129.51, 128.50, 128.24, 126.90, 75.00, 66.16, 56.90, 56.55, 48.79, 47.83, 46.11, 42.88, 41.95, 40.48, 40.22, 35.80, 35.07, 34.80, 34.65, 32.48, 32.36, 29.69 (grease), 28.61, 28.57, 27.05, 26.76, 26.34, 24.86, 24.18, 23.36, 20.87, 18.56, 12.15. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{42}H_{59}NNaO_4$, 664.4336; found, 664.4331. **IR** (KBr, cm^{-1}): ν 3415, 2926, 1622, 1400, 1119, 615.

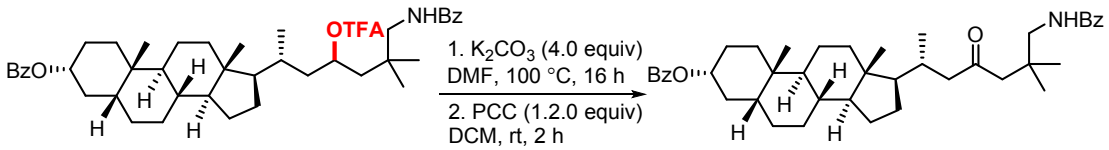
(3R,5R,8R,10S,13R,14S,17R)-17-((2R,4R)-7-benzamido-4-chloro-6,6-dimethylheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (7ag)



7ag

Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.2, 7.5 Hz, 2H), 7.43 (dd, J = 7.2, 7.2 Hz, 2H), 6.49–6.51 (m, 1H), 4.95–5.00 (m, 1H), 4.12–4.16 (m, 1H), 3.63 (dd, J = 13.8, 8.1 Hz, 1H), 3.24 (dd, J = 13.8, 5.1 Hz, 1H), 1.92–2.03 (m, 4H), 1.77–1.89 (m, 5H), 1.67–1.69 (m, 1H), 1.57–1.63 (m, 2H), 1.39–1.47 (m, 4H), 1.27–1.30 (m, 4H), 1.17–1.22 (m, 3H), 1.08–1.14 (dt, J = 16.2, 4.5 Hz, 5H), 1.06 (s, 3H), 1.01 (s, 3H), 0.97 (s, 3H), 0.96 (d, J = 6.0 Hz, 3H), 0.71 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 167.43, 166.13, 134.86, 132.66, 131.39, 130.96, 129.51, 128.62, 128.24, 126.82, 75.02, 58.26, 56.56, 56.51, 49.42, 48.41, 47.35, 42.93, 41.97, 40.50, 40.23, 35.81, 35.33, 35.09, 34.67, 33.32, 32.38, 28.25, 27.05, 26.78, 26.70, 26.35, 25.23, 24.18, 23.38, 20.88, 18.03, 12.14. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{42}H_{58}ClNNaO_3$, 682.3997; found, 682.3998. **IR** (KBr, cm^{-1}): ν 3415, 2927, 1622, 1400, 1118, 616.

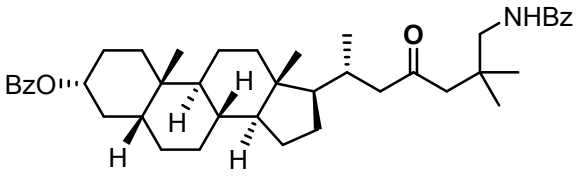
Preparation of 8ag:



3ag **8ag**

Procedure: PCC (5 mg, 0.024 mmol, 1.2 equiv) was added to a solution of **6ag** (10.8 mg, 0.02 mmol, 1.0 equiv) in DCM (0.1 mL), then stired for 2 hours. The vial was allowed to cool to room temperature. The solvent was then removed in vacuo and the residue was further purified with flash column chromatography (PE: EtOAc: DCM = 5:1:0.5) to give the titled compound **8ag**.

(3R,5R,8R,10S,13R,14S,17R)-17-((R)-7-benzamido-6,6-dimethyl-4-oxoheptan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl benzoate (8ag)

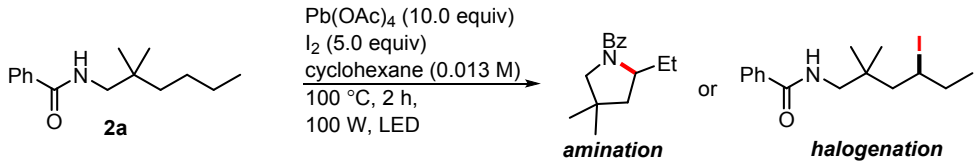


8ag

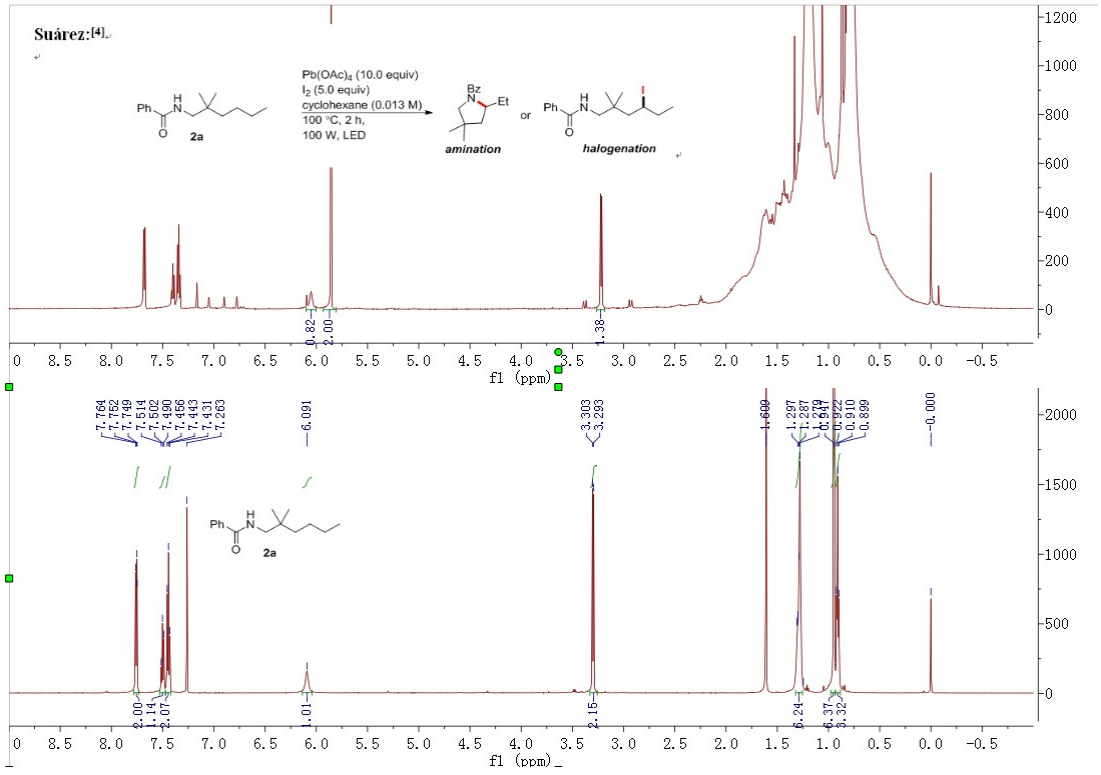
Colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.05 (d, J = 7.8Hz, 2H), 7.86 (d, J = 7.5Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2Hz, 1H), 7.46 (dd, J = 7.8, 7.2 Hz, 2H), 7.44 (dd, J = 7.5, 7.2 Hz, 2H), 7.37 (t, J = 5.4 Hz, 1H), 4.94–5.02 (m, 1H), 3.42 (dd, J = 13.8, 6.3 Hz, 1H), 3.32 (dd, J = 13.8, 6.0 Hz, 1H), 2.51 (dd, J = 16.5, 2.1 Hz, 1H), 2.44 (s, 2H), 2.21 (dd, J = 16.4, 9.9 Hz, 1H), 1.95–2.00 (m, 3H), 1.76–1.90 (m, 4H), 1.67–1.69 (m, 1H), 1.52–1.62 (m, 5H), 1.40–1.47 (m, 4H), 1.25–1.29 (m, 3H), 1.10–1.15 (m, 4H), 1.08 (s, 3H), 1.07 (s, 3H), 0.96 (s, 3H), 0.92 (d, J = 6.3 Hz, 3H), 0.70 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 213.09, 167.31, 166.12, 134.64, 132.68, 131.29, 130.89, 129.49, 128.52, 128.24, 126.94, 74.97, 56.51, 56.04, 52.98, 52.47, 49.50, 42.81, 41.90, 40.41, 40.02, 35.77, 35.41, 35.05, 34.63, 32.57, 32.34, 28.52, 27.00, 26.74, 26.67, 26.43, 26.30, 24.14, 23.34, 20.81, 19.84, 12.07. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{42}H_{57}NNaO_4$, 662.4180; found, 662.4172. **IR** (KBr, cm^{-1}): ν 3415, 1636, 1400, 1119, 616.

Comparative experiments.

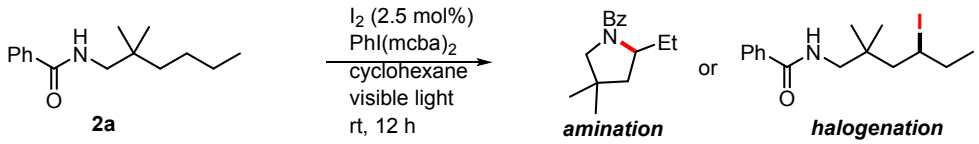
Suárez:[4]



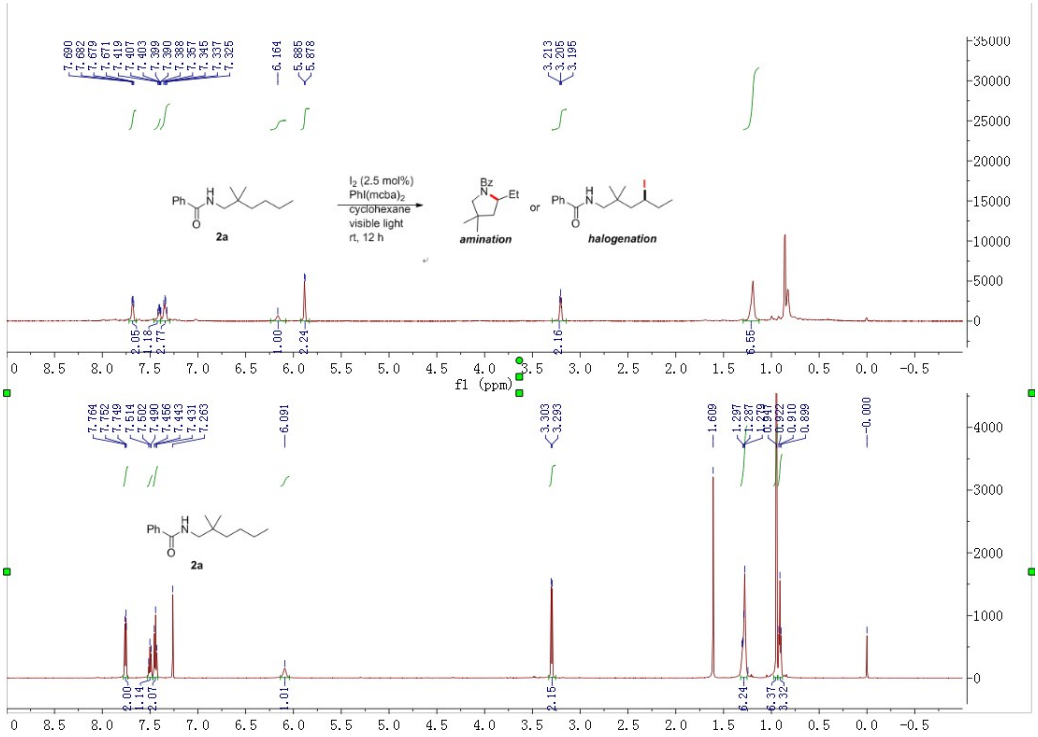
Procedure: To an oven-dried 25 mL round bottom flask with a condenser, **2a** (23.3 mg, 0.10 mmol, 1.0 equiv), $Pb(OAc)_4$ (443.38 mg, 1 mmol, 10 equiv), I_2 (127 mg, 0.5 mmol, 5.0 equiv), 7.5 mL cyclohexane were added sequentially under nitrogen atmosphere. The reaction mixture was irradiation with 100 W LED and stirred at 100 ℃ for 2 hours. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The result was determined by crude ^{1}H NMR.



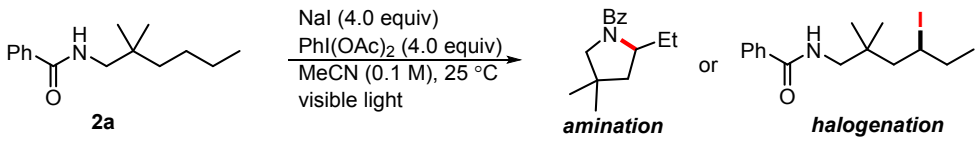
Muñiz:[5]



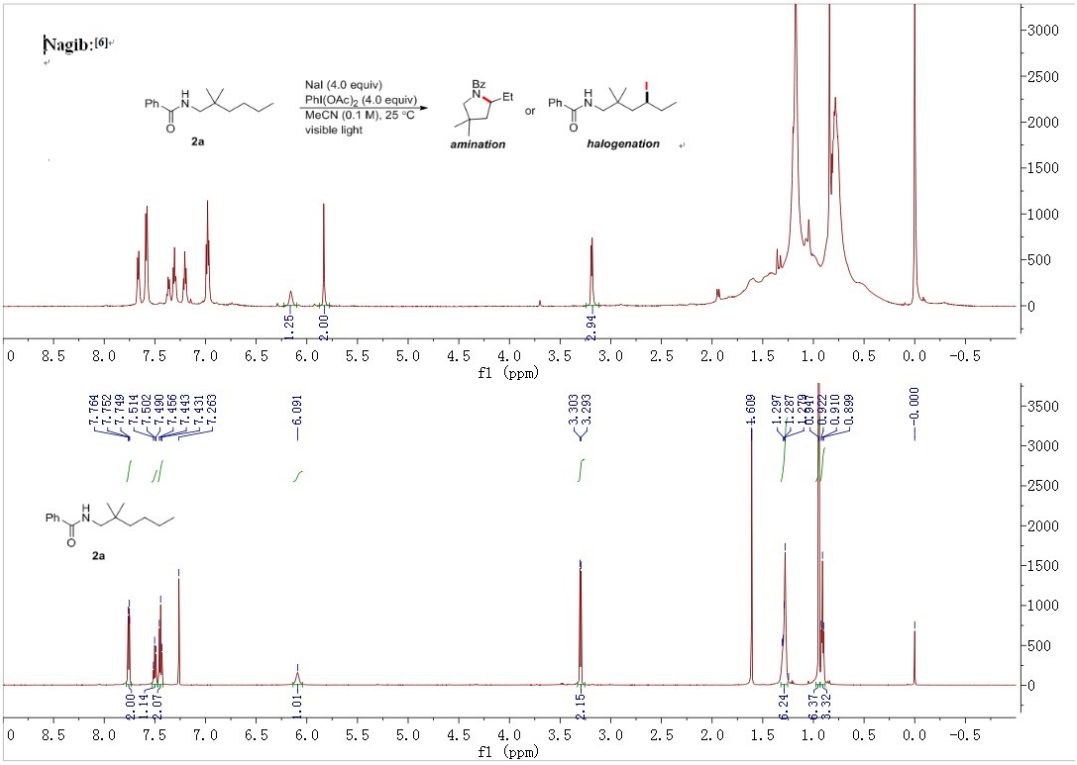
Procedure: A Schlenk tube equipped with a stirrer bar is charged with $PhI(mcba)_2$ (113 mg, 0.22 mmol, 1.0 equiv), and the amide **2a** (23.3 mg, 0.10 mmol, 1.0 equiv), evacuated, and backfilled with argon, before 1.5 mL of absolute dichloroethane are added. The solution is stirred at 25 ºC for 12 h under visible light. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure.The result was determined by crude ^1H NMR. 90 % of SM was recovered. (We have successfully reproduced the Muñiz reaction with sulphoamide under this condition).



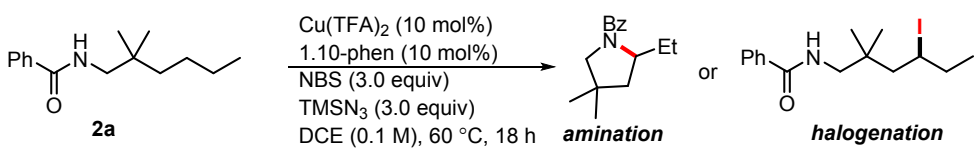
Nagib:[6]



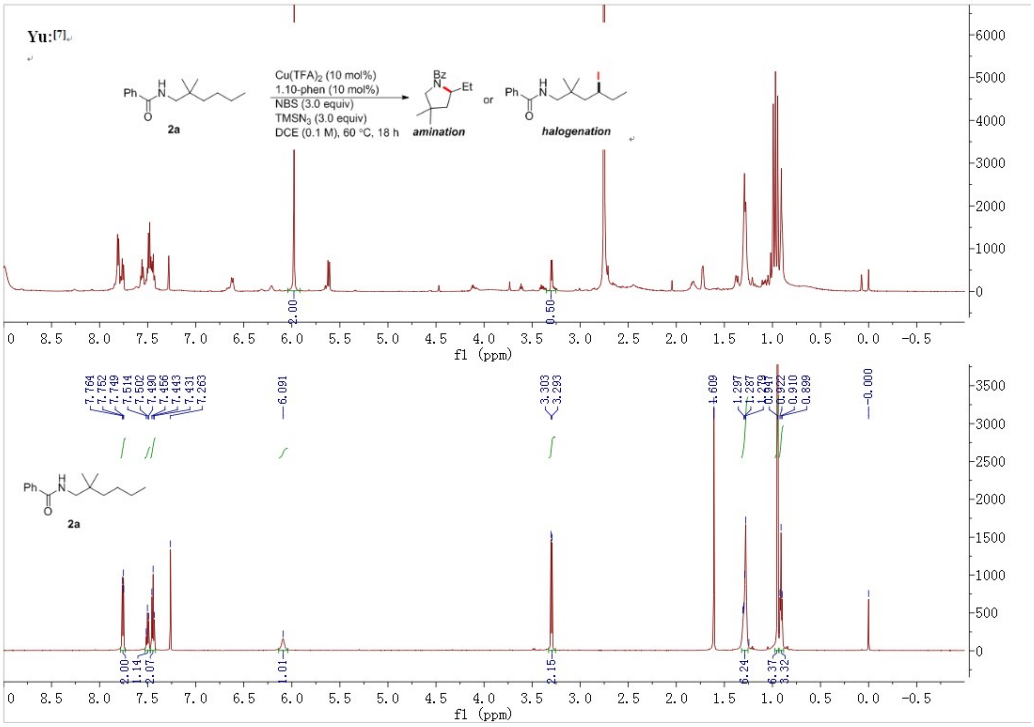
Procedure: To an oven-dried vial with a PTFE septa cap, was added a magnetic stir bar, amide **2a** (46.7 mg, 0.20 mmol, 1.0 equiv), iodobenzene diacetate (256 mg, 0.8 mmol, 4.0 equiv), and dry sodium iodide (148.7 mg, 0.8 mmol, 4.0 equiv).* This vial was sealed and sequentially evacuated and backfilled with nitrogen three times. Separately, acetonitrile was degassed using a freeze-pump-thaw technique three times. Acetonitrile (2 mL) was added to the vial and the vial was stired at 25 °C in oil bath and iriadiation with blue LED light for 10 hours. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure.The result was determined by crude ^{1}H NMR. 85% of SM was recovered. (We have successfully reproduced the Nagib reaction with sulphoamide under this condition).



Yu:[7]

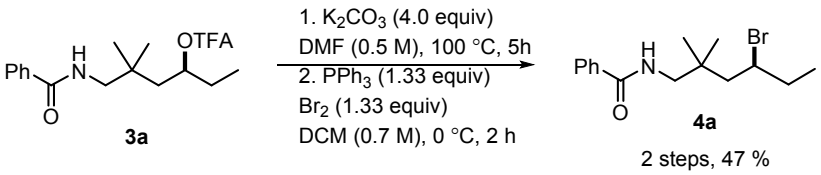


Procedure: A Schlenk tube equipped with a stirrer bar is charged with $Cu(TFA)_2$ (3.1 mg, 0.01 mmol, 10 mol%), 1,10-Phenanthroline (1.8 mg, 0.01 mmol, 10 mol%), NBS (53.4 mg, 0.3 mmol, 3.0 equiv), $TMSN_3$ (37 μL, 0.3 mmol, 3.0 equiv), amide **2a** (23.3 mg, 0.10 mmol, 1.0 equiv) and DCE (1.0 mL) was added sequentially under air.And then tube was sealed with rubber cap. The mixture was stirred at 60 ºC for 18 h. After completion, the reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure.The result was determined by crude ^1H NMR. 55 % of SM was recovered.



Mechanism Studies:

Preparation of 4a:

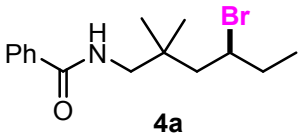


3a (138 mg. 0.4 mmol, 1.0 equiv), K_2CO_3 (221 mg, 1.6 mmol, 4.0 equiv), DMF (0.5 M) were added to an oven-dried vial, and the mixture was heated at 100 ℃ for 5 hours. The reaction was diluted with water, extracted with EtOAc and washed with

brine. The combined solvent was dried with Na_2SO_4 and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 5:1:0.5 as eluent) to give the alcohol .

PPh_3 (122 mg, 0.466 mmol, 1.33 equiv) was dissolved in DCM (0.7 M), then cooled to 0 ℃, then Br_2 (74 mg, 0.466 mmol, 1.33 equiv) was added slowly until the solvent turned to yellow solution, the alcohol was added at one time, the desired mixture was striing 2 hours at that temperature (Detected by TLC). The reaction was diluted with water and sat. $Na_2S_2O_3$ solution, extracted with DCM. The combined organic solvent was dried with Na_2SO_4, and concentrated under reduce pressure. The desired residue was purified by flash column chromatography on silica gel (PE:EA:DCM = 8:1:0.5 as eluent) to give the **4a**.

***N*-(4-bromo-2,2-dimethylhexyl)benzamide (4a)**

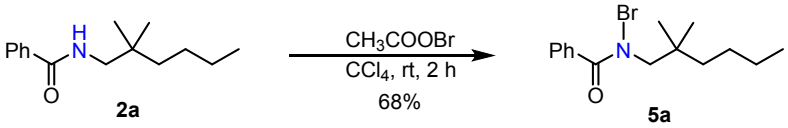


4a

Colourless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 7.2, 7.2 Hz, 2H), 6.54 (br s, 1H), 4.08–4.14 (m, 1H), 3.62 (dd, J = 13.8, 8.1 Hz, 1H), 3.25 (dd, J = 13.8, 5.4 Hz, 1H), 2.16 (dd, J = 15.9, 8.1 Hz, 1H), 1.83–1.94 (m, 2H), 1.80 (dd, J = 15.9, 2.1 Hz, 1H), 1.05 (t, J = 7.2 Hz, 3H), 1.04 (s, 3H), 1.01 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.45, 134.81, 131.42, 128.63, 126.82, 55.11, 48.53, 47.99, 35.44, 34.77, 26.60, 25.08, 12.01. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}BrNNaO$, 334.0777; found, 334.0778. **IR** (KBr, cm^{-1}): ν 3550, 3476, 3414, 1619, 1400, 1117.

Preparation of 5a:[8]

The **5a** was prepared as reference 8

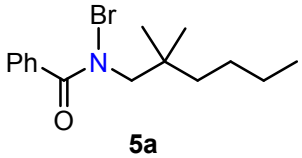


2a **5a**

To a 25 mL flame dried, foil wrapped flask under N_2, amide **2a** (233 mg, 1.0 equiv, 1.0 mmol) was added followed by acetyl hypobromite solution (7.5 mL, 1.47 mmol, 0.20 M) in CCl_4. The reaction was stirred at room temperature for 1.5 hours. When the reaction was complete as judged by ^{1}H NMR analysis (1.5 hours usually sufficient) the reaction was concentrated under reduced pressure to give a yellow solid. The desired residue was purified by flash column chromatography on silica gel (PE:Et_2O = 5:1 as eluent) quickly to give the **5a**.

General storage: All N-Bromo reagents were stored in foil-wrapped vials in the freezer when not in use.

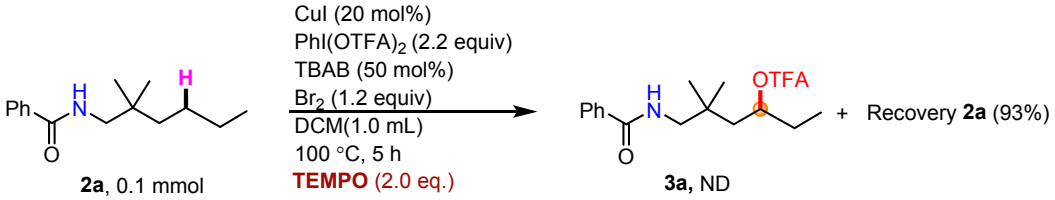
***N*-bromo-*N*-(2,2-dimethylhexyl)benzamide (5a)**



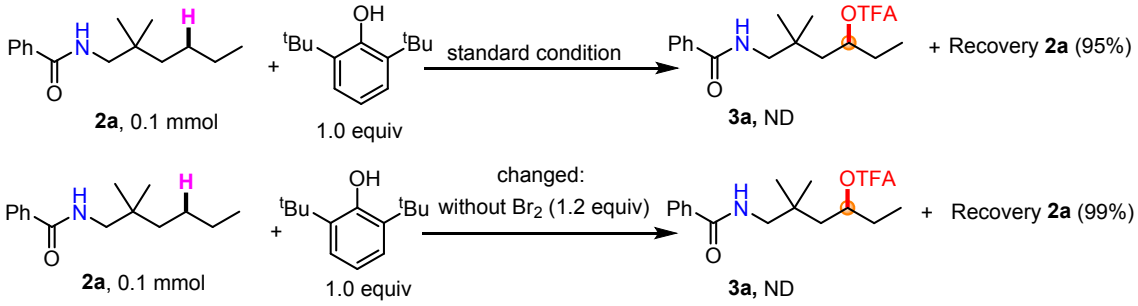
5a

Yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (d, J = 6.9 Hz, 2H), 7.38–7.43 (m, 3H), 3.76 (s, 2H), 1.25–1.28 (m, 4H), 1.19–1.23 (m, 2H), 0.96 (s, 6H), 0.88 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 173.75, 134.97, 130.20, 128.04, 127.66, 65.07, 40.27, 36.79, 25.92, 25.52, 23.45, 14.05. **HRMS–ESI** (*m/z*): $[M+Na]^+$ calcd. for $C_{15}H_{22}BrNNaO$, 334.0777; found, 334.0767. **IR** (KBr, cm^{-1}): ν 3476, 3414, 1639, 1618, 1121, 1094, 713, 616, 479.

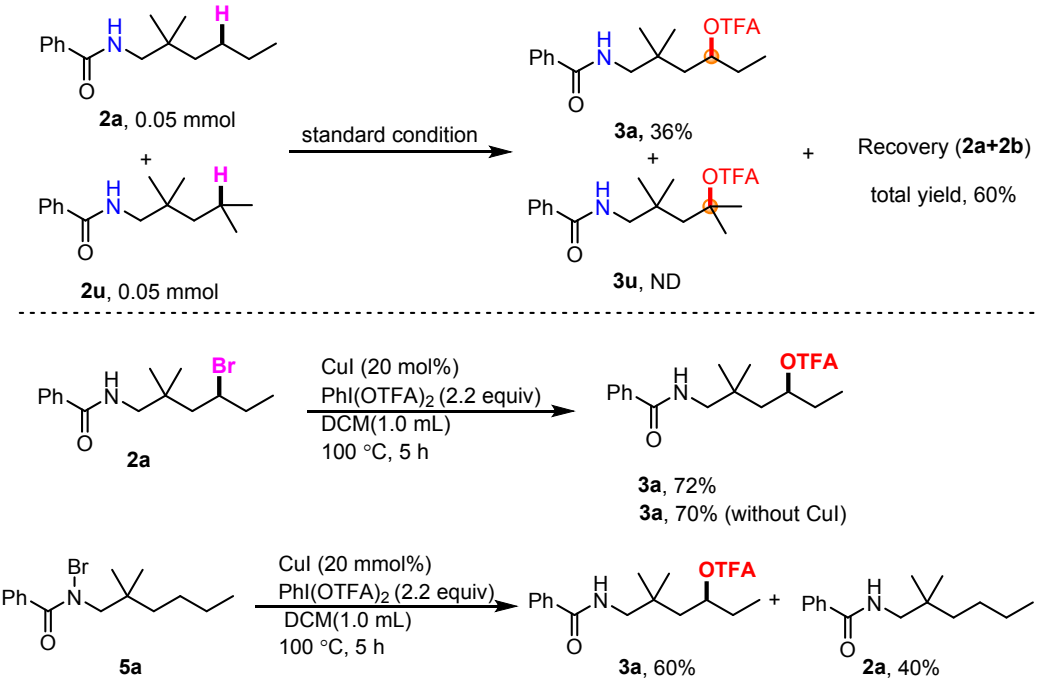
1. TEMPO Control Experiments



2. Radical capture experiments



3. Competition experiments



Results:

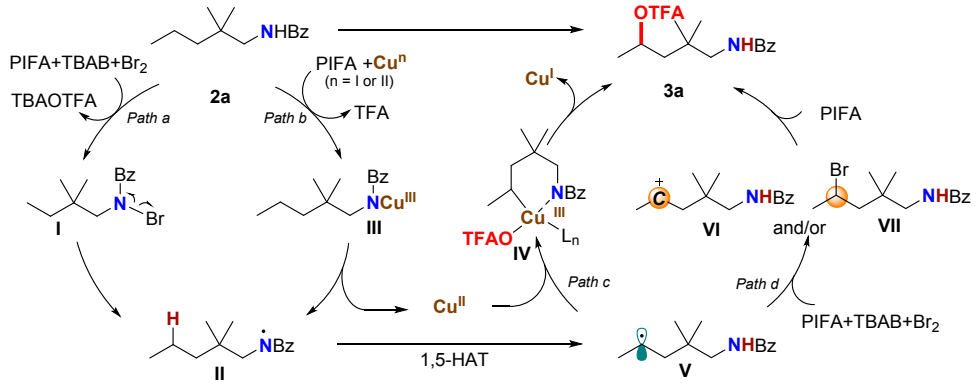
1. By adding TEMPO and 2,6-di-*tert*-butylphenol to the reaction mixture independently, the reaction was completely inhibited.

2. The intermolecular competition experiment showed that this reactio gave the excellent selectivity on the secondary C−H bond than the tertiary one.

3. The conpound **4a** can be transferred to the final product, so it maybe the possible intermediate in this reaction.

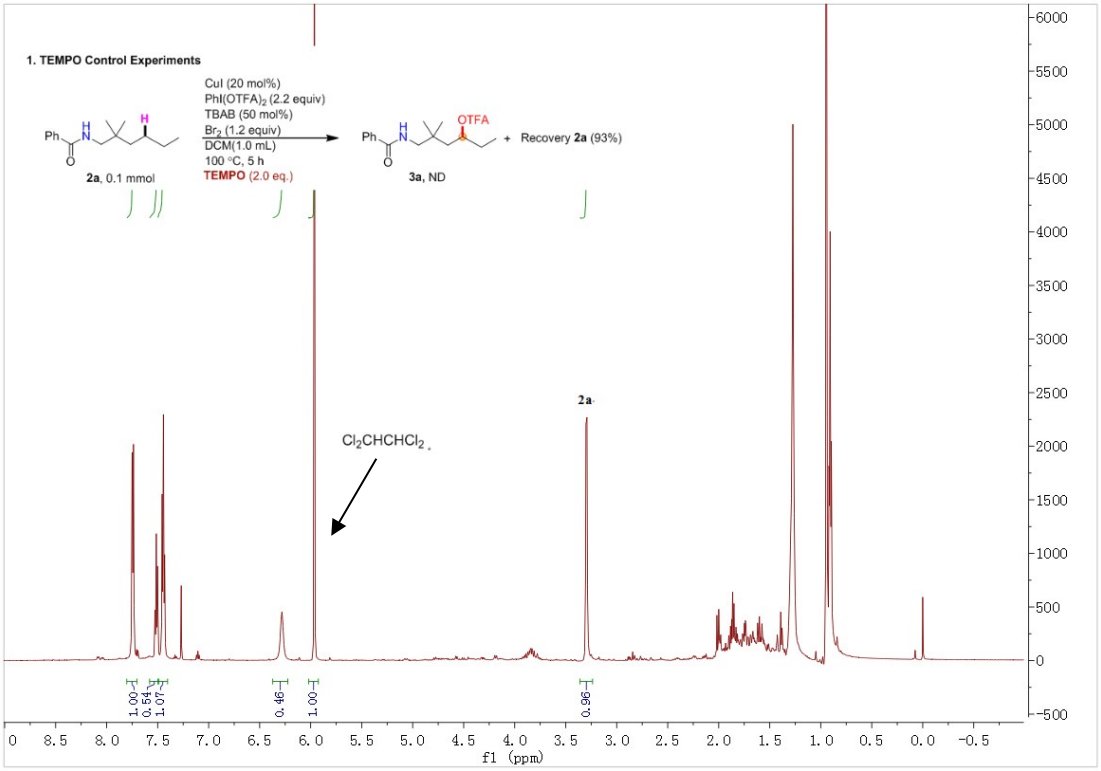
4. The compound **5a** was subjected to the reaction condition of CuI (20 mol%) and PIFA (2.2 equiv) in DCE (1.0 mL) at 100 ℃, 60% trifluoroacetoxylation product **3a** was observed and 40% of protonation product **2a** was observed.

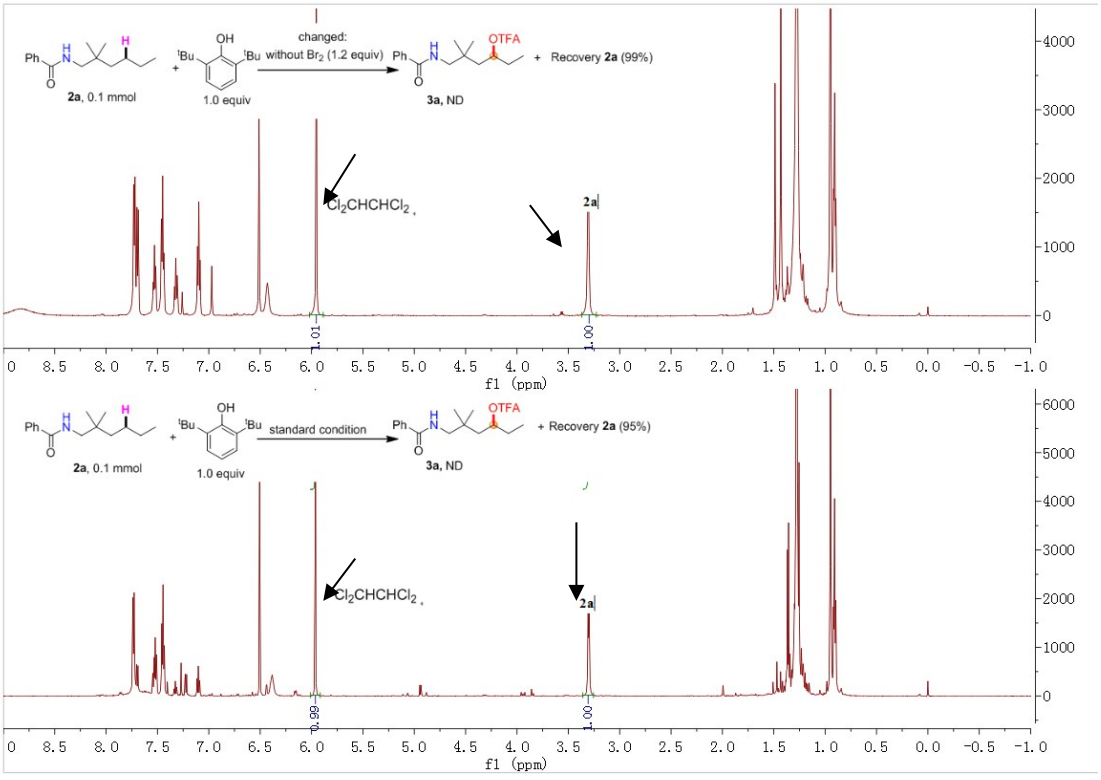
Proposed Mechanism:

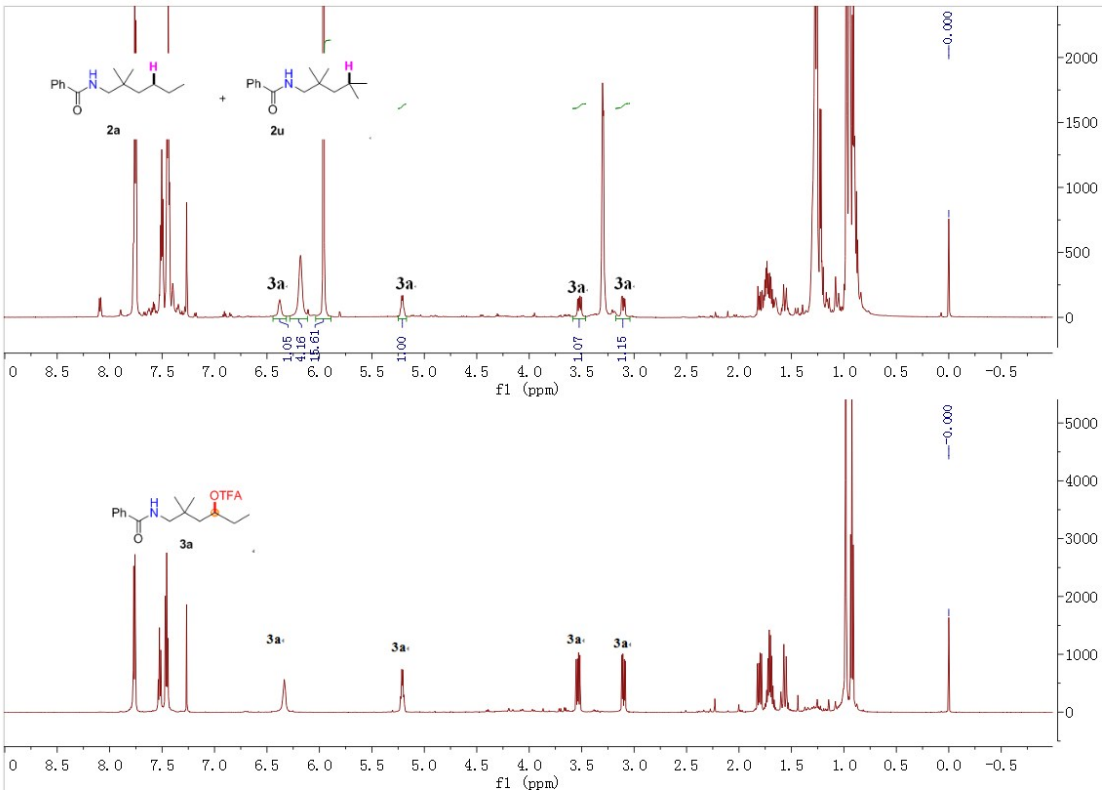


We propose that this transformation is preferred to a single-electron-oxidation process (Scheme 3). With the assistance of PhI(OTFA)2 and copper catalyst, the N-Br intermediate I (path a) or Cu(III)-amidine intermediate III (path b) can be generated.17 Subsequent homolysis of the N-Br or N-Cu bond afforded amidinyl radical II. This was followed by a 1,5-H radical shift to give the corresponding C-radical V, which resulted in the selective C–H bond trifluoroacetoxylation at δ position. For the next step, two possible pathways could be followed: one is the oxidative addition of a carbon radical by a Cu(II) catalyst to generate Cu(III)-amide intermediate IV, and after ligand exchange and reductive elimination to afford the trifluoroacetoxylation product 3a (path c). The other is the oxidation of carbon radical to carbocation (VI) which is captured by OTFA-, to directly give product (path d). Although we didn't detect any δ-brominated product (VII) even with decreased PIFA

or shorter reaction time, the possibility that the product is formed through a substitution reaction of intermediate VII cannot be ruled out.







References

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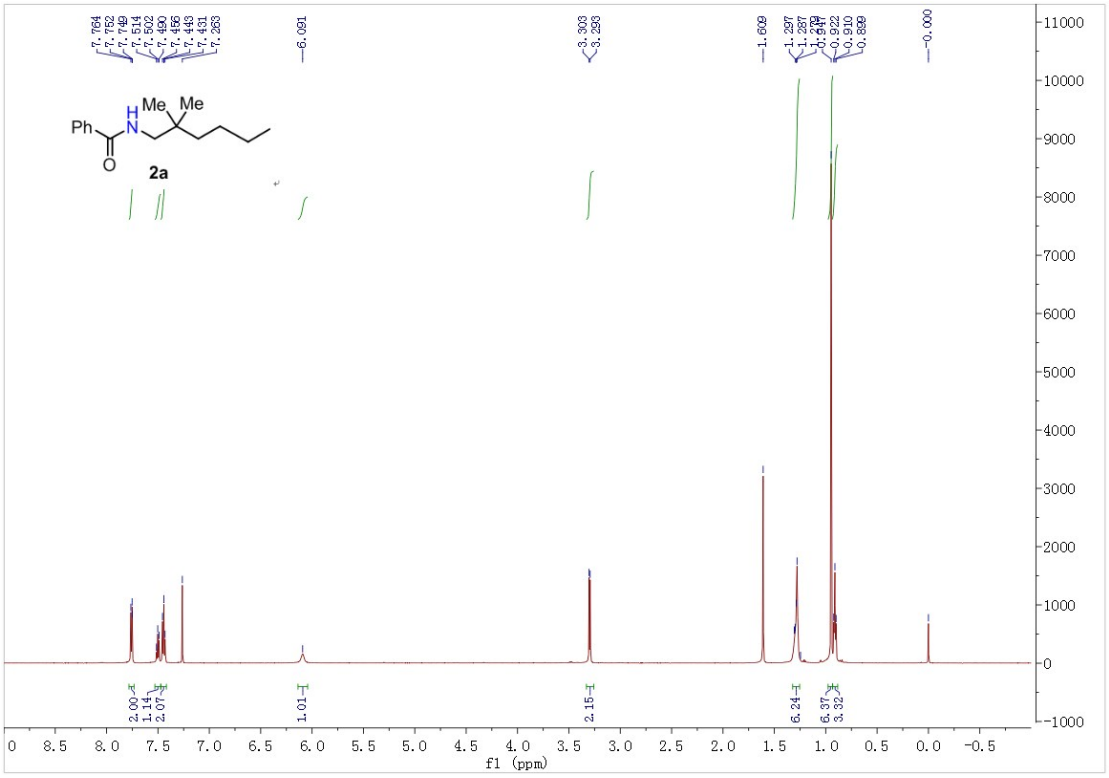
NMR Spectra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7.749
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7.263
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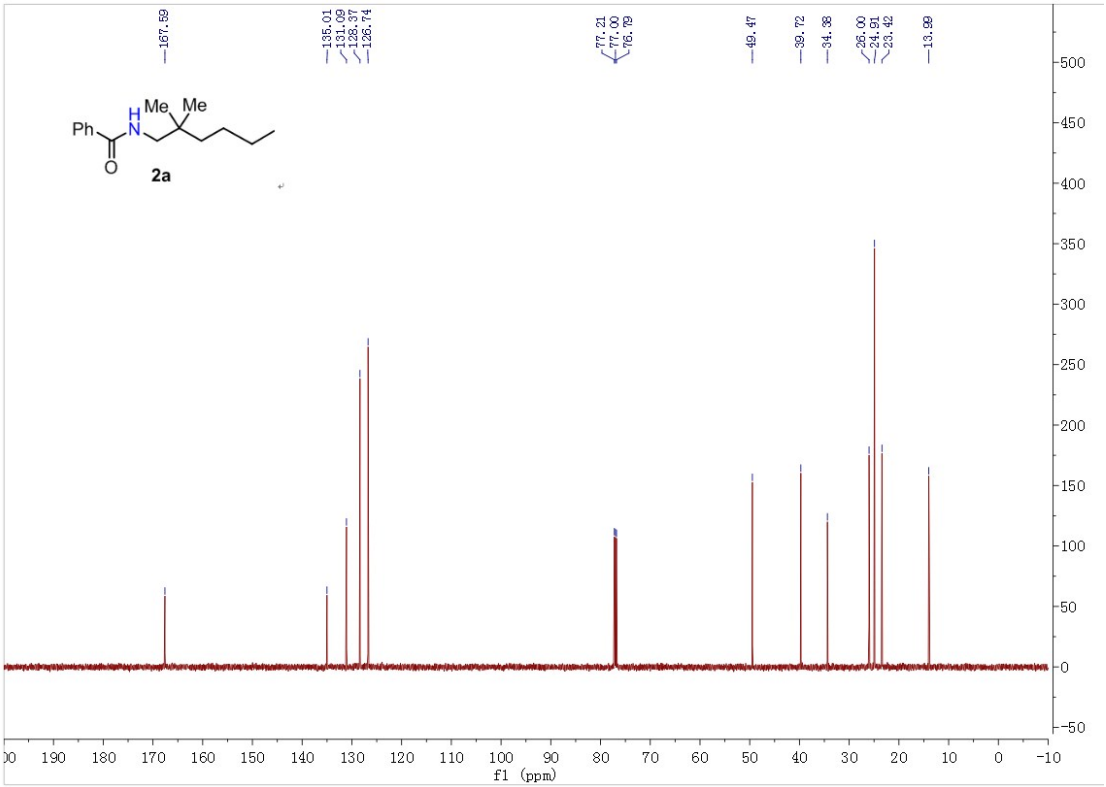
3.293
1.609
1.297
1.287
0.922
0.910
0.899
0.000
Me
Me
Ph
H
N
O
2a
2.00
1.14
2.07
1.01
2.15
6.24
6.37
3.32
f1 (ppm)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131.09
128.37
126.74
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77.00
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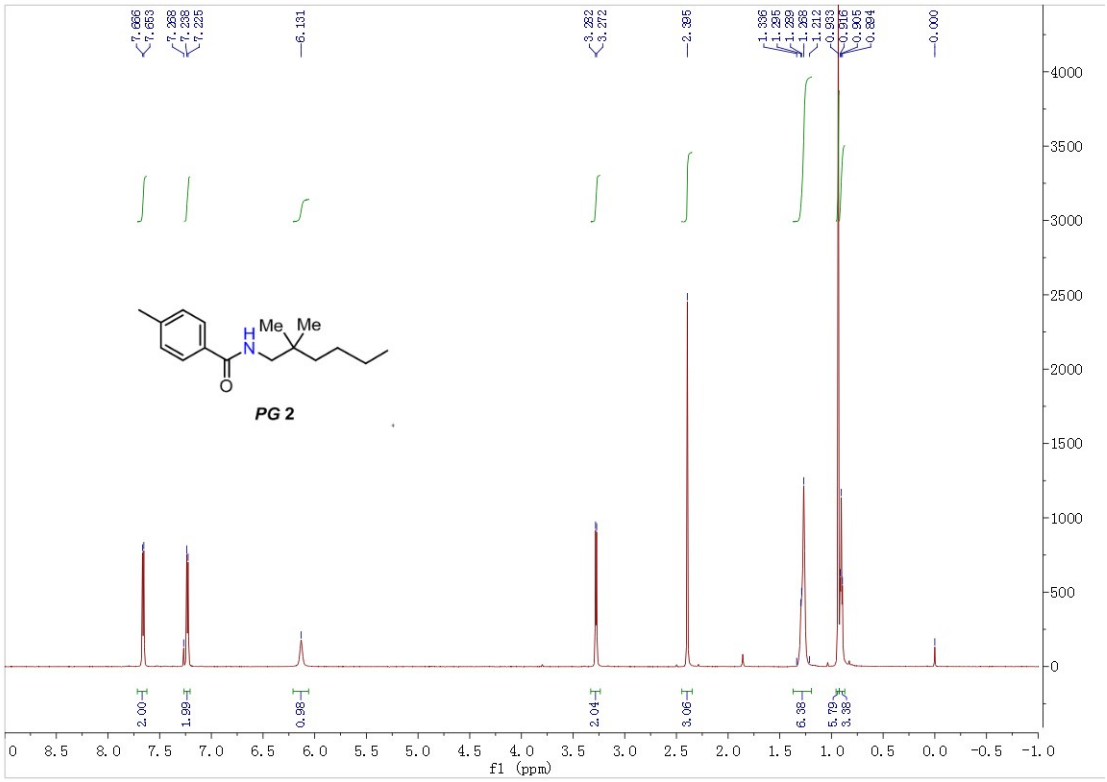
26.00
24.91
23.42
13.99
Me
Me
Ph
H
N
O
2a
f1 (ppm)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6.131
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1.396
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1.268
1.212
0.933
0.916
0.905
0.894
0.000
Me
Me
H
N
O
PG 2
2.00
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0.98
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6.38
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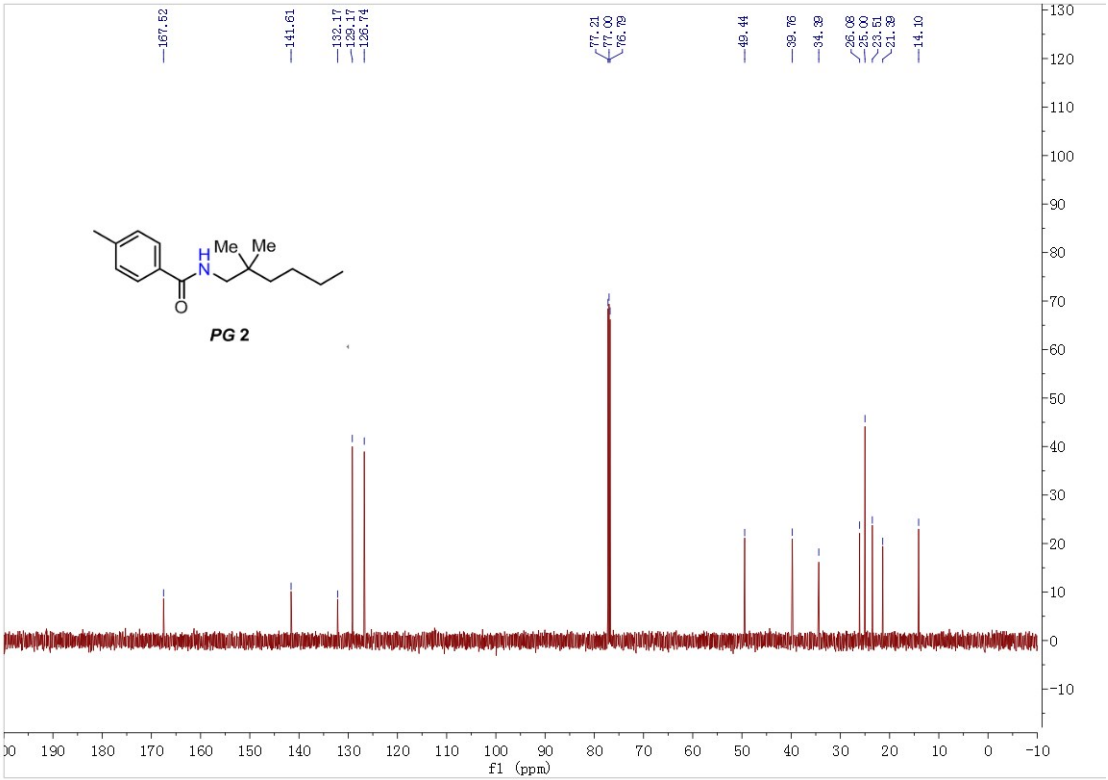
3.38
f1 (ppm)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21.39
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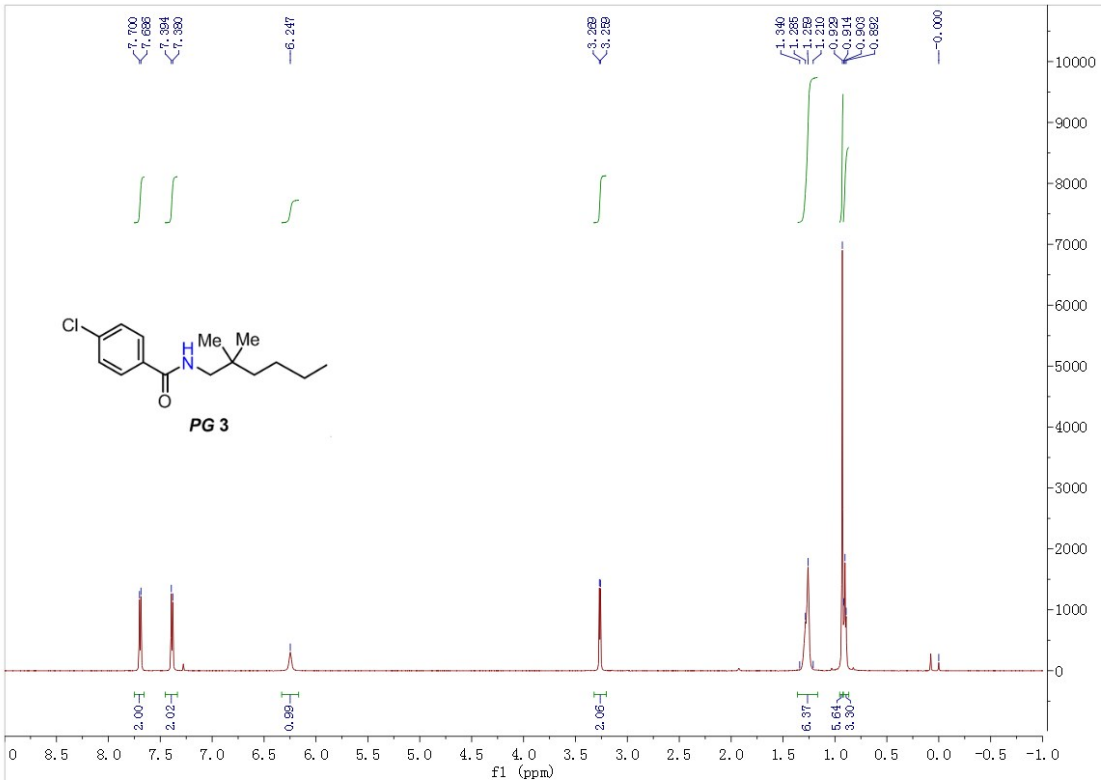
Me
Me
H
N
O
PG 2
f1 (ppm)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0.914
0.903
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0.000
Cl
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H
N
O
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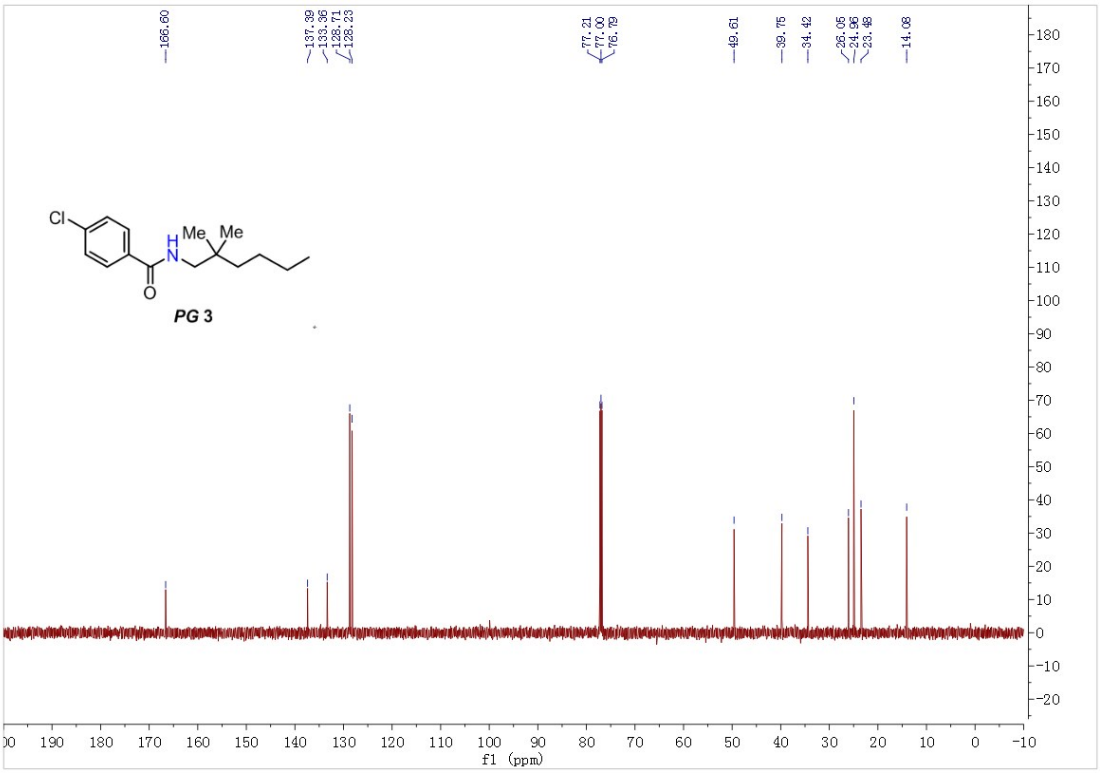
f1 (ppm)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O
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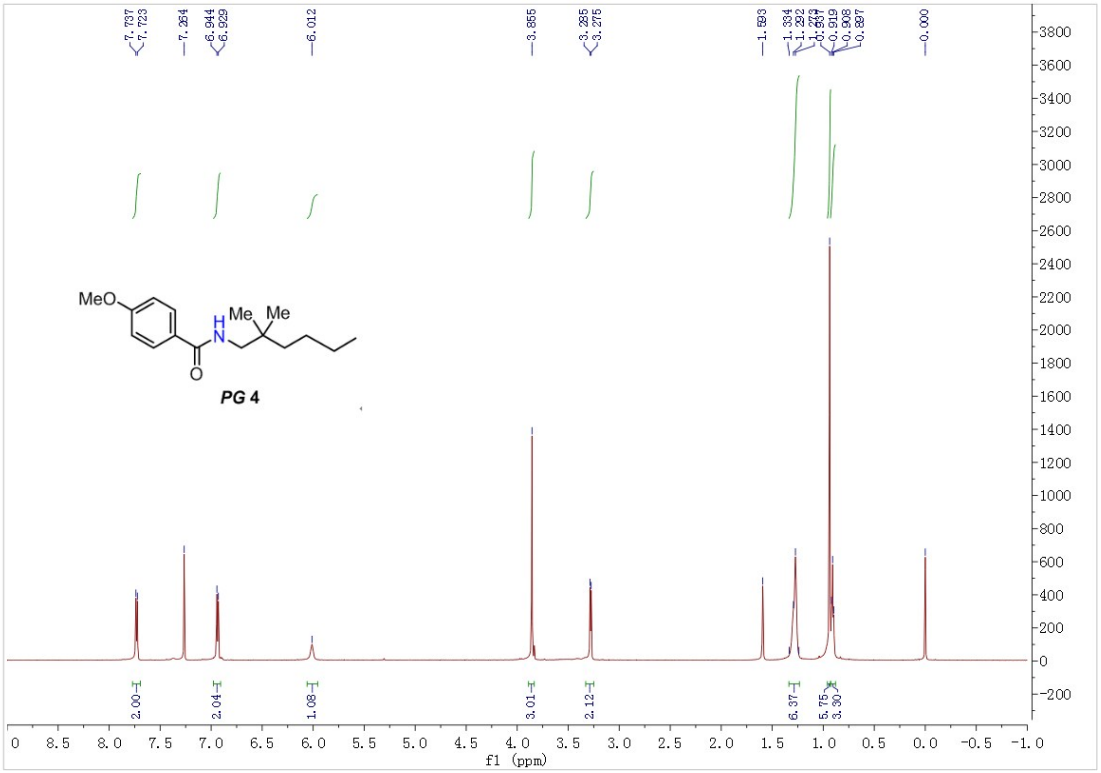
f1 (ppm)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0.937
0.919
0.908
0.897
0.000
MeO
Me
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N
O
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2.12
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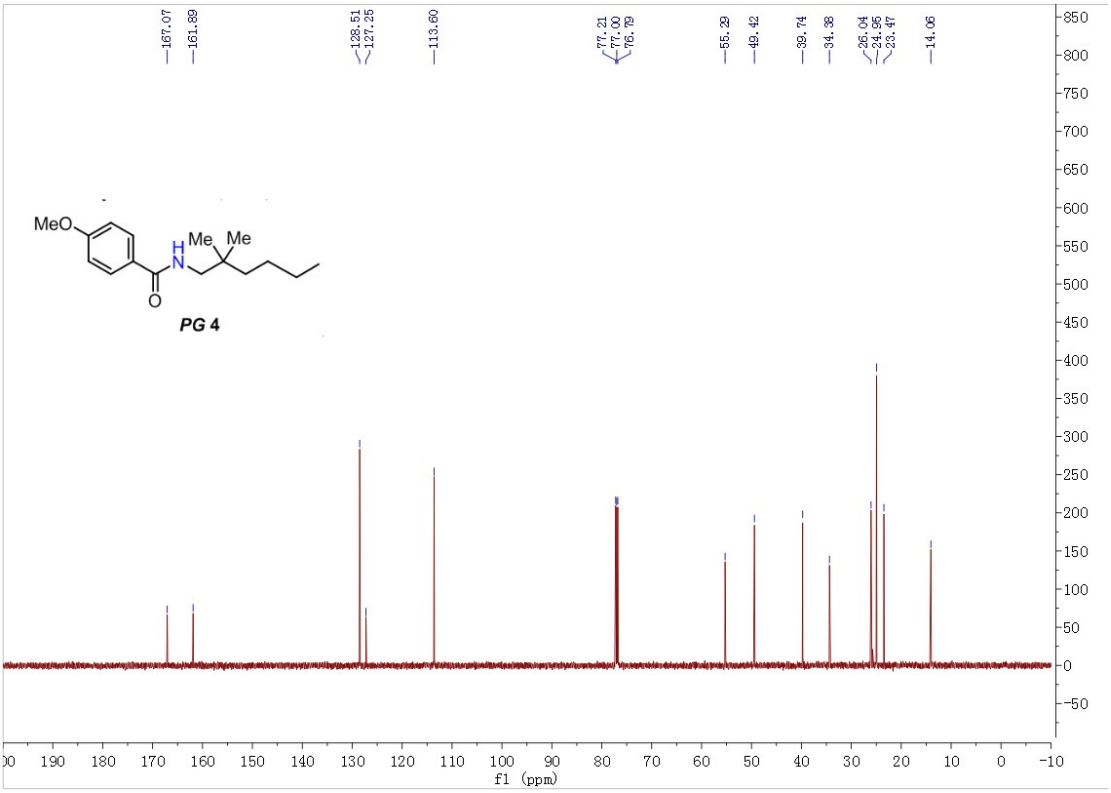
3.30
f1 (ppm)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76.79
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49.42
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24.96
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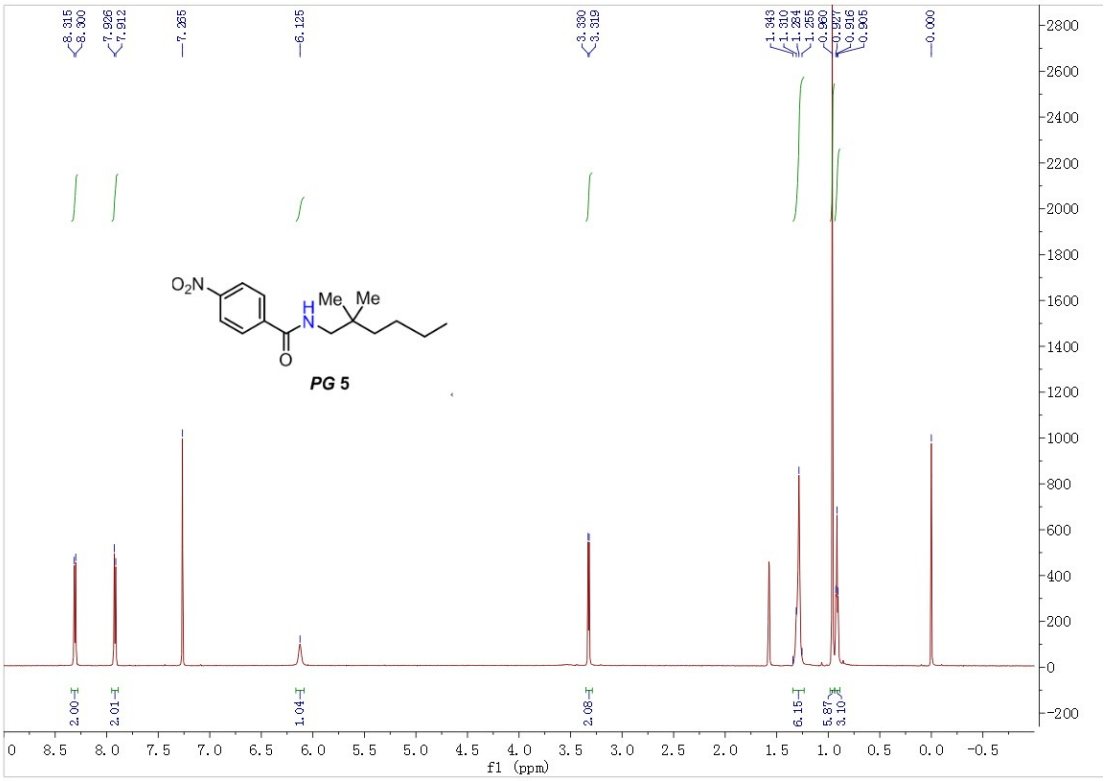
14.06
MeO
Me
Me
H
N
O
PG 4
f1 (ppm)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8.300
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7.912
7.265
6.125
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1.310
1.284
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0.960
0.927
0.916
0.905
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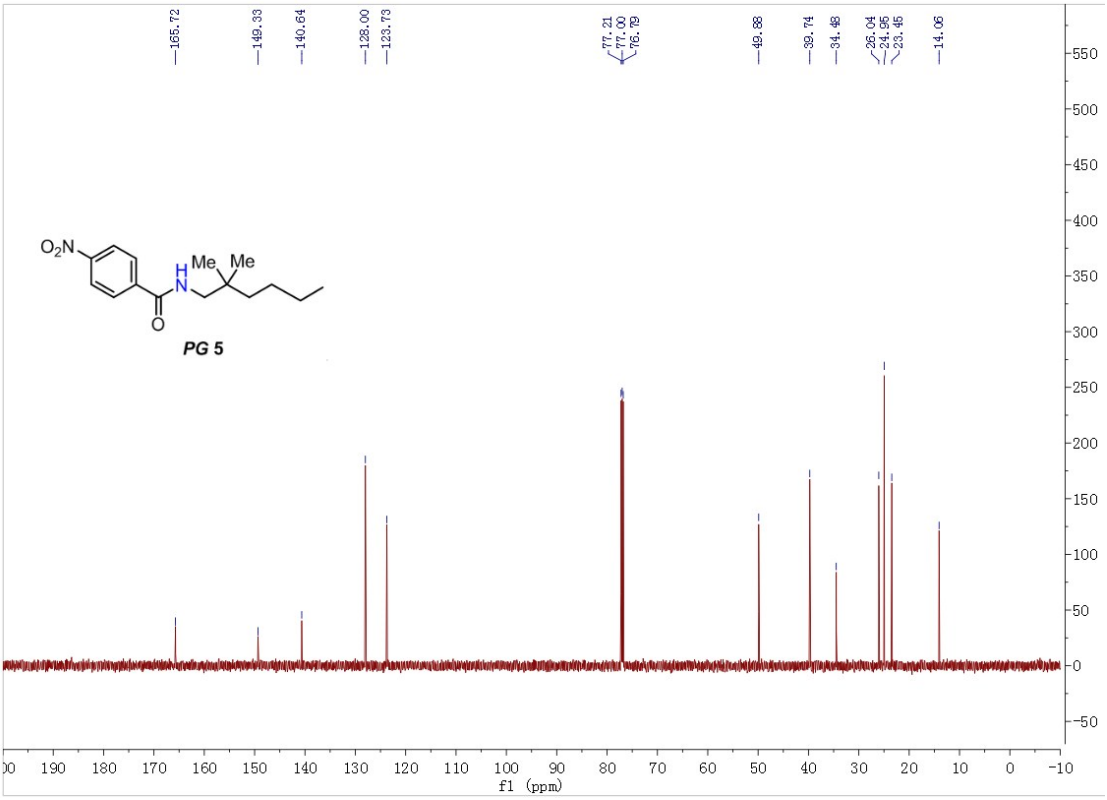
2.01
1.04
2.08
6.15
5.87
3.10
f1 (ppm)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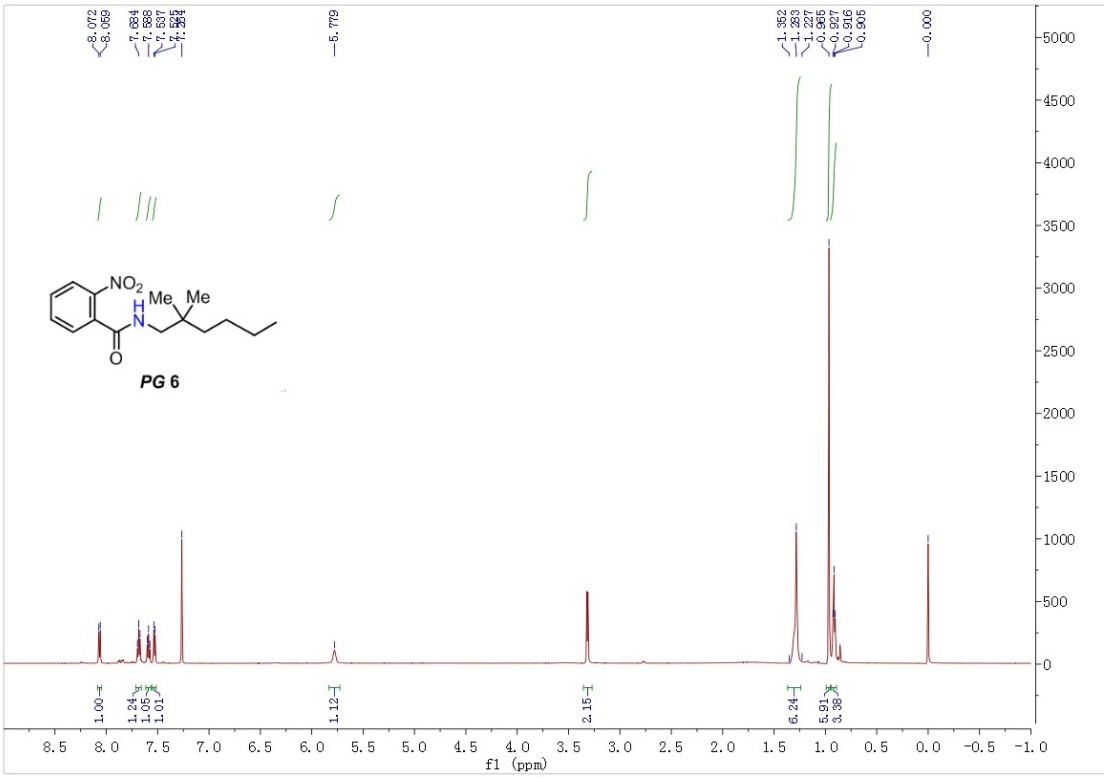
23.45
14.06
f1 (ppm)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8.069
7.694
7.688
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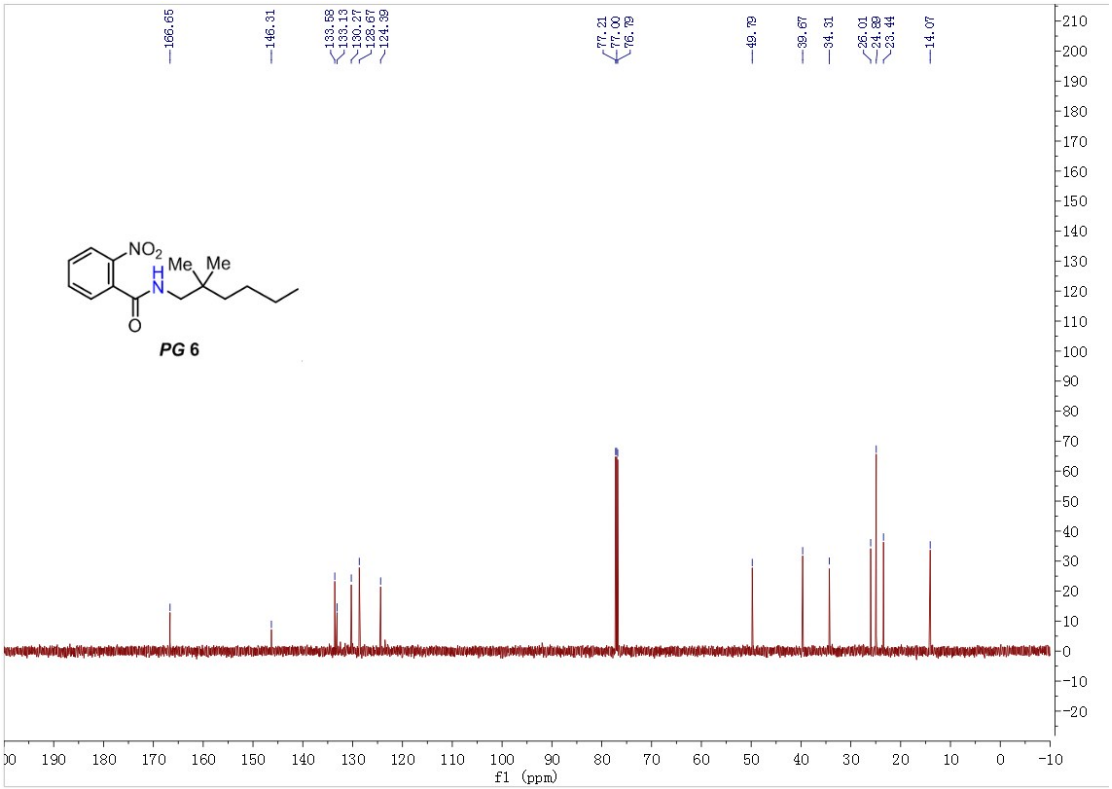
7.531
5.779
1.352
1.283
1.227
0.965
0.927
0.916
0.905
0.000
NO2
Me
Me
H
N
O
PG 6
1.00
1.24
1.05
1.01
1.12
2.15
6.24
5.91
3.38
f1 (ppm)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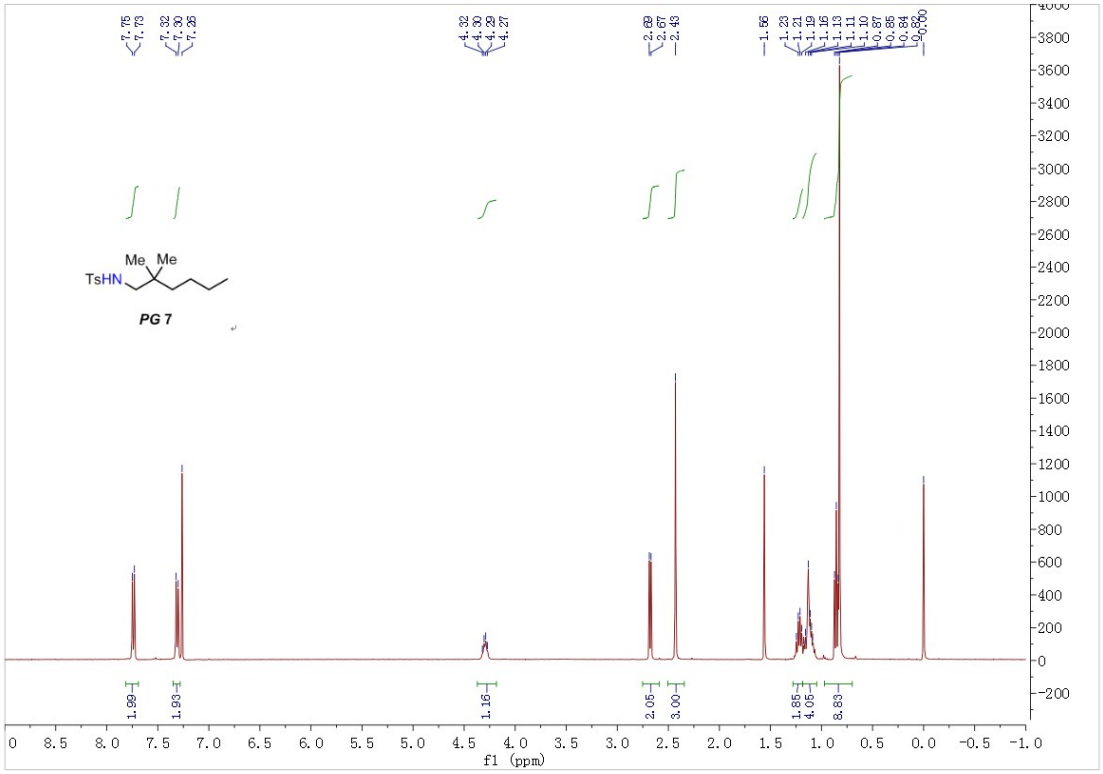
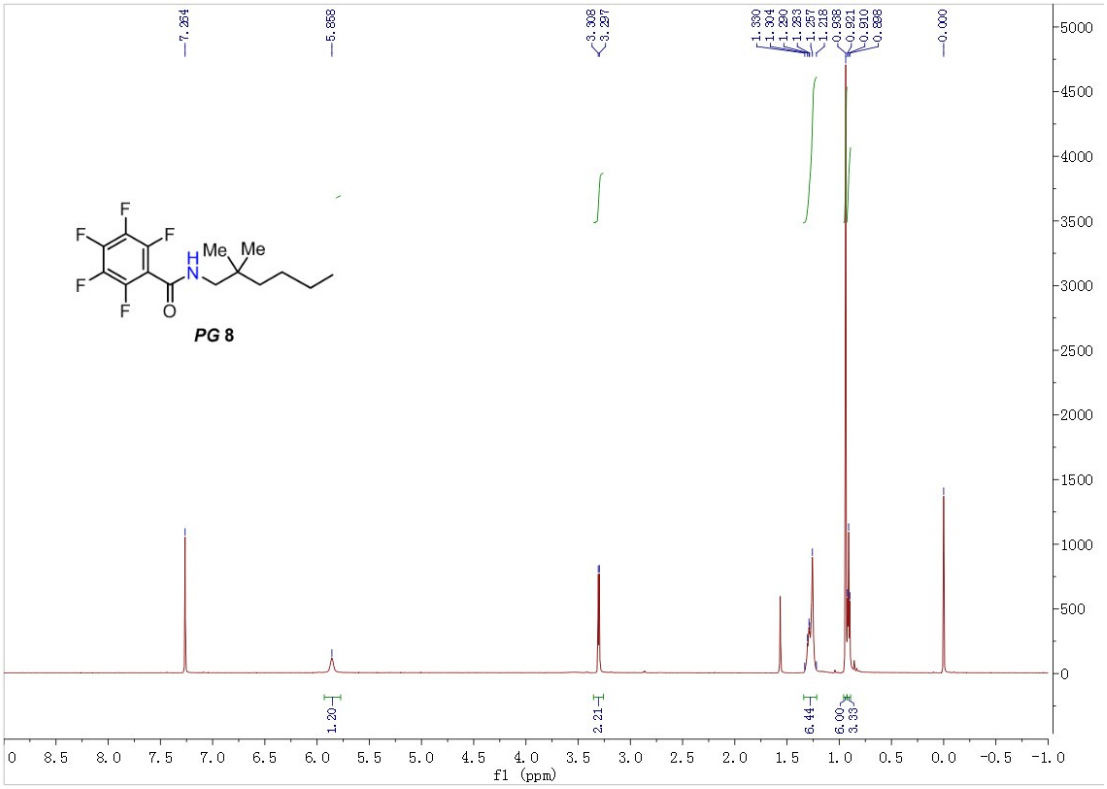
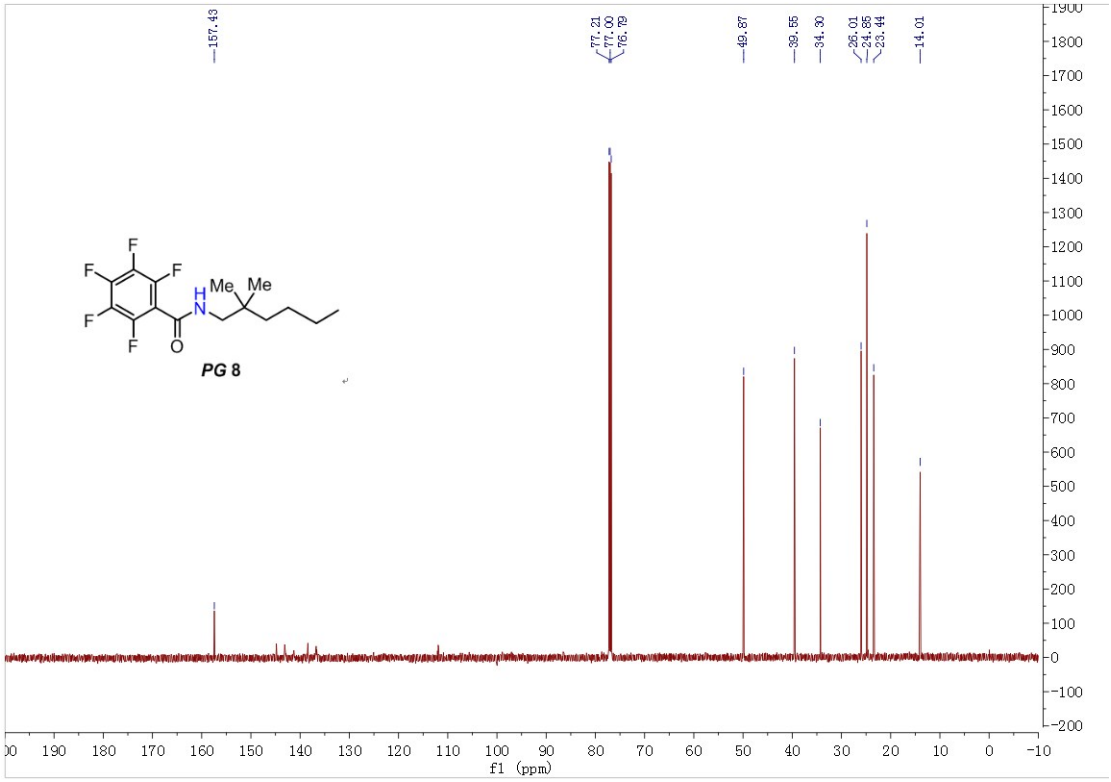
146.31
133.58
133.13
130.27
128.67
124.39
77.21
77.00
76.79
49.79
39.67
34.31
26.01
24.89
23.44
14.07
NO2
Me
Me
H
N
O
PG 6
f1 (ppm)


