Supporting Information

Copper-Mediated C3-Cyanation of Indole by the Combination of Amine and Ammonium

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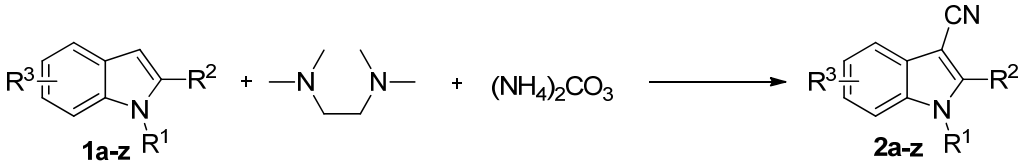
1. General experimental details

Unless otherwise noted, materials were either purchased from commercial suppliers or purified by standard techniques. DMSO was purchased to use without any further purified. Nuclear Magnetic Resonance spectra were recorded on a Bruker 500 MHz instrument or a Bruker 300 MHz instrument. All ^{1}H NMR experiments were reported in δ units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) or DMSO (2.5 ppm) in the deuterated solvent. All ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.0 ppm) or DMSO-d_6 (39.5 ppm) and all were obtained with ^{1}H decoupling. All coupling constants *J*, were reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, brs = broad singlet.

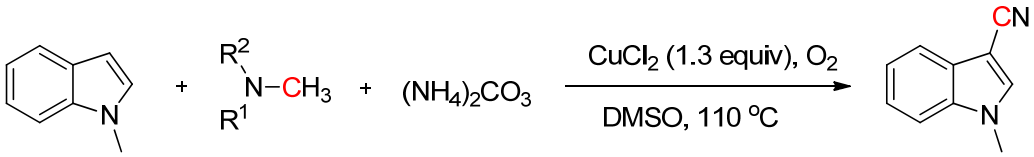
Caution: Work with cyanides is hazardous; the experiments and work-up need to be carried out in a well-ventilated fume-hood.

1.1 Typical experimental procedure for the cyanation of indoles (Fig 1):



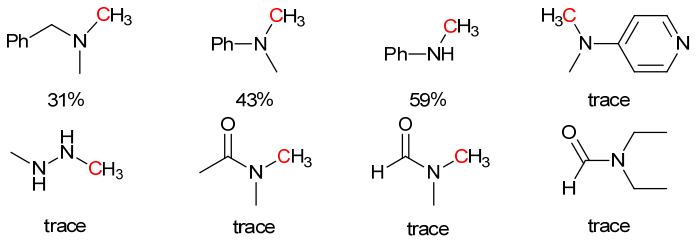
Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with indole **1** (0.2 mmol, 1 equiv), TMEDA (75 μL, 0.5 mmol, 2.5 equiv), $(NH_4)_2CO_3$ (76.8 mg, 0.8 mmol, 4.0 equiv), $CuCl_2$ (35 mg, 0.26 mmol, 1.3 equiv) and DMSO (0.5 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 12-24 h in oil bath. After cooling to room temperature, the resultant mixture was extracted with EtOAc (10 × 2 mL) from brine and the collected organic layer was evaporated under reduced pressure. The residue was purified by flash column chromatography on a silica gel to give the products.

1.2 Typical experimental procedure for the reaction of *N*-methyl containing partners:



Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1-Methylindole (25 μL, 0.2 mmol, 1 equiv), *N*-methyl compound (0.5 mmol, 2.5 equiv), $(NH_4)_2CO_3$ (76.8 mg, 0.8 mmol, 4.0 equiv), $CuCl_2$ (35 mg, 0.26 mmol, 1.3 equiv) and DMSO (0.5 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 18 h in oil bath. After cooling to room temperature, the resultant mixture was extracted with EtOAc (10 × 2 mL) from brine and the collected organic layer was evaporated under reduced pressure. The residue was purified by flash column chromatography on a silica gel to give the products.

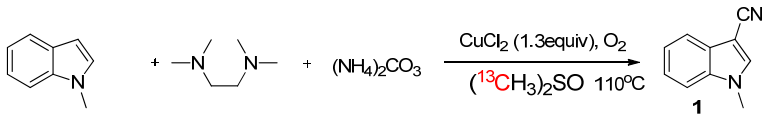
2. Results of Other N-Methyl Containing Partners



3. ^{13}C labeled DMSO and ^{15}N labeled NH_4Cl Study

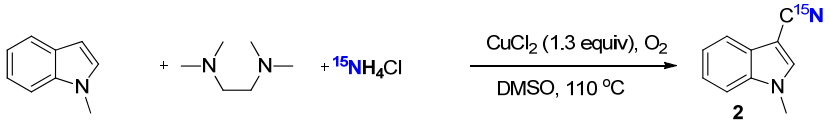
Ammonium chloride (^{15}N, 99%, cat. No. NLM-467-5) and Dimethyl sulfoxide (carbonyl-^{13}C, 99%, cat. No. CLM-503-1) were purchased from Cambridge Isotope Laboratories, Inc.

3.1 The reaction of 1-Methylindole with $(NH_4)_2CO_3$ in $(^{13}CH_3)_2SO$:



Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1-methylindole (25 μL, 0.2 mmol, 1 equiv), TMEDA (75 μL, 0.5 mmol, 2.5 equiv), $(NH_4)_2CO_3$ (76.8 mg, 0.8 mmol, 4.0 equiv), $CuCl_2$ (35 mg, 0.26 mmol, 1.3 equiv) and ^{13}C labeled DMSO (0.3 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 18 h in oil bath. After cooling to room temperature, the resultant mixture was extracted with EtOAc (10 × 2 mL) from brine and the collected organic layer was evaporated under reduced pressure. The residue was purified by flash column chromatography on a silica gel to give the products (21.3 mg, 68% yield) as a brown oil.

3.2 The reaction of 1-Methylindole with $^{15}NH_4Cl$ in DMSO:



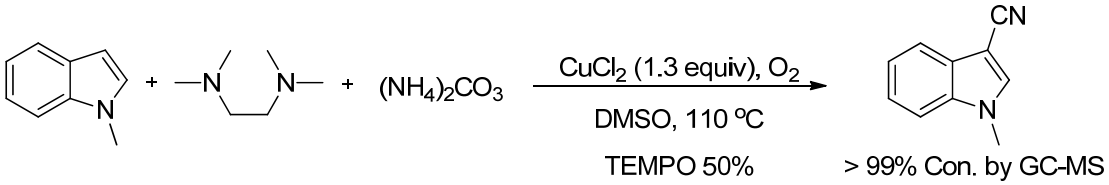
Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1-methylindole (25 μL, 0.2 mmol, 1 equiv), TMEDA (75 μL, 0.5 mmol, 2.5 equiv), $^{15}NH_4Cl$ (76.8 mg, 0.8 mmol, 4.0 equiv), Na_2CO_3 (42.4 mg, 0.4 mmol, 2 equiv), $CuCl_2$ (35 mg, 0.26 mmol, 1.3 equiv) and DMSO (0.3 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 12 h in oil bath. After cooling to room temperature, the resultant mixture was extracted with EtOAc (10 × 2 mL) from brine and the collected organic layer was evaporated under reduced pressure. The residue was purified by flash column chromatography on a silica gel to give the products (15.7 mg, 51% yield) as a brown oil. HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{10}H_9{}^{15}NN$: 158.0730, found : 158.0723.

4. Preliminary Mechanism Study

4.1 Experiment on TEMPO as a Radical Scavenger:

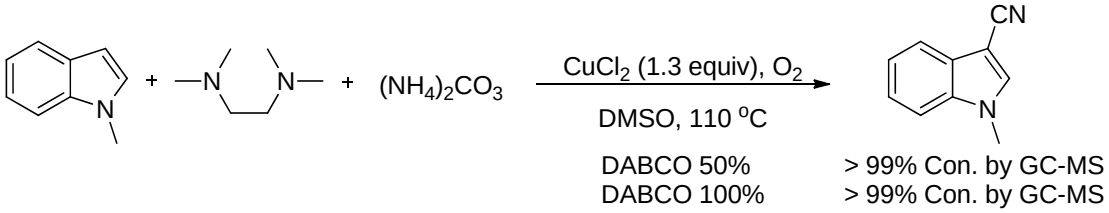
Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1-methylindole **1a** (0.2 mmol), TMEDA (75 μL, 0.5 mmol, 2.5 equiv), $(NH_4)_2CO_3$ (76.8 mg, 0.8 mmol, 4.0 equiv), $CuCl_2$

(35 mg, 0.26 mmol, 1.3 equiv), TEMPO (15.6 mg, 0.1 mmol, 50 mol %) and DMSO (0.5 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 12 h in oil bath. After cooling to room temperature, the resultant mixture was analyzed by GC-MS.



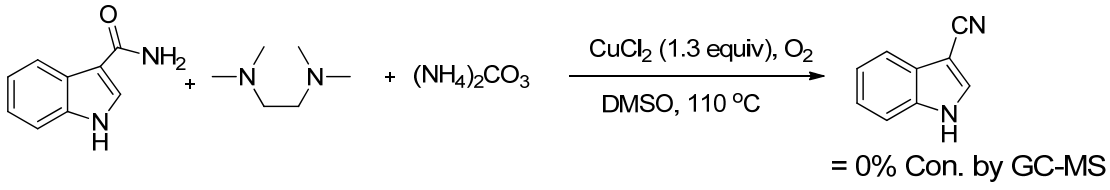
4.2 Experiment on 1,4-Diazabicyclo[2,2,2]octane (DABCO) as a Singlet Oxygen Inhibitor:

Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1-methylindole **1a** (0.2 mmol), TMEDA (75 μL, 0.5 mmol, 2.5 equiv), $(NH_4)_2CO_3$ (76.8 mg, 0.8 mmol, 4.0 equiv), $CuCl_2$ (35 mg, 0.26 mmol, 1.3 equiv), DABCO (11.2 mg, 0.1 mmol, 50 mol % or 22.4 mg, 0.2 mmol, 100 mol %) and DMSO (0.5 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 12h in oil bath. After cooling to room temperature, the resultant mixture was analyzed by GC-MS.



4.3 The reaction of carboxamide compounds to form nitriles (Scheme 2):

Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1H-indole-3-carboxamide (30.0 mg，0.2 mmol), TMEDA (75 μL, 0.5 mmol, 2.5 equiv), $(NH_4)_2CO_3$ (76.8 mg, 0.8 mmol, 4.0 equiv), $CuCl_2$ (35 mg, 0.26 mmol, 1.3 equiv), and DMSO (0.5 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 12h in oil bath. After cooling to room temperature, the resultant mixture was analyzed by GC-MS.



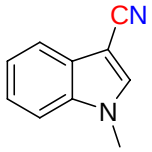
5. Detection of Iminium Ion 3 by HRMS

Under air, a 20 mL of Schlenk tube equipped with a stir bar was charged with 1-methylindole **1a** (0.2 mmol), N-Benzyldimethylamine (75 μL, 0.5 mmol, 2.5 equiv), $(NH_4)_2CO_3$ (76.8 mg, 0.8 mmol, 4.0 equiv), $CuCl_2$ (35 mg, 0.26 mmol, 1.3 equiv) and DMSO (0.5 mL). The tube was sealed with a rubber plug and charged with O_2. The reaction mixture was stirred at 110 °C for 2, 4 and 6h in oil bath respectively. After cooling to room temperature, the resultant mixture was analyzed by HRMS and the

concentration of iminium ion **3** in different reaction time was consistent with reaction tendency.HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{18}H_{19}N_2$: 263.1543, found : 263.1521

6. Characterization Data for the Products

1-methyl-1*H*-indole-3-carbonitrile (2a)[1]

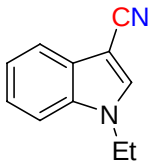


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (25.9 mg, 83% yield) as a brown oil.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 7.30-7.17 (m, 3H), 3.73 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.9, 135.5, 127.7, 123.7, 122.0, 119.7, 115.9, 110.3, 85.2, 33.5.

1-ethyl-1*H*-indole-3-carbonitrile (2b)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (30.9 mg, 91% yield) as a brown soild.

Mp: 88-90 °C.

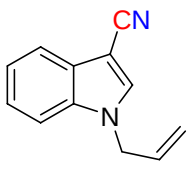
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.61 (s, 1H), 7.42 (s, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.0 Hz, 1H), 7.30-7.25 (m, 1H), 4.21 (q, *J* = 7.5 Hz, 2H), 1.51 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.0, 133.9, 127.9, 123.7, 122.0 119.9, 116.0, 110.4, 85.4, 41.8, 15.1.

IR (prism, cm^{-1}): 2977, 2212, 1527, 1462, 925, 735.

MS (EI) 170 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{11}H_{11}N_2$: 171.0917, found : 171.0911.

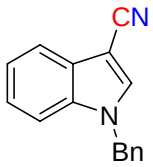
1-allyl-1*H*-indole-3-carbonitrile (2c)[3]



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (23.3 mg, 64% yield) as a brown oil.

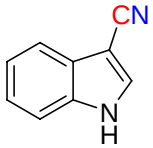
^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.27 (s, 1H), 7.66-7.61 (m, 2H), 7.34-7.26 (m, 2H), 6.04-5.98 (m, 2H), 5.21-5.18 (m, 1H), 5.09-5.05 (m, 1H), 4.93-4.91 (m, 2H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 136.9, 135.2, 133.2, 127.2, 123.5, 122.1, 118.8, 117.8, 116.0, 111.8, 83.7, 48.8.

1-benzyl-1*H*-indole-3-carbonitrile (2d)[1]



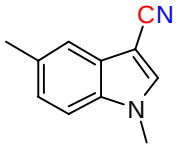
Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (29.2 mg, 63% yield) as a brown oil.
^{1}H NMR (DMSO-d_6, 500 MHz): δ 8.48 (s, 1H), 7.67-7.64 (m, 2H), 7.35-7.26 (m, 7H), 5.52 (s, 2H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 137.2, 136.7, 135.1, 128.7, 127.8, 127.3, 127.2, 123.6, 122.1, 118.8, 115.9, 111.9, 84.0, 49.9.

1*H*-indole-3-carbonitrile (2e)[2]



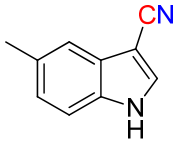
Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (19.6 mg, 69% yield) as a yellow solid.
^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.21 (br, 1H), 8.24 (s, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.30-7.22 (m, 2H).
^{13}C NMR (DMSO-d_6, 125 MHz): δ 135.3, 134.5, 126.8, 123.4, 121.8, 118.5, 116.5, 113.0, 84.2

1,5-dimethyl-1*H*-indole-3-carbonitrile (2f)[1]



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (27.3 mg, 80% yield) as a brown oil.
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (s, 1H), 7.49 (s, 1H), 7.27 (d, J = 9.0 Hz, 1H), 7.16 (d, J = 9.0 Hz, 1H), 3.81 (s, , 3H), 2.48 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.3, 134.4, 131.8, 128.1, 125.4, 119.4, 116.0, 109.9, 84.8, 33.5, 21.3.

5-methyl-1*H*-indole-3-carbonitrile (2g)[4]

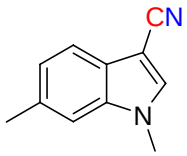


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (26.1 mg, 83% yield) as a white solid.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.08 (br, 1H), 8.17 (d, J =3.0 Hz, 1H), 7.44-7.11 (m, 2H), 7.10 (d, J =3.0 Hz, 1H), 3.37 (s, 3H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 134.2, 133.5, 130.7, 127.0, 124.9, 117.9, 116.5, 112.6, 83.6, 21.0.

1,6-dimethyl-1*H*-indole-3-carbonitrile (2h)[1]

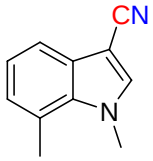


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (30.9 mg, 91% yield) as a yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, J = 8.0 Hz, 1H), 7.47 (s, 1H), 7.17 (s, 1H), 7.12 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H), 2.51 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.3, 135.0, 133.9, 125.5, 123.8, 119.3, 116.1, 110.2, 85.1, 33.5, 21.8.

1,7-dimethyl-1*H*-indole-3-carbonitrile (2i)[1]

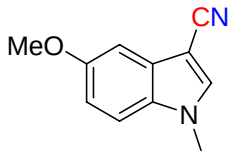


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (20.4 mg, 60% yield) as a yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.57 (d, J = 7.5 Hz, 1H), 7.42 (s, 1H), 7.45 (s, 1H), 7.15-7.12 (m, 1H), 7.01 (d, J = 7.0 Hz, 1H), 4.08 (s, 3H), 2.75 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.7, 134.7, 128.9, 126.4, 112.3, 122.2, 117.9, 115.9, 85.2, 37.6, 19.4.

5-methoxy-1-methyl-1*H*-indole-3-carbonitrile (2j)[1]

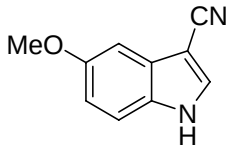


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (26.0 mg, 70% yield) as a yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.49 (s, 1H), 7.26 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 6.97 (dd, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.0, 135.3, 131.0, 128.6, 116.2, 114.6, 111.2, 100.7, 84.8, 55.7, 33.7.

5-methoxy-1*H*-indole-3-carbonitrile (2k)[4]

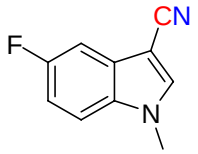


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (21.8 mg, 64% yield) as a white solid.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.05 (br, 1H), 8.15 (s, 1H), 7.44 (d, J = 9.0 Hz, 1H), 7.07 (s, 1H), 6.90 (d, J = 9.0 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 155.3, 134.3, 130.0, 127.5, 116.6, 113.8, 99.7, 84.0, 55.4.

5-fluoro-1-methyl-1*H*-indole-3-carbonitrile (2l)[1]

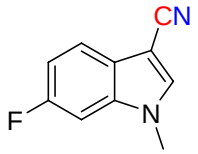


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (22.9 mg, 66% yield) as a pale yellow solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58 (s, 1H), 7.40-7.37 (m, 1H), 7.33-7.30 (m, 1H), 7.11-7.07 (m, 1H), 3.85 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.2 (d, $J_{C\text{-}F}$ = 238.8 Hz), 136.7, 132.6, 128.4 (d, $J_{C\text{-}F}$ = 11.3 Hz), 115.4, 112.5 (d, $J_{C\text{-}F}$ = 26.3 Hz), 111.4 (d, $J_{C\text{-}F}$ = 11.3 Hz), 105.1 (d, $J_{C\text{-}F}$ = 25.0 Hz), 85.6 (d, $J_{C\text{-}F}$ = 3.8 Hz), 33.9.

6-fluoro-1-methyl-1*H*-indole-3-carbonitrile (2m)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (28.5 mg, 82% yield) as a yellow solid.

Mp: 78-80°C.

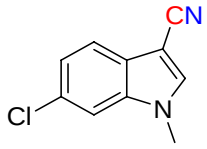
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.68-7.65 (m, 1H), 7.55 (s, 1H), 7.07-7.03 (m, 2 H), 3.80 (s, 3 H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.6 (d, $J_{C\text{-}F}$ = 241.3 Hz), 136.2 (d, $J_{C\text{-}F}$ = 12.5 Hz), 136.0 (d, $J_{C\text{-}F}$ = 3.8 Hz), 124.0, 120.9 (d, $J_{C\text{-}F}$ = 10.0 Hz), 115.4, 111.1 (d, $J_{C\text{-}F}$ = 25.0 Hz), 97.0 (d, $J_{C\text{-}F}$ = 26.3 Hz), 85.9, 33.7.

IR (prism, cm^{-1}):2217, 1626, 1534, 1381, 911, 758.

MS (EI) 174 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{11}H_8FN_2$: 175.0666, found: 175.0677.

5-chloro-1*H*-indole-3-carbonitrile(2n)[2]

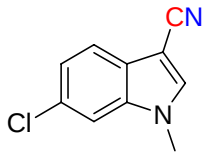


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (28.8 mg, 86% yield) as a white solid.

^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.39 (br, 1H), 8.32 (s, 1H), 7.65 (s, 1H), 7.57 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 136.1, 133.8, 127.8, 126.5, 123.6, 117.8, 115.7, 114.7, 84.1.

6-chloro-1-methyl-1*H*-indole-3-carbonitrile (2o)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (15.6 mg, 41% yield) as a brown solid.

M.p :91-93°C

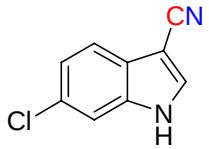
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.66 (d, J = 8.5 Hz, 1H), 7.56 (s, 1H), 7.40 (s, 1H), 7..27 (d, J = 8.5Hz, 1H), 3.83 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.4, 136.1, 130.1, 126.2, 123.0, 120.8, 115.3, 110.5, 86.0, 33.7.

IR (prism, cm^{-1}): 2219, 1537, 1466, 1062, 807.

MS (EI) 190 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{10}H_8ClN_2$: 191.0371, found: 191.0367.

6-chloro-1*H*-indole-3-carbonitrile (2p)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (19 mg, 50% yield) as a yellow solid.

M.p: 174-176 °C.

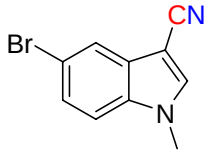
^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.3 (br, 1H), 8.29 (s, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.5 Hz，1H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 135.7, 135.6, 128.0, 125.4, 122.1, 119.9, 115.8, 112.6, 84.6.

