Supporting information

Oxidative cyanation of *N*-aryltetrahydroisoquinoline induced by visible light for the synthesis of α-aminonitrile using potassium thiocyanate as "CN" agent

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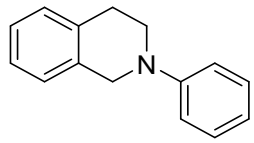
Table of Contents

General information

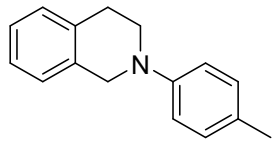
Commercially available reagents were used as received. All solvents were dried using 5Å molecular sieves. Chromatographic purification was performed by flash chromatography using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-AV instrument internally referenced to $SiMe_4$ and chloroform signals (400 MHz and 100 MHz, respectively). MS analyses were performed on a GCMS-QP 2010 Plus instrument (EI mode). All compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS and micro melting point tester. The bulbs used were all from online suppliers.

General procedure for the synthesis of 1

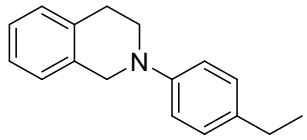
All substrates were synthesized by known methods[1]. Briefly, ethylene glycol (10 mmol, 0.6 mL), isopropanol (5 mL), 1,2,3,4-tetrahydroisoquinoline (5 mmol, 0.56 mL), iodobenzene (5 mmol), copper(I) iodide (0.5 mmol, 100 mg), potassium phosphate (10 mmol, 2.13 g) were added to a 50 mL Schlenk bottle, and the reaction was carried out at 90 ℃ for 24 h in a nitrogen atmosphere with magnetic stirring. After reaction completion, the content was cooled to room temperature and subject to extraction with ethyl acetate. The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography using silica gel.



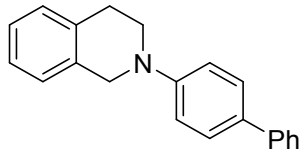
2-phenyl-1,2,3,4-tetrahydroisoquinoline (**1a**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.16 – 7.13 (m, 4H), 6.98 (dd, *J* = 8.5, 3.1 Hz, 2H), 6.82 (td, *J* = 7.3, 3.8 Hz, 1H), 4.40 (s, 2H), 3.55 (t, *J* = 5.4 Hz, 2H), 2.98 (t, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.5, 134.85, 134.4, 129.2, 128.5, 126.5, 126.3, 126.0, 118.63, 115.1, 50.7, 46.5, 29.1.



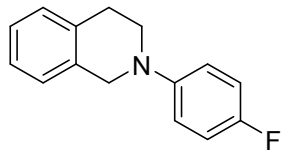
2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (**1b**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.08 (m, 6H), 6.91 (d, *J* = 8.3 Hz, 2H), 4.34 (s, 2H), 3.50 (t, *J* = 5.8 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.6, 134.7, 134.5, 129.7, 128.6, 128.4, 126.5, 126.2, 125.9, 115.8, 51.4, 47.2, 29.0, 20.4.



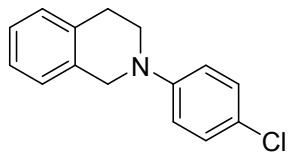
2-(4-ethylphenyl)-1,2,3,4-tetrahydroisoquinoline (**1c**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.07 (m, 6H), 6.93 (d, *J* = 8.5 Hz, 2H), 4.36 (s, 2H), 3.51 (t, *J* = 5.8 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.8, 134.8, 134.8, 134.6, 128.6, 128.5, 126.5, 126.2, 125.9, 115.7, 51.4, 47.1, 29.1, 27.9, 15.8.



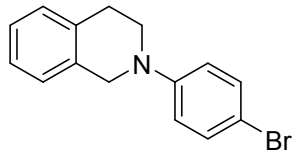
2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroisoquinoline (**1d**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.51 (m, 4H), 7.41 – 7.37 (m, 2H), 7.28 – 7.15 (m, 5H), 7.05 – 7.00 (m, 2H), 4.45 (s, 2H), 3.59 (t, *J* = 5.9 Hz, 2H), 2.99 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.7, 141.0, 134.9, 134.3, 131.1, 128.7, 128.5, 127.8, 126.5, 126.4, 126.4, 126.2, 126.1, 115.0, 50.5, 46.2, 29.1.



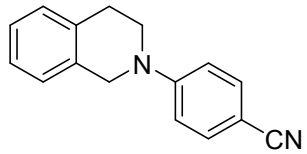
2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1e**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.12 (m, 4H), 7.01 – 6.90 (m, 4H), 4.32 (s, 2H), 3.47 (t, *J* = 5.8 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.7 (d, *J* = 236.0 Hz), 147.3 (d, *J* = 1.0 Hz), 134.5, 134.2, 128.6, 126.5, 126.3, 126.0, 117.1 (d, *J* = 7.0 Hz), 115.6 (d, *J* = 22.0 Hz), 51.9, 47.8, 29.0.



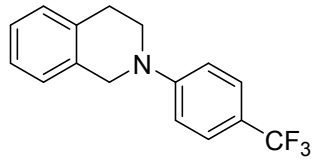
2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1f**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.12 (m, 6H), 6.90 – 6.82 (m, 2H), 4.36 (s, 2H), 3.51 (t, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.0, 134.6, 134.0, 129.0, 128.5, 126.5, 126.4, 126.1, 123.2, 116.1, 50.6, 46.5, 28.9.



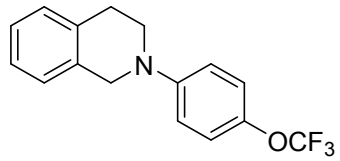
2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (**1g**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.28 (m, 2H), 7.24 – 7.04 (m, 4H), 6.87 – 6.75 (m, 2H), 4.36 (s, 2H), 3.52 (t, *J* = 5.9 Hz, 2H), 2.96 (t, *J* = 5.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.4, 134.7, 134.0, 131.9, 128.5, 126.5, 126.1, 116.4, 110.4, 50.4, 46.3, 28.9.



4-(3,4-dihydroisoquinolin-2(1H)-yl)benzonitrile (**1h**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 9.0 Hz, 2H), 7.24 – 7.16 (m, 4H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.48 (s, 2H), 3.62 (t, *J* = 5.9 Hz, 2H), 2.98 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.1, 134.8, 133.5, 133.3, 128.1, 126.9, 126.5, 126.4, 120.4, 112.6, 98.5, 48.7, 44.5, 28.9.

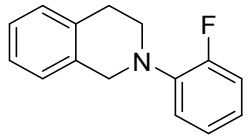


2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (**1i**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 8.7 Hz, 2H), 7.22 – 7.15 (m, 4H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.45 (s, 2H), 3.60 (t, *J* = 5.9 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.1, 134.9, 133.8, 128.3, 126.7, 126.5 (q, *J* = 4.0 Hz), 126.3, 125.0 (q, *J* = 268.6 Hz), 119.0 (q, *J* = 32.5 Hz), 112.9, 49.4, 45.2, 28.9.

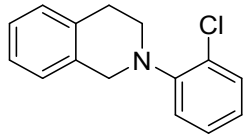


2-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroisoquinoline (**1j**), ^{1}H NMR

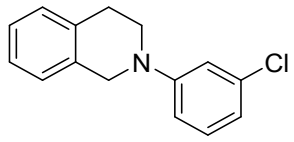
(400 MHz, Chloroform-*d*) δ 7.20 – 7.12 (m, 6H), 6.94 – 6.86 (m, 2H), 4.38 (s, 2H), 3.53 (t, *J* = 5.9 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.2, 141.1 (d, *J* = 1.0 Hz), 134.7, 134.0, 128.5, 126.5, 126.2, 122.1, 118.2 (q, *J* = 253.7 Hz), 115.3, 50.6, 46.5, 29.0.



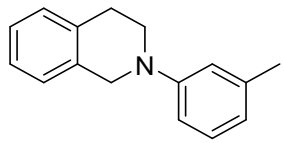
2-(2-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1k**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.11 (m, 3H), 7.11 – 6.95 (m, 4H), 6.94 – 6.89 (m, 1H), 4.29 (s, 2H), 3.43 (t, *J* = 5.9 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.7 (d, J = 244.0 Hz), 139.8 (d, *J* = 9.0 Hz), 134.4, 134.4, 128.9, 126.3, 126.3 125.9, 124.4 (d, *J* = 3.0 Hz), 122.2 (d, *J* = 8.0 Hz), 119.4 (d, *J* = 3.0 Hz), 116.1 (d, *J* = 21.0 Hz), 52.6 (d, *J* = 2.0 Hz), 48.9 (d, *J* = 5.0 Hz), 28.9.



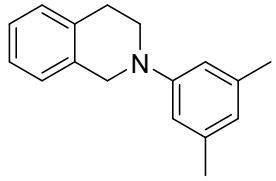
2-(2-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1l**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.07 (m, 6H), 6.97 (t, *J* = 7.6 Hz, 1H), 4.26 (s, 2H), 3.38 (t, *J* = 5.6 Hz, 2H), 3.01 (t, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.1, 134.7, 134.5, 130.7, 128.9, 128.8, 127.5, 126.3, 126.3, 125.8, 123.6, 120.6, 53.2, 49.9, 29.1.



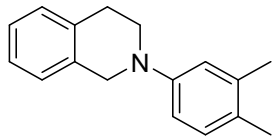
2-(3-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (**1m**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.10 (m, 5H), 6.88 (t, *J* = 2.1 Hz, 1H), 6.78 – 6.73 (m, 2H), 4.35 (s, 2H), 3.49 (t, *J* = 5.9 Hz, 2H), 2.93 (t, *J* = 5.9 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.3, 135.0, 134.7, 133.9, 130.0, 128.3, 126.4, 126.1, 117.9, 114.3, 112.5, 49.9, 45.8, 29.0.



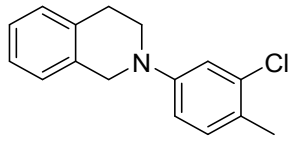
2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline (**1n**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.11 (m, 5H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.65 (d, *J* = 7.4 Hz, 1H), 4.38 (s, 2H), 3.53 (t, *J* = 5.8 Hz, 2H), 2.96 (t, *J* = 5.8 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.6, 138.8, 134.9, 134.5, 129.0, 128.5, 126.5, 126.2, 125.9, 119.6, 115.9, 112.3, 50.8, 46.5, 29.2, 21.8.



2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (**1o**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 – 7.12 (m, 4H), 6.62 (s, 2H), 6.50 (s, 1H), 4.37 (s, 2H), 3.52 (t, *J* = 5.8 Hz, 2H), 2.97 (t, *J* = 5.8 Hz, 2H), 2.30 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.7, 138.7, 134.9, 134.6, 128.5, 126.5, 126.2, 125.9, 120.7, 113.1, 50.9, 46.6, 29.3, 21.7.



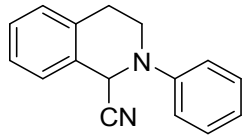
2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (**1p**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.10 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.76 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.34 (s, 2H), 3.49 (t, *J* = 5.9 Hz, 2H), 2.97 (t, *J* = 5.9 Hz, 2H), 2.25 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.1, 137.1, 134.7, 134.6, 130.2, 128.6, 127.2, 126.5, 126.2, 125.87, 117.5, 113.3, 51.5, 47.3, 29.2, 20.3, 18.7.



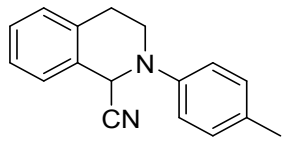
2-(3-chloro-4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (**1q**), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.05 (m, 5H), 6.94 (d, *J* = 2.6 Hz, 1H), 6.76 (dd, *J* = 8.4, 2.6 Hz, 1H), 4.33 (s, 2H), 3.48 (t, *J* = 5.8 Hz, 2H), 2.95 (t, *J* = 5.8 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.6, 134.8, 134.6, 134.1, 131.1, 128.5, 126.5, 126.4, 126.1, 125.5, 115.5, 113.6, 50.7, 46.5, 29.0, 18.9.

General procedure for the synthesis of 3

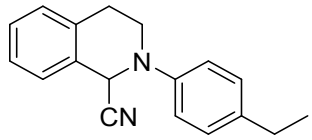
N-Aryltetrahydroisoquinoline (0.2 mmol), potassium thiocyanate (0.1 mmol, 9.75 mg), and acetonitrile (1.5 mL) were added to a round bottom flask of 10 mL equipped with a small polytetrafluoroethylene magnet stirrer. Then the round bottom flask was sealed with a rubber plug that was fixed with inlet and outlet tubes for thorough removal of air and introduction of O_2 (three times). The round bottom flask with its content was then properly sealed and placed under purple LEDs irradiation (30 W) with magnetic stirring for 24 h. After reaction completion, the content was filtered through a sand core funnel. The filtrate was concentrated and purified by silica gel column chromatography to obtain the corresponding product using a mixture of petroleum ether and ethyl acetate as eluent.



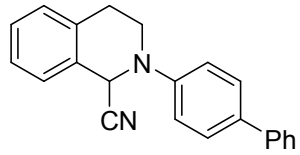
2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3a**)[2, 3-5], white solid, m.p. 99-100 ℃, 92% yield (21.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.30 (m, 2H), 7.28 – 7.16 (m, 4H), 7.04 (d, *J* = 7.9 Hz, 2H), 7.00 – 6.95 (m, 1H), 5.47 (s, 1H), 3.74 – 3.68 (m, 1H), 3.40 (ddd, *J* = 12.4, 10.7, 4.0 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.88 (dt, *J* = 16.3, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.1, 134.4, 129.4, 129.3, 129.2, 128.6, 126.9, 126.7, 121.7, 117.7, 117.3, 52.9, 43.9, 28.3. MS (EI) m/z (%) 234.00, 206.00, 181.00, 129.00, 105.00 (100), 77.00, 51.00.



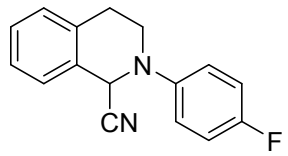
2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3b**)[3-5], white solid, m.p. 117-118 ℃, 79% yield (19.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 4H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.5 Hz, 2H), 5.45 (s, 1H), 3.72 – 3.67 (m, 1H), 3.43 (ddd, *J* = 12.3, 11.1, 4.0 Hz, 1H), 3.19 – 3.11 (m, 1H), 2.93 (dt, *J* = 16.3, 3.1 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.2, 134.5, 131.8, 130.0, 129.5, 129.3, 128.6, 127.0, 126.7, 118.3, 117.7, 54.1, 44.3, 28.5, 20.6. MS (EI) m/z (%) 248.05, 220.00 (100), 204.00, 119.05, 91.00, 65.00, 51.00.



2-(4-ethylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3c**)[3], white solid, m.p. 133-134 ℃, 86% yield (22.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 3H), 7.23 – 7.18 (m, 3H), 7.05 – 7.02 (m, 2H), 5.46 (s, 1H), 3.74 – 3.68 (m, 1H), 3.44 (ddd, *J* = 12.2, 11.0, 4.0 Hz, 1H), 3.19 – 3.10 (m, 1H), 2.94 (dt, *J* = 16.3, 2.8 Hz, 1H), 2.61 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.3, 138.1, 134.5, 129.6, 129.3, 128.9, 128.6, 127.0, 126.7, 118.2, 117.7, 53.9, 44.3, 28.5, 28.0, 15.7. MS (EI) m/z (%) 262.05, 234.05 (100), 219.00, 204.00, 133.05, 103.00, 77.00, 51.00.

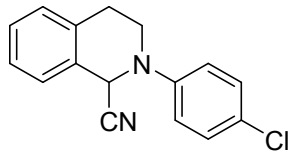


2-([1,1'-biphenyl]-4-yl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3d**)[3], white solid, m.p. 169-170 ℃, 62% yield (19.2 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (t, *J* = 8.9 Hz, 4H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.23 (m, 5H), 7.14 (d, *J* = 8.5 Hz, 2H), 5.56 (s, 1H), 3.85 – 3.80 (m, 1H), 3.52 (ddd, *J* = 12.0, 11.1, 3.9 Hz, 1H), 3.21 – 3.13 (m, 1H), 2.98 (dt, *J* = 16.3, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.5, 140.5, 134.6, 134.5, 129.4, 129.3, 128.8, 128.7, 128.2, 127.0, 126.9, 126.8, 126.7, 117.7, 117.5, 52.9, 44.2, 28.5. MS (EI) m/z (%) 310.05, 284.05 (100), 265.00, 204.00, 180.05, 141.00, 128.00, 103.00, 77.00, 51.00.

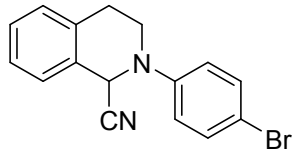


2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3e**)[2, 3-4], white solid, m.p. 124-125 ℃, 76% yield (19.2 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.22 (m, 4H), 7.07 (d, *J* = 6.1 Hz, 4H), 5.40 (s, 1H), 3.62 (dd, *J* = 11.9, 5.5 Hz, 1H), 3.44 (td, *J* = 11.7, 3.9 Hz, 1H), 3.20 – 3.12 (m, 1H), 2.95 (dt, *J* = 16.6, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.5 (d, *J* = 240.0 Hz), 145.0 (d, *J* = 2.4 Hz), 134.2, 129.4, 129.3, 128.8, 127.0, 126.8, 120.4 (d, *J* = 8.0 Hz), 117.4, 116.1 (d, *J* = 23.0 Hz), 54.7, 44.7, 28.5. MS (EI) m/z (%) 252.00, 224.00, 199.00, 129.05 (100),

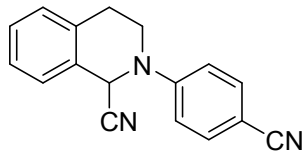
95.00, 75.00, 51.00.



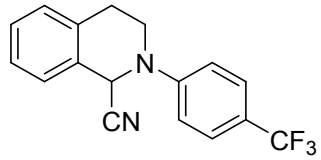
2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3f**)[2, 4-5], white solid, m.p. 152-153 ℃, 83% yield (22.2 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 5H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 5.46 (s, 1H), 3.73 – 3.68 (m, 1H), 3.46 (td, *J* = 11.5, 4.0 Hz, 1H), 3.19 – 3.11 (m, 1H), 2.97 (dt, *J* = 16.3, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.9, 134.3, 129.5, 129.3, 129.2, 128.9, 127.0, 126.9, 118.8, 117.4, 53.1, 44.3, 28.4. MS (EI) m/z (%) 268.00, 240.00 (100), 204.00, 165.05, 139.00, 129.05, 102.05, 75.00, 51.00.



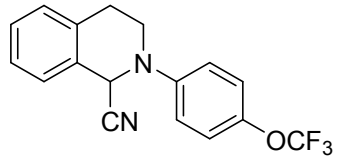
2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3g**)[2,3-4], white solid, m.p. 155-156 ℃, 61% yield (19 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.43 (m, 2H), 7.34 – 7.23 (m, 4H), 6.97 – 6.93 (m, 2H), 5.46 (s, 1H), 3.74 – 3.68 (m, 1H), 3.46 (ddd, *J* = 12.3, 10.7, 4.1 Hz, 1H), 3.19 – 3.10 (m, 1H), 2.97 (dt, *J* = 16.3, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.3, 134.4, 132.4, 129.3, 129.1, 128.9, 127.0, 126.9, 119.0, 117.4, 114.3, 52.8, 44.2, 28.4. MS (EI) m/z (%) 311.95, 285.95, 206.00, 182.90, 154.90, 129.00 (100), 102.00, 76.00, 51.00.



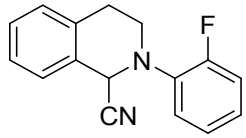
2-(4-cyanophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3h**)[6], white solid, m.p. 155-156 ℃, 83% yield (21.5 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (dd, *J* = 8.8, 1.7 Hz, 2H), 7.39 – 7.26 (m, 4H), 7.02 (dd, *J* = 8.7, 1.6 Hz, 2H), 5.60 (s, 1H), 3.91 – 3.78 (m, 1H), 3.63 – 3.56 (m, 1H), 3.19 – 3.07 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.5, 134.6, 133.8, 129.3, 129.0, 128.7, 127.3, 126.9, 119.4, 117.3, 114.6, 102.4, 50.0, 43.7, 28.1. MS (EI) m/z (%) 259.05, 231.05, 190.5, 129.05 (100), 102.05, 77.00, 51.00.



2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3i**)[4, 5], white solid, m.p. 102-103 ℃, 88% yield (26.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.23 (m, 4H), 7.07 (d, *J* = 8.5 Hz, 2H), 5.57 (s, 1H), 3.83 (dt, *J* = 12.4, 5.0 Hz, 1H), 3.53 (ddd, *J* = 12.6, 9.6, 4.4 Hz, 1H), 3.18 – 3.10 (m, 1H), 3.02 (dt, *J* = 16.2, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.2, 134.5, 129.2, 129.1, 128.93, 127.1, 127.0, 126.8 (q, *J* = 3.6 Hz), 124.4 (q, *J* = 269.3 Hz), 122.4 (q, *J* = 32.7 Hz), 117.5, 115.2, 51.1, 43.8, 28.2. MS (EI) m/z (%) 302.00, 274.00, 172.00, 145.00, 129.05 (100), 102.00, 77.00, 51.00.

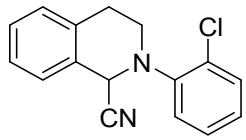


2-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3j**)[2], white solid, m.p. 83-84 ℃, 81% yield (25.8 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.20 (m, 6H), 7.07 (d, *J* = 8.9 Hz, 2H), 5.47 (s, 1H), 3.75 – 3.70 (m, 1H), 3.48 (td, *J* = 12.0, 11.4, 4.0 Hz, 1H), 3.19 – 3.11 (m, 1H), 2.98 (dt, *J* = 16.3, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.0, 143.5 (d, *J* = 1.7 Hz), 134.3, 129.3, 129.1, 128.9, 127.0 (d, *J* = 3.3 Hz), 122.4, 120.5 (q, *J* = 254.9 Hz) 118.4, 117.4, 53.1, 44.4, 28.4. MS (EI) m/z (%) 318.05, 290.00, 265.00, 233.00, 208.00, 189.00, 161.00, 129.05 (100), 90.00, 77.00, 51.00.

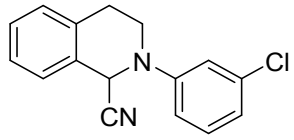


2-(2-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3k**)[2,4], colorless oily liquid, 77% yield (19.4 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 1H), 7.26 – 7.15 (m, 5H), 7.13 – 7.09 (m, 2H), 5.48 (s, 1H), 3.59 – 3.48 (m, 2H), 3.26 – 3.17 (m, 1H), 2.91 (dt, *J* = 16.7, 2.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0 (d, *J* = 245.0 Hz), 136.8 (d, *J* = 9.0 Hz), 133.9, 129.5, 129.2, 128.7, 127.0, 126.7, 125.0 (d, *J* = 3.0 Hz), 124.9, 121.4 (d, *J* = 2.0 Hz), 117.4, 116.4 (d, *J* = 20.0 Hz), 53.8, 53.8, 44.7, 28.5. MS (EI) m/z (%) 252.00, 224.00, 199.00,

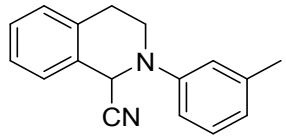
129.05 (100), 102.00, 77.00, 51.00.



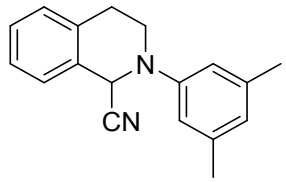
2-(2-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3l**)[2, 4], white solid, m.p. 115-116 ℃, 63% yield (16.9 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.26 – 7.21 (m, 3H), 7.15 – 7.11 (m, 1H), 5.53 (s, 1H), 3.61 (td, *J* = 11.9, 3.7 Hz, 1H), 3.45 (dd, *J* = 11.9, 6.3 Hz, 1H), 3.29 – 3.20 (m, 1H), 2.91 (dd, *J* = 16.4, 2.7 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.9, 134.1, 130.7, 129.7, 129.6, 129.4, 128.8, 128.2, 127.1, 126.7, 126.1, 123.2, 117.4, 53.9, 45.6, 28.8. MS (EI) m/z (%) 268.00, 239.95, 222.00, 203.95, 139.00, 129.05, (100), 102.00, 77.00, 51.00.



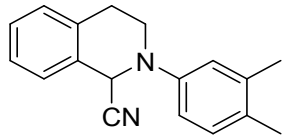
2-(3-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3m**)[2,4], colorless oily liquid, 67% yield (18 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.23 (m, 5H), 7.03 (t, *J* = 2.0 Hz, 1H), 6.98 – 6.92 (m, 2H), 5.49 (s, 1H), 3.78 – 3.72 (m, 1H), 3.48 (ddd, *J* = 12.4, 10.4, 4.2 Hz, 1H), 3.18 – 3.10 (m, 1H), 2.99 (dt, *J* = 16.3, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.3, 135.3, 134.4, 130.5 129.3, 129.1, 128.9, 127.0, 127.0, 121.4, 117.5, 117.1, 114.9, 52.3, 44.0, 28.3. MS (EI) m/z (%) 268.00, 239.95, 204.00, 165.00, 139.00, 129.05 (100), 102.00, 75.00, 51.00.



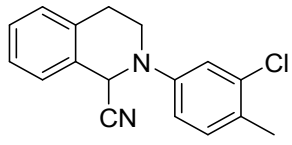
2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3n**)[2, 4-5], colorless oily liquid, 47% yield (11.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 5H), 6.90 – 6.88 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.51 (s, 1H), 3.79 – 3.73 (m, 1H), 3.46 (ddd, *J* = 12.3, 10.8, 4.0 Hz, 1H), 3.19 – 3.11 (m, 1H), 2.96 (dt, *J* = 16.3, 3.2 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.4, 139.4, 134.6, 129.7, 129.4, 129.3, 128.7, 127.0, 126.8, 122.8, 118.4, 117.8, 114.7, 53.3, 44.1, 28.6, 21.7. MS (EI) m/z (%) 248.00, 220.00, 119.00 (100), 204.00, 178.00, 91.00, 65.00, 51.00.



2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3o**), colorless oily liquid, 66% yield (17.3 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 4H), 6.68 (d, *J* = 14.1 Hz, 3H), 5.50 (s, 1H), 3.78 – 3.72 (m, 1H), 3.44 (ddd, *J* = 12.3, 11.1, 4.0 Hz, 1H), 3.18 – 3.10 (m, 1H), 2.94 (dt, *J* = 16.3, 3.1 Hz, 1H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.5, 139.1, 134.7, 129.8, 129.3, 128.6, 127.0, 126.8, 123.8, 117.8, 115.5, 53.4, 44.1, 28.6, 21.6. MS (EI) m/z (%) 262.05, 234.05 (100), 218.00, 133.05, 103.00, 77.00, 51.00.