PG 7
f1 (ppm)


PG 8
f1 (ppm)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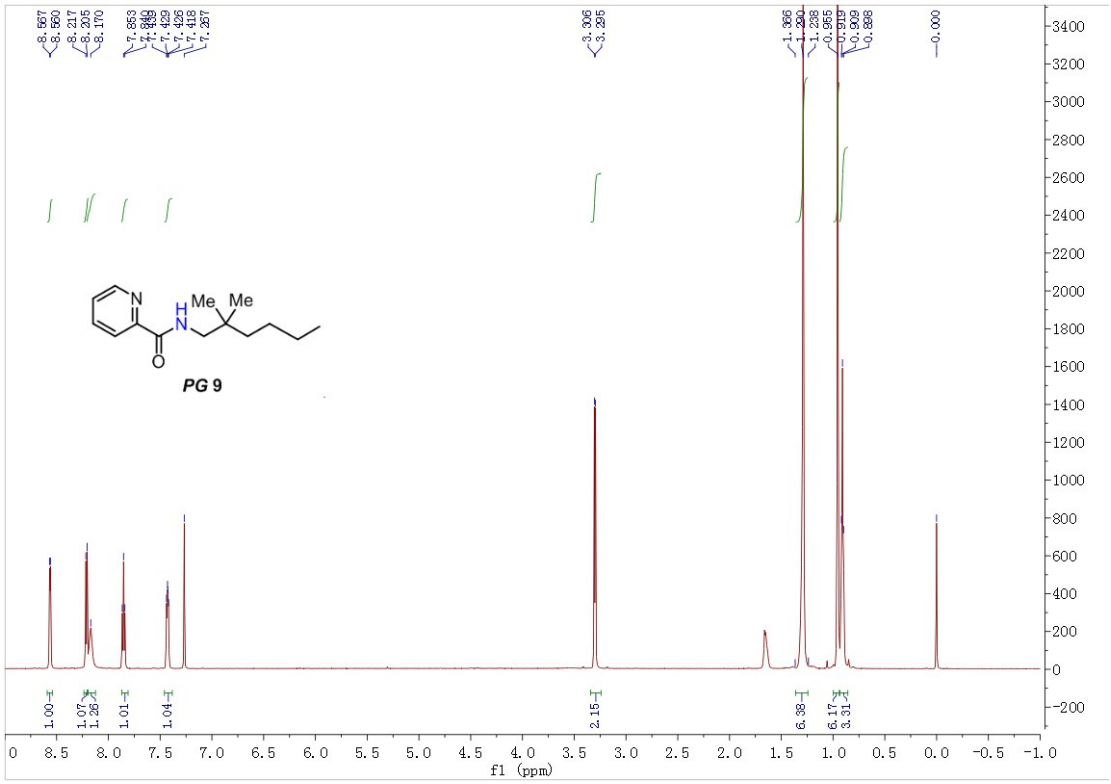
77.00
76.79
49.67
39.55
34.30
26.01
24.95
23.44
14.01
F
F
F
F
F
H
N
Me
Me
O
PG 8
f1 (ppm)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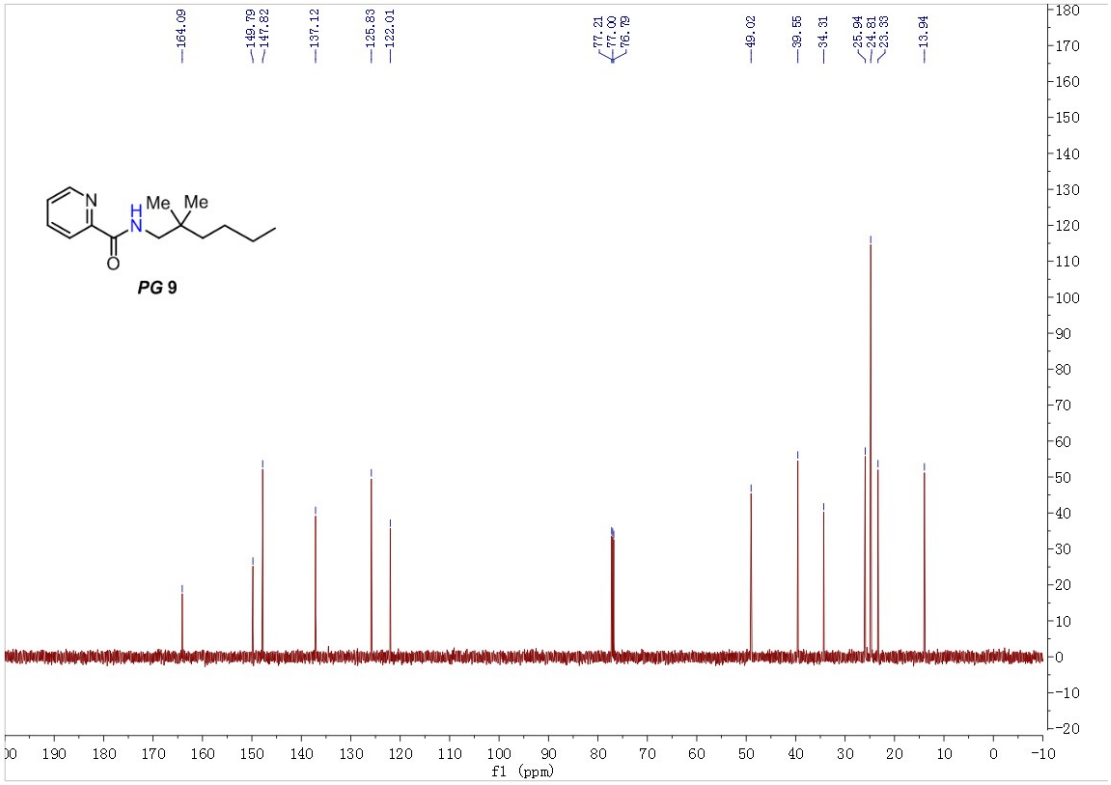
8.550
8.217
8.205
8.170
7.853
7.429
7.426
7.418
7.257
3.306
3.295
1.366
1.290
1.238
0.965
0.919
0.909
0.898
0.000
N
H
N
Me
Me
O
PG 9
1.00
1.07
1.26
1.01
1.04
2.15
6.38
6.17
3.31
f1 (ppm)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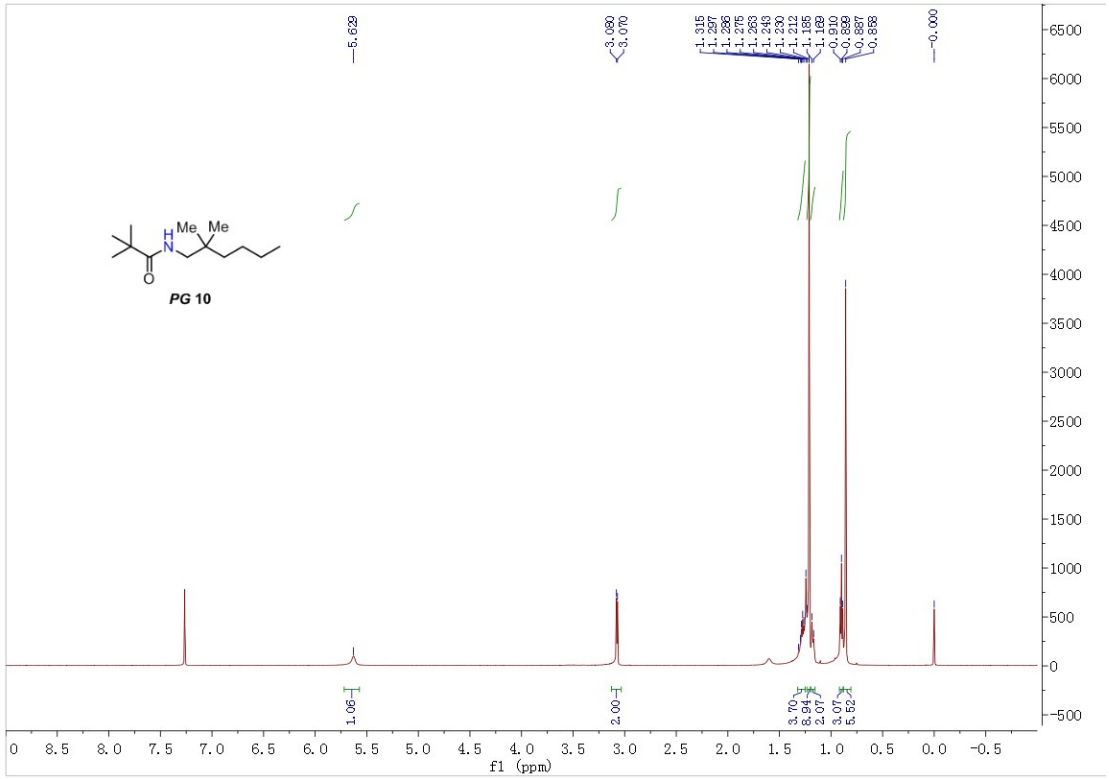
149.79
147.82
137.12
125.83
122.01
77.21
77.00
76.79
49.02
39.55
34.31
25.94
24.81
23.33
13.94
Me Me
PG 9
f1 (ppm)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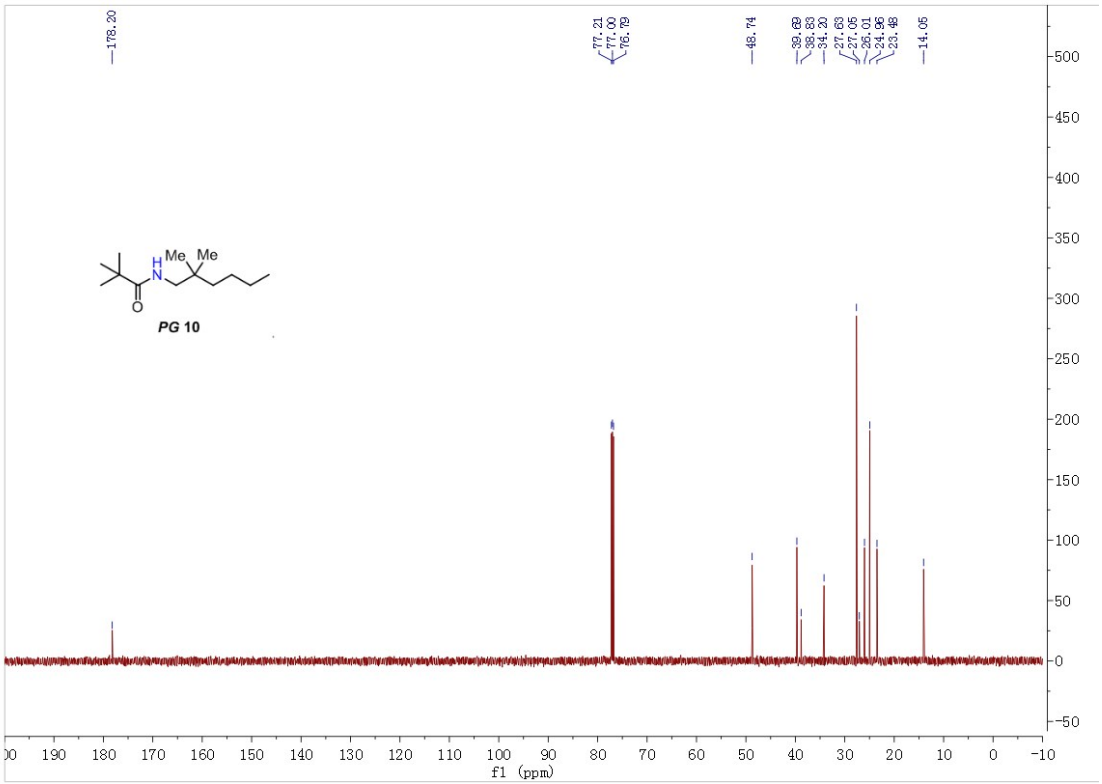
3.070
1.315
1.297
1.286
1.275
1.263
1.243
1.230
1.212
1.185
1.169
0.910
0.889
0.887
0.868
0.000
Me Me
PG 10
1.06
2.00
3.70
8.94
2.07
3.07
5.52
f1 (ppm)


178.20
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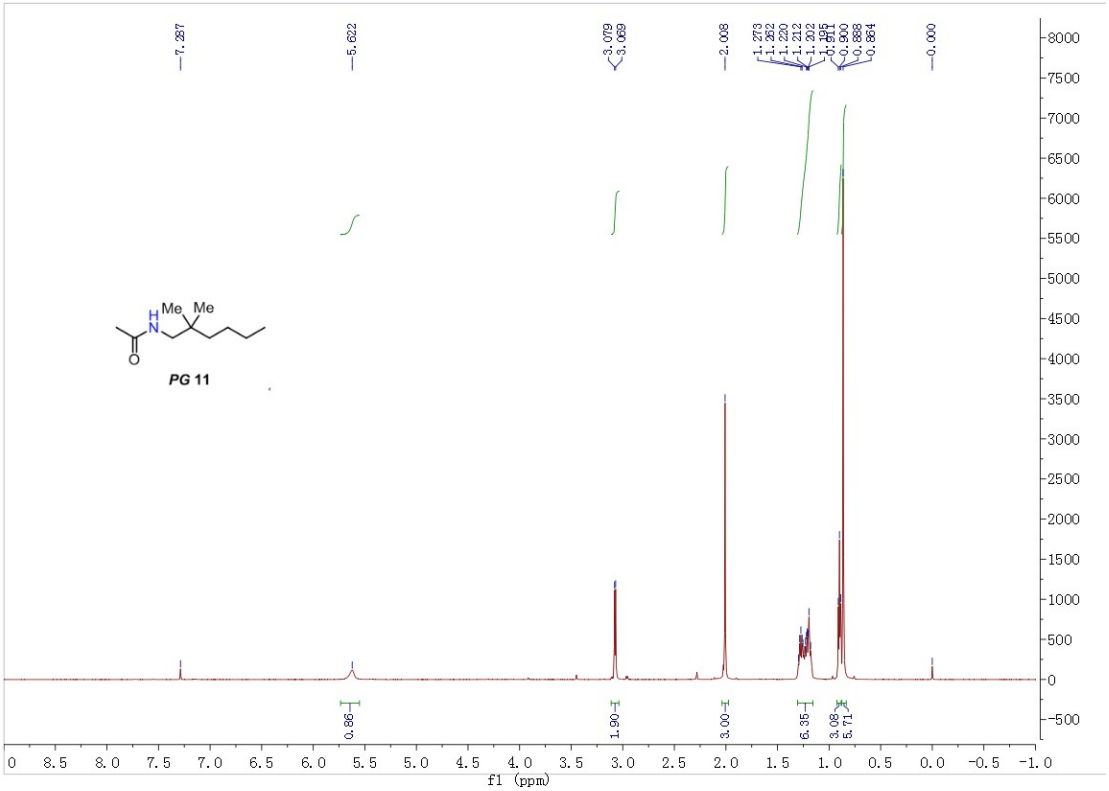
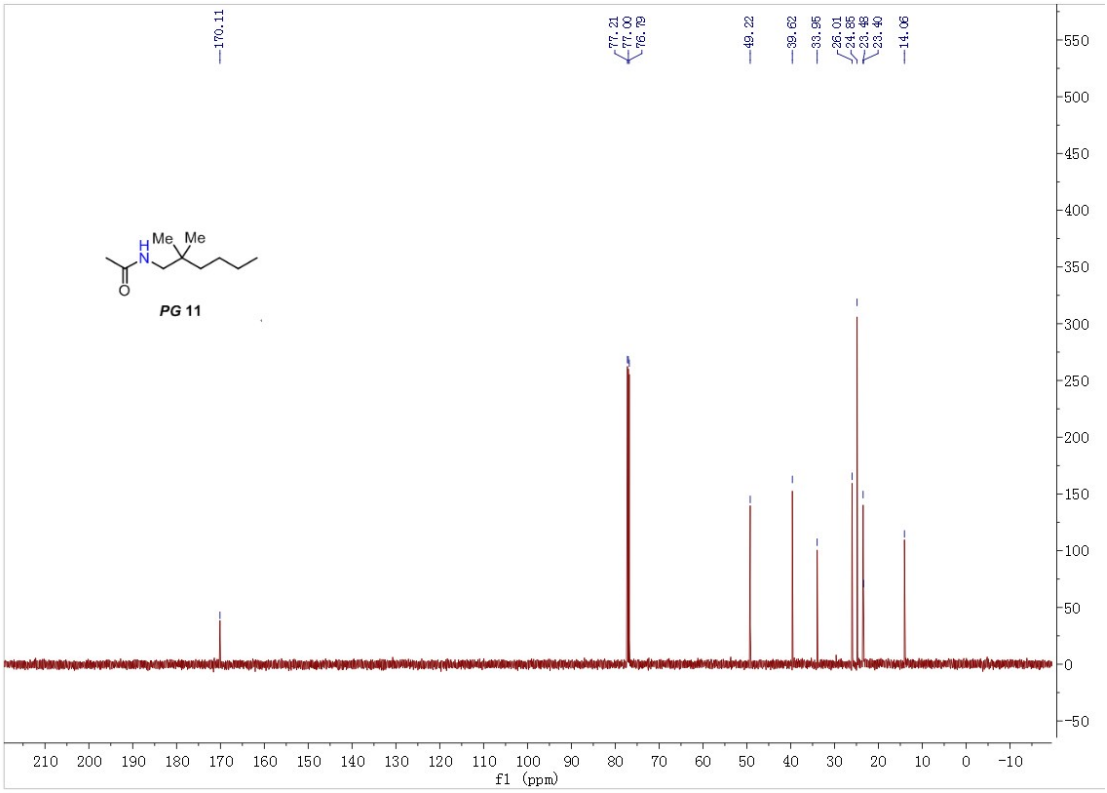
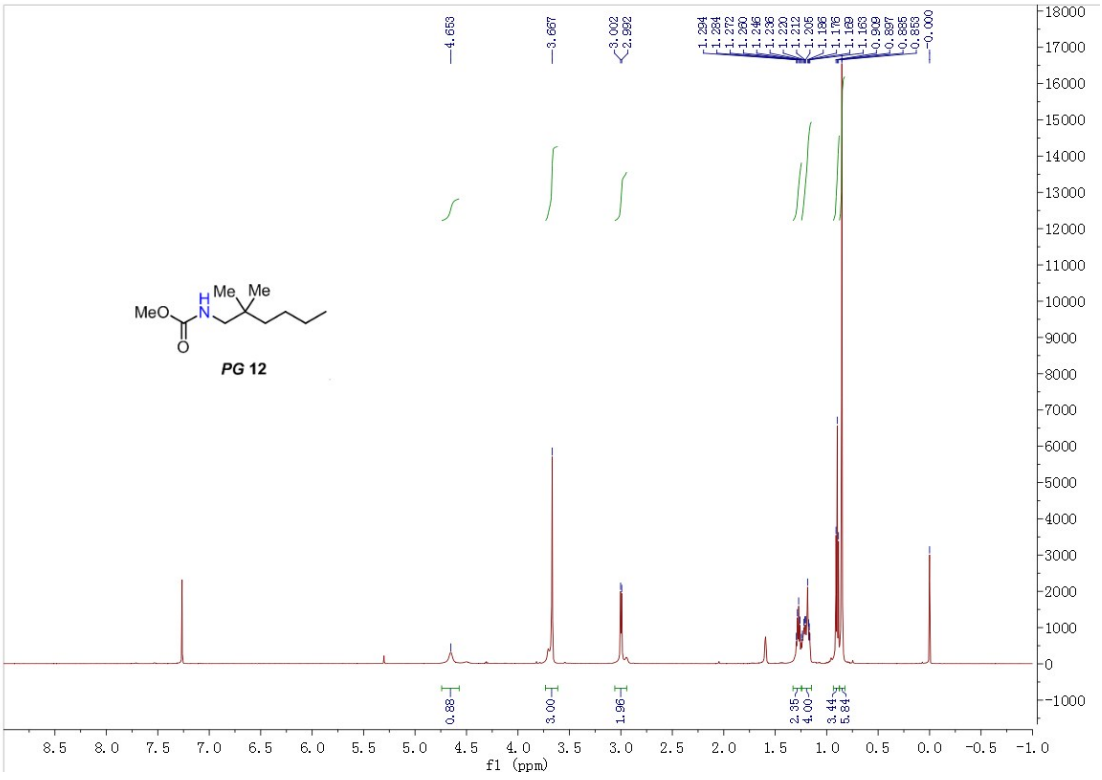
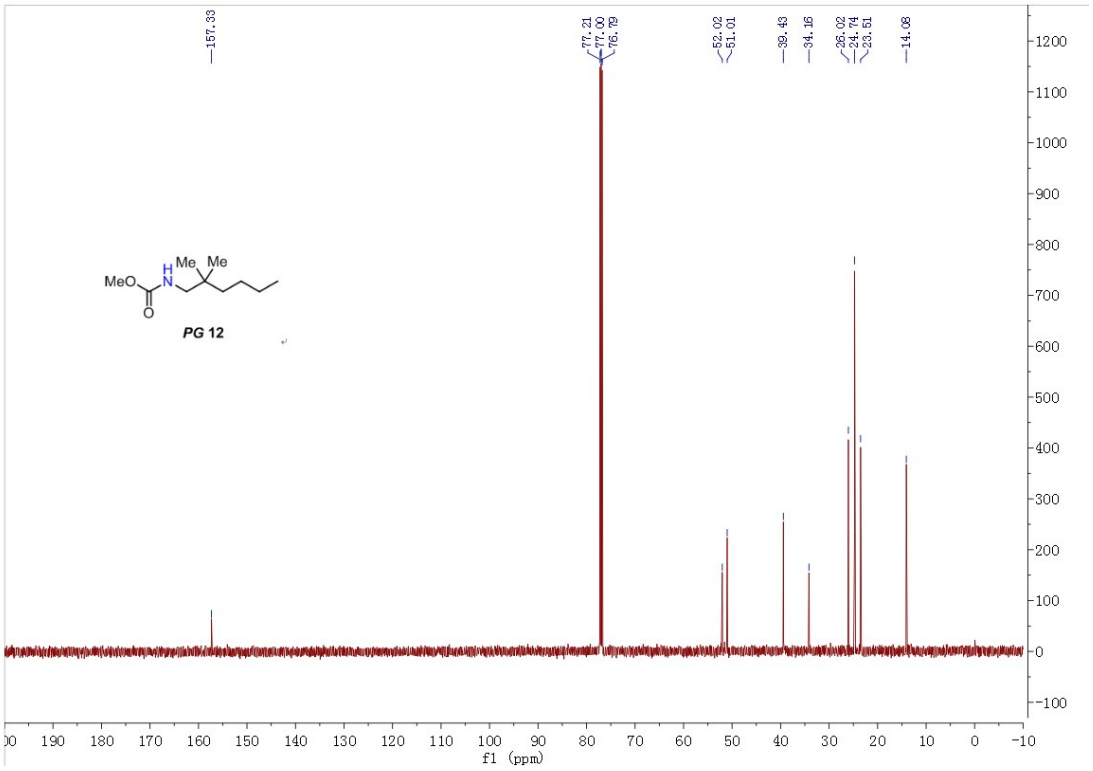
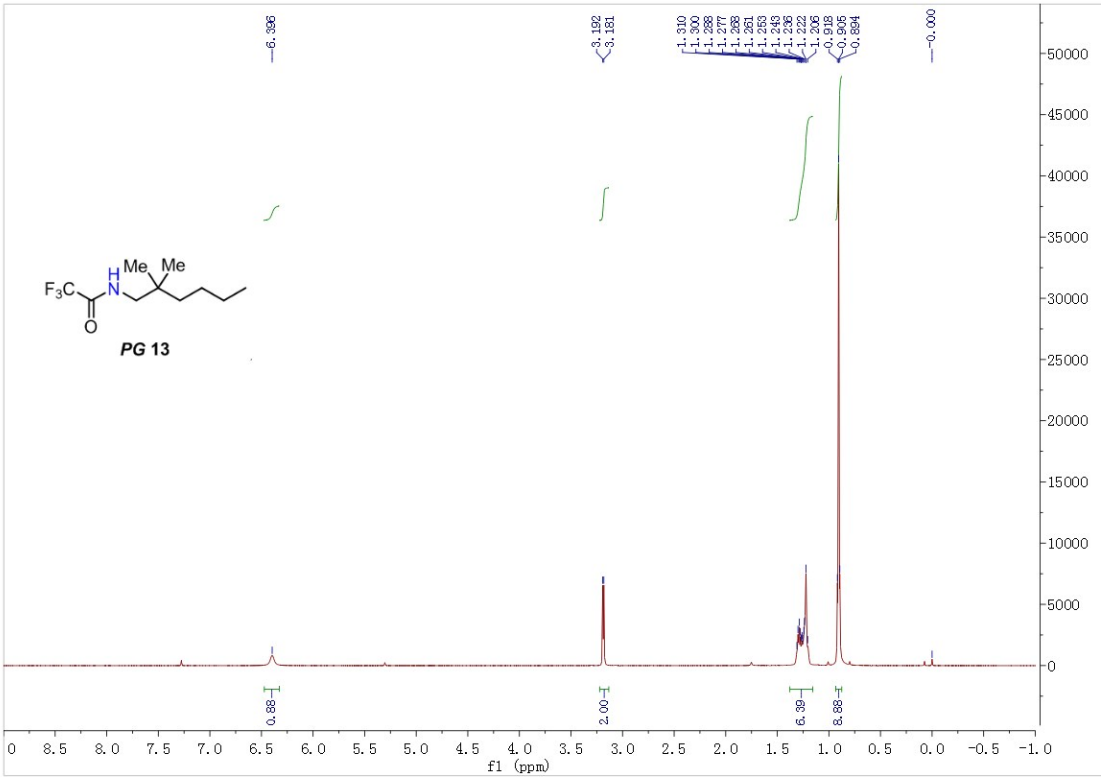
77.00
76.79
48.74
39.69
38.83
34.20
27.63
27.05
26.01
24.96
23.48
14.06
Me
Me
H
N
O
PG 10
f1 (ppm)

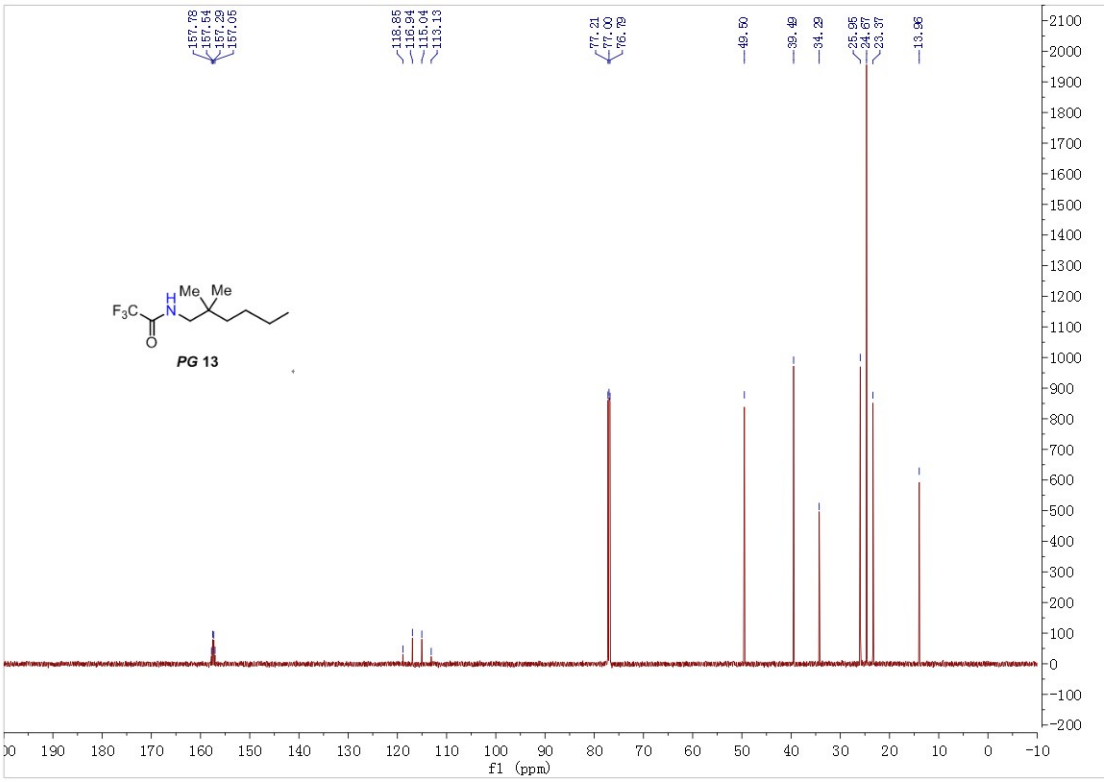

7.287
5.622
3.079
3.069
2.008
1.273
1.262
1.220
1.212
1.202
0.900
0.888
0.864
0.000
Me
Me
H
N
O
PG 11
0.86
1.90
3.00
6.35
3.08
5.71
f1 (ppm)


170.11
77.21
77.00
76.79
49.22
39.62
33.96
26.01
24.85
23.46
23.40
14.06
Me
Me
H
N
O
PG 11
f1 (ppm)


4.653
3.667
3.002
2.992
1.294
1.284
1.272
1.260
1.246
1.236
1.220
1.212
1.205
1.186
1.176
1.169
1.163
0.909
0.897
0.886
0.853
0.000
MeO
Me
Me
H
N
O
PG 12
0.88
3.00
1.96
2.35
4.00
3.44
5.84
f1 (ppm)


157.33
77.21
77.00
76.79
62.02
51.01
39.43
34.16
26.02
24.74
23.51
14.08
MeO
H
N
Me
Me
O
PG 12
f1 (ppm)


