Electrochemical strategies for *N*-cyanation of secondary amines and α *C*-cyanation of tertiary amines under transition metal-free conditions

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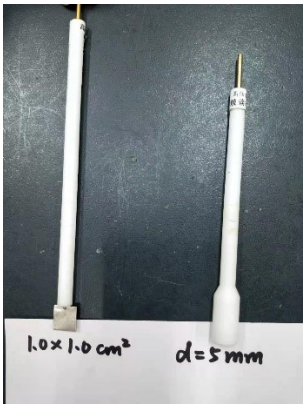
General considerations

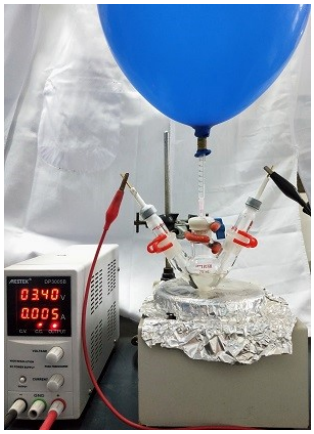
The substrates of **7a**-**8a** and **11a** were brought from commercial suppliers as hydrochloride and were simply disposed with base before adding into reactions,[1] the compounds of **1n**-**19n**,[2] **22n**[2] and **17**-**18n**[3] were prepared following literature procedures,[2,3] all other reagents were commercially available and were used as received unless otherwise noted. The instrument for electrolysis is Adjustable DC Power Supply (DP3005B) (made in China). Column chromatography was performed on silica gel 300-400 mesh. The yields reported are the isolated yields and the average of two runs. ^{1}H and ^{13}C NMR spectra of all compounds were recorded at 400 and 100 MHz with $CDCl_3$ as solvent respectively. All coupling constants (J values) were reported in Hertz (Hz). HRMS (**10**-**11ap**, **13np**, **18np** and **22np**) were performed by Analysis and Testing Center of Nanchang University, HRMS (**2ap**, **4ap**, **5**-**6ap**, **8**-**9ap**, **29ap**, **6np**, **12np** and **17np**) were performed by Analysis and Testing Center of Nanjing University. Cyclic voltammograms were obtained on a IVIUMSTAT potentiostat. The amount of electrocatalytic hydrogen evolution was measured on a gas chromatography (Kexiao, GC-1690 China) (TCD detector, 13X molecular sieve column, N_2 gas carrier).

2. Experimental procedures

General procedure for metal-free electrocatalytic *N*-cyanation of secondary amines (procedure A): secondary amine (0.2 mmol), TMSCN (54 μL, 0.4 mmol, 2 equiv), TBAB (161 mg, 0.5 mmol, 2.5 equiv), KF (46.5 mg, 0.8 mmol, 4 equiv) and CH_3CN (10 mL) were combined and added into oven-dried three-necked flask (25 mL) with a stir bar. The flask was equipped with glassy carbon (d = 5 mm) as the anode and platinum electrodes (1.0 × 1.0 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed under room temperature at a constant current of 5 mA under aerobic conditions for 3 h. When the reaction was finished, the reaction mixtures were diluted with EtOAc and filtered through a short plug of silica gel that was then washed with EtOAc. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.



General procedure for metal-free electrocatalytic α-C-cyanation of aromatic tertiary amines (procedure B): tertiary amine (0.2 mmol), TMSCN (54 μL, 0.4 mmol, 2 equiv), TBAB (161 mg, 0.5 mmol, 2.5 equiv), KF (46.5 mg, 0.8 mmol, 4 equiv) and CH_3CN (10 mL) were combined and added into oven-dried three-necked flask (25 mL) with a stir bar. The flask was equipped with graphite felts (15 × 15 × 0.4 mm^3) as the anode and platinum electrodes (1.0 × 1.0 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed under room temperature at a constant current of 5 mA under N_2 atmosphere for 3 h. When the reaction was finished, the reaction mixtures were diluted with EtOAc and filtered through a short plug of silica gel that was then washed with EtOAc. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to provide corresponding product.



3,4-Dihydro-2(1*H*)-isoquinolinecarbonitrile (1ap)

Procedure A was followed using 1,2,3,4-tetrahydroisoquinoline (26.6 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 27.2 mg (86%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 - 7.19 (m, 2 H), 7.15 - 7.13 (m, 1 H), 7.06 - 7.02 (m, 1 H), 4.40 (s, 2 H), 3.48 (t, J = 5.9 Hz, 2 H), 2.95 (t, J = 5.9 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6, 130.8, 129.2, 127.2, 126.7, 126.0, 118.0, 50.0, 46.8, 27.7.

6-Methoxy-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (2ap)

Procedure A was followed using 6-methoxy-1,2,3,4-tetrahydroisoquinoline (32.6 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 30.3 mg (80%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, J = 8.4 Hz, 1 H), 6.76 (dd, J = 2.8, 8.6 Hz, 1 H), 6.65 (d, J = 2.8 Hz, 1 H), 4.34 (s, 2 H), 3.77 (s, 3 H), 3.45 (t, J = 5.9 Hz, 2 H), 2.91 (t, J = 5.9 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 133.9, 127.1, 122.9, 118.2, 113.9, 113.1, 55.4, 49.7, 46.7, 28.0. HRMS (ESI-Orbitrap MS) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{13}ON_2$: 189.10224; found: 189.10182.

6,7-Dimethoxy-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (3ap)

Procedure A was followed using 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (38.6 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (80:20, petroleum ether: EtOAc) to afford 32.9 mg (75%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.59 (s, 1 H), 6.49 (s, 1 H), 4.31 (s, 2 H), 3.82 (d, J = 5.3 Hz, 6 H), 3.43 (t, J = 5.9 Hz, 2 H), 2.85 (t, J = 5.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 148.0, 124.6, 122.6, 118.1, 111.8, 108.6, 56.0, 56.0, 49.8, 46.9, 27.2.

6-Bromo-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (4ap)

Procedure A was followed using 6-bromo-1,2,3,4-tetrahydroisoquinoline (42.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 38.9 mg (82%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 - 7.29 (m, 2 H), 6.91 (d, J = 8.2 Hz, 1 H), 4.34 (s, 2 H), 3.45 (td, J = 1.8, 6.0 Hz, 2 H), 2.92 (t, J = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.9, 132.1, 129.9, 129.8, 127.7, 120.9, 117.7, 49.8, 46.5, 27.5. HRMS (ESI-Orbitrap MS) *m*/*z*: $[M+H]^+$ Calcd. for $C_{10}H_{10}BrN_2$: 237.00219; found: 237.00165.

7-Bromo-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (5ap)

Procedure A was followed using 7-bromo-1,2,3,4-tetrahydroisoquinoline (42.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 39.8 mg (84%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J = 1.9, 8.2 Hz, 1 H), 7.18 (s, 1 H), 7.01 (d, J = 8.2 Hz, 1 H), 4.35 (s, 2 H), 3.45 (t, J = 6.0 Hz, 2 H), 2.89 (t, J = 5.9 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.9, 131.6, 130.9, 130.4, 128.9, 120.3, 117.6, 49.6, 46.6, 27.2. HRMS (ESI-Orbitrap MS) *m*/*z*: $[M+H]^+$ Calcd. for $C_{10}H_{10}BrN_2$: 237.00219; found: 237.00186.

6-Chloro-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (6ap)

Procedure A was followed using 6-chloro-1,2,3,4-tetrahydroisoquinoline (33.5 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 29.6 mg (77%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 - 7.11 (m, 2 H), 6.96 (d, J = 8.2 Hz, 1 H), 4.35 (s, 2 H), 3.44 (t, J = 5.9 Hz, 2 H), 2.91 (t, J = 5.9 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 132.8, 129.2, 129.0, 127.4, 126.9, 117.7, 49.6, 46.4, 27.5. HRMS (ESI-Orbitrap MS) *m*/*z*: $[M+H]^+$ Calcd. for $C_{10}H_{10}ClN_2$: 193.05270; found: 193.05264.

6-Fluoro-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (7ap)

Procedure A was followed using 6-fluoro-1,2,3,4-tetrahydroisoquinoline (30.2 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified

by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 27.8 mg (79%) of the product as a yellow solid. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (dd, J = 5.5, 8.5 Hz, 1 H), 6.89 (td, J = 2.7, 8.5 Hz, 1 H), 6.83 (dd, J = 2.6, 9.2 Hz, 1 H), 4.35 (s, 2 H), 3.44 (t, J = 6.0 Hz, 2 H), 2.92 (t, J = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6 (d, J = 245 Hz), 134.8 (d, J = 7 Hz), 127.6 (d, J = 8 Hz) , 126.5 (d, J = 3 Hz) , 117.8, 115.6 (d, J = 21 Hz), 114.0 (d, J = 22 Hz), 49.6, 46.4, 27.7 (d, J = 1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -115.0.

5-(Trifluoromethyl)-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (8ap)

Procedure A was followed using 5-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinoline (40.2 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 36.4 mg (80%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8 Hz, 1 H), 7.30 (t, J = 8 Hz, 1 H), 7.22 (d, J = 8 Hz, 1 H), 2.05 (s, 2 H), 3.48 (t, J = 6 Hz, 2 H), 3.09 (t, J = 6 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6, 131.5 (q, J = 1.7 Hz), 129.9 (q, J = 1.5 Hz), 129.0 (q, J = 30 Hz), 124.1 (q, J = 272 Hz), 126.5, 125.0 (q, J = 5.7 Hz), 117.4, 50.1, 46.1, 24.4 (q, J = 2 Hz). HRMS (ESI-Orbitrap MS) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{10}F_3N_2$: 227.07906; found: 227.07866.

3,4-Dihydro-1-methyl-2(1*H*)-isoquinolinecarbonitrile (9ap)

Procedure A was followed using 1-methyl-1,2,3,4-tetrahydroisoquinoline (29.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 28.6 mg (83%) of the product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 - 7.19 (m, 2 H), 7.13 - 7.09 (m, 2 H), 4.54 (q, J = 6.8 Hz, 1 H), 3.59 - 3.53 (m, 1 H), 3.48 - 3.42 (m, 1 H), 2.95 (t, J = 5.6 Hz, 2 H), 1.63 (d, J = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 132.4, 129.2, 127.1, 126.8, 126.2, 117.5, 54.4, 44.7, 28.2, 21.4. HRMS (ESI-Orbitrap MS) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{13}N_2$: 173.10732; found: 173.10707.

1-Phenyl-3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (10ap)

Procedure A was followed using 1-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 17.5 mg (37%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 - 7.34 (m, 3 H), 7.24 - 7.20 (m, 4 H), 7.18 - 7.11 (m, 1 H), 6.87 (d, J = 8 Hz, 1 H), 5.49 (s, 1 H), 3.59 - 3.43 (m, 2 H), 3.07 - 3.01 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 133.8, 133.1, 129.1, 128.9, 128.8, 128.4, 127.6, 126.8, 117.5, 63.2, 44.8, 28.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{15}N_2$: 235.1230; found: 235.1238.

7,8-Dihydro-1,6-naphthyridine-6(5*H*)-carbonitrile (11ap)

Procedure A was followed using 5,6,7,8-tetrahydro-1,6-naphthyridine (26.8 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (50:50, petroleum ether: EtOAc) to afford 14.9 mg (47%) of the product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d,

J = 4.8 Hz, 1 H), 7.39 (d, *J* = 7.7 Hz, 1 H), 7.18 (dd, *J* = 4.8, 7.8 Hz, 1 H), 4.44 (s, 2 H), 3.60 (t, *J* = 6.0 Hz, 2 H), 3.15 (t, *J* = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 148.6, 134.2, 126.7, 122.1, 117.6, 49.6, 47.1, 30.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_{10}N_3$: 160.0869; found: 160.0873.

Pyrrolidine-1-carbonitrile (12ap)

Procedure A was followed using pyrrolidine (14.2 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (60:40, petroleum ether: EtOAc) to afford 11.7 mg (61%) of the product as a light brown oil. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.36 - 3.33 (m, 4 H), 1.88 - 1.85(m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.9, 50.5, 25.7.

2-Phenylpyrrolidine-1-carbonitrile (13ap)

Procedure A was followed using 2-phenylpyrrolidine (29.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (70:30, petroleum ether: EtOAc) to afford 27.9 mg (82%) of the product as a orange oil. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 - 7.33 (m, 2 H), 7.29 - 7.26 (m, 3 H), 4.62 (t, *J* = 7.1 Hz, 1 H), 3.69 - 3.63 (m, 1 H), 3.56 - 3.50 (m, 1 H), 2.32 - 2.24 (m, 1 H), 2.02 - 1.90 (m, 2 H), 1.86 - 1.77 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 128.7, 128.1, 126.3, 116.9, 65.8, 51.4, 35.5, 24.7.

2-(Pyridin-3-yl)pyrrolidine-1-carbonitrile (14ap)

Procedure A was followed using 3-(pyrrolidin-2-yl)pyridine (29.6 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (EtOAc) to afford 31.4 mg (91%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 2 H), 7.66 (d, *J* = 10.4 Hz, 1 H), 7.35 - 7.31 (m, 1 H), 4.69 (t, *J* = 9.6 Hz, 1 H), 3.77 - 3.69 (m, 1 H), 3.65 - 3.57 (m, 1 H), 2.39 (dq, *J* = 8.4, 16.8 Hz, 1 H), 2.10 - 2.01 (m, 2 H),1.93 - 1.81 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 148.1, 135.2, 133.8, 123.6, 116.3, 63.5, 51.4, 35.3, 24.7.

Piperidine-1-carbonitrile (15ap)

Procedure A was followed using piperidine (17.0 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (70:30, petroleum ether: EtOAc) to afford 14.1 mg (64%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 - 3.12 (m, 4 H), 1.63 - 1.58 (m, 4 H), 1.59 - 1.51 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.6, 50.2, 24.6, 23.0.

4-Methylpiperidine-1-carbonitrile (16ap)

Procedure A was followed using 4-methylpiperidine (19.8 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column

chromatography on silica gel (60:40, petroleum ether: EtOAc) to afford 17.0 mg (69%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.32 (d, J = 12.3 Hz, 2 H), 2.93 (td, J = 2.8, 12.5 Hz, 2 H), 1.59 (d, J = 12.0 Hz, 2 H), 1.49 - 1.36 (m, 1 H), 1.24 (qd, J = 4.4, 12.4 Hz, 2 H), 0.90 (d, J = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.5, 49.6, 32.7, 29.6, 21.7.

1,4-Dioxa-8-azaspiro[4.5]decane-8-carbonitrile (17ap)

Procedure A was followed using 1,4-dioxa-8-azaspiro[4.5]decane (28.6 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (75:25, petroleum ether: EtOAc) to afford 24.7 mg (74%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.92 (s, 4 H), 3.30 - 3.27 (m, 4 H), 1.76 - 1.73 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 118.0, 105.4, 64.6, 48.0, 34.1.

Ethyl 1-cyanopiperidine-4-carboxylate (18ap)

Procedure A was followed using ethyl piperidine-4-carboxylate (31.5 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (75:25, petroleum ether: EtOAc) to afford 36.0 mg (99%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.12 (q, J = 7.1 Hz, 2 H), 3.43 - 3.37 (m, 2 H), 3.07 - 3.01 (m, 2 H), 2.43 - 2.36 (m, 2 H), 1.97 - 1.90 (m, 2 H), 1.84 - 1.75 (m, 2 H), 1.23 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 118.0, 60.9, 48.7, 39.5, 26.8, 14.2.

4-Phenylpiperidine-1-carbonitrile (19ap)

Procedure A was followed using 4-phenylpiperidine (32.2 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 34.2 mg (92%) of the product as a off-white solid. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 - 7.29 (m, 2 H), 7.24 - 7.17 (m, 3 H), 3.53 - 3.48 (m, 2 H), 3.16 - 3.09 (m, 2 H), 2.62 - 2.55 (m, 1 H), 1.85 - 1.80 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 128.7, 126.8, 126.6, 50.1, 41.3, 32.0.

4-Benzylpiperidine-1-carbonitrile (20ap)

Procedure A was followed using 4-benzylpiperidine (35.0 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 31.6 mg (79%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, J = 9.6 Hz, 2 H), 7.19 (t, J = 9.6 Hz, 1 H), 7.11 (d, J = 10.0 Hz, 2 H), 3.37 (d, J = 16.8 Hz, 2 H), 2.97 - 2.88 (m, 2 H), 2.54 (d, J = 8.8 Hz, 2 H), 1.67 - 1.54 (m, 3 H), 1.41 - 1.25 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 129.0, 128.4, 126.2, 118.5, 49.7, 42.8, 36.8, 30.7.

Morpholine-4-carbonitrile (21ap)

Procedure A was followed using morpholine (17.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (60:40, petroleum ether: EtOAc) to afford 13.5 mg (60%) of the product as a light brown oil. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.71 - 3.68 (m, 4 H), 3.21 - 3.19 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.2, 65.6, 48.8.

Thiomorpholine-4-carbonitrile (22ap)

Procedure A was followed using thiomorpholine (20.6 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (75:25, petroleum ether: EtOAc) to afford 19.8 mg (77%) of the product as a off-white solid. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 - 3.43 (m, 4 H), 2.69 - 2.67 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.4, 50.9, 26.2.

1-(Pyridin-4-yl)piperazine-1-carbonitrile (23ap)

Procedure A was followed using 1-(pyridin-4-yl)piperazine (32.6 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (20:10:1, petroleum ether: EtOAc: triethylamine) to afford 30.5 mg (81%) of the product as a yellowish solid. Exhibited spectral data in accordance with previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 5.7 Hz, 2 H), 6.62 (d, J = 5.7 Hz, 2 H), 3.40 - 3.30 (m, 8 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 150.5, 117.0, 109.0, 48.4, 45.4.

***N*,*N*-diallylcyanamide (24ap)**

Procedure A was followed using diallylamine (19.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 17.1 mg (81%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 - 5.78 (m, 2 H), 5.34 - 5.29 (m, 4 H), 3.63 - 3.60 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.0, 120.7, 117.7, 53.5.

Benzylmethylcyanamide (25ap)

Procedure A was followed using *N*-methylbenzylamine (24.2 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (75:25, petroleum ether: EtOAc) to afford 21.2 mg (72%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 - 7.31 (m, 5 H), 4.15 (s, 2 H), 2.77 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 129.0, 128.7, 128.5, 118.9, 57.2, 37.9.

***N*-methyl-*N*-phenethylcyanamide (26ap)**

Procedure A was followed using *N*-methyl-phenethylamine (27.0 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (75:25, petroleum ether: EtOAc) to afford 27.9 mg (87%) of the product as a colorless liquid. Exhibited spectral data in accordance with previous report.[4] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 - 7.28 (m, 2 H), 7.25 - 7.20 (m, 3 H), 3.21 - 3.17(m, 2 H), 2.94 - 2.90 (m, 2 H), 2.78 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 128.6, 126.8, 118.2, 54.2, 39.1, 33.8.

***N*,*N*-Dibutylcyanamide (27ap)**

Procedure A was followed using dibutylamine (25.8 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (80:20, petroleum ether: EtOAc) to afford 19.7 mg (64%) of the product as a red oil. Exhibited spectral data in accordance with previous report.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.93 (t, J = 7.2 Hz, 4 H), 1.61 - 1.54 (m, 4 H), 1.33 (dq, J = 7.2, 15.2 Hz, 4 H), 0.89 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 117.9, 51.2, 29.7, 19.7, 13.6.

2-Cyano-1,1,3,3-tetramethylguanidine (28ap)

Procedure A was followed using 1,1,3,3-tetramethylguanidine (23.0 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (20:10:1, petroleum ether: EtOAc:triethylamine) to afford 20.2 mg (72%) of the product as a yellow liquid. Exhibited spectral data in accordance with previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 117.8, 40.1.

2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (1np)

Procedure B was followed using 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 38.4 mg (82%) of the product as a slightly yellow solid. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 - 7.24 (m, 2 H), 7.21 - 7.11 (m, 4 H), 6.98 (d, J = 8.1 Hz, 2 H), 6.91 (t, J = 7.4 Hz, 1 H), 5.41 (s, 1 H), 3.69 - 3.63 (m, 1 H), 3.37 (ddd, J = 4.1, 10.7, 12.4 Hz, 1 H), 3.08 - 3.00 (m, 1 H), 2.85 (dt, J = 3.6, 16.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 134.6, 129.6, 129.4, 128.8, 127.1, 126.9, 121.9, 117.8, 117.6, 53.2, 44.2, 28.5.

2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (2np)

Procedure B was followed using 2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (44.7 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 38.8 mg (78%) of the product as a slightly yellow solid. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 - 7.20 (m, 4 H), 7.15 (d, J = 8.2 Hz, 2 H), 7.01 - 6.97 (m, 2 H), 5.44 (s, 1 H), 3.71 - 3.66 (m, 1 H), 3.43 (ddd, J = 4.1, 11.0, 12.3 Hz, 1 H), 3.18 - 3.10 (m, 1 H), 2.93 (dt, J = 3.4, 16.4 Hz, 1 H),

2.30 (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, 44.5, 28.7, 20.7.

2-(*o*-Tolyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (3np)

Procedure B was followed using 2-(*o*-tolyl)-1,2,3,4-tetrahydroisoquinoline (44.7 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 31.2 mg (63%) of the product as a slightly yellow solid. Exhibited spectral data in accordance with previous report.[9] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 - 7.22 (m, 7 H), 7.14 - 7.10 (m, 1 H), 5.06 (s, 1 H), 3.61 (td, J = 3.9, 11.8 Hz, 1 H), 3.34 (ddt, J = 1.7, 6.2, 12.1 Hz, 1 H), 3.22 - 3.13 (m, 1 H), 2.91 (ddd, J = 1.8, 3.9, 16.4 Hz, 1 H), 2.29 (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, 117.7, 55.1, 46.1, 29.1, 17.7.

2-(2,4-Dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (4np)

Procedure B was followed using 2-(2,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinoline (47.5 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 44.6 mg (85%) of the product as a slightly yellow solid. Exhibited spectral data in accordance with previous report.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 - 7.33 (m, 1 H), 7.31 - 7.26 (m, 4 H), 7.15 (d, J = 12 Hz, 2 H), 5.10 (s, 1 H), 3.65 (td, J = 3.9, 11.8 Hz, 1 H), 3.36 (ddt, J = 1.7, 6.2, 12.1 Hz, 1 H), 3.27 - 3.19 (m, 1 H), 2.96 (ddd, J = 1.8, 3.9, 16.4 Hz, 1 H), 2.39 (s, 3 H), 2.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 134.9, 134.5, 133.2, 131.9, 130.1, 129.7, 128.6, 127.7, 127.0, 126.5, 121.8, 117.8, 55.2, 46.1, 29.1, 20.9, 17.5.

2-(4-(*tert*-Butyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (5np)

Procedure B was followed using 2-(4-(*tert*-butyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (53.1 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (99:1, petroleum ether: EtOAc) to afford 43.2 mg (74%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.8 Hz, 2 H), 7.32 - 7.21 (m, 4 H), 7.05 (d, J = 8.8 Hz, 2 H), 5.50 (s, 1 H), 3.77 - 3.72 (m, 1 H), 3.46 (ddd, J = 4.0, 10.8, 12.4 Hz, 1 H), 3.19 - 3.10 (m, 1 H), 2.94 (dt, J = 3.4, 16.2 Hz, 1 H), 1.33 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 144.8, 134.6, 129.7, 129.4, 128.7, 127.1, 126.8, 126.4, 117.9, 117.6, 53.6, 44.3, 34.2, 31.5, 28.6.

2-(4-(Benzyloxy)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (6np)

Procedure B was followed using 2-(4-(benzyloxy)phenyl)-1,2,3,4-tetrahydroisoquinoline (63.1 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 31.6 mg (46%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 - 7.29 (m, 4 H), 7.26 - 7.13 (m, 5 H), 7.00 - 6.97 (m, 2 H), 6.93 - 6.89 (m, 2 H), 5.28 (s, 1 H), 4.96 (s, 2 H),3.53 - 3.47(m, 1 H), 3.53 - 3.47(m,

1 H), 3.11 - 3.02 (m, 1 H), 2.86 - 2.81 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 142.8, 137.1, 134.4, 129.8, 129.5, 128.7, 128.7, 128.1, 127.6, 127.2, 126.8, 120.9, 117.7, 115.9, 70.5, 55.4, 44.9, 28.7. HRMS (ESI-Orbitrap MS) *m*/*z*: $[M+H]^+$ Calcd. for $C_{23}H_{21}ON_2$: 341.16484; found: 341.16394.

2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (7np)

Procedure B was followed using 2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoline (57.6 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 54.1 mg (78%) of the product as a slightly yellow solid. Exhibited spectral data in accordance with previous report.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 - 7.41 (m, 2 H), 7.29 - 7.20 (m, 4 H), 6.92 (d, J = 8.8 Hz, 2 H), 5.43 (s, 1 H), 3.71 - 3.66 (m, 1 H), 3.43 (td, J = 4.1, 11.6, 12.3 Hz, 1 H), 3.15 - 3.07 (m, 1 H), 2.94 (dt, J = 3.8, 16.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 134.5, 132.5, 129.5, 129.3, 129.0, 127.1, 127.1, 119.1, 117.6, 114.4, 52.9, 44.3, 28.5.

2-(4-Chlorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (8np)

Procedure B was followed using 2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinoline (48.7 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 44.1 mg (82%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 - 7.21 (m, 5 H), 7.23 - 7.21 (m, 1 H), 7.00 - 6.97 (m, 2 H), 5.44 (s, 1 H), 3.71 - 3.66 (m, 1 H), 3.47 - 3.40 (m, 1 H), 3.17 - 3.08 (m, 1 H), 2.95 (dt, J = 3.7, 16.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 134.5, 129.6, 129.5, 129.3, 129.0, 127.1, 127.09, 127.07, 118.9, 117.6, 53.2, 44.4, 28.5.

2-(4-Fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (9np)

Procedure B was followed using 2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (45.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 39.8 mg (79%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 - 7.26 (m, 2 H), 7.24 - 7.22 (m, 2 H), 7.07 - 7.05 (m, 4 H), 5.40 (s, 1 H), 3.65 - 3.59 (m, 1 H), 3.48 - 3.41 (m, 1 H), 3.20 - 3.11 (m, 1 H), 2.97 - 2.91 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8 (d, J = 241 Hz), 145.2, 134.4, 129.6, 129.5, 128.9, 127.2, 127.0, 120.6 (d, J = 8 Hz), 117.5, 116.3 (d, J = 23 Hz), 54.9, 44.9, 28.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -120.7 - -120.8 (m).

2-(2-Fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (10np)

Procedure B was followed using 2-(2-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (45.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 36.1 mg (71%) of the product as a white solid. Exhibited spectral data

in accordance with previous report.[12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 - 7.16 (m, 4 H), 7.14 - 7.09 (m, 2 H), 7.07 - 7.02 (m, 2 H), 5.41 (s, 1 H), 3.53 - 3.42 (m, 2 H), 3.19 - 3.10 (m, 1 H), 2.88 - 2.82 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (d, J = 245 Hz), 136.9, 136.8, 134.0, 129.6, 129.3, 128.7, 127.1, 126.8, 125.1 (t, J = 3.5 Hz), 121.5 (d, J = 3 Hz), 117.5, 116.5 (d, J = 22 Hz), 53.9 (d, J = 5 Hz), 44.8, 28.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -122.5 - -122.6 (m).

2-(3-Fluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (11np)

Procedure B was followed using 2-(3-fluorophenyl)-1,2,3,4-tetrahydroisoquinoline (45.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 40.5 mg (80%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 - 7.10 (m, 5 H), 6.71 - 6.53 (m, 3 H), 5.38 (s, 1 H), 3.65 - 3.59 (m, 1 H), 3.37 - 3.30 (m, 1 H), 3.03 - 2.95 (m, 1 H), 2.87 - 2.81 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8 (d, J = 243 Hz), 149.8 (d, J = 9 Hz), 134.6, 130.8, 130.7, 129.3, 129.2, 129.0, 127.1 (d, J = 2 Hz), 117.7, 112.1 (t, J = 2 Hz), 107.9 (d, J = 18 Hz), 104.0 (d, J = 25 Hz), 52.1, 44.0, 28.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.1 - -111.2 (m).

2-(2,4-Difluorophenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (12np)

Procedure B was followed using 2-(2,4-difluorophenyl)-1,2,3,4-tetrahydroisoquinoline (49.0 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 34.0 mg (63%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 - 7.19 (m, 1 H), 7.17 - 7.08 (m, 4 H), 6.85 - 6.77 (m, 2 H), 5.28 (s, 1 H), 3.46 - 3.34 (m, 2 H), 3.15 - 3.06 (m, 1 H), 2.85 - 2.79 (m, 1 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5 (dd, J = 12 Hz), 156.3 (dd, J = 12 Hz), 133.9, 133.4 (dd, J = 3 Hz), 129.1, 128.4 (d, J = 251 Hz), 127.8 (d, J = 200 Hz), 122.7 (dd, J = 6 Hz), 117.4, 111.7 (dd, J = 4 Hz), 105.1 (dd, J = 24 Hz), 54.3 (d, J = 5 Hz), 45.1, 28.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.9 - -115.0 (m), -118.1 - -118.2 (m). HRMS (ESI-Orbitrap MS) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{13}F_2N_2$: 271.10413; found: 271.10349.

2-(2-Fluoro-4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile(13np)

Procedure B was followed using 2-(2-fluoro-4-methylphenyl)-1,2,3,4-tetrahydroisoquinoline (48.3 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 34 mg (64%) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 - 7.21 (m, 4 H), 7.14 - 7.09 (m, 1 H), 6.99 - 6.92 (m, 2 H), 5.44 (s, 1 H), 3.53 - 3.50 (m, 2 H), 3.25 - 3.16 (m, 1 H), 2.93 - 2.88 (m, 1 H), 2.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2 (d, J = 245 Hz), 135.6 (d, J = 8 Hz), 134.3 (J = 10 Hz), 134.1, 129.6, 129.5, 128.7, 127.2, 126.8, 125.5 (d, J = 3 Hz), 121.5 (d, J = 3 Hz), 117.6, 117.1 (d, J = 20 Hz), 54.2 (d, J = 5 Hz), 44.9 (d, J = 1 Hz), 28.7, 20.8 (d, J = 2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -128.4 (t, J = 10.9 Hz). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{16}FN_2$: 267.1292; found: 267.1304.

2-(4-(Trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (14np)

Procedure B was followed using 2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (55.4 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). With stirring, the reaction mixture was performed for 6 h instead of 3 h. The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 30.6 mg (51%) of the product as a slightly yellow solid. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8 Hz, 2 H), 7.37 - 7.25 (m, 4 H), 7.08 (d, J = 8 Hz, 2 H), 5.57 (s, 1 H), 3.88 - 3.82 (m, 1 H), 3.60 - 3.53 (m, 1 H), 3.20 - 3.12 (m, 1 H), 3.08 - 3.01 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 134.7, 129.4, 129.3, 129.2, 127.3, 127.2, 127.0 (q, J = 3.5 Hz), 122.67 (q, J = 34 Hz), 117.6, 115.5, 51.4, 44.1, 28.5.

2-(Naphthalen-2-yl)-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (15np)

Procedure B was followed using 2-(naphthalen-2-yl)-1,2,3,4-tetrahydroisoquinoline (51.9 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (99:1, petroleum ether: EtOAc) to afford 42.0 mg (70%) of the product as a white solid. Exhibited spectral data in accordance with previous report.[10] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 - 7.78 (m, 3 H), 7.51 - 7.46 (m, 1 H), 7.42 - 7.38 (m, 2 H), 7.36 - 7.25 (m, 5 H), 5.66 (s, 1 H), 3.95 - 3.90 (m, 1 H), 3.61 - 3.54 (m, 1 H), 3.25 - 3.17 (m, 1 H), 3.00 (dt, J = 3.4, 16.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 134.6, 134.4, 129.6, 129.55, 129.52, 129.5, 128.9, 127.6, 127.23, 127.18, 127.0, 126.7, 124.5, 119.4, 117.8, 112.9, 53.3, 44.5, 28.6.

6,7-Dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (16np)

Procedure B was followed using 6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinoline (53.9 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (80:20, petroleum ether: EtOAc) to afford 48.2 mg (82%) of the product as a slightly yellow solid. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 - 7.33 (m, 2 H), 7.08 (d, J = 7.6 Hz, 2 H), 7.01 (t, J = 7.2 Hz, 1 H), 6.76 (s, 1 H), 6.68 (s, 1 H), 5.46 (s, 1 H), 3.87 (d, J = 2.2 Hz, 6 H), 3.80 - 3.74 (m, 1 H), 3.43 (td, J = 4.0, 11.8, 12.4 Hz, 1 H), 3.11 - 3.03 (m, 1 H), 2.84 (dt, J = 3.4, 16.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 148.4, 148.1, 129.5, 126.9, 121.9, 121.1, 117.9, 117.7, 111.5, 109.4, 56.1, 56.0, 53.0, 44.2, 28.1.

2-Methyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (17np)

Procedure B was followed using 2-Methyl-1,2,3,4-tetrahydroisoquinoline (29.5 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (90:10, petroleum ether: EtOAc) to afford 13.4 mg (39 %) of the product as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.14 (m, 4 H), 4.72 (s, 1 H), 3.09 - 3.00 (m, 1 H), 2.91 - 2.87 (m, 1 H), 2.83 - 2.76 (m, 2 H), 2.59 (s, 3 H).^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 129.6, 129.5, 128.6, 127.2,

126.6, 116.6, 56.9, 48.4, 43.8, 28.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{11}H_{12}N_2$: 173.10732; found: 173.10686.

2-Allyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (18np)

Procedure B was followed using 1-Allyl-1,2,3,4-tetrahydroquinoline (34.6 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (95:5, petroleum ether: EtOAc) to afford 16 mg (40 %) of the product as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.22 (m, 1 H), 7.20 (d, J = 3.6 Hz, 2 H), 7.16 (d, J = 7.2 Hz, 1 H), 5.91 - 5.81 (m, 1 H), 5.42 (d, J = 17.2 Hz, 1 H), 5.29 (d, J = 10.0 Hz, 1 H), 4.83 (s, 1 H), 3.35 (qd, J = 13.2, 5.6 Hz, 2 H), 3.07 - 3.01 (m, 2 H), 2.83 - 2.76 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 133.6, 129.6, 129.5, 128.6, 127.4, 126.6, 119.9, 116.60, 58.8, 54.5, 46.6, 28.5. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ Calcd. for $C_{13}H_{14}N_2$: 199.1235; found: 199.1230.

1-Phenyl-1,2,3,4-tetrahydroquinoline-2-carbonitrile (19np)

Procedure B was followed using 1-phenyl-1,2,3,4-tetrahydroquinoline (41.8 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (99:1, petroleum ether: EtOAc) to afford 10.7 mg (23%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.[13] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 - 7.45 (m, 2 H), 7.37 - 7.34 (m, 2 H), 7.33 - 7.29 (m, 1 H), 7.11 (d, J = 8 Hz, 1 H), 6.97 (t, J = 8 Hz, 1 H), 6.80 (td, J = 8 Hz, 1 H), 6.52 (d, J = 8 Hz, 1 H), 4.68 - 4.66 (m, 1 H), 3.33 - 3.24 (m, 1 H), 2.94 (dt, J = 16 Hz, 1 H), 2.40 - 2.34 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 142.1, 130.3, 129.6, 127.2, 127.1, 126.7, 121.7, 119.7, 119.1, 115.6, 52.0, 25.7, 24.4.

1-Phenylpyrrolidine-2-carbonitrile (20np)

Procedure B was followed using 1-phenylpyrrolidine (29.4 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 18.8 mg (55%) of the product as a brown oil. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 - 7.30 (m, 2 H), 6.86 (t, J = 7.3 Hz, 1 H), 6.71 (d, J = 8.2 Hz, 2 H), 4.45 - 4.43 (m, 1 H), 3.49 - 3.34 (m, 2 H), 2.45 - 2.38 (m, 1 H), 2.32 - 2.28 (m, 1 H), 2.27 - 2.15 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 129.5, 119.4, 118.3, 112.8, 49.1, 47.5, 31.6, 24.0.

1-Phenylpiperidine-2-carbonitrile (21np)

Procedure B was followed using 1-phenylpiperidine (32.2 mg, 0.2 mmol) and TMSCN (54 µL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (99:1, petroleum ether: EtOAc) to afford 23.9 mg (64%) of the product as a brown oil. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 - 7.26 (m, 2 H), 7.02 - 6.98 (m, 3 H), 4.63 (t, J = 3.7 Hz, 1 H), 3.45 (d, J = 12.0 Hz, 1 H), 3.04 (td, J = 2.6, 11.8 Hz, 1 H), 2.04 - 2.00 (m, 2 H), 1.87 - 1.85 (m, 2 H), 1.74 - 1.67 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 129.4, 122.2, 118.4, 117.3, 52.1, 46.7, 29.3, 25.2, 20.3.

4-Methyl-1-phenylpiperidine-2-carbonitrile (22np)

Procedure B was followed using 4-methyl-1-phenylpiperidine (35.0 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 16.4 mg (41%) of the product as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 - 7.29 (m, 2 H), 7.02 - 6.97 (m, 3 H), 4.66 - 4.64 (m, 1 H), 3.50 - 3.45 (m, 1 H), 3.07 (td, J = 4, 12 Hz, 1 H), 2.05 - 2.00 (m, 1 H), 1.91 - 1.83 (m, 2 H), 1.71 - 1.63 (m, 1 H), 1.43 - 1.32 (m, 1 H), 1.04 (d, J = 8 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 129.5, 122.2, 118.4, 117.5, 52.0, 46.4, 37.2, 33.8, 27.1, 21.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}N_2$: 201.1386; found: 201.1399.

2-(Methyl(phenyl)amino)acetonitrile (23np)

Procedure B was followed using *N*,*N*-dimethylaniline (24.2 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 15.5 mg (53%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.[8] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 7.9 Hz, 2 H), 6.93 (t, J = 7.3 Hz, 1 H), 6.88 (d, J = 8.1 Hz, 2 H), 4.18 (s, 2 H), 3.02 (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.

2-(Methyl(*p*-tolyl)amino)acetonitrile (24np)

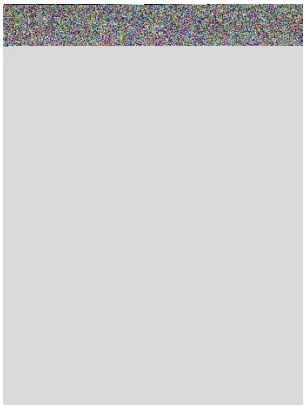
Procedure B was followed using *N*,*N*-dimethyl-*p*-toluidine (27.0 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). With stirring, the reaction mixture was performed for 6 h instead of 3 h. The reaction mixture was purified by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 15.1 mg (47%) of the product as a yellow oil. Exhibited spectral data in accordance with previous report.[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 - 7.10 (m, 2 H), 6.82 - 6.78 (m, 2 H), 4.14 (s, 2 H), 2.97 (s, 3 H), 2.29 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 130.1, 130.1, 115.6, 43.0, 39.6, 20.5.

3. Synthesis of cathepsin K inhibitor 29ap

Procedure A was followed using *tert*-butyl pyrrolidine-2-carboxylate (34.2 mg, 0.2 mmol) and TMSCN (54 μL, 0.4 mmol, 2 equiv). The reaction mixture was purified by flash column chromatography on silica gel (75:25, petroleum ether: EtOAc) to afford 36.0 mg (92%) of the product **29ap** as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.99 (q, J = 4 Hz, 1 H), 3.51 - 3.45 (m, 1 H), 3.41 - 3.35 (m, 1 H), 2.15 - 2.06 (m, 1 H), 1.99 - 1.91 (m, 1 H), 1.88 - 1.81 (m, 2 H), 1.39 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 117.1, 80.0, 55.8, 50.5, 48.6, 31.6, 28.3. HRMS (ESI-Orbitrap MS) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{17}O_2N_2$: 197.12845; found: 197.12810.

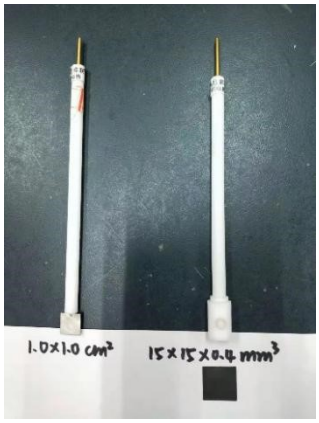
4. Scale-up synthesis of 3,4-dihydroisoquinoline-2(1*H*)-carbonitrile (1ap)

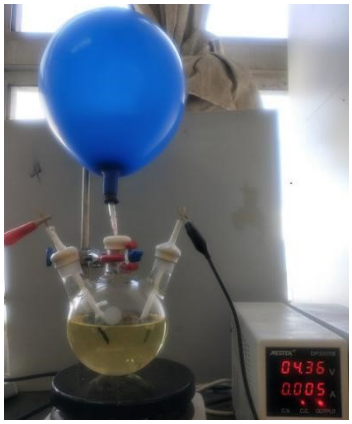
1,2,3,4-Tetrahydroisoquinoline (4 mmol), TMSCN (8 mmol, 2 equiv), TBAB (10 mmol, 2.5 equiv), KF (16 mmol, 4 equiv) and CH_3CN (200 mL) were combined and added into an oven-dried undivided three-necked bottle (500 mL) equipped with a stir bar. The bottle was equipped with glassy carbon (d = 5 mm) as the anode and platinum electrodes (1.0×1.0 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed under room temperature at a constant current of 5 mA (The dual display potentiostat was operating in constant current mode) under aerobic conditions for 36 h. When the reaction was finished, the solution was filtered and washed with EtOAc. The solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (9:1, petroleum ether: EtOAc) to afford 0.484 g (76%) of the **1ap**.



Scale-up synthesis of 2-phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (1np)

2-Phenyl-1,2,3,4-tetrahydroisoquinoline (4 mmol), TMSCN (8 mmol, 2 equiv), TBAB (10 mmol, 2.5 equiv), KF (16 mmol, 4 equiv) and CH_3CN (200 mL) were combined and added into an oven-dried undivided three-necked bottle (500 mL) equipped with a stir bar. The bottle was equipped with graphite felts (15×15×0.4 mm^3) as the anode and platinum electrodes (1.0×1.0 cm^2) as the cathode. The reaction mixture was stirred and electrolyzed under room temperature at a constant current of 5 mA (The dual display potentiostat was operating in constant current mode) under N_2 atmosphere for 36 h. When the reaction was finished, the solution was filtered and washed with EtOAc. The solvent was removed with a rotary evaporator. The pure product was obtained by flash column chromatography on silica gel (98:2, petroleum ether: EtOAc) to afford 0.655 g (70%) of the **1np**.





5. General procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under room temperature. Glassy carbon electrode was used as working electrode, and platinum wire was employed as counter electrode. Ag/AgCl reference electrode was submerged in saturated aqueous KCl solution and separated from reaction by a salt bridge. The mixture of acetonitrile (10 mL) containing 0.1 M $LiClO_4$ was poured into the electrochemical cell in all experiments. The scan rate was 100 mV/s ranging from 0 to 3.0 V.

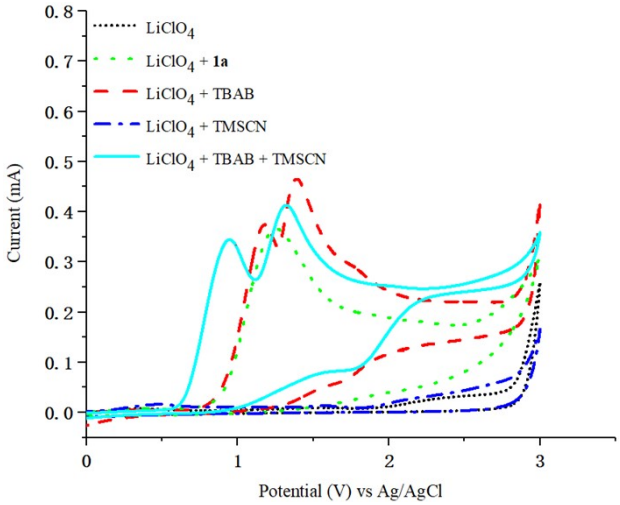


Figure 1. Cyclic voltammograms of reactants and the mixtures in 0.1 M $LiClO_4/CH_3CN$ using a glassy carbon as working electrode, Pt wire as counter, Ag/AgCl as reference electrode, at 100 mV/s scan rate: background ($LiClO_4$ 0.1 M in MeCN); TBAB (0.03 M); tetrahydroisoquinoline **1a** (0.05 M); TMSCN (0.05 M); TBAB (0.03 M) + TMSCN (0.05 M).

