Supporting Information

Exploring the ring-opening reactions of imidazo[1,5-a]quinolines for the synthesis of imides under photochemical conditions

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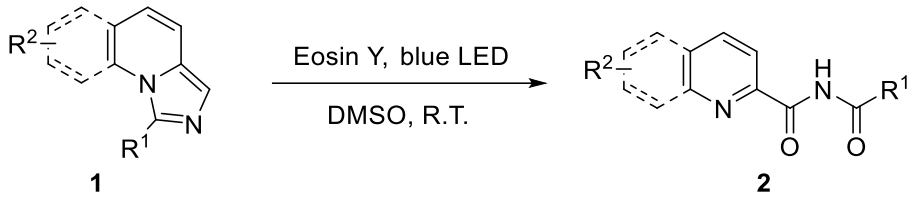
1. General Information

^{1}HNMR and ^{13}CNMR spectra were recorded at 400MHz and 100MHz respectively, The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet of doublets), coupling constants (Hz) and integration, using tetramethylsilane (TMS) as internal reference, in $CDCl_3$. High resolution mass spectra was obtained using electrospray ionization (ESI) method on a TOF mass analyzer. Unless otherwise indicated, all commercial reagents and solvents were used without further purification.

2. General Experimental Procedure

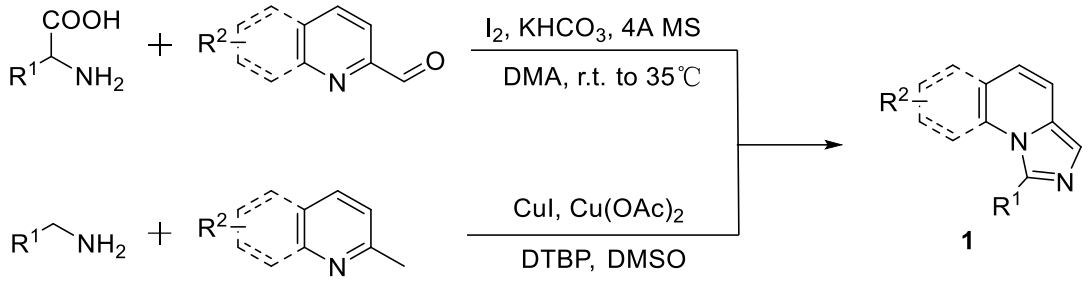
2.1. General Experimental Procedure for the Synthesis of Imides 2



1 **2**

Imidazo[1,5-a]quinoline (**1**, 0.2 mmol), Eosin Y (5.0 mol %), and DMSO (1.5 mL) were added to an oven-dried reaction vessel equipped with a magnetic stir bar, and the reaction vessel was irradiated using 5 W blue LEDs at room temperature under ambient air for 12h. After the reaction was completed, the resulting mixture was extracted with EtOAc, washed by H_2O. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Products were purified by flash chromatography on 200−300 mesh silica gels using petroleum ether/ethyl acetate as eluent to afford the pure products **2**.

2.2. General Experimental Procedure for the Synthesis of 1

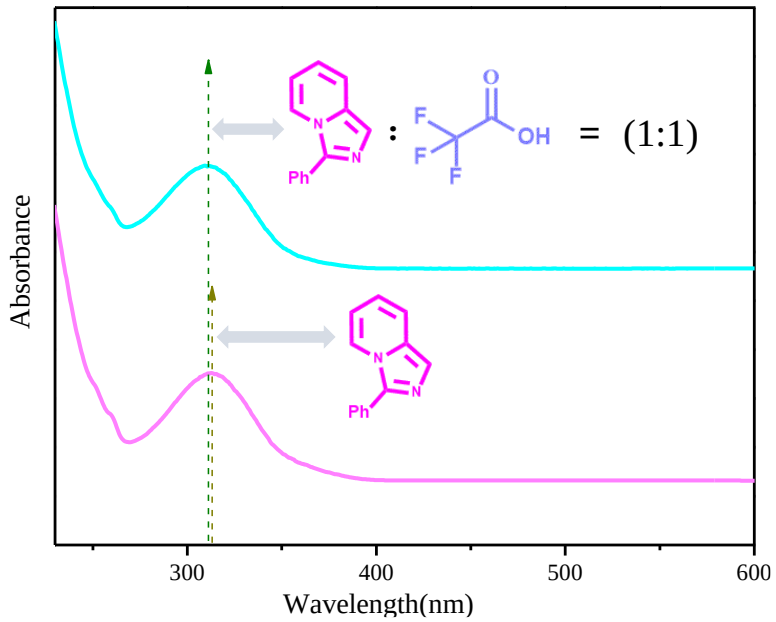


Imidazo[1,5-a]quinolines **1a**, **1b**, **1m-1q** were prepared by using following the reported methodology (*J. Org. Chem.*, 2012, **77**, 11161). L-Phenylglycine (1.84 g, 11 mmol) and potassium bicarbonate (2.00 g, 20 mmol) weighed into a 100 mL round bottom flask, followed by DMA (30 mL). Then, 2-quinolinecarboxaldehyde (0.95 mL, 10 mmol) was added to this mixture, and finally I_2 (2.54g, 10 mmol) was added under stirring. The reaction is carried out under nitrogen atmosphere at room temperature for 12 h. The reaction process was monitored by TLC. After the reaction was completed, the resulting mixture was extracted with EtOAc and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Products were purified by flash chromatography on 200−300 mesh silica gels using petroleum ether/ethyl acetate as the eluent.

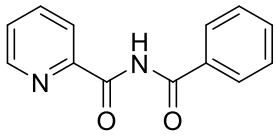
Other imidazo[1,5-a]quinolines were prepared by using following the reported methodology (*J. Org. Chem.*, 2016, **81**, 4386). CuI (38.1 mg, 0.2 mmol) and $Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol) was dissolved in a reaction tube using 1.5 mL of DMSO, and then benzylamine (65.6 μL, 0.6 mmol), 2-methylquinoline (27.1 μL, 0.2 mmol) and DTBP (73.3 μL, 0.4 mmol) were added, sequentially. The mixture was stirred at 110 °C for 24 h, and the reaction process was monitored by TLC. After the reaction was completed, The reaction system was allowed to attain room temperature and extracted with ethyl acetate (3 × 20 mL), and then the organic layer was washed with brine (2 × 10 mL) and dried with anhydrous Na_2SO_4. Subsequently, the solvent was removed under reduced pressure and the remaining crud product was purified by column chromatography over silica gel.

2.3. UV Characterization Data of 1a

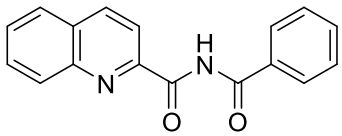
The ultraviolet spectra of the **1a** and **1a** : TFA = 1:1 were recorded on a SHIMADZU Model 2550 UV-visible spectrophotometer (600 to 230 nm). The absorbances and ε of the samples was recorded at 312 nm, red-shift occurred in the addition of TFA and the absorbances and ε of the samples was recorded at 309 nm.



3. Characterization Data of Products

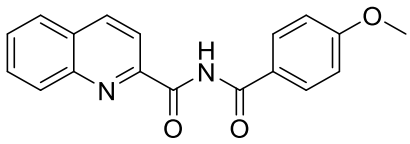


N-benzoylpicolinamide (**2a**): 85% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ11.53 (s, 1H), 8.66-8.64 (m, 1H), 8.33 (d, *J*=7.8 Hz, 1H), 8.00-7.93 (m, 3H), 7.64-7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 161.9, 148.5, 148.3, 138.0, 133.4, 133.0, 128.9, 127.8, 127.7, 123.3; HRMS (ESI): calcd for $C_{13}H_{11}N_2O_2$ $[M+H]^+$ 227.0821, found 227.0823.

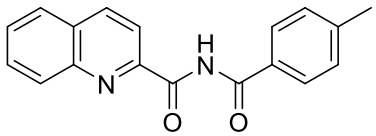


N-benzoylquinoline-2-carboxamide (**2b**): 94% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 8.39 (s, 2H), 8.19 (d, *J*=8.5 Hz, 1H), 8.07-8.05(m, 2H),

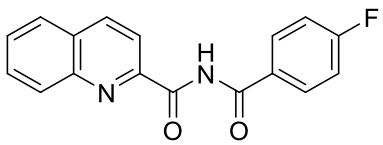
7.93 (d, *J*=7.8 Hz, 1H), 7.85-7.81 (m, 1H), 7.71-7.64 (m, 2H), 7.60-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 162.1, 148.2, 146.1, 138.3, 133.5, 133.1, 130.7, 129.9, 129.9, 129.0, 128.9, 127.9, 127.9, 118.9; HRMS (ESI): calcd for $C_{17}H_{13}N_2O_2$ $[M+H]^+$ 277.0977, found 277.0979.



N-(4-methoxybenzoyl)quinoline-2-carboxamide (**2c**): 76% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 8.38 (s, 2H), 8.19 (d, *J*=8.5 Hz, 1H), 8.05-8.01 (m, 2H), 7.94-7.91 (m, 1H), 7.85-7.80 (m, 1H), 7.70-7.66 (m, 1H), 7.06-7.02 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.5, 162.1, 148.5, 146.1, 138.2, 130.6, 130.0, 129.9, 129.8, 128.8, 127.9, 125.8, 118.9, 114.2, 55.5; HRMS (ESI): calcd for $C_{18}H_{15}N_2O_3$ $[M+H]^+$ 307.1083, found 307.1080.

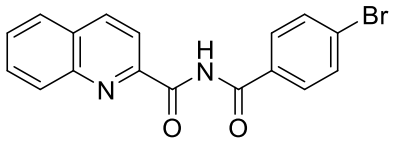


N-(4-methylbenzoyl)quinoline-2-carboxamide (**2d**): 85% yield; yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.71 (s, 1H), 8.39 (s, 2H), 8.18 (d, *J*=8.5 Hz, 1H), 7.97-7.92 (m, 3H), 7.85-7.81 (m, 1H), 7.71-7.67 (m, 1H), 7.38-7.36 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.1, 148.4, 146.1, 143.9, 138.3, 130.8, 130.6, 129.9, 129.8, 129.6, 128.9, 127.9, 127.9, 118.9, 21.6; HRMS (ESI): calcd for $C_{18}H_{15}N_2O_2$ $[M+H]^+$ 291.1134, found 291.1139.

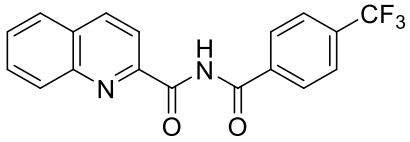


N-(4-fluorobenzoyl)quinoline-2-carboxamide (**2e**): 73% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.68 (s, 1H), 8.42-8.37 (m, 2H), 8.20 (d, *J*=8.5 Hz, 1H), 8.11-8.06 (m, 2H), 7.95 (d, *J*=8.2 Hz, 1H), 7.87-7.83 (m, 1H), 7.73-7.69 (m, 1H), 7.28

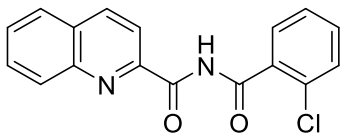
-7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, *J* = 254.7 Hz), 164.0, 162.1, 148.2, 146.1, 138.4, 130.7, 130.5 (d, *J* = 9.3 Hz), 130.0, 129.8, 129.8 (d, *J* = 3.1 Hz), 129.0, 127.9, 118.9, 116.1 (d, *J* = 22.1 Hz).HRMS (ESI): calcd for $C_{17}H_{12}FN_2O_2$ $[M+H]^+$ 295.0883, found 295.0881.



N-(4-bromobenzoyl)quinoline-2-carboxamide (**2f**): 78% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.42-8.36 (m, 2H), 8.18 (d, *J*=8.5 Hz, 1H), 7.95-7.89 (m, 3H), 7.86-7.82 (m, 1H), 7.73-7.68 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 162.0, 148.1, 146.1, 138.4, 132.4, 132.2, 130.8, 130.0, 129.8, 129.5 , 129.0, 128.1, 127.9, 118.9; HRMS (ESI): calcd for $C_{17}H_{12}BrN_2O_2$ $[M+H]^+$ 355.0082, found 355.0086.

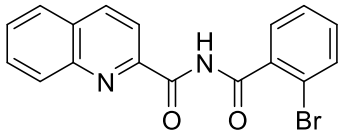


N-(4-(trifluoromethyl)benzoyl)quinoline-2-carboxamide (**2g**): 80% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 8.43-8.37 (m, 2H), 8.19 (d, *J*=8.5 Hz, 1H), 8.15-8.13(m, 2H), 7.95 (d, *J*=8.1 Hz, 1H), 7.87-7.83 (m, 3H), 7.72 (t, *J*=7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 162.1, 147.9, 146.1, 138.5, 136.8, 134.5 (q, *J* = 32.9 Hz), 130.8, 130.0, 129.8, 129.1, 128.4, 127.9, 126.0 (q, *J* = 3.7 Hz), 123.5 (d, *J* = 272.8 Hz), 118.9. HRMS (ESI): calcd for $C_{18}H_{12}F_3N_2O_2$ $[M+H]^+$ 345.0851, found 345.0854.

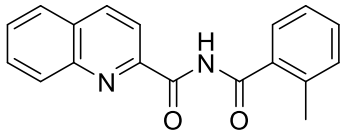


N-(2-chlorobenzoyl)quinoline-2-carboxamide (**2h**): 77% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (s, 1H), 8.37 (d, *J*=8.5 Hz, 1H), 8.30 (d, *J*=8.5 Hz, 1H), 8.16 (d, *J*=8.6 Hz, 1H), 7.92 (d, *J*=8.2 Hz, 1H), 7.84-7.80 (m, 1H), 7.75-7.64 (m, 2H), 7.53-7.45 (m, 2H), 7.42 (td, *J*=7.2, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

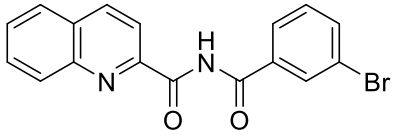
166.0, 162.1, 147.6, 146.2, 138.2, 134.7, 132.0, 130.8, 130.7, 130.1, 129.9, 129.9, 129.0, 127.8, 127.2, 118.9; HRMS (ESI): calcd for $C_{17}H_{12}ClN_2O_2$ $[M+H]^+$ 311.0587, found 311.0589.



N-(2-bromobenzoyl)quinoline-2-carboxamide (**2i**): 65% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ11.36 (s, 1H), 8.37 (d, *J*=8.5 Hz, 1H), 8.29 (d, *J*=8.5 Hz, 1H), 8.17 (d, *J*=8.6 Hz, 1H), 7.92 (d, *J*=8.2 Hz, 1H), 7.85-7.81 (m, 1H), 7.71-7.67 (m, 2H), 7.60 (dd, *J*=7.6, 1.7 Hz, 1H), 7.46 (td, *J*=7.5, 1.2 Hz, 1H), 7.39 (td, *J*=7.7, 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.1, 147.5, 146.2, 138.2, 137.3, 133.2, 131.8, 130.7, 129.9, 129.3, 129.0, 127.8, 127.6, 119.0, 118.9; HRMS (ESI): calcd for $C_{17}H_{12}BrN_2O_2$ $[M+H]^+$ 355.0082, found 355.0087.

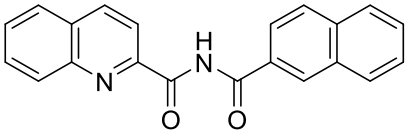


N-(2-methylbenzoyl)quinoline-2-carboxamide (**2j**): 78% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 8.39-8.34 (m, 2H), 8.14 (d, *J*=8.4 Hz, 1H), 7.93 (d, *J*=8.1 Hz, 1H), 7.83-7.79 (m, 1H), 7.71-7.63 (m, 2H), 7.48-7.44 (m, 1H), 7.37-7.33 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 162.2, 148.0, 146.2, 138.2, 137.2, 134.7, 131.5, 131.2, 130.7, 129.9, 129.8, 128.9, 127.8, 127.3, 126.0, 118.9, 20.1; HRMS (ESI): calcd for $C_{18}H_{15}N_2O_2$ $[M+H]^+$ 291.1134, found 291.1138.

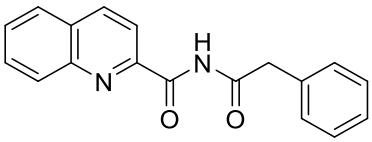


N-(3-bromobenzoyl)quinoline-2-carboxamide (**2k**): 82% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 8.40 (m, 2H), 8.19 (m, 2H), 8.00-7.69 (m, 5H), 7.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 161.0, 146.9, 144.9, 137.4,

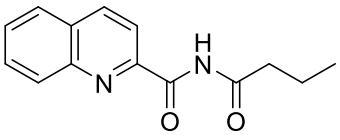
134.9, 134.4, 130.2, 129.7, 129.4, 129.0, 128.8, 128.0, 126.9, 125.2, 122.1, 117.9. HRMS (ESI): calcd for $C_{17}H_{12}BrN_2O_2$ $[M+H]^+$ 355.0082, found 355.0084.



N-(2-naphthoyl)quinoline-2-carboxamide (**2l**): 86% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.48 (s, 1H), 8.48 (d, *J*=8.1 Hz, 1H), 8.39-8.34 (m, 2H), 8.09 (d, *J*=8.6 Hz, 1H), 8.06 (d, *J*=8.3 Hz, 1H), 7.95-7.90 (m, 3H), 7.81-7.77 (m, 1H), 7.70-7.66(m, 1H), 7.63-7.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 162.4, 148.0, 146.2, 138.2, 133.8, 132.5, 132.2, 130.7, 130.2, 129.9, 129.8, 128.9, 127.8, 127.8, 126.7, 126.1, 125.0, 124.7, 118.9; HRMS (ESI): calcd for $C_{21}H_{15}N_2O_2$ $[M+H]^+$ 327.1134, found 327.1132.

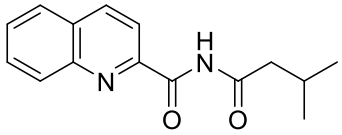


N-(2-phenylacetyl)quinoline-2-carboxamide (**2m**): 63% yield; yellowish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ10.84 (s, 1H), 8.36-8.29 (m, 2H), 8.08 (d, *J*=8.5 Hz, 1H), 7.90 (d, *J*=8.2 Hz, 1H), 7.83-7.79 (m, 1H), 7.69-7.65 (m, 1H), 7.43-7.37 (m, 4H), 7.34 -7.30 (m, 1H), 4.35 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 162.7, 147.6, 146.2, 138.1, 133.7, 130.7, 129.9, 129.8, 128.9, 128.7, 127.7, 127.2, 118.7, 44.0; HRMS (ESI): calcd for $C_{18}H_{15}N_2O_2$ $[M+H]^+$ 291.1134, found 291.1132.

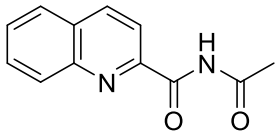


N-butyrylquinoline-2-carboxamide (**2n**): 70% yield; pale yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.36 (d, *J*=8.5 Hz, 1H), 8.29 (d, *J*=8.5 Hz, 1H), 8.14 (d, *J*=8.5 Hz, 1H), 7.90 (d, *J*=8.1 Hz, 1H), 7.83-7.79 (m, 1H), 7.69-7.65 (m, 1H), 3.01 (t, *J*=7.4 Hz, 2H), 1.84-1.75 (m, 2H), 1.05 (t, *J*=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

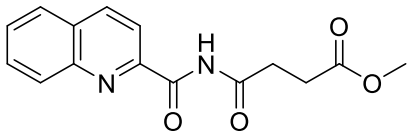
δ 174.8, 162.8, 147.8, 146.2, 138.1, 130.6, 129.9, 129.7, 128.9, 127.7, 118.7, 39.4, 17.6, 13.7; HRMS (ESI): calcd for $C_{14}H_{15}N_2O_2$ $[M+H]^+$ 243.1134, found 243.1135.



N-(3-methylbutanoyl)quinoline-2-carboxamide (**2o**): 60% yield; pale yellow foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ1H NMR (400 MHz, Chloroform-d) δ 10.69 (s, 1H), 8.36 (d, *J*=8.5 Hz, 1H), 8.29 (d, *J*=8.5 Hz, 1H), 8.14 (d, *J*=8.5 Hz, 1H), 7.90 (d, *J*=8.0 Hz, 1H), 7.83-7.79 (m, 1H), 7.70-7.66 (m, 1H), 2.92 (d, *J*=6.9 Hz, 2H), 2.29 (m, 1H), 1.06 (d, *J*=6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 162.7, 147.8, 146.2, 138.1, 130.7, 129.9, 129.7, 128.9, 127.7, 118.7, 46.2, 24.9, 22.5; HRMS (ESI): calcd for $C_{15}H_{17}N_2O_2$ $[M+H]^+$ 257.1290, found 257.1289.

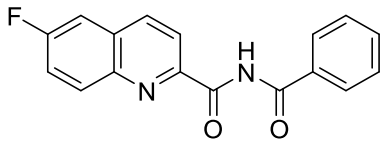


N-acetylquinoline-2-carboxamide (**2p**): 45% yield; pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.84-7.81(m, 1H), 7.70-7.67 (m, 1H), 2.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 163.1, 147.6, 146.2, 138.1, 130.7, 129.9, 129.8, 128.9, 127.7, 118.7, 25.4; HRMS (ESI): calcd for $C_{12}H_{11}N_2O_2$ $[M+H]^+$ 215.0821, found 215.0817.

