Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Aryne triggered dearomatization reaction of isoquinolines and quinolines with chloroform

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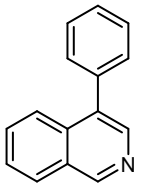
I. General Information

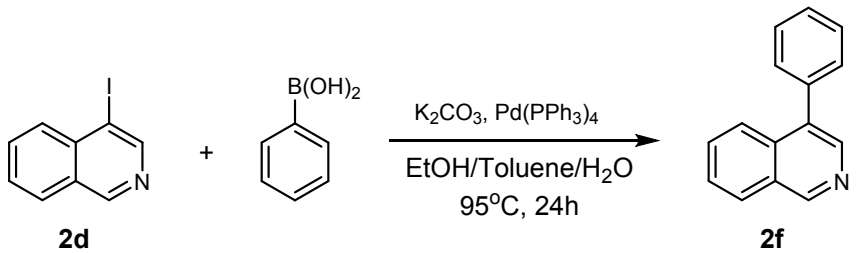
Unless stated otherwise, all reactions were carry out with distilled and dried solvents under an atmosphere of N_2, oven (100 °C) dried glassware with standard vacuum line techniques were used. Organic solvents used for carrying out reactions were dry using standard methods. The reactions were monitored either by thin-layer chromatography on silica Gel 60-F254 coated 0.2mm plates (Yantai Chemical Industry Research Institute) or by GC-MS (Thermo Fisher Trace1300ISQ). Visualization was accomplished by UV light (254nm). The crude products were purified either using a preparative thin-layer chromatography (TLC) plate or flash column chromatography using silica gel (normal phase, 200-300 mesh, Branch of Qingdao Haiyang Chemical) . ^{1}H NMR spectra was recorded on a 400 MHz spectrometer at ambient temperature. Data were report as follows: (1) chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quint = quintet and m = multiplet); (3) coupling constants (Hz).^{13}C NMR spectra were recorded on a 100 MHz spectrometer at ambient temperature. Chemical shifts were report in ppm from $CDCl_3$ (77.00 ppm). All commercial materials were use as received unless otherwise noted. Aryne precursors are all prepared following the literature procedures[1]. Isoquinoline **2b**[2], **2c**[2], **2d**[3], **2g**[2], **2h**[2], **2j**[4], and quinoline **2n**[5] are prepared following the literature procedures. Compound **9** is prepared following the literature procedures[6]. CsF was dried in vacuum at 130°C for 2h before use.

II. Substrates Preparation

Synthesis of 2f:



4-phenylisoquinoline (2f)

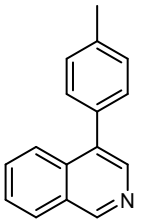


2d **2f**

4-Phenylisoquinoline **2f** was prepared according to the modified literature procedure.[3] In an oven-dried round-bottom flask, 4-iodoisoquinoline **2d** (62mg, 0.25 mmol, 1.0 equiv.) was taken in a mixture of 0.25mL EtOH, 0.5 mL water and 1mL toluene and degassed for 20 min. To the resulting mixture, phenylboronic acid (50 mg, 0.375mmol, 1.5 equiv.), K_2CO_3 (138mg, 1 mmol, 4.0 equiv.) and $Pd(PPh_3)_4$ (14mg, 0.0125 mmol, 0.05 equiv.) were added successively at r.t. The resulting mixture was stirred at 95°C under positive argon pressure for 24h. The reaction mixture was cooled to r.t. quenched

with sat. NH_4Cl solution, extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, concentrated in vacuo to obtain a black oil which was purified by silica gel column chromatography (PE: EA = 5:1 as the eluent) to give 4-phenylisoquinoline **2f** (95% yield) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.50 (s, 1H), 8.07 – 8.02 (m, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.56 – 7.44 (m, 5H).

Synthesis of (2g)

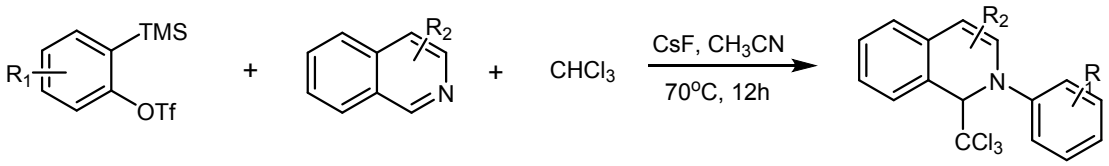


4-(p-tolyl)isoquinoline(2g)

Following the procedure of **2f**, the crude product was purified by silica gel chromatography (PE: EA = 5:1 as the eluent) to give **2g** (98% yield) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.48 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.72 – 7.53 (m, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 2.45 (s, 3H).

III. General procedure for the three-component reaction

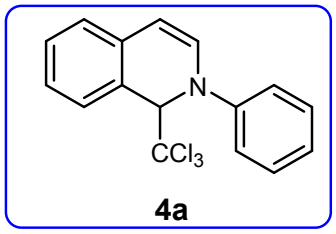
1) Scope of Aryne:



1 **2** **3** **4**

General procedure: To a 10 mL flame-dried schlenk tube containing CsF (0.5 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added aryne precursor (**1**) (0.18 mmol), (iso)quinolone **(2)** (0.15 mmol), acetonitrile (0.4 ml) and chloroform (0.4 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours (general procedure A) or 24 hours (general procedure B). The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (20 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE:EA).

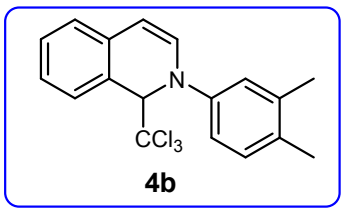
2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (4a)



4a

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4a** (91% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.41 – 7.30 (m, 3H), 7.29 – 7.19 (m, 4H), 7.05 (t, J = 7.2 Hz, 1H), 6.78 (dd, J = 7.3, 1.2 Hz, 1H), 6.12 (d, J = 7.3 Hz, 1H), 5.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.69, 133.14, 129.98, 129.25, 129.13, 129.12, 125.79, 124.19, 123.41, 122.55, 118.52, 108.75, 104.78, 74.54. HR-MS (ESI): Calcd for $C_{16}H_{13}Cl_3N^+$ $[M+H]^+$ requires 324.0108; found 324.0106.

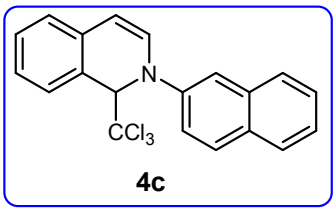
2-(3,4-dimethylphenyl)-1-(trichloromethyl) Naphthalene (4b)



4b

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4b** (85% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.5 Hz, 1H), 7.36 (dd, J = 10.8, 4.1 Hz, 1H), 7.28 – 7.17 (m, 2H), 7.15 – 7.05 (m, 1H), 7.03 (s, 2H), 6.75 (dd, J = 7.3, 1.0 Hz, 1H), 6.05 (d, J = 7.3 Hz, 1H), 5.77 (s, 1H), 2.26 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.05, 137.55, 133.40, 131.12, 130.30, 130.07, 129.99, 129.05, 125.59, 124.07, 123.16, 120.51, 116.46, 107.74, 105.05, 75.01, 20.14, 18.91. HR-MS (ESI): Calcd for $C_{18}H_{17}Cl_3N^+$ $[M+H]^+$ requires 352.0421; found 352.0417.

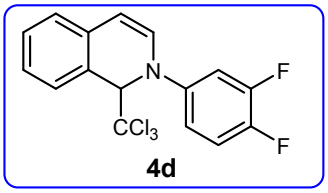
2-(naphthalen-2-yl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4c)



4c

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: DCM = 30:1 as the eluent) to give **4c** (81% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.78 – 7.69 (m, 2H), 7.53 (dd, *J* = 17.1, 5.4 Hz, 3H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.37 (q, *J* = 7.7 Hz, 2H), 7.25 (dd, *J* = 15.4, 7.8 Hz, 2H), 6.90 (d, *J* = 7.2 Hz, 1H), 6.15 (d, *J* = 7.3 Hz, 1H), 5.96 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.46, 134.02, 133.27, 130.14, 129.75, 129.56, 129.26, 129.24, 127.52, 127.14, 126.74, 125.89, 124.66, 124.28, 123.42, 119.24, 115.34, 108.86, 104.84, 74.80. HR-MS (ESI): Calcd for $C_{20}H_{15}Cl_3N^+$ $[M+H]^+$ requires 374.0265; found 374.0261.

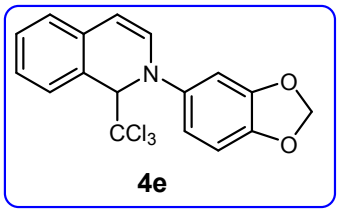
2-(3,4-difluorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4d)



4d

Following the general procedure with 0.25mmol 4,5-difluoro-2-(trimethylsilyl)phenyltrifluoromethanesulfonate instead of 0.15 mmol, for 24h. The crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4d** (90% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.30 (dt, *J* = 8.2, 6.0 Hz, 2H), 7.21 – 7.07 (m, 2H), 7.05 – 6.90 (m, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.20 (d, *J* = 7.3 Hz, 1H), 5.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.39 (dd, J = 247.9, 13.4 Hz), 145.20 (dd, J = 244.5, 12.8 Hz), 142.60 (d, J = 7.6 Hz), 131.75, 129.07, 128.37, 127.57, 125.23, 123.47, 122.31, 116.51 (d, J = 18.0 Hz), 113.22 (dd, J = 5.3, 3.2 Hz), 108.95, 107.23 (d, J = 20.9 Hz) , 103.35, 74.00.HR-MS (ESI): Calcd for $C_{16}H_{11}Cl_3F_2N^+$ $[M+H]^+$ requires 359.9920; found 359.9917.

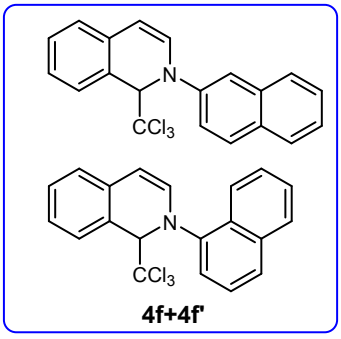
2-(benzo[d][1,3]dioxol-5-yl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4e)



4e

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4e** (85% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.29 (td, *J* = 7.5, 1.2 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.14 (dd, *J* = 11.5, 4.4 Hz, 1H), 6.80 (d, *J* = 2.3 Hz, 1H), 6.70 – 6.65 (m, 1H), 6.55 (dd, *J* = 7.3, 1.3 Hz, 1H), 5.94 (d, *J* = 7.5 Hz, 1H), 5.85 (t, *J* = 4.8 Hz, 2H), 5.58 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.33, 143.74, 142.59, 133.32, 130.78, 130.19, 129.15, 125.66, 124.10, 122.78, 113.32, 108.28, 107.56, 104.87, 102.52, 101.38, 76.08. HR-MS (ESI): Calcd for $C_{17}H_{13}Cl_3O_2N^+$ $[M+H]^+$ requires 368.0006; found 368.0002.

3-(naphthalen-2-yl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4f) and 2-(naphthalen-1-yl) -1-(trichlor omethyl) -1, 2-dihydroisoquinoline (4f')

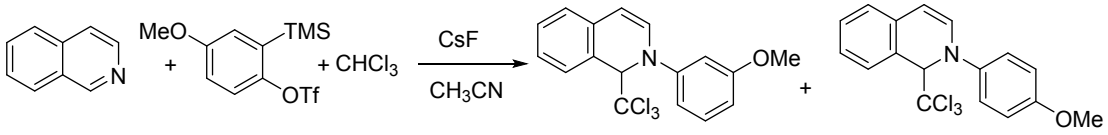


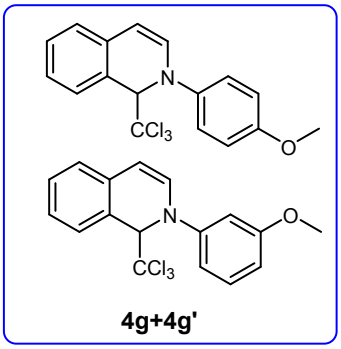
4f+4f'

Following the general procedure A, the crude product was

purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4f** and **4f'** (4:1, 85% yield) as a black solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 8.8 Hz, 4H), 7.78 – 7.70 (m, 8H), 7.62 – 7.47 (m, 14H), 7.43 (dd, J = 15.5, 7.5 Hz, 6H), 7.41 – 7.32 (m, 8H), 7.32 – 7.12 (m, 12H), 6.90 (d, J = 7.3 Hz, 4H) (major), 6.72 (d, J = 7.4 Hz, 1H), 6.15 (d, J = 7.3 Hz, 4H) (major), 5.96 (s, 4H) (major), 5.80 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.46(major), 134.14, 134.02(major), 133.27(major), 131.11, 130.14(major), 129.74, 129.56(major), 129.41, 129.26(major), 129.24(major), 127.52(major), 127.14(major), 126.74(major), 126.26, 125.89(major), 125.23, 124.66(major), 124.28(major), 124.03, 123.42(major), 119.24(major), 115.34(major), 108.86(major), 104.84(major), 102.96, 74.79(major). HR-MS (ESI): Calcd for $C_{20}H_{15}Cl_3N^+$ $[M+H]^+$ requires 374.0265; found 374.0261.

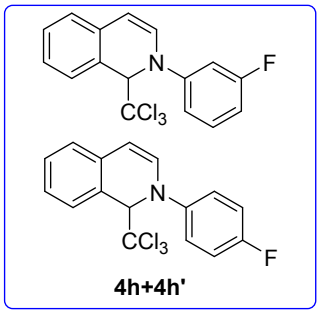
2-(4-methoxyphenyl)-1-(trichloromethyl)-1, 2-dihydroisoquinoline (4g) and 3-(4-methoxyphenyl) -1-(trichloromethyl)-1, 2-dihydroisoquinoline (4g')





Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4g** and **4g'** (1:1.15, 97% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, J = 7.3 Hz, 2H), 7.36 (ddd, J = 7.5, 2.3, 1.2 Hz, 2H), 7.31 – 7.14 (m, 7H), 6.94 – 6.82 (m, 3H), 6.80 (t, J = 2.3 Hz, 1H), 6.76 (dd, J = 7.3, 1.1 Hz, 1H), 6.68 (dd, J = 7.3, 1.0 Hz, 1H), 6.60 (dd, J = 8.2, 2.1 Hz, 1H), 6.12 (d, J = 7.3 Hz, 1H), 6.01 (d, J = 7.3 Hz, 1H)(major), 5.79 (s, 1H), 5.70 (s, 1H)(major), 3.81 (s, 3H), 3.78 (s, 3H)(major). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.49, 155.73, 148.03, 141.08, 133.45, 133.12, 130.82, 130.19, 129.98, 129.15, 129.09, 128.98, 125.88, 125.52, 124.26, 124.01, 123.63, 122.68, 121.44, 114.52, 110.96, 109.09, 107.39, 107.06, 105.14, 105.05, 104.69, 75.81(major), 74.57, 55.54(major), 55.34. HR-MS (ESI): Calcd for $C_{17}H_{14}Cl_3NO^+$ $[M+H]^+$ requires 354.0141; found 354.0211.

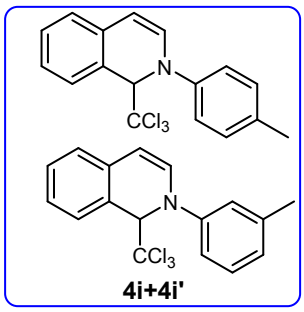
2-(3-fluorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4h) and 2-(4-fluorophenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4h')



Following the general procedure A, Following the general procedure with 0.25 mmol 4-fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate instead of 0.15 mmol, for 24h. The crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4h** and **4h'** (1:2.5, 88% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, J = 7.6 Hz, 4H), 7.41 – 7.34 (m, 4H), 7.30 – 7.25 (m, 4H), 7.25 - 7.20 (m, J = 6.9, 5.2, 2.5 Hz, 9H), 7.07 – 6.99

(m, 6H), 6.96 (dt, *J* = 11.5, 2.3 Hz, 1H), 6.76 – 6.69 (m, 2H), 6.67 (dd, *J* = 7.3, 1.3 Hz, 2H), 6.17 (d, *J* = 7.3 Hz, 1H), 6.08 (d, *J* = 7.3 Hz, 2H) (major), 5.74 (d, *J* = 1.0 Hz, 1H), 5.70 (d, *J* = 1.0 Hz, 2H) (major). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.43 (d, *J* = 245.2 Hz), 157.76 (d, *J* = 242.9 Hz) (major), 147.17 (d, *J* = 10.0 Hz), 142.44 (d, *J* = 2.6 Hz) (major), 132.12(major), 131.82, 129.35 (d, *J* = 9.7 Hz), 129.12(major), 128.99, 128.85(major), 128.29, 128.23(major), 127.12, 125.18, 124.85(major), 123.47, 123.21(major), 122.78, 121.98, 119.93 (d, *J* = 8.0 Hz) (major), 114.93 (d, *J* = 22.6 Hz) (major), 112.44 (d, *J* = 2.6 Hz), 109.14, 108.05 (d, *J* = 21.4 Hz), 107.37(major), 104.57, 104.32, 103.79, 74.41(major), 73.28. HR-MS (ESI): Calcd for $C_{16}H_{11}Cl_3FN^+$ $[M+H]^+$ requires 342.0014; found 342.0010.

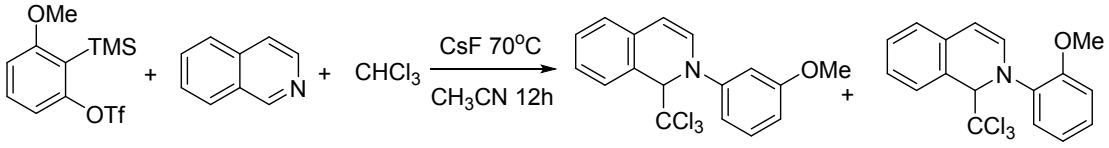
2-(p-tolyl)-1-(trichloromethyl)-1, 2-dihydroisoquinoline (4i) and 2-(m-tolyl)-1-(trichloromethyl)-1, 2-dihydroisoquinoline (4i')

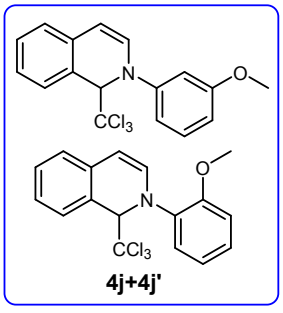


4i+4i'

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4i** and **4i'** (1:1.5, 93% yield) as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 3H), 7.33 – 7.25 (m, 3H), 7.22 – 7.08 (m, 7H), 6.85 – 6.74 (m, 4H), 6.73 (s, 2H), 6.68 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.60 (dd, *J* = 7.3, 0.9 Hz, 1H), 6.52 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.04 (d, *J* = 7.3 Hz, 1H) (major), 5.94 (d, *J* = 7.3 Hz, 1H), 5.71 (s, 1H)(major), 5.63 (s, 1H), 3.73 (s, 4H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.85(major), 144.68, 139.18(major), 133.34, 133.25(major), 132.30, 130.05(major), 130.02, 129.82(major), 129.78, 129.43, 129.09(major), 125.75(major), 125.64, 124.17(major), 124.10, 123.49(major), 123.43, 123.17, 119.46, 118.96(major), 115.78, 108.53(major), 107.91, 104.98, 104.87(major), 74.95, 74.66(major), 21.68(major), 20.56 HR-MS (ESI): Calcd for $C_{17}H_{115}C_{l3}N^+$ $[M+H]^+$ requires 338.0265; found338.0262.

2-(3-methoxyphenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4j) and 2-(2-methoxyphenyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (4j')





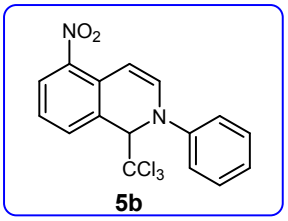
4j+4j'

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **4j** and **4j'** (13:1, 89% yield) as a yellow solid. *For major isomer* : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.28 – 7.23 (m, 1H), 7.23 – 7.18 (m, 2H), 6.86 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.80 (t, *J* = 2.3 Hz, 1H), 6.75 (dd, *J* = 7.3, 1.1 Hz, 1H), 6.59 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.11 (d, *J* = 7.3 Hz, 1H), 5.79 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.49, 148.02, 133.11, 129.98, 129.14, 128.97, 125.88, 124.26, 123.62, 110.96, 109.08, 107.39, 105.14, 104.69, 74.56, 55.33. HR-MS (ESI):

Calcd for $C_{17}H_{14}Cl_3NO^+$ $[M+H]^+$ requires 354.0141; found 354.0210.

2) Scope of (Iso)quinolines:

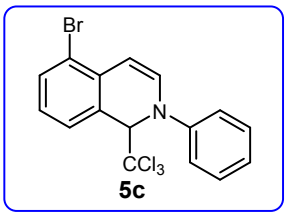
5-nitro-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (5b)



5b

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5b** (76% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.69 (dd, *J* = 19.6, 4.6 Hz, 1H), 7.41 - 7.37 (m, *J* = 4.0, 2.0 Hz, 2H), 7.35 - 7.30 (m, *J* = 8.6, 7.9 Hz, 3H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.04 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 5.89 (d, *J* = 1.3 SHz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.06, 143.68, 135.58, 134.45, 129.65, 128.49, 126.27, 125.04, 124.99, 124.10, 119.69, 103.73, 102.42, 74.73. HR-MS (ESI): Calcd for $C_{16}H_{12}Cl_3N_2O_2^+$ $[M+H]^+$ requires 368.9959; found 368.9959.

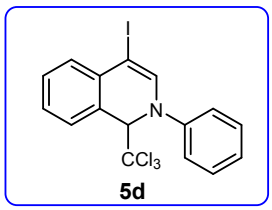
5-bromo-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (5c)



5c

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5c** (70% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 1H), 7.36 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.30 – 7.22 (m, 2H), 7.09 (q, *J* = 7.7 Hz, 2H), 6.88 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 5.78 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.26, 133.22, 132.73, 130.96, 129.39, 126.50, 124.84, 123.14, 119.75, 118.90, 107.44, 104.29, 74.66. HR-MS (ESI): Calcd for $C_{16}H_{11}BrCl_3N^+$ $[M+H]^+$ requires 401.9213; found 401.9214.

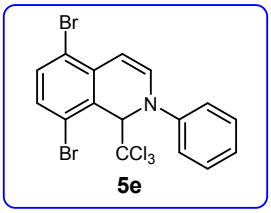
4-**iodo-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline (5d)**



5d

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5d** (96% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.40 – 7.30 (m, 4H), 7.27 – 7.24 (m, 2H), 7.19 (d, J = 1.2 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 5.75 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.47, 140.42, 129.32, 129.25, 128.57, 126.50, 125.09, 124.97, 122.60, 119.61, 103.81, 74.91. HR-MS (ESI): Calcd for $C_{16}H_{11}ICl_3N^+$ $[M+H]^+$ requires 449.9075; found 449.9073.

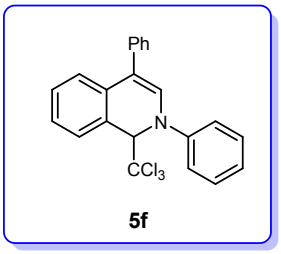
5,8-dibromo-2-phenyl-1-(trichloromethyl)-1,2-dihydronaphthalene (5e)



5e

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5e** (94% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.92 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.46 (d, *J* = 1.2 Hz, 1H), 6.36 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.01, 135.02, 133.90, 132.38, 130.88, 129.64, 123.84, 122.72, 119.80, 119.79, 118.42, 106.64, 103.98, 73.38. HR-MS (ESI): Calcd for $C_{16}H_{11}Br_2Cl_3N^+$ $[M+H]^+$ requires 481.8298; found 481.8293.

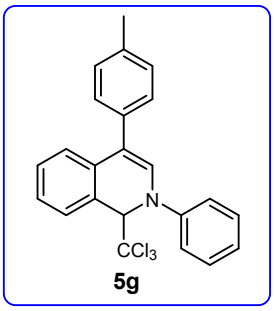
1,4-diphenyl-2-(trichloromethyl)-1,2-dihydroisoquinoline (5f)



5f

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give 5**f** (92% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 10.8, 4.9 Hz, 1H), 7.49 – 7.40 (m, 4H), 7.39 – 7.26 (m, 8H), 7.08 – 7.02 (m, 1H), 6.84 (d, *J* = 1.4 Hz, 1H), 5.85 (d, *J* = 1.0 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 146.12, 137.52, 133.70, 130.17, 129.31, 128.95, 128.91, 128.68, 127.18, 126.80, 126.40, 124.55, 123.63, 123.11, 122.40, 117.98, 103.93, 74.34. HR-MS (ESI): Calcd for $C_{22}H_{16}Cl_3N^+$ $[M+H]^+$ requires 440.0421; found 440.0423.

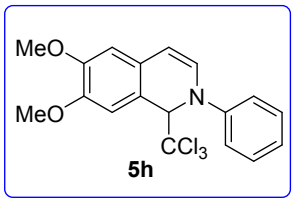
2-phenyl-4-(p-tolyl)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5g)



5g

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5g** (79% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 1H), 7.36 (dt, *J* = 6.9, 5.5 Hz, 4H), 7.32 – 7.29 (m, 4H), 7.24 (dd, *J* = 13.3, 5.4 Hz, 3H), 7.03 (dd, *J* = 9.9, 4.2 Hz, 1H), 6.80 (d, *J* = 1.4 Hz, 1H), 5.83 (d, *J* = 1.2 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.13, 136.90, 134.53, 133.82, 130.13, 129.37, 129.28, 128.90, 128.78, 126.43, 126.34, 124.59, 123.70, 123.11, 122.28, 117.86, 103.95, 74.32, 21.21 HR-MS (ESI): Calcd for $C_{23}H_{19}Cl_3N^+$ $[M+H]^+$ requires 414.0578; found 417.0572.

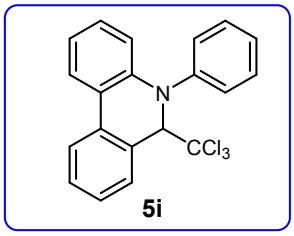
6,7-dimethoxy-2-phenyl-1-(trichloromethyl)-1,2-dihydroisoquinoline(5h)



5h

Following the general procedure A, reacted for 1h. the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **5i** (90% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.9 Hz, 2H), 7.26 (s, 1H), 7.04 (t, *J* = 7.2 Hz, 2H), 6.99 (s, 1H), 6.73 (s, 1H), 6.69 (dd, *J* = 7.3, 1.0 Hz, 1H), 6.06 (d, *J* = 7.3 Hz, 1H), 5.74 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.86, 147.47, 146.88, 129.29, 127.63, 126.90, 122.45, 118.40, 115.83, 113.28, 108.80, 106.91, 105.34, 77.36, 56.22, 55.89. HR-MS (ESI): Calcd for $C_{18}H_{17}Cl_3NO_2^+$ $[M+H]^+$ requires 384.0319; found 384.0315.

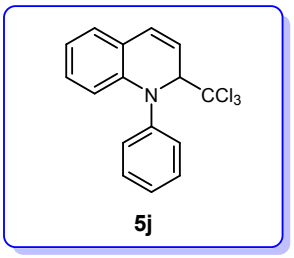
5-phenyl-6-(trichloromethyl)-5,6-dihydrophenanthridine (5i)



5i

Following the general procedure A, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5i** (46% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.37 – 7.29 (m, 4H), 7.29 – 7.19 (m, 3H), 7.19 – 7.12 (m, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 5.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.97, 139.21, 132.45, 130.55, 129.38, 129.07, 128.69, 128.36, 128.33, 126.90, 124.33, 123.46, 123.42, 123.14, 122.62, 120.47, 103.86, 76.67. HR-MS (ESI): Calcd for $C_{20}H_{15}Cl_3N^+$ $[M+H]^+$ requires 374.0265; found 374.0263.

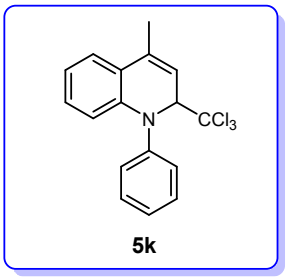
1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5j)



5j

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5j** (95% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.31 (dd, *J* = 10.6, 5.2 Hz, 2H), 7.18 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.15 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.99 (d, *J* = 5.9 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.90, 141.79, 130.27, 129.18, 128.73, 127.04, 125.36, 124.81, 124.66, 121.68, 121.42, 118.35, 104.16, 75.00. HR-MS (ESI): Calcd for $C_{16}H_{13}Cl_3N^+$ $[M+H]^+$ requires 324.0108; found 324.0108.

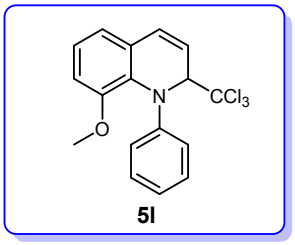
4-methyl-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5k)



5k

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5k** (40% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 7.18 – 7.12 (m, 1H), 7.12 – 7.09 (m, 1H), 7.06 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.99 (td, *J* = 7.5, 1.2 Hz, 1H), 5.97 (dd, *J* = 6.1, 1.3 Hz, 1H), 4.92 (d, *J* = 6.0 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 149.97, 141.44, 135.81, 129.14, 128.43, 127.32, 124.17, 123.87, 123.78, 122.18, 121.76, 115.82, 104.54, 74.84, 18.96. HR-MS (ESI): Calcd for $C_{17}H_{15}Cl_3N^+$ $[M+H]^+$ requires 338.0265; found 338.0263.

8-methoxy-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5l)

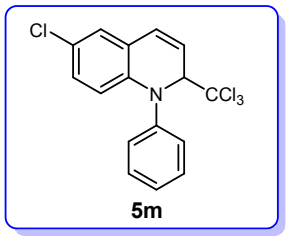


5l

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5l** (48% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (ddd, *J* = 8.9, 5.4, 1.9 Hz, 2H), 7.10 – 7.05 (m, 2H), 6.99 (ddd, *J* = 8.5, 2.3, 1.1 Hz, 1H), 6.93 (ddd, *J* = 6.9, 2.5, 1.2 Hz, 1H), 6.87 (d, *J* = 9.5 Hz, 1H), 6.82 (dd, *J*

= 7.5, 1.2 Hz, 1H), 6.76 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.09 (ddd, *J* = 9.3, 6.0, 1.3 Hz, 1H), 4.88 – 4.84 (m, 1H), 3.54(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.78, 149.66, 129.98, 129.39, 128.62, 128.57, 123.95, 122.79, 120.16, 119.97, 119.60, 113.69, 103.30, 75.08, 56.51. HR-MS (ESI): Calcd for $C_{17}H_{15}OCl_3N^+$ $[M+H]^+$ requires 354.0214; found 354.0214.

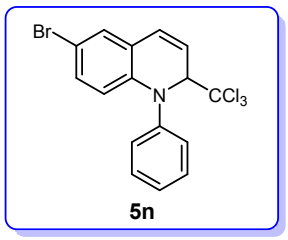
6-chloro-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5m)



5m

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5m** (86% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.26 – 7.19 (m, 2H), 7.11 – 7.04 (m, 2H), 6.98 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.80 (d, *J* = 9.6 Hz, 1H), 6.10 (dd, *J* = 9.6, 5.9 Hz, 1H), 4.90 (dd, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.55, 140.50, 129.40, 129.33, 128.65, 126.58, 125.17, 125.05, 122.68, 119.69, 103.89, 74.99. HR-MS (ESI): Calcd for $C_{16}H_{12}Cl_4N^+$ $[M+H]^+$ requires 357.9718; found 357.97120.

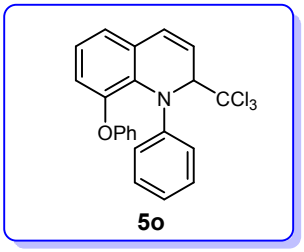
6-bromo-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5n)



5n

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5n** (86% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 7.21 – 7.12 (m, 2H), 6.88 (d, *J* = 3.9 Hz, 1H), 6.86 (d, *J* = 2.9 Hz, 1H), 6.16 (dd, *J* = 9.6, 5.9 Hz, 1H), 4.98 (d, *J* = 5.9 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 149.31, 140.96, 131.40, 129.42, 129.32, 129.13, 126.86, 125.17(two carbon), 122.77, 119.50, 113.80, 103.82, 74.86. HR-MS (ESI): Calcd for $C_{16}H_{12}Cl_3BrN^+$ $[M+H]^+$ requires 401.9213; found 401.9215.

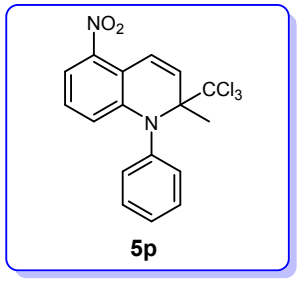
8-phenoxy-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5o)



5o

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5o** (70% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 3H), 7.16 – 7.11 (m, 4H), 7.11 – 7.05 (m, 3H), 7.04 – 7.00 (m, 1H), 6.98 – 6.93 (m, 2H), 6.54 (dd, *J* = 8.6, 0.9 Hz, 2H), 6.17 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.76 (dd, *J* = 6.0, 0.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 157.59, 149.51, 148.20, 132.94, 129.85, 129.77, 129.33, 129.15, 128.69, 123.70, 122.91, 122.34, 122.24, 121.59, 120.13, 117.24, 102.95, 75.46. HR-MS (ESI): Calcd for $C_{22}H_{17}Cl_3NO^+$ $[M+H]^+$ requires 416.0370; found 416.0373.

