

Supporting Information

A Unified Photoredox-Catalysis Strategy for C(sp³)-H Hydroxylation and Amidation Using Hypervalent Iodine

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1. Reagents

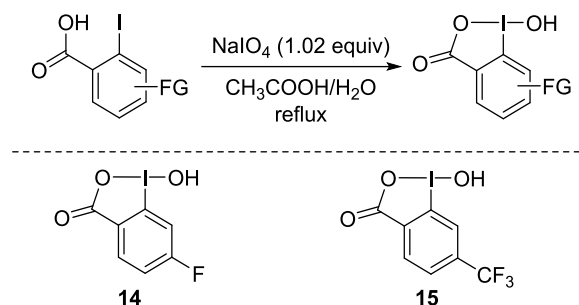
All commercial materials were used as received unless otherwise noted. DCM was dried by distillation over CaH₂. THF was dried by distillation over sodium/benzophenone. Anhydrous CH₃CN was purchased from Acros Organics and stored under nitrogen atmosphere. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching ($\lambda_{\text{max}} = 254 \text{ nm}$). Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China. Zhdankin reagent (azidobenziodoxole, BI-N₃, **11**)¹, acetoxybenziodoxole (BI-OAc, **12**)¹, hydroxylbenziodoxole (BI-OH, **13**)¹, 4-methoxyl hydroxylbenziodoxole (4MOBI-OH, **18**)², and [Ru(bpz)₃](PF₆)₂³ were synthesized according to reported procedures and used as freshly prepared. [Ru(bpy)₃]Cl₂ (98%, Ru > 15.75%, Energy Chemical), HFIP (99.0%, ACS grade, J&K Chemical,) and H₂¹⁸O (97% ¹⁸O, J&K Chemical) were used as received unless otherwise noted.

2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm). Peaks recorded are relative to internal standards: TMS ($\delta = 0.00$) for ¹H and CDCl₃ ($\delta = 77.00$) for ¹³C spectra. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, br s = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on a Waters LCT Premier instrument. All reactions were carried out in a 22 mL glass vial (Thermo SCIENTIFIC National B7999-5, made from clear borosilicate glass), sealed with PTEF cap on bench top.

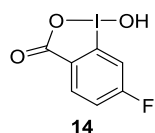
3. Synthesis of hypervalent iodines

3.1 Procedure for synthesis of **14** and **15**:

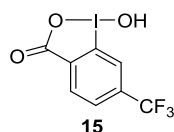


Scheme S1

To a solution of AcOH in water (30% v/v, 30 mL) NaIO₄ (20.4 mmol, 1.02 equiv) and corresponding benzoic acid (20 mmol, 1.00 equiv) were added at room temperature. The suspension mixture was vigorously stirred and refluxed for 4 h under air. The reaction mixture was cooled to room temperature then poured into cold water (50 mL). The mixture is then filtered and the filter cake was further washed with water and acetone. The residue was collected and dried under high vacuum in dark to give the desired product.



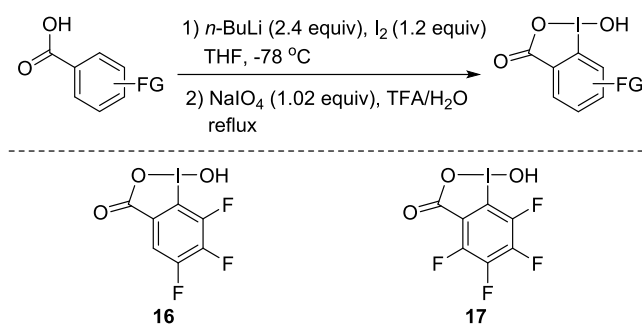
Compound **14** was obtained in 75% yield as white solid. M.p. = 222-223 °C (decomp.); IR (KBr) : $\tilde{\nu}$ = 3083, 2416, 1742, 1609, 1472, 1210, 885, 781, 668 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (br s, 1H), 8.00 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.58-7.53 (m, 2H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 166.85, 166.07 (d, *J* = 255.3 Hz), 132.93, 128.33, 122.86, 118.06 (d, *J* = 20.8 Hz), 113.60 (d, *J* = 28.6 Hz); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -105.53 (s, 1F); HRMS Calcd for C₇H₅FIO₃ [M+H]⁺: 282.9267, Found: 282.9260.



Compound **15** was obtained in 67% yield as white solid. M.p. = 244-245 °C (decomp.);

IR (KBr) : $\tilde{\nu}$ = 3050, 2440, 1830, 1562, 1398, 1321, 1186, 1133, 782, 700 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.40 (br s, 1H), 8.18 (d, J = 7.9 Hz, 1H), 8.09 (d, J = 8.1 Hz, 1H), 8.04 (br s, 1H); ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 166.99, 135.83, 134.42 (q, J = 32.5 Hz), 132.38, 128.08 (q, J = 7.1 Hz), 123.88 (q, J = 273.3 Hz), 123.65 (q, J = 3.8 Hz), 122.52; ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ -61.24 (s, 3F); HRMS Calcd for $\text{C}_8\text{H}_5\text{F}_3\text{IO}_3$ $[\text{M}+\text{H}]^+$: 332.9235, Found: 332.9228.

3.2 Procedure for synthesis of 16 and 17:

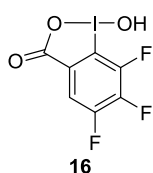


Scheme S2

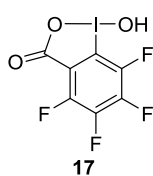
A modified literature procedure was followed for the synthesis of hypervalent iodine **16** and **17**.⁴ To a solution of the corresponding benzoic acid (77 mmol, 1.0 equiv) in anhydrous THF, n -Butyllithium (77 mL, 2.4 M in hexanes, 185 mmol, 2.4 equiv) was added dropwisely at $-78\text{ }^\circ\text{C}$ under Ar atmosphere. The resulting suspension was stirred at $-78\text{ }^\circ\text{C}$ for 3 h. Then a solution of iodine (93 mmol, 1.2 equiv) in anhydrous THF (50 mL) was added slowly until the brown color of the iodine persisted in the solution. After the addition was completed, the reaction mixture was warmed to room temperature. The reaction was carefully quenched by dropwise addition of saturated aqueous solution of NaHSO_3 until the brown color just faded (Note: excessive addition of NaHSO_3 could cause low yield, or even no product was obtained), and the reaction mixture was concentrated *in vacuo*. To the residue, water (100 mL) and ethyl acetate (80 mL) was added. The resulting mixture was acidified with aqueous 2 M H_2SO_4 to pH 1-2 under vigorous stirring at $0\text{ }^\circ\text{C}$. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (80 mL x 2). The combined organic phase was washed with saturated aqueous NaHSO_3 solution (5 mL), water (50 mL), brine (20 mL), dried over Na_2SO_4 and filtrated. The filtrate was concentrated *in vacuo* and the residue was precipitated with petroleum ether (60 mL) for 4 h. The resultant precipitate was collected by filtration, washed with petroleum ether (20 mL), the

S4

desired product was obtained as a white solid and used without further purification . The corresponding 2-iodobenzoic acid (50 mmol) and NaIO₄ (10.9 g, 51 mmol) were added into a solution of TFA (trifluoroacetic acid, 100 mL) in water (100 mL), the resulting mixture was heated at reflux for 3 h then cooled to 35 °C. The resultant precipitate was collected by filtration, carefully washed with water (400 mL) and petroleum ether (50 mL). The residue was collected and dried under high vacuum to give the desired product.

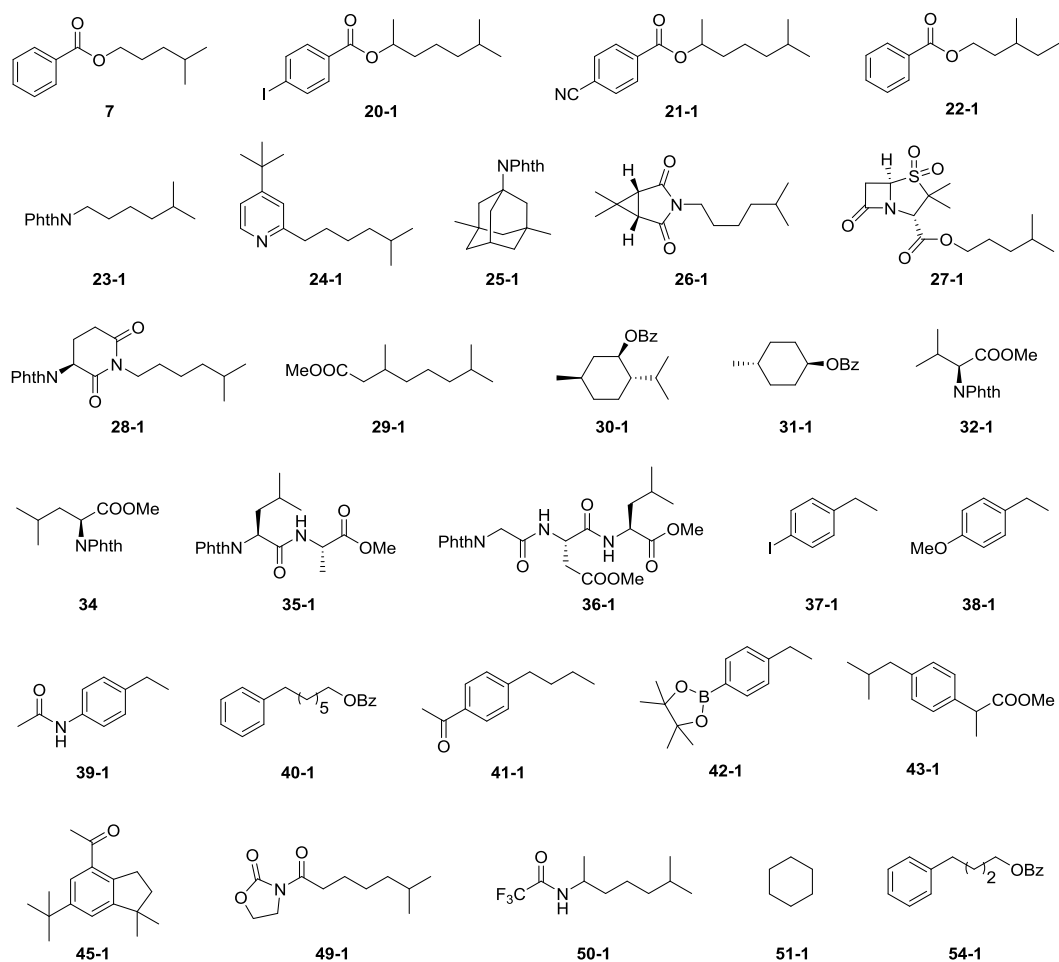


Compound **16** was obtained in 62% yield (for 2 steps) as white solid. M.p. = 219-220 °C (decomp.); IR (KBr) : $\tilde{\nu}$ = 3652, 2994, 1649, 1499, 1354, 1128, 1059, 793, 739 cm⁻¹; ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.87 (br s, 1H), 7.79 (ddd, *J* = 10.7, 7.3, 2.1 Hz, 1H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 165.65, 152.25 (dd, *J* = 253.2, 10.6 Hz), 151.59 (dd, *J* = 259.0, 12.7 Hz), 143.87 (dt, *J* = 257.2, 16.4 Hz), 130.49 (dd, *J* = 5.9, 2.0 Hz), 114.62 (dd, *J* = 18.6, 2.3 Hz), 100.23 (dd, *J* = 12.3, 1.8 Hz); ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -129.90 (dd, *J* = 20.4, 8.8 Hz, 1F), -133.67 (dd, *J* = 20.8, 8.8 Hz, 1F), -151.51 (dd, *J* = 20.4, 20.8 Hz, 1F); HRMS Calcd for C₇HF₃IO₃ [M-H]⁻: 316.8922, Found: 316.8925.



Compound **17** was obtained in 58% yield (for 2 steps) following the above procedure. Spectra data are consistent with those reported in the literature.⁴

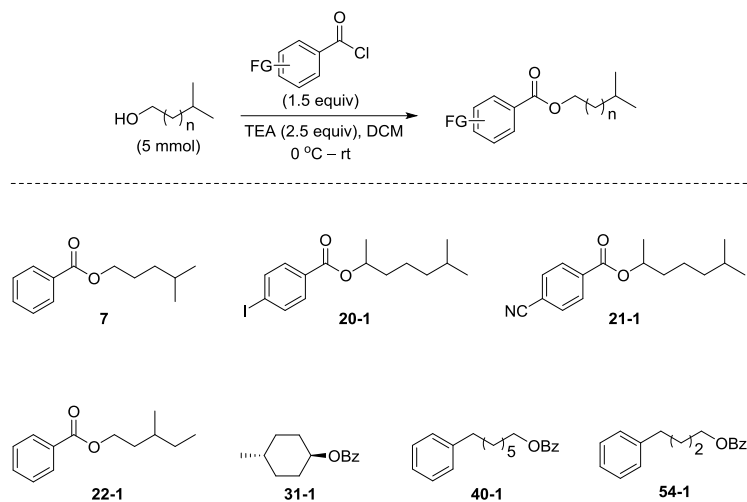
4. Synthesis of substrates for hydroxylation and amidation:



Scheme S3 List of all substrates used in this study

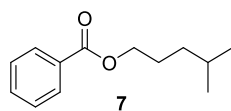
Compounds **37-1**, **38-1**, **39-1**, **41-1**, **42-1**, **45-1**, **51-1** were commercial available and used as received.

4.1 General procedure for synthesis 7, 20-1, 21-1, 22-1, 31-1, 40-1 and 54-1:

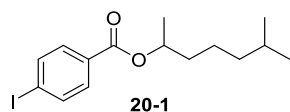


Scheme S4

To a solution of alcohols (5 mmol) and trimethylamine (TEA, 12.5 mmol, 2.5 equiv) in CH_2Cl_2 (50 mL) was added appropriate acyl chloride (7.5 mmol, 1.5 equiv) dropwisely at 0 °C. The reaction mixture was warmed to room temperature and stirred until corresponding alcohol was completely consumed monitoring by TLC. The mixture was diluted with DCM (200 mL), washed with saturated aqueous NaHCO_3 solution (20 mL), 1 M HCl (20 mL), water (20 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4 and filtrated. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel to afford desired product.

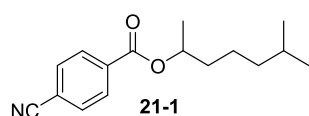


Compound **7** was prepared in 92% yield following the general procedure. Spectra data are consistent with those reported in the literature.⁵

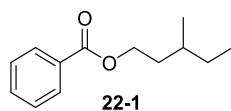


Compound **20-1** was prepared in 89% yield as a colorless oil following the general

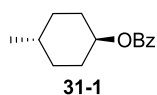
procedure. IR (KBr) : $\tilde{\nu}$ = 3465, 2953, 1717, 1586, 1271, 1108, 1008, 753 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 5.18-5.10 (m, 1H), 1.76-1.67 (m, 1H), 1.62-1.48 (m, 2H), 1.43-1.35 (m, 2H), 1.33 (d, J = 6.2 Hz, 3H), 1.24-1.16 (m, 2H), 0.86 (d, J = 6.6 Hz, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.57, 137.53, 130.91, 130.29, 100.35, 72.02, 38.61, 36.12, 27.73, 23.12, 22.51, 22.47, 19.98; **HRMS** Calcd for $\text{C}_{15}\text{H}_{21}\text{IO}_2$ $[\text{M}]^+$: 360.0586, Found: 360.0581.



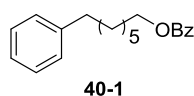
Compound **21-1** was prepared in 97% yield as a white solid following the general procedure. M.p. = 47-48 $^{\circ}\text{C}$; IR (KBr) : $\tilde{\nu}$ = 2954, 2232, 1721, 1464, 1277, 1110, 862, 768 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 5.26-5.09 (m, 1H), 1.80-1.67 (m, 1H), 1.66-1.48 (m, 2H), 1.43-1.29 (m, 5H), 1.27-1.14 (m, 2H), 0.86 (d, J = 6.6 Hz, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.51, 134.68, 132.12, 129.98, 118.03, 116.11, 72.90, 38.62, 36.09, 27.76, 23.13, 22.50, 22.46, 19.94; **HRMS** Calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$ $[\text{M}]^+$: 259.1572, Found: 259.0933.



Compound **22-1** was prepared in 84% yield following the general procedure. Spectra data are consistent with those reported in the literature.⁵

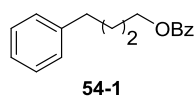


Compound **31-1** was prepared in 78% yield following the general procedure. Spectra data are consistent with those reported in the literature.⁶



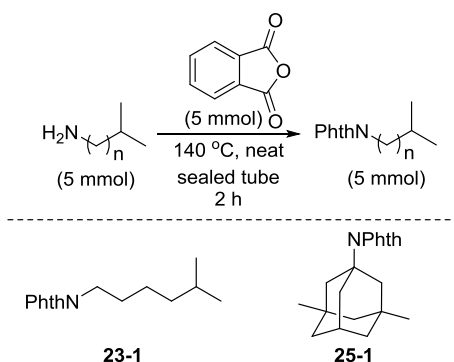
Compound **40-1** was prepared in 70% yield as a colorless oil following the general

procedure. IR (KBr) : $\tilde{\nu}$ = 3424, 2929, 1719, 1452, 1274, 1114, 747, 710 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06-8.03 (m, 2H), 7.58-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 4.31 (t, J = 6.6 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 1.79-1.72 (m, 2H), 1.66-1.59 (m, 2H), 1.46-1.34 (m, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.46, 142.56, 132.64, 130.36, 129.38, 128.24, 128.16, 128.09, 125.46, 64.91, 35.79, 31.28, 29.03, 29.01, 28.57, 25.85; **HRMS** Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 319.1674, Found: 319.1661.



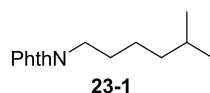
Compound **54-1** was prepared in 74% yield following the general procedure. Spectra data are consistent with those reported in the literature.⁷

4.2 Procedure for synthesis of phthalimide **23-1** and **25-1**:

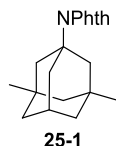


Scheme S5

The corresponding amine (5 mmol, 1.0 equiv) and phthalic anhydride (5mmol, 1.0 equiv) were heated at 140 °C in a sealed tube equipped with a stir bar for 2 h. After been cooled to room temperature, the reaction mixture was dissolved in ethyl acetate (200 mL), washed with water (20 mL), dried over Na_2SO_4 and filtrated. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 5:95 (v/v)) to afford the desired product.

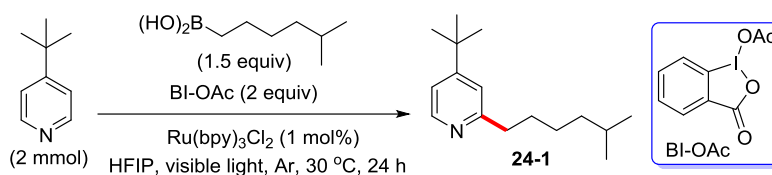


Compound **23-1** was prepared in 82% yield following the general procedure. Spectra data are consistent with those reported in the literature.⁶



Compound **25-1** was prepared in 78% yield following the general procedure. Spectra data are consistent with those reported in the literature.⁸

4.3 Synthesis of compound 24-1:

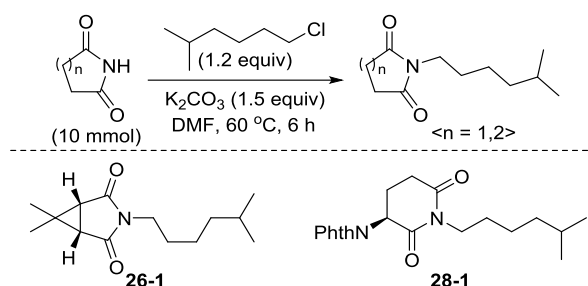


Scheme S6

4-(*tert*-butyl)pyridine (270 mg, 2 mmol, 1.0 equiv), (5-methylhexyl)boronic acid (432 mg, 3 mmol, 1.5 equiv) and BI-OAc (1.22 g, 4 mmol, 2.0 equiv) were added to a solution of Ru(bpy)₃Cl₂ (0.02 mmol, 0.01 equiv) in HFIP (5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the irradiation of fluorescent light for 48 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (30 mL). To the solution was added K₂CO₃ (approximate 1.5 g), and the resulting mixture was vigorously stirred for 5 min. Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel (eluted with ethyl acetate/petroleum ether = 5:95 (v/v)) to afford the desired product **24-1** as a colorless oil (289 mg, 62%). IR (KBr) : $\tilde{\nu}$ = 2957, 2867, 1600, 1465, 836, 743 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 5.3 Hz, 1H), 7.12 (d, *J* = 1.5 Hz, 1H), 7.08 (dd, *J* =

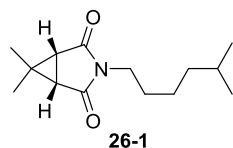
5.3, 1.8 Hz, 1H), 2.76 (t, $J = 7.8$ Hz, 2H), 1.74-1.67 (m, 2H), 1.59-1.49 (m, 1H), 1.40-1.33 (m, 2H), 1.30 (s, 9H), 1.24-1.19 (m, 2H), 0.86 (d, $J = 6.6$ Hz, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.18, 160.10, 148.91, 119.49, 117.95, 38.75, 38.61, 34.50, 30.50, 30.28, 27.81, 27.16, 22.57; **HRMS** Calcd for $\text{C}_{16}\text{H}_{28}\text{N}$ $[\text{M}+\text{H}]^+$: 234.2222, Found: 234.2220.

4.4 Procedure for synthesis of 26-1 and 28-1:



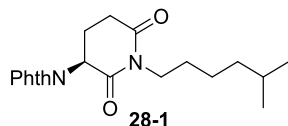
Scheme S7

The corresponding imine (10 mmol, 1.0 equiv), 1-chloro-5-methylhexane (1.62 g, 12 mmol, 1.2 equiv) and K_2CO_3 (2.07 g, 15 mmol, 1.5 equiv) were added into DMF (15 mL). The reaction mixture was heated at 60 °C for 6 h. After been cooled to room temperature, the reaction mixture was poured into brine (200 mL). The aqueous phase was extracted with ethyl ether (20 mL x 4). The combined organic phase was dried over Na_2SO_4 and filtrated. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 10:90 (v/v)) to afford the desired product.



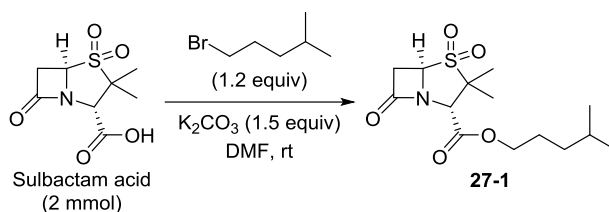
Compound **26-1** was prepared in 85% yield as a colorless oil following the general procedure. IR (KBr) : $\tilde{\nu} = 2955, 1768, 1703, 1403, 1177, 999, 685 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.36 (t, $J = 7.6$ Hz, 2H), 2.31 (s, 3H), 1.55-1.46 (m, 3H), 1.32-1.26 (m, 2H), 1.24 (s, 3H), 1.21 (s, 3H), 1.19-1.14 (m, 2H), 0.85 (d, $J = 6.6$ Hz, 6H); $^{13}\text{C NMR}$

(101 MHz, CDCl₃) δ 173.84, 38.30, 38.16, 35.21, 33.42, 28.11, 27.72, 26.11, 24.69, 22.43, 15.55; **HRMS** Calcd for C₁₄H₂₄NO₂ [M+H]⁺: 238.1807, Found: 238.1800.



Compound **28-1** was prepared in 81% yield as a pale yellow oil following the general procedure. IR (KBr) : $\tilde{\nu}$ = 2954, 2916, 1782, 1718, 1680, 1390, 1266, 1132, 749, 615 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 7.91-7.87 (m, 2H), 7.79-7.75 (m, 2H), 5.00-4.95 (m, 1H), 3.85-3.74 (m, 2H), 3.00-2.95 (m, 1H), 2.85-2.71 (m, 2H), 2.15-2.09 (m, 1H), 1.56-1.49 (m, 3H), 1.34-1.26 (m, 2H), 1.21-1.15 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ 170.79, 168.38, 167.41, 134.36, 131.76, 123.69, 50.15, 40.77, 38.42, 32.02, 27.98, 27.82, 24.63, 22.54, 22.50, 22.00; **HRMS** Calcd for C₂₀H₂₅N₂O₄ [M+H]⁺: 357.1814, Found: 357.1807.

4.5 Synthesis of compound 27-1:

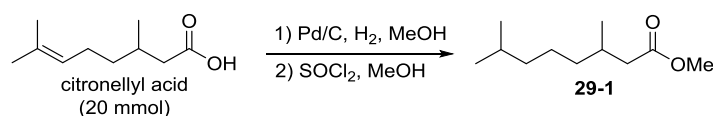


Scheme S8

Sulbactam acid (466 mg, 2.0 mmol, 1.0 equiv), 1-bromo-4-methylpentane (400 mg, 2.4 mmol, 1.2 equiv) and K₂CO₃ (415 mg, 3.0 mmol, 1.5 equiv) were added into DMF (5 mL). The reaction mixture was stirred overnight, then poured into brine (60 mL), the aqueous phase was extracted with ethyl ether (10 mL x 4). The combined organic phase was dried over Na₂SO₄ and filtrated. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 10:90 (v/v)) to afford the desired product as a colorless oil (482 mg, 76%). IR (KBr) : $\tilde{\nu}$ = 3007, 1798, 1752, 1466, 1275, 1262, 751 cm⁻¹; **¹H NMR** (400 MHz, CDCl₃)

δ 4.62 (dd, $J = 4.0, 2.3$ Hz, 1H), 4.39 (s, 1H), 4.19 (t, $J = 6.8$ Hz, 2H), 3.53-3.42 (m, 2H), 1.72-1.65 (m, 2H), 1.62 (s, 3H), 1.60-1.55 (m, 1H), 1.42 (s, 3H), 1.27-1.21 (m, 2H), 0.91 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.75, 166.98, 66.85, 63.18, 62.61, 61.03, 38.25, 34.81, 27.58, 26.26, 22.40, 22.37, 20.30, 18.52; HRMS Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_5\text{SNa}$ $[\text{M}+\text{Na}]^+$: 340.1195, Found: 340.1188.

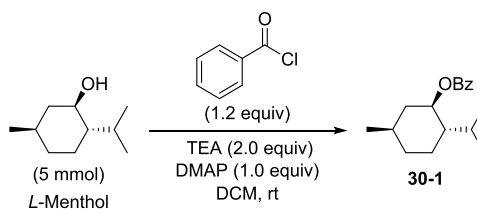
4.6 Synthesis of compound 29-1:



Scheme S9

To a solution of citronellyl acid (3.4 g, 20.0 mmol, 1.0 equiv) in 40 mL of MeOH was added Pd/C (0.6 g, 5% on carbon, wetted with ca. 55% water). The reaction mixture was stirred under H₂ for 24 h at room temperature. The reaction mixture was filtered through a pad of celite and the solvent was removed *in vacuo*. The residue was dissolved in MeOH (50 mL), thionyl chloride (9.5 g, 80 mmol, 4.0 equiv) was dropwisely added at 0 °C. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 2 h. The solvent was removed under reduced pressure and the resulting residue was purified by silica gel column chromatography (EtOAc/petroleum ether 1:100 (v/v)) to give compound **29-1** as a colorless oil (87% yield for 2 steps), spectra data are consistent with those reported in the literature.⁵

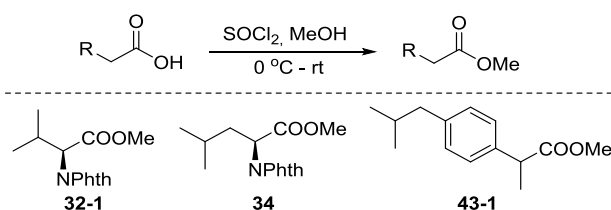
4.7 Synthesis of compound 30-1:



Scheme S10

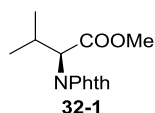
Compound **30-1** was prepared following a reported procedure⁹: To a solution of DMAP (0.61 g, 5 mmol, 1.0 equiv) in CH₂Cl₂ (25 mL) was added trimethylamine (1.01g, 10 mmol, 2.0 equiv), benzoyl chloride (0.84g, 6 mmol, 1.2 equiv), and finally *L*-Menthol (0.78 g, 5 mmol, 1.0 equiv). The mixture was stirred at room temperature for 2 h, and then diluted with ethyl ether (60 mL). The resulting mixture was washed with of 1N HCl (25 mL x 3), saturated aqueous NaHCO₃ solution (25 mL) and brine (25 mL). The organic layer was dried over Na₂SO₄ and filtrated. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 5:95 (v/v)) to afford **30-1** (1.20 g, 92%) as a colorless oil. Spectra data are consistent with those reported in the literature.⁸

4.8 Procedure for synthesis of 32-1, 34 and 43-1:

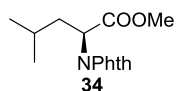


Scheme S11

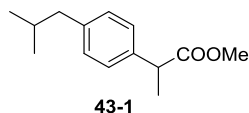
To the solution of the carboxylic acid (10 mmol) in MeOH (100 mL) was added thionyl chloride (4.8 g, 40 mmol, 4.0 equiv) dropwisely at 0 °C. After the addition was completed, the reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the resulting residue was purified by silica gel column chromatography to give the desired product.



Compound **32-1** was prepared in 72% yield following the general procedure. Spectra data are consistent with those reported in the literature.¹⁰

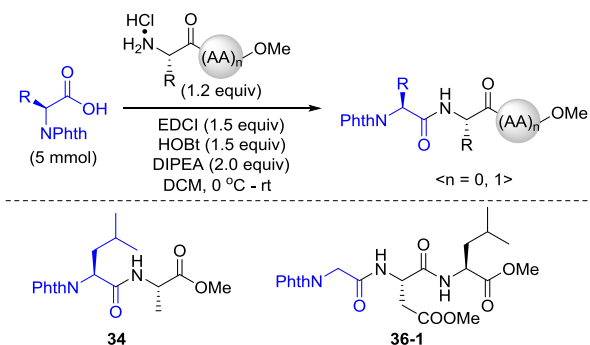


Compound **34** was prepared in 76% yield following the general procedure. Spectra data are consistent with those reported in the literature.¹¹



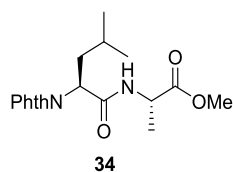
Compound **43-1** was prepared in 99% yield following the general procedure. Spectra data are consistent with those reported in the literature.¹²

4.9 Procedure for synthesis of **34** and **36-1**:

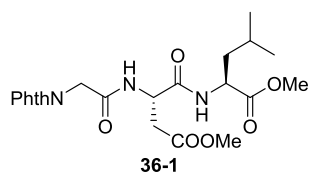


Scheme S12

To a suspension of the carboxylic acid (5 mmol) in 50 mL of DCM was added EDCI (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride, 7.5 mmol, 1.5 equiv) and HOBT (1-hydroxybenzotriazole, 7.5 mmol, 1.5 equiv) at 0 °C. The reaction mixture was stirred for 20 min. at 0 °C. Then corresponding amine hydrochloride (6.0 mmol, 1.2 equiv) and DIPEA (10 mmol, 2.0 equiv) were added successively. The reaction mixture was warmed to room temperature and stirred overnight. Removed the solvent under reduced pressure, and the residue was dissolved in EtOAc (100 mL). The resulting solution was washed with aqueous 1M HCl (20 mL), water (20 mL), brine (20 mL), dried over Na₂SO₄ and filtrated. The solvent was removed under reduced pressure and the resulting residue was purified by silica gel column chromatography to give the desired product.

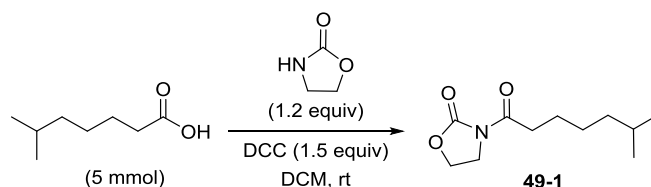


Compound **34** was prepared in 81% yield following the general procedure. Spectra data are consistent with those reported in the literature.¹³



Compound **36-1** was prepared in 70% yield as a white oil following the general procedure. M.p. = 198-199 °C; IR (KBr) : $\tilde{\nu}$ = 3290, 3075, 2956, 2923, 1776, 1730, 1677, 1648, 1550, 1415, 1240, 1194, 743, 712 cm^{-1} ; **¹H NMR** (400 MHz, CDCl_3) δ 7.90-7.86 (m, 2H), 7.78-7.74 (m, 2H), 7.24 (d, J = 7.7 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 4.87-4.83 (m, 1H), 4.54-4.49 (m, 1H), 4.39 (q, J = 16.2 Hz, 2H), 3.71 (s, 3H), 3.70 (s, 3H), 3.04 (dd, J = 17.2, 3.7 Hz, 1H), 2.66 (dd, J = 17.2, 7.2 Hz, 1H), 1.68-1.59 (m, 3H), 0.94 (t, J = 6.5 Hz, 3H); **¹³C NMR** (101 MHz, CDCl_3) δ 172.65, 172.58, 169.85, 167.58, 166.21, 134.18, 131.85, 123.51, 52.16, 52.13, 51.07, 49.18, 40.62, 40.59, 35.50, 24.69, 22.70, 21.59; **HRMS** Calcd for $\text{C}_{14}\text{H}_{23}\text{N}_2\text{NaO}_6$ [$\text{M}+\text{Na}^+$]: 484.1696, Found: 484.1682.

4.10 Procedure for synthesis of 49-1:

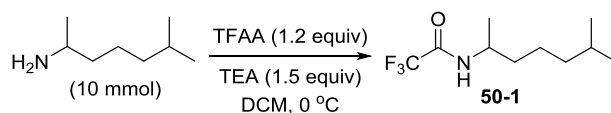


Scheme S13

To a solution of 6-methylheptanoic acid (1.44 g, 10 mmol) and oxazolidin-2-one (1.04 g, 12 mmol, 1.2 equiv) in 50 mL of DCM was added DCC (dicyclohexylcarbodiimide, 3.09 g, 15 mmol, 1.5 equiv). The reaction mixture was stirred overnight at room

temperature. The reaction mixture was washed with water (10 mL), brine (10 mL), dried over Na₂SO₄ and filtrated. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 20:80 (v/v)) to afford **49-1** (1.34 g, 63%) as a white solid. M.p. = 45-46 °C; IR (KBr) : $\tilde{\nu}$ = 3453, 2953, 1765, 1699, 1386, 1042, 757, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.41 (t, *J* = 8.1 Hz, 2H), 4.02 (t, *J* = 8.1 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.68-1.59 (m, 2H), 1.57-1.49 (m, 2H), 1.39-1.32 (m, 2H), 1.23-1.17 (m, 2H), 0.87 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 173.57, 153.52, 61.96, 42.49, 38.59, 35.12, 27.80, 26.89, 24.45, 22.54; HRMS Calcd for C₁₁H₁₉O₃NNa [M+Na⁺]: 236.1263, Found: 236.1252.

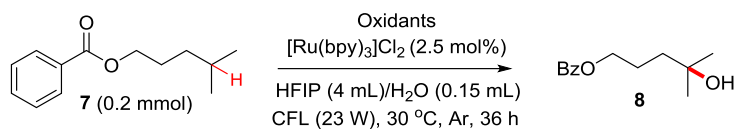
4.11 Synthesis of amide 50-1:



Scheme S14

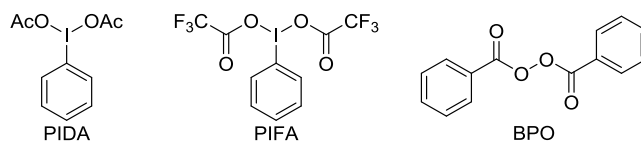
To a solution of 6-methylheptan-2-amine (1.29 g, 10.0 mmol, 1.0 equiv) and TEA (1.52 g, 15.0 mmol, 1.5 equiv) in 50 mL of DCM was added a solution of TFAA (trifluoroacetic anhydride, 2.52 g, 12.0 mmol, 1.2 equiv) in DCM (10 mL) at 0 °C. The reaction mixture was stirred for 1 h. The reaction mixture was washed with aqueous 1M HCl (10 mL), water (10 mL), dried over Na₂SO₄ and filtrated. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (eluted with EtOAc/petroleum ether 5:95 (v/v)) to give compound **50-1** as a colorless oil (1.89 g, 84% yield), spectra data are consistent with those reported in the literature.⁵

5. Optimization for tertiary C-H hydroxylation

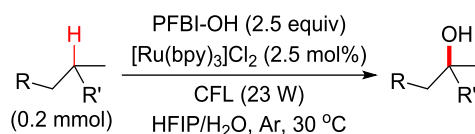


Oxidants	Equiv.	Conversion (%) ^a	Yield (%) ^b
PIDA	2.5	<5	<2
PIFA	2.5	<5	<2
BPO	2.5	22	11
K ₂ S ₂ O ₈	2.5	<5	<2
NaIO ₄	2.5	<5	<2

(a) Based on recovered starting material 7. (b) Isolated yield.

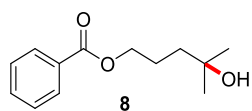


6. General procedures and substrate scope of tertiary C-H hydroxylation with PFBI-OH



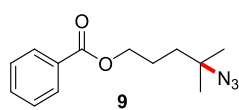
Scheme S15

General condition: To a solution of HFIP (4 mL) and water (0.15 mL) (Note: HFIP and water were bubbled with argon gas for 10 minutes to remove oxygen), were added substrate (0.2 mmol, 1.0 equiv), PFBI-OH (0.5 mmol, 2.5 equiv) and [Ru(bpy)₃]Cl₂ (0.005 mmol, 0.025 equiv). The reaction vial was purged with Ar for 1 min, then sealed with PTEF cap. The mixture was stirred at 30 °C under the irradiation of 23 W fluorescent light for 10-36 h. K₂CO₃ (approximate 150 mg) was added to the solution, and the resulting mixture was vigorously stirred for 5 min. The solvent was removed *in vacuo* and the residue was dissolved in DCM (5 mL). Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford the desired product.



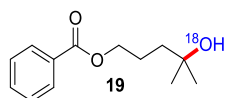
$R_f = 0.26$, 20% EtOAc in Hexane

Compound **8** was isolated in 64% yield as a colorless oil following the general procedure (36 h). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06-8.03 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.43 (m, 2H), 4.35 (t, $J = 6.6$ Hz, 2H), 1.91-1.84 (m, 2H), 1.67-1.60 (m, 2H), 1.27 (s, 6H). Spectra data are consistent with those reported in the literature.⁵



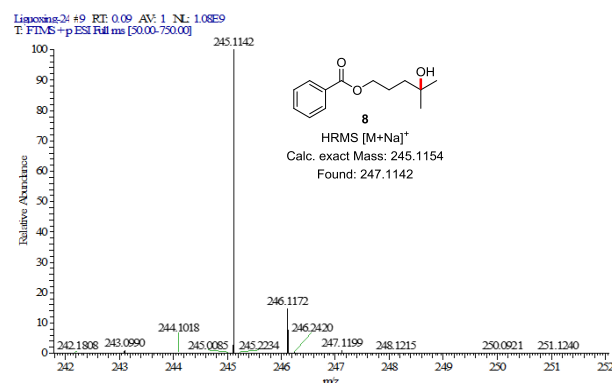
$R_f = 0.50$, 5% EtOAc in Hexane

Compound **9** was isolated in 58% yield as a colorless oil following the general procedure (36 h, 2 equiv of **11** (BI- N_3) was used, without water addition). IR (KBr) : $\tilde{\nu} = 3429, 2925, 2096, 1721, 1456, 1275, 1114, 712$ cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07-8.01 (m, 2H), 7.60-7.53 (m, 1H), 7.49-7.42 (m, 2H), 4.34 (t, $J = 6.5$ Hz, 2H), 1.90-1.82 (m, 2H), 1.66-1.62 (m, 2H), 1.31 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.53, 132.90, 130.22, 129.56, 129.51, 128.33, 64.81, 61.14, 37.80, 25.95, 23.79; **HRMS** Calcd for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_2\text{Na}$ [$\text{M}+\text{Na}^+$]: 270.1218, Found: 270.1212.



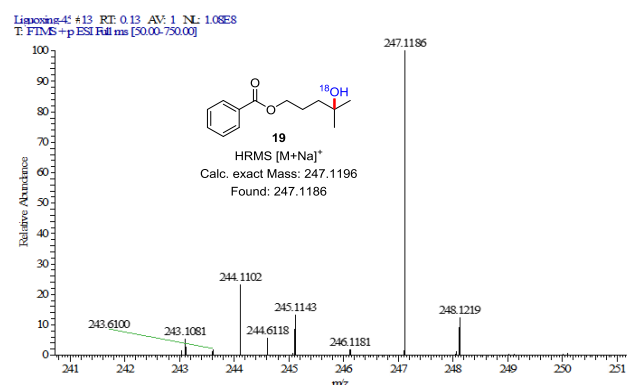
Compound **19** was isolated in 61% yield (88% incorporation of ^{18}O) as a colorless oil following the general procedure (Note: HFIP was dried over anhydrous Na_2SO_4 overnight, then bubbled with argon gas for 10 minutes to remove oxygen before the experiment. 36 h, 0.15 mL of H_2^{18}O was used, 97% ^{18}O).

High Resolution Mass Spectrum (HRMS) of Compound 8:



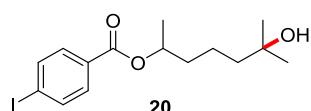
m/z	Abund (NL)
245.1154	1.08*10 ⁹
247.1199	1.05*10 ⁷

High Resolution Mass Spectrum (HRMS) of Compound 19:



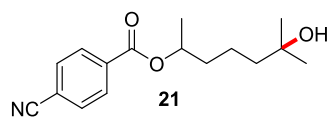
m/z	Abund (NL)
245.1143	1.45*10 ⁷
247.1186	1.08*10 ⁸

88% incorporation of ¹⁸O was estimated based on the relative abundance (NL) of the peaks at 245.1143 and 247.1186.



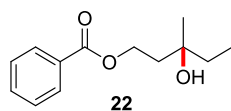
R_f = 0.27, 20% EtOAc in Hexane

Compound **20** was isolated in 67% yield as a colorless oil following the general procedure (24 h, conversion based on RSM **20-1**: 80%, yield based on RSM: 84%). IR (KBr) : $\tilde{\nu}$ = 3394, 2922, 1714, 1586, 1275, 1115, 1007, 754 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 5.20-5.13 (m, 1H), 1.80-1.72 (m, 1H), 1.66-1.44 (m, 6H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.20 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 165.72, 137.62, 130.96, 130.24, 100.45, 71.86, 70.80, 43.47, 36.40, 29.27, 29.19, 20.16, 20.03; HRMS Calcd for C₁₅H₂₁O₃INa [M+Na]⁺: 399.0433, Found: 399.0419.



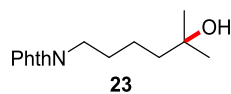
$R_f = 0.20$, 20% EtOAc in Hexane

Compound **21** was isolated in 63% yield as a colorless oil following the general procedure (24 h, conversion based on RSM **21-1**: 77%, yield based on RSM: 82%). IR (KBr) : $\tilde{\nu} = 3730, 2921, 2232, 1719, 1462, 1278, 1112, 863, 768, 691 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.13 (d, $J = 8.1 \text{ Hz}$, 2H), 7.74 (d, $J = 8.1 \text{ Hz}$, 2H), 5.24-5.17 (m, 1H), 1.83-1.74 (m, 1H), 1.68-1.59 (m, 1H), 1.53-1.40 (m, 4H), 1.37 (d, $J = 6.3 \text{ Hz}$, 3H), 1.21 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 164.55, 134.58, 132.20, 132.15, 130.00, 118.02, 116.15, 72.67, 70.77, 43.40, 36.34, 29.29, 29.23, 20.12, 19.98; **HRMS** Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{NNa}$ $[\text{M}+\text{Na}]^+$: 298.1419, Found: 298.1407.



