Electrochemical promoted oxidative α-cyanation of tertiary and secondary amines using cheap AIBN

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1. Typical Experimental Procedure

(a) General

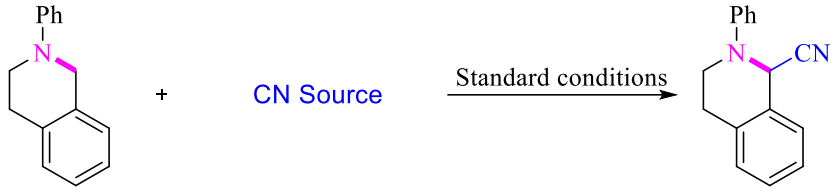
All reactions were carried out in anhydrous solvent and commercially available reagents were used as received unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated aluminium-backed silica gel 60 F_{254} plates (EMD Millipore, 200 μm thickness). TLC plates were visualized with ultraviolet light. Flash column chromatography was performed using Tsingtao silica gel (200-300). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX - 400 spectrometers; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference ($CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.16 ppm). Data for ^{1}H NMR and ^{13}C NMR are reported as follows: chemical shift (δ, ppm), multiplicity, integration, and coupling constant (Hz). Melting points are uncorrected. The instrument for electrolysis is IKA ElectraSyn 2.0. Cyclic voltammograms were obtained on a CHI 660E potentiostat.

(b) General procedure for synthesis of compound 3

To an undivided single-necked bottle (10 mL) were added 1,2,3,4-tetrahydroisoquinolines **1** (0.20 mmol) and AIBN **2** (0.20 mmol) under the presence of $^{n}Bu_4NBr$ (0.006 M) and CH_3CN (5 mL) as the solvent. The bottle was equipped with graphite electrode (1.0×1.0 cm^2) as anode and platinum electrodes as cathode under air. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA at room temperature for 3 h until complete consumption of **1** as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the solution was filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (Petroleum ether/ethyl acetate) to afford the desired products **3**.

(c) Experimental device

(d)



TMSCN	63%
malononitrile	51%
NaCN	trace

Table S1 Screening of other CN sources

(e)

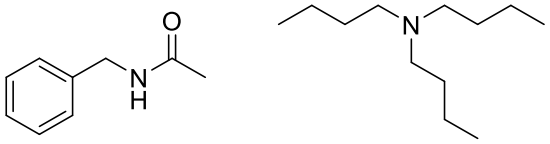
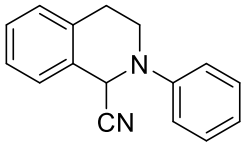


Table S2 ineffective amines

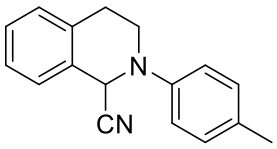
2. Characterization data of products

2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3a)[1]



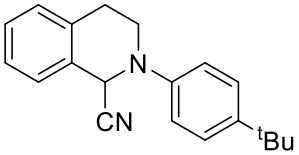
white solid, m.p. 99-100 °C, (44.69 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.6 Hz, 2 H), 7.24 – 7.19 (m, 3 H), 7.15 (d, *J* = 6.8 Hz, 1 H), 7.00 (d, *J* = 8.4 Hz, 2 H), 6.94 (t, *J* = 7.6, 1 H), 5.43 (s, 1 H), 3.72 – 3.67 (m, 1 H), 3.40 (td, *J* = 10.8 Hz, 4.0 Hz, 1 H), 3.12 – 3.04 (m, 1 H), 2.91 – 2.86 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 134.7, 129.7, 129.7, 129.5, 128.9, 127.2, 126.9, 122.0, 117.9, 117.7, 53.3, 44.3, 28.6; MS:m/z 234 (M^+).

2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3b)[1]



white solid, m.p. 117-118 °C, (41.9 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.07 (m, 6 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 5.37 (s, 1 H), 3.64 – 3.59 (m, 1 H), 3.35 (td, *J* = 11.2 Hz, 4.0 Hz, 1 H), 3.11 – 3.02 (m, 1 H), 2.85 (dt, *J* = 16.4 Hz, 2.8 Hz, 1 H), 2.23 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 134.6, 131.9, 130.2, 129.7, 129.5, 128.8, 127.2, 126.9, 118.4, 117.8, 54.2, 44.4, 28.7, 20.7; MS:m/z 248 (M^+).

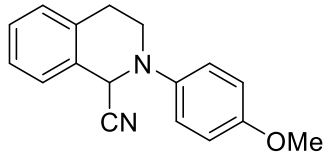
2-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3c)[2]



yellow oil, (50.7 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.8 Hz, 2 H), 7.23 – 7.12 (m, 4 H),

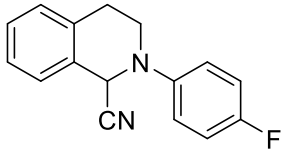
6.95 (d, *J* = 8.4 Hz, 2 H), 5.40 (s, 1 H), 3.67 – 3.63 (m, 1 H), 3.37 (td, *J* = 11.2 Hz, 4.0 Hz, 1 H), 3.10 – 3.01 (m, 1 H), 2.85 (dt, *J* = 16.4 Hz, 3.2 Hz, 1 H), 1.23 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 144.9, 134.7, 129.5, 128.8, 127.2, 126.9, 126.5, 117.9, 117.7, 53.7, 44.4, 34.2, 31.5, 28.7; MS:m/z 290 (M^+).

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3d)[2]



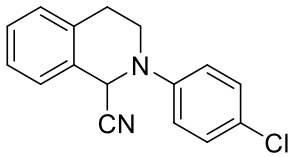
yellow oil, (42.5 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.12 (m, 4 H), 6.99 (d, *J* = 9.2 Hz, 2 H), 6.82 (d, *J* = 9.2 Hz, 2 H), 5.28 (s, 1 H), 3.70 (s, 3 H), 3.51 – 3.46 (m, 1 H), 3.33 (td, *J* = 11.6 Hz, 4.0 Hz, 1 H), 3.11 – 3.02 (m, 1 H), 2.83 (d, *J* = 15.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 142.6, 134.4, 129.7, 129.5, 128.7, 127.1, 126.8, 121.1, 117.7, 114.8, 55.6, 55.6, 44.9, 28.8; MS:m/z 264 (M^+).

2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3e)[1]



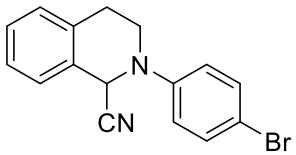
white solid, m.p. 124-125 °C, (43.1 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.12 (m, 4 H), 6.96 (d, *J* = 5.6 Hz, 4 H), 5.30 (s, 1 H), 3.54 – 3.50 (m, 1 H), 3.33 (td, *J* = 12.0 Hz, 4.0 Hz, 1 H), 3.09 – 3.01 (m, 1 H), 2.84 (dt, *J* = 16.4 Hz, 3.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 145.1 (d, *J* = 2.5 Hz), 134.3, 129.4 (d, *J* = 12.2 Hz), 128.9, 127.1, 126.9, 120.5 (d, *J* = 8.0 Hz), 117.5, 116.3, 116.1, 54.7, 44.8, 28.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -120.7. MS:m/z 252 (M^+).

2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3f)[1]



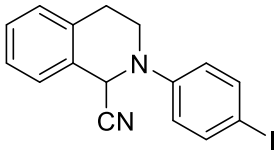
white solid, m.p. 152-153 °C, (44.1 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 – 7.20 (m, 5 H), 7.16 (d, *J* = 7.6 Hz, 1 H), 6.93 (d, *J* = 9.2 Hz, 2 H), 5.38 (s, 1 H), 3.67 – 3.60 (m, 1 H), 3.38 (dt, *J* = 10.8 Hz, 4 Hz, 1 H), 3.11 – 3.03 (m, 1 H), 2.89 (dt, *J* = 16.4 Hz, 3.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 134.5, 129.6, 129.5, 129.3, 129.0, 127.2, 127.1, 127.1, 119.0, 117.6, 53.3, 44.4, 28.5; MS:m/z 268 (M^+).

2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3g)[1]



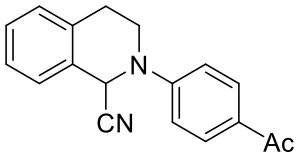
white solid, m.p. 155-156 °C, (56.0 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.8 Hz, 2 H), 7.26 – 7.15 (m, 4 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 5.38 (s, 1 H), 3.66 – 3.60 (m, 1 H), 3.37 (td, *J* = 10.8 Hz, 4.4 Hz, 1 H), 3.10 – 3.02 (m, 1 H), 2.89 (dt, *J* = 16.4 Hz, 3.6 Hz, 1 H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 134.5, 132.5, 129.5, 129.2, 129.0, 127.1, 127.1, 119.2, 117.6, 114.4, 52.9, 44.3, 28.5; MS:m/z 312 (M^+).

2-(4-iodophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3h)[2]



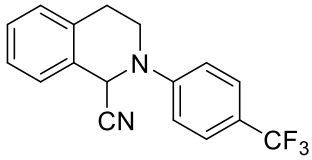
white powder, m.p. 145-147 °C, (61.2 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, 2 H), 7.26 – 7.20 (m, 3 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 5.38 (s, 1 H), 3.66 – 3.61 (m, 1 H), 3.40 – 3.33 (m, 1 H), 3.09 – 3.01 (m, 1 H), 2.88 (dt, *J* = 16.4 Hz, 3.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 138.4, 134.5, 129.4, 129.2, 128.9, 127.1, 127.1, 119.3, 117.6, 84.2, 52.5, 44.1, 28.4; MS:m/z 360 (M^+).

2-(4-acetylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3i)[1]



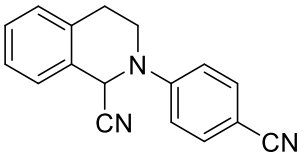
light yellow oil, (37.9 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.8 Hz, 2 H), 7.40 – 7.28 (m, 4 H), 7.04 (d, *J* = 9.2 Hz, 2 H), 5.66 (s, 1 H), 3.94 – 3.88 (m, 1 H), 3.64 – 3.57 (m, 1 H), 3.20 – 3.05 (m, 2 H), 2.57 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 151.2, 134.8, 130.6, 129.3, 129.2, 129.2, 129.0, 127.3, 127.1, 117.6, 114.1, 50.4, 43.7, 28.3, 26.3; MS:m/z 276 (M^+).

2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3j)[1]



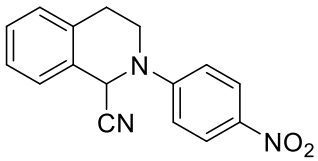
white solid, m.p. 102-103 °C, (45.5 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.8 Hz, 2 H), 7.30 – 7.17 (m, 4 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 5.50 (s, 1 H), 3.80 – 3.73 (m, 1 H), 3.50 – 3.43 (m, 1 H), 3.10 – 3.03 (m, 1 H), 2.95 (dt, *J* = 16.4 Hz, 4.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 134.7, 129.3, 129.2, 129.1, 127.3, 127.1, 127.0 (q, *J* = 3.6 Hz), 126.9 (q, *J* = 269.3 Hz), 126.9 (q, *J* = 32.7 Hz), 126.9, 126.7, 125.8, 123.2, 123.1, 122.7, 122.4, 122.1, 120.4, 117.6, 115.4, 51.2, 43.9, 28.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -61.5. MS:m/z 302 (M^+).

2-(4-cyanophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3k)[1]



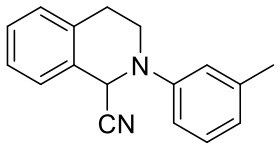
white solid, m.p. 155-156 °C, (39.1 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.8 Hz, 2 H), 7.30 – 7.19 (m, 4 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 5.52 (s, 1 H), 3.81 – 3.73 (m, 1 H), 3.54 – 3.48 (m, 1 H), 3.10 – 2.97 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 134.7, 133.9, 129.4, 129.1, 128.8, 127.4, 127.1, 119.5, 117.5, 114.7, 102.5, 50.1, 43.8, 28.2; MS:m/z 259 (M^+).

2-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3l)[2]



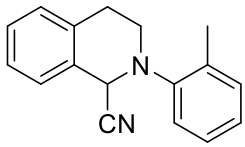
yellow powder, m.p. 102-104 ºC, (37.6 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 9.6 Hz, 2 H), 7.33 – 7.19 (m, 4 H), 6.93 (d, *J* = 9.2 Hz, 2 H), 5.58 (s, 1 H), 3.84 – 3.78 (m, 1 H), 3.65 – 3.58 (m, 1 H), 3.09 (t, *J* = 6.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 140.3, 134.8, 129.6, 129.2, 128.8, 127.7, 127.1, 126.2, 117.3, 113.5, 49.9, 44.2, 28.3; MS:m/z 279 (M^+).

2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3m)[1]



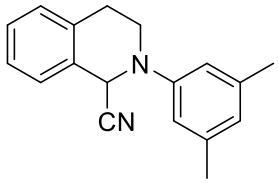
colorless oily liquid, (39.4 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.13 (m, 5 H), 6.80 (d, *J* = 7.2 Hz, 2 H), 6.75 (d, *J* = 7.6 Hz, 1 H), 5.42 (s, 1 H), 3.70 – 3.65 (m, 1 H), 3.37 (td, *J* = 11.2 Hz, 4.4 Hz, 1 H), 3.10 – 3.01 (m, 1 H), 2.86 (dt, *J* = 16.0 Hz, 3.2 Hz, 1 H), 3.28 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 139.5, 134.7, 129.7, 129.5, 129.4, 128.8, 127.1, 126.9, 122.8, 118.5, 117.9, 114.8, 53.4, 44.2, 28.6, 21.8; MS:m/z 248 (M^+).

2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3n)[1]



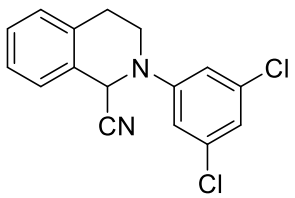
colorless liquid, (46.8 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 7 H), 7.08 – 7.03 (m, 1 H), 4.98 (s, 1 H), 3.53 (td, *J* = 11.6 Hz, 3.6 Hz, 1 H), 3.28 – 3.23 (m, 1 H), 3.14 – 3.06 (m, 1 H), 2.83 (dd, *J* = 13.2 Hz, 2.0 Hz, 1 H), 2.20 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 134.6, 133.4, 131.3, 130.1, 129.8, 128.7, 127.3, 127.1, 126.7, 125.5, 122.1, 117.8, 55.1, 46.1, 29.1, 17.7; MS:m/z 248 (M^+).

2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3o)[1]



colorless oily liquid, (43.7 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 4 H), 6.63 (d, *J* = 14.8 Hz, 3 H), 5.42 (s, 1 H), 3.68 – 3.64 (m, 1 H), 3.35 (td, *J* = 11.2 Hz, 4.0 Hz, 1 H), 3.09 – 2.95 (m, 1 H), 2.85 (dt, *J* = 16.0 Hz, 2.8 Hz, 1 H), 2.24 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 139.2, 134.7, 129.8, 129.4, 128.7, 127.1, 126.6, 123.9, 117.9, 115.6, 53.5, 44.2, 28.7, 21.7; MS:m/z 262 (M^+).

