

Supporting Information

Photoredox-Mediated Minisci C-H Alkylation of *N*-Heteroarenes Using Boronic Acids and Hypervalent Iodine

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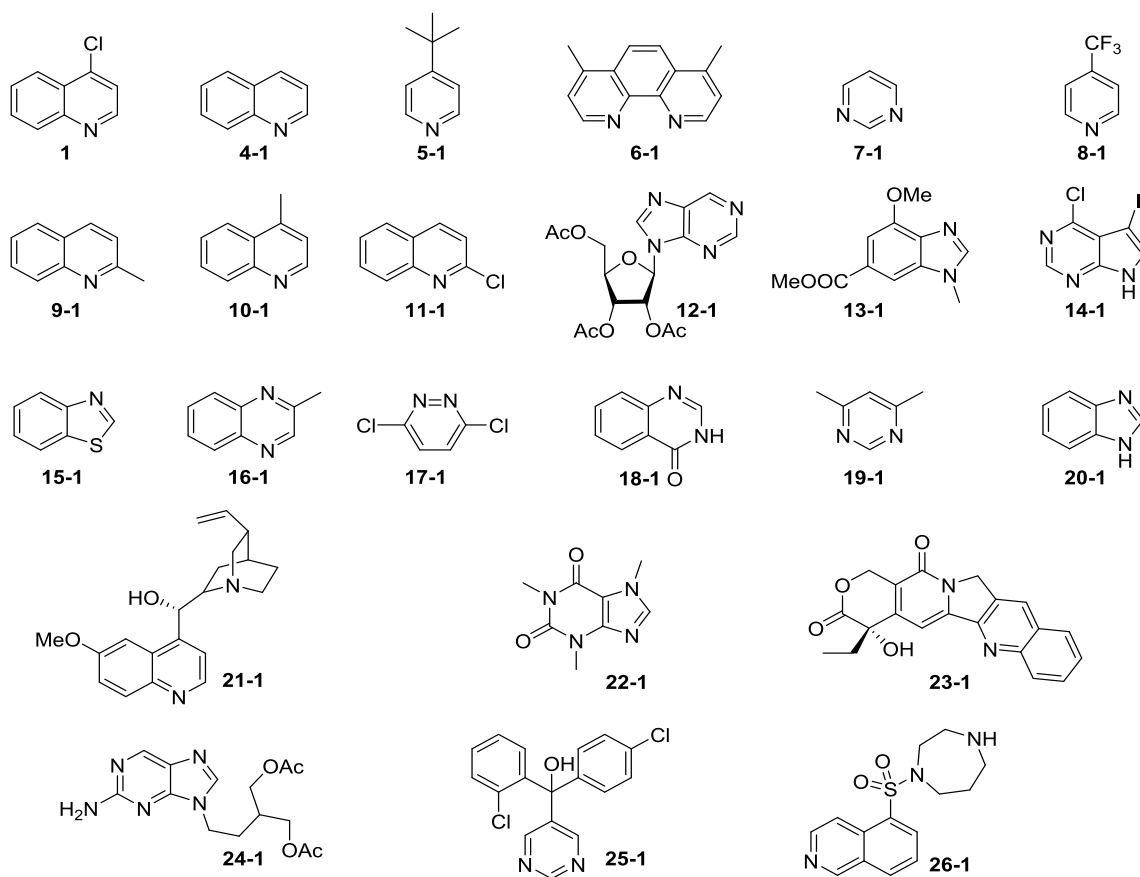
1. Reagents

All commercial materials were used as received unless otherwise noted. DCM was dried by distillation over CaH_2 . Anhydrous CH_3CN 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. Hydroxylbenziodoxole (BI-OH),¹ acetoxybenziodoxole (BI-OAc),¹ azidobenziodoxole (BI-N₃)¹, methoxylbenziodoxole (BI-OMe),² chlorobenziodoxole (BI-Cl)³ were synthesized according to reported procedures and used as freshly prepared. $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (98%, $\text{Ru} > 15.75\%$, Energy Chemical) and HFIP (99.0%, J&K Chemical) were used as received.

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 CDCl_3 ($\delta = 77.00$) for ^{13}C 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 4 mL glass vial (Thermo SCIENTIFIC National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with PTEF cap on bench top.

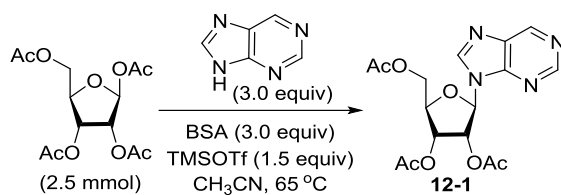
3. Synthesis of *N*-heteroaromatic substrates



Scheme S1. List of all *N*-heteroaromatic substrates used in this study

Compounds **1**, **4-1**, **5-1**, **6-1**, **7-1**, **8-1**, **9-1**, **10-1**, **11-1**, **14-1**, **15-1**, **16-1**, **17-1**, **18-1**, **19-1**, **20-1**, **21-1**, **22-1**, **23-1**, **24-1**, **25-1**, **26-1** were commercial available and used as received.

3.1 Synthesis of **12-1**

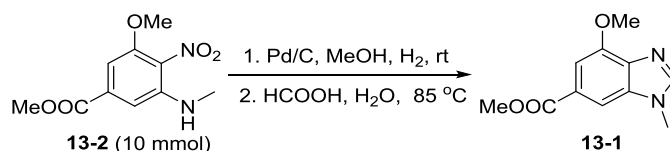


Scheme S2.

Compound **12-1** was prepared following a reported procedure⁴: 1,2,3,5-*O*-Tetracetyl- β -L-ribofuranose (800 mg, 2.5 mmol, 1.0 equiv) and purine (900 mg, 7.5 mmol, 3.0 equiv) were co-evaporated three times with anhydrous CH₃CN under argon. Then anhydrous CH₃CN (50 mL) and BSA (*N,O*-bis(trimethylsilyl)acetamide, 1.85 mL, 7.5 mmol, 3.0 equiv) were added

at room temperature. The mixture was stirred at 60-65 °C until all the base was dissolved. TMSOTf (435 µL, 3.75 mmol, 1.5 equiv) was added, and the resulting mixture was stirred overnight at 65 °C. After cooled to room temperature, the mixture was diluted with DCM (250 mL), washed with saturated aqueous NaHCO₃ solution (20 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 = 4:1) to afford **12-1** (473 mg, 50%) as a colorless oil. Spectra data are consistent with those reported in the literature.⁴

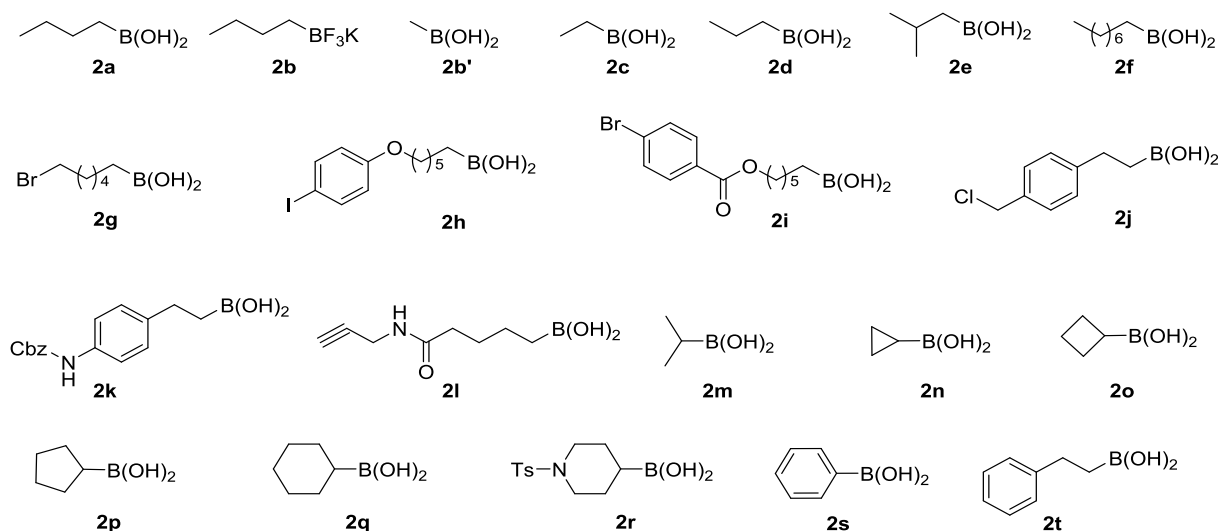
3.2 Synthesis of 13-1



Scheme S3.

To a solution of compound **13-2** (2.41 g, 10 mmol, 1.0 equiv) in anhydrous methanol (100 mL) was added 5% Pd/C (2.12 g). The mixture was stirred at room temperature under an atmosphere of H₂ (balloon) for 20 h then filtrated through a pad of Celite and washed with 20 mL of methanol. The filtrate was concentrated *in vacuo* and the residue was dissolved in a mixture of water (20 mL) and formic acid (20 mL). The solution was then heated at 85 °C for 12 h. After cooled to room temperature, the solvent was removed under reduced pressure. The residue was partitioned between EtOAc (150 mL) and saturated aqueous NaHCO₃ solution (50 mL). The organic layer was washed with brine, dried over Na₂SO₄ and filtrated. The filtrate was concentrated *in vacuo* and the resulting residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 4:1) to afford compound **13-1** (1.40 g, 63% for 2 steps) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.79 (s, 1H), 7.39 (s, 1H), 4.06 (s, 3H), 3.99 (s, 3H), 3.94 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.62, 147.08, 145.20, 145.12, 127.56, 124.77, 116.08, 104.24, 55.74, 52.11, 33.93; HRMS Calcd for C₁₁H₁₃N₂O₃ [M+H⁺]: 221.0926, Found: 221.0925.

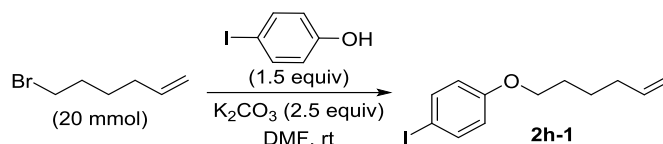
4. Synthesis of alkyl boronic acids



Scheme S4. List of all alkyl boronic acids used in this study

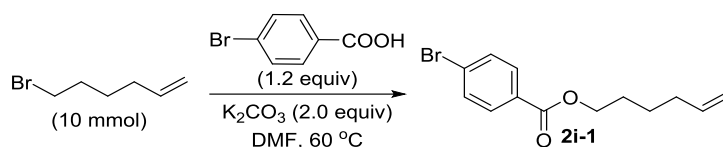
Compounds **2a**, **2b**, **2b'**, **2c**, **2d**, **2e**, **2f**, **2m**, **2n**, **2o**, **2p**, **2q**, **2s**, and **2t** were commercial available and used as received.

4.1 Synthesis of alkene substrates **2h-1**, **2i-1** and **2k-1**



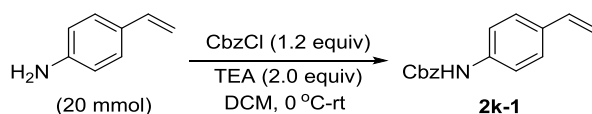
Scheme S5.

To a solution of 6-bromohex-1-ene (3.24 g, 20 mmol, 1.0 equiv) in DMF (30 mL) was added 4-iodophenol (6.60 g, 30 mmol, 1.5 equiv) and K_2CO_3 (7.46 g, 50 mmol, 2.5 equiv). The mixture was stirred at room temperature until 6-bromohex-1-ene was completely consumed monitoring by TLC. The reaction mixture was poured into brine (200 mL) and extracted with Et_2O (40 mL x 3). 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 = 5:95) to afford compound **2h-1** (5.22 g, 86%) as a colorless oil. Spectra data are consistent with those reported in the literature.⁵



Scheme S6.

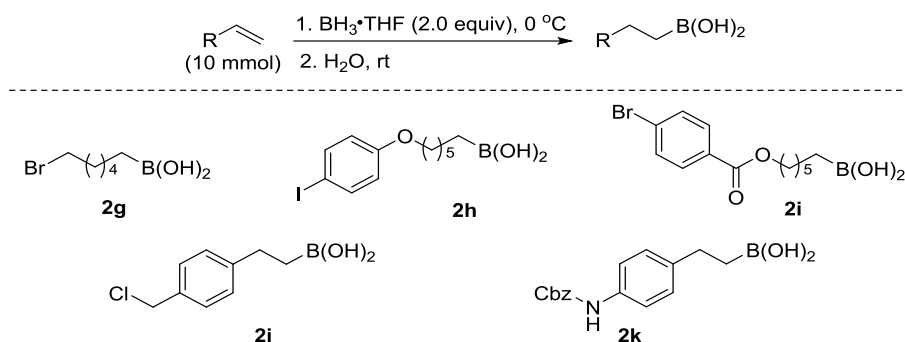
To a solution of 6-bromohex-1-ene (3.24 g, 20 mmol, 1.0 equiv) in DMF (30 mL) was added 4-bromobenzoic acid (4.84 g, 24 mmol, 1.2 equiv) and K_2CO_3 (5.53 g, 40 mmol, 2.0 equiv) at room temperature. Then the mixture was stirred at 60 °C until 6-bromohex-1-ene was completely consumed monitoring by TLC. After cooled to room temperature, the reaction mixture was poured into brine (200 mL) and extracted with Et_2O (40 mL x 3). 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 = 5:95) to afford compound **2h-1** (3.80 g, 67%) as a colorless oil. Spectra data are consistent with those reported in the literature.⁶



Scheme S7.

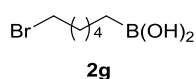
To a solution of 4-vinylaniline (2.39 g, 20 mmol, 1.0 equiv) and TEA (4.07g, 40 mmol, 2.0 equiv) in DCM (50 mL) was slowly added CbzCl (4.10 g, 24 mmol, 1.2 equiv) at 0 °C. After addition completed, the mixture was stirred at room temperature until 4-vinylaniline was completely consumed monitoring by TLC. The reaction mixture was diluted with DCM (100 mL), and washed with 1 N HCl (20 mL), water (20 mL) and brine (20 mL) successively. 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 (ethyl acetate/petroleum ether = 5:95) to afford compound **2k-1** (4.10 g, 81%) as a colorless solid. Spectra data are consistent with those reported in the literature.⁷

4.2 General Procedure for Synthesis of alkyl boronic acids 2g-2k

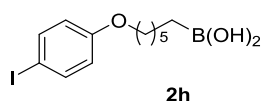


Scheme S8.

The alkyl boronic acid substrates were prepared following a reported procedure⁸: to a solution of alkene (10 mmol, 1.0 equiv) in THF (2 mL) was added a solution of $\text{BH}_3\cdot\text{THF}$ (20 mL, 20 mmol, 2.0 equiv, 1.0 M solution in THF) dropwise at 0 °C. The mixture was stirred for 2 h at room temperature and H_2O (2 mL) was added carefully. After stirred for additional 3 h at room temperature, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in EtOAc (30 mL), washed with saturated aqueous NaHCO_3 solution (20 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4 and filtrated. The filtrate was concentrated *in vacuo* to approximately 5 mL. Petroleum ether was then added under stirring. The resultant precipitate was collected by filtration, washed with petroleum ether and dried under high vacuum to afford the desired alkyl boronic acid as a white solid.

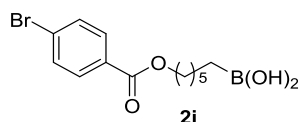


Compound **2g** was prepared in 42% yield following the general procedure. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 7.37 (s, 2H), 3.52 (t, *J* = 6.7 Hz, 2H), 1.82-1.75 (m, 2H), 1.40-1.21 (m, 6H), 0.58 (t, *J* = 7.6 Hz, 2H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 35.75, 32.72, 31.61, 27.92, 24.51, 15.80; HRMS Calcd for $\text{C}_6\text{H}_{14}\text{BBrNaO}_2$ [$\text{M}+\text{Na}^+$]: 231.0168, Found: 231.0134.

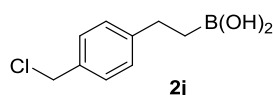


Compound **2h** was prepared in 45% yield following the general procedure. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.40 (s, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.95 (t, *J* = 6.3

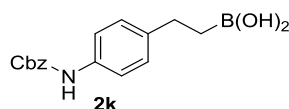
Hz, 2H), 1.74-1.67 (m, 2H), 1.40-1.31 (m, 6H), 0.61 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 159.03, 138.37, 117.67, 83.25, 68.07, 32.29, 29.02, 25.86, 24.64, 15.88; **HRMS** Calcd for $\text{C}_{12}\text{H}_{18}\text{BINA}\text{O}_3$ [$\text{M}+\text{Na}^+$]: 371.0291, Found: 371.0273.



Compound **2i** was prepared in 31% yield following the general procedure. ^1H NMR (DMSO- d_6 , 400 MHz) δ 7.88 (d, $J = 8.5$ Hz, 2H), 7.74 (d, $J = 8.5$ Hz, 2H), 7.39 (s, 2H), 4.25 (t, $J = 6.5$ Hz, 2H), 1.72-1.65 (m, 2H), 1.41-1.23 (m, 6H), 0.58 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 165.56, 132.38, 131.53, 129.51, 127.77, 65.51, 32.17, 28.56, 25.85, 24.57, 15.84; **HRMS** Calcd for $\text{C}_{13}\text{H}_{18}\text{BBrNaO}_4$ [$\text{M}+\text{Na}^+$]: 351.0379, Found: 351.0394.

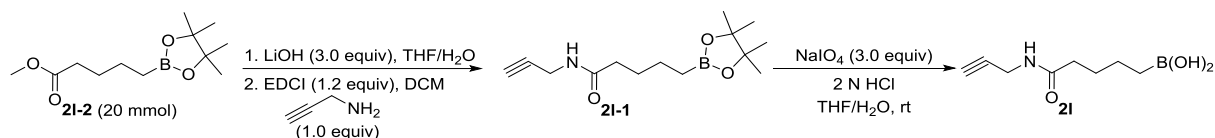


Compound **2j** was prepared in 46% yield following the general procedure. ^1H NMR (DMSO- d_6 , 400 MHz) δ 7.53 (s, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 4.71 (s, 2H), 2.63 (t, $J = 8.2$ Hz, 2H), 0.90 (t, $J = 8.2$ Hz, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 145.90, 134.98, 129.26, 128.47, 46.79, 30.38, 17.84; **HRMS** Calcd for $\text{C}_9\text{H}_{12}\text{BClNaO}_2$ [$\text{M}+\text{Na}^+$]: 221.0517, Found: 221.0509.

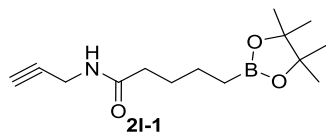


Compound **2k** was prepared in 31% yield following the general procedure. ^1H NMR (DMSO- d_6 , 400 MHz) δ 9.64 (s, 1H), 7.51 (s, 2H), 7.42-7.33 (m, 7H), 7.09 (d, $J = 8.3$ Hz, 2H), 5.14 (s, 2H), 2.57 (t, $J = 8.1$ Hz, 2H), 0.88 (t, $J = 8.1$ Hz, 2H); ^{13}C NMR (DMSO- d_6 , 100 MHz) δ 153.56, 139.34, 136.88, 136.51, 128.58, 128.21, 128.14, 128.08, 118.36, 65.73, 29.65, 17.76; **HRMS** Calcd for $\text{C}_{16}\text{H}_{18}\text{BNNaO}_4$ [$\text{M}+\text{Na}^+$]: 322.1227, Found: 322.1242.

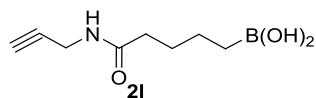
4.3 Synthesis of alkyl boronic acid **2l**



Scheme S9



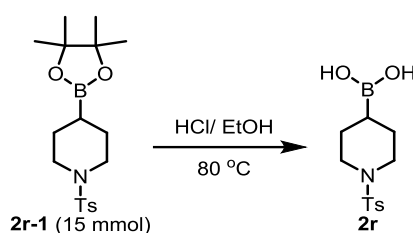
To a solution of compound **21-2** (4.84 g, 20 mmol, 1.0 equiv) in a mixture of THF (40 mL) and H₂O (20 mL) was added LiOH (0.96 g, 60 mmol, 3.0 equiv). The mixture was stirred at room temperature until compound **21-2** was completely consumed monitoring by TLC. The solvent was concentrated *in vacuo*, then ethyl acetate (50 mL) and water (10 mL) were added. Under vigorous stirring, the reaction was acidified with 2N HCl to pH 1-2. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (20 mL x 2). The combined organic phase was dried over Na₂SO₄ and filtrated. The filtrate was concentrated *in vacuo* and the residue was dissolved in DCM (50 mL). To this solution were added EDCI (2.18 g, 24 mmol, 1.2 equiv) and prop-2-yn-1-amine (1.1 g, 20 mmol, 1.0 equiv), and the mixture was stirred at room temperature for 1 h. Then the reaction mixture was diluted with DCM (150 mL), washed with water (20 mL), 1 N HCl (20 mL) and brine (20 mL) successively. 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 = 1:1) to afford compound **21-1** (3.0 g, 56% for 2 steps) as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 5.85 (s, 1H), 4.06-4.05 (m, 2H), 2.23 (t, *J* = 2.6 Hz, 1H), 2.20 (d, *J* = 7.7 Hz, 1H), 1.66-1.61 (m, 2H), 1.49-1.41 (m, 2H), 1.25 (s, 12H), 0.81 (t, *J* = 7.7 Hz, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.66, 83.03, 79.72, 71.45, 36.15, 29.05, 27.95, 24.79, 24.56, 23.48; **HRMS** Calcd for C₁₄H₂₄BNNaO₃ [*M*+Na⁺]: 288.1747, Found: 288.1740.



Compound **21** was prepared following a reported procedure⁹: to a solution of compound **21-1** (662 mg, 2.5 mmol, 1.0 equiv) in a mixture of THF (16 mL) and H₂O (4 mL), 2 N HCl (0.8

mL) and NaIO₄ (1.60 g, 7.5 mmol, 3.0 equiv) were added. The mixture was stirred at room temperature until compound **2l-1** was completely consumed monitoring by TLC. The reaction mixture was extracted with EtOAc, and the combined organic phases were washed with brine, dried over Na₂SO₄ and filtrated. The filtrate was concentrated *in vacuo* to approximately 5 mL. Petroleum ether was then added under stirring. The resultant precipitate was collected by filtration, washed with petroleum ether and dried under high vacuum to afford the desired product **2l** as a white solid (180 mg, 39%). ¹H NMR (DMSO-*d*₆, 400 MHz) δ 8.24 (t, *J* = 4.8 Hz, 1H), 7.39 (s, 2H), 3.83-3.81 (m, 2H), 3.08 (t, *J* = 2.0 Hz, 1H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.49-1.43 (m, 2H), 1.35-1.27 (m, 2H), 0.60 (t, *J* = 7.7 Hz, 2H); ¹³C NMR (DMSO-*d*₆, 100 MHz) δ 172.06, 81.36, 72.72, 35.16, 28.13, 27.66, 23.97, 15.16; HRMS Calcd for C₈H₁₄BNNaO₃ [M+Na⁺]: 206.0964, Found: 206.0928.

4.4 Synthesis of alkyl boronic acid **2r**



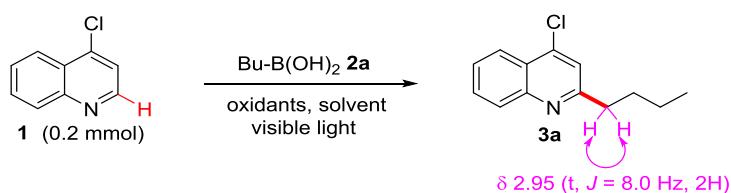
Scheme S10.

Compound **2r** was prepared following a reported procedure⁹: to a mixture of EtOH (10 mL) and concentrated hydrogen chloride (18 mL) was added compound **2r-1** (4.7 g, 15 mmol, 1.0 equiv). The mixture was stirred for 10 minutes at room temperature and then heated at 80 °C until the boronic esters were completely consumed monitoring by TLC. After cooled to room temperature, the reaction mixture was diluted with water and extracted with EtOAc. The combined organic phases were washed with brine, dried over Na₂SO₄ and filtrated. The filtrate was concentrated *in vacuo* and residue was recrystallized from EtOAc and petroleum ether to afford compound **2r** as a white solid (1.06 g, 55%). Spectra data are consistent with those reported in the literature.⁹

5. Reaction optimization for Minisci C-H alkylation of compound **1**

All screening reactions were carried out at a 0.2 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2). The vials were purged with Ar for 1 min, sealed with PTEF cap and stirred on bench top. Stock solution of Ru(bpy)₃Cl₂ (0.04 mmol in 10 mL of HFIP) was used if necessary. A 20 W compact household fluorescent bulb was positioned 10 cm aside from the reaction vials if necessary.

Compound **1** (32.8 mg, 0.2 mmol, 1.0 equiv) and other specified reagents were dispersed in 0.5 mL of solvent containing photocatalyst. The mixture was stirred at specified temperature with or without light irradiation for 24 h. After removal of the solvent *in vacuo*, the residue was dissolved in 3 mL of CDCl₃ along with Cl₂CHCHCl₂ (20 µL) as an internal standard for ¹H NMR analysis. The composition of reaction mixture was analyzed based on the methylene group peaks at 2.95 ppm (t, *J* = 8.0 Hz, 2H) for compound **3a**.

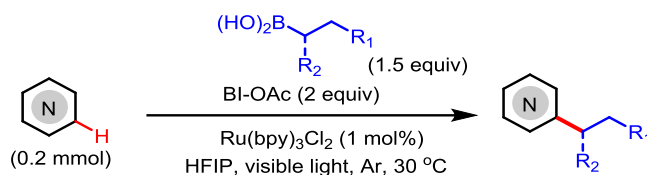


Entry	Reagents (equiv) / atmosphere	Solvents/ mL	t (°C) /Time (h)	Yield (%) ^a 3a
1	2a (1.5), BI-OH (2), Ar	HFIP/0.5	80 / 48	20
2	2a (1.5), BI-OAc (2), Ar	HFIP/0.5	80 / 48	28
3	2a (1.5), BI-OAc (2), Ar	CHCl ₃ /0.5	80 / 48	<2
4	2a (1.5), BI-OAc (2), Ar	CH ₃ CN/0.5	80 / 48	<2
5	2a (1.5), BI-OAc (2), Ar	TFE/0.5	30 / 24	34
6	2a (1.5), PhI(CF ₃ COO) ₂ (2), Ru(bpy) ₃ Cl ₂ (0.01), VL ^b , Ar	HFIP/0.5	30 / 24	<2
7	2a (1.5), BI-OAc (2), Ru(bpy) ₃ Cl ₂ (0.01), VL, Ar	HFIP/0.25	30 / 24	69
8	2a (1.5), BI-OAc (2), Ru(bpy) ₃ Cl ₂ (0.01), VL, Ar	HFIP/1.0	30 / 24	48

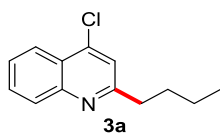
^a) Yields are based on ¹H-NMR analysis on a 0.2 mmol scale. ^b) VL: compact household fluorescent bulb, 20 W.

Table S1. Minisci C-H alkylation of compound 1

6. General procedure and substrate scope for Minisci C-H alkylation

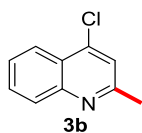


General condition: *N*-heteroaromatic substrate (0.2 mmol, 1.0 equiv), alkyl boronic acid (0.3 mmol, 1.5 equiv) and BI-OAc (0.4 mmol, 2.0 equiv) were added to a solution of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (0.002 mmol, 0.01 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 1-48 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K_2CO_3 (approximate 150 mg), 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 preparative thin layer chromatography or flash chromatography on silica gel to afford the desired product.



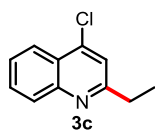
$R_f = 0.6$, 20% EtOAc in Hexane

Compound **3a** was prepared following the general procedure (24 h) in 82% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (dd, $J = 8.3, 0.6$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.75-7.71 (m, 1H), 7.60-7.56 (m, 1H), 7.40 (s, 1H), 2.95 (t, $J = 8.0$ Hz, 2H), 1.83-1.76 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.04, 148.73, 142.48, 130.23, 129.14, 126.60, 124.89, 123.89, 121.33, 38.84, 31.91, 22.59, 13.93; HRMS Calcd for $\text{C}_{13}\text{H}_{15}\text{ClN}$ [$\text{M}+\text{H}^+$]: 220.0893, Found: 220.0929.



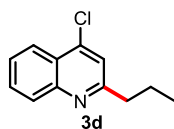
$R_f = 0.2$, 10% Methyl *tert*-butyl ether in Hexane

Compound **3b** was prepared following the general procedure (**2b'** 2.0 equiv, 48 h) in 46% yield as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (dd, $J = 8.4, 0.9$ Hz, 1H), 8.03 (d, $J = 8.4$ Hz, 1H), 7.76-7.72 (m, 1H), 7.61-7.56 (m, 1H), 7.41 (s, 1H), 2.73 (s, 3H). Spectra data are consistent with those reported in the literature.¹⁰



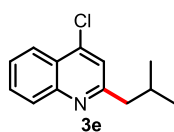
$R_f = 0.5$, 20% EtOAc in Hexane

Compound **3c** was prepared following the general procedure (24 h) in 80% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.19 (dd, $J = 8.4, 0.9$ Hz, 1H), 8.05 (dd, $J = 8.5, 0.4$ Hz, 1H), 7.76-7.72 (m, 1H), 7.60-7.56 (m, 1H), 7.42 (s, 1H), 2.99 (q, $J = 7.6$ Hz, 2H), 1.40 (t, $J = 7.6$ Hz, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 163.91, 148.71, 142.62, 130.27, 129.14, 126.63, 124.92, 123.91, 120.88, 32.11, 13.75; **HRMS** Calcd for $\text{C}_{11}\text{H}_{11}\text{ClN}$ [$\text{M}+\text{H}^+$]: 192.0580, Found: 192.0577.



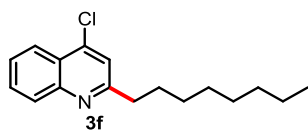
$R_f = 0.5$, 20% EtOAc in Hexane

Compound **3d** was prepared following the general procedure (24 h) in 85% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.4$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.73 (dd, $J = 8.4, 7.2$ Hz, 1H), 7.58 (dd, $J = 8.4, 7.2$ Hz, 1H), 7.40 (s, 1H), 2.93 (t, $J = 7.6$ Hz, 2H), 1.89-1.80 (m, 2H), 1.03 (t, $J = 7.3$ Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 162.82, 148.73, 142.48, 130.24, 129.15, 126.61, 124.91, 123.89, 121.35, 41.01, 23.05, 13.93; **HRMS** Calcd for $\text{C}_{12}\text{H}_{13}\text{ClN}$ [$\text{M}+\text{H}^+$]: 206.0737, Found: 206.0773.



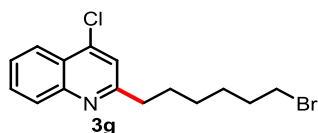
$R_f = 0.6$, 20% EtOAc in Hexane

Compound **3e** was prepared following the general procedure (24 h) in 78% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.19 (dd, $J = 8.4, 0.7$ Hz, 1H), 8.06 (d, $J = 8.2$ Hz, 1H), 7.74-7.72 (m, 1H), 7.60-7.56 (m, 1H), 7.38 (s, 1H), 2.82 (d, $J = 7.4$ Hz, 2H), 2.27-2.16 (m, 1H), 0.99 (d, $J = 6.6$ Hz, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ 162.16, 148.72, 142.26, 130.18, 129.19, 126.59, 124.85, 123.86, 121.89, 121.85, 48.02, 29.30, 22.46; **HRMS** Calcd for $\text{C}_{13}\text{H}_{15}\text{ClN}$ [$\text{M}+\text{H}^+$]: 220.0893, Found: 220.0890.



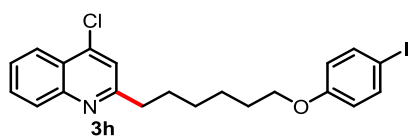
$R_f = 0.6$, 10% EtOAc in Hexane

Compound **3f** was prepared following the general procedure (24 h) in 73% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.18 (dd, $J = 8.4, 1.0$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.76-7.71 (m, 1H), 7.60-7.56 (m, 1H), 7.40 (s, 1H), 2.94 (t, $J = 8.0$ Hz, 2H), 1.84-1.76 (m, 2H), 1.43-1.27 (m, 10H), 0.87 (t, $J = 7.0$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 163.07, 148.73, 142.47, 130.23, 129.15, 126.59, 124.89, 123.89, 121.33, 39.14, 31.82, 29.83, 29.48, 29.42, 29.18, 22.64, 14.09; **HRMS** Calcd for $\text{C}_{17}\text{H}_{23}\text{ClN}$ [$\text{M}+\text{H}^+$]: 276.1519, Found: 276.1515.



$R_f = 0.5$, 10% EtOAc in Hexane

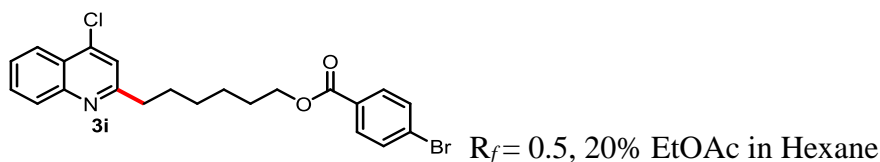
Compound **3g** was prepared following the general procedure (24 h) in 60% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.19 (dd, $J = 8.4, 0.8$ Hz, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.76-7.72 (m, 1H), 7.61-7.57 (m, 1H), 7.40 (s, 1H), 3.41 (t, $J = 6.8$ Hz, 2H), 2.95 (t, $J = 7.8$ Hz, 2H), 1.91-1.80 (m, 4H), 1.55-1.41 (m, 4H); **^{13}C NMR** (100 MHz, CDCl_3) δ 162.65, 148.71, 142.58, 130.31, 129.13, 126.69, 124.92, 123.92, 121.31, 38.90, 33.87, 32.60, 29.50, 28.52, 27.97; **HRMS** Calcd for $\text{C}_{15}\text{H}_{18}\text{BrClN}$ [$\text{M}+\text{H}^+$]: 326.0311, Found: 326.0308.



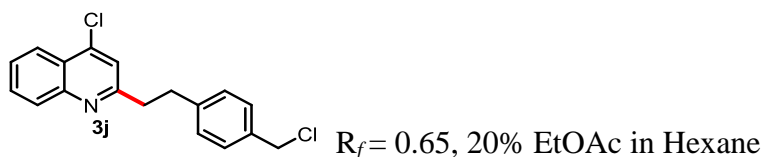
$R_f = 0.4$, 10% EtOAc in Hexane

Compound **3h** was prepared following the general procedure (24 h) in 60% yield as a colorless solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.19 (dd, $J = 8.4, 0.9$ Hz, 1H), 8.05 (d, $J = 8.1$ Hz, 1H), 7.76-7.72 (m, 1H), 7.61-7.56 (m, 1H), 7.54-7.51 (m, 2H), 7.40 (s, 1H), 6.67-6.63 (m, 2H), 3.90 (t, $J = 6.5$ Hz, 2H), 2.95 (t, $J = 7.8$ Hz, 2H), 1.86-1.76 (m, 4H), 1.56-1.43 (m, 4H); **^{13}C NMR** (100 MHz, CDCl_3) δ 162.73, 158.90, 148.69, 142.55, 138.10, 130.29, 129.12, 126.67, 124.90,

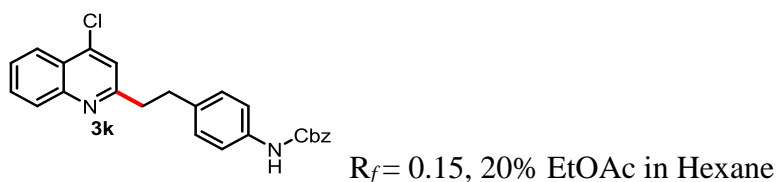
123.91, 121.30, 116.86, 82.41, 67.89, 38.93, 29.60, 29.07, 28.95, 25.82; **HRMS** Calcd for $C_{21}H_{22}ClINO$ $[M+H]^+$: 466.0435, Found: 466.0430.



Compound **3i** was prepared following the general procedure (24 h) in 77% yield as a colorless solid. **1H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, $J = 8.3$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.5$ Hz, 2H), 7.79 -7.69 (m, 1H), 7.61-7.56 (m, 3H), 7.40 (s, 1H), 4.31 (t, $J = 6.6$ Hz, 2H), 2.96 (t, $J = 7.8$ Hz, 3H), 1.89-1.75 (m, 4H), 1.56-1.43 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.86, 162.64, 148.71, 142.52, 131.62, 131.03, 130.27, 129.29, 129.13, 127.87, 126.65, 124.88, 123.89, 121.26, 65.22, 38.91, 29.55, 29.03, 28.52, 25.88; **HRMS** Calcd for $C_{22}H_{22}BrClINO_2$ $[M+H]^+$: 446.0522, Found: 446.0520.

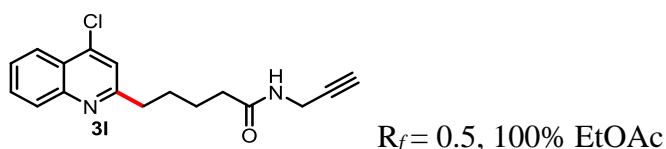


Compound **3j** was prepared following the general procedure (**2j** 2.0 equiv, 10 h) in 55% yield as a colorless solid. **1H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, $J = 8.3$ Hz, 1H), 8.08 (d, $J = 8.4$ Hz, 1H), 7.83-7.71 (m, 1H), 7.65 - 7.54 (m, 1H), 7.35 (s, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 4.57 (s, 2H), 3.27-3.22 (m, 2H), 3.18-3.14 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.41, 148.77, 142.59, 141.55, 135.31, 130.37, 129.19, 128.85, 128.76, 126.84, 125.00, 123.96, 121.47, 46.15, 40.49, 35.19; **HRMS** Calcd for $C_{18}H_{16}Cl_2N$ $[M+H]^+$: 316.0660, Found: 301.0663.

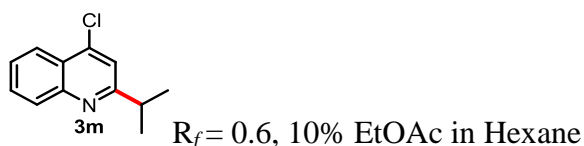


Compound **3k** was prepared following the general procedure (10 h) in 74% yield as a colorless solid. **1H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, $J = 8.3$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.76-

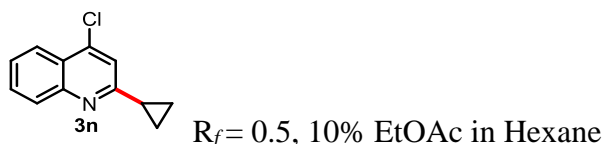
7.72 (m, 1H), 7.61-7.59 (m, 1H), 7.38-7.29 (m, 8H), 7.17 (d, $J = 8.3$ Hz, 2H), 6.72 (s, 1H), 5.19 (s, 2H), 3.24-3.20 (m, 2H), 3.12-3.08 (m, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 161.60, 153.34, 148.74, 142.54, 136.33, 136.05, 135.83, 130.33, 129.15, 129.03, 128.58, 128.30, 128.28, 126.78, 124.98, 123.94, 121.50, 118.84, 66.94, 40.69, 34.88; **HRMS** Calcd for $\text{C}_{25}\text{H}_{22}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}^+]$: 417.1370, Found: 417.1368.



Compound **3l** was prepared following the general procedure (24 h) in 52% yield as a colorless solid. **^1H NMR** (400 MHz, CDCl_3) δ 8.19 (dd, $J = 8.3$, 0.6 Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.76-7.72 (m, 1H), 7.61-7.57 (m, 1H), 7.40 (s, 1H), 5.85 (s, 1H), 4.06-4.04 (m, 2H), 2.97 (t, $J = 7.5$ Hz, 2H), 2.27 (t, $J = 7.3$ Hz, 2H), 2.22 (t, $J = 2.5$ Hz, 1H), 1.91-1.84 (m, 2H), 1.81-1.74 (m, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 172.25, 162.19, 148.66, 142.67, 130.34, 129.07, 126.74, 124.94, 123.94, 121.35, 79.58, 1.54, 38.44, 36.04, 29.11, 28.90, 25.08; **HRMS** Calcd for $\text{C}_{17}\text{H}_{18}\text{ClN}_2\text{O}$ $[\text{M}+\text{H}^+]$: 301.1108, Found: 301.1198.

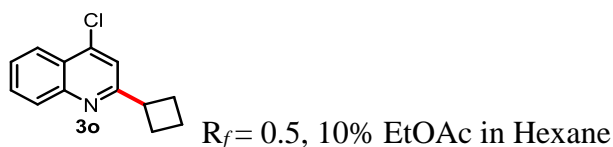


Compound **3m** was prepared following the general procedure (1 h) in 88% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.0$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.75-7.71 (m, 1H), 7.59-7.55 (m, 1H), 7.43 (s, 1H), 3.28-3.18 (m, 1H), 1.39 (d, $J = 6.9$ Hz, 6H). Spectra data are consistent with those reported in the literature.¹¹

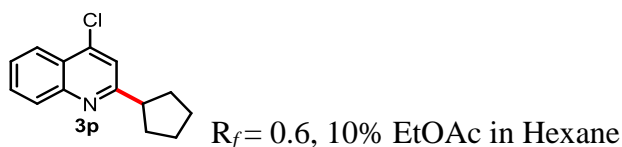


Compound **3n** was prepared following the general procedure (24 h) in 56% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.14 (dd, $J = 8.4$, 0.9 Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H),

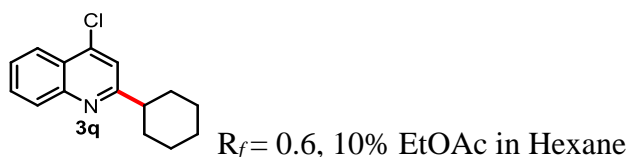
7.72-7.68 (m, 1H), 7.55-7.51 (m, 1H), 7.29 (s, 1H), 2.23-2.17 (m, 1H), 1.19-1.14 (m, 1H), 1.13-1.08 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 163.49, 148.80, 142.13, 130.18, 128.97, 126.09, 124.85, 123.89, 119.56, 17.95, 10.47; **HRMS** Calcd for C₁₂H₁₁ClN [M+H⁺]: 204.0580, Found: 204.0627.



Compound **3o** was prepared following the general procedure (10 h) in 82% yield as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.14 (dd, $J = 8.4$, 0.9 Hz, 1H), 8.07 (d, $J = 8.3$ Hz, 1H), 7.75-7.70 (m, 1H), 7.59-7.54 (m, 1H), 7.43 (s, 1H), 3.87-3.78 (m, 1H), 2.48-2.42 (m, 4H), 2.18-2.06 (m, 1H), 2.00-1.92 (m, 1H). Spectra data are consistent with those reported in the literature.¹²

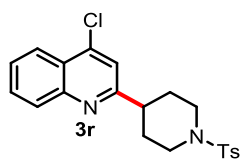


Compound **3p** was prepared following the general procedure (1 h) in 87% yield as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.16 (dd, $J = 8.3$, 1.0 Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.74-7.70 (m, 1H), 7.58-7.54 (m, 1H), 7.43 (s, 1H), 3.39-3.30 (m, 1H), 2.21-2.14 (m, 2H), 1.94-1.73 (m, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.25, 148.49, 142.40, 130.11, 129.24, 126.51, 124.99, 123.82, 120.15, 48.61, 33.45, 25.93; **HRMS** Calcd for C₁₄H₁₅ClN [M+H⁺]: 232.0893, Found: 232.0892.



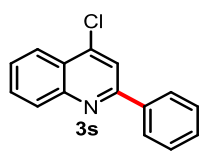
Compound **3q** was prepared following the general procedure (1 h) in 88% yield as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.17 (d, $J = 8.3$ Hz, 1H), 8.05 (d, $J = 8.5$ Hz, 1H), 7.74-7.70 (m, 1H), 7.59-7.54 (m, 1H), 7.42 (s, 1H), 2.92-2.86 (m, 1H), 2.04-2.00 (m, 2H), 1.92-1.87 (m,

2H), 1.80-1.77 (m, 1H), 1.66-1.56 (m, 2H), 1.51-1.40 (m, 2H), 1.38-1.30 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ 166.79, 148.59, 142.57, 130.13, 129.24, 126.55, 125.08, 123.86, 119.74, 47.38, 32.65, 26.38, 25.95; **HRMS** Calcd for C₁₅H₁₇ClN [M+H⁺]: 246.1050, Found: 246.1048.



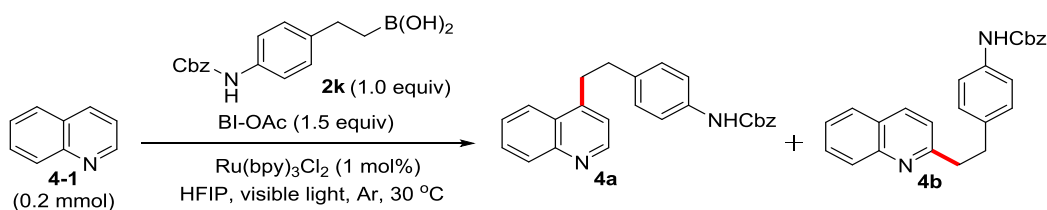
3r R_f = 0.25, 20% EtOAc in Hexane

Compound **3r** was prepared following the general procedure (3 h) in 86% yield as a colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.18 (dd, J = 8.3, 0.7 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.78-7.72 (m, 1H), 7.70 (d, J = 8.2 Hz, 2H), 7.62-7.58 (m, 1H), 7.36 (d, J = 8.2 Hz, 2H), 7.34 (s, 1H), 3.99-3.94 (m, 2H), 2.84-2.76 (m, 1H), 2.49-2.42 (m, 5H), 2.07-1.98 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ 163.62, 148.55, 143.49, 142.92, 133.25, 130.40, 129.62, 129.33, 127.69, 127.00, 125.17, 123.88, 119.42, 46.27, 44.05, 30.74, 21.51; **HRMS** Calcd for C₂₁H₂₂ClN₂O₂S [M+H⁺]: 401.1091, Found: 401.1088.

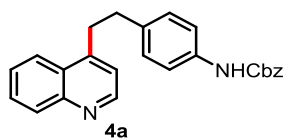


3s R_f = 0.85, 10% EtOAc in Hexane

Compound **1** (32.8 mg, 0.2 mmol, 1.0 equiv), phenyl boronic acid **2t** (36.8 mg, 0.3 mmol, 1.5 equiv), BI-OAc (122.4 mg, 0.4 mmol, 2.0 equiv) and TFA (38.8 mg, 0.4 mmol, 2.0 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.28 mg, 0.002 mmol, 0.01 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 24 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K₂CO₃ (approximate 150 mg), the mixture was vigorously stirred for 5 min. After that, 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 to afford compound **3r** as a colorless solid (10.0 mg, 21% yield). **¹H NMR** (400 MHz, CDCl₃) δ 8.24 (dd, J = 8.3, 0.7 Hz, 1H), 8.20-8.14 (m, 3H), 7.98 (s, 1H), 7.81-7.76 (m, 1H), 7.65-7.61 (m, 1H), 7.56-7.47 (m, 3H). Spectra data are consistent with those reported in the literature.¹³

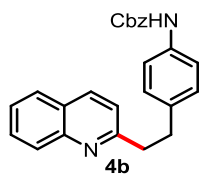


Scheme S11.



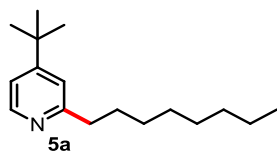
$R_f = 0.25$, 40% EtOAc in Hexane

Compound **4a** was prepared following the general procedure (**2k** 1.0 equiv, BI-OAc 1.5 equiv, 10 h) in 39% yield as a colorless solid. ^1H NMR (400 MHz, CDCl_3) δ 8.77 (d, $J = 4.4$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 7.72-7.68 (m, 1H), 7.59-7.55 (m, 1H), 7.41-7.31 (m, 7H), 7.14 (d, $J = 4.5$ Hz, 1H), 7.12 (d, $J = 8.4$ Hz, 2H), 6.88 (br s, 1H), 5.20 (s, 2H), 3.36-3.32 (m, 2H), 3.04-3.00 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.38, 150.09, 148.24, 147.32, 136.09, 136.03, 130.22, 129.57, 129.06, 128.92, 128.57, 128.31, 128.26, 127.35, 126.42, 123.32, 120.89, 118.89, 66.94, 35.41, 34.07; HRMS Calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}^+]$: 383.1760, Found: 383.1819.



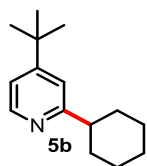
$R_f = 0.6$, 40% EtOAc in Hexane

Compound **4b** was prepared following the general procedure (**2k** 1.0 equiv, BI-OAc 1.5 equiv, 10 h) in 11% yield as a colorless solid. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.6$ Hz, 1H), 8.04 (d, $J = 8.6$ Hz, 1H), 7.78 (d, $J = 8.1$ Hz, 1H), 7.72-7.68 (m, 1H), 7.52-7.48 (m, 1H), 7.41-7.28 (m, 7H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.65 (br s, 1H), 5.19 (s, 2H), 3.28-3.24 (m, 2H), 3.13-3.09 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.70, 147.96, 136.74, 136.20, 136.08, 135.71, 129.39, 129.09, 128.83, 128.60, 128.32, 128.30, 127.52, 126.78, 125.79, 121.58, 118.79, 66.95, 40.98, 35.21; HRMS Calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}^+]$: 383.1760, Found: 383.1819.



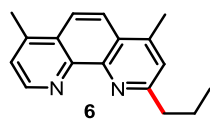
$R_f = 0.4$, 10% EtOAc in Hexane

Compound **5a** was prepared following the general procedure (48 h) in 52% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.41 (d, $J = 5.3$ Hz, 1H), 7.11 (s, 1H), 7.08 (dd, $J = 5.3$, 1.7 Hz, 1H), 2.76 (t, $J = 7.8$ Hz, 2H), 1.75-1.68 (m, 2H), 1.38-1.26 (m, 19H), 0.87 (t, $J = 6.7$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 162.25, 160.18, 148.94, 119.54, 118.00, 38.66, 34.56, 31.85, 30.55, 30.10, 29.50, 29.45, 29.23, 22.65, 14.09; **HRMS** Calcd for $\text{C}_{17}\text{H}_{30}\text{N}$ $[\text{M}+\text{H}^+]$: 248.2378, Found: 248.2376.



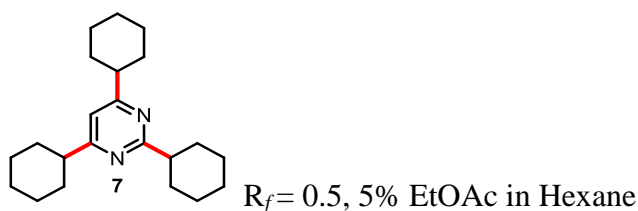
$R_f = 0.4$, 10% EtOAc in Hexane

Compound **5b** was prepared following the general procedure (16 h) in 53% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 8.43 (d, $J = 5.3$ Hz, 1H), 7.12 (d, $J = 1.9$ Hz, 1H), 7.09 (dd, $J = 5.3$, 1.9 Hz, 1H), 2.71-2.64 (m, 1H), 1.96-1.84 (m, 4H), 1.77-1.73 (m, 1H), 1.60-1.51 (m, 2H), 1.47-1.39 (m, 2H), 1.37-1.27 (m, 10H); **^{13}C NMR** (100 MHz, CDCl_3) δ 166.23, 160.18, 148.82, 118.18, 117.90, 46.76, 34.63, 32.99, 30.57, 26.63, 26.05; **HRMS** Calcd for $\text{C}_{15}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}^+]$: 218.1909, Found: 218.1906.

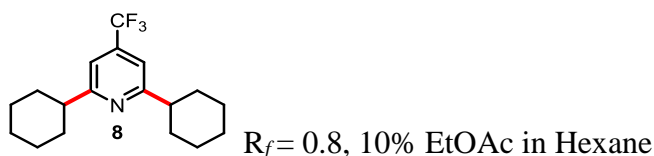


$R_f = 0.2$, 100% EtOAc

Compound **6** was prepared following the general procedure (24 h) in 70% yield as a colorless oil. **^1H NMR** (400 MHz, CDCl_3) δ 9.08 (d, $J = 4.5$ Hz, 1H), 8.01-7.95 (m, 2H), 7.43 (dd, $J = 4.5$, 0.5 Hz, 1H), 7.38 (d, $J = 0.5$ Hz, 1H), 3.17-3.13 (m, 2H), 2.79 (s, 3H), 2.77 (s, 3H), 1.96-1.86 (m, 2H), 1.07 (t, $J = 7.3$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3) δ 162.91, 149.81, 145.97, 145.75, 144.06, 143.98, 127.90, 126.15, 123.66, 123.59, 122.00, 120.93, 41.46, 23.66, 19.11, 14.20; **HRMS** Calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2$ $[\text{M}+\text{H}^+]$: 251.1548, Found: 251.1544.

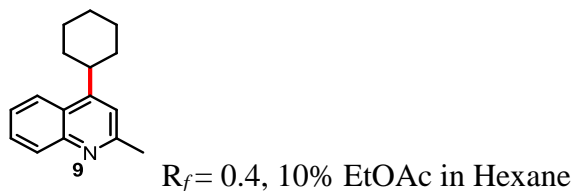


Compound **7-1** (16.2 mg, 0.2 mmol, 1.0 equiv), boronic acid **2q** (115.2 mg, 0.9 mmol, 4.5 equiv) and BI-OAc (367.4 mg, 1.2 mmol, 6.0 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.28 mg, 0.002 mmol, 0.01 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 1 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K₂CO₃ (approximate 450 mg), the mixture was vigorously stirred for 5 min. After that, 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 to afford compound **7** as a colorless oil (41.2 mg, 63% yield). **¹H NMR** (400 MHz, CDCl₃) δ 6.77 (s, 1H), 2.83-2.75 (m, 1H), 2.61-2.55 (m, 2H), 1.95-1.63 (m, 17H), 1.52-1.25 (m, 13H). Spectra data are consistent with those reported in the literature.¹⁴

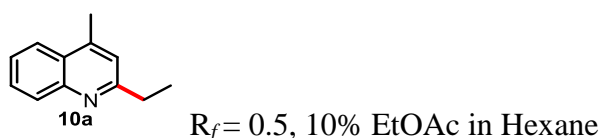


Compound **8-1** (29.5 mg, 0.2 mmol, 1.0 equiv), boronic acid **2q** (76.6 mg, 0.6 mmol, 3.0 equiv) and BI-OAc (244.8 mg, 0.8 mmol, 4.0 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.28 mg, 0.002 mmol, 0.001 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 2 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K₂CO₃ (approximate 450 mg), the mixture was vigorously stirred for 5 min. After that, 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 to afford compound **8** as a colorless oil (51.0 mg, 82% yield). **¹H NMR** (400 MHz, CDCl₃) δ 7.15 (s, 2H), 2.79-2.72 (m, 2H), 1.98-1.74 (m, 10H), 1.56-1.27 (m, 10H); **¹³C NMR** (100 MHz,

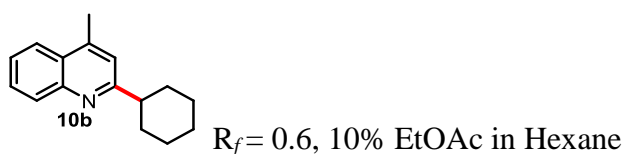
CDCl₃) δ 167.14, 138.67 (q, J = 32.8 Hz), 123.35 (q, J = 272.9 Hz), 138.67 (q, J = 32.8 Hz), 46.56, 32.82, 26.41, 25.99; **HRMS** Calcd for C₁₈H₂₅F₃N [M+H⁺]: 312.1939, Found: 312.1938.



