Supporting Information

Copper-Catalyzed Synthesis of α-Amino Nitriles through Methyl Transfer from DMF to Aromatic Amines

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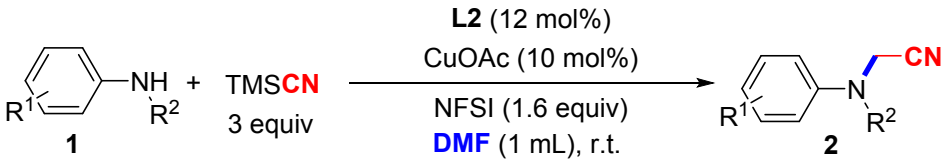
1. General Information

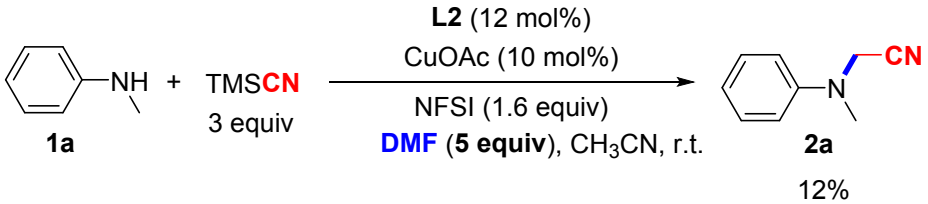
All syntheses were performed in oven-dried glassware under nitrogen atmosphere. All commercially obtained compounds were used as received. Solvents were purified as described in "Purification of Laboratory Chemicals". Thin layer chromatography was performed on GF254 plates (0.25 mm layer thickness). Flash chromatography was performed with 300–400 mesh silica gels. Visualization was accomplished with UV light (254 nm) and phosphomolybdic acid. ^{1}H, ^{13}C NMR spectra were recorded using a Bruker AM-400NMR spectrometer at room temperature. The chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H) $CDCl_3$ (77.0 ppm for ^{13}C). HRMS (EI) were recorded on a Waters AutoSpec Premier P776 spectrometer.

2. General Procedure for The Synthesis of α-amino Nitriles



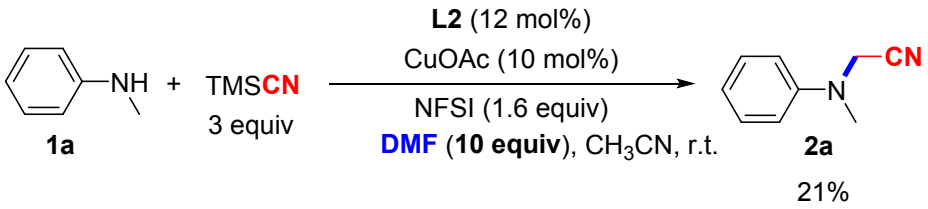
An oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.) and DMF (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and substrate (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine(5 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford the product.

Reducing the amount of DMF



An oven-dried round-bottom flask equipped with a magnetic stirring bar under nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.), DMF (1 mmol, 5 equiv), CH_3CN (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, 1,3-dinitrobenzene (0.4 mmol, 2.0 equiv) NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with

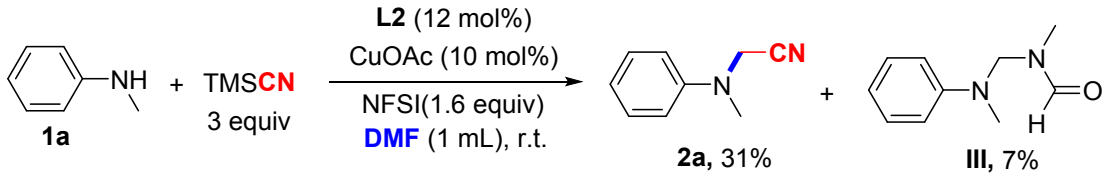
ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford the product as light yellow oil. Yield 12%.



An oven-dried round-bottom flask equipped with a magnetic stirring bar under nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.), DMF (2 mmol, 10 equiv), CH_3CN (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, 1,3-dinitrobenzene (0.4 mmol, 2.0 equiv) NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford the product as light yellow oil. Yield 21%.

3. Procedures for Mechanistic Experiments

Intermediate trapping experiment

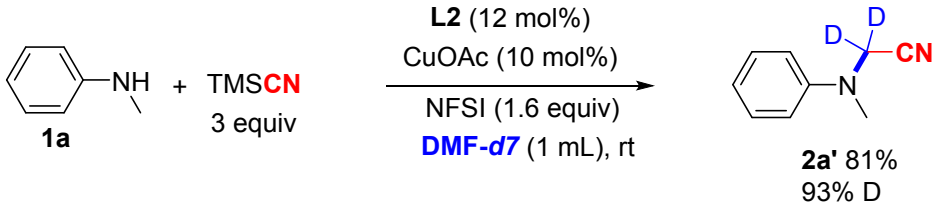


An oven-dried round-bottom flask equipped with a magnetic stirring bar under an nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.) and DMF (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 1h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine(5 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford the products. Products **2a** and **III** were isolated with yield of 31% and 7%, respectively, and 57% of **1a** was recovered.

The compound III exists as a 1.6:1 mixture of rotamers, the major rotamer is denoted

by §, minor rotamer denoted by*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H§), 8.09 (s, 1H*), 7.41 – 7.20 (m, 5H*), 7.02 – 6.70 (m, 5H§), 4.99 (s, 2H*), 4.77 (s, 2H§), 3.00 (s, 3H*), 2.87 (s, 3H§), 2.80 (s, 3H*), 2.79 (s, 3H§); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.93*, 162.13§, 148.30§, 147.77*, 129.31§, 129.23*, 119.05§, 117.99*, 114.19§, 112.85*, 67.54§, 60.79*, 38.05*, 36.16§, 33.12*, 28.81§. HRMS (EI) exact mass calculated for $C_{10}H_{14}N_{20}$:178.1106, found m/z 178.1102.

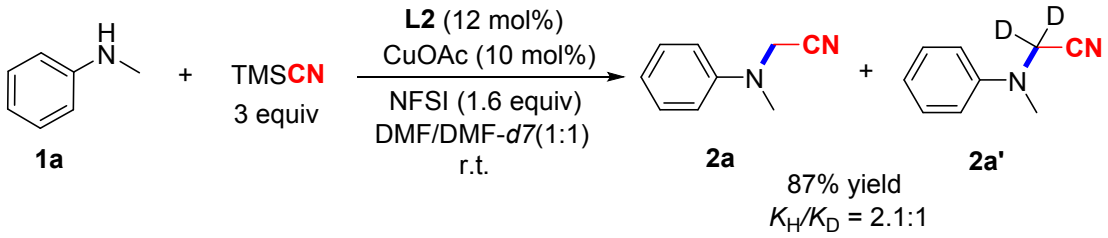
Deuterium labeling experiment



An oven-dried round-bottom flask equipped with a magnetic stirring bar under nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.) and DMF-*d7* (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford the product as light yellow oil. Yield 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 8.0 Hz, 2H), 7.07 – 6.80 (m, 3H), 3.01 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 147.70, 129.41, 120.12, 115.43, 114.78, 41.80 (m, $J_{C\text{-}D}$ =21.7 Hz). HRMS (EI) exact mass calculated for$C_9H_8D_2N_2$:148.0970, found m/z 148.0966.

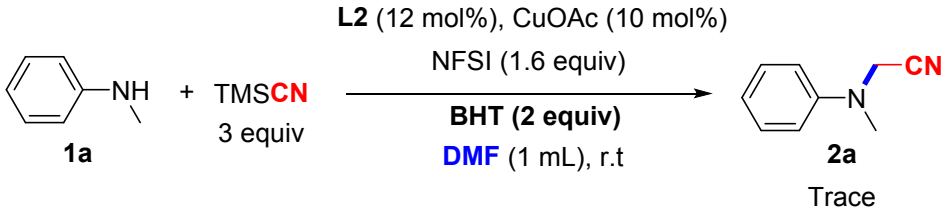
Kinetic isotopic effect



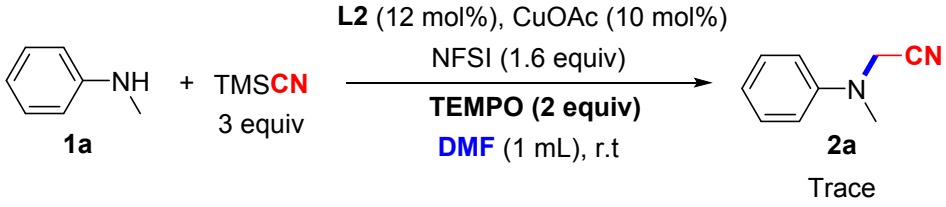
An oven-dried round-bottom flask equipped with a magnetic stirring bar under nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.), DMF-d_7 (0.5 mL) and DMF (0.5 mL). The reaction was allowed to stir at room temperature for 15 min. Then, NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL × 2). The

organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford the product as light yellow oil. Yield 87%. The K_H/K_D ratio was 2.1:1.

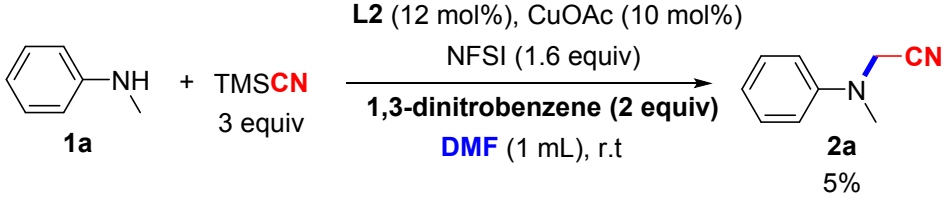
Radical inhibiting experiments



An oven-dried round-bottom flask equipped with a magnetic stirring bar under nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.), and DMF (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, BHT (0.4 mmol, 2.0 equiv) NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL × 2). Trace amount of product was obtained.



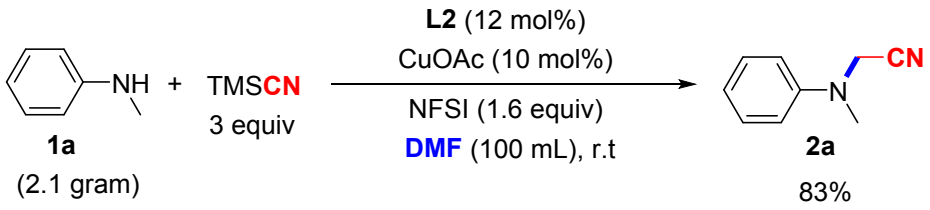
An oven-dried round-bottom flask equipped with a magnetic stirring bar under nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.), and DMF (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, TEMPO (0.4 mmol, 2.0 equiv) NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL × 2). Trace amount of product was obtained.



An oven-dried round-bottom flask equipped with a magnetic stirring bar under

nitrogen atmosphere, was charged with Ligand **L2** (0.024 mmol, 0.12 equiv.), CuOAc (0.02 mmol, 0.1 equiv.), and DMF (1 mL). The reaction was allowed to stir at room temperature for 15 min. Then, 1,3-dinitrobenzene (0.4 mmol, 2.0 equiv) NFSI (0.32 mmol, 1.6 equiv.), TMSCN (0.6 mmol, 3 equiv.) and *N*-methylaniline (0.2 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (30 mL), and washed successively with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford the product as light yellow oil. Yield 5%.

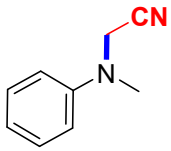
4. Gram-Scale reaction



An oven-dried round-bottom flask equipped with a magnetic stirring bar under a nitrogen atmosphere, was charged with Ligand **L2** (2.4 mmol, 0.12 equiv.), CuOAc (2 mmol, 0.1 equiv.) and DMF (100 mL). The reaction was allowed to stir at room temperature for 15 min. Then, NFSI (32 mmol, 1.6 equiv.), TMSCN (60 mmol, 3 equiv.) and *N*-methylaniline (20 mmol, 1 equiv.) were added to the reaction mixture in turn. The resulting reaction mixture was stirred at room temperature for 16 h, then diluted with ethyl acetate (300 mL), and washed successively with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to afford 2.4 g of product **2a** in 83% yield.

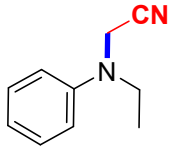
5. Product Characterization

N-Methyl-*N*-phenylaminoacetonitrile (2a)



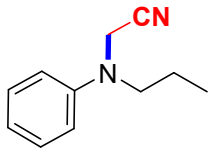
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 98%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.8 Hz, 2H), 7.01 – 6.79 (m, 3H), 4.18 (s, 2H), 3.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.78, 129.46, 120.23, 115.18,114.91, 42.31, 39.26; HRMS (EI) exact mass calculated for $C_9H_{10}N_2$:146.0844, found m/z 146.0842.

N-Ethyl-*N*-phenylaminoacetonitrile(2b)



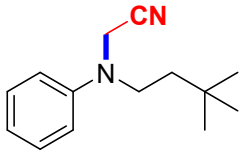
The title compound was prepared according to the general procedure. The product was obtained as light yellow oil. Yield 97%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.6, 7.5 Hz, 2H), 6.95 – 6.84 (m, 3H), 4.15 (s, 2H), 3.45 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.79, 129.47, 119.76, 116.34, 114.86, 46.21, 39.45, 12.16; HRMS (EI) exact mass calculated for $C_{10}H_{12}N_2$: 160.1000, found m/z 160.0999.

N-Propyl-*N*-phenylaminoacetonitrile(2c)



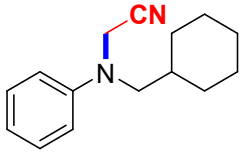
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 90%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.8 Hz, 2H), 6.97 – 6.81 (m, 3H), 4.16 (s, 2H), 3.34 – 3.29 (m, 2H), 1.75 – 1.63 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.16, 129.47, 119.65, 116.29, 114.65, 53.80, 39.98, 20.41, 11.34 ; HRMS (EI) exact mass calculated for $C_{11}H_{14}N_2$: 174.1157, found m/z 174.1162.

N-(3,3-Dimethyl)butyl-*N*-phenylaminoacetonitrile (2d)



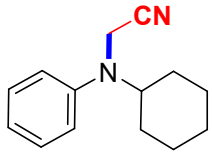
The title compound was prepared according to the general procedure. The product was obtained as light yellow oil. Yield 86%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 6.94 – 6.81 (m, 3H), 4.14 (s, 2H), 3.52 – 3.10 (m, 2H), 1.77 – 1.50 (m, 2H), 0.99 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.94, 129.51, 119.61, 116.34, 114.64, 48.39,40.01, 39.98 (d, *J* = 16.4 Hz), 29.79, 29.29; HRMS (EI) exact mass calculated for $C_{14}H_{20}N_2$:216.1626, found m/z 216.1624.

_N_-Cyclohexylmethyl-_N_-phenylaminoacetonitrile (2e)



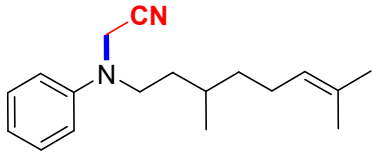
The title compound was prepared according to the general procedure. The product was obtained as brown oil. Yield 78%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.81-6.88 (m, 3H), 4.12 (s, 2H), 3.14 (d, *J* = 7.2 Hz, 2H), 1.81 – 1.63 (m, 6H), 1.36 – 1.11 (m, 3H), 0.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.63, 129.36, 119.39, 116.11, 114.41, 58.89, 40.69, 36.57, 31.08, 26.40, 25.82; HRMS (EI) exact mass calculated for $C_{15}H_{20}N_2$: 228.1626, found m/z 228.1631.

2-(Cyclohexylphenylamino)acetonitrile(2f)



The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 46%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 7.8 Hz, 2H), 6.87 – 6.91 (m, 3H), 4.11 (s, 2H), 3.68 – 3.55 (m, 1H), 1.91 (m, 4H), 1.71 (m, 1H), 1.51 – 1.11 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.35, 129.51, 119.74, 117.81, 115.35, 58.18, 34.73, 30.63, 25.86, 25.68; HRMS (EI) exact mass calculated for $C_{14}H_{18}N_2$: 214.1470, found m/z 214.1465.

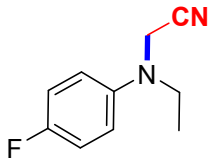
_N_-(3,7-Dimethyloct-6-en-1-yl)-_N_-phenylaminoacetonitrile(2g)



The title compound was prepared according to the general procedure. The product was obtained as light yellow oil. Yield 80%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.14 – 6.73 (m, 3H), 5.10 (t, *J* = 7.1 Hz, 1H), 4.14 (s, 2H), 3.48 – 3.26 (m, 2H), 2.00 (m, 2H), 1.75 – 1.64 (m, 4H), 1.61 (s, 3H), 1.56 – 1.43 (m, 2H), 1.43 – 1.34 (m, 1H), 1.25 – 1.16 (m, 1H), 0.97 (d, *J*

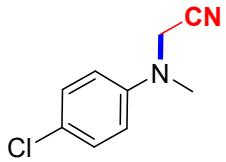
= 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.14, 131.48, 129.49, 124.44, 119.77, 116.26, 114.87, 50.22, 40.06, 36.94, 33.86, 30.47, 25.70, 25.41, 19.54, 17.65; HRMS (EI) exact mass calculated for $C_{18}H_{26}N_2$: 270.2096, found m/z 270.2089.

***N*-(4-Fluorophenyl)-*N*-ethylaminoacetonitrile (2h)**



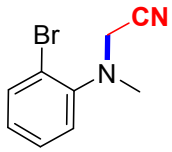
The title compound was prepared according to the general procedure. The product was obtained as light yellow oil.Yield 83%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 6.97 (m, 2H), 6.87 (m, 2H), 4.09 (s, 2H), 3.35 (q, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.59 (d, *J* = 240.0 Hz), 143.64, 117.96 (d, *J* = 7.7 Hz), 116.03 (d, *J* = 22.4 Hz), 115.98, 46.76, 40.83, 12.31; HRMS (EI) exact mass calculated for $C_{10}H_{11}FN_2$: 178.0906, found m/z 178.0905.

***N*-(4-Chlorophenyl)-*N*-methylaminoacetonitrile(2i)**



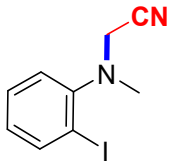
The title compound was prepared according to the general procedure. The product was obtained as light yellow oil. Yield 75%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.15 (s, 2H), 2.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.38, 129.37, 125.36, 116.11, 115.19, 42.39, 39.45; HRMS (EI) exact mass calculated for $C_9H_9ClN_2$: 180.0454, found m/z 180.0452.

***N*-(2-Bromophenyl)-*N*-methylaminoacetonitrile (2j)**



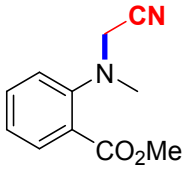
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 71%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.37 – 7.31 (m, 1H), 7.28 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.01-7.05 (m, 1H), 4.09 (s, 2H), 2.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.38, 133.95, 128.55, 126.33, 122.77, 119.74, 115.10, 44.79, 40.59; HRMS (EI) exact mass calculated for $C_9H_9BrN_2$: 223.9949, found m/z 223.9942.

***N*-(2-Iodophenyl)-*N*-methylaminoacetonitrile (2k)**



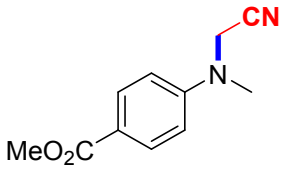
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 59%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.9, 1.4 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.30 – 7.24 (m, 1H), 6.91 (dd, J = 7.8, 1.6 Hz, 1H).4.00 (s, 2H), 2.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.33, 140.19, 129.49, 127.27, 122.81, 115.12, 97.61, 45.60, 40.97 ; HRMS (EI) exact mass calculated for $C_9H_9IN_2$: 271.9810, found m/z 271.9812.

Methyl 2-((cyanomethyl)methylamino)benzoate(2l)



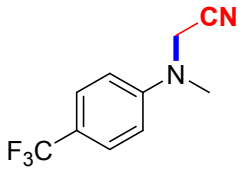
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 90%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 – 7.44 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 4.14 (s, 3H), 3.90 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.14, 149.75, 132.94, 131.63, 125.13, 123.77, 121.29, 52.22, 46.22, 40.91; HRMS (EI) exact mass calculated for $C_{11}H_{12}N_2O_2$: 204.0899, found m/z 204.0903.

Methyl 4-((cyanomethyl)methylamino)benzoate(2m)



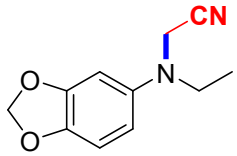
The title compound was prepared according to the general procedure. The product was obtained as yellow powder. Yield 83%;
mp 79.5-80.3°C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 4.25 (s, 2H), 3.88 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.85, 150.85, 131.43, 120.83, 115.07, 112.74, 51.76, 41.18, 39.00; HRMS (EI) exact mass calculated for $C_{11}H_{12}N_2O_2$: 204.0899, found m/z 204.0901.

***N*-methyl-*N*-(4-trifluoromethylphenyl)aminoacetonitrile(2n)**



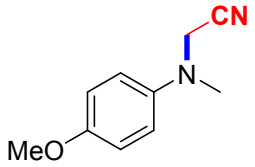
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 82%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.23 (s, 2H), 3.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.82, 126.69 (q, *J* = 3.7 Hz), 124.48 (q, *J* = 270.8 Hz), 121.42, 121.25 (q, *J* = 32.8 Hz), 115.05, 113.34, 41.39, 39.04; HRMS (EI) exact mass calculated for $C_{10}H_9F_3N_2$: 214.0718, found m/z214.0716.

_N_-(benzo[_d_][1,3]dioxol-5-yl)-_N_-ethylaminoacetonitrile(2o)



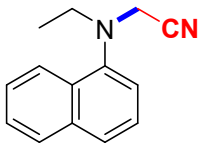
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 81%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 6.39 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.92 (s, 2H), 4.03 (s, 2H), 3.26 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.49, 142.92, 142.52, 115.99, 110.31, 108.44, 101.10, 100.45, 46.95, 41.75, 12.45; HRMS (EI) exact mass calculated for $C_{11}H_{12}N_2O_2$: 204.0899, found m/z 204.0902.

_N_-Methyl-_N_-(4-methoxyphenyl)aminoacetonitrile(2p)



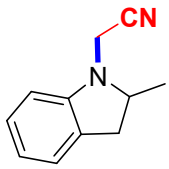
The title compound was prepared according to the general procedure. The product was obtained as colorless oil. Yield 70%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 4H), 4.08 (s, 2H), 3.78 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.34, 142.11, 124.61, 117.76, 114.73, 55.52, 43.94, 39.93; HRMS (EI) exact mass calculated for $C_{10}H_{12}N_2O$: 176.0950, found m/z 176.0954.

2-(Ethyl(naphthalen-1-yl)amino)acetonitrile(2q)



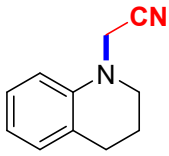
The title compound was prepared according to the general procedure except the reaction time was prolonged to 28 h. The product was obtained as colorless oil. Yield 75%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.36 (m, 4H), 4.10 (s, 2H), 3.36 (dd, *J* = 14.1, 7.0 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.22, 134.78, 129.82, 128.52, 126.16, 126.13, 125.66, 125.63, 47.24, 43.73, 12.87; HRMS (EI) exact mass calculated for $C_{14}H_{14}N_2$: 210.1157, found m/z 210.1160.

2-(2-Methylindolin-1-yl)acetonitrile(3a)



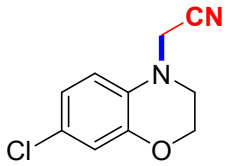
The title compound was prepared according to the general procedure. The product was obtained as yellow oil. Yield 72%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 17.7, 7.6 Hz, 2H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 3.96 (d, *J* = 18.0 Hz, 1H), 3.73 – 3.62 (m, 1H), 3.18 (dd, *J* = 15.3, 8.2 Hz, 1H), 2.68 (dd, *J* = 15.3, 10.7 Hz, 1H), 1.38 (d, *J* = 6.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.40, 129.39, 127.51, 124.59, 120.36, 114.95, 108.07, 60.42, 37.04, 34.91, 18.31; HRMS (EI) exact mass calculated for $C_{11}H_{12}N_2$: 172.1000, found m/z 172.1003.