6. Hydrogen detection experiment

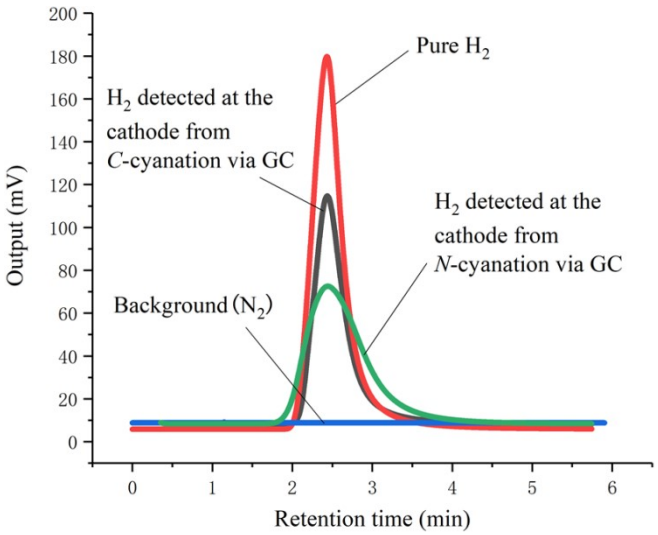


Figure 2. The observation of H_2 gas liberation on cathode was confirmed via GC (KeXiao GC1690) during electrolysis.

7. References

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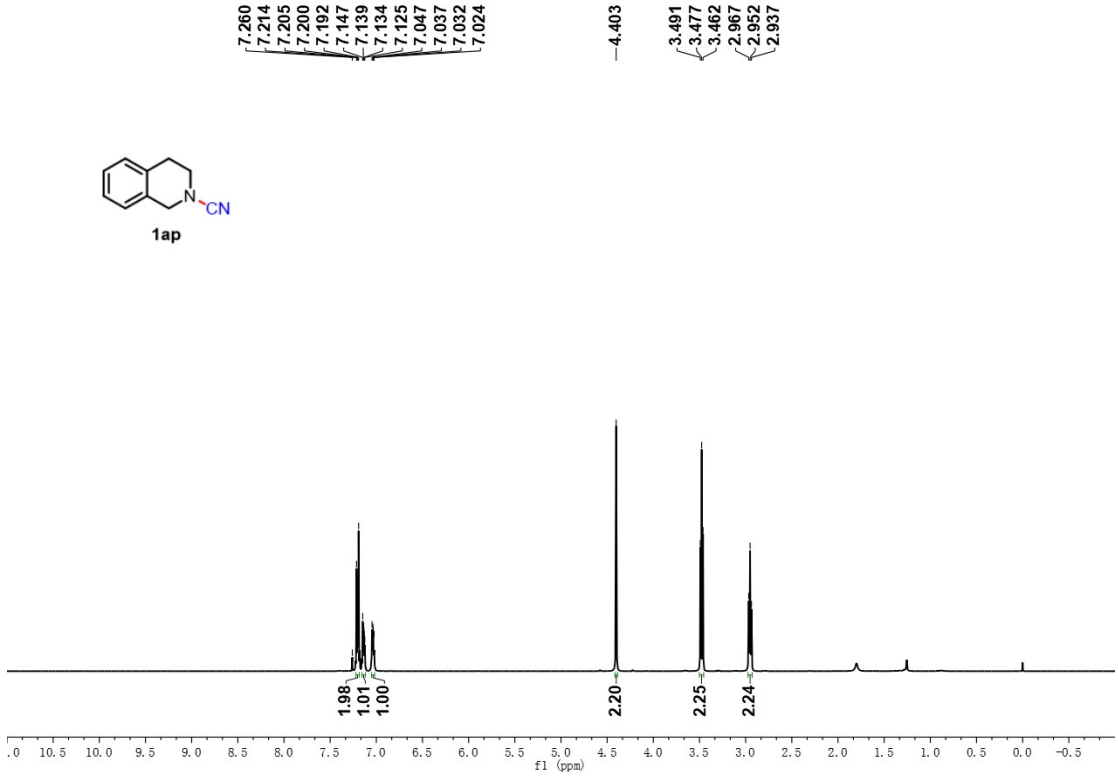
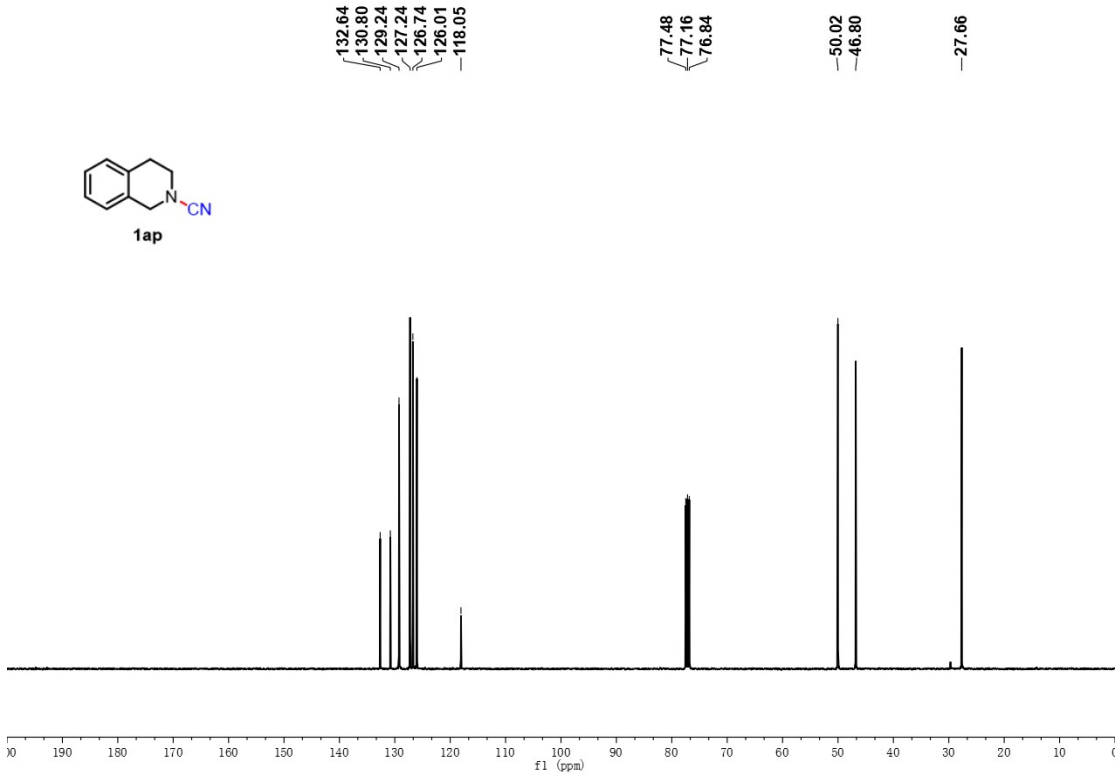
8. ^{1}H, ^{13}C and ^{19}F spectra