IR (prism, cm^{-1}): 3242, 2221, 1624, 1525, 1409, 1016, 736.

MS (EI) 176 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_9H_6ClN_2$: 177.0214, found : 177.0203.

5-bromo-1-methyl-1*H*-indole-3-carbonitrile (2q)[1]

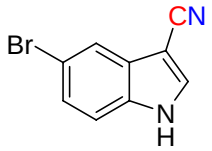


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (14.4 mg, 31% yield) as a brown solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.87 (s, 1H), 7.54 (s, 1H), 7.42 (d, J = 7.0 Hz, 2H), 7.24 (d, J = 7.0 Hz 1H), 3.83 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.3, 134.7, 129.2, 127.0, 122.4, 115.8, 115.1, 111.8, 85.2, 33.8.

5-bromo-1*H*-indole-3-carbonitrile (2r)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:3) to give the products (32.6 mg, 74% yield) as a pale yellow solid.

M.p: 181-182°C

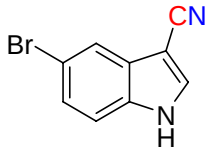
^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.39 (br, 1H), 8.30 (s, 1H), 7.79 (s, 1H), 7.53 (d, J = 8.5 Hz 1H), 7.41 (d, J = 8.5 Hz, 1H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 135.9, 134.0, 128.4, 126.1, 120.7, 115.6, 115.0, 114.4, 84.0.

IR (prism, cm^{-1}): 3108, 2211, 1524, 1487, 1074, 762.

MS (EI) 222 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_9H_6BrN_2$: 220.9709, found: 220.9692

6-bromo-1-methyl-1*H*-indole-3-carbonitrile(2s)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (21.3 mg, 46% yield) as a yellow solid.

Mp: 127-129 °C

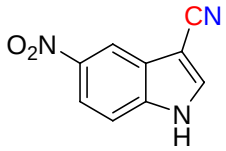
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.60-7.52 (m, 3H), 7.38 (s, d, J = 15.0 Hz, 1H), 3.83 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.8, 136.1, 126.5, 125.5, 121.1, 117.5, 115.2, 113.5, 86.0, 33.7.

IR (prism, cm^{-1}): 2213, 1525, 1467, 1027, 789.

MS (EI) 234 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{10}H_8BrN_2$: 234.9865, found: 234.9881.

5-nitro-1*H*-indole-3-carbonitrile (2u)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:2) to give the products (23.6 mg, 63% yield) as a yellow solid.

Mp: 184-186 °C.

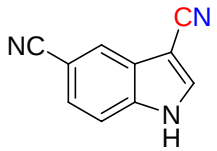
^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.8 (br, 1H), 8.52 (s, 1H), 8.48 (d, J = 2.0 Hz, 1H), 8.13 (dd, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 1H), 7.43 (d, J = 9.0 Hz, 1H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 142.6, 138.5, 138.3, 126.0, 118.6, 115.1, 114.9, 113.8, 86.8.

IR (prism, cm^{-1}): 3100, 2216, 1623, 1538, 1336, 832.

MS (EI) 187 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_9H_6N_3O_2$: 188.0455, found: 188.0477.

1*H*-indole-3,5-dicarbonitrile (2w)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:2) to give the products (25.4 mg, 76% yield) as a yellow solid.

Mp: 246-248°C.

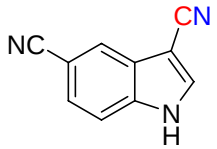
^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.70 (br, 1H), 8.47 (s, 1H), 8.19 (s, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 137.3, 137.0, 126.4, 126.3, 124.1, 119.6, 115.2, 114.3, 104.2, 85.5.

IR (prism, cm^{-1}): 3103, 2218, 2188, 1623, 1524, 763.

MS (EI) 167 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{10}H_6N_3$: 168.0556, found : 168.0553.

1*H*-indole-3,5-dicarbonitrile (2x)



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:2) to give the products (20.4 mg, 66% yield) as a yellow solid.

Mp: 246-248°C.

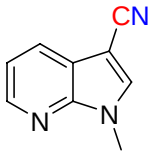
^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.69 (br, 1H), 8.47 (s, 1H), 8.19 (s, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.65 (d, J = 8.5 Hz, 1H).

^{13}C NMR (DMSO-d_6, 125 MHz): δ 137.3, 137.0, 126.4, 126.3, 124.1, 119.6, 115.2, 114.3, 104.1, 85.5.

IR (prism, cm^{-1}): 3106, 2222, 2219, 1621, 1509, 777.

MS (EI) 167 (M^+); HRMS (ESI-TOF, $[M+H]^+$) Calcd. for $C_{10}H_6N_3$: 168.0556, found: 168.0562.

1-methyl-1*H*-pyrrolo[2,3-b]pyridine-3-carbonitrile (2y)[1]

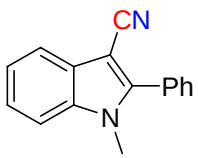


Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl acetate:petroleum ether, 1:5) to give the products (16.3 mg, 52% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.46 (s, 1H), 8.08 (d, J = 9.5 Hz, 1H), 7.75 (s, 1H), 7.28-7.26 (m, 1H), 3.97 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.8, 145.2, 135.8, 128.2, 120.0, 118.1, 115.1, 84.2, 32.0.

1-methyl-2-phenyl-1*H*-indole-3-carbonitrile (2z)[1]



Flash column chromatography on a silica gel (ethyl acetate:petroleum ether, 1:10 → ethyl

acetate:petroleum ether, 1:5) to give the products (29.2 mg, 63% yield) as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79 (d, *J* = 7.0 Hz, 1H), 7.59-7.52 (m, 5H), 7.44-7.32 (m, 3H), 3.77 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.1, 136.8, 129.9, 129.8, 129.0, 128.7, 127.6, 123.8, 122.4, 119.5, 116.6, 110.5, 85.5, 31.7.

7. References

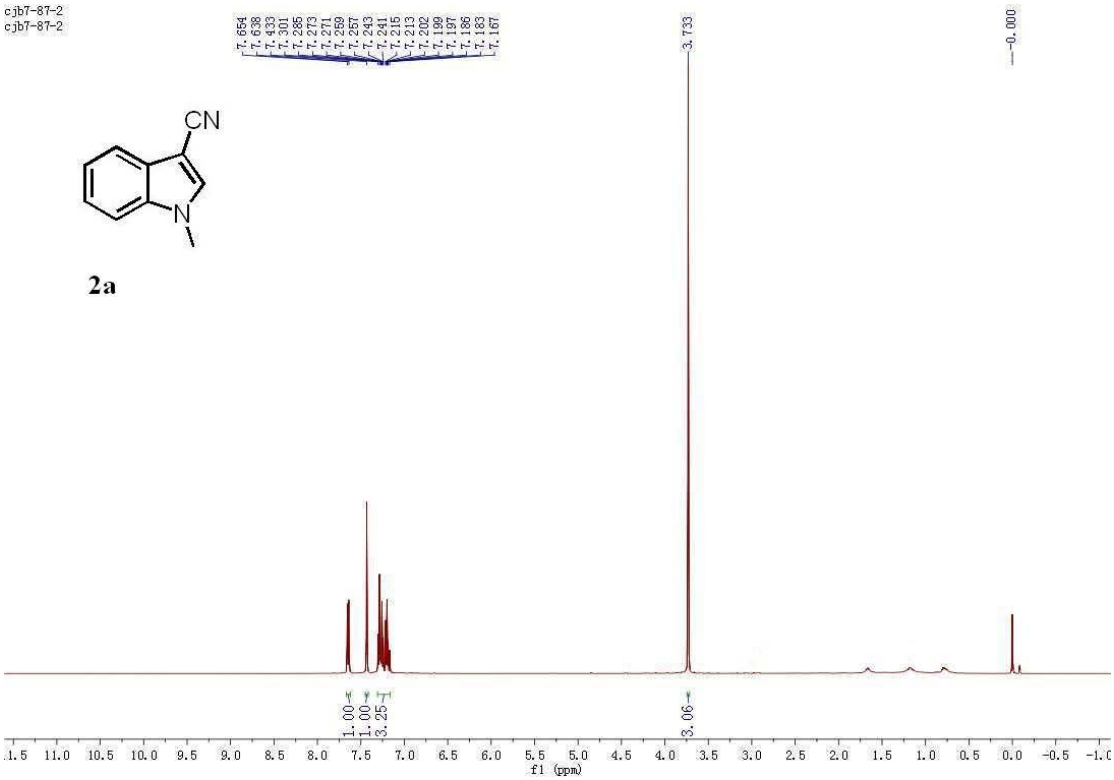
(1). X. Ren, J. Chen, F. Chen and J. Cheng, *Chem. Commun*., 2011, **47**, 6725.

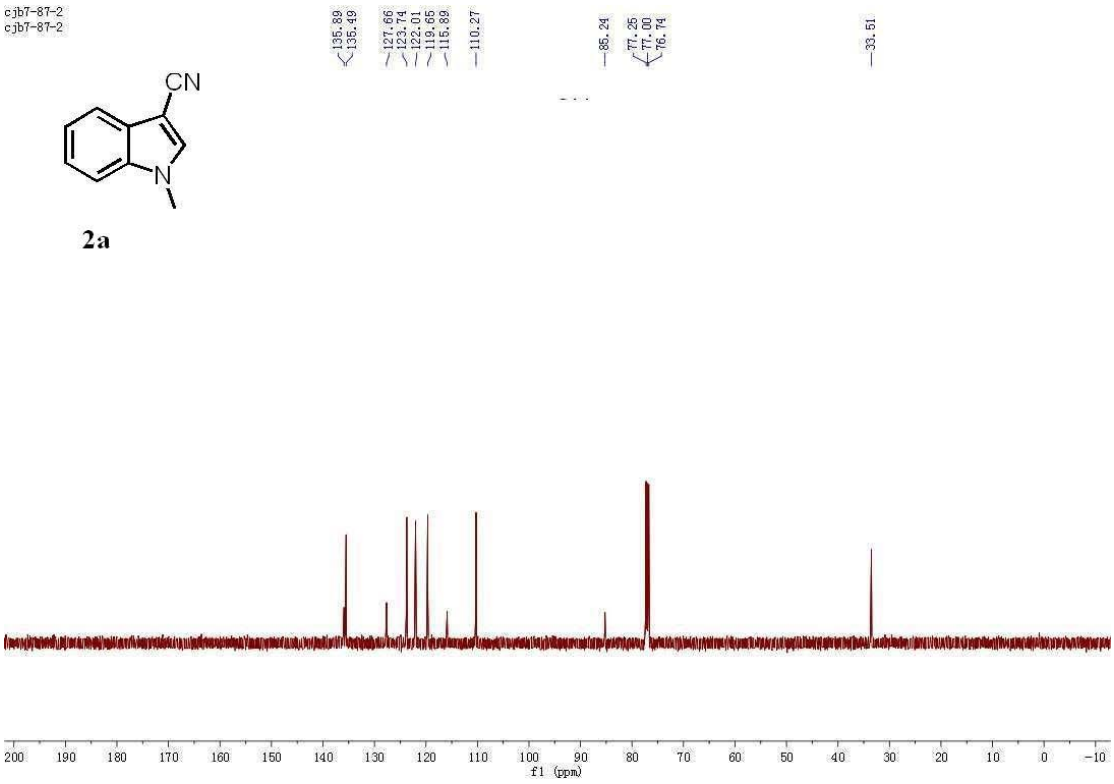
(2). K.Y. Lee, H. S. Lee and J. J. Kim, *Bull. Korean Chem. Soc*., 2007, **28**, 333.

(3). Y. Yang, Y. Zhang and J. Wang, *Org. Lett.*, 2011, **13**, 5608.

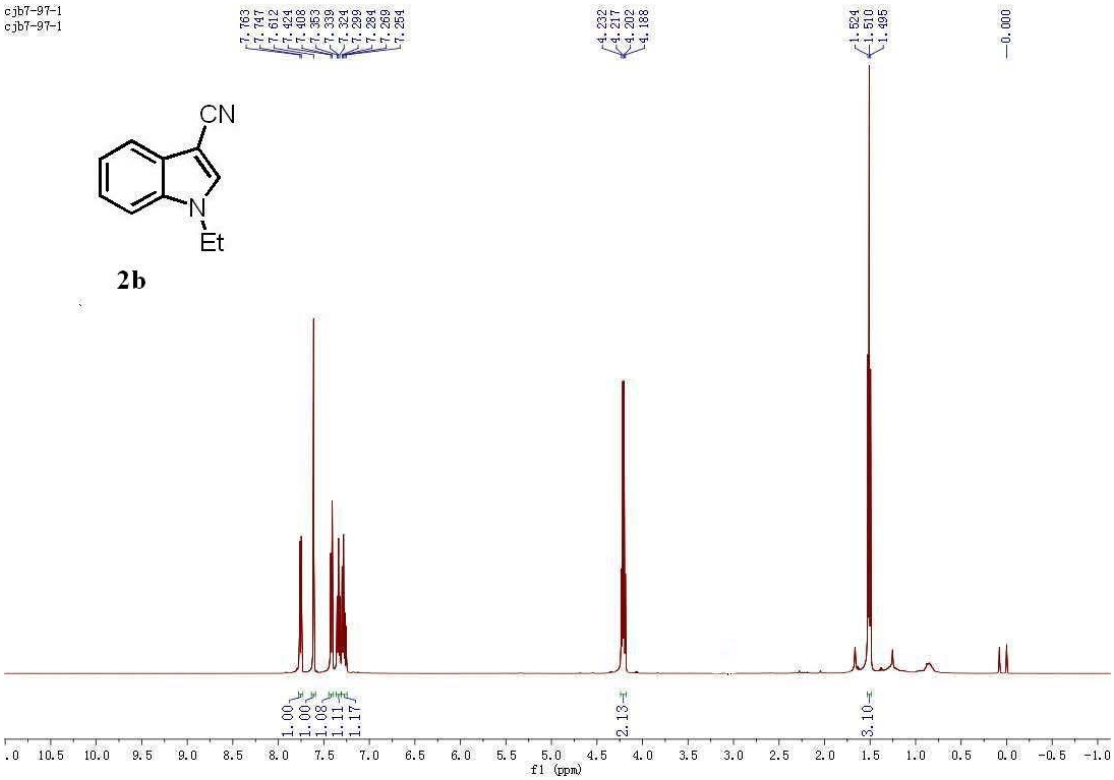
(4). L. Zhang, Q. Wen, J. Jin, C. Wang, P. Lu, Y. Wang, *Tetrahedron*, 2013, **69**, 4236.

8. ^{1}H NMR and ^{13}C NMR Copies of the Products





S14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7.269
7.254
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4.217
4.202
4.188
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1.510
1.495
0.000
CN
N
Et
2b
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1.00
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1.11
1.17
2.13
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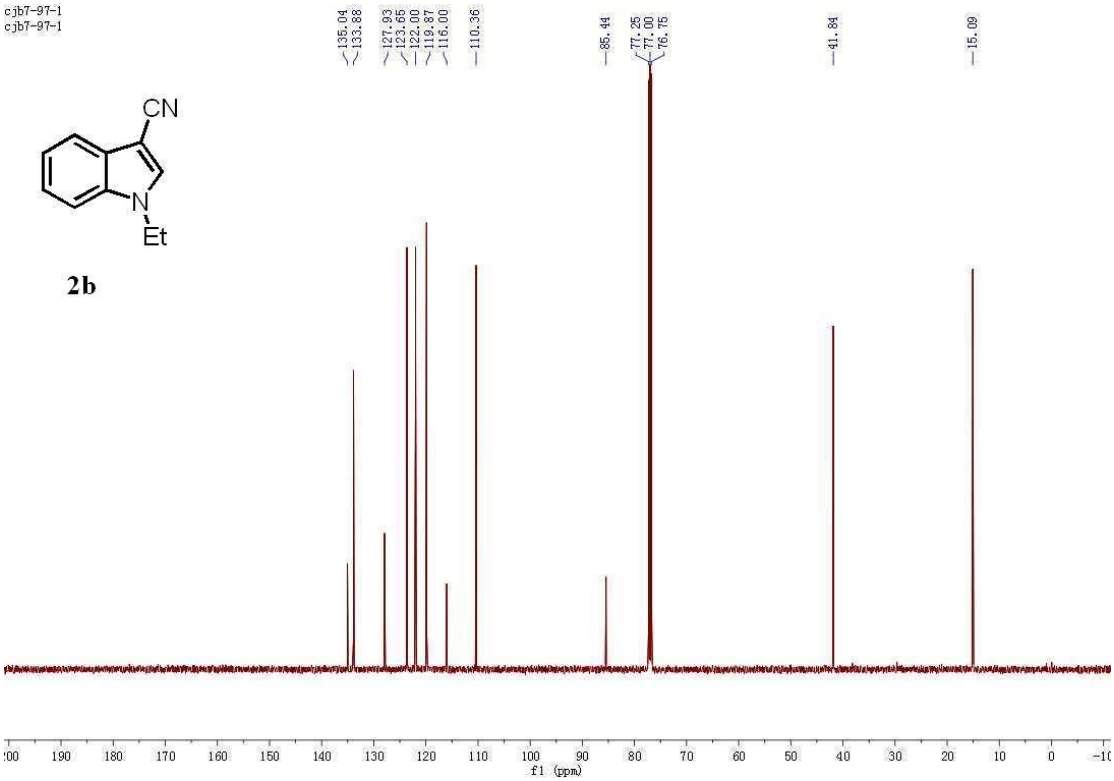
f1 (ppm)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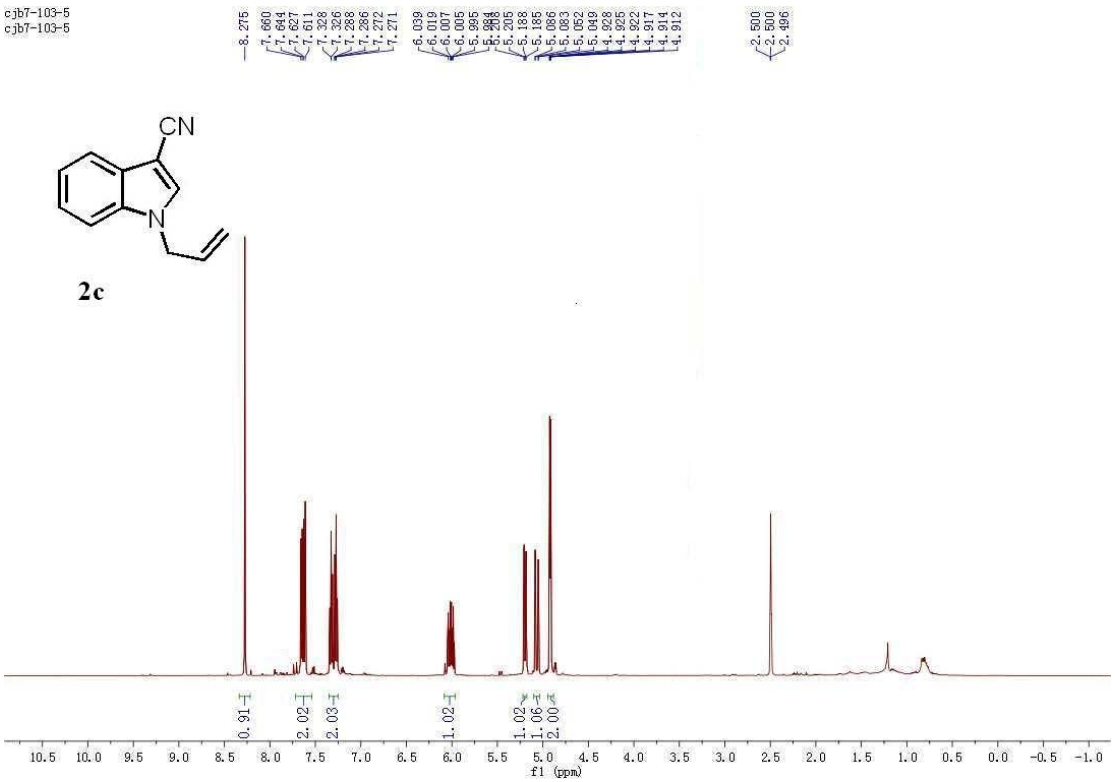
CN
N
Et
2b
f1 (ppm)