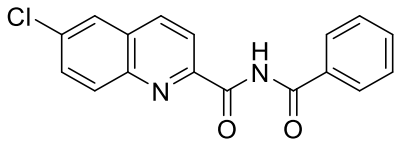


Methyl-4-oxo-4-(quinoline-2-carboxamido)butanoate (**2q**): 65% yield; pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.80 (s, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.84-7.81 (m, 1H), 7.70-7.68 (m, 1H), 3.72 (s, 3H), 3.39(t, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 6.5 Hz, 2H). ^{13}C

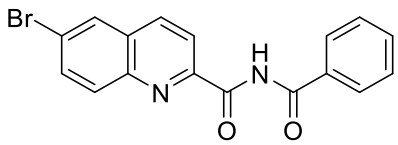
NMR (151 MHz, $CDCl_3$) δ 173.8, 173.3, 163.4, 147.9, 146.5, 138.6, 131.2, 130.2, 130.2, 129.4, 128.1, 119.2, 52.3, 33.1, 28.5; HRMS (ESI): calcd for $C_{15}H_{15}N_2O_4$ $[M+H]^+$ 287.1032, found 287.1026.



N-benzoyl-6-fluoroquinoline-2-carboxamide (**2r**): 76% yield; pale yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1H), 8.41 (d, *J*=8.5 Hz, 1H), 8.35 (d, *J*=8.6 Hz, 1H), 8.21 (dd, *J*=9.1, 5.3 Hz, 1H), 8.05-8.03 (m, 2H), 7.67-7.54 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9 (s), 161.9 (s), 161.8 (d, *J* = 252 Hz), 147.9 (d, *J* = 3.0 Hz), 143.2 (s), 137.7 (d, *J* = 5.7 Hz), 133.5 (s), 133.1 (s), 132.5 (d, *J* = 9.5 Hz), 130.9 (d, *J* = 10.5 Hz), 129.0 (s), 127.8 (s), 121.3 (d, *J* = 26.2 Hz), 119.7 (s), 111.1 (d, *J* = 22.0 Hz); HRMS (ESI): calcd for $C_{17}H_{12}FN_2O_2$ $[M+H]^+$ 295.0883, found 295.0881.

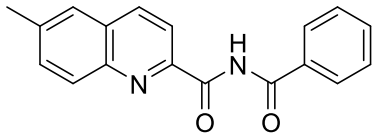


N-benzoyl-6-chloroquinoline-2-carboxamide (**2s**): 85% yield; pale yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.41 (d, *J*=8.5 Hz, 1H), 8.32 (d, *J*=8.5 Hz, 1H), 8.14 (d, *J*=9.0 Hz, 1H), 8.05-8.03 (m, 2H), 7.92-7.92 (m, 1H), 7.78-7.75 (m, 1H), 7.65 (t, *J*=7.3 Hz, 1H), 7.59-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 160.7, 147.5, 143.4, 136.4, 133.9, 132.4, 132.1, 130.7, 130.3, 129.4, 127.9, 126.8, 125.5, 118.9; HRMS (ESI): calcd for $C_{17}H_{12}ClN_2O_2$ $[M+H]^+$ 311.0587, found 311.0585.

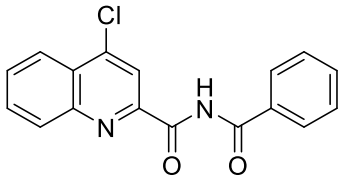


N-benzoyl-6-bromoquinoline-2-carboxamide (**2t**): 90% yield; pale yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.43 (d, *J*=8.5 Hz, 1H), 8.32 (d, *J*=8.5 Hz, 1H), 8.12-8.04 (m, 4H), 7.90 (dd, *J*=9.0, 1.9 Hz, 1H), 7.66 (t, *J*=7.3 Hz, 1H), 7.60-7.56

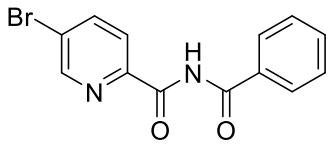
(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 160.7, 147.6, 143.6, 136.3, 133.3, 132.4, 132.1, 130.4, 129.8, 128.9, 127.9, 126.8, 122.2, 118.9; HRMS (ESI): calcd for $C_{17}H_{12}BrN_2O_2$ $[M+H]^+$ 355.0082, found 355.0084.



N-benzoyl-6-methylquinoline-2-carboxamide (**2v**): 90% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 8.33 (d, *J*=8.4 Hz, 1H), 8.27 (d, *J*=8.4 Hz, 1H), 8.07-8.04 (m, 3H), 7.67-7.63 (m, 3H), 7.59-7.55 (m, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.2, 146.4, 143.6, 138.3, 136.4, 132.6, 132.0, 132.0, 129.0, 128.4, 127.9, 126.8, 125.6, 117.9, 22.8; HRMS (ESI): calcd for $C_{18}H_{15}N_2O_2$ $[M+H]^+$ 291.1134, found 291.1135.

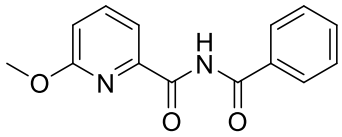


N-benzoyl-4-chloroquinoline-2-carboxamide (**2w**): 78% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.47 (s, 1H), 8.34 (d, *J*=8.4 Hz, 1H), 8.23 (d, *J*=8.4 Hz, 1H), 8.07-8.05 (m, 2H), 7.93-7.89 (m, 1H), 7.81 (t, *J*=7.3 Hz, 1H), 7.67 (t, *J*=7.4 Hz, 1H), 7.61-7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 161.2, 148.2, 146.8, 145.2, 133.4, 133.2, 131.5, 130.3, 129.9, 129.0, 128.0, 127.9, 124.5, 119.2; HRMS (ESI): calcd for $C_{17}H_{12}ClN_2O_2$ $[M+H]^+$ 311.0587, found 311.0588.



N-benzoyl-5-bromopicolinamide (**2x**): 93% yield; pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 8.71 (d, *J*=1.9 Hz, 1H), 8.22 (d, *J*=8.3 Hz, 1H), 8.08 (dd, *J*=8.3, 2.2 Hz, 1H), 7.98-7.96 (m, 2H), 7.63 (t, *J*=7.4 Hz, 1H), 7.56-7.52 (m, 2H); ^{13}C

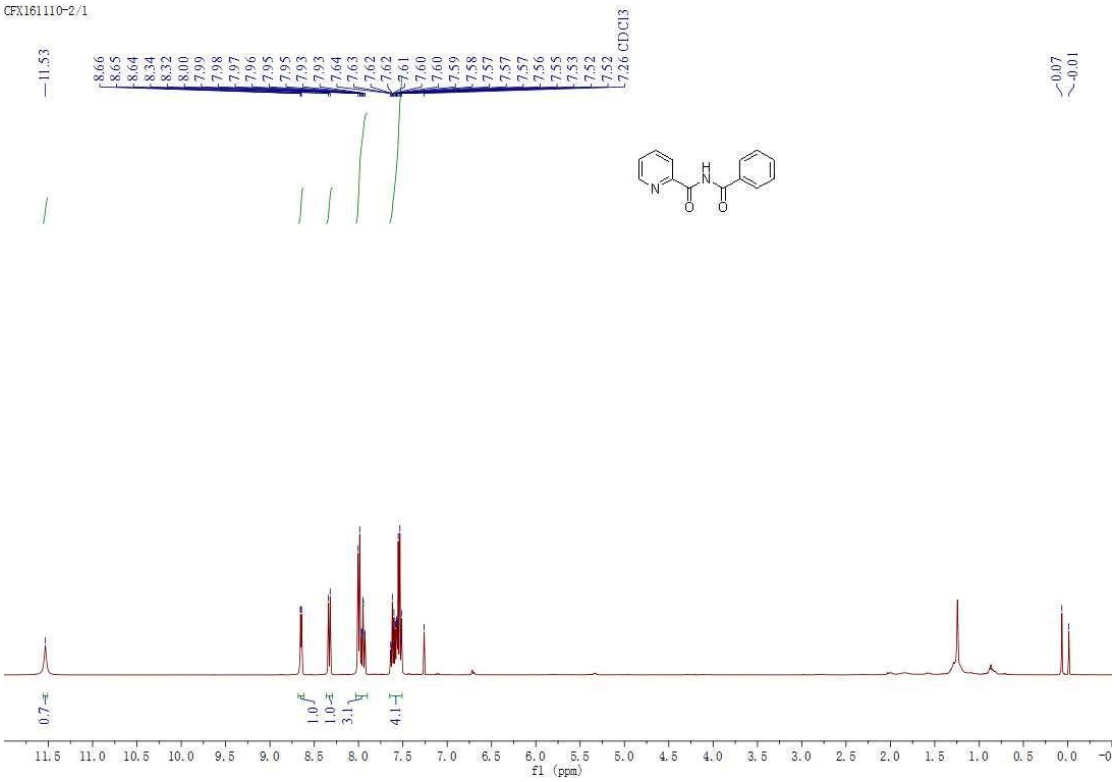
NMR (100 MHz, $CDCl_3$) δ 164.7, 161.2, 149.6, 147.0, 140.8, 133.2, 133.2, 129.0, 127.8, 125.7, 124.6; HRMS (ESI): calcd for $C_{13}H_{10}BrN_2O_2$ $[M+H]^+$ 304.9926, found 304.9930.

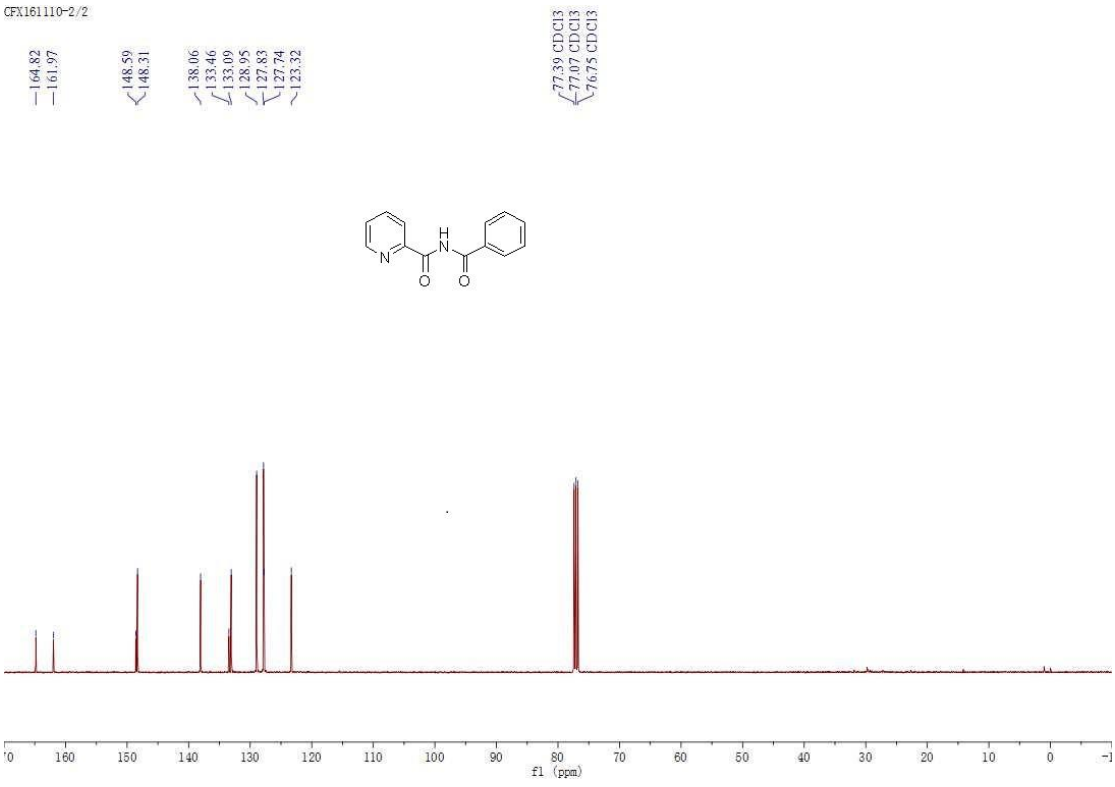


N-benzoyl-6-methoxypicolinamide (**2y**): 75% yield; pale yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 11.27(s, 1H), 7.98-7.94 (m, 3H), 7.82 (t, *J*=7.7 Hz, 1H), 7.63 (t, *J*=7.3 Hz, 1H), 7.55-7.51 (m, 2H), 7.04 (d, *J*=8.2 Hz, 1H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 162.9, 161.6, 145.8, 140.3, 133.6, 133.0, 129.0, 127.6, 116.9, 116.2, 53.5; HRMS (ESI): calcd for $C_{14}H_{13}N_2O_3$ $[M+H]^+$ 257.0926, found 257.0929.

4. Copies of ^{1}H NMR and ^{13}C NMR Spectra

2a





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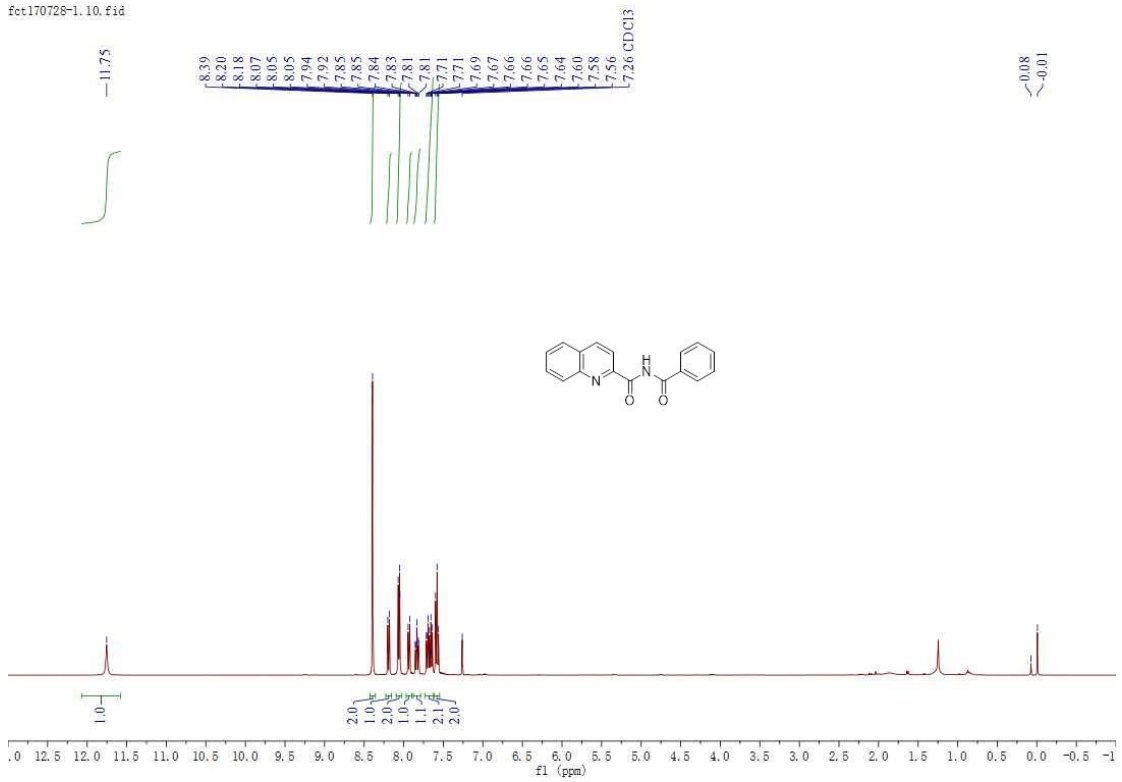
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7.81
7.81
7.71
7.71
7.69
7.67
7.66
7.66
7.65
7.64
7.60
7.58
7.56
7.26 CDCl3
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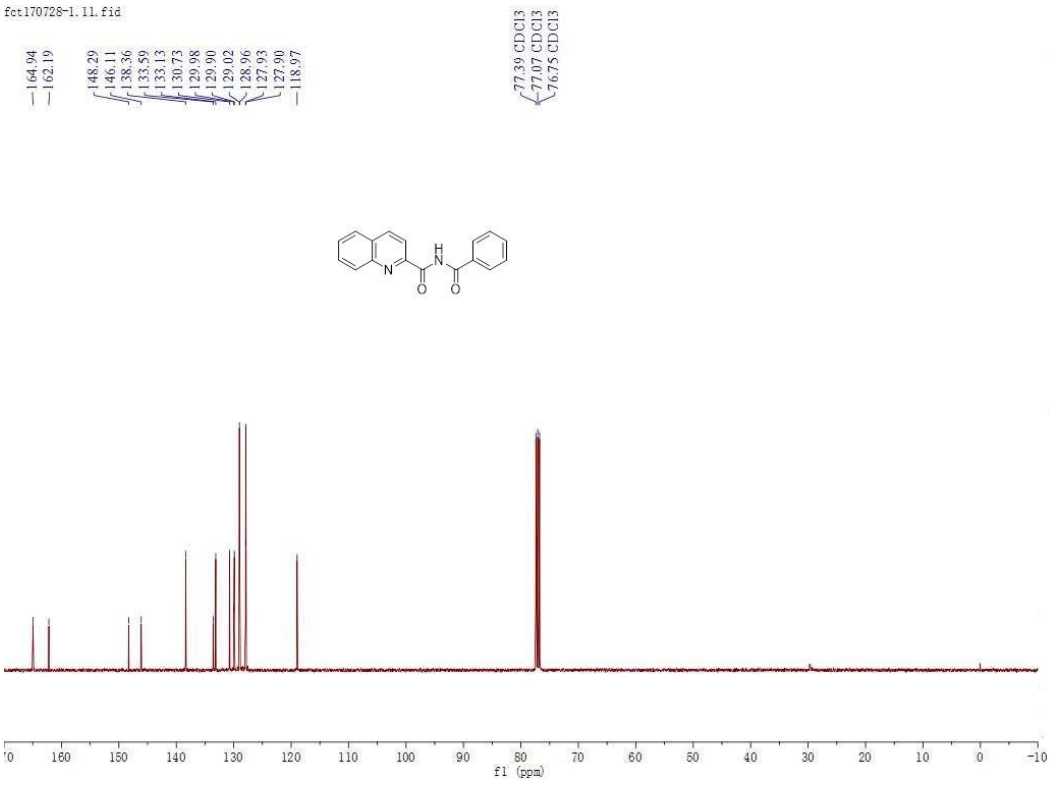
f1 (ppm)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127.90
118.97
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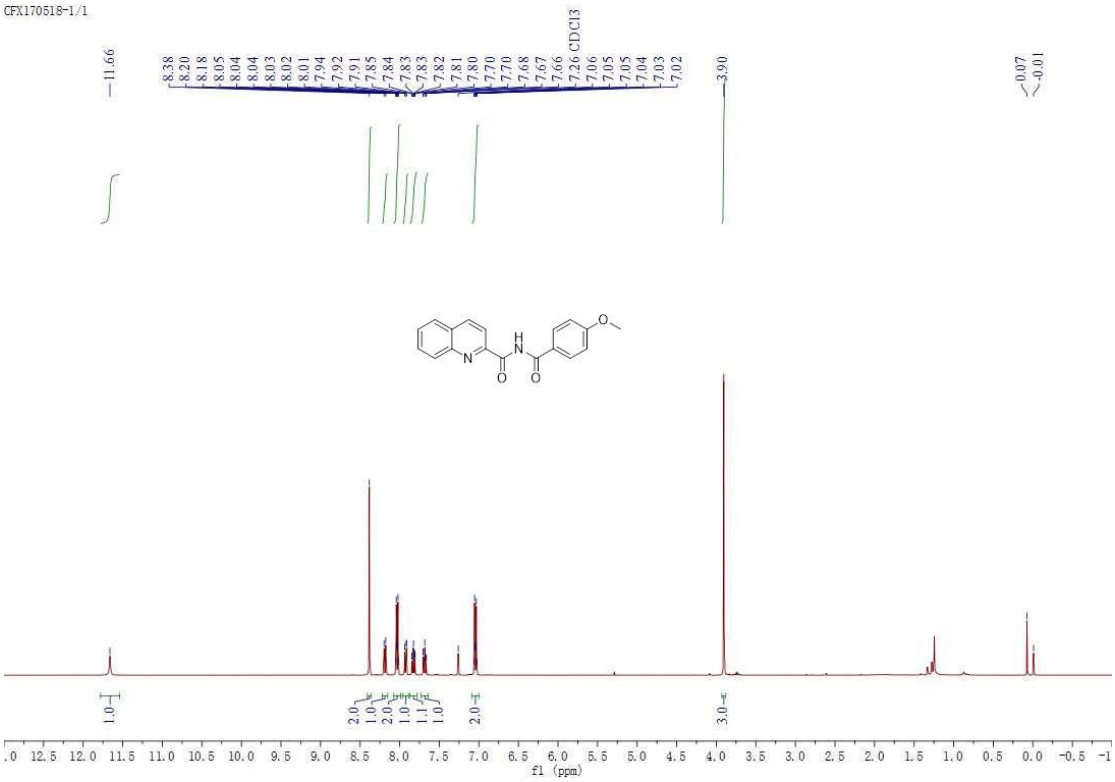
77.07 CDCl3
76.75 CDCl3
f1 (ppm)