2-(3,4-Dihydroquinolin-1(2*H*)-yl)acetonitrile(3b)



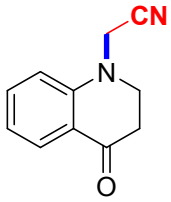
The title compound was prepared according to the general procedure. The product was obtained as yellow powder. Yield 74%;
mp 59.6-61.1°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (td, *J* = 8.0, 1.0 Hz, 1H), 7.04 (d, *J* = 6.9 Hz, 1H), 6.79 (td, *J* = 7.4, 0.8 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 4.16(s, 2H), 3.38 – 3.22 (m, 2H), 2.80 (t, *J* = 6.5 Hz, 2H), 2.10 – 2.01 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.12, 129.54, 127.24, 124.61, 119.14, 115.76, 111.81, 50.00, 40.13, 27.27, 22.16; HRMS (EI) exact mass calculated for $C_{11}H_{12}N_2$: 172.1000, found m/z 172.0998.

2-(7-Chloro-2,3-dihydro-4*H*-benzo[*b*][1,4]oxazin-4-yl)acetonitrile(3c)



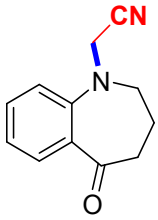
The title compound was prepared according to the general procedure except the ligand L1 instead of L2. The product was obtained as brown oil. Yield63%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (dt, *J* = 7.1, 2.3 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 4.43 – 4.20 (m, 2H), 4.13 (s, 2H), 3.42 – 3.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.74, 131.01, 125.57, 121.34, 117.19, 114.59, 113.96, 64.48, 47.39, 39.70; HRMS (EI) exact mass calculated for $C_{10}H_9ClN_2O$: 208.0403, found m/z 208.0400.

2-(4-Oxo-3,4-dihydroquinolin-1(2H)-yl)acetonitrile(3d)



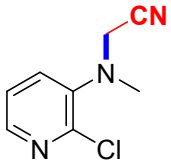
The title compound was prepared according to the general procedure. The product was obtained as light yellow powder. Yield 81%;
mp 137.5-138.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.57 – 7.45 (m, 1H), 6.97 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 4.27 (s, 2H), 3.73 – 3.39 (m, 2H), 2.90 – 2.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.43, 149.15, 135.71, 128.74, 121.71, 120.15, 114.38, 113.15, 50.28, 39.87, 38.10; HRMS (EI) exact mass calculated for $C_{11}H_{10}N_2O$: 186.0793, found m/z 186.0795.

2-(5-Oxo-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepin-1-yl)acetonitrile(3e)



The title compound was prepared according to the general procedure. The product was obtained as colorless crystal. Yield 92%;
mp 109.6-110.3°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.52 – 7.38 (m, 1H), 7.00 (m, 2H), 4.27 (s, 2H), 3.33 (t, *J* = 6.7 Hz, 2H), 2.79 (t, *J* = 6.9 Hz, 2H), 2.38 – 2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.15, 150.06, 133.06, 130.17, 129.21, 121.36, 115.89, 115.09, 54.98, 40.86, 40.44, 27.65; HRMS (EI) exact mass calculated for $C_{12}H_{12}N_2O$: 200.0950, found m/z 200.0955.

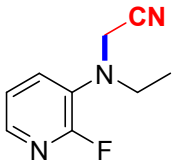
***N*-(2-Chloropyridin-3-yl)-*N*-methylaminoacetonitrile (3f)**



The title compound was prepared according to the general procedure. The product was obtained as light yellow oil. Yield 71%;

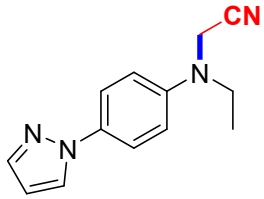
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.57 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.29 (dd, *J* = 7.9, 4.7 Hz, 1H), 4.17 (s, 2H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.15, 144.75, 142.85, 130.29, 123.18, 114.62, 43.72, 40.12; HRMS (EI) exact mass calculated for $C_8H_8ClN_3$: 181.0407, found m/z 181.0408.

_N_-Ethyl-_N_-(2-fluoropyridin-3-yl)aminoacetonitrile(3g)



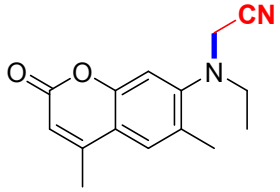
The title compound was prepared according to the general procedure. The product was obtained as brown oil.Yield 63 %;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.81 (m, 1H), 7.58 – 7.40 (m, 1H), 7.20 – 7.07 (m, 1H), 4.12 (s, 2H), 3.27 (q, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.27 (d, *J* = 231.0 Hz), 132.25 (d, *J* = 13.6 Hz), 131.95 (d, *J* = 26.8 Hz), 121.96 (d, *J* = 3.6 Hz), 118.68 (d, *J* = 5.4 Hz), 37.70, 14.45; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.02 (d, *J* = 10.3 Hz). HRMS (EI) exact mass calculated for $C_9H_{10}FN_3$: 179.0859, found m/z 179.0863.

_N_-(4-(1_H_-pyrazol-1-yl)phenyl)-_N_-ethylaminoacetonitrile(3h)



The title compound was prepared according to the general procedure. The product was obtained as yellow powder. Yield 79%;
mp 61.5-62.4°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.1 Hz, 1H), 7.69 (d, *J* = 0.9 Hz, 1H), 7.61 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.44 (d, *J* = 1.9 Hz, 1H), 4.18 (s, 2H), 3.47 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.49, 140.62, 133.41, 126.66, 120.93, 116.09, 115.65, 107.17, 46.56, 39.75, 12.17; HRMS (EI) exact mass calculated for $C_{13}H_{14}N_4$: 226.1218, found m/z 226.1211.

_N_-(4,6-Dimethyl-2-oxo-2_H_-chromen-7-yl)-_N_-ethylaminoacetonitrile(3i)

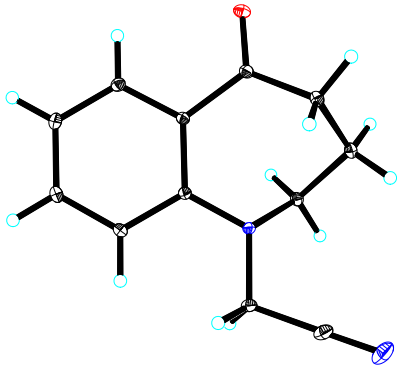


The title compound was prepared according to the general procedure. The product was obtained as light yellow powder. Yield 95%;
mp 168.1-169.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.09 (s, 1H), 6.13 (s,

1H), 3.93 (s, 2H), 3.16 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.00, 152.49, 152.11, 151.13, 129.81, 126.83, 116.62, 115.24, 113.79, 109.80, 46.93, 42.00, 18.58, 17.78, 12.70 ; HRMS (EI) exact mass calculated for $C_{15}H_{16}N_2O$: 256.1212, found m/z 256.1209.

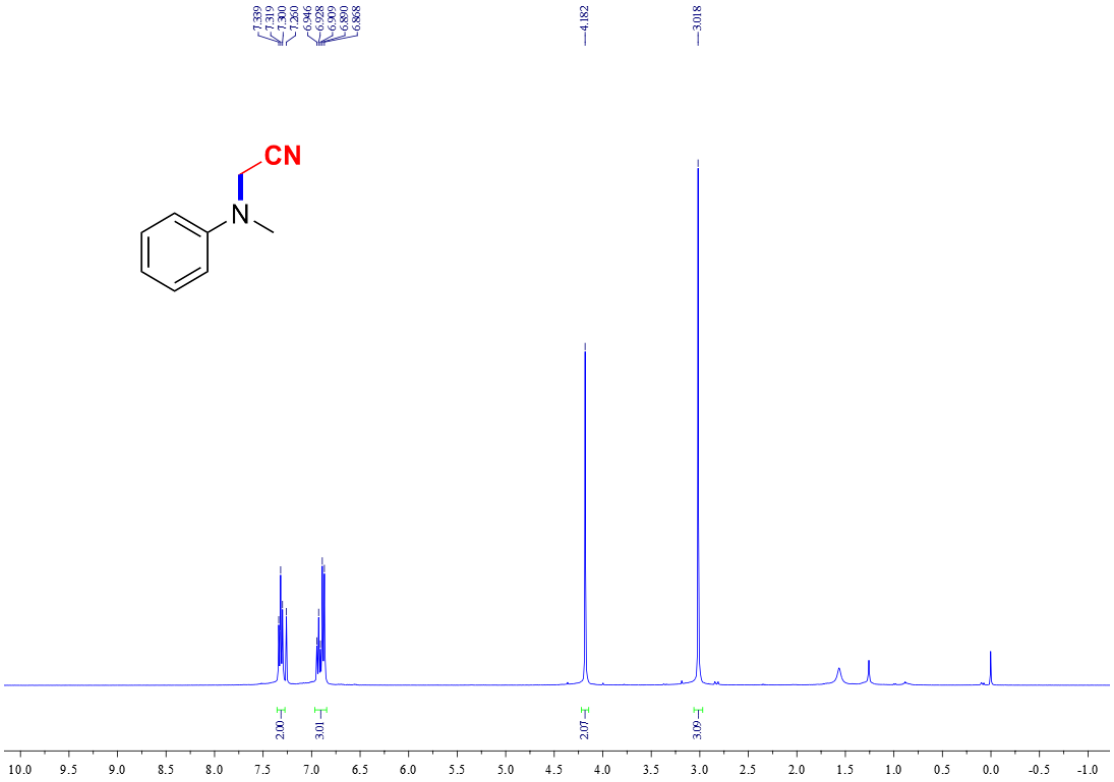
6. X-ray Crystallographic Data of 3e

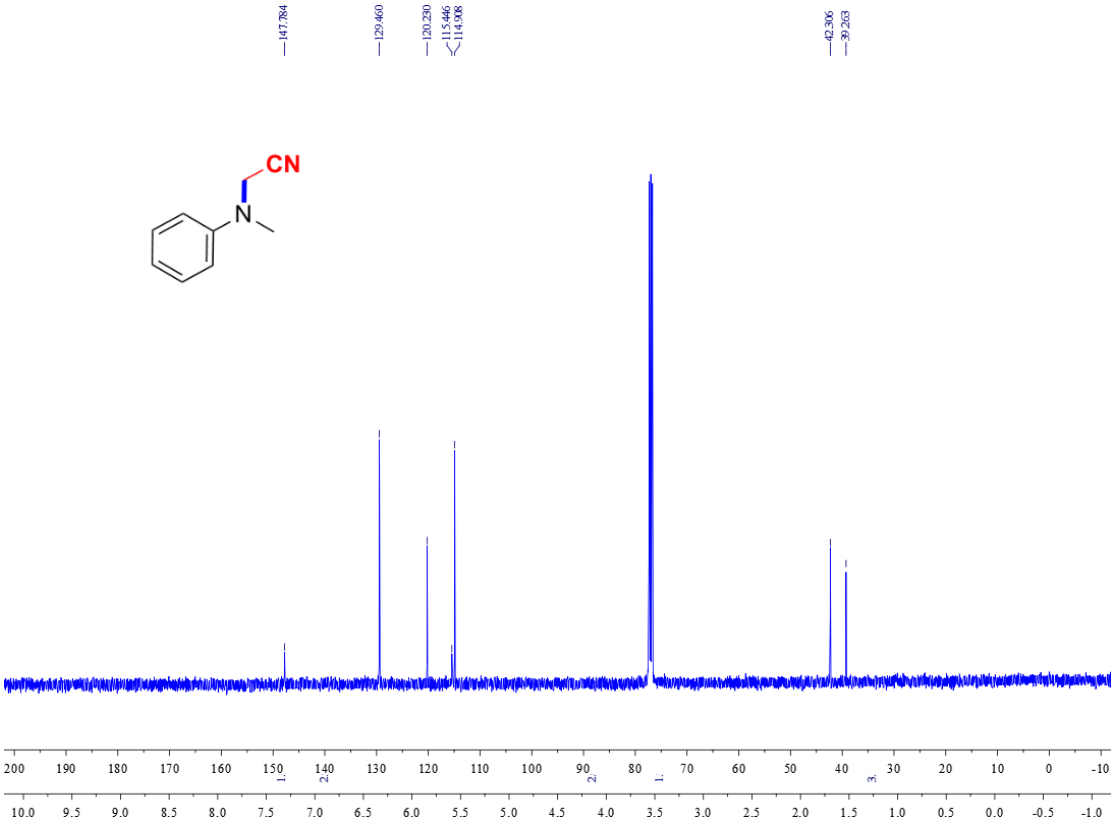
3e was recrystallized from chloroform in a closed tube at room temperature to obtain colorless crystals. Crystal data for **3e**: $C_{12}H_{12}N_2O$, $M = 200.24$, $a = 10.4481(12)$ Å, $b = 7.0131(8)$ Å, $c = 13.7142(16)$ Å, $\alpha = 90°$, $\beta = 99.787(2)°$, $\gamma = 90°$, $V = 990.3(2)$ Å^3, $T = 100(2)$ K, space group $P21/n$, $Z = 4$, μ(MoKα) = 0.088 mm^{-1}, 10505 reflections measured, 2948 independent reflections ($R_{int} = 0.0230$). The final R_1 values were 0.0370 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1014 ($I > 2\sigma(I)$). The final R_1 values were 0.0397 (all data). The final $wR(F^2)$ values were 0.1038 (all data). The goodness of fit on F^2 was 1.094.

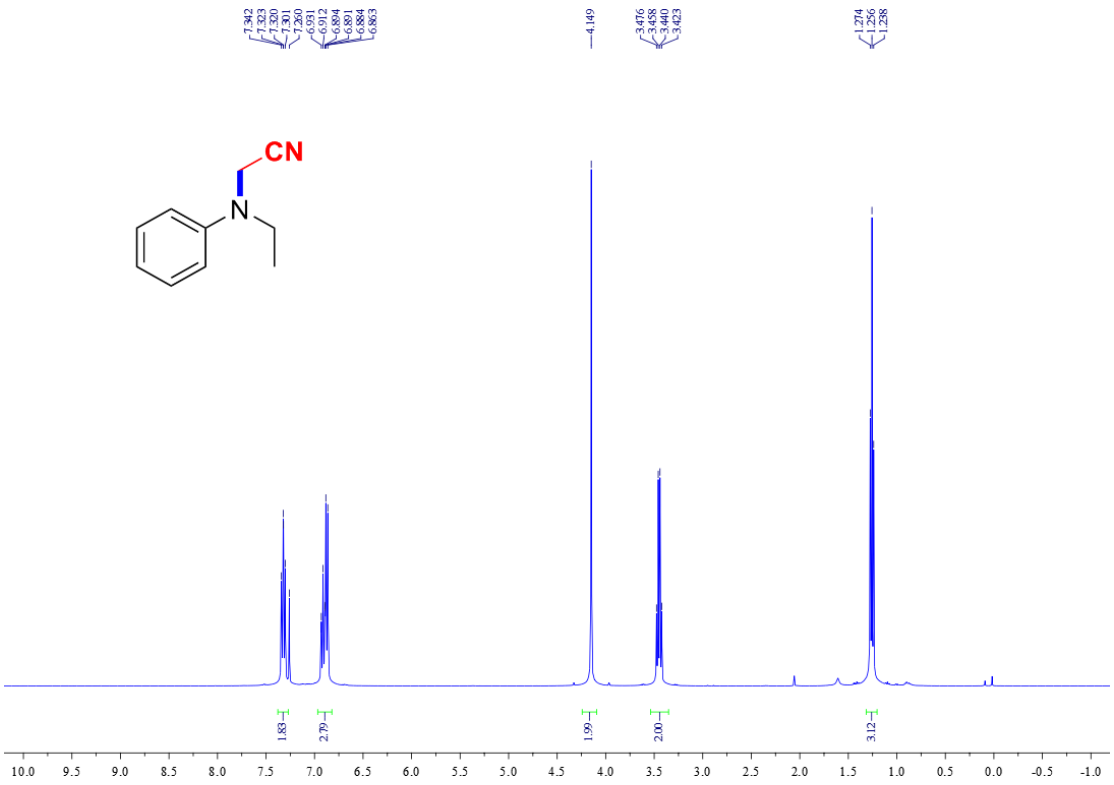


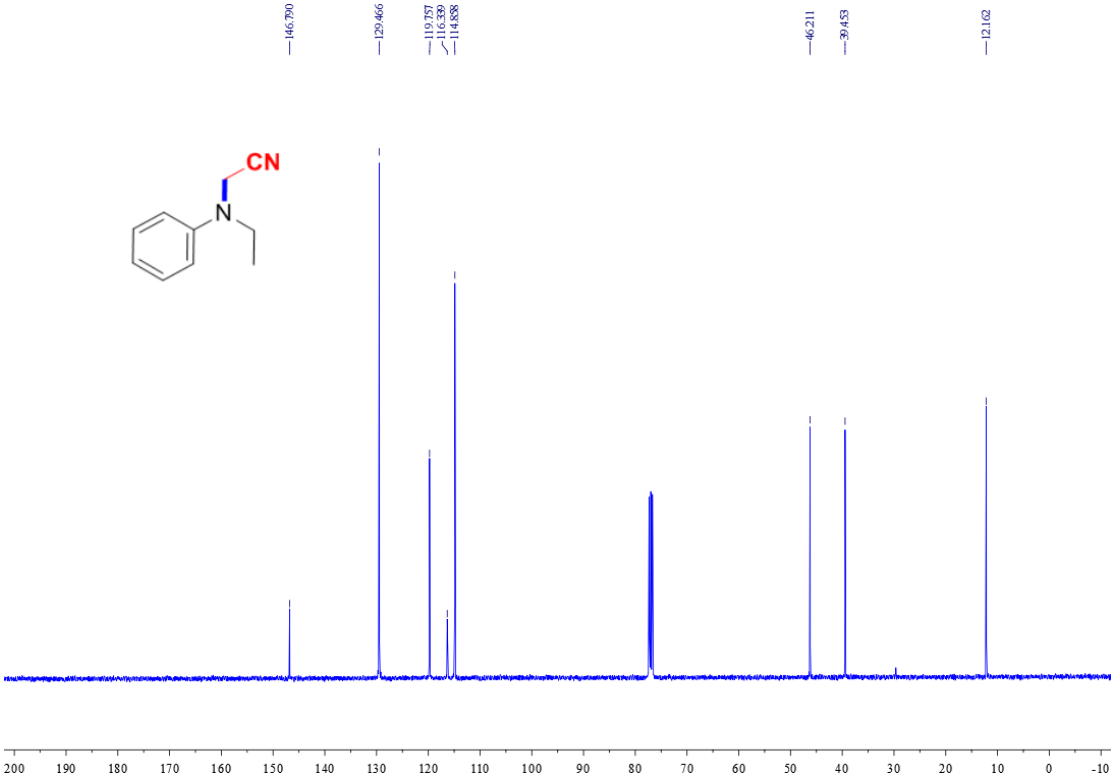
View of a molecule of **3e** with the atom-labelling scheme.
Displacement ellipsoids are drawn at the 30% probability level.

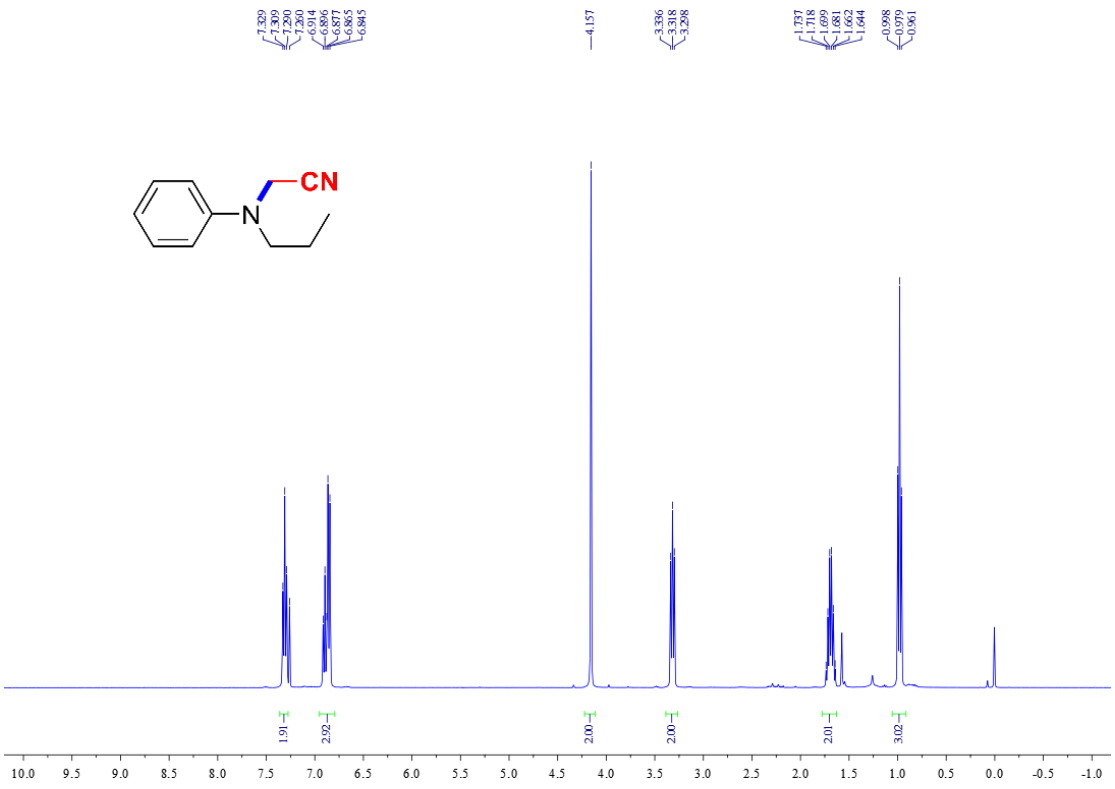
7. ^{1}H-NMR and ^{13}C-NMR Spectral Data






7.342
7.323
7.320
7.301
7.260
6.897
6.893
6.894
6.891
6.884
6.863
4.149
3.476
3.458
3.440
3.423
1.274
1.256
1.238
CN
N
1.83
2.79
1.99
2.00
3.12
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 -1.0