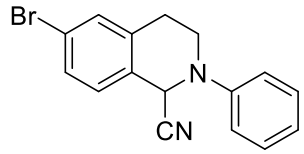
2-(3,5-dichlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3p)[2]



white powder, m.p. 151-152 ºC, (43.7 mg, 72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 3 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 6.84 – 6.83 (m, 1 H), 6.78 (d, *J* = 1.6 Hz, 2 H), 5.37 (s, 1 H), 3.64 – 3.58 (m, 1 H), 3.41

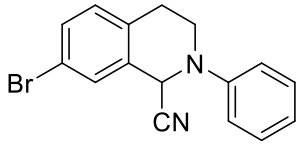
– 3.34 (m, 1 H), 3.05 – 2.97 (m, 1 H), 2.90 (dt, *J* = 16.4 Hz, 4.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7, 135.9, 134.4, 129.3, 129.2, 128.9, 127.3, 127.1, 120.9, 117.4, 114.6, 51.5, 44.0, 28.3; MS:m/z 302 (M^+).

6-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3q)[2]



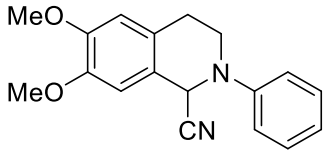
yellow oil, (47.2 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 4 H), 7.07 (d, *J* = 8.8 Hz, 1 H), 6.99 – 6.93 (m, 3 H), 5.37 (m, 1 H), 3.69 – 3.64 (m, 1 H), 3.35 (td, *J* = 10.8 Hz, 4.0 Hz, 1 H), 3.08 – 3.00 (m, 1 H), 2.84 (dt, *J* = 16.4 Hz, 3.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 136.9, 132.4, 130.1, 129.7, 128.7, 122.8, 122.4, 117.9, 117.3, 53.1, 43.9, 28.4; MS:m/z 312 (M^+).

7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3r)[2]



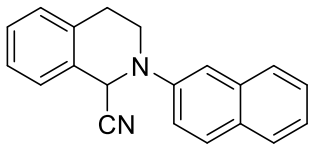
yellow oil, (50.3 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.25 (m, 4 H), 7.02 – 6.92 (m, 4 H), 5.36 (m, 1 H), 3.69 – 3.64 (m, 1 H), 3.35 (td, *J* = 10.8 Hz, 4.0 Hz, 1 H), 3.02 – 2.94 (m, 1 H), 2.80 (dt, *J* = 16.4 Hz, 3.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 133.7, 132.0, 131.6, 131.1, 129.9, 129.7, 122.4, 120.2, 117.9, 117.3, 52.9, 44.1, 28.1; MS:m/z 312 (M^+).

6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3s)[2]



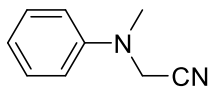
white solid, m.p. 138-140 °C, (43.8 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.6 Hz, 2 H), 7.00 (d, *J* = 8.0 Hz, 2 H), 6.94 (t, *J* = 7.6 Hz, 1 H), 6.67 (s, 1 H), 6.61 (s, 1 H), 5.37 (s, 1 H), 3.81 (s, 6 H), 3.72 – 3.67 (m, 1 H), 3.36 (td, *J* = 11.2 Hz, 4.0 Hz, 1 H), 3.05 – 2.96 (m, 1 H), 2.77 (dt, *J* = 15.6 Hz, 3.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 148.5, 148.1, 129.7, 126.9, 122.1, 121.2, 118.0, 117.9, 111.6, 109.4, 56.2, 56.1, 53.2, 44.3, 28.2; MS:m/z 294 (M^+).

2-(naphthalen-2-yl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3t)[1]



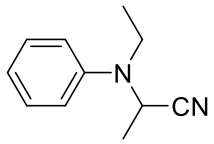
colorless oil, (43.9 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 6.8 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.45 – 7.37 (m, 4 H), 7.29 – 7.26 (m, 1 H), 7.22 – 7.16 (m, 3 H), 5.31 (s, 1 H), 3.70 (td, *J* = 12.0 Hz, 3.6 Hz, 1 H), 3.49 – 3.44 (m, 1 H), 3.28 – 3.27 (s, 1 H), 2.93 (d, *J* = 14.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 134.8, 134.6, 129.9, 129.9, 128.9, 128.9, 127.3, 126.8, 126.5, 126.3, 126.1, 125.9, 122.5, 118.6, 117.4, 56.6, 46.3, 29.3; MS:m/z 284 (M^+).

2-(methyl(phenyl)amino)acetonitrile(3u)[1]



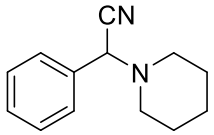
colorless oil, (16.4 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.2 Hz, 2 H), 6.97 – 6.89 (m, 3 H), 4.21 (s, 2 H), 3.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 129.6, 120.4, 115.6, 115.0, 42.5, 39.4; MS:m/z 146 (M^+).

***2-(ethyl(phenyl)amino)propanenitrile*(*3v*)[1]**



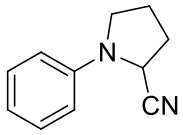
yellow oil, (23.4 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 8.0 Hz, 2 H), 7.01 (t, *J* = 7.6 Hz, 3 H), 4.53 – 4.47 (m, 1 H), 3.44 – 3.30 (m, 2 H), 1.59 (d, *J* = 7.2 Hz, 3 H), 1.21 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 129.5, 121.8, 119.6, 119.0, 48.3, 43.7, 18.6, 13.9; MS:m/z 174 (M^+).

***2-phenyl-2-(piperidin-1-yl)acetonitrile*(*3w*)[3]**



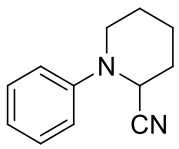
colorless oil, (32.2 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.2 Hz, 2 H), 7.41 – 7.35 (m, 3 H), 4.82 (s, 1 H), 2.54 – 2.50 (m, 4 H), 1.62 – 1.55 (m, 4 H), 1.50 – 1.46 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.7, 128.8, 128.8, 127.9, 115.8, 63.2, 51.1, 25.9, 24.1; MS:m/z 200 (M^+).

***1-phenylpyrrolidine-2-carbonitrile*(*3x*)[1]**



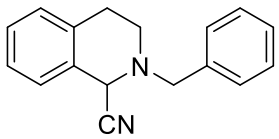
colorless oil, (31.1 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.6 Hz, 2 H), 6.87 (t, *J* = 7.2 Hz, 1 H), 6.73 (d, *J* = 8.4 Hz, 2 H), 4.47 (d, *J* = 5.6 Hz, 1 H), 3.52 – 3.47 (m, 1 H), 3.43 – 3.37 (m, 1 H), 2.48 – 2.42 (m, 1 H), 2.37 – 2.19 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 129.6, 119.4, 118.3, 112.8, 49.2, 47.6, 31.7, 24.1; MS:m/z 172 (M^+).

***1-phenylpiperidine-2-carbonitrile*(*3y*)[1]**



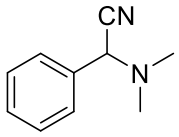
colorless oil, (31.4 mg, 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.2 Hz, 2 H), 7.02 (t, *J* = 7.6 Hz, 3 H), 4.65 (s, 1 H), 3.48 (d, *J* = 11.2 Hz, 1 H), 3.06 (m, *J* = 11.6 Hz, 1 H), 2.09 – 1.99 (m, 2 H), 1.89 – 1.87 (m, 2 H), 1.79 – 1.69 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 129.5, 122.3, 118.4, 117.3, 52.1, 46.7, 29.4, 25.2, 20.3; MS:m/z 186 (M^+).

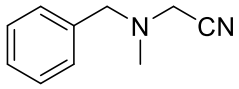
***2-benzyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile*(*3z*)[3]**



colorless oil, (40.4 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2 H), 7.36 – 7.28 (m, 3 H), 7.25 – 7.22 (m, 1 H), 7.18 – 7.14 (m, 2 H), 7.11 (d, *J* = 6.0 Hz, 1 H), 4.67 (s, 1 H), 3.91 (d, *J* = 10.8 Hz, 1 H), 3.82 (d, *J* = 10.8, 1 H), 3.10 – 3.01 (m, 2 H), 2.91 – 2.84 (m, 1 H), 2.78 – 2.74 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 134.5, 129.7, 129.5, 129.2, 128.8, 128.6, 127.9, 127.4, 128.5, 116.7, 60.0, 54.5, 46.7, 28.6; MS:m/z 248 (M^+).

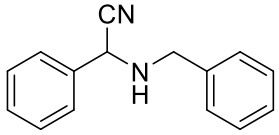
***2-(dimethylamino)-2-phenylacetonitrile*(*3aa*)*/2-(benzyl(methyl)amino)acetonitrile*(*3aa'*)[4]**





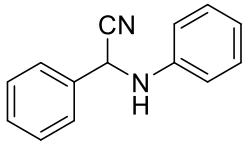
yellowish oil, (20.9 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 6.4 Hz, 2 H), 7.43 – 7.36 (m, 3 H), 7.43 – 7.29 (m, 5 H), 4.85 (s, 1 H), 3.61 (s, 1 H), 3.45 (s, 1 H), 2.44 (s, 3 H), 2.32 (s, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 129.2, 129.1, 128.9, 128.8, 127.9, 127.9, 63.3, 60.3, 44.3, 42.5, 41.9; MS:m/z 160 (M^+).

***2-(benzylamino)-2-phenylacetonitrile*(*3ab*)[4]**



yellowish oil, (15.6 mg, 35%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 5.6 Hz, 2 H), 7.40 – 7.35 (m, 5 H), 7.34 – 7.31 (m, 3 H), 4.71 (s, 1 H), 4.02 (d, *J* = 10.4 Hz, 1 H), 3.92 (d, *J* = 10.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 134.8, 129.1, 129.0, 128.7, 128.5, 128.5, 127.7, 127.4, 118.8, 53.5, 51.3; MS:m/z 222 (M^+).

***2-phenyl-2-(phenylamino)acetonitrile*(*3ac*)[4]**



yellow oil, (13.3 mg, 32%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 4.8 Hz, 2 H), 7.31 (d, *J* = 5.2 Hz, 3 H), 7.14 (t, *J* = 7.6 Hz, 2 H), 6.77 (t, *J* = 7.2 Hz, 1 H), 6.63 (d, *J* = 8.4 Hz, 2 H), 5.27 (d, *J* = 8.0 Hz, 1 H), 4.00 – 3.96 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 133.9, 129.6, 129.5, 129.3, 127.3, 120.2, 118.3, 114.2, 50.1; MS:m/z 208 (M^+).

3. References

1. B. Ullah.; Y.-L. Zhou.; J.-W. Chen.; Z.-B. Bao.; Y.-W. Yang.; Q.-L. Ren.; Z.-G. Zhang., *Tetrahedron Letters*. **2019**, *60*, 348-351.

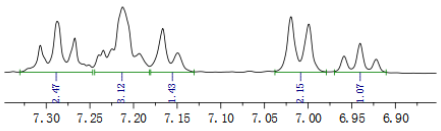
2. B. Yi.; N. Yan.; N.-N. Yi.; Y.-J. Xie.; X.-Y. Wen.; Chak-Tong Au.; D.-H. Lan., *RSC Advances*. **2019**, *51*, 29482-30032.

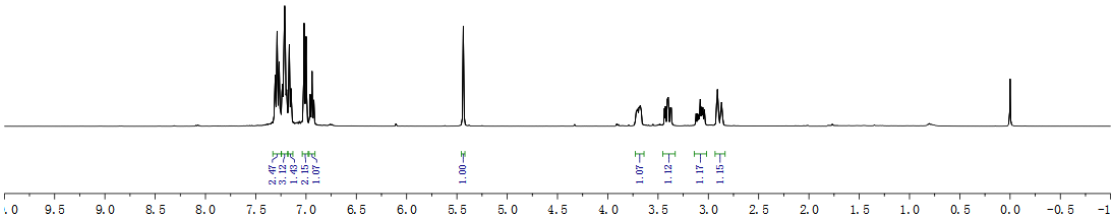
3. K. S. Indalkar.; C. K. Khatri.; G. U. Chaturbhuj., *Tetrahedron Letters*. **2017**, *58*, 2144-2148.

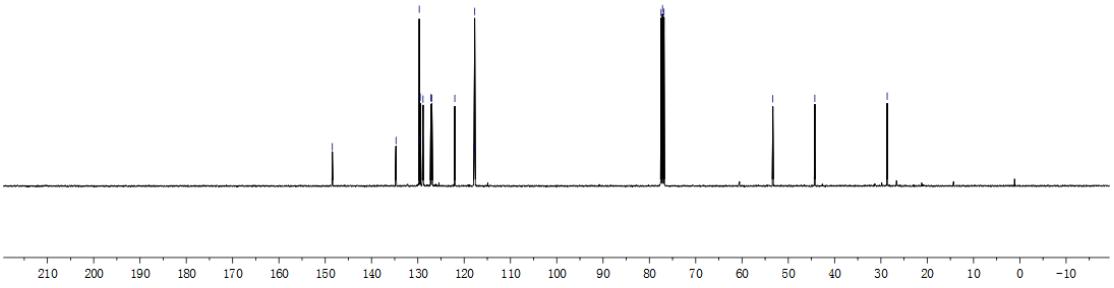
4. P.-C. Li.; Y.-D. Zhang.; Z.-L. Chen.; X.-X. Zhang., *Tetrahedron Letters.* **2017**, *58*, 1854-1858.