2c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7.26 CDCl3
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7.03
7.02
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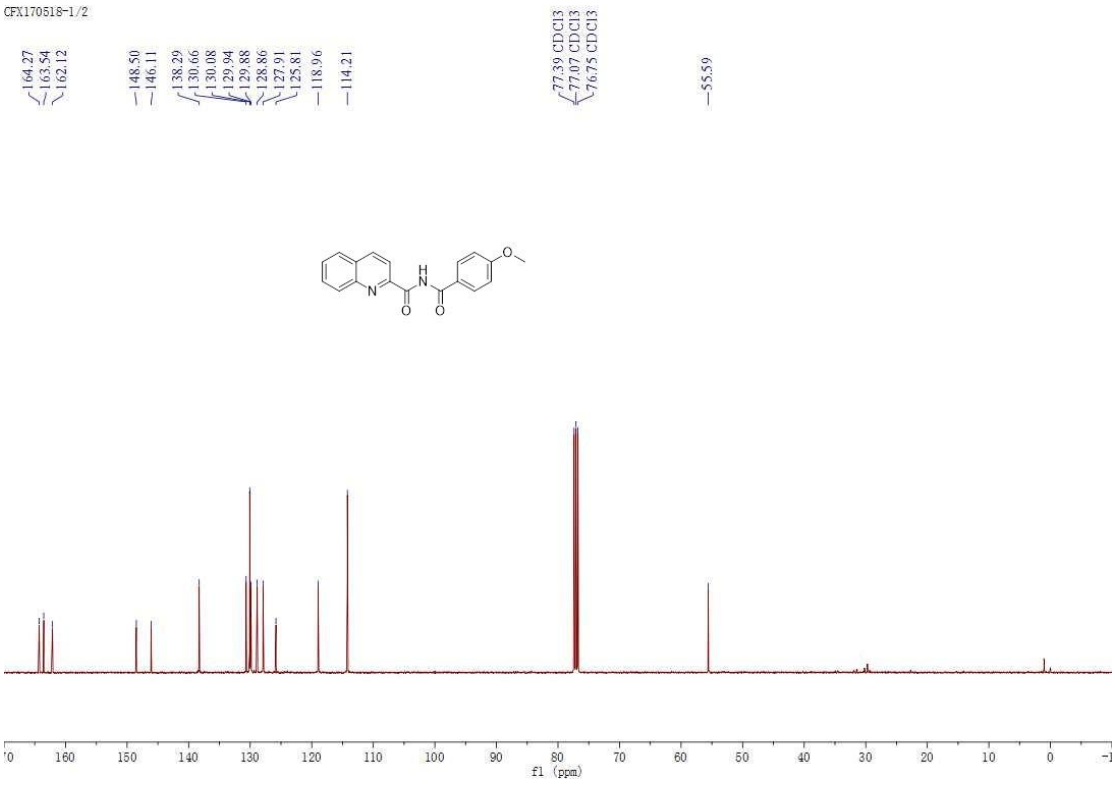
f1 (ppm)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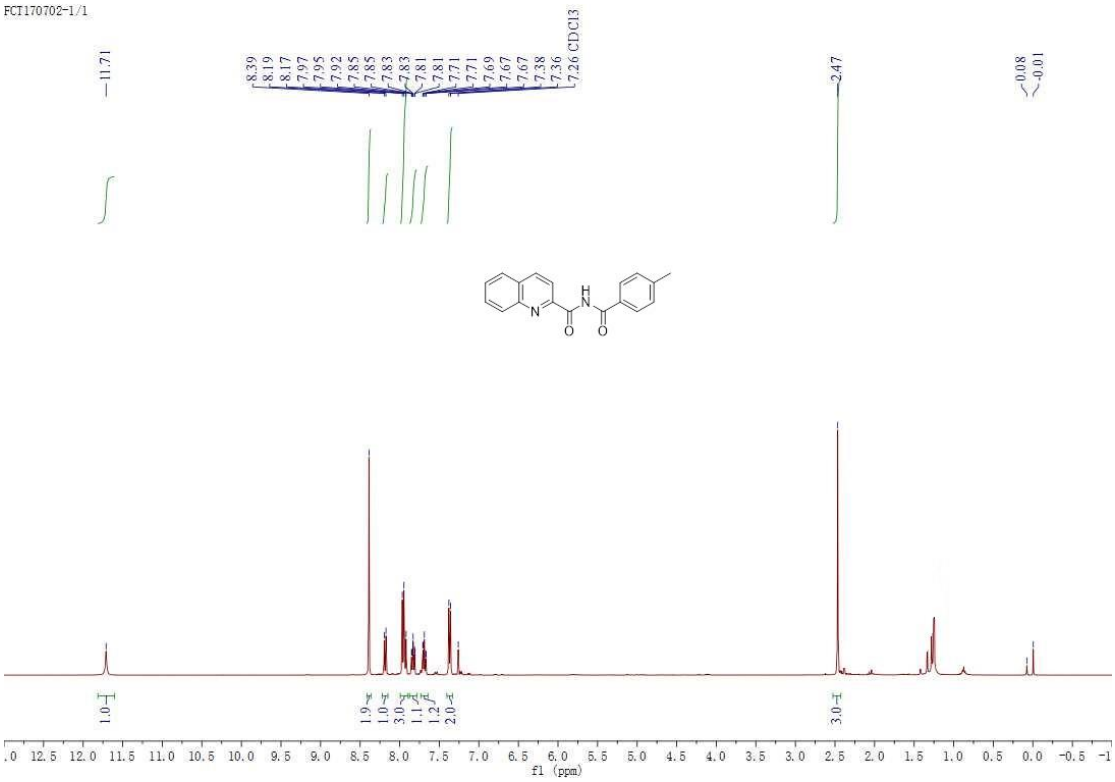
f1 (ppm)

2d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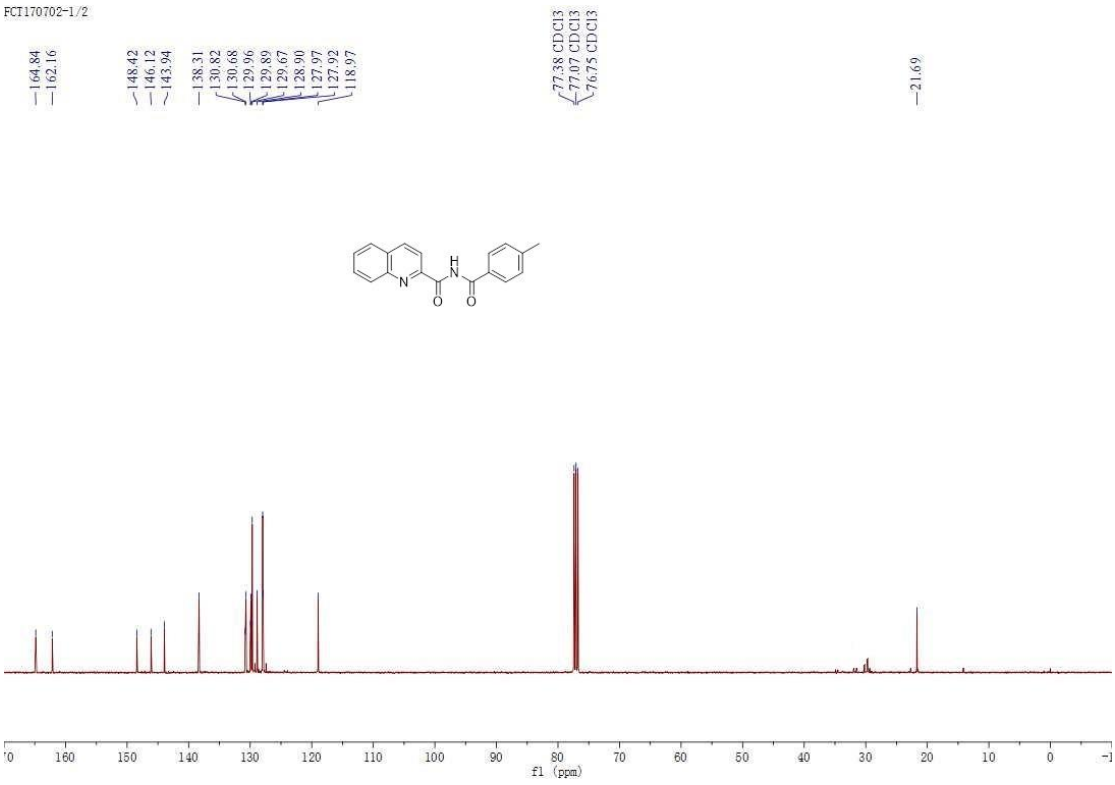
f1 (ppm)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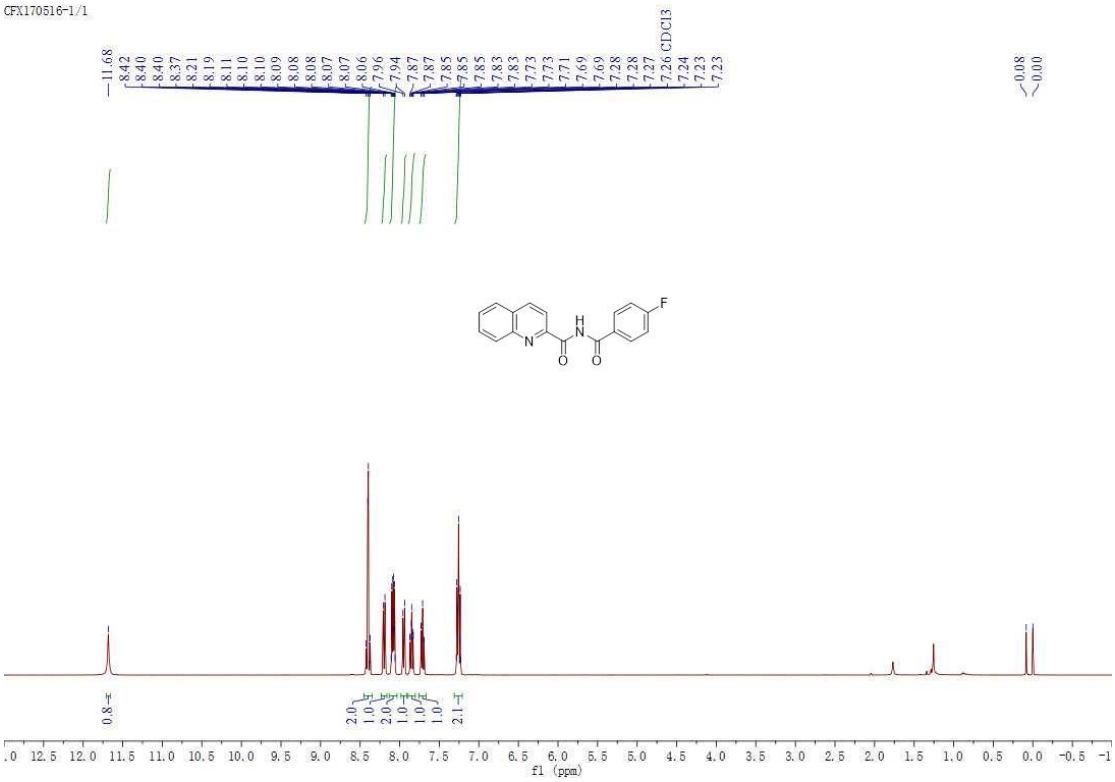
76.75 CDCl3
21.69
f1 (ppm)

2e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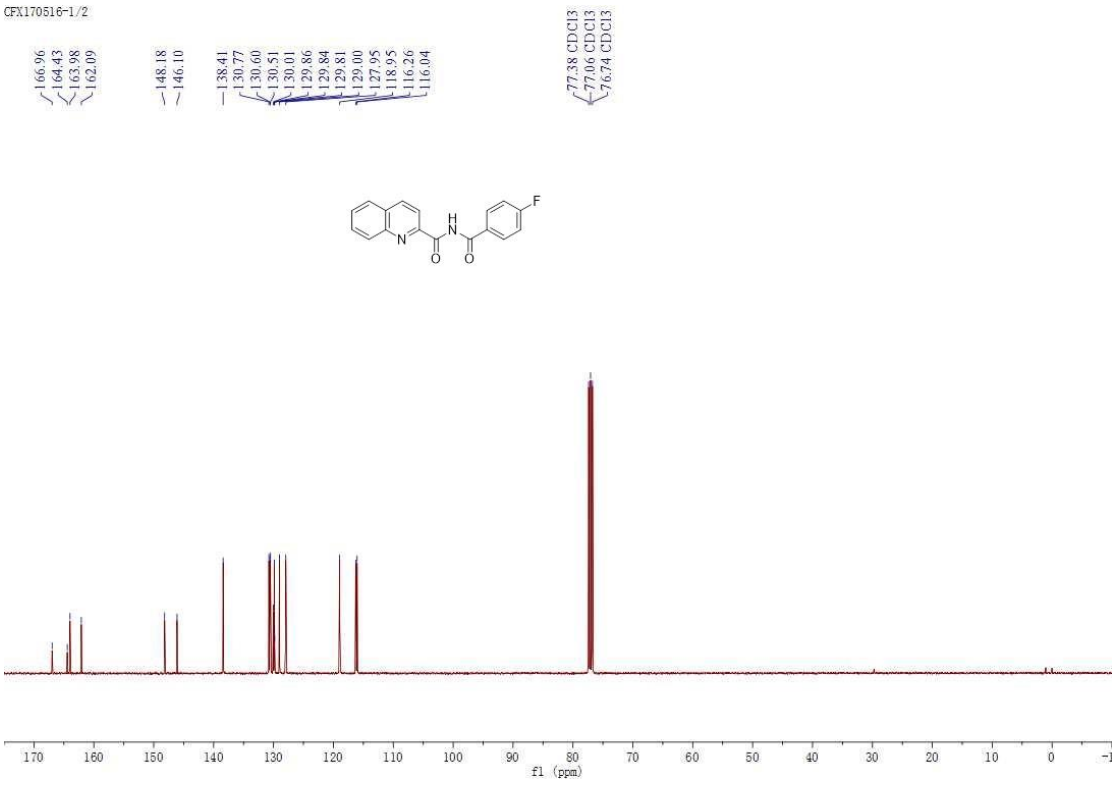
f1 (ppm)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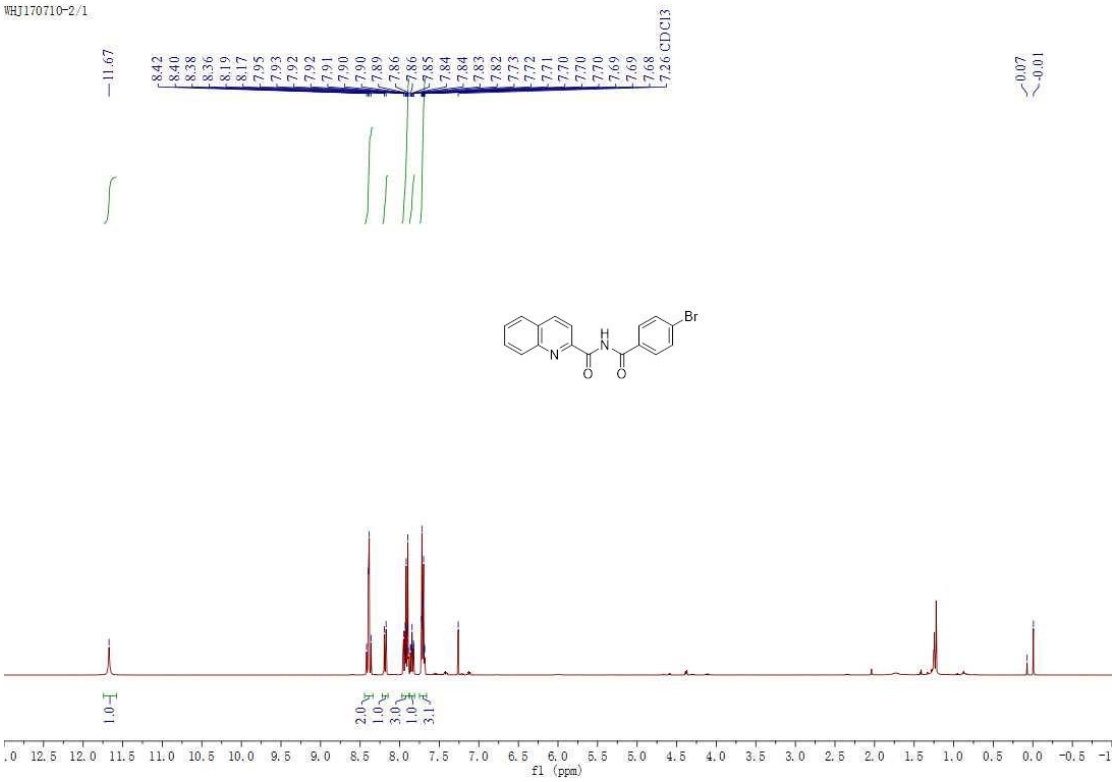
O
f1 (ppm)

2f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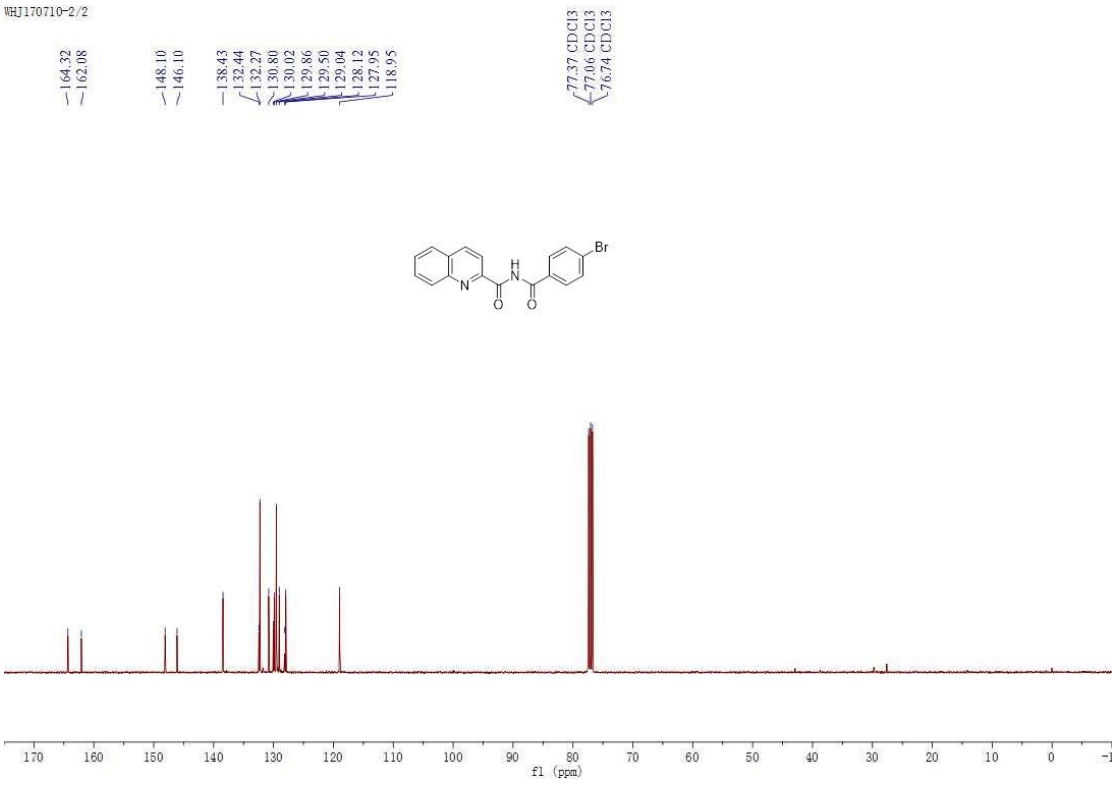
f1 (ppm)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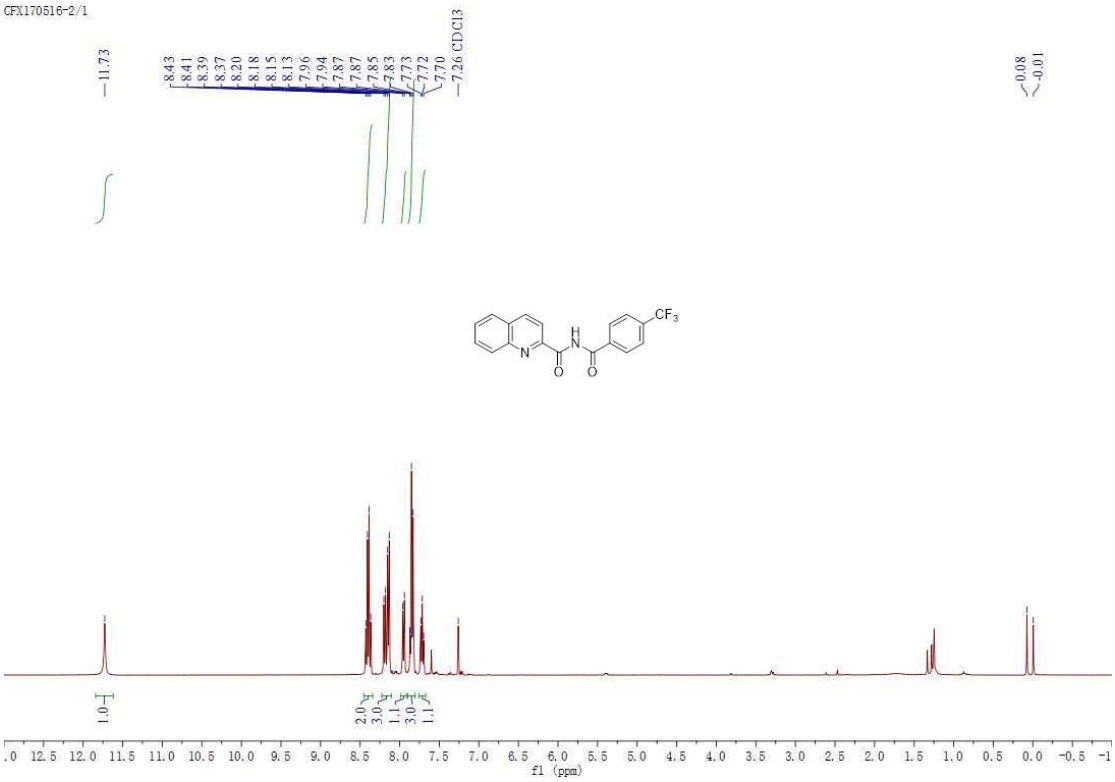
O
f1 (ppm)