6.386
3.192
3.181
1.310
1.300
1.288
1.277
1.268
1.261
1.253
1.243
1.235
1.222
1.206
0.918
0.905
0.894
0.000
F3C
H
N
Me
Me
O
PG 13
0.88
2.00
6.39
8.88
f1 (ppm)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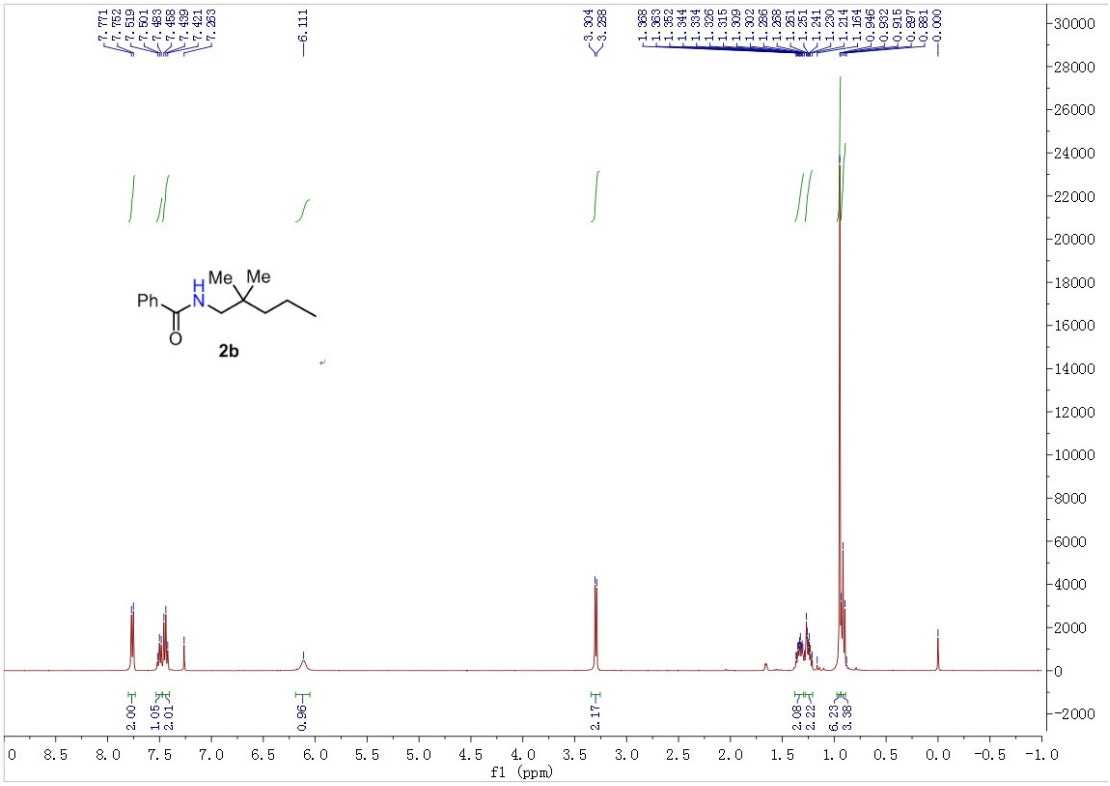
157.54
157.29
157.05
118.85
116.94
115.04
113.13
77.21
77.00
76.79
49.60
39.49
34.29
25.95
24.67
23.37
13.96
Me Me
H
N
F3C
O
PG 13
f1 (ppm)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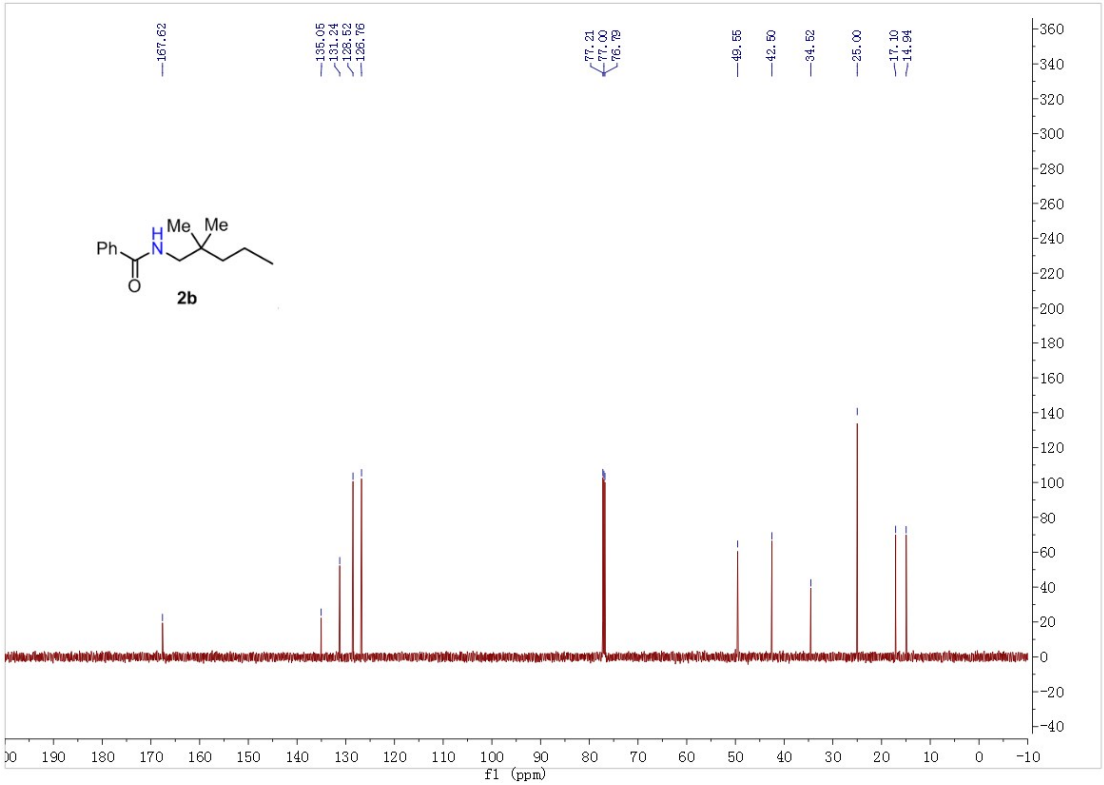
7.501
7.483
7.468
7.439
7.421
7.263
6.111
3.304
3.288
1.388
1.363
1.352
1.344
1.334
1.326
1.315
1.309
1.302
1.286
1.268
1.261
1.251
1.241
1.230
1.214
1.164
0.946
0.932
0.915
0.897
0.881
0.000
Me Me
H
N
Ph
O
2b
2.00
1.05
2.01
0.96
2.17
2.08
2.22
6.23
3.38
f1 (ppm)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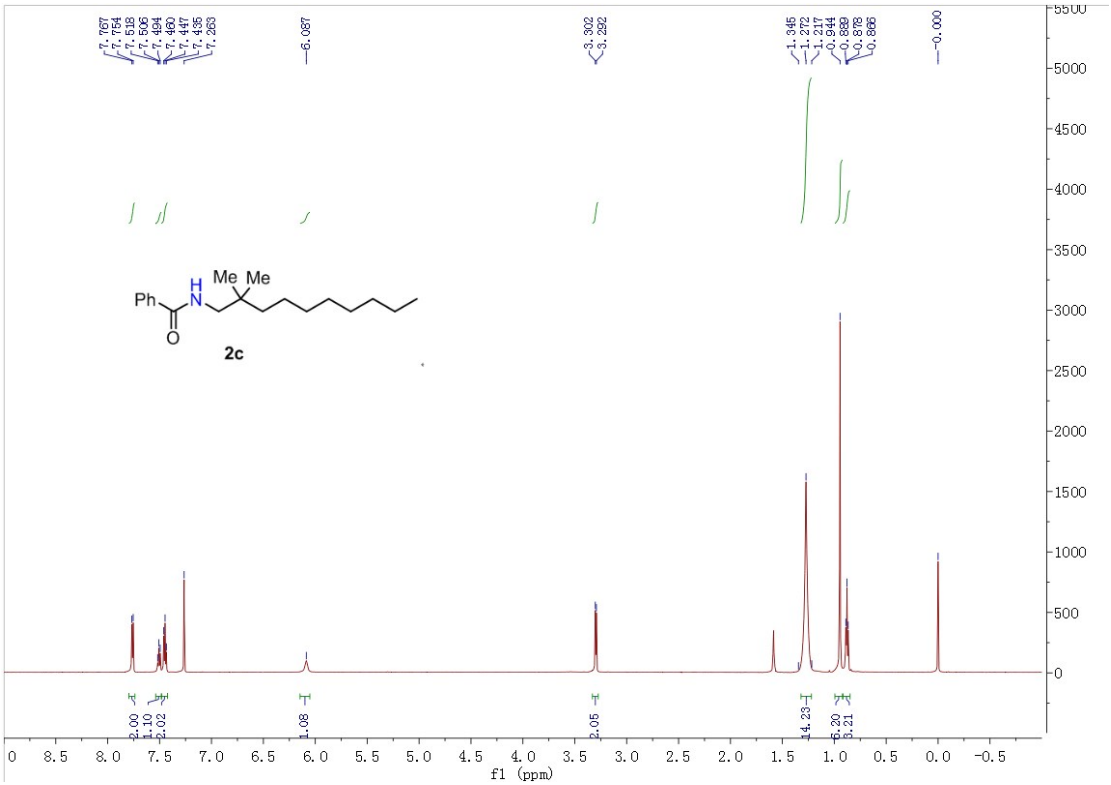
135.05
131.24
128.52
126.76
77.21
77.00
76.79
49.56
42.60
34.62
25.00
17.10
14.94
Ph
N
H
O
Me
Me
2b
f1 (ppm)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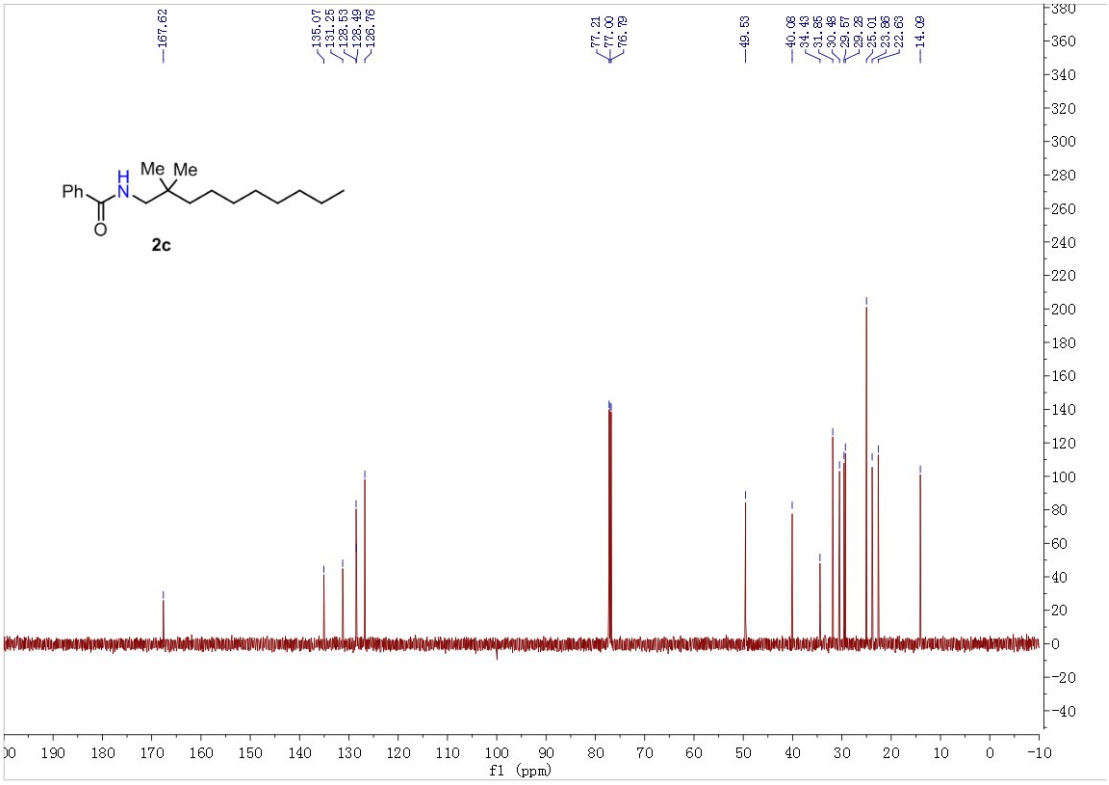
7.754
7.518
7.506
7.494
7.460
7.447
7.435
7.263
6.087
3.302
3.292
1.345
1.272
1.217
0.944
0.889
0.878
0.866
0.000
2.00
1.10
2.02
1.08
2.05
14.23
6.20
3.21
Ph
N
H
O
Me
Me
2c
f1 (ppm)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135.07
131.25
128.53
128.49
126.76
77.21
77.00
76.79
49.53
40.06
34.43
31.85
30.48
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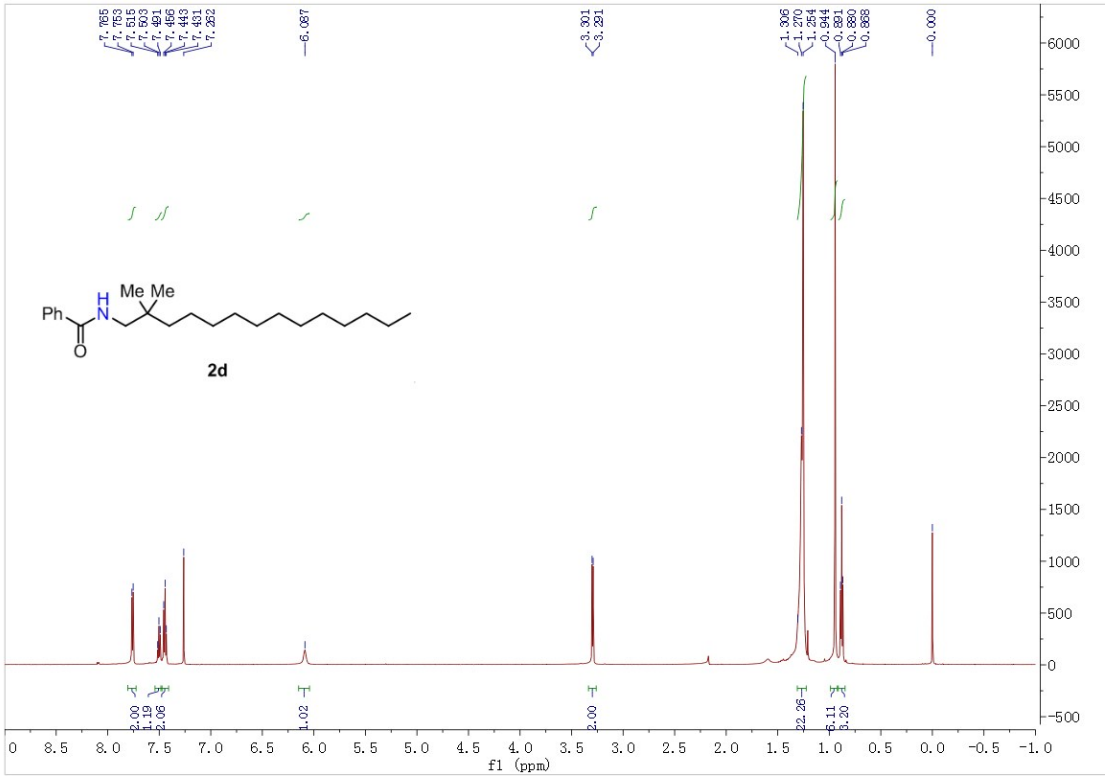
25.01
23.86
22.63
14.09
Ph
H
N
O
Me Me
2c
f1 (ppm)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7.491
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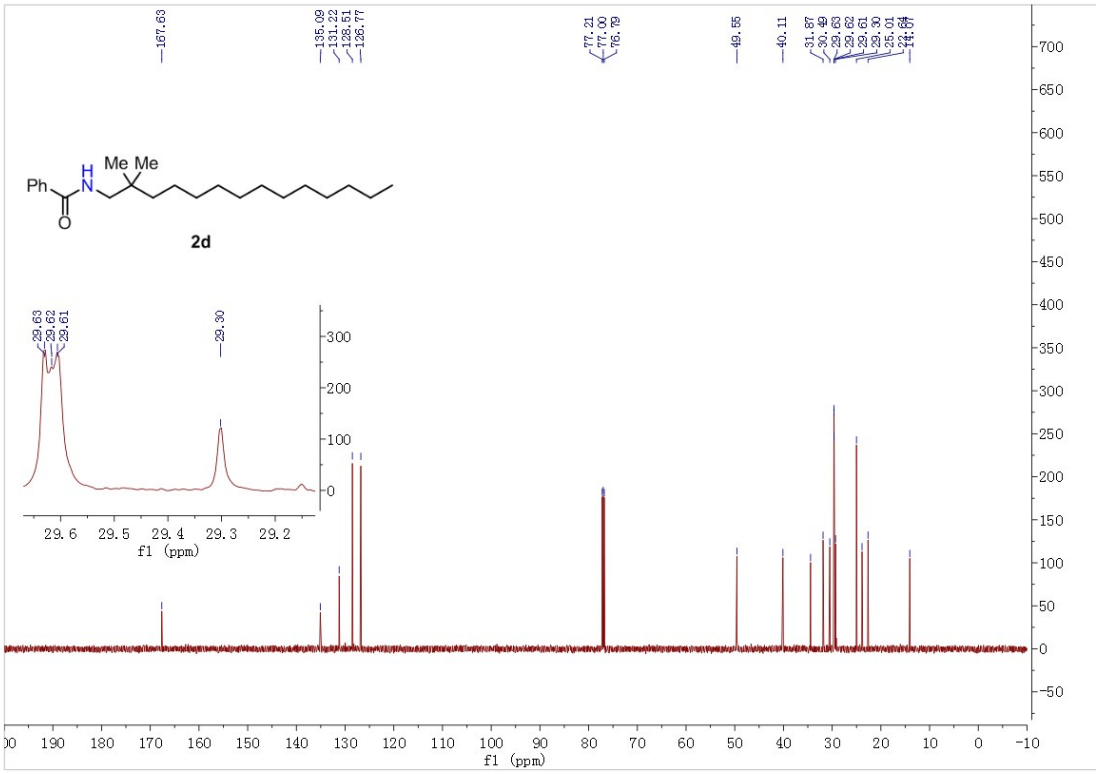
7.443
7.431
7.262
6.067
3.301
3.291
1.306
1.270
1.254
0.944
0.891
0.880
0.868
0.000
2.00
1.19
2.06
1.02
2.00
22.26
6.11
3.20
Ph
H
N
O
Me Me
2d
f1 (ppm)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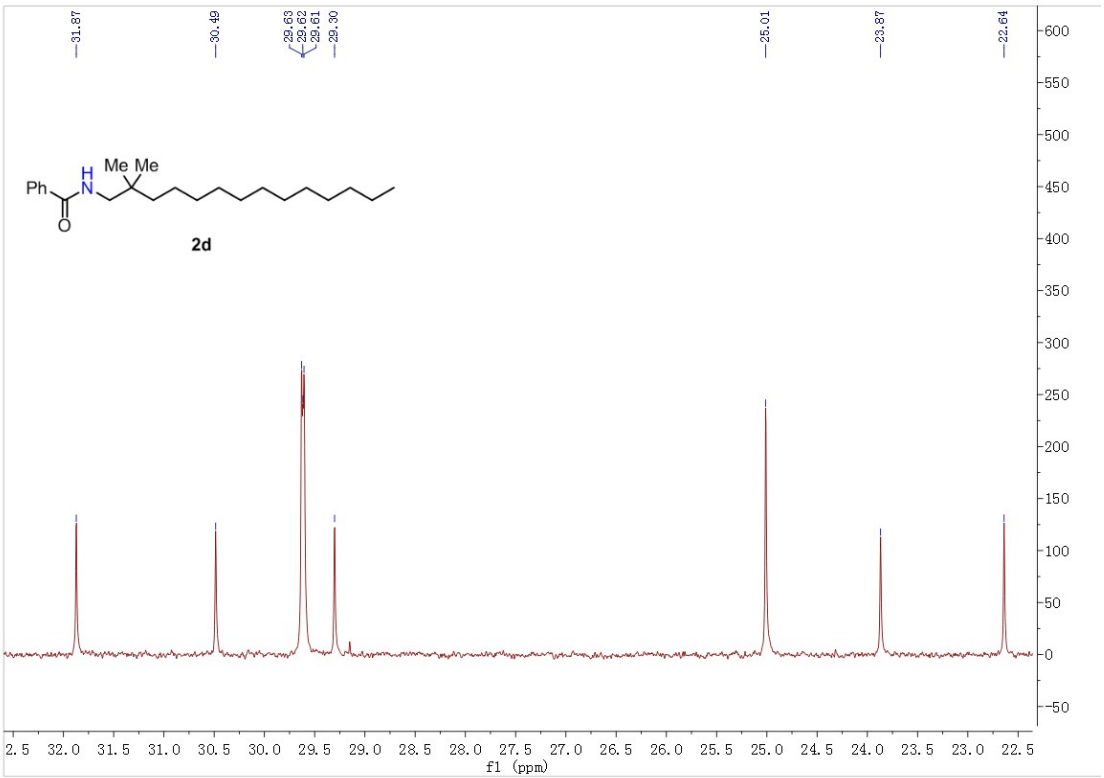
128.51
126.77
77.21
77.00
76.79
49.55
40.11
31.87
30.49
29.63
29.62
29.61
29.30
25.01
23.87
22.64
14.07
Me Me
Ph
H
N
O
2d
29.63
29.62
29.61
29.30
f1 (ppm)
f1 (ppm)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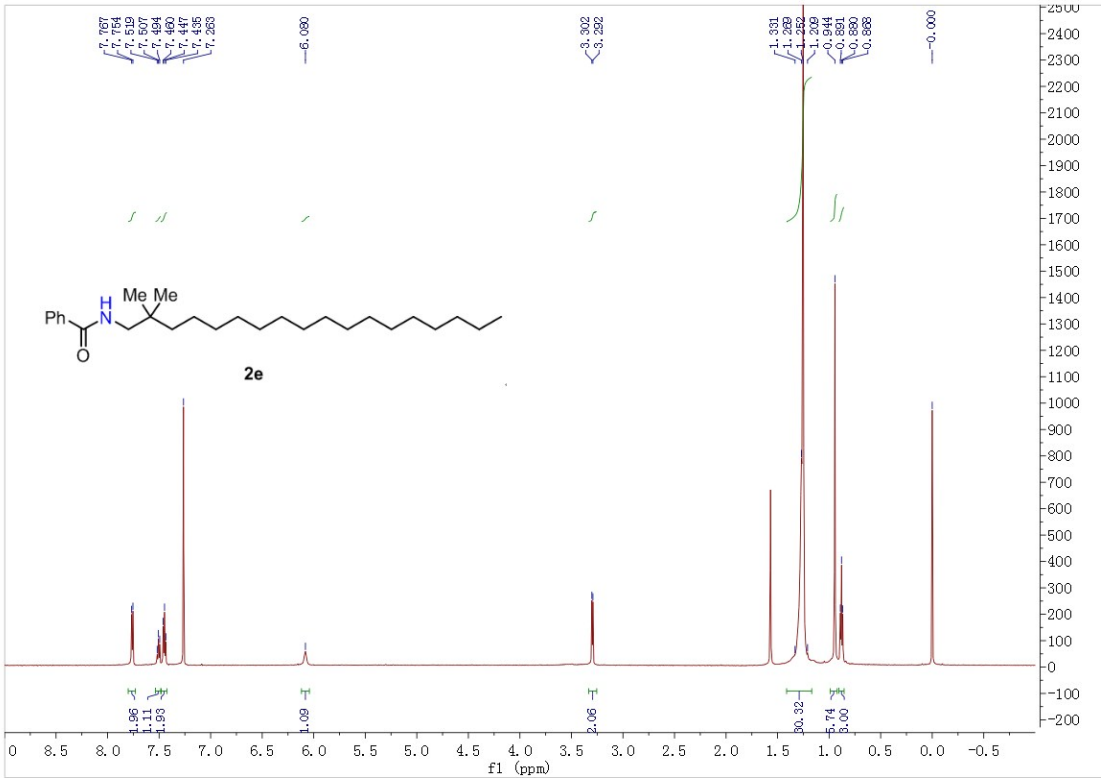
30.49
29.63
29.62
29.61
29.30
25.01
23.87
22.64
Me Me
Ph
H
N
O
2d
f1 (ppm)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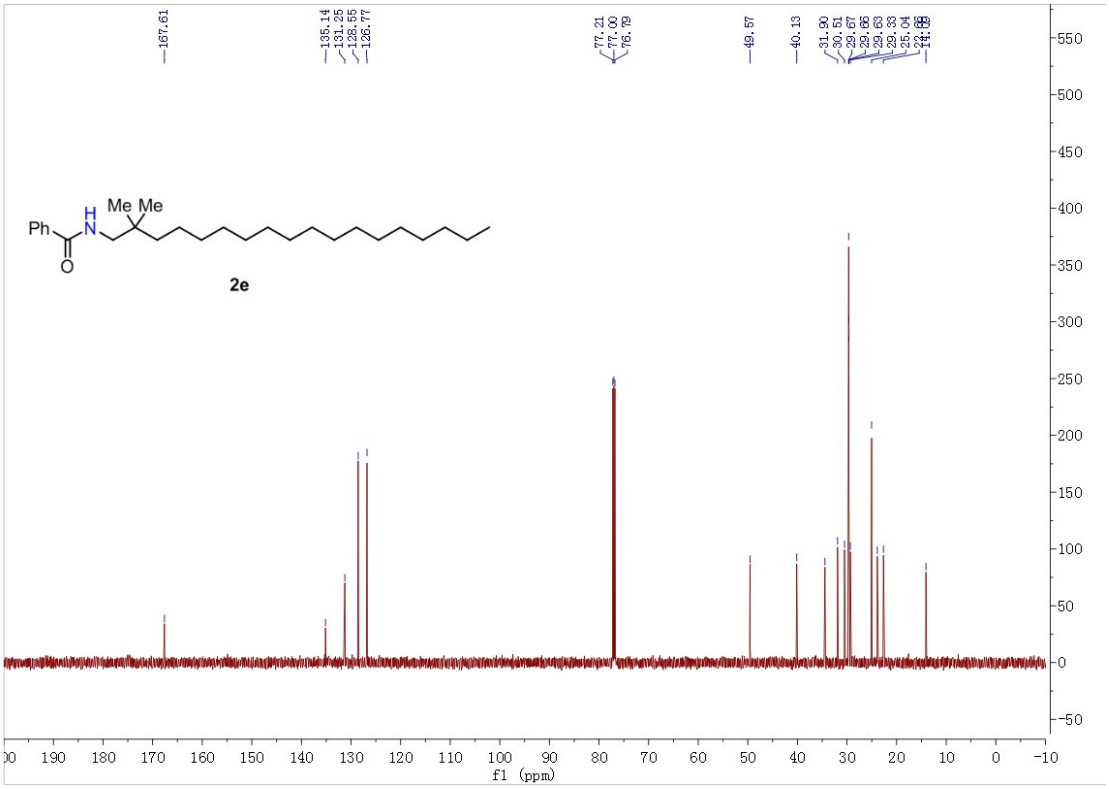
7.460
7.447
7.435
7.263
6.080
3.302
3.292
1.331
1.289
1.252
1.209
0.944
0.891
0.880
0.868
0.000
Ph
H
N
O
Me Me
2e
1.96
1.11
1.93
1.09
2.06
30.32
5.74
3.00
f1 (ppm)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77.21
77.00
76.79
49.57
40.13
31.90
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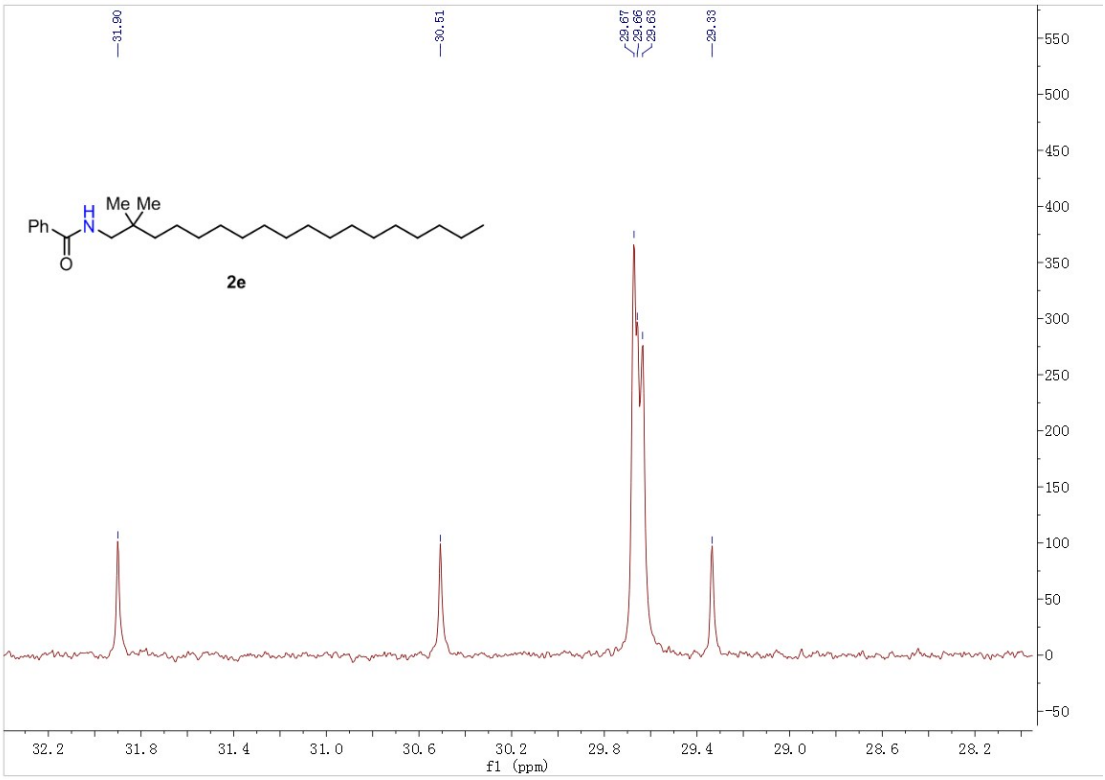
29.63
29.33
25.04
14.09
Ph
H
N
O
Me Me
2e
f1 (ppm)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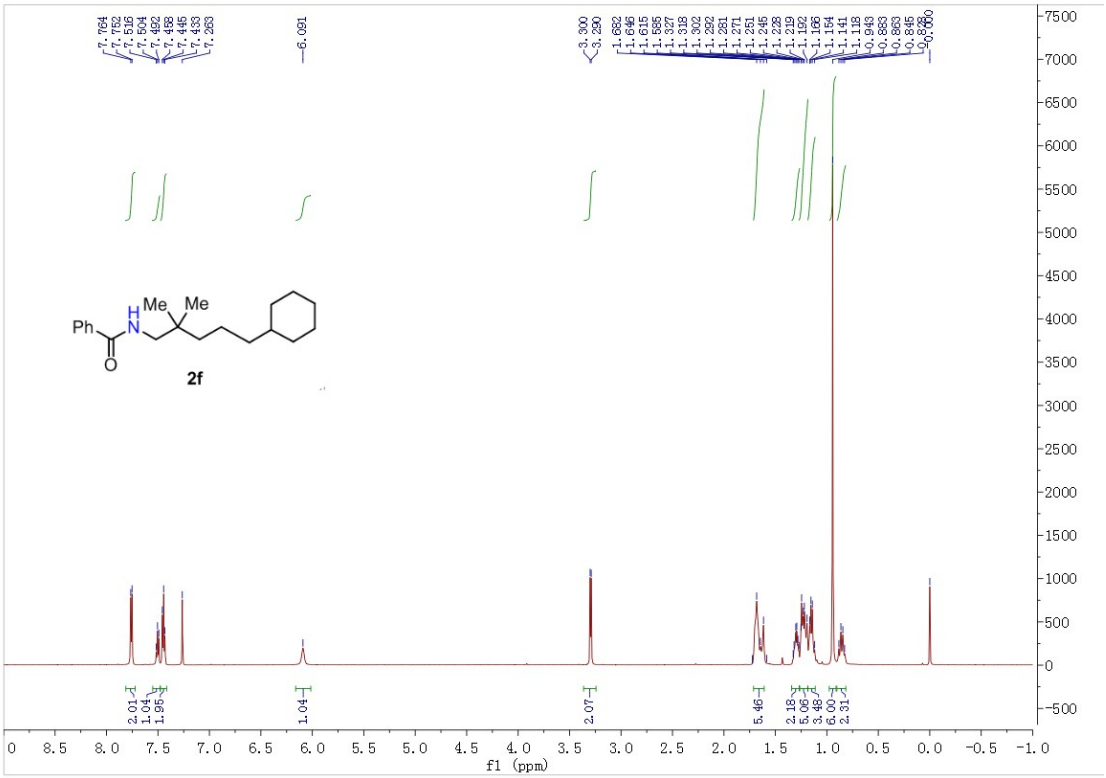
29.67
29.66
29.63
29.33
Ph
H
N
O
Me Me
2e
f1 (ppm)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7.433
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6.091
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1.646
1.615
1.586
1.327
1.318
1.302
1.282
1.261
1.271
1.251
1.245
1.228
1.219
1.192
1.166
1.154
1.141
1.118
0.943
0.883
0.863
0.846
0.808
0.000
Ph
H
N
O
Me Me
2f
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1.04
2.07
5.46
2.18
2.06
3.48
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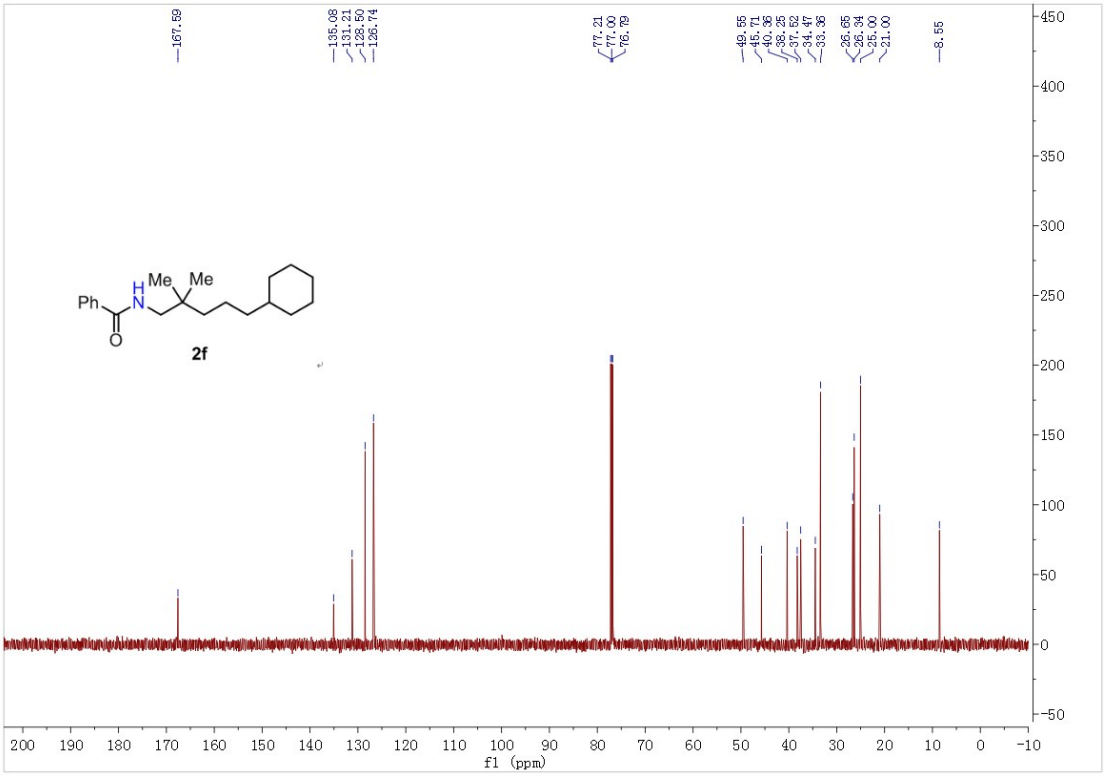
f1 (ppm)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77.21
77.00
76.79
49.55
45.71
40.36
38.25
37.62
34.47
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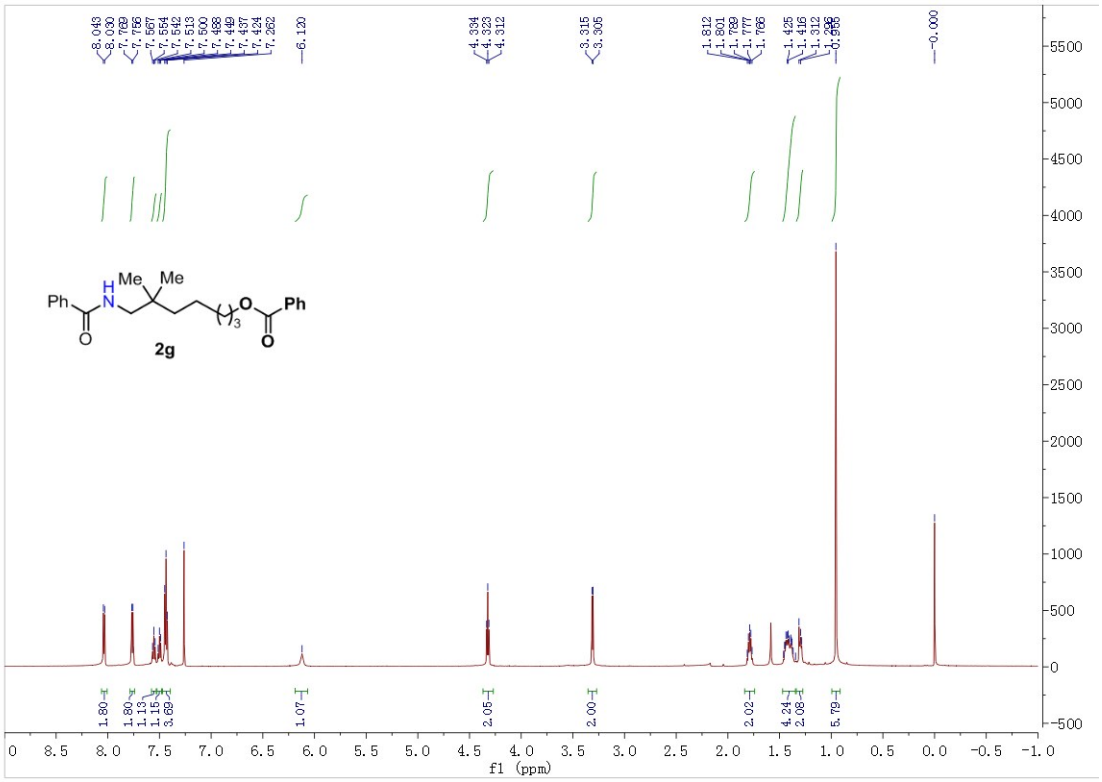
Ph
Me
Me
H
N
O
2f
f1 (ppm)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7.513
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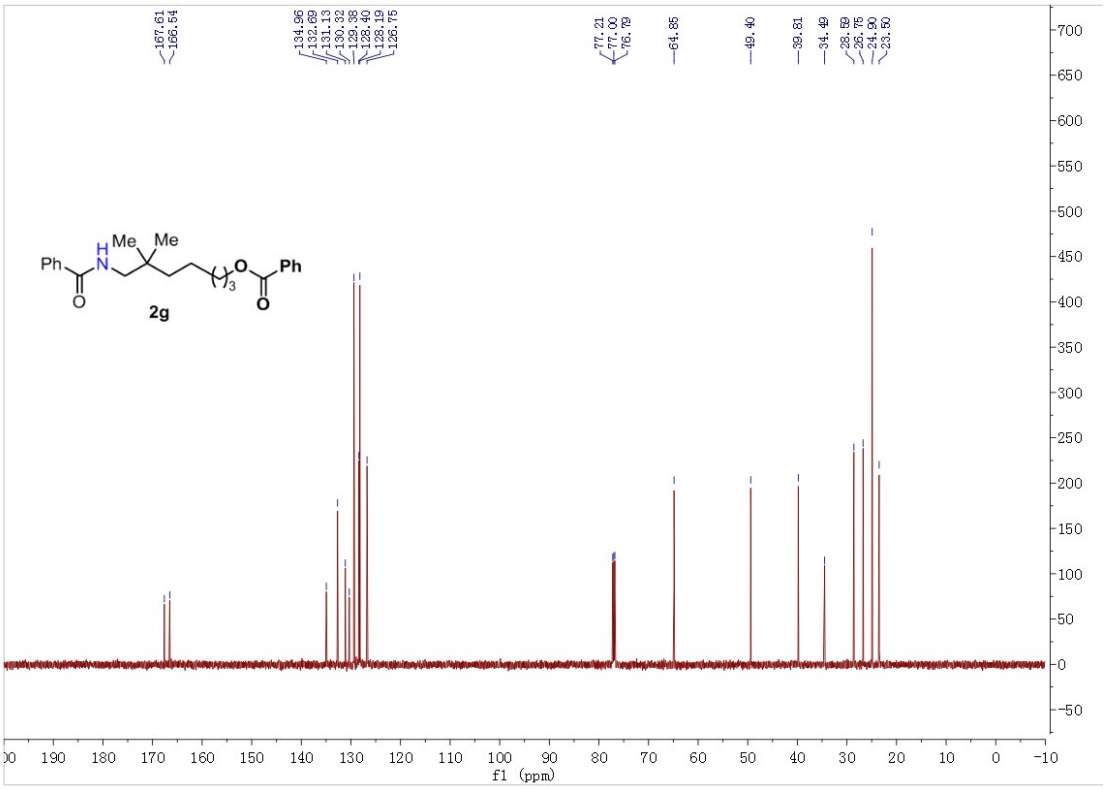
7.488
7.449
7.437
7.424
7.262
6.120
4.334
4.323
4.312
3.315
3.305
1.812
1.801
1.789
1.777
1.766
1.425
1.416
1.312
1.302
0.000
1.80
1.80
1.13
1.15
3.69
1.07
2.05
2.00
2.02
4.24
2.08
5.79
Ph
Me
Me
H
N
O
O
Ph
2g
f1 (ppm)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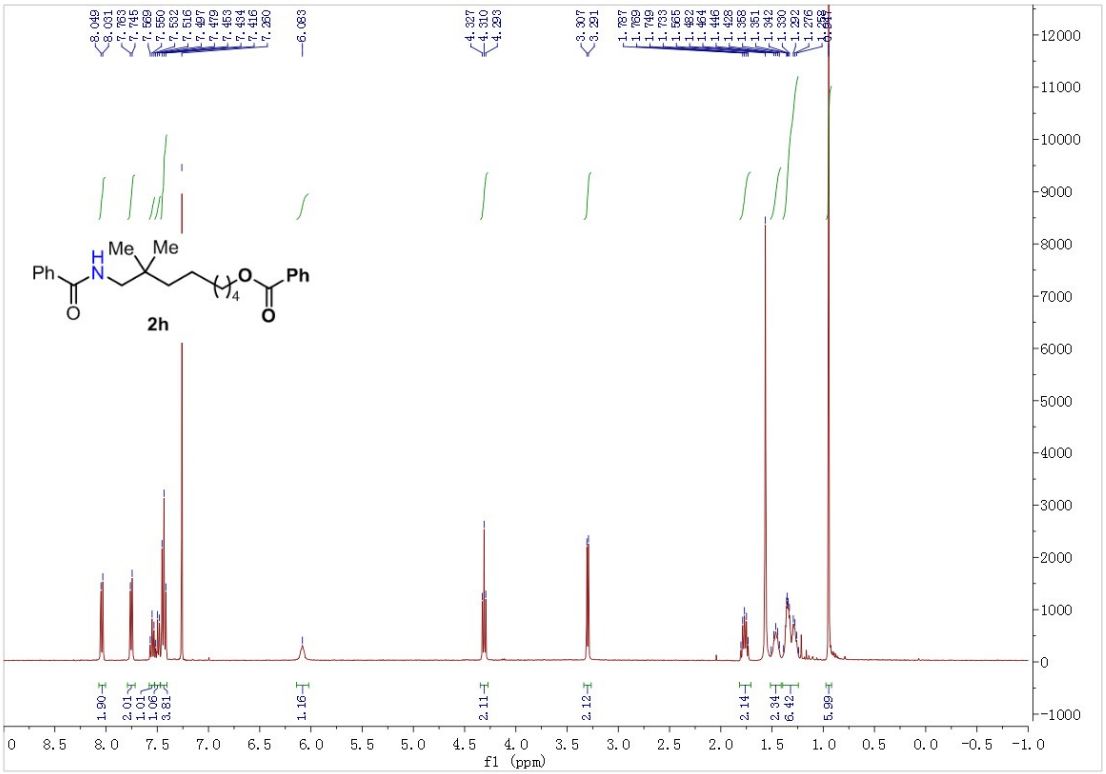
166.54
134.96
132.69
131.13
130.32
129.38
128.40
128.19
126.75
77.21
77.00
76.79
64.86
49.40
39.81
34.49
28.59
26.75
24.90
23.50
Ph
Me
Me
H
N
O
Ph
O
3
O
2g
f1 (ppm)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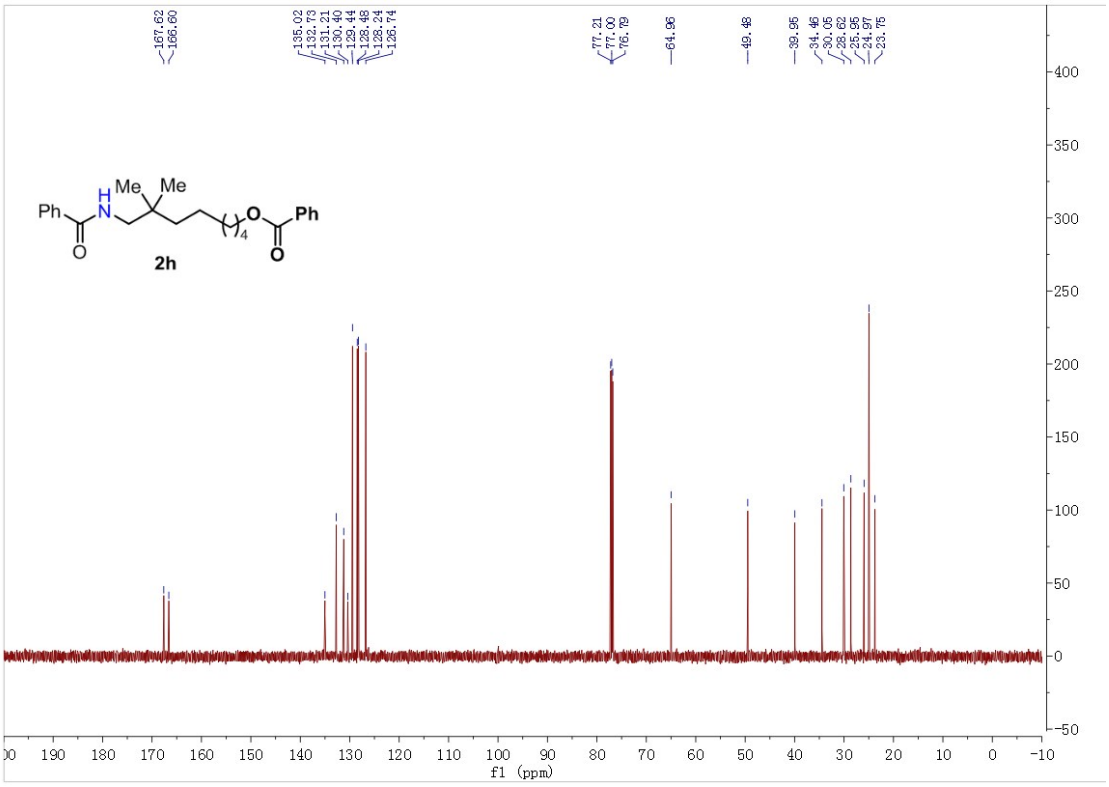
7.453
7.434
7.416
7.250
6.083
4.327
4.310
4.293
3.307
3.291
1.787
1.769
1.749
1.733
1.565
1.482
1.464
1.446
1.428
1.358
1.351
1.342
1.330
1.292
1.276
Ph
Me
Me
H
N
O
Ph
O
4
O
2h
1.90
2.01
2.01
1.06
3.81
1.16
2.11
2.12
2.14
2.34
6.42
5.99
f1 (ppm)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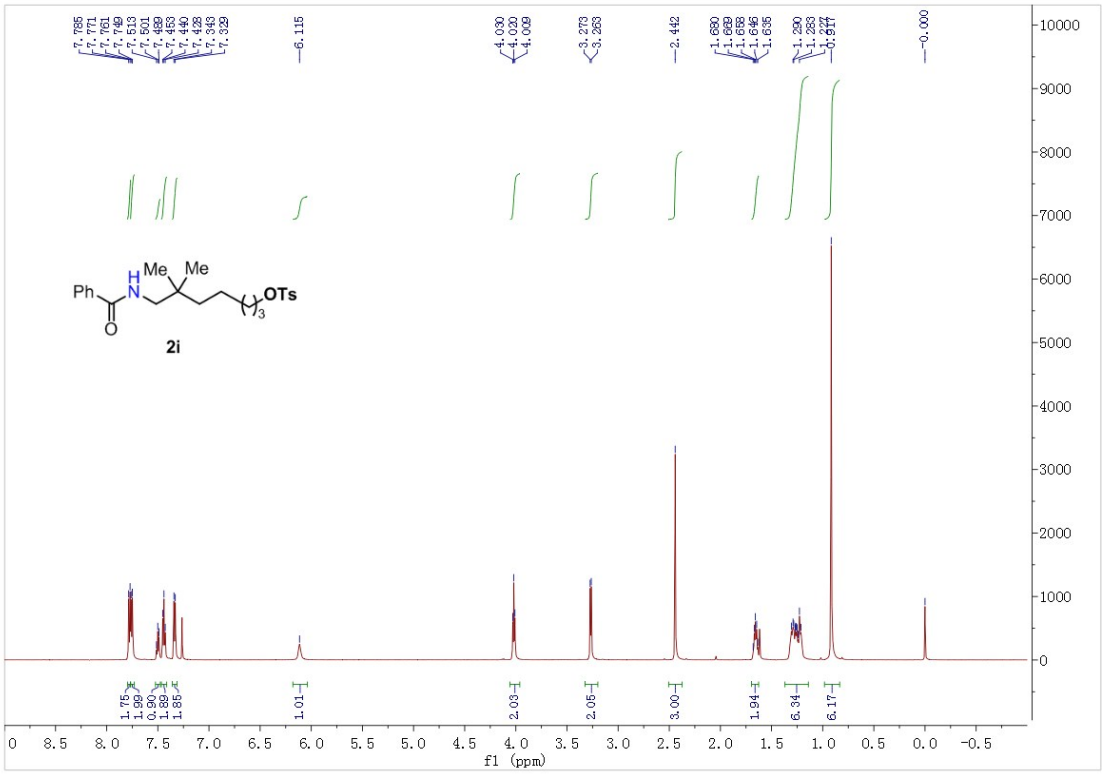
131.21
130.40
129.44
128.48
128.24
126.74
77.21
77.00
76.79
64.96
49.48
39.96
34.46
30.05
28.62
25.96
24.97
23.76
Ph
H
N
Me
Me
O
4
O
Ph
O
2h
f1 (ppm)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7.465
7.440
7.428
7.343
7.329
6.115
4.030
4.020
4.009
3.273
3.263
2.442
1.690
1.669
1.658
1.646
1.635
1.290
1.283
0.877
-0.000
Ph
H
N
Me
Me
OTs
3
O
2i
1.75
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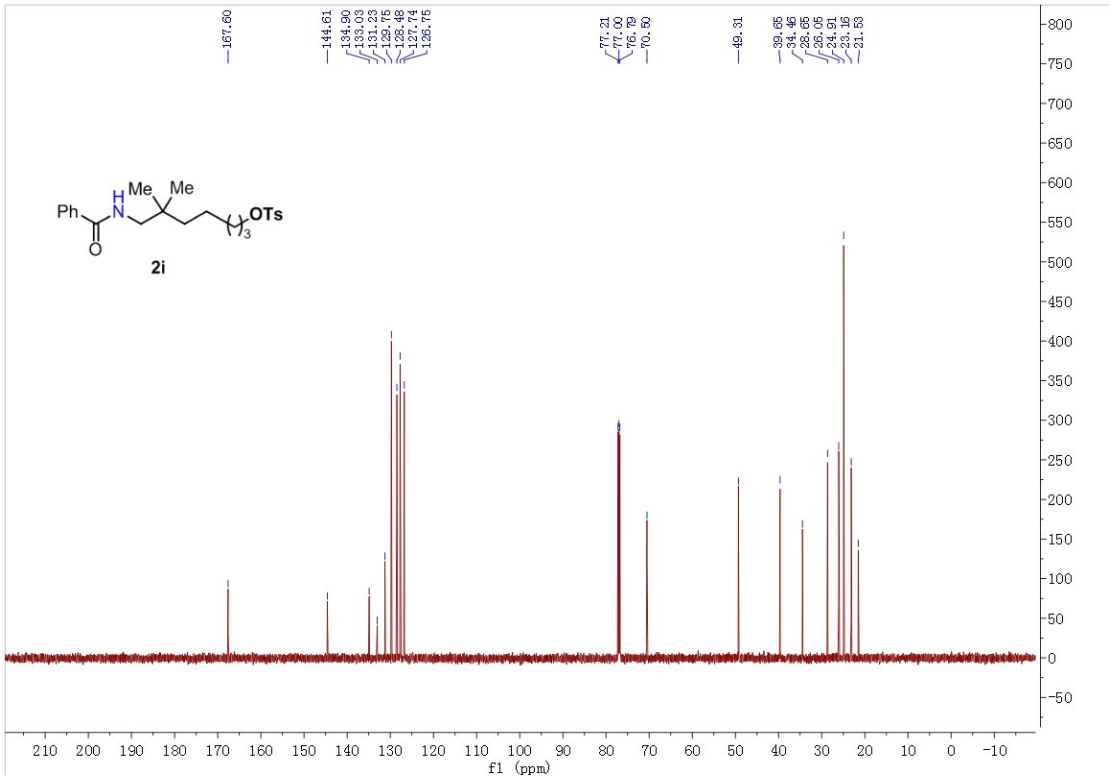
0.90
1.89
1.85
1.01
2.03
2.05
3.00
1.94
6.34
6.17
f1 (ppm)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77.00
76.79
70.50
49.31
39.65
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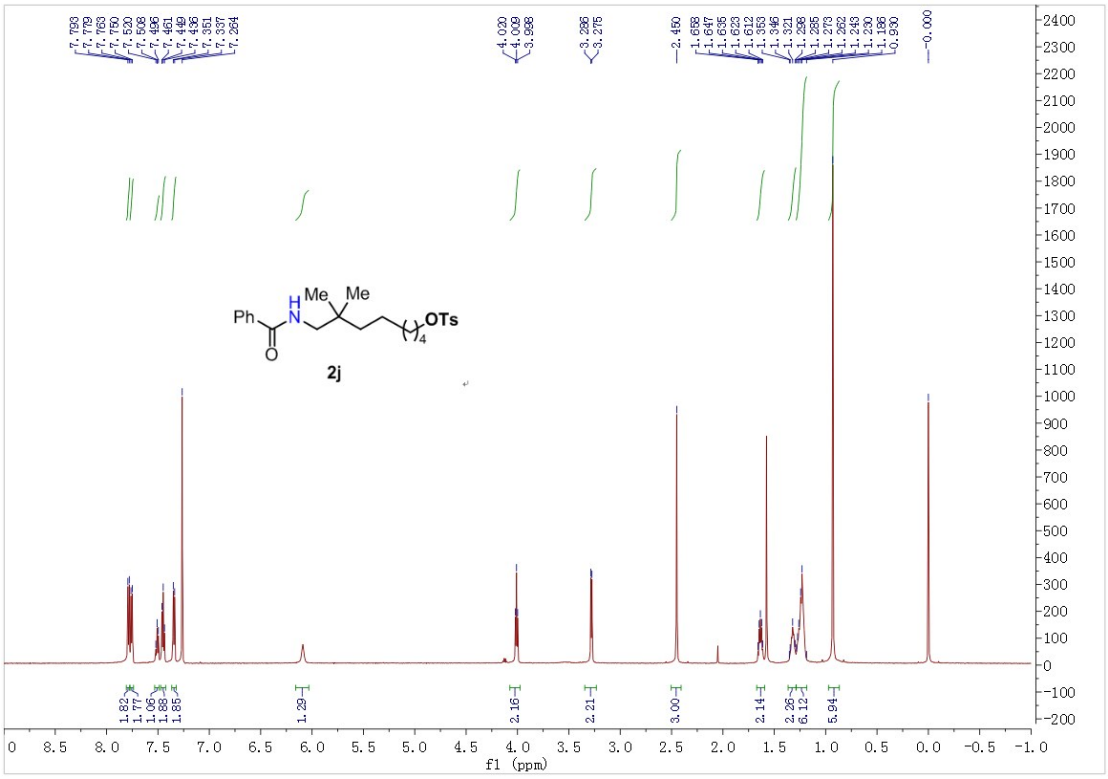
28.65
26.05
24.91
23.16
21.53
Ph
Me
Me
OTs
2i
f1 (ppm)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7.461
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7.436
7.351
7.337
7.294
4.020
4.008
3.988
3.286
3.276
2.460
1.668
1.647
1.635
1.623
1.612
1.363
1.346
1.321
1.288
1.285
1.273
1.262
1.245
1.230
1.208
1.188
0.930
-0.000
Ph
Me
Me
OTs
2j
1.82
1.77
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1.29
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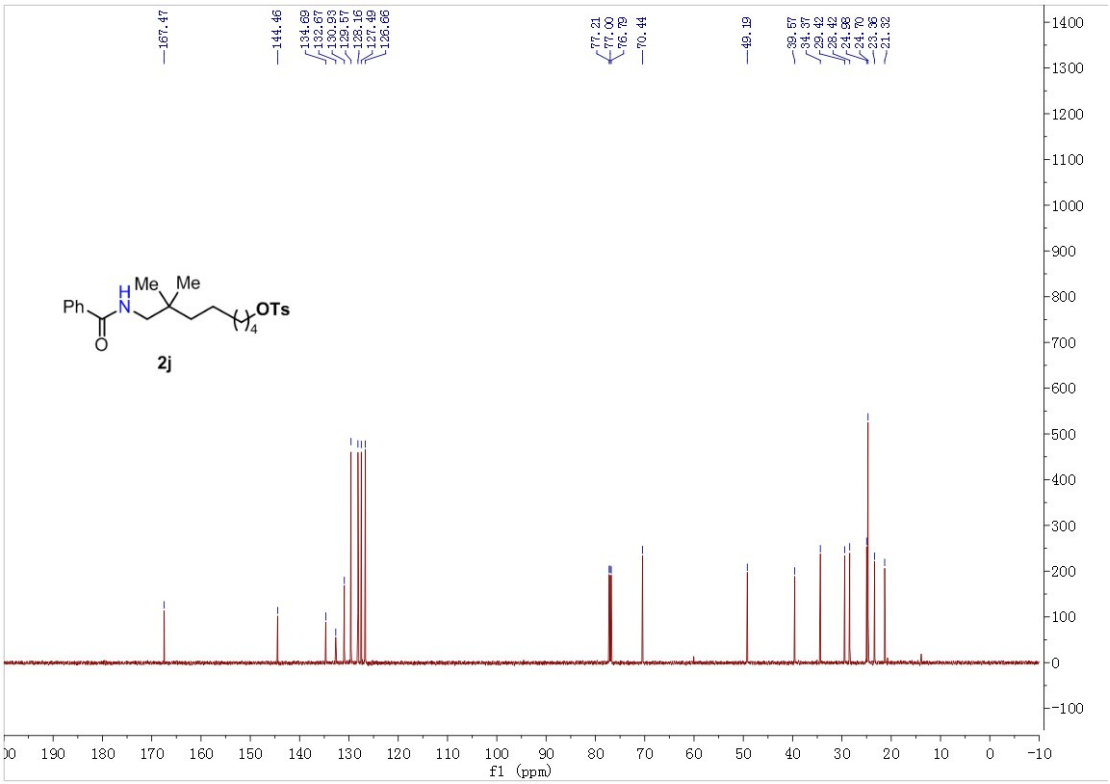
2.21
3.00
2.14
2.26
6.12
5.94
f1 (ppm)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77.21
77.00
76.79
70.44
49.19
39.57
34.37
29.42
28.42
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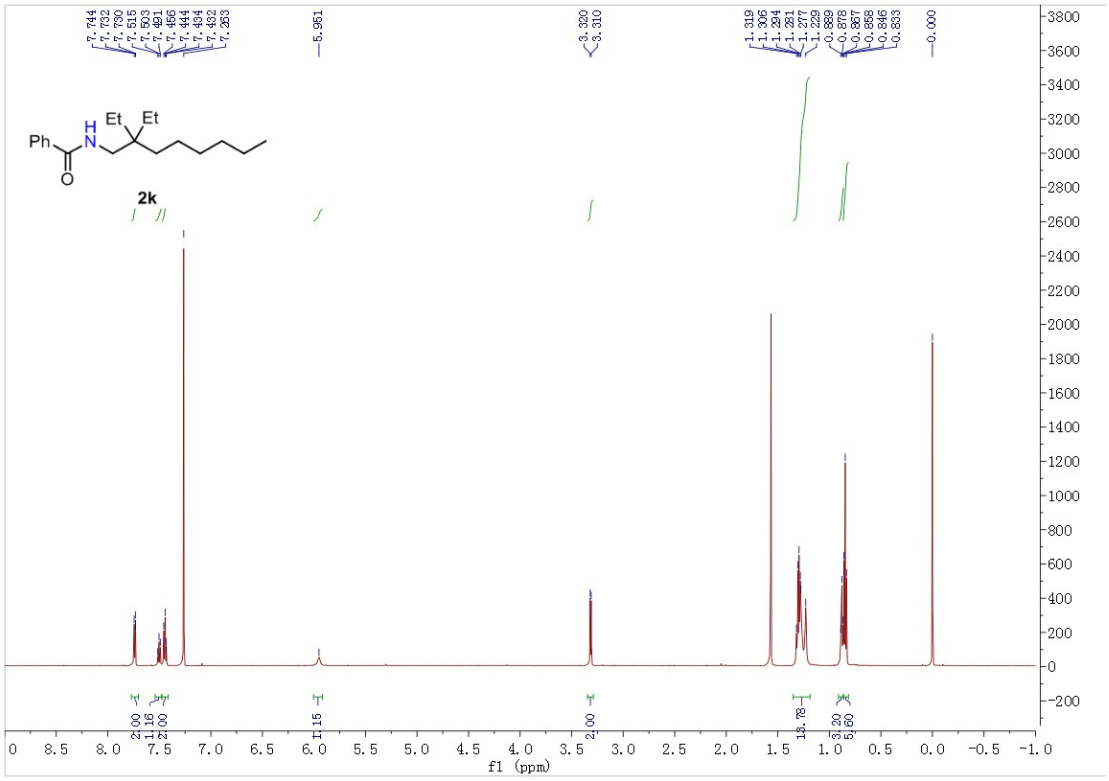
23.36
21.32
Ph
H
N
Me
Me
OTs
4
O
2j
f1 (ppm)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7.491
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7.444
7.434
7.432
7.263
5.951
3.320
3.310
1.319
1.306
1.294
1.281
1.277
1.229
0.889
0.878
0.867
0.858
0.846
0.833
0.000
Ph
H
N
Et
Et
O
2k
2.00
1.16
2.00
1.15
2.00
13.78
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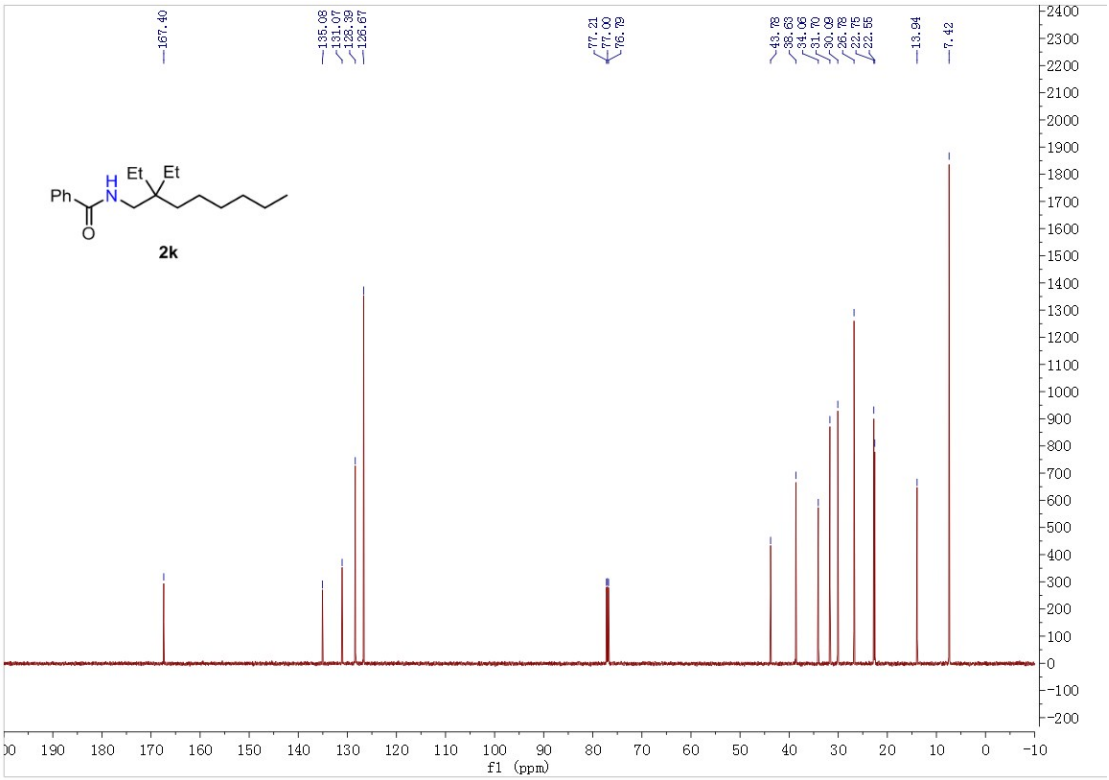
5.60
f1 (ppm)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76.79
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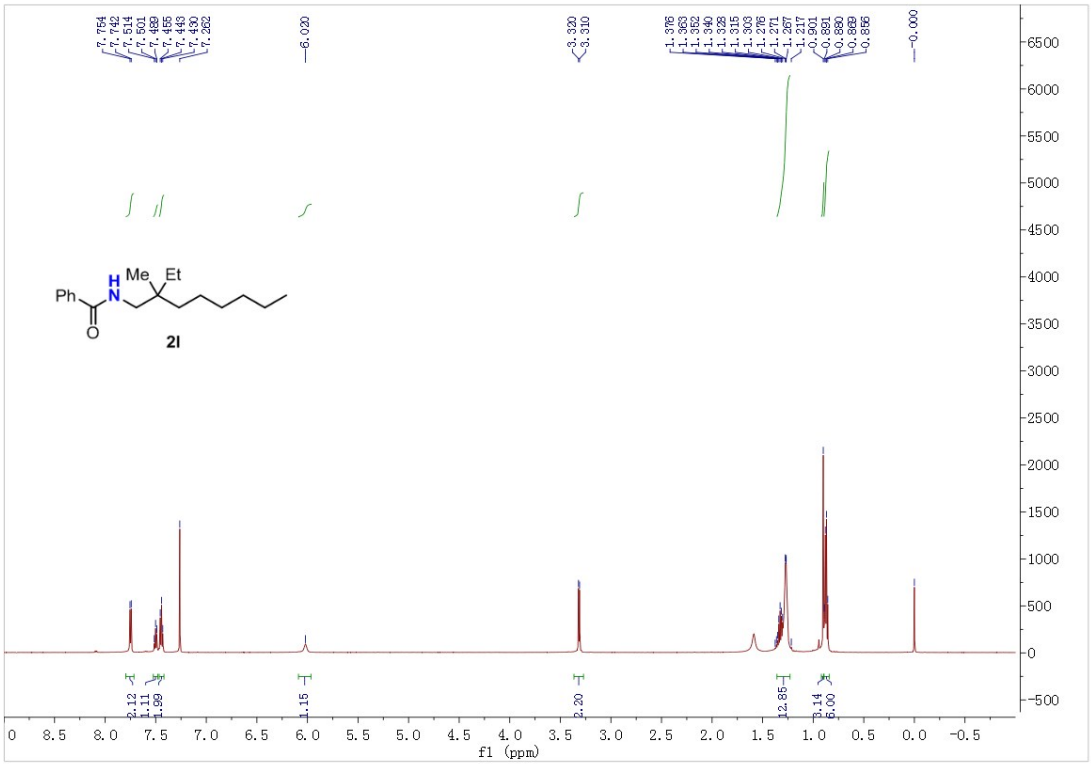
38.63
34.06
31.70
30.09
26.78
22.75
22.55
13.94
7.42
Ph
H
N
O
Et
Et
2k
f1 (ppm)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7.488
7.455
7.449
7.430
7.262
6.020
3.320
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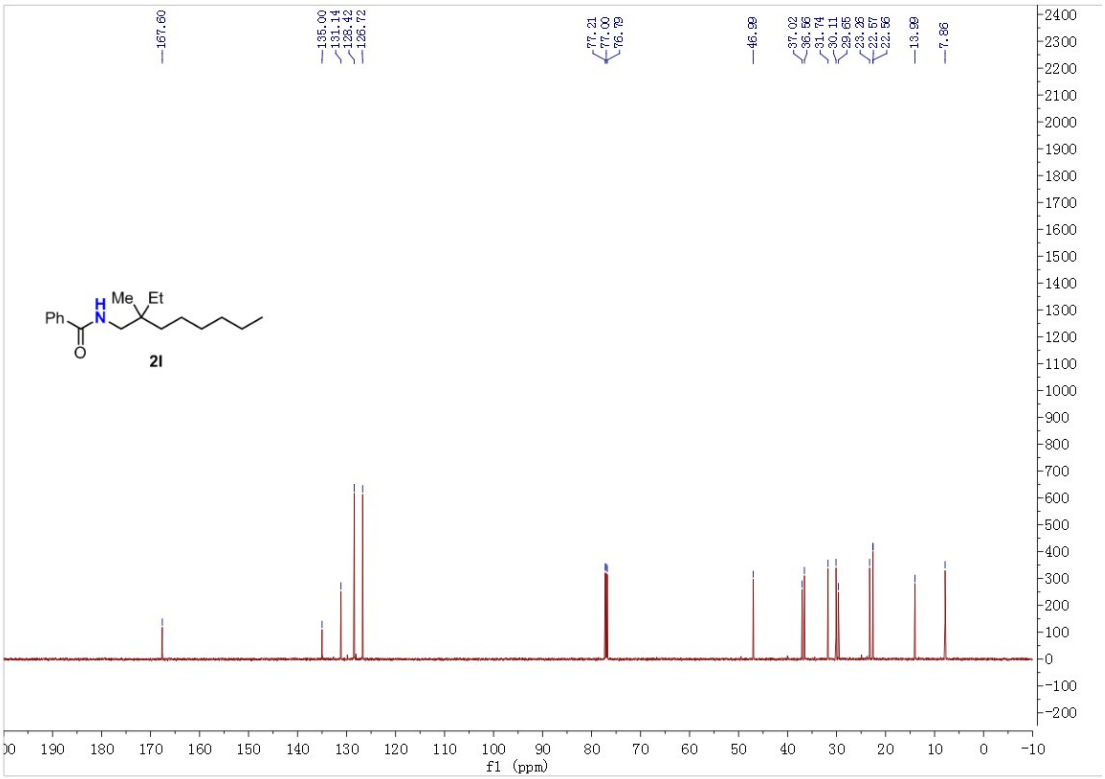
1.376
1.363
1.352
1.340
1.328
1.315
1.303
1.276
1.271
1.267
1.217
0.901
0.891
0.889
0.866
0.000
Ph
H
N
O
Me
Et
2l
2.12
1.11
1.99
1.15
2.20
12.85
3.14
6.00
f1 (ppm)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77.00
76.79
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37.02
36.66
31.74
30.11
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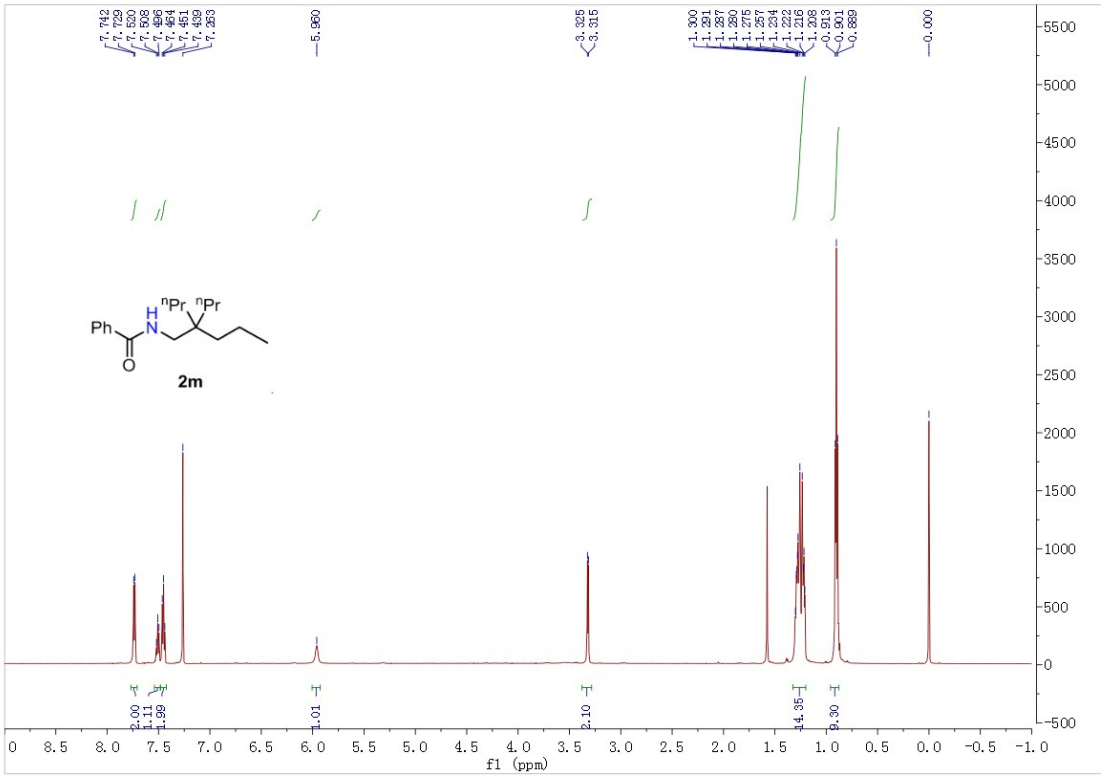
22.67
22.56
13.99
7.86
Ph
H
N
O
Me
Et
2l
f1 (ppm)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7.451
7.439
7.263
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3.315
1.300
1.291
1.287
1.280
1.275
1.257
1.234
1.222
1.216
1.208
0.913
0.901
0.889
0.000
Ph
H
N
O
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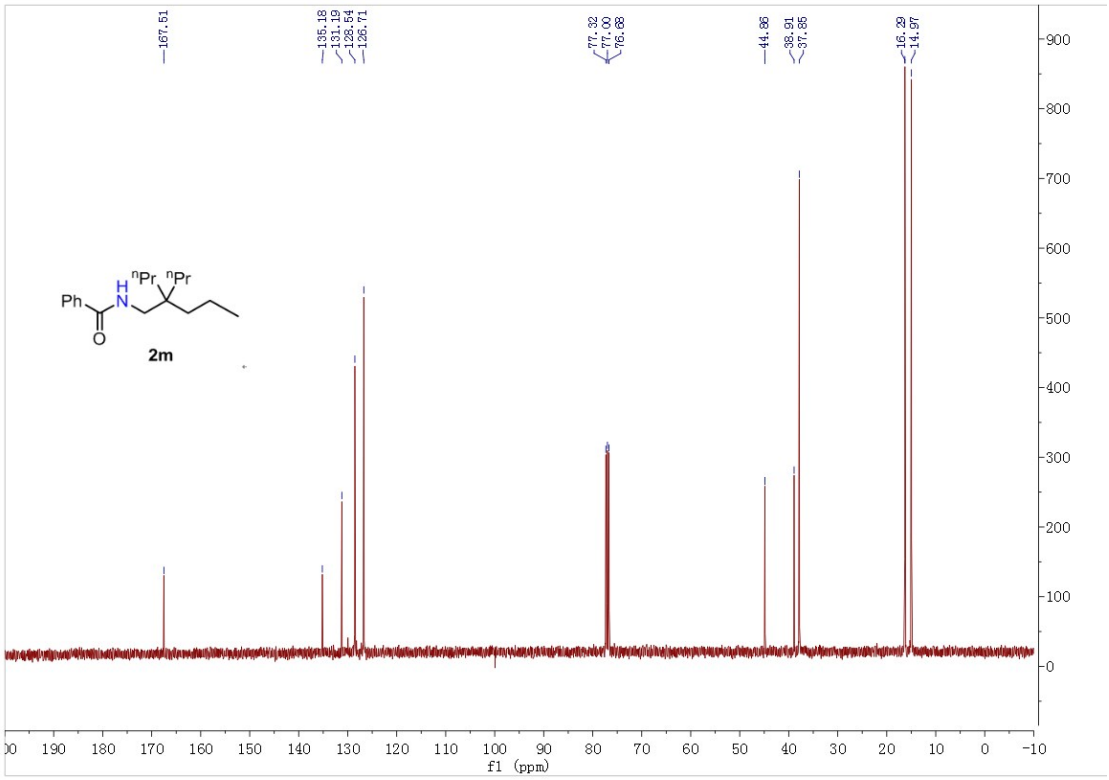
nPr
2m
2.00
1.11
1.99
1.01
2.10
14.35
9.30
f1 (ppm)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77.00
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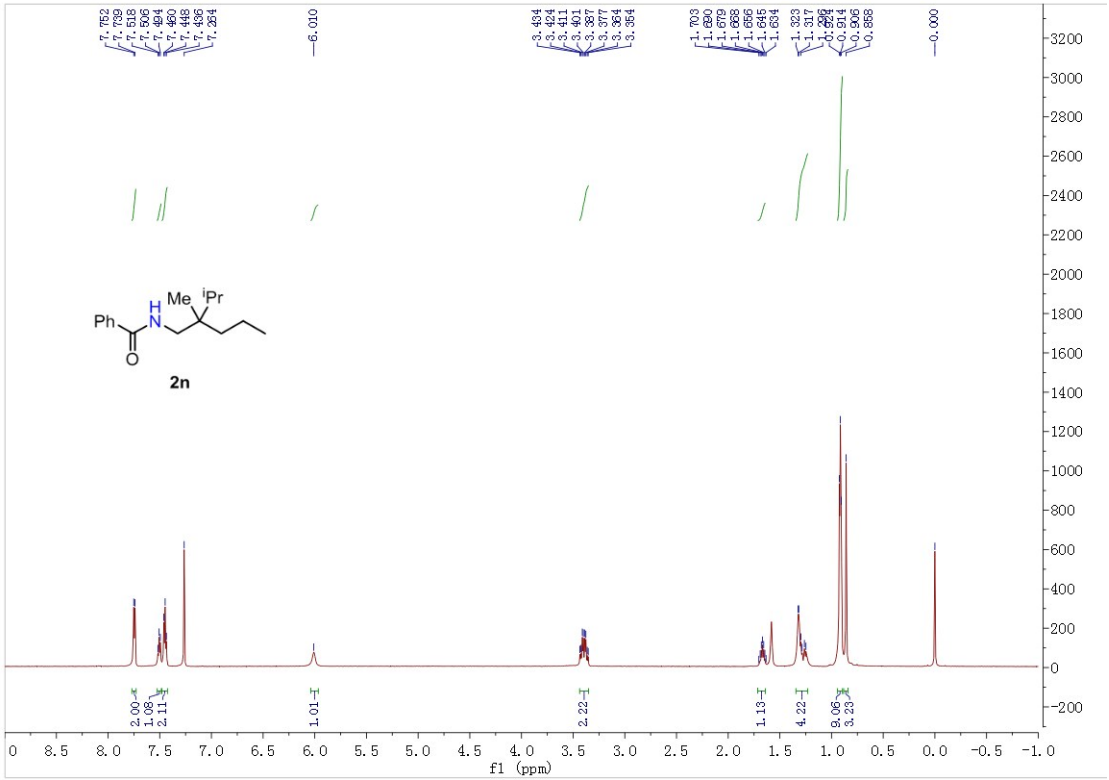
37.85
16.29
14.97
Ph
H
N
O
nPr
nPr
2m
f1 (ppm)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7.436
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3.377
3.364
3.354
1.703
1.690
1.679
1.668
1.656
1.645
1.634
1.323
1.317
0.914
0.906
0.868
0.000
Ph
H
N
O
Me
iPr
2n
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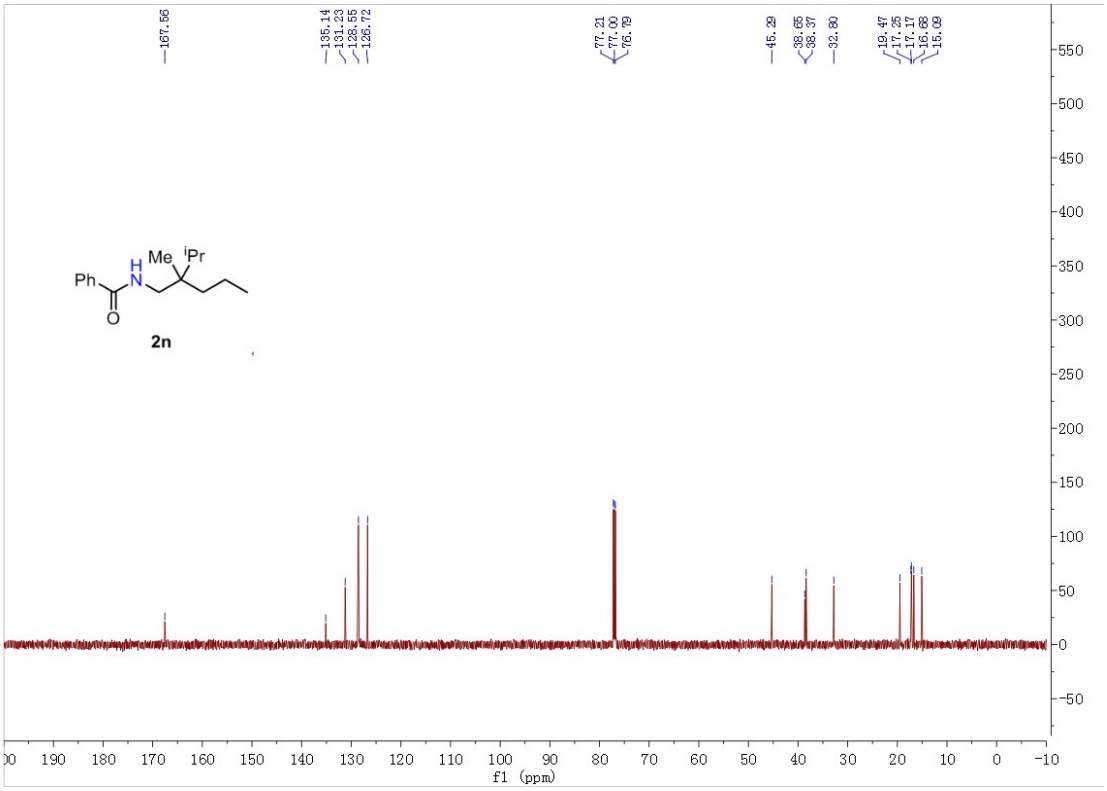
1.08
2.11
1.01
2.22
1.13
4.22
9.06
3.23
f1 (ppm)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76.79
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38.37
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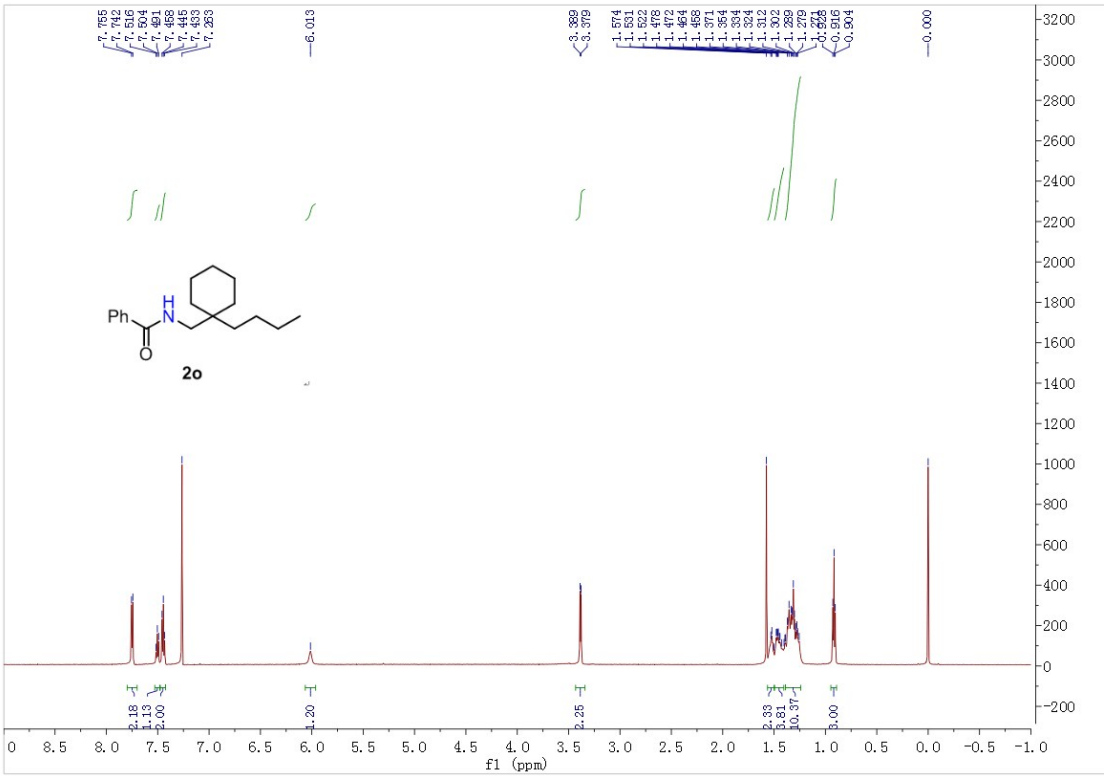
17.17
16.88
15.09
Ph
H
N
O
Me
iPr
2n
f1 (ppm)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7.468
7.445
7.433
7.263
6.013
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3.379
1.574
1.531
1.522
1.478
1.472
1.464
1.458
1.371
1.354
1.334
1.312
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1.289
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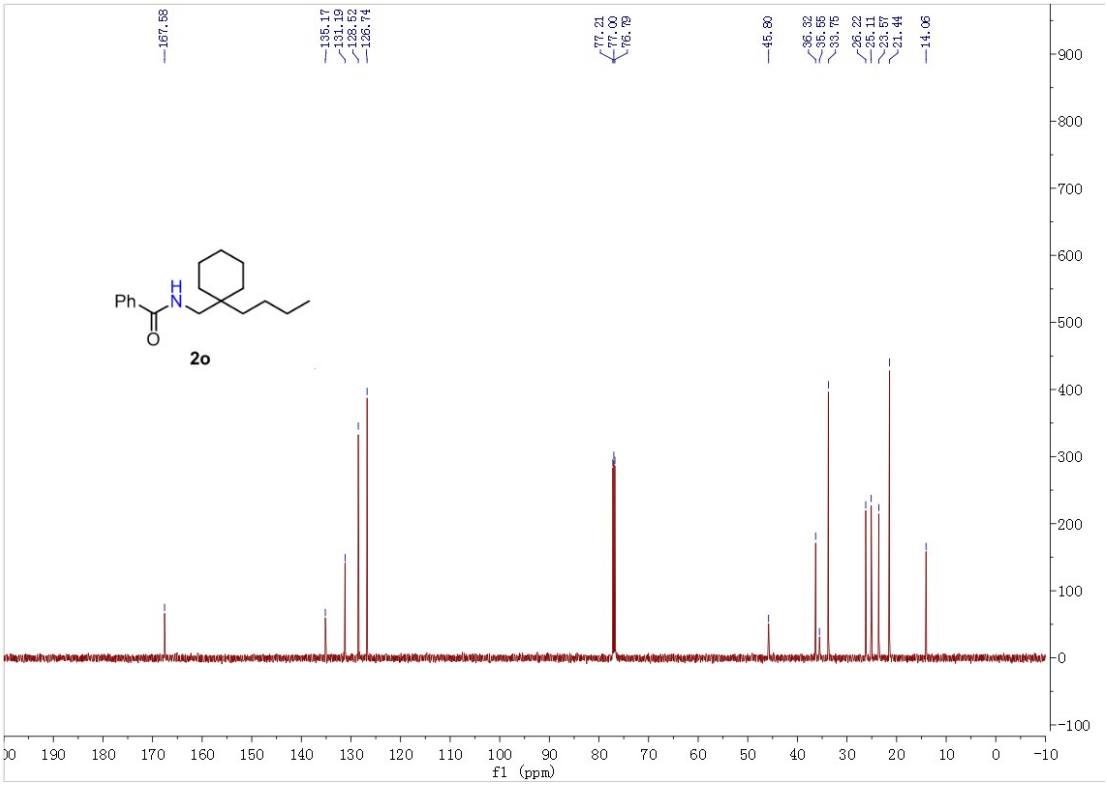
0.928
0.916
0.904
0.000
Ph
H
N
O
2o
f1 (ppm)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76.79
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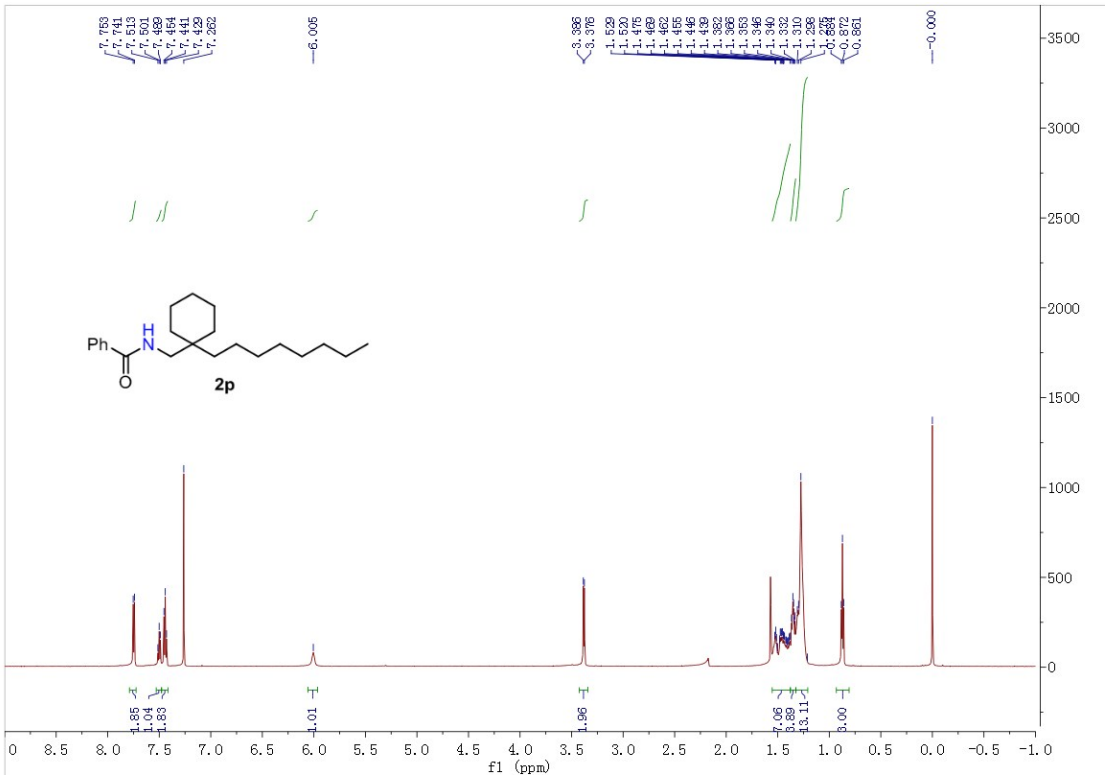
14.06
Ph
H
N
O
2o
f1 (ppm)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7.429
7.262
6.005
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3.376
1.529
1.520
1.475
1.462
1.455
1.446
1.439
1.382
1.366
1.353
1.346
1.340
1.332
1.310
1.298
0.872
0.861
-0.000
Ph
H
N
O
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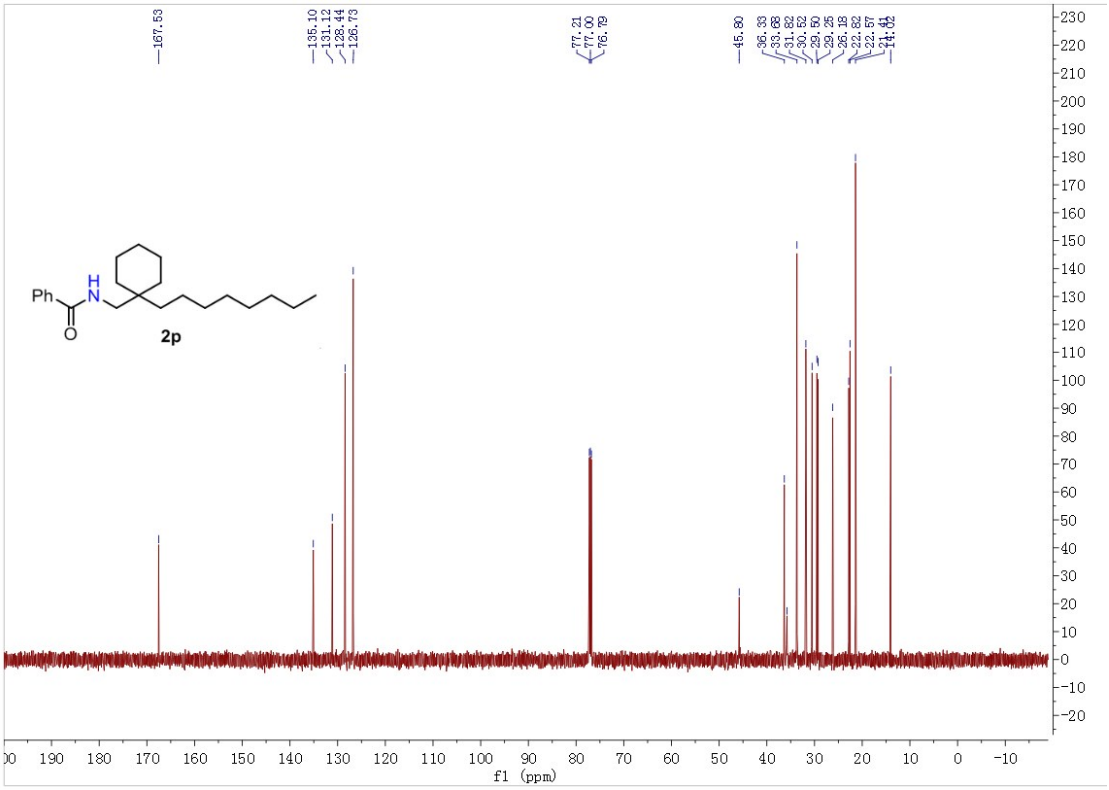
1.04
1.03
1.01
1.96
7.06
3.89
3.11
3.00
f1 (ppm)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33.68
31.82
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26.18
22.82
22.57
21.41
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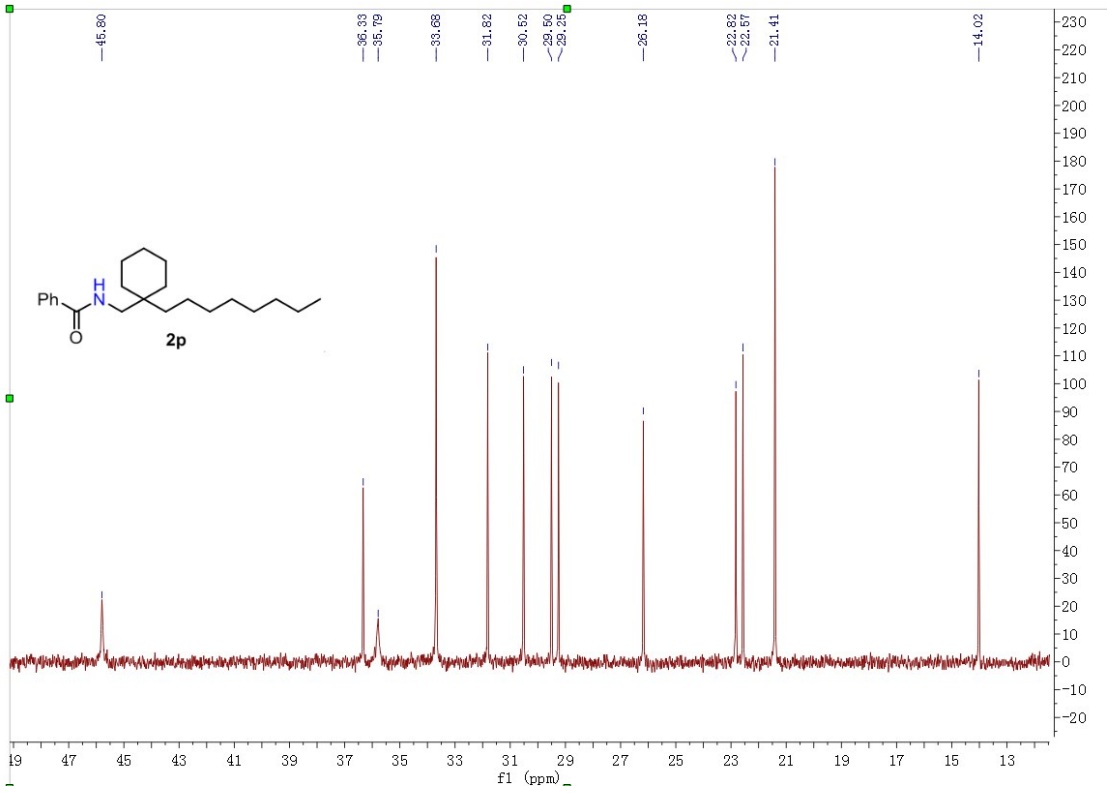
Ph
H
N
O
2p
f1 (ppm)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30.52
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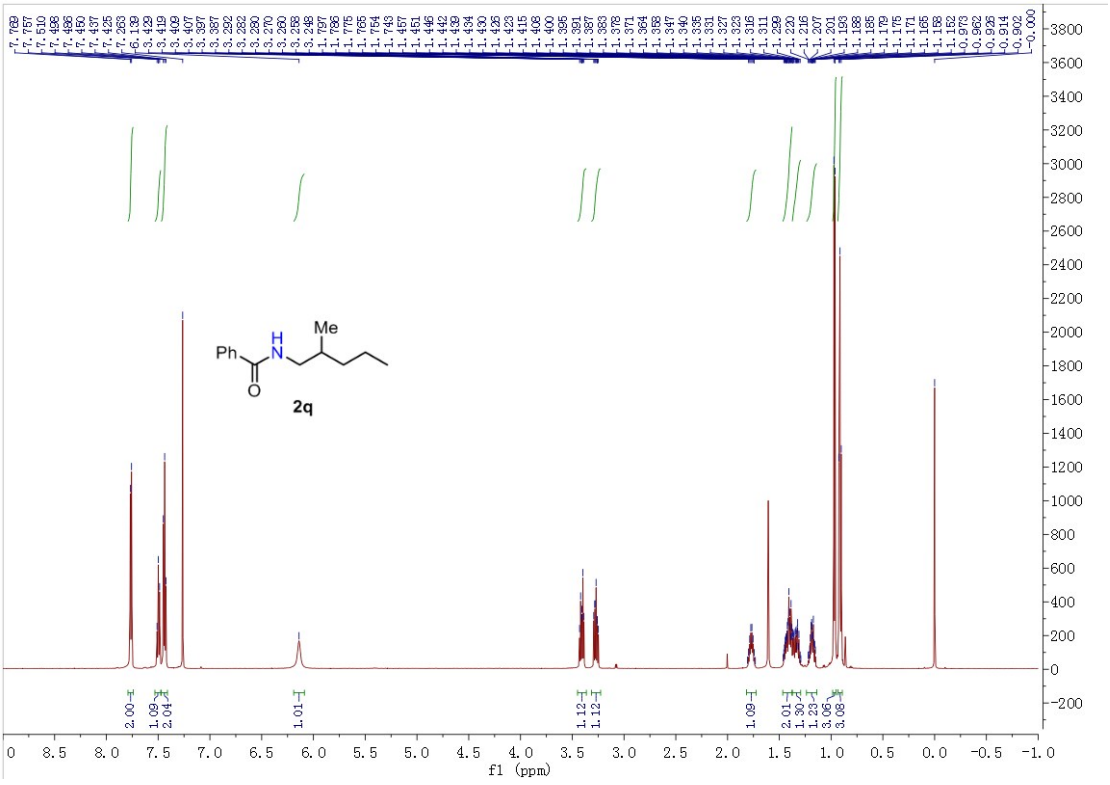
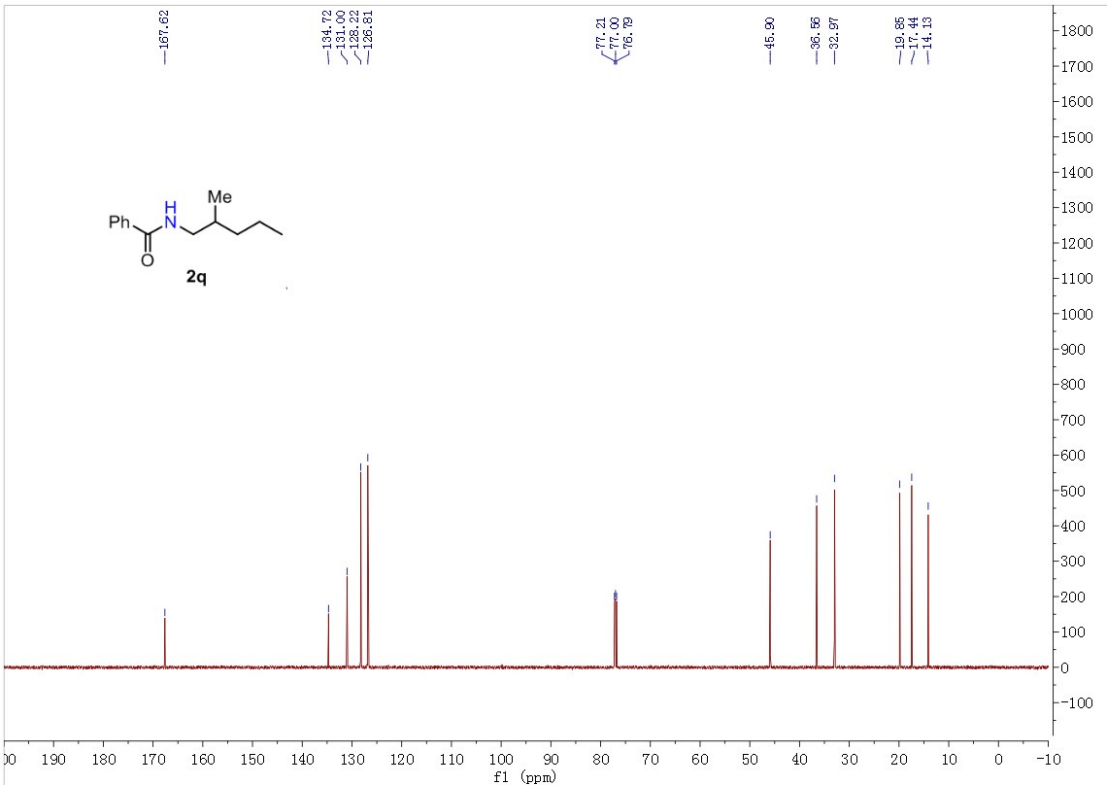
26.18
22.82
22.57
21.41
14.02
Ph
H
N
O
2p
f1 (ppm)