S15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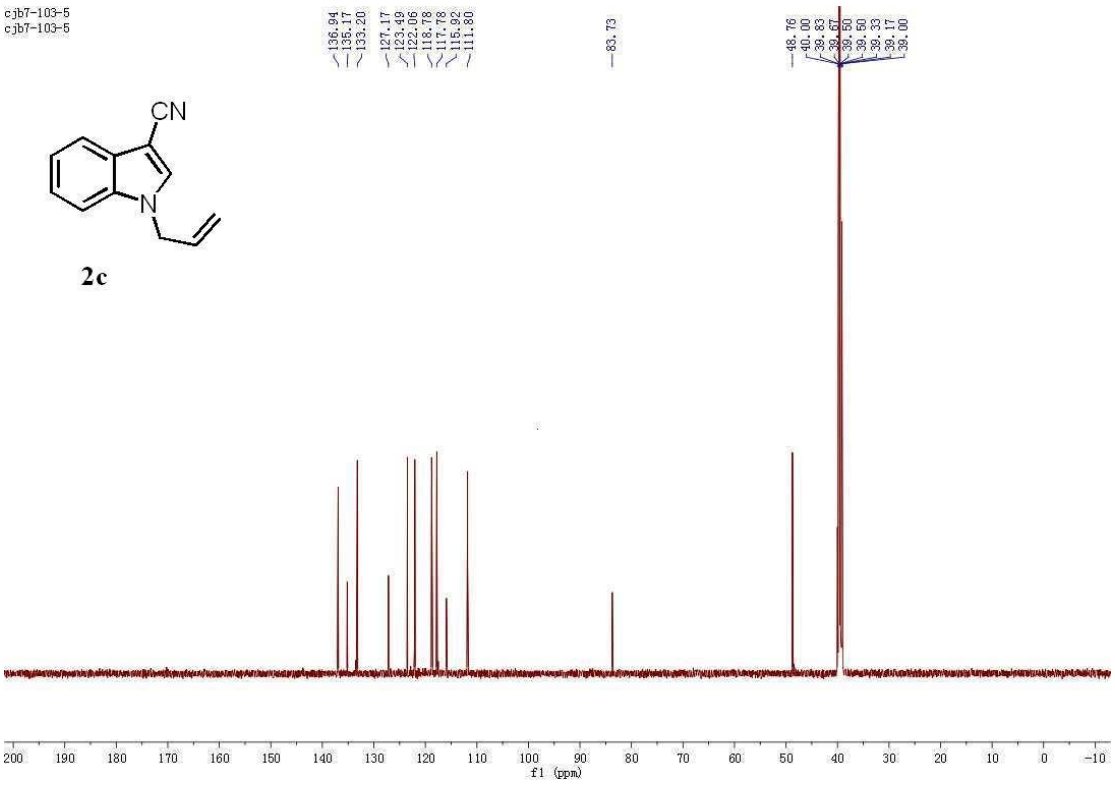
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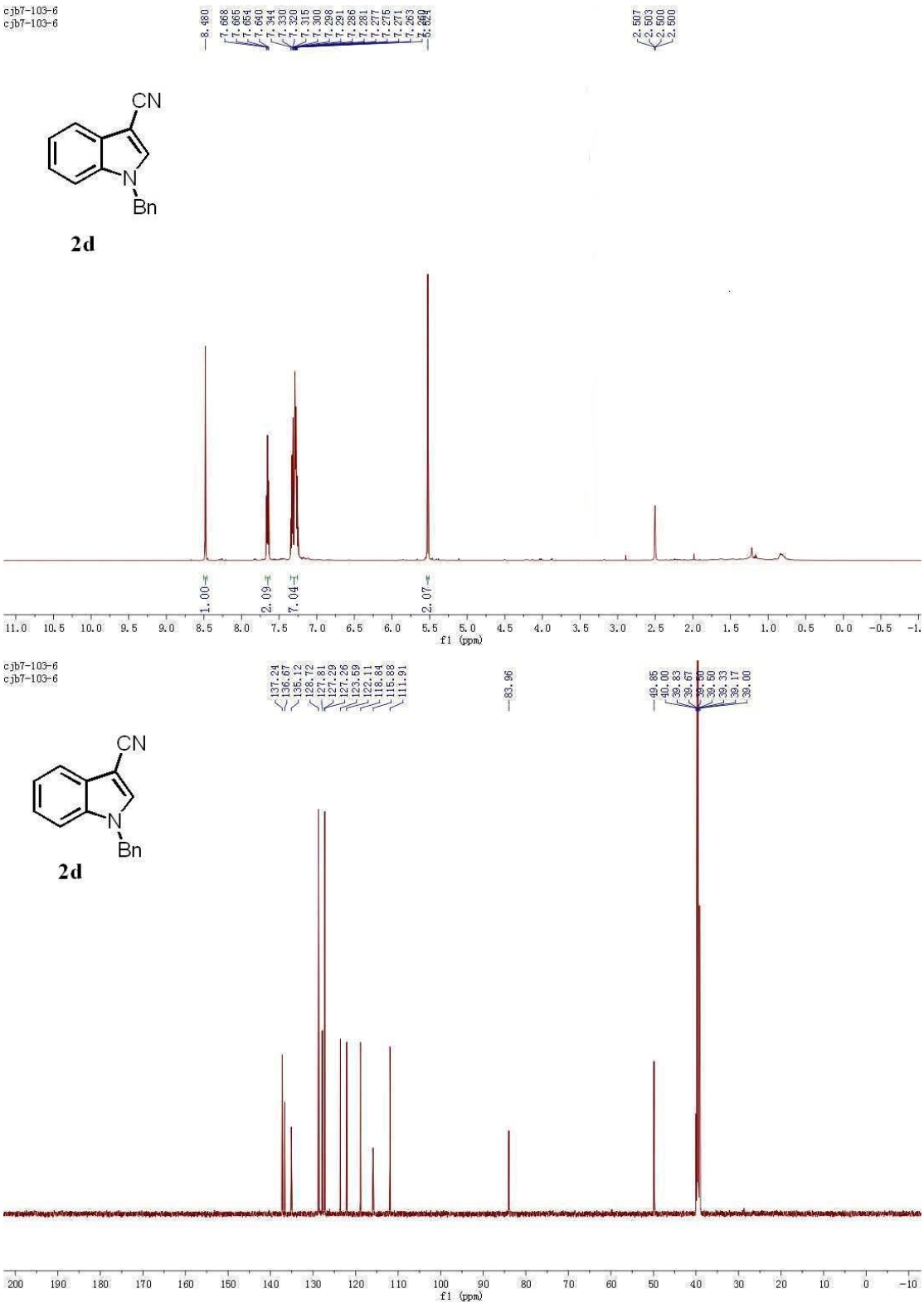
CN
N
2c
f1 (ppm)

S16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Bn
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f1 (ppm)
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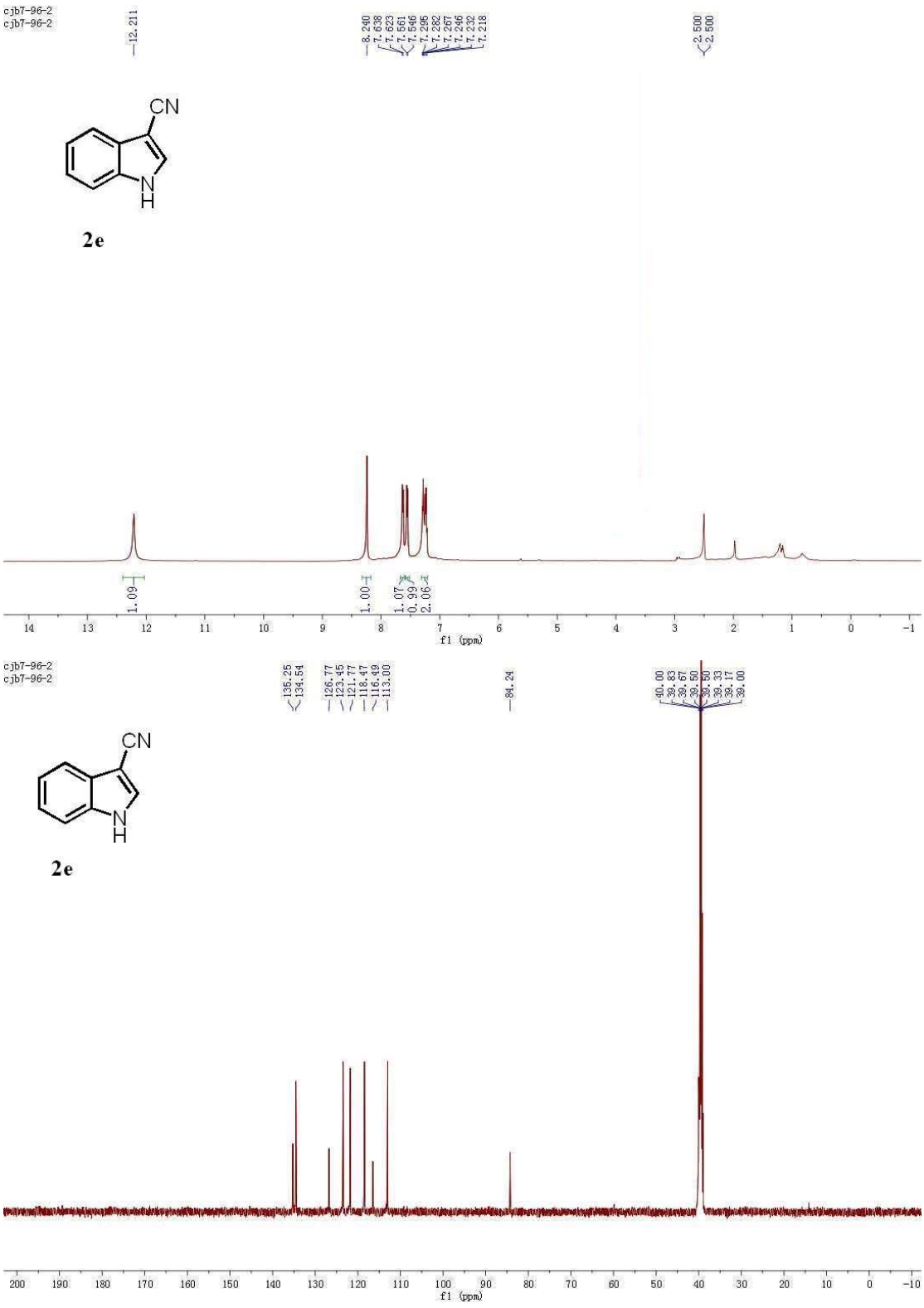
Bn
2d
f1 (ppm)

S17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CN
N
H
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0.99
2.06
f1 (ppm)
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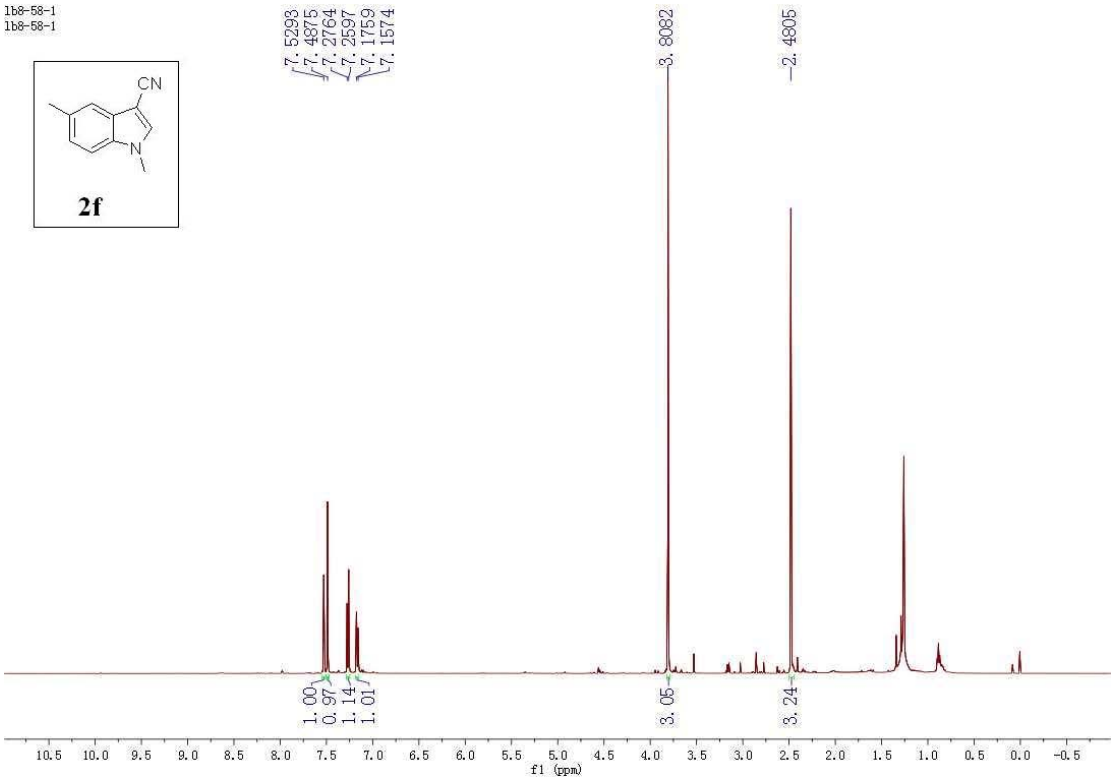
S18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1.01
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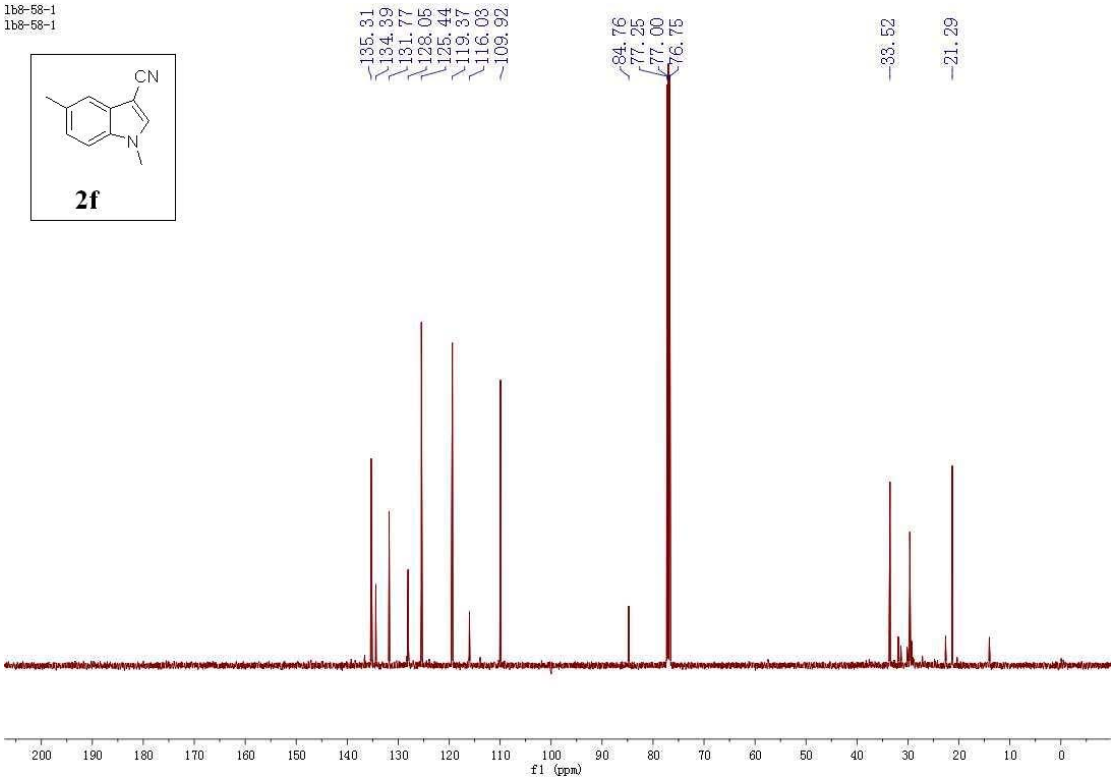
f1 (ppm)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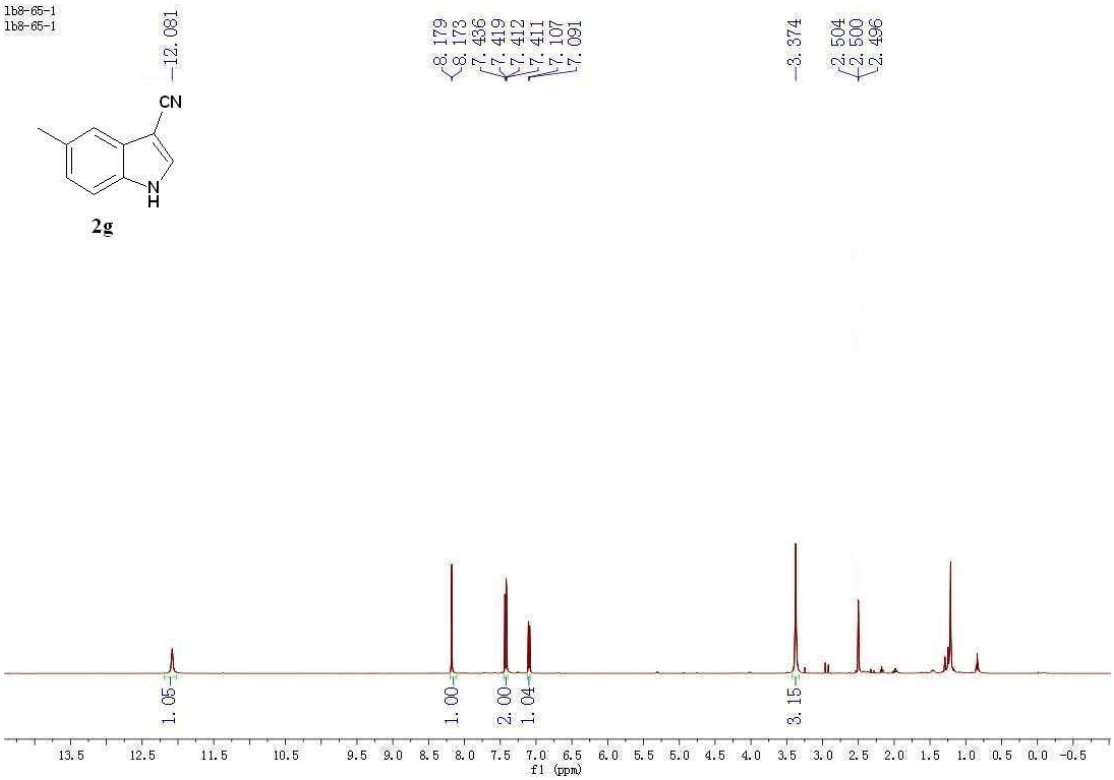
2f
f1 (ppm)

S19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H
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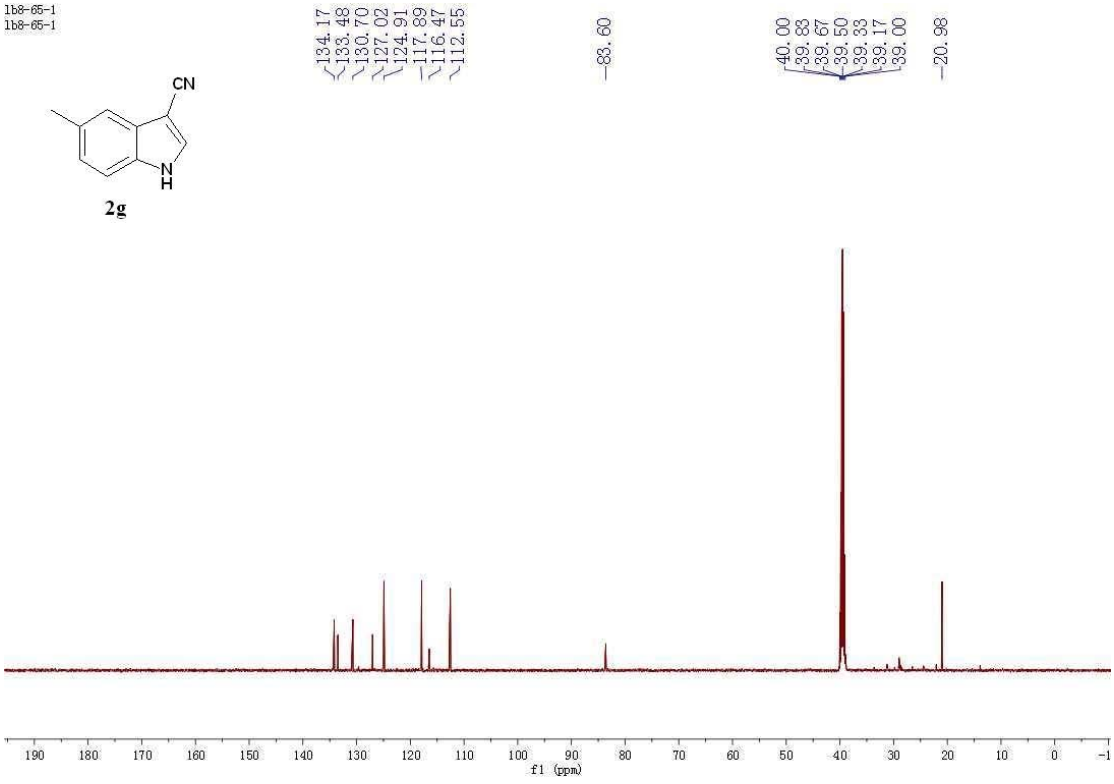
f1 (ppm)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112.55
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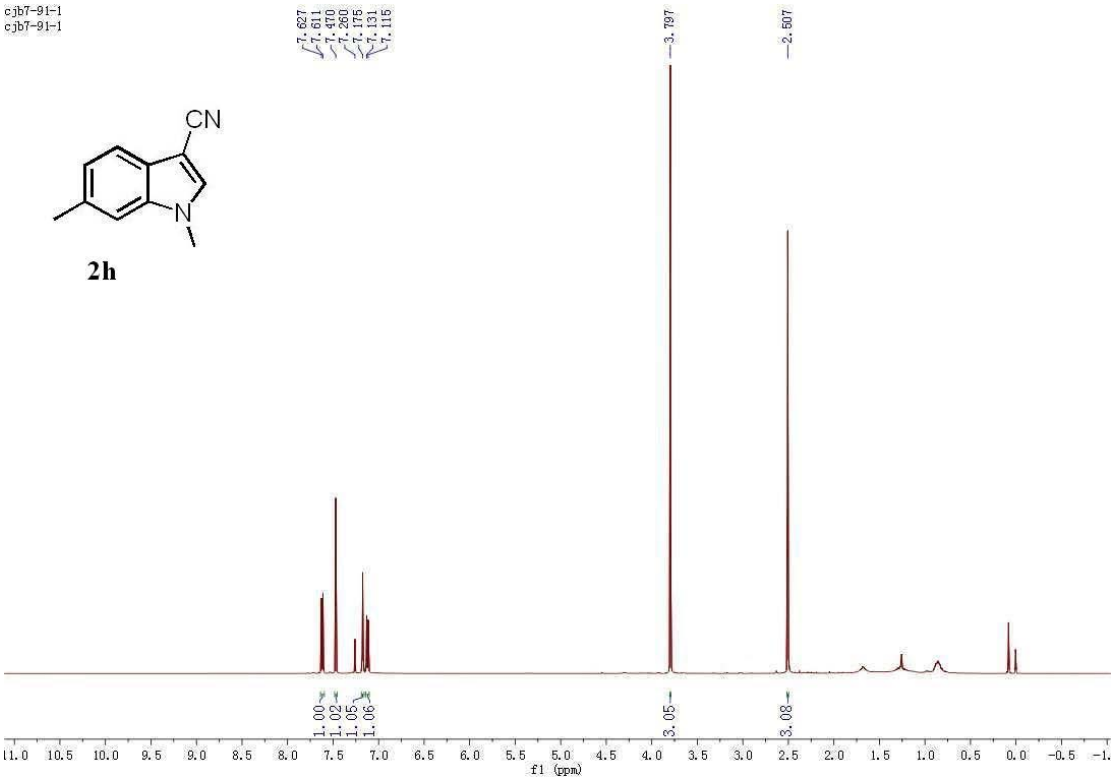
CN
N
H
2g
f1 (ppm)