2g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7.73
7.72
7.70
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CF3
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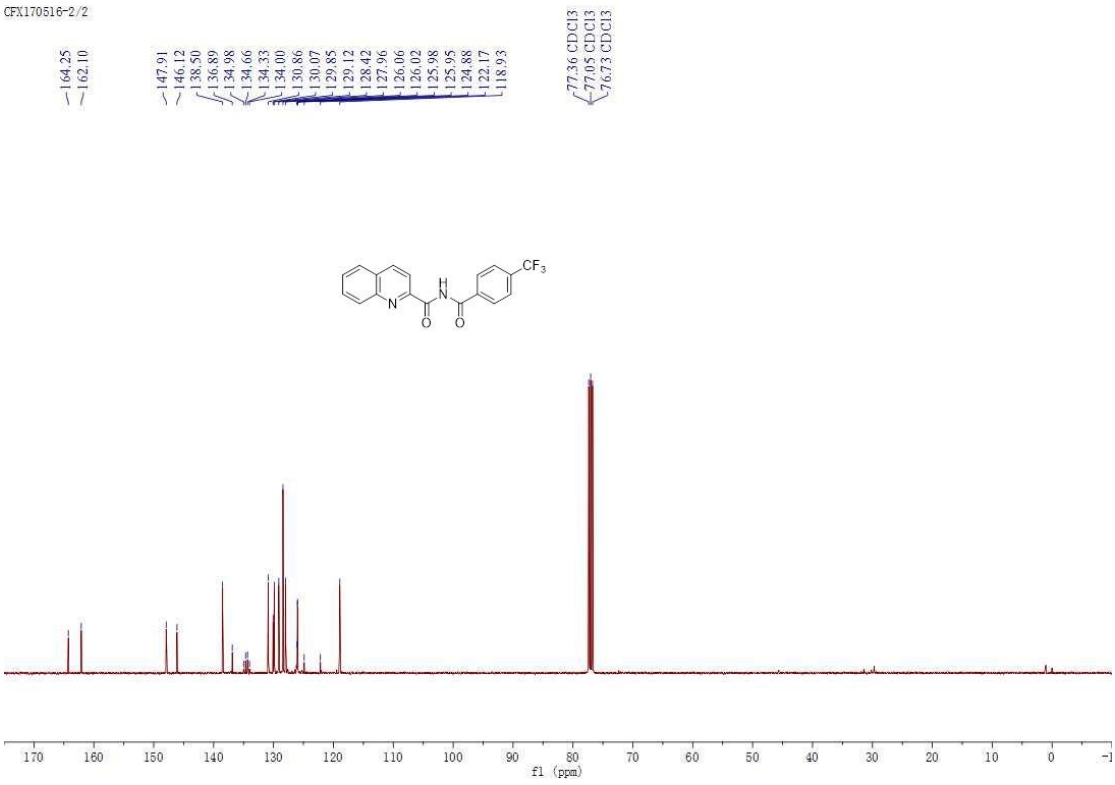
f1 (ppm)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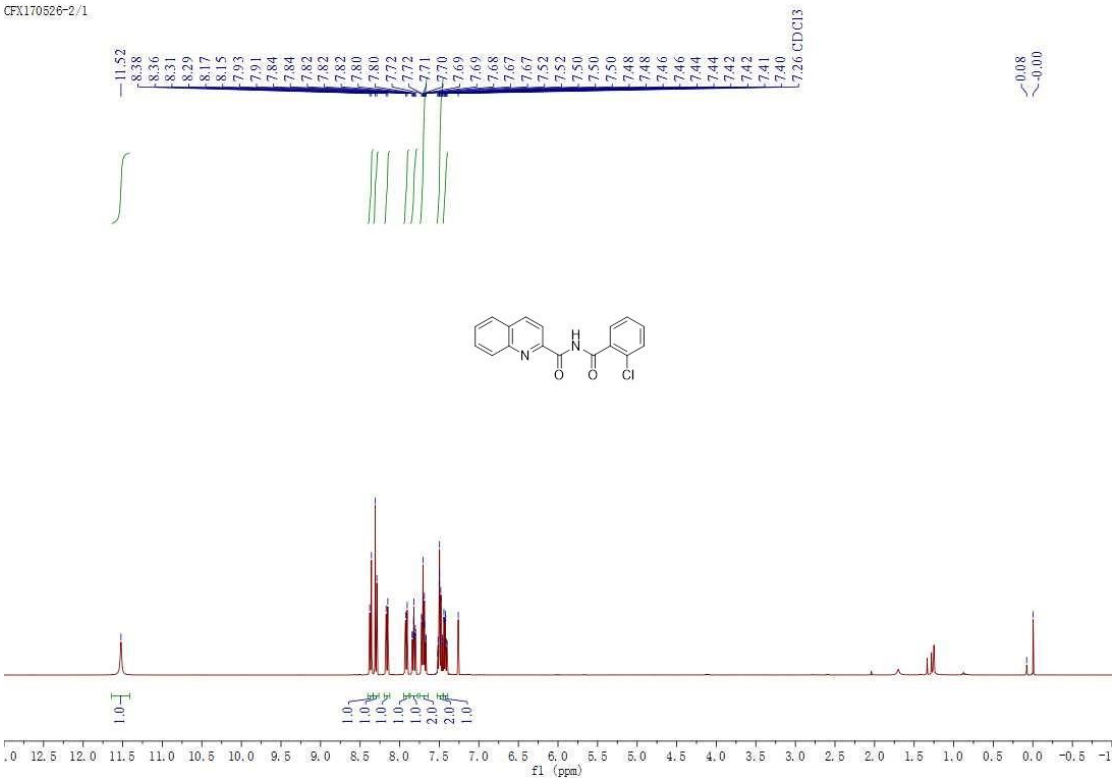
76.73 CDCl3
CF3
f1 (ppm)

2h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7.48
7.48
7.46
7.46
7.44
7.44
7.42
7.42
7.41
7.40
7.26 CDCl3
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H
N
O
O
Cl
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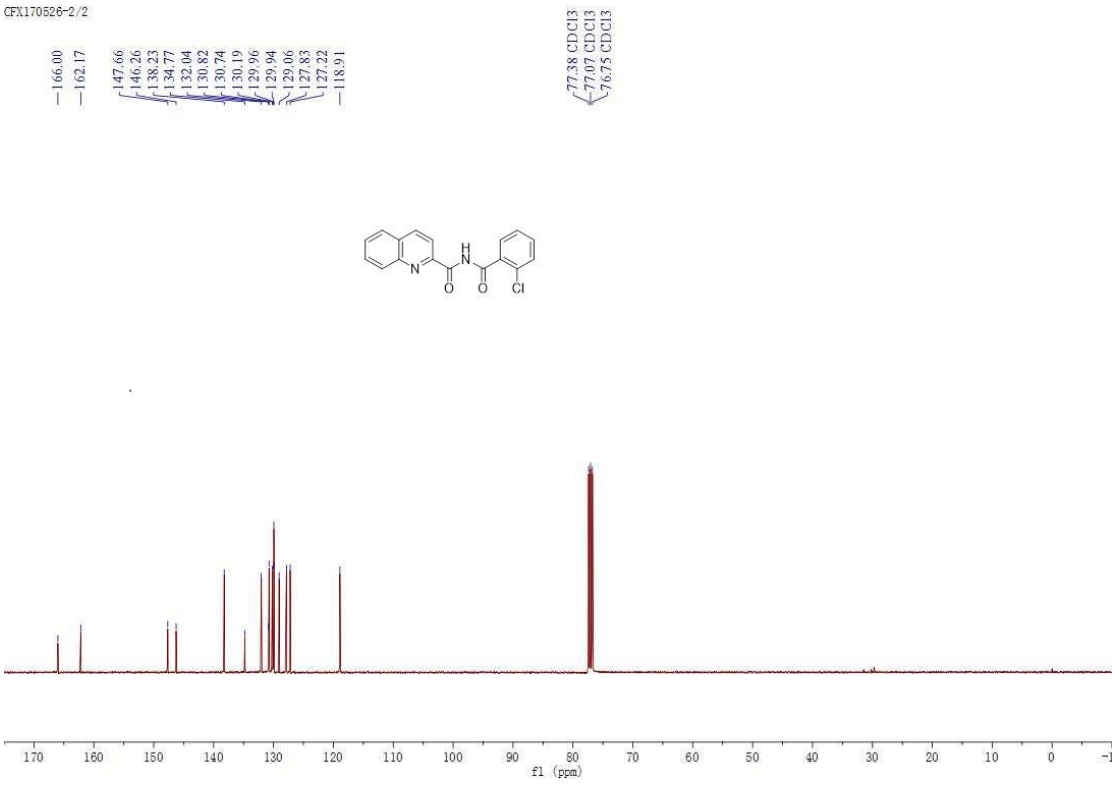
1.0
1.0
1.0
1.0
1.0
2.0
2.0
2.0
1.0
f1 (ppm)


CFX170526-2/2
166.00
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147.66
146.26
138.23
134.77
132.04
130.82
130.74
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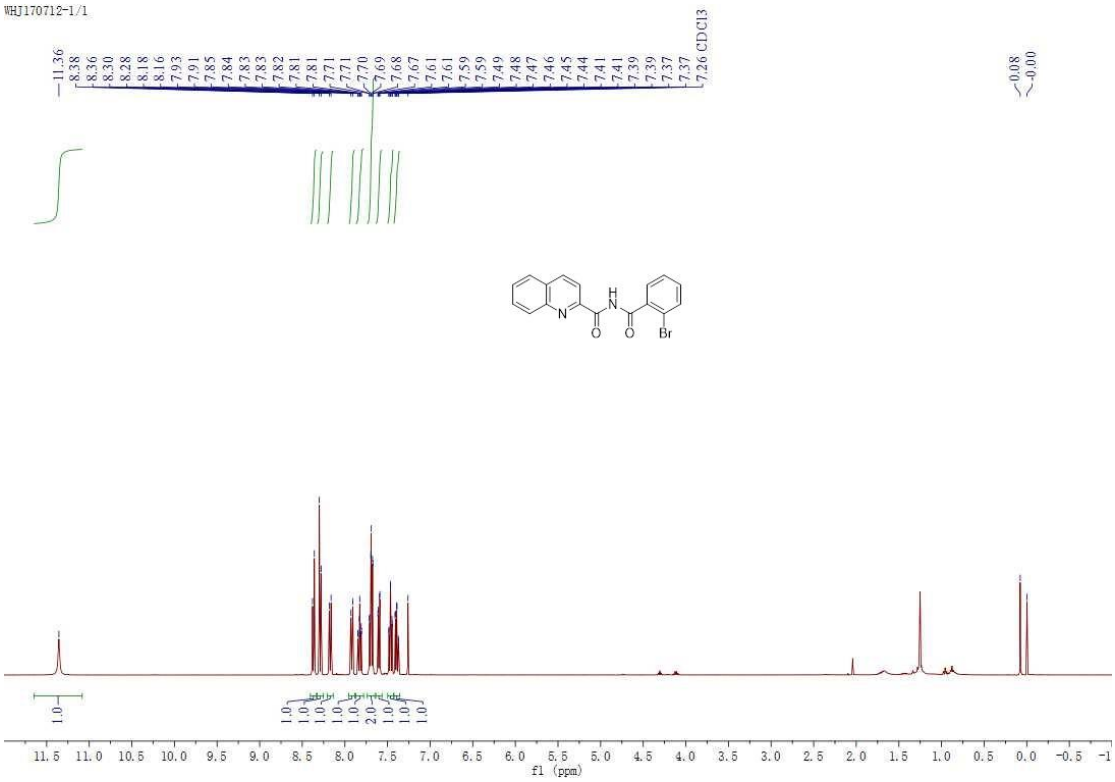
129.96
129.94
129.06
127.83
127.22
118.91
77.38 CDCl3
77.07 CDCl3
76.75 CDCl3
H
N
O
O
Cl
f1 (ppm)

2i


WHJ170712-1/1
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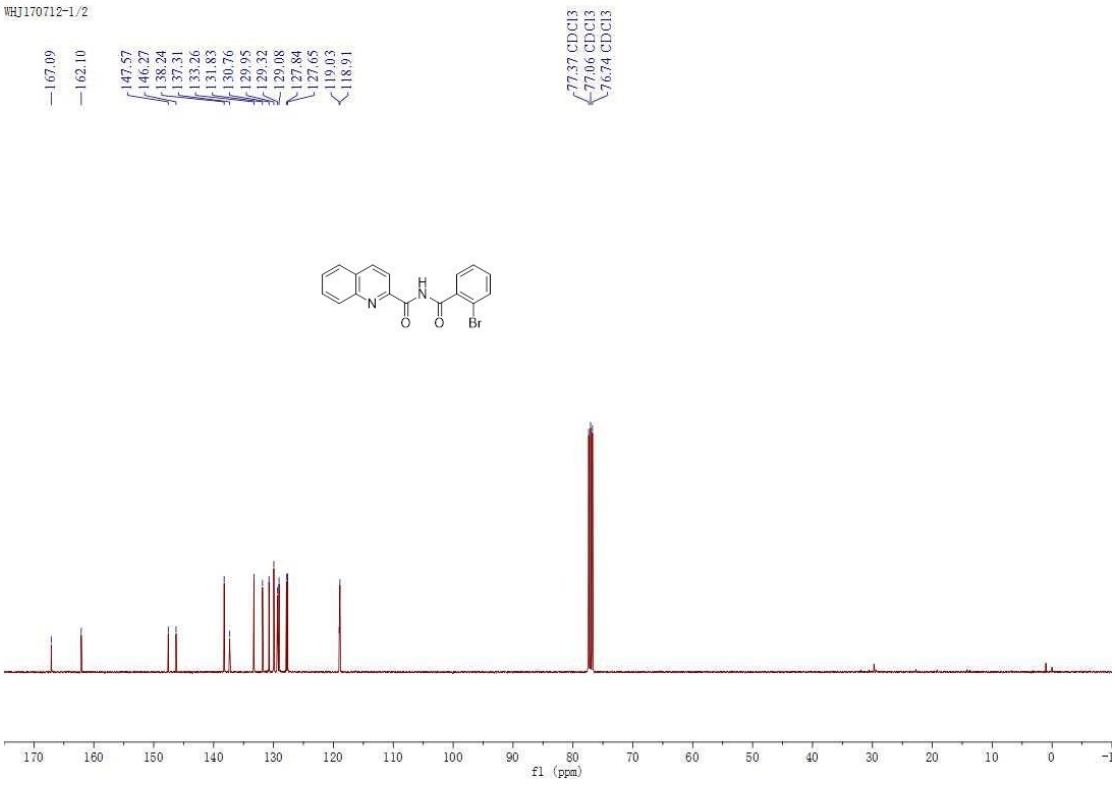
8.38
8.36
8.30
8.28
8.18
8.16
7.93
7.91
7.85
7.84
7.83
7.83
7.82
7.81
7.81
7.71
7.71
7.70
7.69
7.68
7.67
7.61
7.61
7.59
7.59
7.49
7.48
7.47
7.46
7.45
7.44
7.41
7.41
7.39
7.39
7.37
7.37
7.26 CDCl3
0.08
0.00
f1 (ppm)


WHJ170712-1/2
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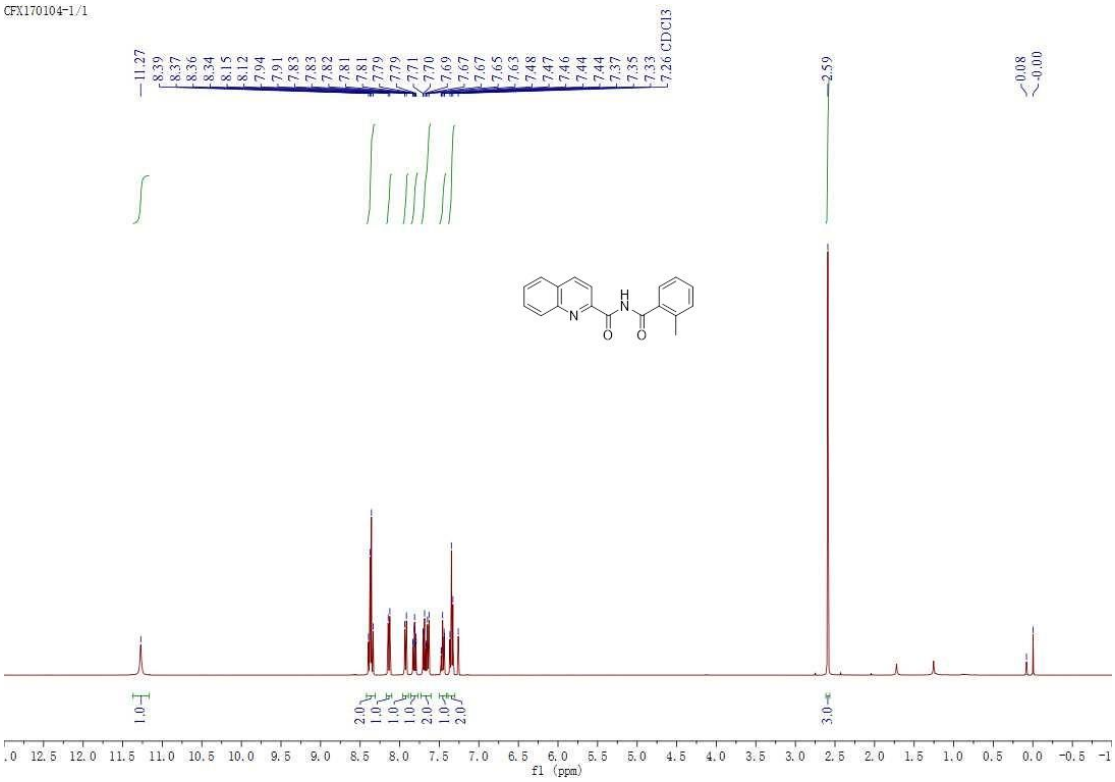
146.27
138.24
137.31
133.26
131.83
130.76
129.95
129.32
129.08
127.84
127.65
119.03
118.91
77.37 CDCl3
77.06 CDCl3
76.74 CDCl3
f1 (ppm)

2j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8.34
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8.12
7.94
7.91
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7.83
7.82
7.81
7.81
7.79
7.79
7.71
7.70
7.69
7.67
7.67
7.65
7.63
7.48
7.47
7.46
7.44
7.44
7.37
7.35
7.33
7.26 CDCl3
2.59
0.08
0.00
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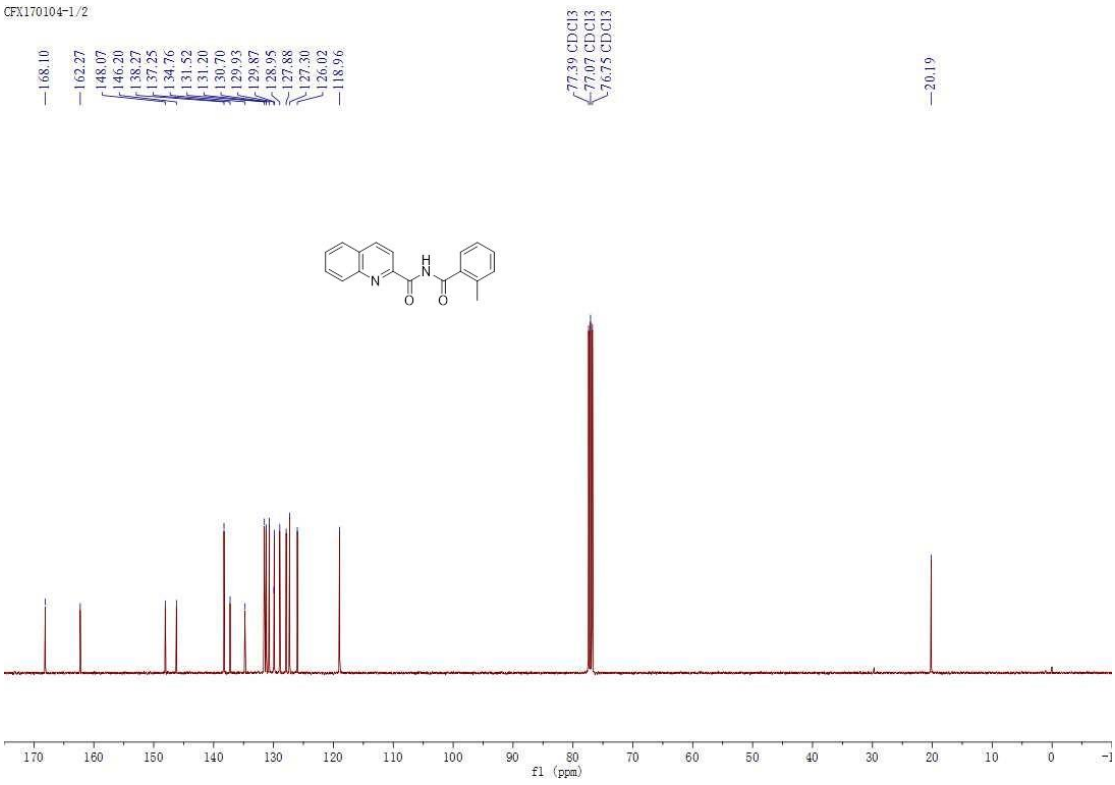
2.0
1.0
1.0
1.0
2.0
1.0
2.0
3.0
f1 (ppm)