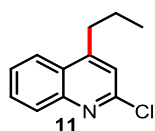
Compound **9** was prepared following the general procedure (2 h) in 93% yield as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.03 (d, J = 9.2 Hz, 2H), 7.66-7.62 (m, 1H), 7.50-7.46 (m, 1H), 7.16 (s, 1H), 3.31-3.26 (m, 1H), 2.71 (s, 3H), 2.01-1.83 (m, 5H), 1.60-1.48 (m, 4H), 1.40-1.28 (m, 1H). Spectra data are consistent with those reported in the literature.¹⁴



Compound **10a** was prepared following the general procedure (24 h) in 80% yield as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 8.3, 0.6 Hz, 1H), 7.69-7.65 (m, 1H), 7.52-7.48 (m, 1H), 7.16 (s, 1H), 2.96 (q, J = 7.6 Hz, 2H), 2.68 (s, 3H), 1.39 (t, J = 7.6 Hz, 3H). Spectra data are consistent with those reported in the literature.¹⁵

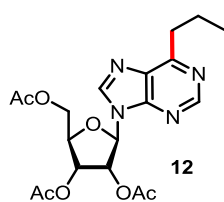


Compound **10b** was prepared following the general procedure (1 h) in 96% yield as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.04 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.68-7.64 (m, 1H), 7.50-7.46 (m, 1H), 7.16 (s, 1H), 2.90-2.84 (m, 1H), 2.67 (s, 3H), 2.01 (d, J = 12.7 Hz, 2H), 1.86-1.91 (m, 2H), 1.80-1.76 (m, 1H), 1.67-1.57 (m, 2H), 1.52-1.41 (m, 2H), 1.39-1.30 (m, 1H). Spectra data are consistent with those reported in the literature.¹²



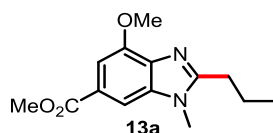
11 $R_f = 0.4$, 10% EtOAc in Hexane

Compound **11** was prepared following the general procedure (24 h) in 62% yield as a colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.03-7.99 (m, 2H), 7.73-7.69 (m, 1H), 7.58-7.54 (m, 1H), 7.24 (s, 1H), 3.02 (t, $J = 7.7$ Hz, 2H), 1.86-1.76 (m, 2H), 1.06 (t, $J = 7.3$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 151.94, 150.61, 148.02, 130.08, 129.31, 126.58, 126.31, 123.62, 121.50, 34.00, 22.96, 14.07; **HRMS** Calcd for C₁₂H₁₃ClN [M+H⁺]: 206.0737, Found: 206.0773.



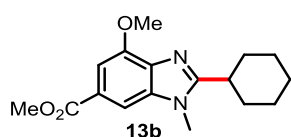
12 $R_f = 0.6$, 100% EtOAc

Compound **12** was prepared following the general procedure (24 h) in 60% yield as a colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.90 (s, 1H), 8.18 (s, 1H), 6.24 (d, $J = 5.1$ Hz, 1H), 5.99 (t, $J = 5.3$ Hz, 1H), 5.71 (t, $J = 5.1$ Hz, 1H), 4.49-4.46 (m, 2H), 4.41-4.36 (m, 1H), 3.18 (t, $J = 7.6$ Hz, 2H), 2.16 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 1.98-1.89 (m, 2H), 1.04 (t, $J = 7.4$ Hz, 3H). Spectra data are consistent with those reported in the literature.¹⁶



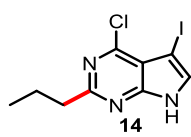
13a $R_f = 0.6$, 100% EtOAc

Compound **13a** was prepared following the general procedure (24 h) in 72% yield as a colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.06 (s, 1H), 7.37 (s, 1H), 4.00 (s, 3H), 3.98 (s, 3H), 3.93 (s, 3H), 2.83 (t, $J = 7.7$ Hz, 2H), 1.94-1.84 (m, 2H), 1.07 (t, $J = 7.4$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 167.78, 156.72, 146.39, 143.42, 128.36, 124.09, 115.03, 104.09, 55.72, 52.06, 32.40, 29.25, 20.86, 13.96; **HRMS** Calcd for C₁₄H₁₉N₂O₃ [M+H⁺]: 263.1396, Found: 263.1391.



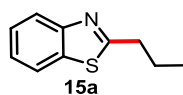
13b $R_f = 0.5$, 50% EtOAc in Hexane

Compound **13b** was prepared following the general procedure (1 h) in 90% yield as a colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.10 (d, *J* = 1.2 Hz, 1H), 7.36 (d, *J* = 1.2 Hz, 1H), 4.02 (s, 3H), 3.98 (s, 3H), 3.92 (m, 3H), 2.84-2.77 (m, 1H), 2.00-1.90 (m, 4H), 1.82-1.73 (m, 4H), 1.47-1.34 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 167.83, 160.47, 146.45, 143.64, 128.33, 123.93, 115.31, 104.03, 55.73, 52.04, 36.02, 32.14, 31.32, 26.25, 25.76; **HRMS** Calcd for C₁₇H₂₃N₂O₃ [M+H⁺]: 303.1709, Found: 303.1708.



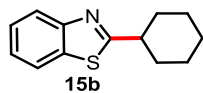
R_f = 0.5, 50% EtOAc in Hexane

Compound **14** was prepared following the general procedure (24 h) in 62% yield as light yellow solid. **¹H NMR** (400 MHz, CDCl₃) δ 11.63 (s, 1H), 8.60 (s, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 1.87-1.78 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 151.93, 151.65, 149.24, 144.13, 117.97, 53.31, 31.08, 22.13, 13.73; **HRMS** Calcd for C₉H₁₀ClIN₃ [M+H⁺]: 321.9608, Found: 321.9605.



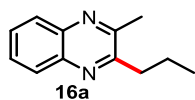
R_f = 0.65, 20% EtOAc in Hexane

Compound **15a** was prepared following the general procedure (24 h) in 82% yield as colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.84 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.47-7.43 (m, 1H), 7.36-7.32 (m, 1H), 3.10 (t, *J* = 7.6 Hz, 2H), 1.96-1.87 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). Spectra data are consistent with those reported in the literature.¹⁷



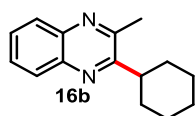
R_f = 0.65, 20% EtOAc in Hexane

Compound **15b** was prepared following the general procedure (2 h) in 88% yield as colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.46-7.42 (m, 1H), 7.35-7.31 (m, 1H), 3.14-3.07 (m, 1H), 2.22-2.18 (m, 2H), 1.91-1.86 (m, 2H), 1.78-1.74 (m, 1H), 1.69-1.59 (m, 2H), 1.50-1.39 (m, 2H), 1.37-1.29 (m, 1H). Spectra data are consistent with those reported in the literature.¹⁸



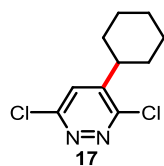
$R_f = 0.65$, 20% EtOAc in Hexane

Compound **16a** was prepared following the general procedure (24 h) in 64% yield as colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.03-7.96 (m, 2H), 7.69-7.65 (m, 2H), 2.99 (t, $J = 7.8$ Hz, 2H), 2.77 (s, 3H), 1.92-1.83 (m, 2H), 1.09 (t, $J = 7.4$ Hz, 3H). Spectra data are consistent with those reported in the literature.¹⁹



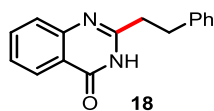
$R_f = 0.4$, 10% EtOAc in Hexane

Compound **16b** was prepared following the general procedure (10 h) in 78% yield as colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.03-7.99 (m, 1H), 7.98-7.94 (m, 1H), 7.66-7.62 (m, 2H), 3.07-3.00 (m, 1H), 2.79 (s, 3H), 1.96-1.91 (m, 4H), 1.82-1.73 (m, 3H), 1.52-1.36 (m, 3H). Spectra data are consistent with those reported in the literature.¹⁴



$R_f = 0.7$, 20% EtOAc in Hexane

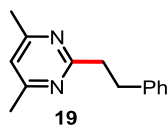
Compound **17** was prepared following the general procedure (2 h) in 65% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.36 (s, 1H), 2.91-2.83 (m, 1H), 1.98-1.90 (m, 4H), 1.85-1.81 (m, 1H), 1.52-1.41 (m, 2H), 1.37-1.26 (m, 3H). Spectra data are consistent with those reported in the literature.²⁰



$R_f = 0.6$, 100% EtOAc

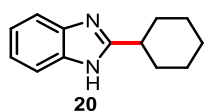
Compound **18** was prepared following the general procedure (24 h) in 67% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 12.0 (br s, 1H), 8.31 (dd, $J = 7.9, 0.9$ Hz, 1H), 7.83-7.78 (m, 1H), 7.75 (d, $J = 7.7$ Hz, 1H), 7.52-7.48 (m, 1H), 7.35 (d, $J = 7.2$ Hz, 2H), 7.31-7.27 (m,

2H), 7.23-7.16 (m, 1H), 3.23-3.19 (m, 2H), 3.12-3.08 (m, 2H). Spectra data are consistent with those reported in the literature.²¹



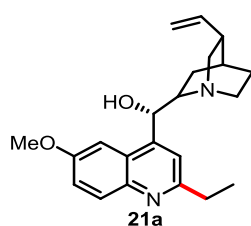
$R_f = 0.5$, 50% EtOAc in Hexane

Compound **19** was prepared following the general procedure (24 h) in 64% yield as colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.28 (d, $J = 4.4$ Hz, 4H), 7.21-7.16 (m, 1H), 6.87 (s, 1H), 3.22-3.17 (m, 2H), 3.14-3.09 (m, 2H), 2.46 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 169.69, 166.53, 141.65, 128.47, 128.27, 125.83, 117.48, 41.27, 34.97, 23.98; **HRMS** Calcd for C₁₄H₁₇N₂ [M+H⁺]: 213.1392, Found: 213.1423.



$R_f = 0.8$, 100% EtOAc

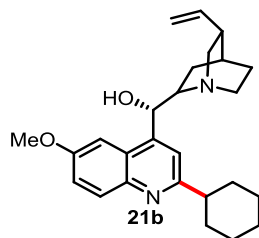
Compound **20** was prepared following the general procedure (10 h) in 76% yield as colorless solid. **¹H NMR** (400 MHz, CD₃OD) δ 7.50-7.46 (m, 2H), 7.19-7.15 (m, 2H), 2.93-2.86 (m, 1H), 2.10-2.06 (m, 2H), 1.91-1.87 (m, 2H), 1.81-1.77 (m, 1H), 1.69-1.62 (m, 2H), 1.53-1.42 (m, 2H), 1.40-1.31 (m, 1H). Spectra data are consistent with those reported in the literature.¹⁴



$R_f = 0.4$, 5% MeOH in DCM

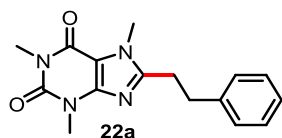
Compound **21a** was prepared following the general procedure (24 h) in 81% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.90 (d, $J = 9.2$ Hz, 1H), 7.41 (s, 1H), 7.25 (d, $J = 2.3$ Hz, 1H), 7.14 (s, 1H), 5.75-5.67 (m, 1H), 5.54 (s, 1H), 4.97-4.90 (m, 2H), 3.84 (s, 3H), 3.54 (br s, 1H), 3.13-3.07 (m, 1H), 2.85 (q, $J = 7.6$ Hz, 2H), 2.76-2.62 (m, 2H), 2.28 (br s, 1H), 1.81-1.68 (m, 3H), 1.56-1.43 (m, 3H), 1.29 (t, $J = 7.6$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 161.01, 157.10, 147.62, 143.83, 141.62, 130.84, 124.81, 121.05, 118.01, 114.49, 101.27, 71.74, 59.92,

56.91, 55.62, 43.28, 39.83, 32.03, 27.85, 27.43, 21.43, 14.03; **HRMS** Calcd for C₂₂H₂₉N₂O₂ [M+H⁺]: 353.2229, Found: 353.2228.



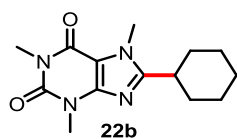
21b $R_f = 0.4$, 5% MeOH in DCM

Compound **21b** was prepared following the general procedure (8 h) in 90% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.95 (d, $J = 9.2$ Hz, 1H), 7.49 (s, 1H), 7.30 (d, $J = 9.2$ Hz, 1H), 7.19 (s, 1H), 5.77-5.67 (m, 2H), 4.99-4.91 (m, 2H), 3.87 (s, 3H), 3.65-3.52 (m, 1H), 3.19-3.11 (m, 2H), 2.87-2.81 (m, 1H), 2.78-2.67 (m, 2H), 2.36-2.26 (m, 1H), 2.00-1.91 (m, 2H), 1.84-1.74 (m, 6H), 1.63-1.26 (m, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 163.90, 157.18, 147.46, 143.74, 141.44, 131.06, 124.94, 120.99, 116.70, 114.60, 101.23, 71.63, 59.83, 56.86, 55.71, 47.29, 43.34, 39.74, 32.81, 27.87, 27.28, 26.46, 25.98, 20.92; **HRMS** Calcd for C₂₆H₃₅N₂O₂ [M+H⁺]: 407.2699, Found: 407.2698.



22a $R_f = 0.45$, 5% MeOH in DCM

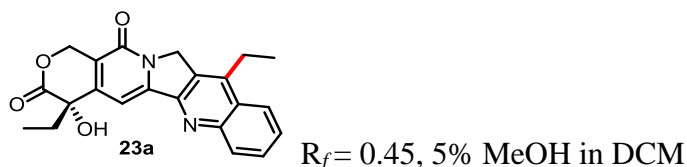
Compound **22a** was prepared following the general procedure (24 h) in 42% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.31-7.21 (m, 4H), 7.13 (d, $J = 7.0$ Hz, 2H), 3.61 (s, 3H), 3.60 (s, 3H), 3.39 (s, 3H), 3.11-3.08 (m, 2H), 3.04-3.00 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃) δ 155.26, 153.34, 151.67, 148.00, 139.97, 128.72, 128.31, 126.69, 107.15, 34.03, 31.39, 29.72, 28.95, 27.85; **HRMS** Calcd for C₁₆H₁₉N₄O₂ [M+H⁺]: 299.1508, Found: 299.1508.



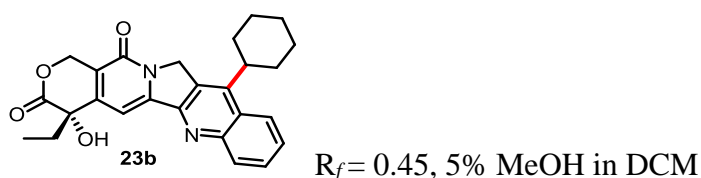
22b $R_f = 0.5$, 5% MeOH in DCM

Compound **22b** was prepared following the general procedure (12 h) in 50% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 3.93 (s, 3H), 3.57 (s, 3H), 3.40 (s, 3H), 2.75-2.68 (m, 1H),

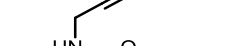
1.92-1.85 (m, 4H), 1.78-1.64 (m, 3H), 1.44-1.31 (m, 3H). Spectra data are consistent with those reported in the literature.¹⁴





(*S*)-camptothecin **23-1** (69.6 mg, 0.2 mmol, 1.0 equiv), ethyl boronic acid **2c** (22.5 mg, 0.3 mmol, 1.5 equiv) and BI-OAc (122.4 mg, 0.4 mmol, 2.0 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.28 mg, 0.002 mmol, 0.01 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 48 h. The solvent was removed *in vacuo* and the residue was purified by preparative thin layer chromatography to afford compound **23a** as a light yellow solid (45.2 mg, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, $J = 8.4$ Hz, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.84-7.79 (m, 1H), 7.70-7.67 (m, 2H), 5.77 (d, $J = 16.2$ Hz, 1H), 5.32 (d, $J = 16.2$ Hz, 1H), 5.27 (s, 2H), 3.74 (s, 1H), 3.22 (q, $J = 7.7$ Hz, 2H), 1.96-1.84 (m, 2H), 1.42 (t, $J = 7.7$ Hz, 3H), 1.05 (t, $J = 7.4$ Hz, 3H). Spectra data are consistent with those reported in the literature.²²



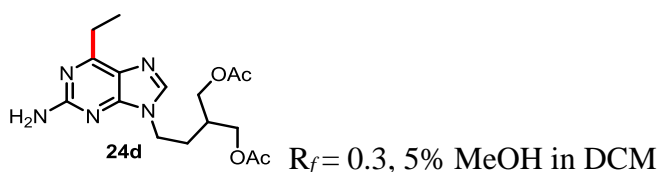
(*S*)-camptothecin **23-1** (69.6 mg, 0.2 mmol, 1.0 equiv), alkyl boronic acid **2q** (38.6 mg, 0.3 mmol, 1.5 equiv) and BI-OAc (122.4 mg, 0.4 mmol, 2.0 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.28 mg, 0.002 mmol, 0.01 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 5 h. The solvent was removed *in vacuo* and the residue was purified by preparative thin layer chromatography to afford compound **23b** as a light yellow solid (78.1 mg, 91% yield). ¹H NMR (400 MHz, CDCl₃) δ 8.26-8.20 (m, 2H), 7.79 (t, $J = 7.5$ Hz, 1H), 7.69-7.04 (m, 2H), 5.76 (d, $J = 16.2$ Hz, 1H), 5.42 (s, 2H), 5.31 (d, $J = 16.2$ Hz, 1H), 3.81 (s,


24a $R_f = 0.25$, 5% MeOH in DCM

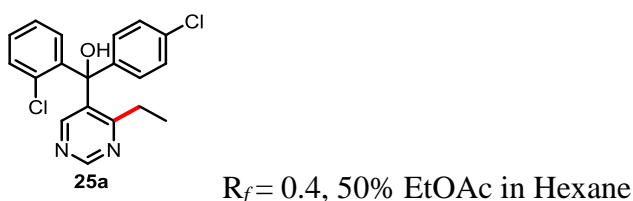
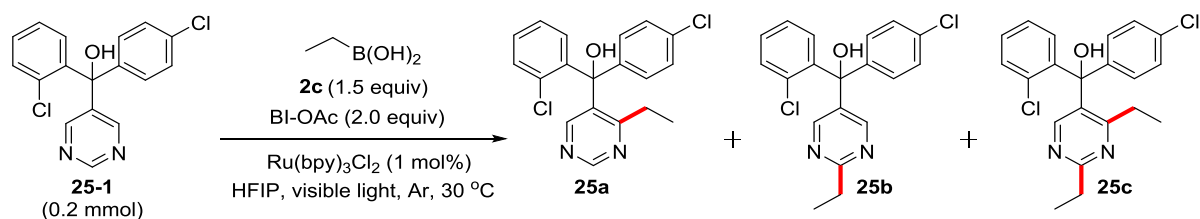

24b $R_f = 0.6$, 5% MeOH in DCM


24c $R_f = 0.3$, 5% MeOH in DCM

Compound **24c** was prepared following the general procedure (4 h) in 50% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (s, 1H), 5.02 (br s, 2H), 4.18 (t, *J* = 7.1 Hz, 2H), 4.14 (d, *J* = 5.4 Hz, 4H), 3.26-3.18 (m, 1H), 2.06 (s, 6H), 2.03-1.75 (m, 10H), 1.50-1.34 (m, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.83, 167.66, 159.71, 152.66, 140.21, 125.83, 63.62, 42.26, 40.73, 34.82, 31.06, 28.80, 26.22, 25.90, 20.79; **HRMS** Calcd for C₂₀H₃₀N₅O₄ [M+H⁺]: 404.2298, Found: 404.2295.

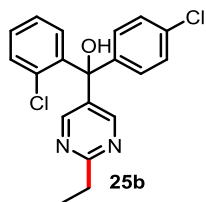


Compound **24d** was prepared following the general procedure (4 h) in 70% yield as colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (s, 1H), 4.95 (s, 2H), 4.19 (t, *J* = 7.1 Hz, 2H), 4.14 (d, *J* = 5.3 Hz, 4H), 3.03 (q, *J* = 7.6 Hz, 2H), 2.06 (s, 6H), 2.02-1.90 (m, 3H), 1.39 (t, *J* = 7.6 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.83, 164.98, 159.66, 152.56, 140.53, 126.37, 63.61, 40.78, 34.84, 28.80, 26.40, 20.78, 12.57; **HRMS** Calcd for C₁₆H₂₄N₅O₄ [M+H⁺]: 350.1828, Found: 350.1825.



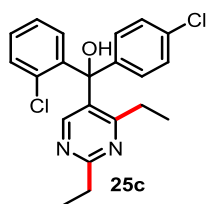
Compound **25a** was prepared following the general procedure (24 h) in 11% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 9.10 (s, 1H), 7.91 (s, 1H), 7.48 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.38-7.34 (m, 3H), 7.21-7.17 (m, 3H), 6.67 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.59 (s, 1H), 2.81-2.67 (m, 2H), 1.14 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 172.45, 157.70, 155.83,

141.95, 141.10, 135.71, 134.26, 132.60, 131.95, 130.64, 130.04, 129.20, 128.67, 127.06, 81.23, 29.96, 12.70; **HRMS** Calcd for C₁₉H₁₇Cl₂N₂O [M+H⁺]: 359.0718, Found: 359.0719.



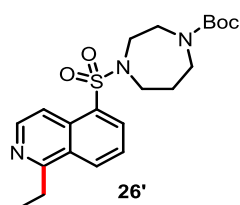
$R_f = 0.5$, 50% EtOAc in Hexane

Compound **25b** was prepared following the general procedure (24 h) in 14% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.52 (s, 2H), 7.44 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.35-7.31 (m, 3H), 7.22-7.18 (m, 3H), 6.76 (dd, $J = 7.9, 1.4$ Hz, 1H), 4.46 (s, 1H), 3.02 (q, $J = 7.6$ Hz, 2H), 1.38 (t, $J = 7.6$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 171.24, 156.37, 142.47, 141.34, 135.09, 134.10, 132.72, 131.82, 130.69, 130.06, 128.78, 128.65, 126.98, 79.77, 32.26, 12.43; **HRMS** Calcd for C₁₉H₁₇Cl₂N₂O [M+H⁺]: 359.0718, Found: 359.0719.



$R_f = 0.7$, 50% EtOAc in Hexane

Compound **25c** was prepared following the general procedure (24 h) in 16% yield as colorless solid. **¹H NMR** (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.45 (dd, $J = 7.9, 0.9$ Hz, 1H), 7.36-7.30 (m, 3H), 7.19-7.16 (m, 3H), 6.69 (dd, $J = 7.9, 1.3$ Hz, 1H), 4.56 (s, 1H), 2.97 (q, $J = 7.6$ Hz, 2H), 2.69 (q, $J = 7.4$ Hz, 2H), 1.37 (t, $J = 7.6$ Hz, 3H), 1.12 (t, $J = 7.4$ Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 170.90, 156.12, 142.37, 141.39, 134.06, 132.65, 132.40, 131.85, 130.68, 129.86, 129.20, 128.55, 126.94, 81.21, 32.16, 30.00, 13.01, 12.41; **HRMS** Calcd for C₂₁H₂₁Cl₂N₂O [M+H⁺]: 387.1031, Found: 387.1028.

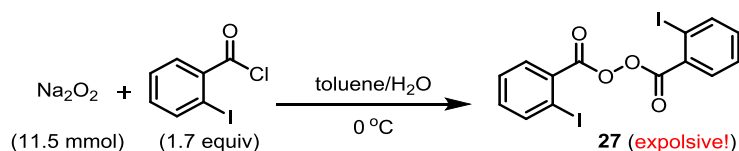


$R_f = 0.3$, 50% EtOAc in Hexane

Fasudil (58.4 mg, 0.2 mmol, 1.0 equiv, prepared from commercial available fasudil hydrochloride by neutralization), ethyl boronic acids **2c** (24.5 mg, 0.3 mmol, 1.5 equiv) and BI-OAc (126.0 mg, 0.4 mmol, 2.0 equiv) were added to a solution of Ru(bpy)₃Cl₂ (1.8 mg, 0.002 mmol, 0.01 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 10 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K₂CO₃ (approximate 300 mg), the mixture was vigorously stirred for 5 min. After that, the mixture was filtrated through a pad of Celite and washed with DCM. The filtrate was concentrated *in vacuo* and the residue was dissolved in DCM (5 mL). To the solution was added Boc₂O (87.5 mg, 0.4 mmol, 2.0 equiv) and TEA (61.0 mg, 0.6 mmol, 3.0 equiv), then the mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 50:50) to afford compound **26'** (51.2 mg, 61% for 2 steps) as a colorless oil. **¹H NMR** (400 MHz, CD₃OD) δ 8.62 (d, *J* = 8.5 Hz, 1H), 8.49 (d, *J* = 6.3 Hz, 1H), 8.40-8.35 (m, 3H), 7.84-7.80 (m, 1H), 3.55-3.38 (m, 10H), 1.90-1.85 (m, 2H), 1.44 (s, 9H), 1.42 (t, *J* = 8.4 Hz, 3H); **¹³C NMR** (100 MHz, CD₃OD) δ 164.45, 155.50, 155.35, 141.80, 141.76, 135.27, 132.66, 132.33, 131.09, 127.30, 126.28, 116.59, 80.06, 79.93, 48.62, 48.36, 47.97, 47.94, , 47.02, 45.76, 45.45, 28.79, 28.63, 28.08, 27.27, 27.24, 13.11; **HRMS** Calcd for C₁₇H₂₂N₃O₄S [M-*t*-Bu+2H⁺]: 364.1331, Found: 364.1436.

7. Mechanism study

7.1 Synthesis of compound 27



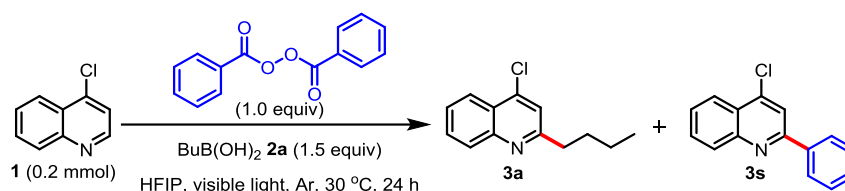
Scheme S13.

Compound **27** was prepared following a reported procedure²⁴: to the solution of *o*-iodobenzoyl chloride (5.2 g, 19.5 mmol, 1.7 equiv) in toluene (5 mL) was added a solution of sodium peroxide (0.9 g, 11.5 mmol, 1.0 equiv) in ice-water (12 mL) dropwise at 0 °C. After addition completed, the mixture was stirred for 1 h at 0 °C. The precipitate was collected by filtration

and the solid product was quickly washed with water, methanol, sodium bicarbonate and again with water and methanol. The solid was then dissolved with chloroform at room temperature. To the clear solution was added cold methanol at 0 °C as soon as possible under stirring (**NOTE:** If the addition of the methanol was delayed, no compound **27** was obtained.) The precipitated peroxide was allowed to stand at 0 °C only until the mother liquor is clear. After filtration, compound **27** was obtained as a colorless crystals (1.3 g, 23%). Spectra data are consistent with those reported in the literature.²⁴ (**NOTE:** Compound **27** is explosive, all the operations above were performed behind a blast shield.)

7.2 Minisci C-H alkylation promoted by BPO

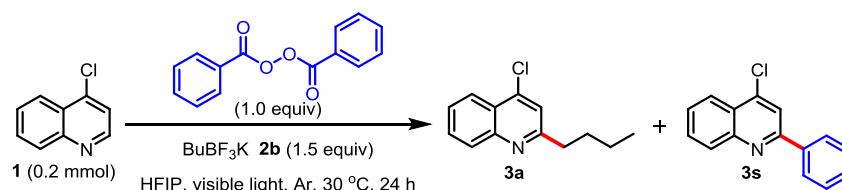
7.2.1 Minisci C-H alkylation with compound **2a** promoted by BPO



Scheme S14.

Compound **1** (32.8 mg, 0.2 mmol, 1.0 equiv), alkyl boronic acids **2a** (30.8 mg, 0.3 mmol, 1.5 equiv) and BPO (benzoyl peroxide, 48.6 mg, 0.2 mmol, 1.0 equiv) were added to HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and then the mixture was stirred at 30 °C under the fluorescent light irradiation for 24 h. The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K₂CO₃ (approximate 150 mg), the mixture was vigorously stirred for 5 min. Filtrated over a Celite plug and the residue was washed with DCM. The filtrate was concentrated *in vacuo* and the residue was purified by preparative thin layer chromatography to afford compound **3a** as a colorless oil in 20% yield. Compound **3s** was isolated in 11% yield (5.1 mg) as a colorless oil.

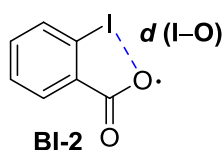
7.2.2 Minisci C-H alkylation with compound **2b** promoted by BPO



Scheme S15.

Single point energies were calculated using M06-2X and 6-311++G(d,p) and the SMD solvation model in HFIP. 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 HFIP² ($\epsilon = 16.7$) 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. All reported Gibbs free energies and enthalpies are corrected to the standard concentration in solution (1 mol/L).

The geometry of the key reaction intermediate, the *ortho*-iodobenzoyloxy radical **BI-2**, was also optimized using a few different levels of theories to evaluate the effects of density functional method, basis set, and solvation models on the weak intramolecular I \cdots O interaction. The optimized I \cdots O distance is highly dependent upon the choice of density functional, basis set. As expected, calculations without diffuse functions significantly overestimate the I \cdots O distance (entries 1 and 4). B3LYP and ω B97X-D also predict longer I \cdots O distance than M06-2X when using the same basis set (entries 1, 9 versus 5). Interestingly, calculations using the 6-31+G(d) and 6-311++G(d,p) basis sets give almost identical results (entries 2 versus 3, 5 versus 6). Replacing the SDD basis set with the LANL2DZ basis set for iodine leads to slight decrease of the I \cdots O distance (entries 7 and 8). Finally, using solvation model in the geometry optimization also noticeably decreases the I \cdots O distance (entries 10-12).



entry	method for geometry optimization	$d(\text{I-O}) / \text{\AA}$
1	B3LYP/6-31G(d)-SDD	2.81
2	B3LYP/6-31+G(d)-SDD	2.71
3	B3LYP/6-311++G(d,p)-SDD	2.71
4	M06-2X/6-31G(d)-SDD	2.78
5	M06-2X/6-31+G(d)-SDD	2.59
6	M06-2X/6-311++G(d,p)-SDD	2.59
7	M06-2X/6-31+G(d)-LANL2DZ	2.56
8	M06-2X/6-311++G(d,p)-LANL2DZ	2.56

9	ω B97X-D/6-31+G(d)-SDD	2.68
10	M06-2X/6-31G(d)-SDD/SMD(HFIP)	2.50
11	M06-2X/6-31+G(d)-SDD/SMD(HFIP)	2.47
12	M06-2X/6-311++G(d,p)-SDD/SMD(HFIP)	2.48

Table S2. Geometry of BI-2 optimized at different levels of theories.

8.2 The reaction energy of the one electron reduction of BI-OAc using the excited state $\text{Ru(II)}^*(\text{bpy})_3^{2+*}$

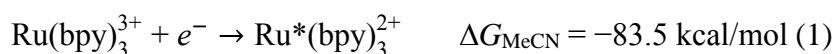
The photoexcited $\text{Ru(II)}^*(\text{bpy})_3^{2+}$ is a potent reductant with an experimental standard reduction potential (SRP) of -0.81 V vs. SCE in MeCN.²⁶ Thus, the absolute SRP in MeCN can be calculated as follows.²⁷

$$E_{\text{Ru(bpy)}_3^{3+/2+*}}^{\ominus, \text{abs}} = E_{\text{Ru(bpy)}_3^{3+/2+*}}^{\ominus, \text{SCE}} + 4.429\text{V} = -0.81\text{V} + 4.429\text{V} = 3.62\text{V}$$

Since

$$\Delta G = -nFE$$

where n is the number of electron transferred (one), F is the Faraday constant, the Gibbs free energy of the following reduction half reaction is

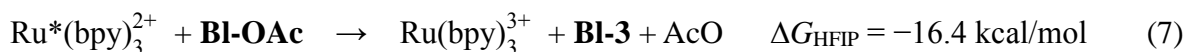
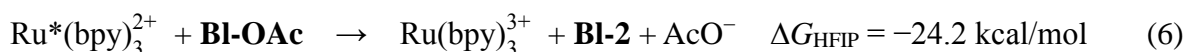
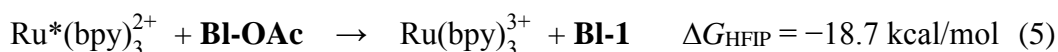


The reaction Gibbs free energies of the following reduction half reactions are calculated using the DFT-computed Gibbs free energy in HFIP solution (see Computational Details) and the Gibbs free energy of electron (-0.867 kcal/mol).²⁸





The reaction energies of the SET reactions (eq. 5-7) can be calculated from equations 1-4. Since the experimental reduction potential of $\text{Ru}(\text{bpy})_3^{3+}/\text{Ru}^*(\text{bpy})_3^{2+}$ in HFIP is not available, the reduction half reaction energy in MeCN (eq. 1) was used in the calculations.



8.3 Cartesian coordinates and energies of optimized structures

BI-OAc

M06-2X/6-31+G(d) SCF energy: -659.12988545 a.u.

M06-2X/6-31+G(d) enthalpy: -658.968934 a.u.

M06-2X/6-31+G(d) free energy: -659.025297 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -659.33123735 a.u.

M06-2X/6-311++G(d,p) enthalpy: -659.170286 a.u.

M06-2X/6-311++G(d,p) free energy: -659.226649 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.186805	0.120762	-0.000647
C	-0.927377	0.691416	0.000044
C	-0.698798	2.057019	0.001759
C	-1.826774	2.881309	0.002990
C	-3.114640	2.340859	0.002362
C	-3.298844	0.961995	0.000464
C	-2.323585	-1.378609	-0.002036
H	0.305464	2.462057	0.002153
H	-1.690132	3.958426	0.004523

H	-3.975843	3.001240	0.003419
H	-4.285923	0.508927	-0.000044
O	-1.157565	-2.004279	-0.001678
O	-3.396361	-1.933395	-0.003267
I	0.590771	-0.805851	-0.000220
O	1.938123	0.857653	-0.001870
C	3.192014	0.434703	0.004572
O	3.474299	-0.751826	0.013357
C	4.206736	1.549693	-0.009164
H	4.115226	2.109978	-0.943825
H	4.012274	2.239723	0.815499
H	5.208559	1.129629	0.075526

BI-1

M06-2X/6-31+G(d) SCF energy: -659.22774316 a.u.

M06-2X/6-31+G(d) enthalpy: -659.068338 a.u.

M06-2X/6-31+G(d) free energy: -659.128858 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -659.48981655 a.u.

M06-2X/6-311++G(d,p) enthalpy: -659.330411 a.u.

M06-2X/6-311++G(d,p) free energy: -659.390931 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.292165	0.239393	-0.000132
C	0.955654	0.617448	-0.000059
C	0.550822	1.950195	-0.000076
C	1.534851	2.937929	-0.000167
C	2.887448	2.590254	-0.000242
C	3.257938	1.249699	-0.000224
C	2.734746	-1.226952	-0.000112
H	-0.506314	2.196755	-0.000018
H	1.237647	3.983572	-0.000179
H	3.649032	3.366114	-0.000314

H	4.298181	0.936896	-0.000278
O	1.785153	-2.074538	0.000043
O	3.948227	-1.458906	-0.000238
I	-0.534303	-0.905164	0.000092
O	-2.374768	1.069516	0.000119
C	-3.449737	0.382201	0.000112
O	-3.535200	-0.856580	0.000089
C	-4.736464	1.218898	0.000130
H	-4.749433	1.865555	0.882798
H	-4.749428	1.865606	-0.882501
H	-5.613442	0.568872	0.000109

BI-2

M06-2X/6-31+G(d) SCF energy: -430.74156239 a.u.

M06-2X/6-31+G(d) enthalpy: -430.639153 a.u.

M06-2X/6-31+G(d) free energy: -430.684410 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -659.48981655 a.u.

M06-2X/6-311++G(d,p) enthalpy: -659.387407 a.u.

M06-2X/6-311++G(d,p) free energy: -659.432664 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	-1.899331	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

BI-3

M06-2X/6-31+G(d) SCF energy: -430.87638502 a.u.
M06-2X/6-31+G(d) enthalpy: -430.774583 a.u.
M06-2X/6-31+G(d) free energy: -430.820810 a.u.
M06-2X/6-311++G(d,p) SCF energy in solution: -431.07893180 a.u.
M06-2X/6-311++G(d,p) enthalpy: -430.977130 a.u.
M06-2X/6-311++G(d,p) free energy: -431.023357 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.343638	0.381596	-0.000009
C	0.337462	-0.583752	0.000027
C	0.625294	-1.953013	0.000056
C	1.946294	-2.388786	0.000026
C	2.975961	-1.448051	-0.000041
C	2.665427	-0.093633	-0.000051
C	1.162498	1.943047	0.000013
H	-0.185769	-2.674862	0.000114
H	2.161700	-3.454732	0.000047
H	4.014485	-1.771223	-0.000093
H	3.437745	0.669957	-0.000084
O	-0.012577	2.350335	0.000006
O	2.237323	2.579354	0.000039
I	-1.765388	-0.138700	-0.000009

AcO-

M06-2X/6-31+G(d) SCF energy: -228.43236595 a.u.
M06-2X/6-31+G(d) enthalpy: -228.378045 a.u.
M06-2X/6-31+G(d) free energy: -228.411558 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -228.60628795 a.u.

M06-2X/6-311++G(d,p) enthalpy: -228.551967 a.u.

M06-2X/6-311++G(d,p) free energy: -228.585480 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.347532	-0.051596	-0.000001
H	-1.729639	0.476278	0.882045
H	-1.729649	0.476376	-0.881983
C	0.209652	0.001190	-0.000002
O	0.802793	-1.103892	0.000000
O	0.697592	1.157847	0.000000
H	-1.716512	-1.081858	-0.000052

AcO radical

M06-2X/6-31+G(d) SCF energy: -228.30816108 a.u.

M06-2X/6-31+G(d) enthalpy: -228.254162 a.u.

M06-2X/6-31+G(d) free energy: -228.288393 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -228.38359529 a.u.

M06-2X/6-311++G(d,p) enthalpy: -228.329596 a.u.

M06-2X/6-311++G(d,p) free energy: -228.363827 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.353003	-0.104275	-0.001640
H	-1.685989	-0.335956	1.013724
H	-1.790422	0.846417	-0.314459
C	0.154364	-0.062290	-0.006706
O	0.910535	-1.003143	0.001711
O	0.631980	1.177475	0.000993
H	-1.671876	-0.905726	-0.670817

BzO radical

M06-2X/6-31+G(d) SCF energy: -419.97383060 a.u.
 M06-2X/6-31+G(d) enthalpy: -419.862909 a.u.
 M06-2X/6-31+G(d) free energy: -419.904056 a.u.
 M06-2X/6-311++G(d,p) SCF energy in solution: -420.09336129 a.u.
 M06-2X/6-311++G(d,p) enthalpy: -419.982440 a.u.
 M06-2X/6-311++G(d,p) free energy: -420.023587 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.833234	-1.210020	0.000249
C	-0.442239	-1.222506	0.000257
C	0.252718	-0.011936	-0.000018
C	-0.428048	1.207680	-0.000306
C	-1.819831	1.212859	-0.000315
C	-2.519219	0.005659	-0.000034
H	-2.383836	-2.145467	0.000467
H	0.117705	-2.152981	0.000471
H	-2.358461	2.155184	-0.000552
H	-3.605222	0.012262	-0.000034
C	1.734670	-0.058667	0.000032
O	2.435591	-1.050045	-0.000005
O	2.368883	1.106193	0.000130
H	0.125123	2.143400	-0.000542

Ph radical

M06-2X/6-31+G(d) SCF energy: -231.45729696 a.u.
 M06-2X/6-31+G(d) enthalpy: -231.363600 a.u.
 M06-2X/6-31+G(d) free energy: -231.396927 a.u.
 M06-2X/6-311++G(d,p) SCF energy in solution: -231.52000248 a.u.
 M06-2X/6-311++G(d,p) enthalpy: -231.426306 a.u.
 M06-2X/6-311++G(d,p) free energy: -231.459633 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.223860	-0.769470	0.000127
C	-0.000018	-1.400238	0.000085
C	1.224016	-0.769268	-0.000243
C	1.212335	0.631345	0.000121
C	-0.000156	1.322902	-0.000004
C	-1.212302	0.631388	-0.000169
H	-2.158310	-1.322692	0.000058
H	-0.000053	2.408699	0.000167
H	-2.151432	1.178126	-0.000029
H	2.151258	1.178331	0.000202
H	2.158445	-1.322422	0.000106

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M06-2X/6-31+G(d) SCF energy: -242.22393023 a.u.

M06-2X/6-31+G(d) enthalpy: -242.139205 a.u.

M06-2X/6-31+G(d) free energy: -242.178367 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -231.52000248 a.u.

M06-2X/6-311++G(d,p) enthalpy: 0.000000 a.u.

M06-2X/6-311++G(d,p) free energy: 0.000000 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.645211	-1.269303	0.000000
C	-1.271348	-1.172315	0.000000
C	-0.569594	0.000607	0.000001
C	-1.284613	1.201078	0.000001
C	-2.679794	1.154193	0.000000
C	-3.359334	-0.065173	0.000000
H	-3.153922	-2.228532	-0.000001
H	-3.240120	2.084082	-0.000001
H	-4.445334	-0.082819	-0.000001
H	-0.761876	2.153180	-0.000001

I 1.555861 -0.019253 0.000000

CO₂

M06-2X/6-31+G(d) SCF energy: -188.51469500 a.u.

M06-2X/6-31+G(d) enthalpy: -188.499178 a.u.

M06-2X/6-31+G(d) free energy: -188.523423 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -188.57200890 a.u.

M06-2X/6-311++G(d,p) enthalpy: -188.556492 a.u.

M06-2X/6-311++G(d,p) free energy: -188.580737 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.163071
O	0.000000	0.000000	-1.163071

BuB(OH)₂

M06-2X/6-31+G(d) SCF energy: -334.31712425 a.u.

M06-2X/6-31+G(d) enthalpy: -334.148920 a.u.

M06-2X/6-31+G(d) free energy: -334.192915 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -334.44056789 a.u.

M06-2X/6-311++G(d,p) enthalpy: -334.272364 a.u.

M06-2X/6-311++G(d,p) free energy: -334.316359 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.173103	-0.572452	-0.000387
H	-2.211836	-1.230077	-0.879756
H	-2.211822	-1.231304	0.878062
C	-0.848326	0.188145	0.000155
H	-0.806721	0.850683	-0.874427
H	-0.807007	0.849916	0.875341
C	0.376504	-0.731075	-0.000109

H	0.333232	-1.401439	0.873193
H	0.333140	-1.400880	-0.873839
B	1.765279	0.022714	-0.000009
O	1.797506	1.386853	-0.000218
H	2.704750	1.725556	-0.000146
O	2.977231	-0.629947	0.000254
H	2.902412	-1.592263	0.000349
C	-3.384664	0.357659	0.000277
H	-3.378880	1.005767	-0.883286
H	-4.324976	-0.202720	-0.000292
H	-3.379052	1.004273	0.884935

TS-1

M06-2X/6-31+G(d) SCF energy: -765.05578593 a.u.

M06-2X/6-31+G(d) enthalpy: -764.785473 a.u.

M06-2X/6-31+G(d) free energy: -764.852915 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -765.30591138 a.u.

M06-2X/6-311++G(d,p) enthalpy: -765.035598 a.u.

M06-2X/6-311++G(d,p) free energy: -765.103040 a.u.

Imaginary frequency: -270.7239 cm⁻¹

Cartesian coordinates

ATOM	X	Y	Z
C	-4.059280	1.895144	-0.258200
C	-3.546927	0.608836	-0.424762
C	-2.189456	0.402334	-0.212224
C	-1.335022	1.436375	0.155893
C	-1.867827	2.716999	0.323198
C	-3.222943	2.946961	0.116041
H	-5.118339	2.069864	-0.421713
H	-4.198990	-0.210060	-0.711152
H	-1.190642	3.512487	0.619633
H	-3.630225	3.944273	0.246340

C	0.134423	1.235192	0.397933
O	0.846437	2.112622	0.824396
O	0.570769	0.022003	0.061058
B	1.590015	-0.938544	1.026843
C	2.993866	-0.110049	0.990802
H	2.871416	0.768727	1.633234
H	3.714395	-0.779943	1.485830
C	3.514943	0.309803	-0.379064
H	3.553339	-0.552039	-1.066863
H	2.817383	1.028664	-0.828764
C	4.908894	0.937814	-0.321559
H	5.613382	0.217085	0.114839
H	4.879965	1.795627	0.362811
O	0.954855	-0.990809	2.282713
H	0.608428	-1.876599	2.455218
O	1.539234	-2.183283	0.325745
H	2.140256	-2.205784	-0.430562
I	-1.365305	-1.543545	-0.425871
C	5.411114	1.386998	-1.692519
H	6.408965	1.833414	-1.630809
H	5.464686	0.540189	-2.386918
H	4.736025	2.132024	-2.128674

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M06-2X/6-31+G(d) SCF energy: -607.41390059 a.u.

M06-2X/6-31+G(d) enthalpy: -607.270208 a.u.

M06-2X/6-31+G(d) free energy: -607.325398 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -607.60702977 a.u.

M06-2X/6-311++G(d,p) enthalpy: -607.463337 a.u.

M06-2X/6-311++G(d,p) free energy: -607.518527 a.u.

Cartesian coordinates

ATOM	X	Y	Z
------	---	---	---

C	-3.304999	1.495311	-0.447941
C	-2.675995	0.255999	-0.362228
C	-1.310459	0.176803	-0.087168
C	-0.563757	1.345231	0.109006
C	-1.222778	2.580751	0.047517
C	-2.578912	2.664415	-0.235775
H	-4.366720	1.537959	-0.671804
H	-3.251524	-0.652643	-0.504594
H	-0.632648	3.474230	0.226215
H	-3.064602	3.633308	-0.290619
C	0.908725	1.440816	0.380080
O	1.402878	2.346200	0.996757
I	-0.550985	-1.808729	0.129771
O	1.608222	0.424082	-0.159474
B	2.997073	0.350287	-0.297630
O	3.764717	1.461439	-0.342097
H	4.697815	1.249525	-0.482148
O	3.531690	-0.893507	-0.454789
H	2.863536	-1.592814	-0.410895

n-butyl radical

M06-2X/6-31+G(d) SCF energy: -157.68966288 a.u.

M06-2X/6-31+G(d) enthalpy: -157.564109 a.u.

M06-2X/6-31+G(d) free energy: -157.599579 a.u.

M06-2X/6-311++G(d,p) SCF energy in solution: -157.73738981 a.u.

M06-2X/6-311++G(d,p) enthalpy: -157.611836 a.u.

M06-2X/6-311++G(d,p) free energy: -157.647306 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.503443	0.523498	-0.070447
H	-0.392725	1.268630	0.728414

H	-0.407185	1.067497	-1.018313
C	0.636519	-0.493999	0.037510
H	0.510920	-1.056713	0.980751
H	0.537711	-1.241700	-0.761714
C	1.987876	0.132763	-0.014419
H	2.859889	-0.435585	-0.315515
H	2.151057	1.110746	0.426803
C	-1.880258	-0.129869	0.019243
H	-2.682016	0.610265	-0.064437
H	-2.017661	-0.864917	-0.781809
H	-2.004150	-0.652581	0.974496

9. References

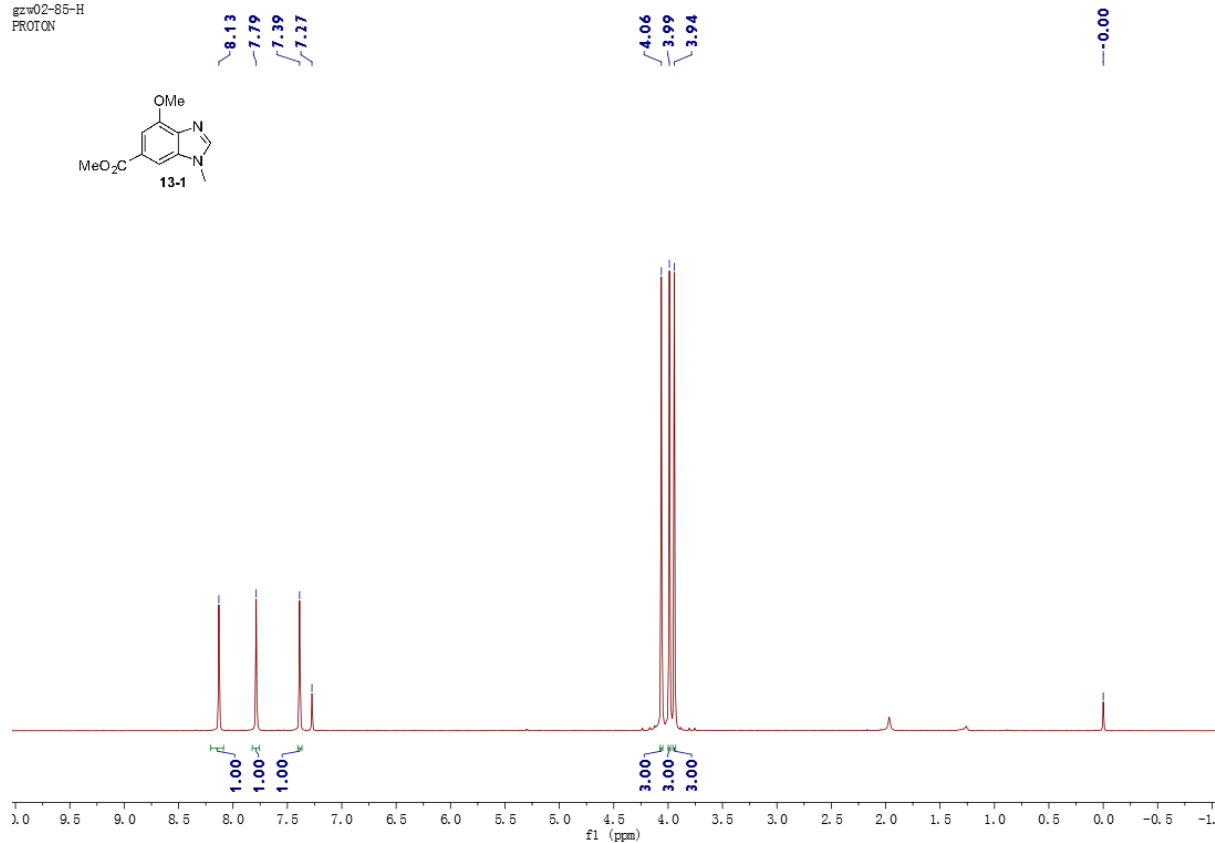
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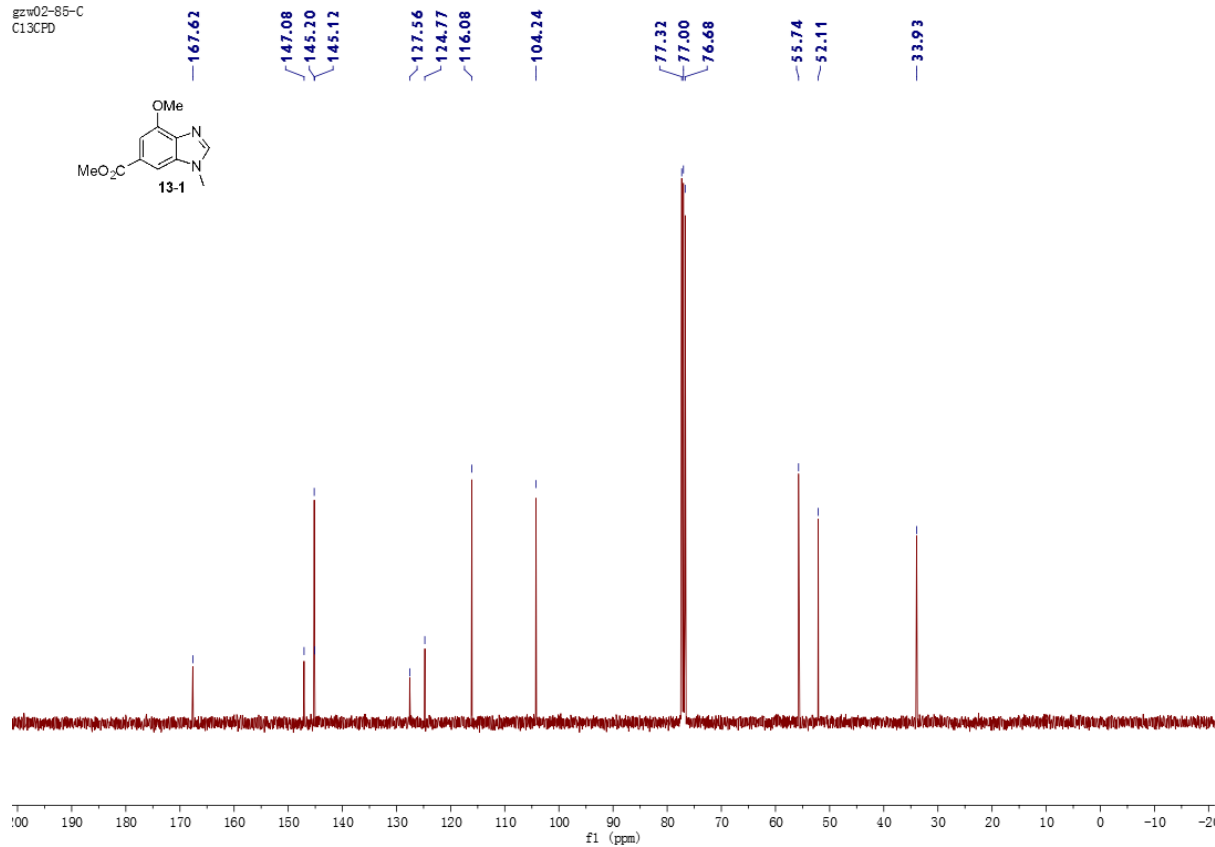
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10. ^1H -NMR and ^{13}C -NMR spectra

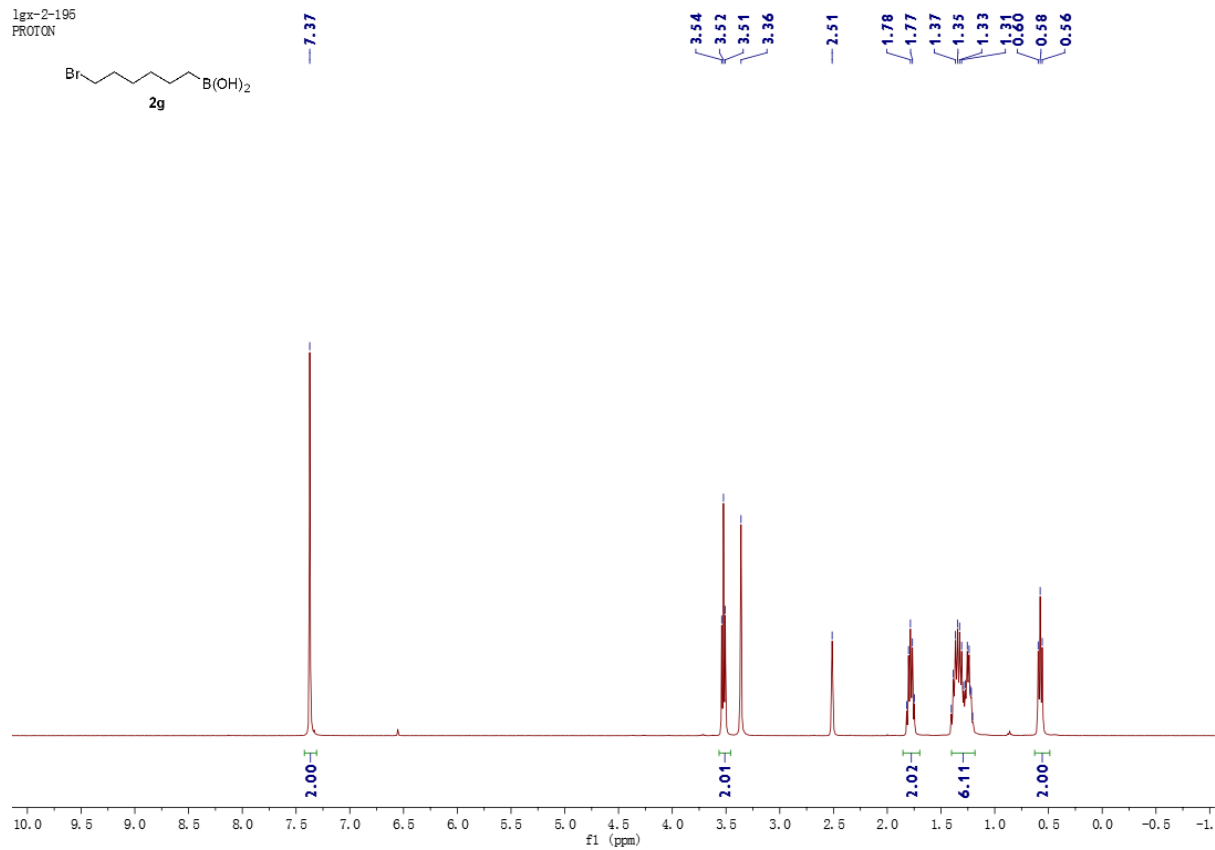
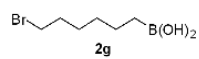
gzw02-85-H
PROTON