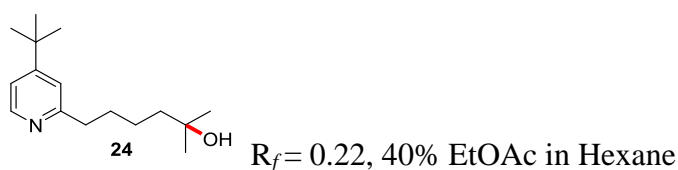
$R_f = 0.28$, 20% EtOAc in Hexane

Compound **22** was isolated in 54% yield as a colorless oil following the general procedure (36 h, conversion based on RSM **22-1**: 67%, yield based on RSM: 80%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04-8.02 (m, 2H), 7.58-7.54 (m, 1H), 7.47-7.42 (m, 2H), 4.50 (t, $J = 6.9 \text{ Hz}$, 2H), 1.97 (td, $J = 6.9, 2.6 \text{ Hz}$, 2H), 1.59 (q, $J = 7.5 \text{ Hz}$, 2H), 1.26 (s, 3H), 0.96 (t, $J = 7.5 \text{ Hz}$, 3H). Spectra data are consistent with those reported in the literature.⁵

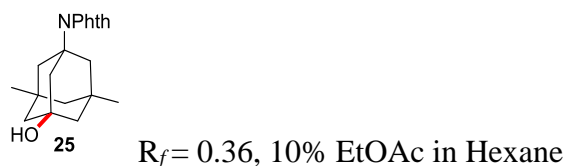


$R_f = 0.13$, 20% EtOAc in Hexane

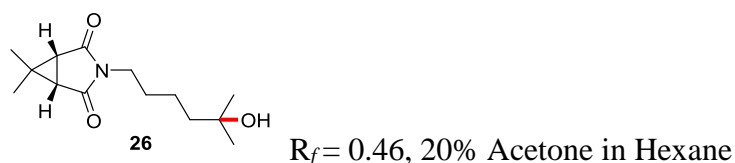
Compound **23** was isolated in 77% yield as a white solid following the general procedure (24 h). M.p. = 54-55 °C; IR (KBr) : $\tilde{\nu} = 3396, 2923, 1770, 1710, 1398, 1186, 1038, 720 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85-7.82 (m, 2H), 7.74-7.69 (m, 2H), 3.71 (t, $J = 7.2 \text{ Hz}$, 2H), 1.74-1.66 (m, 2H), 1.55-1.50 (m, 1H), 1.47-1.38 (m, 3H), 1.21 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.48, 133.87, 132.11, 123.17, 70.77, 43.13, 37.74, 29.20, 28.94, 21.40; **HRMS** Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3\text{NNa}$ $[\text{M}+\text{Na}]^+$: 284.1263, Found: 284.1250.



Compound **24** was isolated in 57% yield as a colorless oil following the general procedure (24 h, conversion based on RSM **24-1**: 78%, yield based on RSM: 73%). IR (KBr) : $\tilde{\nu} = 3358, 2925, 1724, 1632, 1467, 1210, 954, 736 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.43 (d, $J = 4.6 \text{ Hz}$, 1H), 7.14 (s, 1H), 7.12 (d, $J = 4.6 \text{ Hz}$, 1H), 2.81 (t, $J = 7.6 \text{ Hz}$, 2H), 1.79-1.71 (m, 2H), 1.55-1.51 (m, 2H), 1.48-1.42 (m, 2H), 1.31 (s, 9H), 1.21 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.73, 160.70, 148.61, 119.77, 118.25, 70.92, 43.52, 38.12, 34.64, 30.50, 30.42, 29.20, 23.97; **HRMS** Calcd for $\text{C}_{16}\text{H}_{28}\text{NO}$ $[\text{M}+\text{H}]^+$: 250.2171, Found: 250.2169.

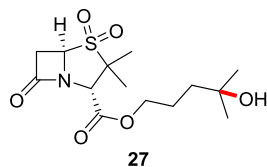


Compound **25** was isolated in 81% yield as a white solid following the general procedure (10 h). M.p. = 161-162 °C; IR (KBr) : $\tilde{\nu} = 3454, 2948, 1769, 1706, 1505, 1456, 1353, 1114, 966, 720 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78-7.75 (m, 2H), 7.71-7.68 (m, 2H), 2.91 (s, 2H), 2.25-2.16 (m, 4H), 2.02 (s, 4H), 1.57 (br s, 1H), 1.28 (s, 2H), 1.04 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.40, 133.90, 131.67, 122.72, 85.75, 62.02, 49.07, 45.84, 44.97, 42.40, 34.50, 29.35; **HRMS** Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_3$ $[\text{M}]^+$: 325.1678, Found: 325.1675.



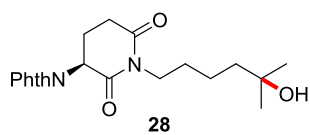
Compound **26** was isolated in 74% yield as a colorless oil following the general procedure (24 h). IR (KBr) : $\tilde{\nu} = 3368, 2936, 1766, 1697, 1504, 1370, 1017, 751, 686 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.39 (t, $J = 7.5 \text{ Hz}$, 2H), 2.32 (s, 2H), 1.58-1.47

(m, 4H), 1.40-1.34 (m, 2H), 1.24 (s, 3H), 1.21 (s, 3H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.01, 70.70, 43.08, 37.93, 35.44, 33.50, 29.12, 28.29, 26.16, 21.55, 15.62; HRMS Calcd for $\text{C}_{14}\text{H}_{22}\text{NO}_2$ $[\text{M}-\text{OH}]^+$: 236.1651, Found: 236.1642.



$R_f = 0.23$, 50% EtOAc in Hexane

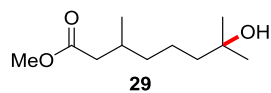
To a solution of HFIP (4 mL) and water (0.15 mL), were added compound **27-1** (64.0 mg, 0.2 mmol, 1.0 equiv), PFBI-OH (168.8 mg, 0.5 mmol, 2.5 equiv) and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (3.4 mg, 0.005 mmol, 0.025 equiv). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the irradiation of fluorescent light for 24 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (MeOH/DCM = 2:98 (v/v)) to afford compound **27** as a colorless oil (38.0 mg, 65%). IR (KBr) : $\tilde{\nu} = 3391, 2920, 1796, 1752, 1646, 1466, 1373, 1221, 1119, 951, 749\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3) δ 4.60 (dd, $J = 4.1, 2.3\text{ Hz}$, 1H), 4.37 (s, 1H), 4.21 (t, $J = 6.8\text{ Hz}$, 2H), 3.50-3.40 (m, 2H), 1.81-1.74 (m, 2H), 1.60 (s, 3H), 1.52-1.48 (m, 2H), 1.40 (s, 3H), 1.22 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.78, 166.94, 70.36, 66.86, 63.22, 62.66, 61.07, 39.49, 38.28, 29.34, 29.30, 23.49, 20.29, 18.58; HRMS Calcd for $\text{C}_{14}\text{H}_{24}\text{NO}_6\text{S}$ $[\text{M}+\text{H}]^+$: 334.1324, Found: 334.1318.



$R_f = 0.68$, 5% MeOH in DCM

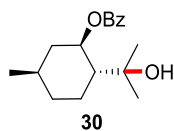
Compound **28** was isolated in 62% yield as a colorless oil following the general procedure (24 h). IR (KBr) : $\tilde{\nu} = 3476, 2966, 1717, 1678, 1391, 1193, 1081, 890, 721\text{ cm}^{-1}$; ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.88 (m, 2H), 7.78-7.76 (m, 2H), 5.01-4.97 (m, 1H), 3.84 (t, $J = 7.3\text{ Hz}$, 2H), 3.03-2.94 (m, 1H), 2.85-2.71 (m, 2H), 2.17-2.10 (m, 1H), 1.60-1.54 (m, 2H), 1.51-1.45 (m, 2H), 1.43-1.33 (m, 2H), 1.20 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.86, 168.53, 167.42, 134.41, 131.69, 123.70, 70.75, 50.11,

43.25, 40.42, 31.96, 29.16, 29.07, 28.11, 21.96, 21.34; **HRMS** Calcd for C₂₀H₂₃N₂O₄ [M-OH]⁺: 355.1658, Found: 355.1651.



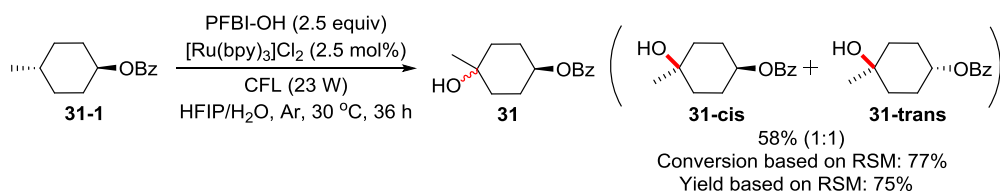
R_f = 0.32, 20% EtOAc in Hexane

Compound **29** was isolated in 80% yield as a colorless oil following the general procedure (24 h). **¹H NMR** (400 MHz, CDCl₃) δ 3.67 (s, 3H), 2.31 (dd, *J* = 14.7, 6.0 Hz, 1H), 2.13 (dd, *J* = 14.7, 8.0 Hz, 1H), 2.03-1.93 (m, 1H), 1.48-1.29 (m, 6H), 1.21 (s, 6H), 0.95 (d, *J* = 6.6 Hz, 3H). Spectra data are consistent with those reported in the literature.⁵

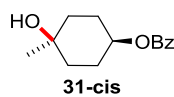


R_f = 0.45, 20% EtOAc in Hexane

Compound **30** was isolated in 52% yield as a colorless oil following the general procedure (24 h, conversion based on RSM **30-1**: 84%, yield based on RSM: 62%). **¹H NMR** (400 MHz, CDCl₃) δ 8.04-8.01 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.43 (m, 2H), 5.10 (td, *J* = 10.8, 4.2 Hz, 1H), 2.76 (br s, 1H), 2.19-2.14 (m, 1H), 2.00-1.94 (m, 1H), 1.90-1.83 (m, 1H), 1.78-1.70 (m, 1H), 1.67-1.55 (m, 1H), 1.19 (s, 3H), 1.17 (s, 3H), 1.14-0.96 (m, 3H), 0.94 (d, *J* = 6.5 Hz, 3H). Spectra data are consistent with those reported in the literature.¹⁴



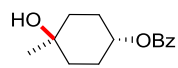
Scheme S16



R_f = 0.2, 20% EtOAc in Hexane

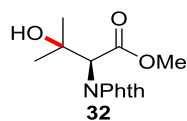
Compound **31-cis** was isolated in 30% yield as a colorless oil following the general

procedure (36 h, conversion based on RSM: 77%, yield based on RSM: 39%). ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.58-7.53 (m, 1H), 7.46-7.42 (m, 2H), 5.03-4.96 (m, 1H), 1.95-1.86 (m, 3H), 1.81-1.75 (m, 2H), 1.62-1.54 (m, 3H), 1.29 (s, 3H). Spectra data are consistent with those reported in the literature.¹⁵



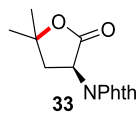
31-trans $R_f = 0.3$, 20% EtOAc in Hexane

Compound **31-trans** was isolated in 28% yield as a colorless oil following the general procedure (36 h, conversion based on RSM: 77%, yield based on RSM: 36%). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 5.23-5.20 (m, 1H), 2.06-2.00 (m, 2H), 1.84-1.78 (m, 4H), 1.60-1.57 (m, 2H), 1.32 (s, 3H). Spectra data are consistent with those reported in the literature.¹⁵



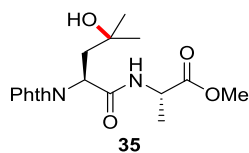
32 $R_f = 0.26$, 20% EtOAc in Hexane

Compound **32** was isolated in 29% yield as a colorless solid following the general procedure (36 h, conversion based on RSM: 36%, yield based on RSM: 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.90 (m, 2H), 7.80-7.78 (m, 2H), 4.90 (s, 1H), 4.40 (s, 1H), 3.76 (s, 3H), 1.53 (s, 3H), 1.30 (s, 3H). Spectra data are consistent with those reported in the literature.¹⁶



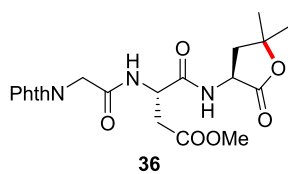
33 $R_f = 0.38$, 20% EtOAc in Hexane

Compound **33** was isolated in 52% yield as a white solid following the general procedure (36 h, conversion based on RSM: 59%, yield based on RSM: 88%). ¹H NMR (400 MHz, CDCl₃) δ 7.90-7.86 (m, 2H), 7.78-7.74 (m, 2H), 5.24 (dd, *J* = 11.5, 9.6 Hz, 1H), 2.60 (t, *J* = 12.0 Hz, 1H), 2.44 (dd, *J* = 12.3, 9.6 Hz, 1H), 1.64 (s, 3H), 1.52 (s, 3H). Spectra data are consistent with those reported in the literature.¹³



$R_f = 0.28$, 60% EtOAc in Hexane

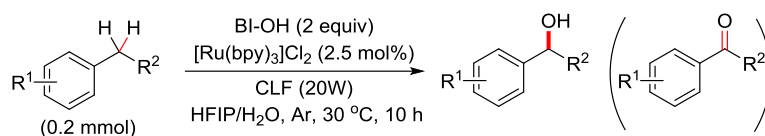
Compound **35** was isolated in 44% yield as a white solid following the general procedure (36 h, conversion based on RSM: 49%, yield based on RSM: 90%). **¹H NMR** (400 MHz, CDCl₃) δ 7.88-7.85 (m, 2H), 7.75-7.73 (m, 2H), 7.41 (d, $J = 7.2$ Hz, 1H), 5.12 (t, $J = 5.6$ Hz, 1H), 4.62-4.55 (m, 1H), 3.74 (s, 3H), 2.63 (dd, $J = 15.3, 6.0$ Hz, 1H), 2.20 (dd, $J = 15.3, 5.3$ Hz, 1H), 2.07 (br s, 1H), 1.40 (d, $J = 7.2$ Hz, 3H), 1.35 (s, 3H), 1.31 (s, 3H). Spectra data are consistent with those reported in the literature.¹³



$R_f = 0.50$, 5% MeOH in DCM

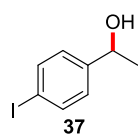
Compound **36** was isolated in 39% yield as a white solid following the general procedure (36 h, conversion based on RSM: 51%, yield based on RSM: 76%). M.p. = 188-190 °C; IR (KBr) : $\tilde{\nu} = 3435, 2922, 2852, 1772, 1721, 1652, 1547, 1419, 1377, 1193, 1160, 1113, 956, 712$ cm⁻¹; **¹H NMR** (400 MHz, CDCl₃) δ 7.88-7.84 (m, 2H), 7.76-7.73 (m, 2H), 7.51 (d, $J = 8.3$ Hz, 1H), 7.42 (d, $J = 7.5$ Hz, 1H), 4.93-4.88 (m, 1H), 4.80-4.73 (m, 1H), 4.47-4.33 (m, 2H), 3.71 (s, 3H), 3.04 (dd, $J = 17.1, 4.7$ Hz, 1H), 2.77 (dd, $J = 17.1, 6.0$ Hz, 1H), 2.51 (dd, $J = 12.5, 9.1$ Hz, 1H), 2.14 (dd, $J = 12.5, 11.7$ Hz, 1H), 1.52 (s, 3H), 1.43 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 174.02, 172.52, 170.32, 167.77, 166.66, 134.27, 131.90, 123.61, 82.42, 52.26, 50.35, 49.40, 40.80, 35.15, 28.81, 27.16; **HRMS** Calcd for C₂₂H₂₇O₈N₂Na [M+Na⁺]: 468.1383, Found: 468.1367.

7. General procedures and substrate scope of benzylic C-H hydroxylation with BI-OH



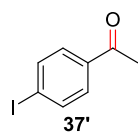
Scheme S17

General condition: To a solution of HFIP (4 mL) and water (0.45 mL) (Note: HFIP and water were bubbled with argon gas for 10 minutes to remove oxygen), were added substrate (0.2 mmol, 1.0 equiv), BI-OH (0.4 mmol, 2.0 equiv) and [Ru(bpy)₃]Cl₂ (0.005 mmol, 0.025 equiv). The reaction vial was purged with Ar for 1 min, then sealed with PTEF cap. The reaction mixture was stirred at 30 °C under the irradiation of fluorescent light for 10 h. K₂CO₃ (approximate 20 mg) was added to the solution, and the resulting mixture was vigorously stirred for 5 min. The solvent was removed *in vacuo* and the residue was dissolved in DCM (5 mL). Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford the desired product.



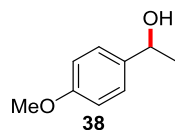
$R_f = 0.44$, 20% EtOAc in Hexane

Compound **37** was isolated in 71% yield as a colorless oil following the general procedure. ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.63 (m, 2H), 7.13-7.11 (m, 2H), 4.85 (q, *J* = 6.5 Hz, 1H), 1.84 (br s, 1H), 1.46 (d, *J* = 6.5 Hz, 3H). Spectra data are consistent with those reported in the literature.¹⁷



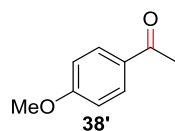
$R_f = 0.44$, 20% EtOAc in Hexane

Compound **37'** was isolated in 8% yield as a light yellow solid following the general procedure. **¹H NMR** (400 MHz, CDCl₃) δ 7.85-7.82 (m, 2H), 7.69-7.65 (m, 2H), 2.58 (s, 3H). Spectra data are consistent with those reported in the literature.¹⁸



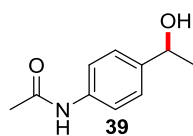
$R_f = 0.32$, 20% EtOAc in Hexane

Compound **38** was isolated in 82% yield as colorless oil following the general procedure (1.5 equiv. BI-OH was used). **¹H NMR** (400 MHz, CDCl₃) δ 7.32-7.28 (m, 2H), 6.90-6.86 (m, 2H), 4.85 (q, $J = 6.4$ Hz, 1H), 3.80 (s, 3H), 1.86 (br s, 1H), 1.48 (d, $J = 6.4$ Hz, 3H). Spectra data are consistent with those reported in the literature.¹⁹



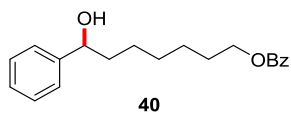
$R_f = 0.32$, 20% EtOAc in Hexane

Compound **38'** was isolated in 10% yield as a white solid following the general procedure (1.5 equiv. BI-OH was used). **¹H NMR** (400 MHz, CDCl₃) δ 7.96-7.93 (m, 2H), 6.96-6.92 (m, 2H), 3.88 (s, 3H), 2.57 (s, 3H). Spectra data are consistent with those reported in the literature.²⁰



$R_f = 0.17$, 60% EtOAc in Hexane

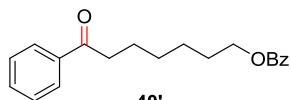
Compound **39** was isolated in 76% yield as a colorless oil following the general procedure (16 h, 4.0 equiv. BI-OH was used). **¹H NMR** (400 MHz, CDCl₃) δ 7.49 (br s, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 4.86 (q, $J = 6.2$ Hz, 1H), 2.15 (s, 3H), 2.10 (br s, 1H), 1.47 (d, $J = 6.4$ Hz, 3H). Spectra data are consistent with those reported in the literature.²¹



40

$R_f = 0.43$, 20% EtOAc in Hexane

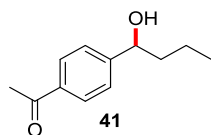
Compound **40** was isolated in 78% yield as a colorless oil following the general procedure. IR (KBr) : $\tilde{\nu} = 3365, 2929, 1717, 1452, 1315, 1274, 1116, 742, 709 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.05-8.02 (m, 2H), 7.57-7.53 (m, 1H), 7.46-7.41 (m, 2H), 7.37-7.32 (m, 4H), 7.30-7.25 (m, 1H), 4.67 (dd, $J = 7.1, 6.1 \text{ Hz}$, 1H), 4.29 (t, $J = 6.6 \text{ Hz}$, 2H), 1.89 (br s, 1H), 1.86-1.67 (m, 4H), 1.49-1.27 (m, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.63, 144.82, 132.74, 130.36, 129.45, 128.34, 128.24, 127.39, 125.80, 74.46, 64.96, 38.90, 29.07, 28.55, 25.87, 25.62; **HRMS** Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 335.1623, Found: 335.1609.



40'

$R_f = 0.77$, 20% EtOAc in Hexane

Compound **40'** was isolated in 6% yield as a colorless oil following the general procedure. IR (KBr) : $\tilde{\nu} = 3416, 3062, 2932, 2857, 1967, 1912, 1718, 1685, 1451, 1276, 1116, 971, 804, 714 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (dd, $J = 8.0, 0.9 \text{ Hz}$, 2H), 7.96 (dd, $J = 8.0, 0.9 \text{ Hz}$, 2H), 7.58-7.54 (m, 2H), 7.48-7.42 (m, 4H), 4.33 (t, $J = 6.6 \text{ Hz}$, 2H), 2.99 (t, $J = 7.3 \text{ Hz}$, 2H), 1.83-1.75 (m, 4H), 1.55-1.43 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 200.32, 166.66, 137.02, 132.91, 132.81, 130.45, 129.52, 128.56, 128.31, 128.02, 64.94, 38.42, 28.98, 28.58, 25.94, 24.13; **HRMS** Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 333.1467, Found: 333.1453.

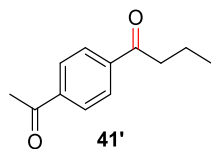


41

$R_f = 0.19$, 20% EtOAc in Hexane

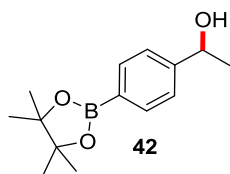
Compound **41** was isolated in 57% yield as a pale yellow oil following the general procedure (16 h, 4.0 equiv. BI-OH was used). IR (KBr) : $\tilde{\nu} = 3440, 2958, 1931, 1679, 1607, 1414, 1360, 1271, 960, 836, 750 \text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.2 \text{ Hz}$, 2H), 7.44 (d, $J = 8.2 \text{ Hz}$, 2H), 4.76 (dd, $J = 7.3, 5.8 \text{ Hz}$, 1H), 2.60 (s, 3H), 2.04 (br s, 1H), 1.82-1.65 (m, 2H), 1.49-1.28 (m, 2H), 0.94 (t, $J = 7.4 \text{ Hz}$, 3H); $^{13}\text{C NMR}$

NMR (101 MHz, CDCl₃) δ 197.85, 150.29, 136.28, 128.53, 125.95, 73.83, 41.27, 26.61, 18.83, 13.88; **HRMS** Calcd for C₁₂H₁₅O₂ [M-H]⁻: 191.1072, Found: 191.1068.



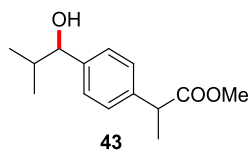
41' $R_f = 0.58$, 20% EtOAc in Hexane

Compound **41'** was isolated in 9% yield as a white solid following the general procedure (16 h, 4.0 equiv. BI-OH was used). **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (br s, 4H), 2.99 (t, $J = 7.2$ Hz, 2H), 2.65 (s, 3H), 1.83-1.74 (m, 2H), 1.02 (t, $J = 7.4$ Hz, 3H). Spectra data are consistent with those reported in the literature.²²



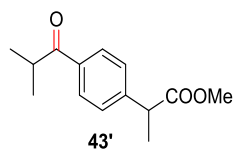
42 $R_f = 0.38$, 20% EtOAc in Hexane

Compound **42** was isolated in 50% yield as a colorless oil following the general procedure (4.0 equiv. BI-OH was used). **¹H NMR** (400 MHz, CDCl₃) δ 7.80 (d, $J = 7.9$ Hz, 2H), 7.38 (d, $J = 7.9$ Hz, 2H), 4.92 (q, $J = 6.3$ Hz, 1H), 1.82 (br s, 1H), 1.49 (d, $J = 6.5$ Hz, 3H), 1.34 (s, 12H). Spectra data are consistent with those reported in the literature.²³



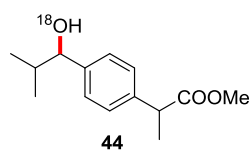
43 $R_f = 0.36$, 20% EtOAc in Hexane

Compound **43** was isolated in 64% yield as a colorless oil following the general procedure. **¹H NMR** (400 MHz, CDCl₃) δ 7.27 (s, 4H), 4.34 (d, $J = 6.9$ Hz, 1H), 3.72 (q, $J = 7.2$ Hz, 1H), 3.66 (s, 3H), 1.99-1.90 (m, 1H), 1.49 (d, $J = 7.2$ Hz, 3H), 1.00 (d, $J = 6.7$ Hz, 3H), 0.80 (d, $J = 6.8$ Hz, 3H). Spectra data are consistent with those reported in the literature.²⁴



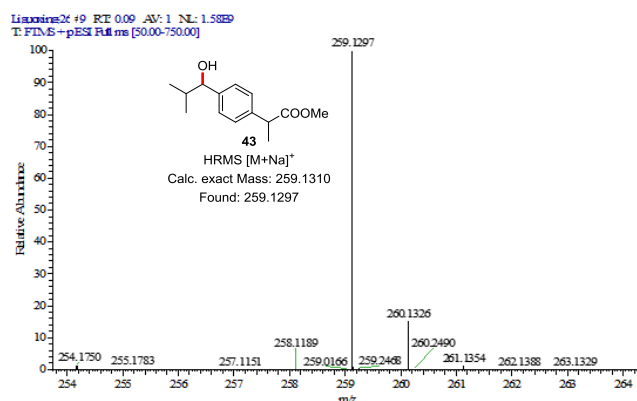
$R_f = 0.4$, DCM

Compound **43'** was isolated in 10% yield as a colorless oil following the general procedure. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.3$ Hz, 2H), 7.39 (d, $J = 8.3$ Hz, 2H), 3.79 (q, $J = 7.2$ Hz, 1H), 3.68 (s, 3H), 3.59-3.48 (m, 1H), 1.53 (d, $J = 7.2$ Hz, 3H), 1.21 (d, $J = 6.8$ Hz, 6H). Spectra data are consistent with those reported in the literature.²⁵



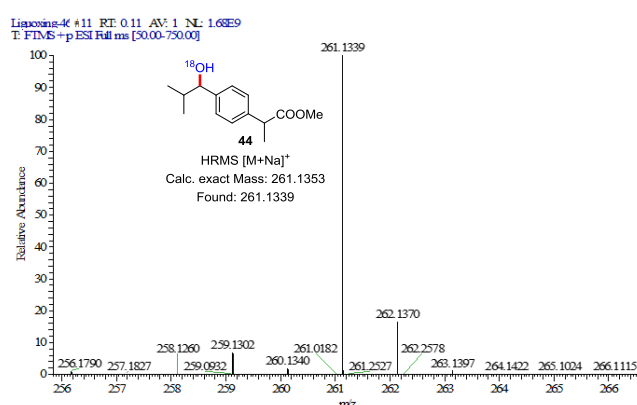
Compound **44** was isolated in 60% yield (93% incorporation of ^{18}O) as a colorless oil following the general procedure (Note: HFIP was dried over anhydrous Na_2SO_4 overnight, then bubbled with argon gas for 10 minutes to remove oxygen before the experiment. 10 h, 0.45 mL of H_2^{18}O was used, 97% ^{18}O).

High Resolution Mass Spectrum (HRMS) of Compound 43:



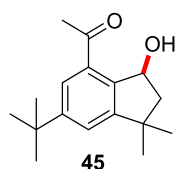
m/z	Abund (NL)
259.1297	1.58*10 ⁹
261.1354	1.85*10 ⁷

High Resolution Mass Spectrum (HRMS) of Compound 44:



m/z	Abund (NL)
259.1302	1.18*10 ⁸
261.1339	1.68*10 ⁹

93% incorporation of ¹⁸O was estimated based on the relative abundance (NL) of the peaks at 259.1302 and 261.1339.



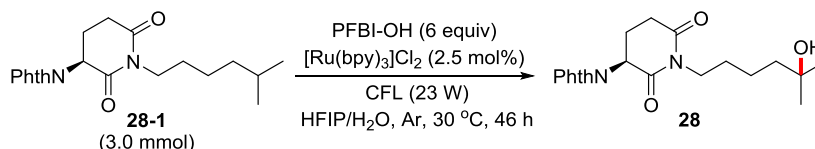
$R_f = 0.63$, 20% EtOAc in Hexane

Compound **45** was isolated in 90% yield as a white solid following the general procedure (1.5 equiv. BI-OH was used). M.p. = 59-60 °C; IR (KBr) : $\tilde{\nu} = 3494, 2954, 2865, 1792, 1664, 1460, 1362, 1238, 1060, 889, 778, 704 \text{ cm}^{-1}$; ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, $J = 1.6 \text{ Hz}$, 1H), 7.43 (d, $J = 1.6 \text{ Hz}$, 1H), 5.38 (ddd, $J = 7.6, 3.9, 1.6 \text{ Hz}$, 1H), 4.53 (d, $J = 1.6 \text{ Hz}$, 1H), 2.68 (s, 3H), 2.30 (dd, $J = 13.5, 7.6 \text{ Hz}$, 1H), 2.05 (dd, $J = 13.6, 3.9 \text{ Hz}$, 1H), 1.40 (s, 3H), 1.37 (s, 9H), 1.26 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 202.70, 154.34, 152.22, 142.21, 133.62, 126.21, 124.63, 73.19, 48.71, 42.79, 34.88, 31.40, 30.92, 29.88, 27.96; HRMS Calcd for C₁₇H₂₄NaO₂ [M+Na]⁺: 283.1674,

Found: 283.1660.

8. Scale-up reaction for hydroxylation

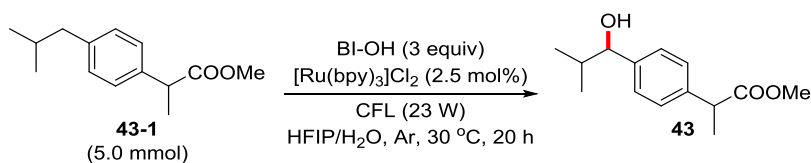
8.1 Scale-up reaction for hydroxylation of 28-1:



Scheme S18

Reaction condition: To a solution of HFIP (60 mL) and water (2.25 mL) (Note: HFIP and water were bubbled with argon gas for 10 minutes to remove oxygen), were added compound **28-1** (1.07 g, 3.0 mmol, 1.0 equiv), PFBI-OH (2.54 g, 7.5 mmol, 2.5 equiv) and [Ru(bpy)₃]Cl₂ (48.0 mg, 0.075 mmol, 0.025 equiv). The reaction vial was purged with Ar for 5 min, sealed with PTEF cap. The reaction mixture was stirred at 30 °C under the irradiation of fluorescent light for 46 h. K₂CO₃ (1.05 g) was added to the solution, and the resulting mixture was vigorously stirred for 10 min. The solvent was removed *in vacuo* and the residue was dissolved in MeOH (50 mL). Then silica gel (8.0 g) was added into the solution. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 50:50 (v/v)) to afford compound **28** as a colorless oil (667 mg, 60%). 119 mg of starting material **28-1** was recovered. Conversion based on RSM: 89%. Yield based on RSM: 67%.

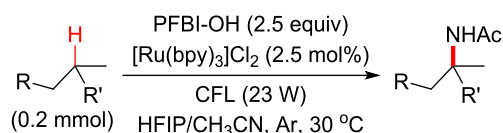
8.2 Scale-up reaction for hydroxylation of 43-1:



Scheme S19

Reaction condition: To a solution of HFIP (100 mL) and water (11.25 mL) (Note: HFIP and water were bubbled with argon gas for 10 minutes to remove oxygen), were added compound **43-1** (1.10 g, 5.0 mmol, 1.0 equiv), BI-OH (2.66 g, 10.0 mmol, 2.0 equiv) and [Ru(bpy)₃]Cl₂ (80.0 mg, 0.125 mmol, 0.025 equiv). The reaction vial was purged with Ar for 5 min, sealed with PTEF cap. The reaction mixture was stirred at 30 °C under the irradiation of fluorescent light for 20 h. K₂CO₃ (3.75 g) was added to the solution, and the resulting mixture was vigorously stirred for 10 min. The solvent was removed *in vacuo* and the residue was dissolved in MeOH (50 mL). Then silica gel (10.0 g) was added into the solution. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 15:85 (v/v)) to afford compound **43** as a colorless oil (680 mg, 58%). 137 mg of starting material **43-1** was recovered. Conversion based on RSM: 88%. Yield based on RSM: 66%.

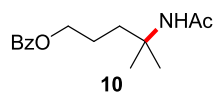
9. General procedures and substrate scope of C(sp³)-H amidation with PFBI-OH



Scheme S20

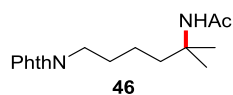
General condition: To a solution of HFIP (4 mL) and acetonitrile (3 mL) (Note: HFIP and acetonitrile were dried over 4 Å molecular sieves overnight, then bubbled with argon gas for 10 minutes to remove oxygen before the experiment), were added substrate (0.2 mmol, 1.0 equiv), PFBI-OH (0.5 mmol, 2.5 equiv) and [Ru(bpy)₃]Cl₂ (0.005 mmol, 0.025 equiv). The reaction vial was purged with Ar for 1 min, then sealed with PTEF cap. The mixture was stirred at 30 °C under the irradiation of 23 W fluorescent light for 10-24 h. K₂CO₃ (approximate 150 mg) was added to the solution, and the resulting mixture was vigorously stirred for 5 min. The solvent was removed *in*

vacuo and the residue was dissolved in DCM (5 mL). Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford the desired product.



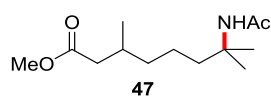
$R_f = 0.38$, 50% EtOAc in Hexane

Compound **10** was isolated in 56% yield as a white solid following the general procedure (36 h). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.04 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.61 – 7.53 (m, 1H), 7.46-7.43 (m, 2H), 5.30 (br s, 1H), 4.32 (t, $J = 6.6$ Hz, 2H), 1.94 (s, 3H), 1.91-1.86 (m, 2H), 1.78-1.72 (m, 2H), 1.33 (s, 6H). Spectra data are consistent with those reported in the literature.²⁶



$R_f = 0.20$, 40% EtOAc in Hexane

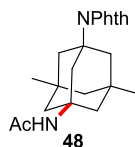
Compound **46** was isolated in 67% yield as a white solid following the general procedure (24 h). M.p. = 142-143 °C; IR (KBr) : $\tilde{\nu} = 3303, 2928, 1771, 1712, 1657, 1545, 1439, 1397, 1369, 1041, 720$ cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86-7.83 (m, 2H), 7.74-7.71 (m, 2H), 5.42 (br s, 1H), 3.70 (t, $J = 7.0$ Hz, 2H), 1.94 (s, 3H), 1.73-1.66 (m, 4H), 1.35-1.26 (m, 2H), 1.31 (s, 6H), 0.96 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.57, 168.58, 133.94, 132.04, 123.18, 77.32, 77.00, 76.68, 53.41, 39.75, 37.44, 28.65, 26.73, 24.42, 21.01; HRMS Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_3\text{Na}$ [$\text{M}+\text{Na}^+$]: 325.1528, Found: 325.1522.



$R_f = 0.22$, 20% Acetone in Hexane

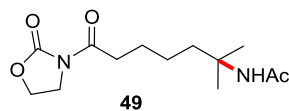
Compound **47** was isolated in 71% yield as a colorless oil following the general procedure (24 h). M.p. = 142-143 °C; IR (KBr) : $\tilde{\nu} = 3306, 3080, 2925, 1737, 1656, 1548, 1460, 1372, 1192$ cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.19 (br s, 1H), 3.67 (s,

3H), 2.30 (dd, $J = 14.7, 6.1$ Hz, 1H), 2.12 (dd, $J = 14.7, 8.0$ Hz, 1H), 1.98-1.93 (m, 1H), 1.92 (s, 3H), 1.70-1.63 (m, 2H), 1.31-1.17 (m, 4H), 1.29 (s, 6H), 0.93 (d, $J = 6.6$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.74, 169.36, 53.66, 51.38, 41.62, 40.12, 36.91, 30.28, 26.95, 26.89, 24.51, 21.46, 19.74; **HRMS** Calcd for $\text{C}_{13}\text{H}_{25}\text{NO}_3\text{Na}$ [$\text{M}+\text{Na}^+$]: 266.1732, Found: 266.1725.



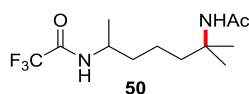
$R_f = 0.19$, 20% Acetone in Hexane

Compound **48** was isolated in 60% yield as a white solid following the general procedure (10 h). M.p. = 186-187 °C; IR (KBr) : $\tilde{\nu} = 3304, 3068, 2922, 1770, 1708, 1656, 1548, 1348, 1316, 720$ cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77-7.73 (m, 2H), 7.70-7.66 (m, 2H), 5.28 (br s, 1H), 2.61 (s, 2H), 2.14 (s, 4H), 1.92 (s, 3H), 1.78-1.70 (m, 4H), 1.22 (s, 2H), 0.96 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.56, 169.37, 133.79, 131.77, 122.60, 61.73, 54.29, 49.23, 46.27, 45.14, 42.59, 33.38, 29.53, 24.60; **HRMS** Calcd for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$ [$\text{M}+\text{Na}^+$]: 389.1841, Found: 389.1834.



$R_f = 0.32$, EtOAc

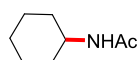
Compound **49** was isolated in 71% yield as a white solid following the general procedure (24 h). M.p. = 86-87 °C; IR (KBr) : $\tilde{\nu} = 3386, 3081, 2923, 1778, 1698, 1656, 1545, 1386, 1221, 1037, 761$ cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.19 (br s, 1H), 4.42 (t, $J = 8.1$ Hz, 2H), 4.02 (t, $J = 8.1$ Hz, 1H), 2.93 (t, $J = 7.4$ Hz, 1H), 1.92 (s, 3H), 1.74-1.62 (m, 4H), 1.37-1.25 (m, 2H), 1.30 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 173.28, 169.43, 153.53, 61.98, 53.57, 42.46, 39.72, 34.95, 26.88, 24.45, 23.61; **HRMS** Calcd for $\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_4\text{Na}$ [$\text{M}+\text{Na}^+$]: 293.1477, Found: 293.1469.



$R_f = 0.54$, 40% Acetone in Hexane

Compound **50** was isolated in 64% yield as a colorless oil following the general

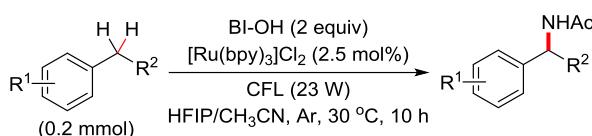
procedure (24 h). IR (KBr) : $\tilde{\nu}$ = 3363, 3082, 2924, 1706, 1658, 1552, 1460, 1373, 1188, 1159 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.28 (d, J = 6.9 Hz, 1H), 5.34 (br s, 1H), 4.11-4.00 (m, 1H), 1.93 (s, 3H), 1.76-1.69 (m, 2H), 1.54-1.43 (m, 2H), 1.33-1.20 (m, 2H), 1.29 (s, 3H), 1.28 (s, 3H), 1.23 (d, J = 6.6 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 170.07, 156.85 (q, J = 36.5 Hz), 115.93 (q, J = 287.9 Hz), 53.59, 46.18, 39.31, 36.52, 27.28, 26.67, 24.10, 20.59, 20.42; **HRMS** Calcd for $\text{C}_{12}\text{H}_{21}\text{F}_3\text{N}_2\text{O}_2\text{Na}$ [$\text{M}+\text{Na}^+$]: 305.1453, Found: 305.1447.



51 R_f = 0.21, 20% Acetone in Hexane

Compound **51** was isolated in 63% yield as a white solid following the general procedure (24 h, 0.5 mmol scale, 1.0 equiv of cyclohexane was used). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.50 (br s, 1H), 3.79-3.70 (m, 1H), 1.98 (s, 3H), 1.93-1.89 (m, 2H), 1.73-1.68 (m, 2H), 1.64-1.60 (m, 1H), 1.41-1.30 (m, 2H), 1.20-1.06 (m, 3H). Spectra data are consistent with those reported in the literature.²⁷

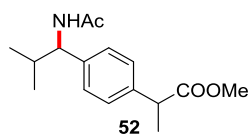
10. General procedures and substrate scope of benzylic C-H amidation with BI-OH



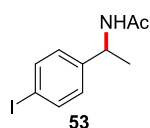
Scheme S21

General condition: To a solution of HFIP (4 mL) and acetonitrile (1.5 mL) (Note: HFIP and acetonitrile were dried over 4 Å molecular sieves overnight, then bubbled with argon gas for 10 minutes to remove oxygen before the experiment), were added substrate (0.2 mmol, 1.0 equiv), BI-OH (0.4 mmol, 2.0 equiv) and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (0.005 mmol, 0.025 equiv). The reaction vial was purged with Ar for 1 min, then sealed with PTEF cap. The reaction mixture was stirred at 30 °C under the irradiation of fluorescent

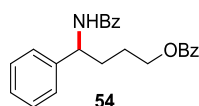
light for 10 h. K_2CO_3 (approximate 20 mg) was added to the solution, and the resulting mixture was vigorously stirred for 5 min. The solvent was removed *in vacuo* and the residue was dissolved in DCM (5 mL). Then the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin layer chromatography or flash chromatography on silica gel to afford the desired product.



Compound **52** was isolated in 67% yield as a colorless oil following the general procedure. IR (KBr) : $\tilde{\nu}$ = 3292, 2926, 1737, 1646, 1546, 1460, 1375, 1210, 1166, 856 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.1 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 5.94 (d, J = 8.9 Hz, 1H), 4.74 (dd, J = 8.9, 8.3 Hz, 1H), 3.71 (q, J = 7.2 Hz, 1H), 3.66 (s, 3H), 2.05-1.96 (m, 1H), 1.98 (s, 3H), 1.48 (d, J = 7.2 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.99, 174.95, 169.29, 140.47, 139.18, 127.49, 127.18, 58.75, 51.99, 44.98, 44.96, 33.27, 23.43, 19.75, 18.78, 18.53, 18.50; HRMS Calcd for $C_{16}H_{23}NO_3Na$ [$M+Na^+$]: 300.1576, Found: 300.1568.



Compound **53** was isolated in 74% yield as a pale yellow solid following the general procedure. M.p. = 103-104 $^{\circ}C$; IR (KBr) : $\tilde{\nu}$ = 3426, 3064, 2925, 1647, 1545, 1374, 1274, 821, 754 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 5.85 (d, J = 5.4 Hz, 1H), 5.09-5.01 (m, 1H), 1.99 (s, 3H), 1.45 (d, J = 6.9 Hz, 3H), ; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.48, 142.80, 137.67, 128.16, 92.68, 48.43, 23.29, 21.55; HRMS Calcd for $C_{10}H_{13}INO$ [$M+H^+$]: 290.0042, Found: 290.0033.



Compound **54** was isolated in 62% yield as a white solid following the general procedure (2.5 mL PhCN was used). M.p. = 146-147 °C; IR (KBr) : $\tilde{\nu}$ = 3315, 3062, 2924, 1717, 1637, 1533, 1276, 1116, 708 cm^{-1} ; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 (dd, J = 8.3, 1.2 Hz, 2H), 7.77 (dd, J = 8.4, 1.2 Hz, 2H), 7.58-7.52 (m, 1H), 7.51-7.47 (m, 1H), 7.45-7.34 (m, 8H), 7.31-7.27 (m, 1H), 6.40 (d, J = 8.0 Hz, 1H), 5.29-5.23 (m, 1H), 4.35 (td, J = 6.4, 0.9 Hz, 2H), 2.17-2.01 (m, 2H), 1.96-1.85 (m, 1H), 1.85-1.74 (m, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.77, 166.55, 141.74, 134.43, 132.88, 131.47, 130.19, 129.51, 128.82, 128.50, 128.31, 127.62, 126.92, 126.62, 64.48, 53.66, 32.55, 25.85; **HRMS** Calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3\text{Na}$ [$\text{M}+\text{Na}^+$]: 396.1576, Found: 396.1566.

11. Measurement of quantum yield (Φ) for C-H hydroxylation of **7**²⁸

11. 1 Determination of light intensity

11. 1. 1 Determination of the light intensity at 436 nm:

A 0.15 M solution of ferrioxalate was prepared by dissolving 2.3848 g of potassium ferrioxalate hydrate ($\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$) in 30.00 mL of 0.05 M H_2SO_4 . A buffer of phenanthroline was prepared by dissolving 50.0 mg of phenanthroline and 11.25 g of sodium acetate in 50.00 mL of 0.5 M H_2SO_4 . The above solutions were both stored in the dark after preparation. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 436$ nm with an emission slit width at 10.0 nm. After irradiation completed, 0.35 mL of the phenanthroline solution was added to the cuvette. Then the solution was allowed to rest in dark for 1 h. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using equation 1:

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \epsilon} \quad \text{(Equation 1)}$$

In the equation 1, V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ϵ is the molar absorptivity at 510 nm (11,100 L mol⁻¹ cm⁻¹). The photon flux can be calculated using equation 2:

$$\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} \quad (\text{Equation 2})$$

In the equation 2, Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at $\lambda = 436$ nm), t is the time (90.0 s), and f is the fraction of light absorbed at $\lambda = 436$ nm (0.99990, *vide infra*). The photon flux was calculated (average of three experiments) to be 4.29×10^{-10} einstein s⁻¹.

Sample calculation:

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \epsilon} = \frac{0.00235 \text{ L} \cdot 0.184}{1 \text{ cm} \cdot 11100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 3.90 \times 10^{-8} \text{ mol}$$

$$\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} = \frac{3.90 \times 10^{-8}}{1.01 \cdot 90 \text{ s} \cdot 0.99990} = 4.29 \times 10^{-10} \text{ einstein s}^{-1}$$

11. 1. 2 Determination of fraction of light absorbed at 436 nm for the ferrioxalate solution:

The absorbance of the above ferrioxalate solution at 436 nm was measured to be 4.009. The fraction of light absorbed (f) was calculated using equation 3, where A (absorbance) is the measured absorbance at 436 nm.

$$f = 1 - 10^{-A} \quad (\text{Equation 3})$$

$$f = 1 - 10^{-4.009} = 1 - 10^{-4.009} = 0.99990$$

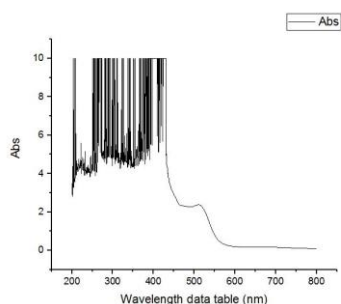
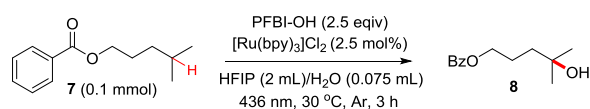


Figure S1. Absorbance of the ferrioxalate actinometer solution.