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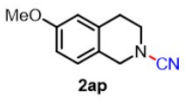
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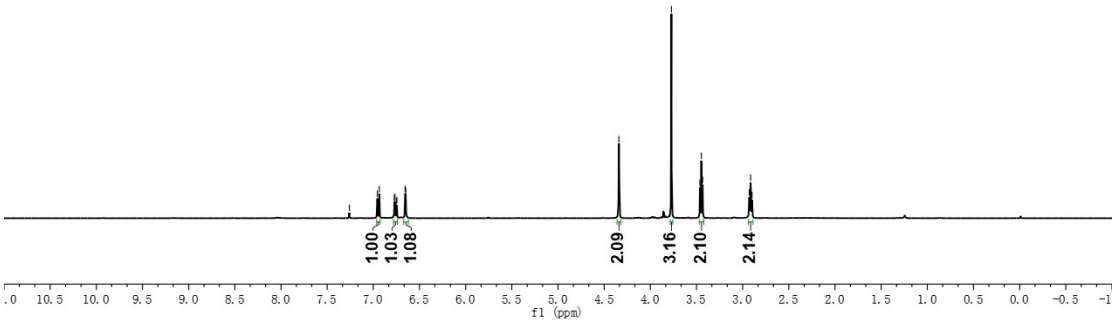
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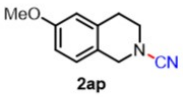
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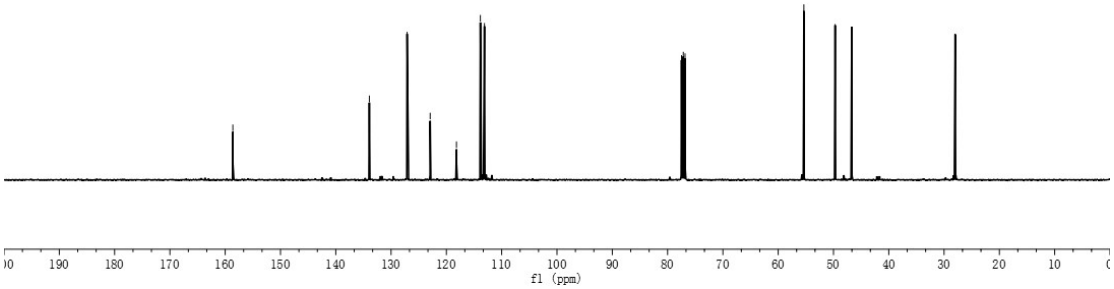
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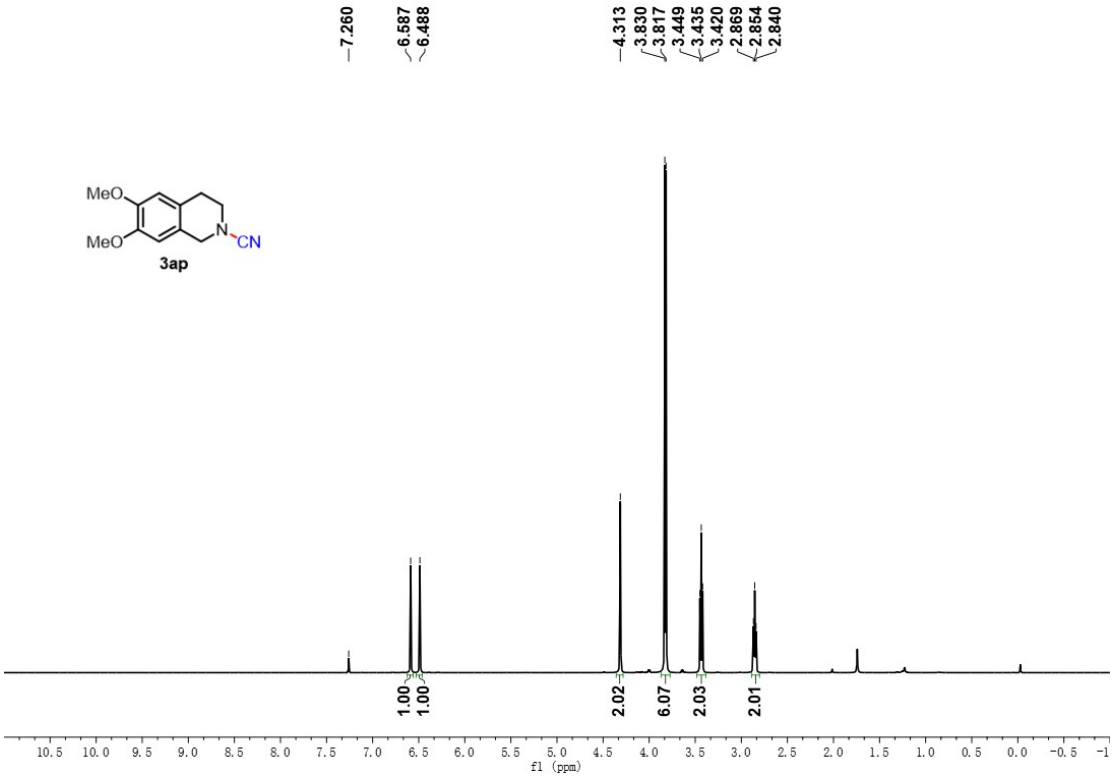
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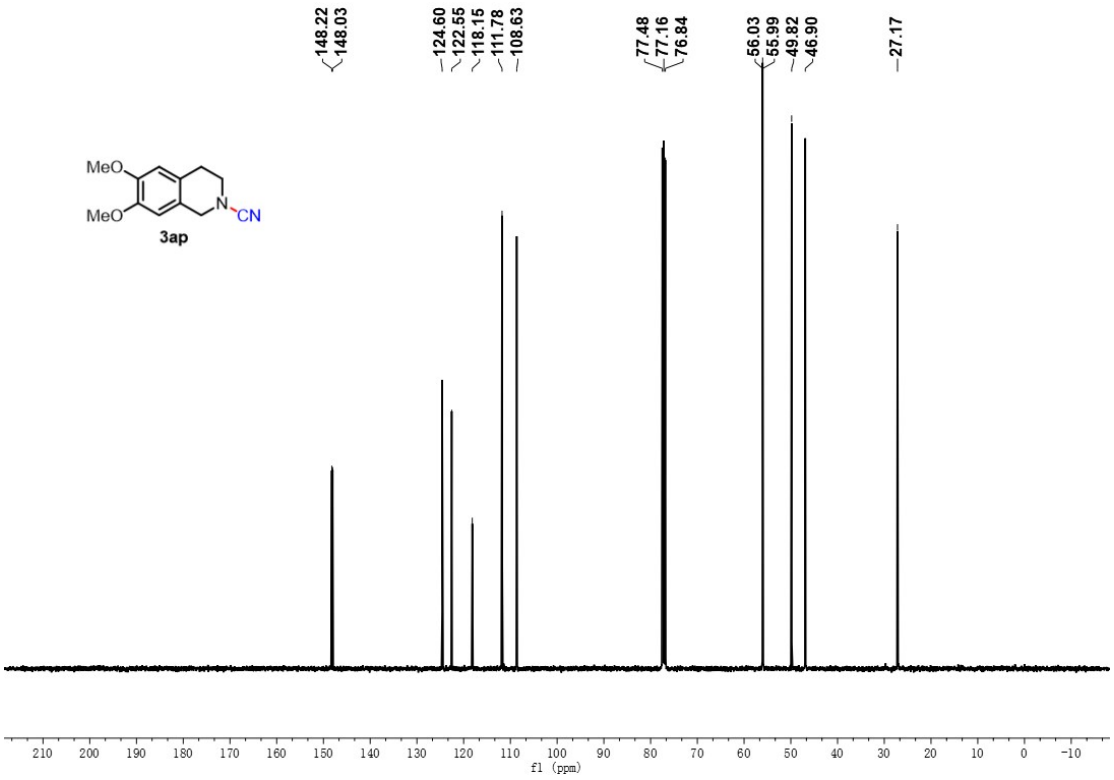
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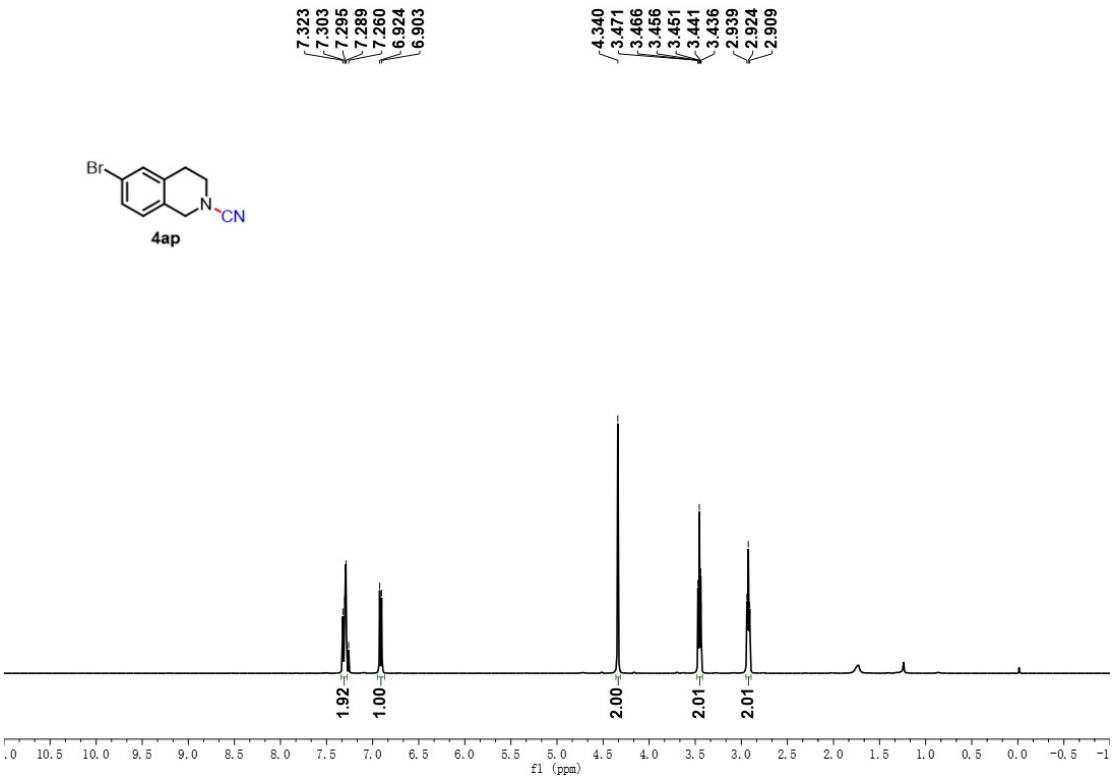
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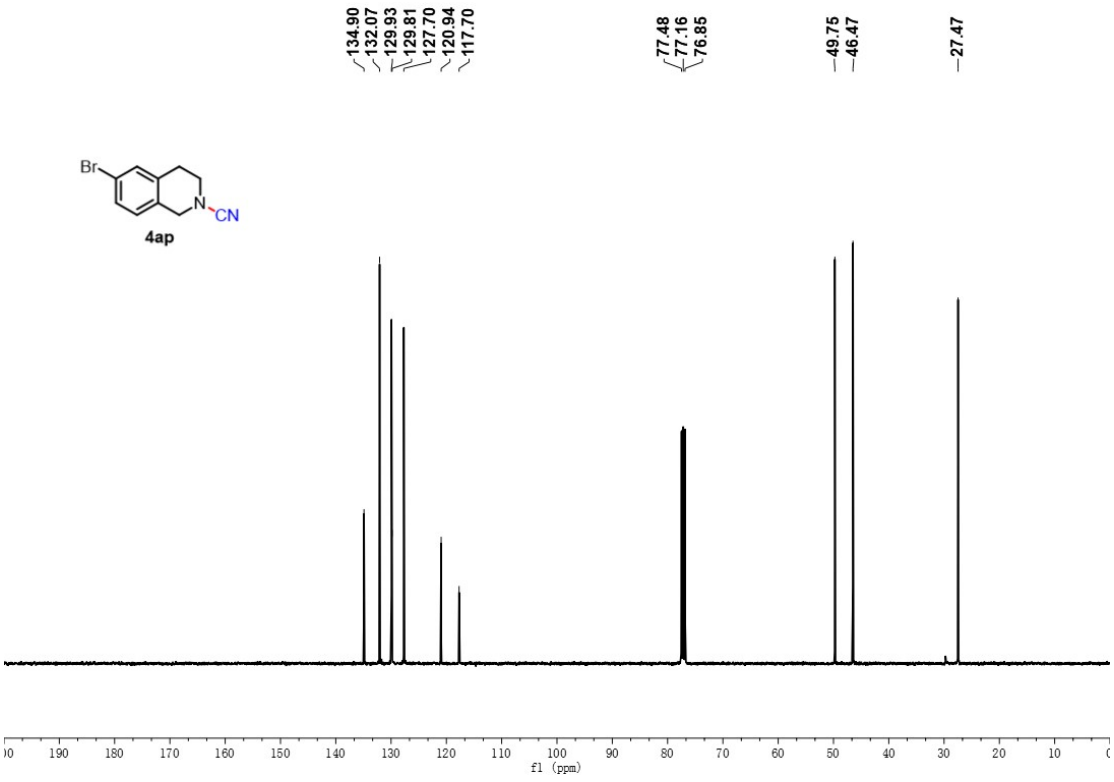
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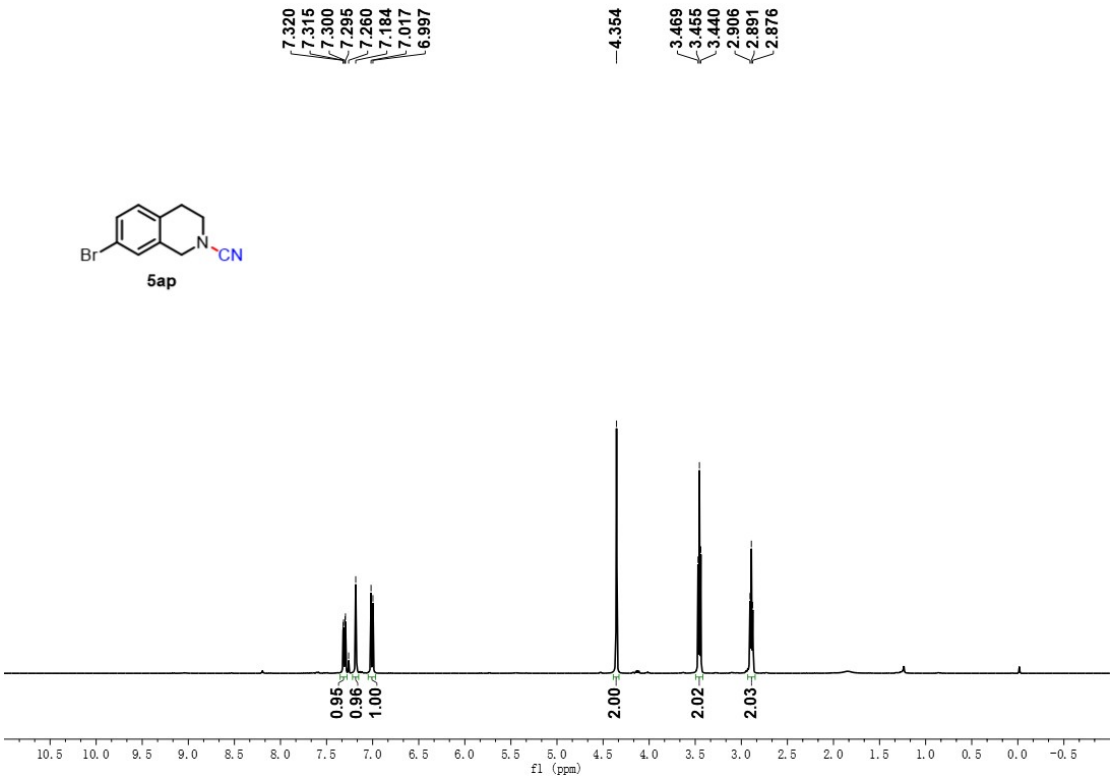
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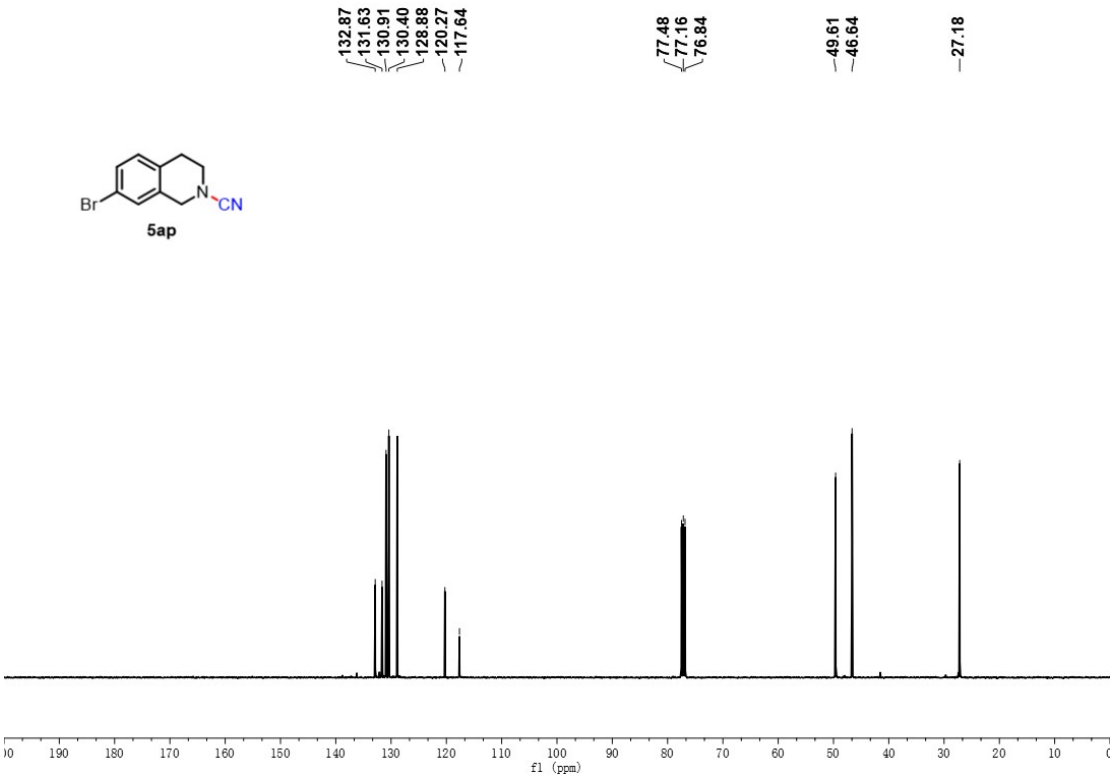
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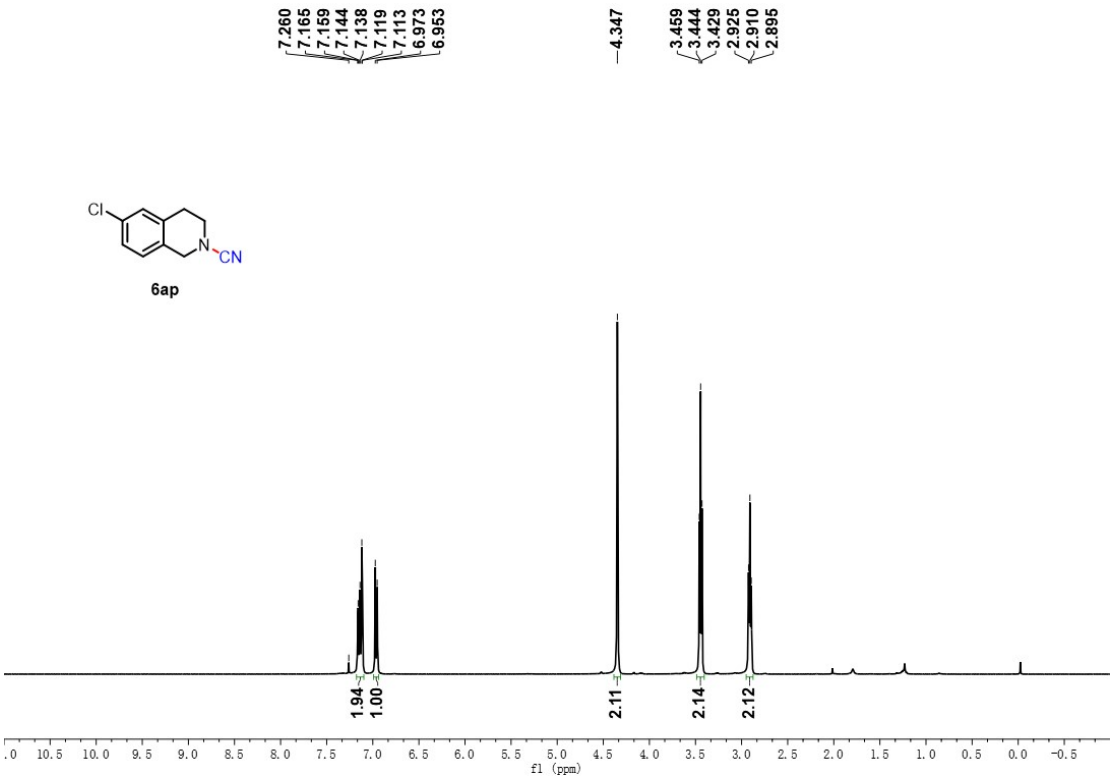
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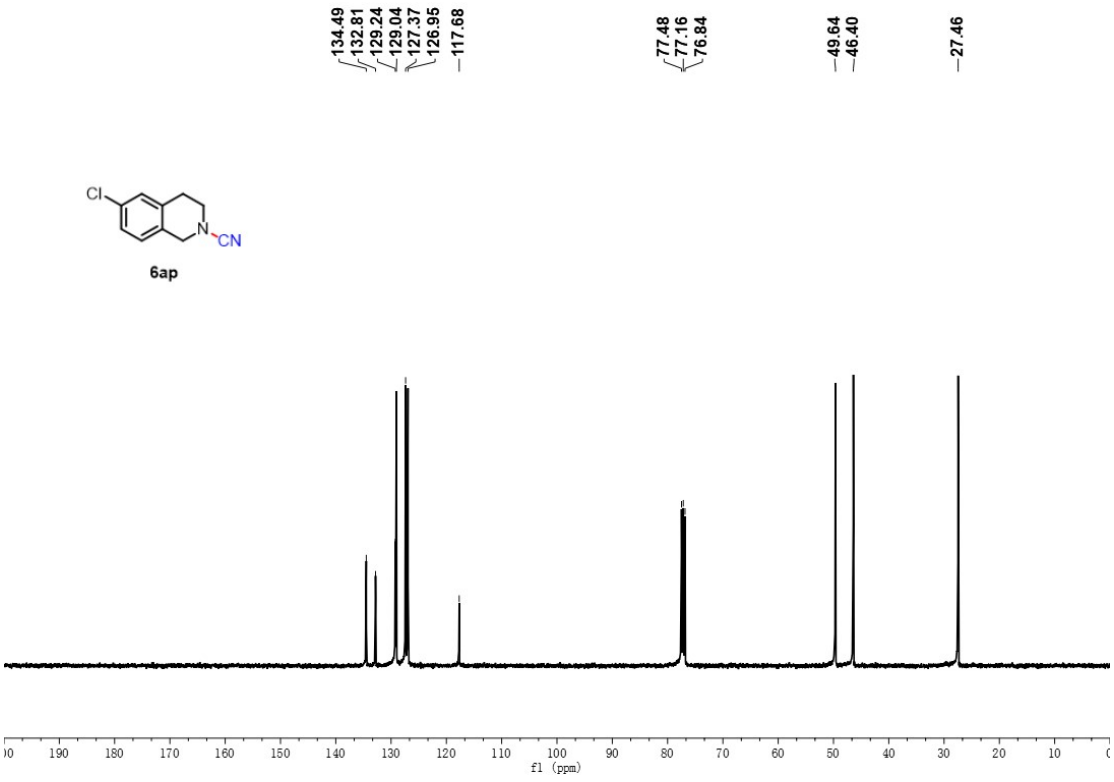
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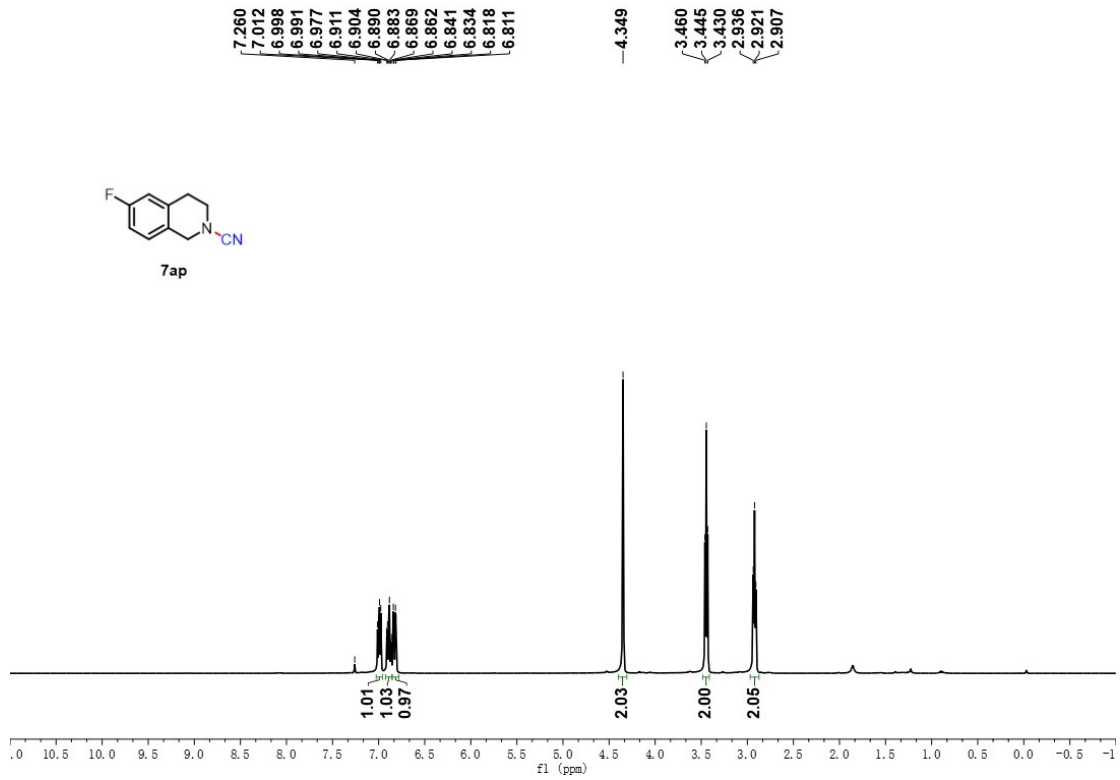
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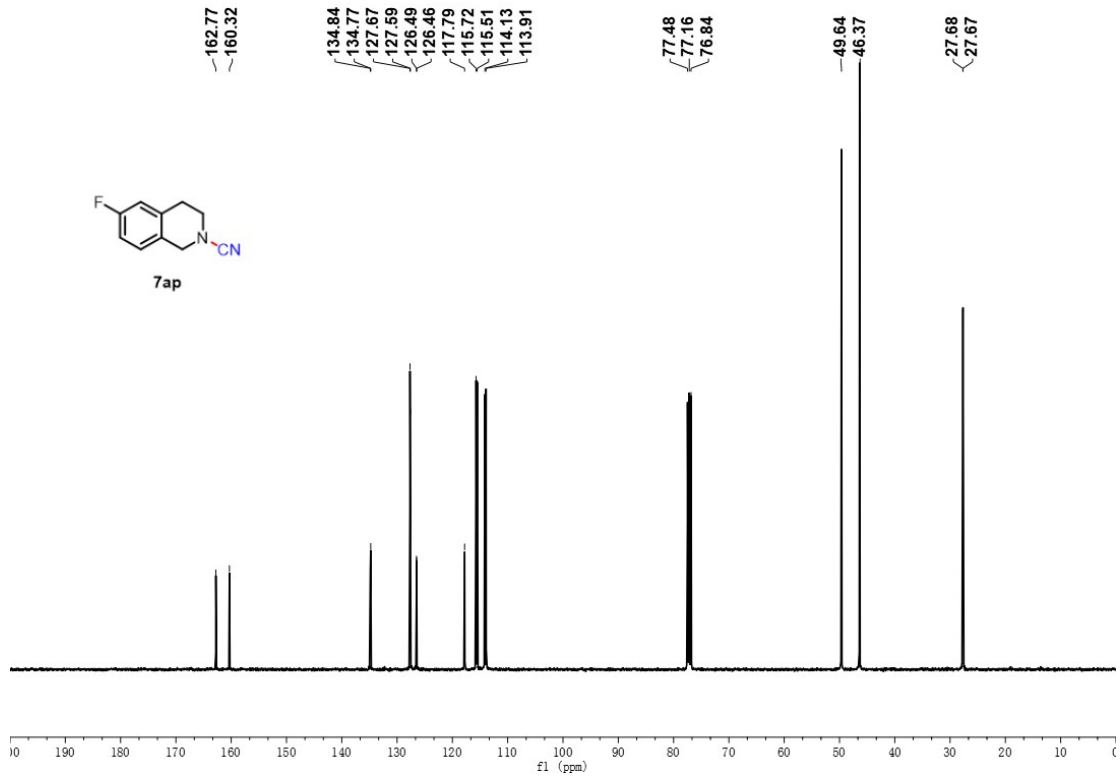
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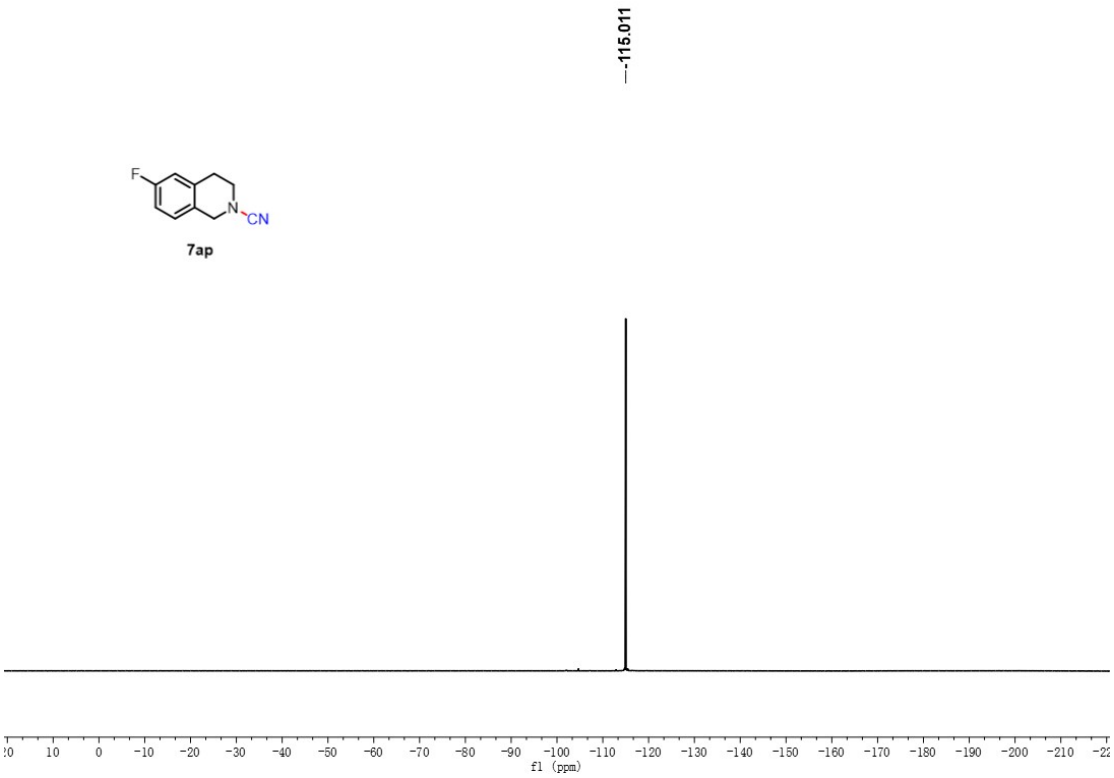
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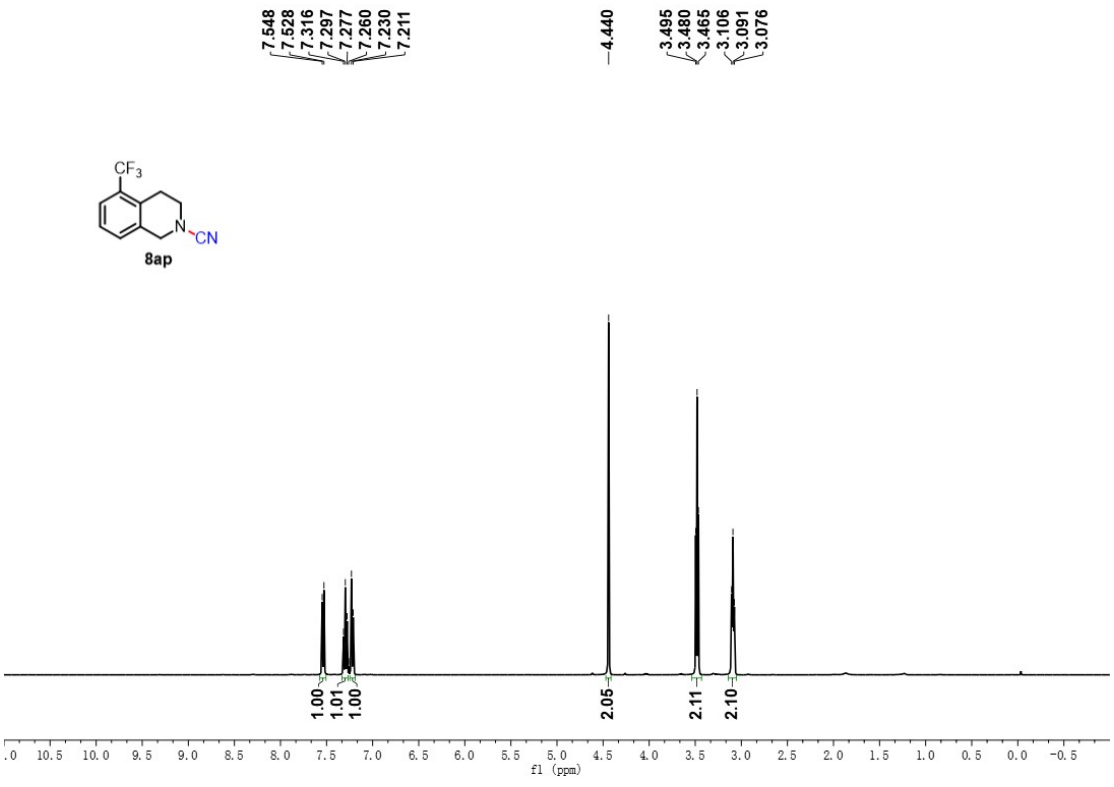
f1 (ppm)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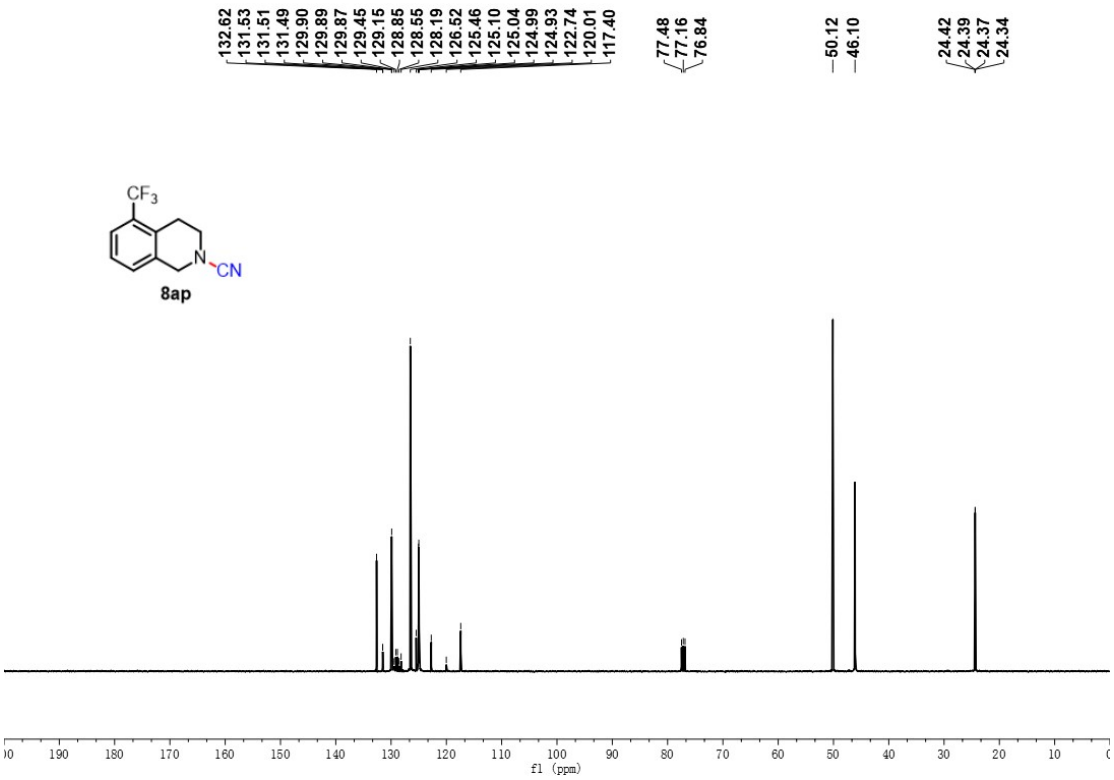
3.480
3.465
3.106
3.091
3.076
CF3
N
CN
8ap
1.00
1.01
1.00
2.05
2.11
2.10
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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129.45
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128.85
128.55
128.19
126.52
125.46
125.10
125.04
124.99
124.93
122.74
120.01
117.40
77.48
77.16
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50.12
46.10
24.42
24.39
24.37
24.34
CF3
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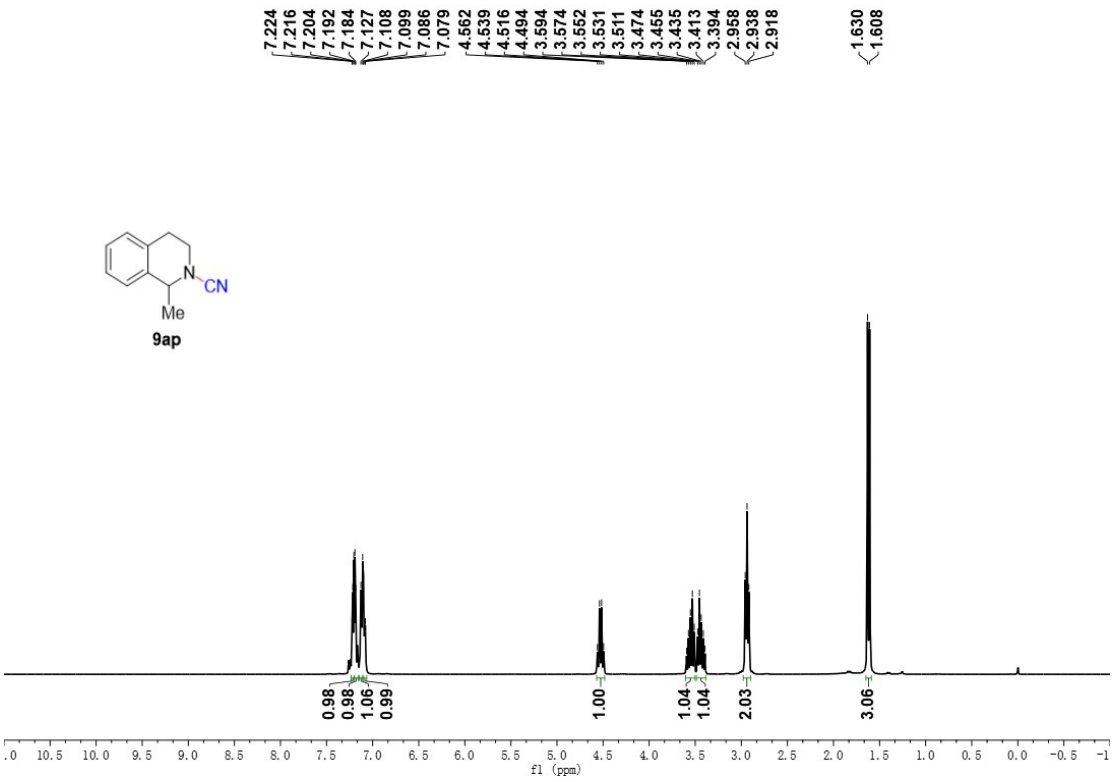
CN
8ap
f1 (ppm)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7.127
7.108
7.099
7.086
7.079
4.562
4.539
4.516
4.494
3.594
3.574
3.552
3.531
3.511
3.474
3.455
3.435
3.413
3.394
2.958
2.938
2.918
1.630
1.608
N
CN
Me
9ap
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0.98
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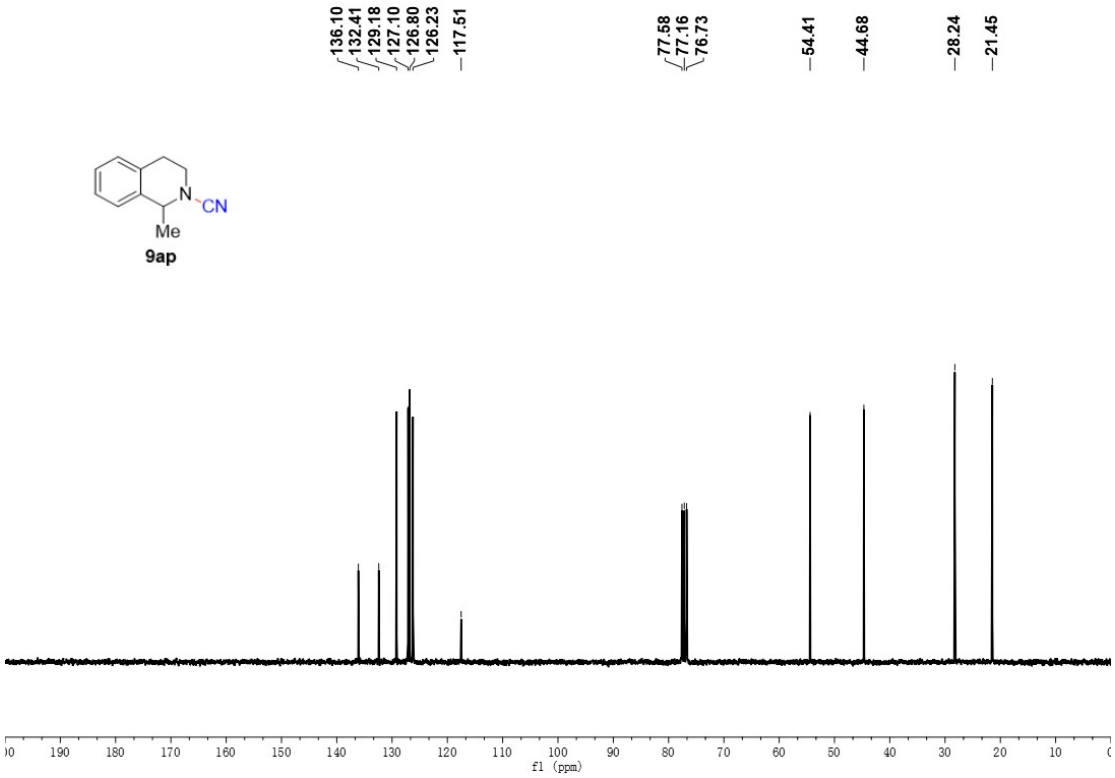
0.99
1.00
1.04
1.04
2.03
3.06
f1 (ppm)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132.41
129.18
127.10
126.80
126.23
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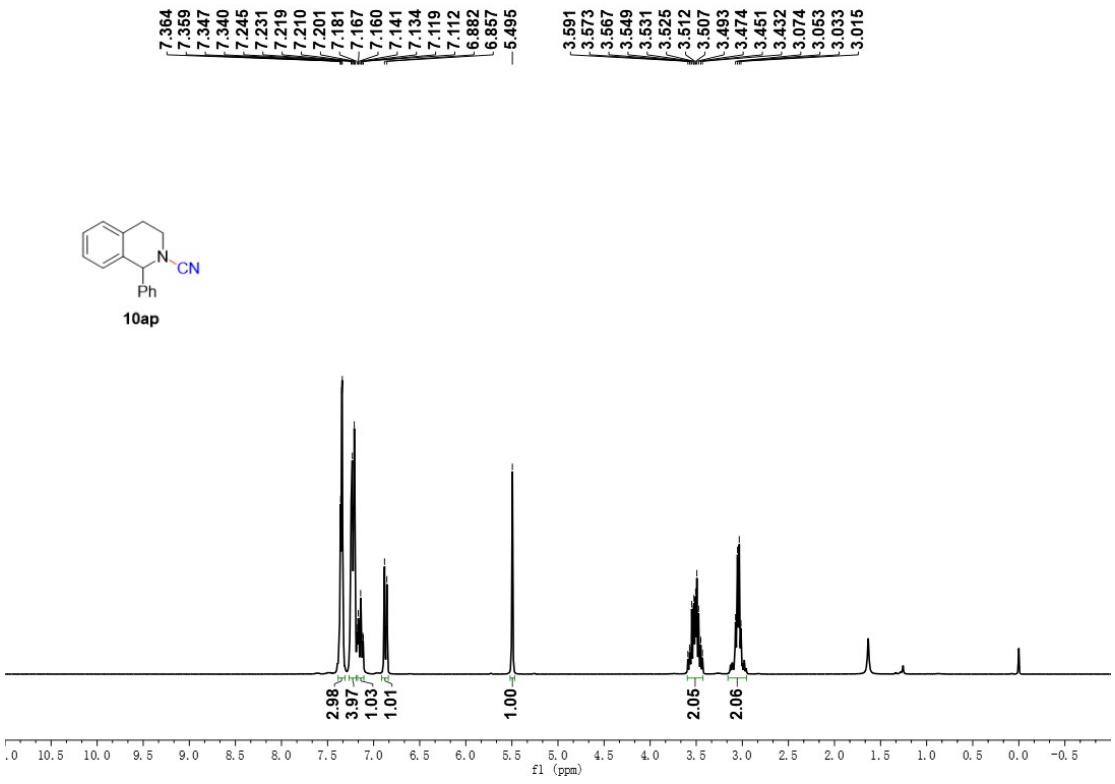
77.58
77.16
76.73
54.41
44.68
28.24
21.45
N
CN
Me
9ap
f1 (ppm)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7.219
7.210
7.201
7.181
7.167
7.160
7.141
7.134
7.119
7.112
6.882
6.857
5.495
3.591
3.573
3.567
3.549
3.531
3.525
3.512
3.507
3.493
3.474
3.451
3.432
3.074
3.053
3.033
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Ph
10ap
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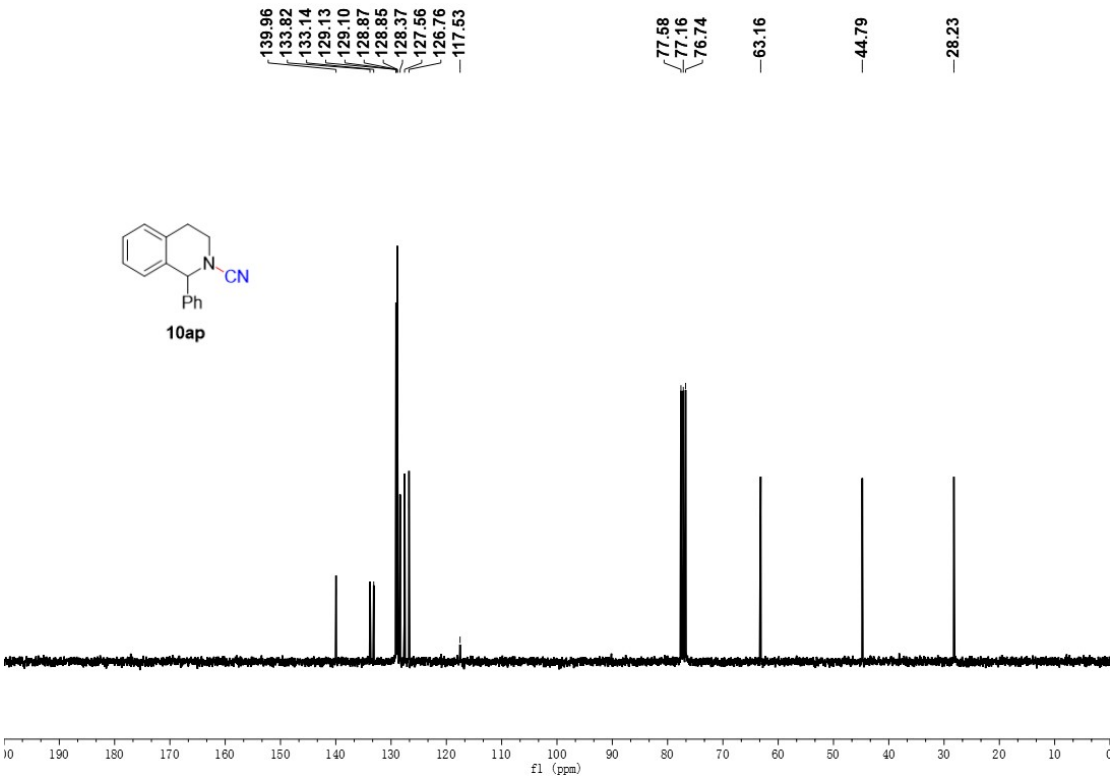
3.97
1.03
1.01
1.00
2.05
2.06
f1 (ppm)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76.74
63.16
44.79
28.23
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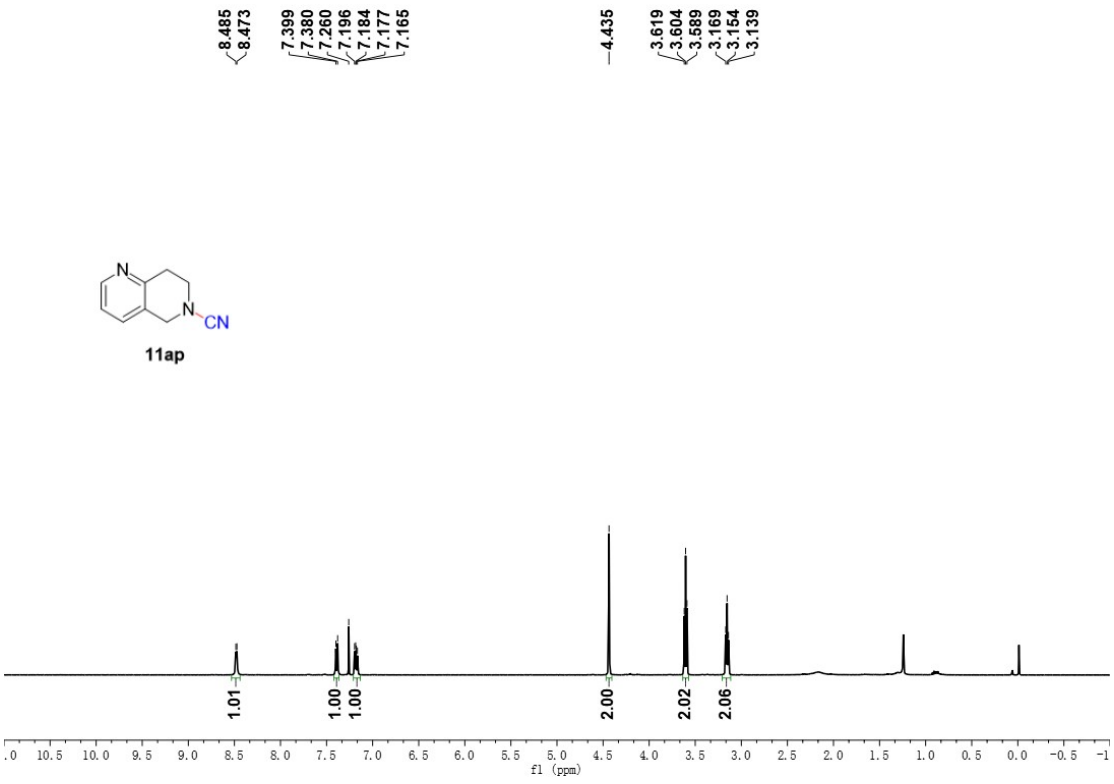
CN
Ph
10ap
f1 (ppm)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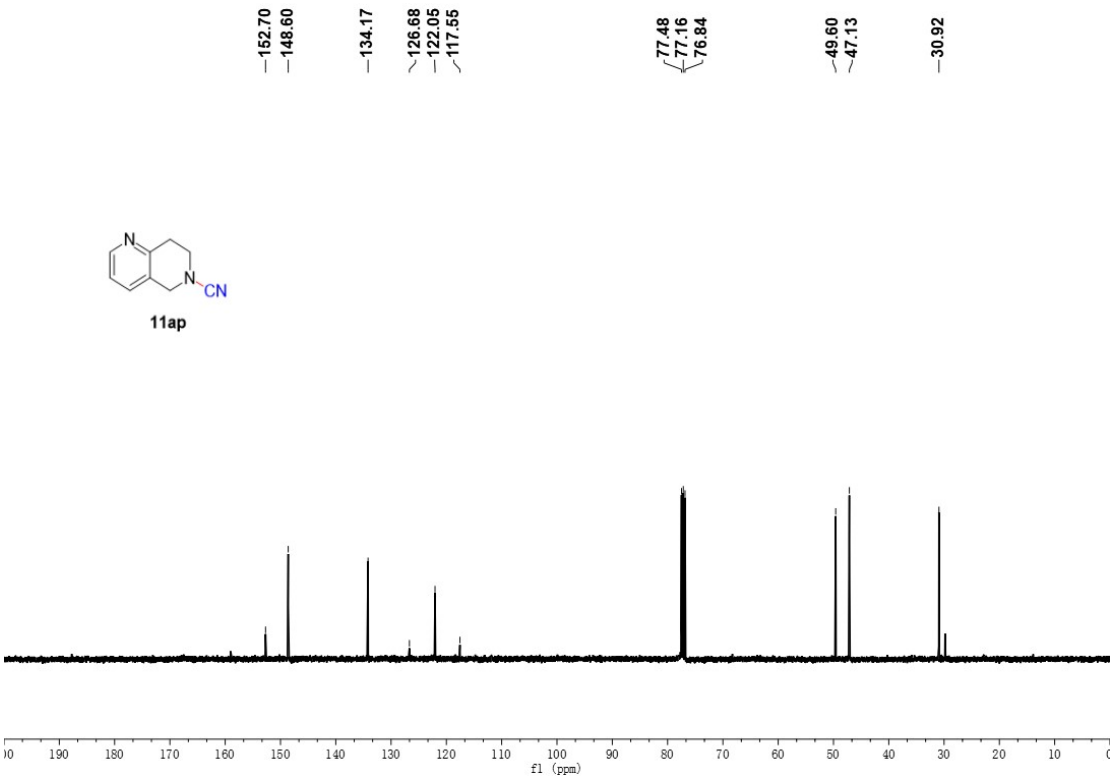
7.184
7.177
7.165
4.435
3.619
3.604
3.589
3.169
3.154
3.139
N
N
CN
11ap
1.01
1.00
1.00
2.00
2.02
2.06
f1 (ppm)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148.60
134.17
126.68
122.05
117.55
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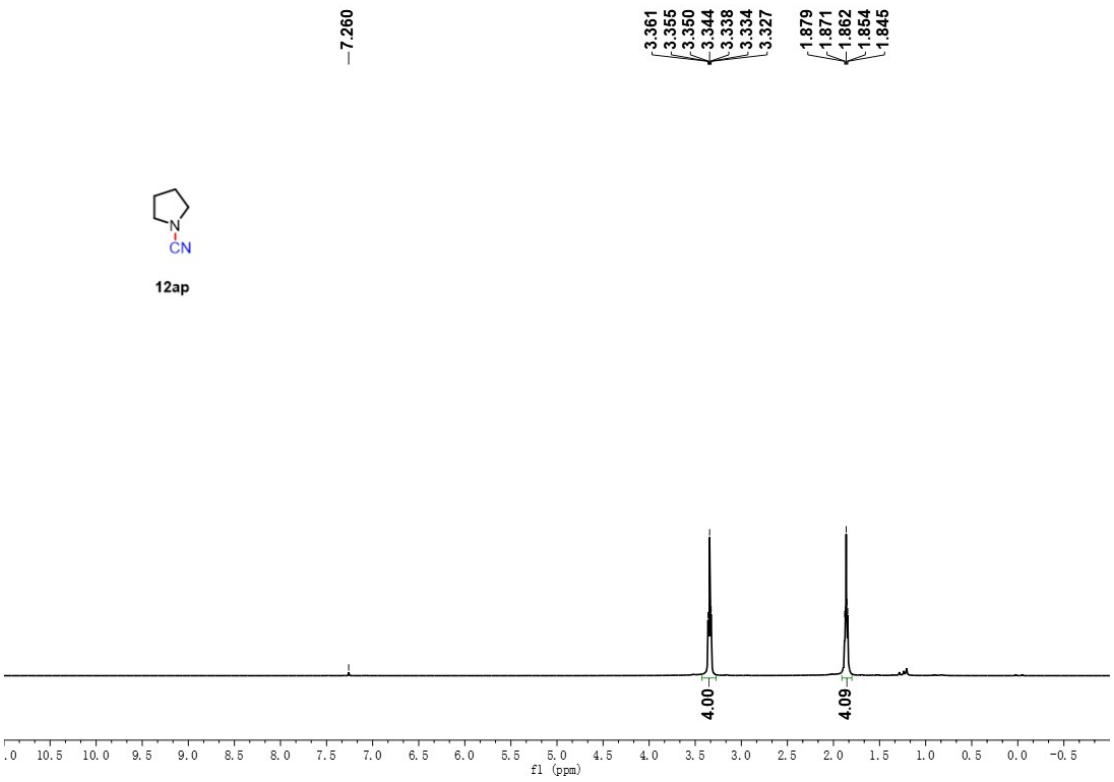
77.16
76.84
49.60
47.13
30.92
N
N
CN
11ap
fl (ppm)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3.355
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3.338
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3.327
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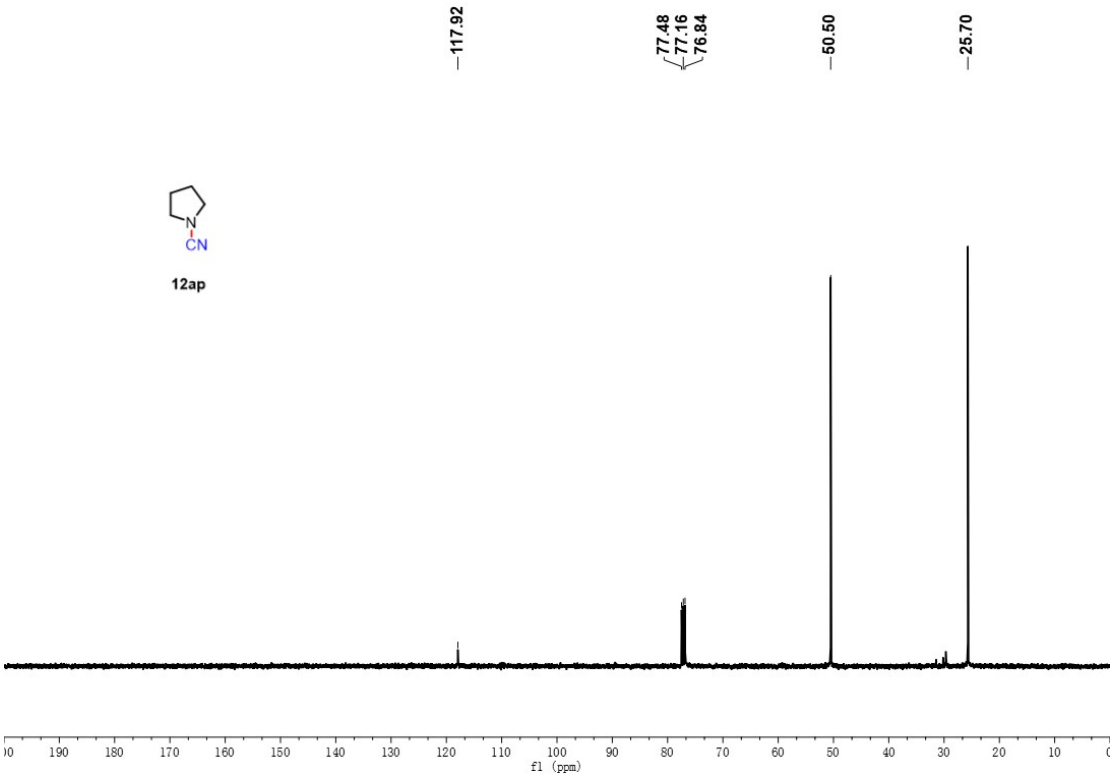
1.871
1.862
1.854
1.845
N
CN
12ap
4.00
4.09
fl (ppm)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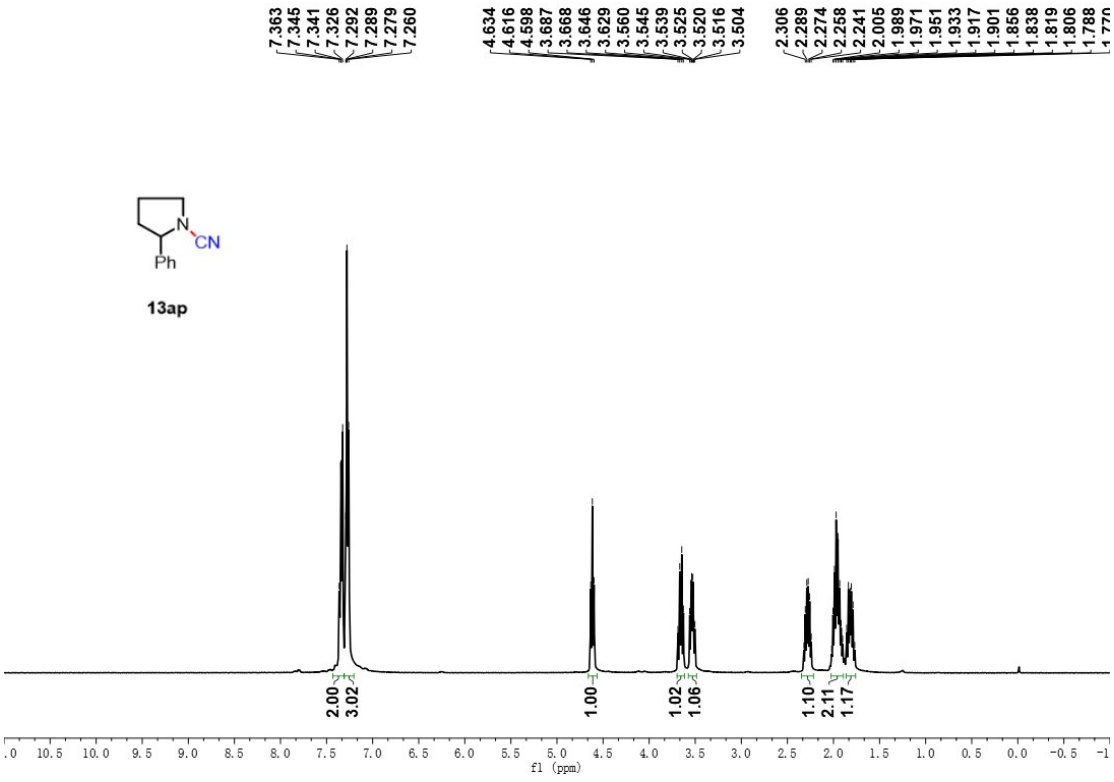
77.48
77.16
76.84
50.50
25.70
CN
12ap
f1 (ppm)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7.292
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7.279
7.260
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4.616
4.598
3.687
3.668
3.646
3.629
3.560
3.545
3.539
3.525
3.520
3.516
3.504
2.306
2.289
2.274
2.258
2.241
2.005
1.989
1.971
1.951
1.933
1.917
1.901
1.856
1.838
1.819
1.806
1.788
CN
Ph
13ap
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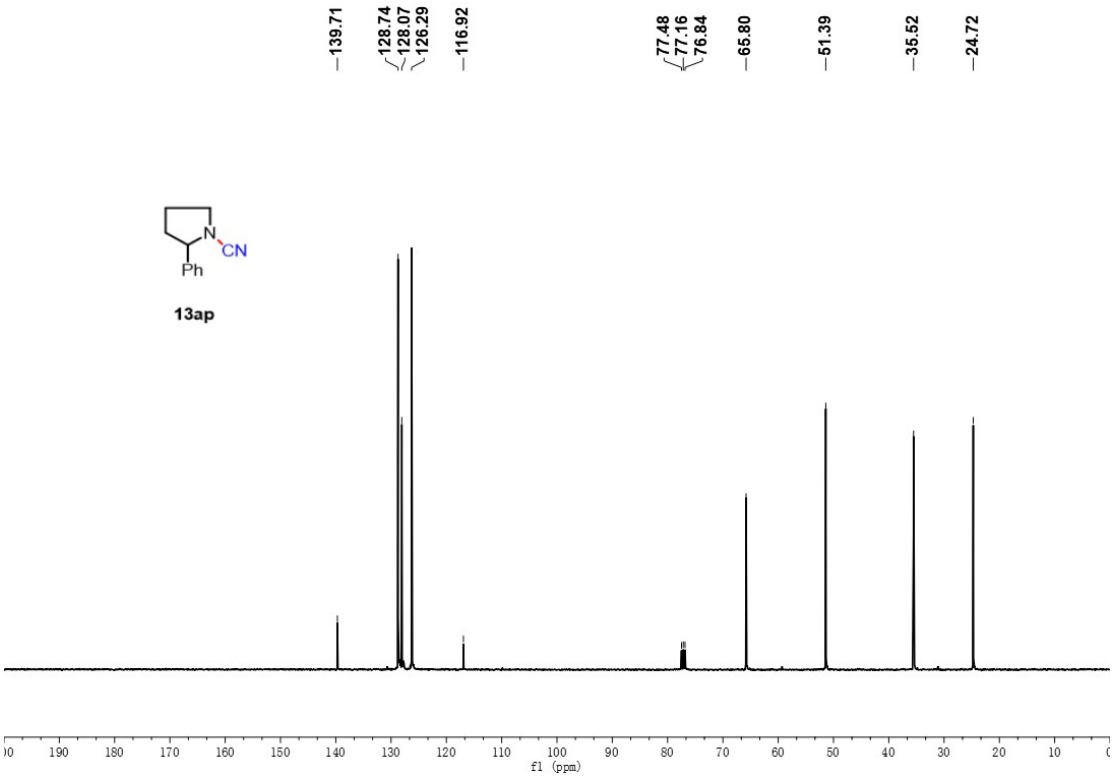
3.02
1.00
1.02
1.06
1.10
2.11
1.17
f1 (ppm)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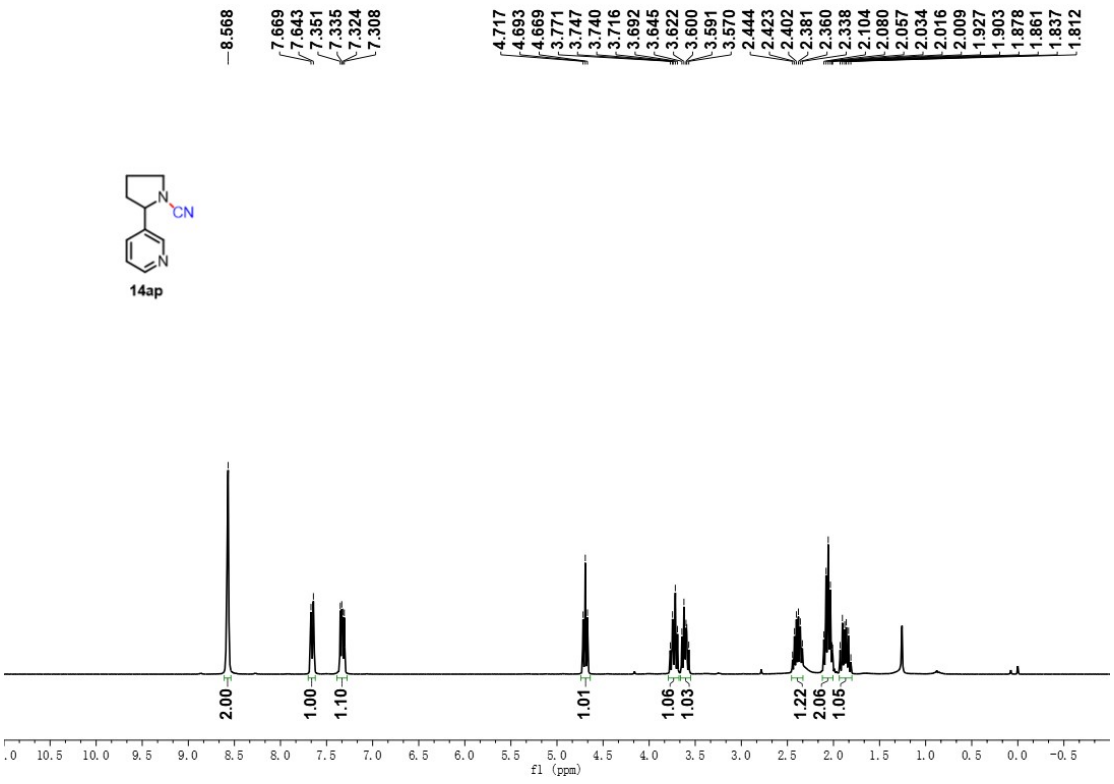
51.39
35.52
24.72
CN
Ph
13ap
f1 (ppm)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7.324
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4.717
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4.669
3.771
3.747
3.740
3.716
3.692
3.645
3.622
3.600
3.591
3.570
2.444
2.423
2.402
2.381
2.360
2.338
2.104
2.080
2.057
2.034
2.016
2.009
1.927
1.903
1.878
1.861
1.837
1.812
CN
N
14ap
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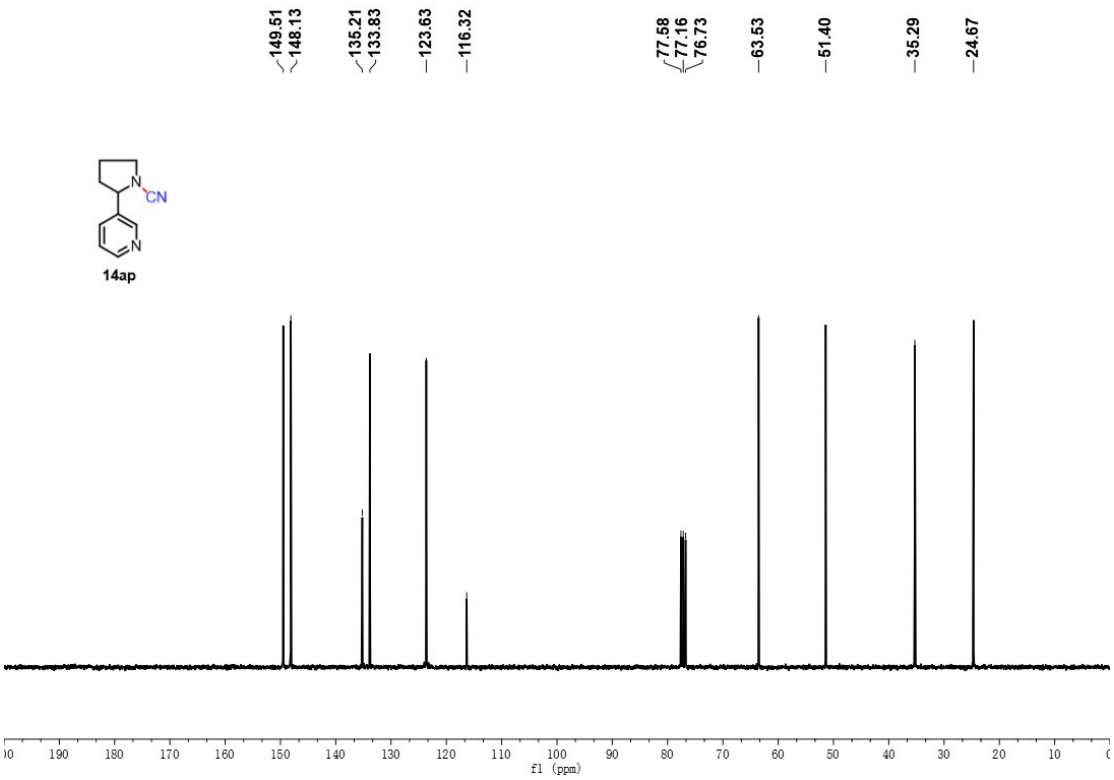
1.00
1.10
1.01
1.06
1.03
1.22
2.06
1.05
f1 (ppm)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135.21
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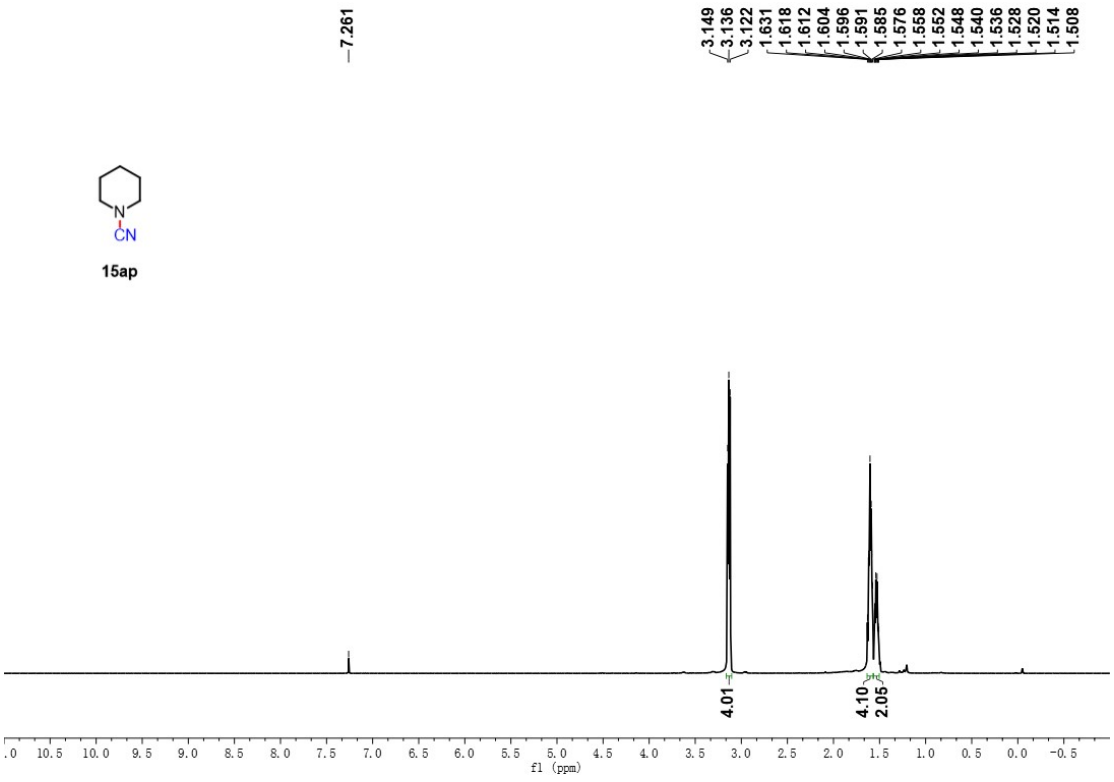
77.16
76.73
63.53
51.40
35.29
24.67
CN
N
14ap
f1 (ppm)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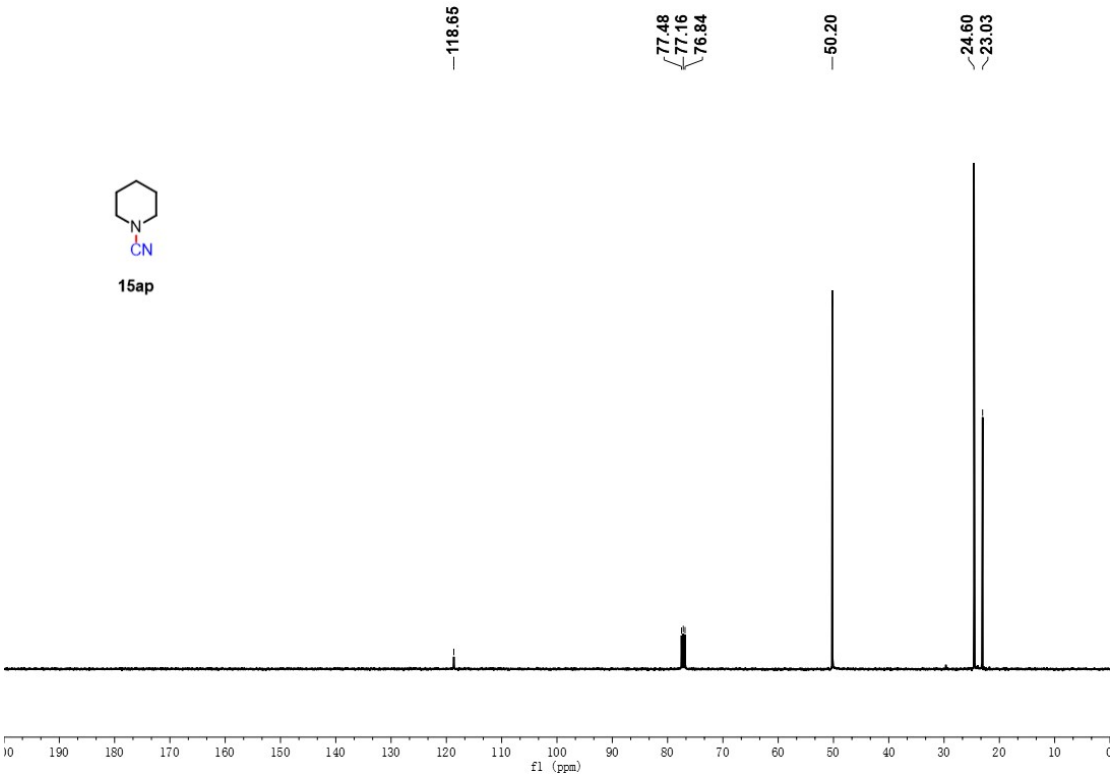
1.604
1.596
1.591
1.585
1.576
1.558
1.552
1.548
1.540
1.536
1.528
1.520
1.514
1.508
N
CN
15ap
4.01
4.10
2.05
f1 (ppm)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76.84
50.20
24.60
23.03
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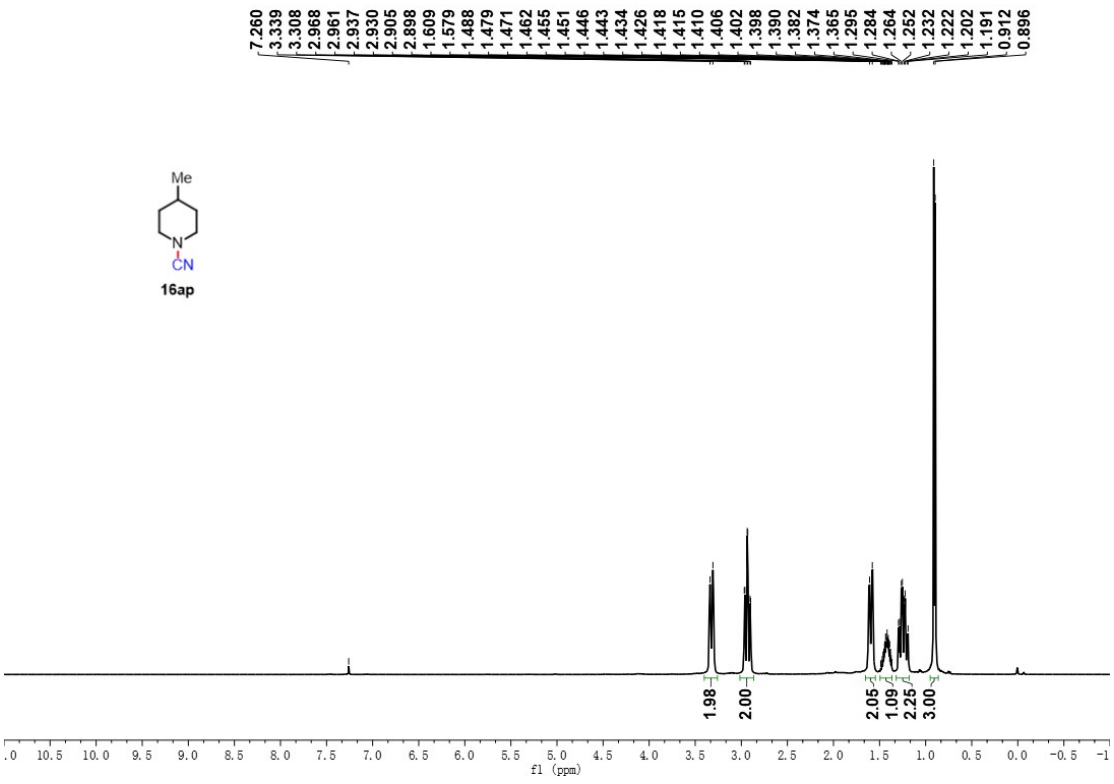
CN
15ap
f1 (ppm)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2.930
2.905
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1.488
1.479
1.471
1.462
1.455
1.451
1.446
1.443
1.434
1.426
1.418
1.415
1.410
1.406
1.402
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1.390
1.382
1.374
1.365
1.295
1.284
1.264
1.252
1.232
1.222
1.202
1.191
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Me
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CN
16ap
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1.09
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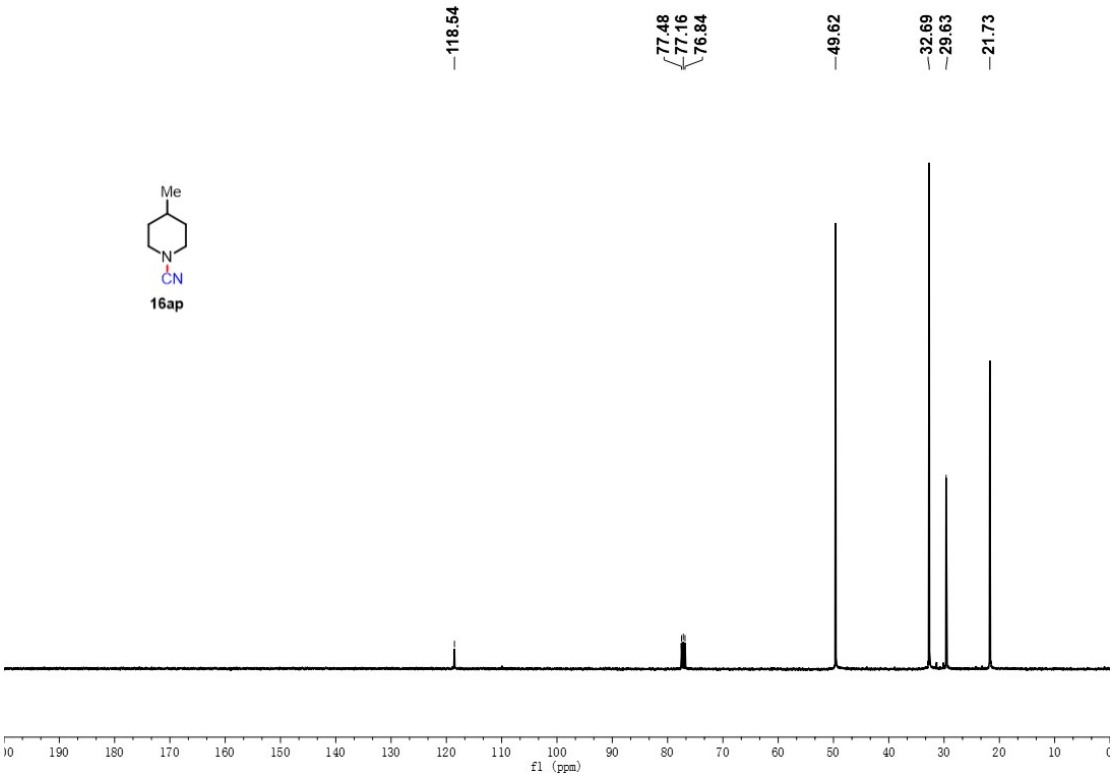
3.00
f1 (ppm)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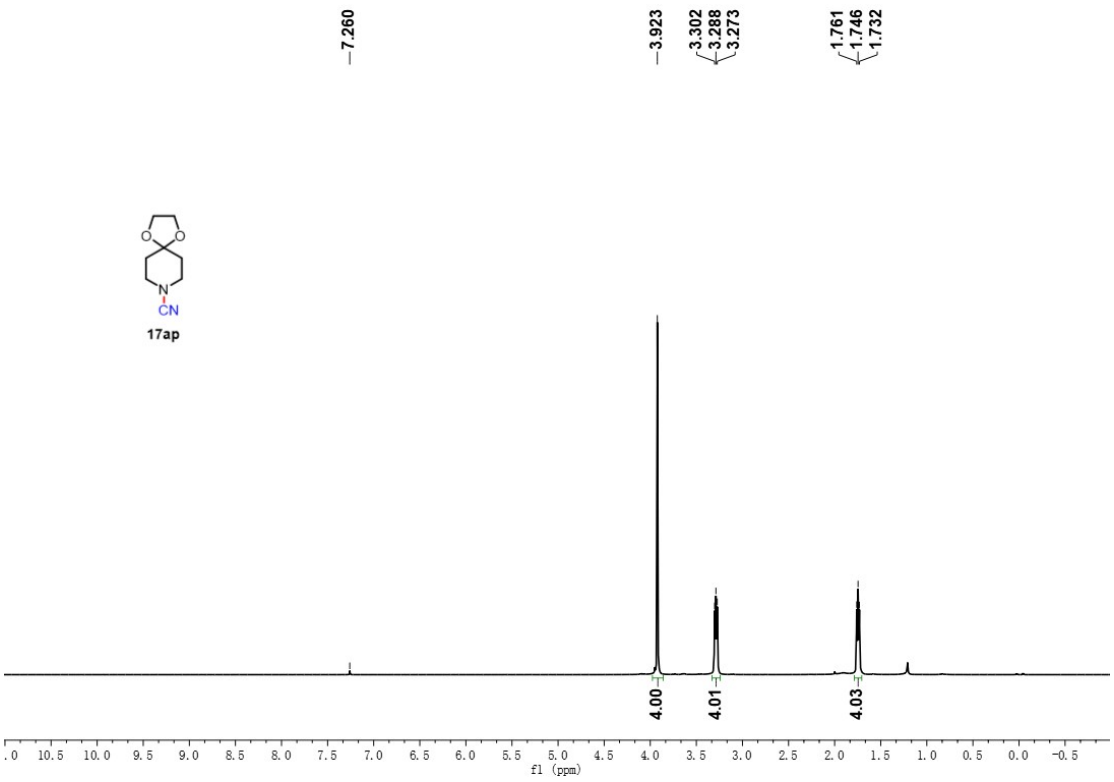
29.63
21.73
Me
N
CN
16ap
f1 (ppm)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1.746
1.732
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O
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17ap
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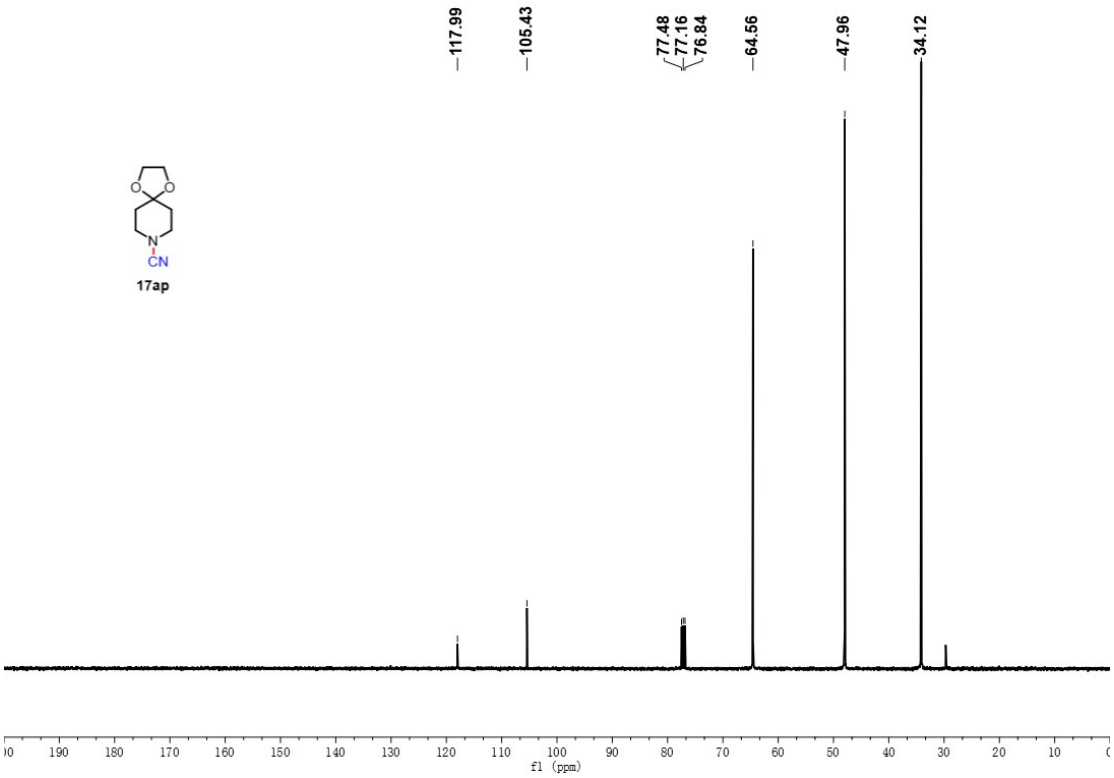
4.03
f1 (ppm)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64.56
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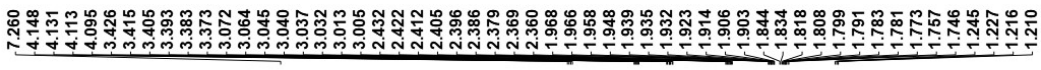
34.12
O
O
N
CN
17ap
fl (ppm)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3.383
3.373
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3.040
3.037
3.032
3.013
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2.422
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2.405
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1.939
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1.746
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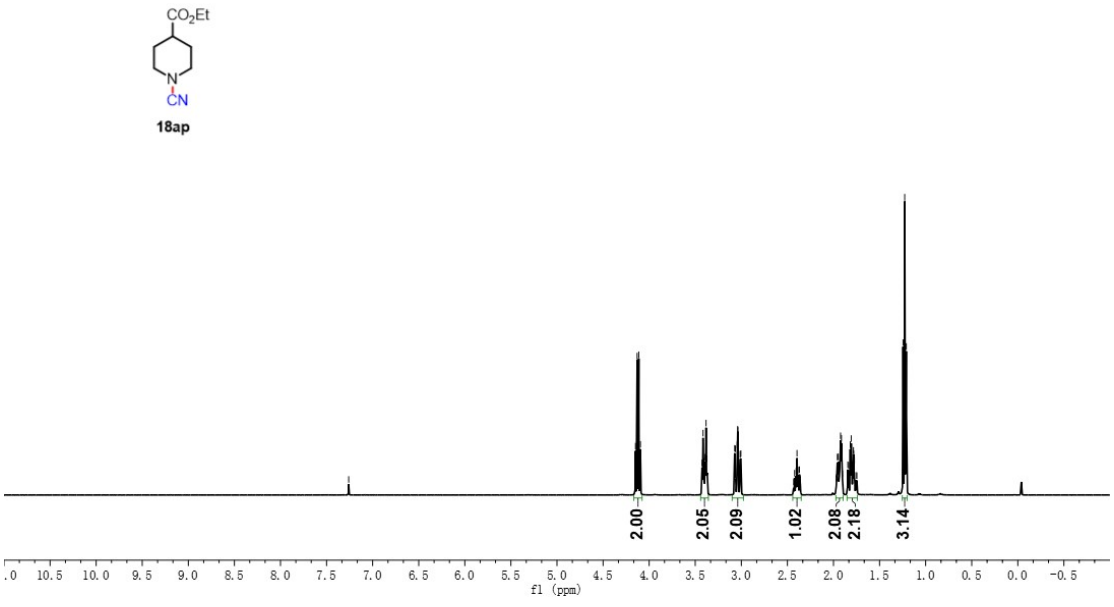
1.227
1.216
1.210