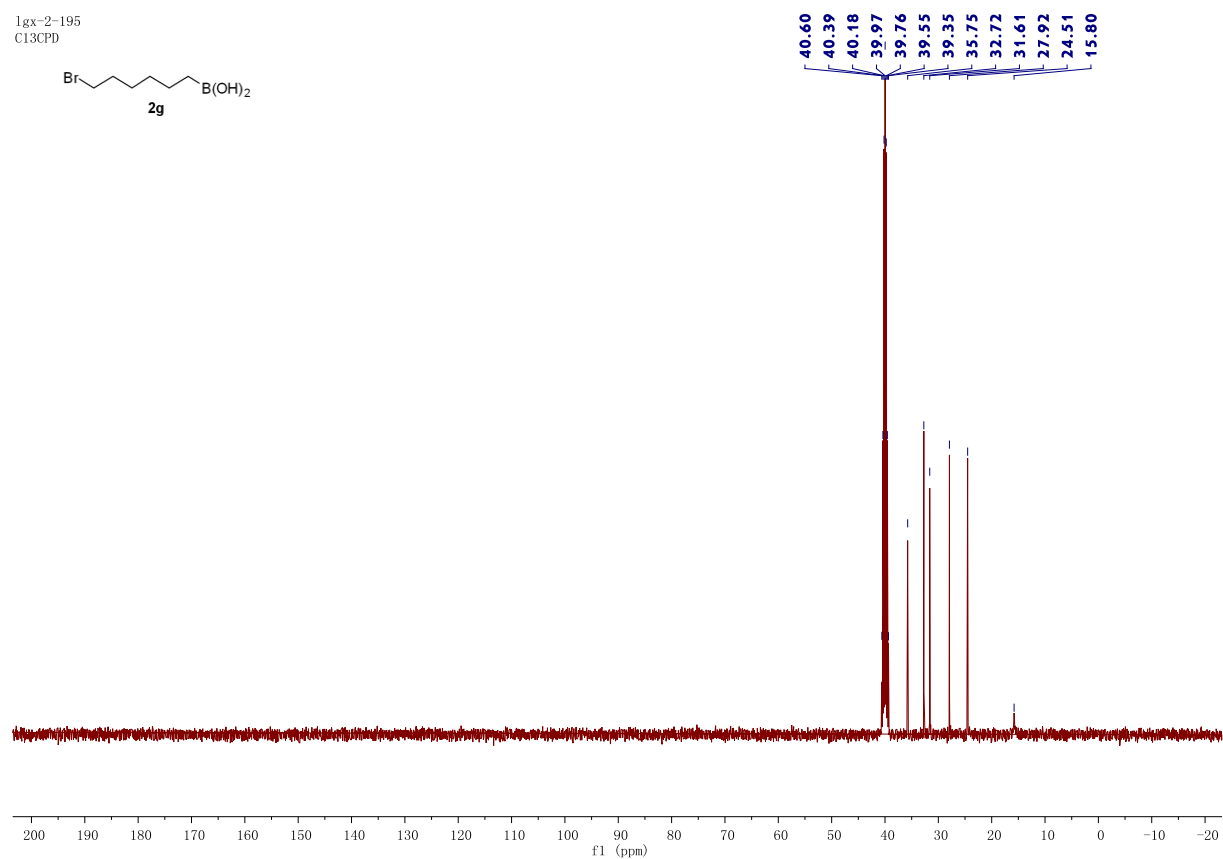
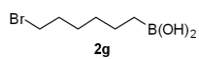
gzw02-85-C
C13CPD



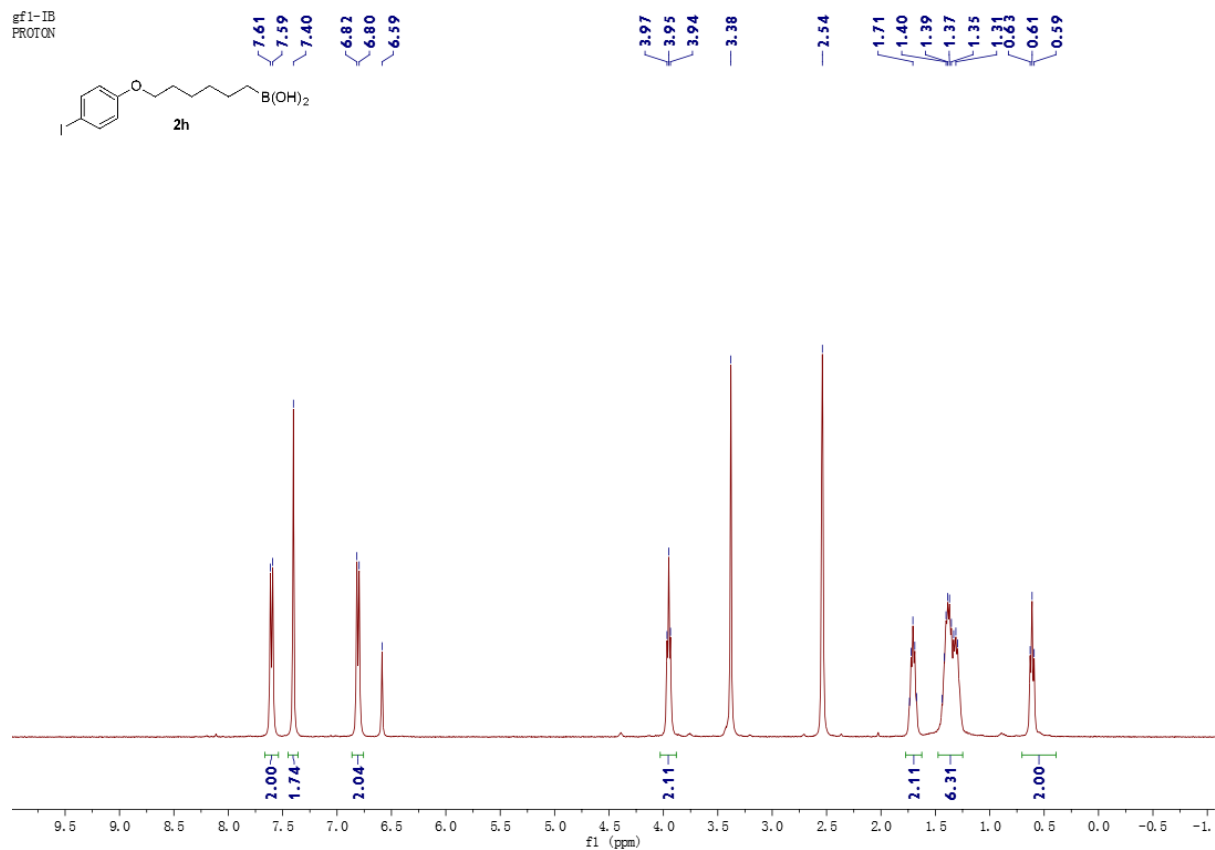
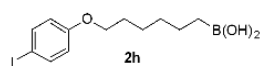
1gx-2-195
PROTON



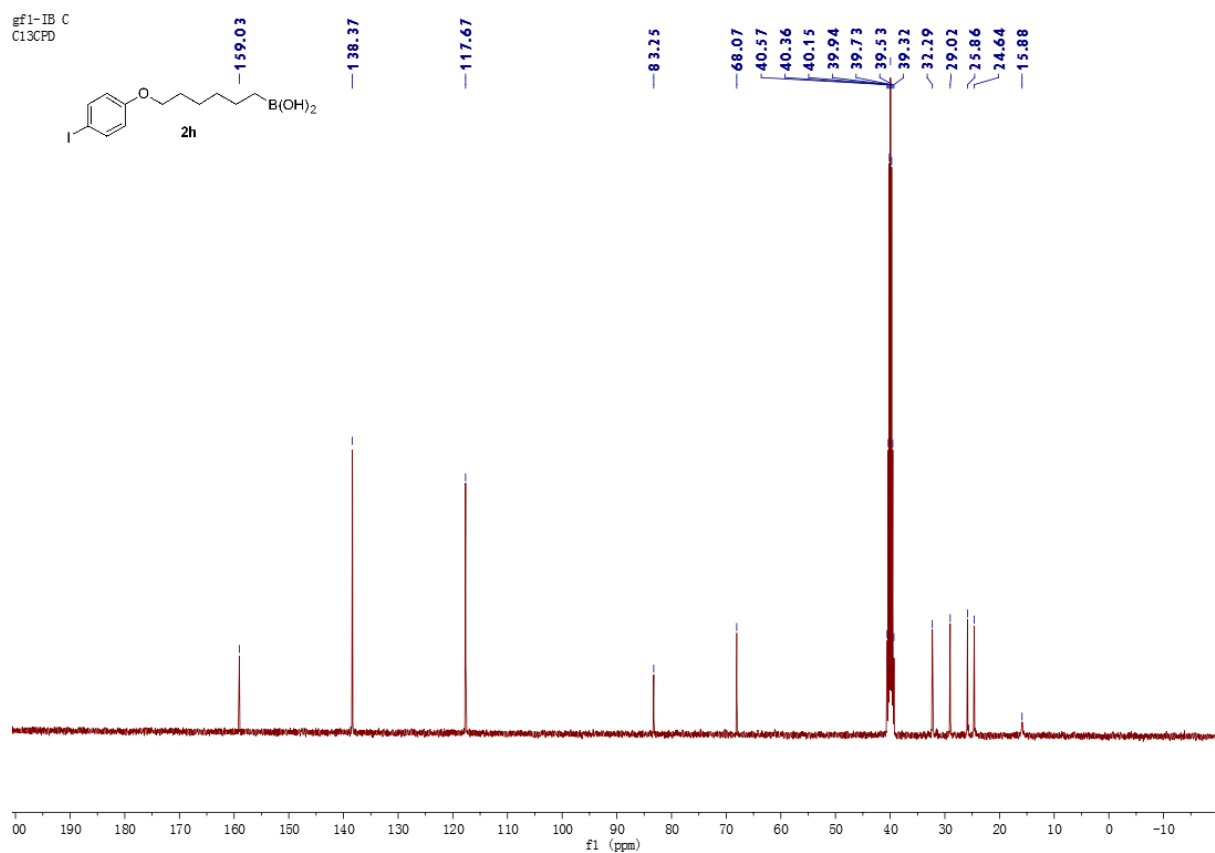
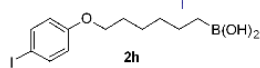
1gx-2-195
C13CPD



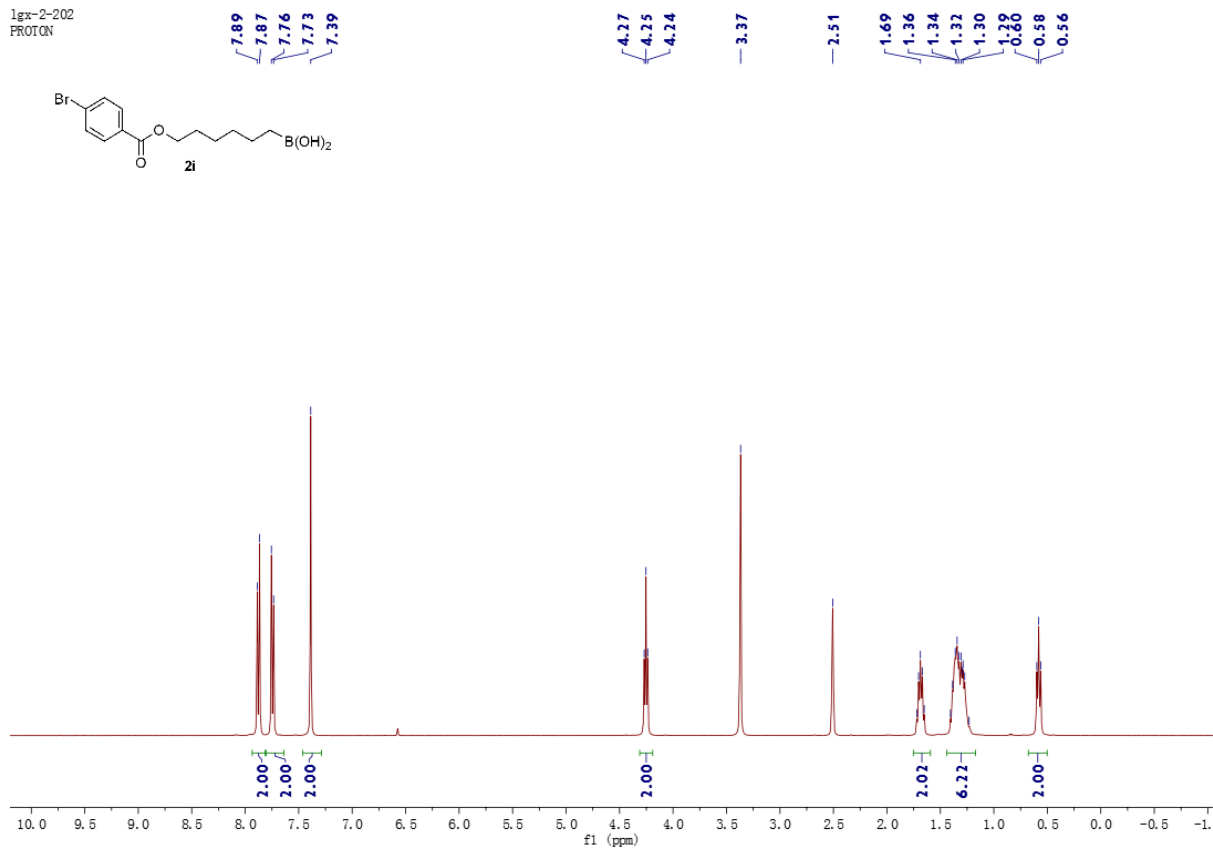
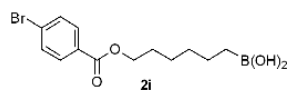
gf1-IB
PROTON



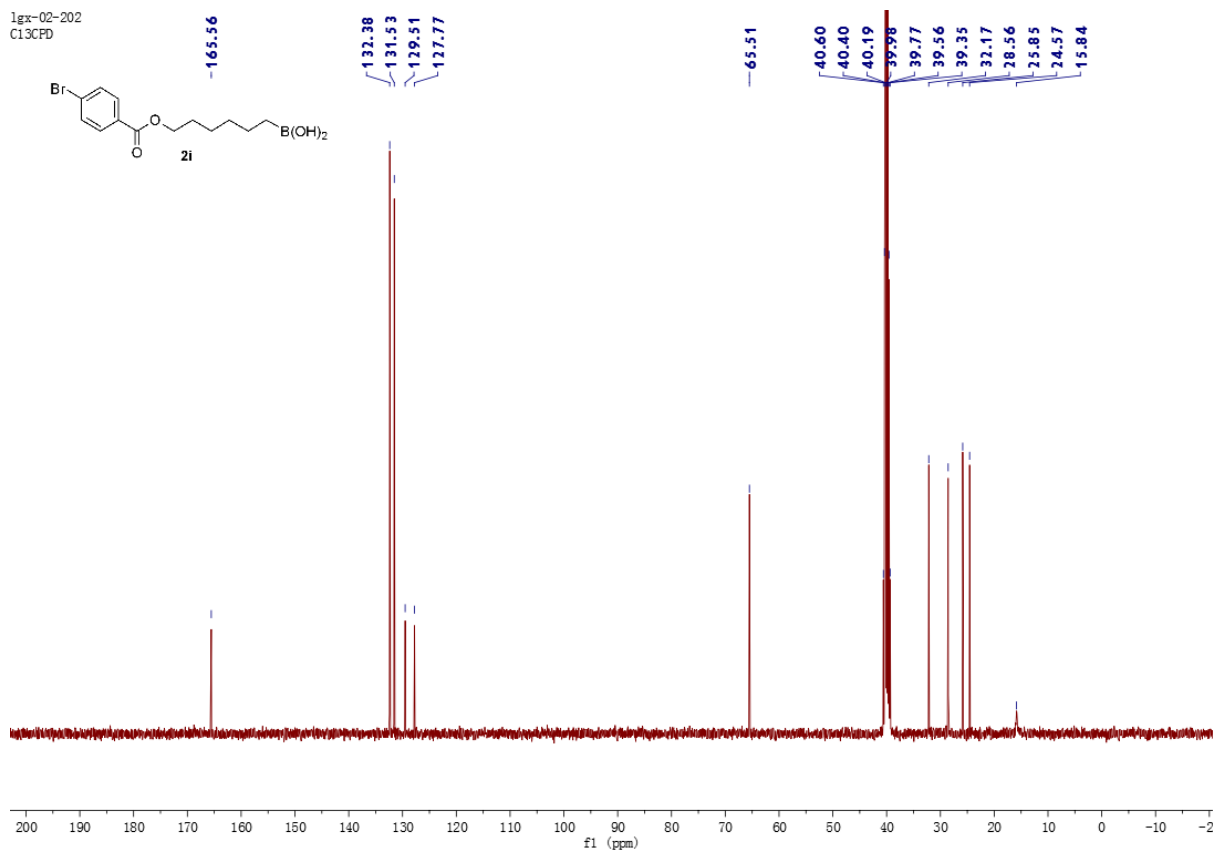
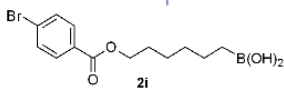
gf1-IB C
C13CPD



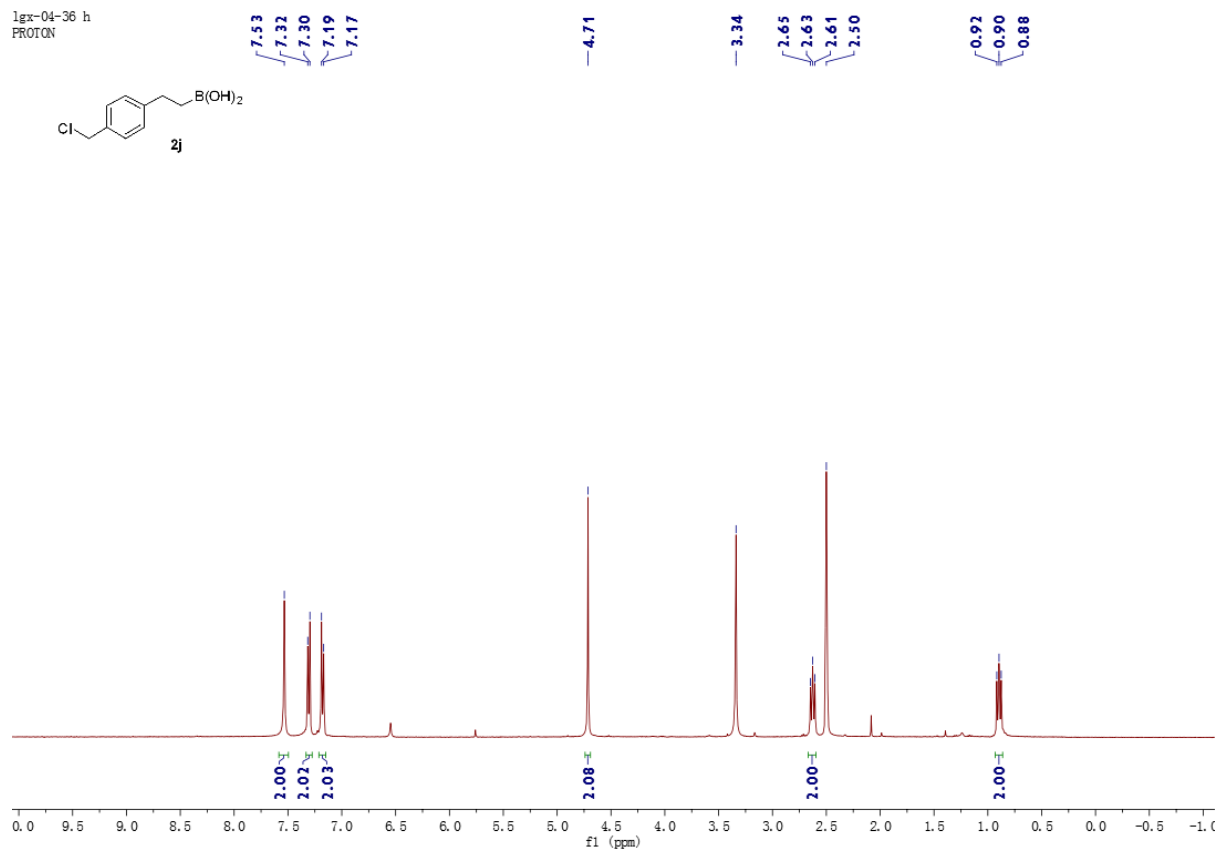
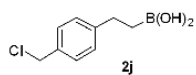
1gx-2-202
PROTON



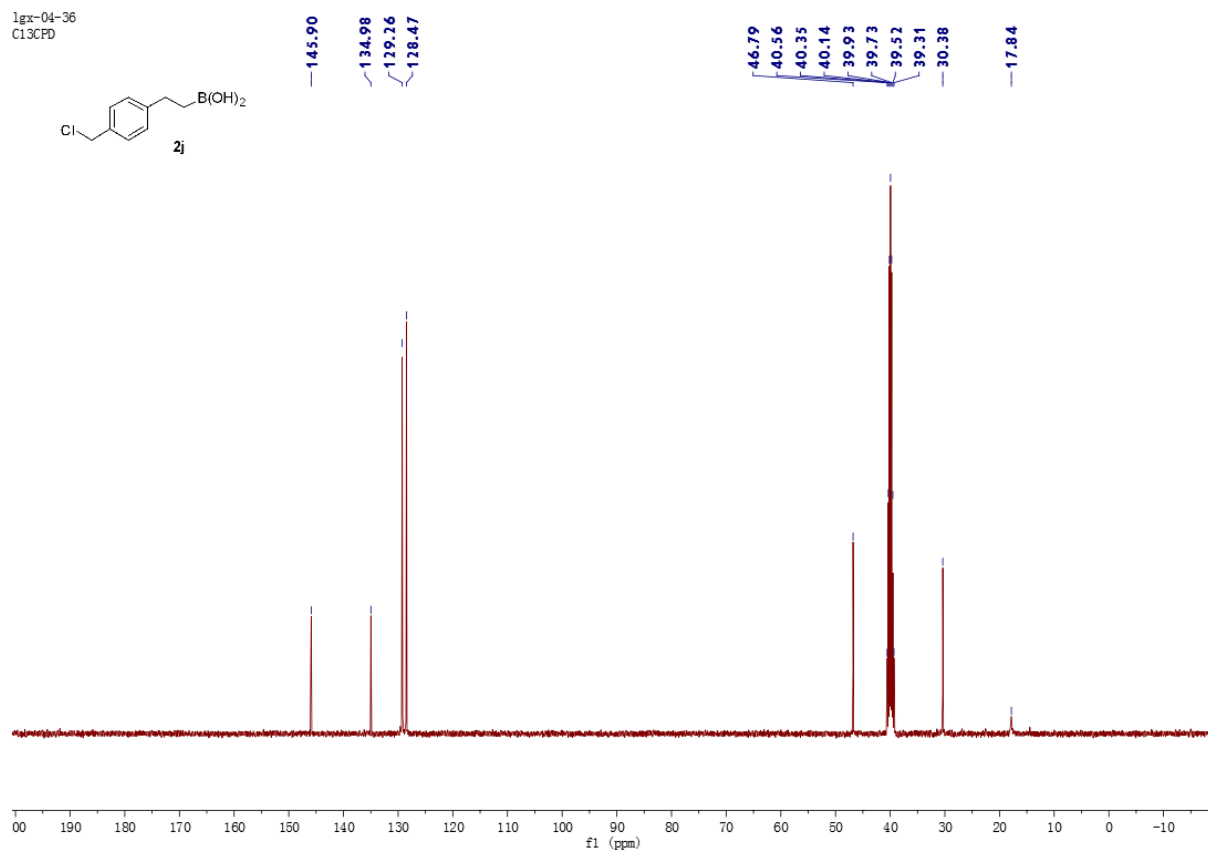
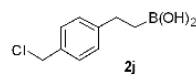
1gx-02-202
C13CPD



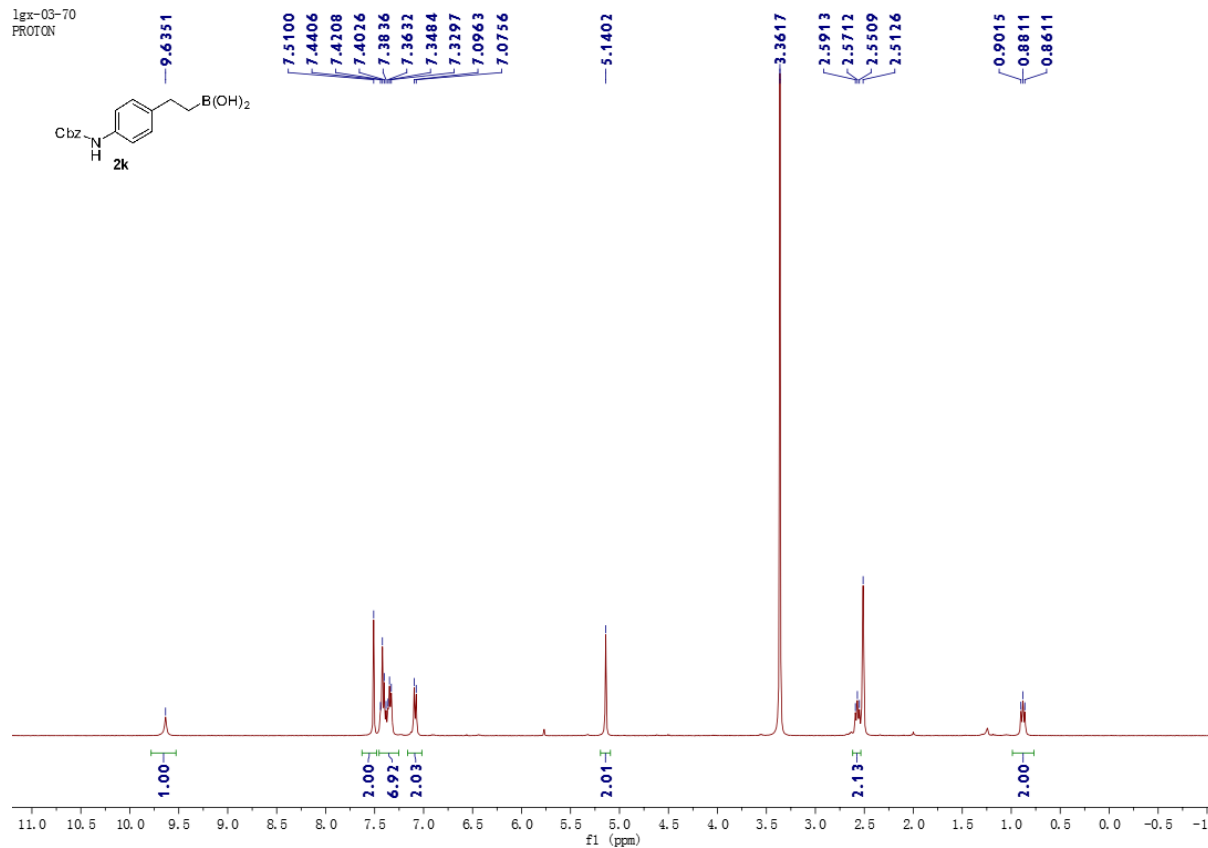
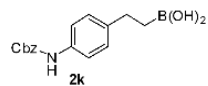
1gx-04-36 h
PROTON



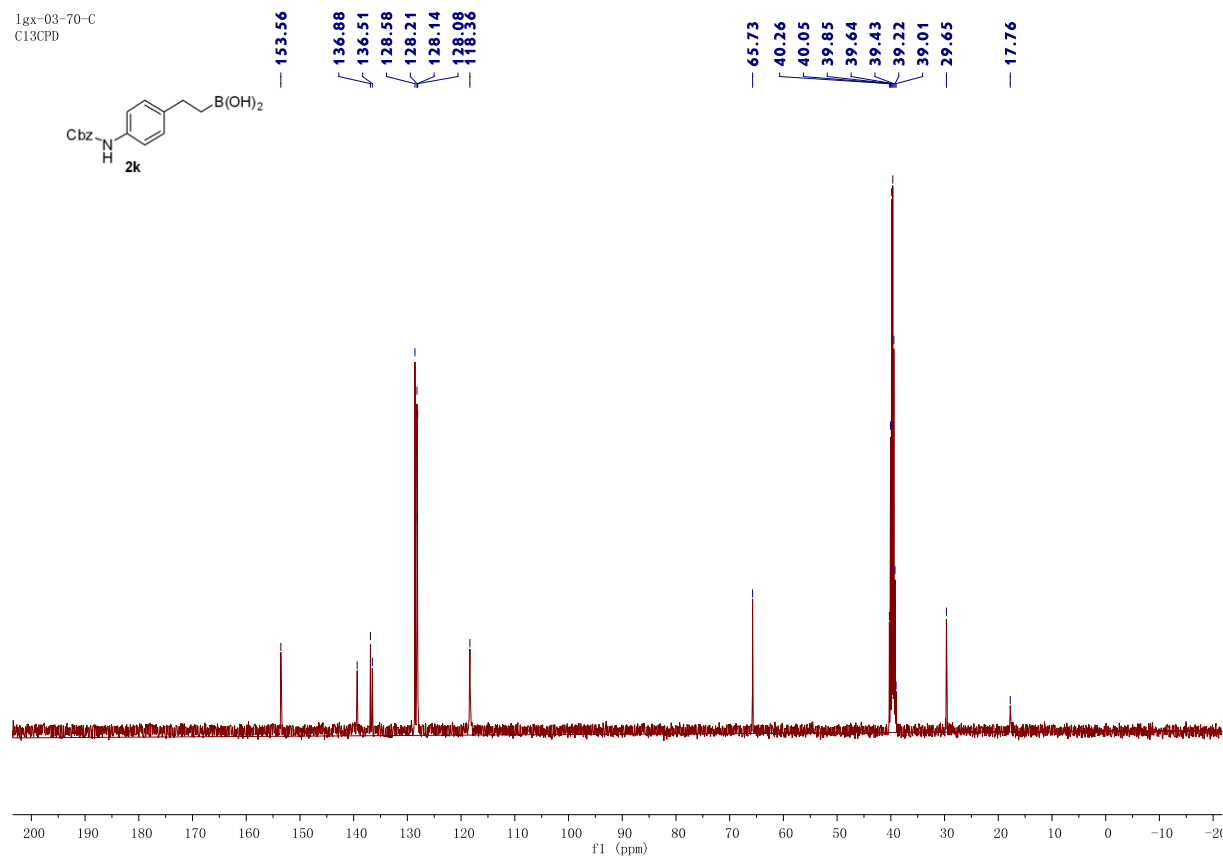
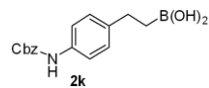
1gx-04-36
C13CPD



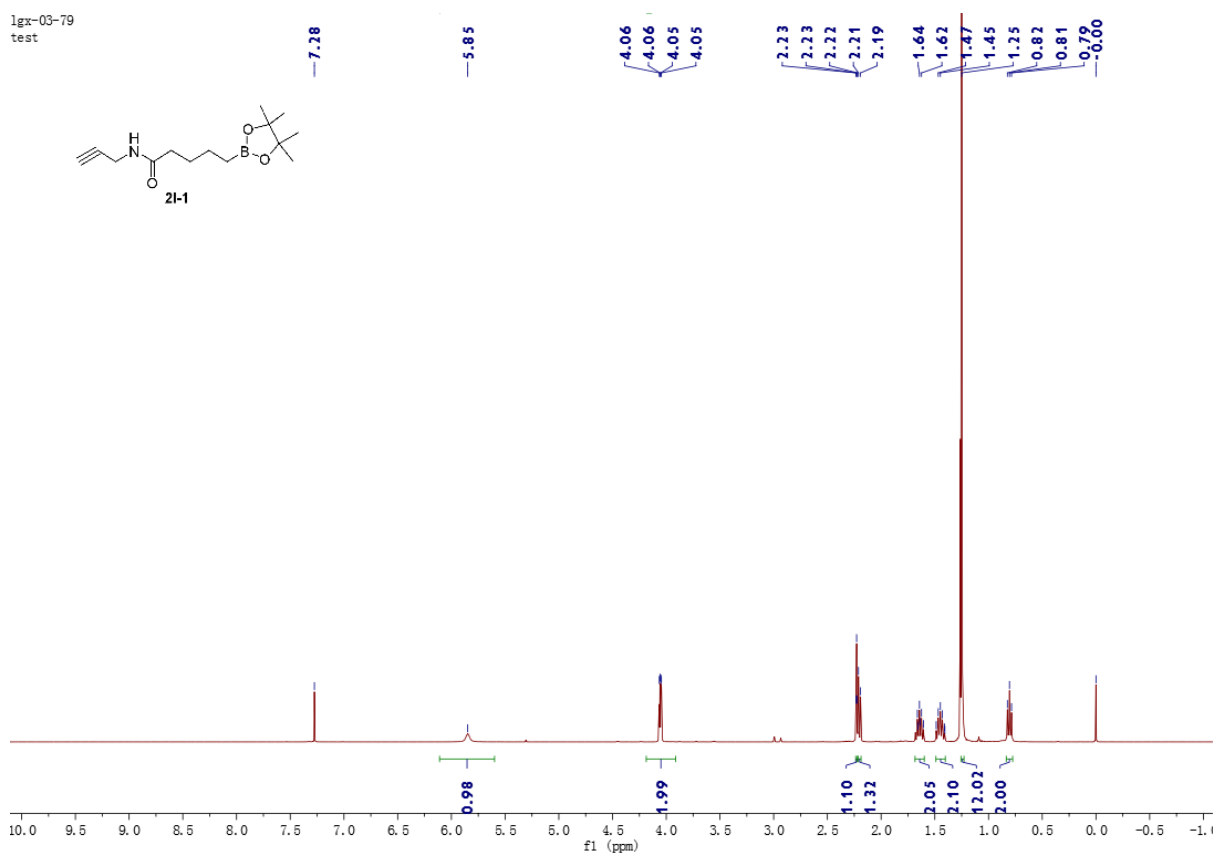
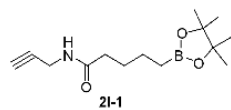
1gx-03-70
PROTON



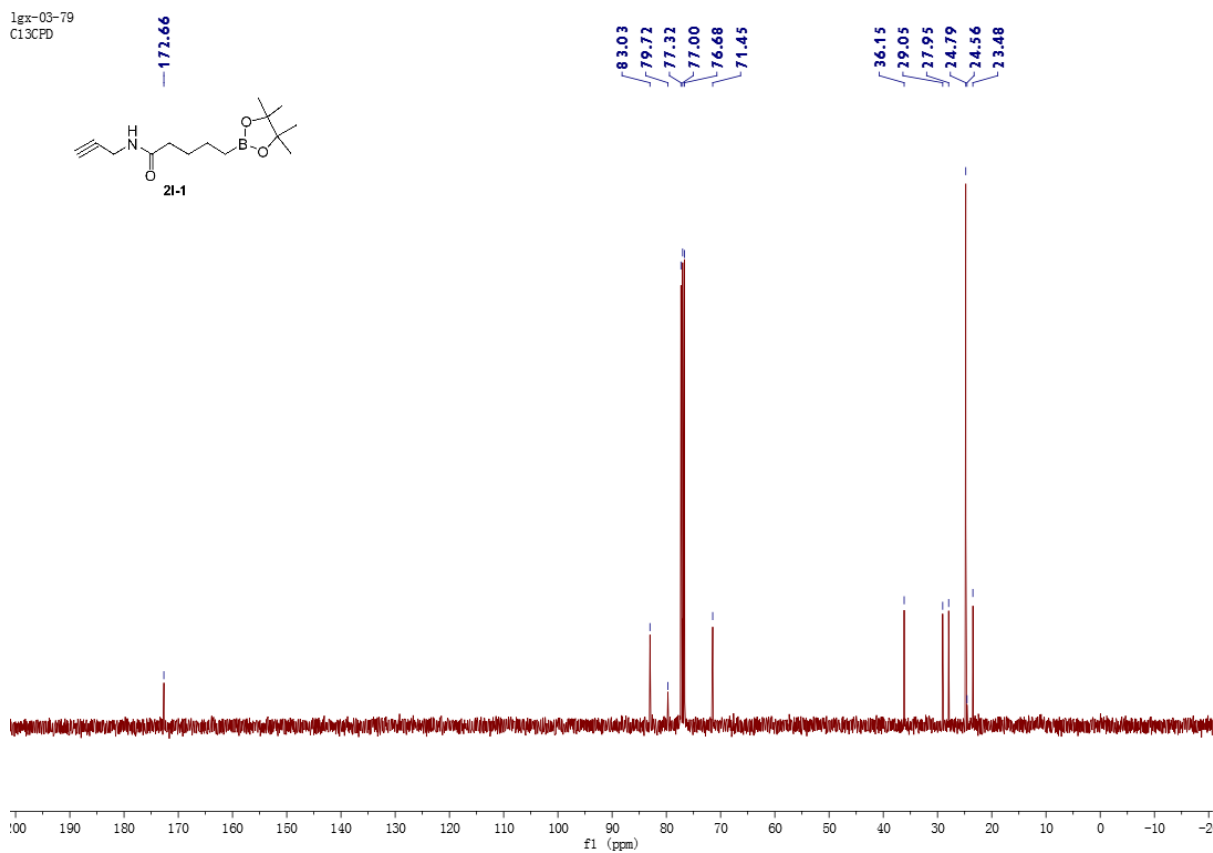
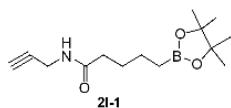
1gx-03-70-C
C13CPD



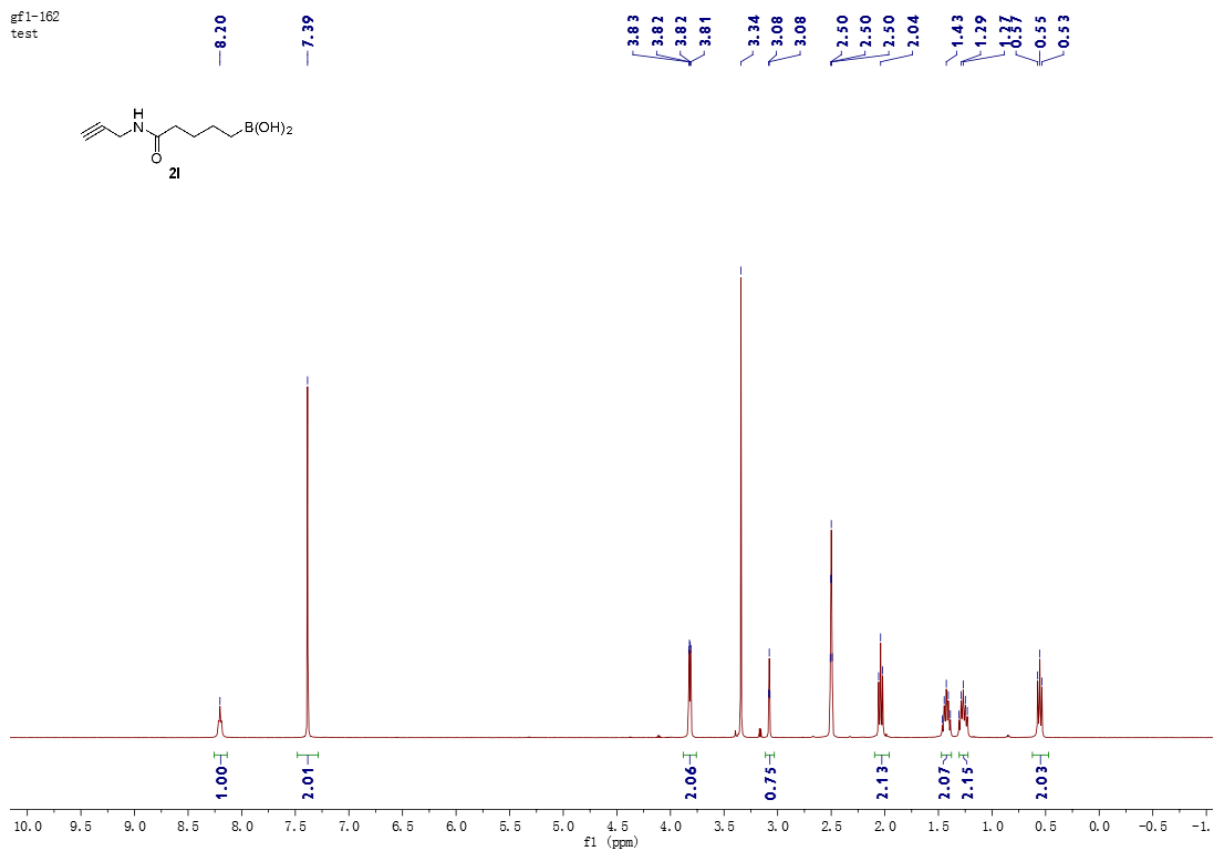
lgx-03-79
test



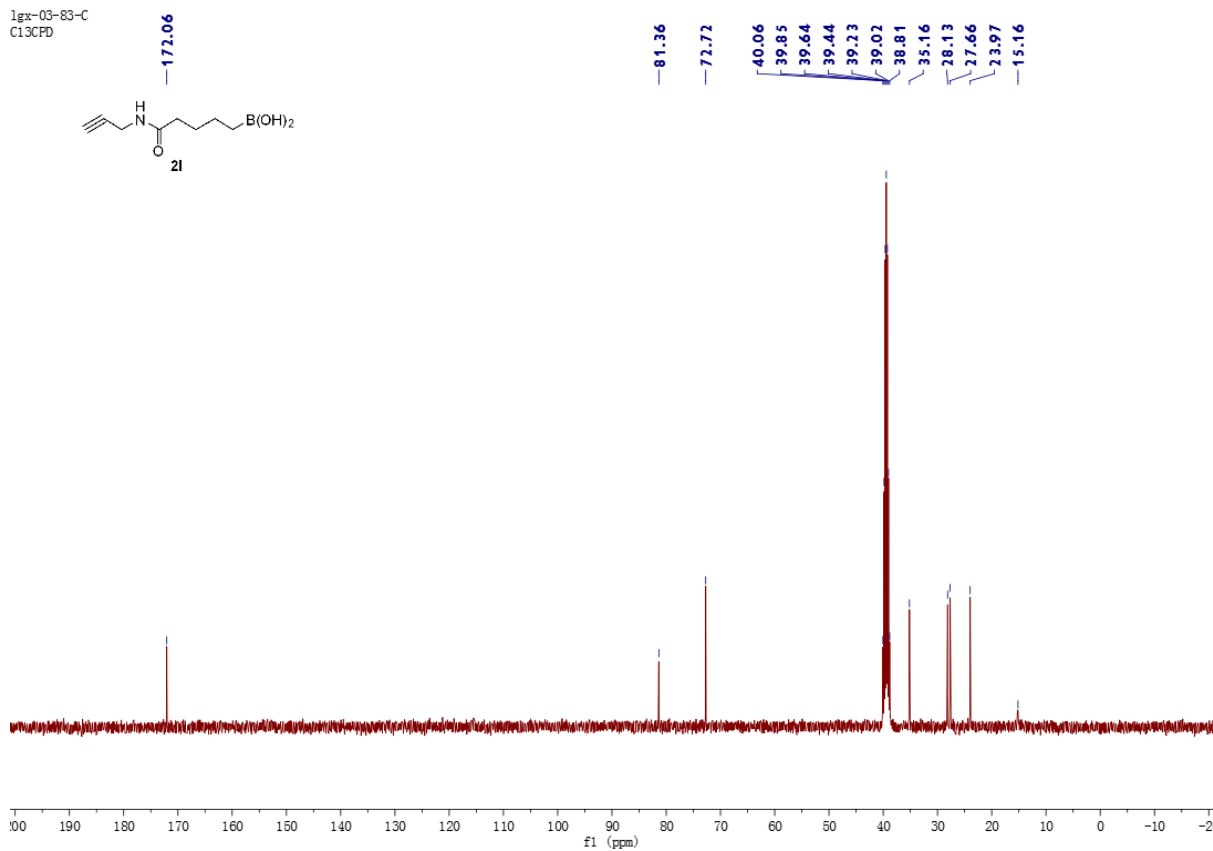
lgx-03-79
C13CPD

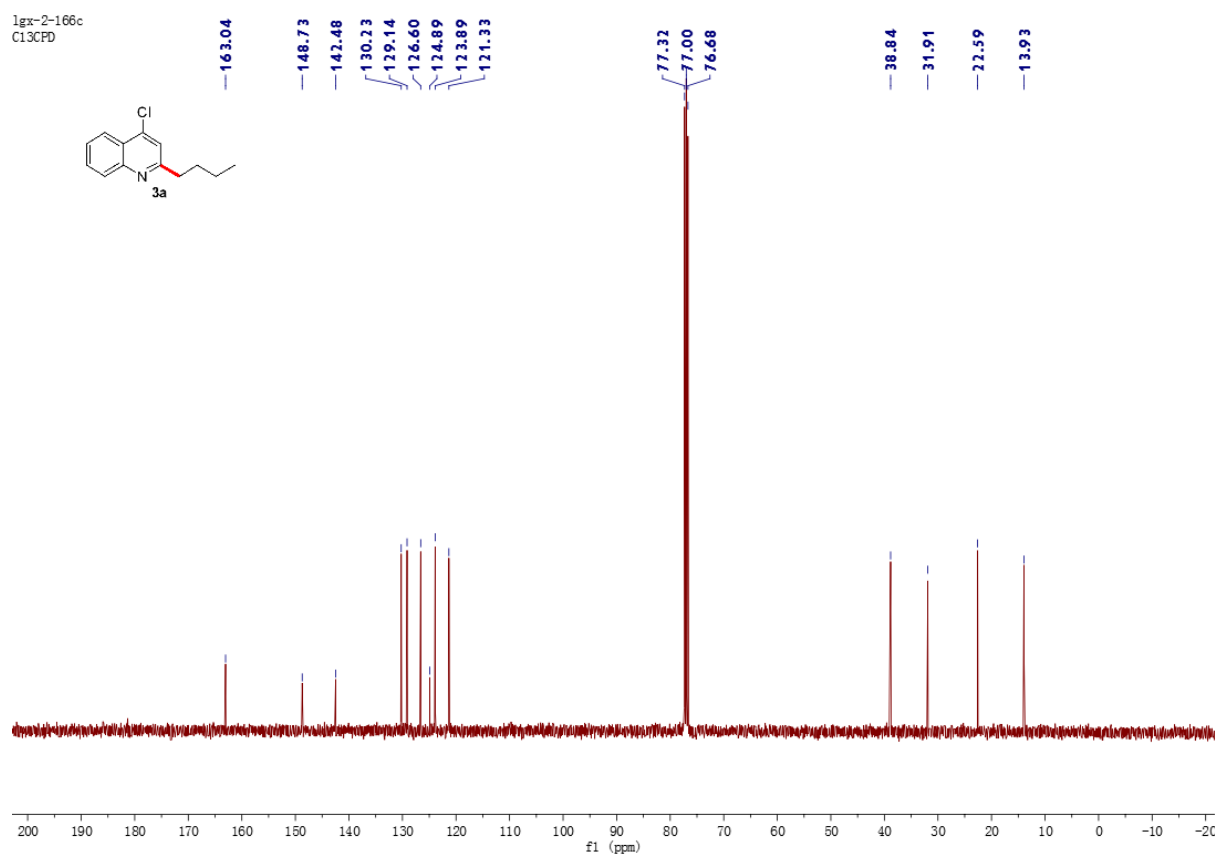
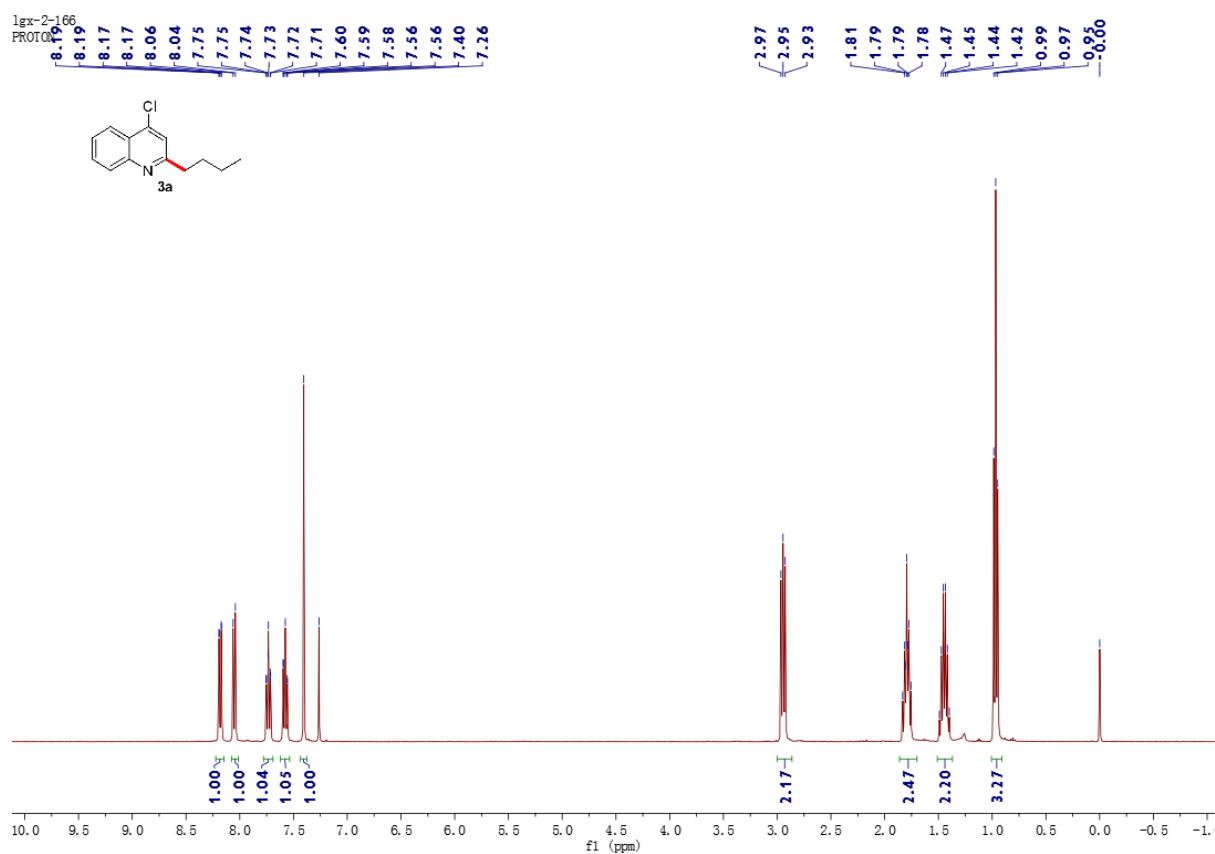


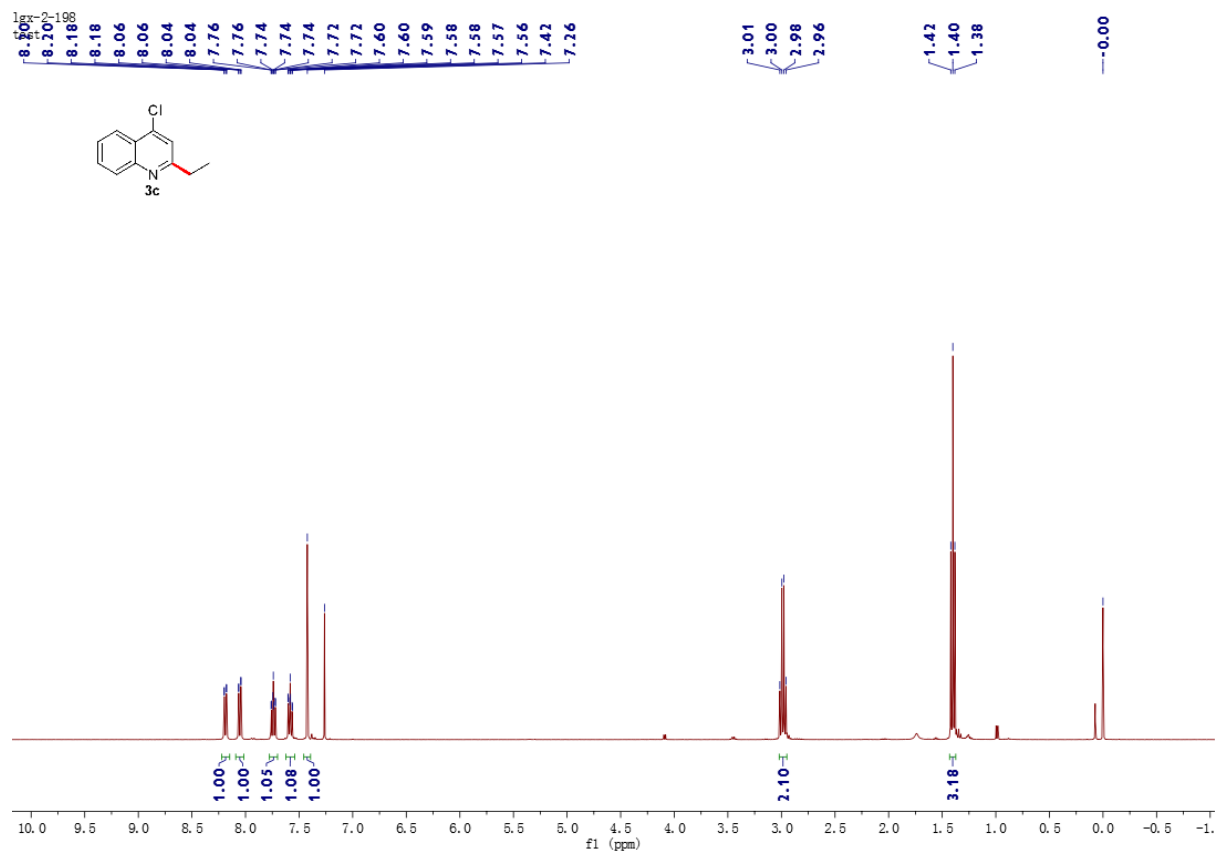
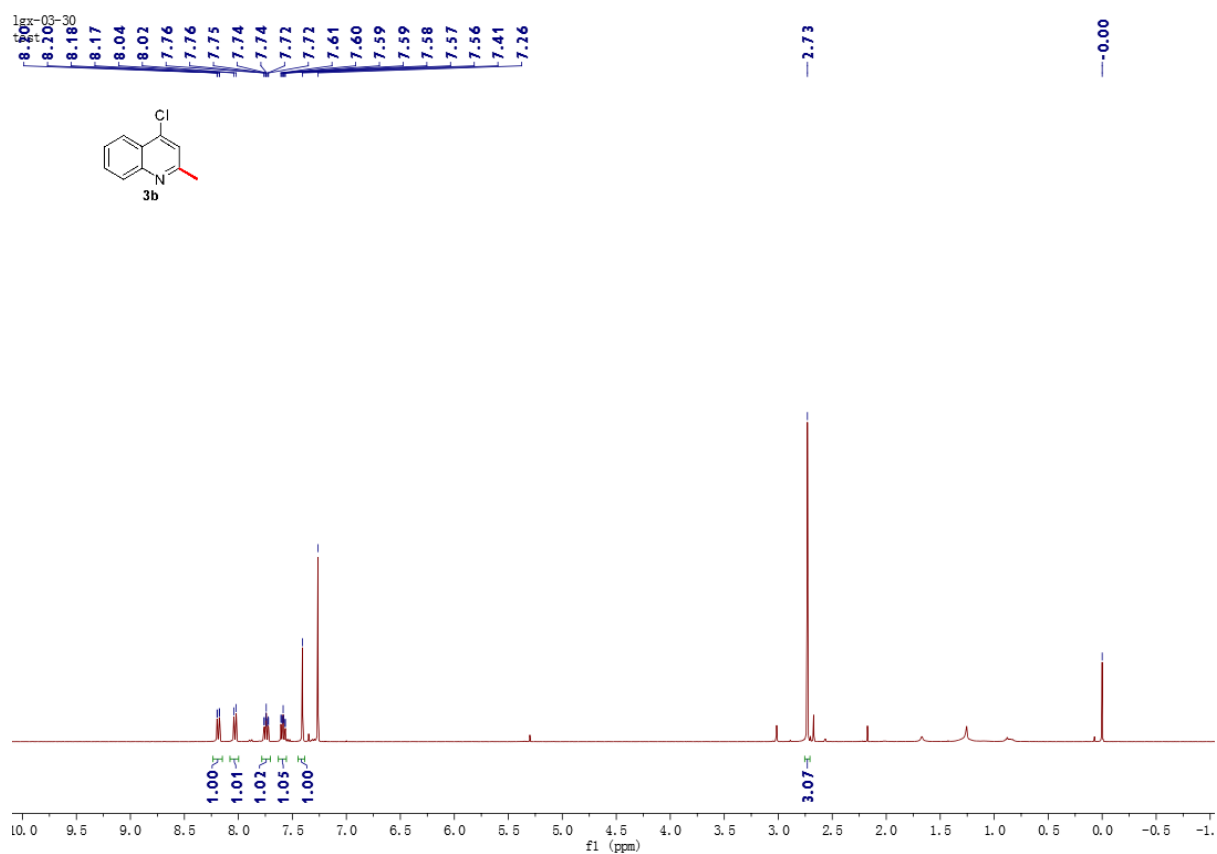
gf1-162
test