4. ^{1}H, ^{13}C and ^{19}F NMR spectra of products

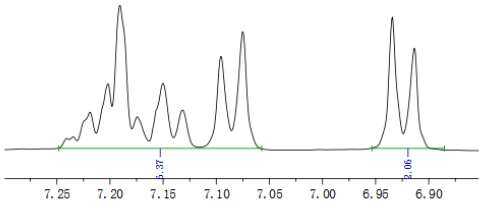
2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3a)

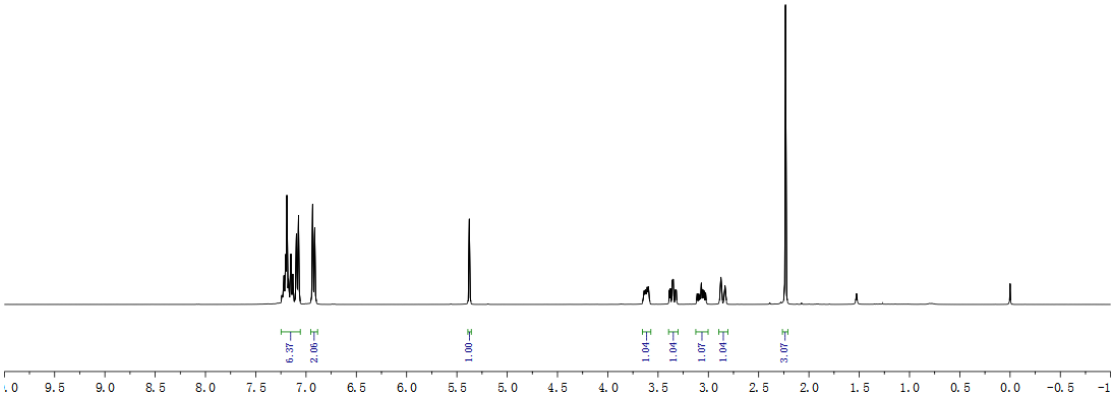


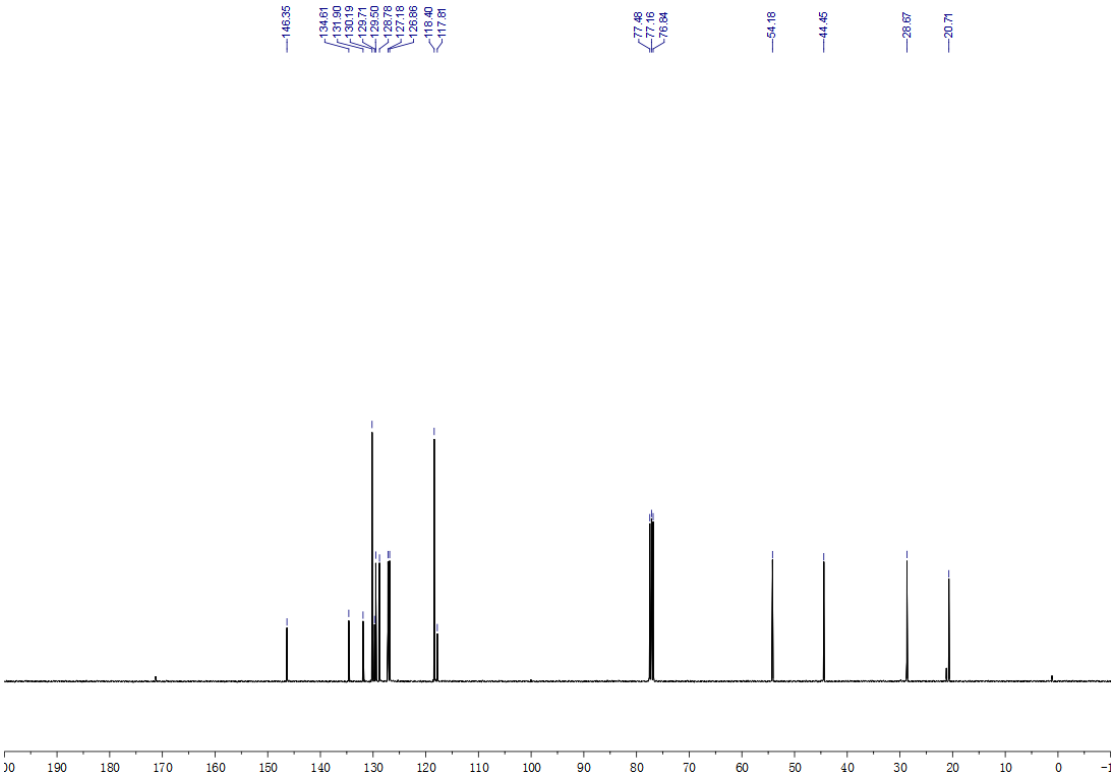




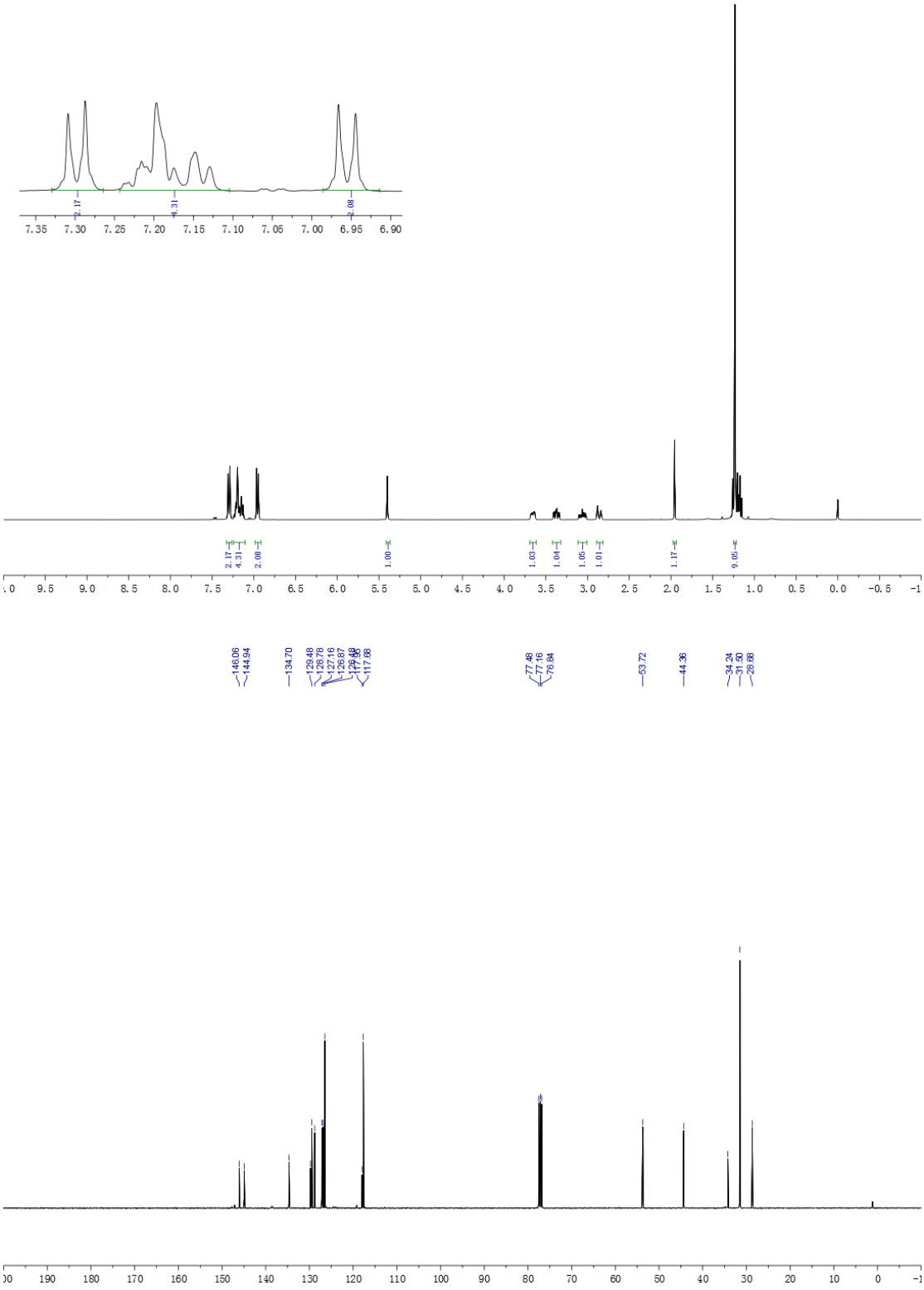
2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3b)



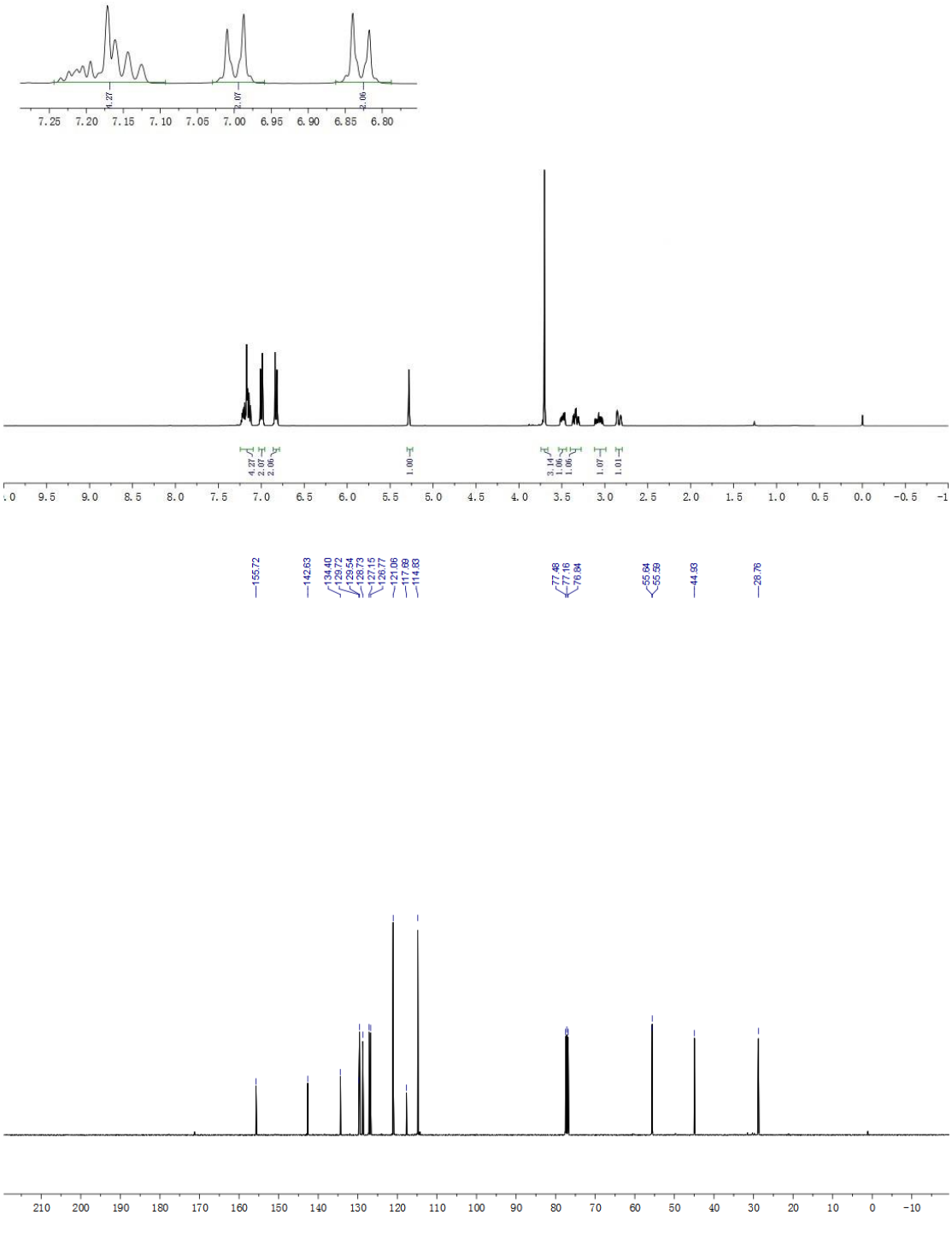




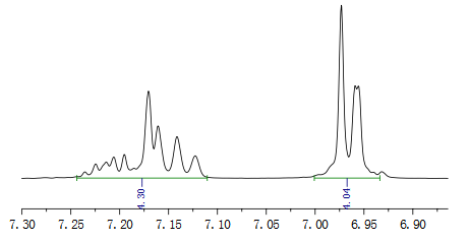
2-(4-(tert-butyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3c)

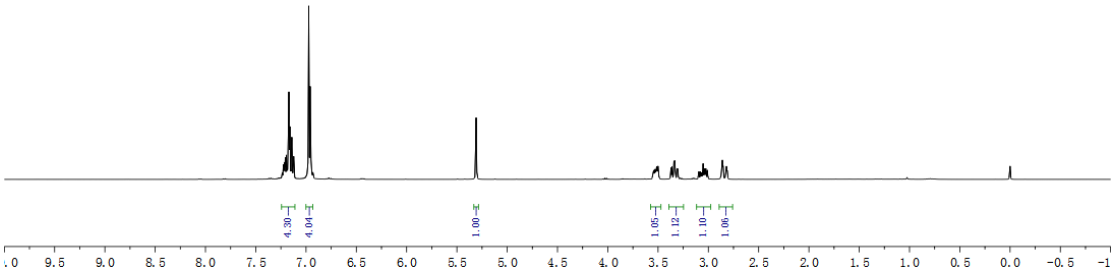


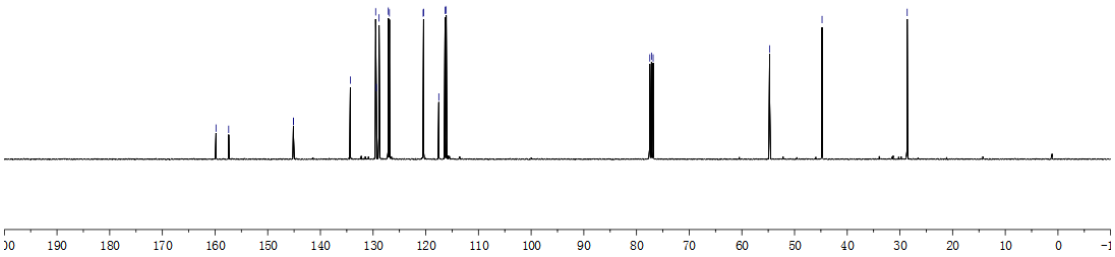
2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3d)

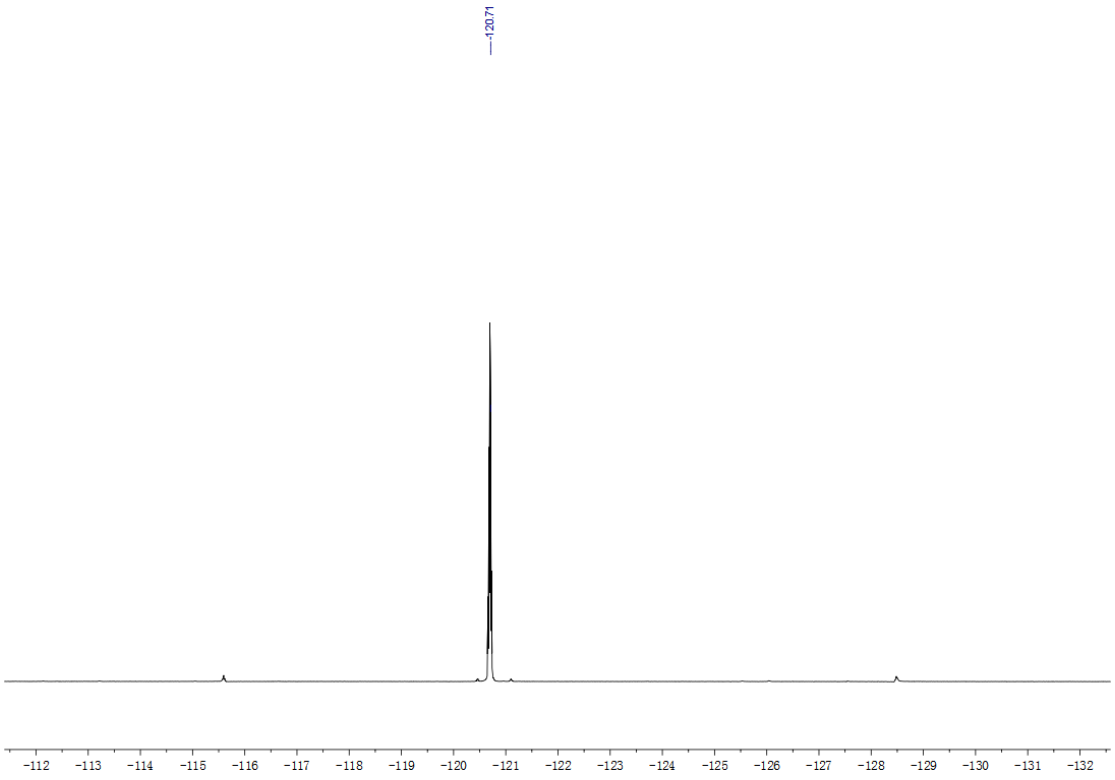


2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3e)