CO2Et
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CN
18ap
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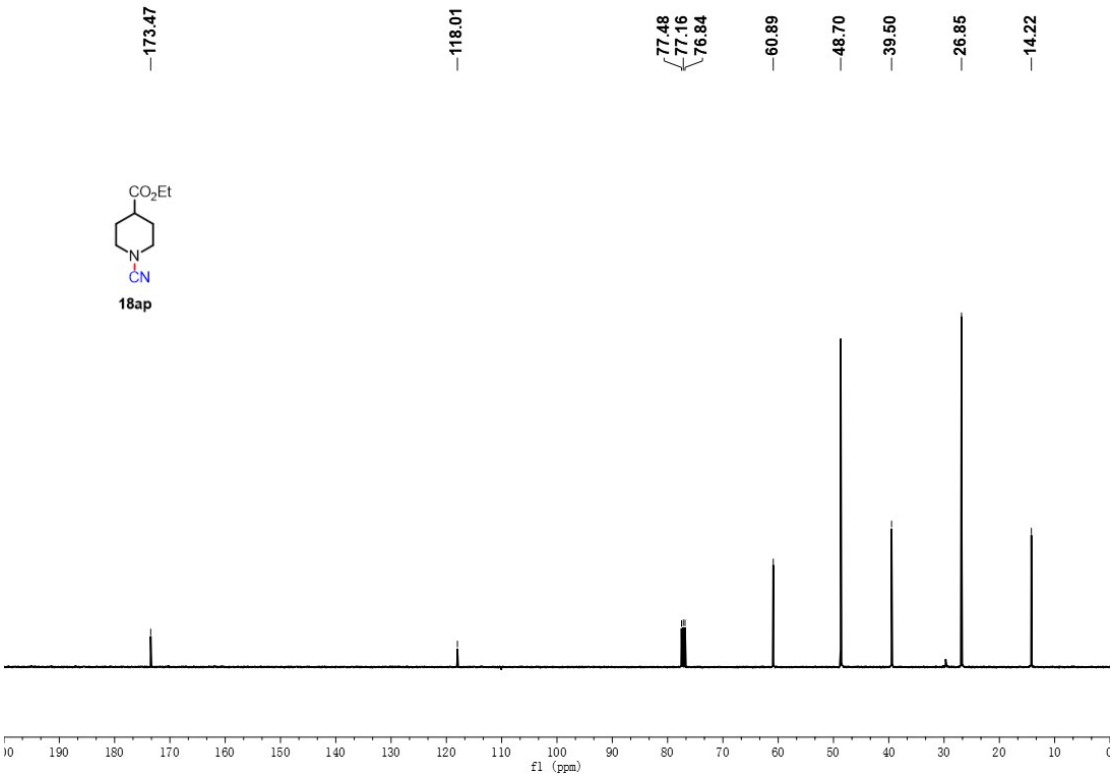
2.09
1.02
2.08
2.18
3.14
fl (ppm)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39.50
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CO2Et
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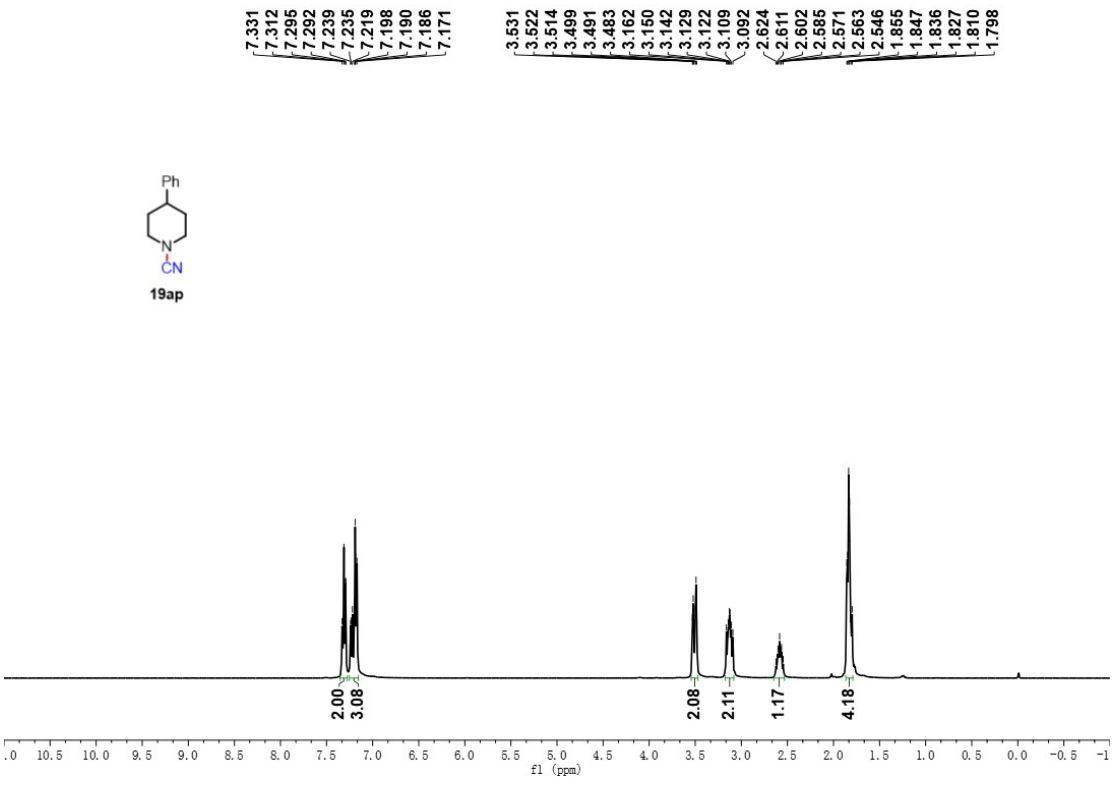
CN
18ap
f1 (ppm)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3.522
3.514
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2.563
2.546
1.855
1.847
1.836
1.827
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CN
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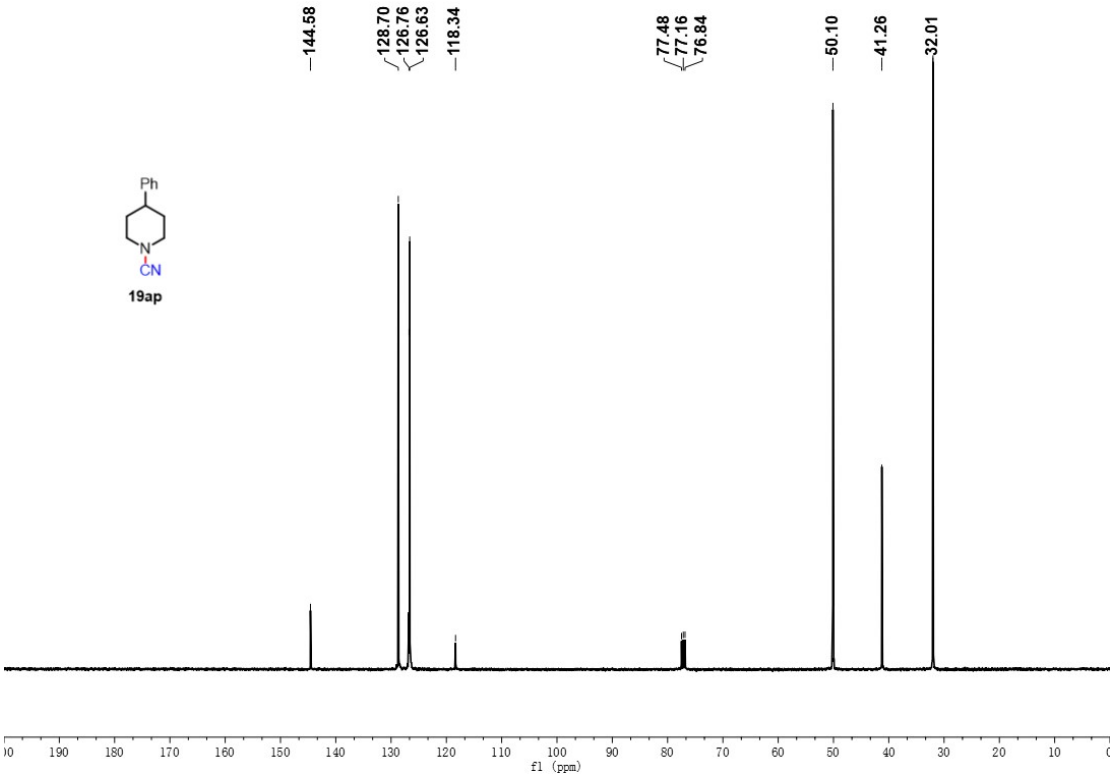
3.08
2.08
2.11
1.17
4.18
f1 (ppm)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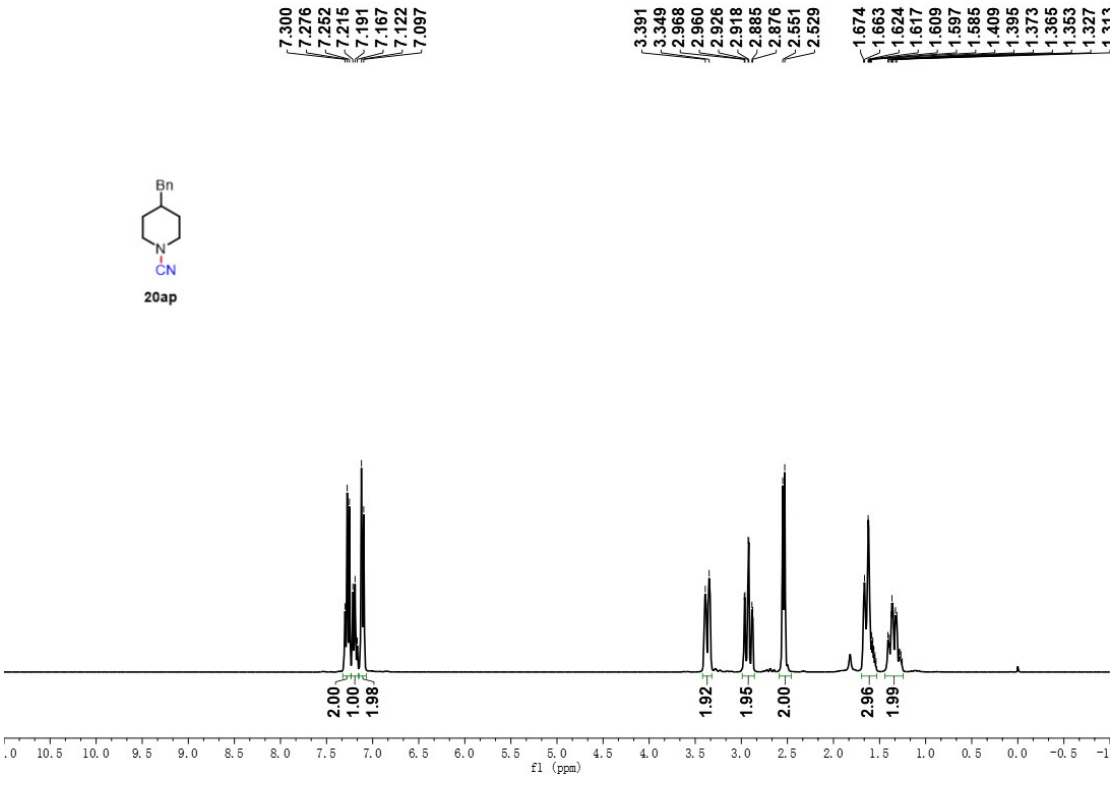
41.26
32.01
Ph
N
CN
19ap
f1 (ppm)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2.918
2.885
2.876
2.551
2.529
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1.663
1.624
1.617
1.609
1.597
1.585
1.409
1.395
1.373
1.365
1.353
1.327
Bn
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20ap
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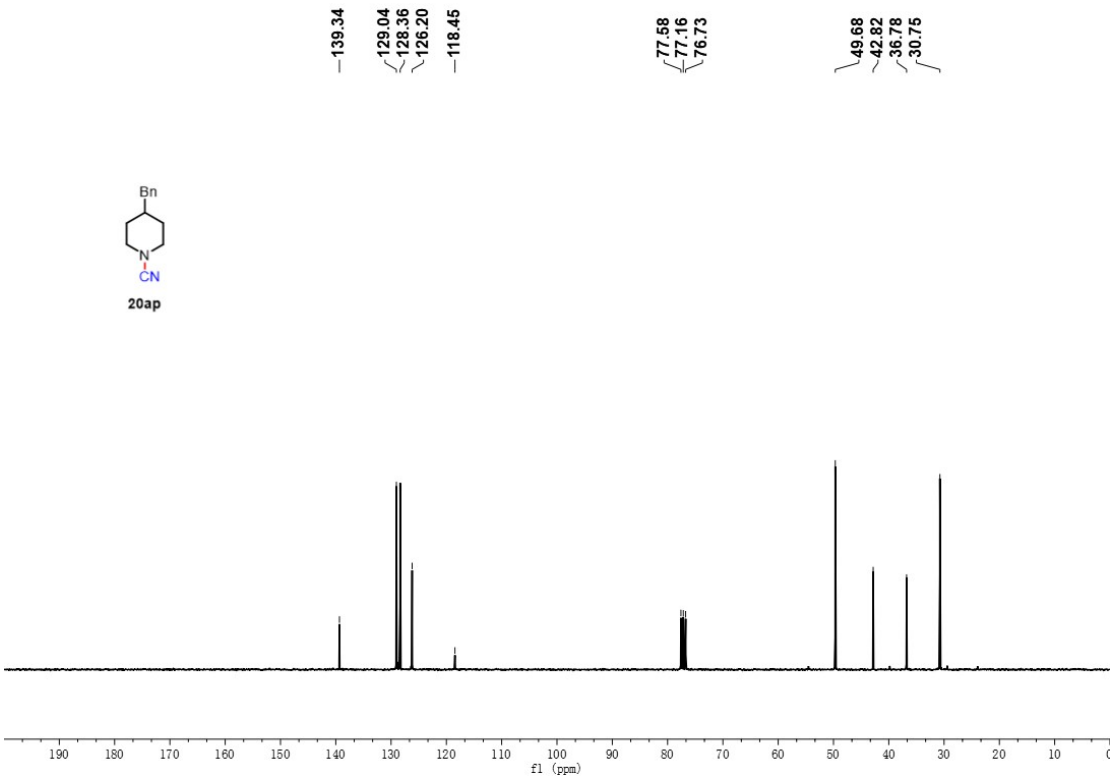
1.92
1.95
2.00
2.96
1.99
f1 (ppm)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42.82
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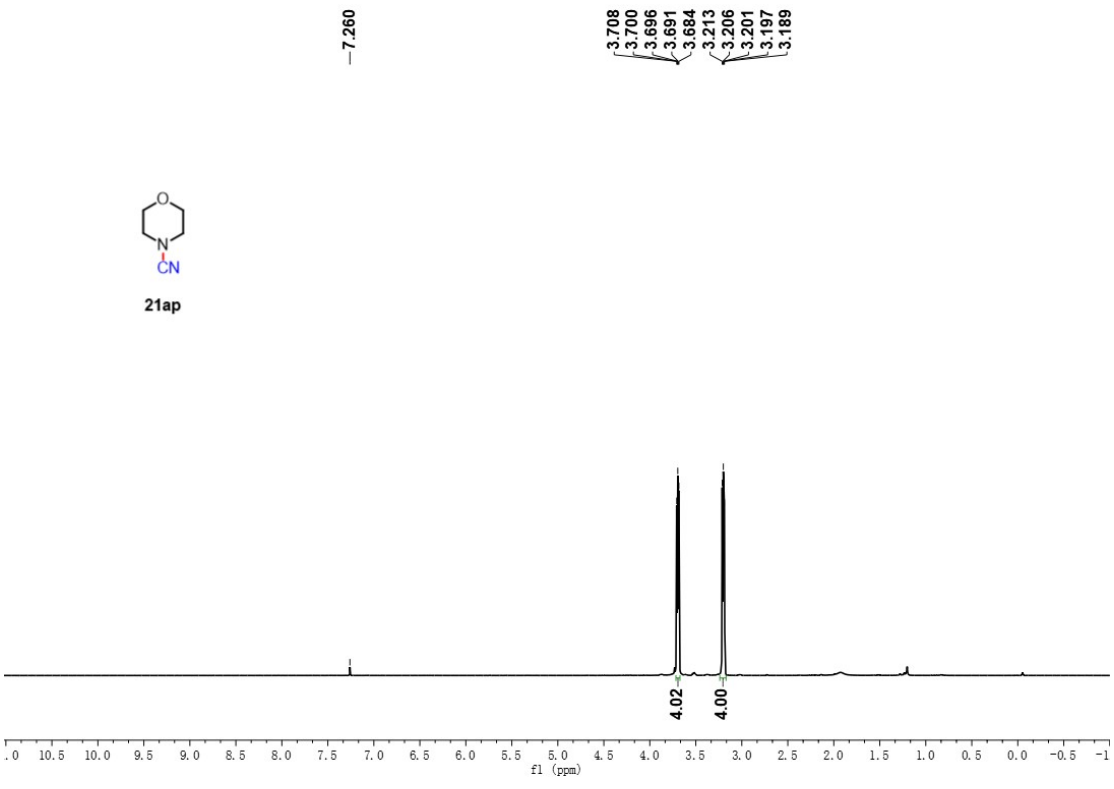
Bn
N
CN
20ap
f1 (ppm)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O
N
CN
21ap
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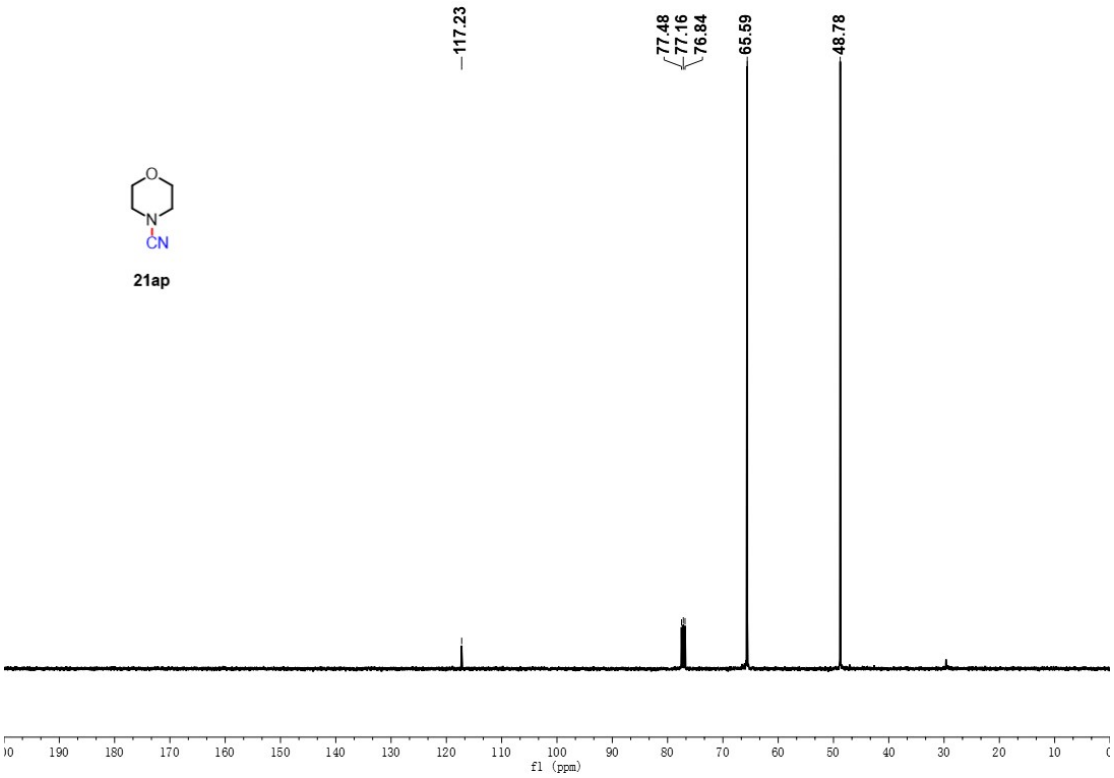
4.00
f1 (ppm)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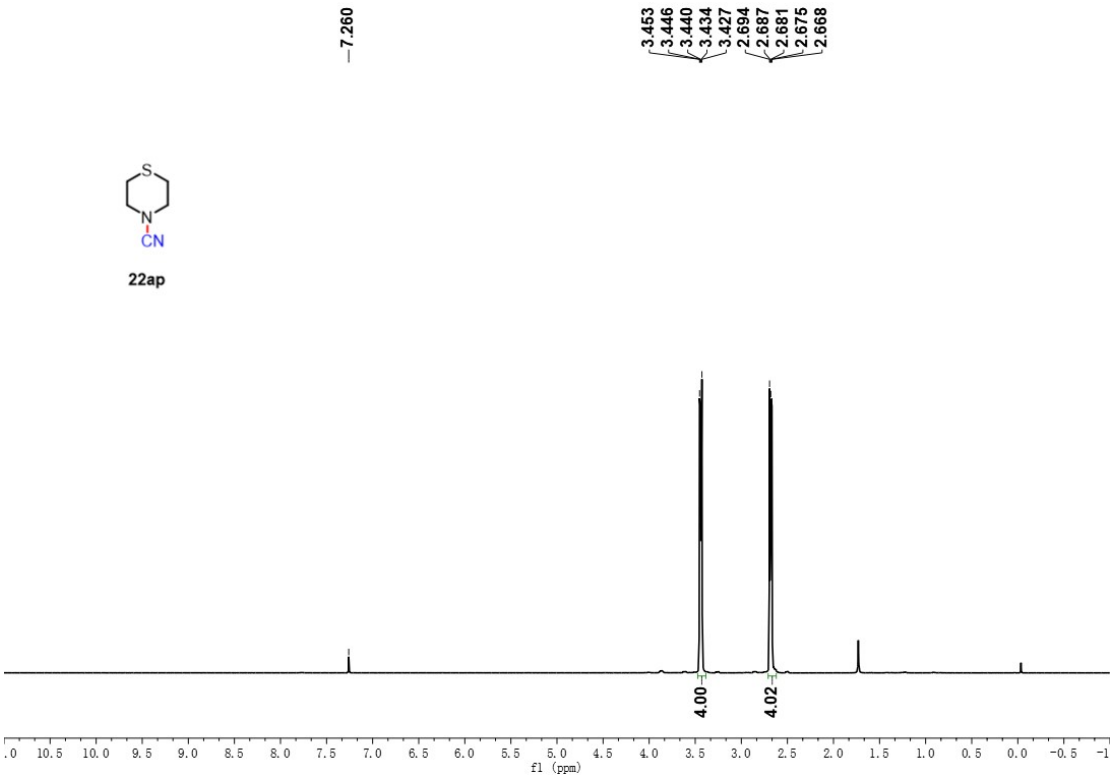
76.84
65.59
48.78
O
N
CN
21ap
f1 (ppm)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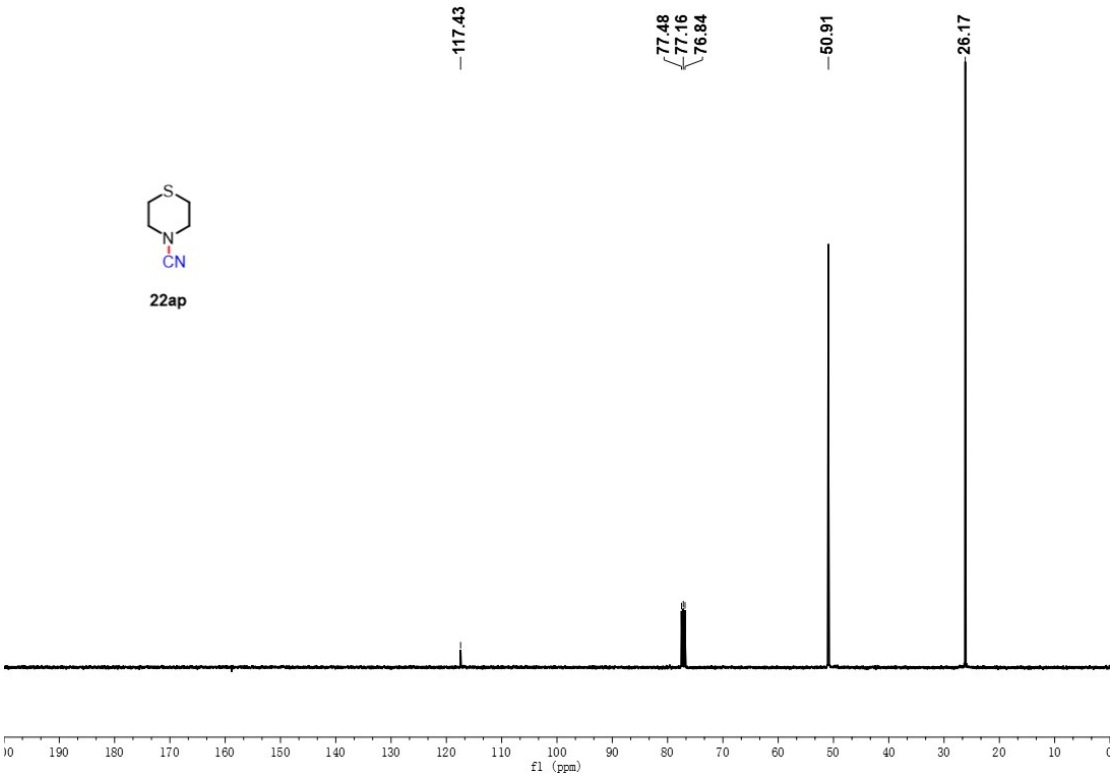
CN
22ap
4.00
4.02
f1 (ppm)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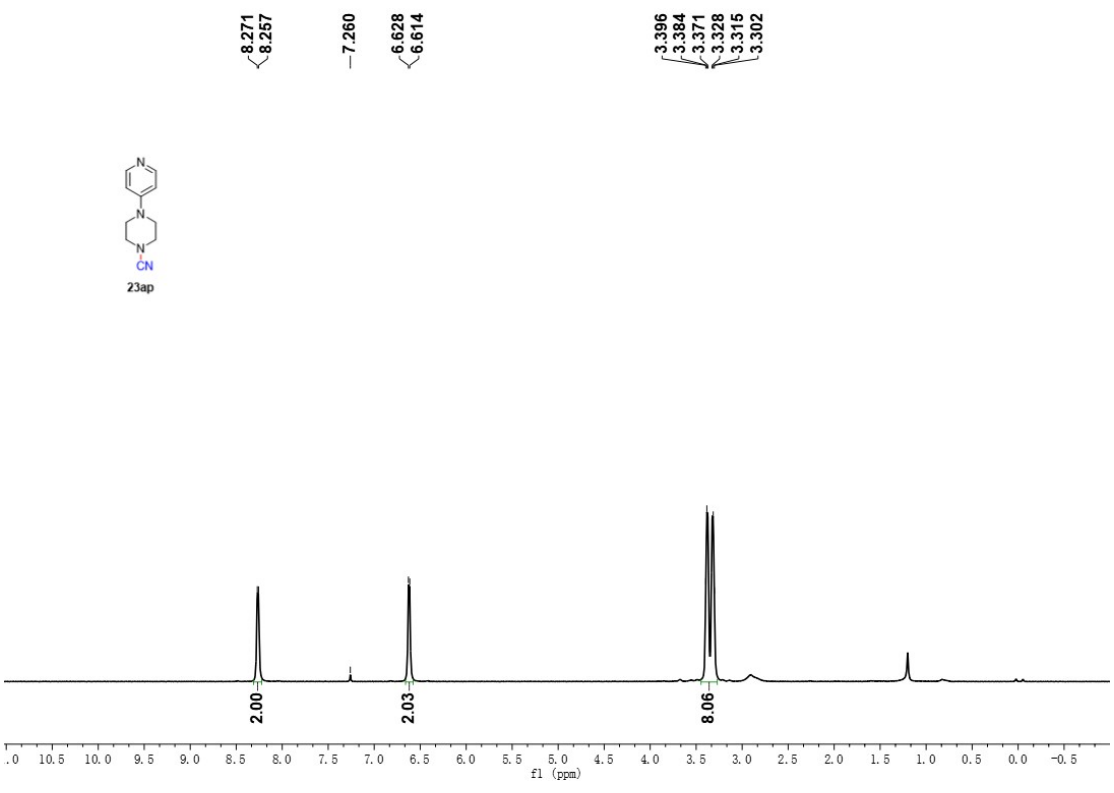
26.17
22ap
f1 (ppm)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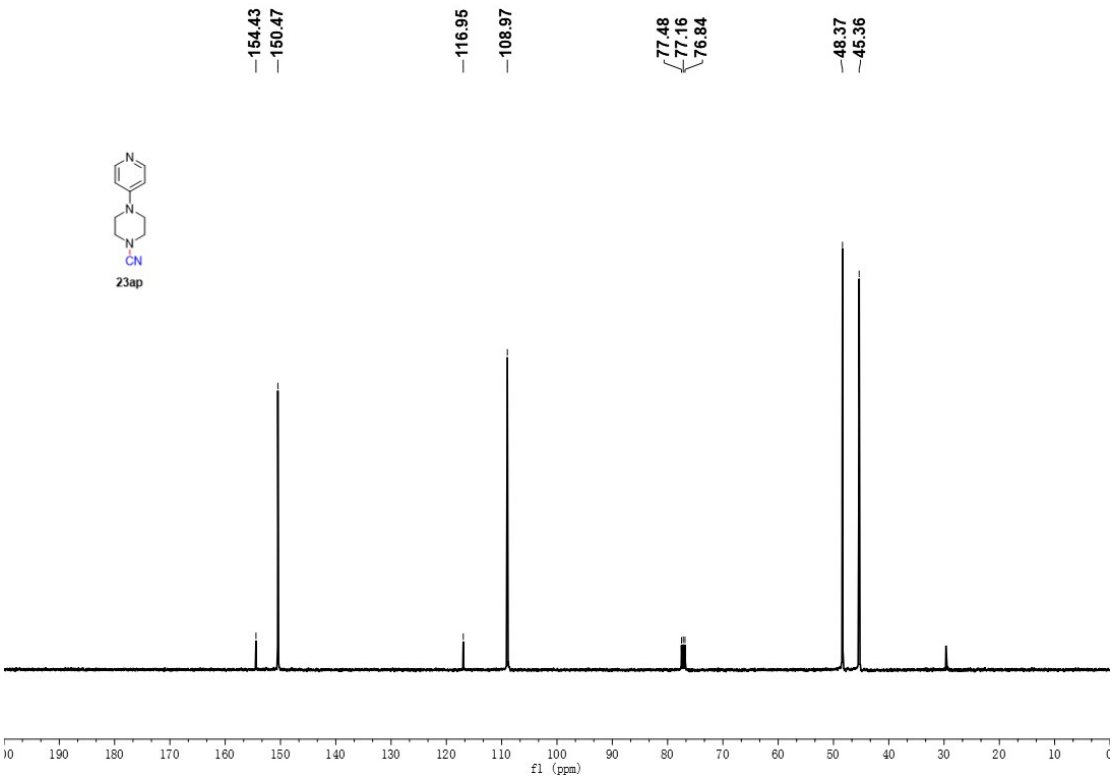
8.257
7.260
6.628
6.614
3.396
3.384
3.371
3.328
3.315
3.302
23ap
2.00
2.03
8.06
f1 (ppm)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150.47
116.95
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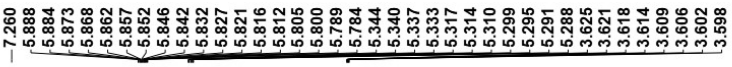
77.48
77.16
76.84
48.37
45.36
23ap
f1 (ppm)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5.888
5.884
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5.852
5.846
5.842
5.832
5.827
5.821
5.816
5.812
5.805
5.800
5.789
5.784
5.344
5.340
5.337
5.333
5.317
5.314
5.310
5.299
5.295
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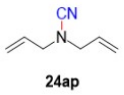
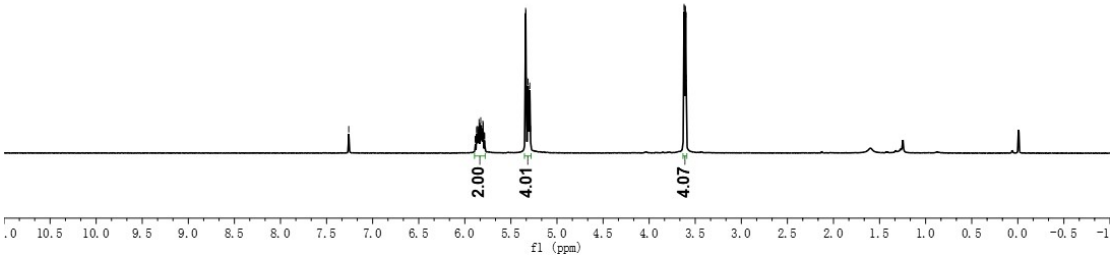
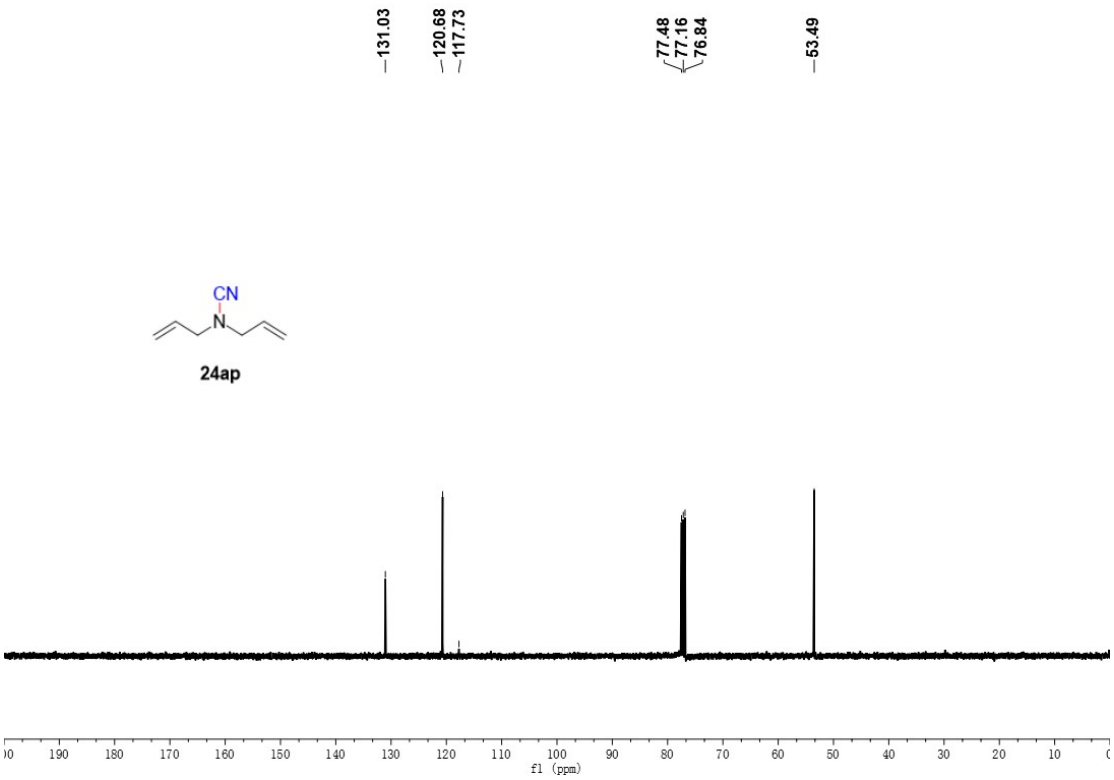
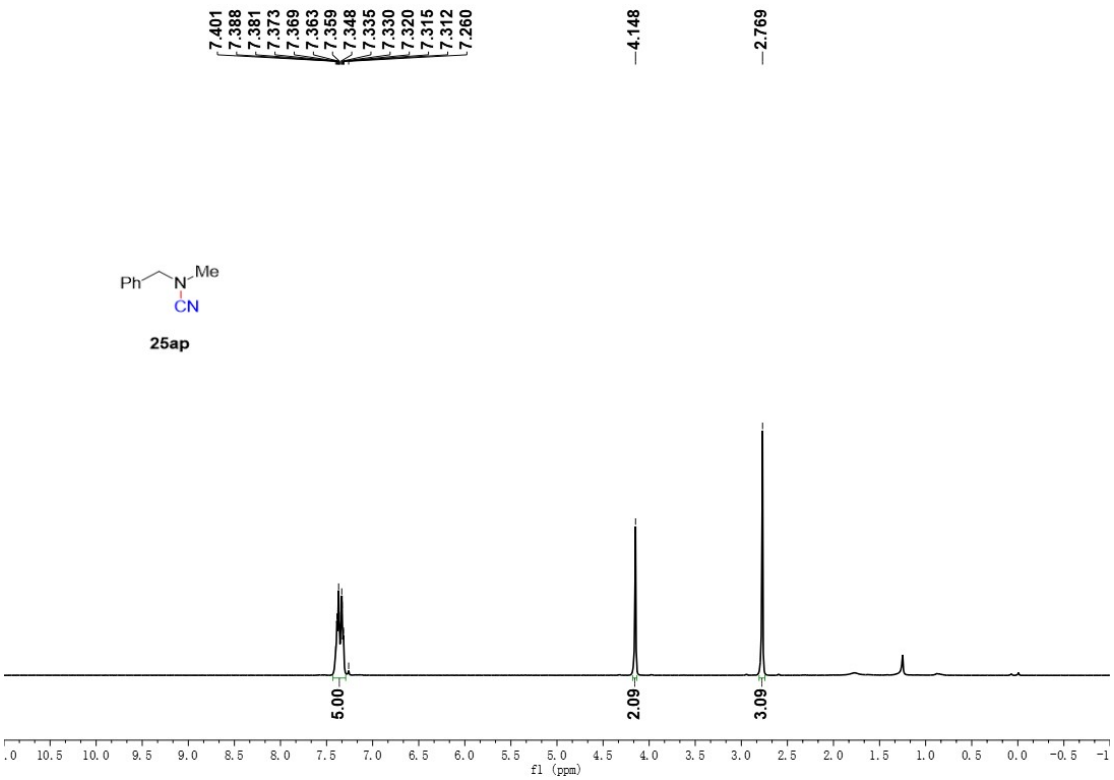
5.288
3.625
3.621
3.618
3.614
3.609
3.606
3.602
3.598


