Suporting Information

Synthesis of Isoquinolones by Visible-Light-Induced Deaminative [4+2] Annulation

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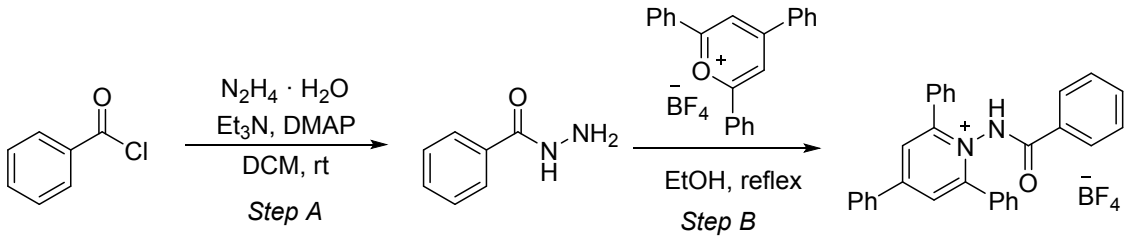
1. General Information

Chemicals were purchased from commercial sources without further purification unless otherwise noted. Glassware was dried in oven and cooled before use. All reactions were performed with solvents dried by anhydrous $MgSO_4$. Reactions were monitored by TLC and visualized by UV lamp (254nm) and stained with ethanolic solution of concentrated sulfuric acid or potassium permanganate. Yields generally referred to chromatographically isolated yields, unless otherwise noted. ^{1}H NMR (600MHz) and ^{13}C NMR (151 MHz) spectra are recorded on a Bruker AV-400 spectrometer in $CDCl_3$-*d* or DMSO-d_6. For ^{1}H NMR (600MHz), $CDCl_3$-*d* (δ= 7.26 ppm) serverd as internal standard and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (in Hz), and integration. For ^{13}C NMR (151 MHz), $CDCl_3$-*d* (δ= 77.25 ppm) was used as internal standard. For ^{1}H NMR (600 MHz), DMSO-d_6 (δ= 2.50 ppm) was used as internal standard. For ^{13}C NMR (151 MHz), DMSO-d_6 (δ= 39.52 ppm) was used as internal standard. HR-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

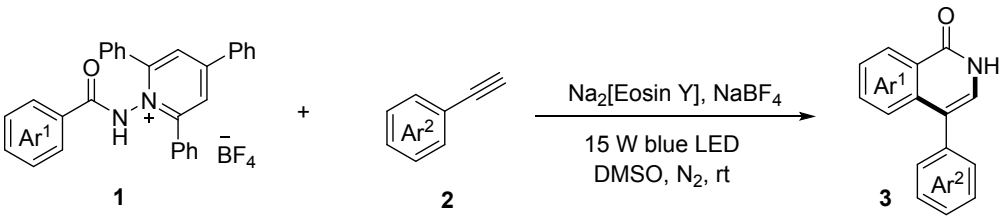
2. General Procedure for Synthesis of Pyridinium Salts



Step A: To a 100 mL round bottom flask equipped with magnetic stir bar was added Hydrazine (20.0 mmol, 80% aq.) in 10 mL CH_2Cl_2. Then triethylamine (25.0 mmol) and DMAP (1.6 mmol) were added followed by stirring the mixture under the ice bath. When cooling to 0 ℃, benzoyl chloride was added into the mixture and stirred for 30 min. Thereafter the mixture was allowed to stir overnight at room temperature, and then was concentrated and purified by Silica column chromatography to give the pure benzohydrazide in 81% yield.

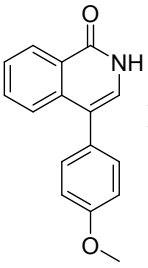
Step B: To a 50 mL round bottom flask equipped with magnetic stir bar was added the obtained benzohydrazide (1.8 g), 2,4,6-triphenylpyrylium tetrafluoroborate (3.5 g) in 10 mL methanol. The mixture was refluxed for 4 h, and then was cooled and added ethoxyethane (40 mL) slowly to precipitate white solid. The white solid was obtained via vacuum filtration to give the final product.

3. General Procedure for [4+2] Annulation Reaction

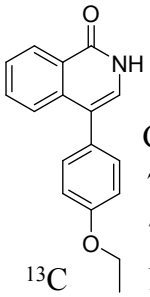


1 (0.1 mmol), **2** (0.4 mmol), 0.15 mmol $NaBF_4$ and photocatalyst Na_2[Eosin Y] (5 mol%) were combined in a 5 ml flask. 1 ml anhydrous DMSO was added via syringe. The flask was evacuated and back-filled with N_2. And then the starting mixture was exposed to a 15 W blue LED bulb for irradiation. After reaction, the mixture was quenched with water and extracted with DCM. The combined organic layer was dried with anhydrous $MgSO_4$ and then filtered. The filtrate was concentrated for purification by chromatography on silica gel to afford final product **3**.

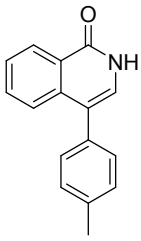
4. Characterizations of [4+2] Annulation Products



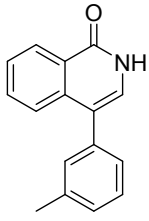
4-(4-methoxyphenyl)isoquinolin-1(2H)-one (**3aa**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 72% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.42 (s, 1H), 8.29 (d, J = 7.9 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.04 (d, J = 7.2 Hz, 3H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.2, 158.6, 136.9, 132.3, 130.9, 128.3, 127.4, 127.2, 126.4, 125.8, 124.3, 117.0, 114.0, 55.1. HRMS (ESI): calc. for $C_{16}H_{14}NO_2$ $[M+H]^+$: 252.1019, found: 252.1043.



(4-ethoxyphenyl)isoquinolin-1(2H)-one (**3ab**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 68% isolated yield. ^{1}H NMR (600 MHz, Chloroform-d) δ 11.66 (s, 1H), 8.51 (d, J = 7.8 Hz, 1H), 7.63 (dt, J = 15.2, 7.5 Hz, 2H), 7.53 (t, J = 6.8 Hz, 1H), 7.32 (d, J = 7.5 Hz, 2H), 7.15 (s, 1H), 7.00 (d, J = 7.6 Hz, 2H), 4.11 (q, J = 6.0 Hz, 2H), 1.47 (t, J = 6.3 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 158.6, 137.8, 132.5, 131.1, 128.7, 128.4, 127.6, 127.4, 126.7, 126.5, 125.1, 119.9, 114.6, 63.6, 14.9. HRMS (ESI): calc. for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176, found: 266.1172.

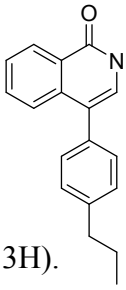


4-(p-tolyl)isoquinolin-1(2H)-one (**3ac**), white solid, R_f = 0.3 (50% DCM in petroleum), 58% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.44 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.31 (s, 4H), 7.06 (d, J = 5.2 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.7, 137.2, 137.1, 133.7, 132.9, 130.1, 129.7, 128.0, 127.7, 126.9, 126.4, 124.8, 117.8, 21.3. HRMS (ESI): calc. for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1070, found: 236.1060.

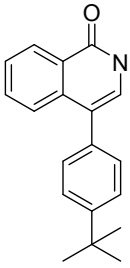


4-(m-tolyl)isoquinolin-1(2H)-one (**3ad**), white solid, R_f = 0.3 (50% DCM in petroleum), 54% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.46 (s, 1H), 8.30 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 6.4 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.37 (d, J = 6.9 Hz, 1H), 7.23 (d, J = 11.3 Hz, 3H), 7.08 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.7, 138.4, 137.1, 136.6, 132.9, 130.8, 129.0, 128.5, 128.1, 127.7, 127.3, 127.0, 126.4, 124.8, 118.0,

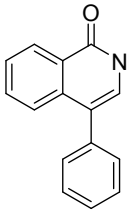
21.5. HRMS (ESI): calc. for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1070, found: 236.1060.



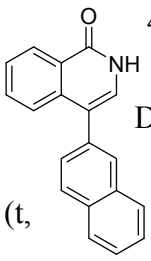
4-(4-propylphenyl)isoquinolin-1(2H)-one (**3ae**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 56% isolated yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.75 (s, 1H), 8.51 (d, *J* = 7.9 Hz, 1H), 7.64 (s, 2H), 7.57 – 7.50 (m, 1H), 7.33 (d, *J* = 6.9 Hz, 2H), 7.28 (d, *J* = 6.9 Hz, 2H), 7.18 (s, 1H), 2.67 (t, *J* = 6.9 Hz, 2H), 1.72 (q, *J* = 6.9 Hz, 2H), 1.01 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.0, 142.1, 137.5, 133.5, 132.4, 129.8, 128.7, 127.6, 126.7, 126.6, 125.8, 125.0, 120.1, 37.8, 24.5, 13.9. HRMS (ESI): calc. for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383, found: 264.1376.



4-(4-(tert-butyl)phenyl)isoquinolin-1(2H)-one (**3af**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 59% isolated yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.56 (s, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.1 Hz, 2H), 7.17 (s, 1H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.9, 150.6, 137.6, 133.3, 132.5, 129.6, 127.6, 126.8, 126.5, 125.6, 125.2, 120.1, 34.7, 31.4. HRMS (ESI): calc. for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found: 278.1535.

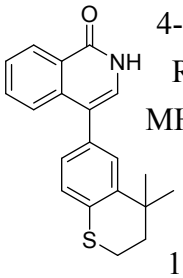


4-phenylisoquinolin-1(2H)-one (**3ag**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum) 54% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.48 (s, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.44 (t, *J* = 6.9 Hz, 3H), 7.10 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.8, 137.1, 136.7, 132.9, 130.2, 129.2, 128.3, 127.9, 127.8, 127.0, 126.4, 124.7, 117.9. HRMS (ESI): calc. for $C_{15}H_{11}NO$ $[M+H]^+$: 222.0913, found: 222.0906.

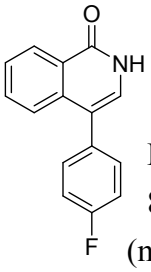


4-(naphthalen-2-yl)isoquinolin-1(2H)-one (**3ah**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 74% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.55 (s, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.99 (s, 2H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 9.8 Hz, 4H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 4.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.8, 137.2, 134.3, 133.7, 133.0, 132.6,

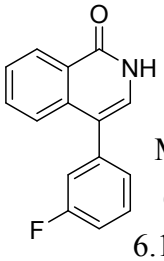
128.7, 128.6, 128.4, 128.4, 128.1, 127.9, 127.8, 127.1, 126.9, 126.7, 126.4, 124.8, 117.8. HRMS (ESI): calc. for $C_{19}H_{20}NO$ $[M+H]^+$: 272.1070, found: 272.1078.



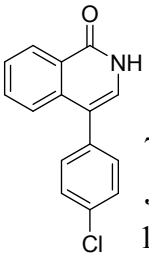
4-(4,4-dimethylthiochroman-6-yl)isoquinolin-1(2H)-one (**3ai**), white solid, R_f = 0.4 (50% DCM in petroleum), 63% isolated yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.65 (s, 1H), 8.52 (d, *J* = 7.9 Hz, 1H), 7.65 (q, *J* = 8.7, 8.2 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 1H), 7.40 (s, 1H), 7.20 – 7.15 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 3.12 – 3.05 (m, 2H), 2.07 – 1.99 (m, 2H), 1.37 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.9, 142.4, 137.6, 132.6, 132.0, 131.4, 128.1, 127.7, 127.6, 126.8, 126.7, 126.5, 125.0, 120.2, 37.7, 33.1, 30.3, 23.2. HRMS (ESI)**:** calc. for $C_{20}H_{20}NOS$ $[M+H]^+$: 322.1260, found: 322.1255.



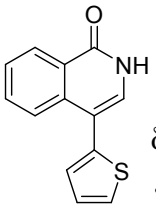
4-(4-fluorophenyl)isoquinolin-1(2H)-one (**3aj**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 63% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.49 (s, 1H), 8.30 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.70 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.48 – 7.44 (m, 3H), 7.34 – 7.29 (m, 2H), 7.10 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 162.4, 161.3, 160.8, 136.6, 132.5, 131.8, 131.7, 128.0, 127.2, 126.5, 125.8, 124.1, 116.3, 115.5, 115.4. ^{19}F NMR (376 MHz, DMSO) δ -114.24. HRMS (ESI): calc. for $C_{15}H_{11}FNO$ $[M+H]^+$: 240.0819, found: 240.0818.



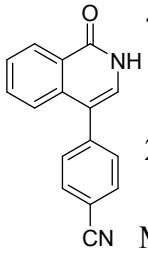
4-(3-fluorophenyl)isoquinolin-1(2H)-one (**3ak**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 61% isolated yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 11.52 (s, 1H), 8.52 (d, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 6.9 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 6.8 Hz, 1H), 7.44 (q, *J* = 6.1 Hz, 1H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.19 (s, 1H), 7.17 – 7.10 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.8, 162.6, 161.0, 137.5, 137.5, 135.9, 131.8, 129.2, 129.2, 126.8, 126.0, 125.8, 124.8, 124.7, 124.7, 123.7, 118.0, 116.0, 115.9, 113.7, 113.6. ^{19}F NMR (376 MHz, DMSO) δ -113.52. HRMS (ESI): calc. for $C_{15}H_{11}FNO$ $[M+H]^+$: 240.0819, found: 240.0814.



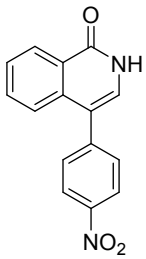
4-(4-chlorophenyl)isoquinolin-1(2H)-one (**3al**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 67% isolated yield. ^{1}H NMR (600 MHz, DMSO) δ 11.54 (s, 1H), 8.30 (t, *J* = 11.0 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.14 (d, *J* = 5.3 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ 161.3, 136.3, 135.1, 132.6, 131.6, 128.6, 128.2, 128.1, 127.4, 127.3, 126.6, 124.0, 116.1. HRMS (ESI): calc. for $C_{15}H_{11}ClNO$ [M+H]+: 256.0524, found: 256.0541.



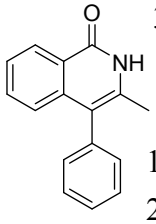
4-(thiophen-2-yl)isoquinolin-1(2H)-one (**3am**), white solid, R_f = 0.4 (50% DCM in petroleum), 64% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.56 (s, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 3.4 Hz, 2H), 7.64 (d, *J* = 5.1 Hz, 1H), 7.57 (dt, *J* = 8.0, 4.1 Hz, 1H), 7.26 (d, *J* = 4.6 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.22 – 7.18 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.1, 136.5, 132.8, 129.1, 127.7, 127.5, 127.2, 126.8, 126.1, 125.7, 124.1, 109.93. HRMS (ESI): calc. for $C_{13}H_{10}NOS$ $[M+H]^+$: 228.0478, found: 228.0475



4-(1-oxo-1,2-dihydroisoquinolin-4-yl)benzonitrile (**3an**), white solid, R_f = 0.4 (50% DCM in petroleum), 45% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.64 (s, 1H), 8.31 (d, *J* = 7.9 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.23 (d, *J* = 5.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.8, 141.9, 136.2, 133.2, 133.1, 131.2, 129.5, 127.9, 127.3, 126.3, 124.3, 119.3, 116.4, 110.5. HRMS (ESI): calc. for $C_{16}H_{11}N_2O$ $[M+H]^+$: 247.0866, found: 247.0866

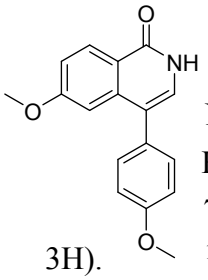


4-(4-nitrophenyl)isoquinolin-1(2H)-one (**3ao**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 32% isolated yield. ^{1}H NMR (400 MHz, DMSO) δ 11.69 (s, 1H), 8.35 (d, *J* = 7.2 Hz, 3H), 7.76 (d, *J* = 8.1 Hz, 3H), 7.58 (dd, *J* = 18.7, 7.6 Hz, 2H), 7.30 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.8, 147.0, 144.0, 136.1, 133.3, 131.4, 129.8, 128.7, 127.9, 127.4, 126.3, 124.3, 115.9. HRMS (ESI): calc. for $C_{15}H_{11}N_2O_3$ $[M+H]^+$: 267.0764, found: 267.0765.

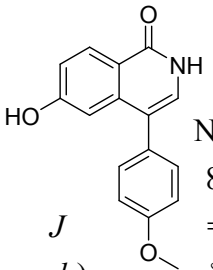


3-methyl-4-phenylisoquinolin-1(2H)-one (**3ap**), white solid, R_f = 0.5 (18% ethyl acetate in petroleum), 42% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.45 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.1 Hz, 2H), 7.43 (q, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.2, 138.8, 136.7, 136.0, 132.8, 131.4, 129.2, 127.9, 127.2, 125.8, 124.8,

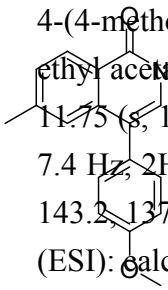
124.7, 115.1, 17.8. HRMS (ESI): calc. for $C_{16}H_{14}NO$ $[M+H]^+$: 236.1060, found: 236.1071.



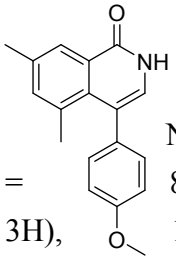
5-methoxy-4-(4-methoxyphenyl)isoquinolin-1(2H)-one (**3ba**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 76% isolated yield. ^1H NMR (600 MHz, DMSO-d_6) δ 11.25 (d, J = 4.8 Hz, 1H), 8.21 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 7.3 Hz, 2H), 7.14 (d, J = 8.9 Hz, 1H), 7.05 (d, J = 7.4 Hz, 2H), 7.01 (d, J = 5.4 Hz, 1H), 6.88 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ 162.2, 160.9, 158.6, 138.9, 130.7, 129.4, 128.4, 128.2, 119.6, 116.7, 115.0, 114.1, 106.1, 55.2, 55.1. HRMS (ESI): calc. for $C_{17}H_{16}NO_3$ $[M+H]^+$: 282.1125, found: 282.1125.



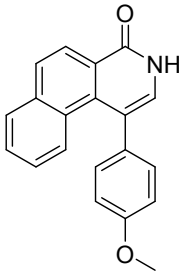
6-hydroxy-4-(4-methoxyphenyl)isoquinolin-1(2H)-one (**3ca**), white solid, R_f = 0.3 (25% ethyl acetate in petroleum), 72% isolated yield. ^1H NMR (600 MHz, DMSO-d_6) δ 11.09 (s, -1H), 10.20 (s, -1H), 8.12 (d, J = 8.6 Hz, -1H), 7.31 (d, J = 7.0 Hz, -2H), 7.05 (d, J = 7.1 Hz, -2H), 6.94 (d, J = 7.1 Hz, -2H), 6.79 (s, -1H), 3.81 (s, -4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 161.0, 160.9, 158.5, 139.2, 130.8, 129.5, 128.7, 127.7, 118.5, 116.6, 116.0, 114.0, 108.1, 55.1. HRMS (ESI): calc. for $C_{17}H_{16}NO_3$ $[M+H]^+$: 268.0968, found: 268.0971.



4-(4-methoxyphenyl)-6-methylisoquinolin-1(2H)-one (**3da**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 67% isolated yield. ^1H NMR (600 MHz, Chloroform-d) δ 11.75 (s, 1H), 8.39 (d, J = 7.9 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.13 (s, 1H), 7.02 (d, J = 7.4 Hz, 2H), 3.89 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 159.1, 143.2, 137.9, 131.1, 128.8, 128.4, 127.6, 126.7, 124.7, 119.6, 114.1, 55.4, 22.1.HRMS (ESI): calc. for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176, found: 266.1178.

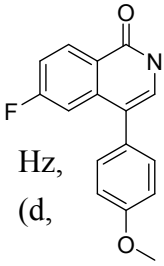


4-(4-methoxyphenyl)-5,7-dimethylisoquinolin-1(2H)-one (**3ea**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 63% isolated yield. ^1H NMR (600 MHz, Chloroform-d) δ 11.42 (s, 1H), 8.24 (s, 1H), 7.20 (d, J = 8.1 Hz, 2H), 6.96 (s, 1H), 6.91 (d, J = 8.2 Hz, 2H), 3.87 (s, 3H), 2.45 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 158.9, 137.9, 136.5, 134.9, 134.0, 132.7, 131.2, 127.1, 125.7, 119.7, 113.4, 55.3, 23.8, 21.1. HRMS (ESI): calc. for $C_{18}H_{18}NO_2$ $[M+Na]^+$: 302.1151, found: 302.1170.

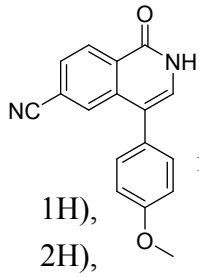


1-(4-methoxyphenyl)benzo[f]isoquinolin-4(3H)-one (**3fa**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 69% isolated yield. ^1H

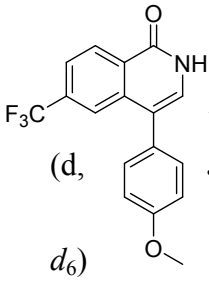
NMR (600 MHz, DMSO-d_6) δ 11.81 (s, 1H), 8.32 (d, J = 8.7 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.12 (s, 1H), 7.04 (d, J = 8.1 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.7, 159.0, 136.2, 135.7, 133.2, 131.6, 131.0, 129.3, 128.9, 128.3, 128.0, 127.7, 125.7, 124.9, 123.7, 117.6, 114.9, 55.7. HRMS (ESI): calc. for $C_{20}H_{16}NO_2$ $[M+H]^+$: 302.1176, found: 302.1186.



6-fluoro-4-(4-methoxyphenyl)isoquinolin-1(2H)-one (**3ga**), white solid, R_f = 0.4 (50% DCM in petroleum), 65% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.52 (s, 1H), 8.42 – 8.31 (m, 1H), 7.95 (d, J = 6.0 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 7.12 (s, 1H), 7.06 (d, J = 7.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.8, 161.1, 159.3, 131.3, 130.6, 130.5, 129.5, 128.2, 123.2, 117.0, 115.7, 115.5, 115.2, 114.7, 109.8, 109.6, 55.6. ^{19}F NMR (376 MHz, DMSO) δ -105.72. HRMS (ESI): calc. for $C_{16}H_{13}FNO_2$ $[M+H]^+$: 270.0925, found: 270.0931.