11. 2 Determination of quantum yield:



Scheme S22

A cuvette was charged with compound **7** (0.1 mmol, 1.0 equiv), PFBI-OH (0.25 mmol, 2.5 equiv) and [Ru(bpy)₃]Cl₂ (0.0025 mmol, 0.025 equiv). HFIP (2 mL) and water (0.075 mL) (Note: HFIP and water were bubbled with argon gas for 10 minutes to remove oxygen), The reaction cuvette was purged with Ar for 1 min, then sealed with PTEF cap. The sample was stirred to make a clear solution (about 5 min.) and irradiated ($\lambda = 436$ nm, slit width = 10.0 nm) for 10800 s (3 h). After irradiation, the solvent was removed under reduced pressure. The yield of product formed was determined by ¹H NMR based on a TCE (1,1,2,2-tetrachloroethane, ~20 μ L) standard to be 3.9%. The quantum yield was determined using equation 4:

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot t \cdot f} \quad (\text{Equation 4})$$

$$\Phi = \frac{3.93 \times 10^{-6} \text{ mol}}{4.29 \times 10^{-10} \text{ einstein s}^{-1} \cdot 10800 \text{ s} \cdot 1.00} = 0.85$$

The quantum yield was calculated to be Φ (3.9%) = 0.85, indicating that a chain reaction mechanism can be excluded.

11. 3 Absorbance of catalyst:

The A (absorbance) of [Ru(bpy)₃] Cl₂ in HFIP was measured at the reaction concentration of 1.25×10^{-3} M and also at a substantially more dilute concentration of 1.25×10^{-5} M. The A at 436 nm for a 1.25×10^{-3} M solution is >10, while the A for 1.25×10^{-5} M solution is 0.188. This result indicated that the fraction of light absorbed (f) is about 1.00.

$$f = 1 - 10^{-A} = 1 - 10^{-10} = 1.00$$

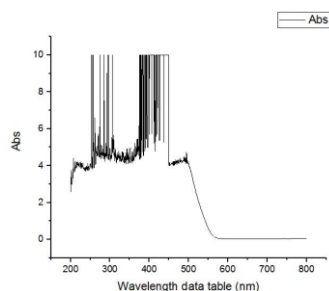


Figure S2. Absorbance of a 1.25×10^{-3} M solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in HFIP.

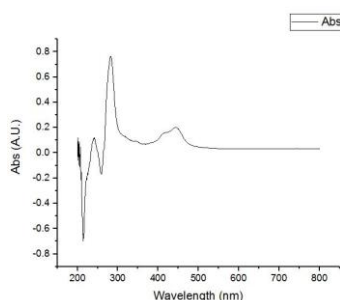


Figure S3. Absorbance of a 1.25×10^{-5} M solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ in HFIP.

12. The luminescence quenching (Stern-Volmer) experiments

The luminescence quenching experiments were carried out on a fluorescence spectrophotometer. To a glass cuvette with a PTEF cap, photocatalyst $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, quencher PFBI-OH (compound **17**) or compound **7**, and HFIP were added to obtain a total volume of 200 μL . Before determination, the solution was degassed by three freeze-pump-thaw cycles and backfilled with argon. The concentration of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was 1.0×10^{-4} M. All samples were irradiated at 452 nm, and emission was determined at 567 nm. It should be noted that all samples were measured within 1 minute after preparation.

The result showed that the excited state of $\text{Ru}(\text{II})^*$ can be quenched by PFBI-OH, while no obvious change of $\text{Ru}(\text{II})^*$ luminescence in the presence of variable concentrations of compound **7** was observed.

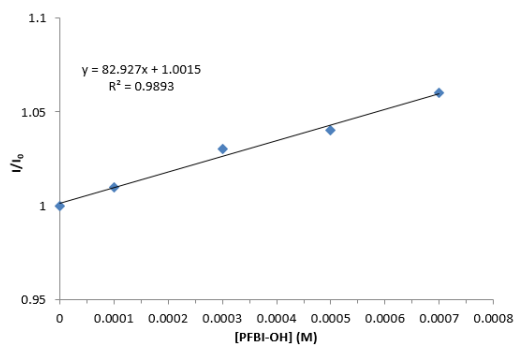


Figure S4. Stern-Volmer quenching studies for PFBI-OH.

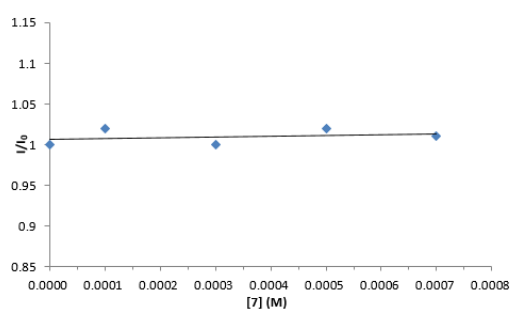


Figure S5. Stern-Volmer quenching studies for 7.

13. DFT calculations

13.1 Computational details

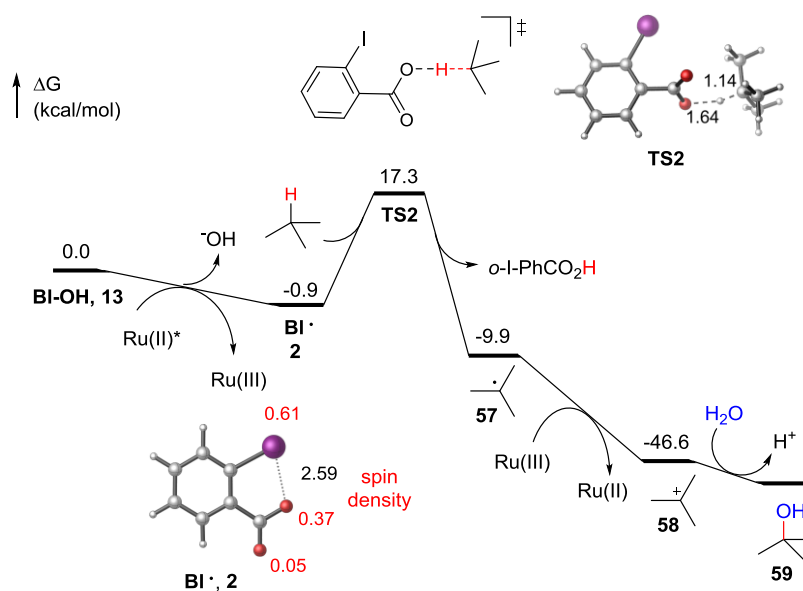
All DFT calculations were performed with the Gaussian 09 software package.²⁹ Geometries were optimized using the M06-2X functional and the 6-31+G(d) basis set in the gas phase. Single point energies were calculated using M06-2X and 6-311++G(d,p) and the SMD solvation model in HFIP.³⁰ Since the solvent parameters for HFIP are not available in Gaussian 09. The parameters of isopropanol were used and the dielectric constant of the solvent was modified to the dielectric constant of HFIP³¹ ($\epsilon = 16.7$) by using the “scrf=(smd,solvent=2-propanol,read)” keywords in the Gaussian 09 calculations. The reported Gibbs free energies and enthalpies include zero-point vibrational energies and thermal corrections computed at 298 K.

The experimental redox potentials of $E_{\text{Ru}(\text{bpy})_3^{3+/2+}}^{\ominus}$ (-0.81 V vs SCE in MeCN) and

$E_{\text{Ru}(\text{bpy})_3^{3+/2+}}^{\ominus}$ ($+1.29$ V vs SCE in MeCN)³² were used in the computation of the SET

reaction energies with Ru(II)* and Ru(III)m including the initial SET reduction with Ru(II) and in the subsequent SET oxidation with Ru(III).⁶

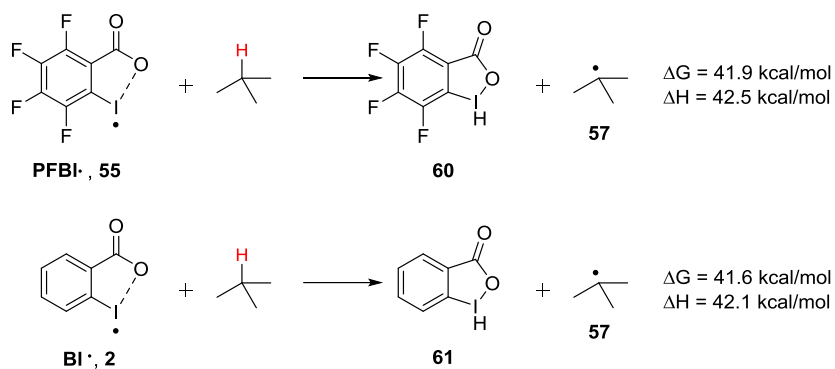
13.2 Potential energy profile of C(sp³)-H hydroxylation with BI-OH



Scheme S23

13.3 H-atom abstraction of *tert*-butane with PFBI• and BI• through the I-centered pathway

Although the computed spin densities of PFBI• and BI• are delocalized over the O and I atoms, the H-abstraction occurs exclusively via the *O*-centered pathway to form *ortho*-iodo benzoic acid and its perfluorinated derivative. This *O*-centered pathway is exergonic by 13.7 kcal/mol and 9.0 kcal/mol for the reactions with PFBI• and BI•, respectively. In contrast, the H-abstraction via the *I*-centered pathway to form **60** and **61** is highly endergonic.



Scheme S24

The transition states for these processes could not be located by calculations. Scan of the H-abstraction reaction coordinates to form the H-I bond indicated a highly endothermic and barrierless transformation with both PFBI• and BI•. These results indicate the H-atom abstraction takes place via the *O*-centered pathway exclusively.

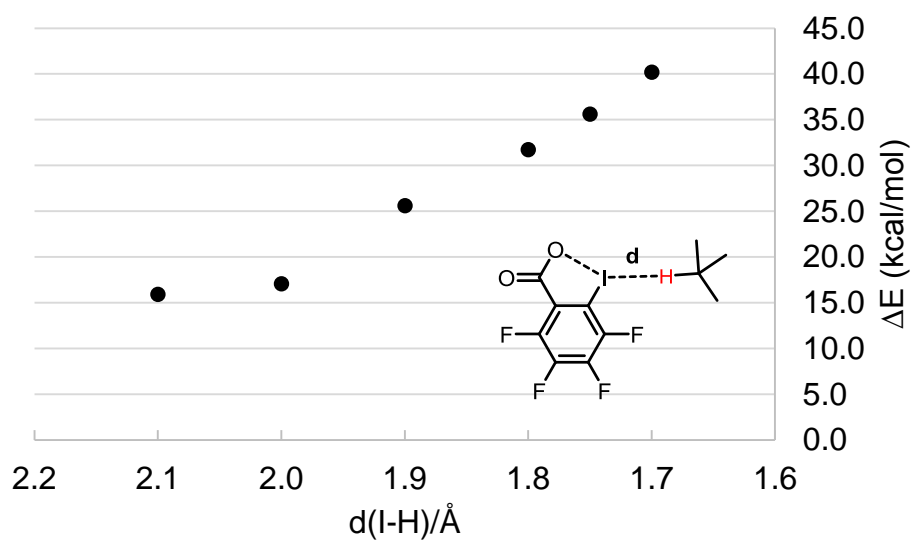


Chart 1

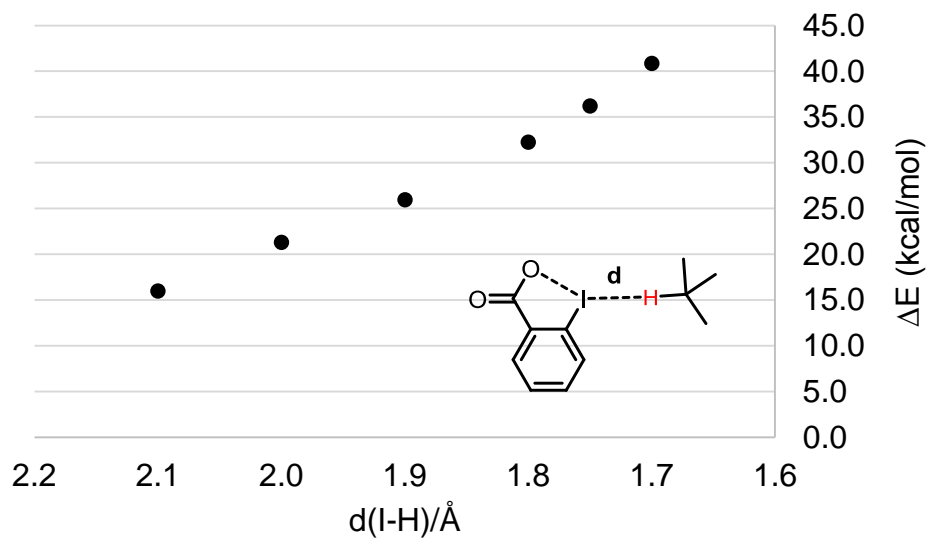


Chart 2

13.4 Cartesian coordinates and energies of optimized structures

PFBI-OH

M06-2X/6-31+G(d) SCF energy: -903.31356630 a.u.
M06-2X/6-31+G(d) enthalpy: -903.223347 a.u.
M06-2X/6-31+G(d) free energy: -903.278767 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -903.59971492 a.u.
M06-2X/6-311++G(d,p) enthalpy: -903.509496 a.u.
M06-2X/6-311++G(d,p) free energy: -903.564916 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.704924	0.991232	0.012661
C	-0.049290	-0.234725	-0.015761
C	-0.739258	-1.432811	-0.050404
C	-2.132182	-1.404469	-0.019237
C	-2.808355	-0.195764	0.036731
C	-2.096440	1.000864	0.044450
C	0.121651	2.267728	-0.045013
O	1.400567	2.014839	-0.169365
O	-0.385090	3.361103	-0.000702
I	2.078588	-0.024863	0.004282
O	2.376022	-1.999664	0.309679
H	2.256397	-2.535499	-0.490713
F	-0.159598	-2.625831	-0.151212
F	-2.810831	-2.542565	-0.055974
F	-4.133559	-0.187965	0.062844
F	-2.796097	2.121991	0.073934

55

M06-2X/6-31+G(d) SCF energy: -827.54891344 a.u.
M06-2X/6-31+G(d) enthalpy: -827.475533 a.u.
M06-2X/6-31+G(d) free energy: -827.529063 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -827.79532614 a.u.
M06-2X/6-311++G(d,p) enthalpy: -827.721946 a.u.
M06-2X/6-311++G(d,p) free energy: -827.775476 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.490788	0.981398	-0.000037
C	0.093871	-0.285450	-0.000006
C	-0.670247	-1.437062	0.000030

C	-2.058074	-1.345042	0.000027
C	-2.662398	-0.096924	-0.000024
C	-1.884536	1.058416	-0.000028
C	0.357247	2.227600	0.000014
O	1.658595	2.045384	-0.000021
O	-0.103467	3.347442	0.000091
F	-0.109030	-2.645384	0.000088
F	-2.800132	-2.442593	0.000020
F	-3.985564	-0.009900	-0.000091
F	-2.526483	2.214391	0.000035
I	2.193196	-0.449223	-0.000017

Isobutane

M06-2X/6-31+G(d) SCF energy:	-158.36179771 a.u.
M06-2X/6-31+G(d) enthalpy:	-158.222321 a.u.
M06-2X/6-31+G(d) free energy:	-158.256686 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution:	-158.40978520 a.u.
M06-2X/6-311++G(d,p) enthalpy:	-158.270308 a.u.
M06-2X/6-311++G(d,p) free energy:	-158.304673 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.000082	0.000024	-0.381074
H	-0.000129	-0.000025	-1.480296
C	-0.029637	-1.452044	0.096502
H	-0.030007	-1.493040	1.193314
H	-0.927262	-1.970727	-0.257930
H	0.845669	-2.006965	-0.258778
C	-1.242864	0.751720	0.096506
H	-1.278782	0.771472	1.193335
H	-1.242751	1.788769	-0.256955
H	-2.161172	0.271921	-0.259739
C	1.272470	0.700305	0.096451
H	2.170479	0.182723	-0.258742
H	1.315882	1.736188	-0.257818
H	1.308755	0.719654	1.193296

TS1

M06-2X/6-31+G(d) SCF energy:	-985.91034576 a.u.
M06-2X/6-31+G(d) enthalpy:	-985.698697 a.u.

M06-2X/6-31+G(d) free energy: -985.770350 a.u.
 M06-2X/6-311++G(d,p) SCF energy in solution: -986.19376847 a.u.
 M06-2X/6-311++G(d,p) enthalpy: -985.982120 a.u.
 M06-2X/6-311++G(d,p) free energy: -986.053773 a.u.
 Imaginary frequency: -188.3224 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.728307	1.896208	0.052610
C	-1.352459	1.976484	-0.117270
C	-0.571888	0.828657	-0.181985
C	-1.169341	-0.428110	-0.040978
C	-2.542277	-0.505633	0.132668
C	-3.321873	0.648263	0.178042
C	0.920434	0.981516	-0.423054
O	1.459172	0.870166	-1.492742
I	-0.035993	-2.203505	-0.077023
O	1.455178	1.238183	0.746772
C	4.157921	0.796504	0.272176
C	3.908166	-0.696320	0.106263
H	3.314636	-0.897935	-0.791633
H	4.865411	-1.226180	0.010940
H	3.378405	-1.107715	0.972909
C	4.925763	1.112892	1.549572
H	5.923461	0.655487	1.504765
H	5.056470	2.191769	1.682153
H	4.412952	0.715075	2.431531
C	4.794811	1.413829	-0.965952
H	4.925851	2.494922	-0.852082
H	5.786444	0.969554	-1.128852
H	4.183406	1.227771	-1.853561
H	3.142642	1.281107	0.389145
F	-3.161604	-1.675575	0.266983
F	-4.633750	0.555867	0.344503
F	-3.472011	2.994012	0.098679
F	-0.790695	3.177847	-0.231041

56

M06-2X/6-31+G(d) SCF energy: -828.22716198 a.u.
 M06-2X/6-31+G(d) enthalpy: -828.140268 a.u.
 M06-2X/6-31+G(d) free energy: -828.194685 a.u.
 M06-2X/6-311++G(d,p) SCF energy in solution: -828.47380042 a.u.

M06-2X/6-311++G(d,p) enthalpy: -828.386906 a.u.
M06-2X/6-311++G(d,p) free energy: -828.441323 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.506351	0.956738	0.000206
C	0.126608	-0.289936	0.015356
C	-0.645280	-1.443545	0.023499
C	-2.034864	-1.373688	0.023416
C	-2.665271	-0.139272	0.008812
C	-1.894032	1.016085	-0.008405
C	0.243595	2.258954	-0.044151
O	0.221907	3.012680	-0.979357
F	-0.087356	-2.652249	0.025896
F	-2.758017	-2.486417	0.036147
F	-3.990558	-0.067935	0.015646
F	-2.517901	2.192748	-0.007122
I	2.224942	-0.491682	-0.049778
O	0.917789	2.480914	1.091822
H	1.398553	3.323061	0.991018

57

M06-2X/6-31+G(d) SCF energy: -157.70081077 a.u.
M06-2X/6-31+G(d) enthalpy: -157.575321 a.u.
M06-2X/6-31+G(d) free energy: -157.611634 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -157.74850228 a.u.
M06-2X/6-311++G(d,p) enthalpy: -157.623013 a.u.
M06-2X/6-311++G(d,p) free energy: -157.659326 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000150	-0.000077	-0.188259
C	1.439547	-0.346451	0.019683
H	1.691368	-0.400229	1.094475
H	1.686765	-1.322688	-0.412386
H	2.104195	0.403825	-0.423442
C	-1.019864	-1.073152	0.019669
H	-1.199138	-1.258129	1.094416
H	-1.986572	-0.802478	-0.419990
H	-0.698683	-2.025937	-0.416117
C	-0.419655	1.419634	0.019619
H	0.298472	2.122089	-0.418170

H	-1.404871	1.617628	-0.417563
H	-0.492608	1.666192	1.094508

58

M06-2X/6-31+G(d) SCF energy: -157.45073926 a.u.
M06-2X/6-31+G(d) enthalpy: -157.325618 a.u.
M06-2X/6-31+G(d) free energy: -157.362308 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -157.59472172 a.u.
M06-2X/6-311++G(d,p) enthalpy: -157.469600 a.u.
M06-2X/6-311++G(d,p) free energy: -157.506290 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.002960	0.001259	0.008702
C	-1.408991	0.401326	0.011228
H	-1.592008	0.823086	-0.997031
H	-2.106416	-0.421148	0.172397
H	-1.587475	1.237156	0.697475
C	0.353320	-1.415836	-0.014658
H	-0.348271	-2.005719	-0.614734
H	1.393749	-1.611490	-0.277080
H	0.191229	-1.757103	1.027942
C	1.052629	1.014789	0.008884
H	0.702491	2.029458	0.195539
H	1.857552	0.729930	0.700171
H	1.525164	0.966594	-0.989618

59

M06-2X/6-31+G(d) SCF energy: -233.55853272 a.u.
M06-2X/6-31+G(d) enthalpy: -233.413903 a.u.
M06-2X/6-31+G(d) free energy: -233.450696 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -233.64296474 a.u.
M06-2X/6-311++G(d,p) enthalpy: -233.498335 a.u.
M06-2X/6-311++G(d,p) free energy: -233.535128 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.682400	1.258692	-0.512776
H	0.631241	1.306413	-1.605900
H	0.202908	2.151308	-0.099271

H	1.741638	1.271920	-0.226292
C	-1.484749	-0.001192	-0.347041
H	-1.616025	-0.000966	-1.433730
H	-1.972196	-0.889052	0.067310
H	-1.973736	0.885563	0.067865
C	0.684502	-1.257434	-0.513029
H	1.743797	-1.268902	-0.226663
H	0.206584	-2.150949	-0.099640
H	0.633329	-1.305065	-1.606155
C	-0.005242	-0.000003	0.016259
O	0.024122	-0.000111	1.445552
H	0.948022	0.000238	1.737575

BI-OH

M06-2X/6-31+G(d) SCF energy:	-506.51406153 a.u.
M06-2X/6-31+G(d) enthalpy:	-506.394811 a.u.
M06-2X/6-31+G(d) free energy:	-506.441483 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution:	-506.68248934 a.u.
M06-2X/6-311++G(d,p) enthalpy:	-506.563239 a.u.
M06-2X/6-311++G(d,p) free energy:	-506.609911 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.483420	0.446000	-0.015623
C	-0.565543	-0.584021	-0.002860
C	-0.892175	-1.926239	0.029705
C	-2.254746	-2.234497	0.025923
C	-3.218230	-1.222878	-0.002684
C	-2.838761	0.116482	-0.020518
C	-0.991579	1.873773	-0.012062
H	-0.119375	-2.686367	0.070603
H	-2.561717	-3.275661	0.051217
H	-4.271600	-1.484830	-0.004308
H	-3.564518	0.924327	-0.033884
O	0.319473	1.962361	0.020619
O	-1.756625	2.812034	-0.033267
I	1.443989	0.118637	0.013608
O	2.082121	-1.829842	0.020237
H	2.292735	-2.133363	-0.876845

2

M06-2X/6-31+G(d) SCF energy: -430.74156239 a.u.
M06-2X/6-31+G(d) enthalpy: -430.639154 a.u.
M06-2X/6-31+G(d) free energy: -430.684411 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -430.87128459 a.u.
M06-2X/6-311++G(d,p) enthalpy: -430.768876 a.u.
M06-2X/6-311++G(d,p) free energy: -430.814133 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.261548	0.516621	-0.000005
C	0.459383	-0.617658	-0.000047
C	0.995309	-1.899332	0.000029
C	2.382684	-2.039015	0.000175
C	3.208614	-0.914240	0.000272
C	2.648845	0.358264	0.000190
C	0.700006	1.909792	-0.000153
H	0.352160	-2.773122	0.000015
H	2.814777	-3.035214	0.000251
H	4.287237	-1.033062	0.000405
H	3.260865	1.255478	0.000238
O	-0.606247	2.036954	-0.000780
O	1.410723	2.897249	0.000386
I	-1.643192	-0.335364	-0.000010

TS2

M06-2X/6-31+G(d) SCF energy: -589.09544762 a.u.
M06-2X/6-31+G(d) enthalpy: -588.855364 a.u.
M06-2X/6-31+G(d) free energy: -588.920283 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -589.26501924 a.u.
M06-2X/6-311++G(d,p) enthalpy: -589.024936 a.u.
M06-2X/6-311++G(d,p) free energy: -589.089855 a.u.
Imaginary frequency: -238.1348 cm⁻¹

Cartesian coordinates

ATOM	X	Y	Z
C	2.583013	3.006222	-0.118467
C	1.246090	2.669031	0.059677
C	0.861815	1.326209	0.129259
C	1.818606	0.321584	-0.027326
C	3.157165	0.656056	-0.211966
C	3.535596	1.997777	-0.252007

H	2.879196	4.049474	-0.157678
H	0.488279	3.440567	0.159227
H	3.901939	-0.124332	-0.327943
H	4.581877	2.249749	-0.396419
C	-0.591284	1.007387	0.409975
O	-1.018556	0.586011	1.457417
I	1.264906	-1.727498	-0.013748
O	-1.267900	1.291623	-0.680286
C	-3.738806	0.220432	-0.170000
C	-3.247871	-1.219840	-0.160348
H	-2.577663	-1.398517	0.686158
H	-4.103527	-1.903722	-0.075227
H	-2.711652	-1.462295	-1.084475
C	-4.614566	0.530924	-1.376058
H	-5.529738	-0.075679	-1.336352
H	-4.911010	1.584754	-1.395852
H	-4.097833	0.298641	-2.313006
C	-4.378830	0.625468	1.149773
H	-4.679224	1.678609	1.142726
H	-5.279800	0.020432	1.323671
H	-3.687475	0.464511	1.981593
H	-2.807303	0.866620	-0.289909

o-I-PhCO₂H

M06-2X/6-31+G(d) SCF energy:	-431.41442373 a.u.
M06-2X/6-31+G(d) enthalpy:	-431.298633 a.u.
M06-2X/6-31+G(d) free energy:	-431.344367 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution:	-431.54393562 a.u.
M06-2X/6-311++G(d,p) enthalpy:	-431.428145 a.u.
M06-2X/6-311++G(d,p) free energy:	-431.473879 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.342260	0.359581	0.008533
C	-0.330068	-0.607949	0.049395
C	-0.666237	-1.962230	0.086626
C	-2.000632	-2.358901	0.088657
C	-3.014528	-1.405997	0.028350
C	-2.679520	-0.060309	-0.020434
C	-1.163600	1.845143	-0.005538
O	-1.964621	2.606006	-0.496199
I	1.756308	-0.188413	-0.060807

O	-0.063849	2.271254	0.630687
H	-0.050339	3.242665	0.560833
H	0.118948	-2.710359	0.108417
H	-2.240676	-3.417296	0.126575
H	-4.056626	-1.708404	0.016836
H	-3.446827	0.705175	-0.079333

60

M06-2X/6-31+G(d) SCF energy: -828.11136219 a.u.
M06-2X/6-31+G(d) enthalpy: -828.029603 a.u.
M06-2X/6-31+G(d) free energy: -828.082158 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -828.38325054 a.u.
M06-2X/6-311++G(d,p) enthalpy: -828.301491 a.u.
M06-2X/6-311++G(d,p) free energy: -828.354046 a.u.

Cartesian coordinates

ATOM	X	Y	Z
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C	1.861428	1.107003	0.000077
C	0.473217	0.977722	0.000107
C	-0.037268	-0.309962	0.000053
C	0.753784	-1.443030	0.000044
C	2.135143	-1.291351	0.000053
C	-0.486734	2.192076	0.000218
O	-1.718409	1.828966	0.000641
I	-2.171326	-0.426089	-0.000056
O	-0.022778	3.312163	-0.000833
H	-2.015586	-2.116610	-0.000467
F	0.244835	-2.678667	0.000013
F	2.922377	-2.359060	0.000036
F	4.003761	0.119706	0.000026
F	2.464443	2.282584	0.000081

61

M06-2X/6-31+G(d) SCF energy: -431.30576710 a.u.
M06-2X/6-31+G(d) enthalpy: -431.195268 a.u.
M06-2X/6-31+G(d) free energy: -431.239359 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -431.45960752 a.u.
M06-2X/6-311++G(d,p) enthalpy: -431.349108 a.u.
M06-2X/6-311++G(d,p) free energy: -431.393199 a.u.

Cartesian coordinates

ATOM	X	Y	Z
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C	2.640053	0.495263	0.000062
C	1.245570	0.575829	0.000011
C	0.546708	-0.610531	-0.000015
C	1.122823	-1.868873	-0.000022
C	2.517094	-1.922154	0.000008
H	4.353827	-0.802172	0.000088
H	3.197349	1.427265	0.000086
H	0.527172	-2.776790	-0.000049
H	3.010959	-2.889075	0.000002
C	0.523878	1.924526	-0.000027
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I	-1.585054	-0.340841	-0.000001
O	1.188690	2.945749	0.000176
H	-1.710600	-2.048594	0.000249

14. References

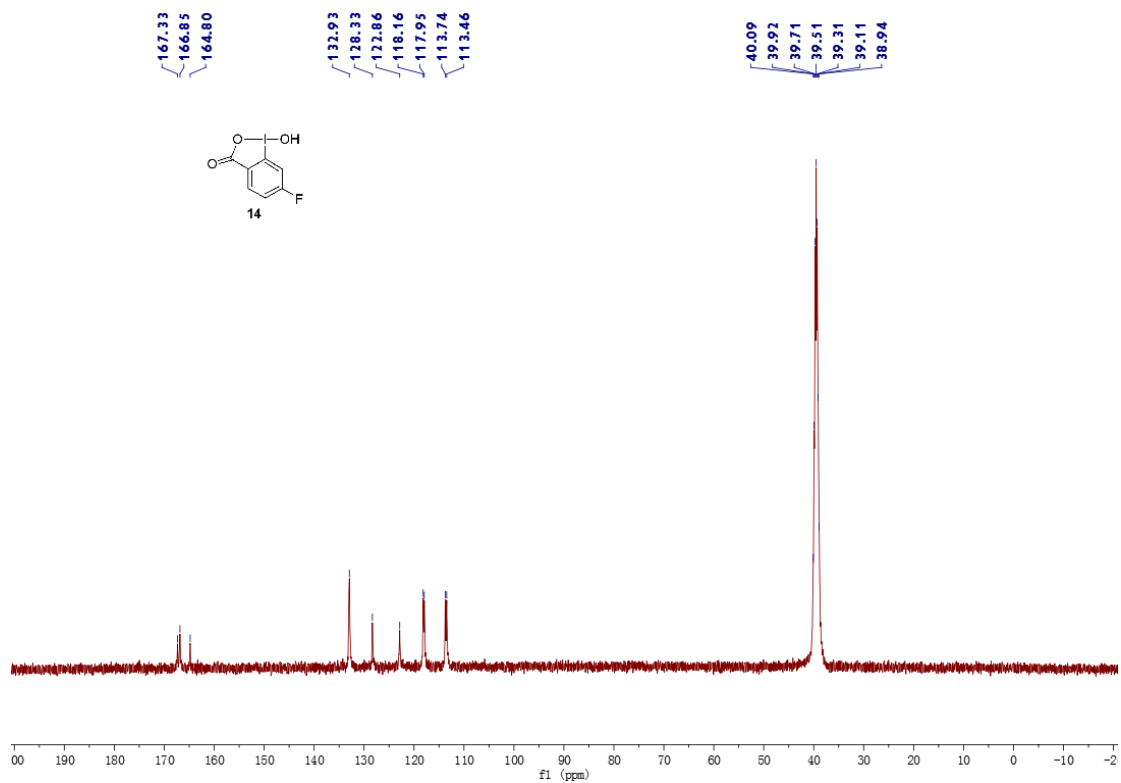
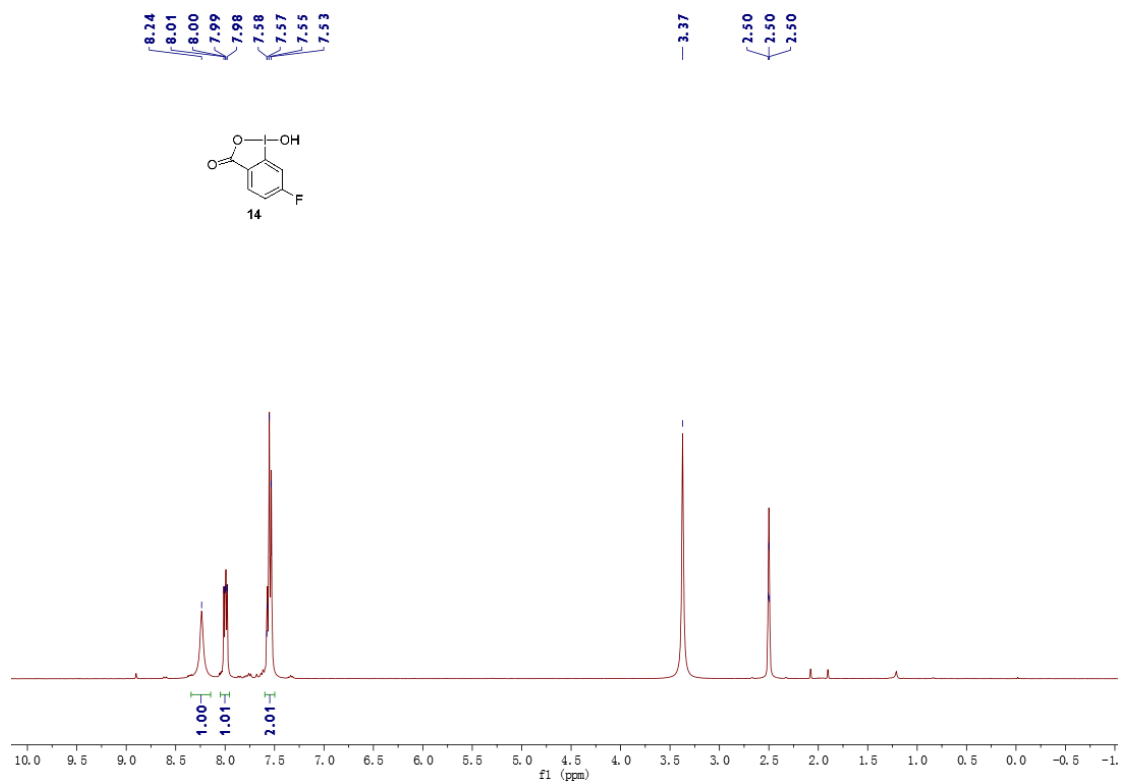
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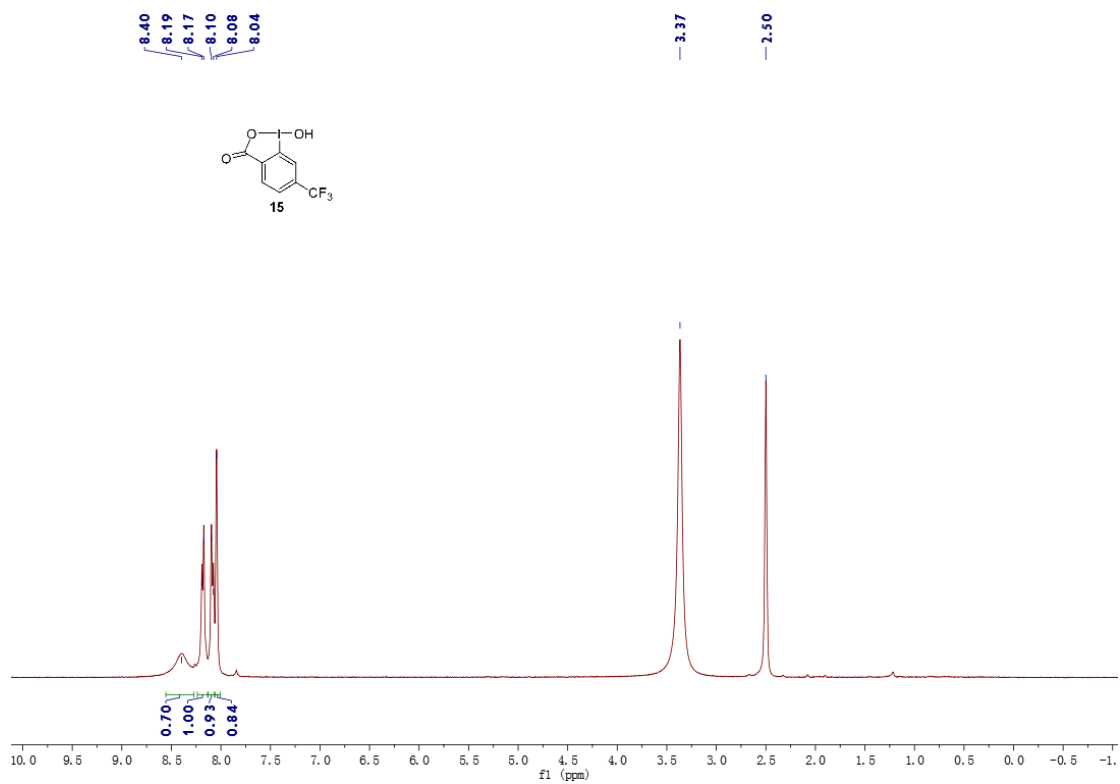
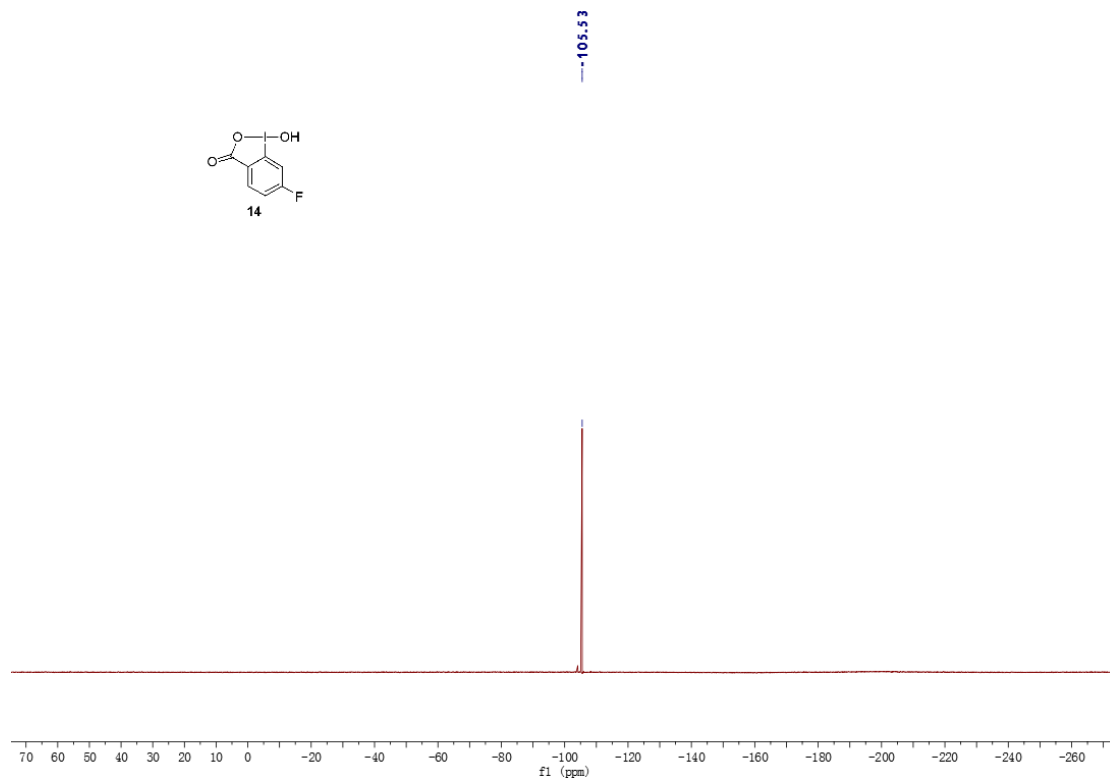
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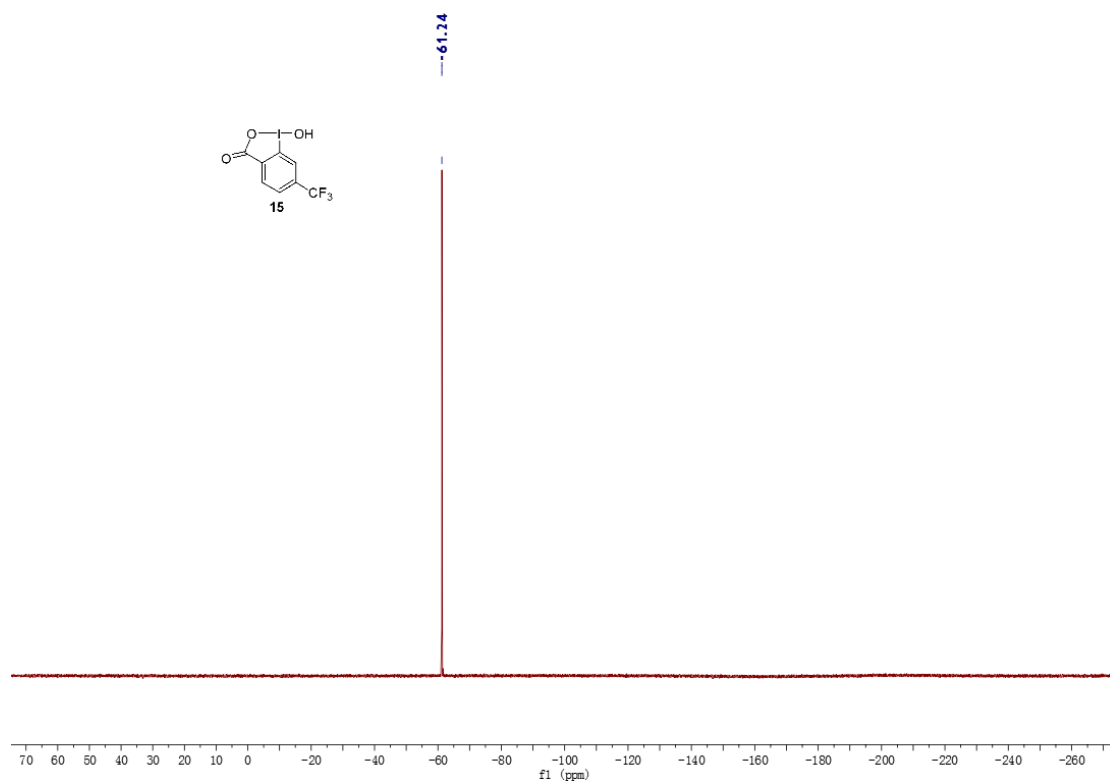
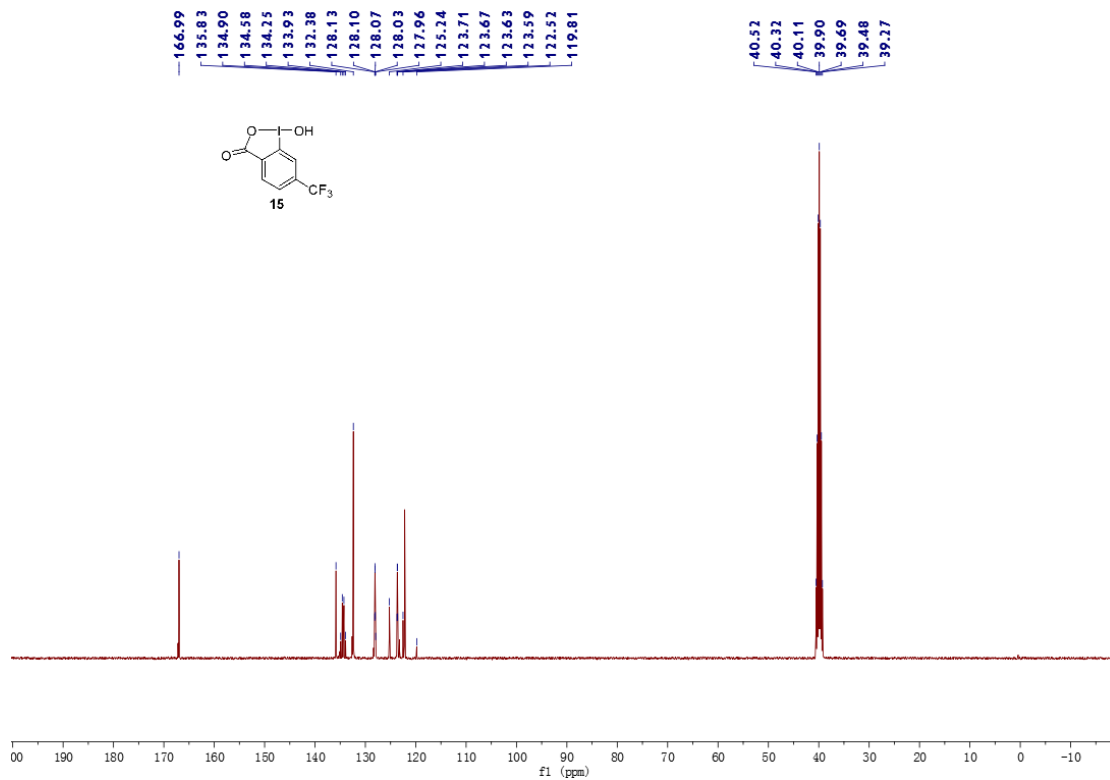
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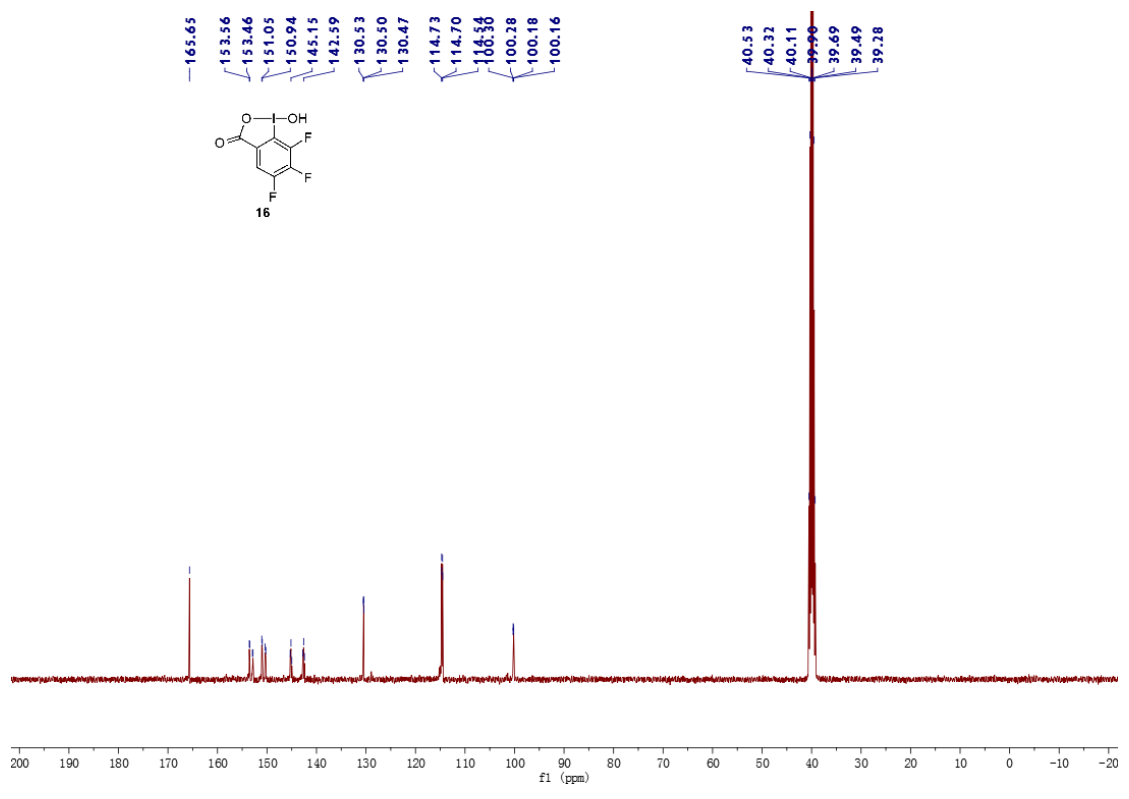
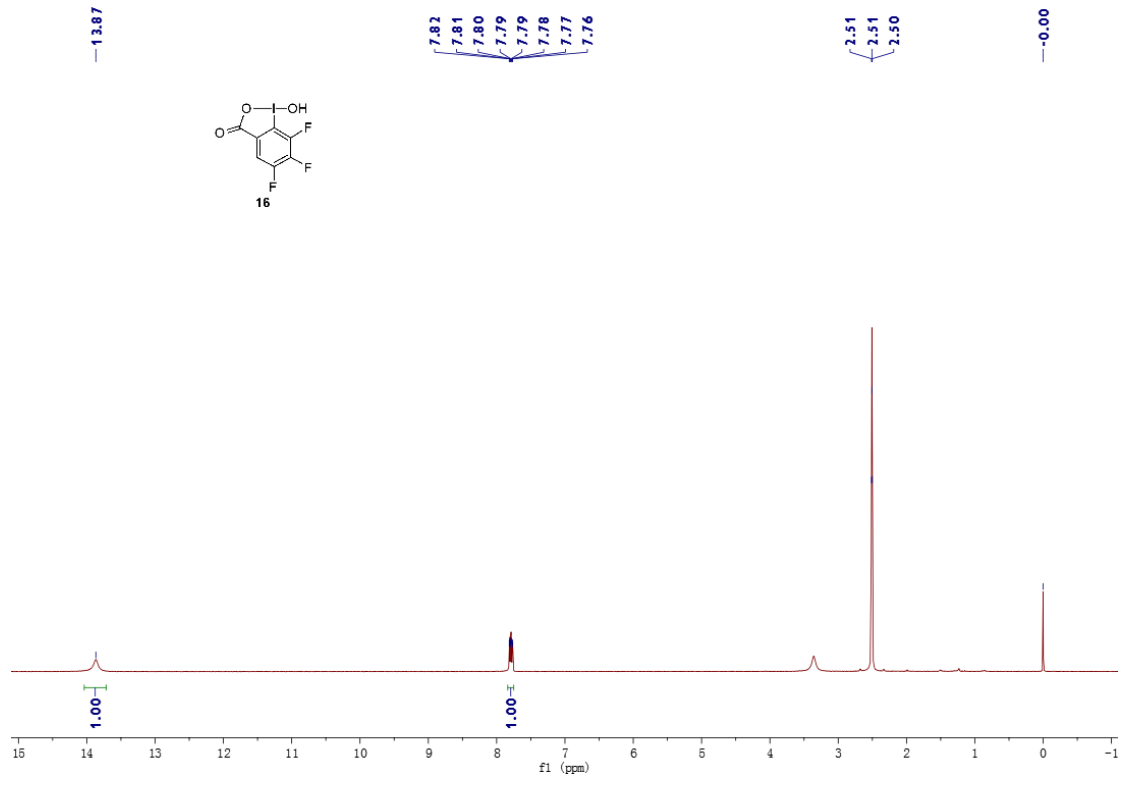
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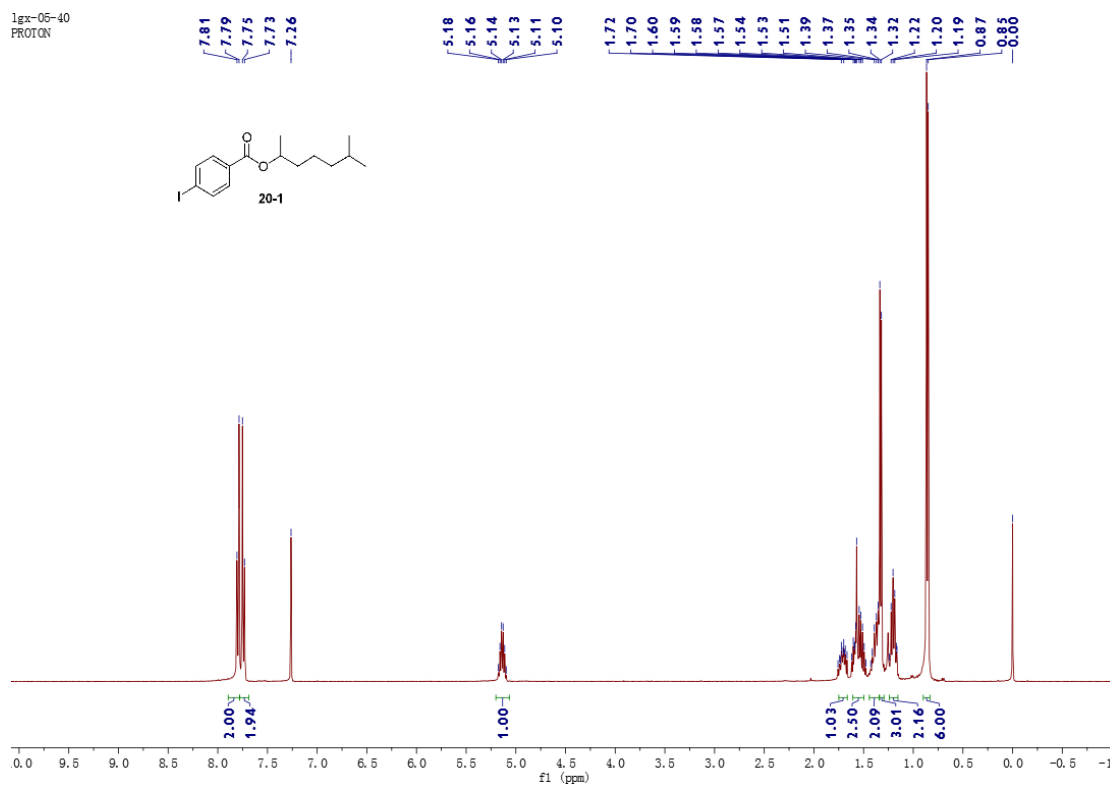
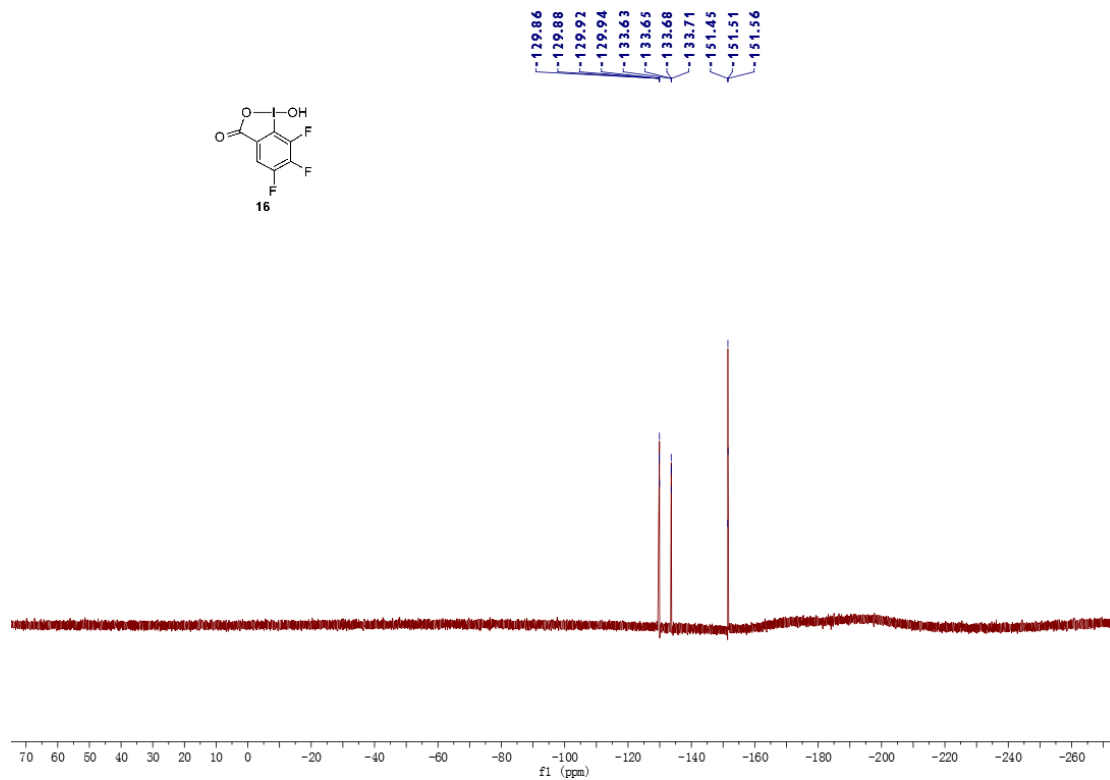
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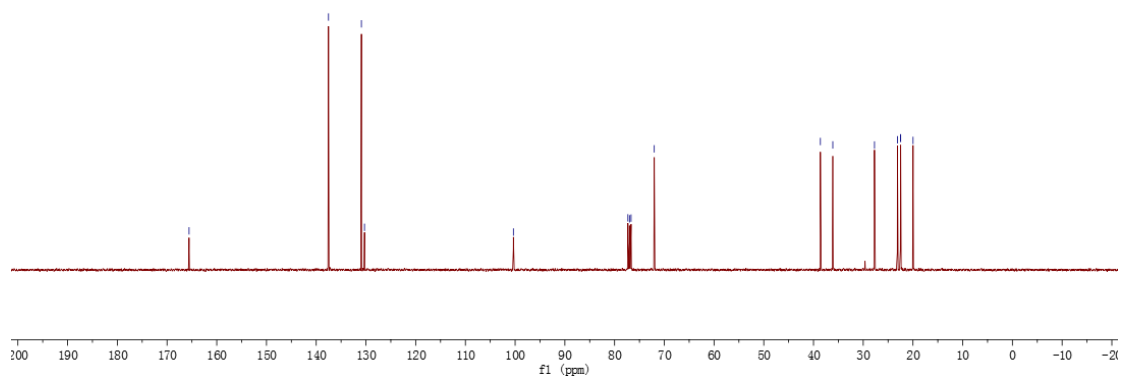
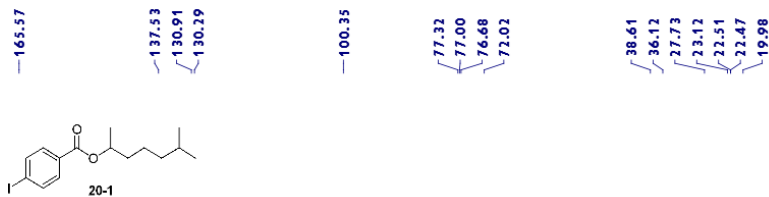