Me
Ph
H
N
O
2q
f1 (ppm)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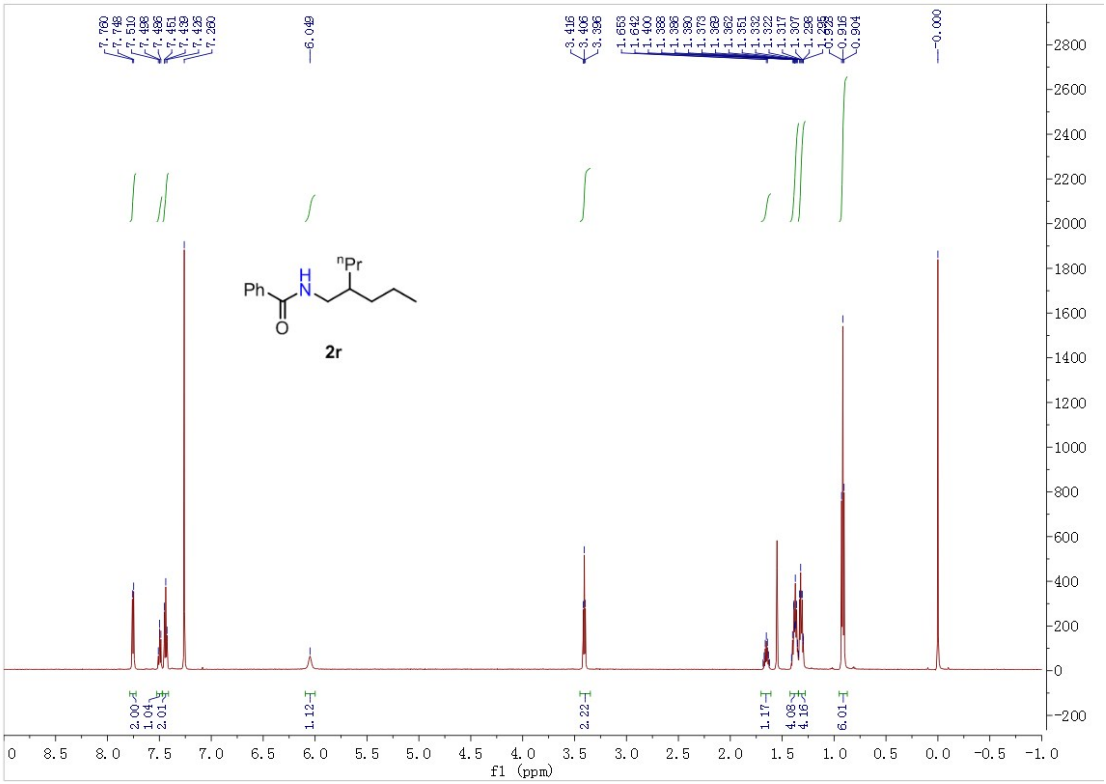
17.44
14.13
Me
Ph
H
N
O
2q
f1 (ppm)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7.426
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6.049
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3.396
1.653
1.642
1.400
1.388
1.386
1.380
1.373
1.369
1.362
1.351
1.332
1.322
1.317
1.307
1.228
0.928
0.916
0.904
0.000
2.00
1.04
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1.12
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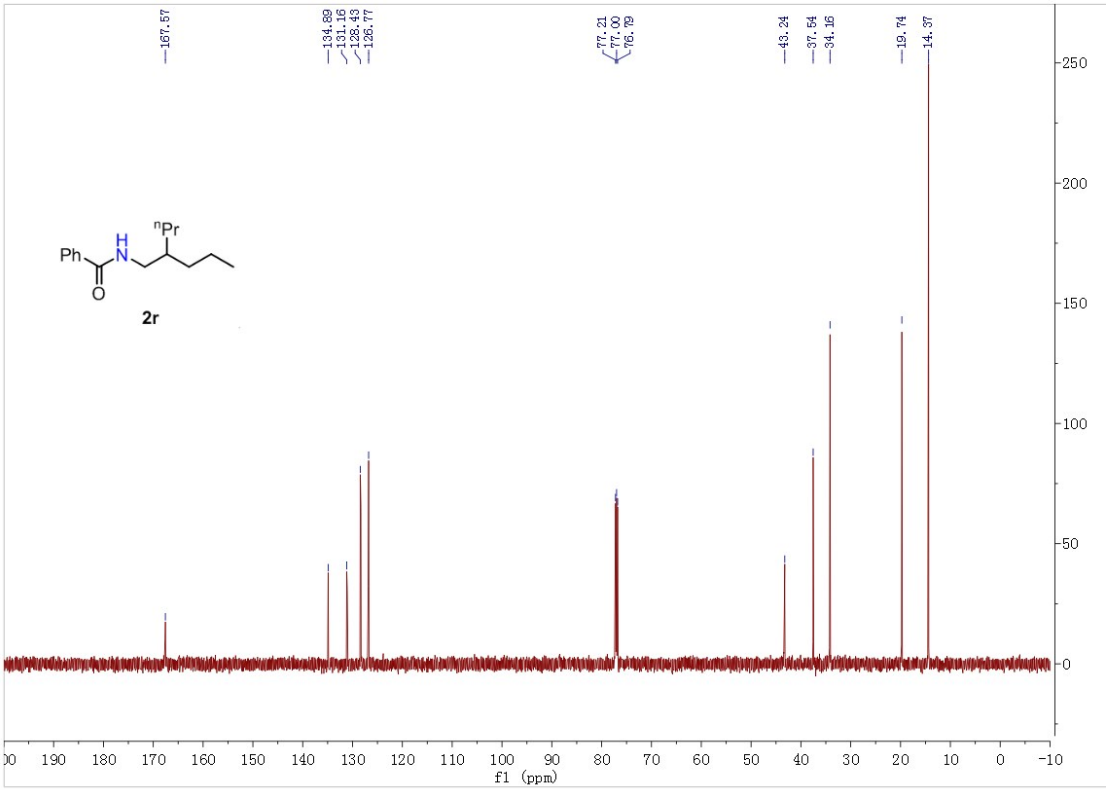
1.17
4.08
4.16
6.01
Ph
N
H
O
nPr
2r
f1 (ppm)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19.74
14.37
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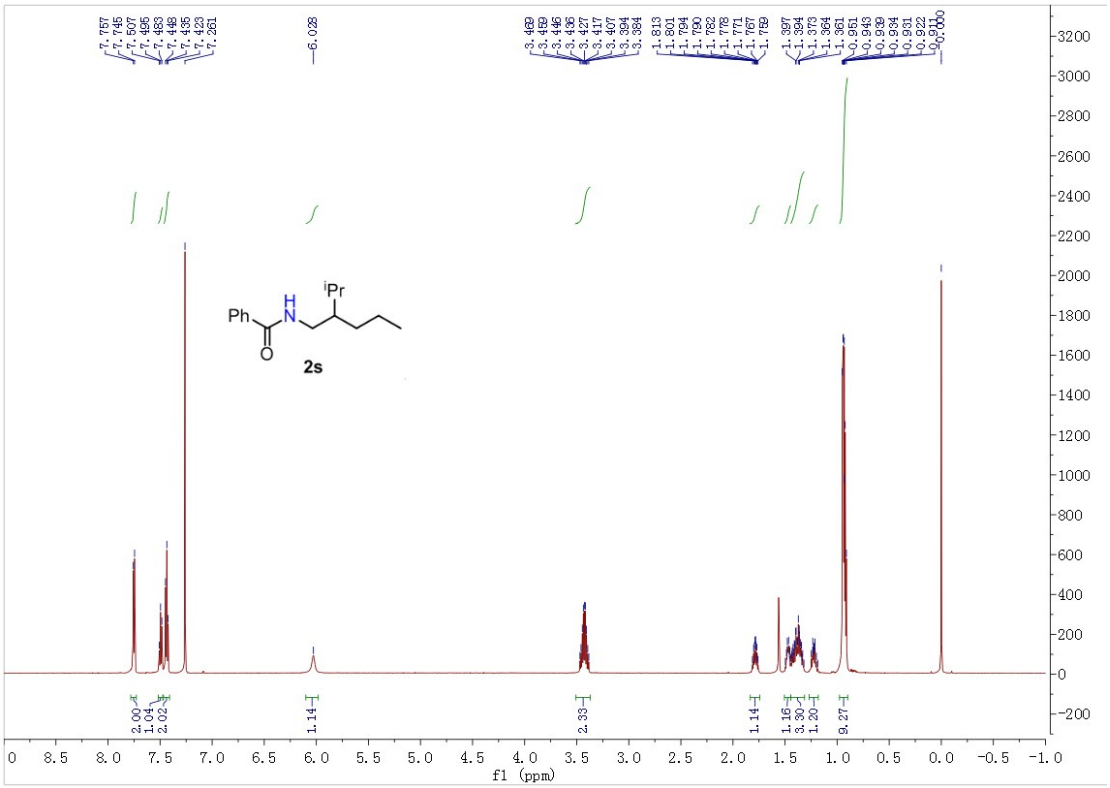
N
H
O
nPr
2r
f1 (ppm)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3.446
3.435
3.427
3.417
3.407
3.394
3.384
1.813
1.801
1.794
1.790
1.782
1.778
1.771
1.767
1.759
1.397
1.394
1.373
1.364
1.361
0.951
0.945
0.939
0.934
0.931
0.922
0.911
0.000
Ph
N
H
iPr
O
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2.02
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2.33
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3.30
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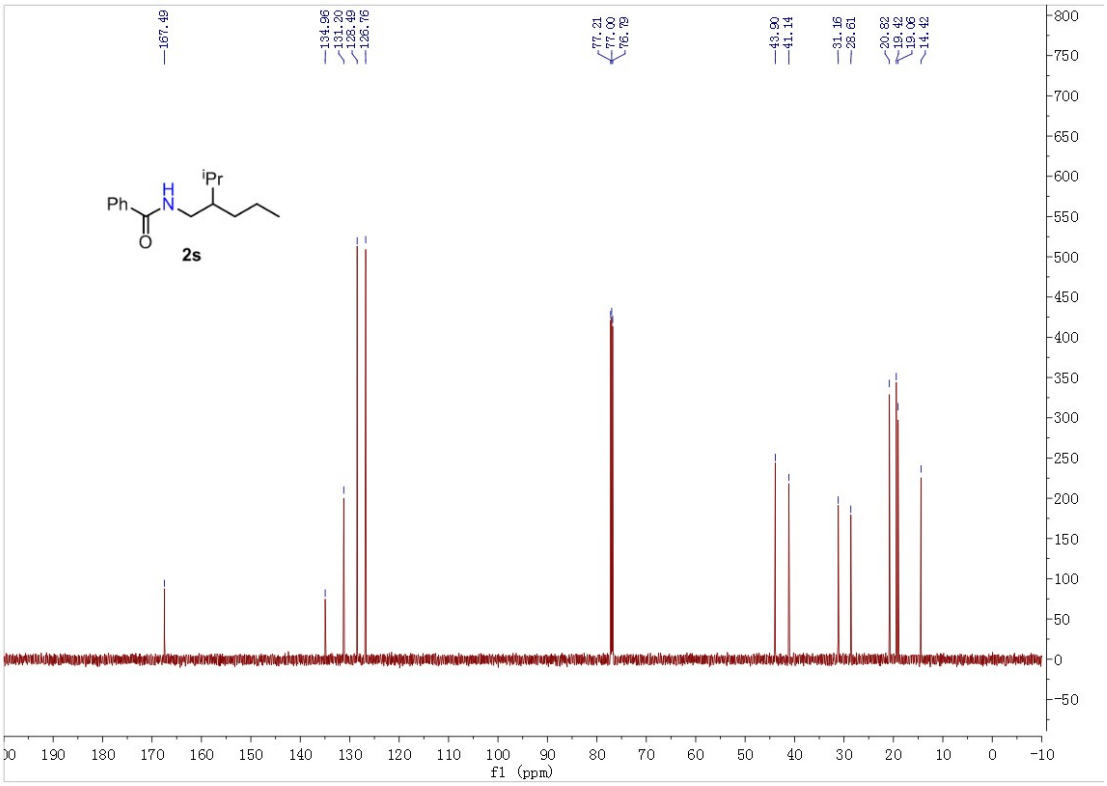
f1 (ppm)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77.00
76.79
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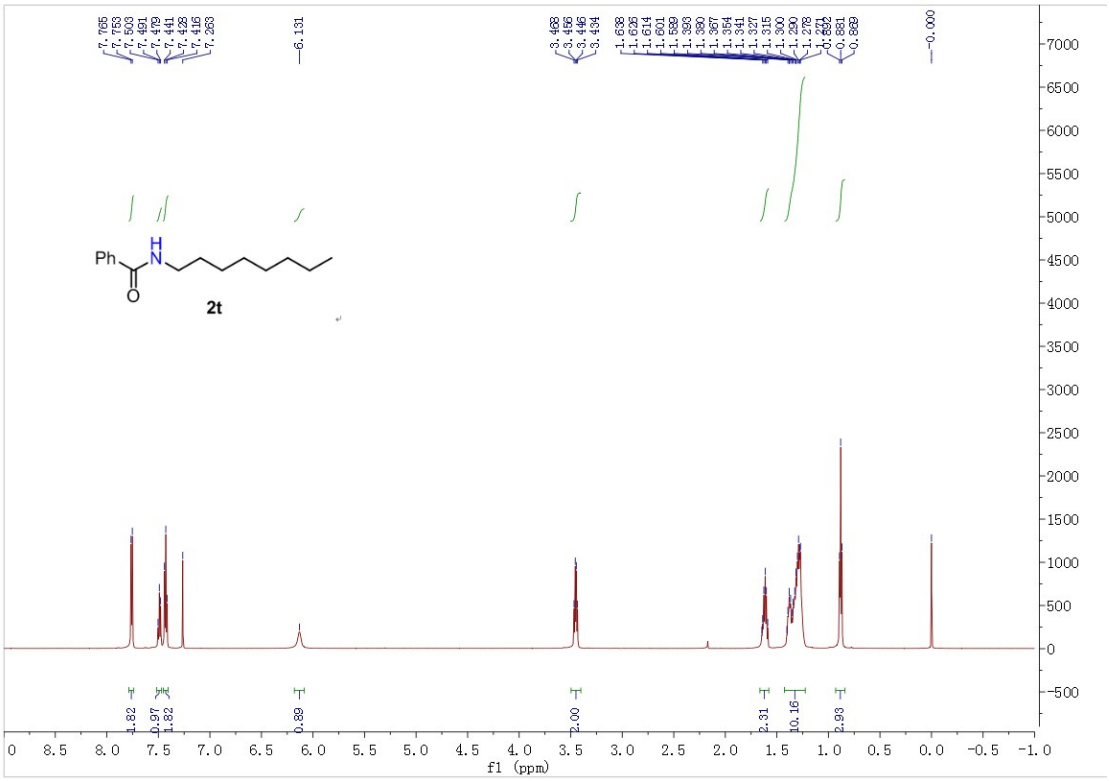
19.42
19.06
14.42
Ph
N
H
iPr
O
2s
f1 (ppm)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7.416
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6.131
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3.456
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3.434
1.638
1.626
1.614
1.601
1.589
1.393
1.380
1.367
1.354
1.341
1.327
1.315
1.300
1.289
1.278
1.271
0.892
0.881
0.869
0.000
Ph
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O
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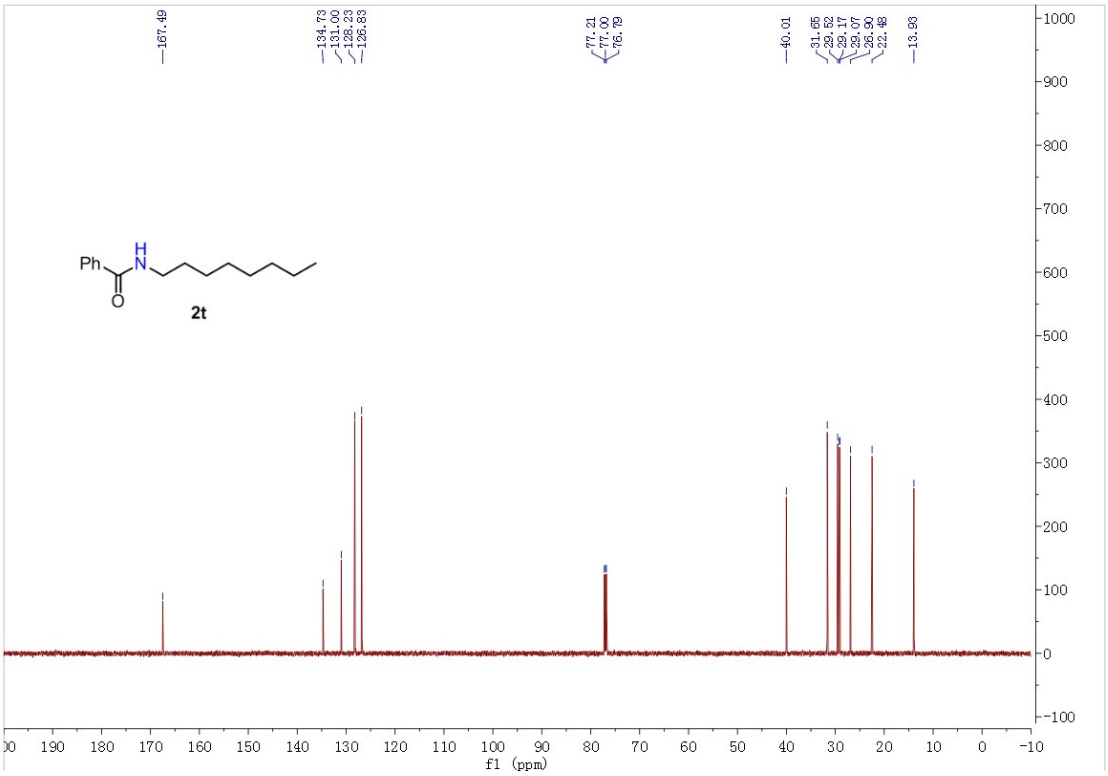
2.31
10.16
2.93
f1 (ppm)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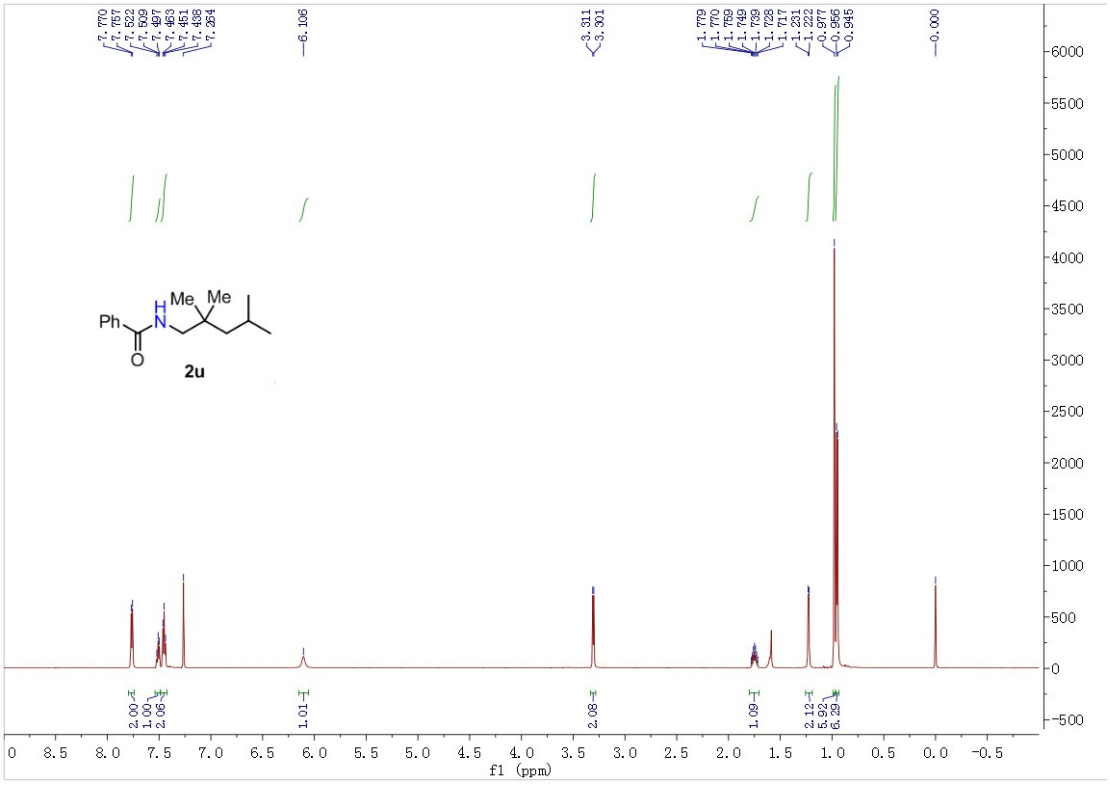
29.07
26.90
22.48
13.93
Ph
H
N
O
2t
f1 (ppm)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7.463
7.451
7.438
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6.106
3.311
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0.000
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H
O
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2.12
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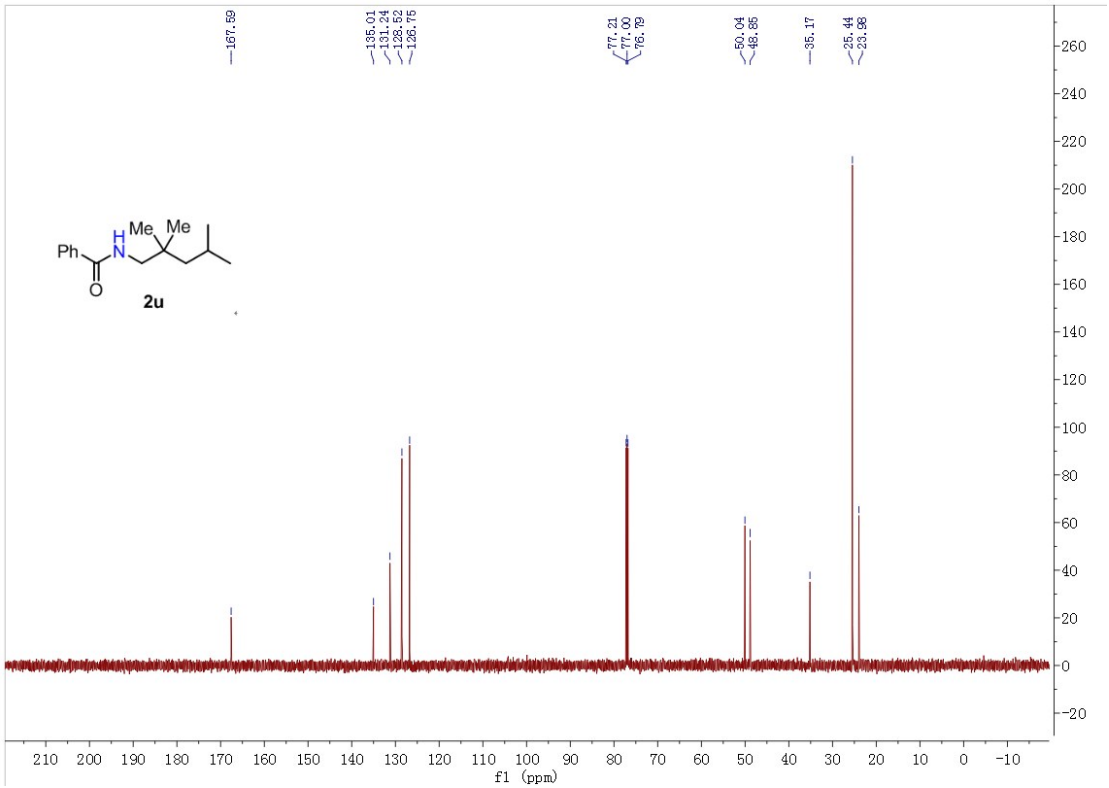
6.29
f1 (ppm)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50.04
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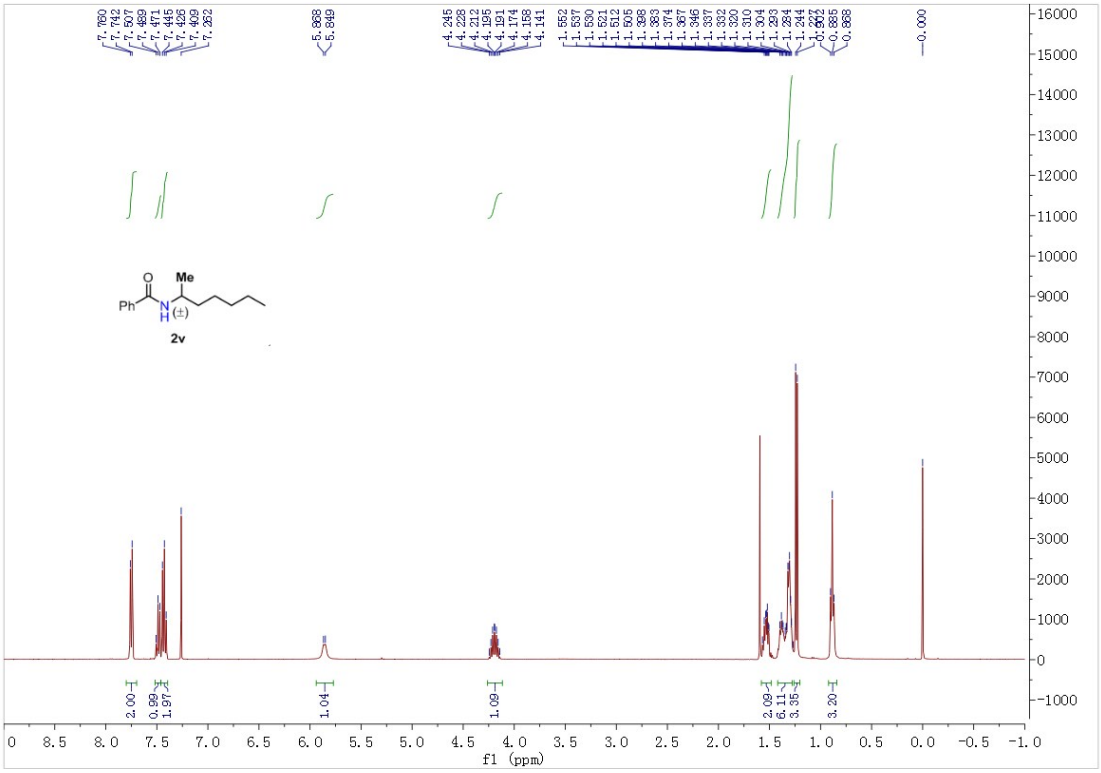
36.17
25.44
23.98
Ph
N
H
O
Me
Me
2u
f1 (ppm)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7.426
7.409
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5.849
4.245
4.228
4.212
4.195
4.174
4.171
4.158
4.141
1.562
1.537
1.530
1.521
1.512
1.506
1.398
1.383
1.374
1.367
1.346
1.337
1.332
1.320
1.310
1.304
1.293
1.284
1.244
0.907
0.885
0.868
0.000
Me
Ph
N
H
(±)
2v
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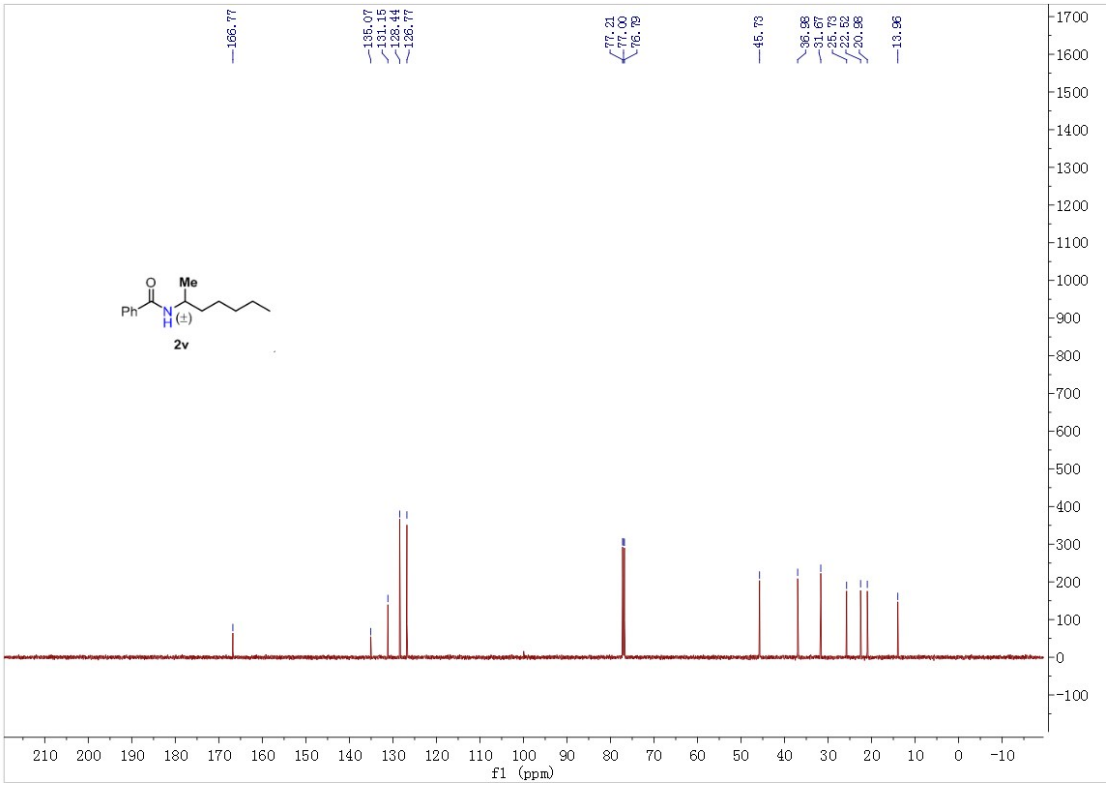
0.99
1.97
1.04
1.09
2.09
6.11
3.35
3.20
f1 (ppm)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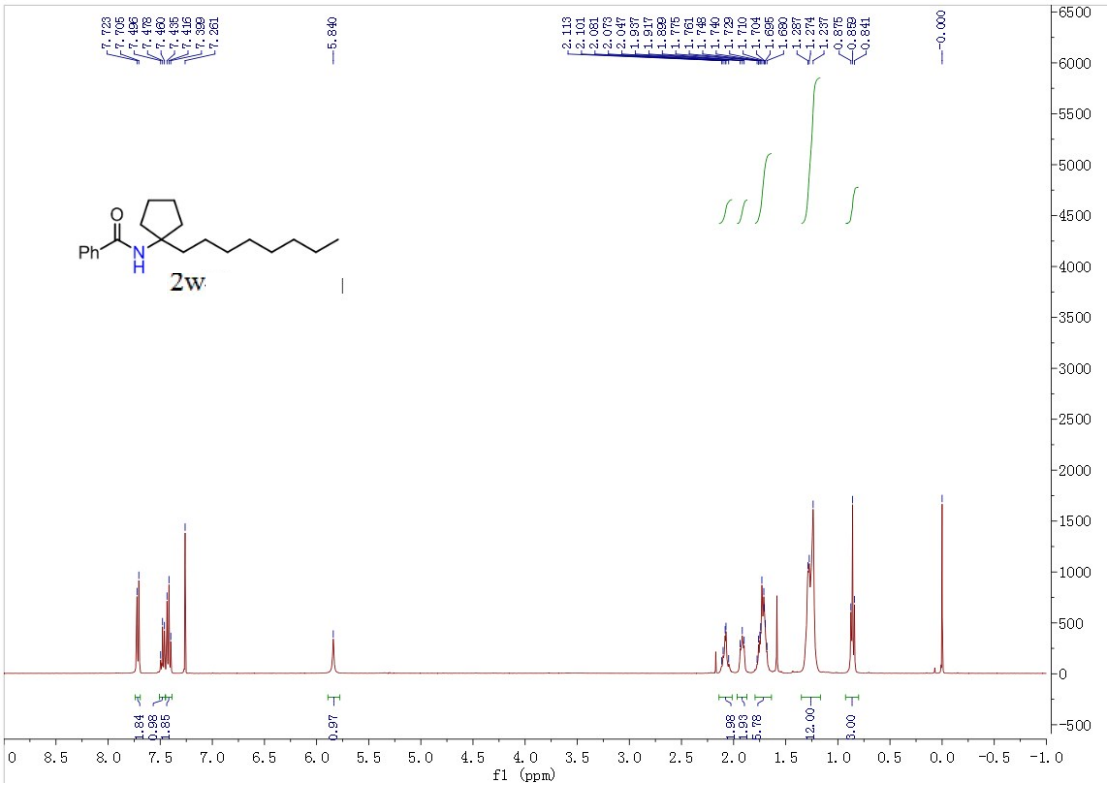
131.15
128.44
126.77
77.21
77.00
76.79
46.73
36.98
31.67
25.73
22.52
20.98
13.96
Me
Ph
N
H
(±)
2v
f1 (ppm)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7.435
7.416
7.389
7.261
5.840
2.113
2.101
2.081
2.073
2.047
1.937
1.917
1.889
1.775
1.761
1.748
1.740
1.729
1.710
1.704
1.695
1.680
1.287
1.274
1.237
0.875
0.839
0.841
0.000
Ph
N
H
O
2w
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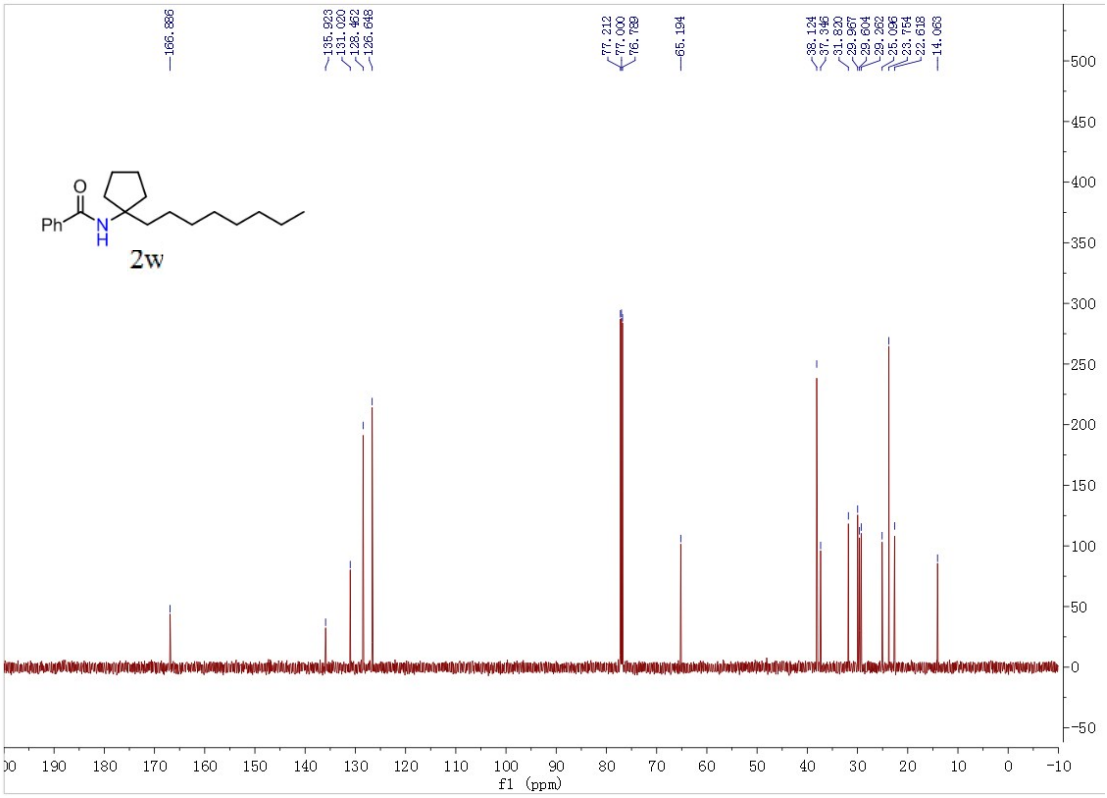
0.98
1.85
0.97
1.98
1.93
5.78
12.00
3.00
f1 (ppm)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77.000
76.789
65.194
38.124
37.946
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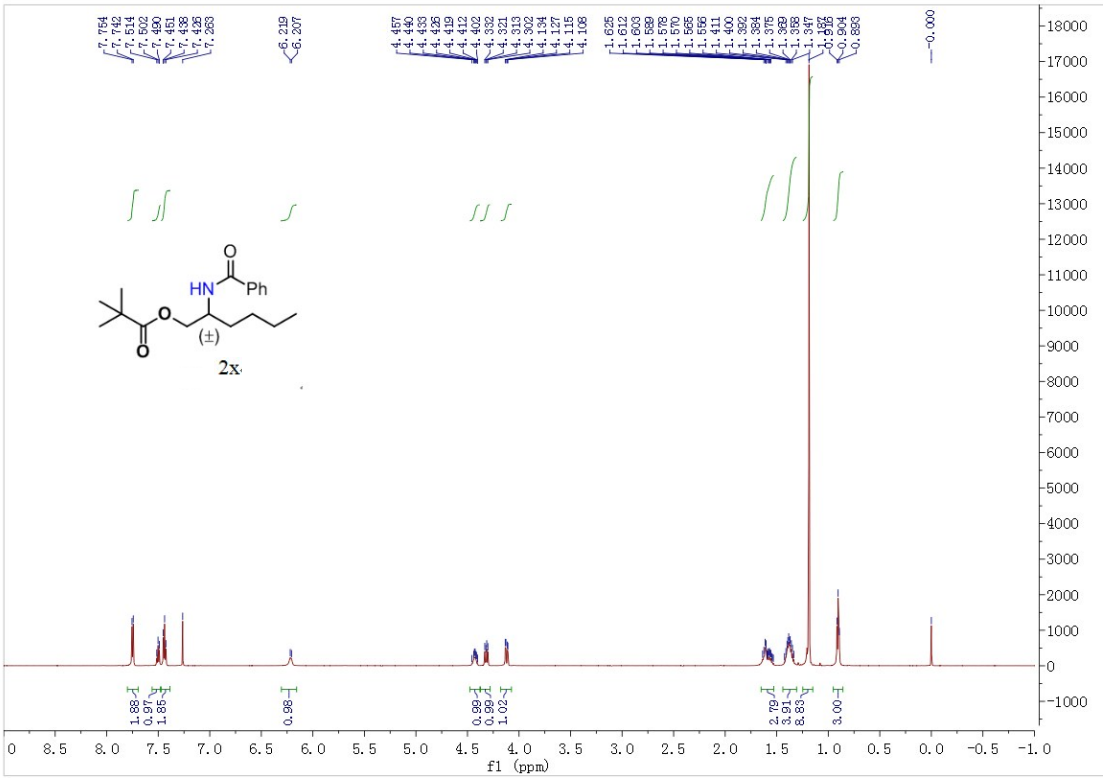
29.262
25.096
23.754
22.618
14.063
Ph
N
H
O
2w
f1 (ppm)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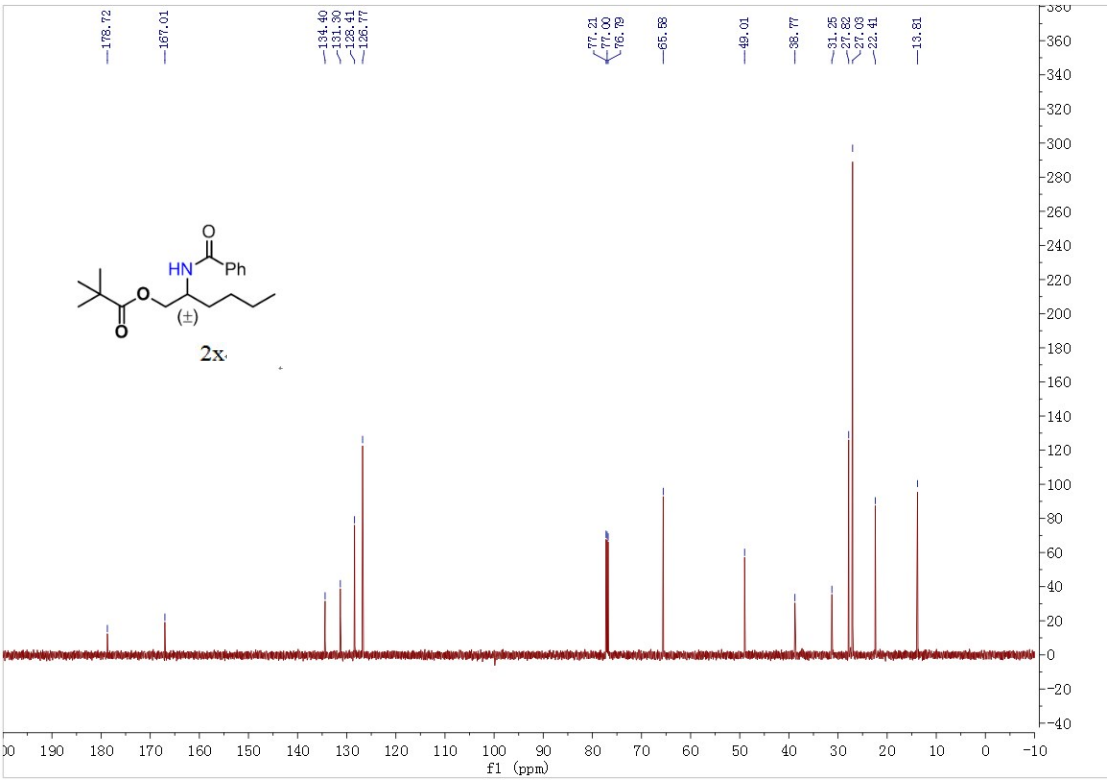
Ph
O
O
(±)
2x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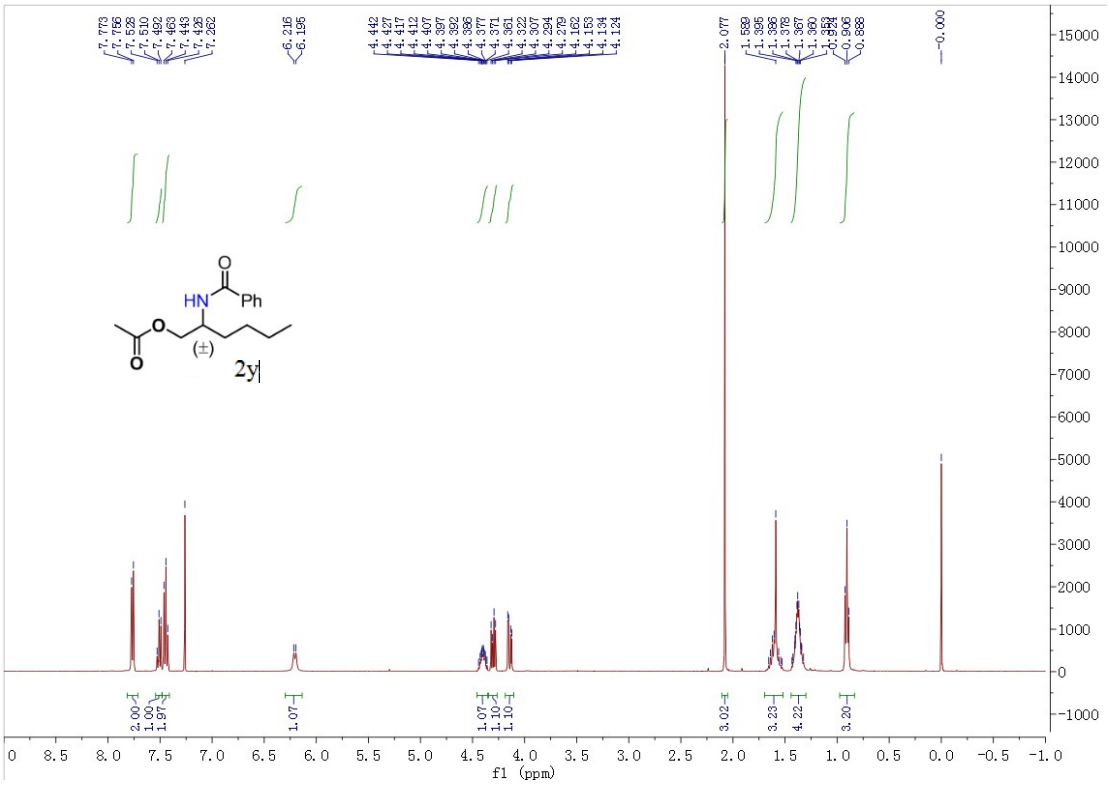
Ph
O
O
(±)
2x
f1 (ppm)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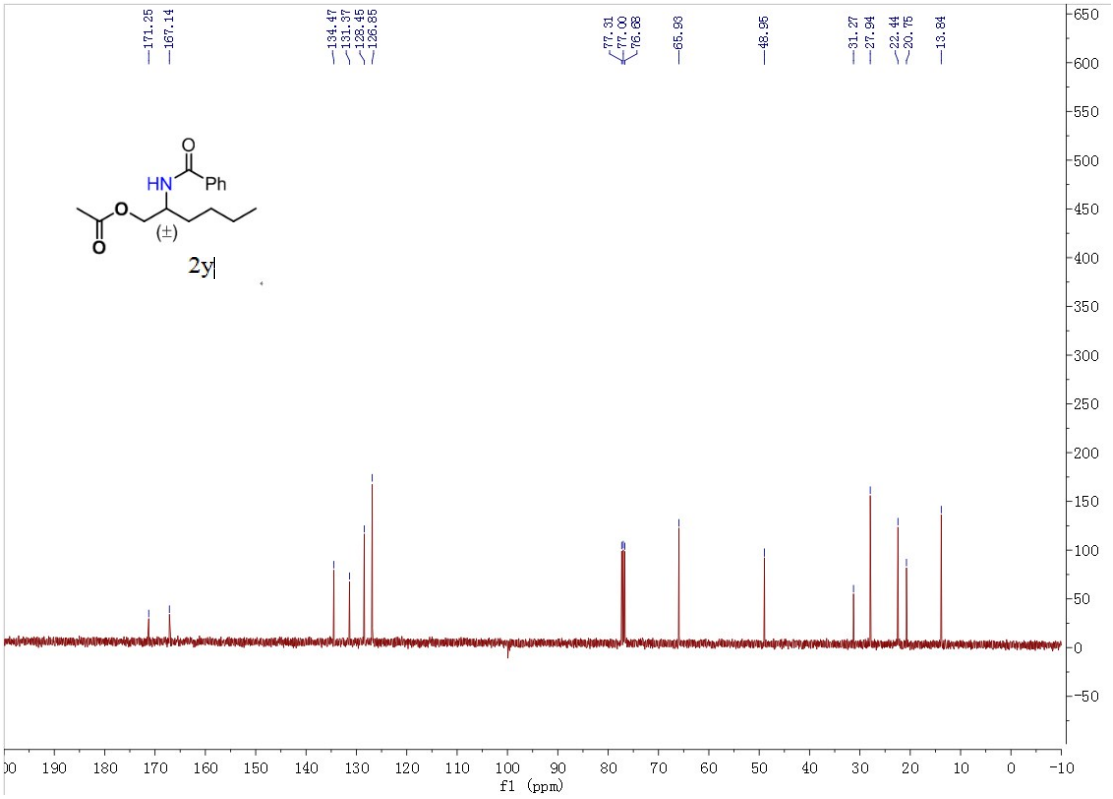
7.492
7.463
7.443
7.426
7.262
6.216
6.195
4.442
4.427
4.417
4.412
4.407
4.397
4.392
4.386
4.377
4.371
4.361
4.322
4.307
4.294
4.279
4.162
4.153
4.134
4.124
2.077
1.589
1.395
1.386
1.378
1.367
1.360
0.906
0.888
0.000
HN
Ph
O
(±)
2y
2.00
1.00
1.97
1.07
1.07
1.10
1.10
3.02
3.23
4.22
3.20
f1 (ppm)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167.14
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131.37
128.45
126.85
77.31
77.00
76.68
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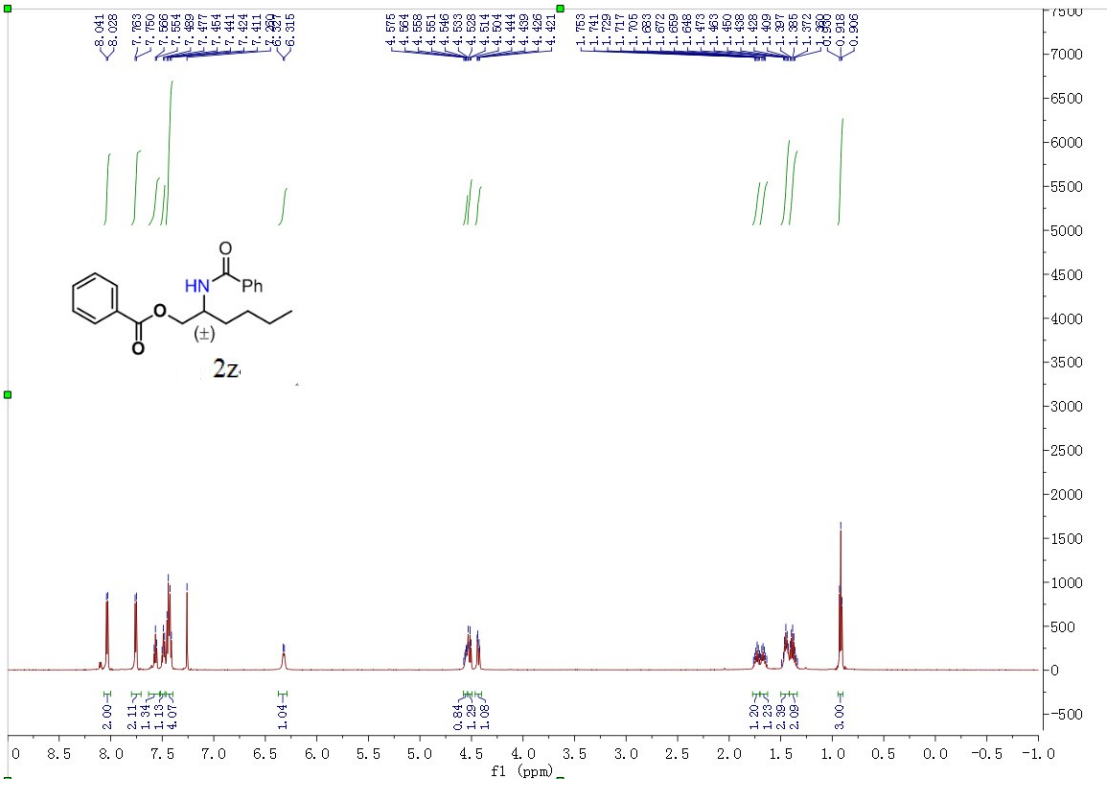
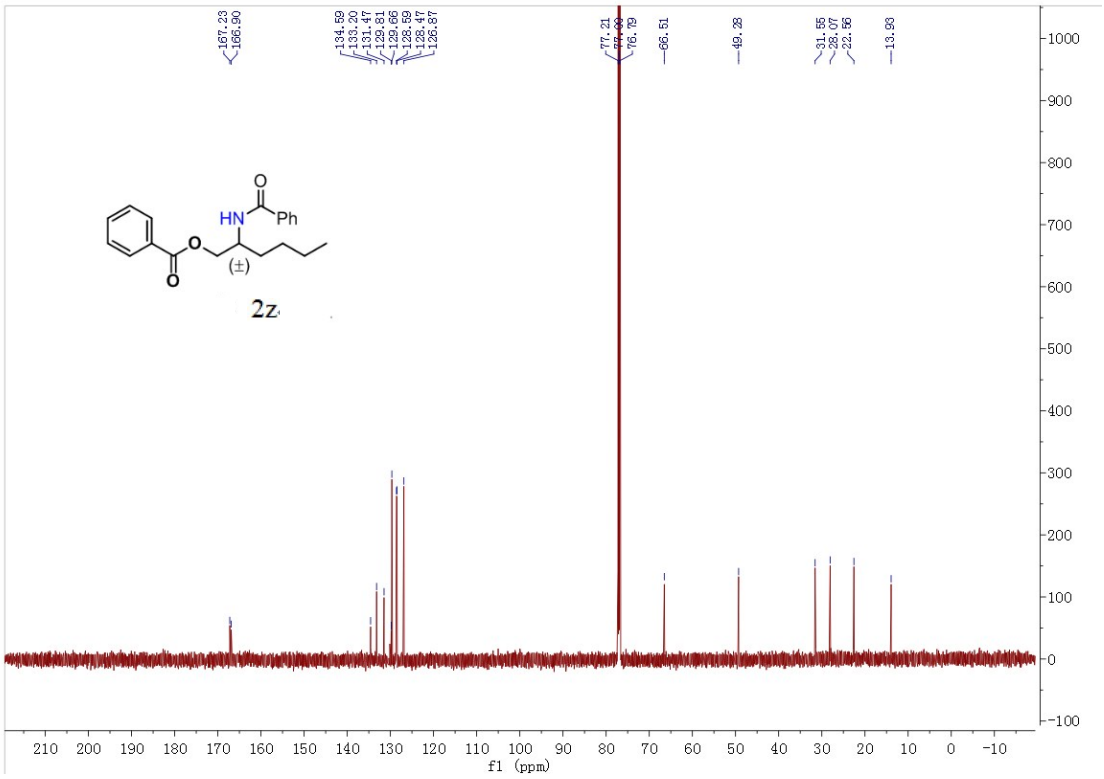
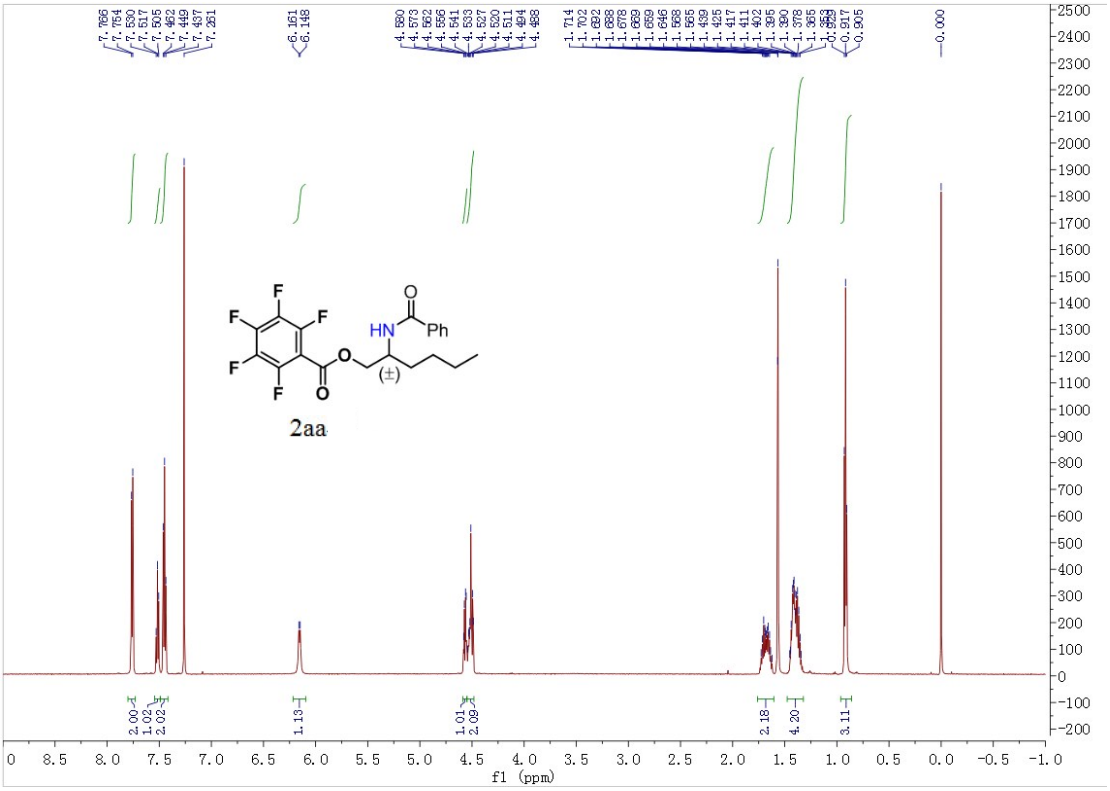
48.96
31.27
27.94
22.44
20.75
13.84
HN
Ph
O
(±)
2y
f1 (ppm)


HN
Ph
O
O
(±)
2z
f1 (ppm)


HN
Ph
O
O
(±)
2z
f1 (ppm)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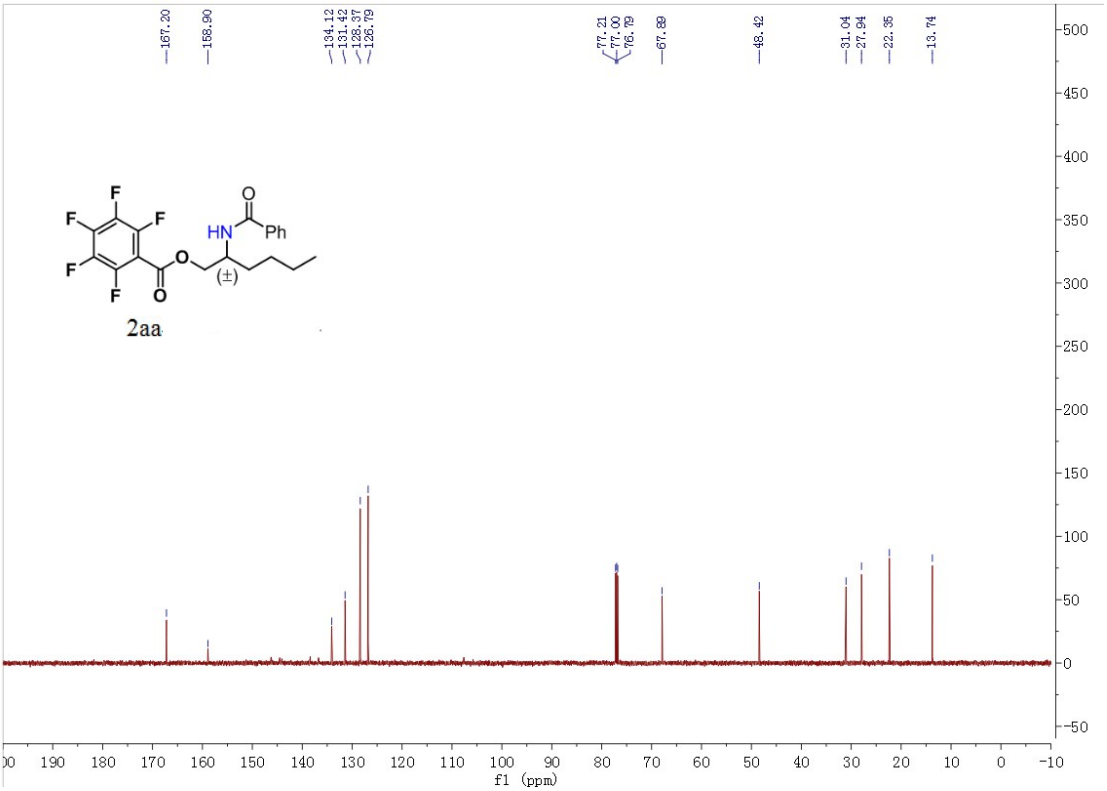
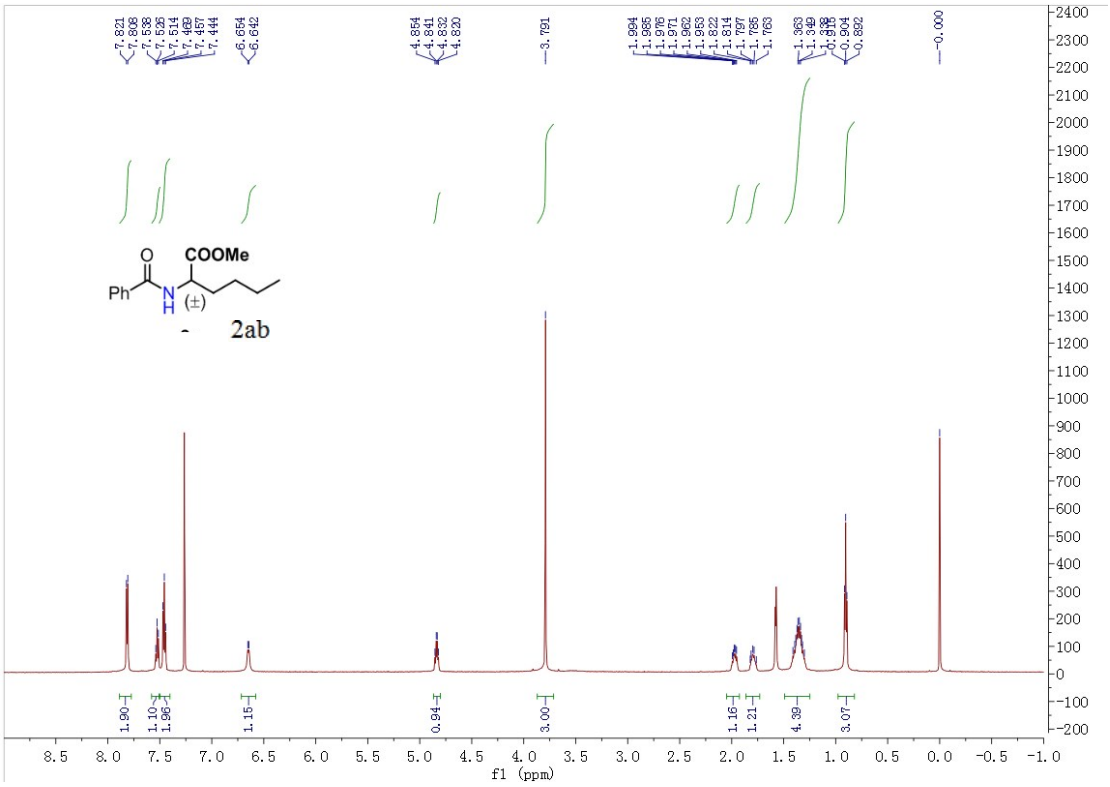
f1 (ppm)


2aa
f1 (ppm)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7.457
7.444
6.654
6.642
4.854
4.841
4.832
4.820
3.791
1.994
1.985
1.976
1.971
1.962
1.953
1.822
1.814
1.797
1.788
1.763
1.363
1.349
0.918
0.904
0.892
0.000
COOMe
Ph
N
H
(±)
2ab
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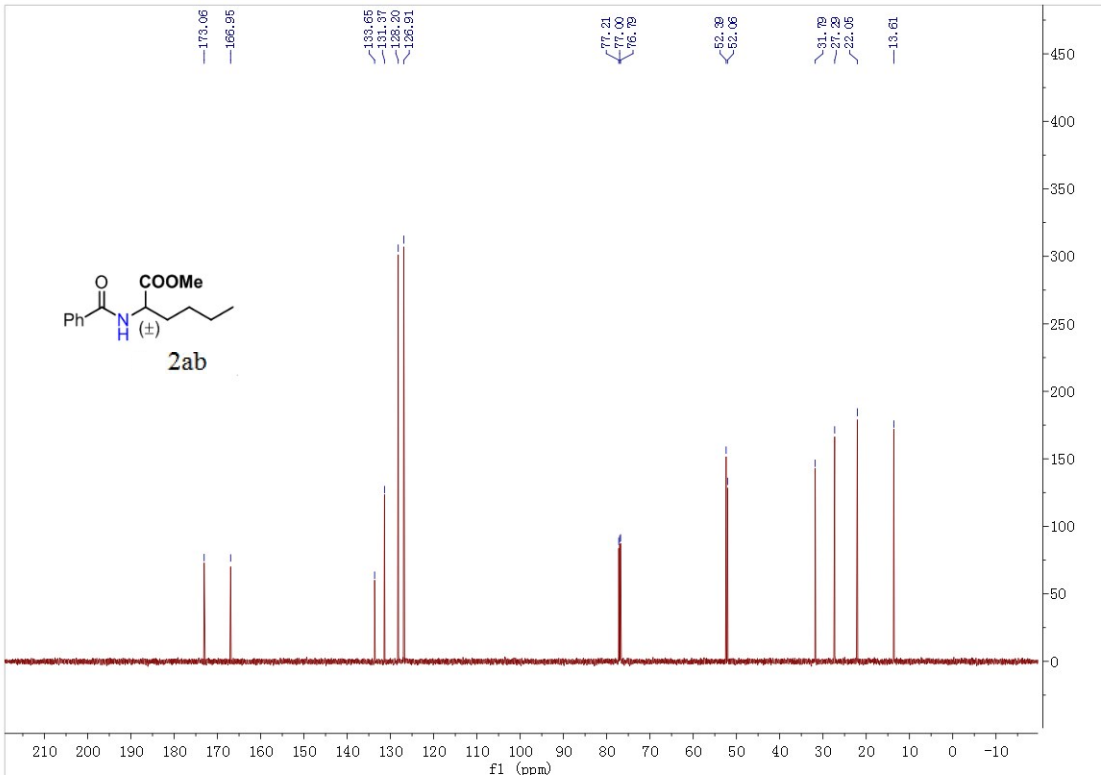
1.98
1.15
0.94
3.00
1.16
1.21
4.39
3.07
f1 (ppm)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77.00
76.79
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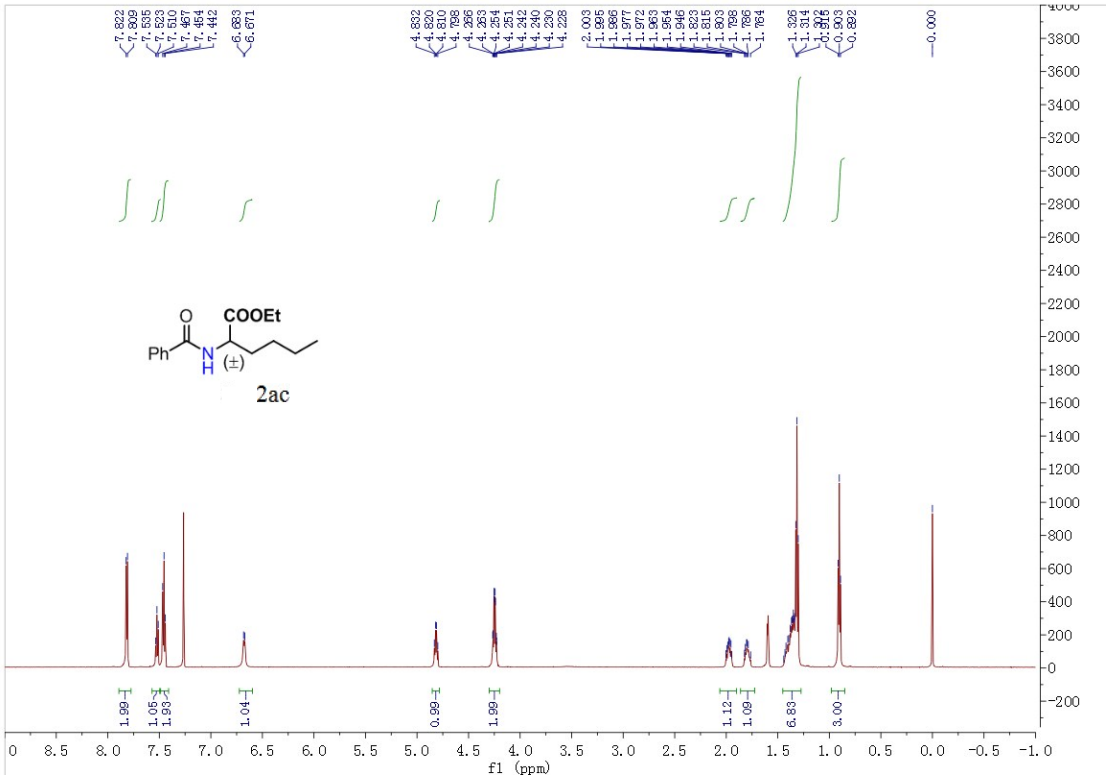
27.29
22.05
13.61
COOMe
Ph
N
H
(±)
2ab
f1 (ppm)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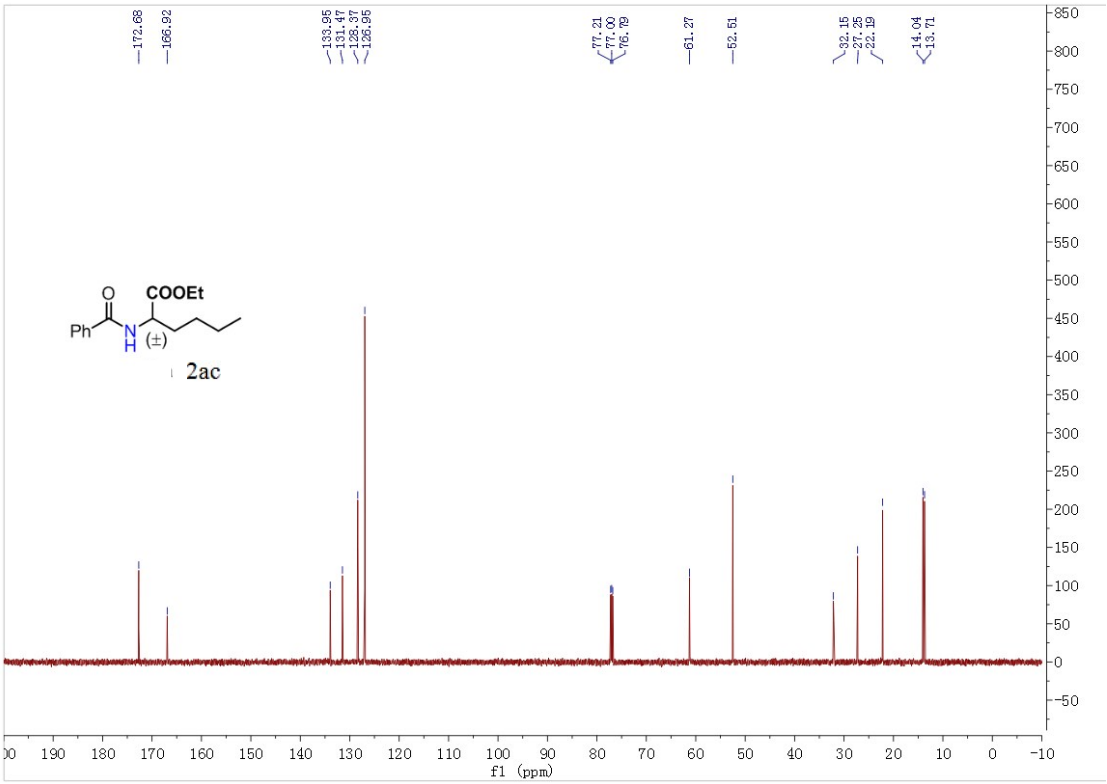
7.467
7.454
7.442
6.683
6.671
4.832
4.820
4.810
4.798
4.266
4.263
4.254
4.251
4.242
4.240
4.230
4.228
2.003
1.995
1.986
1.977
1.972
1.963
1.964
1.946
1.823
1.815
1.803
1.798
1.786
1.764
1.326
1.314
0.918
0.903
0.892
0.000
COOEt
Ph
N
H
(±)
2ac
1.99
1.05
1.93
1.04
0.99
1.99
1.12
1.09
6.83
3.00
f1 (ppm)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77.00
76.79
61.27
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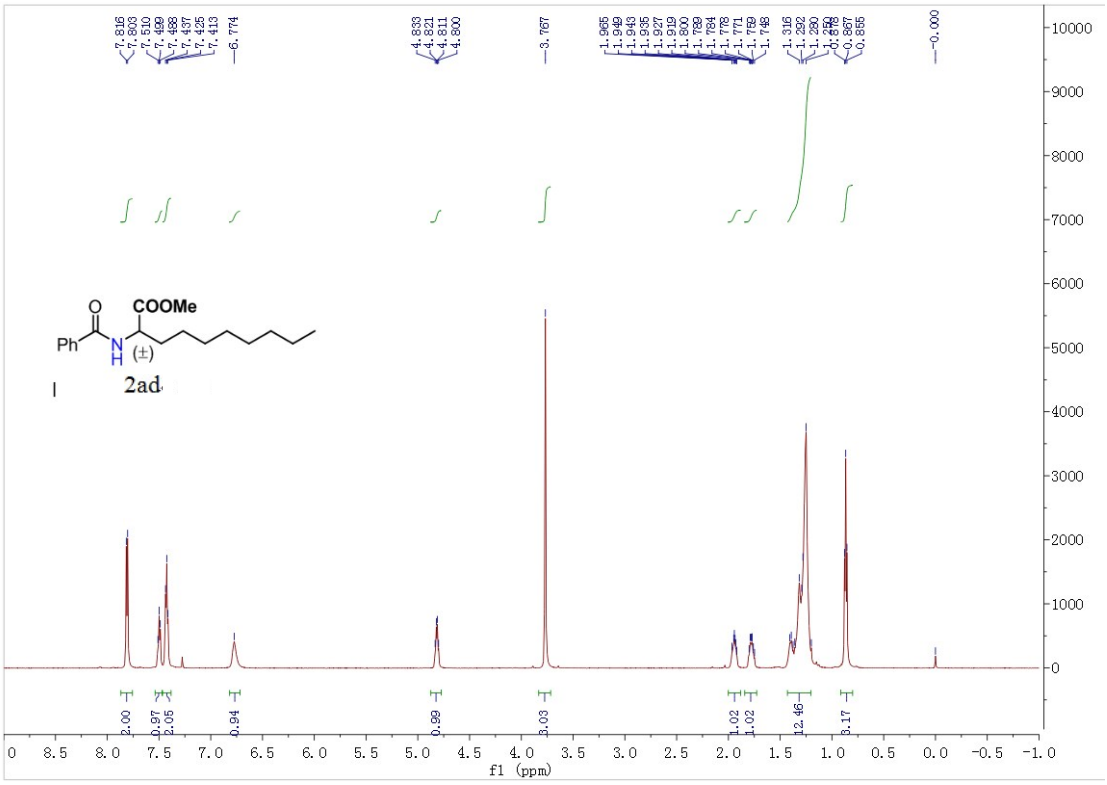
27.25
22.19
14.04
13.71
COOEt
Ph
N
H
(±)
2ac
f1 (ppm)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7.413
6.774
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4.821
4.811
4.800
3.767
1.965
1.949
1.943
1.935
1.927
1.919
1.800
1.789
1.784
1.778
1.771
1.759
1.748
1.316
1.292
1.280
0.867
0.855
0.000
COOMe
Ph
N
H
(±)
2ad
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2.05
0.94
0.99
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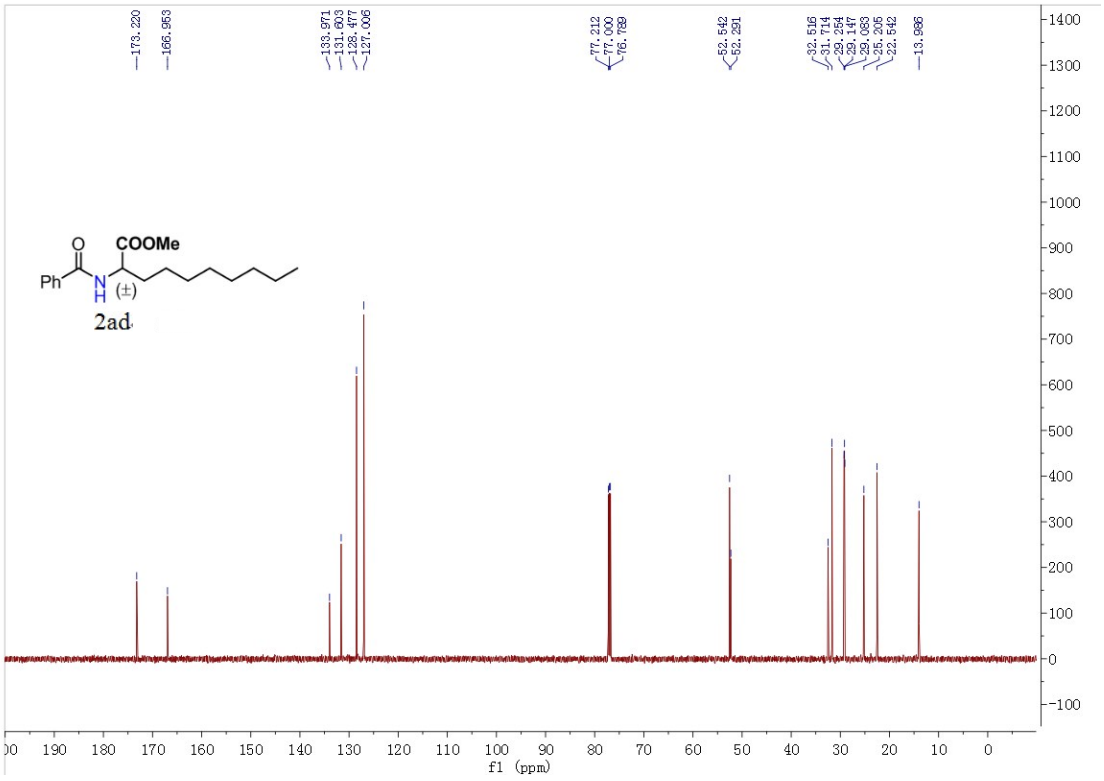
1.02
1.02
12.46
3.17
f1 (ppm)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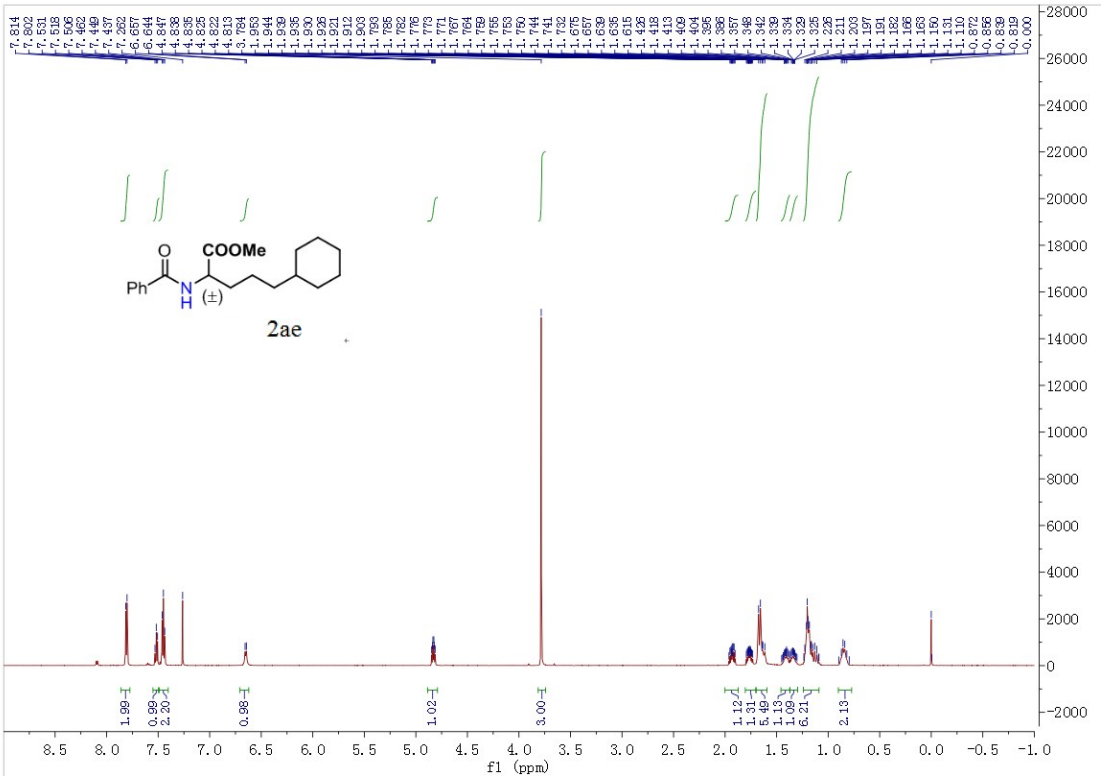
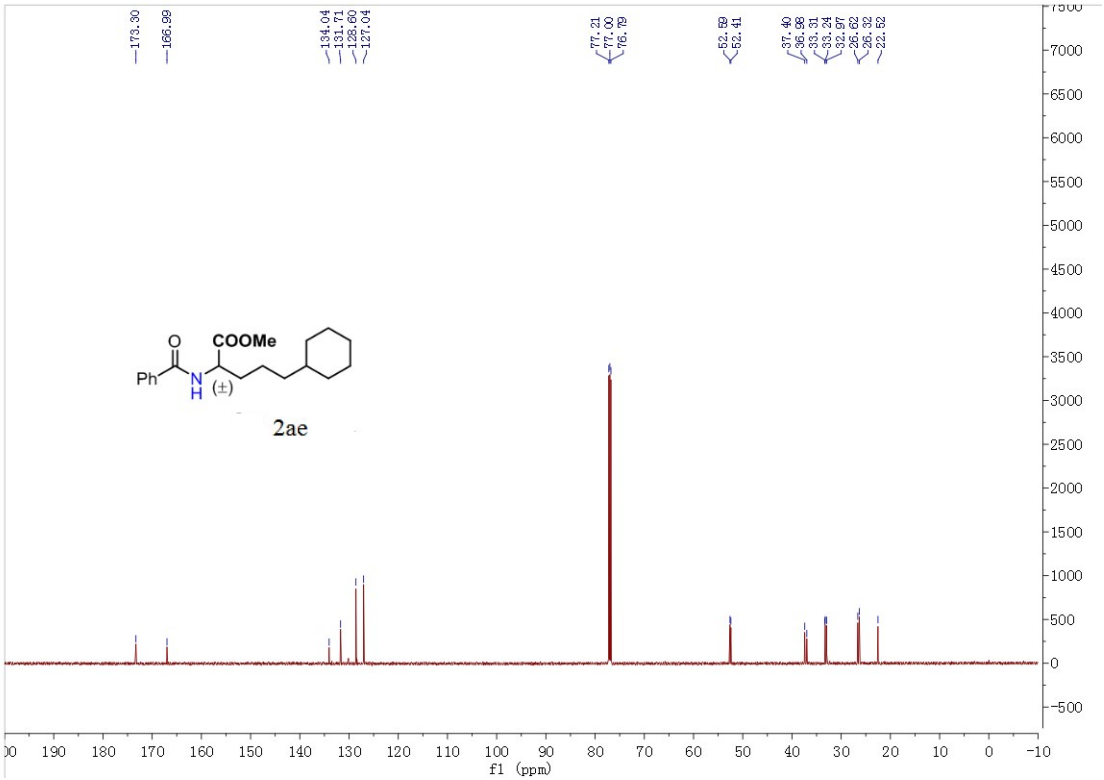
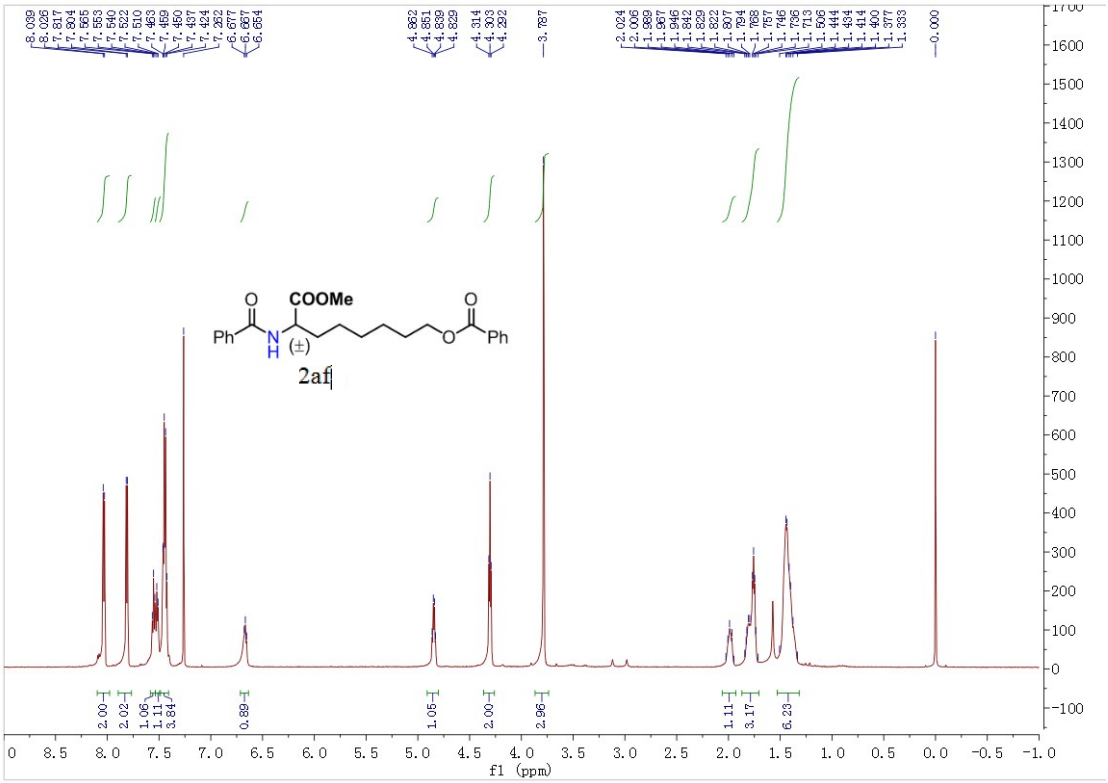
127.006
77.212
77.000
76.789
62.542
62.291
32.516
31.714
29.254
29.147
29.083
25.205
22.542
13.986
COOMe
Ph
N
H
(±)
2ad
f1 (ppm)


COOMe
Ph
N
H
(±)
2ae
f1 (ppm)


COOMe
Ph
N
H
(±)
2ae
f1 (ppm)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7.522
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7.463
7.459
7.450
7.437
7.424
7.262
6.677
6.654
4.862
4.851
4.839
4.829
4.314
4.303
4.292
3.787
2.024
2.006
1.989
1.967
1.946
1.842
1.829
1.822
1.807
1.794
1.768
1.757
1.746
1.736
1.713
1.696
1.444
1.434
1.414
1.400
1.377
1.333
0.000
COOMe
Ph
N
H
(±)
O
Ph
2af
2.00
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1.05
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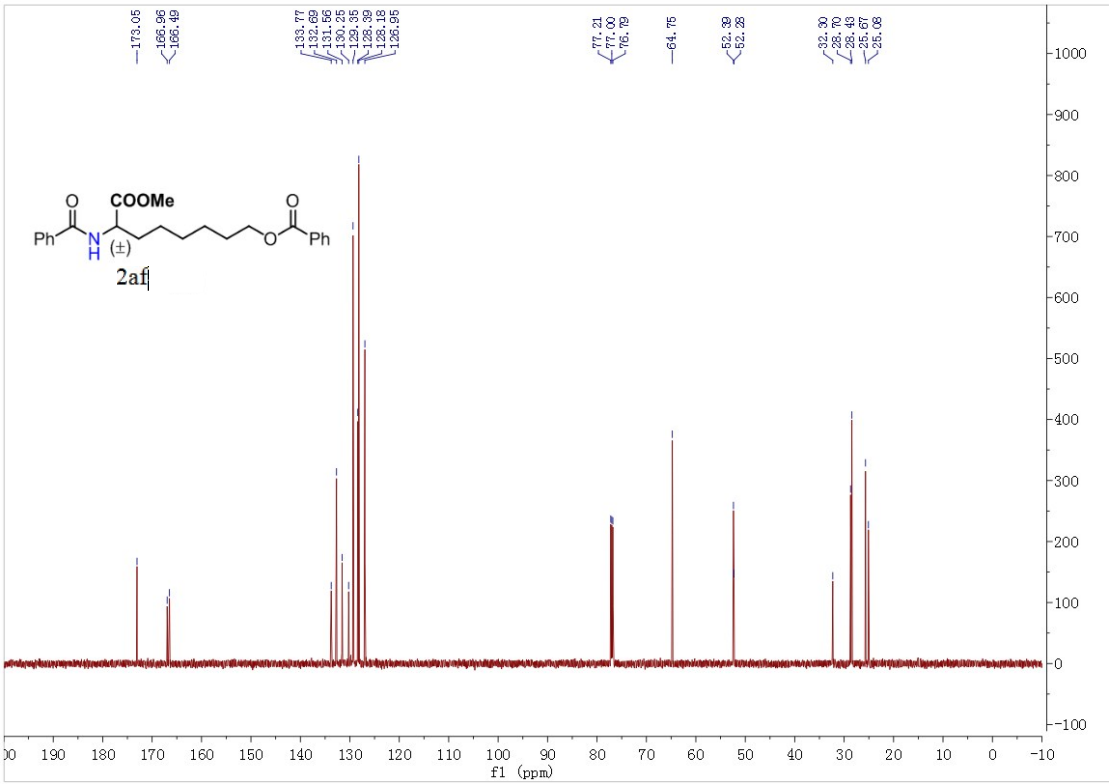
1.11
3.17
6.23
f1 (ppm)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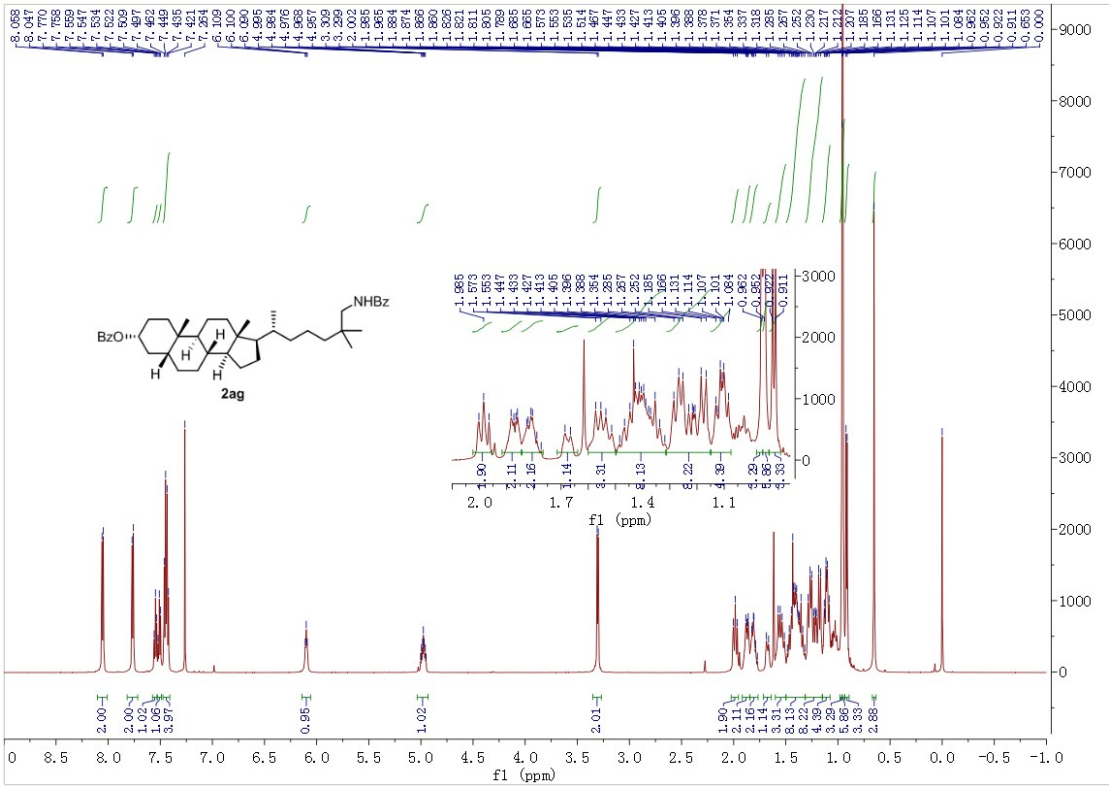
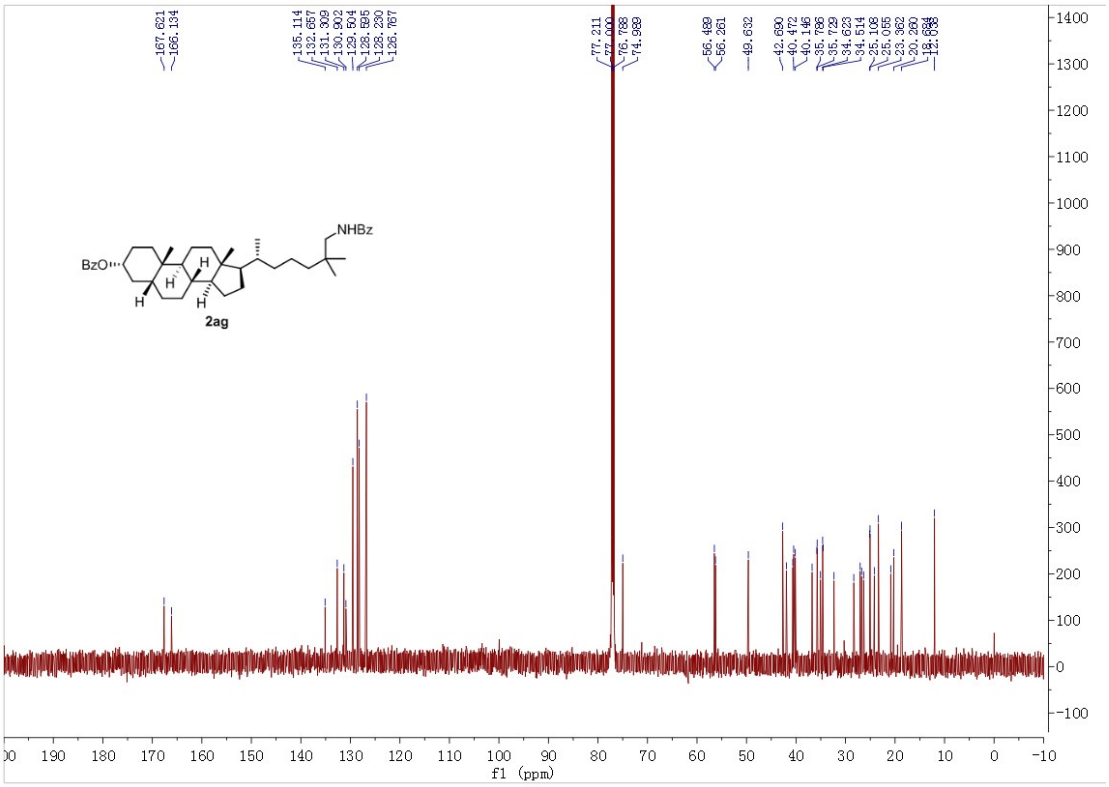
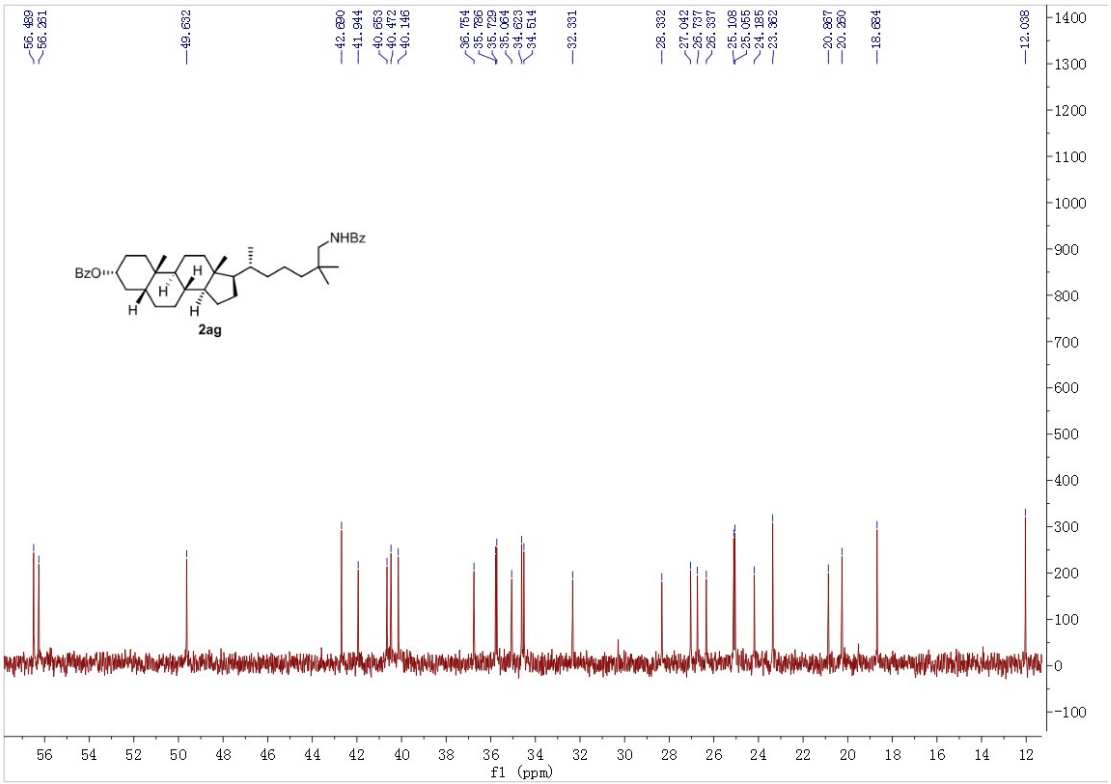
129.35
128.39
128.18
126.95
77.21
77.00
76.79
64.75
52.39
52.28
32.30
28.70
28.43
25.67
25.08
COOMe
Ph
N
H
(±)
O
Ph
2af
f1 (ppm)


NHBz
BzO
H
H
H
2ag
f1 (ppm)


NHBz
BzO
H
H
H
2ag
f1 (ppm)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56.261
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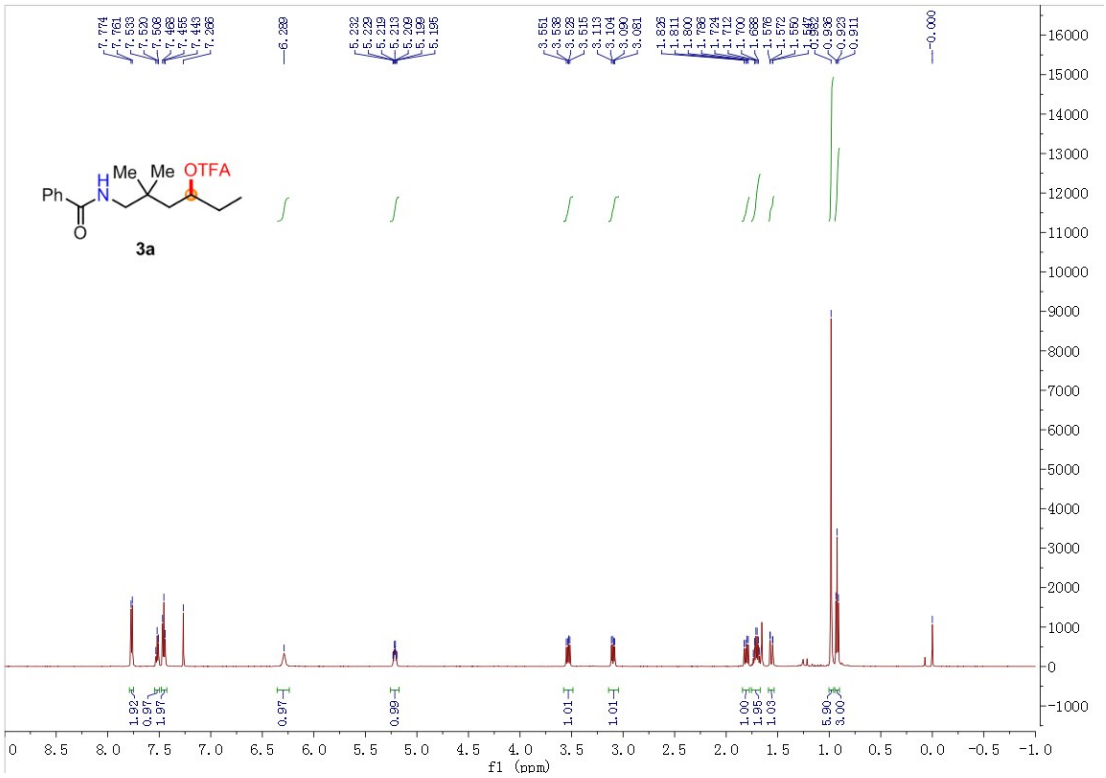
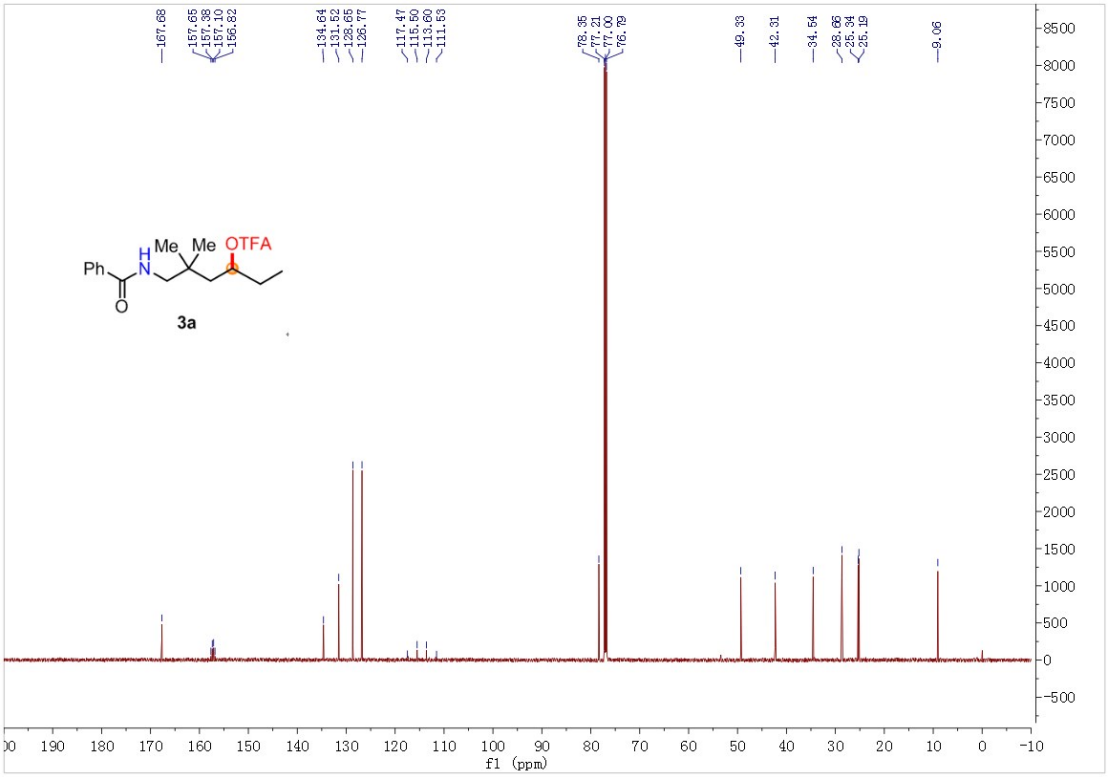
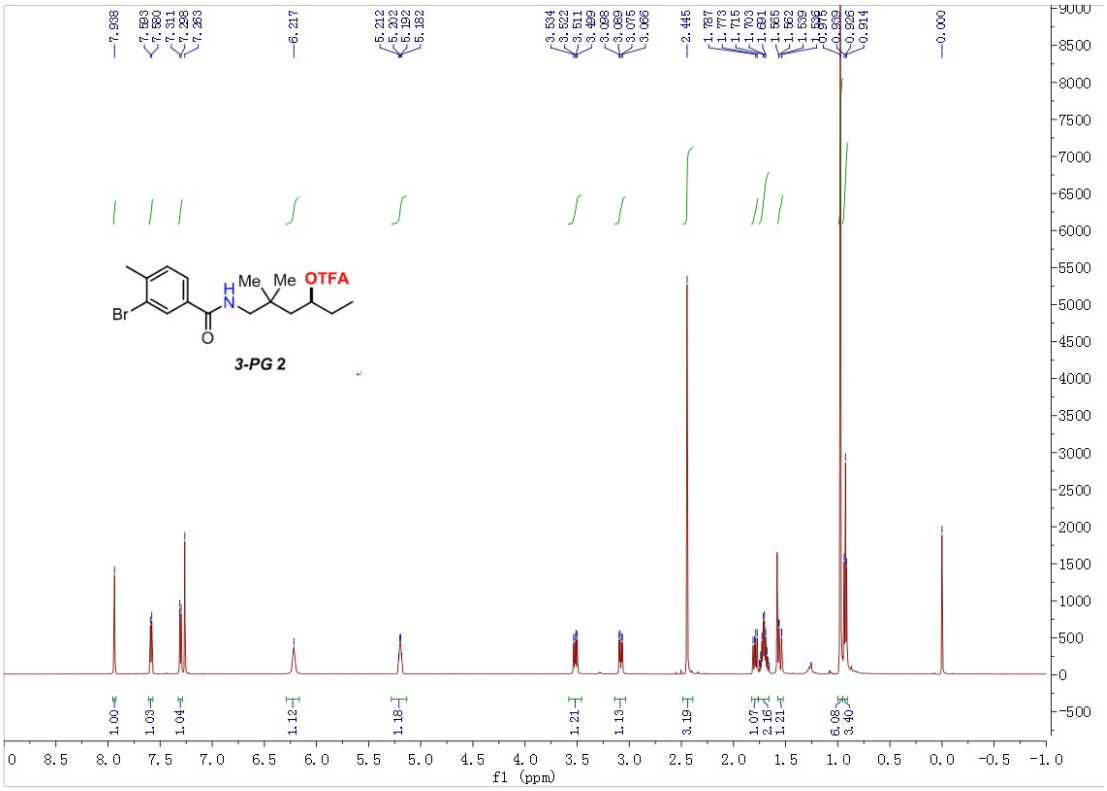
42.890
41.944
40.653
40.472
40.146
36.754
35.786
35.729
35.064
34.623
34.514
32.331
28.332
27.042
26.737
26.337
25.108
25.055
24.185
23.362
20.867
20.260
18.684
12.038
NHBz
BzO
H
H
H
2ag
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12
f1 (ppm)