2-methyl-5-nitro-1-phenyl-2-(trichloromethyl)-1,2-dihydroquinoline (5p)

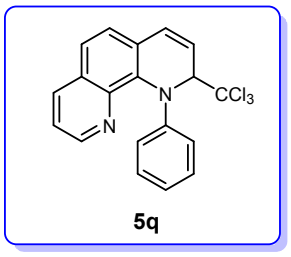


5p

Following the general procedure B, reacted for 24h, the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5p** (46% yield) as a yellow liquid.

^{1}H NMR (400 MHz, DMSO) ^{1}H NMR (400 MHz, DMSO) δ 8.15 (d, *J* = 2.7 Hz, 1H), 7.86 (dd, *J* = 9.2, 4.5 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.61 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 7.20 – 7.15 (m, 2H), 6.21 – 6.07 (m, 2H), 1.65 (s, 3H).^{13}C NMR (100 MHz, DMSO) ^{13}C NMR (100 MHz, DMSO) δ 150.80, 140.72, 138.51, 133.79, 131.56, 130.18, 128.80, 127.02, 125.64, 124.68, 122.64, 120.99, 115.37, 72.05, 40.15, 39.94, 39.73, 39.53, 39.32, 39.11, 38.90, 24.60. HR-MS (ESI): Calcd for $C_{17}H_{14}Cl_3N_2O_2^+$ $[M+H]^+$ requires 383.0115; found 383.0109.

1-phenyl-2-(trichloromethyl)-1,2-dihydro-1,10-phenanthroline (5q)



5q

Following the general procedure B, the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **5q** (43% yield) as a yellow solid. ^{1}H NMR (400 MHz, CDCl3) δ 8.68 (d, *J* = 2.6 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.20 (m, 1H), 7.20 – 7.09 (m, 5H), 6.98 (t, *J* = 6.7 Hz, 1H), 6.31 (dd, *J* = 9.3, 6.0 Hz, 1H), 5.13 (d, *J* = 6.0 Hz, 1H).^{13}C NMR (100 MHz, CDCl3) δ 151.18, 149.46, 142.74, 136.51, 135.84, 129.88, 129.20, 128.72, 127.59, 125.26, 123.24, 122.85, 121.04, 120.90, 120.78, 103.16, 75.57. HR-MS (ESI): Calcd for $C_{19}H_{14}Cl_3N_2^+$ $[M+H]^+$ requires 357.0217; found 357.0213.

3) Substrate Scope with $CDCl_3$

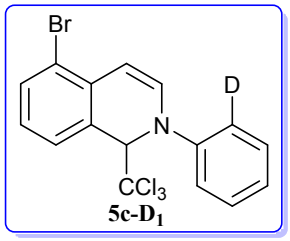
General procedure C: To a 10 mL flame-dried schlenk tube containing CsF (0.5 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added aryne precursor (**1**) (0.18 mmol), (iso)quinoline (0.15 mmol), acetonitrile (0.4 ml) and deuterated chloroform (0.4 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours. The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (20 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA). Percentage of exchanged protons at the specified position are determined by ^{1}H NMR.

2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5a-D_1)

5a-D_1

Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5a-D_1** (73% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, J = 7.9 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.29 – 7.20 (m, 3H), 7.04 (tt, J = 7.8, 3.9 Hz, 1H), 6.78 (dd, J = 7.3, 1.3 Hz, 1H), 6.12 (d, J = 7.3 Hz, 1H), 5.81 (d, J = 1.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.75, 133.25, 130.07, 129.33, 129.22(three carbon), 125.88, 124.28, 123.54, 122.62, 118.60, δ 118.21 (m).108.86, 104.86, 74.66. HR-MS (ESI): Calcd for $C_{16}H_{12}DCl_3N^+$ $[M+H]^+$ requires 325.0171; found 325.0168.

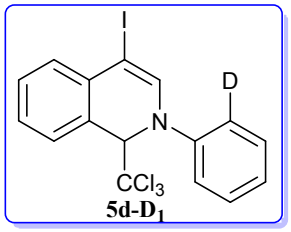
5-bromo-2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5c-D_1)



5c-D$_1$

Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5c-D$_1$** (90% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 8.1 Hz, 1H), 7.33 (dd, *J* = 16.2, 14.4 Hz, 2H), 7.29 – 7.20 (m, 1H), 7.09 (q, *J* = 7.7 Hz, 2H), 6.88 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.44 (d, *J* = 7.5 Hz, 1H), 5.78 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 146.20, 133.22, 132.72, 130.94, 129.39, 129.39, 129.28, 126.50, 124.84, 123.12, 119.75, 118.86, 118.48 (m), 107.45, 104.30, 74.66.

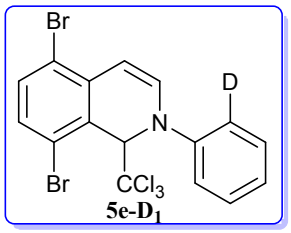
4-iodo-2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5d-D$_1$)



5d-D$_1$

Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5d-D$_1$** (79% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.29 (m, 4H), 7.24 (d, *J* = 6.8 Hz, 1H), 7.19 (d, *J* = 0.9 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 5.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.42, 135.41, 133.21, 130.02, 129.83, 129.45, 129.35, 128.22, 127.36, 124.22, 123.35, 118.56, 118.40(m), 103.74, 76.55, 74.82.

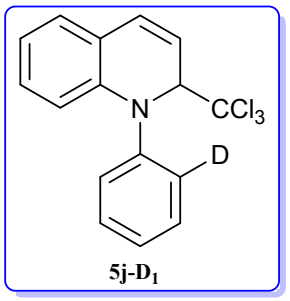
5,8-dibromo-2-(phenyl-2-d)-1-(trichloromethyl)-1,2-dihydroisoquinoline (5e-D$_1$)



5e-D$_1$

Following the general procedure C, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5e-D$_1$** (74% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.32 (dd, *J* = 12.3, 8.4 Hz, 2H), 7.12 (dd, *J* = 14.8, 7.5 Hz, 1H), 6.93 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.45 (d, *J* = 0.8 Hz, 1H), 6.36 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl3) δ 145.95, 135.02, 133.91, 132.36, 130.89, 129.64, 129.54, 123.83, 122.73, 119.79, 119.75, 119.36(m), 118.43, 106.67, 103.98, 73.38.

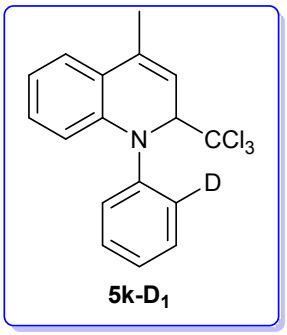
1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline (5j-D$_1$)



5j-D$_1$

Following the general procedure C, reacted for 24h. The crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **5j-D$_1$** (90% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 1H), 7.32 – 7.26 (m, 2H), 7.19 – 7.16 (m, 1H), 7.15 – 7.08 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.13 (dd, *J* = 9.5, 5.9 Hz, 1H), 4.99 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.87, 141.80, 130.31, 129.24, 129.13, 128.78, 127.10, 125.41, 124.59(m), 124.76, 124.68, 121.75, 121.49, 118.42, 104.21, 75.02.

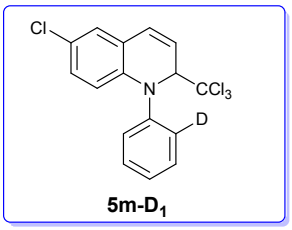
4-methyl-1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline (5k-D$_1$)



5k-D$_1$

Followingthe general procedure C, reacted for 24h. The crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5k-D$_1$** (40% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.36 – 7.30 (m, 2H), 7.22 – 7.17 (m, 1H), 7.15 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.07 – 7.00 (m, 1H), 6.01 (dd, *J* = 6.1, 1.1 Hz, 1H), 4.96 (d, *J* = 5.9 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.94, 141.37, 135.77, 129.09, 128.98, 128.39(m), 127.29, 124.10, 123.74, 122.15, 121.73, 115.79, 104.53, 18.93.

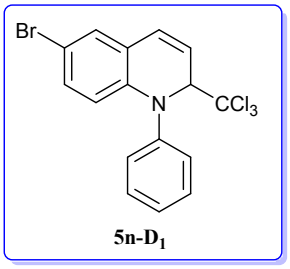
6-chloro-1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline (5m-D$_1$)



5m-D$_1$

Following the general procedure C, reacted for 24h the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5m-D$_1$** (86% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 1H), 7.33 – 7.28 (m, 2H), 7.18 – 7.12 (m, 2H), 7.06 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.91 (dd, *J* = 17.3, 9.1 Hz, 2H), 6.18 (dd, *J* = 9.6, 5.9 Hz, 1H), 4.98 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.40, 140.40, 129.31, 129.24, 129.20, 128.56, 126.49, 126.46, 125.06, 124.90(m), 122.60, 119.61, 103.80, 74.90.

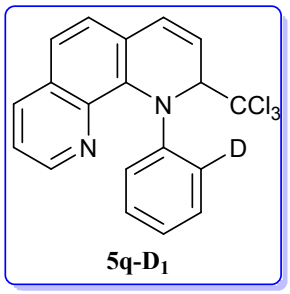
6-bromo-1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydroquinoline (5n-D$_1$)



5n-D$_1$

Following the general procedure C, reacted for 24h the crude product was purified by silica gel chromatography (PE: EA = 100:1 as the eluent) to give **5n-D$_1$** (86% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 1H), 7.34 – 7.27 (m, 3H), 7.21 – 7.12 (m, 2H), 6.87 (dd, *J* = 9.1, 3.5 Hz, 2H), 6.17 (dd, *J* = 9.6, 5.9 Hz, 1H), 4.98 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.35, 141.05, 131.50, 129.52, 129.40, 129.29, 129.23, 126.97, 125.26, 125.19(m), 122.88, 119.60, 113.90, 103.90, 74.96.

1-(phenyl-2-d)-2-(trichloromethyl)-1,2-dihydro-1,10-phenanthroline (5q-D$_1$)



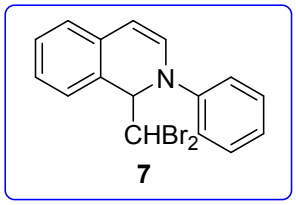
5q-D$_1$

Following the general procedure C, reacted for 24h the crude product was purified by silica gel chromatography (PE: EA = 20:1 as the eluent) to give **5q-D$_1$** (43% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.04 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.19 – 7.10 (m, 1H), 6.32 (dd, *J* = 9.3, 6.0 Hz, 1H), 5.05 (dd, *J* = 63.4, 8.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.16, 149.50, 142.79, 136.54, 135.86, 129.91, 129.24, 128.74, 128.64, 127.62, 125.28, 123.29, 122.86, 121.05, 121.03, 120.94, 120.81, 75.61.

4） Reaction of benzyne precursor 1a, Isoquinoline 2a, and Nucleophile

General procedure D: To a 10 mL flame-dried schlenk tube containing CsF (0.5 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added **1a** (0.18 mmol), isoquinoline (0.15 mmol), acetonitrile (0.4 ml) and nucleophile (0.4 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours (general procedure A) or 24 hours (general procedure B). The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (20 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE:EA).

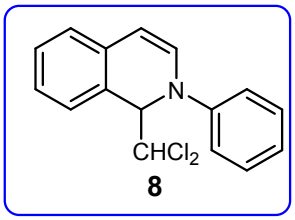
1-(dibromomethyl)-2-phenyl-1,2-dihydroisoquinoline (7)



7

Following the procedure D, using dibromomethane as nucleophile, the crude product was further purified by silica gel flash chromatography (PE: EA = 200:1 as the eluent) to give **5f** (52% yield) as a maroon solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 4H), 7.16 - 7.19 (m, 4H), 7.02 (t, J = 7.3 Hz, 1H), 6.66 (dd, J = 7.2, 1.5 Hz, 1H), 6.07 (d, J = 7.3 Hz, 1H), 5.69 (d, J = 8.3 Hz, 1H), 5.49 (dd, J = 8.3, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.96, 131.08, 129.32, 129.22, 128.66, 127.50, 125.77, 125.18, 123.96, 122.09, 117.53, 107.25, 67.27, 49.12. HR-MS (ESI): Calcd for $C_{16}H_{13}Br_2N^+$ $[M+H]^+$ requires 378.9467; found 379.9463.

1-(dichloromethyl)-2-phenyl-1,2-dihydroisoquinolin (8)

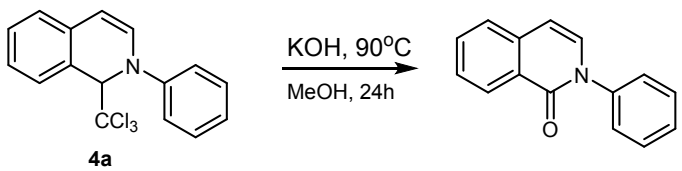


8

Following the procedure D, using dichloromethane as nucleophile, the crude product was purified by silica gel chromatography (PE: EA = 200:1 as the eluent) to give **8** (50% yield) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 4H), 7.23 – 7.13 (m, 4H), 7.08 – 6.92 (m, 1H), 6.66 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.07 (d, *J* = 7.3 Hz, 1H), 5.77 (d, *J* = 8.1 Hz, 1H), 5.35 (dd, *J* = 8.1, 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.13, 131.35, 129.27, 129.11, 128.75, 127.84, 125.87, 125.07, 123.85, 122.13, 117.63, 107.13, 73.17, 67.34. Calcd for $C_{16}H_{13}Cl_2N^+$ $[M+H]^+$ requires 290.0498; found 290.0494.

5) Synthetic Applications

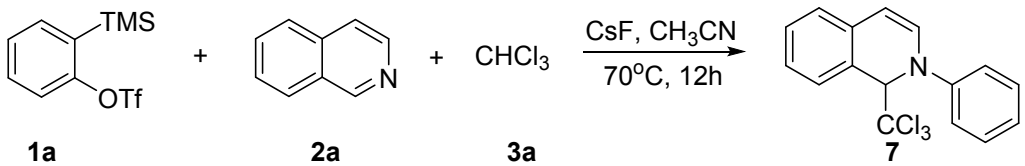
2-phenylisoquinolin-1(2H)-one (10)



4a

To stirred a suspension of **4a** (0.0323g, 0.1mmol) in MeOH (1.5ml), a solution of KOH (0.023g, 5equiv.) in MeOH (2ml) was cautiously added over a period of 30min. The reaction mixture was heated at 90°C for 24h with intensive stirring. Cooled to room temperature. The reaction mixture was then treated with water (10 mL), extracted, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA = 20:1 as the eluent) to give **10** (yield=62%) as a purple liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.1 Hz, 1H), 7.59 – 7.47 (m, 4H), 7.47 – 7.38 (m, 3H), 7.19 (d, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 7.4 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 162.01, 141.38, 137.06, 132.53, 132.16, 129.26, 128.28, 128.06, 127.14, 126.84, 126.58, 125.92, 106.16.

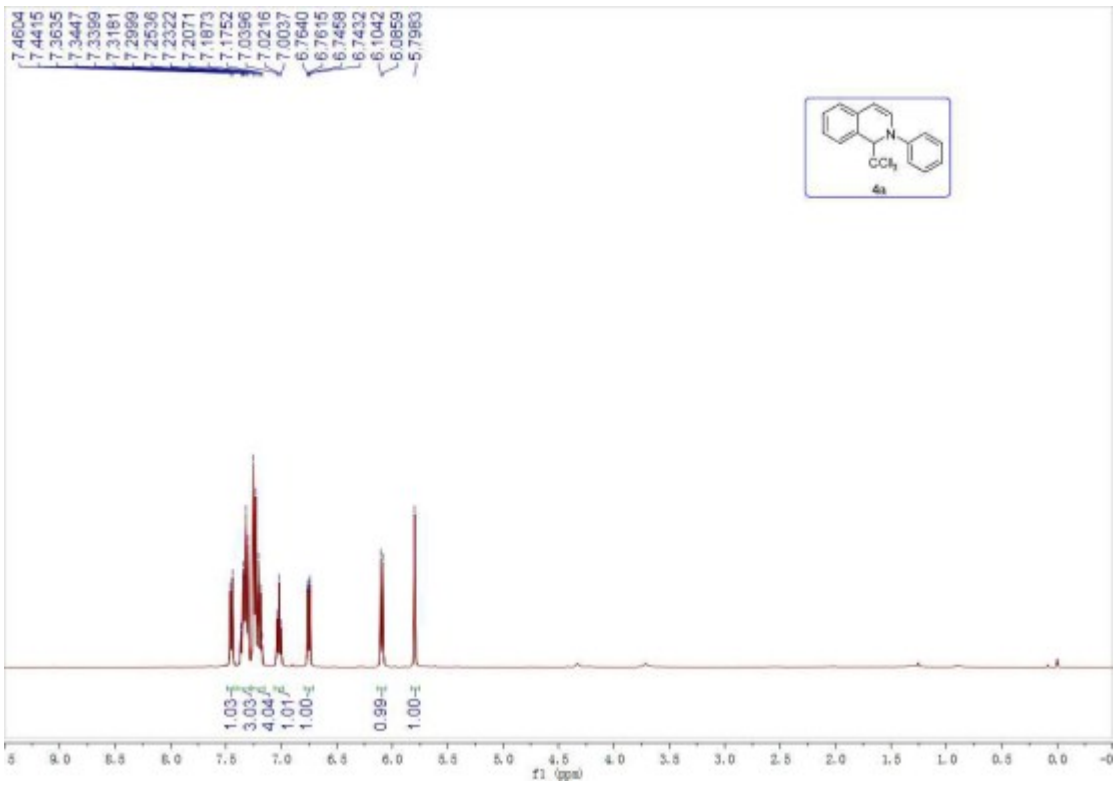
6) Gram-scale reaction



1a **2a** **3a** **7**

To a 50 mL flame-dried schlenk tube containing CsF (10 mmol) was evacuated and purged with nitrogen gas for three times. To the flask were then added **1a** (3.6 mmol), isoquinoline (3 mmol), acetonitrile (8 ml) and chloroform (8 ml) via syringes. The reaction mixture was allowed to stir at 70°C for 12 hours (general procedure A) or 24 hours (general procedure B). The reaction mixture was then cooled to room temperature and treated with water (20 mL), extracted with ethyl acetate (40 ml), dried over sodium sulfate, filtered and concentrated in vacuo. The crude product was further purified by silica gel flash chromatography (PE: EA =200: 1 as the eluent) to give **4a** (0.8772g, 89%) as a white soild.