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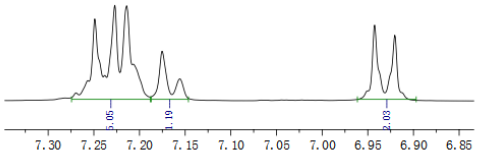
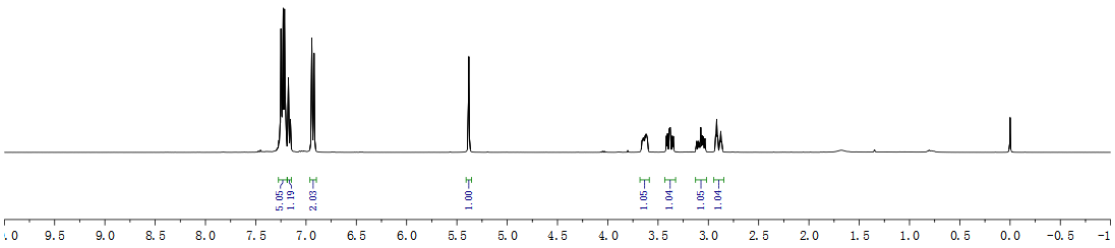
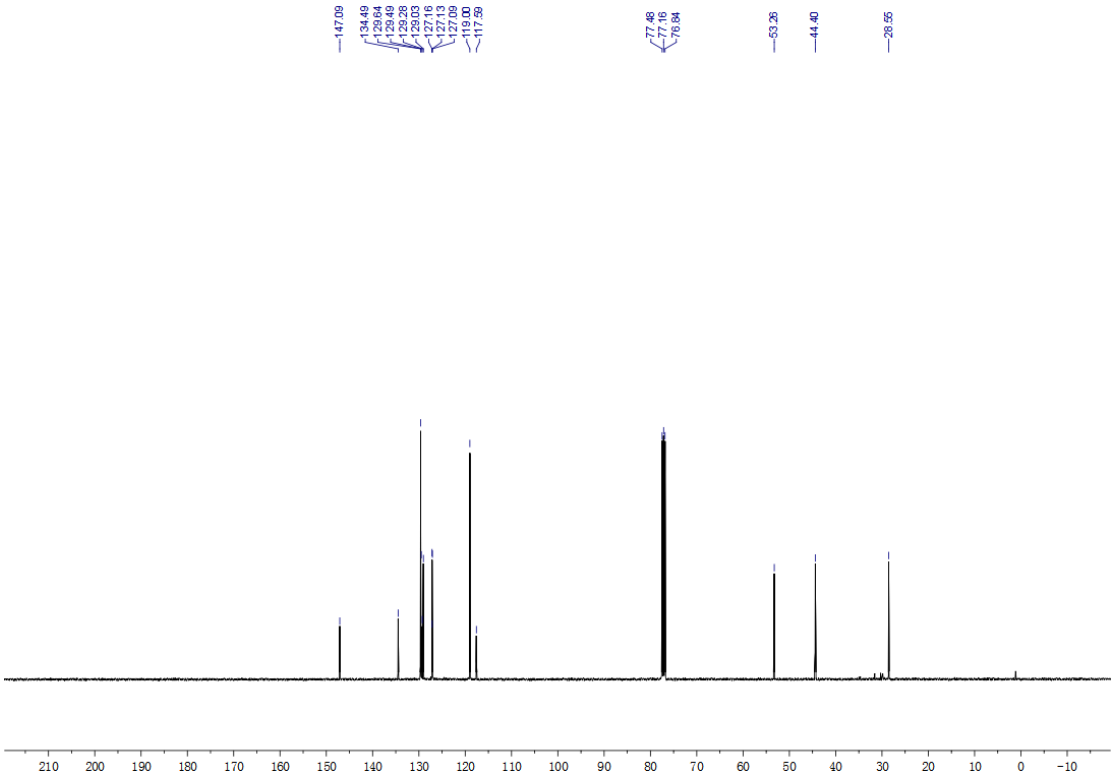
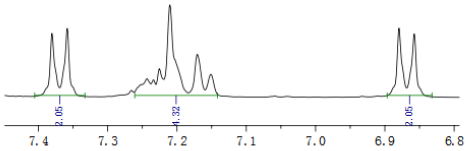
2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3f)

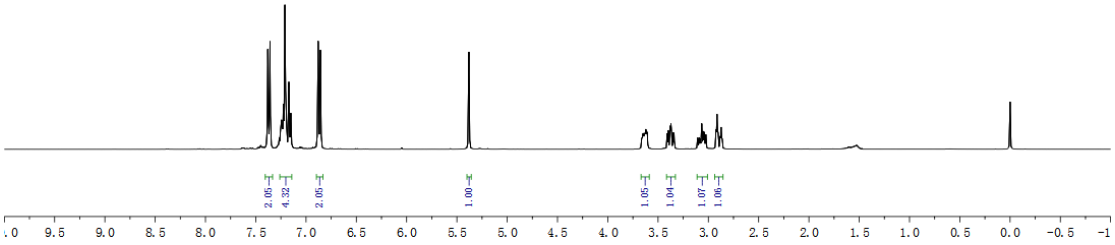


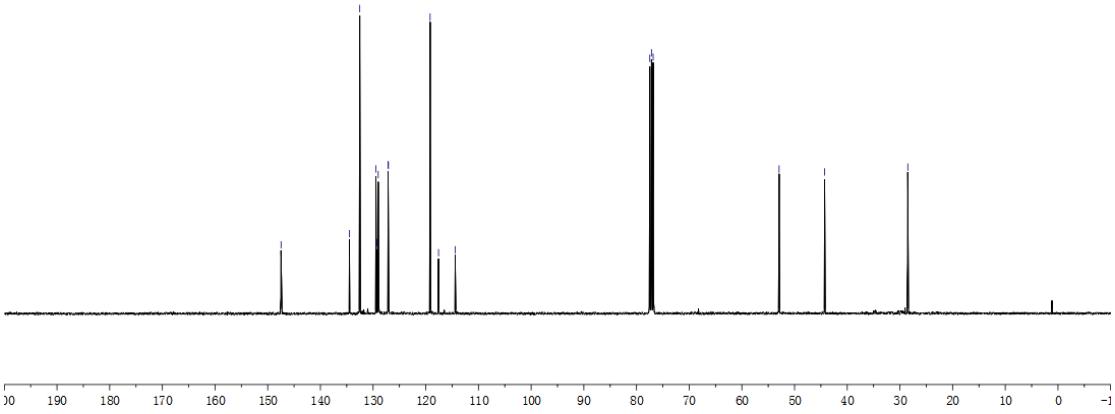




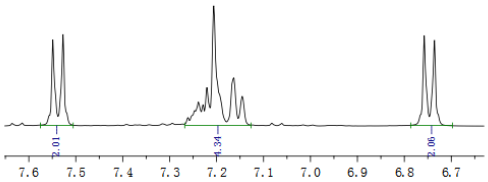
2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3g)

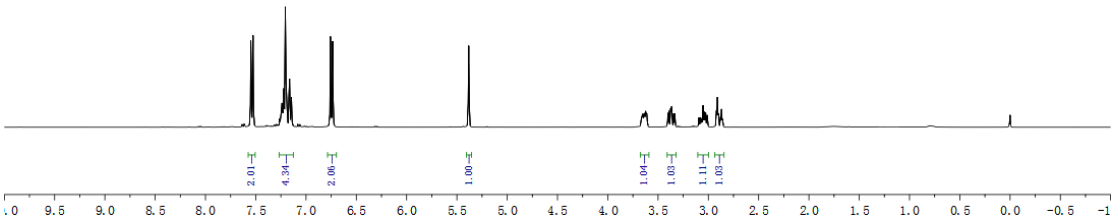


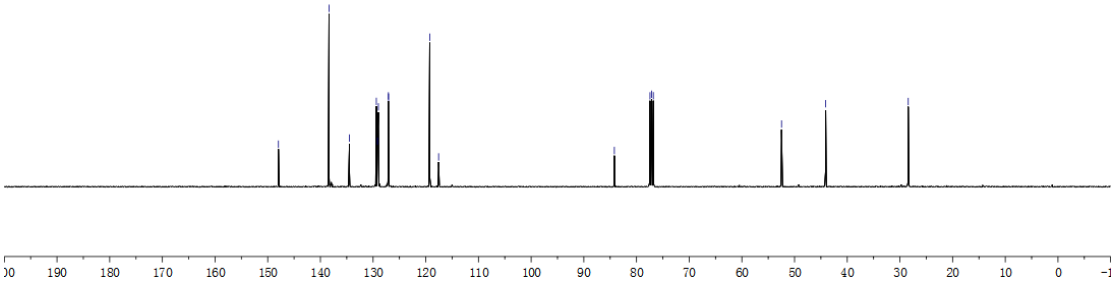




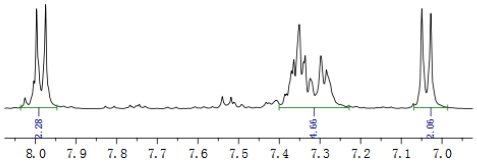
2-(4-iodophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3h)

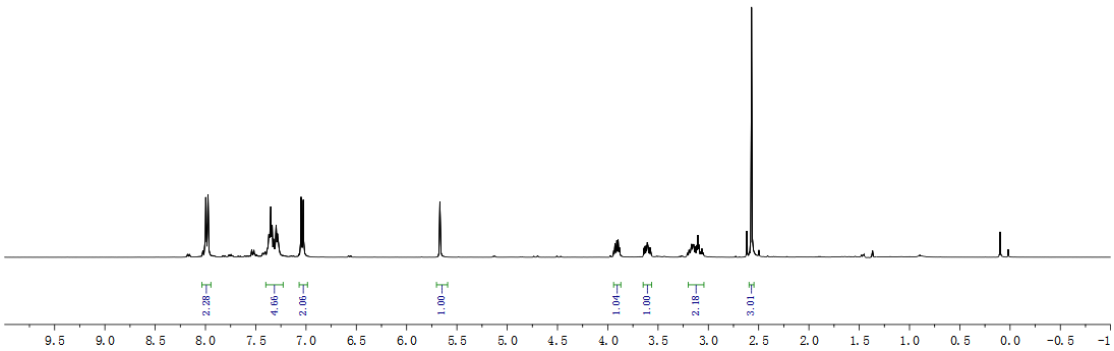


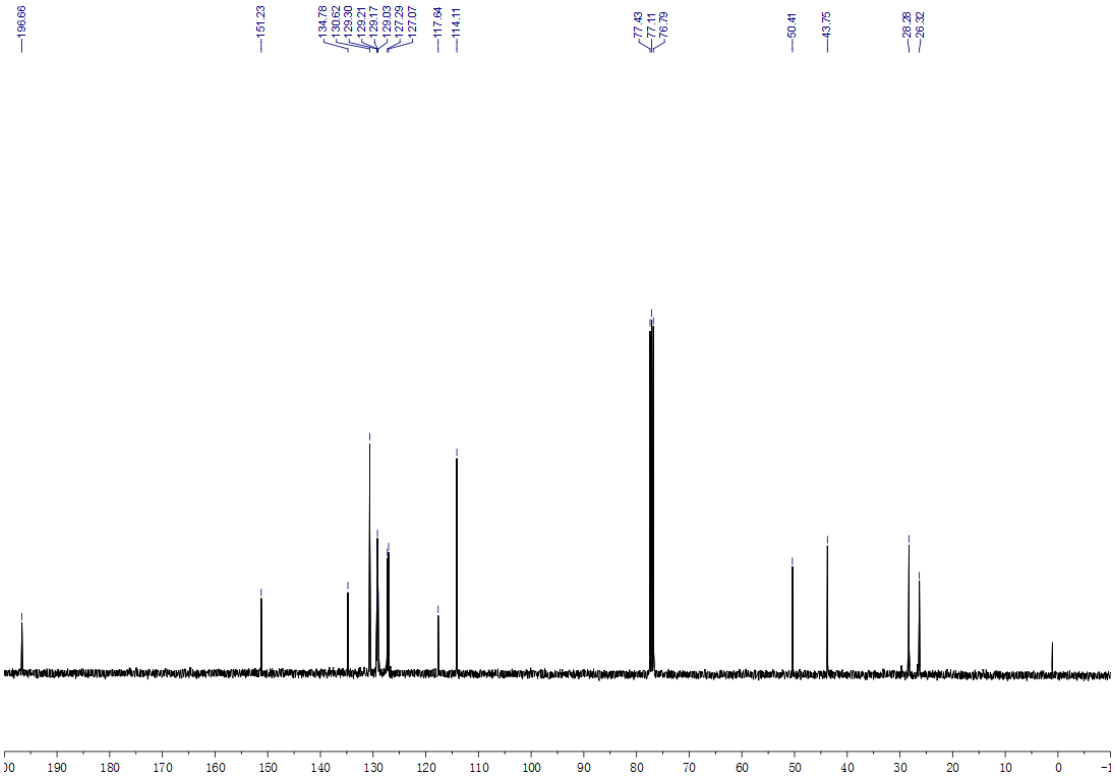




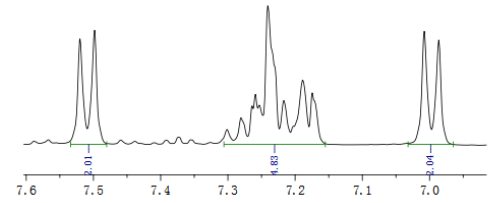
2-(4-acetylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3i)