146.790
129.466
119.757
116.339
114.858
46.211
39.453
12.162
CN
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.329
7.309
7.290
7.260
6.914
6.906
6.887
6.865
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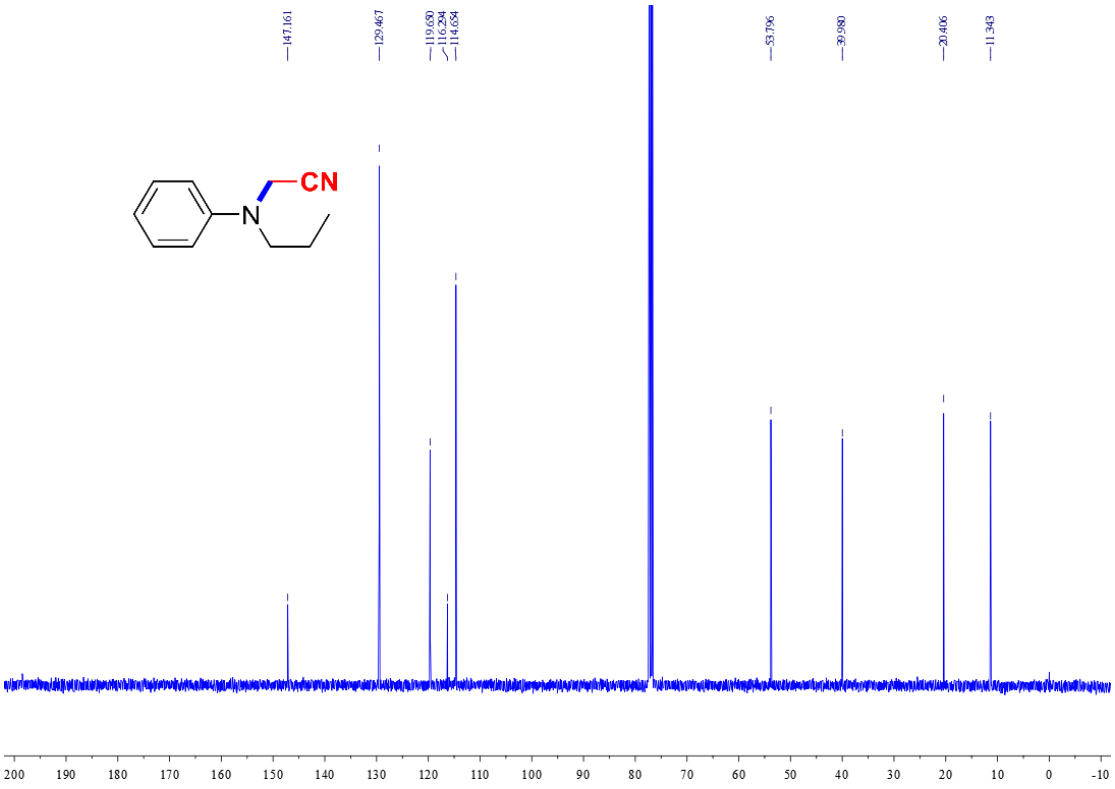
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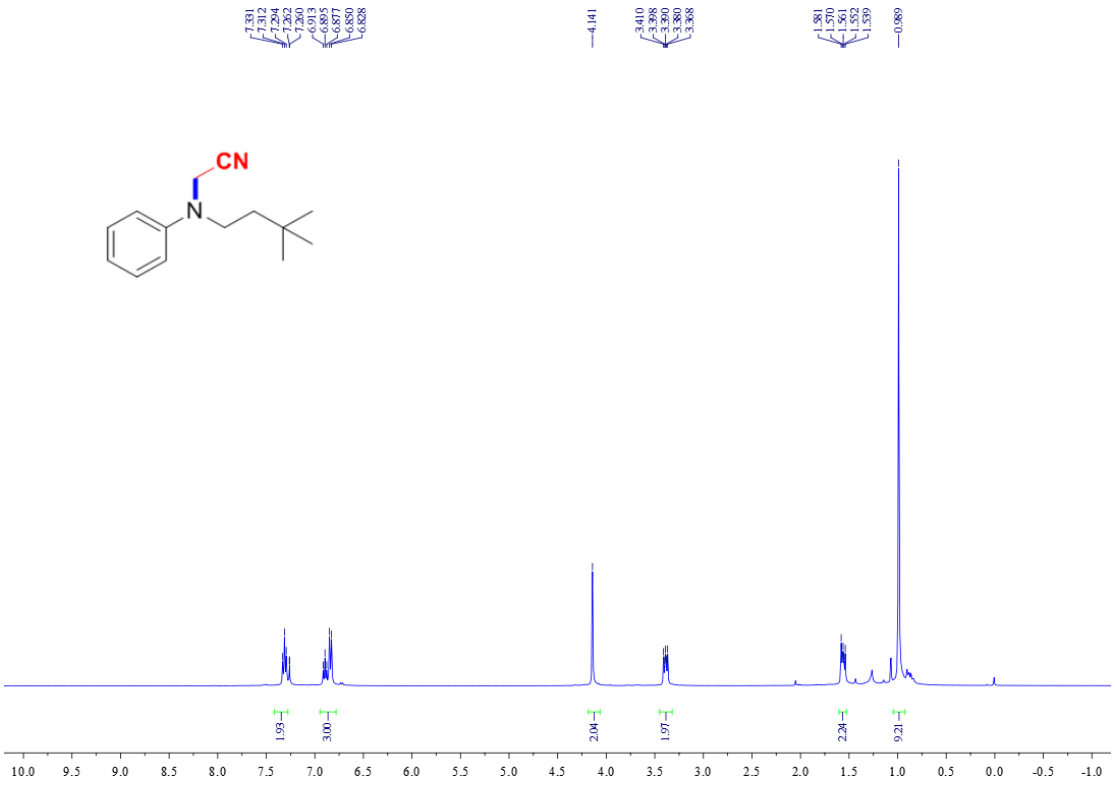
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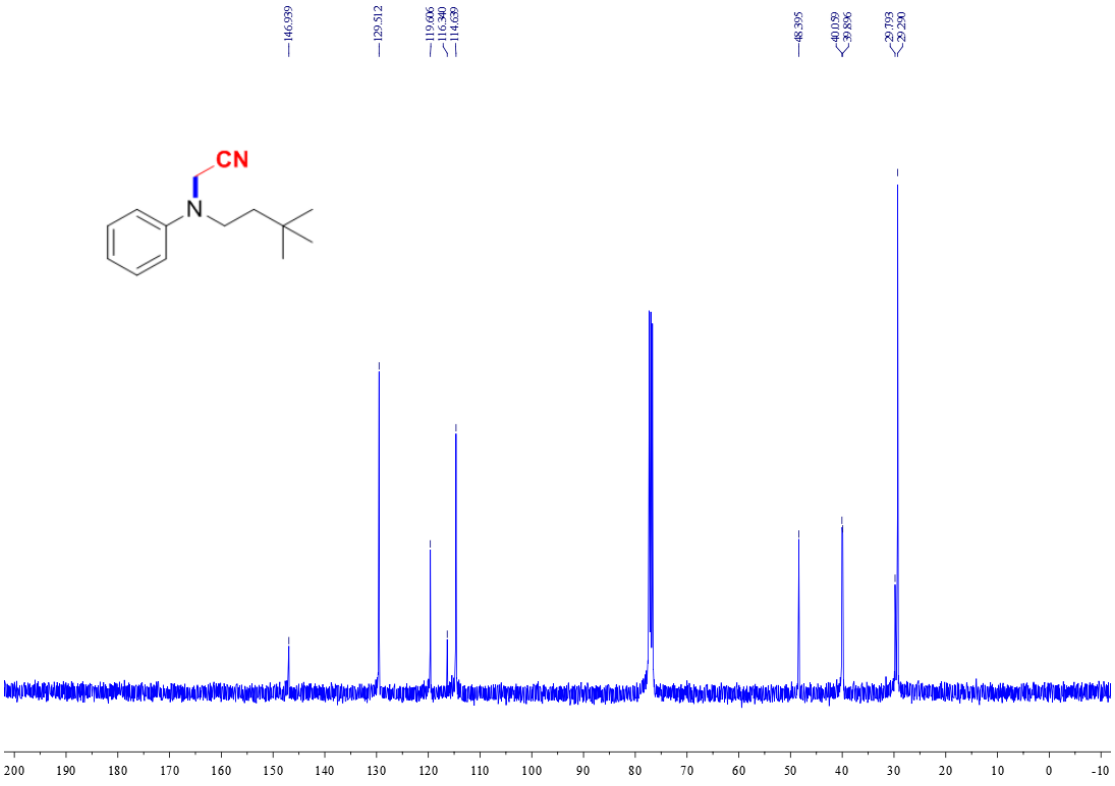
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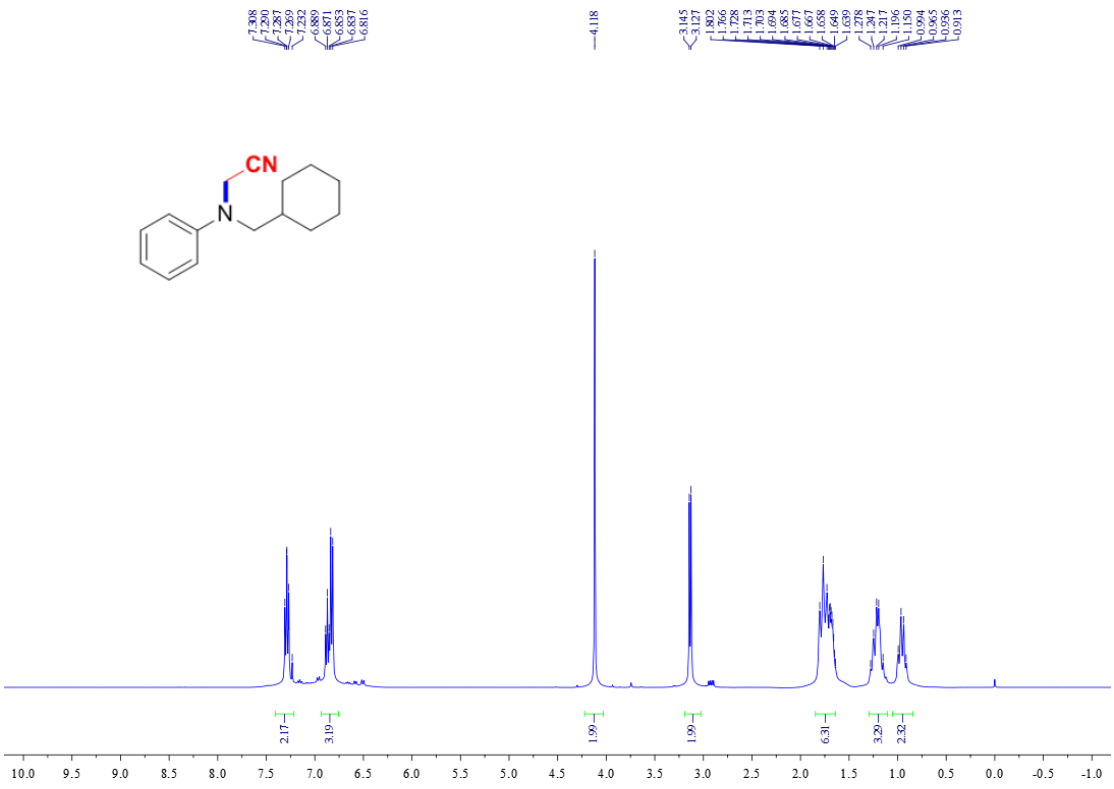
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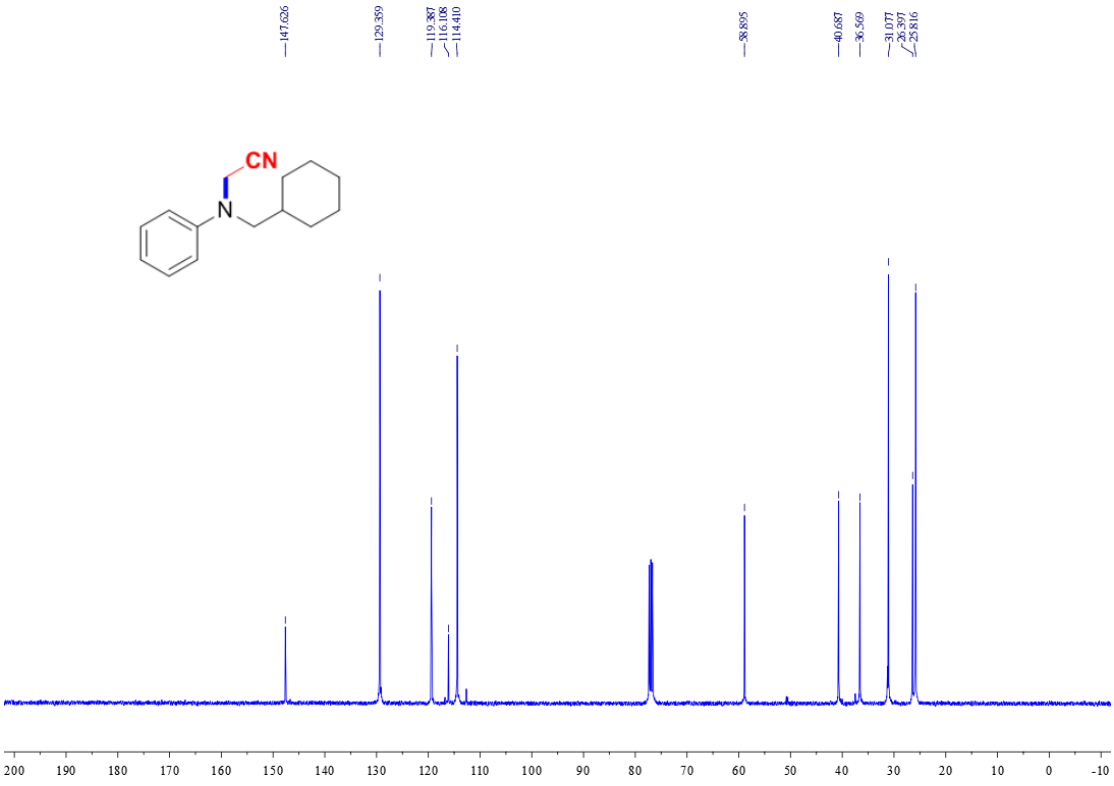
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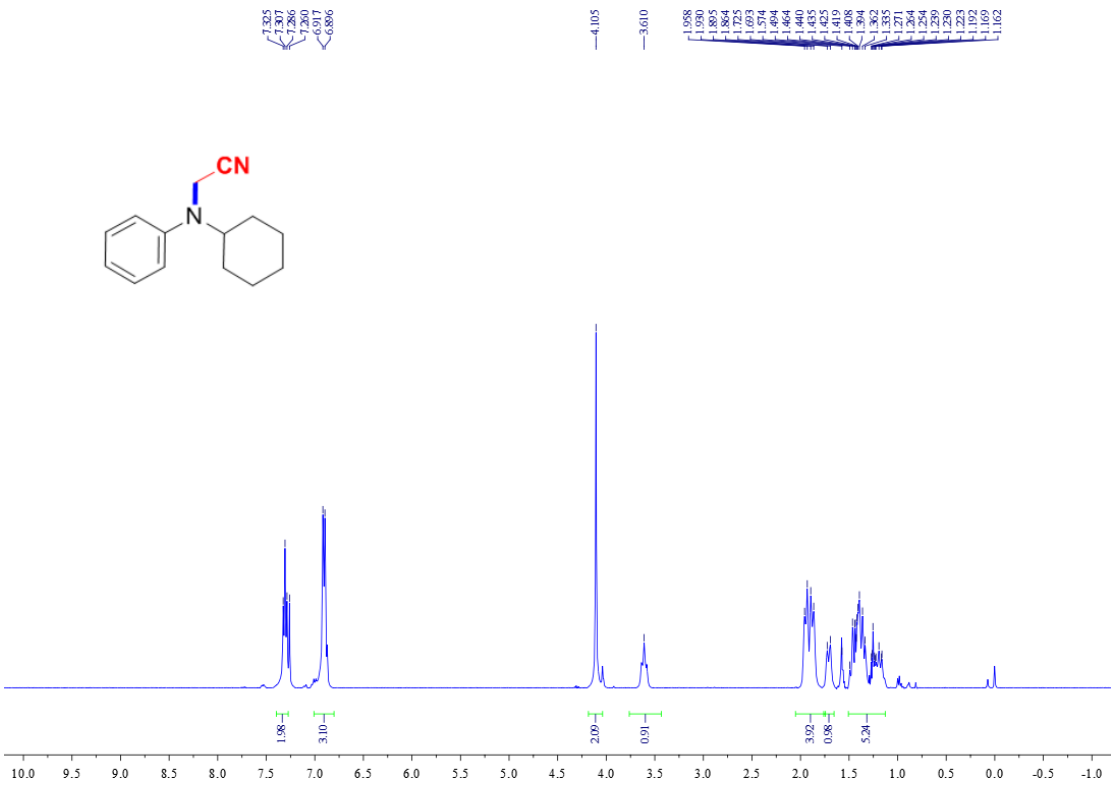
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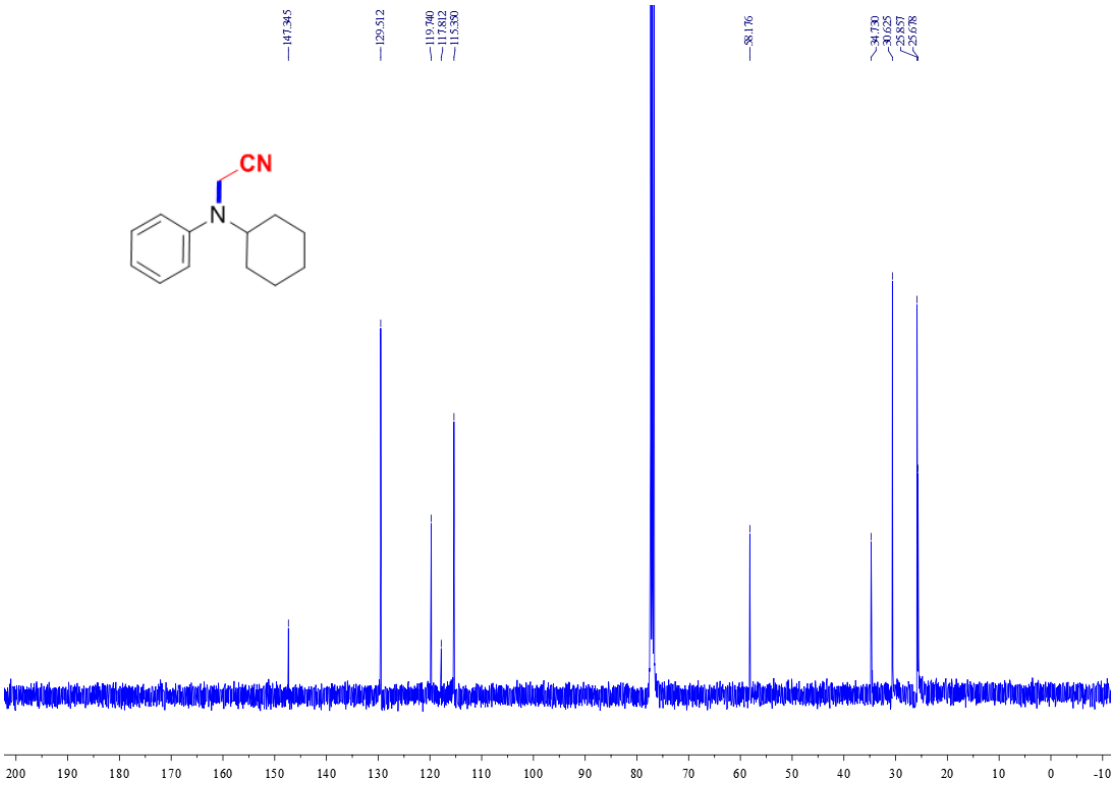
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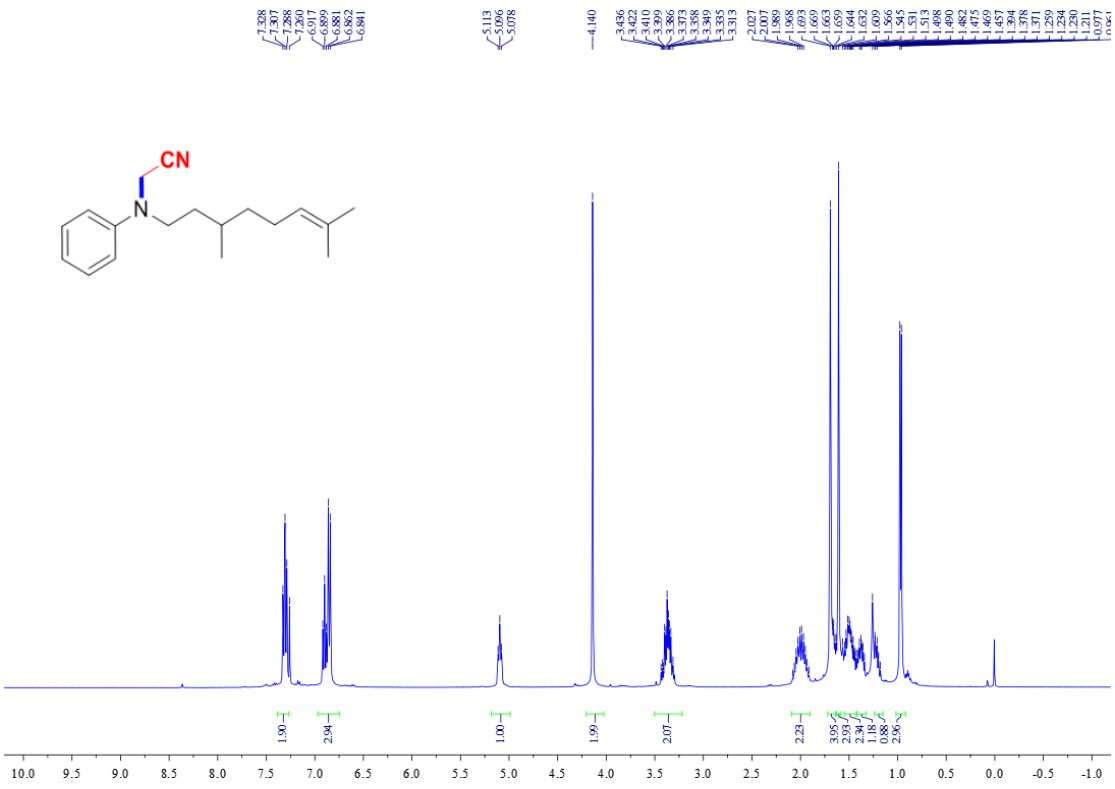
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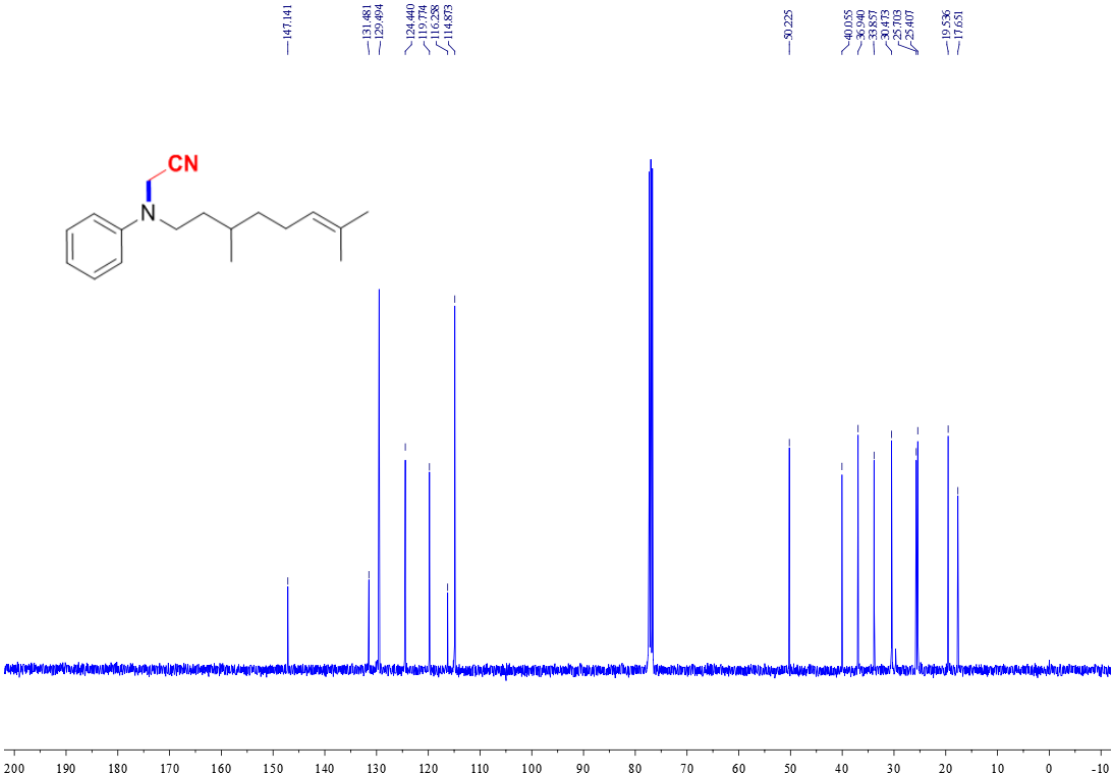
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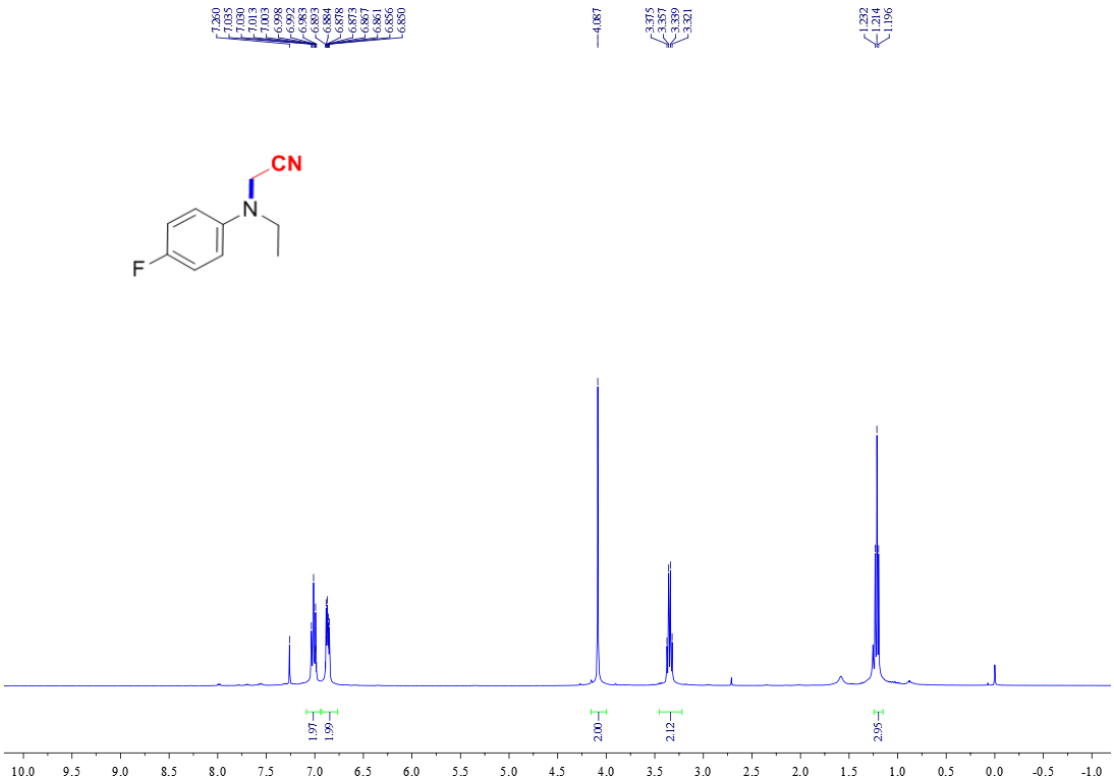