S20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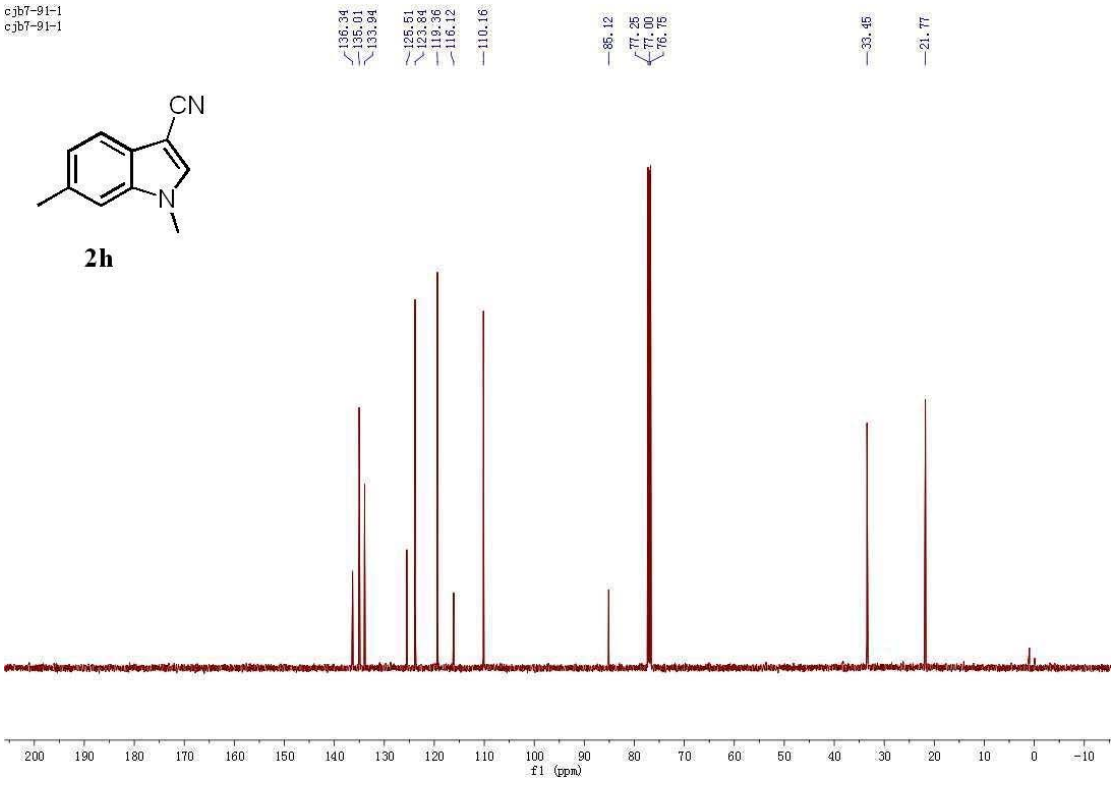
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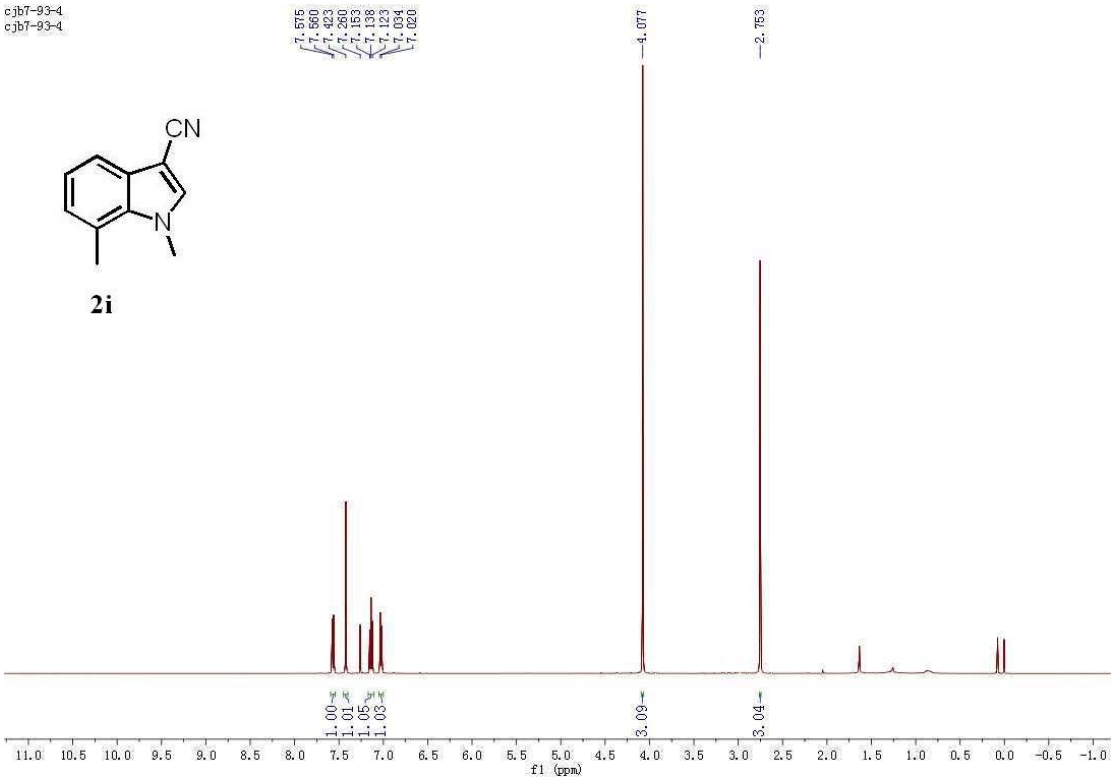
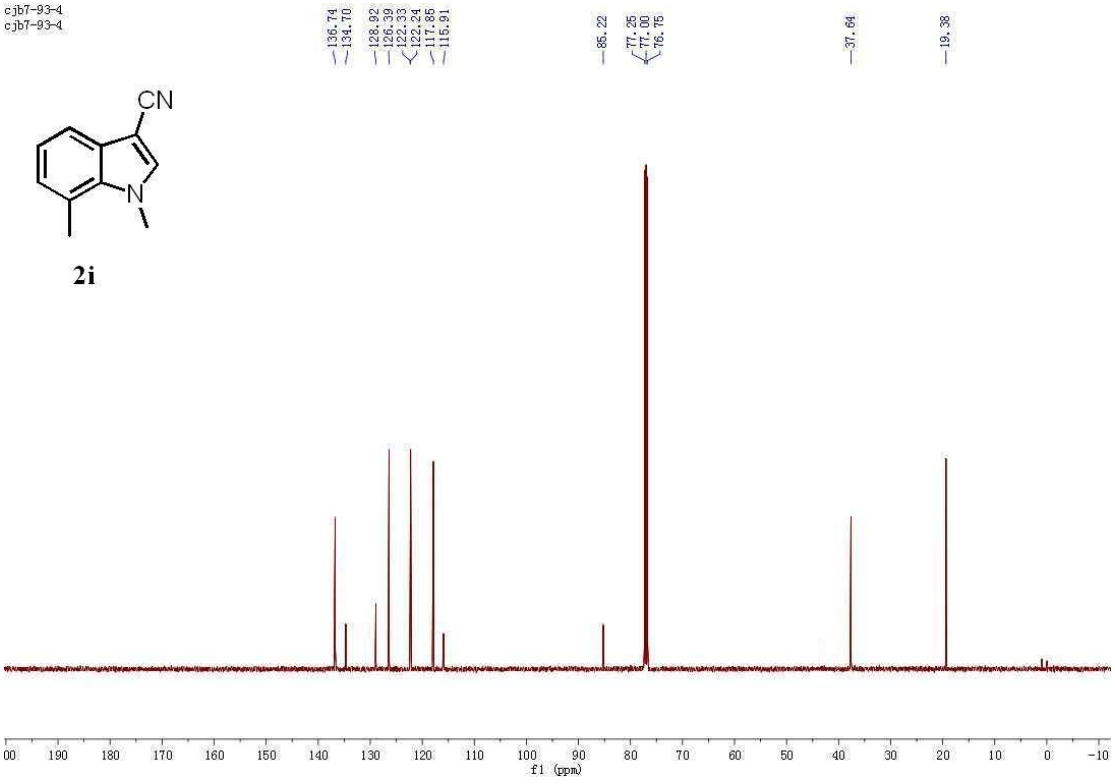
33.45
21.77
CN
N
2h
f1 (ppm)

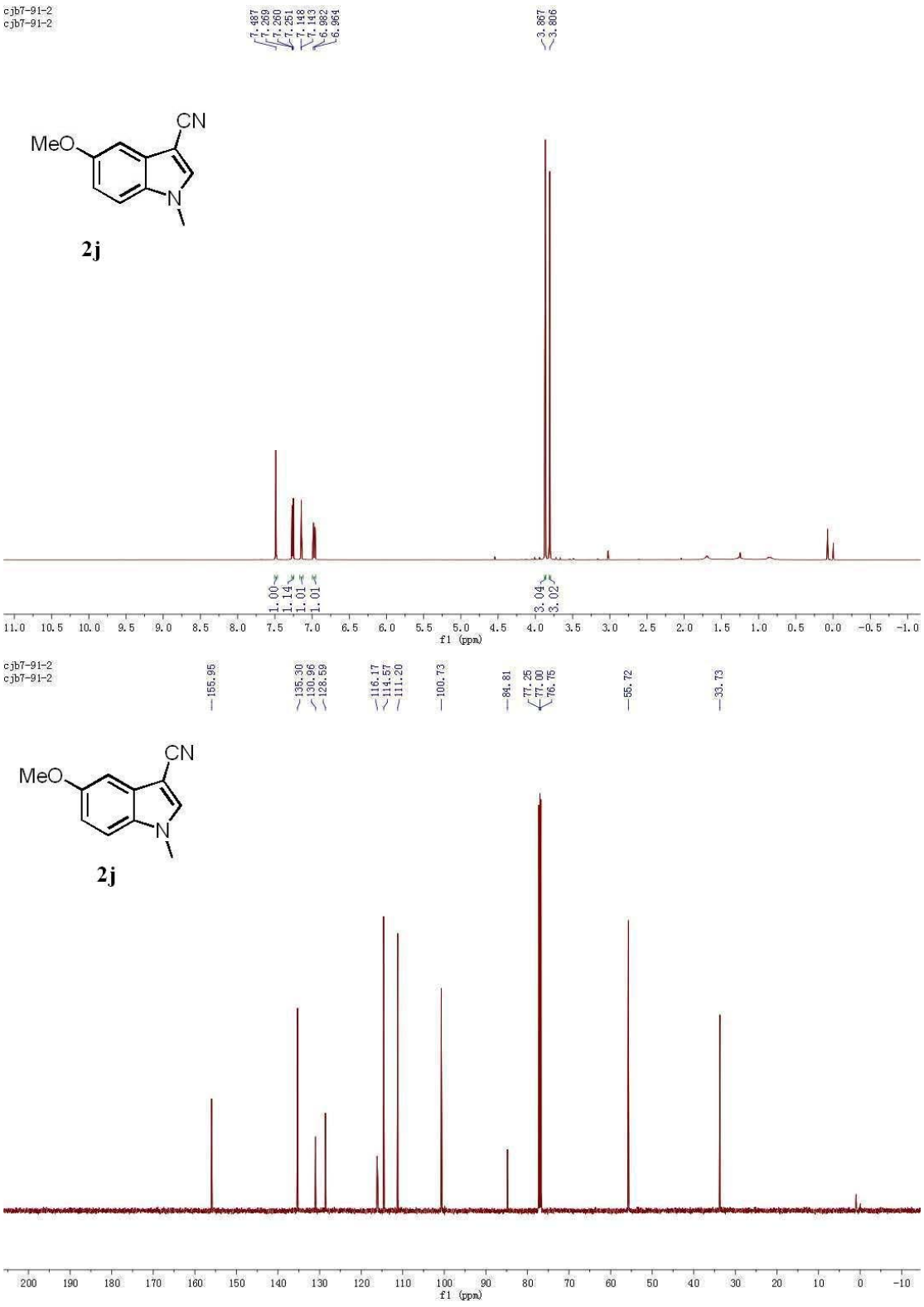
S21


cjb7-93-4
cjb7-93-4
7.575
7.560
7.423
7.260
7.153
7.138
7.123
7.034
7.020
4.077
2.763
CN
N
1.00
1.01
1.05
1.03
3.09
3.04
f1 (ppm)

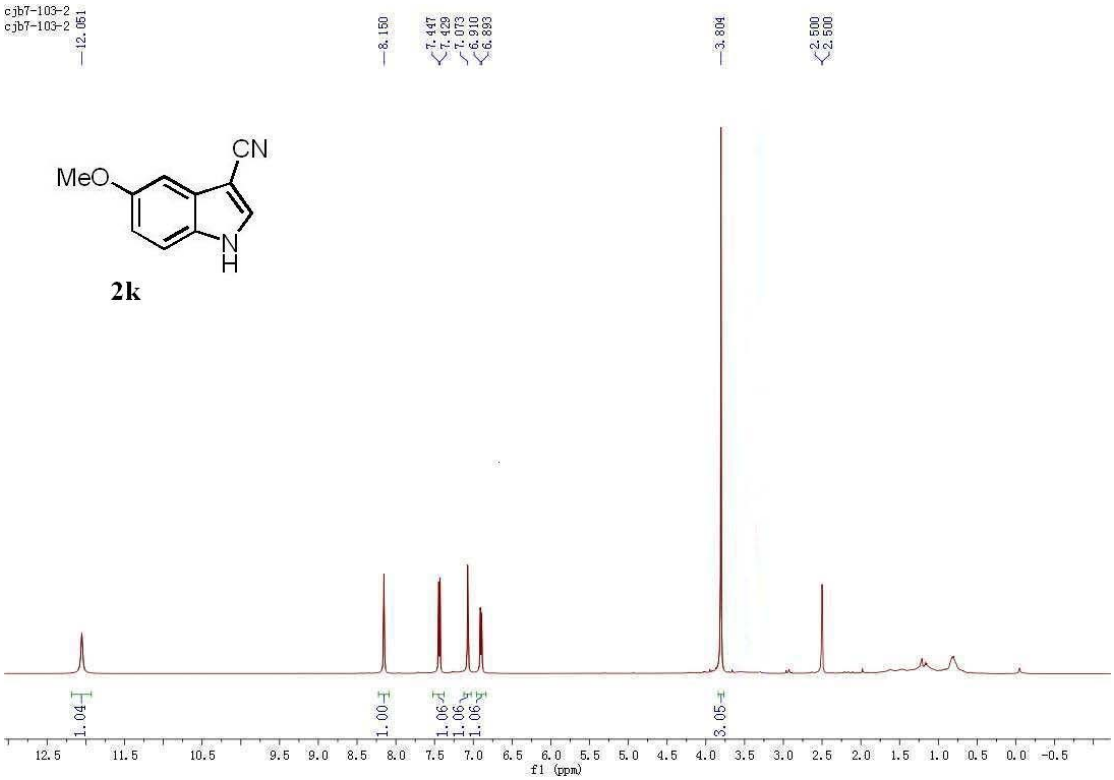
2i

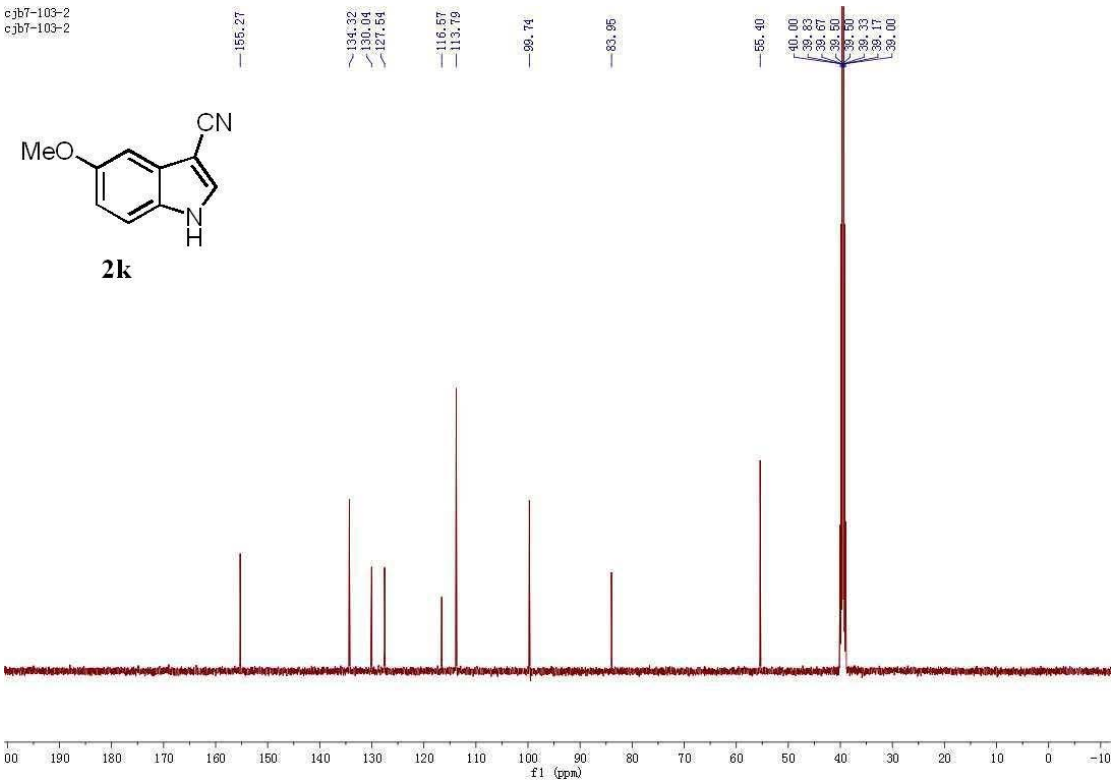

cjb7-93-4
cjb7-93-4
136.74
134.70
128.92
126.39
122.33
122.24
117.85
115.91
86.22
77.25
77.00
76.75
37.64
19.38
CN
N
f1 (ppm)

