Supporting Information

Photoredox-mediated Remote C(sp^3)-H Heteroarylation of Free Alcohols

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Content

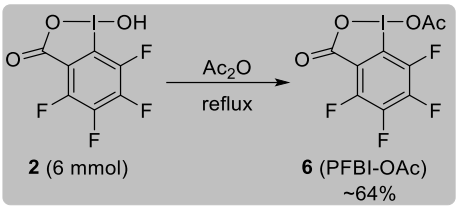
1. Reagents

All commercial materials were used as received unless otherwise noted. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using Silica gel (200–300 mesh) purchased from Qingdao Haiyang Chemical Co., China. [Bis(trifluoroacetoxy)iodo]benzene ($PhI(OTFA)_2$, **7**), and (diacetoxyiodo)benzene ($PhI(OAc)_2$,) were purchased from sigma-aldrich®. Acetoxybenziodoxole (BI–OAc, **1**)[1], perfluorohydroxylbenziodoxole (PFBI–OH, **2**),[2] and hydroxylbenziodoxole (BI–OH, **5**)[1] were synthesized according to reported procedures and used as freshly prepared. $[Ru(bpy)_3]Cl_2$ (98%, Ru＞15.75%, Energy Chemical) and HFIP (99.0%, ACS grade, J&K Chemical) were used as received unless otherwise noted.

2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 500 instruments and all NMR experiments were reported in units, parts per million (ppm). Peaks recorded are relative to internal standards: TMS (δ = 0.00) for ^1H and $CDCl_3$ (δ = 77.00) for ^{13}C spectra. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of 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 clear borosilicate glass) unless otherwise noted, sealed with PTEF cap on bench top. The energy saver CFL bulb (23 W, MINI SPIRAL, SOFT WHITE) was purchased from SATCO®.

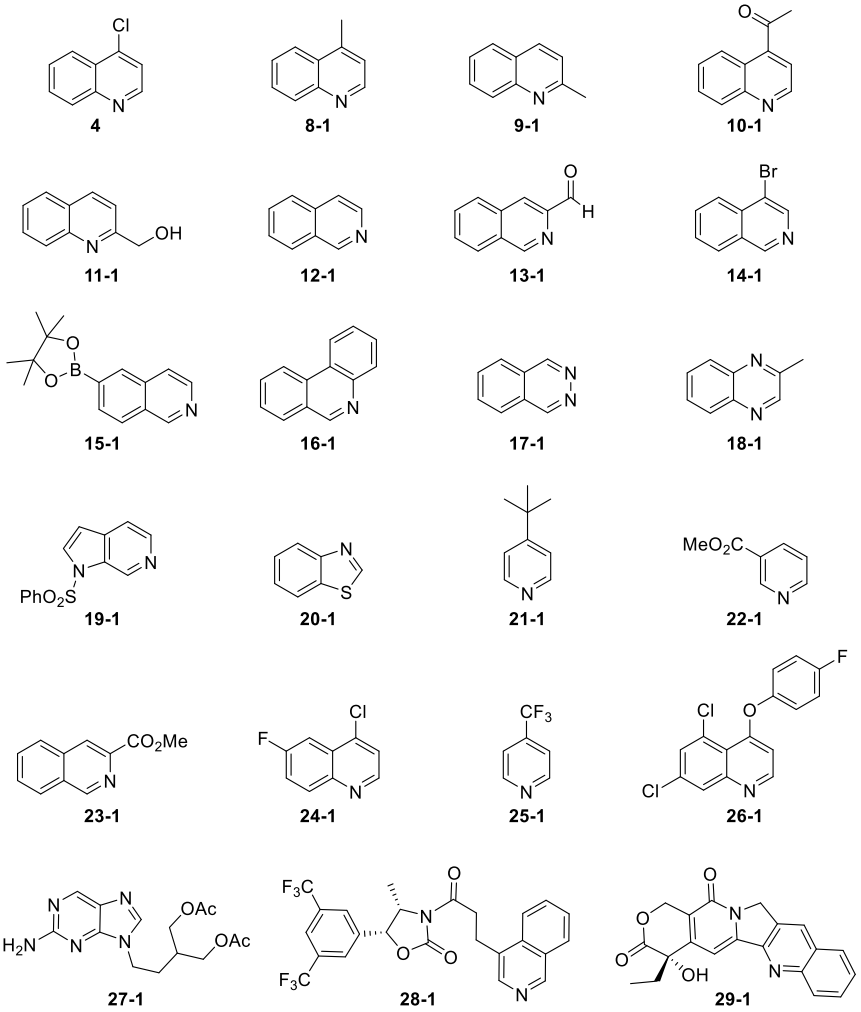
3. Synthesis of PFBI-OAc 6



Scheme S1

PFBI-OH **2** (2.0 g, 6.0 mmol, 1.0 equiv) was heated in Ac_2O (4 mL) to reflux until the solution turned clear (without suspension). The mixture was heated for another 15 min, then left to cool down and slightly yellowish crystals started to form. The crystallization was continued at room temperature over night under Ar. The crystal were then collected and dried overnight under high vacuum to give compound **6** (1.4 g, ~64%). **Note**: compound **6** is very sensitive to moisture, and easily hydrolyzed to form PFBI-OH **2** and acetic acid. **^{1}H NMR** (500 MHz, DMSO-d6) δ 2.21 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d6) δ 179.28, 24.42; **^{19}F NMR** (470 MHz, DMSO-d6) δ -137.27–-137.38(m, 1F), -139.12–-139.24(m, 1F), -144.36–-144.52(m, 1F), -148.99–-149.12(m, 1F).

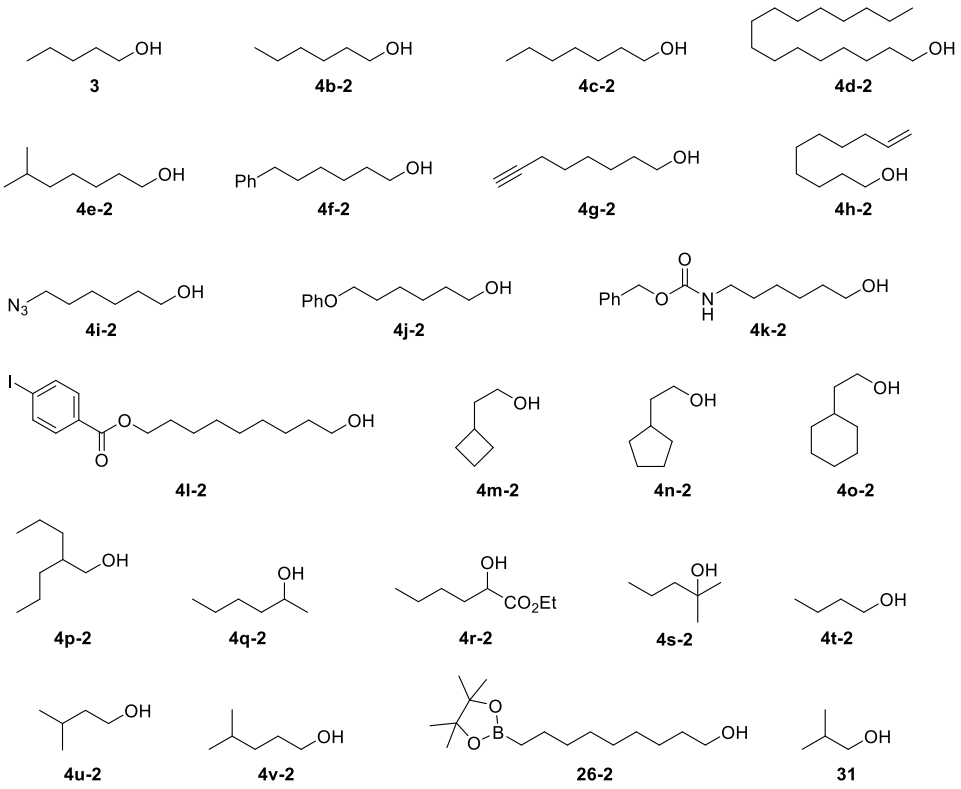
4. *N*-Heteroaromatic substrates



Scheme S2. List of all *N*-heteroaromatic substrates used in this study

All *N*-heteroaromatics substrated were commercial available and used as received unless otherwise noted.

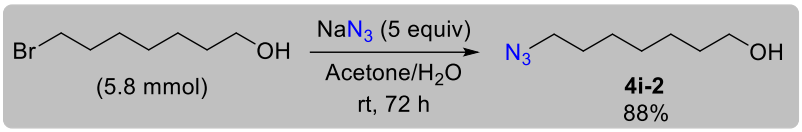
5. Alcohol substrates



Scheme S3. List of all alcohols used in this study

Compounds **3**, **4b-2**, **4c-2**, **4d-2**, **4e-2**, **4f-2**, **4g-2**, **4h-2**, **4k-2**, **4l-2**, **4m-2**, **4n-2**, **4o-2**, **4p-2**, **4q-2**, **4r-2**, **4s-2**, **4t-2**, **4u-2**, **4v-2, 26-2** and **31** were commercial available and used as received.

5.1 Synthesis of alkane substrates 4i-2:

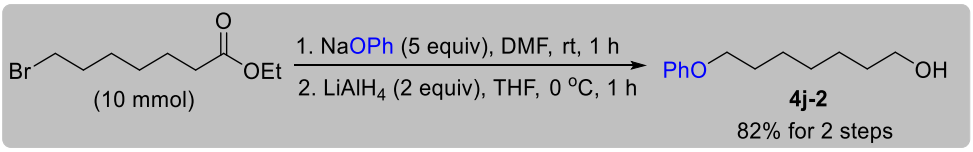


Scheme S4.

To a solution of acetone (20 mL) and water (10 mL), 7-bromo-heptan-1-ol (1.0 g, 5.8 mmol) and sodium azide (1.89 g, 29.0 mmol) were added. The reaction mixture was stirred at ambient temperature for 72 hours. After removal of the organic solvent *in vacuo*, the residual aqueous solution was extracted with EtOAc (50 mL x 3). The combined organic phase was washed with brine, 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 = 1:4) to afford compound **4i-2** (0.80 g, 88%) as a colorless oil. R_f = 0.23 (1:4 ethyl acetate/hexanes). Spectra data are consistent with those reported in the literature.[3]

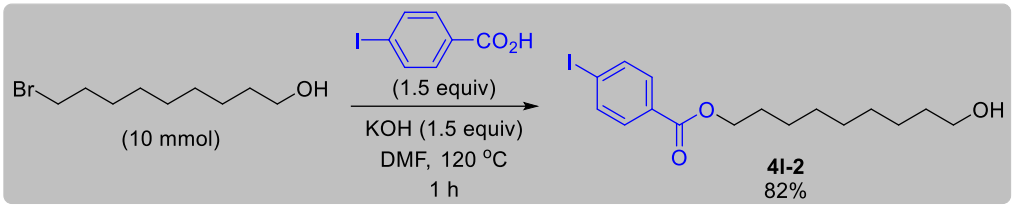
5.2 Synthesis of alkane substrates 4j-2:



Scheme S5.

To a solution of ethyl 7-bromoheptanoate (2.44 g, 10 mmol) in DMF (15 mL), sodium phenolate (3.50 g, 30 mmol) was added, and the mixture was stirred for 2 hour at room temperature. Then the reaction mixture was poured into brine (200 mL) and extracted with Et_2O (50 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 dissolved in THF (50 mL). To the resulting solution, $LiAlH_4$ (760 mg, 20 mmol) was carefully added portionwise at 0 °C. After completing the addition of $LiAlH_4$, the reaction mixture was further stirred at 0 °C for another 1 hour. Then water (1 mL) was added carefully into the reaction solution at 0 °C to quench the reaction. After removal of the organic solvent *in vacuo*, 30 mL of 1M HCl (aq.) and EtOAc (50 mL) were added into the residue. The aquoue phase was further extracted with EtOAc (50 mL x 2). The combined organic phase was wshed with brine, 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 = 1:3) to afford compound **4j-2** (1.71 g, 82% for 2 steps) as a colorless oil. R_f = 0.15 (1:4 ethyl acetate/hexanes). Spectra data are consistent with those reported in the literature.[4]

5.3 Synthesis of alkane substrates 4l-2:



Scheme S6.

To a solution of 4-iodobenzoic acid (3.73 g, 15 mmol) in DMF (15 mL), potassium hydroxide (0.84 g, 15 mmol) was added, and the mixture was stirred for 10 minutes at room temperature. 9-Bromononan-1-ol (2.23 g, 10 mmol) was added into the suspension, then the mixture was heated to 120 °C and stirred for another 1 hour. After being cooled to room temperature, the resulting clear solution was poured into brine (200 mL) and extracted with Et_2O (50 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 = 1:3) to afford compound **4l-2** (3.27 g, 82%) as a white solid. R_f = 0.20 (1:4 ethyl acetate/hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.75–7.73 (m, 2H), 4.30 (t, J = 6.7 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 1.78–1.72 (m, 2H), 1.59–1.54 (m, 2H), 1.46–1.33 (m, 11H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.15, 137.64, 130.96, 129.92, 100.53, 65.34, 62.96, 32.70, 29.40, 29.27, 29.12, 28.59, 25.93, 25.66; **HRMS** Calcd for $C_{16}H_{24}IO_3$ [M+H$^+$]: 391.0770, Found: 391.0780.

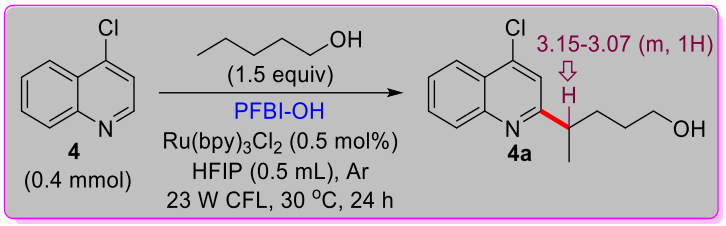
6. Optimization for alkylation of *N*-heteroarenes with alcohols

All screening reactions were carried out at a 0.4 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 $Ru(bpy)_3Cl_2$ in HFIP was used if necessary. A 23 W compact household fluorescent bulb was positioned 10 cm aside from the reaction vials.

4-Chloroquinoline **4** (65.2 mg, 0.4 mmol, 1.0 equiv), 1-pentanol **3** and other specified

reagents were dispersed in 0.5 mL of solvent containing photocatalyst. The mixture was stirred at specified temperature with light irradiation for 24 h. After removal of the solvent *in vacuo*, the residue was dissolved in 3 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an internal standard for ^1H NMR analysis. The composition of reaction mixture was analyzed based on the integration of methenyl group peaks at **3.15–3.07** (m, 1H) for compound **4a**.

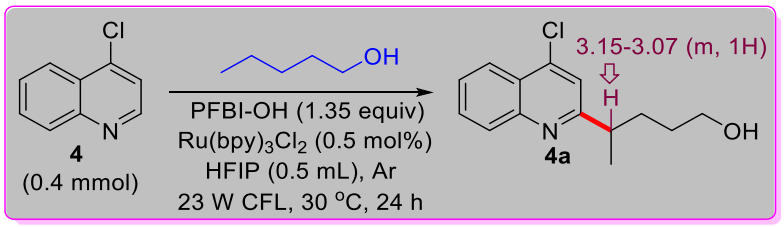
*Evaluation of the loading of PFBI-OH **2**:*



Entry	PFBI-OH (equiv)	Yield (%, NMR)
1	1.20	63
2	1.25	65
3	1.30	75
4	1.35	84(80)[a]
5	1.40	76
6	1.45	72
7	1.50	70

[a] Isolated yield.

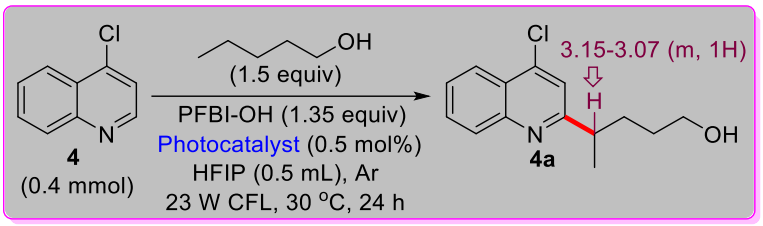
*Evaluation of the loading of alcohol **3**:*



Entry	Alkanol (equiv)	Yield (%, NMR)
1	1.0	42
2	1.25	57
3	1.50	84(80)[a]
4	1.75	86(81)[a]
5	2.0	86(81)[a]

[a] Isolated yield.

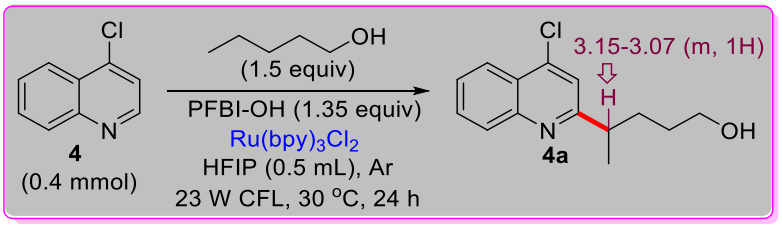
Screening of photocatalysts:



Entry	Photocatalyst	Yield (%, NMR)
1	$Ru(bpy)_3Cl_2$	84(80)[a]
2	$Ir(ppy)_3$	13
3	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$	32
4	$[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$	33
5	$[Ir(ppy)_2(dtbpy)]PF_6$	16

[a] Isolated yield.

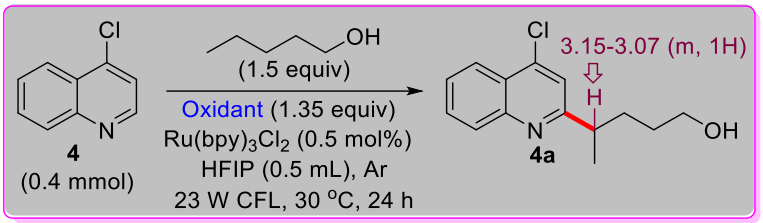
Evaluation of the loading of photocatalyst $Ru(bpy)_3Cl_2$:



Entry	$Ru(bpy)_3Cl_2$ (mol%)	Yield (%, NMR)
1	0	<2 (ND)
2	0.25	70
3	0.5	84(80)[a]
4	1.0	61

[a] Isolated yield.

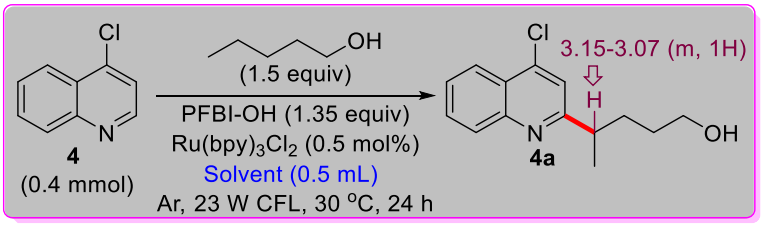
Screening of oxidants:



Entry	Oxidant	Yield (%, NMR)
1	BI-OH	3
2	BI-OAc	25
3	PFBI-OH	84(80)[a]
4	PFBI-OAc	30
5	PIDA	28
6	PIFA	4

[a] Isolated yield.

Evaluation of solvents:

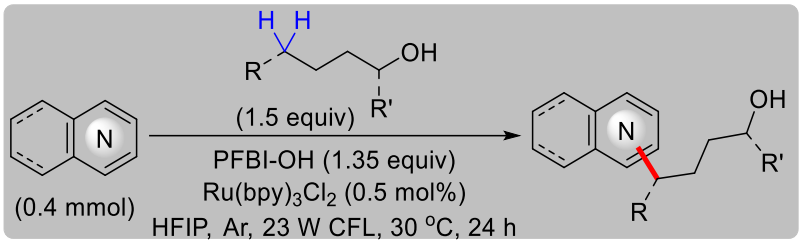


Entry	Solvent	Yield (%, NMR)
1	HFIP	84(80)[a]
2	TFE	38
3	DCM	3
4	CH_3CN	4
5	THF	<1
6	DMF	<1
7	HFIP/DCM (v/v 1:5)	8

[a] Isolated yield.

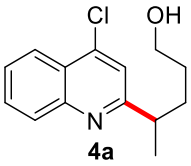
The optimized conditions as following: 4-chloroquinoline **4** (65.2 mg, 0.4 mmol, 1.0 equiv), 1-pentanol **3** (53.0 mg, 0.6 mmol, 1.5 equiv) and PFBI-OH **2** (181.2 mg, 0.54 mmol, 1.35 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The mixture was stirred at 30 ºC under the fluorescent light irradiation (23 W) for 24 h.

7. General procedure and substrate scope



Scheme S7.

General procudure: *N*-heteroaromatic substrate (0.4 mmol, 1.0 equiv), alcohols (0.6 mmol, 1.5 equiv) and PFBI-OH (0.54 mmol, 1.35 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 24 h. (**NOTE**: the vials were placed approximately 5 cm away from the CFL bulb. The reaction temperature was kept at around 30±1 °C, owing to the radiation of light source. Stirring rate: 500 rmp). The solvent was removed *in vacuo* and the residue was dissolved in DCM (3 mL). To the solution was added K_2CO_3 (approximate 80 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.

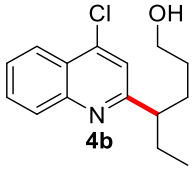


4a

R_f = 0.40, 50% EtOAc in Hexane

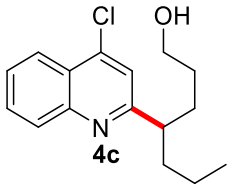
Compound **4a** was isolated in 80% yield (80.2 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 0.6 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.77–7.69 (m, 1H), 7.59–7.56 (m, 1H), 7.40 (s, 1H), 3.67–3.59 (m, 2H), 3.15–3.07 (m, 1H), 2.39 (br s, 1H), 1.96–1.89 (m, 1H), 1.81–1.74 (m, 1H), 1.67–

1.58 (m, 1H), 1.52–1.44 (m, 1H), 1.37 (d, J = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.58, 148.14, 142.82, 130.19, 128.82, 126.63, 124.94, 123.74, 119.58, 62.02, 42.06, 32.81, 30.43, 20.54; **HRMS** Calcd for $C_{14}H_{17}ClNO$ [M+H$^+$]: 250.0999, Found: 250.1001.



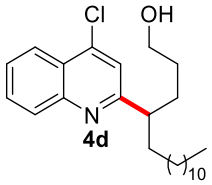
R_f = 0.44, 50% EtOAc in Hexane

Compound **4b** was isolated in 83% yield (87.5 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.4, 1.1 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.38 (s, 1H), 3.64–3.56 (m, 2H), 2.92–2.86 (m, 1H), 2.02 (br s, 1H), 1.89–1.77 (m, 4H), 1.60–1.52 (m ,1H), 1.46–1.39 (m, 1H), 0.85 (t, J = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.65, 148.29, 142.78, 130.22, 129.00, 126.70, 125.04, 123.84, 120.08, 62.34, 49.77, 31.24, 30.50, 28.47, 12.01; **HRMS** Calcd for $C_{15}H_{19}ClNO_4$ [M+H$^+$]: 264.1155, Found: 264.1163.



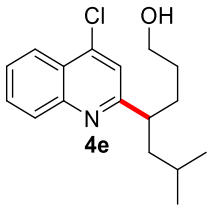
R_f = 0.51, 50% EtOAc in Hexane

Compound **4c** was isolated in 84% yield (93.4 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.4, 1.0 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.75–7.71 (m, 1H), 7.60–7.57 (m, 1H), 7.37 (s, 1H), 3.63–3.55 (m, 2H), 3.01–2.95 (m, 1H), 2.12 (br s, 1H), 1.88–1.82 (m, 2H), 1.81–1.67 (m, 2H), 1.60–1.52 (m, 1H), 1.46–1.38 (m, 1H), 1.35–1.24 (m, 1H), 1.23–1.14 (m, 1H), 0.87 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.85, 148.27, 142.77, 130.21, 128.99, 126.69, 125.03, 123.83, 120.04, 62.32, 47.91, 37.78, 31.56, 30.50, 20.63, 14.08; **HRMS** Calcd for $C_{16}H_{21}ClNO$ [M+H$^+$]: 278.1312, Found: 278.1318.



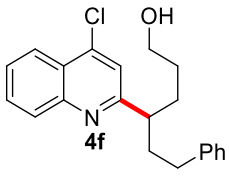
R_f = 0.57, 25% EtOAc in Hexane

Compound **4d** was isolated in 76% yield (122.5 mg) as a white solid following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.4, 0.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.37 (s, 1H), 3.63–3.55 (m, 2H), 2.99–2.93 (m, 1H), 1.90 (br s, 1H), 1.88–1.81 (m, 2H), 1.80–1.69 (m, 2H), 1.60–1.51 (m, 1H), 1.45–1.37 (m, 1H), 1.31–1.11 (m, 20 H), 0.87 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.89, 148.42, 142.76, 130.22, 129.18, 126.71, 125.10, 123.88, 120.15, 62.57, 48.24, 35.69, 31.86, 31.60, 30.58, 29.66, 29.60, 29.57, 29.52, 29.41, 29.30, 27.50, 22.64, 14.08; **HRMS** Calcd for $C_{25}H_{39}ClNO$ [M+H$^+$]: 404.2720, Found: 404.2708.



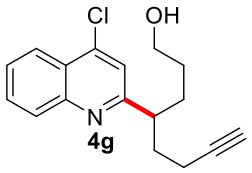
R_f = 0.57, 25% EtOAc in Hexane

Compound **4e** was isolated in 62% yield (72.6 mg) as a white solid following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.38 (s, 1H), 3.63–3.55 (m, 2H), 3.11–3.05 (m, 1H), 1.85–1.80 (m, 2H), 1.77–1.72 (m, 1H), 1.59–1.51 (m, 2H), 1.46–1.35 (m, 2H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.93, 148.48, 142.74, 130.24, 129.23, 126.74, 125.11, 123.90, 120.21, 62.70, 45.95, 44.88, 32.04, 30.55, 25.73, 23.22, 22.22; **HRMS** Calcd for $C_{17}H_{23}ClNO$ [M+H$^+$]: 292.1468, Found: 292.1460.



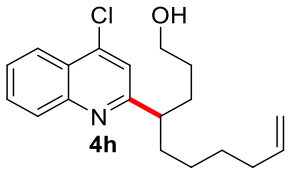
R_f = 0.58, 50% EtOAc in Hexane

Compound **4f** was isolated in 77% yield (104.2 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.77–7.74 (m, 1H), 7.62–7.59 (m, 1H), 7.37 (s, 1H), 7.24–7.22 (m, 2H), 7.16–7.11 (m, 3H), 3.63–3.54 (m, 2H), 3.05–2.99 (m, 1H), 2.63–2.55 (m, 1H), 2.52–2.47 (m, 1H), 2.20–2.13 (m, 1H), 2.10–2.03 (m, 1H), 1.96–1.84 (m, 2H), 1.78 (br s, 1H), 1.60–1.51 (m, 1H), 1.45–1.37 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.23, 148.52, 142.85, 141.95, 130.32, 129.23, 128.28, 128.27, 126.84, 125.75, 125.15, 123.92, 120.39, 62.53, 47.76, 37.25, 33.74, 31.58, 30.47; **HRMS** Calcd for $C_{21}H_{23}ClNO$ [M+H$^+$]: 340.1468, Found: 340.1458.



R_f = 0.44, 50% EtOAc in Hexane

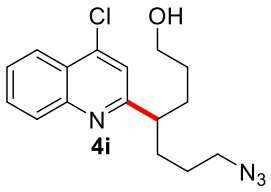
Compound **4g** was isolated in 64% yield (73.8 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.3, 0.4 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.76–7.73 (m, 1H), 7.62–7.58 (m, 1H), 7.40 (s, 1H), 3.64–3.55 (m, 2H), 3.15–3.09 (m, 1H), 2.17–2.06 (m, 3H), 2.02–1.81 (m, 4H), 1.70 (br s, 1H), 1.62–1.53 (m, 1H), 1.46–1.38 (m,1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.38, 148.64, 142.81, 130.32, 129.30, 126.90, 125.17, 123.92, 120.85, 83.86, 68.81, 62.52, 46.82, 34.01, 31.18, 30.45, 16.56; **HRMS** Calcd for $C_{17}H_{19}ClNO$ [M+H$^+$]: 288.1155, Found: 288.1148.



R_f = 0.60, 50% EtOAc in Hexane

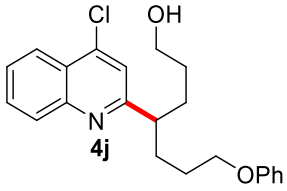
Compound **4h** was isolated in 65% yield (82.3 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.76–7.73 (m, 1H), 7.61–7.58 (m, 1H), 7.37 (s, 1H), 5.74 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 4.94 (d, *J* = 17.0 Hz, 1H), 4.89 (d, *J* = 10.2 Hz, 1H), 3.63–3.55 (m

2H), 3.00–2.94 (m, 1H), 2.00–1.96 (m, 2H), 1.91–1.70 (m, 5H), 1.59–1.51 (m, 1H), 1.45–1.26 (m, 4H), 1.21–1.13 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.73, 148.43, 142.81, 138.79, 130.27, 129.20, 126.77, 125.12, 123.91, 120.17, 114.29, 62.64, 48.18, 35.49, 33.50, 31.60, 30.57, 28.90, 26.96; **HRMS** Calcd for $C_{19}H_{25}ClNO$ [M+H$^+$]: 318.1625, Found: 318.1616.



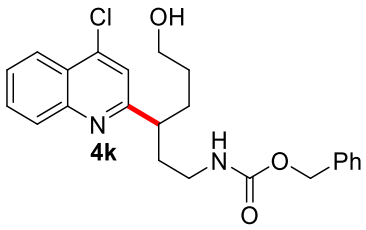
4i R_f = 0.38, 50% EtOAc in Hexane

Compound **4i** was isolated in 76% yield (96.6 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.61–7.58 (m, 1H), 7.37 (s, 1H), 3.63–3.55 (m, 2H), 3.23 (t, *J* = 6.8 Hz, 2H), 3.01–2.95 (m, 1H), 2.29 (br s, 1H), 1.92–1.79 (4H), 1.60–1.51 (m, 2H), 1.48–1.36 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.81, 148.46, 143.02, 130.38, 129.20, 126.93, 125.15, 123.92, 120.08, 62.46, 51.29, 47.70, 32.47, 31.65, 30.43, 26.82; **HRMS** Calcd for $C_{16}H_{20}ClN_4O$ [M+H$^+$]: 319.1326, Found: 319.1313.



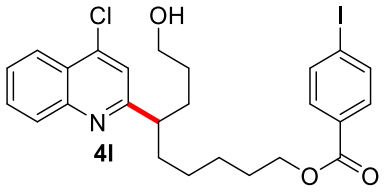
4j R_f = 0.41, 50% EtOAc in Hexane

Compound **4j** was isolated in 60% yield (88.5 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.40 (s, 1H), 7.25–7.22 (m, 2H), 6.91–6.88 (m, 1H), 6.84–6.83 (m, 2H), 3.91 (t, *J* = 6.2 Hz, 2H), 3.63–3.56 (m, 2H), 3.07–3.01 (m, 1H), 2.11 (br s, 1H), 1.89–1.84 (m, 4H), 1.81–1.73 (m, 1H), 1.67–1.52 (m, 2H), 1.46–1.38 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.20, 158.83, 148.46, 142.96, 130.35, 129.35, 129.21, 126.87, 125.17, 123.93, 120.51, 120.25, 114.38, 67.47, 62.60, 47.85, 31.95, 31.68, 30.51, 27.21; **HRMS** Calcd for $C_{22}H_{25}ClNO_2$ [M+H$^+$]: 370.1574, Found: 370.1553.



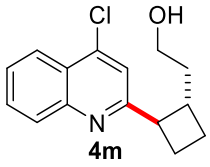
R_f = 0.50, EtOAc

Compound **4k** was isolated in 70% yield (115.0 mg) as a white solid following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.75–7.71 (m, 1H), 7.61–7.58 (m, 1H), 7.38 (s, 1H), 7.34–7.30 (m, 5H), 5.09 (br s, 1H), 5.04 (s, 2H), 3.63–3.55 (m, 2H), 3.26–3.19 (m, 1H), 3.08–3.02 (m, 2H), 2.02–1.98 (m, 2H), 1.94–1.83 (m, 3H), 1.57–1.48 (m, 1H), 1.46–1.38 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.65, 156.35, 148.36, 143.12, 136.52, 130.42, 129.09, 128.40, 127.96, 126.98, 125.14, 123.93, 120.16, 66.49, 62.21, 45.36, 38.98, 35.23, 31.20, 30.31; **HRMS** Calcd for $C_{23}H_{26}ClN_2O_3$ [M+H$^+$]: 413.1632, Found: 413.1614.



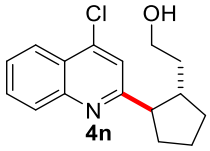
R_f = 0.80, 50% EtOAc in Hexane

Compound **4l** was isolated in 73% yield (160.8 mg) as a white solid following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 0.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.78–7.76 (m, 2H), 7.75–7.72 (m, 1H), 7.71–7.69 (m, 2H), 7.61–7.58 (m ,1H), 7.37 (s, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 3.63–3.55 (m, 2H), 3.00–2.94 (m, 1H), 1.92 (br s, 1H), 1.88–1.66 (m ,6H), 1.59–1.50 (m, 1H), 1.47–1.31 (m, 4H), 1.29–1.17 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.02, 165.52, 148.40, 142.79, 137.56, 130.88, 130.79, 130.26, 129.77, 129.14, 126.77, 125.06, 123.87, 120.08, 100.52, 65.16, 62.49, 48.11, 35.46, 31.61, 30.50, 28.41, 27.15, 26.07; **HRMS** Calcd for $C_{25}H_{28}ClINO_3$ [M+H$^+$]: 552.0802, Found: 552.0772.



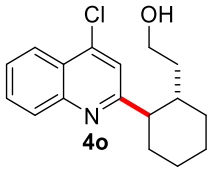
R_f = 0.50, 50% EtOAc in Hexane

Compound **4m** was isolated in 80% yield (83.1 mg) as a white solid following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.3, 0.9 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.76–7.73 (m, 1H), 7.62–7.59 (m, 1H), 7.35 (s, 1H), 6.43(br s, 1H), 3.76–3.67 (m ,2H), 3.56–3.50 (m, 1H), 3.01–2.93 (m, 1H), 2.50–2.45 (m, 1H), 2.18–2.07 (m, 2H), 2.04–1.98 (m, 1H), 1.85–1.76 (m, 1H), 1.69–1.63 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.19, 147.46, 143.29, 130.70, 128.35, 127.00, 124.86, 123.89, 119.55, 59.92, 46.53, 39.73, 38.22, 25.12, 24.95; **HRMS** Calcd for $C_{15}H_{17}ClNO$ [M+H$^+$]: 262.0999, Found: 262.0993.



R_f = 0.51, 50% EtOAc in Hexane

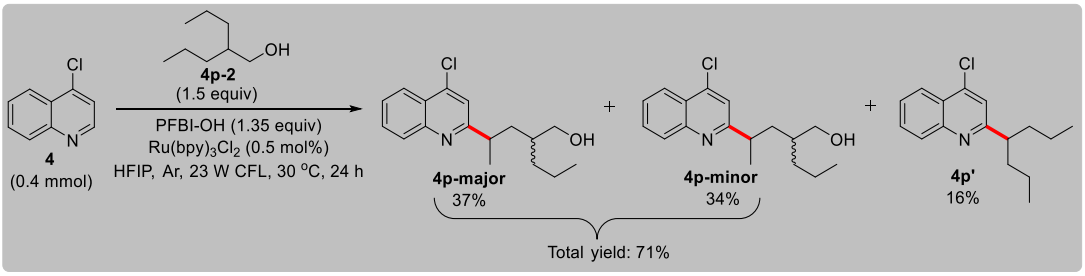
Compound **4n** was isolated in 83% yield (91.7 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.61–7.57 (m, 1H), 7.45 (s, 1H), 4.07 (br s, 1H), 3.59–3.54 (m, 1H), 3.53–3.48 (m ,1H), 3.11–3.06 (m, 1H), 2.67–2.59 (m, 1H), 2.31–2.25 (m, 1H), 2.10–2.04 (m, 1H), 1.90–1.76 (m, 4H), 1.61–1.54 (m, 1H), 1.49–1.42 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.65, 147.90, 142.95, 130.50, 128.73, 126.83, 125.02, 123.86, 120.49, 60.84, 53.19, 41.43, 38.49, 34.48, 33.70, 24.84; **HRMS** Calcd for $C_{16}H_{19}ClNO$ [M+H$^+$]: 276.1155, Found: 276.1147.



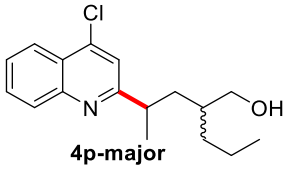
R_f = 0.51, 50% EtOAc in Hexane

Compound **4o** was isolated in 91% yield (105.2 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.61–7.57 (m, 1H), 7.41 (s, 1H), 3.58–3.51 (m, 2H), 2.71 (td, *J* = 11.5, 3.5 Hz, 1H), 2.60 (br s, 1H), 2.12–2.04 (m ,1H), 2.01–1.95 (m, 2H), 1.89–1.81 (m, 2H), 1.57–1.46 (m, 1H), 1.47–1.31 (m, 4H), 1.25–1.18 (m, 1H); **^{13}C**

NMR (125 MHz, $CDCl_3$) δ 165.94, 148.28, 142.97, 130.41, 128.92, 126.80, 125.08, 123.91, 120.72, 60.39, 52.68, 37.54, 37.46, 34.61, 32.50, 26.35, 26.14; **HRMS** Calcd for $C_{17}H_{21}ClNO$ [M+H$^+$]: 290.1312, Found: 290.1301.

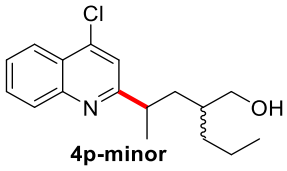


Scheme S8.



R_f = 0.33, 25% EtOAc in Hexane

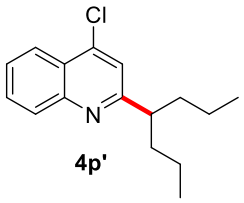
Compound **4p-major** was isolated in 37% yield (43.0 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.74–7.71 (m, 1H), 7.60–7.57 (m, 1H), 7.43 (s, 1H), 3.47 (ddd, *J* = 16.8, 10.7, 5.2 Hz, 2H), 3.22–3.15 (m, 1H), 2.23–2.17 (m, 1H), 1.55–1.49 (m, 1H), 1.48–1.44 (m, 1H), 1.40–1.26 (m, 4H), 1.35 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.58, 148.15, 143.00, 130.49, 128.87, 126.88, 125.09, 123.93, 120.67, 65.31, 40.58, 39.18, 37.48, 34.53, 22.35, 20.12, 14.40; **HRMS** Calcd for $C_{17}H_{23}ClNO$ [M+H$^+$]: 292.1468, Found: 292.1464.



R_f = 0.28, 25% EtOAc in Hexane

Compound **4p-minor** was isolated in 34% yield (38.8 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.44 (s, 1H), 3.59 (dd, *J* = 10.9, 4.5 Hz, 1H), 3.44 (dd, *J* = 10.9, 6.8 Hz, 1H), 3.35–3.28 (m, 1H), 1.96–1.90 (m, 1H),

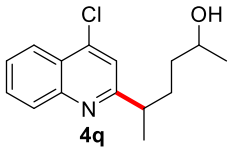
1.75–1.66 (m, 1H), 1.50–1.43 (m, 1H), 1.37 (d, J = 7.0 Hz, 3H), 1.32–1.17 (m, 4H), 0.82 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.74, 148.02, 143.19, 130.46, 128.99, 126.88, 125.09, 123.92, 119.68, 65.87, 39.46, 38.69, 38.17, 33.99, 21.62, 19.98, 14.28; **HRMS** Calcd for $C_{17}H_{23}ClNO$ [M+H$^+$]: 292.1468, Found: 292.1464.



4p'

R_f = 0.81, 25% EtOAc in Hexane

Compound **4p'** was isolated in 16% yield (17.0 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.3, 0.5 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.74–7.71 (m, 1H), 7.59–7.56 (m, 1H), 7.36 (s, 1H), 2.98–2.92 (m, 1H), 1.78–1.66 (m, 4H), 1.33–1.23 (m, 2H), 1.21–1.11 (m, 2H), 0.87 (t, J = 7.3 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.44, 148.67, 142.42, 130.06, 129.40, 126.55, 125.10, 123.88, 120.18, 48.41, 37.82, 20.76, 14.18; **HRMS** Calcd for $C_{16}H_{21}ClN$ [M+H$^+$]: 262.1363, Found: 262.1368.

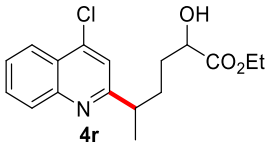


4q

R_f = 0.45, 50% EtOAc in Hexane

Compound **4q** was isolated in 68% yield (72.3 mg) as a colorless oil following the general procedure, 36 h. The two diastereoisomers were obtained as an inseparable mixture. The *dr* ratio was determined by the integration of peaks at **3.85–3.78 ppm** (m, 1H) for one isomer and **3.77–3.71 ppm** (m, 1H) for the other isomer. Data for one diastereoisomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.41 (s, 1H), 3.85–3.78 (m, 1H), 3.13–3.06 (m, 1H), 2.02–1.90 (m, 1H), 1.86–1.80 (m, 1H), 1.40–1.30 (m, 2H), 1.38 (d, J = 7.0 Hz, 3H), 1.16 (d, J = 6.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.60, 148.44, 142.80, 130.32, 129.20, 126.73, 125.10, 123.89, 119.88, 67.94, 42.49, 36.99, 32.46, 23.43, 20.93; Data for the other diastereoisomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ

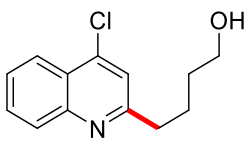
8.19 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.41 (s, 1H), 3.77–3.71 (m, 1H), 3.13–3.06 (m, 1H), 2.02–1.90 (m, 1H), 1.79–1.72 (m, 1H), 1.56–1.48 (m, 2H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.52, 148.35, 142.89, 130.25, 129.15, 126.76, 125.10, 123.89, 119.88, 67.64, 42.41, 37.13, 32.58, 23.53, 21.01; **HRMS** Calcd for $C_{15}H_{19}ClNO$ [M+H$^+$]: 264.1155, Found: 264.1154.



4r

R_f = 0.15, 25% EtOAc in Hexane

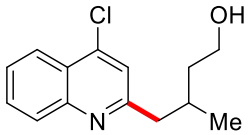
Compound **4r** was isolated in 44% yield (53.8 mg) as a colorless oil following the general procedure. The two diastereoisomers were obtained as an inseparable mixture. The *dr* ratio was determined by the integration of peaks at 7.41 **ppm** (s, 1H) for one isomer and **7.39 ppm** (s, 1H) for the other isomer. Data for one diastereoisomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.05 (d, *J* = 5.7 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.41 (s, 1H), 4.23–4.14 (m, 3H), 3.15–3.07 (m, 1H), 2.05–1.49 (m, 4H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 174.98, 166.16, 148.50, 142.85, 130.28, 129.26, 126.78, 125.13, 123.89, 119.79, 70.42, 61.60, 42.32, 32.25, 31.57, 20.67, 14.15; Data for the other diastereoisomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.07 (d, *J* = 5.7 Hz, 1H), 7.75–7.72 (m, 1H), 7.60–7.57 (m, 1H), 7.39 (s, 1H), 4.23–4.14 (m, 3H), 3.15–3.07 (m, 1H), 2.05–1.49 (m, 4H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.02, 166.15, 148.43, 142.89, 130.26, 129.26, 126.78, 125.13, 123.89, 119.64, 70.25, 61.57, 42.23, 32.12, 31.72, 20.97, 14.11; **HRMS** Calcd for $C_{17}H_{21}ClNO_3$ [M+H$^+$]: 322.1210, Found: 322.1204.



4t

R_f = 0.50, 80% EtOAc in Hexane

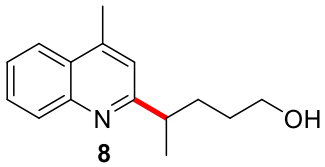
Compound **4t** was isolated in 63% yield (59.0 mg) as a colorless oil following the general procedure, 3 equiv of 1-butanol **4t-2** and 2 equiv of PFBI-OH **2** were used, 36 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.3, 0.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H); 7.76–7.73 (m, 1H), 7.61–7.58 (m ,1H), 7.41 (s, 1H), 3.71 (t, *J* = 6.3 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.45 (br s, 1H), 1.98–1.92 (m ,2H), 1.73–1.67 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.43, 148.40, 142.84, 130.46, 128.91, 126.82, 124.95, 123.94, 121.45, 62.24, 38.08, 32.13, 25.34; **HRMS** Calcd for $C_{13}H_{15}ClNO$ [M+H$^+$]: 236.0842, Found: 236.0840.



4u

R_f = 0.50, 80% EtOAc in Hexane

Compound **4u** was isolated in 74% yield (74.5 mg) as a colorless oil following the general procedure, 3 equiv of 3-methyl-1-butanol **4u-2** and 2 equiv of PFBI-OH **2** were used, 36 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.74–7.71 (m, 1H), 7.59–7.56 (m, 1H), 7.37 (s, 1H), 3.80–3.75 (m, 1H), 3.73–3.69 (m, 1H), 3.65 (br s, 1H), 2.99 (dd, *J* = 13.8, 6.8 Hz, 1H), 2.82 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.36–2.27 (m, 1H), 1.65–1,58 (m, 2H), 0.99 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.64, 148.23, 142.65, 130.42, 128.77, 126.81, 124.85, 123.89, 122.12, 60.34, 45.31, 39.26, 30.47, 20.34; **HRMS** Calcd for $C_{14}H_{17}ClNO$ [M+H$^+$]: 250.0999, Found: 250.0993.

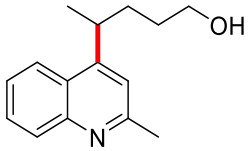


8

R_f = 0.50, 80% EtOAc in Hexane

Compound **8** was isolated in 70% yield (64.1 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.68–7.65 (m, 1H), 7.52–7.49 (m, 1H), 7.15 (s, 1H), 3.66–3.57 (m, 2H), 3.14–3.07 (m, 1H), 2.69 (s, 3H), 2.51 (br s, 1H), 1.99–1.91 (m, 1H), 1.81–1.74 (m, 1H),

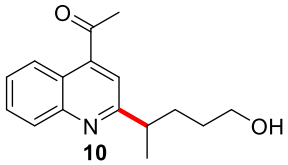
1.68–1.59 (m, 1H), 1.52–1.44 (m, 1H), 1.37 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.19, 147.21, 144.68, 129.19, 129.09, 126.99, 125.55, 123.55, 120.23, 62.51, 42.13, 32.88, 30.64, 21.03, 18.84; **HRMS** Calcd for $C_{15}H_{20}NO$ [M+H$^+$]: 230.1545, Found: 230.1537.



9

R_f = 0.32, 50% EtOAc in Hexane

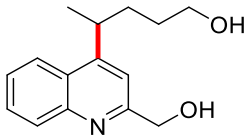
Compound **9** was isolated in 71% yield (65.6 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.67–7.64 (m, 1H), 7.50–7.47 (m, 1H), 7.17 (s, 1H), 3.65 (t, J = 6.4 Hz, 2H), 3.61–3.56 (m, 1H), 2.72 (s, 3H), 1.91–1.84 (m, 1H), 1.82–1.75 (m, 1H), 1.69 (br s, 1H), 1.67–1.58 (m, 1H), 1.57–1.50 (m, 1H), 1.38 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.59, 153.46, 147.93, 129.26, 128.90, 125.39, 122.72, 118.41, 62.46, 33.38, 33.07, 30.64, 25.28, 21.17; **HRMS** Calcd for $C_{15}H_{20}NO$ [M+H$^+$]: 230.1545, Found: 230.1537.