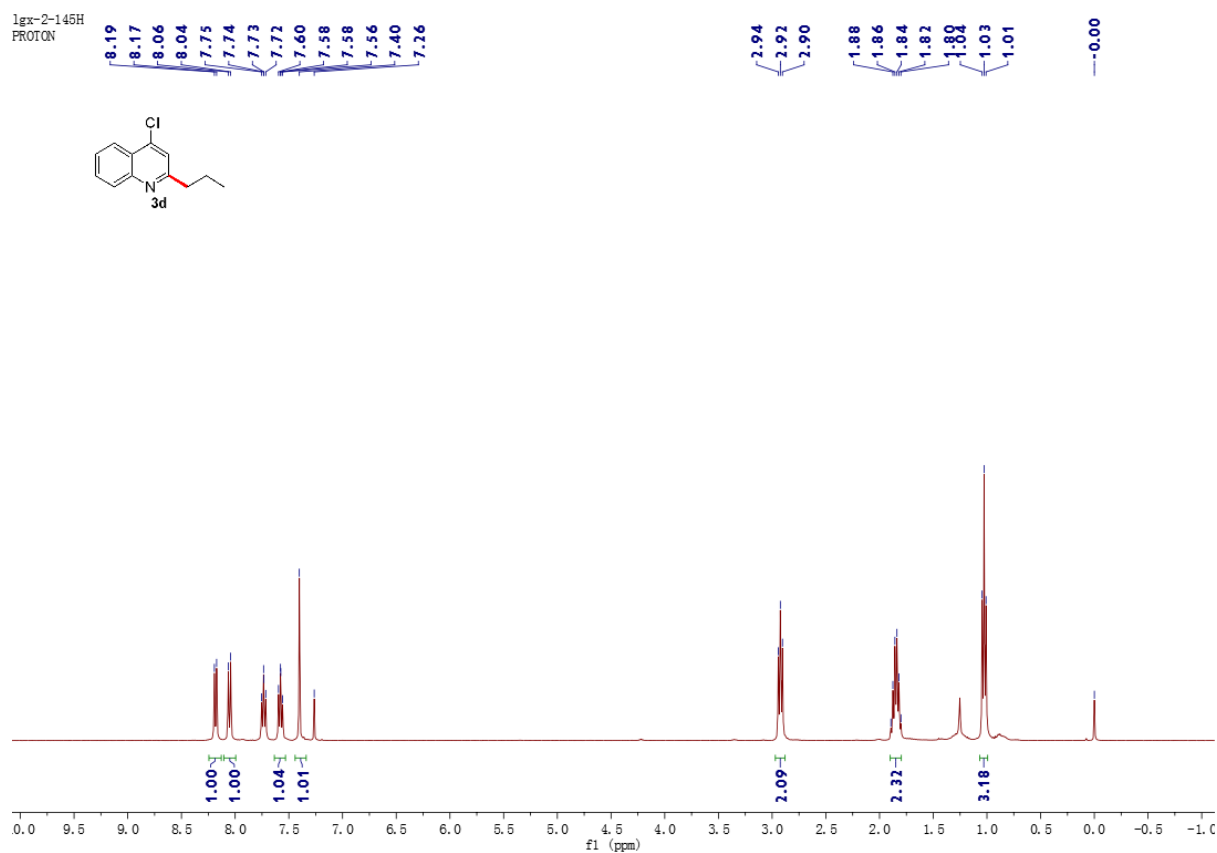
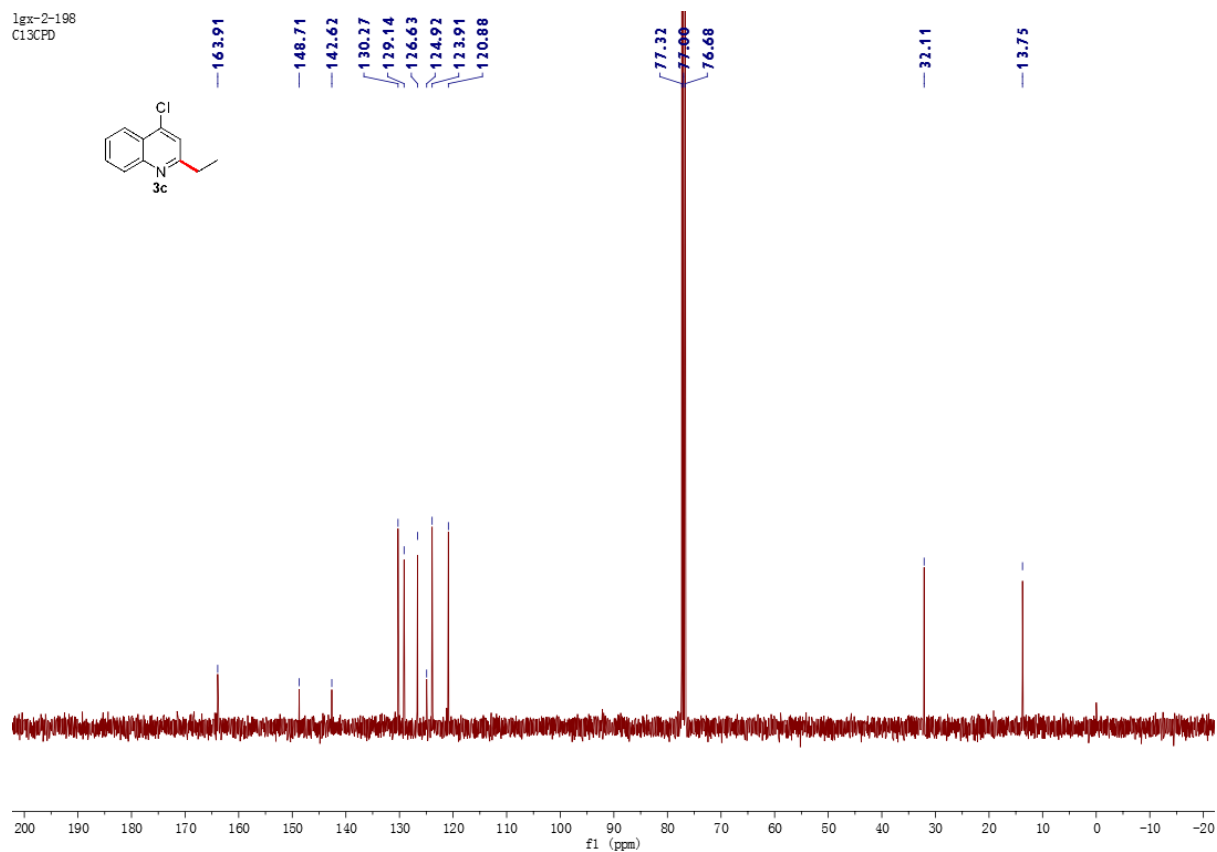


1gx-03-83-C
C13CPD

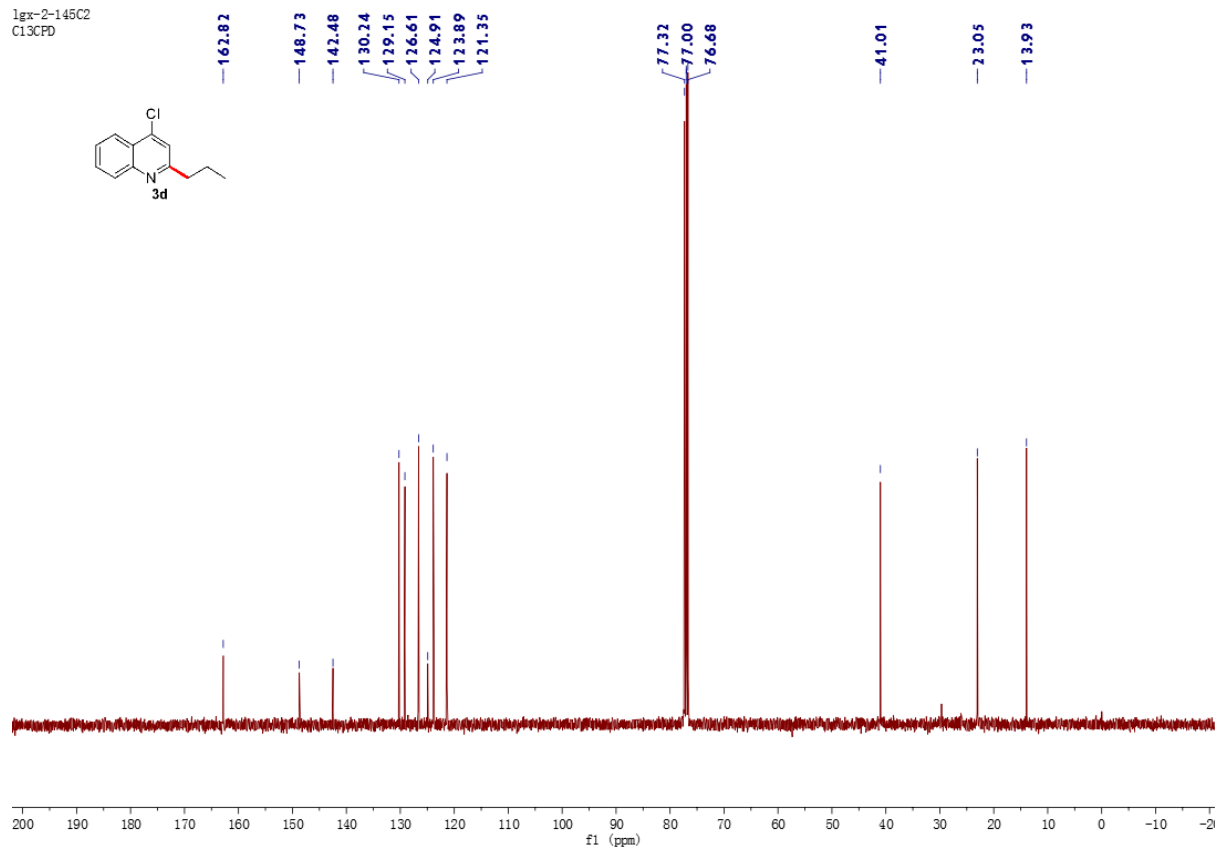
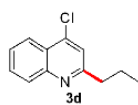




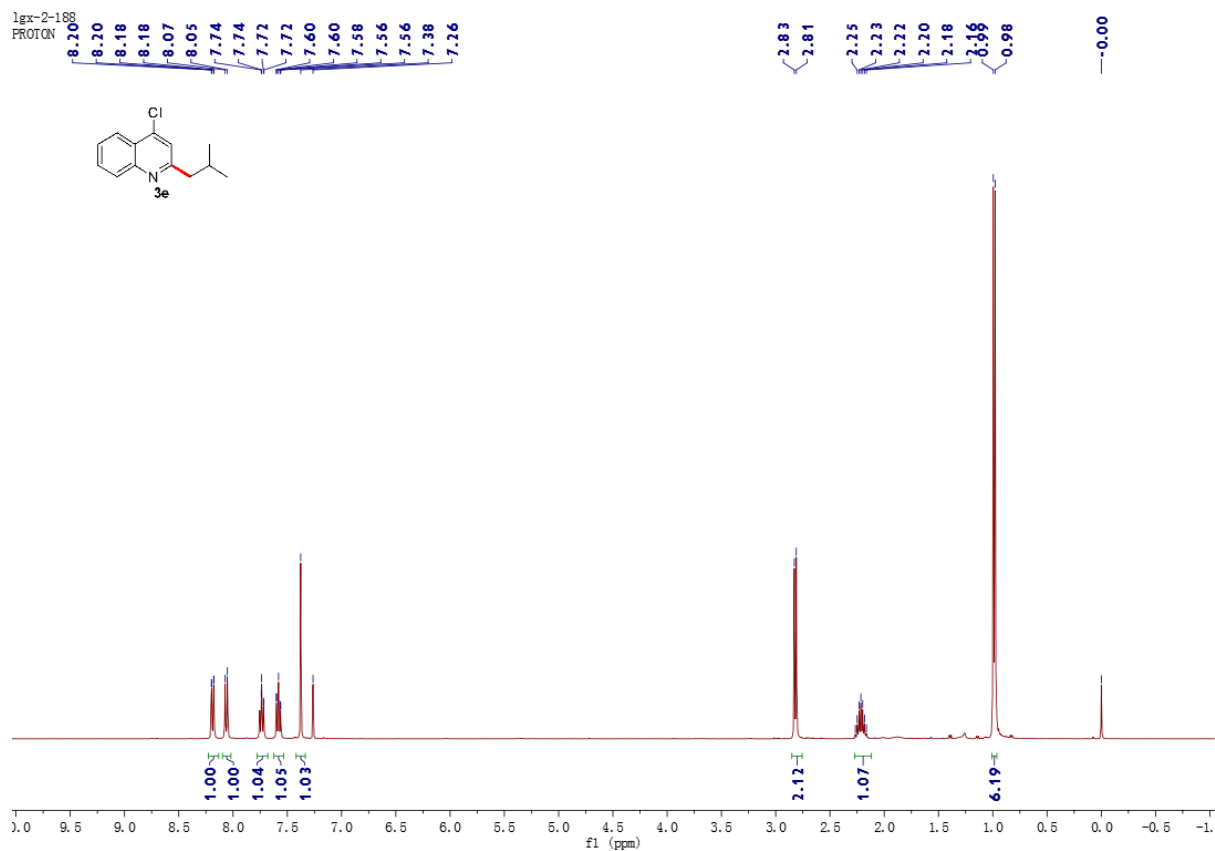
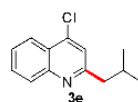


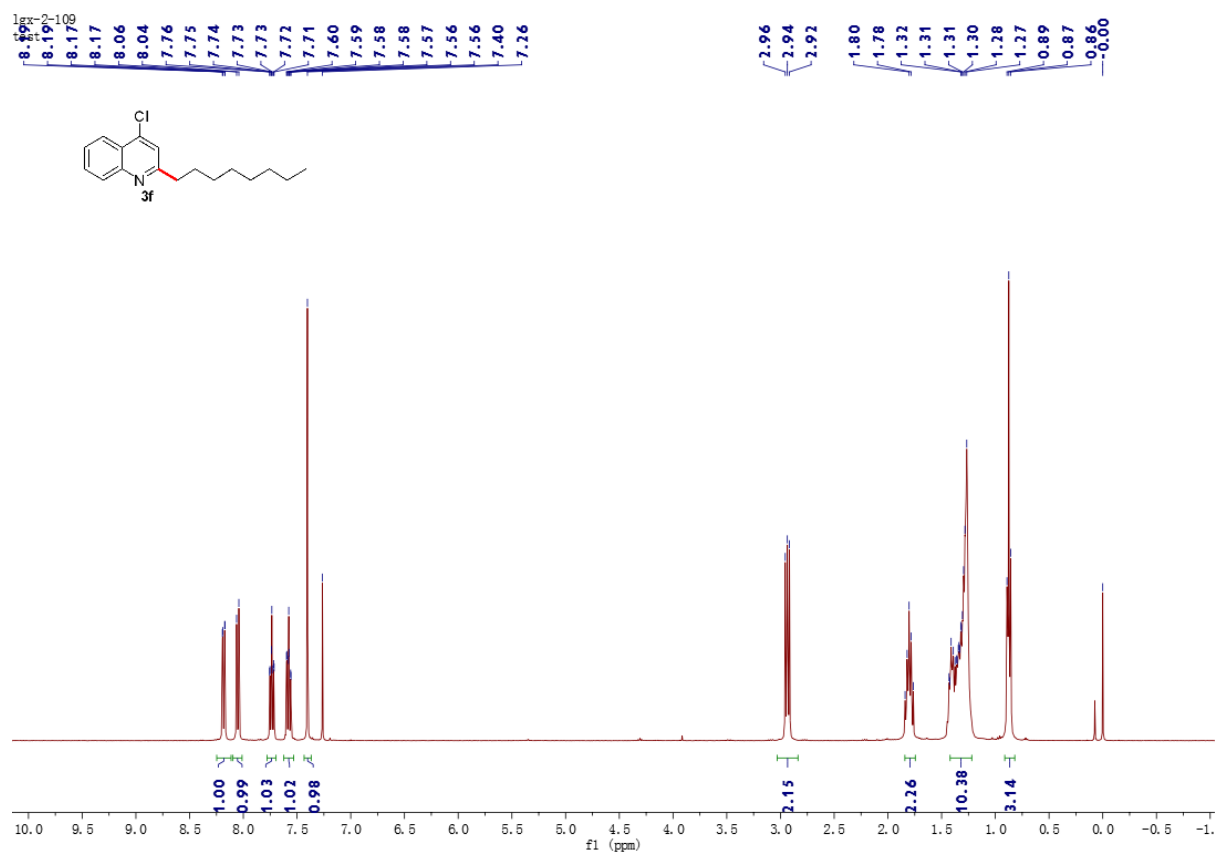
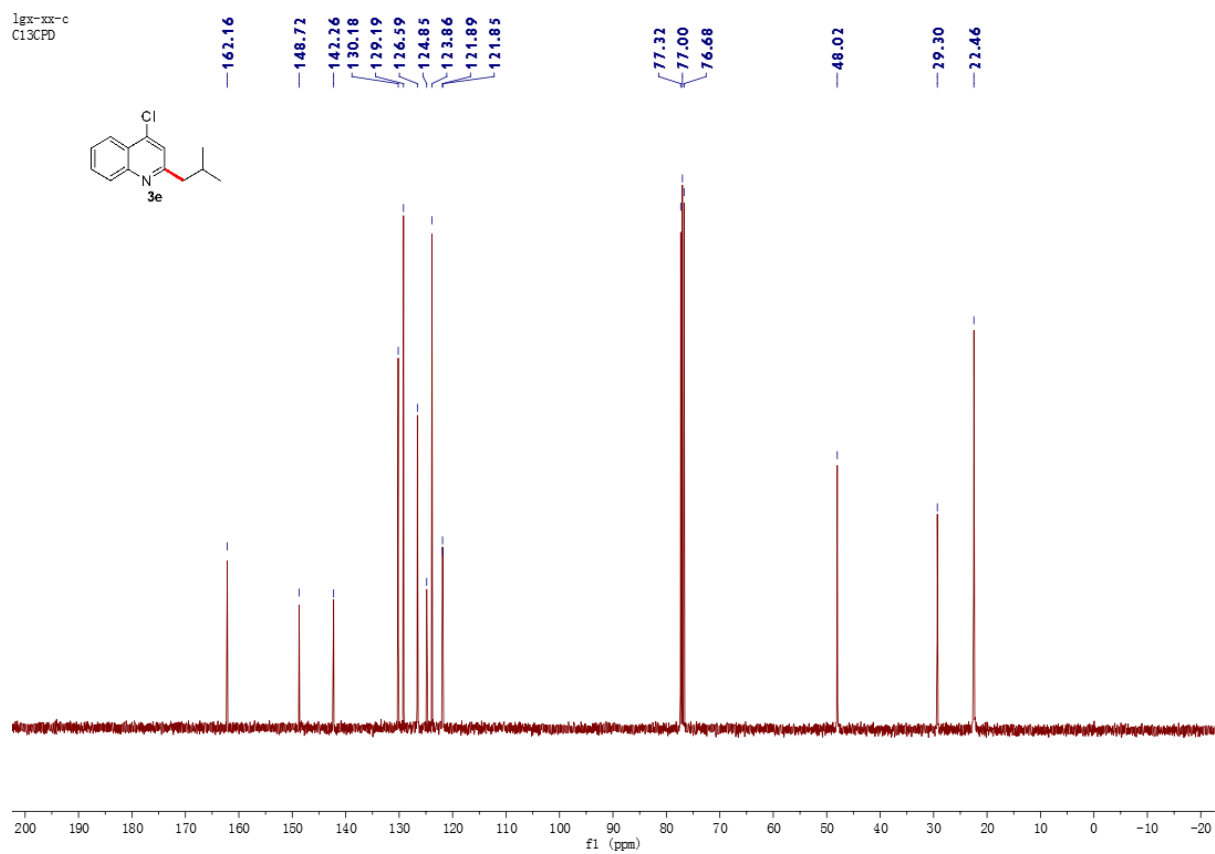


1gx-2-145C2
C13CPD

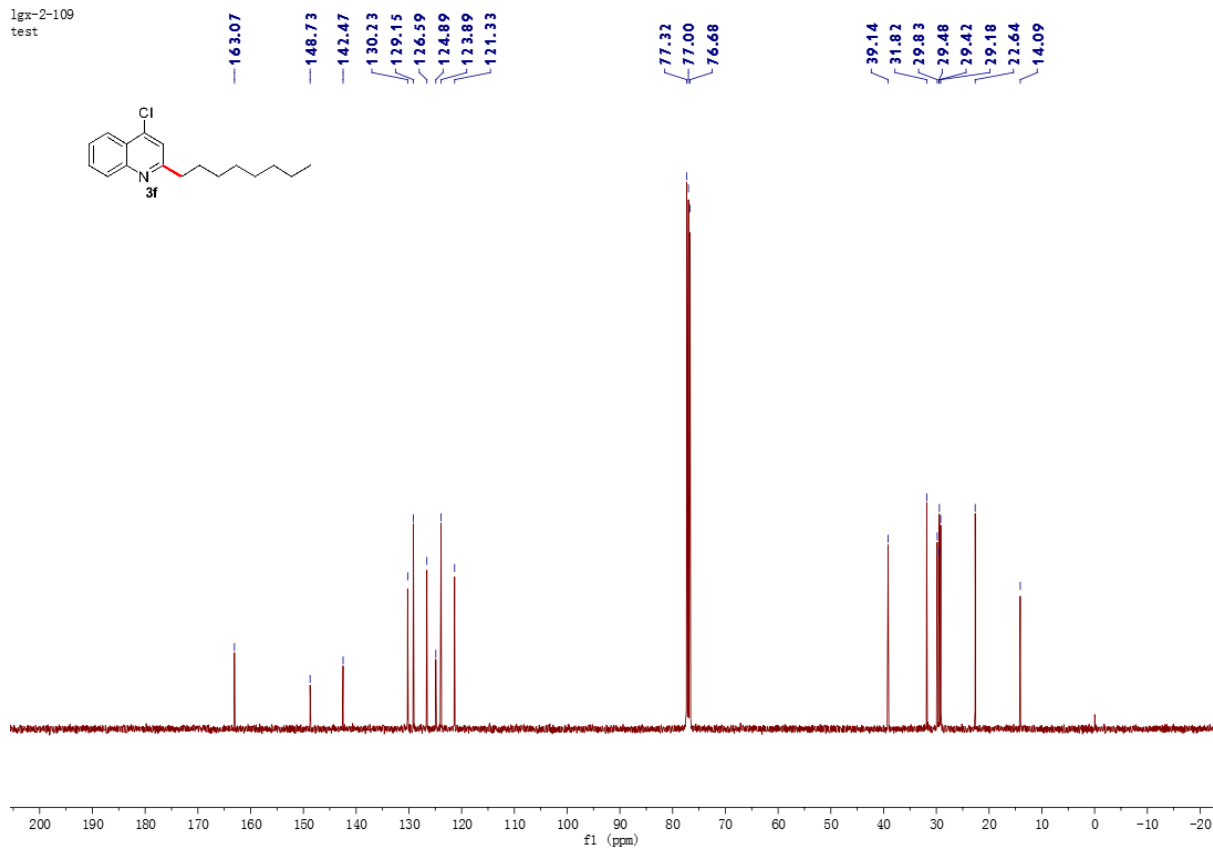
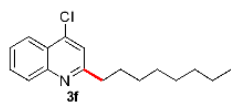


1gx-2-188
PROTON

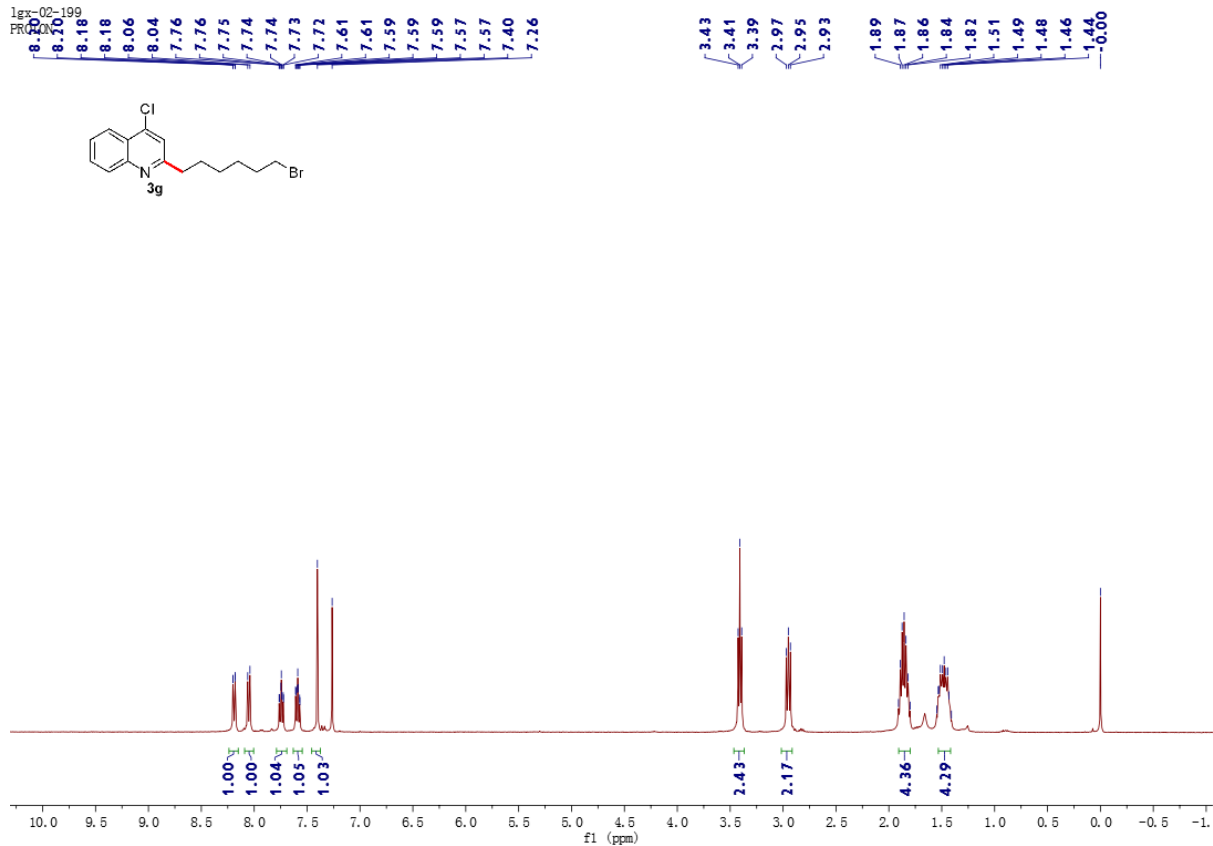
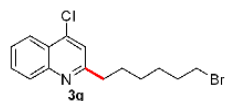




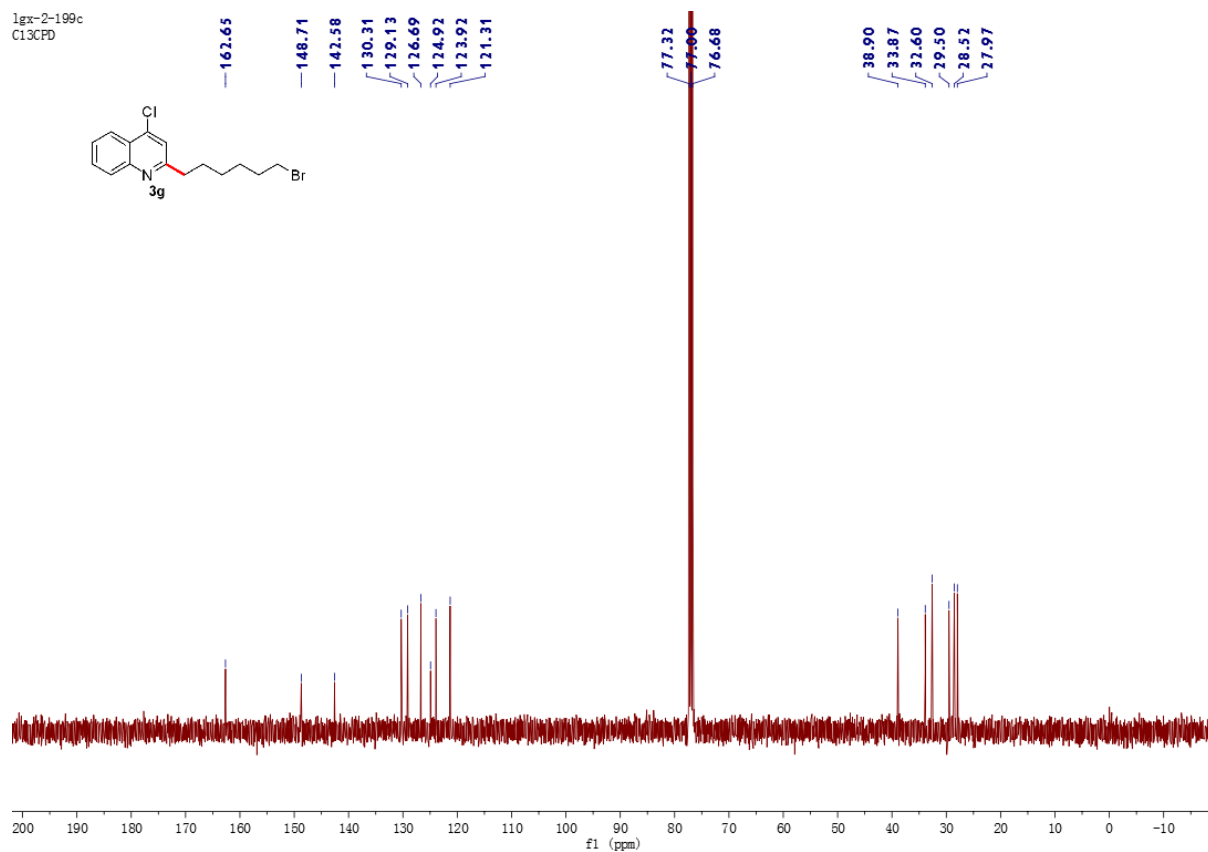
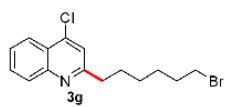
lgx-2-109
test



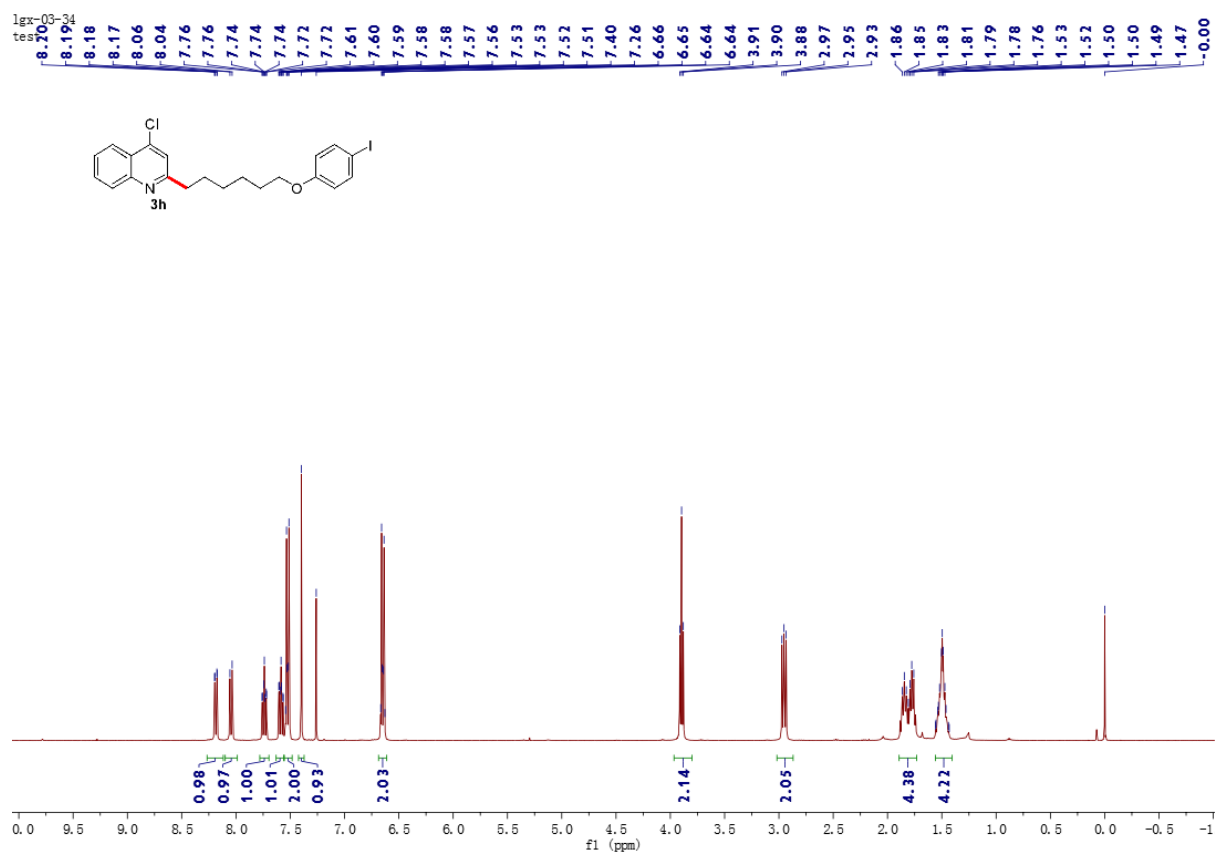
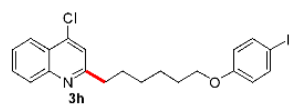
lgx-02-199
PROD



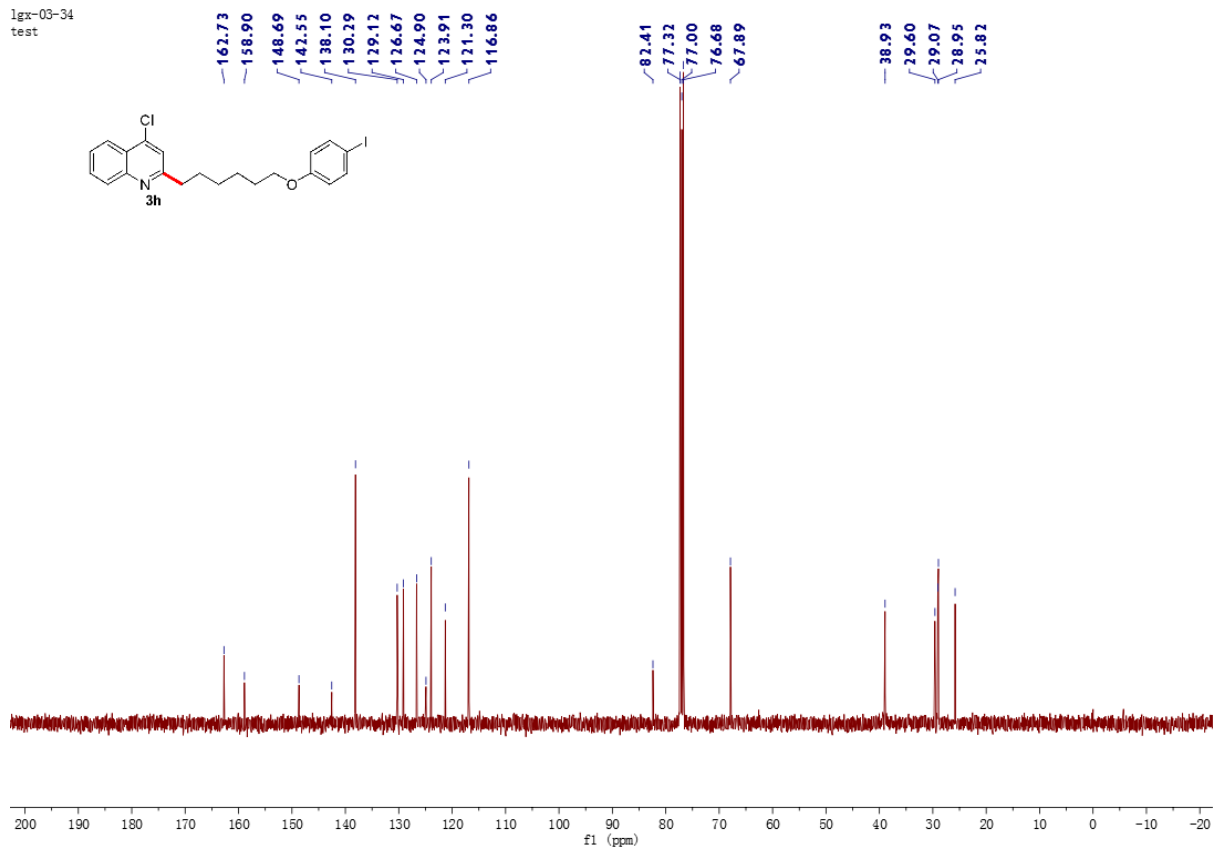
1gx-2-199c
C13CPD



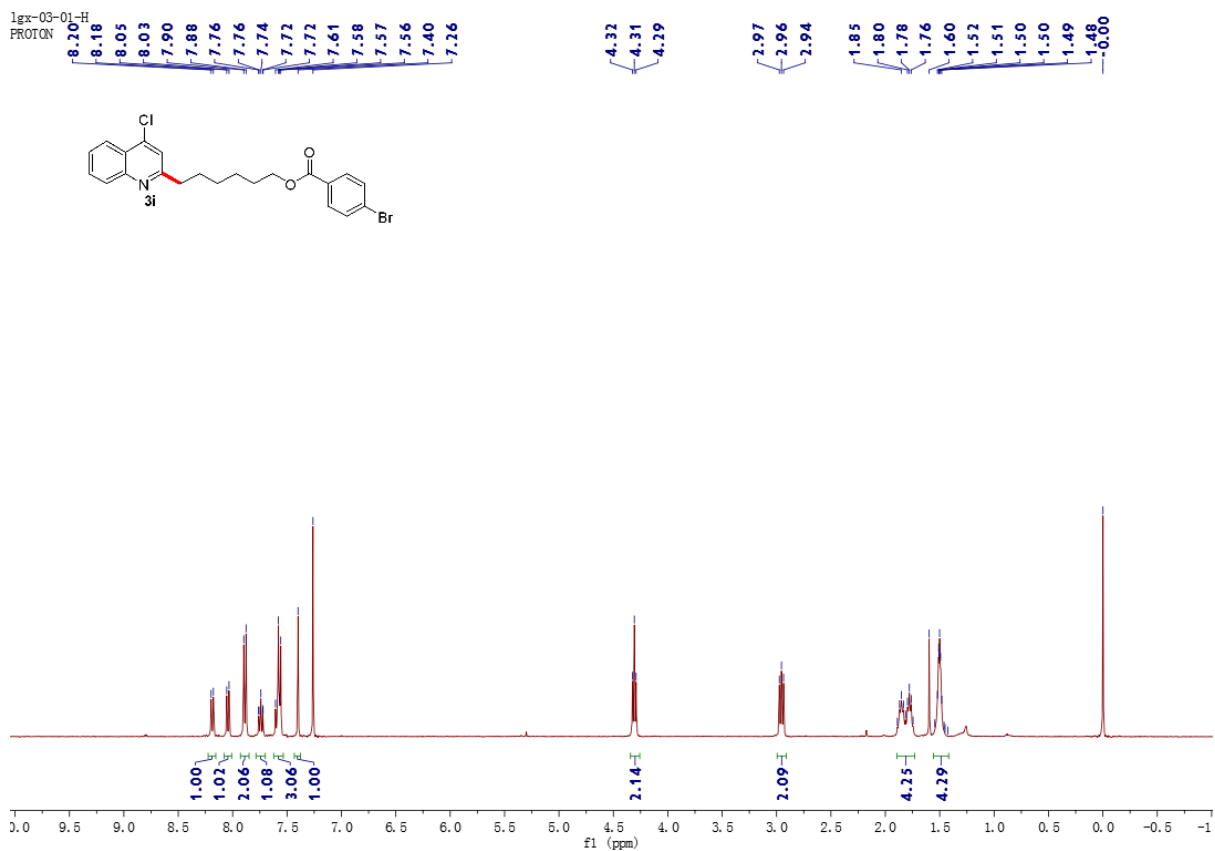
1gx-03-34
tecv



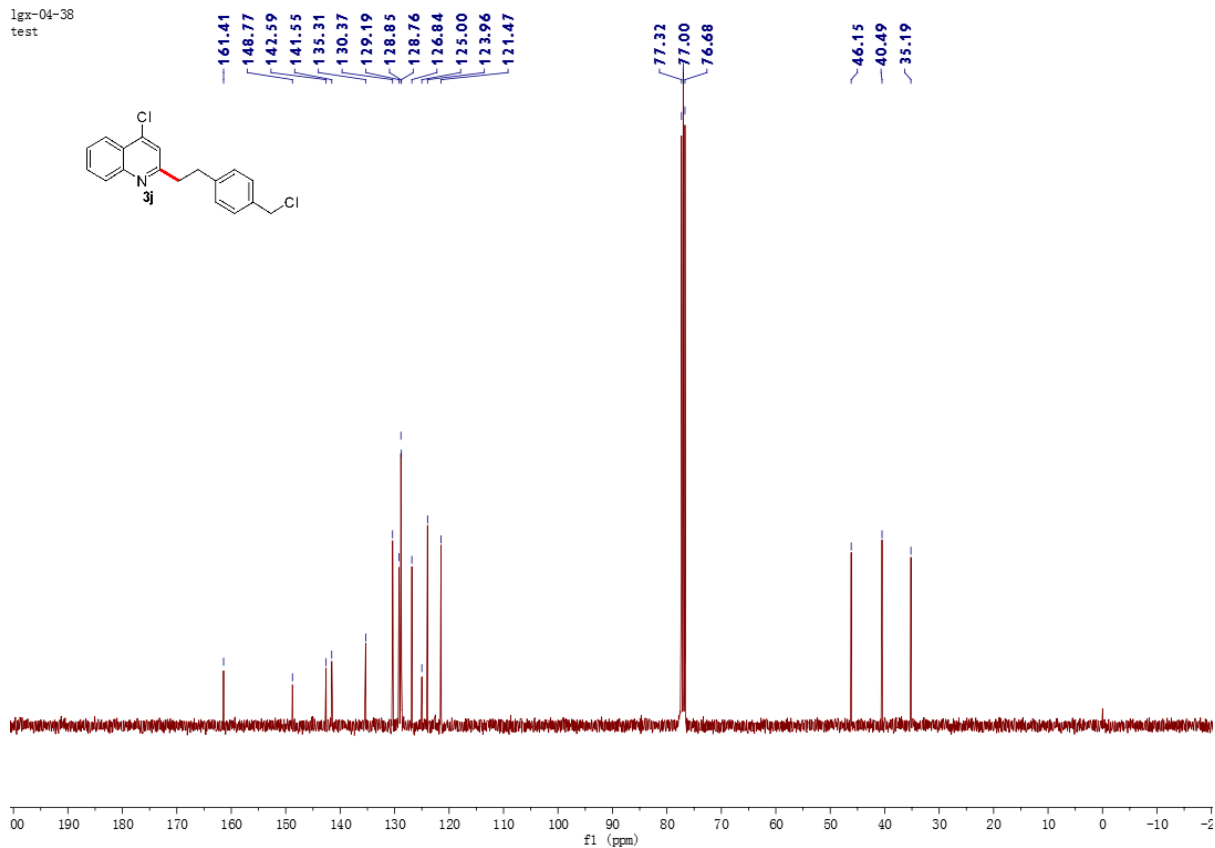
lgx-03-34
test



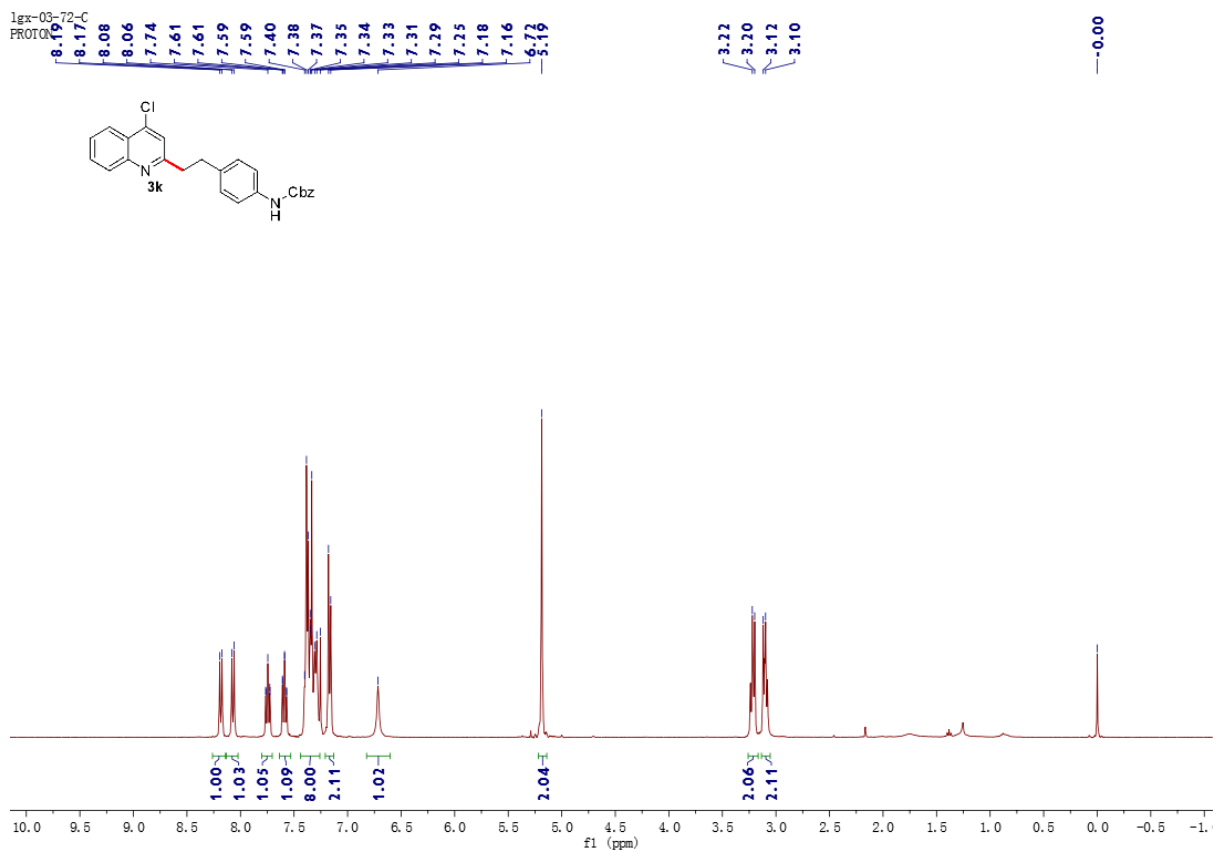
lgx-03-01-H
PROTON

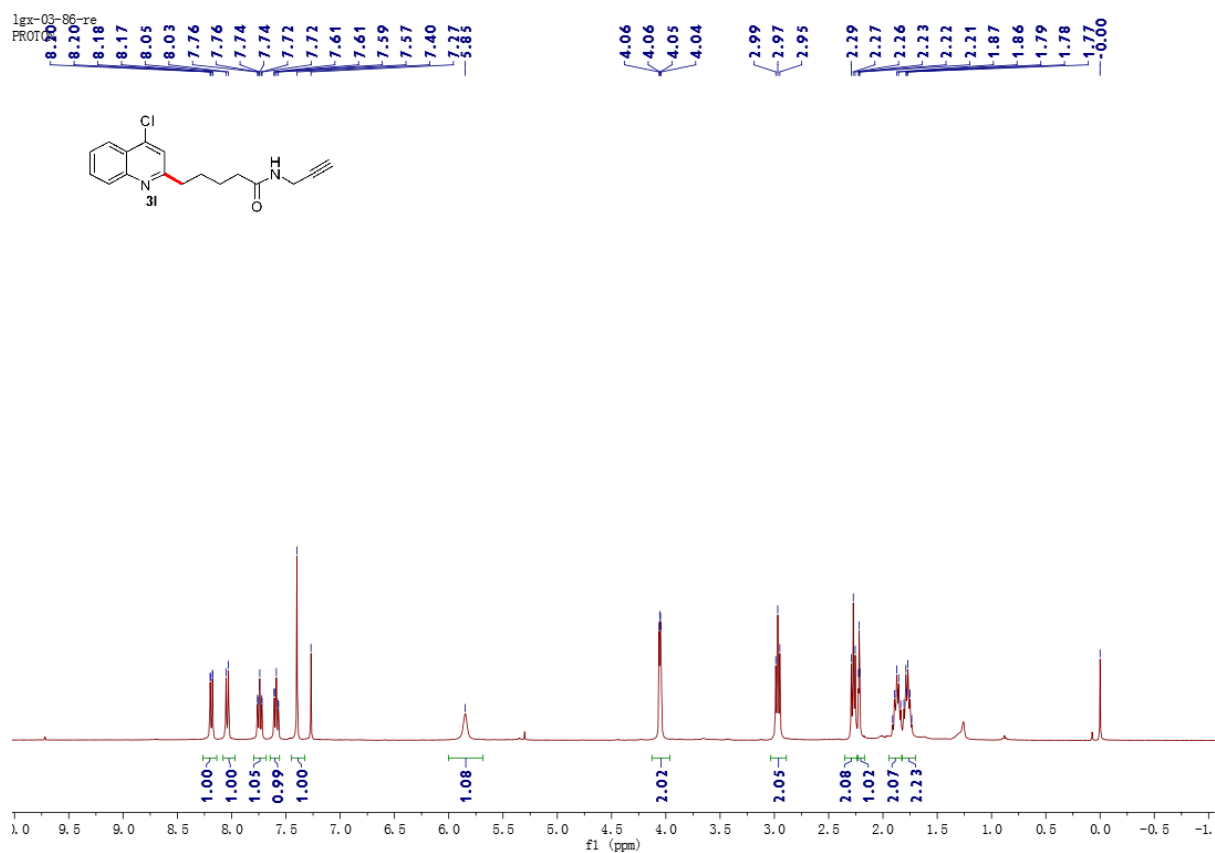
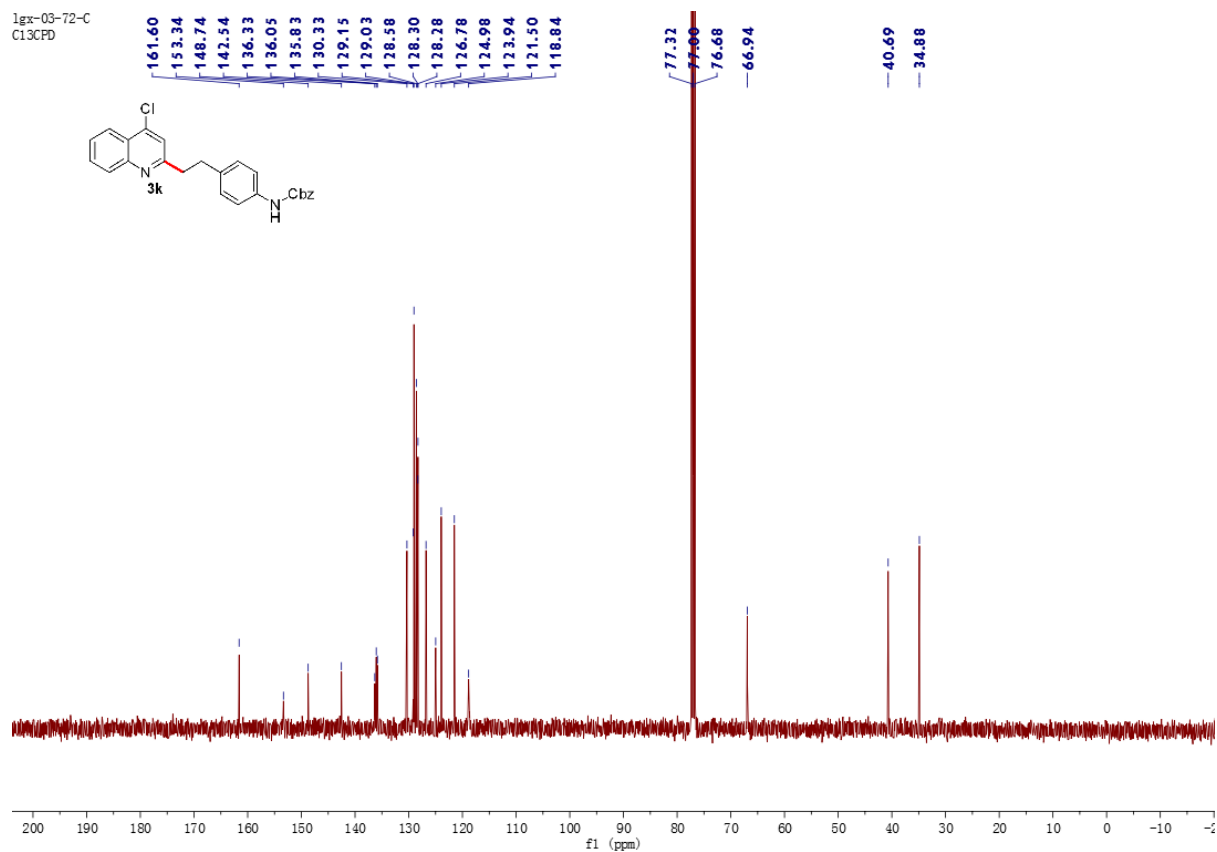