Spectra of product:



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7.298
7.263
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5.212
5.202
5.192
5.182
3.534
3.522
3.511
3.499
3.098
3.089
3.075
3.066
2.445
1.787
1.773
1.715
1.703
1.691
1.665
1.662
1.539
0.975
0.926
0.914
0.000
Me
Me
OTFA
Br
3-PG 2
1.00
1.03
1.04
1.12
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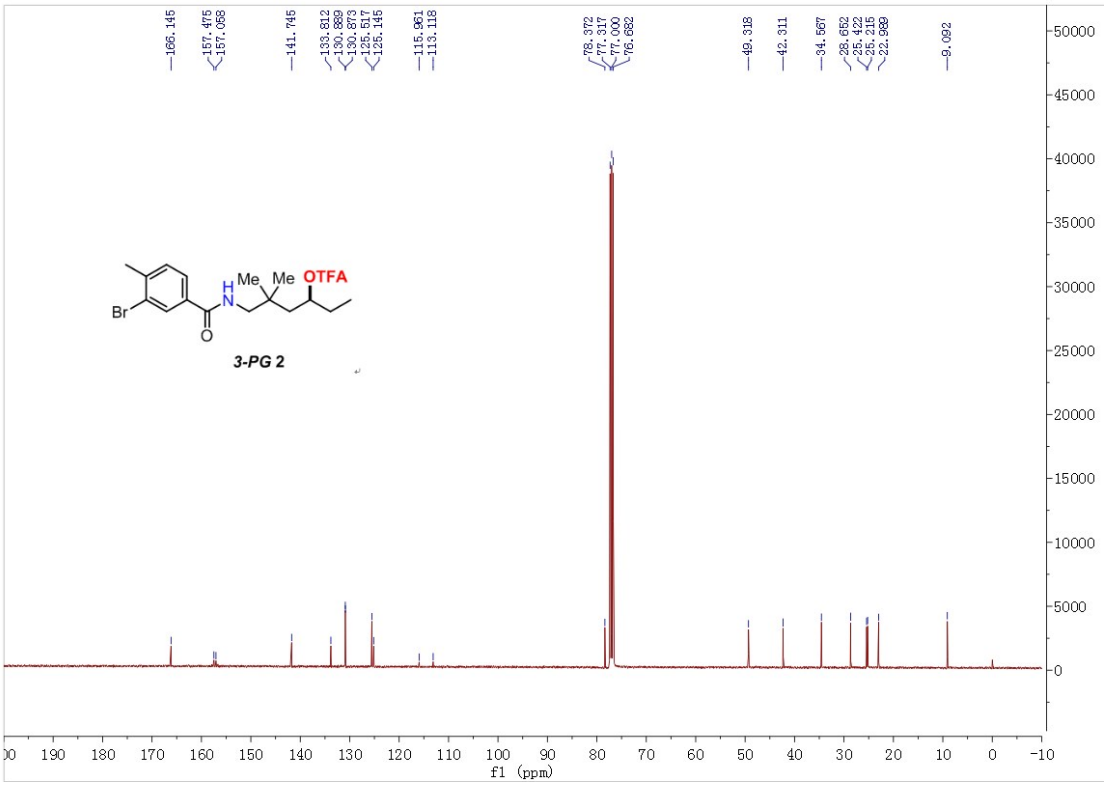
1.21
1.13
3.19
1.07
2.16
1.21
6.08
3.40
f1 (ppm)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125.517
125.145
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77.317
77.000
76.682
49.318
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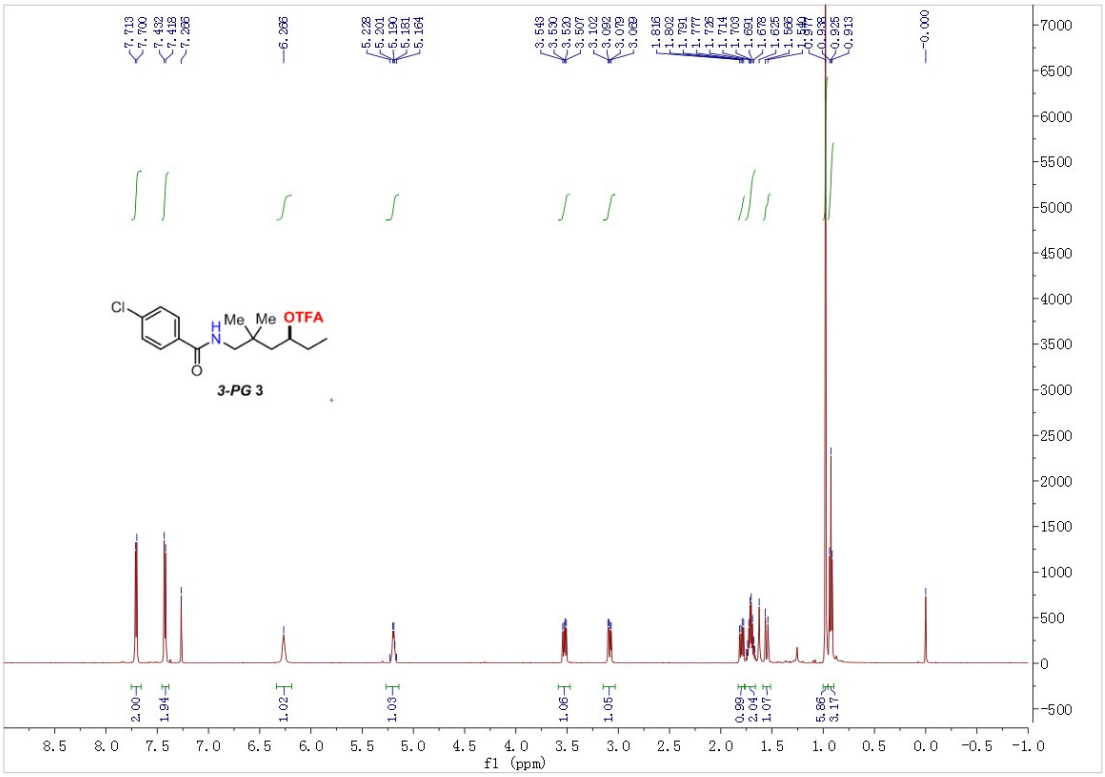
25.422
25.215
22.989
9.092
Me
Me
OTFA
Br
3-PG 2
f1 (ppm)


7.713
7.700
7.432
7.418
7.295
6.295
5.228
5.201
5.190
5.181
5.164
3.543
3.530
3.507
3.102
3.092
3.079
3.069
1.816
1.802
1.791
1.777
1.725
1.714
1.703
1.691
1.678
1.625
1.566
1.544
0.938
0.925
0.913
0.000
Cl
Me
Me
OTFA
H
N
O
3-PG 3
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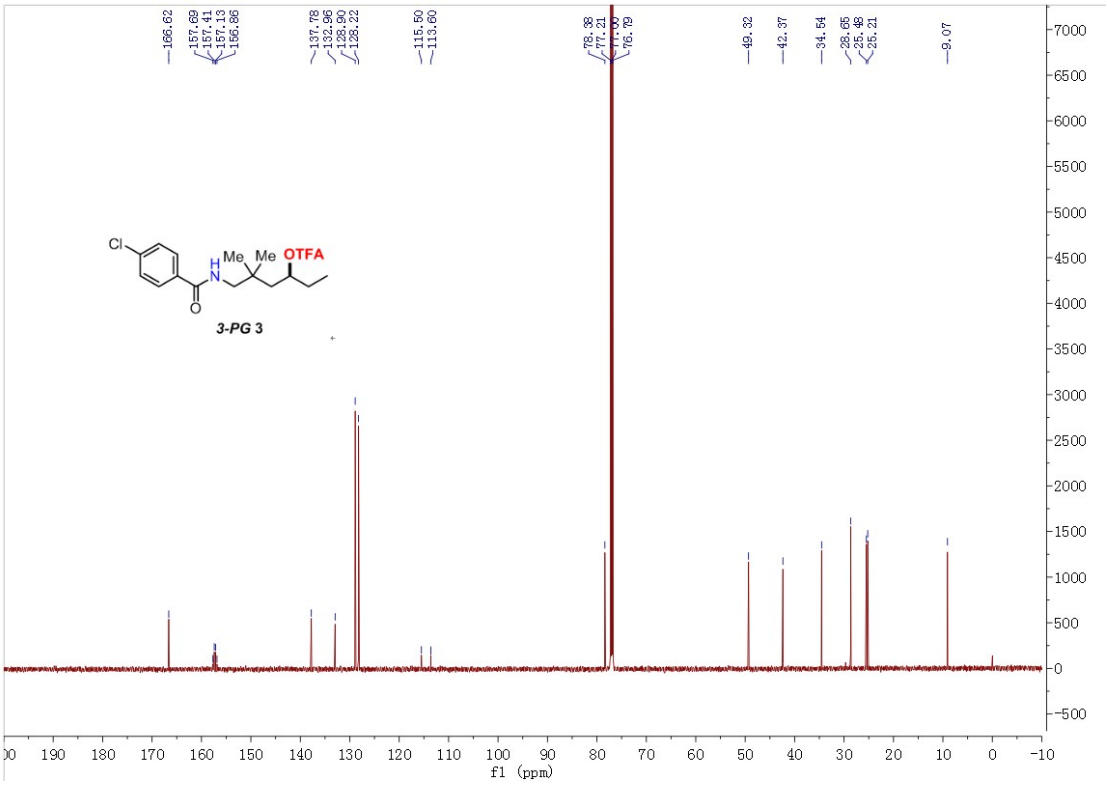
2.04
1.07
5.86
3.17
f1 (ppm)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77.21
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76.79
49.32
42.37
34.54
28.65
25.48
25.21
9.07
Cl
Me
Me
OTFA
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O
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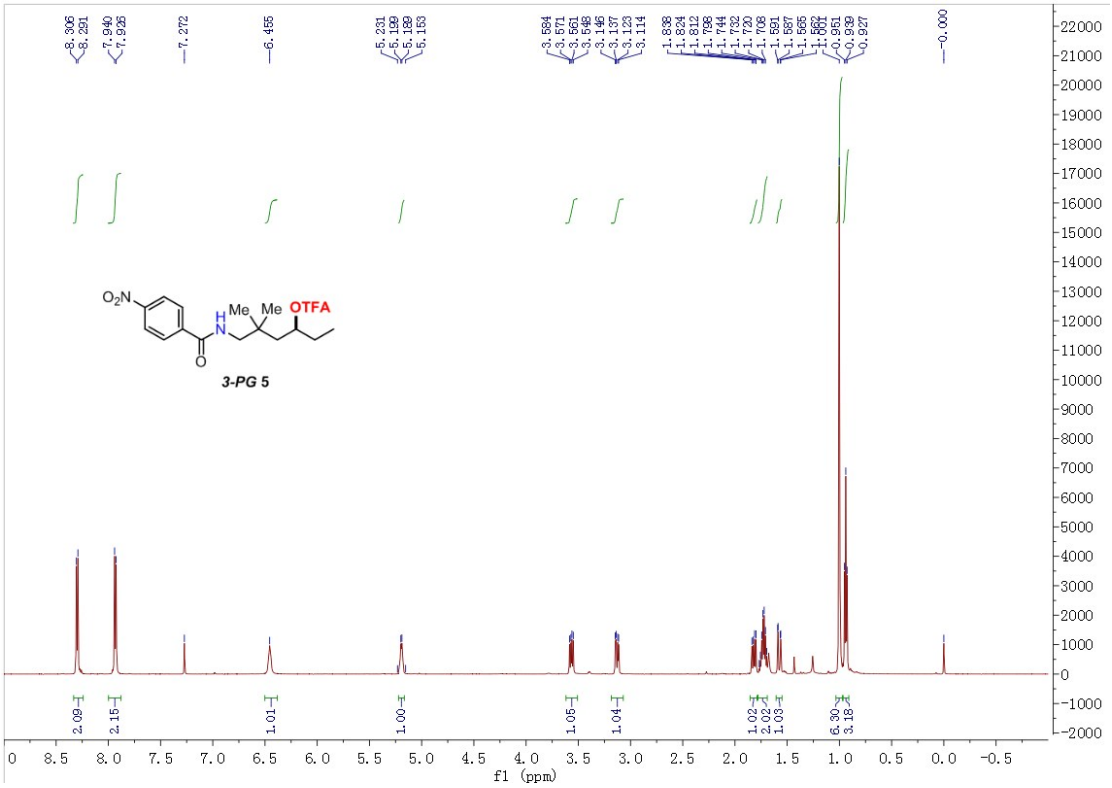
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3.561
3.548
3.146
3.137
3.123
3.114
1.838
1.824
1.812
1.798
1.744
1.732
1.720
1.708
1.591
1.587
1.565
0.951
0.939
0.927
0.000
O2N
H
N
Me
Me
OTFA
O
3-PG 5
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1.04
1.02
2.02
1.03
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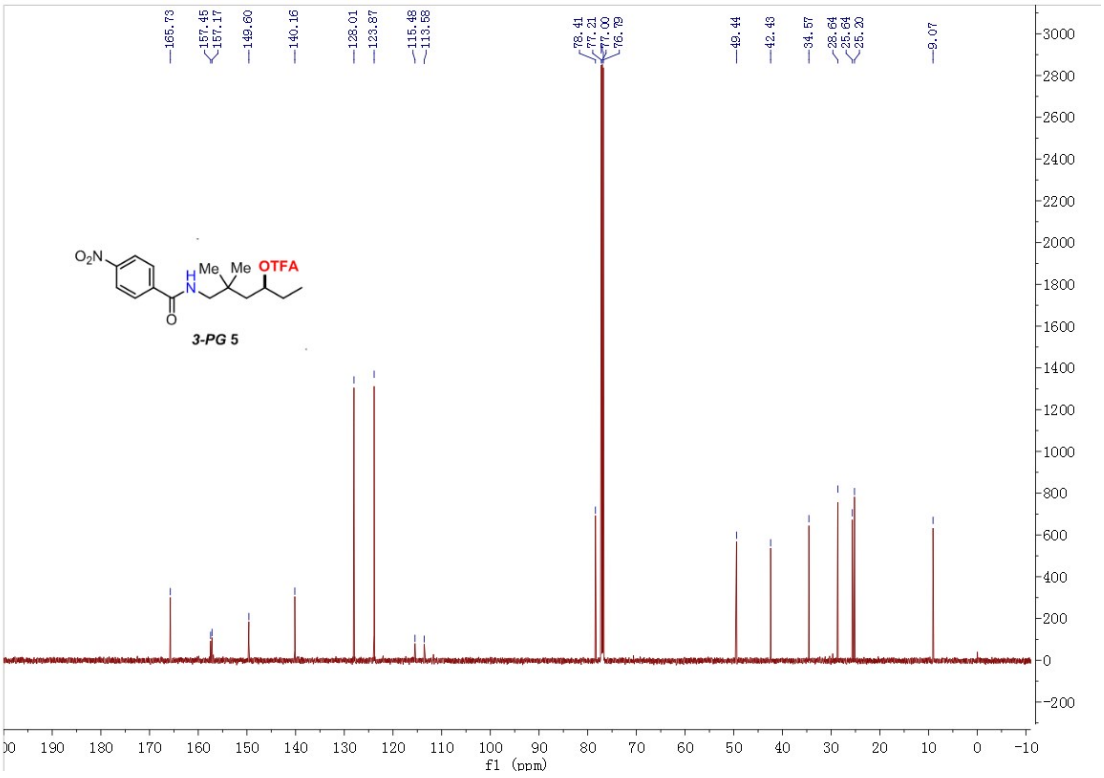
f1 (ppm)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76.79
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42.43
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H
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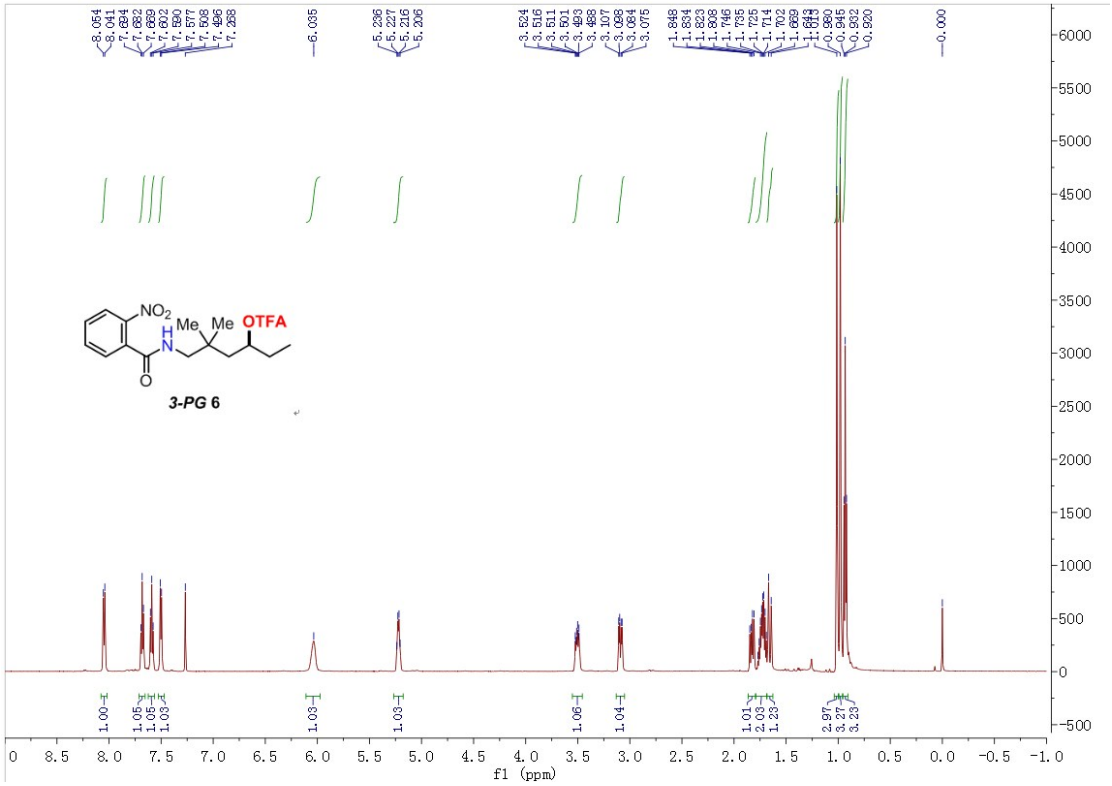
Me
Me
OTFA
O
3-PG 5
f1 (ppm)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7.496
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5.217
5.216
5.205
3.524
3.516
3.511
3.501
3.493
3.488
3.107
3.098
3.084
3.075
1.848
1.834
1.823
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1.735
1.725
1.714
1.702
1.669
1.613
0.980
0.945
0.902
0.920
0.000
NO2
Me
Me
OTFA
H
N
O
3-PG 6
1.00
1.05
1.05
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1.23
2.97
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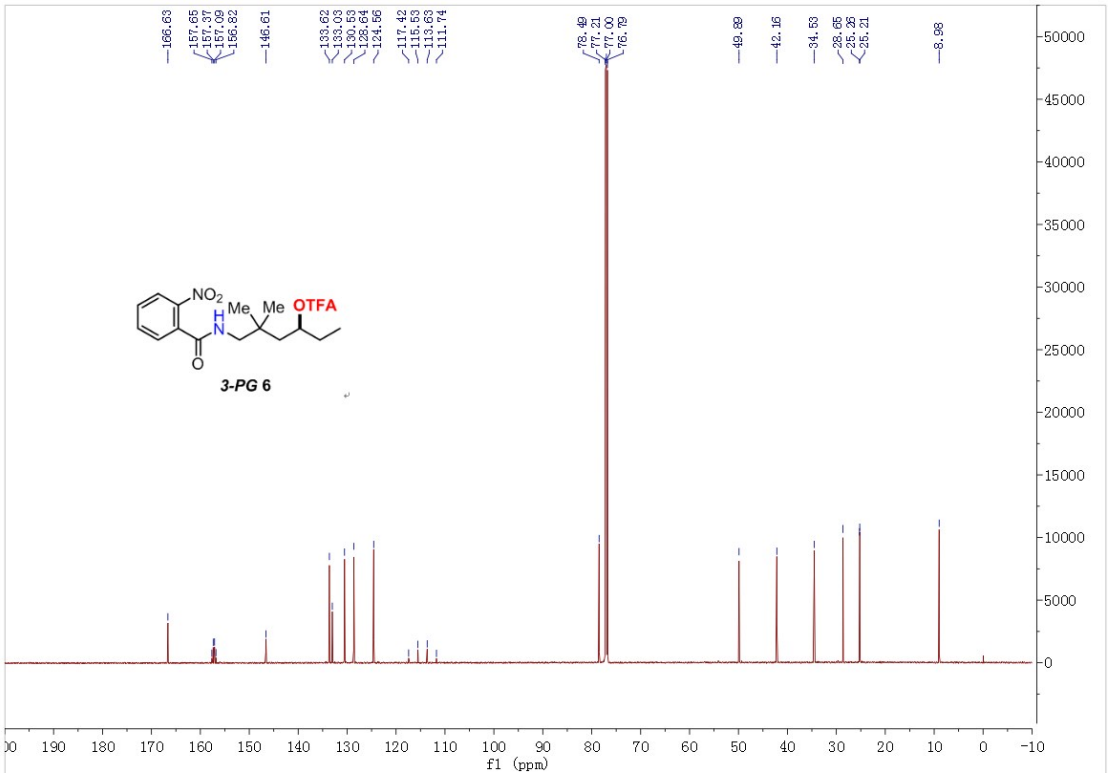
3.23
f1 (ppm)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111.74
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77.21
77.00
76.79
49.89
42.16
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25.21
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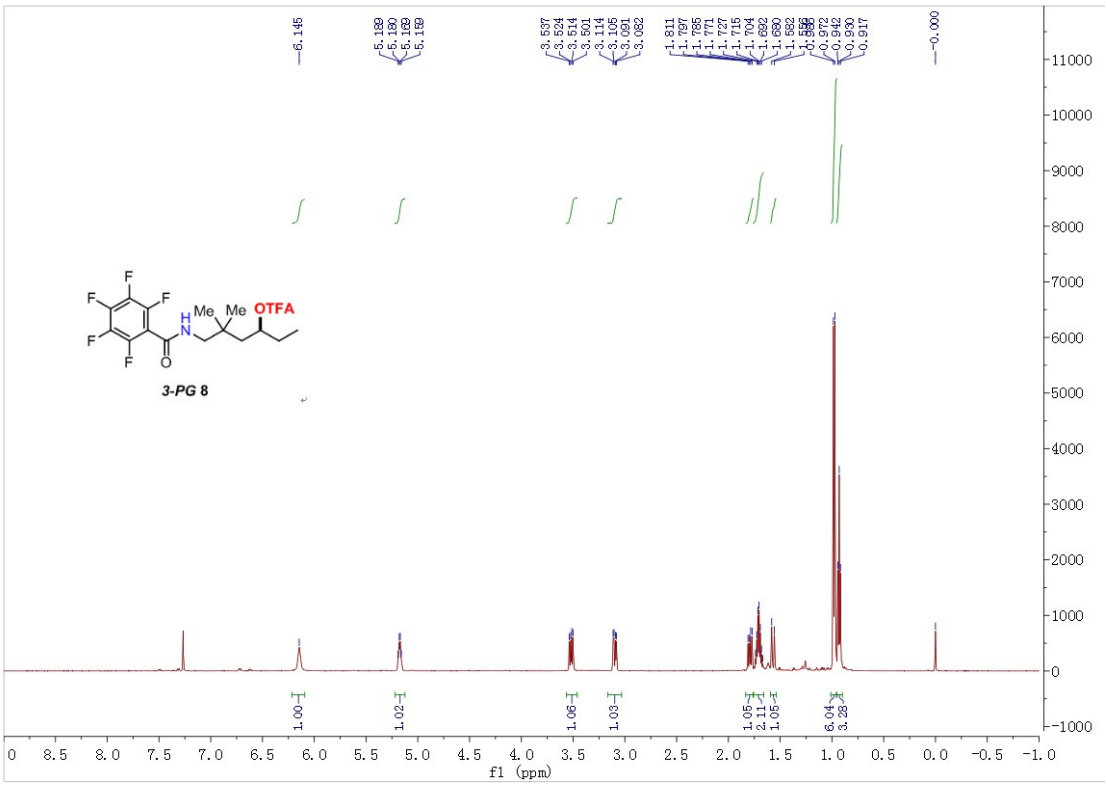
Me
Me
OTFA
H
N
O
3-PG 6
f1 (ppm)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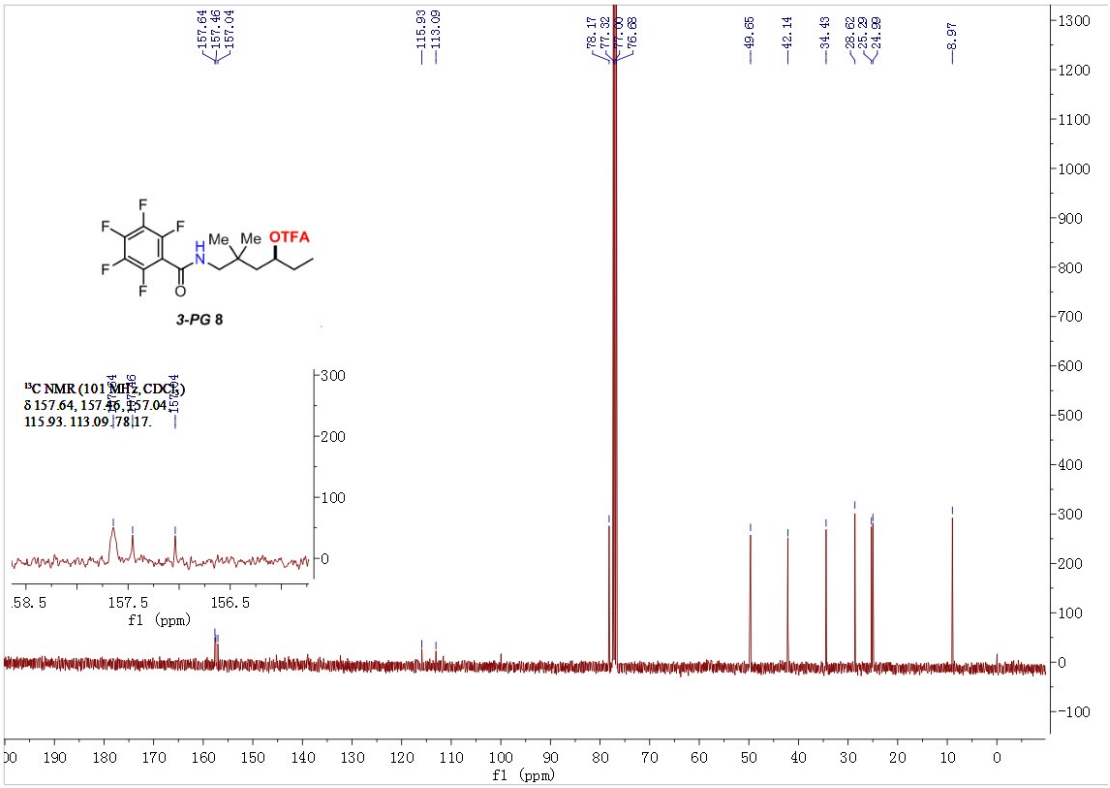
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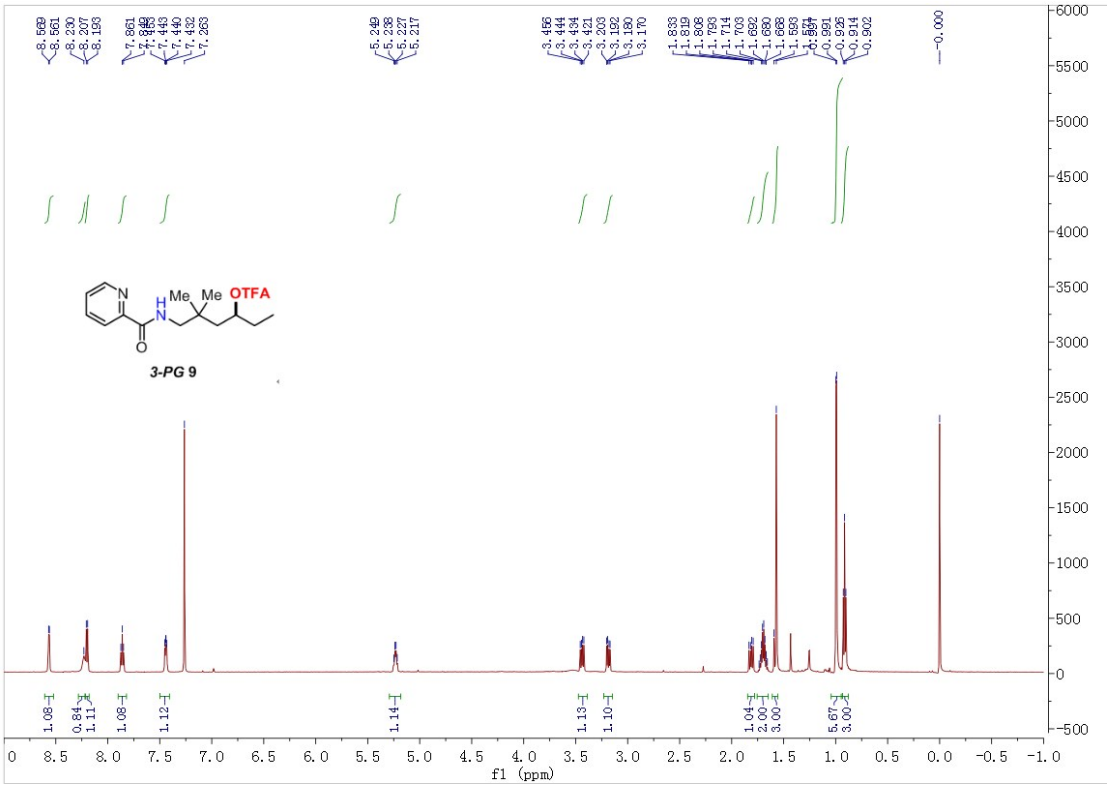
Me Me OTFA
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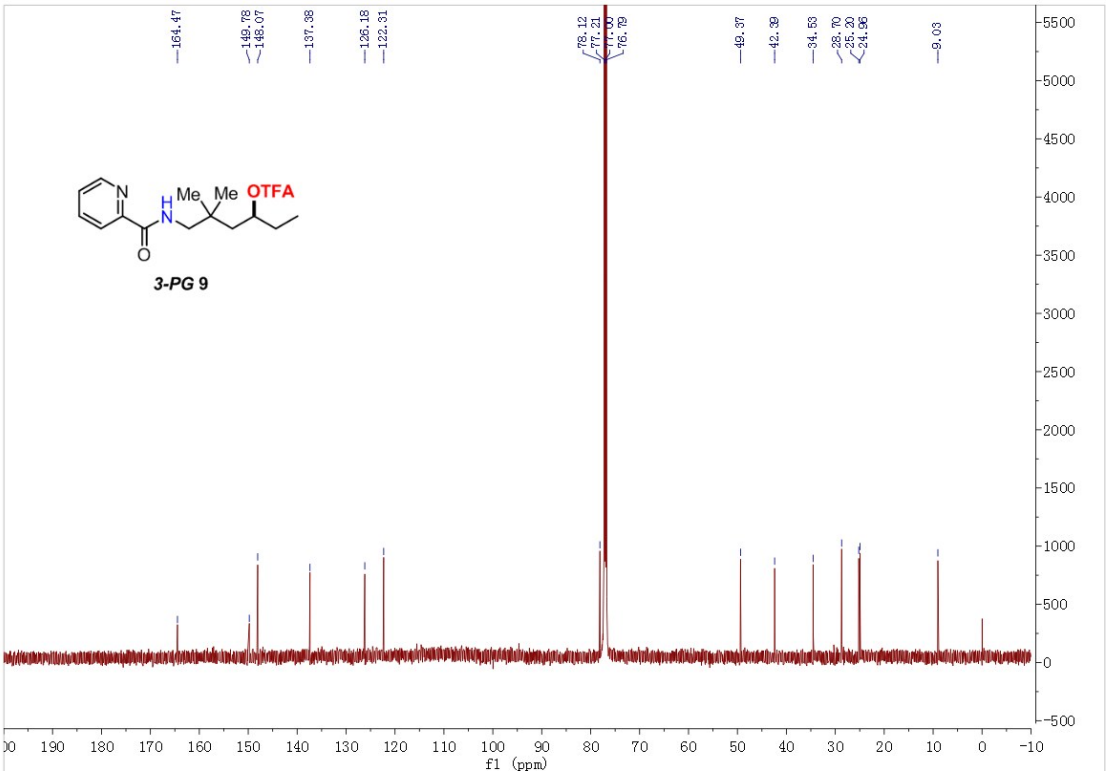
f1 (ppm)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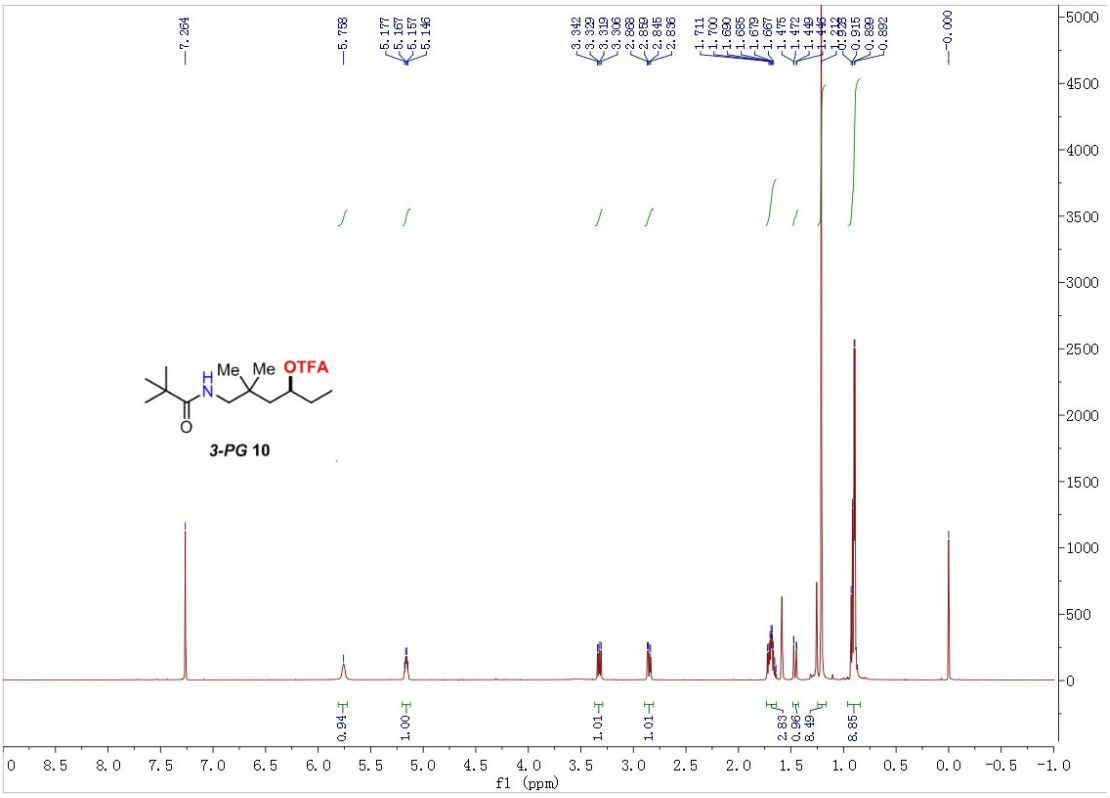
3-PG 9
f1 (ppm)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5.146
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3.329
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3.306
2.868
2.859
2.845
2.836
1.711
1.700
1.690
1.685
1.679
1.667
1.475
1.472
1.469
1.446
1.212
0.928
0.915
0.869
0.862
0.000
Me
Me
OTFA
H
N
O
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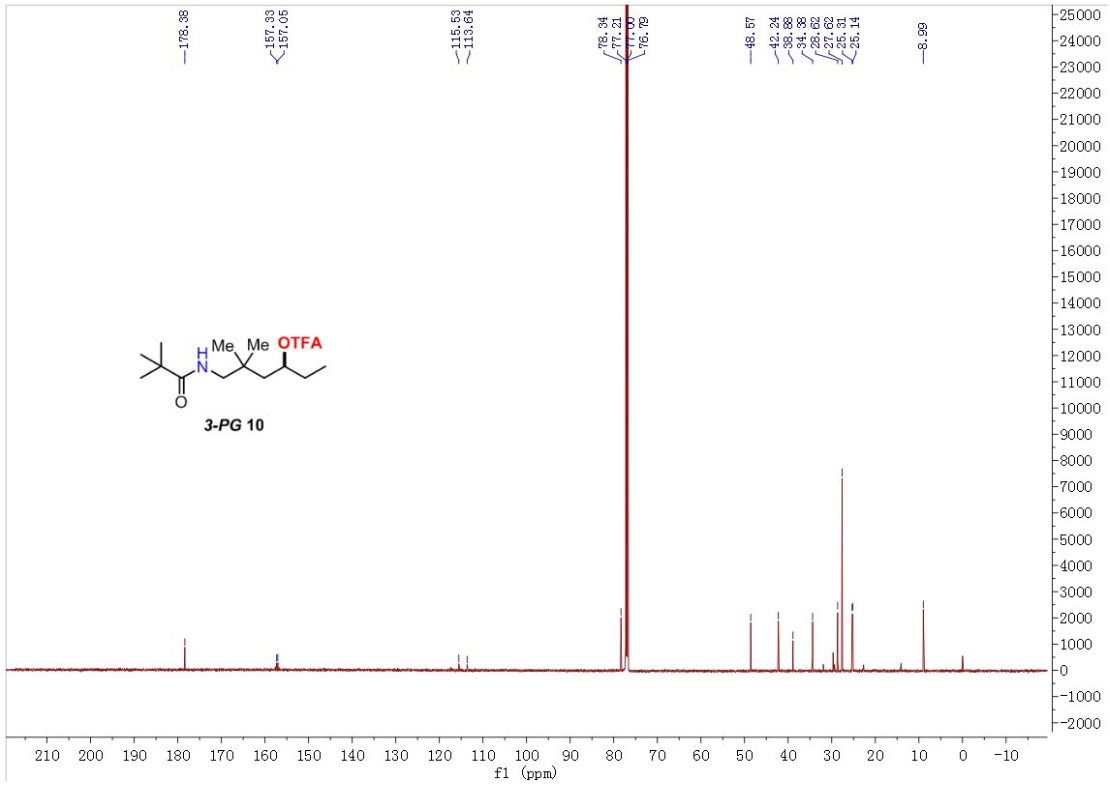
1.00
1.01
1.01
2.83
0.96
8.49
8.85
f1 (ppm)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157.05
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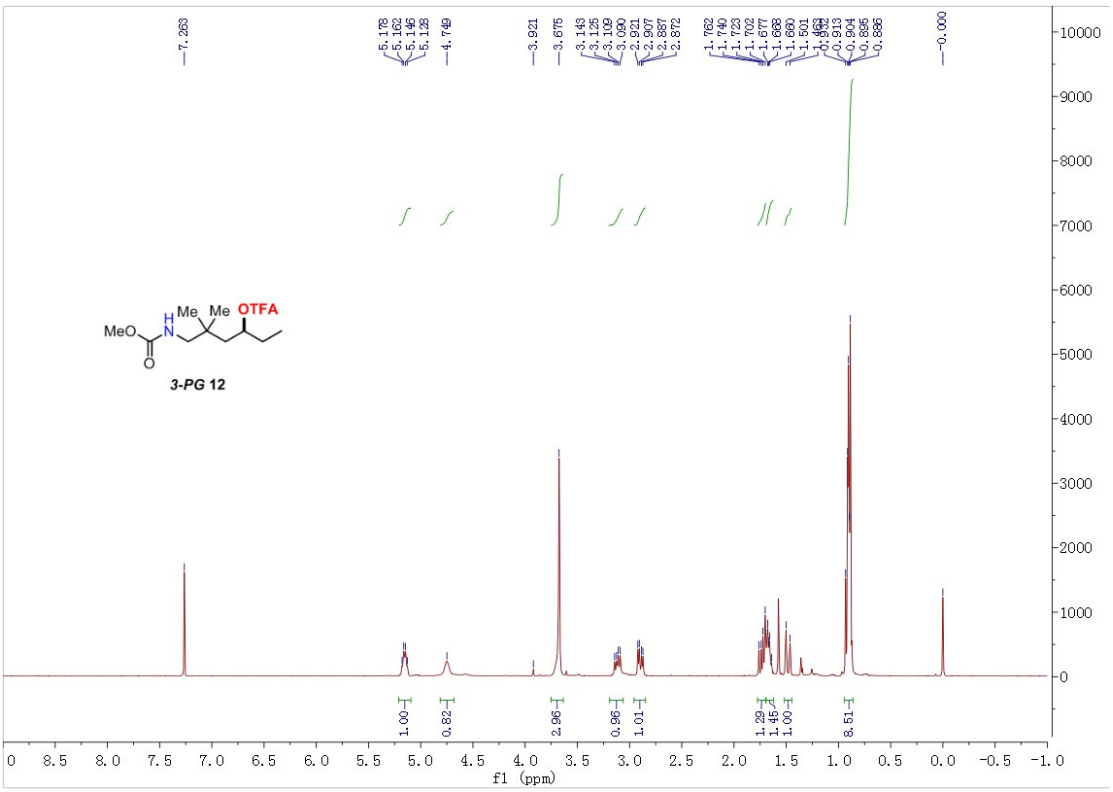
113.64
78.34
77.21
76.79
48.57
42.24
38.88
34.38
28.62
27.62
25.31
25.14
8.99
Me
Me
OTFA
H
N
O
3-PG 10
f1 (ppm)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3.125
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2.921
2.907
2.887
2.872
1.762
1.740
1.723
1.702
1.677
1.660
1.501
0.913
0.904
0.895
0.886
0.000
MeO
Me
Me
OTFA
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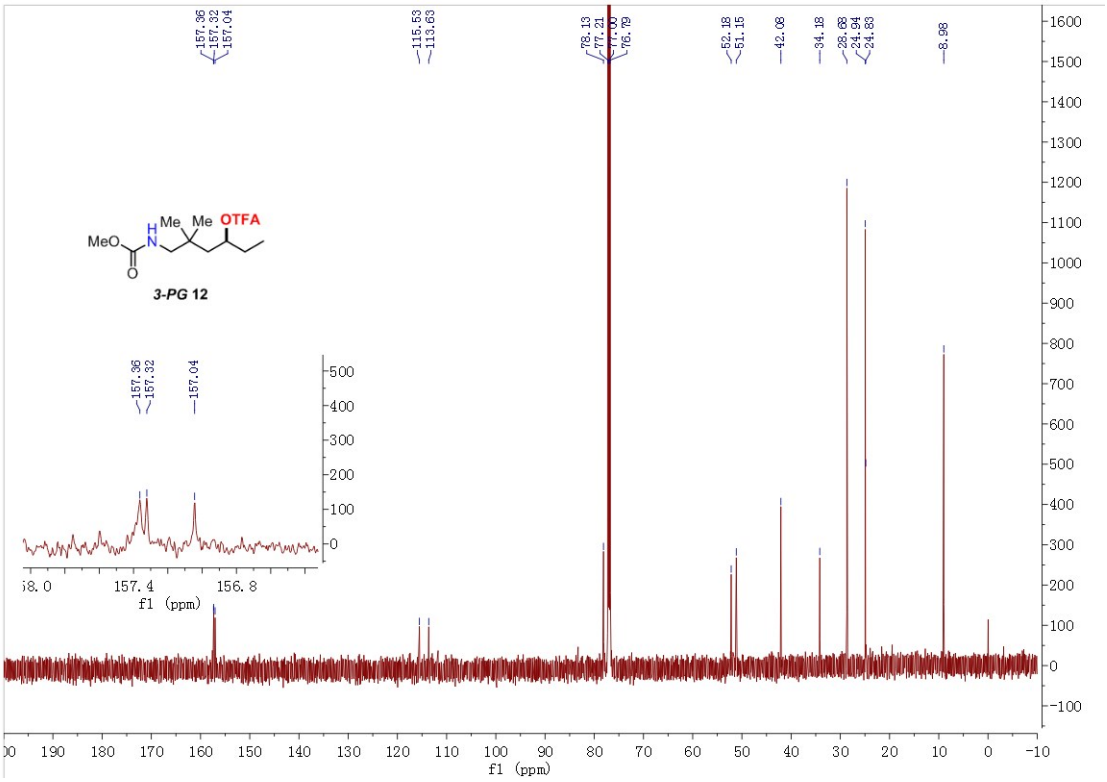
2.96
0.96
1.01
1.29
1.45
1.00
8.51
f1 (ppm)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78.13
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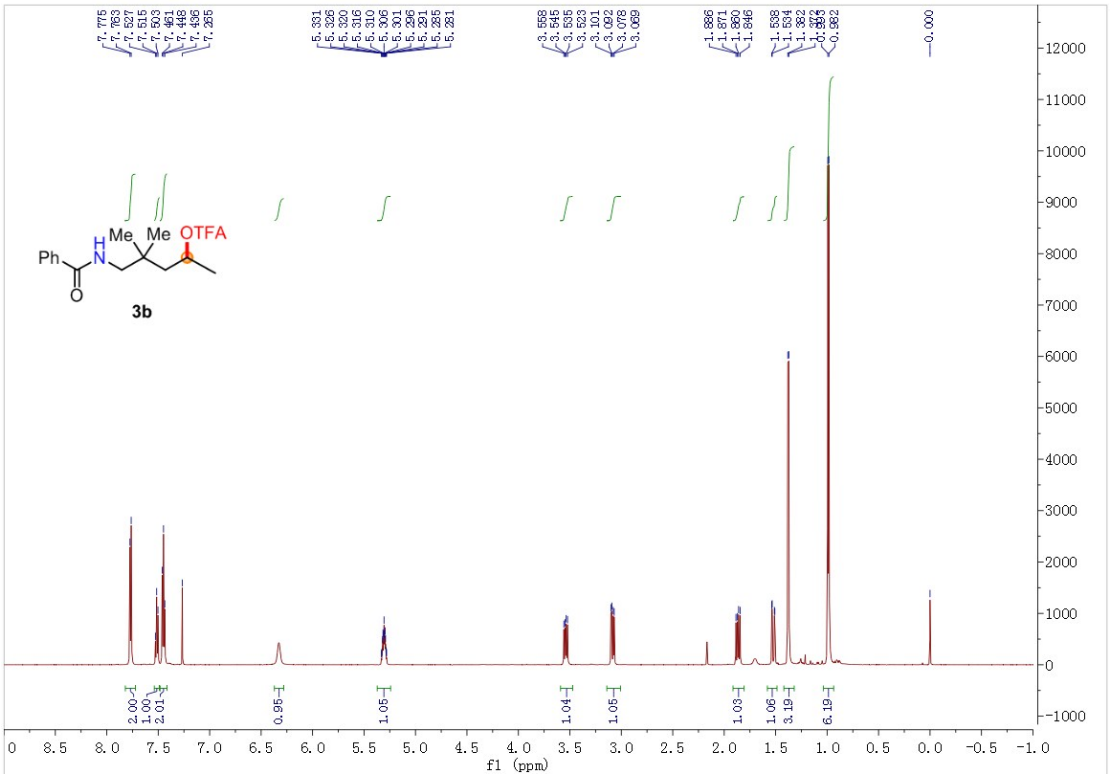
77.00
76.79
62.18
61.15
42.08
34.18
28.88
24.94
24.83
8.98
MeO
Me
Me
OTFA
3-PG 12
157.4
156.8
f1 (ppm)
f1 (ppm)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5.306
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5.296
5.291
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5.281
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3.545
3.535
3.523
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3.092
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3.069
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1.871
1.860
1.846
1.538
1.534
1.382
0.982
0.000
Me
Me
OTFA
Ph
H
N
O
3b
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1.04
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1.06
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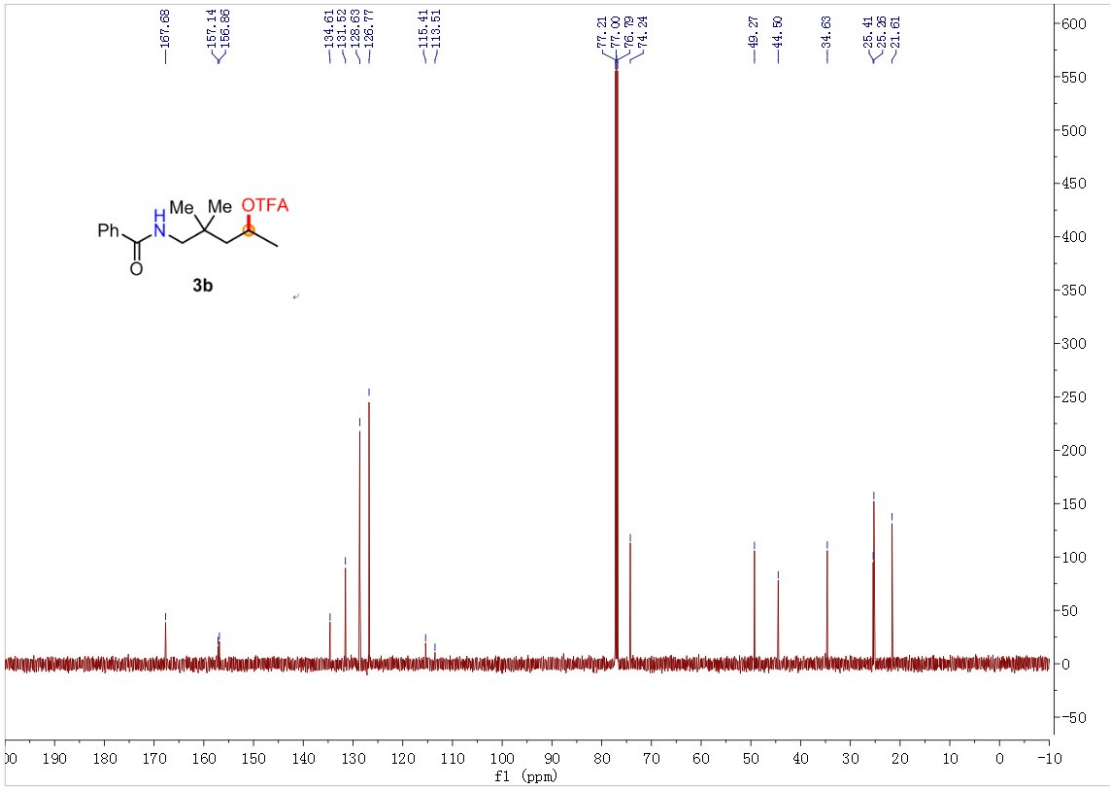
6.19
f1 (ppm)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115.41
113.51
77.21
77.00
76.79
74.24
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25.41
25.25
21.61
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Me
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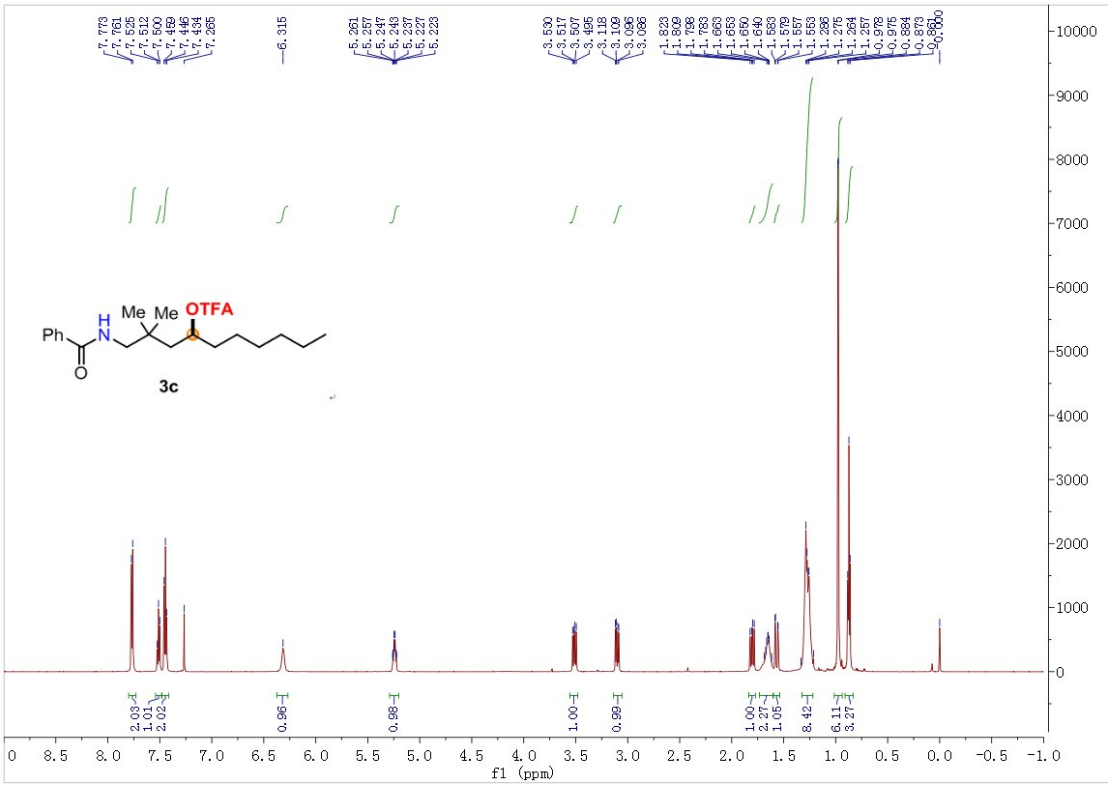
Ph
H
N
O
3b
f1 (ppm)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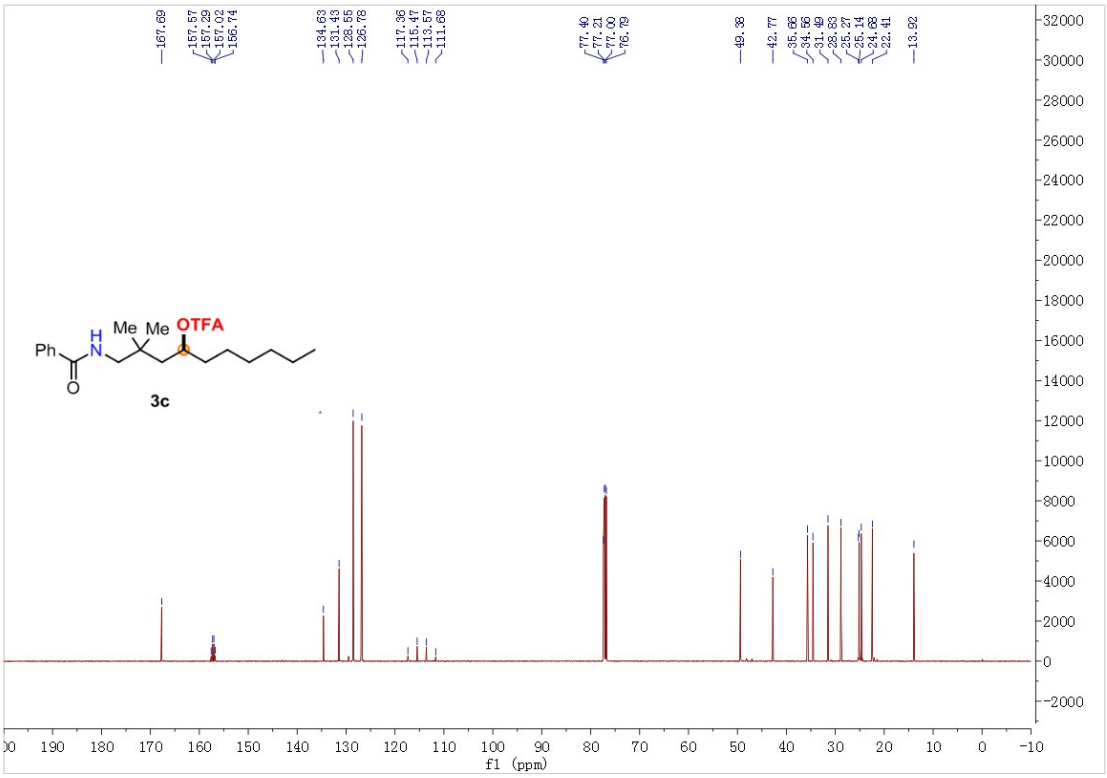
f1 (ppm)


