

## Supporting Information

### **A Combined Experimental and Computational Study on NHC-Promoted Desulfonylation of Tosylated Aldimine**

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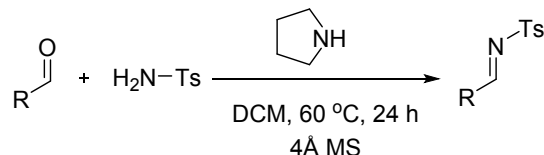
## 1 General information

Unless otherwise mentioned, all reactions were carried out under an atmosphere of nitrogen in dry sealed Schlenk tube and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was accomplished by flash chromatography using silica gel (200-300 mesh). Melting points (°C) are uncorrected. <sup>1</sup>H NMR spectra were measured on a 400 MHz spectrometer in CDCl<sub>3</sub> (100 MHz, <sup>13</sup>C NMR) with a chemical shift ( $\delta$ ) given in ppm relative to TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant *J* (Hz), integration. GC-MS was performed on an Agilent 6890-5973N system with electron ionisation (EI) mass spectrometry.

## 2 Preparation of Imines

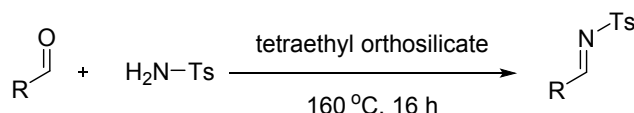
The starting materials (**1a-1q**, **1t**, **1u**, **1v**, **1x** and **3**),<sup>1a</sup> (**1r**, **1s** and **1w**)<sup>1b</sup> and (**4**, **1y**)<sup>1c, 1d</sup> were prepared according to the known procedures.

### 2.1 Procedures for the synthesis of tosylated imines **1a-1q**, **1t**, **1u**, **1v**, **1x** and **3**



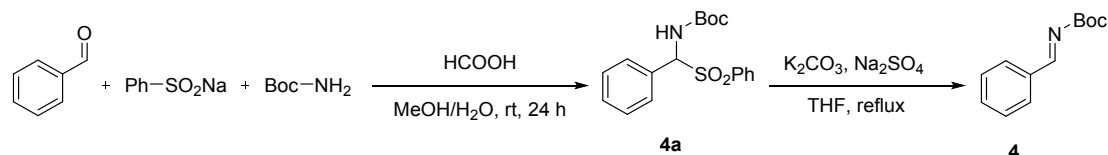
To a solution of 4-methylbenzenesulfonamide (5.8 mmol, 1.0 eq.) in dry DCM (18.0 mL, 0.32 M) were added benzaldehyde (6.96 mmol, 1.2 eq.), molecular sieves of 4Å (1 g/mol) and 10 mol% of pyrrolidine (0.58 mmol, 10 mol%). The mixture was heated to reflux (60 °C) in a seal vial during 24 h. The reaction mixture was filtrated through a pad of Celite and the filtrate was concentrated in vacuo. The product was recrystallized from ethyl acetate and petroleum ether (EA:PE = 1:5) to yield the corresponding pure tosylated imine.

### 2.2 Procedures for the synthesis of tosylated imines **1r**, **1s** and **1w**.



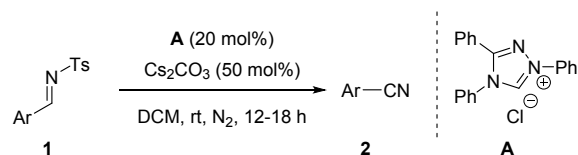
To an oven-dried 50 mL round-bottom flask with a magnetic stirring bar under an nitrogen atmosphere were added 4-methylbenzenesulfonamide (10.0 mmol 1.0 eq.), tetraethyl orthosilicate (20 mL), and the respective aldehyde (10.0 mmol, 1.0 eq.). The flask was connected to a short distillation head and a receptor flask. The reaction mixture was heated at 160 °C for 16 h; the by-product, ethanol, was collected in the receptor flask. The reaction mixture was cooled to room temperature and washed with petroleum ether (10 mL). The mixture was filtered to give a solid, which was recrystallized from ethyl acetate and petroleum ether (EA:PE = 1:5) to yield the corresponding pure tosylated imine.

### 2.3 Procedures for the synthesis of N-Boc imine



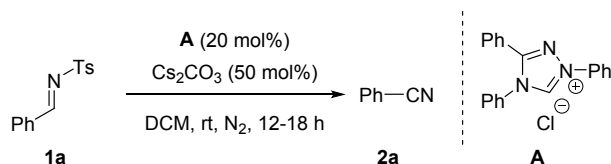
A mixture of benzaldehyde (20.0 mmol, 2.0 eq.), tert-butyl carbamate (10.0 mmol, 1.0 equiv), benzenesulfinic acid sodium salt (25.0 mmol, 2.5 eq.) and formic acid (20.0 mmol, 2.0 eq.) in methanol (10 mL) and water (20 mL) was stirred at room temperature for 24 h. The resulting precipitate was filtered and washed well with diethyl ether. After drying under vacuum, the product **4a** was obtained as a white solid. Then, a THF solution (40 mL) of the obtained product (8 mmol), potassium carbonate (48 mmol), and sodium sulfate (56 mmol) was refluxed for 18 h. The reaction mixture was filtered and concentrated to give the target imine **4**.

### 3 General procedure for the desulfonylation



In the glove box filled with nitrogen, an oven-dried 15 mL sealed tube equipped with a magnetic stir bar was charged with **1** (0.5 mmol), trisaryltriazolium salt **A** (0.1 mmol, 33.4 mg), and Cs<sub>2</sub>CO<sub>3</sub> (0.25 mmol, 81.5 mg). Freshly distilled DCM (2.0 mL) was added into the mixture with a syringe under nitrogen. Then the mixture was stirred at rt until completion (monitored by TLC). After concentrated in vacuo (due to the volatility of the product **2**, the system needed to be placed at -20°C), the crude product was purified by flash column chromatography (mixtures of petroleum ether/ethyl acetate, 80:1 to 10:1, v/v) to yield the desired product **2**.

#### 3.1 Procedure for Gram-scale Experiment



In the glove box filled with nitrogen, an oven-dried 48 mL sealed tube equipped with a magnetic stir bar was charged with the corresponding tosylated aldimine **1a** (10 mmol), trisaryltriazolium salt **A** (2 mmol, 668 mg), and Cs<sub>2</sub>CO<sub>3</sub> (5 mmol, 1.63 g). Freshly distilled DCM (20.0 mL) was added into the mixture with a syringe under nitrogen. Then the mixture was stirred at rt until completion (monitored by TLC). After concentrated in vacuo (due to the volatility of the product **2**, the system needed to be placed at -20°C), the crude product was purified by flash column chromatography (mixtures of petroleum ether/ethyl acetate, 70:1, v/v) to yield the desired product **2a**.

## 4 DFT Computational Study on Mechanism

### Computational Method:

Gaussian 09 program<sup>2</sup> and density functional theory (DFT) were used for all the calculations. All structures were optimized and at the M06-2X/6-31G\*\*<sup>3</sup> level in dichloromethane solvent using the IEFPCM model. Then, frequency calculations at the same level of theory were carried out to identify all of the stationary points as minima (zero imaginary frequencies), and to confirm each transition state has only one imaginary frequency, which connected to the expected intermediates.

**Table S1** The absolute energies (E), zero-point energy (ZPE), E+ZPE, Gibbs free energy correction (GFEC), and GFEC+E of all the stationary points involved in the reaction calculated at the M06-2X/6-31G(d, p)/IEFPCM<sub>dichloromethane</sub> level (Unit in a.u)

	ZPE	E	E+ZPE	GFEC	GFEC+E
NHC	0.304867	-935.014442	-934.709575	0.257631	-934.756811
R1	0.244165	-1144.314610	-1144.070445	0.198472	-1144.116138
HCO <sub>3</sub> <sup>-</sup>	0.026983	-264.428853	-264.401870	0.001236	-264.427617
TS1	0.549386	-2079.323018	-2078.773632	0.481807	-2078.841211
M1	0.551955	-2079.363400	-2078.811445	0.485121	-2078.878279
TS1'	0.545291	-2079.284105	-2078.738814	0.474650	-2078.809455
TS2	0.575977	-2343.788923	-2343.212946	0.504171	-2343.284752
M2	0.579407	-2343.792810	-2343.213403	0.504756	-2343.288054
TS3	0.574773	-2343.762584	-2343.187811	0.499393	-2343.263191
M3	0.406838	-1259.361957	-1258.955119	0.350127	-1259.01183
TsH	0.166607	-1084.427699	-1084.261092	0.123074	-1084.304625
TS4	0.406520	-1259.361197	-1258.954677	0.349894	-1259.011303
P	0.100234	-324.365280	-324.265046	0.069961	-324.295319

### Cartesian Coordinates of the Listed Complexes

#### NHC

0 1

C	0.97713500	-1.27460400	0.04926400
C	-0.24099400	0.64047700	-0.00397300
N	0.99892300	1.03199200	-0.01017300
N	1.71122500	-0.13924400	0.02292300
N	-0.28831600	-0.74550000	0.03657200
C	-1.38535600	1.56354800	-0.08409900
C	-1.32754300	2.77535600	0.61045400
C	-2.49538000	1.27163600	-0.88410200
C	-2.37599000	3.68389900	0.51197800
H	-0.45981400	2.99512500	1.22368900
C	-3.54031000	2.18429400	-0.97824700
H	-2.53548900	0.33945400	-1.43870500

C	-3.48410300	3.38891000	-0.27959300
H	-2.32812700	4.62161800	1.05546100
H	-4.39731300	1.95552900	-1.60276300
H	-4.30182000	4.09816800	-0.35480200
C	-1.45771500	-1.56488500	0.11277900
C	-1.58430400	-2.62863700	-0.77565600
C	-2.43417300	-1.31056300	1.07285200
C	-2.70793100	-3.44629700	-0.70434400
H	-0.80068300	-2.80419600	-1.50433900
C	-3.55916800	-2.12818200	1.12876300
H	-2.30916400	-0.48549900	1.76651700
C	-3.69831200	-3.19467400	0.24271800
H	-2.81028600	-4.27716500	-1.39417400
H	-4.32351100	-1.93552700	1.87401600
H	-4.57596900	-3.83031200	0.29261200
C	3.13521300	-0.08281400	0.00947300
C	3.86443000	-1.27214500	0.02417300
C	3.78235800	1.15020100	-0.02230600
C	5.25311600	-1.21793300	0.00623300
H	3.33284300	-2.21555000	0.04878500
C	5.17409500	1.18685800	-0.04059600
H	3.19856600	2.06166700	-0.03453900
C	5.91495300	0.00847800	-0.02658500
H	5.82036000	-2.14290700	0.01720600
H	5.67846300	2.14730700	-0.06747700
H	6.99899800	0.04401400	-0.04187700

## R1

01

C	-5.23950200	1.55738600	0.00792500
C	-4.24013000	1.73109900	0.96923800
C	-3.06654700	0.99542300	0.89250100
C	-2.88804300	0.07954600	-0.15275700
C	-3.89139500	-0.09212300	-1.11199200
C	-5.06684100	0.64691900	-1.03162200
H	-6.15594300	2.13504400	0.07282400
H	-4.38219200	2.44231100	1.77579600
H	-2.28031900	1.11600600	1.63043800
H	-3.74600700	-0.80563200	-1.91811600
H	-5.84427600	0.51317200	-1.77573000
C	-1.66626500	-0.71637600	-0.27703900
H	-1.60994000	-1.40858600	-1.12482900
N	-0.69848200	-0.61185200	0.55725300
S	0.61901300	-1.63726700	0.27339200

O	0.45704700	-2.38623900	-0.97312900
O	0.82244300	-2.37372600	1.51686500
C	1.92807800	-0.46864700	0.06736900
C	2.49517100	-0.29440100	-1.19000900
C	3.53558100	0.61841900	-1.33097300
C	4.00245400	1.35366100	-0.23820200
C	3.41029300	1.15235600	1.01544000
C	2.37480100	0.24321700	1.17914500
H	2.13283000	-0.87300900	-2.03279400
H	3.99501100	0.75824400	-2.30489400
H	3.77220600	1.71142200	1.87326000
H	1.92517900	0.07750300	2.15281700
C	5.10851900	2.36128500	-0.40445600
H	5.74502500	2.39655000	0.48238300
H	5.72916500	2.12682300	-1.27141500
H	4.69146900	3.36254000	-0.55207600