2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3p**)[2], white solid, m.p. 145-146 ℃, 60% yield (15.7 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.21 (m, 4H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.90 – 6.83 (m, 2H), 5.46 (s, 1H), 3.73 – 3.67 (m, 1H), 3.43 (ddd, *J* = 12.3, 11.0, 4.0 Hz, 1H), 3.19 – 3.11 (m, 1H), 2.93 (dt, *J* = 16.3, 3.0 Hz, 1H), 2.27 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 146.6, 137.7, 134.5, 130.5, 129.7, 129.4, 128.6, 127.1, 126.7, 119.8, 117.7, 115.6, 54.1, 44.3, 28.6, 20.2, 18.9. MS (EI) m/z (%) 262.05, 234.00 (100), 218.00, 133.05, 105.05, 77.00, 51.00.



2-(3-chloro-4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (**3q**)[2], white solid, m.p. 128-129 ℃, 80% yield (22.6 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.18 (m, 5H), 7.07 (d, *J* = 2.6 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.6 Hz, 1H), 5.45 (s, 1H), 3.73 – 3.67 (m, 1H), 3.44 (ddd, *J* = 12.3, 10.7, 4.1 Hz, 1H), 3.18 – 3.10 (m, 1H), 2.96 (dt, *J* = 16.3, 3.3 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.4, 135.2, 134.4, 131.6, 129.3, 129.3, 129.3, 128.8, 127.0, 126.9, 118.4, 117.4, 116.0, 53.2, 44.2, 28.4, 19.1. MS (EI) m/z (%) 282.00, 254.00 (100), 247.00, 218.00,

178.05, 153.00, 129.00, 89.00, 77.00, 51.00.

References

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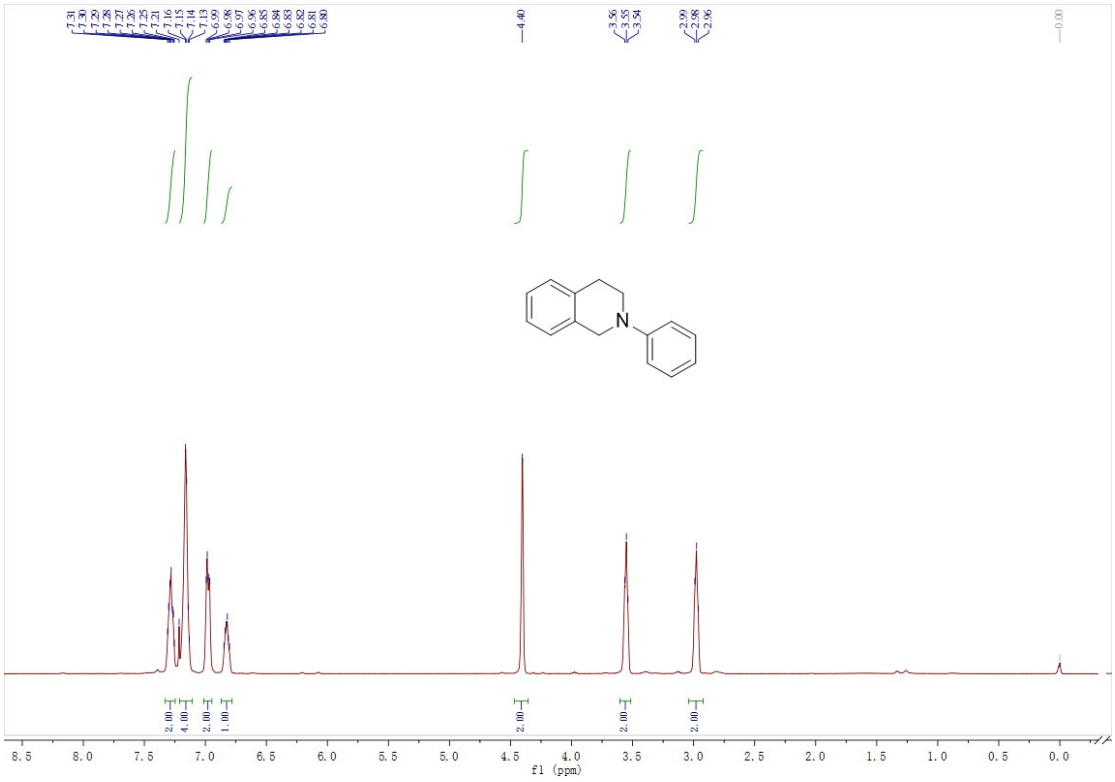
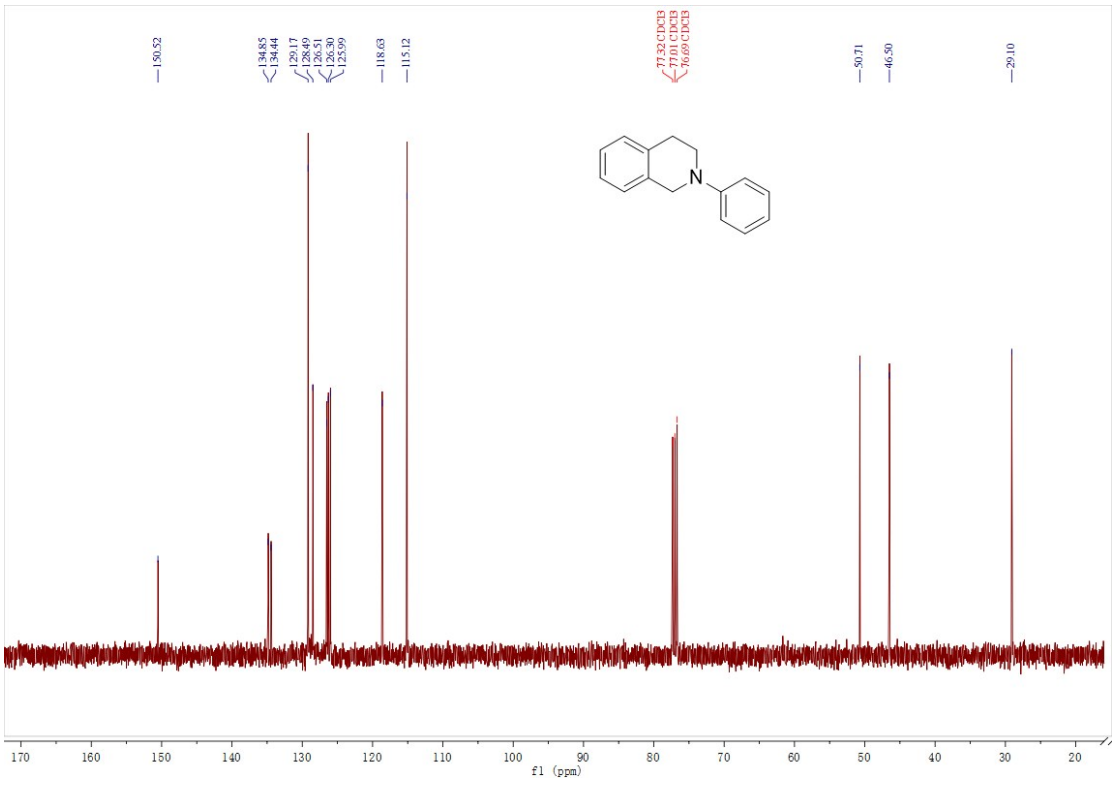
Copies of ^{1}H and ^{13}C NMR spectra of all substrates