10

R_f = 0.20, 50% EtOAc in Hexane

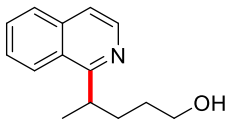
Compound **10** was isolated in 63% yield (65.0 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 7.74–7.71 (m, 1H), 7.58–7.55 (m, 1H), 7.49 (s, 1H), 3.67–3.59 (m, 2H), 3.22–3.15 (m, 1H), 2.74 (s, 3H), 2.28 (br s, 1H), 2.02–1.94 (m, 1H), 1.85–1.77 (m, 1H), 1.69–1.61 (m, 1H), 1.54–1.46 (m, 1H), 1.41 (d, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 201.71, 165.99, 148.52, 143.67, 129.80, 129.35, 127.39, 125.16, 122.31, 118.55, 62.56, 42.33, 32.78, 30.60, 30.17, 20.87; **HRMS** Calcd for $C_{16}H_{20}NO_2$ [M+H$^+$]: 258.1494, Found: 258.1493.



11

R_f = 0.34, 60% Acetone in Hexane

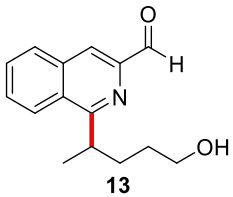
Compound **11** was isolated in 62% yield (60.7 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.70 (ddd, *J* = 8.2, 6.9, 1.0 Hz, 1H), 7.55 (ddd, *J* = 8.2, 6.9, 1.0 Hz, 1H), 7.18 (s, 1H), 4.89 (s, 2H), 3.66–3.59 (m, 3H), 1.92–1.85 (m, 1H), 1.82–1.75 (m, 1H), 1.67–1.58 (m, 1H), 1.58–1.49 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.62, 154.30, 146.98, 129.54, 129.27, 126.55, 126.10, 122.99, 114.74, 64.14, 62.72, 33.37, 33.31, 30.60, 21.21; **HRMS** Calcd for $C_{15}H_{20}NO_2$ [M+H$^+$]: 246.1494, Found: 246.1489.



12

R_f = 0.16, 50% EtOAc in Hexane

Compound **12** was isolated in 80% yield (68.9 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.6 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.68–7.65 (m, 1H), 7.61–7.58 (m, 1H), 7.50 (d, *J* = 5.6 Hz, 1H), 3.87–3.80 (m, 1H), 3.63–3.52 (m, 2H), 2.21–2.14 (m, 1H), 1.89 (br s, 1H), 1.86–1.79 (m, 1H), 1.70–1.61 (m, 1H), 1.53–1.45 (m, 1H), 1.41 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.39, 141.68, 136.37, 129.68, 127.53, 126.98, 126.72, 124.64, 119.07, 62.64, 35.95, 31.96, 30.92, 21.17; **HRMS** Calcd for $C_{14}H_{18}NO$ [M+H$^+$]: 216.1388, Found: 216.1380.

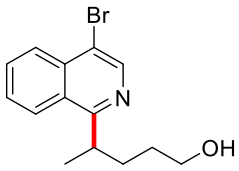


13

R_f = 0.50, 50% EtOAc in Hexane

Compound **13** was isolated in 62% yield (61.3 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.30–8.28 (m, 1H),

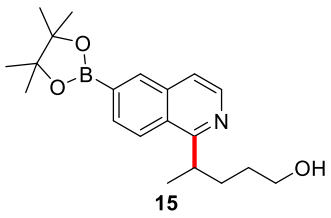
8.23 (s, 1H), 8.03–8.00 (m, 1H), 7.78–7.75 (m, 2H), 3.90–3.83 (m, 1H), 3.66–3.57 (m, 2H), 2.29–2.21 (m, 1H), 1.90–1.83 (m, 1H), 1.71–1.62 (m, 2H), 1.56–1.49 (m, 1H), 1.46 (d, J = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.34, 166.33, 145.77, 135.85, 130.47, 129.80, 128.83, 124.86, 119.71, 62.82, 36.26, 31.88, 30.92, 20.97; **HRMS** Calcd for $C_{15}H_{18}NO_2$ [M+H$^+$]: 244.1338, Found: 244.1337.



14

R_f = 0.50, 50% EtOAc in Hexane

Compound **14** was isolated in 74% yield (87.4 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.24–8.20 (m, 2H), 7.80–7.77 (m, 1H), 7.68–7.65 (m, 1H), 3.83–3.76 (m, 1H), 3.63–3.55 (m, 2H), 2.17–2.10 (m, 1H), 1.84–1.78 (m, 1H), 1.67–1.59 (m, 2H), 1.52–1.44 (m, 1H), 1.40 (d, J = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.05, 143.48, 134.89, 130.93, 128.05, 127.91, 126.86, 124.98, 117.62, 62.70, 35.92, 32.02, 30.83, 21.06; **HRMS** Calcd for $C_{14}H_{17}BrNO$ [M+H$^+$]: 294.0494, Found: 294.0491.

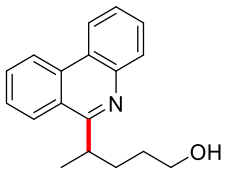


15

R_f = 0.41, 50% EtOAc in Hexane

Compound **15** was isolated in 69% yield (94.0 mg) as a light brown oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, J = 5.7 Hz, 1H), 8.33 (s, 1H), 8.19 (d, J = 8.6 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H), 7.53 (d, J = 5.7 Hz, 1H), 3.87–3.80 (m, 1H), 3.62–3.51 (m, 2H), 2.19–2.12 (m, 1H), 1.86–1.79 (m, 1H), 1.68–1.59 (m, 1H), 1.53–1.43 (m, 1H), 1.40 (d, J = 7.0 Hz, 3H), 1.40 (s, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.34, 141.72, 135.63, 135.58, 131.65, 127.89, 123.52, 119.49, 84.26, 62.68, 35.93, 31.94, 30.91, 24.87, 24.52, 21.20; **HRMS** Calcd for $C_{20}H_{29}BNO_3$ [M+H$^+$]: 342.2240,

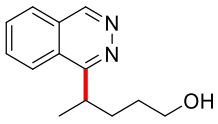
Found: 342.2250.



16

R_f = 0.74, 50% EtOAc in Hexane

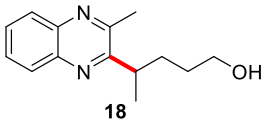
Compound **16** was isolated in 84% yield (88.8 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.84–7.81 (m, 1H), 7.72–7.68 (m, 2H), 7.63–7.60 (m, 1H), 3.90–3.84 (m, 1H), 3.64–3.59 (m, 1H), 3.55–3.50 (m, 1H), 2.43–2.36 (m, 1H), 2.34 (br s, 1H), 1.90–1.83 (m, 1H), 1.79–1.71 (m, 1H), 1.60–1.52 (m, 1H), 1.46 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.97, 143.42, 133.03, 130.10, 129.54, 128.51, 127.17, 126.29, 125.58, 124.97, 123.33, 122.54, 121.79, 62.46, 36.56, 30.98, 30.91, 21.18; **HRMS** Calcd for $C_{18}H_{20}NO$ [M+H$^+$]: 266.1545, Found: 266.1557.



17

R_f = 0.22, EtOAc

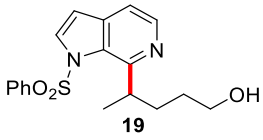
Compound **17** was isolated in 72% yield (62.0 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.98–7.87 (m, 3H), 3.83–3.76 (m, 1H), 3.68–3.61 (m, 2H), 2.48 (br s, 1H), 2.31–2.24 (m, 1H), 1.95–1.88 (m, 1H), 1.72–1.64 (m, 1H), 1.62–1.54 (m, 1H), 1.50 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.16, 132.64, 132.40, 131.78, 127.15, 126.23, 125.33, 123.42, 62.57, 35.39, 31.92, 30.81, 20.70; **HRMS** Calcd for $C_{13}H_{17}N_2O$ [M+H$^+$]: 217.1341, Found: 217.1343.



18

R_f = 0.25, 50% EtOAc in Hexane

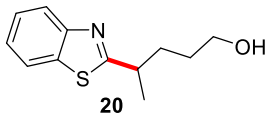
Compound **18** was isolated in 63% yield (58.0 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01–7.96 (m, 2H), 7.66–7.65 (m, 2H), 3.66–3.57 (m, 2H), 3.35–3.28 (m, 1H), 2.79 (s, 3H), 2.16–2.09 (m, 1H), 1.89 (br s, 1H), 1.81–1.74 (m, 1H), 1.70–1.62 (m, 1H), 1.53–1,45 (m, 1H), 1.35 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 160.22, 152.82, 141.21, 140.58, 128.86, 128.68, 128.60, 128.17, 62.70, 37.25, 31.50, 30.77, 22.79, 20.15; **HRMS** Calcd for $C_{14}H_{19}N_2O$ [M+H$^+$]: 231.1497, Found: 231.1501.



19

R_f = 0.26, EtOAc

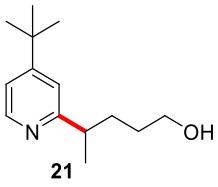
Compound **19** was isolated in 58% yield (80.3 mg) as a pale yellow following the general procedure, 3.0 equiv of 1-pentanol and 2.0 equiv of PFBI-OH were used, 36 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.42 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.58–7.56 (m, 1H), 7.46–7.43 (m, 2H), 7.39 (d, *J* = 3.4 Hz, 1H), 6.48 (s, 1H), 3.64–3.57 (m, 3H), 2.09 (br s, 1H), 1.90–1.83 (m, 1H), 1.68–1.61 (m, 1H), 1.56–1.50 (m, 2H), 1.30 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.40, 142.33, 138.55, 136.49, 135.81, 134.23, 129.49, 126.30, 114.90, 106.48, 106.25, 62.38, 33.97, 31.94, 30.10, 21.26; **HRMS** Calcd for $C_{18}H_{21}N_2O_3S$ [M+H$^+$]: 345.1273, Found: 345.1281.



20

R_f = 0.57, 50% EtOAc in Hexane

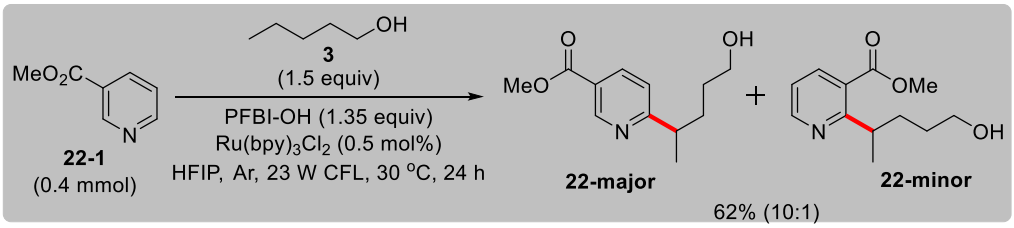
Compound **20** was isolated in 66% yield (58.3 mg) as a colorless oil following the general procedure, 24 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.46–7.43 (m, 1H), 7.36–7.33 (m, 1H), 3.69–3.62 (m, 2H), 3.37–3.30 (m, 1H), 2.01–1.93 (m, 1H), 1.89–1.82 (m, 2H), 1.73–1.56 (m, 2H), 1.48 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.67, 152.87, 134.56, 125.88, 124.68, 122.56, 121.56, 62.47, 39.16, 33.60, 30.33, 21.39; **HRMS** Calcd for $C_{12}H_{16}NOS$ [M+H$^+$]: 222.0953, Found: 222.0957.



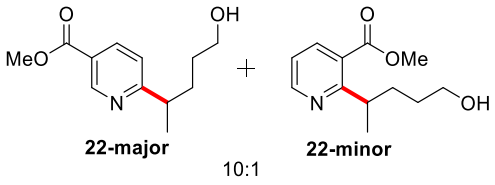
21

R_f = 0.16, 60% EtOAc in Hexane

Compound **21** was isolated in 49% yield (43.0 mg) as a colorless oil following the general procedure, 24 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 5.2 Hz, 1H), 7.12 (s, 1H), 7.10 (dd, *J* = 5.2, 1.6 Hz, 1H), 3.65–3.57 (m, 2H), 2.95–2.88 (m, 1H), 2.47 (br s, 1H), 1.87–1.80 (m, 1H), 1.71–1.63 (m, 1H), 1.62–1.54 (m, 1H), 1.49–1.41 (m, 1H), 1.31 (s, 9H), 1.30 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.78, 160.57, 148.68, 118.46, 118.39, 62.72, 41.54, 34.67, 33.16, 30.71, 30.55, 21.01; **HRMS** Calcd for $C_{14}H_{24}NO$ [$M+H^+$]: 222.1858, Found: 222.1865.



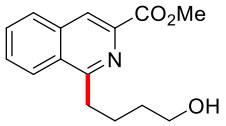
Scheme S9



R_f = 0.20, 60% EtOAc in Hexane

Compound **22** was isolated in 62% yield (55.0 mg) as a colorless oil following the general procedure, an inseparable mixture. Data for **22-major**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.21 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 3.94 (s, 3H), 3.65–3.58 (m, 2H), 3.04–2.97 (m, 1H), 2.10 (br s, 1H), 1.88–1.81 (m, 1H), 1.74–1.67 (m, 1H), 1.61–1.52 (m, 1H), 1.47–1.38 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.82, 165.87, 150.36, 137.55, 123.70, 121.23, 62.57, 52.23, 41.74, 32.95, 30.54, 20.65; Data for **22-minor**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 4.7, 1.8 Hz, 1H), 8.07 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.18 (dd, *J* = 7.9, 4.7 Hz, 1H), 3.92 (s, 3H), 3.79–3.72 (m, 1H), 3.65–3.58 (m, 2H), 1.99–1.91 (m, 1H), 1.67–1.62

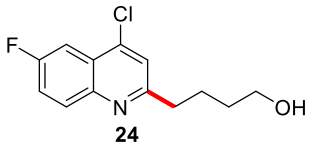
(m, 2H), 1.47–1.38 (m, 1H), 1.29 (d, J = 6.7 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.50, 166.48, 151.86, 137.95, 125.68, 120.51, 62.57, 52.41, 36.79, 32.40, 30.59, 20.58; **HRMS** Calcd for $C_{12}H_{18}NO_3$ [M+H$^+$]: 224.1287, Found: 224.1291.



23

R_f = 0.32, EtOAc

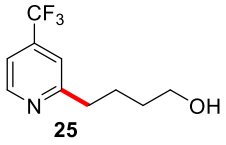
Compound **23** was isolated in 76% yield (79.2 mg) as a white solid following the general procedure, 3.0 equiv of 1-butanol **4t-2** and 2.0 equiv of PFBI-OH were used, 36 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.24 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.78–7.72 (m, 2H), 4.04 (s, 3H), 3.69 (t, J = 6.1 Hz, 2H), 3.44 (t, J = 7.3 Hz, 2H), 2.60 (br s, 1H), 2.10–2.04 (m, 2H), 1.78–1.73 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 166.39, 162.45, 140.12, 135.76, 130.58, 129.40, 128.87, 128.36, 125.37, 122.92, 61.84, 52.74, 34.40, 32.48, 24.54; **HRMS** Calcd for $C_{15}H_{18}NO_3$ [M+H$^+$]: 260.1287, Found: 260.1290.



24

R_f = 0.40, EtOAc

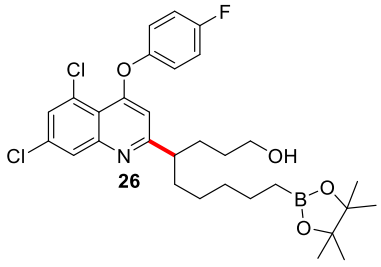
Compound **24** was isolated in 65% yield (65.0 mg) as a white solid following the general procedure, 3.0 equiv of 1-butanol **4t-2** and 2.0 equiv of PFBI-OH were used, 36 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (dd, J = 9.2, 5.3 Hz, 1H), 7.79 (dd, J = 9.2, 2.8 Hz, 1H), 7.50 (td, J = 8.9, 2.8 Hz, 1H), 7.43 (s, 1H), 3.71 (t, J = 6.3 Hz, 2H), 2.99 (t, J = 7.6 Hz, 2H), 2.44 (br s, 1H), 1.96–190 (m, 2H), 1.72–1.66 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.75 (d, J = 2.6 Hz), 160.72 (d, J = 248.8 Hz), 145.47, 141.97 (d, J = 5.5 Hz), 131.52 (d, J = 9.1 Hz), 125.81 (d, J = 10.2 Hz), 122.04, 120.55 (d, J = 25.6 Hz), 107.77 (d, J = 24.3 Hz), 62.18, 37.99, 32.09, 25.39; **HRMS** Calcd for $C_{13}H_{14}ClFNO$ [M+H$^+$]: 254.0748, Found: 254.0762.



25

R_f = 0.38, EtOAc

Compound **25** was isolated in 60% yield (52.9 mg) as a colorless oil following the general procedure, 3.0 equiv of 1-butanol **4t-2** and 2.0 equiv of PFBI-OH were used, 36 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.71 (br s, 1H), 7.39 (s, 1H), 7.35 (d, *J* = 4.4 Hz, 1H), 3.70 (t, *J* = 6.3 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.18 (br s, 1H), 1.90–1.84 (m, 2H), 1.69–1.63 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.61, 150.04, 138.68 (q, *J* = 33.6 Hz), 122.83 (q, *J* = 273.2 Hz), 118.47, 116.75, 62.27, 37.69, 32.02, 25.67; **HRMS** Calcd for $C_{10}H_{13}F_3NO$ [M+H$^+$]: 220.0949, Found: 220.0960.

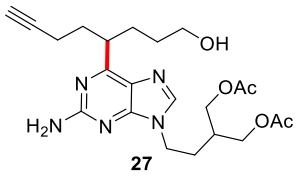


26

R_f = 0.25, 30% EtOAc in Hexane

Quinoxyfen **26-1** (125.3 mg, 0.4 mmol, 1.0 equiv), alcohol **26-2** (166.4 mg, 0.6 mmol, 1.5 equiv) and PFBI-OH (181.4 mg, 0.54 mmol, 1.35 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (1.0 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 24 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 80 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 to afford the desired compound **26** in 67% yield (155.6 mg) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 2.0 Hz, 1H), 7.18–7.09 (m, 4H), 6.49 (s, 1H), 3.58–3.50 (m, 2H), 2.79–2.73 (m, 1H), 1.99 (br s, 1H), 1.74–1.66 (m, 2H), 1.61–1.56 (m, 3H), 1.53–1.45 (m, 1H), 1.37–1.16 (m, 5H), 1.22 (s, 12H), 0.69 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.62,

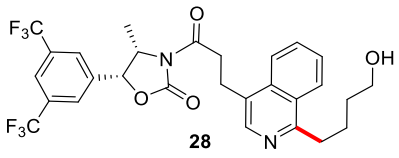
162.25, 159.81 (d, J = 244.3 Hz), 151.20, 150.27 (d, J = 2.6 Hz), 134.86, 129.89, 128.72, 127.39, 121.82, 121.75, 117.10, 117.00, 116.91, 106.42, 82.84, 62.60, 48.09, 35.30, 32.33, 31.19, 30.49, 27.15, 24.75, 23.77, 11.03; **HRMS** Calcd for $C_{30}H_{38}BCl_2FNO_4$ [M+H$^+$]: 576.2255, Found: 576.2275.



27

R_f = 0.46, 5% MeOH in DCM

Compound **27** was isolated in 53% yield (94.5 mg) as a colorless oil following the general procedure. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 5.13 (br s, 2H), 4.18 (t, J = 6.9 Hz, 2H), 4.14 (d, J = 4.7 Hz, 4H), 3.67–3.59 (m, 2H), 3.49 (br s, 1H), 2.85 (br s, 1H), 2.27–2.20 (m, 1H), 2.12 (t, J = 7.1 Hz, 2H), 2.07 (s, 6H), 2.04–1.93 (m, 5H), 1.83–1.76 (m, 1H), 1.62–1.54 (m, 1H), 1.48–1.40 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 170.90, 165.33, 159.64, 152.73, 140.84, 126.90, 84.15, 68.44, 63.63, 62.35, 41.24, 40.86, 34.90, 32.46, 30.44, 30.30, 28.75, 20.82, 16.70; **HRMS** Calcd for $C_{22}H_{32}N_5O_5$ [M+H$^+$]: 446.2403, Found: 446.2417.

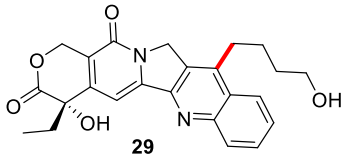


28

R_f = 0.26, EtOAc

Compound **28** was isolated in 78% yield (172.3 mg) as a white solid following the general procedure, 3.0 equiv of 1-butanol **4t-2** and 2.0 equiv of PFBI-OH were used, 36 h. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.92 (s, 1H), 7.79 (s, 2H), 7.75 (ddd, J = 8.4, 6.9, 1.0 Hz, 1H), 7.62 (ddd, J = 8.4, 6.9, 0.8 Hz, 1H), 5.75 (d, J = 7.4 Hz, 1H), 4.94–4.88 (m, 1H), 3.71 (t, J = 6.2 Hz, 2H), 3.47–3.31 (m, 6H), 2.61 (br s, 1H), 2.04–1.98 (m, 2H), 1.77–1.71 (m, 2H), 0.93 (d, J = 6.6 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.55, 160.85, 152.03, 141.23, 136.13, 134.86, 132.46 (q, $J_{C\text{-}F}$ = 33.9 Hz), 130.20, 127.79, 126.86, 126.68, 126.02, 125.98, 125.96, 123.31, 122.93 (hept, $J_{C\text{-}F}$ = 3.6 Hz), 122.84 (q, $J_{C\text{-}F}$ = 272.8 Hz), 77.54,

62.22, 54.30, 36.34, 34.19, 32.33, 25.08, 24.43, 14.86; **HRMS** Calcd for $C_{28}H_{27}F_6N_2O_4$ [M+H$^+$]: 569.1875, Found: 569.1905.



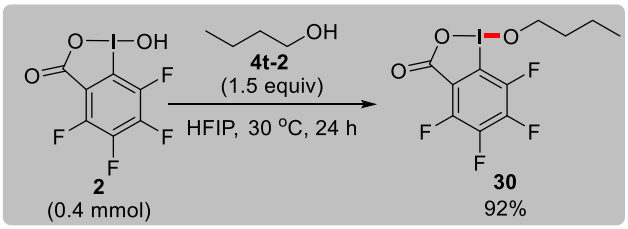
29

R_f = 0.27, 5% MeOH in DCM

Camptothecin **29-1** (139.9 mg, 0.4 mmol, 1.0 equiv), 1-butanol **4t-2** (89.7 mg, 1.2 mmol, 3 equiv) and PFBI-OH (268.8 mg, 0.8 mmol, 2 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (1.0 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 ºC under the fluorescent light irradiation (23 W) for 36 h. The solvent was removed *in vacuo* and the residue was purified by preparative thin layer chromatography on silica gel to afford the desired compound **29** in 58% yield (98.4 mg) as a light yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.79–7.76 (m, 1H), 7.65–7.63 (m, 2H), 5.73 (d, *J* = 16.2 Hz, 1H), 5.29 (d, *J* = 16.2 Hz, 1H), 5.25 (s, 2H), 3.95 (s, 1H), 3.74 (t, *J* = 6.0 Hz, 2H), 3.22 (t, *J* = 7.8 Hz, 2H), 1.96–1.83 (m, 4H), 1.80–1.74 (m, 2H), 1.73 (br s, 1H), 1.03 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.88, 157.62, 151.74, 150.23, 149.35, 146.98, 144.13, 130.60, 130.05, 127.71, 127.24, 127.17, 123.57, 118.46, 98.04, 72.77, 66.30, 62.15, 49.65, 32.52, 31.58, 29.59, 26.28, 7.82; **HRMS** Calcd for $C_{24}H_{25}N_2O_5$ [M+H$^+$]: 421.1763, Found: 421.1790.

8. Mechanism studies

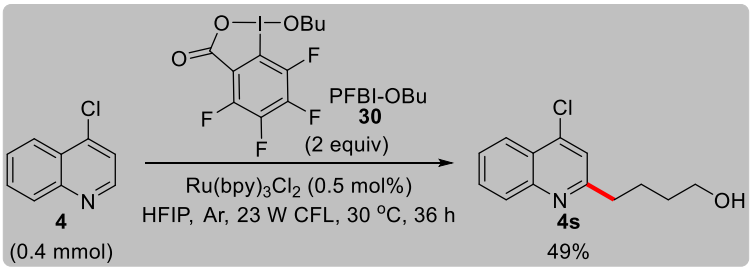
8.1 Alcoholysis of PFBI-OH 2 for preparation of PFBI-OBu 30



Scheme S10.

To the solution of 1-butanol **4t-2** (46.0 mg, 0.6 mmol, 1.5 equiv) in HFIP (1.0 mL), PFBI-OH **2** (134.4 mg, 0.4 mmol, 1.0 equiv) were added. The reaction vial was sealed with PTEF cap, and stirred at 30 °C for 24 h. The solvent was removed *in vacuo* to afford the desired compound **30** in 92% yield (145.0 mg) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.36 (t, *J* = 6.6 Hz, 2H), 1.64–1.57 (m, 2H), 1.45–1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 76.43 (d, *J* = 4.2 Hz), 34.96, 18.70, 13.81; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.41–-134.50 (m, 1F), -142.01–-142.10 (m, 1F), -143.12–-143.23 (m, 1F), -146.07–-146.17 (m, 1F); Compound **30** underwent hydrolysis under aqueous conditions for HRMS analysis procedure, affording PFBI-OH **2**. **HRMS** Calcd for $C_7H_2F_4IO_3$ $[M+H^+]$: 336.8985, Found: 336.8990.

8.2 PFBI-OBu 30 as alkylation reagent



Scheme S11.

4-Chloroquinoline **4** (65.2 mg, 0.4 mmol, 1.0 equiv) and PFBI-OBu **30** (316.0 mg, 0.8 mmol, 2 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 36 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 120 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 (ethyl acetate) to afford compound **4s** in 49% yield (46.0 mg).

8.3 ^{1}H NMR monitored alcoholysis procedure of PFBI-OH with 4t-2

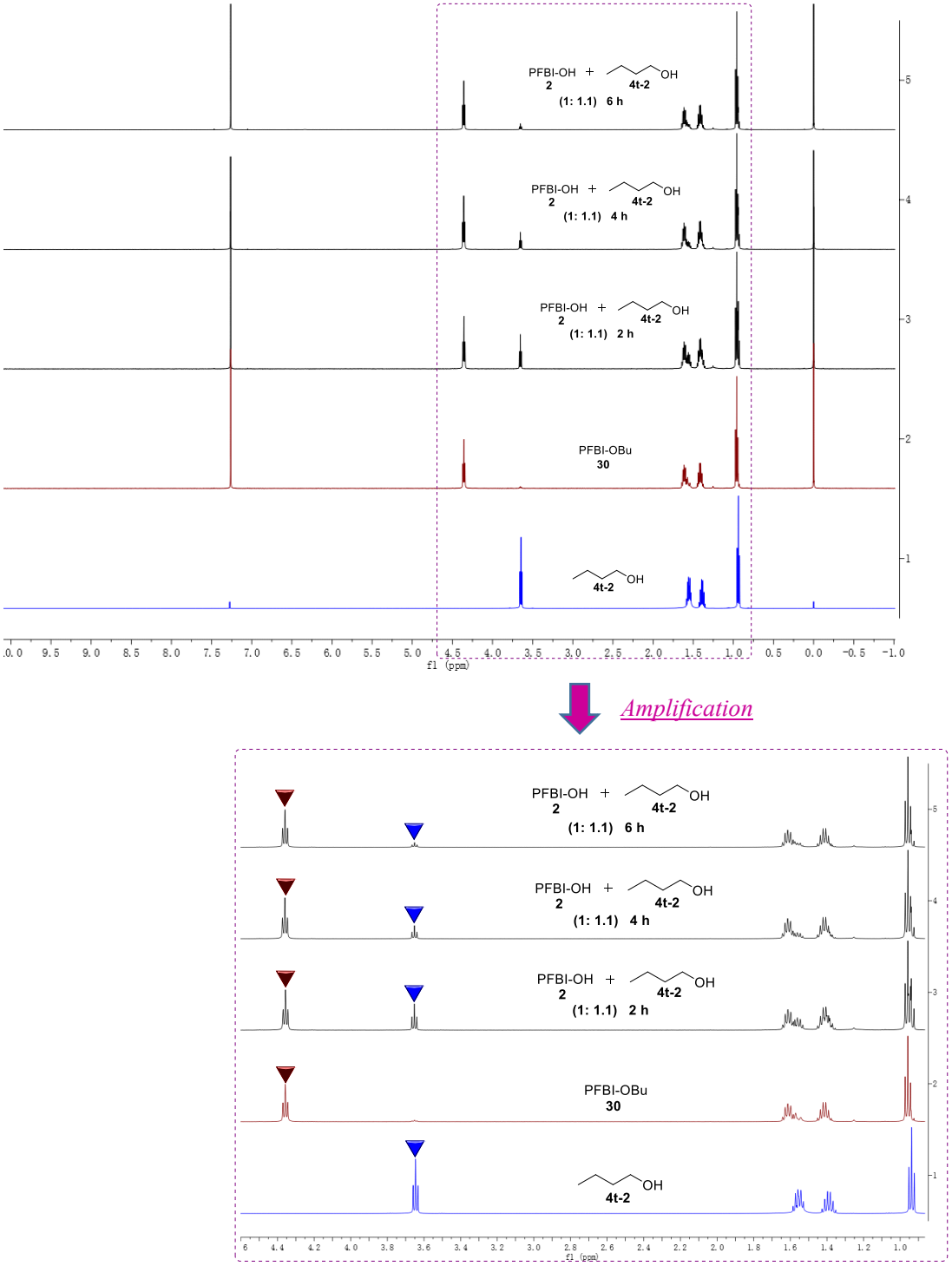


Figure S1.

Three parallel reactions were conducted. To the solution of 1-butanol **4t-2** (46.0 mg, 0.44 mmol, 1.1 equiv) in HFIP (1.0 mL), PFBI-OH **2** (134.4 mg, 0.4 mmol, 1.0 equiv)

was added. The reaction vial was sealed with PTEF cap, and stirred at 30 °C for 2, 4 and 6 hours, respectively. After removal of the solvent *in vacuo* (water bath for rotary evaporation, 40 °C), the residue was dissolved in 3 mL of $CDCl_3$ for ^1H NMR analysis. The results indicated that PFBI-OBu **30** formed *in situ* after the mixture of PFBI-OH **2** and 1-butanol **4t-2** in HFIP, and increased gradually as the extension of reaction time.

8.4 The Stern-Volmer quenching experiments

The luminescence quenching experiments were carried out on a fluorescence spectrophotometer. To a glass cuvette with a PTEF cap, photocatalyst $[Ru(bpy)_3]Cl_2$, quencher PFBI-OBu **30** or compound **4**, and HFIP were added to obtain a total volume of 200 μL. Before determination, the solution was degassed by three freeze-pump-thaw cycles and backfilled with argon. The concentration of $[Ru(bpy)_3]Cl_2$ was 1.0×10^{-4} M. All samples were irradiated at 452 nm, and emission was determined at 568 nm. It should be noted that all samples were measured within 1 minute after preparation.

The results showed that the excited state of Ru (Ⅱ) * can be quenched by PFBI-OBu **30**, while no obvious change of Ru (Ⅱ) * luminescence in the presence of variable concentrations of compound **4** was observed. (NOTE: I_0 is emission intensity of Ru (Ⅱ) * without quencher; I is emission intensity of Ru (Ⅱ) * in presence of a quencher.)

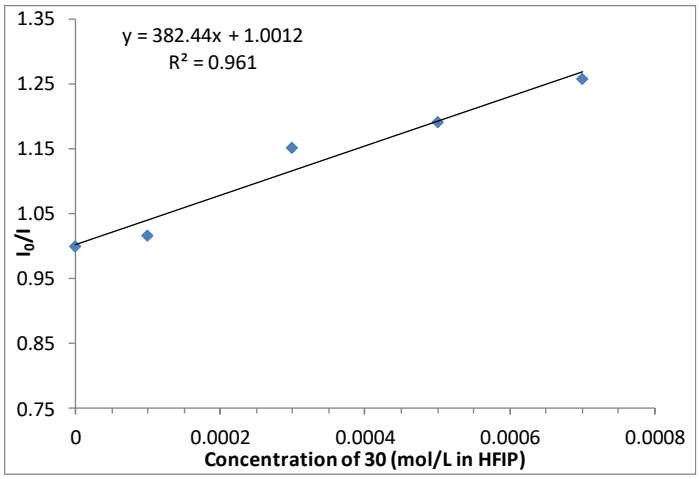


Figure S2. Stern-Volmer quenching experiment for PFBI-OBu **30**.

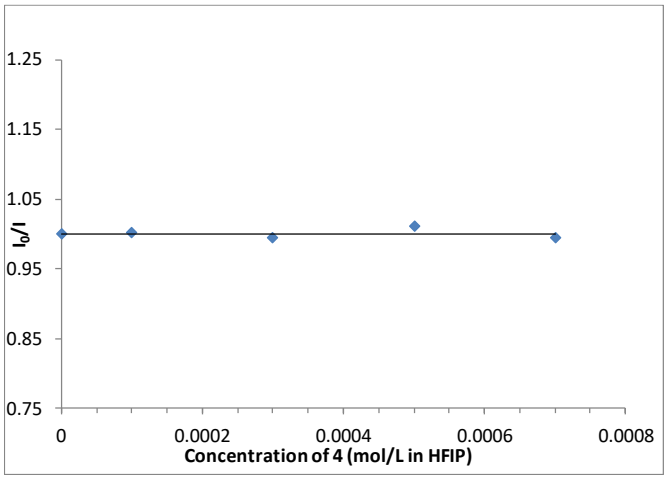
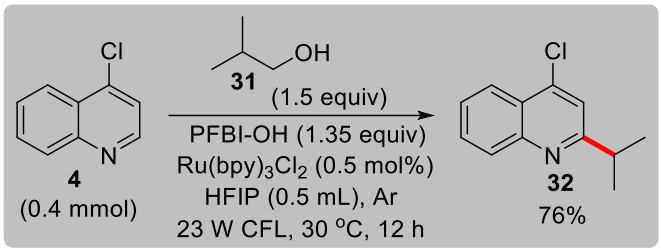


Figure S3. Stern-Volmer quenching experiment for **4**.

8.5 Alkoxyl radical-induced β-C-Cscission in Minisci alkylation reaction

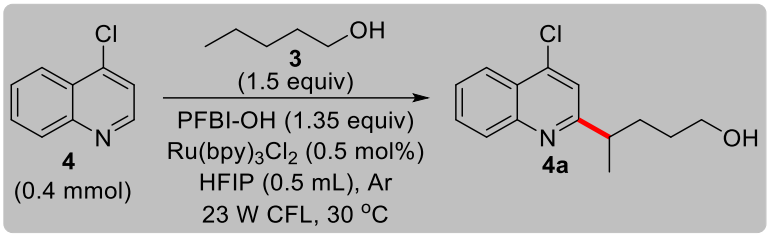


Scheme S12.

4-Chloroquinoline **4** (65.2 mg, 0.4 mmol, 1.0 equiv), *iso*butanol **31** (46.0 mg. 6 mmol, 1.5 equiv) and PFBI-OH (0.54 mmol, 1.35 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap, then the mixture was stirred at 30 °C under the fluorescent light irradiation (23 W) for 12 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 80 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 to afford compound **32** in 76% yield (62.3 mg) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.4, 0.9 Hz, 1H), 8.07–8.05 (m, 1H), 7.73

(ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.57 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.43 (s, 1H), 3.27–3.19 (m, 1H), 1.39 (d, J = 6.9 Hz, 6H). Spectra data are consistent with those reported in the literature.[5]

9. Light ON/OFF experiments



Scheme S13.

4-Chloroquinoline **4** (65.2 mg, 0.4 mmol, 1.0 equiv), 1-pentanol **3** (52.8 mg, 0.6 mmol, 1.5 equiv) and PFBI-OH (181.4 mg, 0.54 mmol, 1.35 equiv) were added to a solution of $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002 mmol, 0.005 equiv) in HFIP (0.5 mL). The reaction vial was purged with Ar for 1 min and sealed with PTEF cap. The reactions were stirred at 30 °C under the fluorescent light irradiation (23 W), and kept in the dark in 1 h intervals. After each interval, one vial was take out. After removal of the solvent *in vacuo*, the residue was dissolved in 3 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an internal standard for ^1H NMR analysis.

Table S1. Yields of light ON/OFF experiments

Vial	Time (h)/condition						Yield (%)[a]
1	0-1/hv						5
2	0-1/hv	1-2/dark					5
3	0-1/hv	1-2/dark	2-3/hv				14
4	0-1/hv	1-2/dark	2-3/hv	3-4/dark			14
5	0-1/hv	1-2/dark	2-3/hv	3-4/dark	4-5/hv		18
6	0-1/hv	1-2/dark	2-3/hv	3-4/dark	4-5/hv	5-6/dark	18

[a] NMR yield, average of three experiments

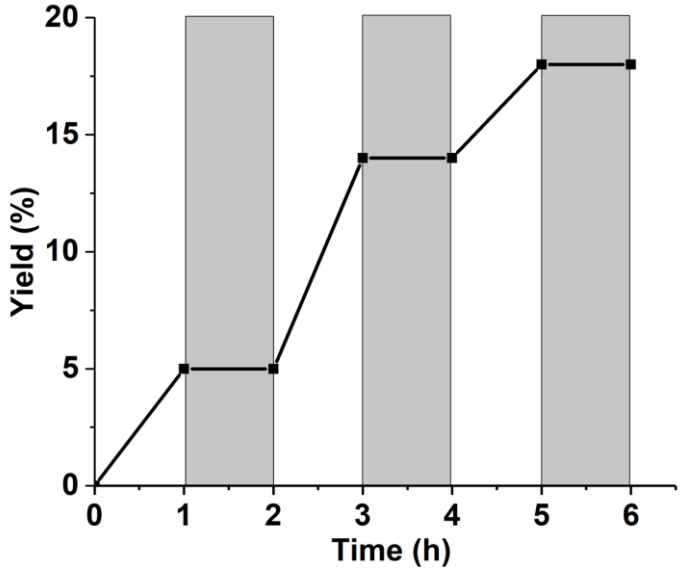


Figure S4. Light ON/OFF experiments using **3** and **4**.

10. References

[1] M. V. Vita, J. Waser, *Org*. *Lett*. **2013**, *15*, 3246.

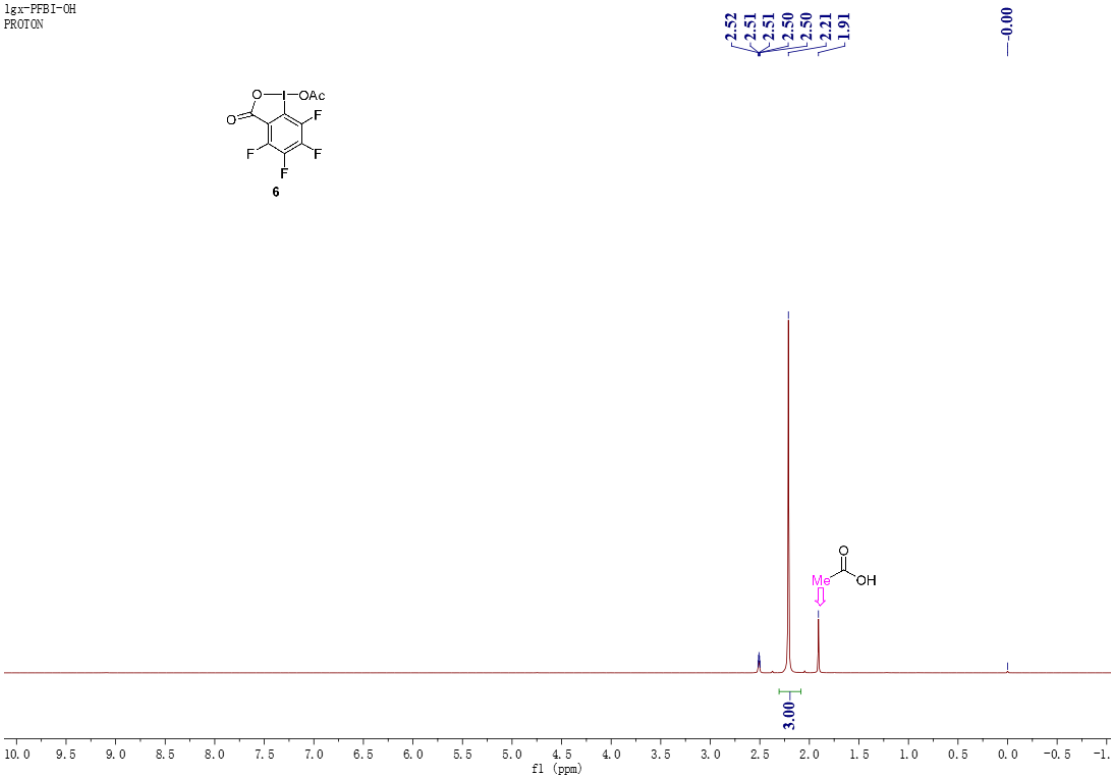
[2] R. D. Richardson, J. M. Zayed, S. Altermann, D. Smith, T. Wirth, *Angew. Chem*. *Int*. *Ed*. **2007**, *46*, 6529.

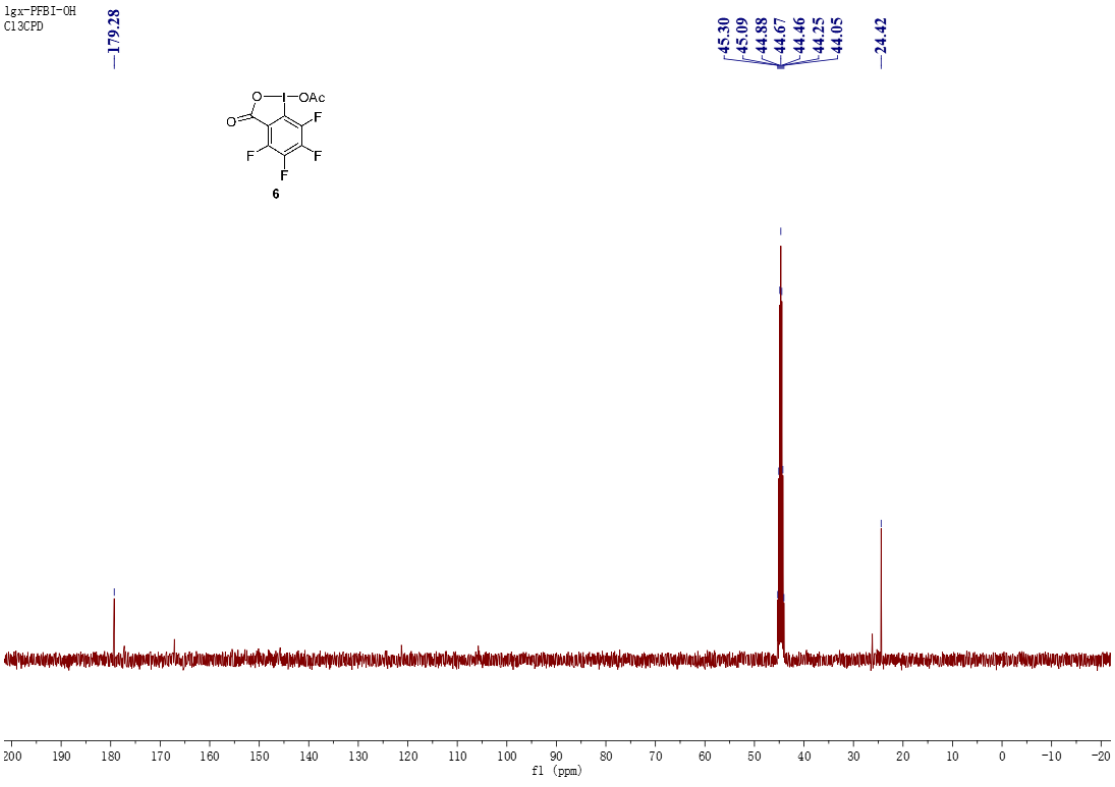
[3] A. Nilsen, P. M. England, *J*. *Am*. *Chem. Soc*. **2007**, *129*, 4902.

[4] E. R. Littmann, C. S. Marven, *J*. *Am*. *Chem. Soc*. **1930**, *52*, 287.

[5] G.-X. Li, C. A. Morales-Rivera, Y. Wang, F. Gao, G. He, P. Liu, G. Chen, *Chem*. *Sci*. **2016**, *7*, 6407.