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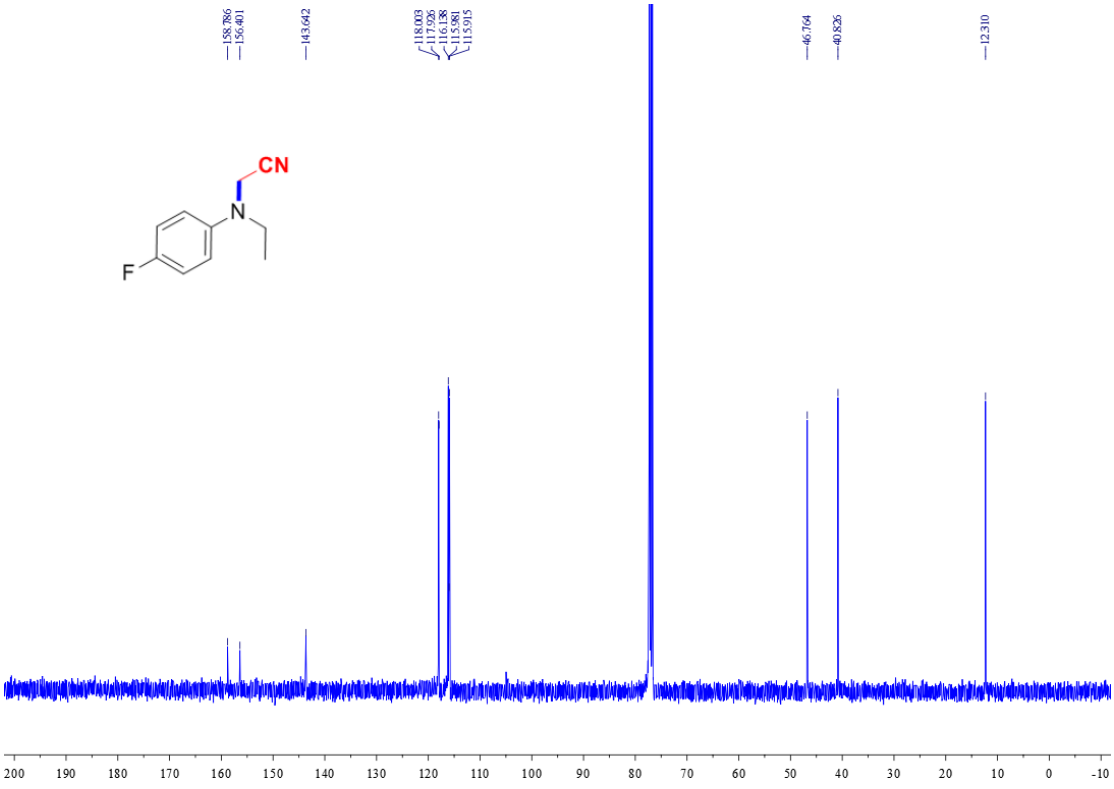
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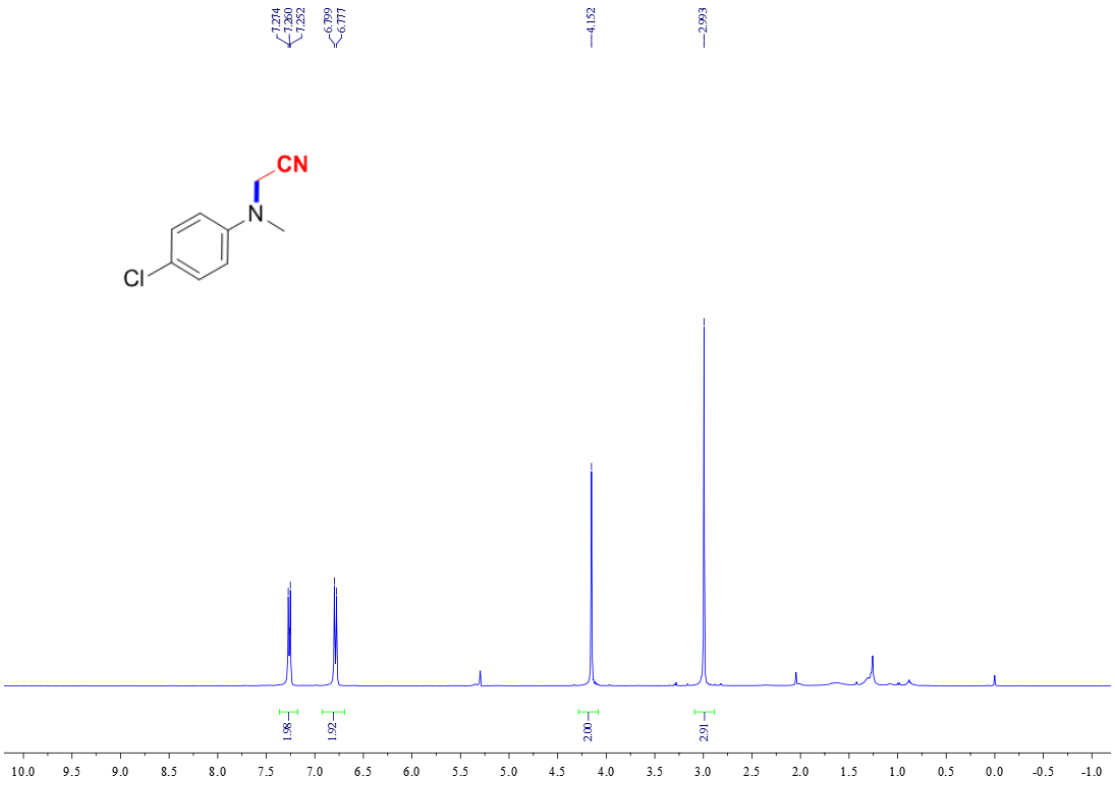
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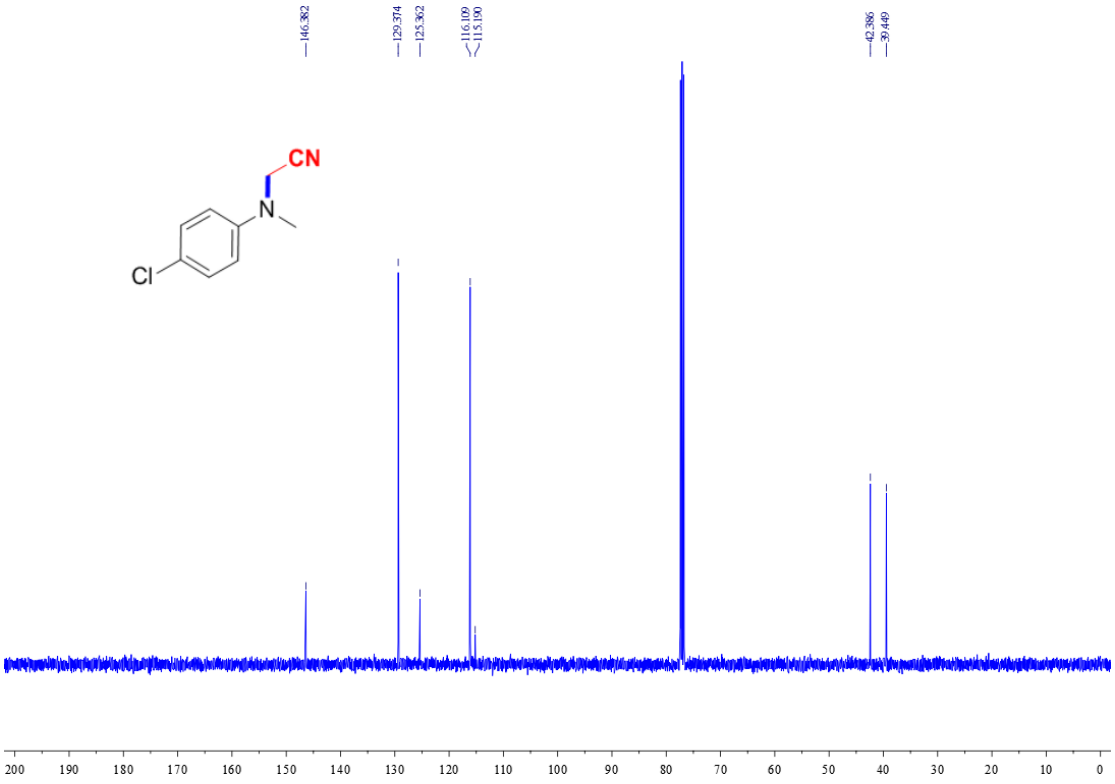
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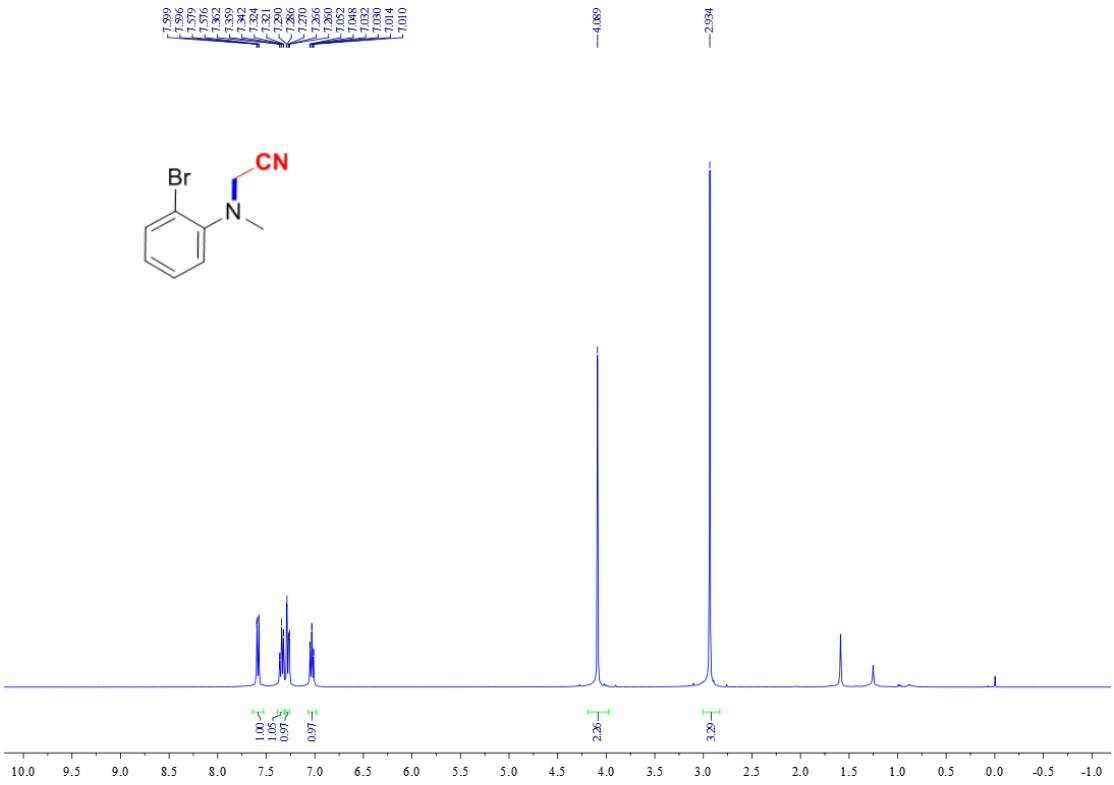
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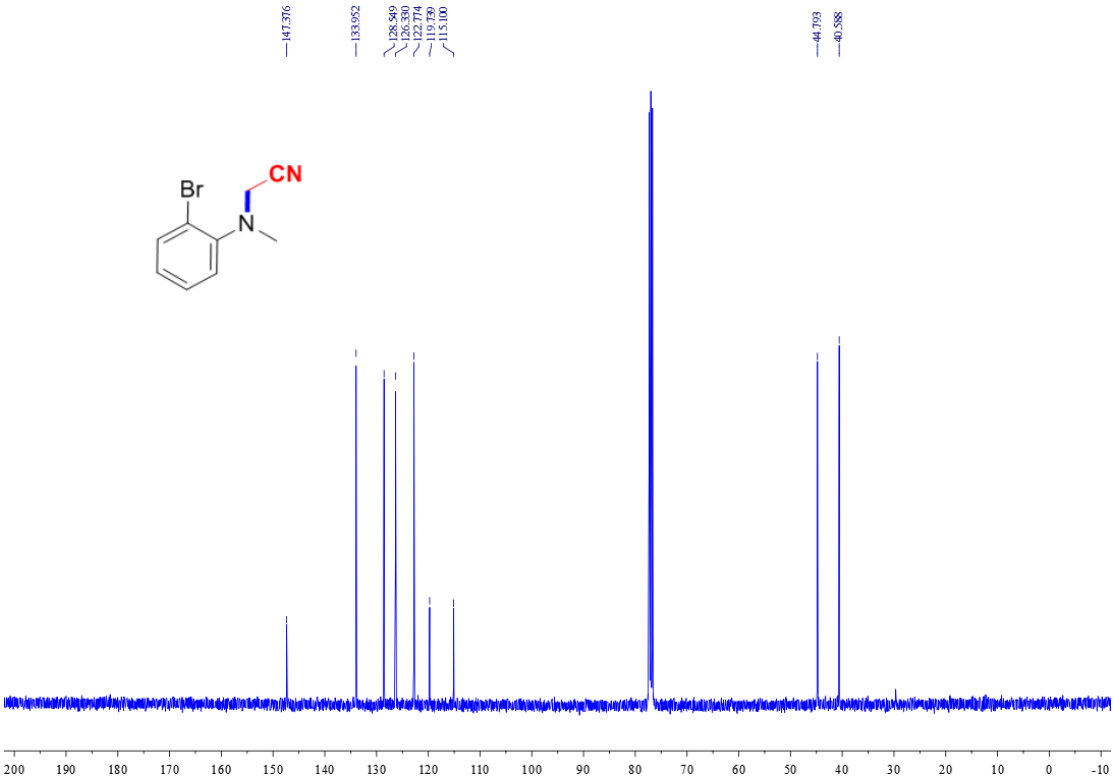
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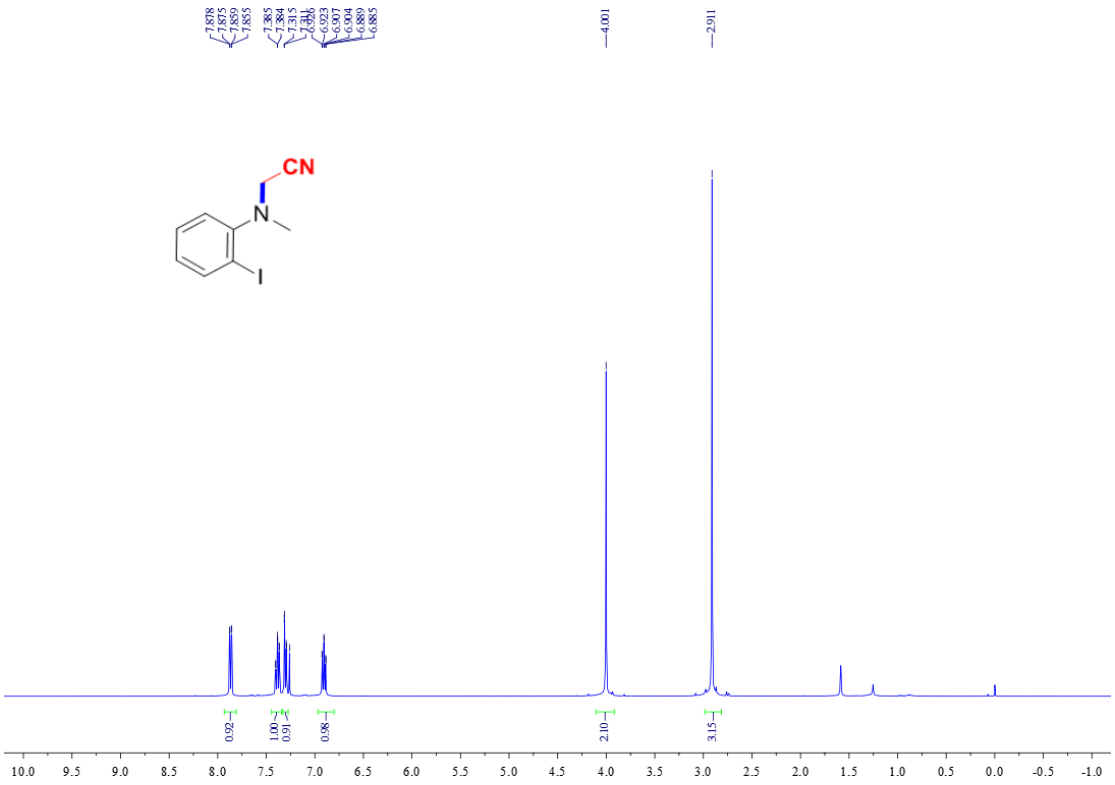
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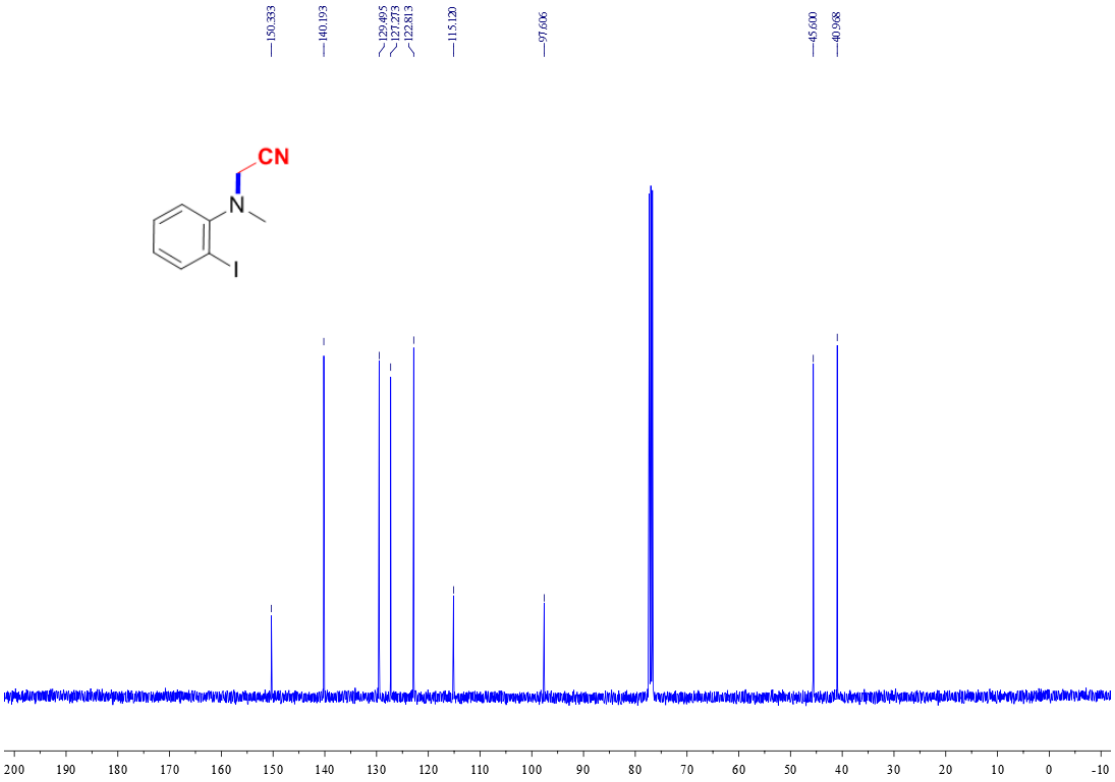
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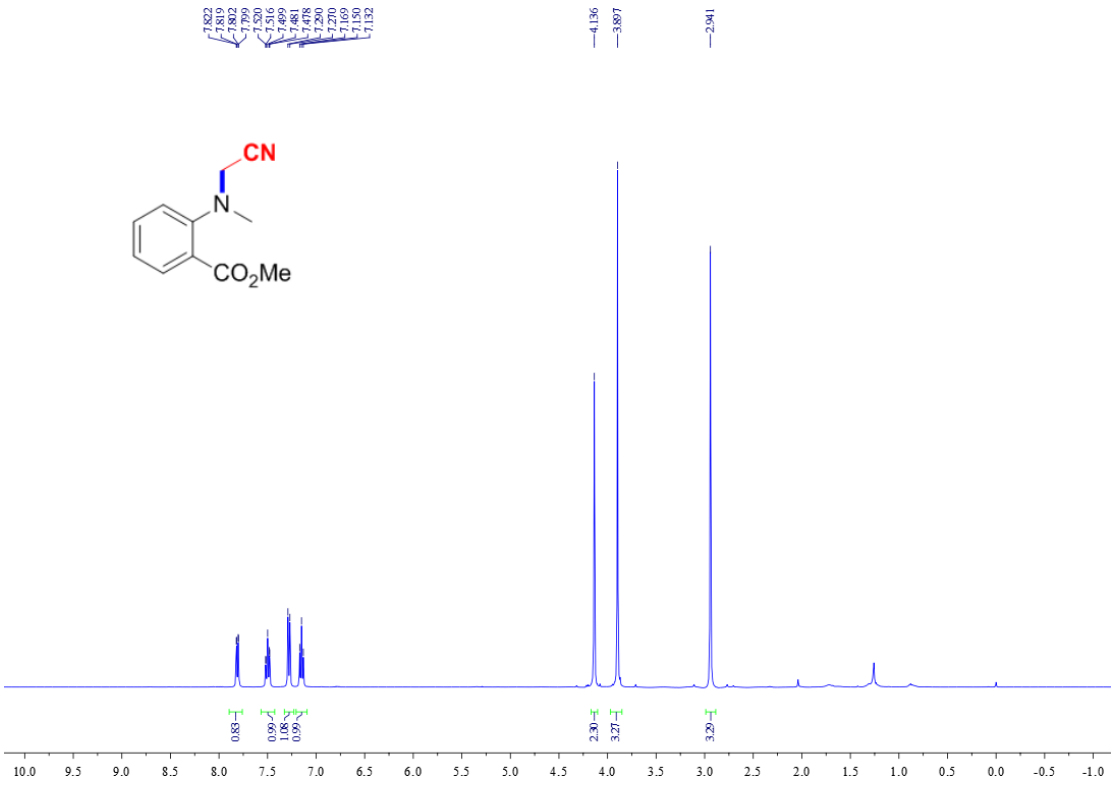
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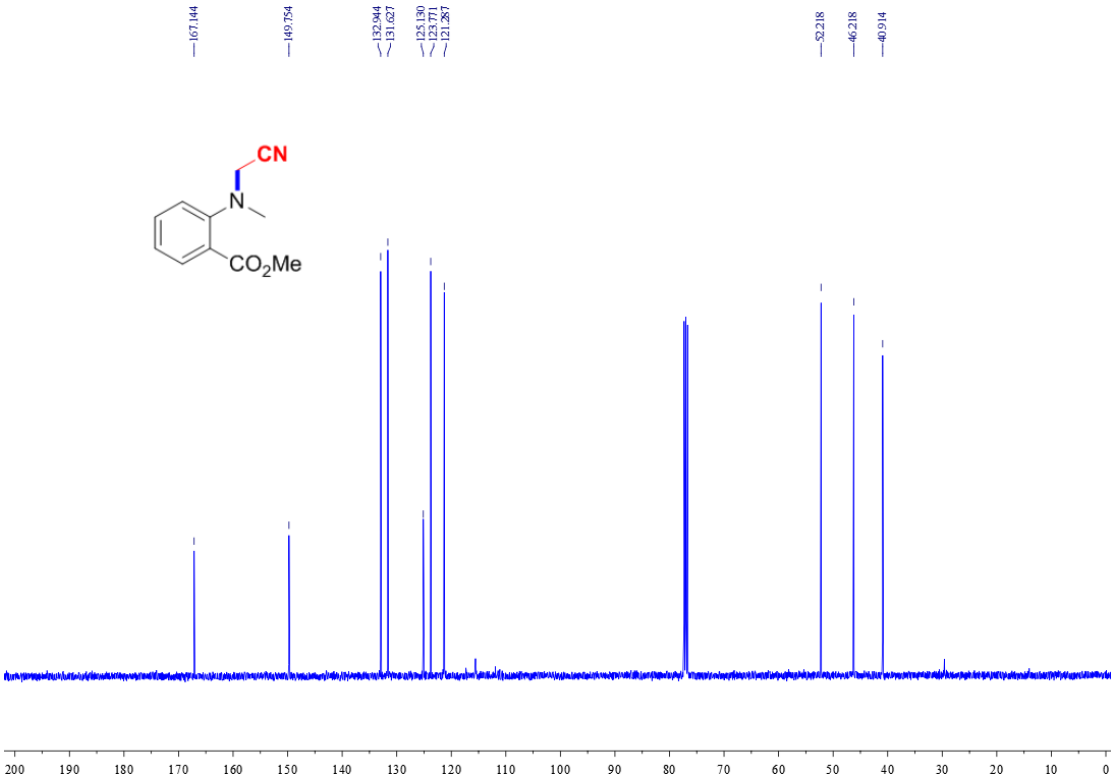
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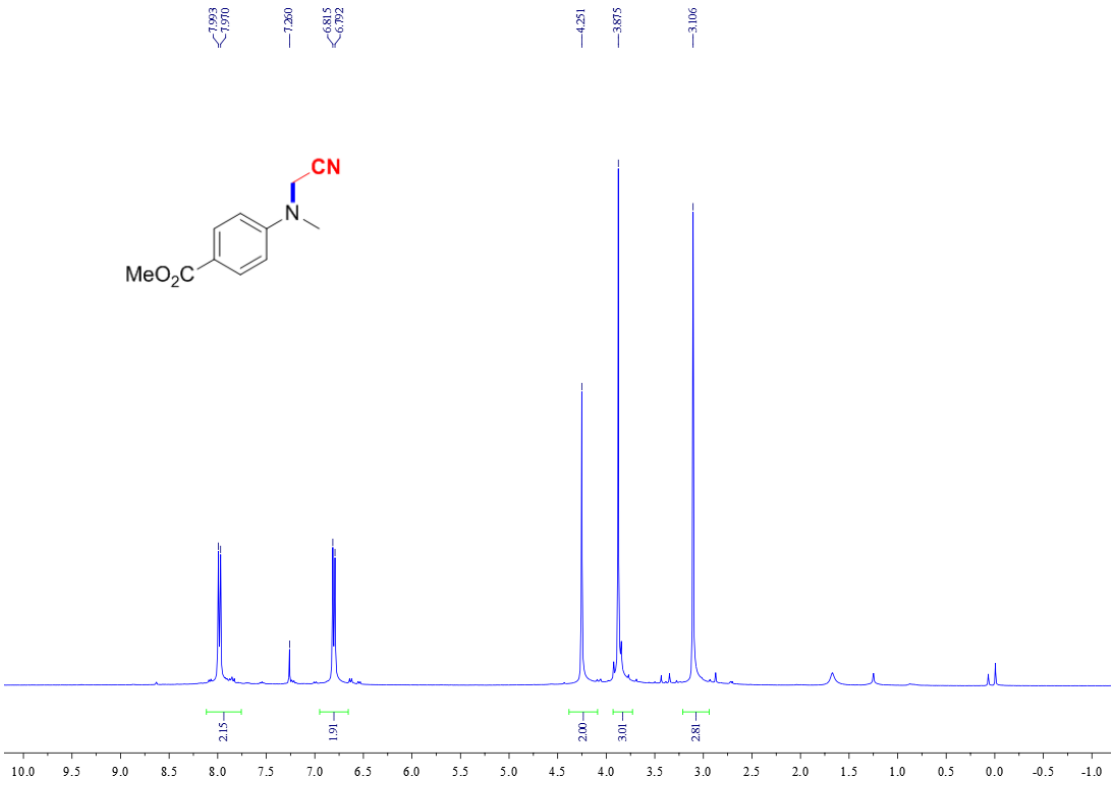
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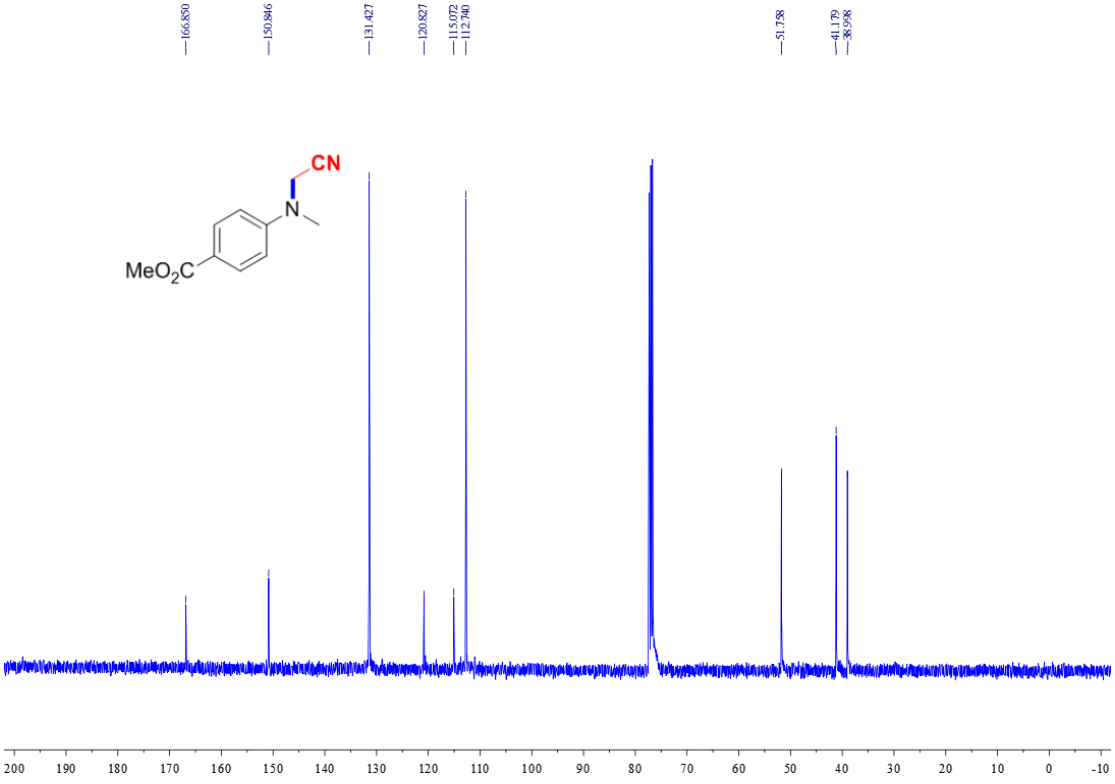
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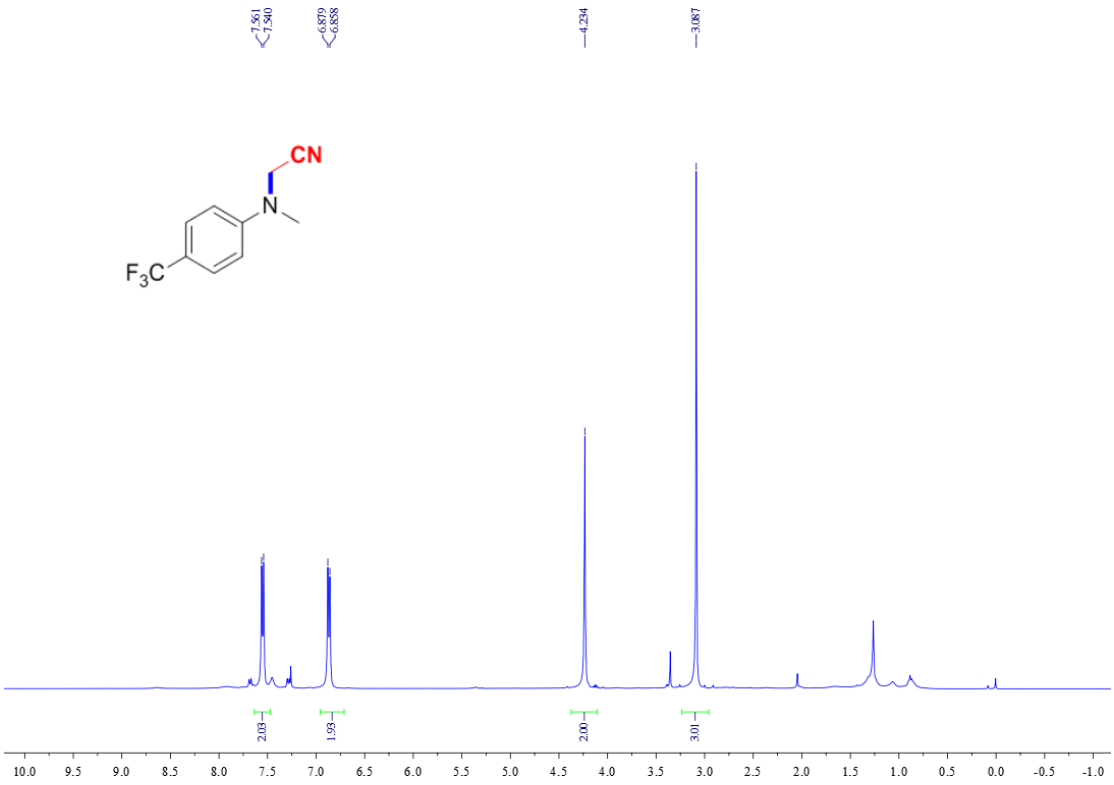