Ph
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N
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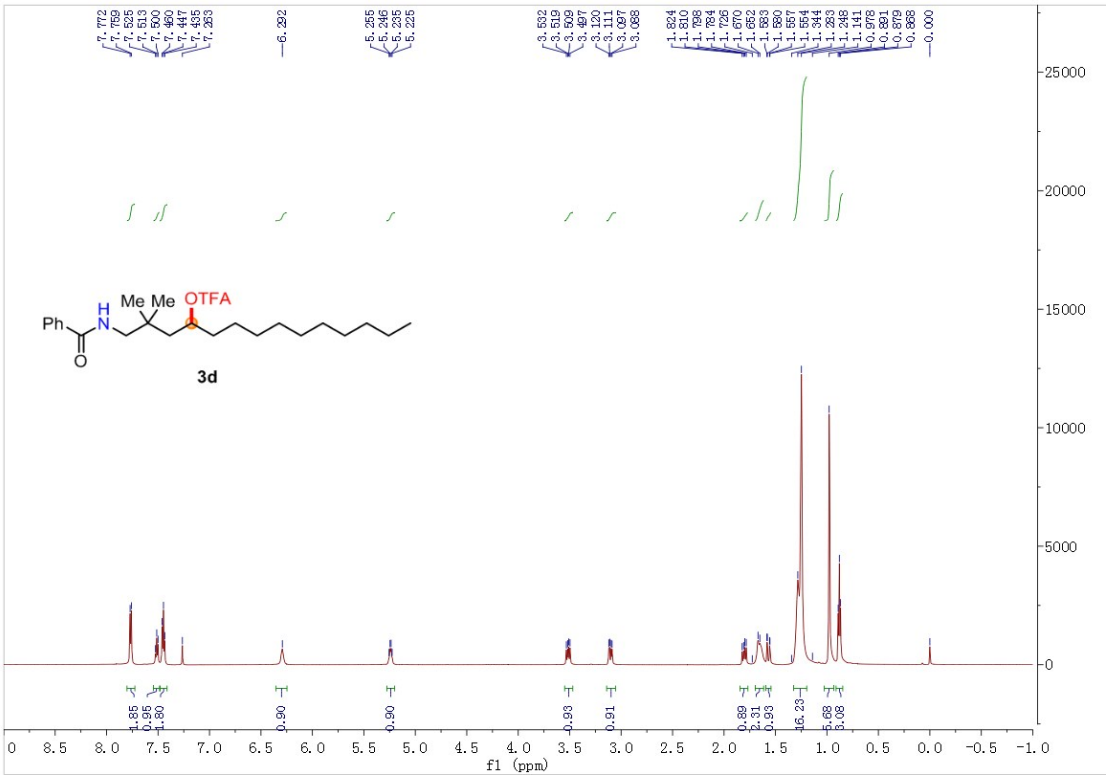
Me Me
OTFA
3c
f1 (ppm)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N
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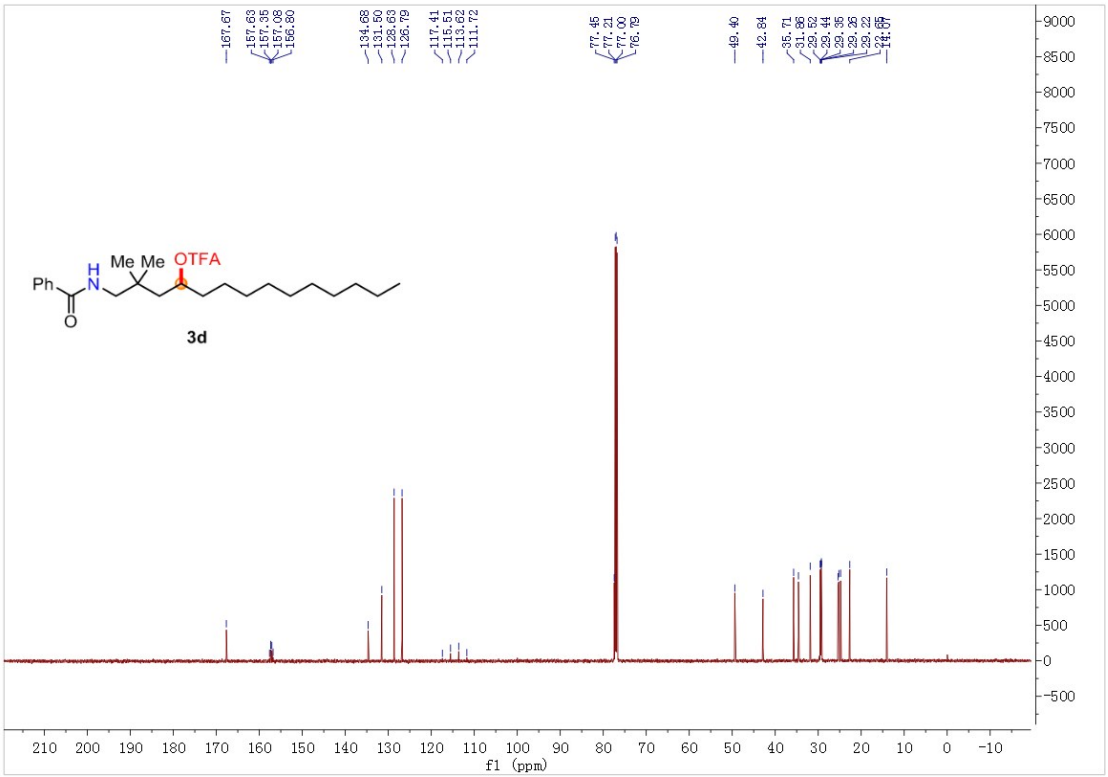
Me Me
OTFA
3d
f1 (ppm)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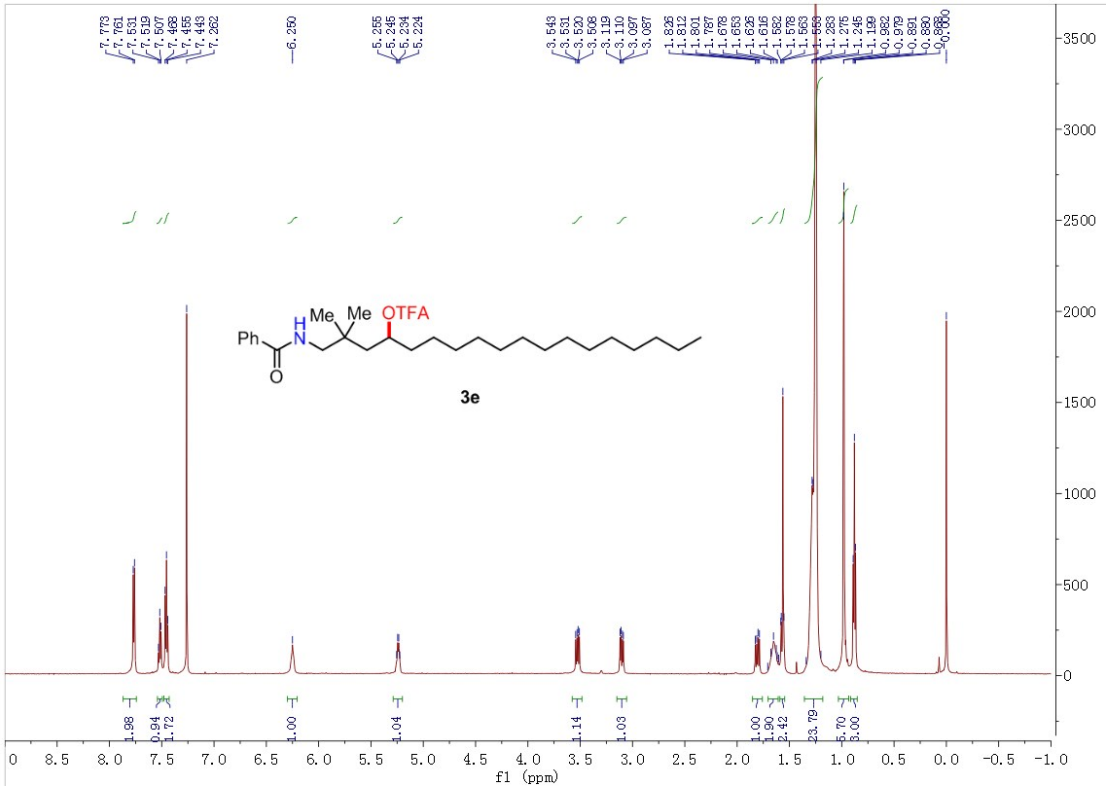
N
O
Me Me
OTFA
3d
f1 (ppm)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Me
Me
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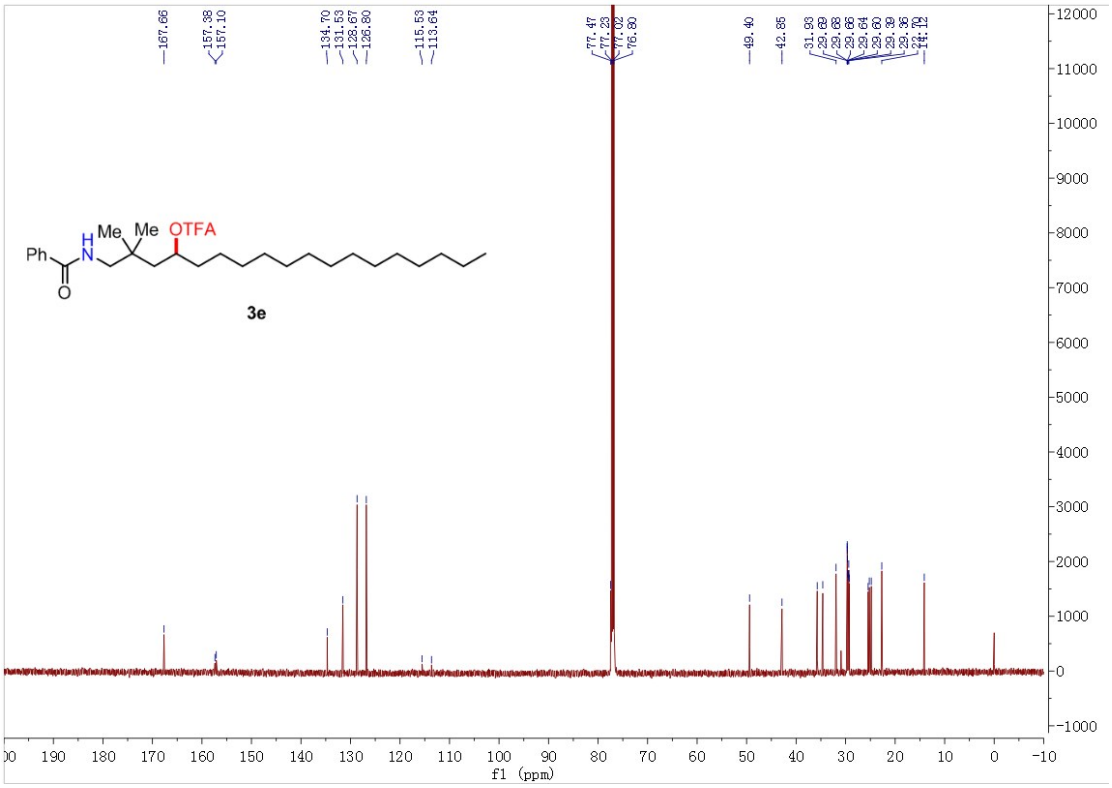
3e
f1 (ppm)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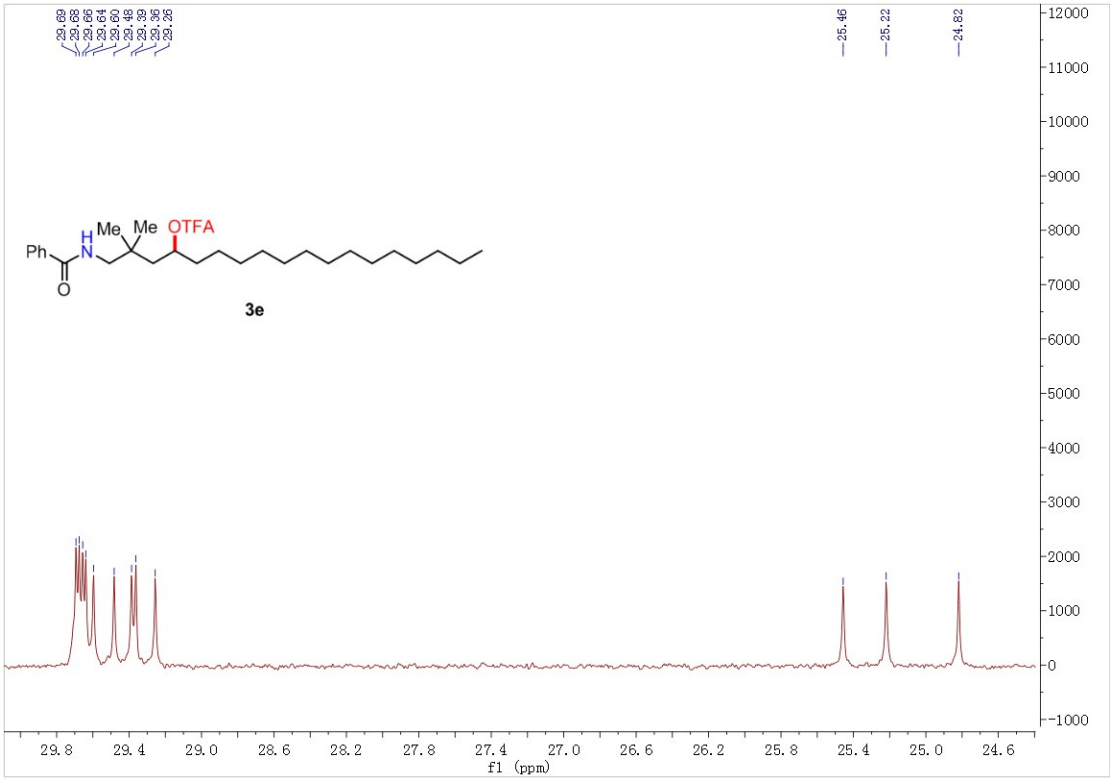
f1 (ppm)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Me
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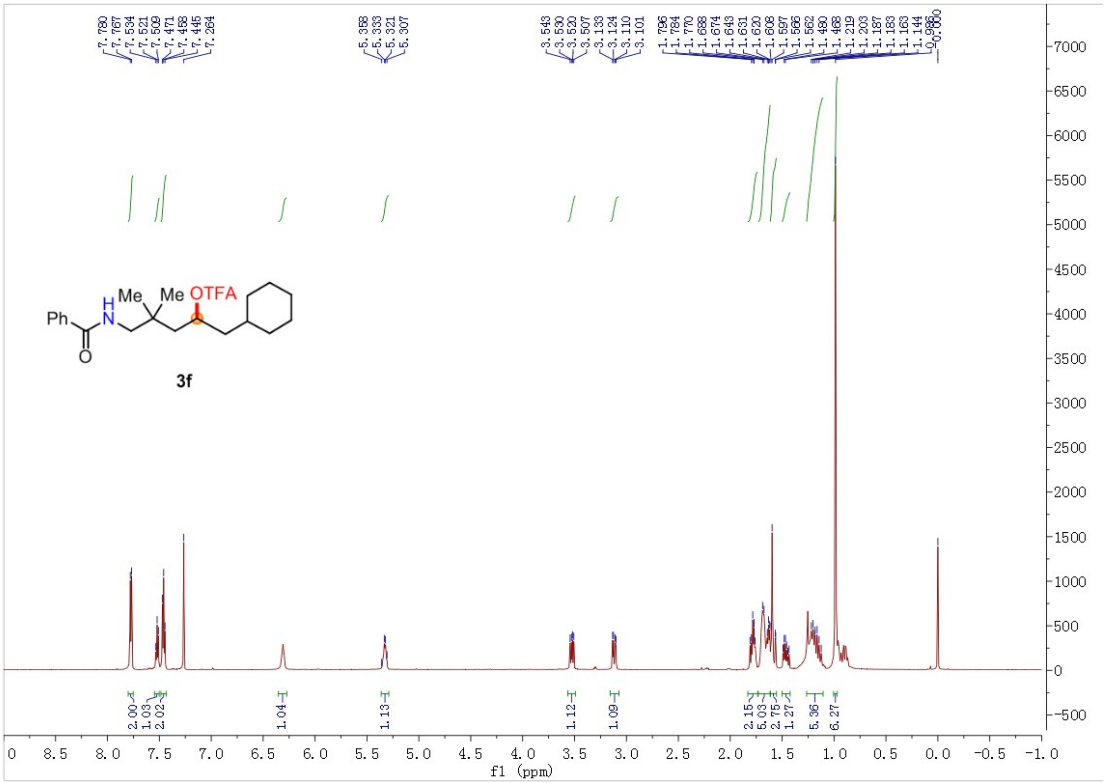
H
N
O
3e
f1 (ppm)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3.110
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1.620
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1.490
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1.219
1.203
1.187
1.183
1.163
1.144
1.094
0.000
Ph
Me
Me
OTFA
H
N
O
3f
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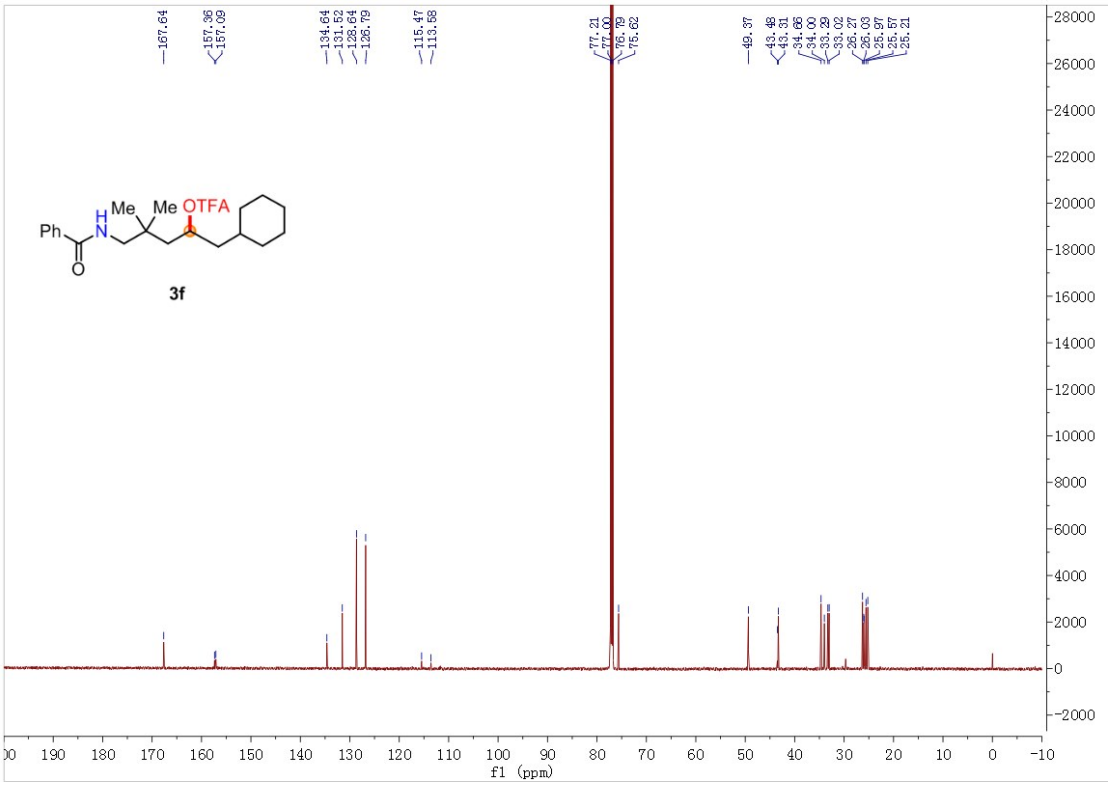
f1 (ppm)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43.31
34.86
34.00
33.29
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25.21
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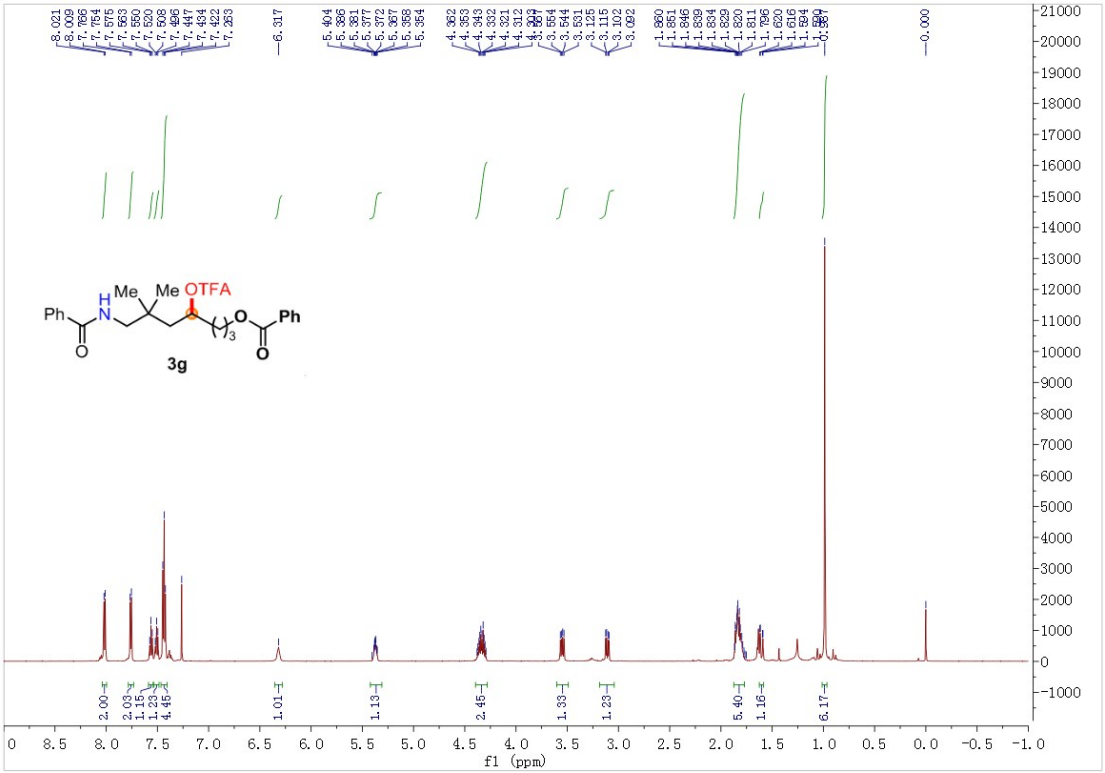
N
H
Me
Me
OTFA
O
3f
f1 (ppm)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1.589
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Ph
N
H
Me
Me
OTFA
O
O
Ph
3g
2.00
2.03
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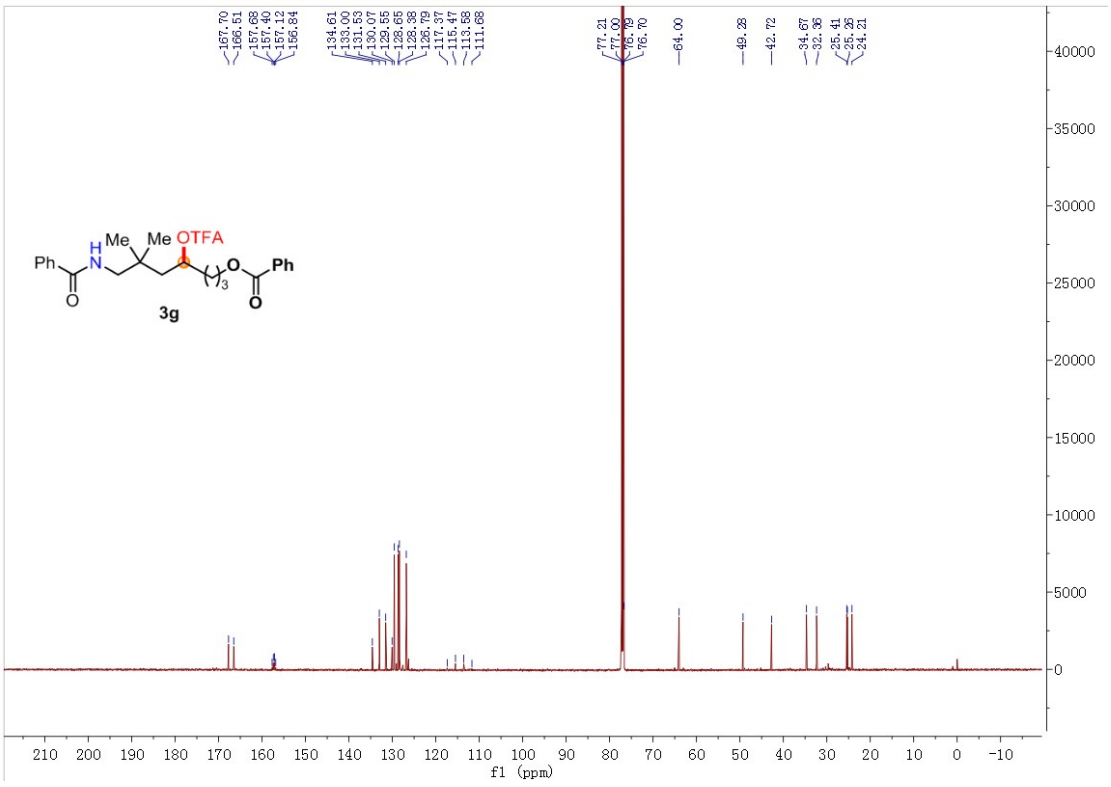
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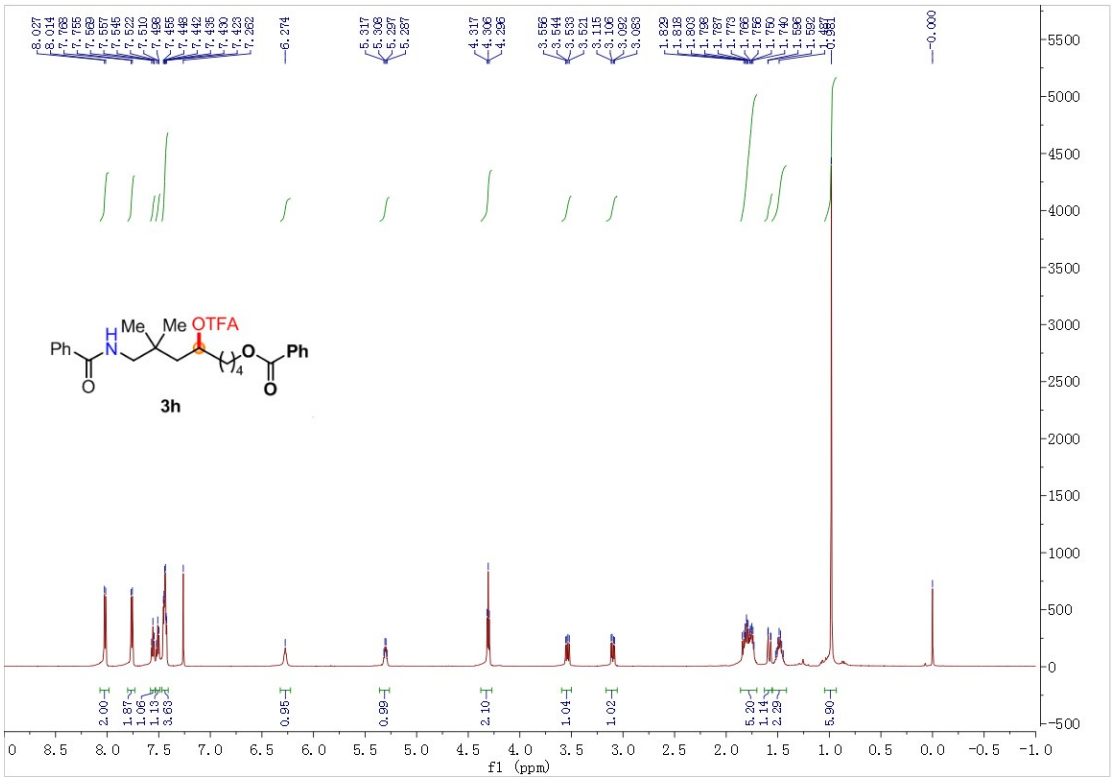
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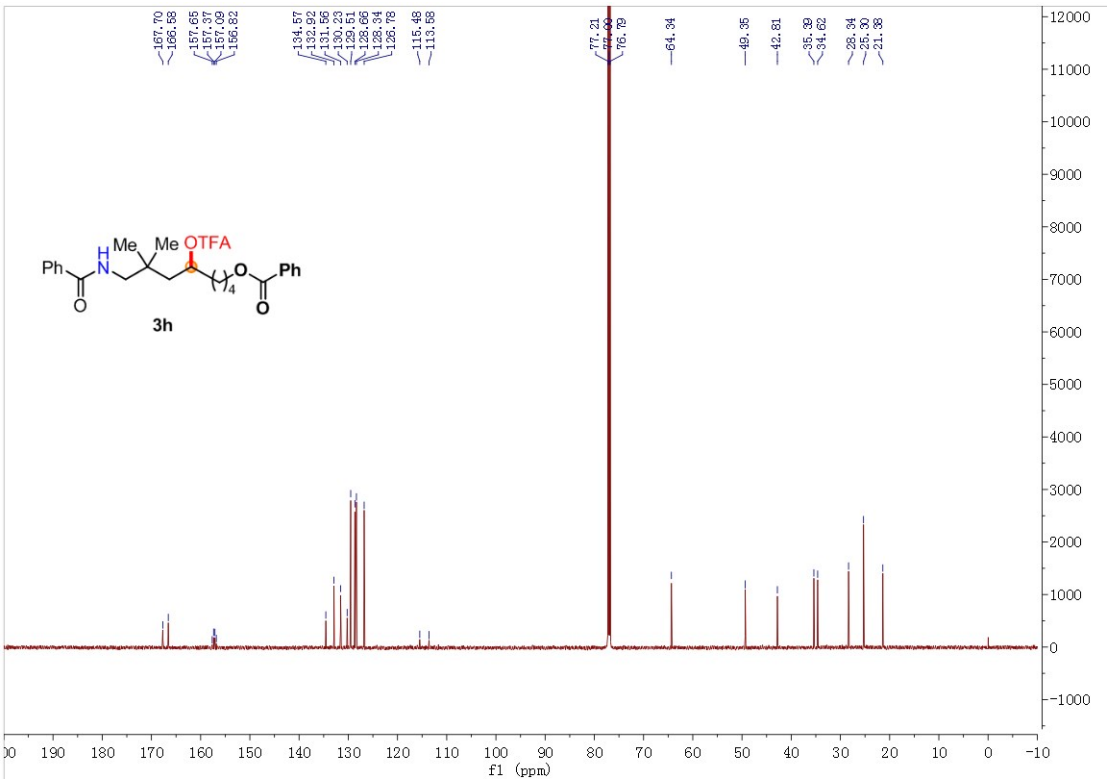
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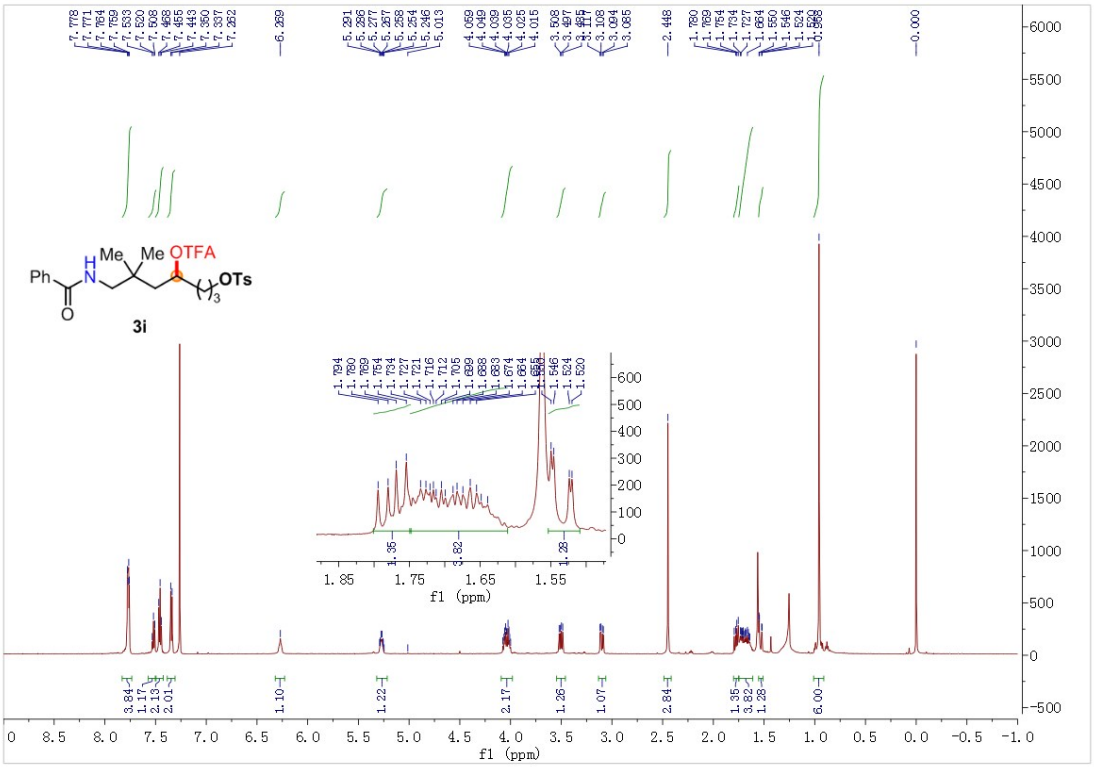
Me
OTFA
O
4
O
Ph
O
3h
f1 (ppm)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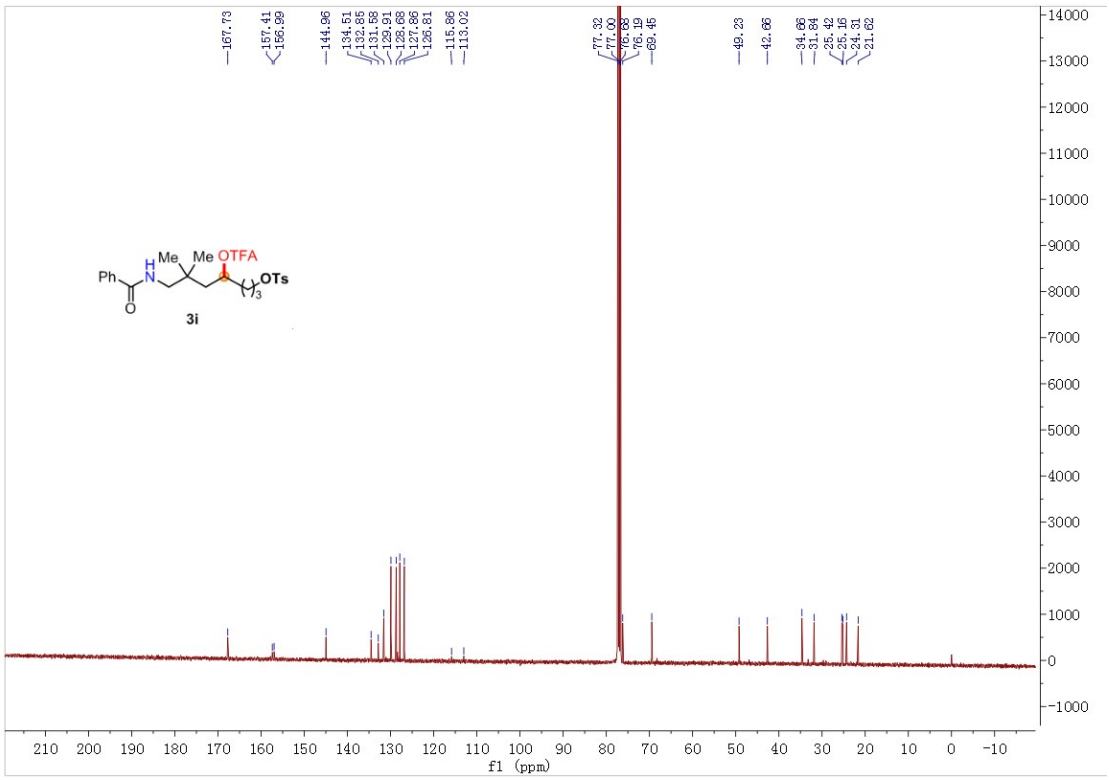
Me
Me
OTFA
3
OTs
O
3i
f1 (ppm)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77.32
77.00
76.68
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69.45
49.23
42.66
34.06
31.84
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24.31
21.62
Ph
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H
O
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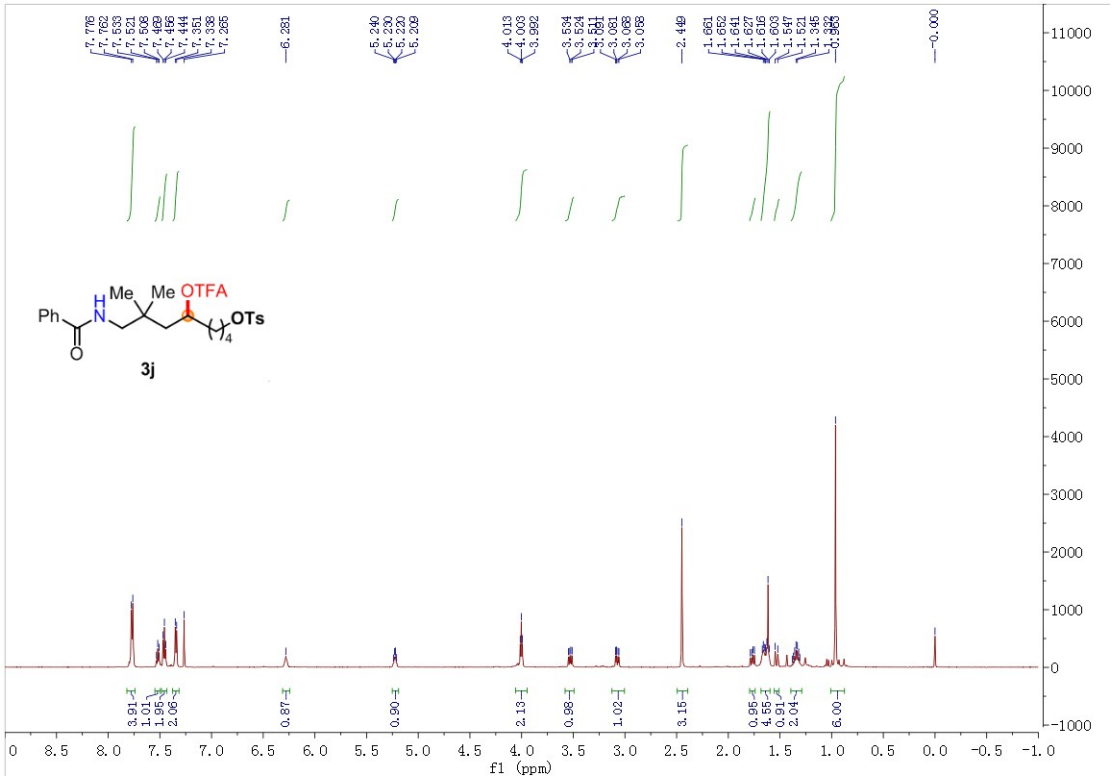
Me
OTFA
OTs
3
3i
f1 (ppm)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7.265
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5.240
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5.209
4.013
4.003
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1.616
1.603
1.547
1.521
1.345
0.000
Ph
N
H
O
Me
Me
OTFA
OTs
4
3j
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1.01
1.95
2.06
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0.98
1.02
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0.95
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0.91
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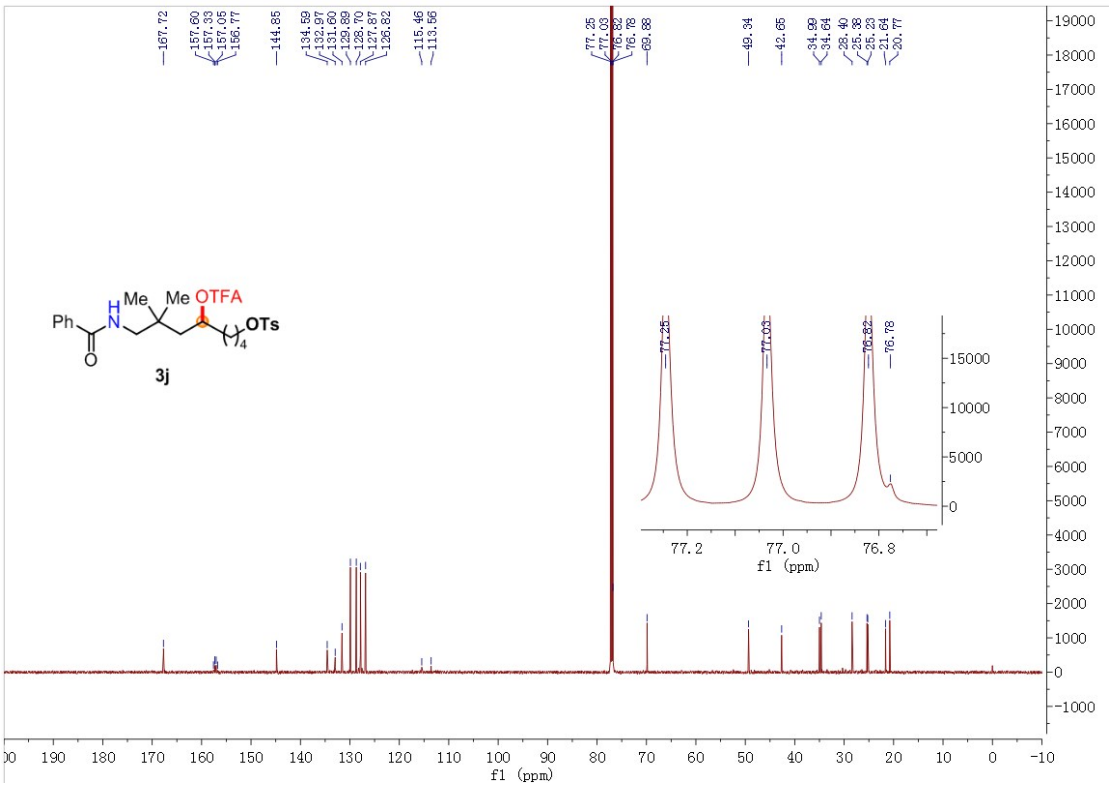
6.00
f1 (ppm)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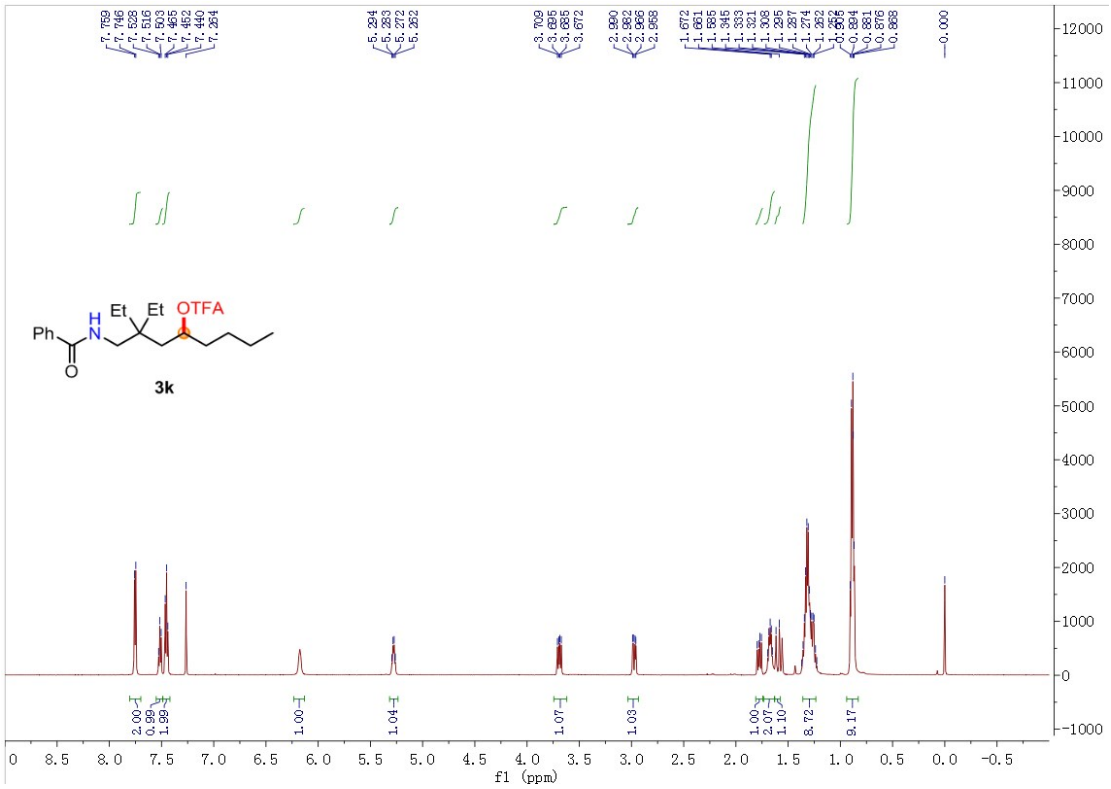
Me
Me
OTFA
OTs
4
3j
f1 (ppm)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N
O
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Et
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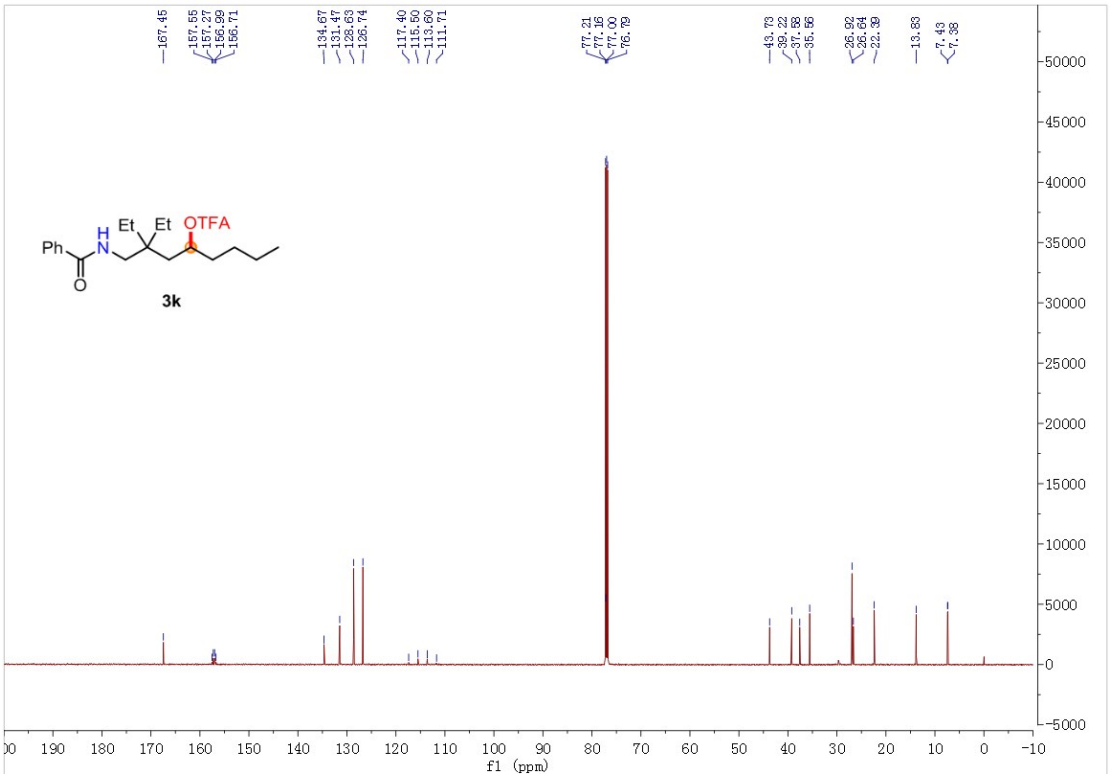
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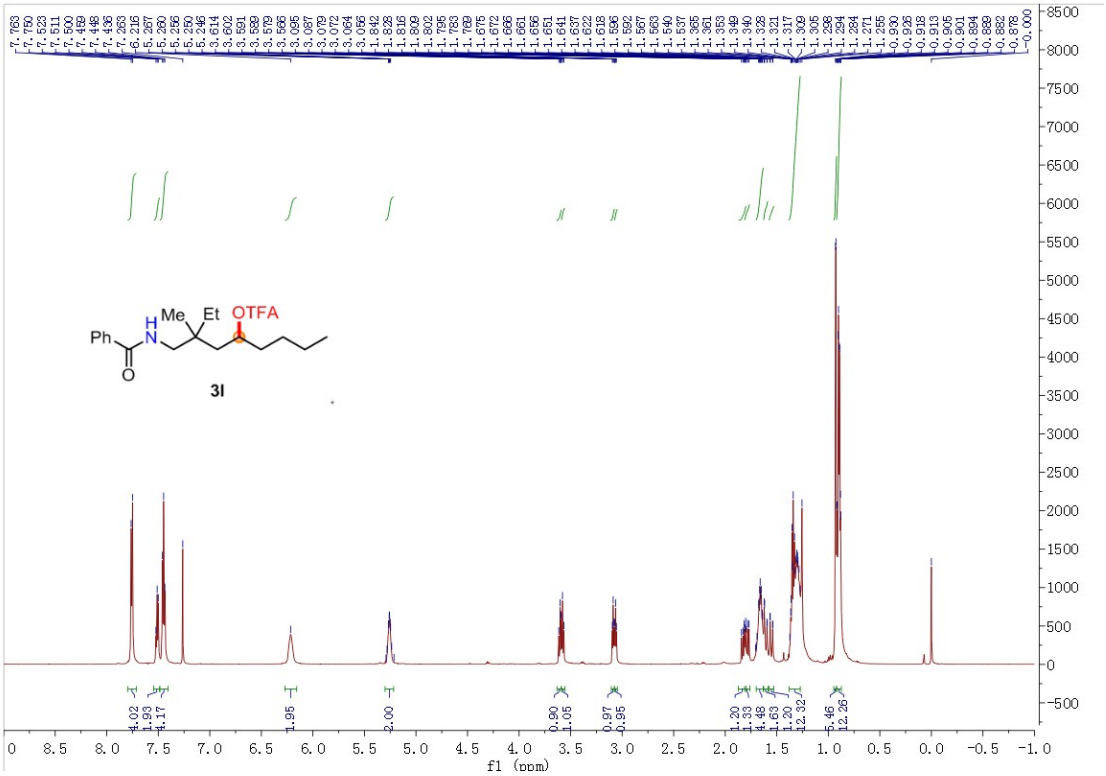
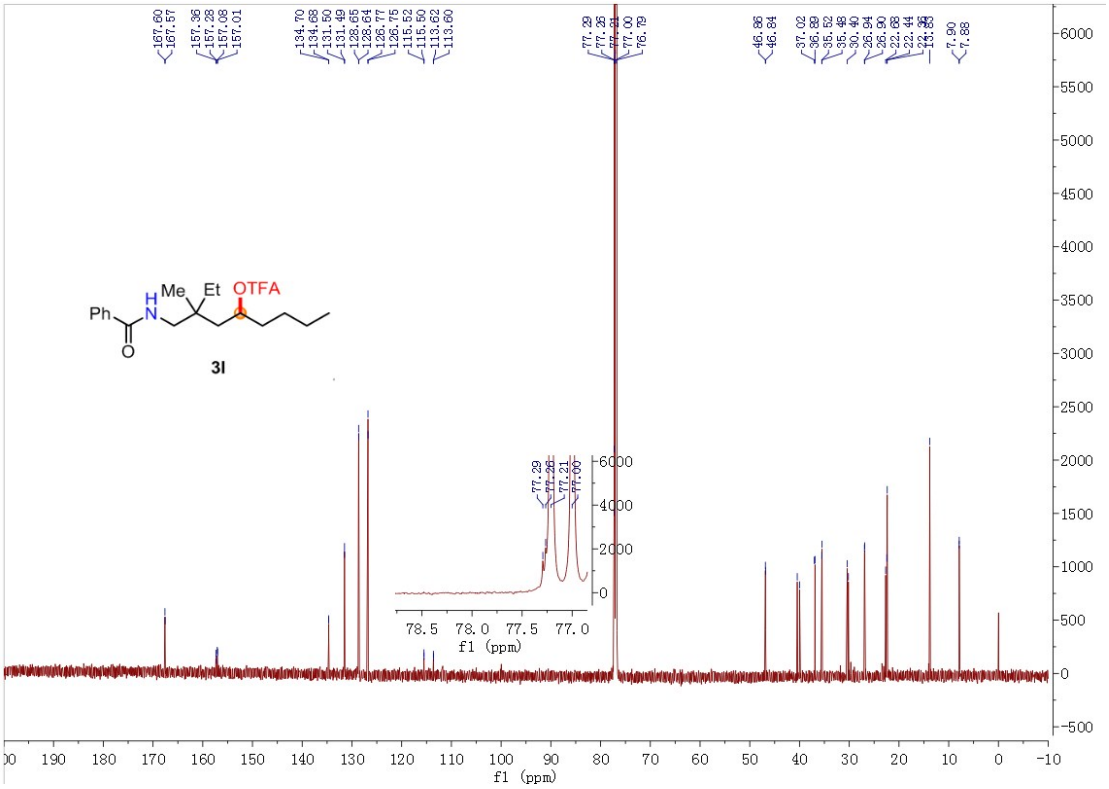
Et
Et
OTFA
3k
f1 (ppm)


Ph
H
N
O
Me
Et
OTFA
3l
f1 (ppm)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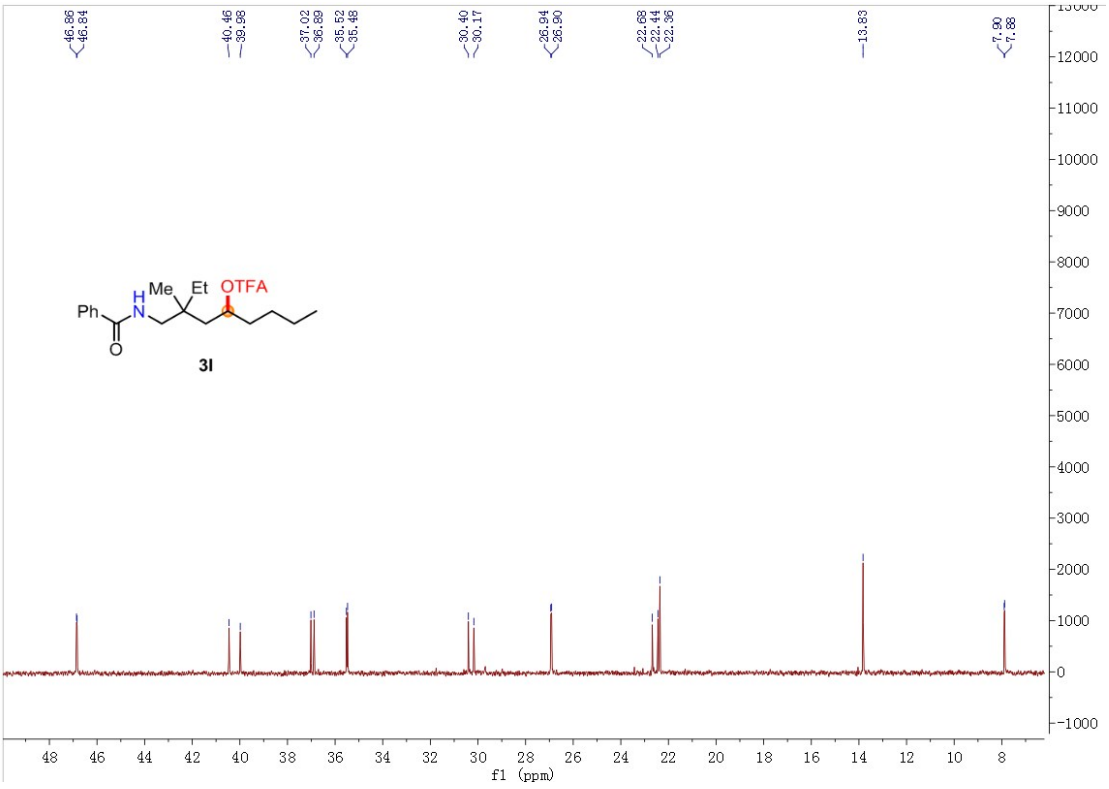
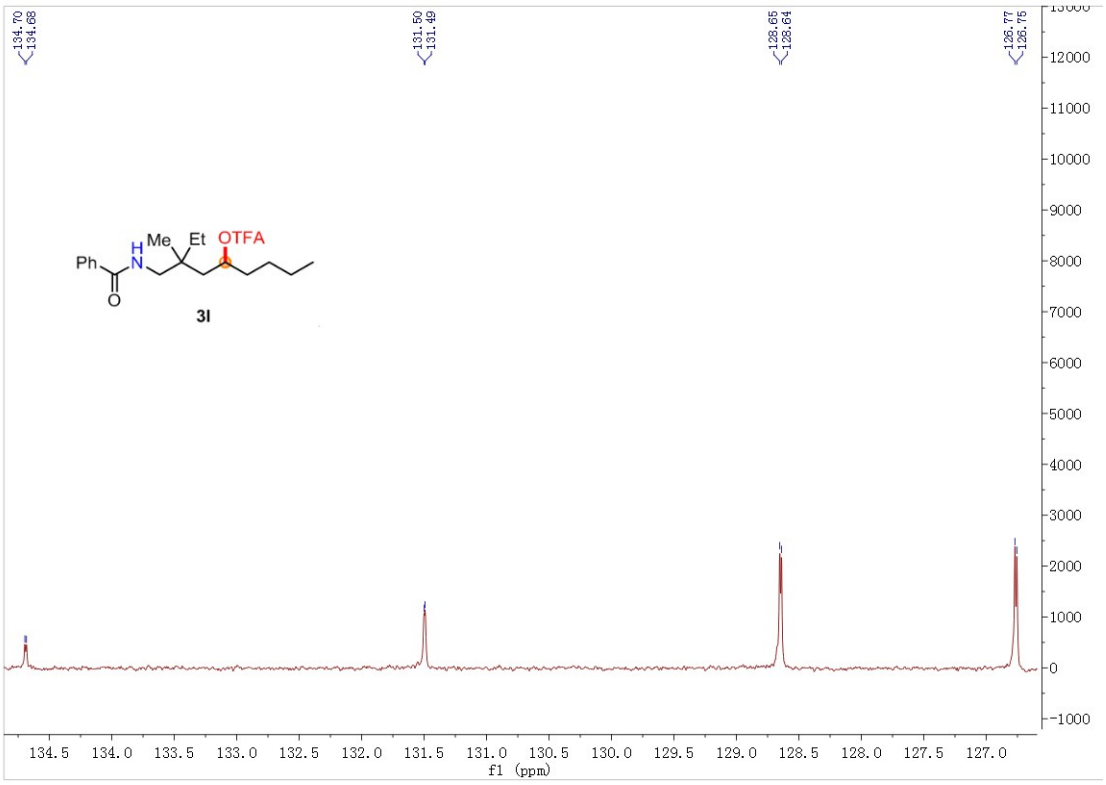
O
Me
Et
OTFA
3l
f1 (ppm)


Ph
N
H
O
Me
Et
OTFA
3l
f1 (ppm)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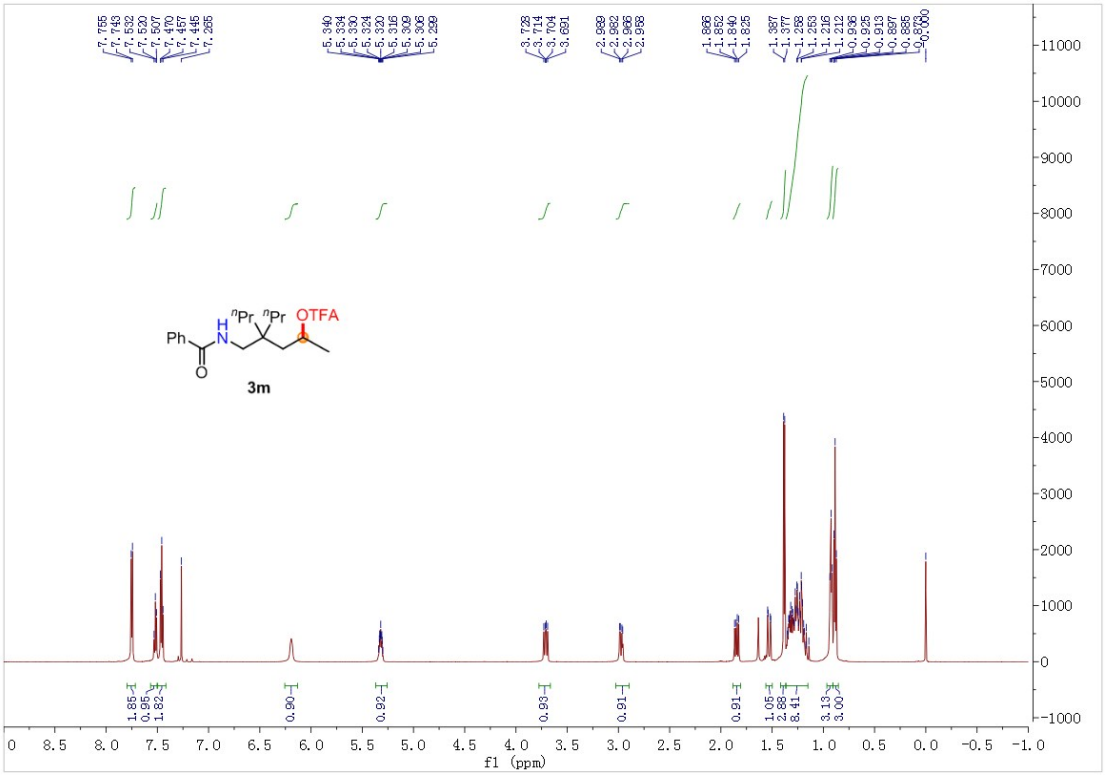
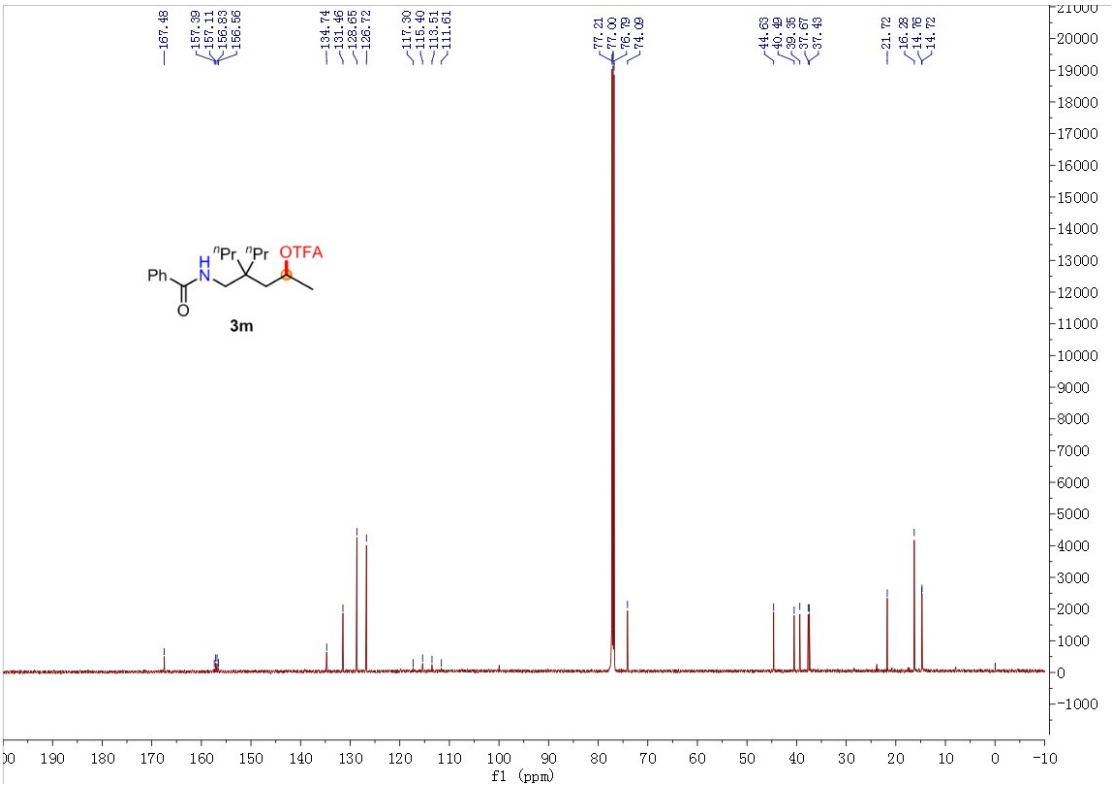
134.68
131.50
131.49
128.65
128.64
126.77
126.75
Ph
Me
Et
OTFA
H
N
O
3l
f1 (ppm)


Ph
nPr
nPr
OTFA
H
N
O
3m
f1 (ppm)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157.11
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134.74
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128.65
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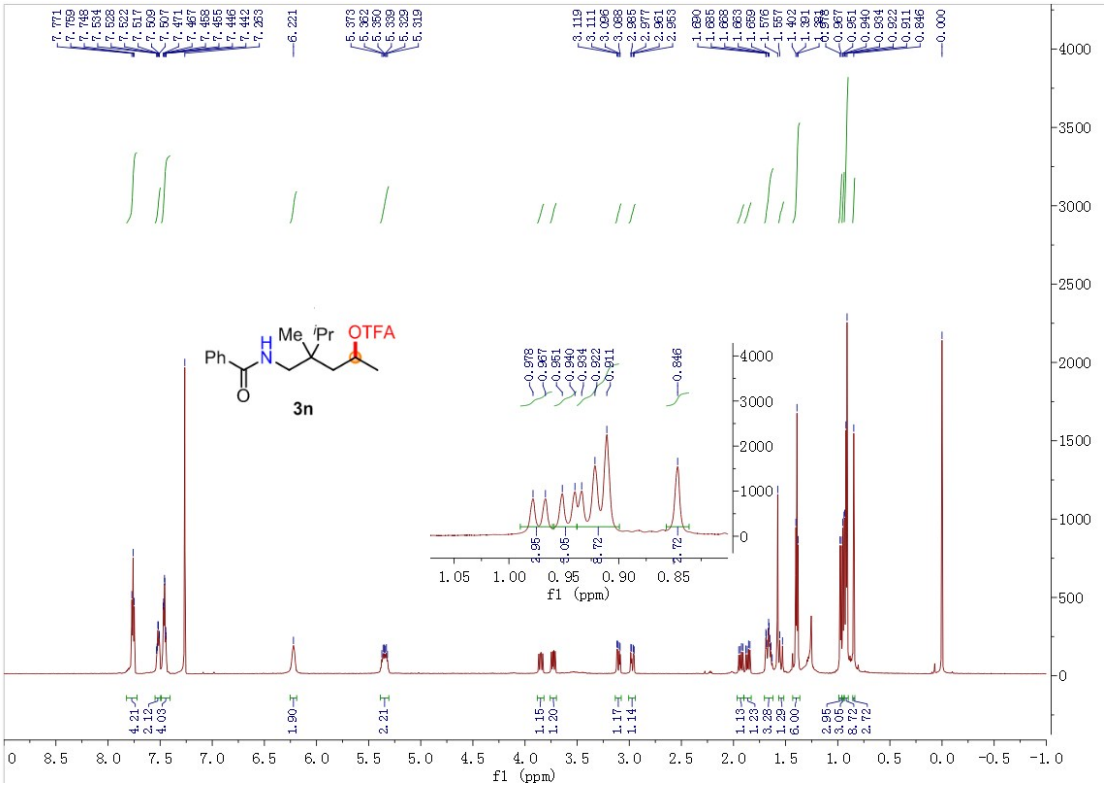
117.30
115.40
113.51
111.61
77.21
77.00
76.79
74.09
44.63
40.49
39.35
37.67
37.43
21.72
16.28
14.76
14.72
Ph
H
N
O
nPr
nPr
OTFA
3m
f1 (ppm)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7.522
7.517
7.509
7.507
7.471
7.467
7.458
7.455
7.446
7.442
7.263
6.221
5.373
5.362
5.350
5.339
5.329
5.319
3.119
3.111
3.096
3.088
2.985
2.977
2.961
2.953
1.690
1.685
1.668
1.663
1.659
1.576
1.557
1.492
1.481
0.978
0.967
0.961
0.940
0.934
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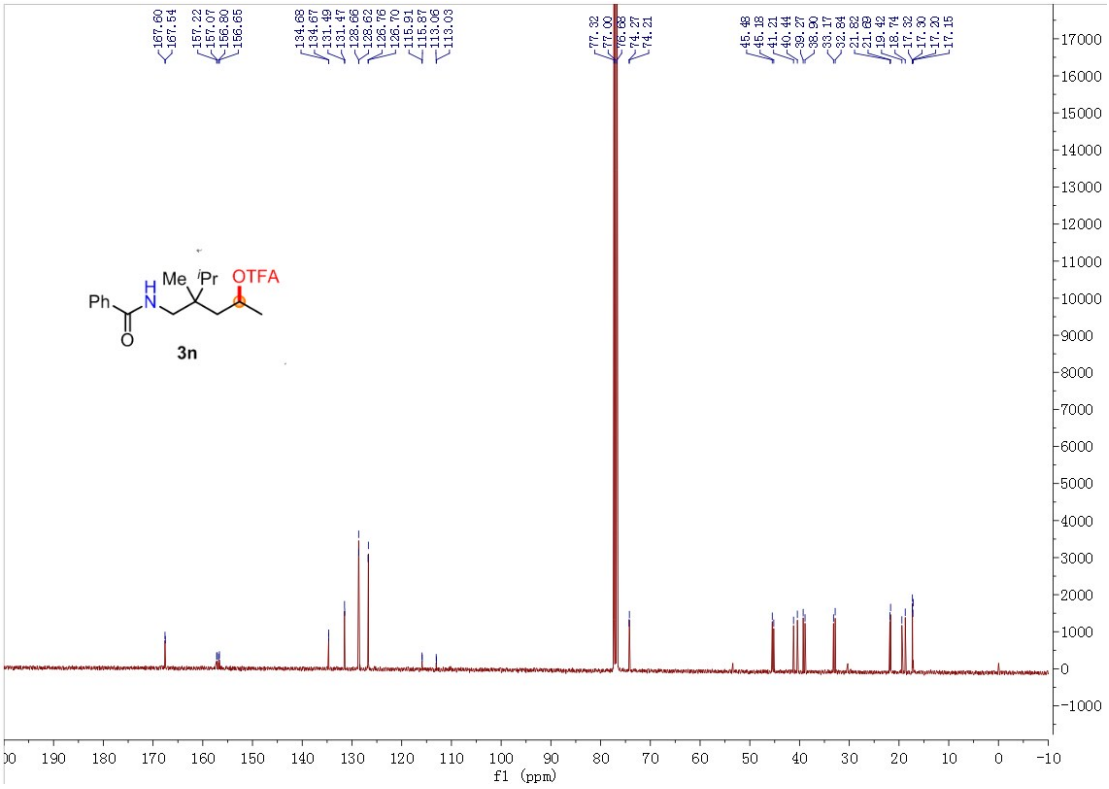
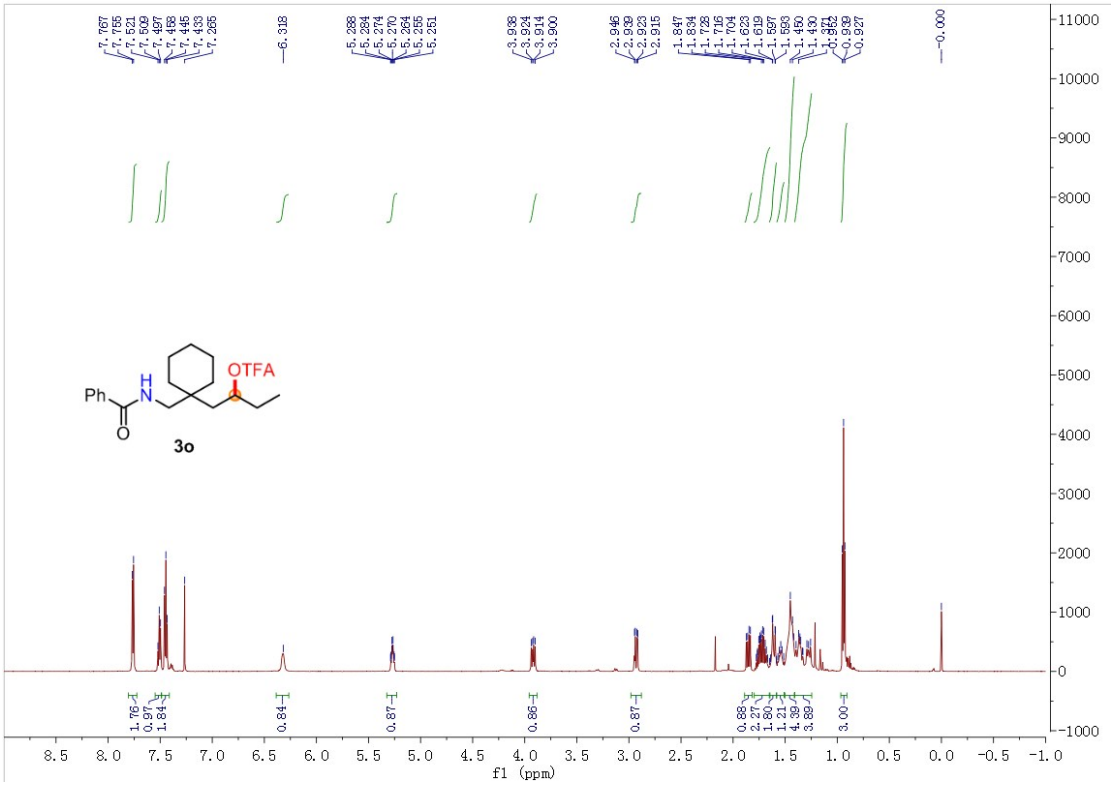
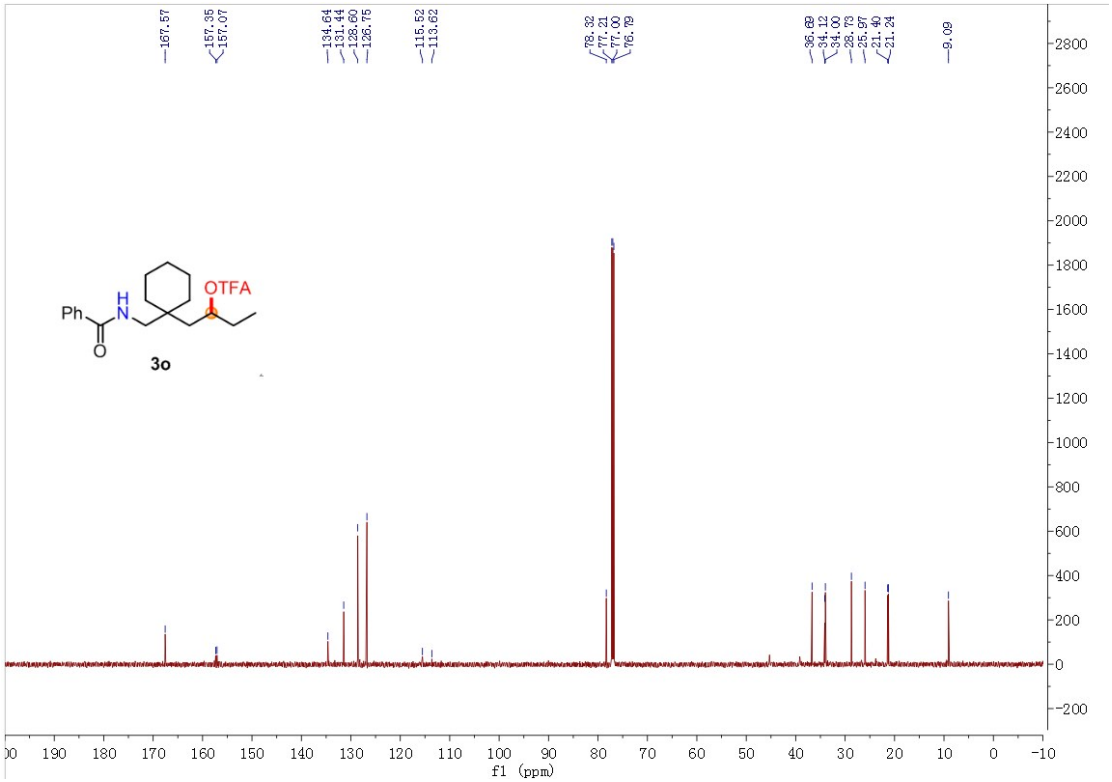
0.911
0.846
0.000
Ph
H
N
O
Me
iPr
OTFA
3n
f1 (ppm)


Ph
H
N
O
Me
iPr
OTFA
3n
f1 (ppm)


Ph
H
N
O
OTFA
3o
f1 (ppm)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157.07
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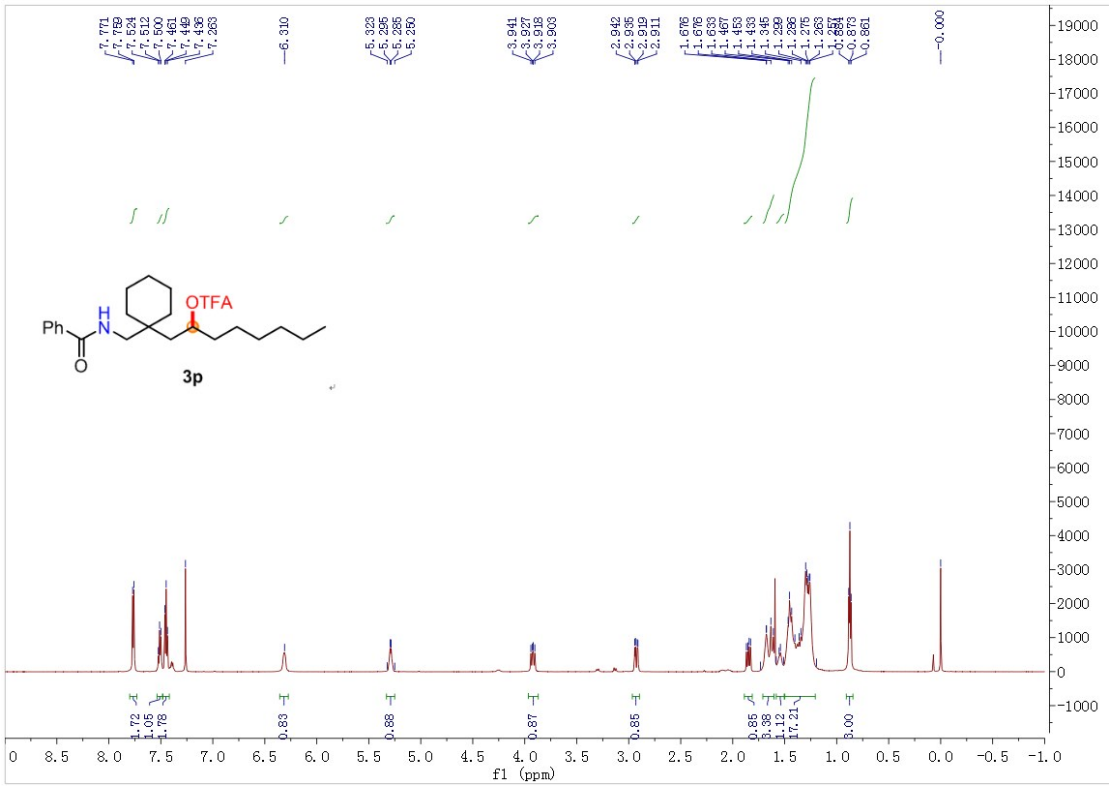
128.60
126.75
115.52
113.62
78.32
77.21
77.00
76.79
36.69
34.12
34.00
28.73
25.97
21.40
21.24
9.09
OTFA
Ph
H
N
O
3o
f1 (ppm)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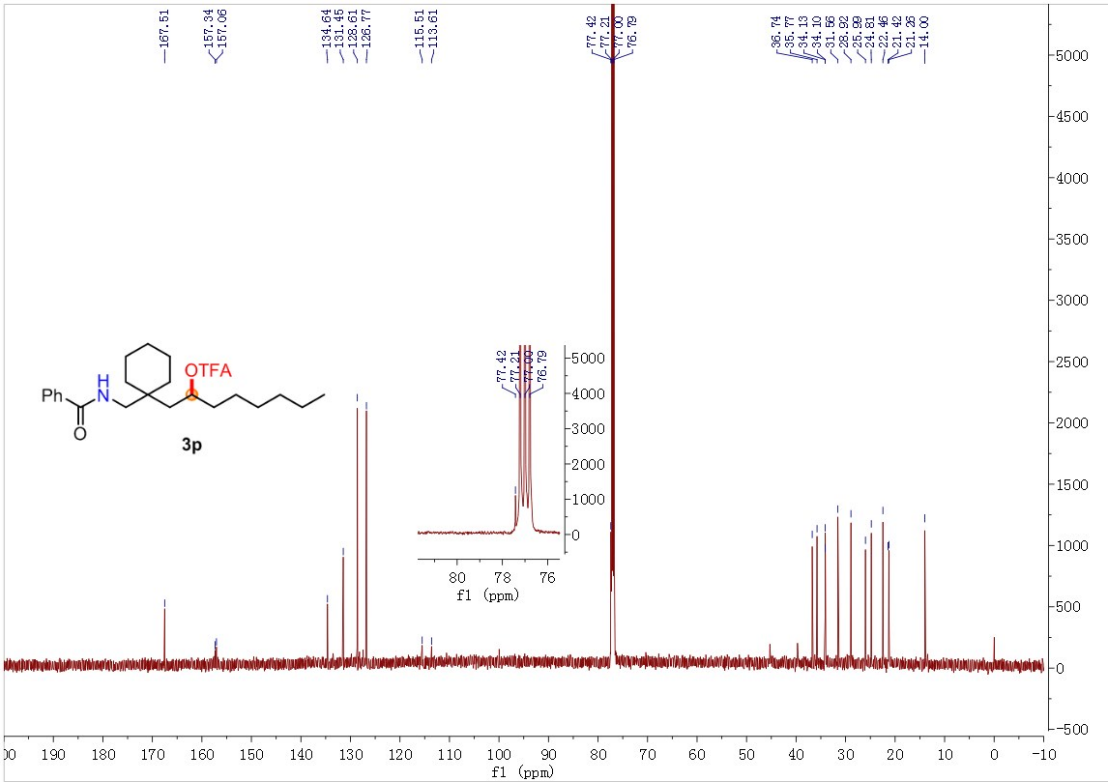
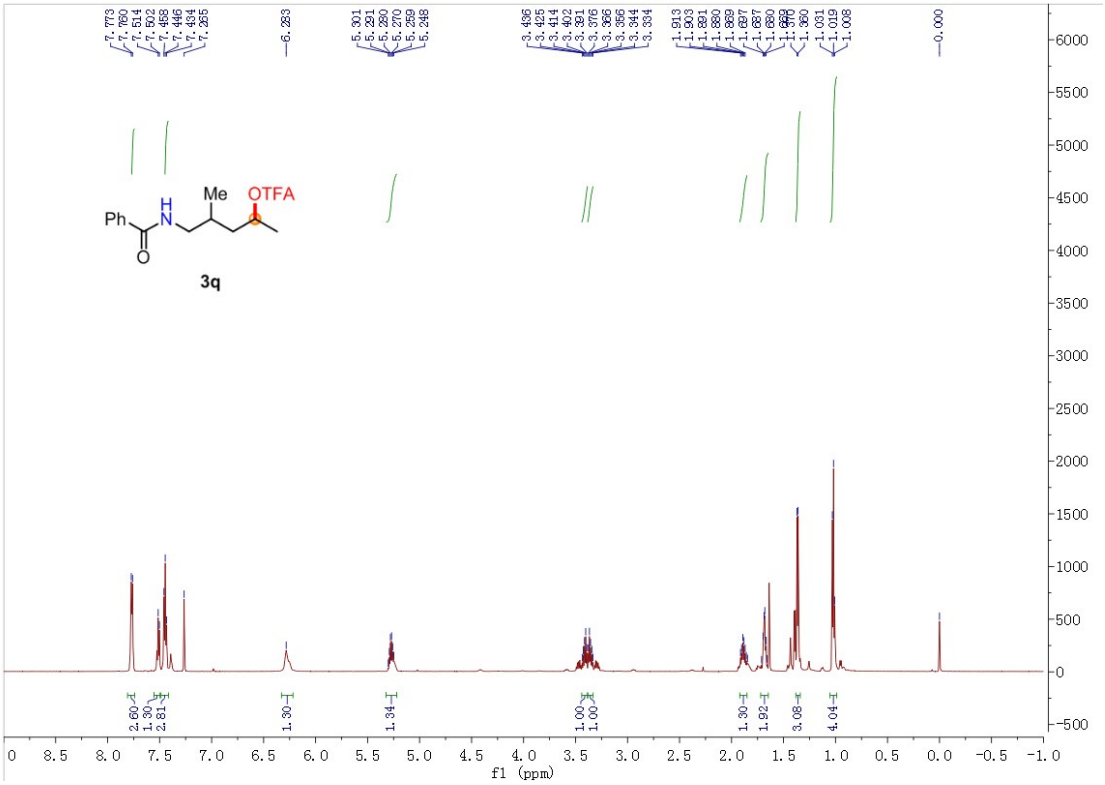
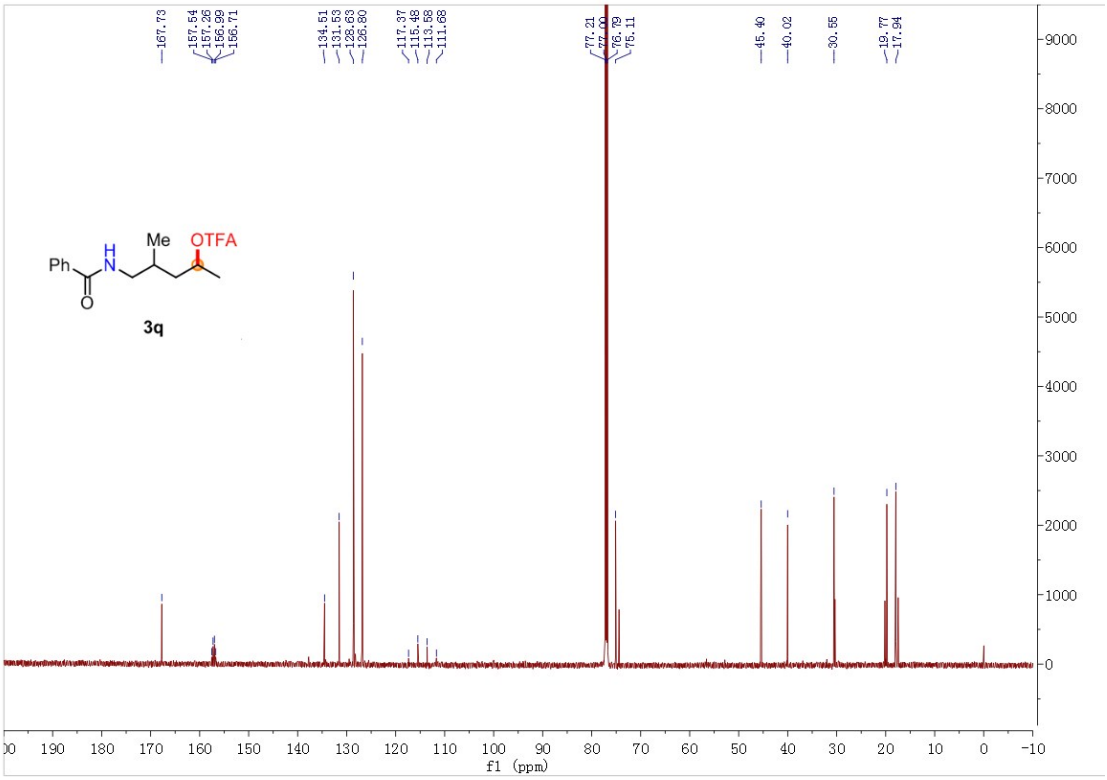
7.789
7.524
7.512
7.500
7.461
7.449
7.436
7.263
6.310
5.323
5.295
5.285
5.280
3.941
3.927
3.918
3.903
2.942
2.935
2.919
2.911
1.676
1.656
1.633
1.467
1.453
1.433
1.345
1.299
1.286
1.275
1.263
0.873
0.861
0.000
OTFA
Ph
H
N
O
3p
1.72
1.05
1.78
0.83
0.88
0.87
0.85
0.85
3.38
1.12
17.21
3.00
f1 (ppm)


OTFA
Ph
H
N
O
3p
f1 (ppm)


Me
OTFA
Ph
H
N
O
3q
f1 (ppm)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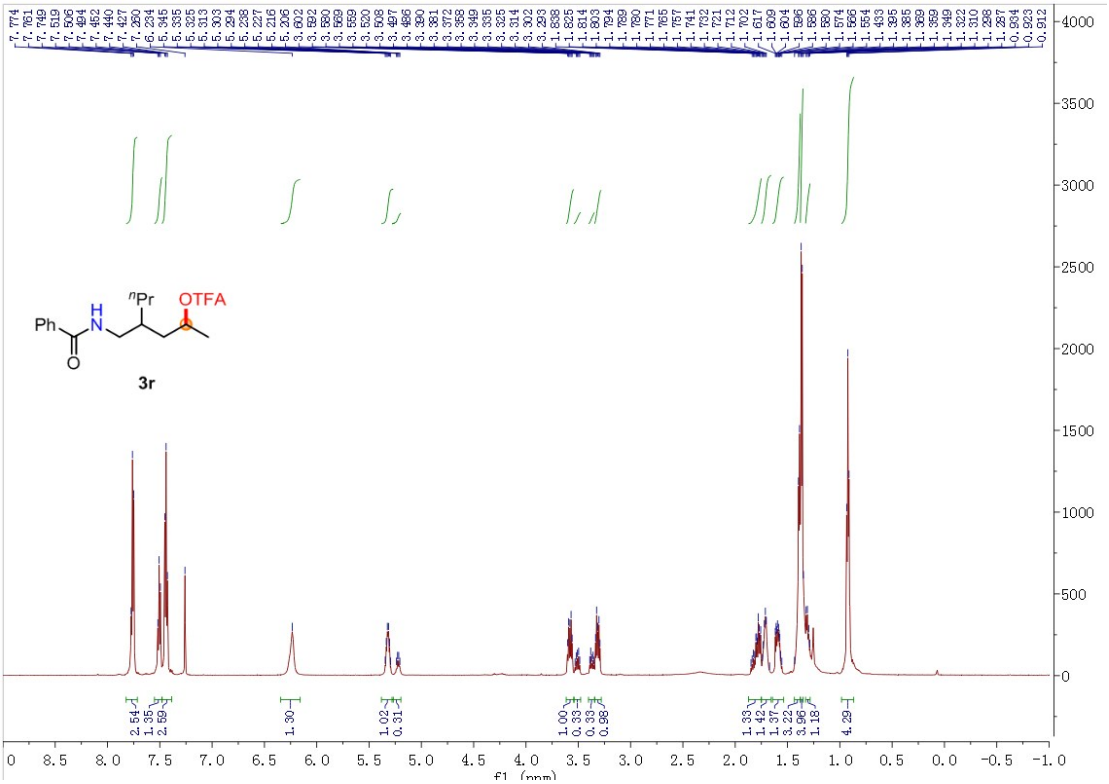
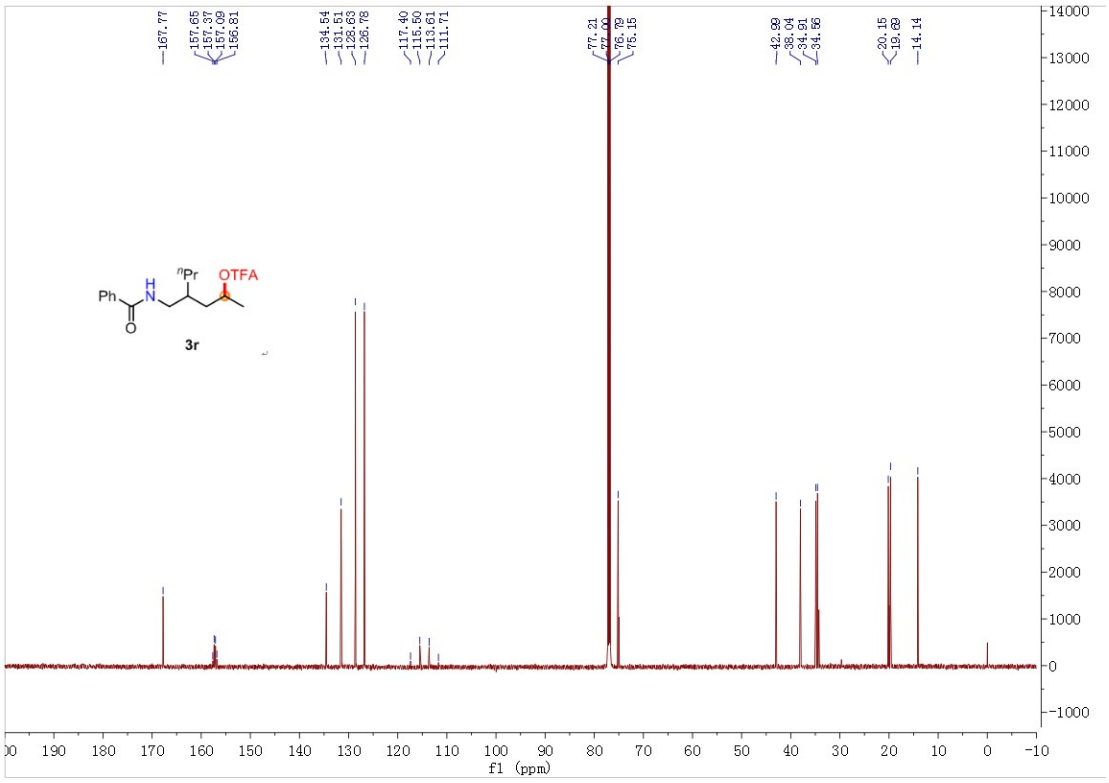
134.51
131.53
128.63
126.80
117.97
115.48
113.88
111.68
77.21
77.00
76.79
75.11
45.40
40.02
30.55
19.77
17.94
Ph
H
N
O
Me
OTFA
3q
f1 (ppm)