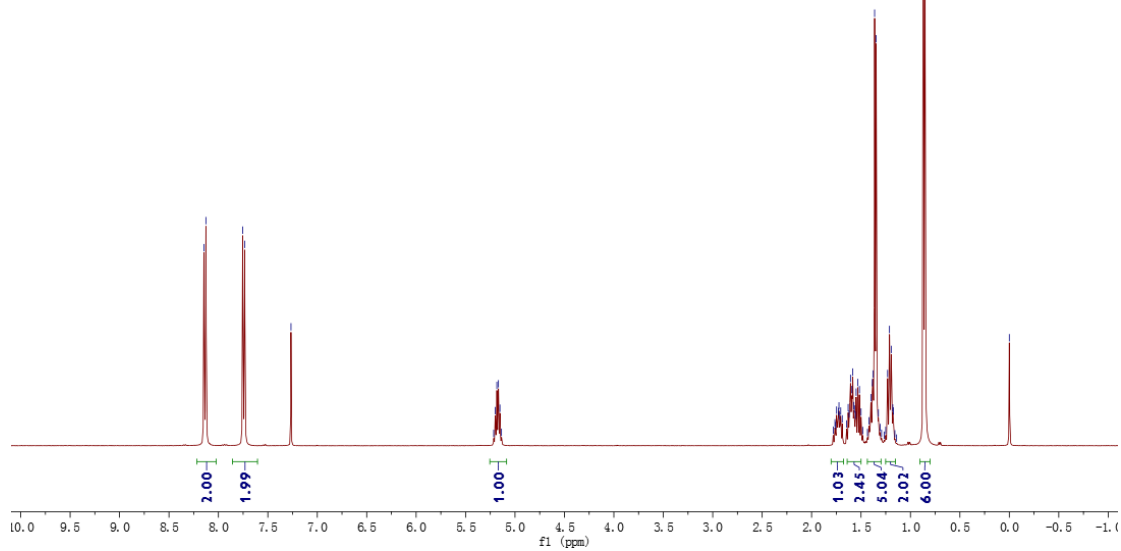
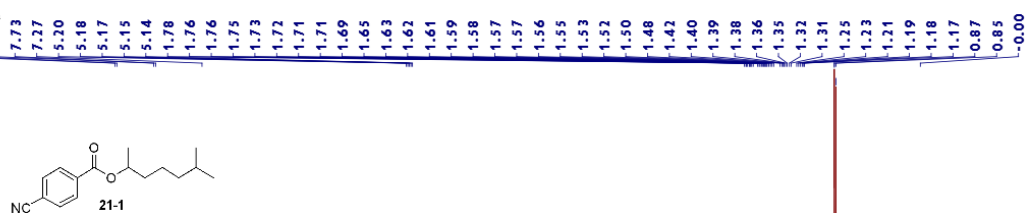




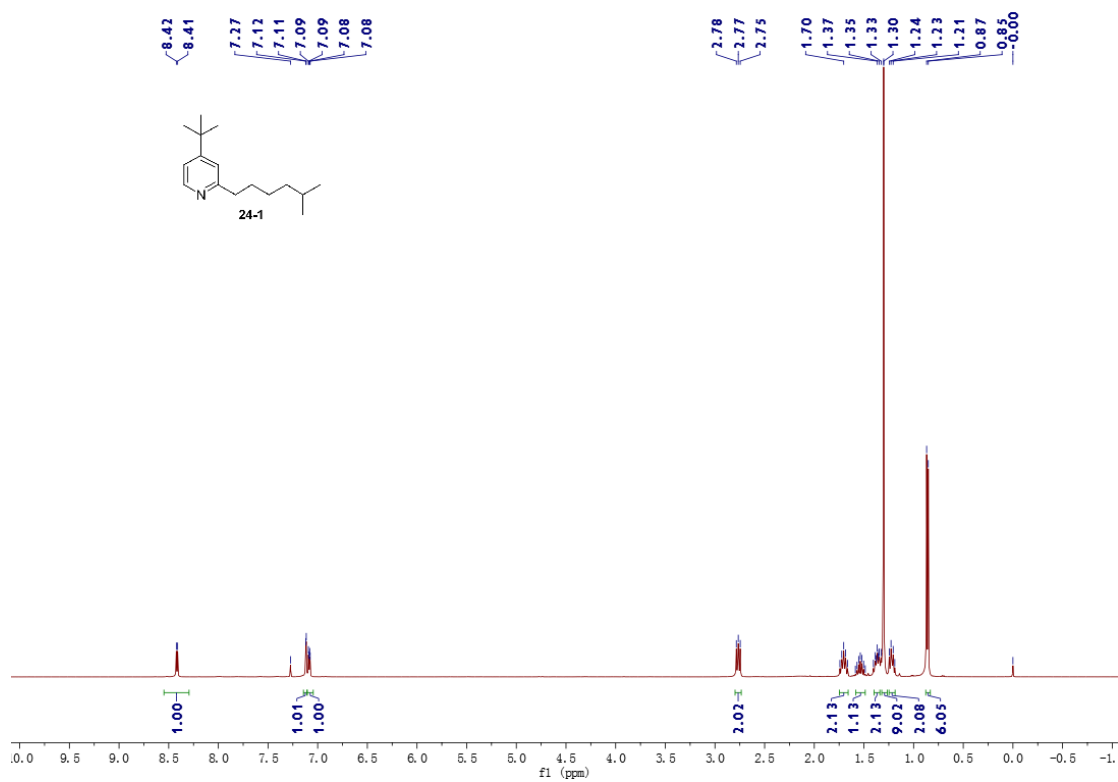
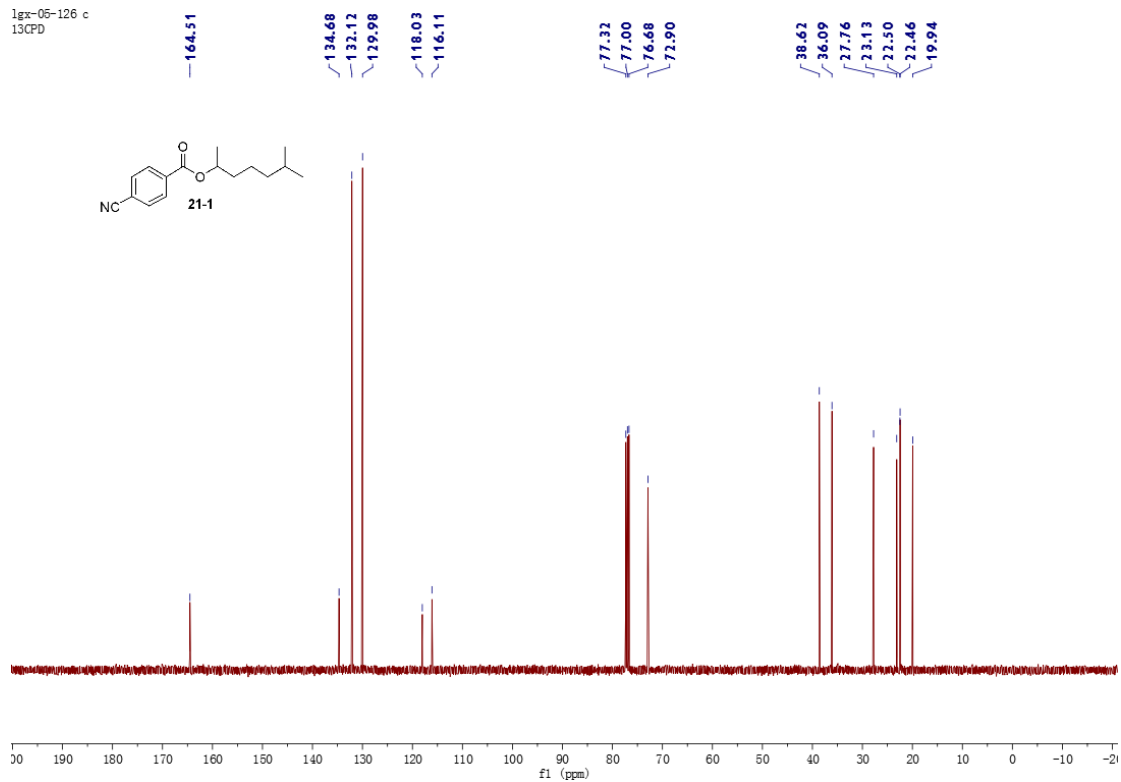
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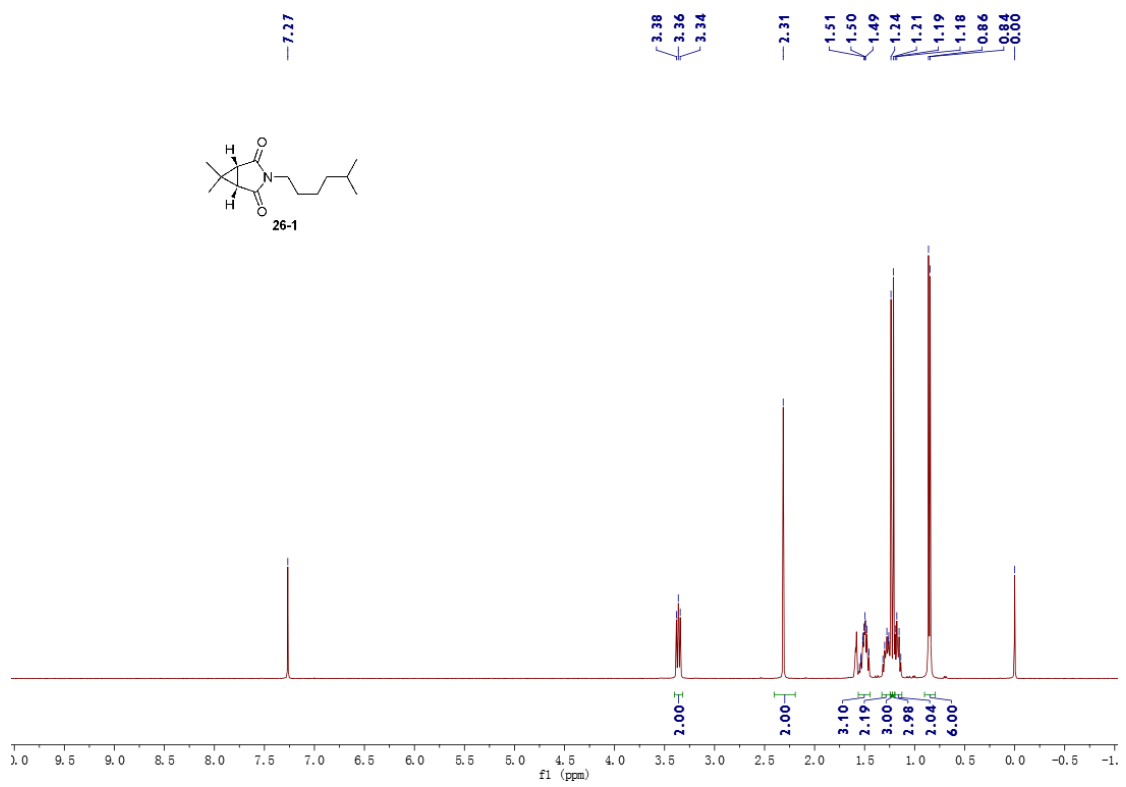
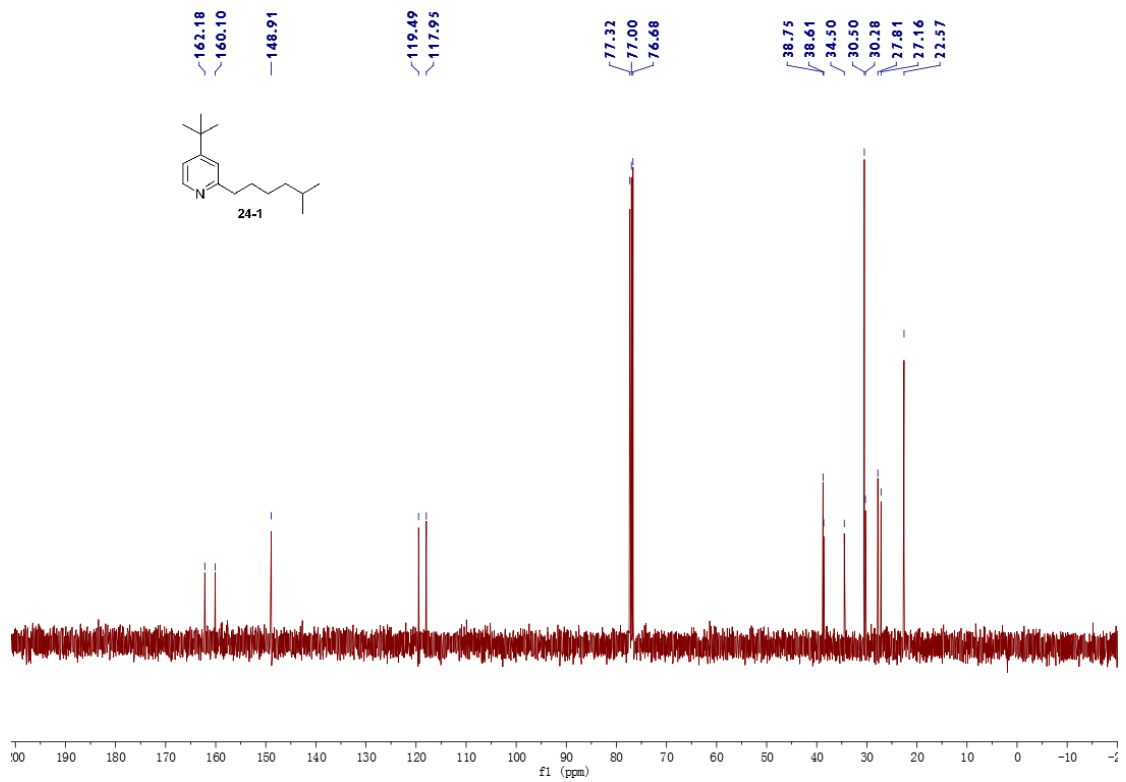


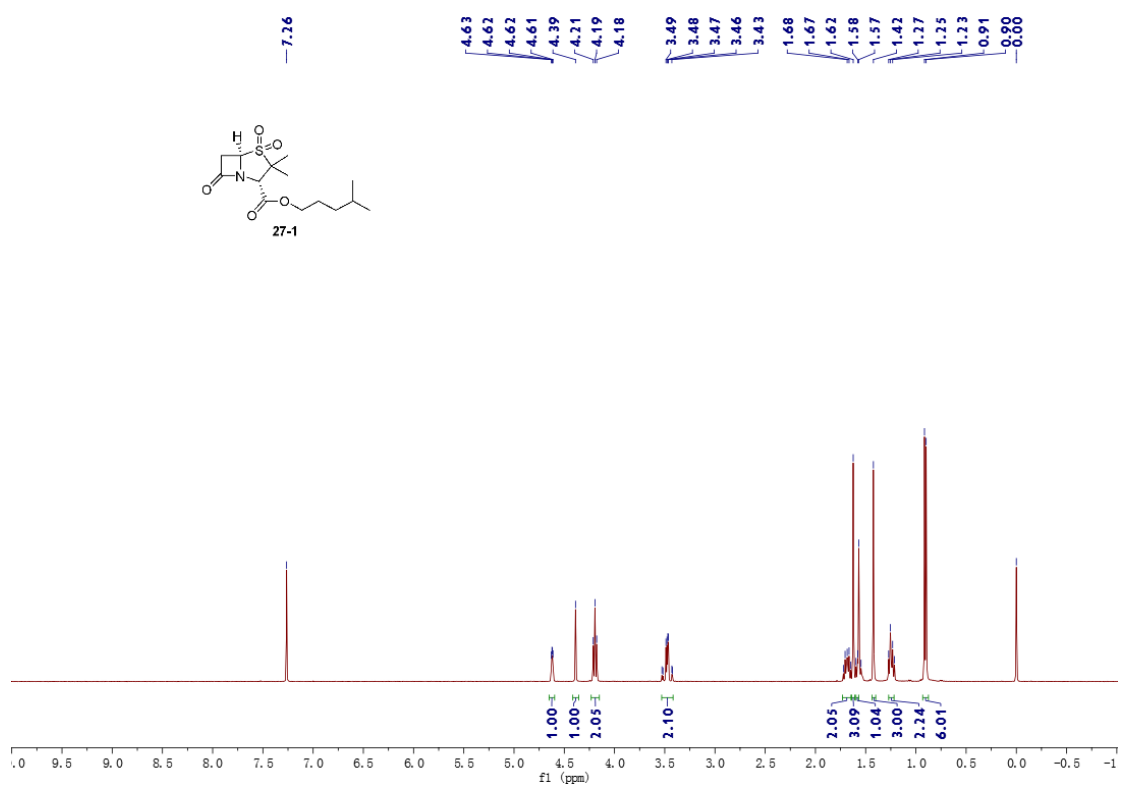
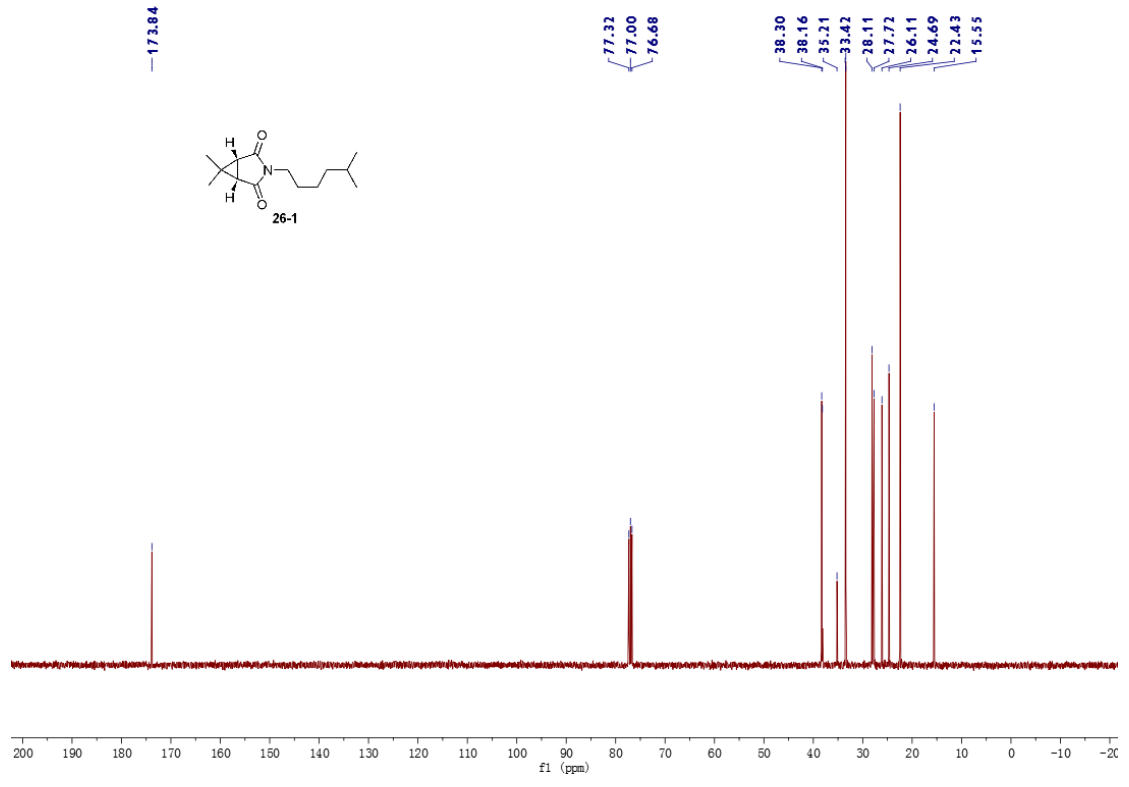
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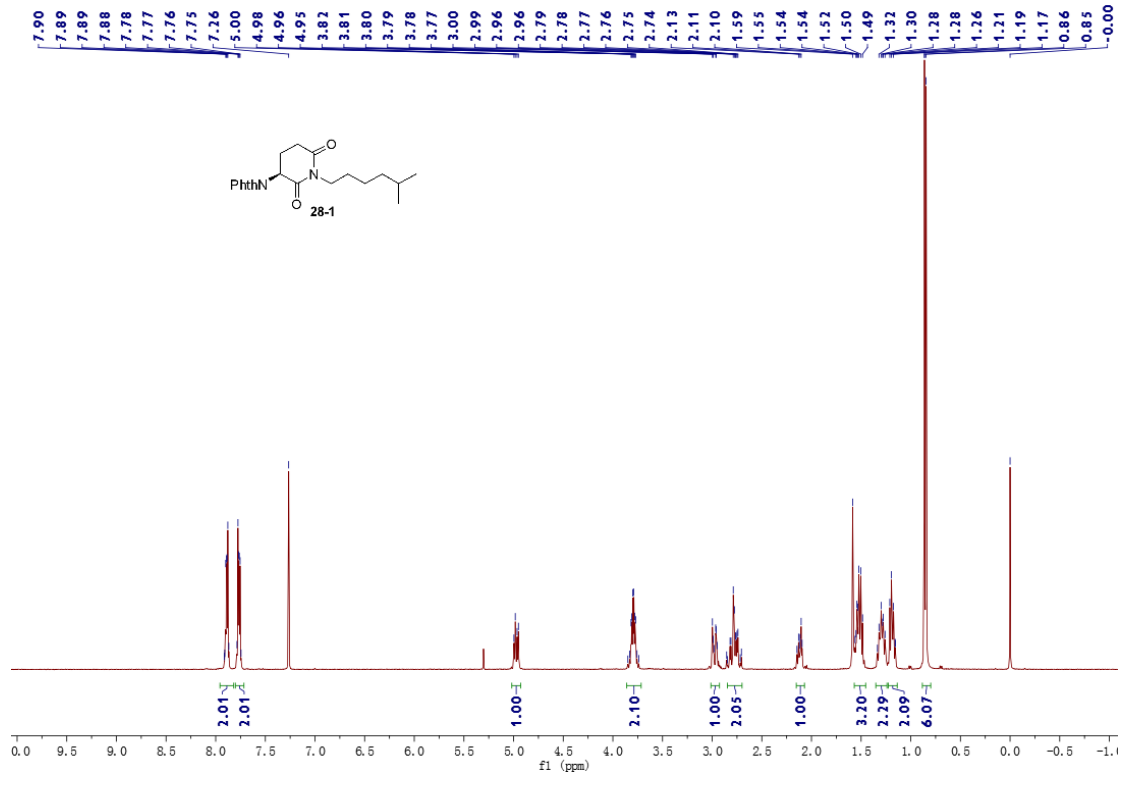
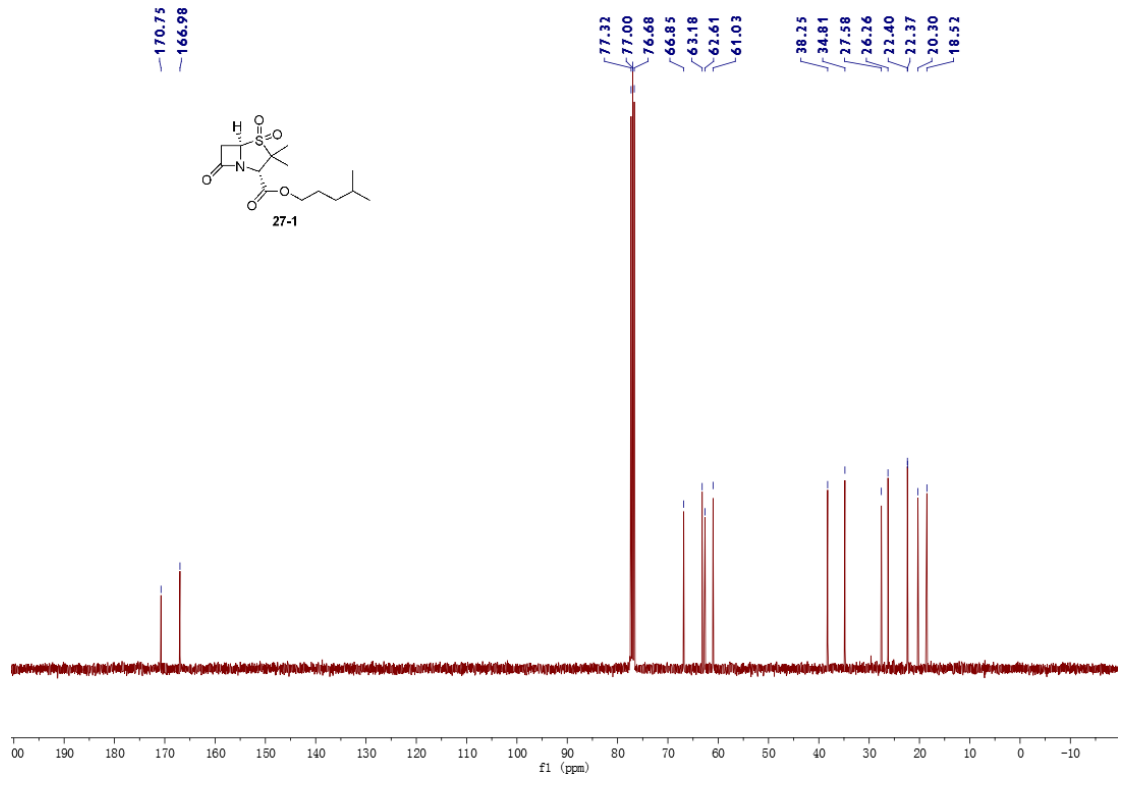


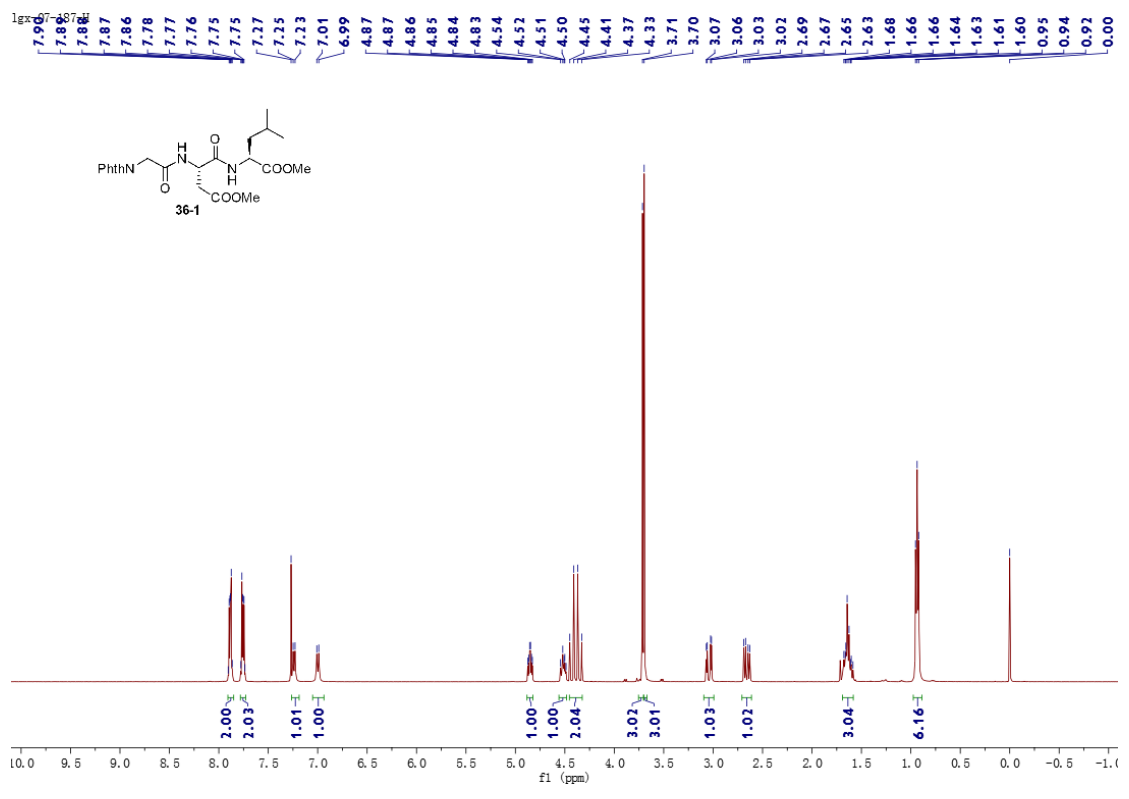
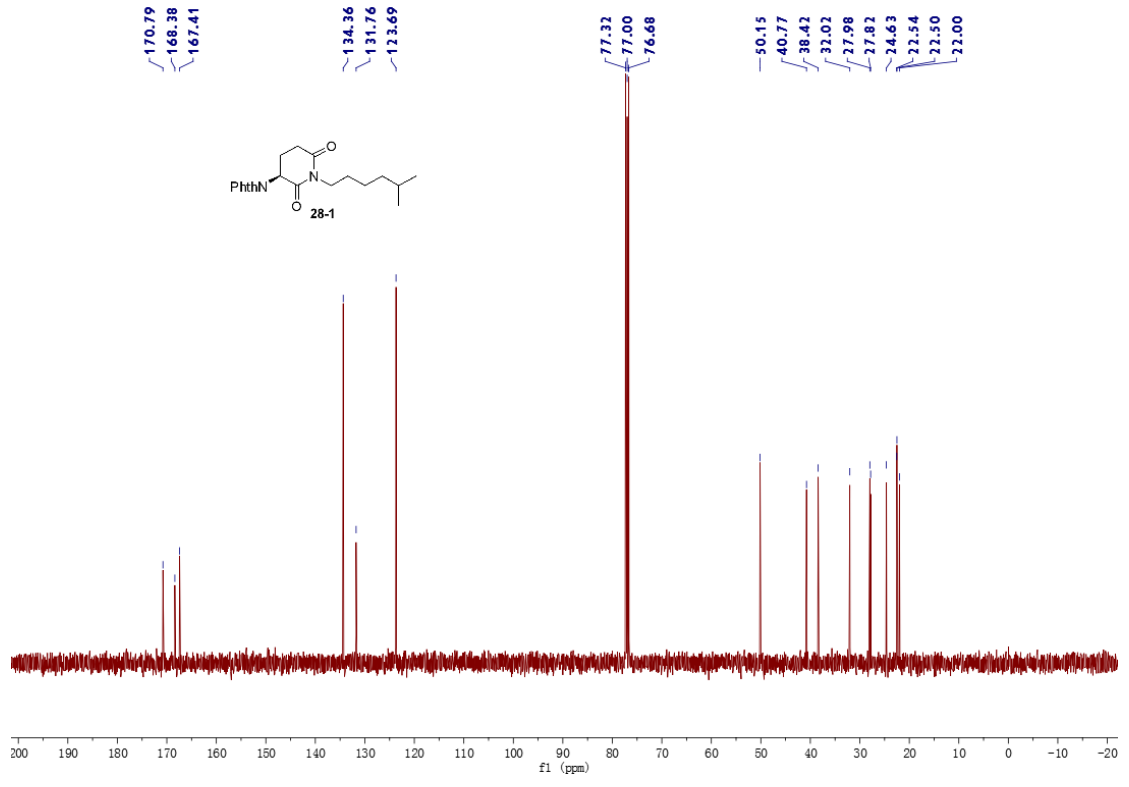
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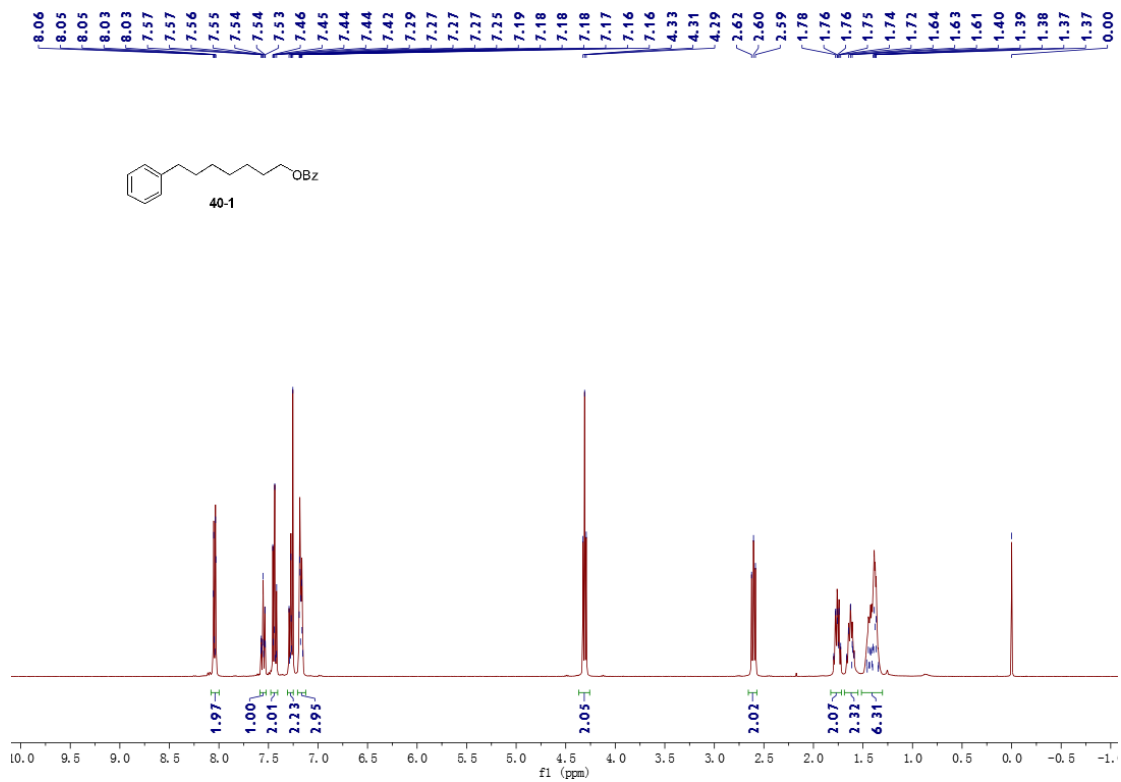
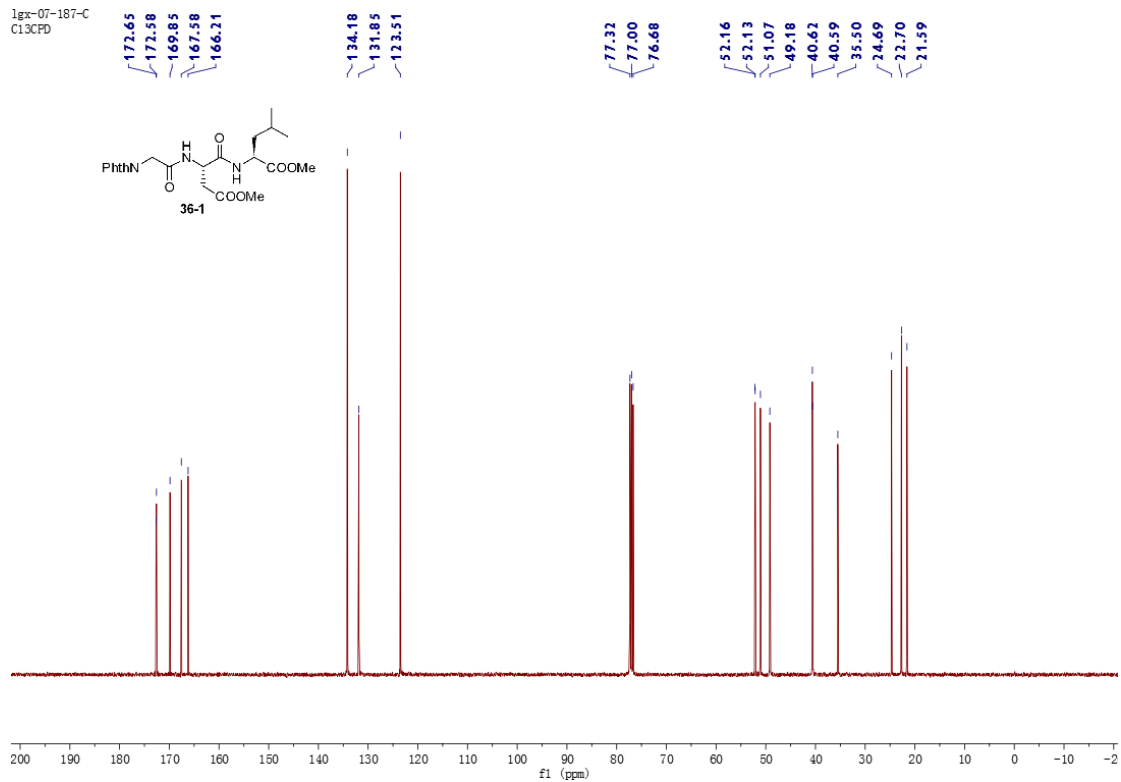