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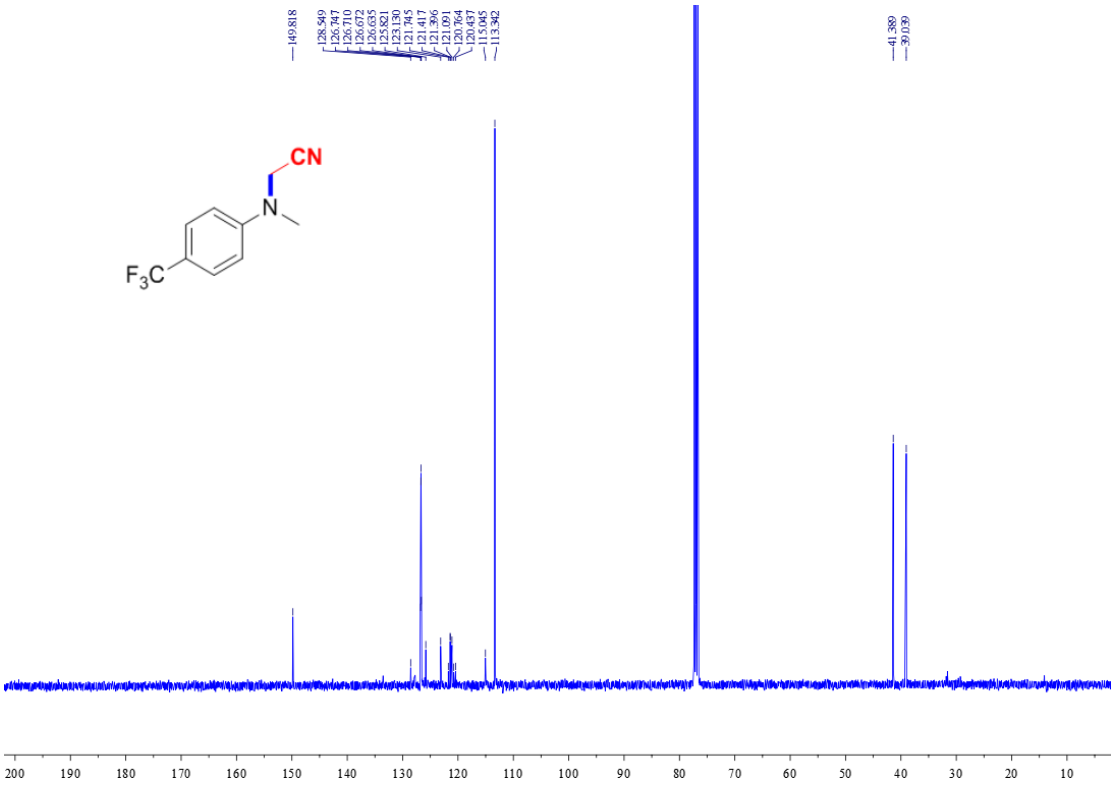
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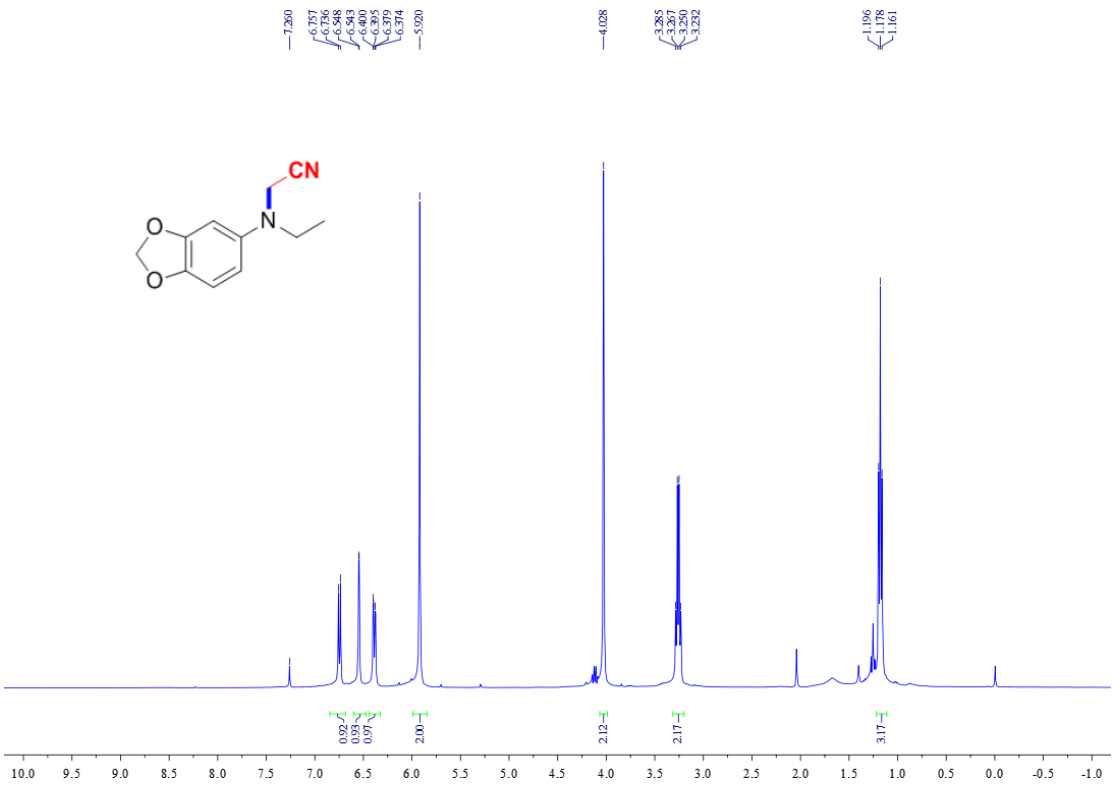
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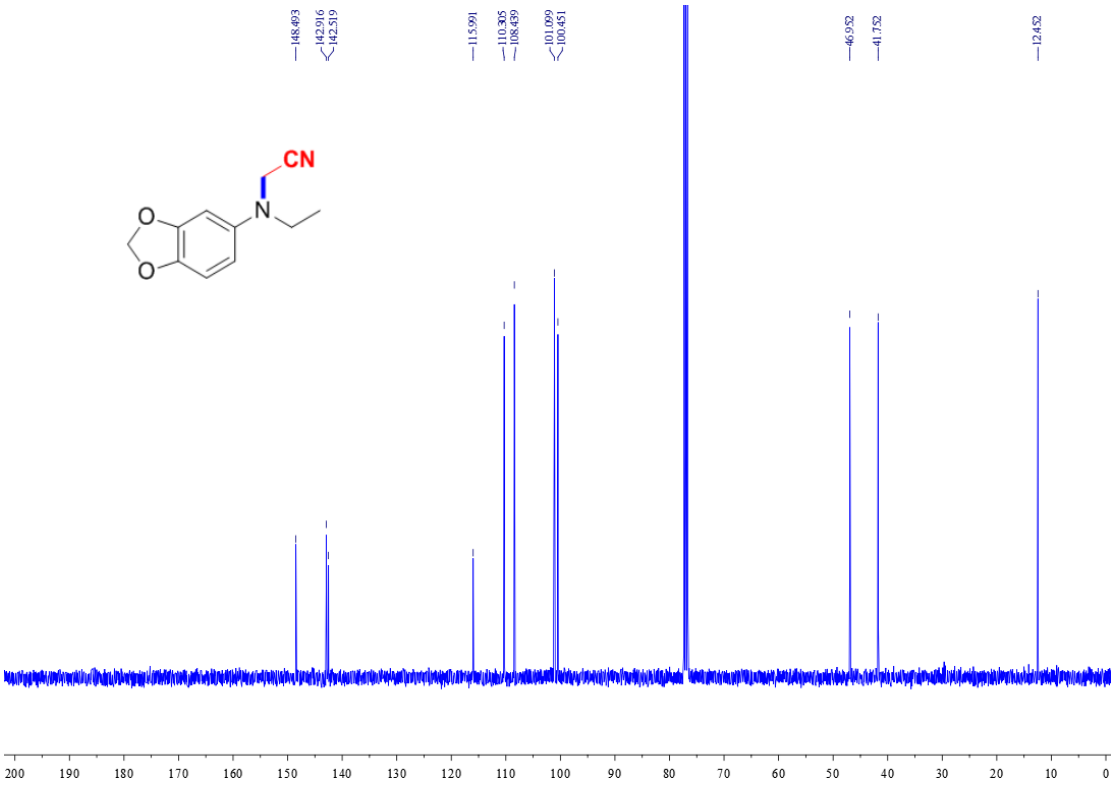
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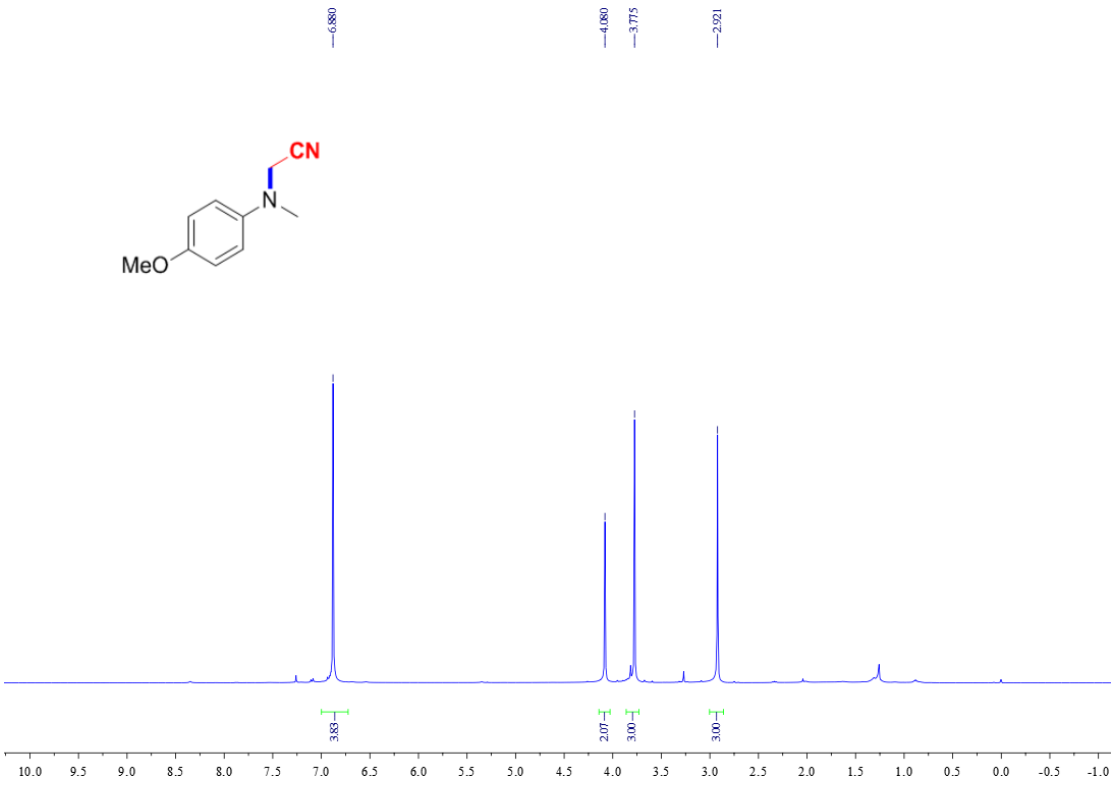
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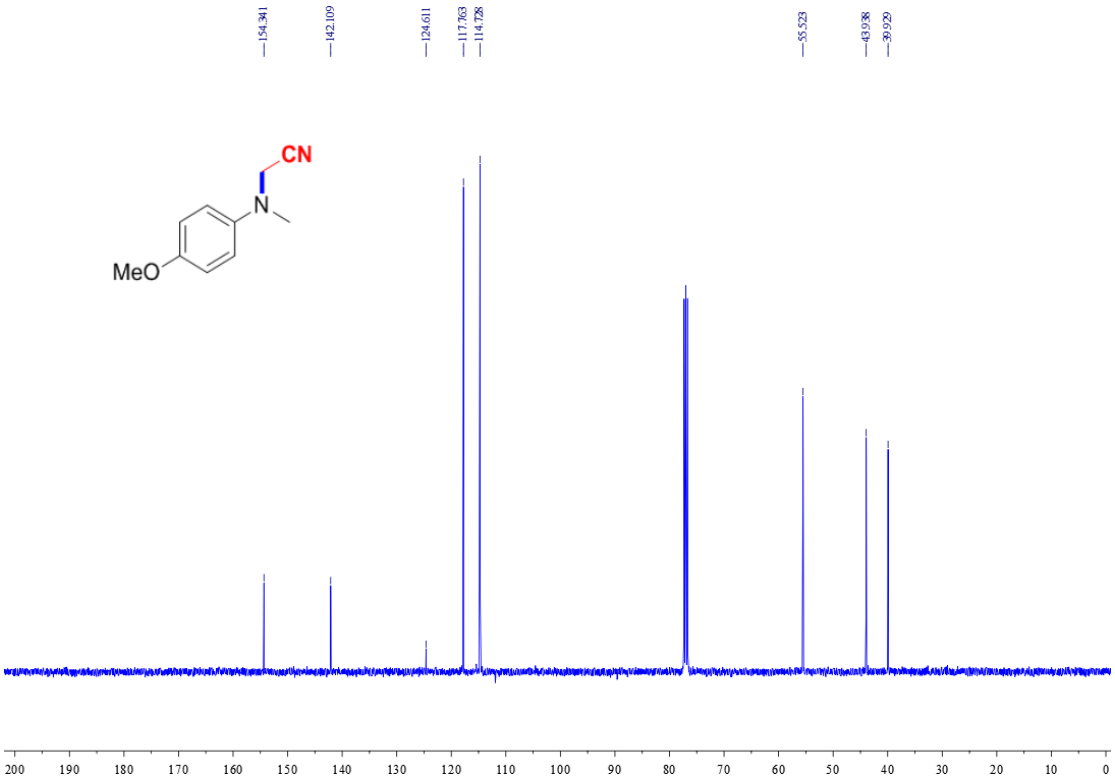
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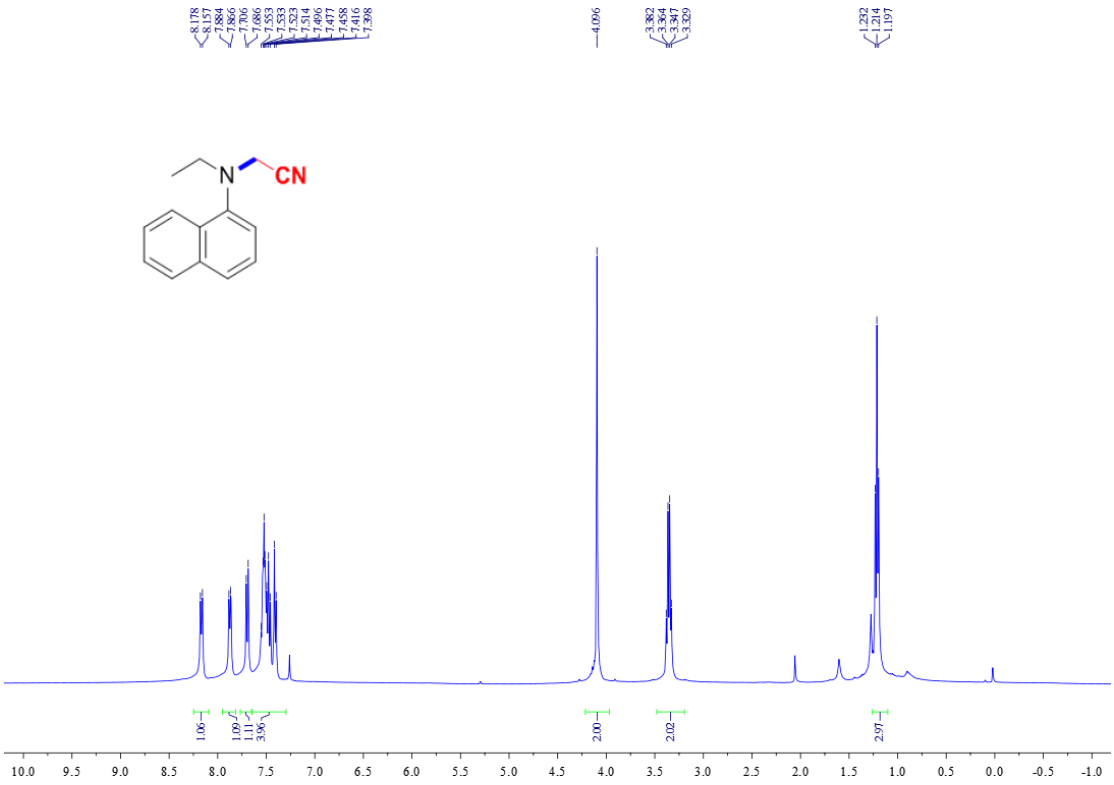
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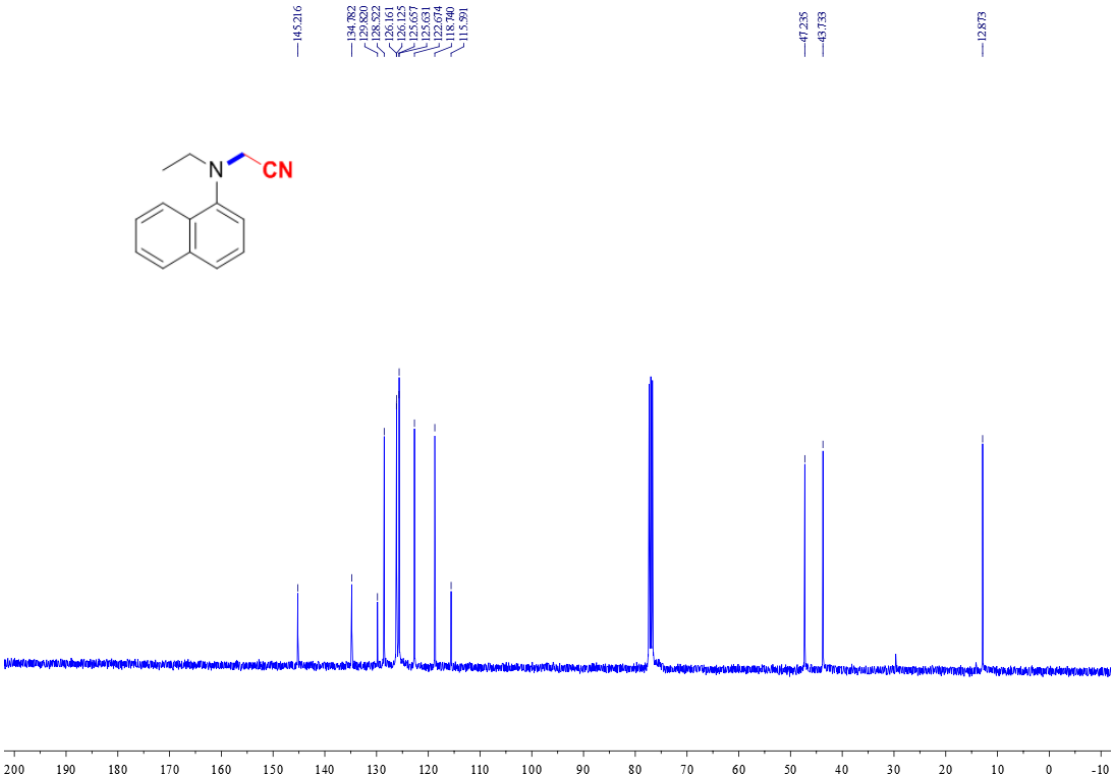
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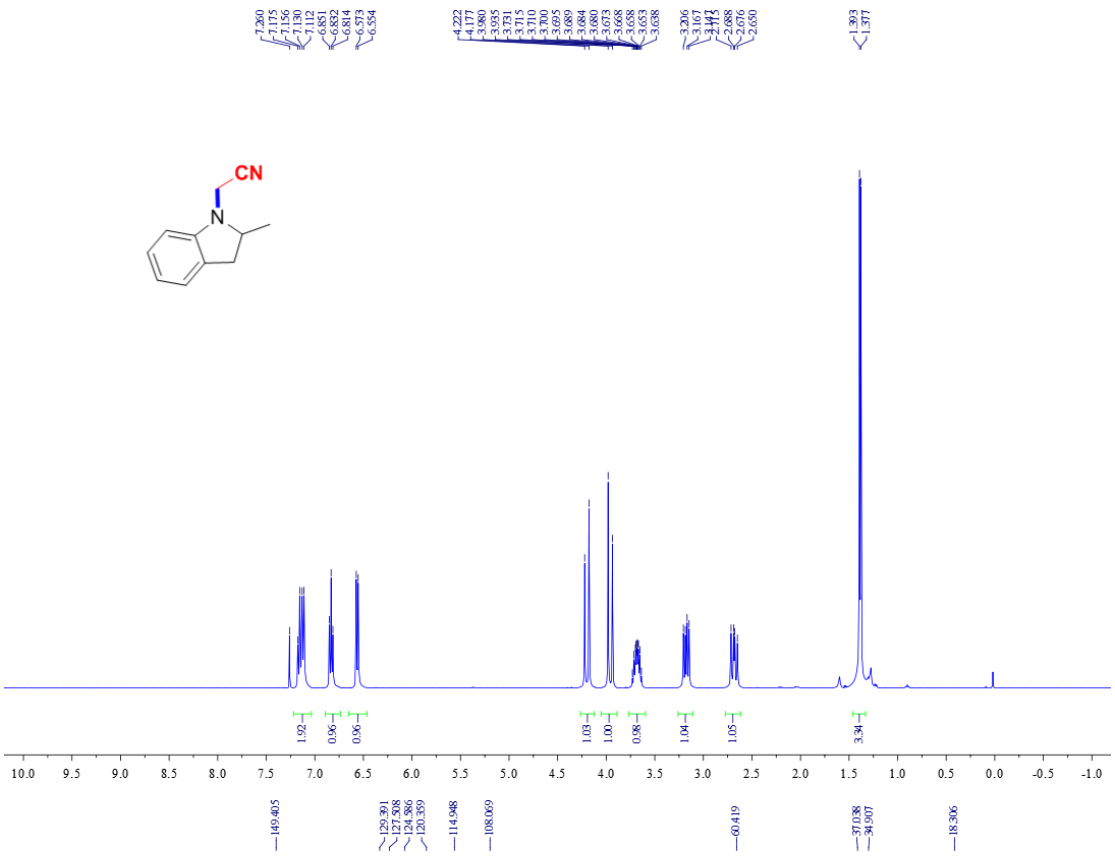
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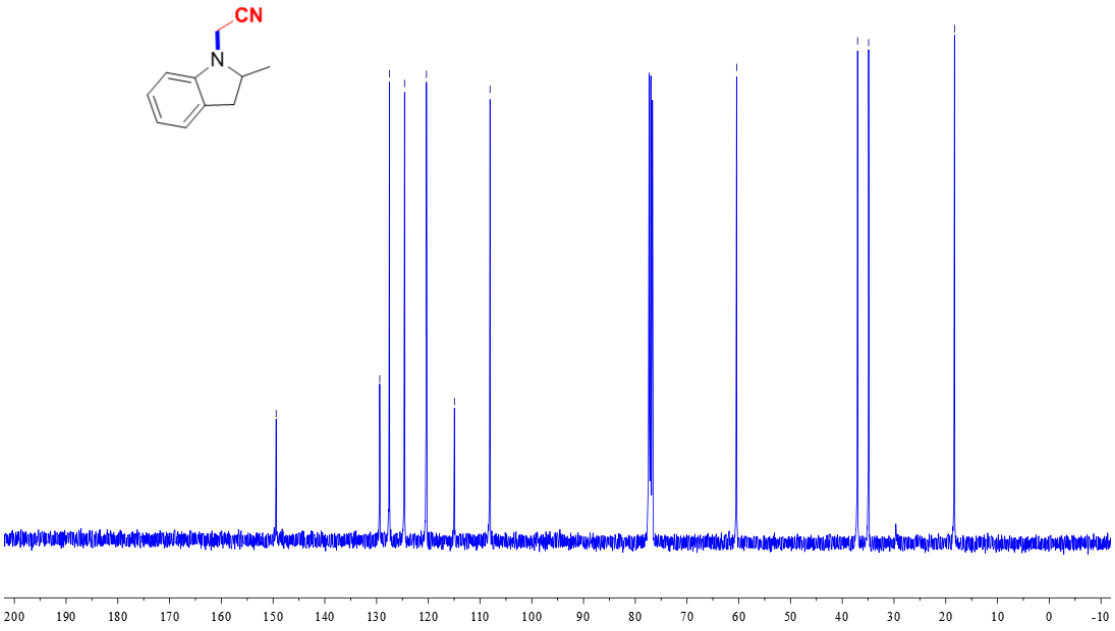
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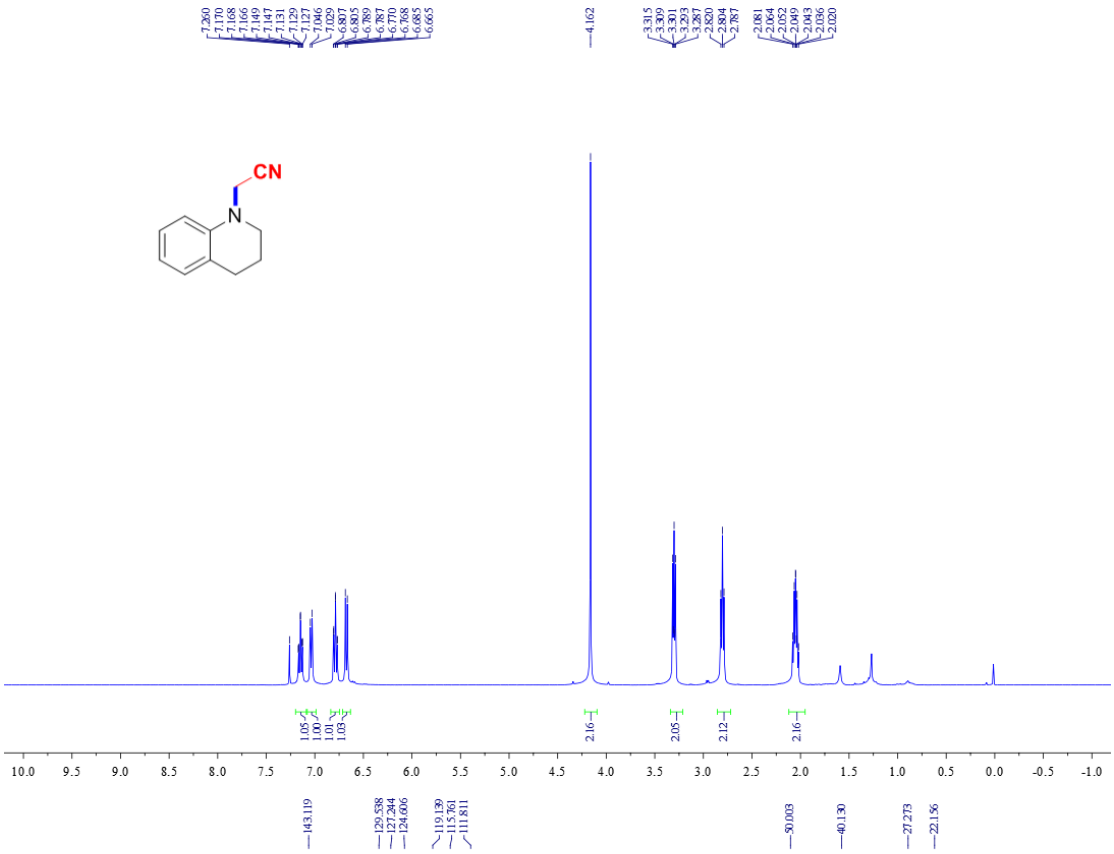
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2.043
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1.01
1.03
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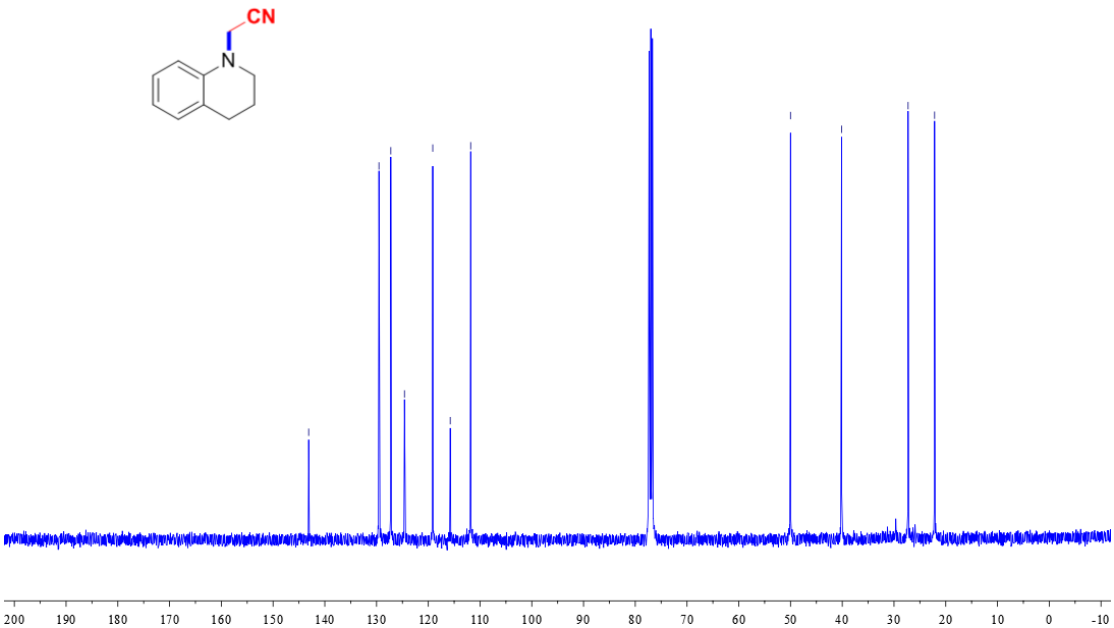