IV. Spectrum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7.3399
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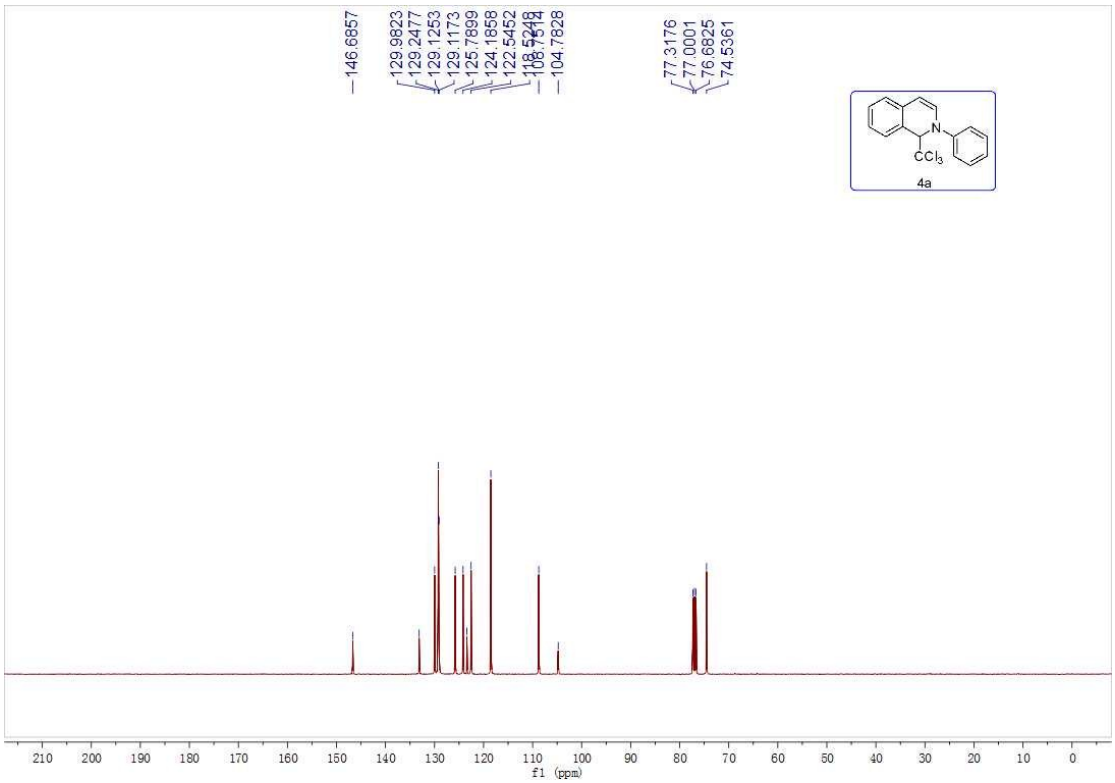
7.2322
7.2071
7.1873
7.1752
7.0396
7.0216
7.0037
6.7640
6.7615
6.7458
6.7432
6.1042
6.0859
5.7963
1.03
3.03
4.04
1.01
1.00
0.99
1.00
f1 (ppm)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129.1253
129.1173
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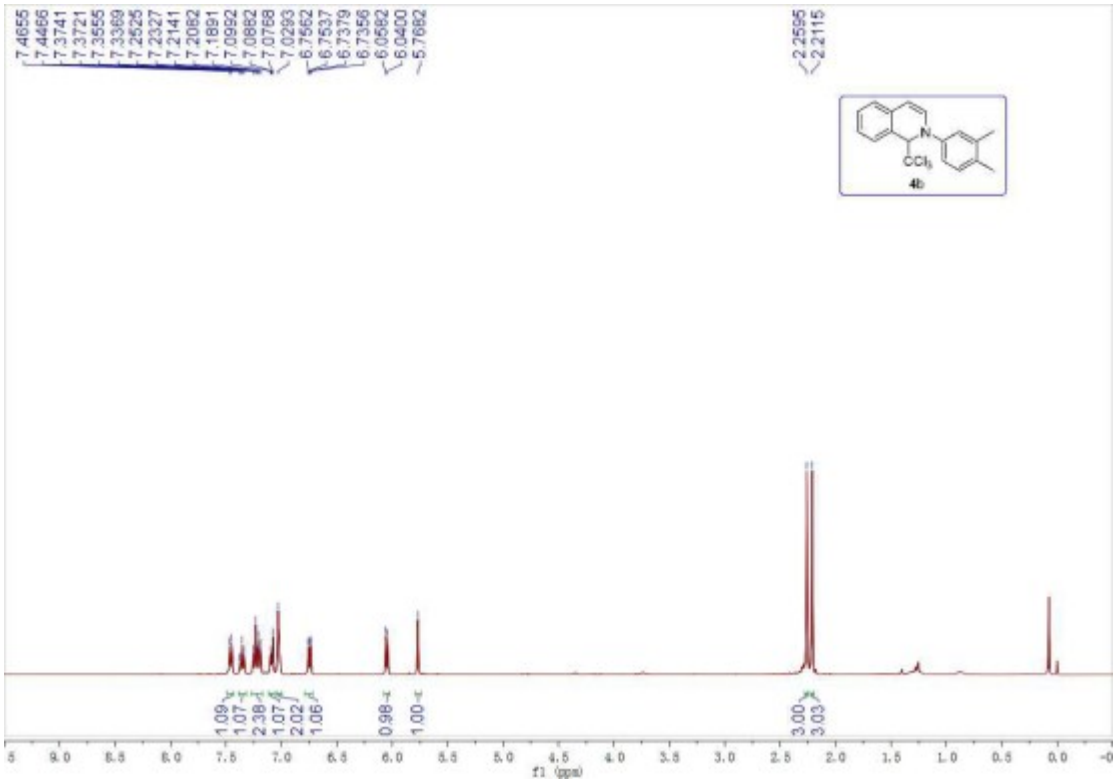
76.6825
74.5361
4a
f1 (ppm)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7.0992
7.0882
7.0768
7.0293
6.7562
6.7537
6.7379
6.7356
6.0582
6.0400
5.7682
2.2595
2.2115
1.09
1.07
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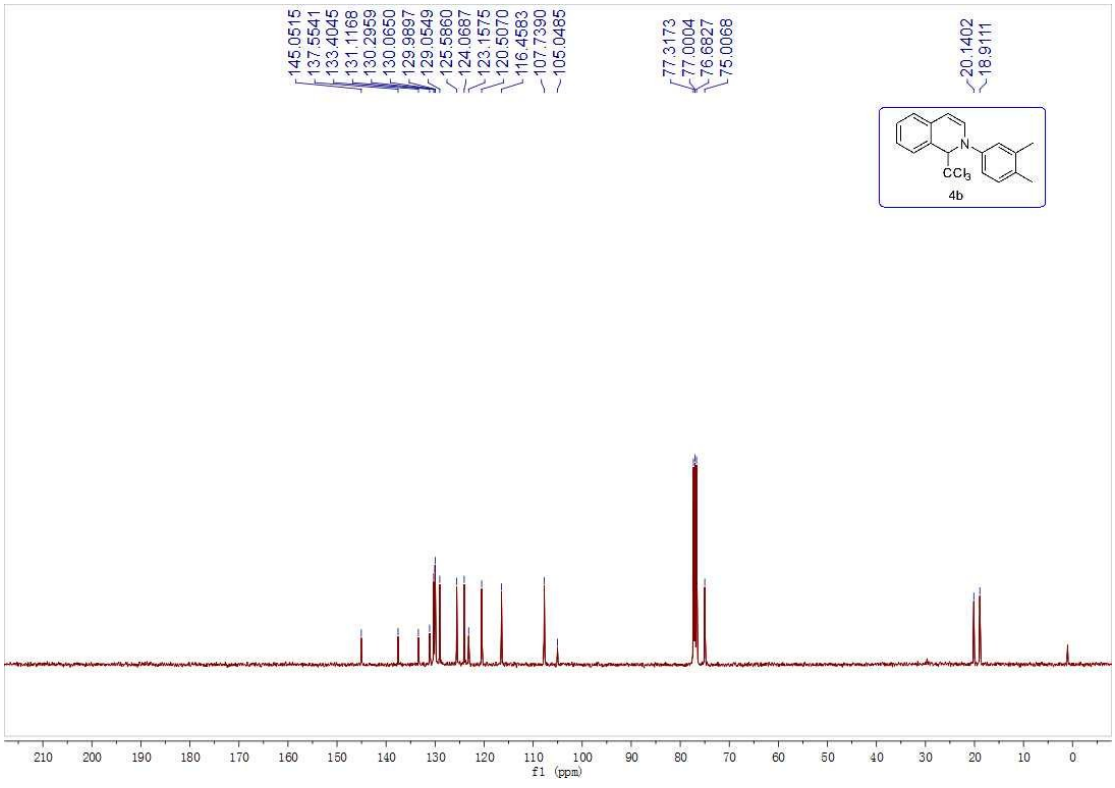
1.07
2.02
1.06
0.98
1.00
3.00
3.03
f1 (ppm)
4b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120.5070
116.4583
107.7390
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77.3173
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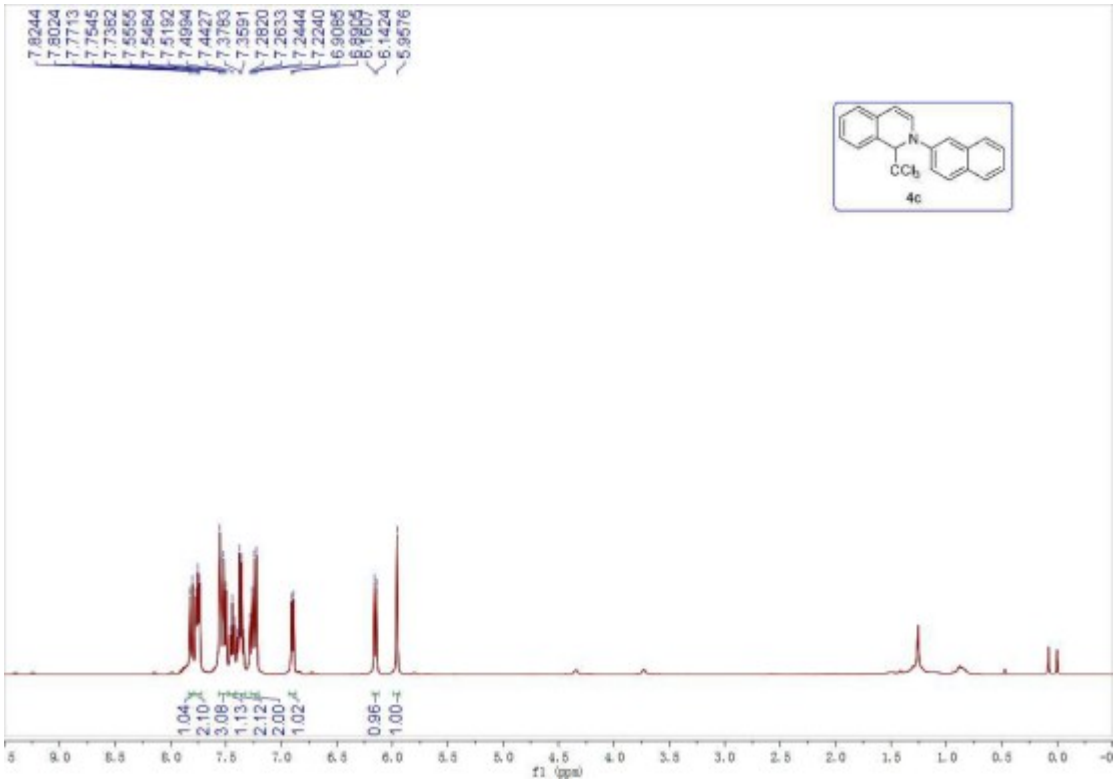
75.0068
20.1402
18.9111
f1 (ppm)
4b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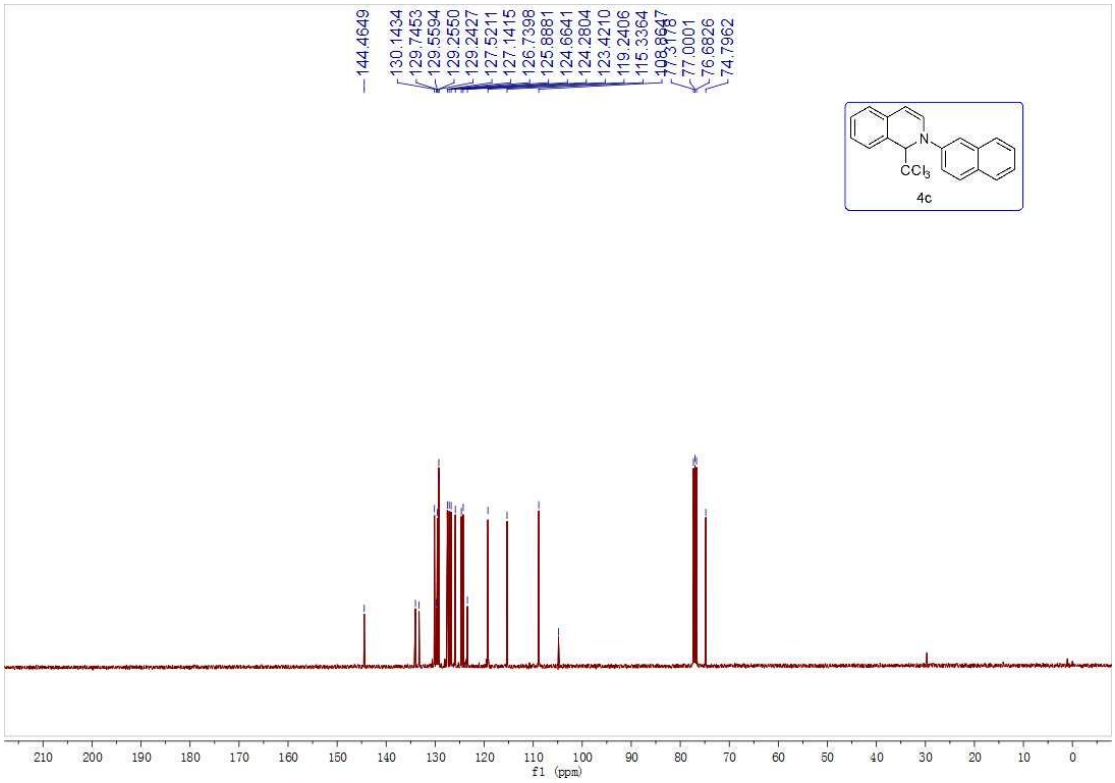
7.3591
7.2820
7.2633
7.2444
7.2240
6.9085
6.1607
6.1424
5.9576
1.04
2.10
3.08
1.13
2.12
2.00
1.02
0.96
1.00
f1 (ppm)
4c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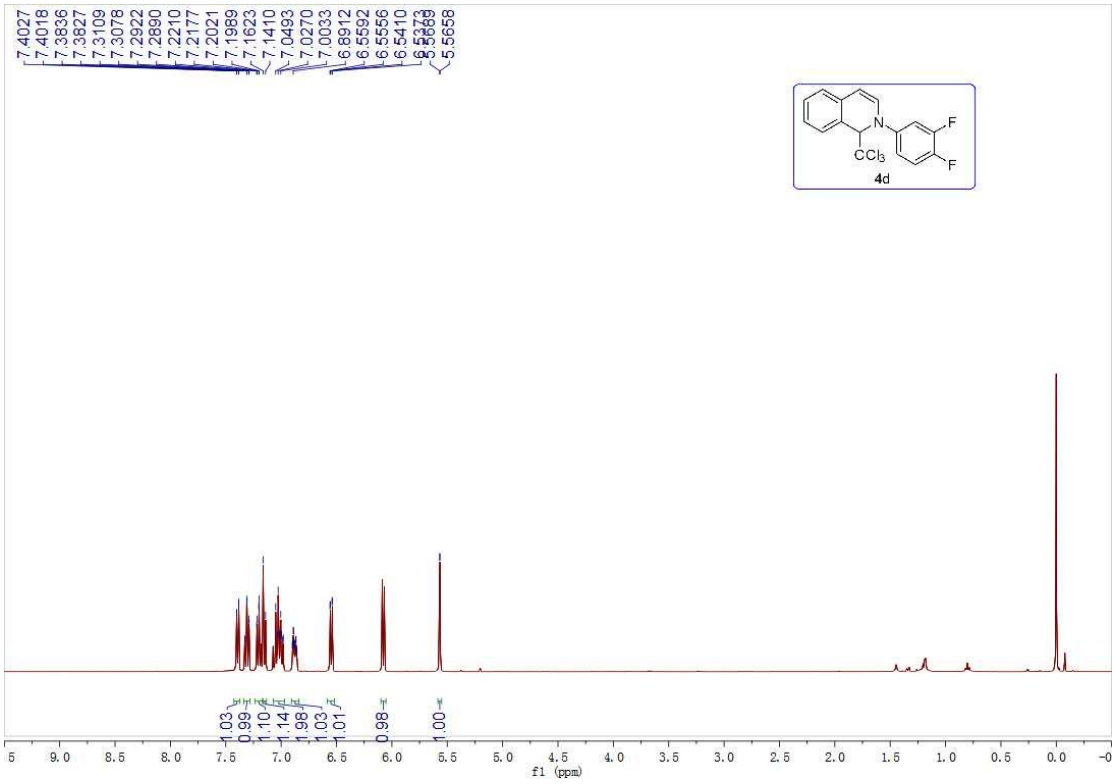
76.6826
74.7962
f1 (ppm)
4c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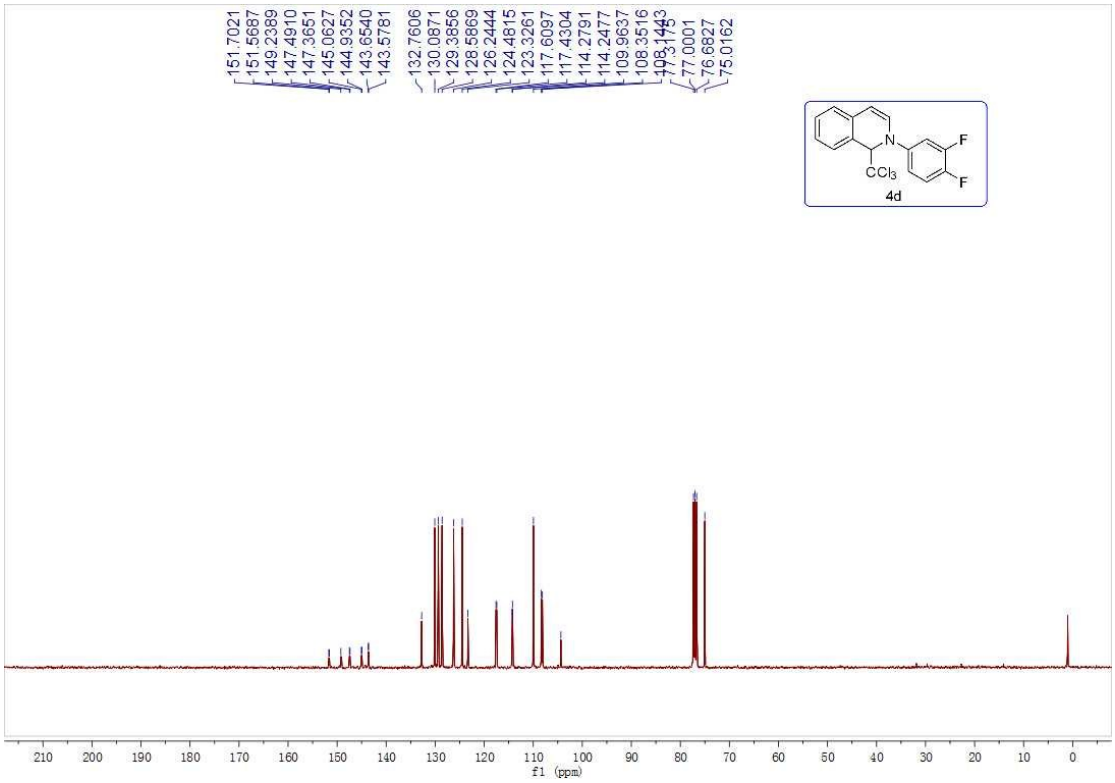
7.1989
7.1623
7.1410
7.0493
7.0270
7.0033
6.8912
6.5592
6.5556
6.5410
5.5658
F
F
CCl3
4d
1.03
0.99
1.10
1.14
1.98
1.03
1.01
0.98
1.00
f1 (ppm)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129.3856
128.5869
126.2444
124.4815
123.3261
117.6097
117.4304
114.2791
114.2477
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108.1443
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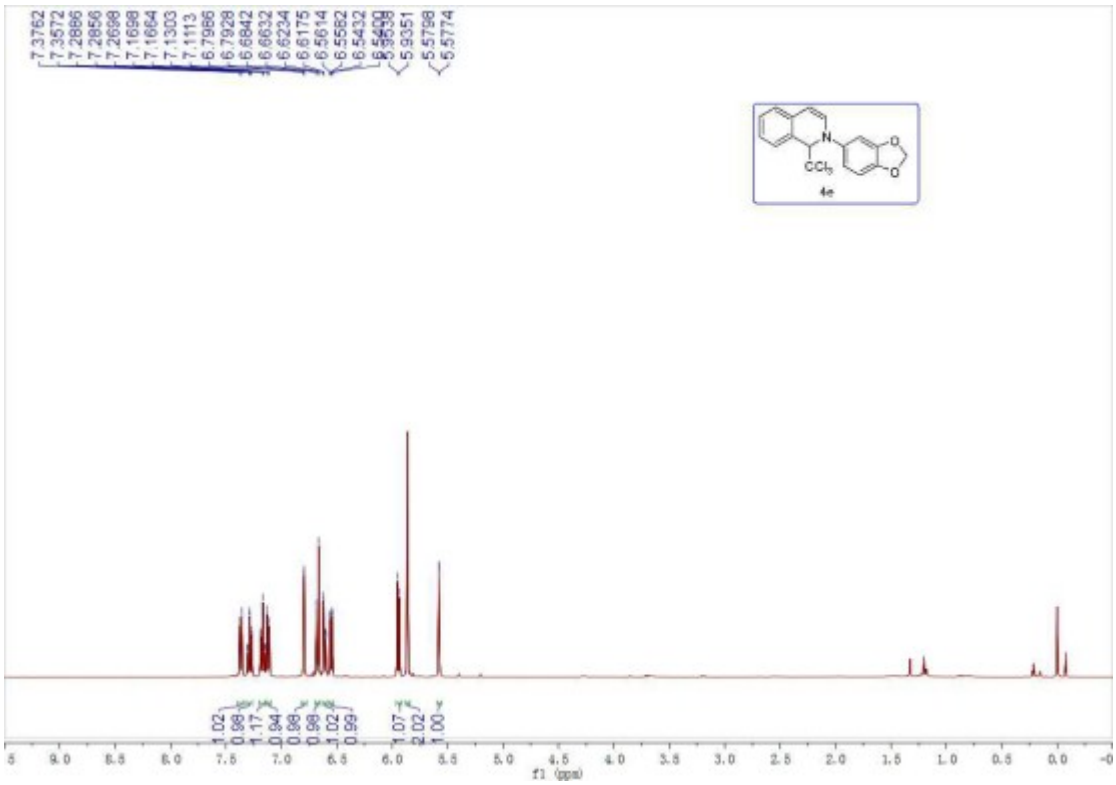
76.6827
75.0162
F
F
CCl3
4d
f1 (ppm)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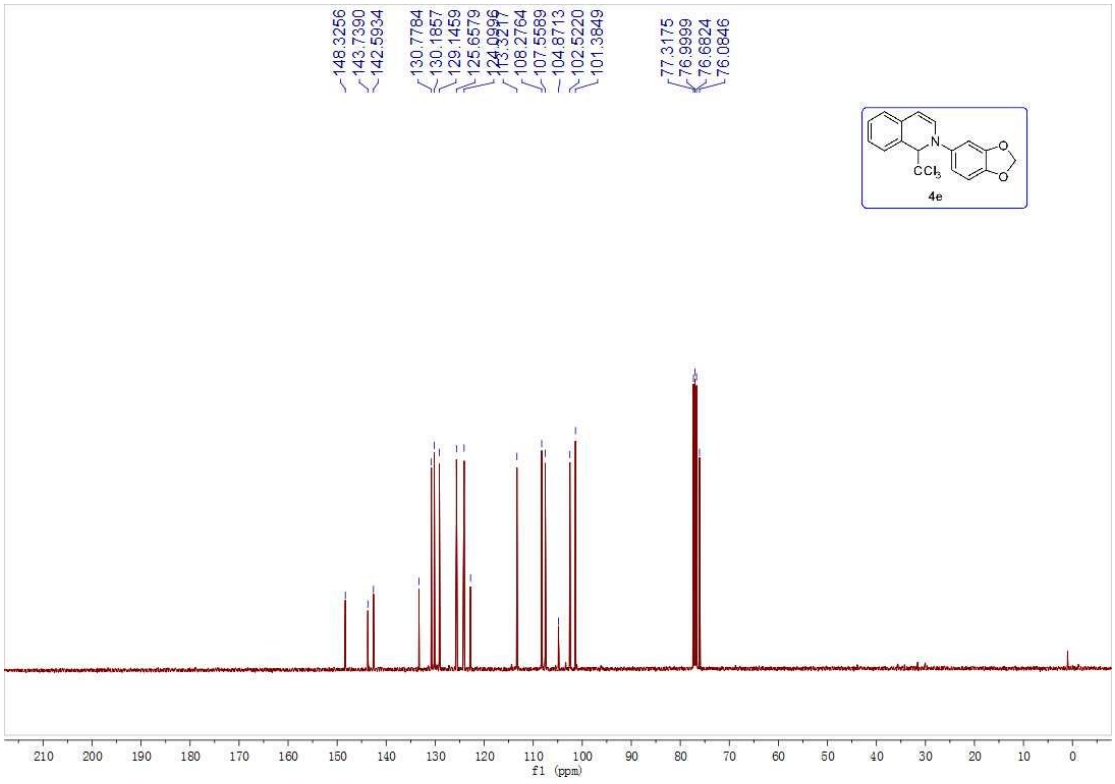
7.2886
7.2856
7.2698
7.1698
7.1664
7.1303
7.1113
6.7966
6.7928
6.6842
6.6632
6.6234
6.6175
6.5614
6.5562
6.5432
5.9351
5.5798
5.5774
4e
f1 (ppm)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130.1657
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125.6579
108.2764
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102.5220
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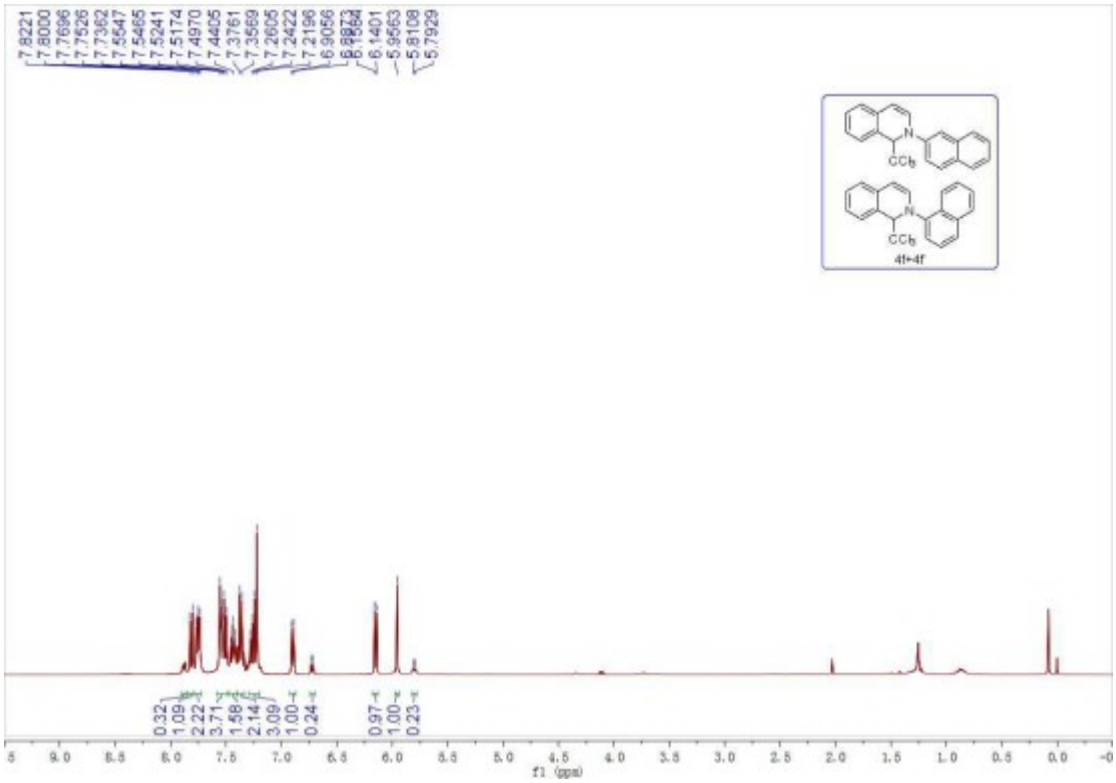
77.3175
76.9999
76.6824
76.0846
4e
f1 (ppm)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7.7696
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7.7362
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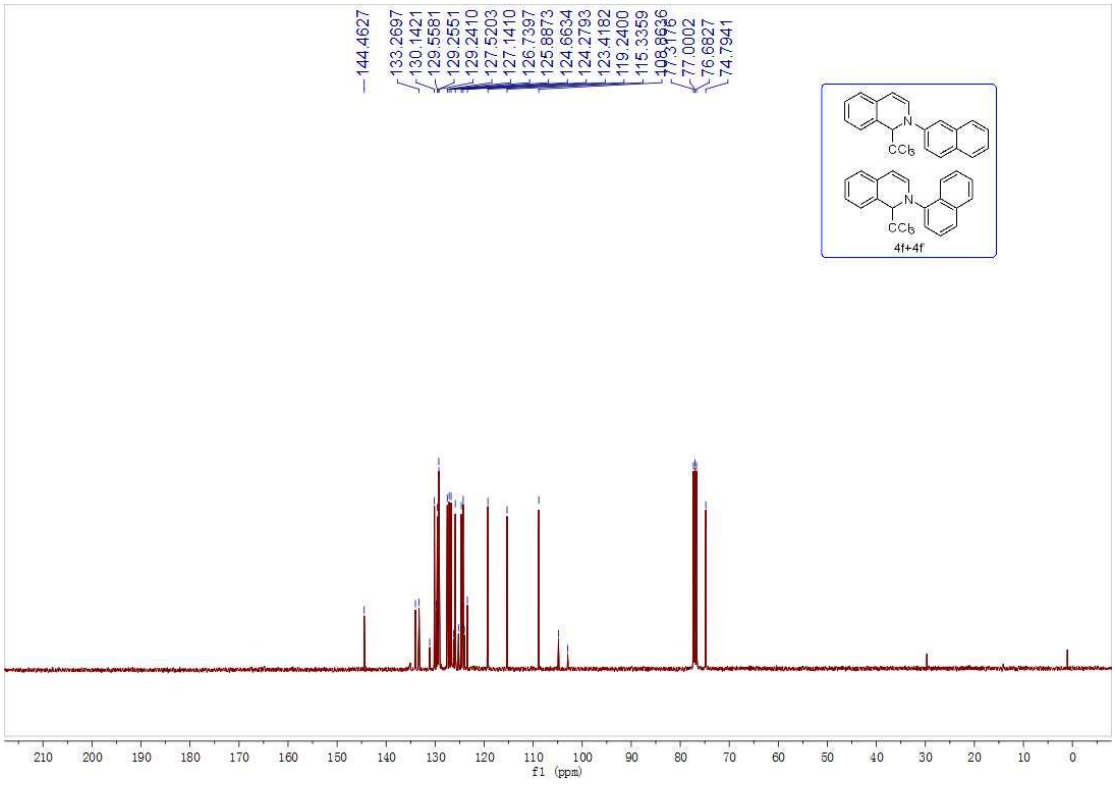
7.5465
7.5241
7.5174
7.4970
7.4405
7.3761
7.3569
7.2605
7.2422
7.2196
6.9056
6.1401
5.9563
5.9108
5.7929
4f+4f
0.32
1.09
2.22
3.71
1.58
2.14
3.09
1.00
0.24
0.97
1.00
0.23
f1 (ppm)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129.2410
127.5203
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125.8873
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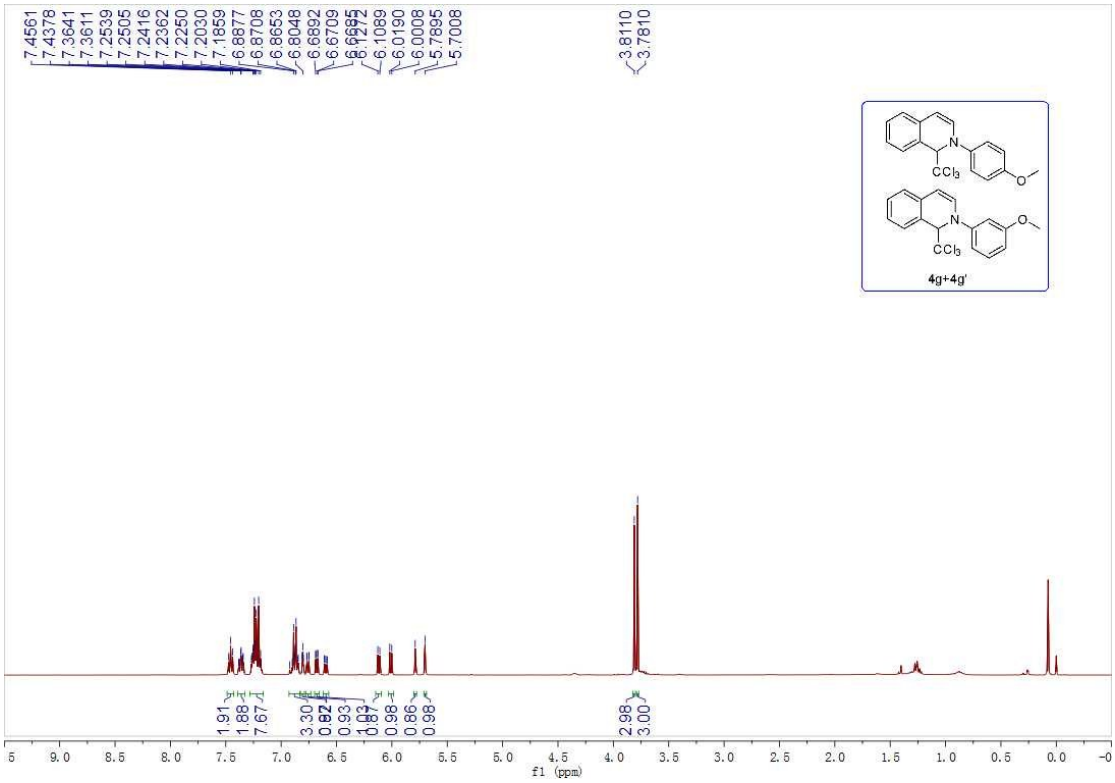
124.2793
123.4182
119.2400
115.3359
77.0002
76.6827
74.7941
4f+4f
f1 (ppm)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7.3641