4-(4-methoxyphenyl)-1-oxo-1,2-dihydroisoquinoline-6-carbonitrile (**3ha**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 49% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.61 (s, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 7.3 Hz, 2H), 7.27 (s, 1H), 7.06 (d, J = 7.3 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.1, 158.9, 140.1, 134.3, 132.2, 131.1, 131.0, 127.2, 125.8, 125.7, 118.5, 116.6, 114.2, 108.5, 55.2. HRMS (ESI): calc. for $C_{17}H_{13}N_2O_2$ $[M+H]^+$: 277.0972, found: 277.0972.



4-(4-methoxyphenyl)-6-(trifluoromethyl)isoquinolin-1(2H)-one (**3ia**), white solid, R_f = 0.4 (25% ethyl acetate in petroleum), 61% isolated yield. ^{1}H NMR (600 MHz, DMSO-d_6) δ 11.80 (s, 1H), 8.53 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.37 (d, J = 7.5 Hz, 2H), 7.25 (s, 1H), 7.07 (d, J = 7.3 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 160.6, 158.8, 139.9, 131.0, 130.3, 128.3, 127.5, 126.0, 125.6, 124.3, 116.6, 114.2, 55.2. ^{19}F NMR (376 MHz, DMSO) δ -60.95. HRMS (ESI): calc. for $C_{18}H_{13}F_3N_2O_2$ $[M+H]^+$: 320.0893, found: 320.0887.

5. Mechanistic Studies

Fluorescence quenching experiments: As shown in Figure S1 a, pyridinium salt **1a** was capable of quenching the excited state of photocatalyst . The emission intensity of the solution (1 mL) of photocatalyst with different concentration of quencher **1a** (0, 0.2, 0.4, 0.6, 0.8, 1.0 mM) was collected after degassed with a nitrogen stream for 5 minutes. The Stern-Volmer plots, as depicted in Figure S1 b, indicated that pyridinium salt **1a** was able to quench the excited photocatalyst much more efficiently than alkyne **2a**.

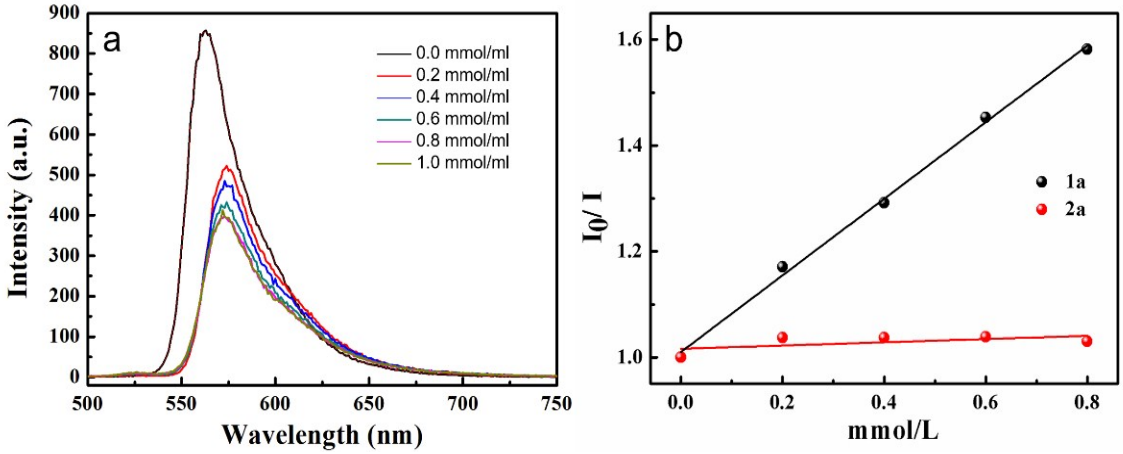


Figure S1 a) Fluorescence spectra of a solution of photocatalyst in DMSO containing different concentration of **1a**. b) Stern-Volmer plots. I_0 and I are respective luminescence intensities in the absence and presence of the indicated concentrations of the corresponding quencher: pyridinium salt **1a** and alkyne **2a**.

Cyclic Voltammetry experiment of pyridinium salt 1a: Further Cyclic Voltammetry (CV) test for evaluation of the redox potential of **1a** was conducted. Cyclic Voltammogram was showed as Figure S2.

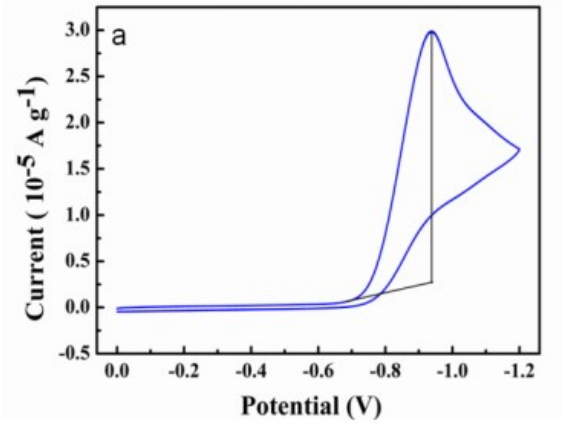
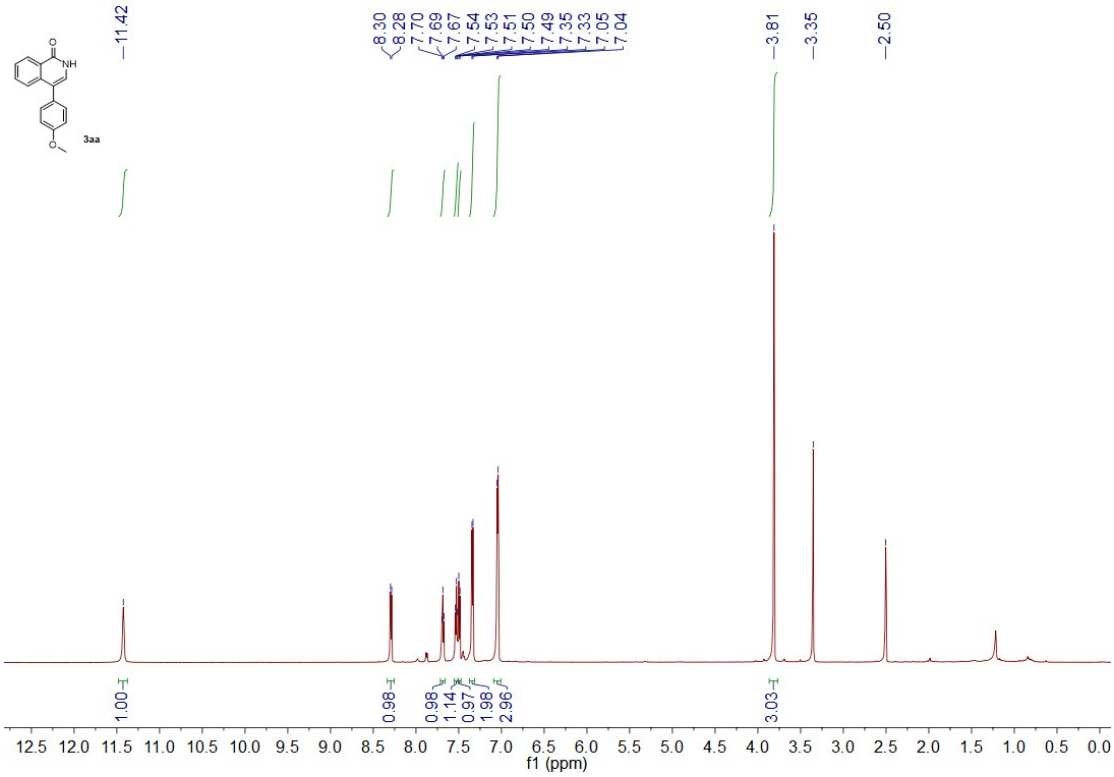
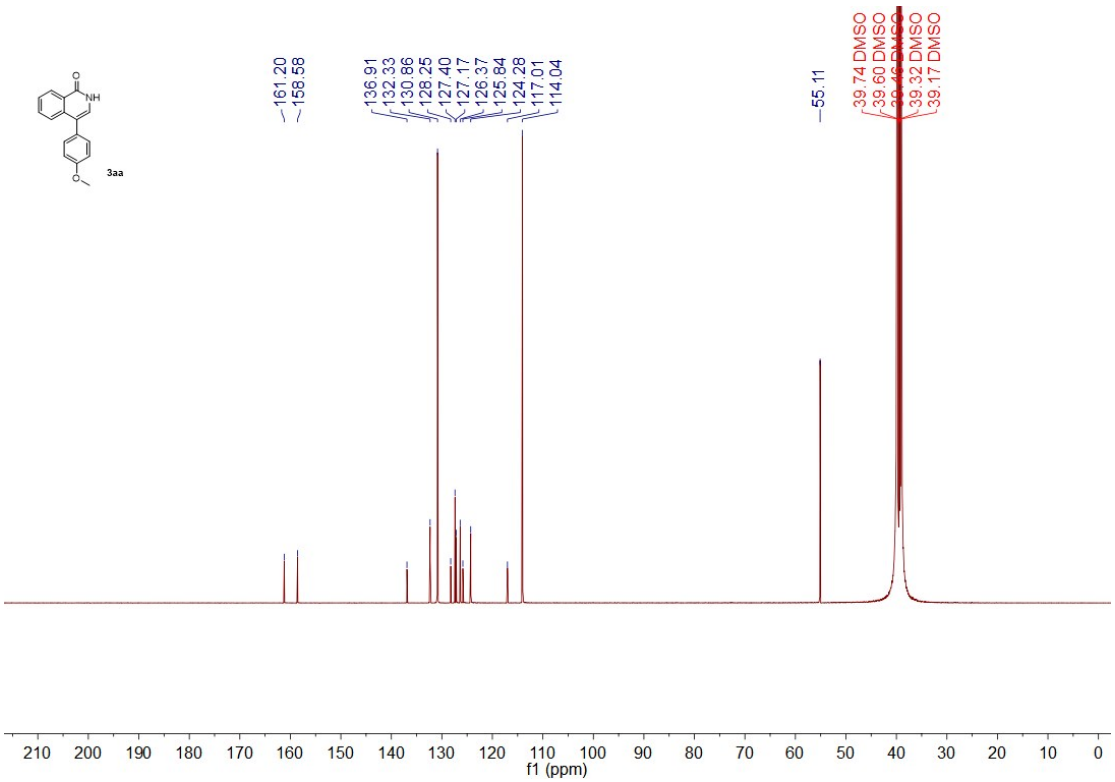
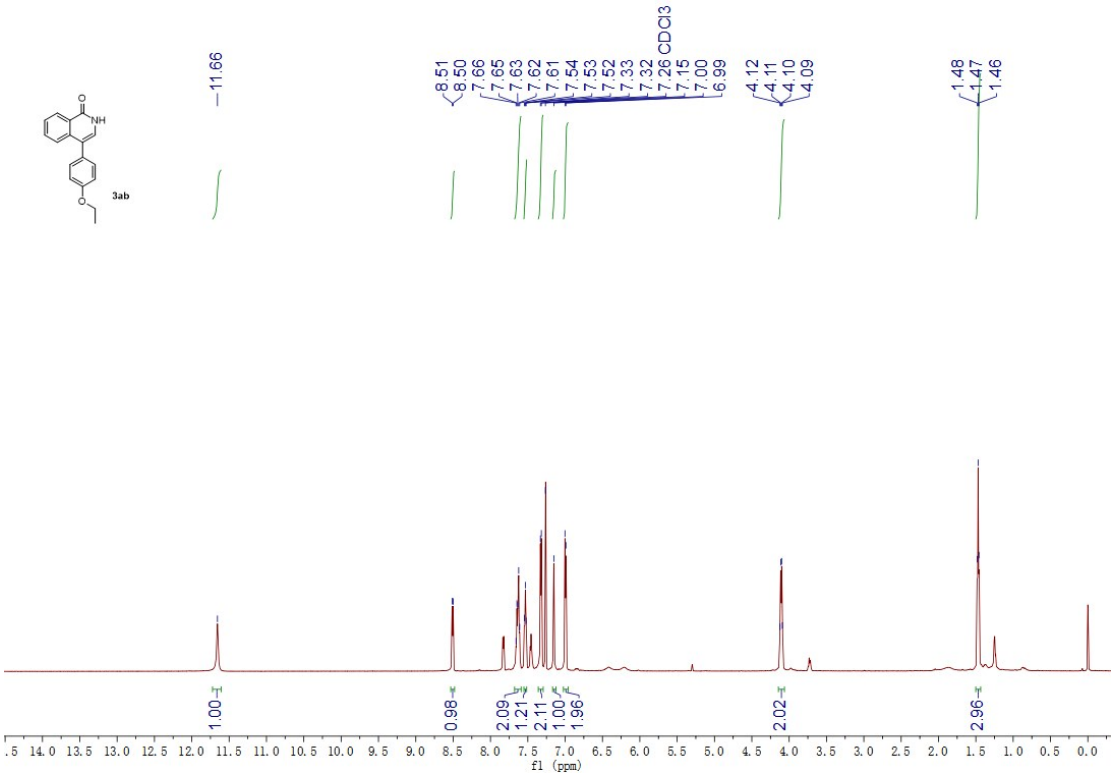


Figure S2 Cyclic Voltammogram of pyridinium salt **1a**.

6. NMR Spectra




3aa
161.20
158.58
136.91
132.33
130.86
128.25
127.40
127.17
126.37
125.84
124.28
117.01
114.04
55.11
39.74 DMSO
39.60 DMSO
39.46 DMSO
39.32 DMSO
39.17 DMSO
f1 (ppm)


3ab
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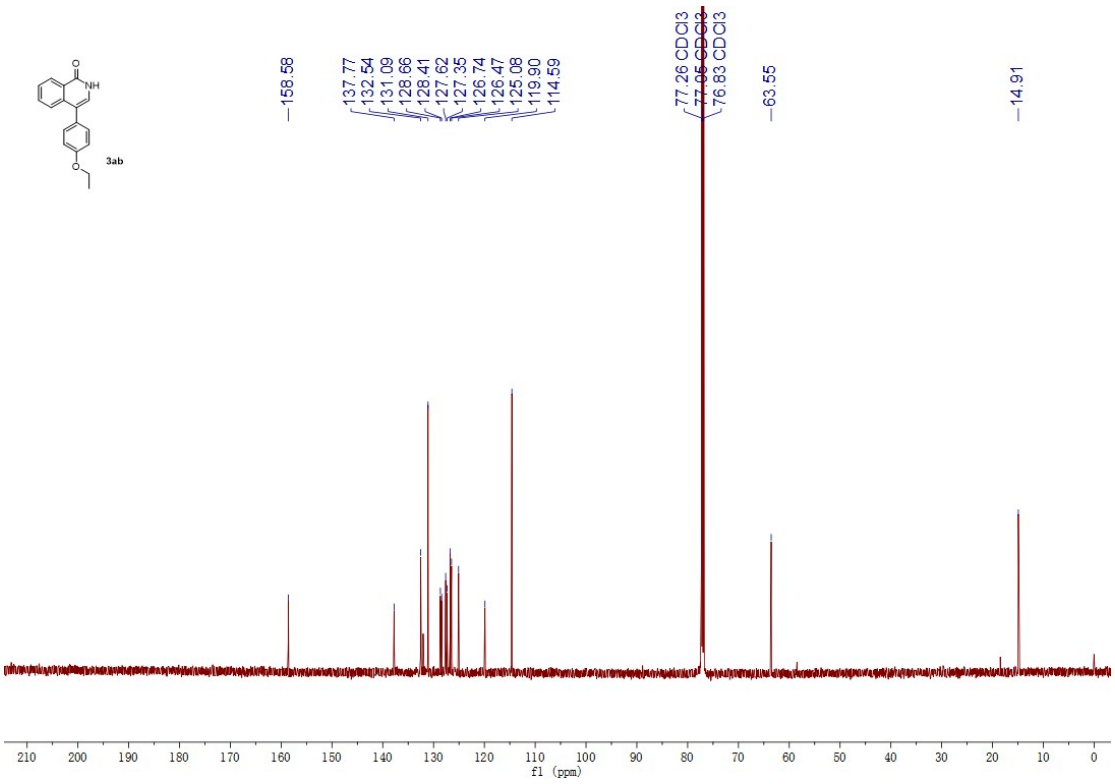
8.51
8.50
7.66
7.65
7.63
7.62
7.61
7.54
7.53
7.52
7.33
7.32
CDCl3
7.26
7.15
7.00
6.99
4.12
4.11
4.10
4.09
1.48
1.47
1.46
1.00
0.98
2.09
1.21
2.11
1.00
1.96
2.02
2.96
f1 (ppm)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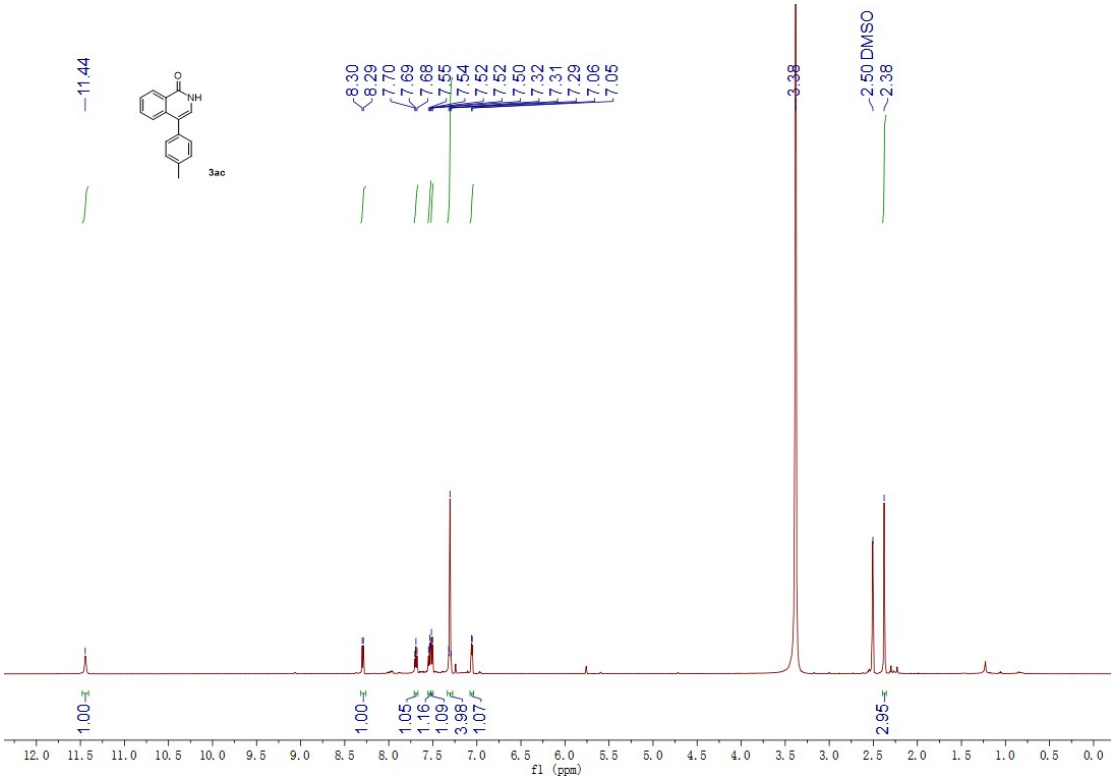
132.54
131.09
128.66
128.41
127.62
127.35
126.74
126.47
125.08
119.90
114.59
77.26 CDCl3
77.05 CDCl3
76.83 CDCl3
63.55
14.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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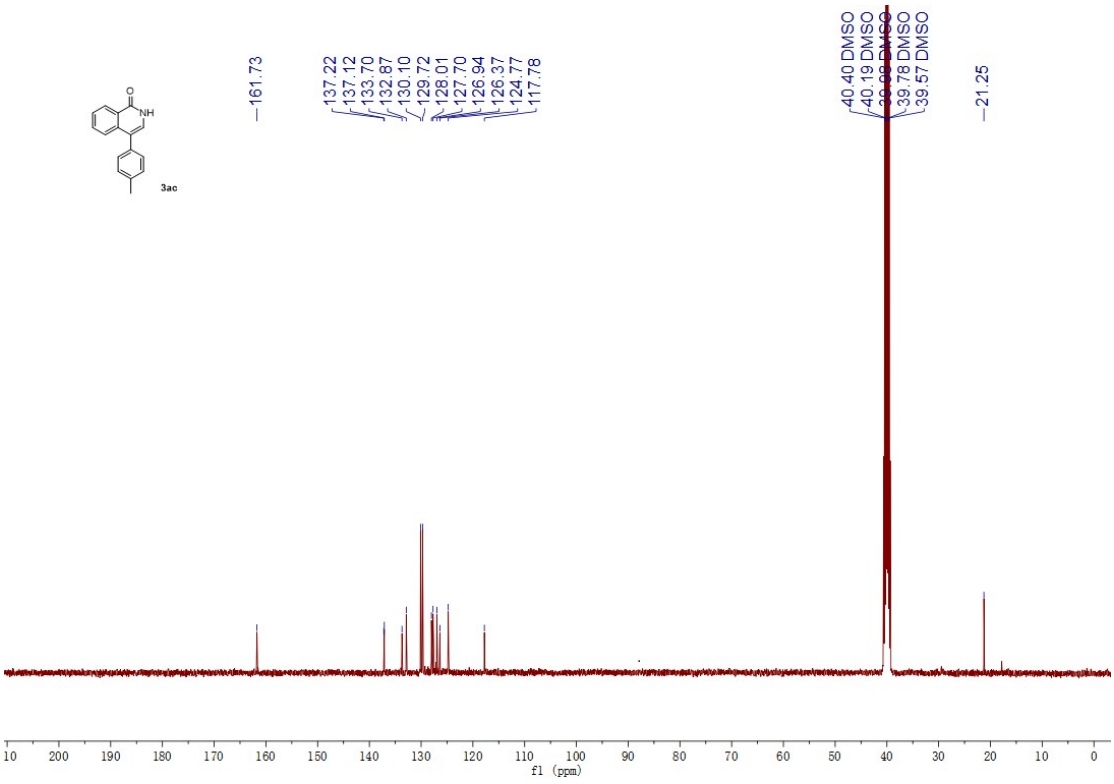
7.70
7.69
7.68
7.55
7.54
7.52
7.52
7.50
7.32
7.31
7.29
7.06
7.05
3.38
2.50 DMSO
2.38
3ac
1.00
1.00
1.05
1.16
1.09
3.98
1.07
2.95
f1 (ppm)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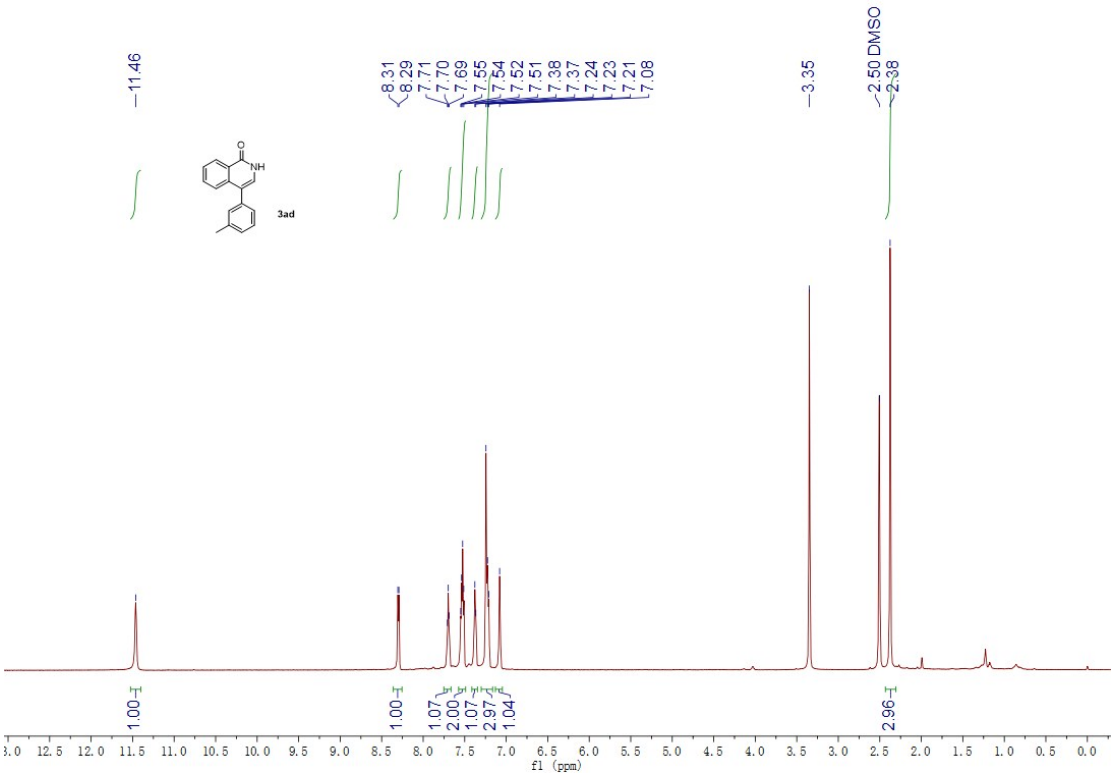
137.12
133.70
132.87
130.10
129.72
128.01
127.70
126.94
126.37
124.77
117.78
40.40 DMSO
40.19 DMSO
39.78 DMSO
39.57 DMSO
21.25
3ac
f1 (ppm)