2i

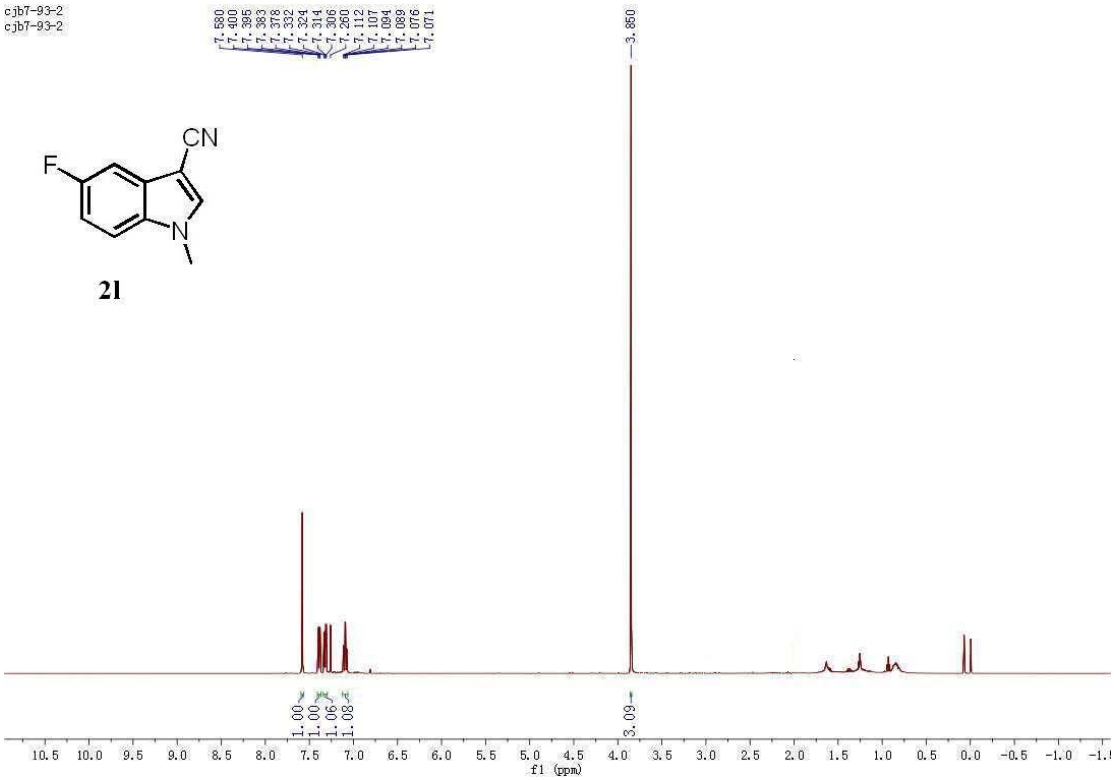

cjb7-91-2
cjb7-91-2
7.487
7.269
7.260
7.251
7.148
7.143
6.982
6.964
3.867
3.806
MeO
CN
N
2j
1.00
1.14
1.01
1.01
3.04
3.02
f1 (ppm)
cjb7-91-2
cjb7-91-2
155.95
136.30
130.96
128.59
116.17
114.57
111.20
100.73
84.81
77.25
77.00
76.75
55.72
33.73
MeO
CN
N
2j
f1 (ppm)

S23

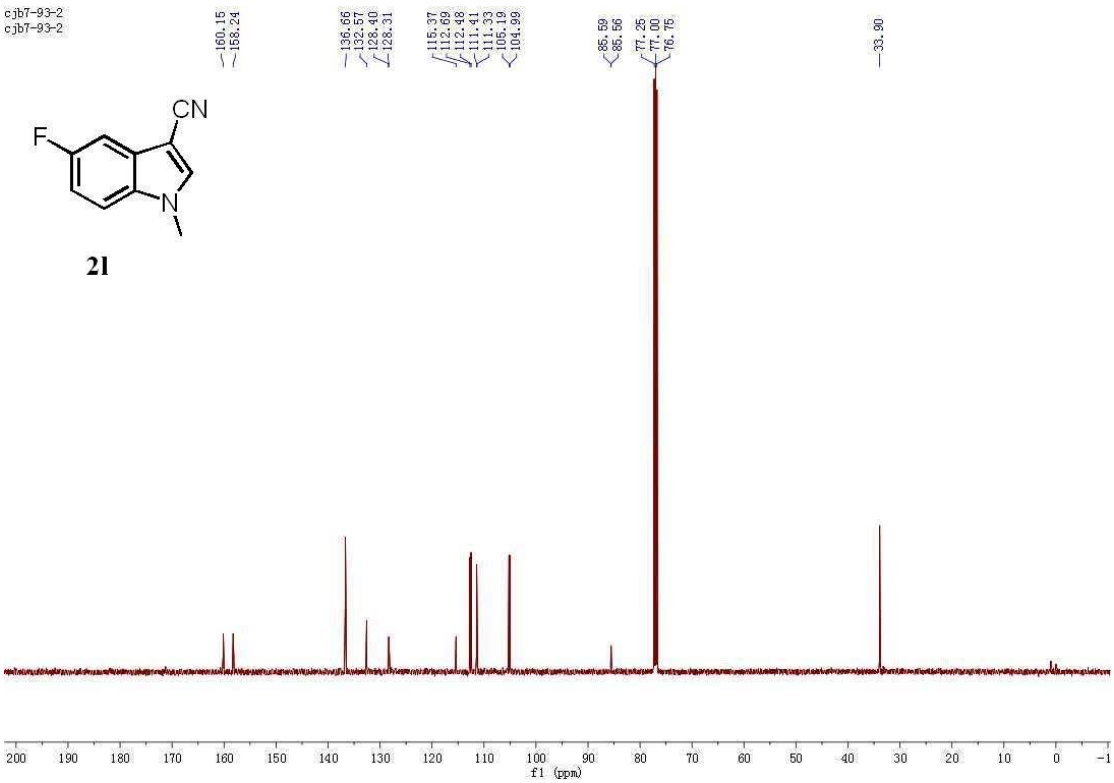

cjb7-103-2
cjb7-103-2
12.061
8.150
7.447
7.429
7.073
6.910
6.893
3.804
2.500
2.500
CN
MeO
N
H
2k
1.04
1.00
1.06
1.06
1.06
3.05
f1 (ppm)


cjb7-103-2
cjb7-103-2
155.27
134.32
130.04
127.64
116.57
113.79
99.74
83.96
55.40
40.00
39.83
39.67
39.50
39.33
39.17
39.00
CN
MeO
N
H
2k
f1 (ppm)

S24

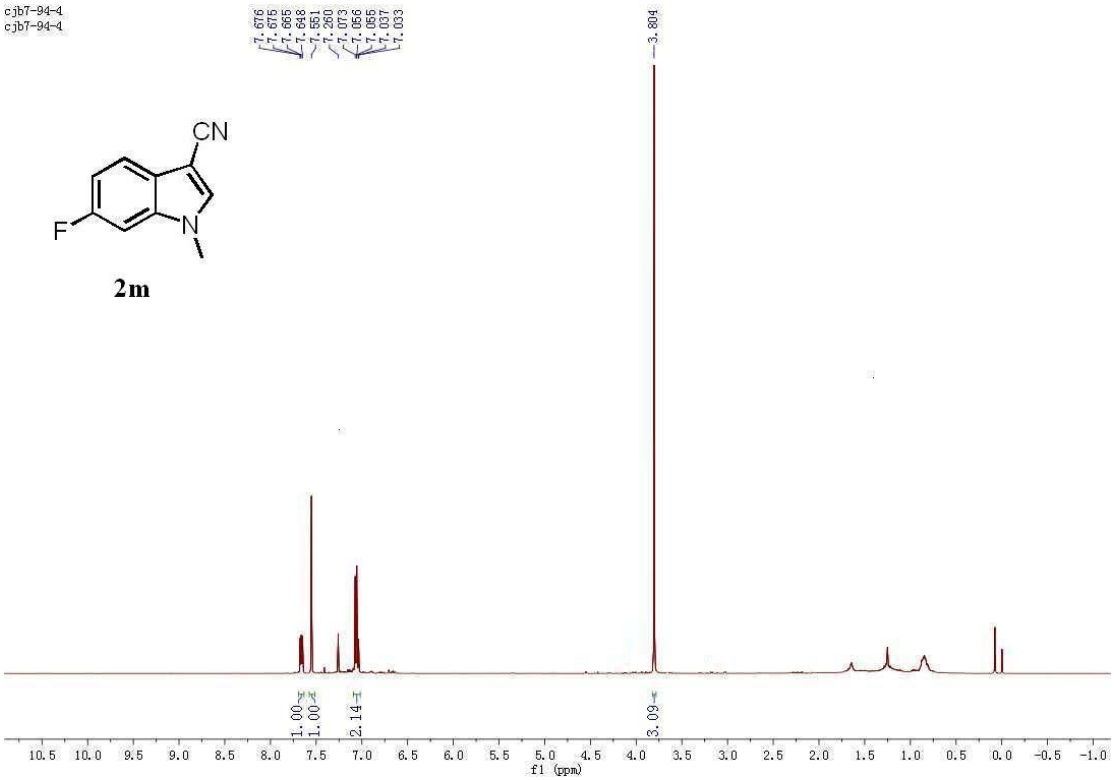

cjb7-93-2
cjb7-93-2
7.580
7.400
7.395
7.383
7.378
7.332
7.324
7.314
7.306
7.260
7.112
7.107
7.094
7.089
7.076
7.071
3.850
CN
F
N
1.00
1.00
1.06
1.08
3.09
f1 (ppm)

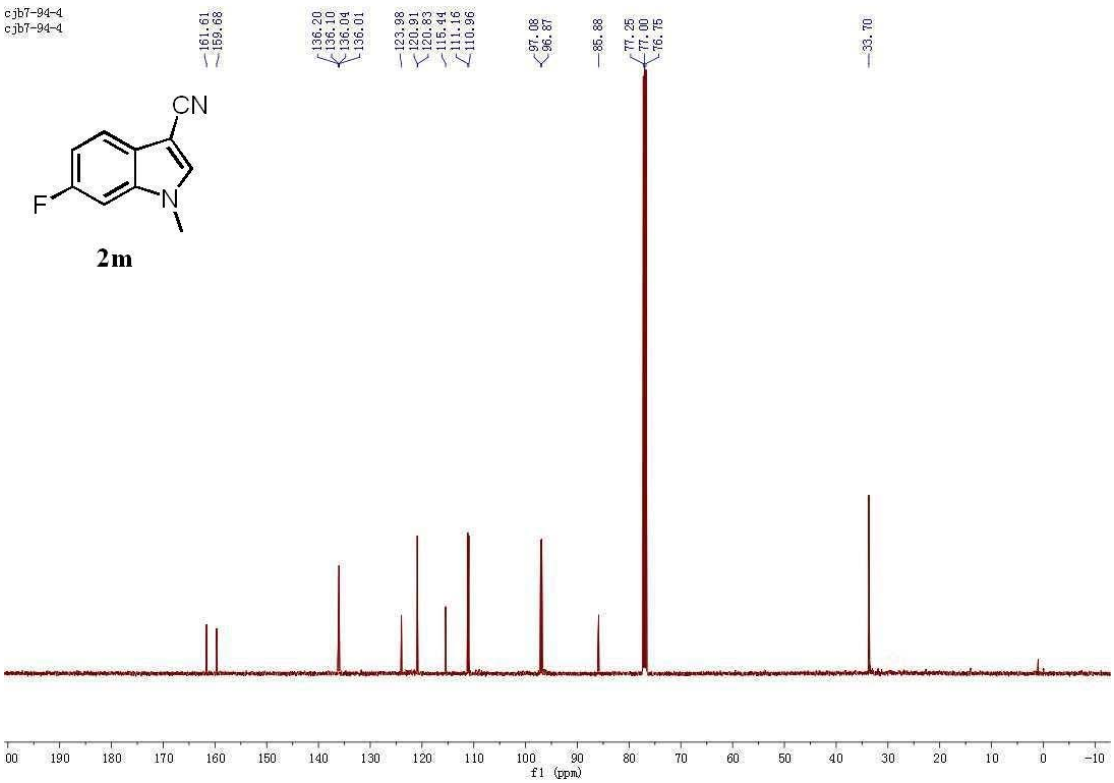
2l


cjb7-93-2
cjb7-93-2
160.15
158.24
136.66
132.57
128.40
128.31
115.37
112.69
112.48
111.41
111.33
106.19
104.99
85.59
85.56
77.25
77.00
76.75
33.90
CN
F
N
f1 (ppm)

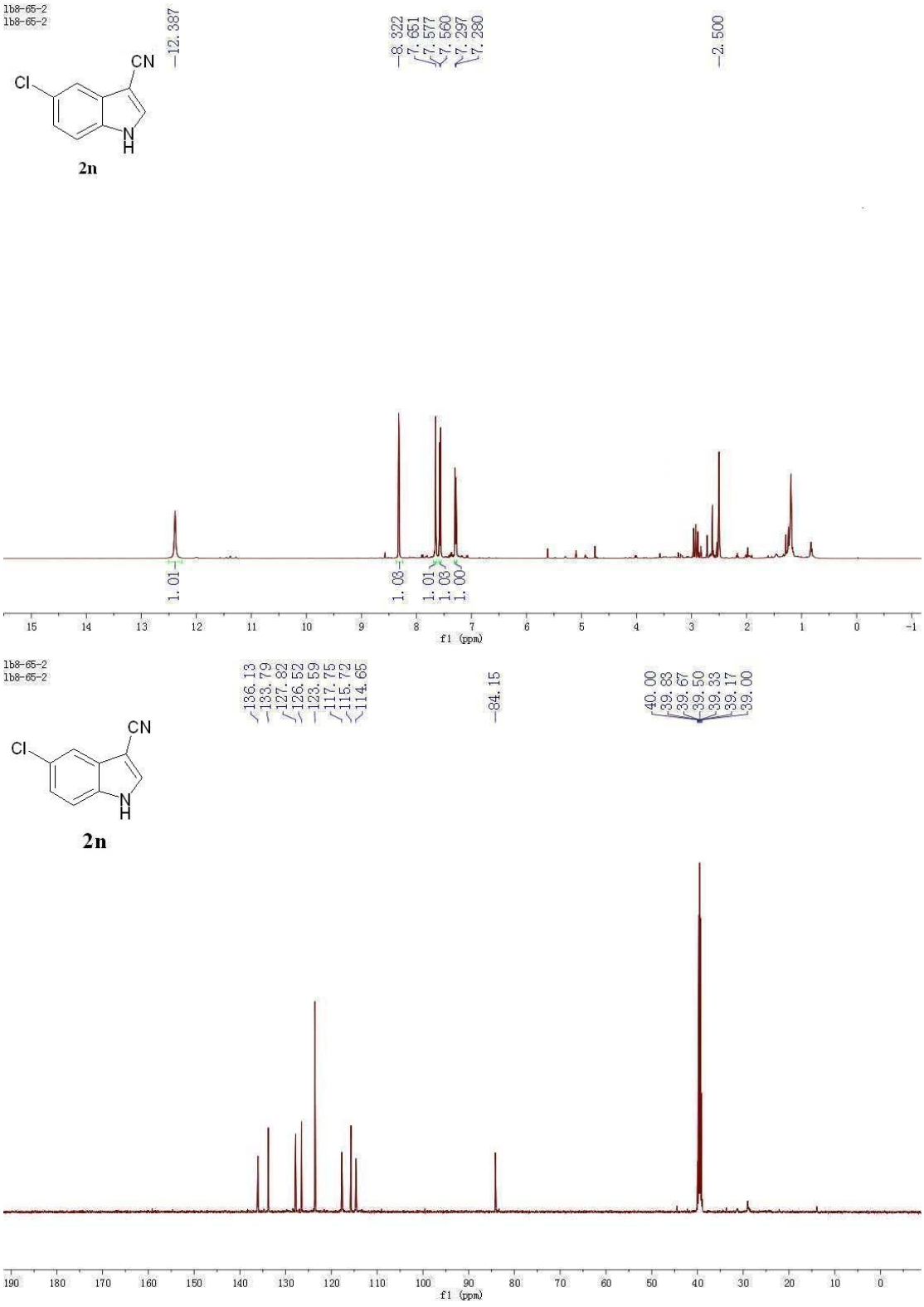
2l

S25

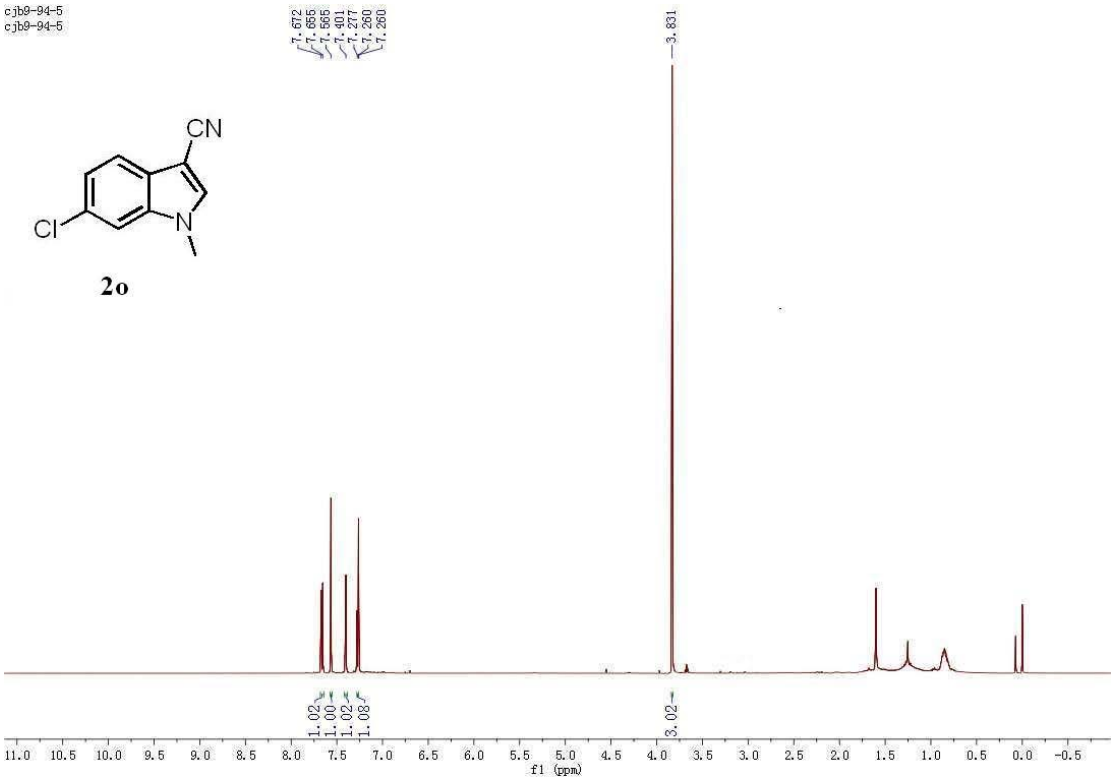

cjb7-94-4
cjb7-94-4
7.676
7.675
7.665
7.648
7.551
7.260
7.073
7.056
7.055
7.037
7.033
3.804
CN
F
N
2m
1.00
1.00
2.14
3.09
f1 (ppm)

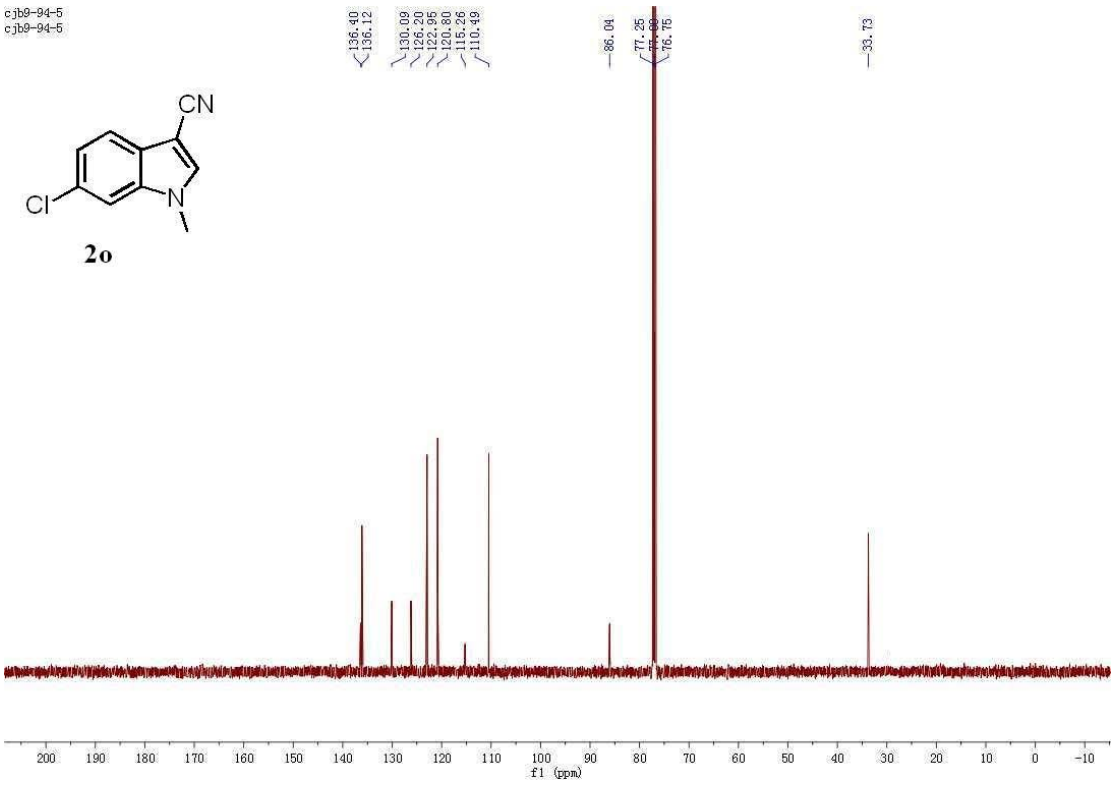

cjb7-94-4
cjb7-94-4
161.61
159.68
136.20
136.10
136.04
136.01
123.98
120.91
120.83
115.44
111.16
110.96
97.08
96.87
86.88
77.25
77.00
76.75
33.70
CN
F
N
2m
f1 (ppm)