**TS1**

01

C	1.22242400	0.73607000	-0.25737800
C	3.43686100	0.35770400	-0.13667300
N	3.29915300	1.64696200	-0.00663700
N	1.95001500	1.84962200	-0.08364600
N	2.18997500	-0.22429700	-0.30175300
C	4.73556100	-0.33064300	-0.05356600
C	5.70745300	0.21772200	0.79179800
C	5.03152900	-1.47594900	-0.80059400
C	6.95906200	-0.37660600	0.89372700
H	5.46711200	1.10551300	1.36683400
C	6.28683600	-2.06648500	-0.69118200
H	4.29624800	-1.89828800	-1.47592400
C	7.24963400	-1.52252100	0.15550400
H	7.70521700	0.05090100	1.55494700
H	6.51362000	-2.95223400	-1.27483700
H	8.22554400	-1.98940300	0.23925500
C	1.91326300	-1.62096700	-0.49468000
C	1.61236600	-2.07647400	-1.77437800
C	1.94503600	-2.48176100	0.59609600
C	1.33066300	-3.42740300	-1.96179700
H	1.61289700	-1.37963300	-2.60731900
C	1.66052600	-3.82911400	0.39819300
H	2.16989700	-2.09040500	1.58298000
C	1.35524900	-4.30127000	-0.87739100
H	1.09464600	-3.79439300	-2.95486400

H	1.67039600	-4.50824800	1.24386000
H	1.13316200	-5.35280800	-1.02588000
C	1.44050700	3.18030500	-0.01628100
C	0.18074600	3.38399800	0.53242800
C	2.20176900	4.23596300	-0.50909600
C	-0.34500800	4.67142300	0.55704500
H	-0.37485800	2.54778200	0.94010300
C	1.67141800	5.52155800	-0.45920600
H	3.18375500	4.04571800	-0.92652000
C	0.39788600	5.74176700	0.06370600
H	-1.33639100	4.82641500	0.96979300
H	2.25427500	6.35321800	-0.84093100
H	-0.01118700	6.74620700	0.08968900
C	-1.47054000	-2.98113100	2.07126000
C	-0.99153500	-1.74763300	2.51342200
C	-0.77243800	-0.71454800	1.60823900
C	-1.03448700	-0.90893500	0.25024200
C	-1.48348600	-2.15479100	-0.19302300
C	-1.71095400	-3.18532200	0.71536200
H	-1.64085400	-3.78348600	2.78214000
H	-0.78577900	-1.59006400	3.56735100
H	-0.40419100	0.24696600	1.94748100
H	-1.66153800	-2.31556500	-1.25331300
H	-2.06514800	-4.14783800	0.36043300
C	-0.87846500	0.14557200	-0.80555400
H	-0.38869400	-0.22148000	-1.70859000
N	-1.67912500	1.15964500	-1.04525500
S	-2.83079900	1.66521200	0.02771600
O	-3.35355600	2.91447400	-0.52653000
O	-2.38054400	1.68730400	1.42703300
C	-4.13011600	0.45290000	-0.09255100
C	-5.01697000	0.53382800	-1.16409800
C	-6.02294400	-0.41636200	-1.28109300
C	-6.15560200	-1.44423700	-0.33998800
C	-5.25173100	-1.50070600	0.72407300
C	-4.23759600	-0.55698100	0.85814900
H	-4.91976300	1.33764700	-1.88630800
H	-6.71968500	-0.36019700	-2.11265200
H	-5.34023600	-2.29504900	1.45994800
H	-3.53435000	-0.60437800	1.68414700
C	-7.27044900	-2.44962800	-0.46067400
H	-7.02611300	-3.37691100	0.06160200
H	-8.19252500	-2.05382900	-0.02274700
H	-7.47880400	-2.68334600	-1.50735800



**TS1'**

0 1

C	-1.32460800	0.45085800	-0.11821800
C	-2.61666200	-1.29468300	-0.41987400
N	-3.24276300	-0.28403600	-0.96481000
N	-2.42529800	0.78330000	-0.77040000
N	-1.41344900	-0.86576800	0.11383900
C	-3.14122600	-2.66583900	-0.38337000
C	-2.98715300	-3.47050600	0.75003600
C	-3.84276400	-3.13827100	-1.49618700
C	-3.52779700	-4.75111600	0.75891000
H	-2.46205200	-3.09479700	1.62250800
C	-4.38038000	-4.41998500	-1.47756100
H	-3.95379300	-2.50064000	-2.36702000
C	-4.22006500	-5.22713000	-0.35316700
H	-3.41360400	-5.37556500	1.63827800
H	-4.92020100	-4.78907400	-2.34282100
H	-4.63765800	-6.22844300	-0.34138000
C	-0.36962500	-1.60710800	0.76678600
C	0.15506000	-2.74624100	0.16504300
C	0.11624800	-1.11631400	1.97423500
C	1.19036400	-3.41683400	0.80912900
H	-0.23170200	-3.09146200	-0.78775000
C	1.16963700	-1.78374100	2.59237800
H	-0.32025800	-0.22731300	2.42048200
C	1.70009600	-2.93553900	2.01555800
H	1.61119300	-4.30777700	0.35599000
H	1.56400900	-1.40044400	3.52739000
H	2.51500700	-3.45905600	2.50426500
C	-2.78071200	2.09292000	-1.22438200
C	-1.76300900	3.01777700	-1.44234800
C	-4.12292700	2.39913900	-1.41538600
C	-2.11783100	4.30084900	-1.84704000
H	-0.72198500	2.72565600	-1.32403800
C	-4.45328600	3.68394600	-1.83391000
H	-4.88237300	1.64706200	-1.23779100
C	-3.45634000	4.63490700	-2.04337600
H	-1.33999700	5.03576900	-2.02204700
H	-5.49514500	3.94147400	-1.98969400
H	-3.72282200	5.63608200	-2.36435200
C	-0.19453100	2.35908600	4.98711800
C	-0.99892500	2.84956000	3.95950400
C	-0.56960400	2.78268100	2.63734700

C	0.69614000	2.26453900	2.32703700
C	1.50588300	1.78165700	3.36823400
C	1.05538800	1.81952300	4.68388600
H	-0.54058500	2.39204200	6.01489500
H	-1.97372600	3.27057200	4.18594100
H	-1.20888800	3.13832700	1.83280000
H	2.47966700	1.36504000	3.12778100
H	1.68867900	1.43588800	5.47833100
C	1.09742300	2.09029300	0.92731000
H	-0.45500700	1.09409600	0.15445200
N	2.18098900	2.41494900	0.44522000
S	2.18359600	1.63735200	-1.50562900
O	2.63427700	2.56673700	-2.57781900
O	0.85562700	0.97648800	-1.69779700
C	3.38203100	0.30859500	-1.45227400
C	4.56067000	0.39687200	-2.18518000
C	5.50131100	-0.62337700	-2.08230500
C	5.28804100	-1.71704000	-1.23791600
C	4.10107100	-1.77310000	-0.49944600
C	3.14667900	-0.76684400	-0.59796800
H	4.71871500	1.25153500	-2.83513800
H	6.41675900	-0.57195400	-2.66586500
H	3.92146100	-2.61856900	0.15921900
H	2.22347100	-0.81768300	-0.02542500
C	6.32984400	-2.79791400	-1.10859900
H	5.89381100	-3.72596200	-0.73266100
H	6.80559700	-3.00329400	-2.07067000
H	7.11766000	-2.49378300	-0.41167400

**M1**

01

C	-0.84301100	0.40404300	-0.06043800
C	-0.80191500	2.56731200	-0.46702000
N	-1.94173100	2.13608100	-0.93695600
N	-1.94719300	0.80158500	-0.68312900
N	-0.09126900	1.51360200	0.08211300
C	-0.37217400	3.97173800	-0.51376600
C	-1.35138600	4.96069100	-0.37413900
C	0.96289200	4.32835900	-0.73065300
C	-0.99298900	6.30174900	-0.44017300
H	-2.38357000	4.67000400	-0.20889900
C	1.31178200	5.67270900	-0.79425300
H	1.72245900	3.56509100	-0.86261800
C	0.33816800	6.65864000	-0.64542000

H	-1.75239400	7.06739800	-0.32528300
H	2.34627600	5.94908700	-0.96624600
H	0.61725600	7.70606500	-0.69201900
C	1.18312700	1.57498100	0.74661300
C	2.25963100	0.90076700	0.18353300
C	1.29697700	2.32196000	1.91393500
C	3.49812700	0.98803000	0.81360200
H	2.12211800	0.32143300	-0.72487200
C	2.54191100	2.40206200	2.52877500
H	0.43027100	2.83255400	2.32164900
C	3.63822300	1.73920800	1.97867700
H	4.34719700	0.46587000	0.38687600
H	2.65332300	2.98083000	3.43893900
H	4.60650600	1.80818700	2.46274900
C	-3.08259900	0.00161400	-1.05606100
C	-4.29230800	0.24479100	-0.41592000
C	-2.92886600	-0.98610800	-2.01985300
C	-5.38567600	-0.54715200	-0.74693000
H	-4.36096400	1.02157300	0.33832800
C	-4.03530900	-1.76807500	-2.34094900
H	-1.95495600	-1.15964400	-2.46224800
C	-5.25550000	-1.55222800	-1.70526100
H	-6.33662600	-0.38475700	-0.25164300
H	-3.93717300	-2.55043000	-3.08540600
H	-6.11133700	-2.16975800	-1.95688100
C	-4.01435100	-2.17657300	2.69053000
C	-3.63124900	-2.91764200	1.57398800
C	-2.49210300	-2.56798700	0.85242100
C	-1.73412600	-1.46853100	1.24284200
C	-2.11049400	-0.73578900	2.36962500
C	-3.24729300	-1.08508200	3.09279300
H	-4.90391800	-2.45137300	3.24836600
H	-4.22464100	-3.77088700	1.26016500
H	-2.19161700	-3.12653100	-0.02801100
H	-1.51173700	0.11880800	2.68294100
H	-3.53219800	-0.50847400	3.96714500
C	-0.52302500	-0.98711600	0.42976000
H	0.30773900	-0.85849900	1.14551700
N	-0.16481200	-1.74179700	-0.75024800
S	0.72448700	-3.02318200	-0.46534300
O	0.57140300	-3.95057800	-1.59895800
O	0.53474600	-3.58225400	0.88971100
C	2.45773200	-2.54695700	-0.50897700
C	2.99063600	-2.02132000	-1.68746500

C	4.33567100	-1.68200900	-1.74137500
C	5.17202600	-1.87023600	-0.63103700
C	4.61824700	-2.39391100	0.53745300
C	3.26548500	-2.72854800	0.60599700
H	2.34984400	-1.88756200	-2.55472800
H	4.75326900	-1.27803600	-2.65996100
H	5.25292700	-2.54619900	1.40649000
H	2.83357300	-3.14634400	1.50876600
C	6.62693400	-1.48267800	-0.69776900
H	7.19754400	-1.94983100	0.10748900
H	7.06961300	-1.77819600	-1.65234100
H	6.74611100	-0.39740500	-0.60577500

**HCO<sub>3</sub><sup>-</sup>**

-1 1

C	-0.13997300	0.06463100	0.00022800
O	0.99783600	-0.76923200	0.00010900
O	0.10788200	1.28854000	-0.00008800
O	-1.21813600	-0.54874700	-0.00020400
H	1.73917700	-0.15228200	0.00009400

**TS2**

-1 1

C	0.75197500	0.58053000	-0.55709100
C	2.96441300	0.77559300	-0.43267700
N	2.52061100	1.99441300	-0.43587900
N	1.16278400	1.87262000	-0.55641700
N	1.93040900	-0.13084900	-0.55567800
C	4.39696700	0.45829400	-0.30978200
C	5.18179100	1.30804400	0.47713700
C	4.99118600	-0.61815600	-0.97647600
C	6.54843200	1.08375900	0.59626300
H	4.70563700	2.13480900	0.99335200
C	6.35903500	-0.83763600	-0.85062600
H	4.39019200	-1.27763500	-1.59293700
C	7.13897100	0.00908600	-0.06548400
H	7.15098800	1.74357800	1.21165000
H	6.81737900	-1.67212500	-1.37069400
H	8.20498900	-0.16935700	0.03155600
C	2.08812100	-1.54750800	-0.36662700
C	1.92355700	-2.41671800	-1.43948100
C	2.49679300	-2.00016300	0.88105500
C	2.17211300	-3.77066800	-1.25109700
H	1.58031100	-2.02851300	-2.39034400