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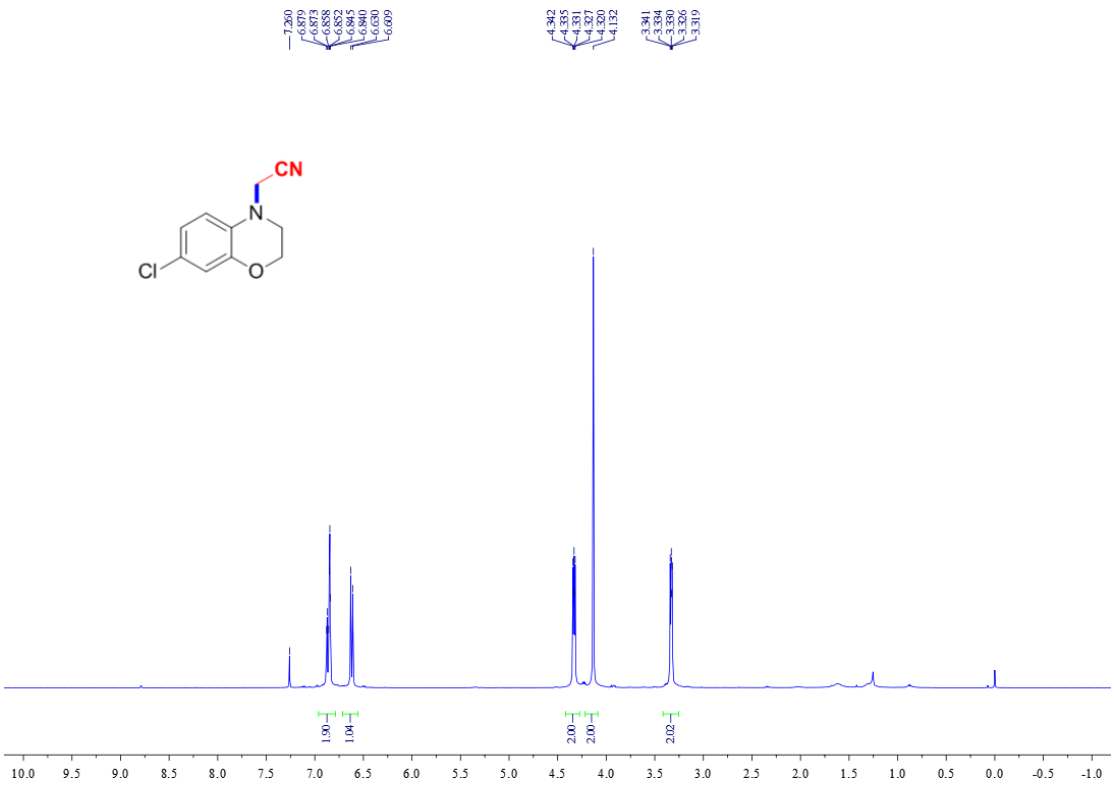
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4.320
4.132
3.341
3.334
3.330
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3.319
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Cl
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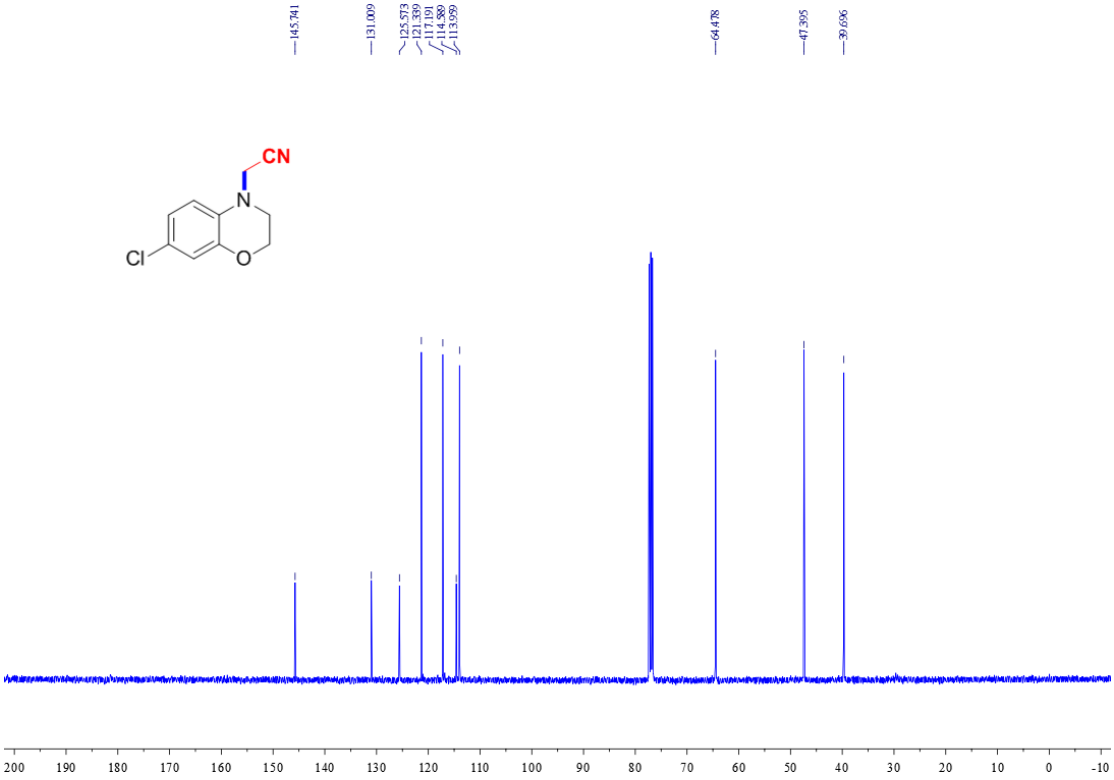
2.00
2.00
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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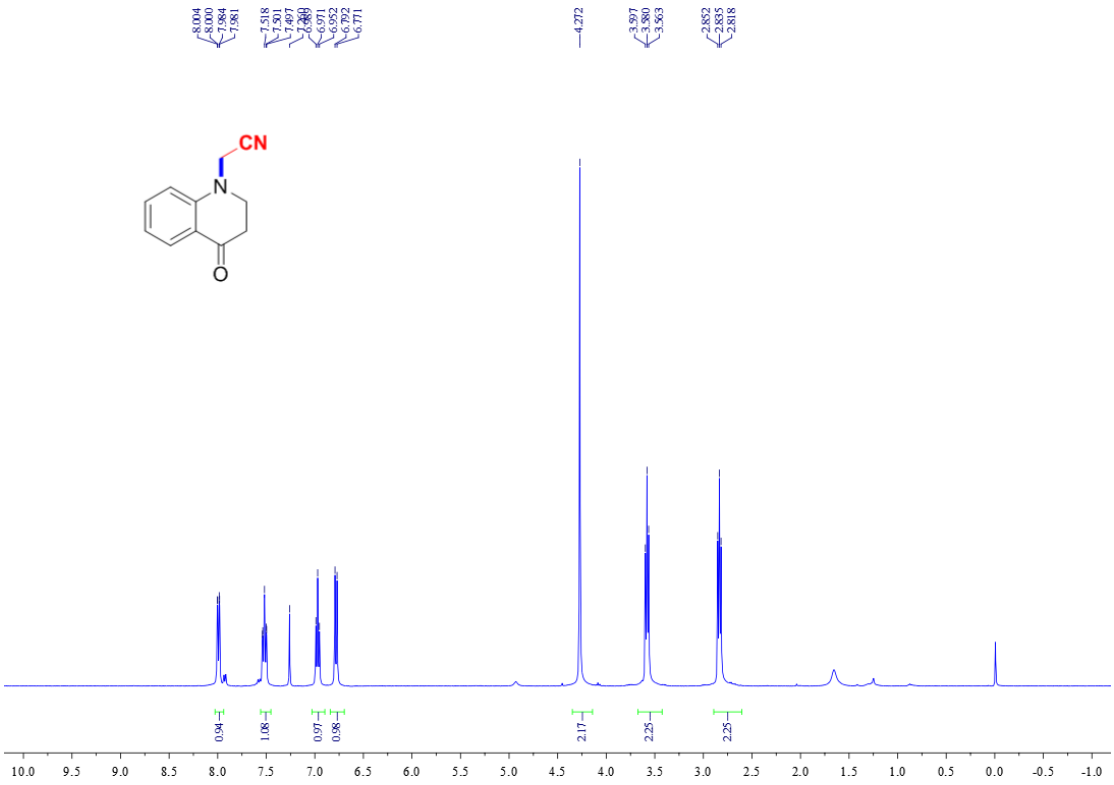
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0.97
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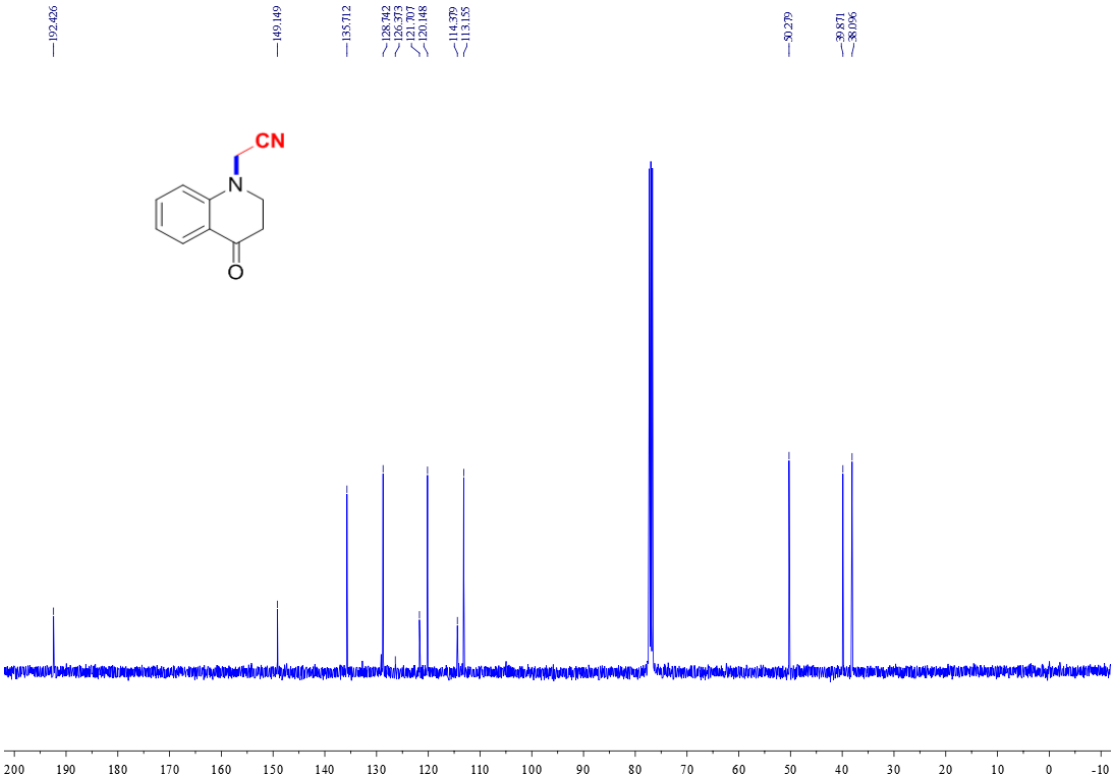
2.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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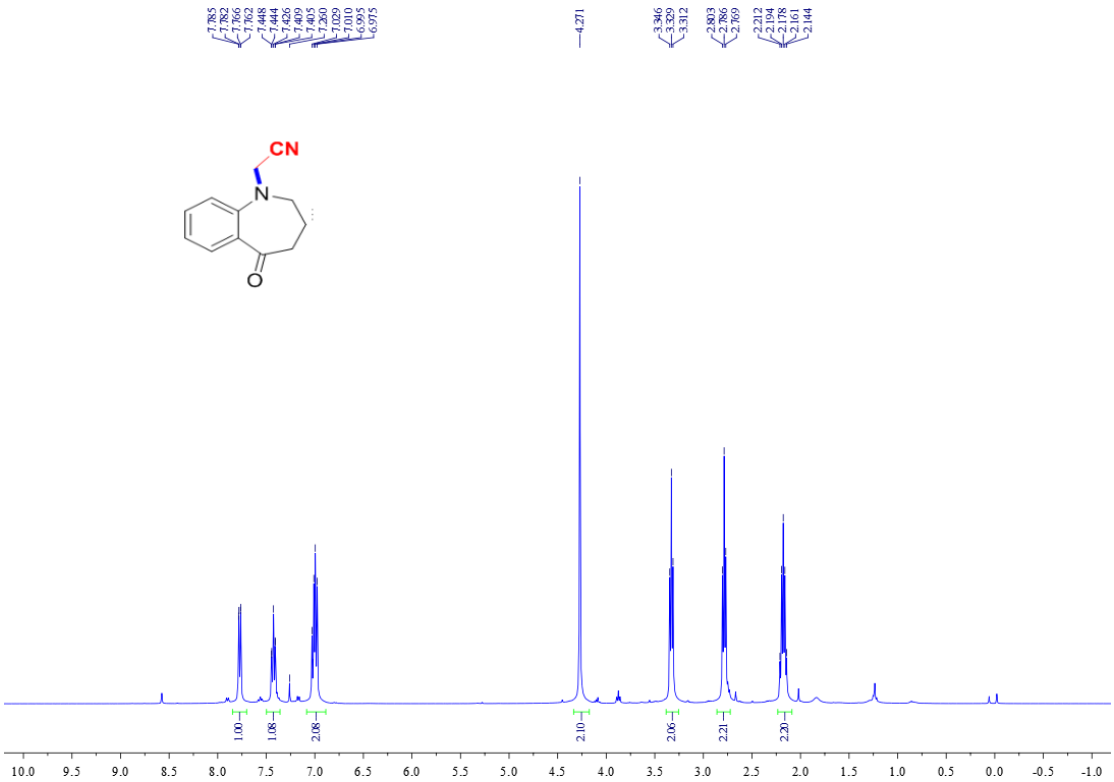
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7.029
7.010
6.995
6.975
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3.329
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2.178
2.161
2.144