CFX170104-1/2
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162.27
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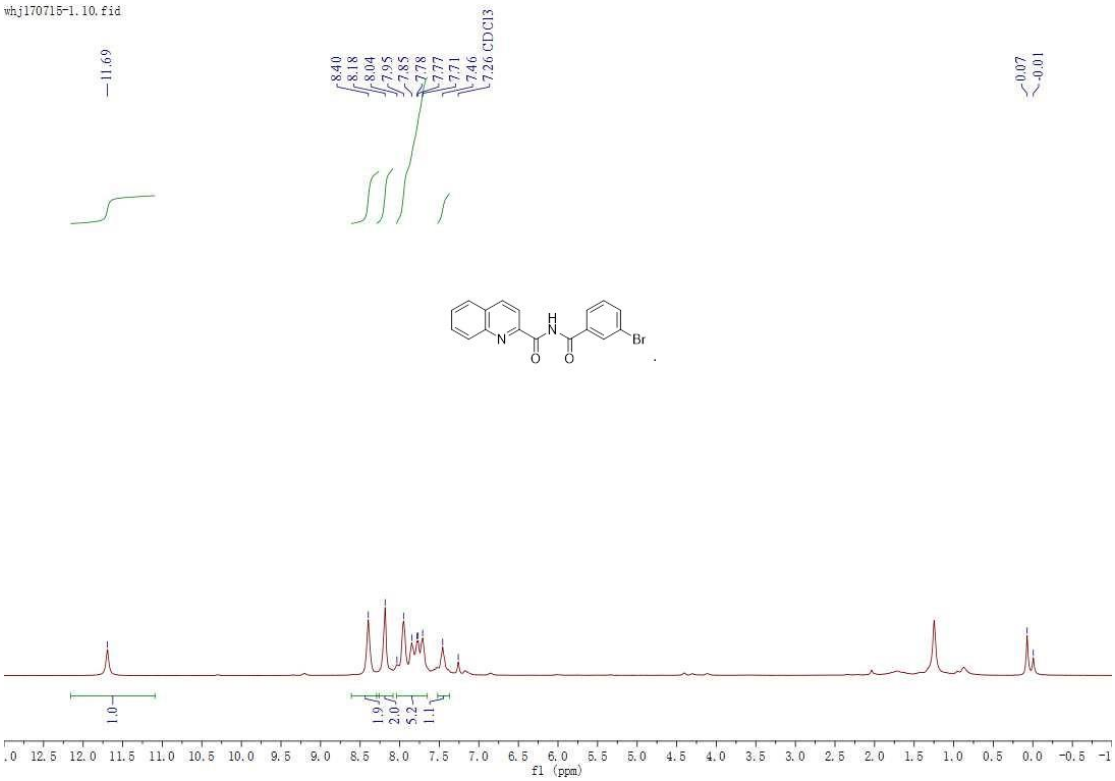
138.27
137.25
134.76
131.52
131.20
130.70
129.93
129.87
128.95
127.88
127.30
126.02
118.96
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
20.19
f1 (ppm)

2k


whj170715-1.10.fid
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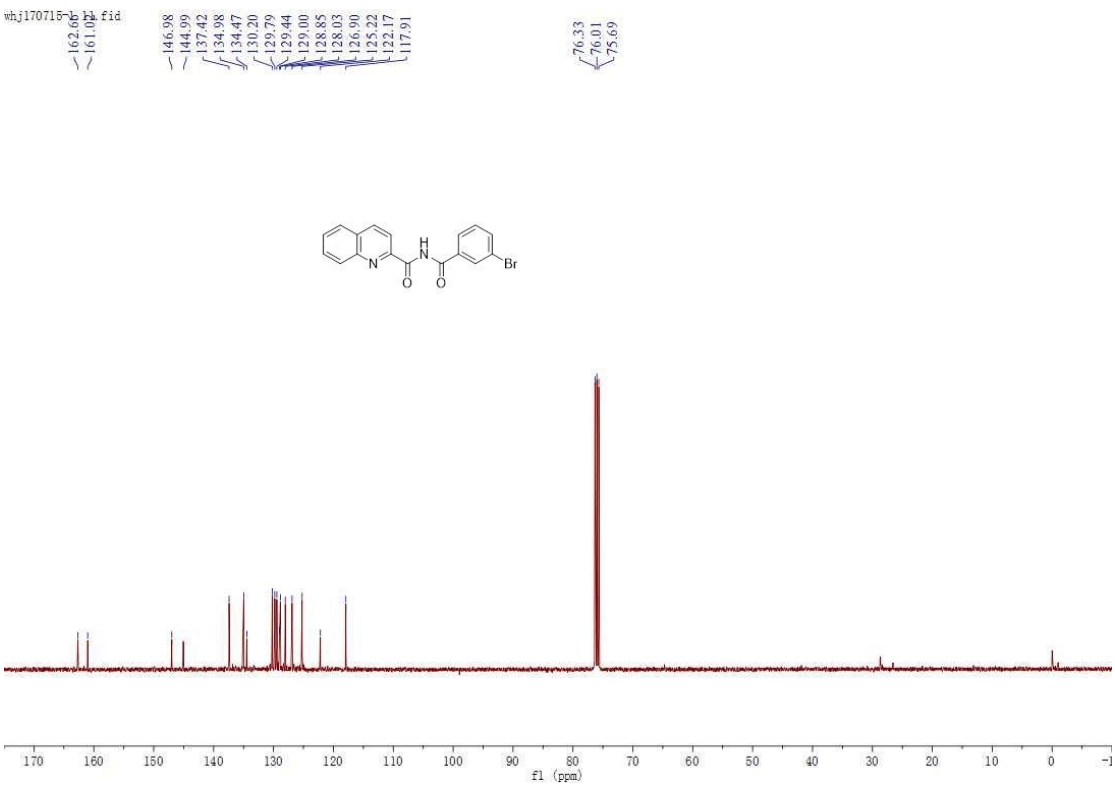
8.40
8.18
8.04
7.95
7.85
7.78
7.77
7.71
7.46
7.26 CDCl3
0.07
-0.01
Br
1.0
1.9
2.0
5.2
1.1
f1 (ppm)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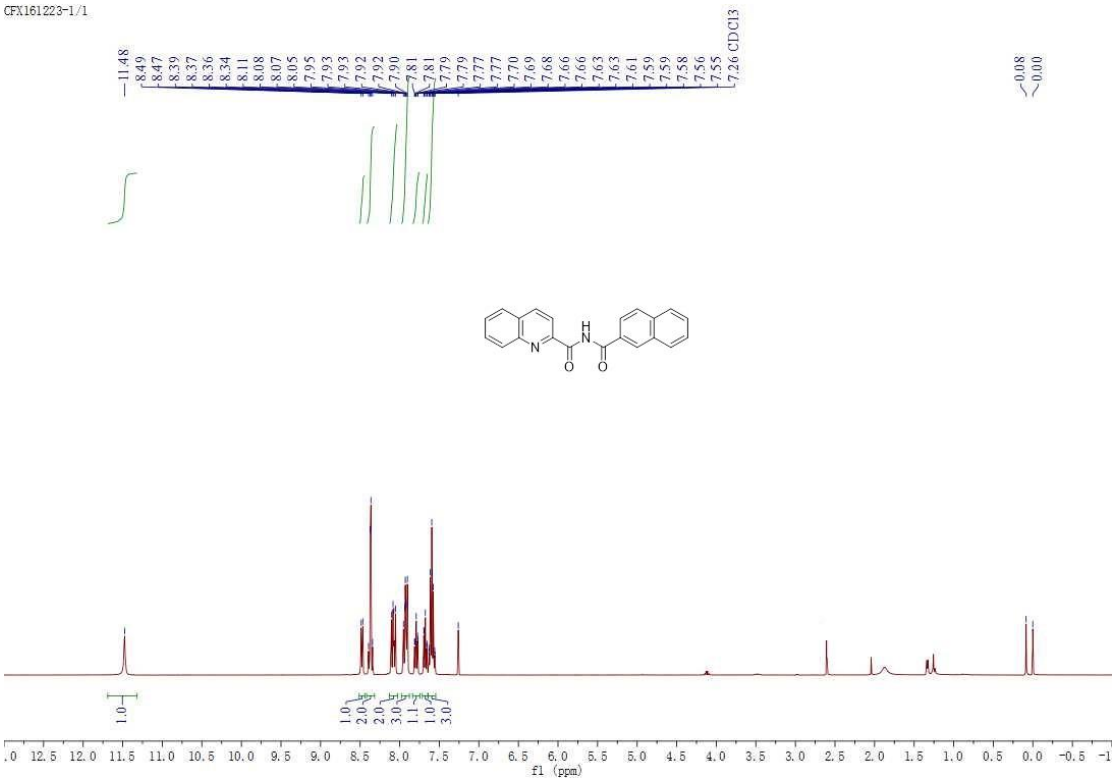
162.66
161.02
146.98
144.99
137.42
134.98
134.47
130.20
129.79
129.44
129.00
128.85
128.03
126.90
125.22
122.17
117.91
76.33
76.01
75.69
Br
f1 (ppm)

2l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8.37
8.36
8.34
8.11
8.08
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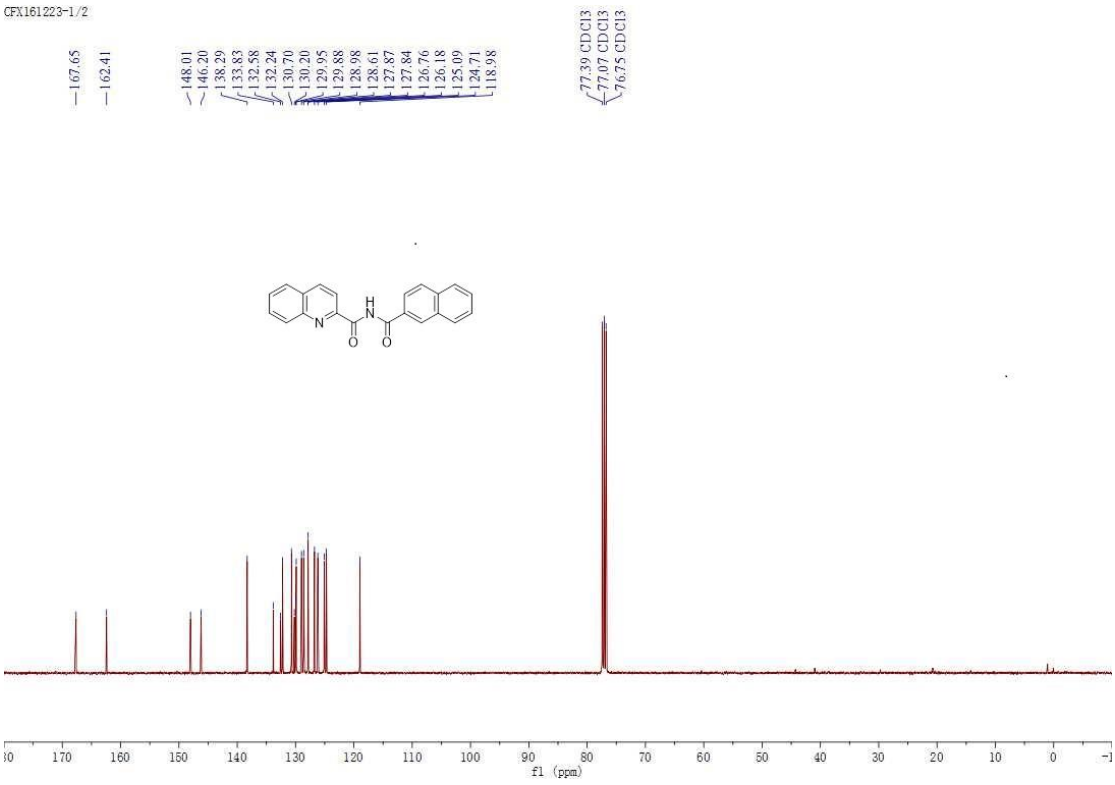
8.05
7.95
7.93
7.93
7.92
7.92
7.90
7.81
7.81
7.79
7.79
7.77
7.77
7.70
7.69
7.68
7.66
7.66
7.63
7.63
7.61
7.59
7.59
7.58
7.56
7.55
7.26 CDCl3
0.08
0.00
1.0
1.0
2.0
2.0
3.0
1.1
1.0
3.0
f1 (ppm)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138.29
133.83
132.58
132.24
130.70
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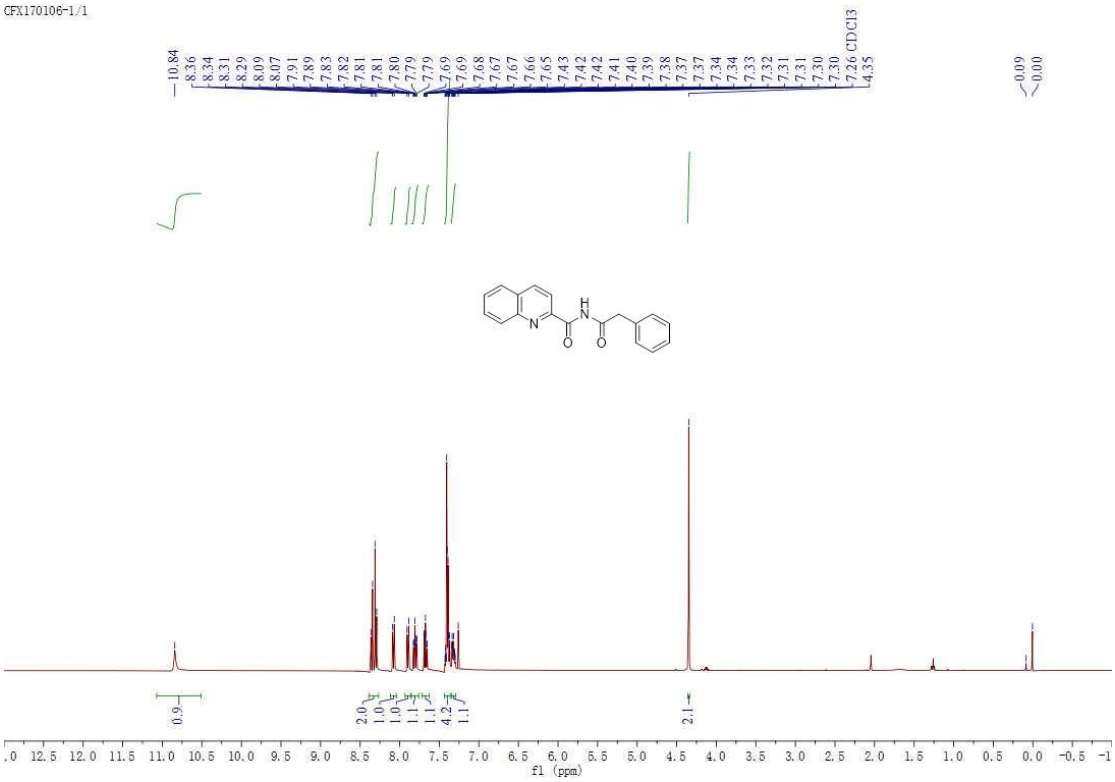
129.95
129.88
128.98
128.61
127.87
127.84
126.76
126.18
125.09
124.71
118.98
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
f1 (ppm)

2m


CFX170106-1/1
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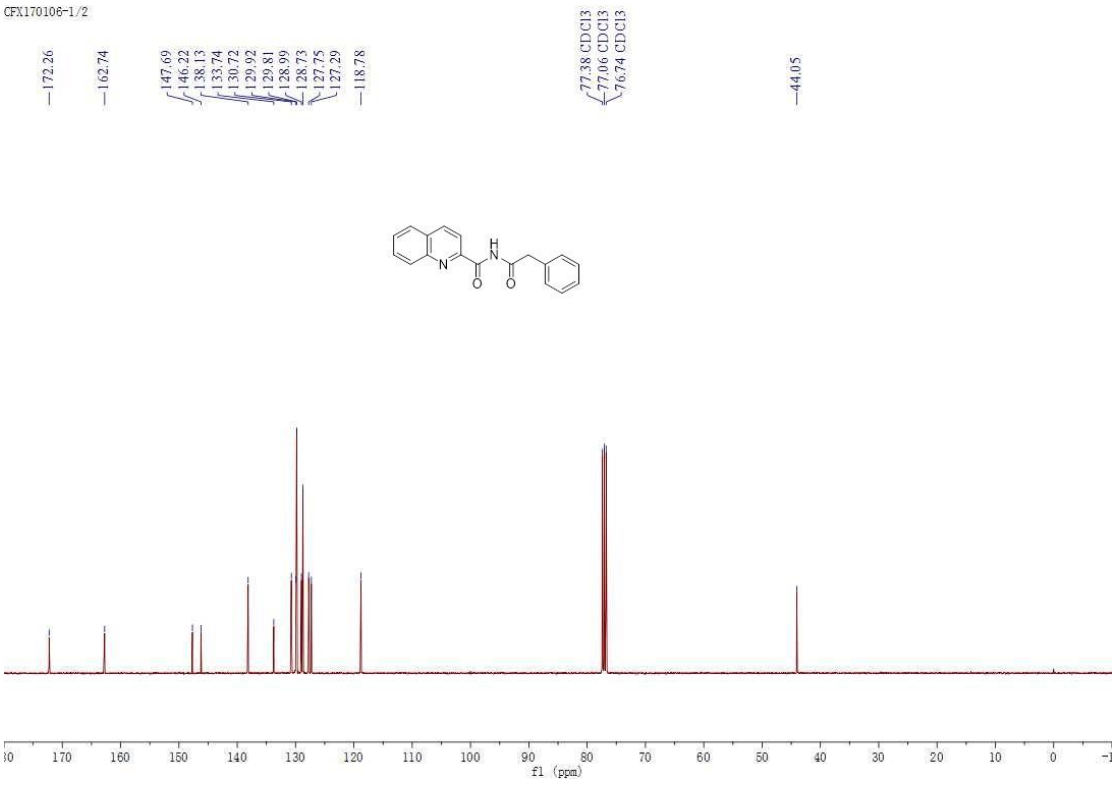
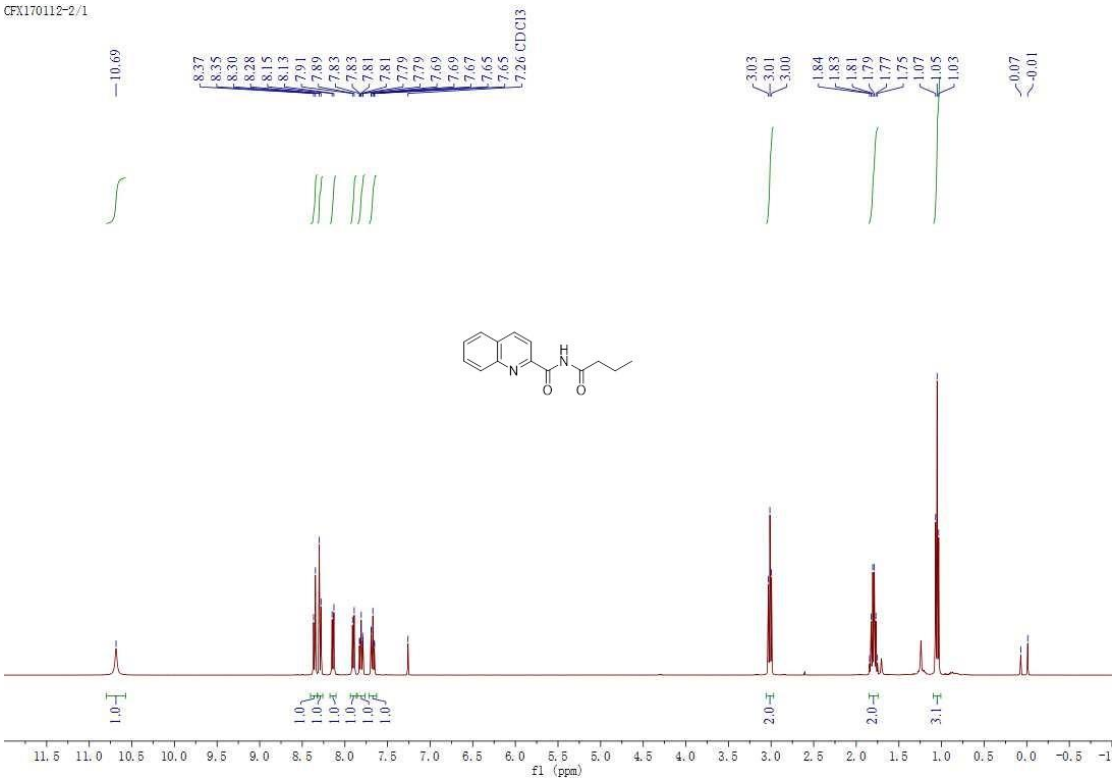
8.36
8.34
8.31
8.29
8.09
8.07
7.91
7.89
7.83
7.82
7.81
7.81
7.80
7.79
7.79
7.69
7.69
7.68
7.67
7.67
7.66
7.65
7.43
7.42
7.42
7.41
7.40
7.39
7.38
7.37
7.37
7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.26 CDCl3
4.35
0.09
0.00
0.9
2.0
1.0
1.0
1.1
1.1
4.2
1.1
2.1
f1 (ppm)