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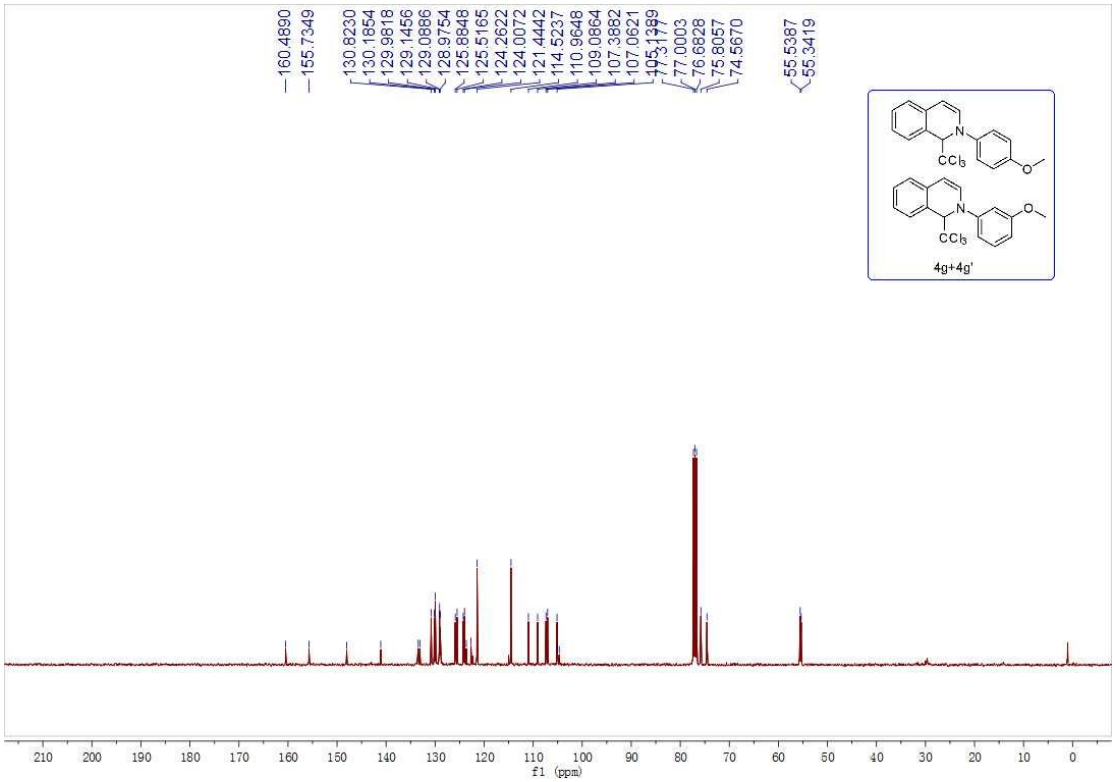
7.2539
7.2505
7.2416
7.2362
7.2250
7.2030
7.1859
6.8877
6.8708
6.8653
6.8048
6.6892
6.6709
6.1089
6.0190
6.0008
5.7895
5.7008
3.8110
3.7810
1.91
1.88
7.67
3.30
0.93
1.03
0.87
0.98
0.86
0.98
2.98
3.00
f1 (ppm)
4g+4g'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129.1456
129.0886
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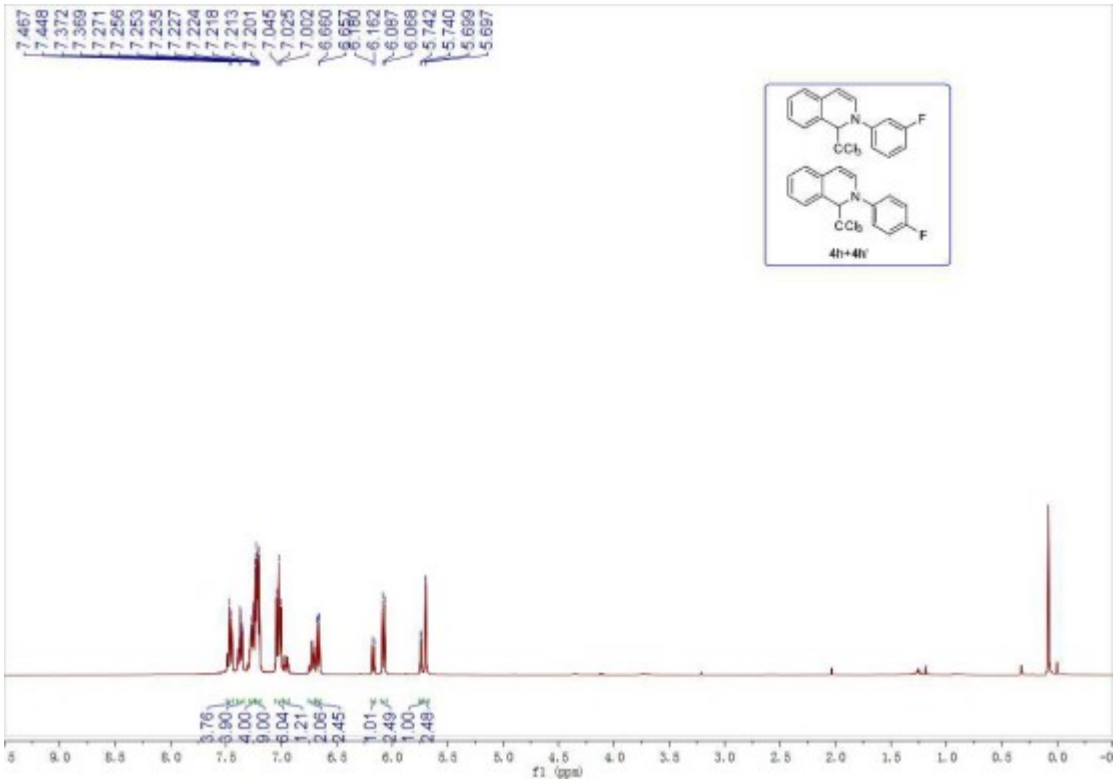
125.8848
125.5165
124.2622
124.0072
121.4442
114.5237
110.9648
109.0864
107.3882
107.0621
77.3177
77.0003
76.6828
75.8057
74.5670
55.5387
55.3419
f1 (ppm)
4g+4g'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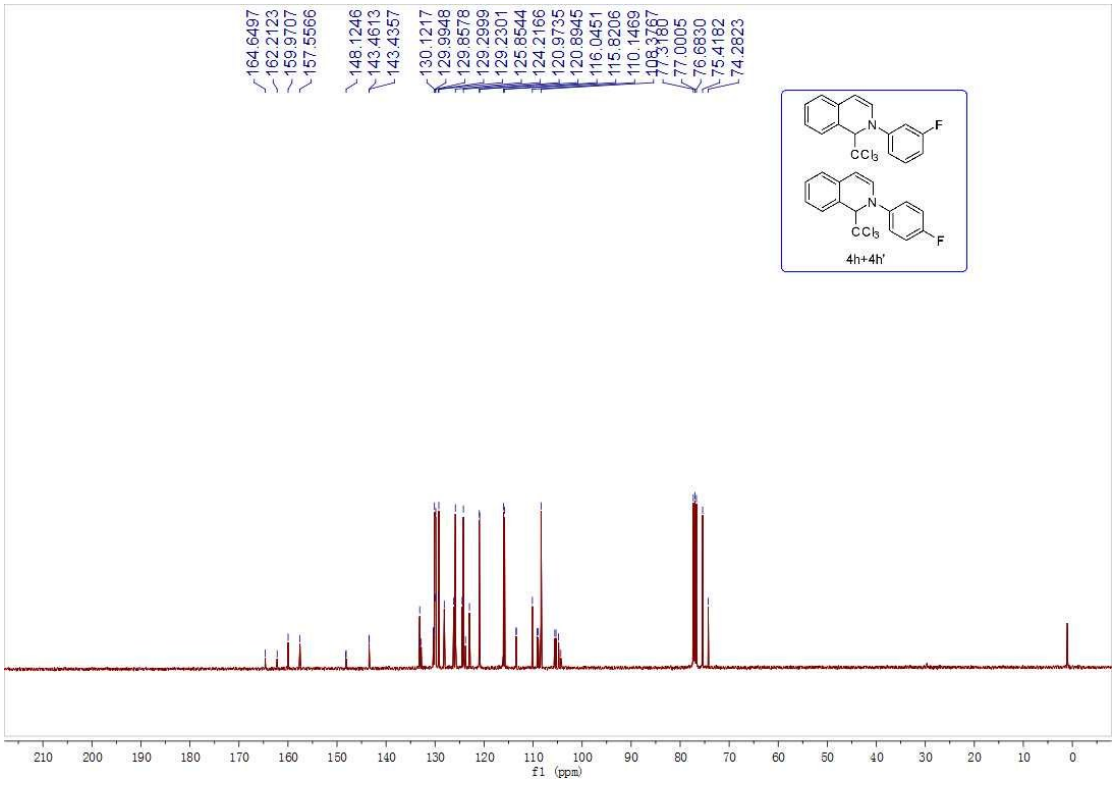
7.448
7.372
7.369
7.271
7.256
7.253
7.235
7.227
7.224
7.218
7.213
7.201
7.045
7.025
7.002
6.660
6.657
6.180
6.162
6.087
6.068
5.742
5.740
5.699
5.697
4h+4h'
3.76
3.90
4.00
9.00
6.04
1.21
2.06
2.45
1.01
2.49
1.00
2.48
f1 (ppm)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148.1246
143.4613
143.4357
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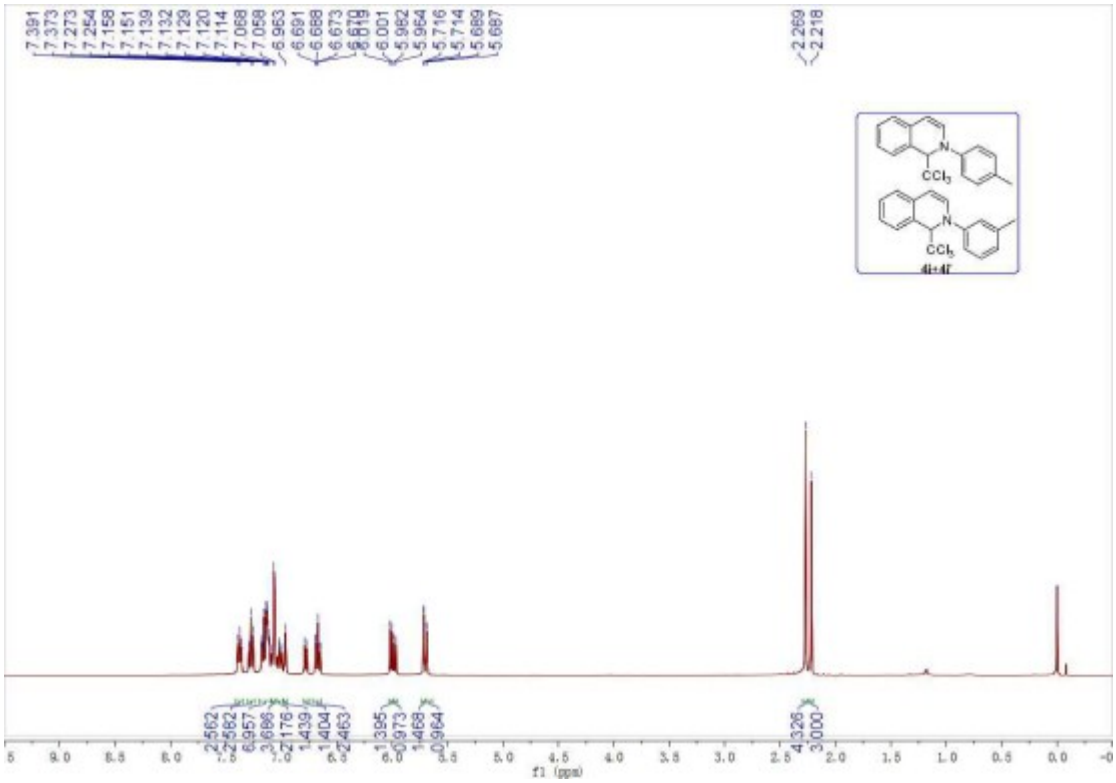
129.9948
129.8578
129.2999
129.2301
125.8544
124.2166
120.9735
120.8945
116.0451
115.8206
110.1469
108.3787
77.3180
77.0005
76.6830
75.4182
74.2823
4h+4h'
f1 (ppm)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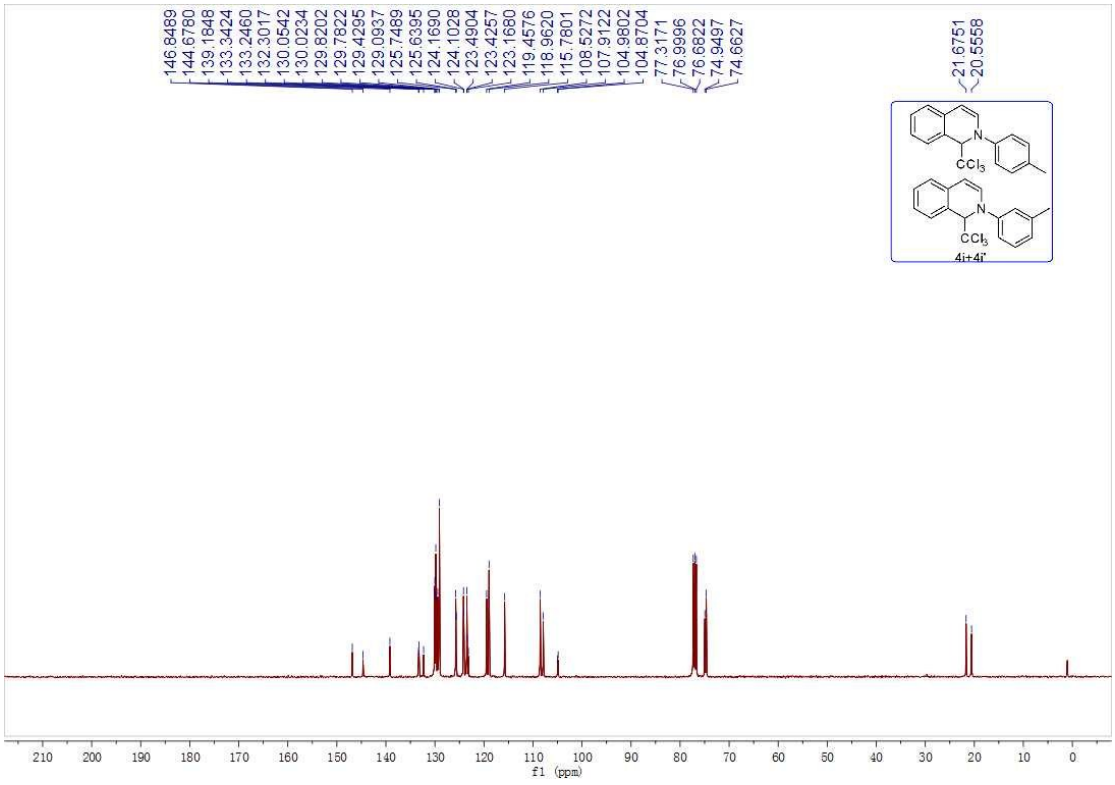
7.373
7.273
7.254
7.158
7.151
7.139
7.132
7.129
7.120
7.114
7.068
7.058
6.963
6.691
6.688
6.673
6.619
6.001
5.962
5.954
5.716
5.714
5.689
5.687
2.269
2.218
CCl3
CCl3
4i+4i'
2.562
2.582
6.957
3.686
2.176
1.439
1.404
2.463
1.395
0.973
1.468
0.964
4.326
3.000
f1 (ppm)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129.8202
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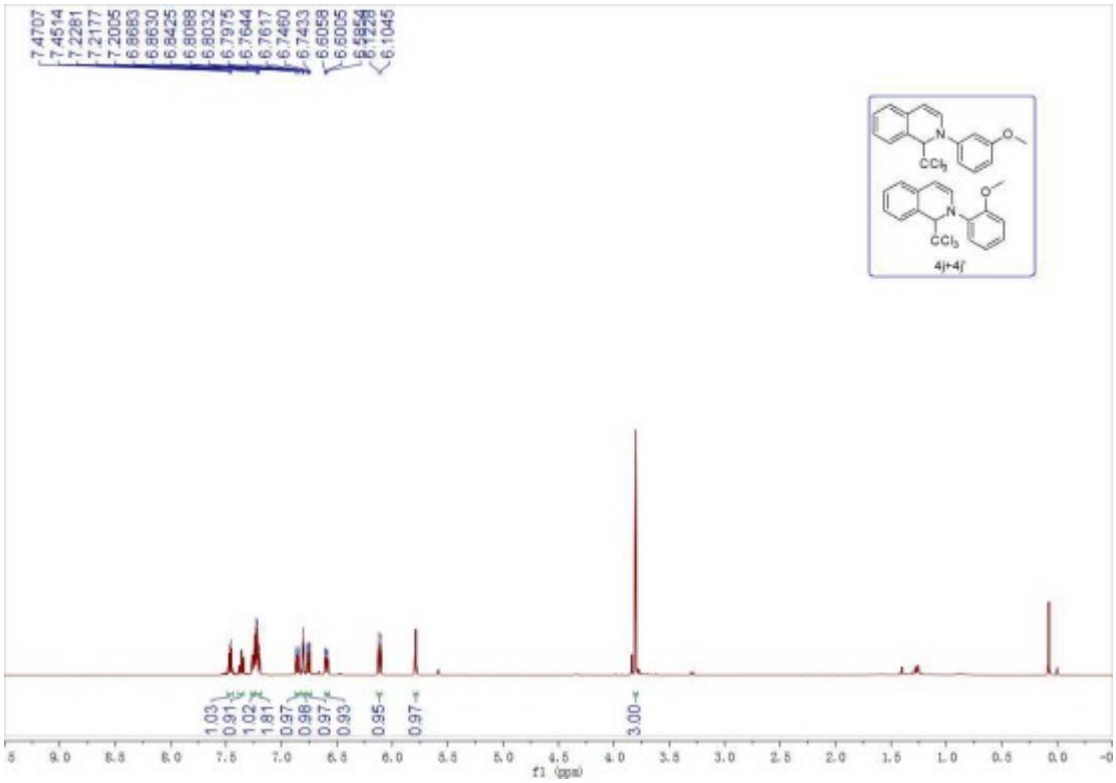
129.0937
125.7489
125.6395
124.1690
124.1028
123.4904
123.4257
123.1680
119.4576
118.9620
115.7801
108.5272
107.9122
104.9802
104.8704
77.3171
76.9996
76.6822
74.9497
74.6627
21.6751
20.5558
CCl3
CCl3
4i+4i'
f1 (ppm)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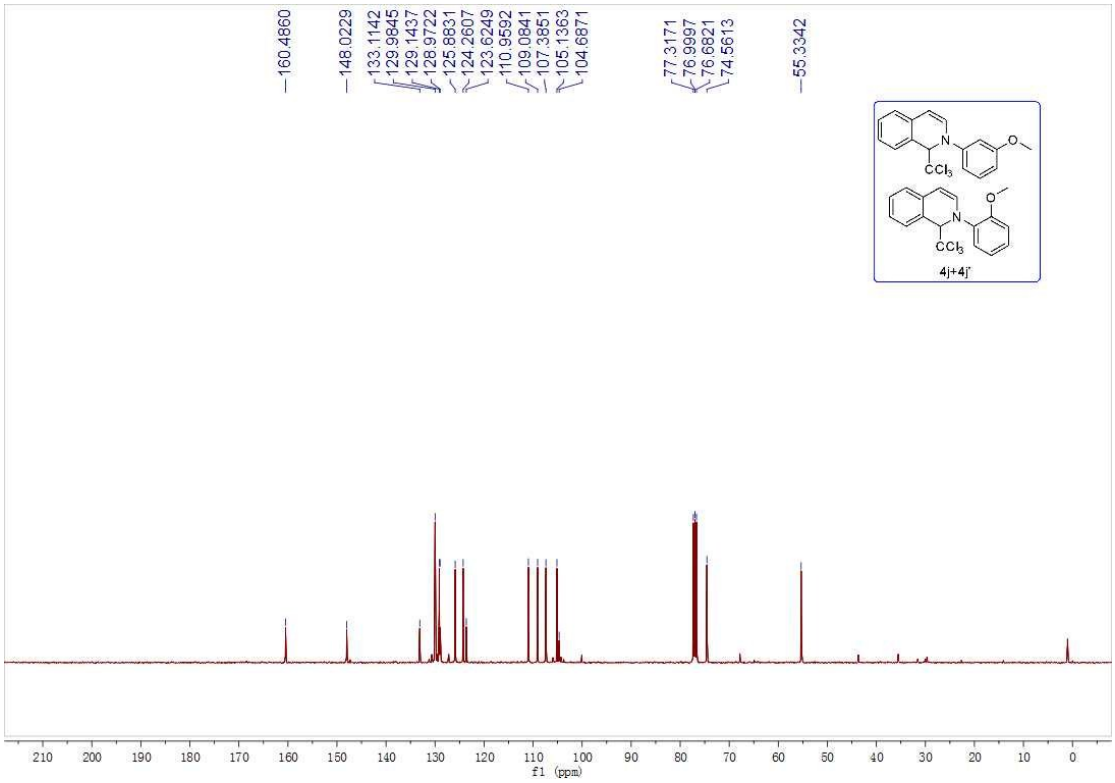
7.4514
7.2281
7.2177
7.2005
6.8663
6.8630
6.8425
6.8088
6.8032
6.7975
6.7644
6.7617
6.7460
6.7433
6.6058
6.6005
6.1228
6.1045
4j+4j'
1.03
0.91
1.02
1.81
0.97
0.98
0.97
0.93
0.95
0.97
3.00
f1 (ppm)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129.1437
128.9722
125.8831
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123.6249
110.9592
109.0841
107.3851
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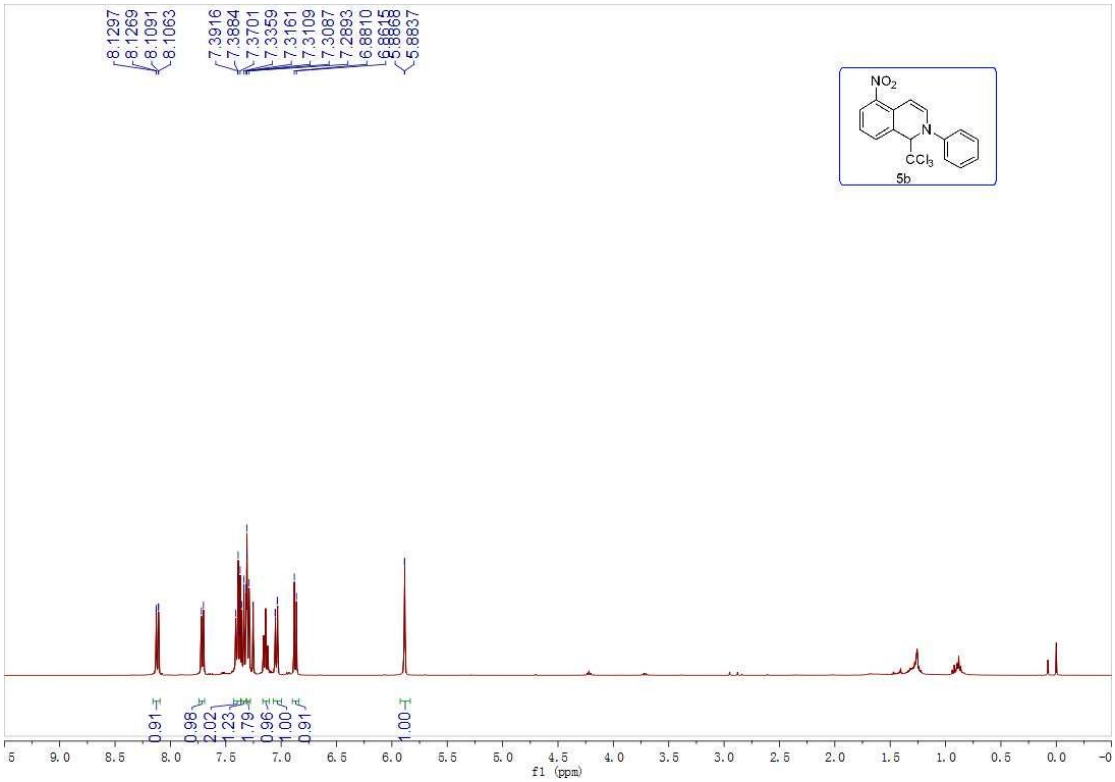
77.3171
76.9997
76.6821
74.5613
55.3342
4j+4j'
f1 (ppm)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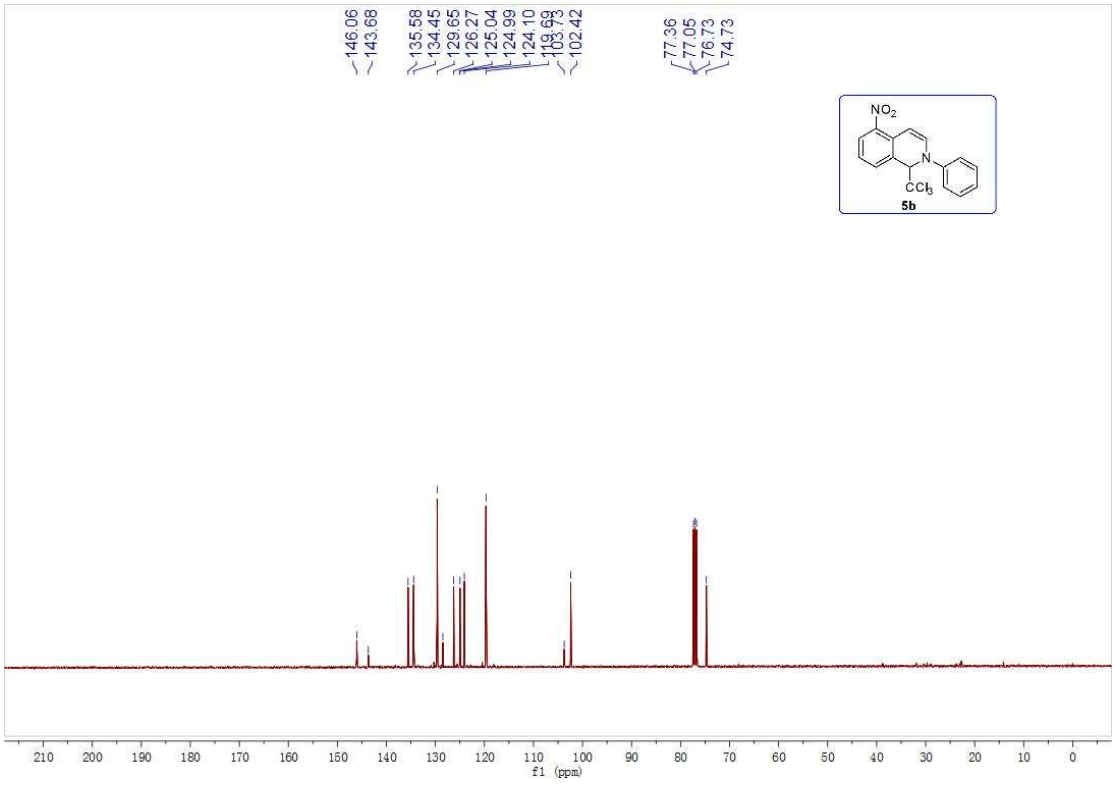
8.1269
8.1091
8.1063
7.3916
7.3884
7.3701
7.3359
7.3161
7.3109
7.3087
7.2893
6.8810
5.8868
5.8837
NO2
N
CCl3
5b
0.91
0.98
2.02
1.23
1.79
0.96
1.00
0.91
1.00
f1 (ppm)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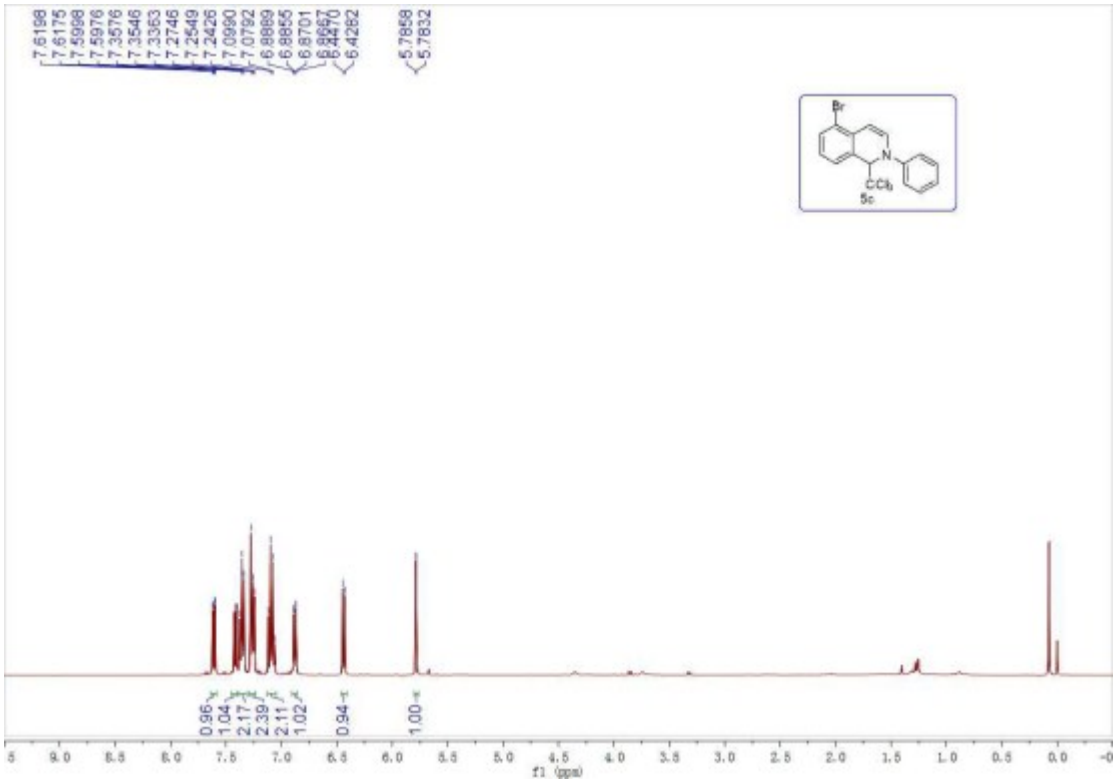
143.68
135.58
134.45
129.65
126.27
125.04
124.99
124.10
119.69
103.73
102.42
77.36
77.05
76.73
74.73
NO2
N
CCl3
5b
f1 (ppm)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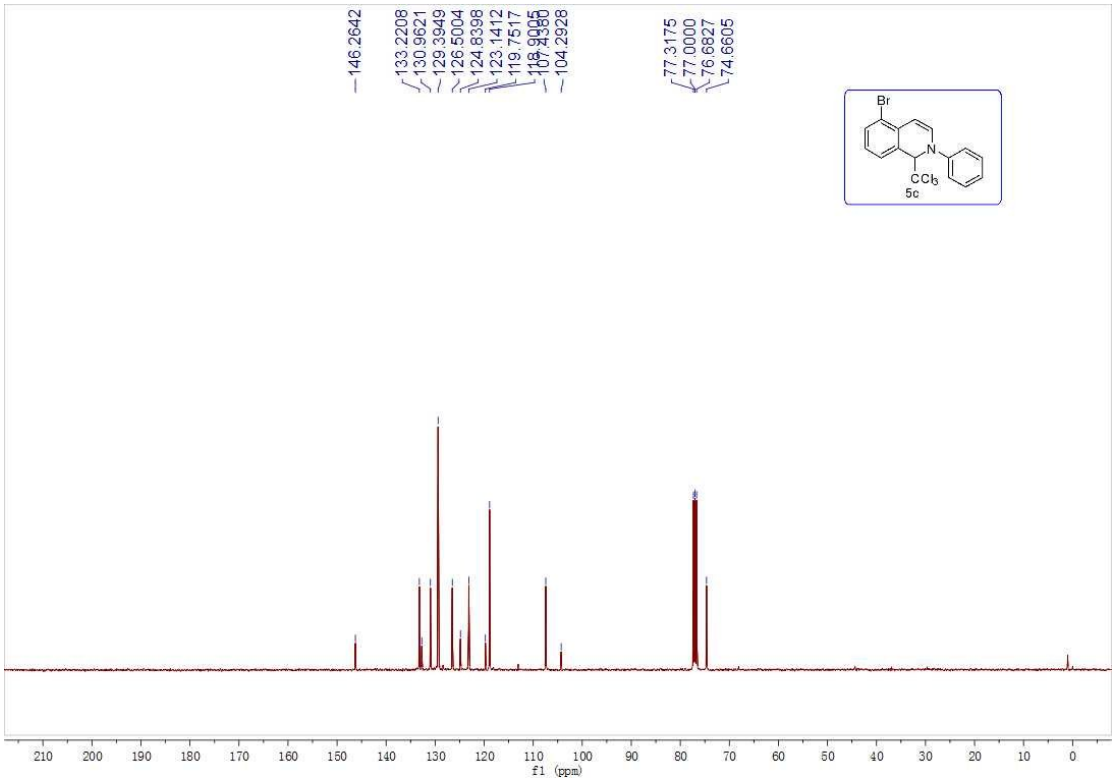
7.5998
7.5976
7.3576
7.3546
7.3363
7.2746
7.2549