11. NMR spectra





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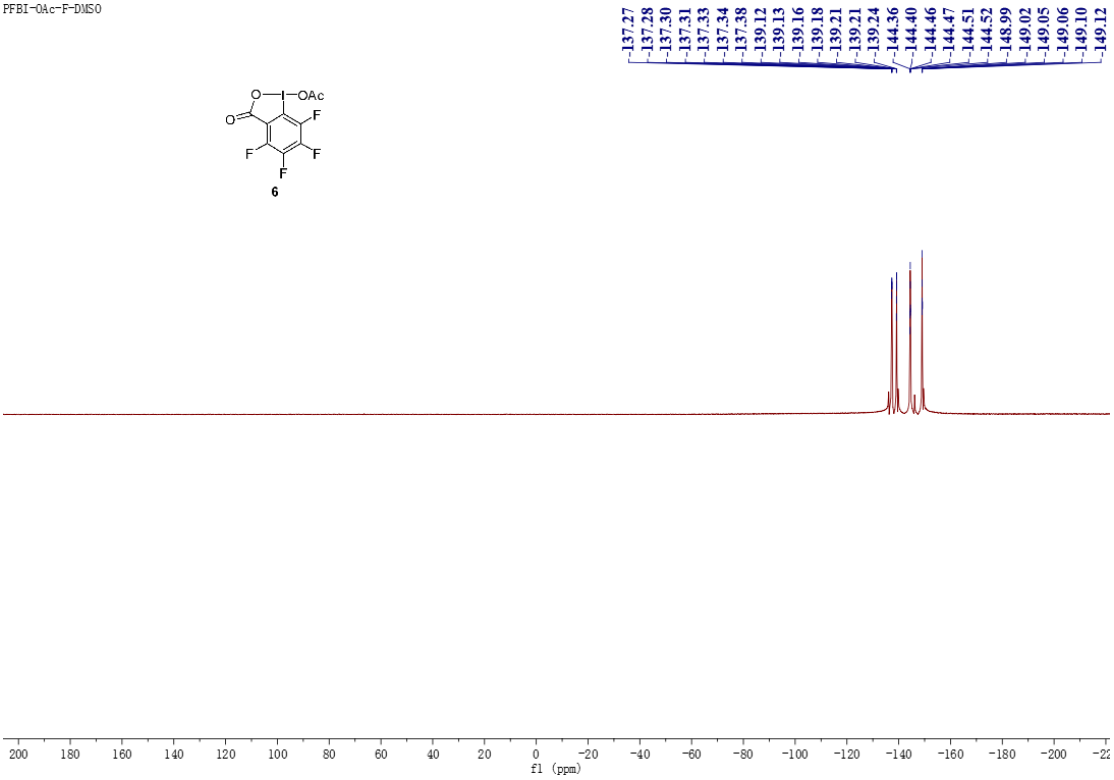

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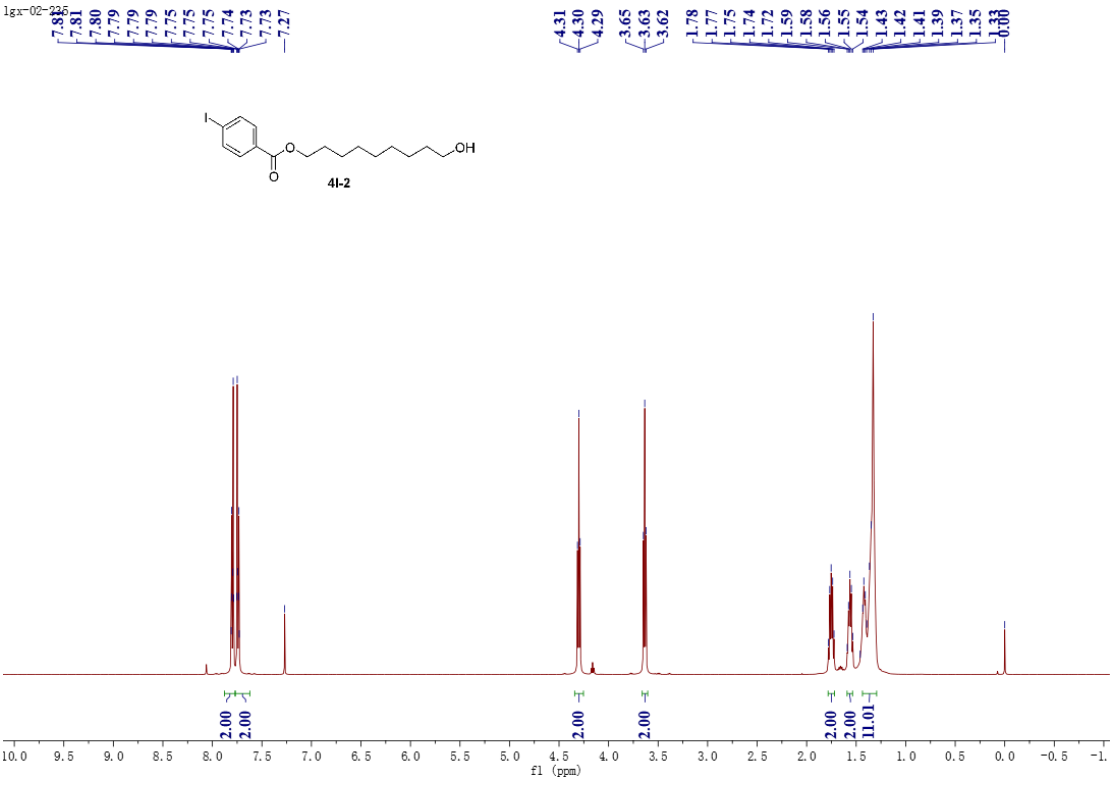

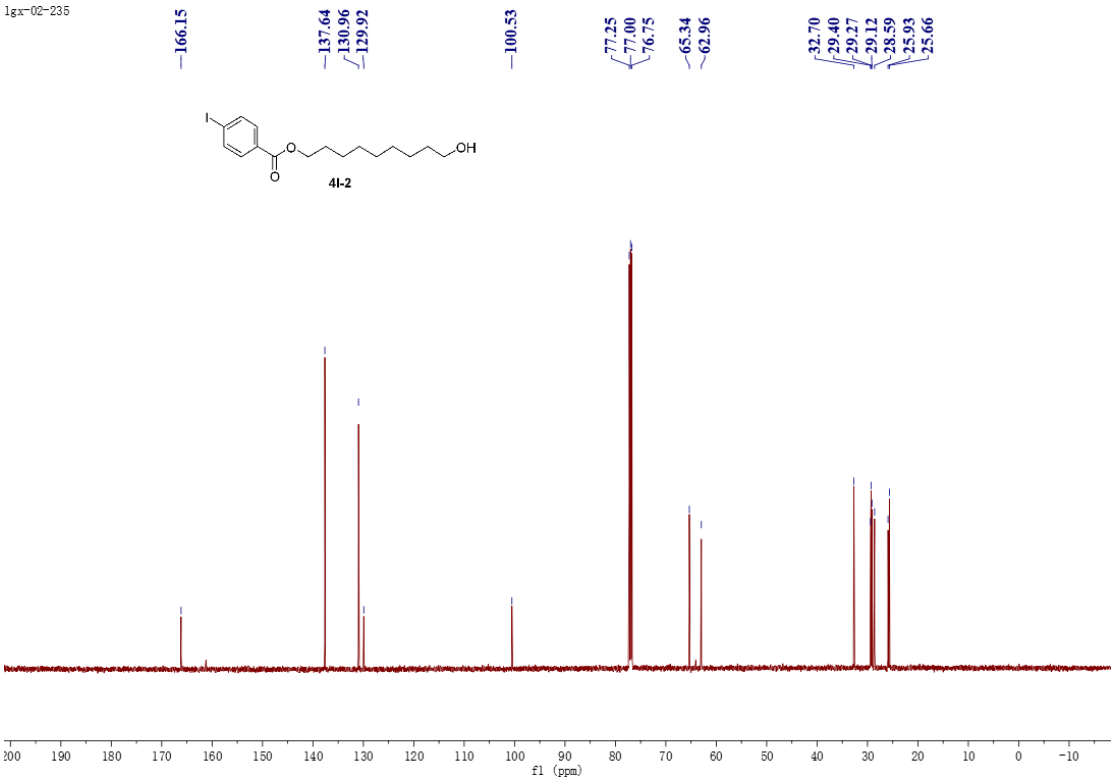
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OH
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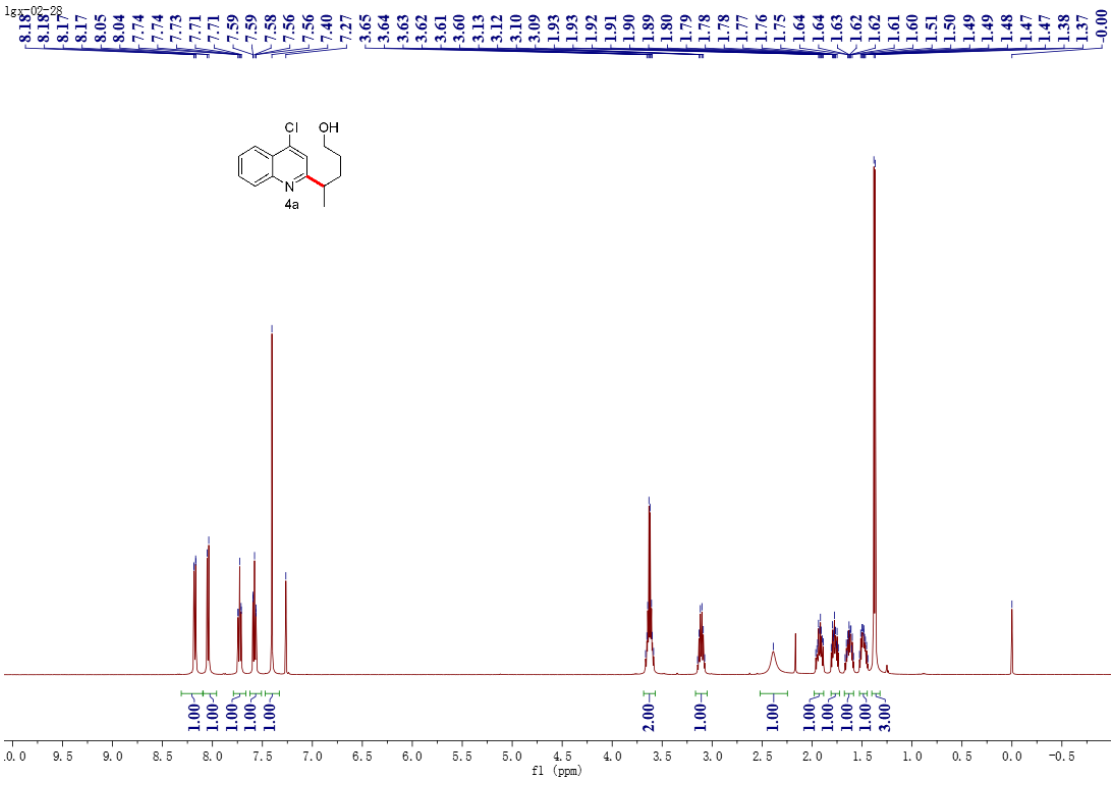
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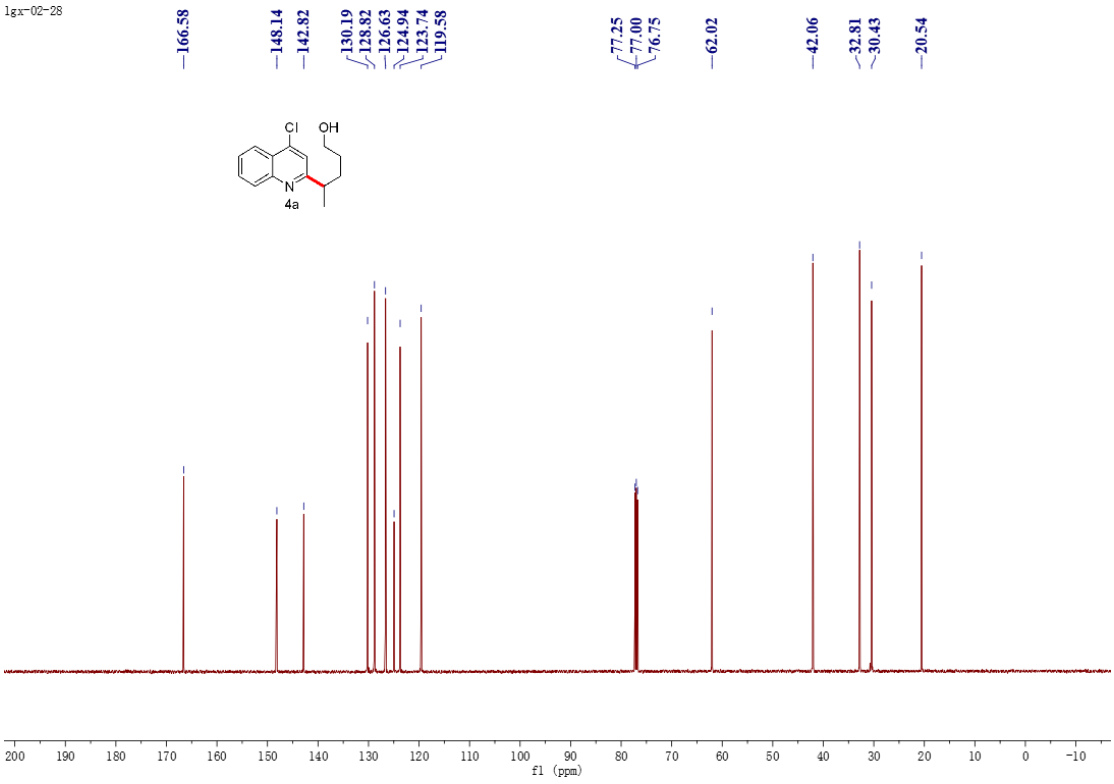
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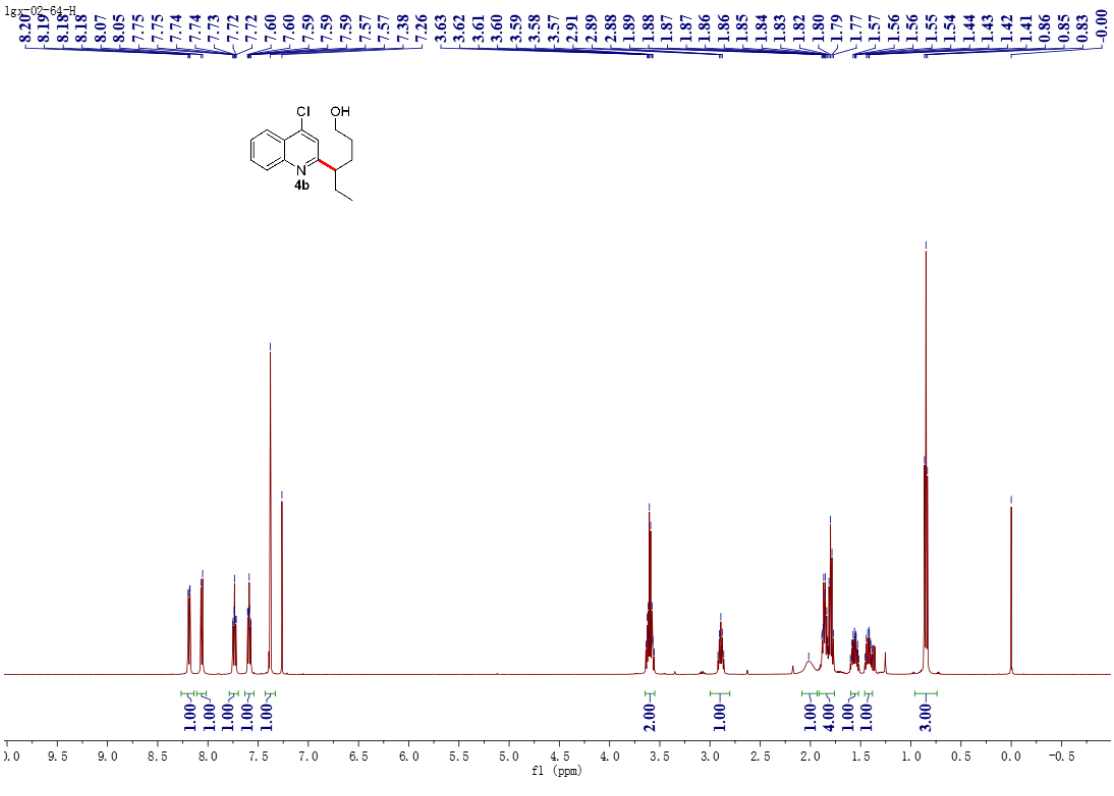
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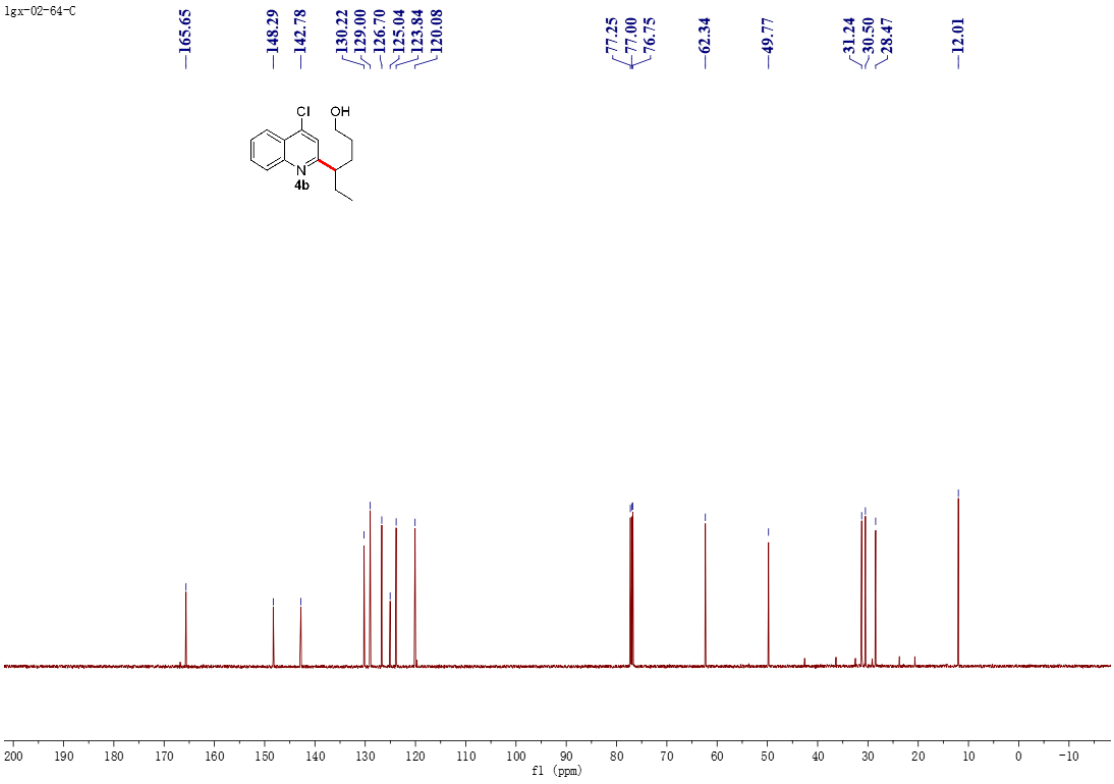
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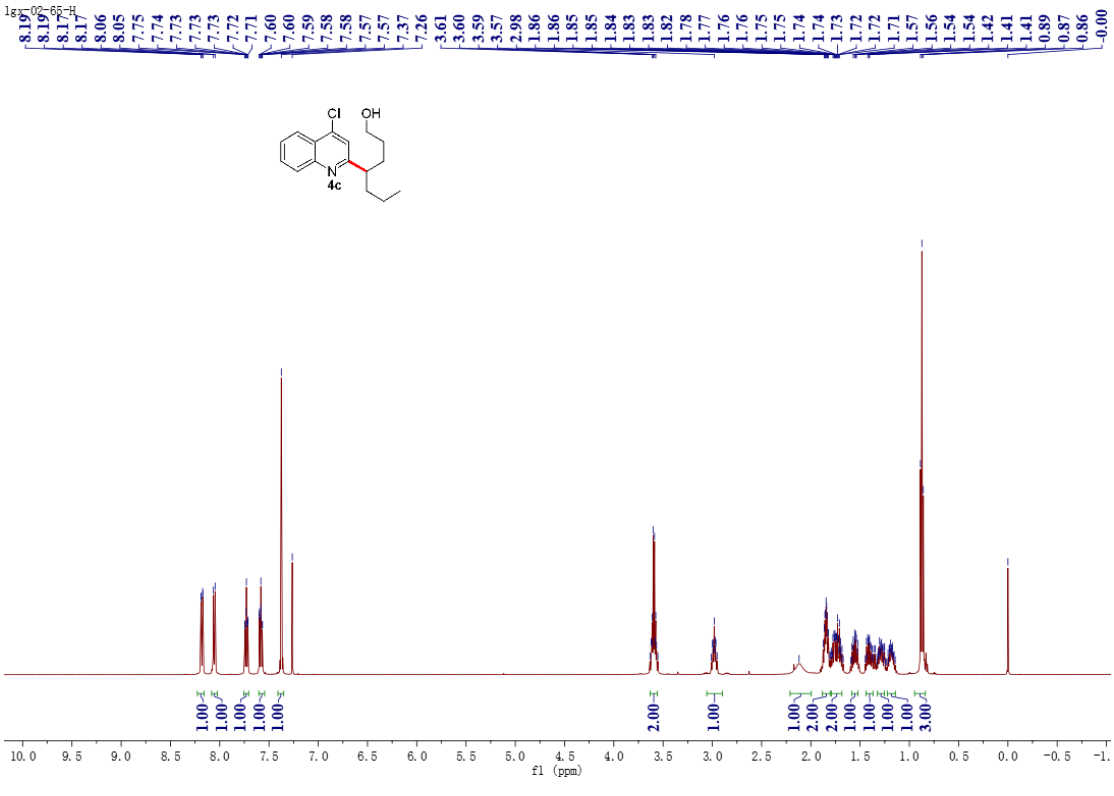
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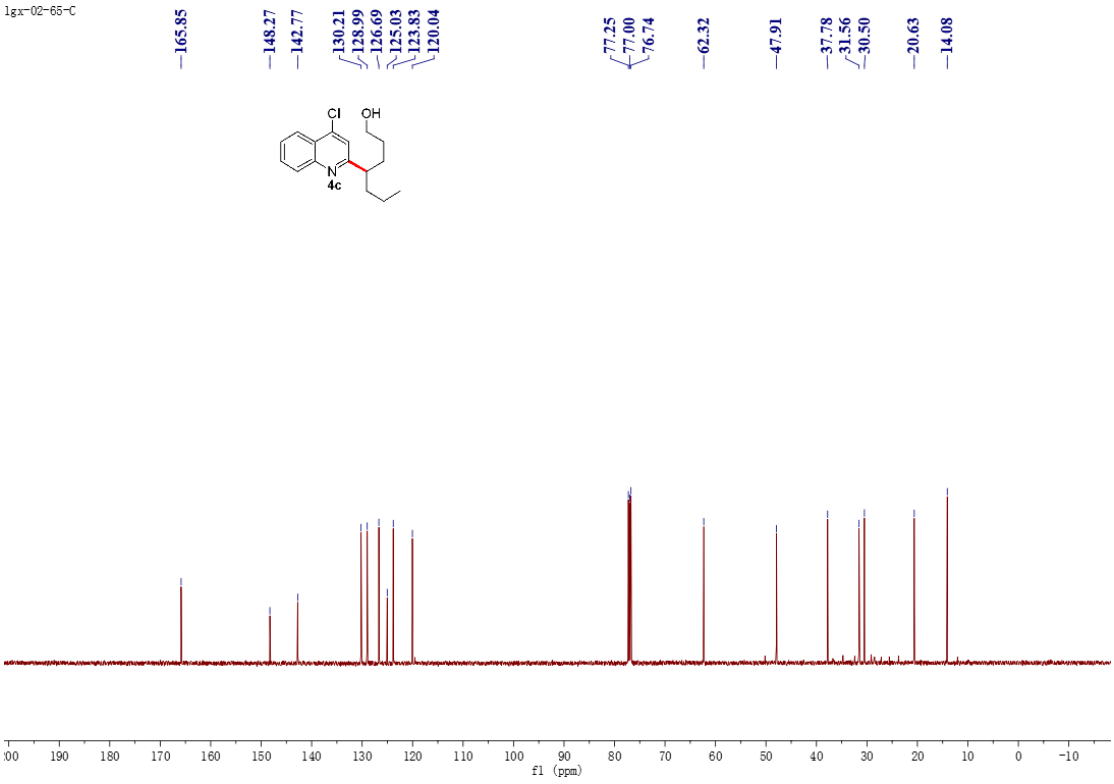
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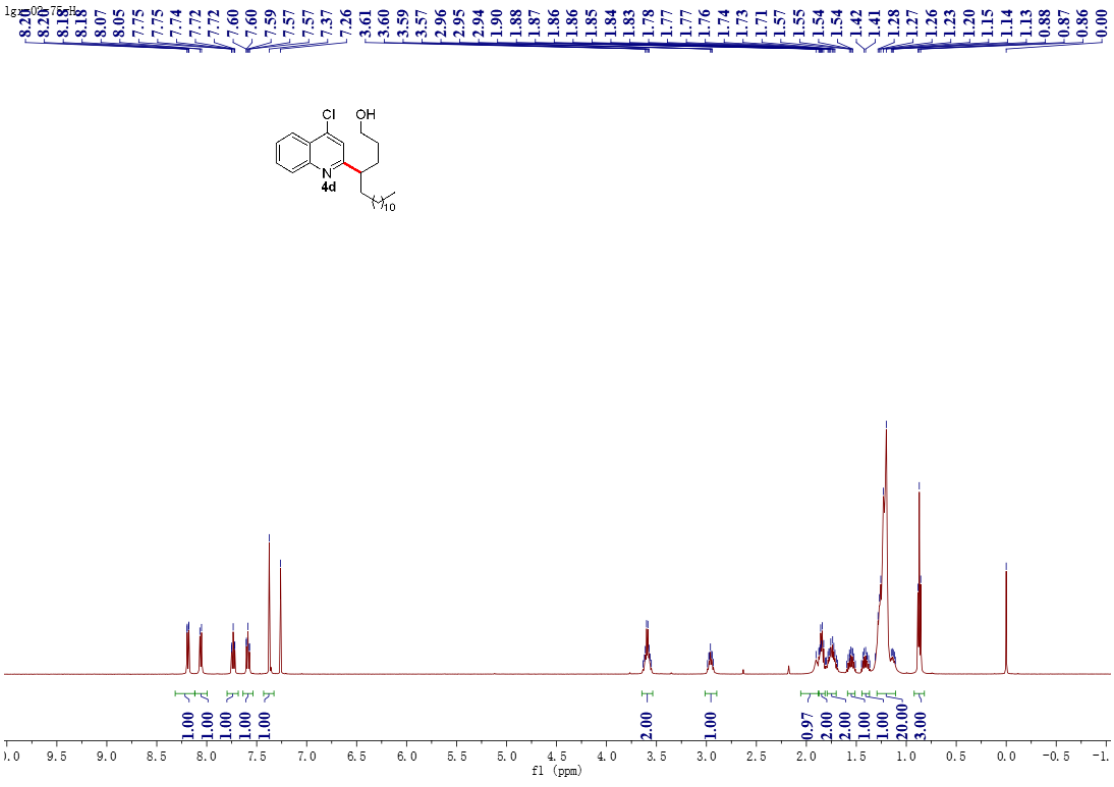
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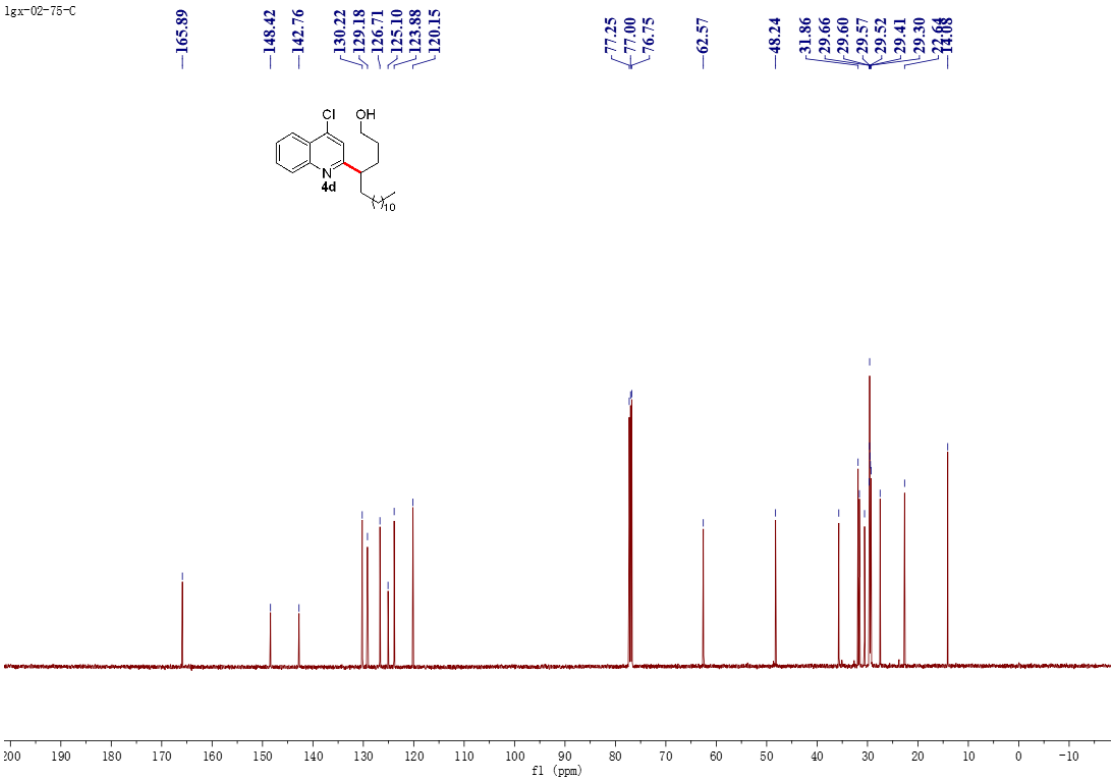
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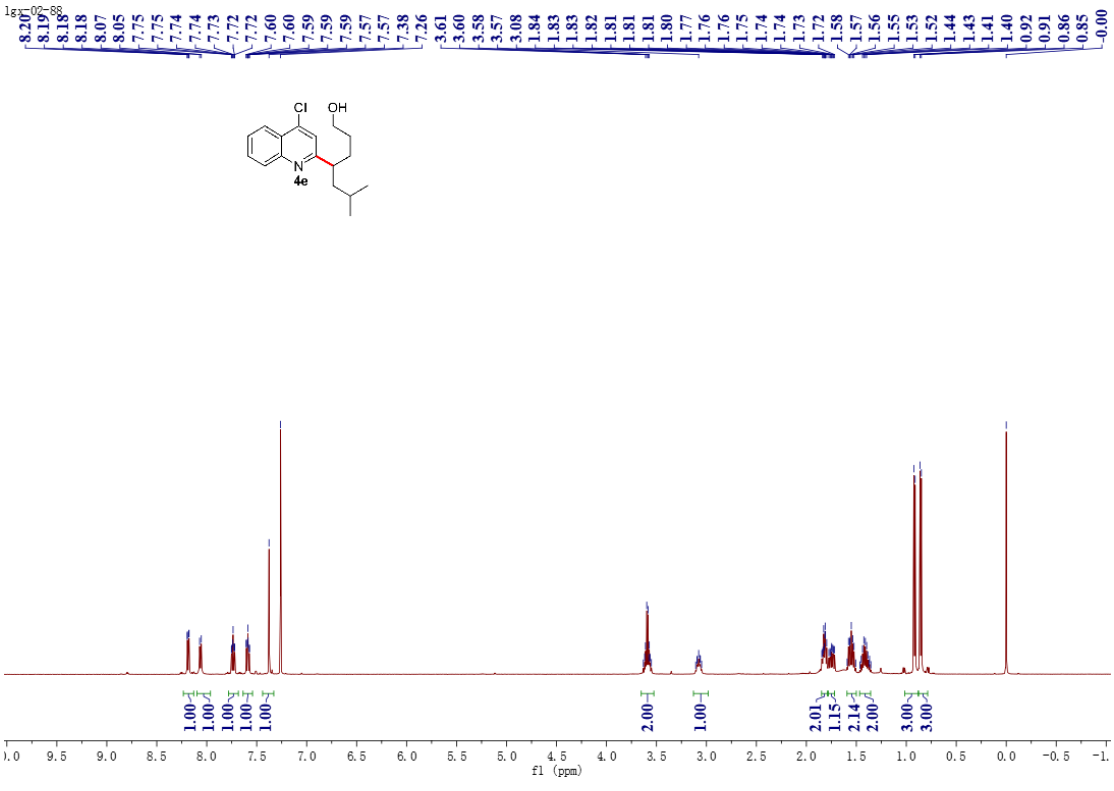
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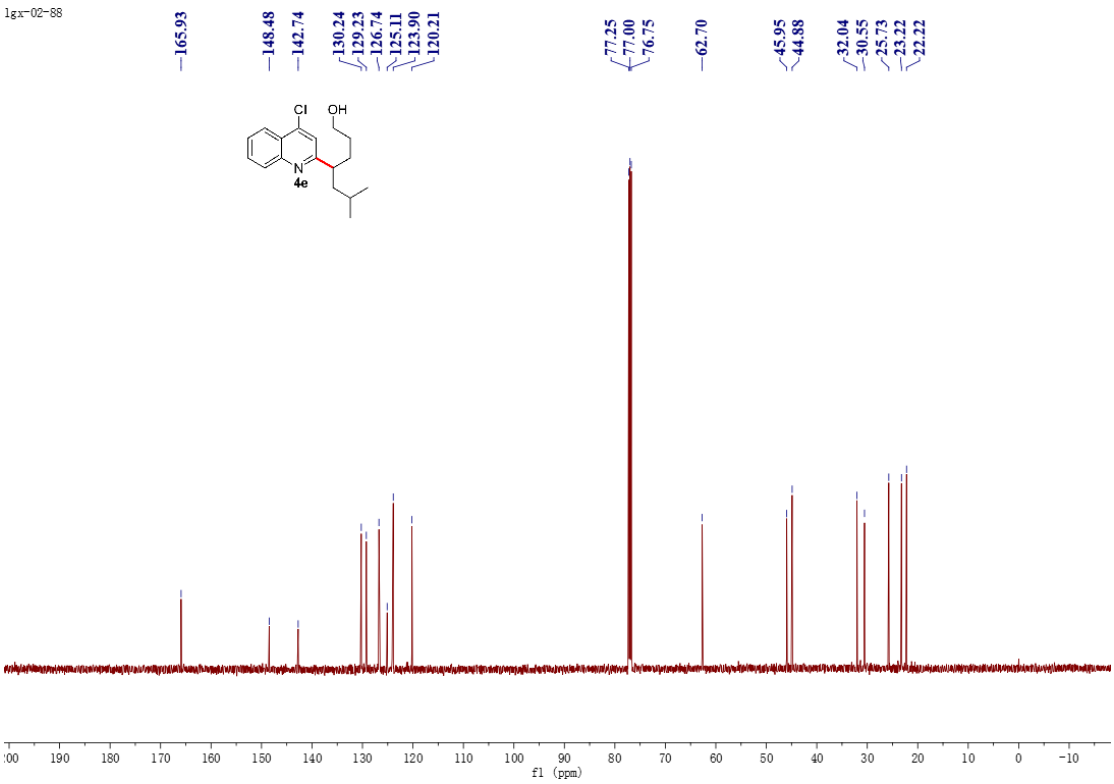
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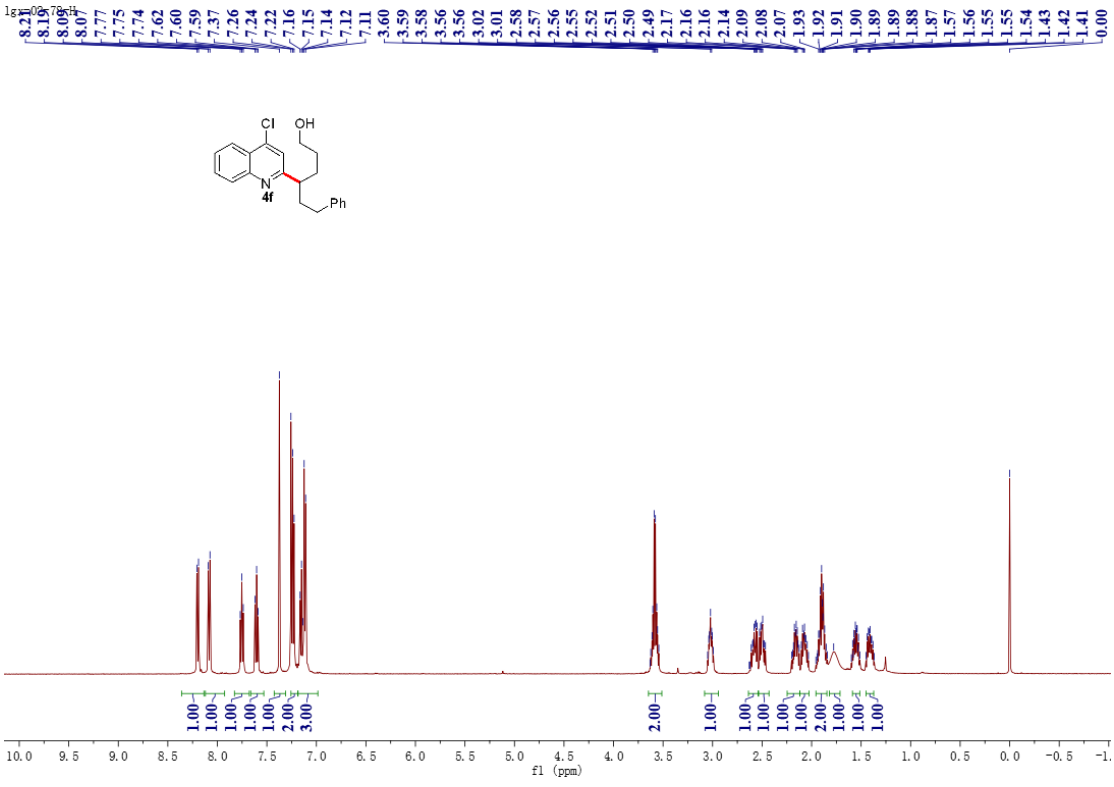
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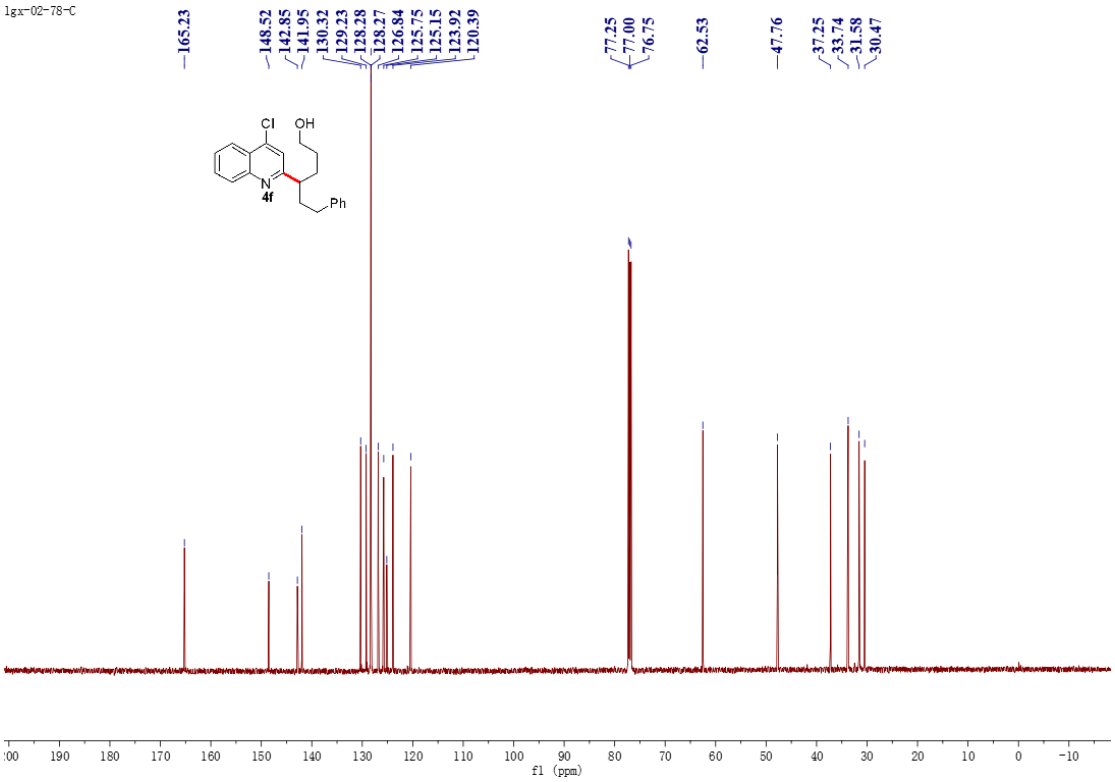
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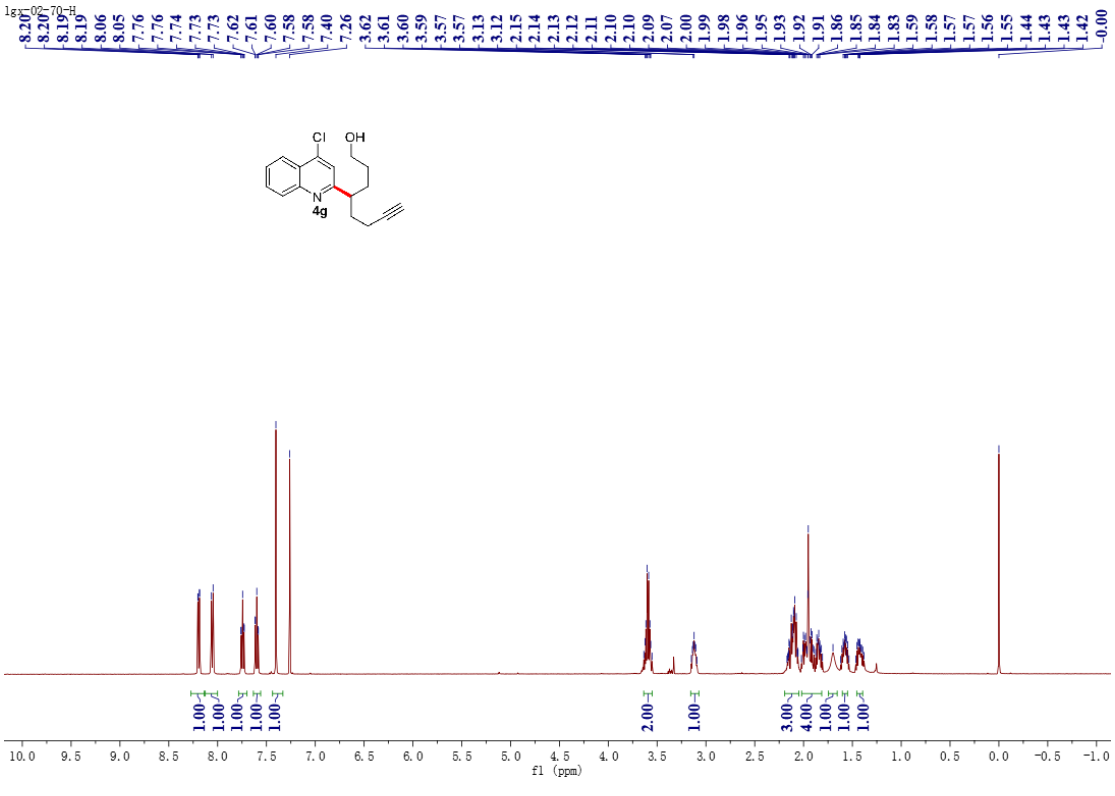
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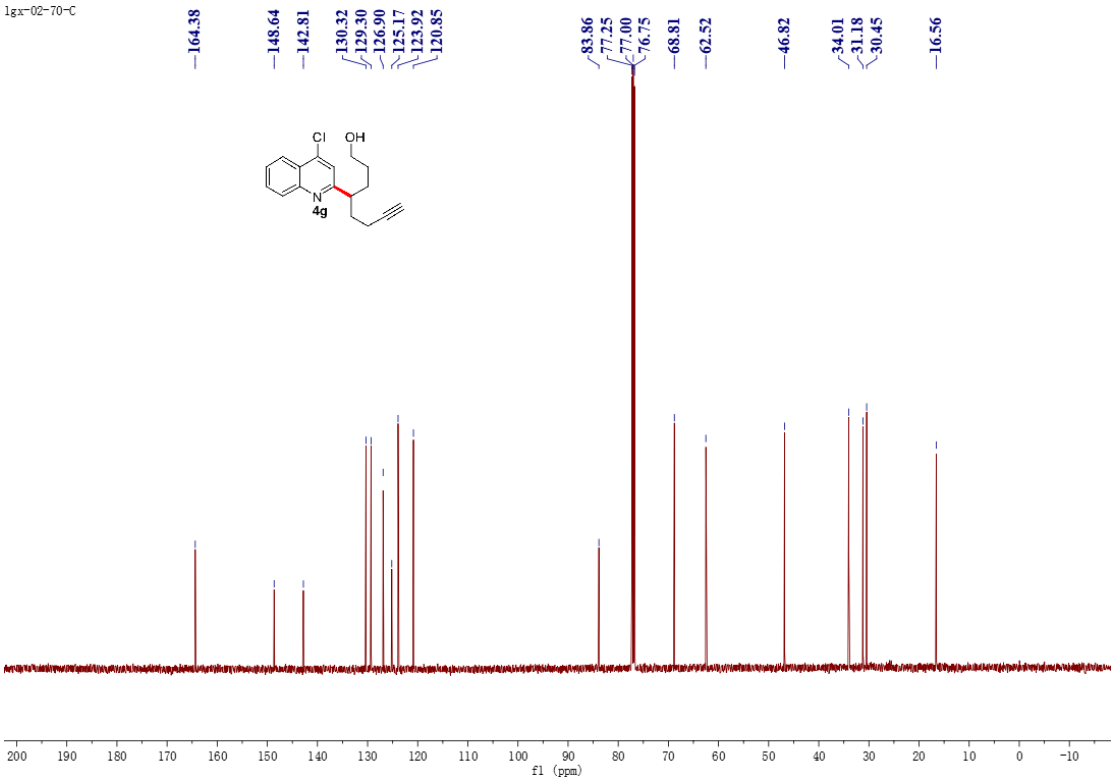
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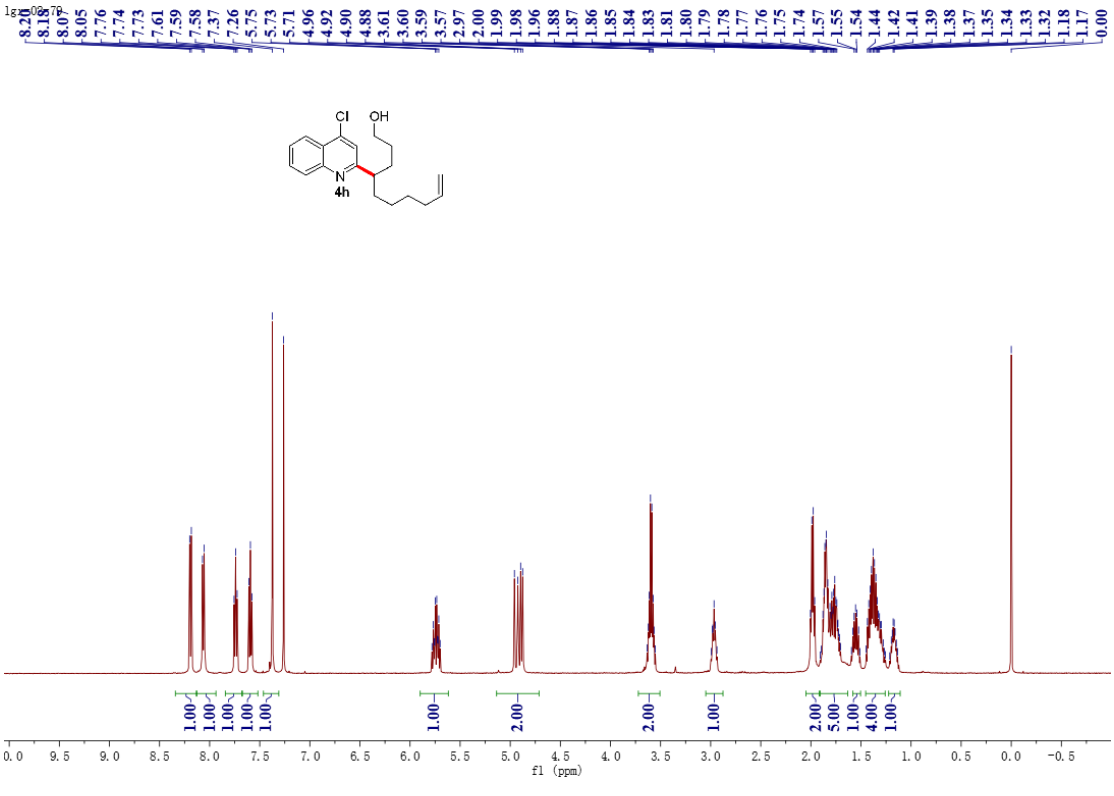
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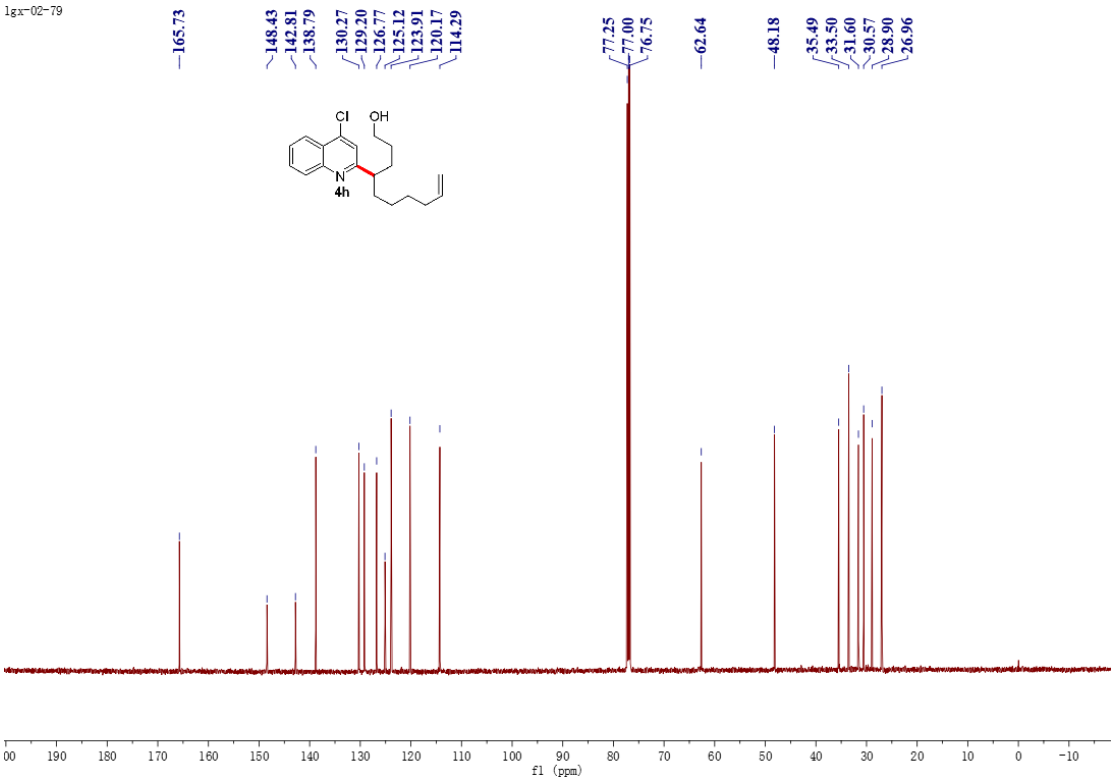
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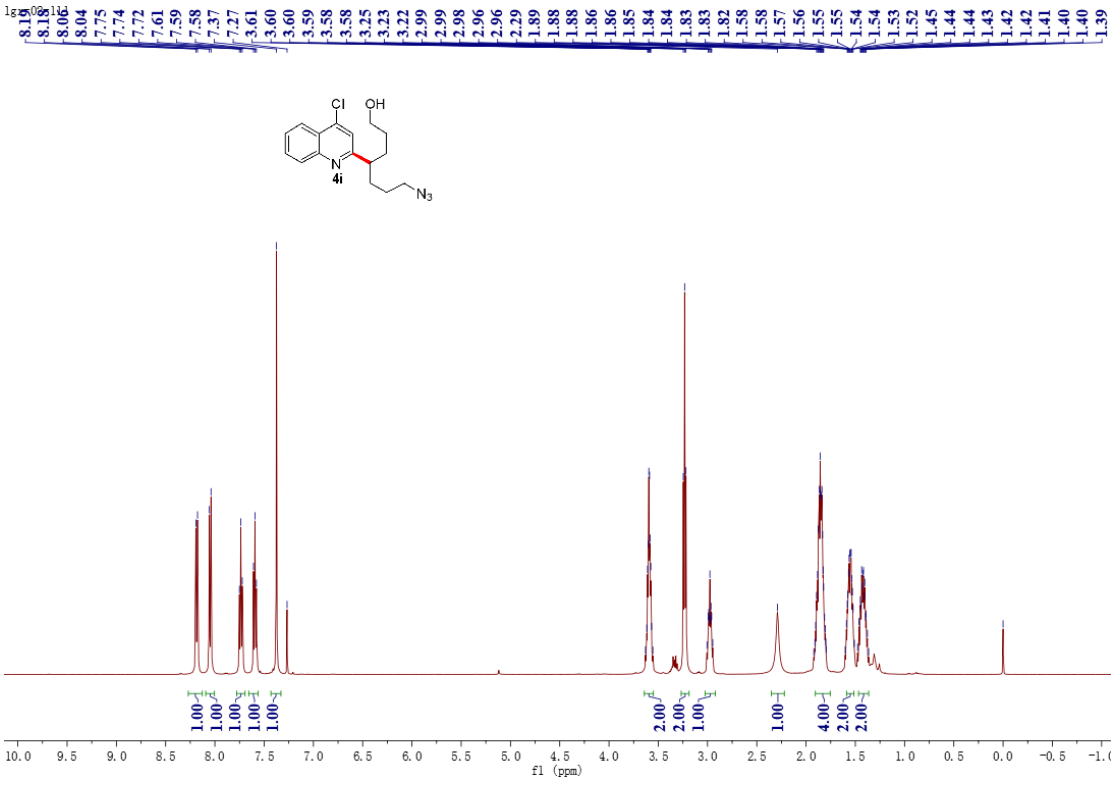
4h
f1 (ppm)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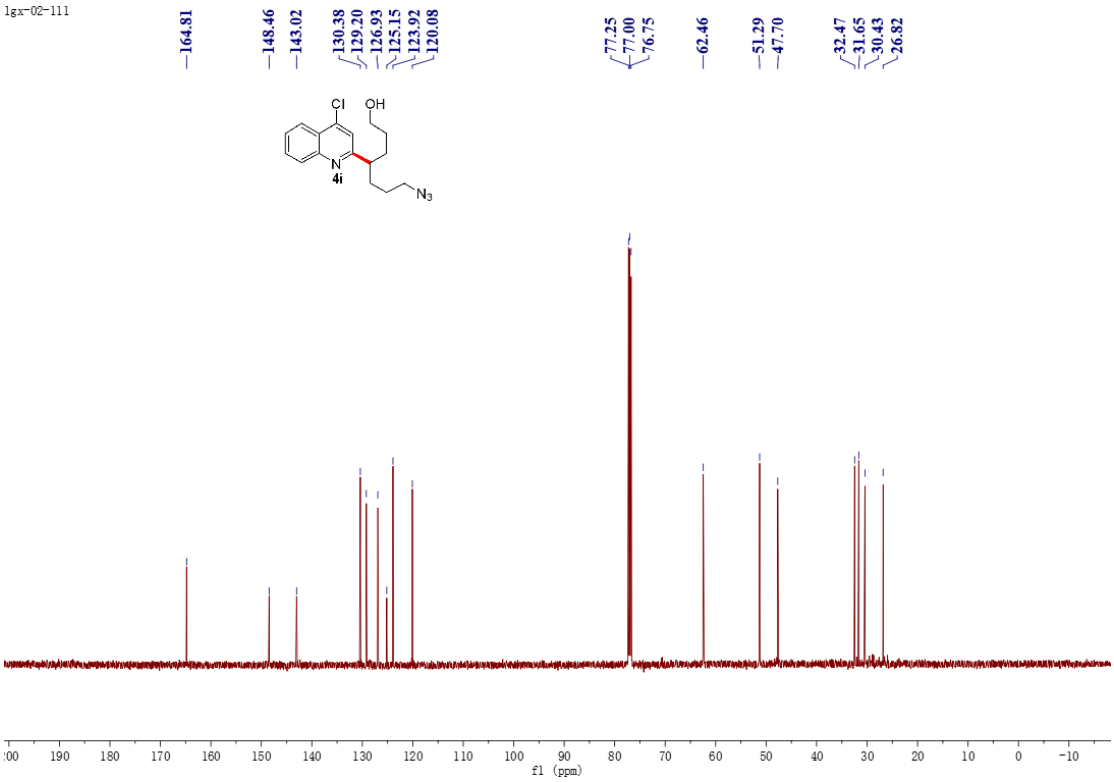
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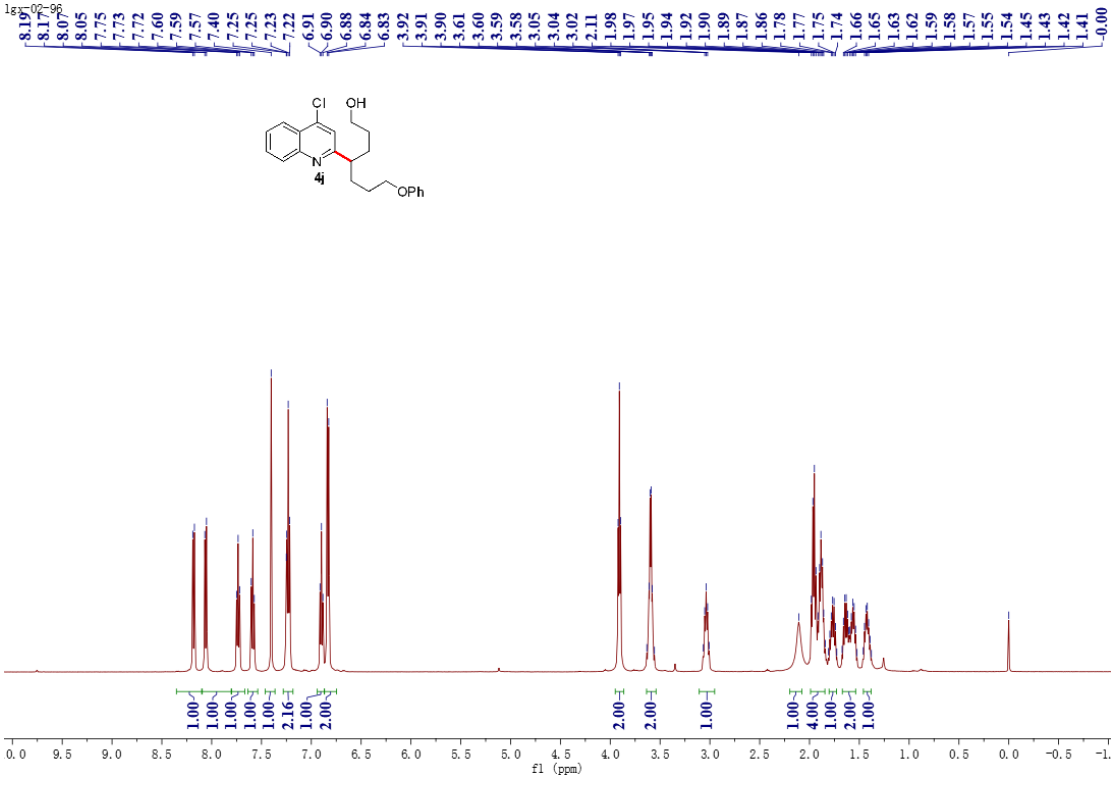
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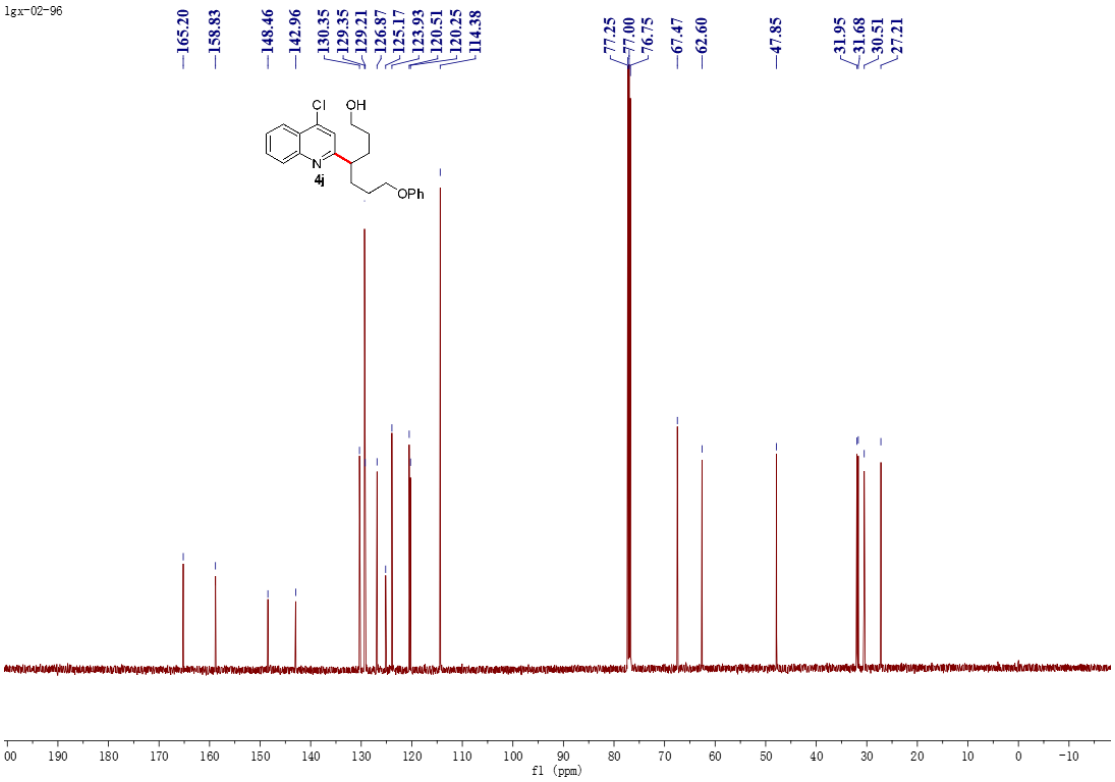
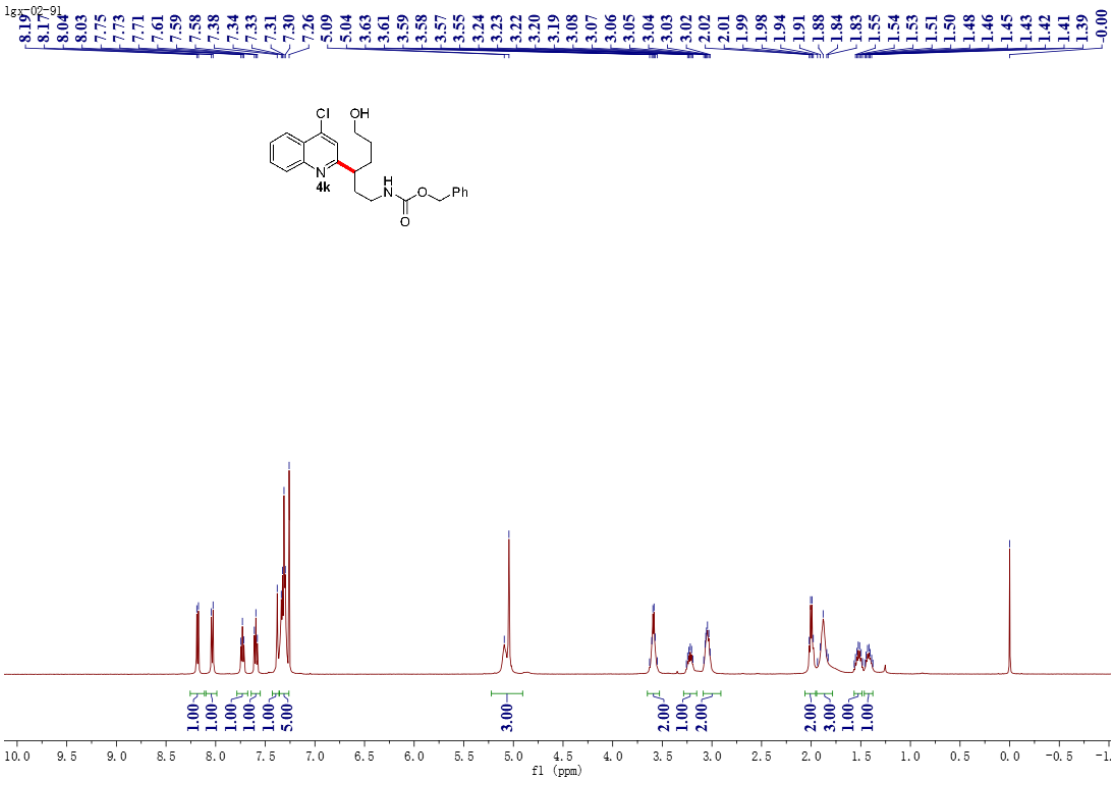
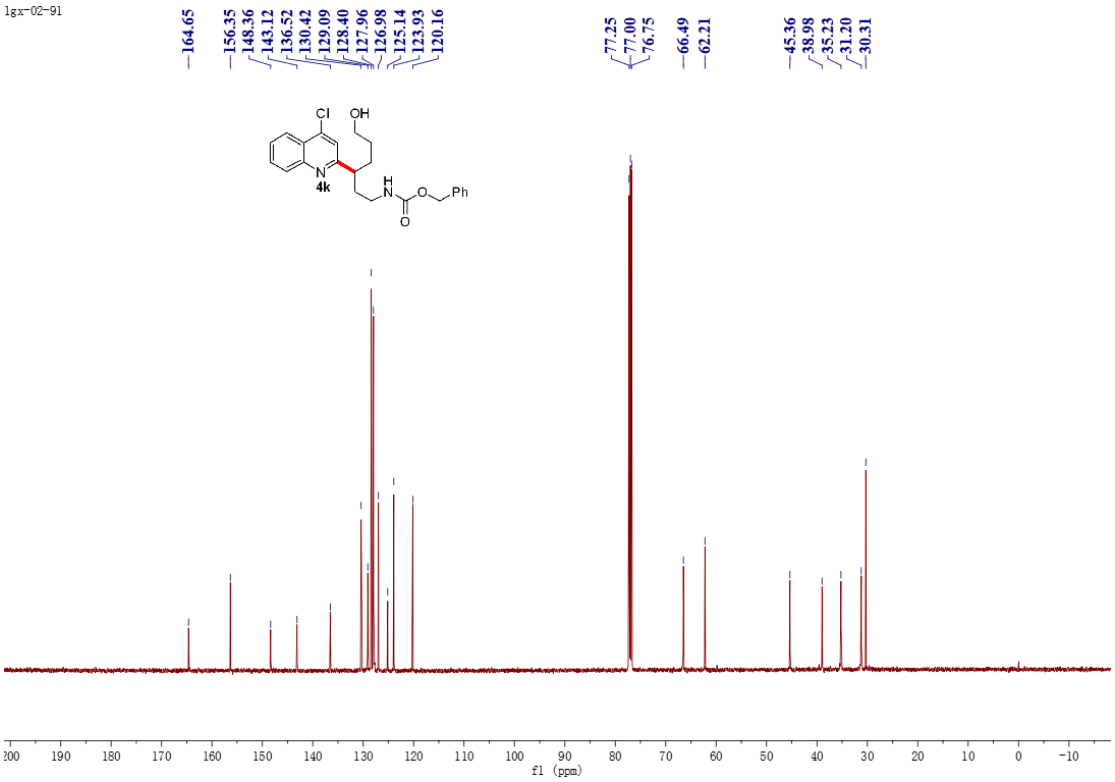
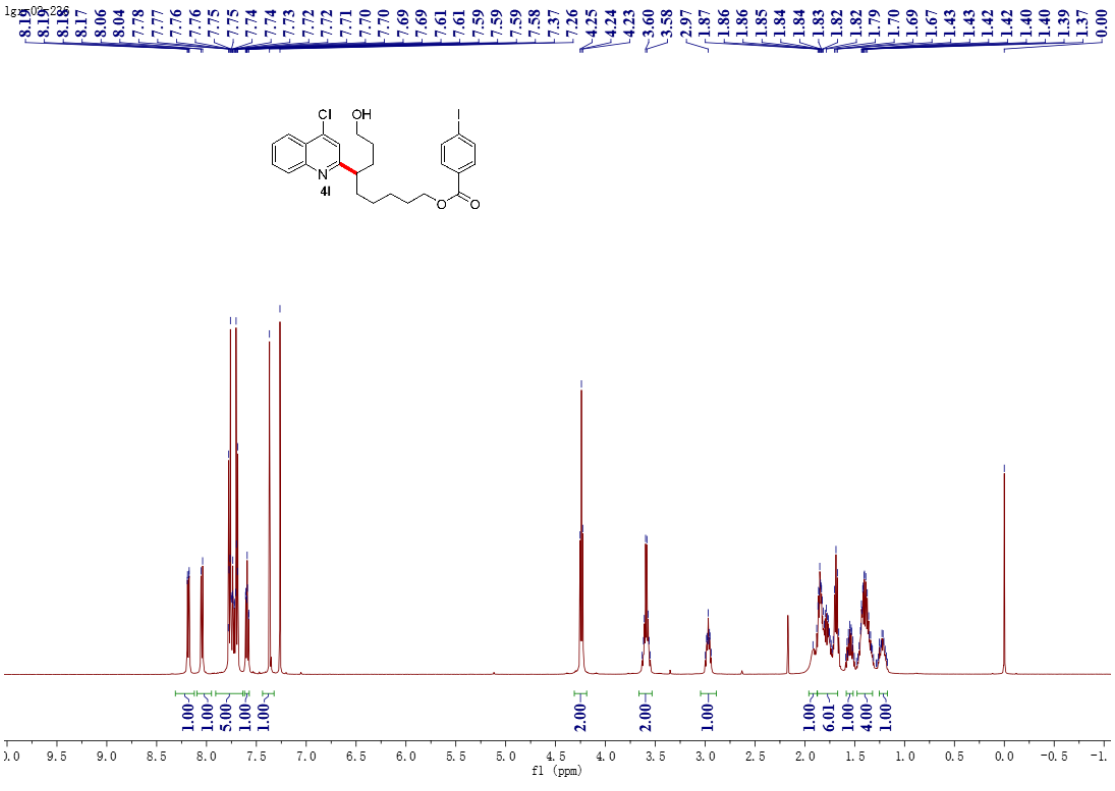
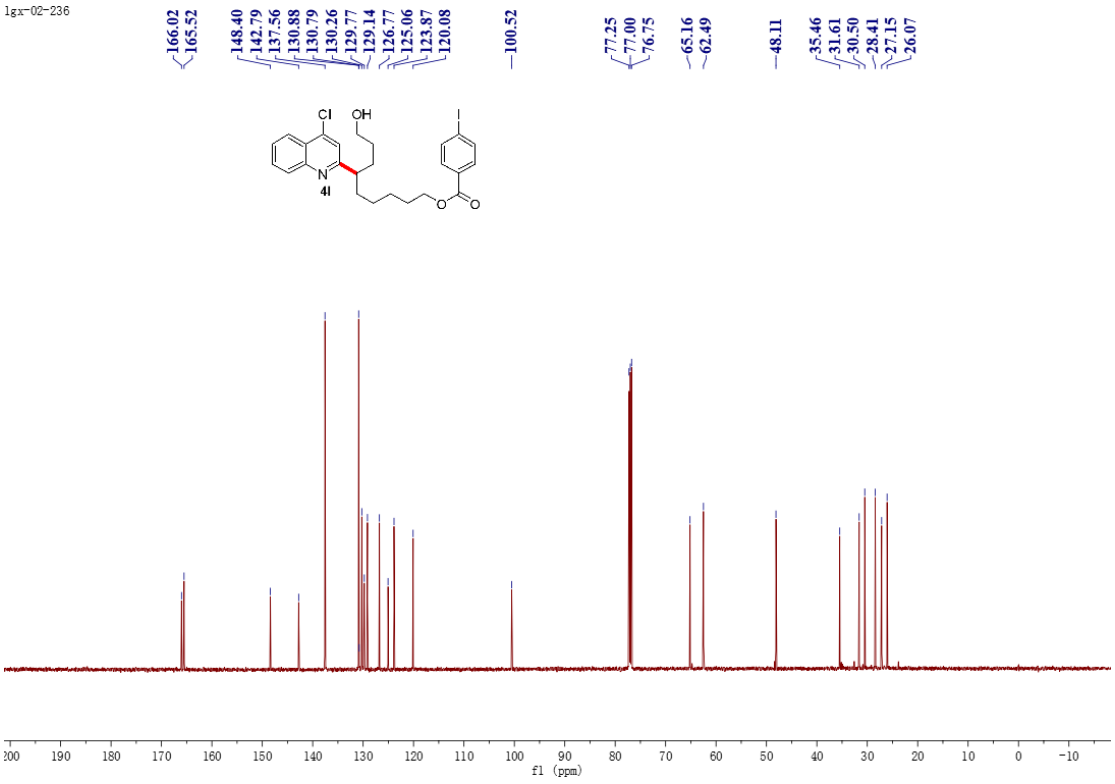
7.25
7.25
7.23
7.22
6.91
6.90
6.88
6.84
6.83
3.92
3.91
3.90
3.61
3.60
3.59
3.58
3.05
3.04
3.02
2.11
1.98
1.97
1.95
1.94
1.92
1.90
1.89
1.87
1.86
1.78
1.77
1.75
1.74
1.66
1.65
1.63
1.62
1.59
1.58
1.57
1.55
1.54
1.45
1.43
1.42
1.41
0.00
Cl
OH
N
4j
OPh
1.00
1.00
1.00
1.00
1.00
2.16
1.00
2.00
2.00
2.00
1.00
1.00
4.00
1.00
2.00
1.00
f1 (ppm)