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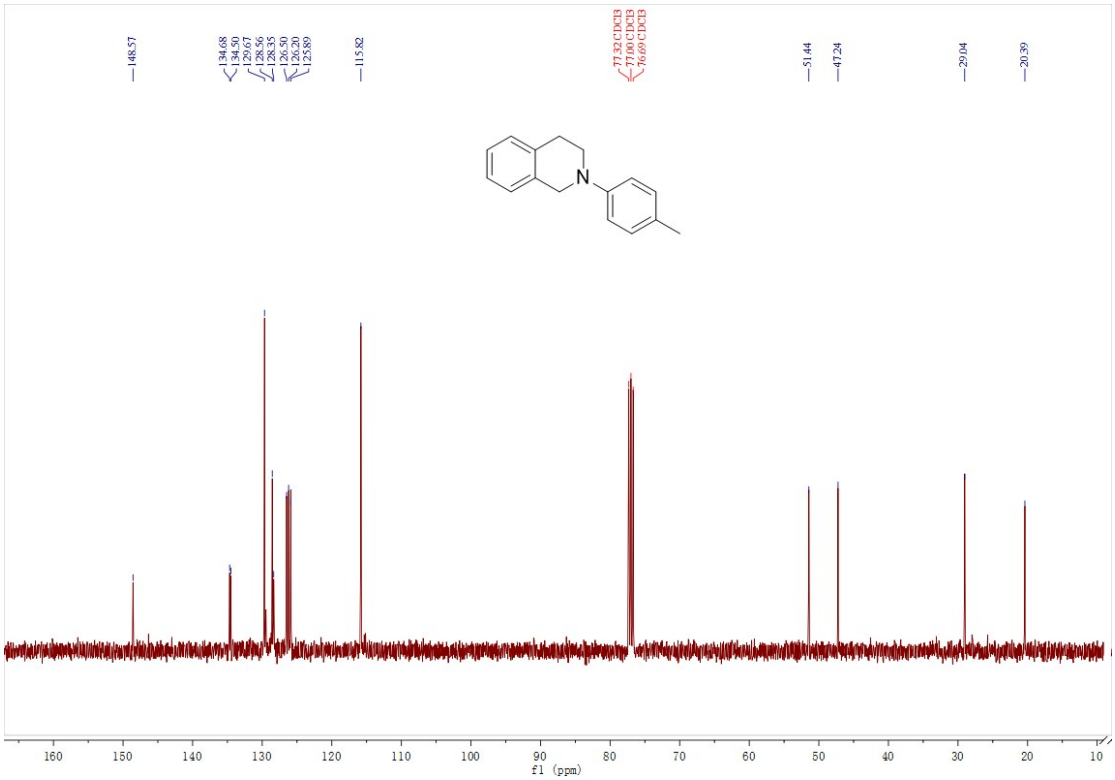
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80
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20
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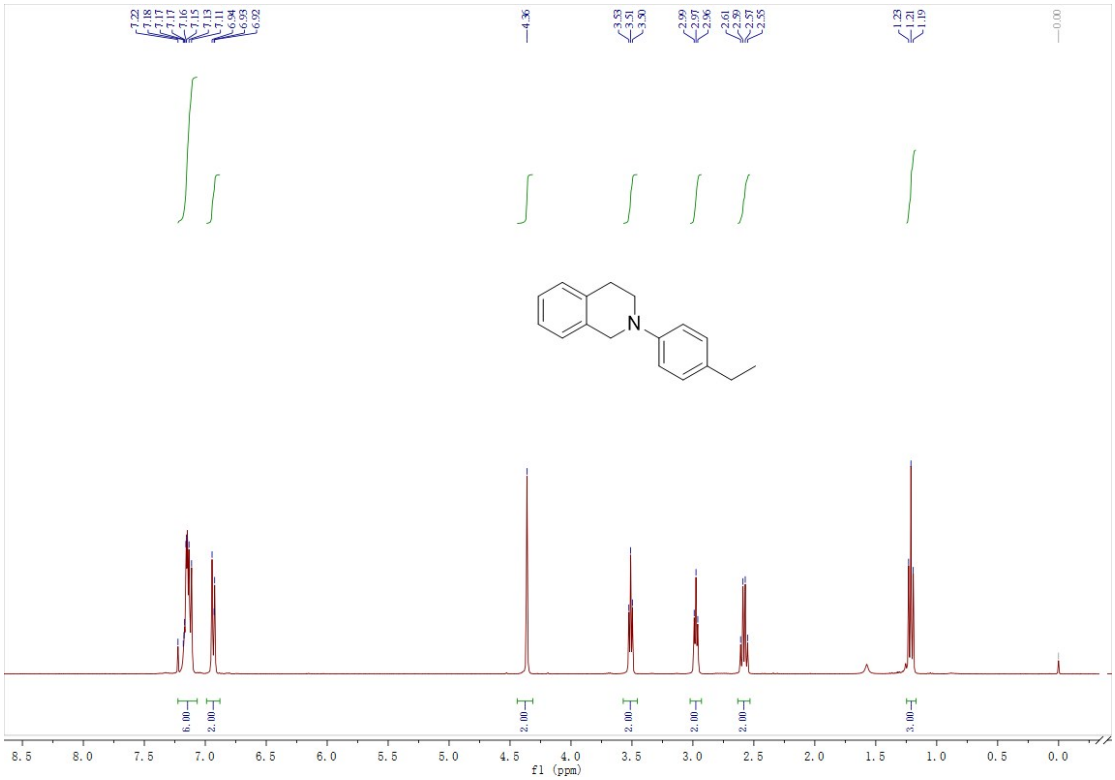
f1 (ppm)
N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7.11
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6.93
6.92
4.36
3.53
3.51
3.50
2.99
2.97
2.96
2.61
2.59
2.57
2.55
1.23
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1.19
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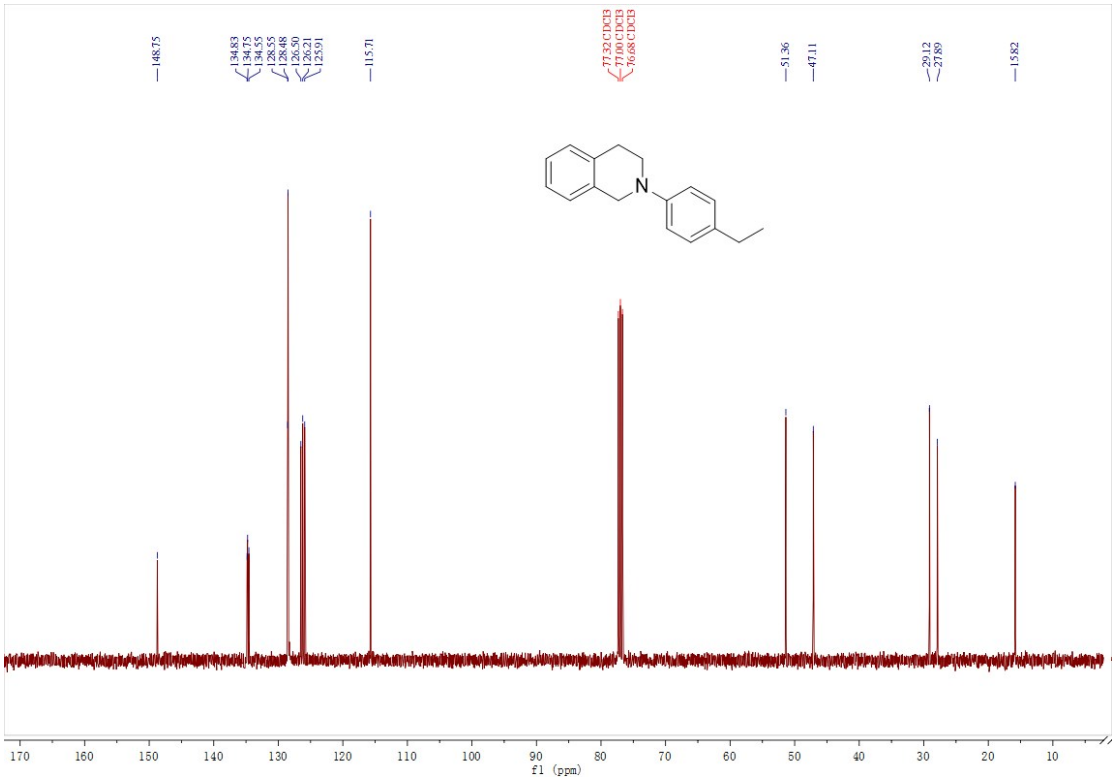
N
6.00
2.00
2.00
2.00
2.00
2.00
3.00
f1 (ppm)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115.71
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77.00 CDCl3
76.68 CDCl3
51.36
47.11
29.12
27.89
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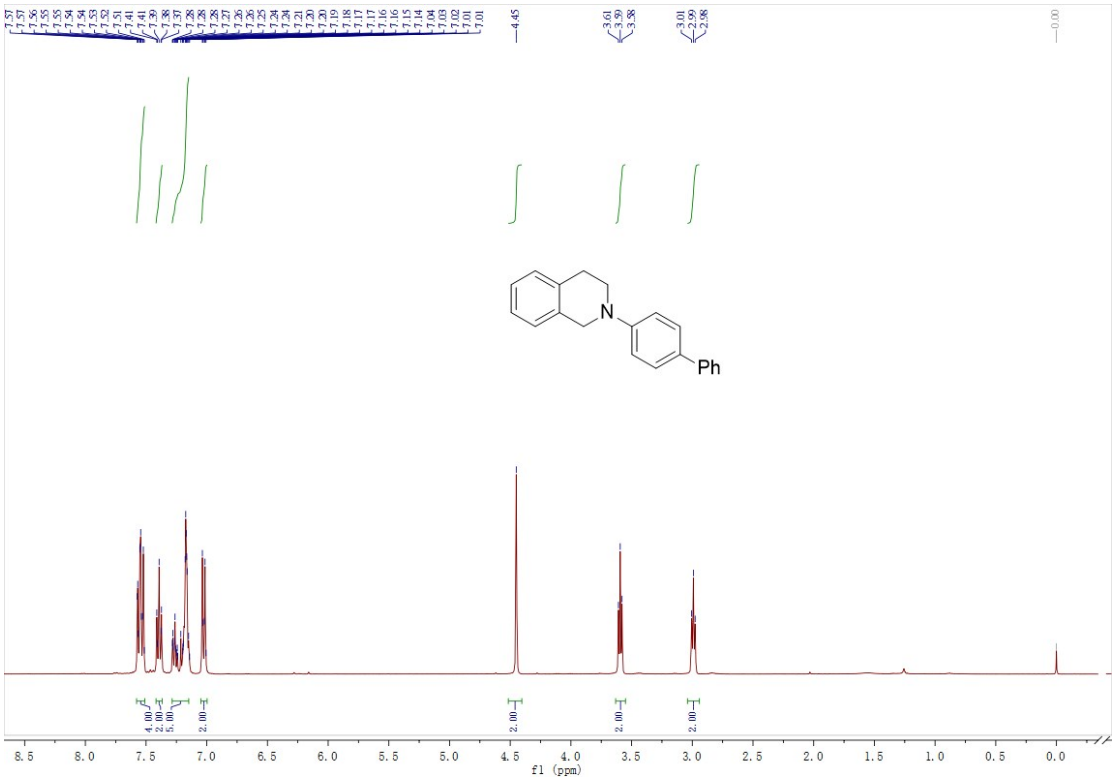
N
f1 (ppm)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7.37
7.28
7.28
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.21
7.20
7.20
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.04
7.03
7.02
7.01
7.01
4.45
3.61
3.60
3.58
3.01
2.99
2.98
0.00
N
Ph
4.00
2.00
5.00
2.00
2.00
2.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
1.5
1.0
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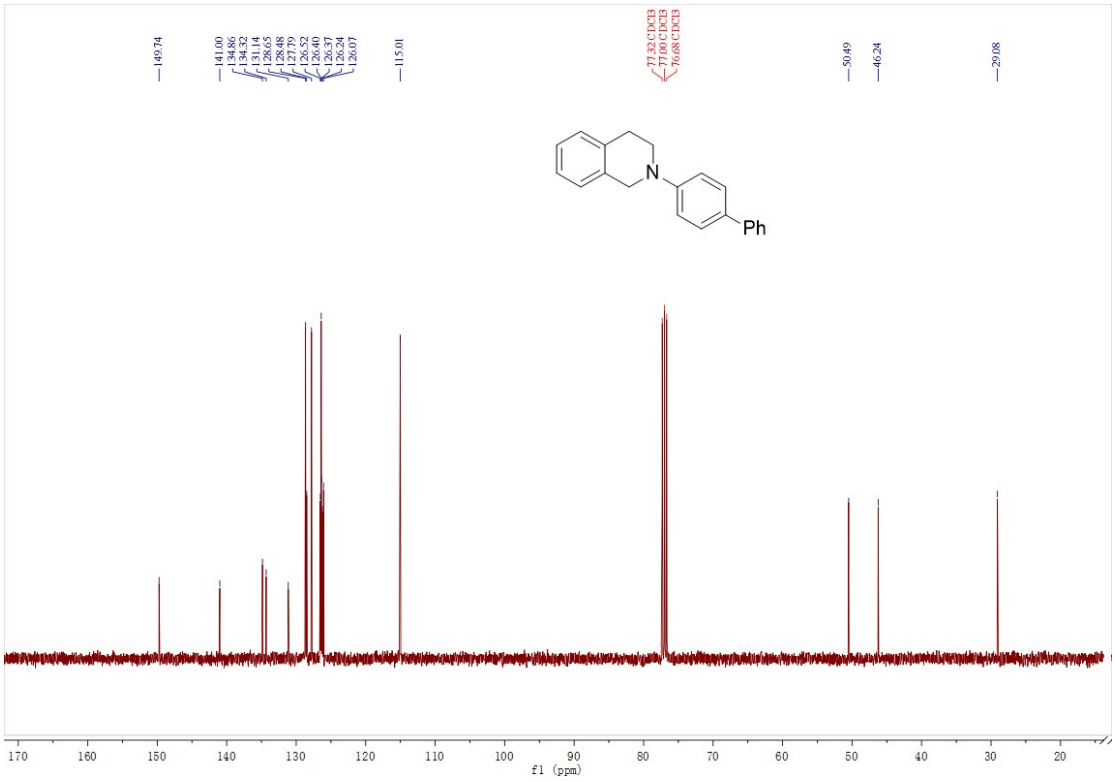
0.0
f1 (ppm)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126.24
126.07
115.01
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
50.49
46.24
29.08
N
Ph
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150
140
130
120
110
100
90
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70
60
50
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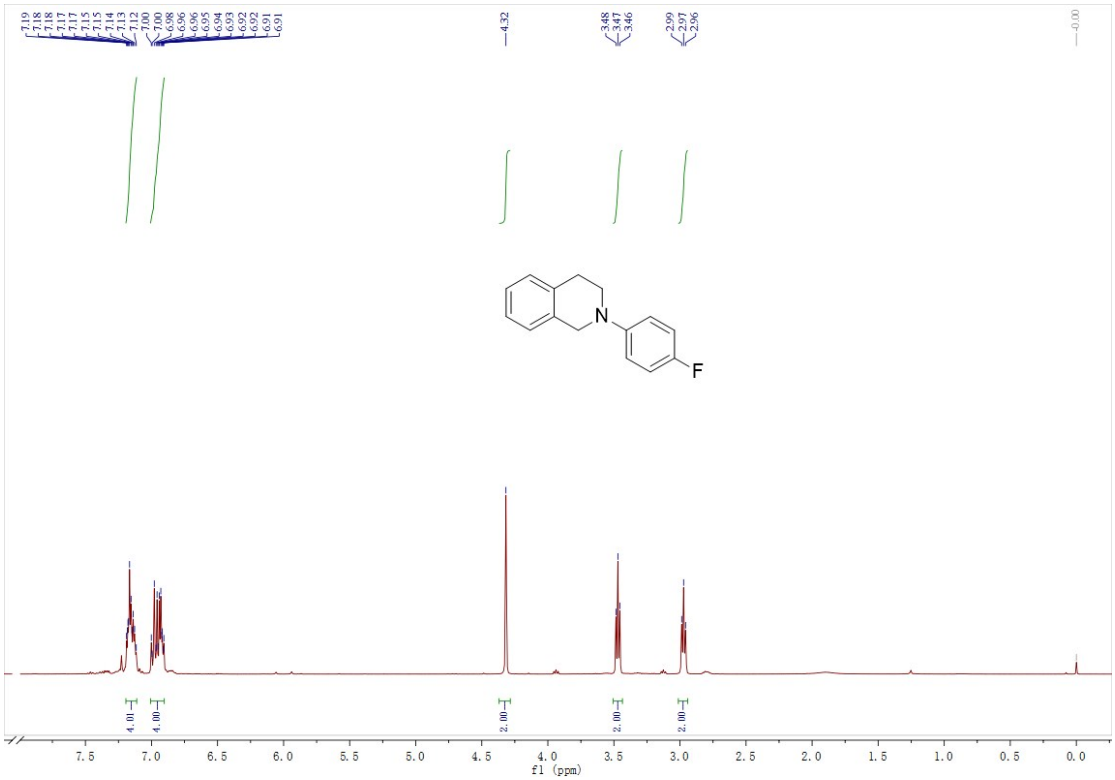
30
20
f1 (ppm)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7.15
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6.96
6.96
6.95
6.94
6.93
6.92
6.92
6.91
6.91
4.32
3.48
3.47
3.46
2.99
2.97
2.96
0.00
N
F
4.01
4.00
2.00
2.00
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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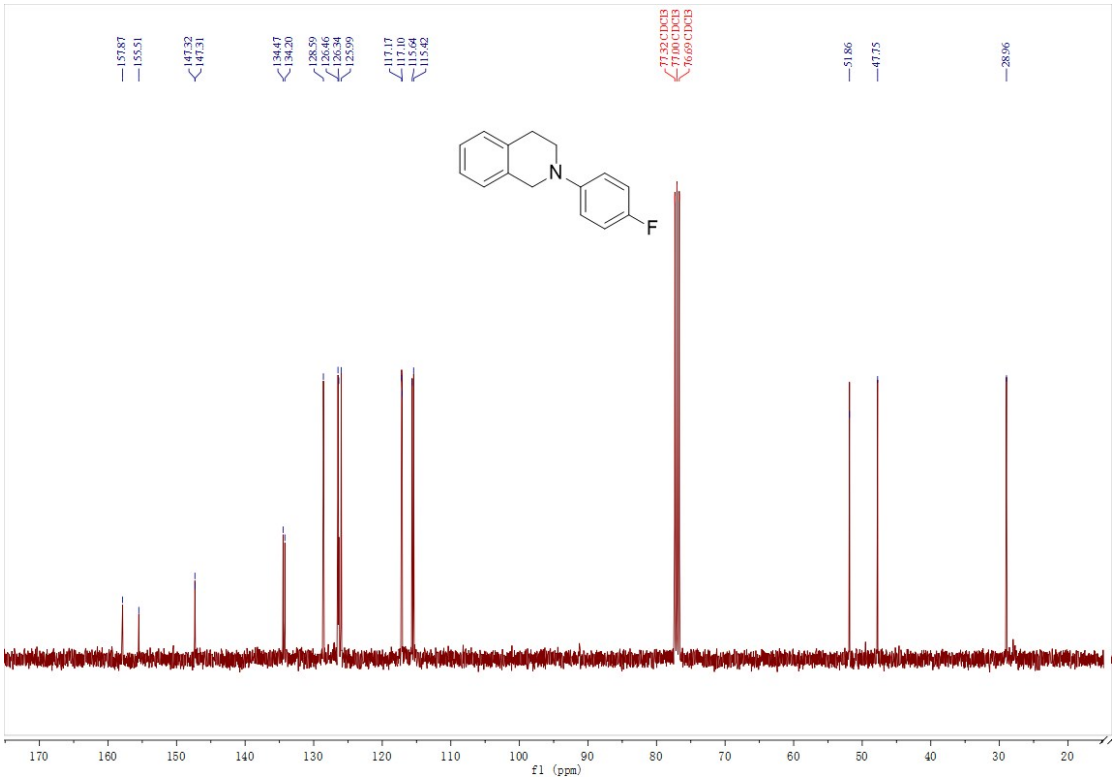
0.0
f1 (ppm)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134.20
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126.46
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125.99
117.17
117.10
115.64
115.42
77.32 CDCl3
77.00 CDCl3
76.69 CDCl3
51.86
47.75
28.96
N
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.12
6.88
6.87
6.86
6.85
4.36
3.52
3.51
3.49
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2.96
2.95
N
Cl
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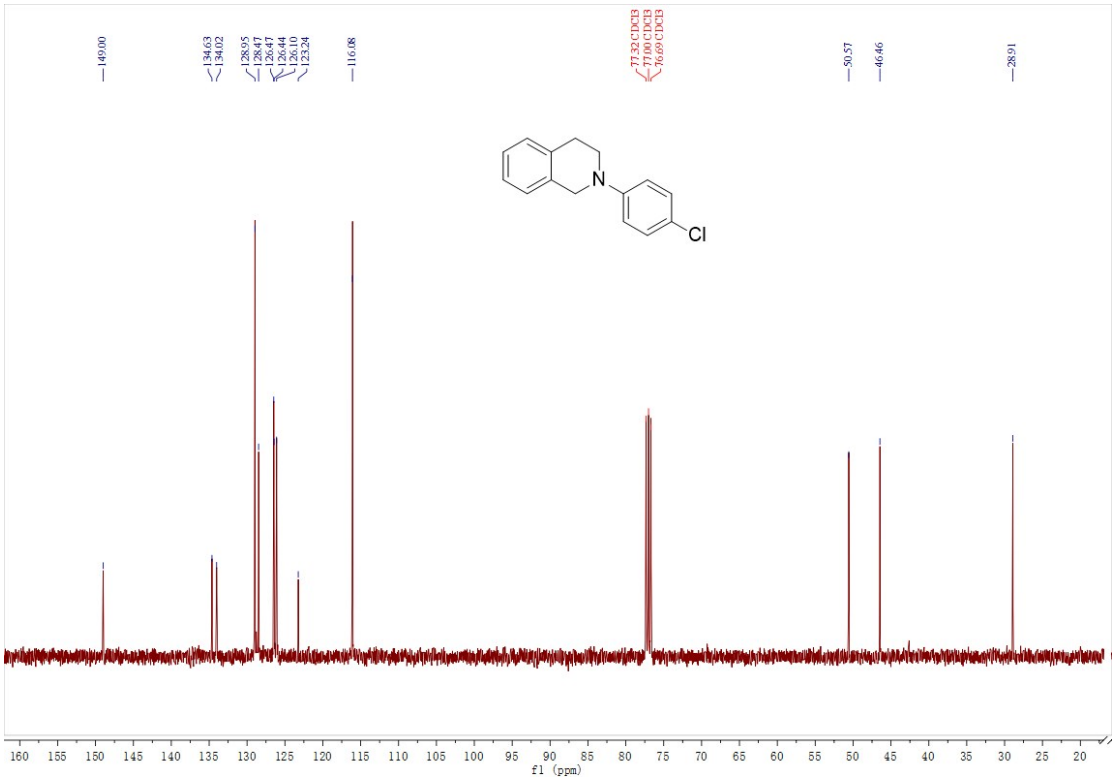
2.00
2.00
2.00
2.00
f1 (ppm)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126.44
126.10
123.24
116.08
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77.00 CDCl3
76.69 CDCl3
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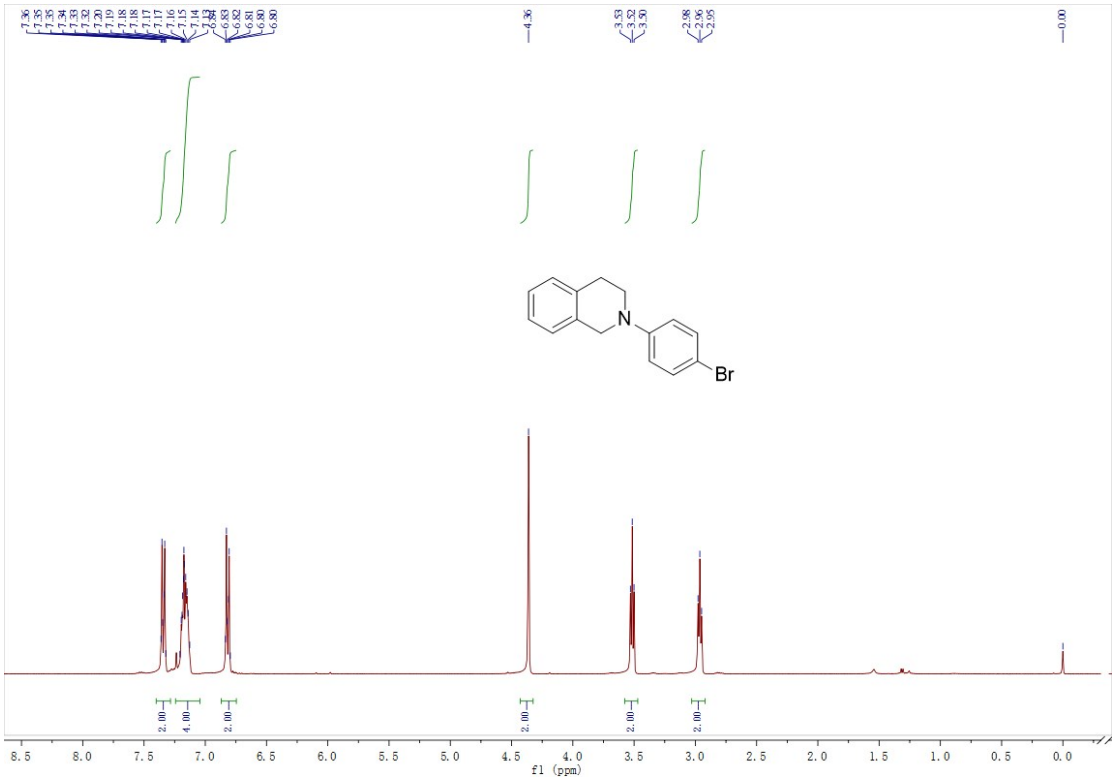
46.46
28.91
N
Cl
f1 (ppm)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7.18
7.17
7.17
7.16
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7.14
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6.82
6.81
6.80
6.80
4.36