11.46
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7.70
7.69
7.55
7.54
7.52
7.51
7.38
7.37
7.24
7.23
7.21
7.08
3.35
2.50 DMSO
2.38
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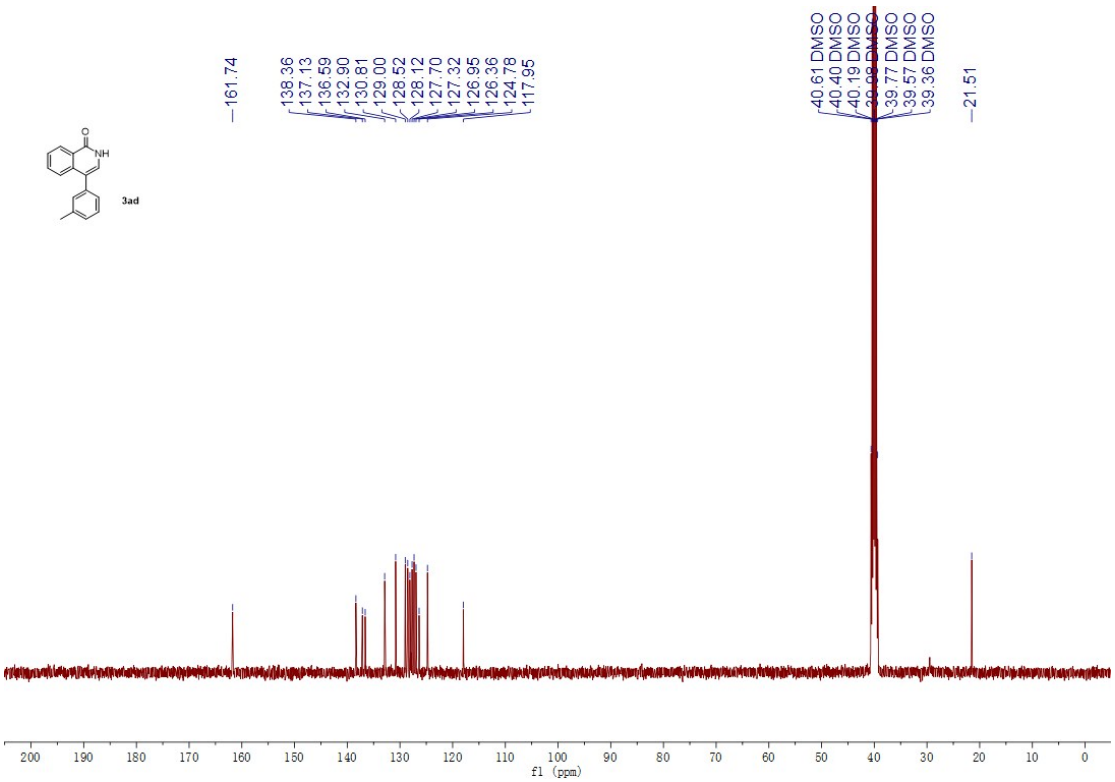
1.00
1.07
2.00
1.07
2.97
1.04
2.96
f1 (ppm)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137.13
136.59
132.90
130.81
129.00
128.52
128.12
127.70
127.32
126.95
126.36
124.78
117.95
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40.19 DMSO
39.98 DMSO
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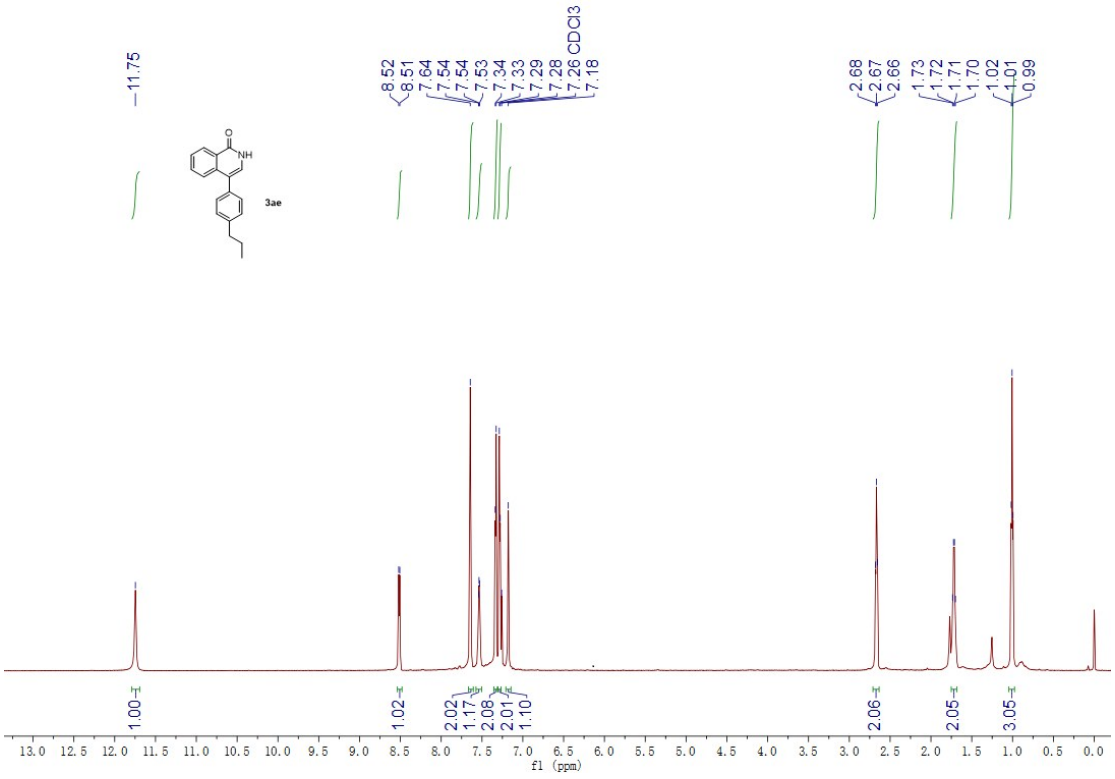
39.57 DMSO
39.36 DMSO
21.51
3ad
f1 (ppm)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7.54
7.54
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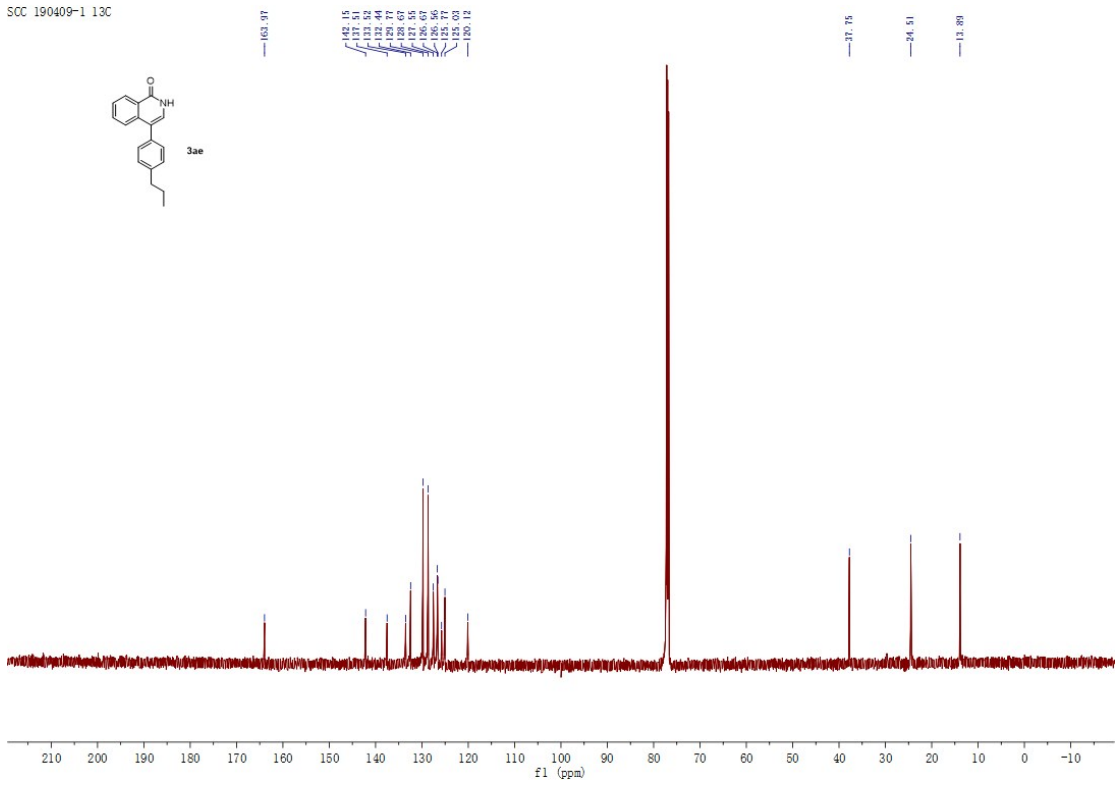
7.34
7.33
7.29
7.28
7.26 CDCl3
7.18
2.68
2.67
2.66
1.73
1.72
1.71
1.70
1.02
1.01
0.99
3ae
1.00
1.02
2.02
1.17
2.08
2.01
1.10
2.06
2.05
3.05
f1 (ppm)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129.77
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127.55
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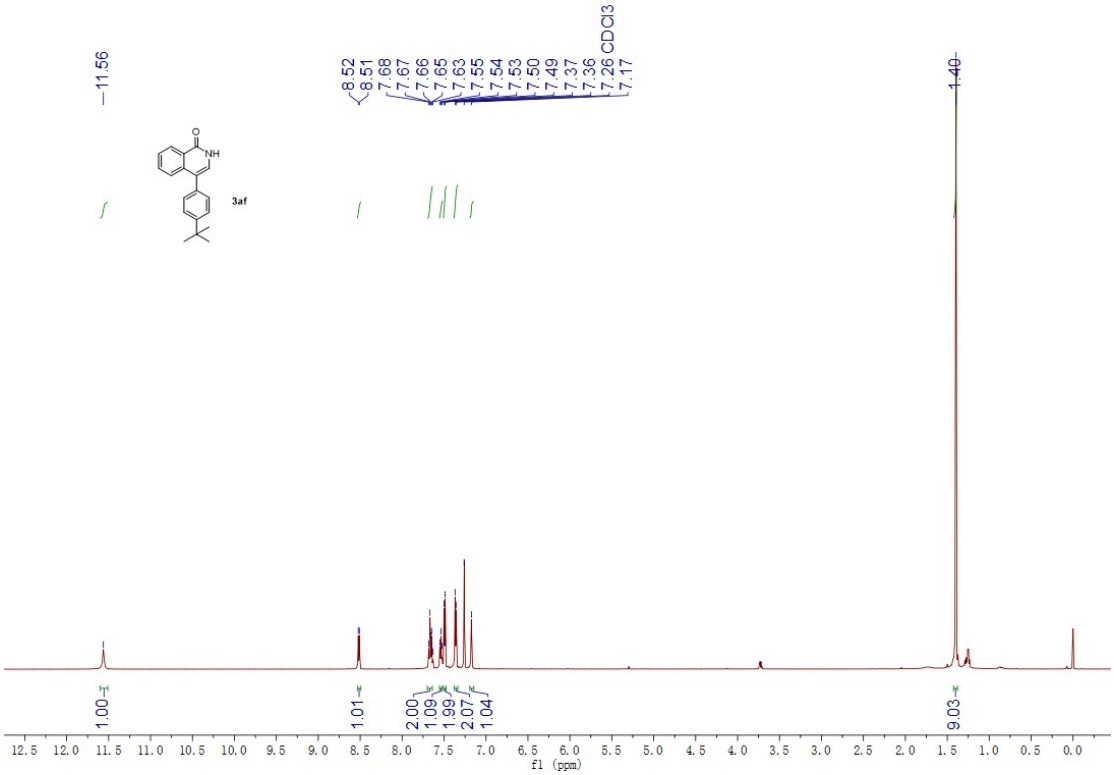
125.77
125.03
120.12
37.75
24.51
13.89
NH
3ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.66
7.65
7.63
7.55
7.54
7.53
7.50
7.49
7.37
7.36
7.26 CDCl3
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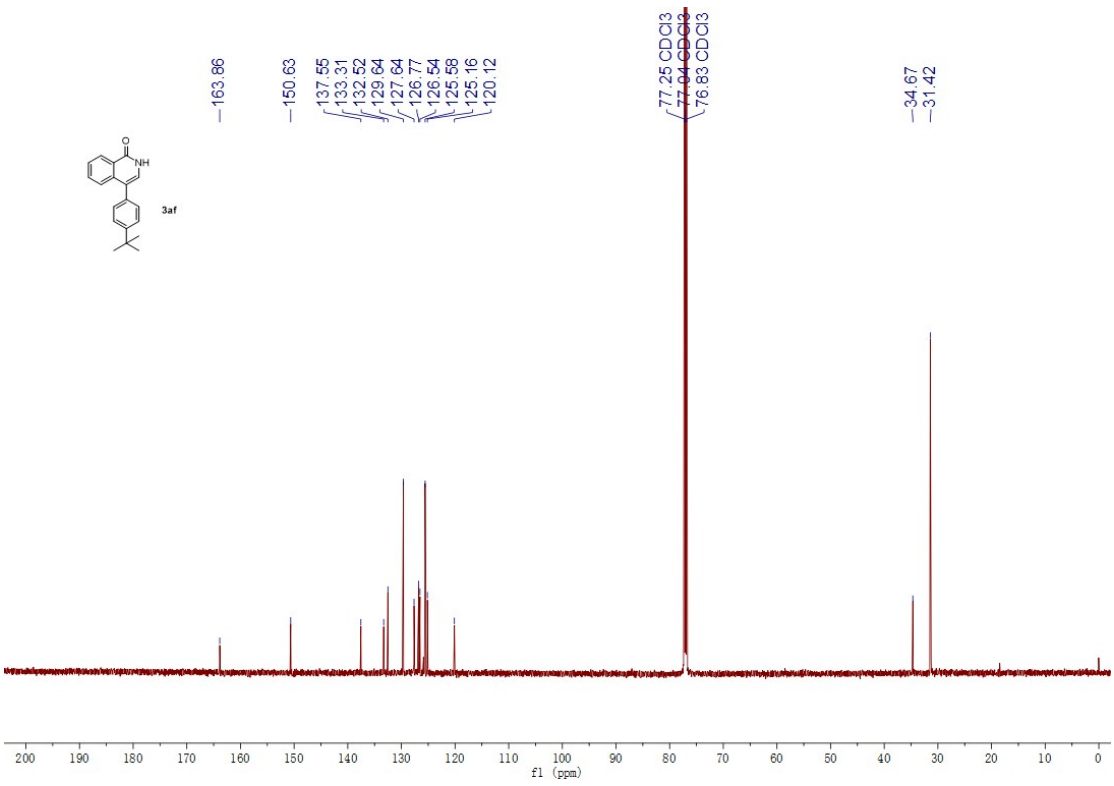
1.99
2.07
1.04
9.03
f1 (ppm)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132.52
129.64
127.64
126.77
126.54
125.58
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120.12
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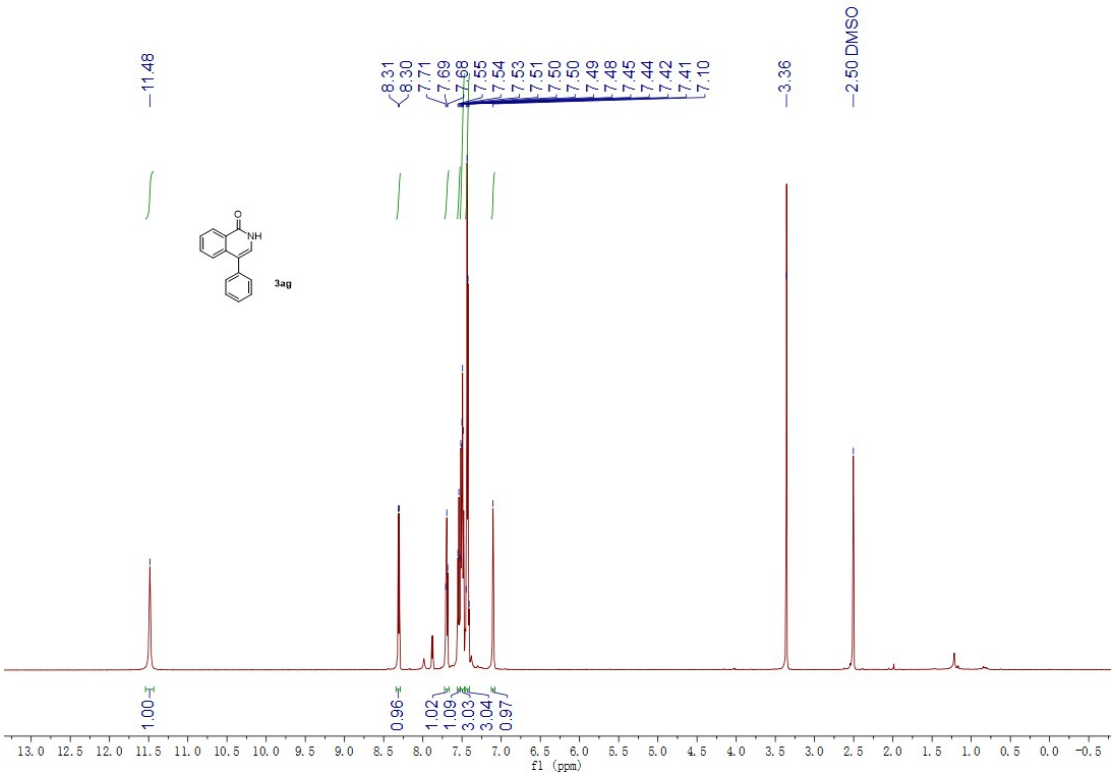
77.04 CDCl3
76.83 CDCl3
34.67
31.42
3af
f1 (ppm)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7.51
7.50
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7.49
7.48
7.45
7.44
7.42
7.41
7.10
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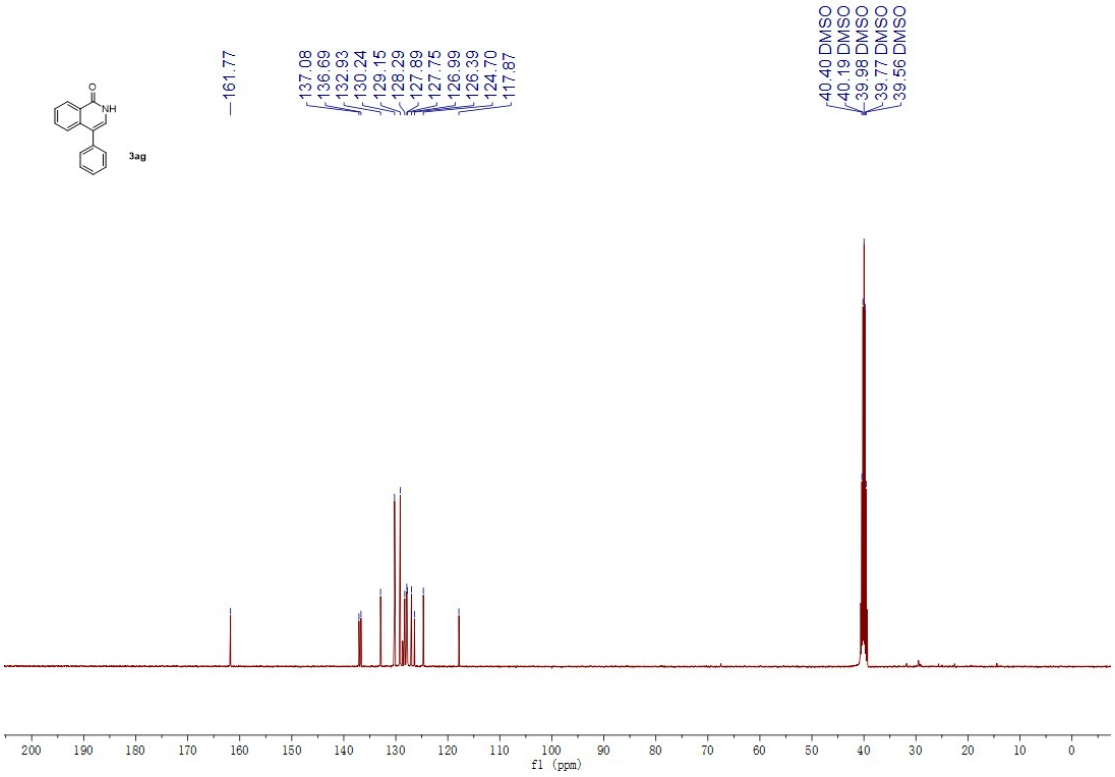
1.02
1.09
3.03
3.04
0.97
f1 (ppm)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39.98 DMSO
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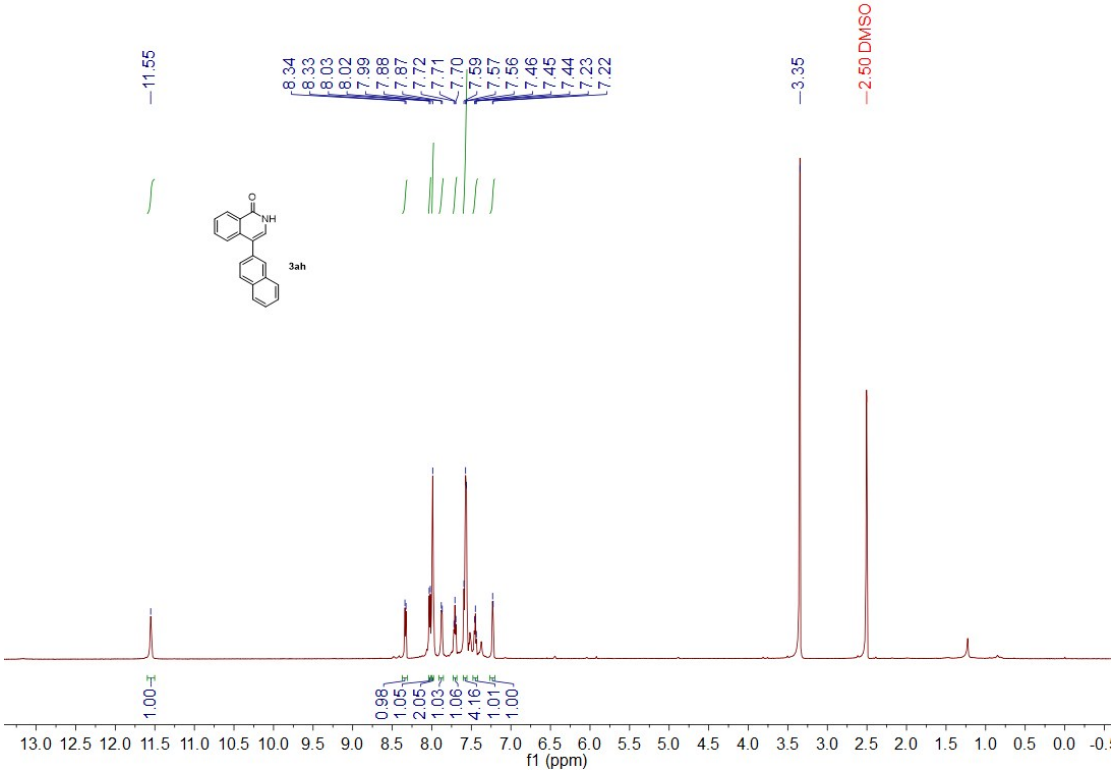
39.56 DMSO
f1 (ppm)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7.71
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7.57
7.56
7.46
7.45
7.44
7.23
7.22
3.35