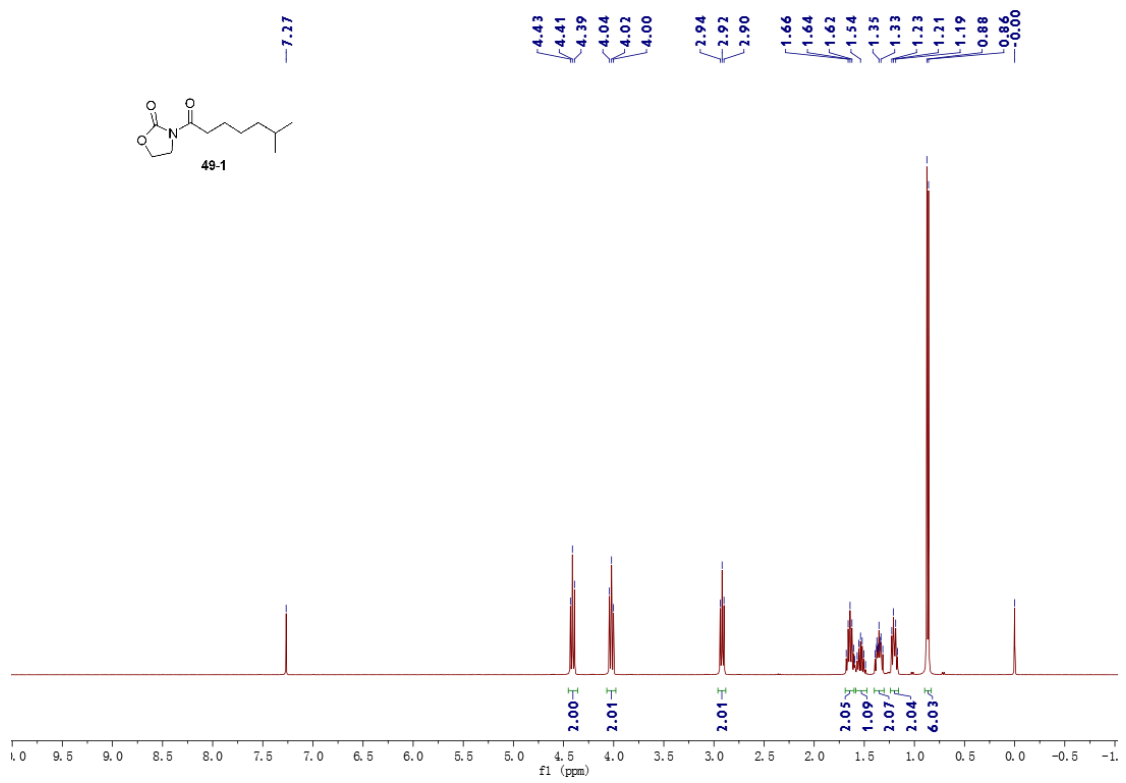
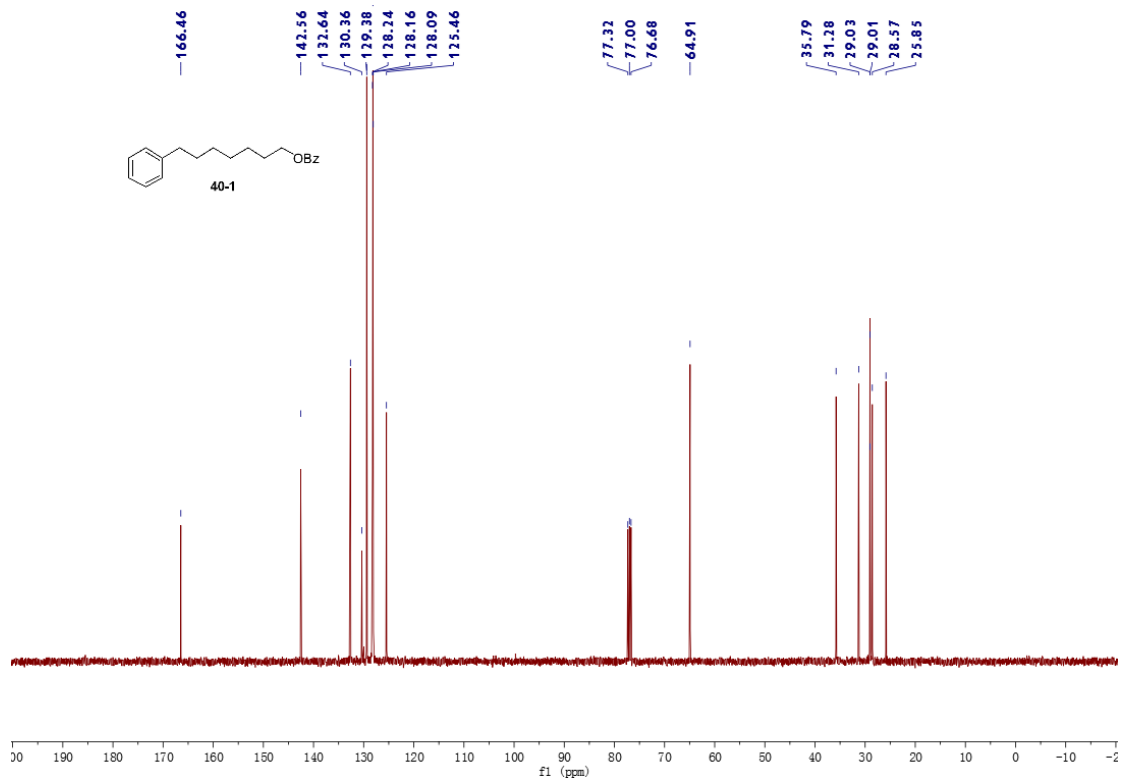


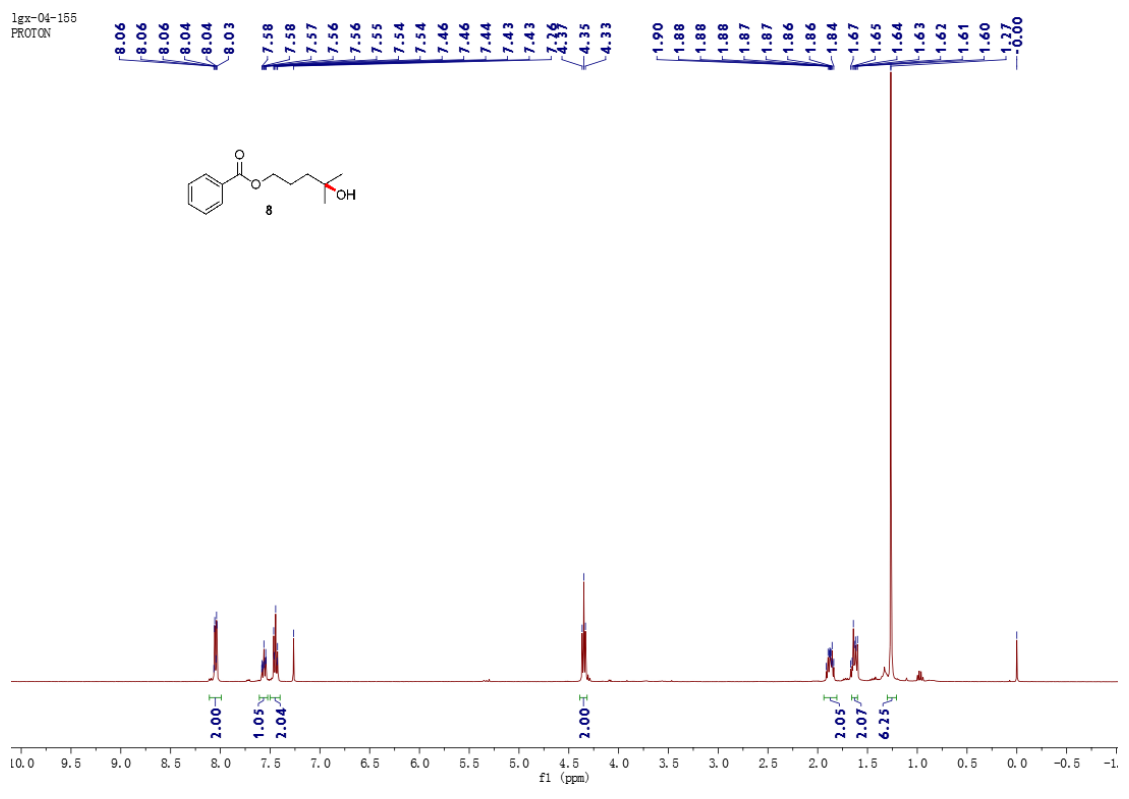
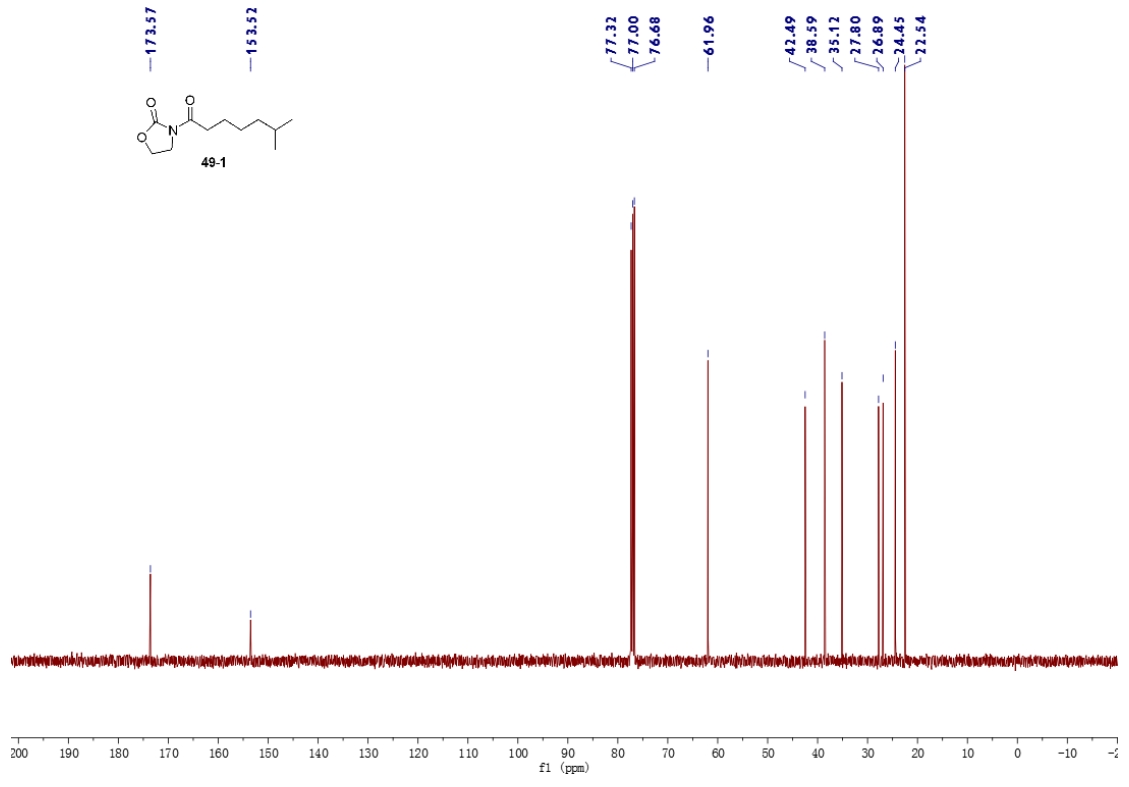




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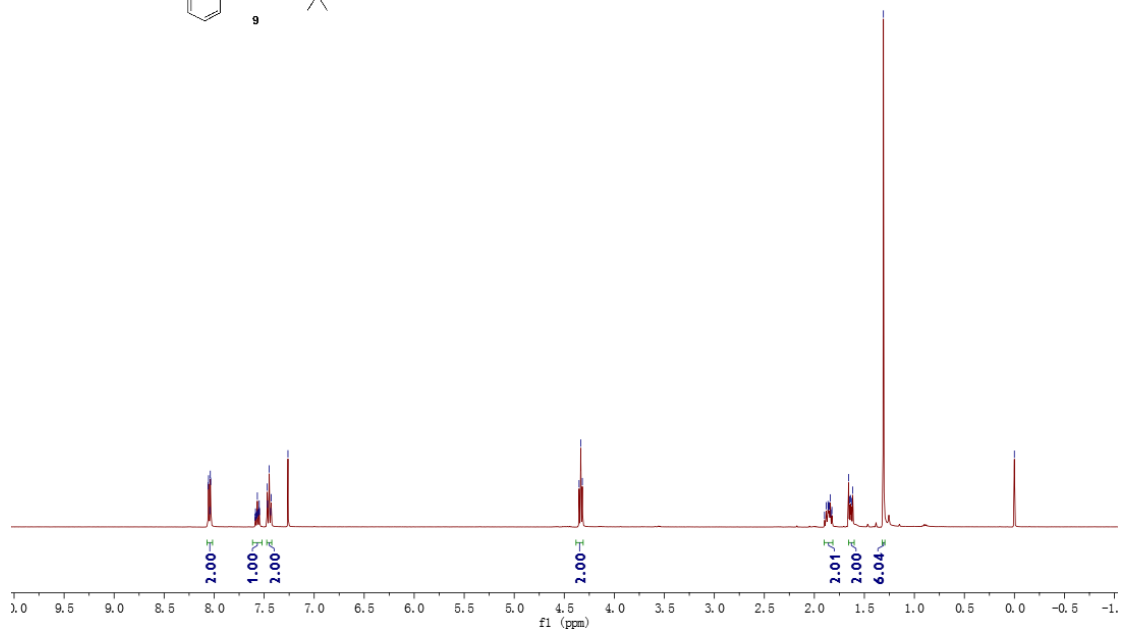
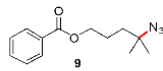






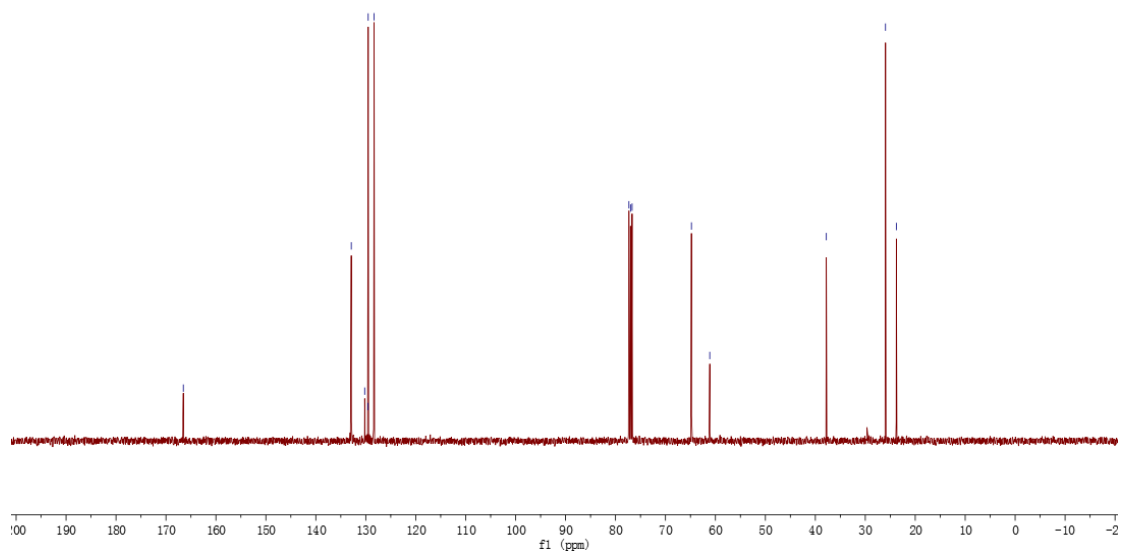
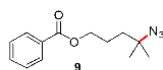
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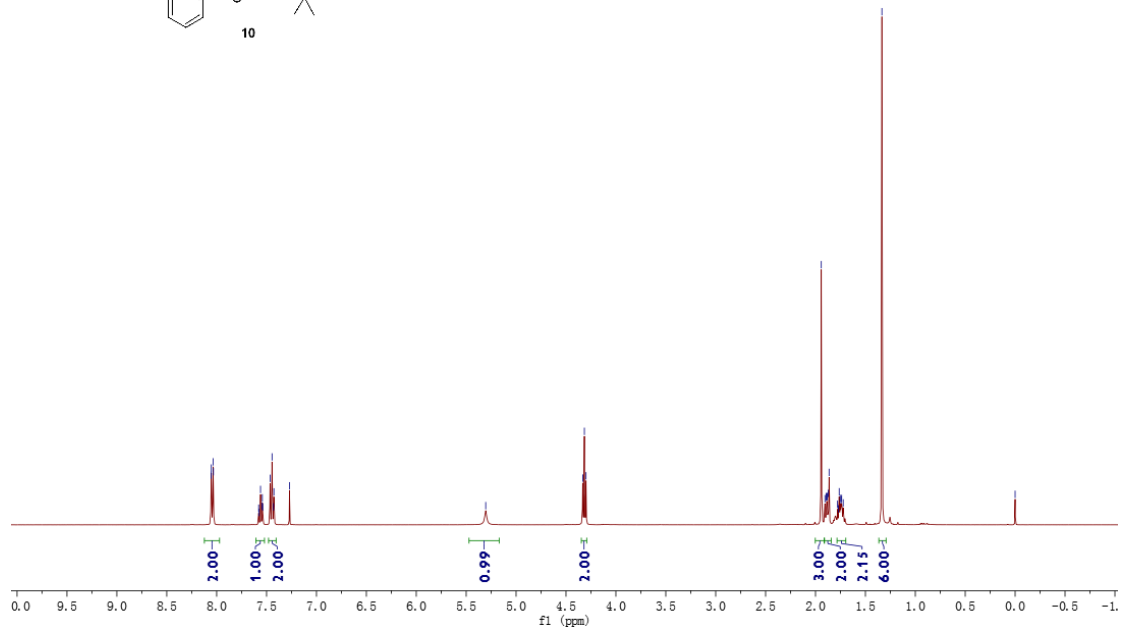
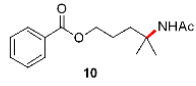


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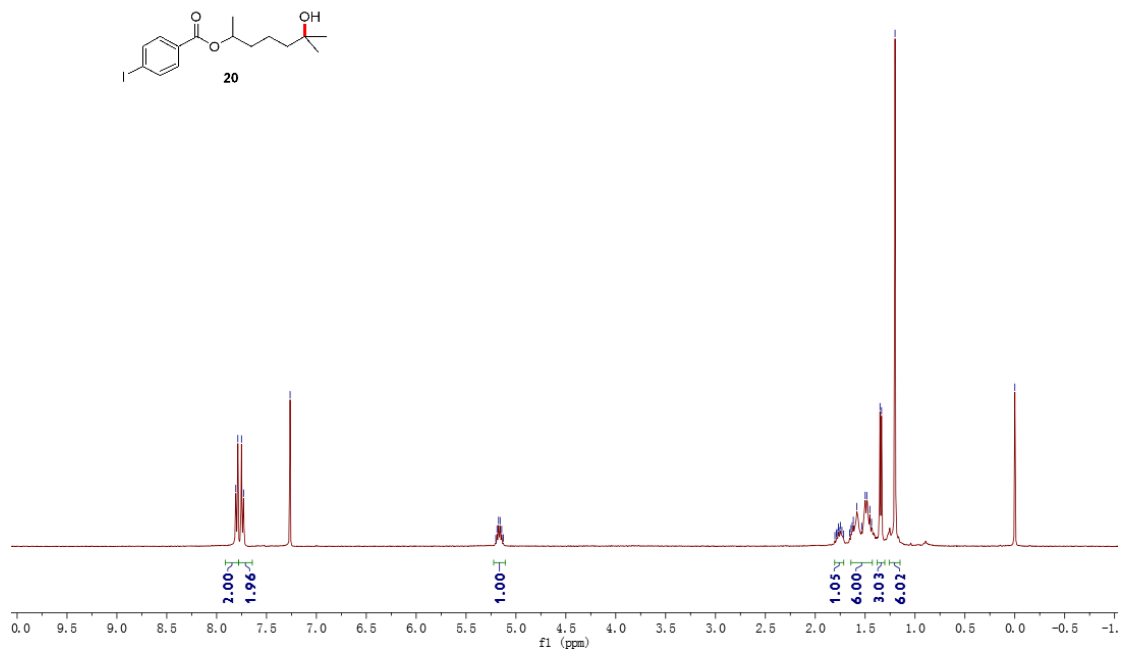
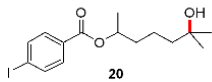
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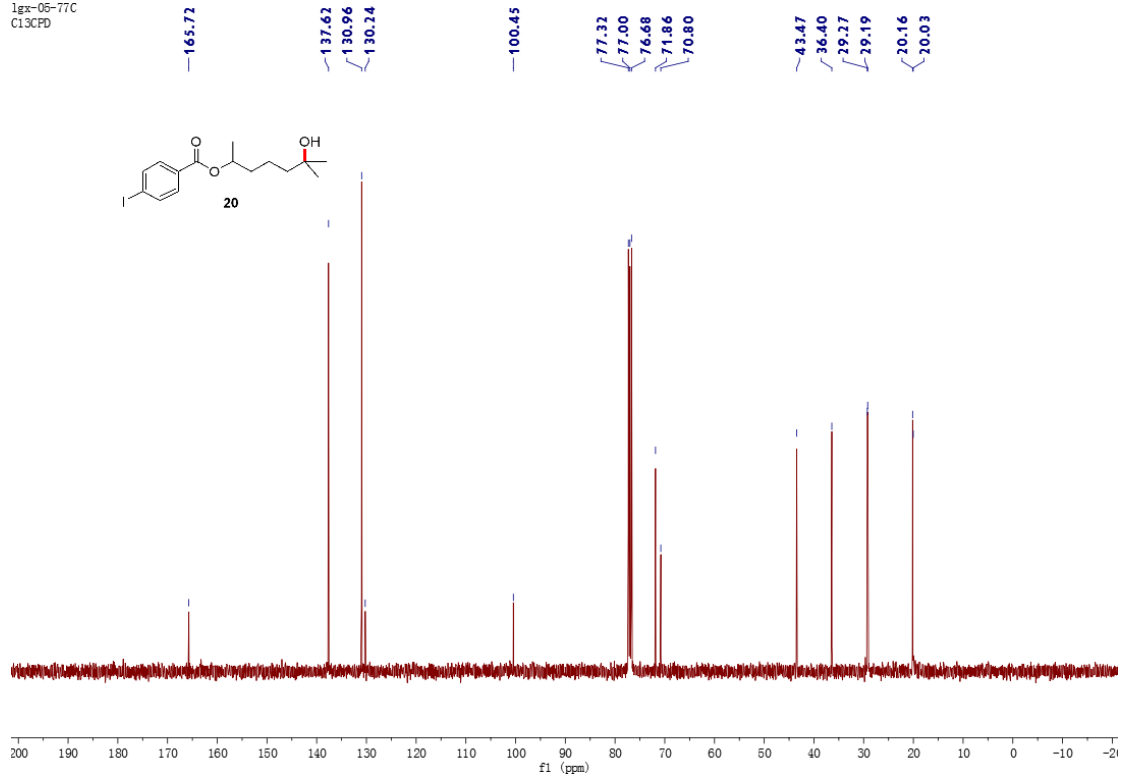
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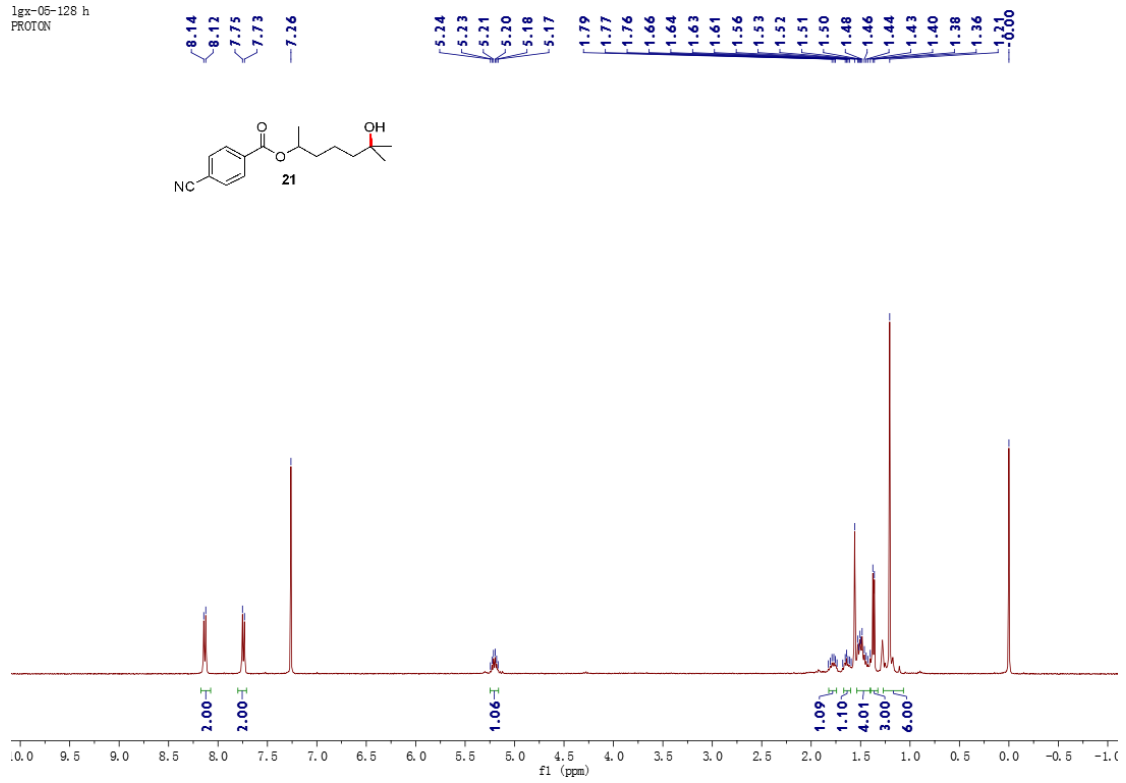
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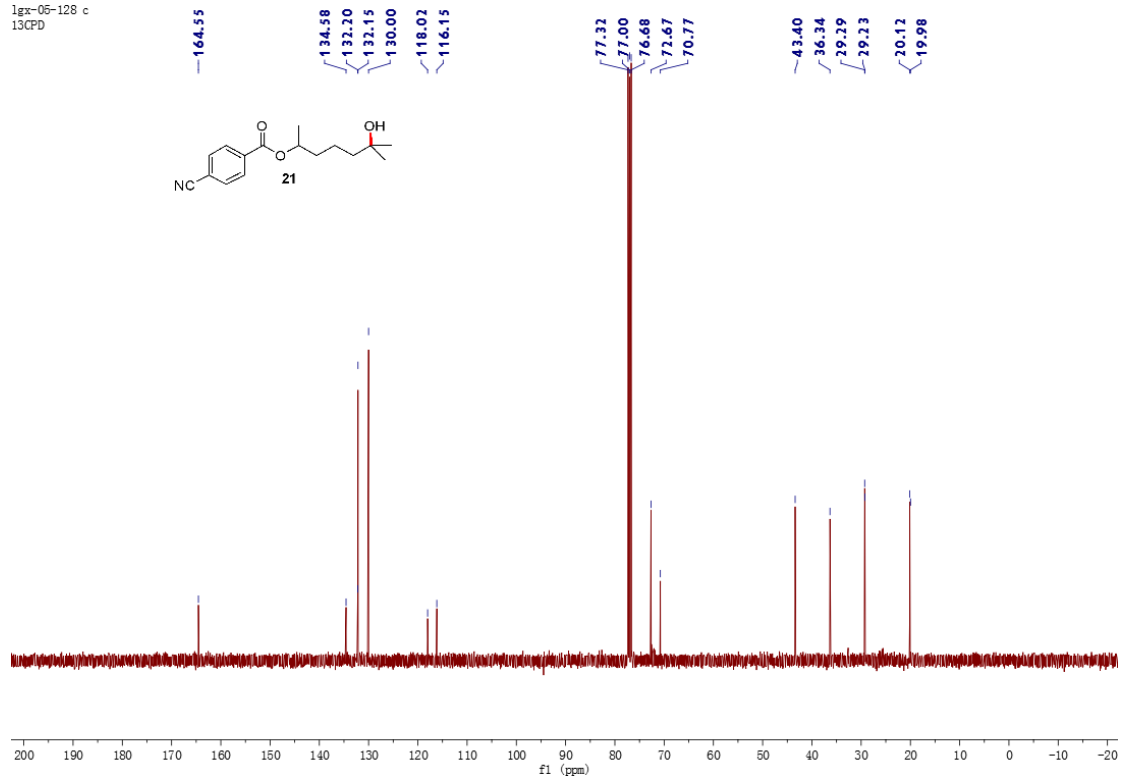
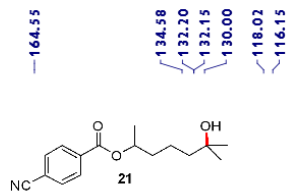
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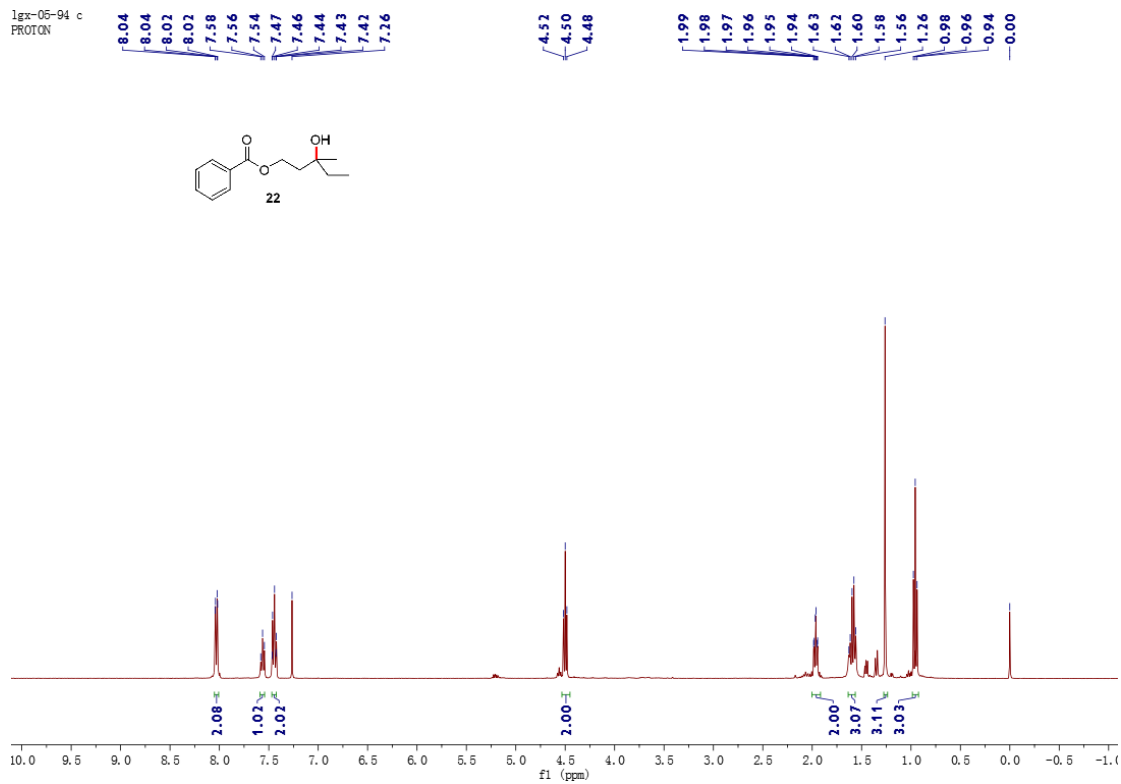
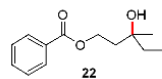
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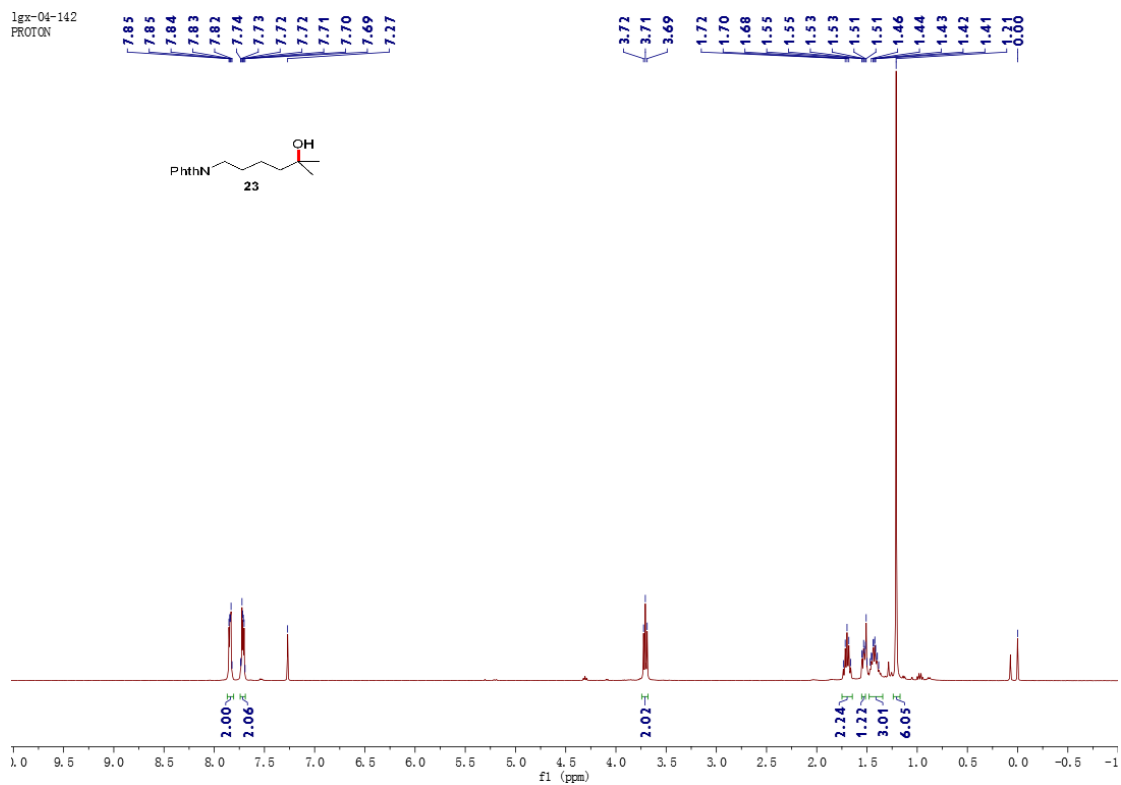
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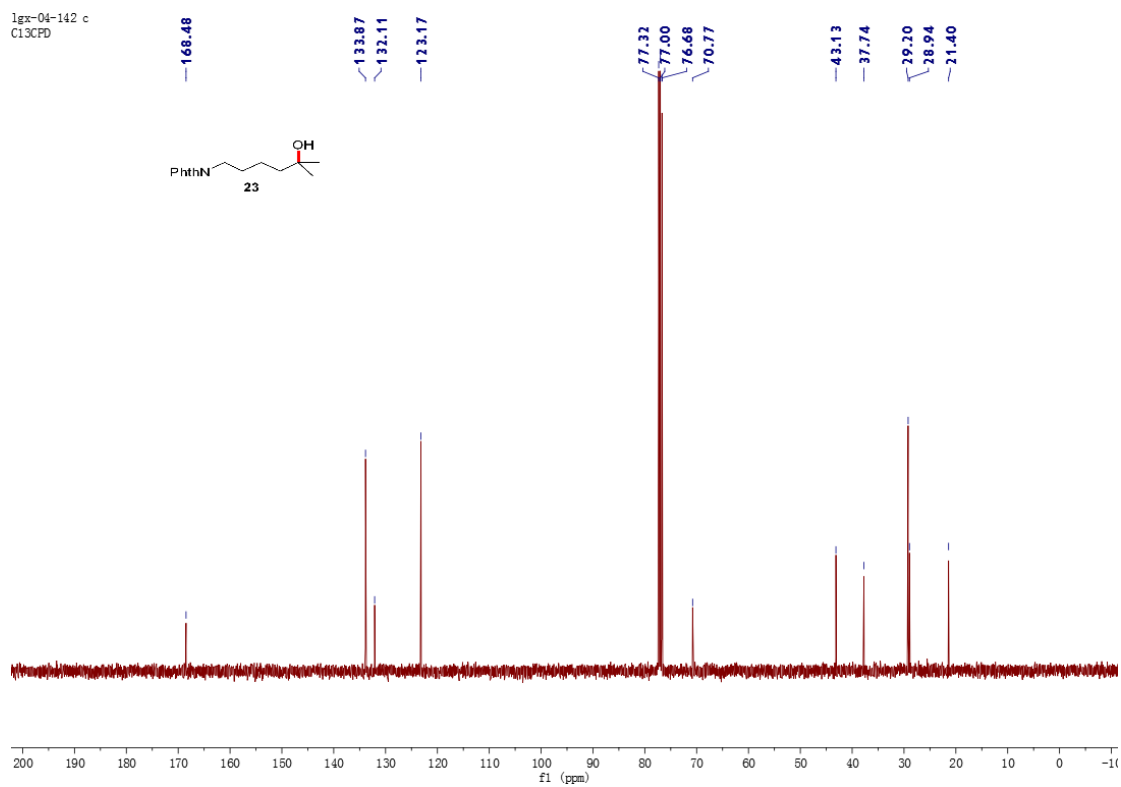
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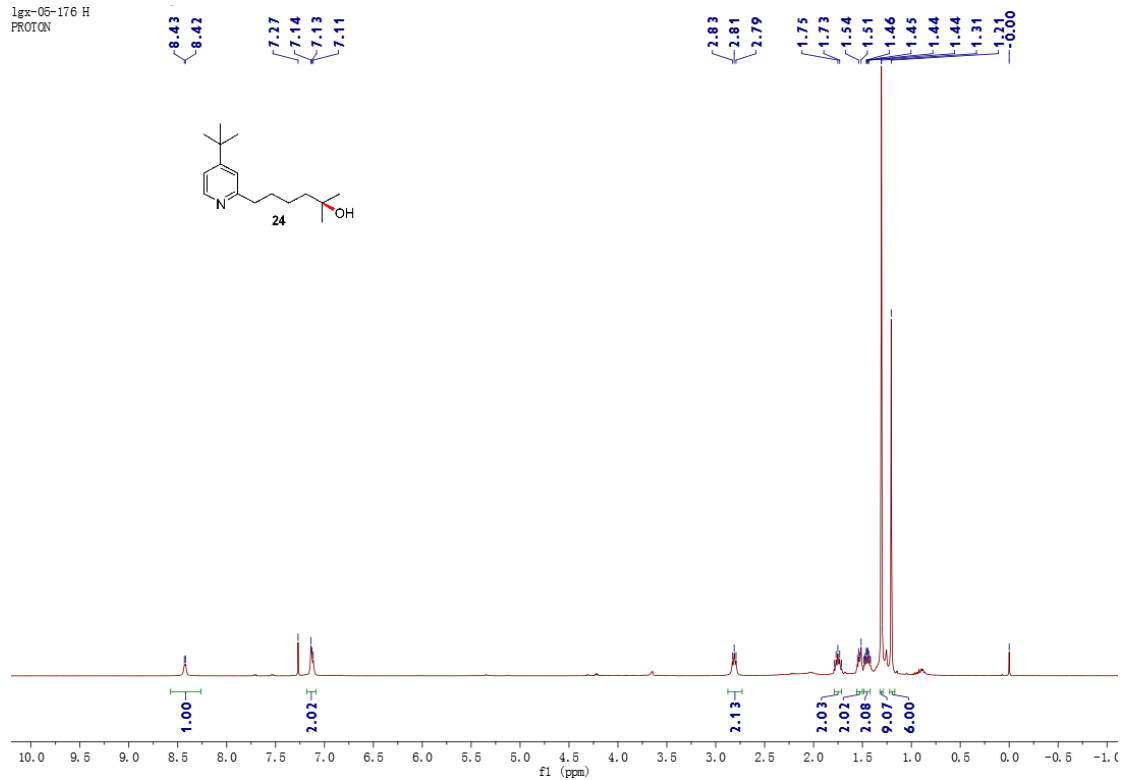
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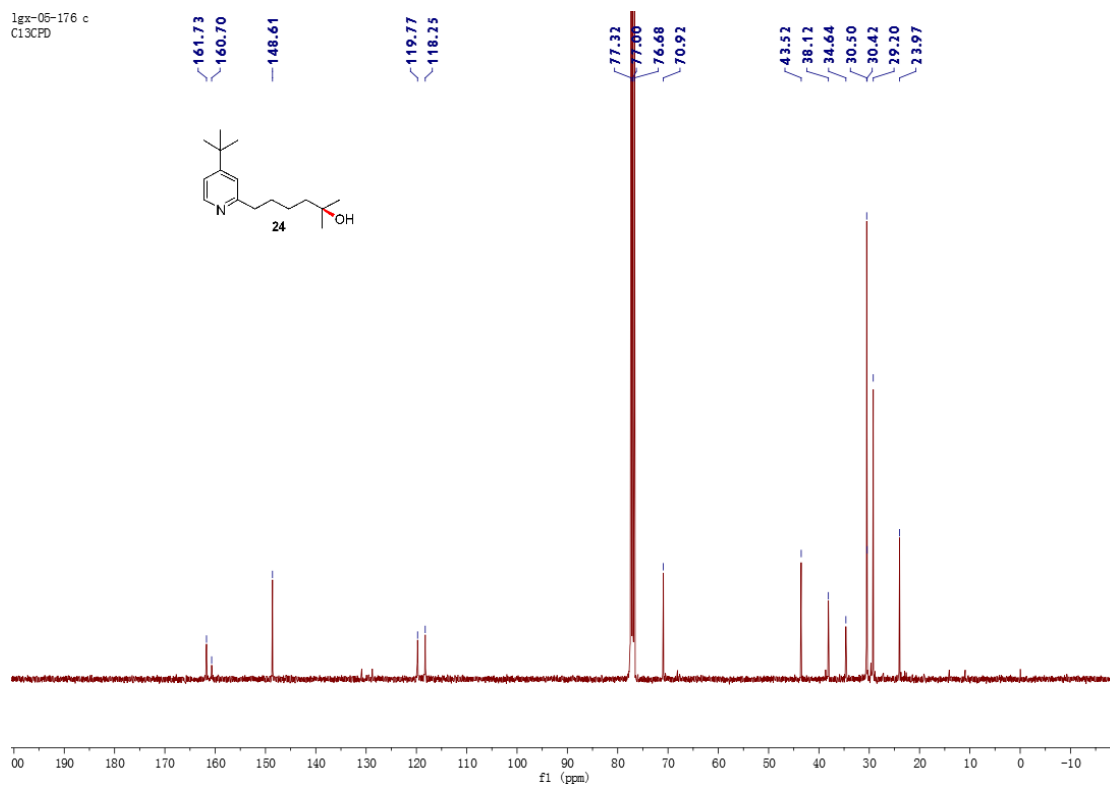
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C13CPD