C	2.74464900	-3.35886000	1.05869200
H	2.63178000	-1.28273900	1.68453100
C	2.58289000	-4.24143900	-0.00447600
H	2.03740200	-4.46065400	-2.07721400
H	3.06661000	-3.72330700	2.02851400
H	2.77708500	-5.29991100	0.13686700
C	0.41767800	3.07492200	-0.72097600
C	0.65469500	4.12057200	0.16577600
C	-0.50820800	3.19305800	-1.75224400
C	-0.06685100	5.30109000	0.02760600
H	1.38461000	3.98796500	0.95706500
C	-1.23822400	4.37087900	-1.86786900
H	-0.66472100	2.36229400	-2.43199900
C	-1.02043100	5.42407700	-0.98108100
H	0.10688000	6.11973800	0.71805100
H	-1.97790200	4.46546700	-2.65586400
H	-1.59145800	6.34164400	-1.07856400
C	-3.88339500	2.66975100	0.30875600
C	-3.89713200	1.80592000	-0.78483700
C	-2.81632600	0.96413900	-1.03017700
C	-1.70237400	0.95540500	-0.18412900
C	-1.70866600	1.81487200	0.92388800
C	-2.77809400	2.67141000	1.15938200
H	-4.72487700	3.32868300	0.50141300
H	-4.75586700	1.78531400	-1.45095700
H	-2.82035900	0.28401900	-1.87509700
H	-0.84468700	1.83112100	1.58442000
H	-2.75279500	3.33831600	2.01672000
C	-0.56092600	-0.00109300	-0.41339900
H	-0.34848500	-0.42932400	0.94738000
N	-0.79050500	-1.04758900	-1.39417400
S	-1.37483900	-2.41424500	-0.85821200
O	-0.69644900	-2.99198700	0.32184900
O	-1.51968100	-3.32135900	-2.01891900
C	-3.05561100	-2.12152600	-0.28429800
C	-4.11986000	-2.20696000	-1.17571200
C	-5.39323900	-1.81834300	-0.76875300
C	-5.61759500	-1.33359200	0.52246800
C	-4.53914500	-1.27826000	1.41064400
C	-3.26386000	-1.66869300	1.01719900
H	-3.94069500	-2.57727100	-2.18053100
H	-6.22636500	-1.88738300	-1.46418800
H	-4.70157200	-0.91234900	2.42178800
H	-2.42113200	-1.60419500	1.69992400

C	-6.98196600	-0.84992200	0.94230300
H	-7.19725300	-1.11712000	1.98021100
H	-7.04132400	0.24158600	0.86676700
H	-7.76609900	-1.26995600	0.30781500
C	0.61463600	-0.00483100	2.74429000
O	0.69057000	-0.30993700	4.06843100
O	1.38657200	0.82876500	2.26535800
O	-0.29840400	-0.67165800	2.14727600
H	1.39919400	0.24228100	4.42583700

## M2

-1 1

C	0.63774600	0.52994600	-0.56658100
C	2.82379800	0.68701600	-0.07279200
N	2.37625600	1.87911900	0.14483300
N	1.03053900	1.84290000	-0.23497400
N	1.86825000	-0.16697200	-0.58510300
C	4.23021200	0.32166600	0.17718600
C	4.83400400	0.75249500	1.36069200
C	4.97996900	-0.39009400	-0.76519600
C	6.17774100	0.48050200	1.59782700
H	4.23416500	1.28142500	2.09242000
C	6.32265100	-0.66018900	-0.52256300
H	4.51445500	-0.72689300	-1.68595700
C	6.92397400	-0.22623300	0.65765300
H	6.63961000	0.81421500	2.52142000
H	6.90039300	-1.20966300	-1.25858800
H	7.97091500	-0.44220900	0.84520700
C	2.09568200	-1.54256300	-0.88542200
C	2.01126300	-1.97433900	-2.20796000
C	2.47358000	-2.41648400	0.12916800
C	2.30388500	-3.29667700	-2.51676000
H	1.70084700	-1.27140200	-2.97418100
C	2.77396700	-3.73949000	-0.19108900
H	2.50216700	-2.04770800	1.14934200
C	2.69040500	-4.18105200	-1.50850200
H	2.23130400	-3.63939100	-3.54389800
H	3.06606000	-4.42762500	0.59576100
H	2.92149300	-5.21327700	-1.75174000
C	0.49163300	3.04743300	-0.72648900
C	0.76886300	4.23353100	-0.03896200
C	-0.30967700	3.08168000	-1.87178200
C	0.24343800	5.43773000	-0.49301300
H	1.39505600	4.19424600	0.84528200

C	-0.83901700	4.29120600	-2.30840900
H	-0.52108900	2.16104600	-2.40357600
C	-0.56891600	5.47523800	-1.62552900
H	0.46475000	6.35194200	0.04909300
H	-1.46356900	4.30461700	-3.19623900
H	-0.98538800	6.41548800	-1.97128200
C	-4.24481000	2.26954600	-0.13006800
C	-4.13180600	1.32913700	-1.15320400
C	-2.94325500	0.63242900	-1.33419400
C	-1.83694700	0.85228300	-0.49986600
C	-1.96433200	1.79902700	0.52805600
C	-3.15377300	2.49818800	0.70706100
H	-5.17384300	2.81244200	0.01732200
H	-4.97625300	1.13099800	-1.80787200
H	-2.86029100	-0.12334300	-2.10952300
H	-1.13135100	1.96964700	1.20306100
H	-3.23238200	3.22099400	1.51436700
C	-0.61980800	0.02415600	-0.69530300
H	-0.38421500	-0.97059300	2.03640400
N	-0.79047800	-1.31681600	-1.14040200
S	-1.26699400	-2.35550100	-0.06818800
O	-0.58793500	-2.23636100	1.27520800
O	-1.20596400	-3.71346200	-0.63259200
C	-2.99900600	-2.07896200	0.32099400
C	-3.96348800	-2.59601700	-0.53754300
C	-5.29944300	-2.24452400	-0.36466700
C	-5.68467200	-1.37003000	0.65364000
C	-4.70153600	-0.87808200	1.51808600
C	-3.36639500	-1.22647900	1.35990400
H	-3.66081600	-3.26566300	-1.33661300
H	-6.05300000	-2.64772200	-1.03621300
H	-4.98647100	-0.19804500	2.31705300
H	-2.61215200	-0.81649800	2.02307200
C	-7.11772800	-0.93103500	0.80703700
H	-7.44610200	-1.00226900	1.84770800
H	-7.23016200	0.11517900	0.50171700
H	-7.78835100	-1.53490200	0.19190500
C	0.83013600	0.42118300	2.59344100
O	0.78923000	1.73613100	2.87724700
O	1.87548700	-0.18179800	2.43958200
O	-0.37861400	-0.07292200	2.53815000
H	1.69649600	2.05982100	2.77520900

Pre-TS3

-1 1

C	1.30390000	-0.34988000	-0.18557000
C	3.33075800	-1.31181700	-0.30836600
N	2.51157100	-2.30360400	-0.29587600
N	1.23906100	-1.75180000	-0.23207300
N	2.69838500	-0.05764900	-0.30901200
C	4.78945200	-1.48225800	-0.36405500
C	5.36685200	-2.61000300	0.22845700
C	5.59875900	-0.55812000	-1.03138400
C	6.74002100	-2.81113700	0.15083300
H	4.72885800	-3.31646200	0.74928000
C	6.97269300	-0.76328700	-1.10378400
H	5.14852900	0.30784600	-1.50443600
C	7.54605700	-1.88719000	-0.51243600
H	7.18319100	-3.68648500	0.61423900
H	7.59585100	-0.04593800	-1.62765600
H	8.61859900	-2.04270500	-0.56809500
C	3.25557500	0.98380000	0.52251300
C	3.73687700	2.15600500	-0.04841500
C	3.28786500	0.80231600	1.90366700
C	4.25069500	3.15850900	0.76991300
H	3.68217000	2.28266000	-1.12446300
C	3.80810600	1.80337200	2.71812300
H	2.89541200	-0.11808400	2.32802400
C	4.28808100	2.98309300	2.15156000
H	4.61784500	4.07856600	0.32699100
H	3.83738100	1.66266200	3.79363600
H	4.68822700	3.76592500	2.78771600
C	0.17553500	-2.53248100	-0.72735500
C	-0.79208300	-1.98406300	-1.57255900
C	0.10524600	-3.88167100	-0.36596800
C	-1.83587500	-2.78121100	-2.02895000
H	-0.74377500	-0.93618900	-1.84348900
C	-0.93962300	-4.66941300	-0.83761400
H	0.86863600	-4.29491600	0.28424000
C	-1.92017600	-4.12377700	-1.66565800
H	-2.59373500	-2.33759100	-2.66752800
H	-0.99028600	-5.71445400	-0.54752400
H	-2.74300300	-4.73733100	-2.01750900
C	0.89609000	4.72563400	-0.41836800
C	0.50870400	4.22504000	0.82584900
C	0.29523900	2.86262300	0.99741200
C	0.48321100	1.97383100	-0.06804200
C	0.84337900	2.48879400	-1.31769600



C	1.05415300	3.85438100	-1.49268100
H	1.06026800	5.79073500	-0.54988700
H	0.37595100	4.90227300	1.66424200
H	-0.01029300	2.46743700	1.96148900
H	0.96338600	1.80118100	-2.15107600
H	1.33667800	4.23732800	-2.46886700
C	0.29950500	0.51291000	0.11741800
N	-0.87690700	-0.02120300	0.69215200
S	-2.25533000	0.53233000	0.24690500
O	-2.44769900	0.69993300	-1.23959500
O	-2.72329100	1.79396100	0.92010400
C	-3.40348000	-0.70941600	0.80720900
C	-4.73499500	-0.32509400	0.96686300
C	-5.68043100	-1.27726400	1.32329800
C	-5.31489100	-2.61284600	1.52938100
C	-3.97558900	-2.97035600	1.36468600
C	-3.01521100	-2.02988100	0.99994700
H	-5.02177300	0.71302900	0.82585600
H	-6.71838500	-0.98103900	1.44870100
H	-3.67476900	-4.00346800	1.51731100
H	-1.97634600	-2.31181100	0.86491400
C	-6.34942100	-3.63030300	1.93451600
H	-6.69767500	-3.44446900	2.95541900
H	-7.22342400	-3.58338900	1.27910500
H	-5.94428300	-4.64348900	1.89569700
C	-5.13394700	2.92692700	-1.30819100
O	-4.56512300	1.96350200	-2.02404400
O	-4.62661200	3.19220500	-0.10712900
O	-6.09431100	3.53655500	-1.72762300
H	-3.73270600	1.55014900	-1.64443000
H	-3.83992800	2.63670800	0.18025600

**TS3**

-1 1

C	1.48446800	-0.17580900	-0.45632800
C	3.44451000	-1.25070100	-0.41415900
N	2.57804900	-2.14471000	-0.77526600
N	1.37700000	-1.48092800	-0.83665600
N	2.85208800	-0.00718300	-0.25497700
C	4.86616000	-1.55528600	-0.19276700
C	5.19894100	-2.79732700	0.35814600
C	5.87755900	-0.65866300	-0.54834400
C	6.53236000	-3.13517100	0.55676600
H	4.40471000	-3.48382600	0.63189500

C	7.21004900	-1.00191800	-0.34458100
H	5.62645900	0.29497200	-0.99790800
C	7.53961900	-2.23663300	0.20973800
H	6.78478200	-4.09765200	0.98918900
H	7.99216100	-0.30454100	-0.62534500
H	8.58028900	-2.49863000	0.37042800
C	3.38361100	1.06344300	0.54480500
C	4.01007700	2.14955200	-0.05577300
C	3.21490200	1.00042200	1.92473700
C	4.48550100	3.18612000	0.74148200
H	4.10250500	2.18526700	-1.13640900
C	3.69024500	2.04215800	2.71542300
H	2.70471500	0.14840500	2.36322700
C	4.32414700	3.13326800	2.12447100
H	4.97252900	4.03820800	0.27981000
H	3.56217900	2.00171900	3.79170300
H	4.68938300	3.94627800	2.74319700
C	0.23596900	-2.16165500	-1.31231200
C	-0.78942100	-1.46324900	-1.95026500
C	0.15492700	-3.54522900	-1.13281100
C	-1.90767800	-2.16017500	-2.39966700
H	-0.72047900	-0.39020600	-2.08937300
C	-0.96431400	-4.22668800	-1.59556300
H	0.96278600	-4.06554600	-0.63195500
C	-2.00025900	-3.53803100	-2.22760800
H	-2.71453700	-1.60145700	-2.86003800
H	-1.03052800	-5.30030900	-1.45126900
H	-2.87881600	-4.07301400	-2.57258800
C	0.87378200	4.93683500	-0.76228100
C	0.21752500	4.47727000	0.38115800
C	0.08786000	3.11395100	0.61697900
C	0.62593600	2.18116700	-0.27869200
C	1.25526100	2.65259600	-1.43738500
C	1.38512100	4.01806000	-1.67616500
H	0.97149900	6.00238000	-0.94559700
H	-0.19447900	5.18880900	1.09071600
H	-0.44264500	2.73875600	1.48609400
H	1.64327600	1.93604000	-2.15928900
H	1.87666800	4.36482800	-2.58062400
C	0.45656300	0.72603600	-0.02465000
N	-0.54278300	0.17693700	0.63596400
S	-2.42989300	0.54158800	-0.05320200
O	-3.13892300	0.58014800	-1.42449700
O	-2.89250300	1.78243800	0.70546900

C	-3.27053000	-0.79040400	0.82721200
C	-4.53769700	-0.54389400	1.35262600
C	-5.24610000	-1.58160900	1.94531800
C	-4.70280700	-2.86952100	2.02643300
C	-3.42955100	-3.09040000	1.49835500
C	-2.70982400	-2.05968000	0.89666600
H	-4.95336600	0.45866500	1.30754700
H	-6.23519700	-1.39388300	2.35570900
H	-2.99213300	-4.08404700	1.55632600
H	-1.71548200	-2.22893900	0.49641500
C	-5.47766500	-3.98009400	2.68830200
H	-5.54825800	-3.81623000	3.76834700
H	-6.49889500	-4.03125400	2.30040000
H	-5.00011000	-4.94864500	2.52569700
C	-6.00235300	2.25341300	-0.71912100
O	-5.58297700	1.20605400	-1.41444000
O	-5.15537100	2.80464900	0.14548400
O	-7.12911800	2.69156900	-0.85103000
H	-4.57768600	1.00124600	-1.36901800
H	-4.25374400	2.34659900	0.26172900