Ph
H
N
O
nPr
OTFA
3r
f1 (ppm)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117.40
115.60
113.61
111.71
77.21
77.00
76.79
76.15
42.89
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20.15
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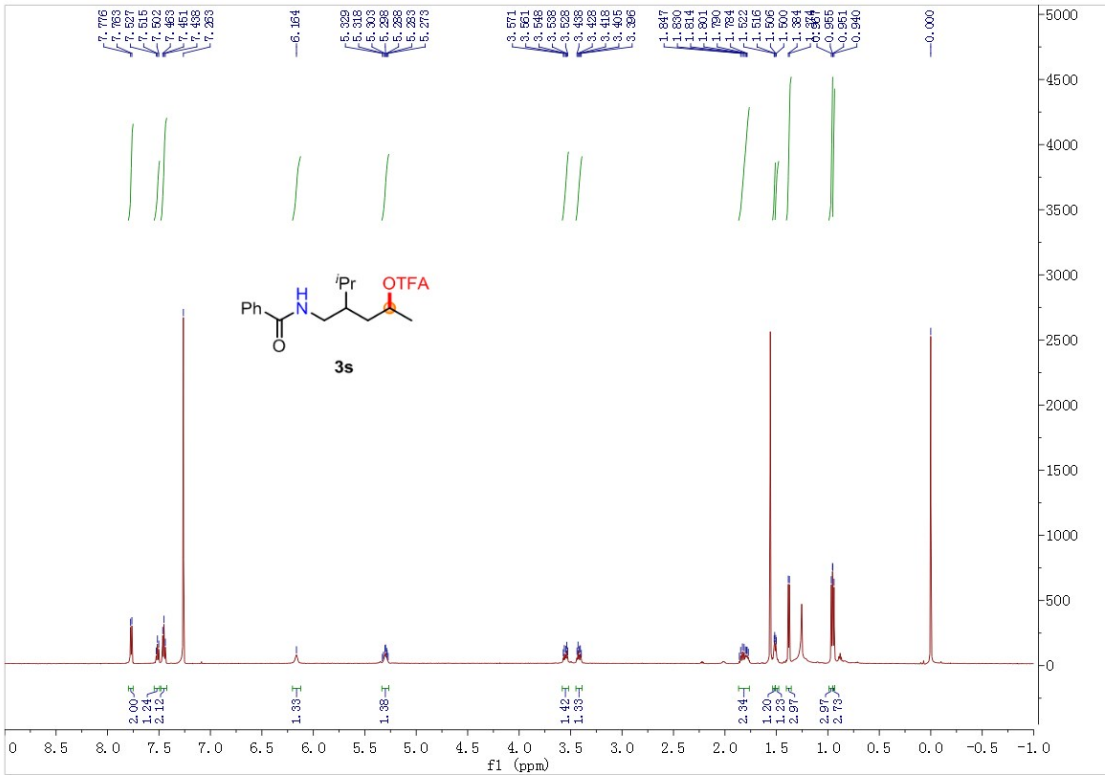
14.14
Ph
H
N
O
iPr
OTFA
3r
f1 (ppm)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7.502
7.463
7.451
7.438
7.263
6.164
5.329
5.313
5.303
5.298
5.288
5.283
5.273
3.571
3.561
3.548
3.538
3.528
3.438
3.428
3.418
3.405
3.396
1.847
1.830
1.814
1.801
1.790
1.784
1.522
1.516
1.506
1.500
1.384
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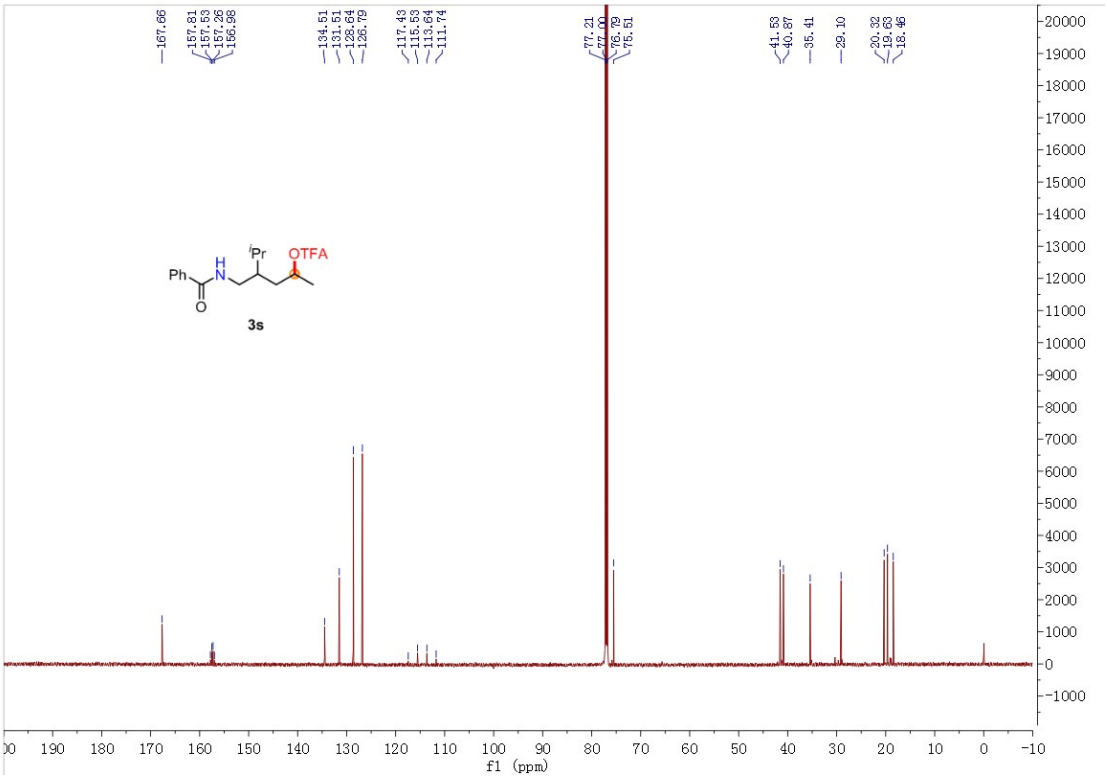
0.961
0.940
0.000
Ph
H
N
O
iPr
OTFA
3s
f1 (ppm)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131.51
128.64
126.79
117.43
115.53
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111.74
77.21
77.00
76.79
75.51
41.53
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20.32
19.63
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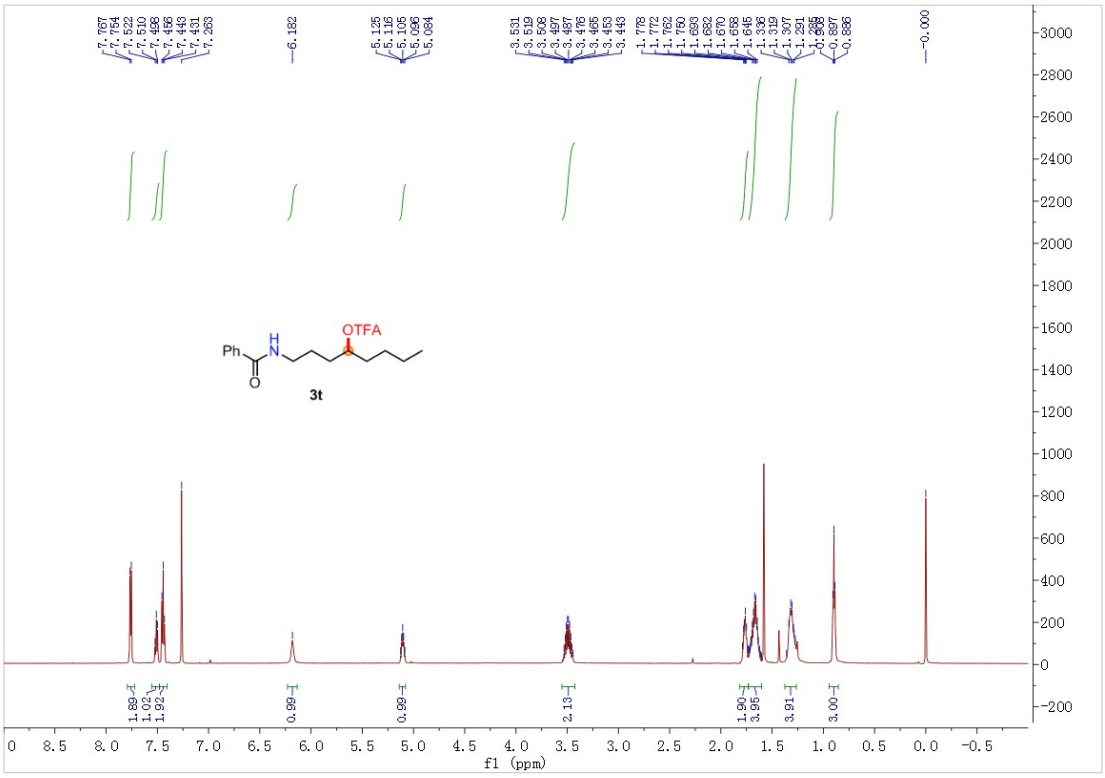
Ph
H
N
O
iPr
OTFA
3s
f1 (ppm)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7.466
7.443
7.431
7.263
6.182
5.135
5.116
5.105
5.086
5.084
3.531
3.519
3.506
3.497
3.487
3.476
3.465
3.453
3.443
1.778
1.772
1.762
1.753
1.688
1.682
1.670
1.668
1.645
1.336
1.319
1.307
1.291
0.897
0.888
-0.000
1.89
1.02
1.92
0.99
0.99
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1.90
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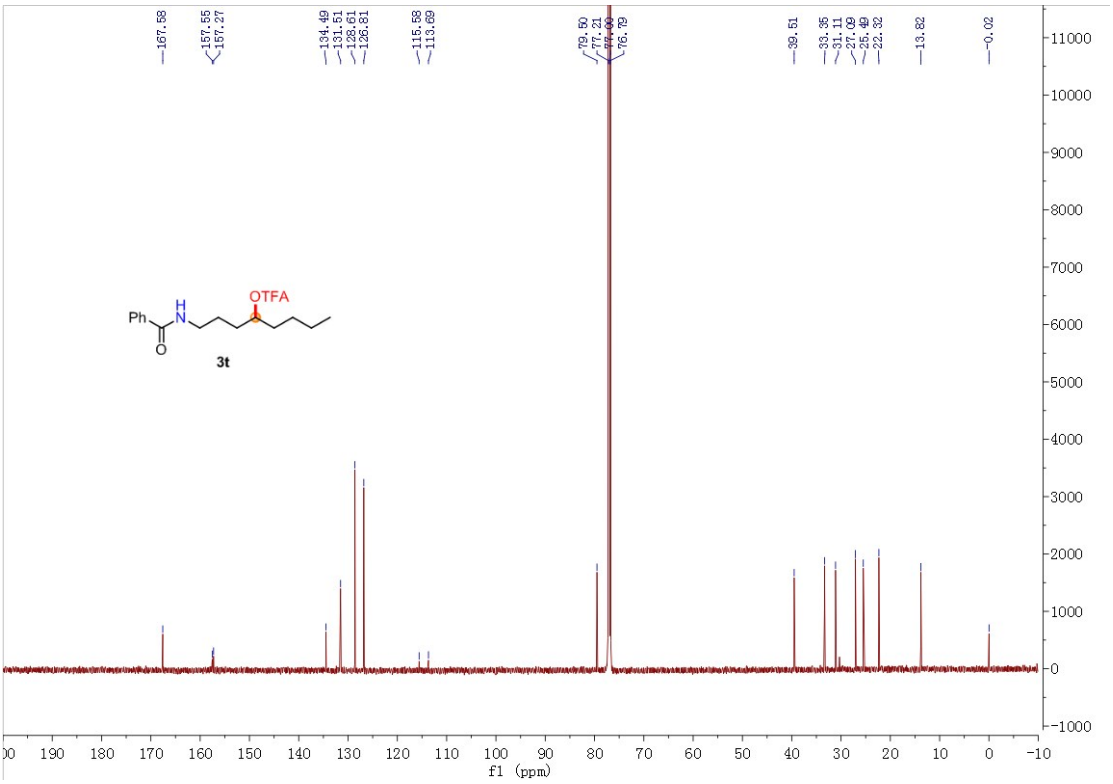
3.91
3.00
Ph
H
N
O
OTFA
3t
f1 (ppm)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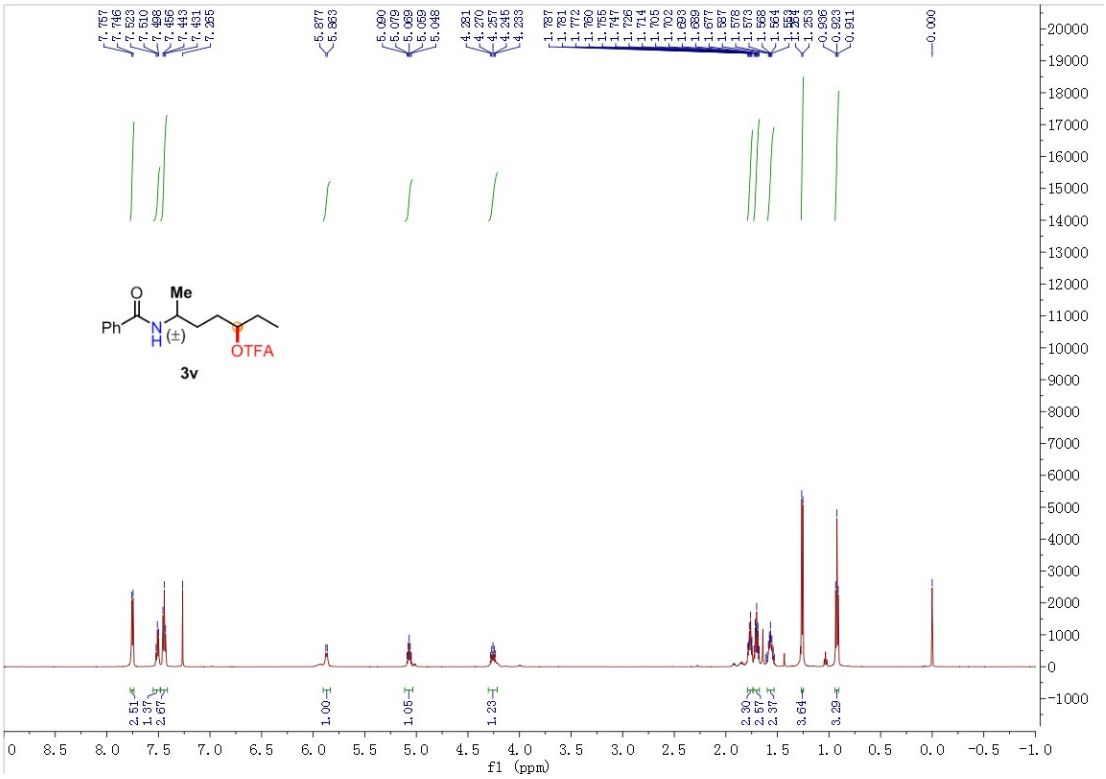
128.61
126.81
115.58
113.69
79.50
77.21
77.00
76.79
39.61
33.35
31.11
27.09
25.49
22.32
13.82
-0.02
OTFA
Ph
H
N
O
3t
f1 (ppm)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5.079
5.069
5.059
5.048
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4.270
4.257
4.245
4.233
1.787
1.781
1.772
1.760
1.755
1.747
1.726
1.714
1.705
1.702
1.693
1.689
1.677
1.668
1.573
1.564
1.253
0.936
0.923
0.911
-0.000
O
Me
Ph
N
H
(±)
OTFA
3v
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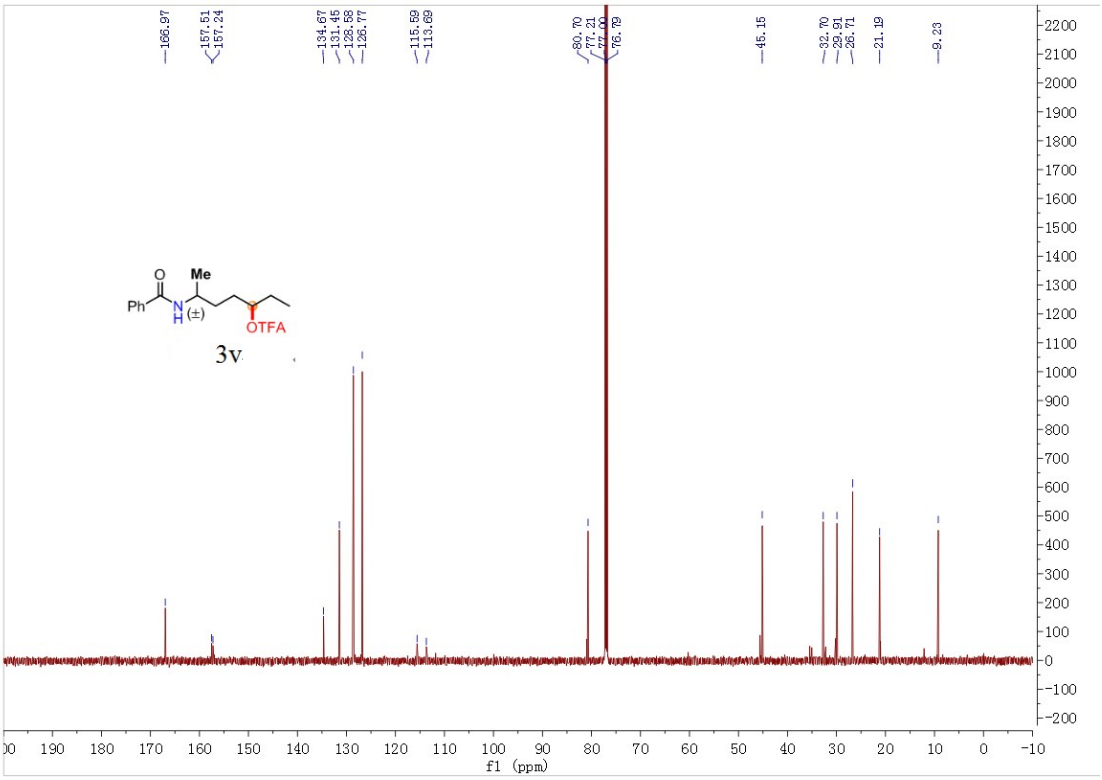
1.37
2.67
1.00
1.05
1.23
2.30
2.57
2.37
3.64
3.29
f1 (ppm)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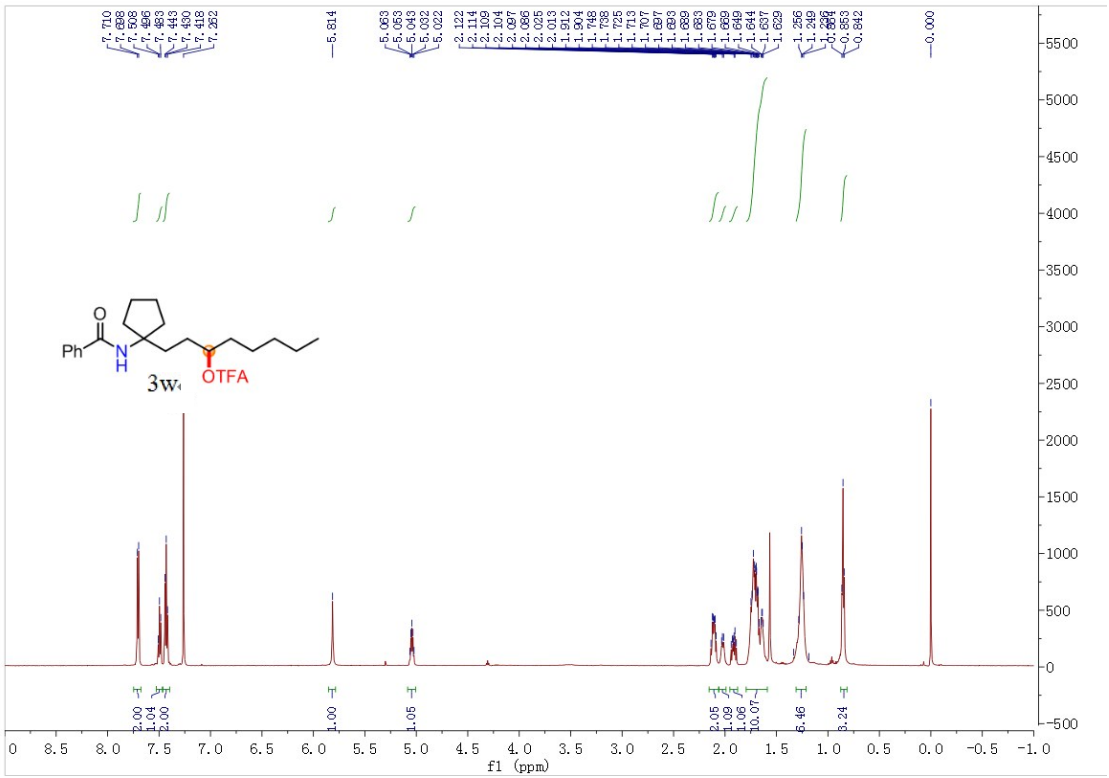
128.58
126.77
115.59
113.69
80.70
77.21
76.79
45.15
32.70
29.91
26.71
21.19
9.23
Ph
N
H
(±)
Me
OTFA
3v
f1 (ppm)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5.814
5.063
5.053
5.043
5.032
5.022
2.122
2.114
2.109
2.104
2.097
2.086
2.025
2.013
1.912
1.904
1.748
1.738
1.725
1.713
1.707
1.697
1.693
1.683
1.679
1.669
1.649
1.644
1.637
1.629
1.256
1.249
0.863
0.842
0.000
Ph
N
H
OTFA
3w
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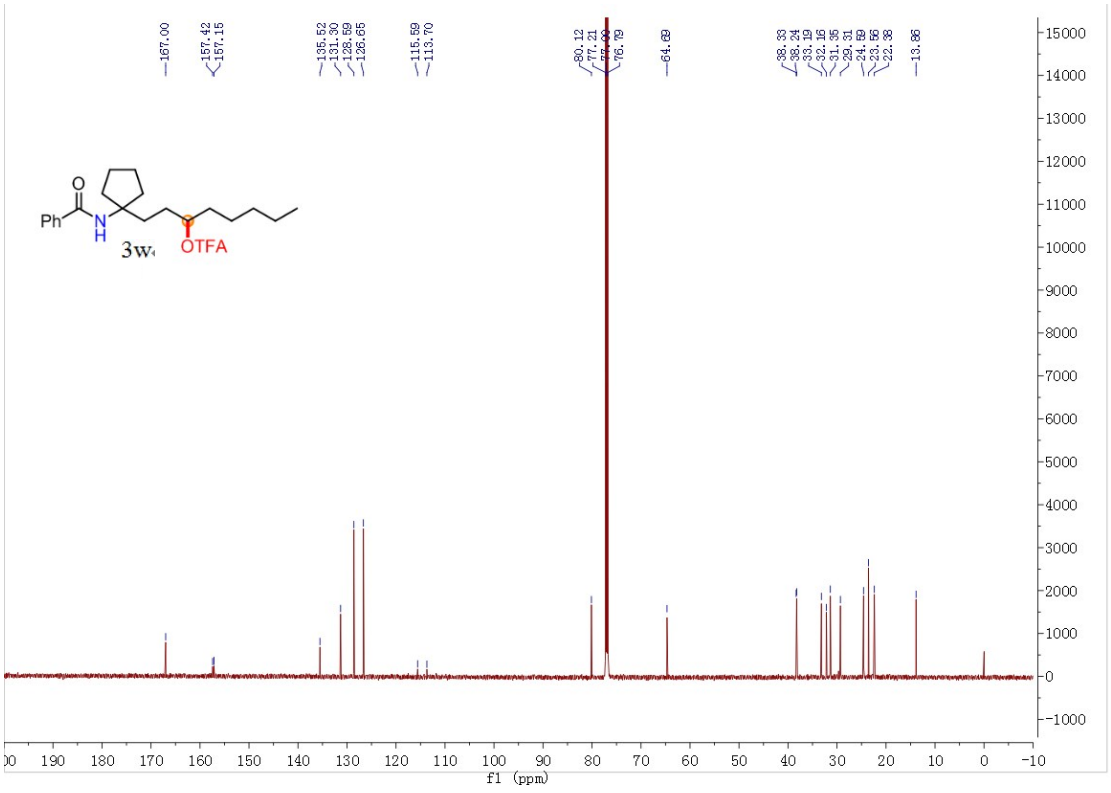
1.00
1.05
2.05
1.09
1.06
10.07
6.46
3.24
f1 (ppm)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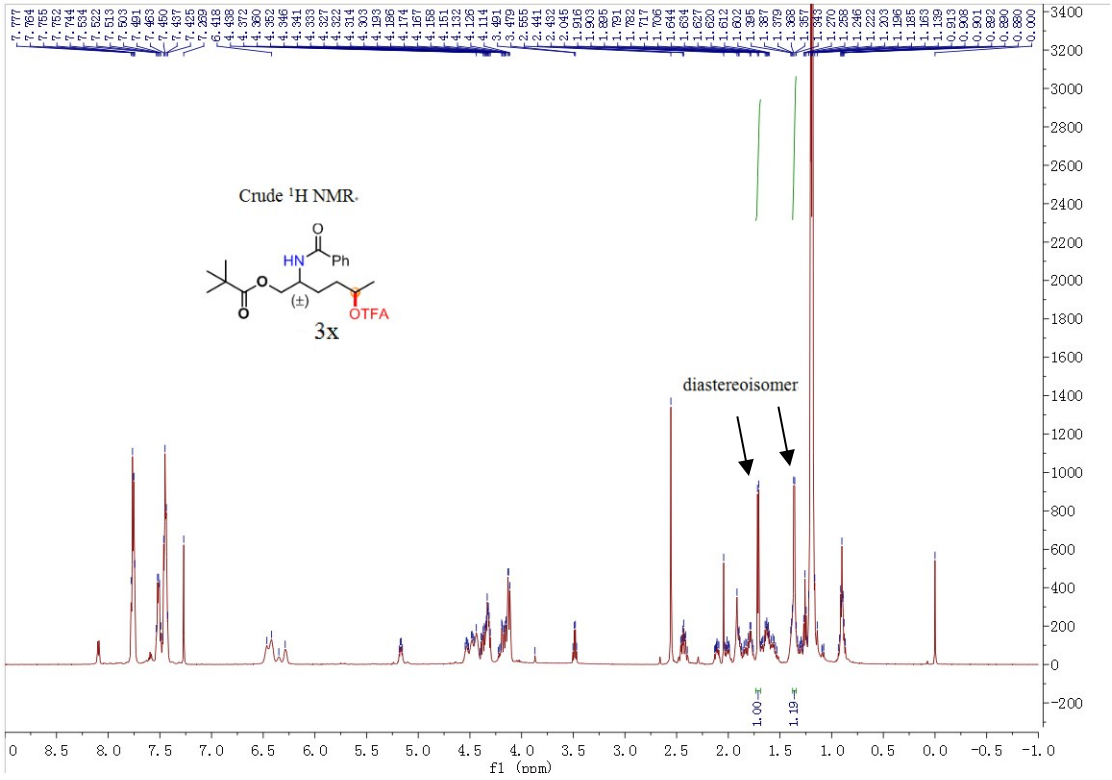
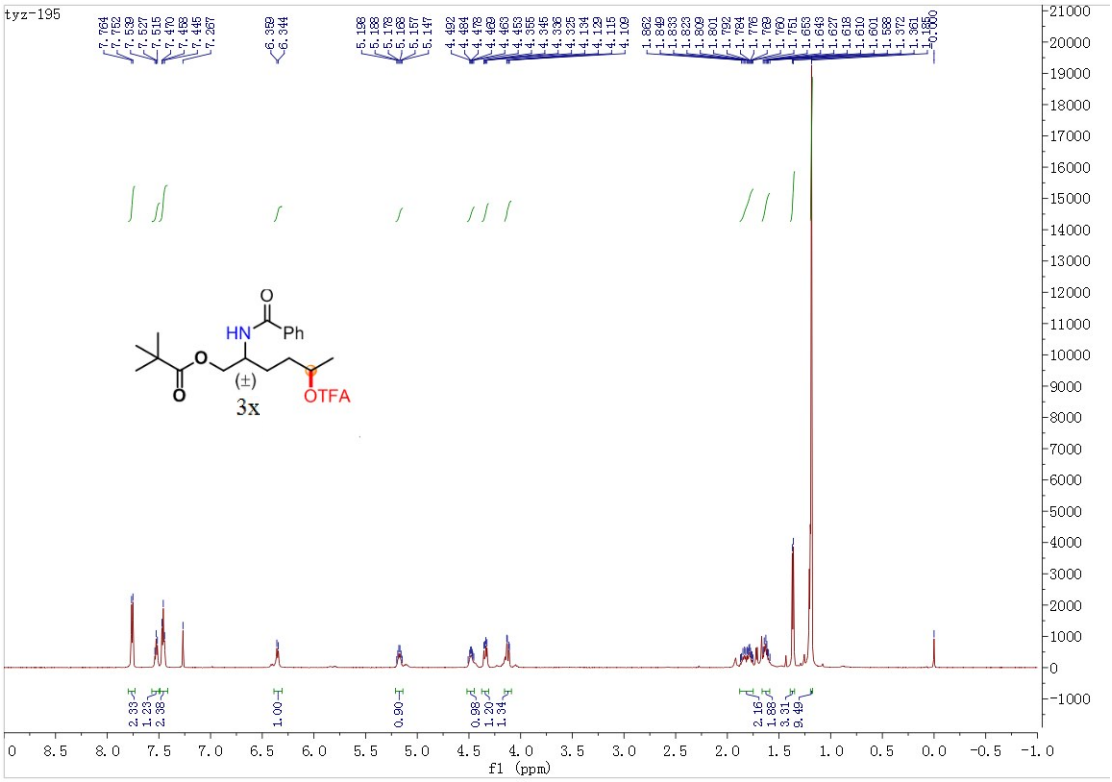
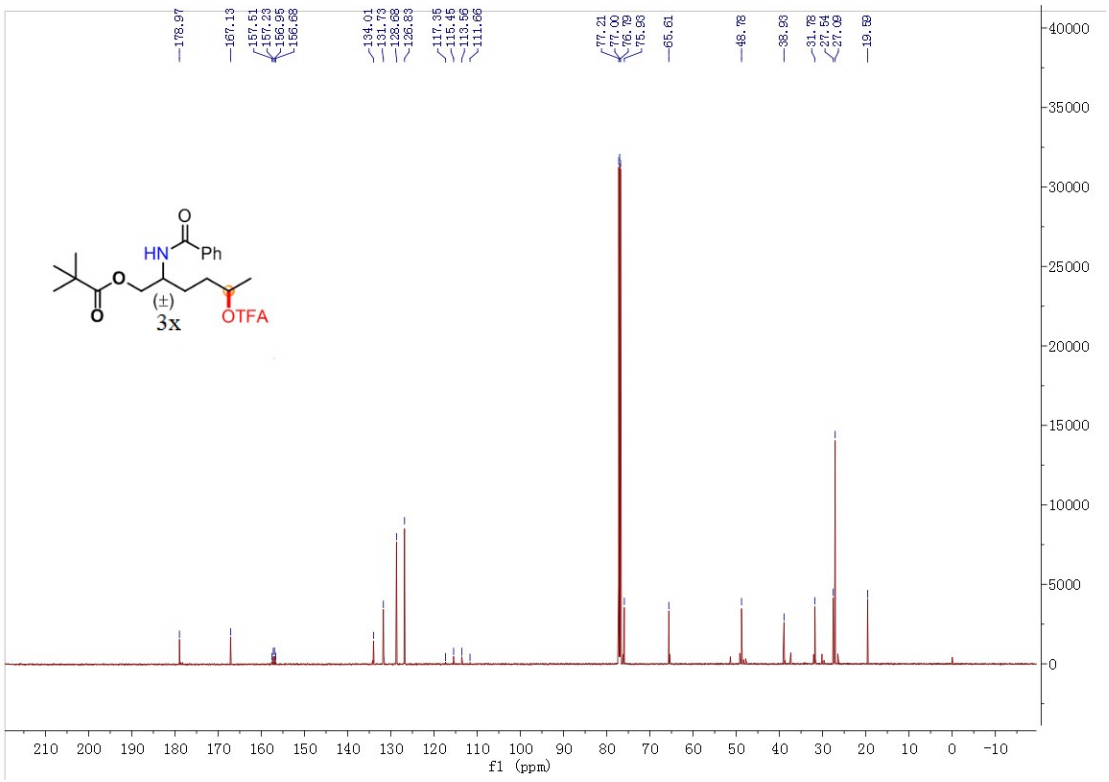
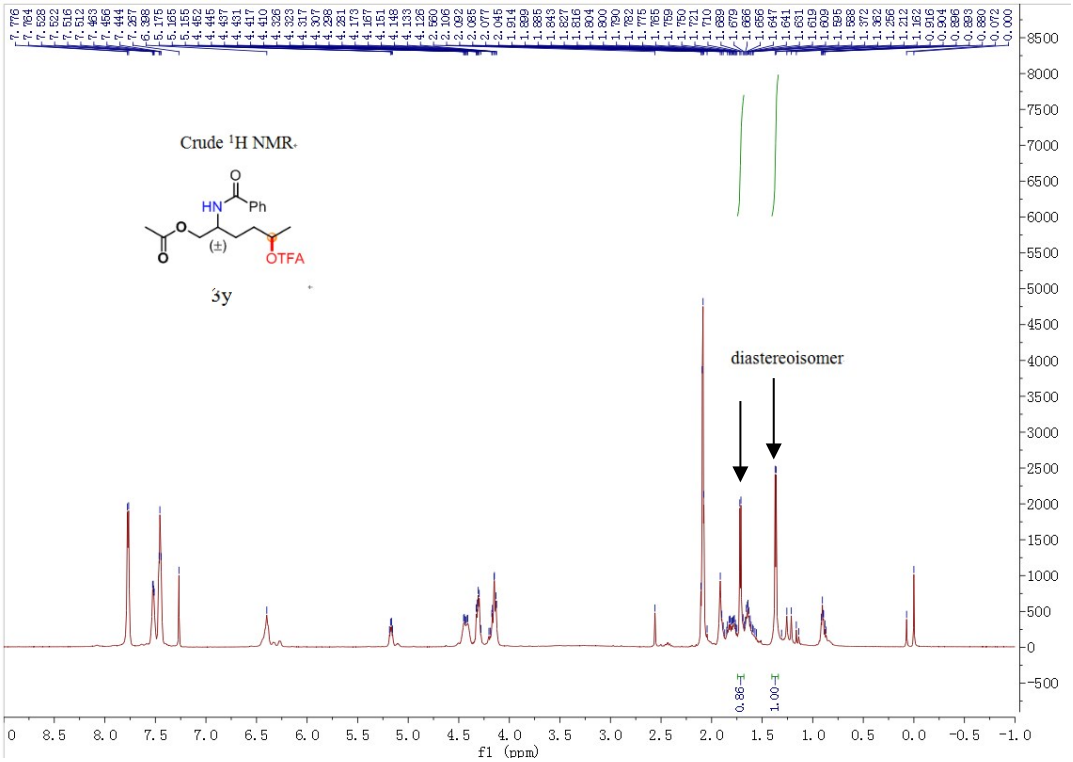
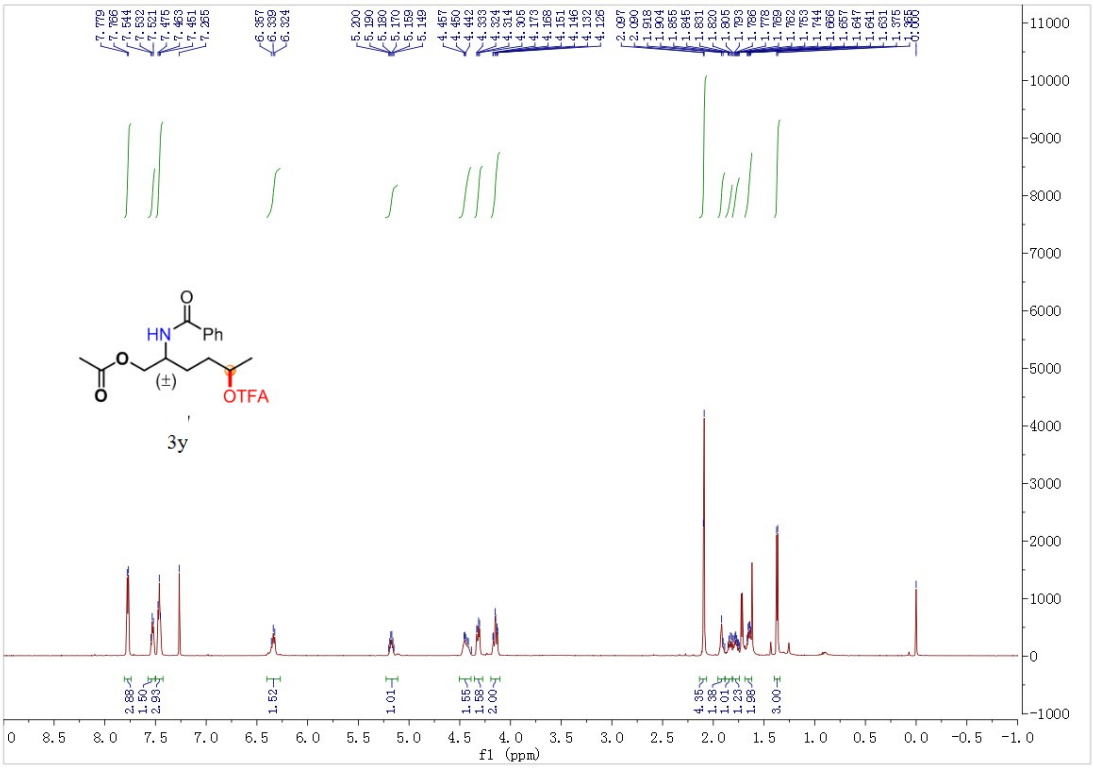
128.59
126.65
115.69
113.70
80.12
77.21
76.79
64.09
38.33
38.24
33.19
32.16
31.35
29.31
24.69
23.66
22.38
13.86
Ph
N
H
O
OTFA
3w
f1 (ppm)


Crude ¹H NMR
HN
Ph
O
(±)
OTFA
3x
diastereoisomer
1.00
1.19
f1 (ppm)


tyz-195
HN
Ph
(±)
3x
OTFA
f1 (ppm)


HN
Ph
(±)
3x
OTFA
f1 (ppm)


Crude ^{1}H NMR
HN
Ph
O
(±)
OTFA
3y
diastereoisomer
0.86
1.00
f1 (ppm)


HN
Ph
O
(±)
OTFA
3y
2.88
1.50
2.93
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1.01
1.55
1.58
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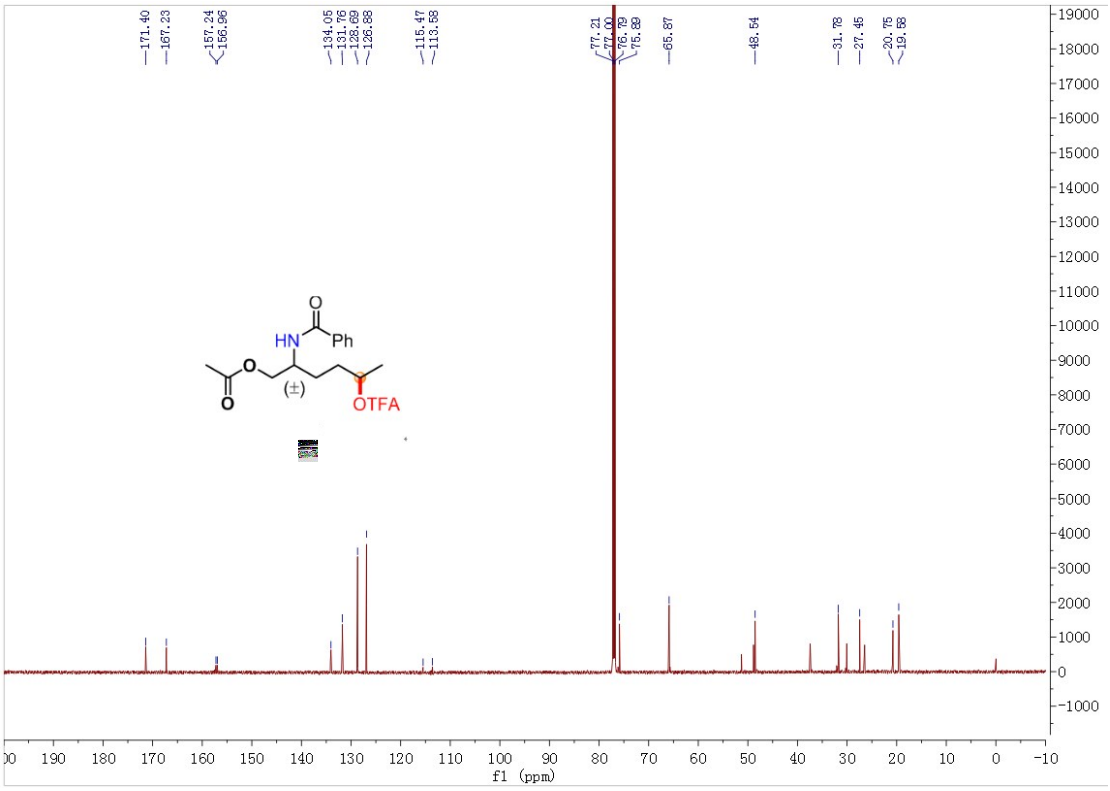
1.01
1.23
1.98
3.00
f1 (ppm)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134.05
131.76
128.69
126.88
115.47
113.58
77.21
77.00
76.79
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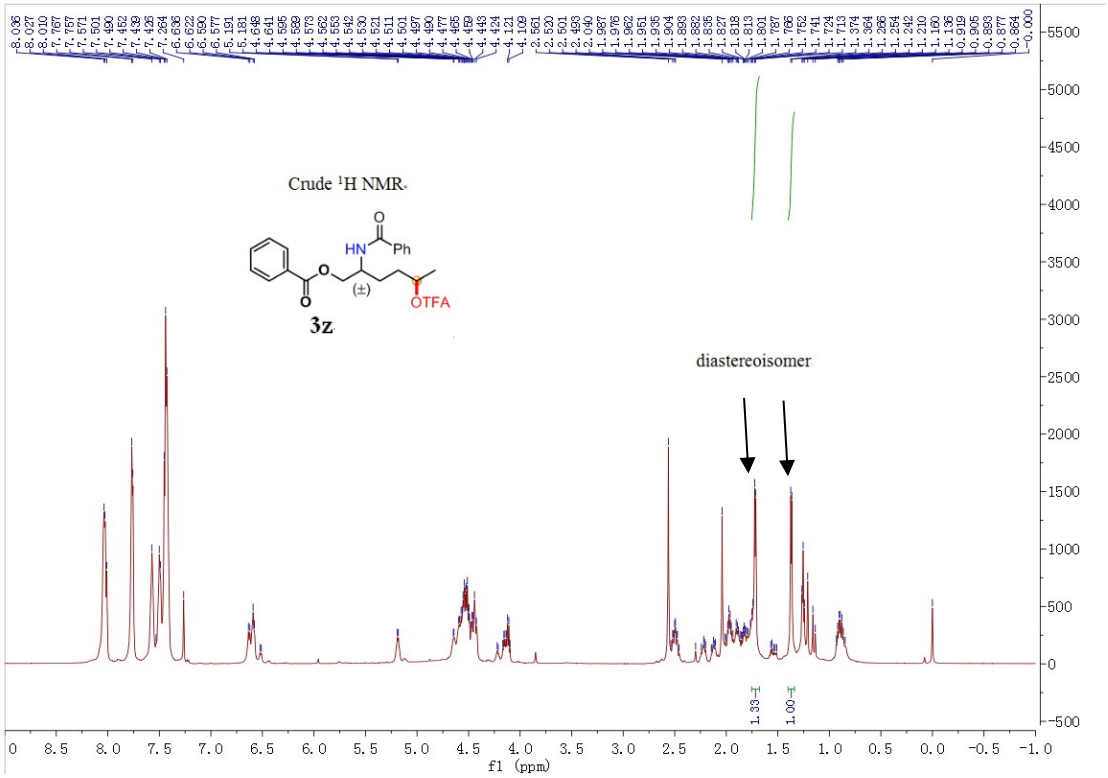
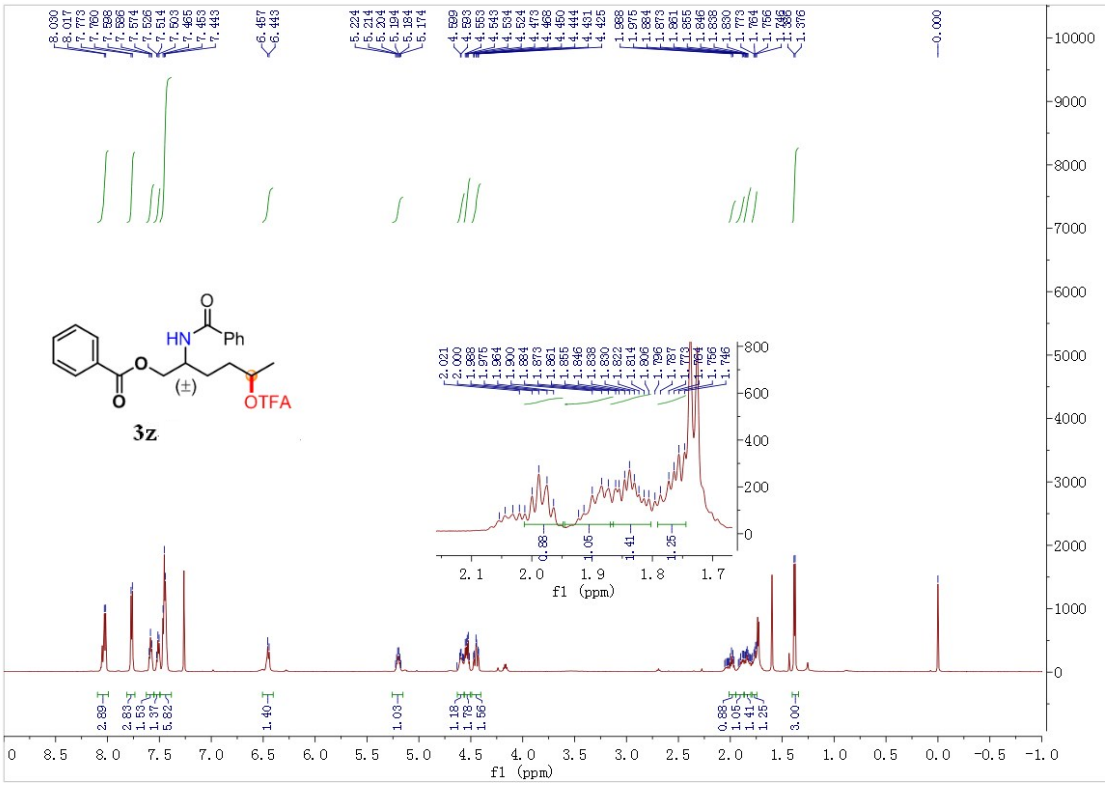
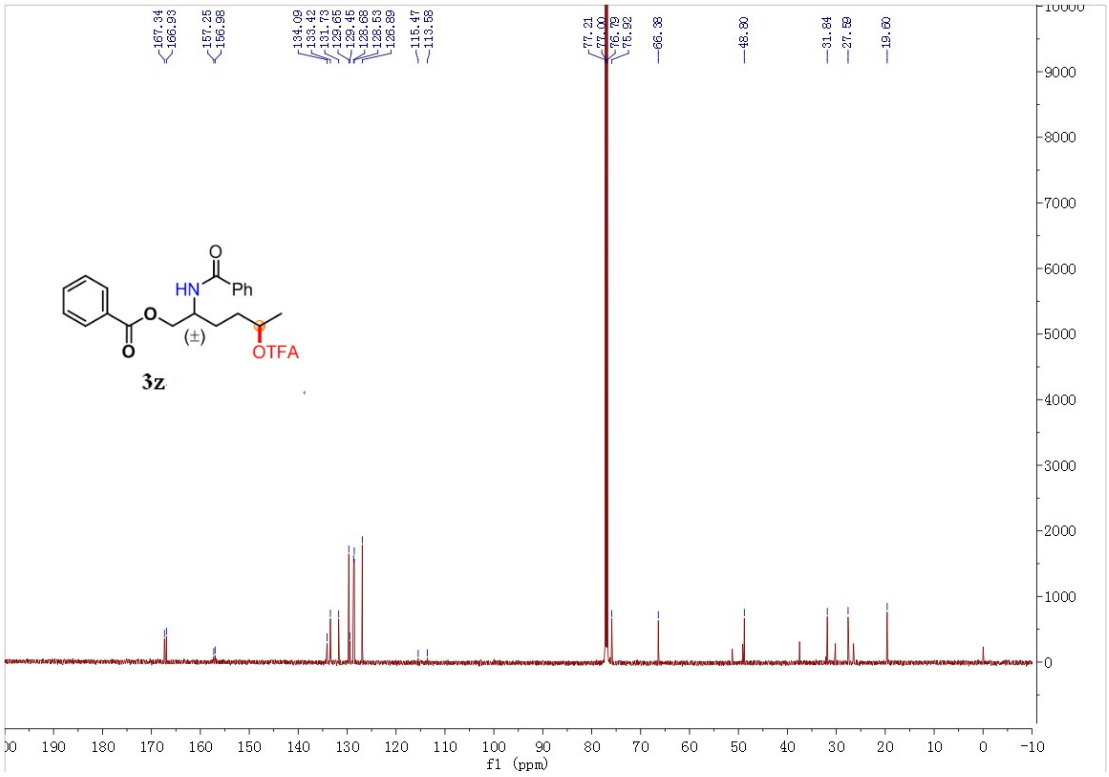
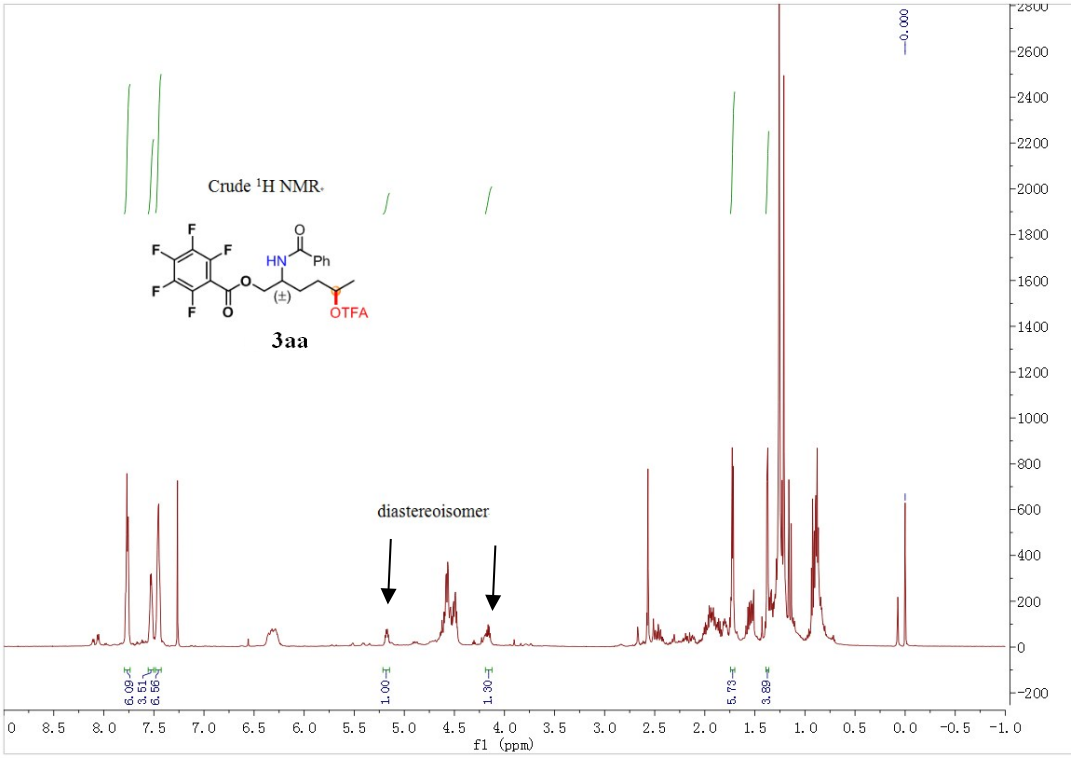
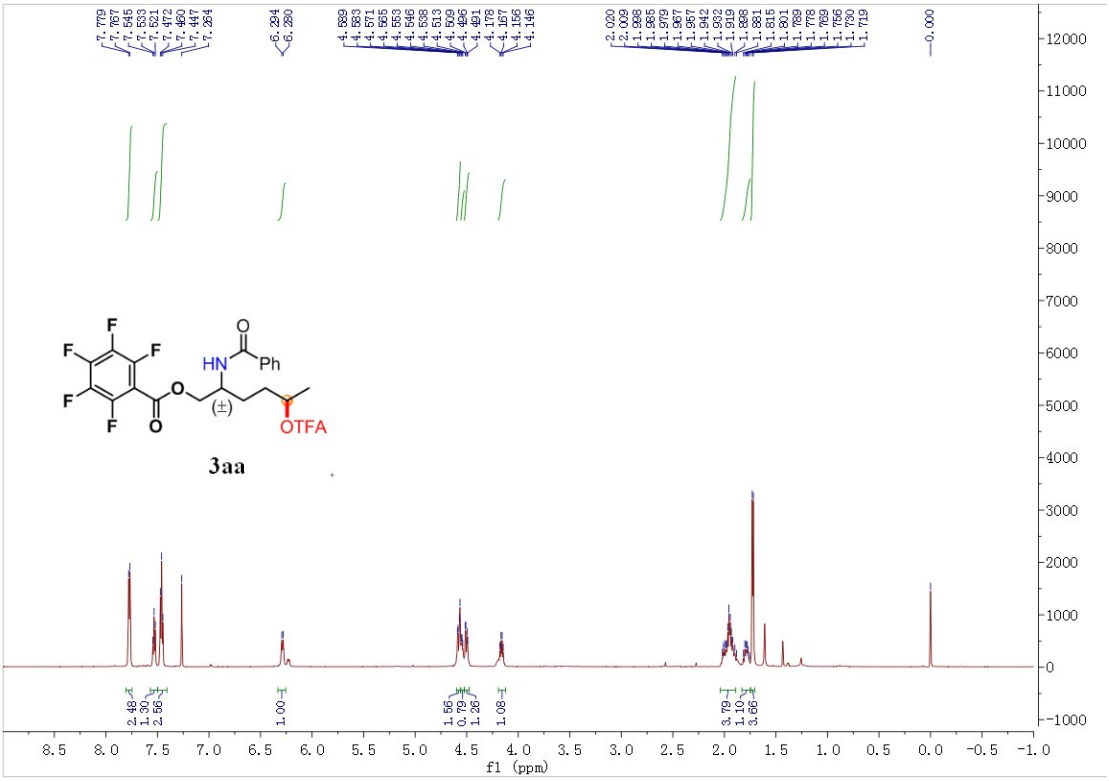
65.87
48.54
31.78
27.45
20.75
19.58
HN
Ph
O
(±)
OTFA
f1 (ppm)

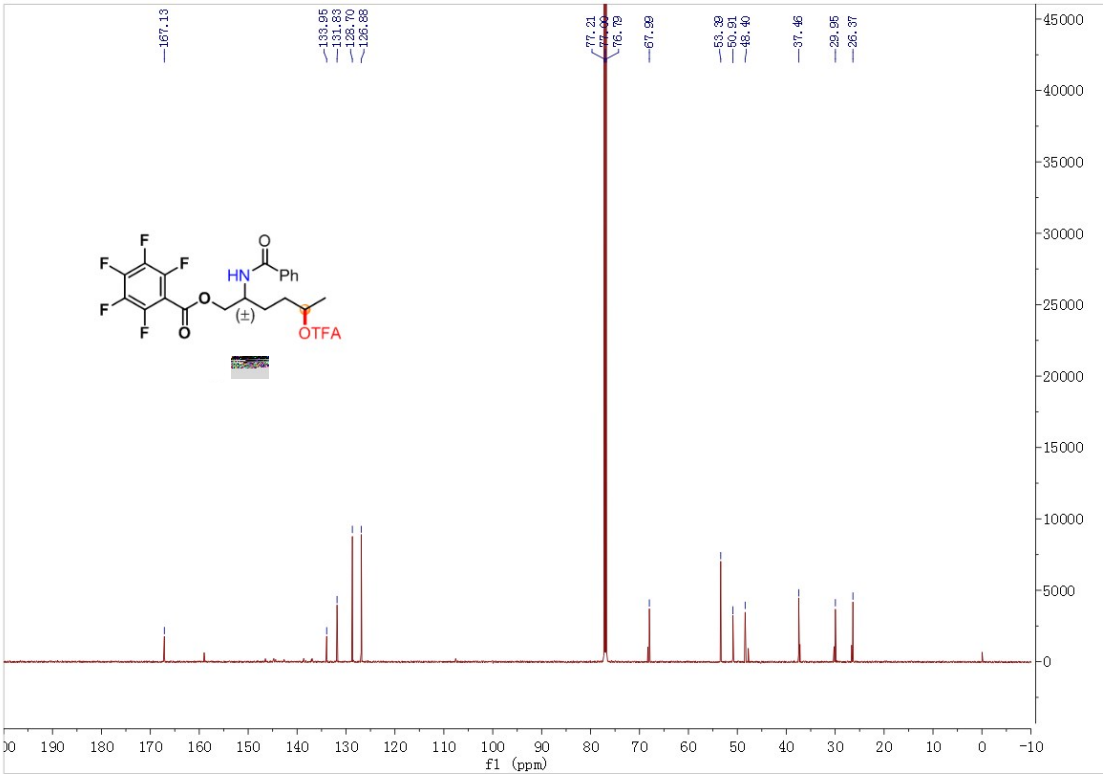

Crude ¹H NMR
HN
Ph
O
(±)
OTFA
3z
diastereoisomer
1.33
1.00
f1 (ppm)

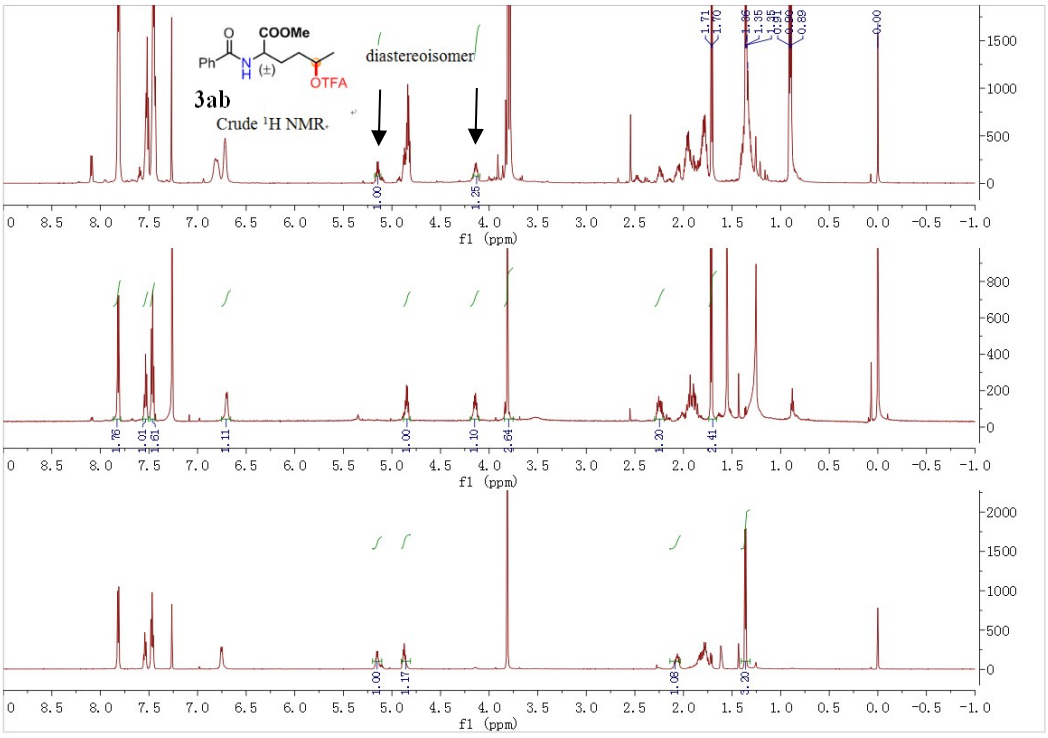

HN
Ph
O
(±)
OTFA
3z
f1 (ppm)

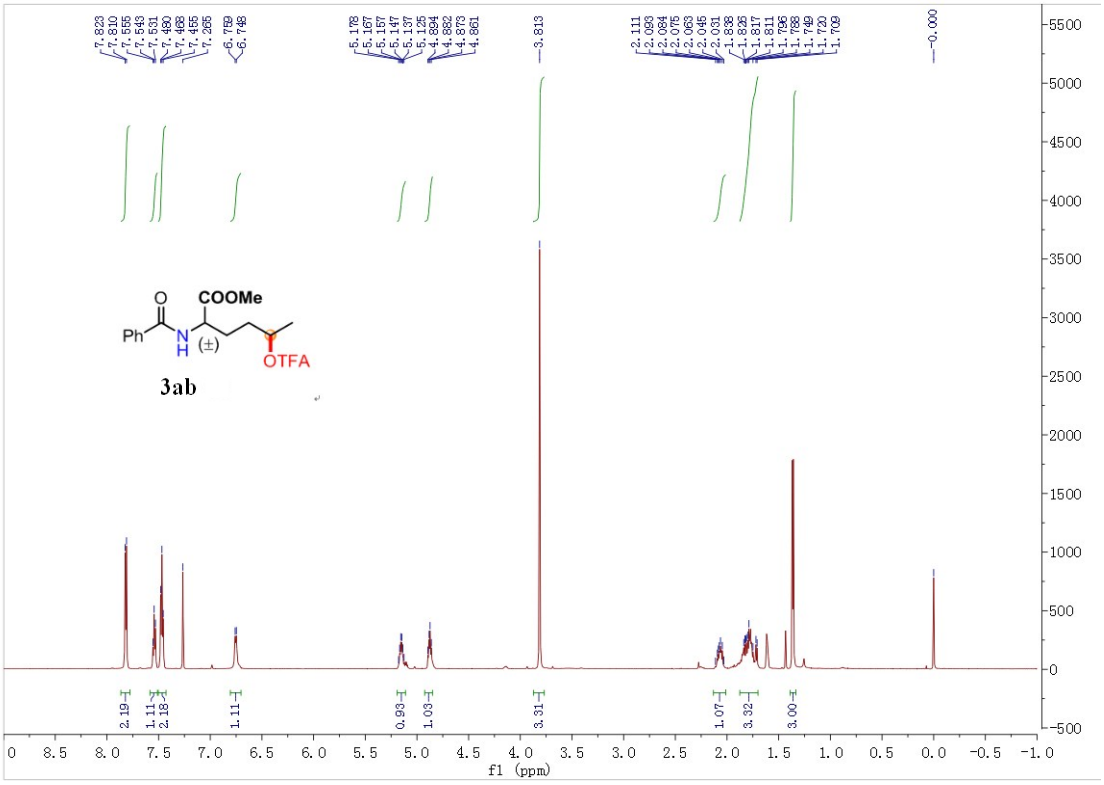

HN
Ph
O
(±)
OTFA
3z
f1 (ppm)

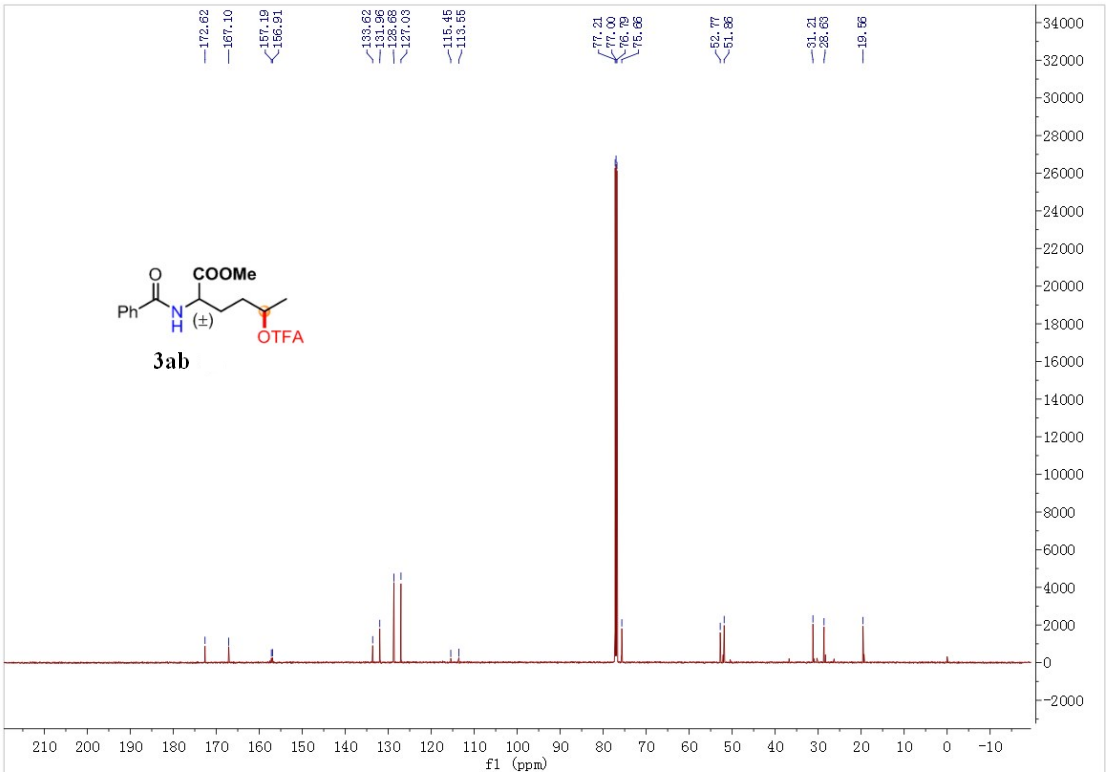

Crude ¹H NMR
3aa
diastereoisomer
f1 (ppm)

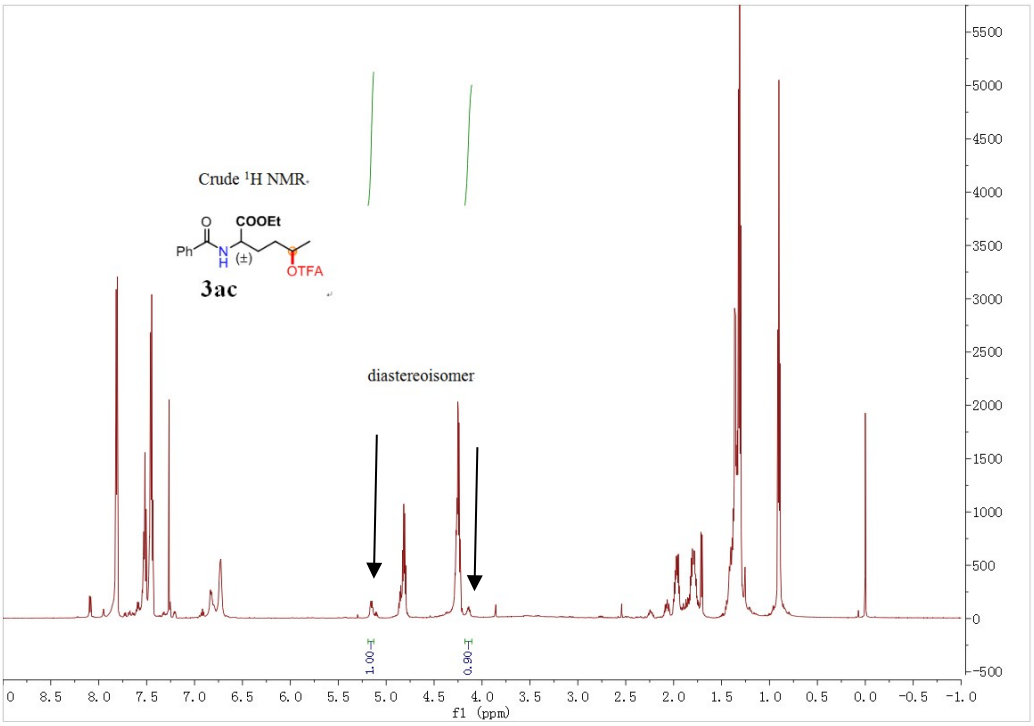

3aa
f1 (ppm)

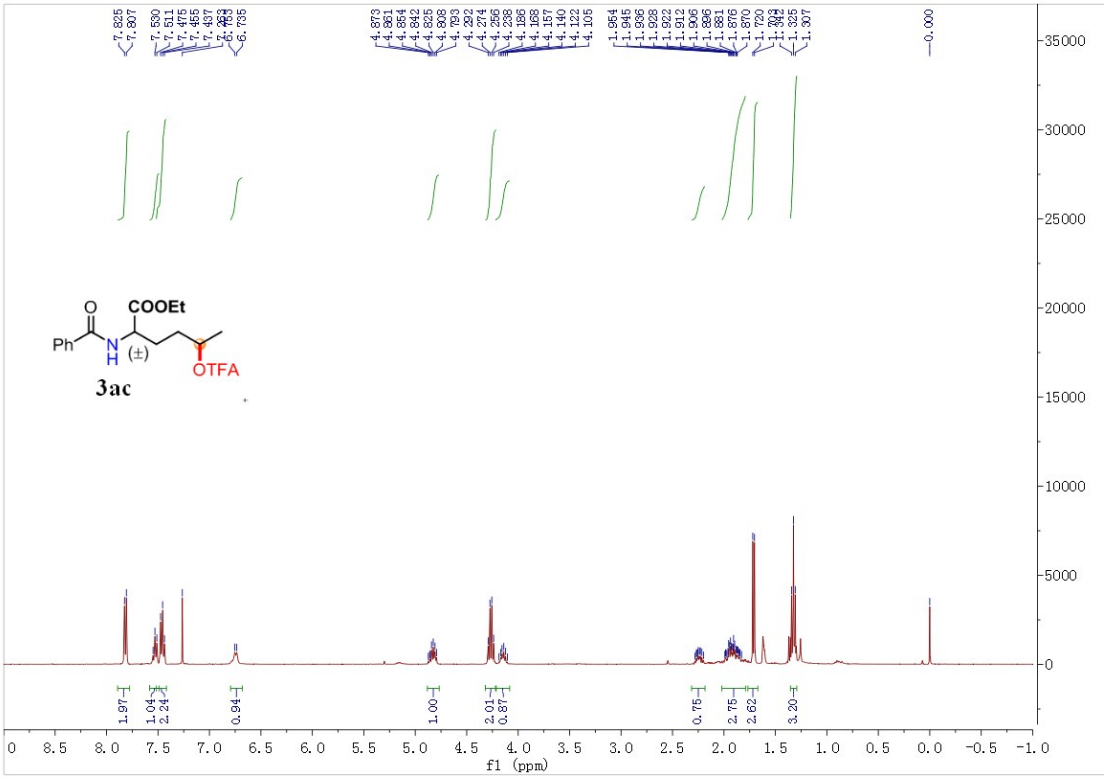

167.13
133.95
131.83
128.70
126.88
77.21
77.00
76.79
67.99
53.39
50.91
43.40
37.46
29.95
26.37
F
F
F
F
O
HN
O
Ph
(±)
OTFA
f1 (ppm)

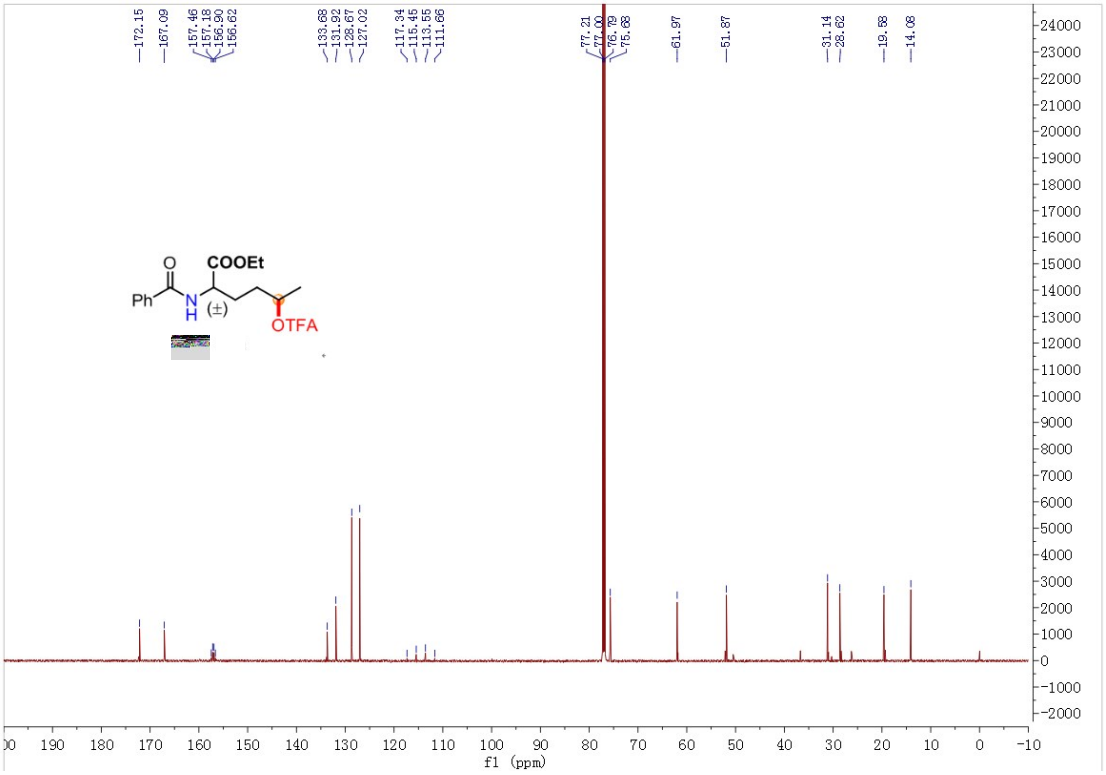

COOMe
Ph
N
H
(±)
OTFA
3ab
Crude ¹H NMR
diastereoisomer
1.71
1.70
1.35
0.89
0.00
1.00
1.25
f1 (ppm)

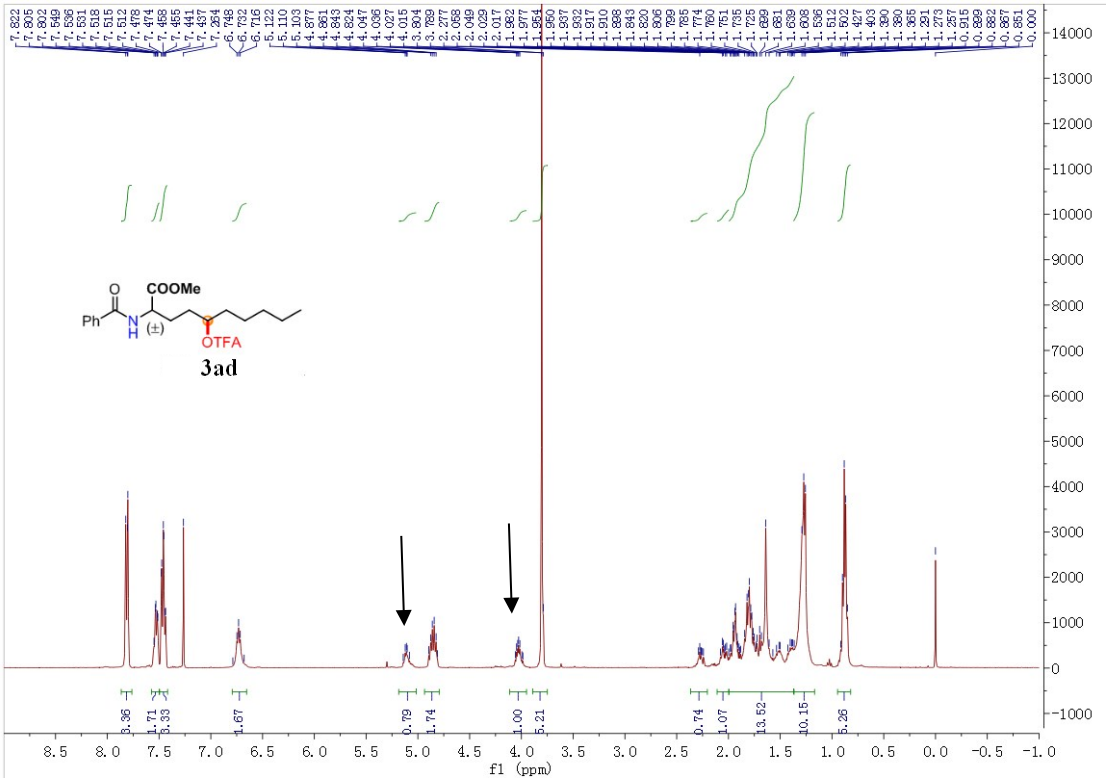

7.823
7.810
7.555
7.543
7.531
7.480
7.468
7.455
7.265
6.759
6.748
5.178
5.167
5.157
5.147
5.137
5.125
4.894
4.882
4.873
4.861
3.813
2.111
2.094
2.084
2.075
2.063
2.045
2.031
1.838
1.826
1.817
1.811
1.796
1.788
1.749
1.720
1.709
0.000
COOMe
Ph
N
H
(±)
OTFA
3ab
2.19
1.11
2.18
1.11
0.93
1.03
3.31
1.07
3.32
3.00
f1 (ppm)

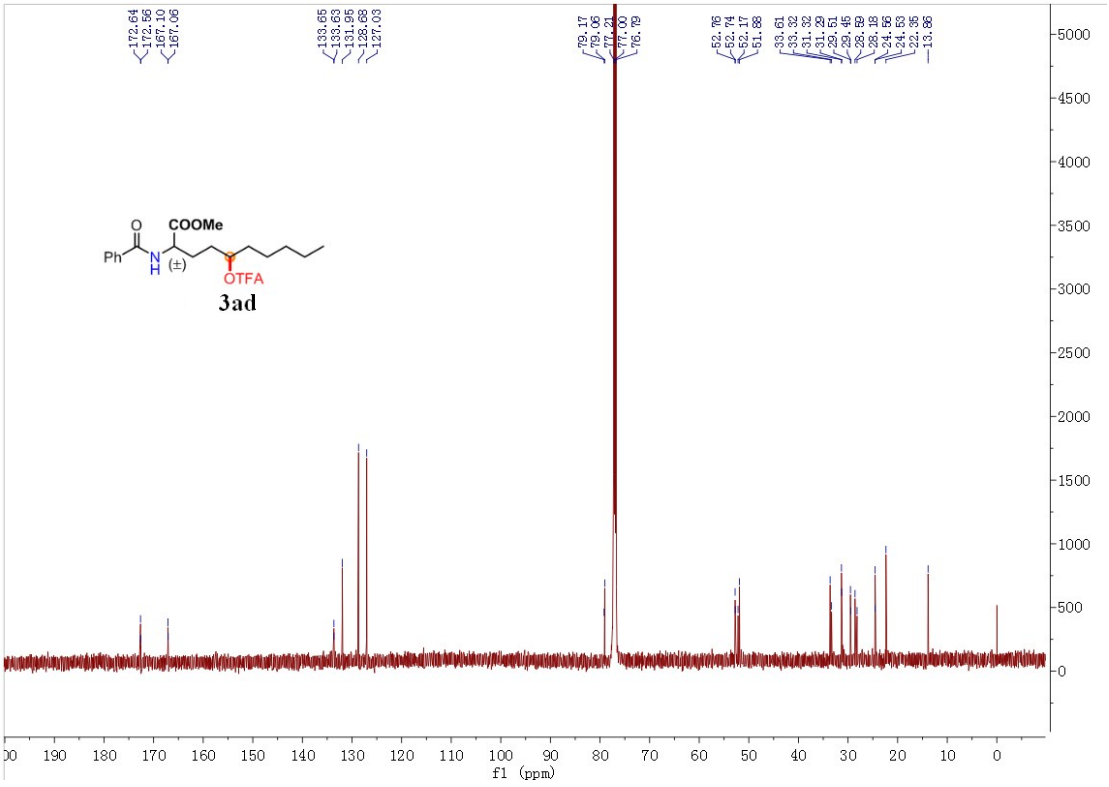

172.62
167.10
157.19
156.91
133.62
131.96
128.68
127.03
115.45
113.65
77.21
77.00
76.79
75.66
52.77
51.86
31.21
28.63
19.66
COOMe
Ph
N
H
(±)
OTFA
3ab
f1 (ppm)

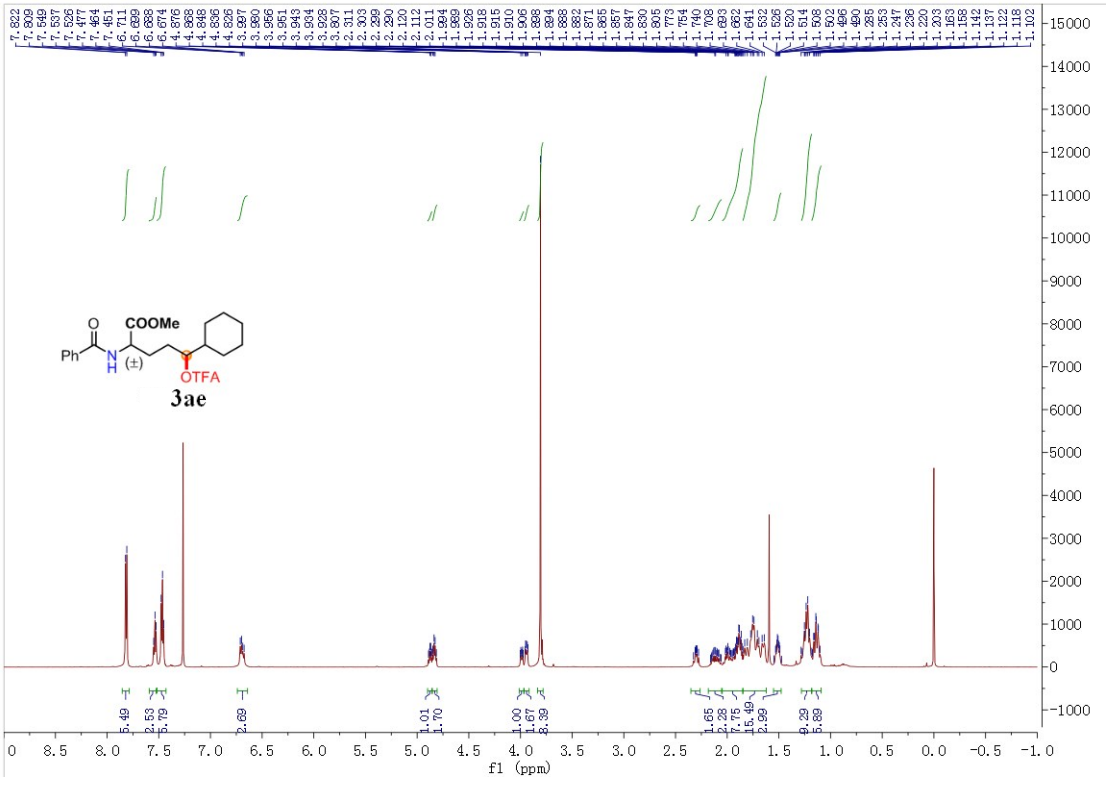

Crude ^{1}H NMR
COOEt
Ph
N
H
(±)
OTFA
3ac
diastereoisomer
1.00
0.90
f1 (ppm)

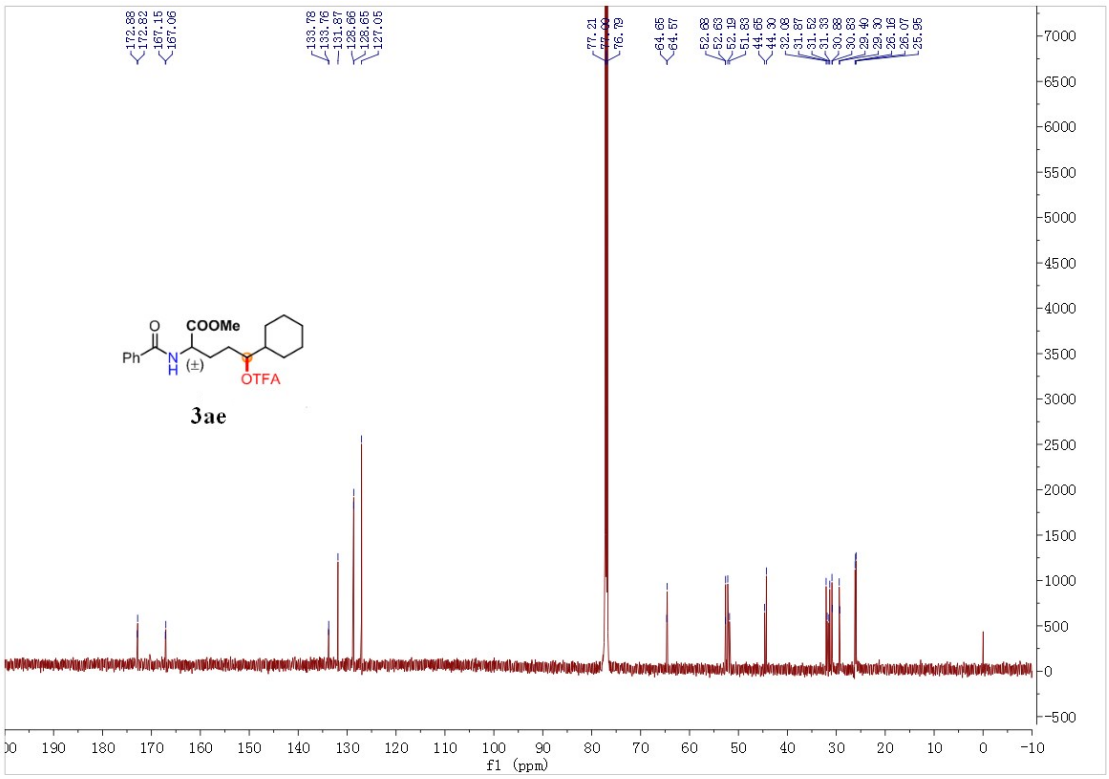

COOEt
Ph
N
H
(±)
OTFA
3ac
1.97
1.04
2.24
0.94
1.00
2.01
0.87
0.75
2.75
2.62
3.20
f1 (ppm)