CN
N
24ap


2.00
4.01
4.07
f1 (ppm)


131.03
120.68
117.73
77.48
77.16
76.84
53.49
CN
N
24ap
f1 (ppm)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7.388
7.381
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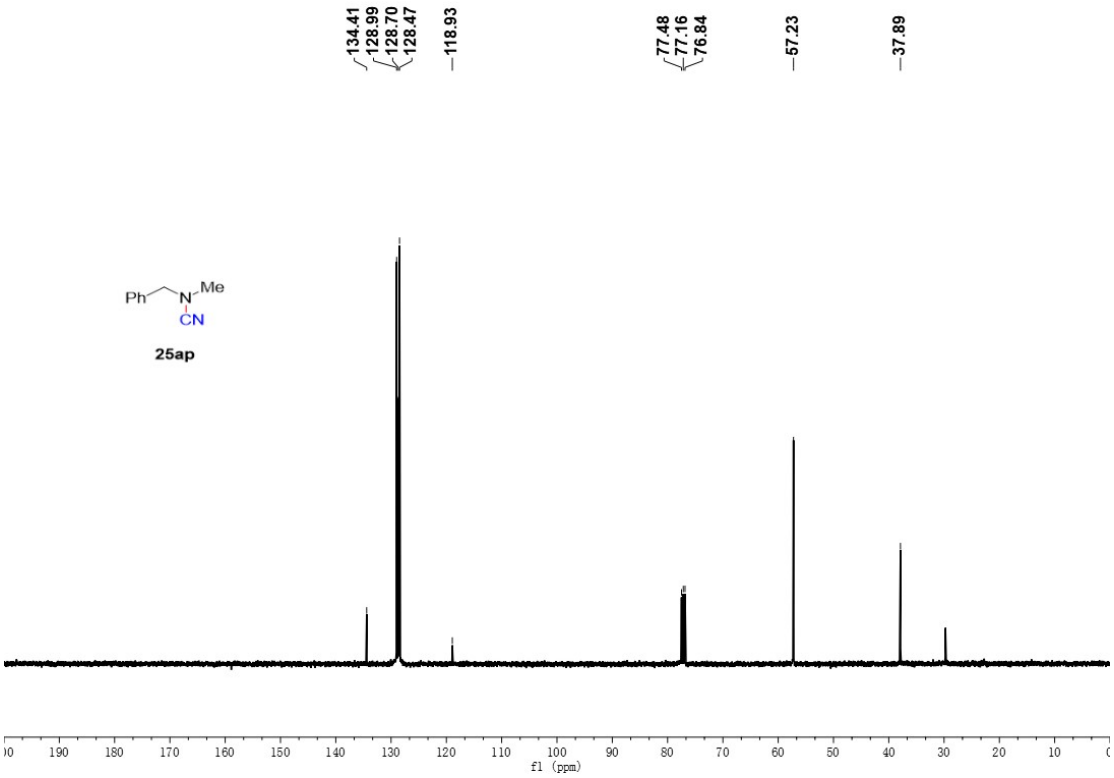
7.363
7.359
7.348
7.335
7.330
7.320
7.315
7.312
7.260
4.148
2.769
Ph
N
Me
CN
25ap
5.00
2.09
3.09
f1 (ppm)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128.99
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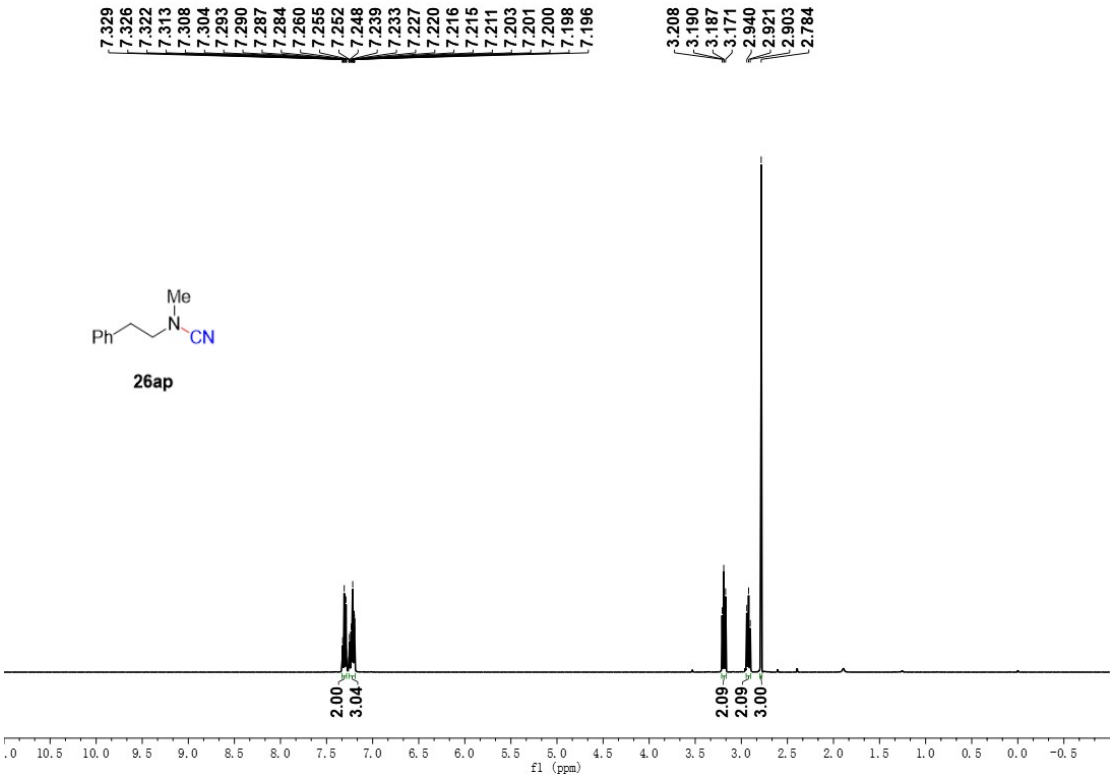
77.48
77.16
76.84
57.23
37.89
Ph
N
Me
CN
25ap
f1 (ppm)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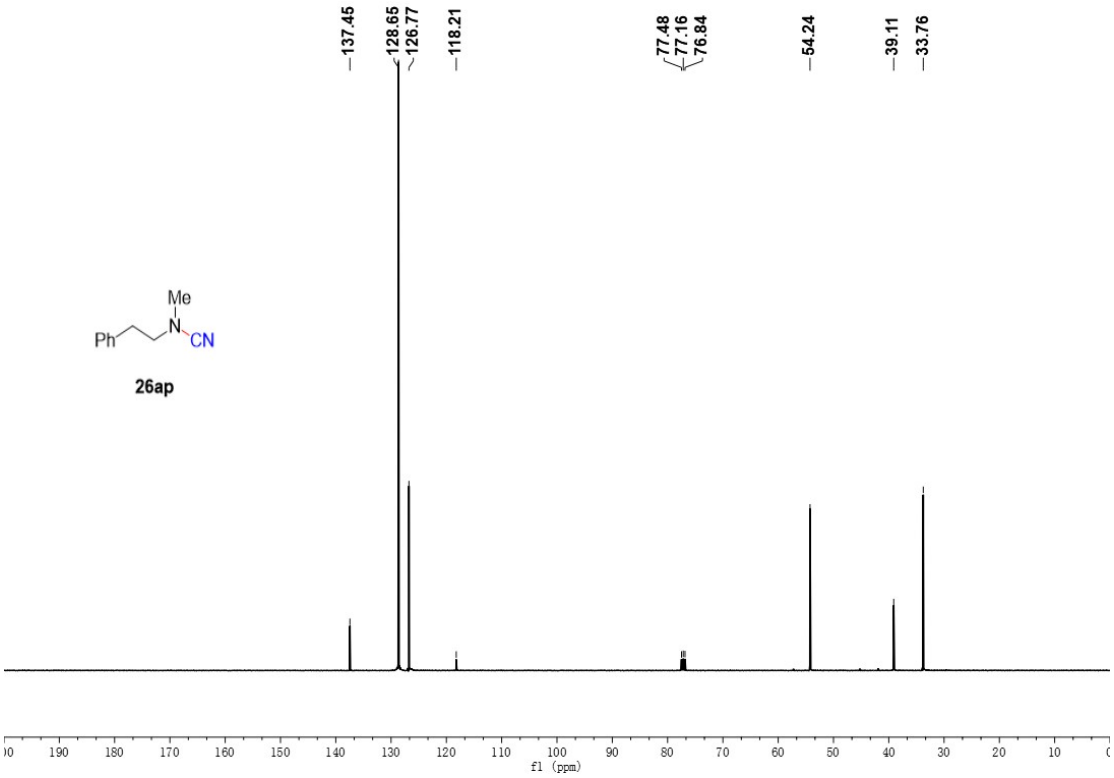
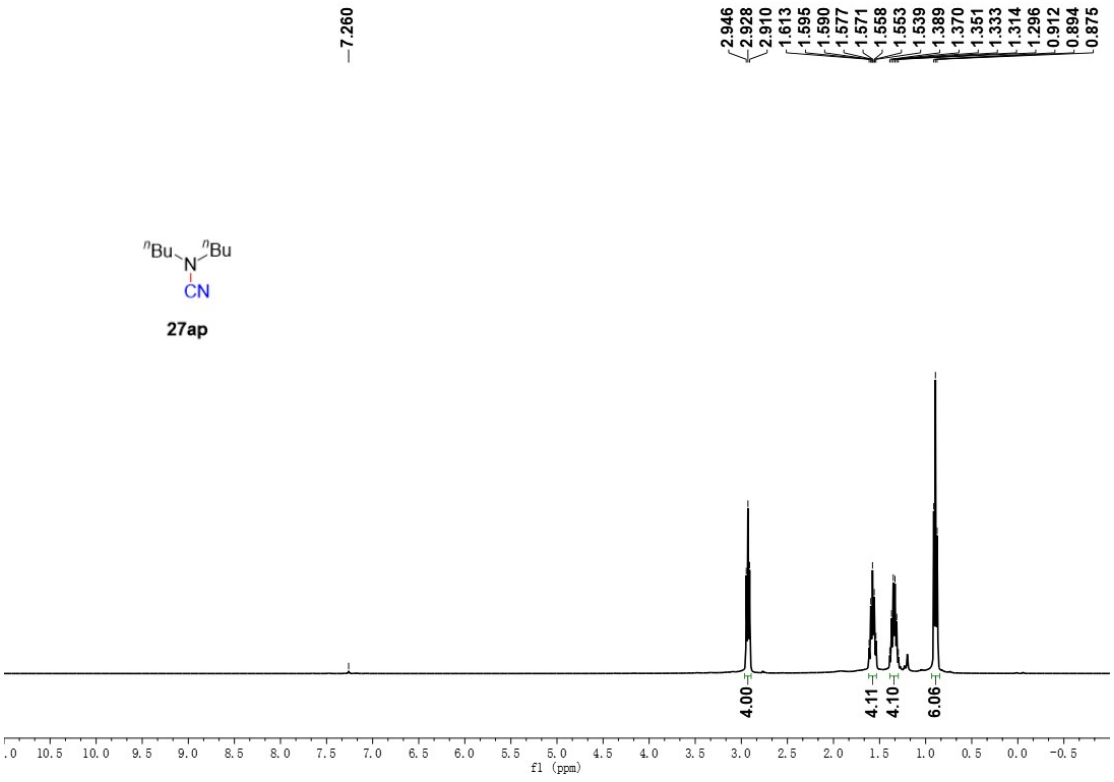
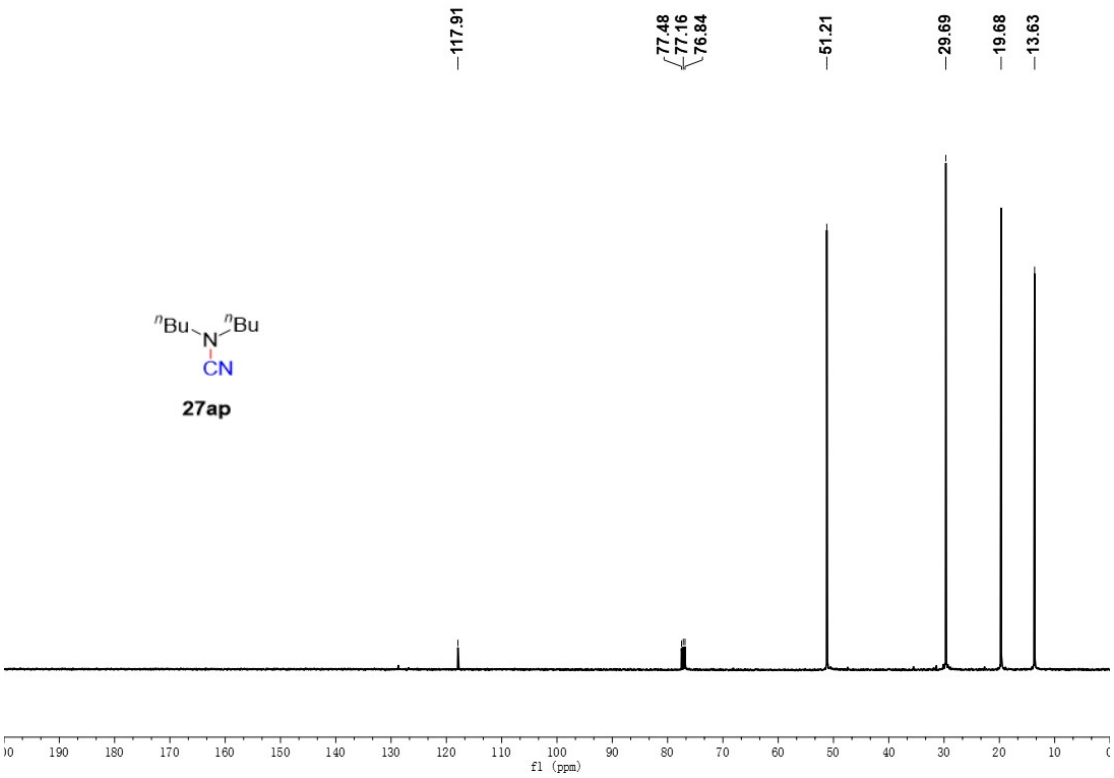
7.304
7.293
7.290
7.287
7.284
7.260
7.255
7.252
7.248
7.239
7.233
7.227
7.220
7.216
7.215
7.211
7.203
7.201
7.200
7.198
7.196
3.208
3.190
3.187
3.171
2.940
2.921
2.903
2.784
Me
N
Ph
CN
26ap
2.00
3.04
2.09
2.09
3.00
f1 (ppm)


137.45
128.65
126.77
118.21
77.48
77.16
76.84
54.24
39.11
33.76
Me
N
Ph
CN
26ap
f1 (ppm)


7.260
2.946
2.928
2.910
1.613
1.595
1.590
1.577
1.571
1.558
1.553
1.539
1.389
1.370
1.351
1.333
1.314
1.296
0.912
0.894
0.875
nBu
N
nBu
CN
27ap
4.00
4.11
4.10
6.06
f1 (ppm)


117.91
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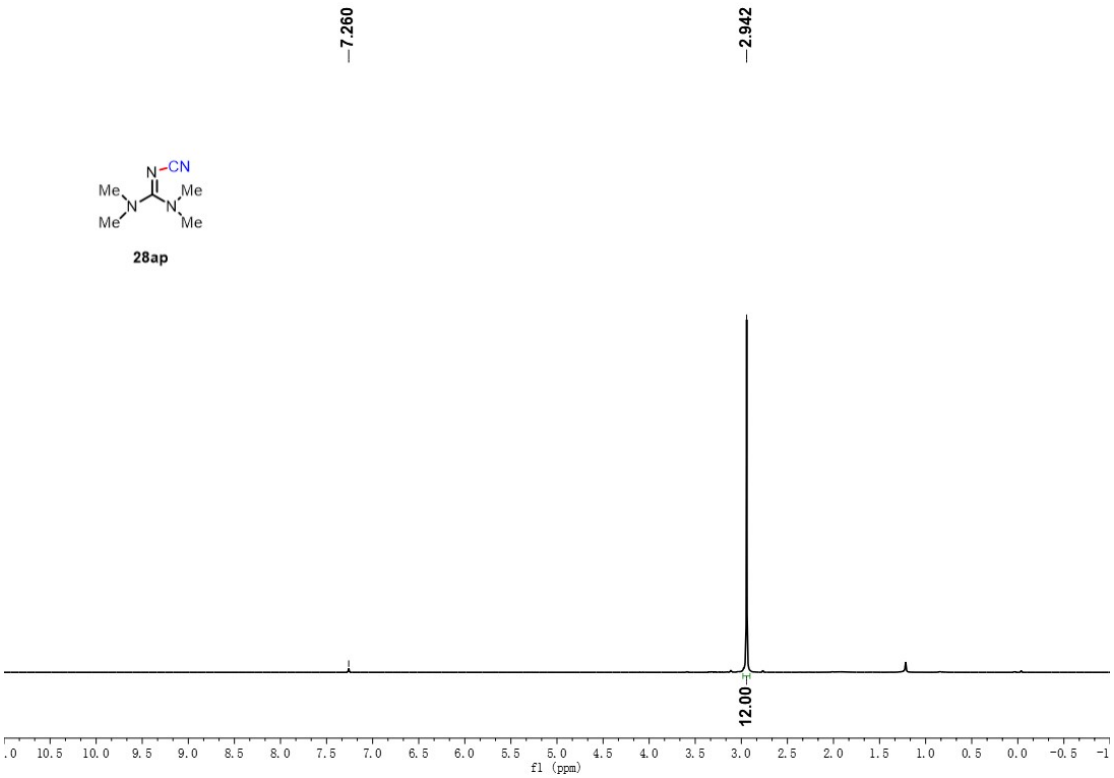
77.16
76.84
51.21
29.69
19.68
13.63
nBu
nBu
N
CN
27ap
f1 (ppm)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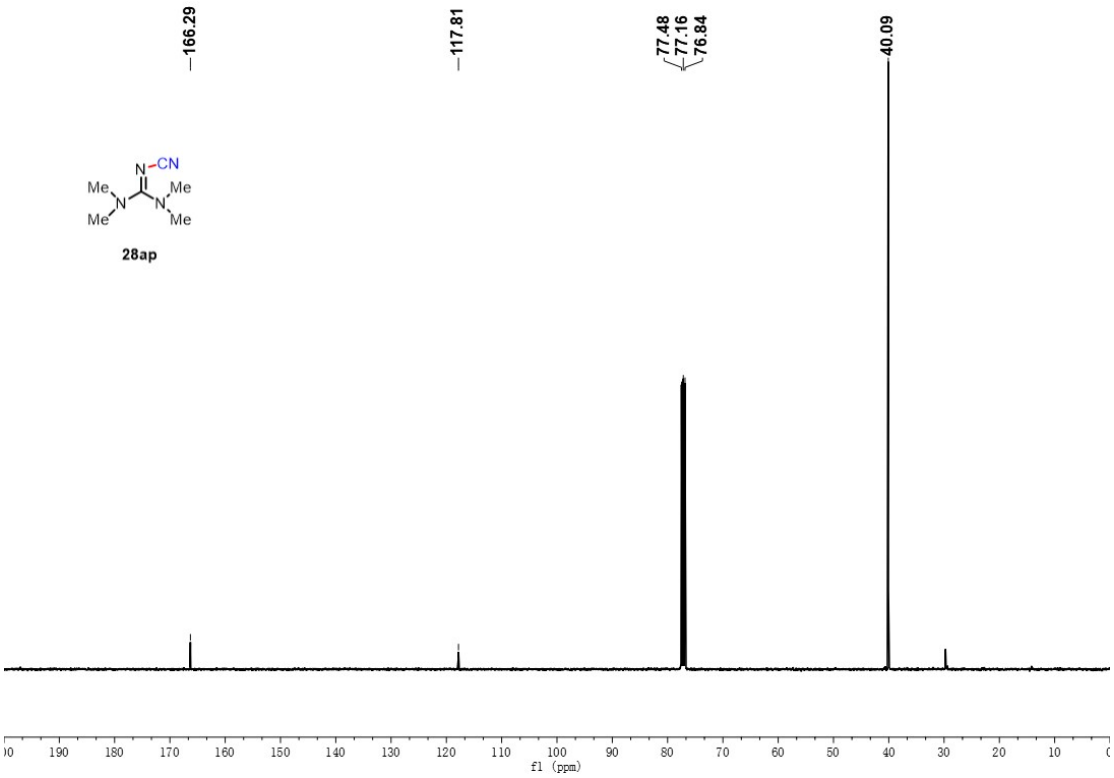
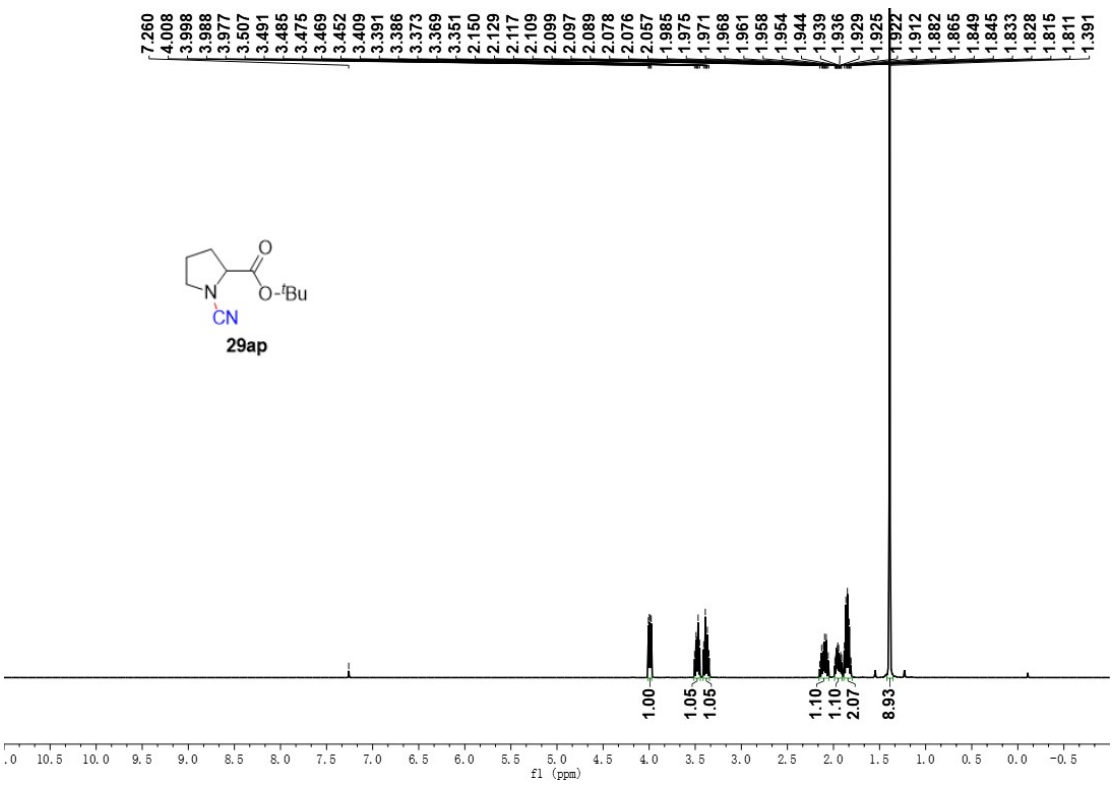
2.942
N-CN
Me
Me
N
N
Me
Me
28ap
12.00
f1 (ppm)


166.29
117.81
77.48
77.16
76.84
40.09
N-CN
Me
Me
N
N
Me
Me
28ap
f1 (ppm)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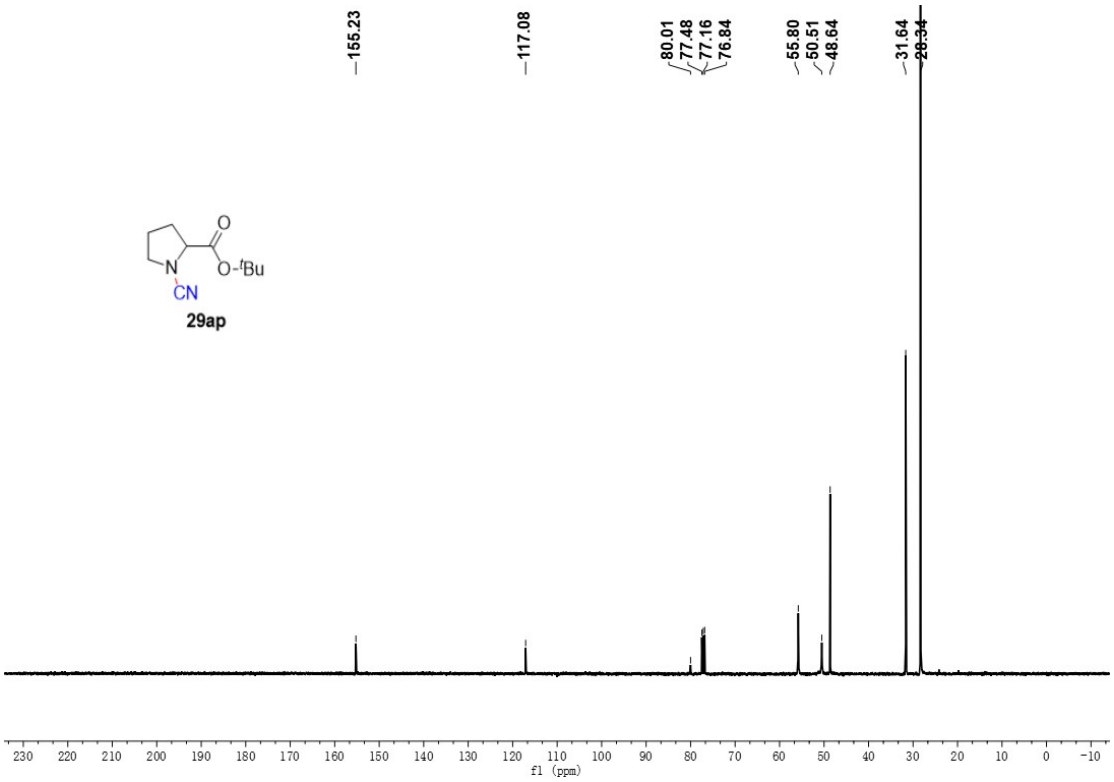
3.998
3.988
3.977
3.507
3.491
3.485
3.475
3.469
3.452
3.409
3.391
3.386
3.373
3.369
3.351
2.150
2.129
2.117
2.109
2.099
2.097
2.089
2.078
2.076
2.057
1.985
1.975
1.971
1.968
1.961
1.958
1.954
1.944
1.939
1.936
1.929
1.925
1.922
1.912
1.882
1.865
1.849
1.845
1.833
1.828
1.815
1.811
1.391
O
O-tBu
N
CN
29ap
1.00
1.05
1.05
1.10
1.10
2.07
8.93
f1 (ppm)


155.23
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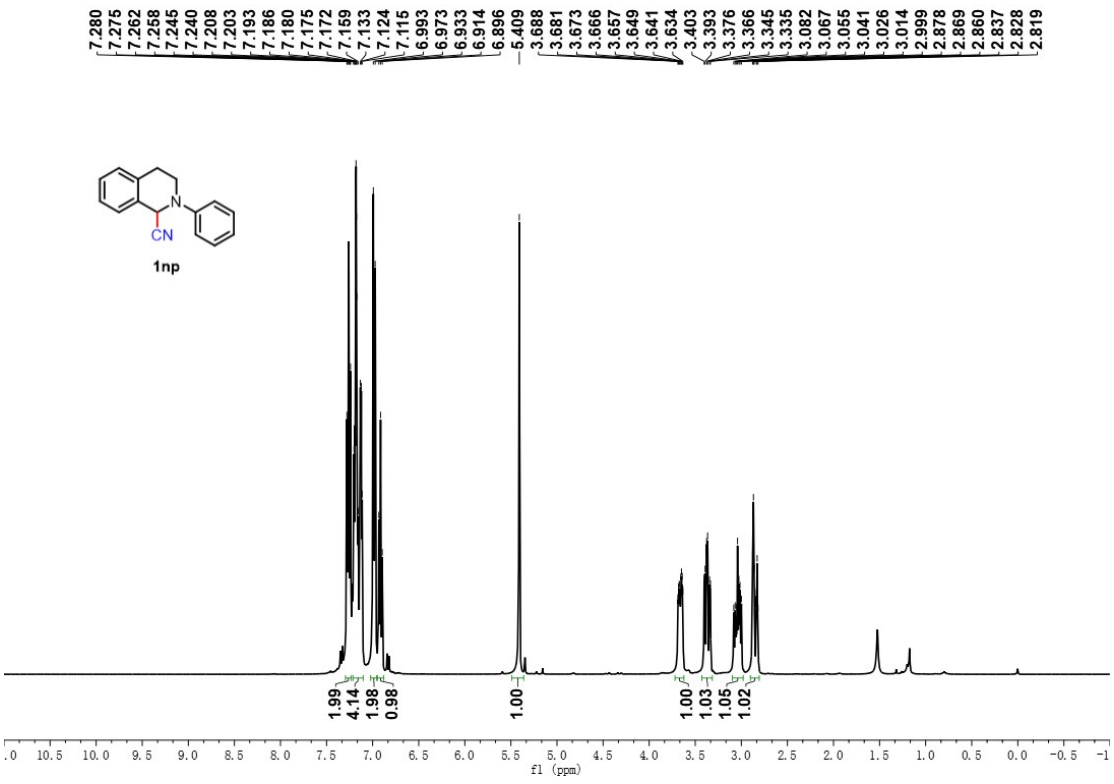
80.01
77.48
77.16
76.84
55.80
50.51
48.64
31.64
28.34
O
O-tBu
N
CN
29ap
fl (ppm)