1gx-02-96
165.20
158.83
148.46
142.96
130.35
129.35
129.21
126.87
125.17
123.93
120.51
120.25
114.38
77.25
77.00
76.75
67.47
62.60
47.85
31.95
31.68
30.51
27.21
Cl
OH
N
4j
OPh
f1 (ppm)


1gx-02-91
8.19
8.17
8.04
8.03
7.75
7.73
7.71
7.61
7.59
7.58
7.38
7.34
7.33
7.31
7.30
7.26
5.09
5.04
3.63
3.61
3.59
3.58
3.57
3.55
3.24
3.23
3.22
3.20
3.19
3.08
3.07
3.06
3.05
3.04
3.03
3.02
2.02
2.01
1.99
1.98
1.94
1.91
1.88
1.84
1.83
1.55
1.54
1.53
1.51
1.50
1.48
1.46
1.45
1.43
1.42
1.41
1.39
0.00
Cl
OH
N
4k
H
N
O
O
Ph
1.00
1.00
1.00
1.00
1.00
5.00
3.00
2.00
1.00
2.00
2.00
3.00
1.00
1.00
f1 (ppm)


lgx-02-91
164.65
156.35
148.36
143.12
136.52
130.42
129.09
128.40
127.96
126.98
125.14
123.93
120.16
77.25
77.00
76.75
66.49
62.21
45.36
38.98
35.23
31.20
30.31
Cl
OH
N
4k
H
N
O
O
Ph
O
f1 (ppm)


8.19
8.18
8.17
8.06
8.04
7.78
7.77
7.76
7.76
7.75
7.75
7.74
7.74
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.69
7.61
7.61
7.59
7.59
7.59
7.58
7.37
7.26
4.25
4.24
4.23
3.60
3.58
2.97
1.87
1.86
1.86
1.85
1.84
1.84
1.83
1.82
1.82
1.79
1.70
1.69
1.67
1.43
1.43
1.42
1.42
1.40
1.40
1.39
1.37
0.00
Cl
OH
I
N
4l
O
O
1.00
1.00
5.00
1.00
1.00
2.00
2.00
1.00
1.00
6.01
1.00
4.00
1.00
f1 (ppm)


lgx-02-236
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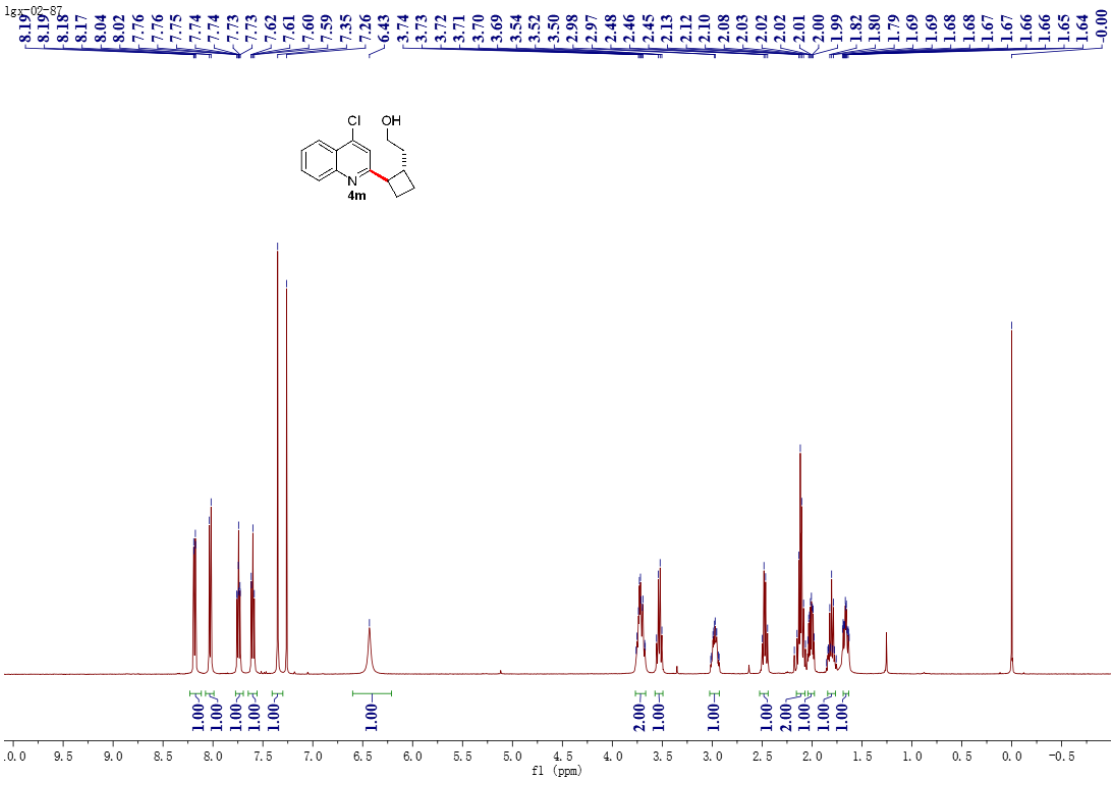
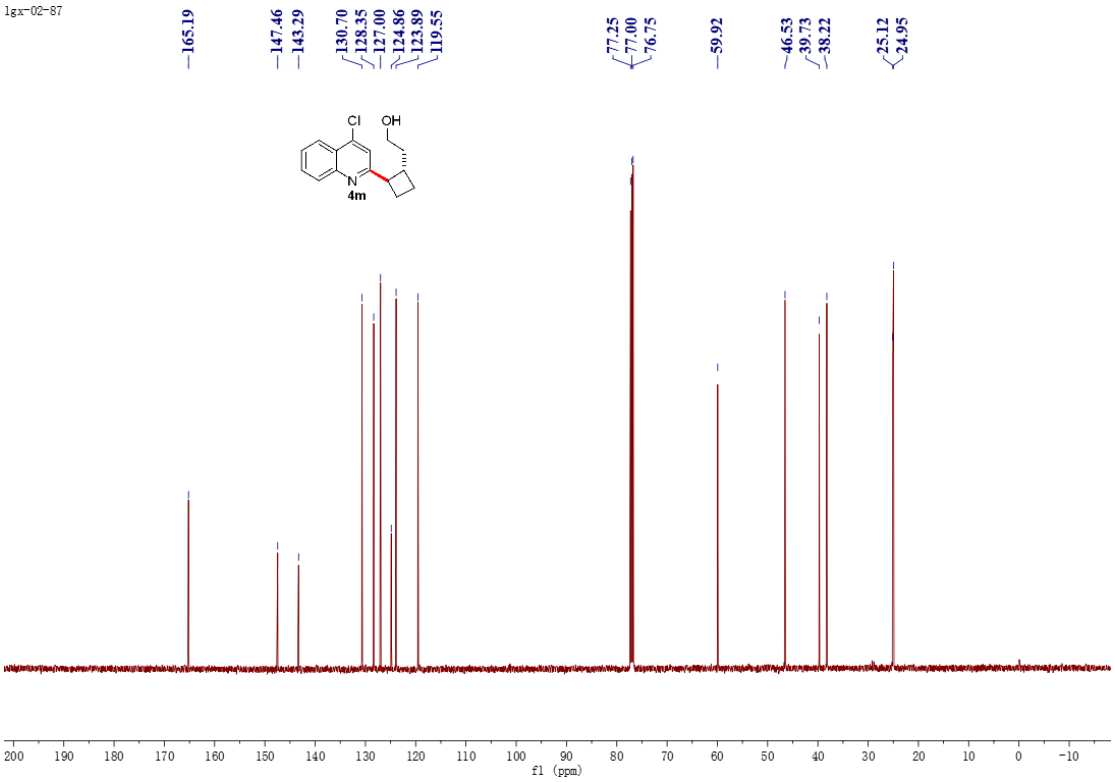
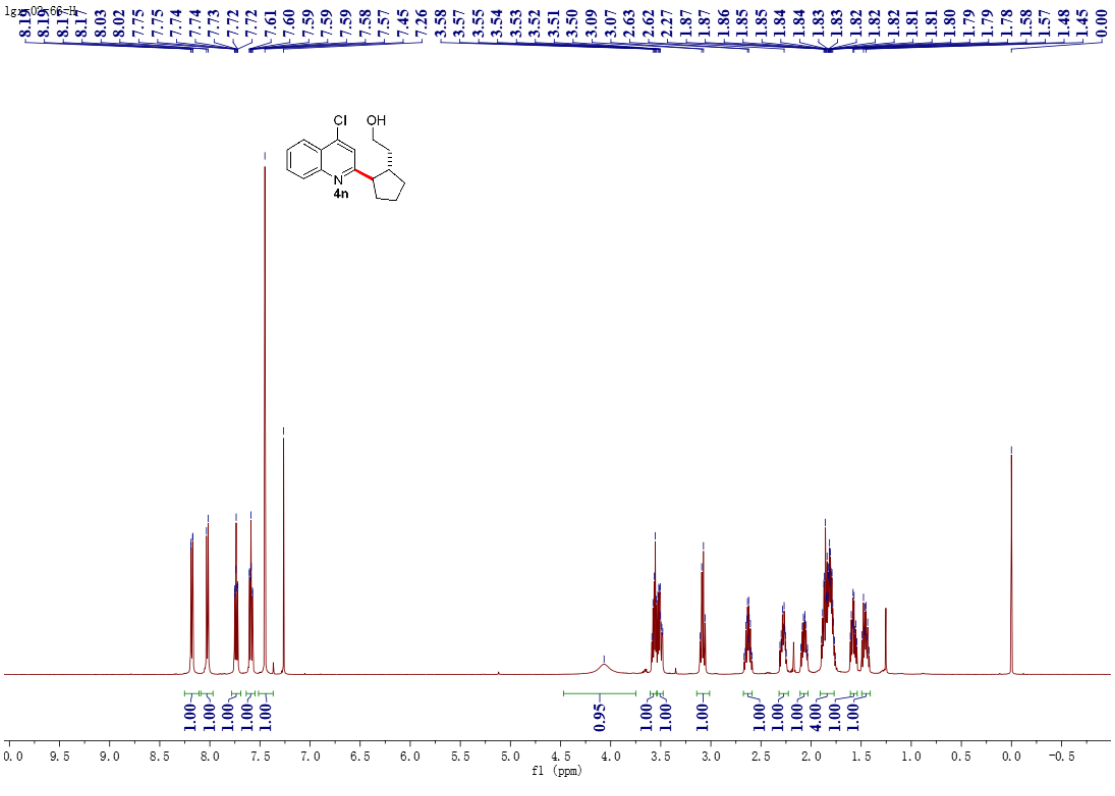
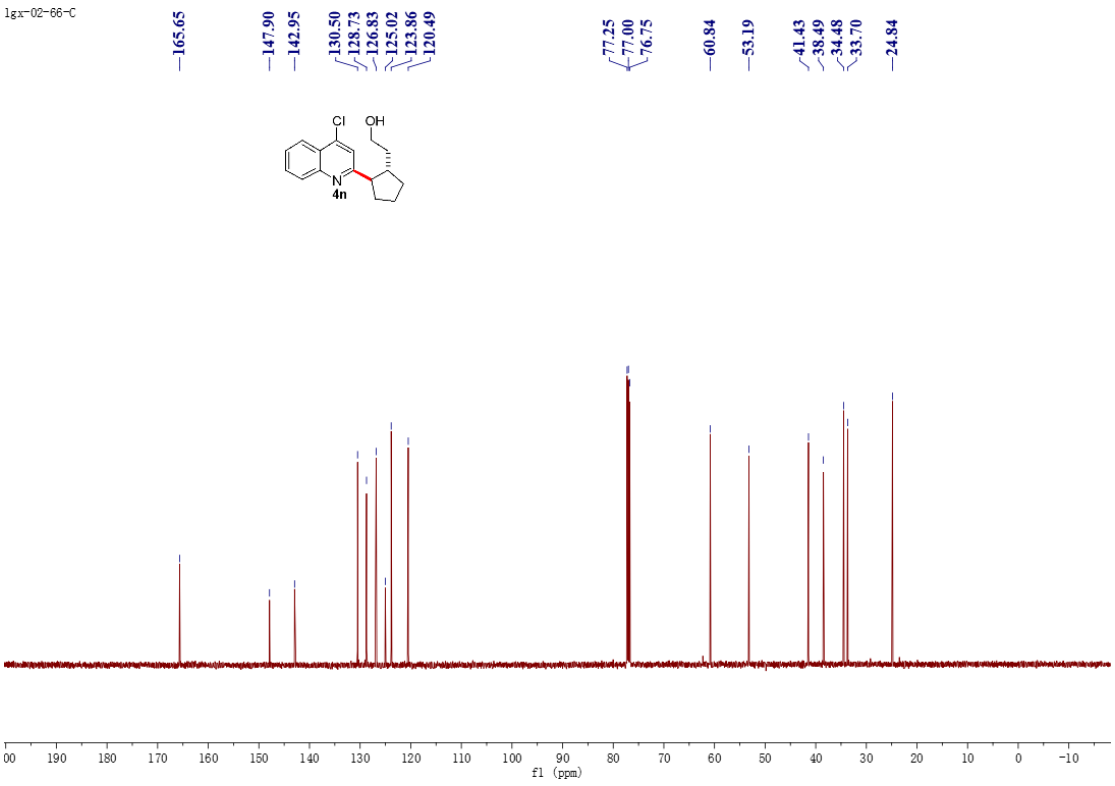
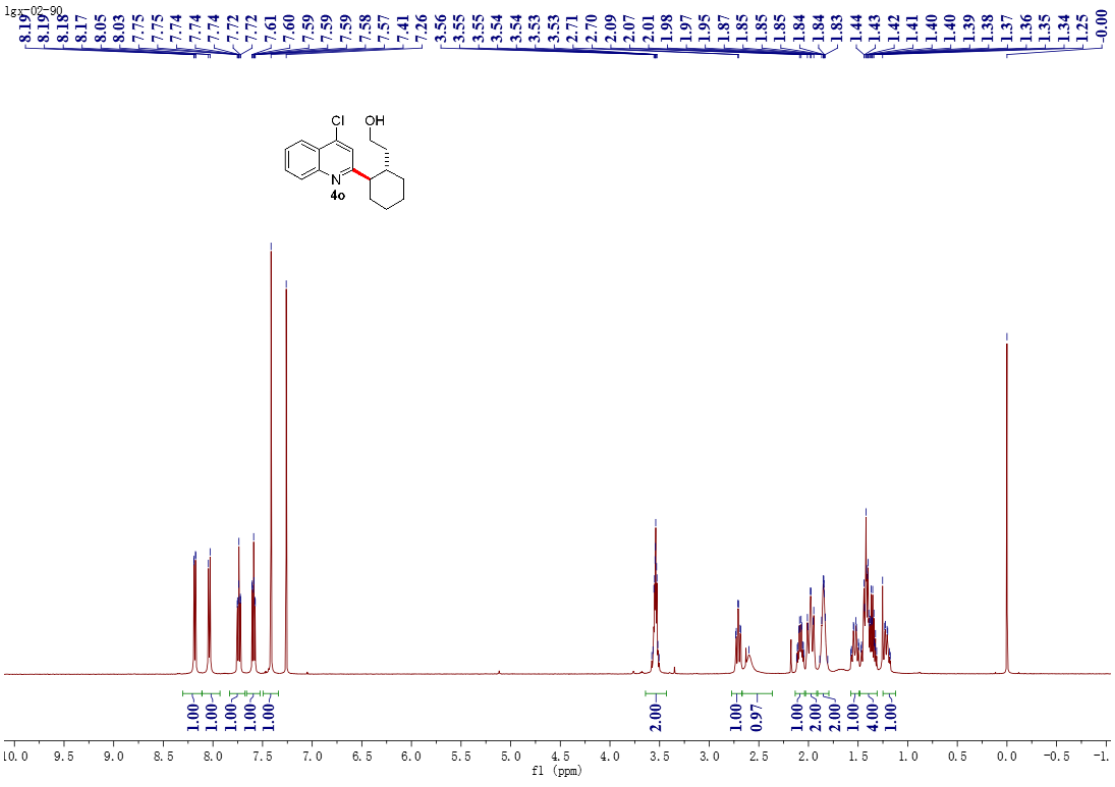
165.52
148.40
142.79
137.56
130.88
130.79
130.26
129.77
129.14
126.77
125.06
123.87
120.08
100.52
77.25
77.00
76.75
65.16
62.49
48.11
35.46
31.61
30.50
28.41
27.15
26.07
Cl
OH
I
N
O
O
4l
f1 (ppm)

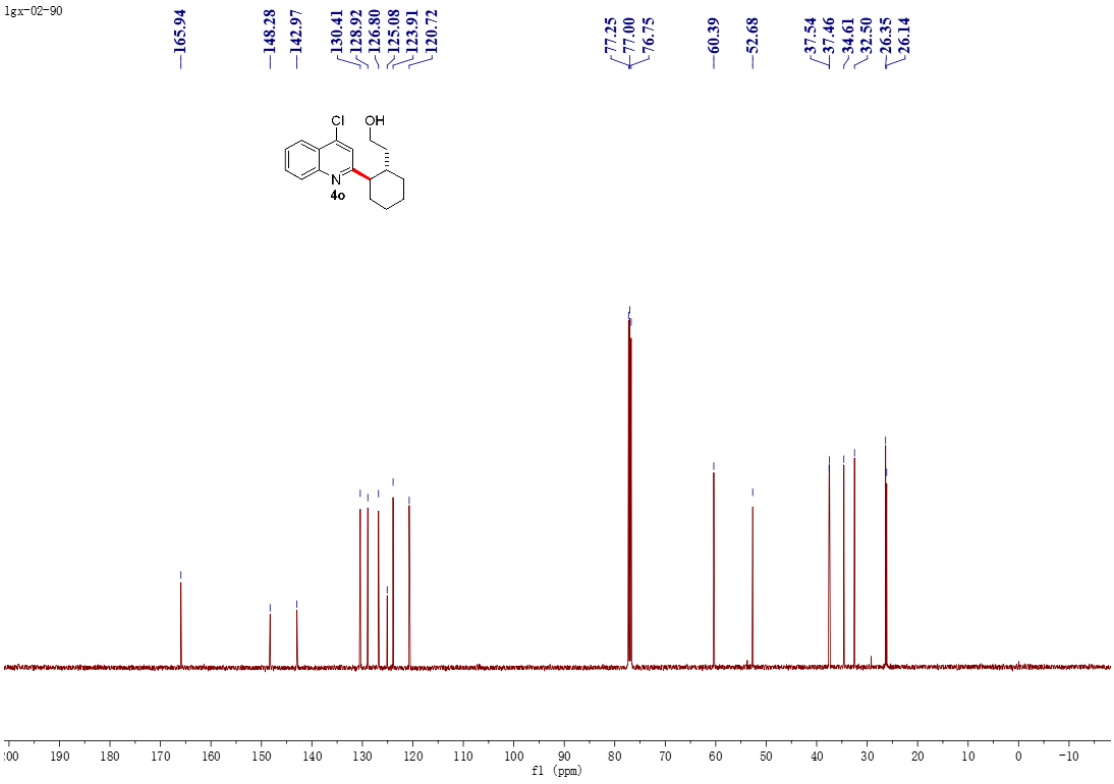

lgx-02-87
8.19
8.19
8.18
8.17
8.04
8.02
7.76
7.76
7.75
7.74
7.74
7.73
7.73
7.62
7.61
7.60
7.59
7.35
7.26
6.43
3.74
3.73
3.72
3.71
3.70
3.69
3.54
3.52
3.50
2.98
2.97
2.48
2.46
2.45
2.13
2.12
2.10
2.08
2.03
2.02
2.02
2.01
2.00
1.99
1.82
1.80
1.79
1.69
1.69
1.68
1.68
1.67
1.67
1.66
1.66
1.65
1.64
0.00
Cl
OH
N
4m
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
f1 (ppm)

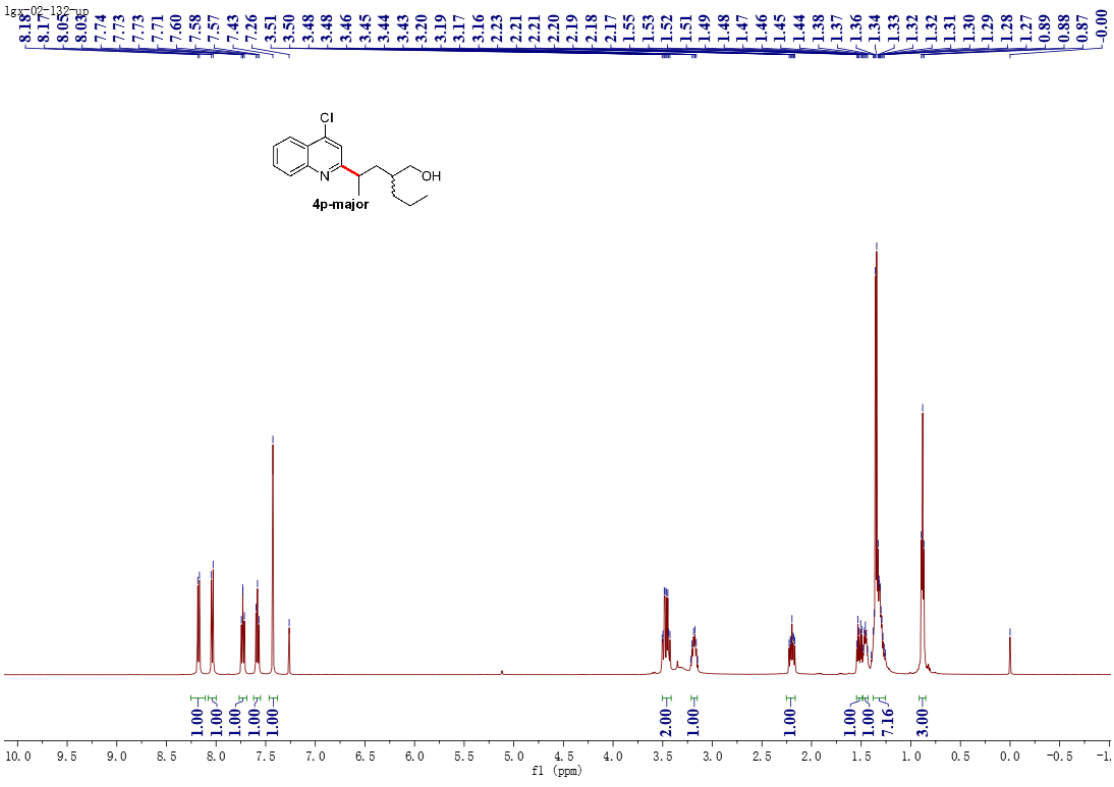

lgx-02-87
165.19
147.46
143.29
130.70
128.35
127.00
124.86
123.89
119.55
77.25
77.00
76.75
59.92
46.53
39.73
38.22
25.12
24.95
Cl
OH
N
4m
f1 (ppm)