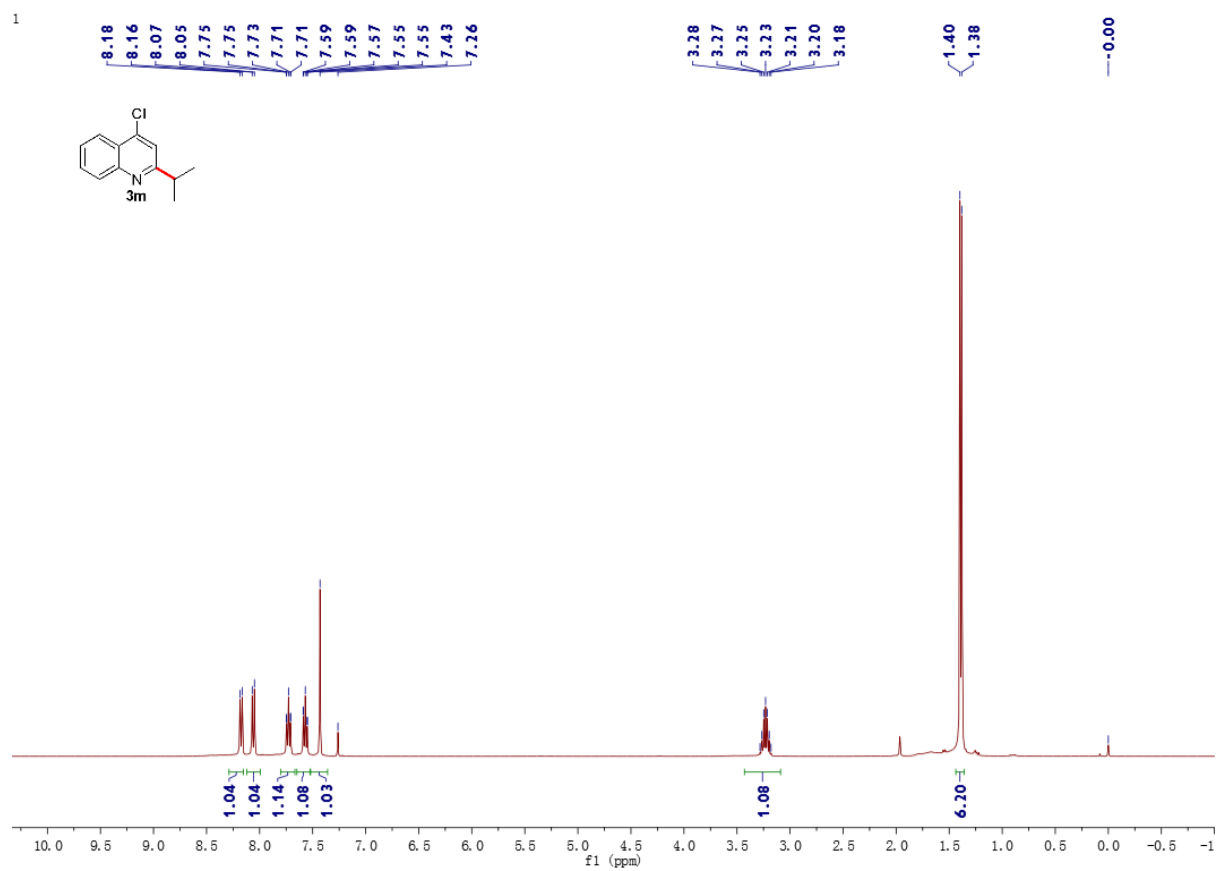
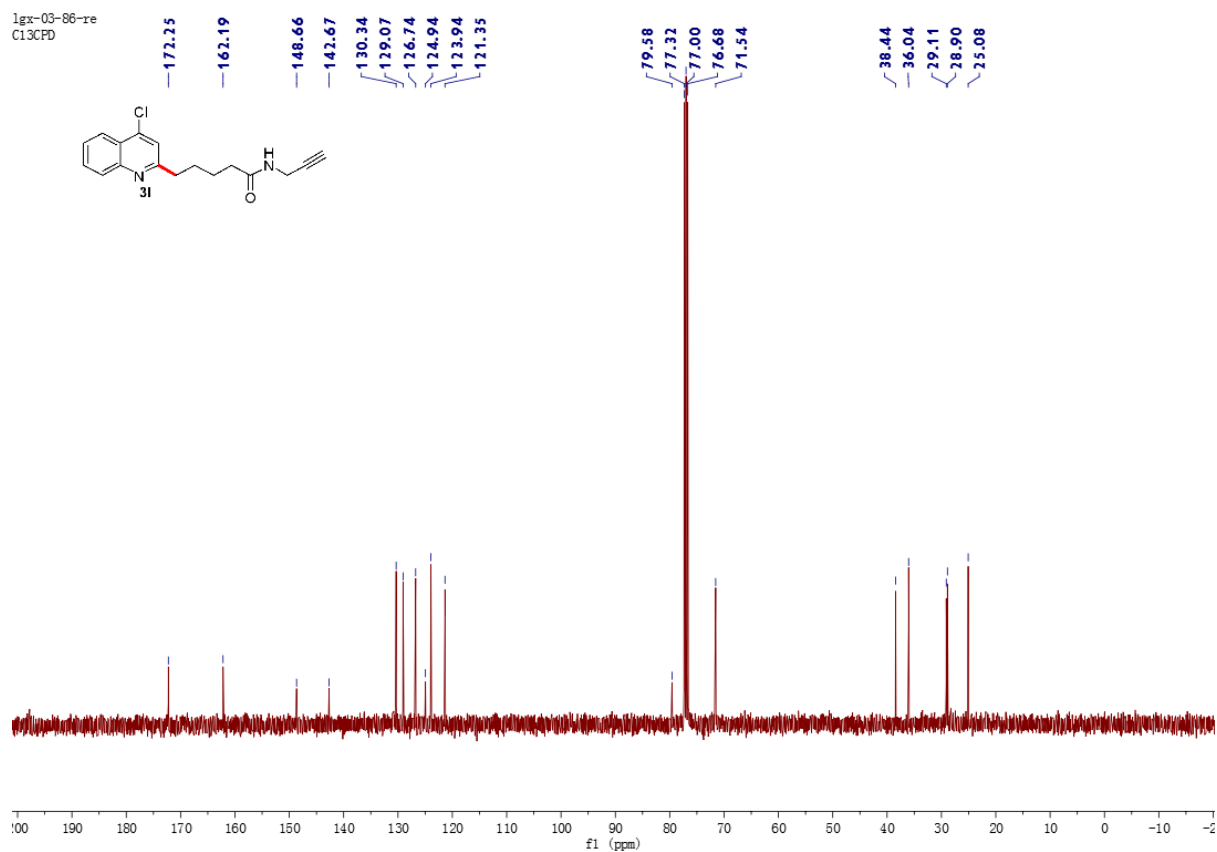
lgx-04-38
test

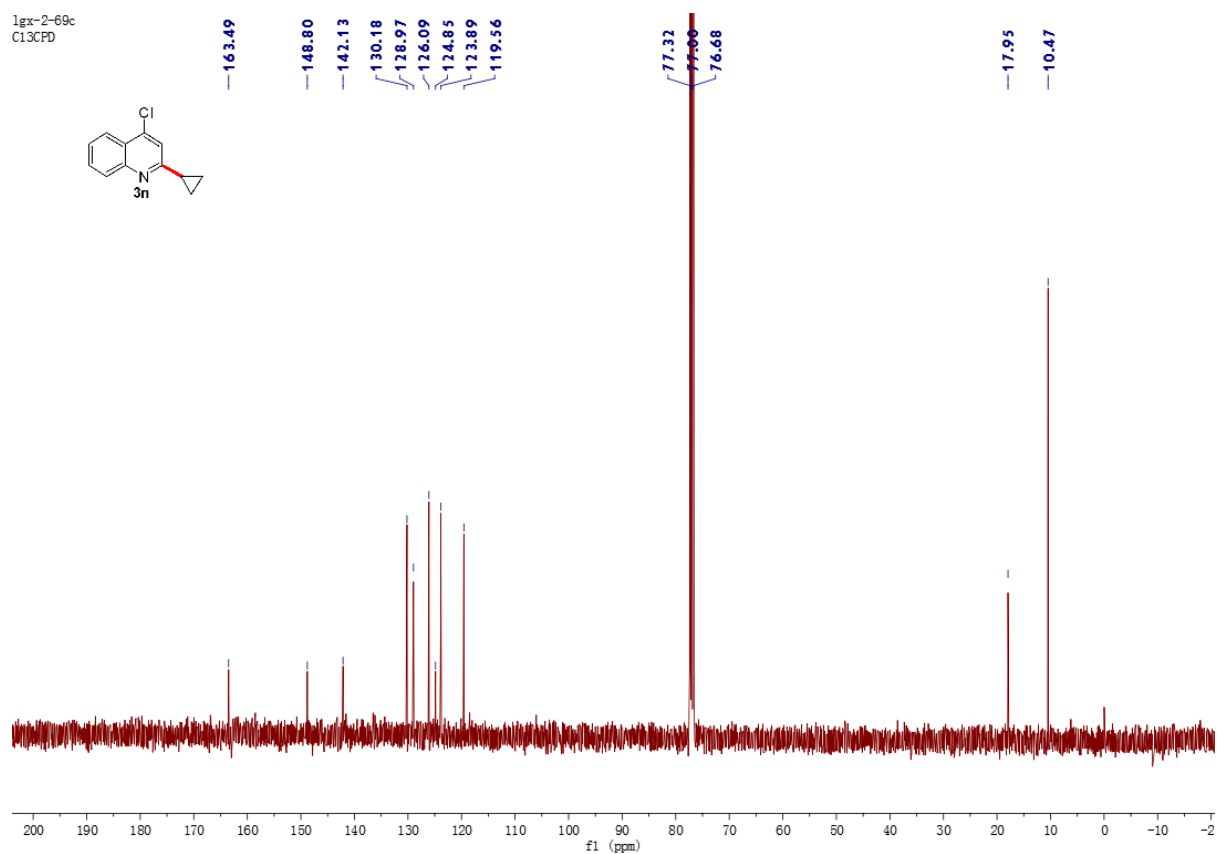
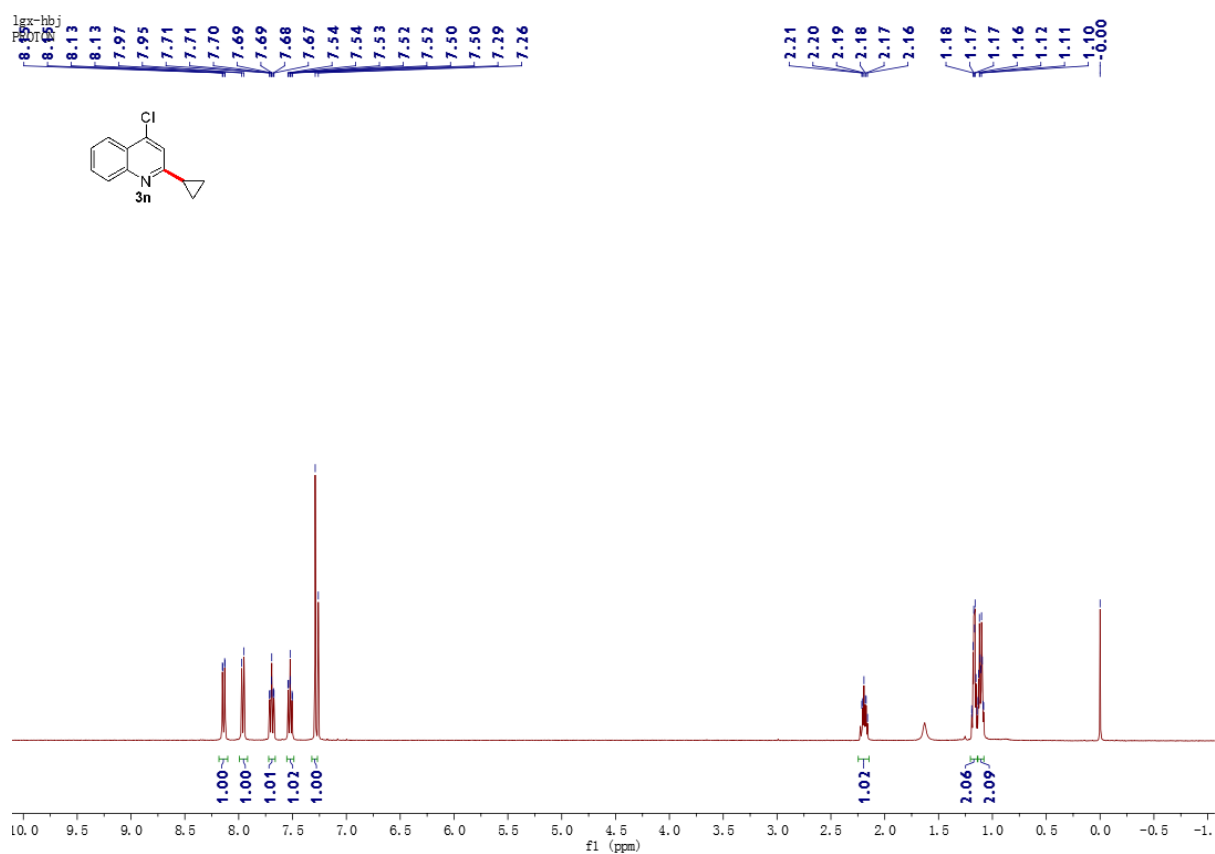


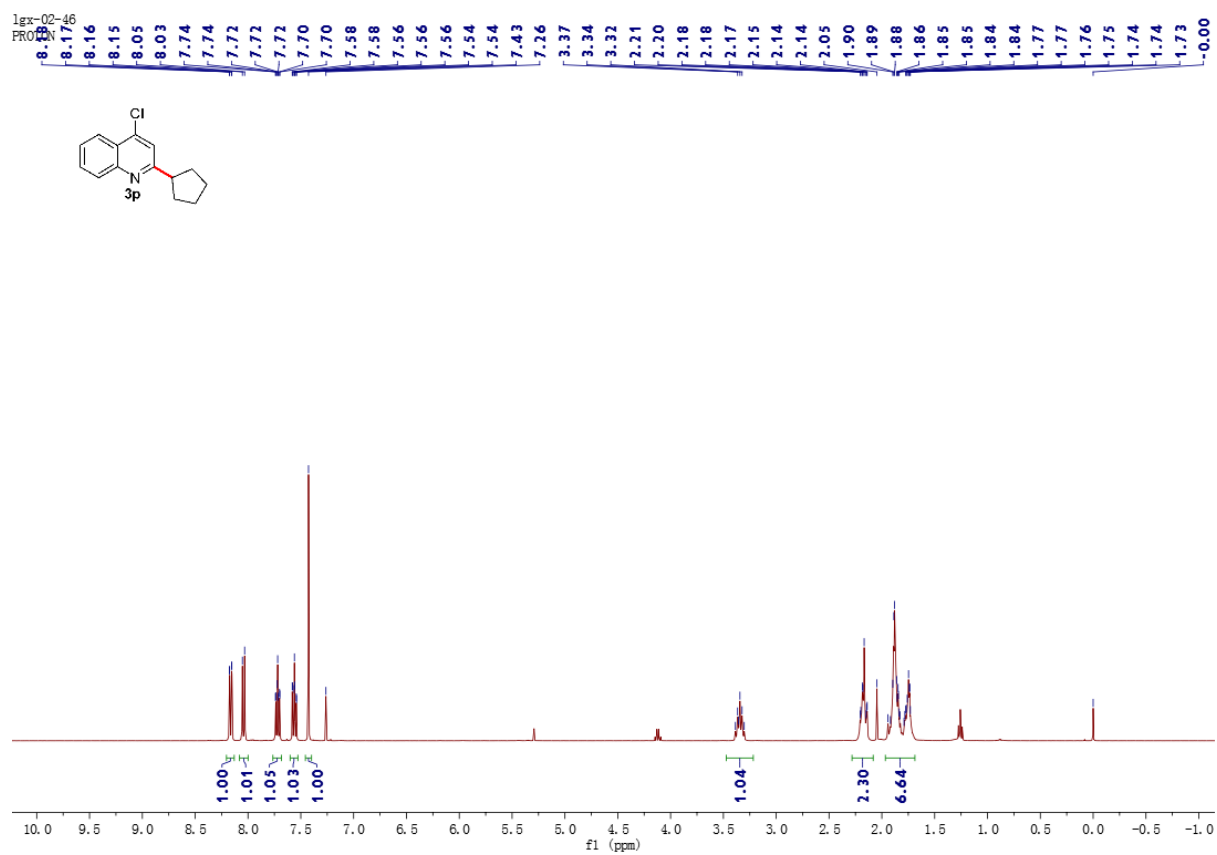
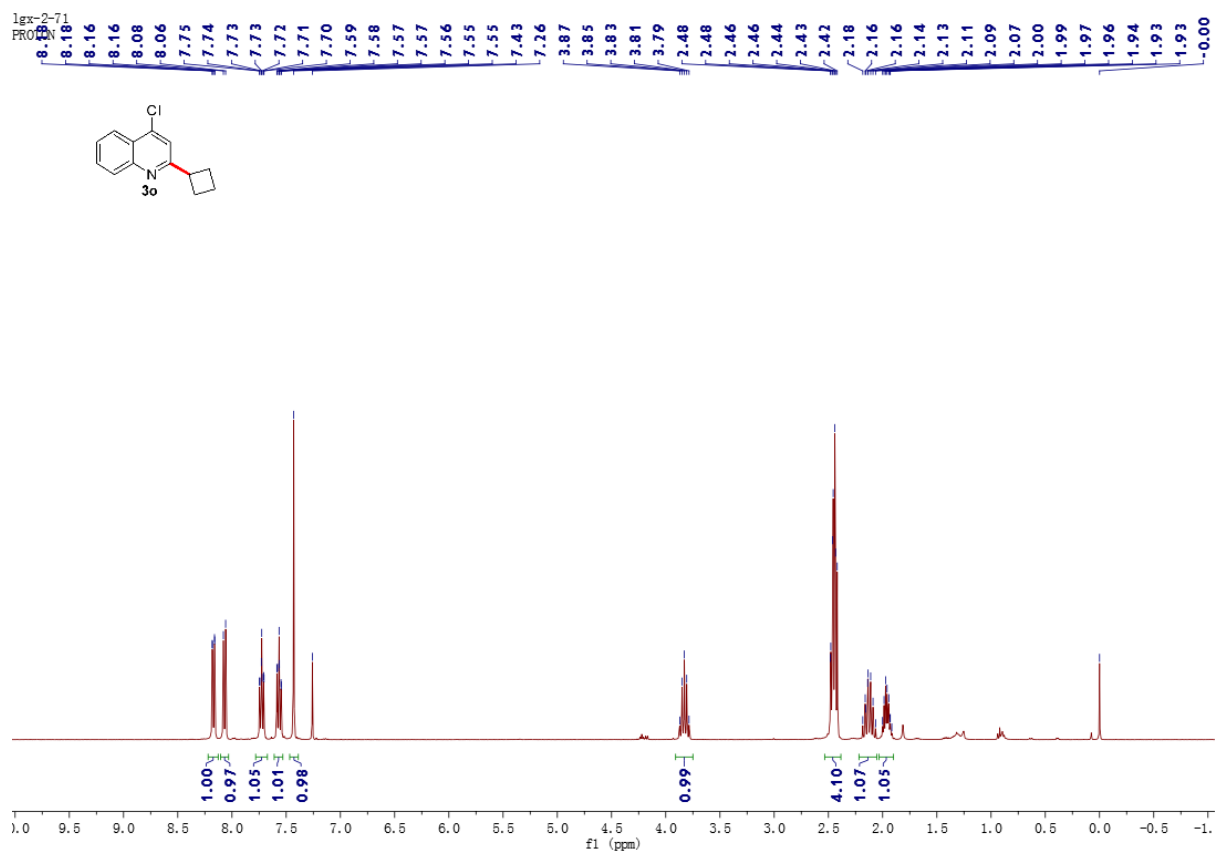
lgx-03-72-C
PROTO



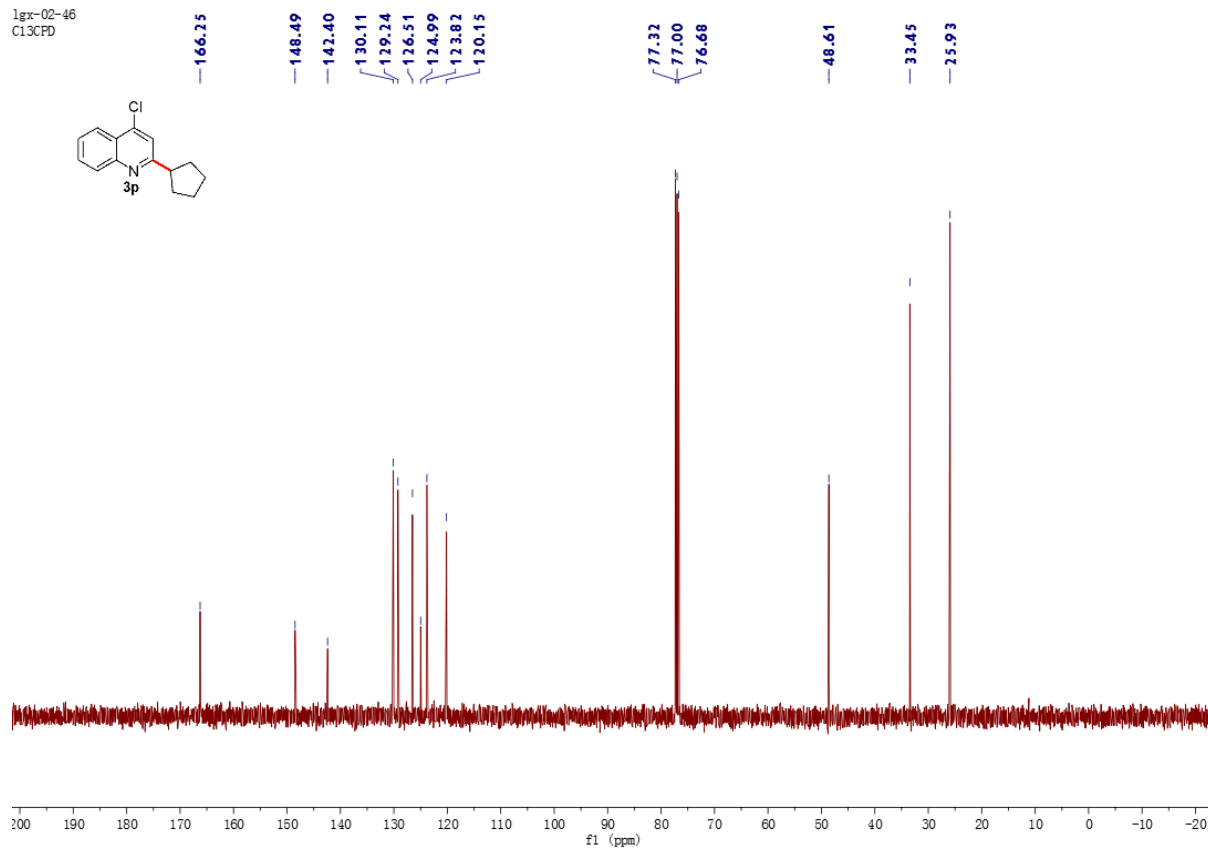
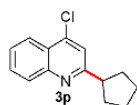




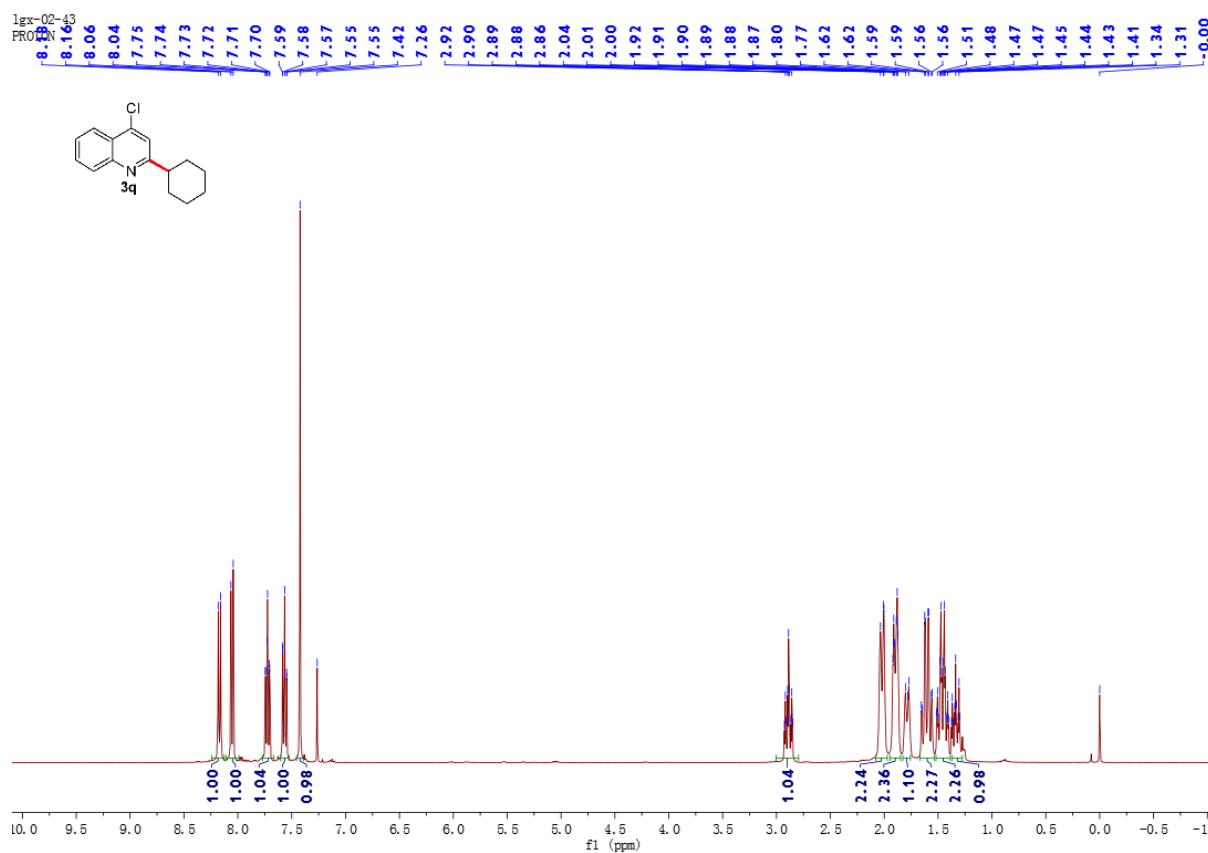
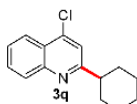




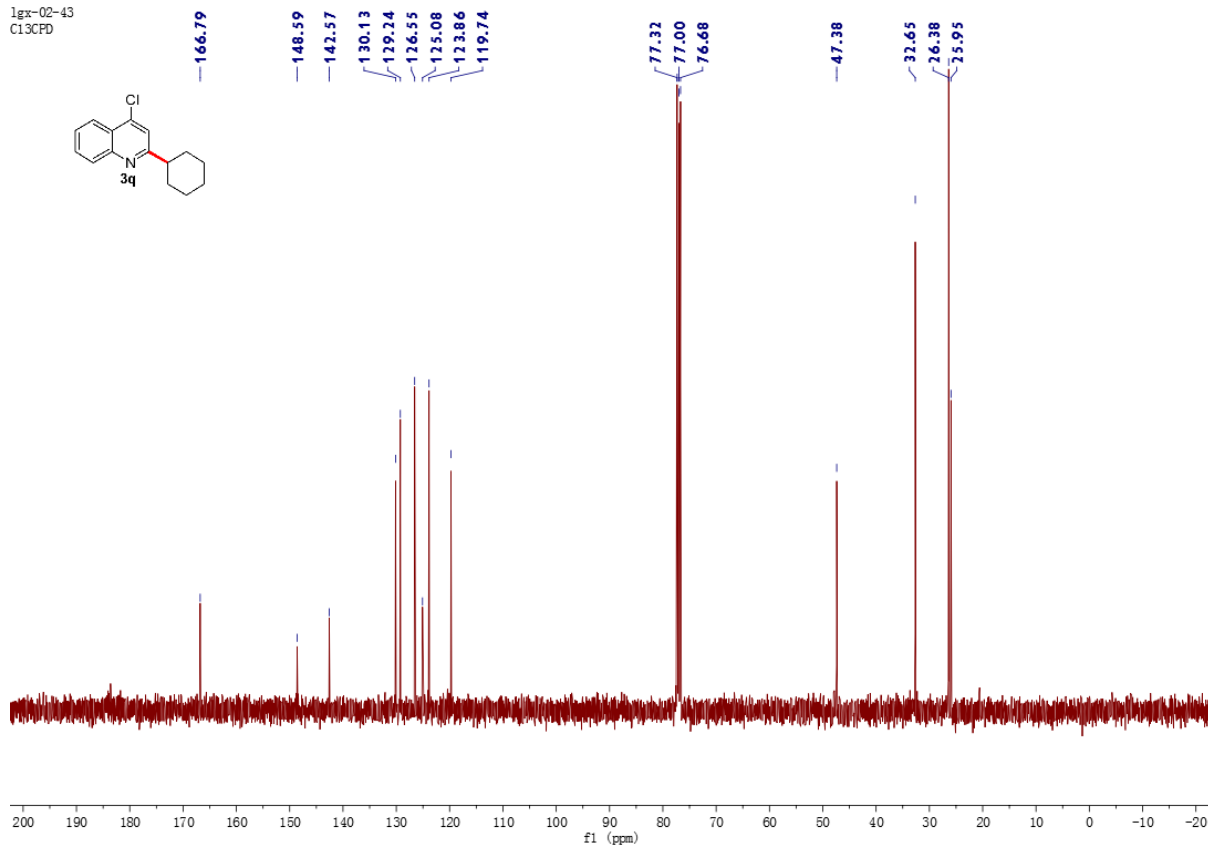
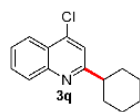
1gx-02-46
C13CPD



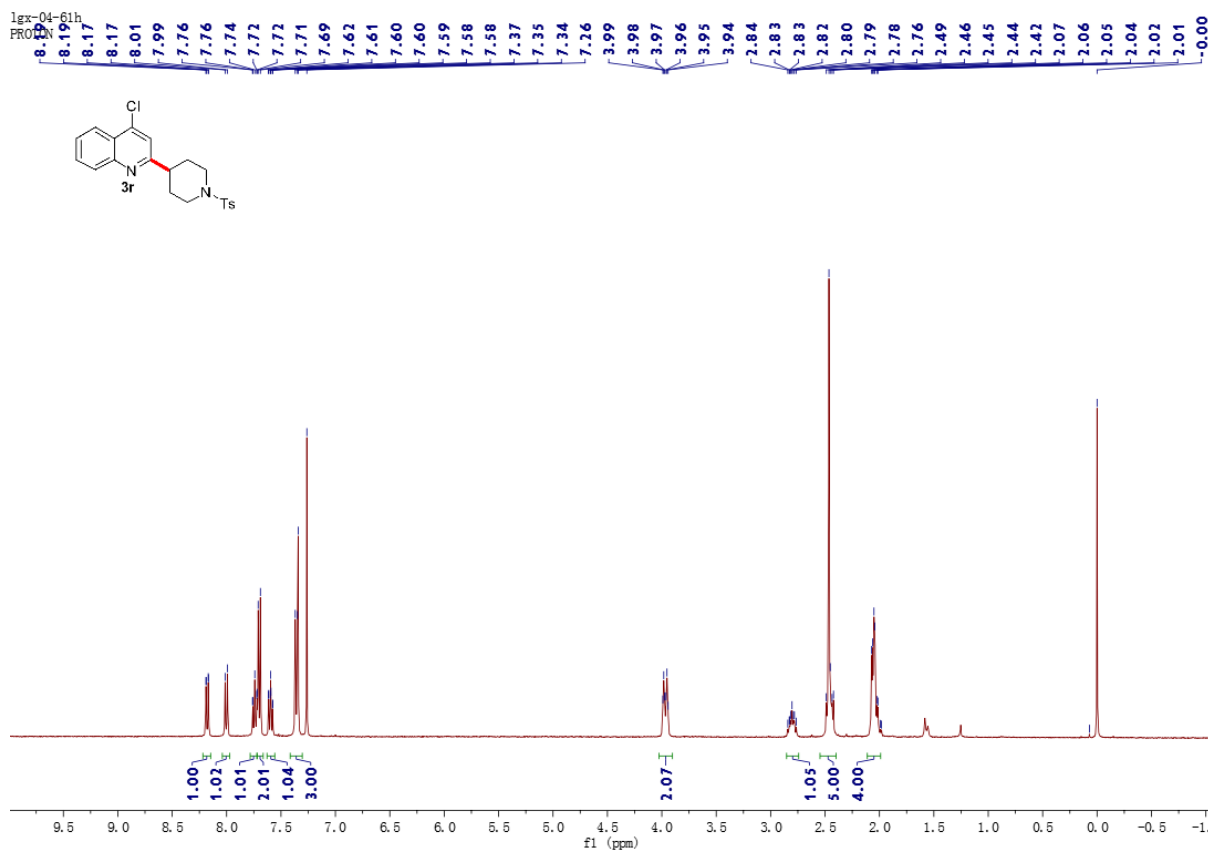
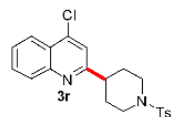
1gx-02-43
PROTON



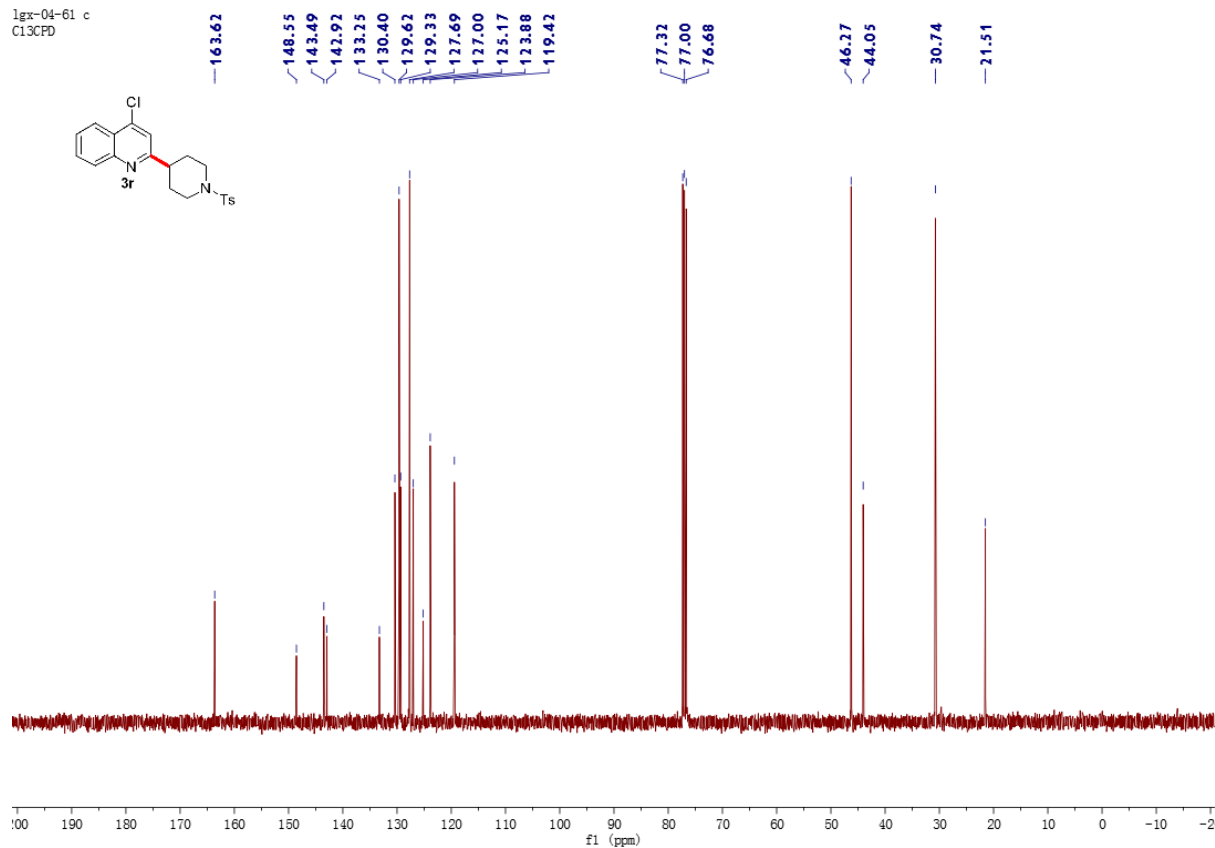
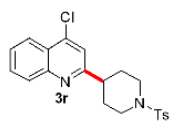
1gx-02-43
C13CPD



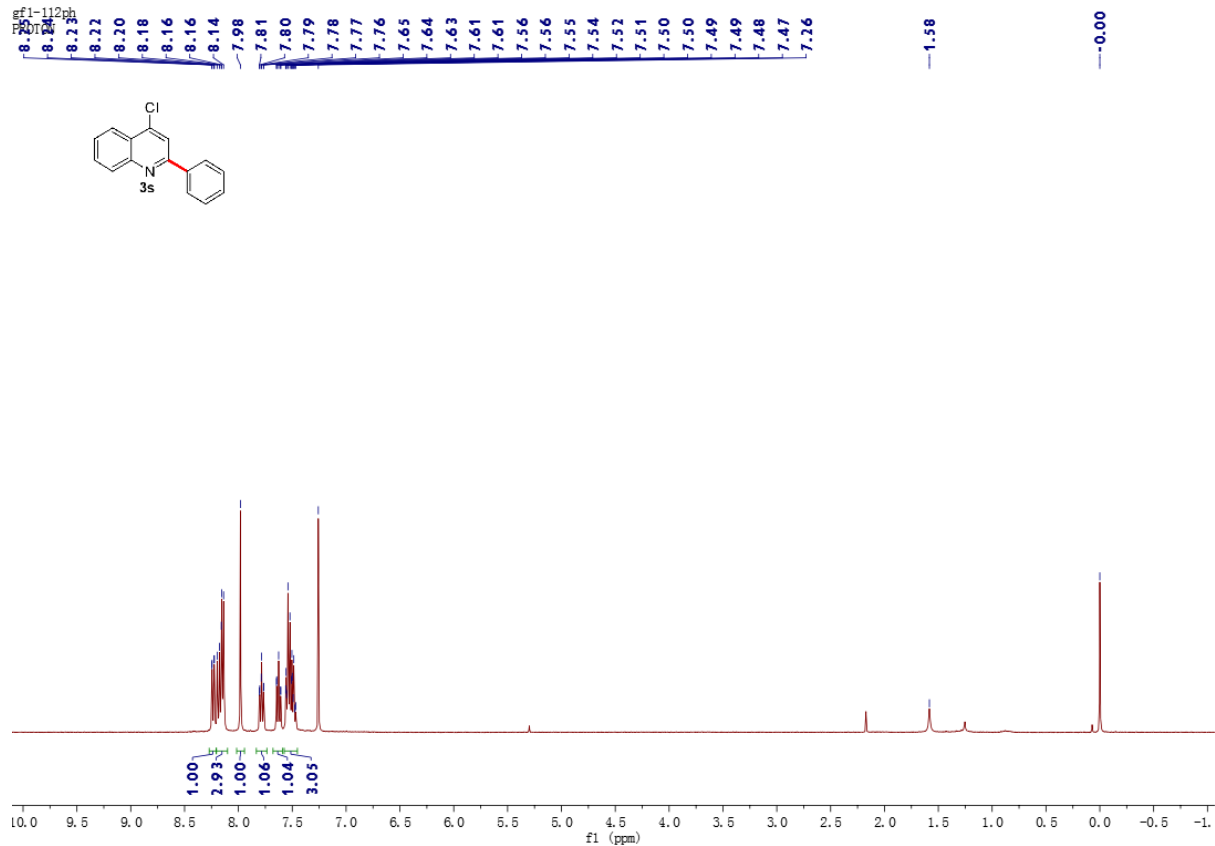
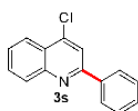
1gx-04-61h
PRO



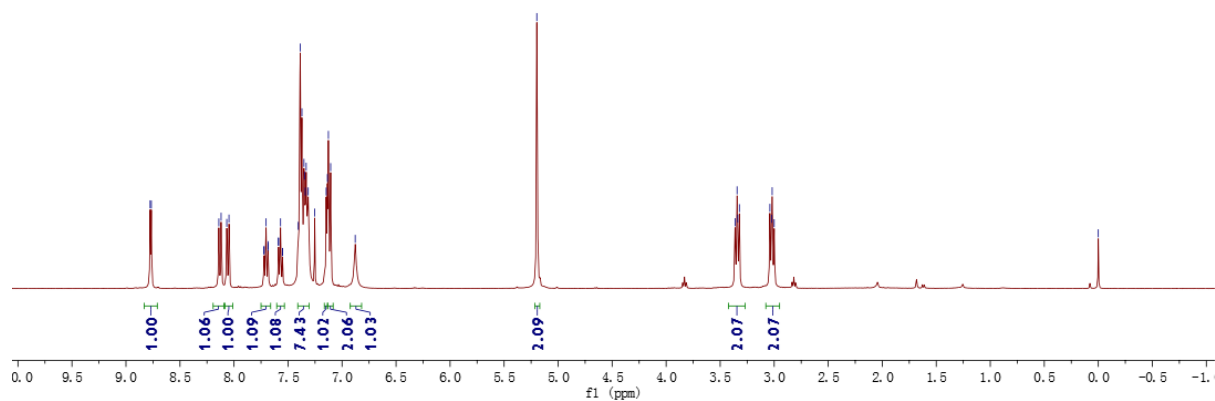
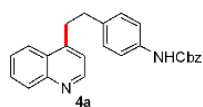
1gx-04-61 c
C13CPD



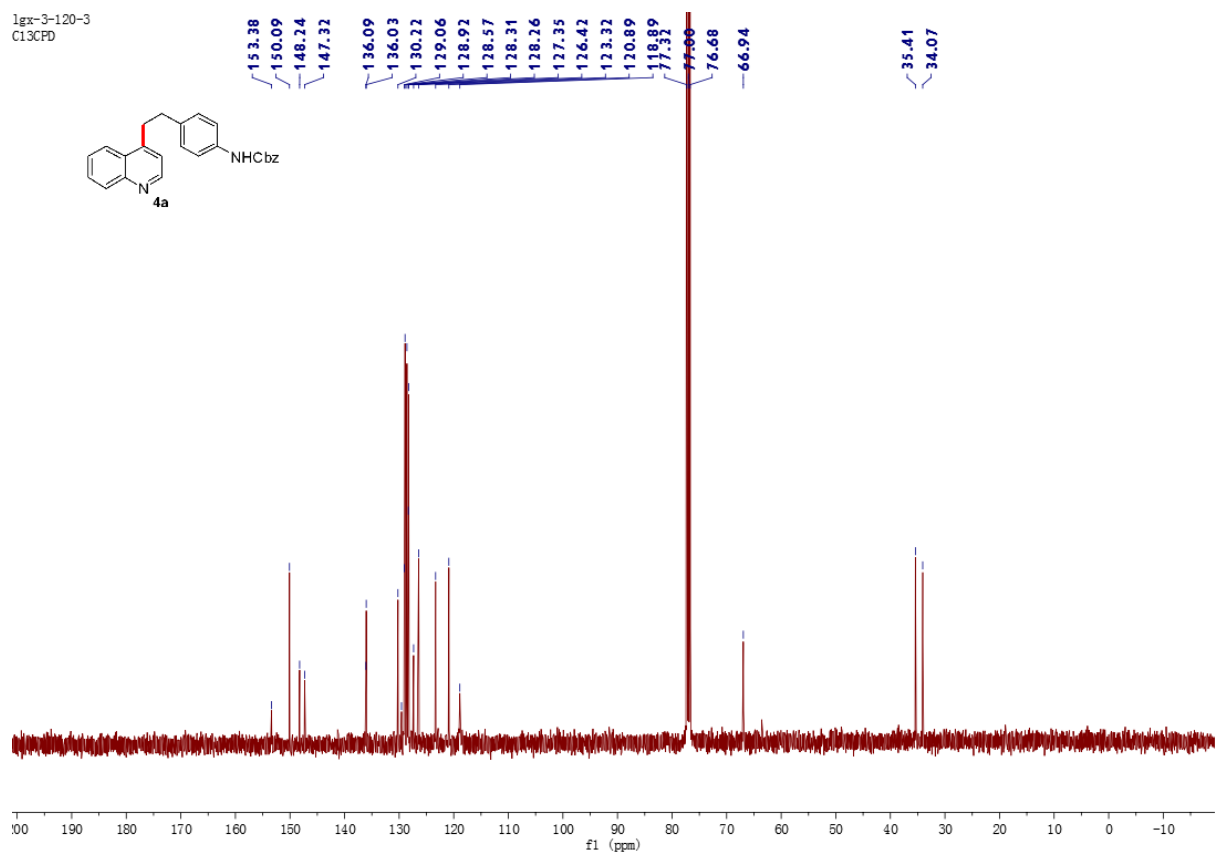
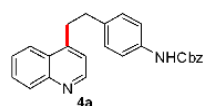
ef1-112ph

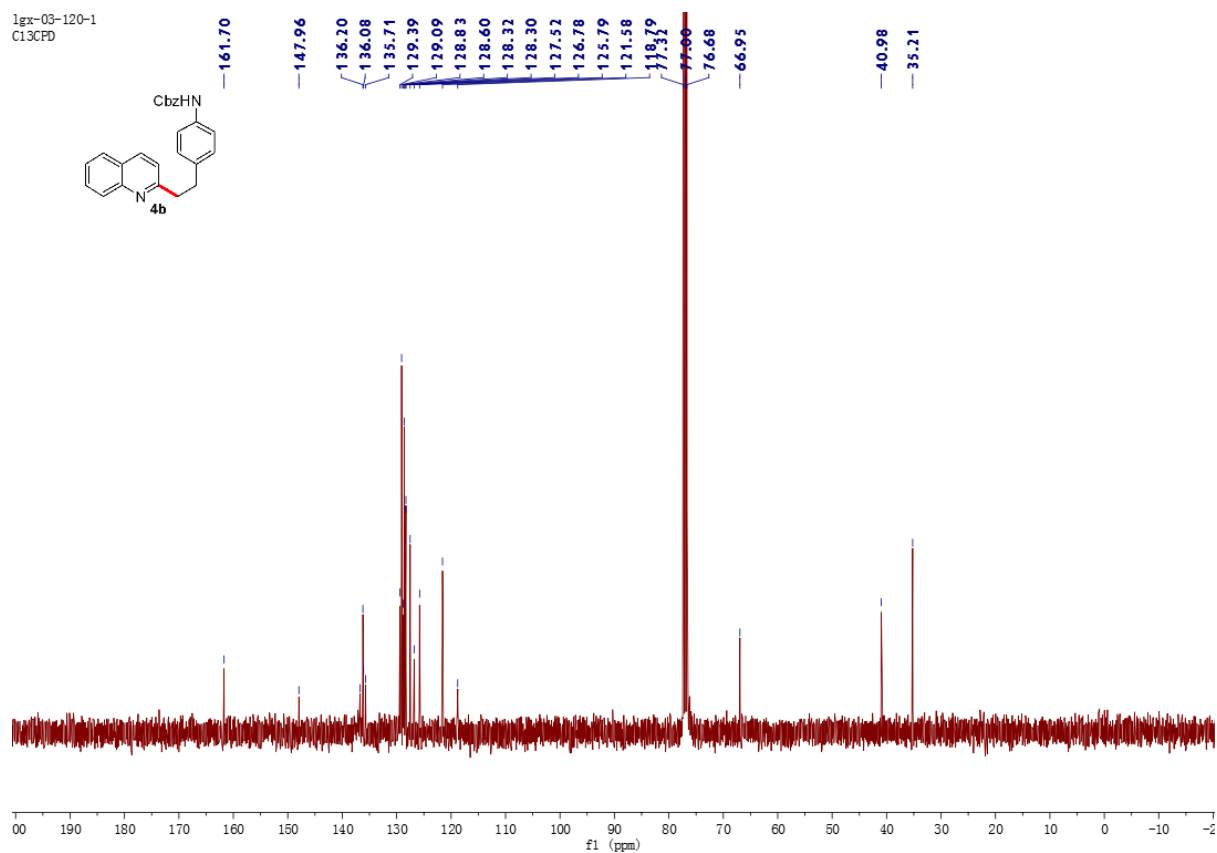
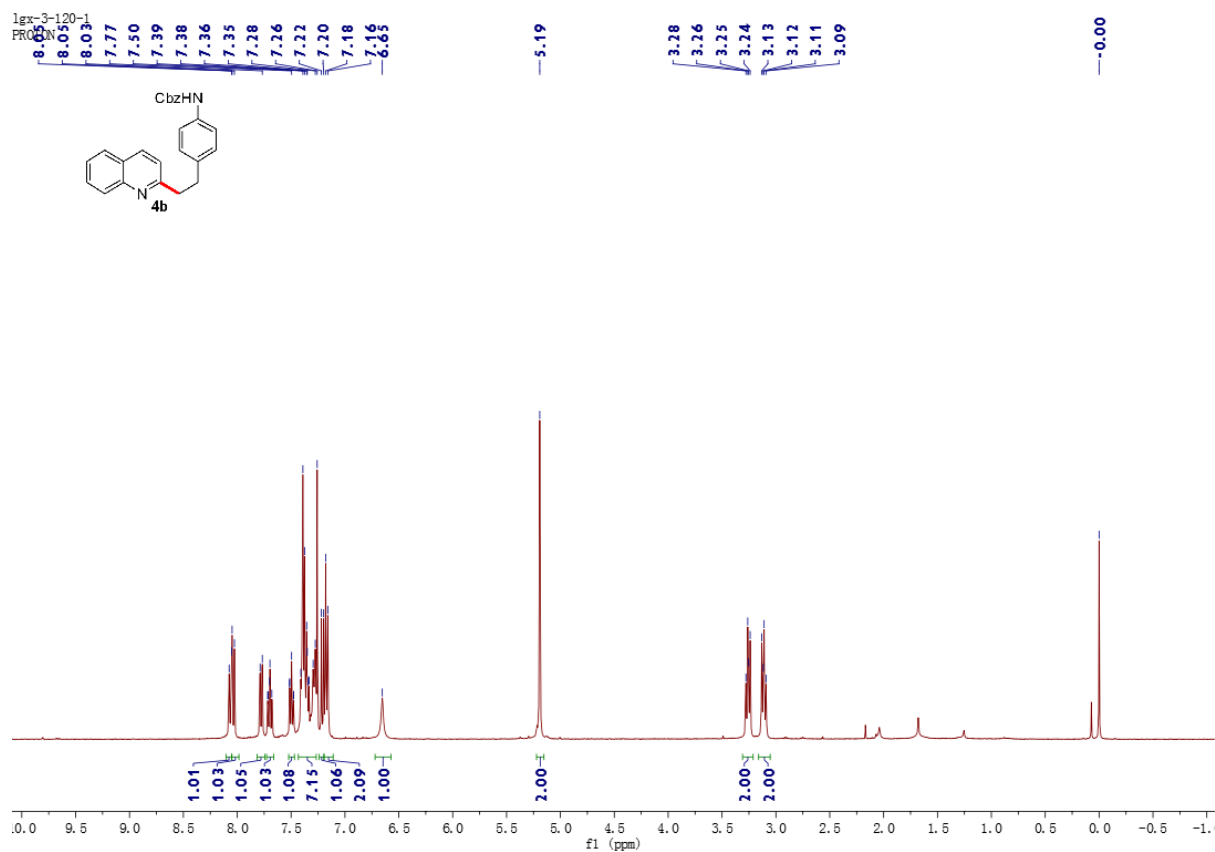