S26

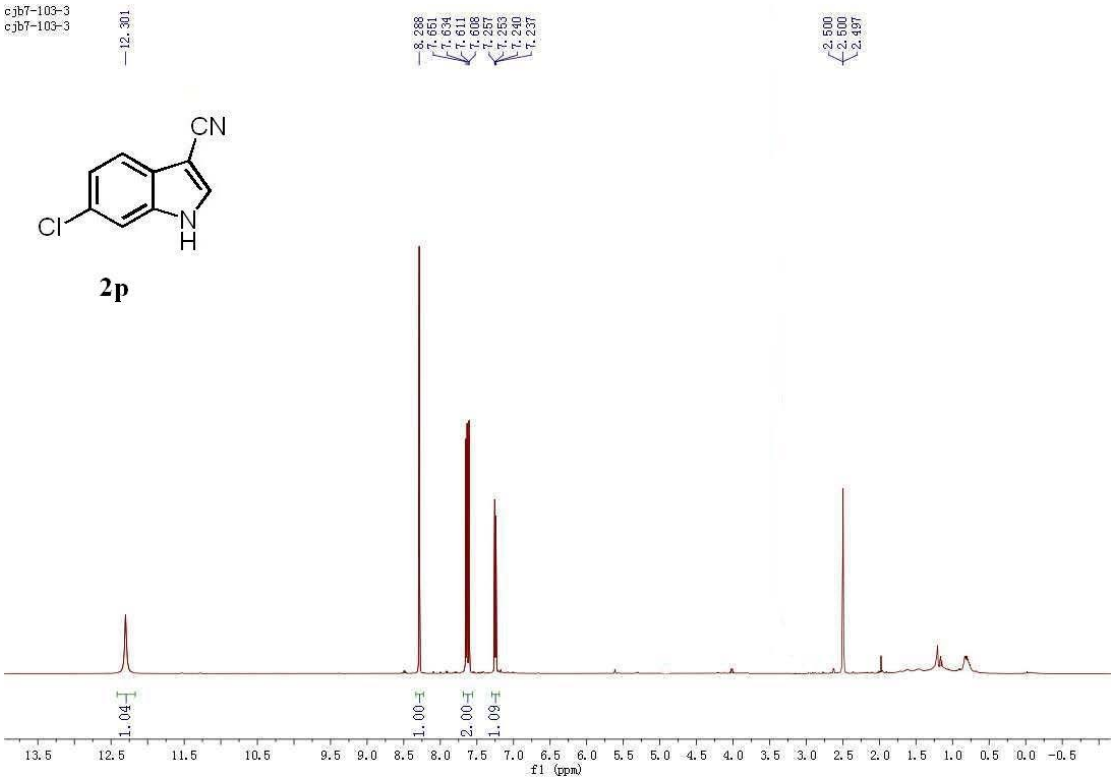

1b8-65-2
1b8-65-2
12.387
8.322
7.651
7.577
7.560
7.297
7.280
2.500
CN
Cl
N
H
2n
1.01
1.03
1.01
1.03
1.00
f1 (ppm)
1b8-65-2
1b8-65-2
136.13
133.79
127.82
126.52
123.59
117.75
115.72
114.65
84.15
40.00
39.83
39.67
39.50
39.33
39.17
39.00
CN
Cl
N
H
2n
f1 (ppm)

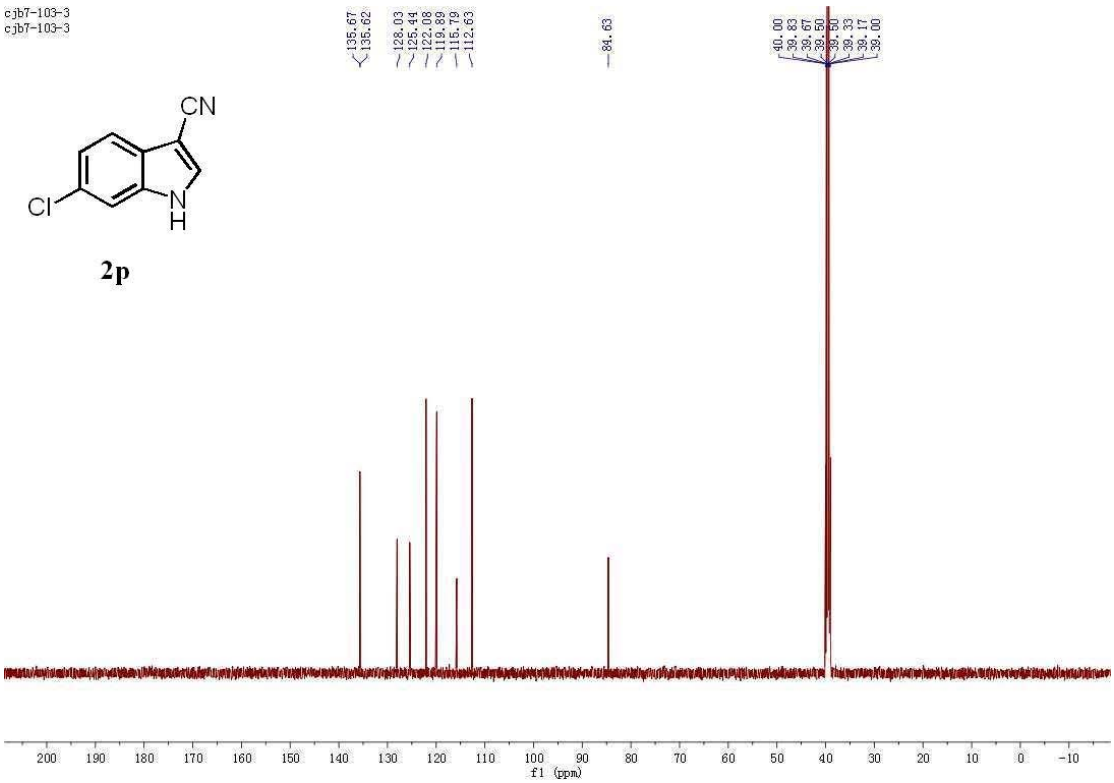
S27


cjb9-94-5
cjb9-94-5
7.672
7.665
7.665
7.401
7.277
7.260
7.260
3.831
CN
Cl
N
2o
1.02
1.00
1.02
1.08
3.02
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

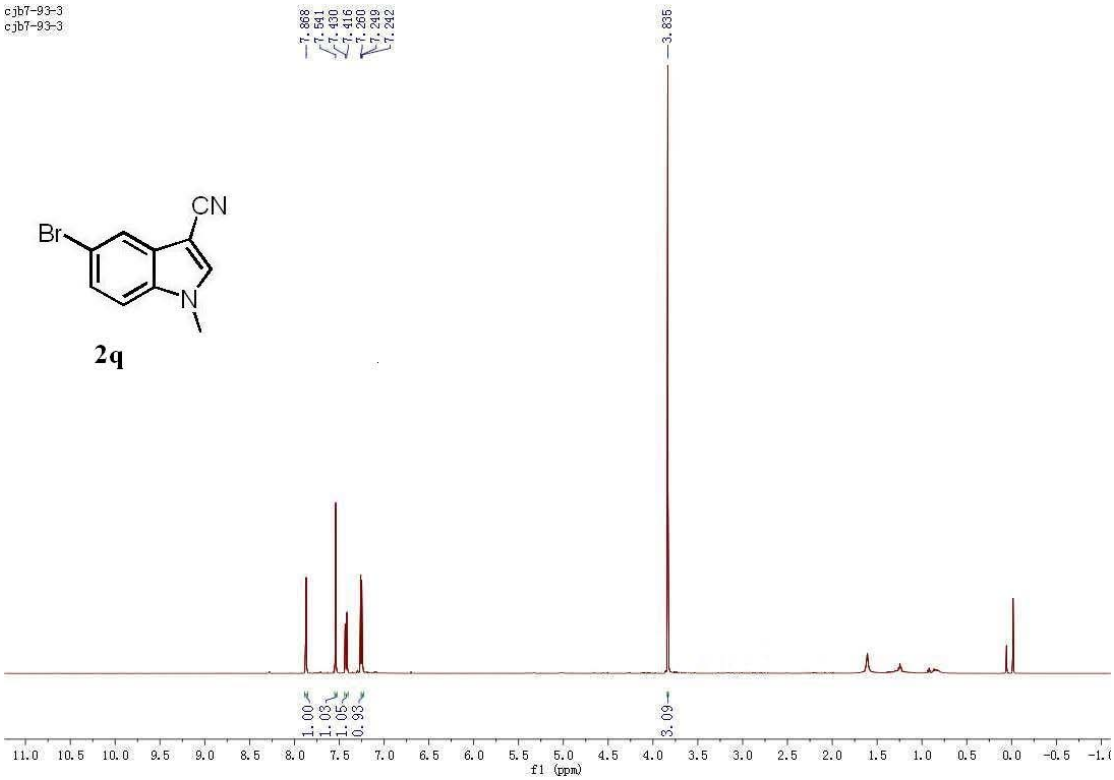

cjb9-94-5
cjb9-94-5
136.40
136.12
130.09
126.20
122.95
120.80
115.26
110.49
86.04
77.25
77.00
76.75
33.73
CN
Cl
N
2o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

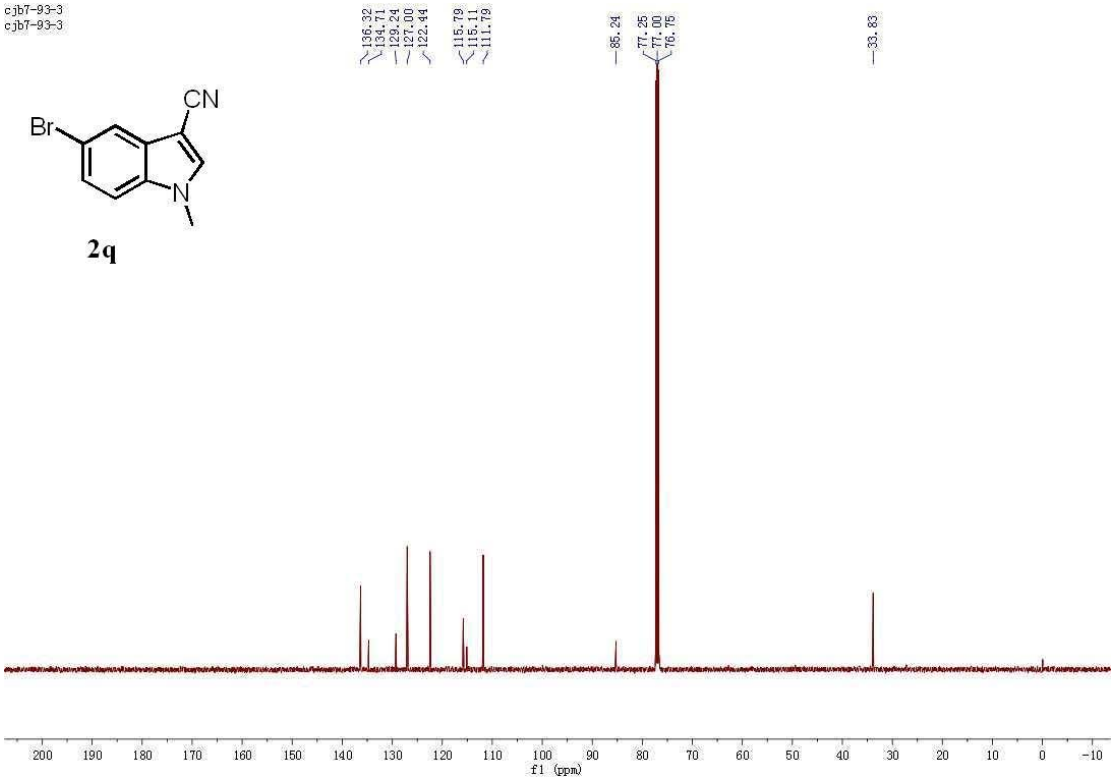
S28


cjb7-103-3
cjb7-103-3
12.301
8.288
7.651
7.634
7.611
7.608
7.257
7.253
7.240
7.237
2.500
2.500
2.497
CN
Cl
N
H
2p
1.04
1.00
2.00
1.09
f1 (ppm)

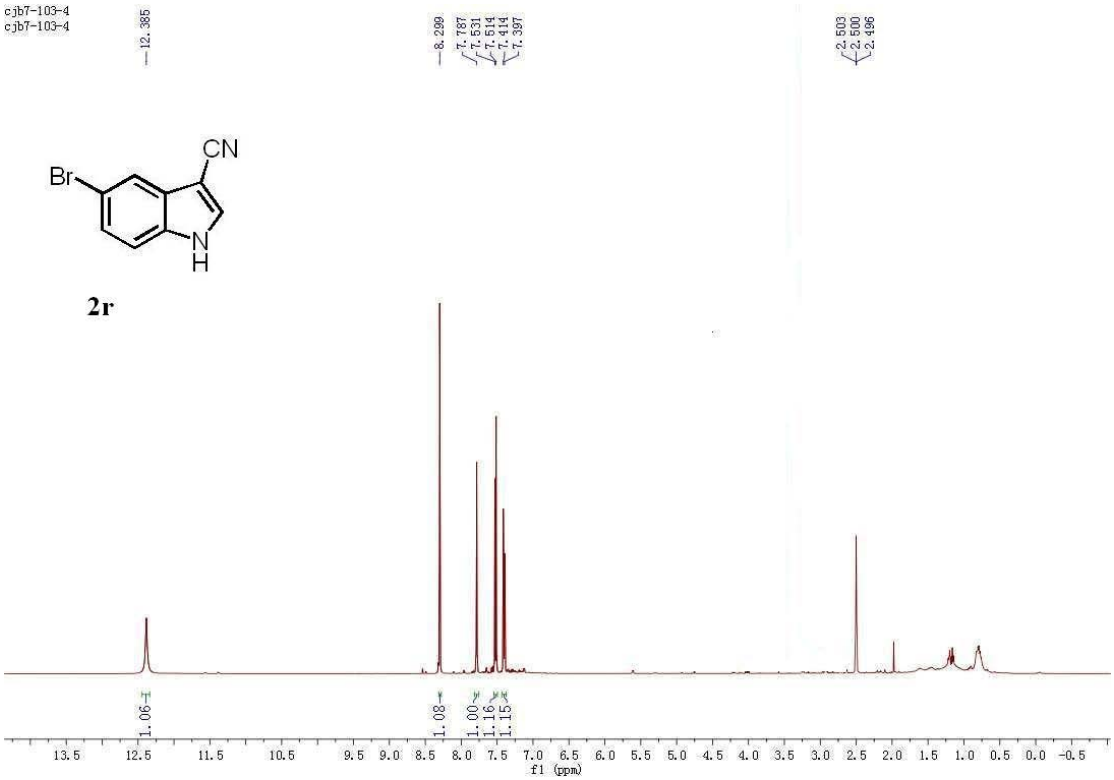

cjb7-103-3
cjb7-103-3
135.67
135.62
128.03
125.44
122.08
119.89
116.79
112.63
84.63
40.00
39.83
39.67
39.50
39.33
39.17
39.00
CN
Cl
N
H
2p
f1 (ppm)

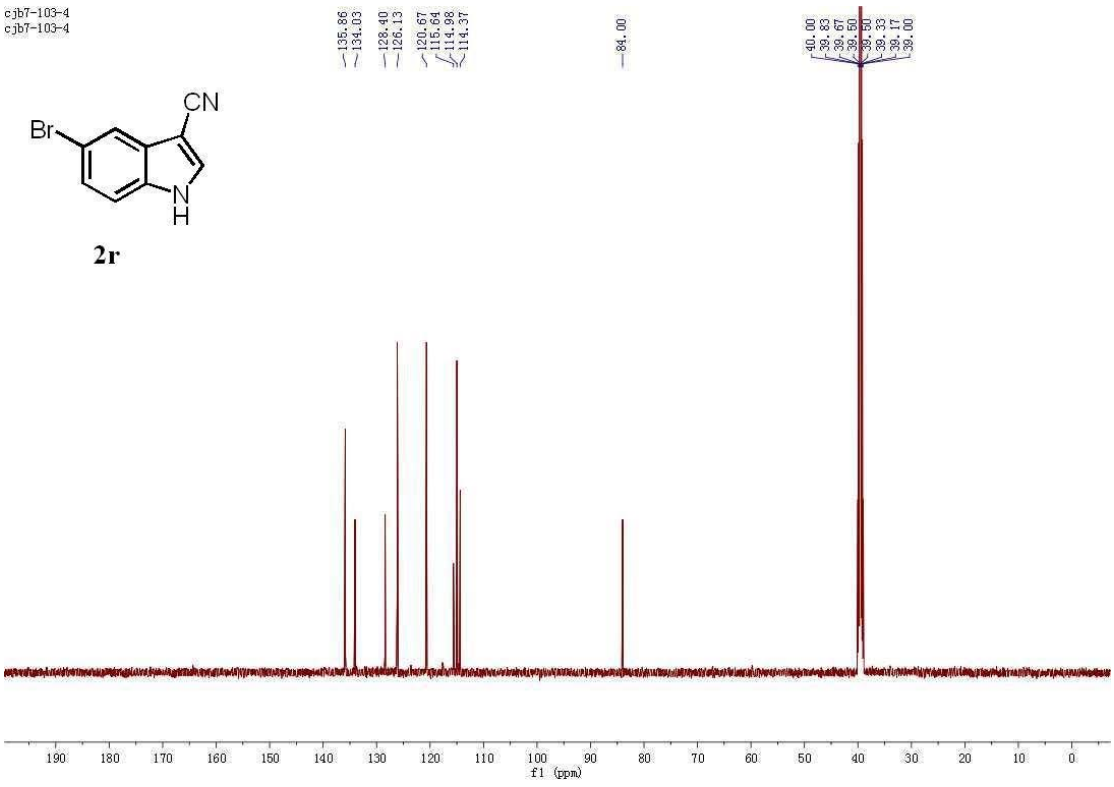
S29


cjb7-93-3
cjb7-93-3
7.868
7.541
7.430
7.416
7.260
7.249
7.242
3.835
CN
Br
N
2q
1.00
1.03
1.05
0.93
3.09
f1 (ppm)

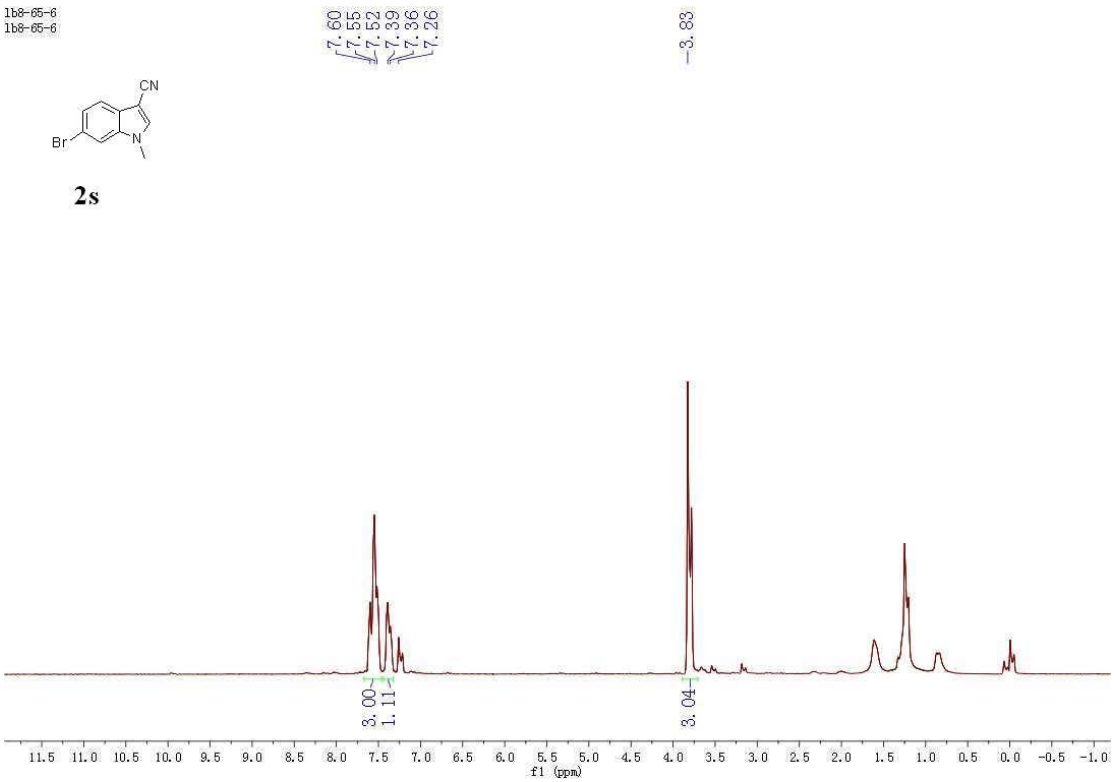

cjb7-93-3
cjb7-93-3
136.32
134.71
129.24
127.00
122.44
115.79
115.11
111.79
86.24
77.25
77.00
76.75
33.83
CN
Br
N
2q
f1 (ppm)