CFX170106-1/2
172.26
162.74
147.69
146.22
138.13
133.74
130.72
129.92
129.81
128.99
128.73
127.75
127.29
118.78
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
44.05
f1 (ppm)

2n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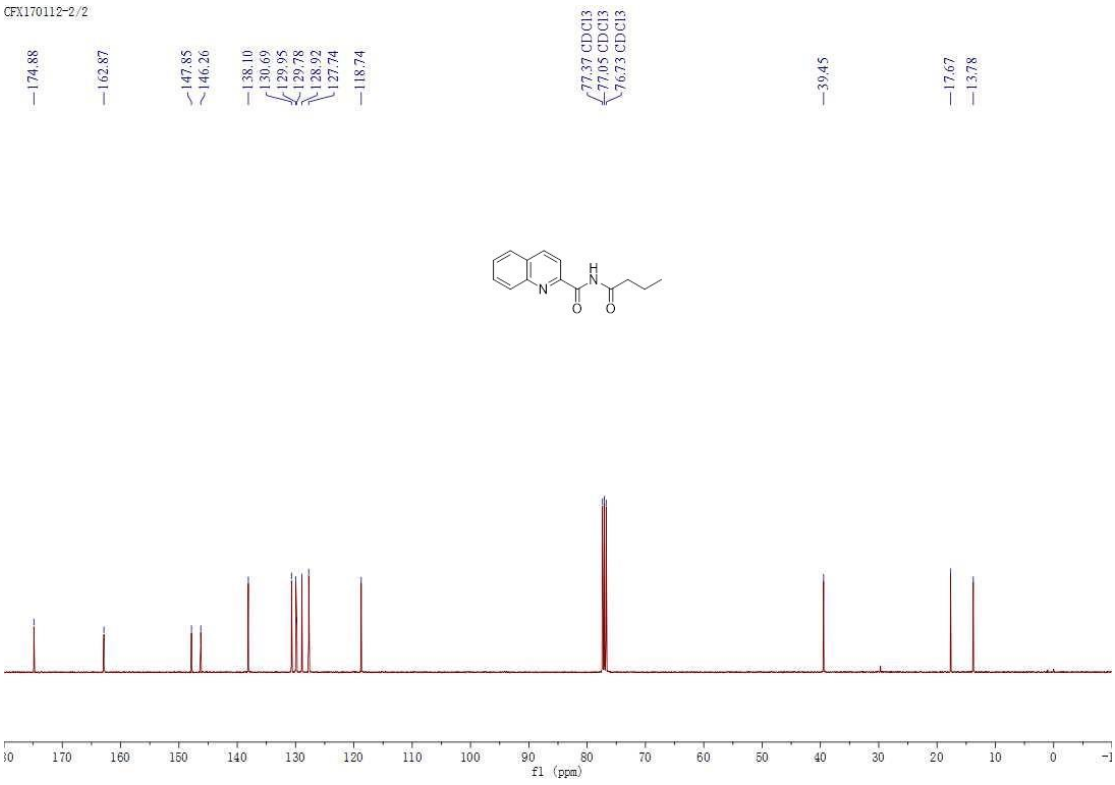
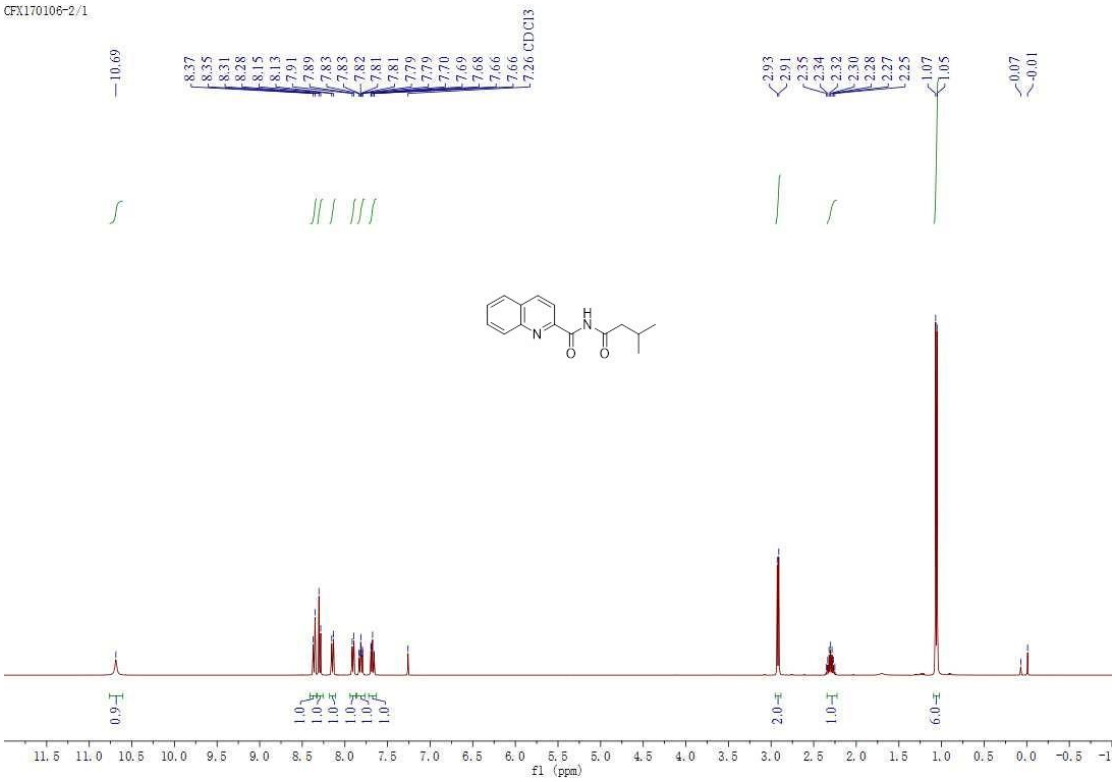
8.37
8.35
8.30
8.28
8.15
8.13
7.91
7.89
7.83
7.81
7.79
7.69
7.67
7.65
7.26 CDCl3
3.03
3.01
3.00
1.84
1.83
1.81
1.79
1.77
1.75
1.07
1.05
1.03
0.07
-0.01
1.0
1.0
1.0
1.0
1.0
1.0
2.0
2.0
3.1
f1 (ppm)


CFX170112-2/2
174.88
162.87
147.85
146.26
138.10
130.69
129.95
129.78
128.92
127.74
118.74
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
39.45
17.67
13.78
f1 (ppm)

2o


CFX170106-2/1
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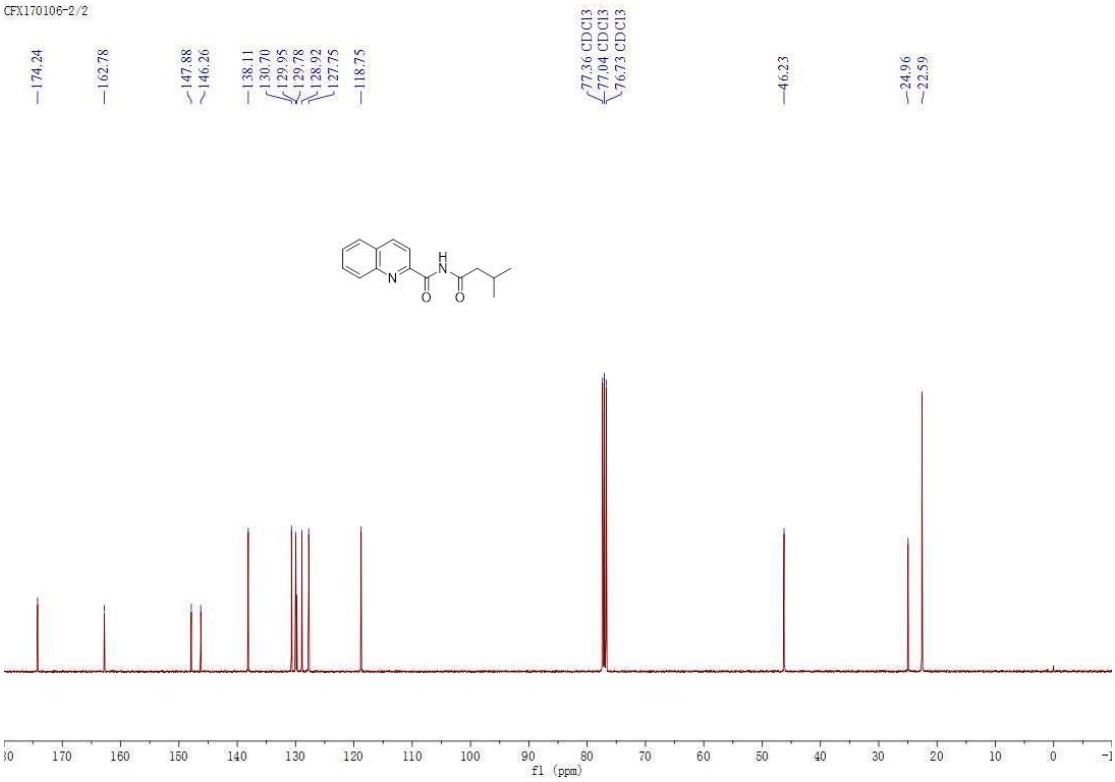
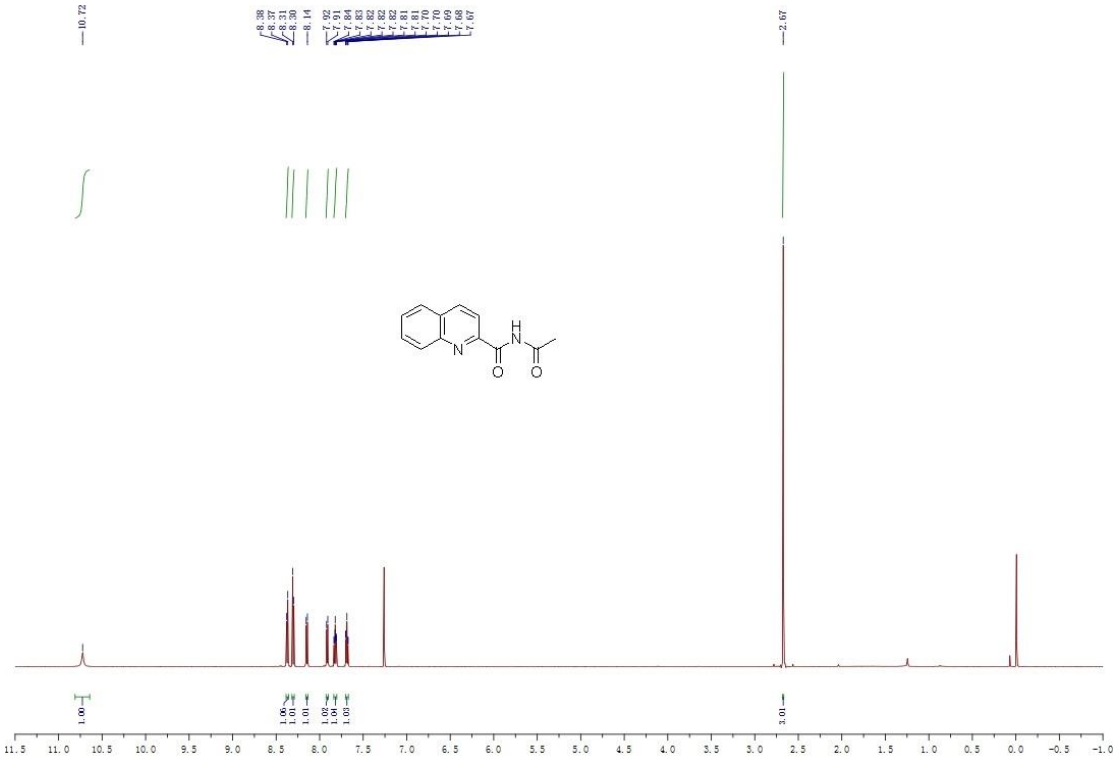
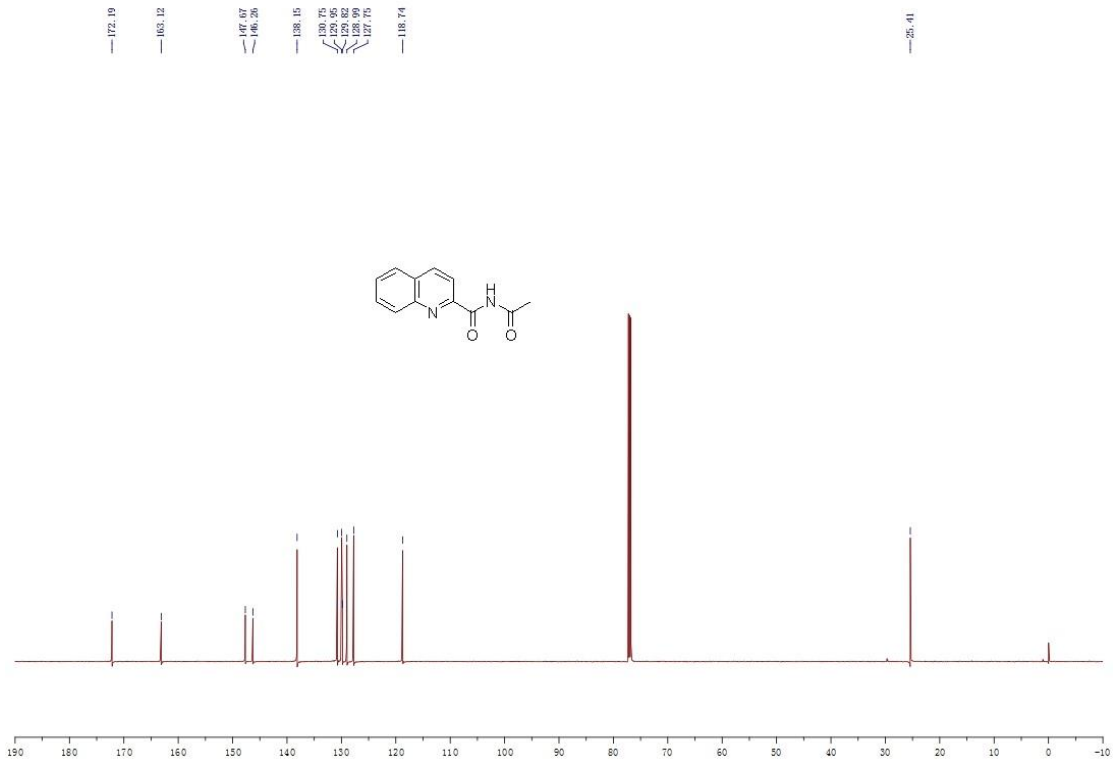
8.37
8.35
8.31
8.28
8.15
8.13
7.91
7.89
7.83
7.83
7.82
7.81
7.81
7.79
7.79
7.70
7.69
7.68
7.66
7.66
7.26 CDCl3
2.93
2.91
2.35
2.34
2.32
2.30
2.28
2.27
2.25
1.07
1.05
0.07
-0.01
0.9
1.0
1.0
1.0
1.0
1.0
1.0
2.0
1.0
6.0
f1 (ppm)

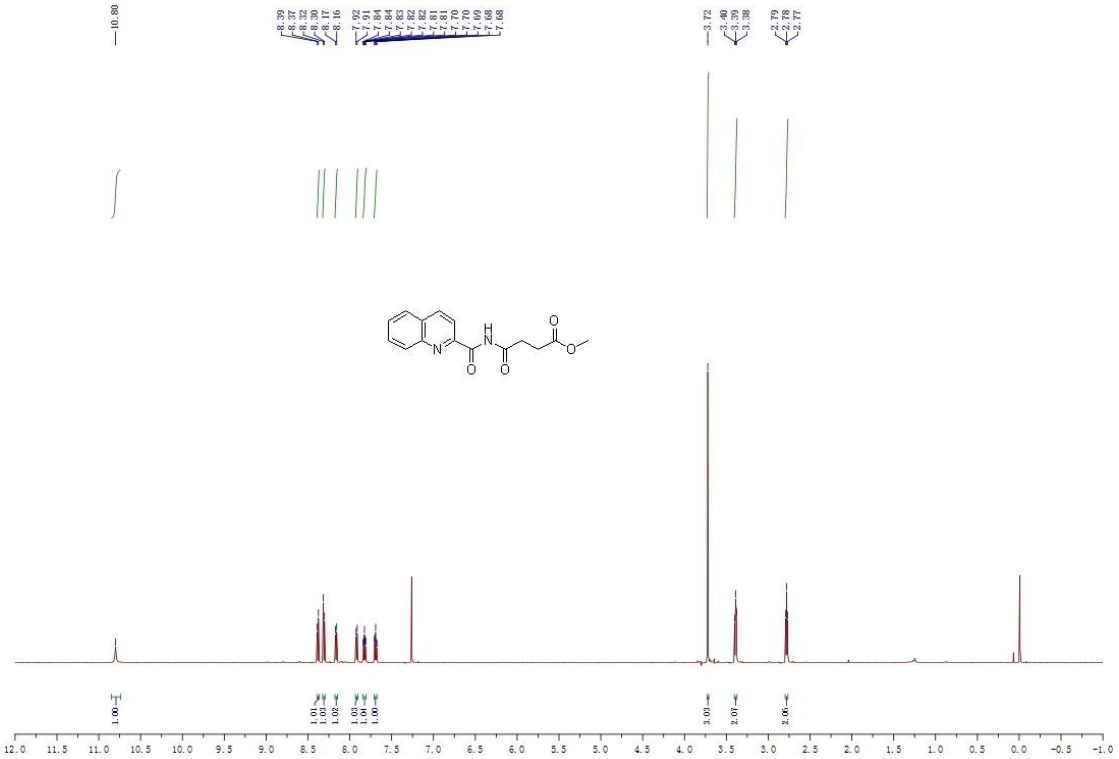

CFX170106-2/2
174.24
162.78
147.88
146.26
138.11
130.70
129.95
129.78
128.92
127.75
118.75
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
46.23
24.96
22.59
f1 (ppm)