1gx-3-120-3
PROTON

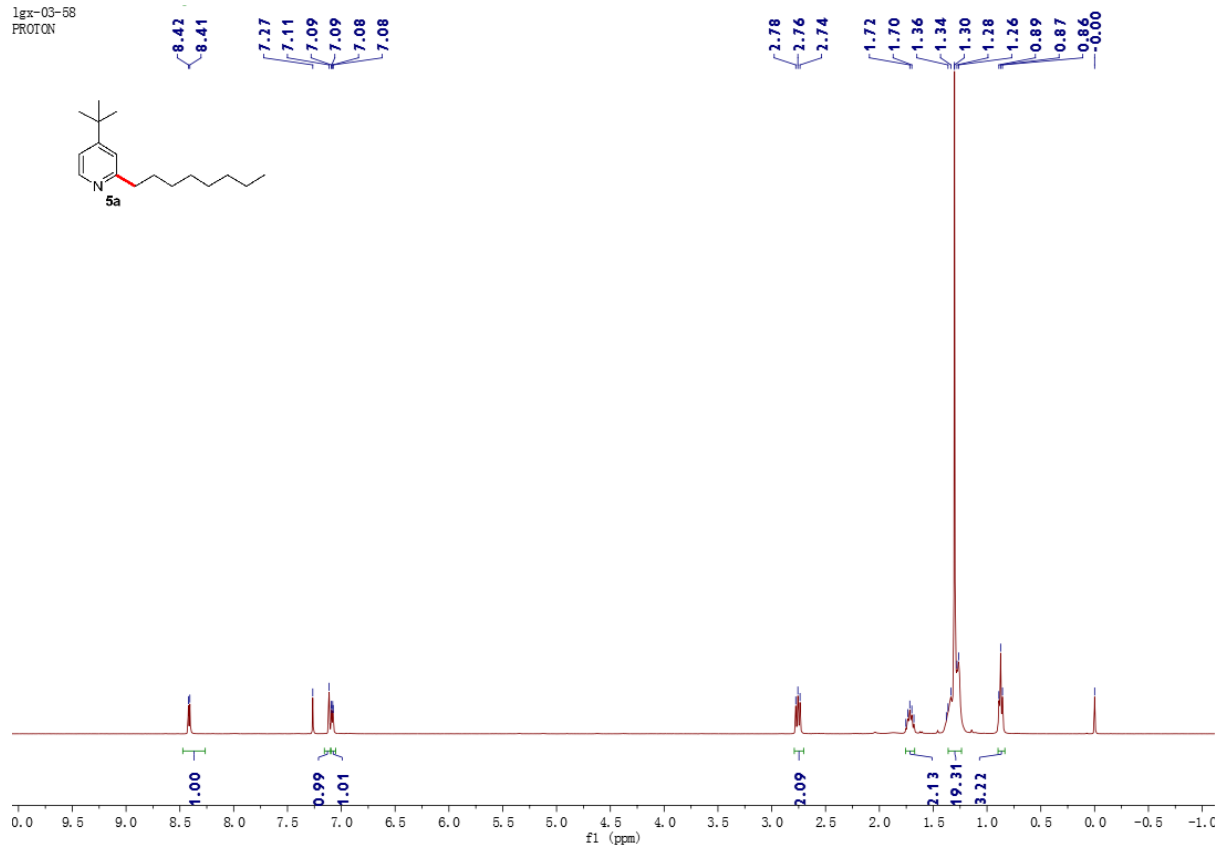


1gx-3-120-3
C13CPD

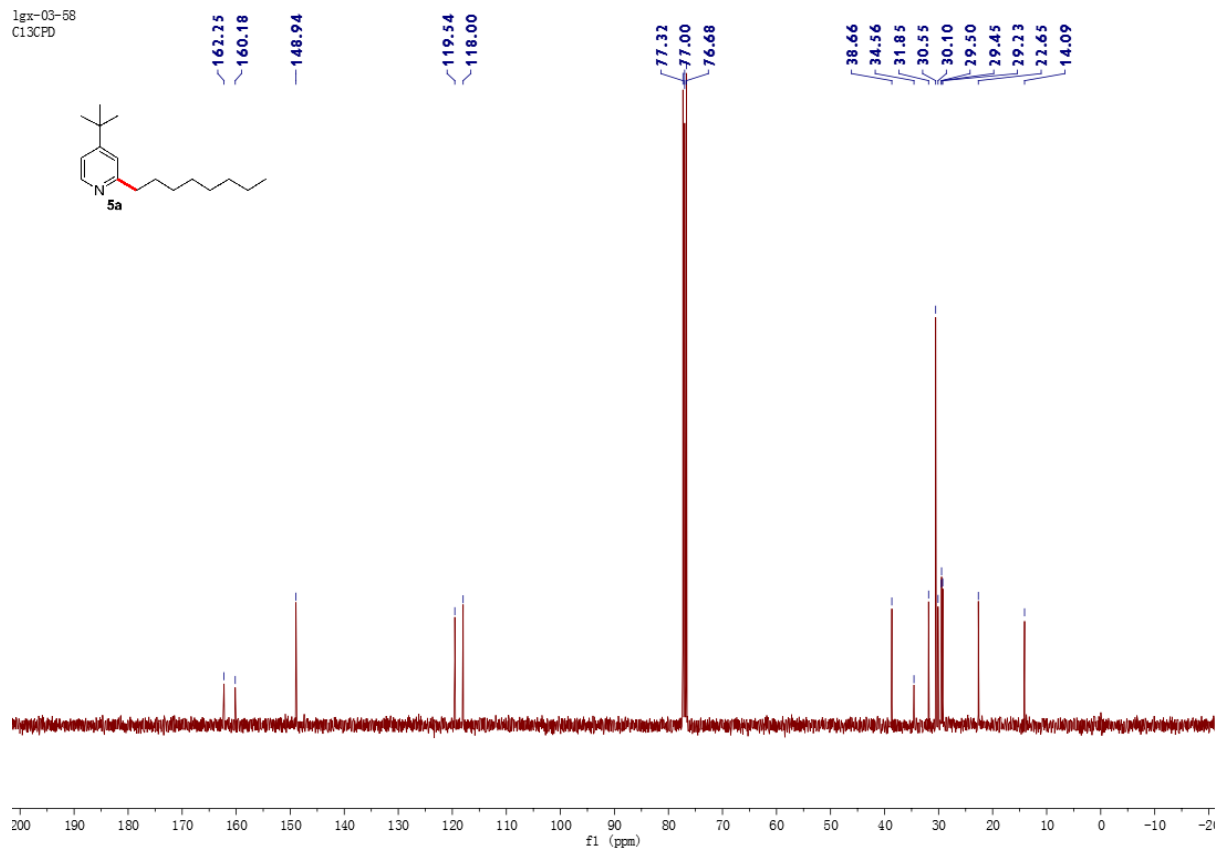


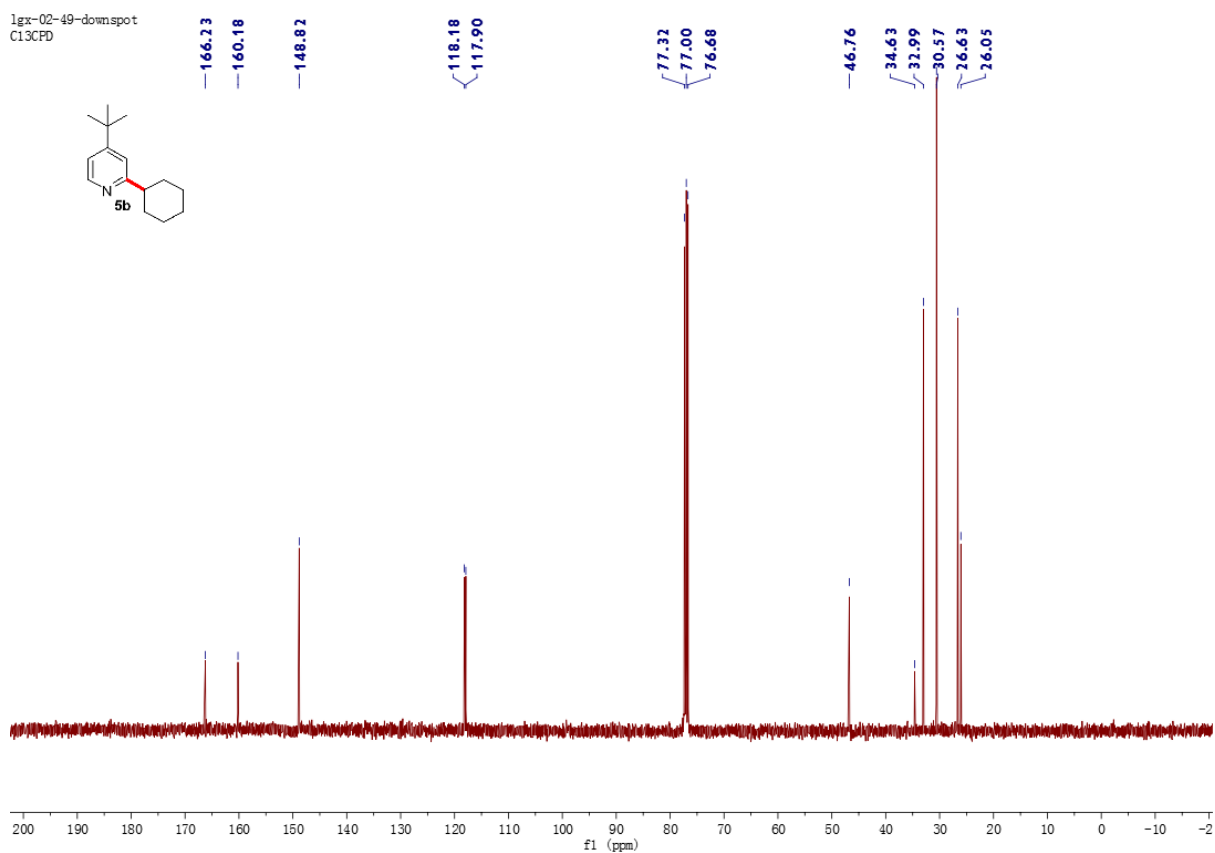
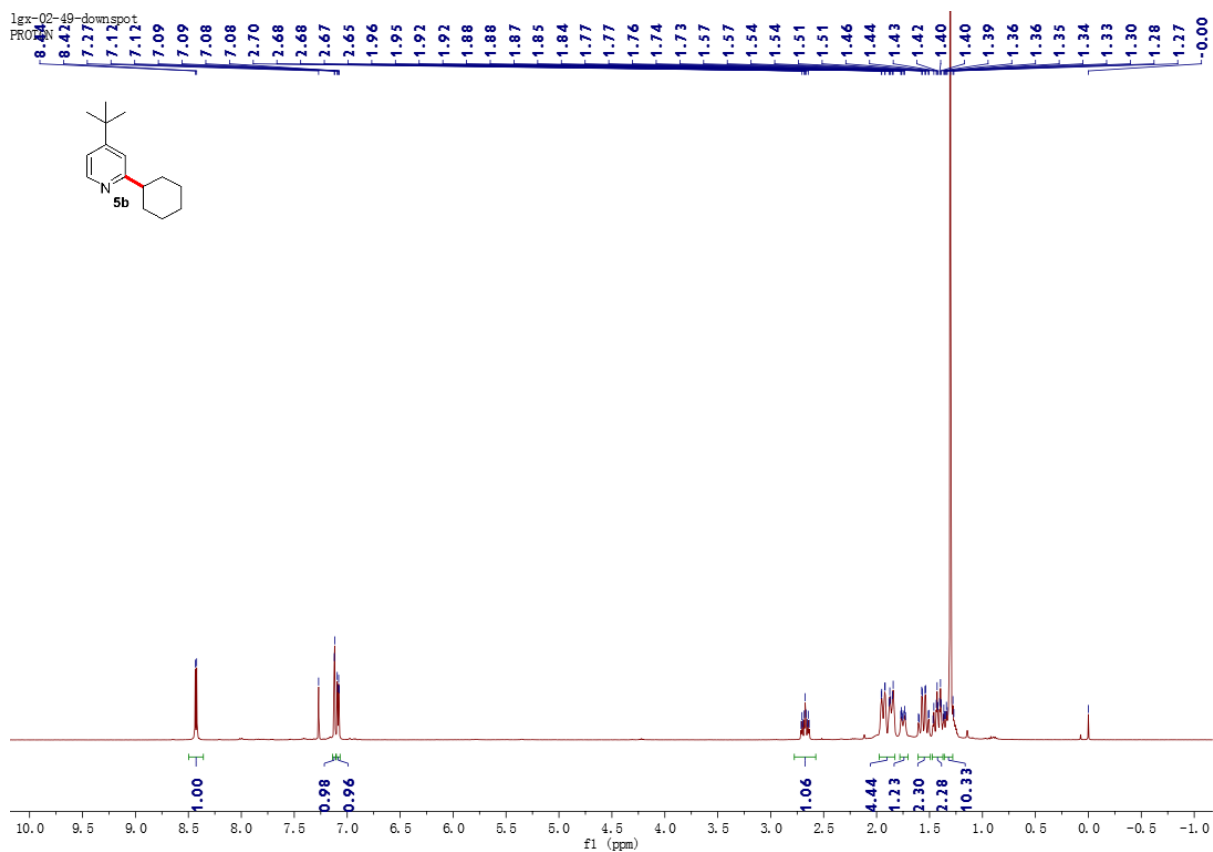


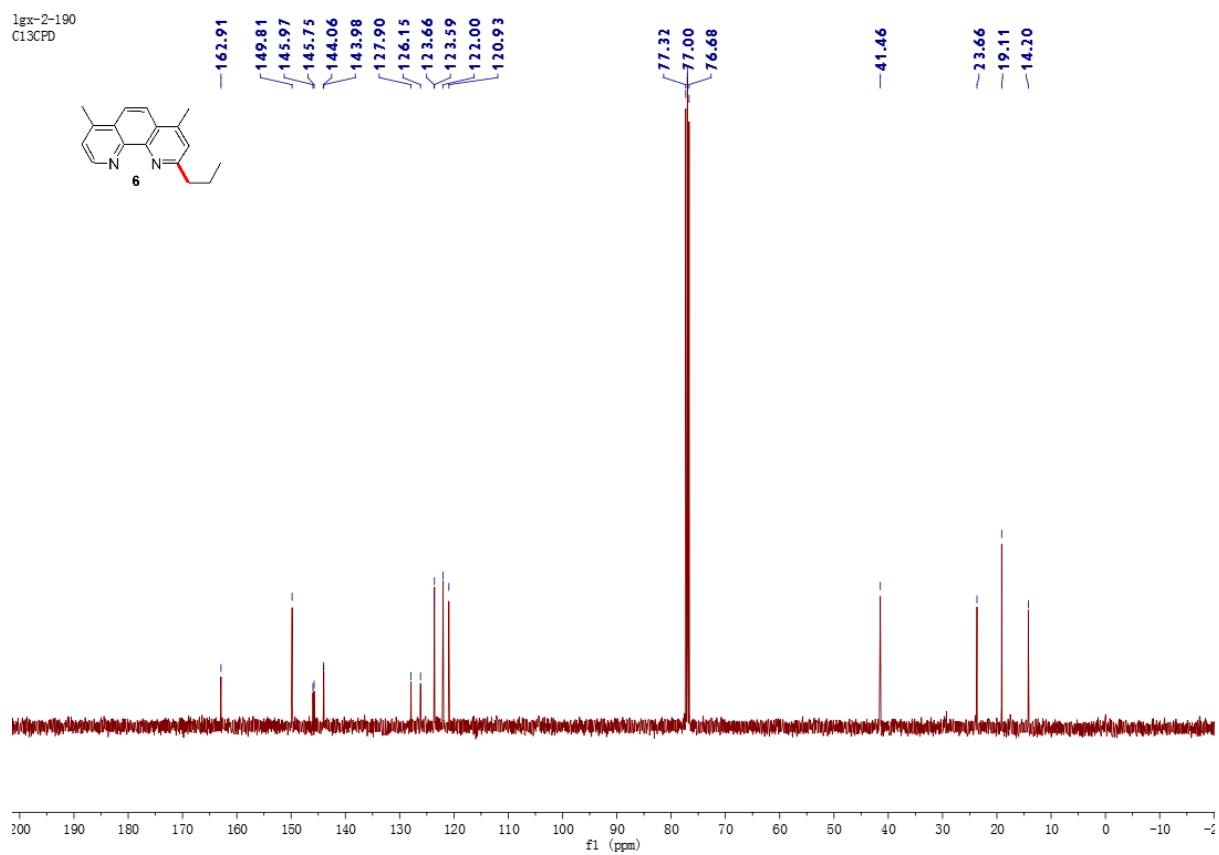
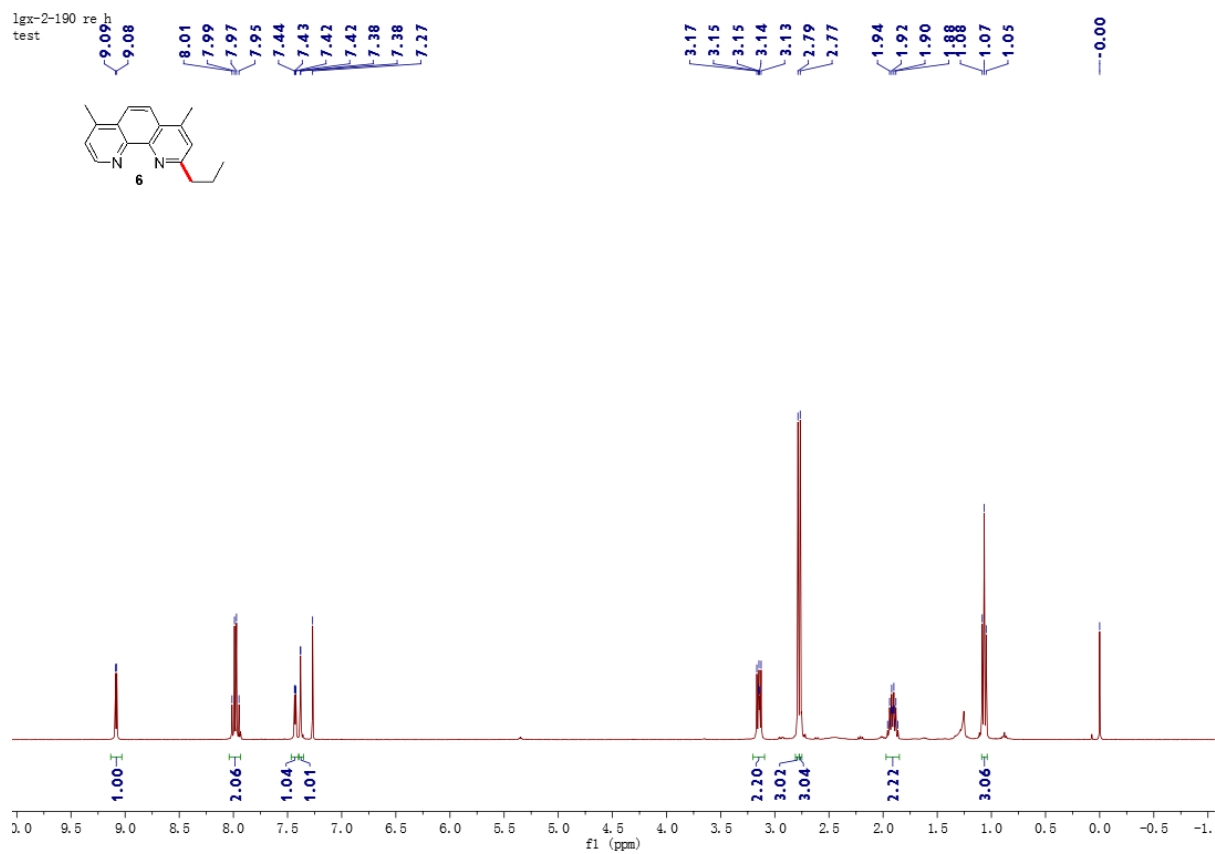
1gx-03-58
PROTON



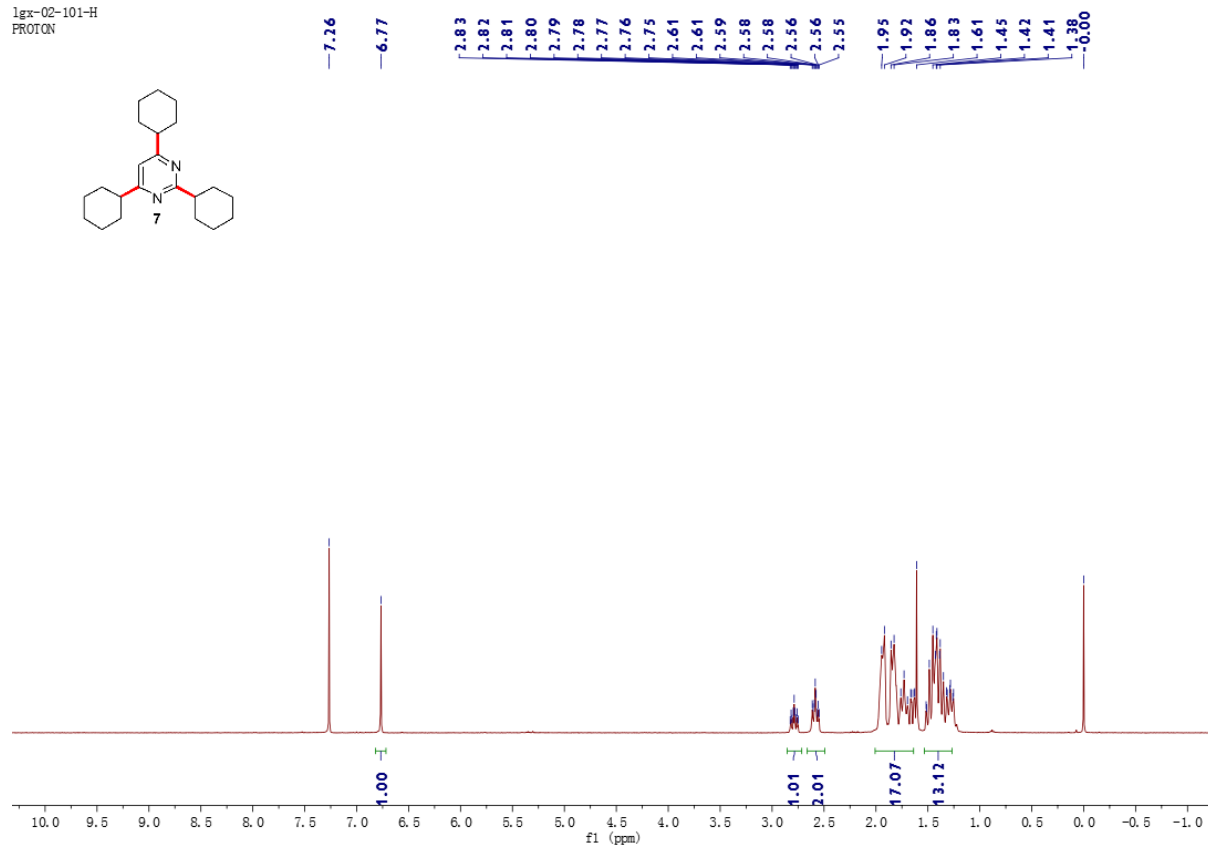
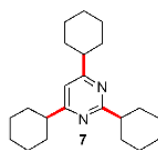
1gx-03-58
C13CPD



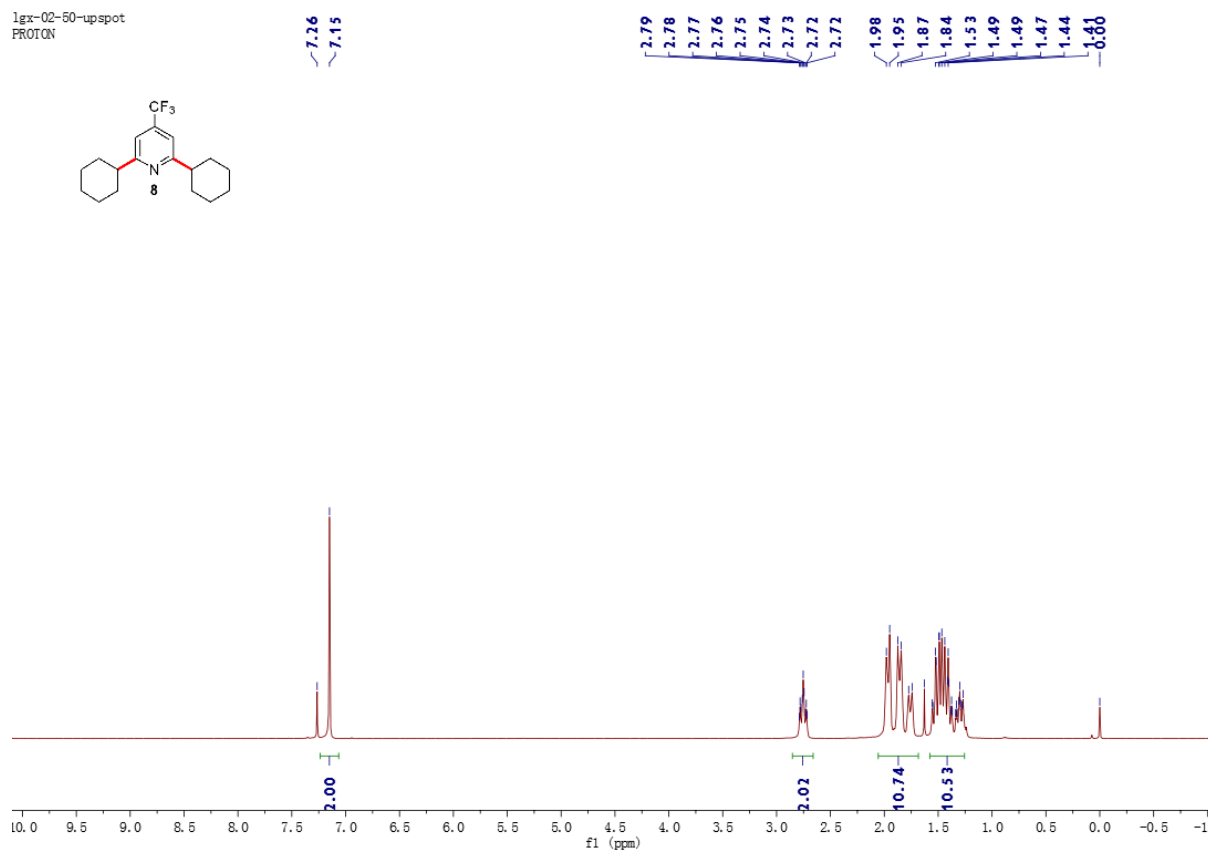
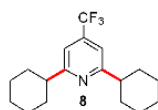




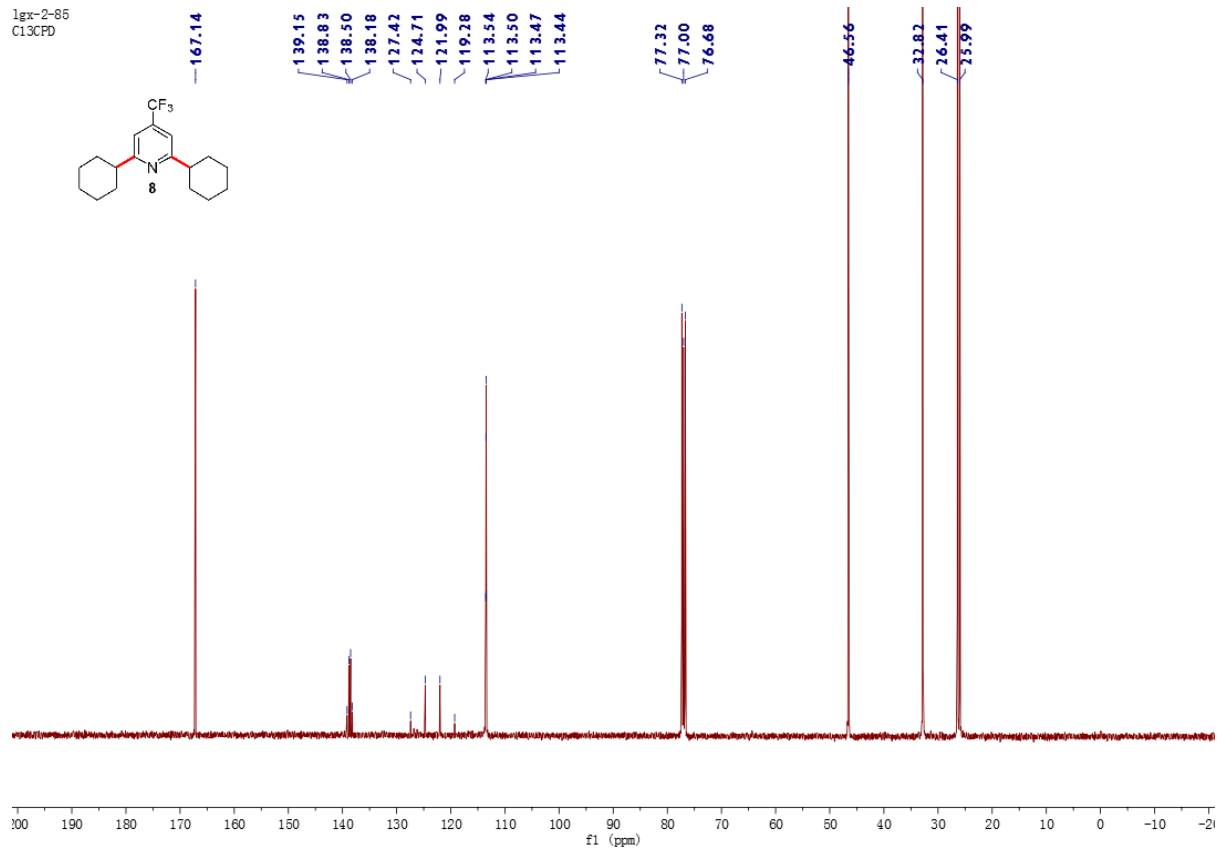
1gx-02-101-H
PROTON



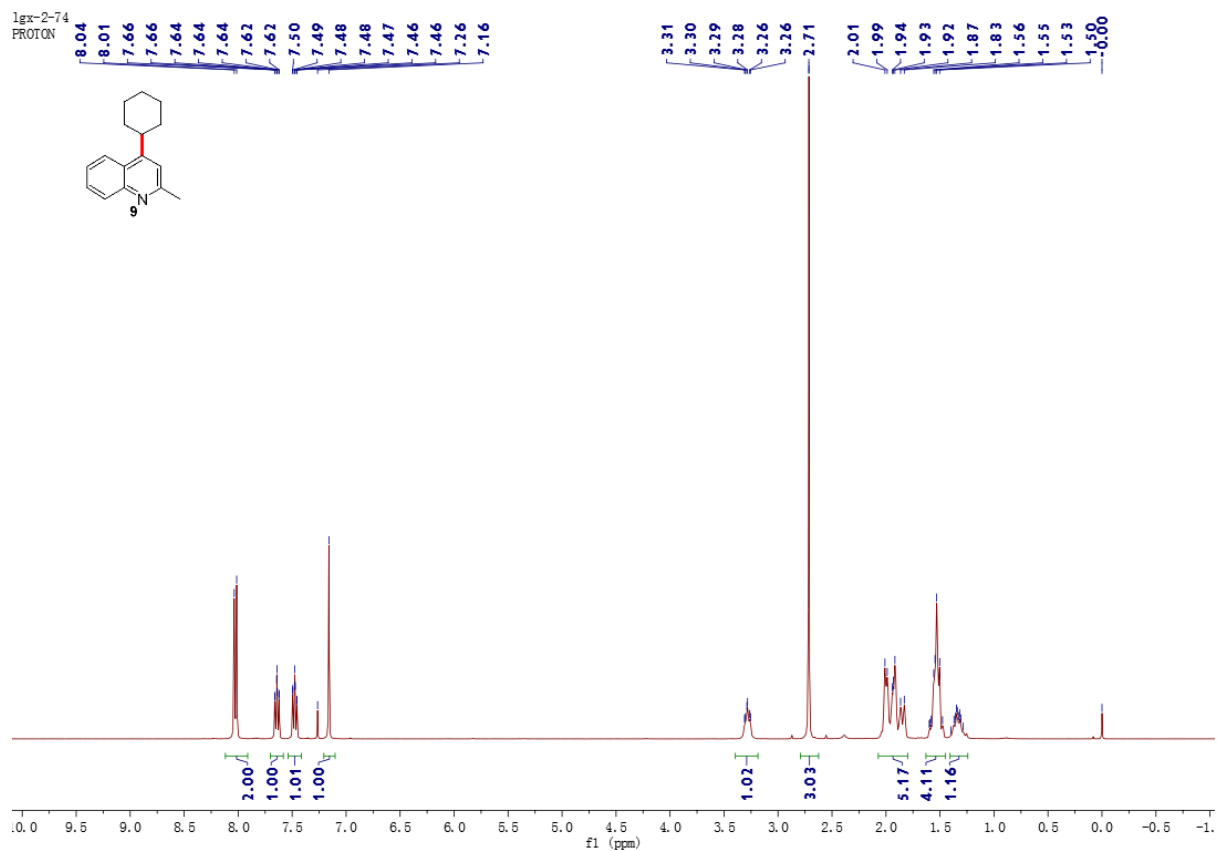
1gx-02-50-upspot
PROTON

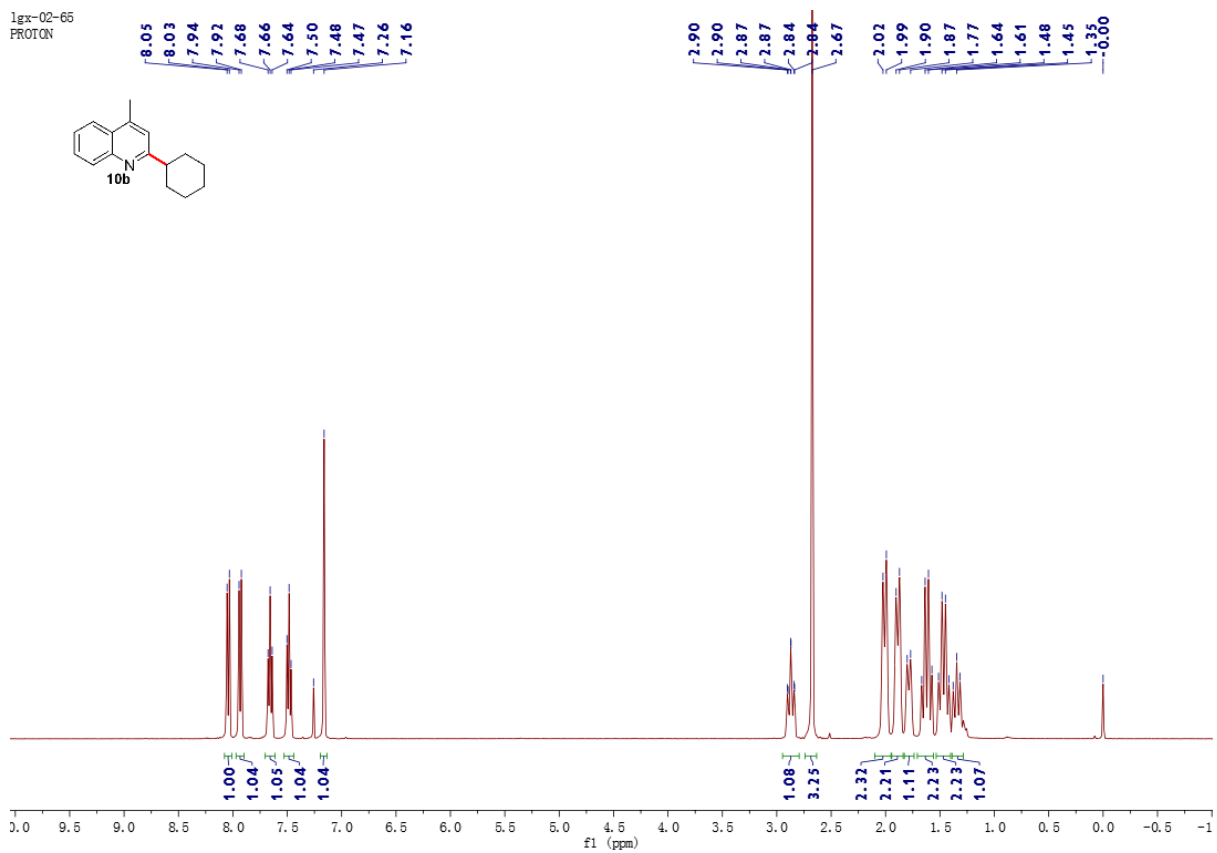
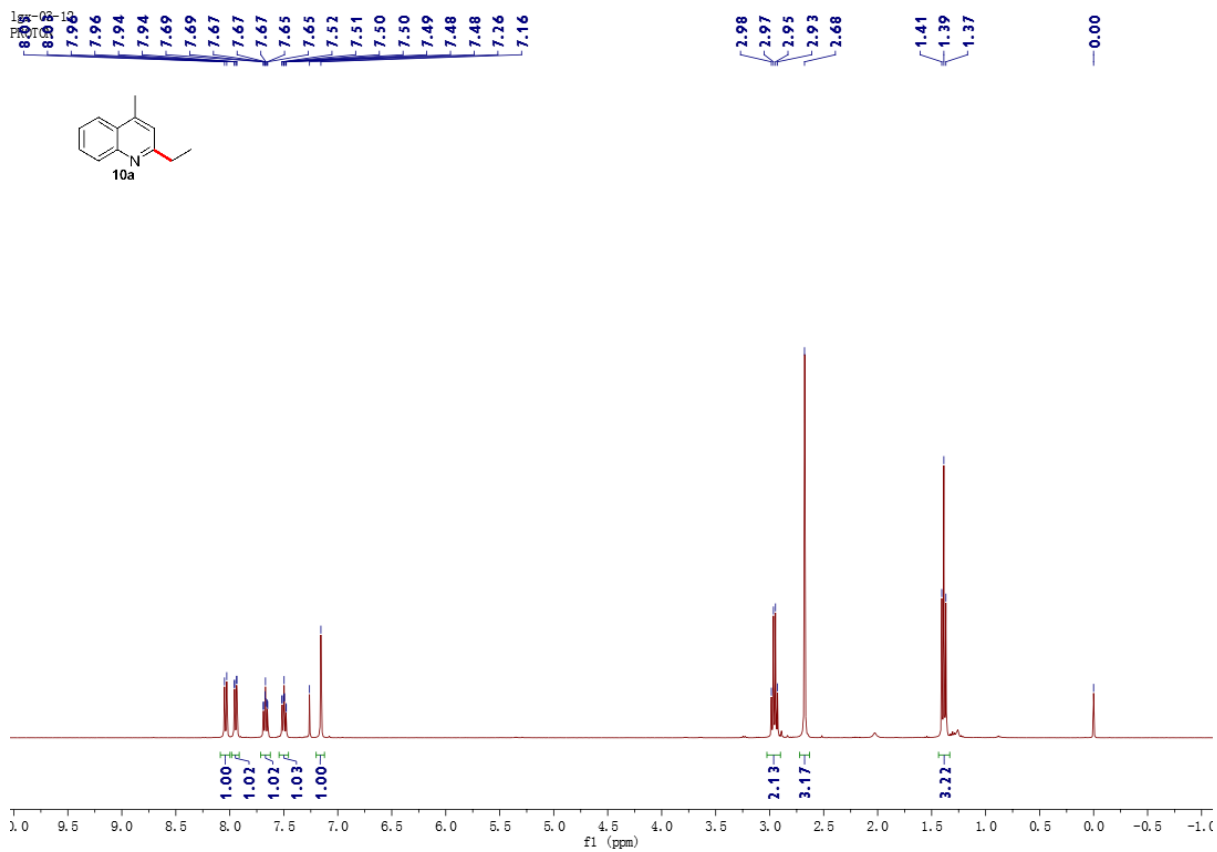


1gx-2-85
C13CPD

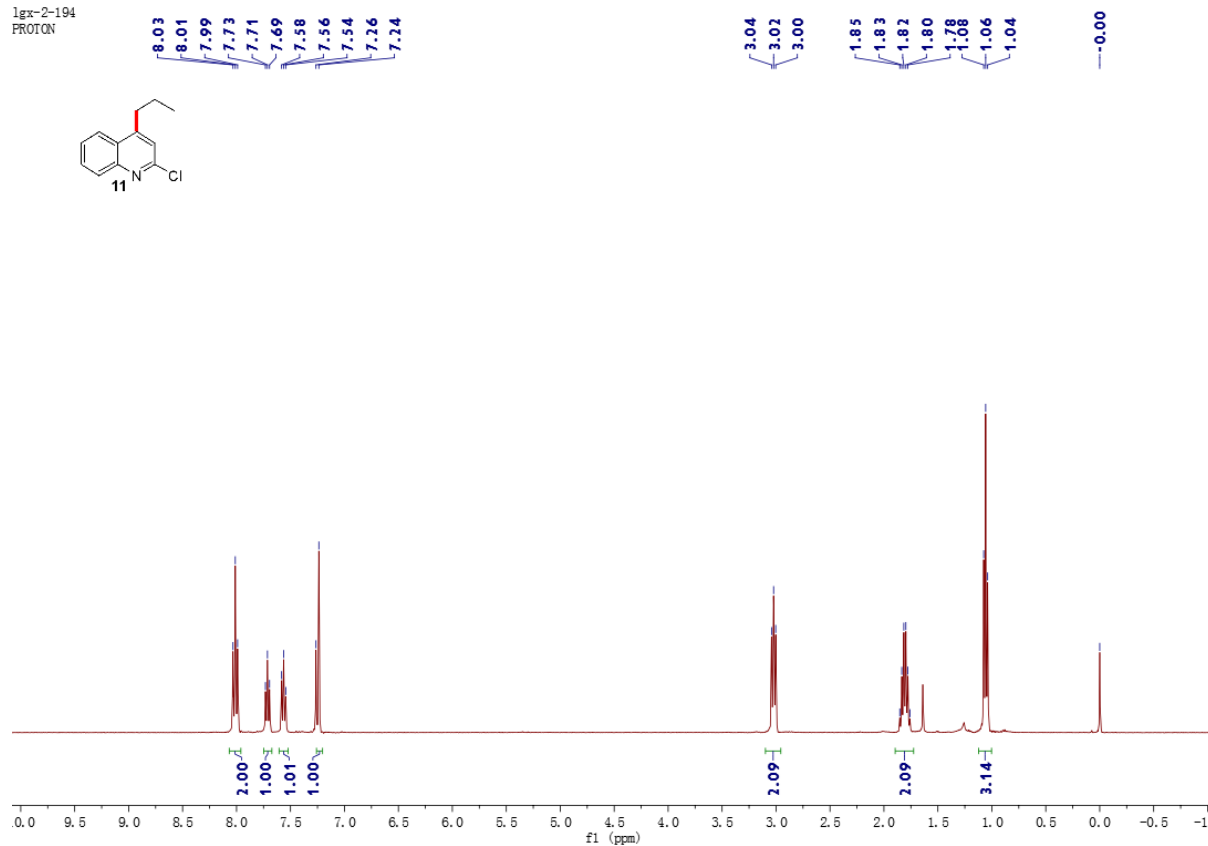
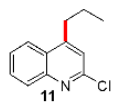


1gx-2-74
PROTON

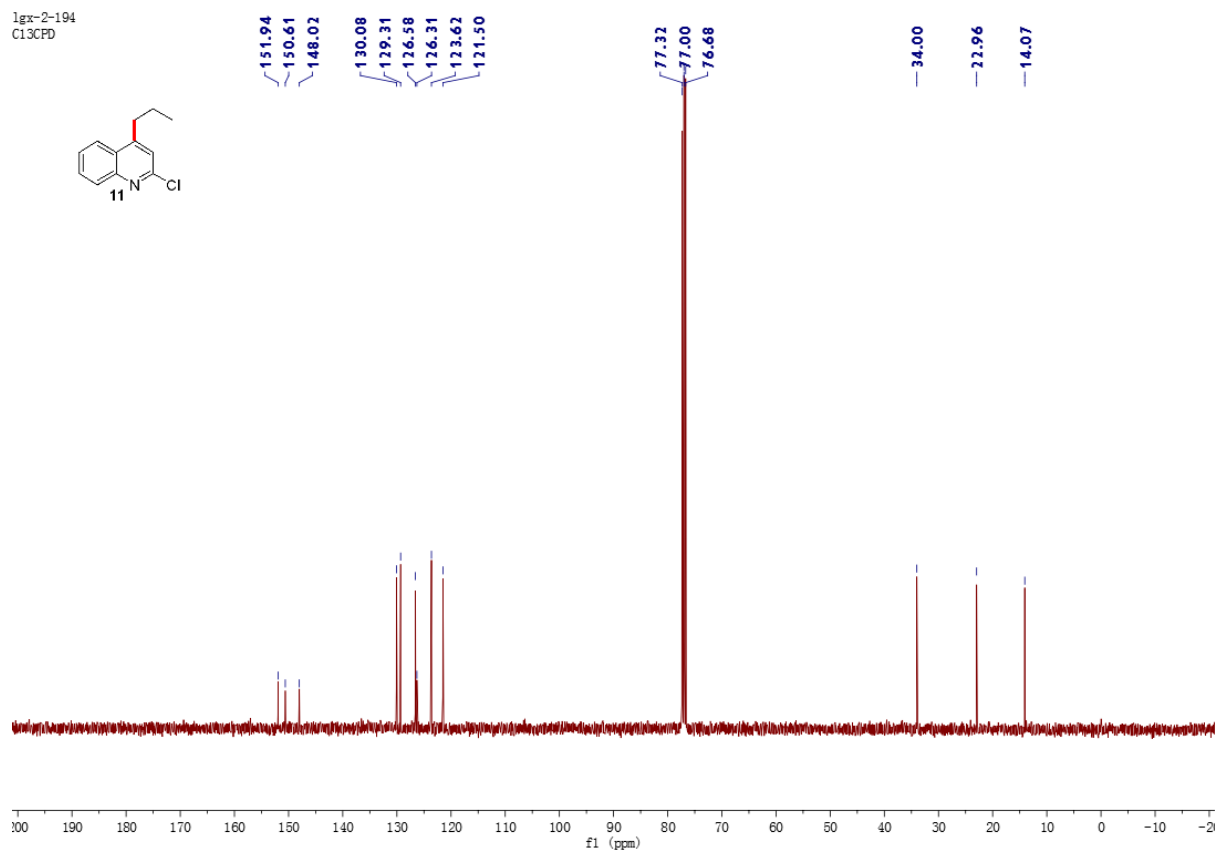
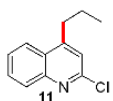




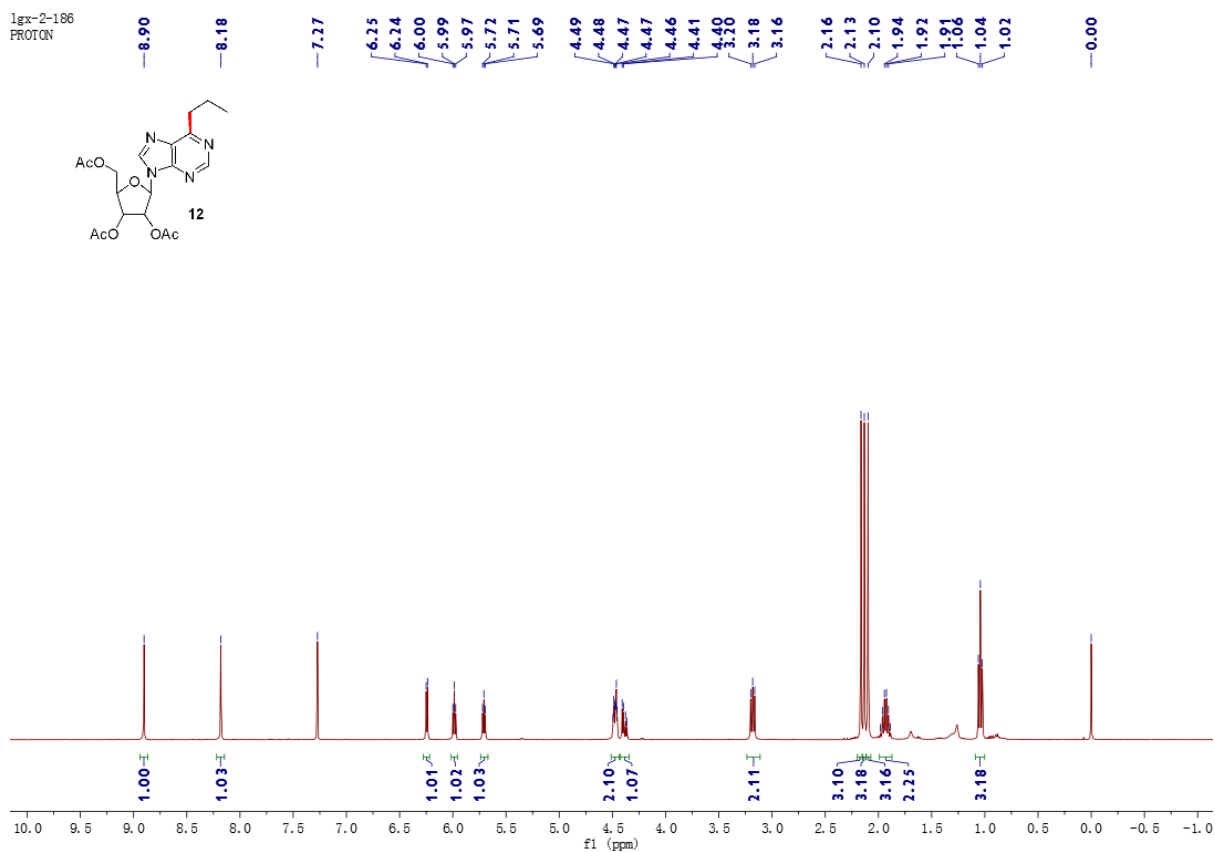
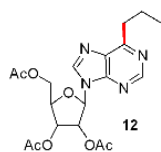
1gx-2-194
PROTON



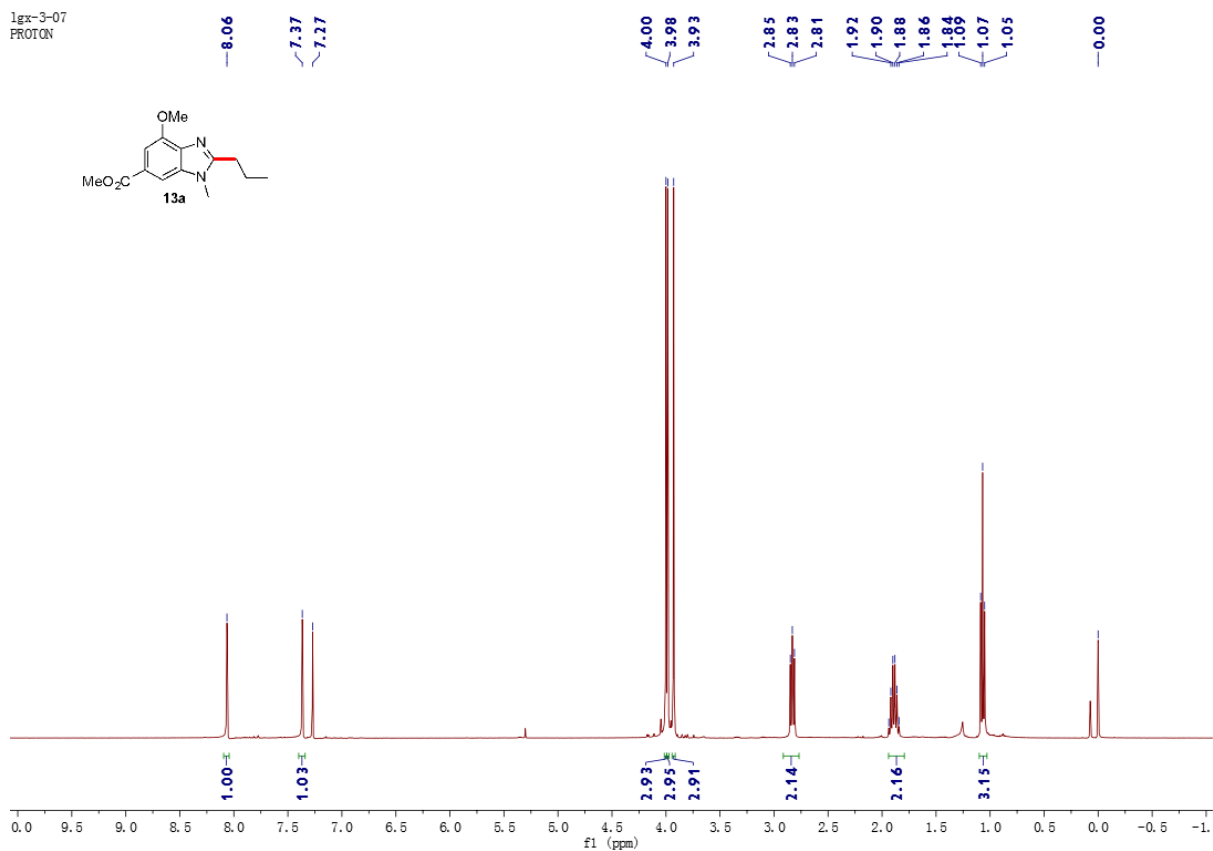
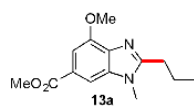
1gx-2-194
C13CPD

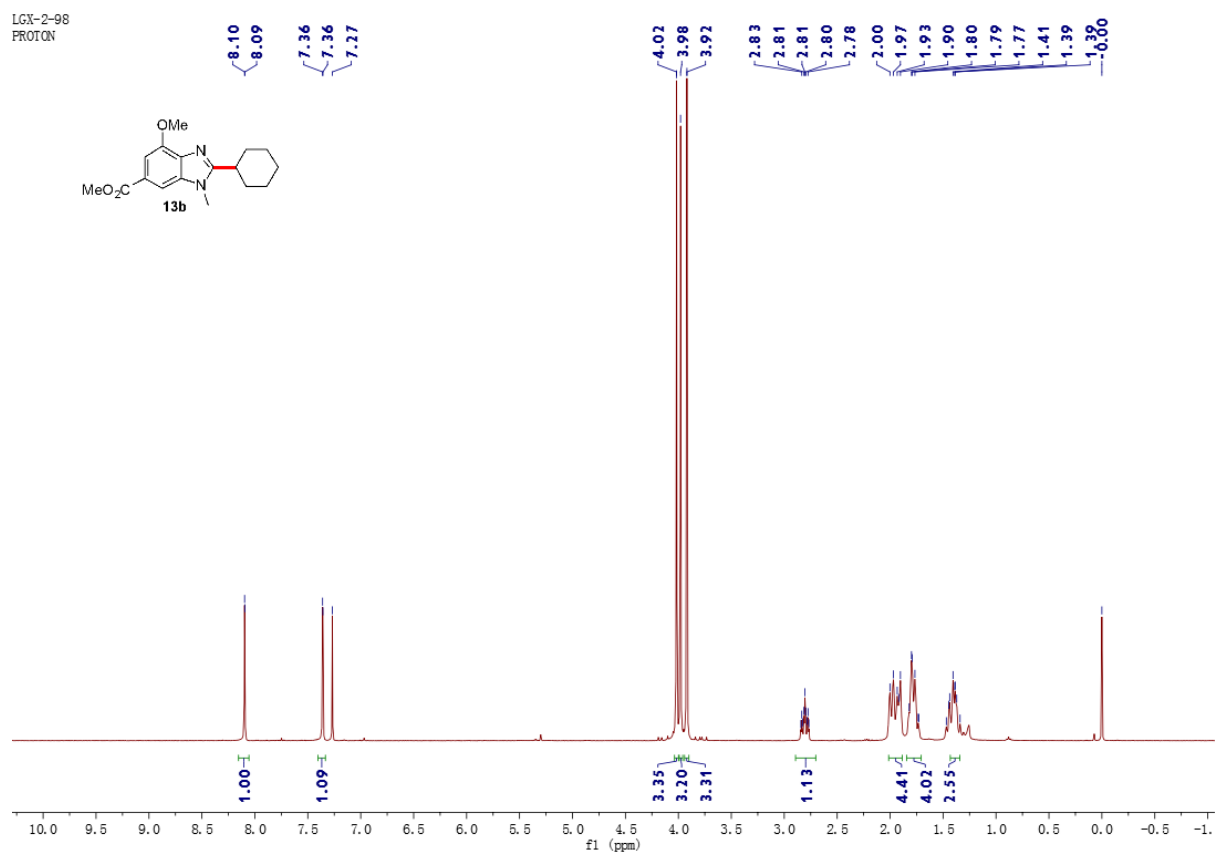
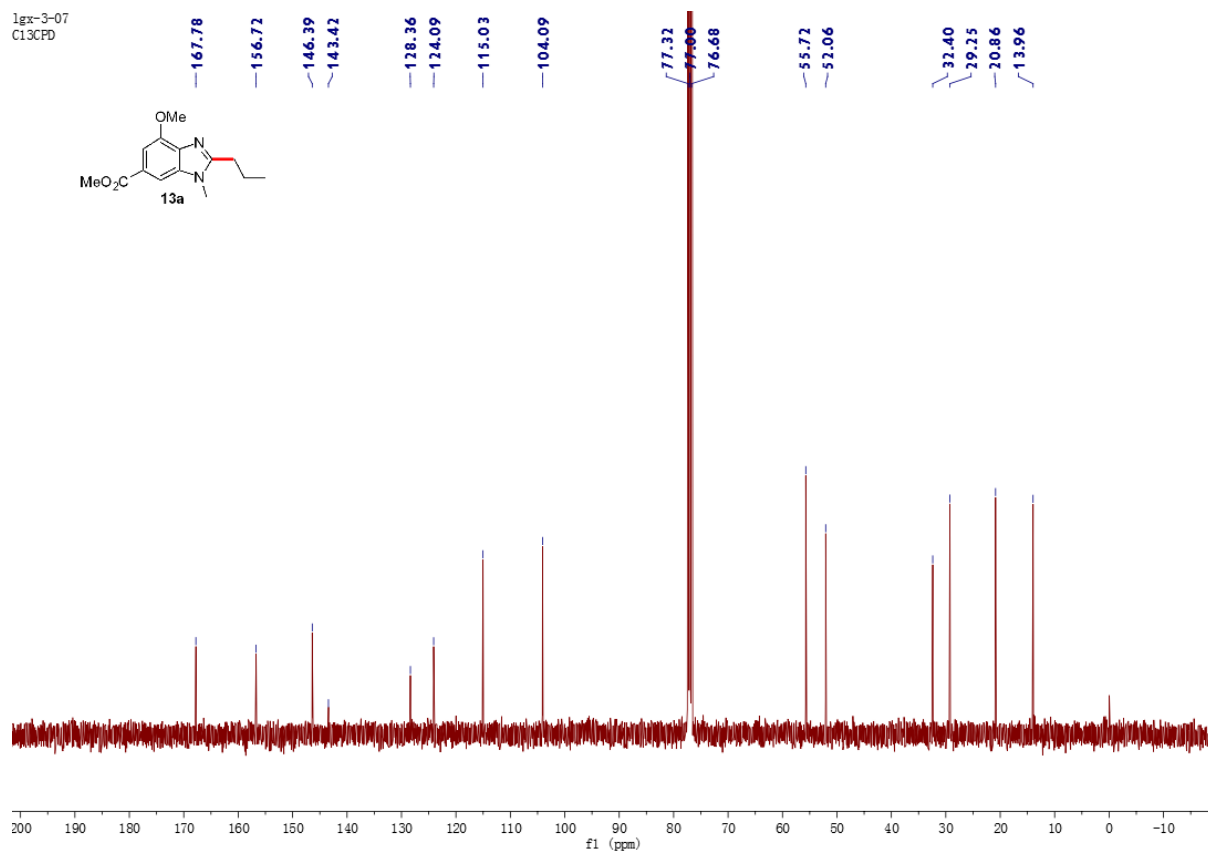