7.2426
7.0990
7.0792
6.8989
6.8855
6.8701
6.4470
6.4262
5.7858
5.7832
Br
N
CCl3
5c
0.96
1.04
2.17
2.39
2.11
1.02
0.94
1.00
f1 (ppm)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124.8398
123.1412
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77.0000
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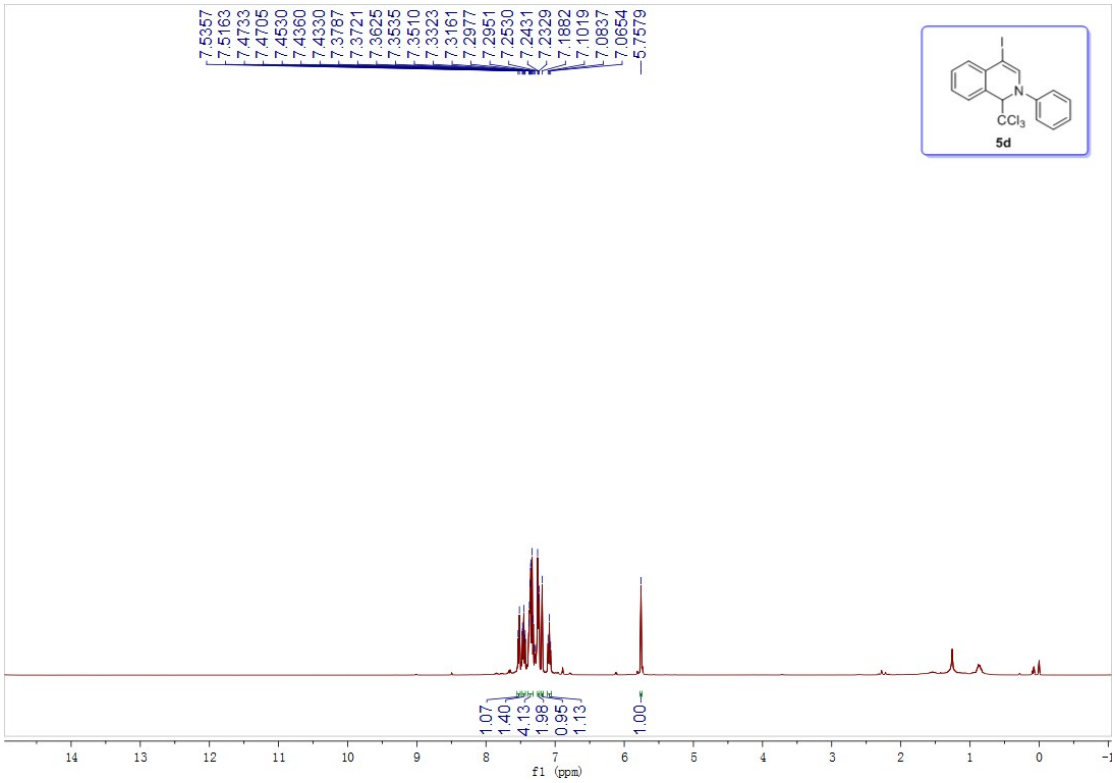
Br
N
CCl3
5c
f1 (ppm)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7.4705
7.4530
7.4360
7.4330
7.3787
7.3721
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7.3535
7.3510
7.3323
7.3161
7.2977
7.2951
7.2530
7.2431
7.2329
7.1882
7.1019
7.0837
7.0654
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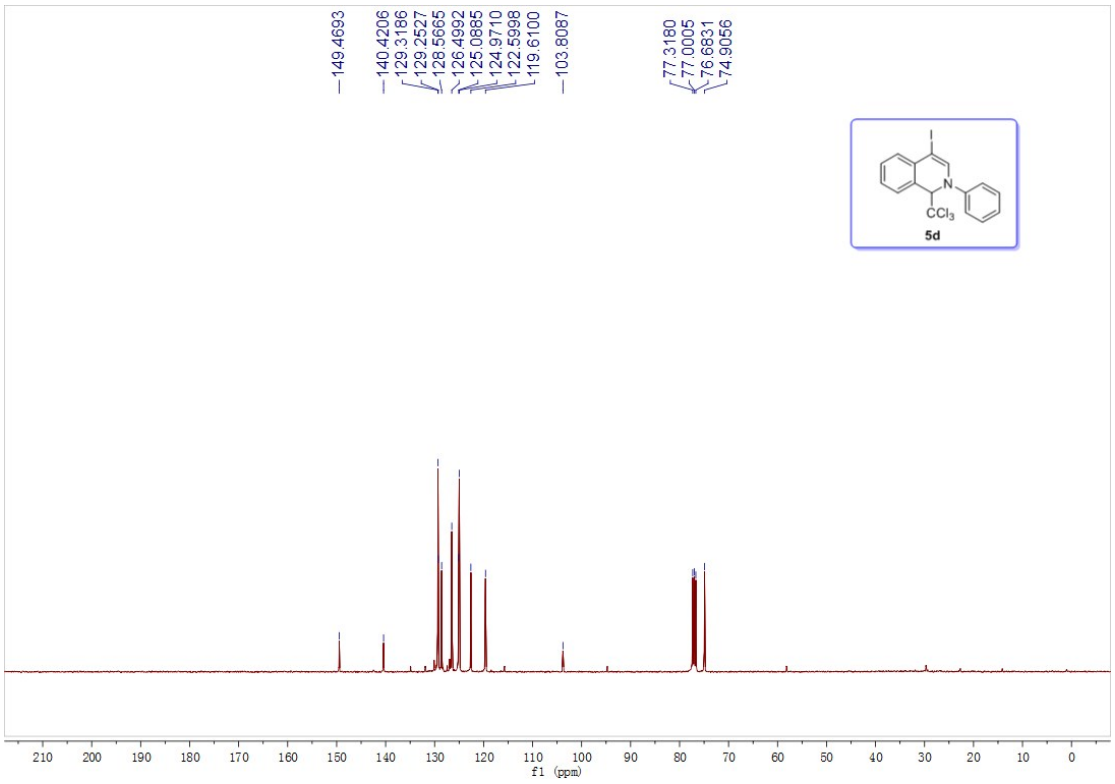
1.07
1.40
4.13
1.98
0.95
1.13
1.00
f1 (ppm)
5d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119.6100
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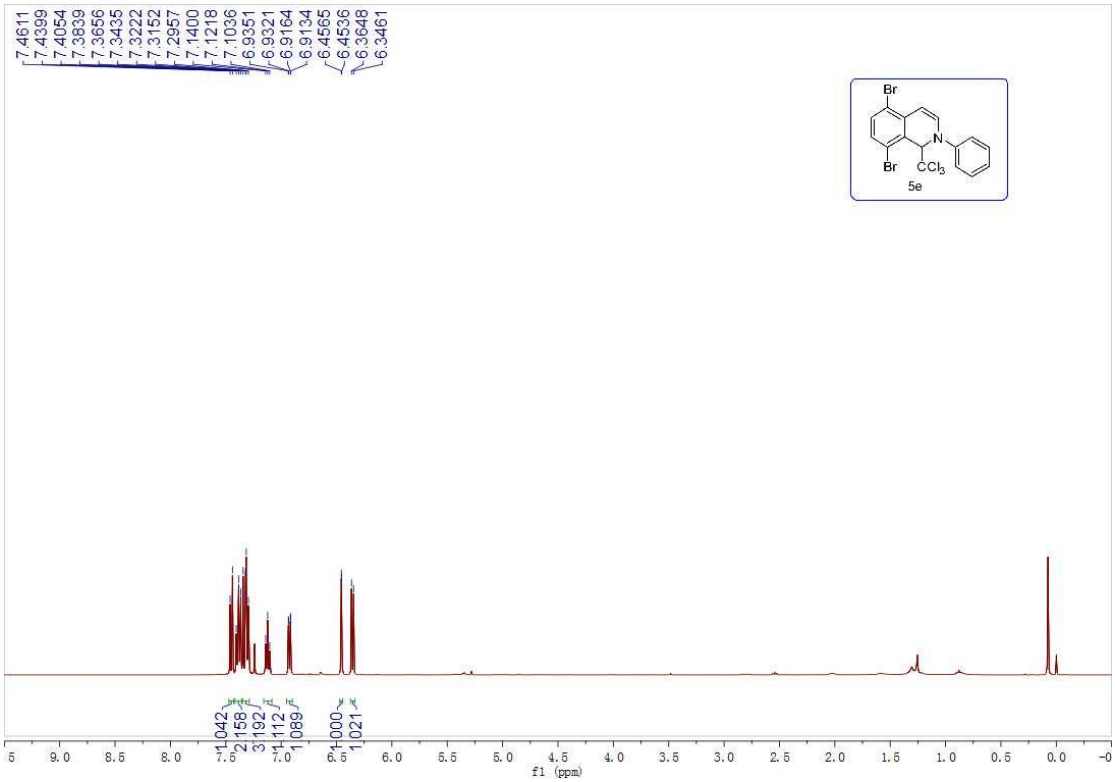
77.0005
76.6831
74.9056
f1 (ppm)
5d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7.3656
7.3435
7.3222
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7.2957
7.1400
7.1218
7.1036
6.9351
6.9321
6.9164
6.9134
6.4565
6.4536
6.3648
6.3461
Br
Br
N
CCl3
5e
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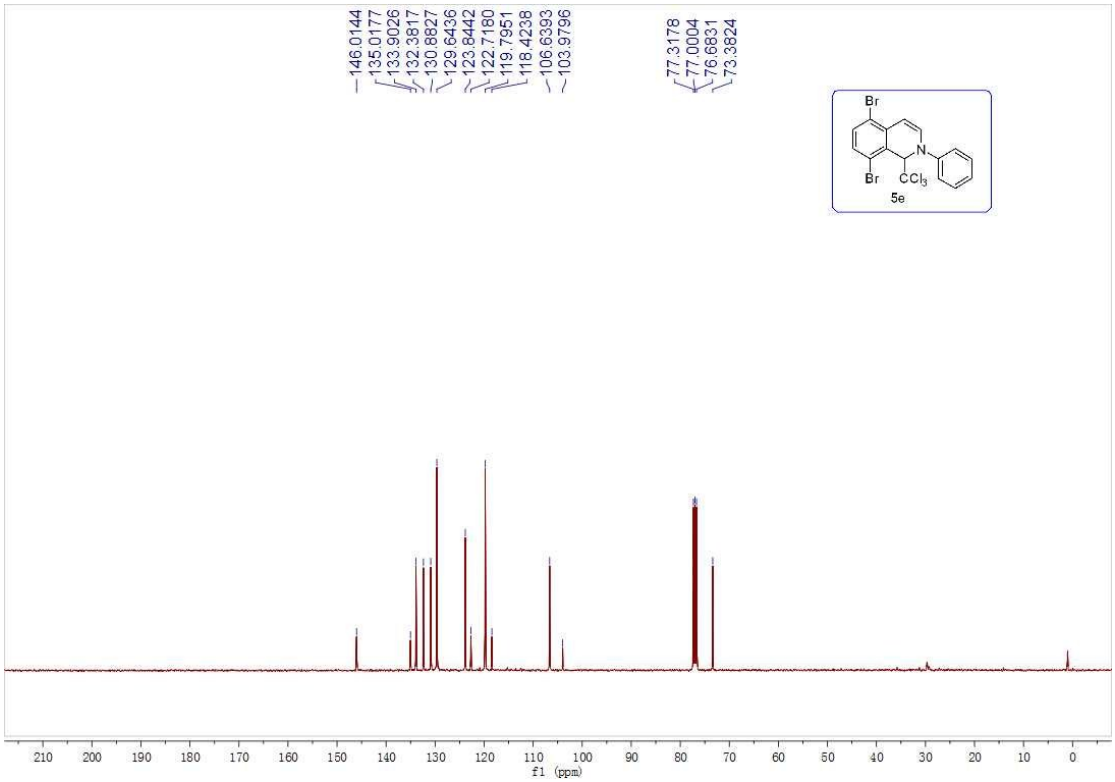
2.158
3.192
1.112
1.089
1.000
1.021
f1 (ppm)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119.7951
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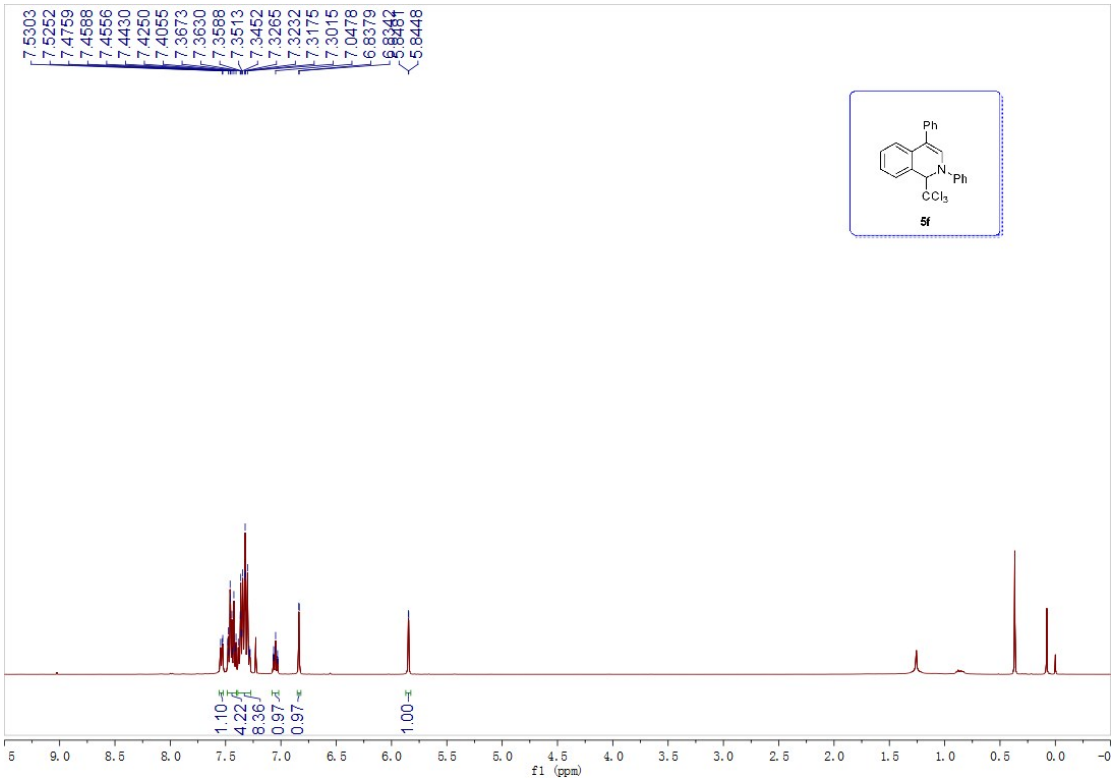
76.6831
73.3824
Br
Br
N
CCl3
5e
f1 (ppm)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7.3673
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7.3588
7.3513
7.3452
7.3265
7.3232
7.3175
7.3015
7.0478
6.8379
5.8448
Ph
N
Ph
CCl3
5f
1.10
4.22
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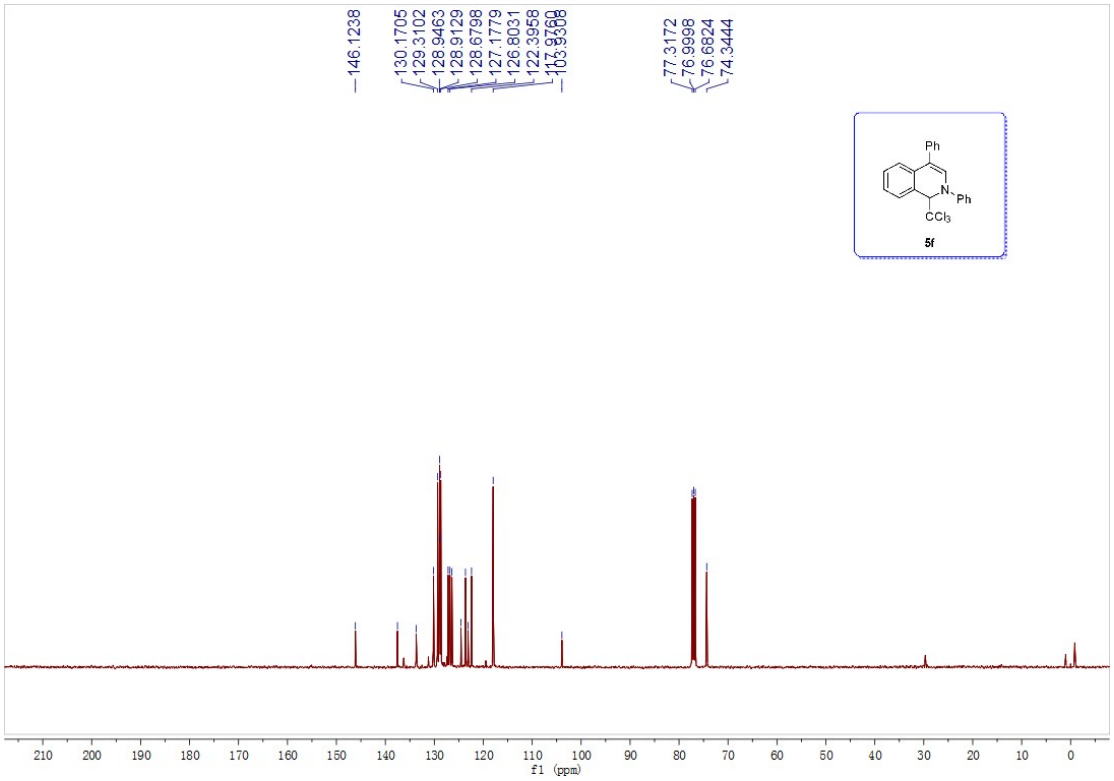
0.97
1.00
f1 (ppm)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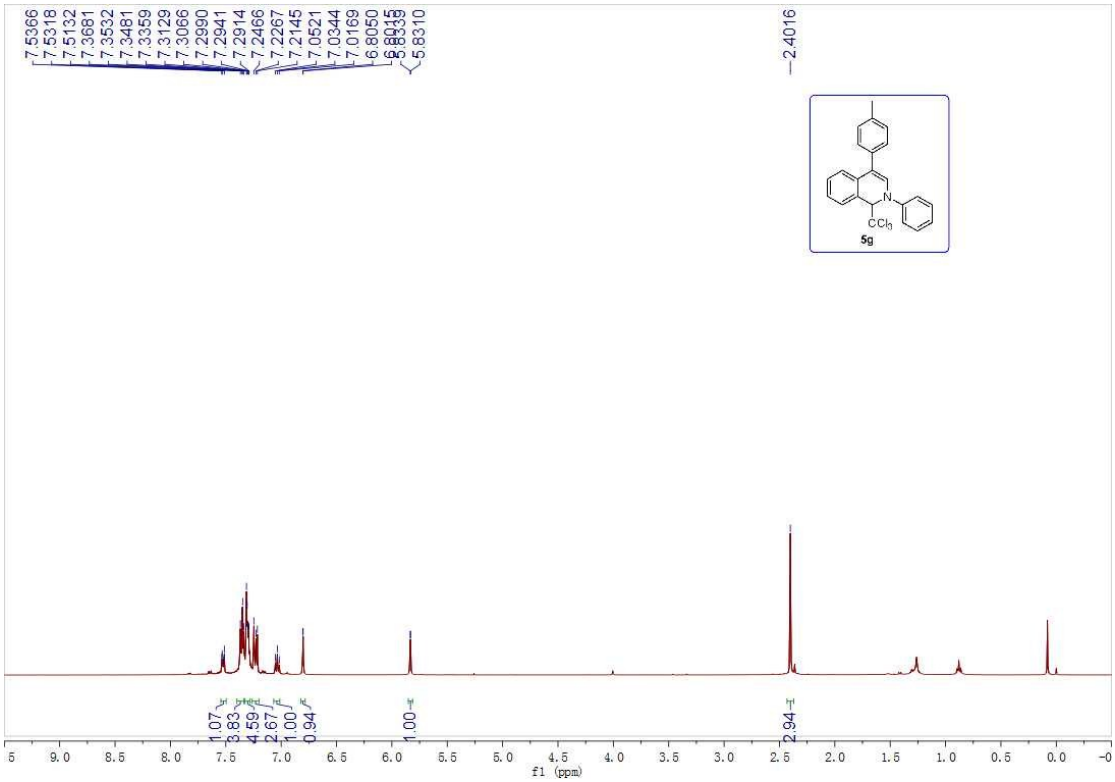
Ph
N
Ph
CCl3
5f
f1 (ppm)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7.3481
7.3359
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7.2914
7.2466
7.2267
7.2145
7.0521
7.0344
7.0169
6.8050
5.8310
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5g
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4.59
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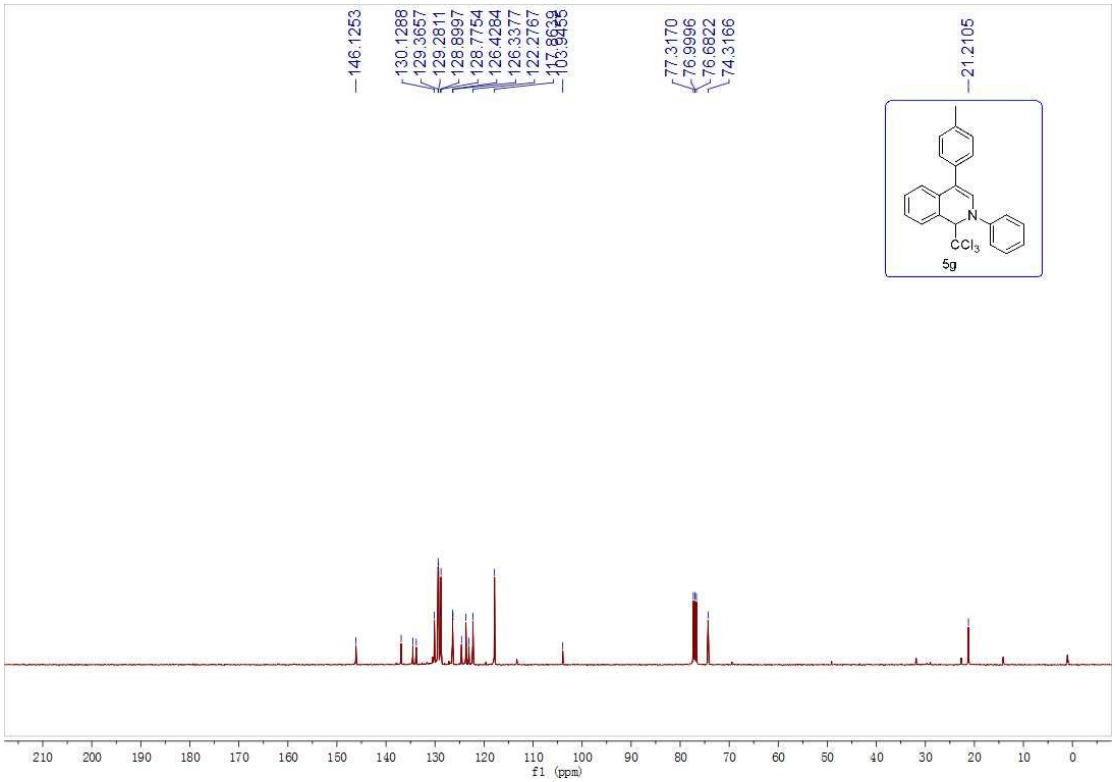
2.94
f1 (ppm)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76.6822
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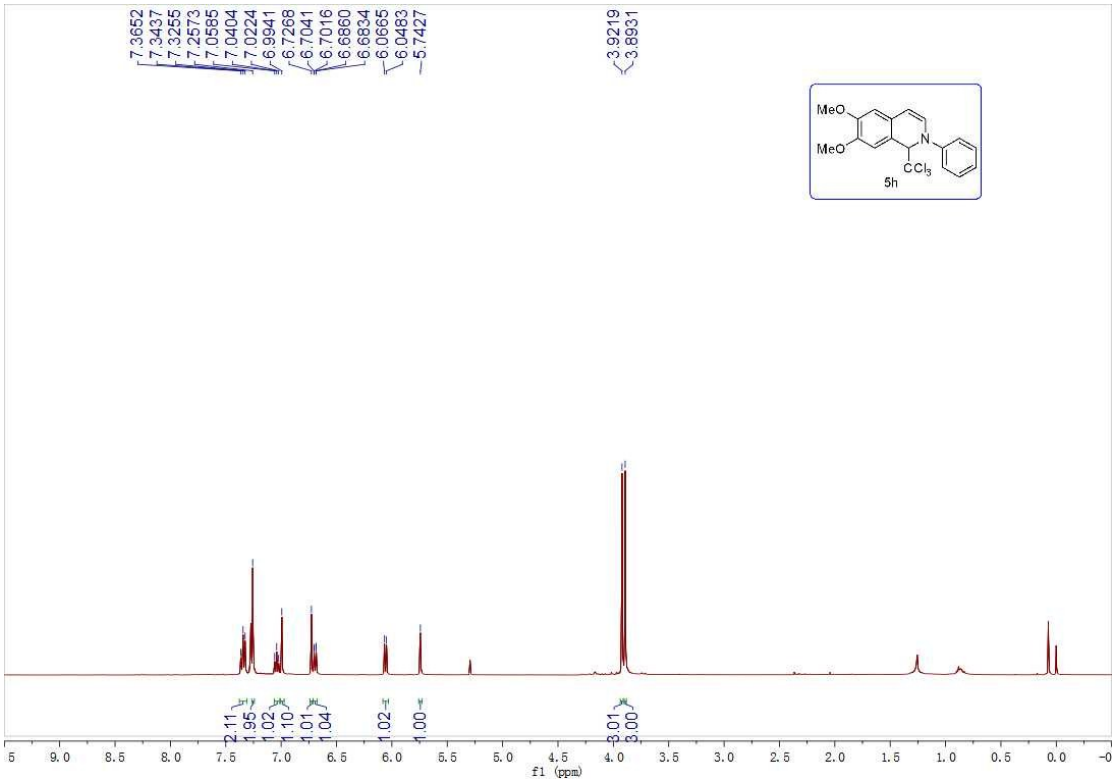
5g
f1 (ppm)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7.0224
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6.7016
6.6860
6.6834
6.0665
6.0483
5.7427
3.9219
3.8931
MeO
MeO
N
CCl3
5h
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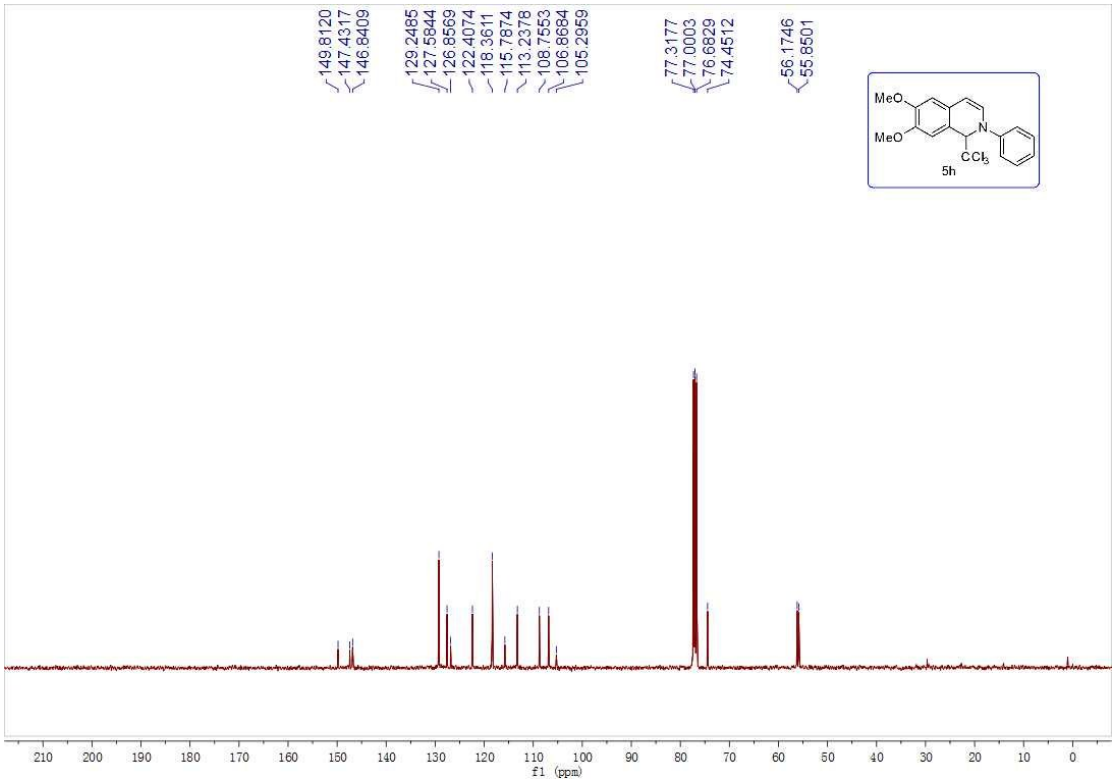
1.02
1.10
1.01
1.04
1.02
1.00
3.01
3.00
f1 (ppm)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106.8684
105.2959
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74.4512
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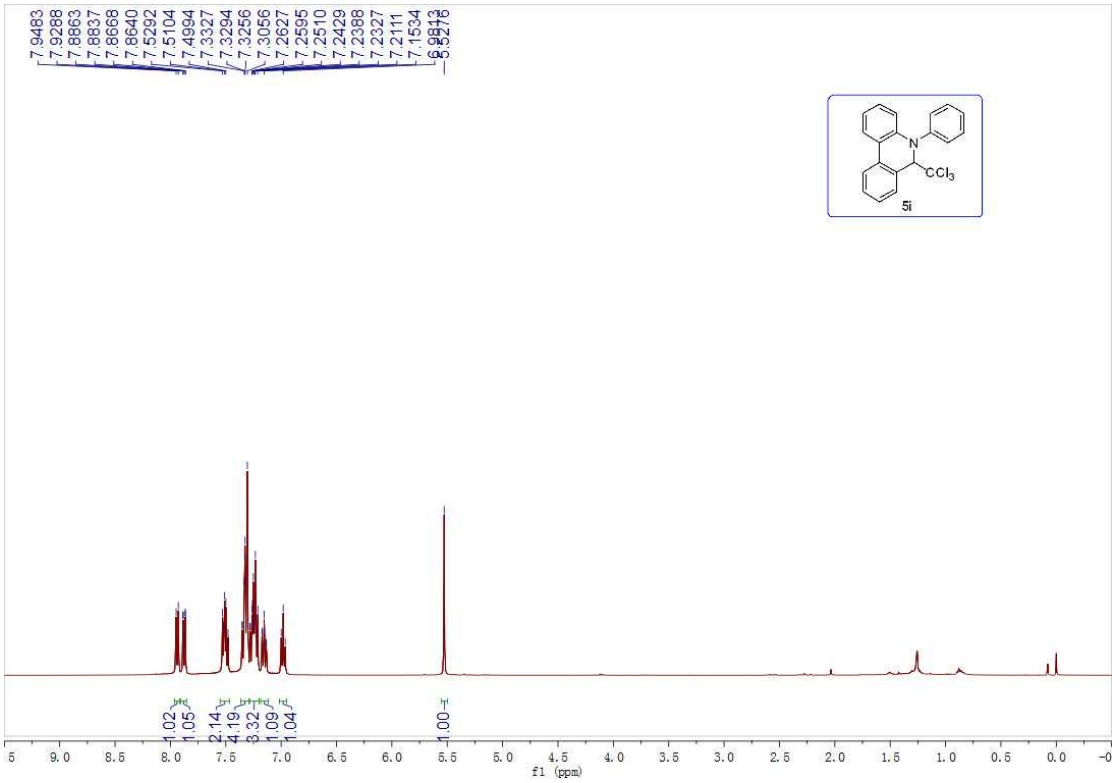
MeO
MeO
N
CCl3
5h
f1 (ppm)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7.3056
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7.2595
7.2510
7.2429
7.2388
7.2327
7.2111
7.1534
6.9813