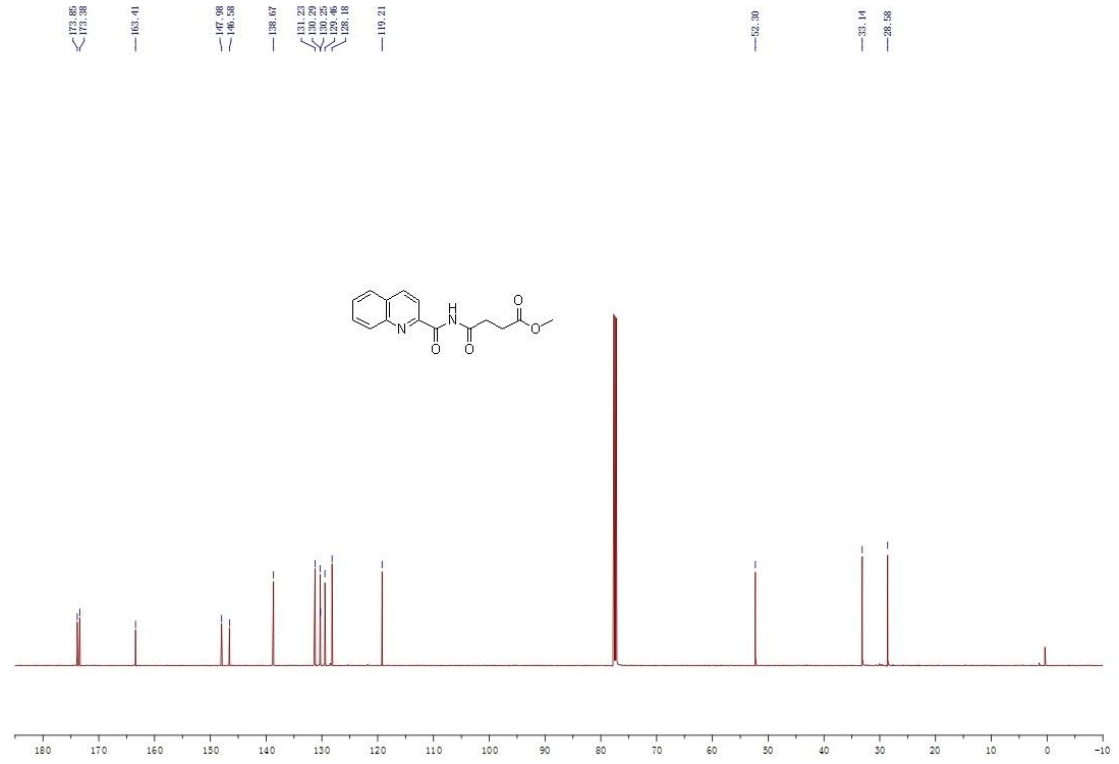
2p



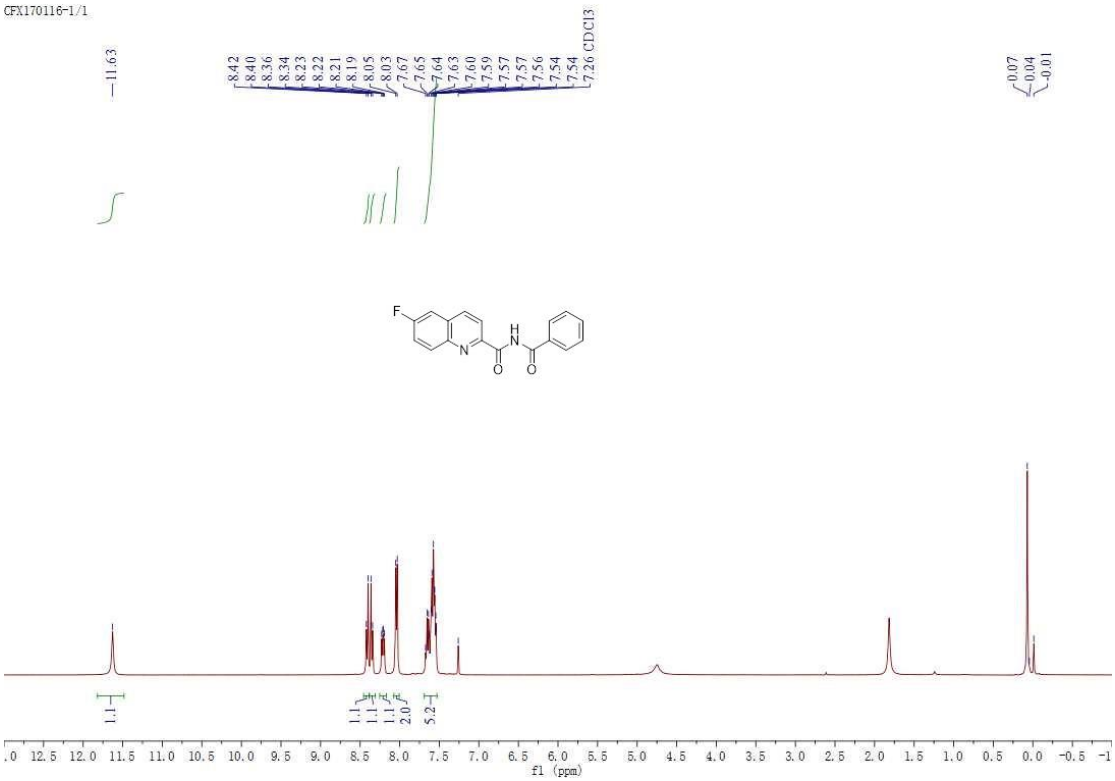


2q





2r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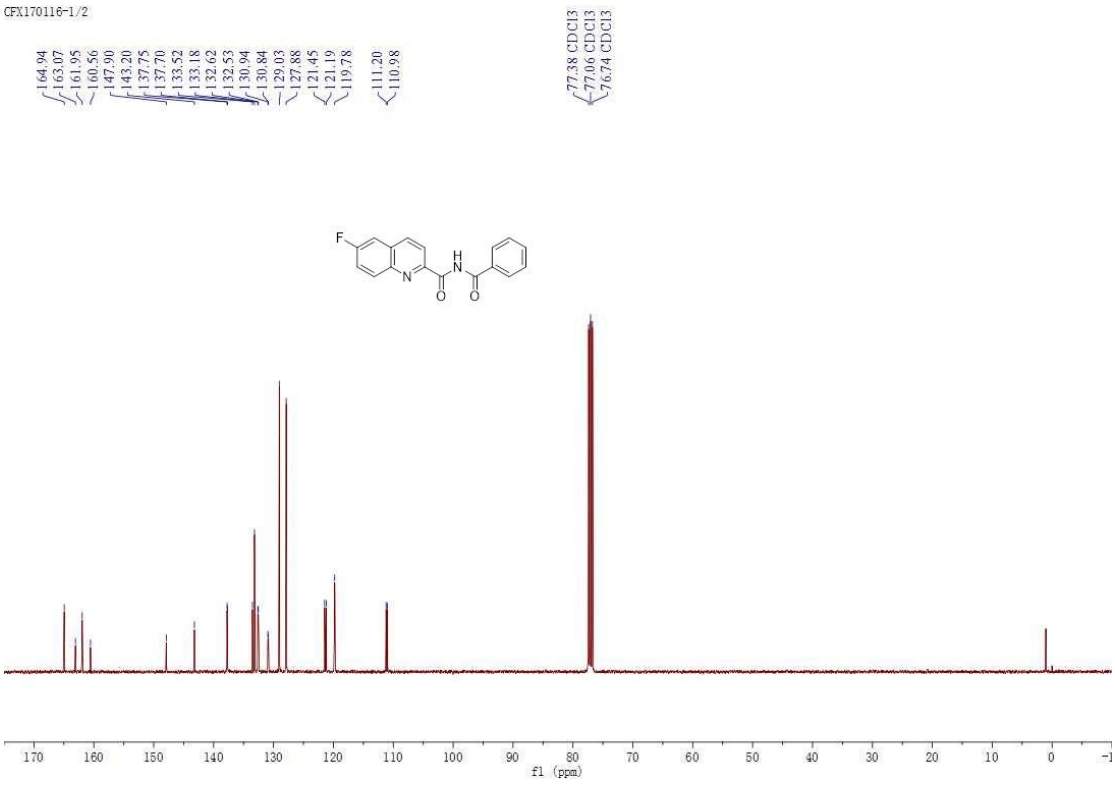
8.40
8.36
8.34
8.23
8.22
8.21
8.19
8.05
8.03
7.67
7.65
7.64
7.63
7.60
7.59
7.57
7.57
7.56
7.54
7.54
7.26 CDCl3
0.07
0.04
-0.01
F
N
H
N
O
O
1.1
1.1
1.1
1.1
2.0
5.2
f1 (ppm)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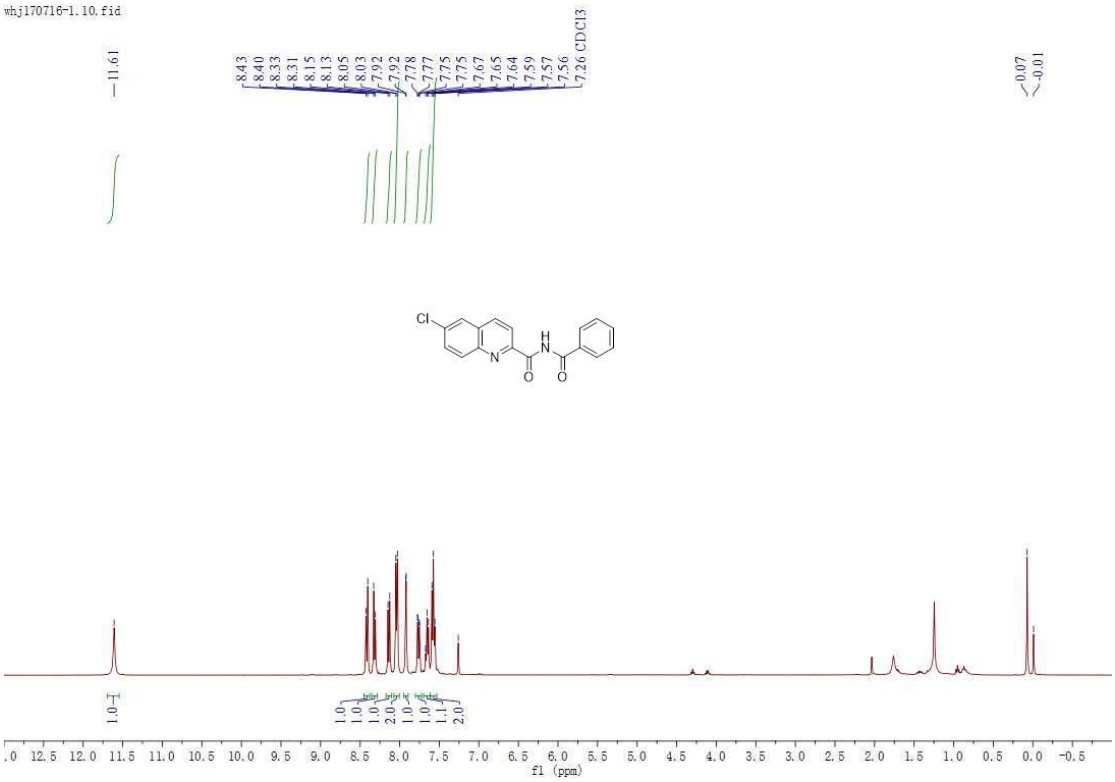
160.56
147.90
143.20
137.75
137.70
133.52
133.18
132.62
132.53
130.94
130.84
129.03
127.88
121.45
121.19
119.78
111.20
110.98
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
F
N
H
N
O
O
f1 (ppm)

2s


whj170716-1.10.fid
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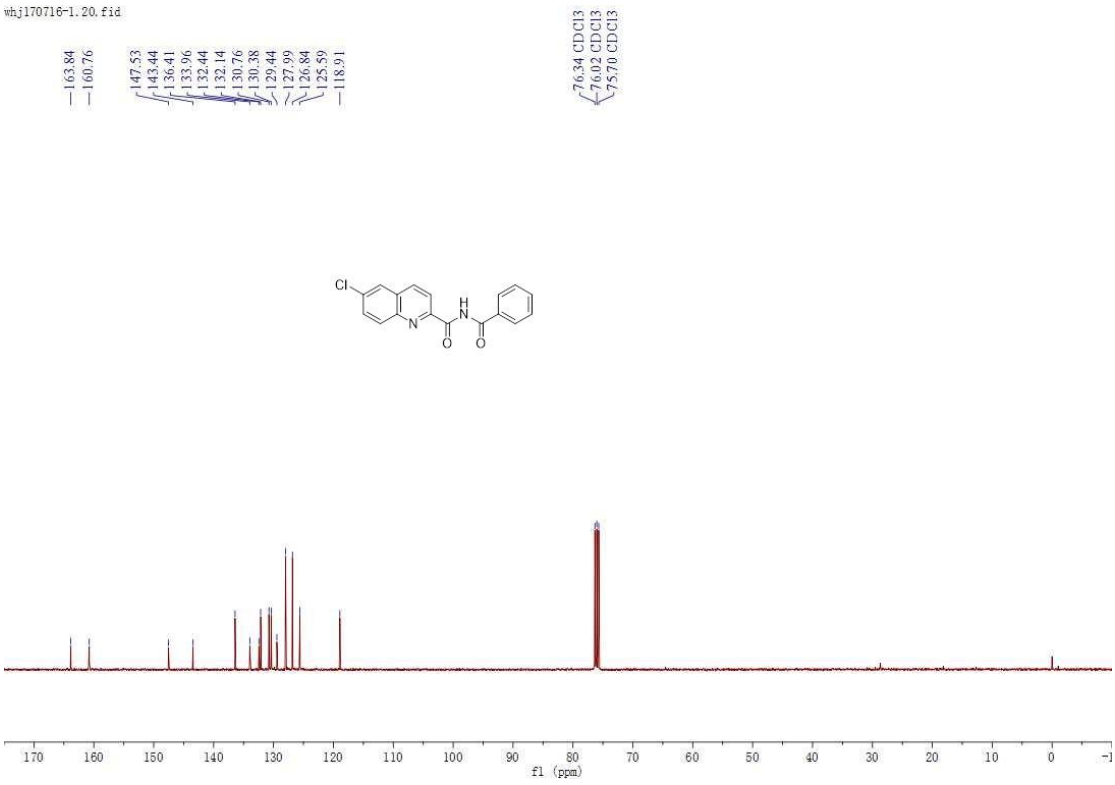
8.40
8.33
8.31
8.15
8.13
8.05
8.03
7.92
7.92
7.78
7.77
7.75
7.75
7.67
7.65
7.64
7.59
7.57
7.56
7.26 CDCl3
0.07
-0.01
Cl
H
N
O
O
1.0
1.0
1.0
1.0
2.0
1.0
1.0
1.1
2.0
f1 (ppm)


whj170716-1.20.fid
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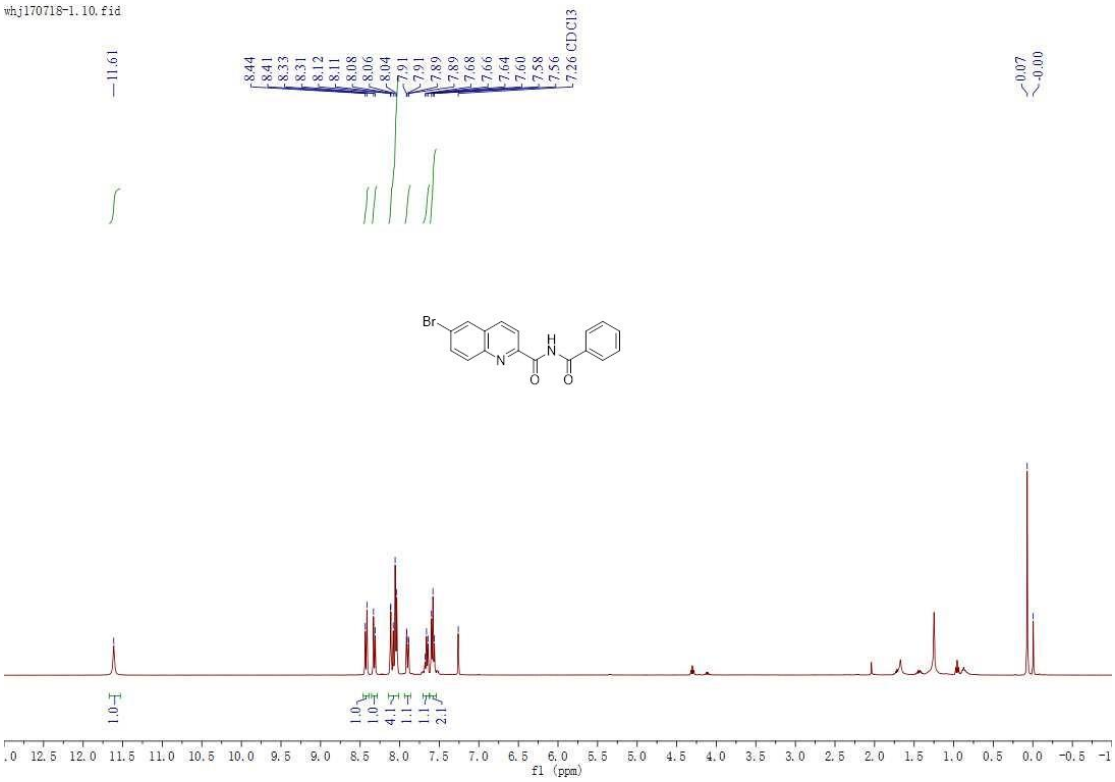
160.76
147.53
143.44
136.41
133.96
132.44
132.14
130.76
130.38
129.44
127.99
126.84
125.59
118.91
76.34 CDCl3
76.02 CDCl3
75.70 CDCl3
Cl
H
N
O
O
f1 (ppm)

2t


whj170718-1.10.fid
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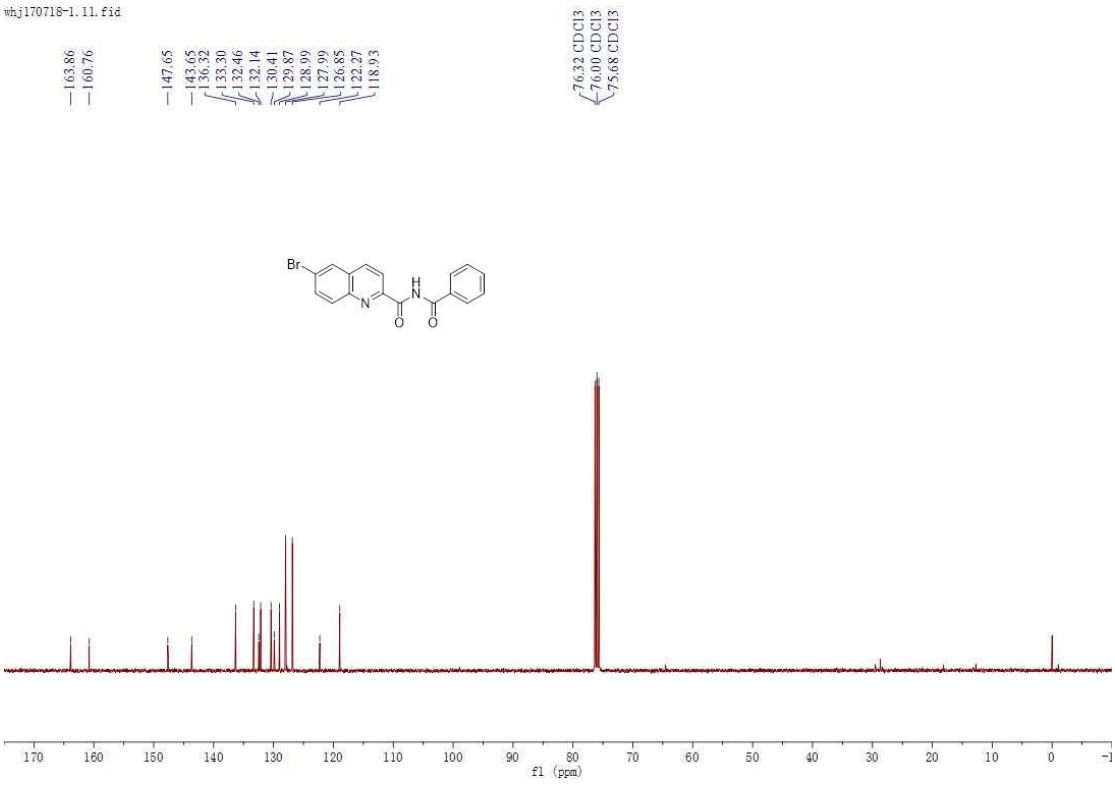
8.41
8.33
8.31
8.12
8.11
8.08
8.06
8.04
7.91
7.91
7.89
7.89
7.68
7.66
7.64
7.60
7.58
7.56
7.26 CDCl3
0.07
-0.00
Br
N
H
O
O
1.0
1.0
1.0
4.1
1.1
1.1
2.1
f1 (ppm)


whj170718-1.11.fid
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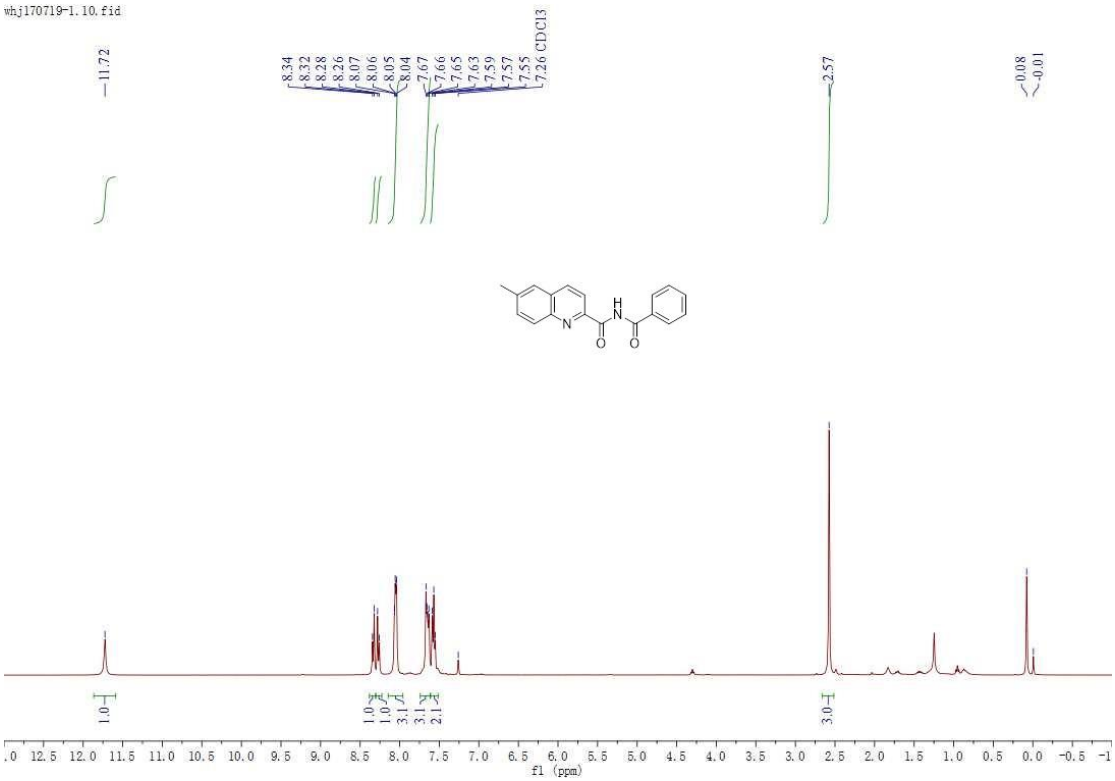
143.65
136.32
133.30
132.46
132.14
130.41
129.87
128.99
127.99
126.85
122.27
118.93
76.32 CDCl3
76.00 CDCl3
75.68 CDCl3
Br
N
H
O
O
f1 (ppm)