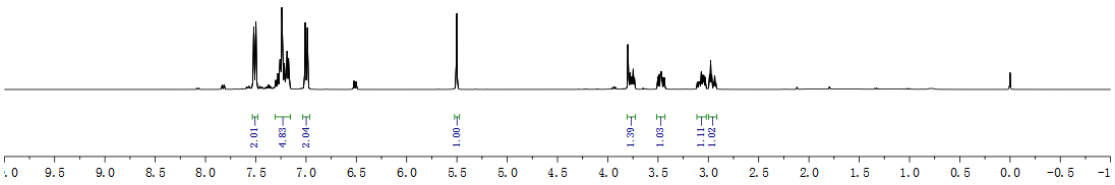


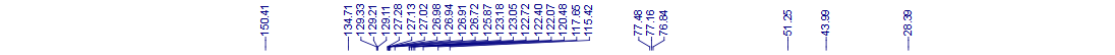


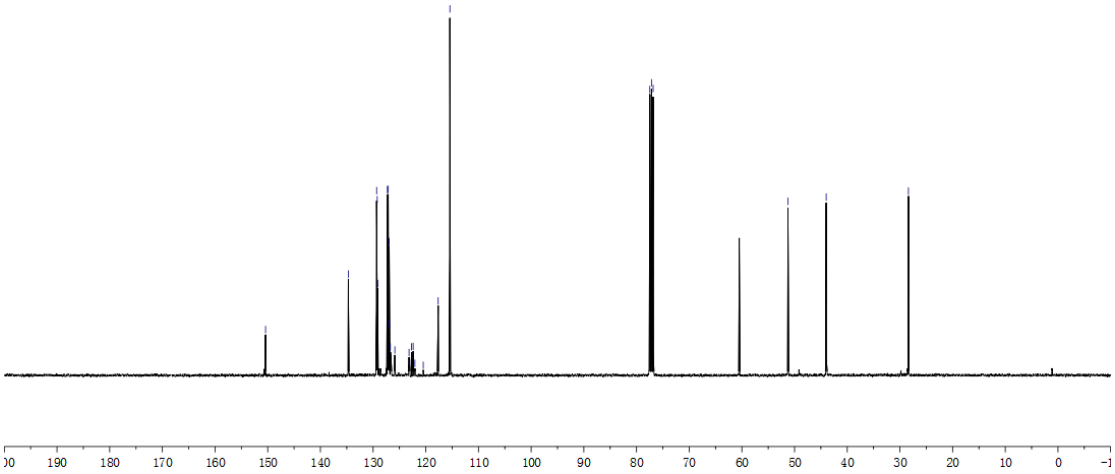


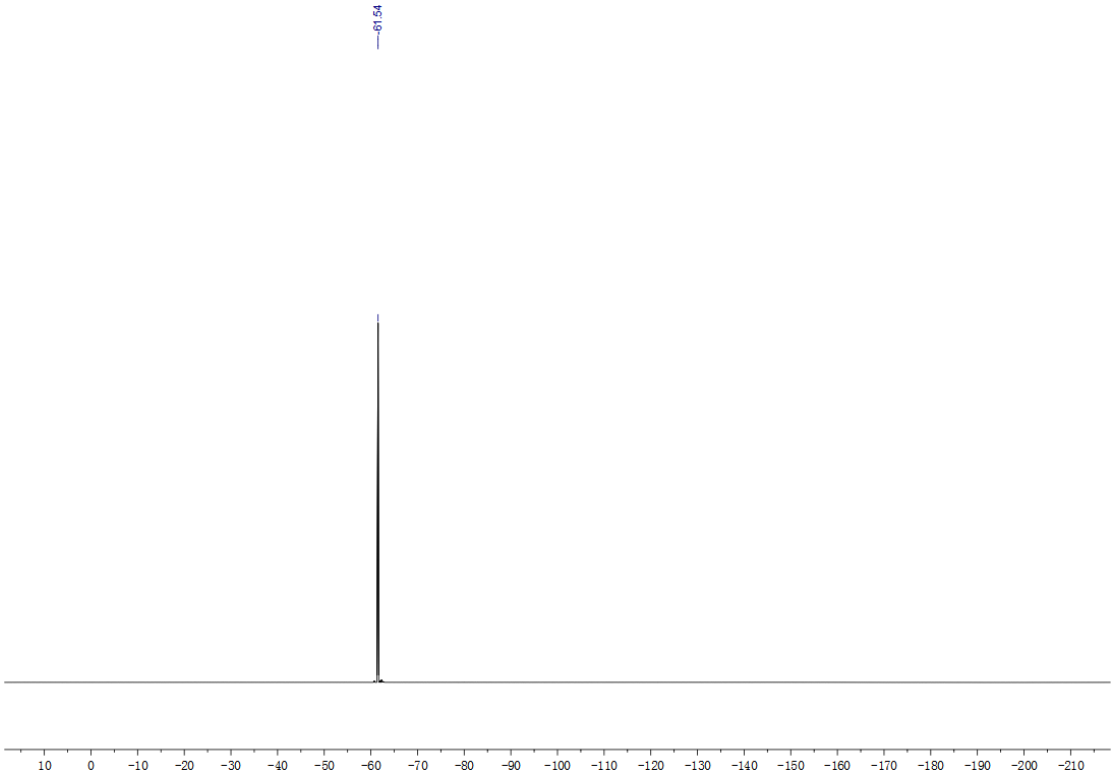
2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3j)







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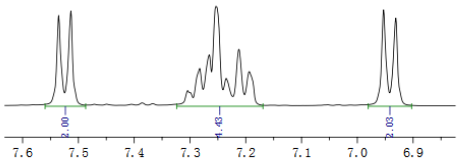
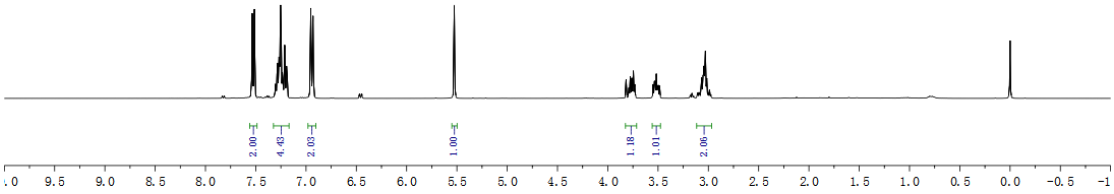
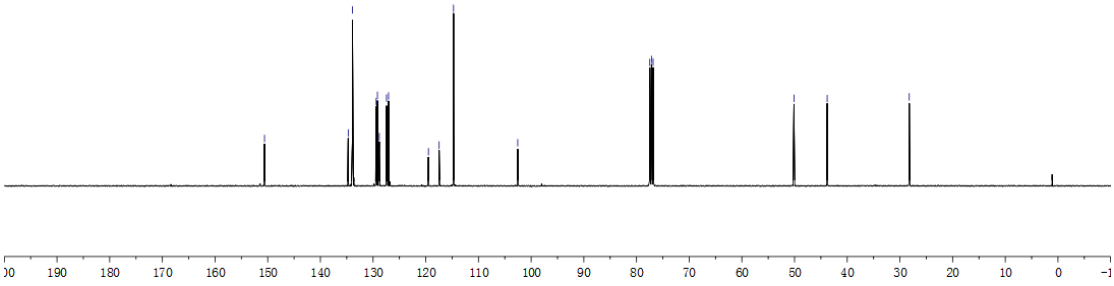
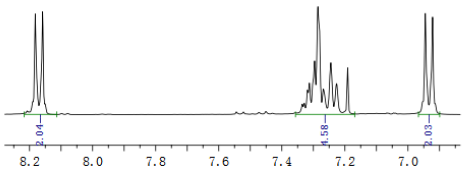
2-(4-cyanophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3k)

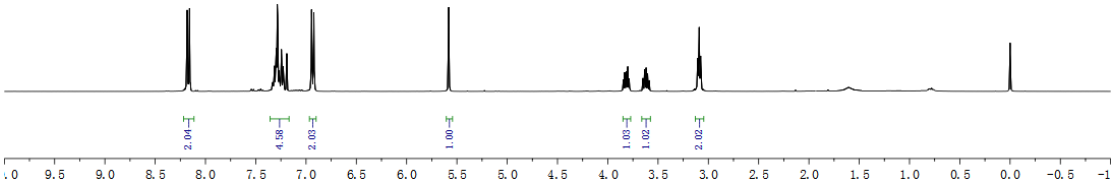


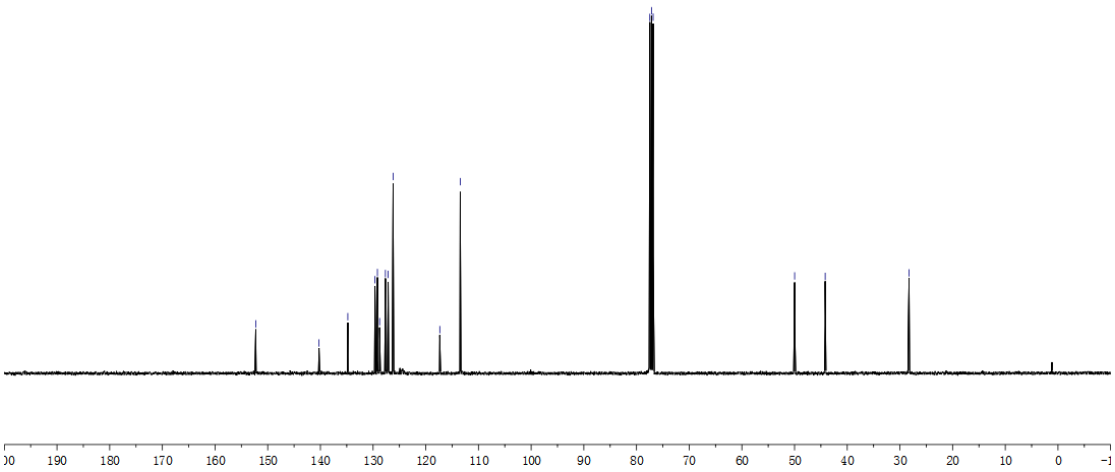




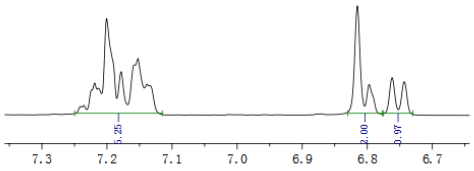
2-(4-nitrophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3l)

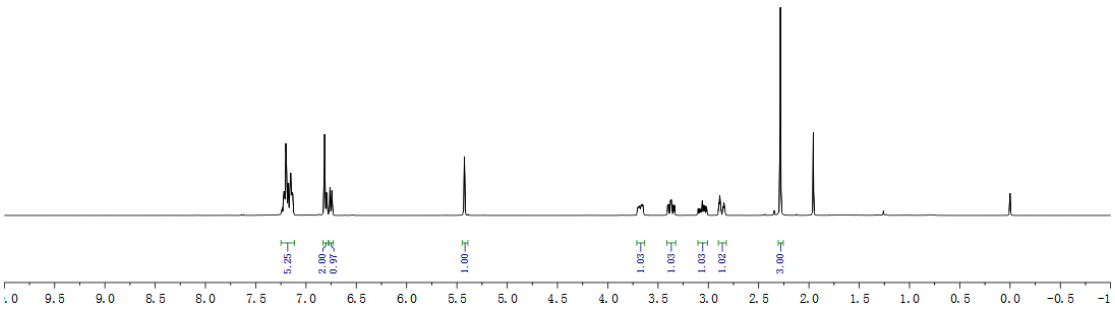


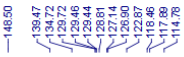


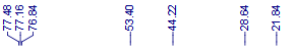


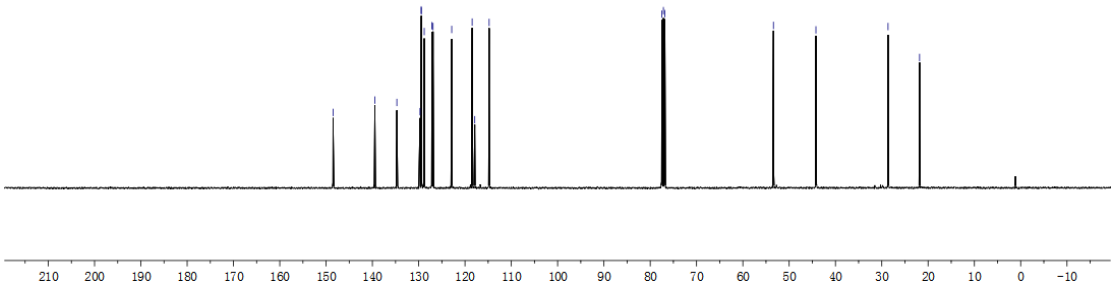
2-(m-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3m)