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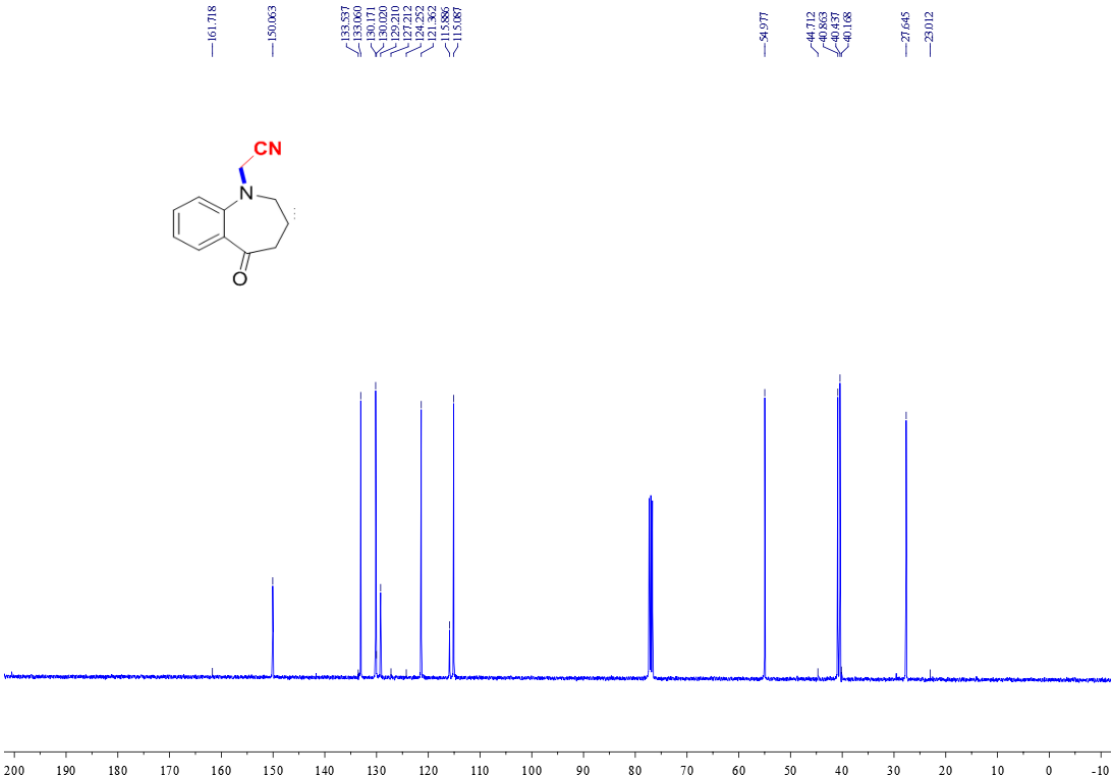
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23.012
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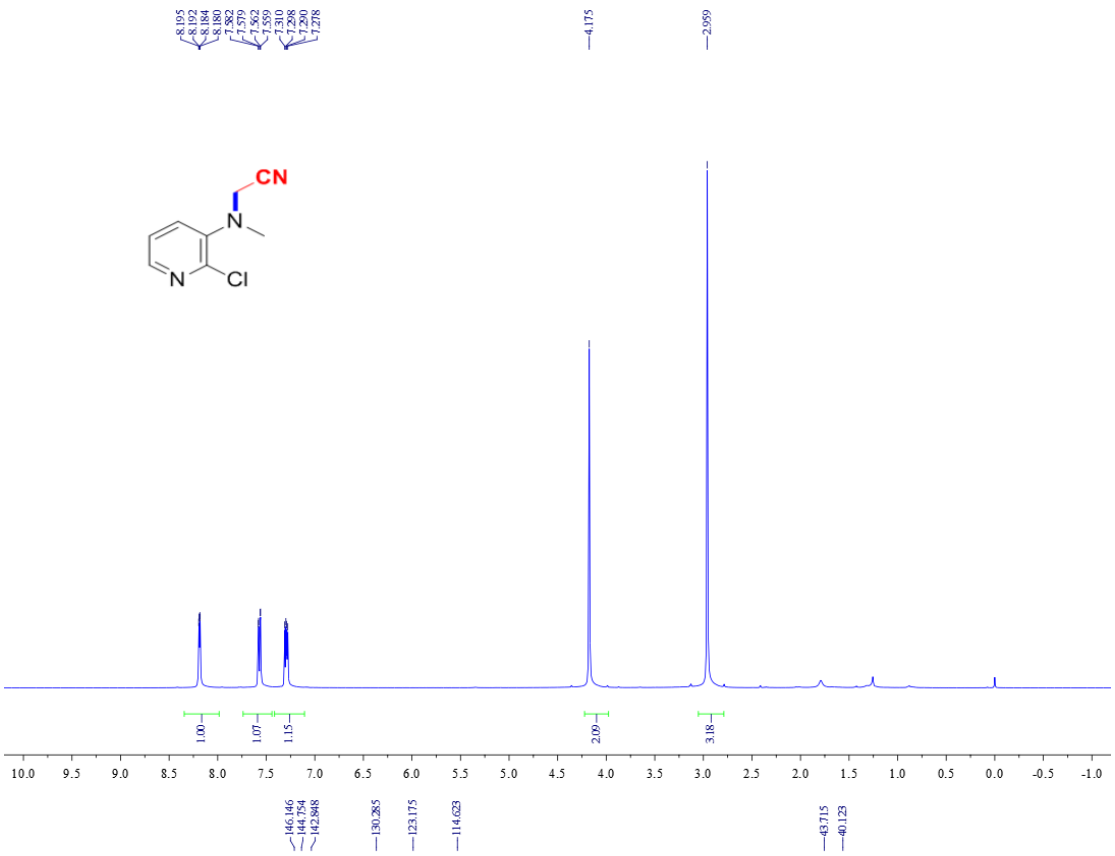
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4.175
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N
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1.07
1.15
2.09
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9.5
9.0
8.5
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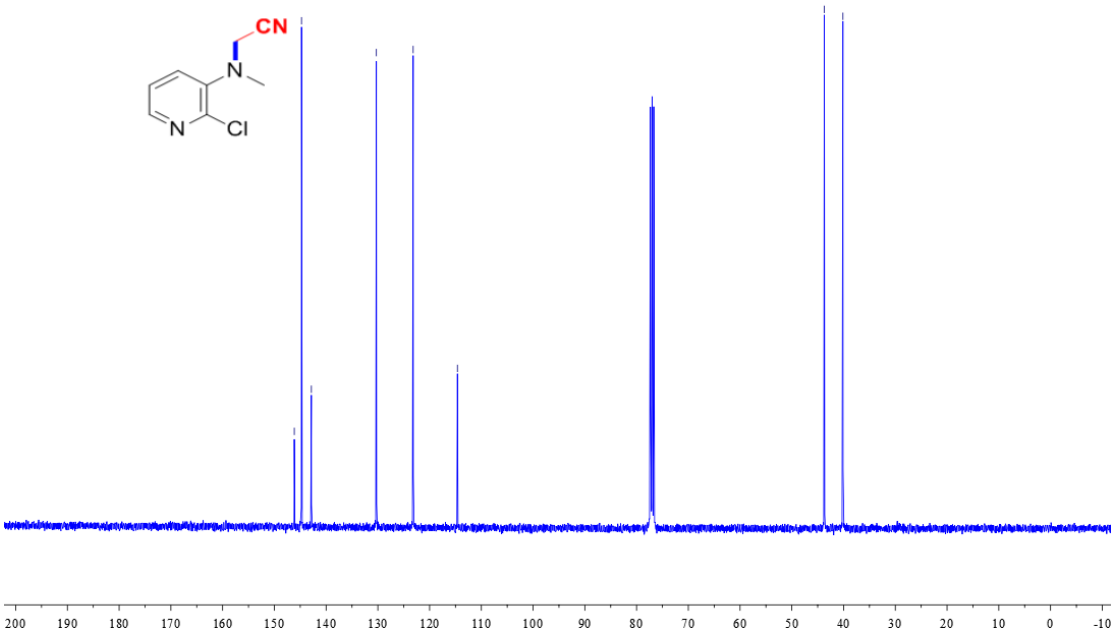
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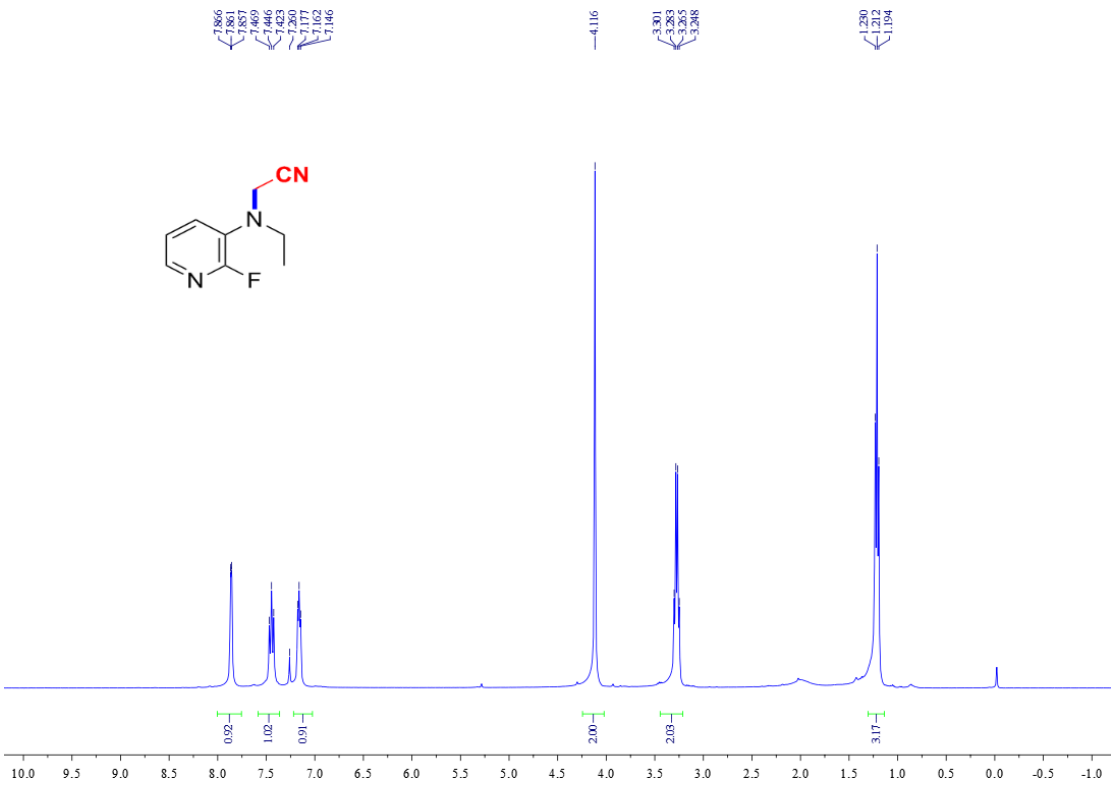
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1.230
1.212
1.194
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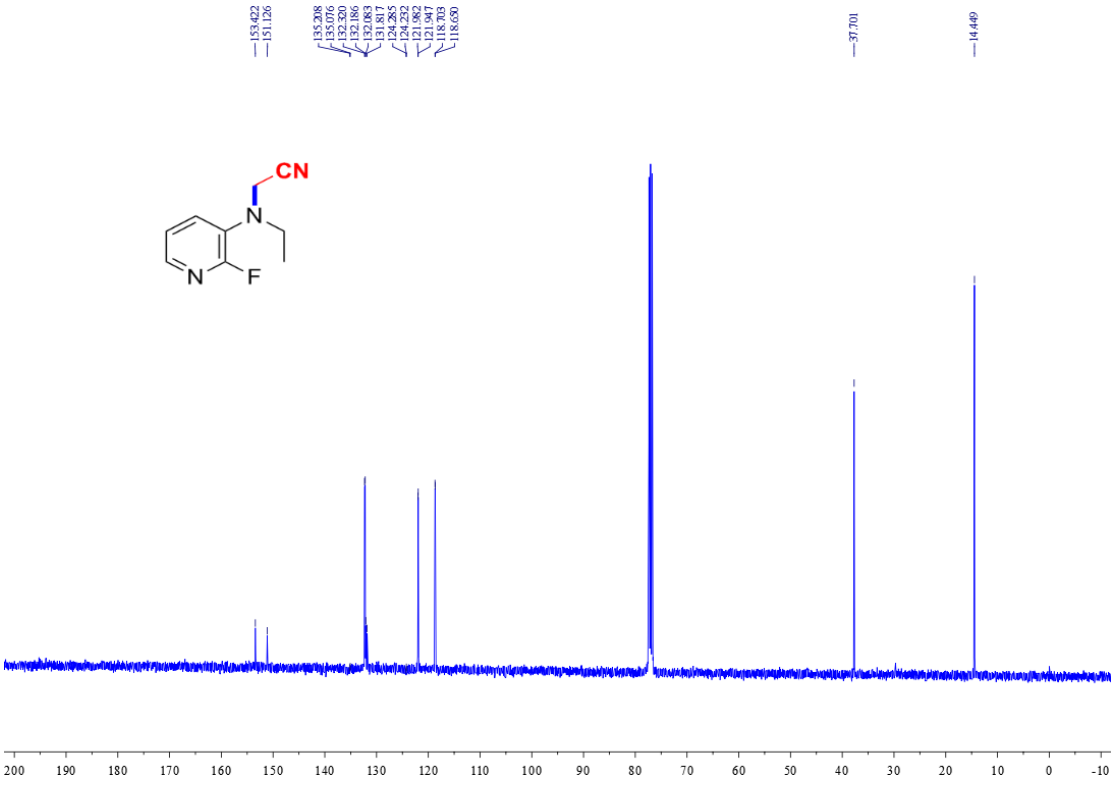
1.02
0.91
2.00
2.03
3.17
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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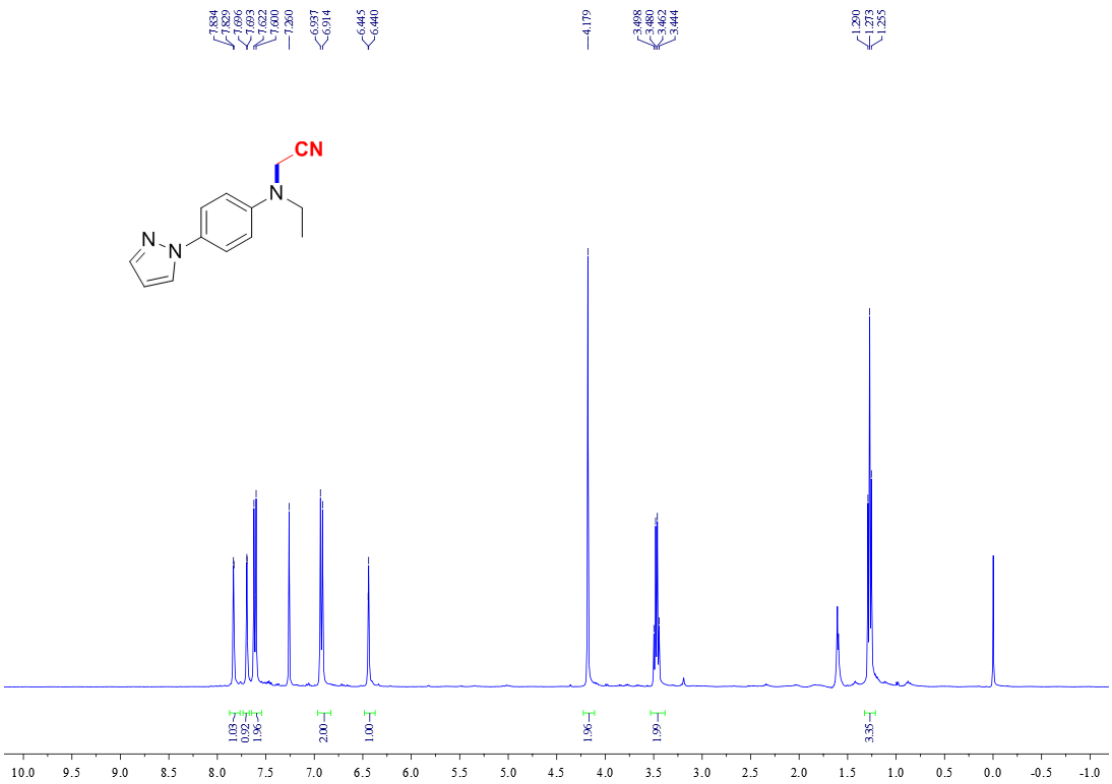
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1.99
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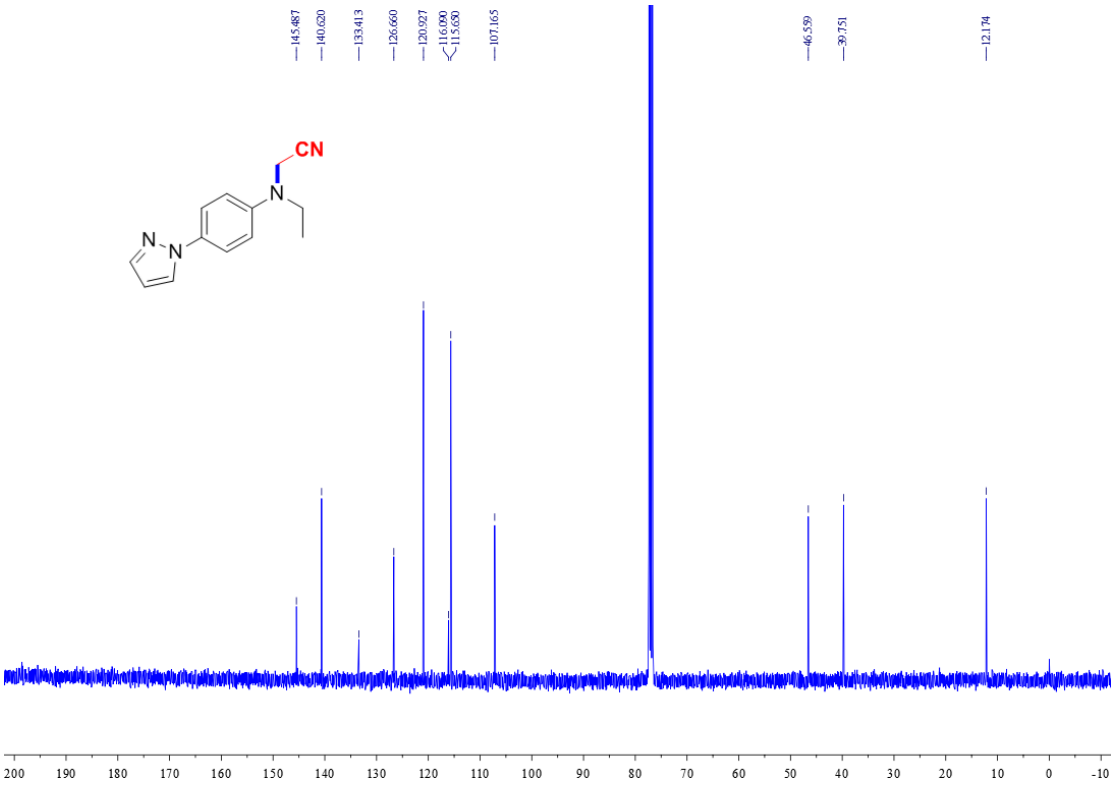