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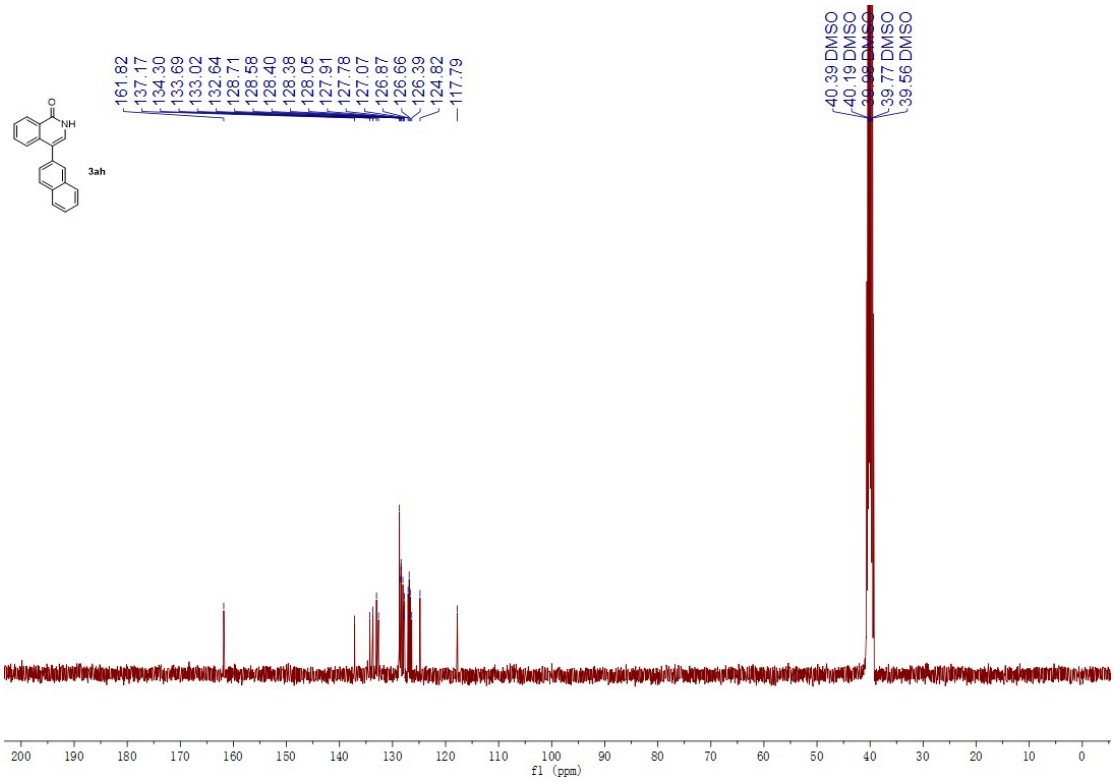
1.05
2.05
1.03
1.06
4.16
1.01
1.00
f1 (ppm)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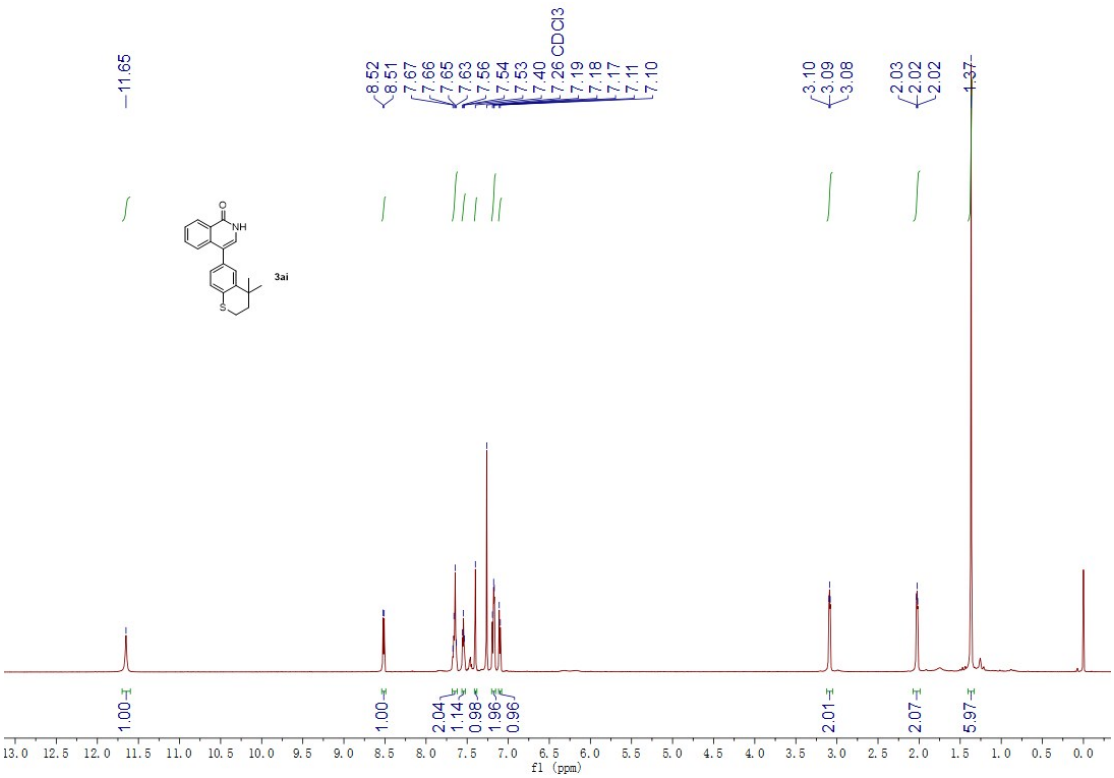
132.64
128.71
128.58
128.40
128.38
128.05
127.91
127.78
127.07
126.87
126.66
126.39
124.82
117.79
40.39 DMSO
40.19 DMSO
39.77 DMSO
39.56 DMSO
NH
O
3ah
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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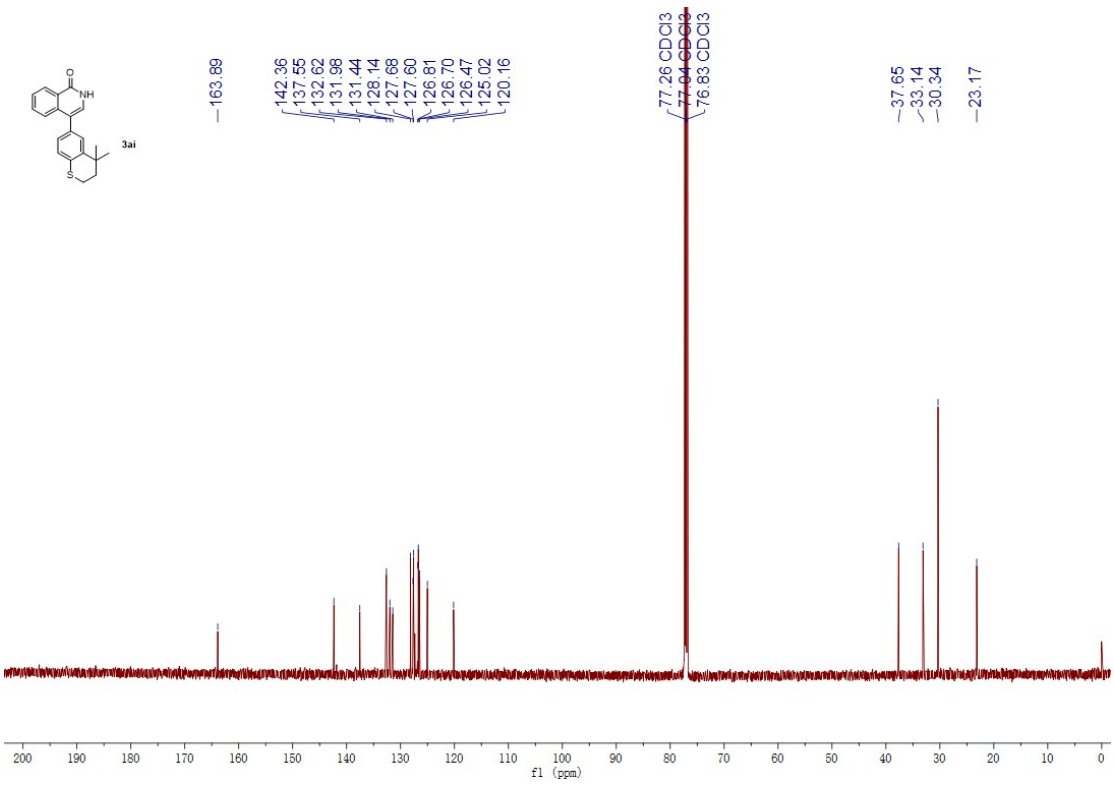
7.67
7.66
7.65
7.63
7.56
7.54
7.53
7.40
7.26 CDCl3
7.19
7.18
7.17
7.11
7.10
3.10
3.09
3.08
2.03
2.02
2.02
1.37
3ai
1.00
1.00
2.04
1.14
0.98
1.96
0.96
2.01
2.07
5.97
f1 (ppm)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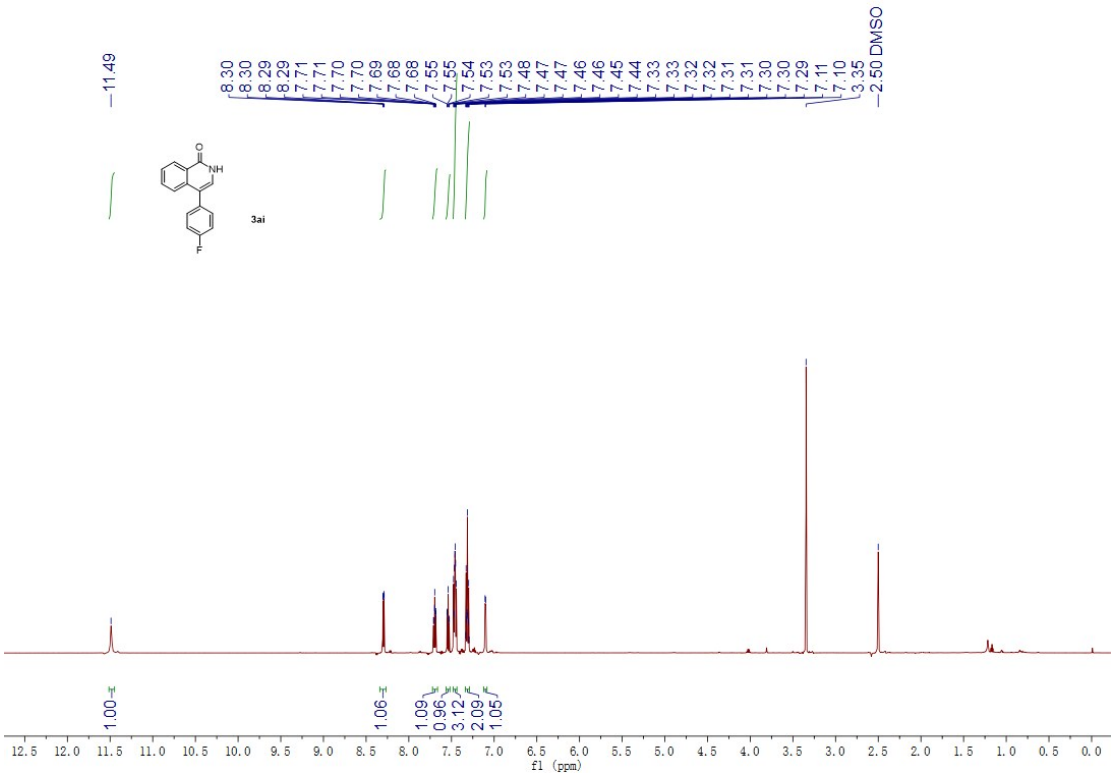
131.44
128.14
127.68
127.60
126.81
126.70
126.47
125.02
120.16
77.26 CDCl3
77.04 CDCl3
76.83 CDCl3
37.65
33.14
30.34
23.17
3ai
f1 (ppm)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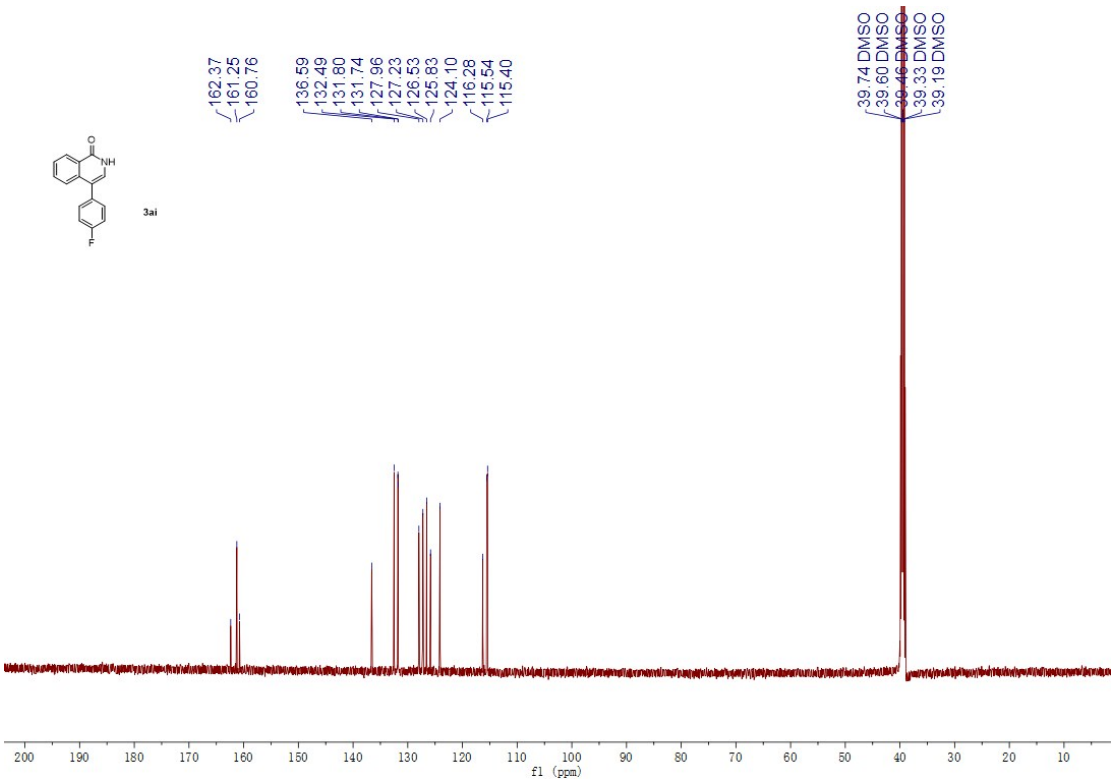
7.71
7.70
7.70
7.69
7.68
7.68
7.55
7.55
7.54
7.53
7.53
7.48
7.47
7.47
7.46
7.46
7.45
7.44
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.11
7.10
3.35
2.50 DMSO
NH
O
F
3ai
1.00
1.06
1.09
0.96
3.12
2.09
1.05
f1 (ppm)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131.80
131.74
127.96
127.23
126.53
125.83
124.10
116.28
115.54
115.40
39.74 DMSO
39.60 DMSO
39.46 DMSO
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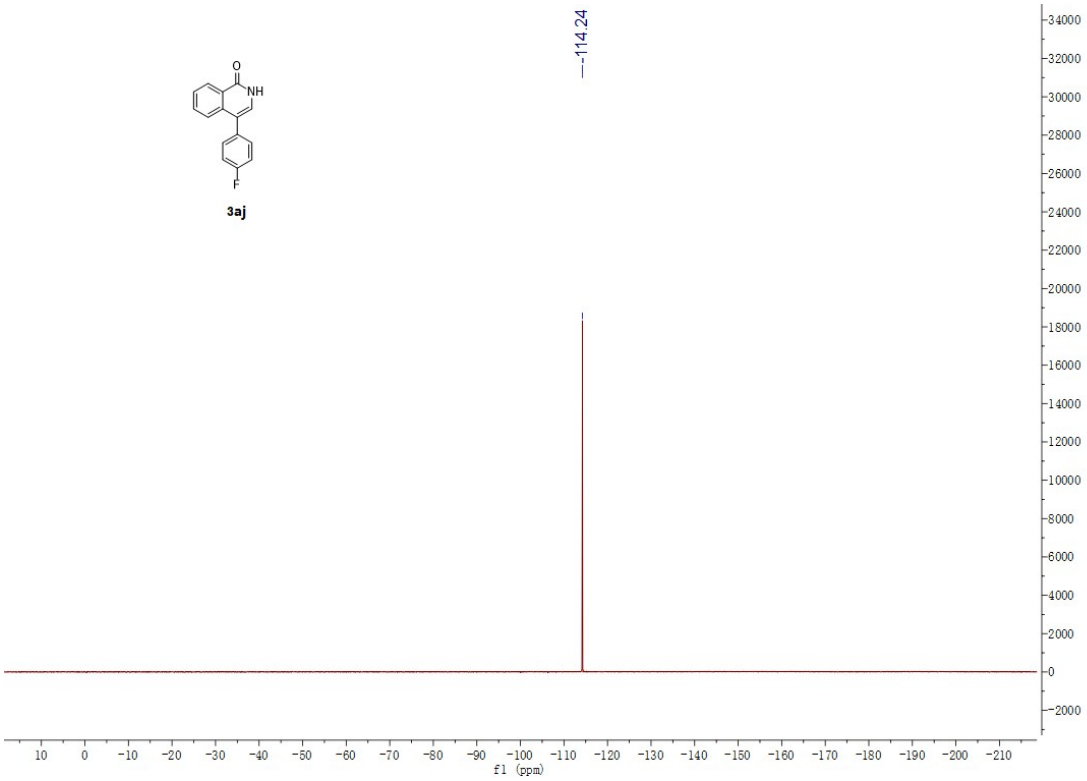
39.19 DMSO
O
NH
F
3ai
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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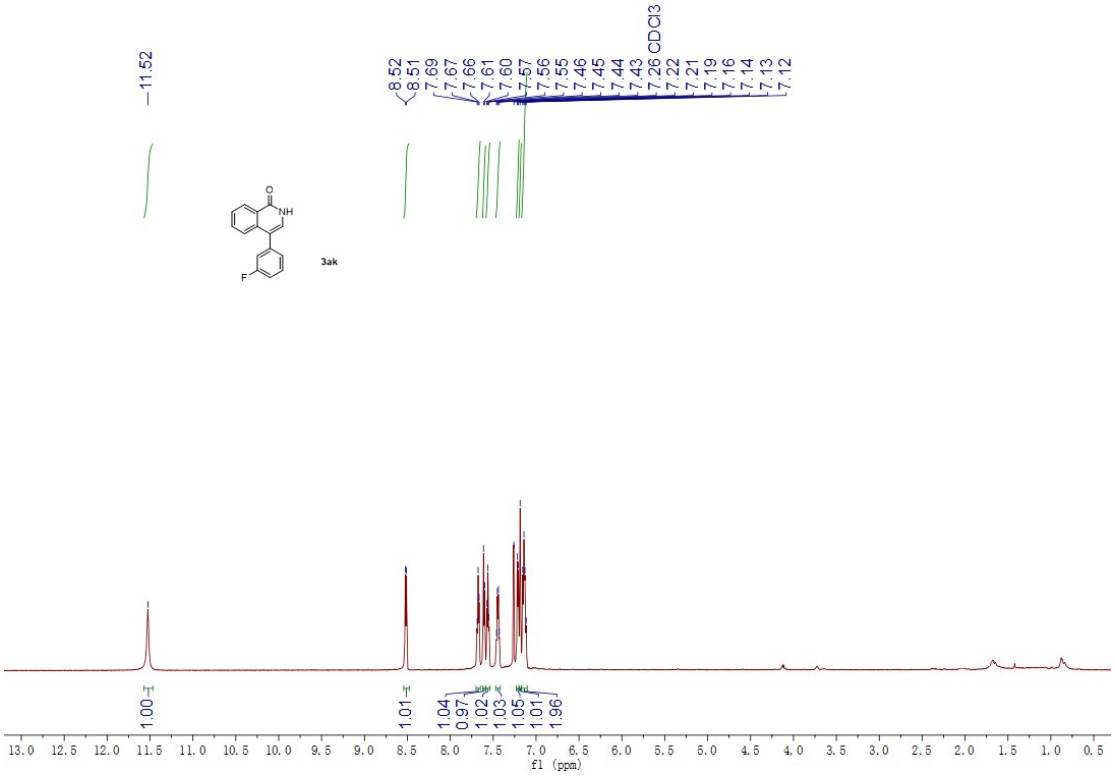
NH
F
3aj
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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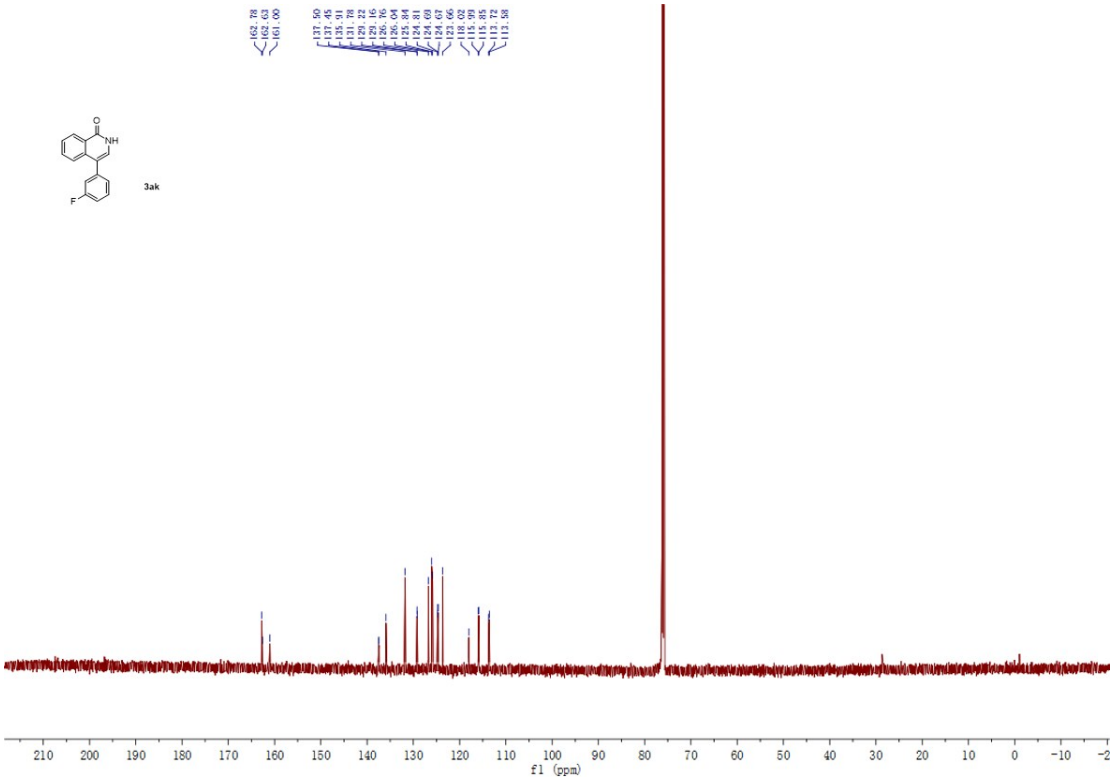
7.66
7.61
7.60
7.57
7.56
7.55
7.46
7.45
7.44
7.43
7.26 CDCl3
7.22
7.21
7.19
7.16
7.14
7.13
7.12
O
NH
F
3ak
1.00
1.01
1.04
0.97
1.02
1.03
1.05
1.01
1.96
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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162.63
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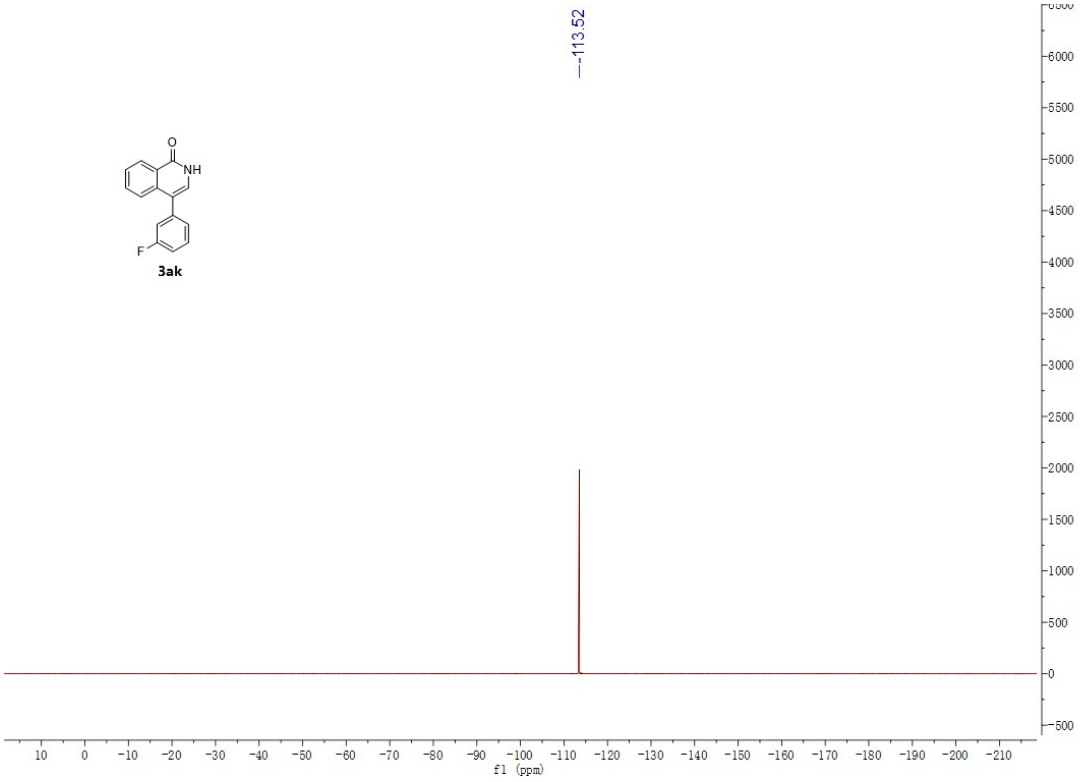
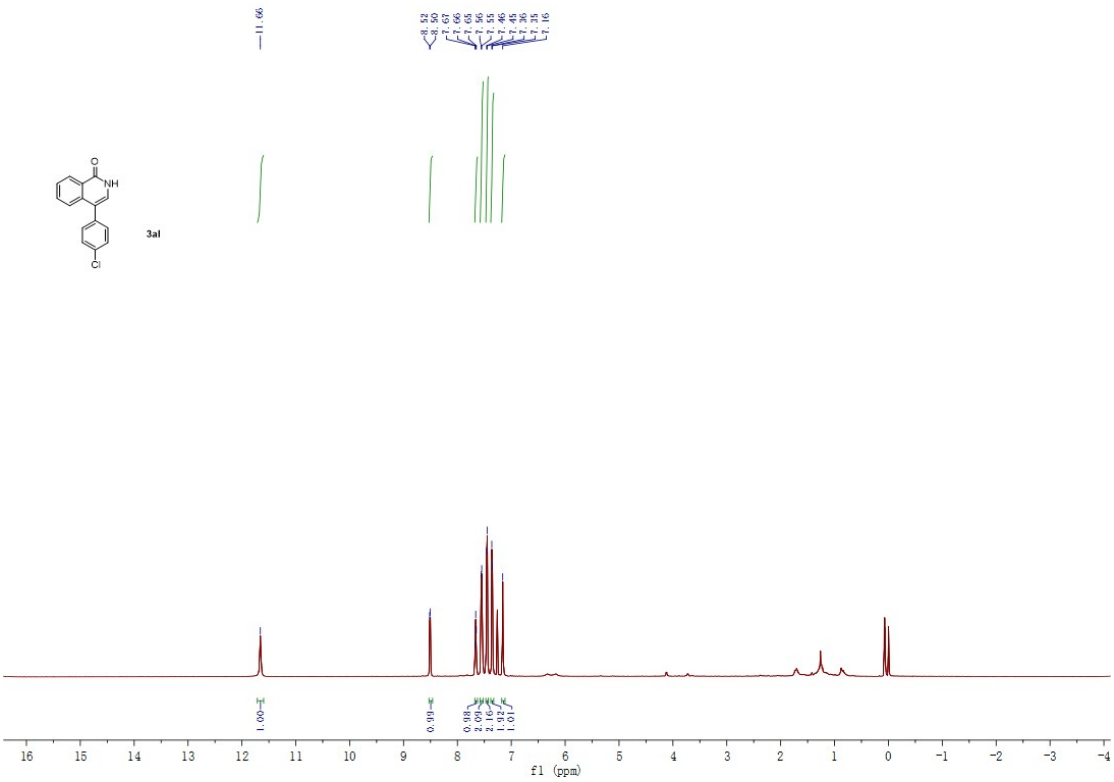
133.78
129.22
129.16
126.76
126.64
125.84
124.81
124.69
124.67
123.66
118.02
115.99
115.85
113.72
113.58
O
NH
F
3ak
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)