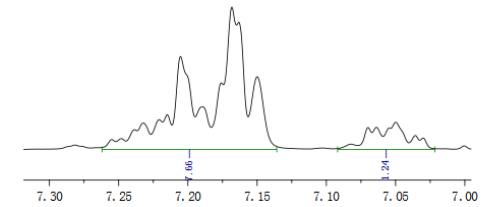


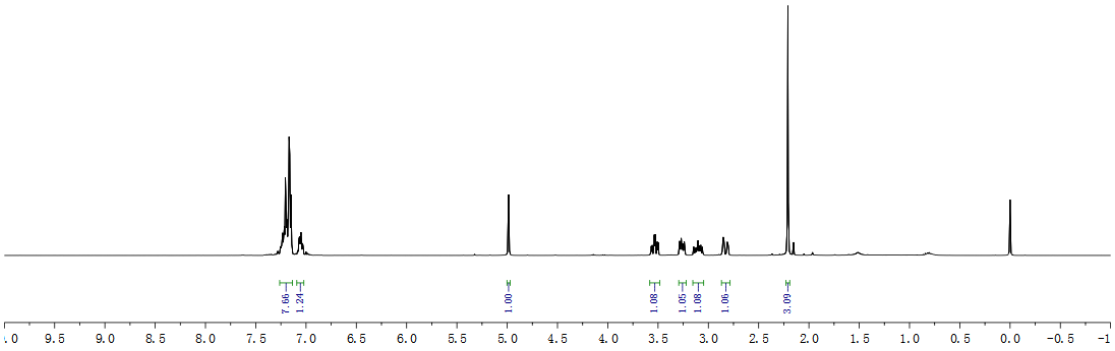


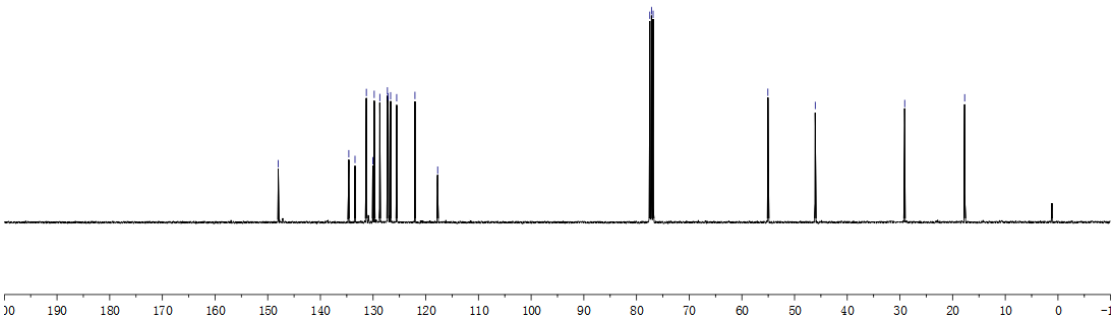




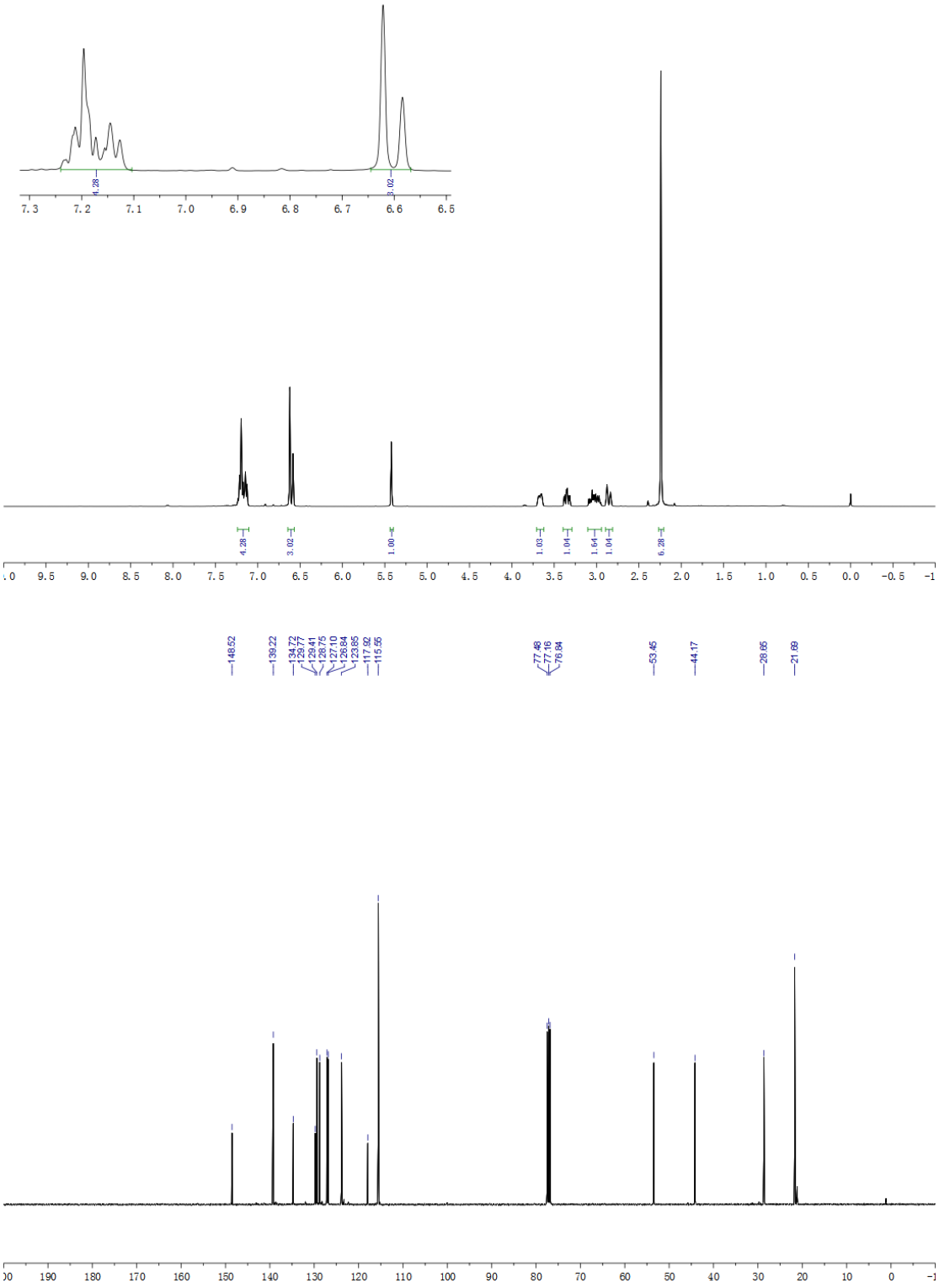
2-(o-tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3n)



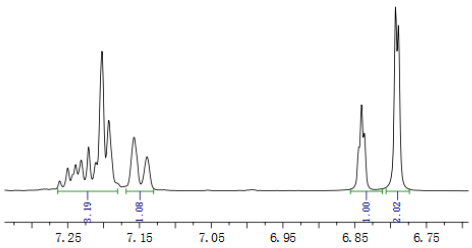


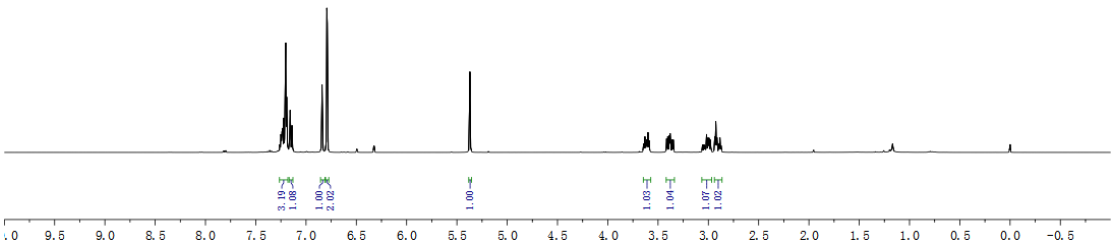


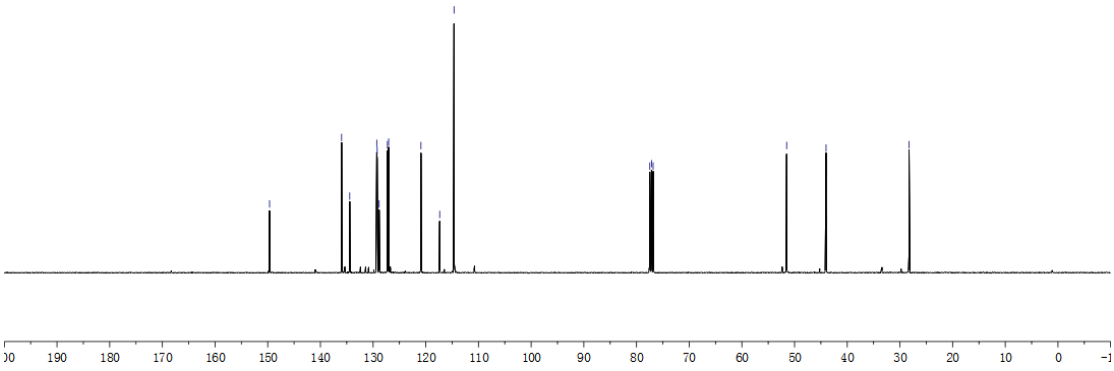
2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3o)



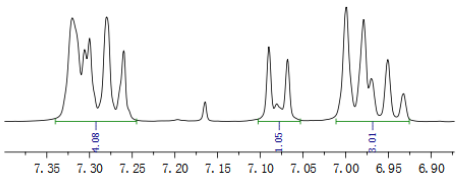
***2-(3,5-dichlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile*(*3p*)**

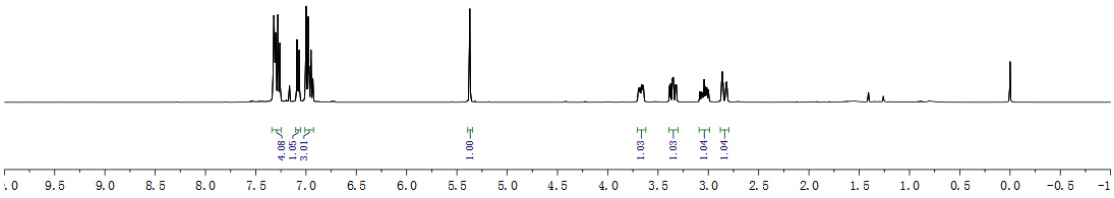


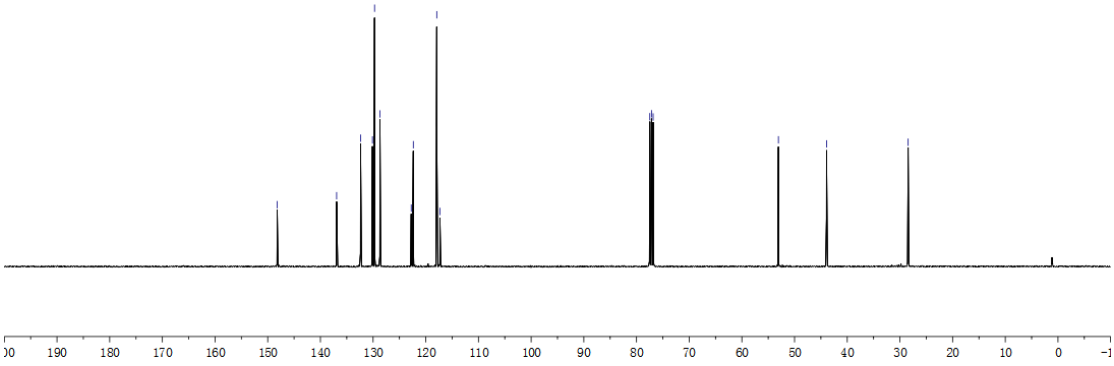




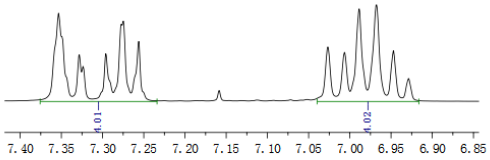
6-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3q)

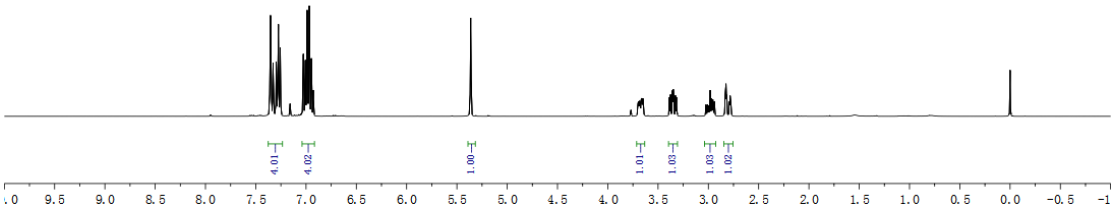


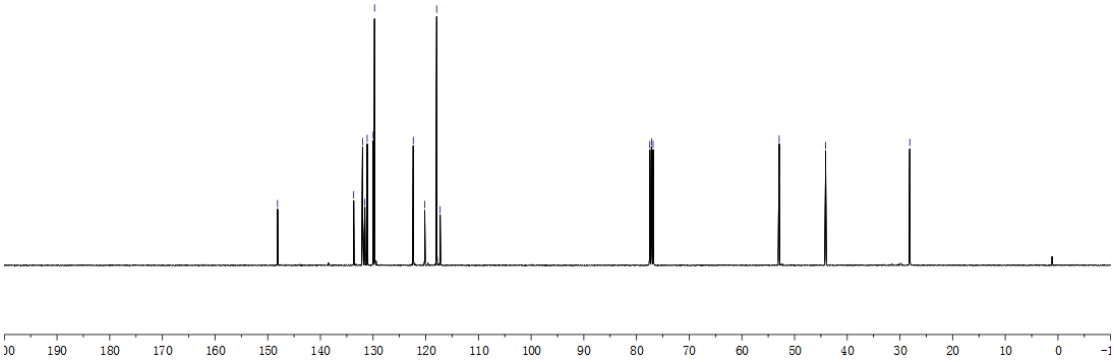




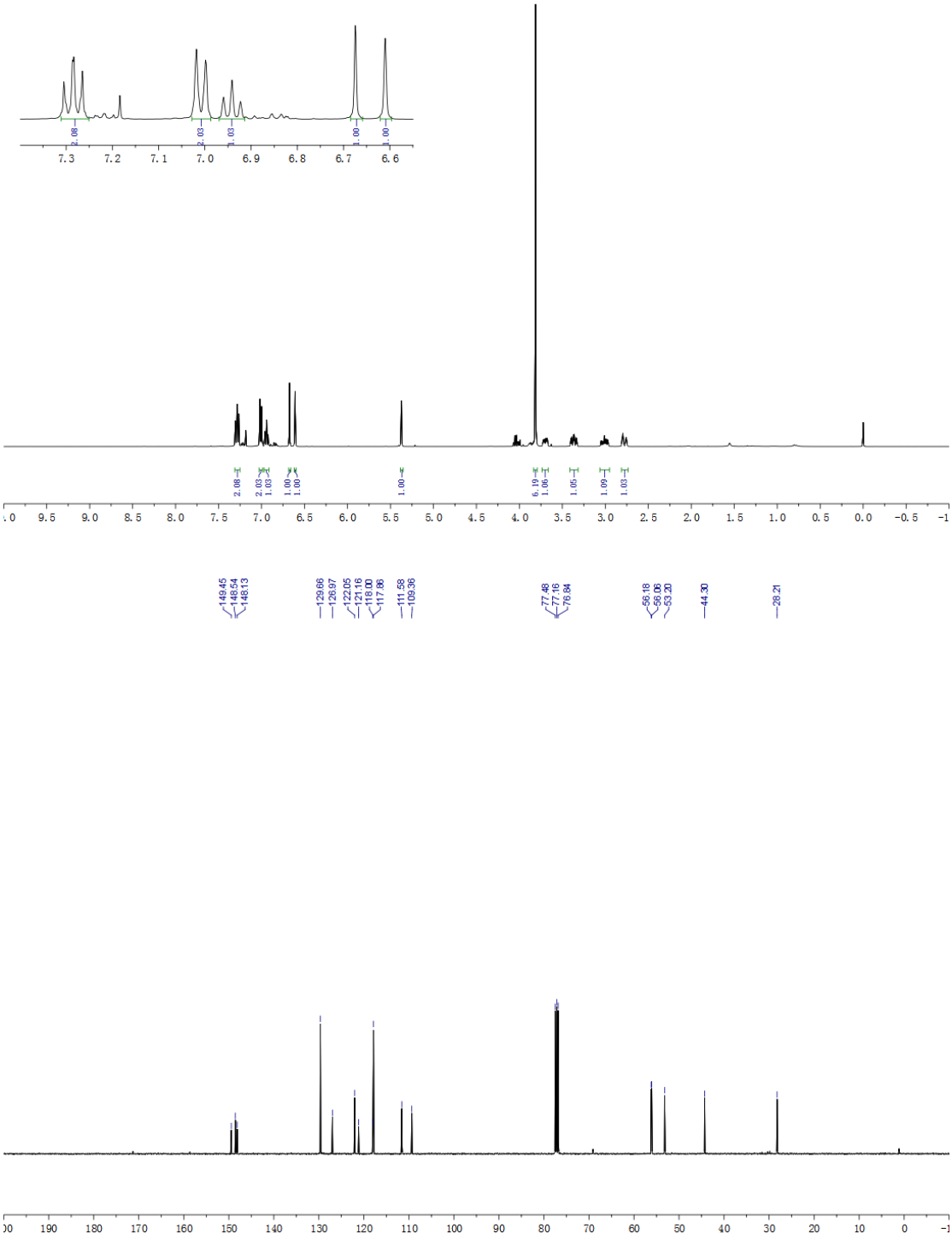
7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3r)