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CCl3
5i
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1.05
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4.19
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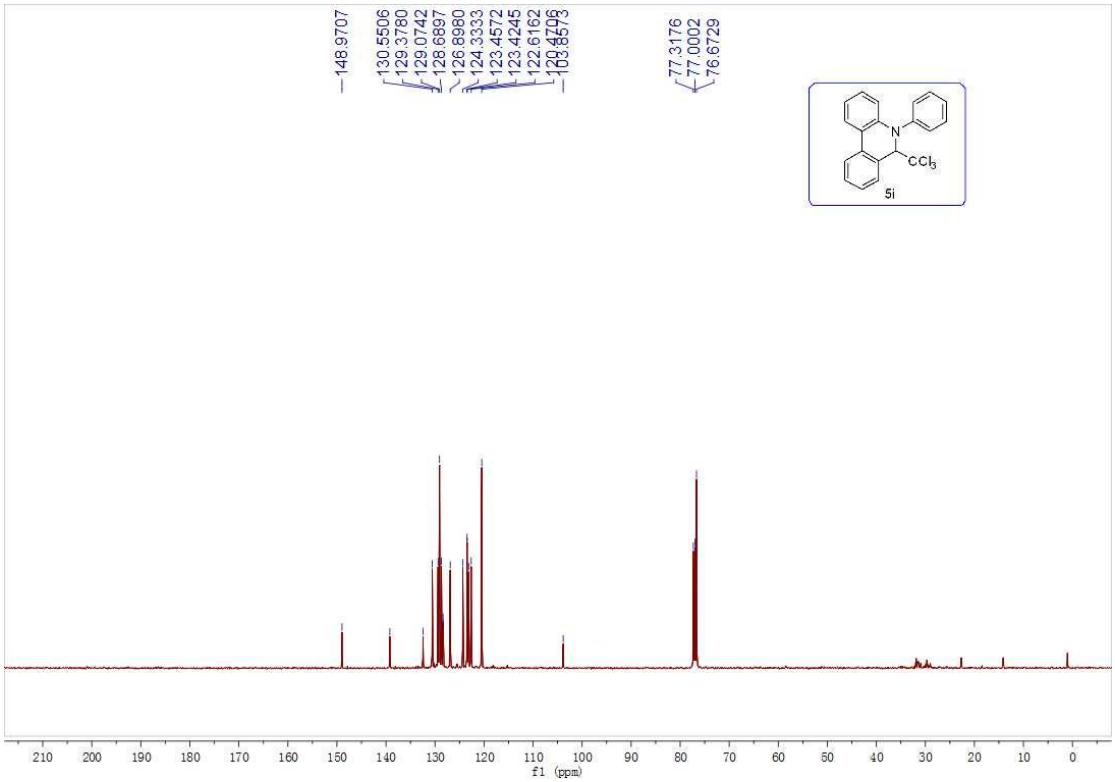
1.09
1.04
1.00
f1 (ppm)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123.4245
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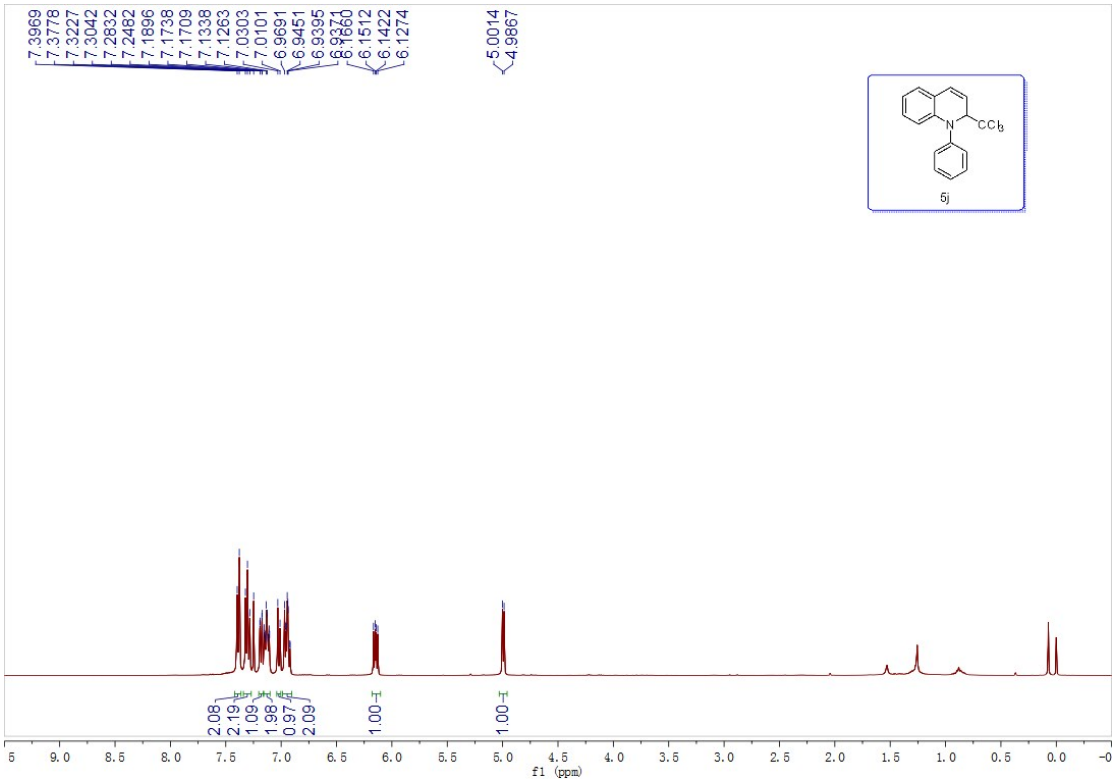
103.8573
77.3176
77.0002
76.6729
CCl3
5i
f1 (ppm)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7.0303
7.0101
6.9691
6.9451
6.9395
6.9371
6.9160
6.1512
6.1422
6.1274
5.0014
4.9867
CCl3
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2.08
2.19
1.09
1.98
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2.09
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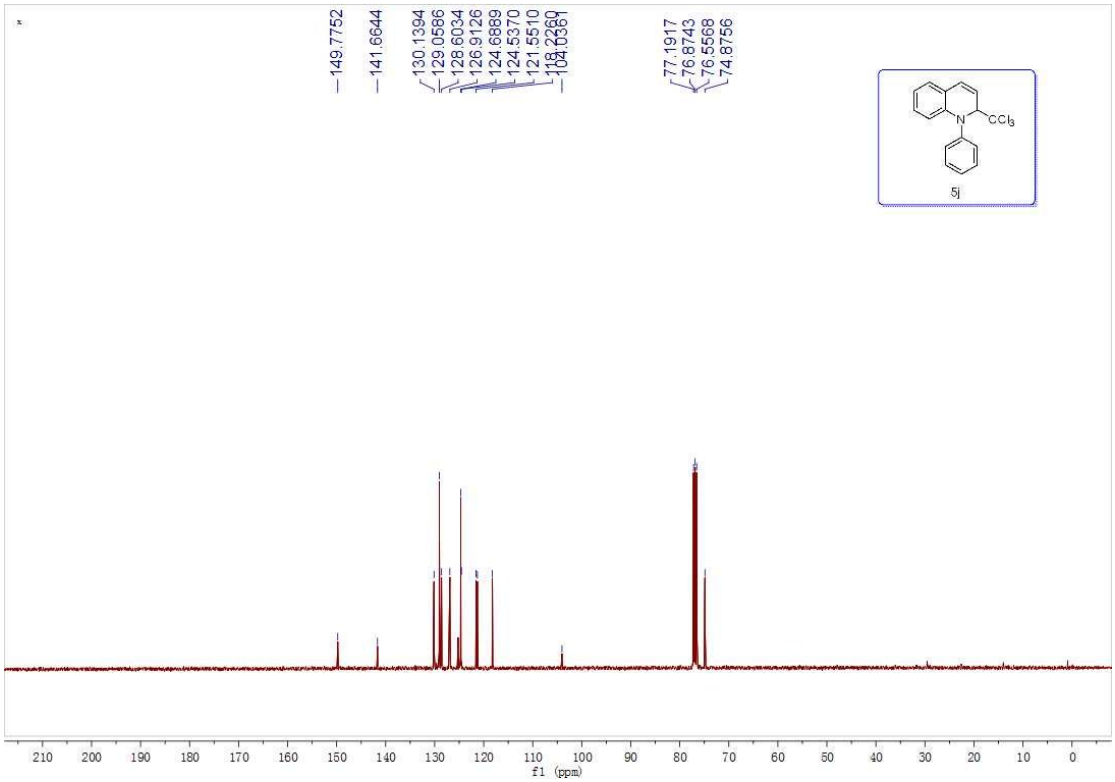
1.00
f1 (ppm)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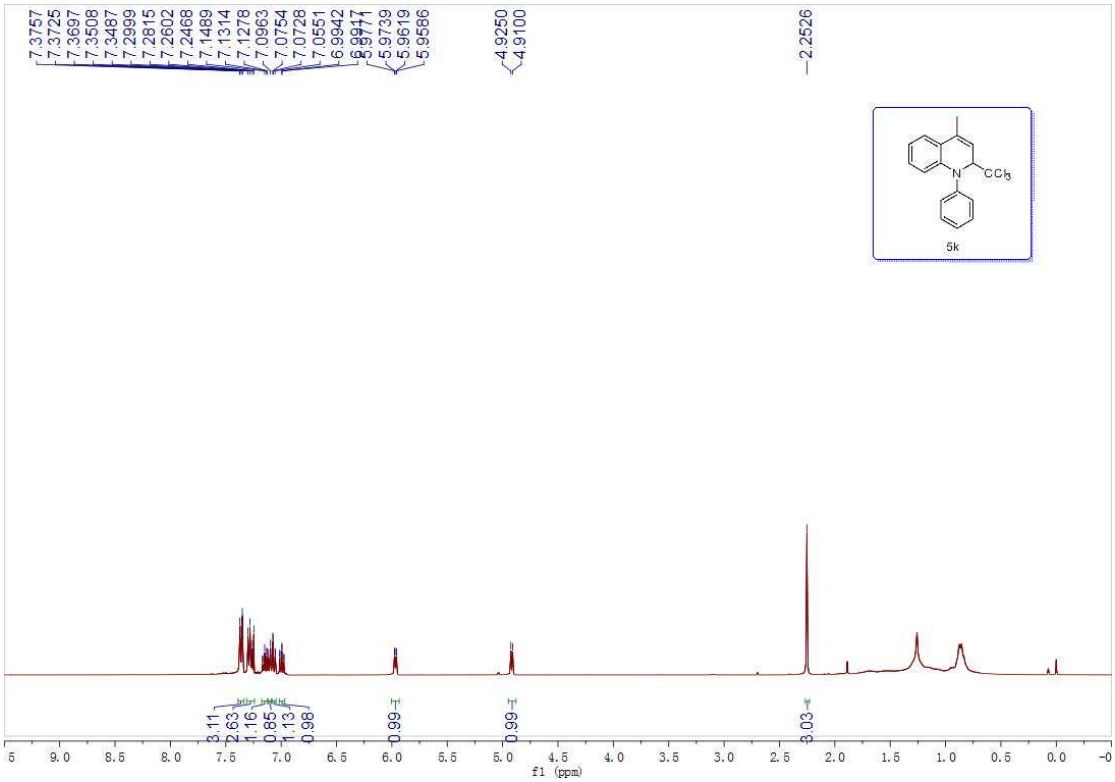
76.8743
76.5568
74.8756
CCl3
N
5j
f1 (ppm)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7.1278
7.0963
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7.0728
7.0551
6.9942
5.9739
5.9619
5.9586
4.9250
4.9100
2.2526
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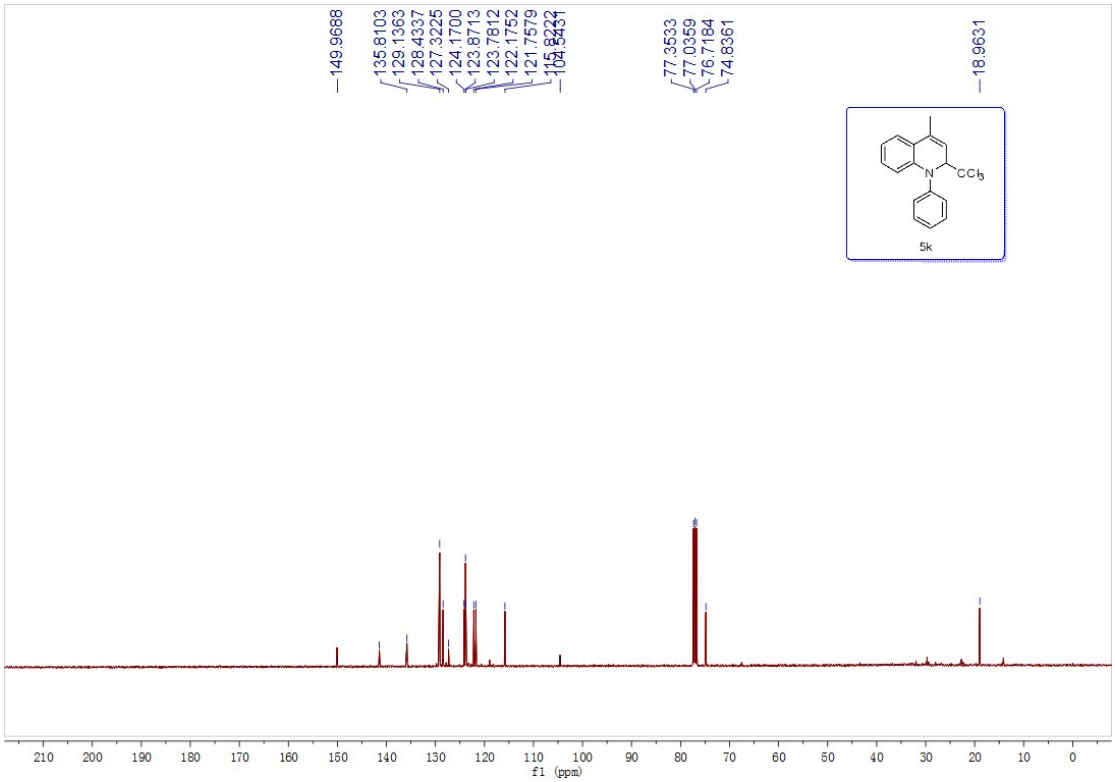
0.99
3.03
CCl3
5k
f1 (ppm)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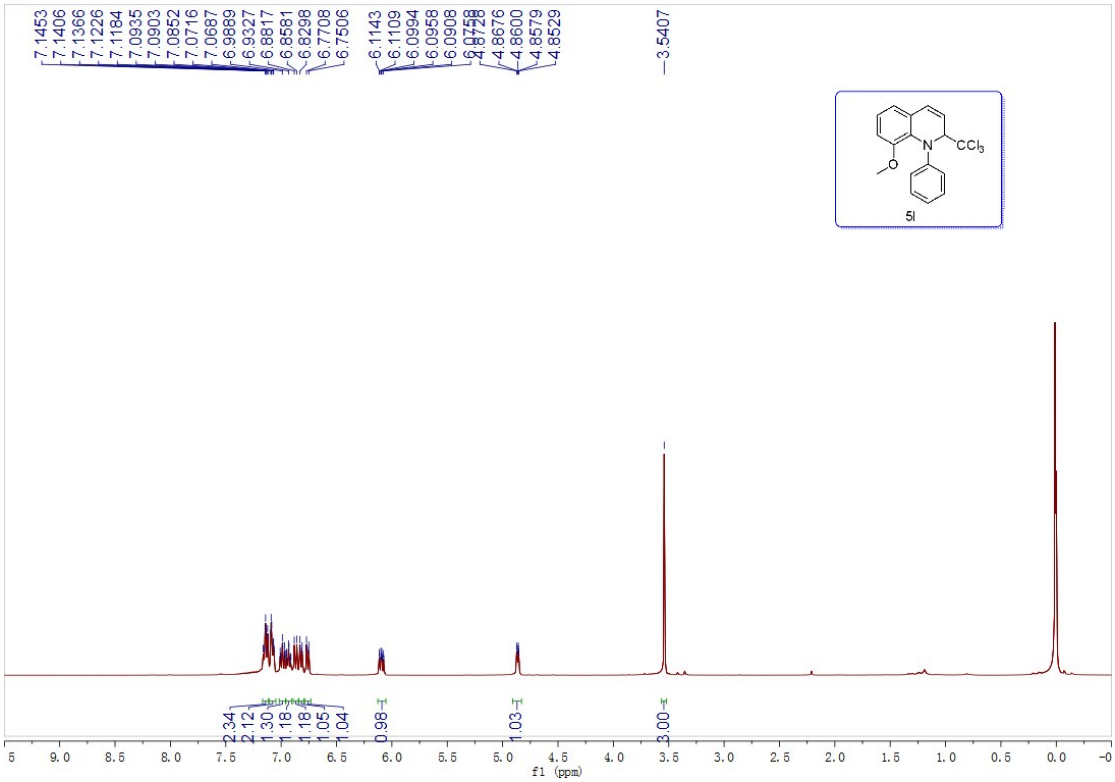
CCl3
5k
f1 (ppm)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6.0908
4.8676
4.8600
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4.8529
3.5407
CCl3
N
O
5l
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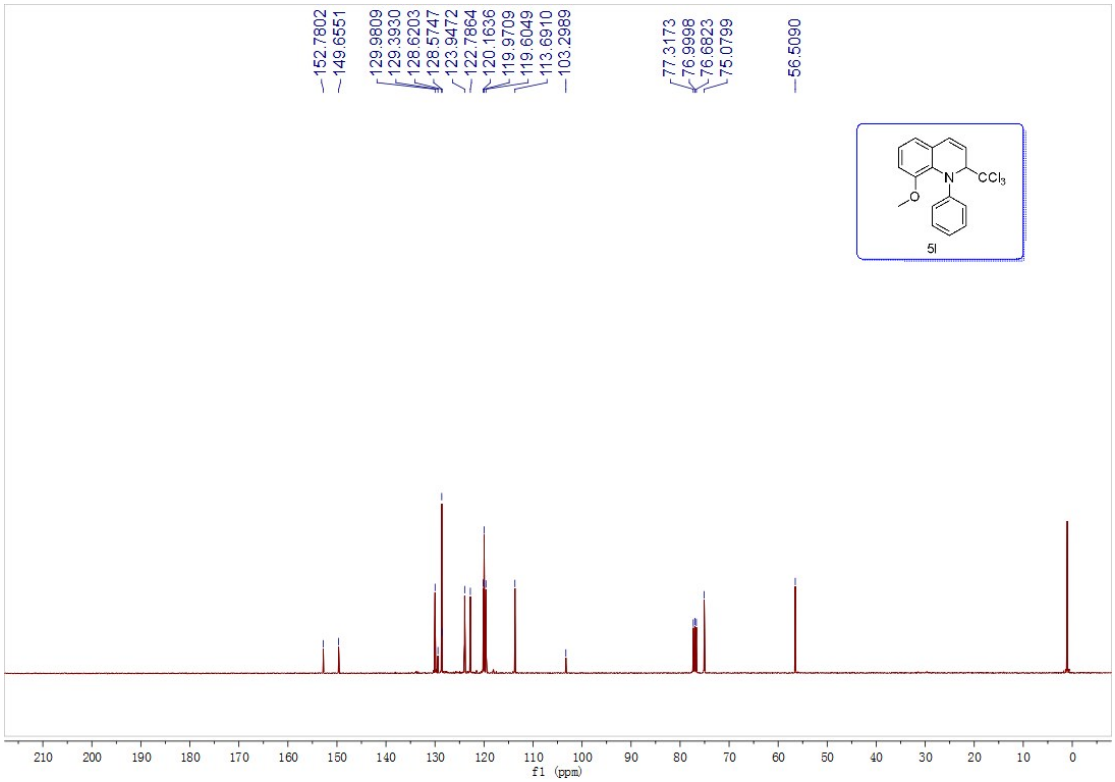
2.12
1.30
1.18
1.05
1.04
0.98
1.03
3.00
f1 (ppm)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75.0799
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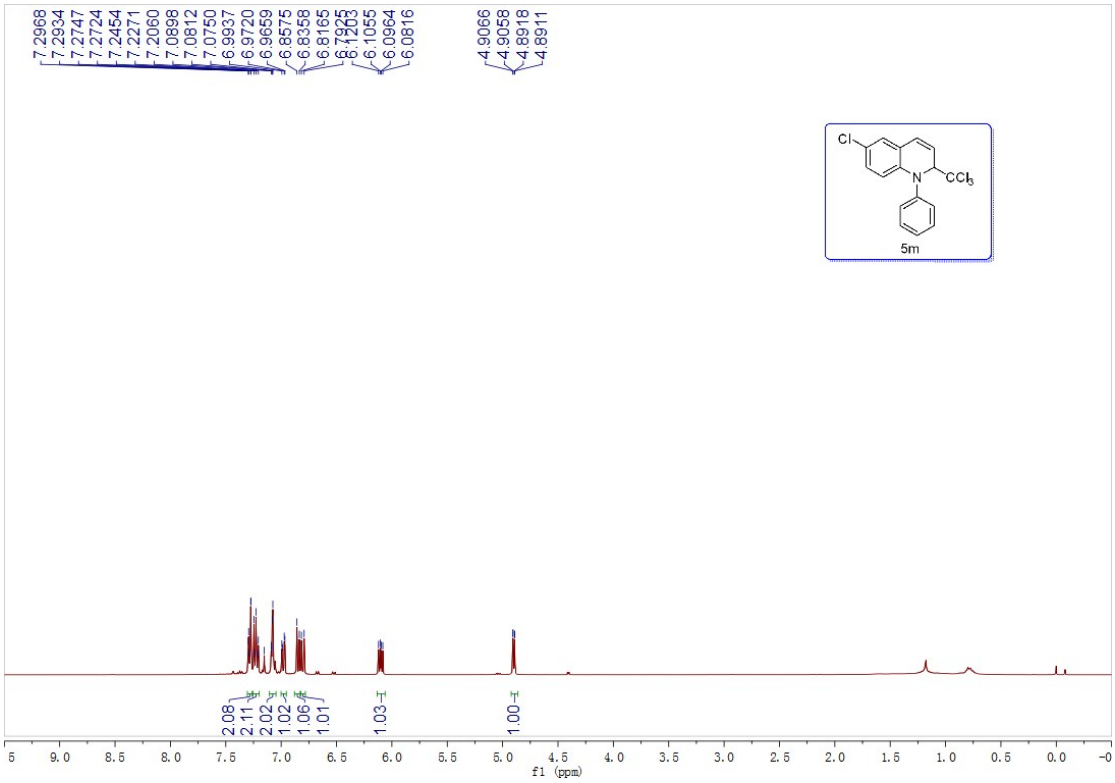
CCl3
N
O
5l
f1 (ppm)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6.8358
6.8165
6.1203
6.1055
6.0964
6.0816
4.9066
4.9058
4.8918
4.8911
Cl
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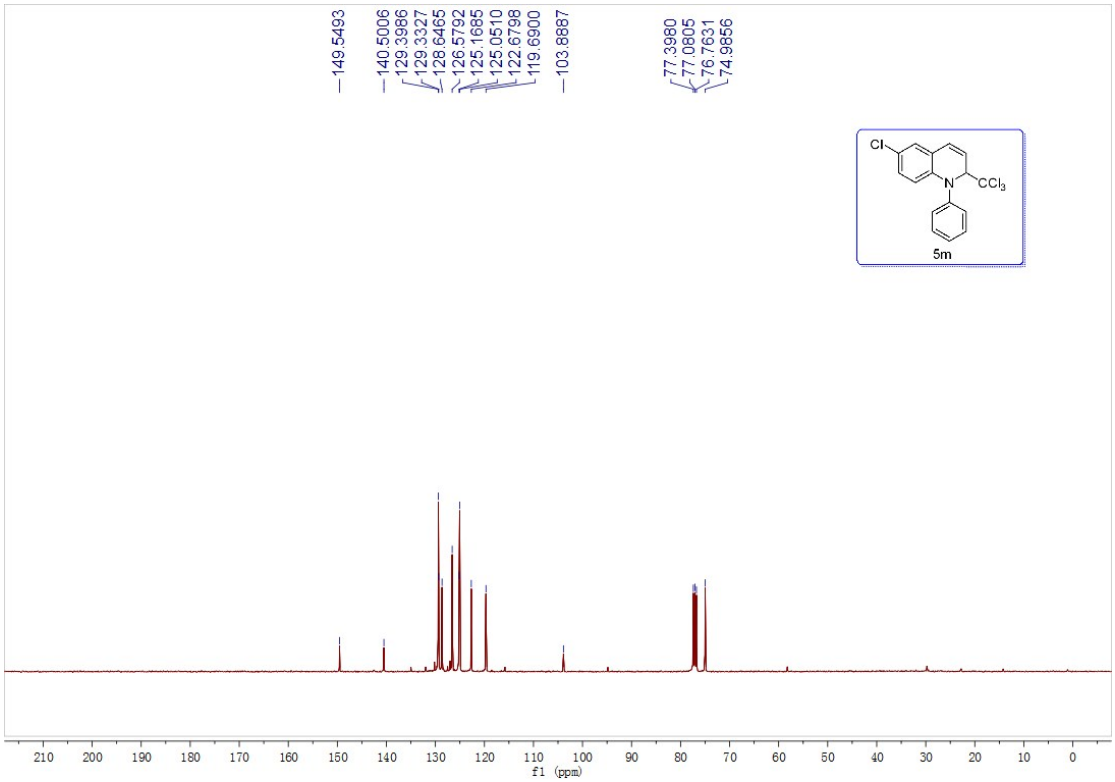
CCl3
5m
2.08
2.11
2.02
1.02
1.06
1.01
1.03
1.00
f1 (ppm)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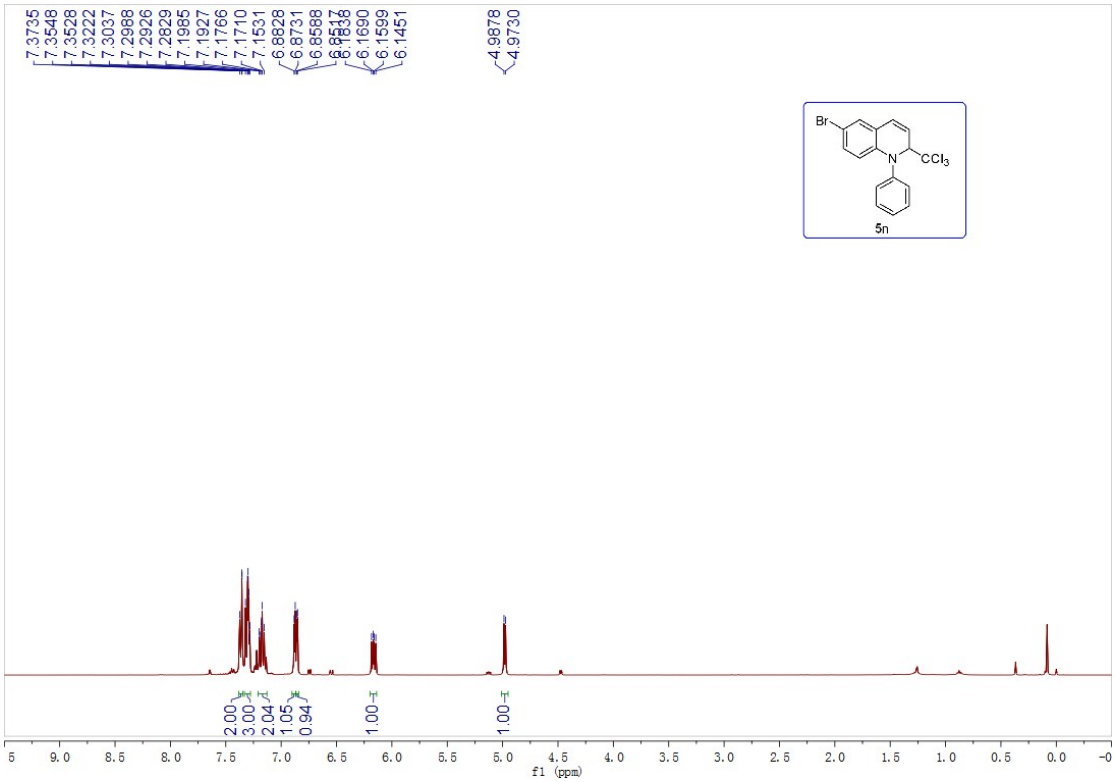
Cl
N
CCl3
5m
f1 (ppm)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7.1710
7.1531
6.8828
6.8731
6.8588
6.8517
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6.1690
6.1599
6.1451
4.9878
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Br
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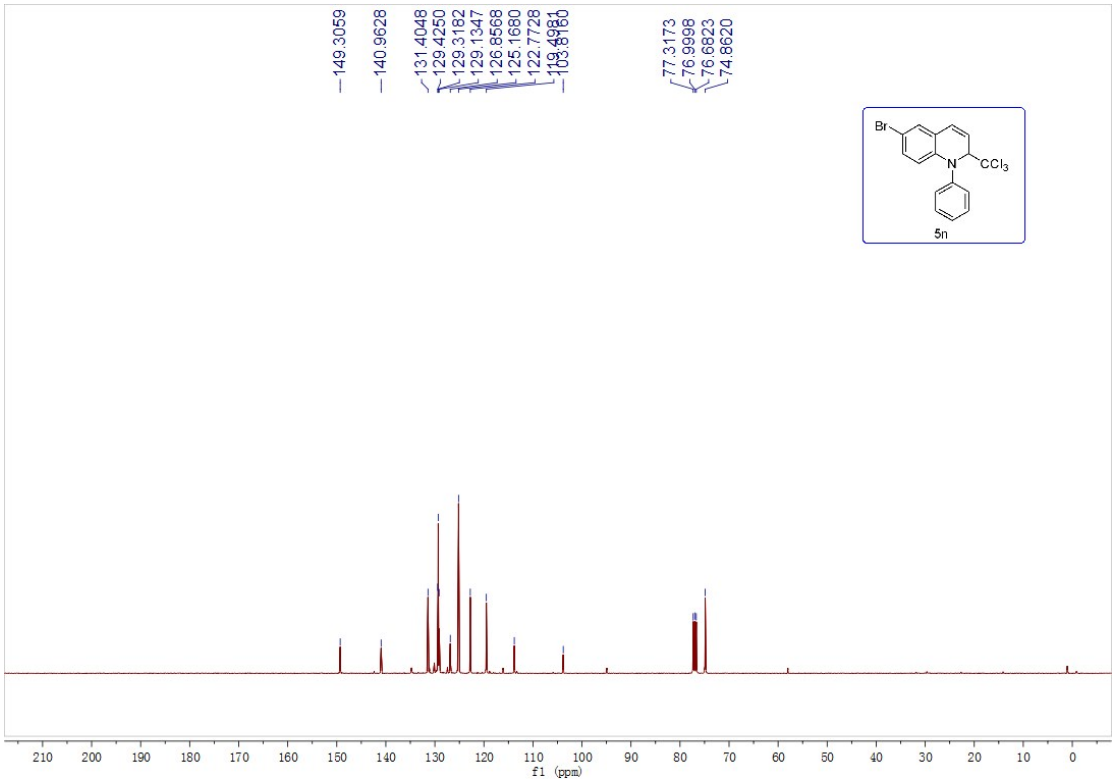
CCl3
5n
2.00
3.00
2.04
1.05
0.94
1.00
1.00
f1 (ppm)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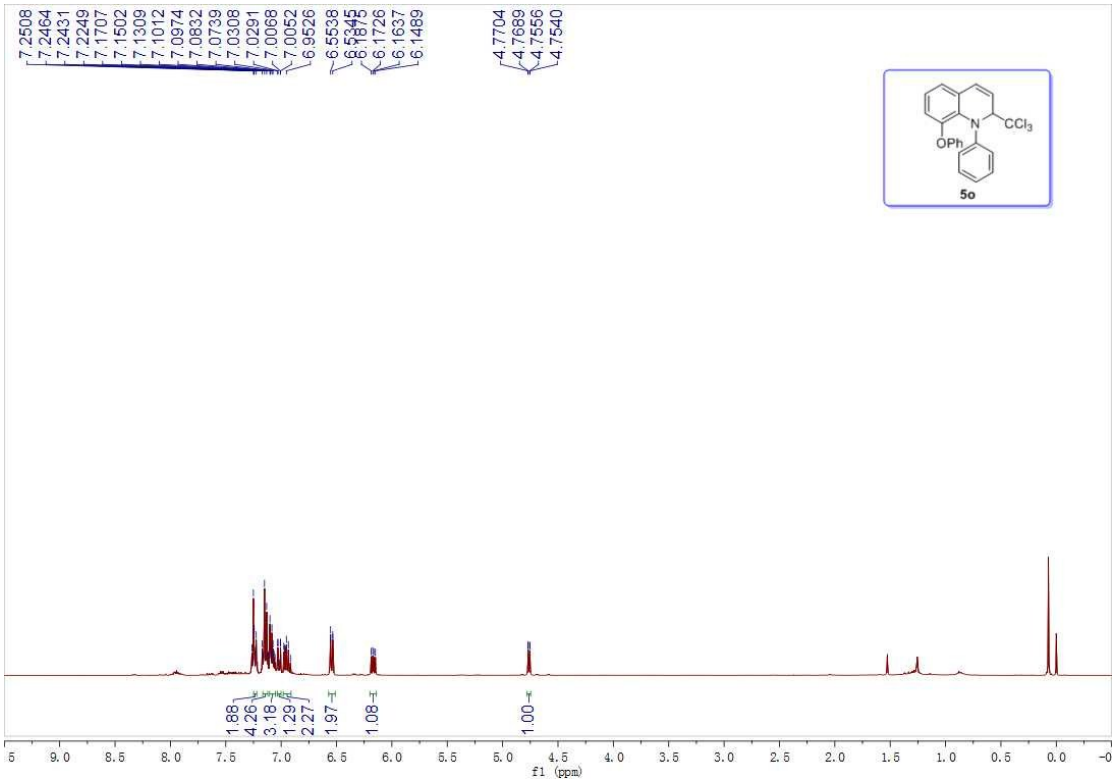
76.6823
74.8620
Br
N
CCl3
5n
f1 (ppm)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6.1845
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6.1637
6.1489
4.7704
4.7689
4.7556
4.7540
CCl3
OPh
N
5o
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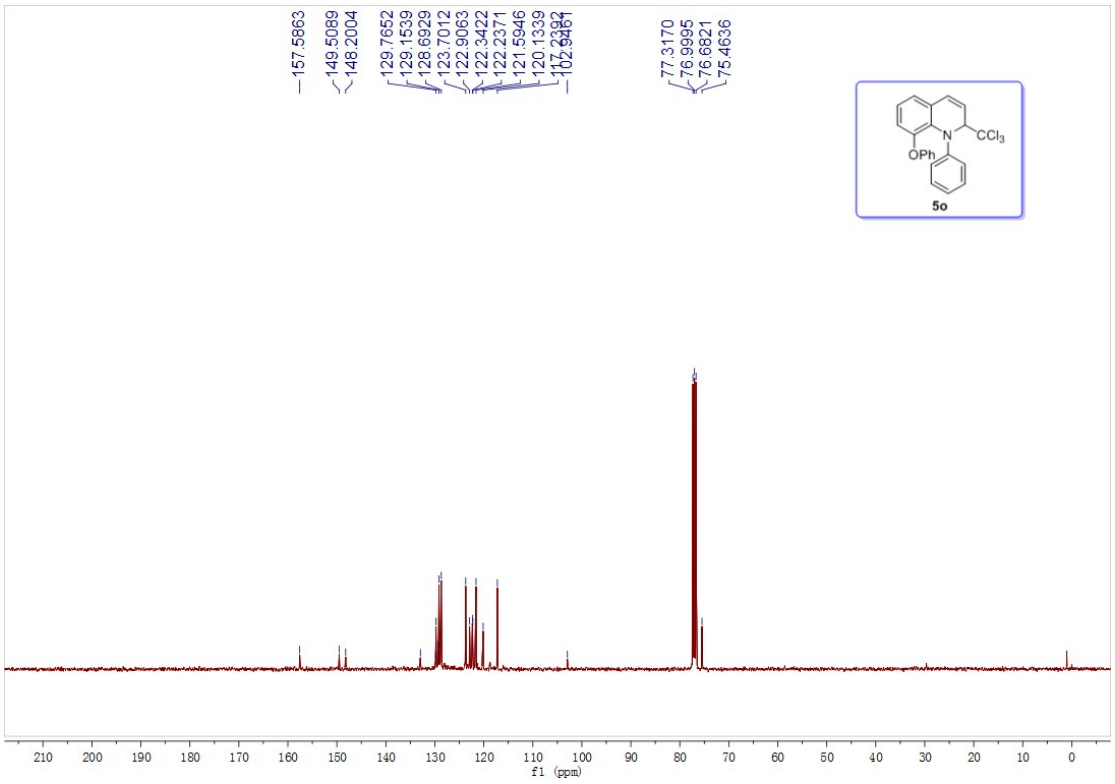
3.18
1.29
2.27
1.97
1.08
1.00
f1 (ppm)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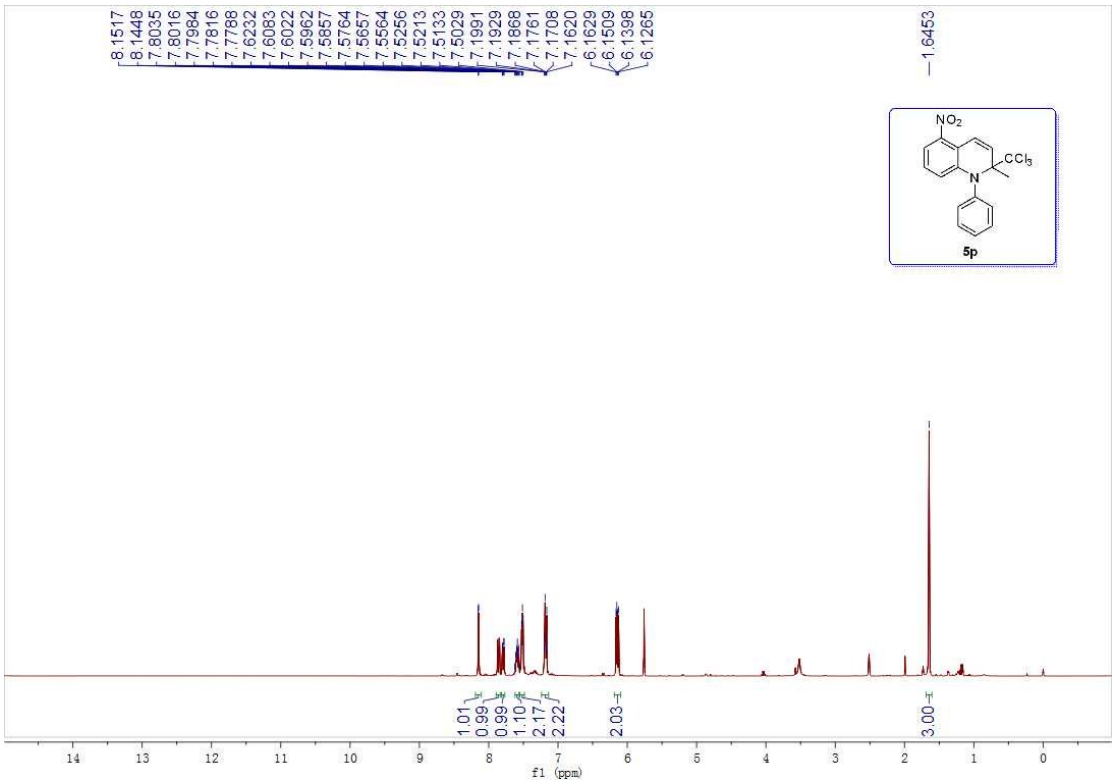
CCl3
OPh
N
5o
f1 (ppm)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7.5564