7.280
7.275
7.262
7.258
7.245
7.240
7.208
7.203
7.193
7.186
7.180
7.175
7.172
7.159
7.133
7.124
7.115
6.993
6.973
6.933
6.914
6.896
5.409
3.688
3.681
3.673
3.666
3.657
3.649
3.641
3.634
3.403
3.393
3.376
3.366
3.345
3.335
3.082
3.067
3.055
3.041
3.026
3.014
2.999
2.878
2.869
2.860
2.837
2.828
2.819
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CN
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4.14
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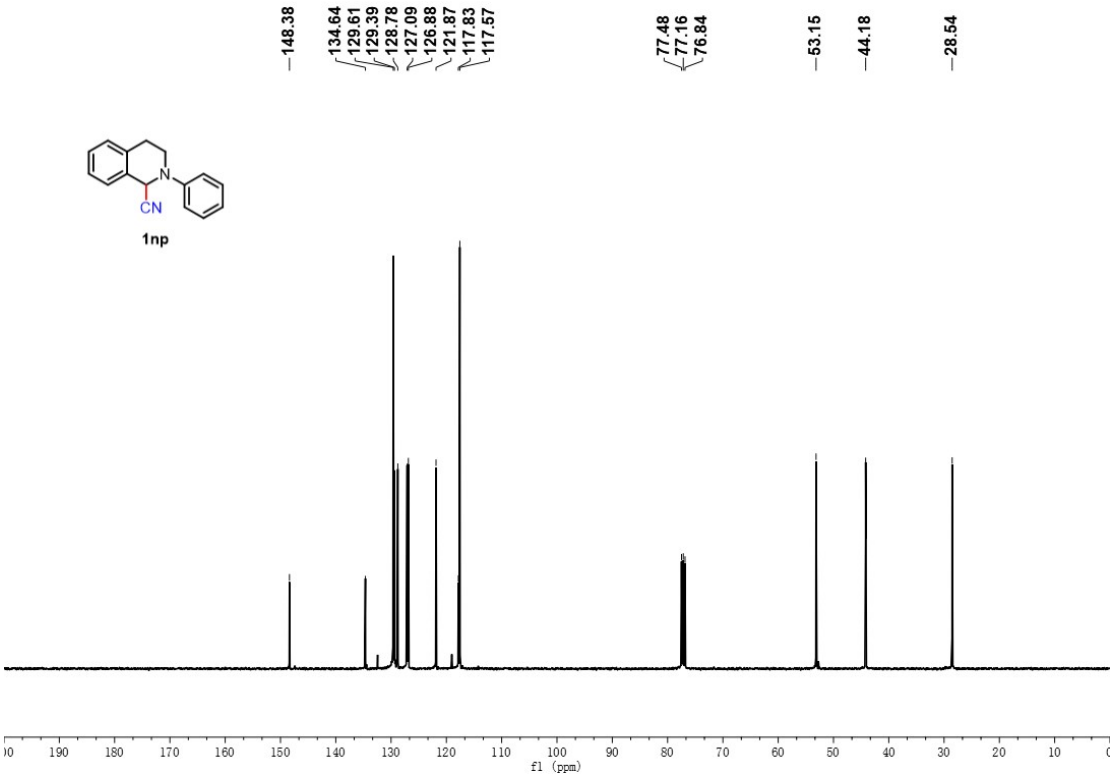
0.98
1.00
1.00
1.03
1.05
1.02
fl (ppm)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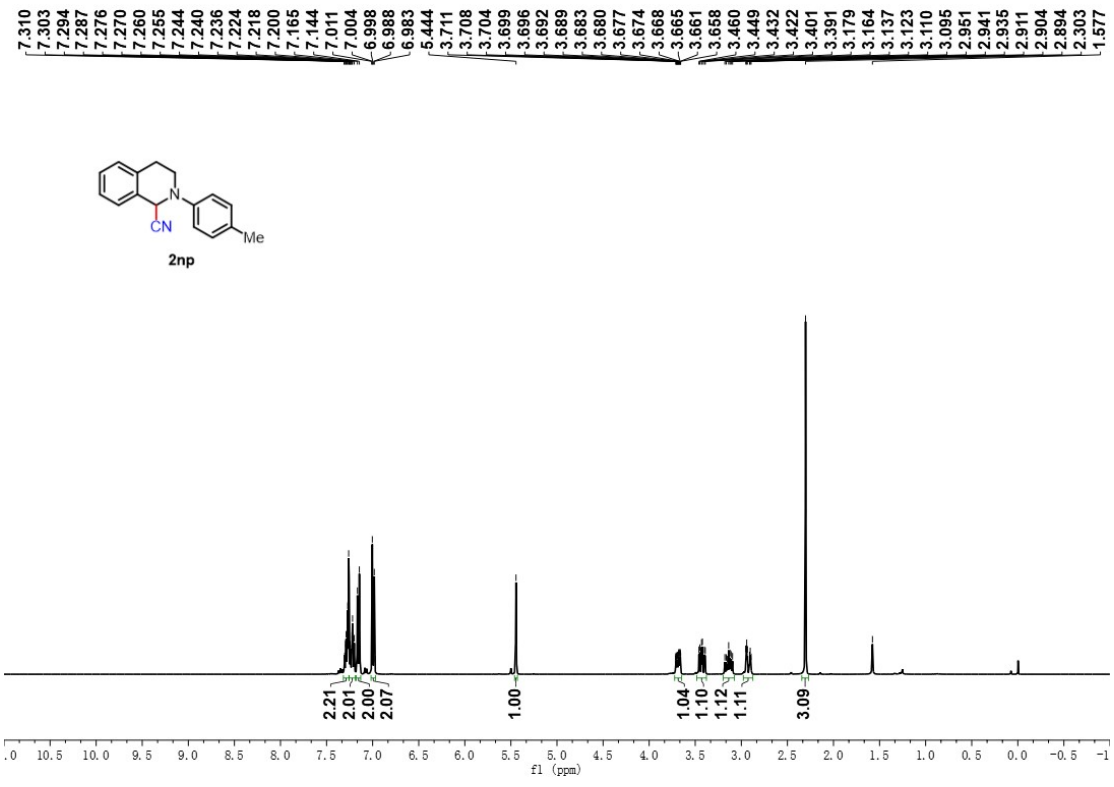
129.39
128.78
127.09
126.88
121.87
117.83
117.57
77.48
77.16
76.84
53.15
44.18
28.54
CN
1np
f1 (ppm)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7.276
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7.255
7.244
7.240
7.236
7.224
7.218
7.200
7.165
7.144
7.011
7.004
6.998
6.988
6.983
5.444
3.711
3.708
3.704
3.699
3.696
3.692
3.689
3.683
3.680
3.677
3.674
3.668
3.665
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3.658
3.460
3.449
3.432
3.422
3.401
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3.164
3.137
3.123
3.110
3.095
2.951
2.941
2.935
2.911
2.904
2.894
2.303
1.577
CN
Me
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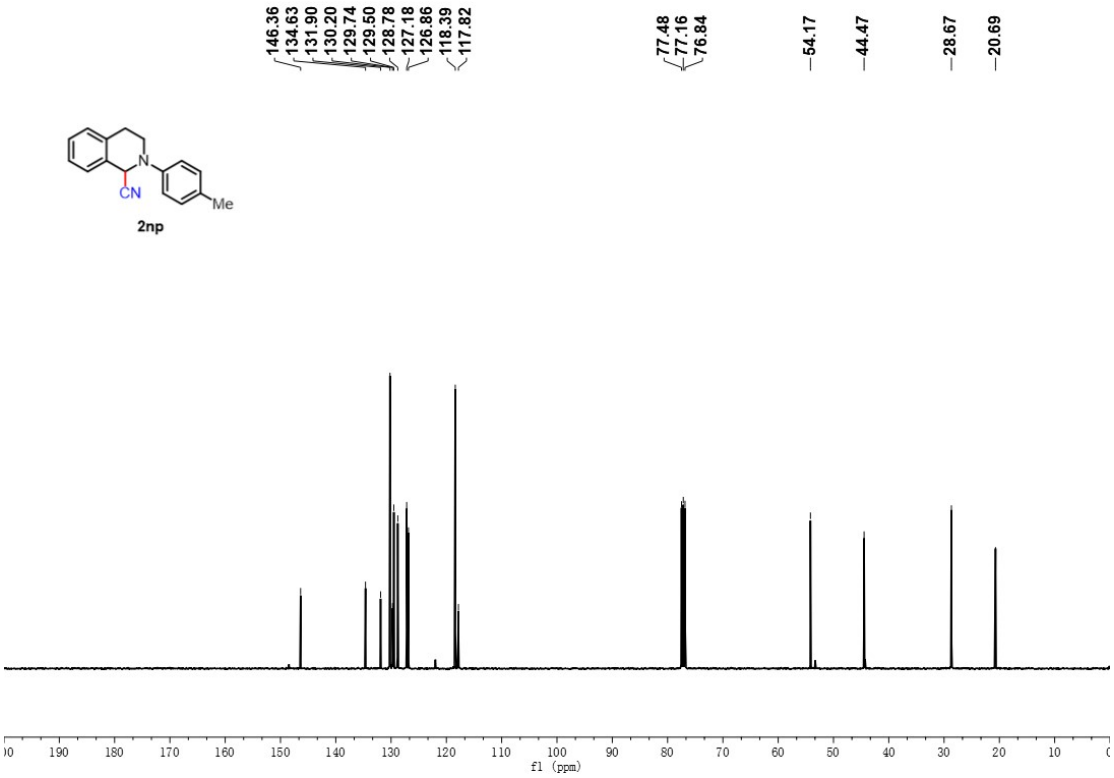
1.00
1.04
1.10
1.12
1.11
3.09
f1 (ppm)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127.18
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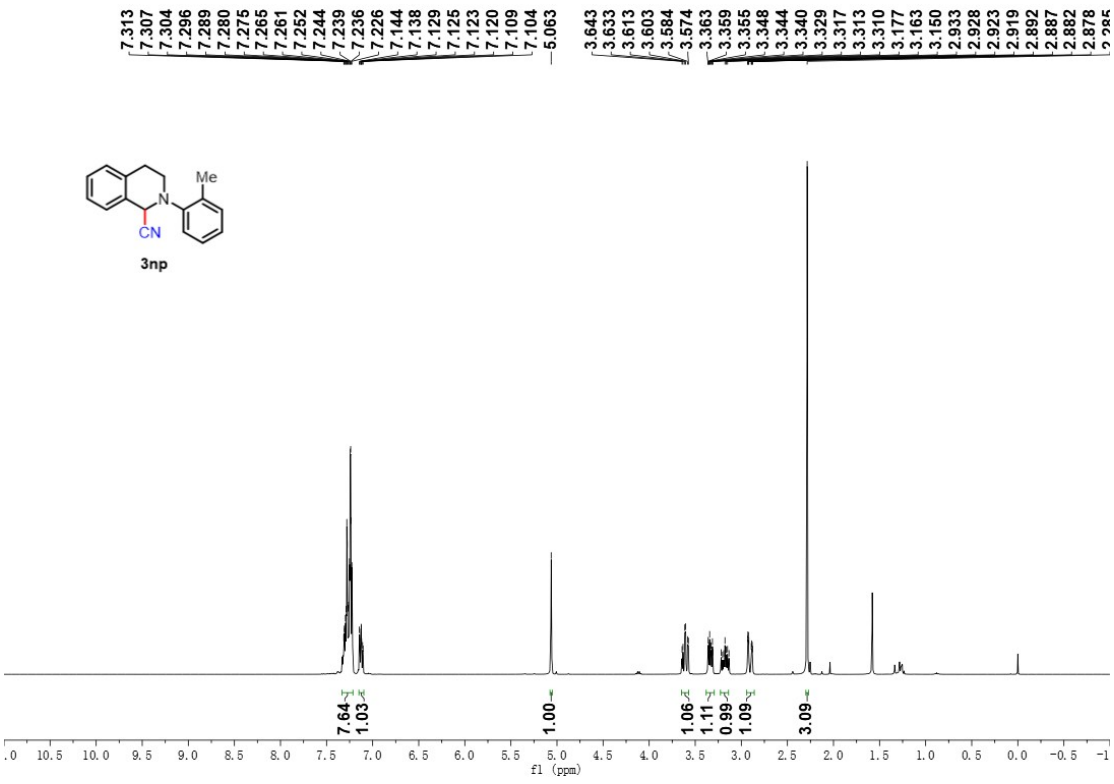
77.16
76.84
54.17
44.47
28.67
20.69
CN
Me
2np
f1 (ppm)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7.236
7.226
7.144
7.138
7.129
7.125
7.123
7.120
7.109
7.104
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3.633
3.613
3.603
3.584
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3.359
3.355
3.348
3.344
3.340
3.329
3.317
3.313
3.310
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3.163
3.150
2.933
2.928
2.923
2.919
2.892
2.887
2.882
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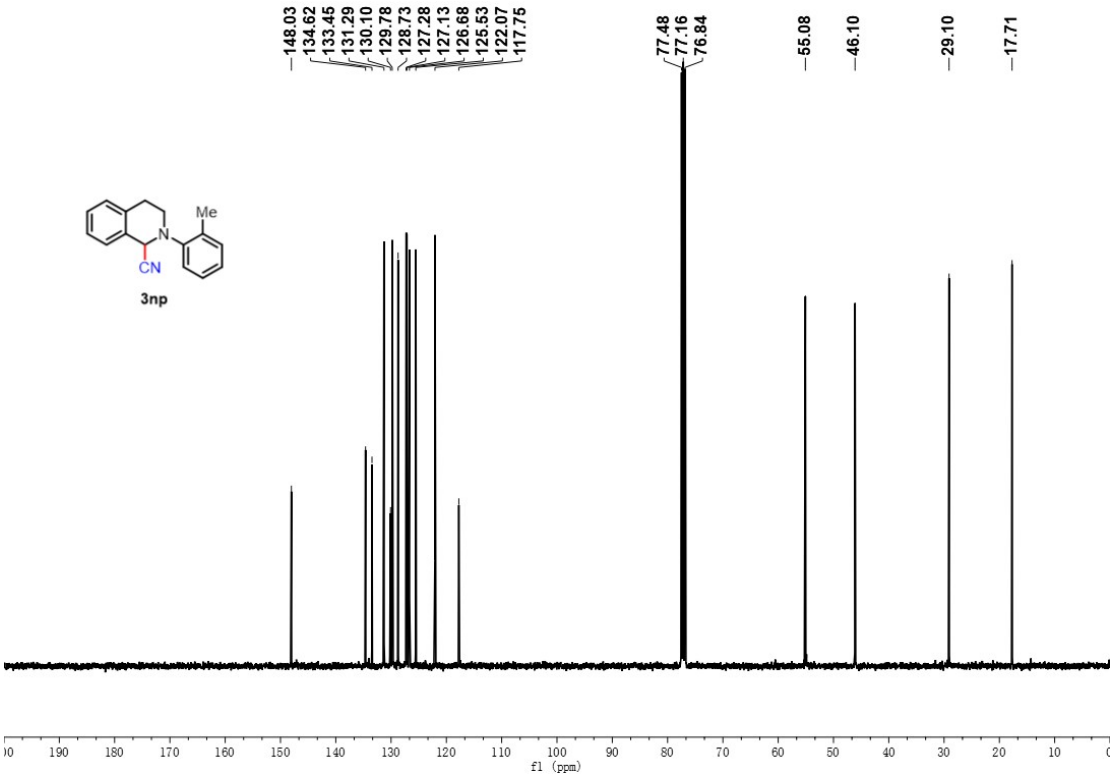
3.09
f1 (ppm)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125.53
122.07
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77.16
76.84
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46.10
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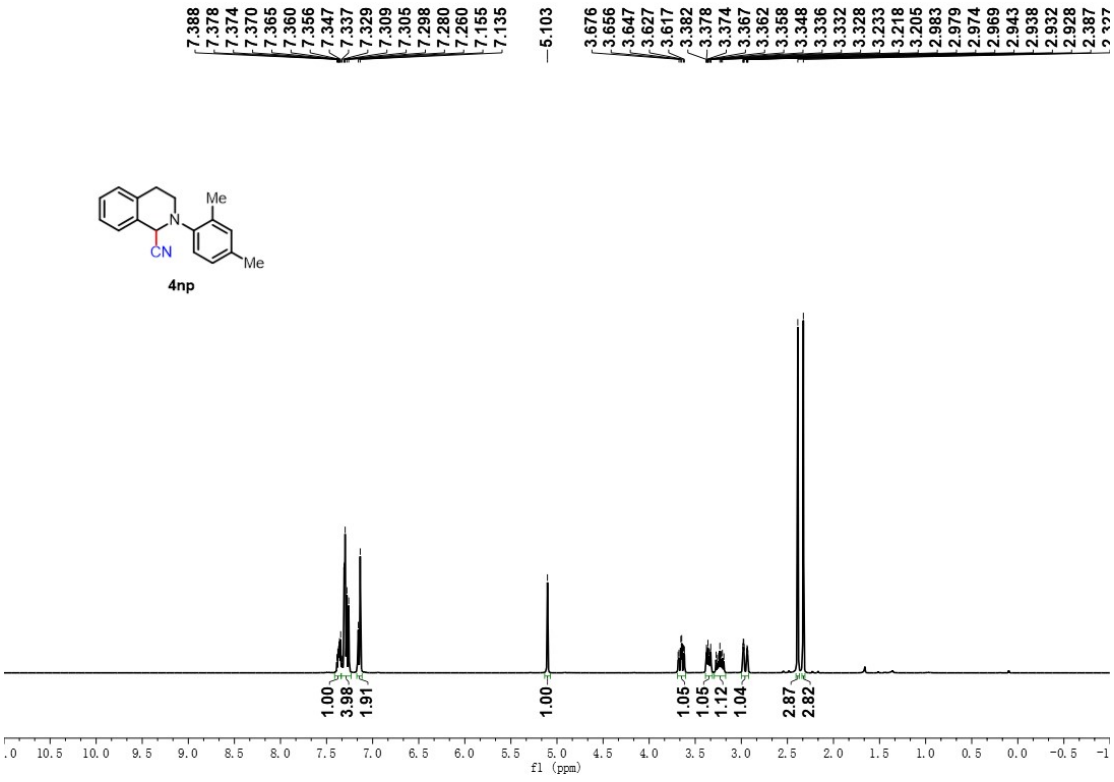
17.71
Me
N
CN
3np
fl (ppm)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7.260
7.155
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3.647
3.627
3.617
3.382
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3.374
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3.362
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3.348
3.336
3.332
3.328
3.233
3.218
3.205
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2.943
2.938
2.932
2.928
2.387
Me
N
CN
Me
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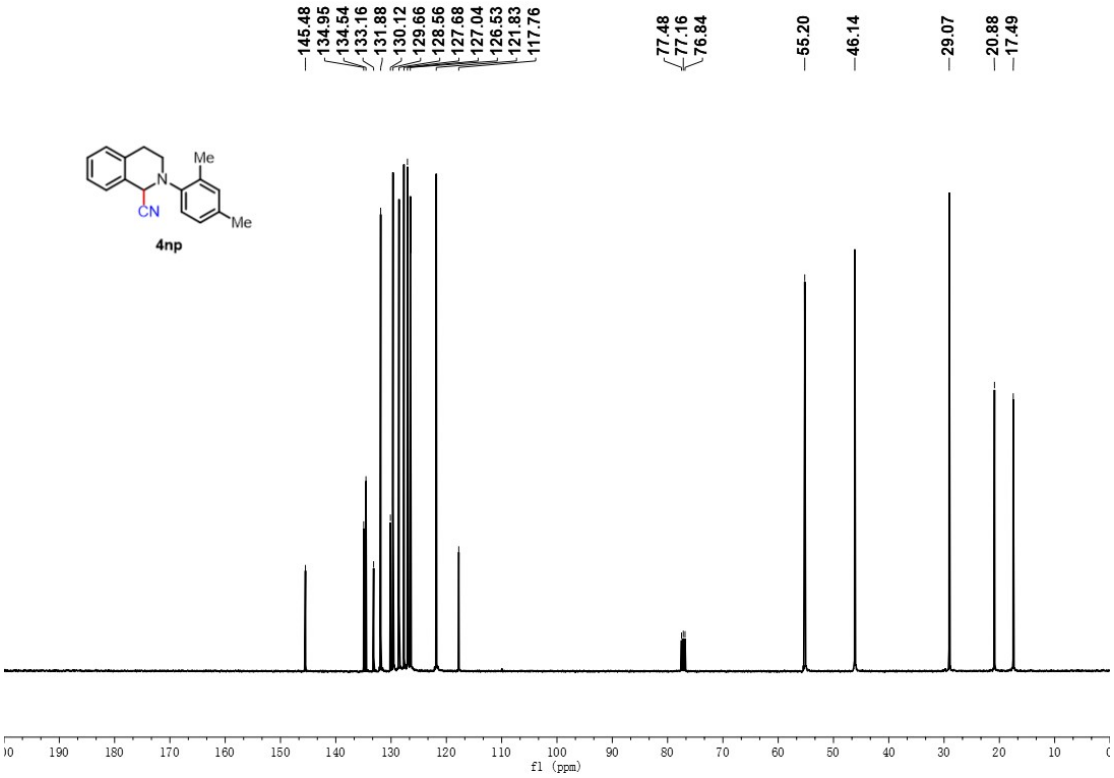
1.05
1.12
1.04
2.87
2.82
fl (ppm)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127.04
126.53
121.83
117.76
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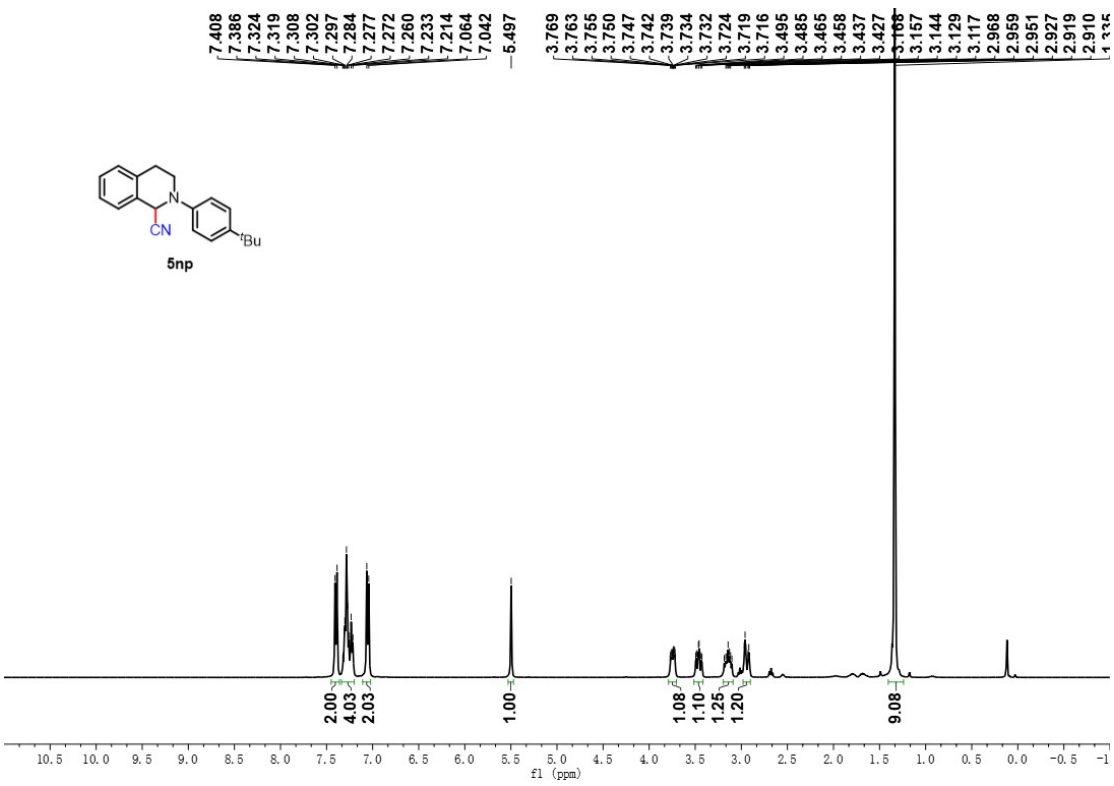
55.20
46.14
29.07
20.88
17.49
Me
N
CN
Me
4np
f1 (ppm)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7.272
7.260
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7.064
7.042
5.497
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3.763
3.755
3.750
3.747
3.742
3.739
3.734
3.732
3.724
3.719
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3.495
3.485
3.465
3.458
3.437
3.427
3.157
3.144
3.129
3.117
2.968
2.959
2.951
2.927
2.919
2.910
N
CN
tBu
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2.03
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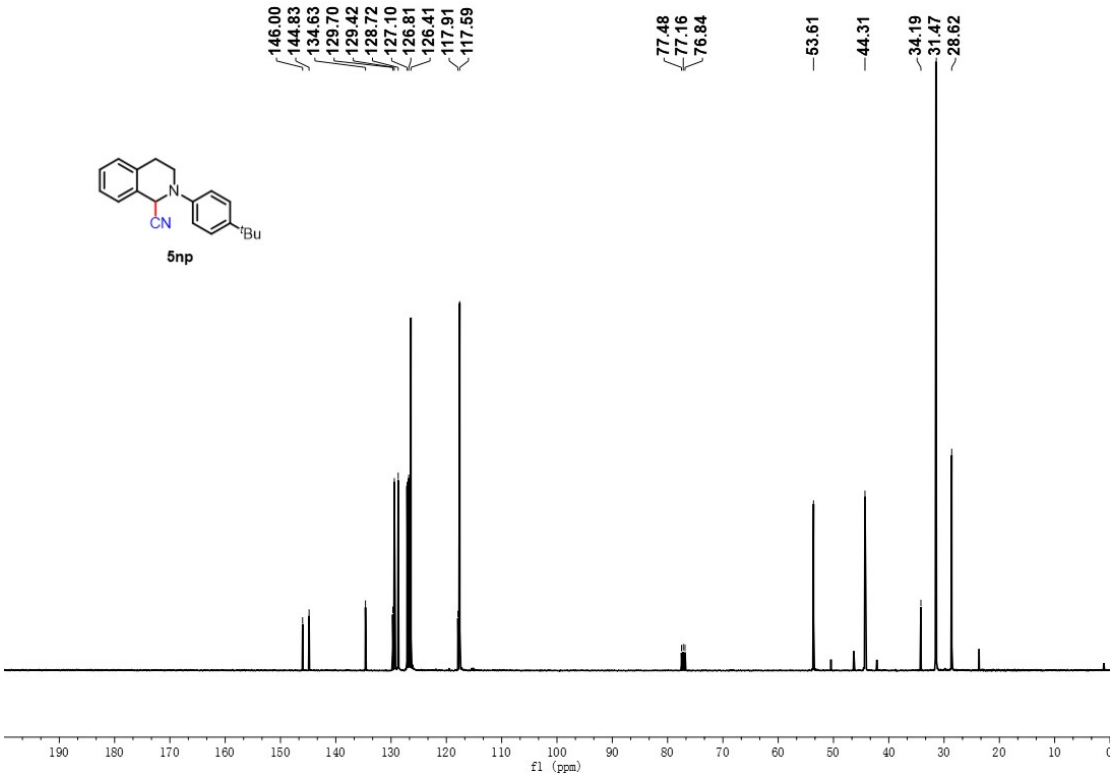
1.08
1.10
1.25
1.20
9.08
f1 (ppm)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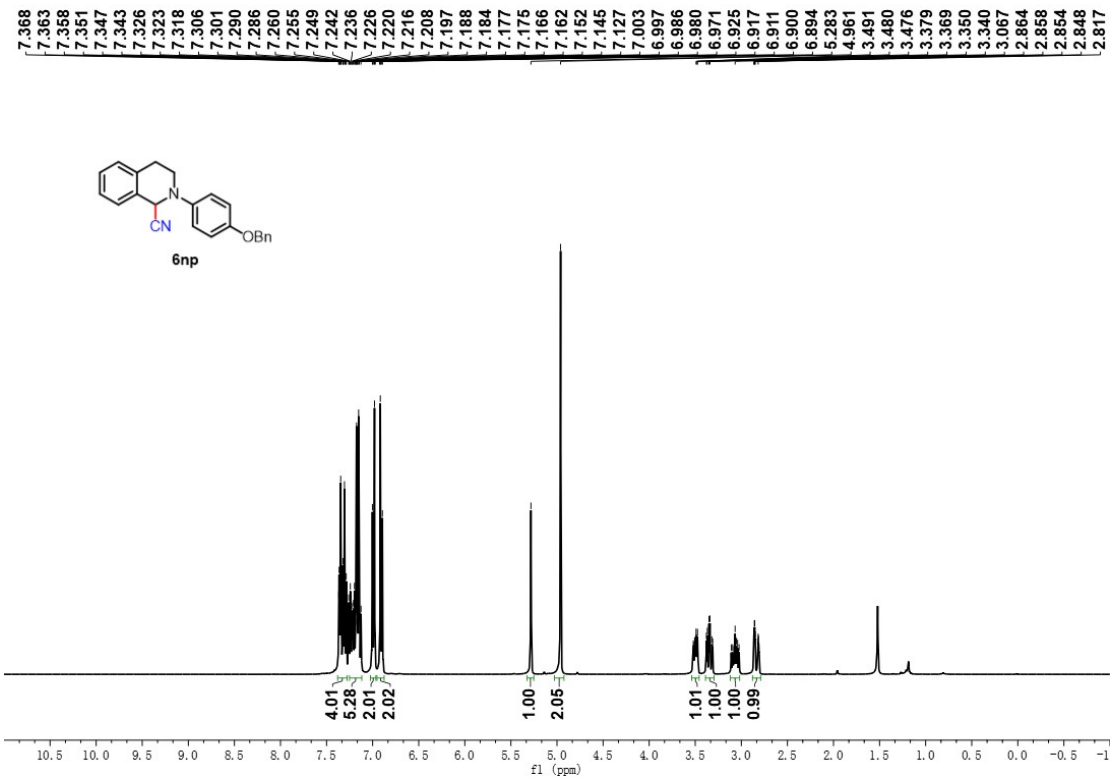
76.84
53.61
44.31
34.19
31.47
28.62
CN
tBu
5np
f1 (ppm)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7.286
7.260
7.255
7.249
7.242
7.236
7.226
7.220
7.216
7.208
7.197
7.188
7.184
7.177
7.175
7.166
7.162
7.152
7.145
7.127
7.003
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6.971
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6.917
6.911
6.900
6.894
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3.491
3.480
3.476
3.379
3.369
3.350
3.340
3.067
2.864
2.858
2.854
2.848
2.817
CN
OBn
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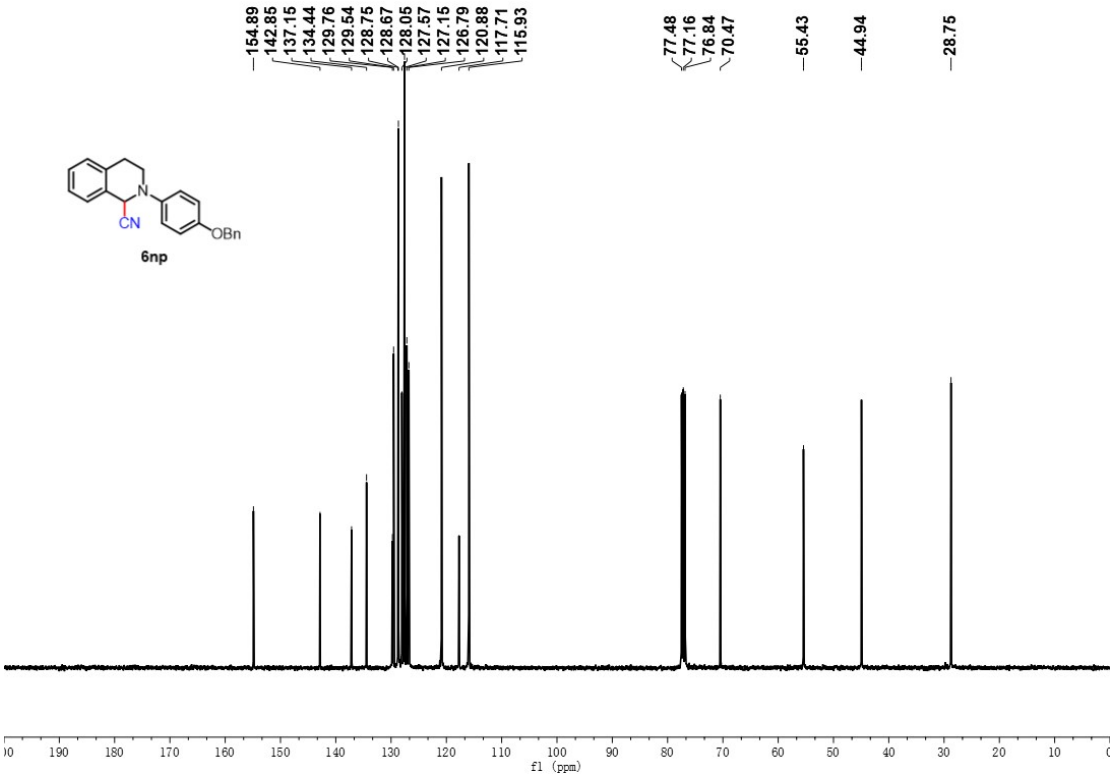
2.01
2.02
1.00
2.05
1.01
1.00
1.00
0.99
f1 (ppm)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129.54
128.75
128.67
128.05
127.57
127.15
126.79
120.88
117.71
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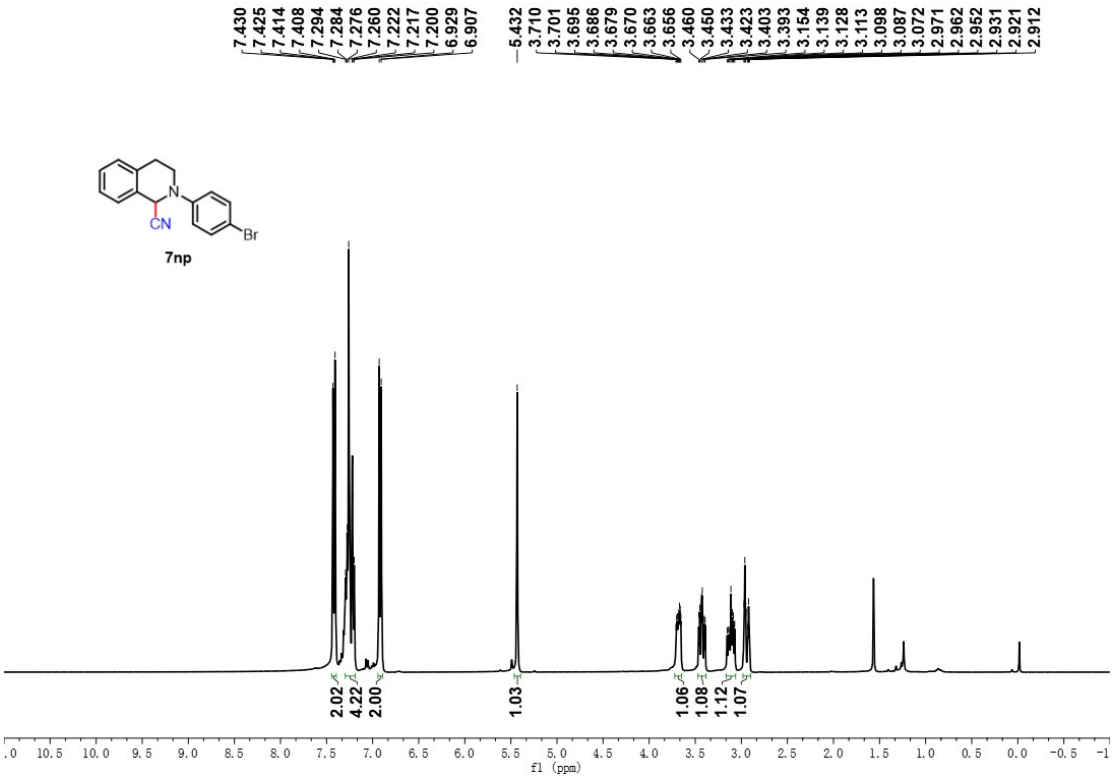
77.16
76.84
70.47
55.43
44.94
28.75
CN
OBn
6np
f1 (ppm)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7.408
7.294
7.284
7.276
7.260
7.222
7.217
7.200
6.929
6.907
5.432
3.710
3.701
3.695
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3.072
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2.962
2.952
2.931
2.921
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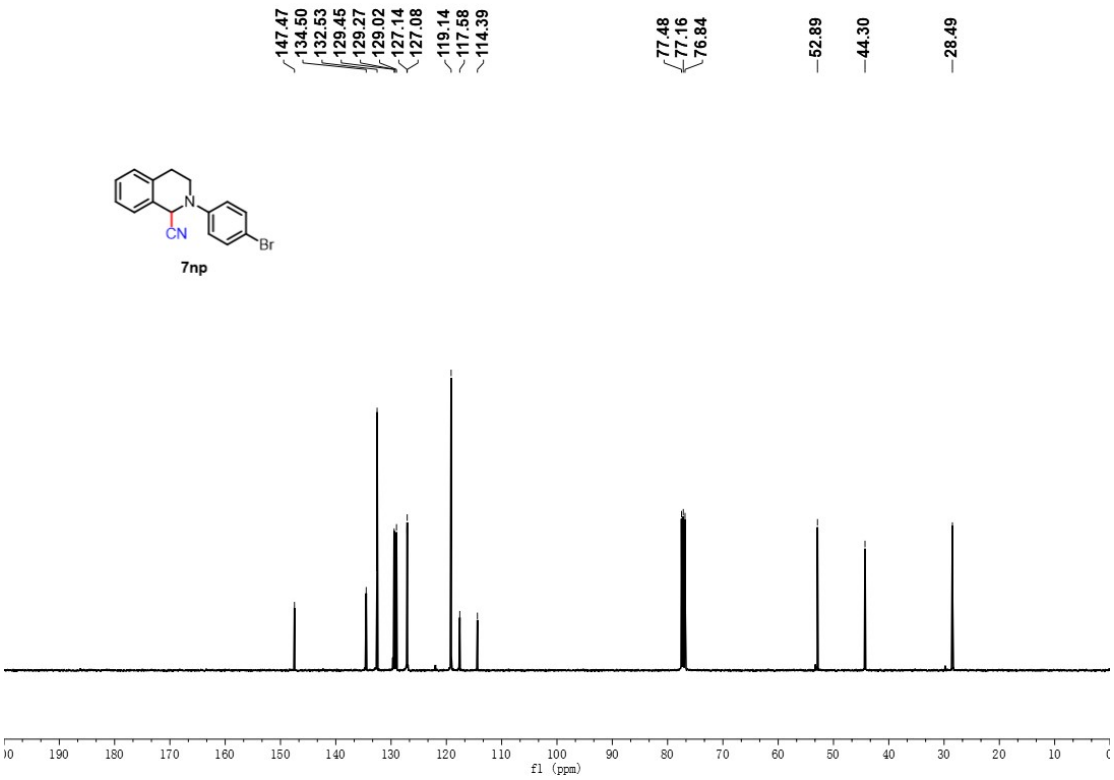
1.07
f1 (ppm)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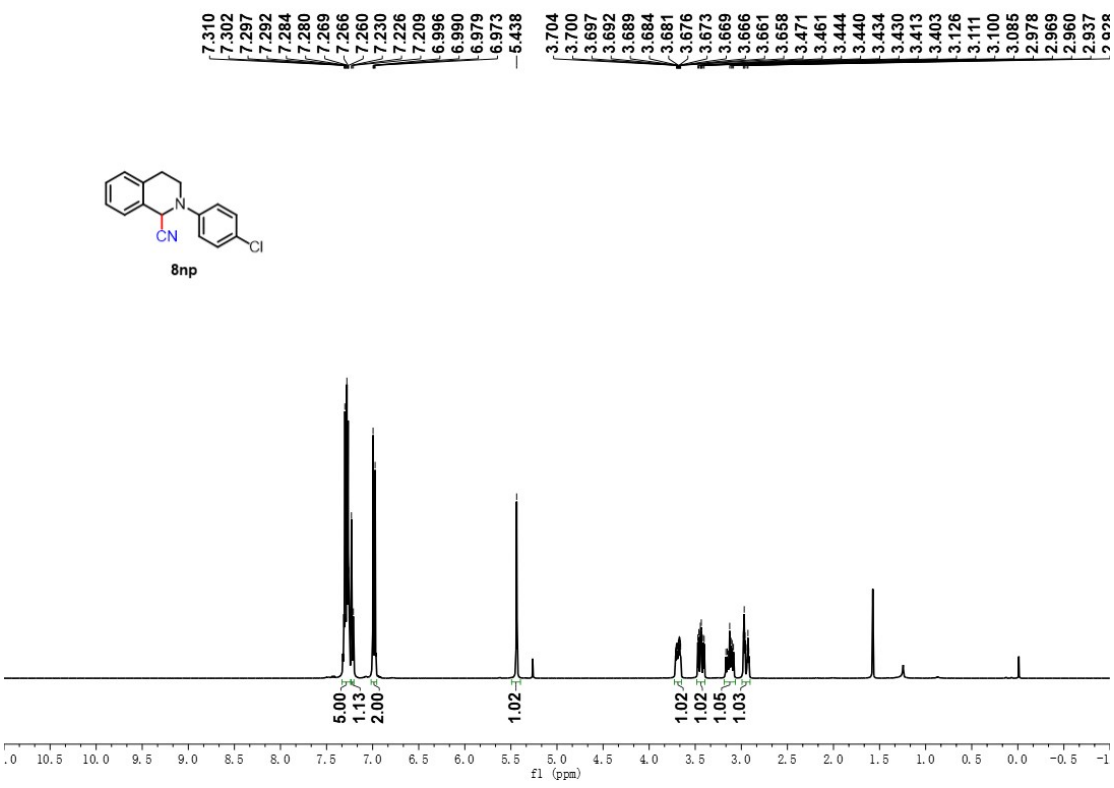
Br
7np
f1 (ppm)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3.403
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3.111
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3.085
2.978
2.969
2.960
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2.00
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1.02
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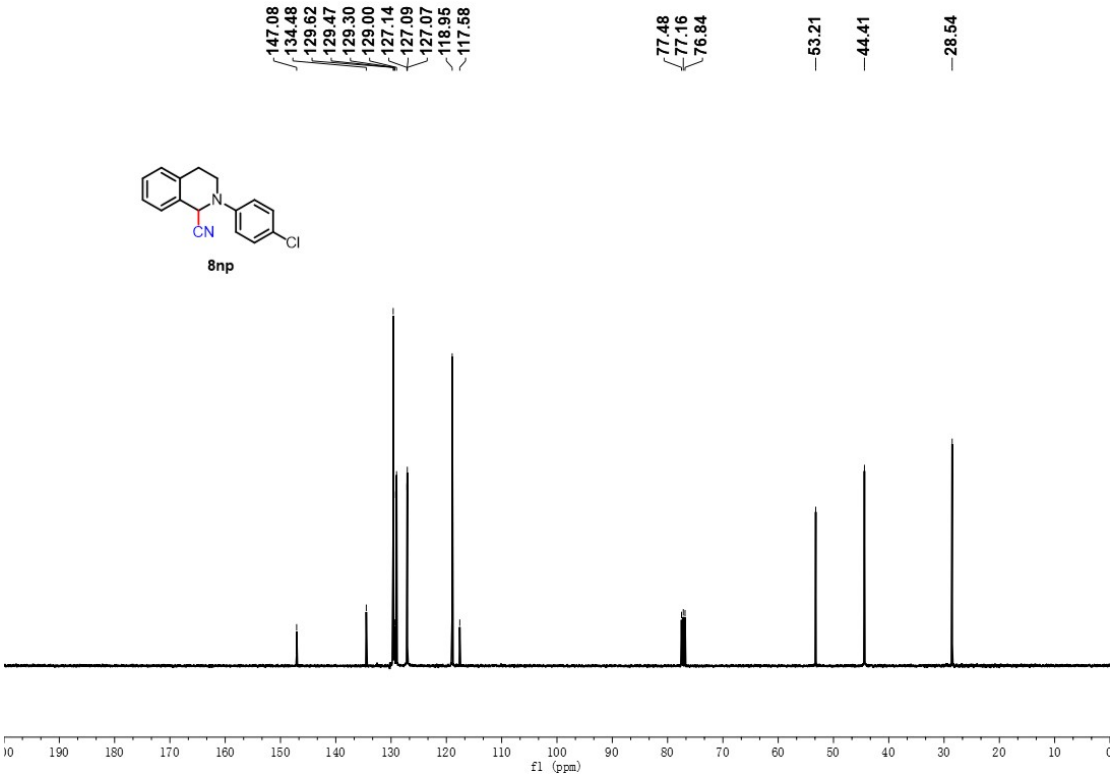
1.03
f1 (ppm)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8np
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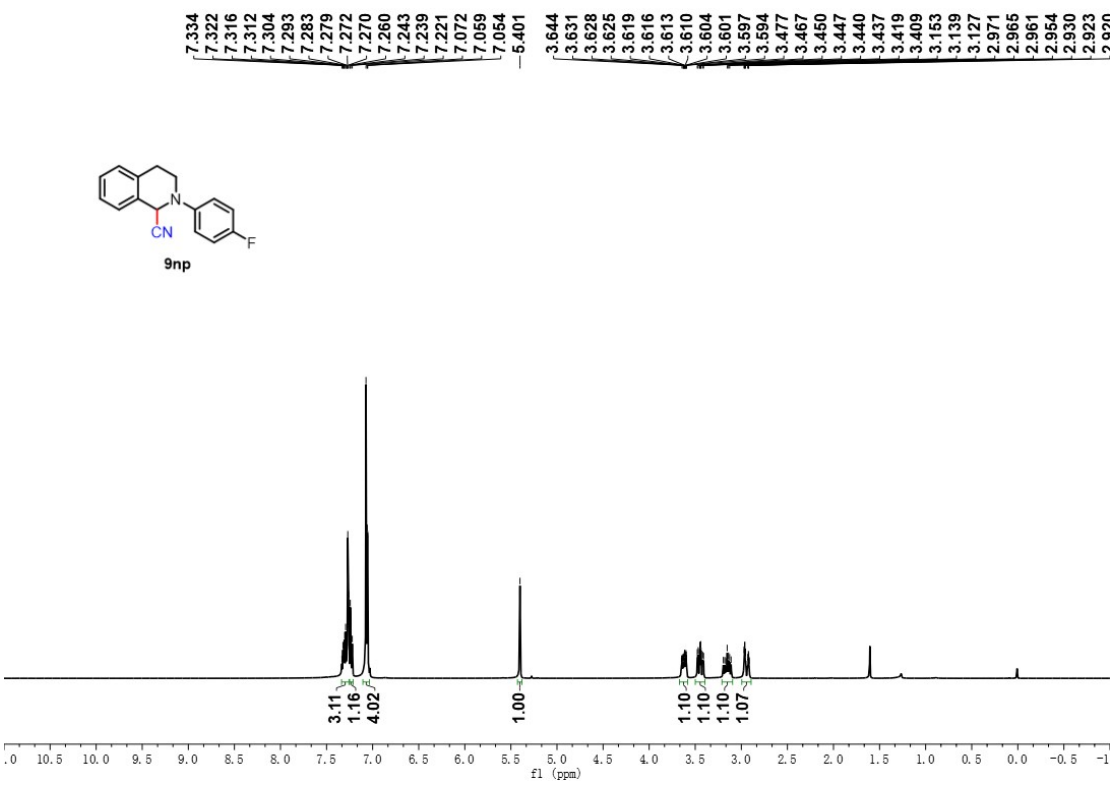
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2.961
2.954
2.930
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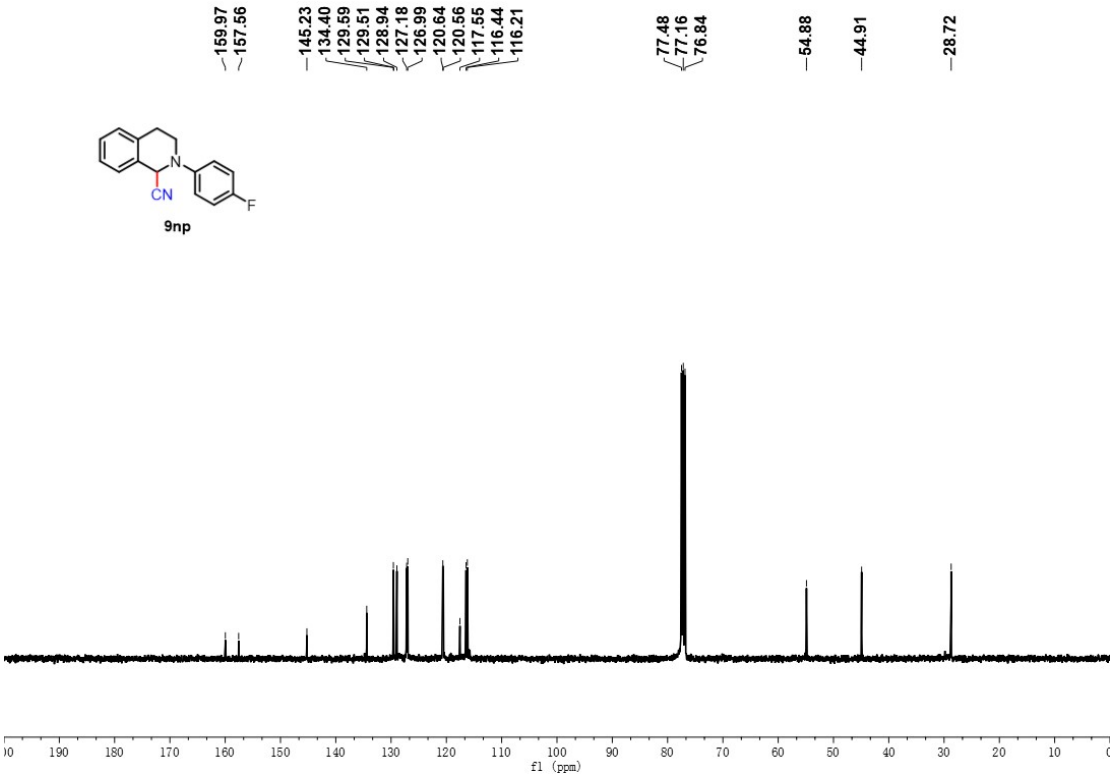
1.10
1.07
f1 (ppm)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129.51
128.94
127.18
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120.56
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77.48
77.16
76.84
54.88
44.91
28.72
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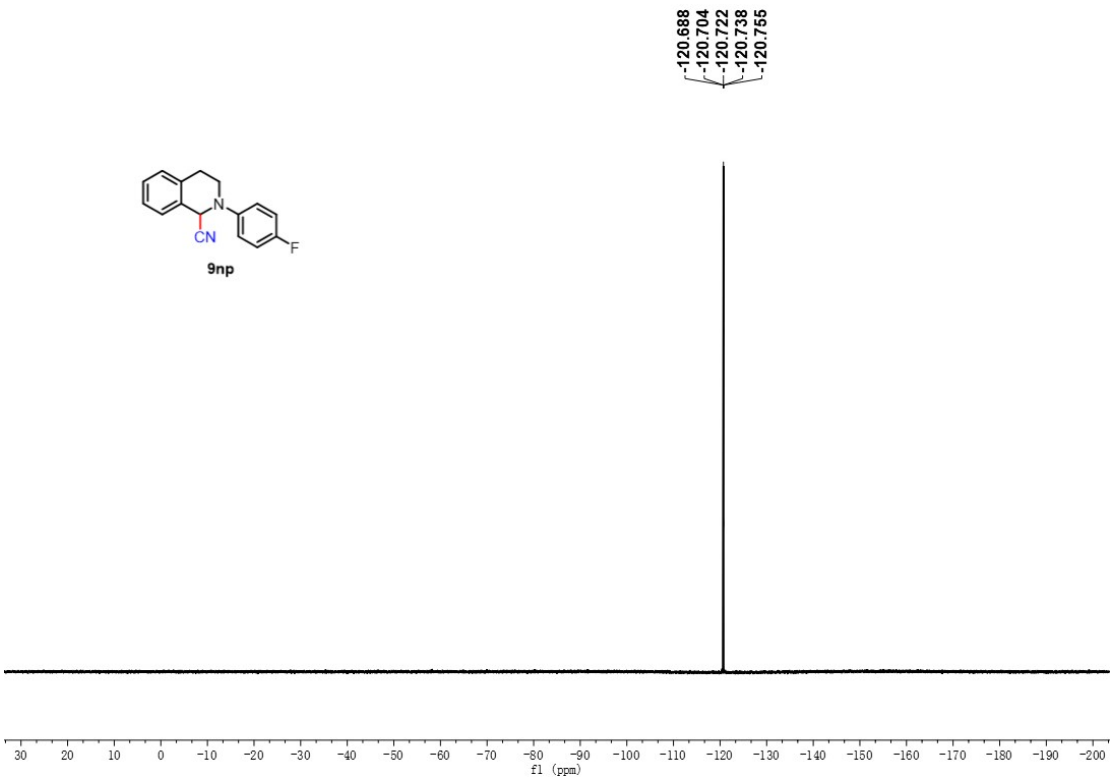
9np
f1 (ppm)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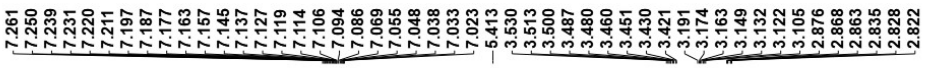
F
9np
f1 (ppm)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7.127
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7.086
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3.430
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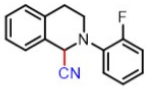
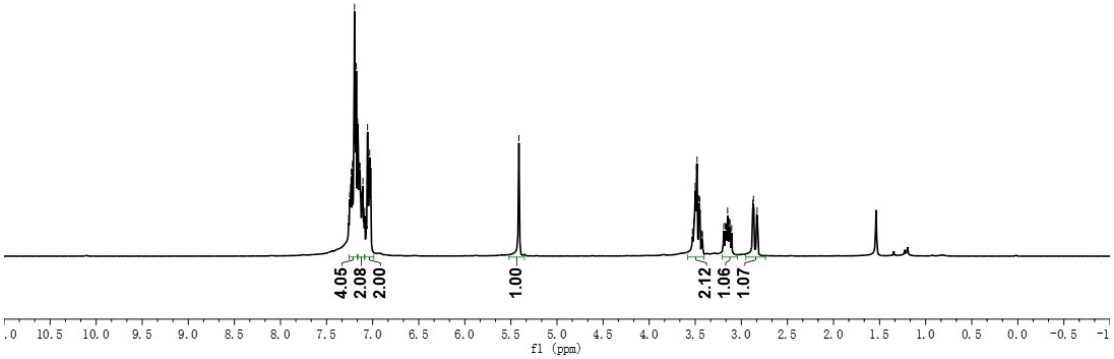
2.828
2.822


F
N
CN

10np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2.08
2.00
1.00
2.12
1.06
1.07
f1 (ppm)


157.31
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134.00
129.62
129.31
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127.12
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125.10
125.07
125.03
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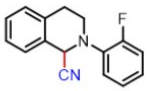
44.78
28.57