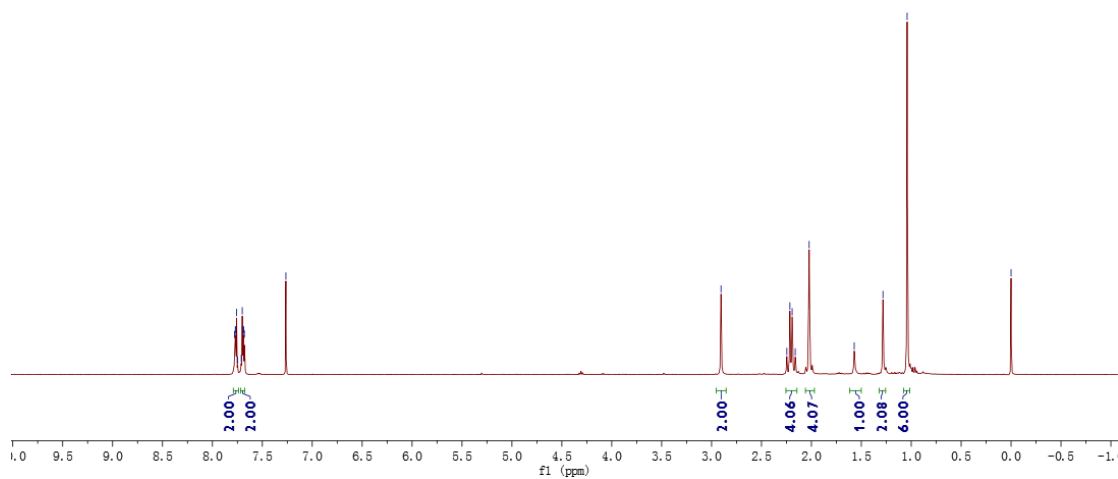
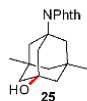


1gx-05-93 H
PROTON

7.78
7.77
7.76
7.76
7.75
7.71
7.70
7.69
7.68
7.26

2.91
2.25
2.22
2.19
2.16
2.02
1.57
1.28
1.04

0.00



1gx-05-87 C
C13CPD

169.40

133.90
131.67

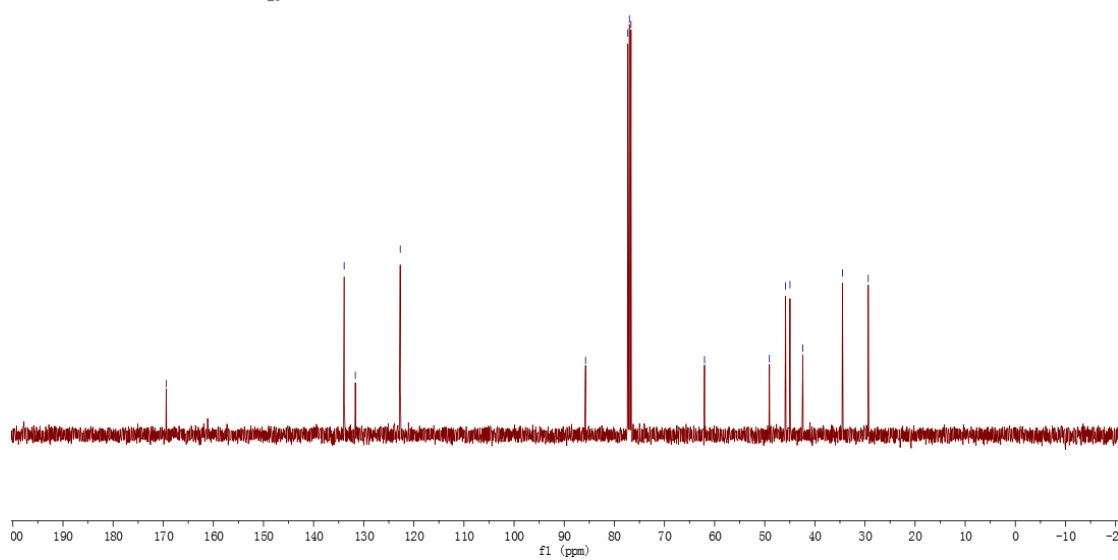
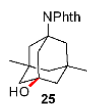
122.72

85.75
77.32
77.00
76.68

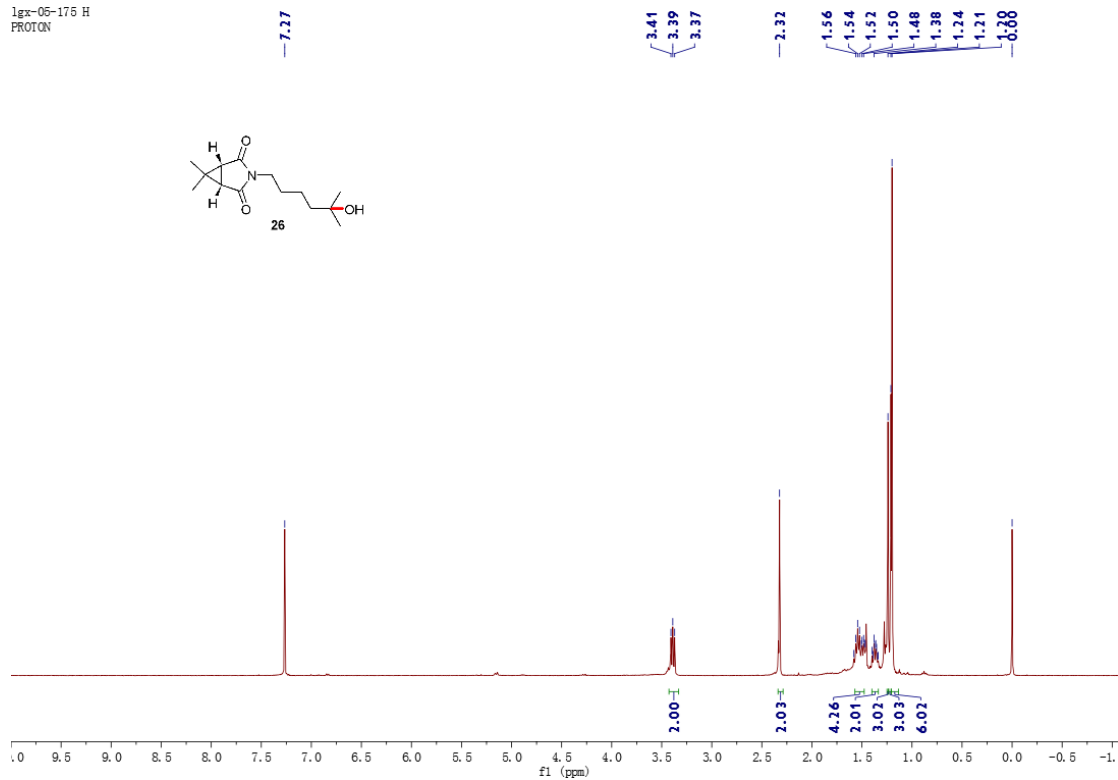
62.02

49.07
45.84
44.97
42.40

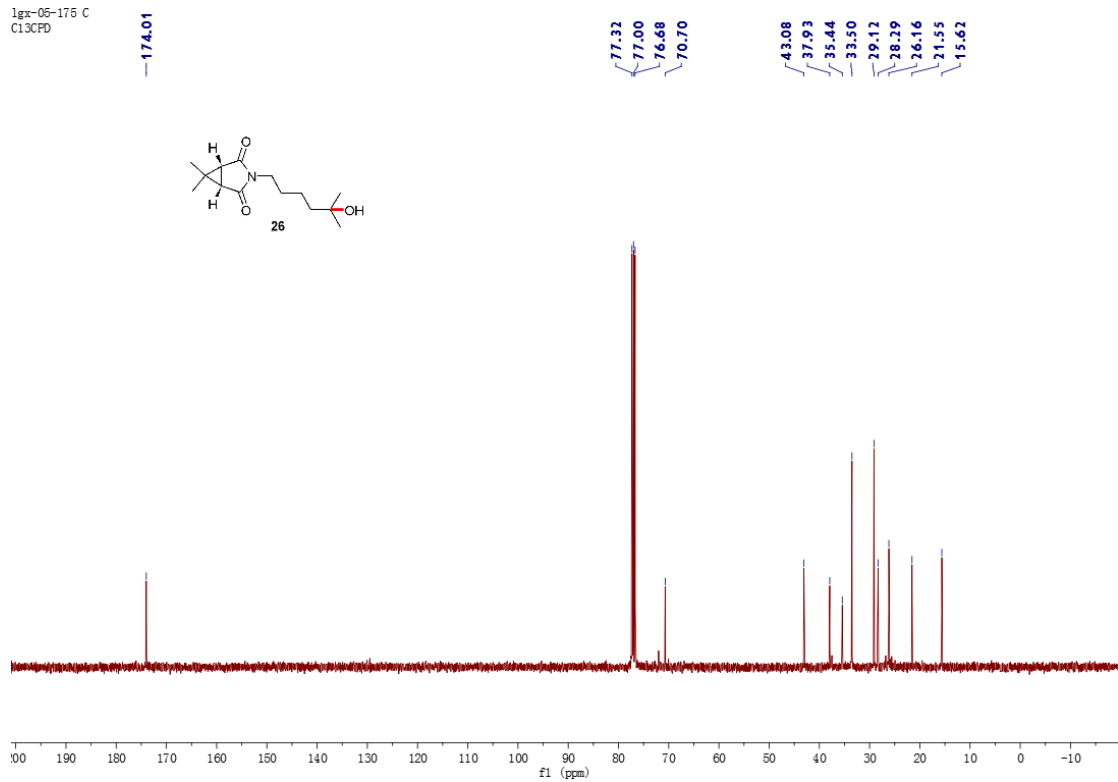
34.50
29.35



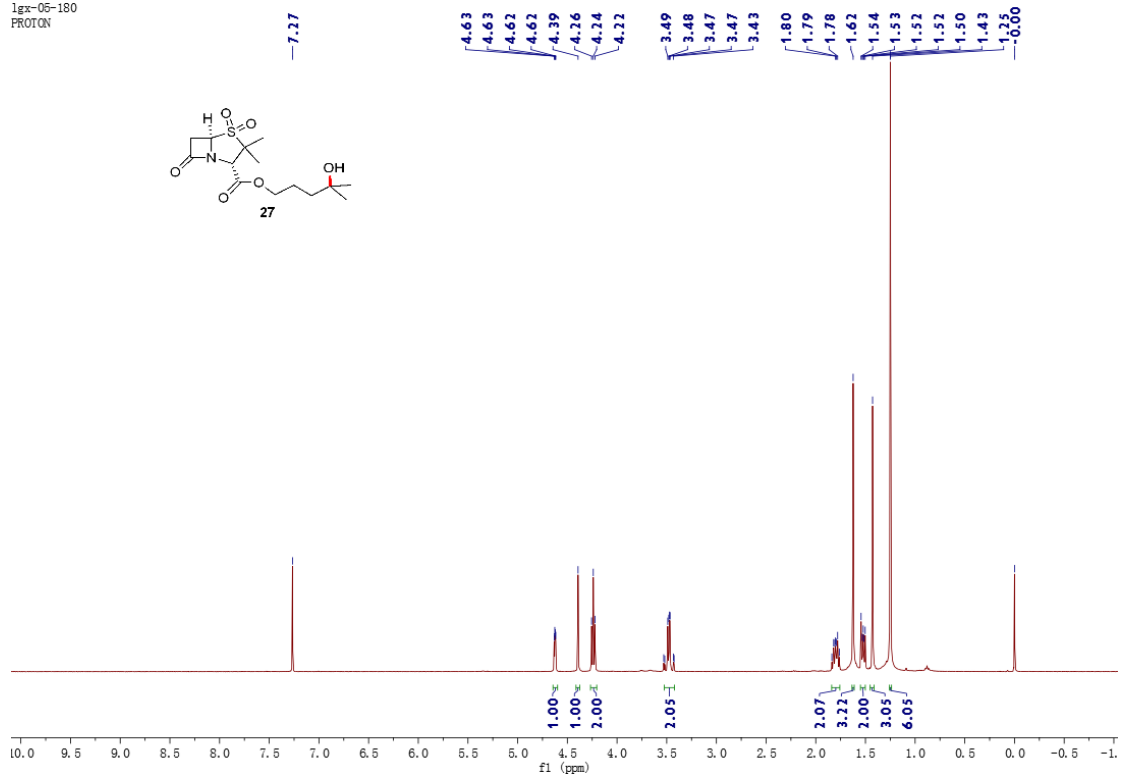
lgx-05-175 H
PROTON



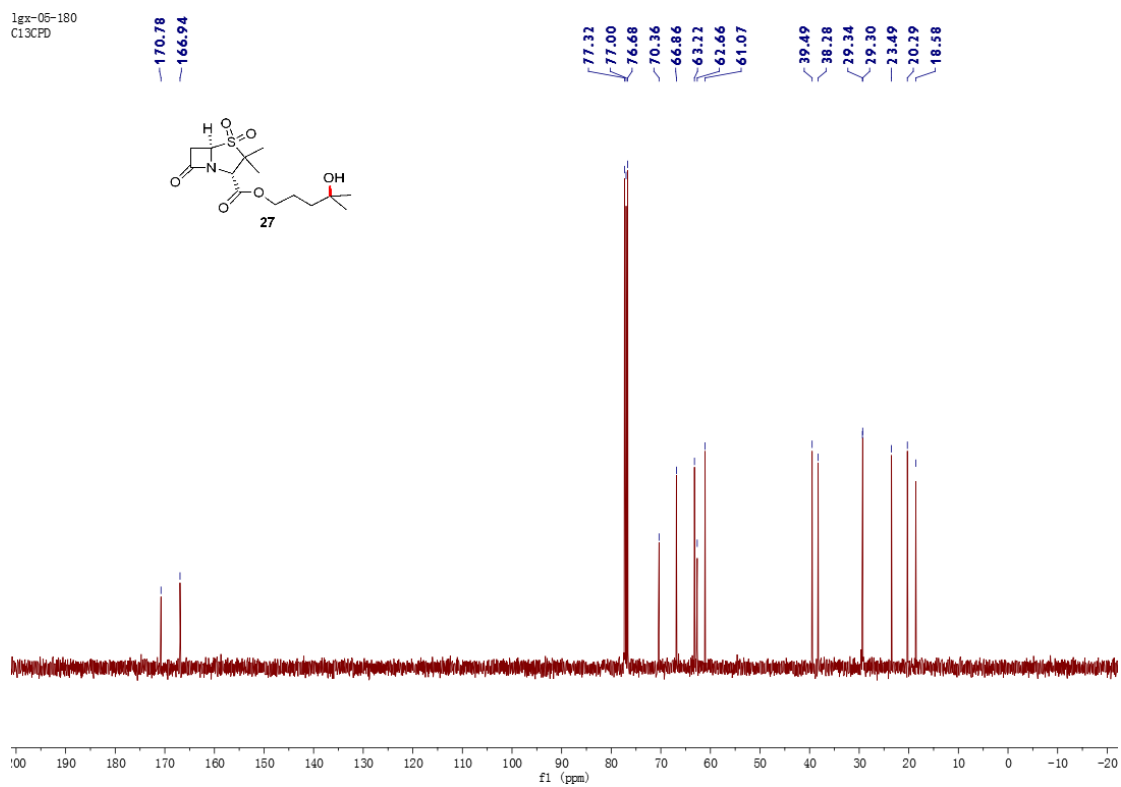
lgx-05-175 C
C13CPD

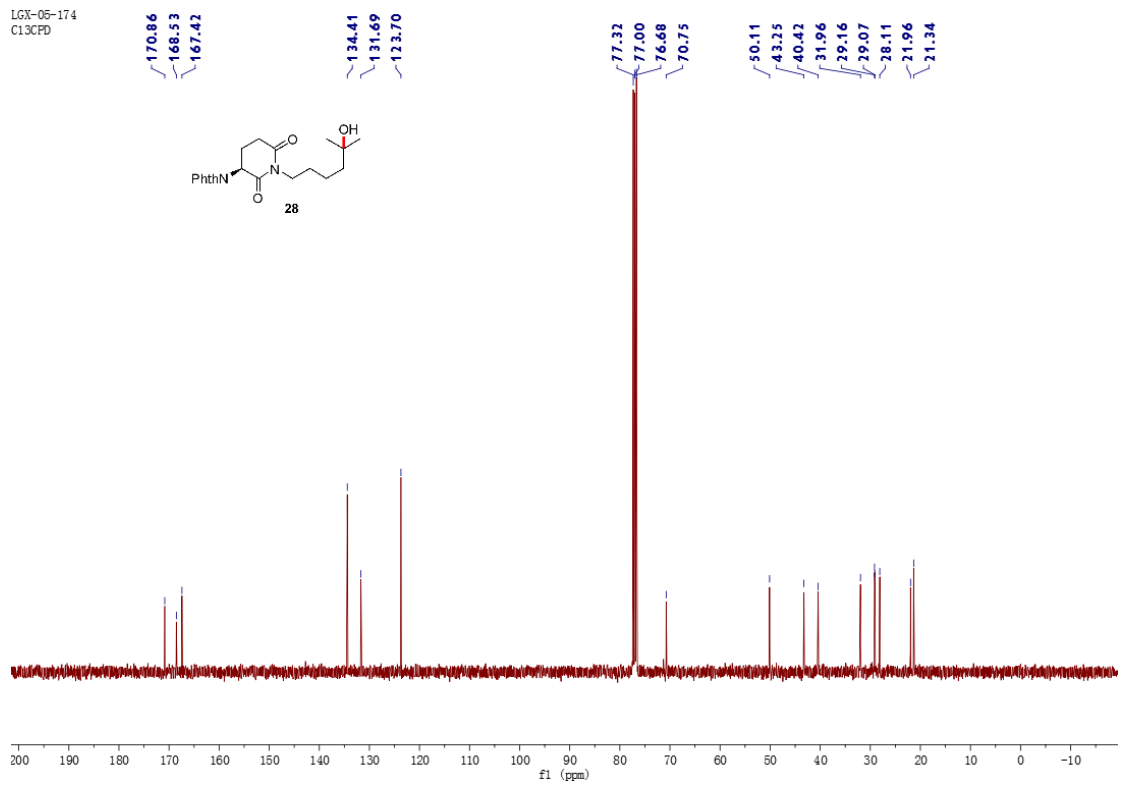
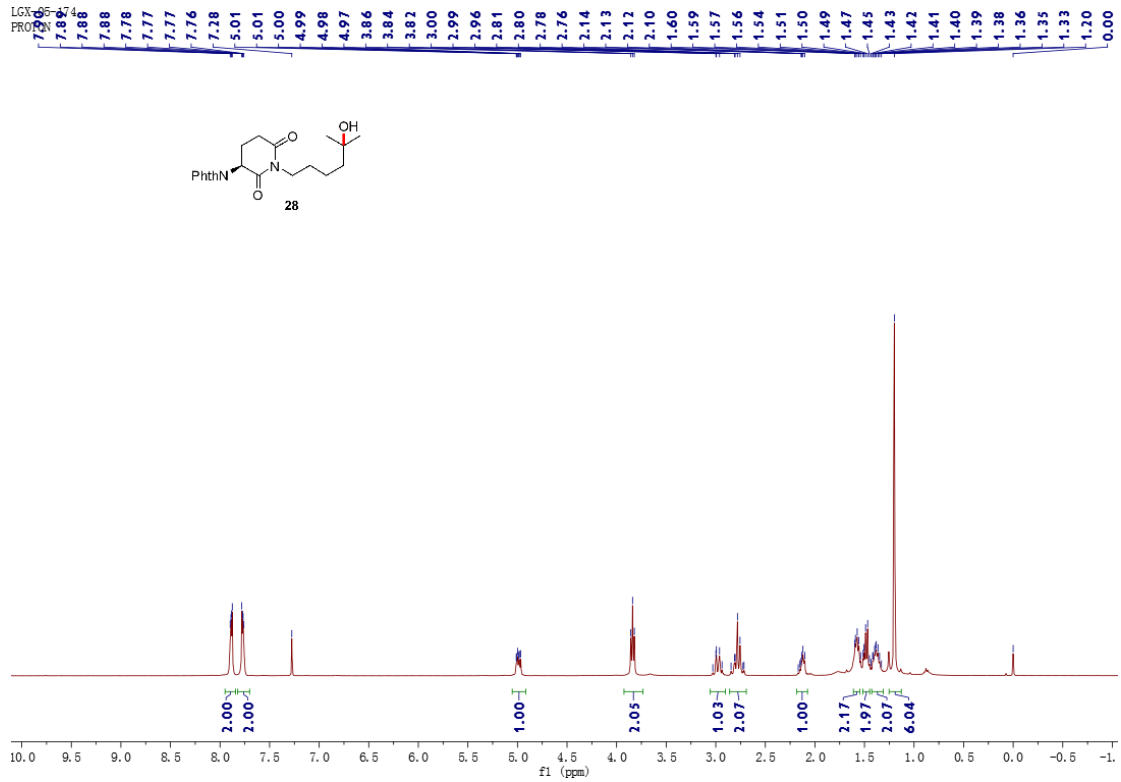


1gx-05-180
PROTON

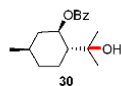
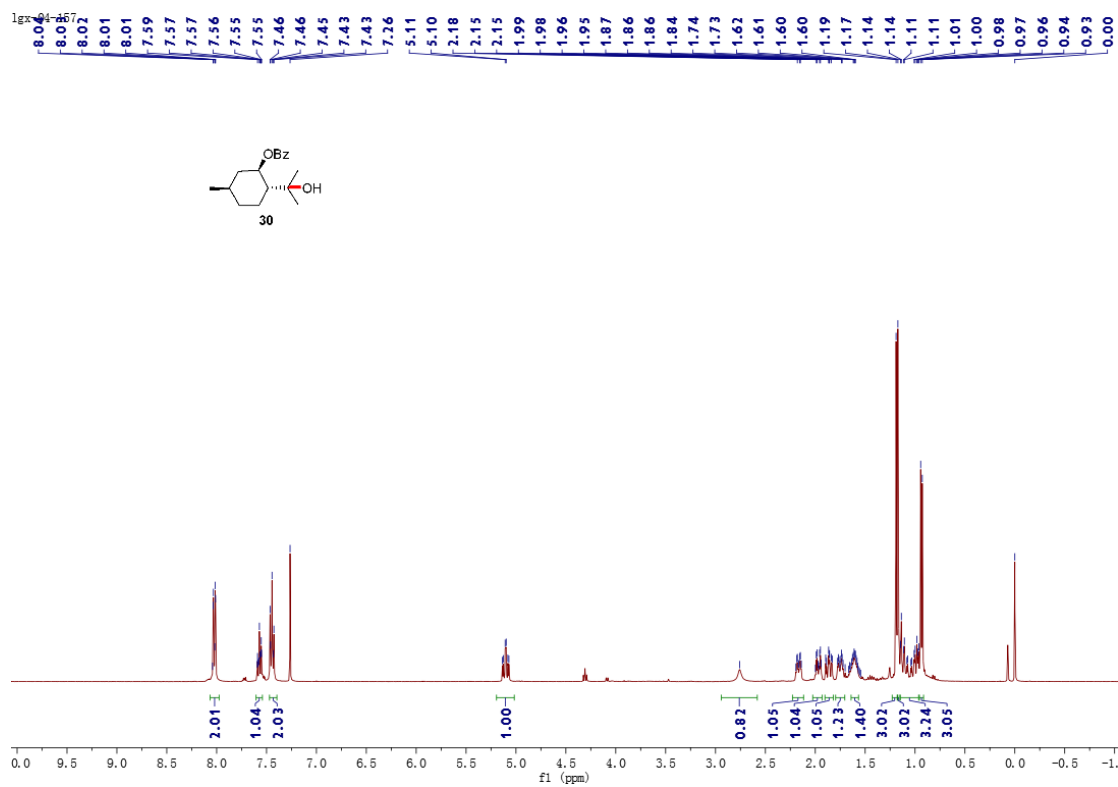
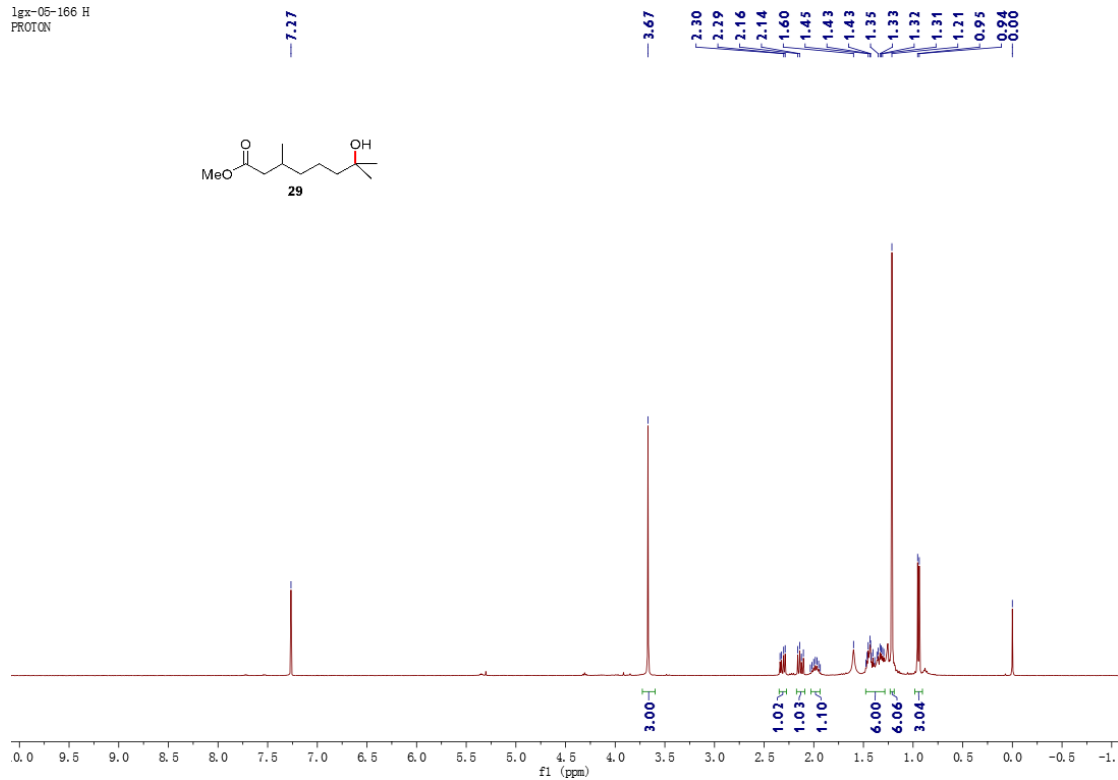
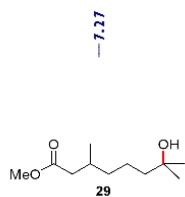


1gx-05-180
C13CPD

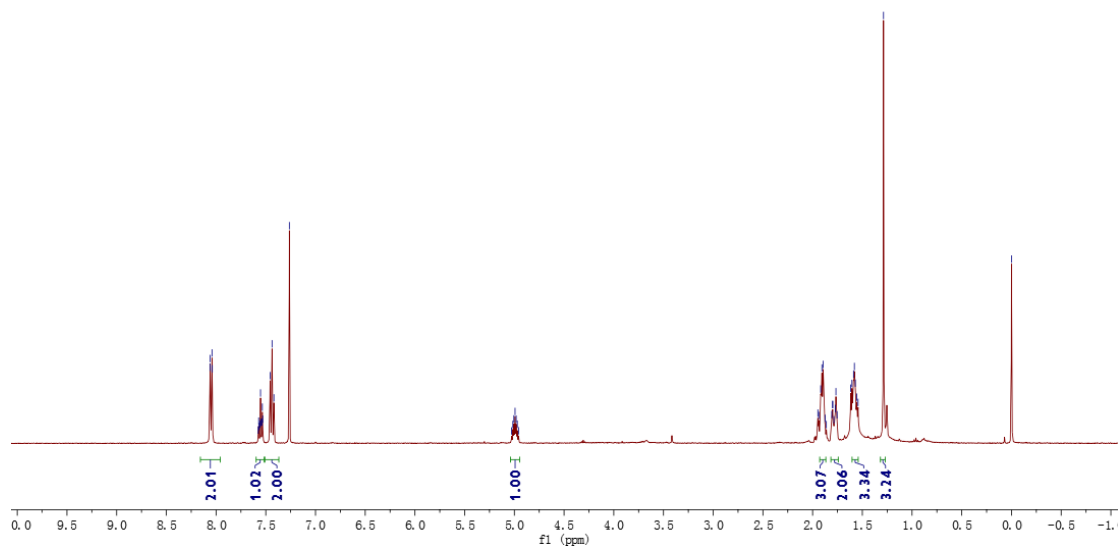
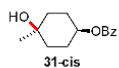
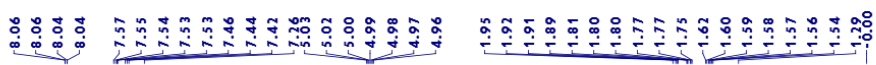




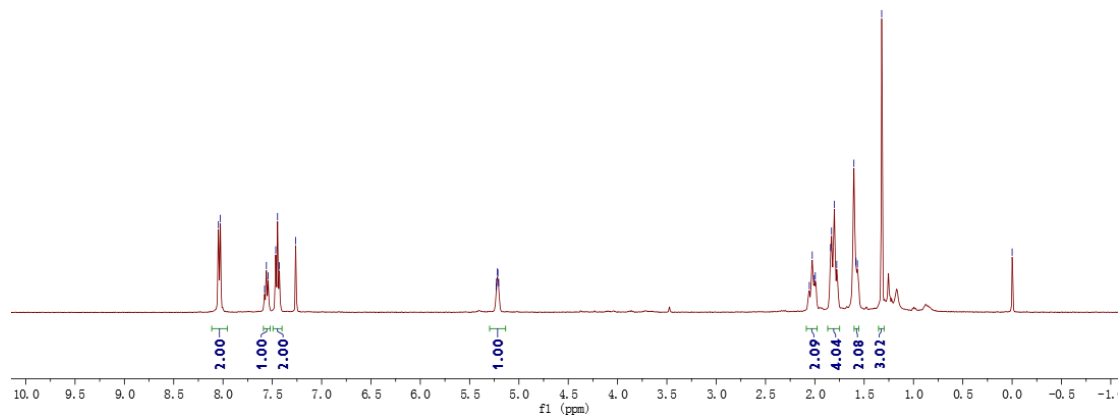
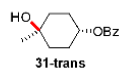
lgx-05-166 H
PROTON

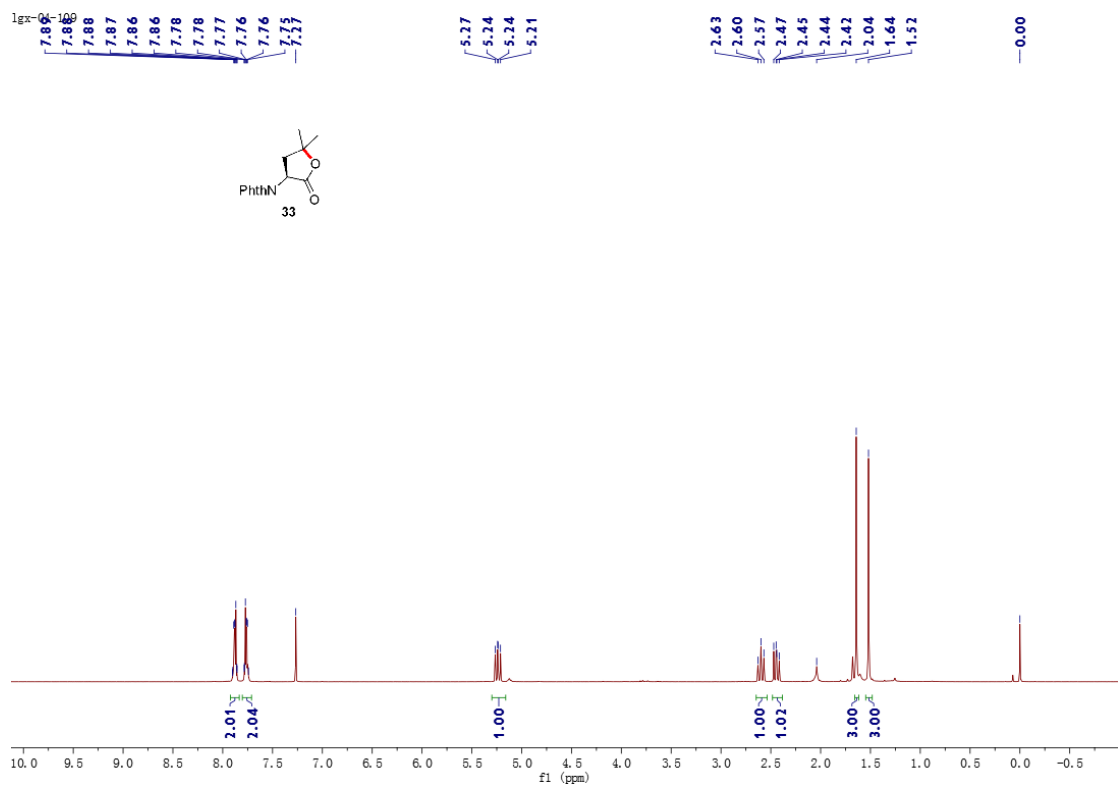
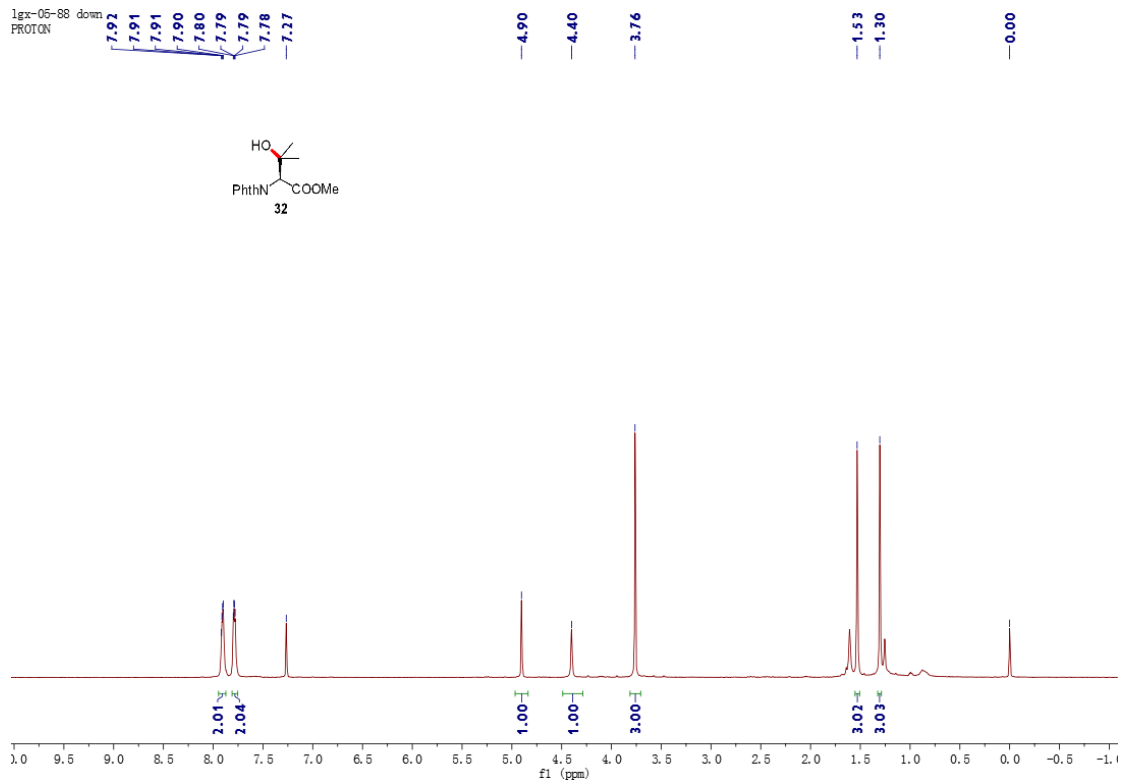


1gx-05-162 UP
PROTON



1gx-05-86 down H
PROTON





lgx-07-168-H

7.88
7.87
7.87
7.86
7.85
7.75
7.74
7.73
7.73
7.42
7.40
7.27

5.14
5.12
5.11

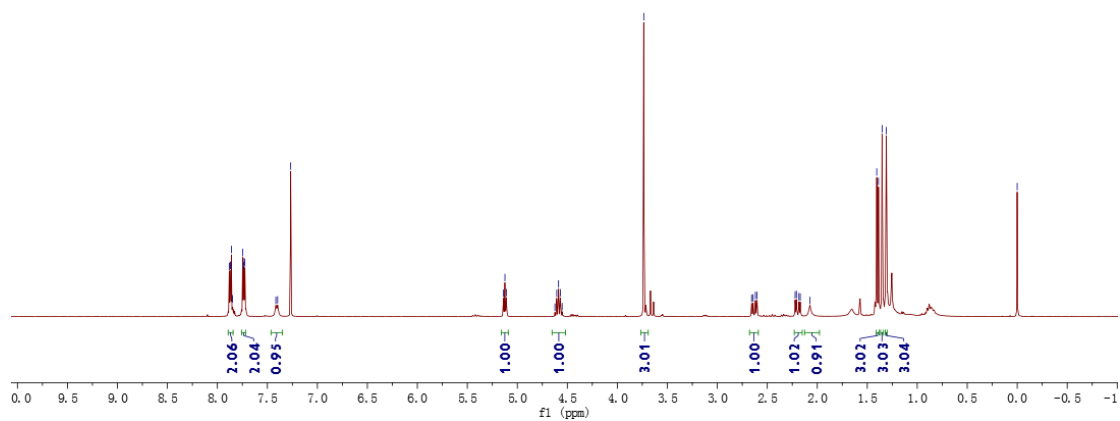
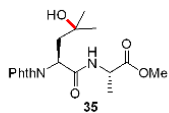
4.61
4.59
4.57
4.55
4.54

2.66
2.64
2.62
2.60

2.22
2.21
2.18
2.17

1.39
1.35
1.31

0.00



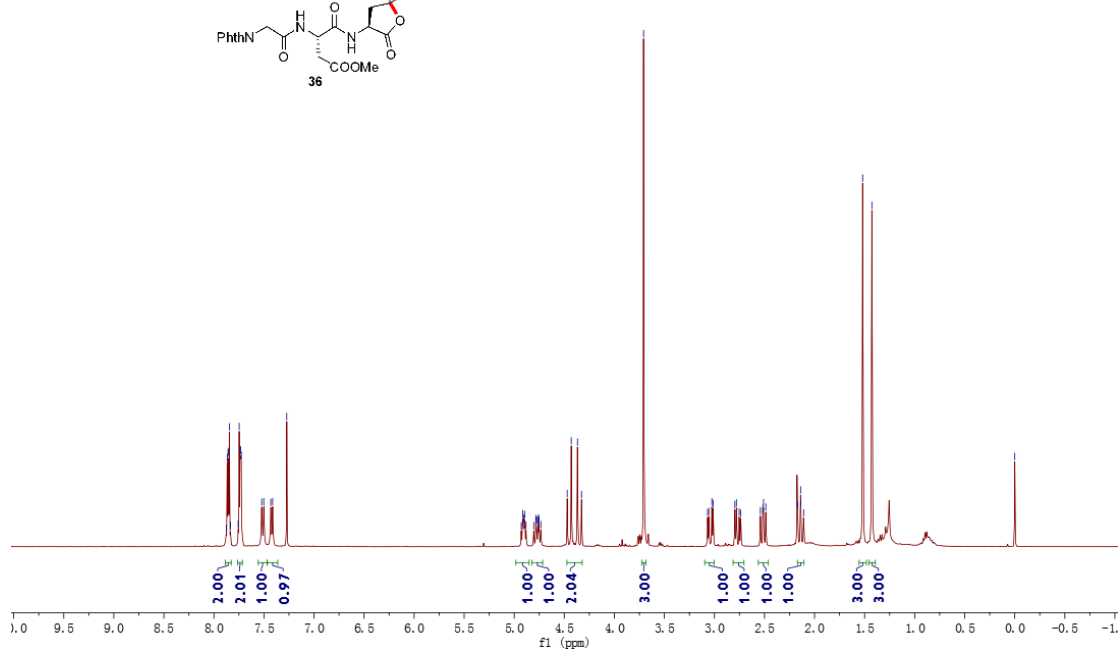
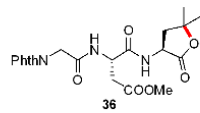
lgx-07-168-H

7.86
7.85
7.84
7.76
7.75
7.73
7.73
7.52
7.50
7.43
7.41
7.27

4.92
4.91
4.90
4.90
4.79
4.78
4.78
4.76
4.76
4.75
4.73
4.47
4.43
4.37
4.33
3.71

3.07
3.06
3.03
3.01
2.80
2.78
2.75
2.74
2.54
2.52
2.51
2.49
2.17
2.14
2.14
2.11
1.52
1.43