1gx-2-186
PROTON

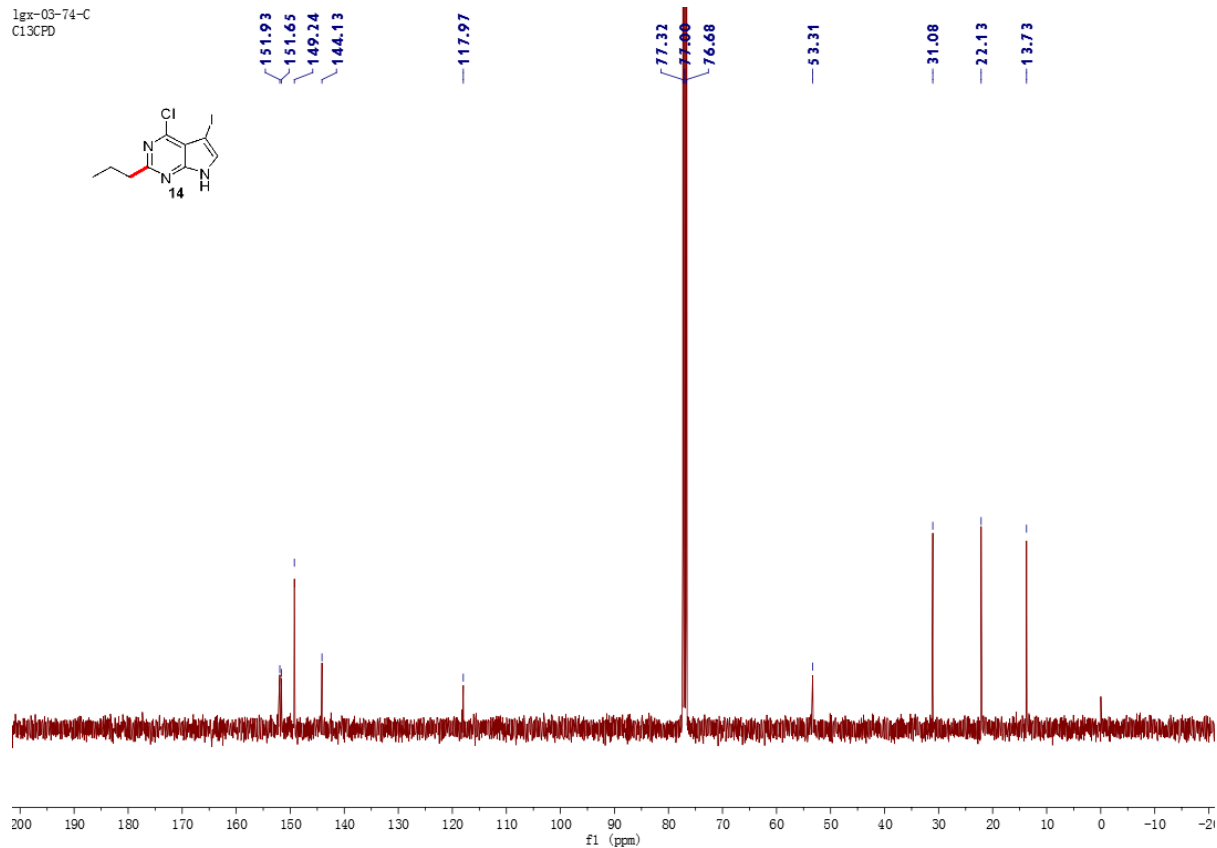
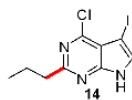


1gx-3-07
PROTON

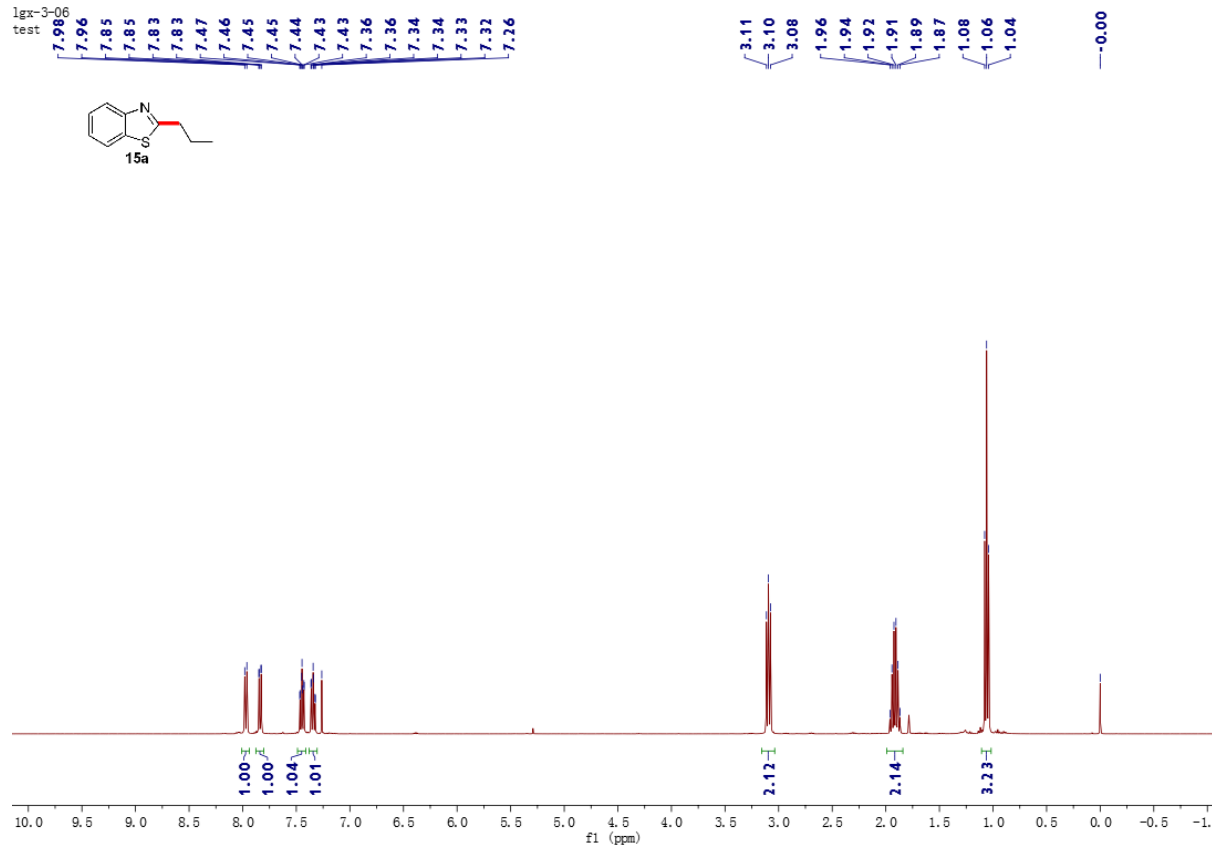
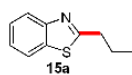


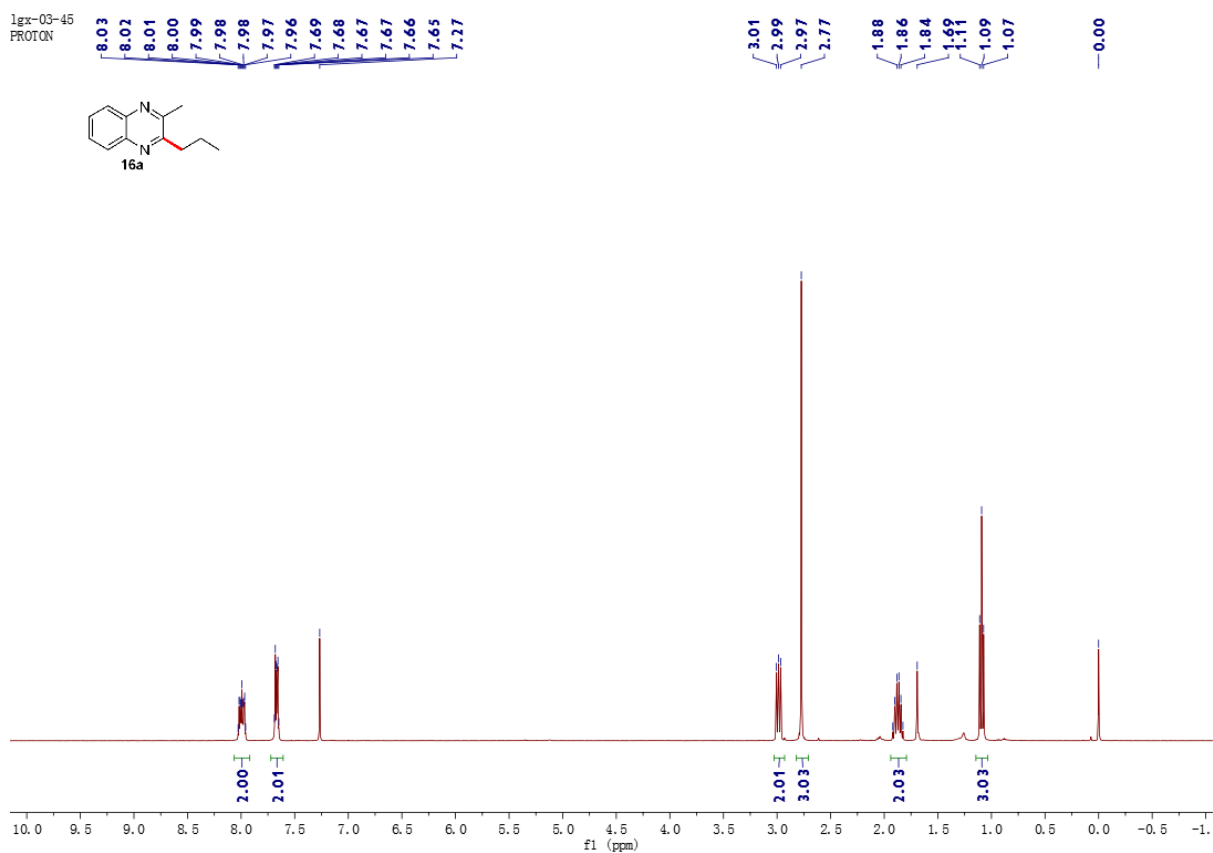
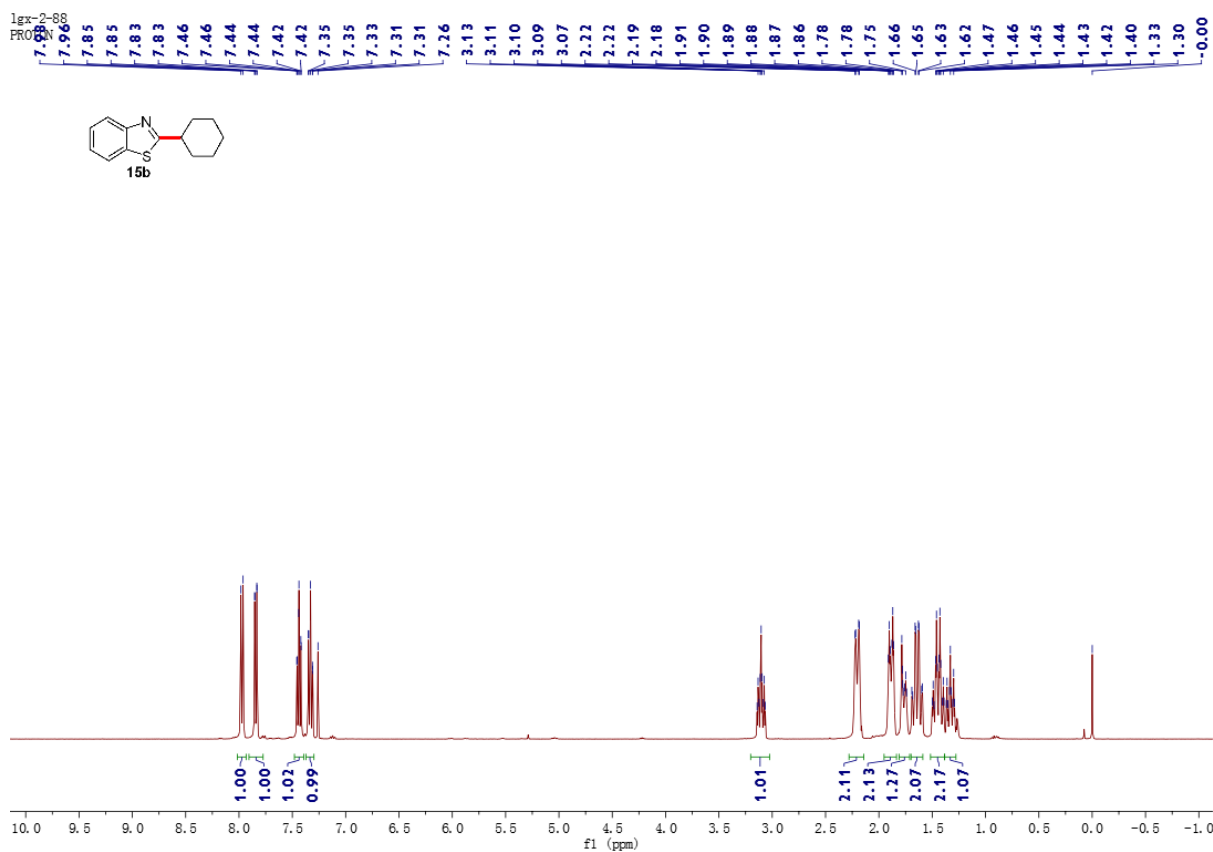


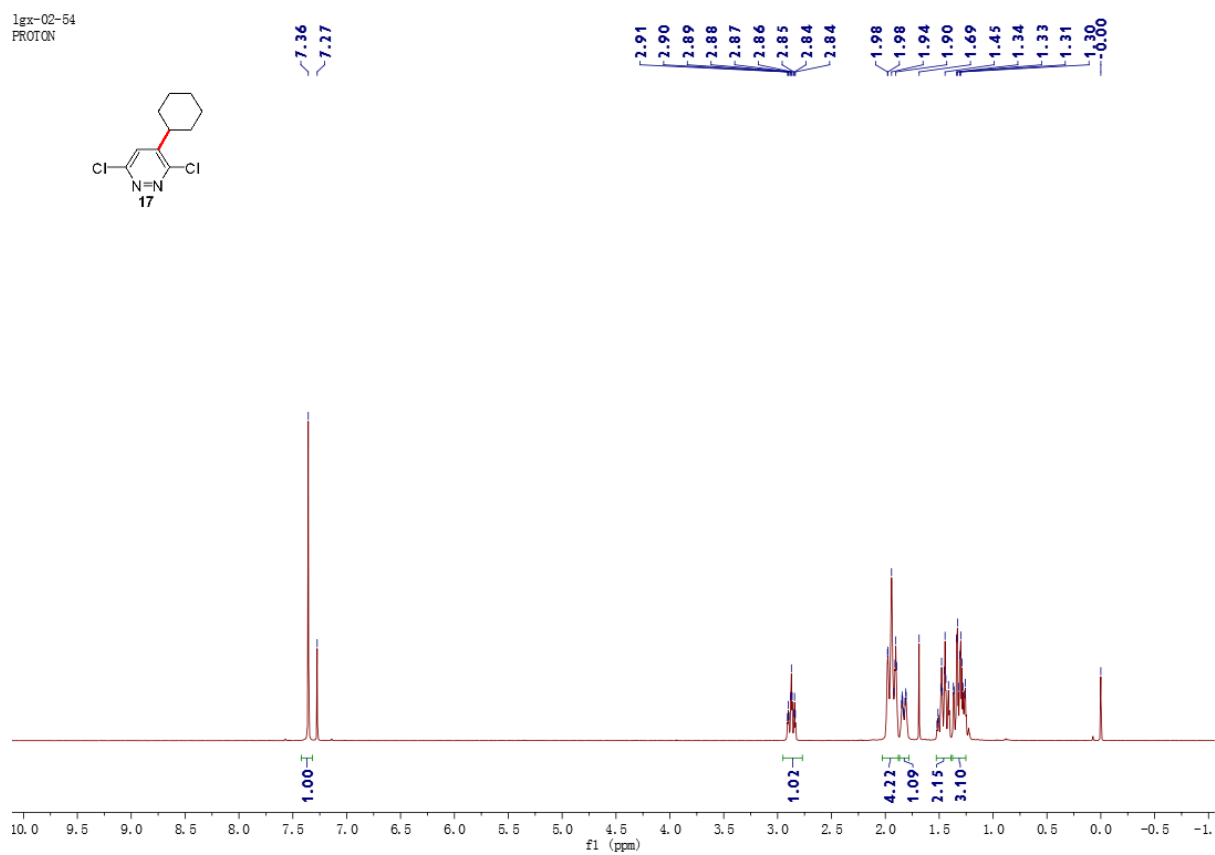
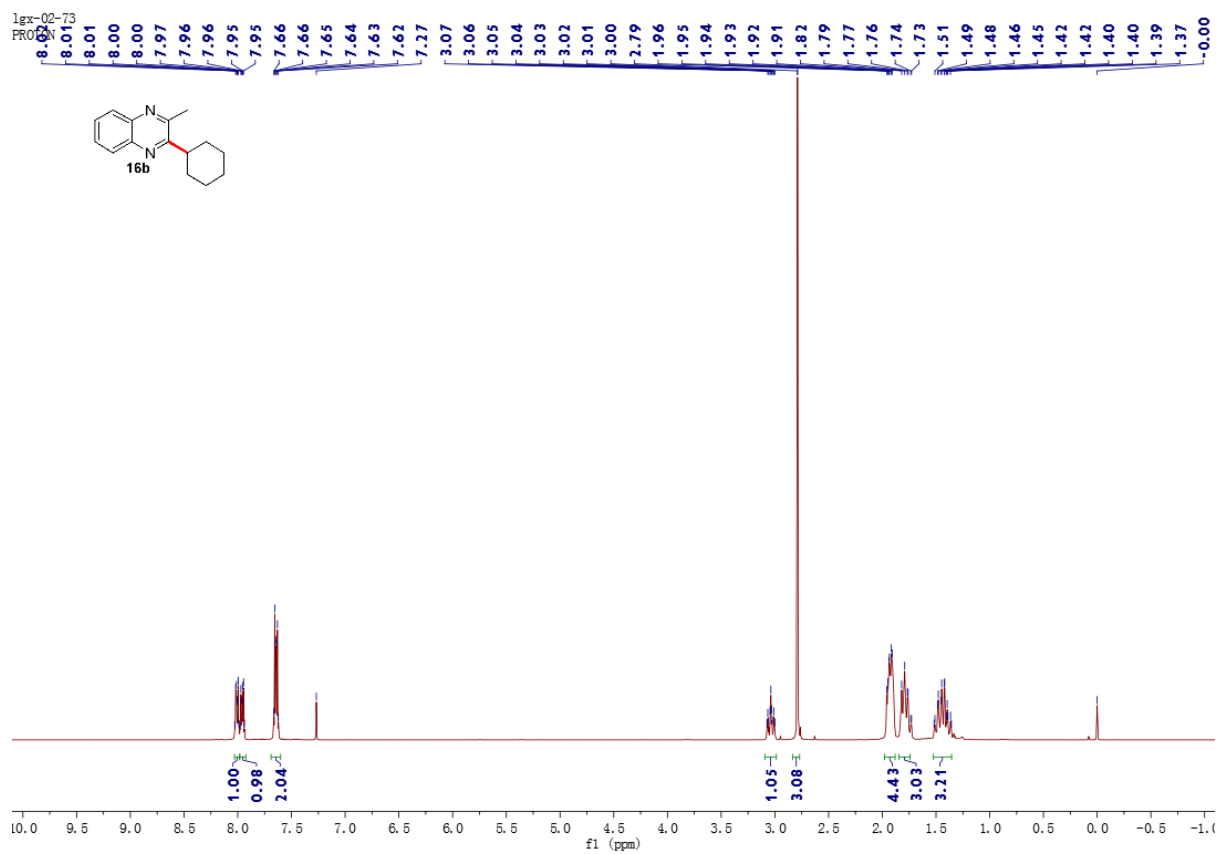
lgx-03-74-C
C13CPD



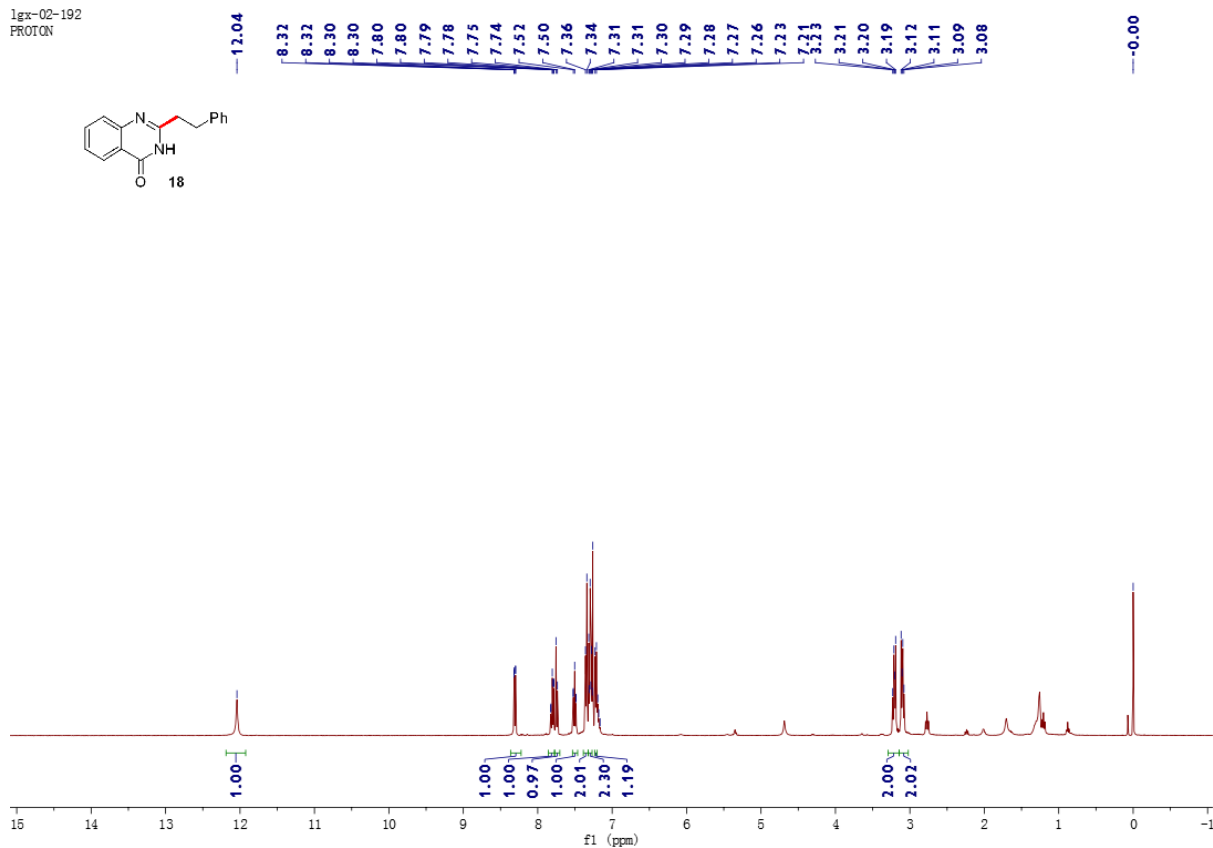
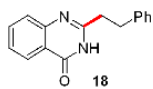
lgx-3-06
test



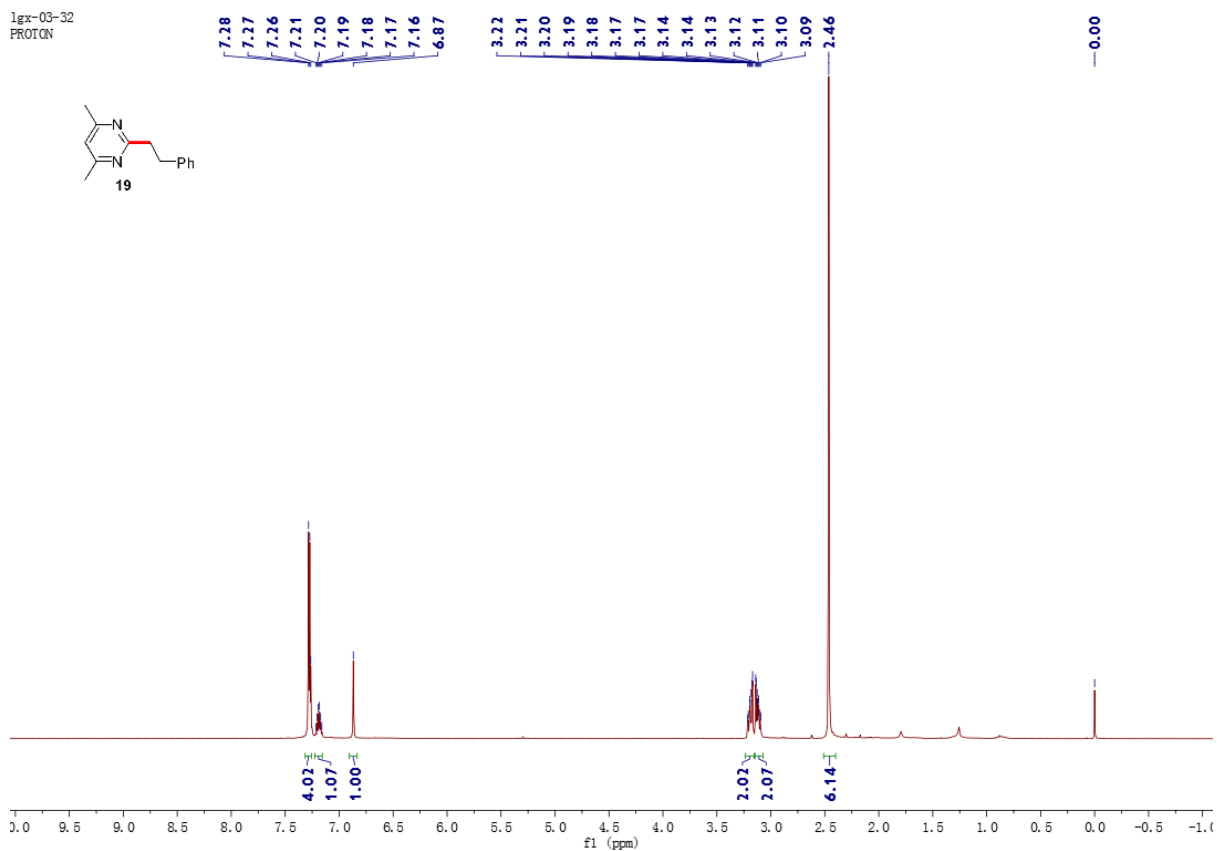
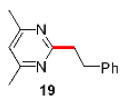




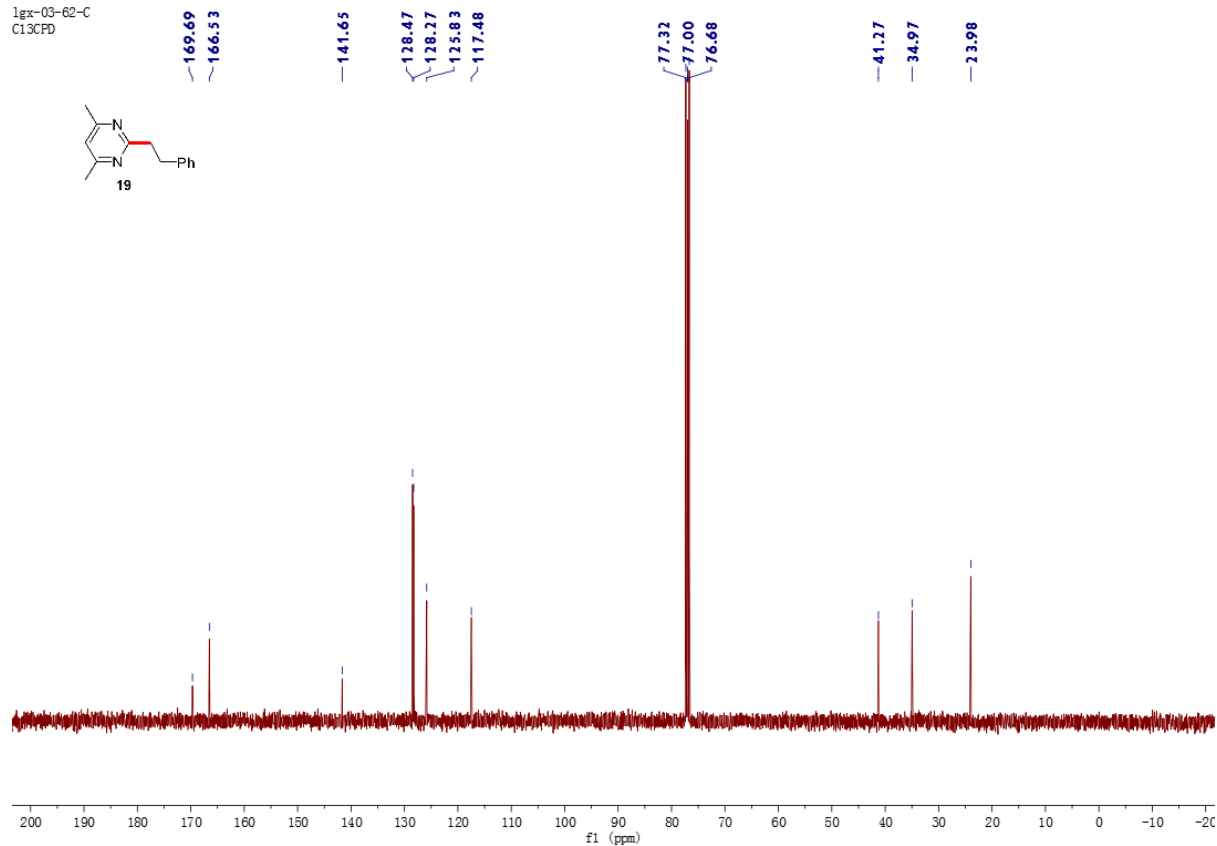
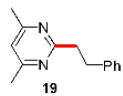
1gx-02-192
PROTON



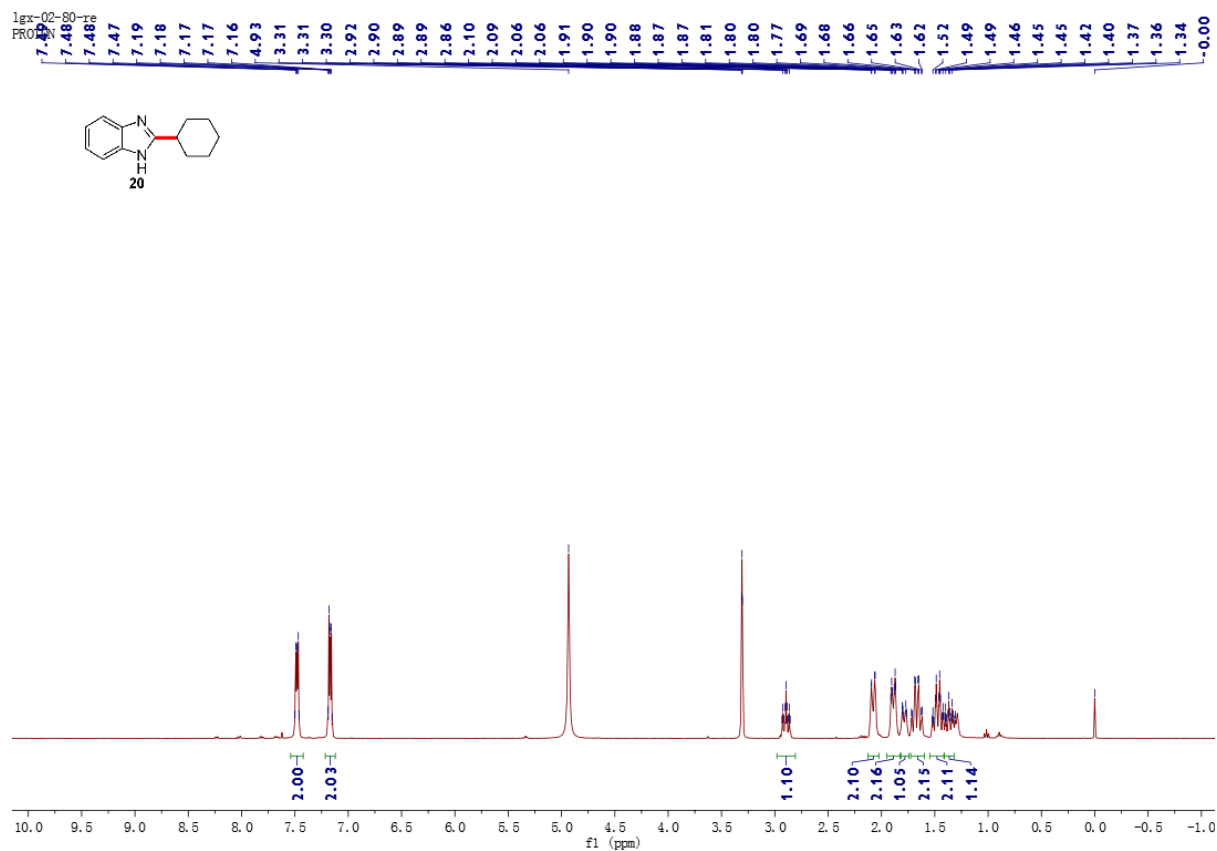
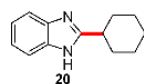
1gx-03-32
PROTON

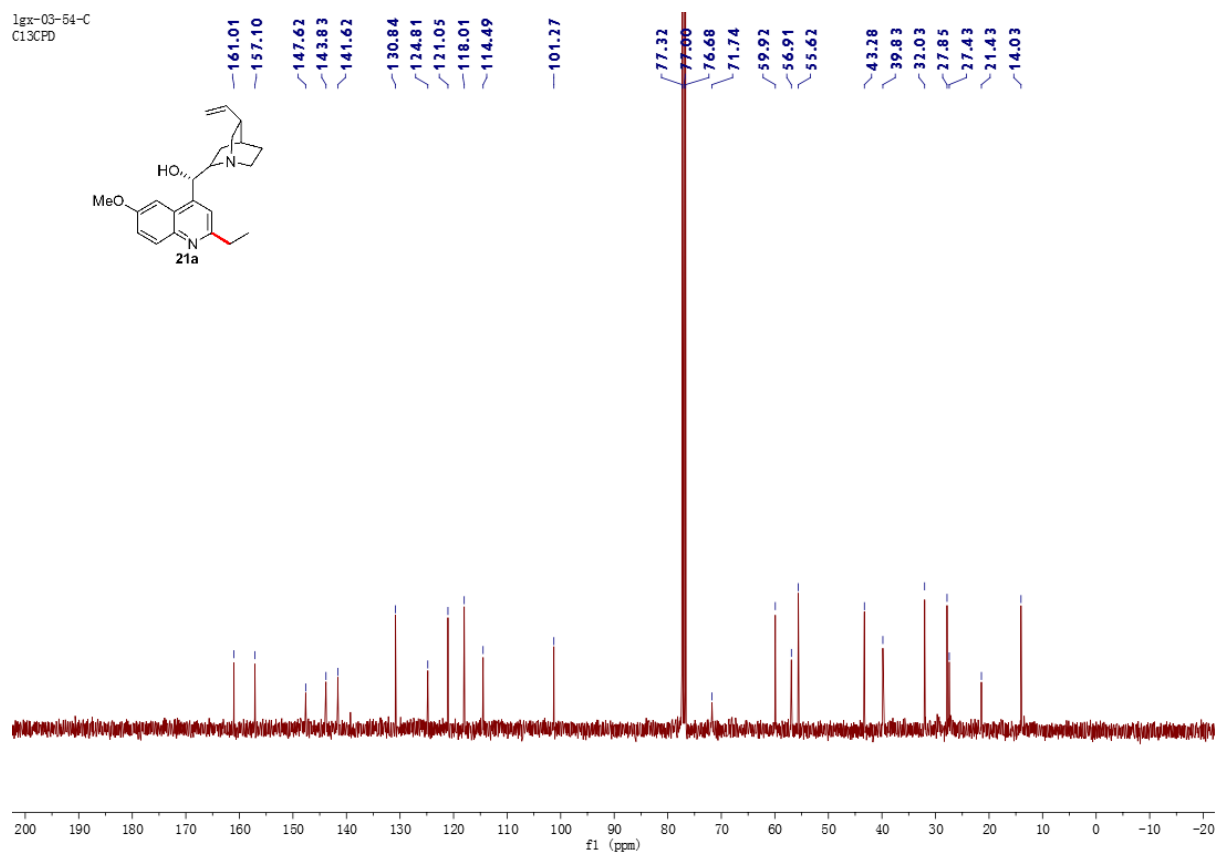
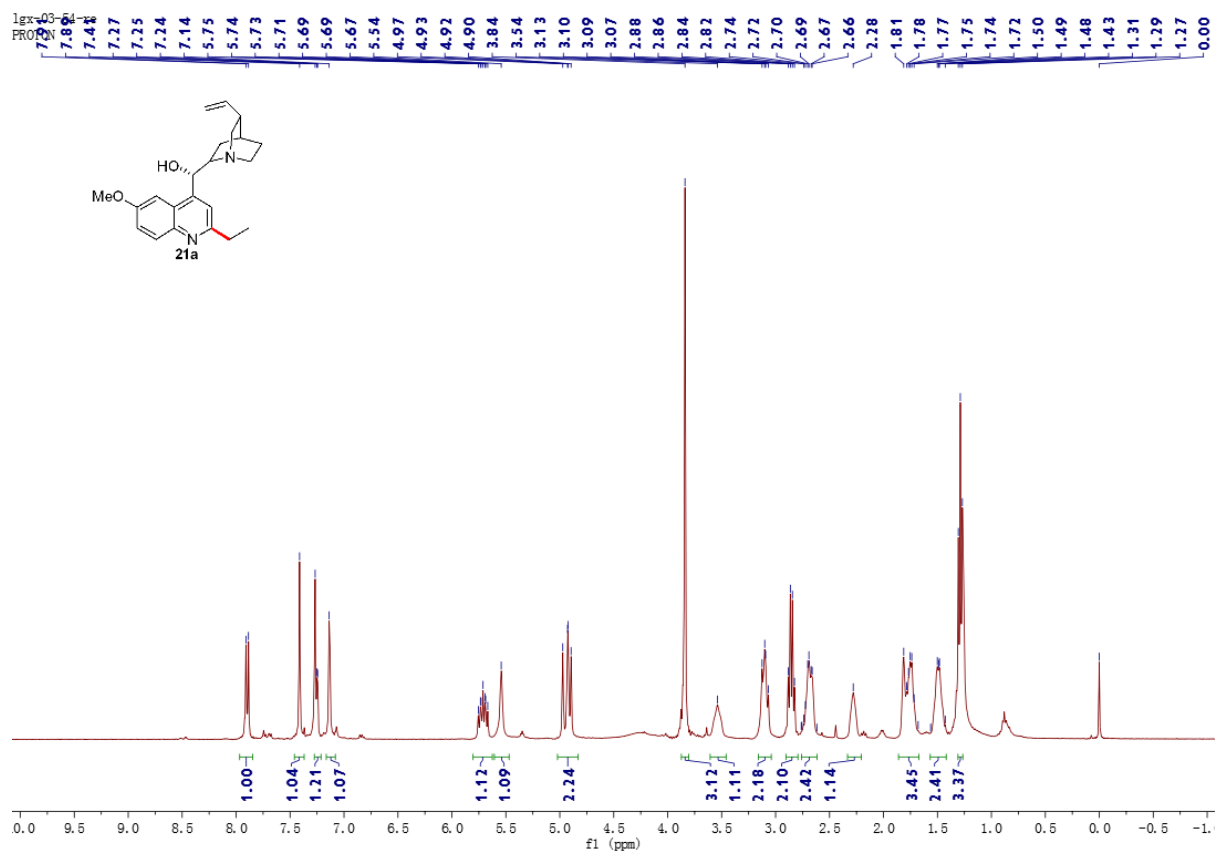


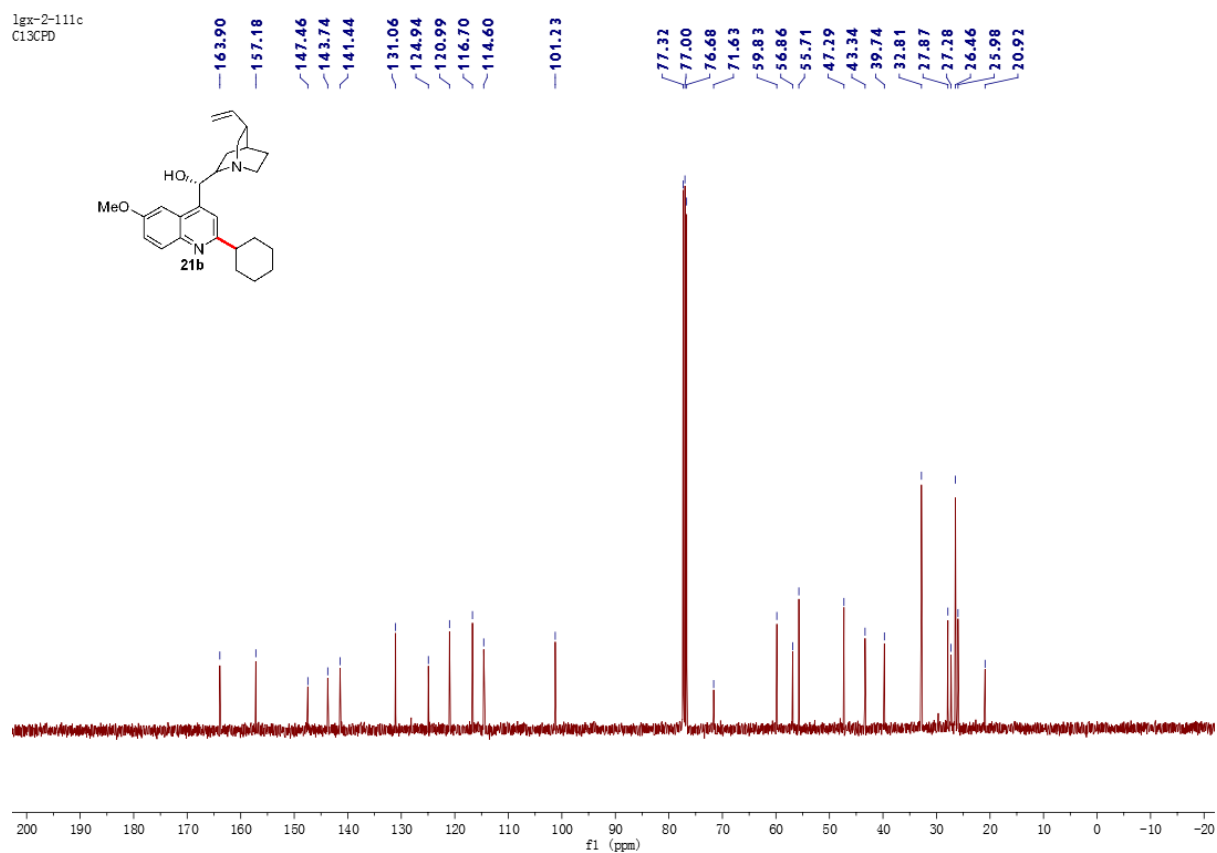
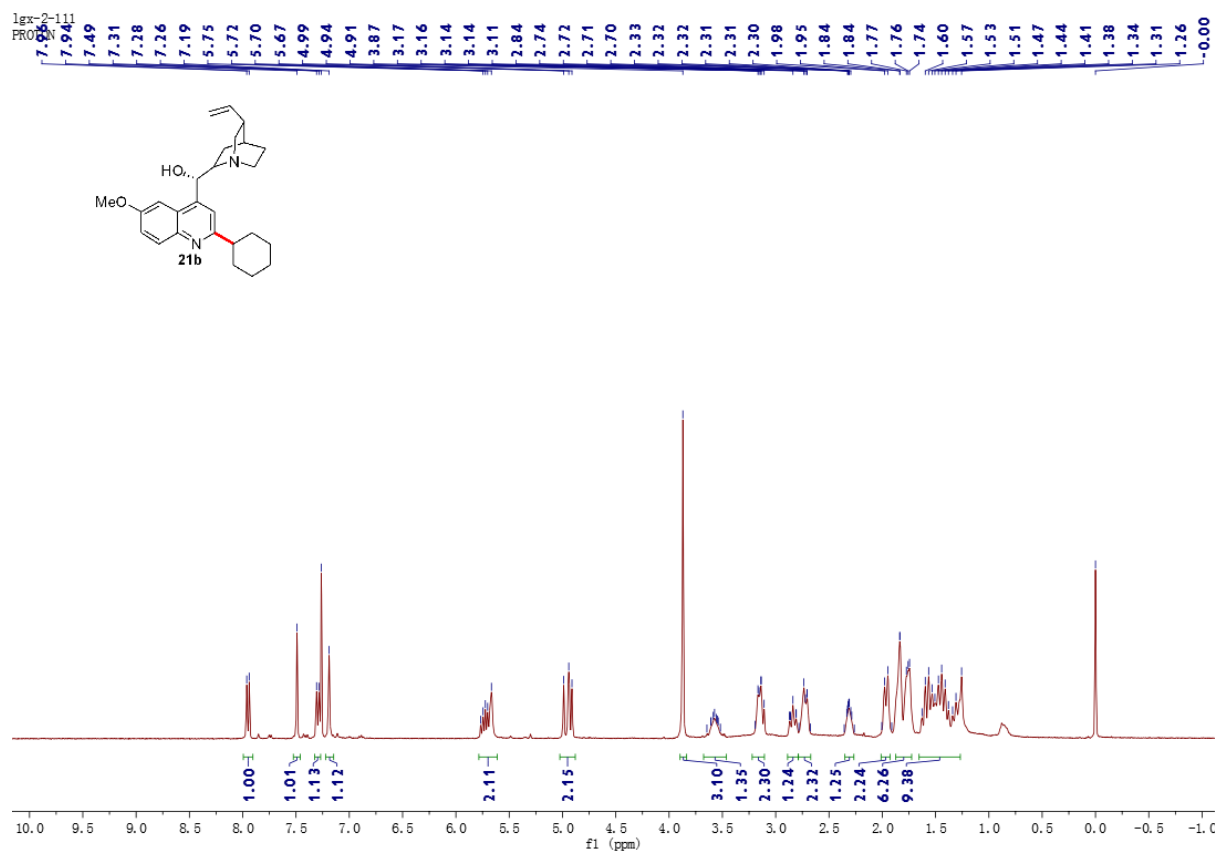
1gx-03-62-C
C13CPD



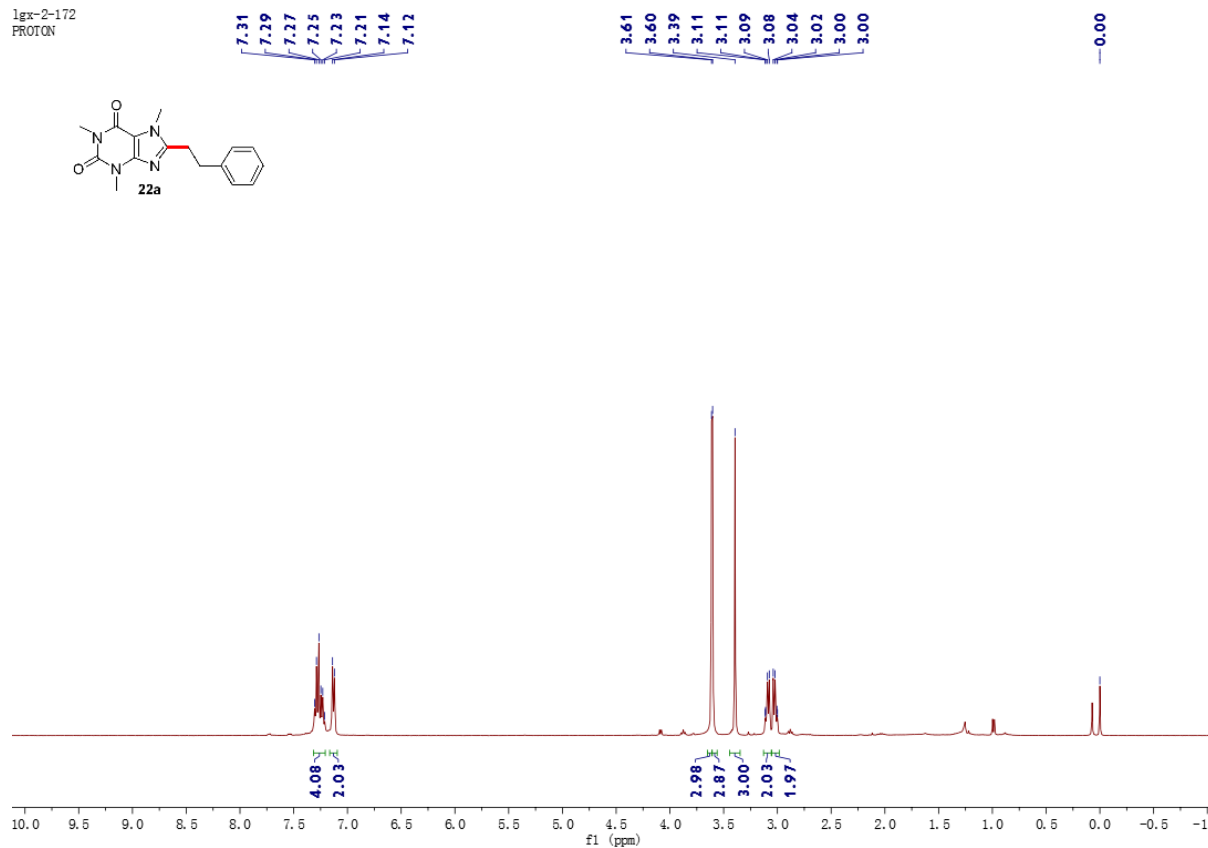
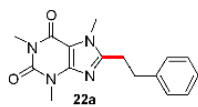
1gx-02-80-re
PROTON



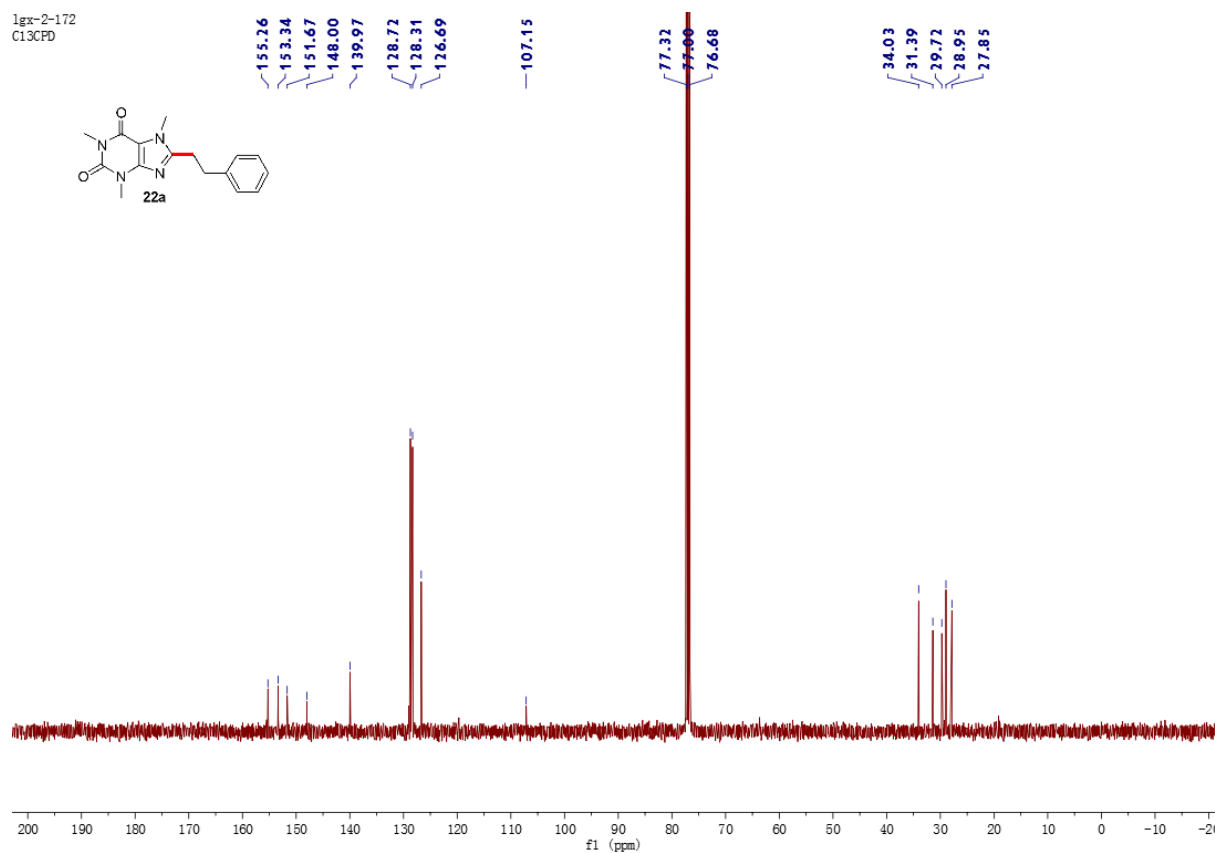
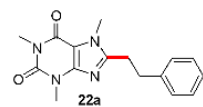




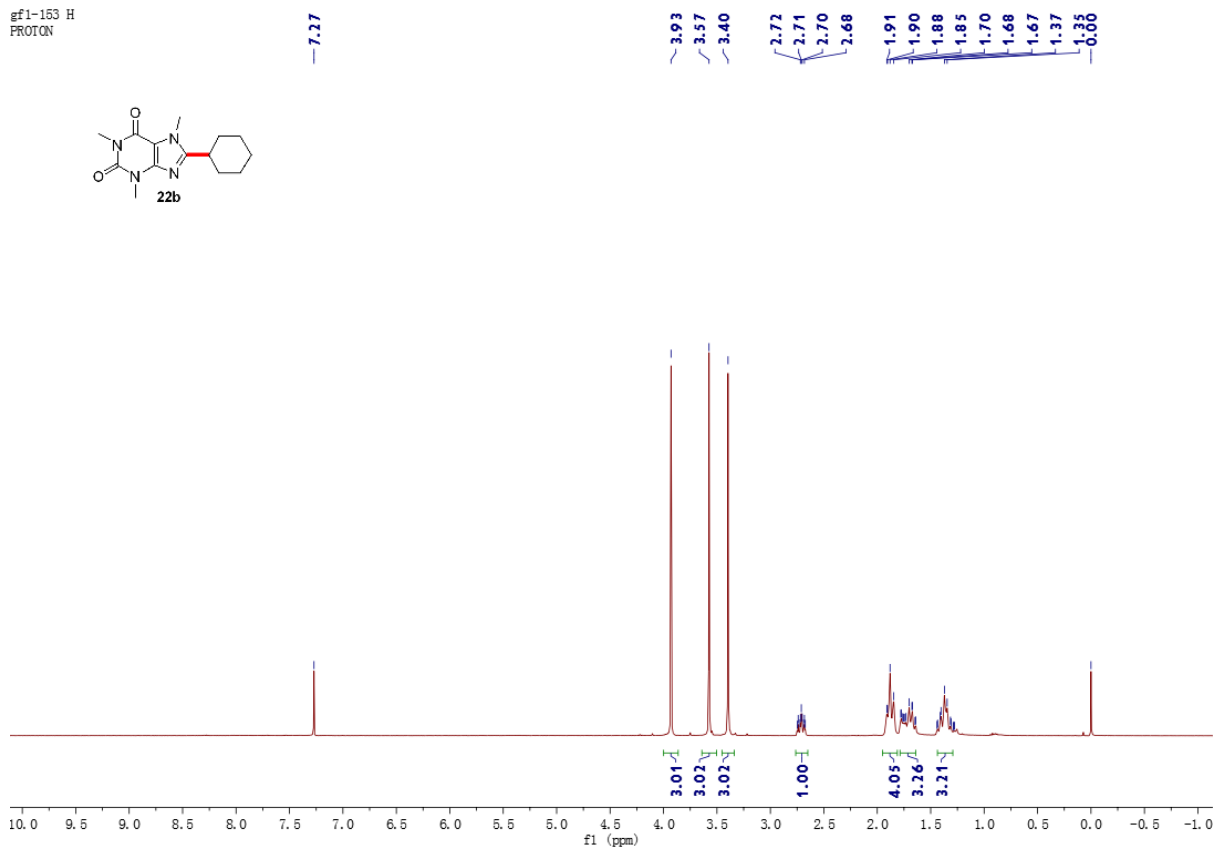
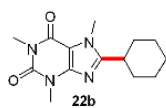
1gx-2-172
PROTON