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7.5213
7.5133
7.5029
7.1991
7.1929
7.1868
7.1761
7.1708
7.1620
6.1629
6.1509
6.1398
6.1265
1.6453
NO2
CCl3
N
5p
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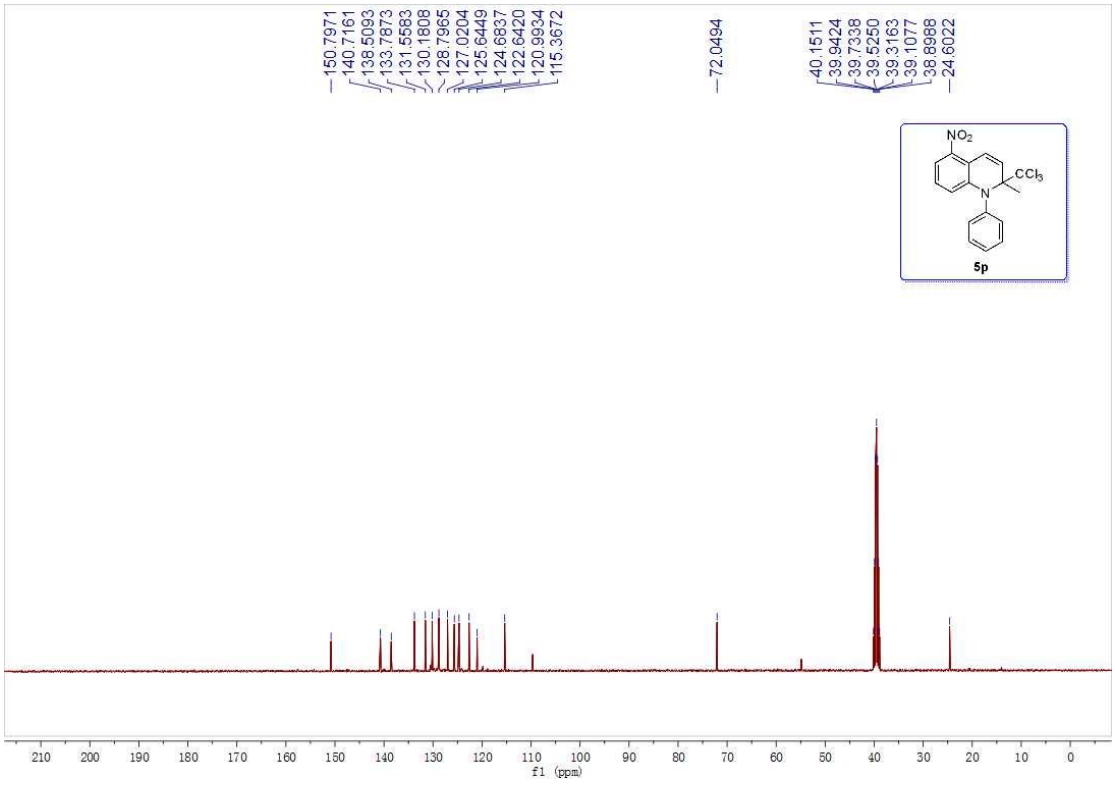
0.99
0.99
1.10
2.17
2.22
2.03
3.00
f1 (ppm)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120.9934
115.3672
72.0494
40.1511
39.9424
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39.1077
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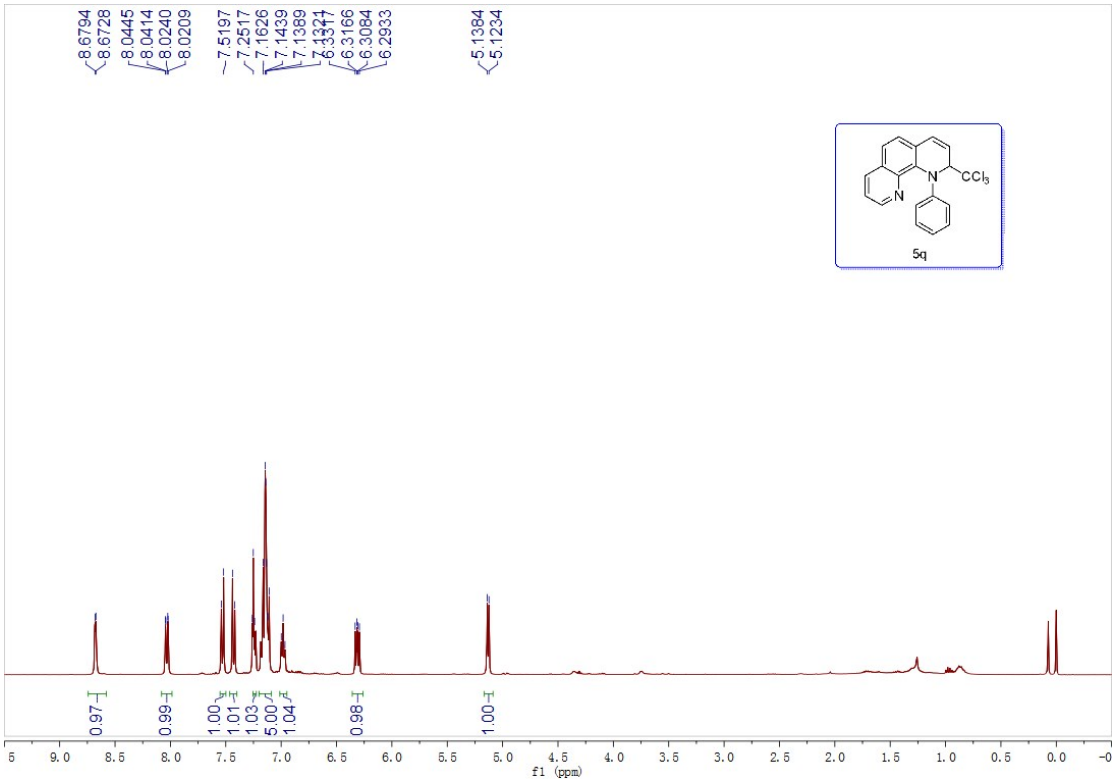
NO2
CCl3
N
5p
f1 (ppm)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7.5197
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7.1389
6.3317
6.3166
6.3084
6.2933
5.1384
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0.97
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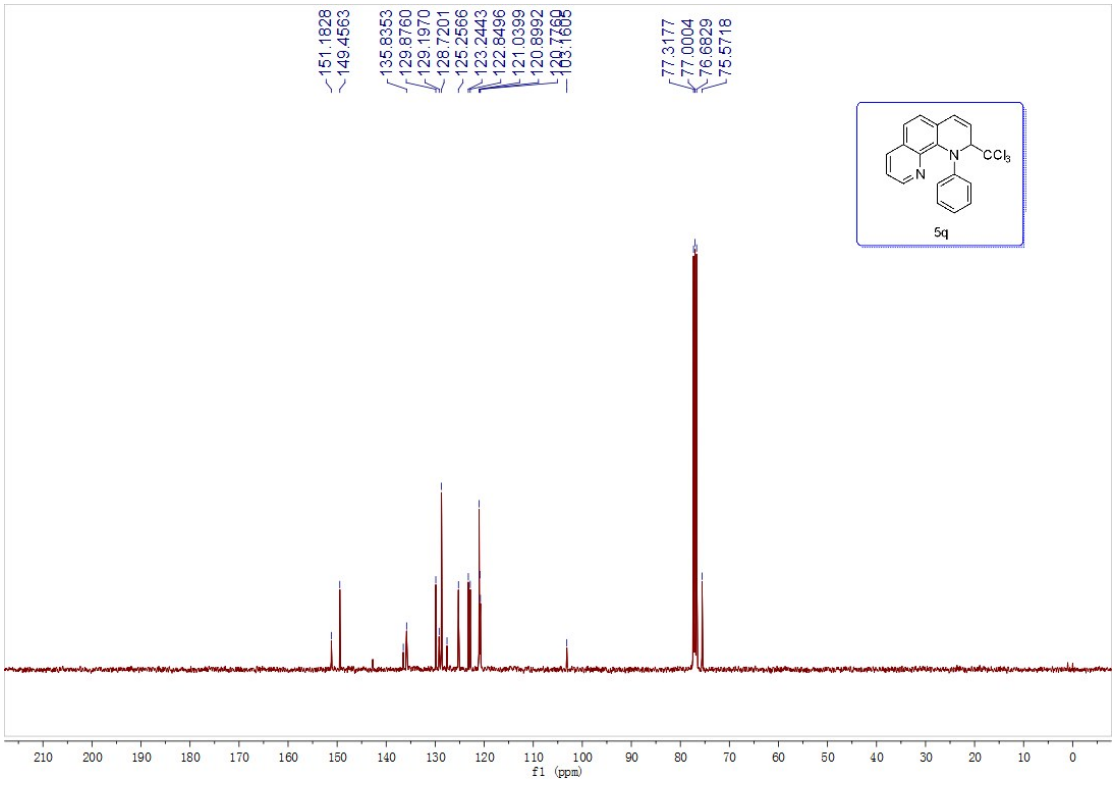
1.00
1.01
1.03
5.00
1.04
0.98
1.00
f1 (ppm)
5q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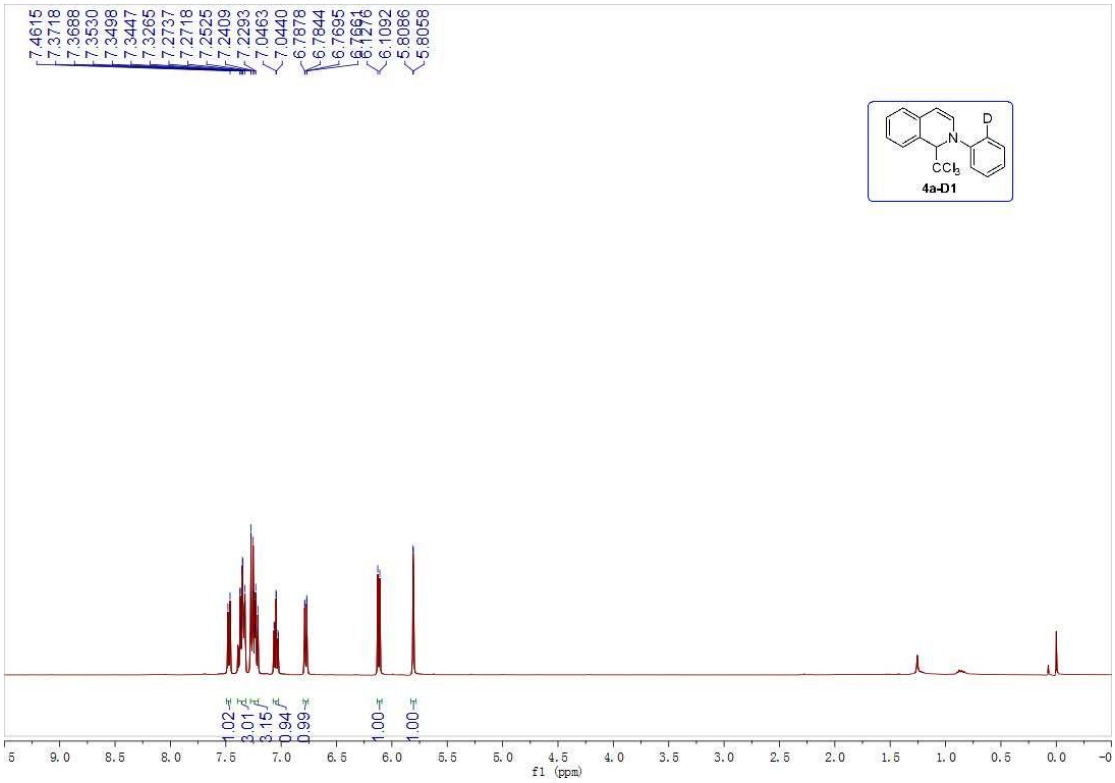
f1 (ppm)
5q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7.2293
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7.0440
6.7878
6.7844
6.7695
6.1276
6.1092
5.8086
5.8058
D
N
CCl3
4a-D1
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3.15
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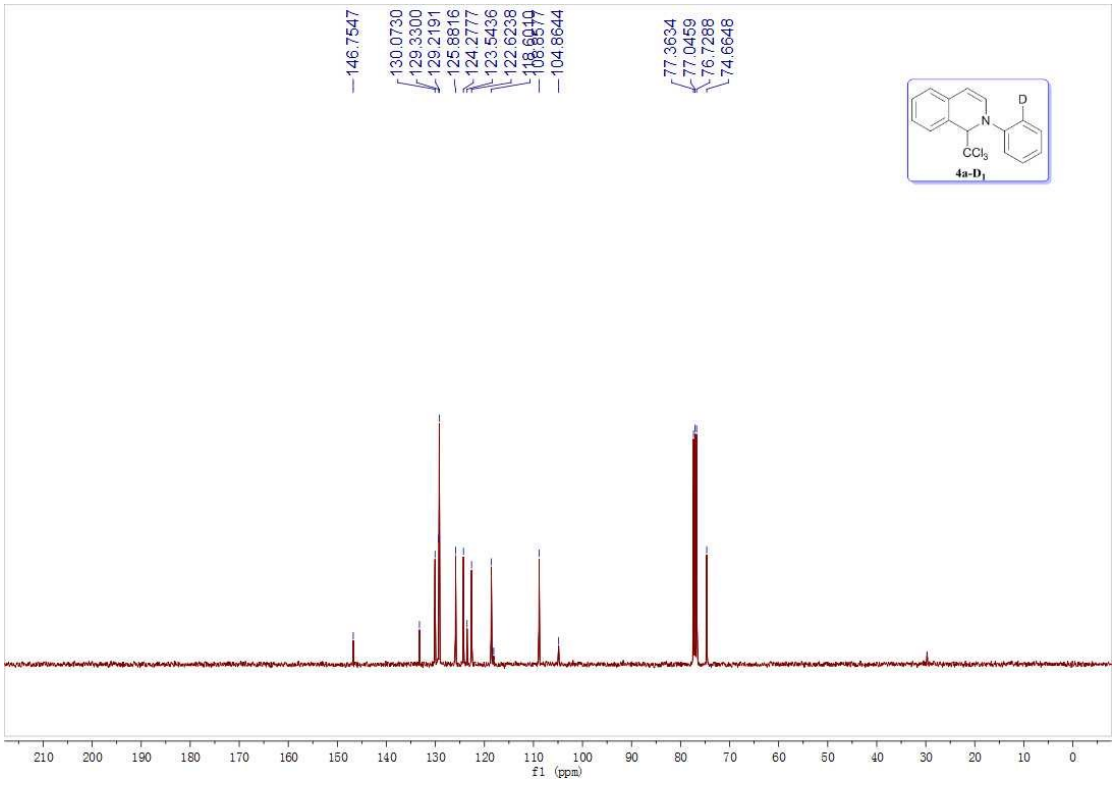
0.99
1.00
1.00
f1 (ppm)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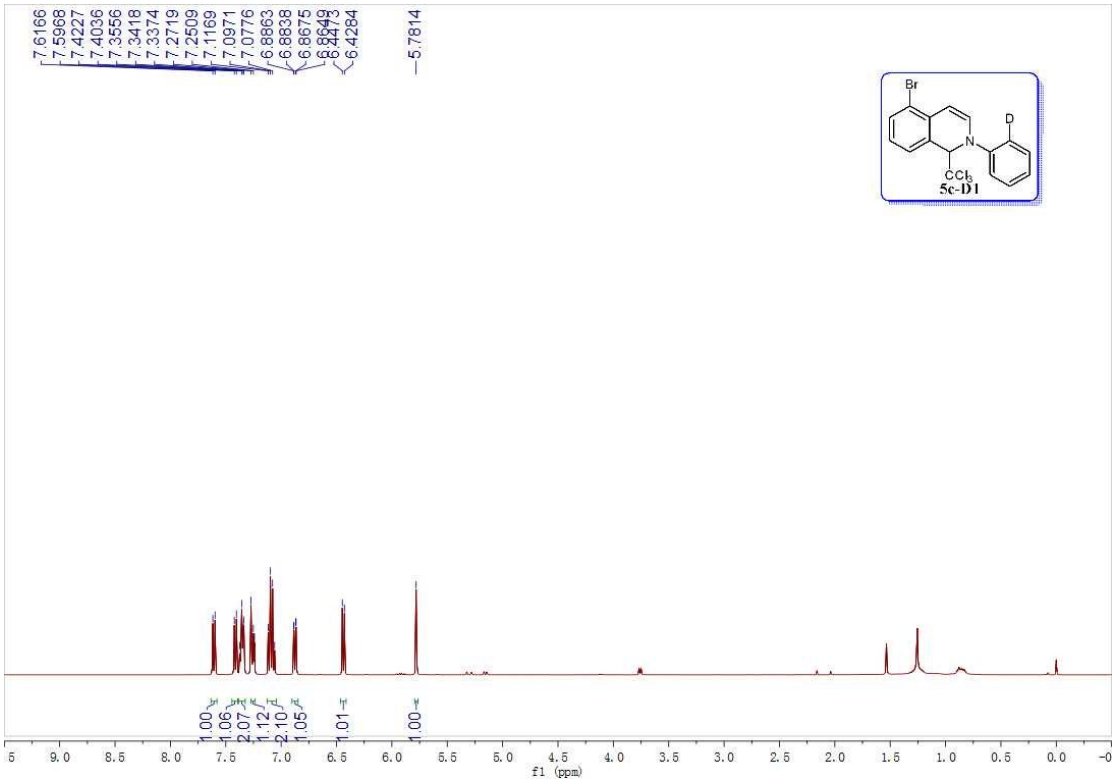
D
N
CCl3
4a-D1
f1 (ppm)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Br
D
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1.05
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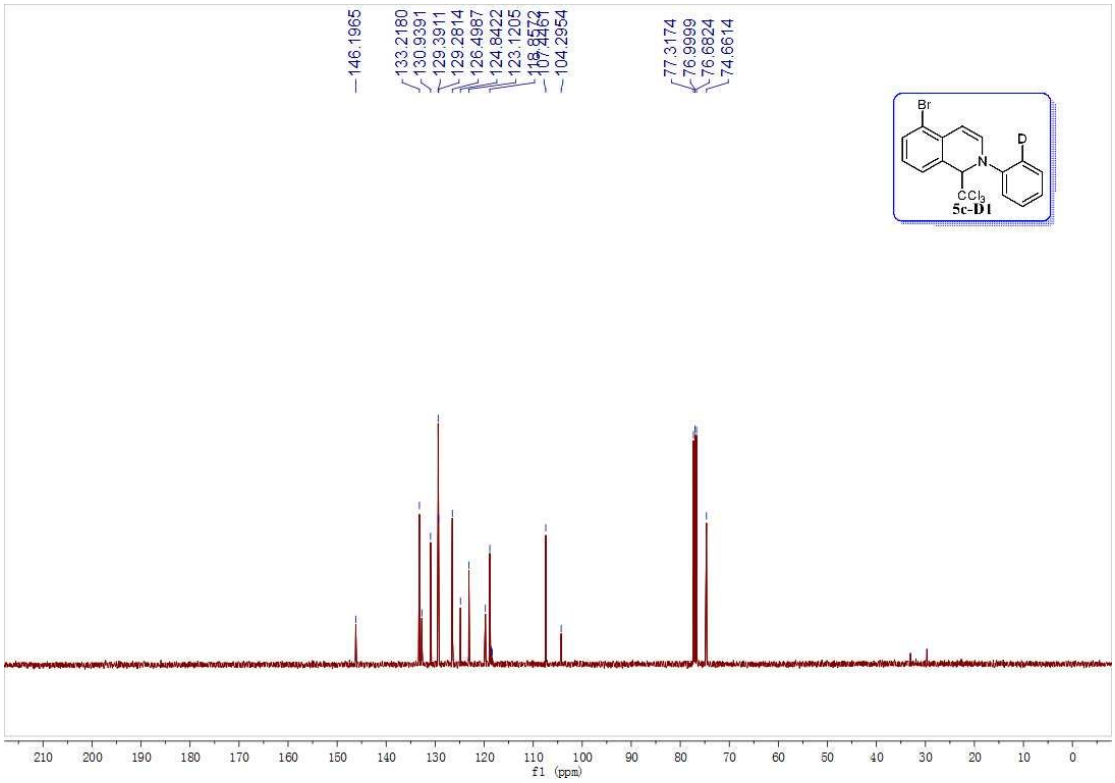
1.00
f1 (ppm)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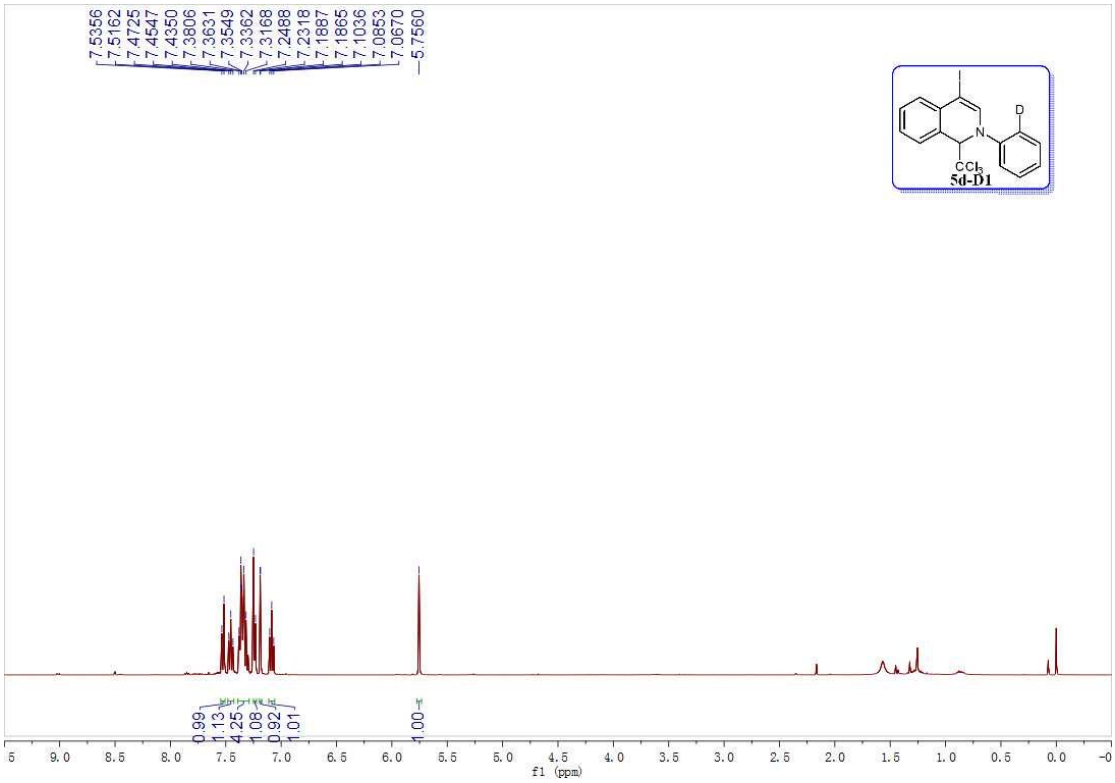
Br
D
N
CCl3
5c-D1
f1 (ppm)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7.0853
7.0670
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f1 (ppm)
D
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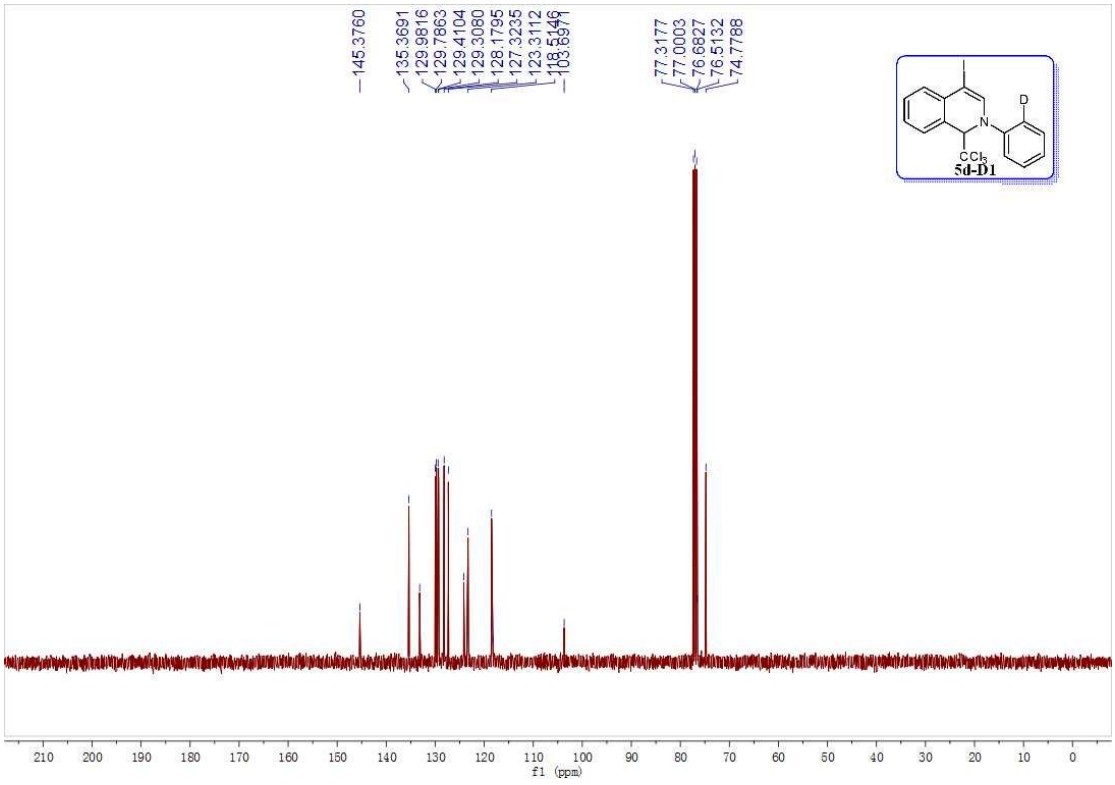
CCl3
5d-D1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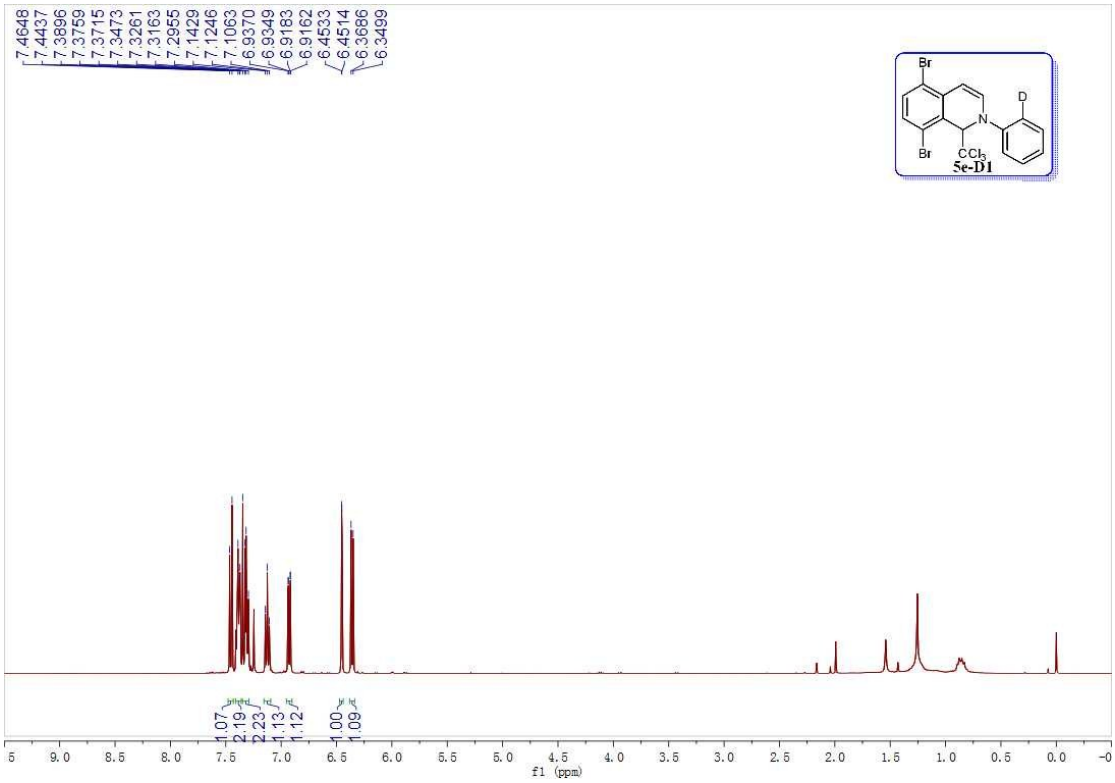
f1 (ppm)
D
N
CCl3
5d-D1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Br
D
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5e-D1
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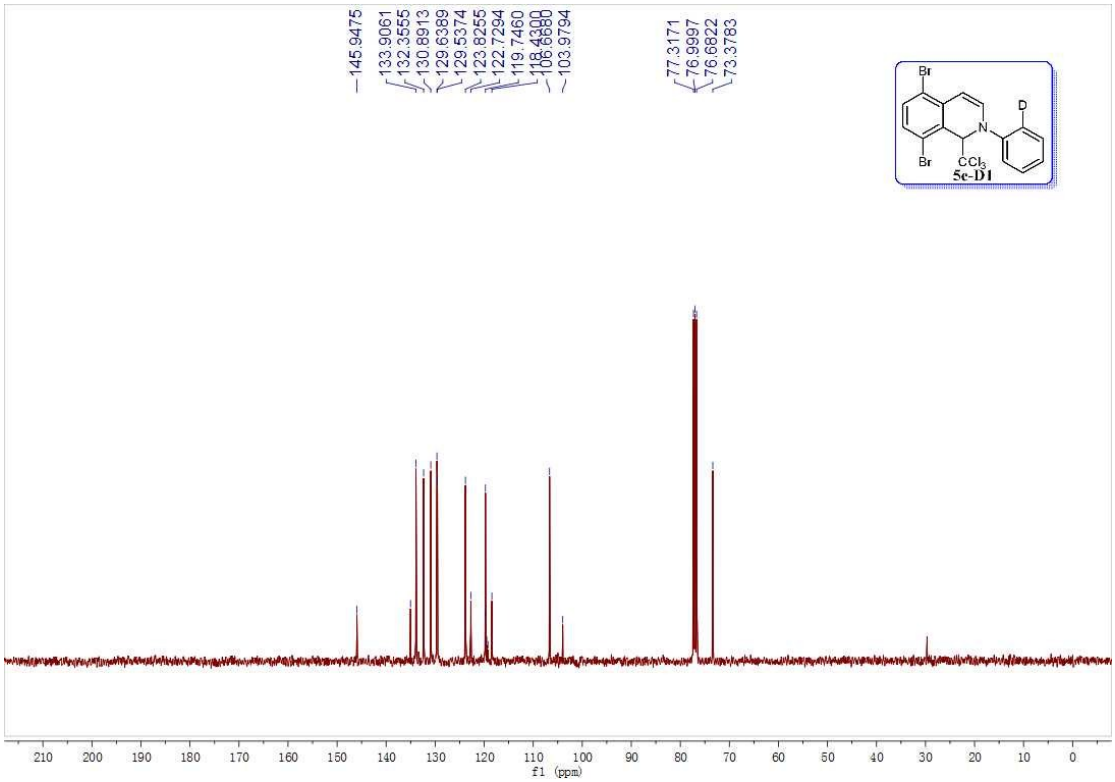
1.12
1.00
1.09
f1 (ppm)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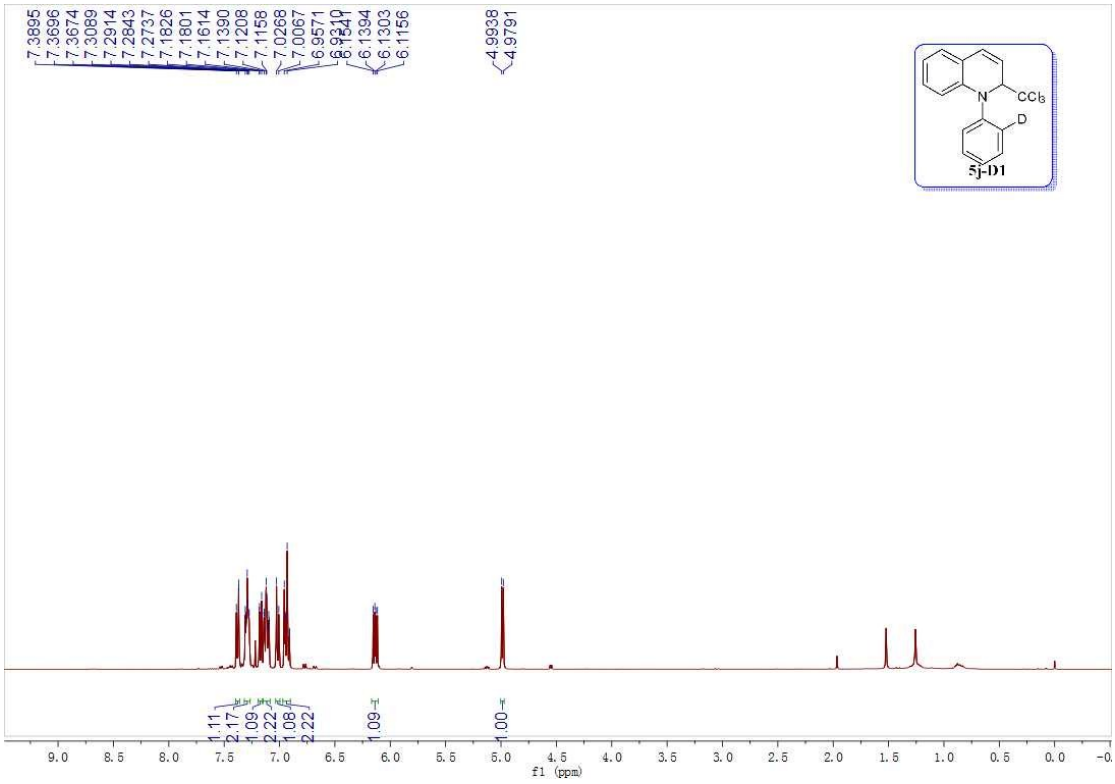
Br
CCl3
5e-D1
f1 (ppm)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6.1303
6.1156
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4.9791
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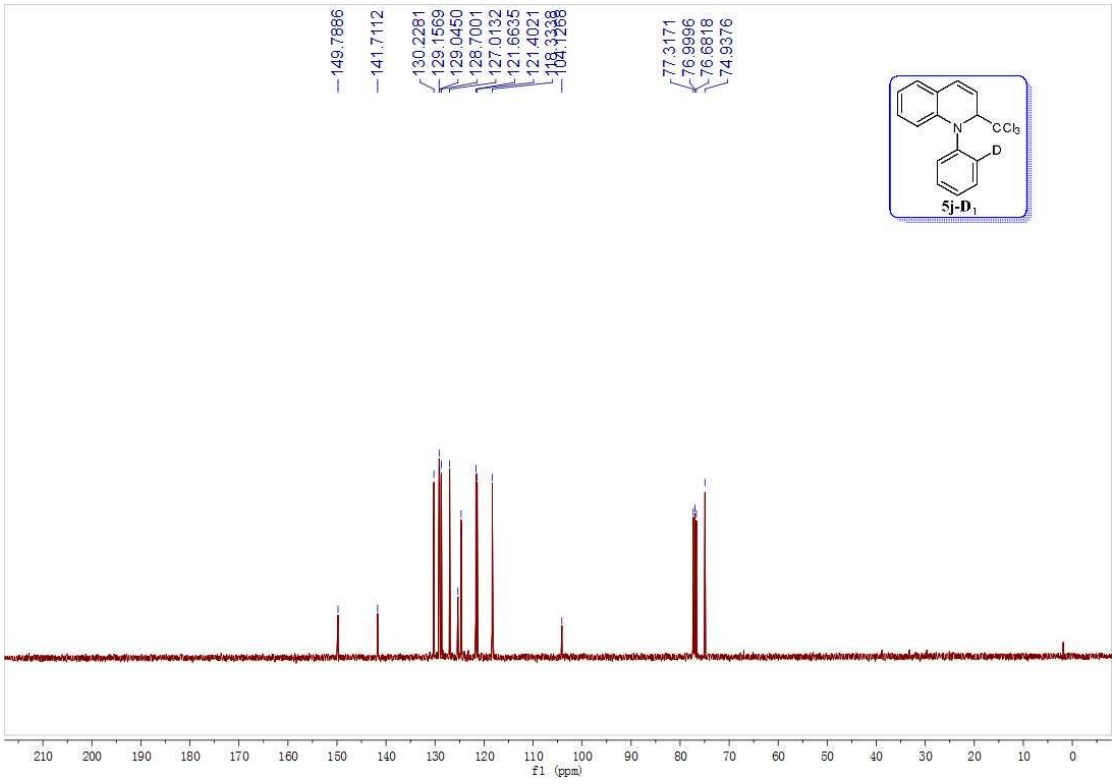
1.00
f1 (ppm)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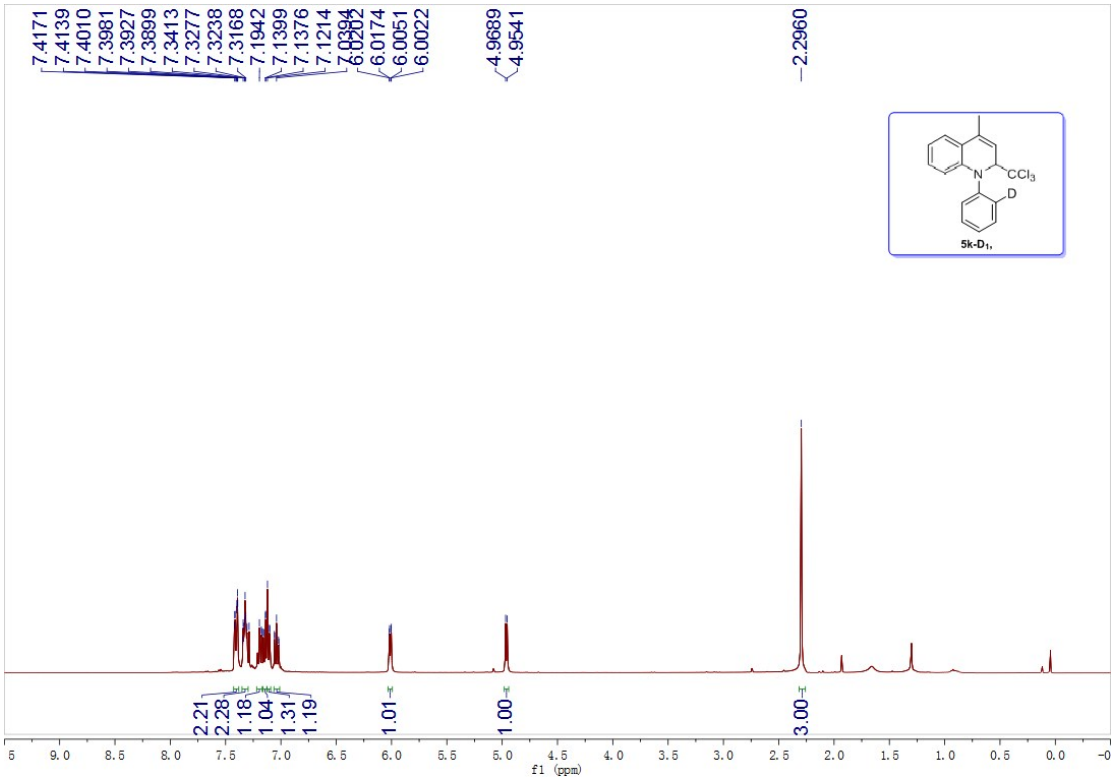
CCl3
D
5j-D1
f1 (ppm)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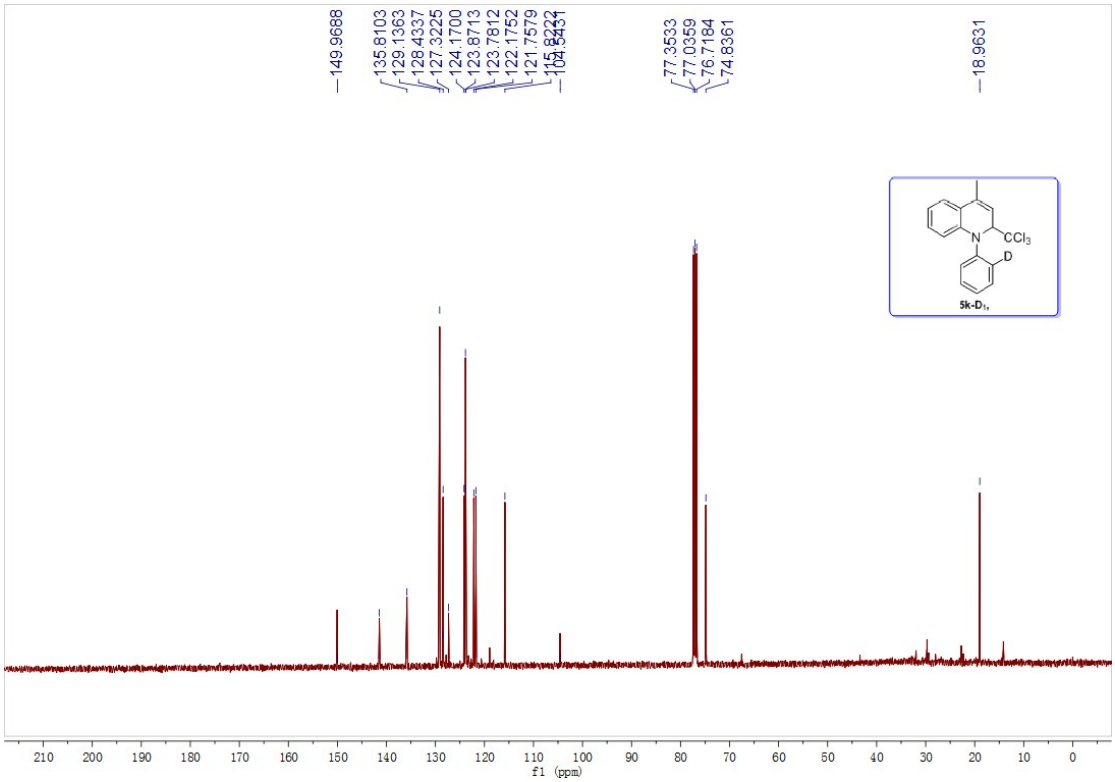
3.00
f1 (ppm)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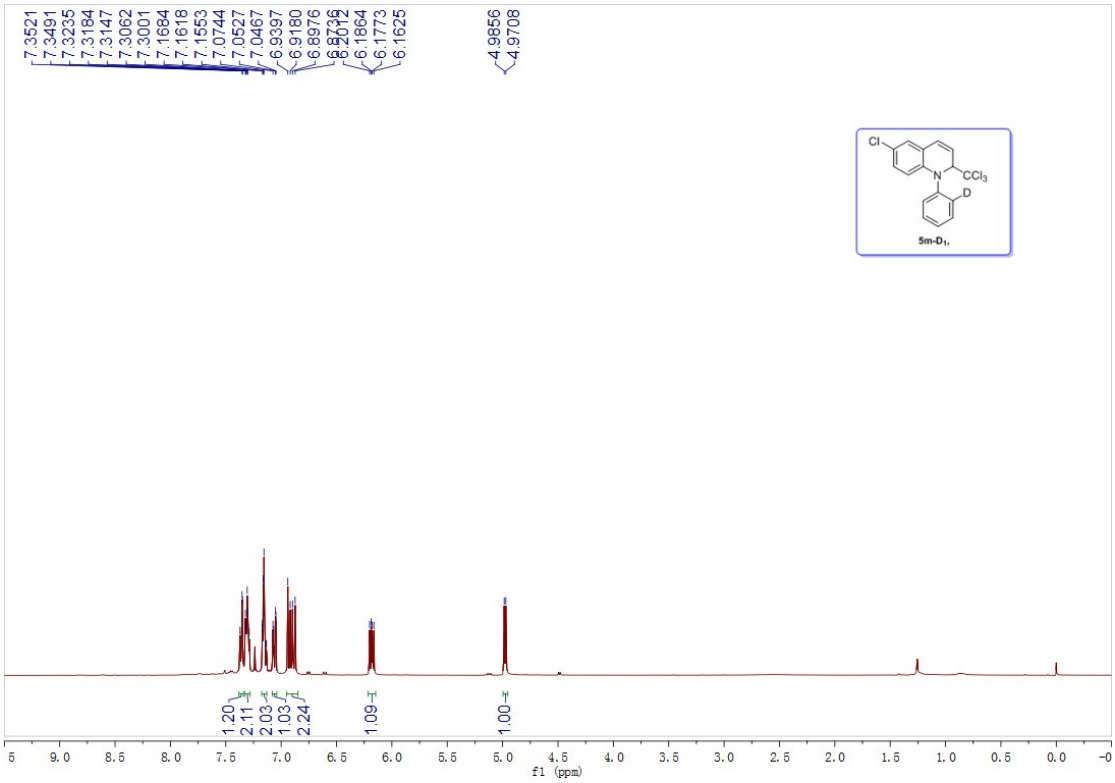
f1 (ppm)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6.9180
6.8976
6.8736
6.2012
6.1864
6.1773
6.1625
4.9856
4.9708
Cl
CCl3
N
D
5m-D1.