0.00



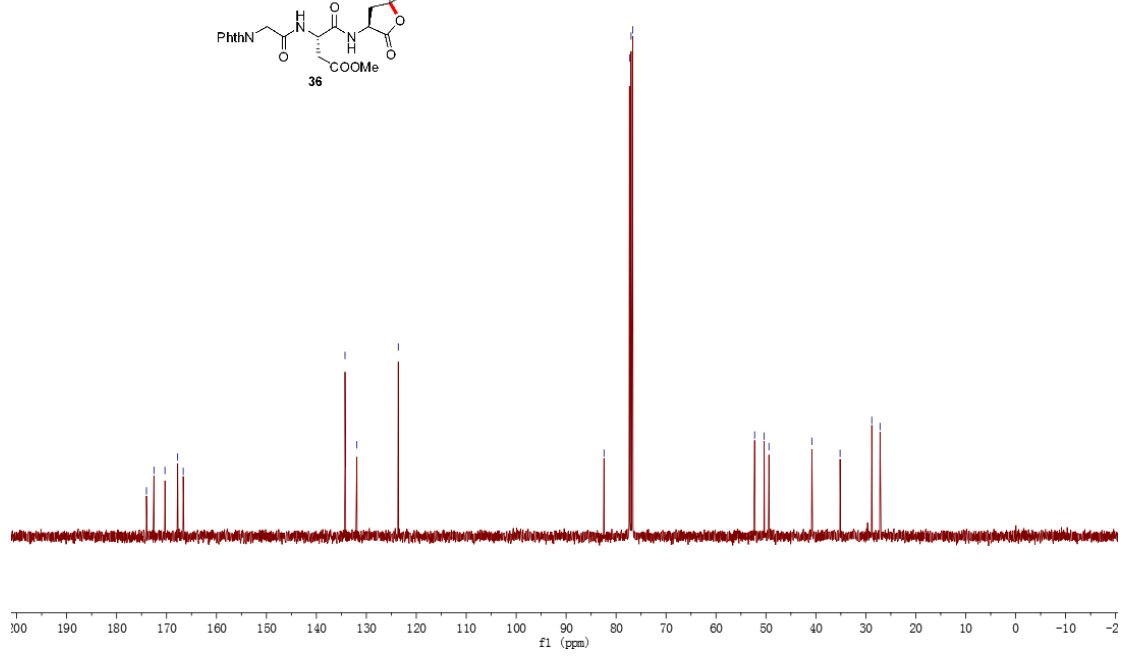
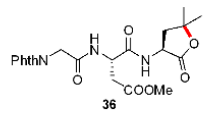
lgx-07-197-1-p-H492
C13CPD

174.00
172.52
170.32
167.77
166.66

134.27
131.90
123.61

82.42
77.32
77.00
76.68

52.26
50.35
49.40
40.80
35.15
28.81
27.16



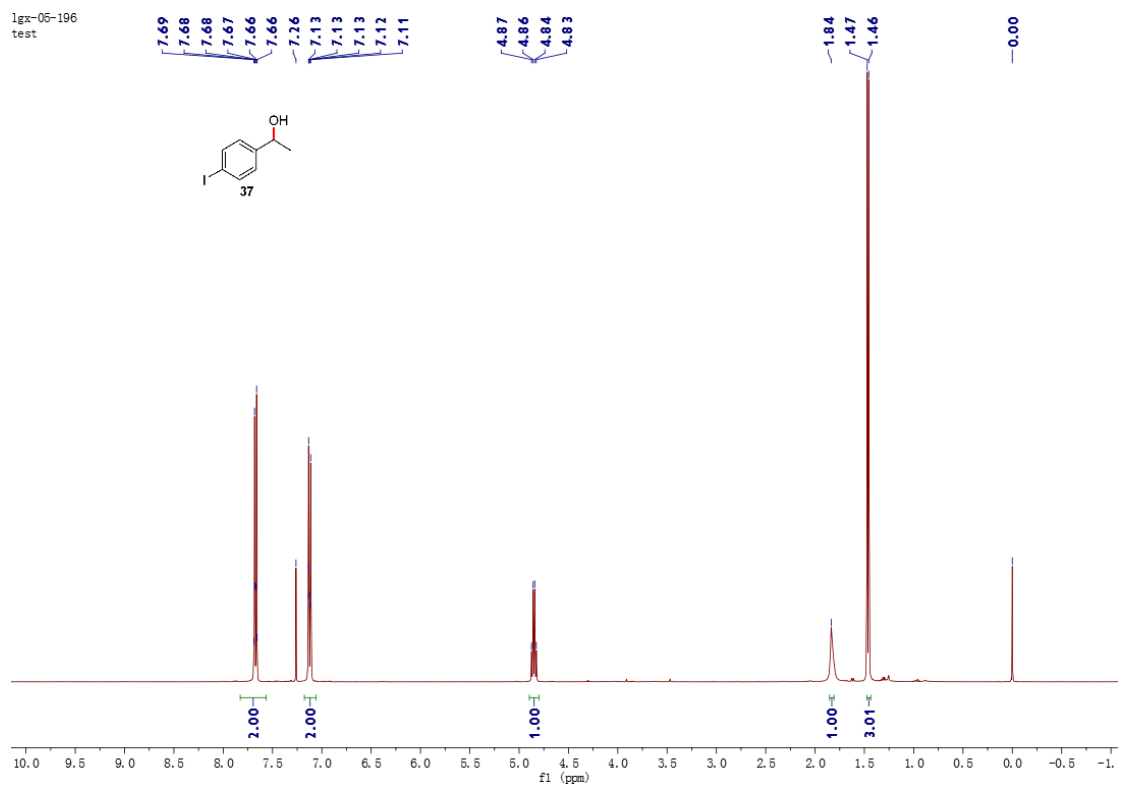
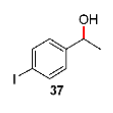
lgx-05-196
test

7.69
7.68
7.68
7.67
7.66
7.66
7.26
7.13
7.13
7.13
7.12
7.11

4.87
4.86
4.84
4.83

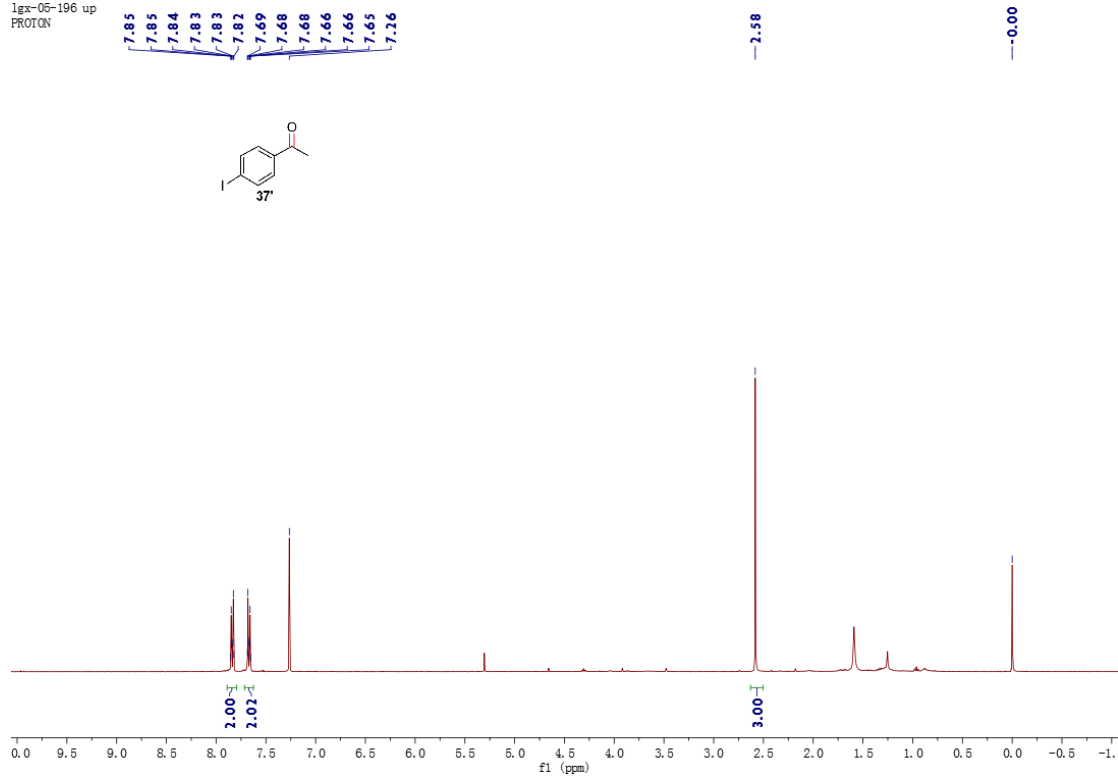
1.84
1.47
1.46

0.00



lgx-05-196 up
PROTON

7.85
7.85
7.84
7.83
7.83
7.82
7.69
7.68
7.68
7.66
7.66
7.65
7.16



lgx-05-191
test

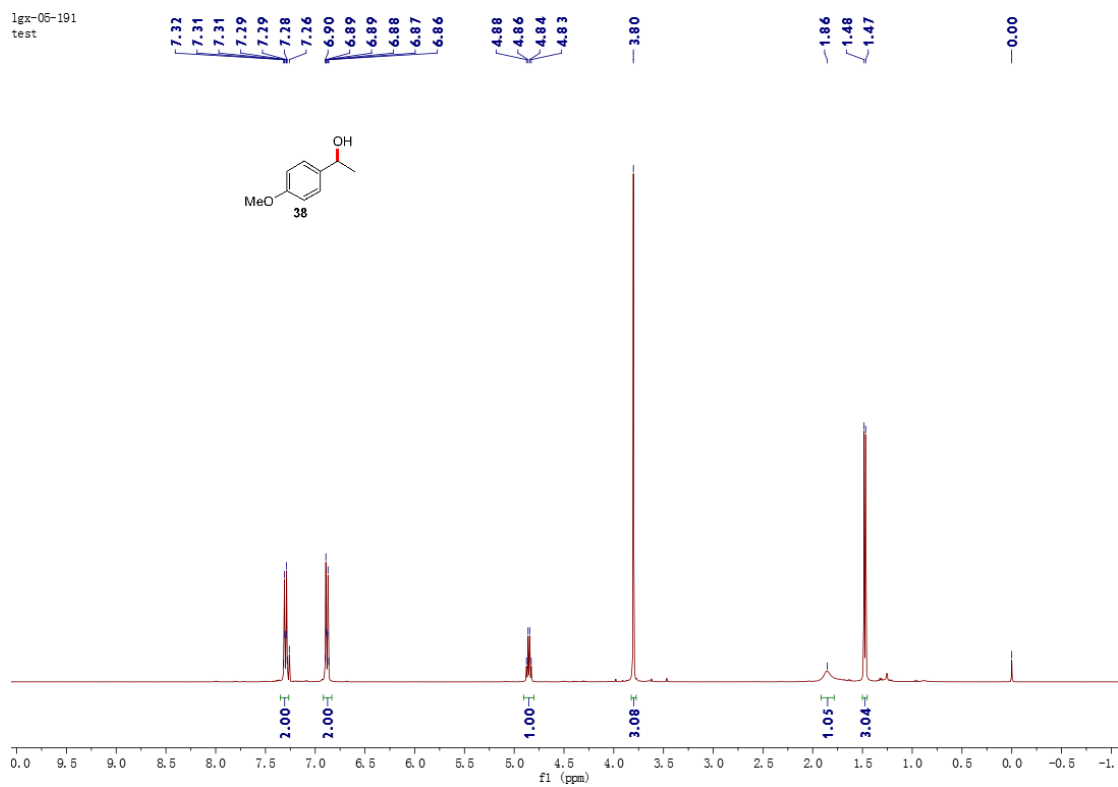
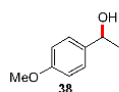
7.32
7.31
7.31
7.29
7.29
7.28
7.26
6.90
6.89
6.89
6.88
6.87
6.86

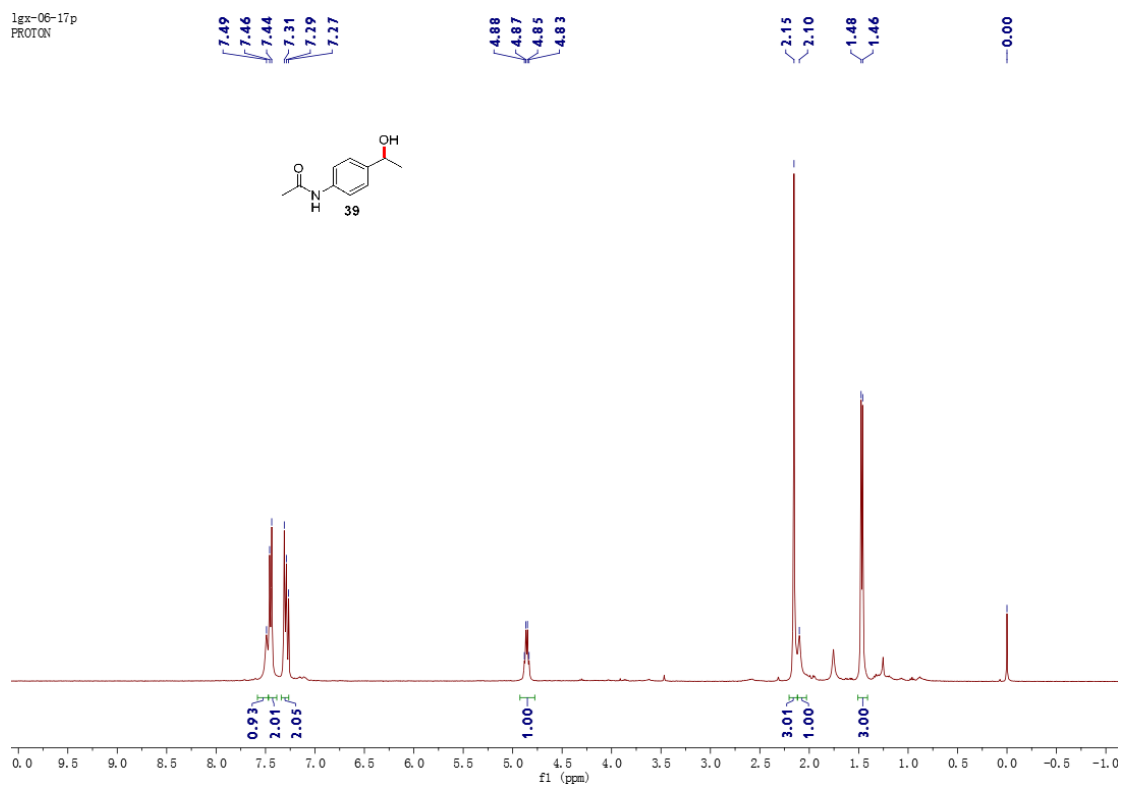
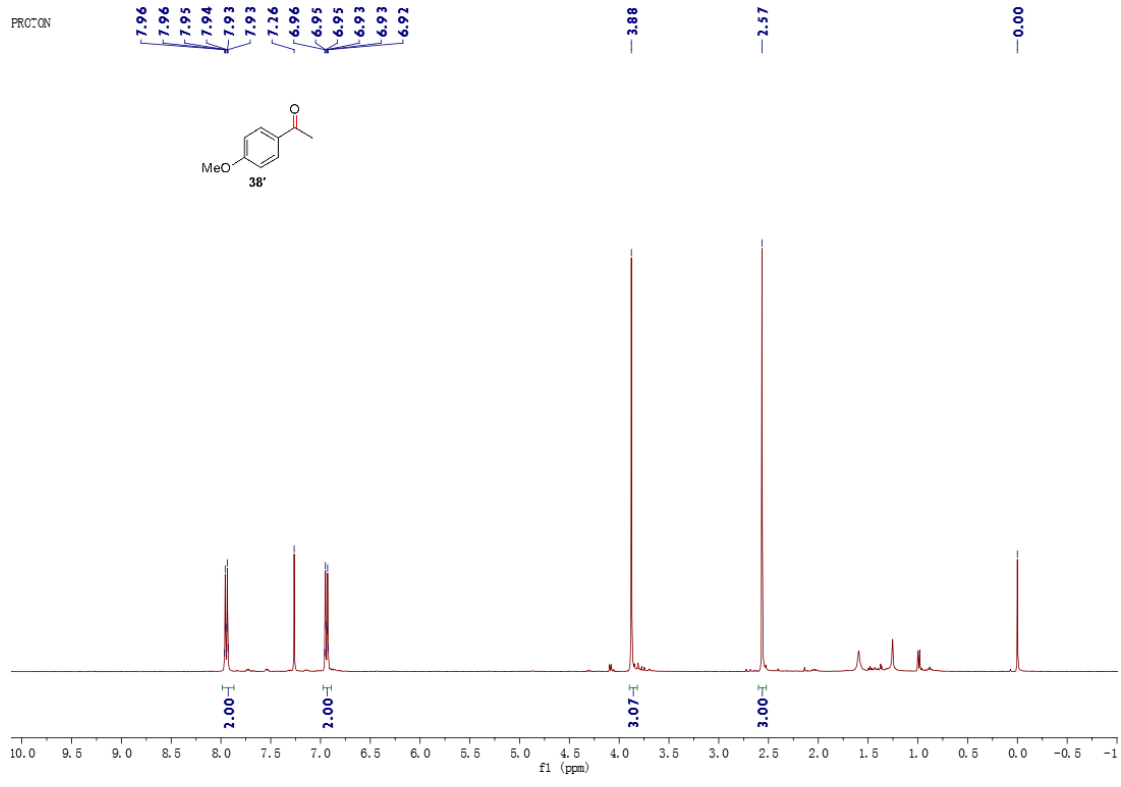
4.88
4.86
4.84
4.83

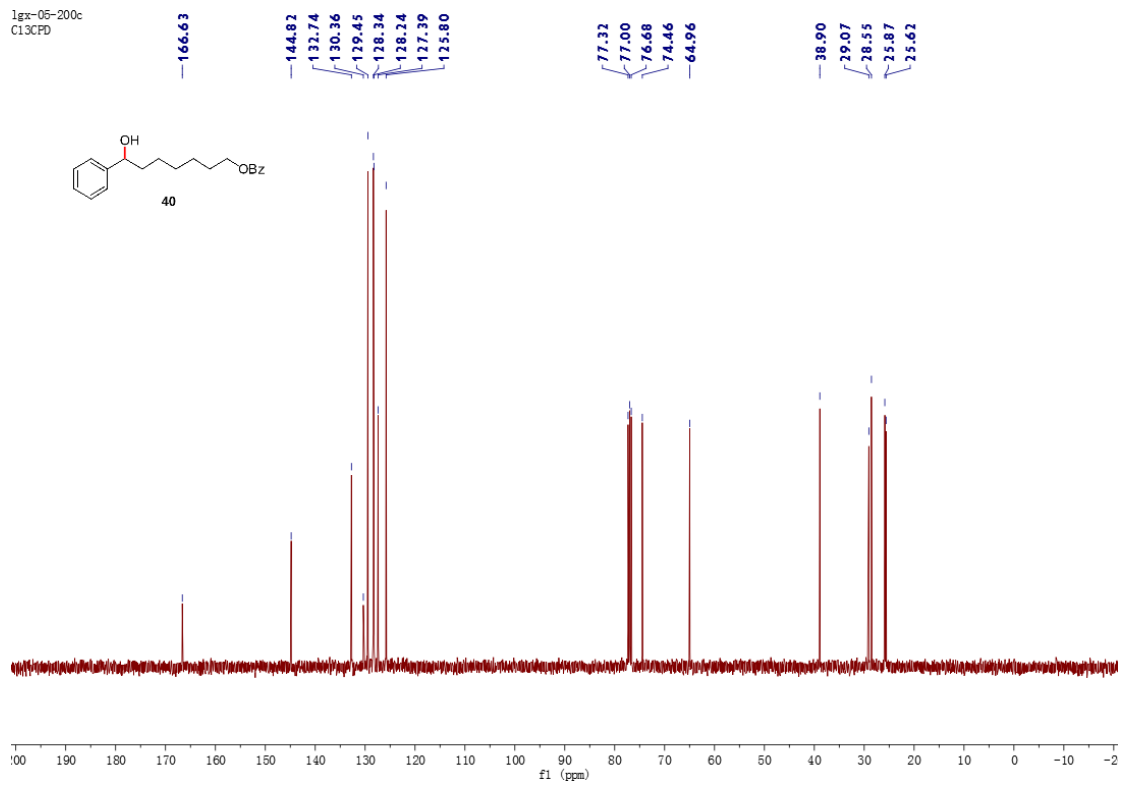
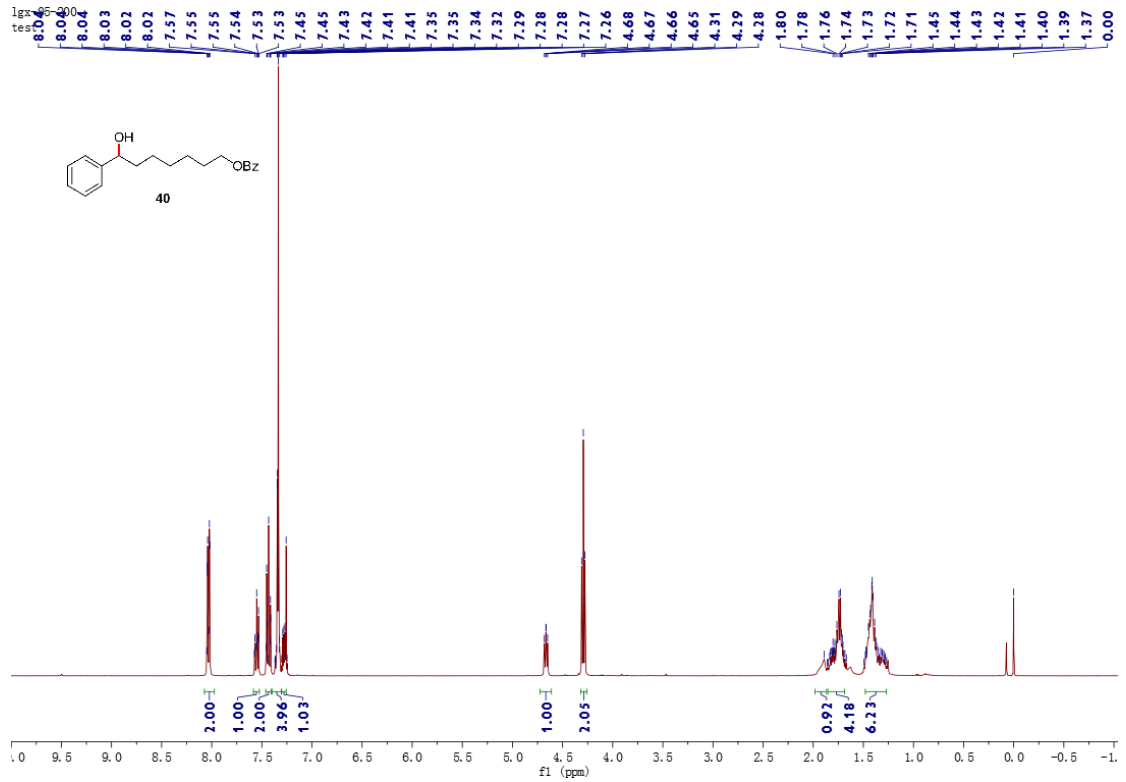
3.80

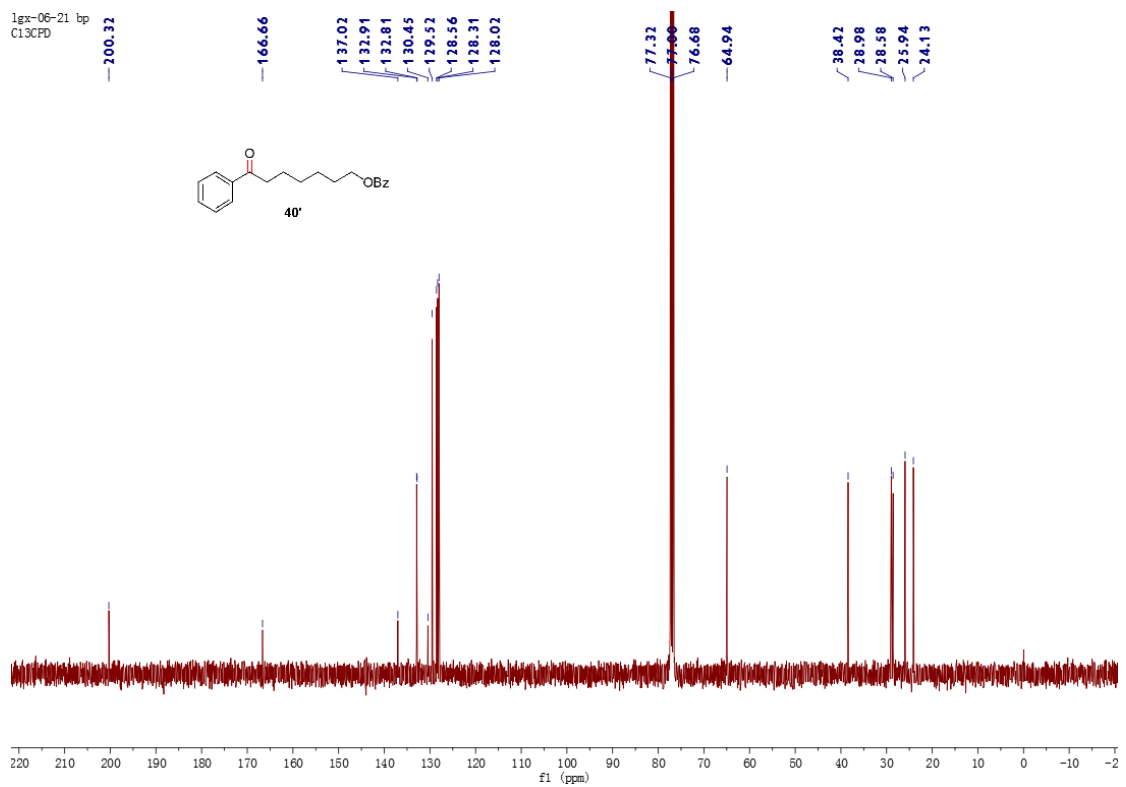
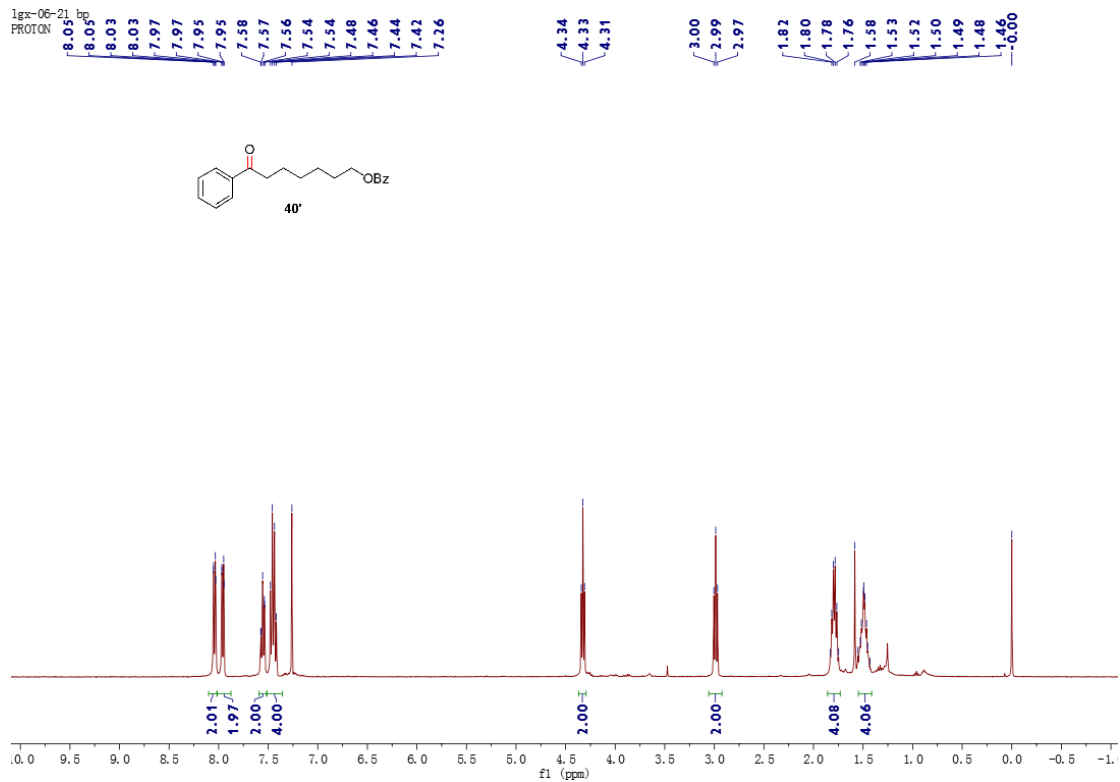
1.86
1.48
1.47

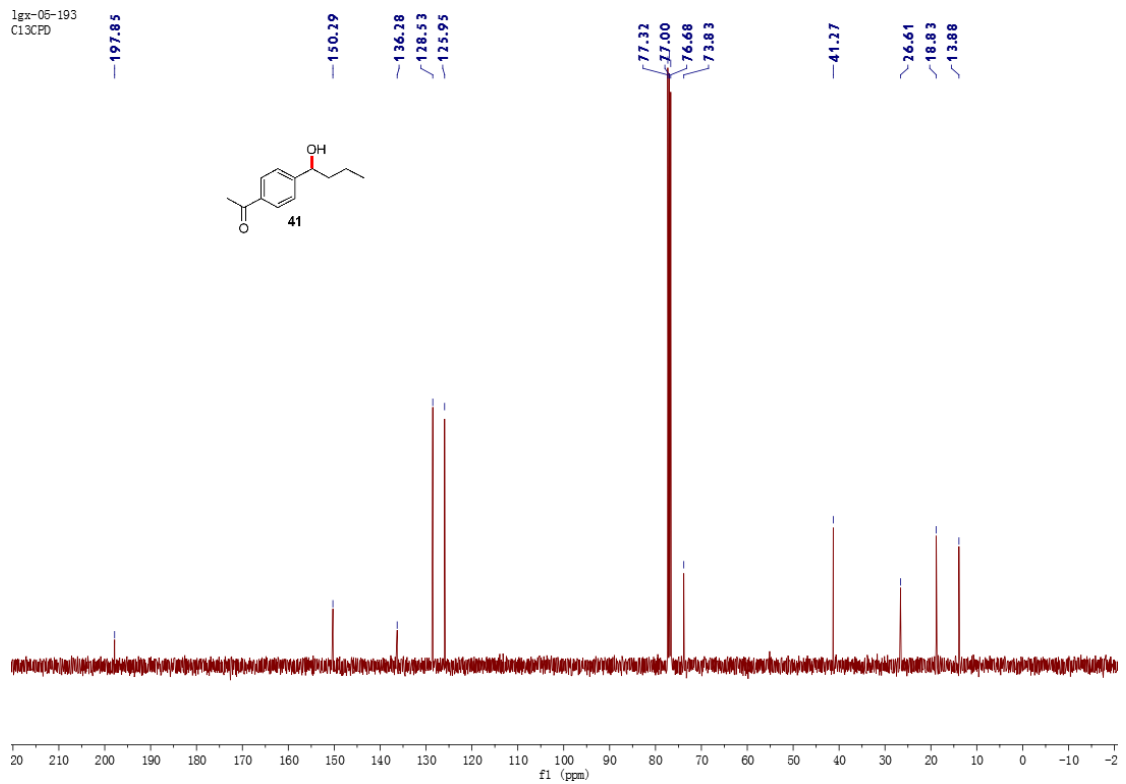
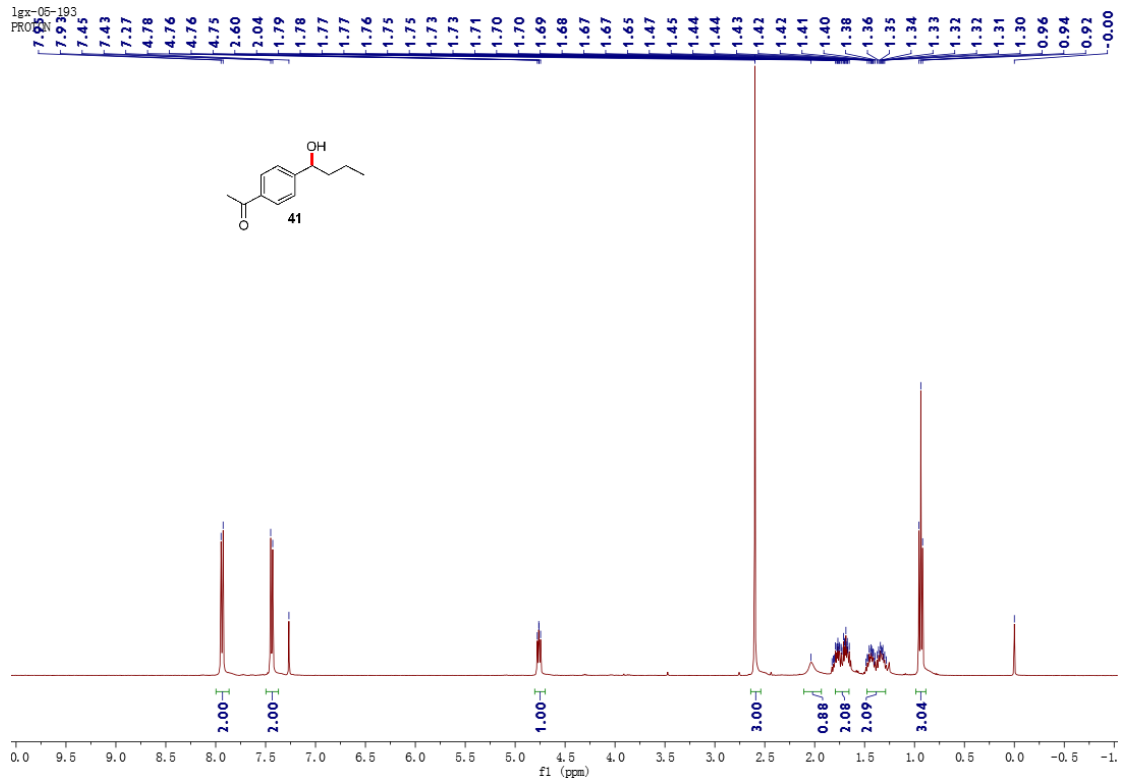
0.00



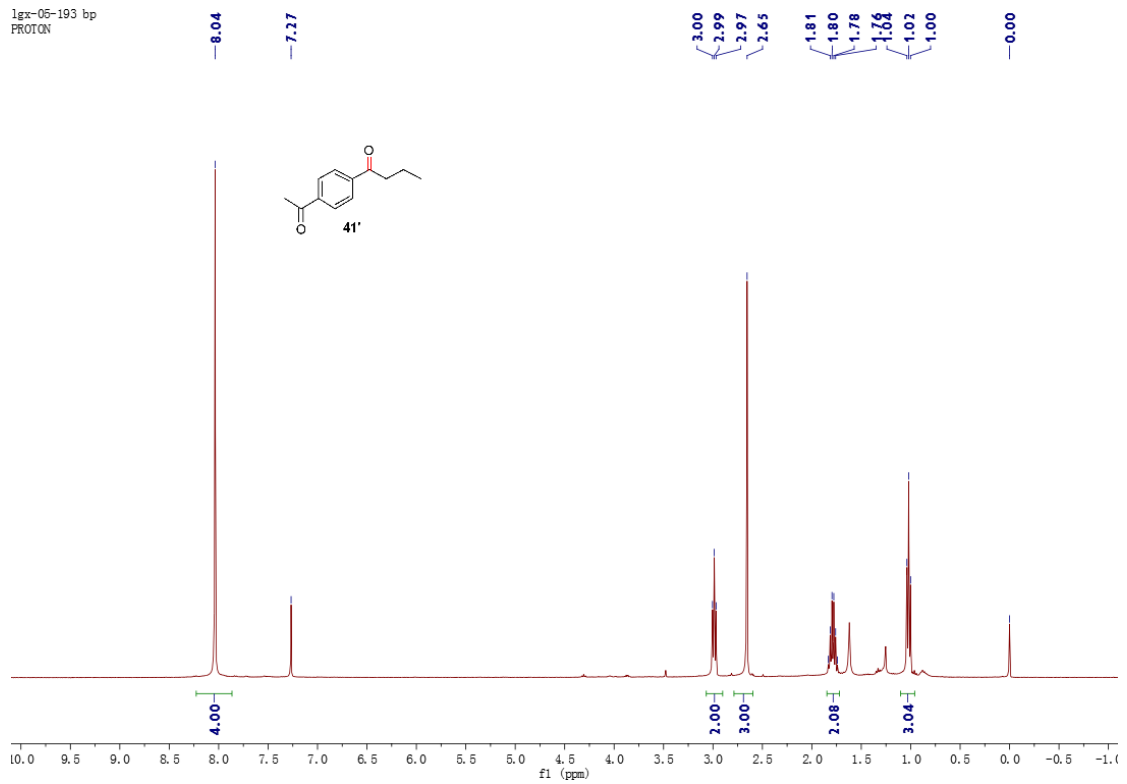




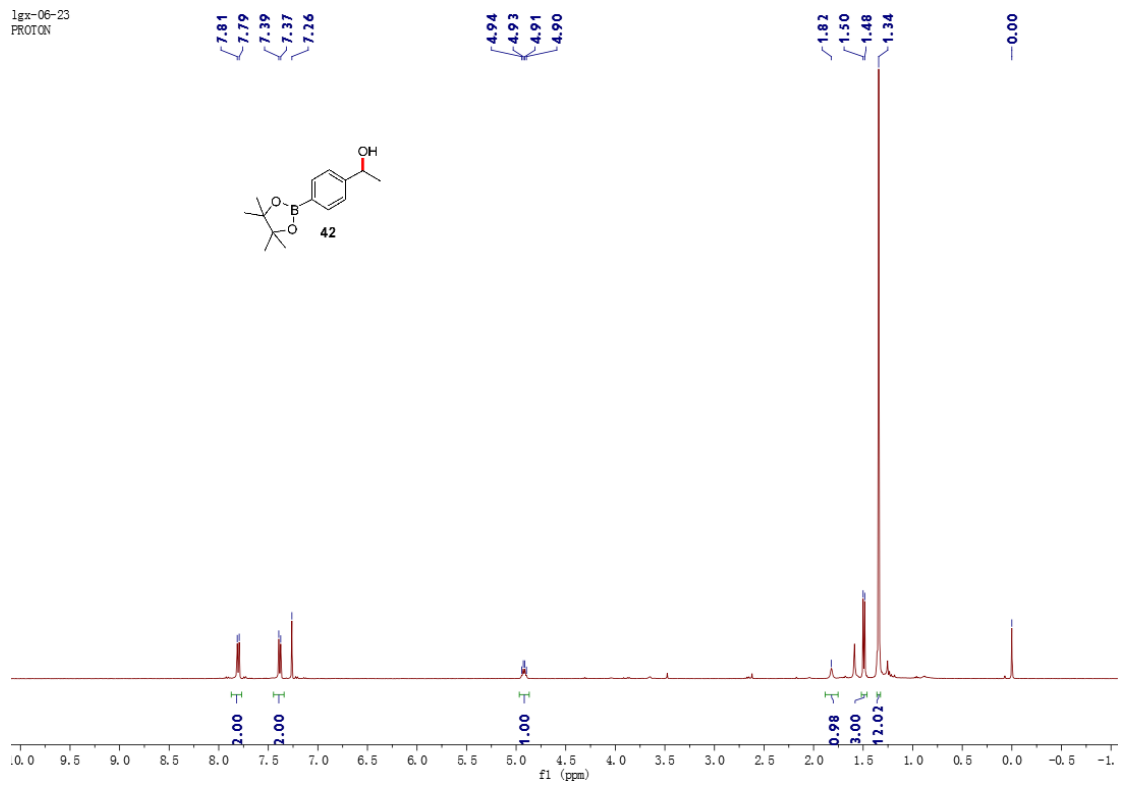




1gz-05-193 bp
PROTON



1gz-06-23
PROTON



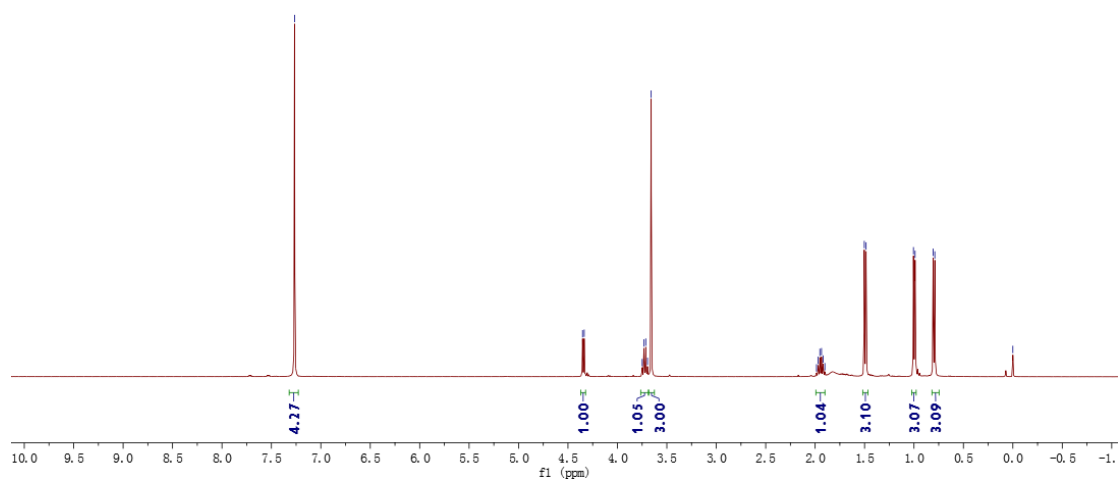
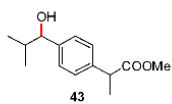
lgx-04-119-3
PROTON

7.27

4.35
4.34
3.75
3.73
3.71
3.70
3.66

1.97
1.95
1.94
1.92
1.90
1.50
1.48
1.01
0.99
0.81
0.79

0.00



lgx-05-181-bp
PROTON

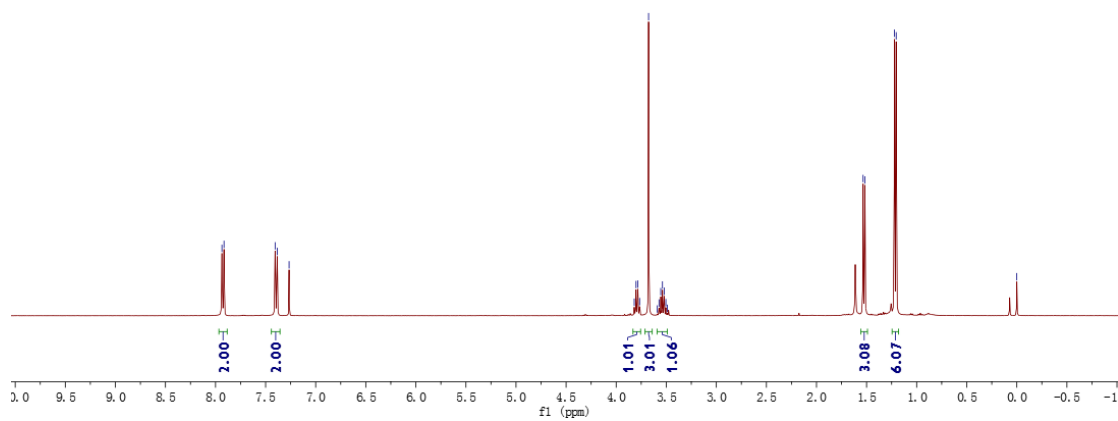
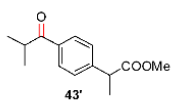
7.94
7.92

7.40
7.38
7.27

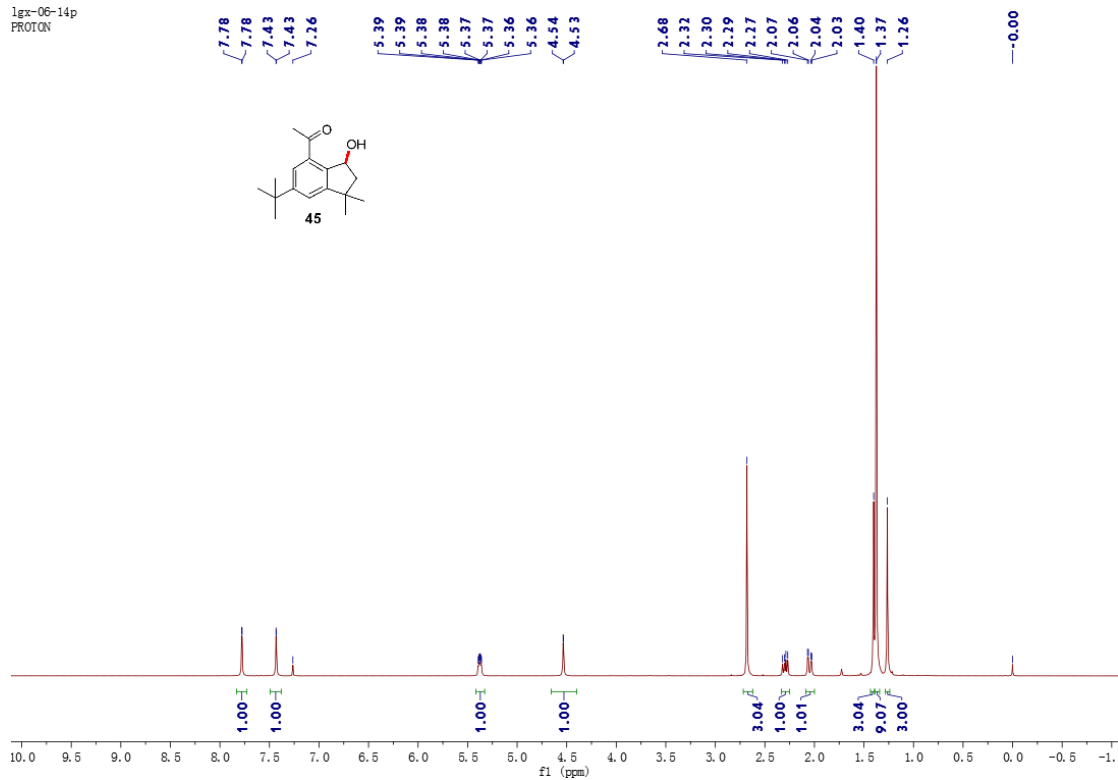
3.82
3.80
3.78
3.77
3.68
3.59
3.57
3.56
3.54
3.52
3.50
3.49