S30

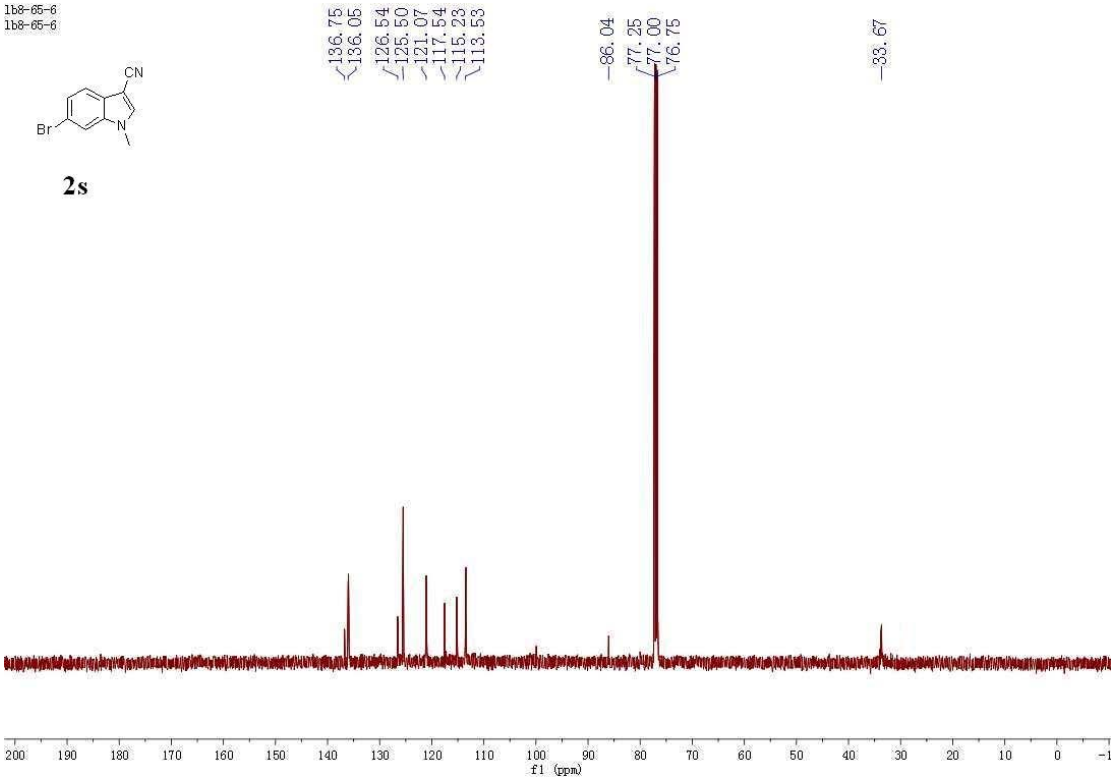

cjb7-103-4
cjb7-103-4
12.385
8.299
7.787
7.531
7.514
7.414
7.397
2.503
2.500
2.496
Br
CN
N
H
2r
1.06
1.08
1.00
1.16
1.15
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


cjb7-103-4
cjb7-103-4
135.86
134.03
128.40
126.13
120.67
115.64
114.98
114.37
84.00
40.00
39.83
39.67
39.50
39.50
39.33
39.17
39.00
Br
CN
N
H
2r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

S31

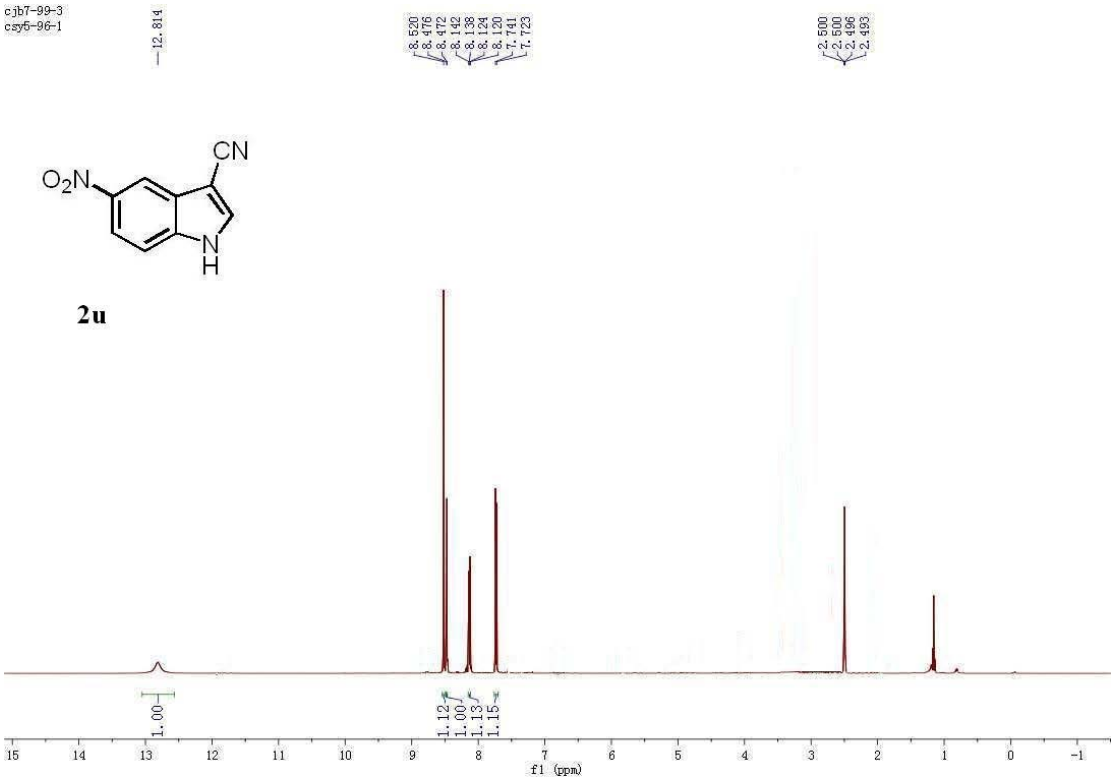

1b8-65-6
1b8-65-6
7.60
7.55
7.52
7.39
7.36
7.26
3.83
CN
Br
N
3.00
1.11
3.04
f1 (ppm)

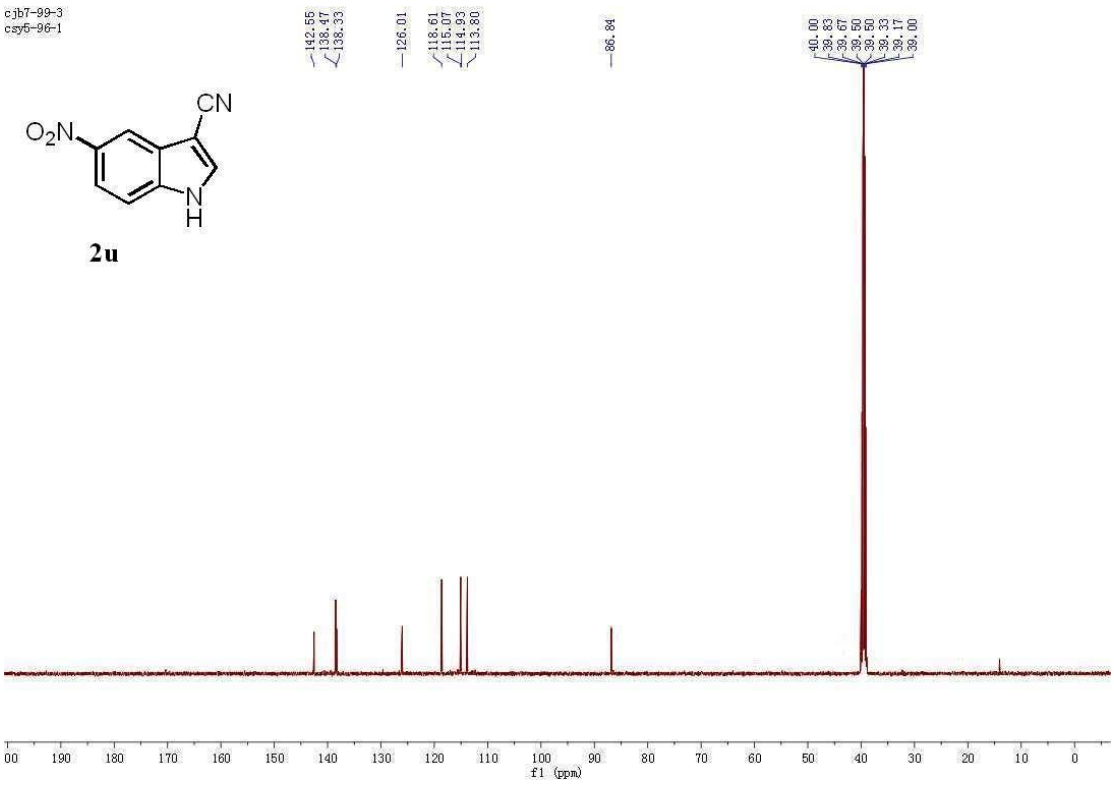
2s


1b8-65-6
1b8-65-6
136.75
136.05
126.54
125.50
121.07
117.54
115.23
113.53
86.04
77.25
77.00
76.75
33.67
CN
Br
N
f1 (ppm)

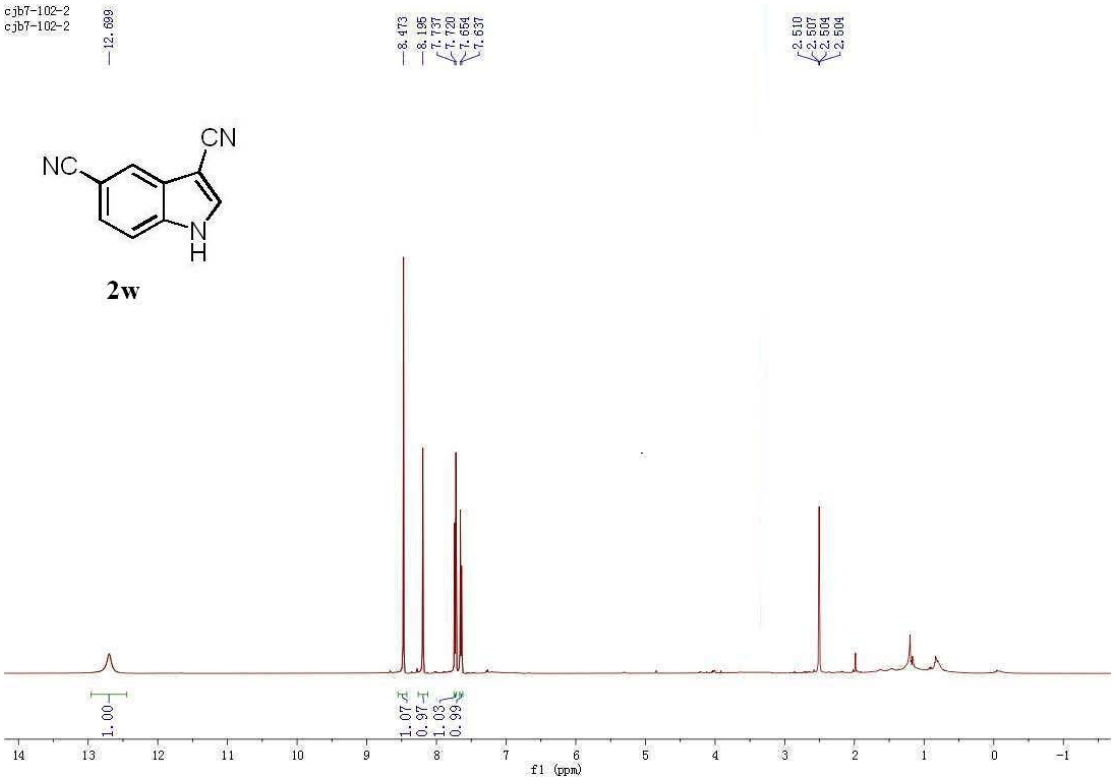
2s

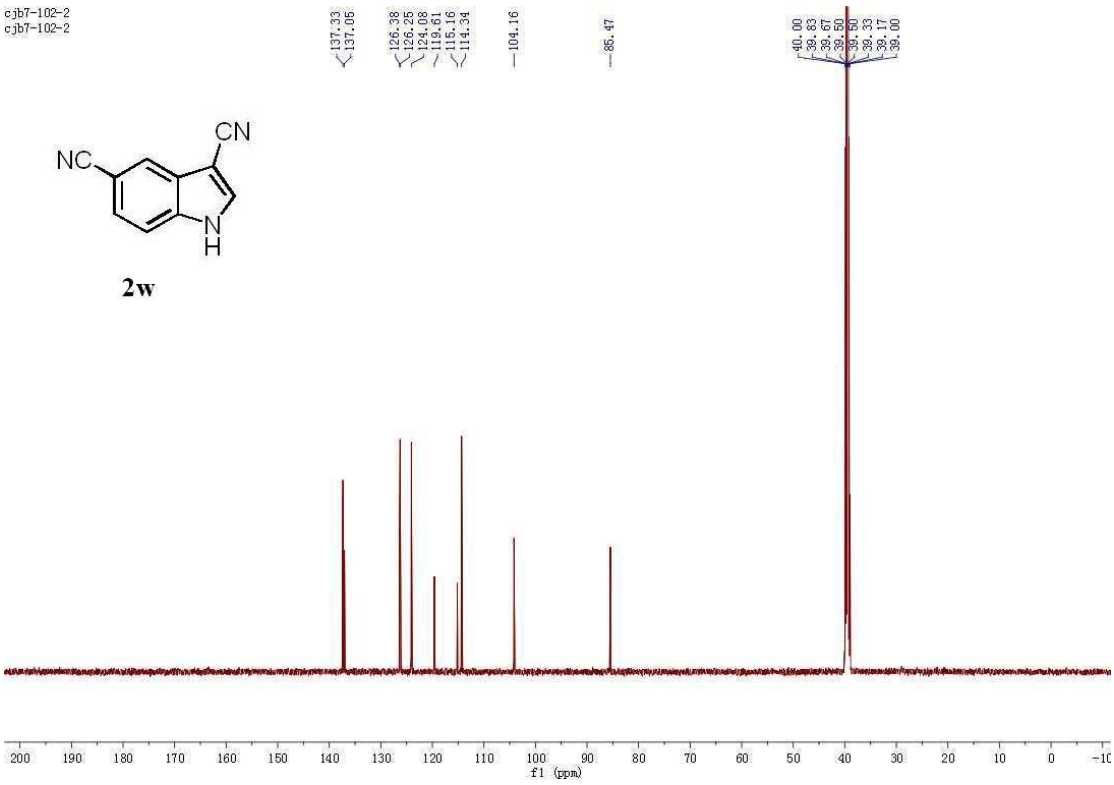
S32


cjb7-99-3
csy5-96-1
12.814
8.520
8.476
8.472
8.142
8.138
8.124
8.120
7.741
7.723
2.500
2.500
2.496
2.493
CN
O2N
N
H
2u
1.00
1.12
1.00
1.13
1.15
f1 (ppm)

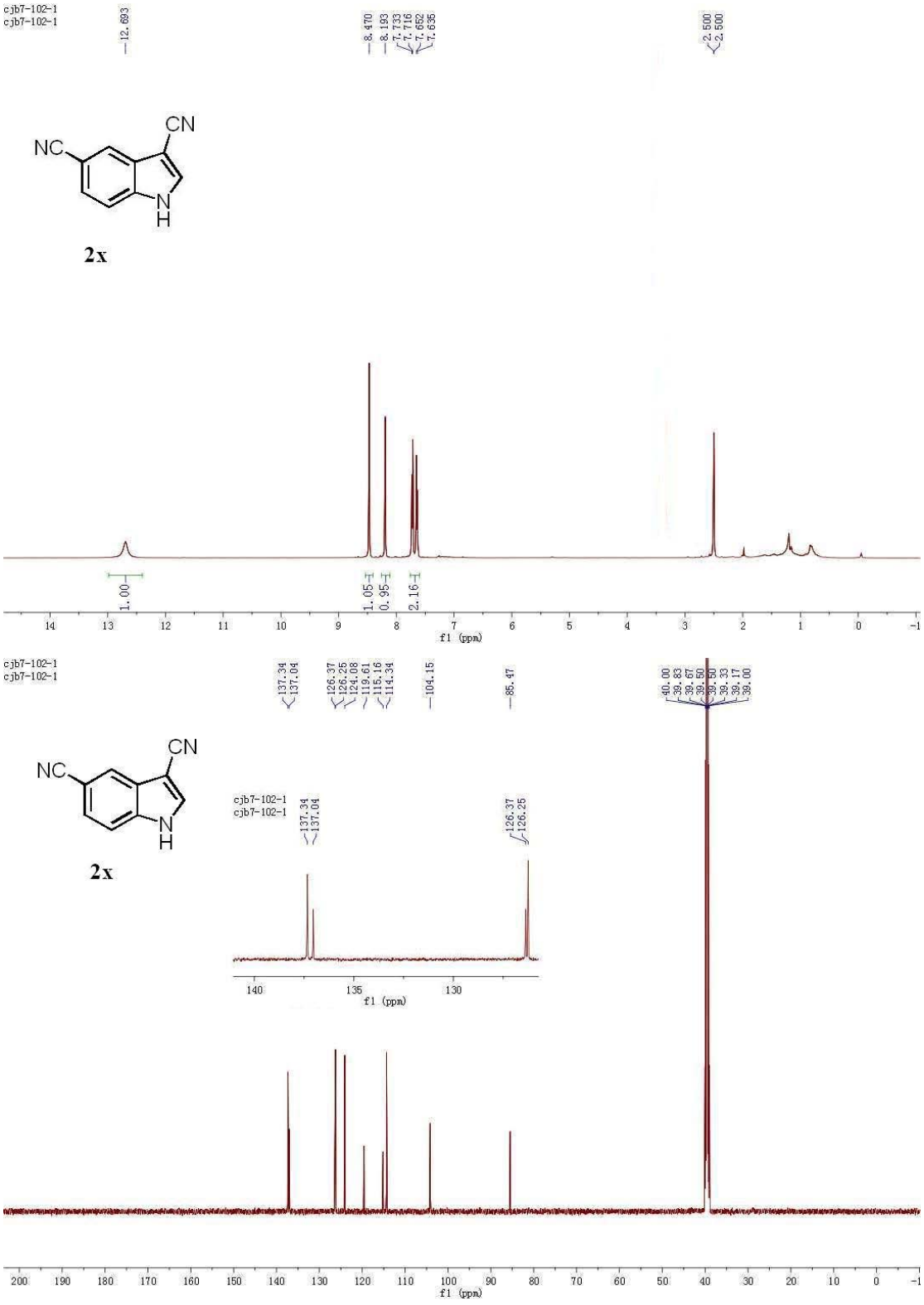

cjb7-99-3
csy5-96-1
142.55
138.47
138.33
126.01
118.61
115.07
114.93
113.80
86.84
40.00
39.83
39.67
39.50
39.33
39.17
39.00
CN
O2N
N
H
2u
f1 (ppm)

S33

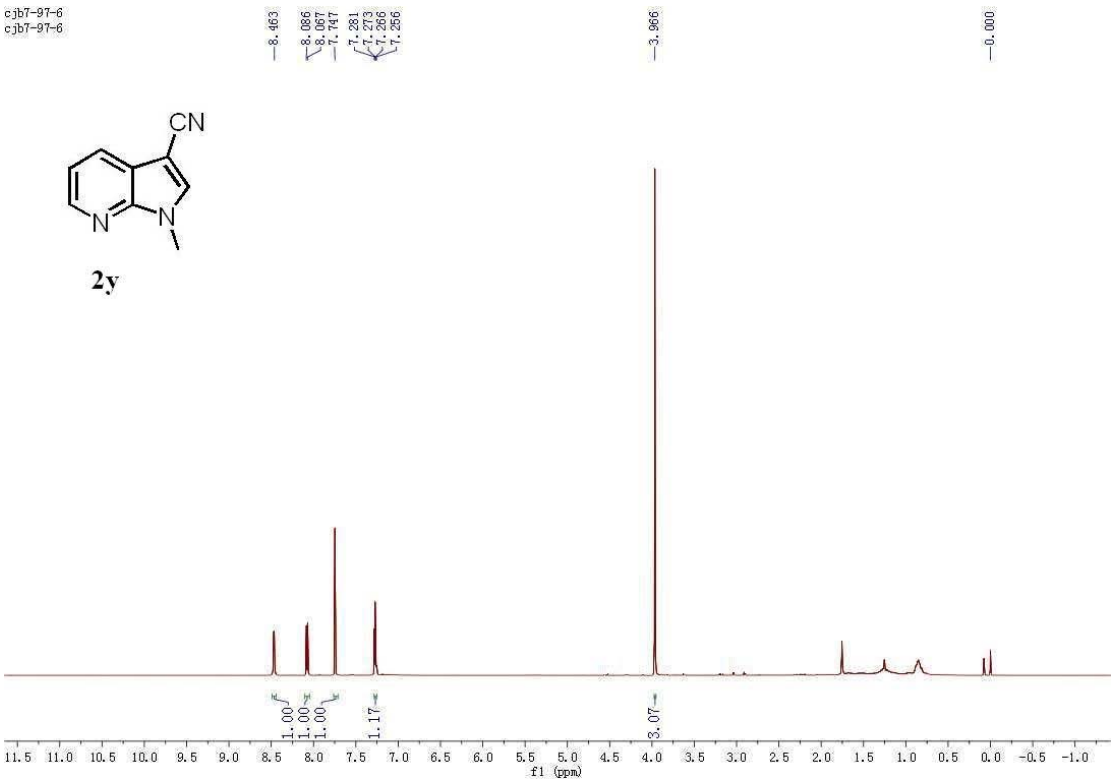

cjb7-102-2
cjb7-102-2
12.699
8.473
8.196
7.737
7.720
7.654
7.637
2.510
2.507
2.504
2.504
CN
NC
N
H
2w
1.00
1.07
0.97
1.03
0.99
f1 (ppm)