COOEt
Ph
N
H
(±)
OTFA
f1 (ppm)

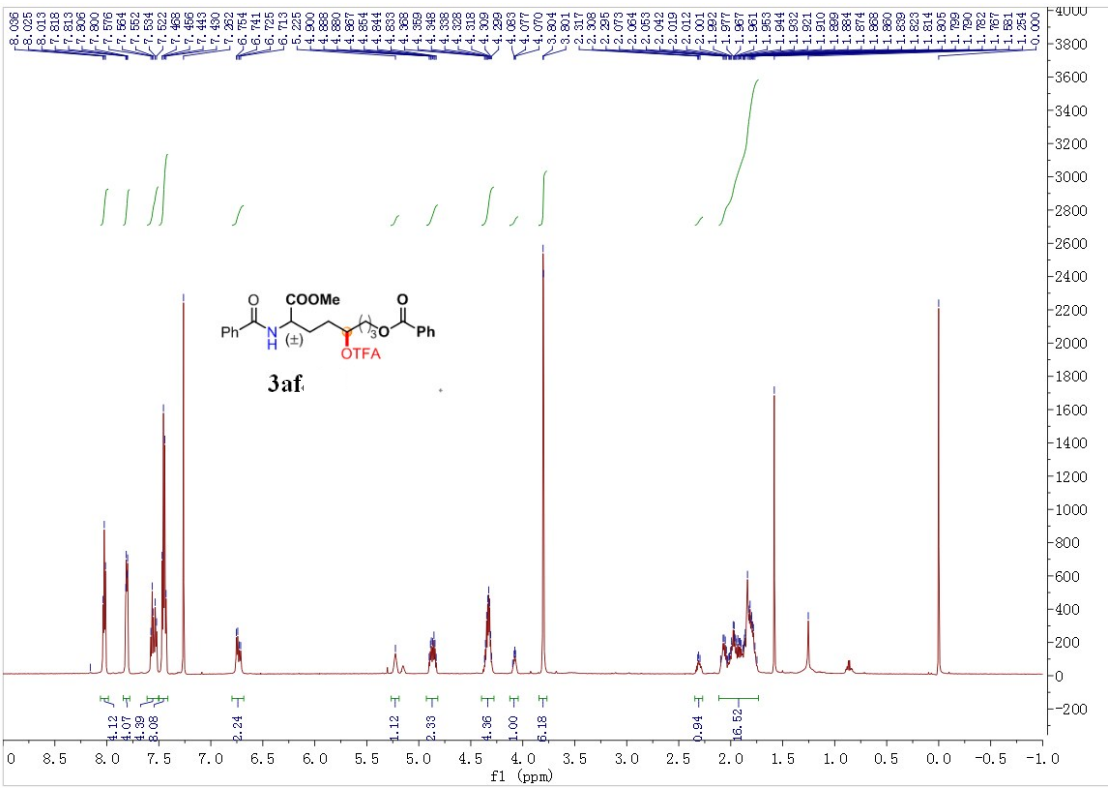

COOMe
Ph
N
H
(±)
OTFA
3ad
f1 (ppm)


COOMe
Ph
N
H
(±)
OTFA
3ad
f1 (ppm)

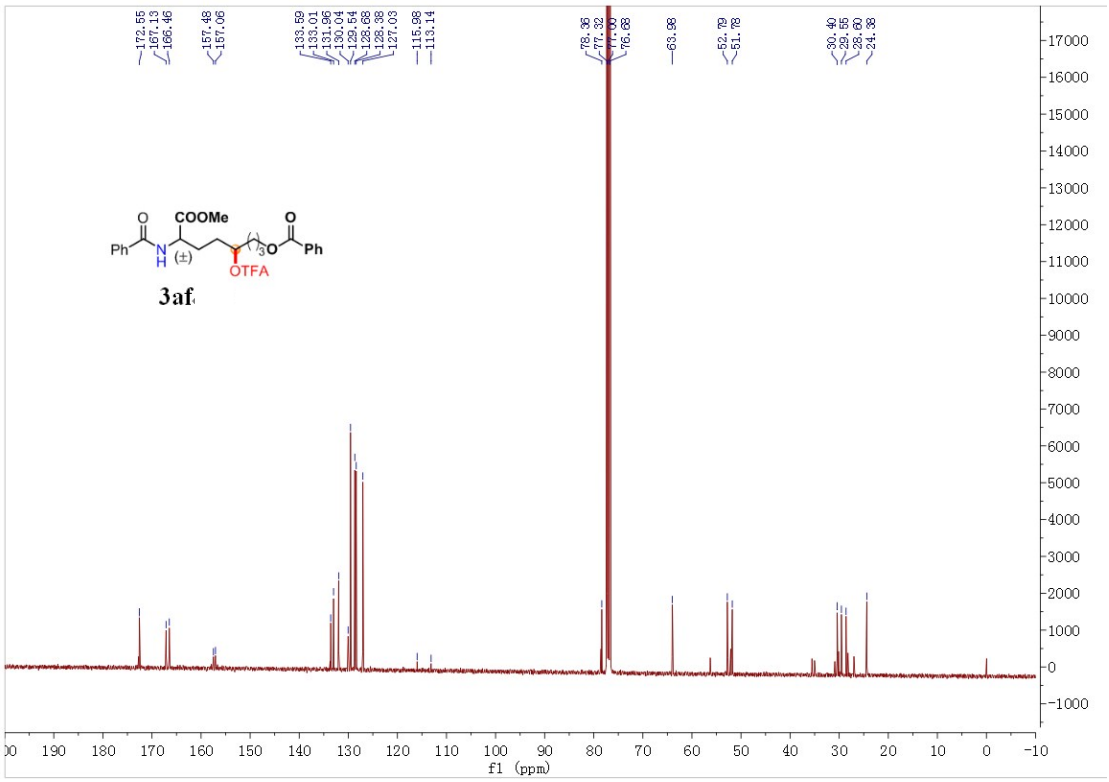

COOMe
Ph
N
H
(±)
OTFA
3ae
f1 (ppm)

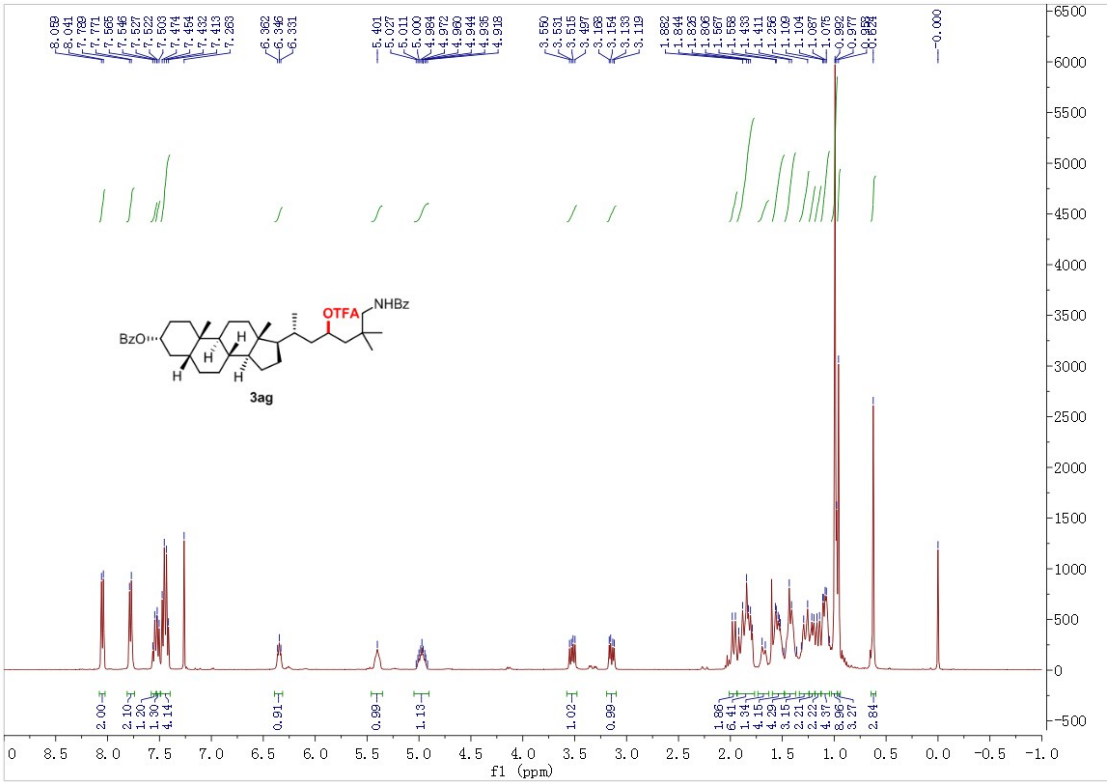

172.88
172.82
167.15
167.06
133.78
133.76
131.87
128.66
128.65
127.05
77.21
77.00
76.79
64.65
64.57
52.68
52.63
52.19
51.83
44.65
44.30
32.08
31.87
31.52
31.33
30.88
30.83
29.40
28.93
28.15
26.07
25.96
COOMe
Ph
N
H
(±)
OTFA
f1 (ppm)

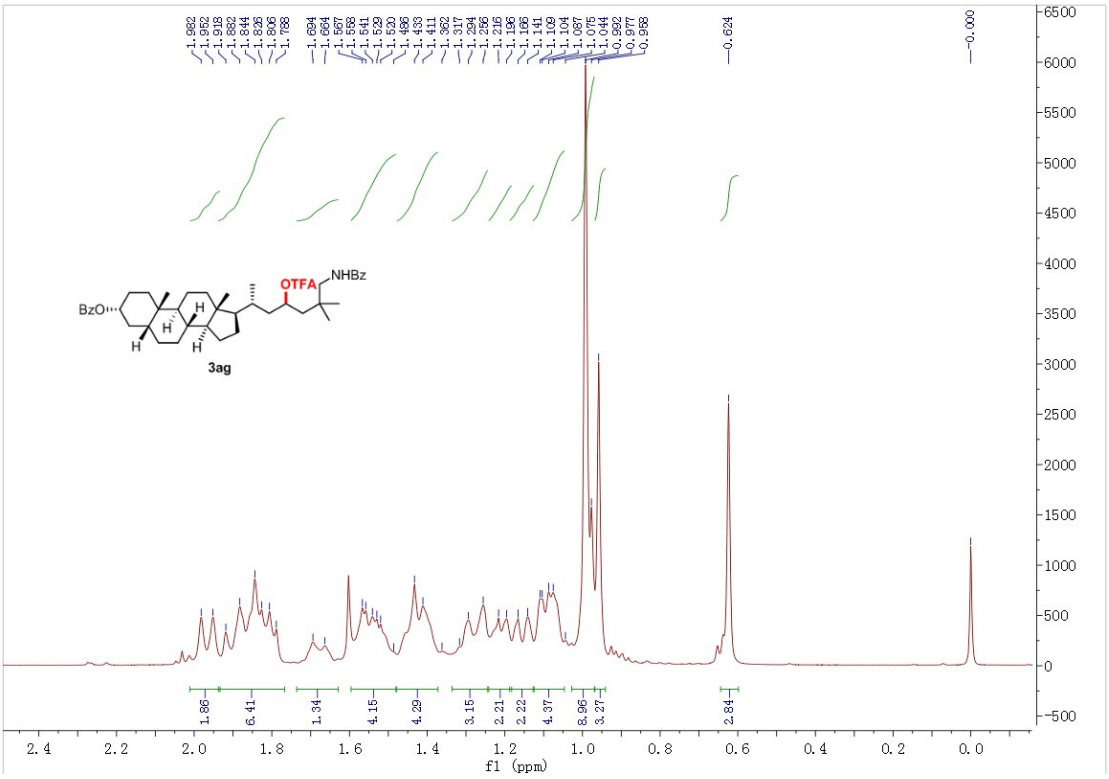
3ae

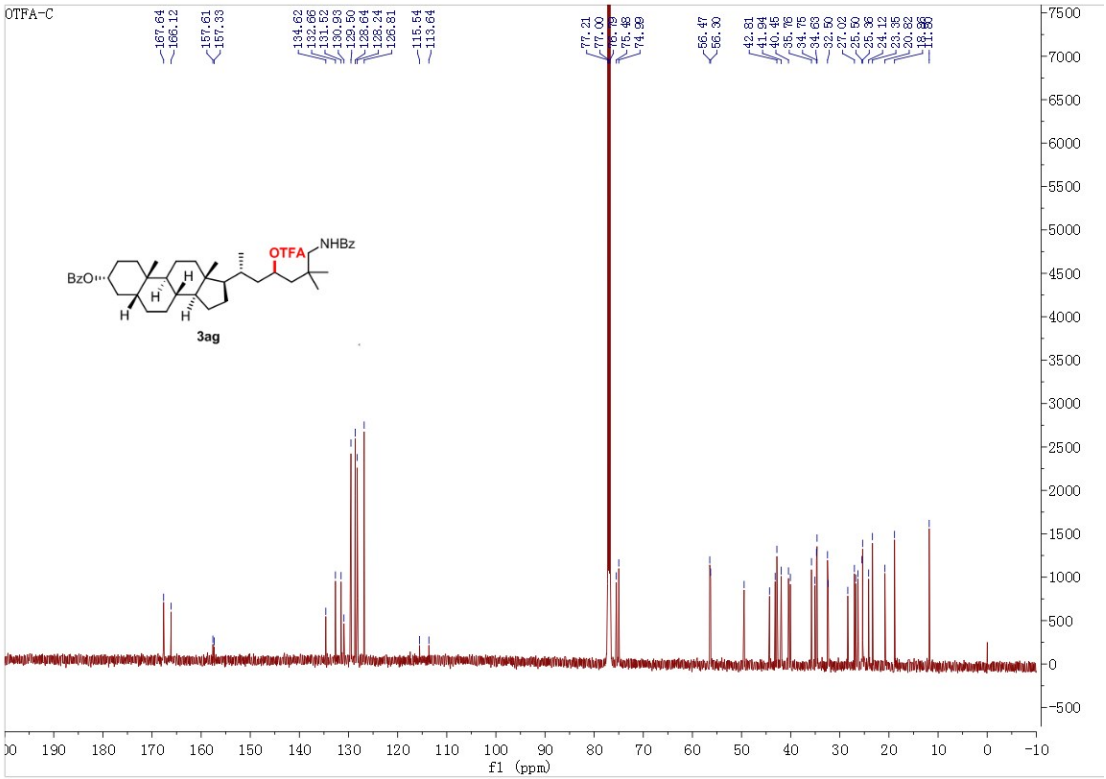

COOMe
Ph
N
H
(±)
OTFA
O
Ph
4.12
4.07
4.39
8.08
2.24
4.12
2.33
4.36
1.00
6.18
0.94
16.52
f1 (ppm)

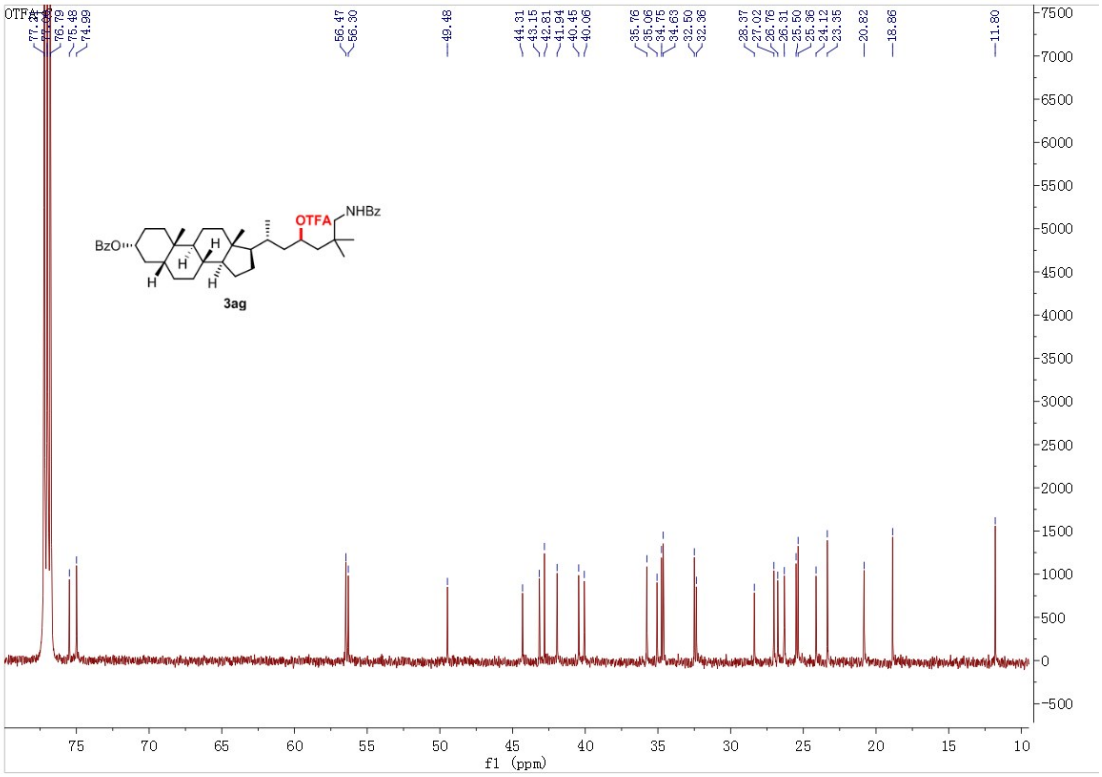
3af


COOMe
Ph
Ph
OTFA
3af


OTFA
NHBz
BzO
3ag


OTFA
NHBz
BzO
3ag
f1 (ppm)


OTFA-C
OTFA
NHBz
BzO
3ag
f1 (ppm)


OTFA
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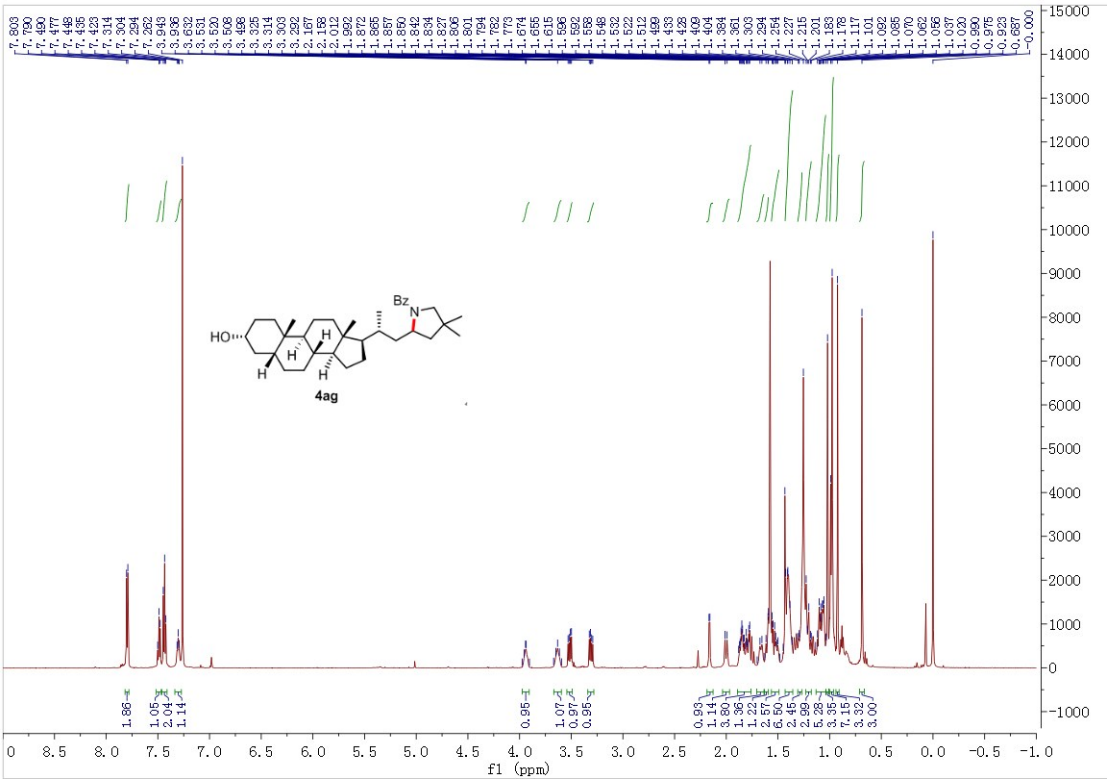
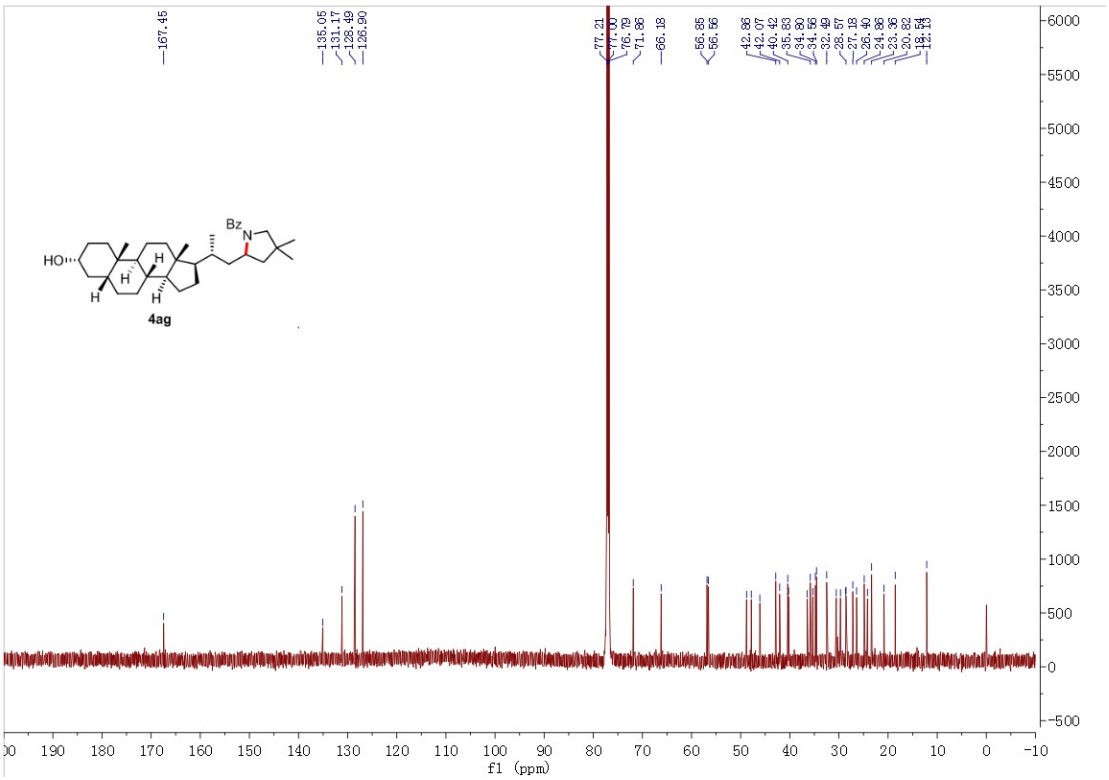
76.79
76.48
74.99
56.47
56.30
49.48
44.31
43.15
42.81
41.94
40.45
40.06
35.76
35.06
34.75
34.63
32.50
32.36
28.37
27.02
26.76
26.31
25.50
25.36
24.12
23.35
20.82
18.86
11.80
BzO
OTFA
NHBz
H
H
H
3ag
f1 (ppm)


HO
Bz
N
H
H
H
4ag
1.86
1.05
2.04
1.14
0.95
1.07
0.97
0.95
0.93
1.14
3.88
1.95
2.27
6.50
2.45
2.99
5.28
3.35
7.15
3.32
3.00
f1 (ppm)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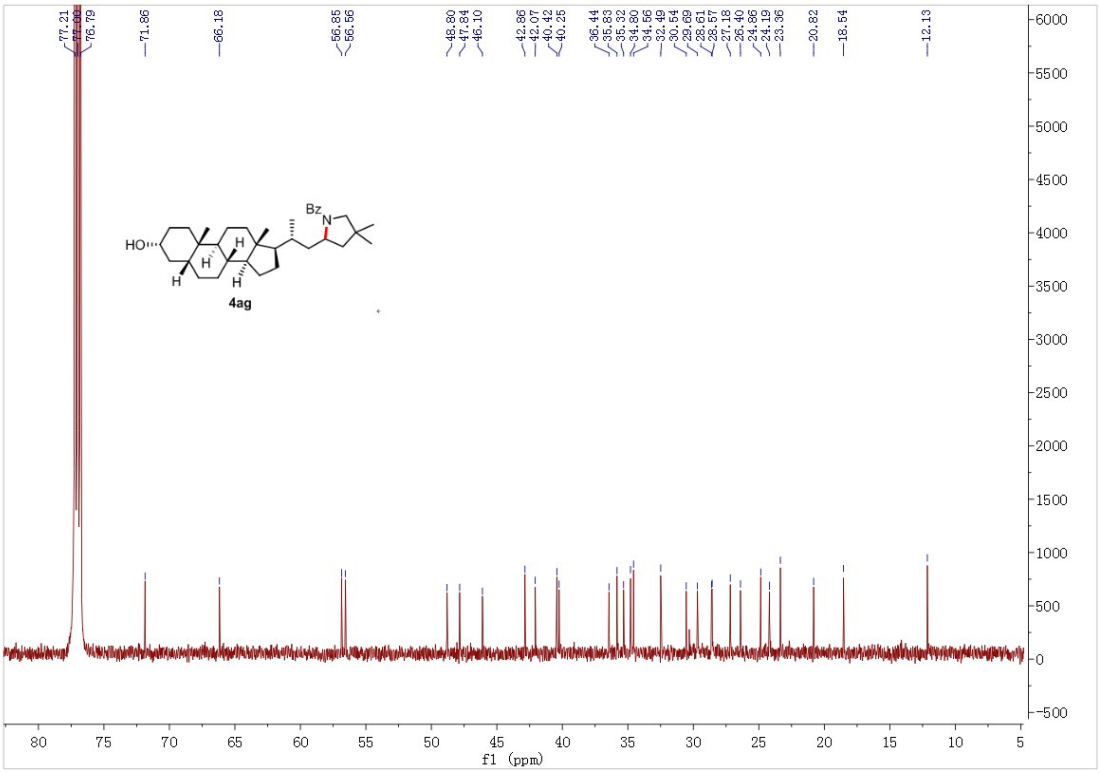
135.05
131.17
128.49
126.90
77.21
77.00
76.79
71.86
66.18
56.85
56.56
42.86
42.07
40.42
35.83
34.80
34.56
32.49
28.57
27.18
26.40
24.86
23.36
20.82
18.54
12.13
HO
Bz
N
H
H
H
4ag
f1 (ppm)


77.21
77.00
76.79
71.86
66.18
56.85
56.56
48.80
47.84
46.10
42.86
42.07
40.42
40.25
36.44
35.83
35.32
34.80
34.56
32.49
30.54
29.69
28.61
28.57
27.18
26.40
24.86
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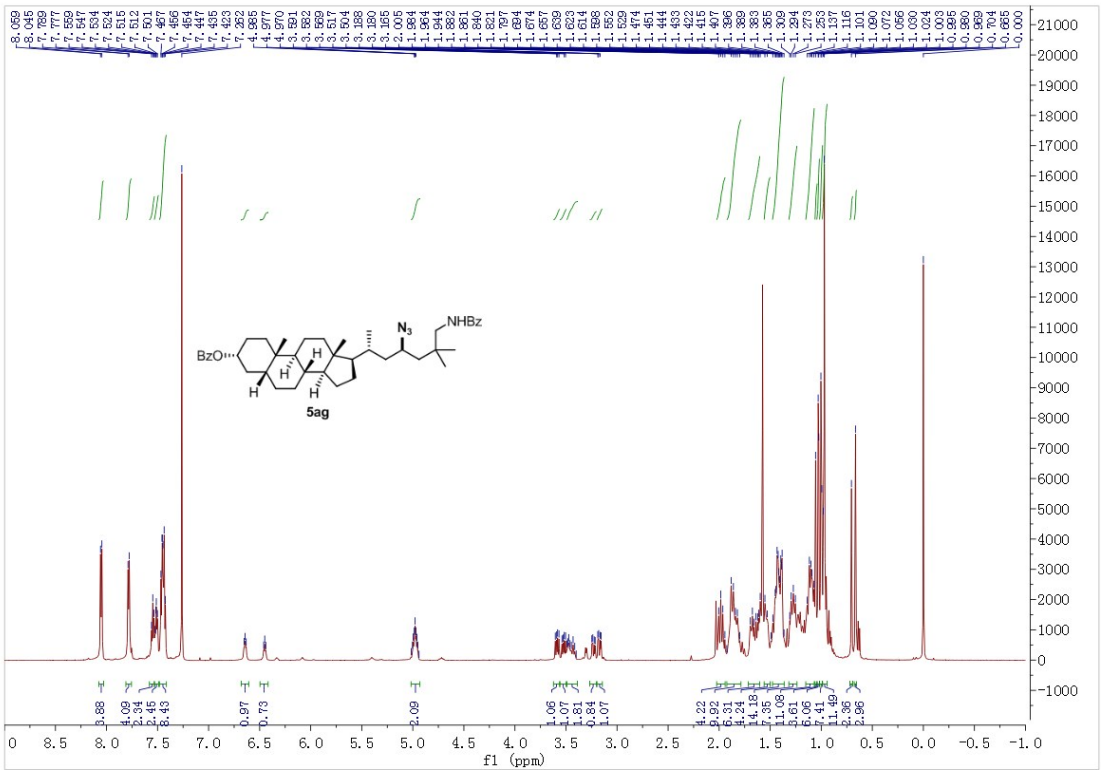
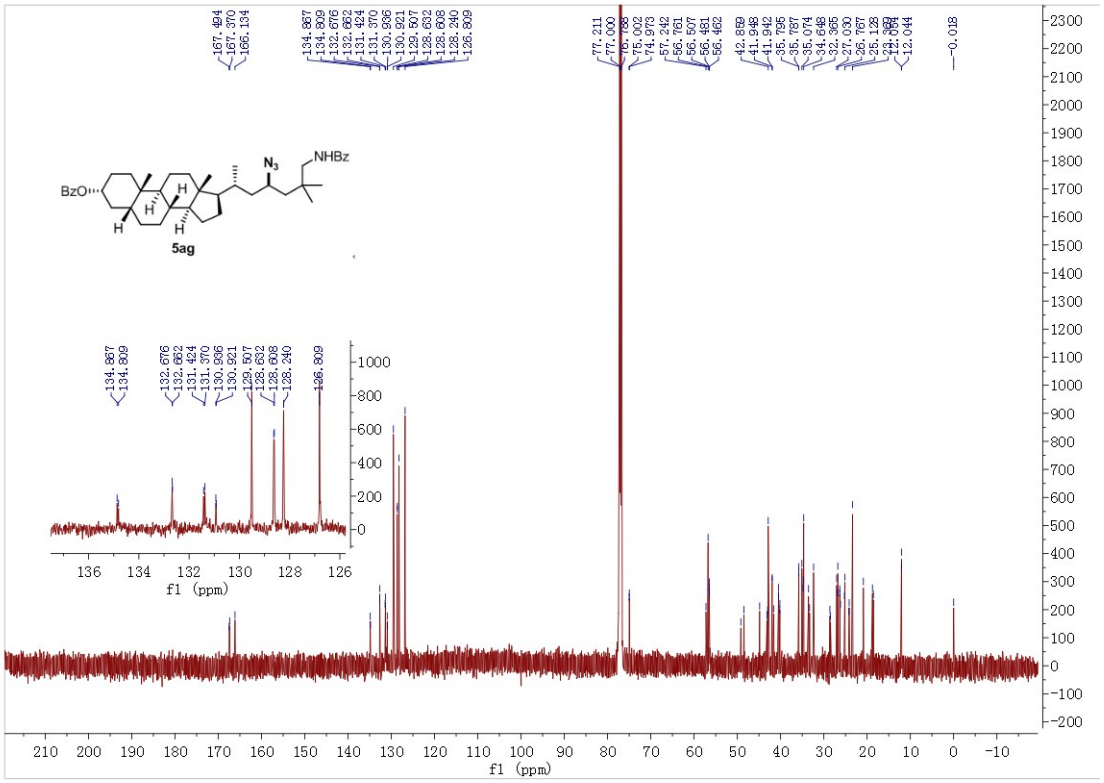
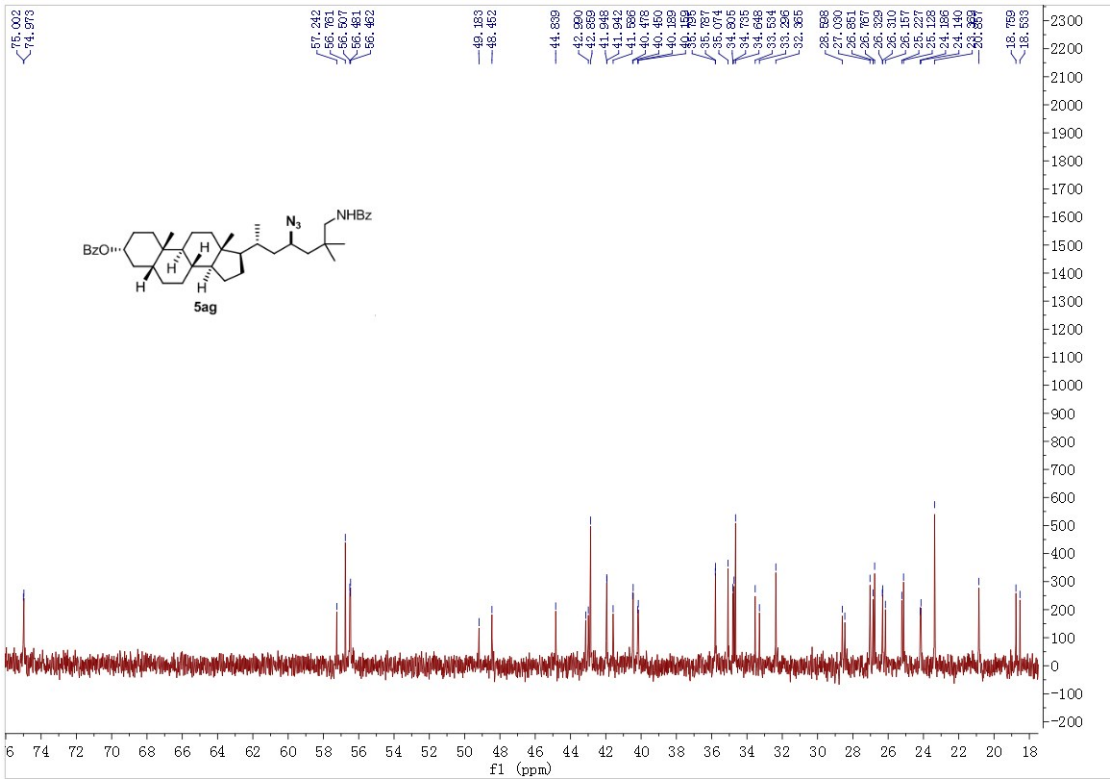
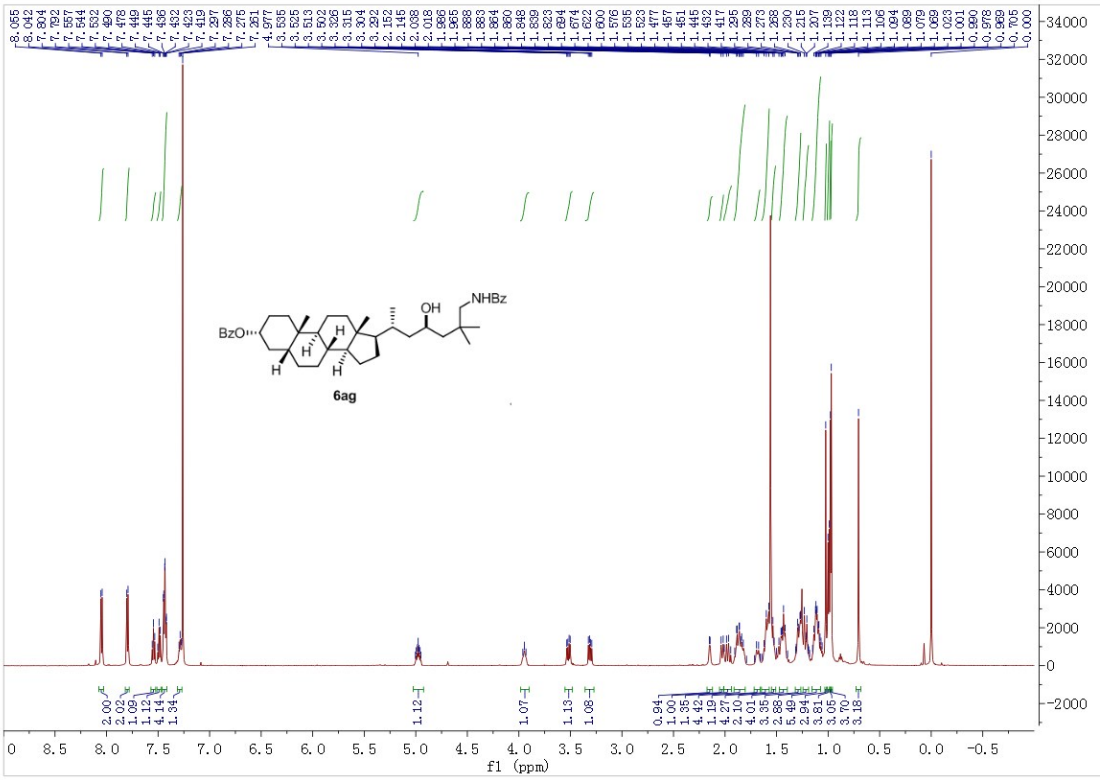
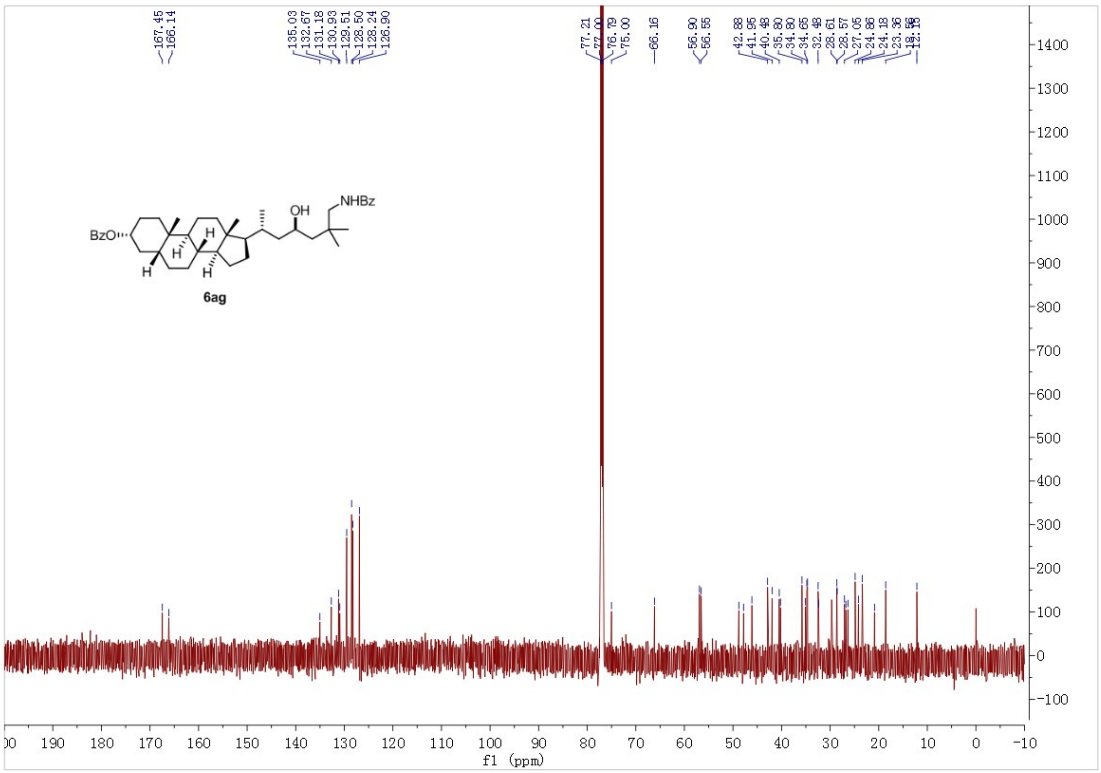
HO
Bz
N
H
H
H
4ag
f1 (ppm)


BzO
N3
NHBz
5ag
f1 (ppm)


BzO
N3
NHBz
5ag
f1 (ppm)
f1 (ppm)


NHBz
N3
BzO
H
H
H
5ag
f1 (ppm)


NHBz
OH
BzO
H
H
H
6ag
f1 (ppm)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129.51
128.50
128.24
126.90
77.21
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75.00
66.16
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34.65
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28.61
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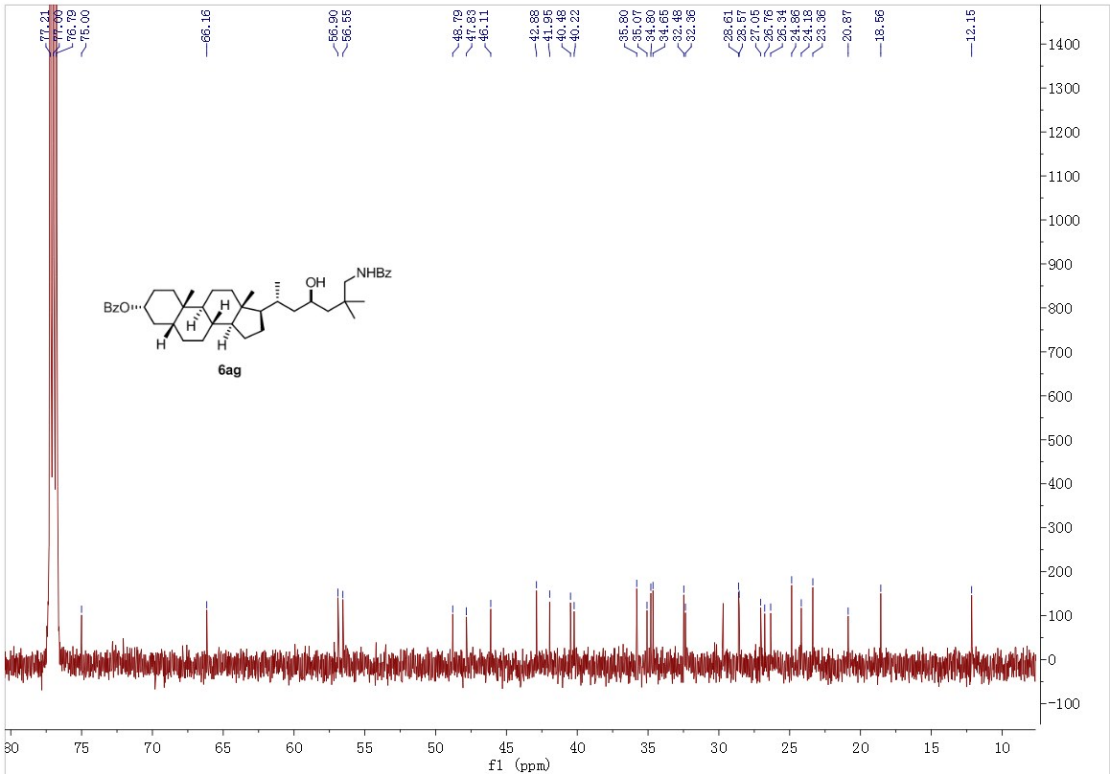
NHBz
BzO
H
H
H
6ag
f1 (ppm)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75.00
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46.11
42.88
41.95
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40.22
35.80
35.07
34.80
34.65
32.48
32.36
28.61
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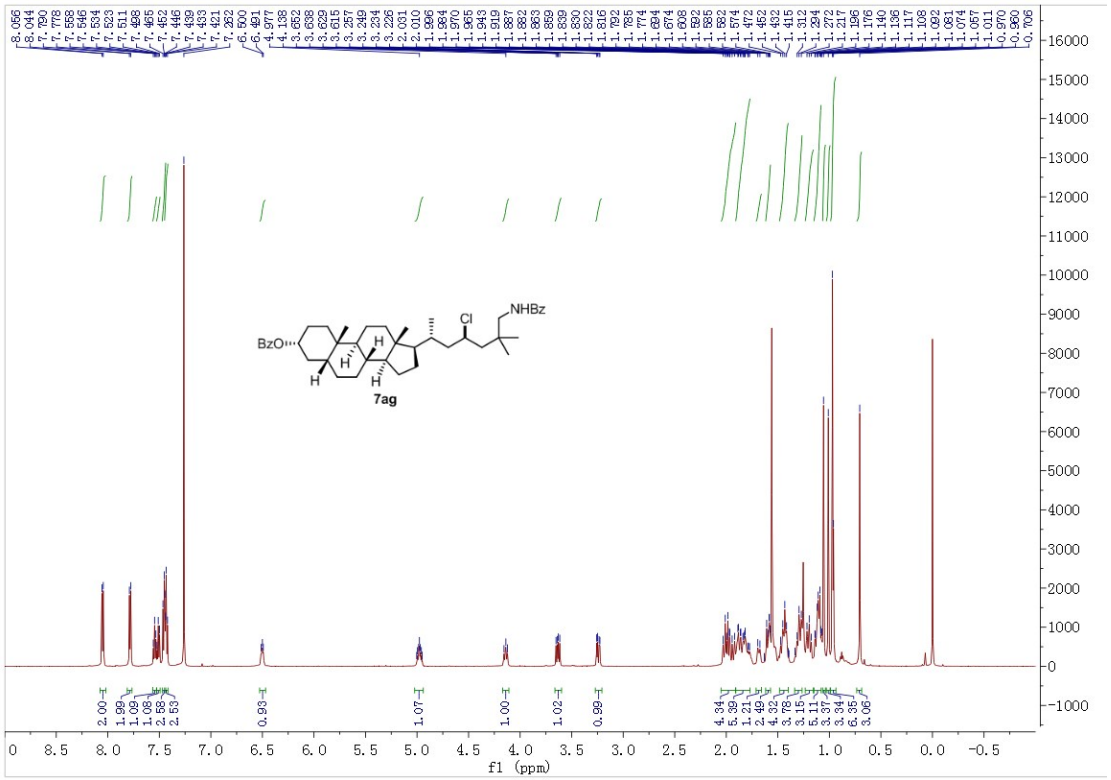
NHBz
BzO
H
H
H
6ag
f1 (ppm)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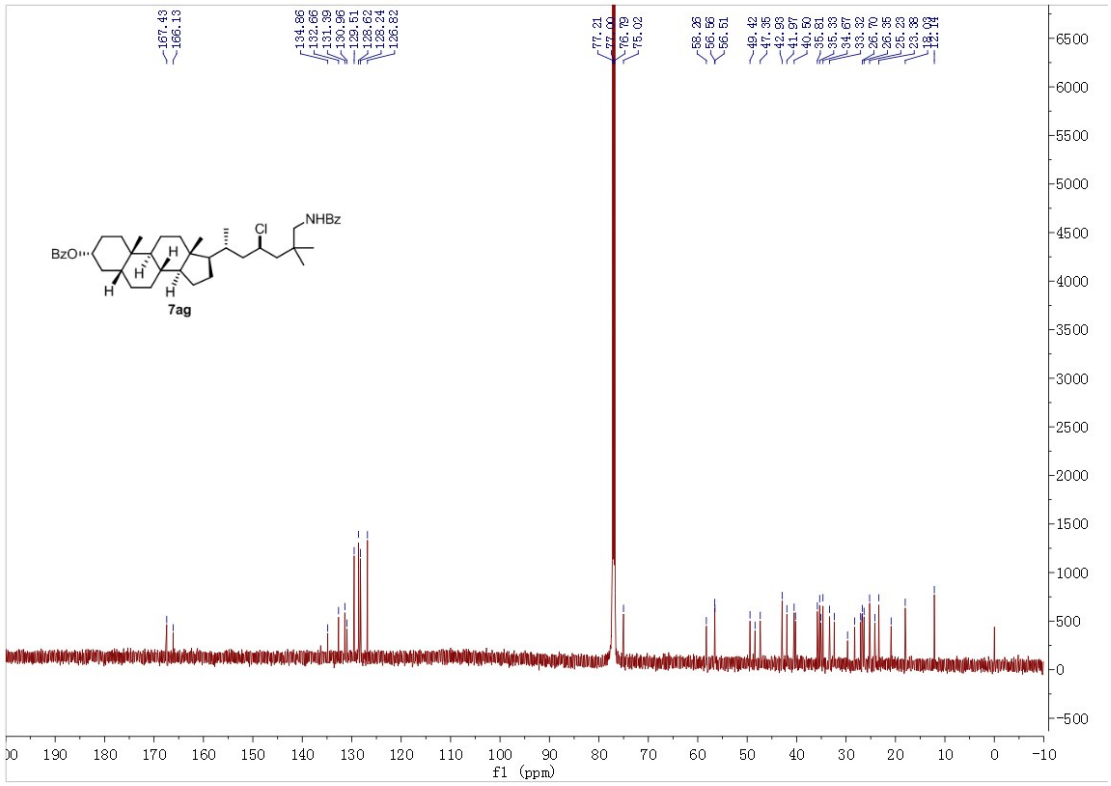
Cl
BzO
H
H
H
7ag
f1 (ppm)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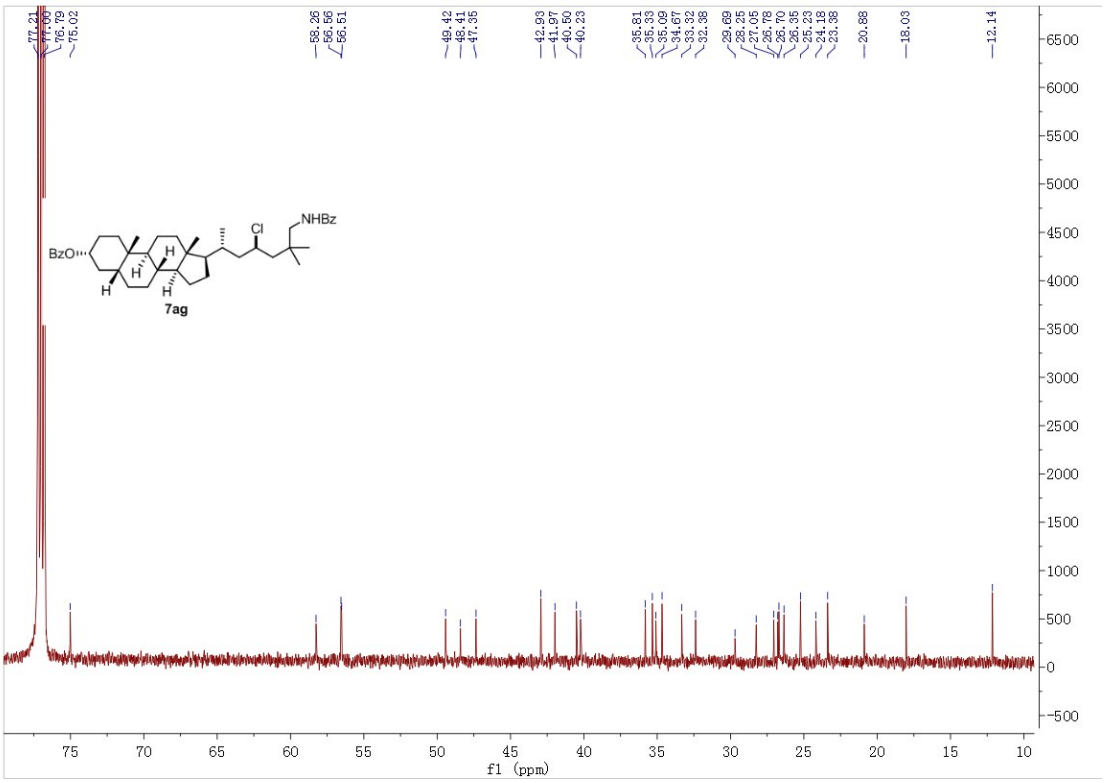
Cl
BzO
H
H
H
7ag
f1 (ppm)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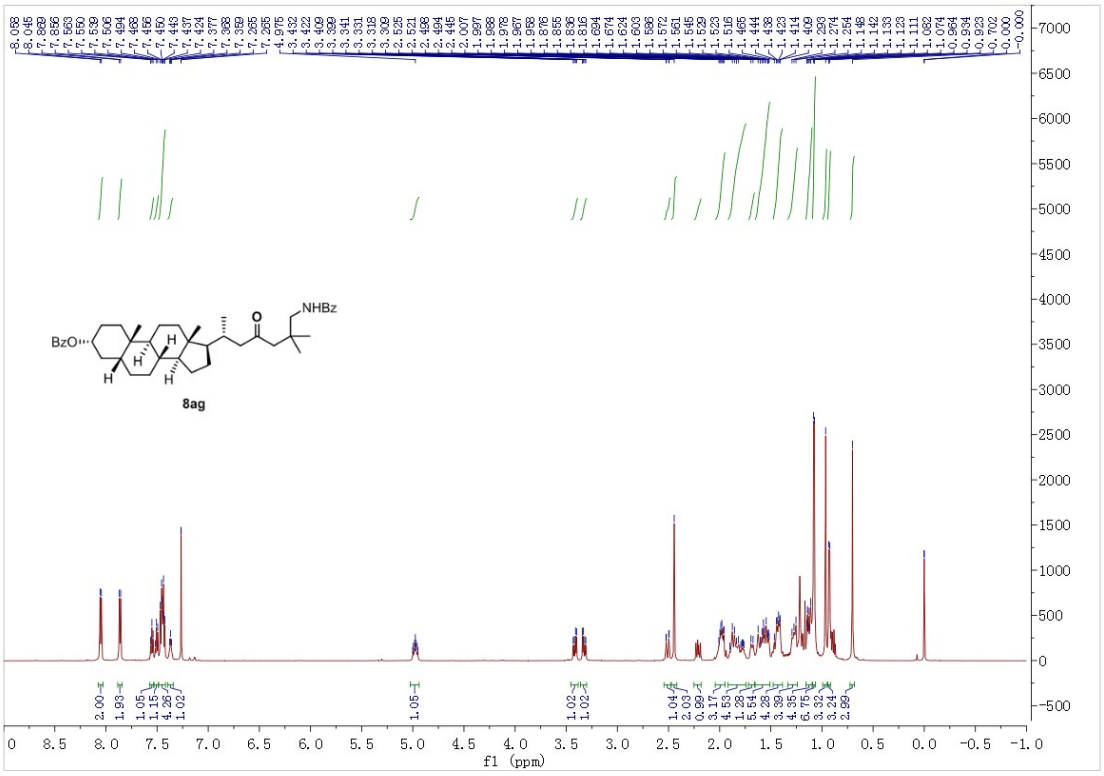
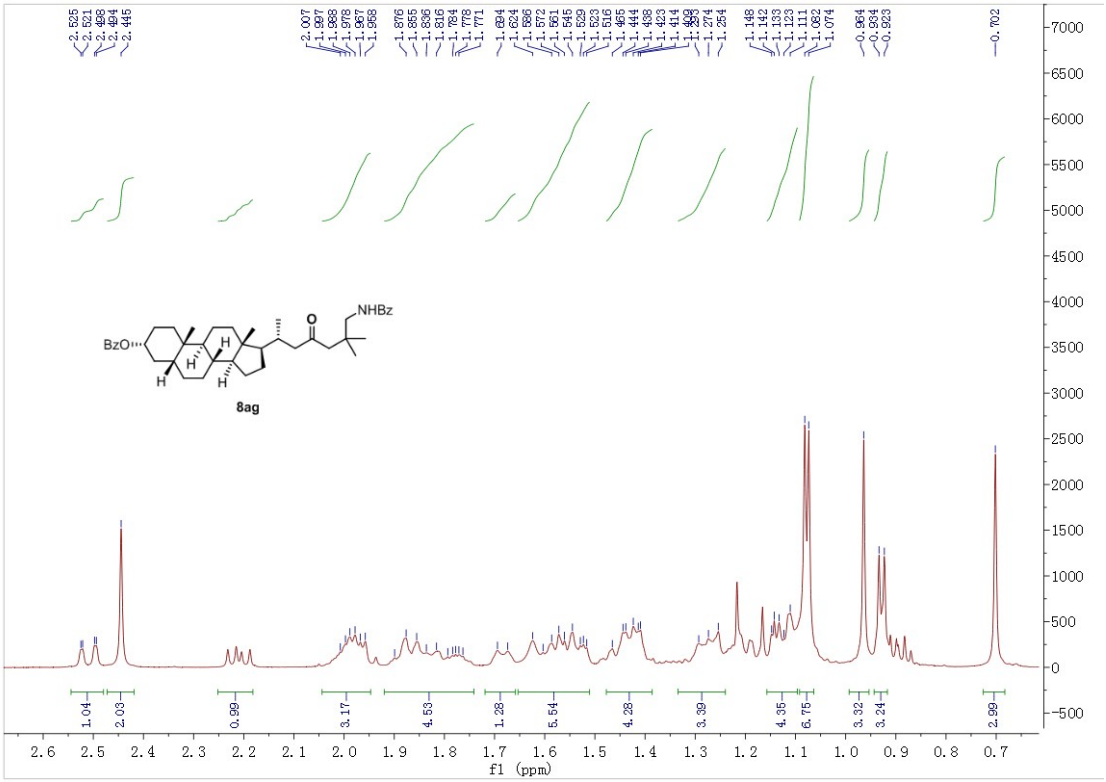
Cl
BzO
H
H
H
7ag
f1 (ppm)


NHBz
O
BzO
H
H
H
8ag
f1 (ppm)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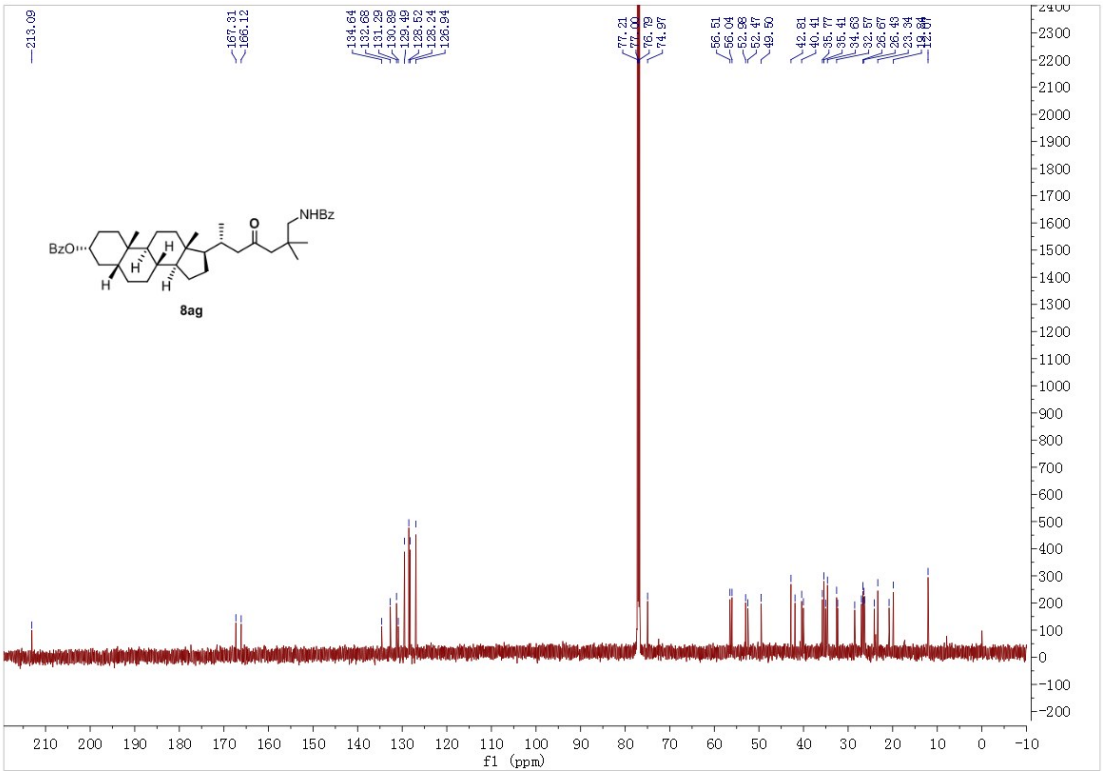
BzO
8ag
f1 (ppm)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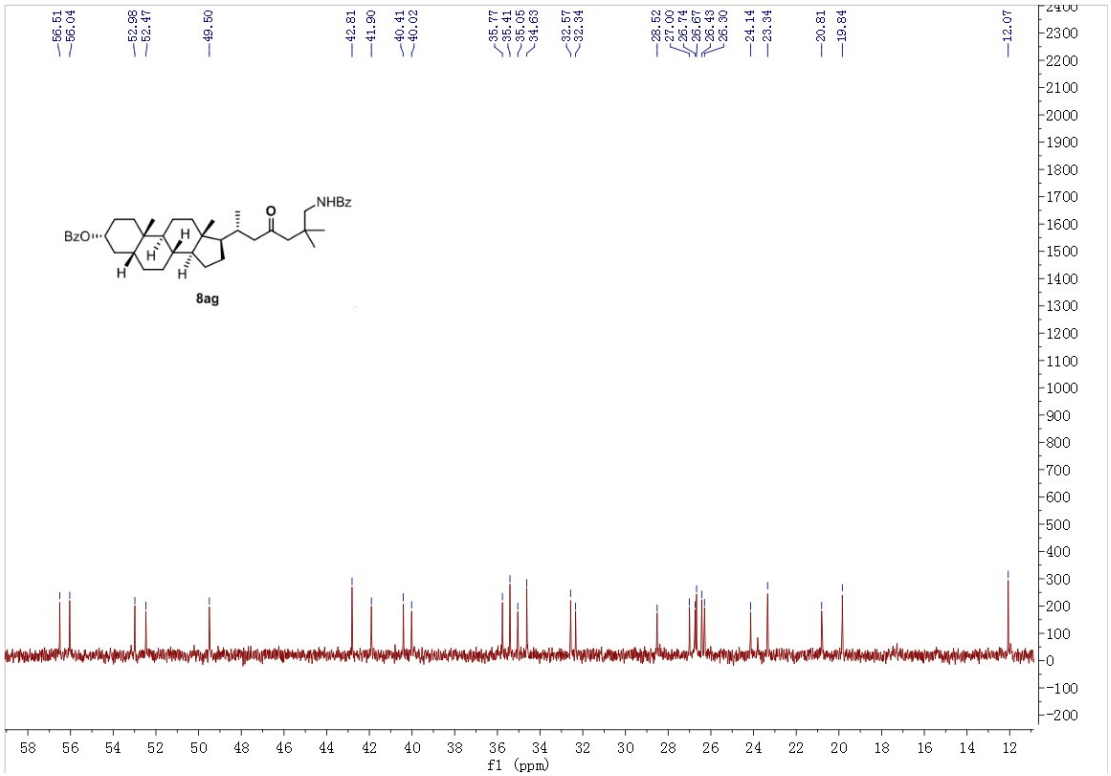
BzO
8ag
f1 (ppm)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35.41
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34.63
32.57
32.34
28.52
27.00
26.74
26.67
26.43
26.30
24.14
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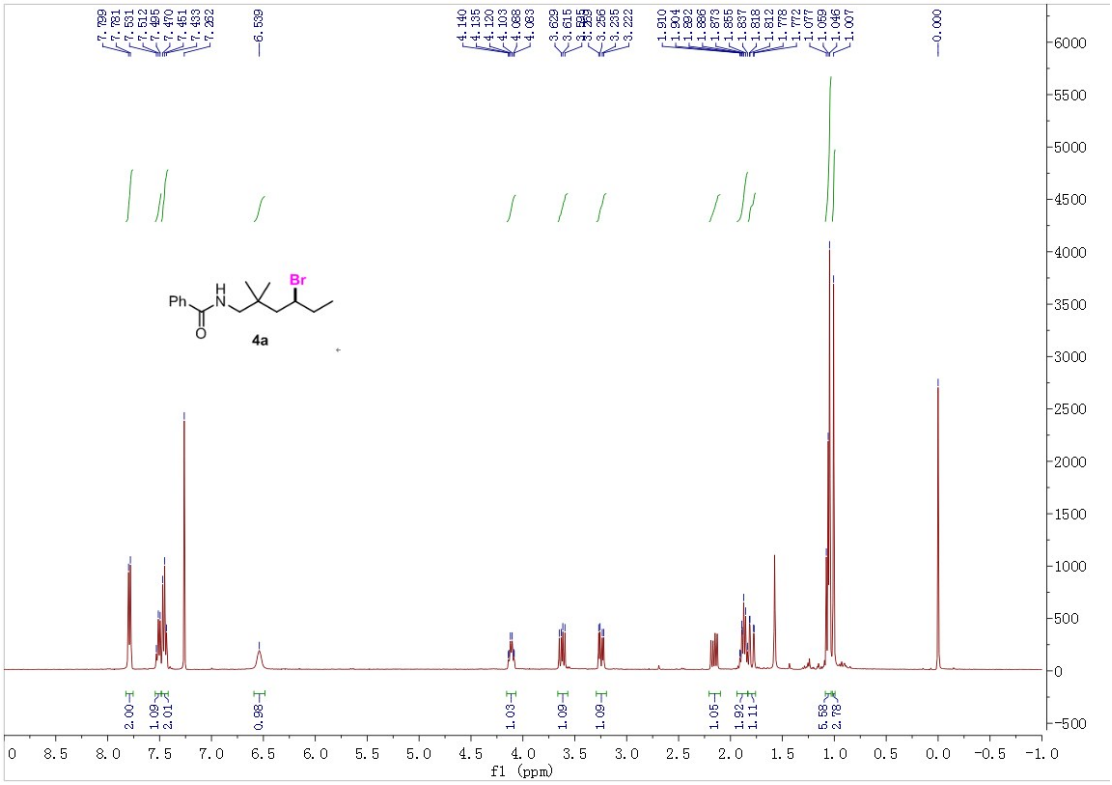
20.81
19.84
12.07
NHBz
O
BzO
H
H
H
8ag
f1 (ppm)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7.470
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7.453
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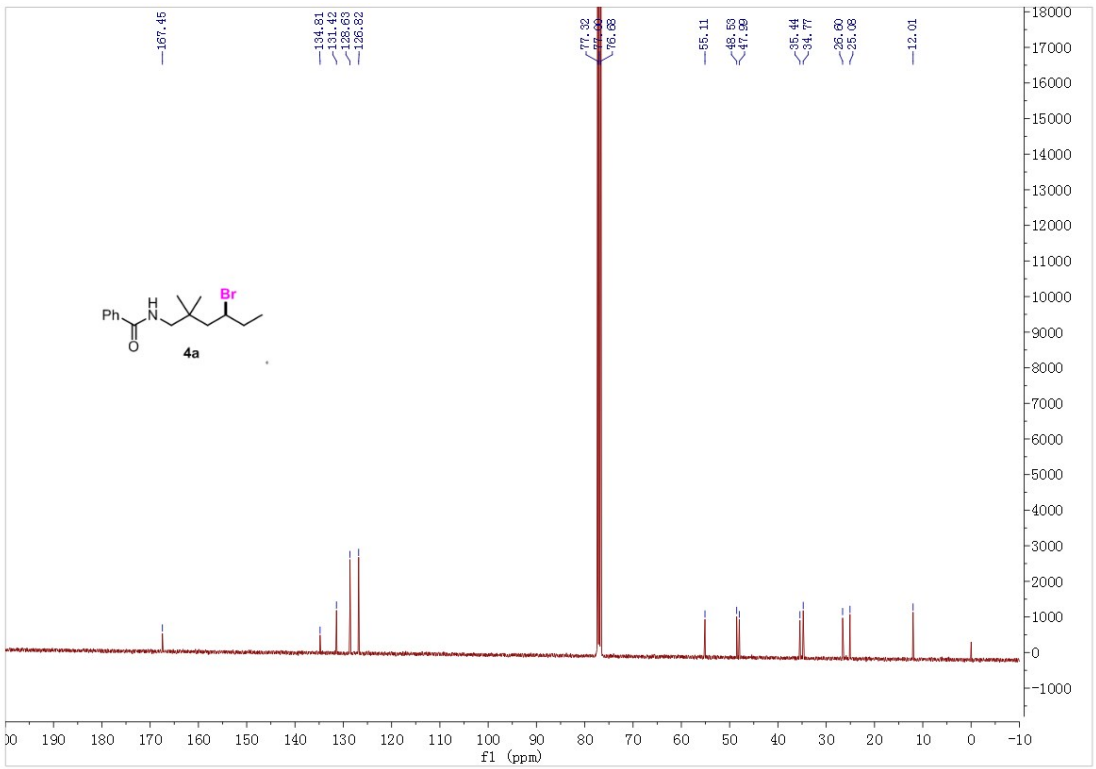
4.129
4.123
4.068
4.063
3.629
3.615
3.255
3.222
1.910
1.904
1.892
1.886
1.873
1.855
1.837
1.818
1.812
1.778
1.772
1.077
1.069
1.046
1.007
0.000
Br
Ph
H
N
O
4a
2.00
1.09
2.01
0.98
1.03
1.09
1.09
1.05
1.92
1.11
5.58
2.78
f1 (ppm)


167.46
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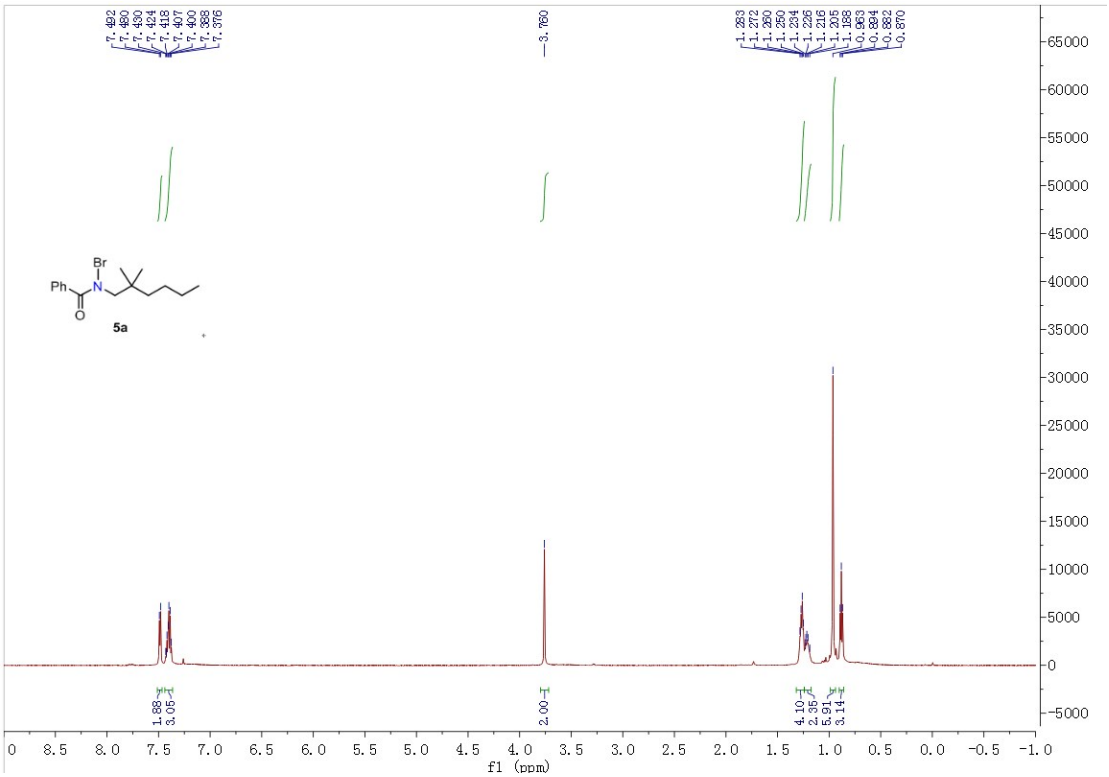
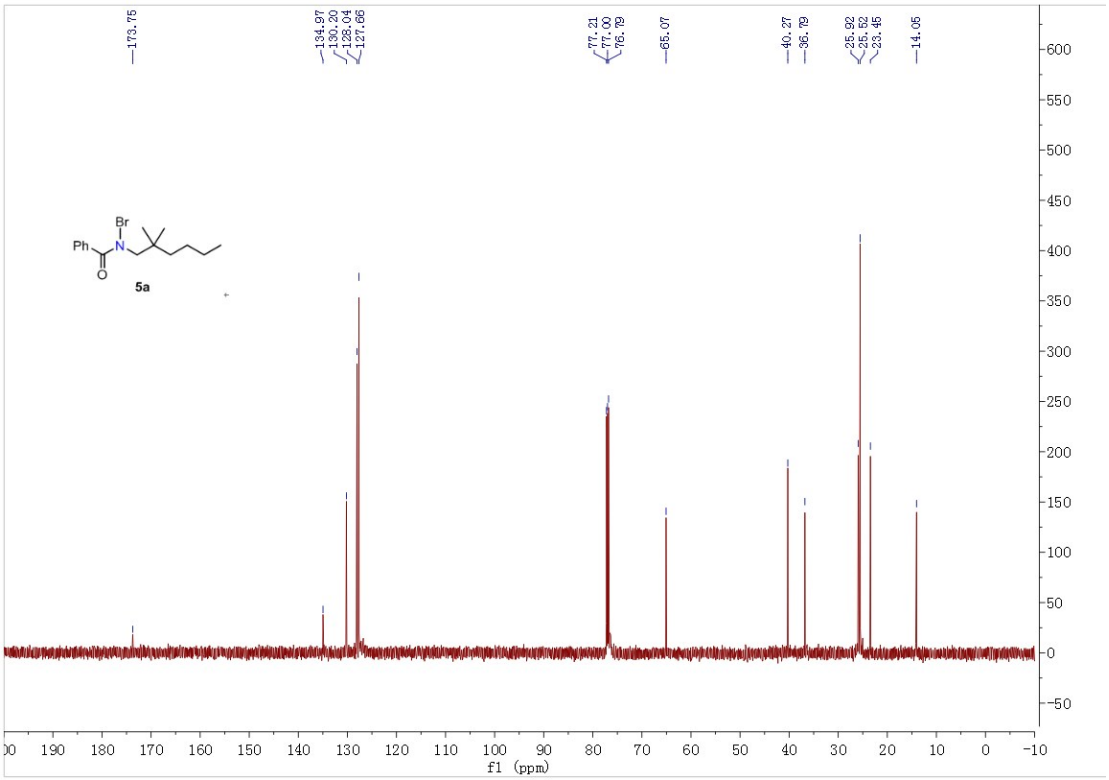
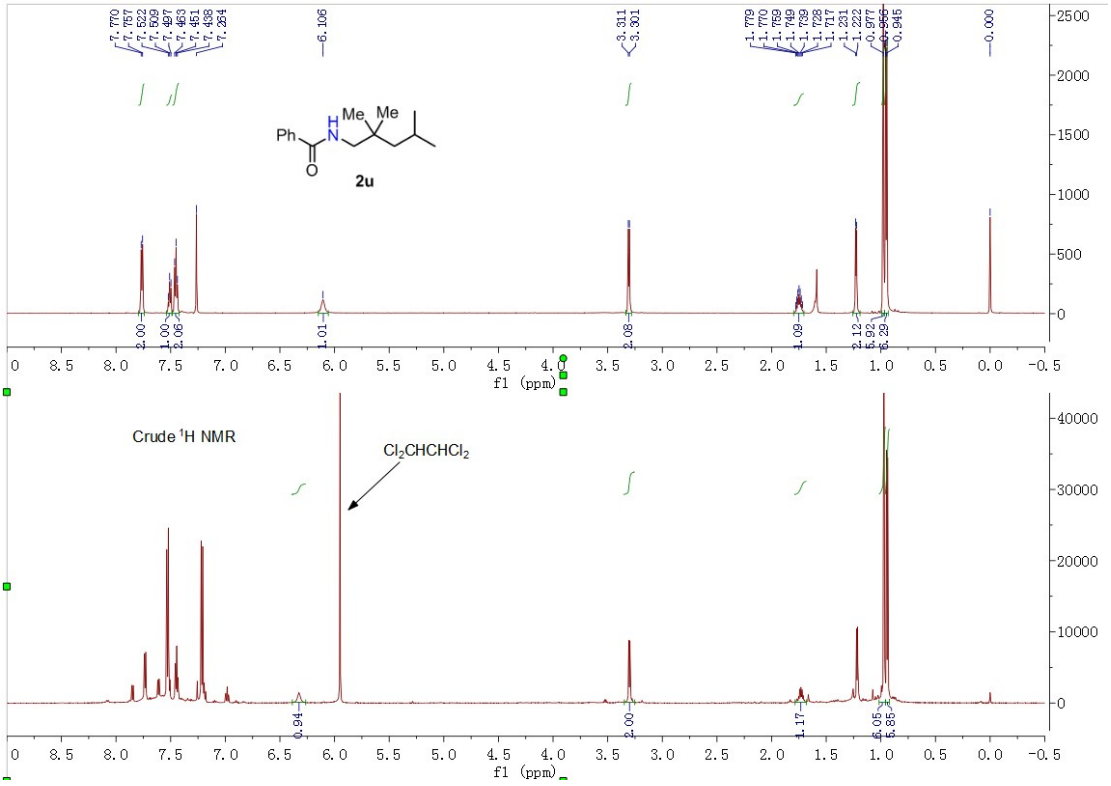
131.42
128.63
126.82
77.32
77.00
76.68
55.11
48.53
47.99
35.44
34.77
26.60
25.08
12.01
Br
Ph
H
N
O
4a
f1 (ppm)


7.492
7.490
7.490
7.414
7.413
7.407
7.400
7.388
7.376
3.760
1.263
1.272
1.260
1.250
1.234
1.226
1.216
1.205
1.188
0.963
0.894
0.882
0.870
Br
Ph
N
O
5a
1.88
3.05
2.00
4.10
2.35
5.91
3.14
f1 (ppm)


173.75
134.97
130.20
128.64
127.66
77.21
77.00
76.79
65.07
40.27
36.79
25.92
25.52
23.45
14.06
Br
Ph
N
O
5a
f1 (ppm)


7.770
7.757
7.522
7.509
7.497
7.463
7.451
7.438
7.264
6.106
3.311
3.301
1.779
1.770
1.759
1.749
1.739
1.728
1.717
1.231
1.222
0.977
0.966
0.945
0.000
Me
Me
H
N
Ph
O
2u
2.00
1.00
2.06
1.01
2.08
1.09
2.12
5.92
6.29
f1 (ppm)
Crude ¹H NMR
Cl2CHCHCl2
0.94
2.00
1.17
6.05
5.85
f1 (ppm)