**M3**

0 1

C	-0.49670600	0.25211400	-0.11535500
C	1.59014800	0.95757300	0.18036300
N	0.85252700	2.02907600	0.22321000
N	-0.42938900	1.58179900	0.06242000
N	0.79484300	-0.16166000	0.00161800
C	3.05122900	0.96310700	0.34194000
C	3.77069100	2.05716100	-0.14846600
C	3.71587300	-0.07065900	1.01021700
C	5.14888500	2.11269600	0.02379400
H	3.24321100	2.85241000	-0.66453500
C	5.09492100	-0.00764000	1.17732000
H	3.15950900	-0.91251700	1.40923000
C	5.81247000	1.07972600	0.68345100
H	5.70524500	2.96074900	-0.36089500
H	5.60824700	-0.80812500	1.69895200
H	6.88864600	1.12322300	0.81455900
C	1.22166700	-1.50467900	-0.26210500
C	0.80655800	-2.53057900	0.57933800
C	2.03198700	-1.74603100	-1.36728600
C	1.22113200	-3.83142000	0.30678300
H	0.17488500	-2.30854500	1.43292100

C	2.44836500	-3.04821500	-1.62205200
H	2.32346300	-0.92389800	-2.01268100
C	2.04388900	-4.08876100	-0.78733900
H	0.90424900	-4.64148000	0.95440800
H	3.08178000	-3.25096400	-2.47865500
H	2.36829600	-5.10333800	-0.99266000
C	-1.50112300	2.51660100	0.00485200
C	-2.79207900	2.11272300	0.33664400
C	-1.22949100	3.82542700	-0.38723200
C	-3.82746400	3.03839100	0.25863100
H	-2.98530200	1.09557600	0.65927500
C	-2.27449200	4.74065300	-0.44842600
H	-0.21541100	4.11031200	-0.63982100
C	-3.57395600	4.35128900	-0.13098000
H	-4.83521000	2.72921300	0.51402600
H	-2.06973900	5.76141800	-0.75307600
H	-4.38553000	5.06883700	-0.18547800
C	-4.31598000	-3.06773300	1.17781700
C	-4.31132000	-3.03415800	-0.21823000
C	-3.42039300	-2.21002900	-0.89407100
C	-2.52041600	-1.41033300	-0.18430700
C	-2.53105300	-1.44599300	1.21066200
C	-3.42525400	-2.27061400	1.89150600
H	-5.01252400	-3.71176400	1.70511400
H	-5.00538000	-3.65418500	-0.77731000
H	-3.39567200	-2.16561300	-1.97889600
H	-1.83725000	-0.82041200	1.77118400
H	-3.42596600	-2.28917200	2.97675800
C	-1.57136100	-0.54516200	-0.95256900
N	-1.40225300	-0.34699400	-2.15607800

**H<sub>2</sub>CO<sub>3</sub>- Ts<sup>-</sup>**

-1 1

S	-1.16796700	-1.87877200	-0.01764700
O	-1.82266700	-1.30077800	1.24795100
O	-1.84044600	-1.27547700	-1.26148300
C	0.42240600	-1.00985100	-0.01829500
C	1.01062400	-0.64294800	-1.22284700
C	2.25517100	-0.01669400	-1.21606500
C	2.92156300	0.24441100	-0.01696700
C	2.30957400	-0.13183700	1.18457200
C	1.06776300	-0.75530600	1.19013500
H	0.48216800	-0.82835000	-2.15277700
H	2.71295400	0.28072000	-2.15577800

H	2.81267200	0.07564400	2.12573200
H	0.58124200	-1.02608300	2.12222200
C	4.26153400	0.93402800	-0.00250700
H	4.18120900	1.92849500	0.44732300
H	4.98794700	0.36786500	0.58751500
H	4.65854500	1.05200200	-1.01278700
C	-1.80464000	1.92378300	0.03399600
O	-1.77862400	1.23625100	1.16780900
O	-1.88116200	1.25988400	-1.11179000
O	-1.76020100	3.14051300	0.04414300
H	-1.83522100	0.21555800	1.11920500
H	-1.89320000	0.23783600	-1.08348400

**TS4**

0 1

C	0.48260800	0.29032300	-0.05245000
C	-1.65521800	0.92273300	-0.18471900
N	-0.96817400	2.02780200	-0.20737100
N	0.33772000	1.62369200	-0.14162500
N	-0.79990000	-0.16402500	-0.11414000
C	-3.12186900	0.86701300	-0.26936200
C	-3.86539100	1.88825000	0.33004400
C	-3.77246400	-0.15442800	-0.96955900
C	-5.25233400	1.88285300	0.23514500
H	-3.34875500	2.67532400	0.86918400
C	-5.16014200	-0.15298300	-1.05928100
H	-3.19846400	-0.93915100	-1.45162900
C	-5.90109100	0.86146500	-0.45642900
H	-5.82625800	2.67394200	0.70575000
H	-5.66278200	-0.94429700	-1.60488400
H	-6.98378000	0.85664800	-0.52698400
C	-1.15021600	-1.53633100	0.10074700
C	-0.68852300	-2.50450900	-0.78386300
C	-1.92088300	-1.86991500	1.21113700
C	-1.01406500	-3.83845200	-0.55202700
H	-0.08932200	-2.21211300	-1.63959300
C	-2.24935600	-3.20406600	1.42509000
H	-2.24881700	-1.09250900	1.89357800
C	-1.79638600	-4.18714800	0.54651200
H	-0.65815700	-4.60243800	-1.23453800
H	-2.85019900	-3.47625200	2.28587300
H	-2.05029600	-5.22717100	0.72160900
C	1.37368200	2.59711900	-0.08949000
C	2.68367300	2.22628000	-0.38601700

C	1.05734700	3.90678900	0.26495700
C	3.68902300	3.18467400	-0.31455600
H	2.91319200	1.20632400	-0.67380700
C	2.07356200	4.85457500	0.32203100
H	0.03120000	4.16769500	0.49244500
C	3.38977800	4.49891500	0.03690200
H	4.71036500	2.89963400	-0.54317200
H	1.83200900	5.87571700	0.59733600
H	4.17822500	5.24209500	0.08790900
C	4.49490300	-2.96919100	-0.94903100
C	4.41973100	-2.92695500	0.44420700
C	3.47718300	-2.11965000	1.06818700
C	2.59513800	-1.34618600	0.30534000
C	2.67381800	-1.39232700	-1.08557500
C	3.62142200	-2.19916800	-1.71204300
H	5.23228600	-3.59964200	-1.43550500
H	5.09783300	-3.52655200	1.04319100
H	3.40132600	-2.07263400	2.14992400
H	1.99161400	-0.78763200	-1.67853000
H	3.67641600	-2.22521100	-2.79561200
C	1.60745100	-0.50611900	1.03116900
N	1.33093800	-0.24934600	2.17671400

**P**

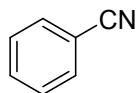
01

C	-2.17187900	-0.00001300	0.00000800
C	-1.47927300	1.20967800	-0.00002900
C	-0.08965800	1.21713200	0.00003000
C	0.60073200	0.00002400	0.00000600
C	-0.08966900	-1.21711300	-0.00001900
C	-1.47928200	-1.20969700	0.00001700
H	-3.25678800	0.00004500	-0.00000700
H	-2.02199600	2.14849200	-0.00004700
H	0.46239700	2.15045400	0.00002300
H	0.46245500	-2.15038700	-0.00002200
H	-2.02192200	-2.14856400	0.00000800
C	2.04047100	-0.00000200	0.00000000
N	3.19817200	-0.00001300	-0.00000500

## 5 Characterization of products

### 5.1 Spectral data

#### Benzonitrile (2a)<sup>4a</sup>

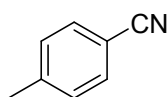


**Aspect:** colorless oil (41.8 mg, 81% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.67 – 7.65 (m, 2H), 7.63 – 7.59 (m, 1H), 7.50 – 7.46 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  132.8, 132.2, 129.1, 118.9, 112.5.

#### 4-Methylbenzonitrile (2b)<sup>4b</sup>

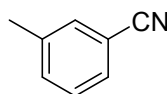


**Aspect:** colorless oil (43.9 mg, 75% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.54 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.7, 132.1, 129.9, 119.2, 109.3, 21.8.

#### 3-Methylbenzonitrile (2c)<sup>4e</sup>

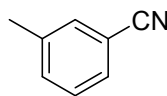


**Aspect:** colorless oil (48.6 mg, 83% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47 – 7.43 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.37 – 7.33 (m, 1H), 2.39 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  139.2, 133.6, 132.5, 129.3, 129.0, 119.1, 112.3, 21.2.

#### 3,4-Dimethylbenzonitrile (2d)<sup>4g</sup>



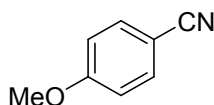
**Aspect:** white solid (51.8 mg, 79% yield).

**MP:** 63 – 64 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.42 – 7.37 (m, 2H), 7.21 (d, *J* = 7.7 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.5, 137.9, 132.9, 130.3, 129.7, 119.3, 109.5, 20.2, 19.6.

#### 4-Methoxybenzonitrile (2e)<sup>4a</sup>



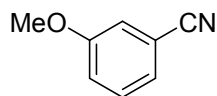
**Aspect:** white solid (47.9 mg, 72% yield).

**MP:** 59 – 61 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 7.57 (m, 2H), 6.98 – 6.93 (m, 2H), 3.86 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.8, 134.0, 119.2, 114.8, 104.0, 55.6.

### 3-Methoxybenzonitrile (2f)<sup>4b</sup>

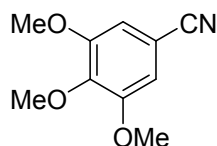


**Aspect:** colorless oil (52.6 mg, 79% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.35 (m, 1H), 7.27 – 7.23 (m, 1H), 7.15 – 7.12 (m, 2H), 3.84 (s, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 159.6, 130.3, 124.5, 119.3, 118.8, 116.8, 113.2, 55.5.

### 3,4,5-Trimethoxybenzonitrile (2g)<sup>4c</sup>



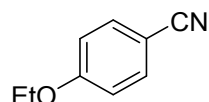
**Aspect:** white solid (83.1 mg, 86% yield).

**MP:** 92 – 93 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 6.87 (s, 2H), 3.91 (s, 3H), 3.88 (s, 6H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.5, 142.3, 119.0, 109.4, 106.7, 61.0, 56.4.

### 4-Ethoxybenzonitrile (2h)<sup>4h</sup>



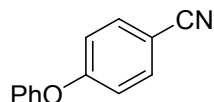
**Aspect:** white solid (54.5 mg, 74% yield).

**MP:** 61 – 63 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.60 – 7.55 (m, 2H), 6.96 – 6.91 (m, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 162.3, 134.0, 119.3, 115.1, 103.7, 63.9, 14.6.

### 4-Phenoxybenzonitrile (2i)<sup>4i</sup>



**Aspect:** white solid (83.9 mg, 86% yield).

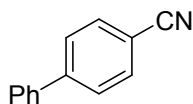
**MP:** 43 – 45 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.57 (m, 2H), 7.45 – 7.38 (m, 1H), 7.26 – 7.21 (m, 1H), 7.09 – 7.04 (m, 2H), 7.02 – 6.98 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 161.7, 154.8, 134.1, 130.2, 125.2, 120.4, 118.9, 117.9, 105.8.

### [1,1'-Biphenyl]-4-carbonitrile (2j)<sup>4c</sup>





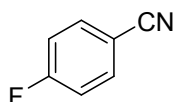
**Aspect:** white solid (68.1 mg, 76% yield).

**MP:** 86 – 87 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.74 – 7.68 (m, 4H), 7.61 – 7.58 (m, 2H), 7.51 – 7.47 (m, 2H), 7.45 – 7.41 (m, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 145.7, 139.2, 132.6, 129.1, 128.7, 127.7, 127.2, 119.0, 110.9.

#### 4-Fluorobenzonitrile (2k)<sup>4b</sup>



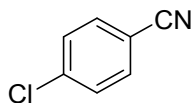
**Aspect:** white solid (44.8 mg, 74% yield).

**MP:** 34 – 35 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.66 (m, 2H), 7.21 – 7.15 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 165.1 (d, *J* = 256.5 Hz), 134.7 (d, *J* = 9.3 Hz), 118.1, 116.9 (d, *J* = 22.7 Hz), 108.6 (d, *J* = 3.6 Hz).