3.93
3.92
3.90
2.98
2.96
2.95
0.00
N
Br
2.00
4.00
2.00
2.00
2.00
2.00
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
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1.0
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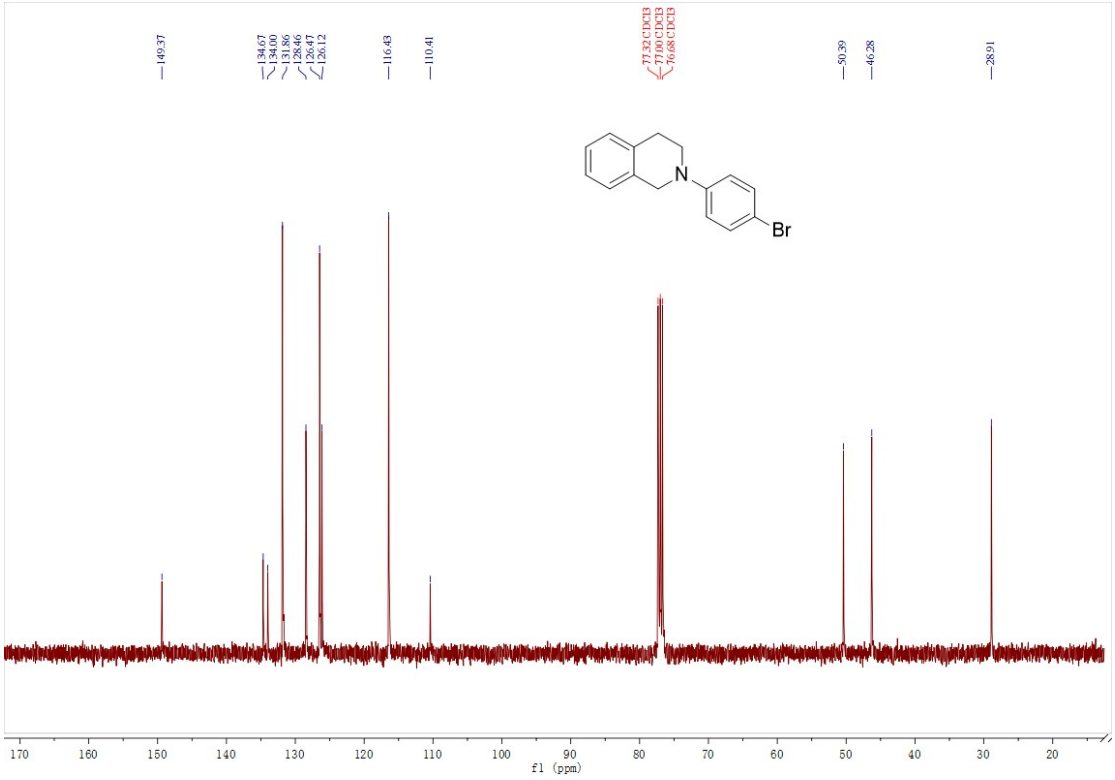
0.0
f1 (ppm)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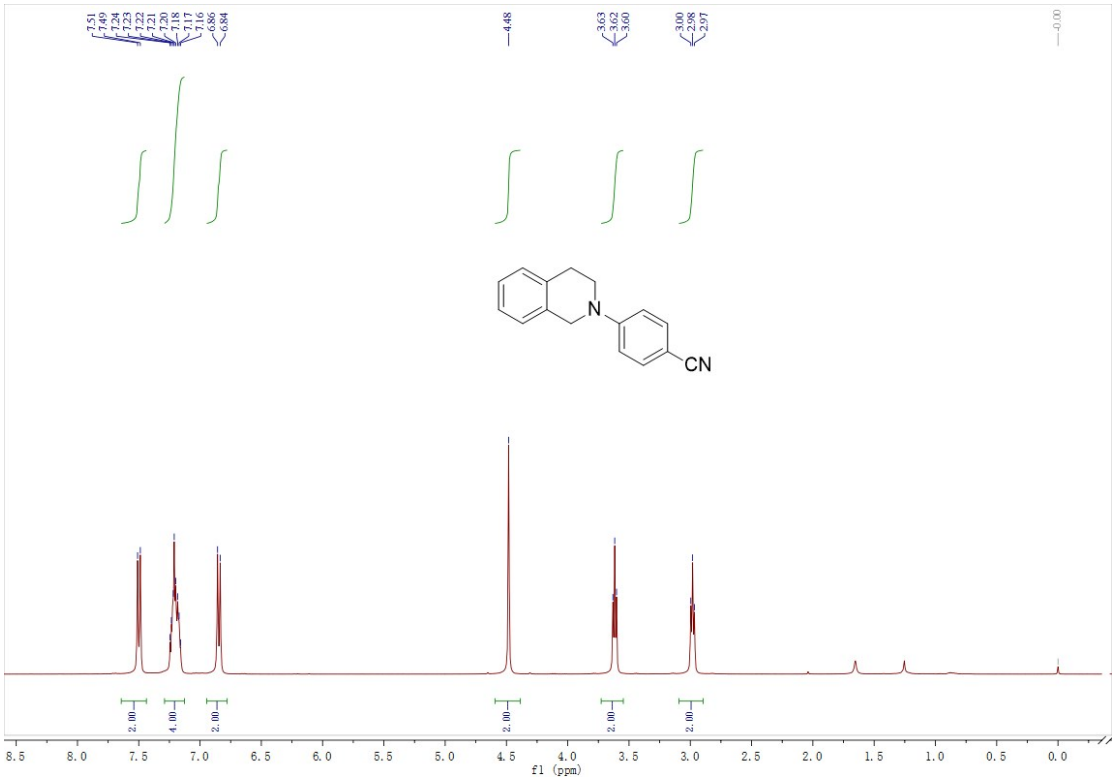
126.47
120.12
116.43
110.41
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
50.39
46.28
28.91
N
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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7.16
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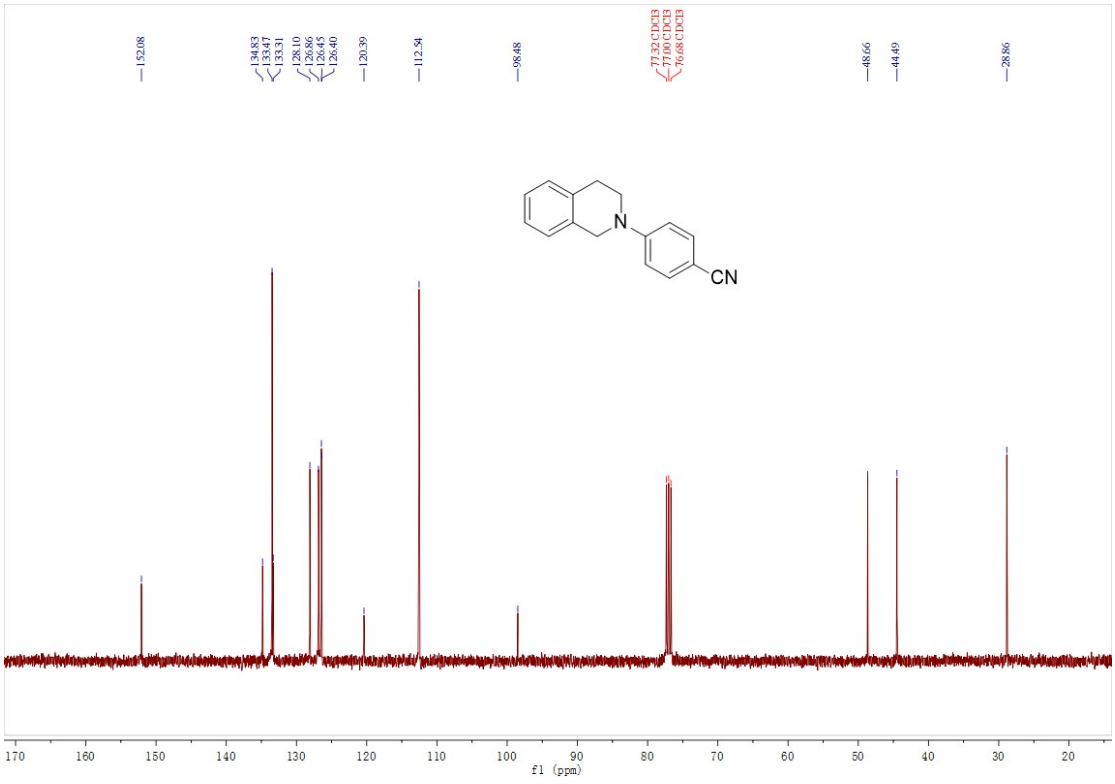
6.84
4.48
3.63
3.62
3.60
3.00
2.98
2.97
0.00
N
CN
2.00
4.00
2.00
2.00
2.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.10
126.86
126.45
126.40
120.39
112.54
98.48
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
48.66
44.49
28.86
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CN
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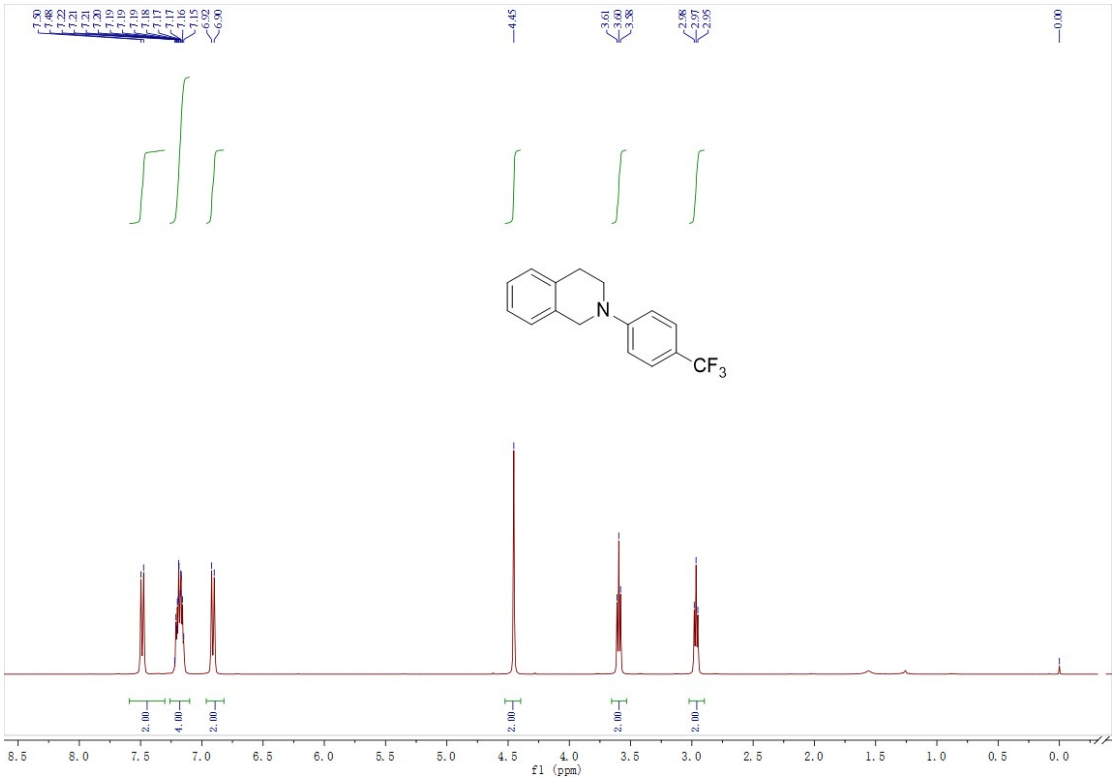
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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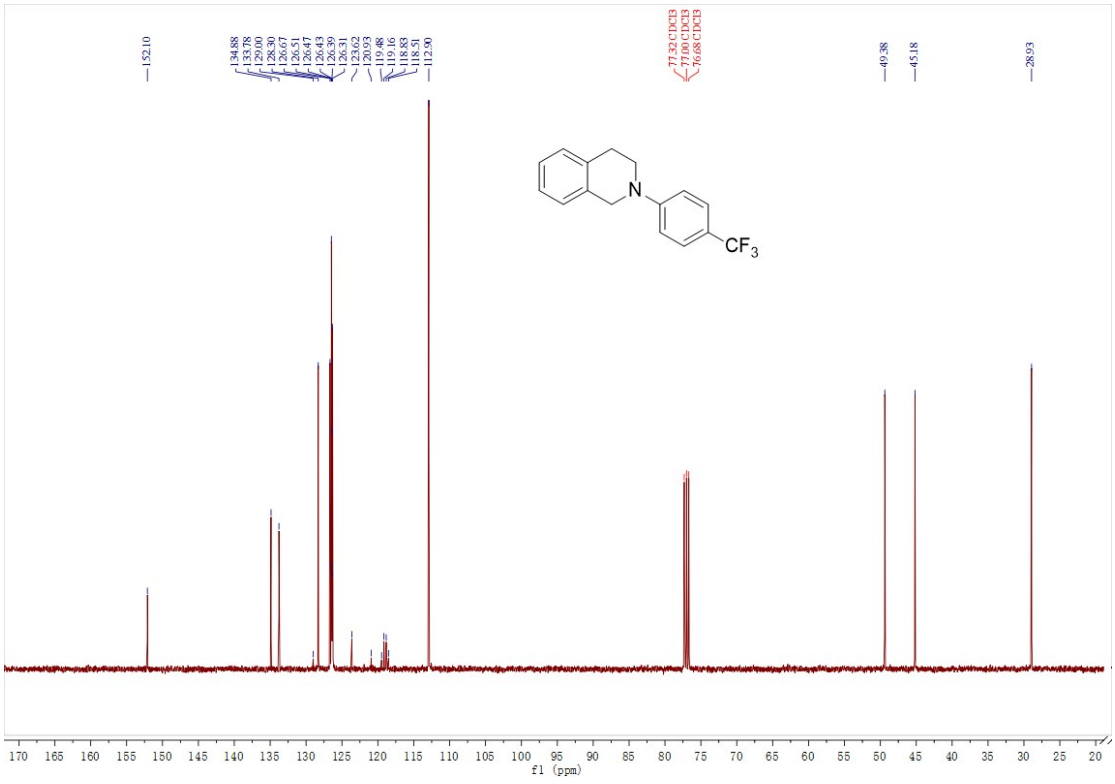
7.18
7.17
7.17
7.16
7.15
6.92
6.90
4.45
3.61
3.60
3.58
2.98
2.97
2.95
0.00
N
CF3
2.00
4.00
2.00
2.00
2.00
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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123.62
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119.48
119.46
118.83
118.51
112.90
77.32 CDCl3
77.06 CDCl3
76.68 CDCl3
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N
CF3
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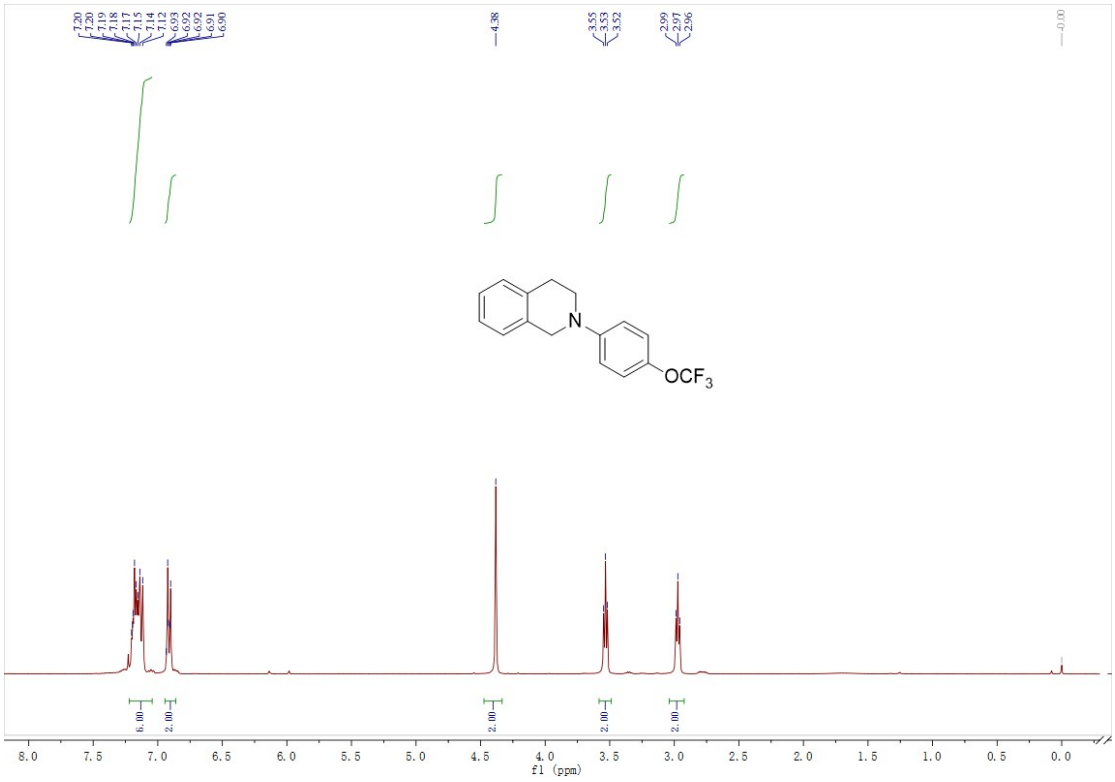
f1 (ppm)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7.12
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6.92
6.92
6.91
6.90
4.38
3.55
3.53
3.52
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2.97
2.96
0.00
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OCF3
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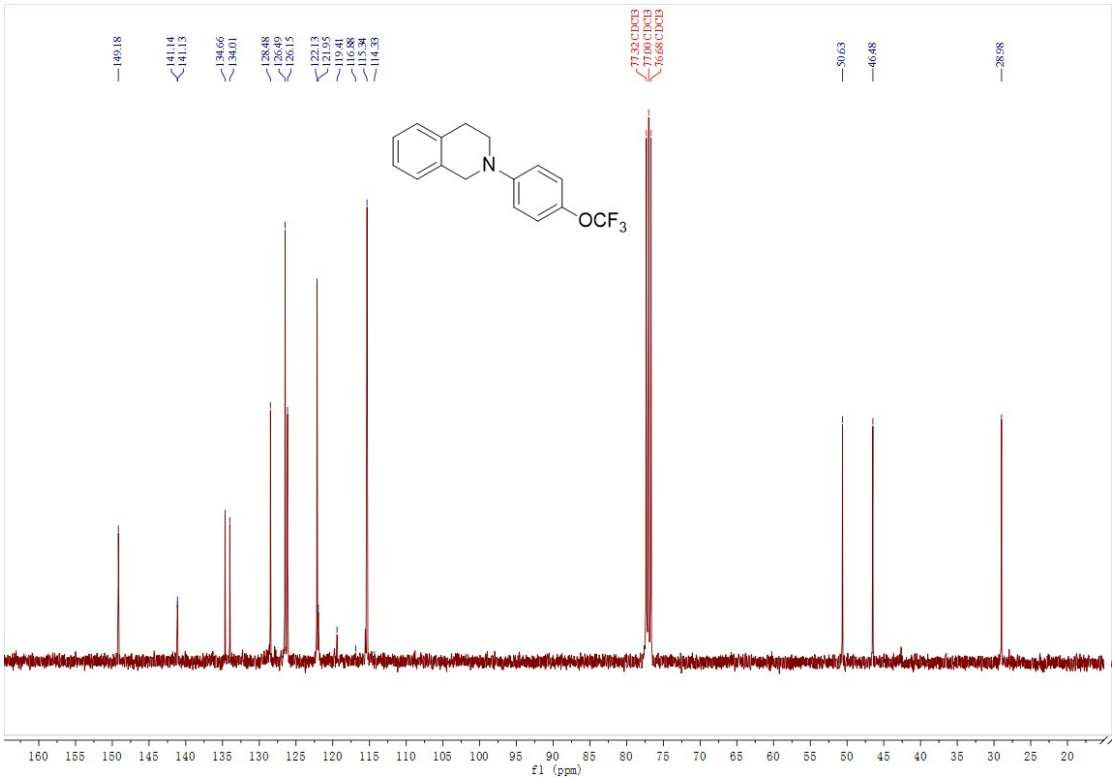
2.00
2.00
2.00
2.00
f1 (ppm)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119.41
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115.34
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77.00 CDCl3
76.68 CDCl3
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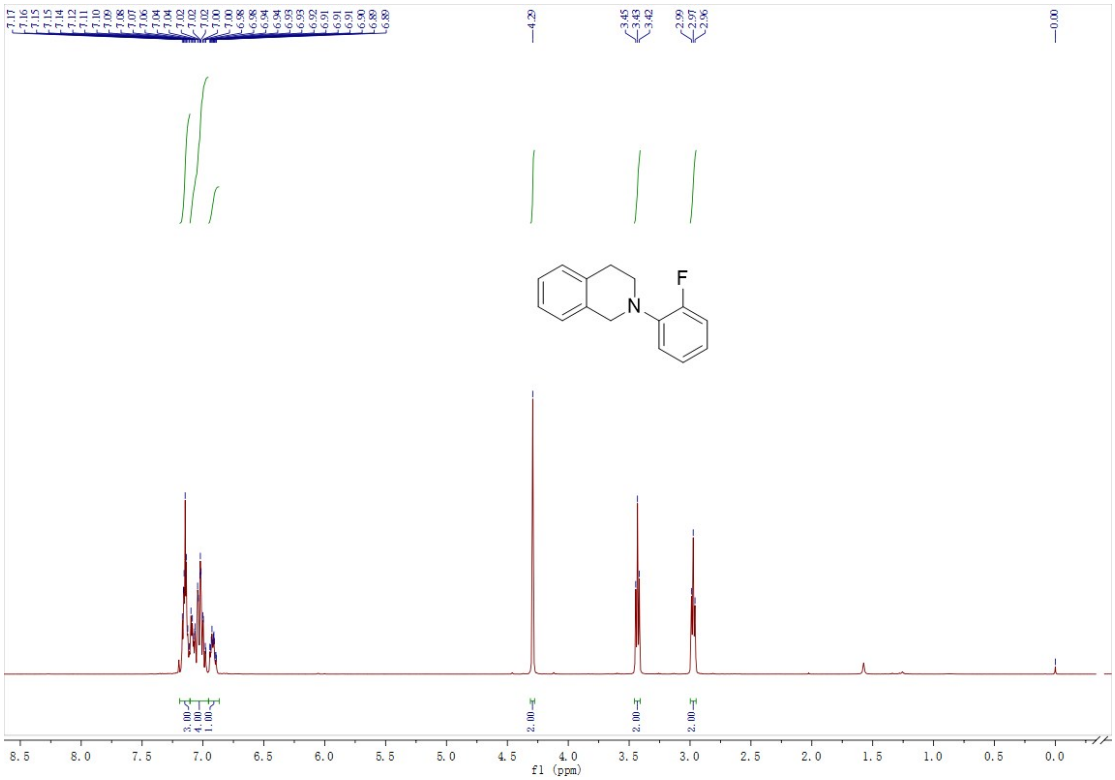
46.48
28.98
N
OCF3
f1 (ppm)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7.12
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7.09
7.08
7.07
7.06
7.04
7.04
7.02
7.02
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6.91
6.91
6.90
6.89
6.89
4.29
3.45
3.43
3.42
2.99
2.97
2.96
0.00
F
N
3.00
4.00
1.00
2.00
2.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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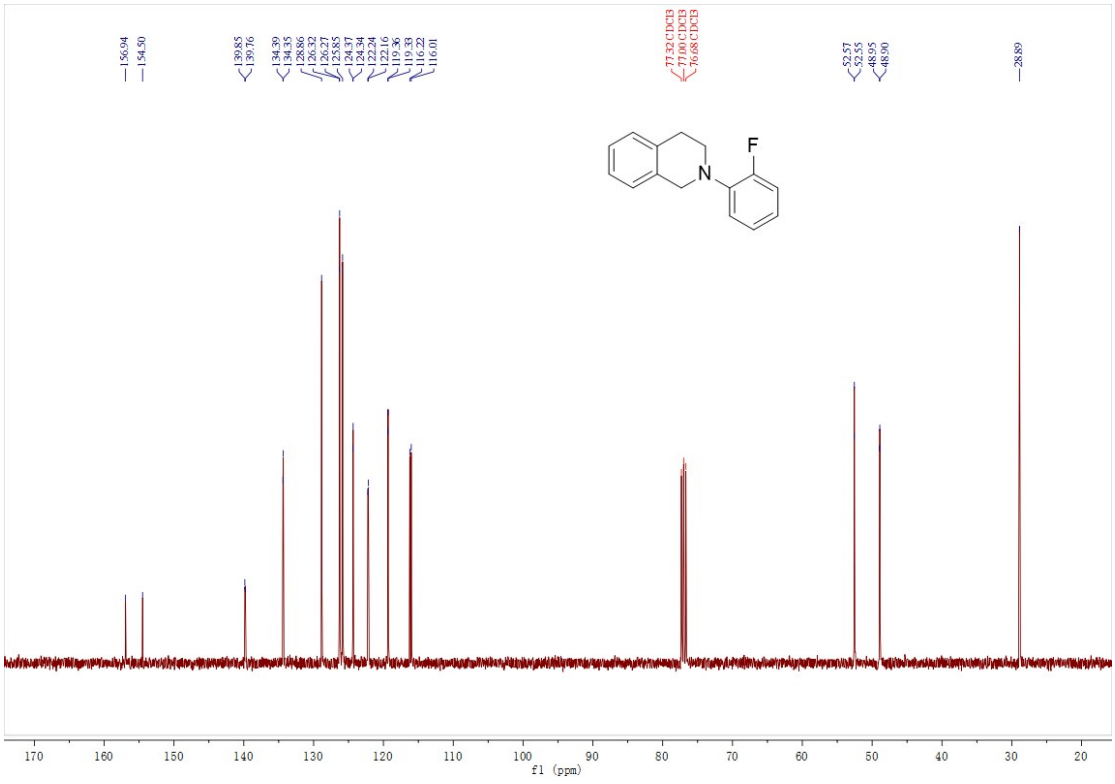
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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122.24
122.16
119.36
119.33
116.22
116.01
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
52.57
52.55
48.95
48.90
28.89
F
N
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150
140
130
120
110
100
90