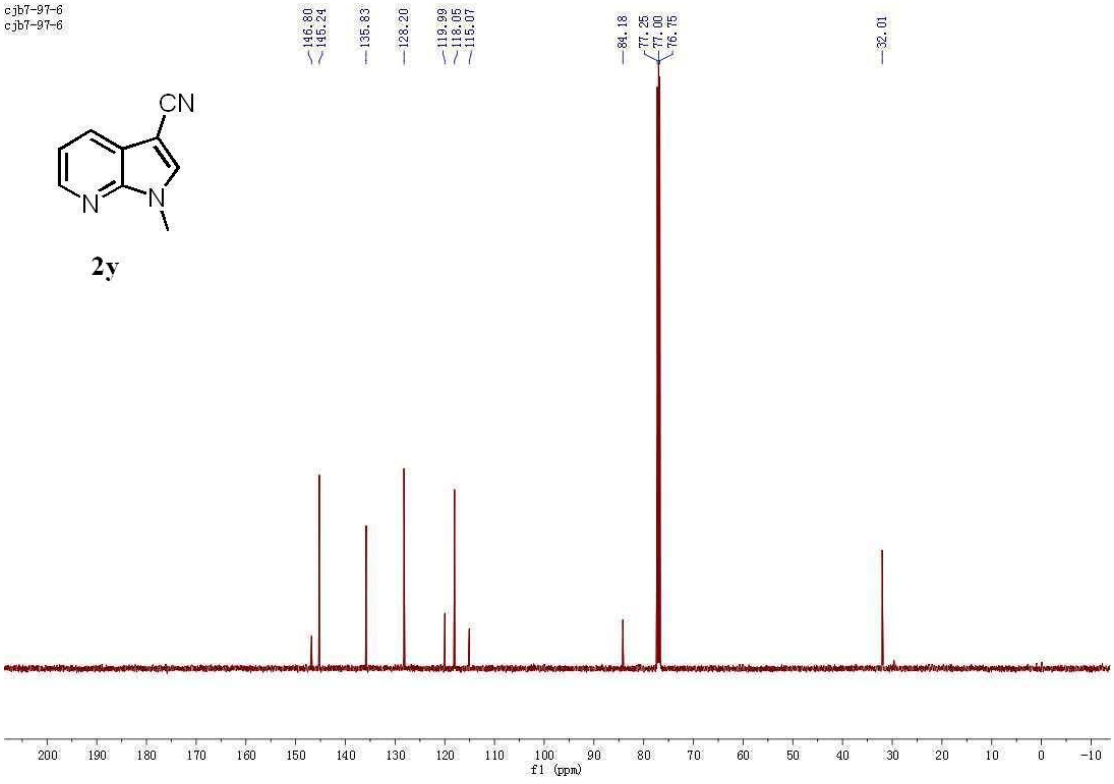

cjb7-102-2
cjb7-102-2
137.33
137.05
126.38
126.25
124.88
119.61
115.16
114.94
104.16
85.47
40.00
39.83
39.67
39.50
39.50
39.33
39.17
39.00
CN
NC
N
H
2w
f1 (ppm)

S34

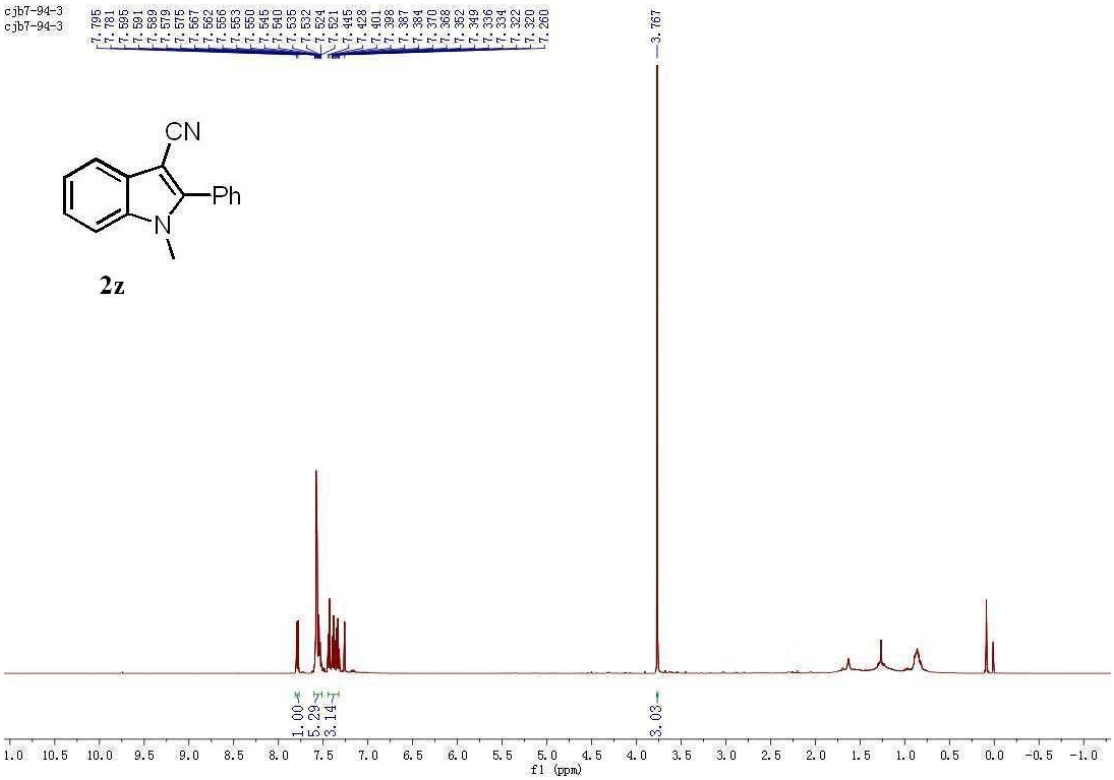

cjb7-102-1
cjb7-102-1
12.693
8.470
8.193
7.733
7.716
7.692
7.635
2.500
2.500
CN
NC
N
H
2x
1.00
1.05
0.95
2.16
f1 (ppm)
cjb7-102-1
cjb7-102-1
137.34
137.04
126.37
126.25
124.08
119.61
115.16
114.34
104.15
85.47
40.00
39.83
39.67
39.50
39.33
39.17
39.00
CN
NC
N
H
2x
cjb7-102-1
cjb7-102-1
137.34
137.04
126.37
126.25
f1 (ppm)
f1 (ppm)

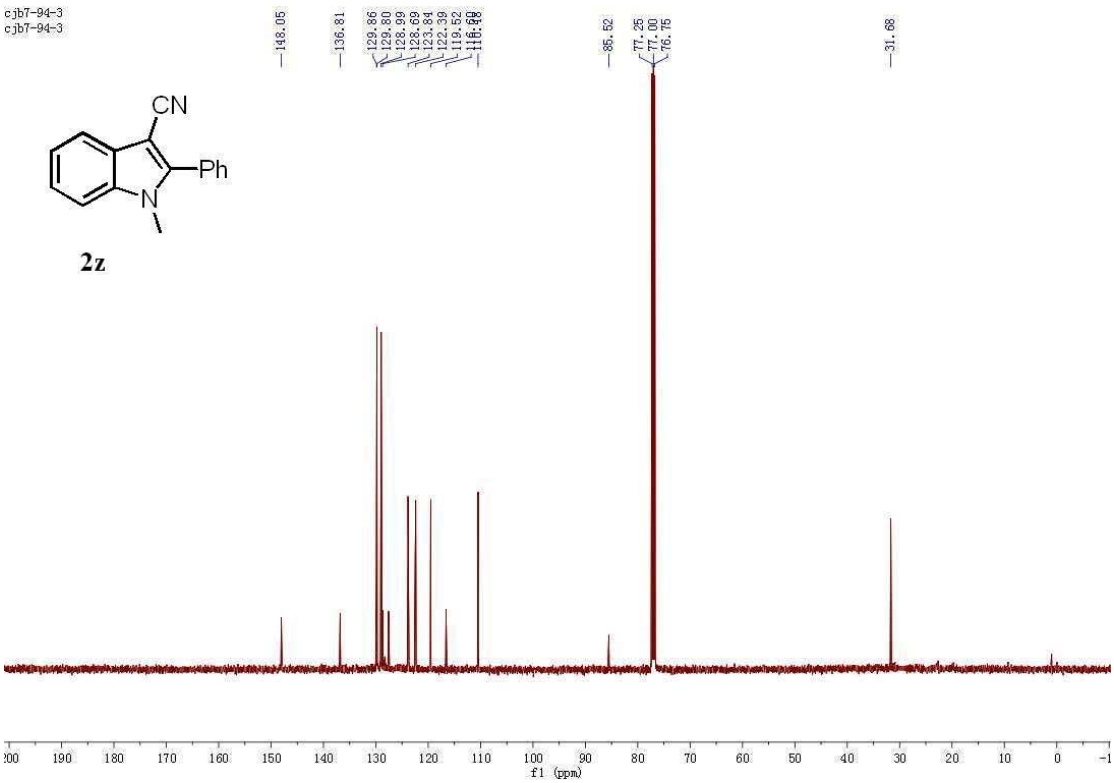
S35


cjb7-97-6
cjb7-97-6
8.463
8.086
8.067
7.747
7.281
7.273
7.266
7.256
3.966
0.000
CN
N
N
2y
1.00
1.00
1.00
1.17
3.07
f1 (ppm)

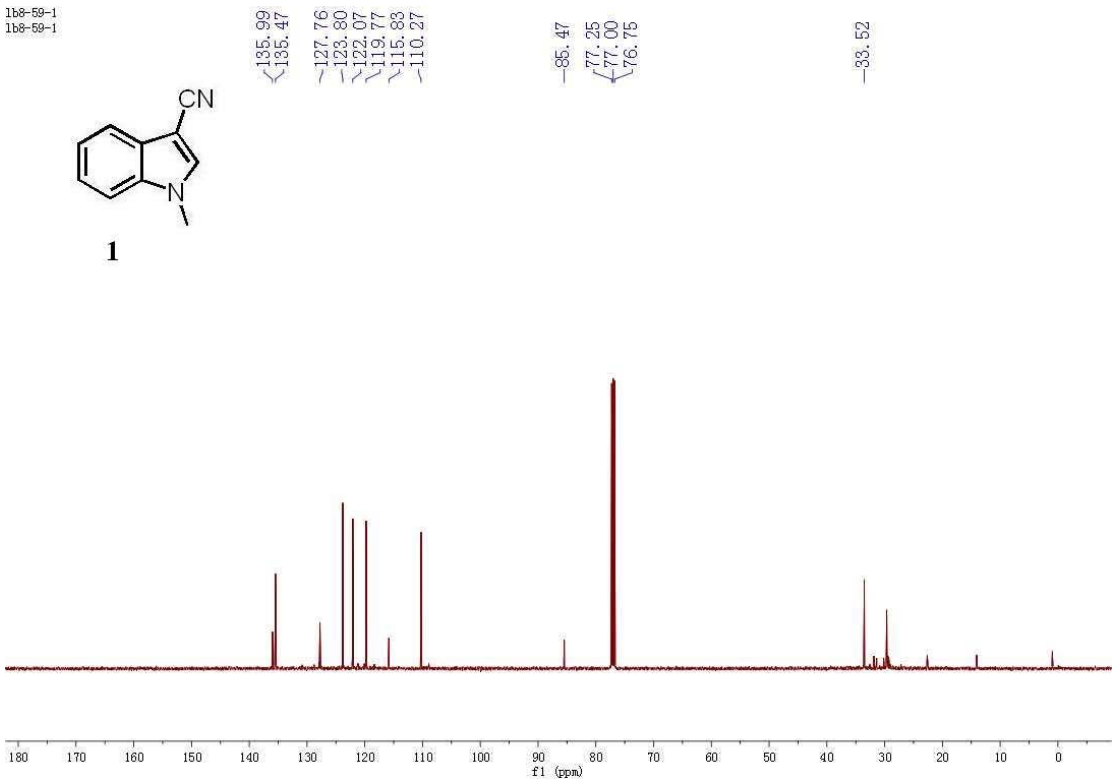

cjb7-97-6
cjb7-97-6
146.80
145.24
135.83
128.20
119.99
118.05
115.07
84.18
77.25
77.00
76.75
32.01
CN
N
N
2y
f1 (ppm)

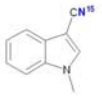
S36


cjb7-94-3
cjb7-94-3
CN
Ph
N
2z
f1 (ppm)


cjb7-94-3
cjb7-94-3
CN
Ph
N
2z
f1 (ppm)

S37

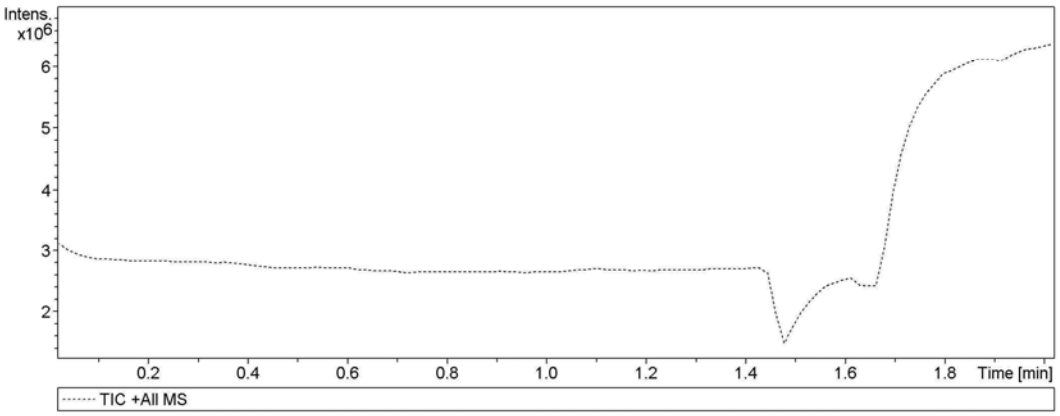

1b8-59-1
1b8-59-1
135.99
135.47
127.76
123.80
122.07
119.77
115.83
110.27
85.47
77.25
77.00
76.75
33.52
CN
N
1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

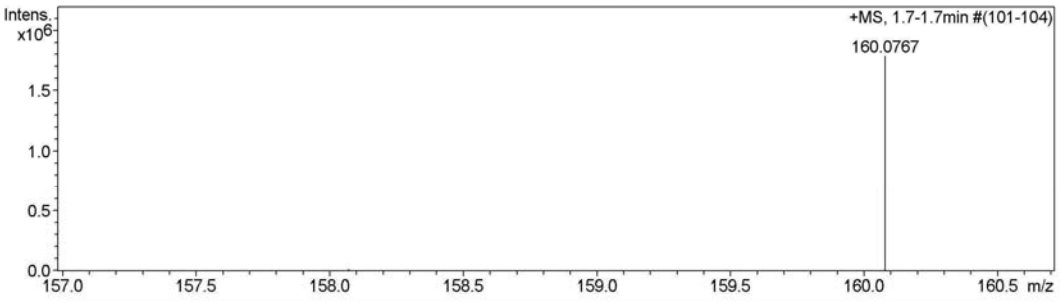


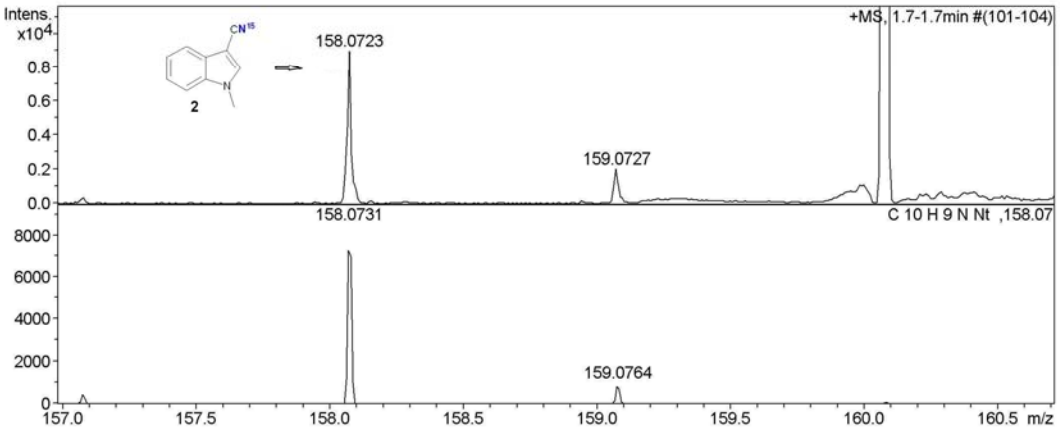
Generic Display Report

Analysis Info

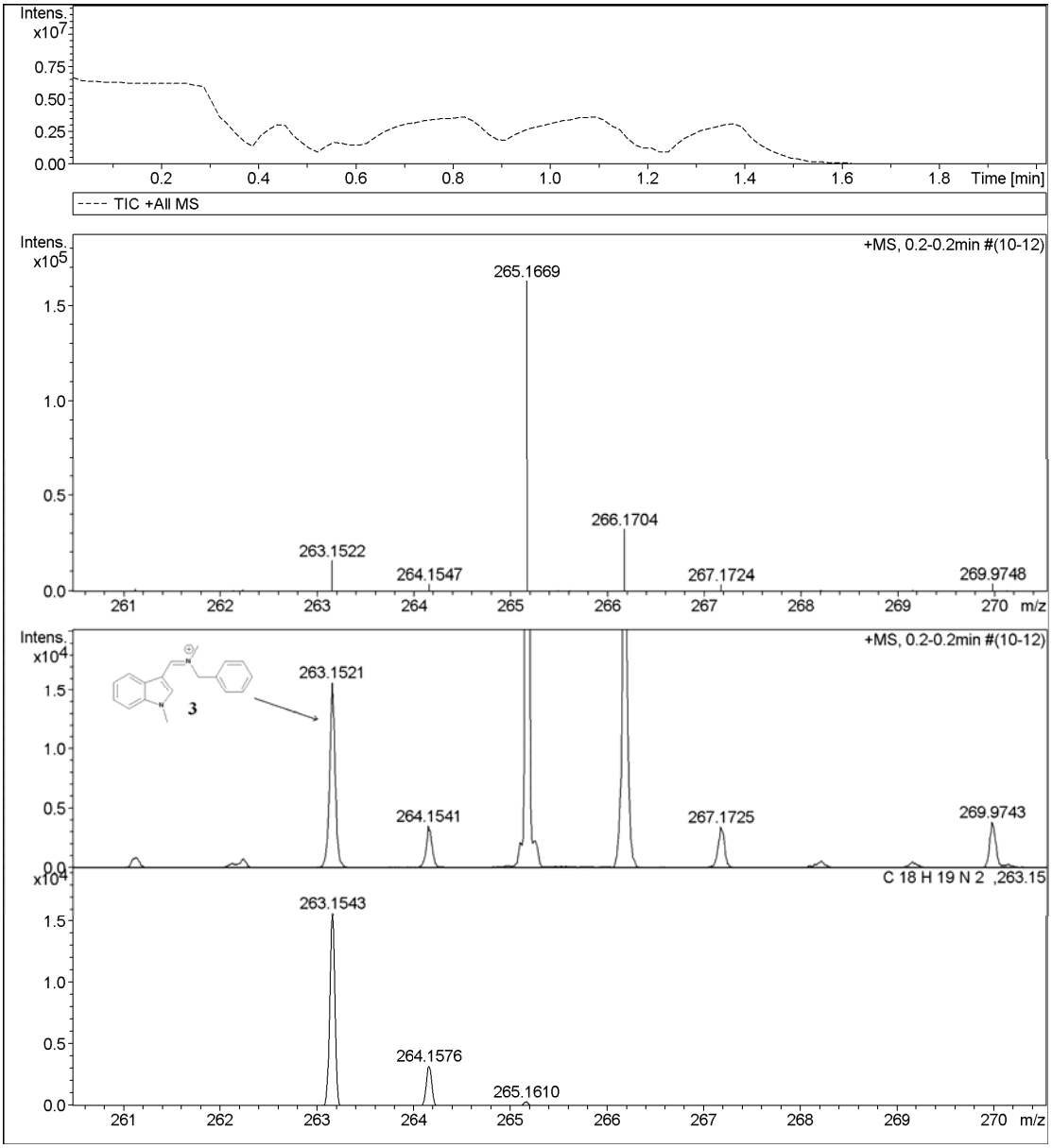
Analysis Name	D:\Data\hbl\hbl120302.d		
Method	tune_150-800.m	Operator	BDAL@DE
Sample Name	hbl120302	Instrument	micrOTOF-Q II
Comment			







S39


Intens.
x10^7
0.75
0.50
0.25
0.00
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
Time [min]
TIC +All MS
Intens.
x10^5
+MS, 0.2-0.2min #(10-12)
265.1669
266.1704
263.1522
264.1547
267.1724
269.9748
261
262
263
264
265
266
267
268
269
270
m/z
Intens.
x10^4
+MS, 0.2-0.2min #(10-12)
263.1521
264.1541
267.1725
269.9743
3
x10^4
C 18 H 19 N 2 ,263.15
263.1543
264.1576
265.1610