#### 4-Chlorobenzonitrile (2l)<sup>4b</sup>



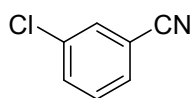
**Aspect:** white solid (47.5 mg, 69% yield).

**MP:** 93 – 95 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.63 – 7.59 (m, 2H), 7.49 – 7.45 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 139.6, 133.4, 129.7, 118.0, 110.8.

#### 3-Chlorobenzonitrile (2m)<sup>4f</sup>



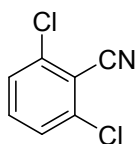
**Aspect:** white solid (53.0 mg, 77% yield).

**MP:** 39 – 41 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 (t, *J* = 1.7 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.43 (t, *J* = 7.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 135.3, 133.3, 132.0, 130.5, 130.3, 117.5, 114.0.

#### 2,6-Dichlorobenzonitrile (2n)<sup>4j</sup>



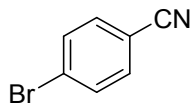
**Aspect:** white solid (67.1 mg, 78% yield).

**MP:** 144 – 145 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.42 (m, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.5, 133.9, 128.2, 114.4, 113.4.

**4-Bromobenzonitrile (2o)**<sup>4f</sup>



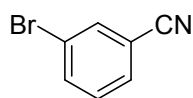
**Aspect:** white solid (69.2 mg, 76% yield).

**MP:** 111 – 112 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 – 7.62 (m, 2H), 7.55 – 7.51 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  133.4, 132.7, 128.0, 118.1, 111.3.

**3-Bromobenzonitrile (2p)**<sup>4f</sup>



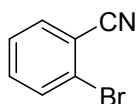
**Aspect:** white solid (75.5 mg, 83% yield).

**MP:** 38 – 39 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.80 (t, *J* = 1.6 Hz, 1H), 7.75 (ddd, *J* = 8.1, 1.9, 1.0 Hz, 1H), 7.61 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.1, 134.8, 130.7, 130.6, 122.9, 117.3, 114.2.

**2-Bromobenzonitrile (2q)**<sup>4a</sup>



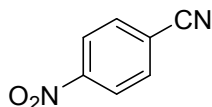
**Aspect:** white solid (71.9 mg, 79% yield).

**MP:** 53 – 55 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.72 – 7.65 (m, 2H), 7.50 – 7.40 (m, 2H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  134.4, 133.9, 133.2, 127.6, 125.4, 117.2, 115.9.

**4-Nitrobenzonitrile (2r)**<sup>4b</sup>



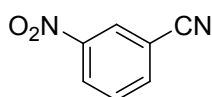
**Aspect:** yellow solid (65.2 mg, 88% yield).

**MP:** 143 – 145 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 – 8.34 (m, 1H), 7.93 – 7.88 (m, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.0, 133.5, 124.3, 118.3, 116.8.

**3-Nitrobenzonitrile (2s)**<sup>4d</sup>



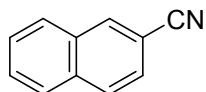
**Aspect:** white solid (64.4 mg, 87% yield).

**MP:** 112 – 114 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.55 (t, 1H, *J* = 1.8 Hz), 8.49 (ddd, 1H, *J* = 8.3, 2.3, 1.0 Hz), 8.01 (dt, 1H, *J* = 7.8, 1.3 Hz), 7.75 (t, 1H, *J* = 8.3 Hz).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 148.3, 137.6, 130.7, 127.5, 127.3, 116.5, 114.2.

#### 2-Naphthonitrile (2t)<sup>4c</sup>



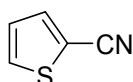
**Aspect:** white solid (62.0 mg, 81% yield).

**MP:** 36 – 38 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.24 (s, 1H), 7.94 – 7.88 (m, 3H), 7.69 – 7.56 (m, 3H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 134.7, 134.2, 132.3, 129.2, 129.1, 128.4, 128.1, 127.7, 126.4, 119.3, 109.4.

#### Thiophene-2-carbonitrile (2u)<sup>4a</sup>

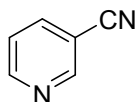


**Aspect:** colorless oil (37.7 mg, 69% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.65 – 7.61 (m, 2H), 7.14 (dd, *J* = 5.0, 3.8 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 137.4, 132.6, 127.7, 114.2, 109.9.

#### Nicotinonitrile (2v)<sup>4b</sup>



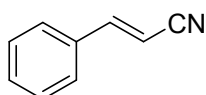
**Aspect:** white solid (40.1 mg, 77% yield).

**MP:** 50 – 51 °C.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.91 (d, *J* = 1.5 Hz, 1H), 8.84 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.98 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.46 (ddd, *J* = 8.0, 5.0, 0.9 Hz, 1H).

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 153.0, 152.5, 139.3, 123.6, 116.5, 110.2.

#### Cinnamonitrile (2w)<sup>4a</sup>



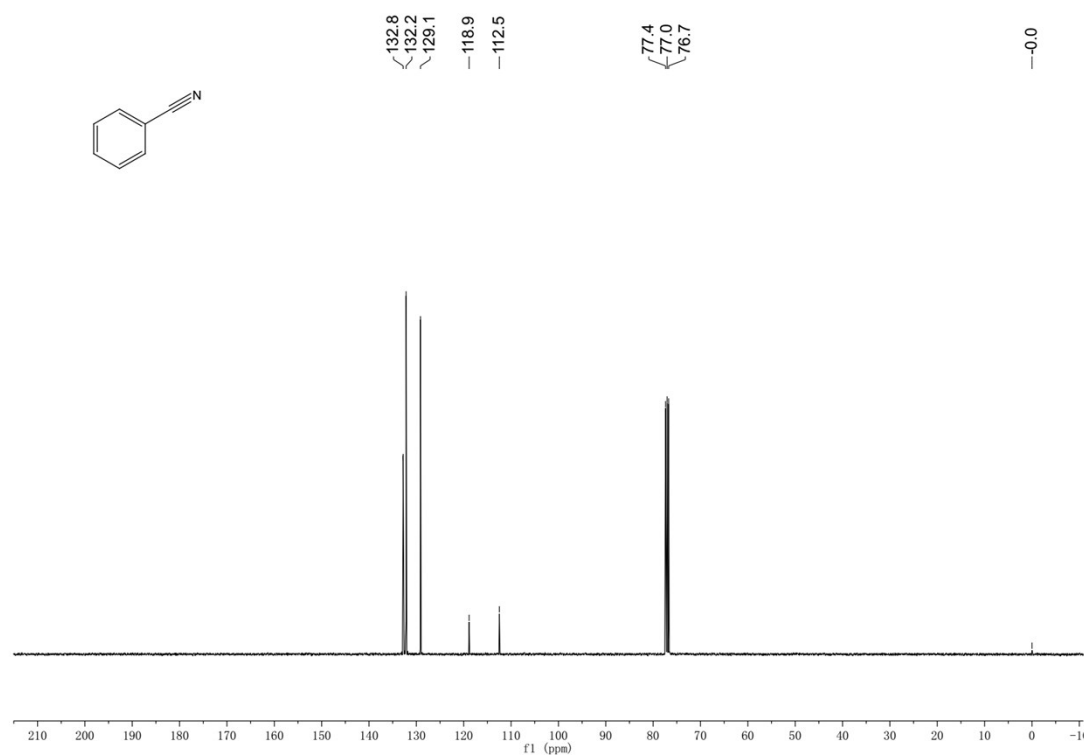
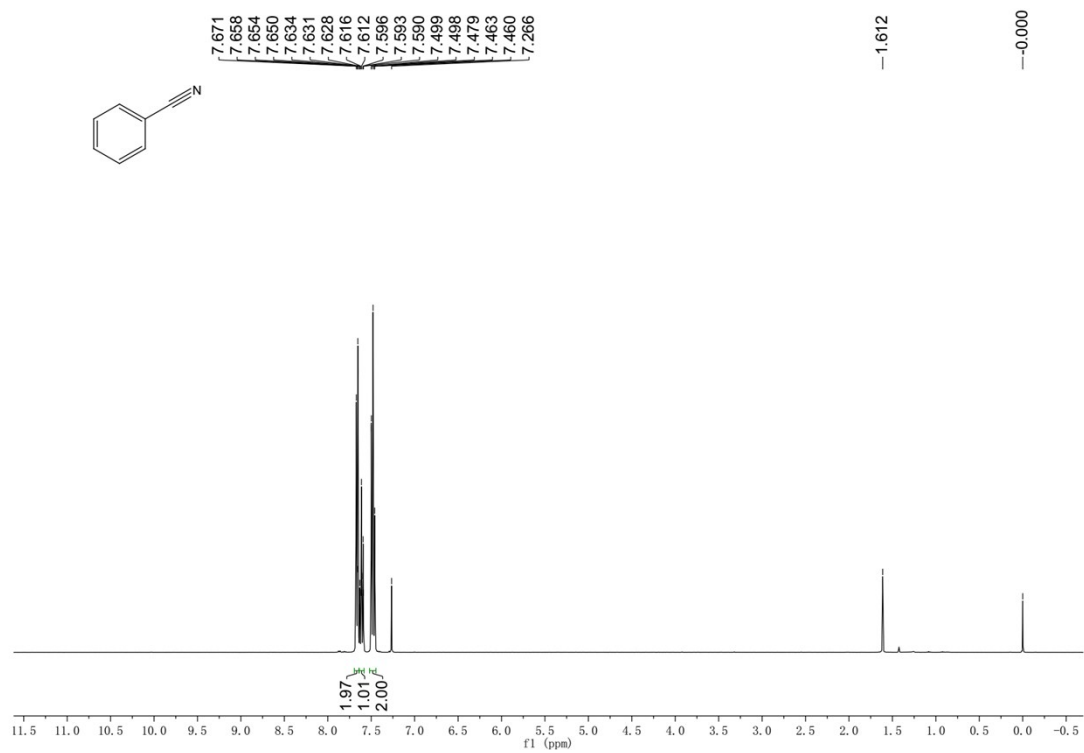
**Aspect:** colorless oil (15.5 mg, 24% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.47 – 7.38 (m, 6H), 5.89 (d, *J* = 16.7 Hz, 1H).

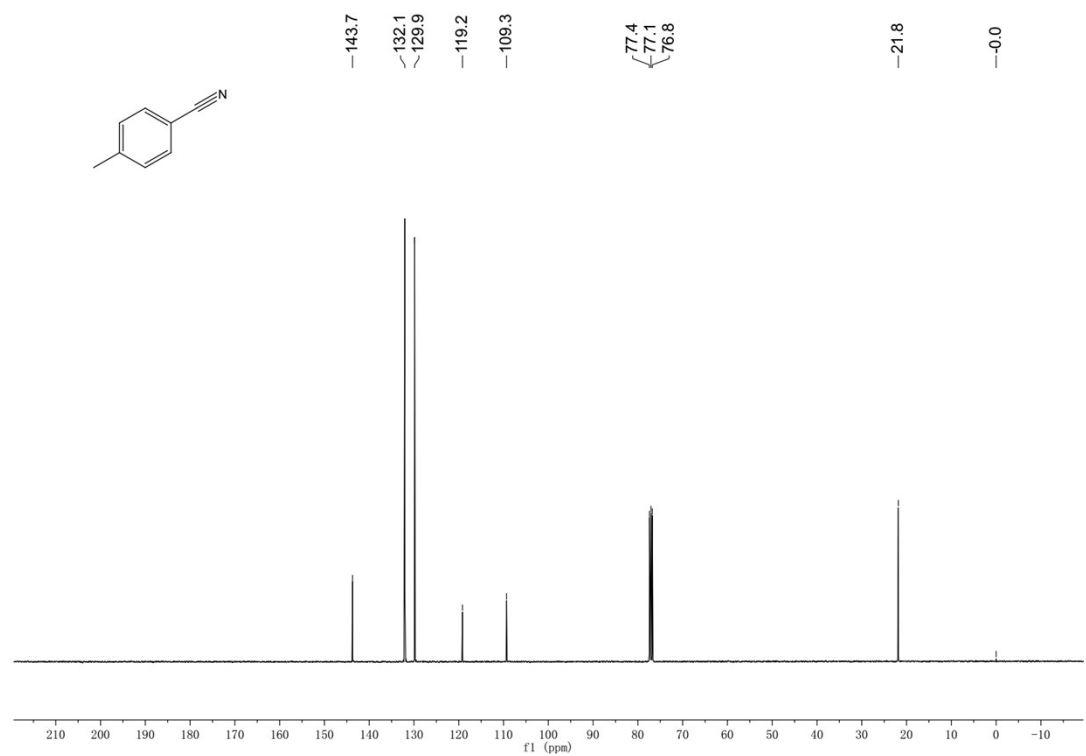
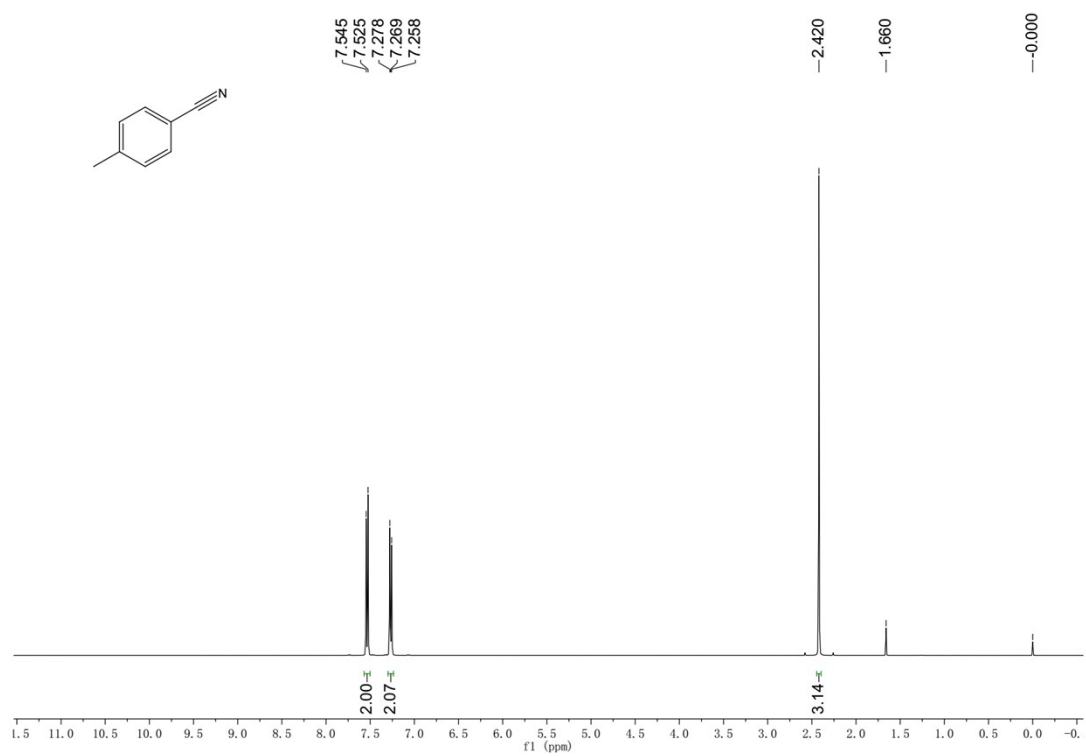
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 150.6, 133.5, 131.2, 129.1, 127.4, 118.2, 96.3.