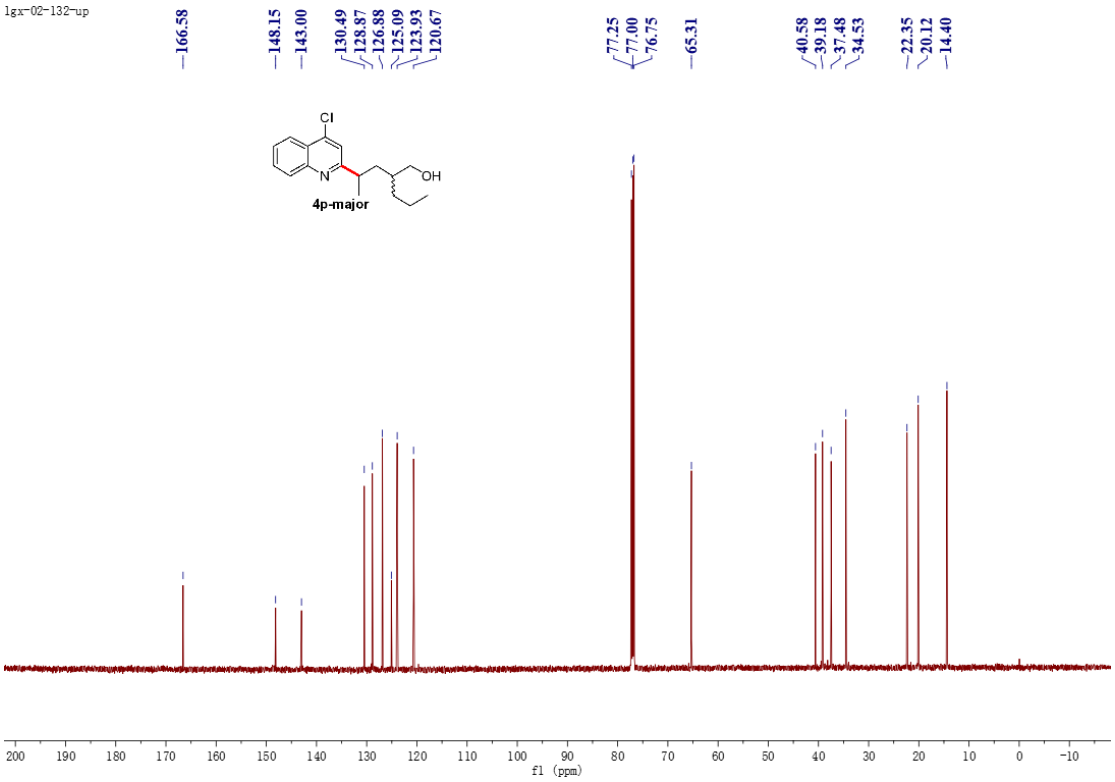

Cl
OH
N
4n
1.00
1.00
1.00
1.00
1.00
0.95
1.00
1.00
1.00
1.00
1.00
1.00
4.00
1.00
1.00
f1 (ppm)

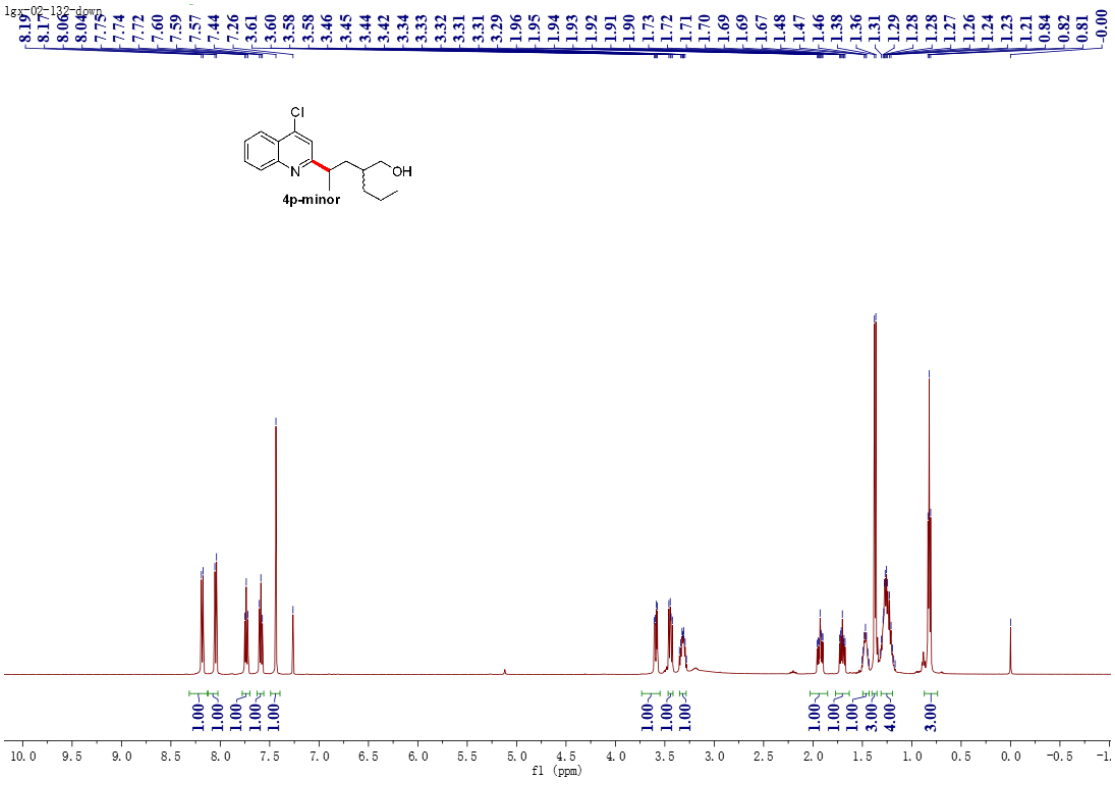

lgx-02-66-C
165.65
147.90
142.95
130.50
128.73
126.83
125.02
123.86
120.49
77.25
77.00
76.75
60.84
53.19
41.43
38.49
34.48
33.70
24.84
Cl
OH
N
4n
f1 (ppm)

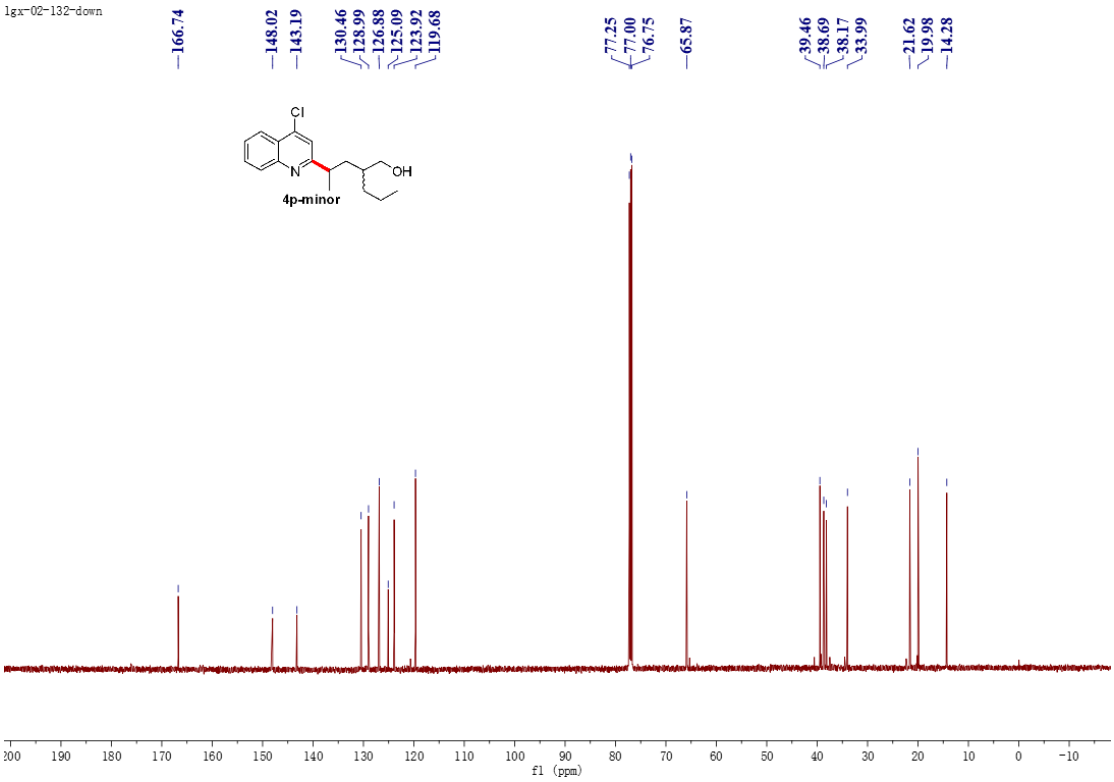

lgx-02-90
8.19
8.19
8.18
8.17
8.05
8.03
7.75
7.75
7.74
7.74
7.74
7.72
7.72
7.61
7.60
7.59
7.59
7.59
7.58
7.57
7.41
7.26
3.56
3.55
3.55
3.54
3.54
3.53
2.71
2.70
2.09
2.07
2.01
1.98
1.97
1.95
1.87
1.85
1.85
1.85
1.84
1.84
1.83
1.44
1.43
1.42
1.41
1.40
1.40
1.39
1.38
1.37
1.36
1.35
1.34
1.25
0.00
Cl
OH
N
4o
1.00
1.00
1.00
1.00
1.00
2.00
1.00
0.97
1.00
2.00
2.00
1.00
4.00
1.00
f1 (ppm)

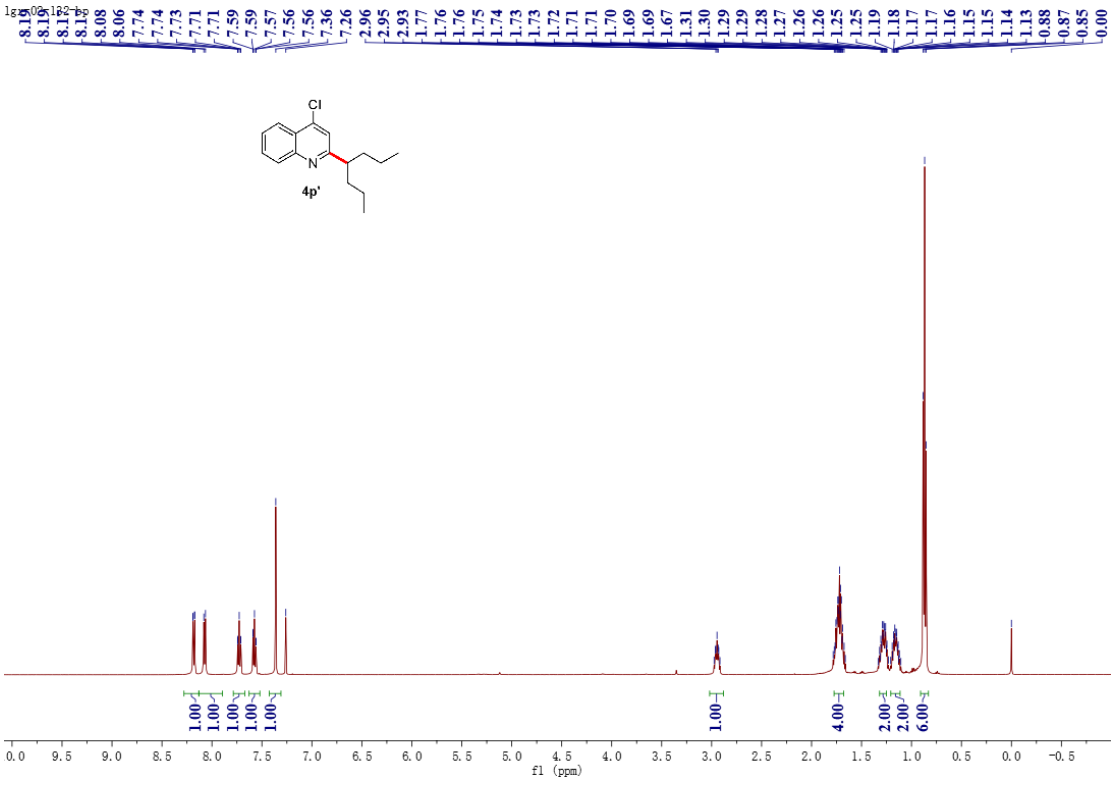

lgx-02-90
165.94
148.28
142.97
130.41
128.92
126.80
125.08
123.91
120.72
77.25
77.00
76.75
60.39
52.68
37.54
37.46
34.61
32.50
26.35
26.14
Cl
OH
N
4o
f1 (ppm)

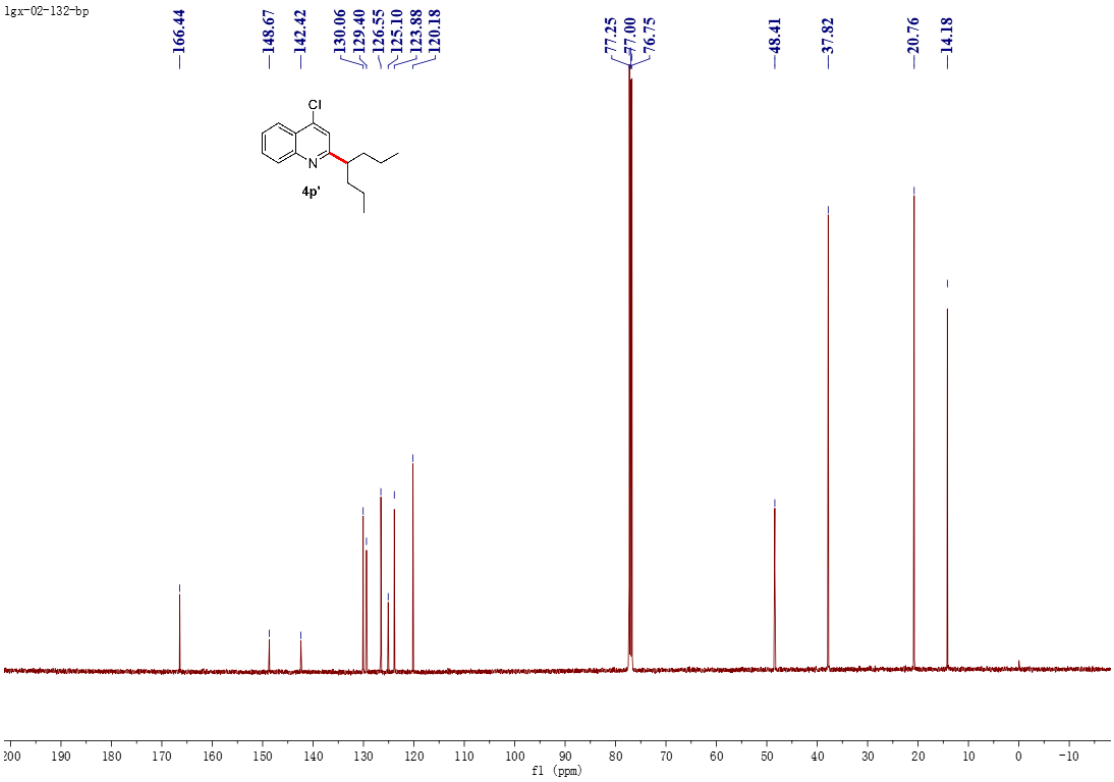

lgx-02-132-up
Cl
OH
N
4p-major
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
7.16
3.00
f1 (ppm)

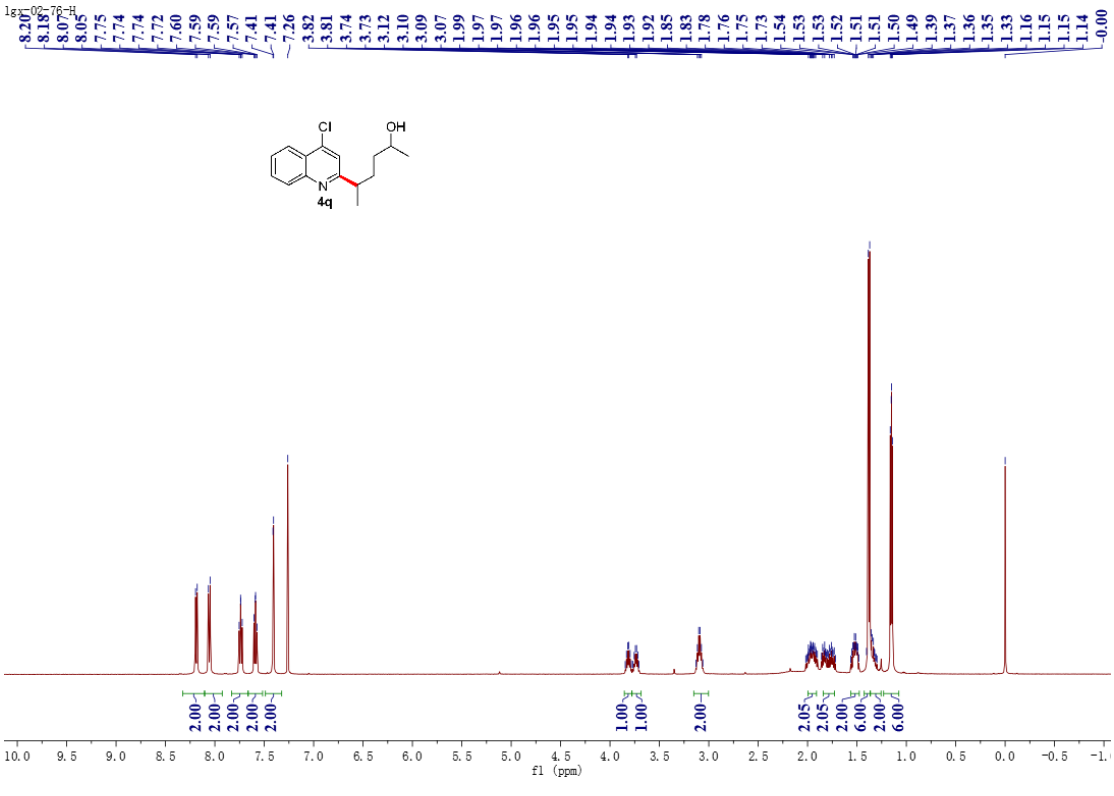

lgx-02-132-up
166.58
148.15
143.00
130.49
128.87
126.88
125.09
123.93
120.67
77.25
77.00
76.75
65.31
40.58
39.18
37.48
34.53
22.35
20.12
14.40
Cl
N
OH
4p-major
f1 (ppm)

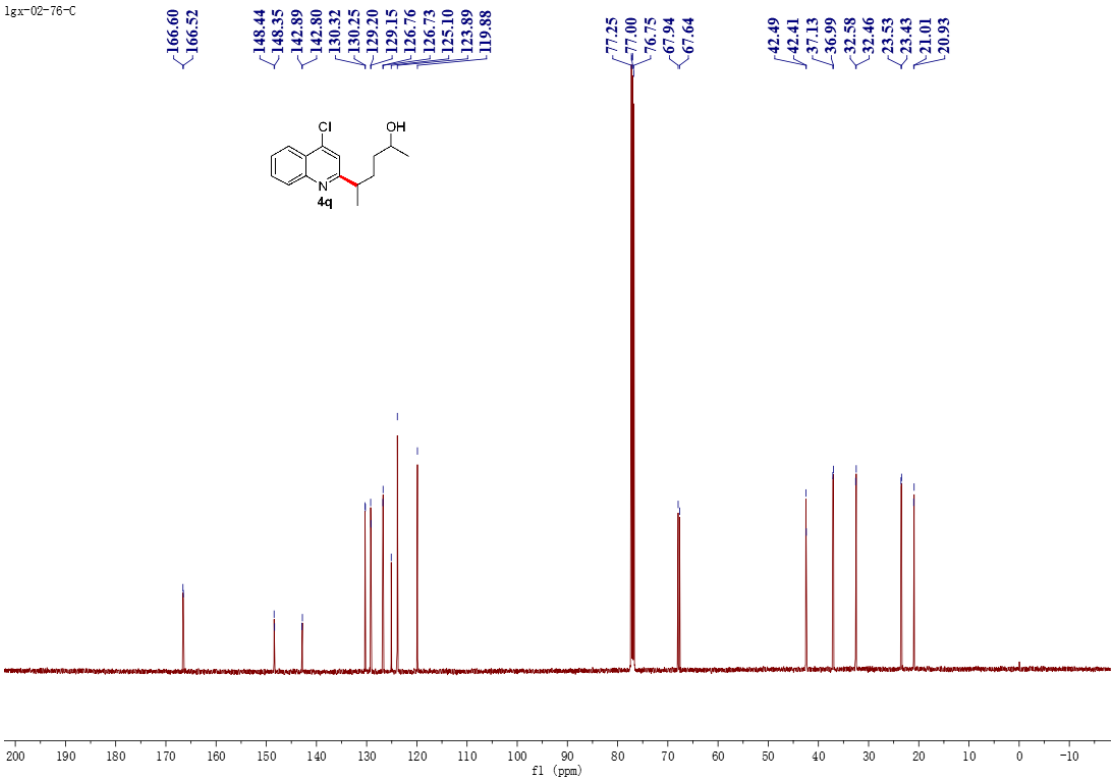

lgx-02-132-down
Cl
N
OH
4p-minor
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
4.00
3.00
f1 (ppm)

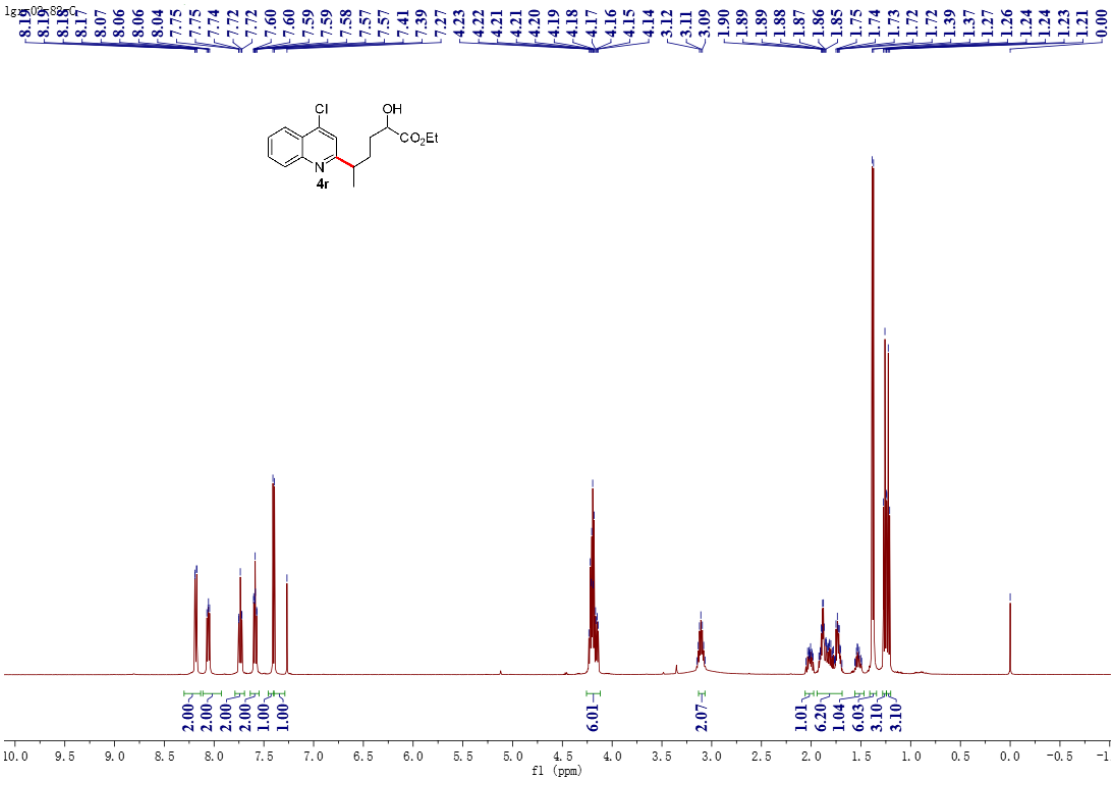

lgx-02-132-down
166.74
148.02
143.19
130.46
128.99
126.88
125.09
123.92
119.68
77.25
77.00
76.75
65.87
39.46
38.69
38.17
33.99
21.62
19.98
14.28
Cl
N
OH
4p-minor
f1 (ppm)

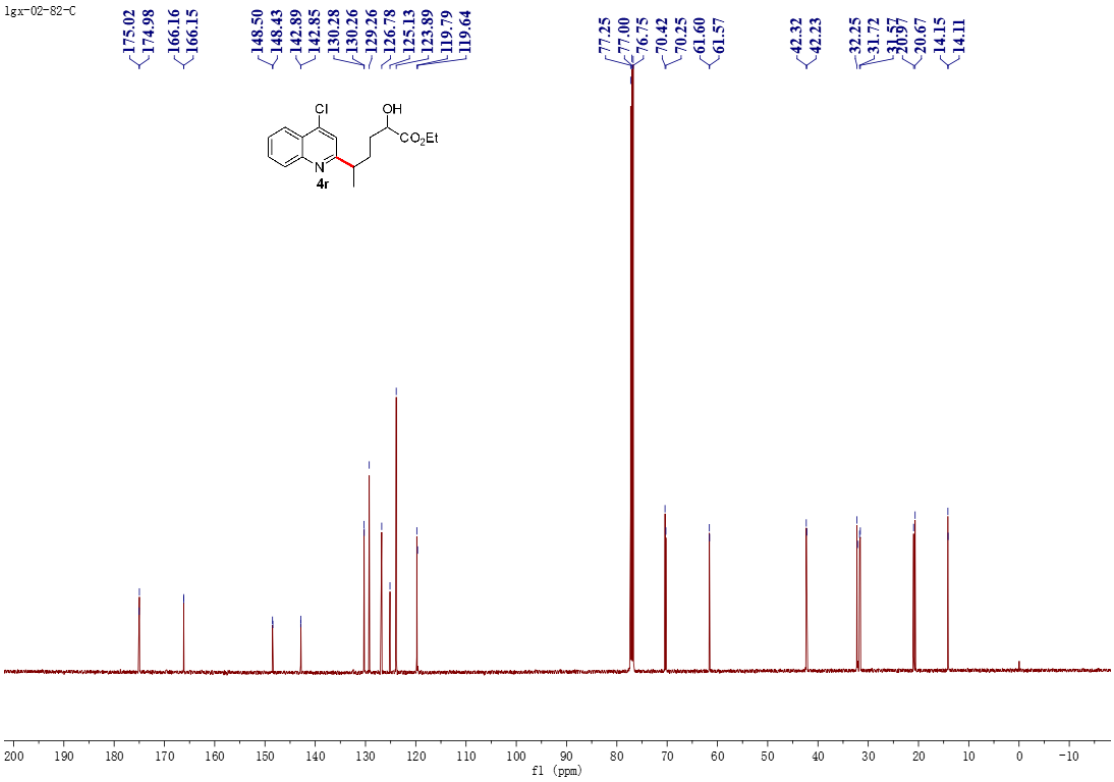

Cl
N
4p'
1.00
1.00
1.00
1.00
1.00
1.00
4.00
2.00
2.00
6.00
f1 (ppm)

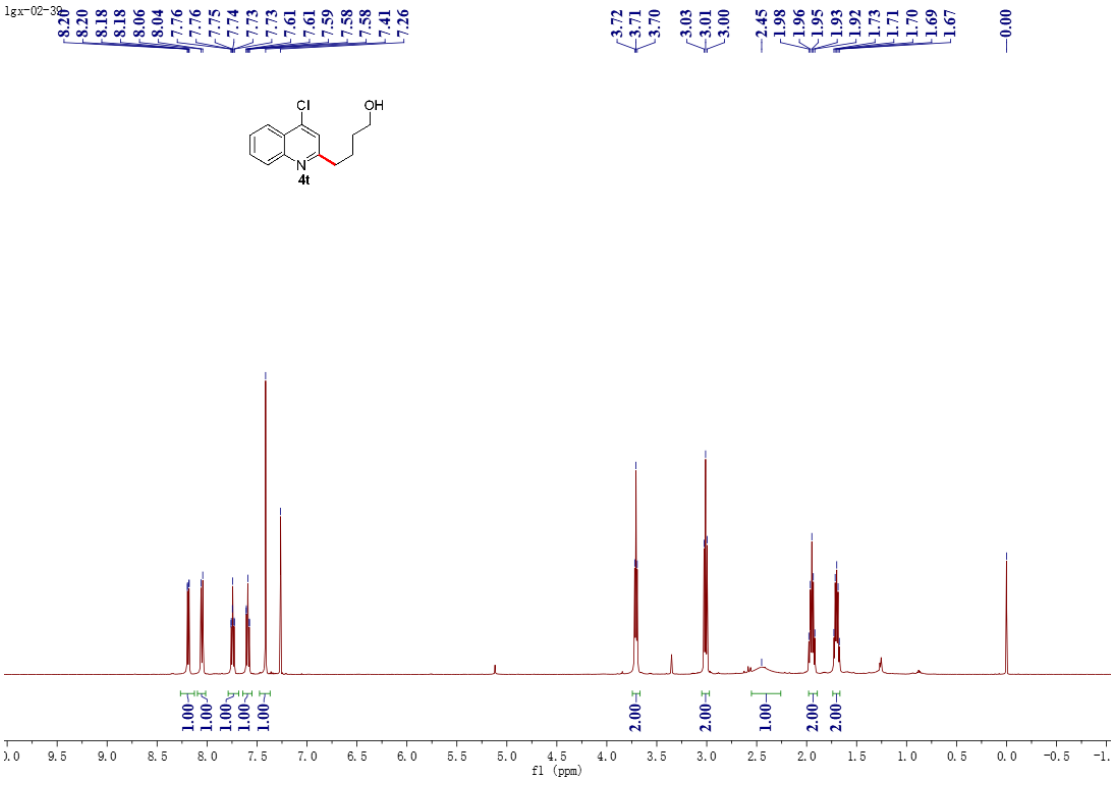

lgx-02-132-bp
166.44
148.67
142.42
130.06
129.40
126.55
125.10
123.88
120.18
77.25
77.00
76.75
48.41
37.82
20.76
14.18
Cl
N
4p'
f1 (ppm)

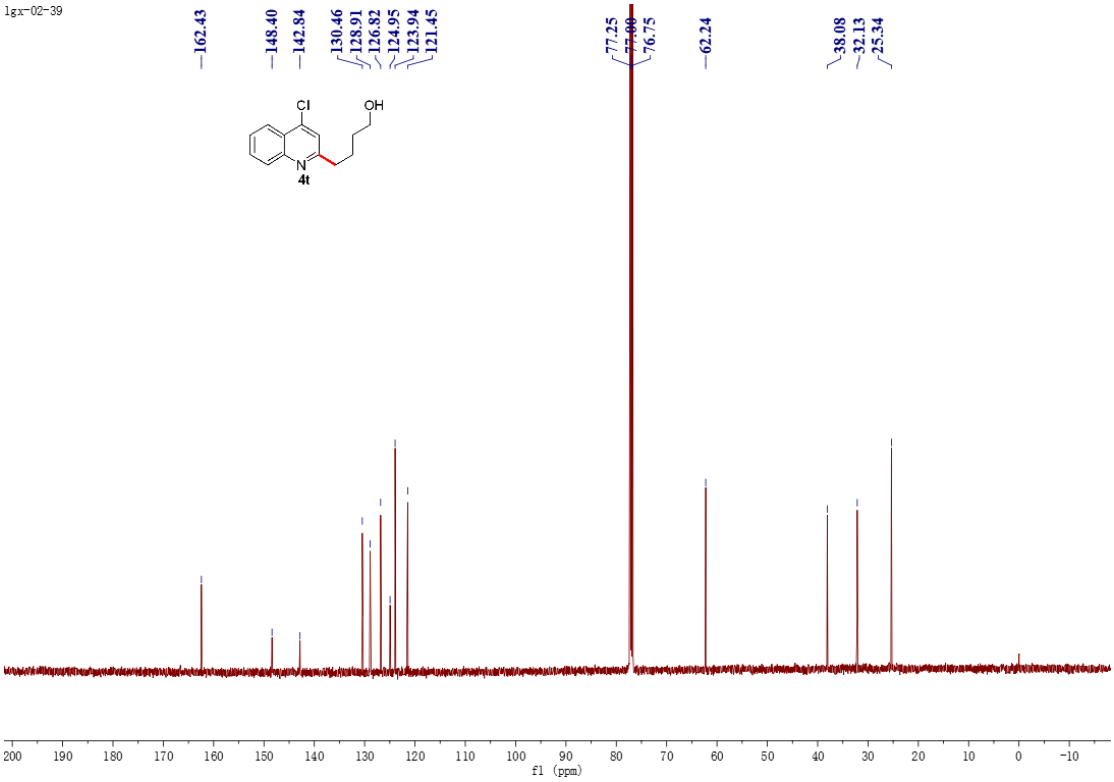

lgx-02-76-H
8.20
8.18
8.07
8.05
7.75
7.74
7.74
7.72
7.60
7.59
7.59
7.57
7.41
7.41
7.26
3.82
3.81
3.74
3.73
3.12
3.10
3.09
3.07
1.99
1.97
1.97
1.96
1.96
1.95
1.95
1.94
1.94
1.93
1.92
1.85
1.83
1.78
1.76
1.75
1.73
1.54
1.53
1.53
1.52
1.51
1.51
1.50
1.49
1.39
1.37
1.36
1.35
1.33
1.16
1.15
1.15
1.14
0.00
Cl
OH
N
4q
2.00
2.00
2.00
2.00
2.00
1.00
1.00
2.00
2.05
2.05
2.00
6.00
2.00
6.00
f1 (ppm)

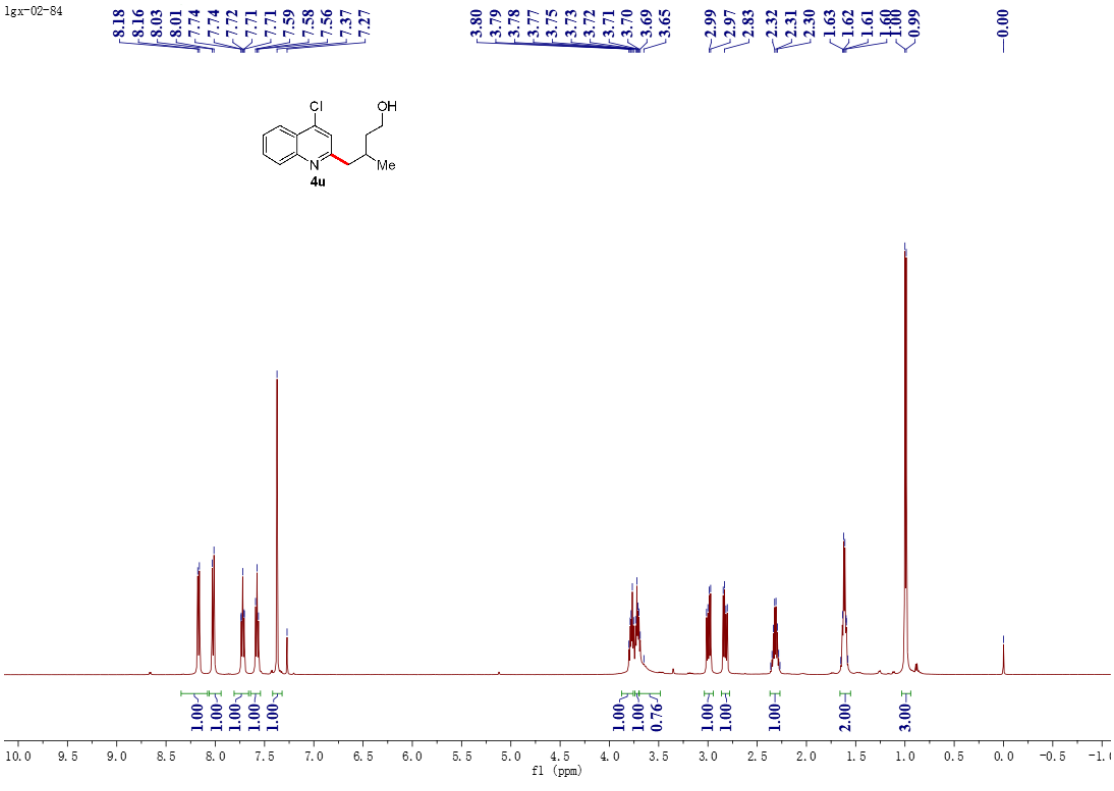

1gx-02-76-C
166.60
166.52
148.44
148.35
142.89
142.80
130.32
130.25
129.20
129.15
126.76
126.73
125.10
123.89
119.88
77.25
77.00
76.75
67.94
67.64
42.49
42.41
37.13
36.99
32.58
32.46
23.53
23.43
21.01
20.93
Cl
OH
N
4q
f1 (ppm)

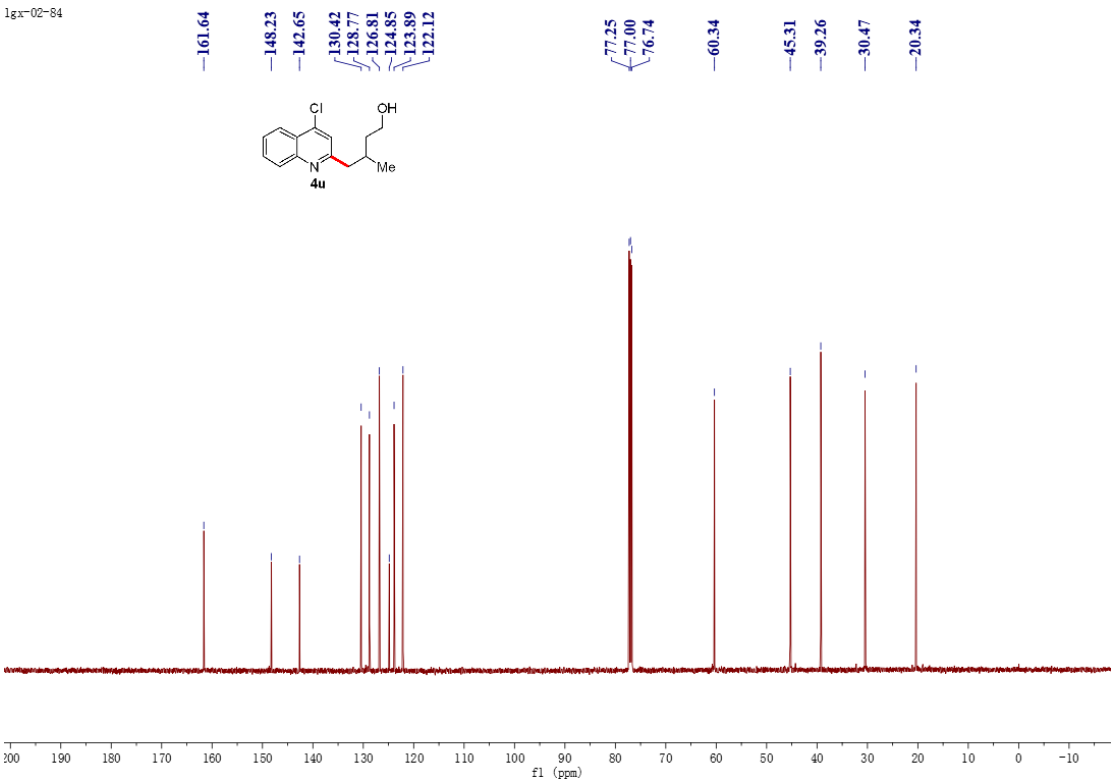

8.19
8.18
8.17
8.07
8.06
8.06
8.04
7.75
7.75
7.74
7.72
7.72
7.60
7.60
7.59
7.59
7.58
7.57
7.57
7.41
7.39
7.27
4.23
4.22
4.21
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
3.12
3.11
3.09
1.90
1.89
1.89
1.88
1.87
1.86
1.85
1.75
1.74
1.73
1.72
1.72
1.39
1.37
1.27
1.26
1.24
1.24
1.23
1.21
0.00
Cl
OH
CO2Et
N
4r
2.00
2.00
2.00
2.00
1.00
1.00
6.01
2.07
1.01
6.20
1.04
6.03
3.10
3.10
f1 (ppm)

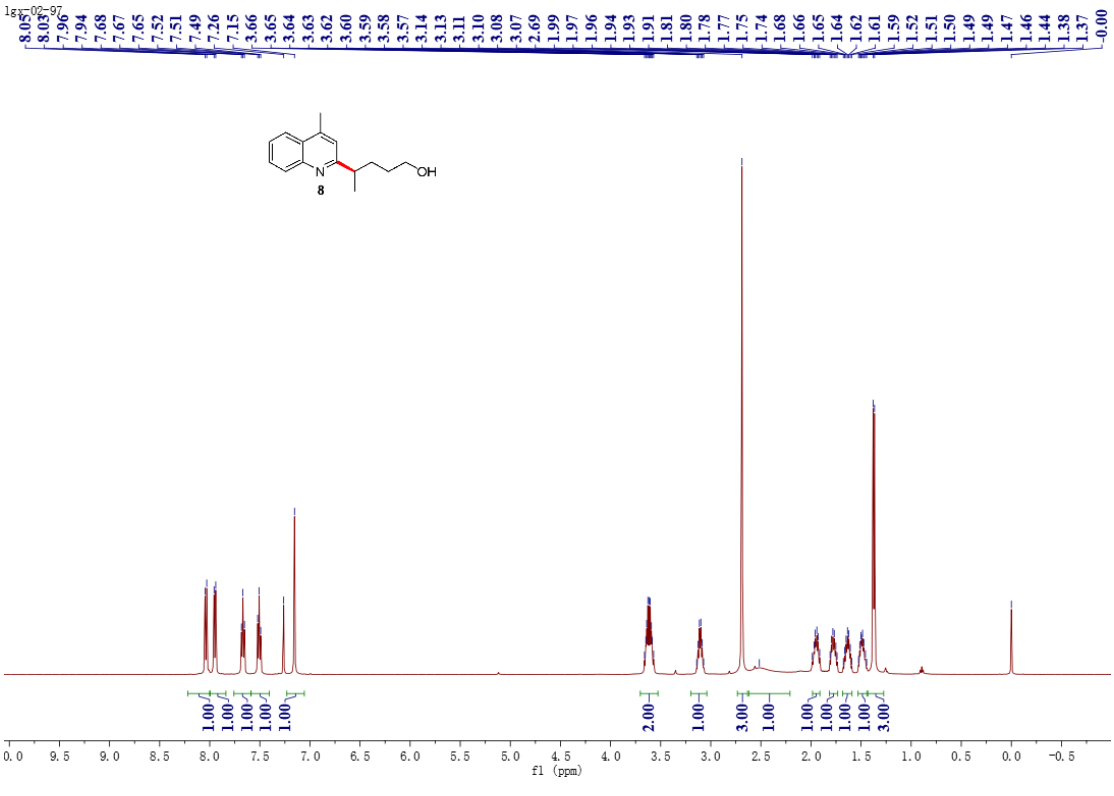

lgx-02-82-C
175.02
174.98
166.16
166.15
148.50
148.43
142.89
142.85
130.28
130.26
129.26
126.78
125.13
123.89
119.79
119.64
77.25
77.00
76.75
70.42
70.25
61.60
61.57
42.32
42.23
32.25
31.72
31.57
20.97
20.67
14.15
14.11
Cl
OH
CO2Et
N
4r
f1 (ppm)

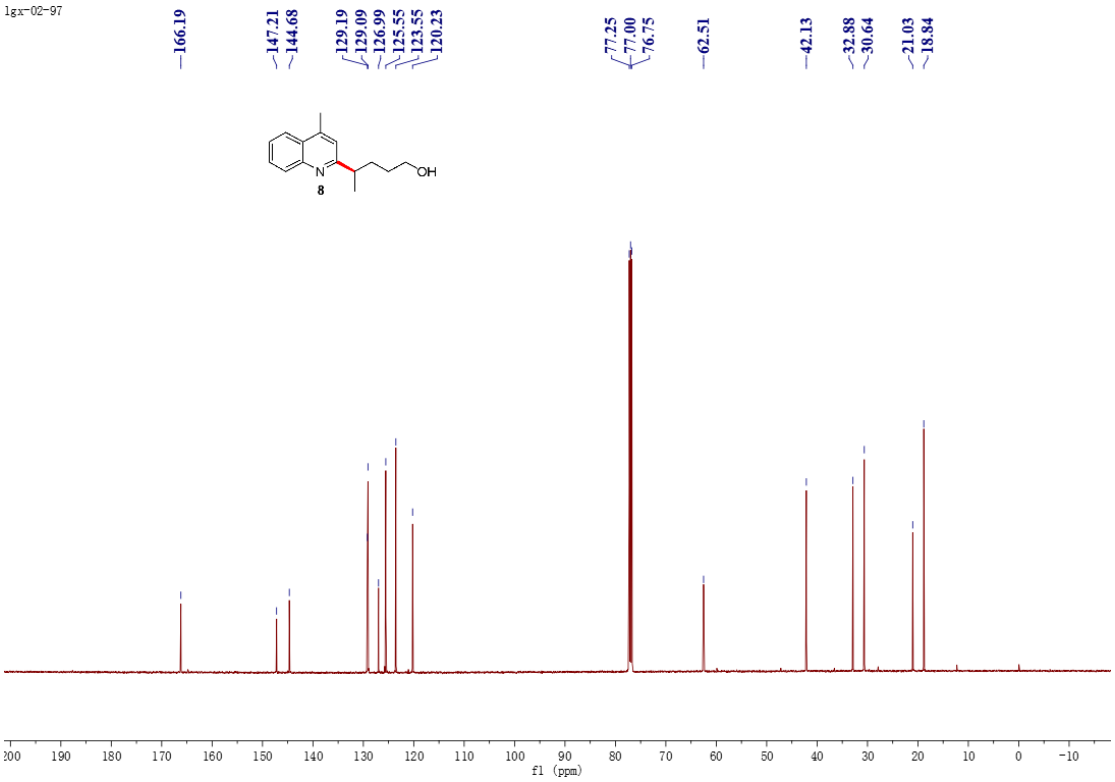

lgx-02-39
8.20
8.20
8.18
8.18
8.06
8.04
7.76
7.76
7.75
7.74
7.73
7.73
7.61
7.61
7.59
7.58
7.58
7.41
7.26
3.72
3.71
3.70
3.03
3.01
3.00
2.45
1.98
1.96
1.95
1.93
1.92
1.73
1.71
1.70
1.69
1.67
0.00
Cl
OH
N
4t
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
2.00
2.00
f1 (ppm)

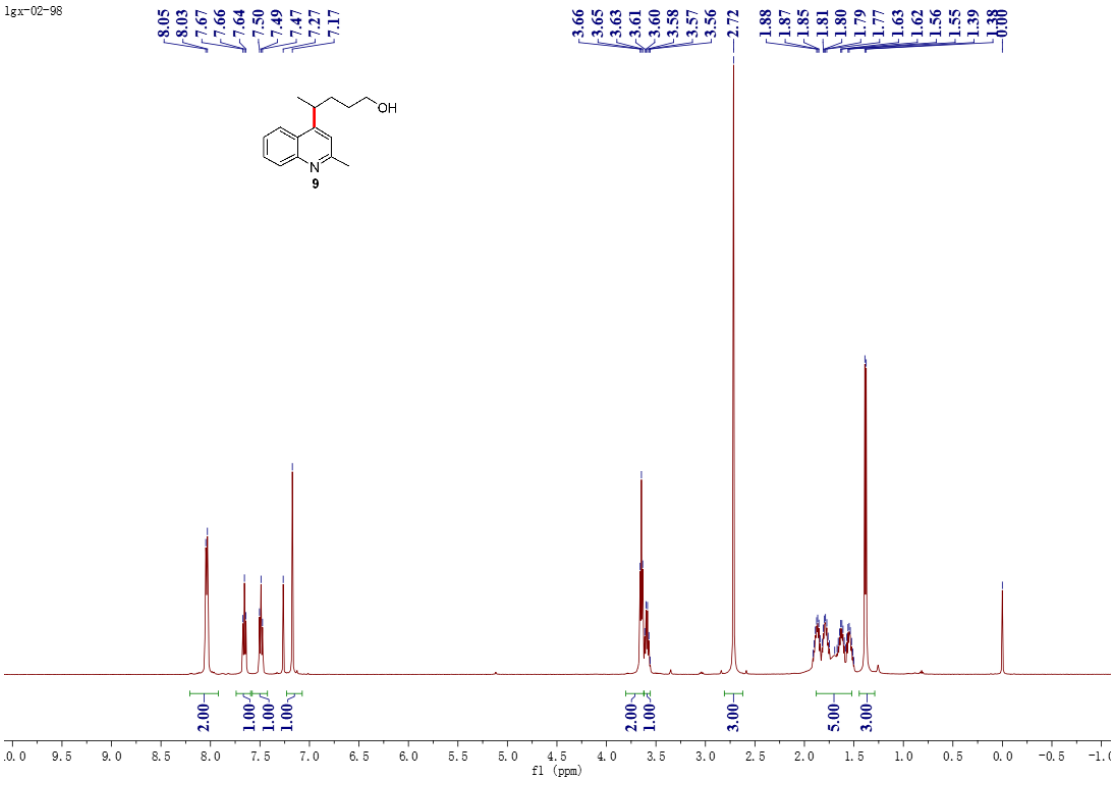

1gx-02-39
162.43
148.40
142.84
130.46
128.91
126.82
124.95
123.94
121.45
77.25
77.00
76.75
62.24
38.08
32.13
25.34
Cl
OH
N
4t
f1 (ppm)