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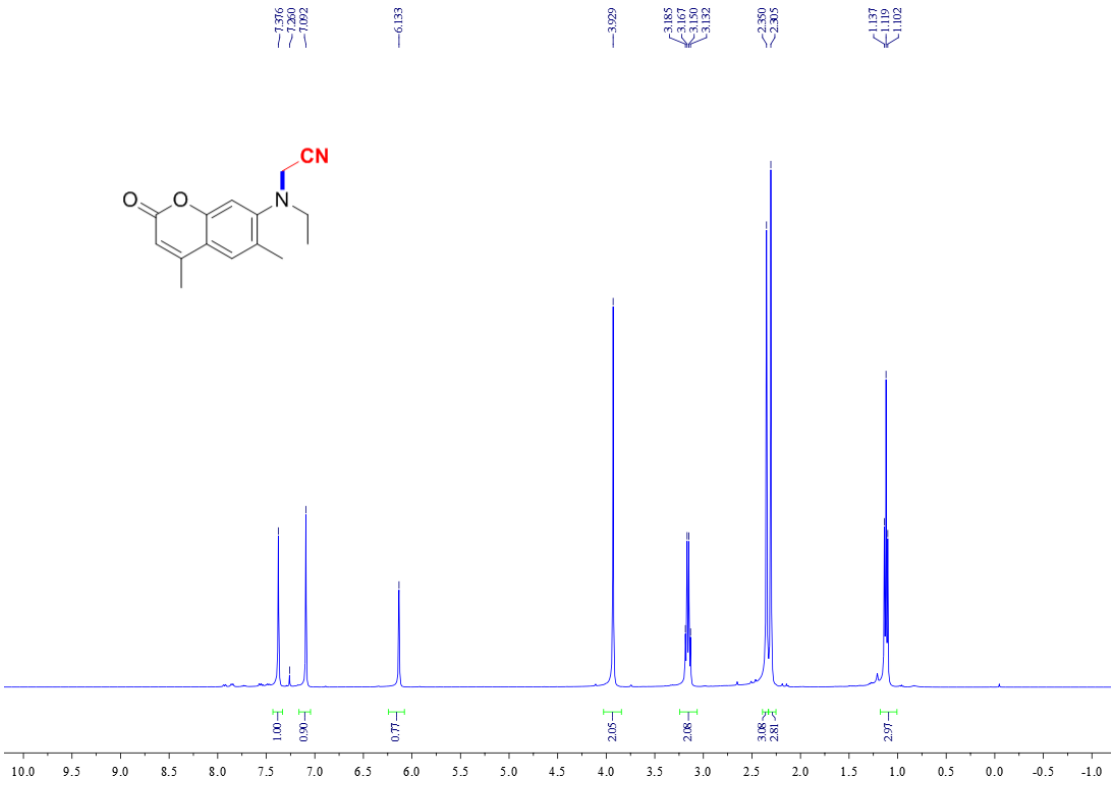
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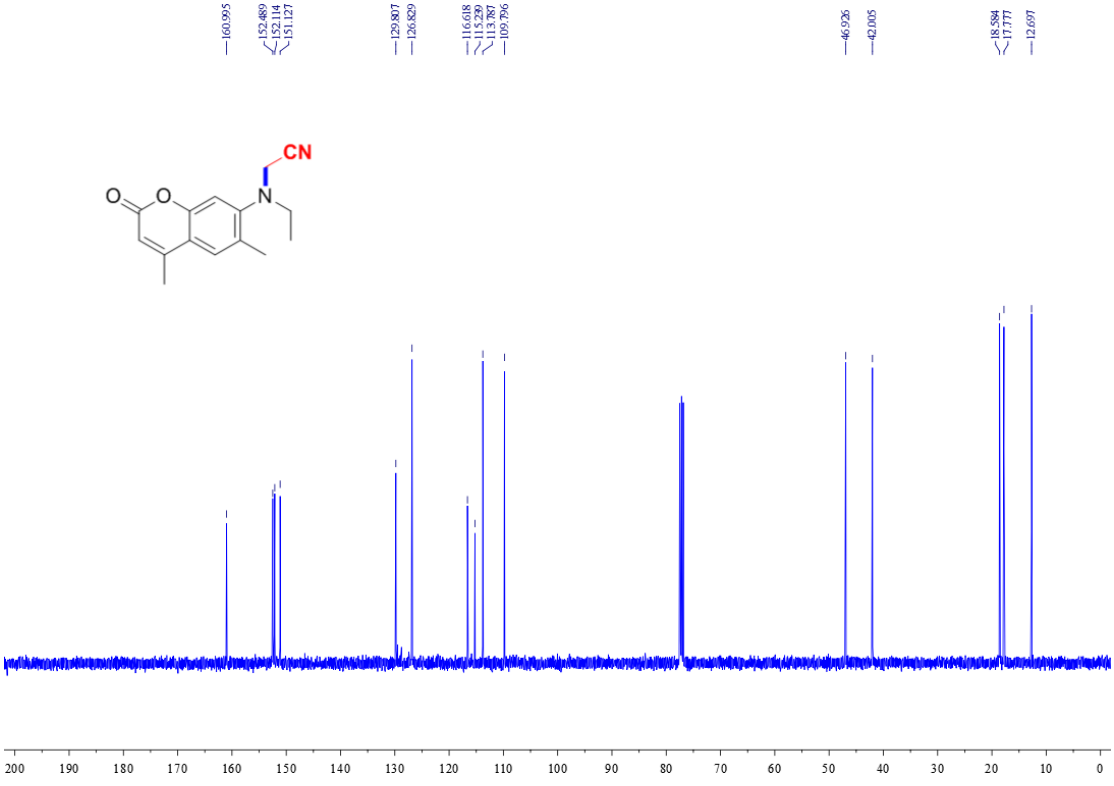
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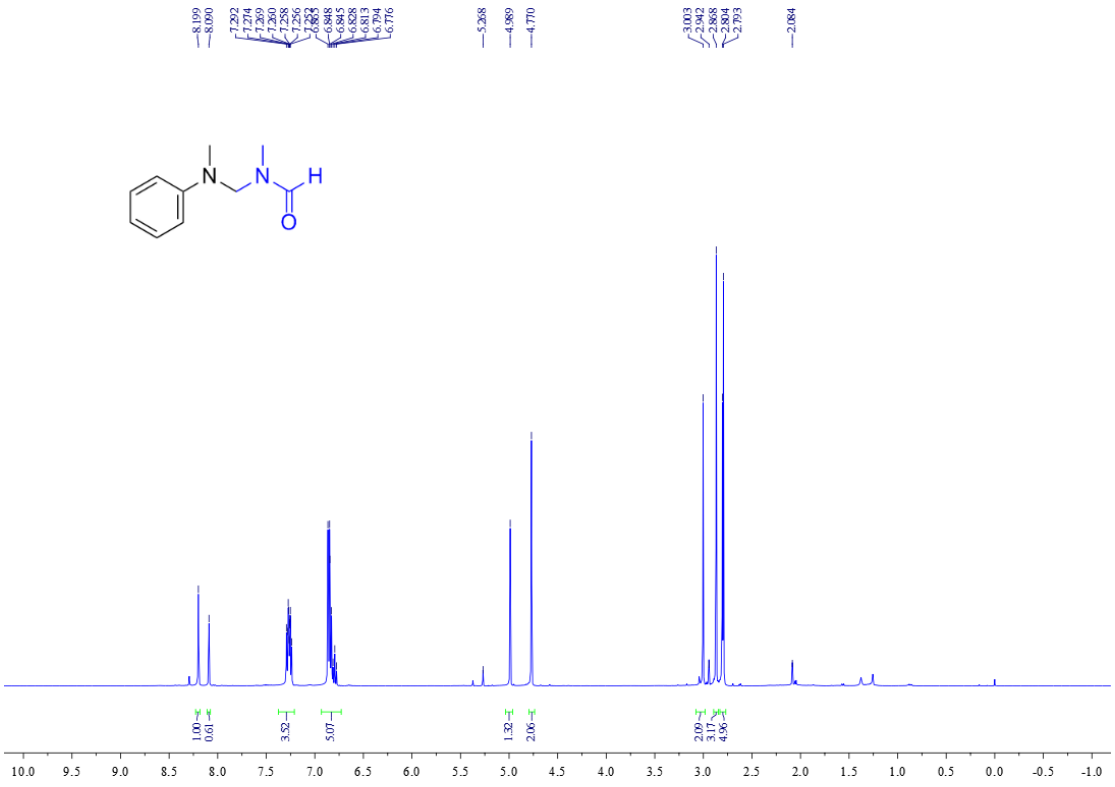
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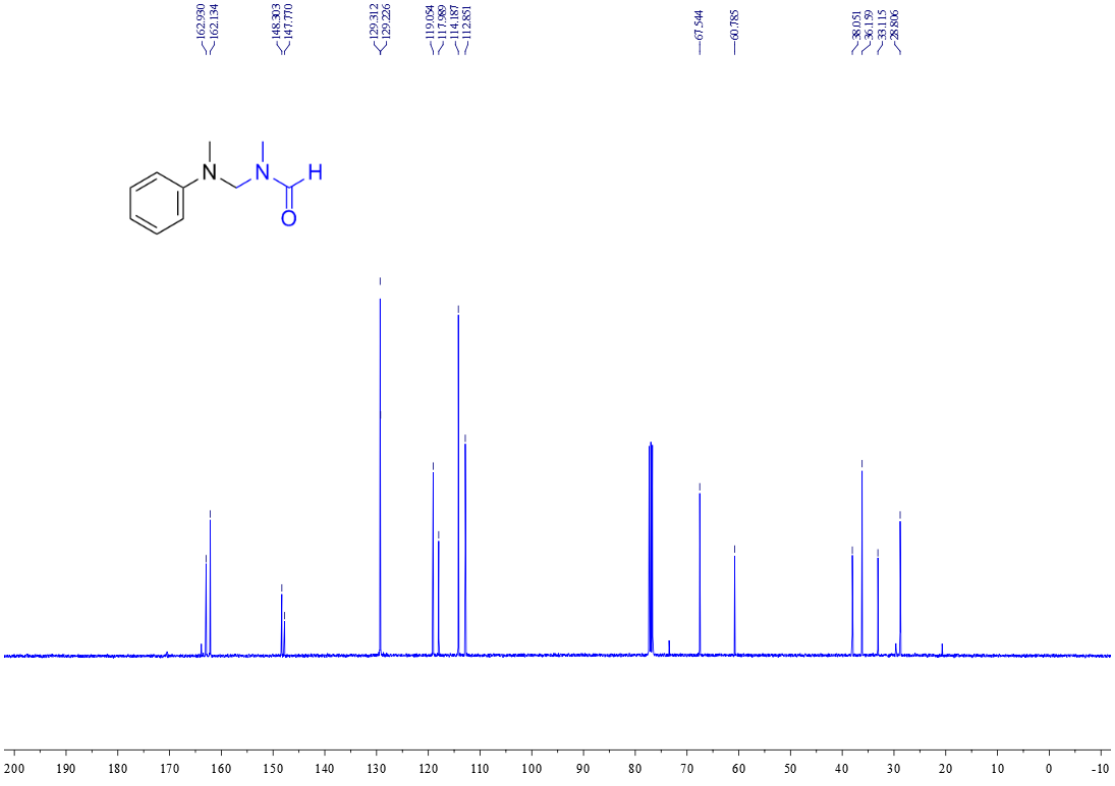
5.07
1.32
2.06
2.09
3.17
4.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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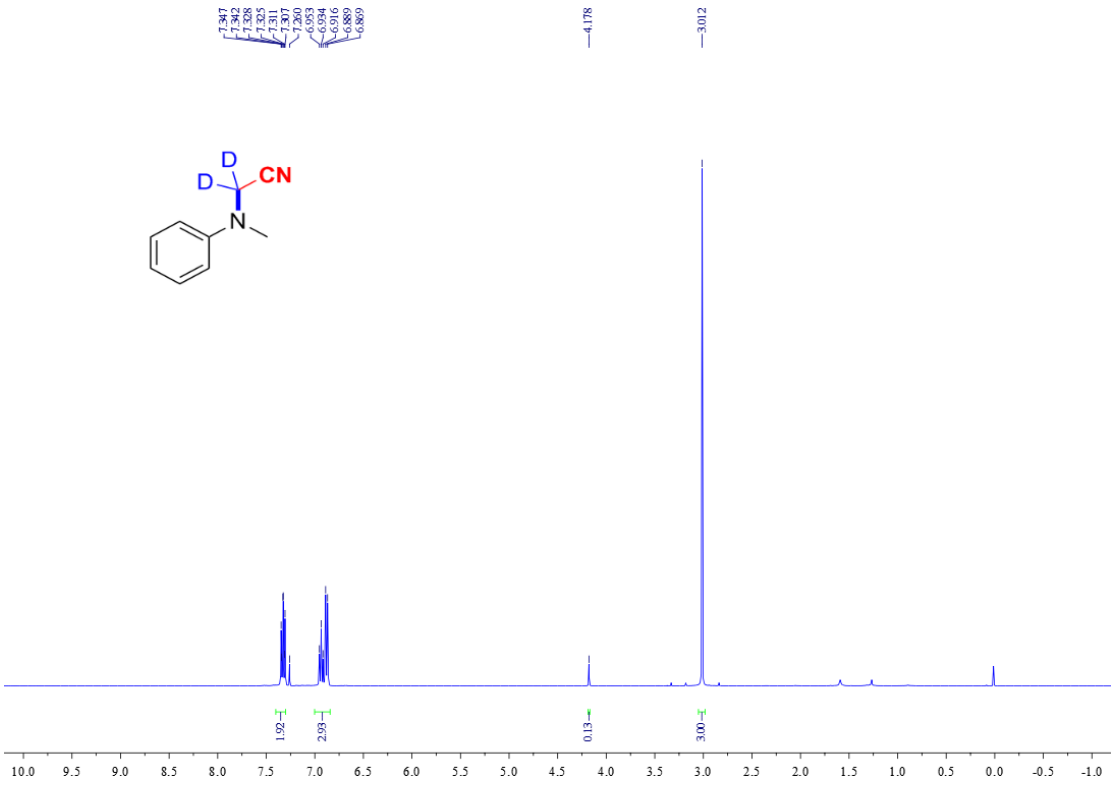
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4.178
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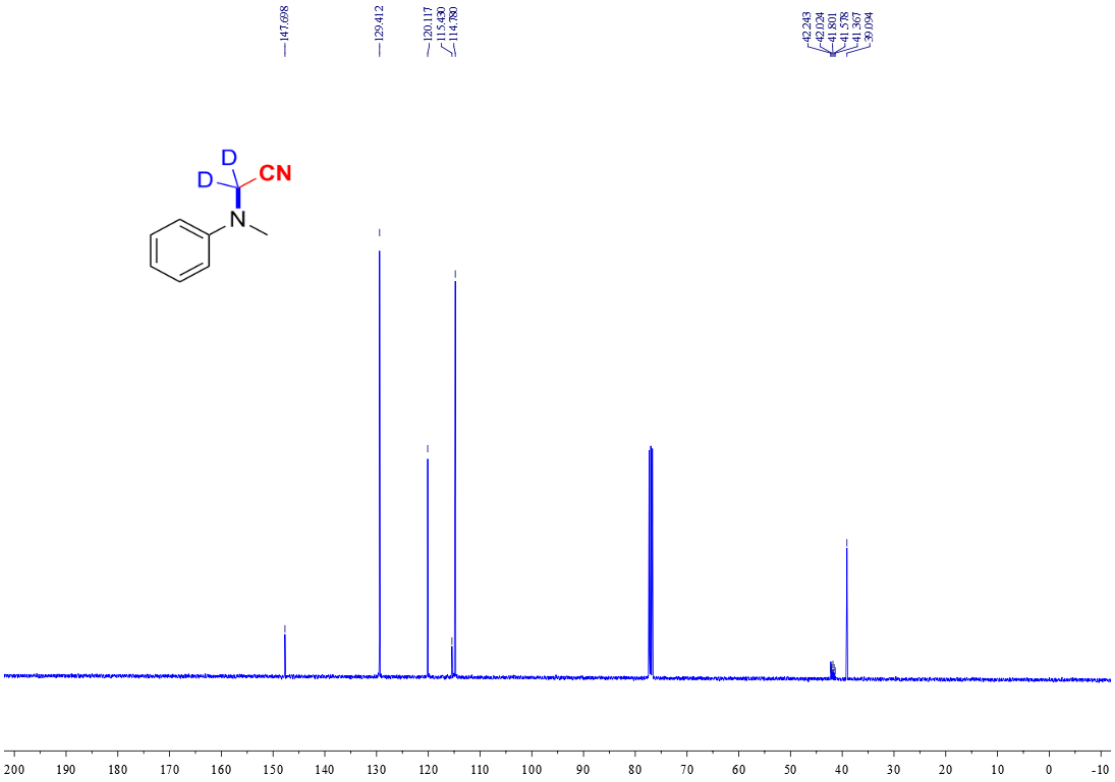
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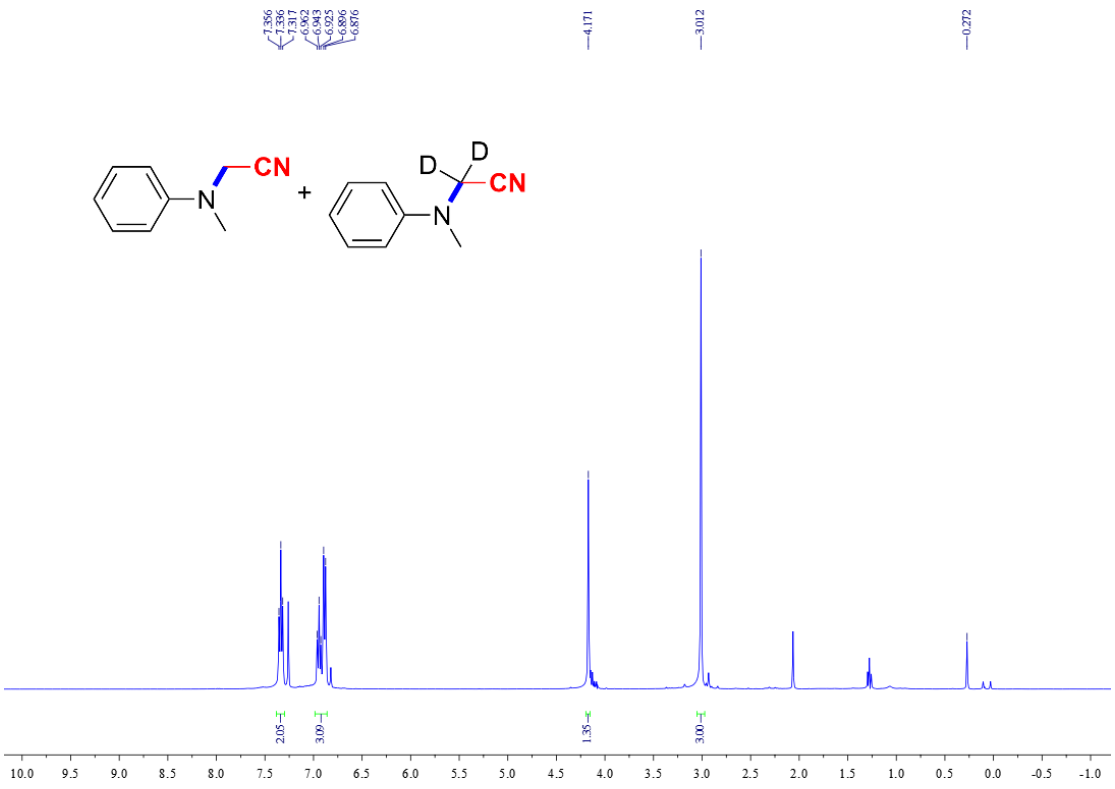
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D
D
CN
N
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3.09
1.35
3.00
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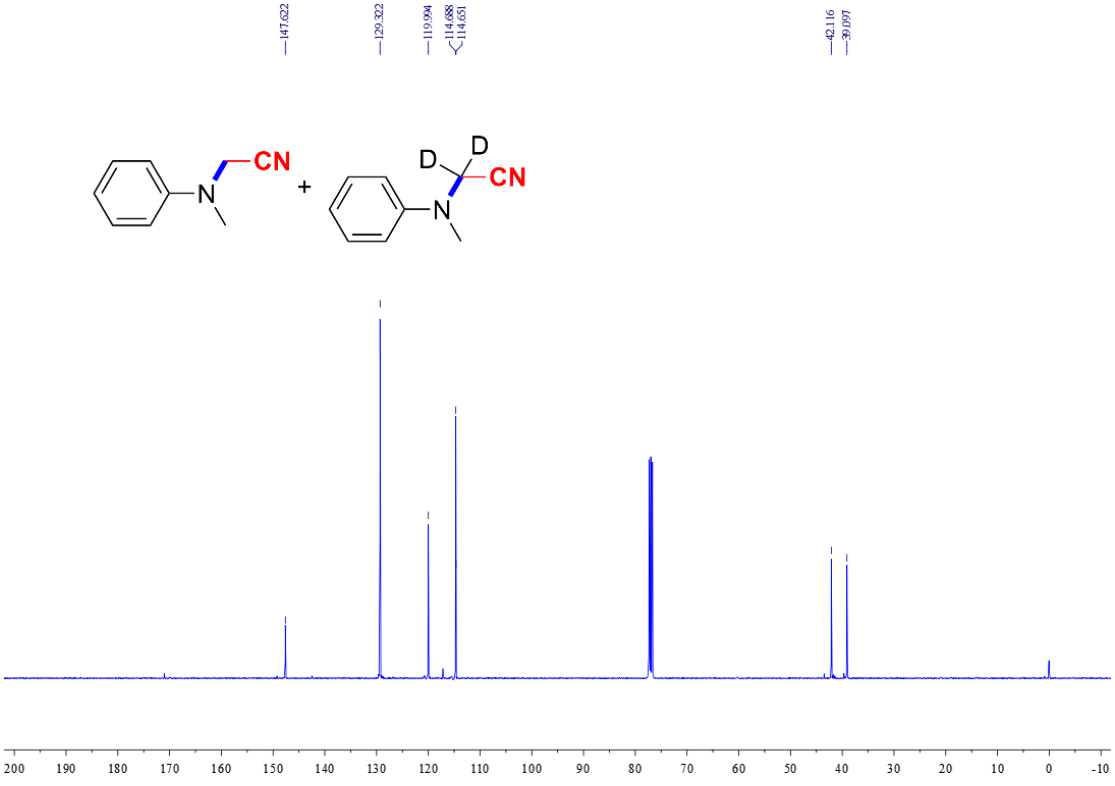
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