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70
60
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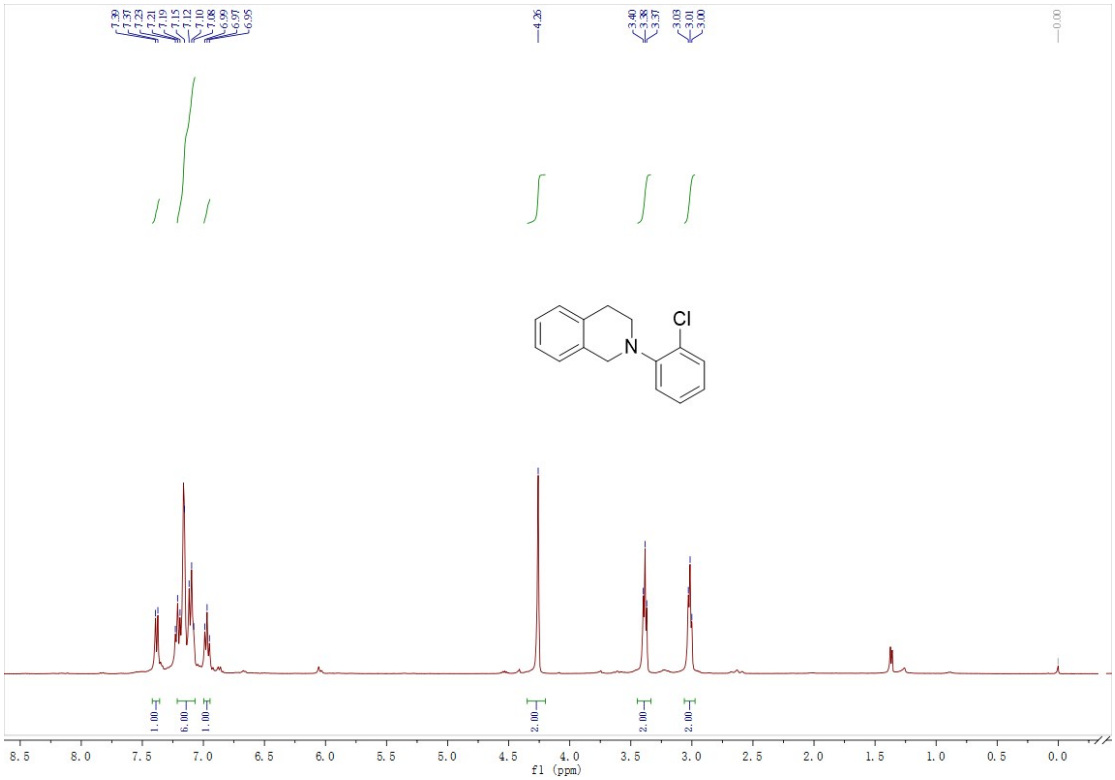
30
20
f1 (ppm)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7.15
7.12
7.10
7.08
6.99
6.97
6.95
4.26
3.40
3.38
3.37
3.03
3.01
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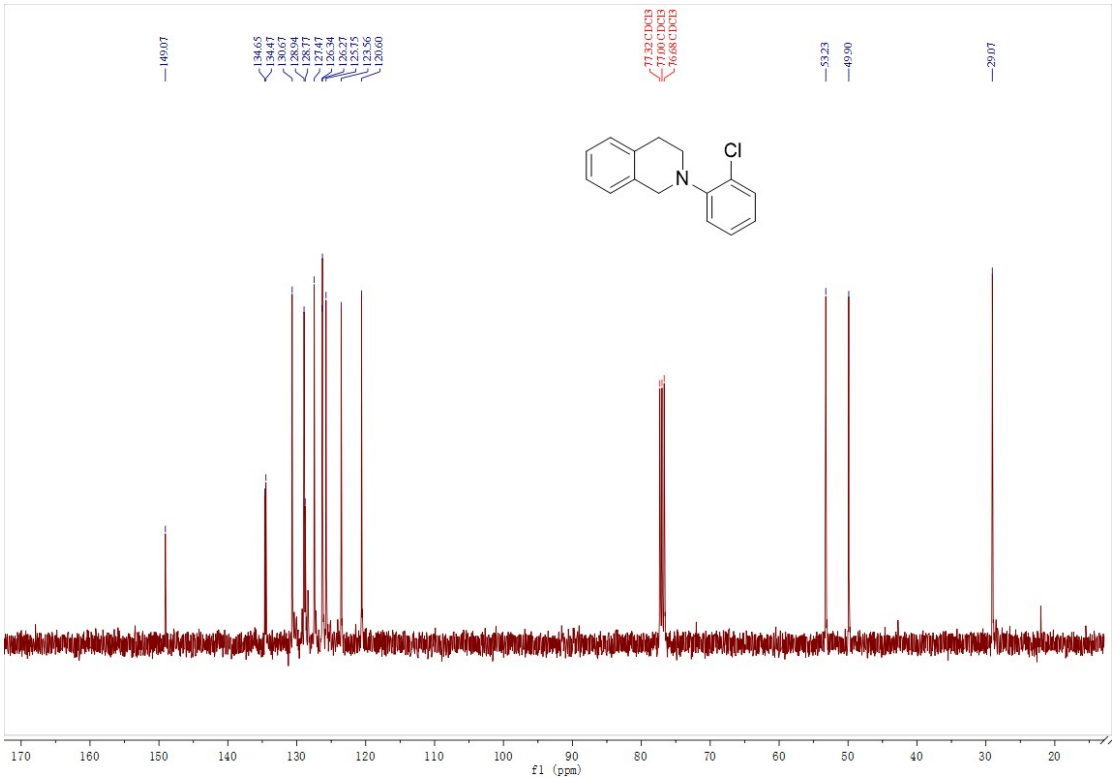
0.00
Cl
N
1.00
6.00
1.00
2.00
2.00
2.00
f1 (ppm)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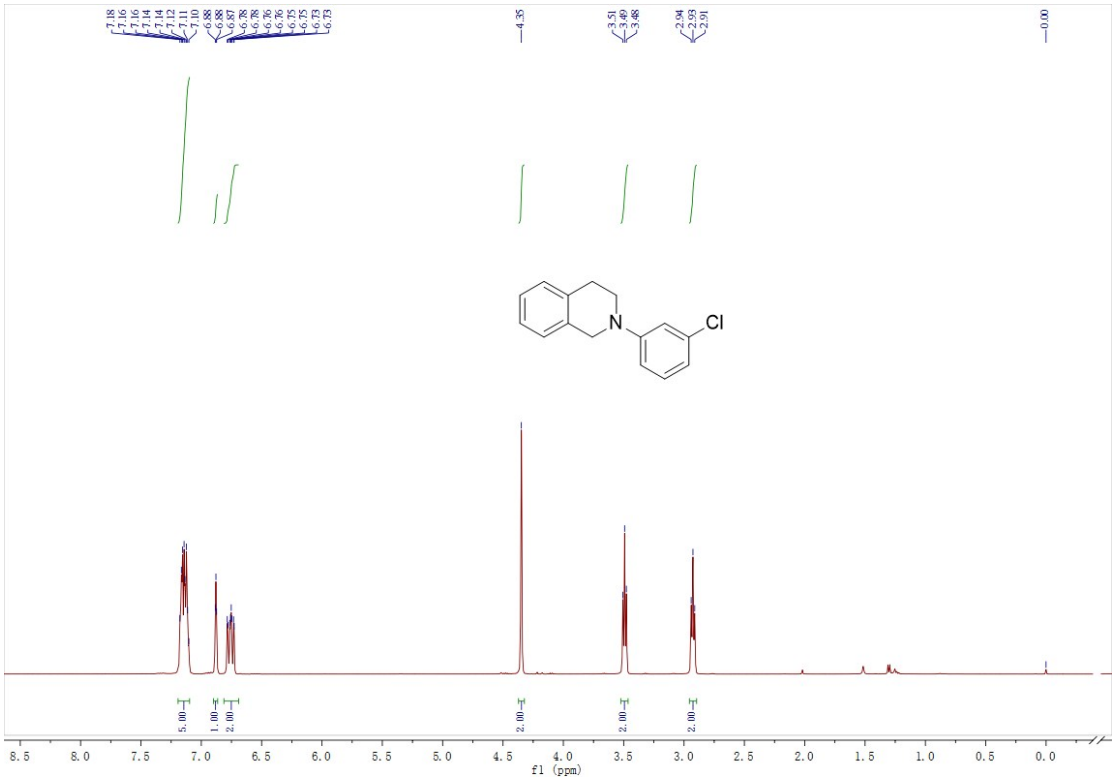
53.23
49.90
29.07
Cl
N
f1 (ppm)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6.76
6.75
6.75
6.73
6.73
4.35
3.51
3.49
3.48
2.94
2.93
2.91
0.00
N
Cl
5.00
1.00
2.00
2.00
2.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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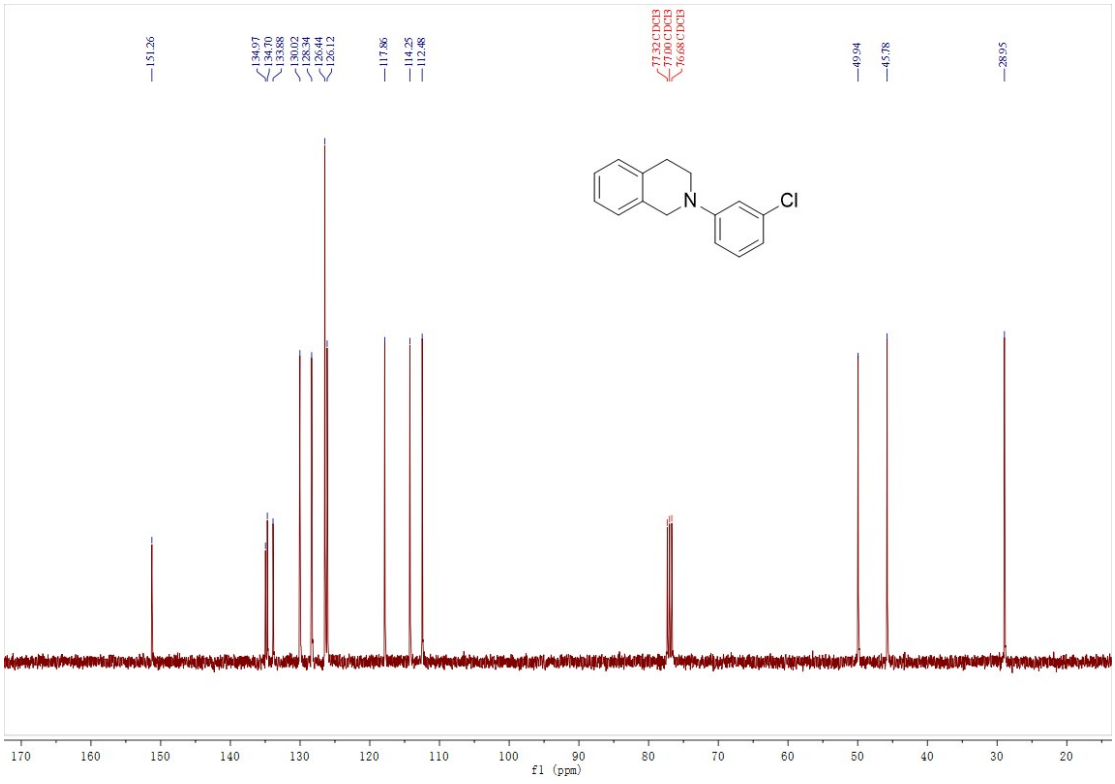
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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130.02
128.34
126.44
126.12
117.86
114.25
112.48
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
49.94
45.78
28.95
N
Cl
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150
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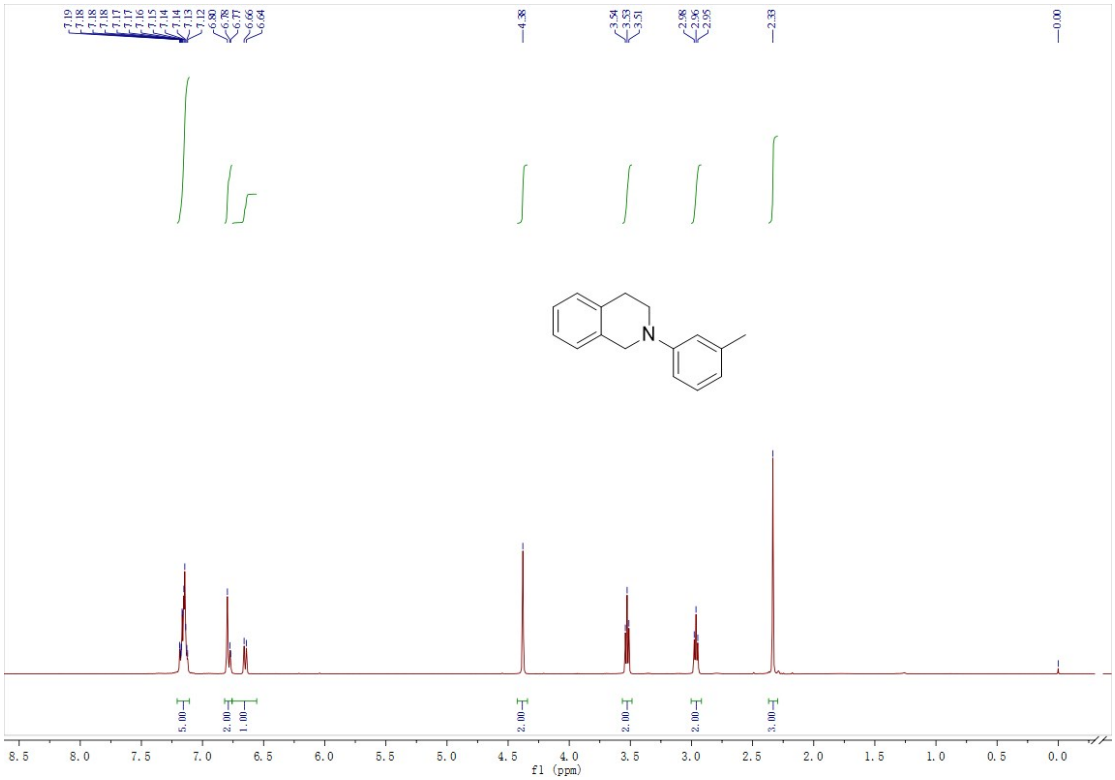
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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7.14
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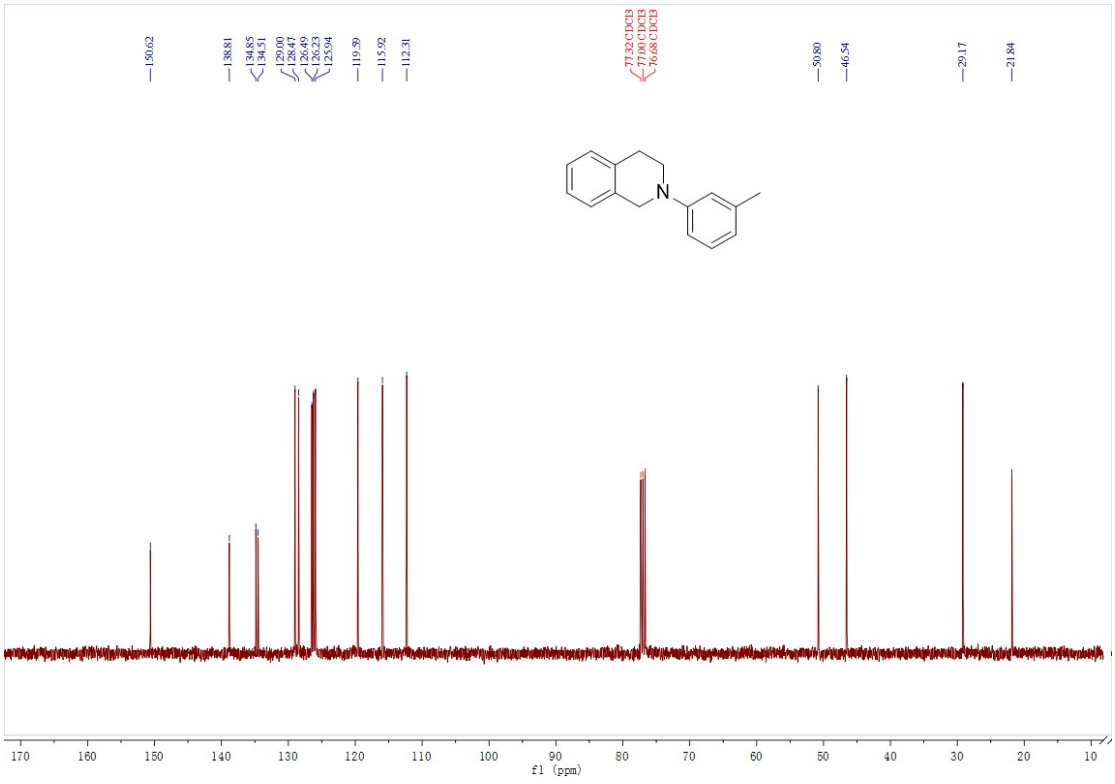
7.13
7.12
6.80
6.78
6.77
6.66
6.64
4.38
3.54
3.53
3.51
2.98
2.96
2.95
2.33
0.00
N
5.00
2.00
1.00
2.00
2.00
2.00
3.00
f1 (ppm)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125.94
119.59
115.92
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50.80
46.54
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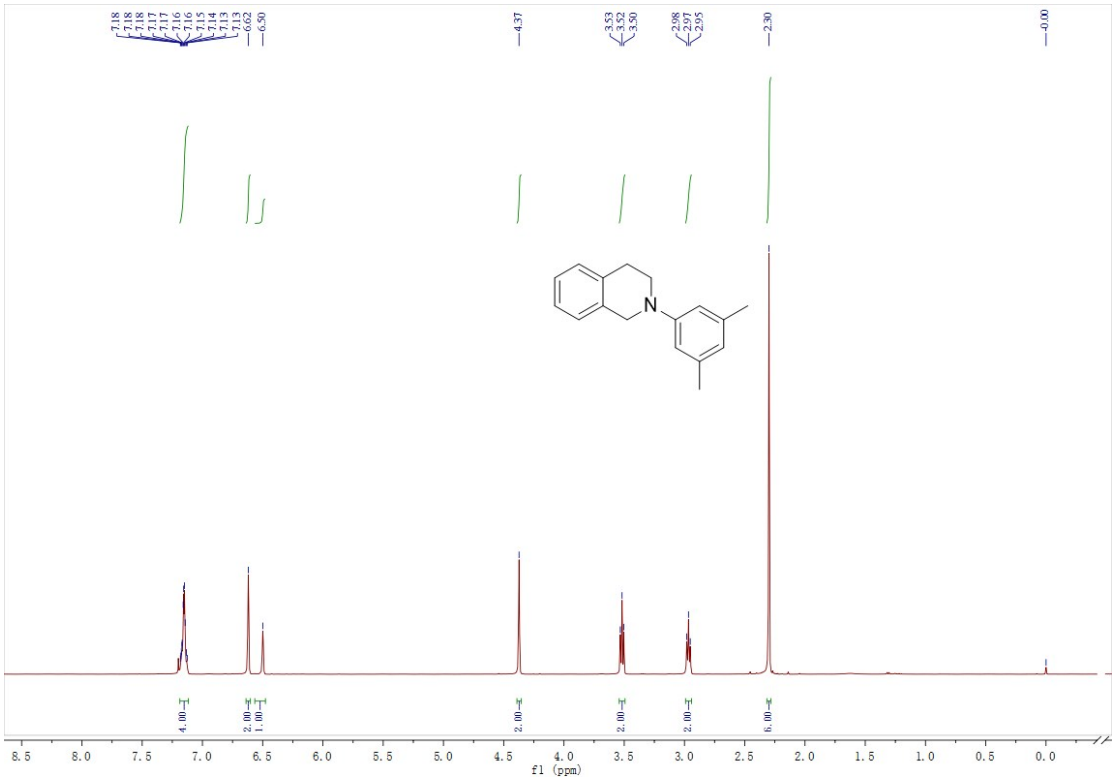
N
f1 (ppm)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7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.13
7.13
6.62
6.50
4.37
3.53
3.52
3.50
2.98
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2.95
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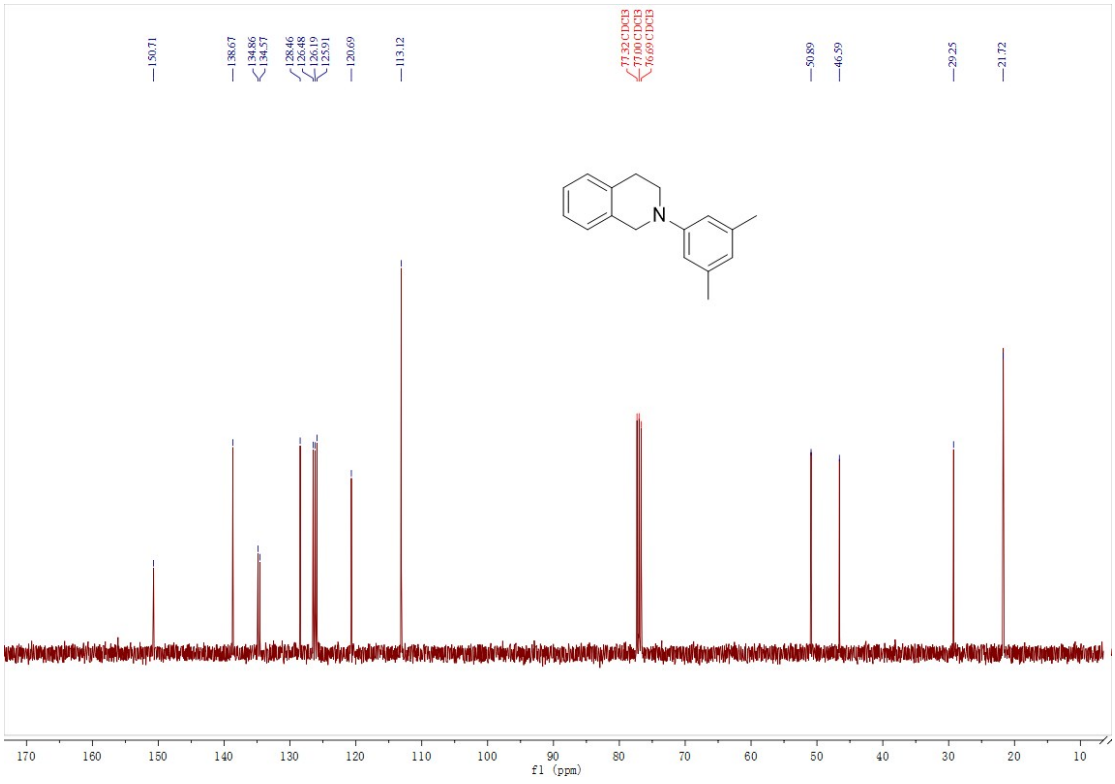
4.00
2.00
1.00
2.00
2.00
2.00
6.00
f1 (ppm)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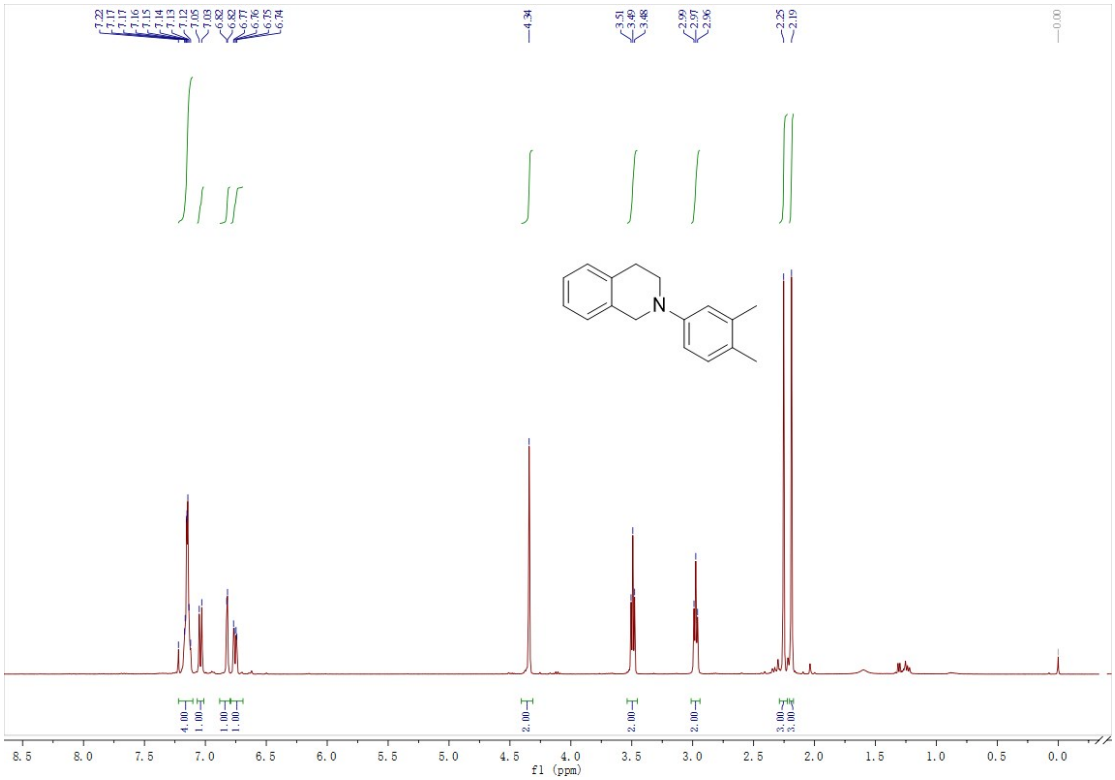
134.57
128.46
126.48
126.19
125.91
120.69
113.12
77.32 CDCl3
77.00 CDCl3
76.69 CDCl3
50.89
46.59
29.25
21.72
f1 (ppm)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2.96
2.25
2.19
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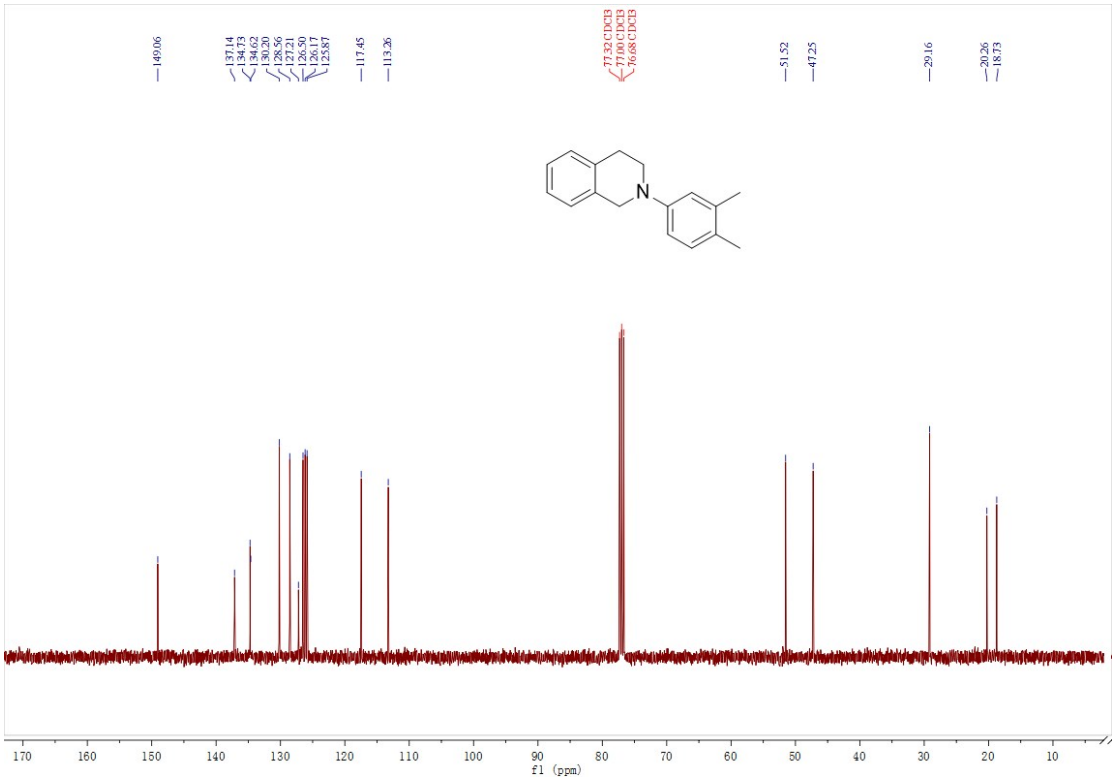
f1 (ppm)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113.26
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76.68 CDCl3
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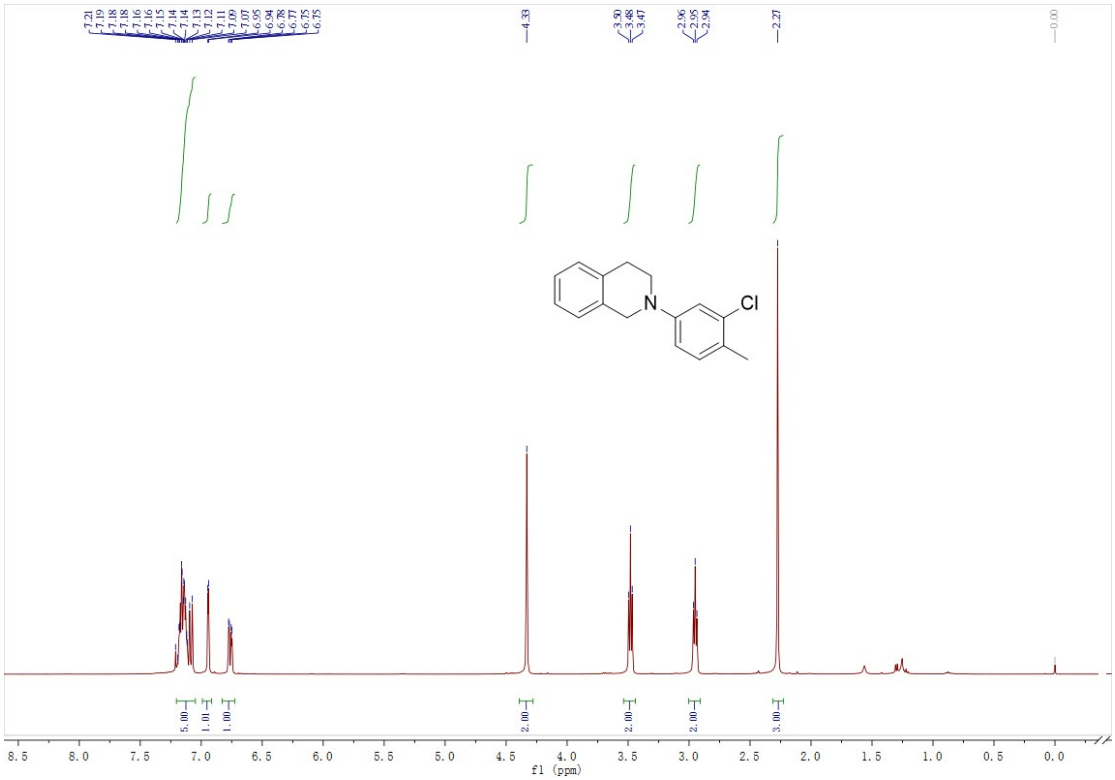
f1 (ppm)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6.94
6.78
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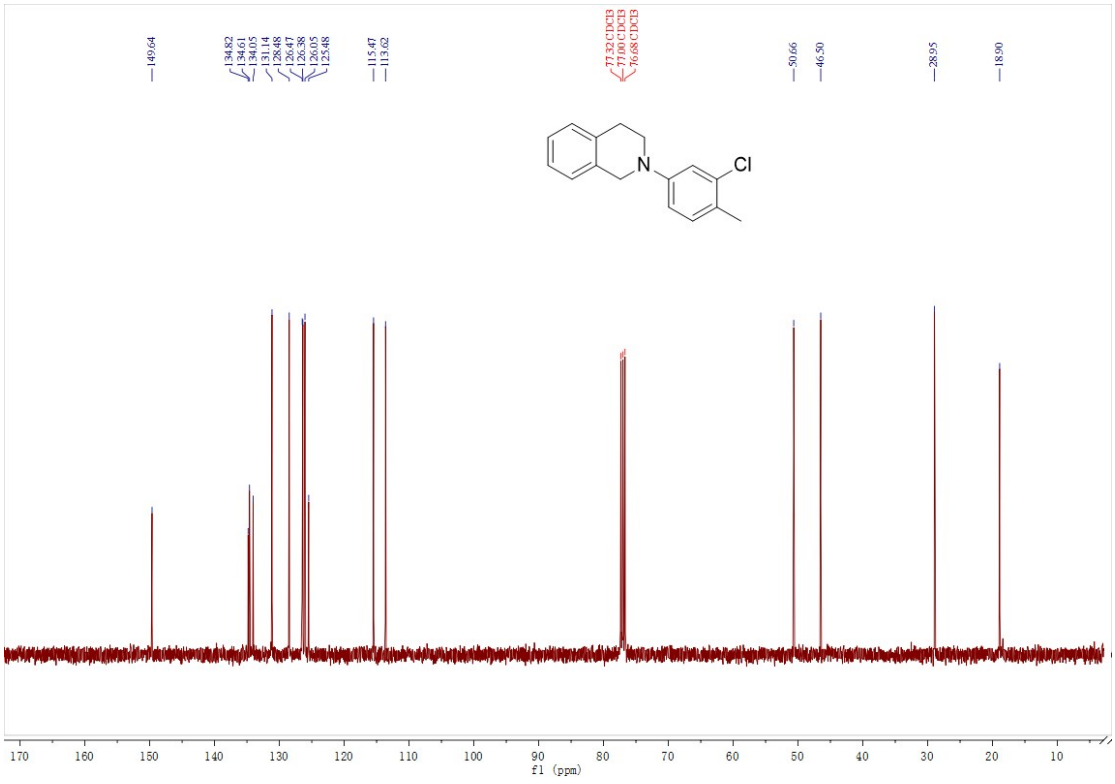
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113.62
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77.00 CDCl3
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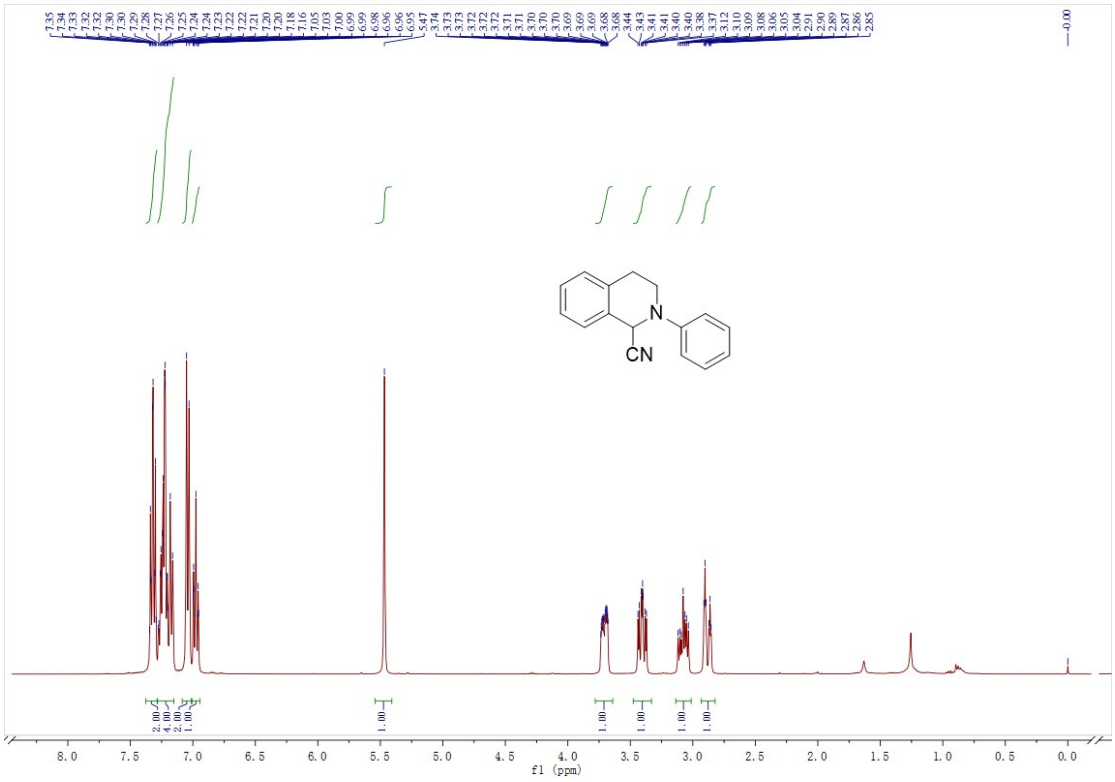
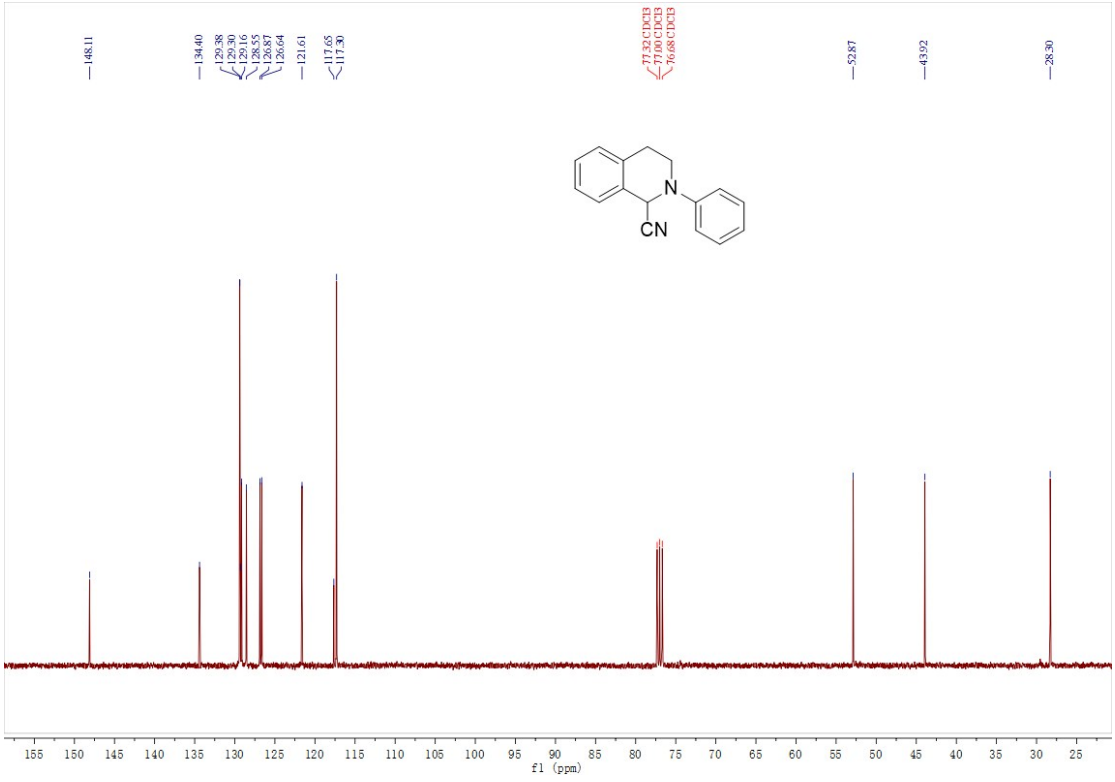
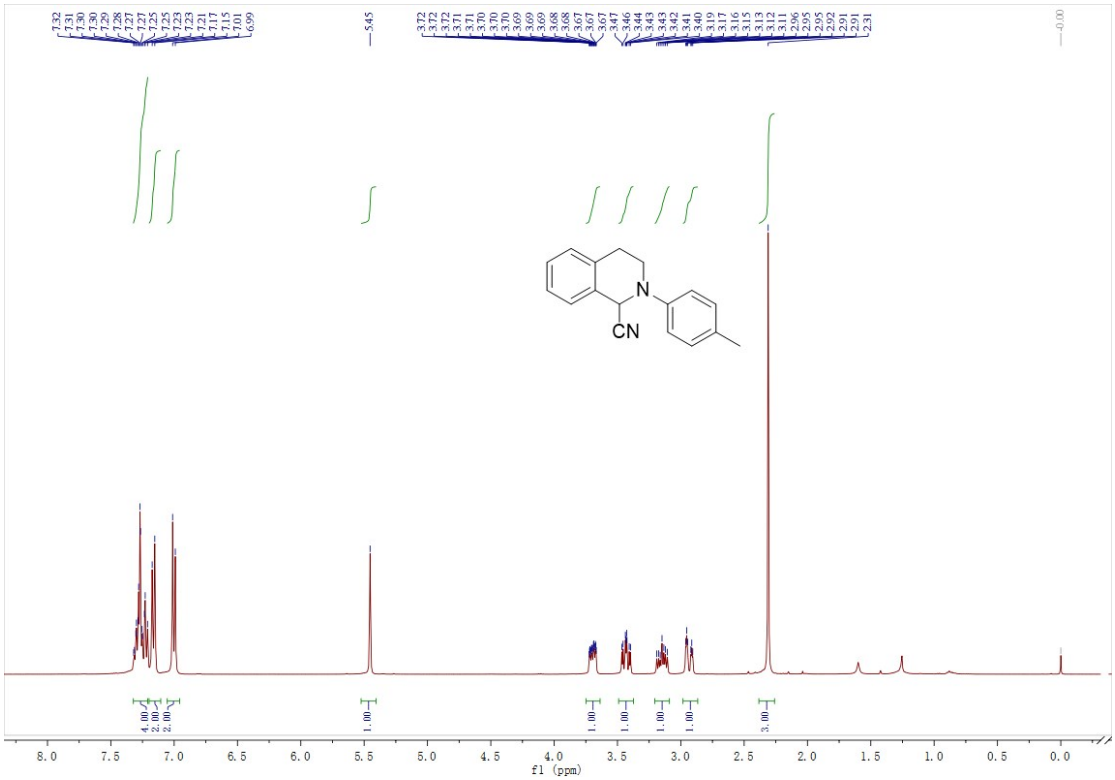
18.90
N
Cl
f1 (ppm)