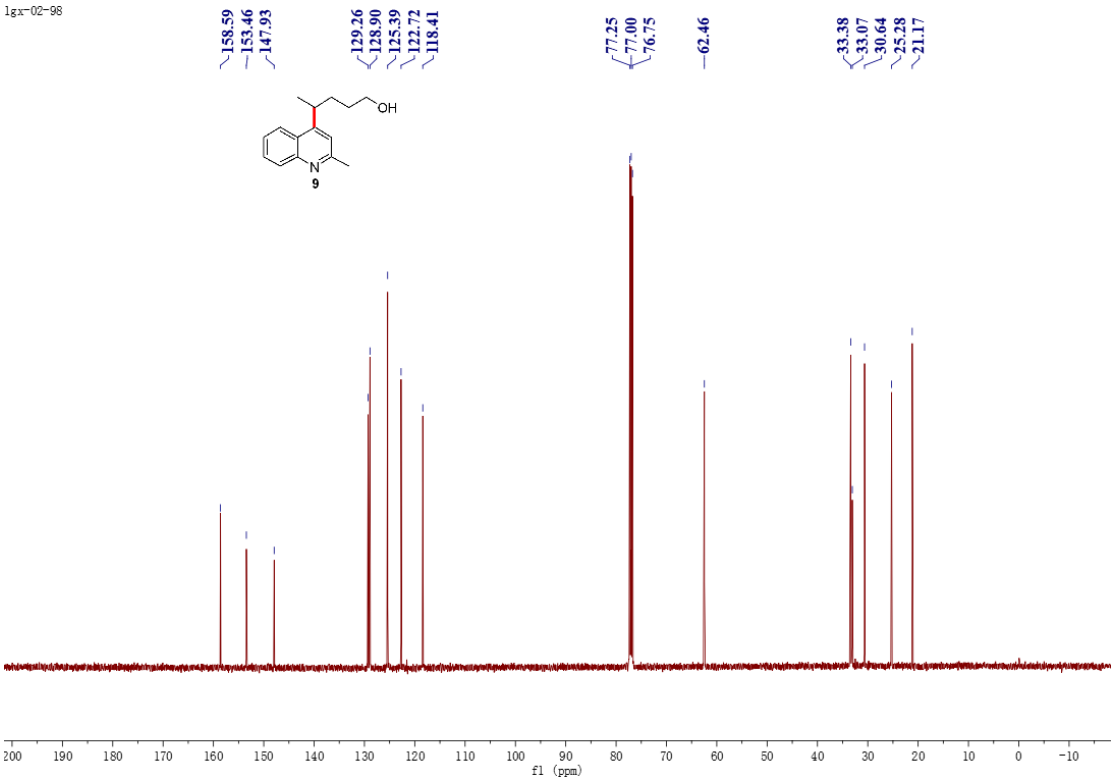

1gx-02-84
8.18
8.16
8.03
8.01
7.74
7.74
7.72
7.71
7.71
7.59
7.58
7.56
7.37
7.27
3.80
3.79
3.78
3.77
3.75
3.73
3.72
3.71
3.70
3.69
3.65
2.99
2.97
2.83
2.32
2.31
2.30
1.63
1.62
1.61
1.00
0.99
0.00
Cl
OH
N
Me
4u
1.00
1.00
1.00
1.00
1.00
1.00
1.00
0.76
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

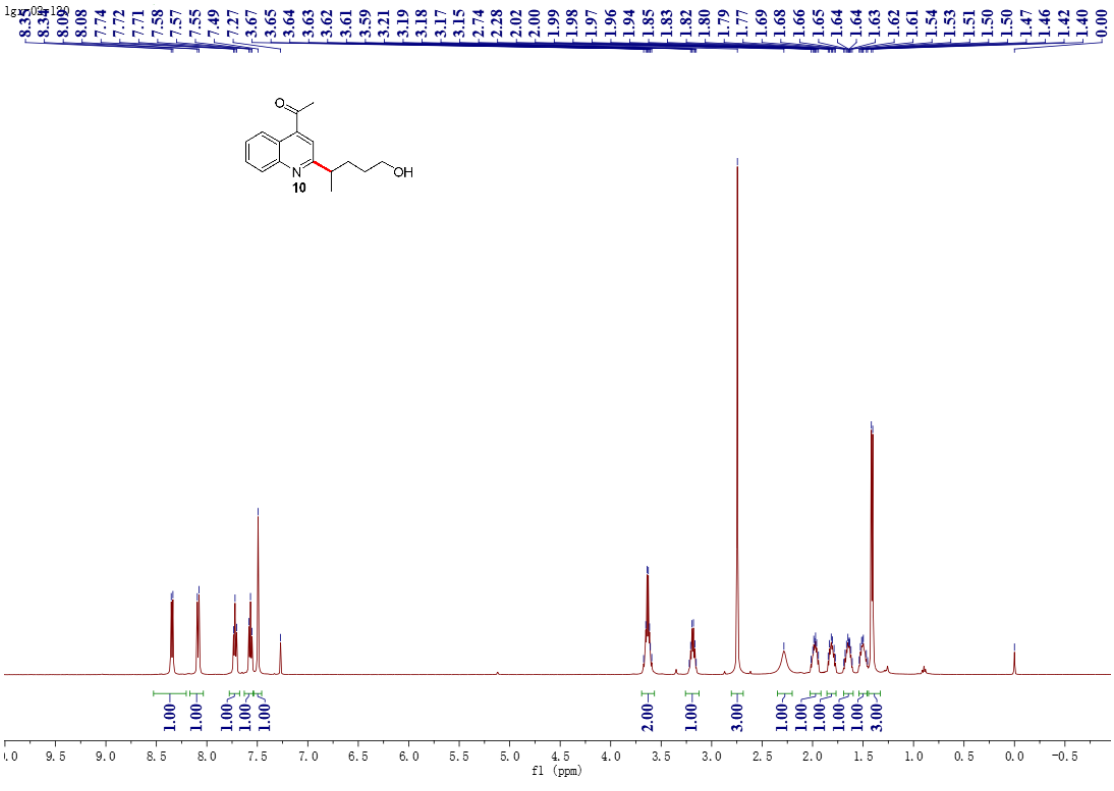

lgx-02-84
161.64
148.23
142.65
130.42
128.77
126.81
124.85
123.89
122.12
77.25
77.00
76.74
60.34
45.31
39.26
30.47
20.34
Cl
OH
N
Me
4u
f1 (ppm)

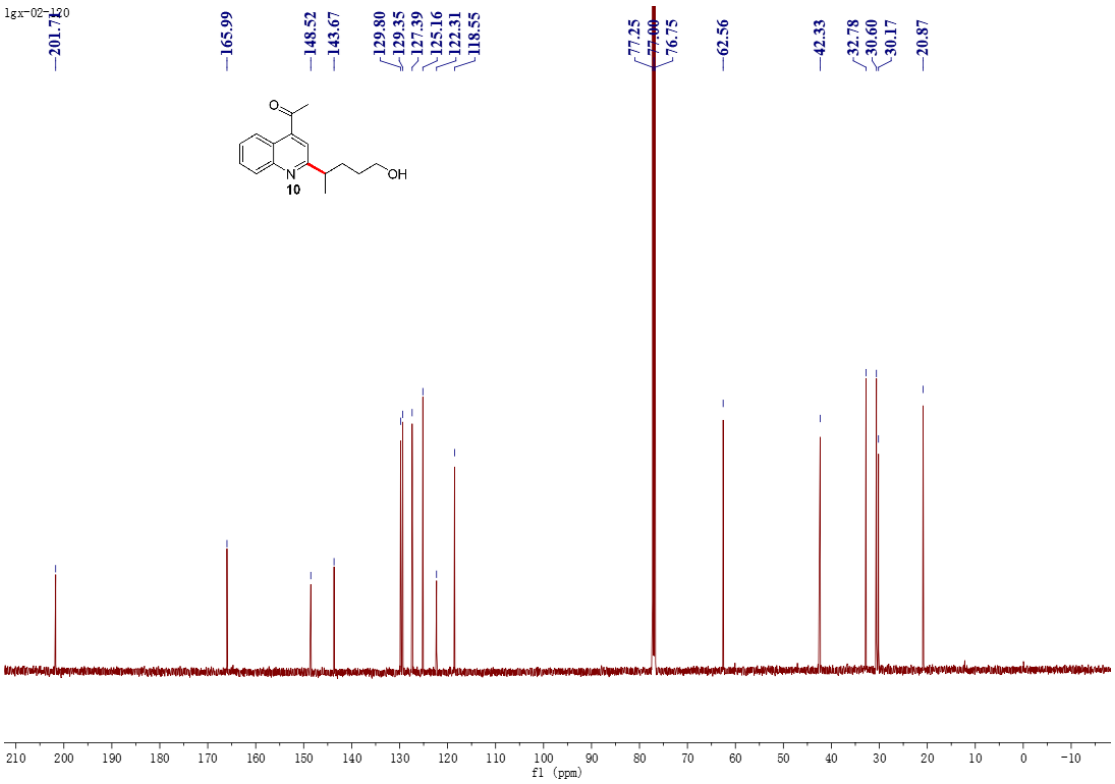

lgx-02-97
8.05
8.03
7.96
7.94
7.68
7.67
7.65
7.52
7.51
7.49
7.26
7.15
3.66
3.65
3.64
3.63
3.62
3.60
3.59
3.58
3.57
3.14
3.13
3.11
3.10
3.08
3.07
2.69
1.99
1.97
1.96
1.94
1.93
1.91
1.81
1.80
1.78
1.77
1.75
1.74
1.68
1.66
1.65
1.64
1.62
1.61
1.59
1.52
1.51
1.50
1.49
1.49
1.47
1.46
1.44
1.38
1.37
0.00
N
OH
8
1.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

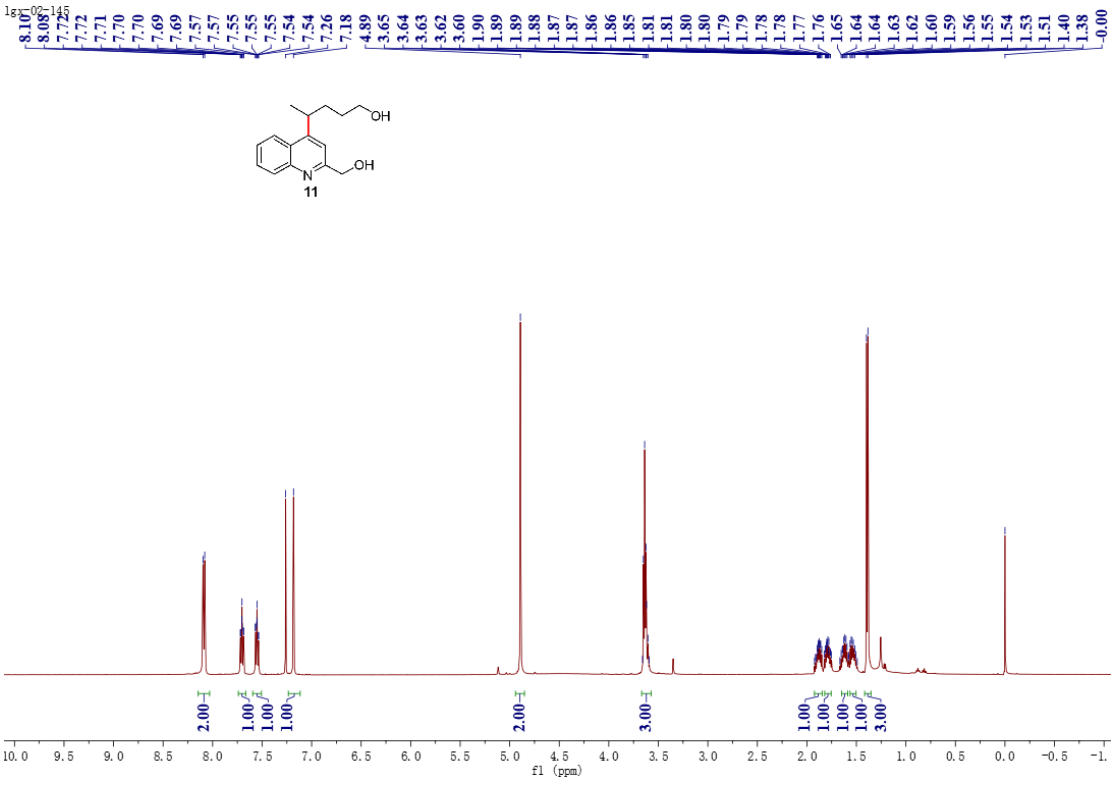

1gx-02-97
166.19
147.21
144.68
129.19
129.09
126.99
125.55
123.55
120.23
77.25
77.00
76.75
62.51
42.13
32.88
30.64
21.03
18.84
OH
8
f1 (ppm)

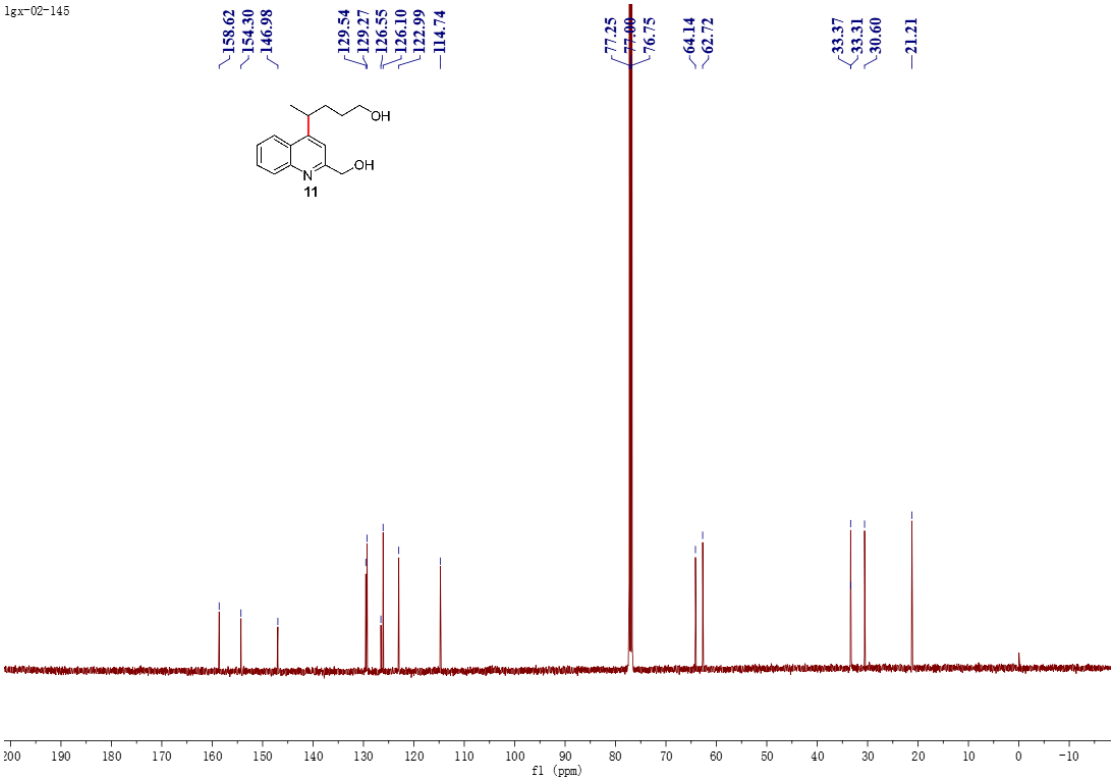

1gx-02-98
8.05
8.03
7.67
7.66
7.64
7.50
7.49
7.47
7.27
7.17
3.66
3.65
3.63
3.61
3.60
3.58
3.57
3.56
2.72
1.88
1.87
1.85
1.81
1.80
1.79
1.77
1.63
1.62
1.56
1.55
1.39
1.38
0.00
OH
9
2.00
1.00
1.00
1.00
2.00
1.00
3.00
5.00
3.00
f1 (ppm)

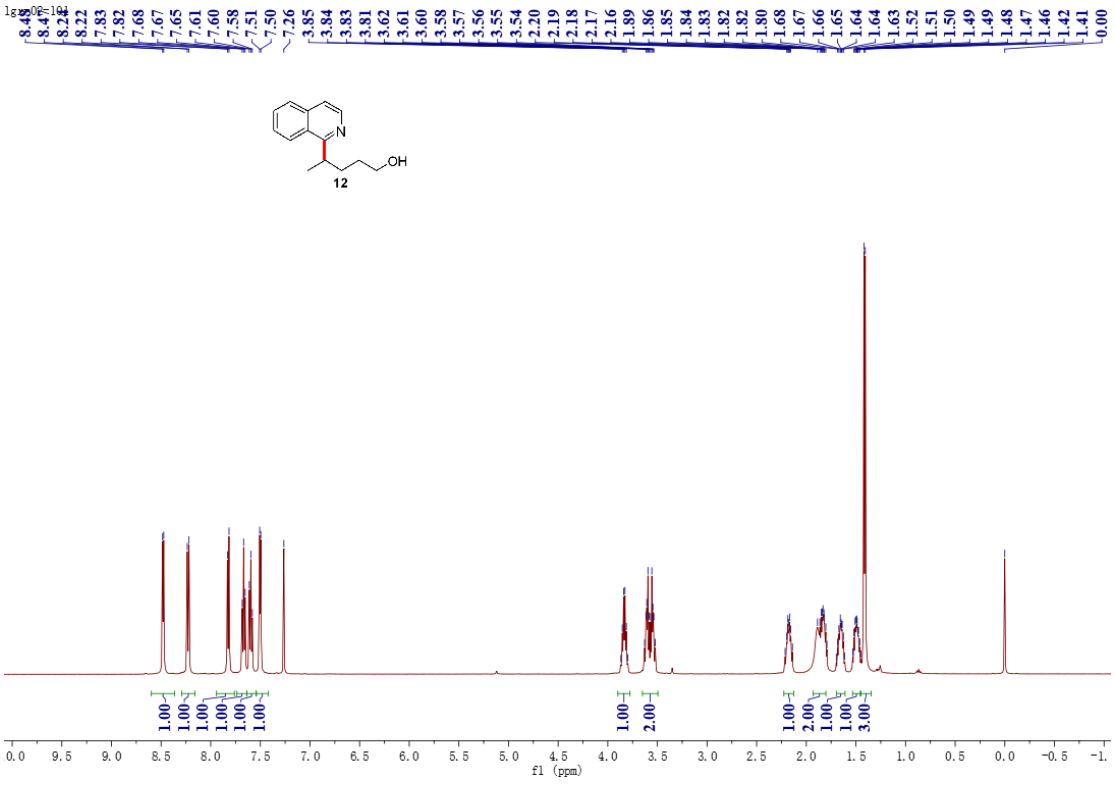

lgx-02-98
158.59
153.46
147.93
129.26
128.90
125.39
122.72
118.41
77.25
77.00
76.75
62.46
33.38
33.07
30.64
25.28
21.17
OH
N
9
f1 (ppm)

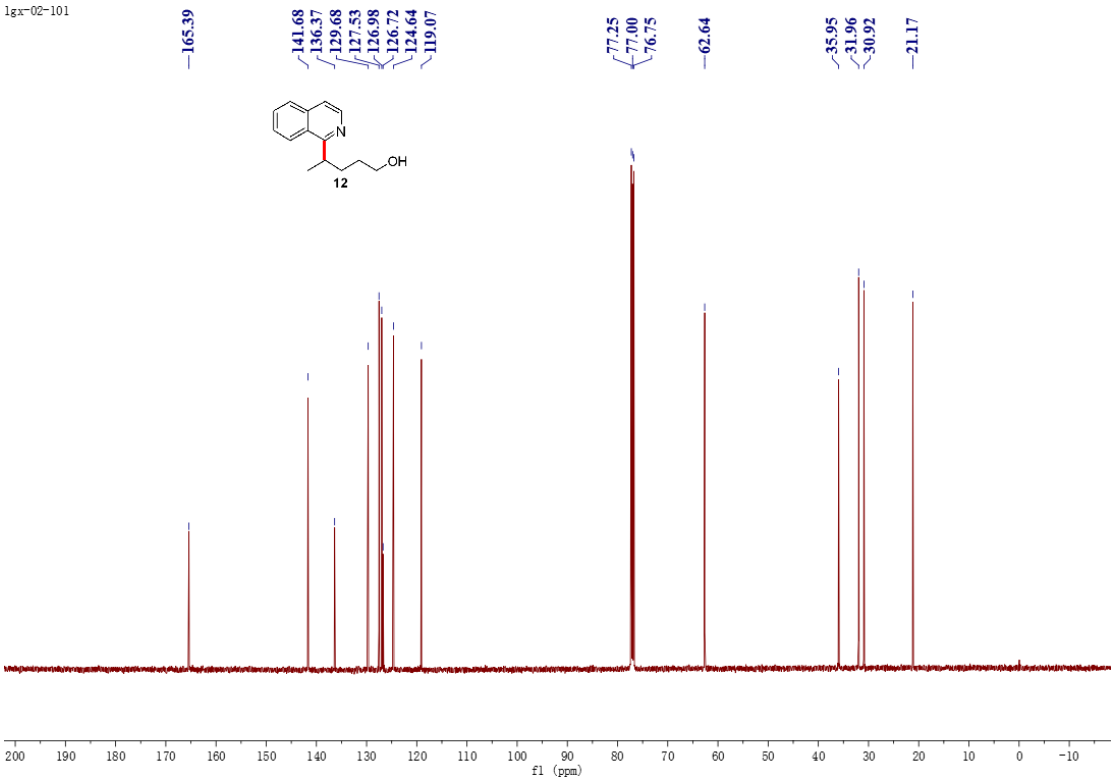

O
N
OH
10
1.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

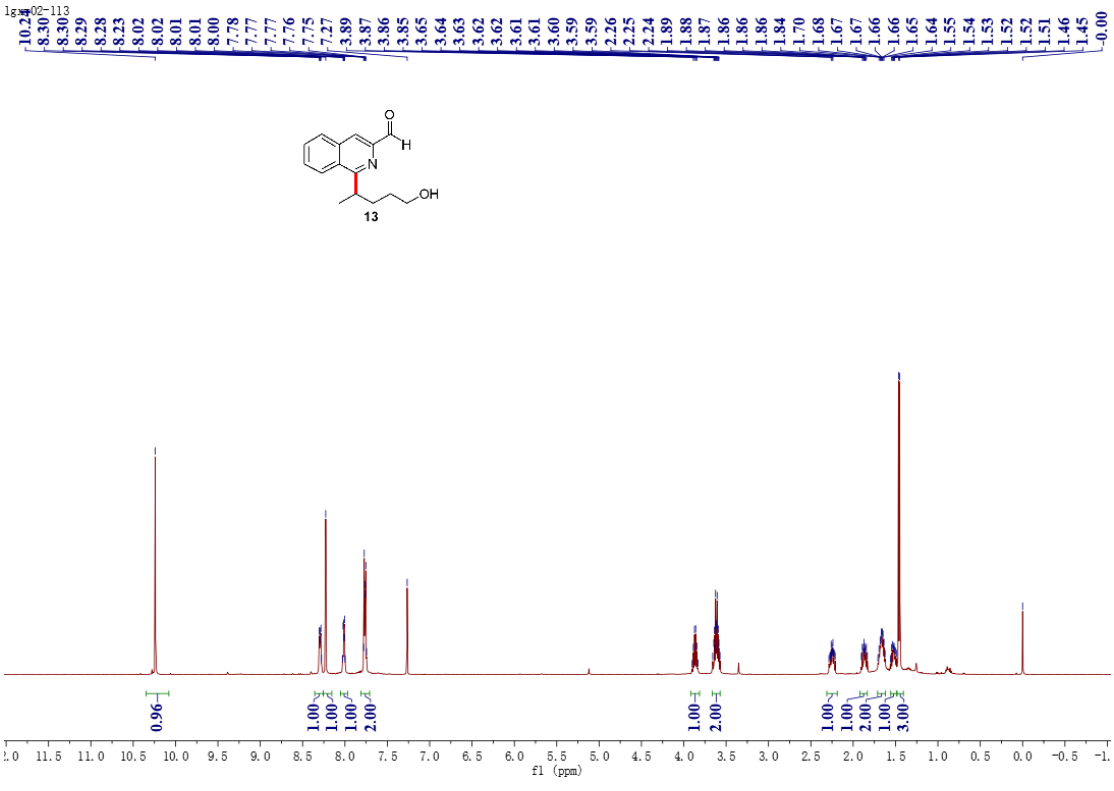

lgx-02-120
201.71
165.99
148.52
143.67
129.80
129.35
127.39
125.16
122.31
118.55
77.25
77.00
76.75
62.56
42.33
32.78
30.60
30.17
20.87
O
N
OH
10
f1 (ppm)

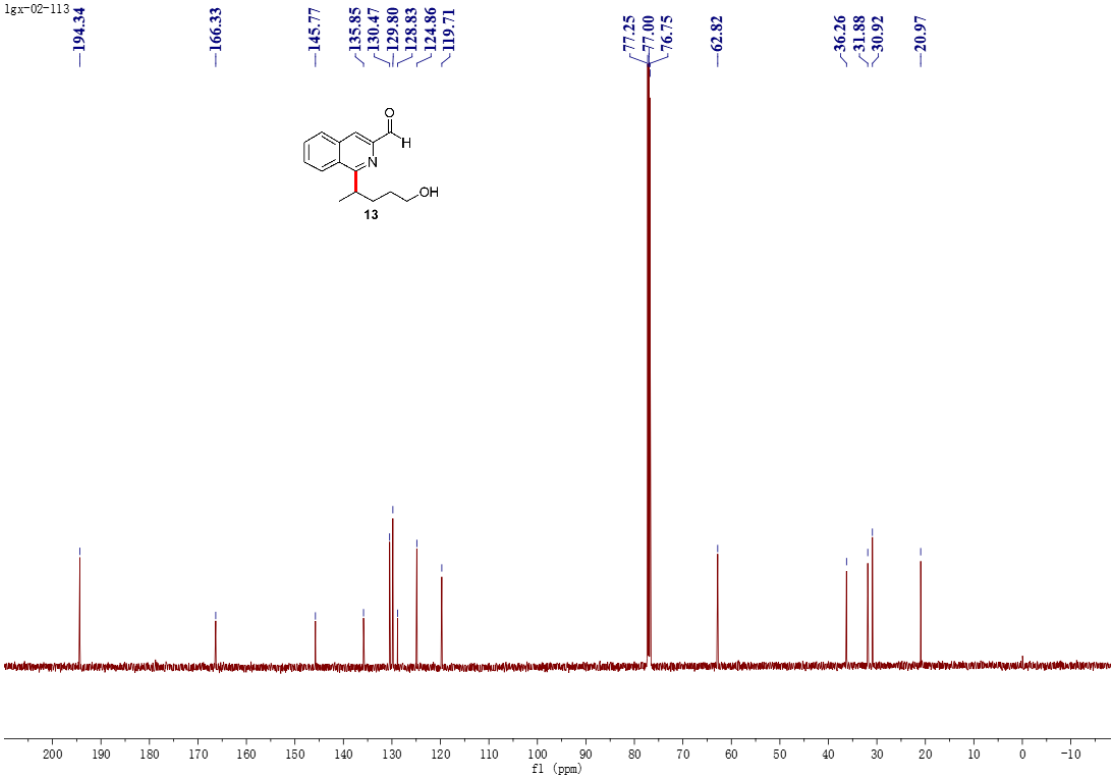

lgx-02-145
OH
OH
N
11
2.00
1.00
1.00
1.00
2.00
3.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

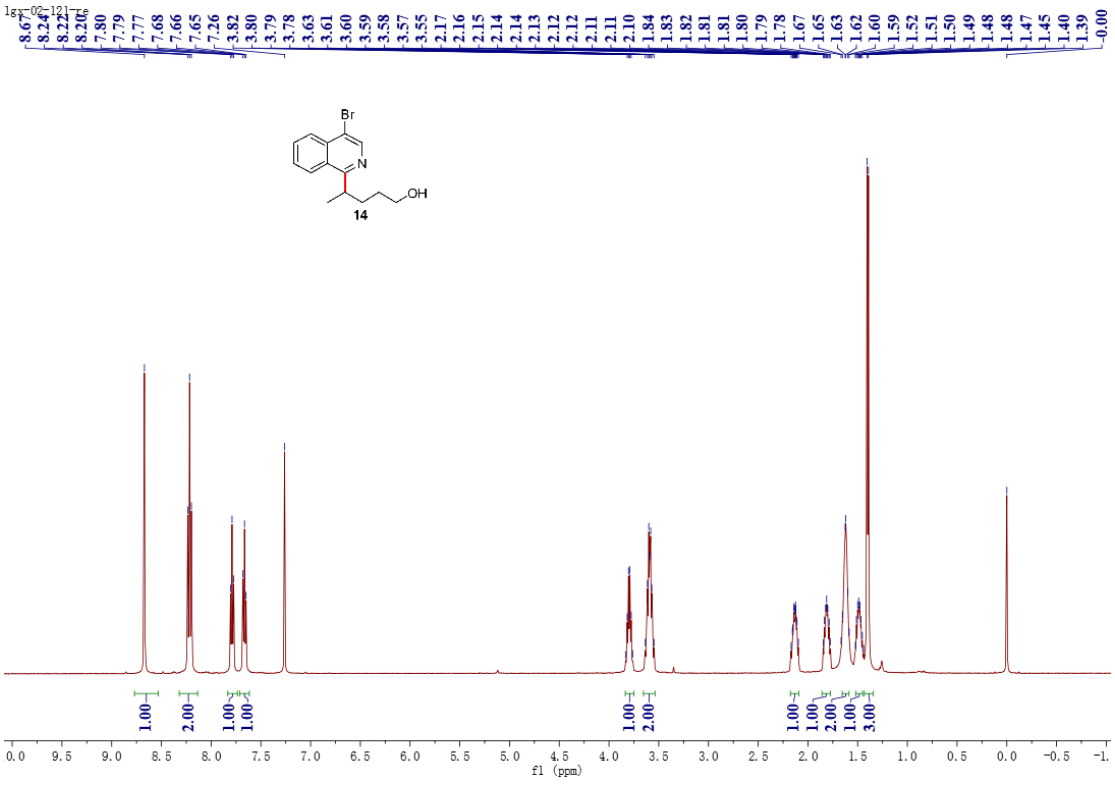

lgx-02-145
158.62
154.30
146.98
129.54
129.27
126.55
126.10
122.99
114.74
77.25
77.00
76.75
64.14
62.72
33.37
33.31
30.60
21.21
OH
OH
N
11
f1 (ppm)

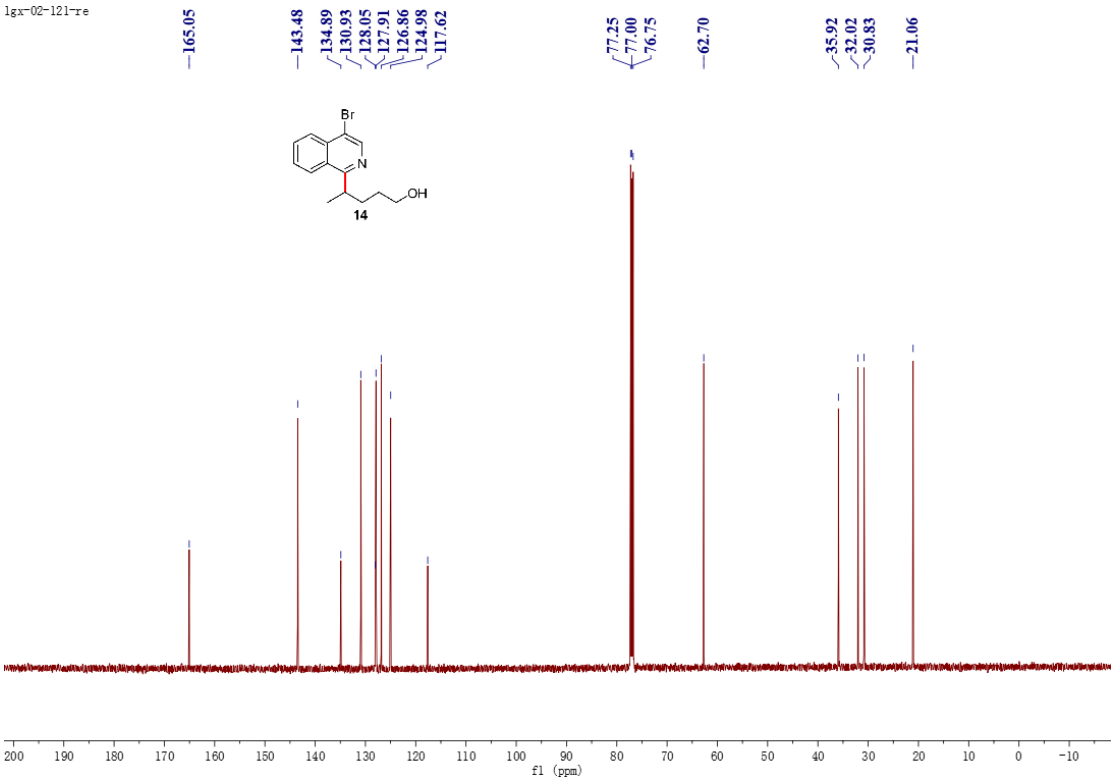

8.45
8.44
8.24
8.22
7.83
7.82
7.68
7.67
7.65
7.61
7.60
7.58
7.51
7.50
7.26
3.85
3.84
3.83
3.81
3.62
3.61
3.60
3.58
3.57
3.56
3.55
3.54
2.20
2.19
2.18
2.17
2.16
1.89
1.86
1.85
1.84
1.83
1.82
1.82
1.80
1.68
1.67
1.66
1.65
1.64
1.64
1.63
1.52
1.51
1.50
1.49
1.49
1.48
1.47
1.46
1.42
1.41
0.00
N
OH
12
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
2.00
1.00
1.00
3.00
f1 (ppm)

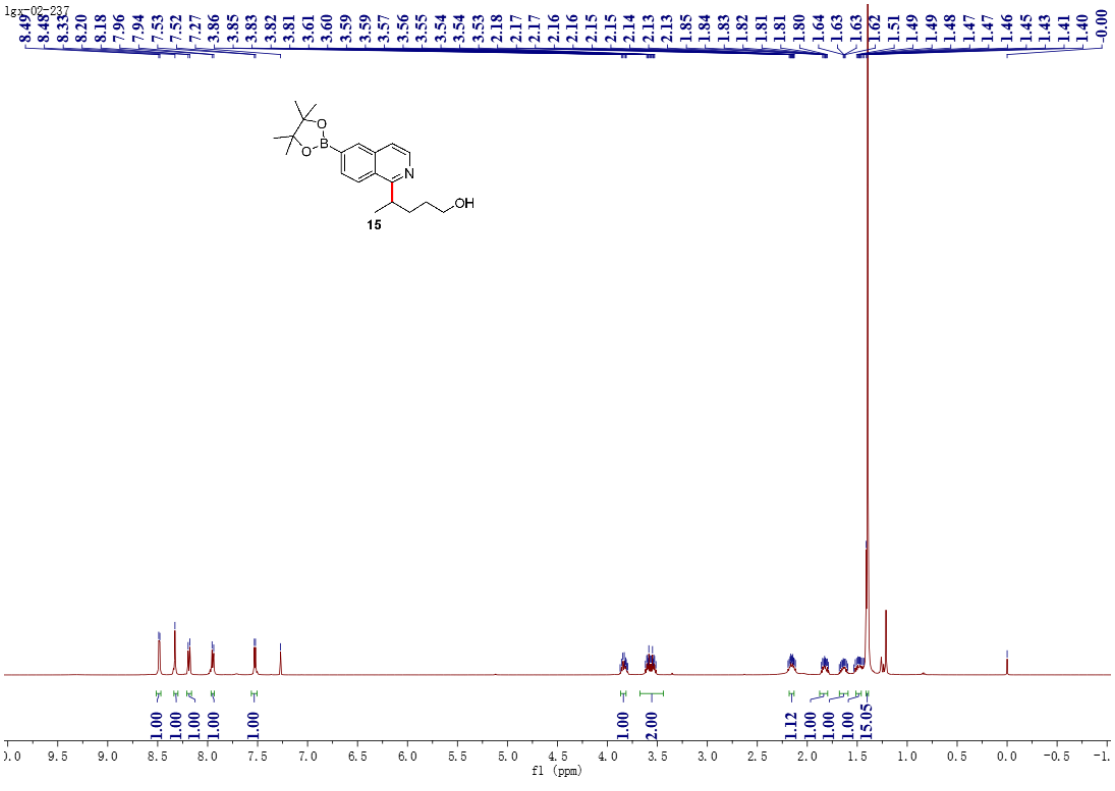

lgx-02-101
165.39
141.68
136.37
129.68
127.53
126.98
126.72
124.64
119.07
77.25
77.00
76.75
62.64
35.95
31.96
30.92
21.17
N
OH
12
f1 (ppm)

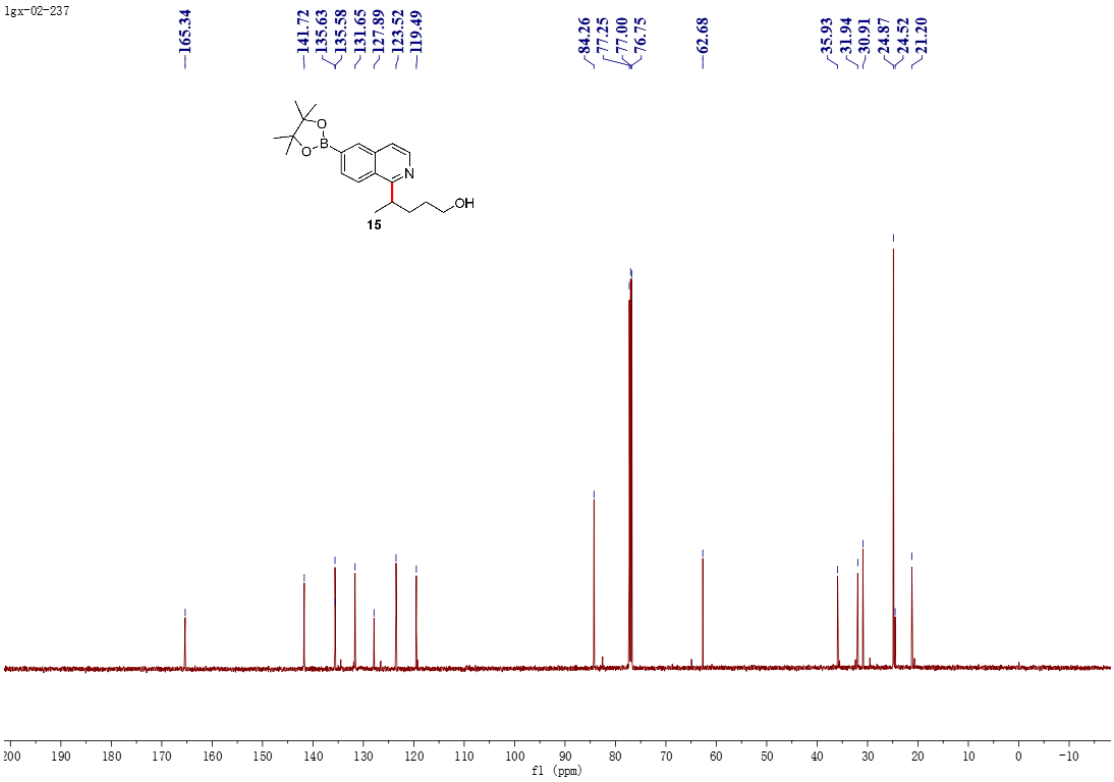

lgx-02-113
10.24
8.30
8.30
8.29
8.28
8.23
8.02
8.02
8.01
8.01
8.00
7.78
7.77
7.77
7.76
7.75
7.27
3.89
3.87
3.86
3.85
3.65
3.64
3.63
3.62
3.62
3.61
3.61
3.60
3.59
3.59
2.26
2.25
2.24
1.89
1.88
1.87
1.86
1.86
1.86
1.84
1.70
1.68
1.67
1.67
1.66
1.66
1.65
1.64
1.55
1.54
1.53
1.52
1.52
1.51
1.46
1.45
0.00
O
H
N
OH
13
0.96
1.00
1.00
1.00
2.00
1.00
2.00
1.00
1.00
2.00
1.00
3.00
f1 (ppm)

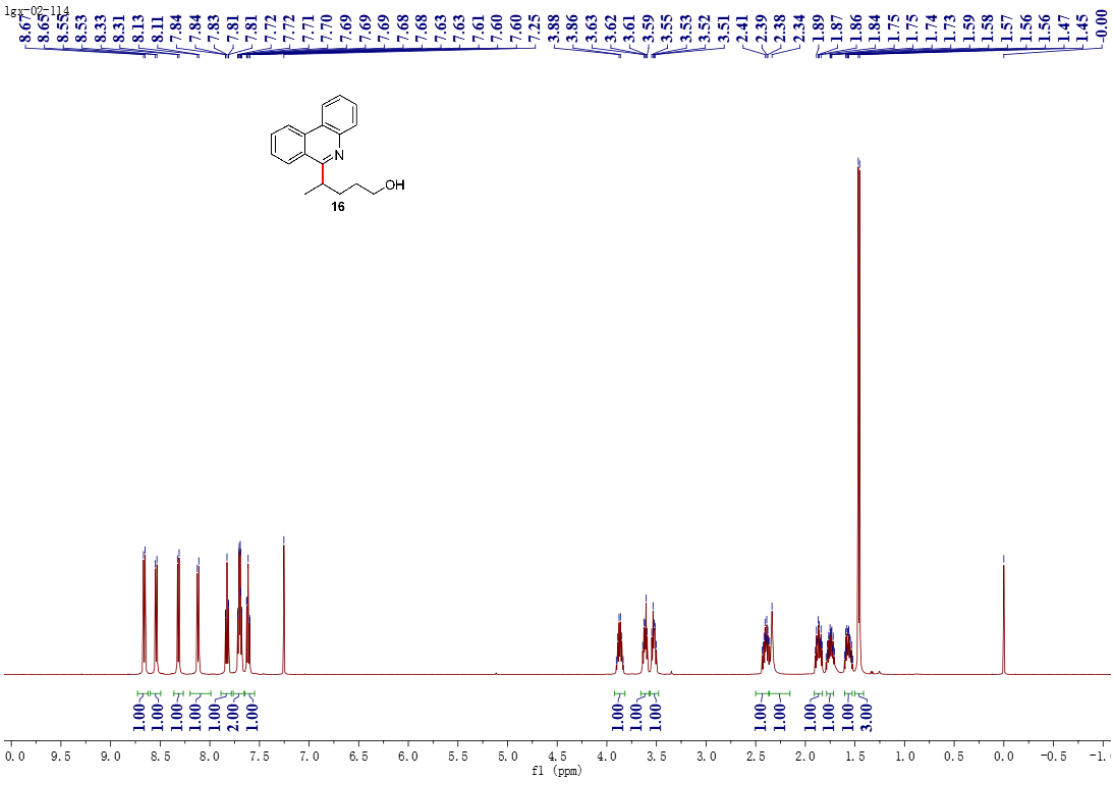

lgx-02-113
194.34
166.33
145.77
135.85
130.47
129.80
128.83
124.86
119.71
77.25
77.00
76.75
62.82
36.26
31.88
30.92
20.97
O
H
N
OH
13
f1 (ppm)

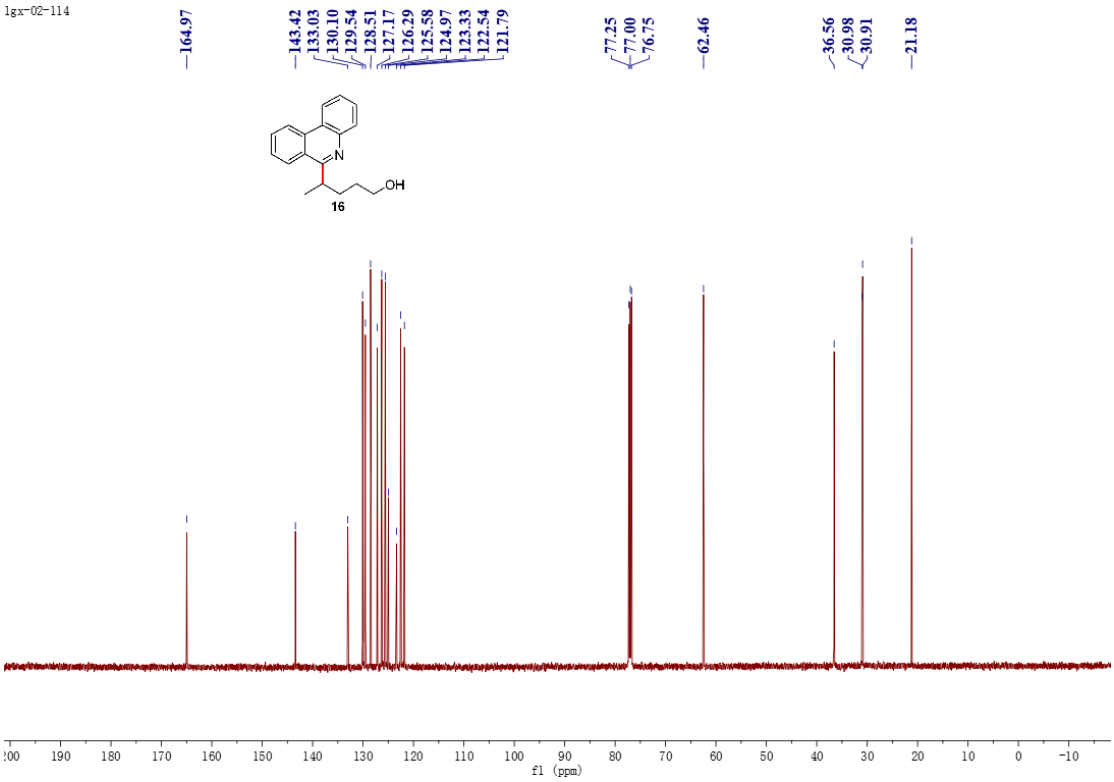

lgx-02-121-re
8.67
8.24
8.22
8.20
7.80
7.79
7.77
7.68
7.66
7.65
7.26
3.82
3.80
3.79
3.78
3.63
3.61
3.60
3.59
3.58
3.57
3.55
2.17
2.16
2.15
2.14
2.14
2.13
2.12
2.12
2.11
2.11
2.10
1.84
1.83
1.82
1.81
1.81
1.80
1.79
1.78
1.67
1.65
1.63
1.62
1.60
1.59
1.52
1.51
1.50
1.49
1.48
1.48
1.47
1.45
1.40
1.39
0.00
Br
N
OH
14
1.00
2.00
1.00
1.00
1.00
2.00
1.00
1.00
2.00
1.00
3.00
f1 (ppm)