-113.52
O
NH
F
3ak
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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8.52
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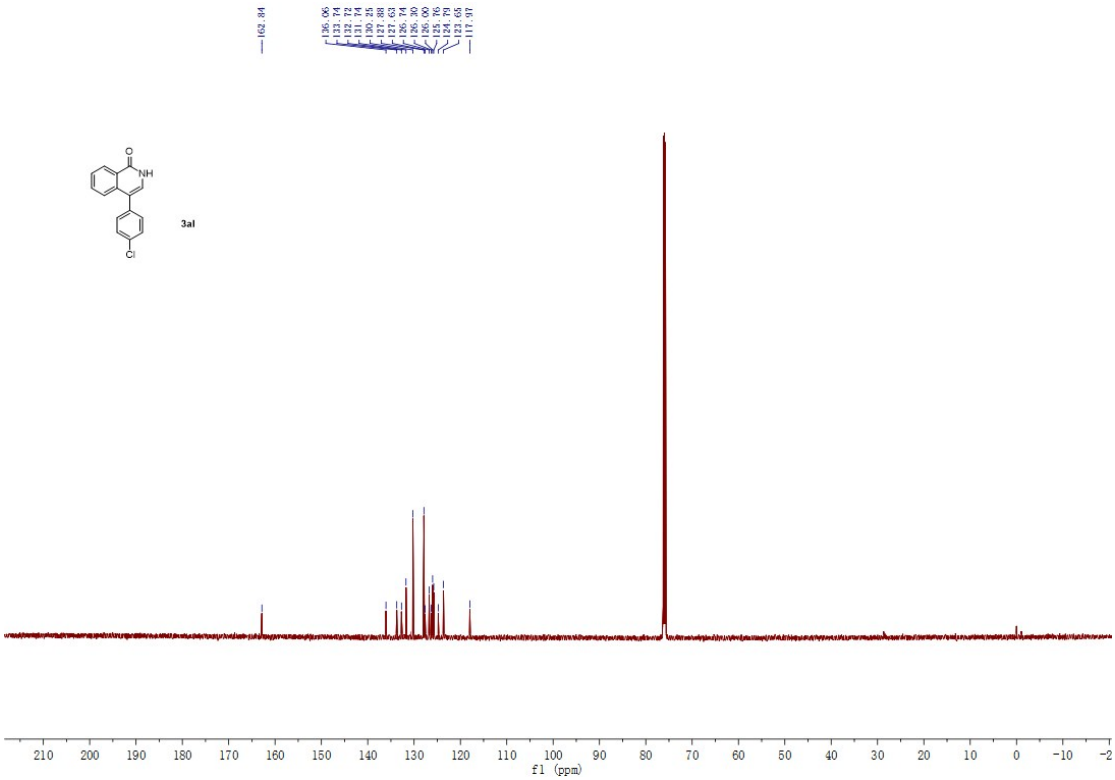
7.67
7.66
7.65
7.56
7.55
7.46
7.45
7.36
7.35
7.16
O
NH
Cl
3al
1.00
0.99
0.98
2.09
2.06
1.92
1.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
f1 (ppm)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132.72
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130.25
129.88
127.65
126.74
126.30
126.00
125.75
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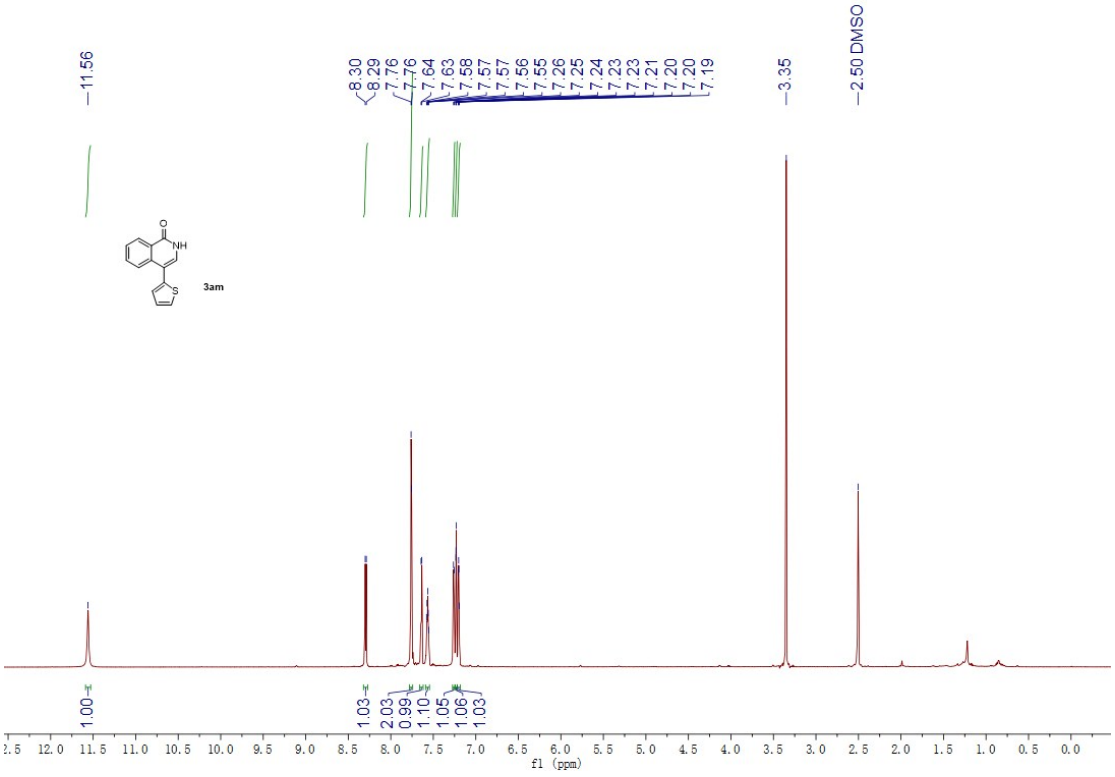
123.65
117.97
O
NH
Cl
3al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)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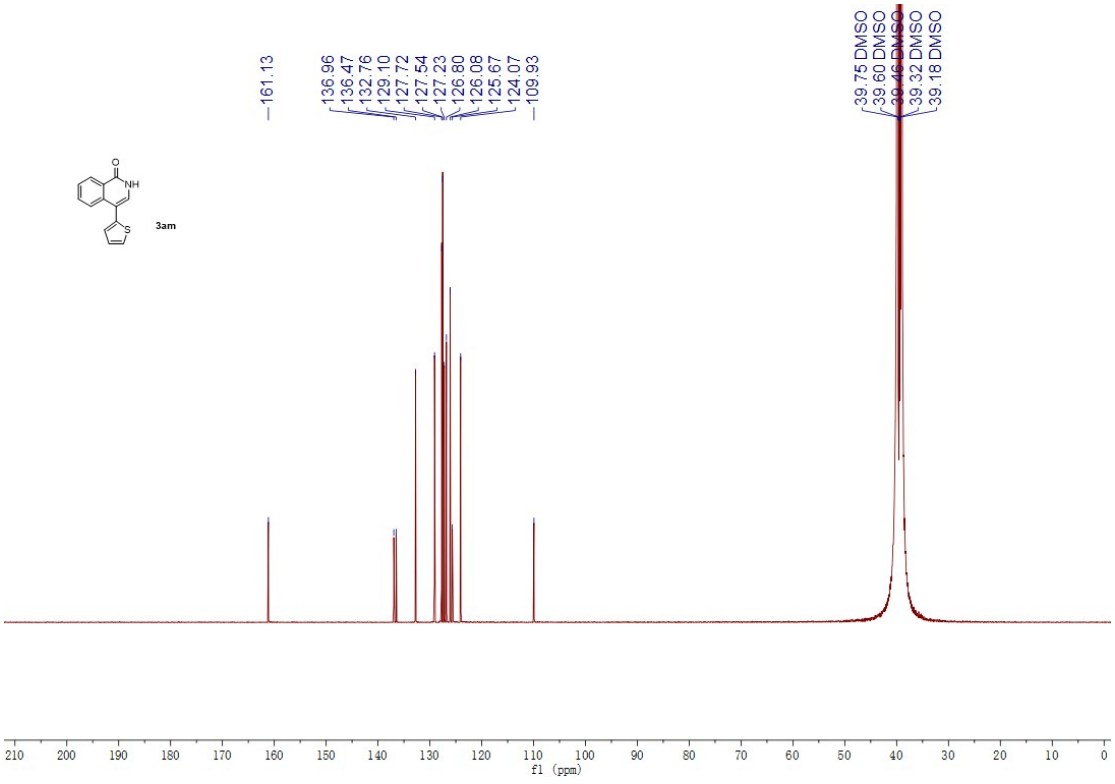
7.64
7.63
7.58
7.57
7.57
7.56
7.55
7.26
7.25
7.24
7.23
7.23
7.21
7.20
7.20
7.19
3.35
2.50 DMSO
O
NH
S
3am
1.00
1.03
2.03
0.99
1.10
1.05
1.06
1.03
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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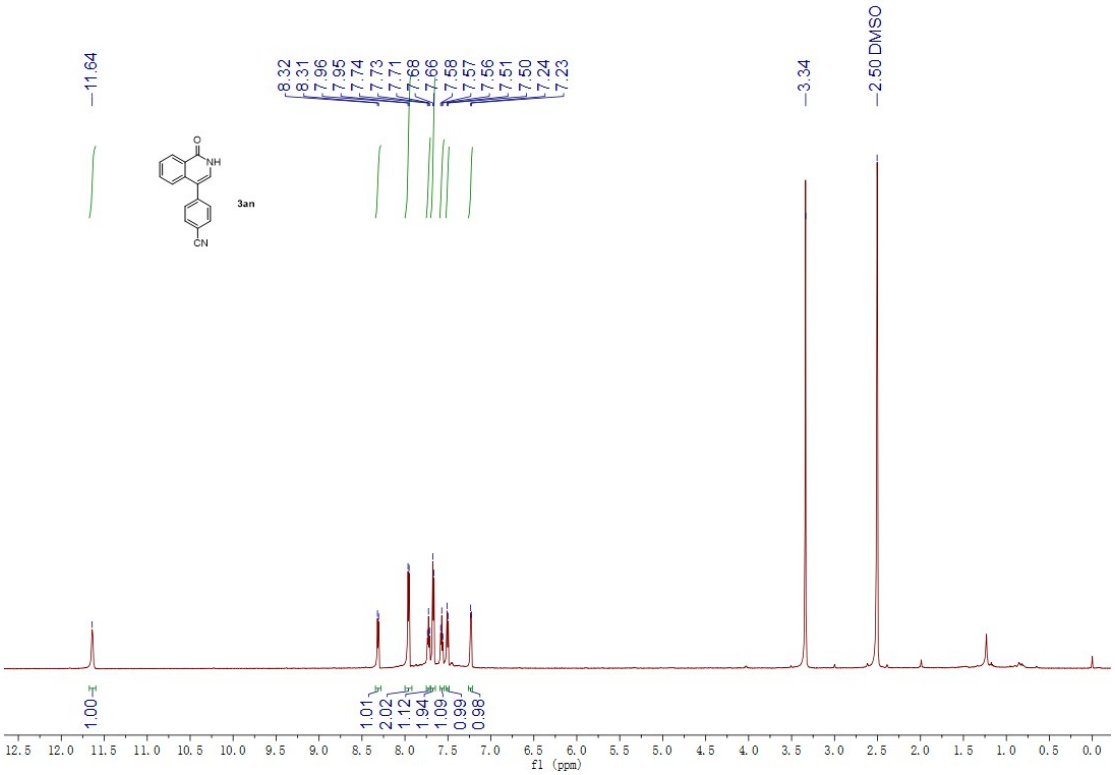
136.96
136.47
132.76
129.10
127.72
127.54
127.23
126.80
126.08
125.67
124.07
109.93
39.75 DMSO
39.60 DMSO
39.46 DMSO
39.32 DMSO
39.18 DMSO
O
NH
S
3am
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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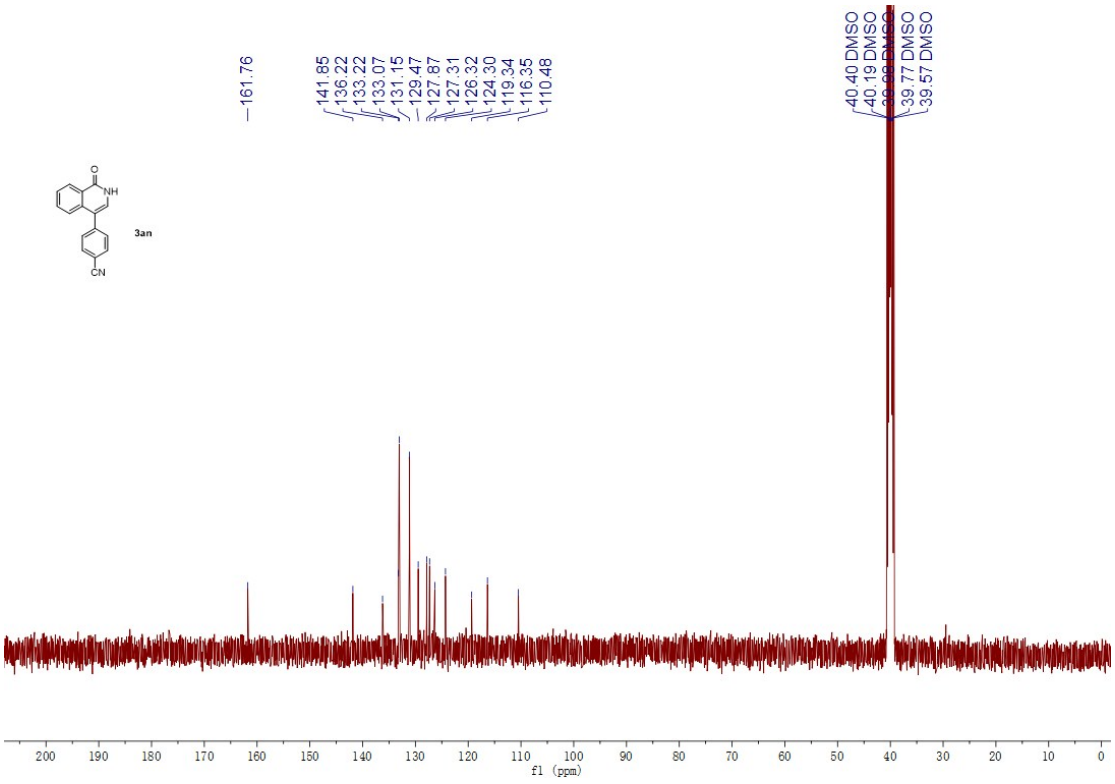
7.95
7.74
7.73
7.71
7.68
7.66
7.58
7.57
7.56
7.51
7.50
7.24
7.23
3.34
2.50 DMSO
3an
1.00
1.01
2.02
1.12
1.94
1.09
0.99
0.98
f1 (ppm)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133.22
133.07
131.15
129.47
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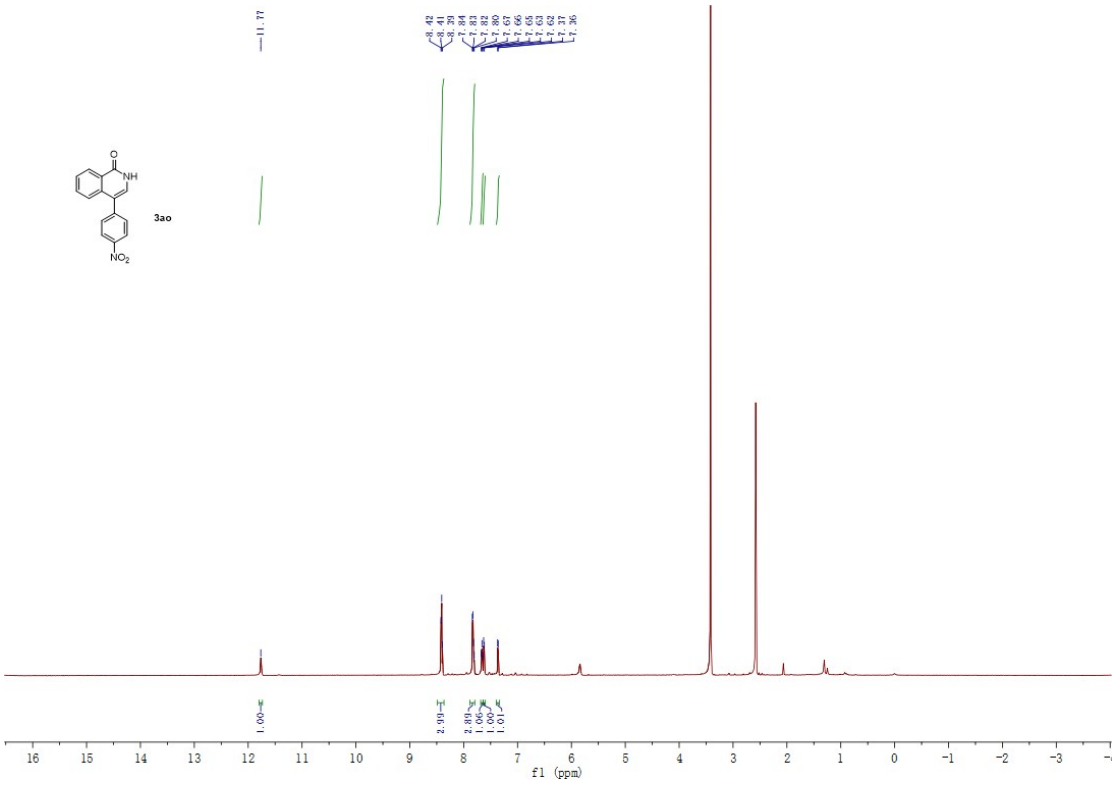
127.31
126.32
124.30
119.34
116.35
110.48
40.40 DMSO
40.19 DMSO
39.77 DMSO
39.57 DMSO
3an