F
N
CN

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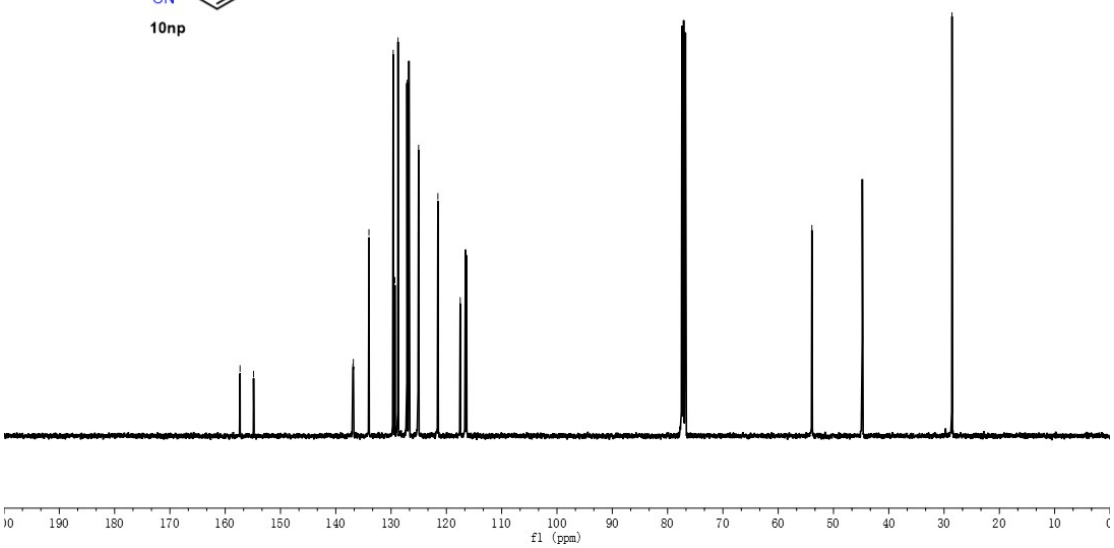
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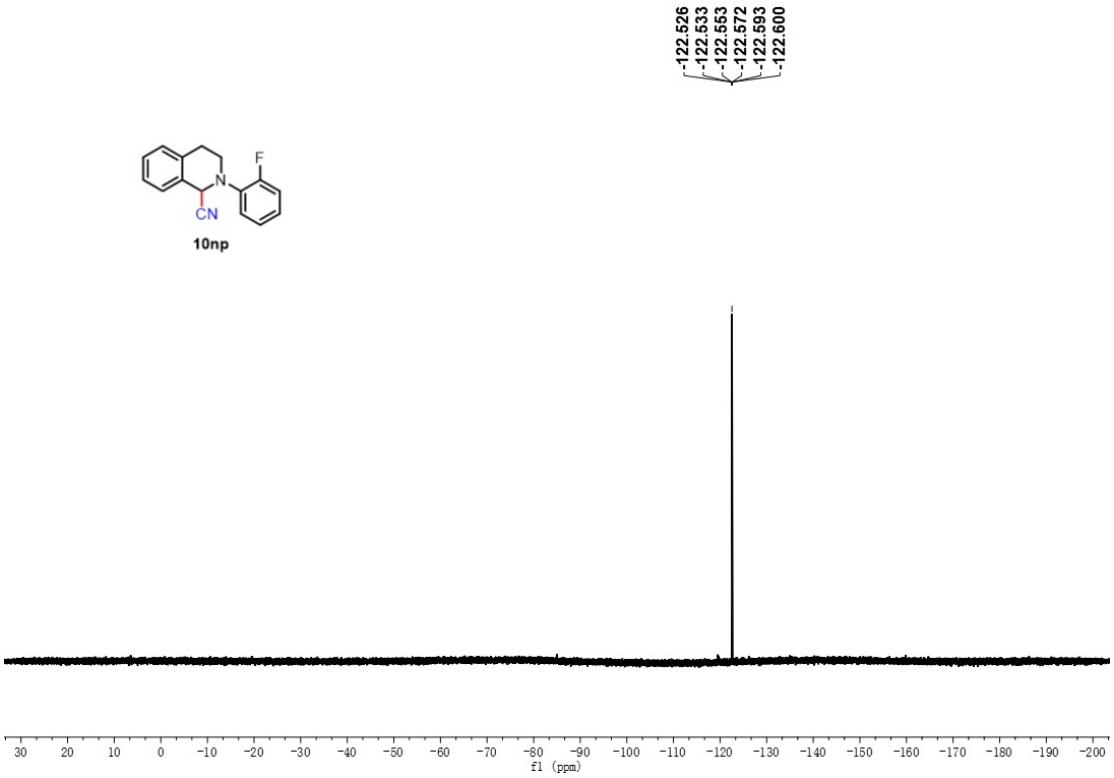
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F
N
CN
10np
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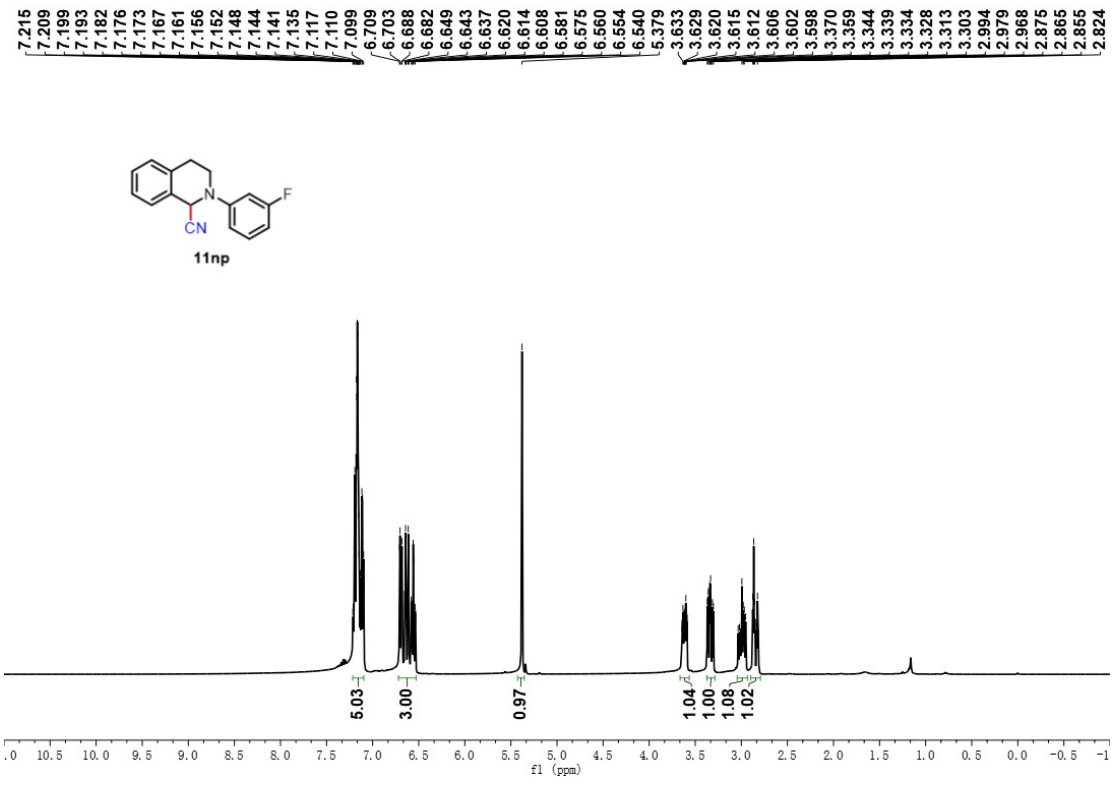
f1 (ppm)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7.141
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6.682
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6.643
6.637
6.620
6.614
6.608
6.581
6.575
6.560
6.554
6.540
5.379
3.633
3.629
3.620
3.615
3.612
3.606
3.602
3.598
3.370
3.359
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3.339
3.334
3.328
3.313
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2.994
2.979
2.968
2.875
2.865
2.855
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F
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CN
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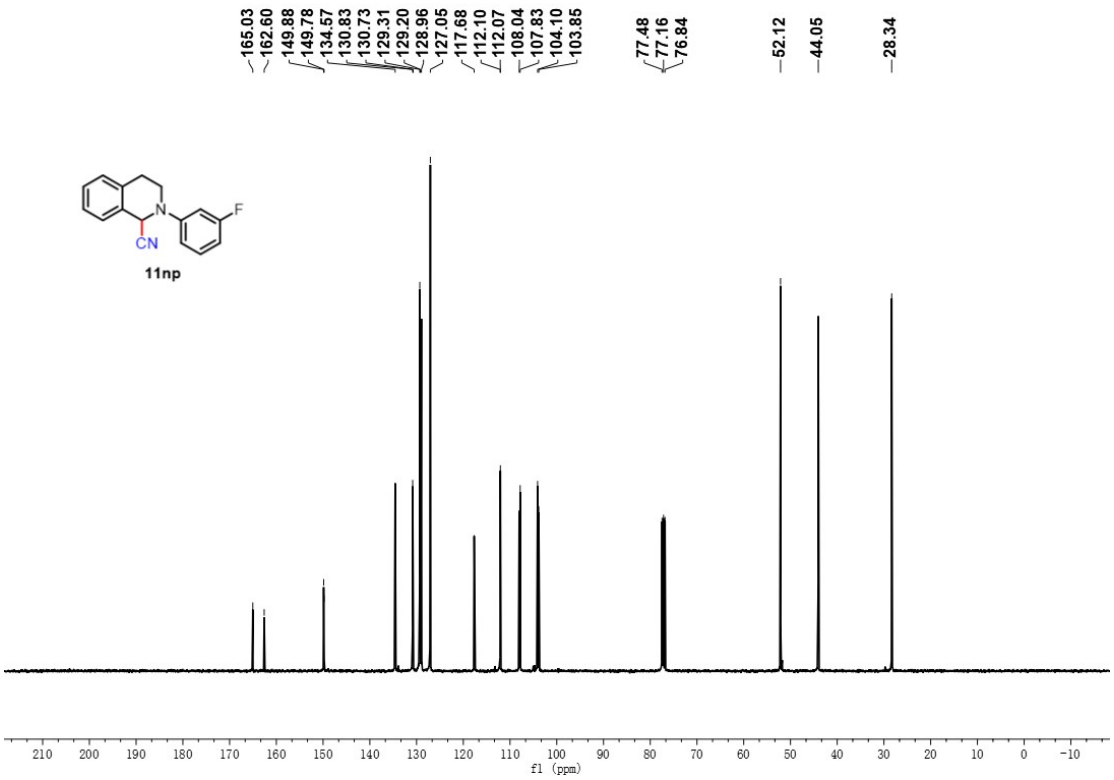
1.00
1.08
1.02
f1 (ppm)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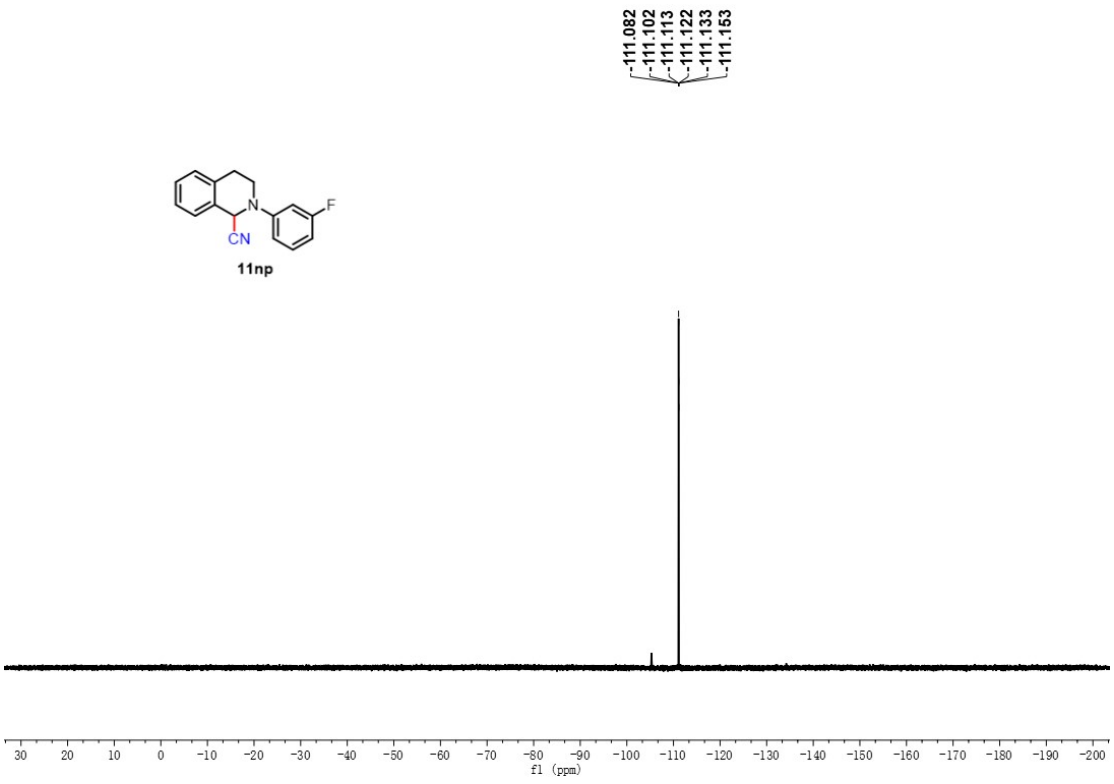
128.96
127.05
117.68
112.10
112.07
108.04
107.83
104.10
103.85
77.48
77.16
76.84
52.12
44.05
28.34
F
N
CN
11np
f1 (ppm)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CN
11np
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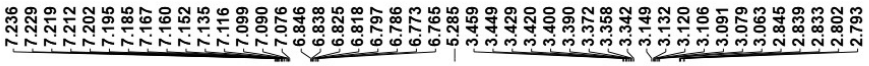
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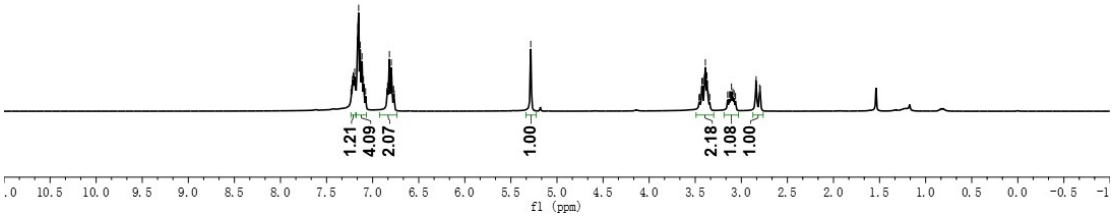
F
N
CN
F

12np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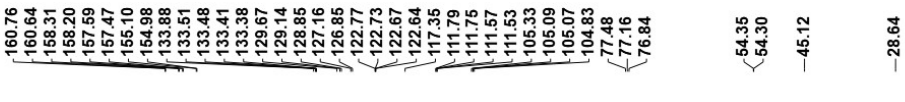
1.00
f1 (ppm)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128.85
127.16
126.85
122.77
122.73
122.67
122.64
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111.75
111.57
111.53
105.33
105.09
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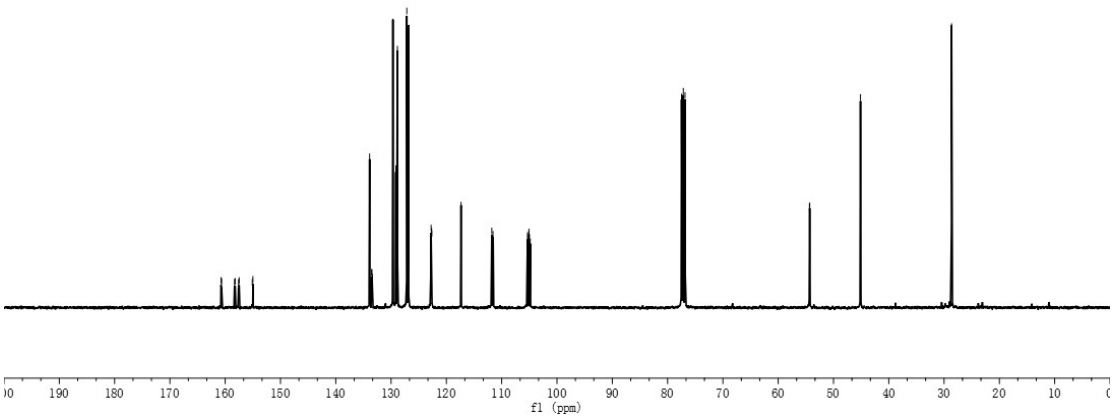
F
N
CN
F

12np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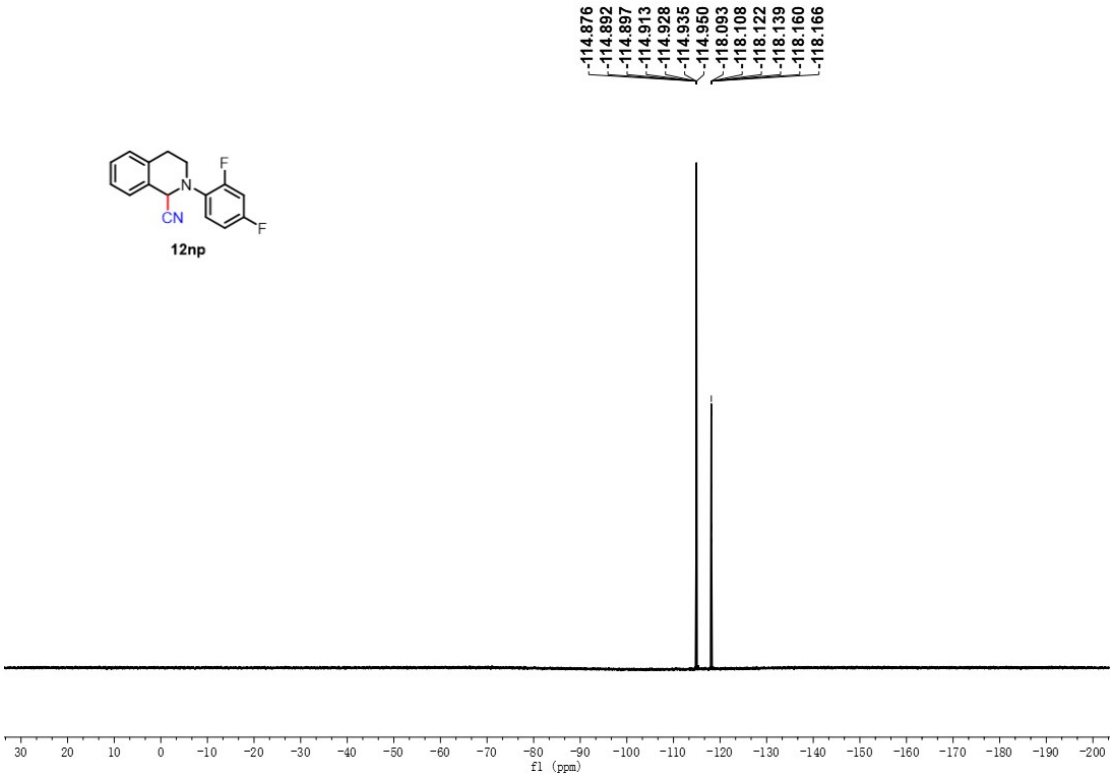
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-118.139
-118.160
-118.166
F
N
CN
F
12np
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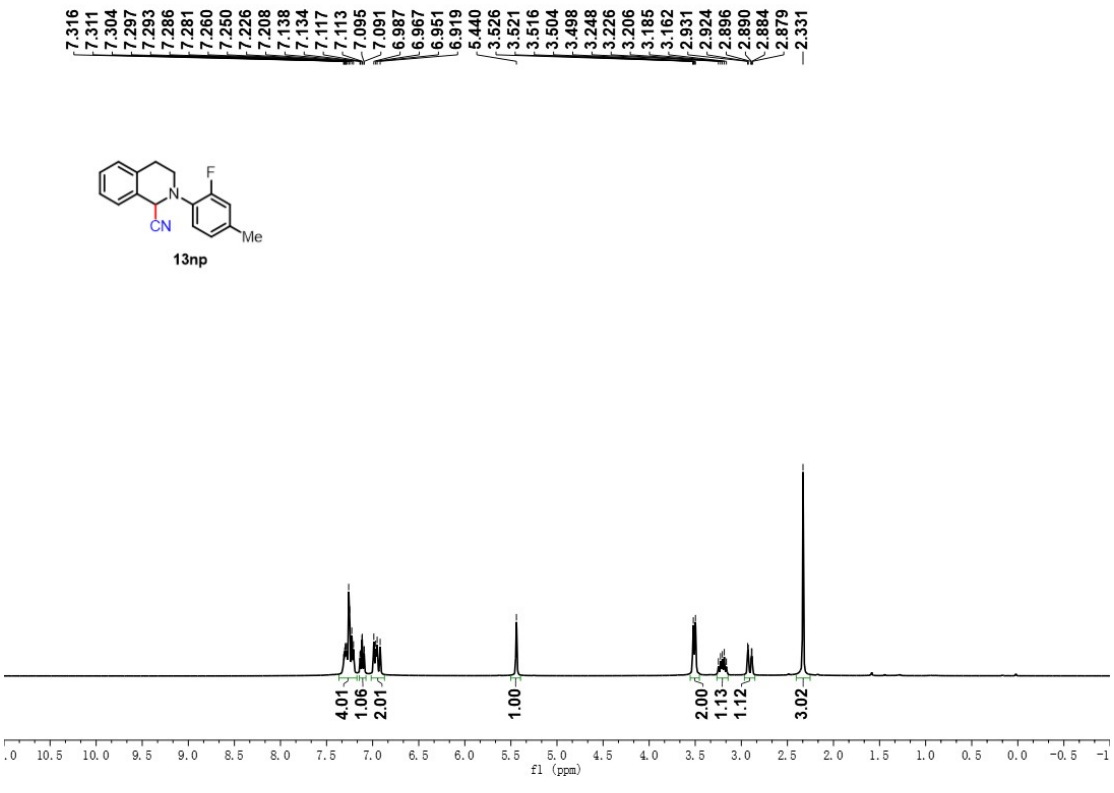
f1 (ppm)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7.113
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6.919
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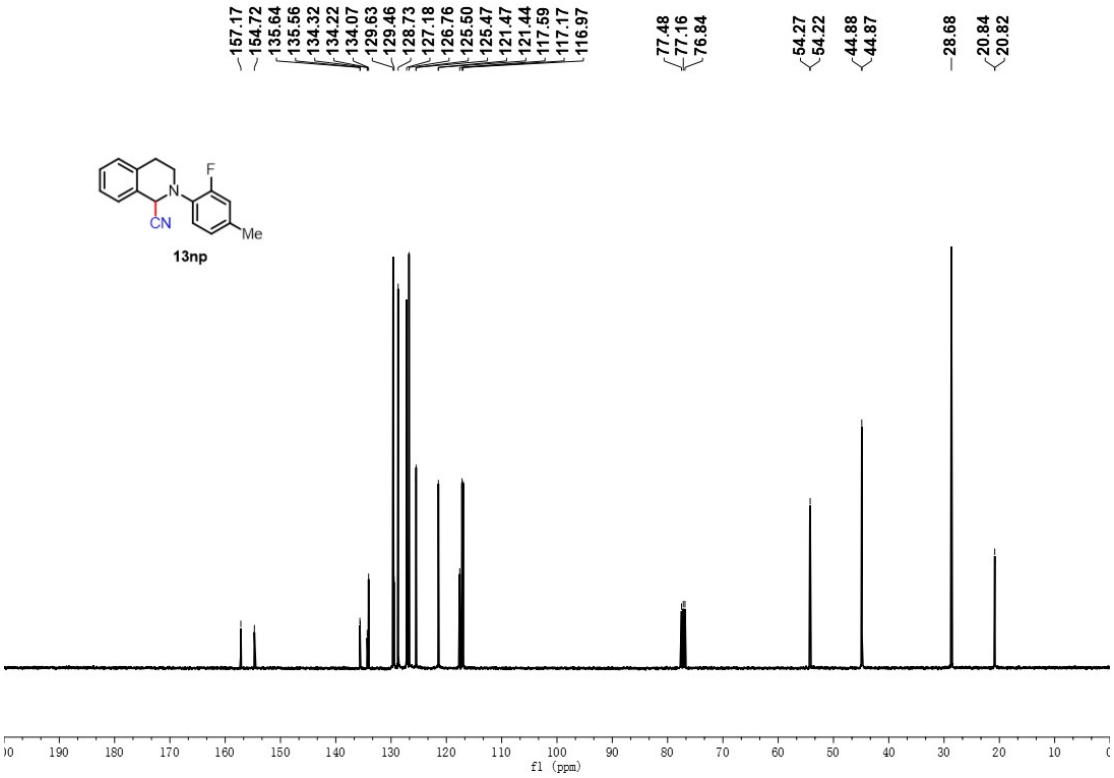
2.884
2.879
2.331
F
N
CN
Me
13np
4.01
1.06
2.01
1.00
2.00
1.13
1.12
3.02
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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117.17
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77.16
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44.87
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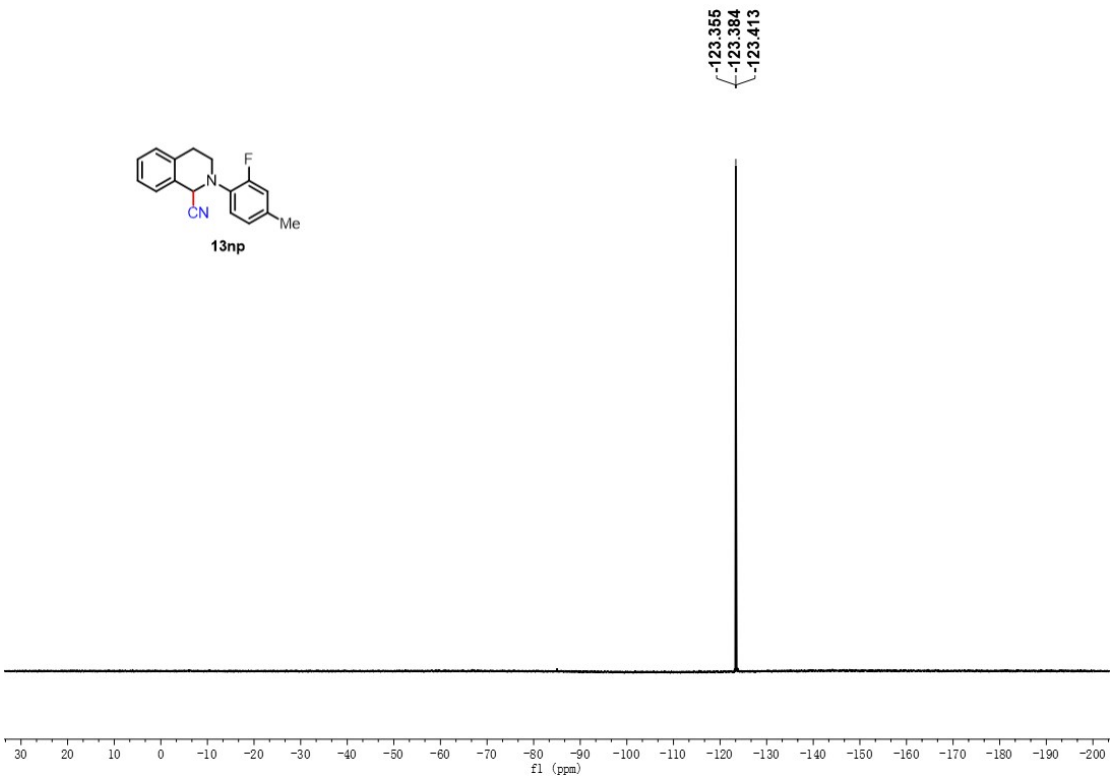
F
N
CN
Me
13np
f1 (ppm)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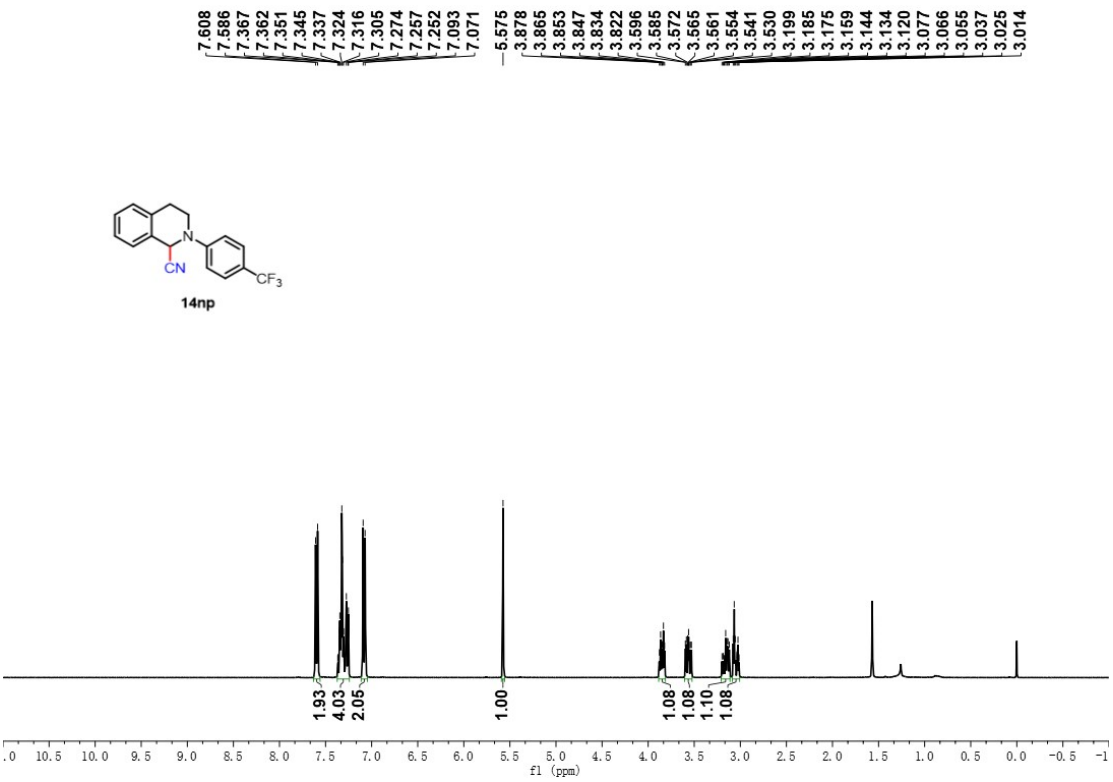
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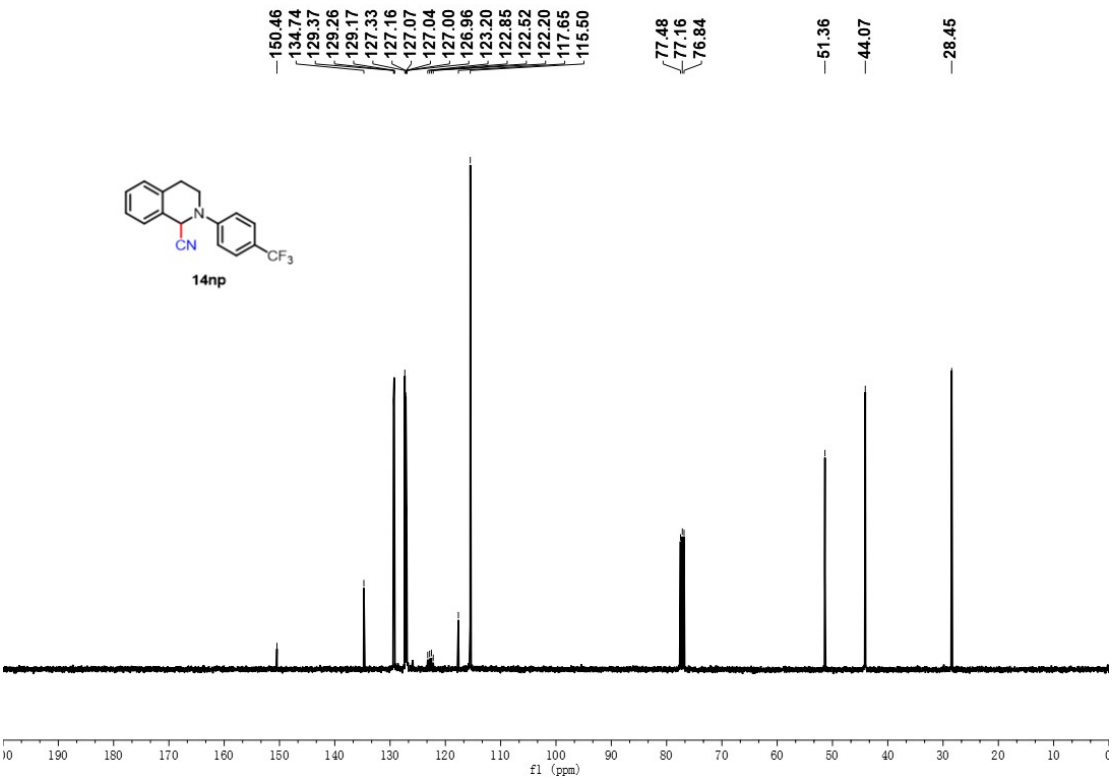
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122.85
122.52
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77.16
76.84
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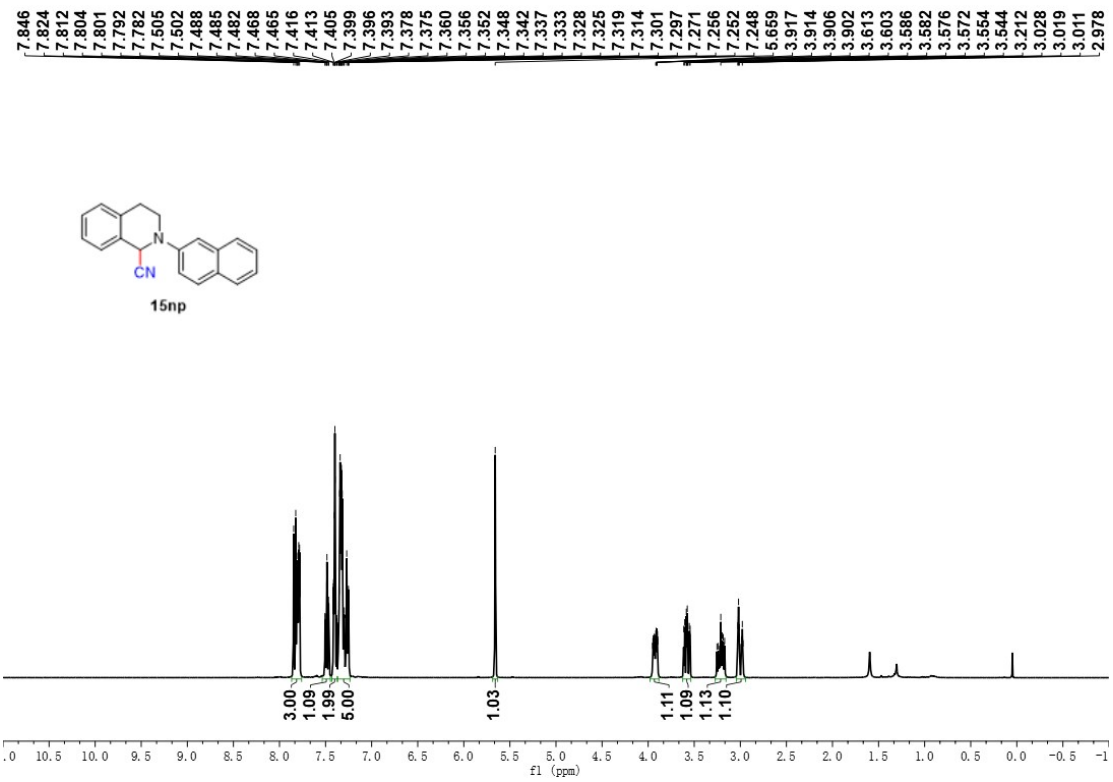
28.45
CN
CF3
14np
f1 (ppm)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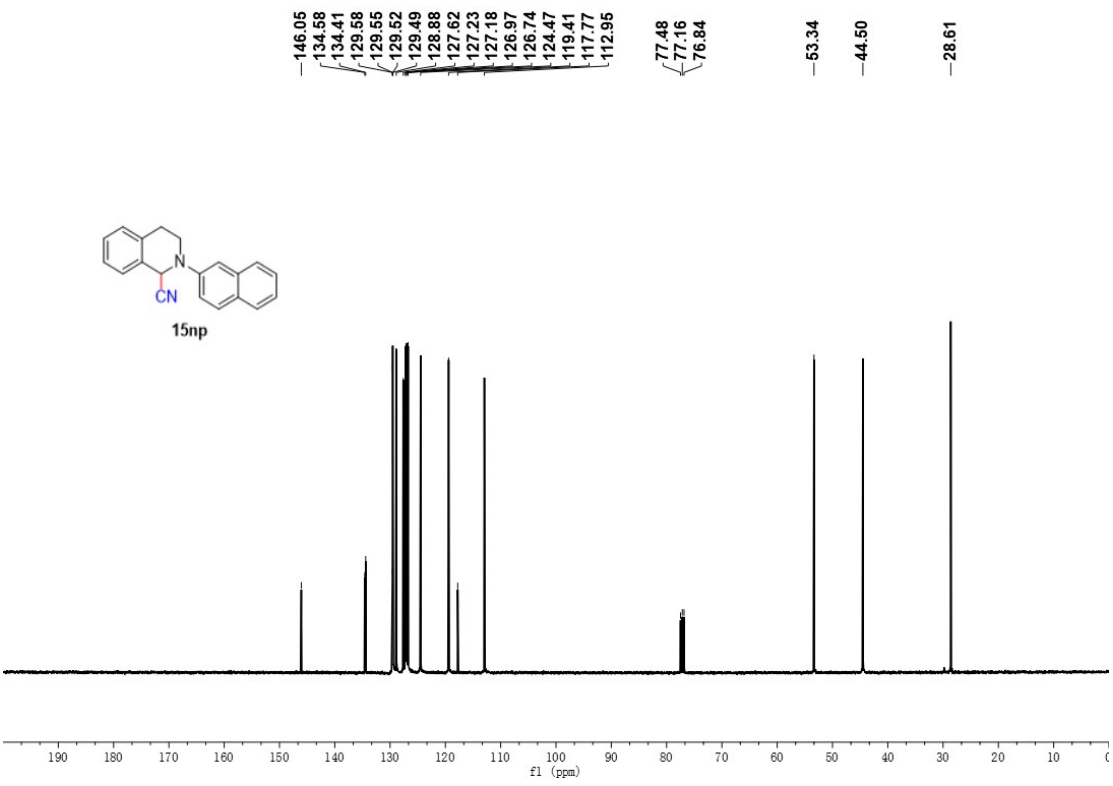
1.10
f1 (ppm)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76.84
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44.50
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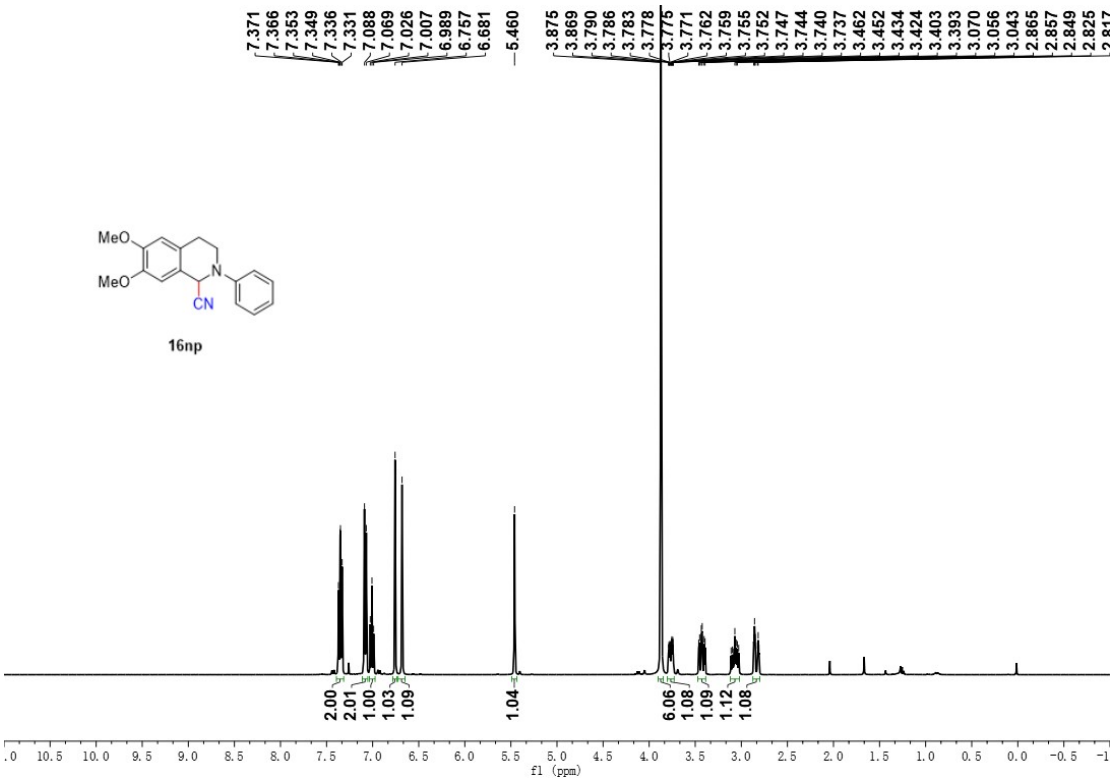
CN
15np
f1 (ppm)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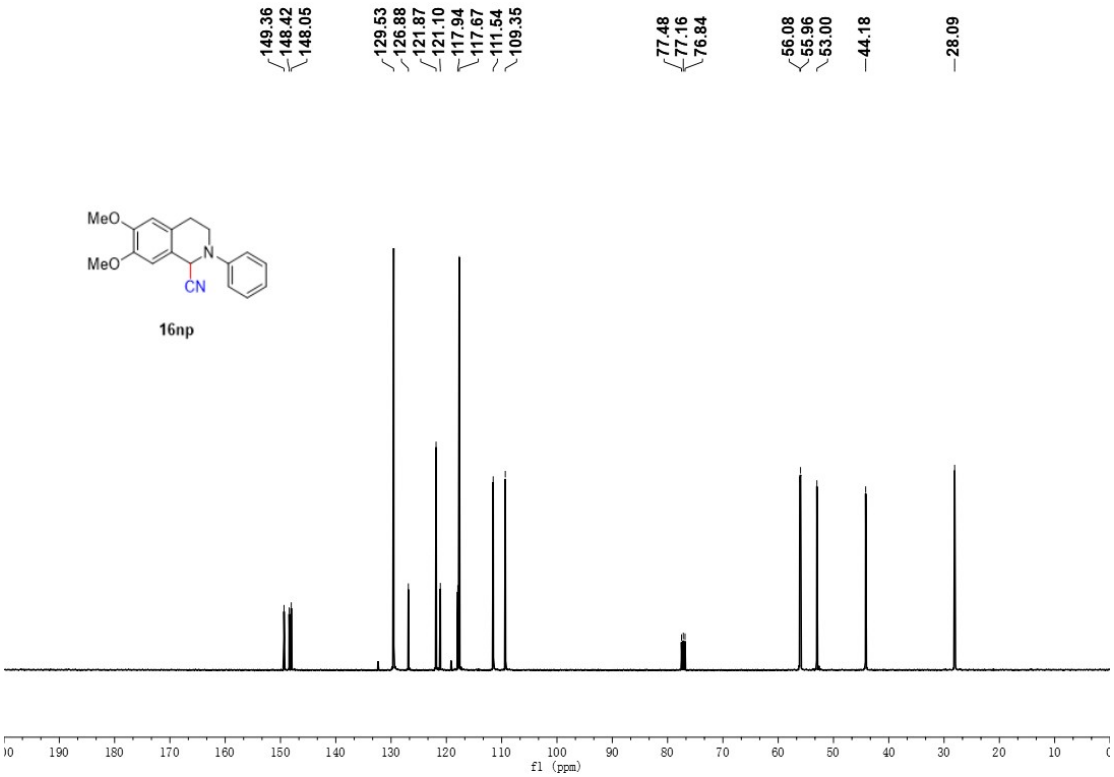
3.056
3.043
2.865
2.857
2.849
2.825
MeO
MeO
N
CN
16np
2.00
2.01
1.00
1.03
1.09
1.04
6.06
1.08
1.09
1.12
1.08
f1 (ppm)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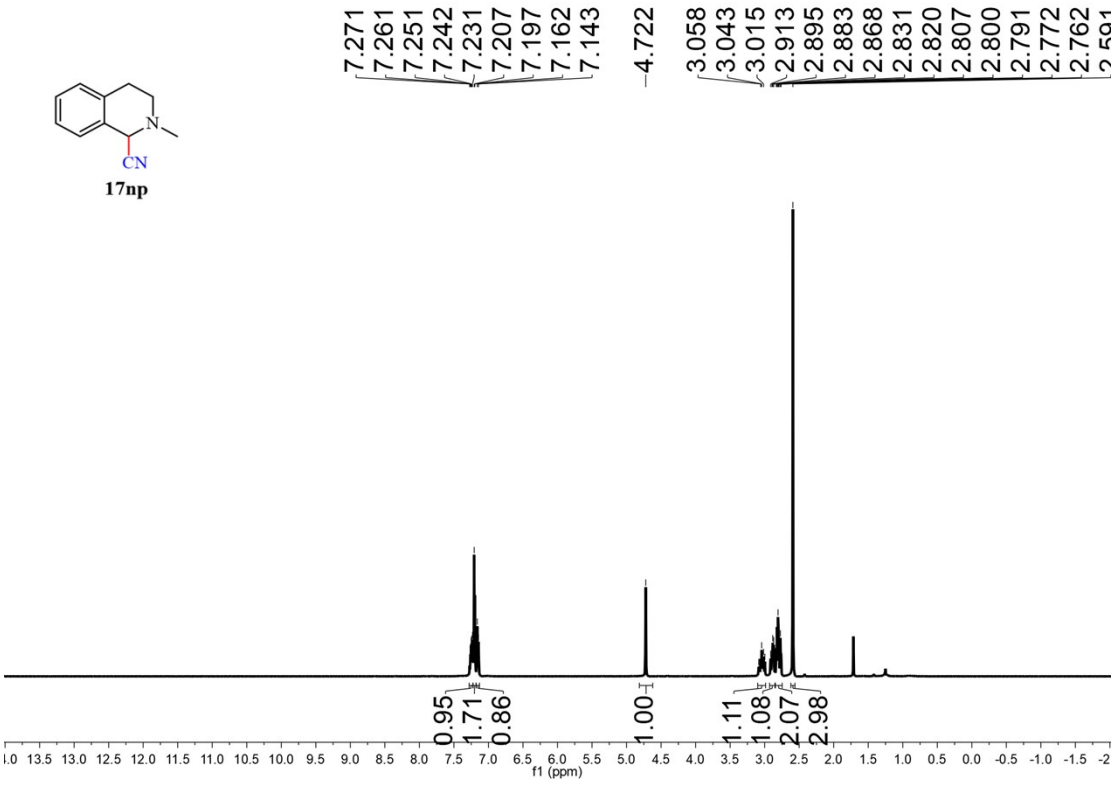
148.42
148.05
129.53
126.88
121.87
121.10
117.94
117.67
111.54
109.35
77.48
77.16
76.84
56.08
55.96
53.00
44.18
28.09
MeO
MeO
N
CN
16np
f1 (ppm)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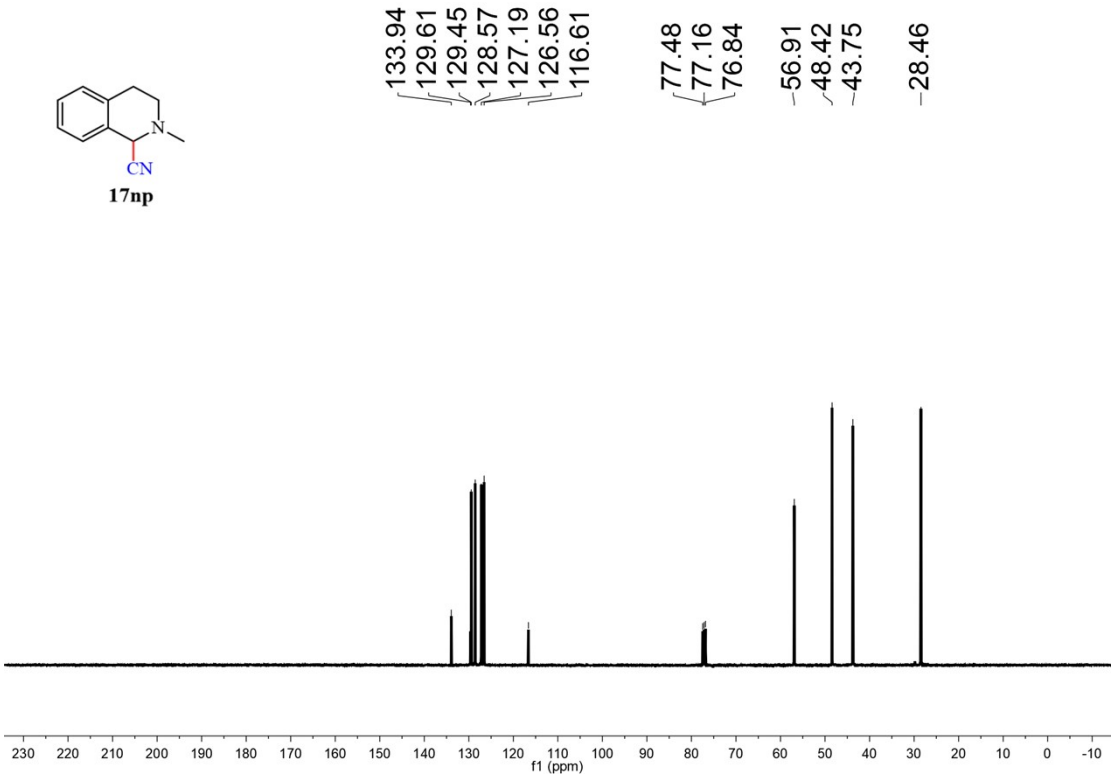
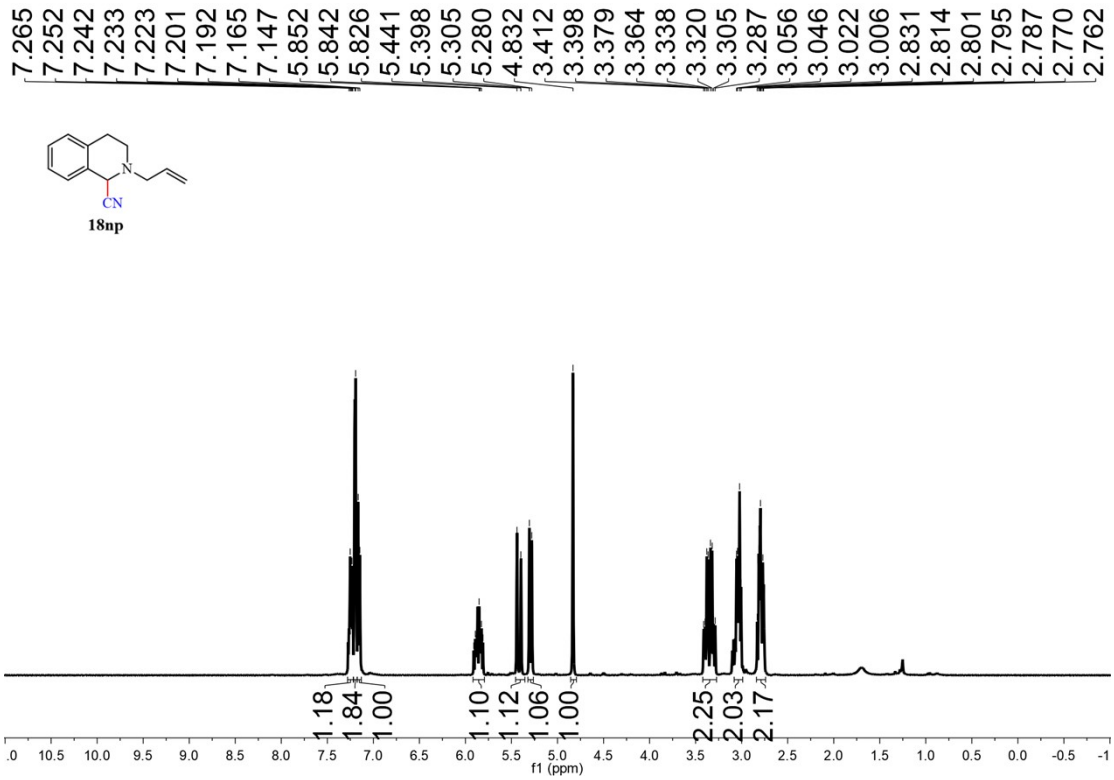
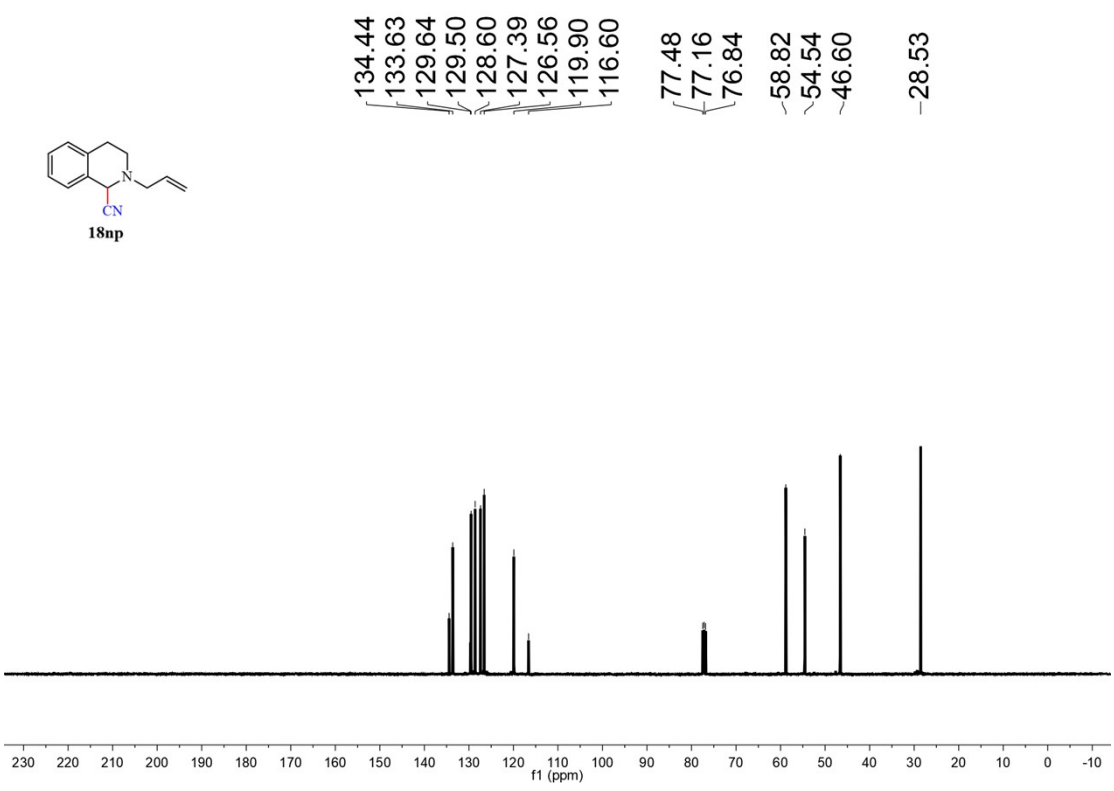
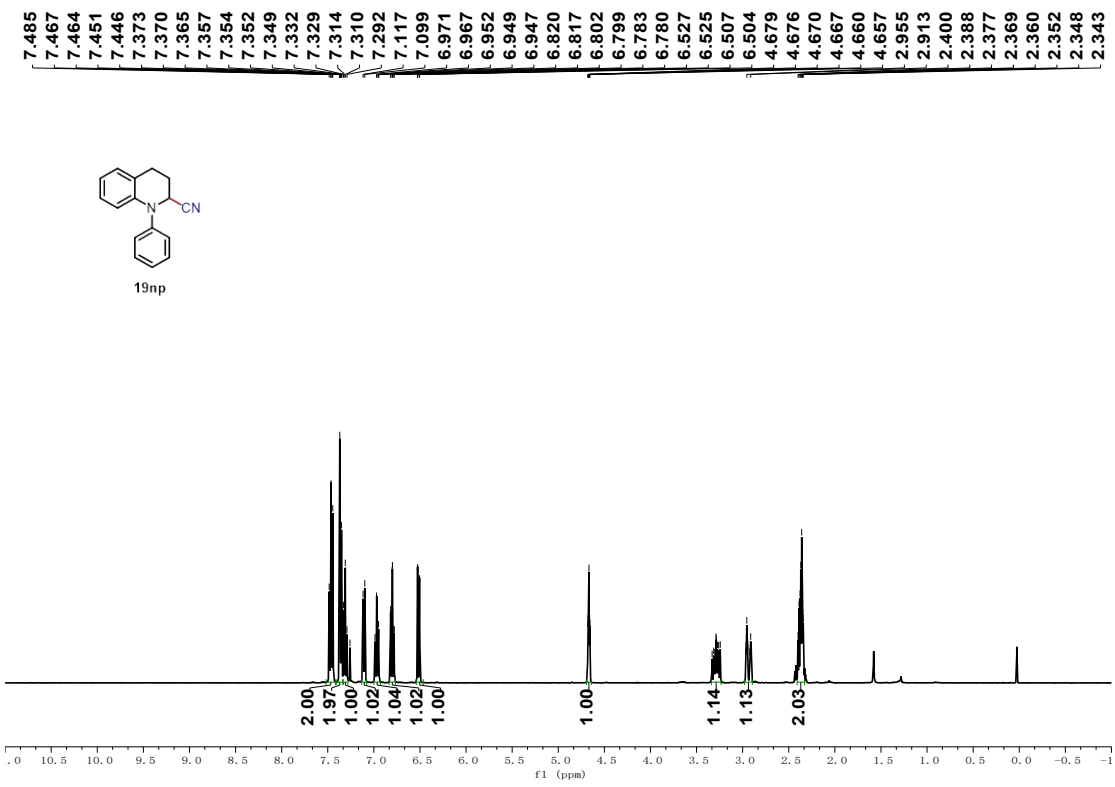
7.261
7.251
7.242
7.231
7.207
7.197
7.162
7.143
4.722
3.058
3.043
3.015
2.913
2.895
2.883
2.868
2.831
2.820
2.807
2.800
2.791
2.772
2.762
CN
17np
0.95
1.71
0.86
1.00
1.11
1.08
2.07
2.98
f1 (ppm)