1.53
1.52
1.22
1.20

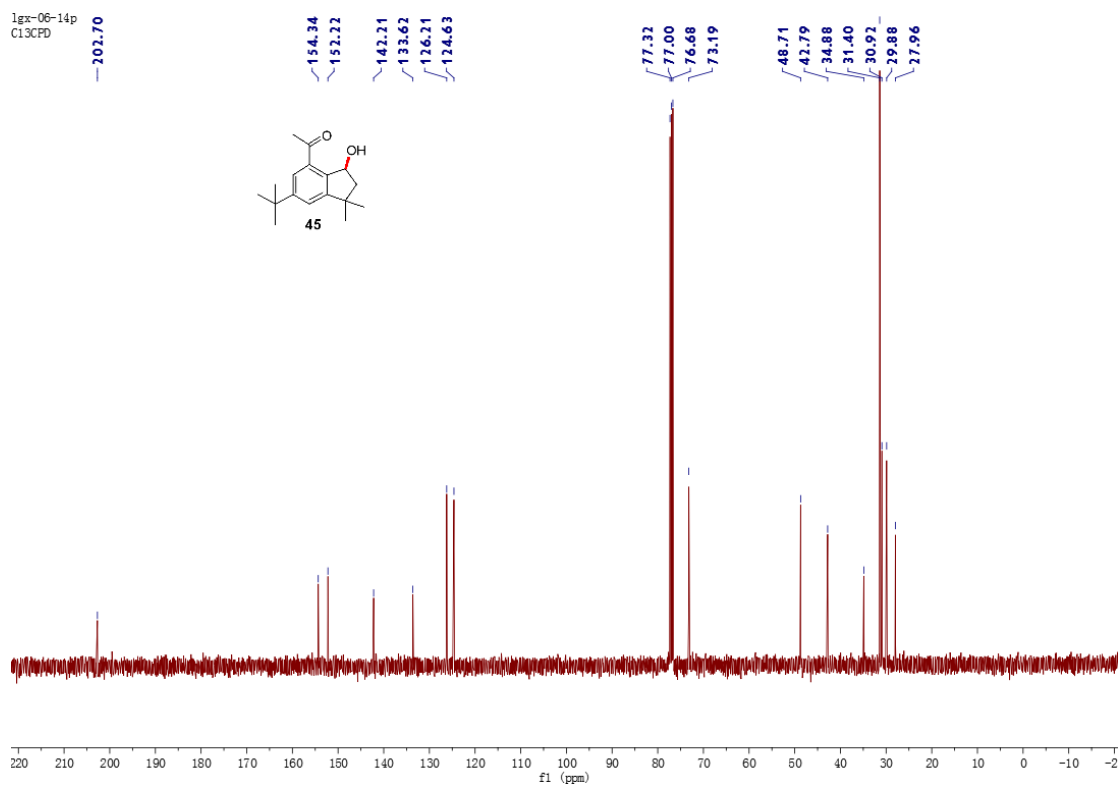
0.00

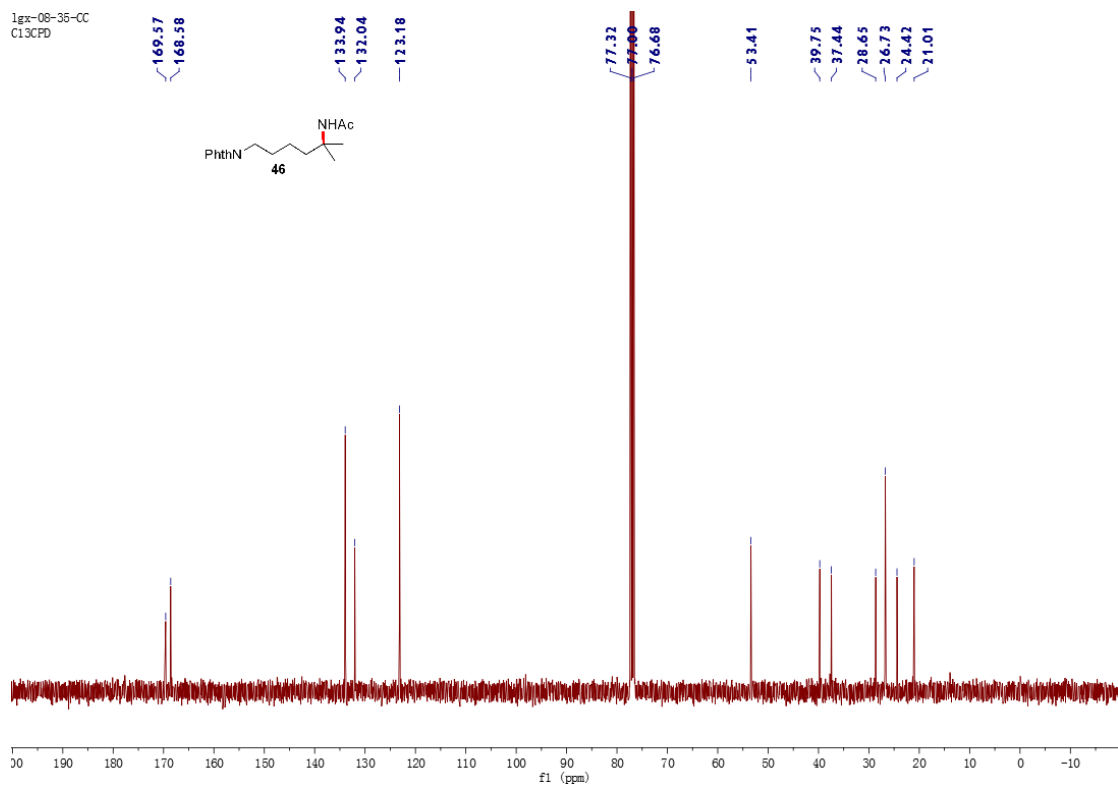
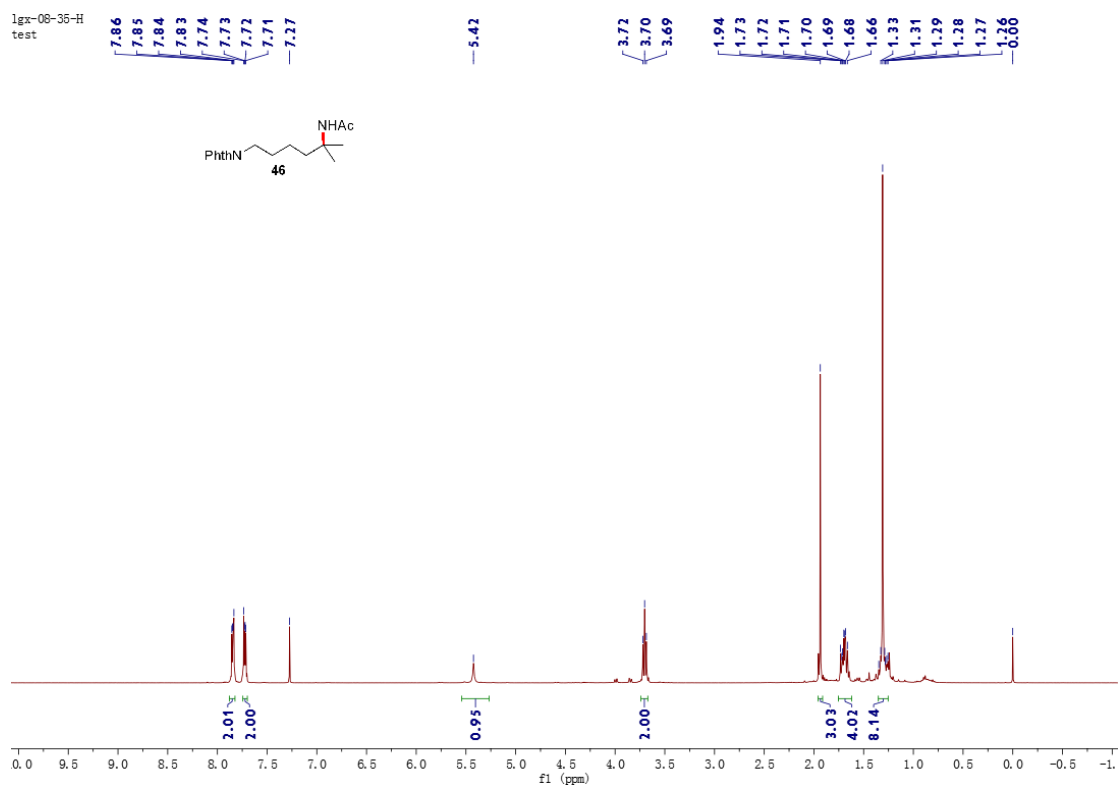


lgx-06-14p
PROTON

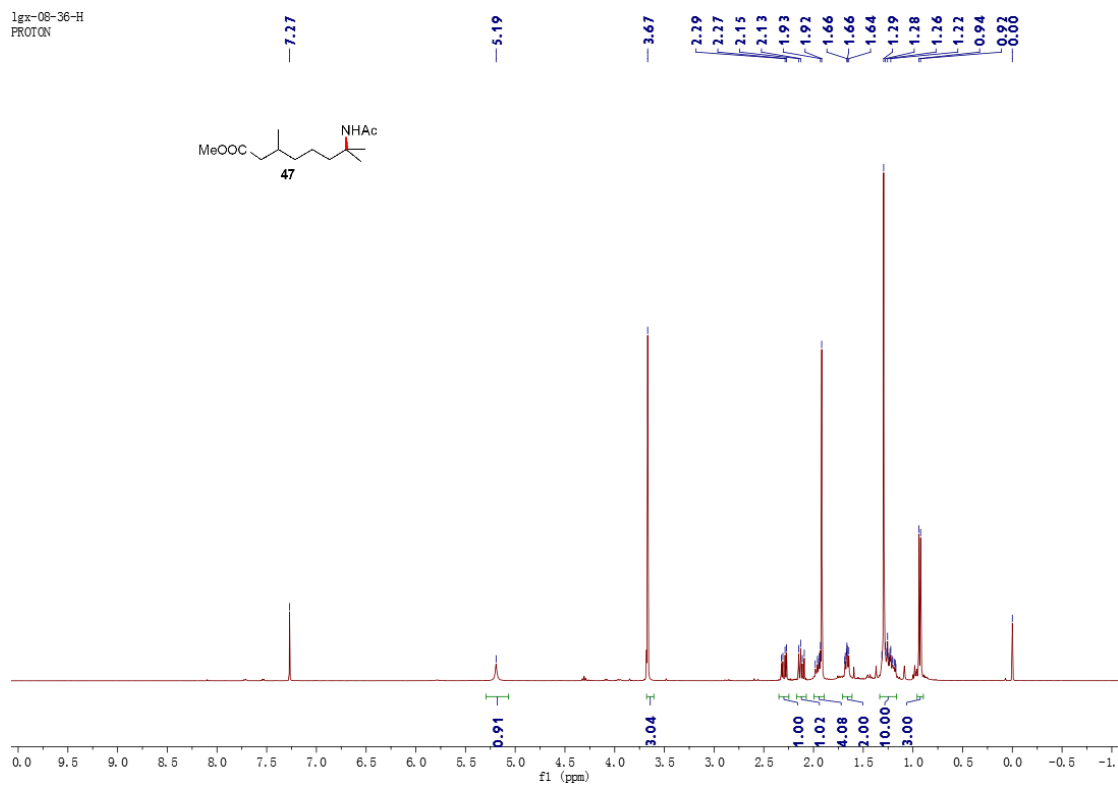


lgx-06-14p
C13CPD

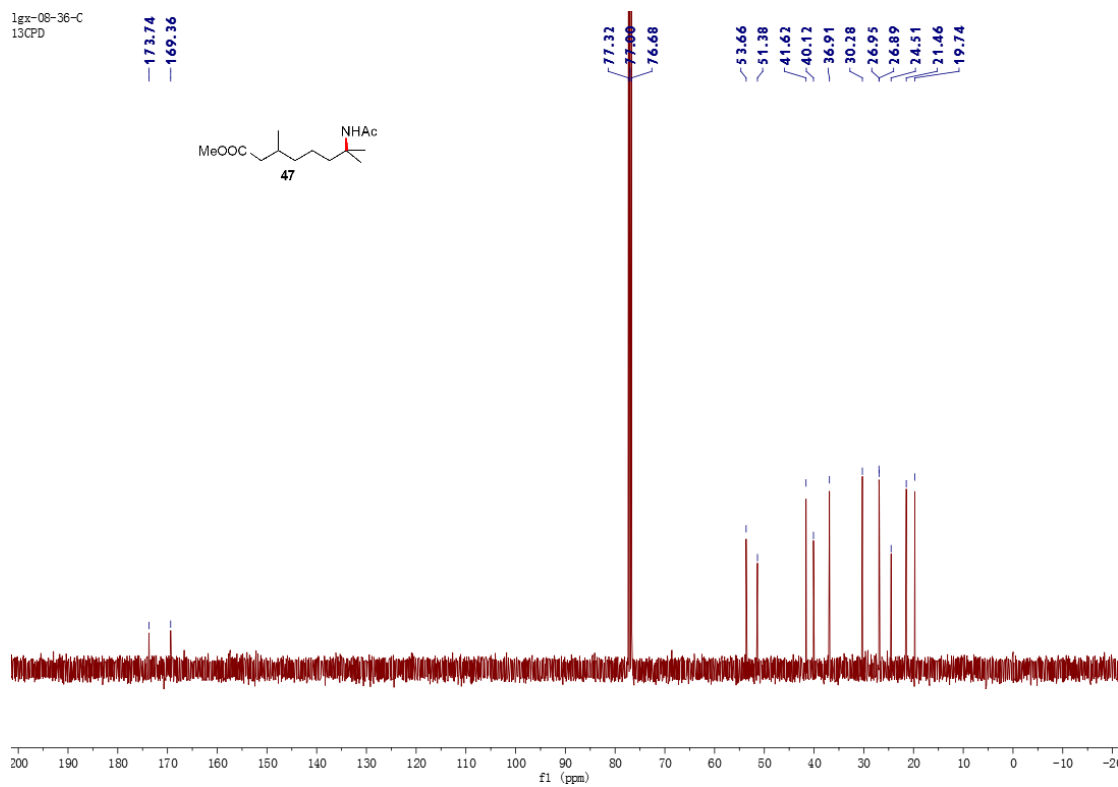




1gx-08-36-H
PROTON



1gx-08-36-C
13CPD



lgx-08-19-AM-H
test

7.77
7.76
7.75
7.74
7.74
7.73
7.70
7.69
7.68
7.67
7.66
7.37

5.28

2.61

2.14

1.92

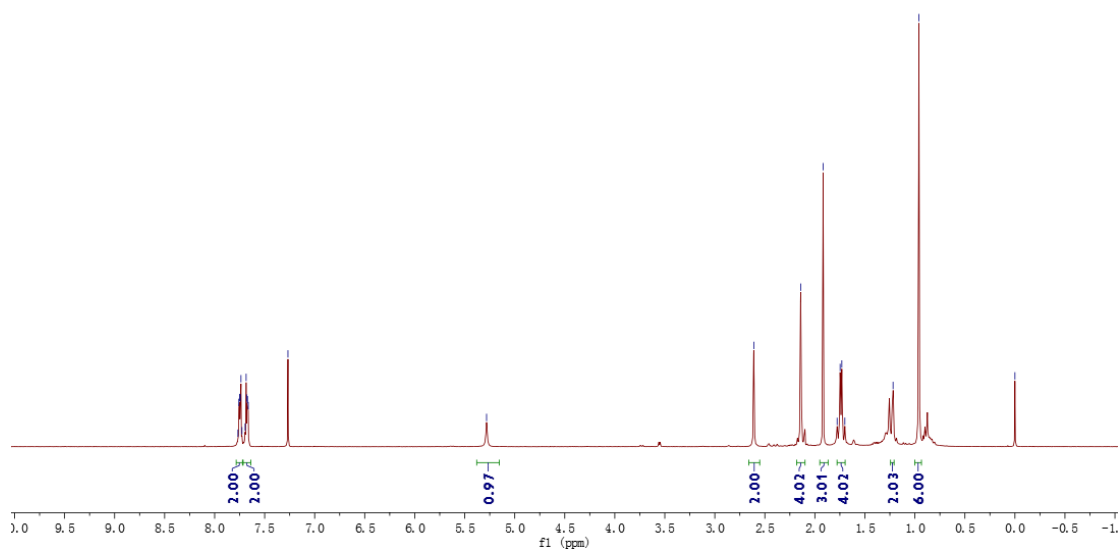
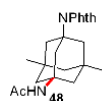
1.75

1.73

1.59

0.96

0.00



lgx-08-19-AM-C
13CPD

169.56
169.37

133.79
131.77

122.60

77.32
77.00
76.68

61.73

54.29

49.23

46.27

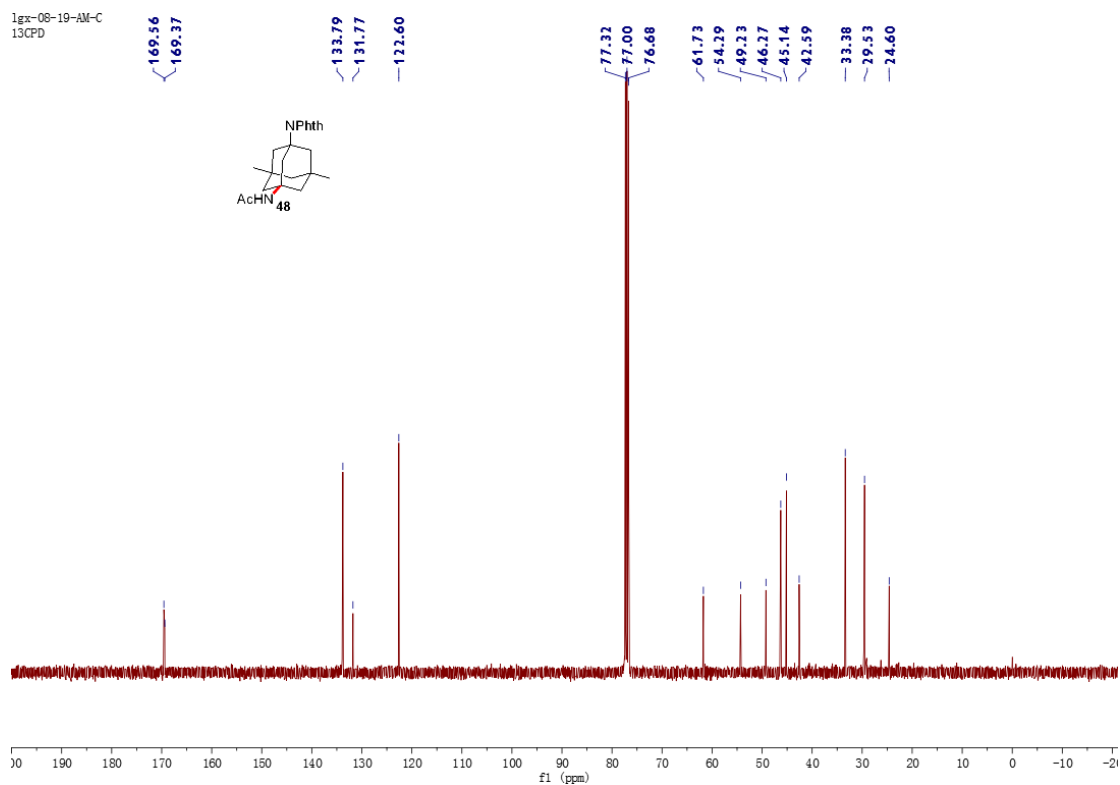
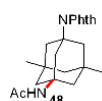
45.14

41.59

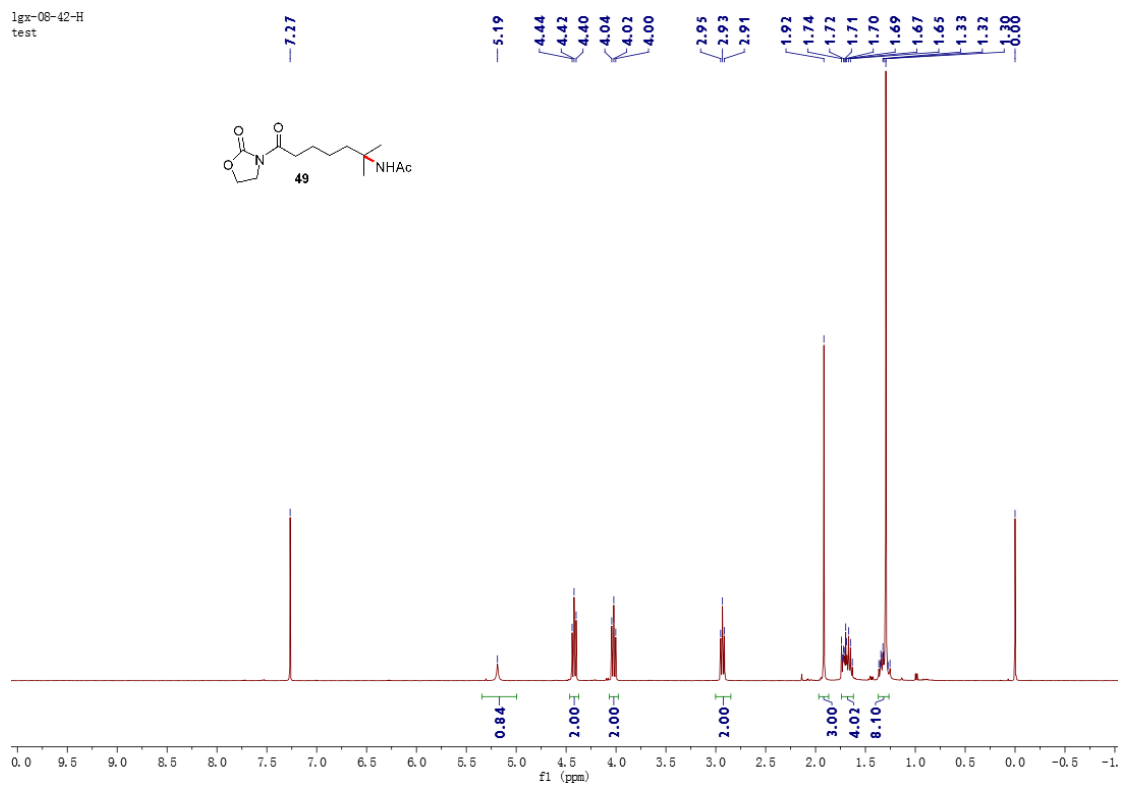
33.38

29.53

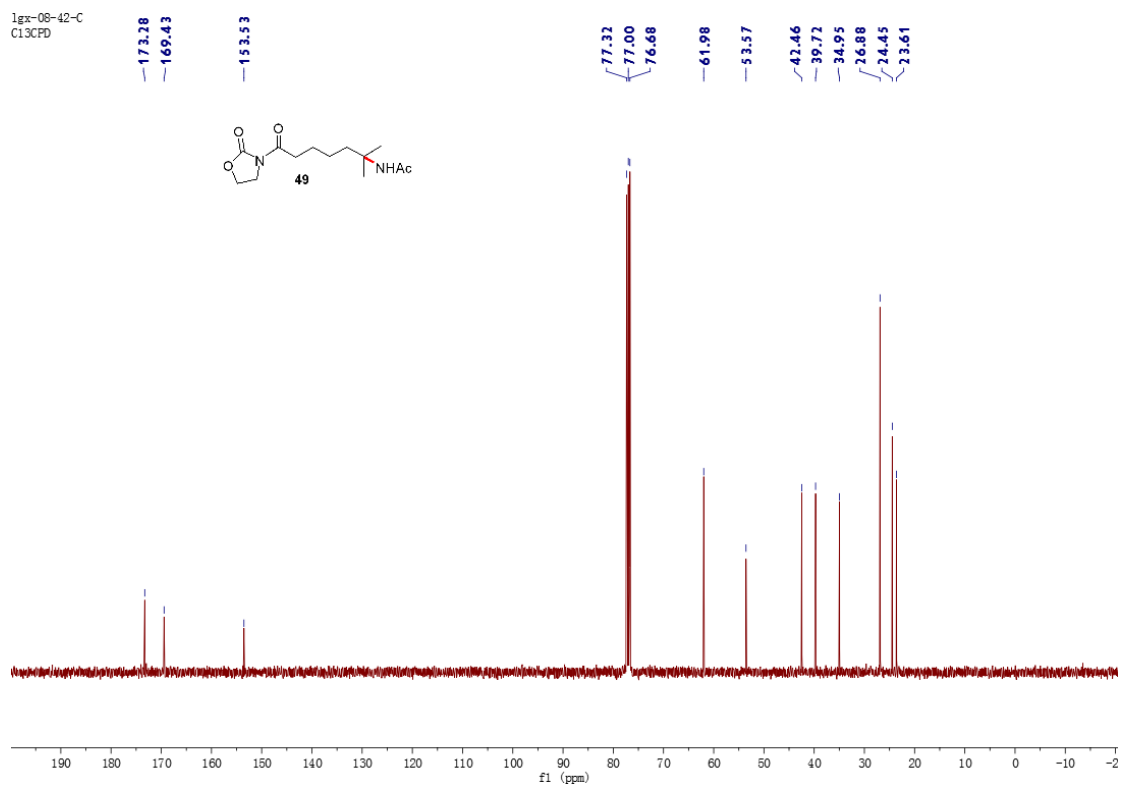
24.60



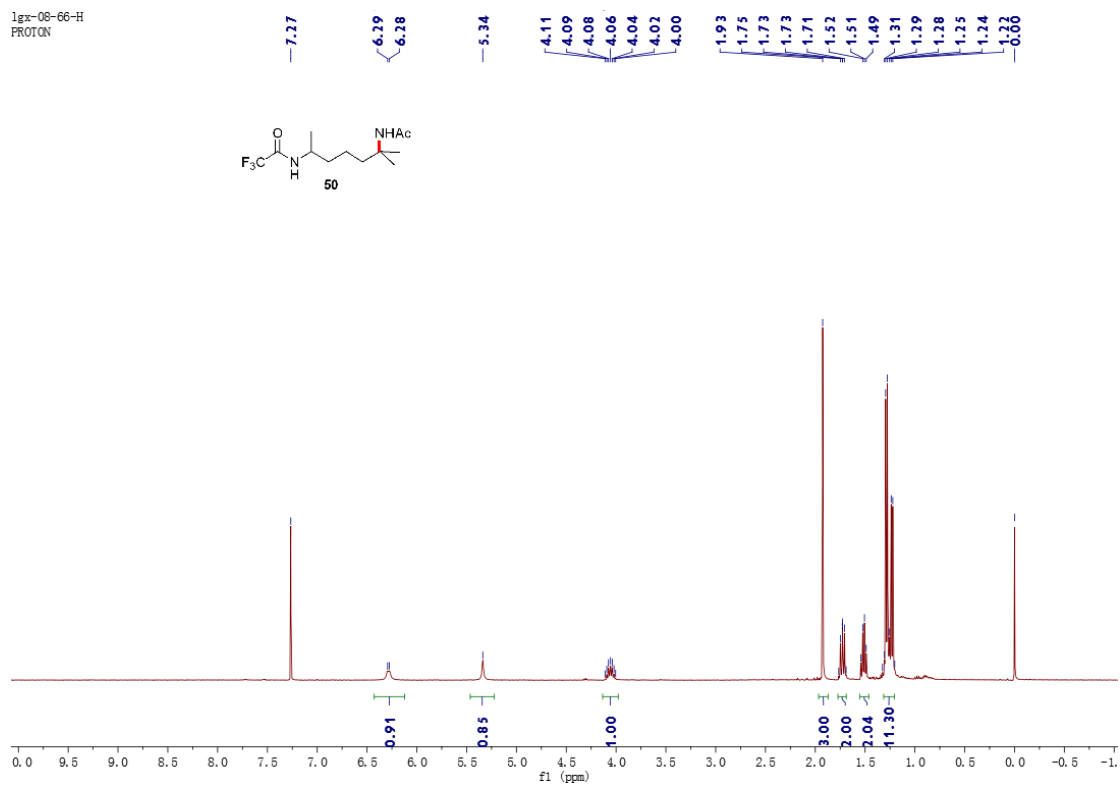
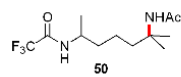
lgx-08-42-H
test



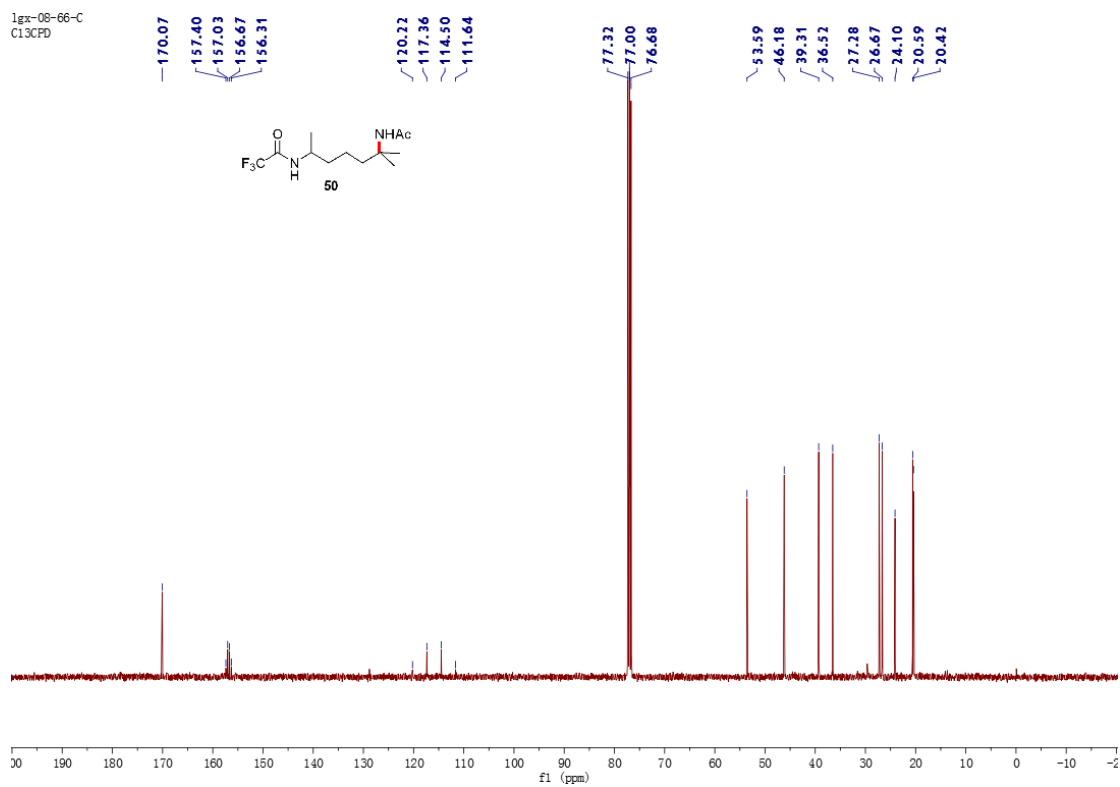
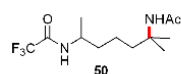
lgx-08-42-C
C13CPD



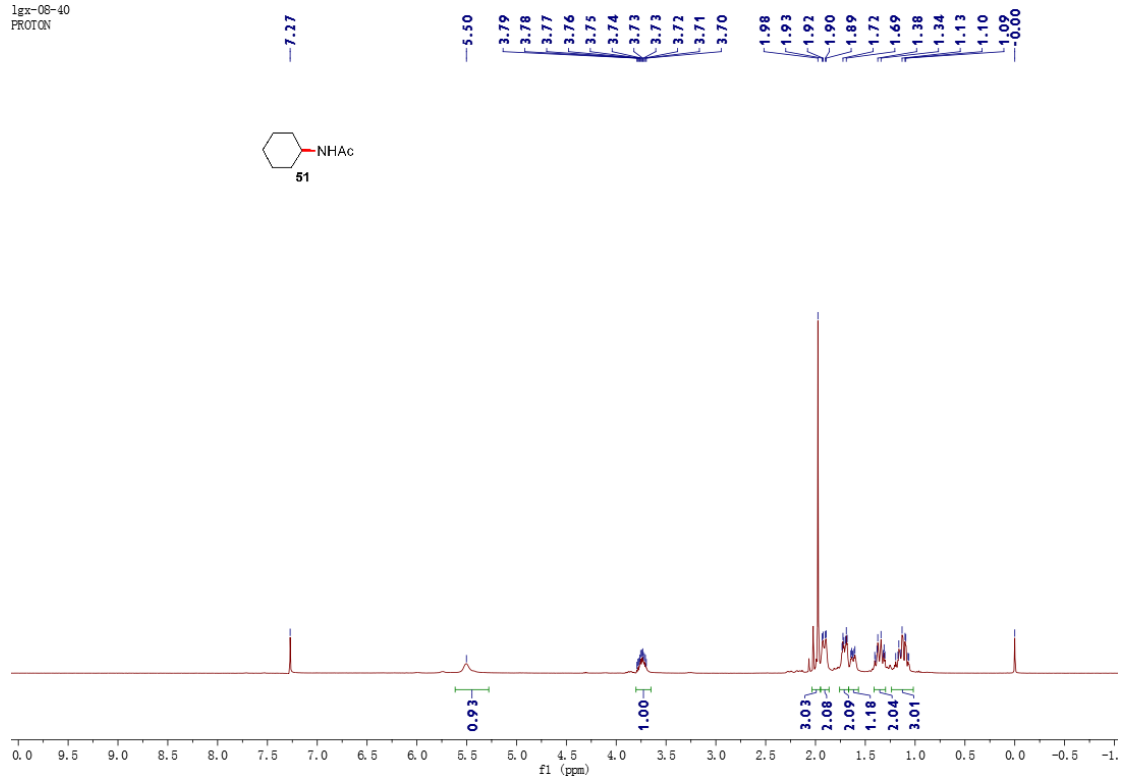
1gx-08-66-H
PROTON



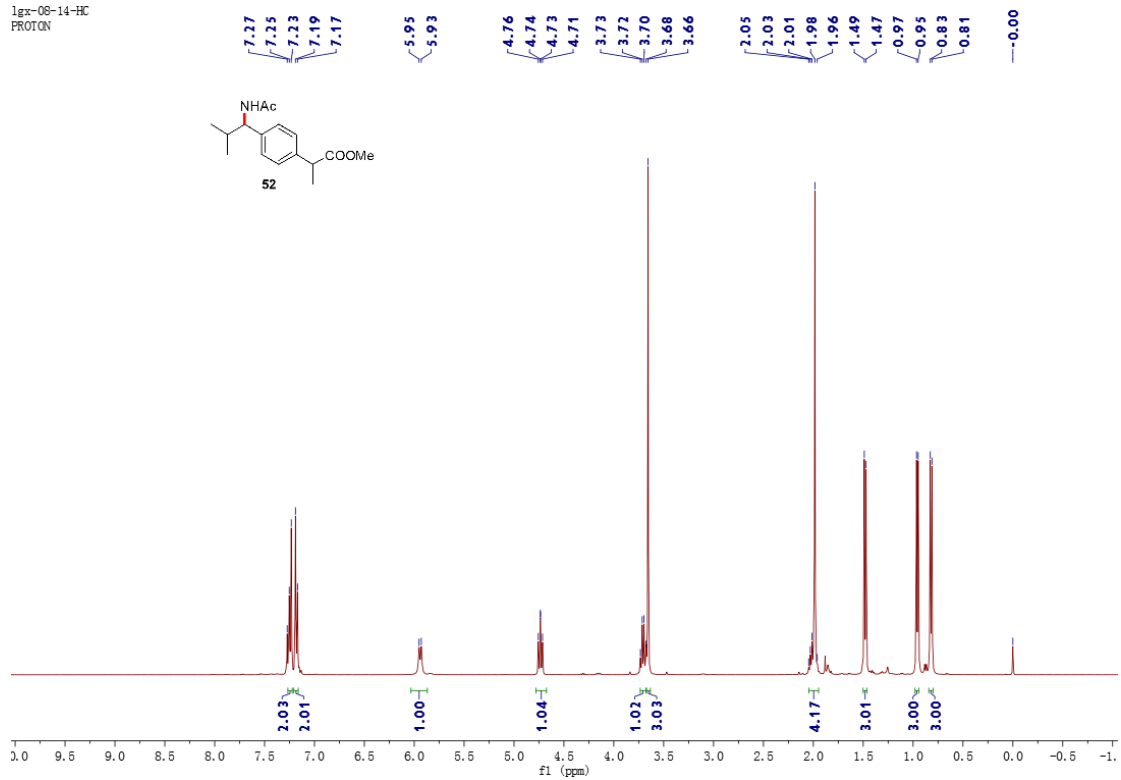
1gx-08-66-C
C13CPD



lgx-08-40
PROTON



lgx-08-14-HC
PROTON



lgx-08-14-C
C13CPD

174.99
174.95
169.29

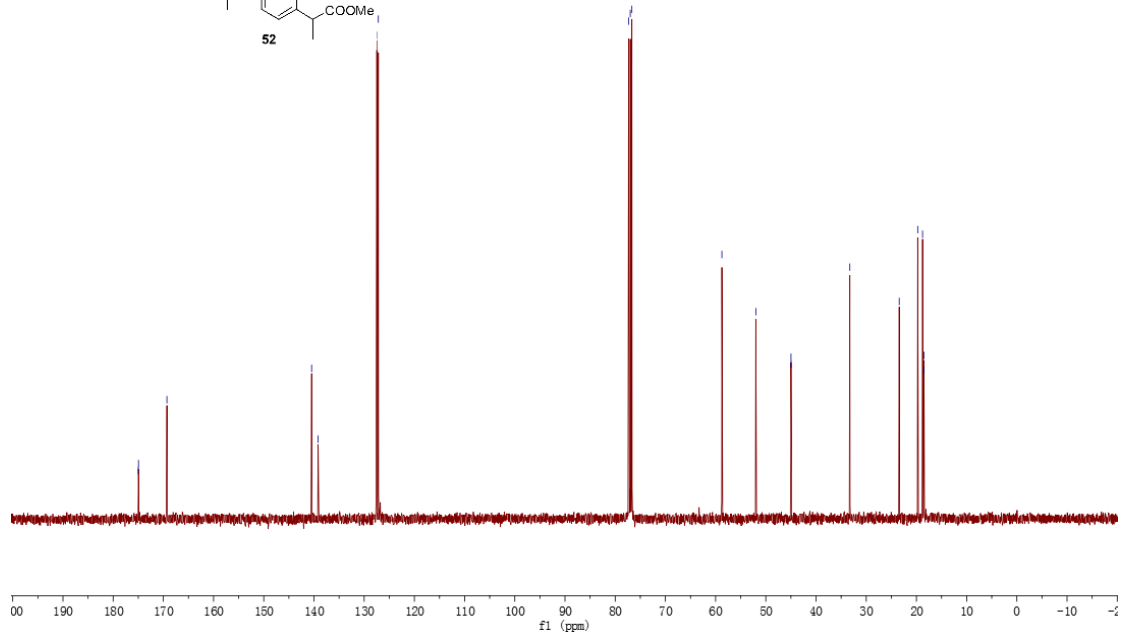
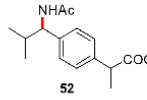
140.47
139.18

127.49
127.18

77.32
77.00
76.68

58.75
51.99
44.98
44.96

33.27
23.43
19.75
18.78
18.53
18.50



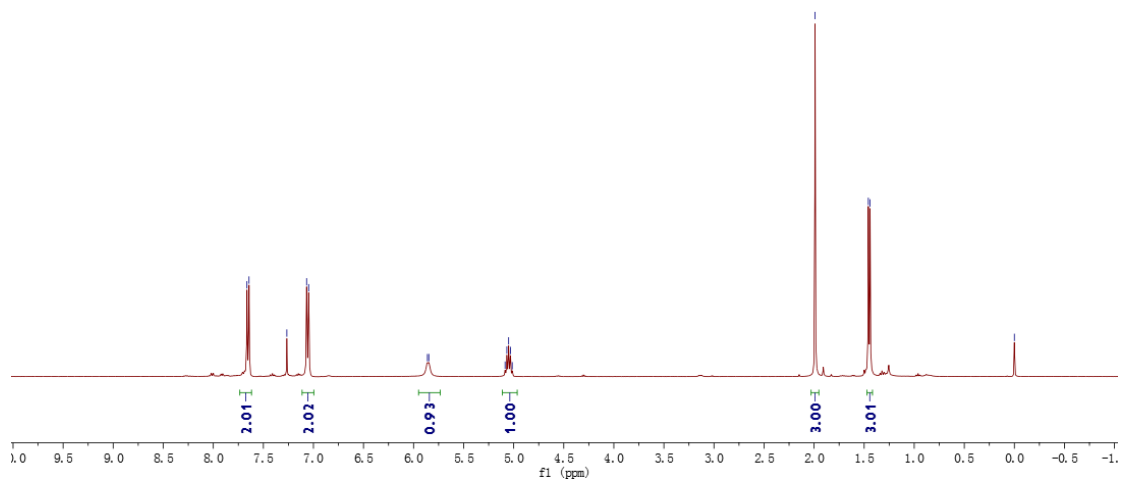
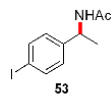
lgx-08-16-HC
PROTON

7.66
7.64
7.27
7.07
7.05

5.86
5.85
5.09
5.07
5.05
5.03
5.01

1.99
1.46
1.44

0.00



lgx-08-16-HC-c
C13CPD

169.48

142.80

137.67

128.16

92.68

77.32

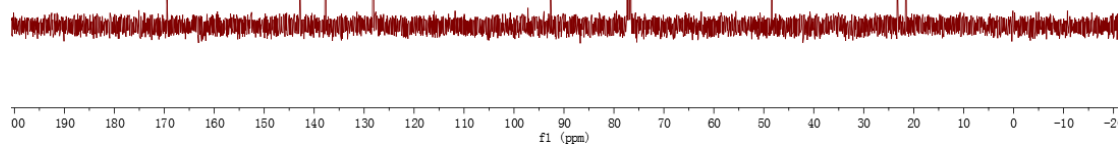
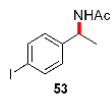
77.00

76.68

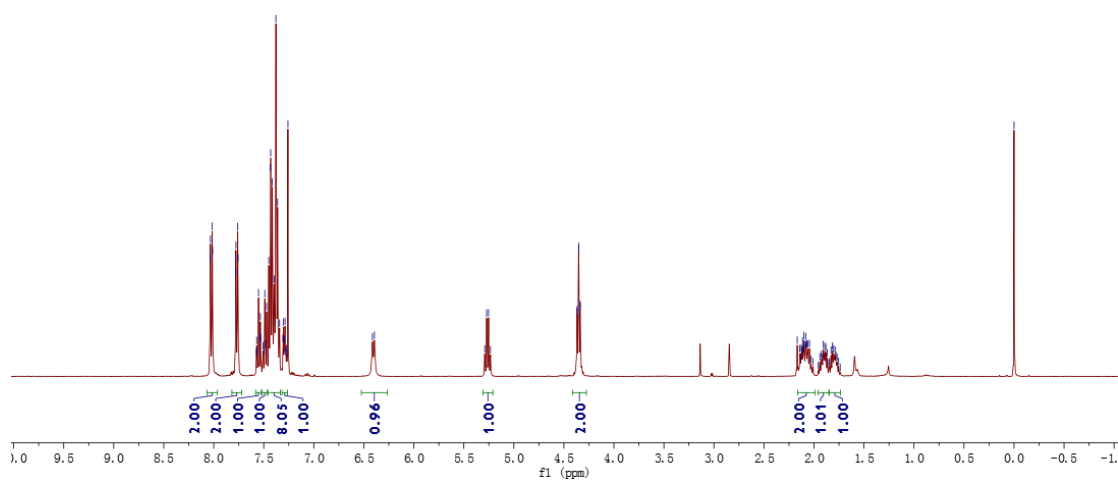
48.43

23.29

21.55



lgx-08-55-H
8.04
8.03
8.01
7.78
7.76
7.76
7.57
7.55
7.54
7.53
7.53
7.49
7.48
7.47
7.45
7.43
7.43
7.41
7.40
7.38
7.36
7.34
7.31
7.30
7.29
7.26
6.41
6.39
5.27
5.25
4.37
4.35
4.35
4.34
4.34
2.17
2.11
2.10
2.10
2.08
2.08
2.07
2.06
2.04
1.91
-0.00



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13CPD

166.77
166.55
141.74
134.43
132.88
131.47
130.19
129.51
128.82
128.50
128.31
127.62
126.92
126.62
77.32
77.00
76.68
64.48
53.66
32.55
25.85