f1 (ppm)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8.39
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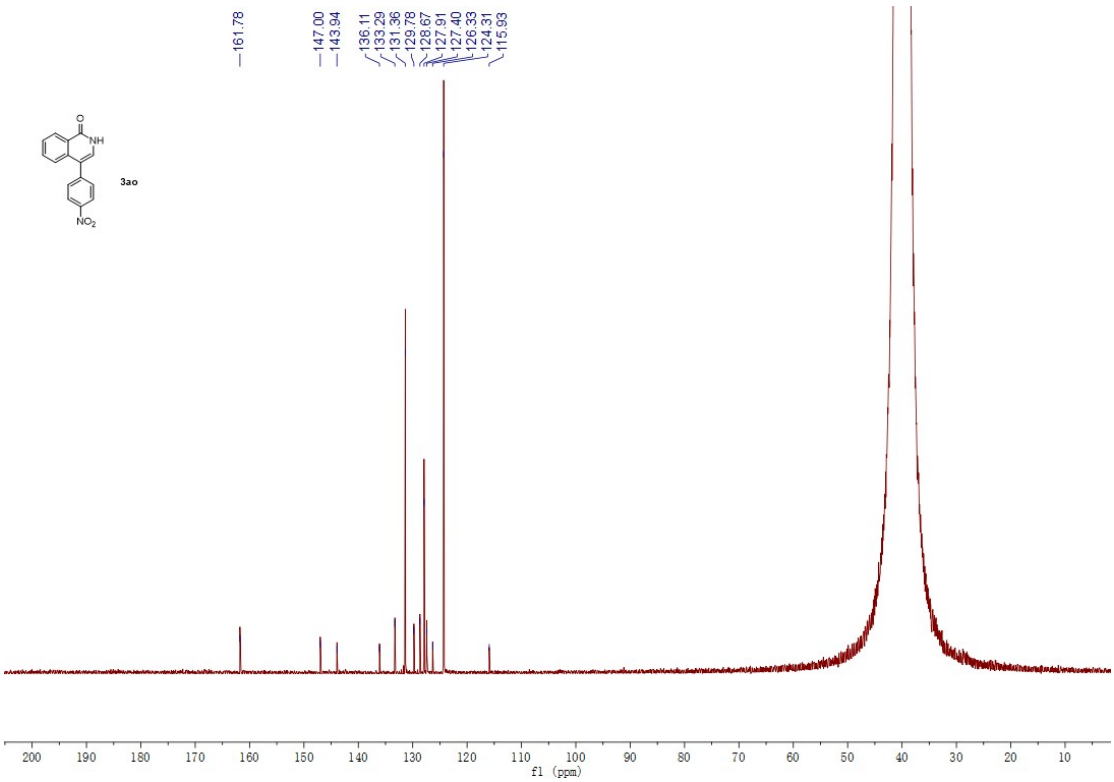
7.83
7.82
7.80
7.67
7.66
7.65
7.63
7.62
7.37
7.36
O
NH
NO2
3ao
1.00
2.99
2.89
1.06
1.00
1.01
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)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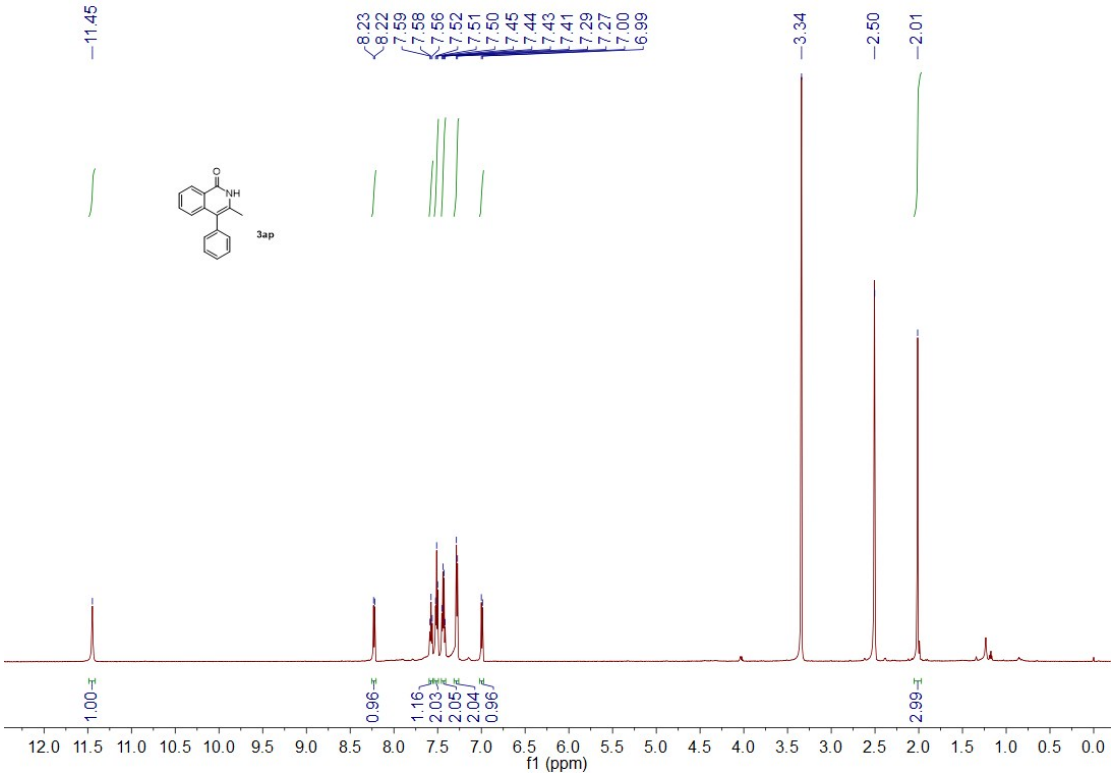
128.67
127.91
127.40
126.33
124.31
115.93
3ao
f1 (ppm)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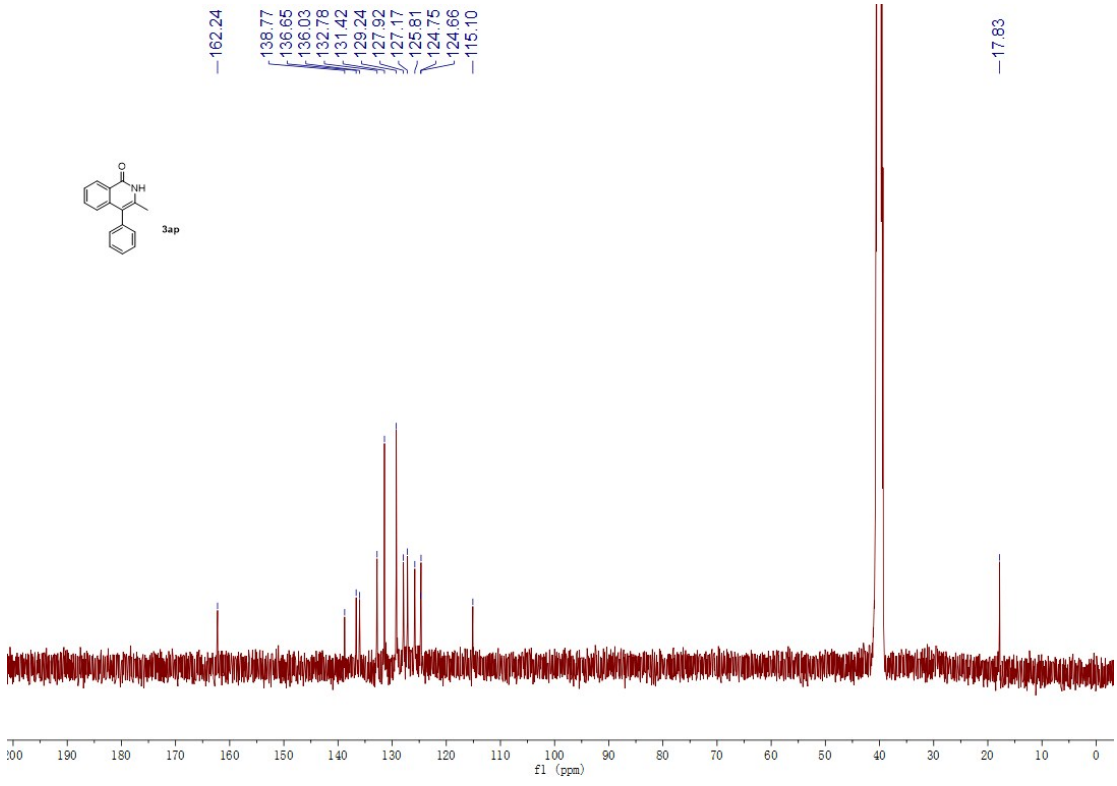
7.52
7.51
7.50
7.45
7.44
7.43
7.41
7.29
7.27
7.00
6.99
3.34
2.50
2.01
3ap
1.00
0.96
1.16
2.03
2.05
2.04
0.96
2.99
f1 (ppm)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136.03
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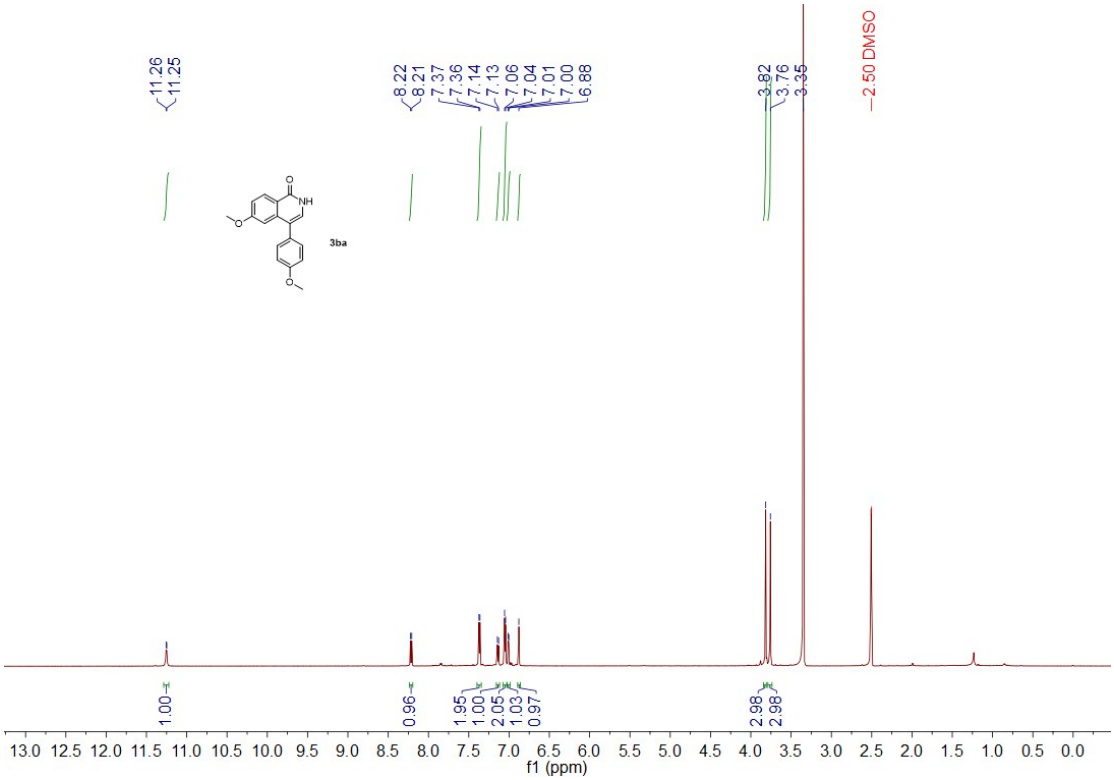
131.42
129.24
127.92
127.17
125.81
124.75
124.66
115.10
17.83
NH
O
3ap
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.22
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7.36
7.14
7.13
7.06
7.04
7.01
7.00
6.88
3.82
3.76
3.35
2.50 DMSO
3ba
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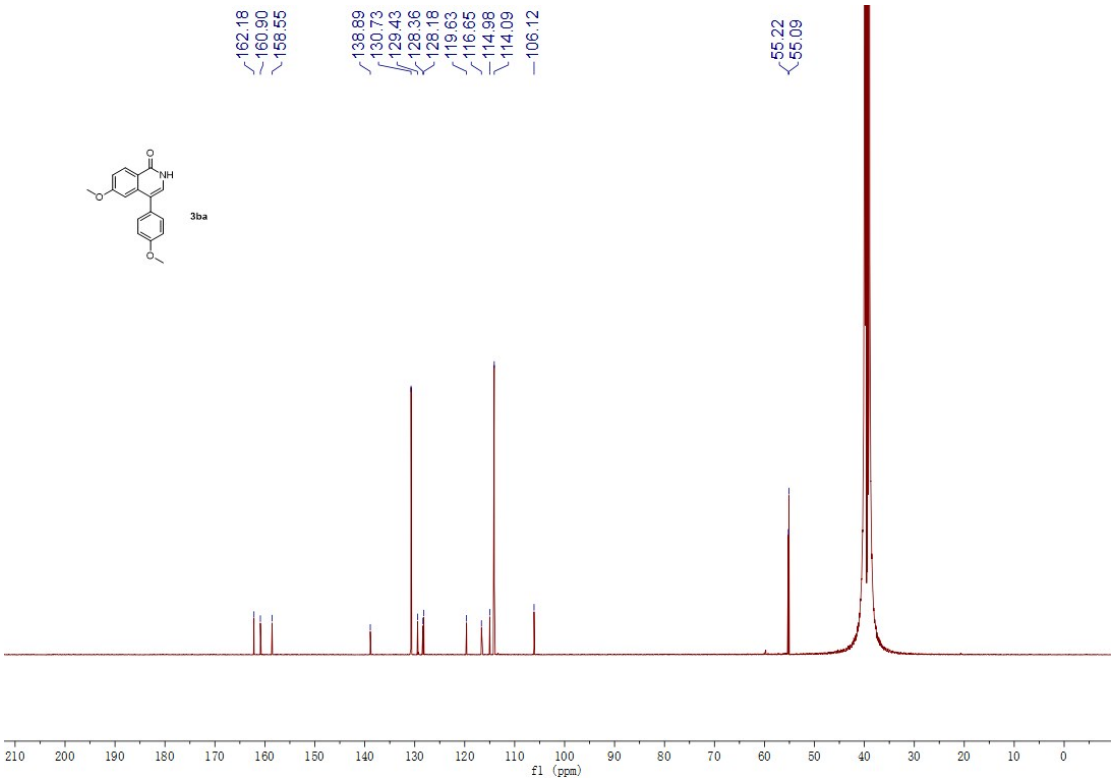
0.96
1.95
1.00
2.05
1.03
0.97
2.98
2.98
f1 (ppm)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129.43
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128.18
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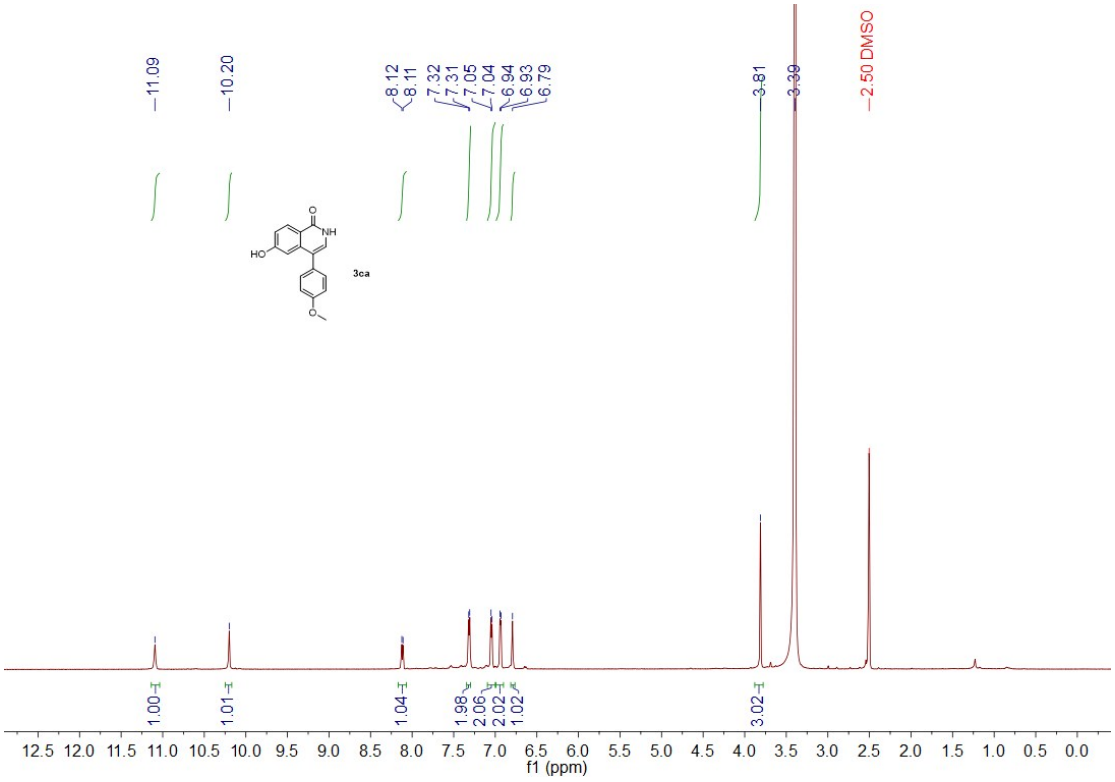
114.98
114.09
106.12
55.22
55.09
3ba
f1 (ppm)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10.20
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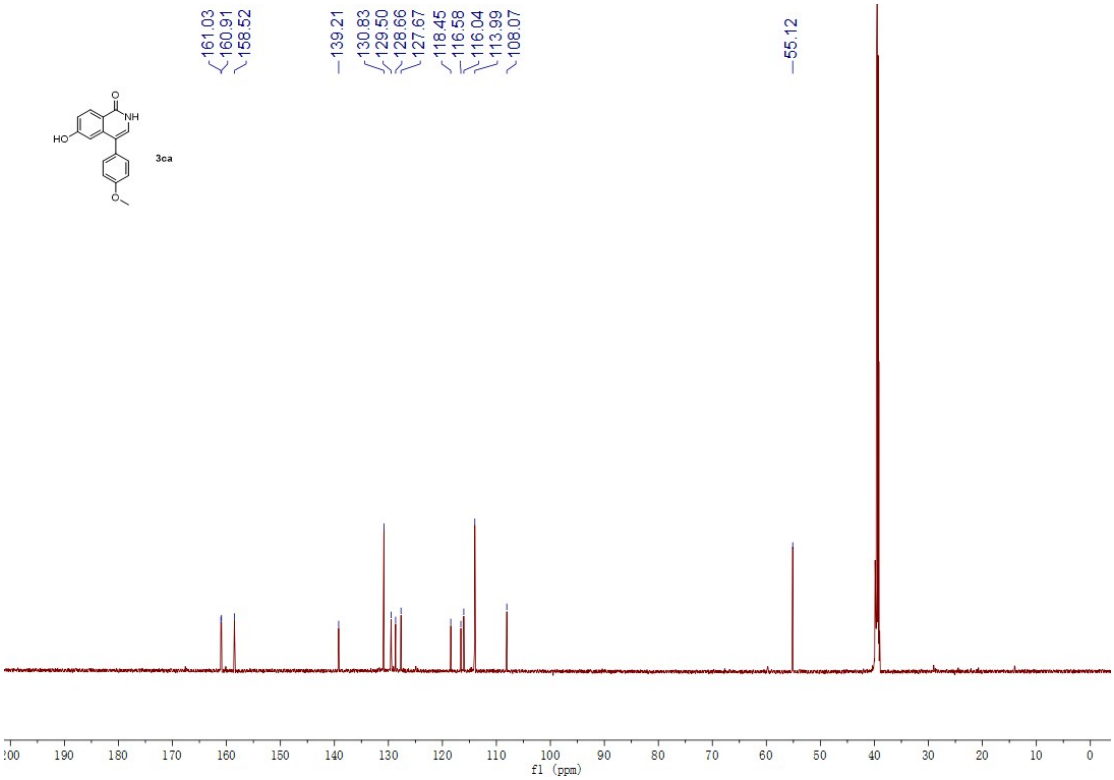
8.11
7.32
7.31
7.05
7.04
6.94
6.93
6.79
3.81
3.39
2.50 DMSO
HO
NH
O
O
3ca
1.00
1.01
1.04
1.98
2.06
2.02
1.02
3.02
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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139.21