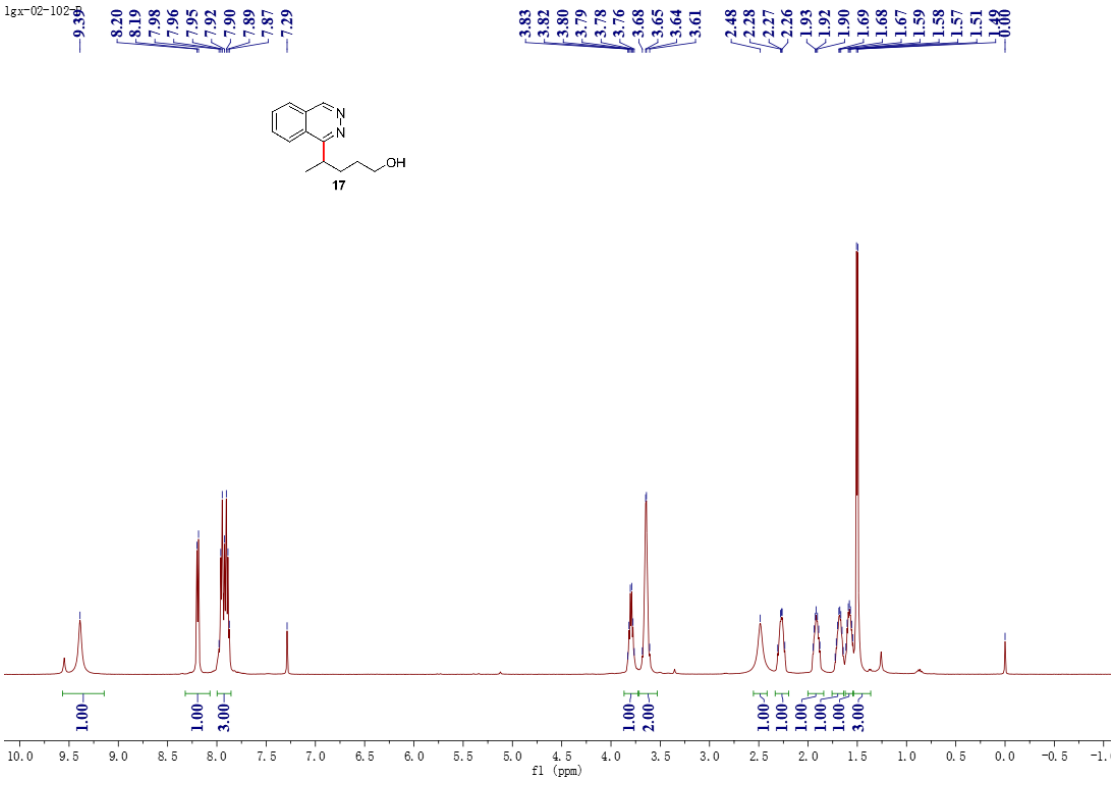

lgx-02-121-re
165.05
143.48
134.89
130.93
128.05
127.91
126.86
124.98
117.62
77.25
77.00
76.75
62.70
35.92
32.02
30.83
21.06
Br
N
OH
14
f1 (ppm)

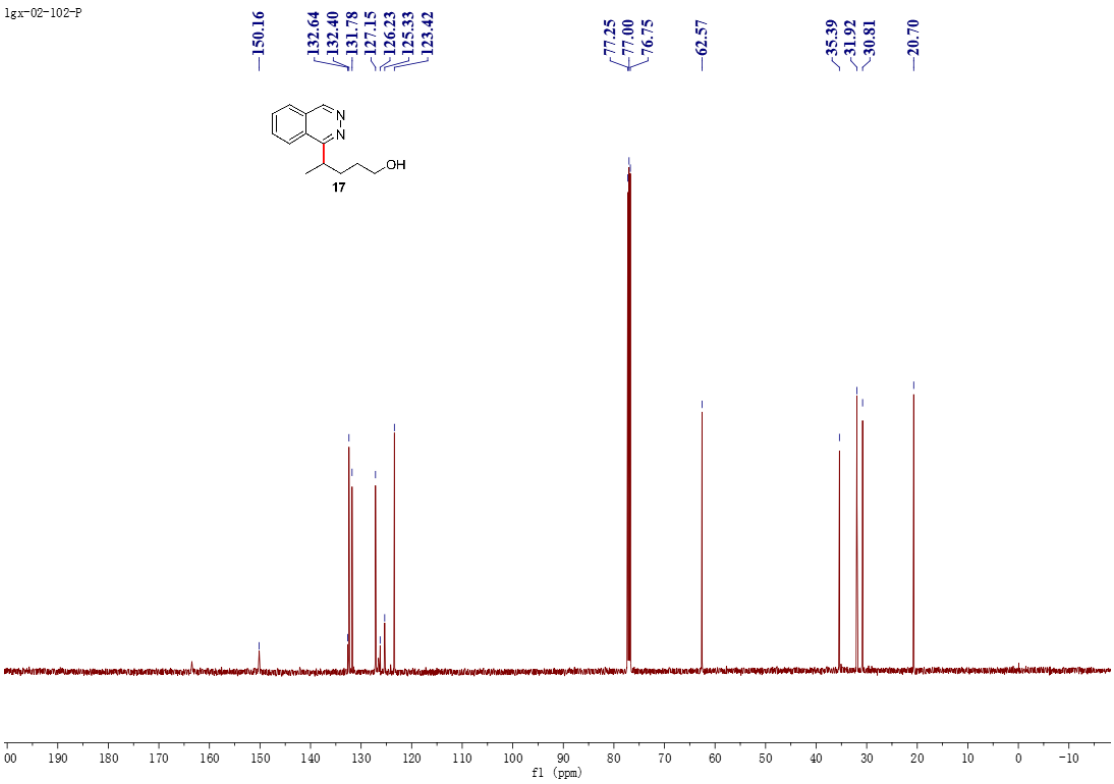

lgx-02-237
8.49
8.48
8.33
8.20
8.18
7.96
7.94
7.53
7.52
7.27
3.86
3.85
3.83
3.82
3.81
3.61
3.60
3.59
3.59
3.57
3.56
3.55
3.54
3.54
3.53
2.18
2.17
2.17
2.16
2.16
2.15
2.15
2.14
2.13
2.13
1.85
1.84
1.83
1.82
1.81
1.81
1.80
1.64
1.63
1.63
1.62
1.51
1.49
1.49
1.48
1.47
1.47
1.46
1.45
1.43
1.41
1.40
0.00
O
O
B
N
OH
15
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.12
1.00
1.00
1.00
15.05
f1 (ppm)

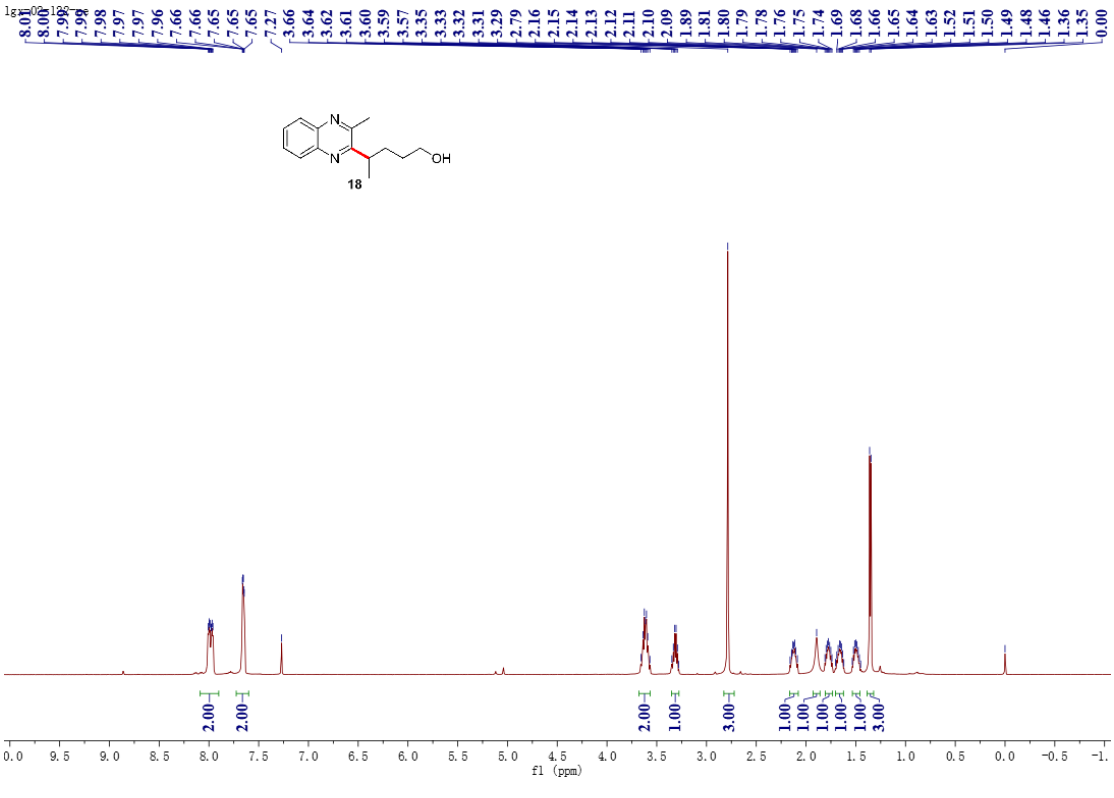

lgx-02-237
165.34
141.72
135.63
135.58
131.65
127.89
123.52
119.49
84.26
77.25
77.00
76.75
62.68
35.93
31.94
30.91
24.87
24.52
21.20
O
O
B
N
OH
15
f1 (ppm)

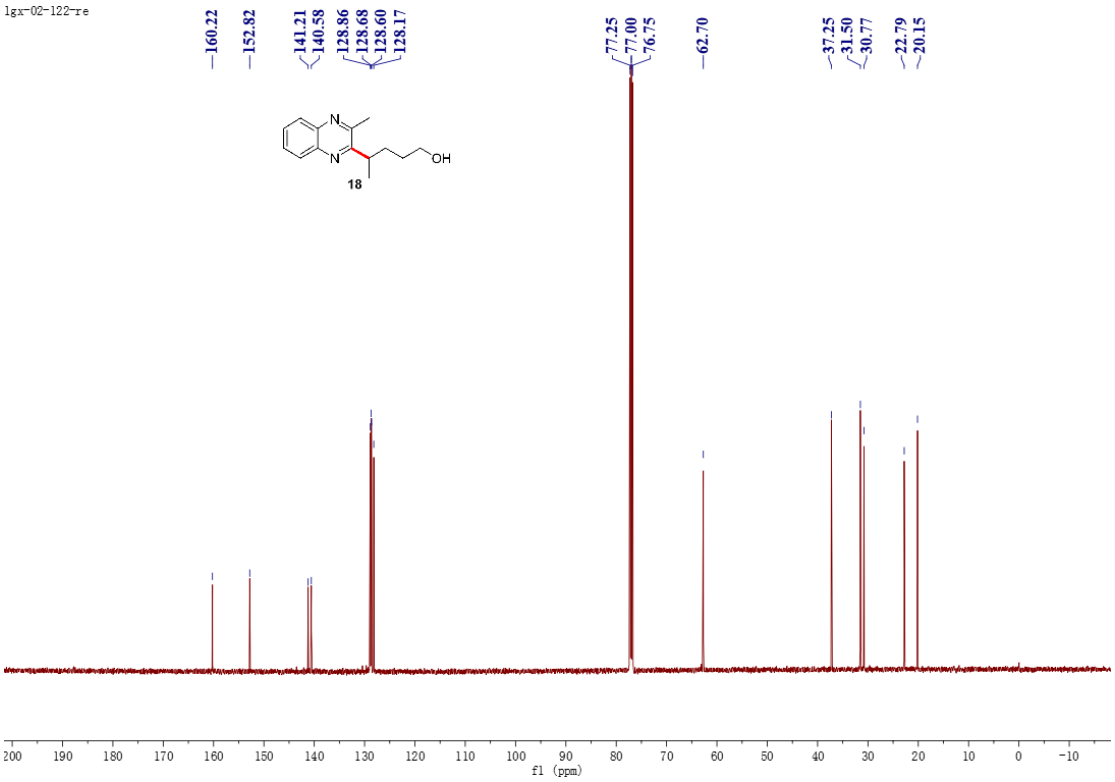

lgx-02-114
8.67
8.65
8.55
8.53
8.33
8.31
8.13
8.11
7.84
7.84
7.83
7.81
7.81
7.72
7.72
7.71
7.70
7.69
7.69
7.69
7.68
7.68
7.63
7.63
7.61
7.60
7.60
7.25
3.88
3.86
3.63
3.62
3.61
3.59
3.55
3.53
3.52
3.51
2.41
2.39
2.38
2.34
1.89
1.87
1.86
1.84
1.75
1.75
1.74
1.73
1.59
1.58
1.57
1.56
1.56
1.47
1.45
0.00
N
OH
16
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

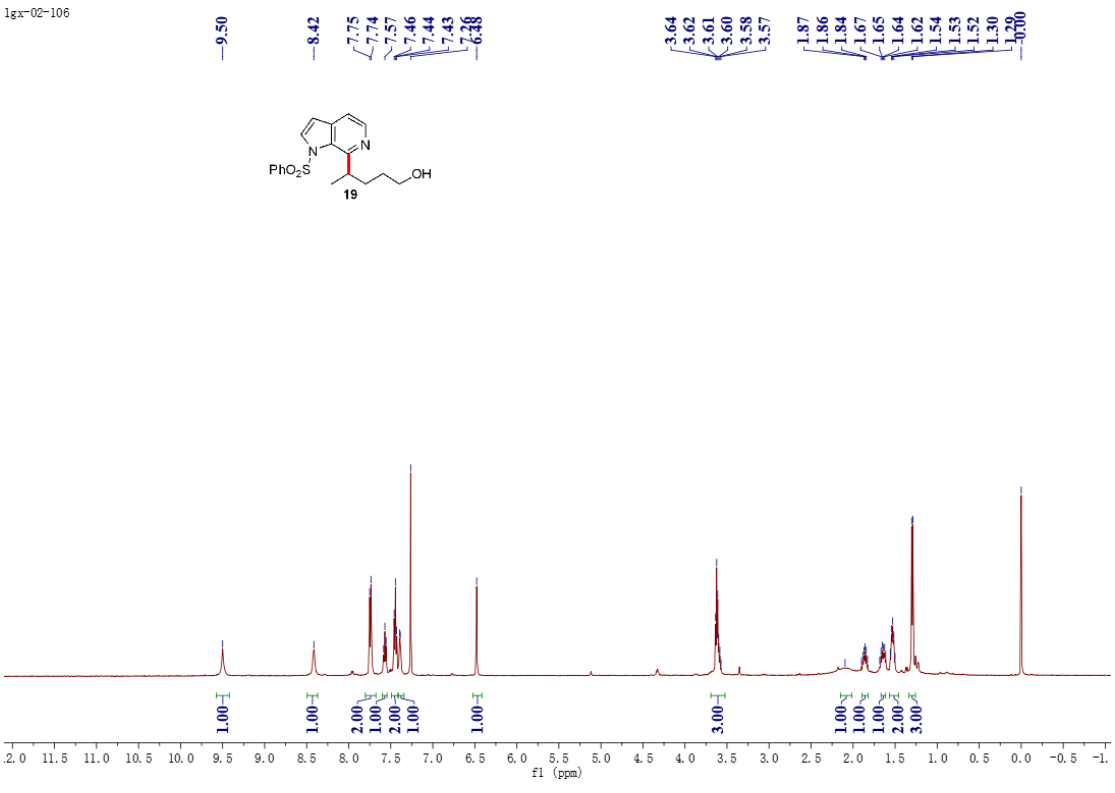

lgx-02-114
164.97
143.42
133.03
130.10
129.54
128.51
127.17
126.29
125.58
124.97
123.33
122.54
121.79
77.25
77.00
76.75
62.46
36.56
30.98
30.91
21.18
OH
16
f1 (ppm)

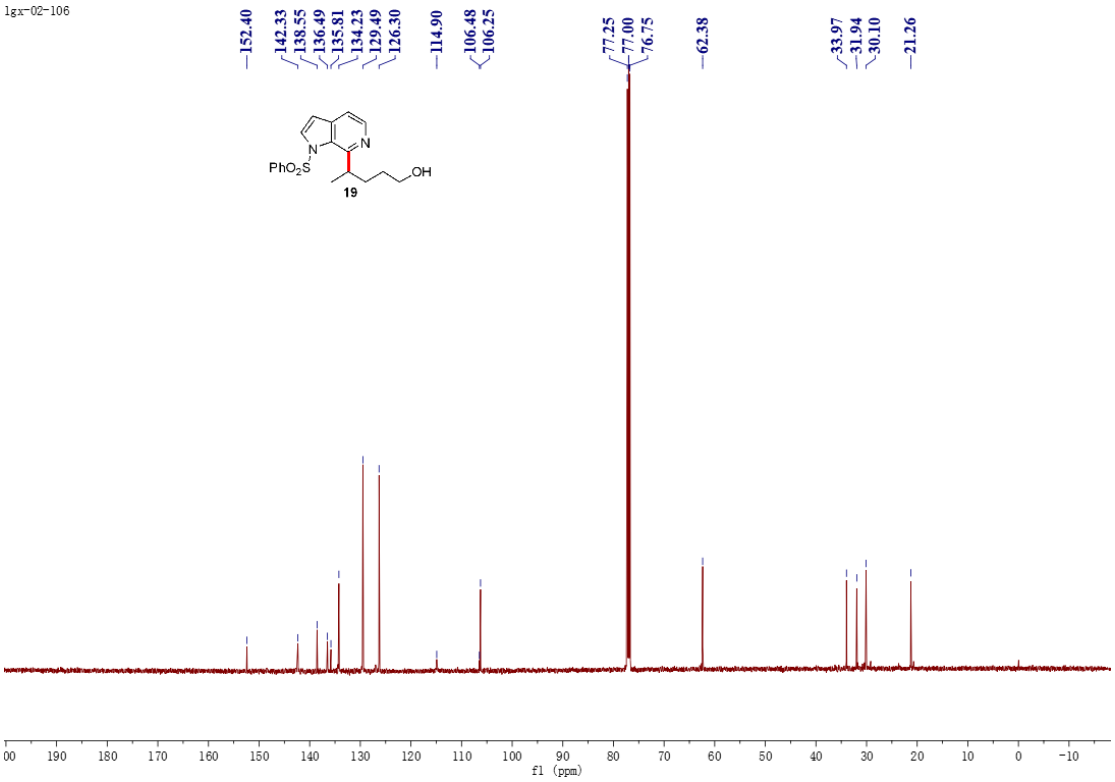

lgx-02-102-5
9.39
8.20
8.19
7.98
7.96
7.95
7.92
7.90
7.89
7.87
7.29
3.83
3.82
3.80
3.79
3.78
3.76
3.68
3.65
3.64
3.61
2.48
2.28
2.27
2.26
1.93
1.92
1.90
1.69
1.68
1.67
1.59
1.58
1.57
1.51
1.49
0.00
OH
17
1.00
1.00
3.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

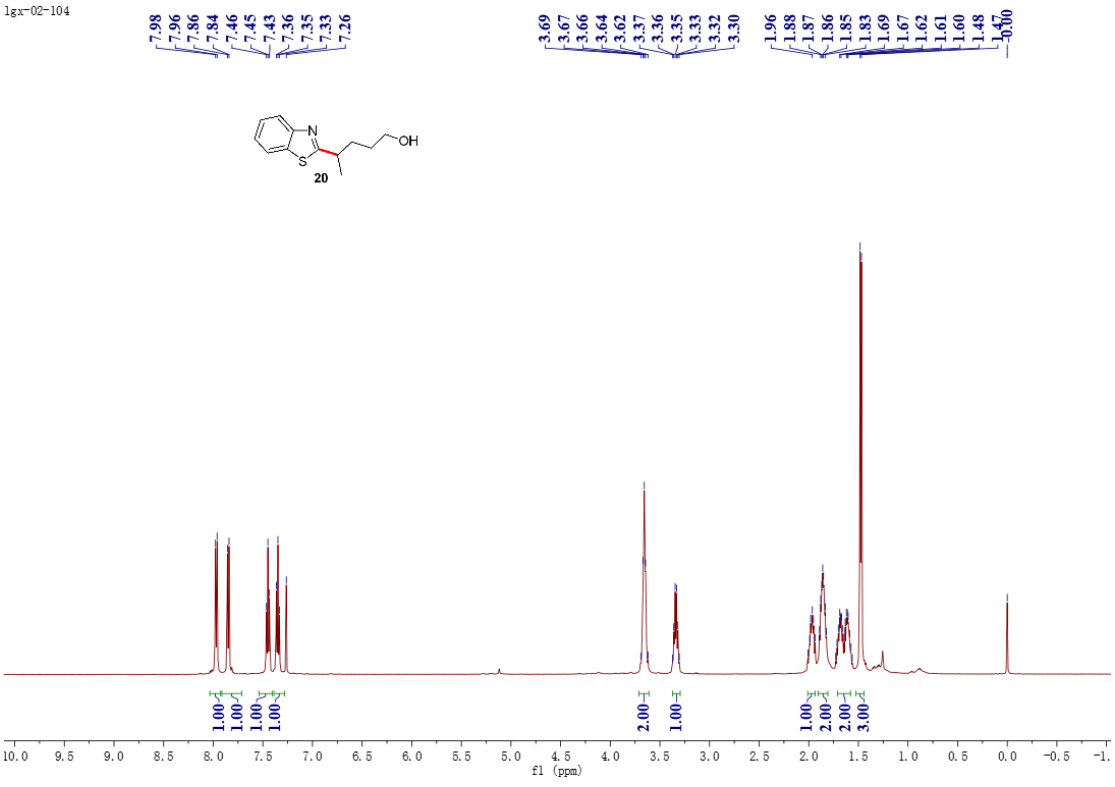

lgx-02-102-P
150.16
132.64
132.40
131.78
127.15
126.23
125.33
123.42
77.25
77.00
76.75
62.57
35.39
31.92
30.81
20.70
N
N
OH
17
f1 (ppm)

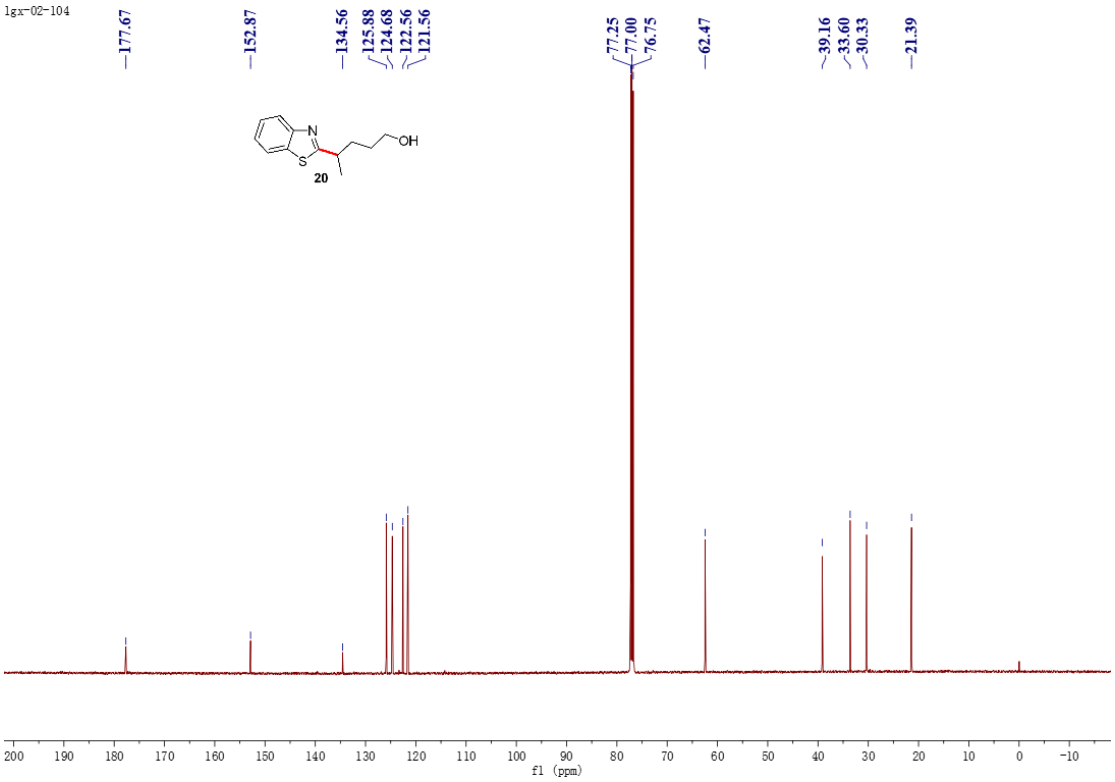

8.01
8.00
7.99
7.98
7.97
7.96
7.66
7.65
7.65
7.27
3.66
3.64
3.62
3.61
3.60
3.59
3.57
3.35
3.33
3.32
3.31
3.29
2.79
2.16
2.15
2.14
2.13
2.12
2.11
2.10
2.09
1.89
1.81
1.80
1.79
1.78
1.76
1.75
1.74
1.69
1.68
1.66
1.65
1.64
1.63
1.52
1.51
1.50
1.49
1.48
1.46
1.36
1.35
0.00
N
N
OH
18
2.00
2.00
2.00
1.00
3.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

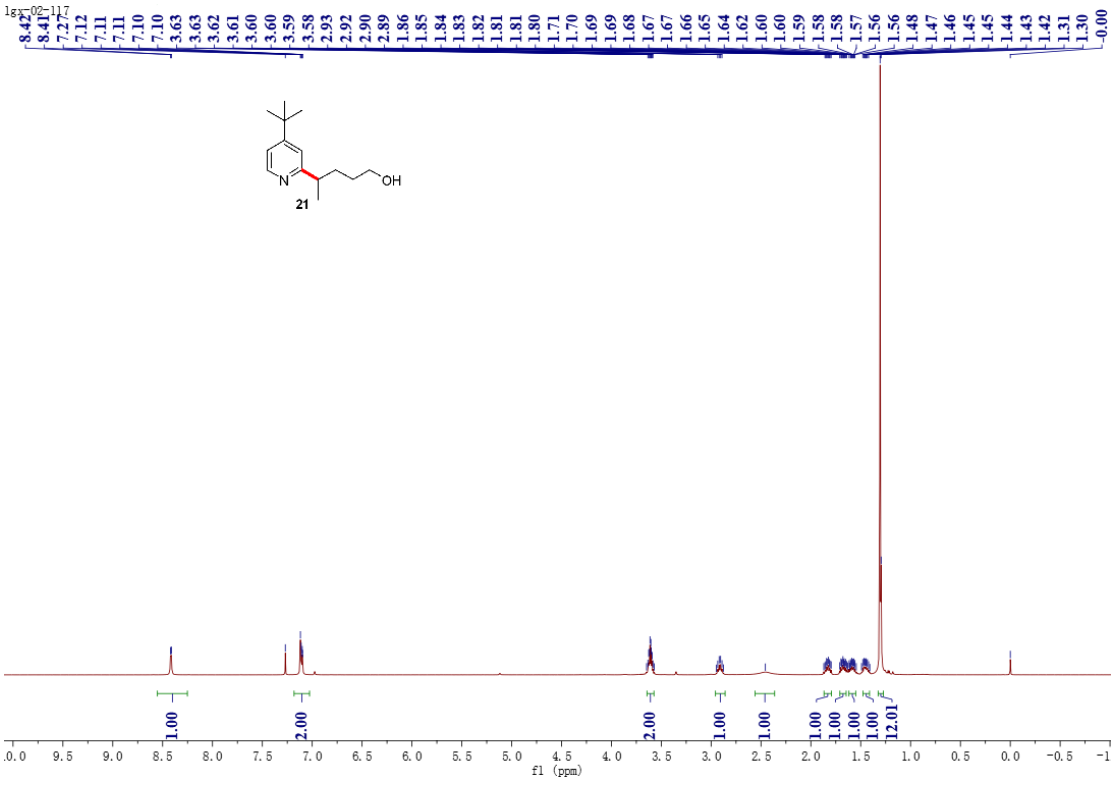

lgx-02-122-re
160.22
152.82
141.21
140.58
128.86
128.68
128.60
128.17
77.25
77.00
76.75
62.70
37.25
31.50
30.77
22.79
20.15
N
N
OH
18
f1 (ppm)

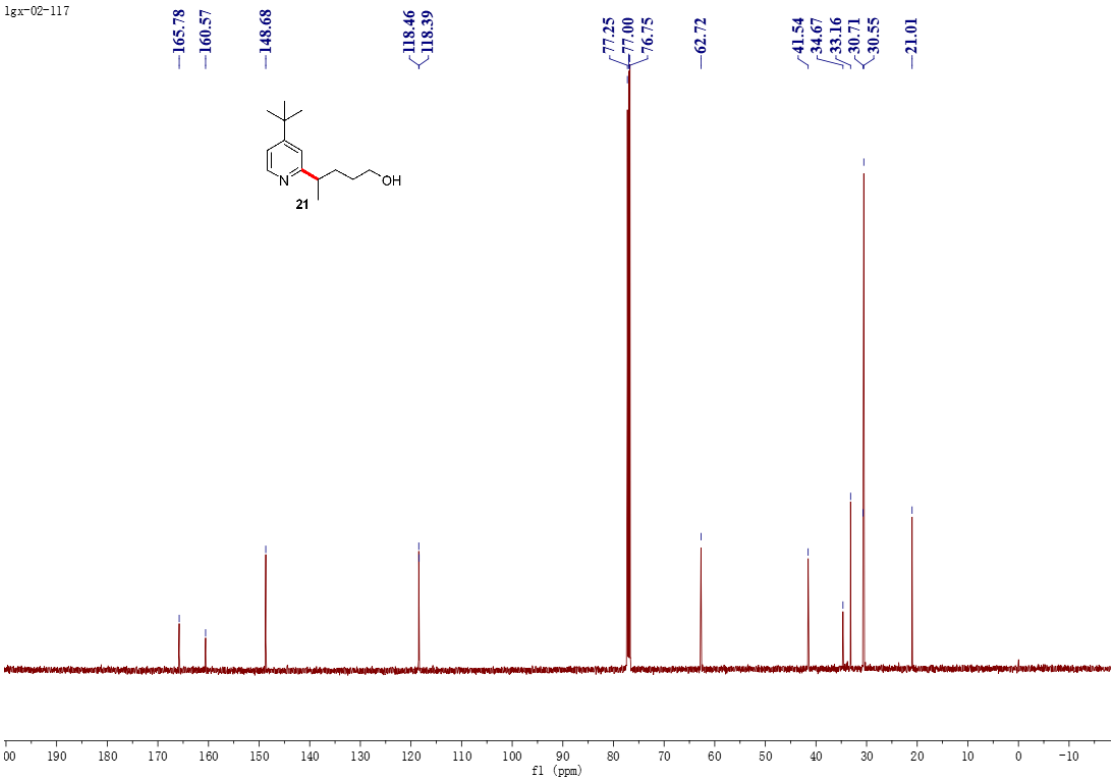

lgx-02-106
9.50
8.42
7.75
7.74
7.57
7.46
7.44
7.43
3.64
3.62
3.61
3.60
3.58
3.57
1.87
1.86
1.84
1.67
1.65
1.64
1.62
1.54
1.53
1.52
1.30
1.29
0.00
N
N
PhO2S
OH
19
1.00
1.00
2.00
1.00
2.00
1.00
1.00
3.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

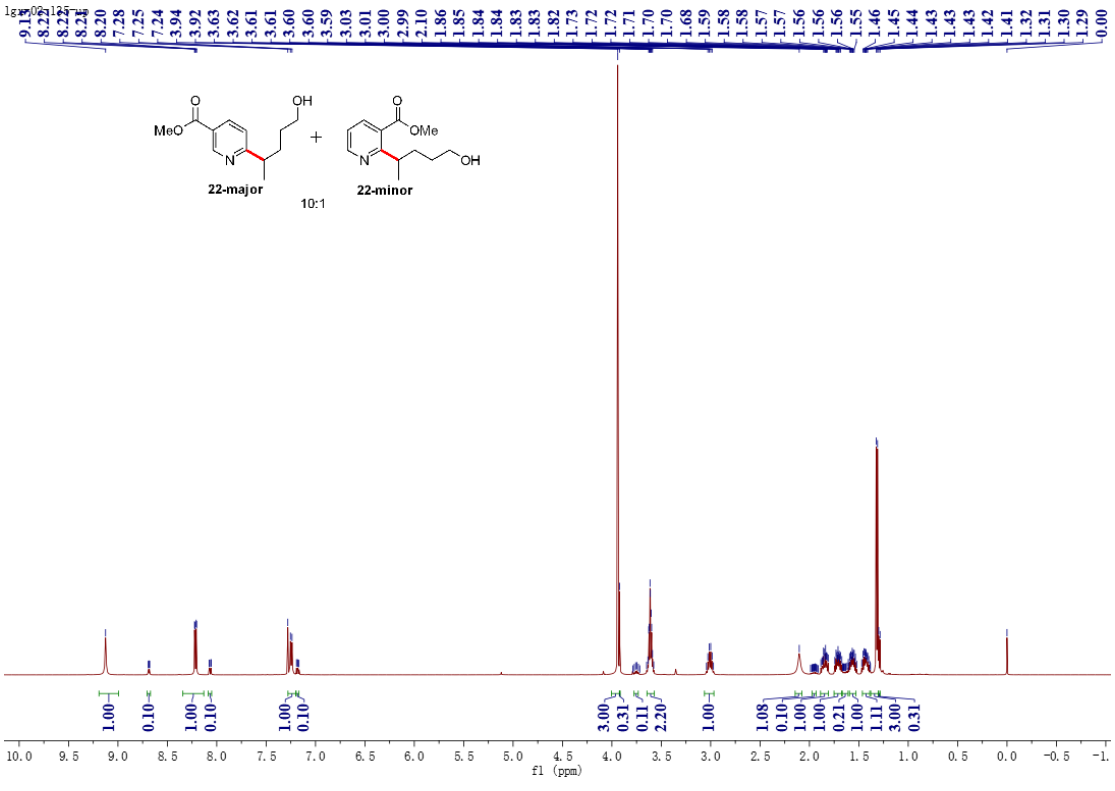

lgx-02-106
152.40
142.33
138.55
136.49
135.81
134.23
129.49
126.30
114.90
106.48
106.25
77.25
77.00
76.75
62.38
33.97
31.94
30.10
21.26
PhO2S
N
OH
19
f1 (ppm)

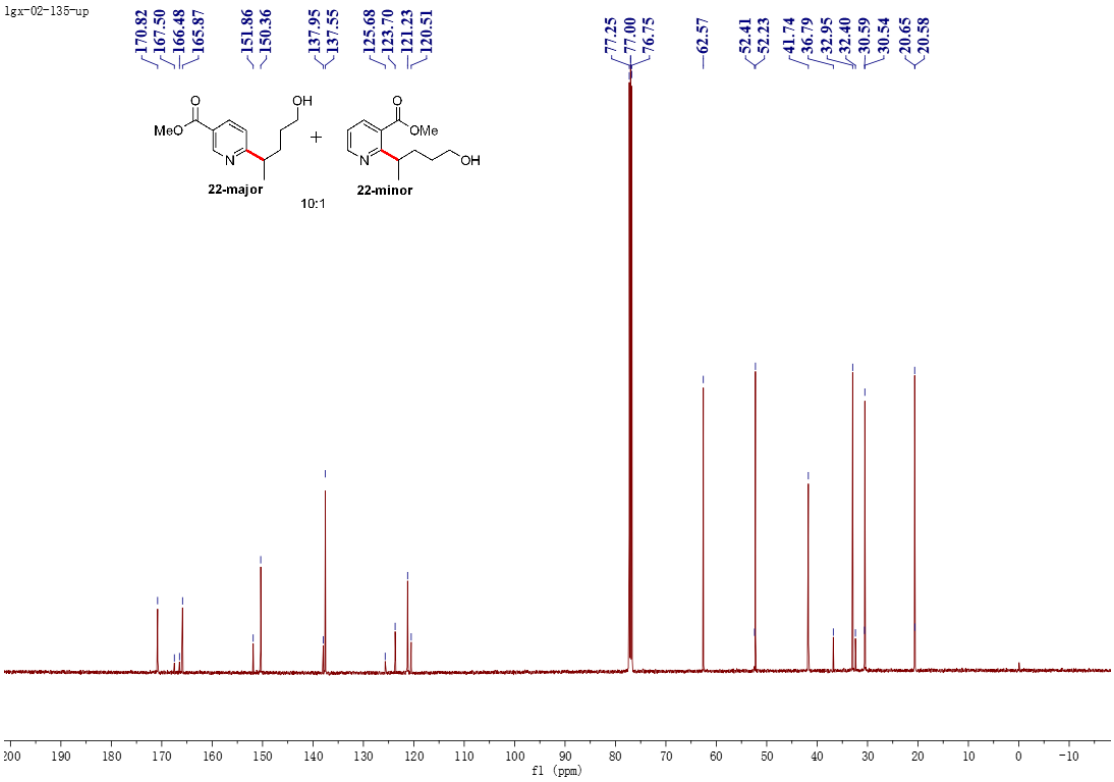

lgx-02-104
7.98
7.96
7.86
7.84
7.46
7.45
7.43
7.36
7.35
7.33
7.26
3.69
3.67
3.66
3.64
3.62
3.37
3.36
3.35
3.33
3.32
3.30
1.96
1.88
1.87
1.86
1.85
1.83
1.69
1.67
1.62
1.61
1.60
1.48
1.47
0.00
N
S
OH
20
1.00
1.00
1.00
1.00
2.00
1.00
1.00
2.00
2.00
3.00
f1 (ppm)

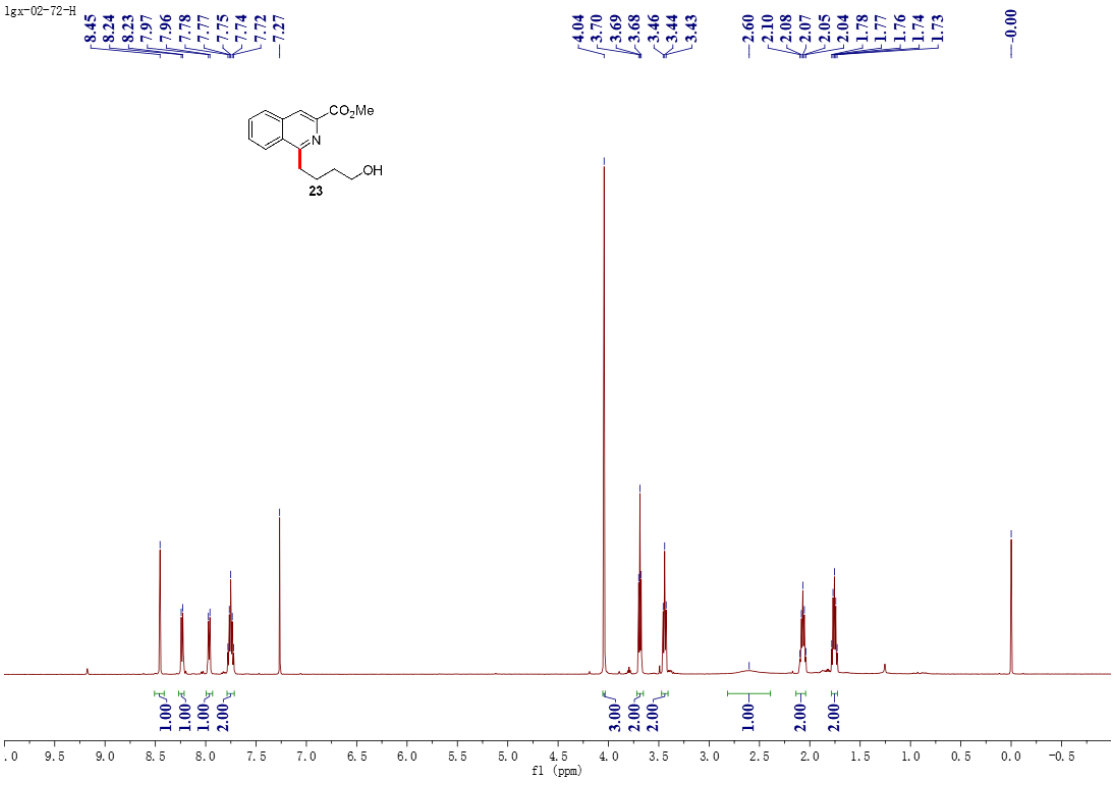

lgx-02-104
177.67
152.87
134.56
125.88
124.68
122.56
121.56
77.25
77.00
76.75
62.47
39.16
33.60
30.33
21.39
N
S
OH
20
f1 (ppm)

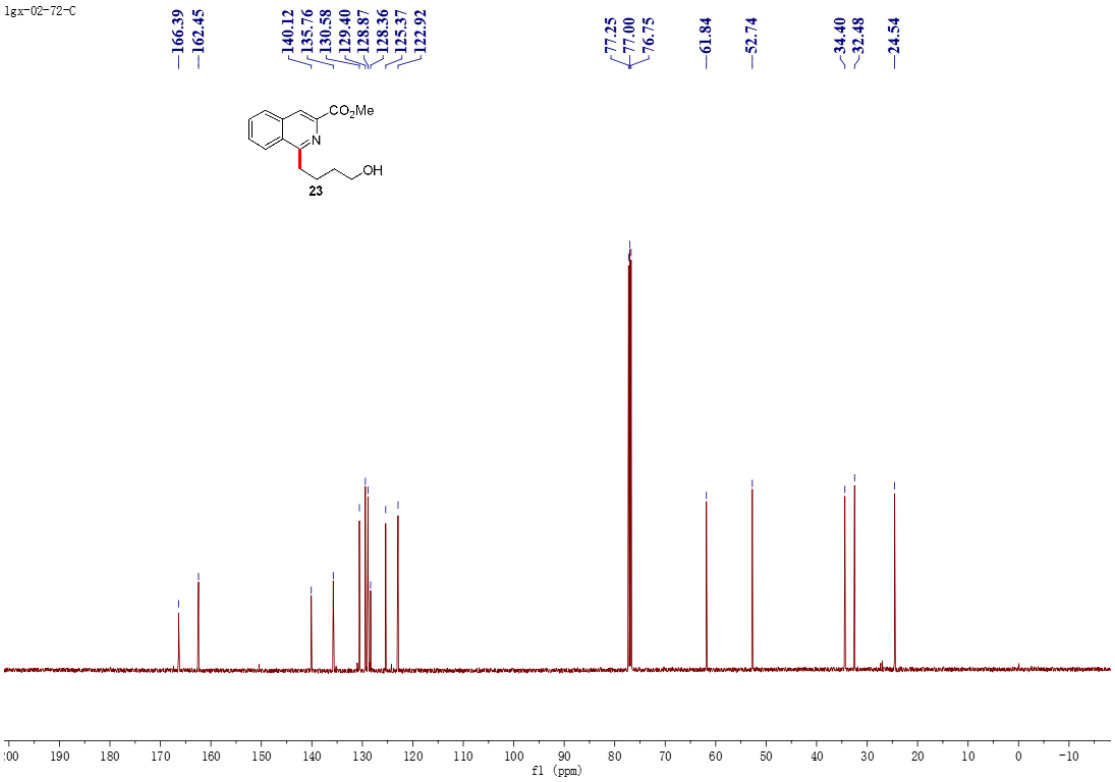

lgx-02-117
8.42
8.41
7.27
7.12
7.11
7.11
7.10
7.10
3.63
3.63
3.62
3.61
3.60
3.60
3.59
3.58
2.93
2.92
2.90
2.89
1.86
1.85
1.84
1.83
1.82
1.81
1.81
1.80
1.71
1.70
1.69
1.69
1.68
1.67
1.67
1.66
1.65
1.64
1.62
1.60
1.60
1.59
1.58
1.58
1.57
1.56
1.56
1.48
1.47
1.46
1.45
1.45
1.44
1.43
1.42
1.31
1.30
0.00
N
OH
21
1.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
12.01
f1 (ppm)

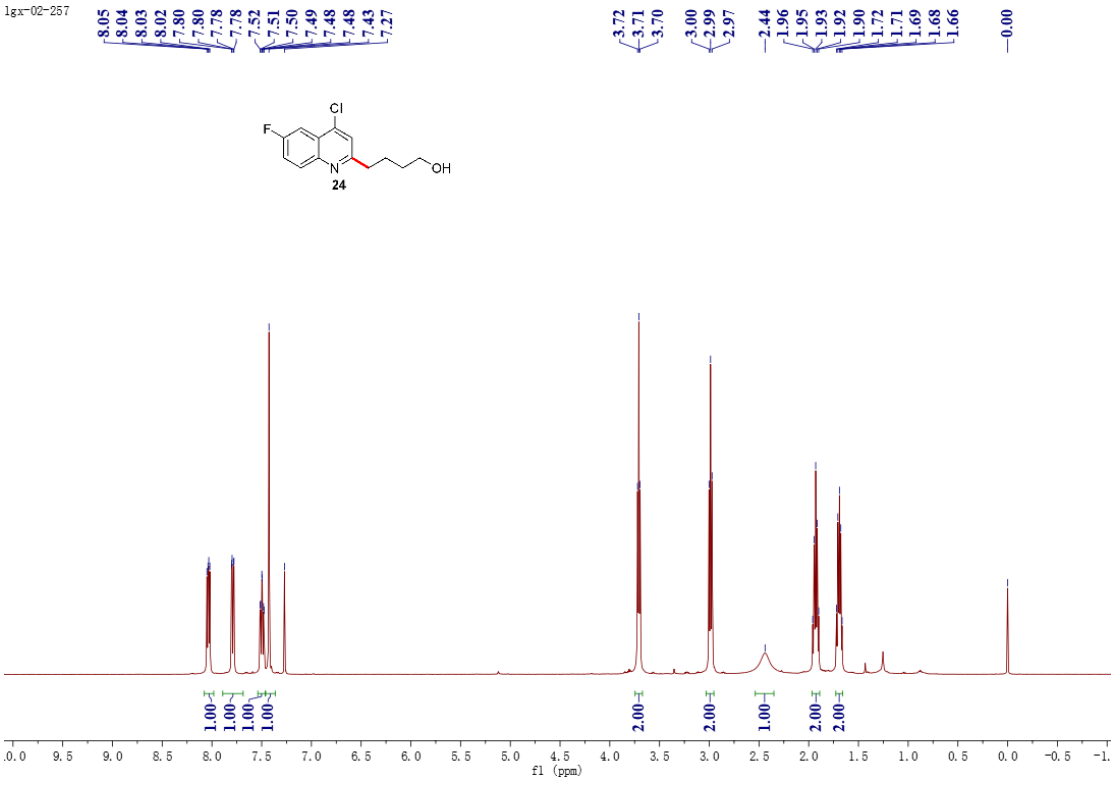

lgx-02-117
165.78
160.57
148.68
118.46
118.39
77.25
77.00
76.75
62.72
41.54
34.67
33.16
30.71
30.55
21.01
OH
N
21
f1 (ppm)