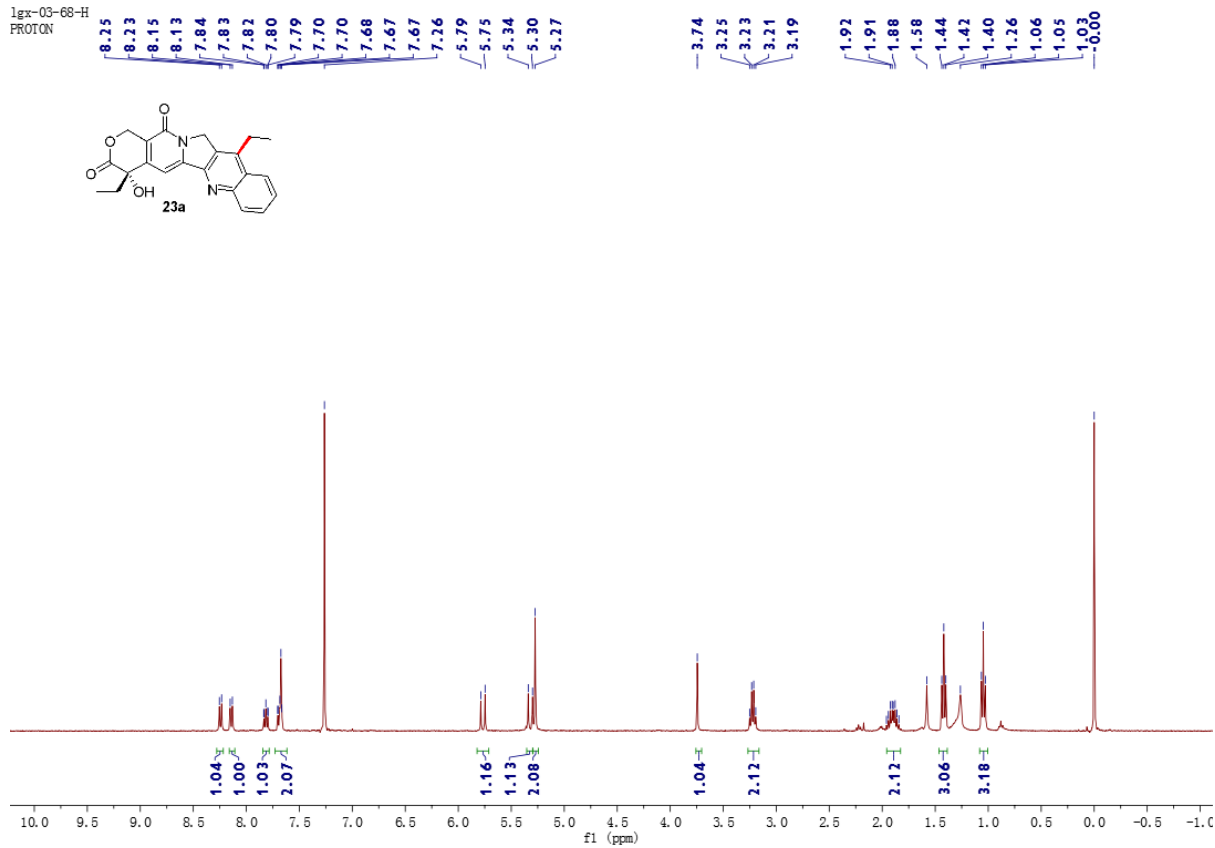
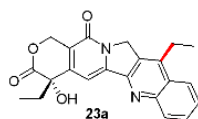
1gx-2-172
C13CPD



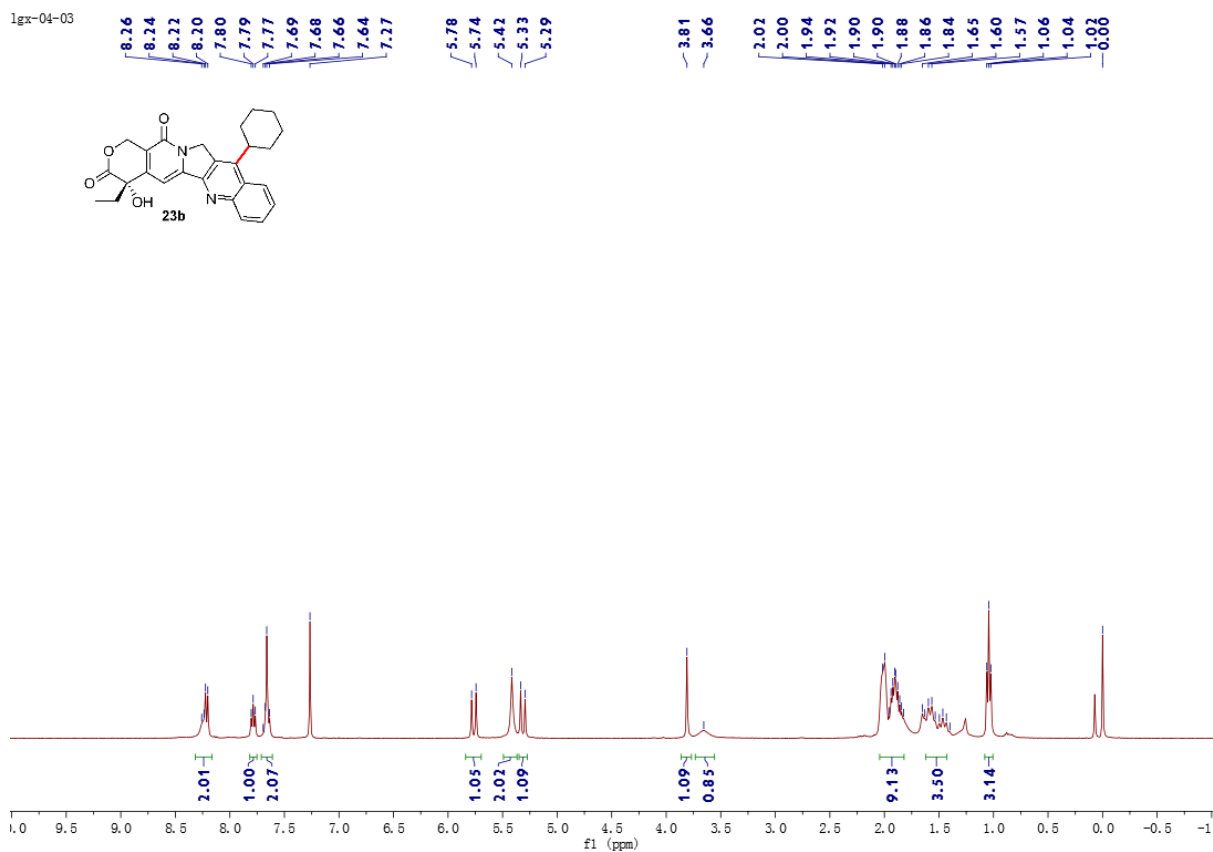
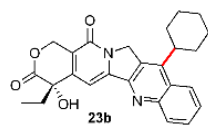
gf1-163 H
PROTON



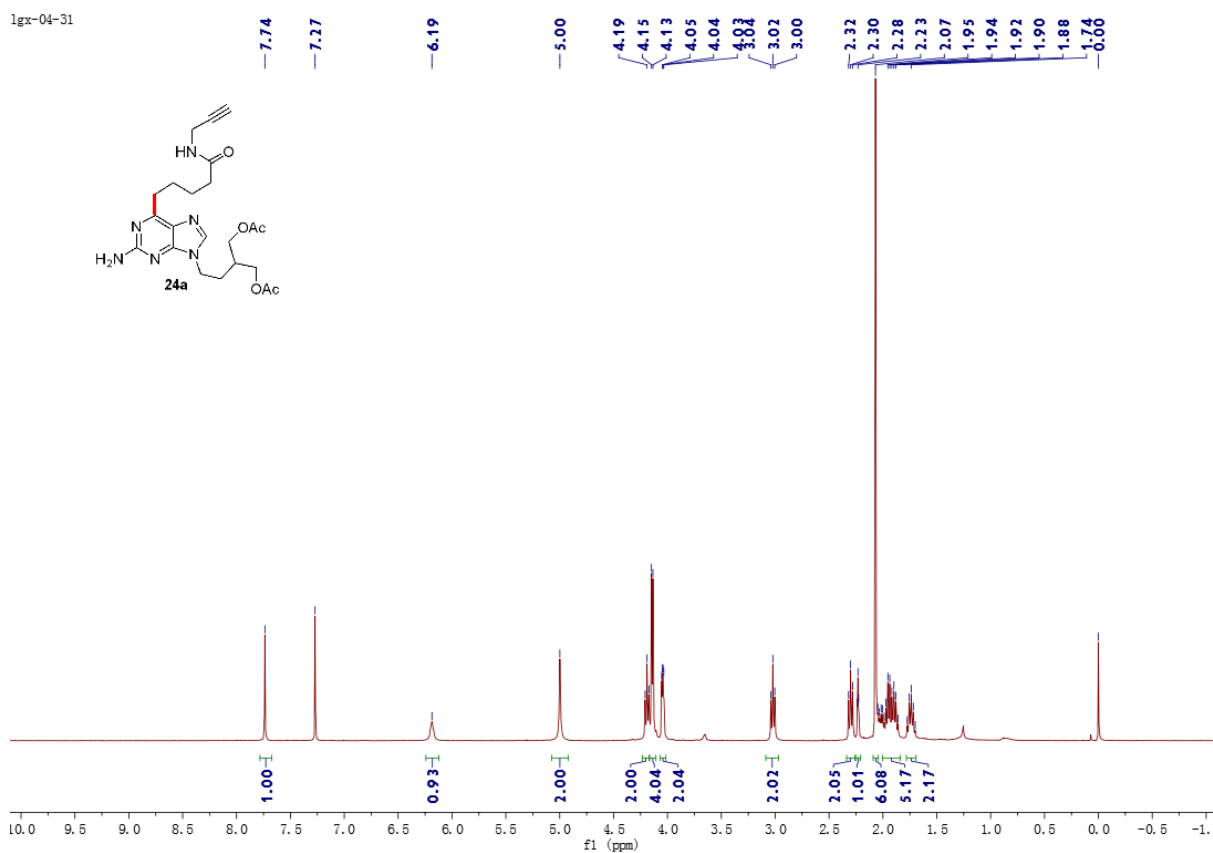
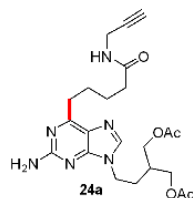
1gx-03-68-H
PROTON



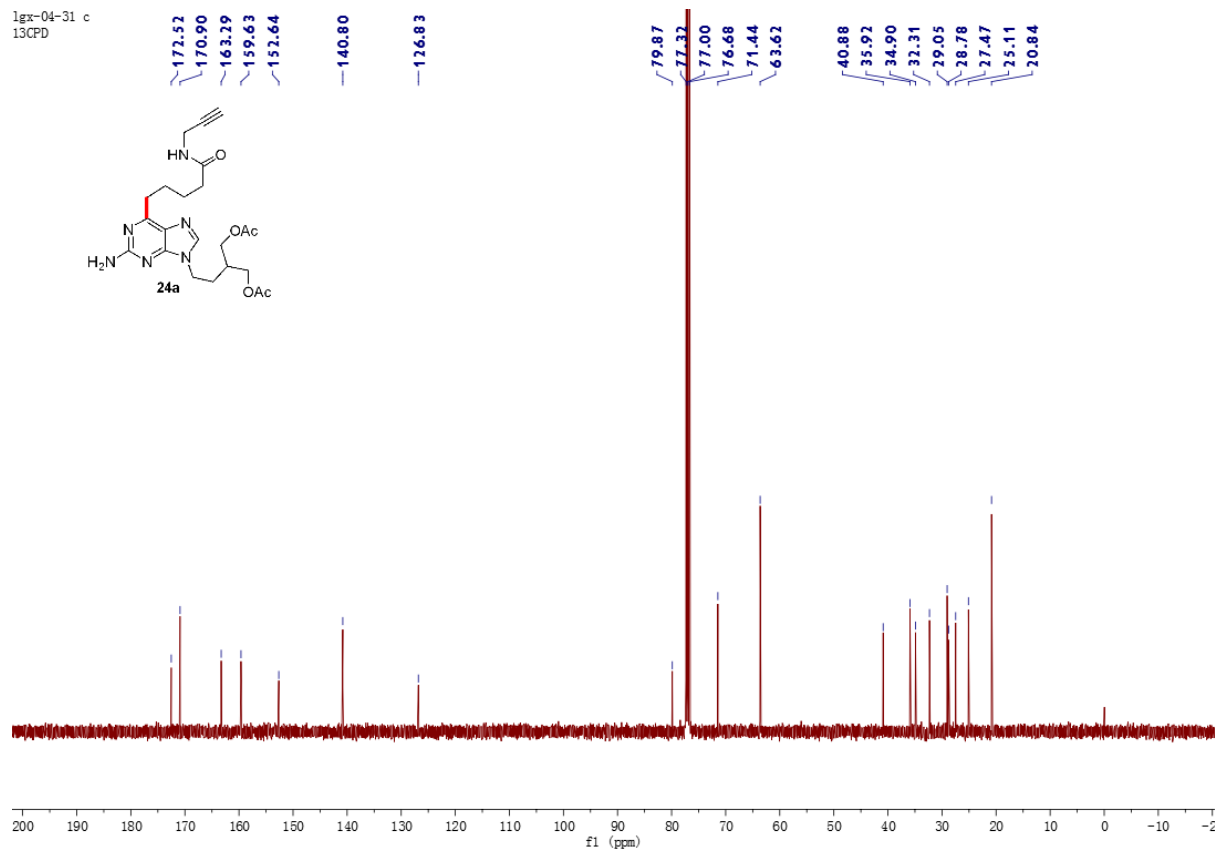
lgx-04-03



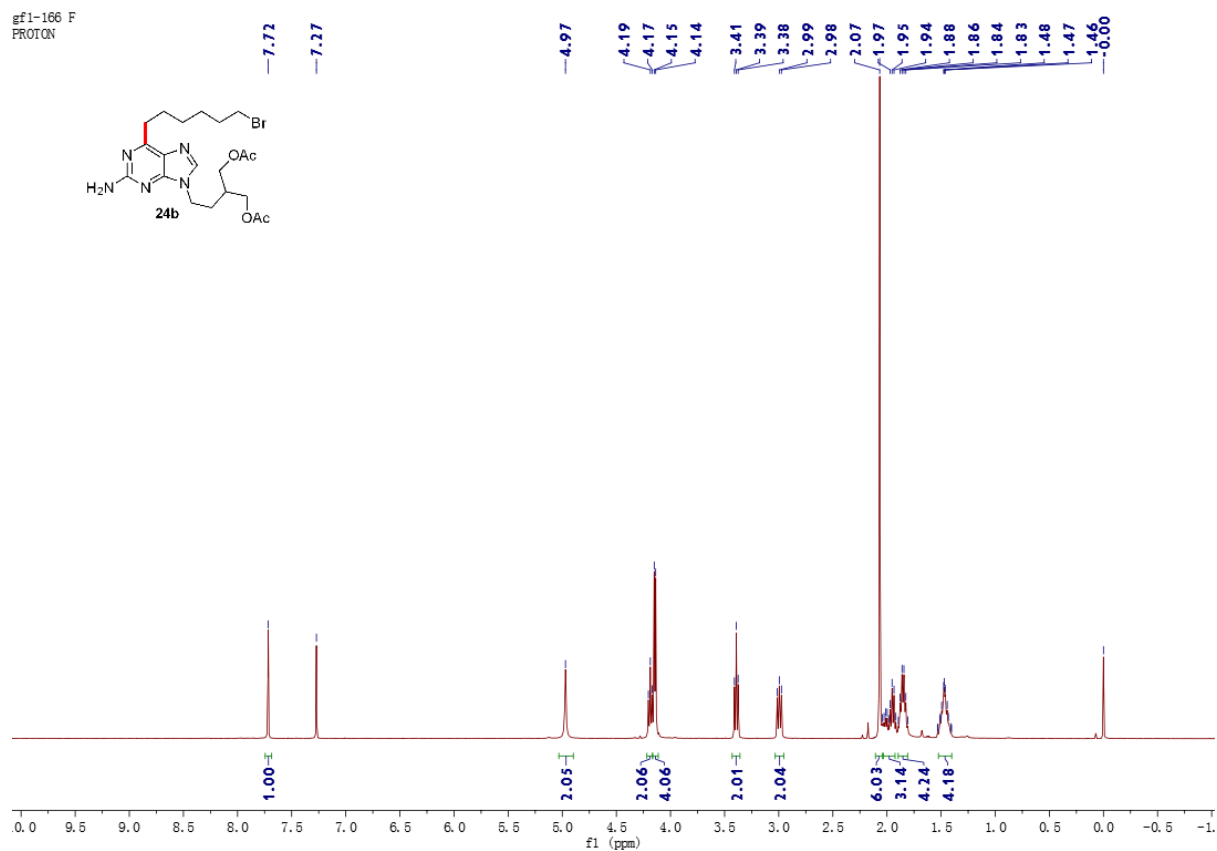
lgx-04-31

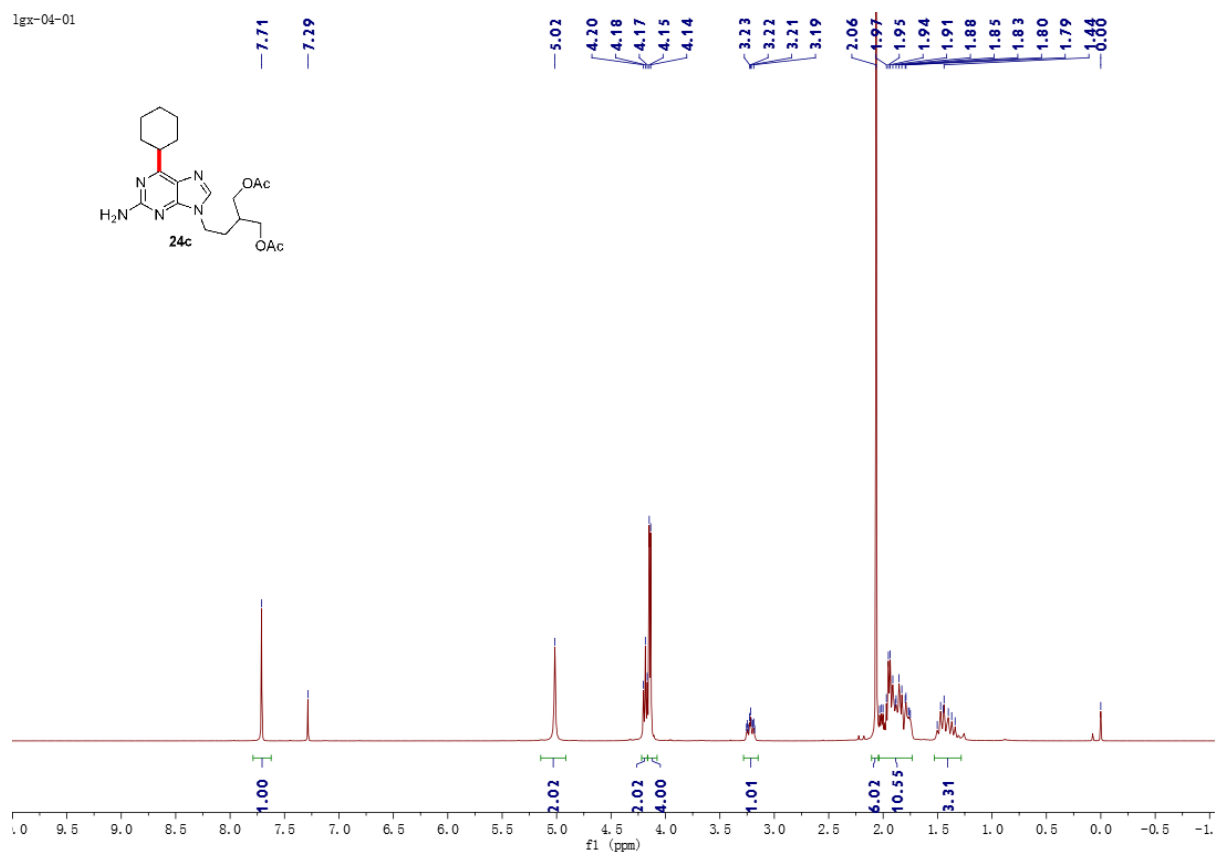
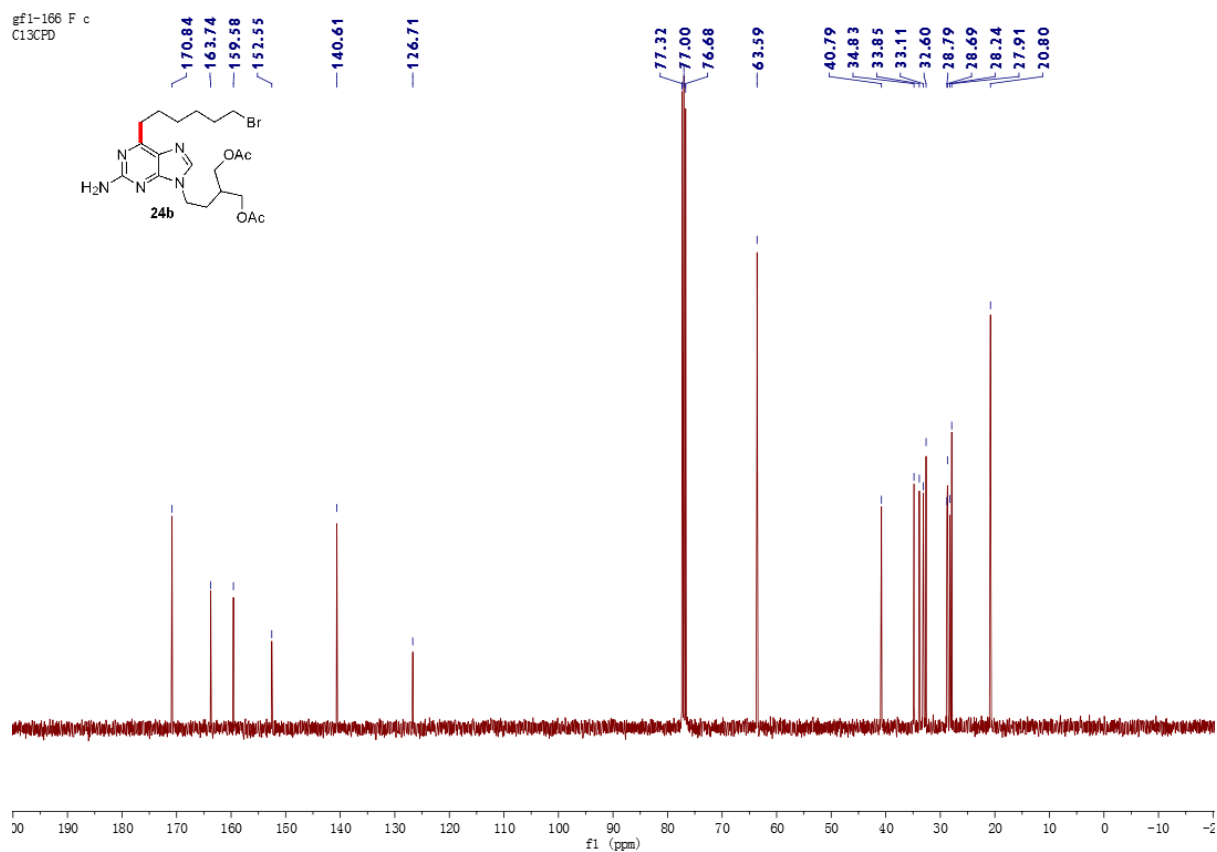


1gx-04-31 c
13CPD

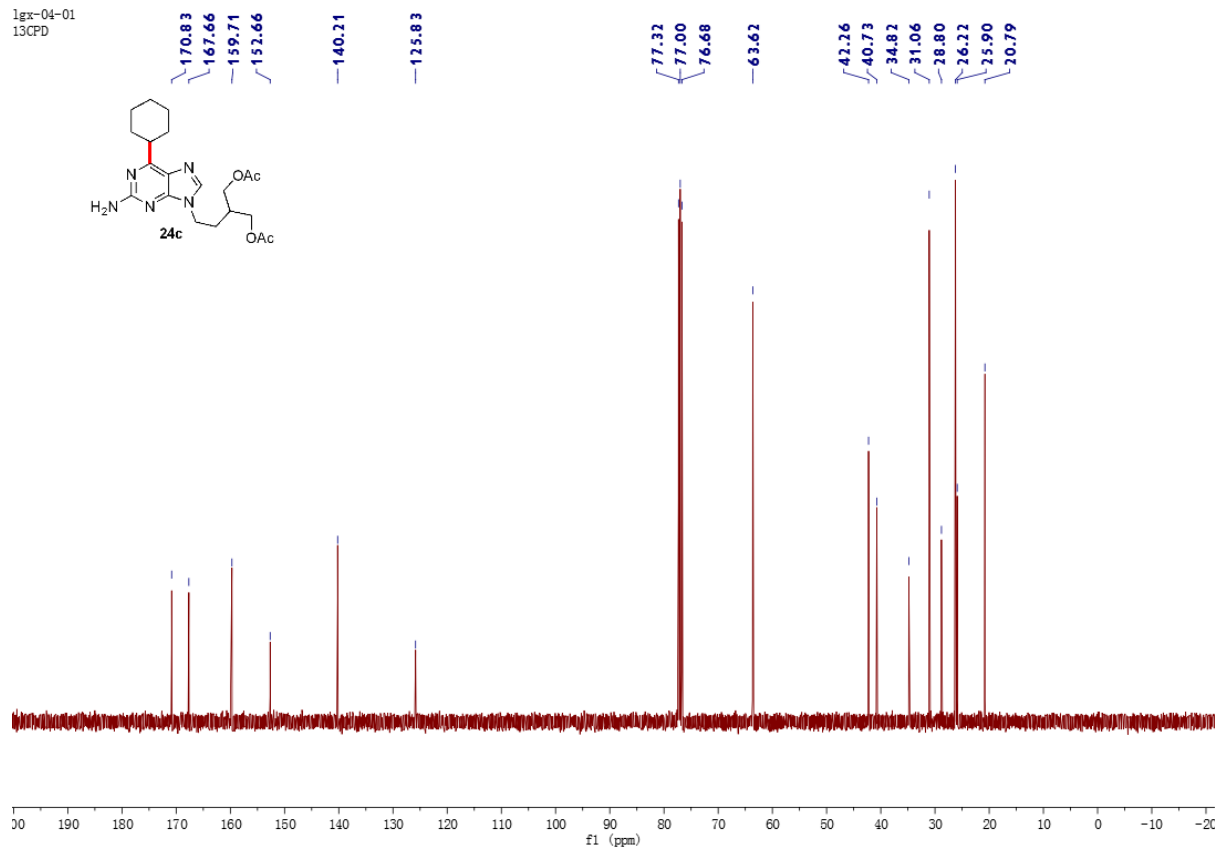


gf1-166 F
PROTON

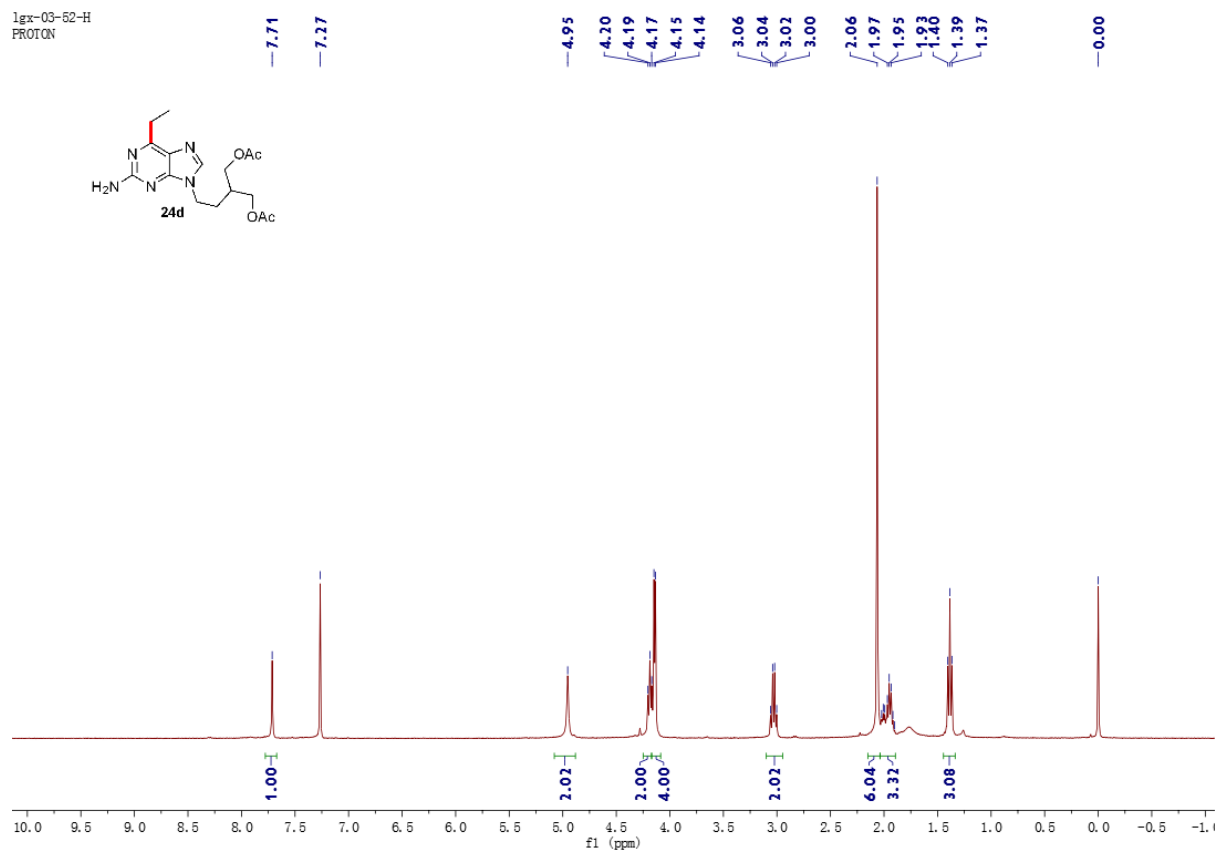


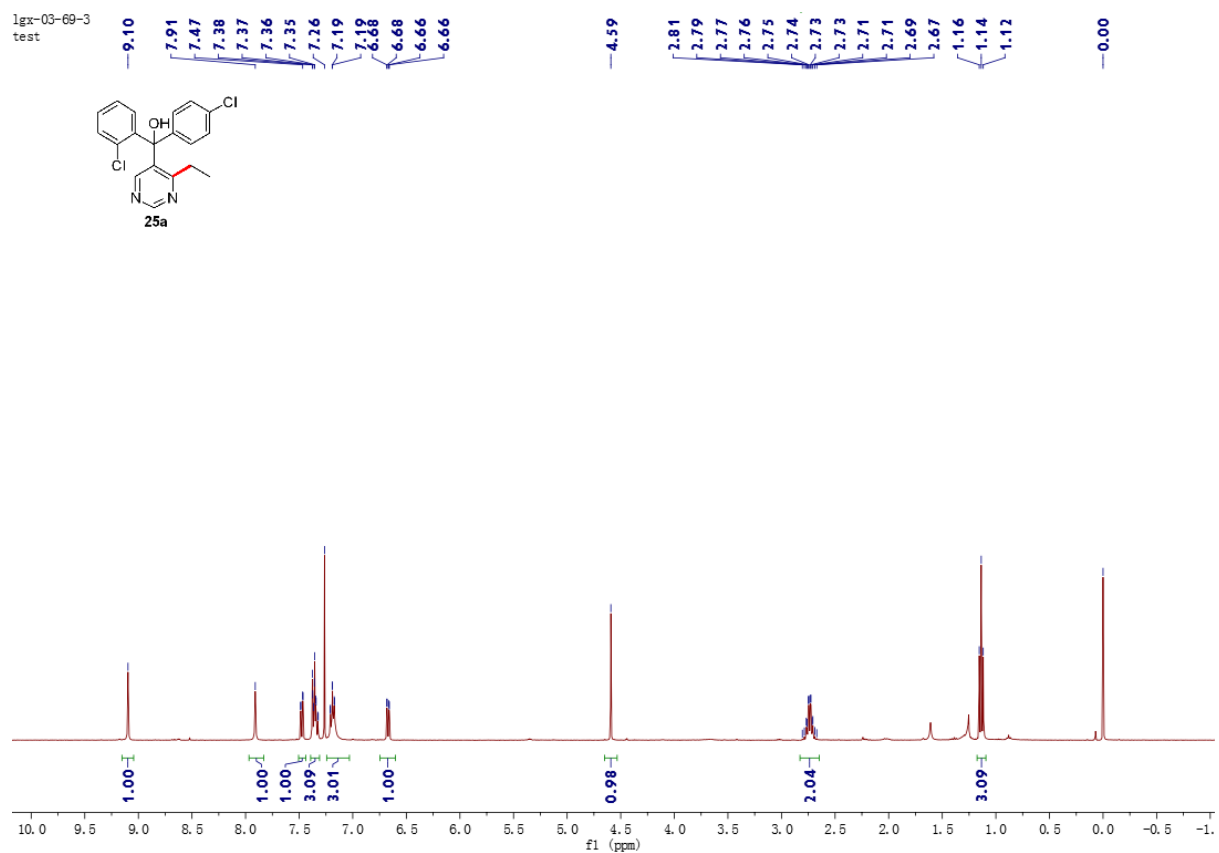
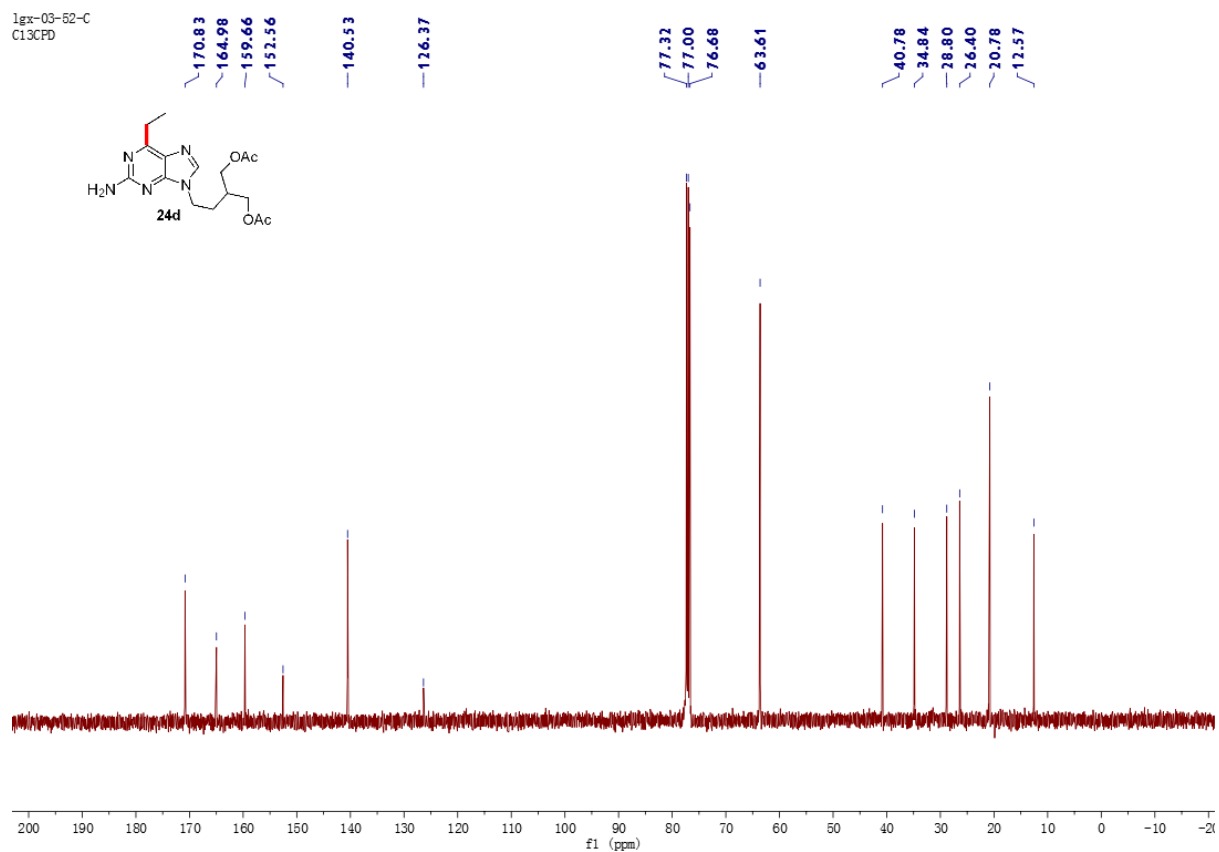


1gx-04-01
13CPD

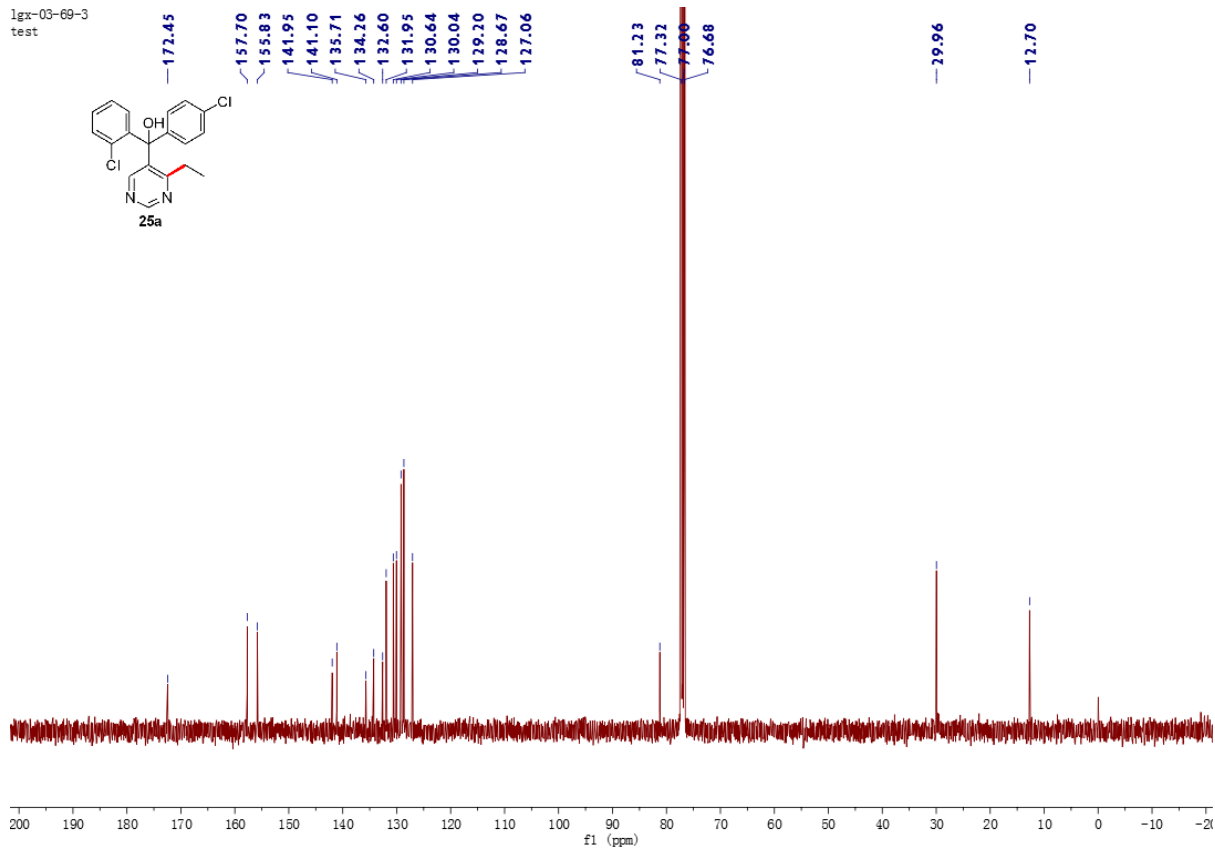


1gx-03-52-H
PROTON

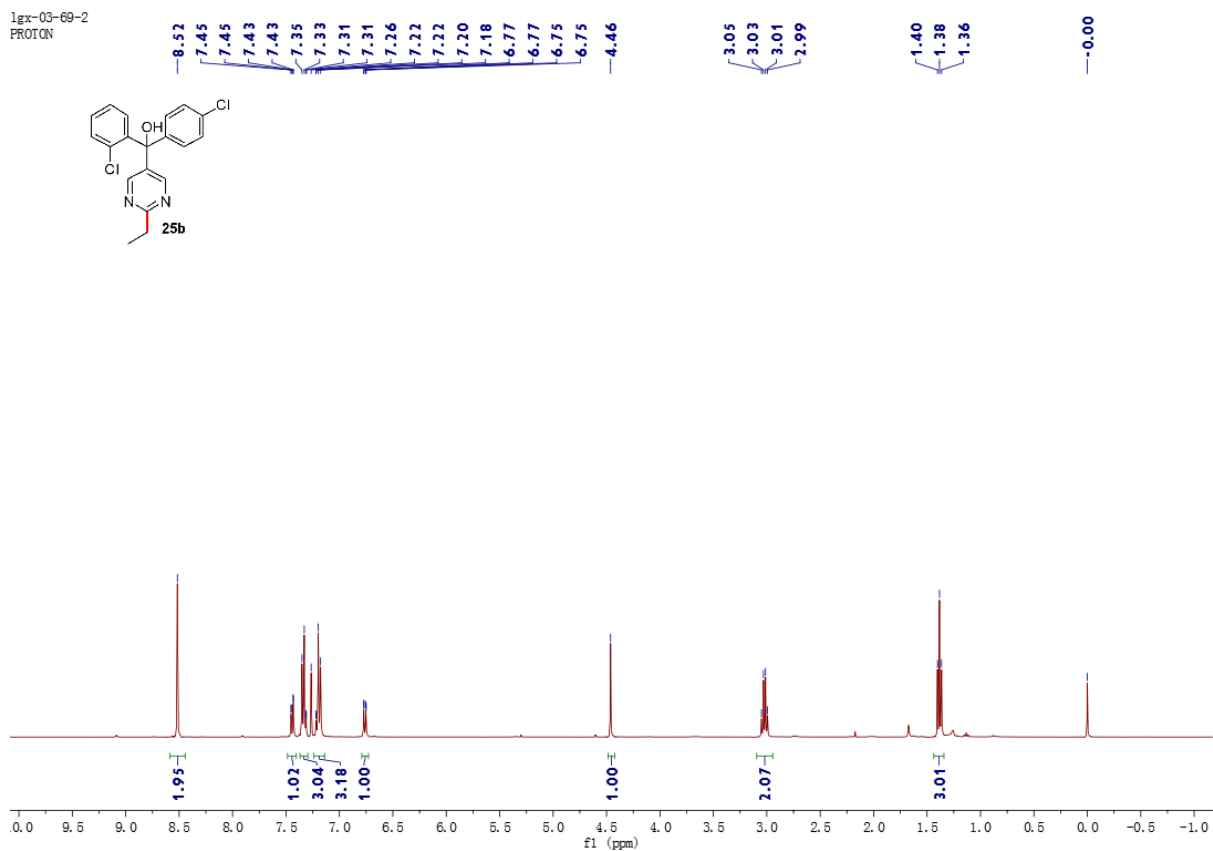


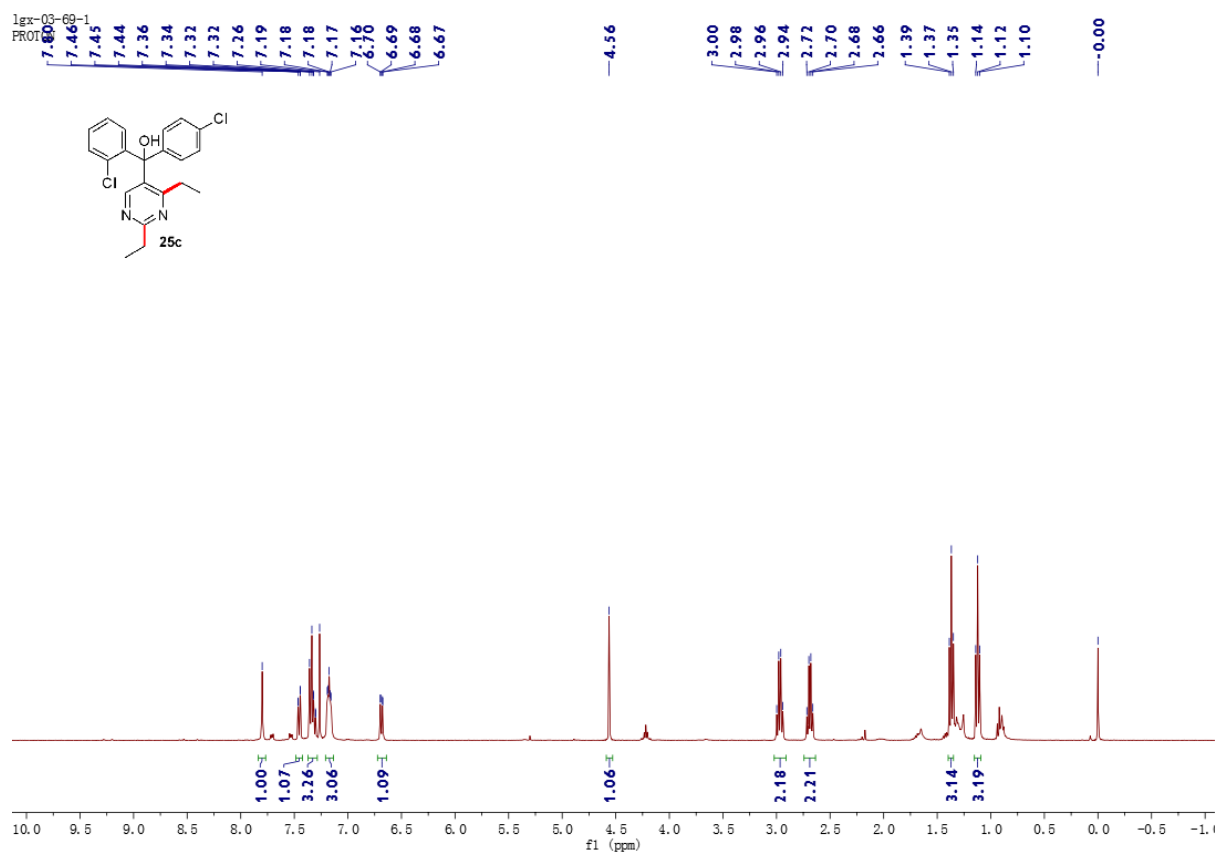
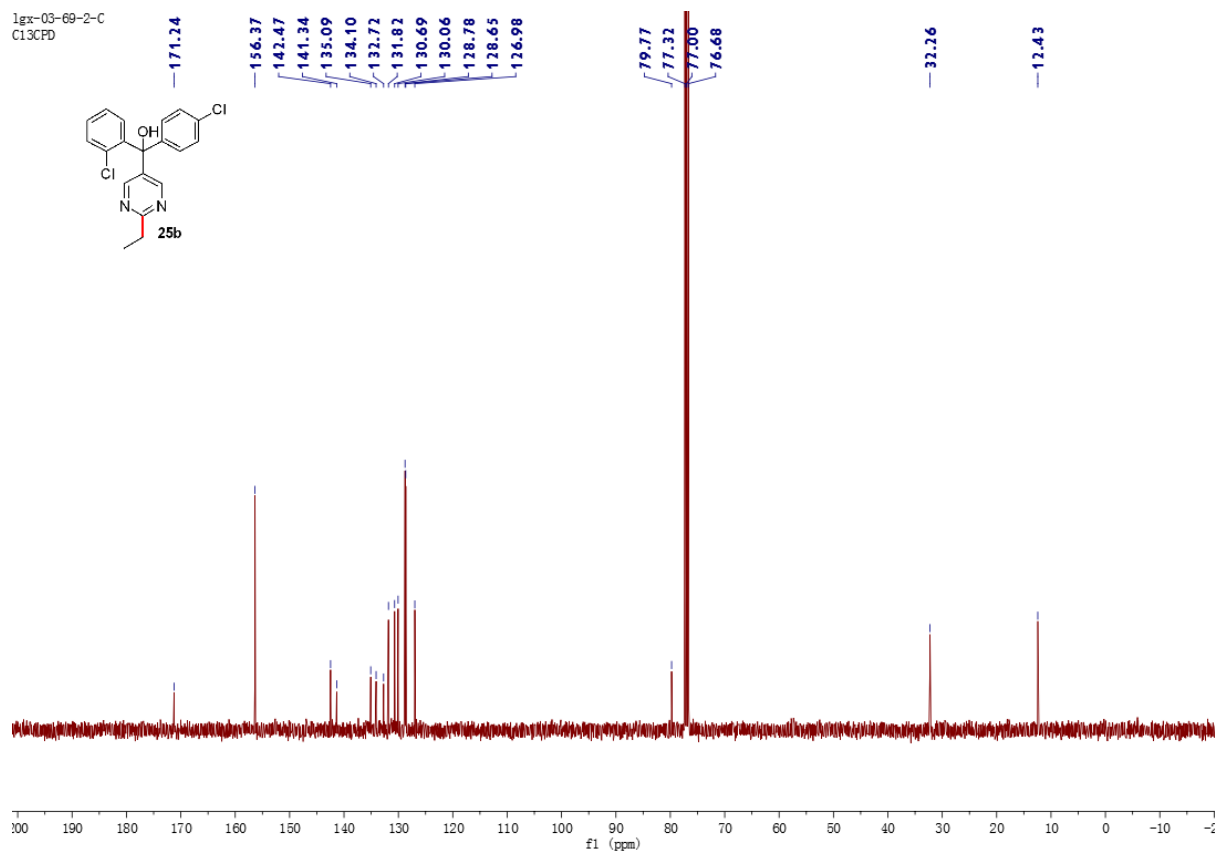


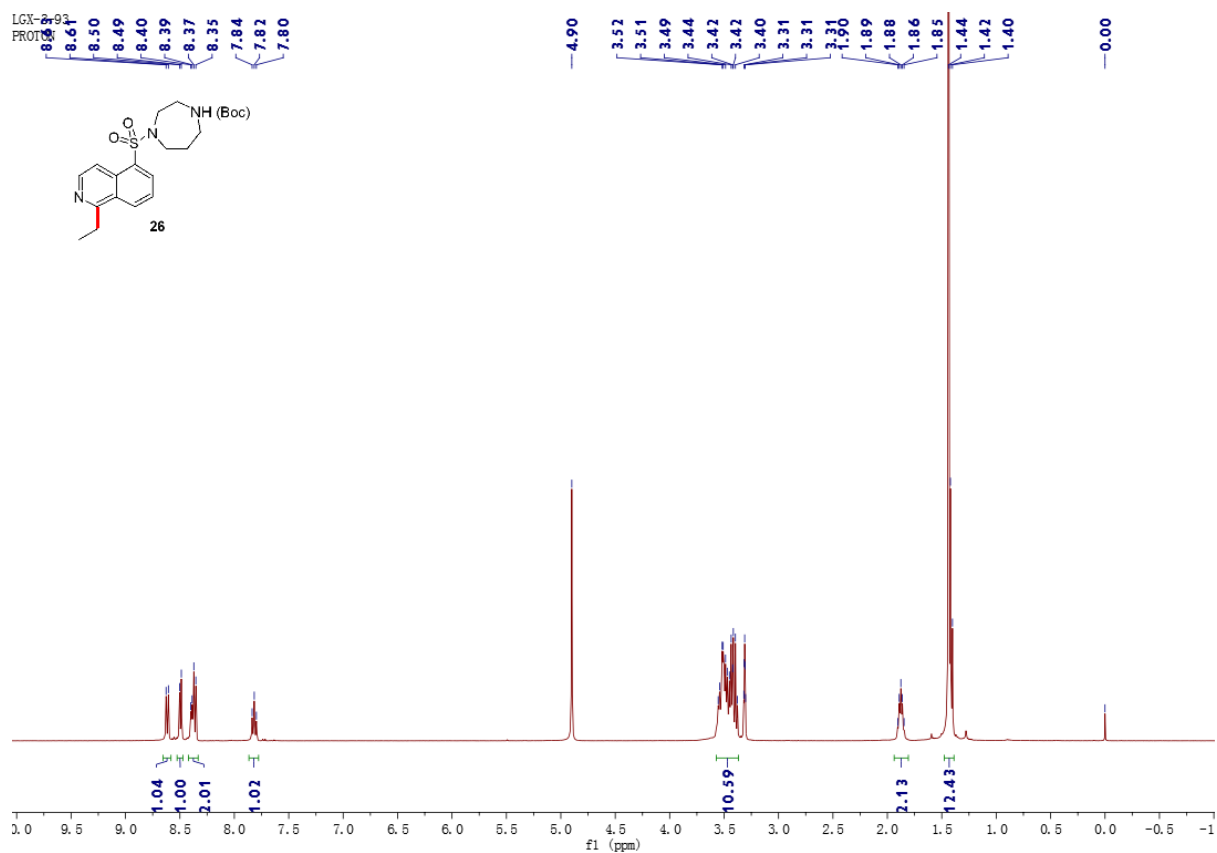
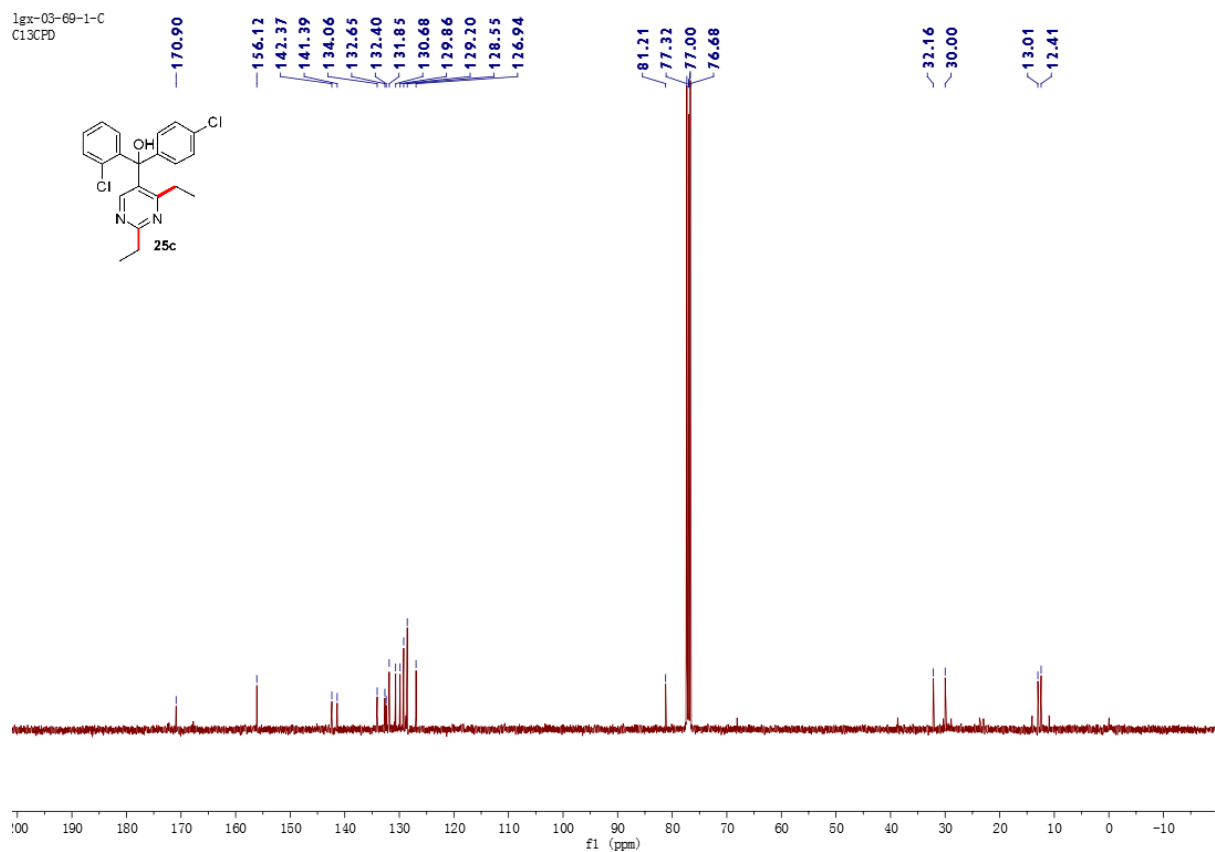
lgx-03-69-3
test



lgx-03-69-2
PROTON







LGX-3-XC
C13CPD