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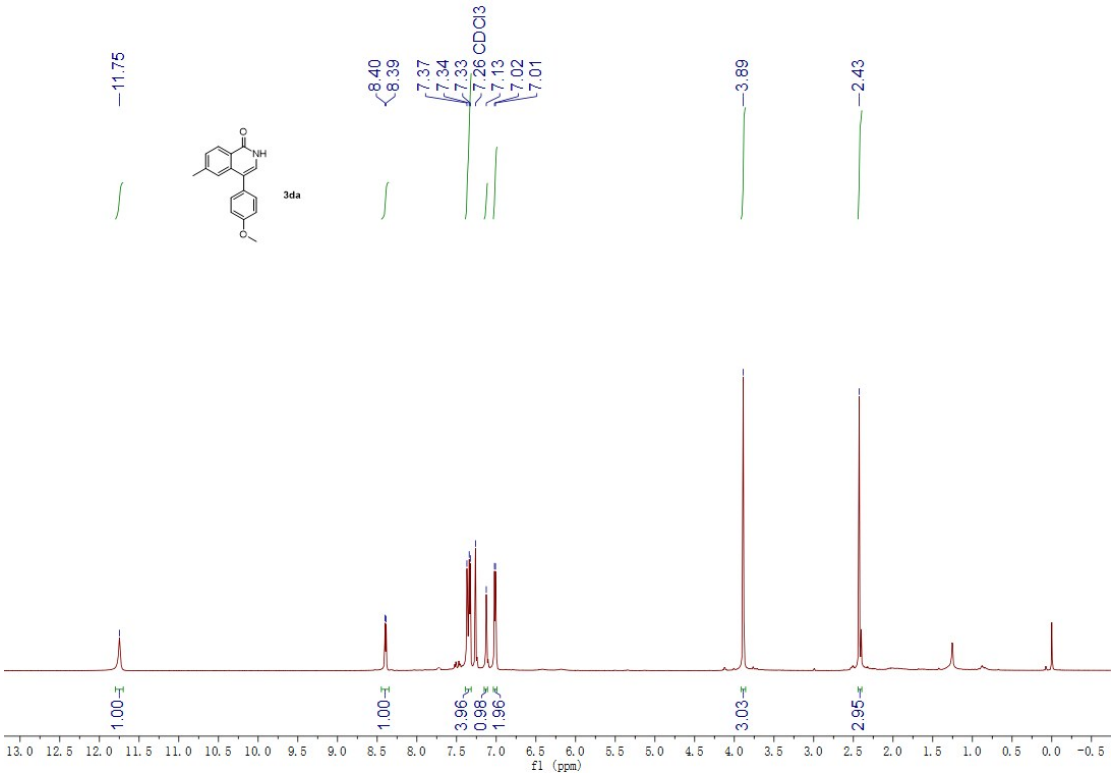
127.67
118.45
116.58
116.04
113.99
108.07
55.12
3ca
f1 (ppm)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7.34
7.33
7.26 CDCl3
7.13
7.02
7.01
3.89
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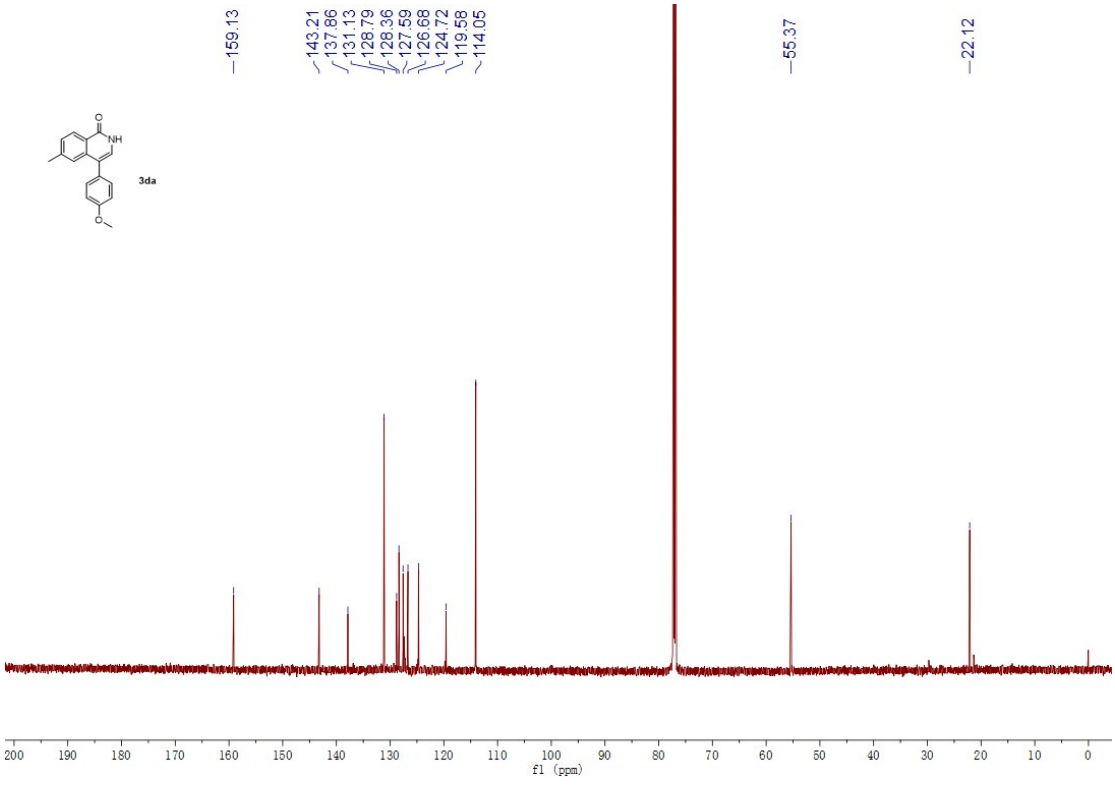
3da
1.00
1.00
3.96
0.98
1.96
3.03
2.95
f1 (ppm)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143.21
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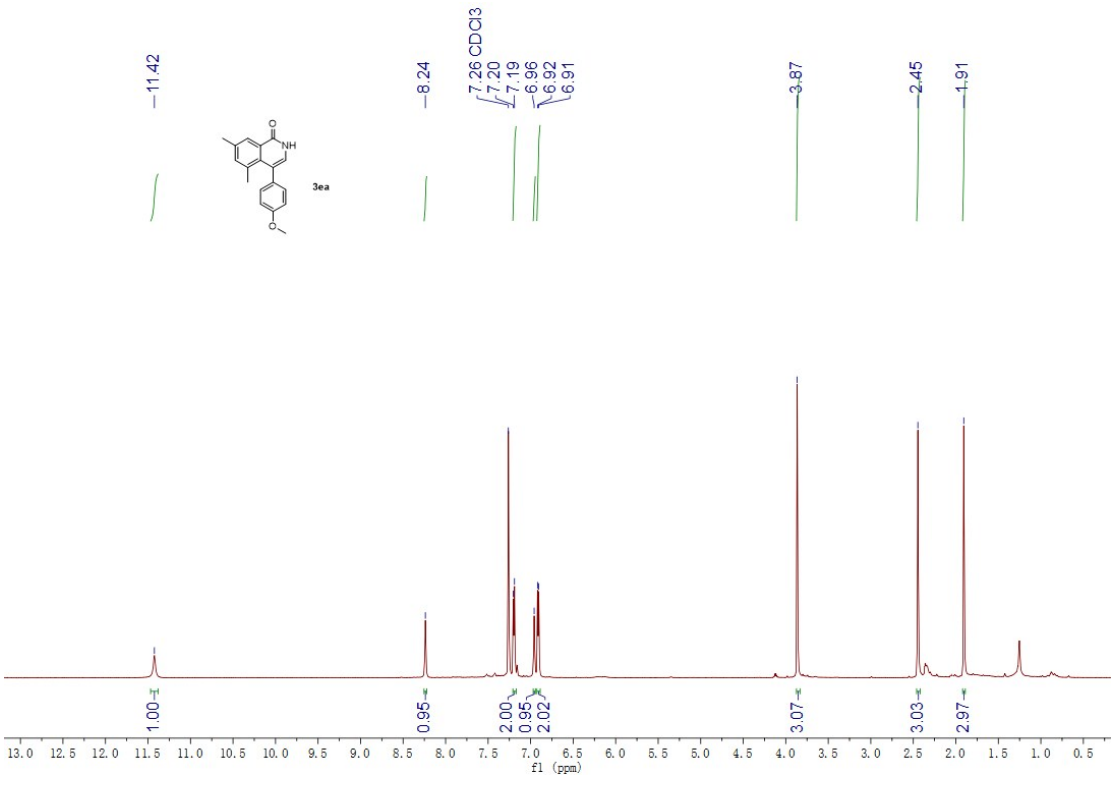
131.13
128.79
128.36
127.59
126.68
124.72
119.58
114.05
55.37
22.12
3da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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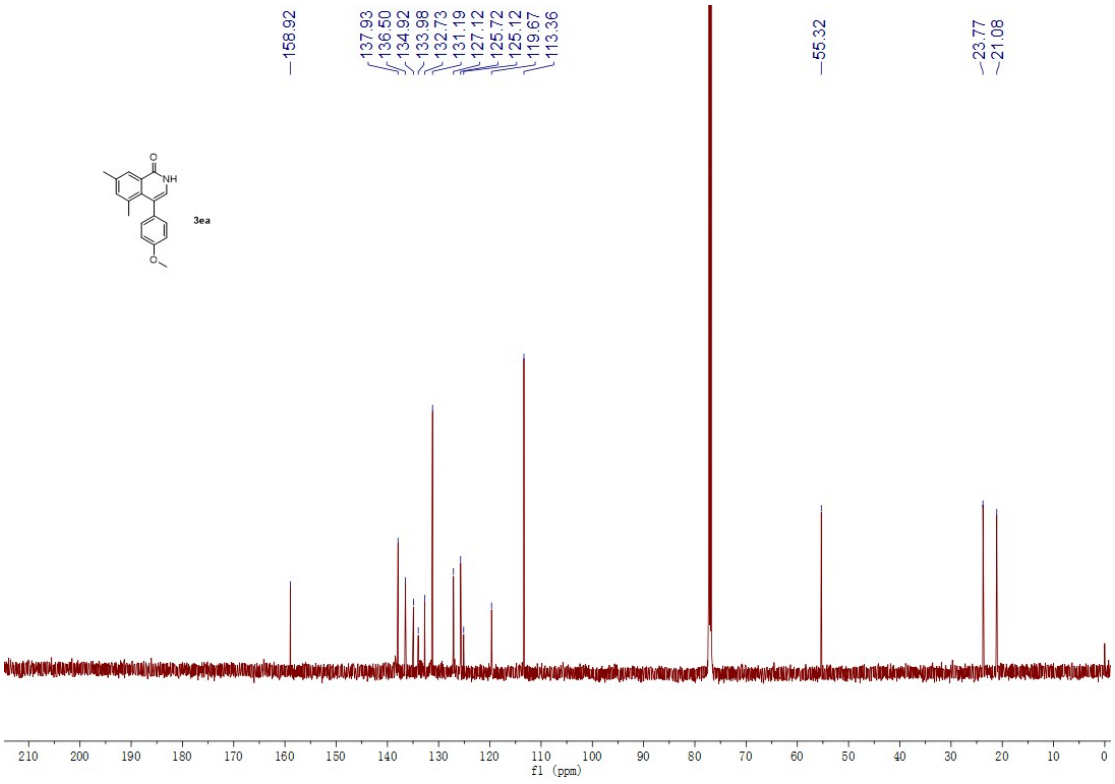
8.24
7.26 CDCl3
7.20
7.19
6.96
6.92
6.91
3.87
2.45
1.91
3ea
1.00
0.95
2.00
0.95
2.02
3.07
3.03
2.97
f1 (ppm)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125.12
119.67
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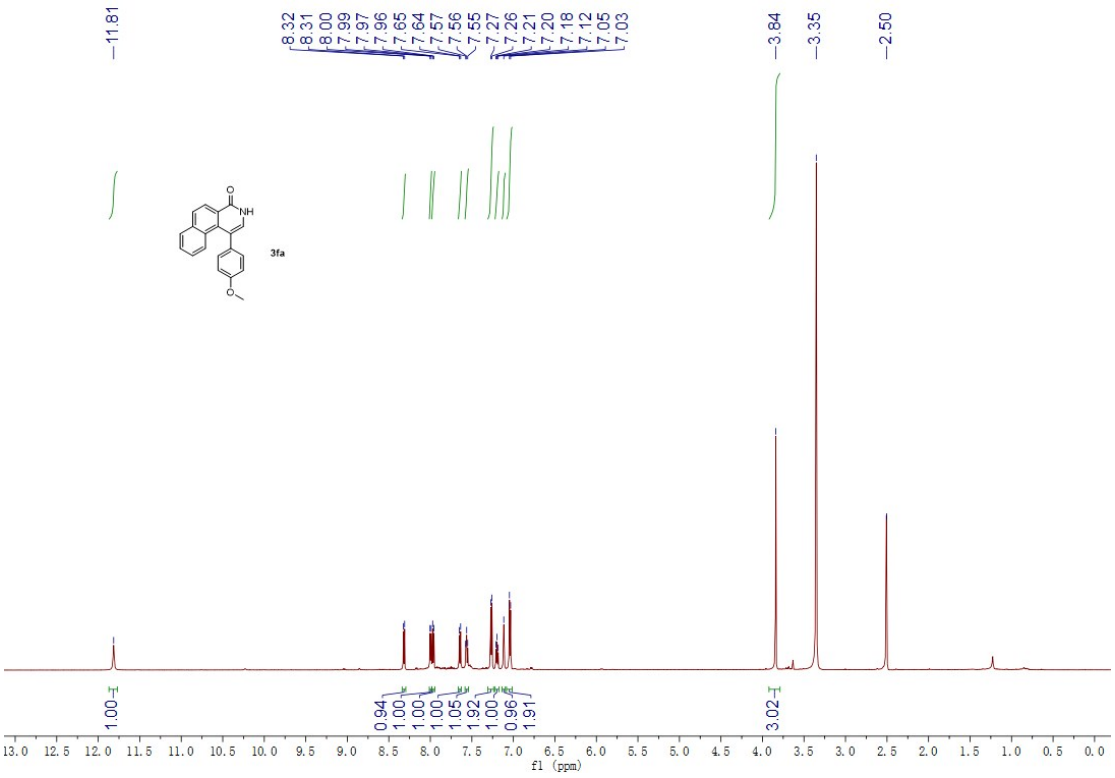
55.32
23.77
21.08
3ea
f1 (ppm)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7.56
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7.27
7.26
7.21
7.20
7.18
7.12
7.05
7.03
3.84
3.35
2.50
3fa
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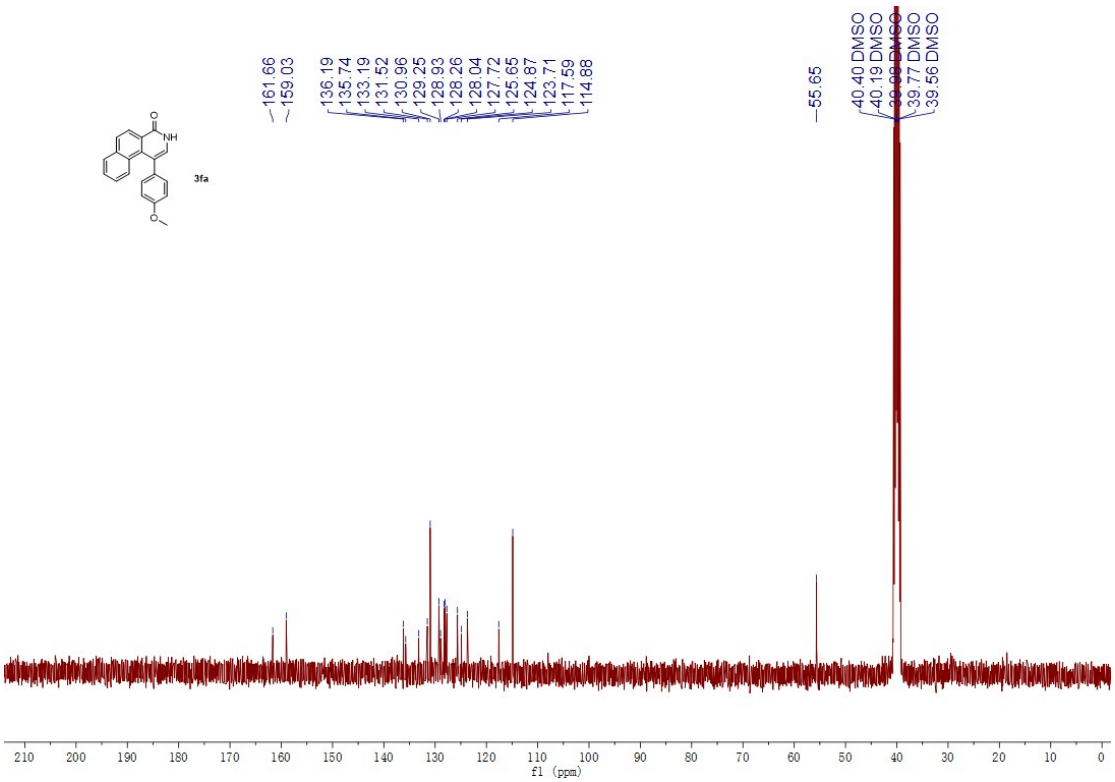
1.00
1.00
1.05
1.92
1.00
0.96
1.91
3.02
f1 (ppm)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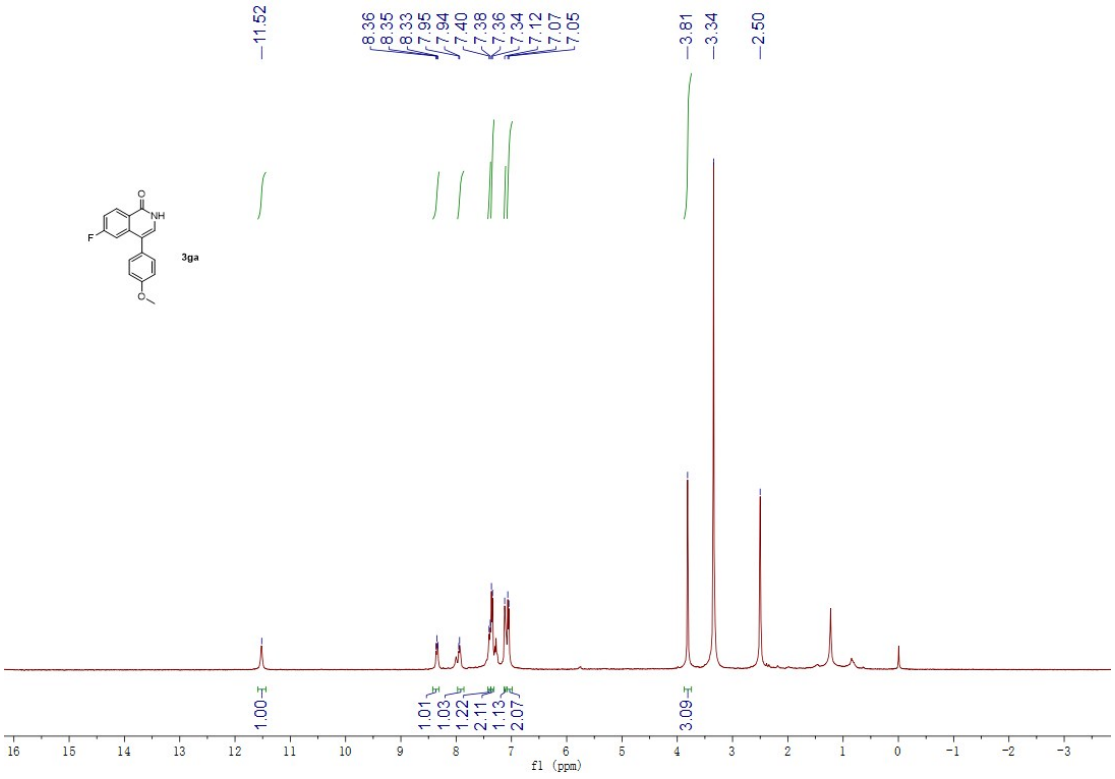
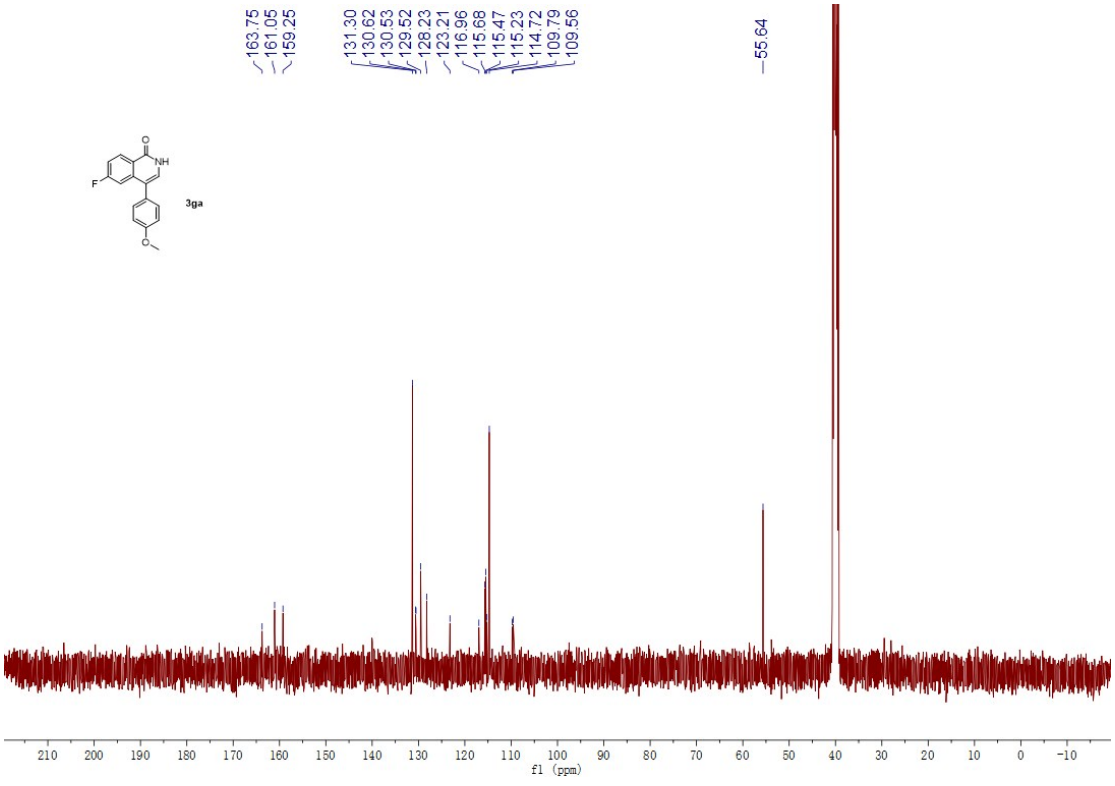
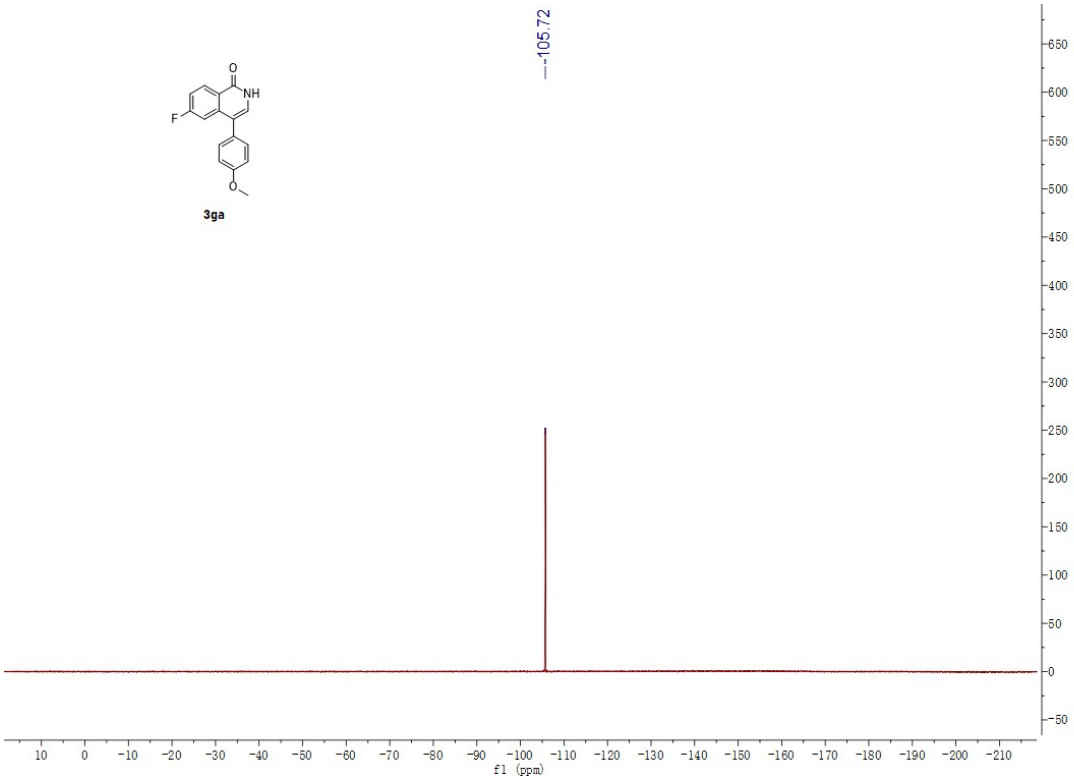
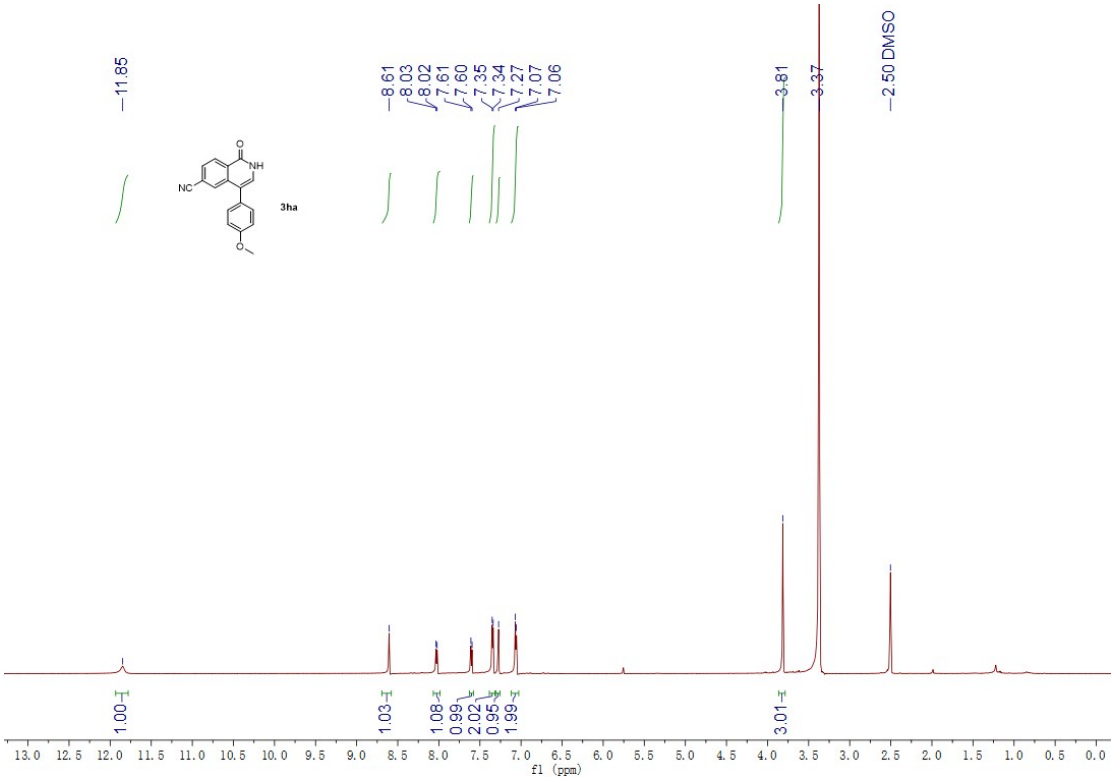
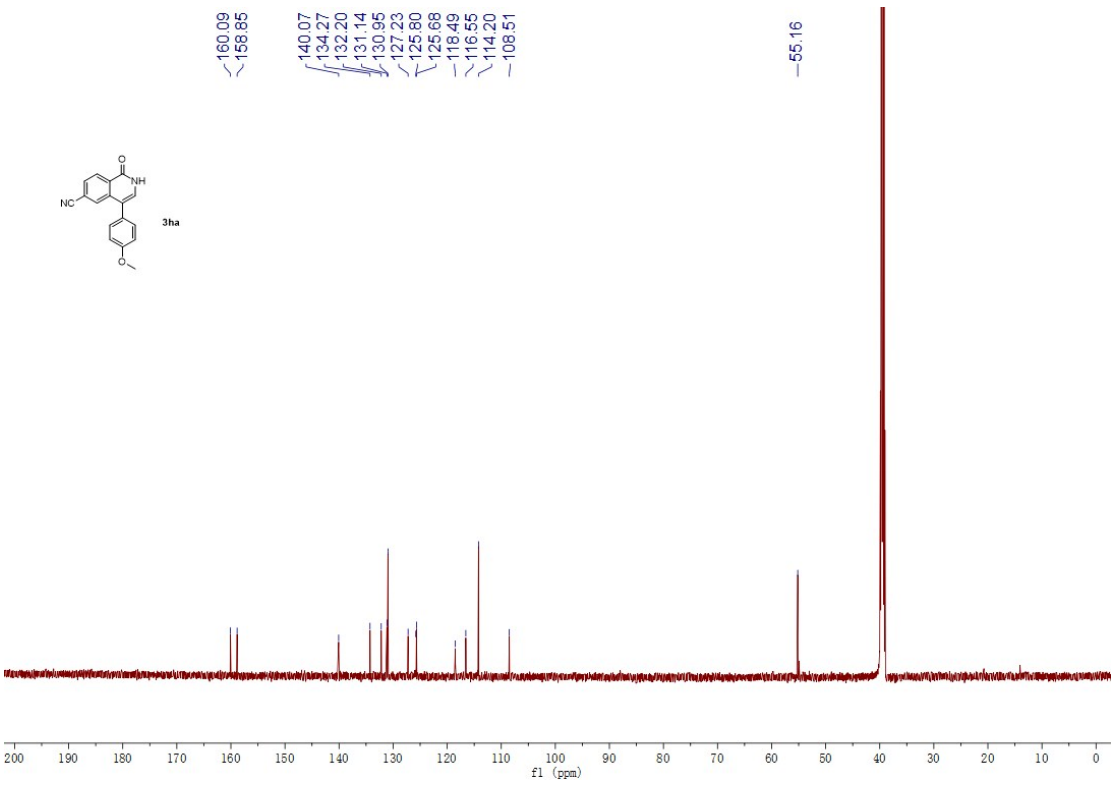
128.93
128.26
128.04
127.72
125.65
124.87
123.71
117.59
114.88
55.65
40.40 DMSO
40.19 DMSO
39.77 DMSO
39.56 DMSO
3fa
f1 (ppm)