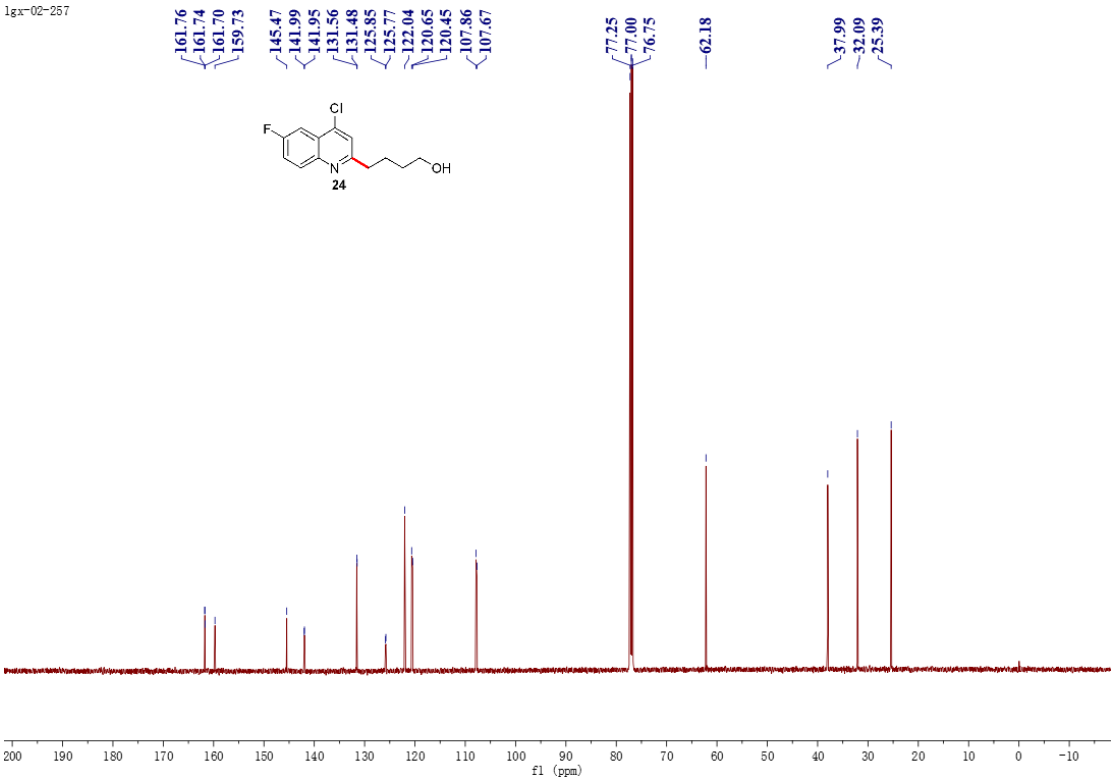

MeO
O
OH
N
22-major
10:1
OMe
22-minor
f1 (ppm)

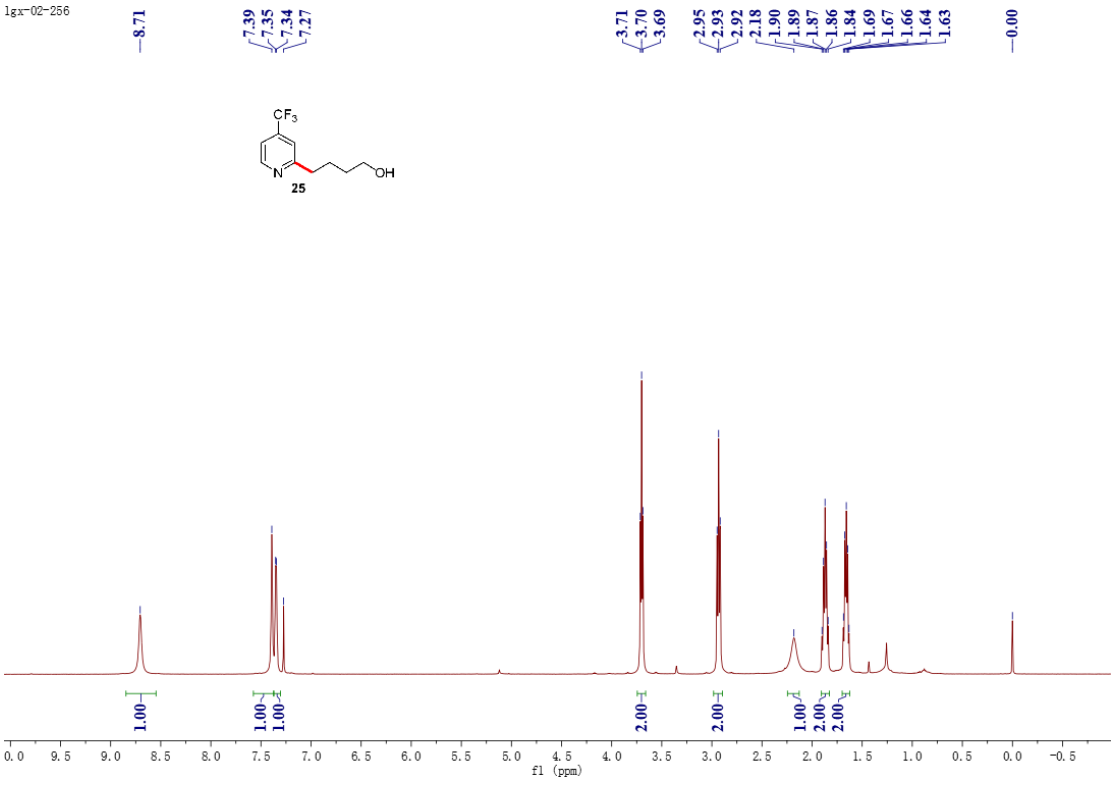

lgx-02-136-up
170.82
167.50
166.48
165.87
151.86
150.36
137.95
137.55
125.68
123.70
121.23
120.51
77.25
77.00
76.75
62.57
52.41
52.23
41.74
36.79
32.95
32.40
30.59
30.54
20.65
20.58
MeO
OH
22-major
10:1
OMe
OH
22-minor
f1 (ppm)

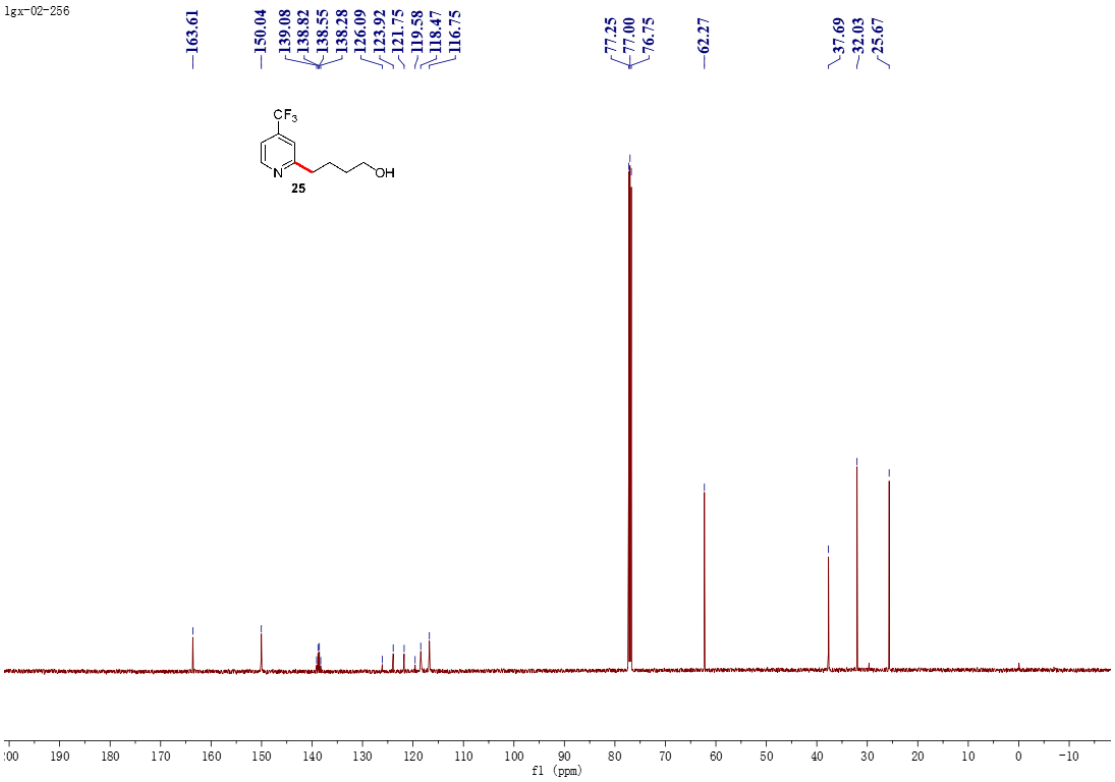

lgx-02-72-H
8.45
8.24
8.23
7.97
7.96
7.78
7.77
7.75
7.74
7.72
7.27
4.04
3.70
3.69
3.68
3.46
3.44
3.43
2.60
2.10
2.08
2.07
2.05
2.04
1.78
1.77
1.76
1.74
1.73
0.00
CO2Me
OH
23
1.00
1.00
1.00
2.00
3.00
2.00
2.00
1.00
2.00
2.00
f1 (ppm)

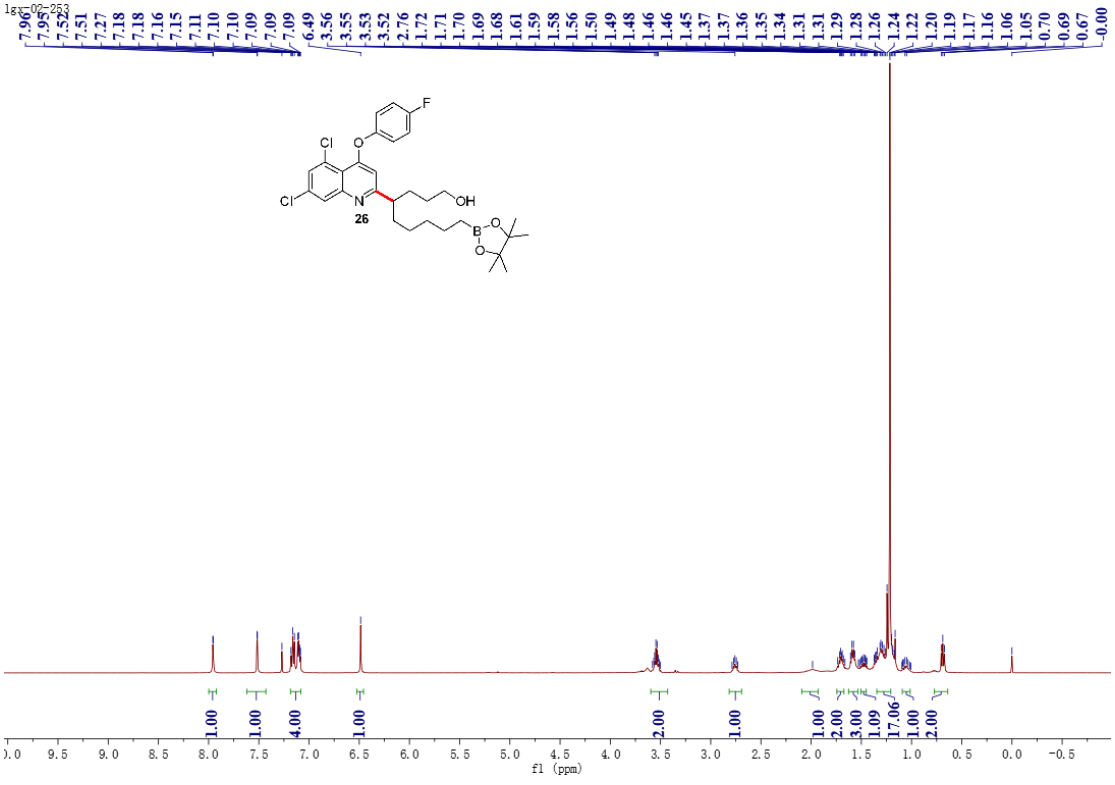

lgx-02-72-C
166.39
162.45
140.12
135.76
130.58
129.40
128.87
128.36
125.37
122.92
77.25
77.00
76.75
61.84
52.74
34.40
32.48
24.54
CO2Me
N
OH
23
f1 (ppm)

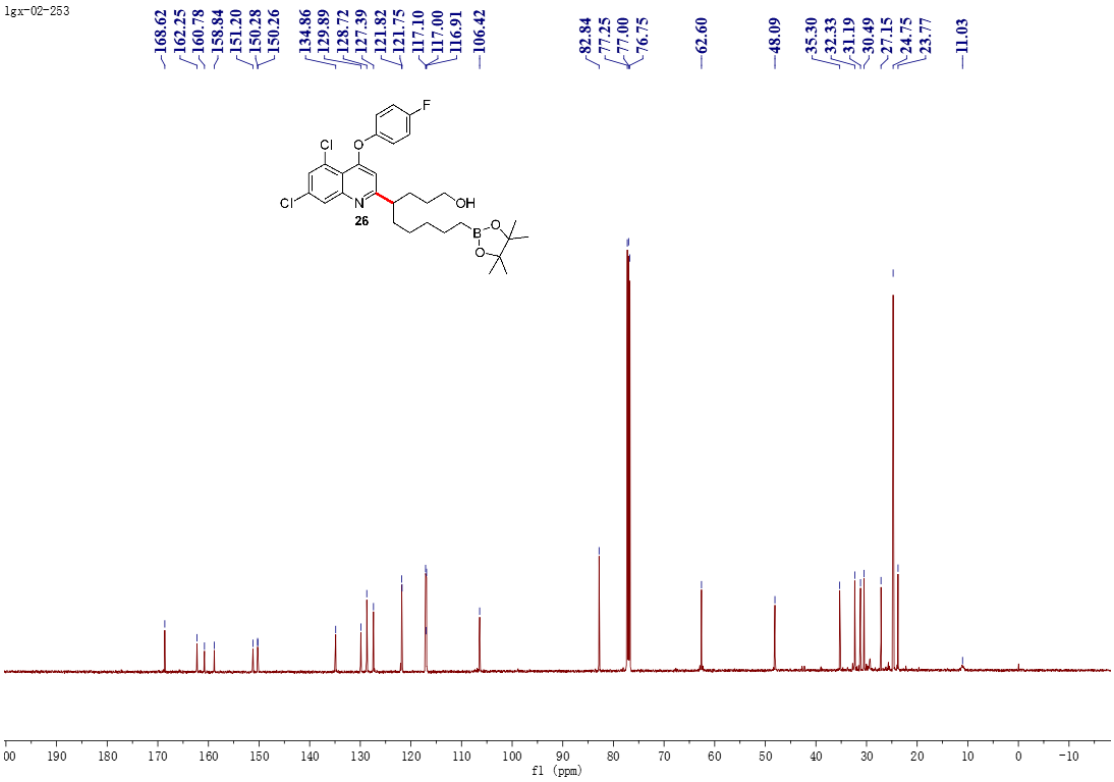

lgx-02-257
8.05
8.04
8.03
8.02
7.80
7.80
7.78
7.78
7.52
7.51
7.50
7.49
7.48
7.48
7.43
7.27
3.72
3.71
3.70
3.00
2.99
2.97
2.44
1.96
1.95
1.93
1.92
1.90
1.72
1.71
1.69
1.68
1.66
0.00
Cl
F
N
OH
24
1.00
1.00
1.00
1.00
2.00
2.00
1.00
2.00
2.00
f1 (ppm)

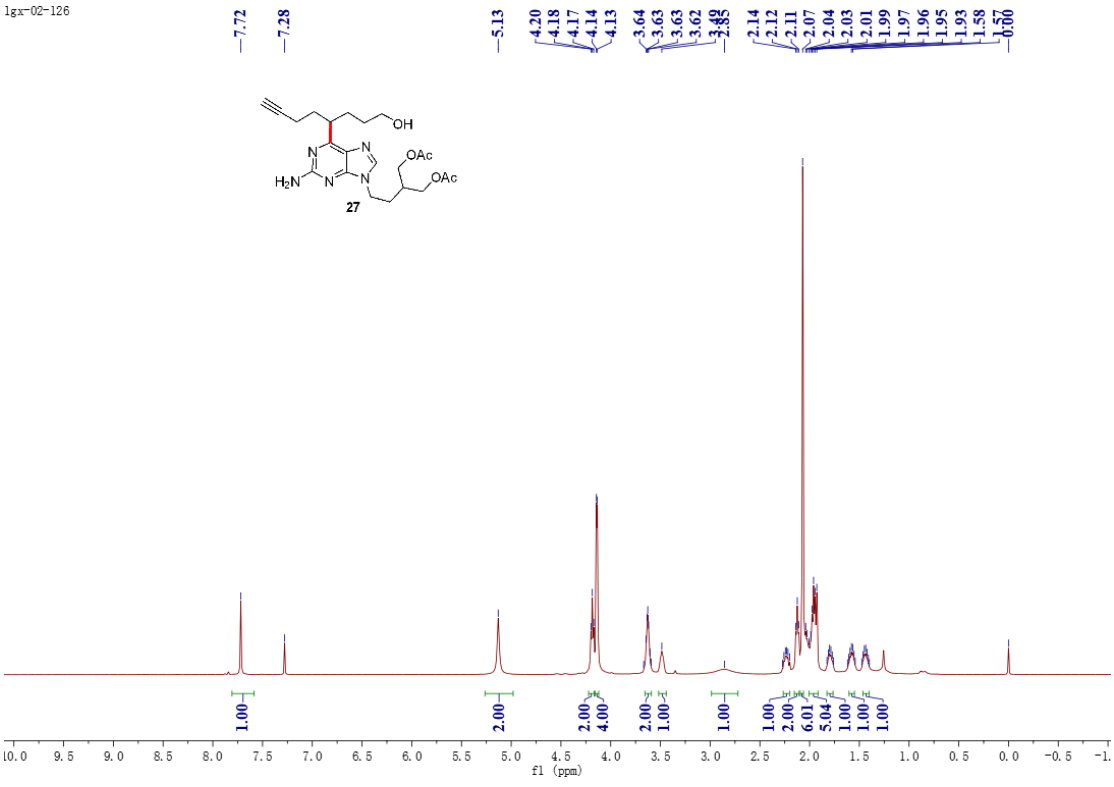

1gx-02-257
161.76
161.74
161.70
159.73
145.47
141.99
141.95
131.56
131.48
125.85
125.77
122.04
120.65
120.45
107.86
107.67
77.25
77.00
76.75
62.18
37.99
32.09
25.39
Cl
F
N
OH
24
f1 (ppm)

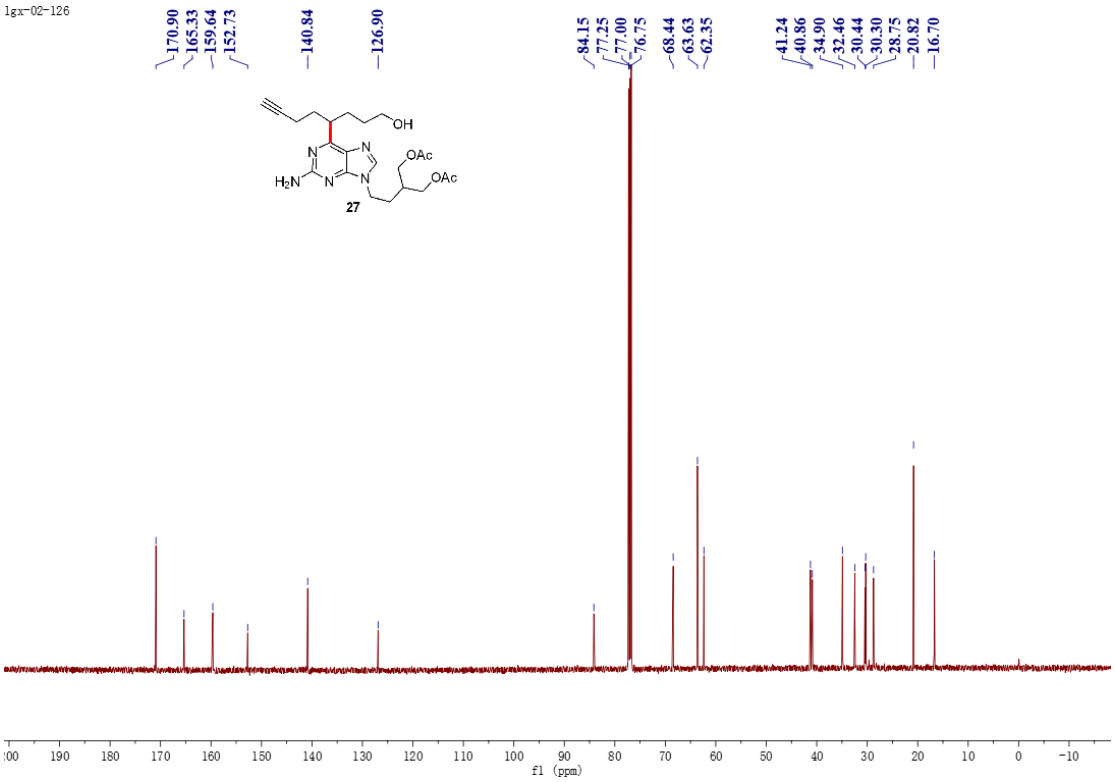

1gx-02-256
8.71
7.39
7.35
7.34
7.27
3.71
3.70
3.69
2.95
2.93
2.92
2.18
1.90
1.89
1.87
1.86
1.84
1.69
1.67
1.66
1.64
1.63
0.00
CF3
N
OH
25
1.00
1.00
1.00
2.00
2.00
1.00
2.00
2.00
f1 (ppm)

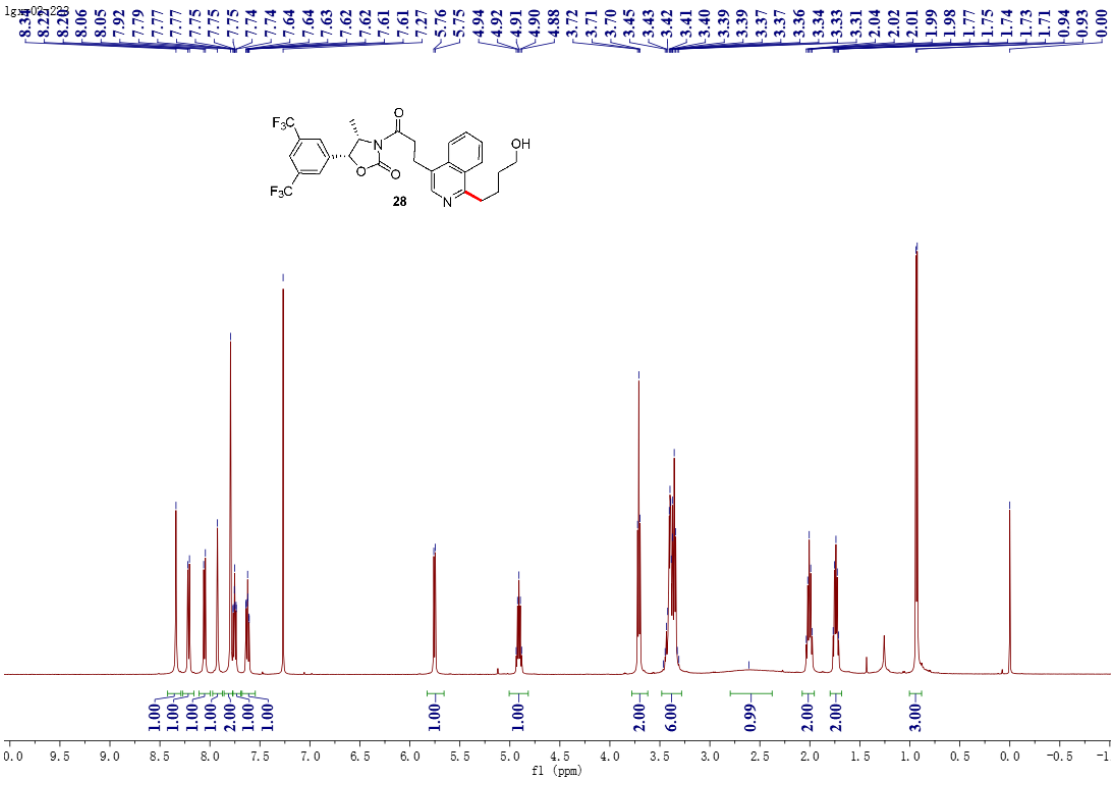

lgx-02-256
163.61
150.04
139.08
138.82
138.55
138.28
126.09
123.92
121.75
119.58
118.47
116.75
77.25
77.00
76.75
62.27
37.69
32.03
25.67
CF3
N
OH
25
f1 (ppm)

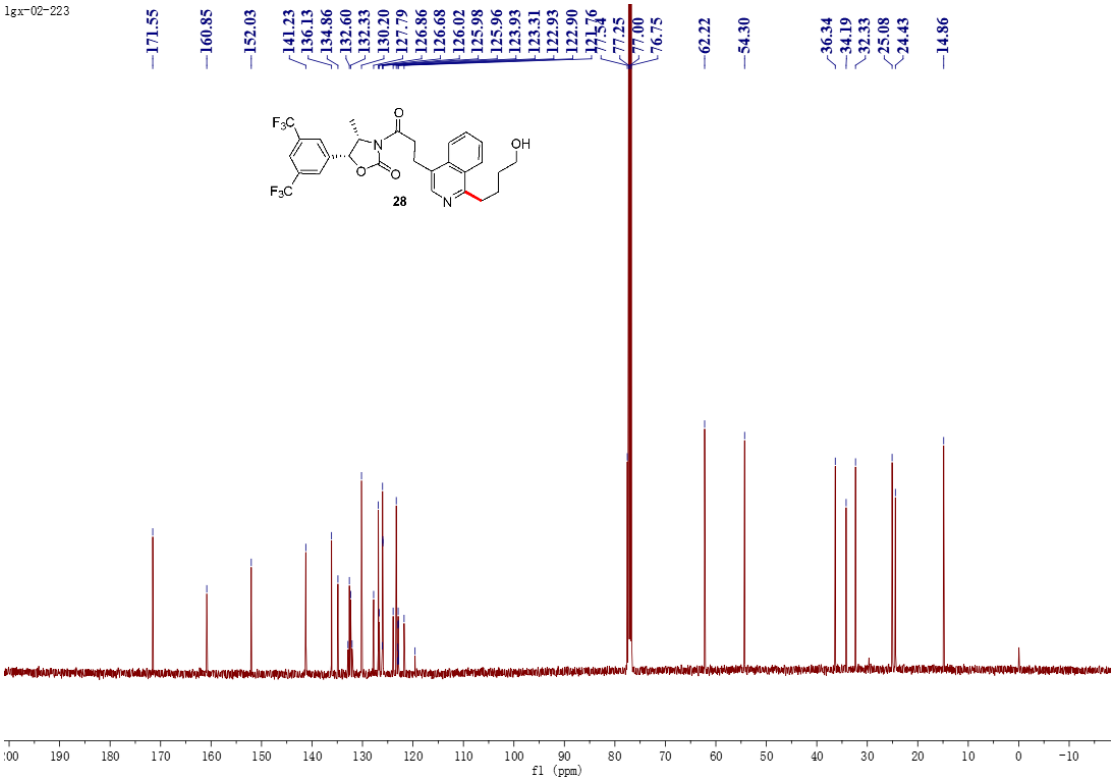

lgx-02-253
F
Cl
O
Cl
N
OH
B
O
O
26
1.00
1.00
4.00
1.00
2.00
1.00
1.00
2.00
3.00
1.09
17.06
1.00
2.00
f1 (ppm)

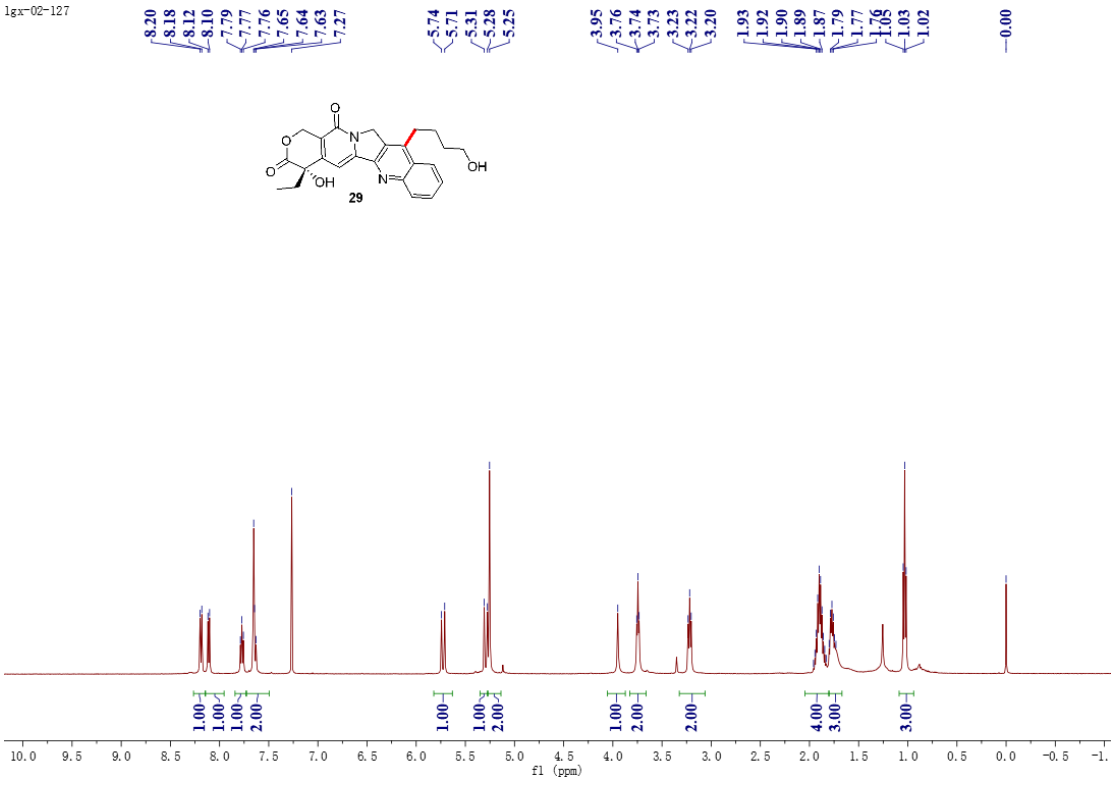

1gx-02-253
168.62
162.25
160.78
158.84
151.20
150.28
150.26
134.86
129.89
128.72
127.39
121.82
121.75
117.10
117.00
116.91
106.42
82.84
77.25
77.00
76.75
62.60
48.09
35.30
32.33
31.19
30.49
27.15
24.75
23.77
11.03
F
O
Cl
Cl
N
OH
B
O
O
26
f1 (ppm)

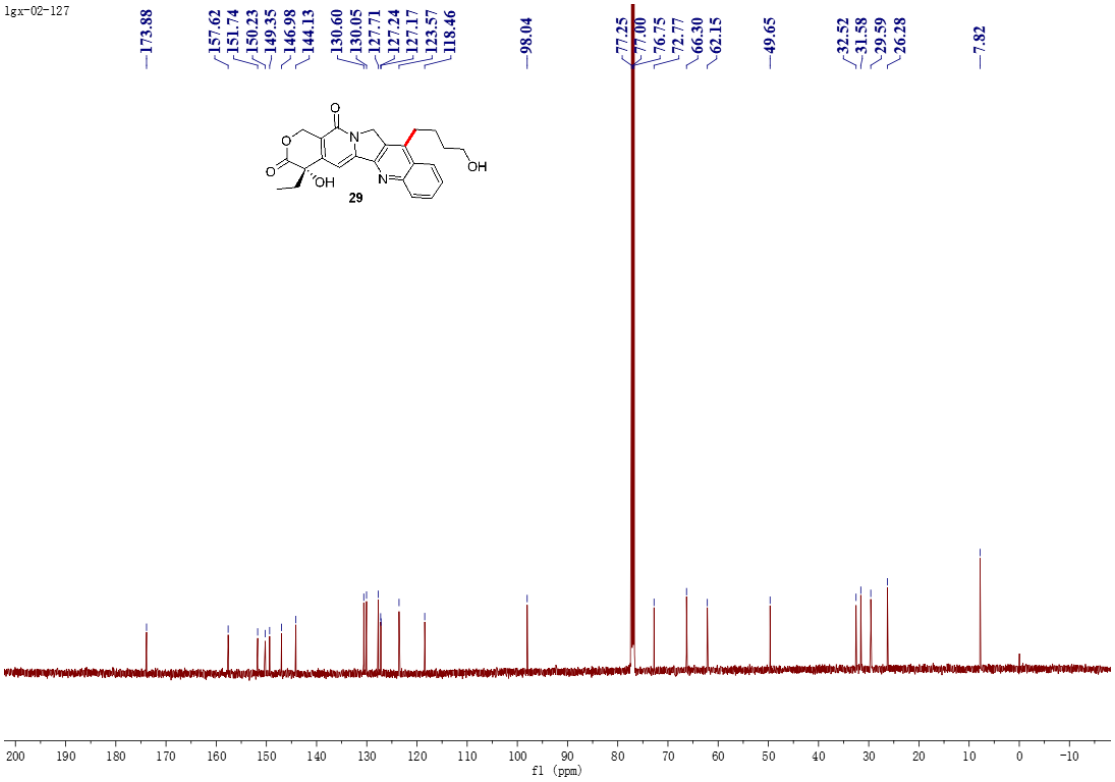

1gx-02-126
7.72
7.28
5.13
4.20
4.18
4.17
4.14
4.13
3.64
3.63
3.63
3.62
2.14
2.12
2.11
2.07
2.04
2.03
2.01
1.99
1.97
1.96
1.95
1.93
1.58
0.00
OH
N
N
N
H2N
OAc
OAc
27
1.00
2.00
2.00
4.00
2.00
1.00
1.00
1.00
2.00
6.01
5.04
1.00
1.00
1.00
f1 (ppm)

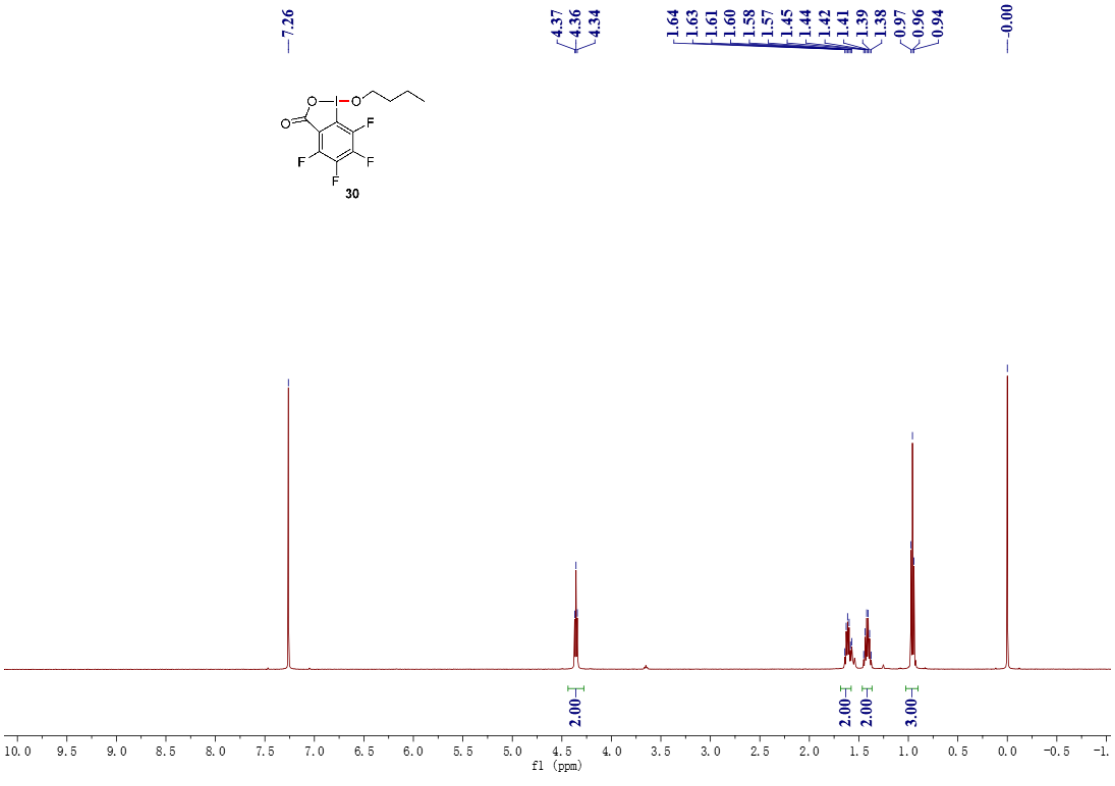

lgx-02-126
170.90
165.33
159.64
152.73
140.84
126.90
84.15
77.25
77.00
76.75
68.44
63.63
62.35
41.24
40.86
34.90
32.46
30.44
30.30
28.75
20.82
16.70
OH
OAc
OAc
N
N
N
N
H2N
27
f1 (ppm)

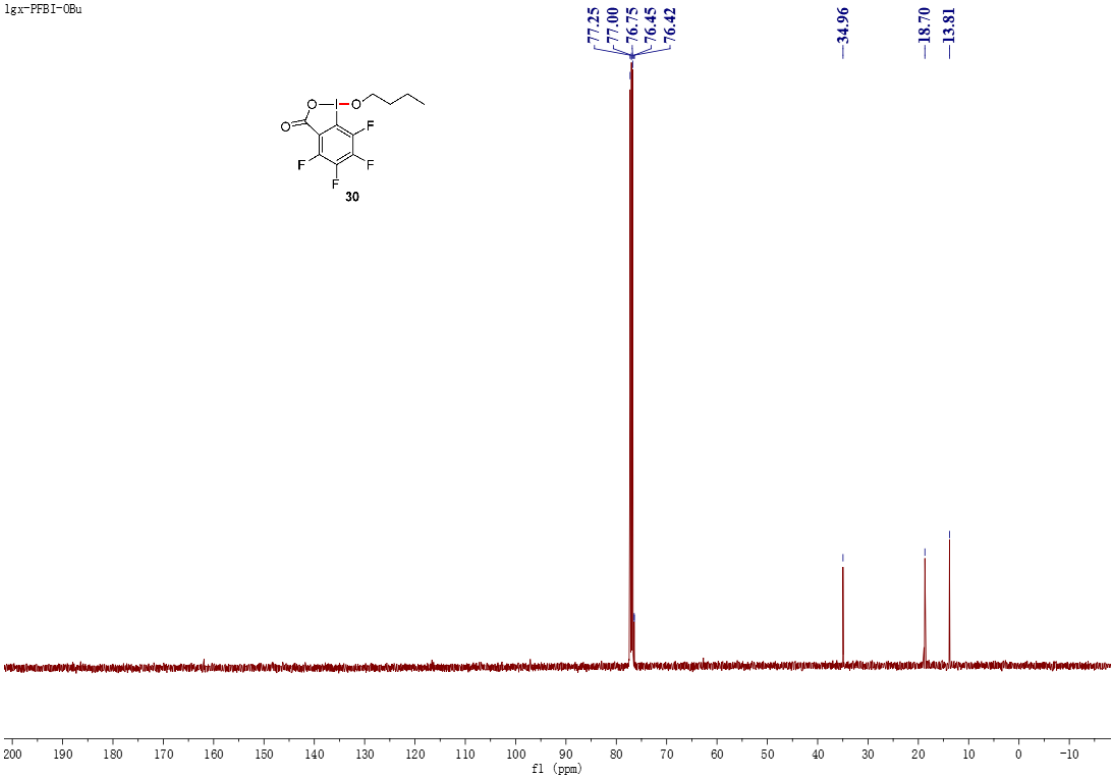

F3C
F3C
O
N
O
O
OH
N
28
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
2.00
6.00
0.99
2.00
2.00
3.00
f1 (ppm)

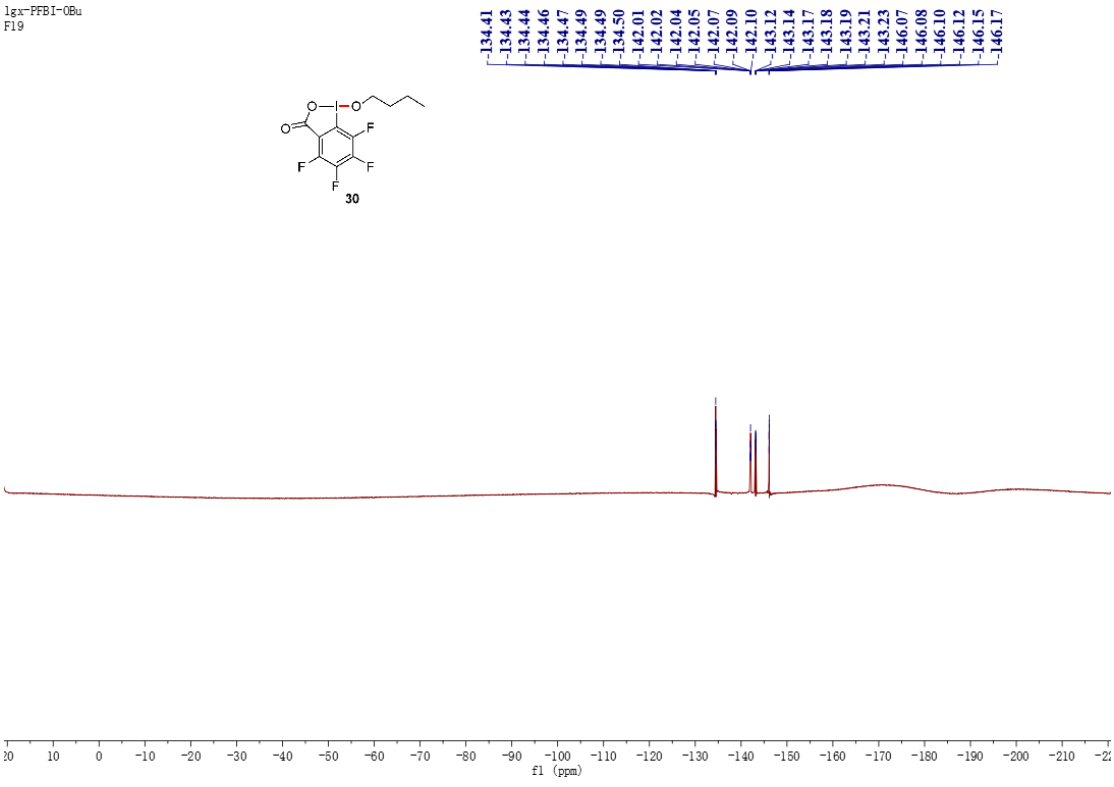

lgx-02-223
171.55
160.85
152.03
141.23
136.13
134.86
132.60
132.33
130.20
127.79
126.86
126.68
126.02
125.98
125.96
123.93
123.31
122.93
122.90
121.76
121.54
77.25
77.00
76.75
62.22
54.30
36.34
34.19
32.33
25.08
24.43
14.86
F3C
F3C
O
N
O
O
OH
N
28
f1 (ppm)

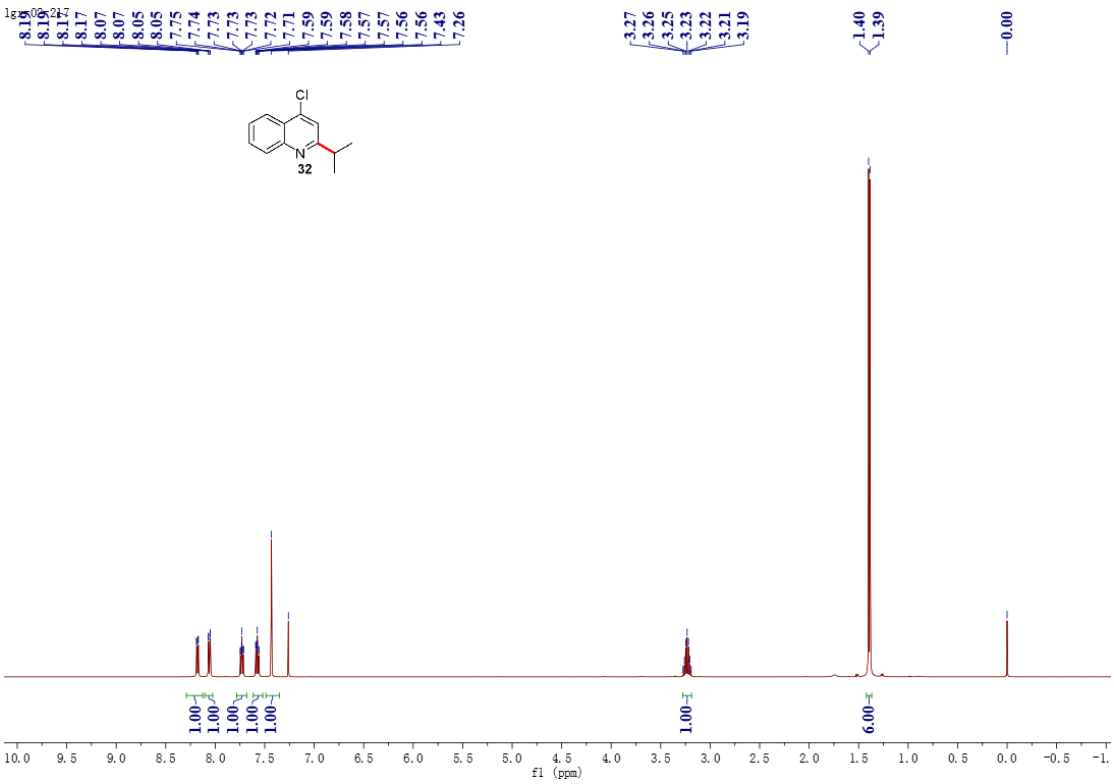

lgx-02-127
8.20
8.18
8.12
8.10
7.79
7.77
7.76
7.65
7.64
7.63
7.27
5.74
5.71
5.31
5.28
5.25
3.95
3.76
3.74
3.73
3.23
3.22
3.20
1.93
1.92
1.90
1.89
1.87
1.79
1.77
1.76
1.05
1.03
1.02
0.00
O
O
N
OH
OH
N
29
1.00
1.00
1.00
2.00
1.00
1.00
2.00
1.00
2.00
2.00
4.00
3.00
3.00
f1 (ppm)


lgx-02-127
173.88
157.62
151.74
150.23
149.35
146.98
144.13
130.60
130.05
127.71
127.24
127.17
123.57
118.46
98.04
77.25
77.00
76.75
72.77
66.30
62.15
49.65
32.52
31.58
29.59
26.28
7.82
OH
OH
29
f1 (ppm)


7.26
4.37
4.36
4.34
1.64
1.63
1.61
1.60
1.58
1.57
1.45
1.44
1.42
1.41
1.39
1.38
0.97
0.96
0.94
0.00
F
F
F
F
30
2.00
2.00
2.00
3.00
f1 (ppm)


lgx-PFBI-OBu
77.25
77.00
76.75
76.45
76.42
34.96
18.70
13.81
30
f1 (ppm)


lgx-PFBI-OBu
F19
134.41
134.43
134.44
134.46
134.47
134.49
134.49
134.50
142.01
142.02
142.04
142.05
142.07
142.09
142.10
143.12
143.14
143.17
143.18
143.19
143.21
143.23
146.07
146.08
146.10
146.12
146.15
146.17
30
f1 (ppm)


8.19
8.19
8.17
8.17
8.07
8.07
8.05
8.05
7.75
7.74
7.73
7.73
7.73
7.72
7.71
7.59
7.58
7.57
7.57
7.56
7.56
7.43
7.26
3.27
3.26
3.25
3.23
3.22
3.21
3.19
1.40
1.39
0.00
Cl
N
32
1.00
1.00
1.00
1.00
1.00
1.00
6.00
f1 (ppm)