## 5.2 Copies of the $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra

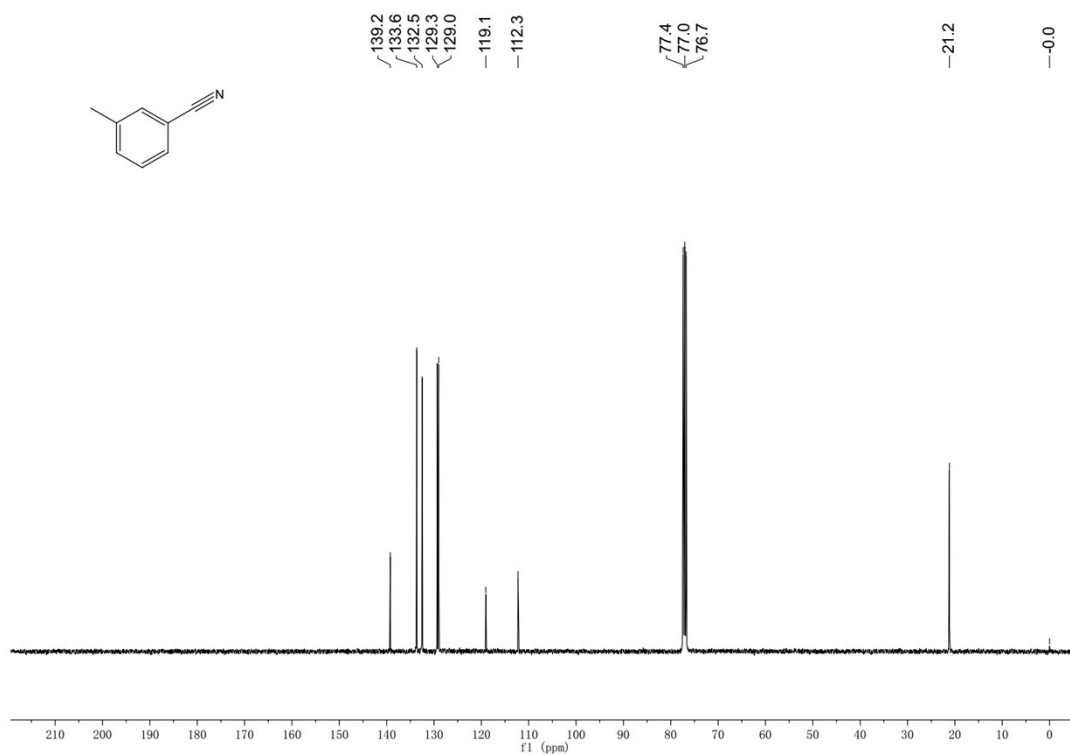
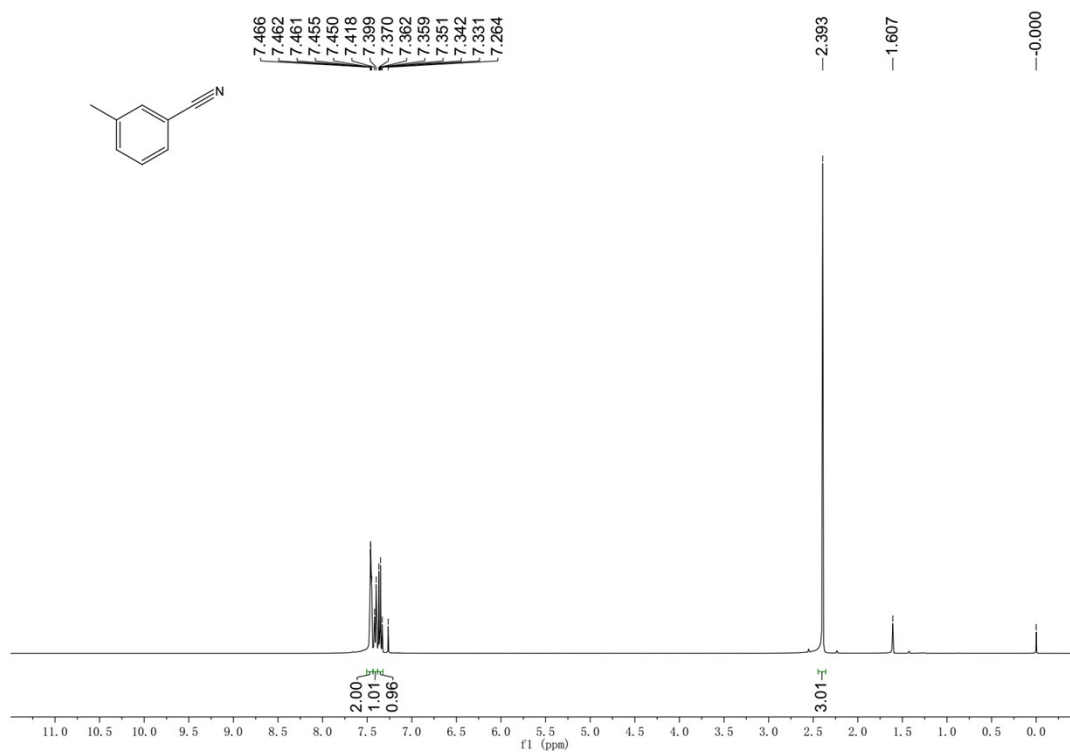
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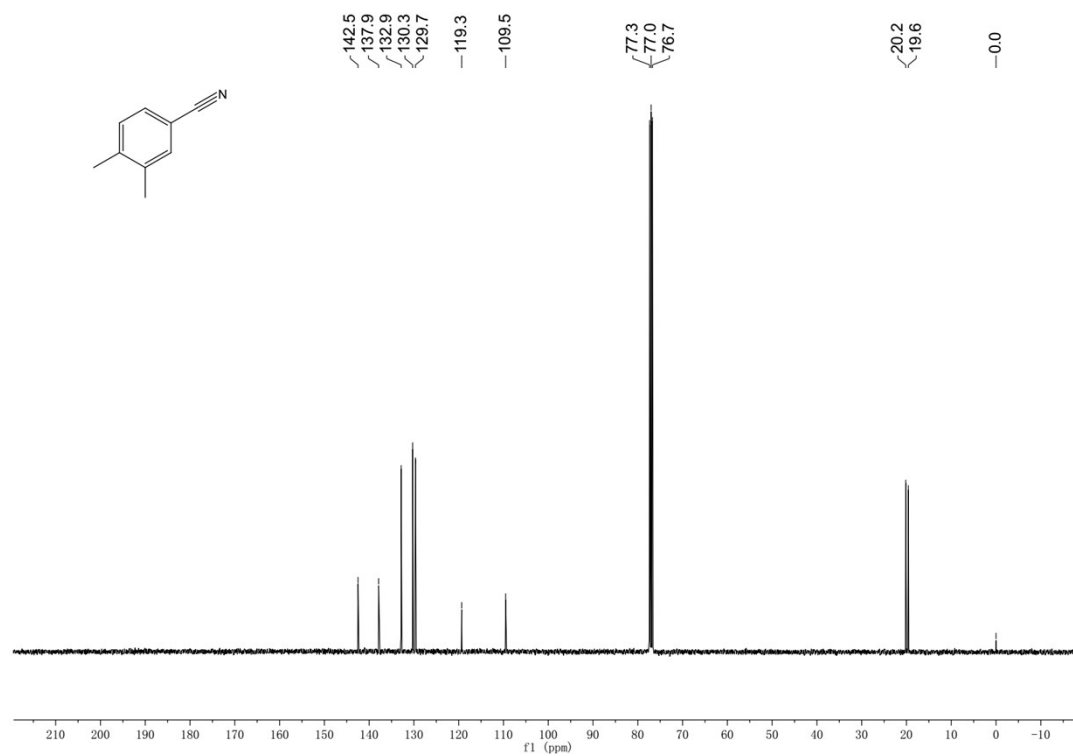
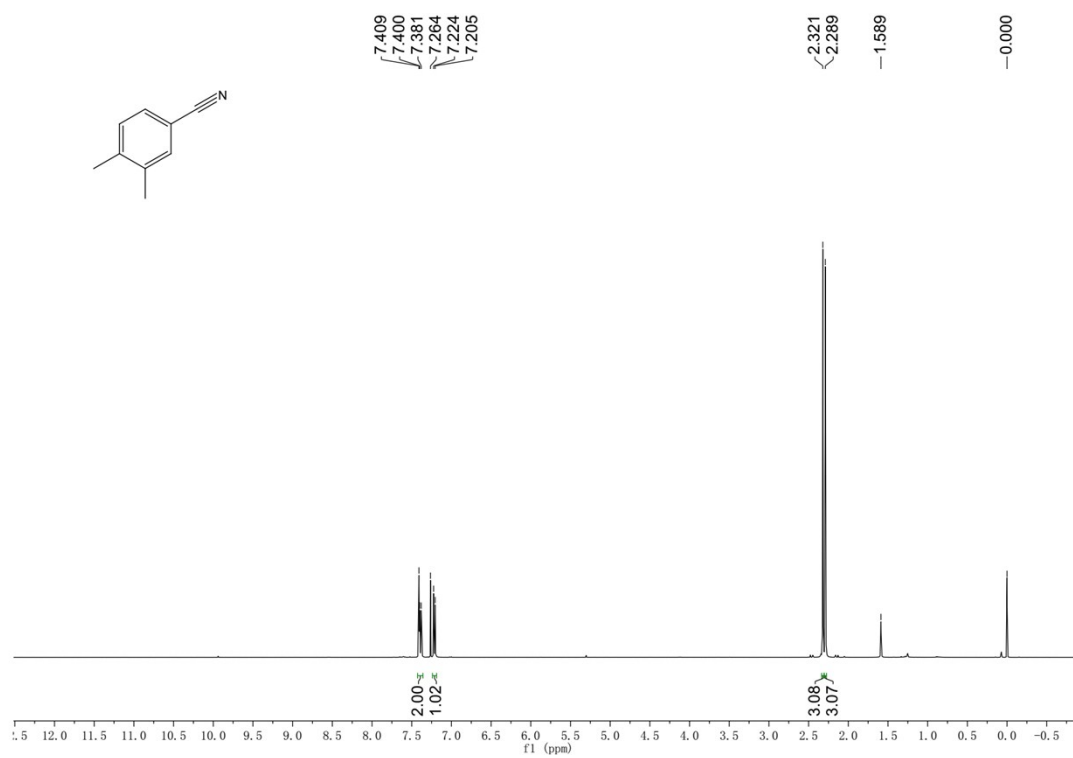
2b