Copies of ^{1}H and ^{13}C NMR spectra of all products



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CN
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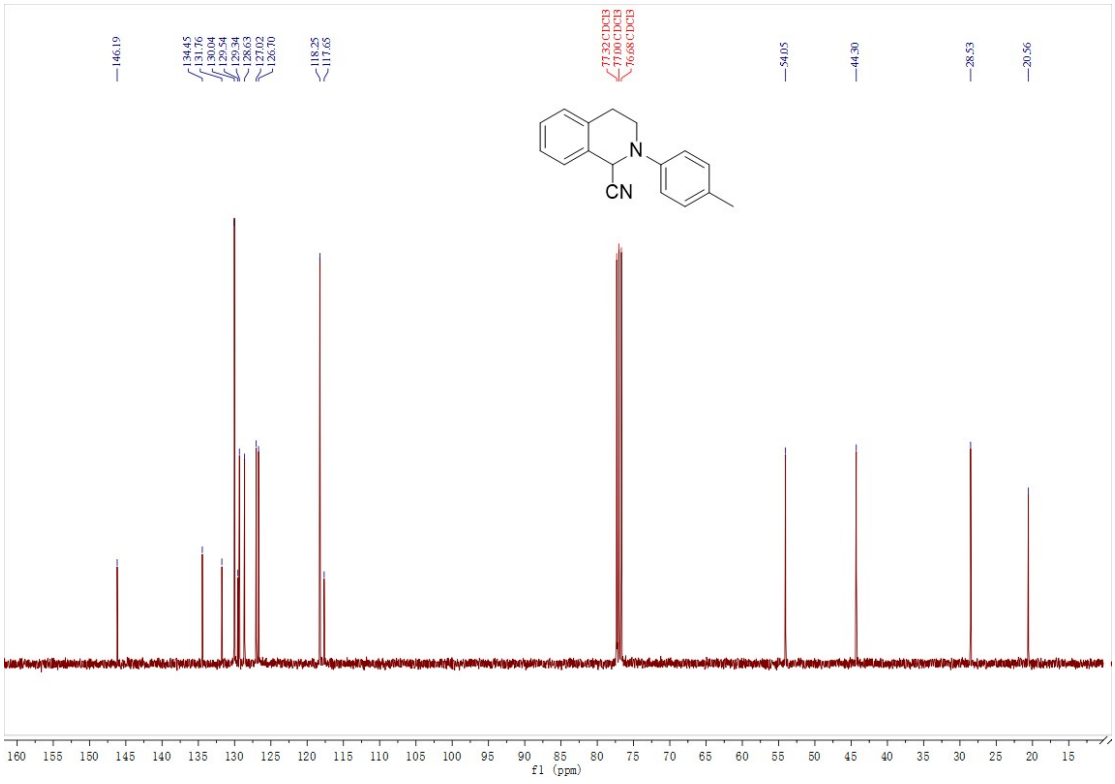
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117.65
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77.00 CDCl3
76.68 CDCl3
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44.30
28.53
20.56
N
CN
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155
150
145
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135
130
125
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115
110
105
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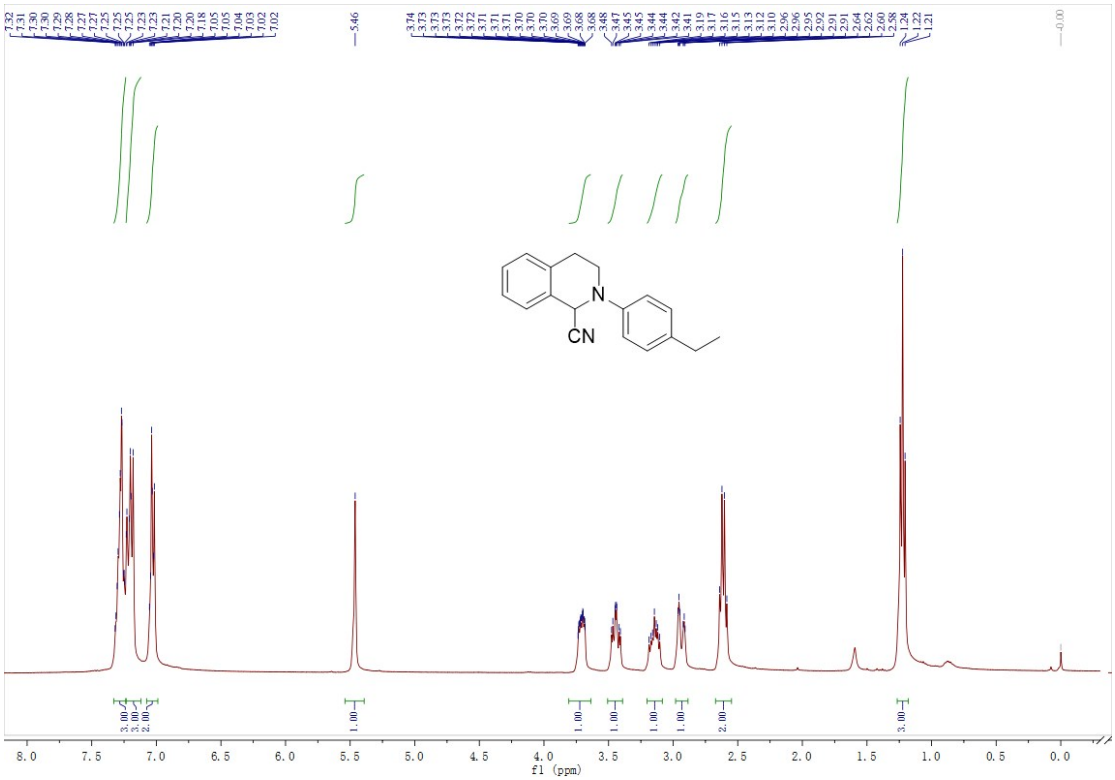
f1 (ppm)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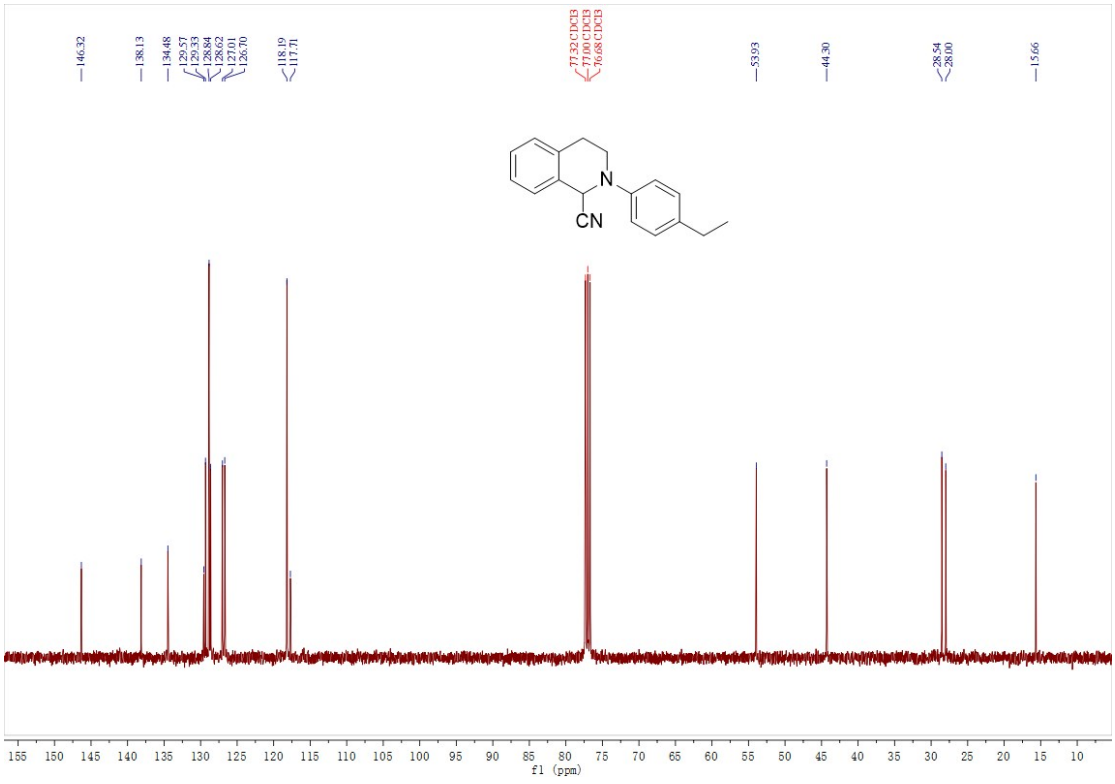
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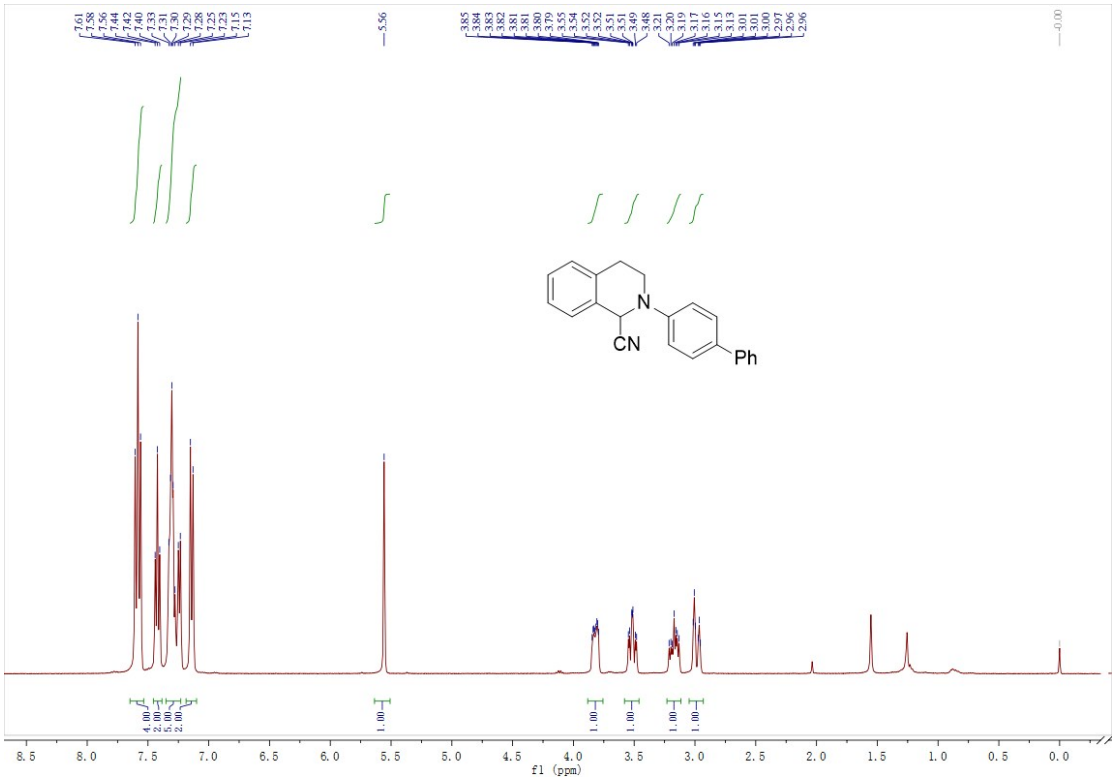
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3.16
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3.13
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3.01
3.00
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2.96
2.96
0.00
N
CN
Ph
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2.00
2.00
1.00
1.00
1.00
1.00
1.00
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6.0
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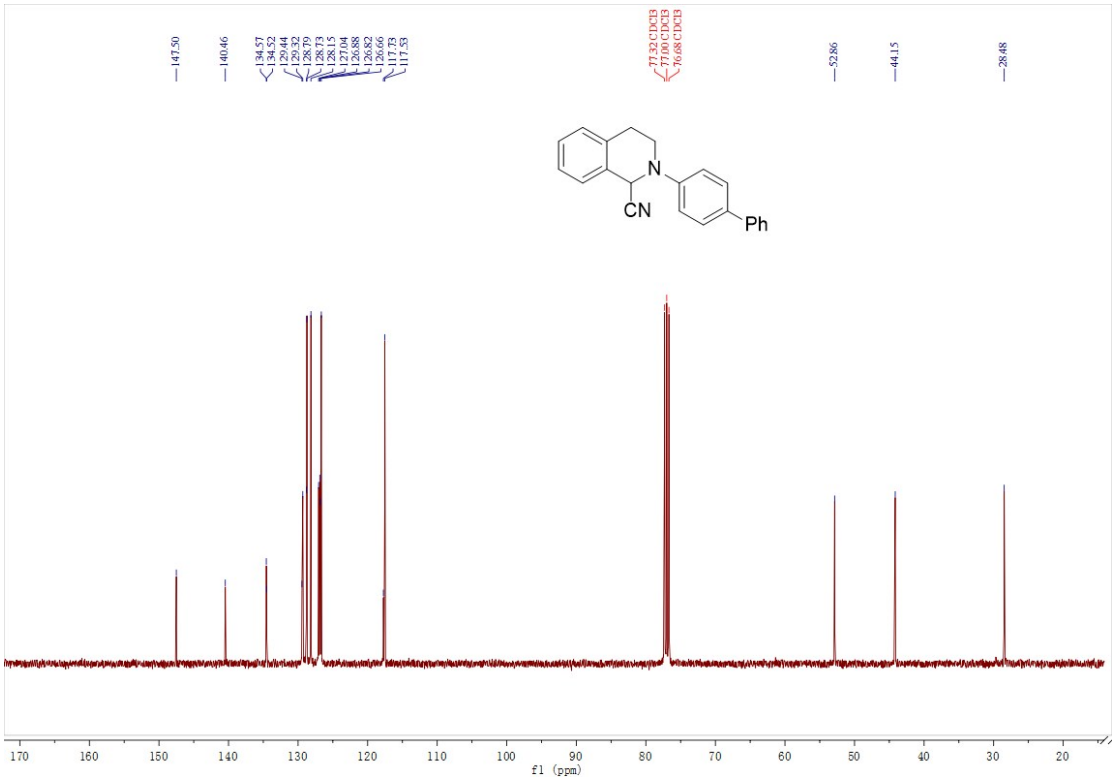
f1 (ppm)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117.53
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77.00/CDCl3
76.68/CDCl3
52.86
44.15
28.48
N
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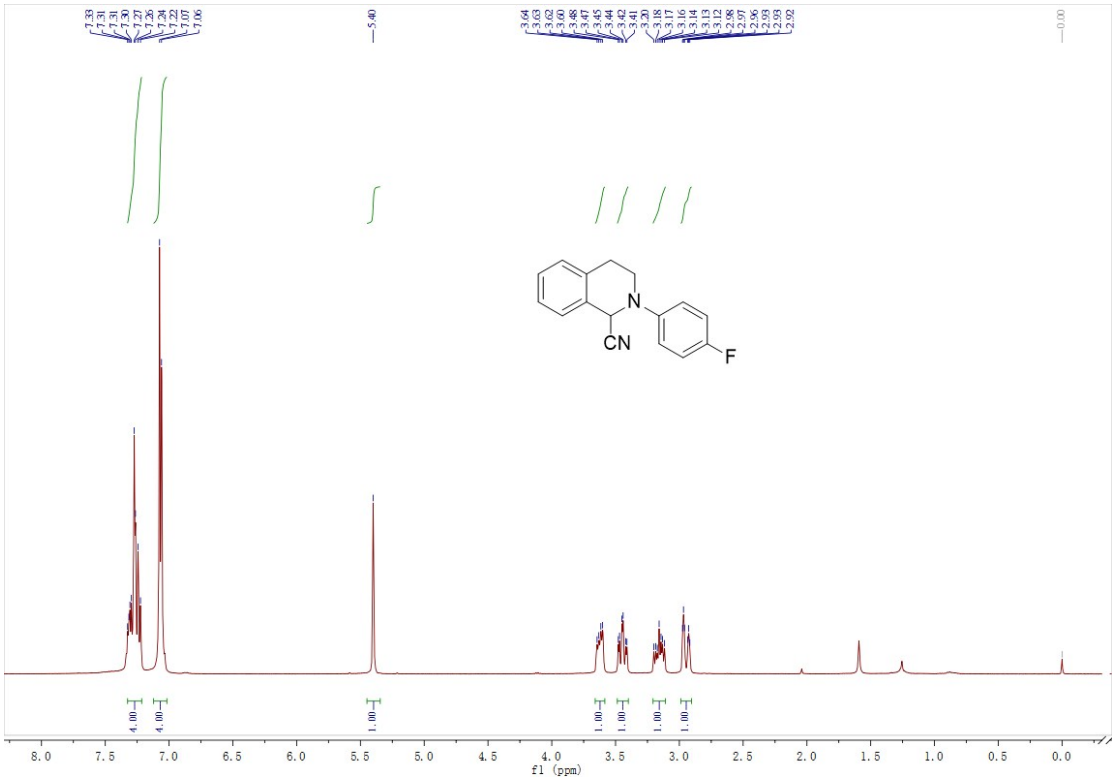
f1 (ppm)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3.13
3.12
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2.96
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2.93
2.92
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1.00
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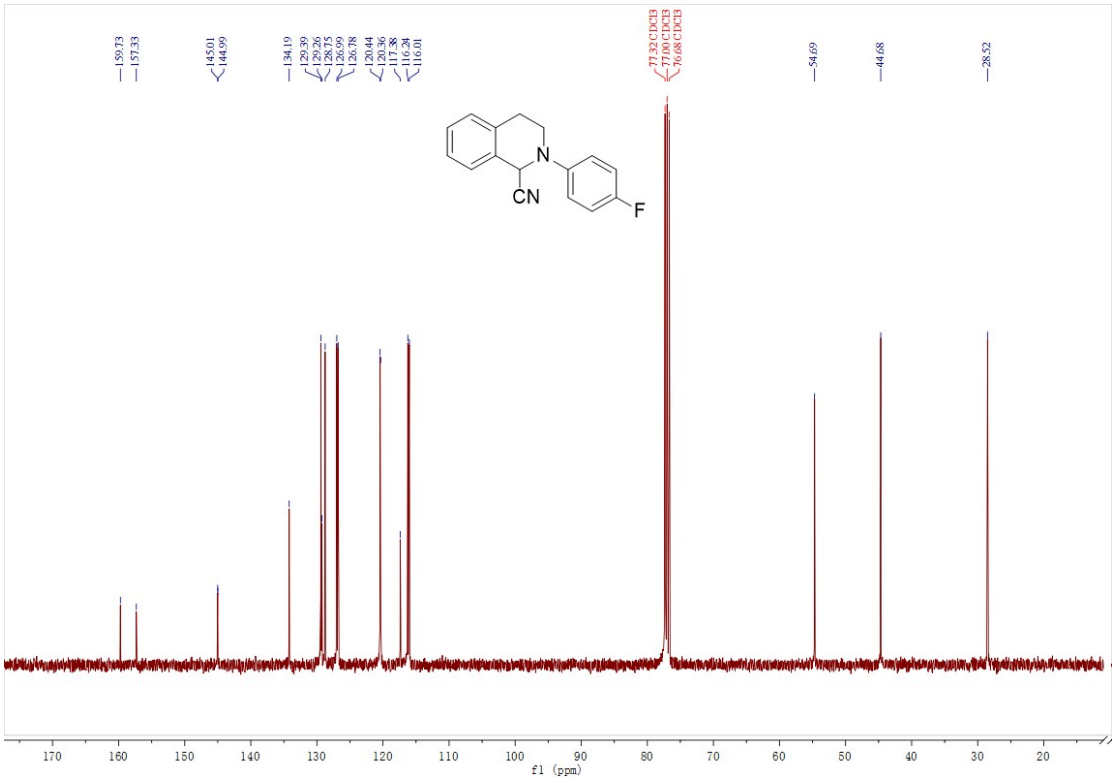
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116.01
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76.68 CDCl3
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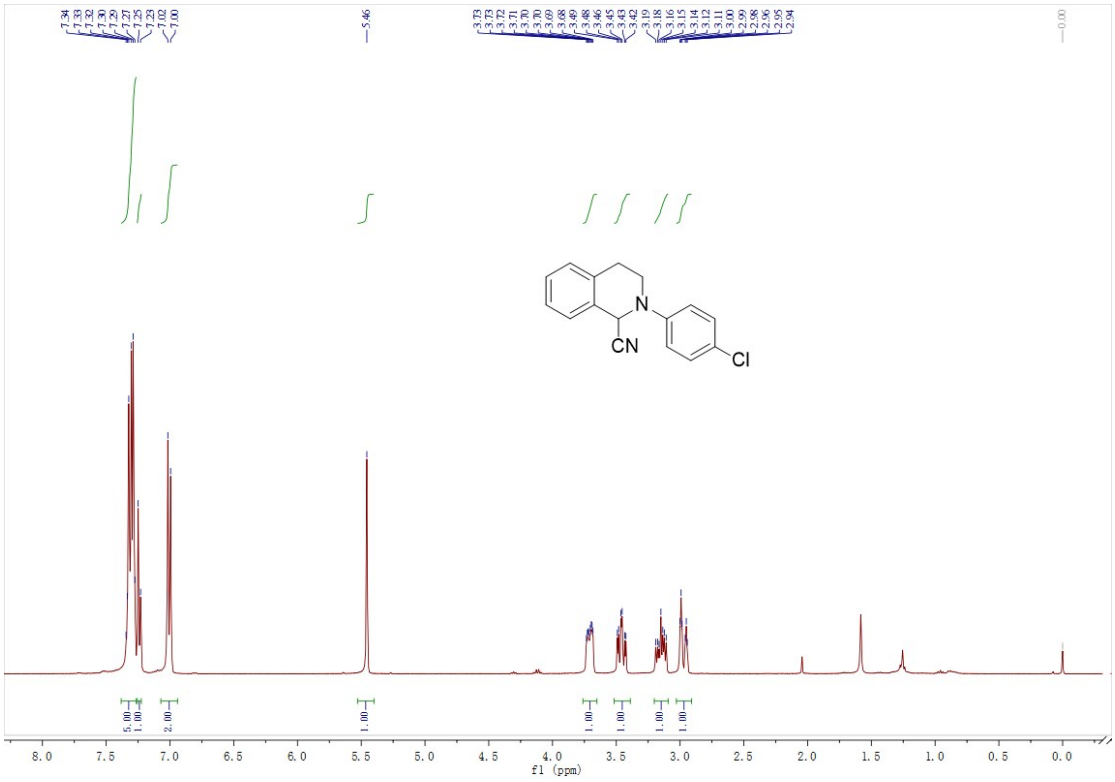
f1 (ppm)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CN