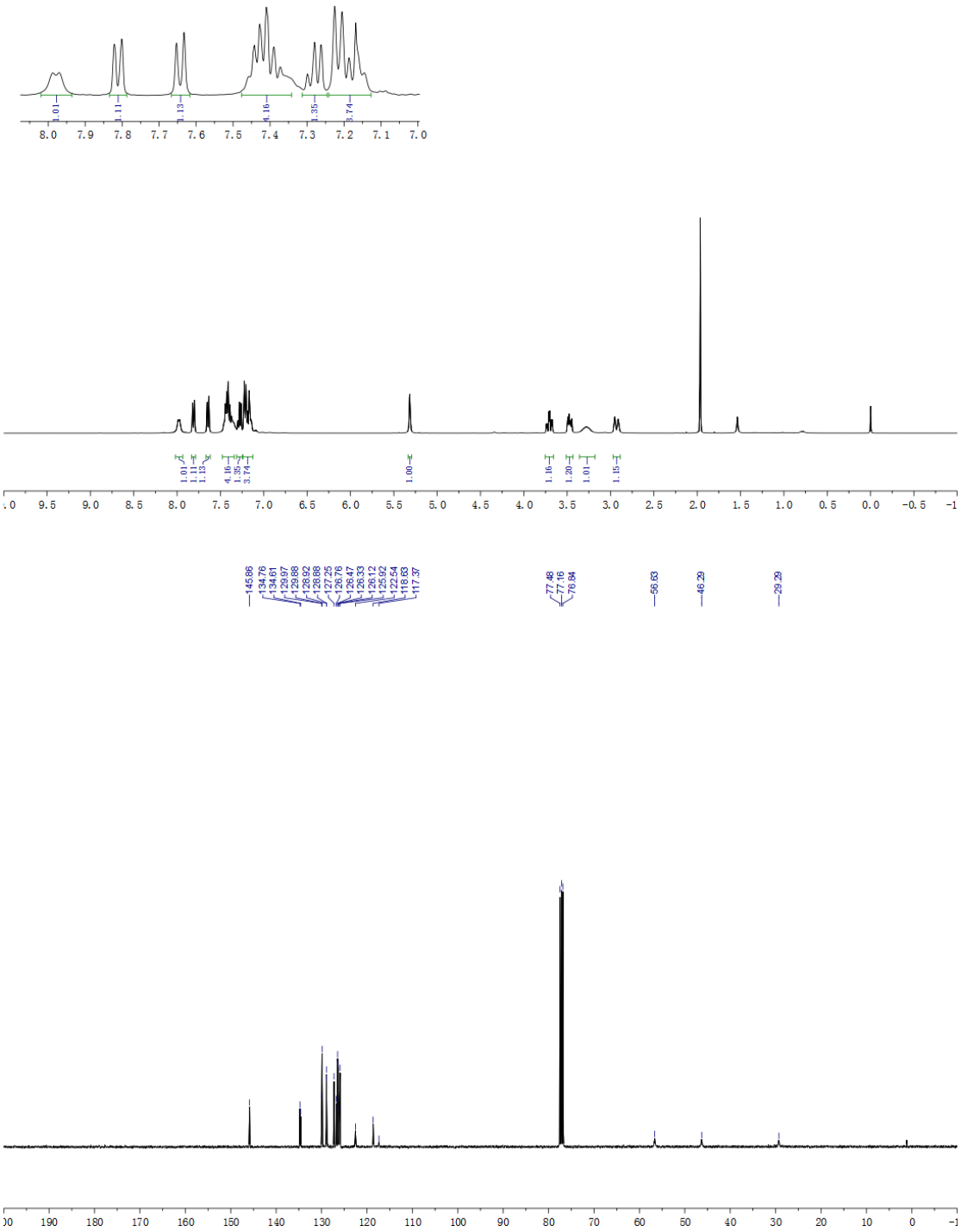




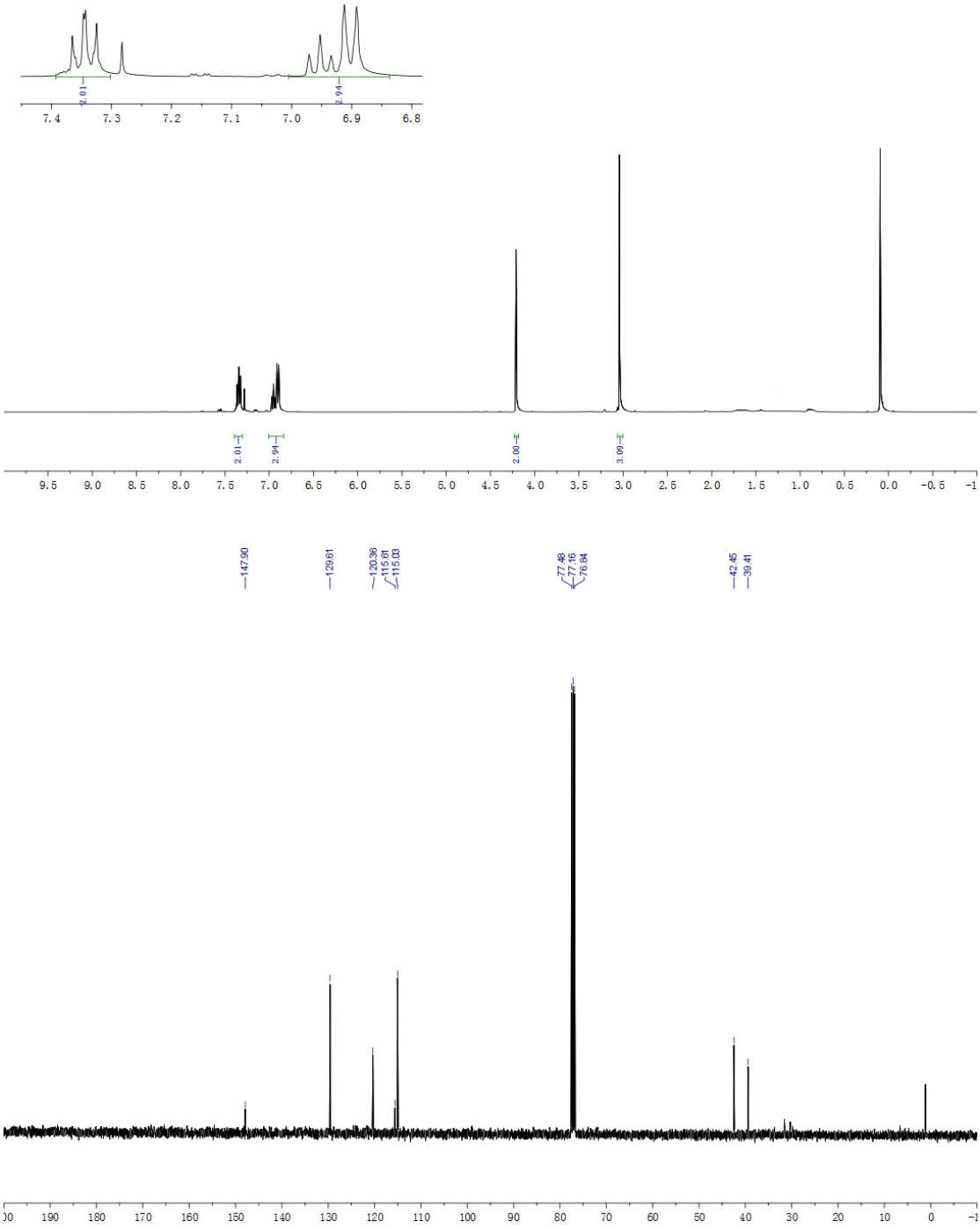
6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(3s)



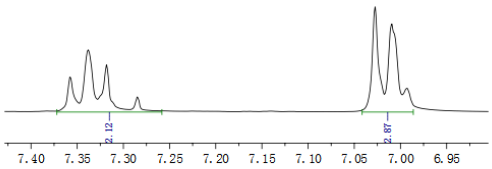
***2-(naphthalen-2-yl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile*(*3t*)**

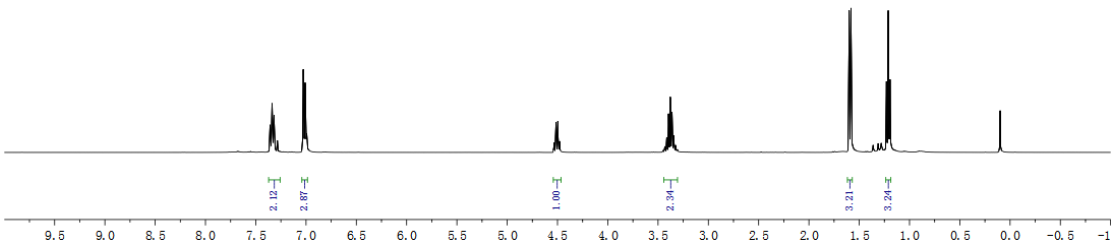


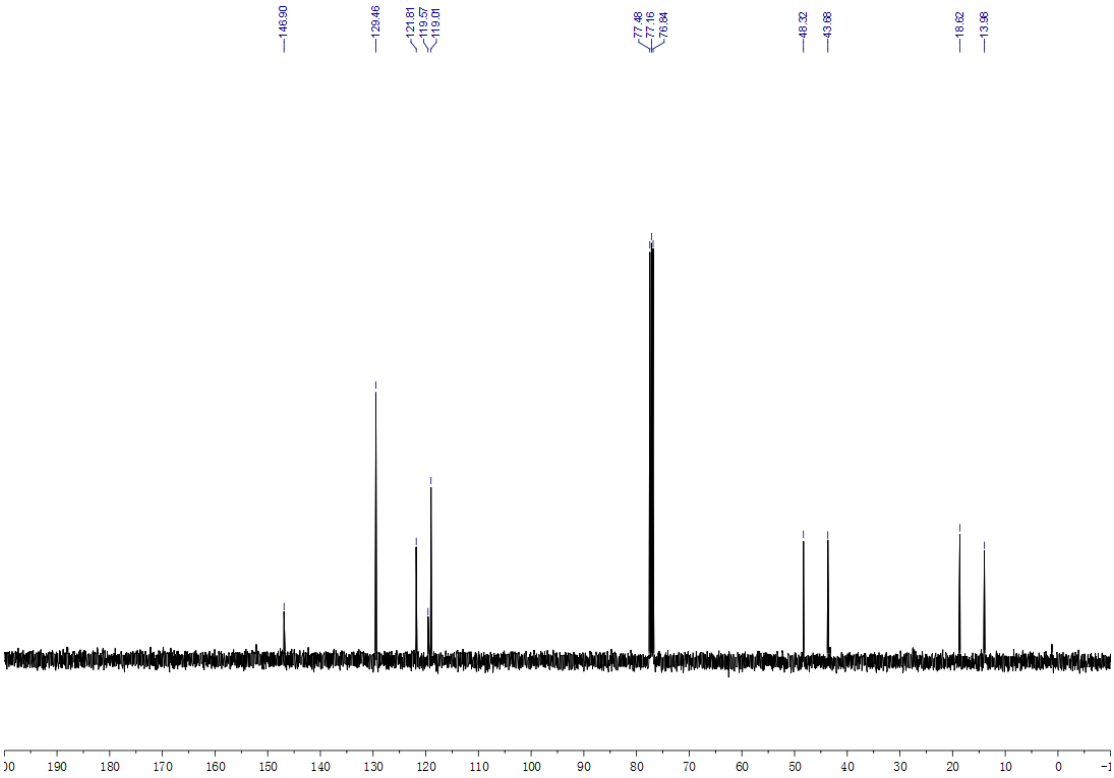
***2-(methyl(phenyl)amino)acetonitrile*(*3u*)**



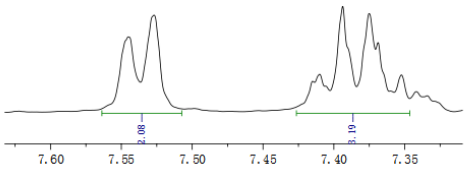
2-(ethyl(phenyl)amino)propanenitrile(3v)

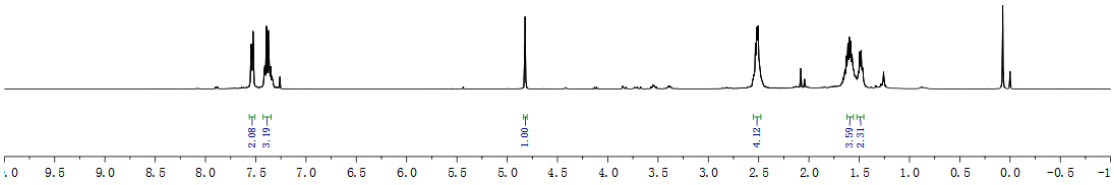


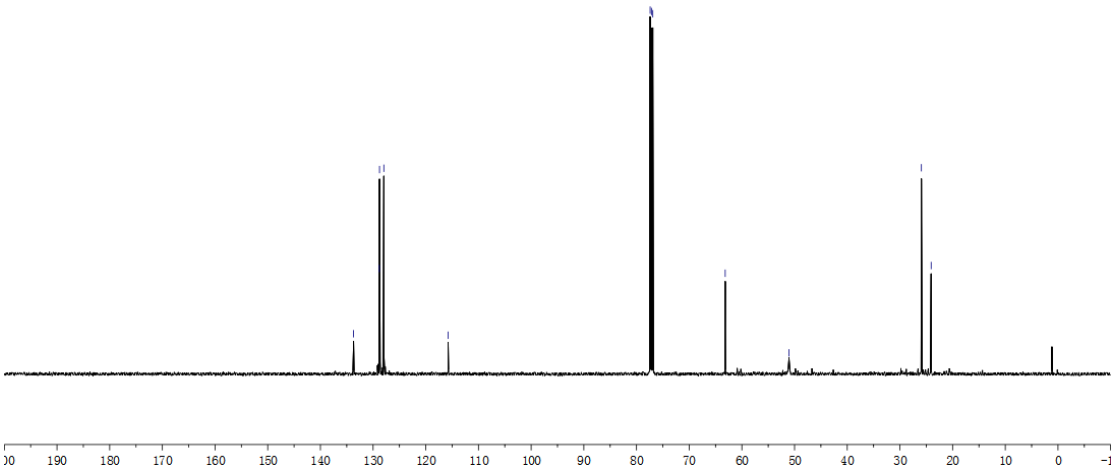




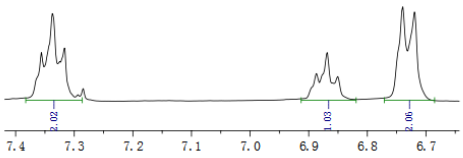
***2-phenyl-2-(piperidin-1-yl)acetonitrile*(*3w*)**