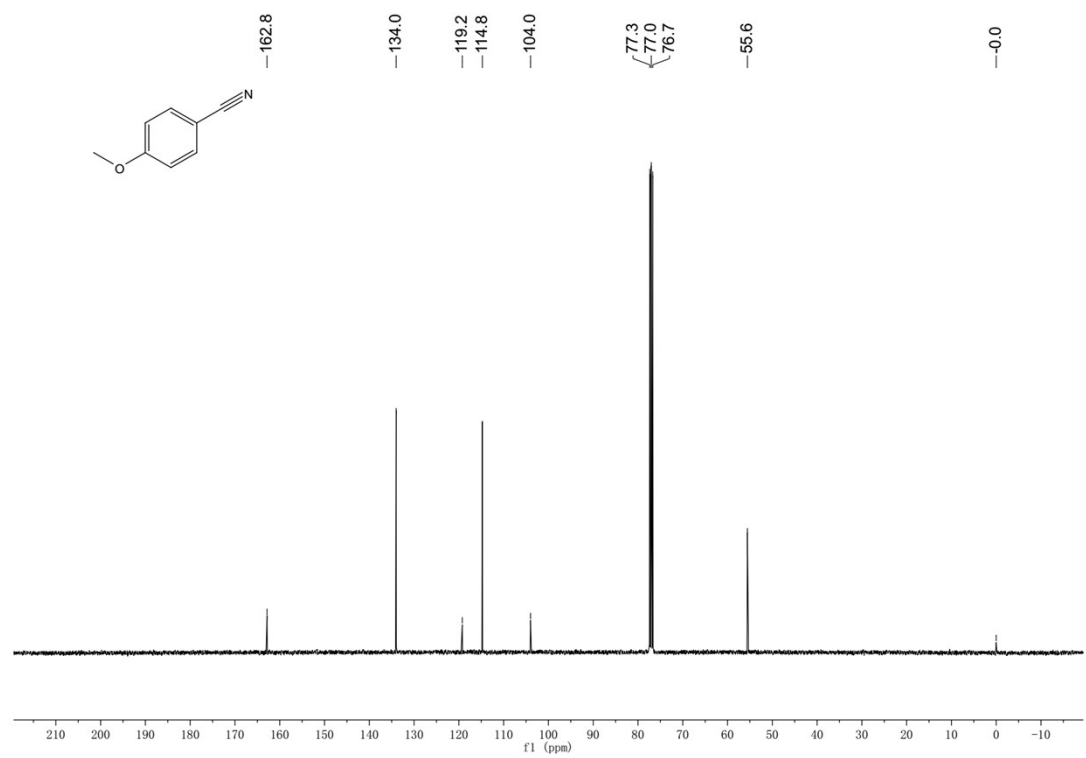
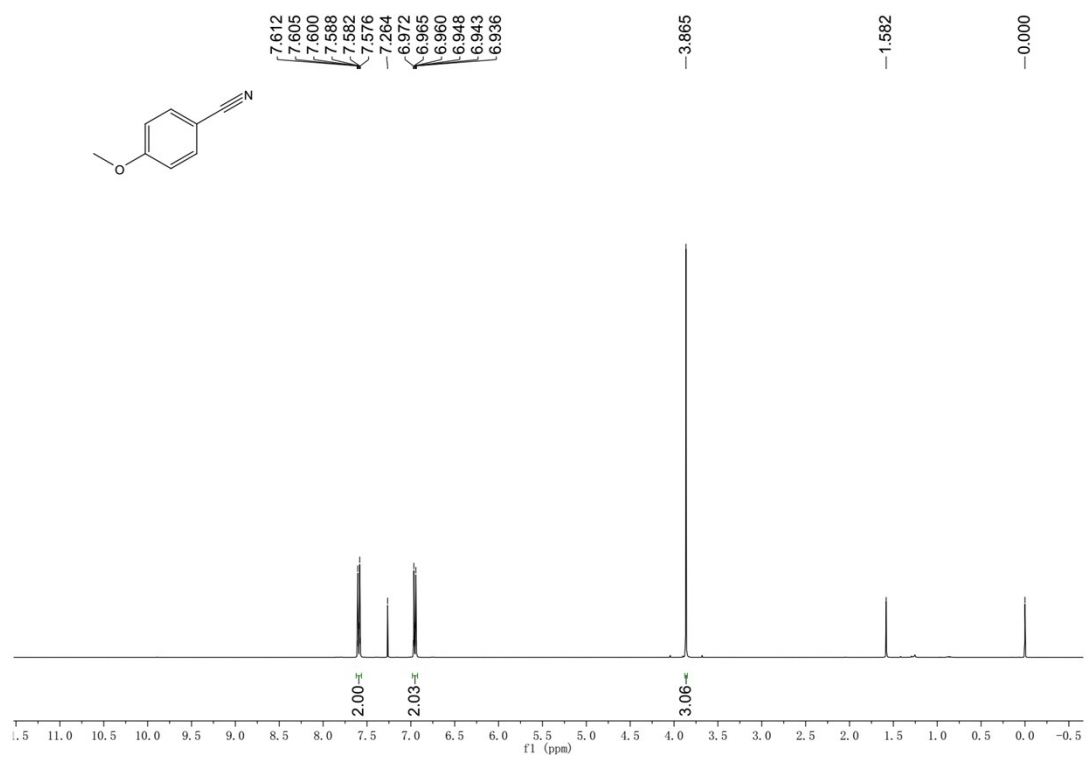
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2d

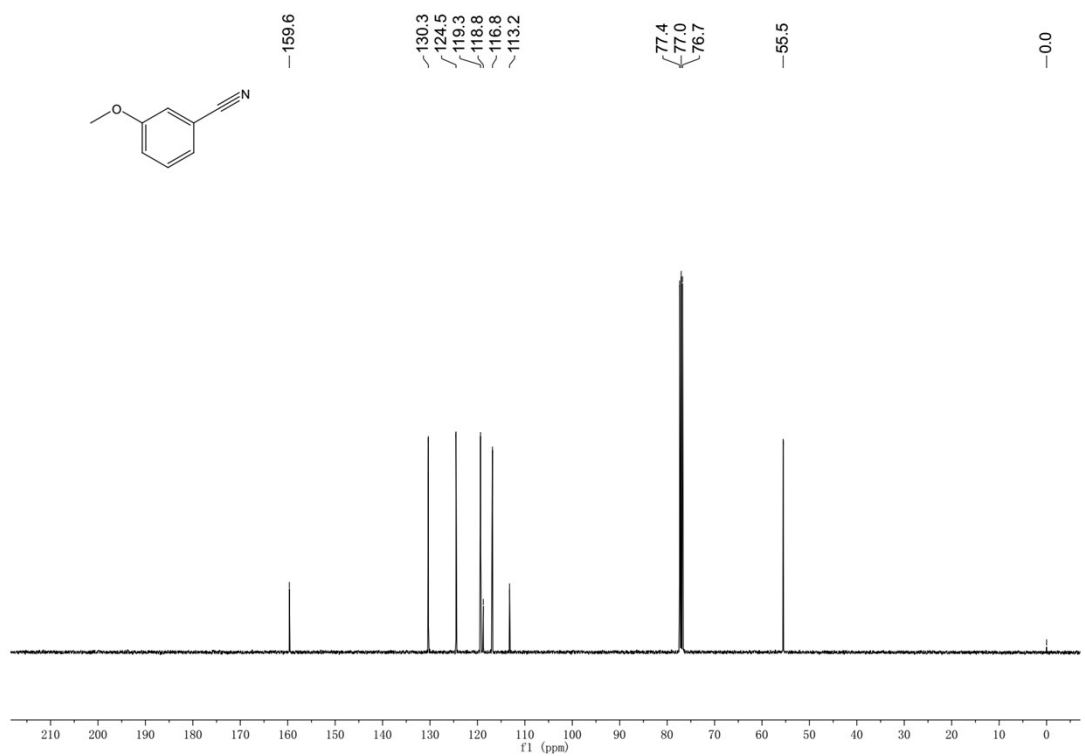
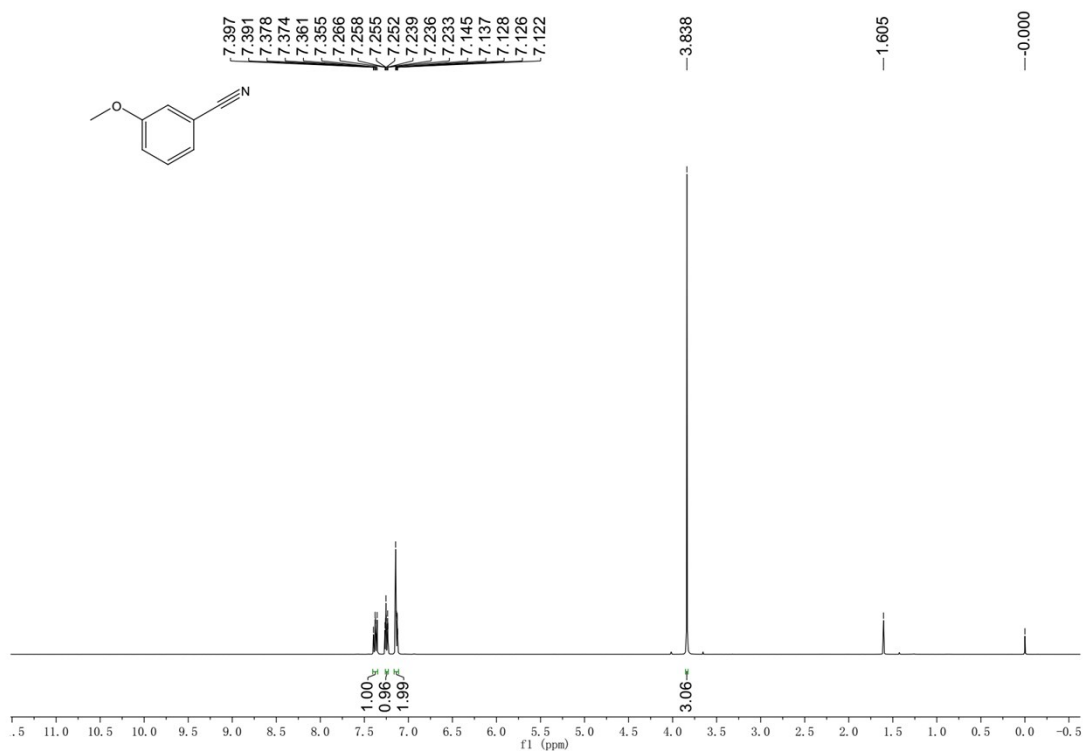


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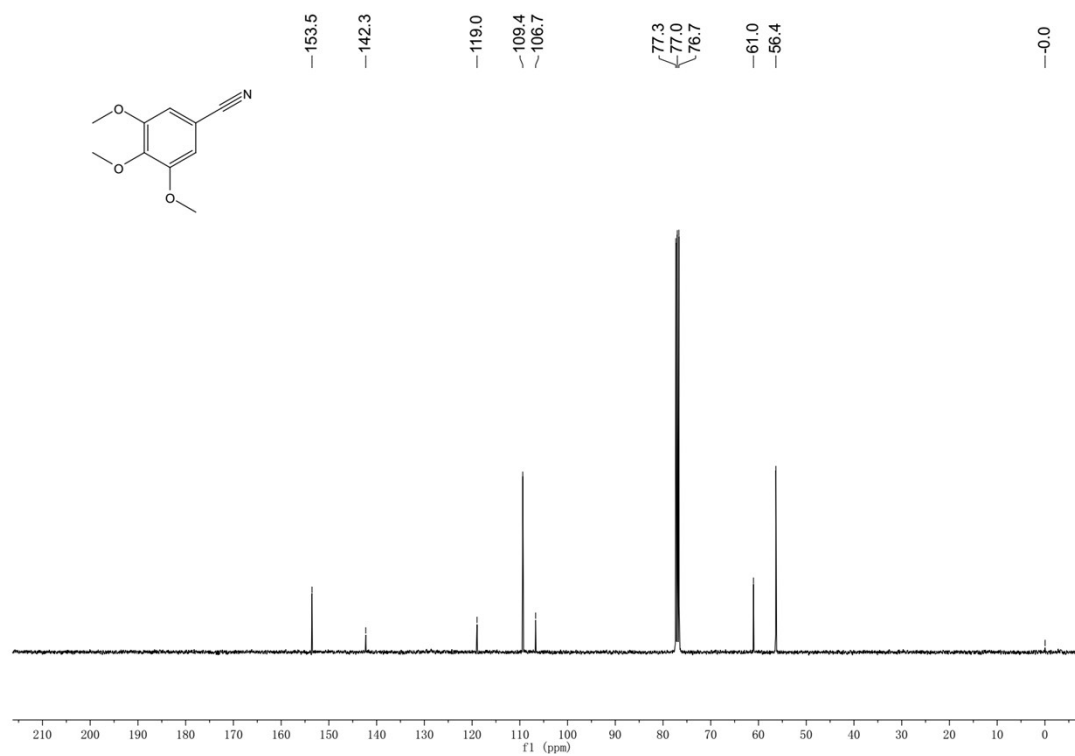
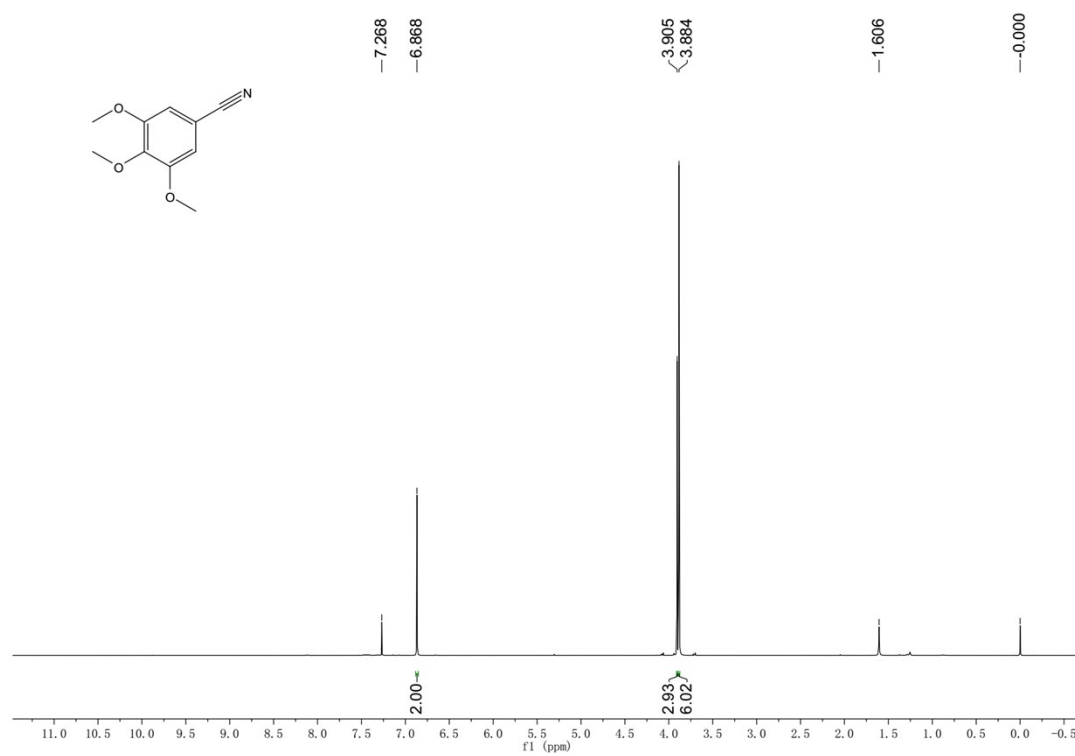