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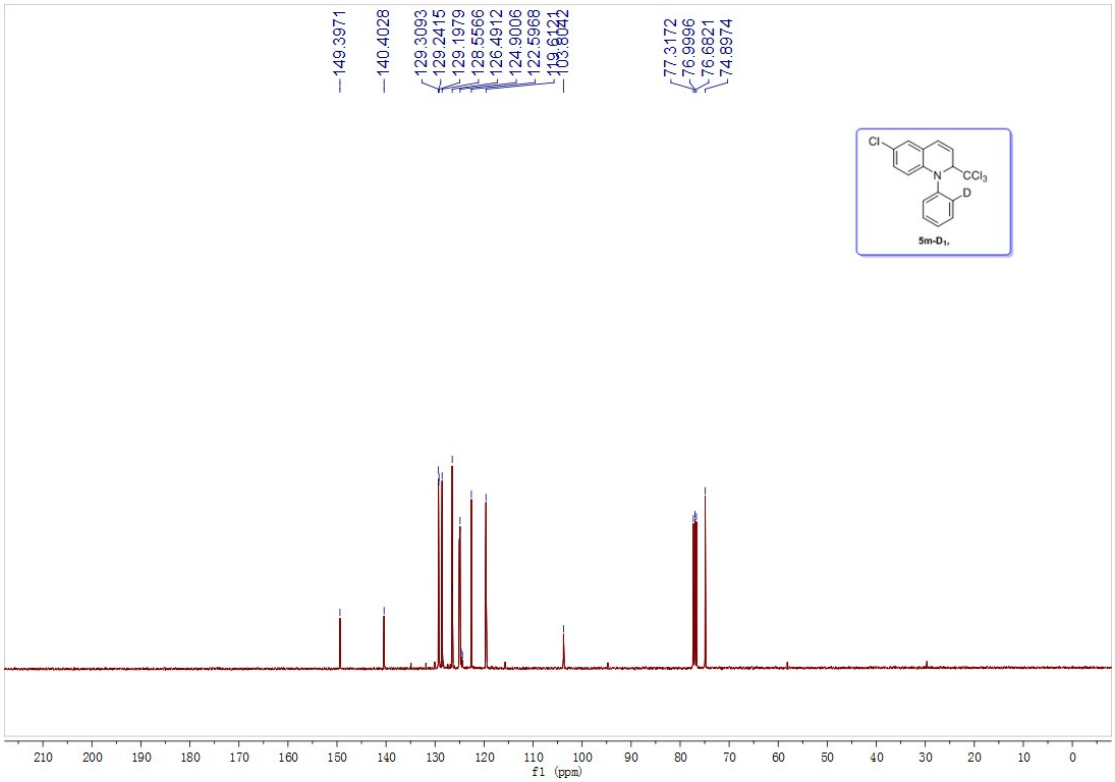
2.11
2.03
1.03
2.24
1.09
1.00
f1 (ppm)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126.4912
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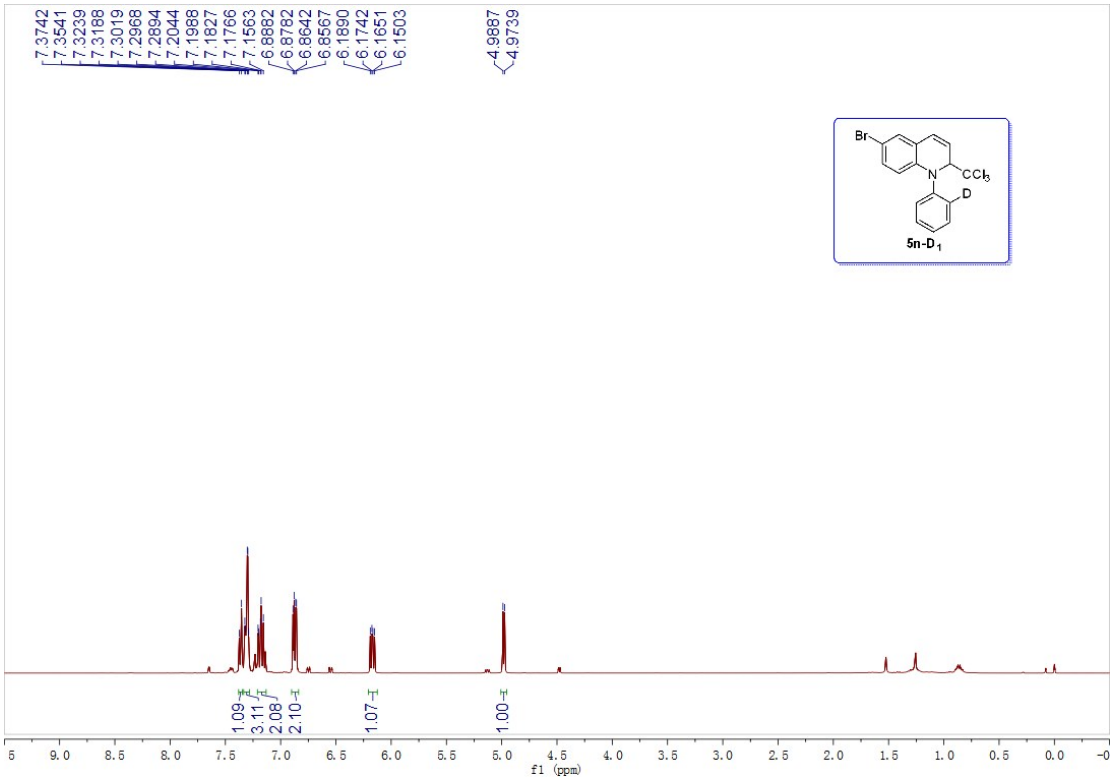
76.6821
74.8974
Cl
CCl3
N
D
5m-D1.
f1 (ppm)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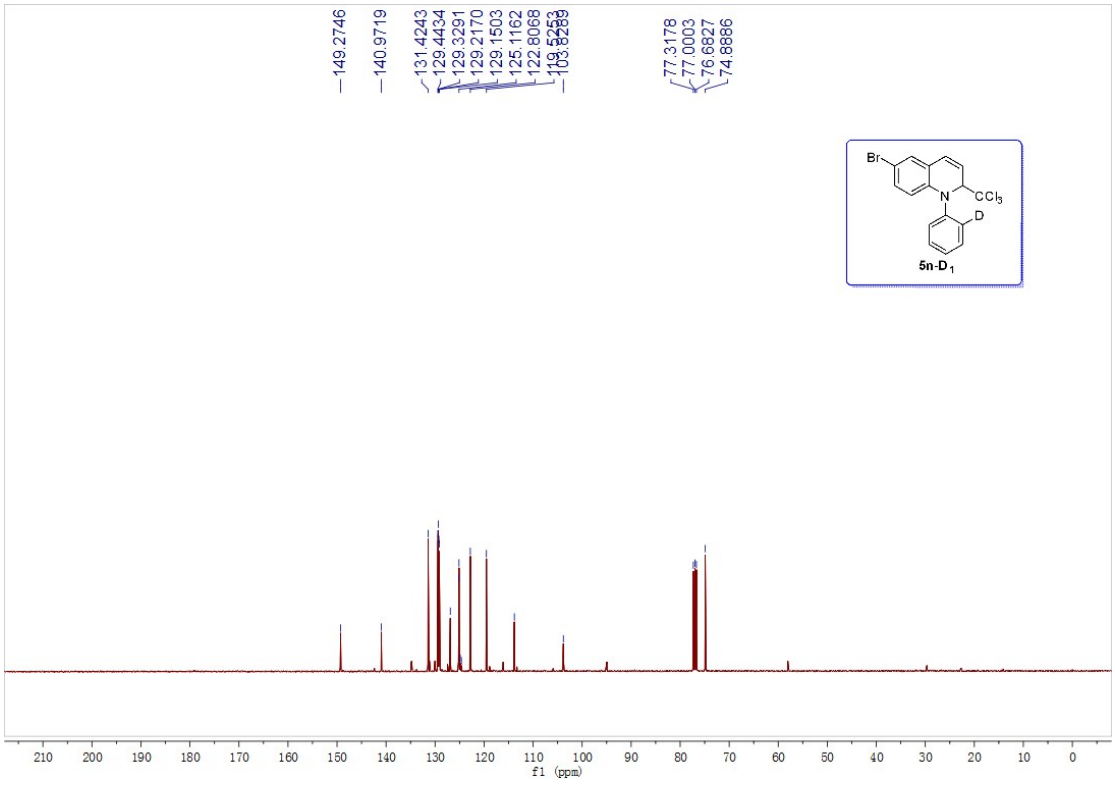
7.3239
7.3188
7.3019
7.2968
7.2894
7.2044
7.1988
7.1827
7.1766
7.1563
6.8882
6.8782
6.8642
6.8567
6.1890
6.1742
6.1651
6.1503
4.9887
4.9739
Br
N
CCl3
D
5n-D1
1.09
3.11
2.08
2.10
1.07
1.00
f1 (ppm)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131.4243
129.4434
129.3291
129.2170
129.1503
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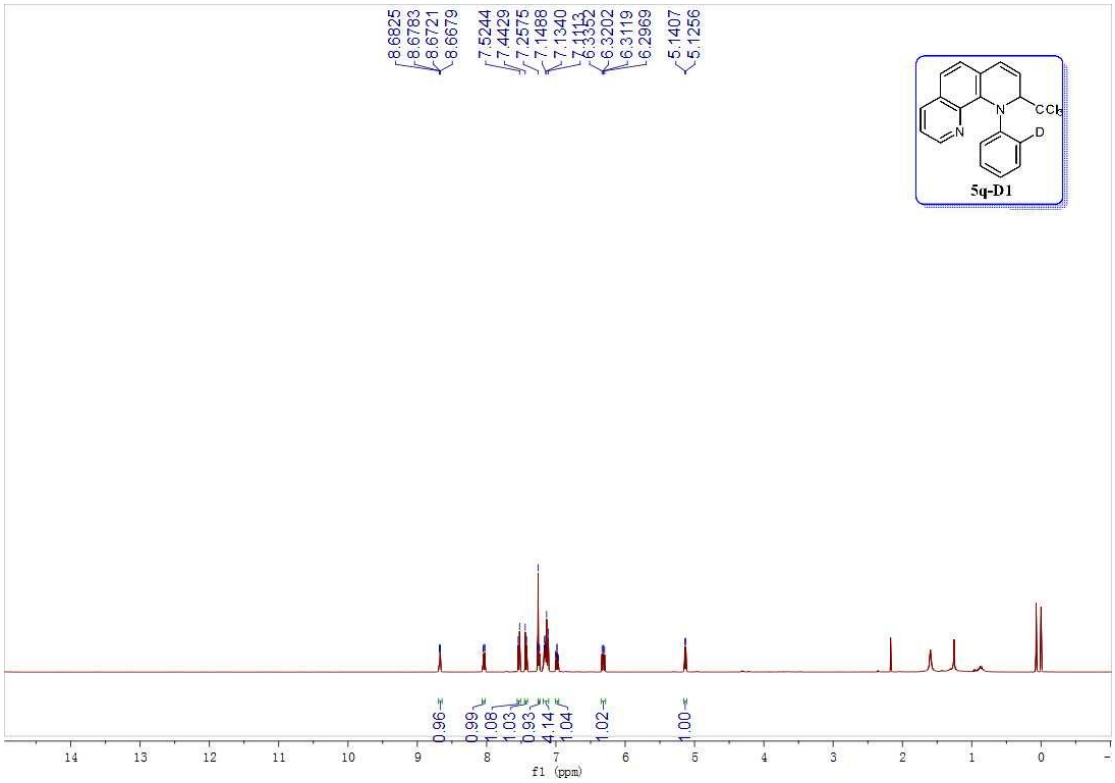
122.8068
77.3178
77.0003
76.6827
74.8886
Br
N
CCl3
D
5n-D1
f1 (ppm)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8.6721
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7.5244
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7.2575
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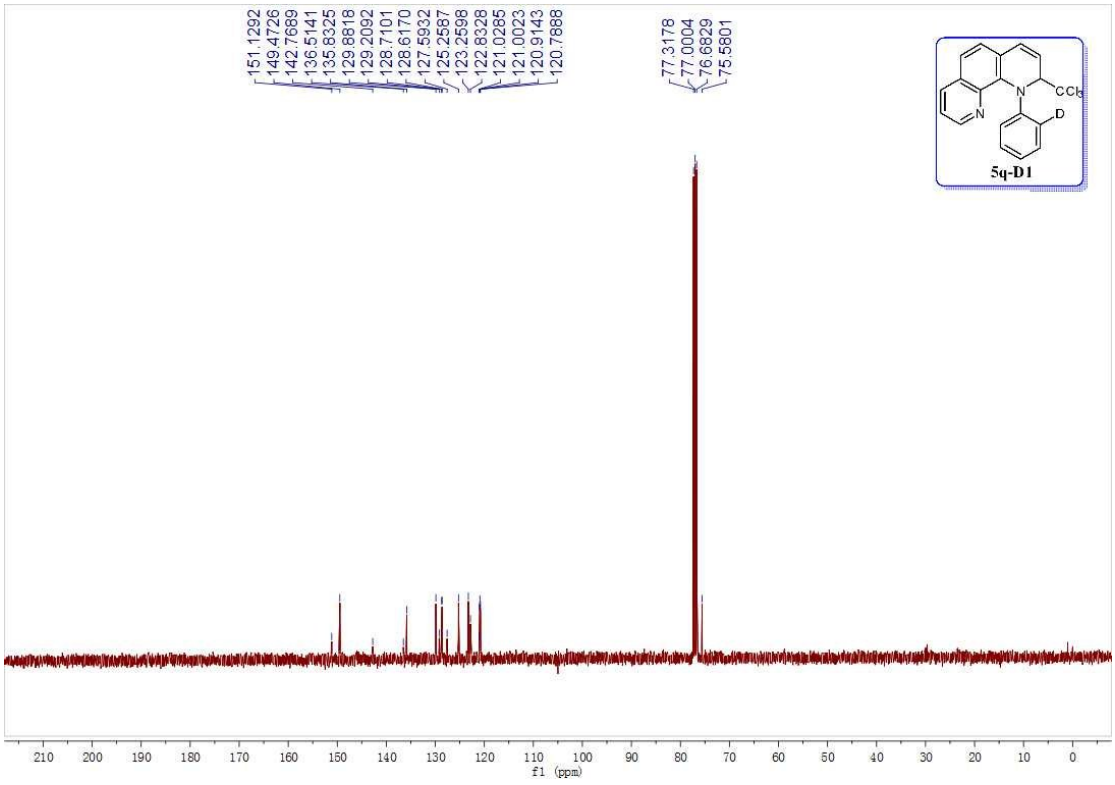
7.1340
6.3352
6.3202
6.3119
6.2969
5.1407
5.1256
5q-D1
0.96
0.99
1.08
1.03
0.93
4.14
1.04
1.02
1.00
f1 (ppm)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125.2587
123.2598
122.8328
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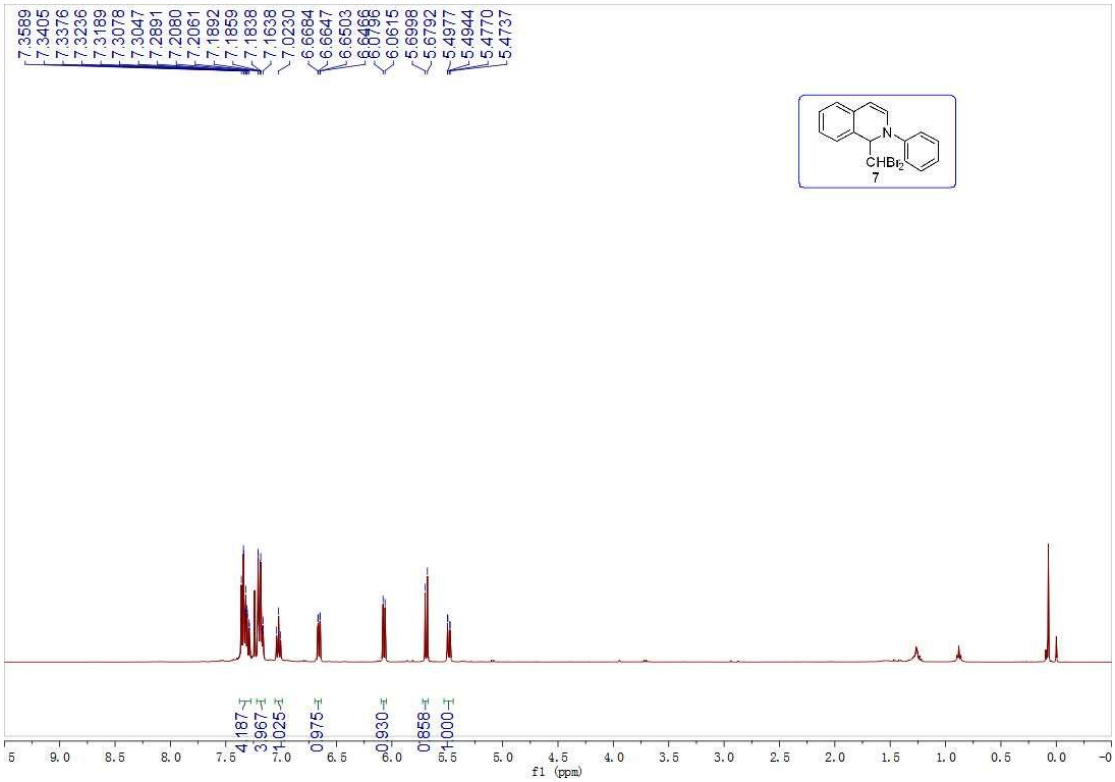
121.0023
120.9143
120.7888
77.3178
77.0004
76.6829
75.5801
5q-D1
f1 (ppm)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7.3189
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7.2891
7.2080
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7.1892
7.1859
7.1838
7.1638
7.0230
6.6684
6.6647
6.6503
6.6466
6.0798
6.0615
5.6998
5.6792
5.4977
5.4944
5.4770
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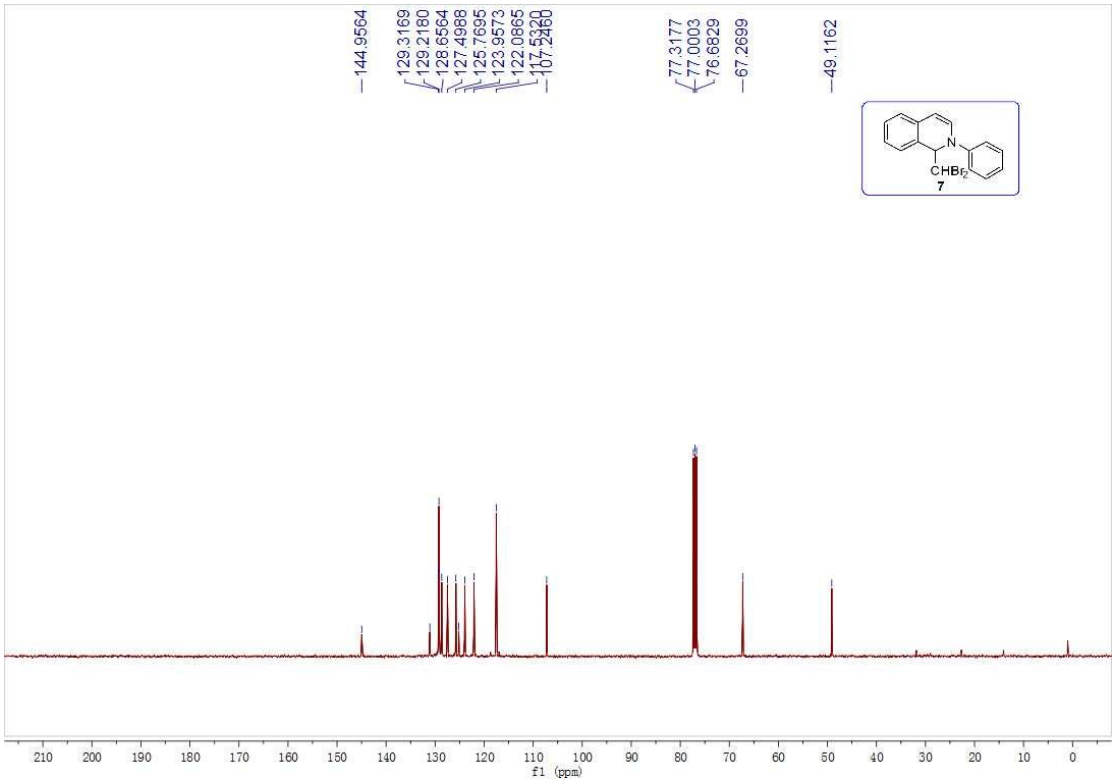
CHBr2
7
4.1187
3.9677
7.1025
0.9750
0.9300
0.8580
1.1000
f1 (ppm)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129.2180
128.6564
127.4988
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123.9573
122.0865
77.3177
77.0003
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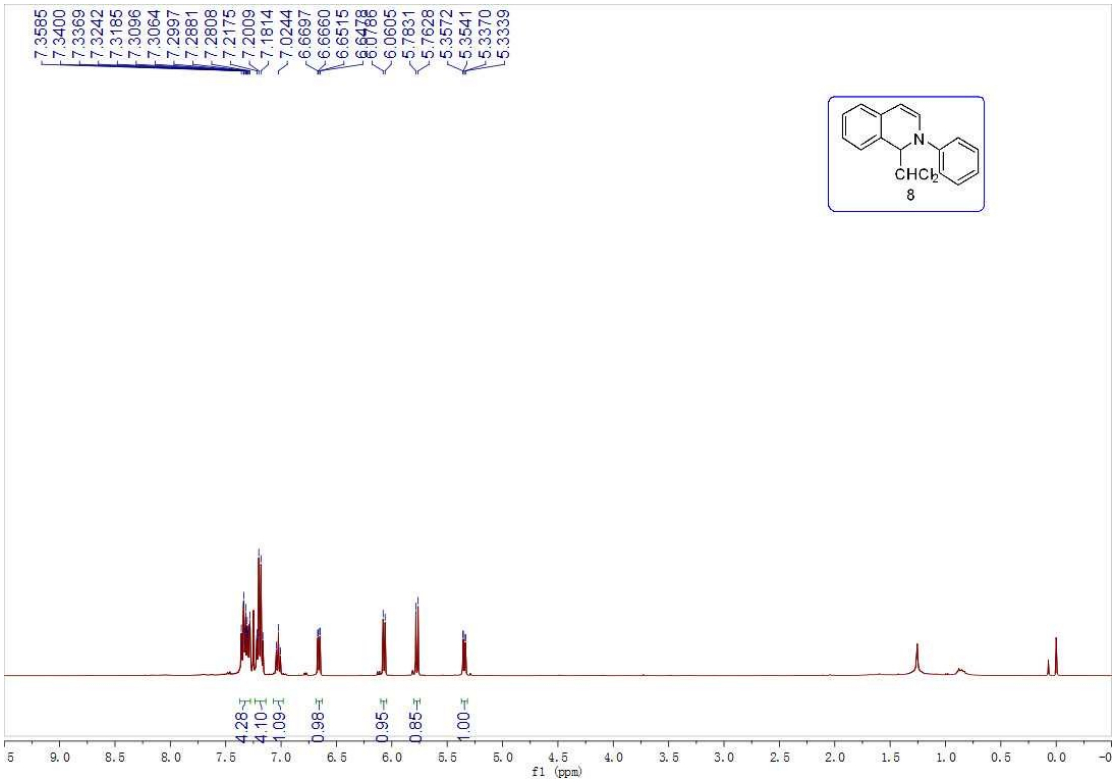
67.2699
49.1162
CHBr2
7
f1 (ppm)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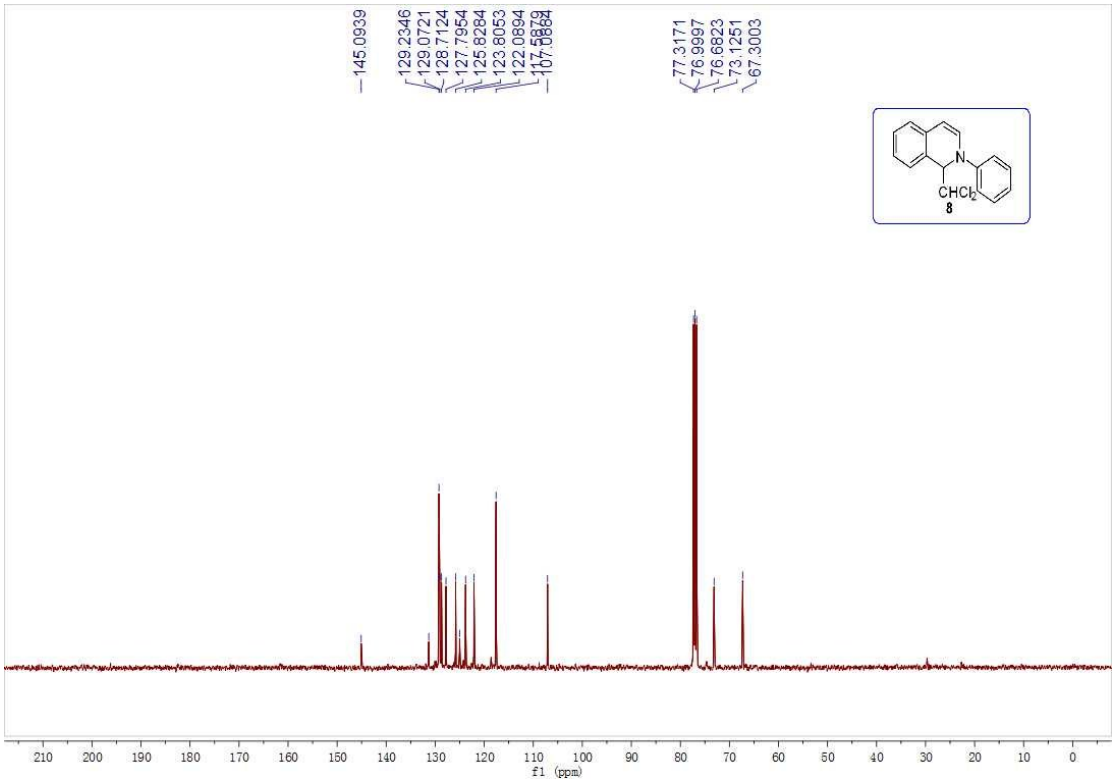
7.3064
7.2997
7.2881
7.2808
7.2175
7.2009
7.1814
7.0244
6.6697
6.6660
6.6515
6.6478
6.0788
6.0605
5.7831
5.7628
5.3572
5.3541
5.3370
5.3339
N
CHCl2
8
4.28
4.10
1.09
0.98
0.95
0.85
1.00
f1 (ppm)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129.0721
128.7124
127.7954
125.8284
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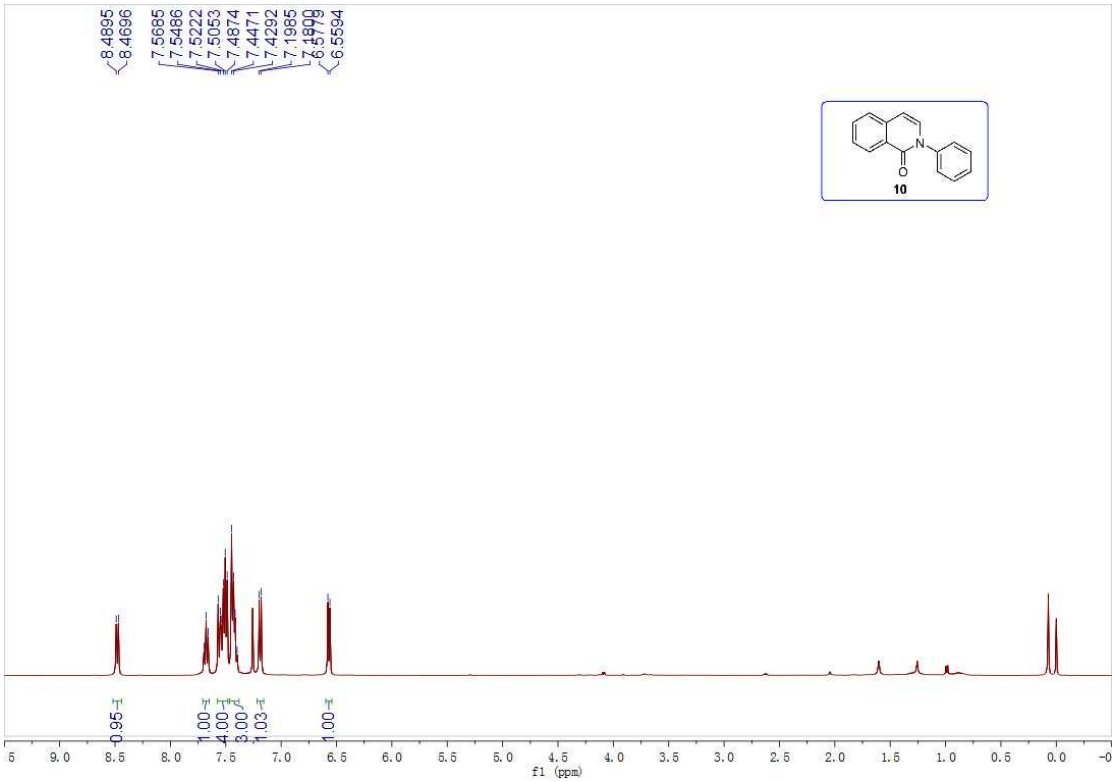
77.3171
76.9997
76.6823
73.1251
67.3003
N
CHCl2
8
f1 (ppm)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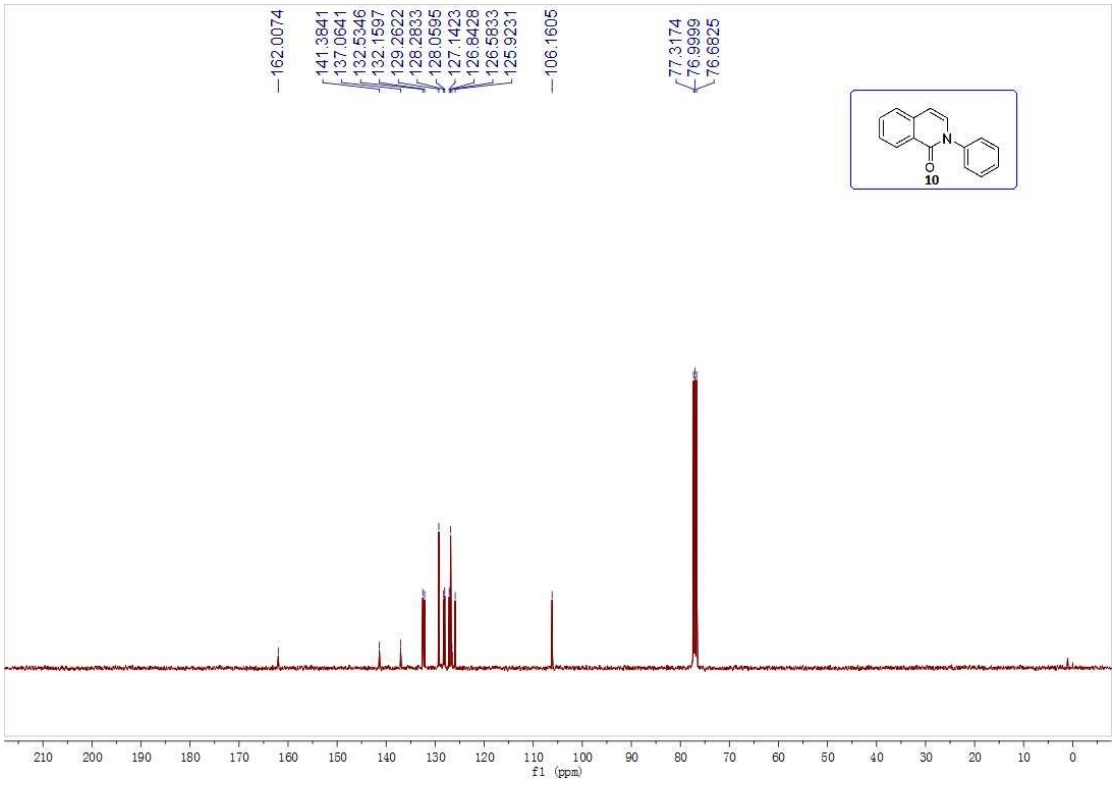
8.4696
7.5685
7.5486
7.5222
7.5053
7.4874
7.4471
7.4292
7.1985
7.1800
6.5779
6.5594
10
0.95
1.00
4.00
3.00
1.03
1.00
f1 (ppm)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137.0641
132.5346
132.1597
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128.2833
128.0595
127.1423
126.8428
126.5833
125.9231
106.1605
77.3174
76.9999
76.6825
10
f1 (ppm)

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