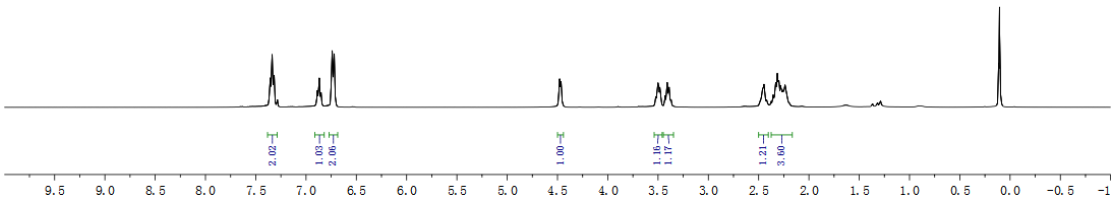


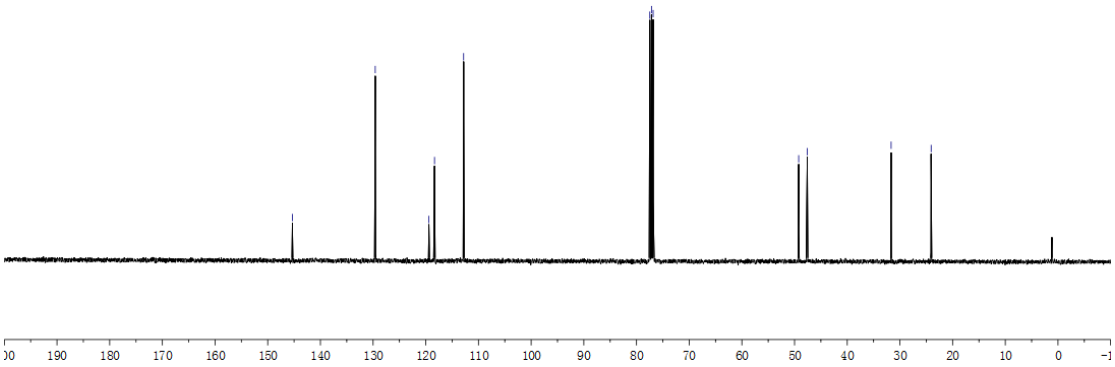




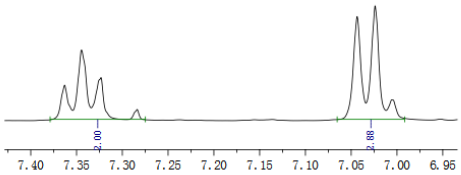
***1-phenylpyrrolidine-2-carbonitrile*(*3x*)**

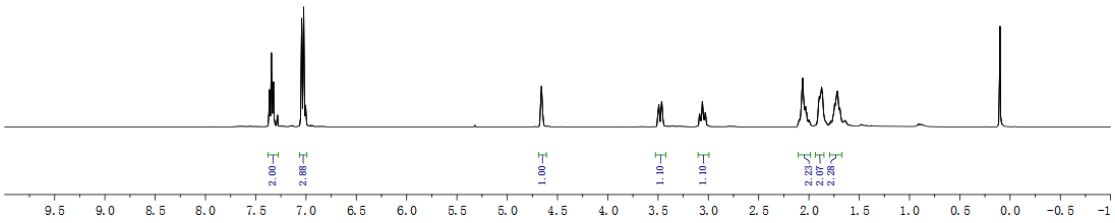


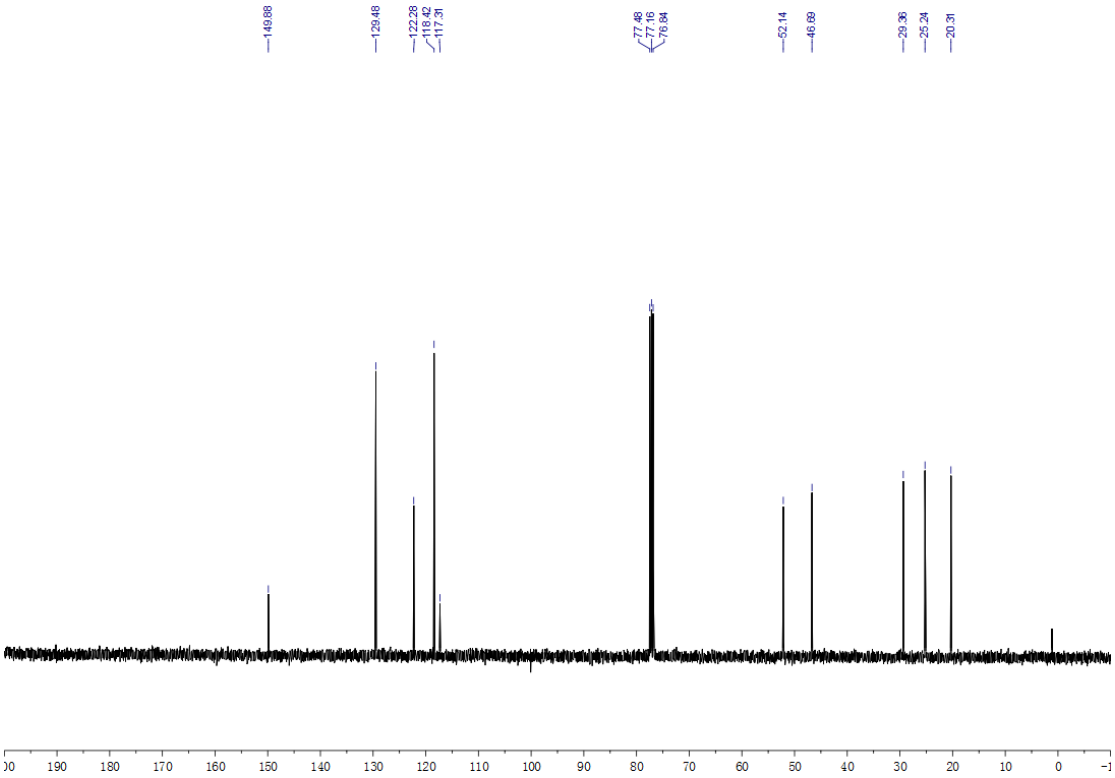




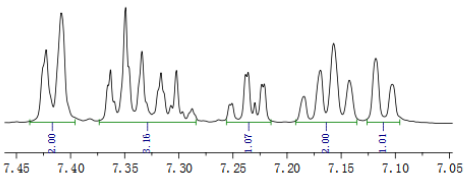
***1-phenylpiperidine-2-carbonitrile*(*3y*)**

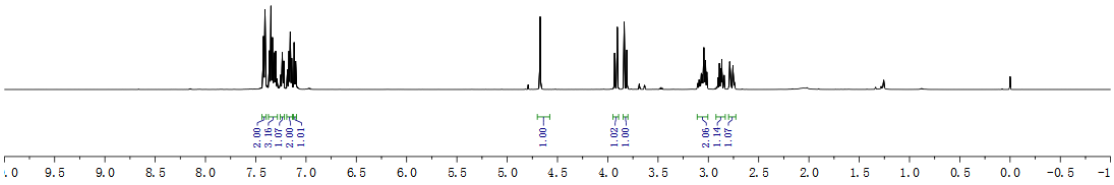


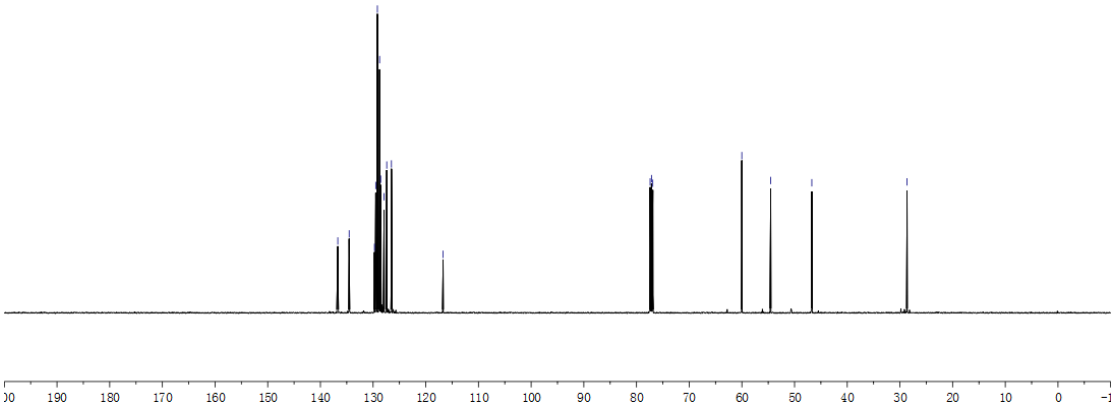




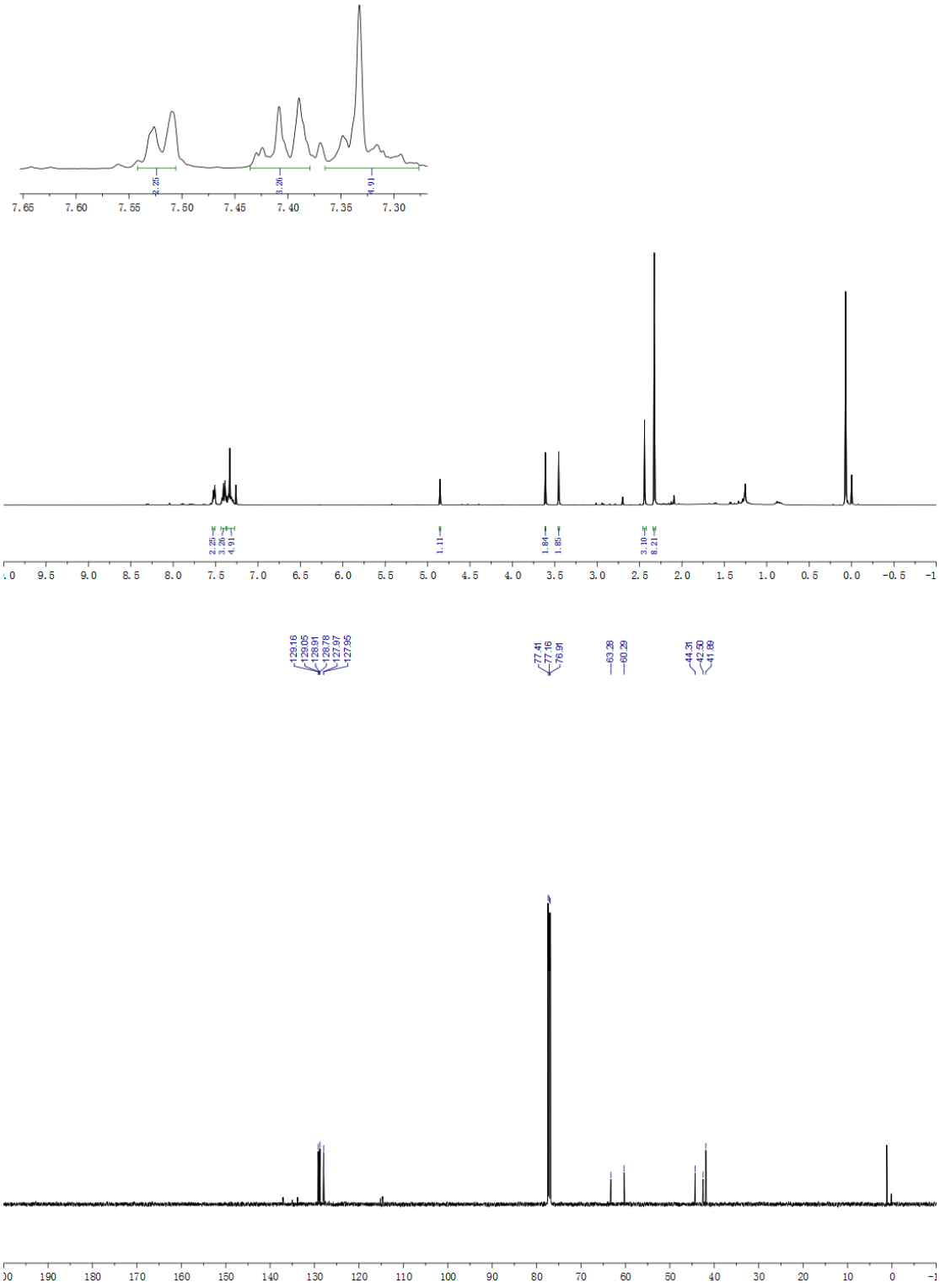
***2-benzyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile*(*3z*)**



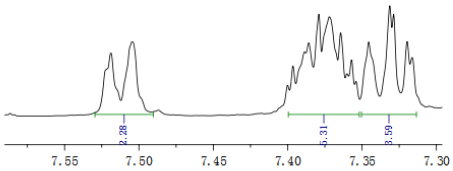


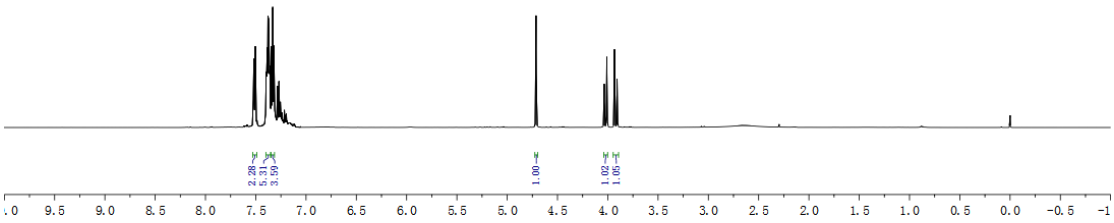


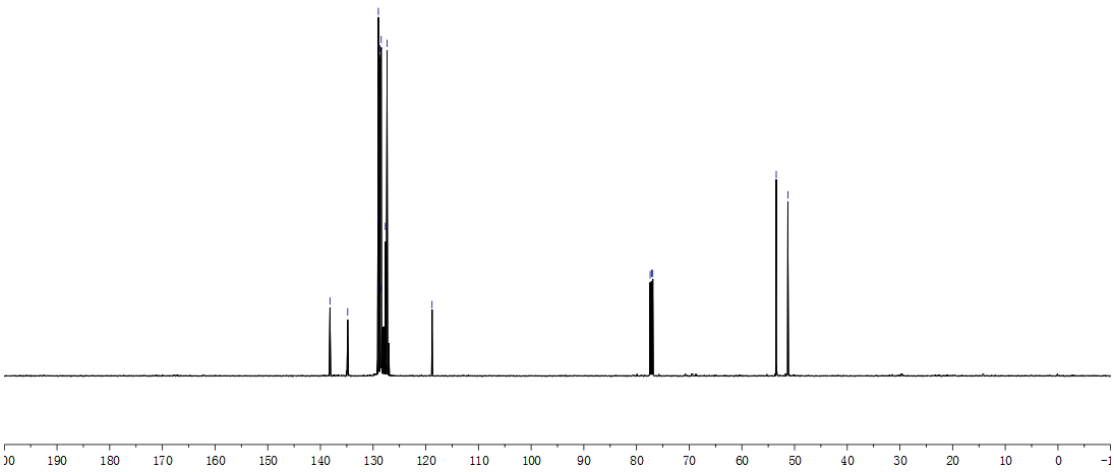
***2-(dimethylamino)-2-phenylacetonitrile*(*3aa*)*/2-(benzyl(methyl)amino)acetonitrile*(*3aa'*)**



***2-(benzylamino)-2-phenylacetonitrile*(*3ab*)**







***2-phenyl-2-(phenylamino)acetonitrile*(*3ac*)**