2v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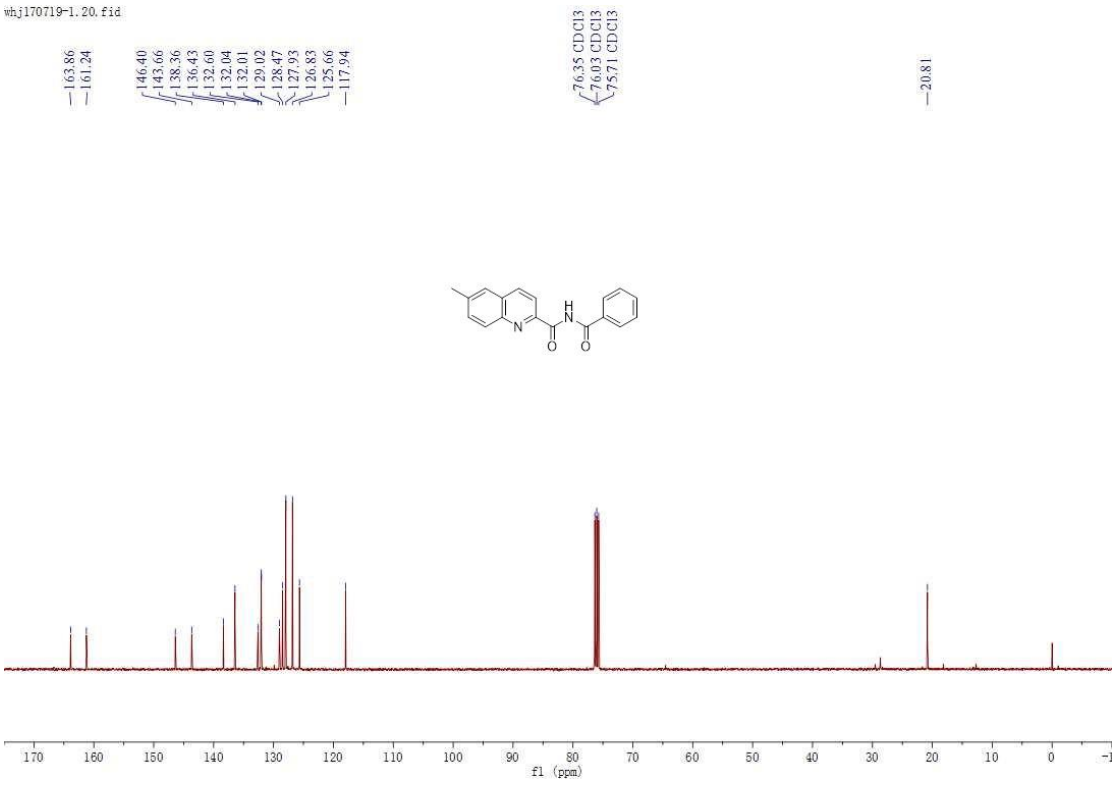
8.32
8.28
8.26
8.07
8.06
8.05
8.04
7.67
7.66
7.65
7.63
7.59
7.57
7.55
7.26 CDCl3
2.57
0.08
-0.01
1.0
1.0
3.1
3.1
2.1
3.0
f1 (ppm)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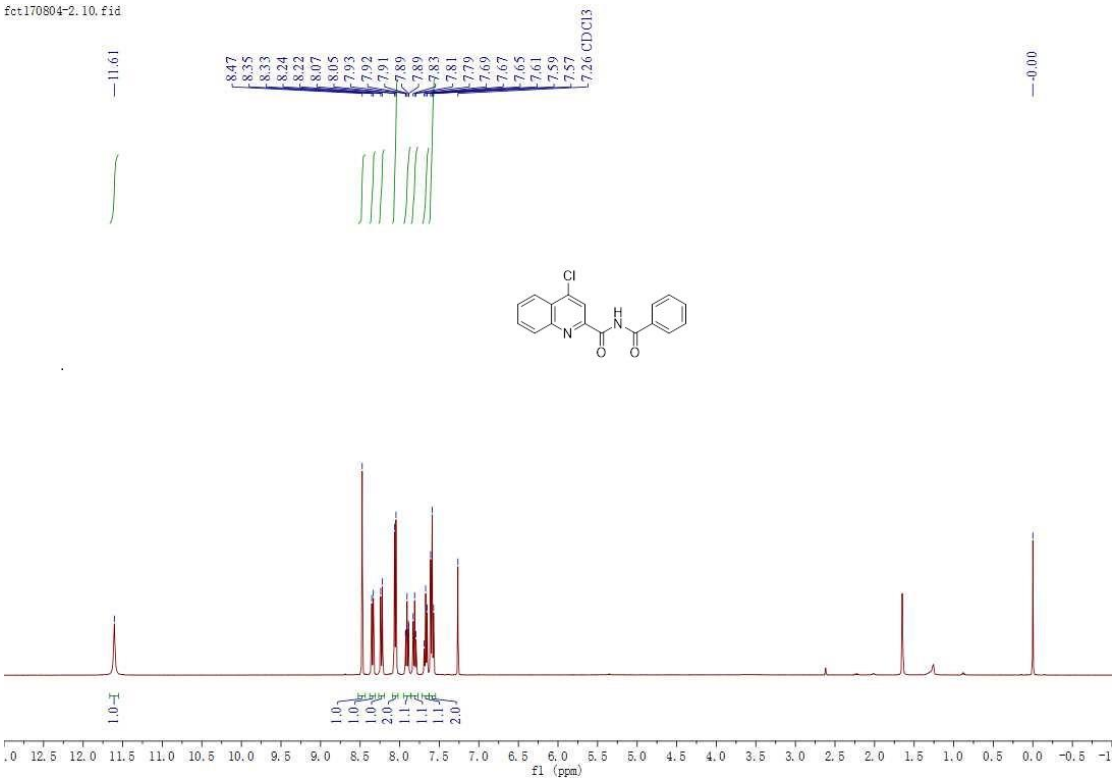
146.40
143.66
138.36
136.43
132.60
132.04
132.01
129.02
128.47
127.93
126.83
125.66
117.94
76.35 CDCl3
76.03 CDCl3
75.71 CDCl3
20.81
f1 (ppm)

2w


fct170804-2.10.fid
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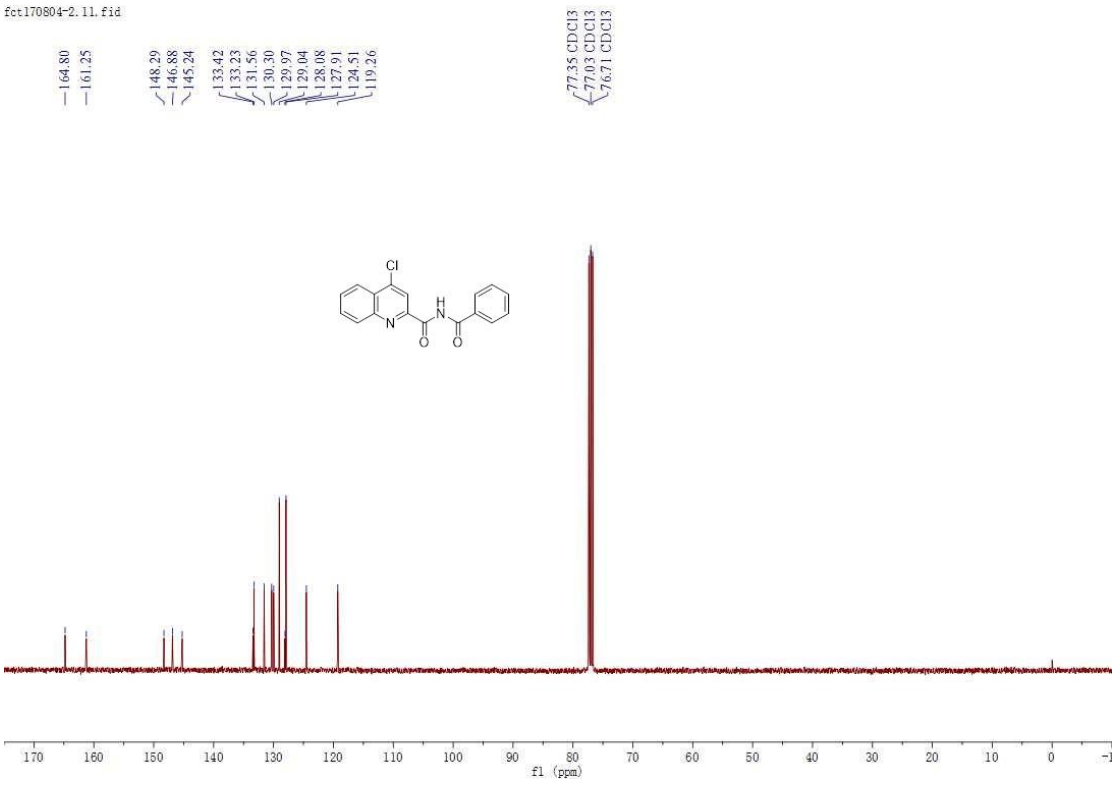
8.35
8.33
8.24
8.22
8.07
8.05
7.93
7.92
7.91
7.89
7.89
7.83
7.81
7.79
7.69
7.67
7.65
7.61
7.59
7.57
7.26 CDCl3
0.00
Cl
N
H
O
O
1.0
1.0
1.0
2.0
1.1
1.1
1.1
2.0
f1 (ppm)


fct170804-2.11.fid
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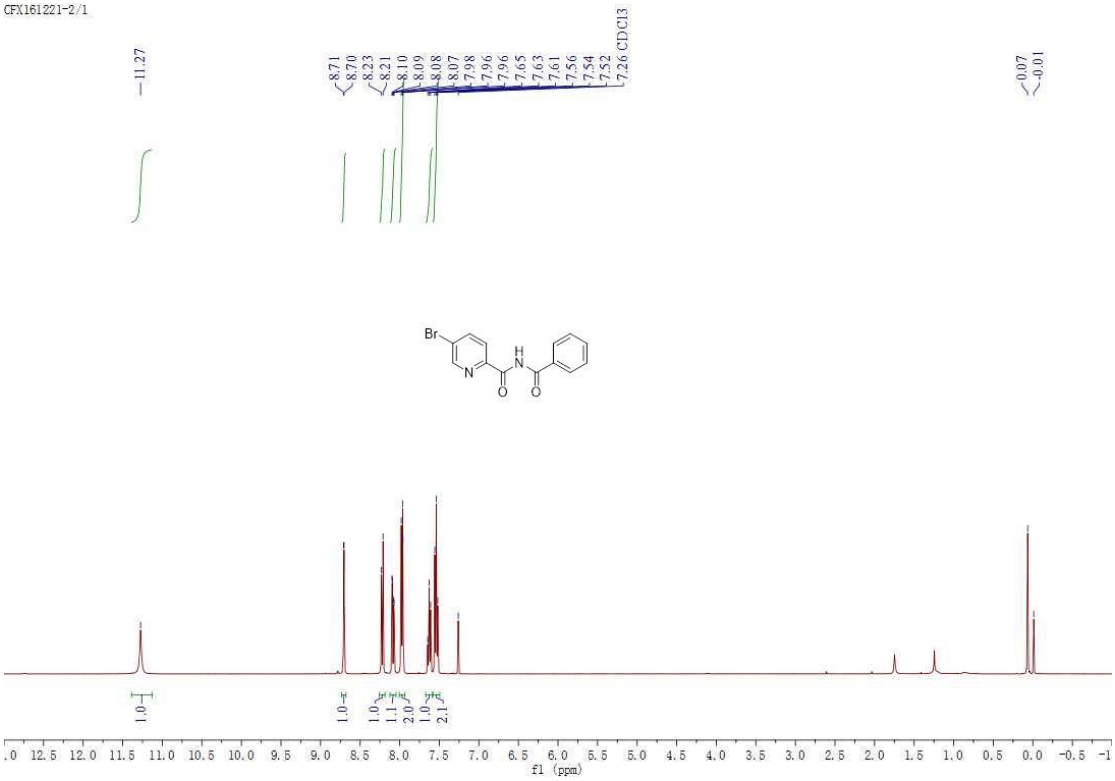
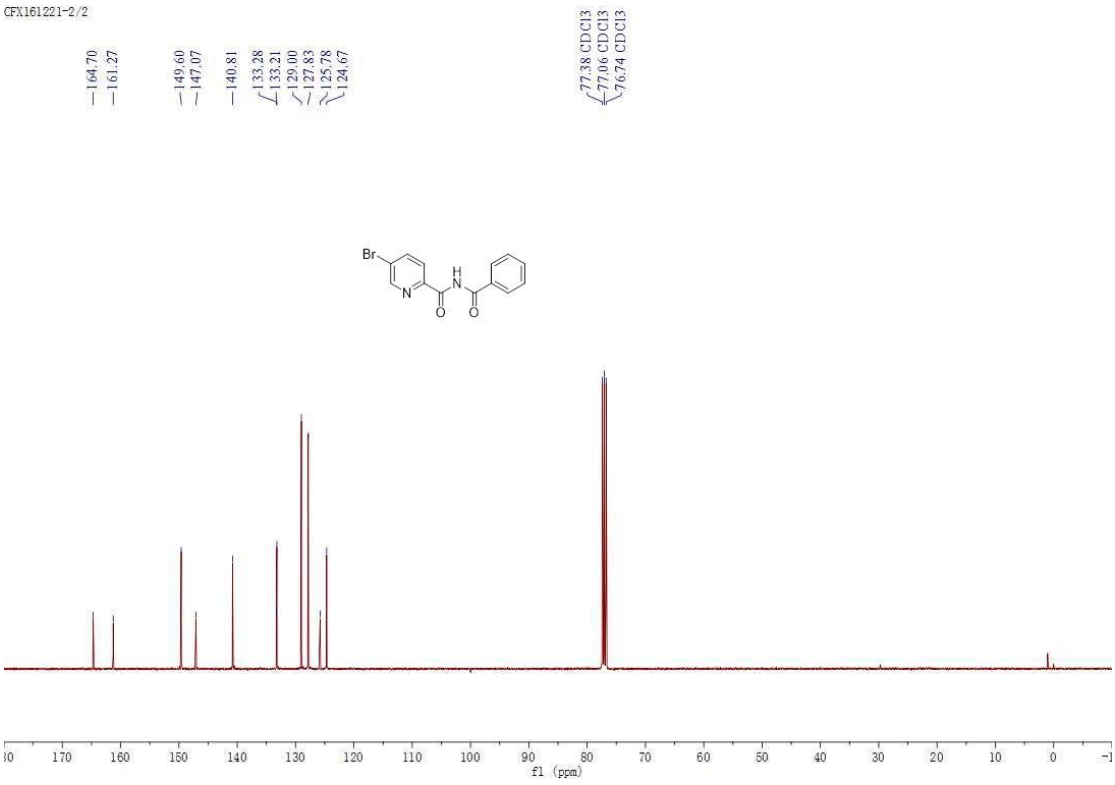
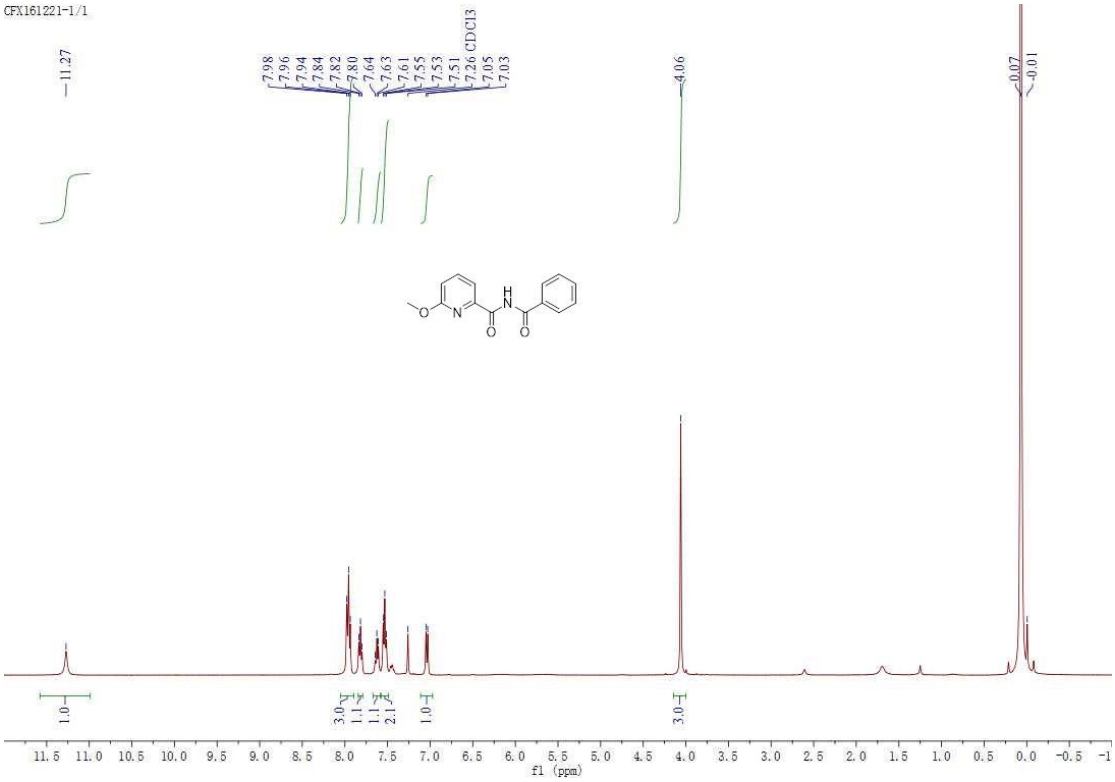
161.25
148.29
146.88
145.24
133.42
133.23
131.56
130.30
129.97
129.04
128.08
127.91
124.51
119.26
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
Cl
N
H
O
O
f1 (ppm)

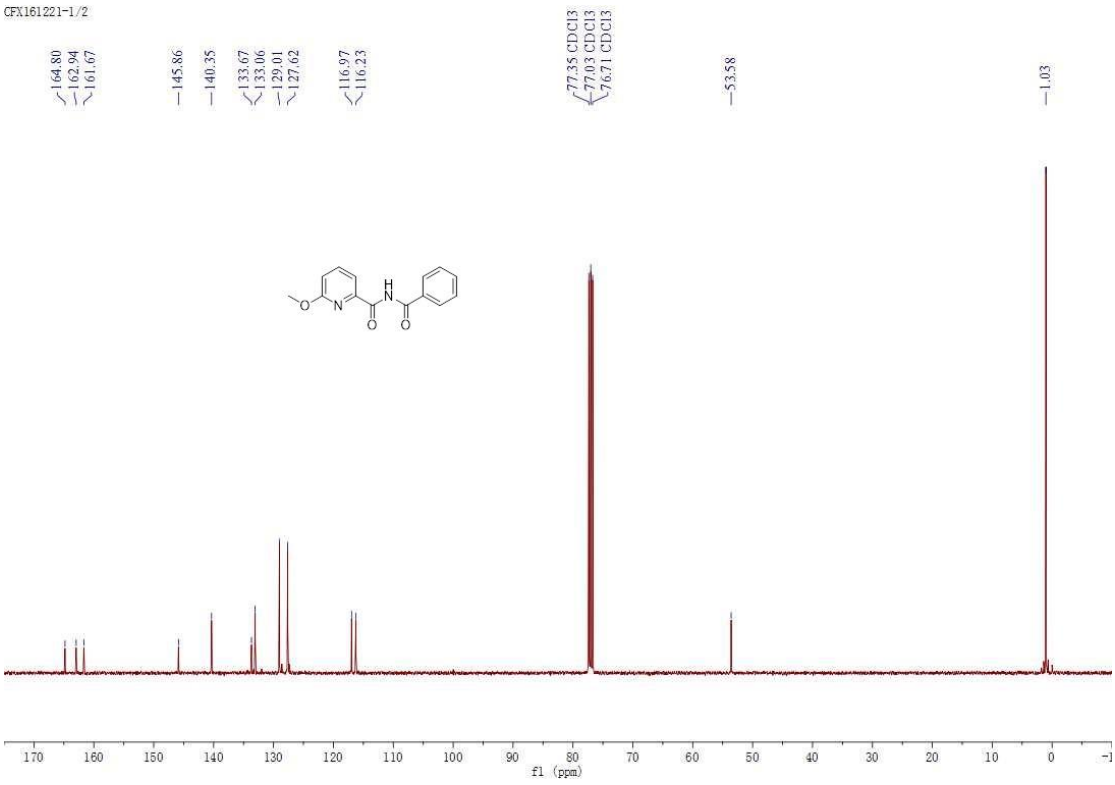
2x


CFX161221-2/1
11.27
8.71
8.70
8.23
8.21
8.10
8.09
8.08
8.07
7.98
7.96
7.96
7.65
7.63
7.61
7.56
7.54
7.52
7.26 CDCl3
0.07
-0.01
Br
N
H
O
O
1.0
1.0
1.1
2.0
1.0
2.1
f1 (ppm)


CFX161221-2/2
164.70
161.27
149.60
147.07
140.81
133.28
133.21
129.00
127.83
125.78
124.67
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
Br
N
H
O
O
f1 (ppm)

2y


CFX161221-1/1
11.27
7.98
7.96
7.94
7.84
7.82
7.80
7.64
7.63
7.61
7.55
7.53
7.51
7.26 CDCl3
7.05
7.03
4.06
0.07
-0.01
1.0
3.0
1.1
1.1
2.1
1.0
3.0
f1 (ppm)


CFX161221-1/2
164.80
162.94
161.67
145.86
140.35
133.67
133.06
129.01
127.62
116.97
116.23
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
53.58
1.03
f1 (ppm)