133.94
129.61
129.45
128.57
127.19
126.56
116.61
77.48
77.16
76.84
56.91
48.42
43.75
28.46
CN
17np
f1 (ppm)


7.265
7.252
7.242
7.233
7.223
7.201
7.192
7.165
7.147
5.852
5.842
5.826
5.441
5.398
5.305
5.280
4.832
3.412
3.398
3.379
3.364
3.338
3.320
3.305
3.287
3.056
3.046
3.022
3.006
2.831
2.814
2.801
2.795
2.787
2.770
2.762
CN
18np
1.18
1.84
1.00
1.10
1.12
1.06
1.00
2.25
2.03
2.17
f1 (ppm)


134.44
133.63
129.64
129.50
128.60
127.39
126.56
119.90
116.60
77.48
77.16
76.84
58.82
54.54
46.60
28.53
CN
18np
f1 (ppm)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7.464
7.451
7.446
7.373
7.370
7.365
7.357
7.354
7.352
7.349
7.332
7.329
7.314
7.310
7.292
7.117
7.099
6.971
6.967
6.952
6.949
6.947
6.820
6.817
6.802
6.799
6.783
6.780
6.527
6.525
6.507
6.504
4.679
4.676
4.670
4.667
4.660
4.657
2.955
2.913
2.400
2.388
2.377
2.369
2.360
2.352
2.348
2.343
CN
19np
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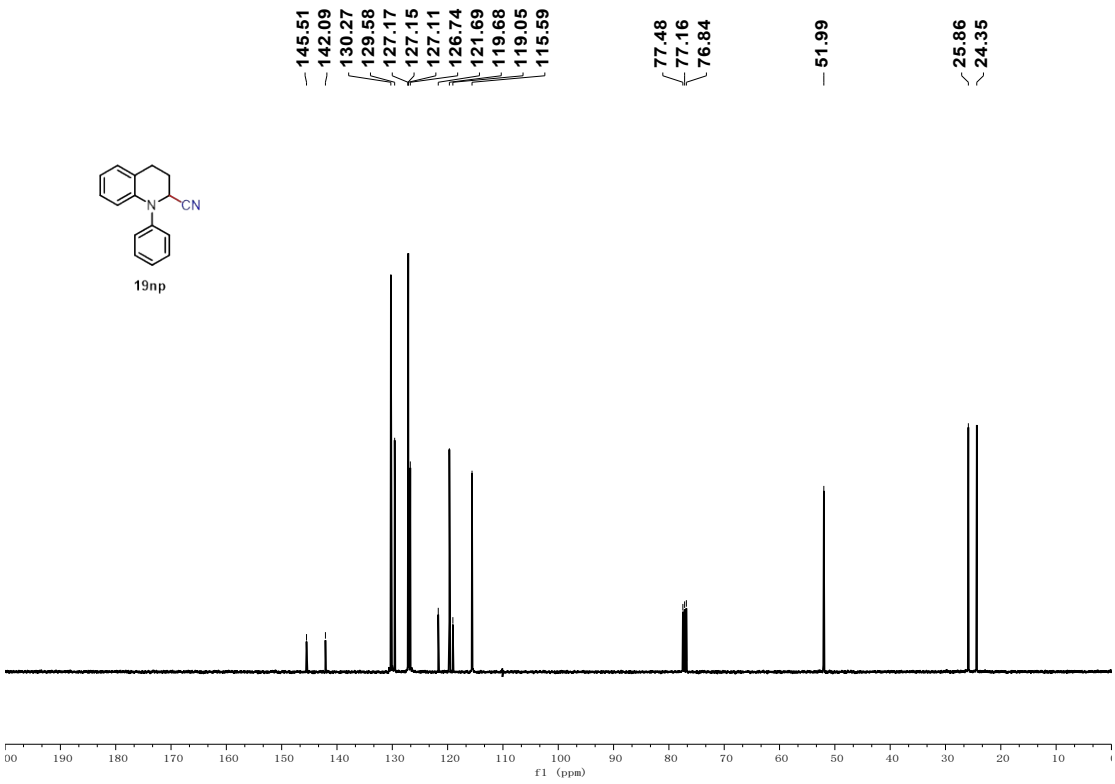
1.97
1.00
1.02
1.04
1.02
1.00
1.00
1.14
1.13
2.03
f1 (ppm)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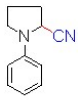
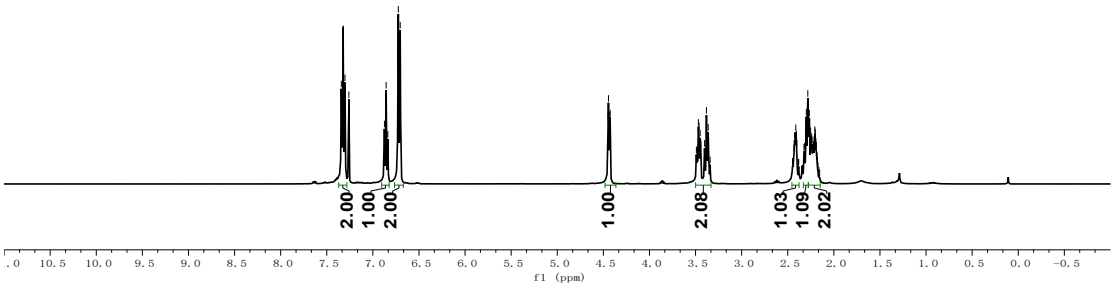
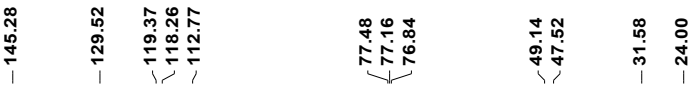
142.09
130.27
129.58
127.17
127.15
127.11
126.74
121.69
119.68
119.05
115.59
77.48
77.16
76.84
51.99
25.86
24.35
CN
19np
f1 (ppm)


7.342
7.337
7.324
7.320
7.307
7.302
7.260
6.874
6.856
6.838
6.724
6.704
4.449
4.445
4.431
4.426
3.491
3.483
3.470
3.462
3.450
3.443
3.402
3.382
3.363
3.342
2.432
2.427
2.420
2.413
2.407
2.401
2.324
2.316
2.299
2.283
2.272
2.266
2.252
2.247
2.241
2.233
2.227
2.221
2.215
2.206
2.202
2.196
2.190
2.183


N
CN

20 np


2.00
1.00
2.00
1.00
2.08
1.03
1.09
2.02
f1 (ppm)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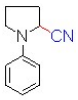
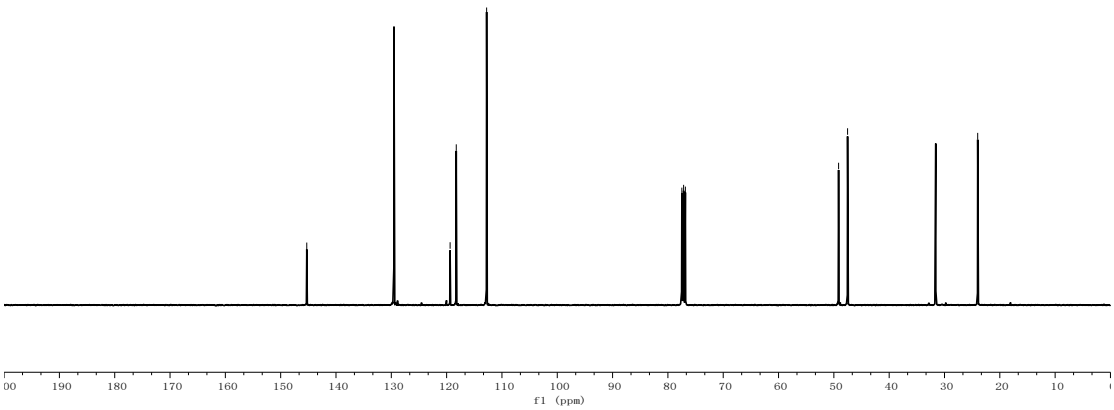
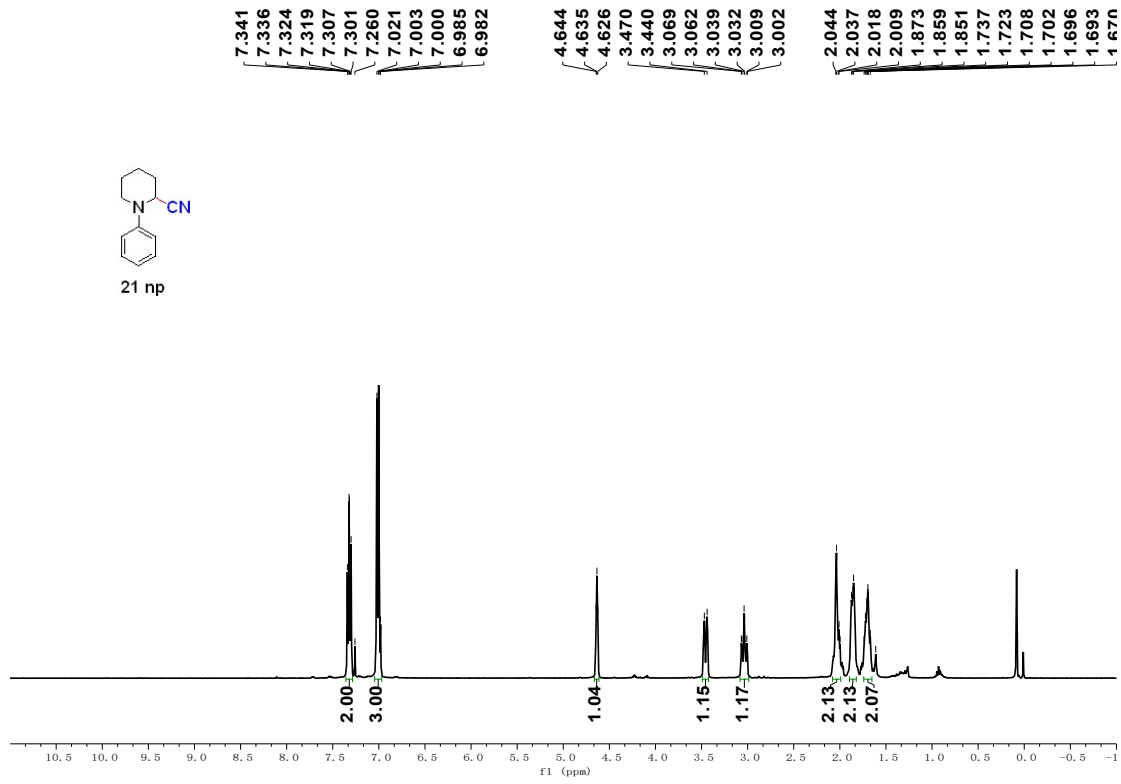
119.37
118.26
112.77
77.48
77.16
76.84
49.14
47.52
31.58
24.00


N
CN

20 np


f1 (ppm)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7.336
7.324
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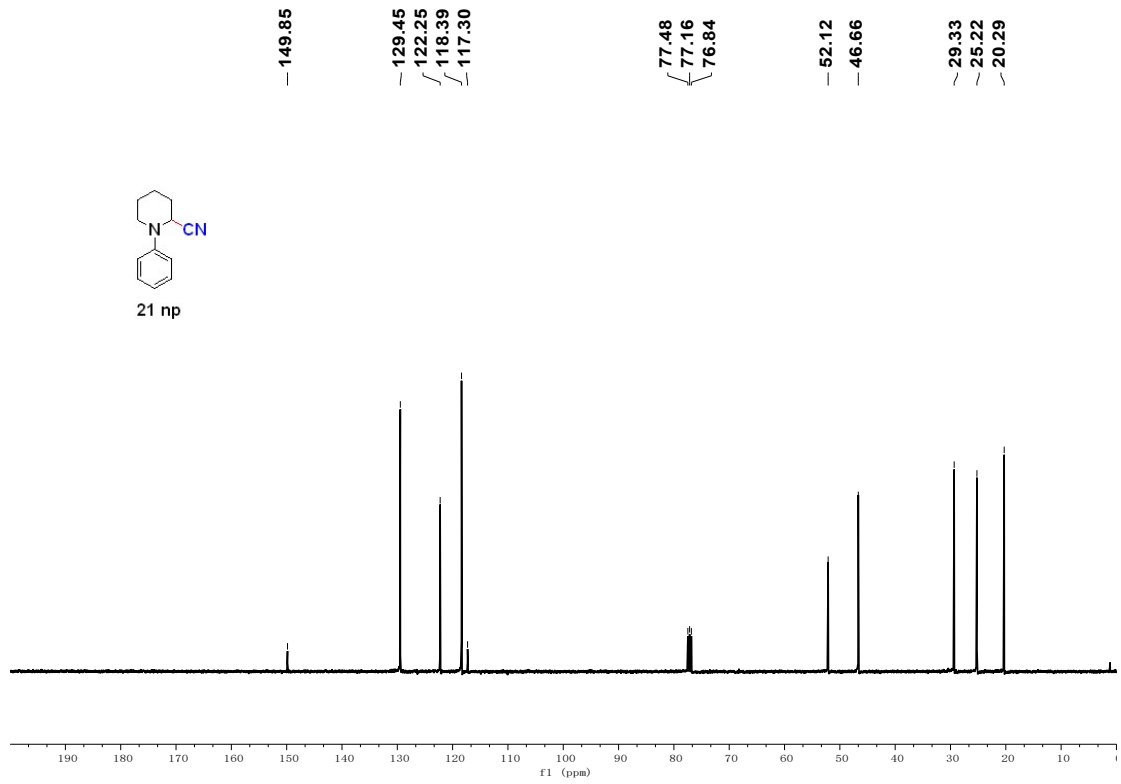
7.307
7.301
7.260
7.021
7.003
7.000
6.985
6.982
4.644
4.635
4.626
3.470
3.440
3.069
3.062
3.039
3.032
3.009
3.002
2.044
2.037
2.018
2.009
1.873
1.859
1.851
1.737
1.723
1.708
1.702
1.696
1.693
CN
21 np
2.00
3.00
1.04
1.15
1.17
2.13
2.13
2.07
f1 (ppm)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122.25
118.39
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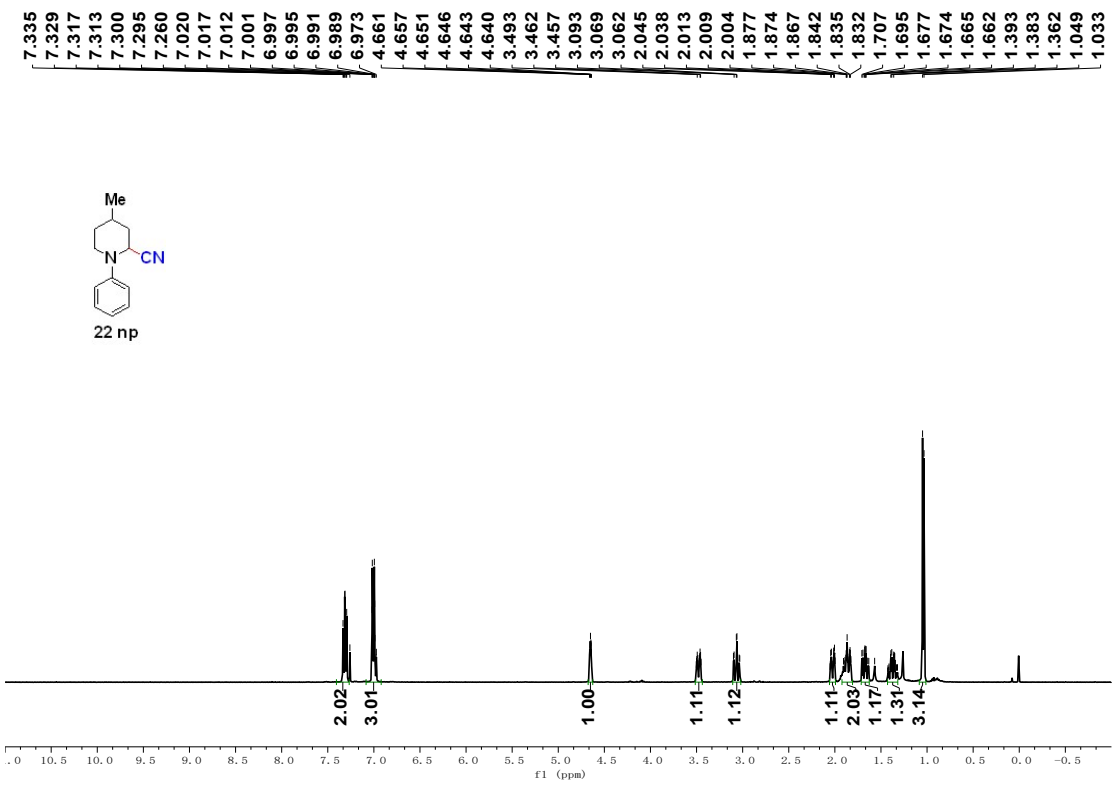
77.16
76.84
52.12
46.66
29.33
25.22
20.29
CN
21 np
f1 (ppm)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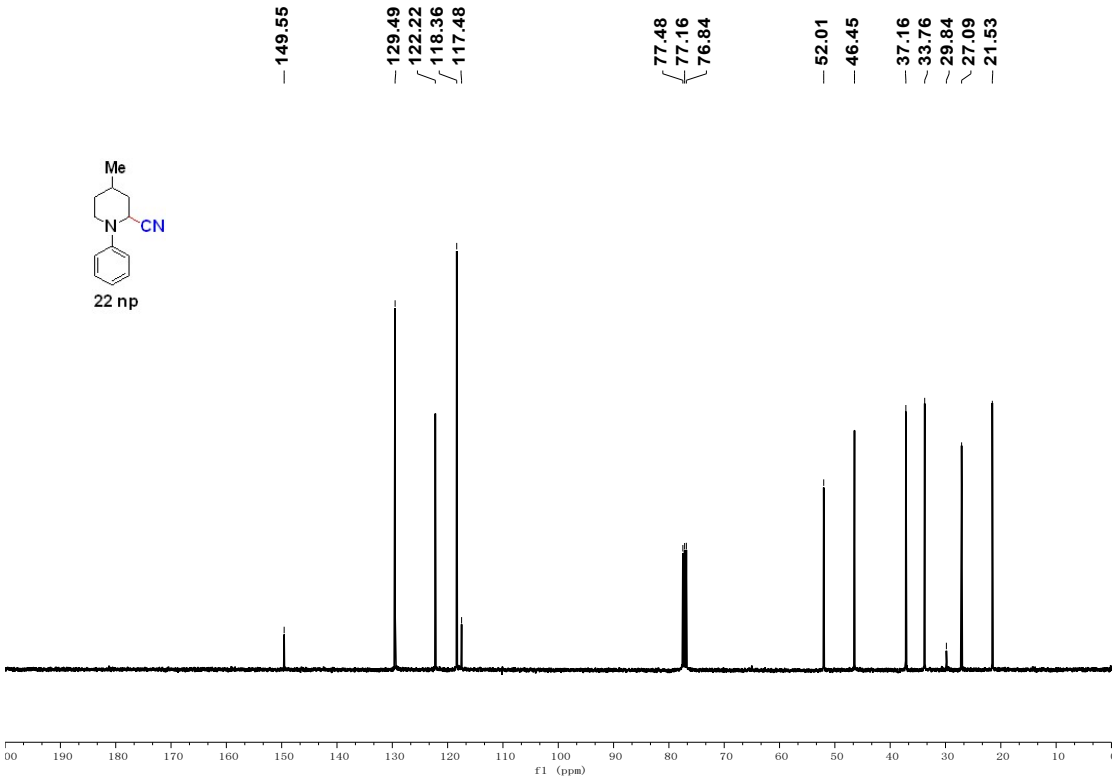
7.329
7.317
7.313
7.300
7.295
7.260
7.020
7.017
7.012
7.001
6.997
6.995
6.991
6.989
6.973
4.661
4.657
4.651
4.646
4.643
4.640
3.493
3.462
3.457
3.093
3.069
3.062
2.045
2.038
2.013
2.009
2.004
1.877
1.874
1.867
1.842
1.835
1.832
1.707
1.695
1.677
1.674
1.665
1.662
1.393
1.383
1.362
1.049
1.033
Me
CN
N
22 np
2.02
3.01
1.00
1.11
1.12
1.11
2.03
1.17
1.31
3.14
f1 (ppm)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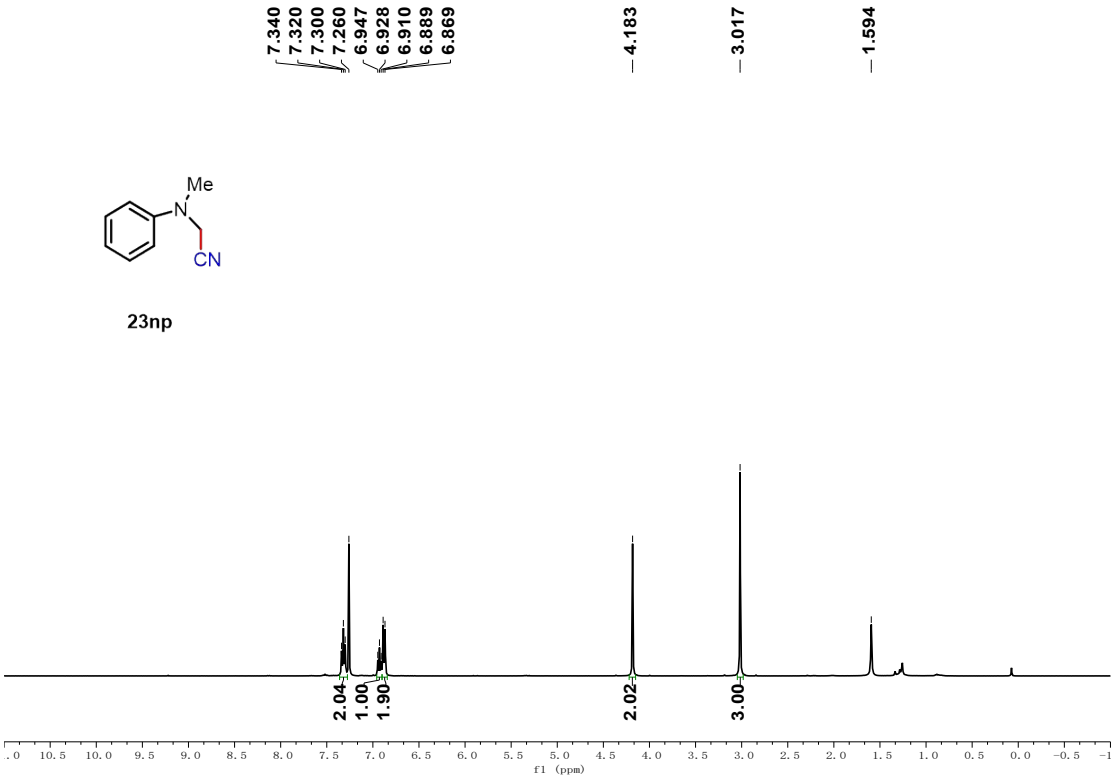
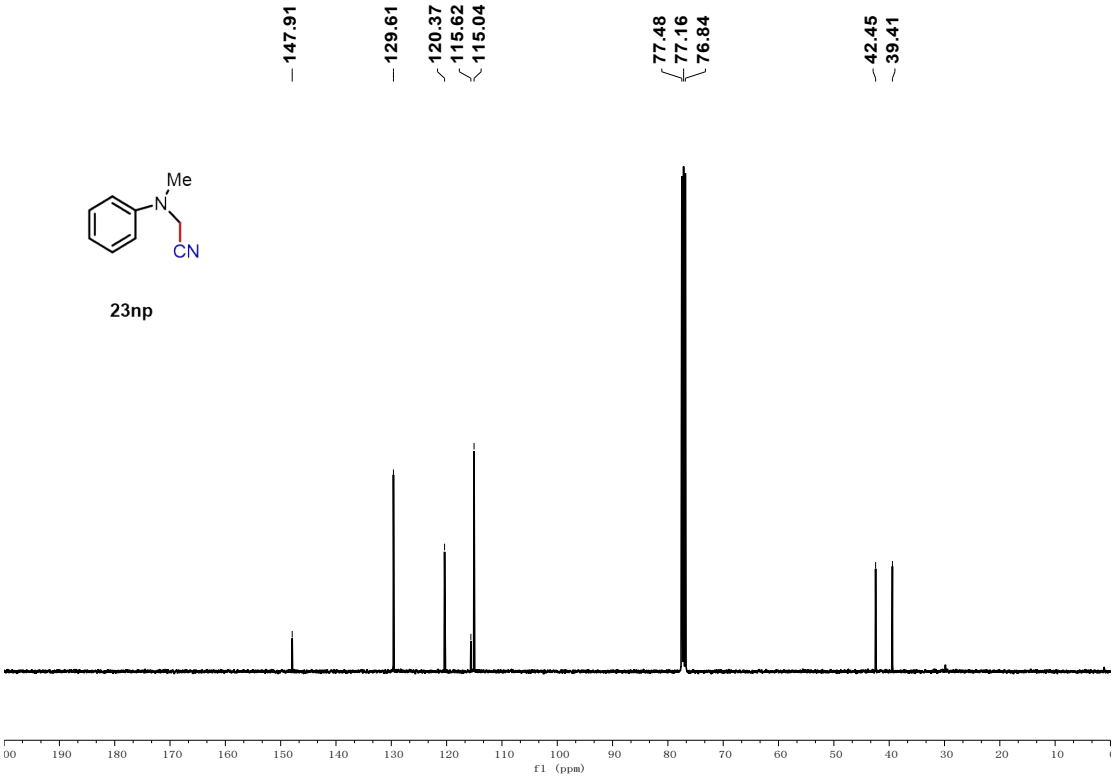
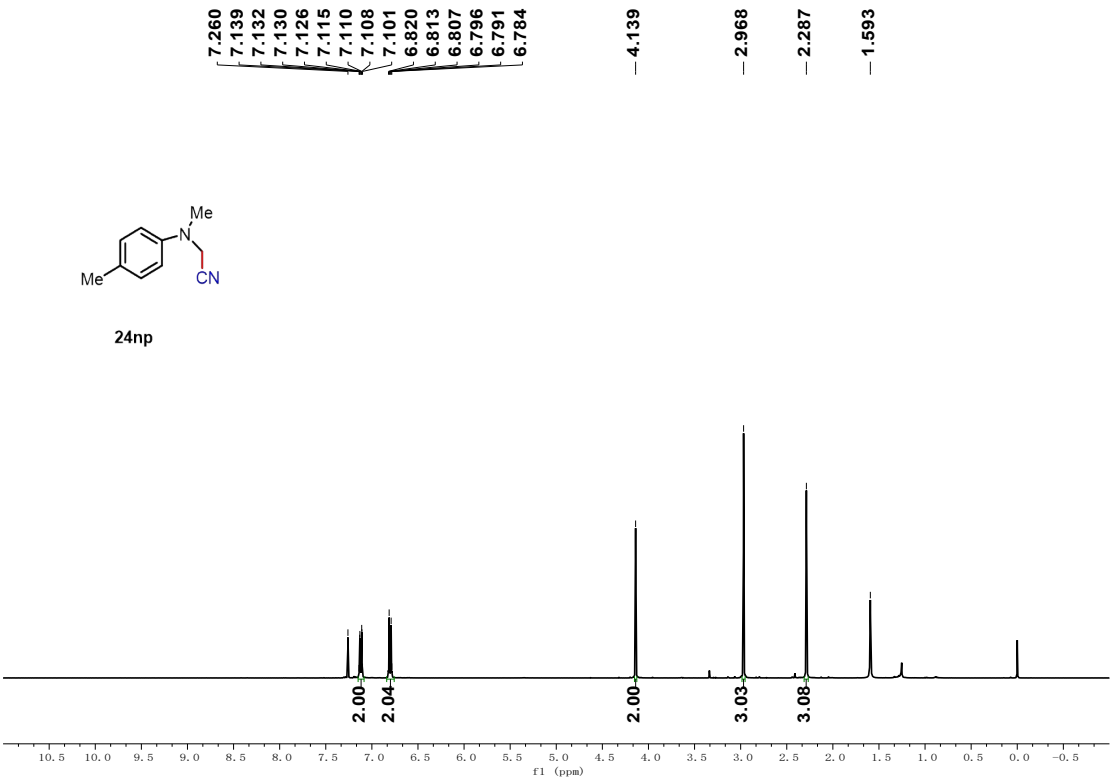
122.22
118.36
117.48
77.48
77.16
76.84
52.01
46.45
37.16
33.76
29.84
27.09
21.53
Me
CN
N
22 np
f1 (ppm)


7.340
7.320
7.300
7.260
6.947
6.928
6.910
6.889
6.869
4.183
3.017
1.594
Me
N
CN
2.04
1.00
1.90
2.02
3.00
f1 (ppm)

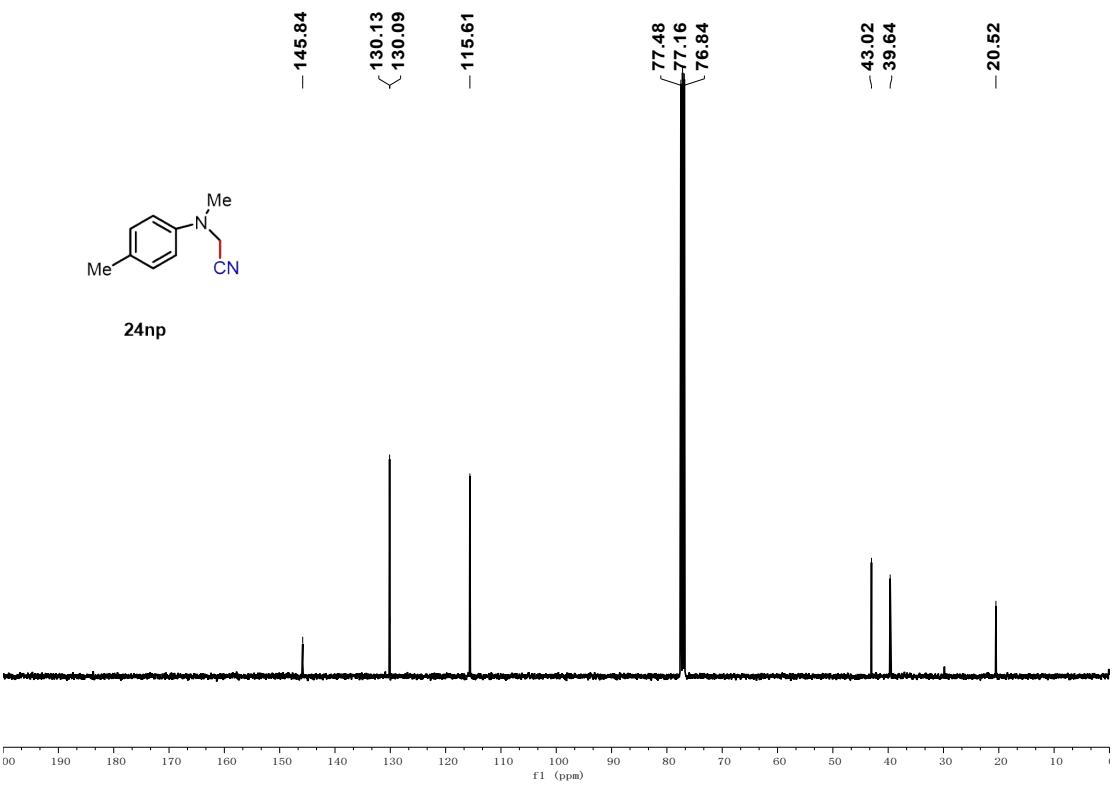
23np


147.91
129.61
120.37
115.62
115.04
77.48
77.16
76.84
42.45
39.41
Me
N
CN
f1 (ppm)

23np


7.260
7.139
7.132
7.130
7.126
7.115
7.110
7.108
7.101
6.820
6.813
6.807
6.796
6.791
6.784
4.139
2.968
2.287
1.593
Me
N
Me
CN
2.00
2.04
2.00
3.03
3.08
f1 (ppm)

24np


145.84
130.13
130.09
115.61
77.48
77.16
76.84
43.02
39.64
20.52
Me
N
Me
CN
f1 (ppm)

24np