Cl
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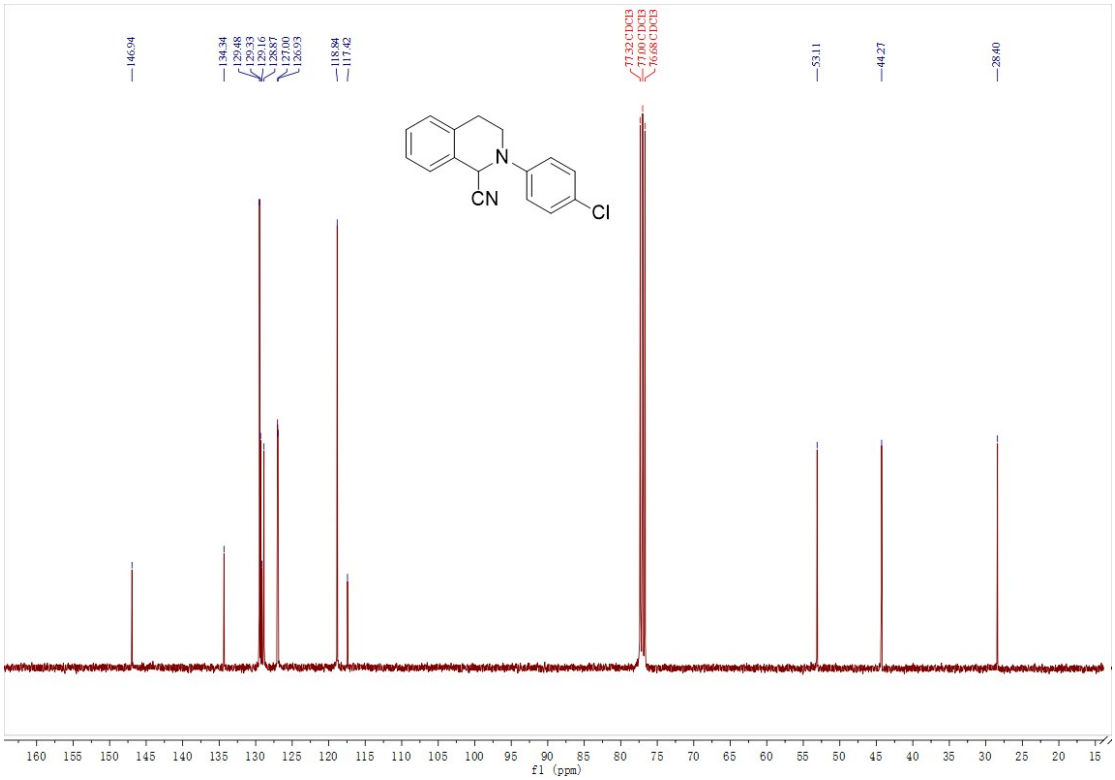
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76.68 CDCl3
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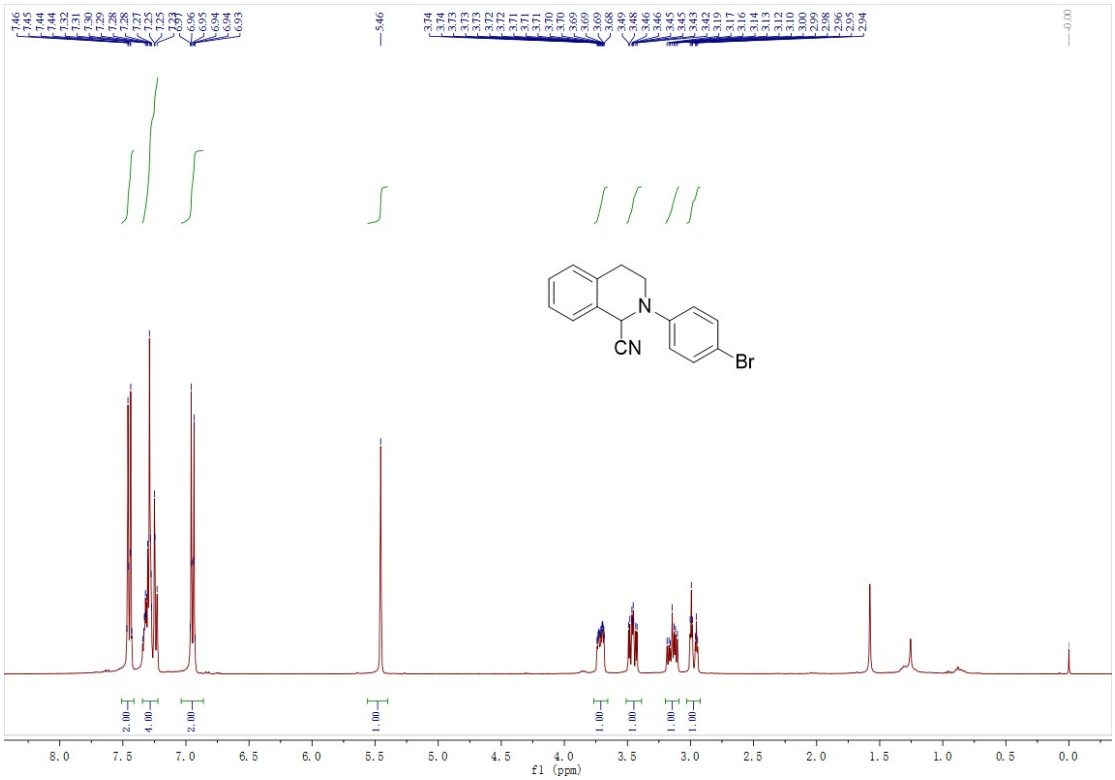
f1 (ppm)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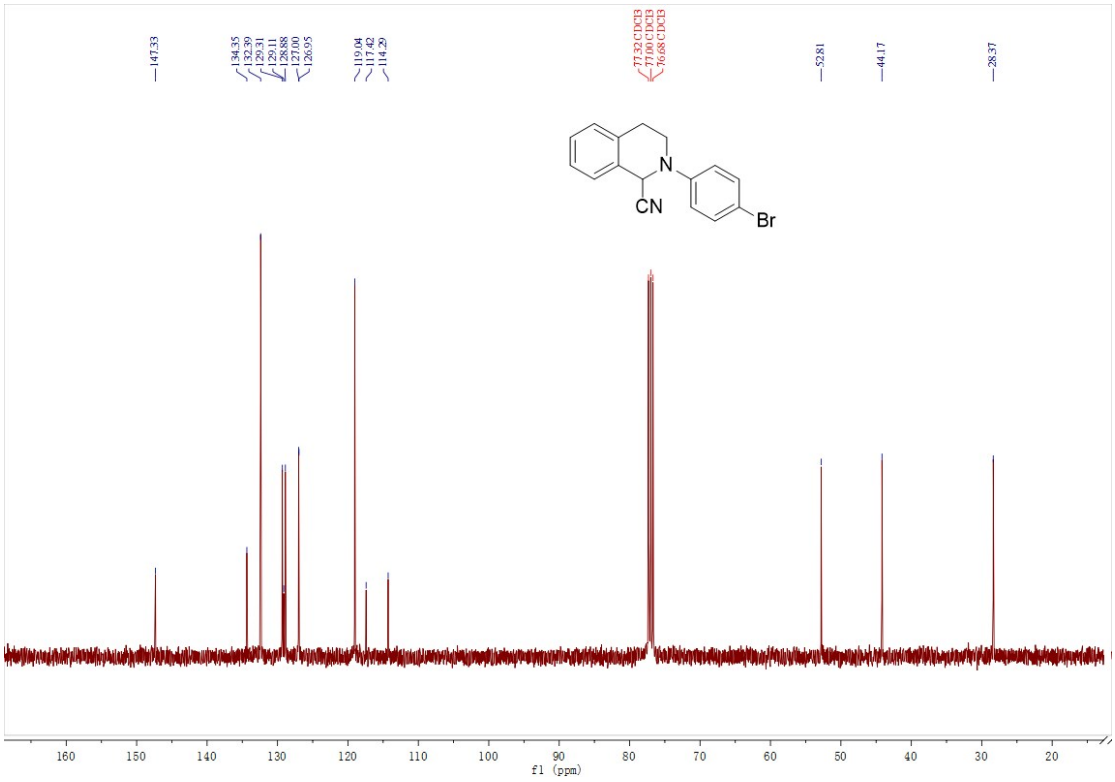
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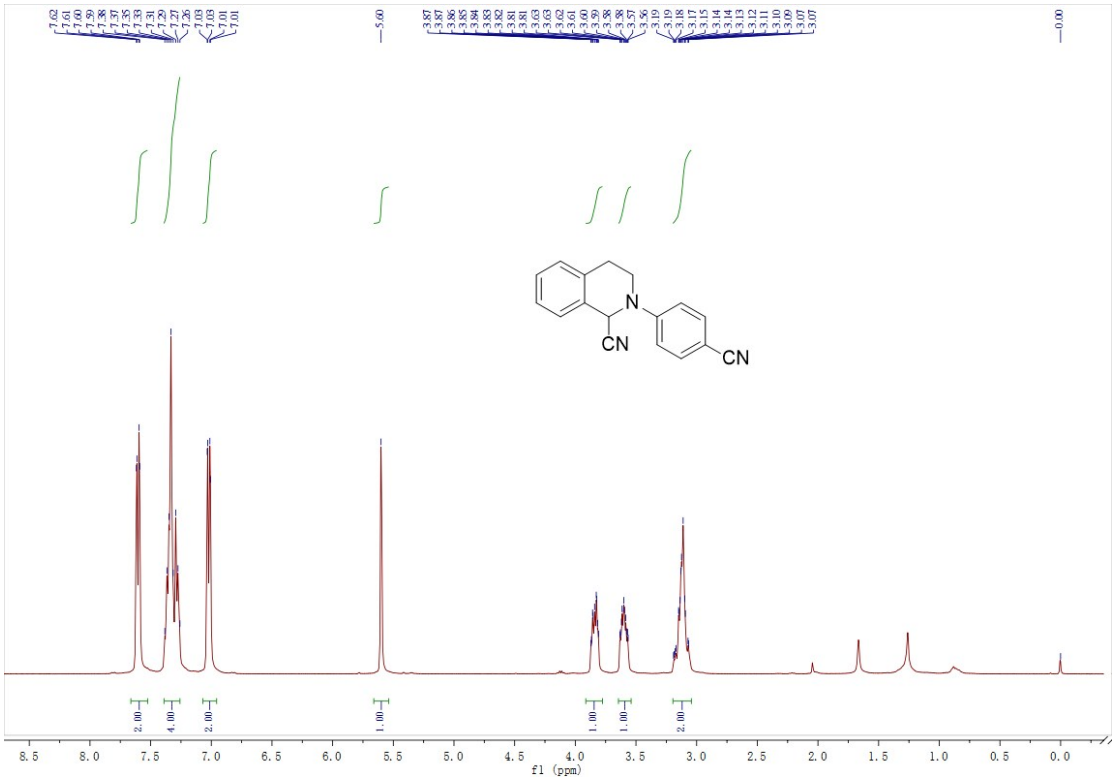
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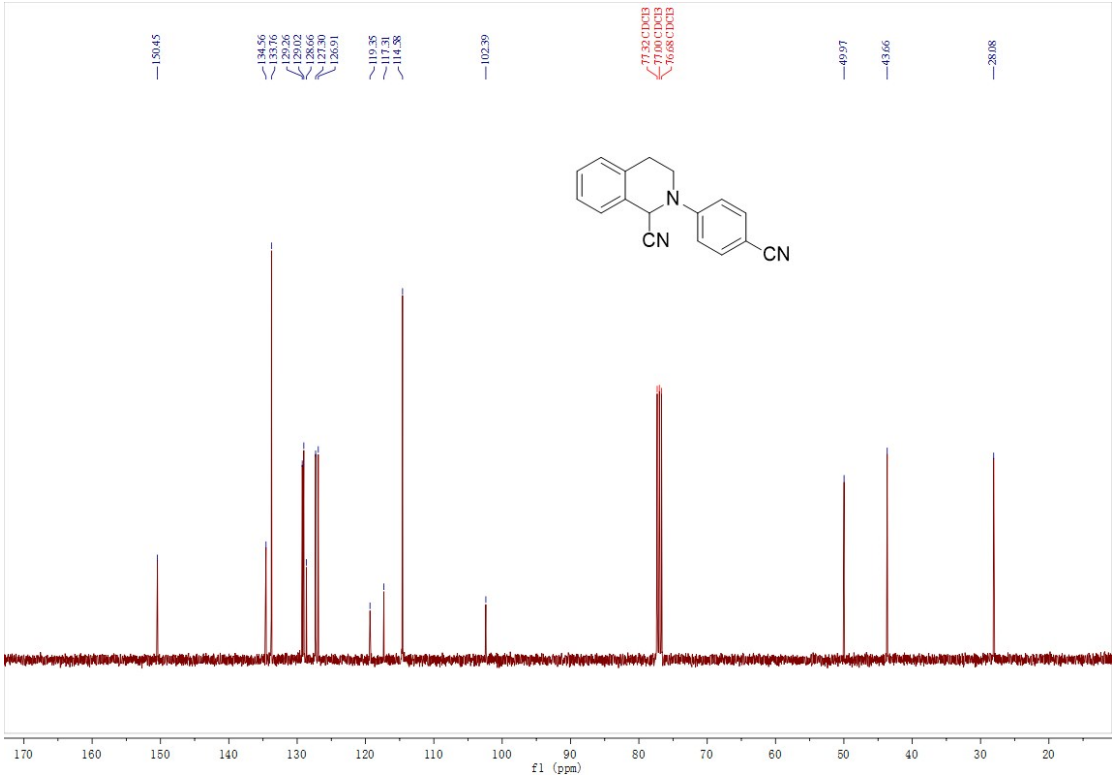
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76.68 CDCl3
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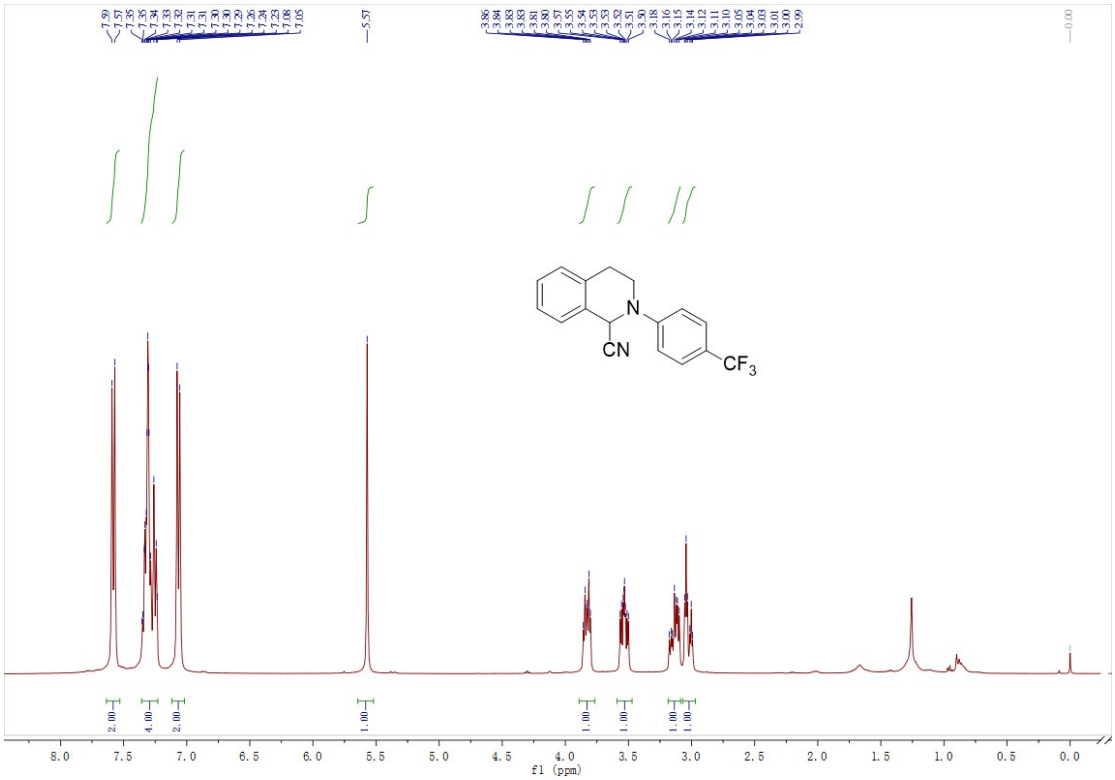
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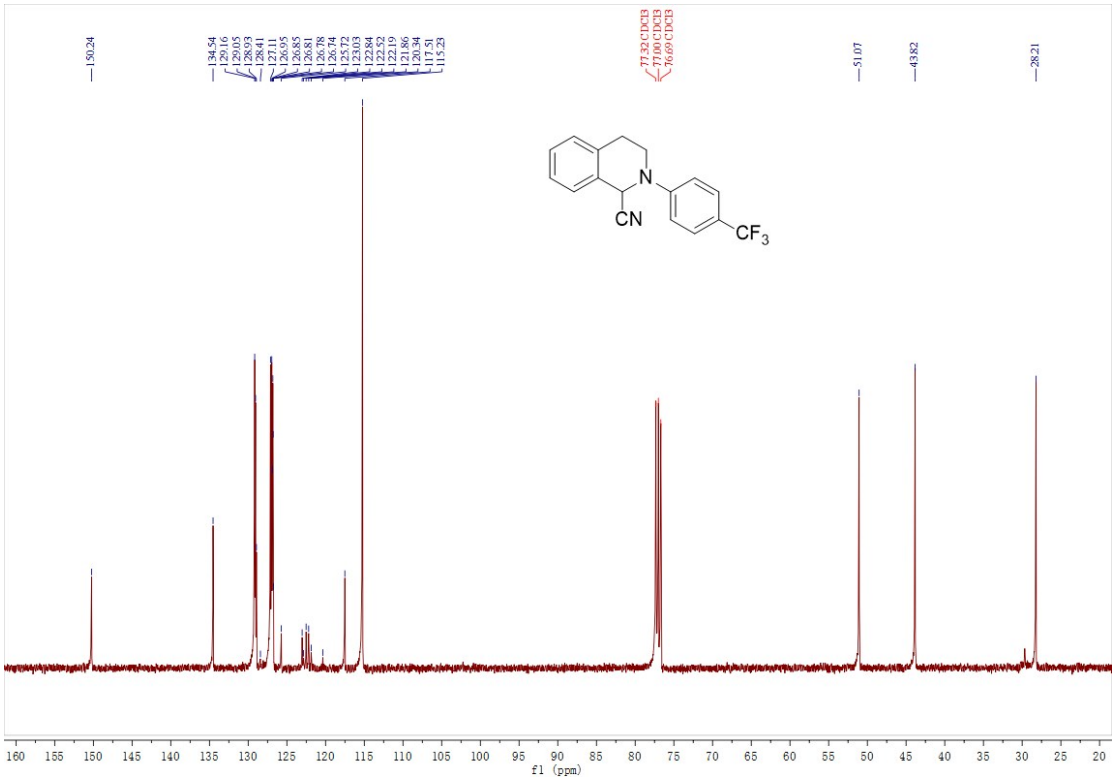
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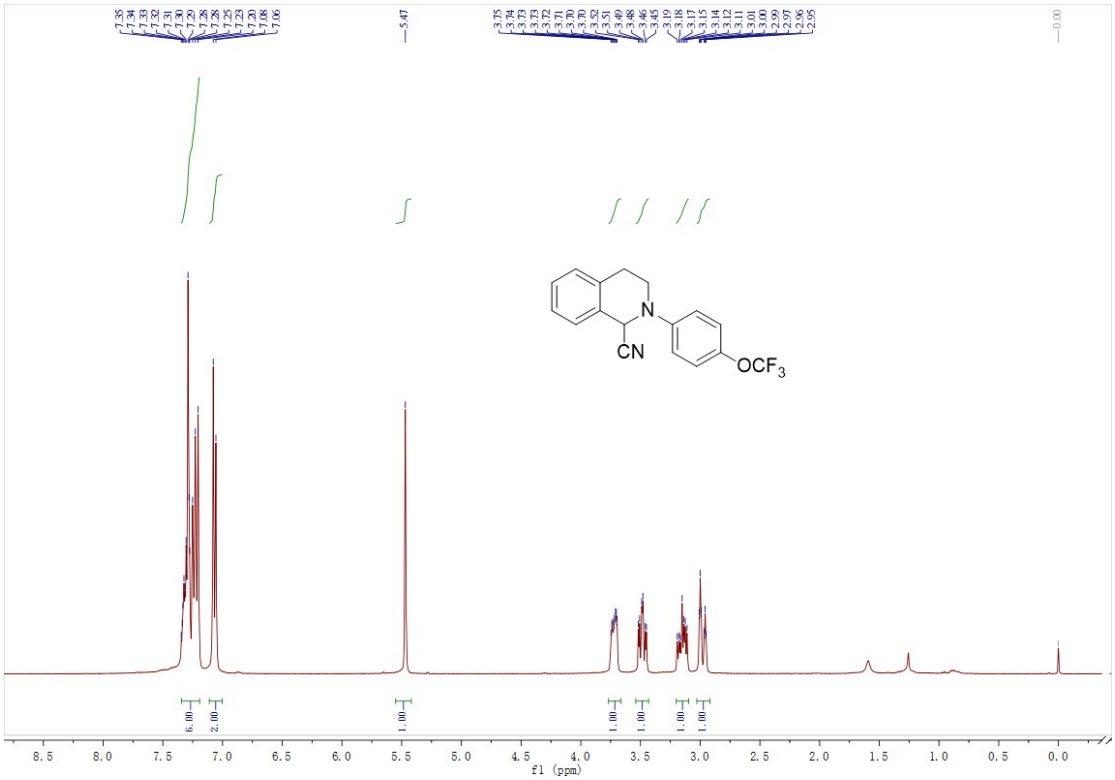
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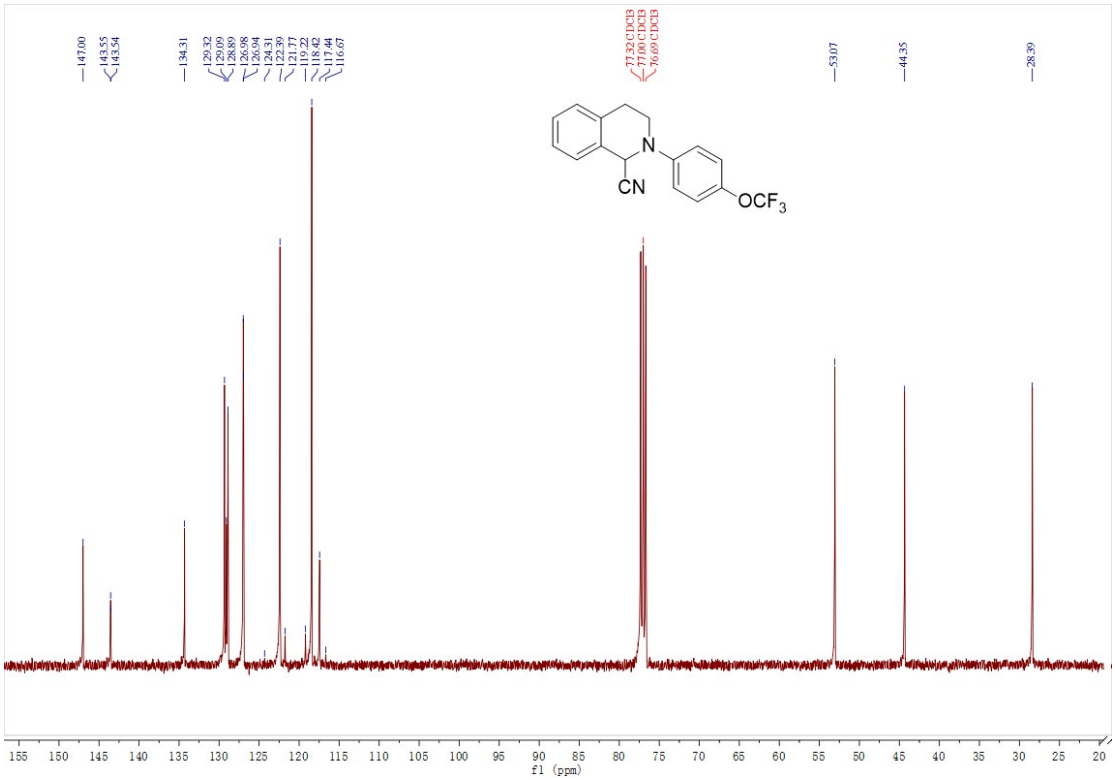
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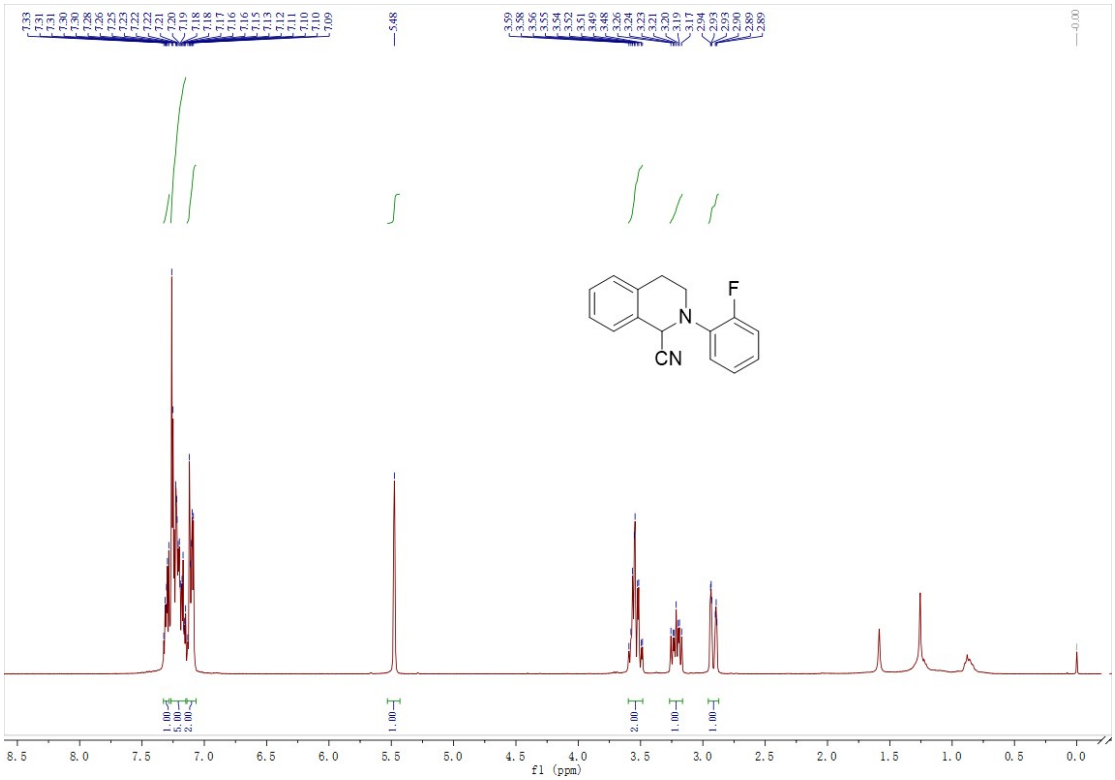
f1 (ppm)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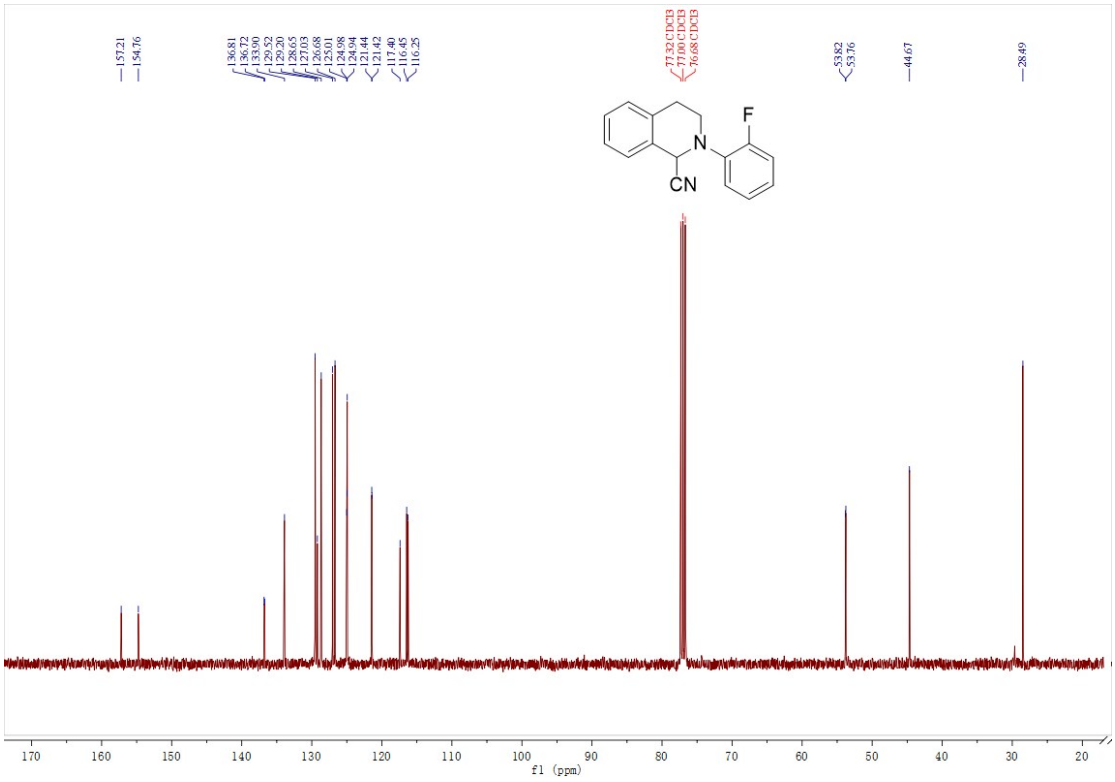
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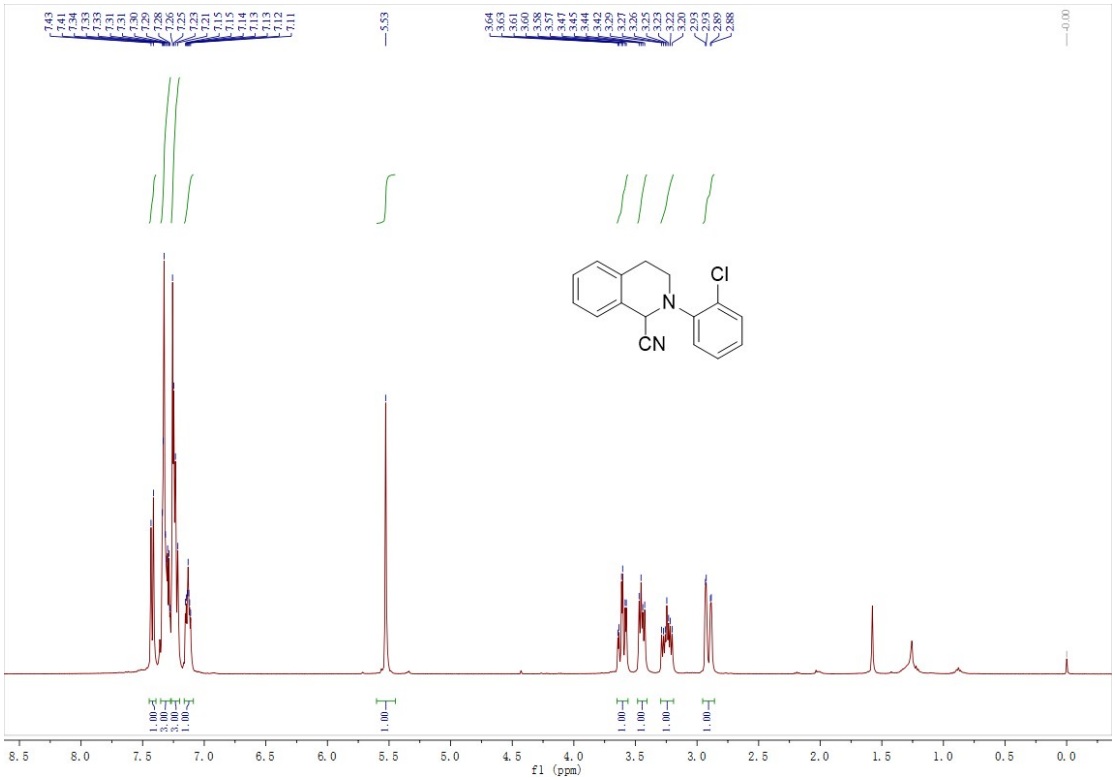
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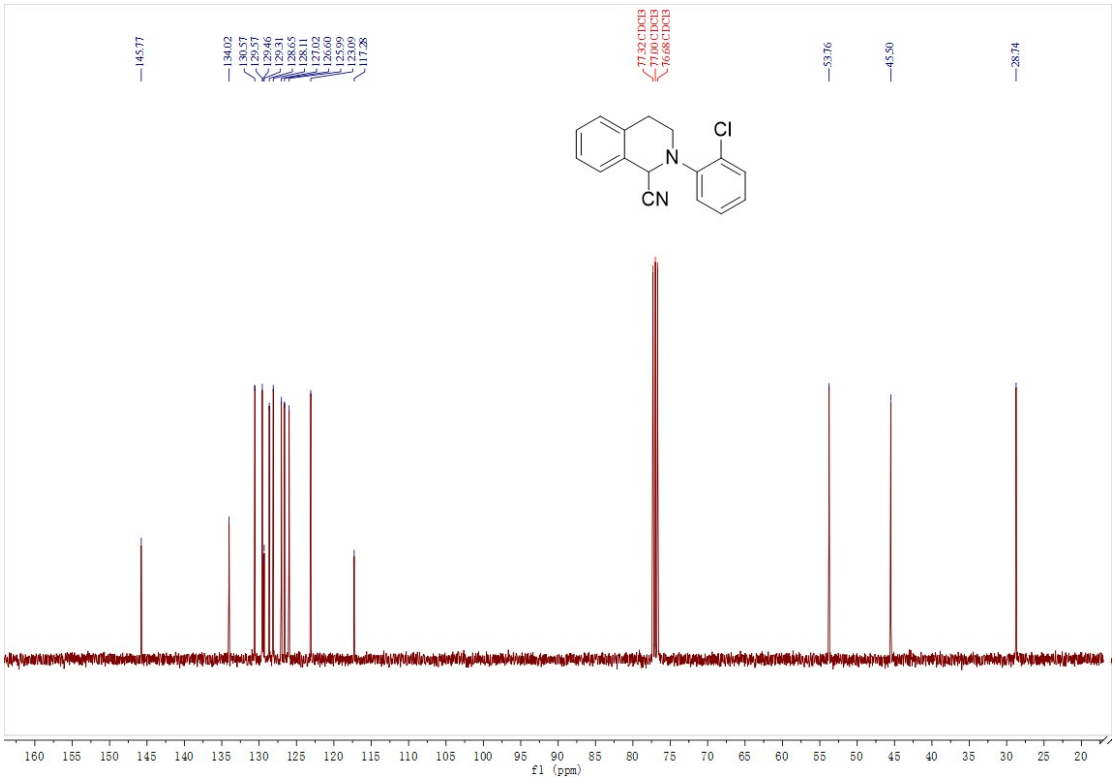
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127.02
126.60
125.99
123.99
117.28
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
53.76
45.50
28.74
Cl
N
CN
160
155
150
145
140
135
130
125
120
115
110
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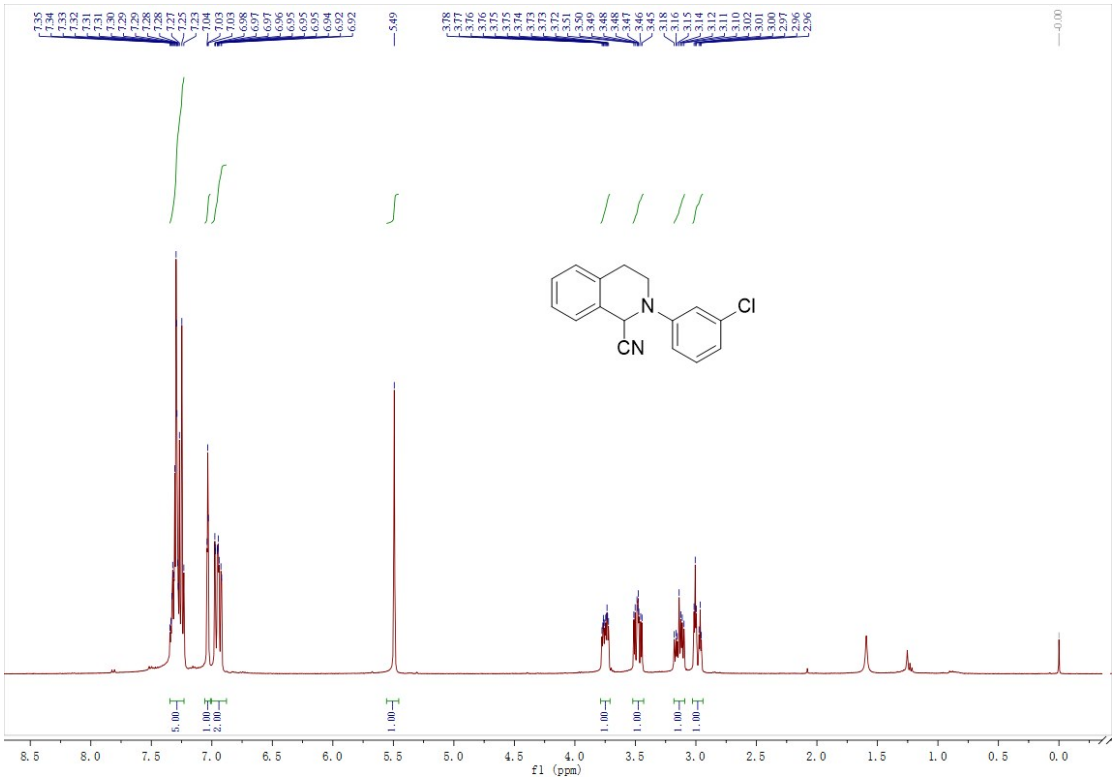
f1 (ppm)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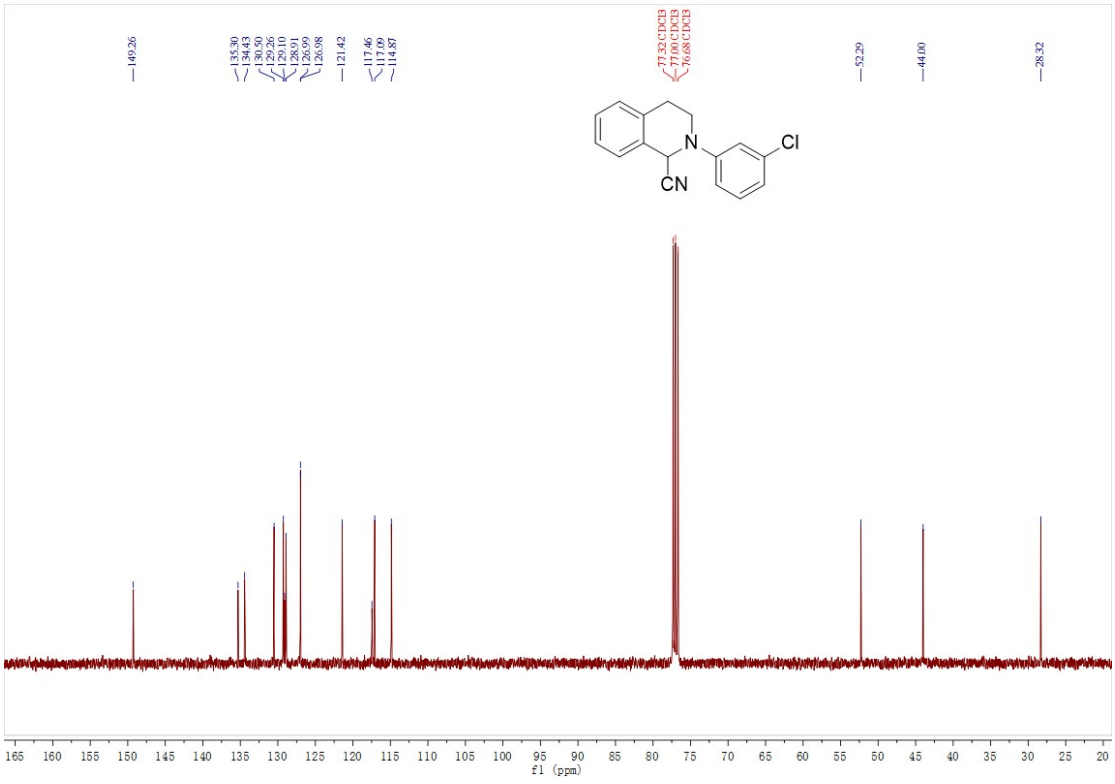
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CN
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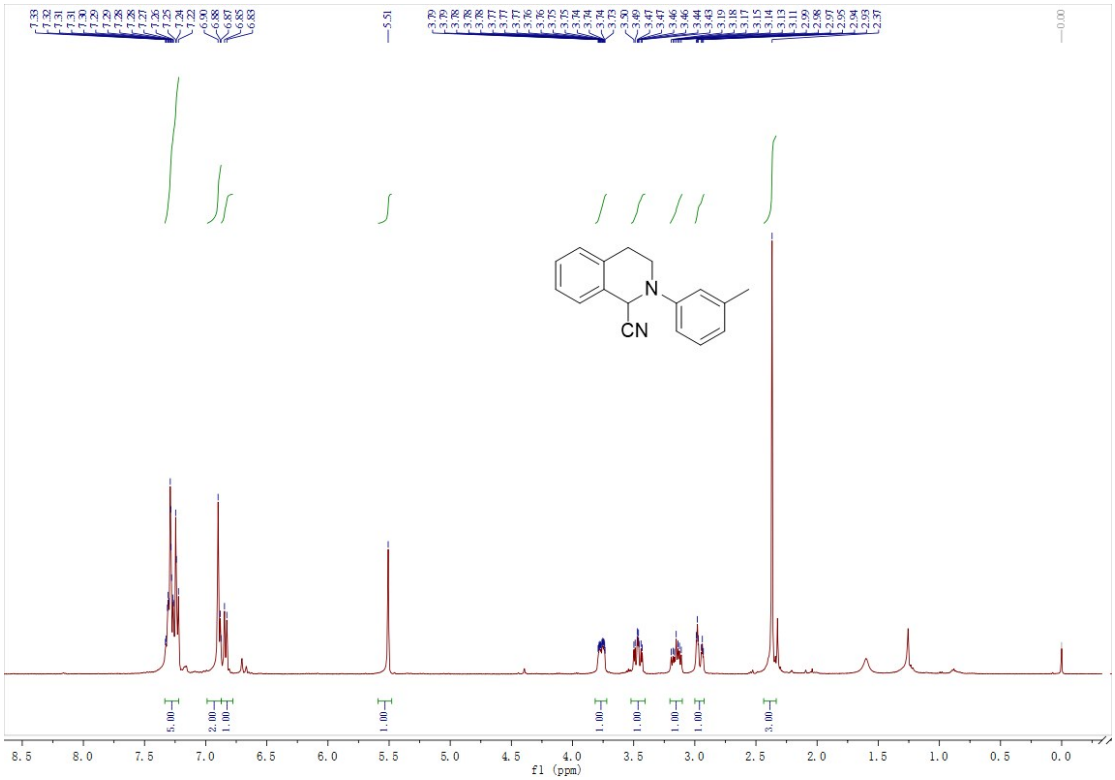
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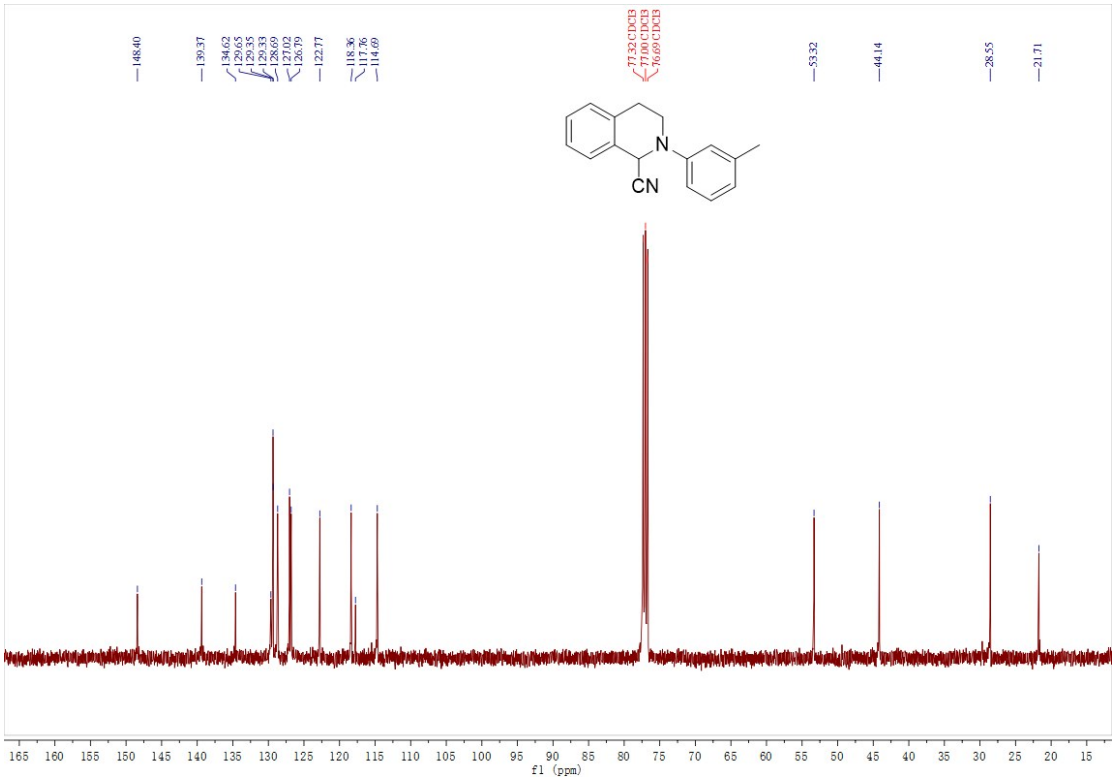
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129.33
128.69
127.02
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122.77
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117.76
114.69
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77.00 CDCl3