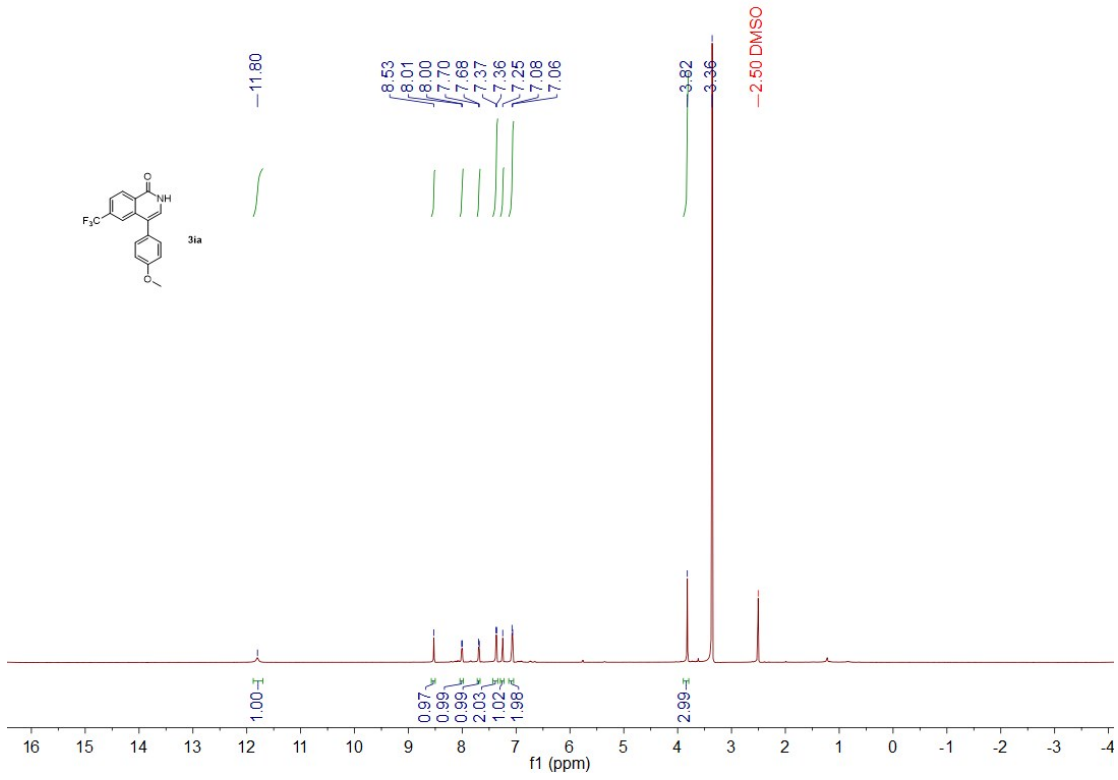

11.52
8.36
8.35
8.33
7.95
7.94
7.40
7.38
7.36
7.34
7.12
7.07
7.05
3.81
3.34
2.50
3ga
1.00
1.01
1.03
1.22
2.11
1.13
2.07
3.09
f1 (ppm)


163.75
161.05
159.25
131.30
130.62
130.53
129.52
128.23
123.21
116.96
115.68
115.47
115.23
114.72
109.79
109.56
55.64
O
NH
F
O
3ga
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-105.72
O
NH
F
O
3ga
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


11.85
8.61
8.03
8.02
7.61
7.60
7.35
7.34
7.27
7.07
7.06
3.81
3.37
2.50 DMSO
NC
NH
O
O
3ha
1.00
1.03
1.08
0.99
2.02
0.95
1.99
3.01
f1 (ppm)


160.09
158.85
140.07
134.27
132.20
131.14
130.95
127.23
125.80
125.68
118.49
116.55
114.20
108.51
55.16
NC
NH
O
O
3ha
f1 (ppm)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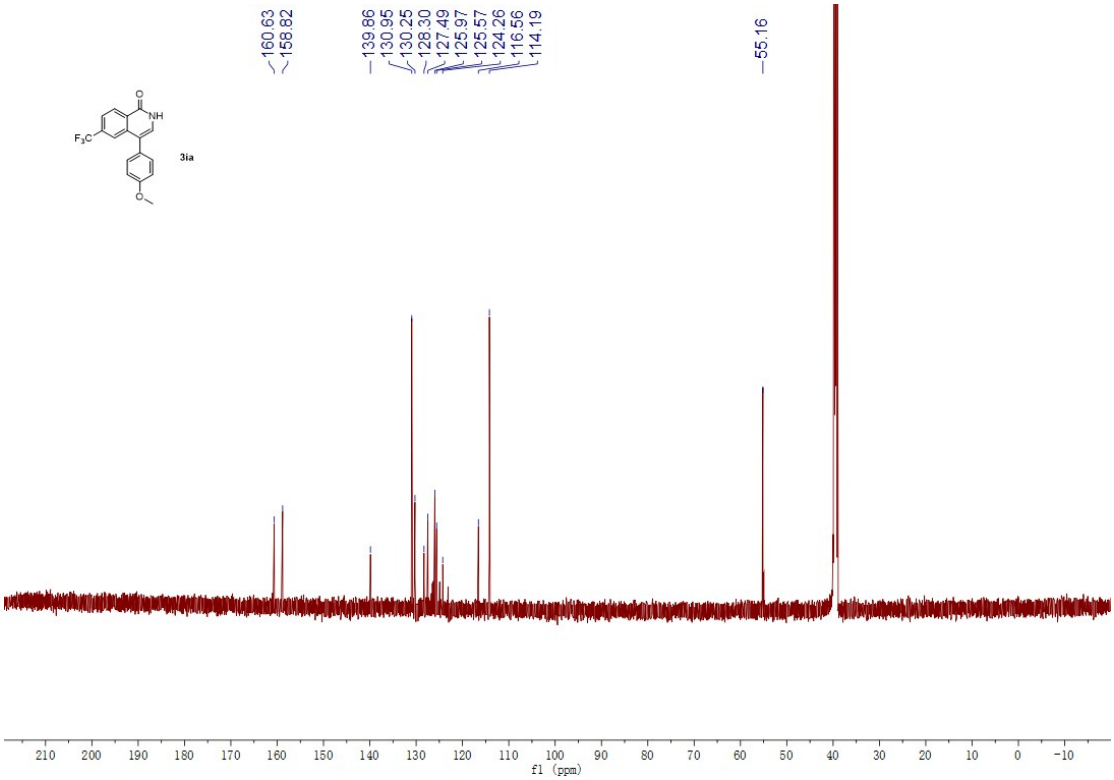
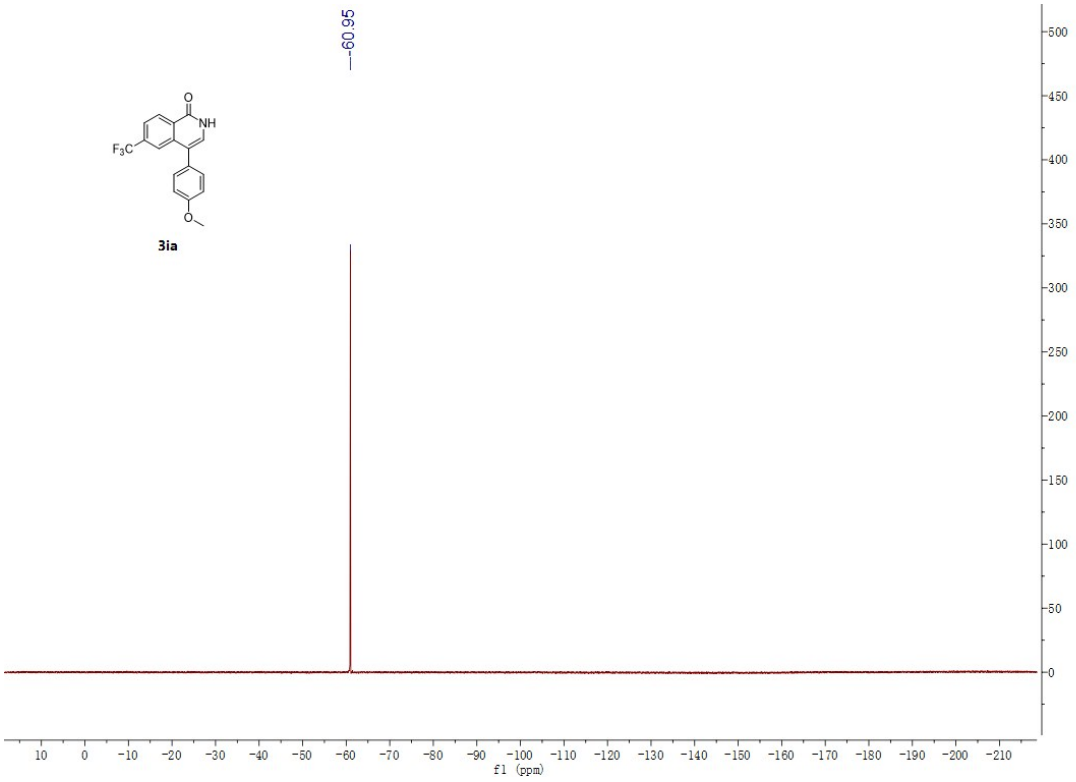
8.53
8.01
8.00
7.70
7.68
7.37
7.36
7.25
7.08
7.06
3.82
3.36
2.50 DMSO
3ia
1.00
0.97
0.99
0.99
2.03
1.02
1.98
2.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


160.63
158.82
139.86
130.95
130.25
128.30
127.49
125.97
125.57
124.26
116.56
114.19
55.16
3ia
f1 (ppm)


-60.95
3ia
f1 (ppm)