76.69 CDCl3
53.32
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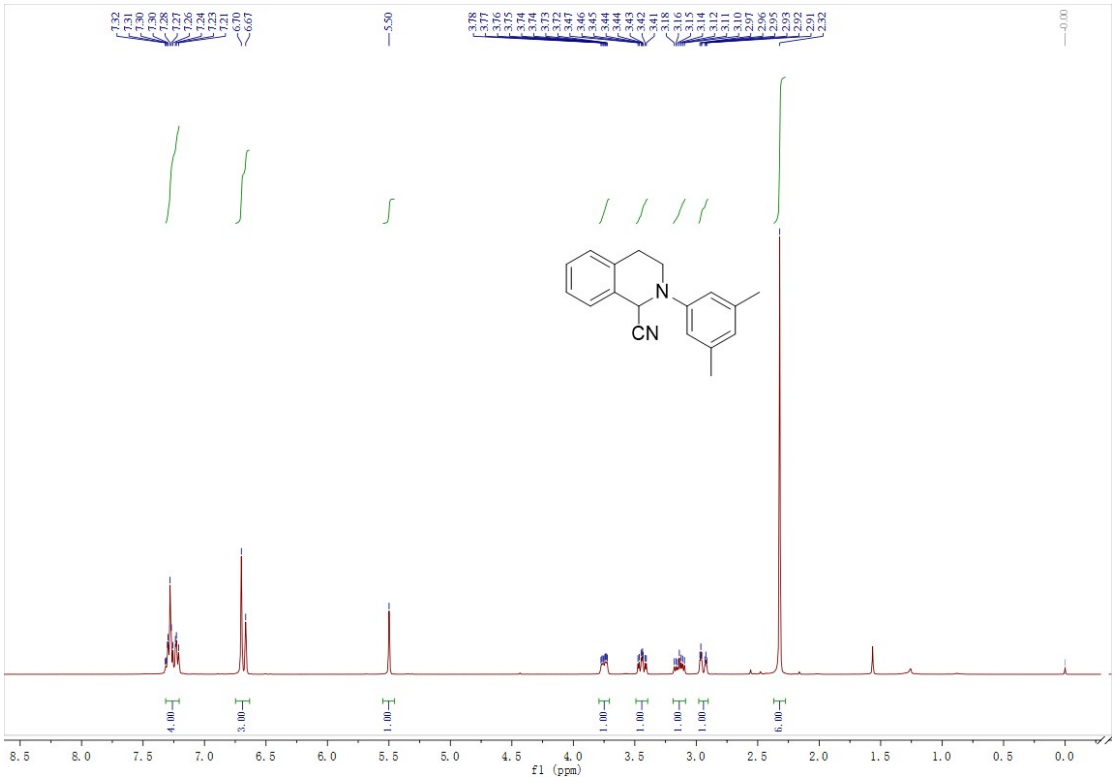
28.55
21.71
N
CN
f1 (ppm)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5.50
3.78
3.77
3.76
3.75
3.74
3.74
3.73
3.72
3.347
3.346
3.345
3.344
3.343
3.342
3.341
3.18
3.16
3.15
3.14
3.12
3.11
3.10
2.97
2.96
2.95
2.93
2.92
2.91
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CN
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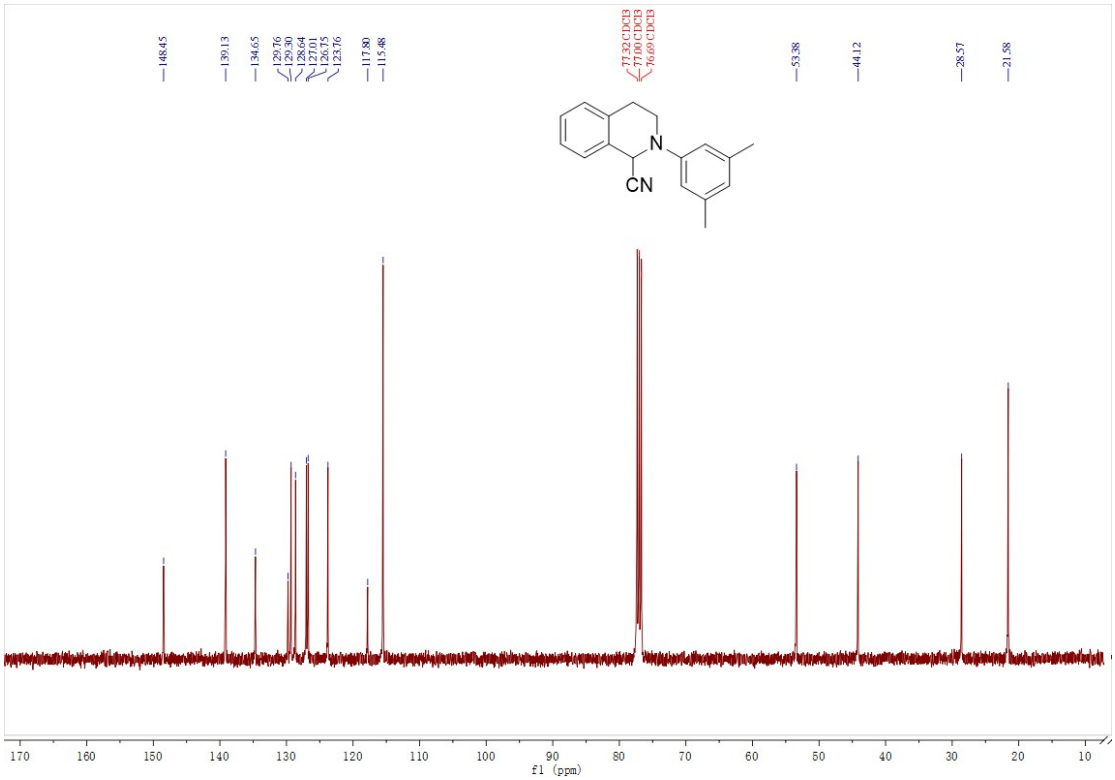
f1 (ppm)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76.69 CDCl3
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28.57
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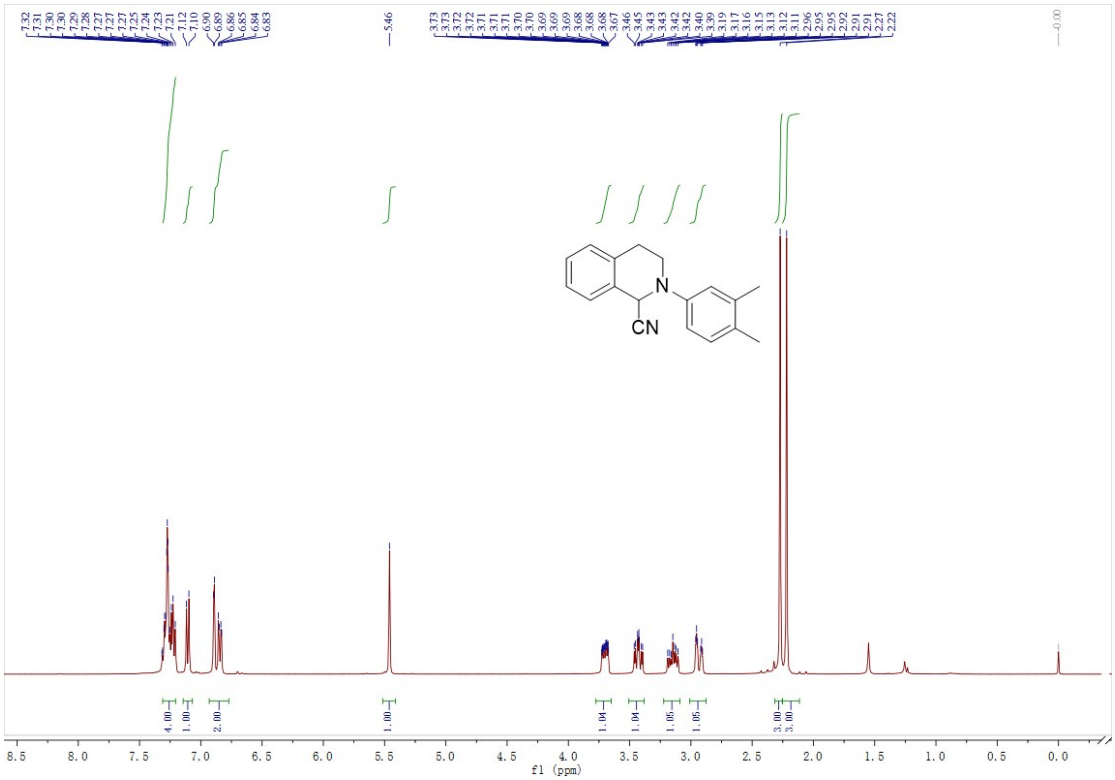
N
CN
f1 (ppm)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7.21
7.12
7.10
6.90
6.89
6.86
6.85
6.84
6.83
5.46
3.73
3.73
3.72
3.72
3.71
3.71
3.71
3.70
3.70
3.69
3.69
3.69
3.68
3.68
3.68
3.67
3.46
3.45
3.43
3.43
3.42
3.42
3.40
3.39
3.19
3.17
3.16
3.15
3.13
3.12
3.11
2.96
2.95
2.92
2.91
2.27
2.22
0.00
N
CN
4.00
1.00
2.00
1.00
1.04
1.04
1.05
1.05
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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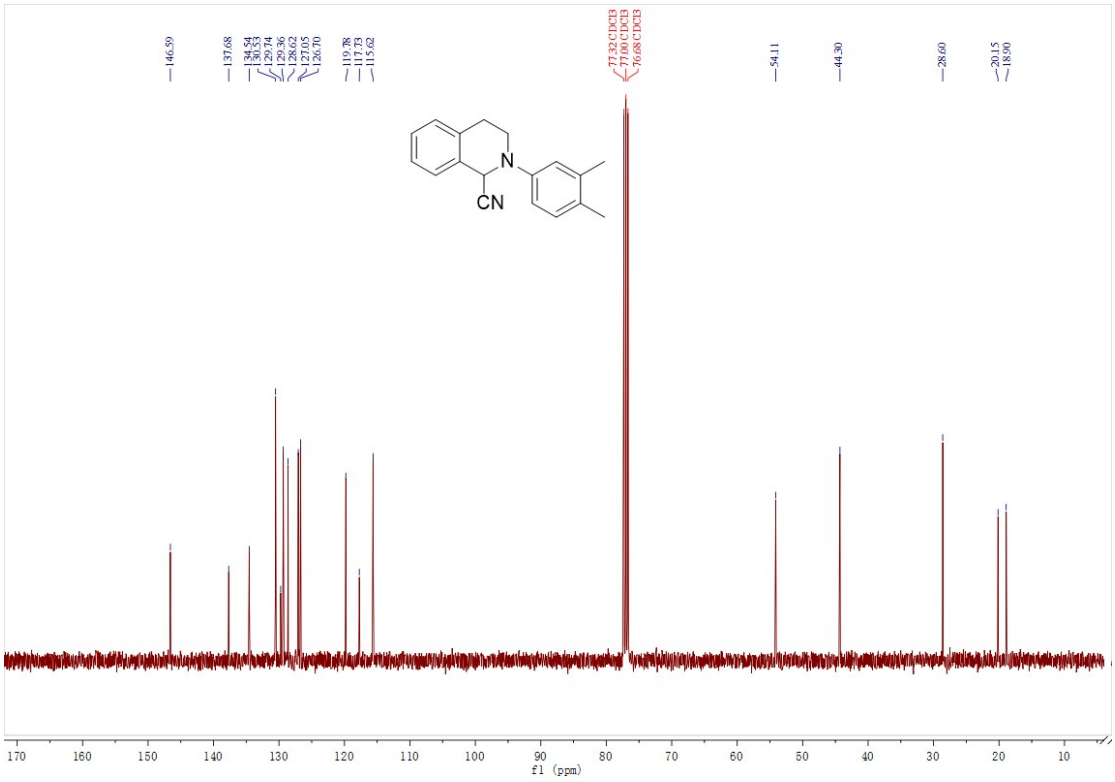
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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119.78
117.73
115.62
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
54.11
44.30
28.60
20.15
18.90
N
CN
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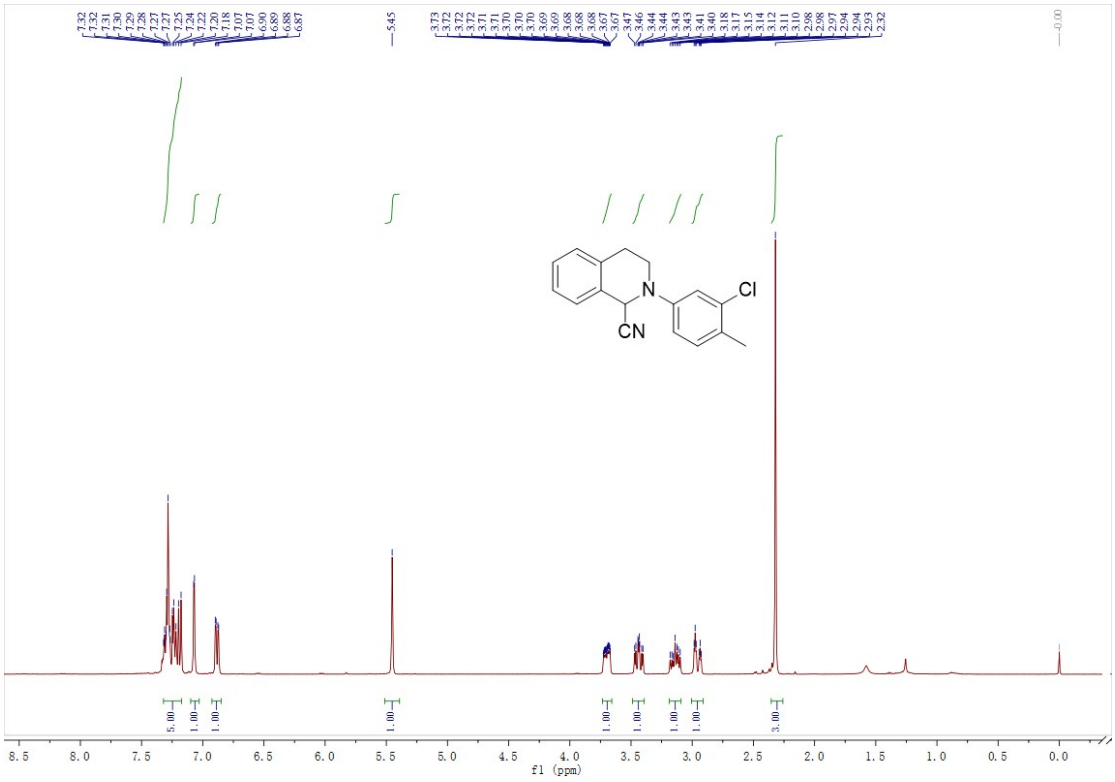
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.32
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7.07
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6.89
6.88
6.87
5.45
3.73
3.72
3.72
3.72
3.71
3.71
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3.68
3.68
3.68
3.67
3.67
3.47
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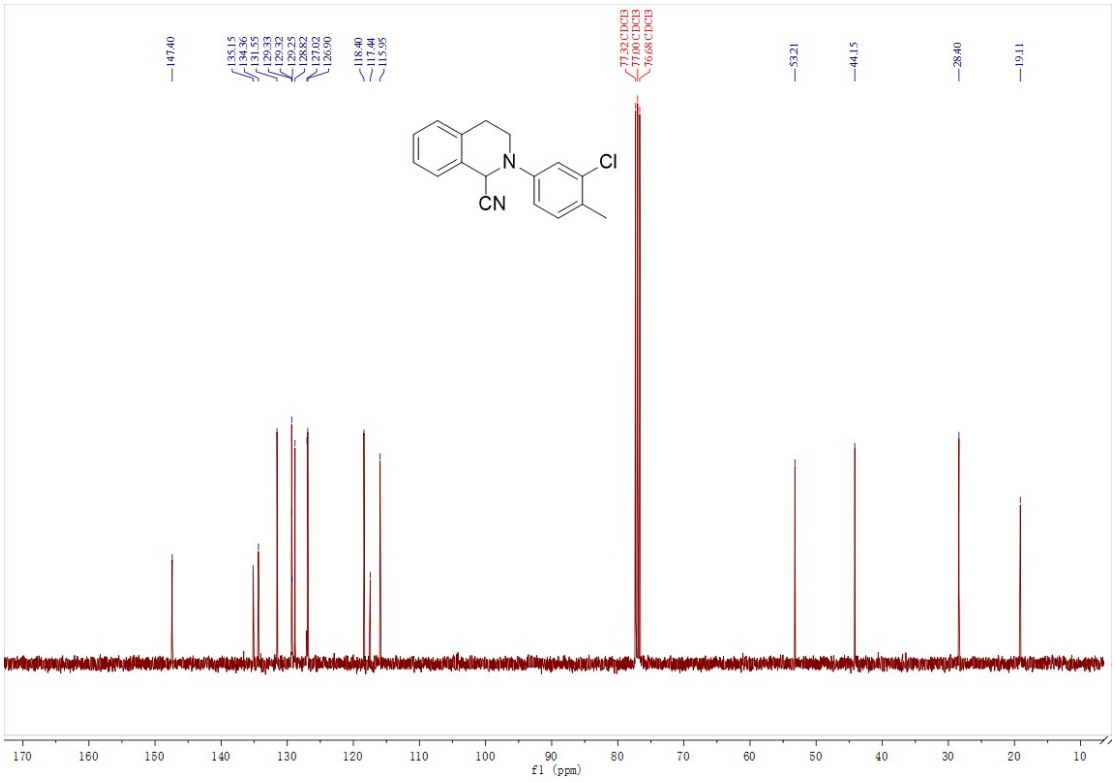
3.44
3.44
3.43
3.43
3.41
3.40
3.18
3.17
3.15
3.14
3.12
3.11
3.10
2.98
2.98
2.97
2.94
2.94
2.93
2.92
0.00
N
Cl
CN
5.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.32
129.25
128.82
127.02
126.90
118.40
117.44
115.95
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
53.21
44.15
28.40
19.11
N
Cl
CN
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)