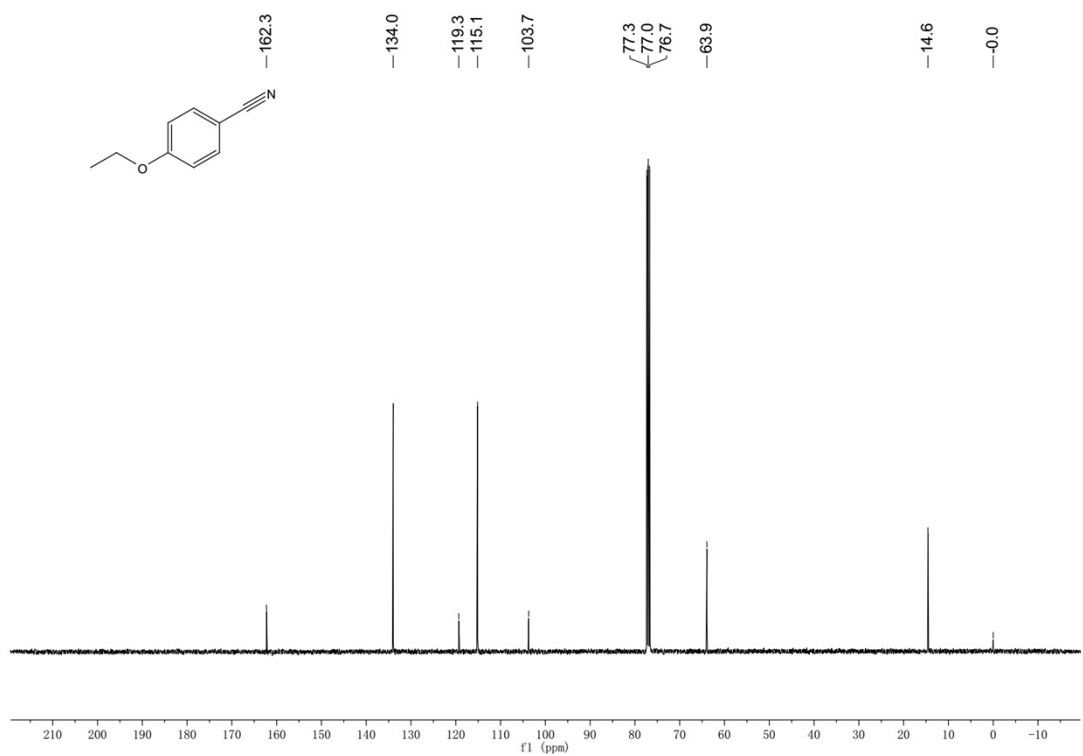
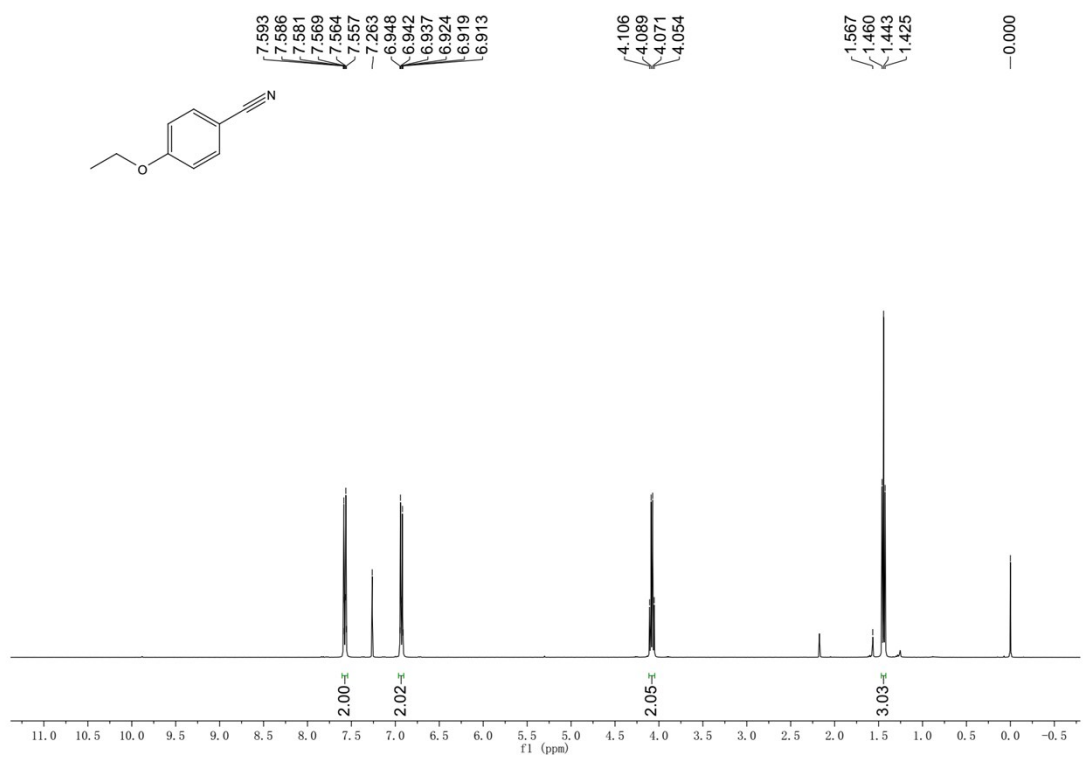
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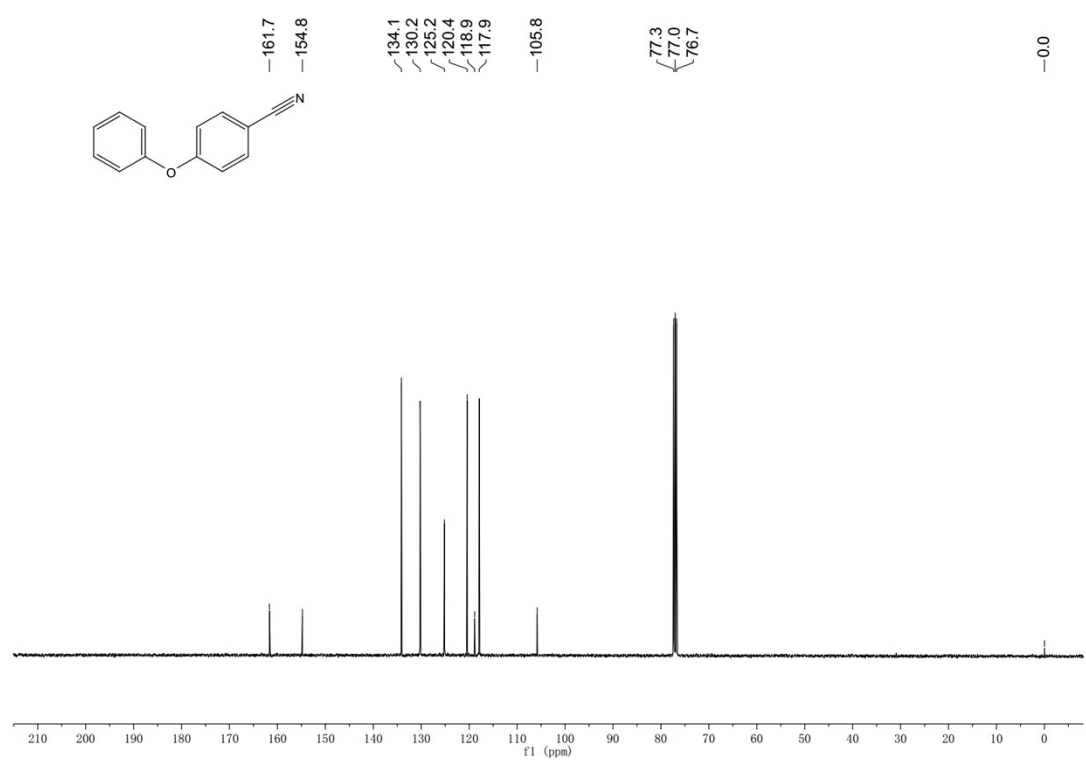
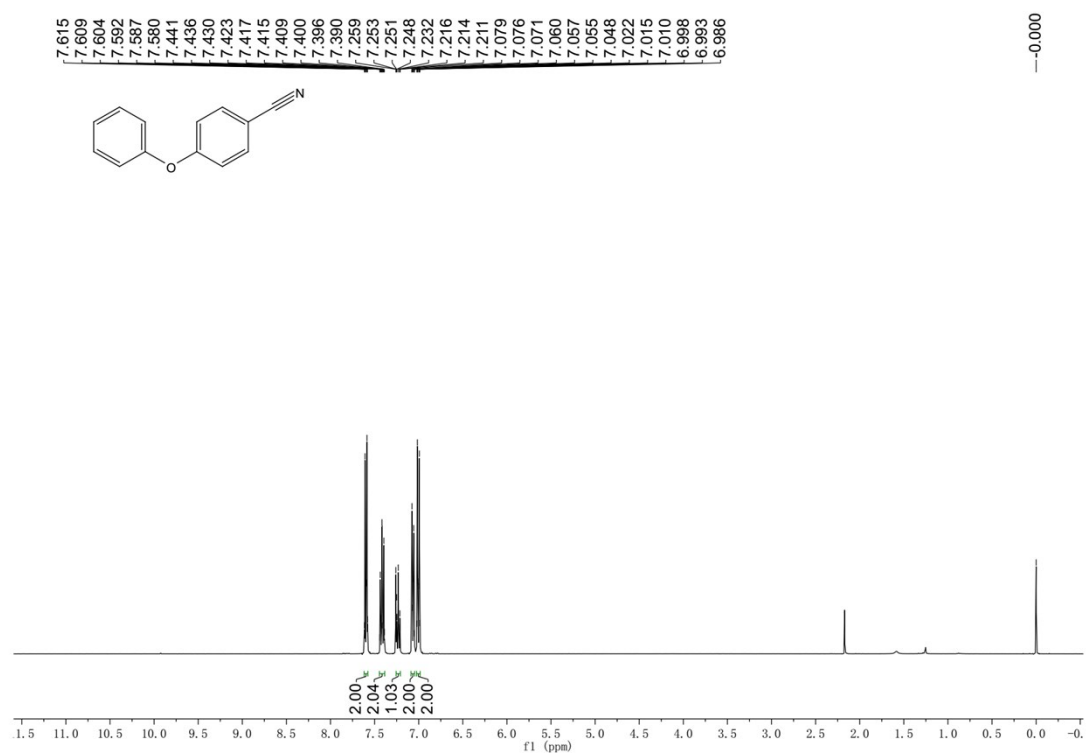
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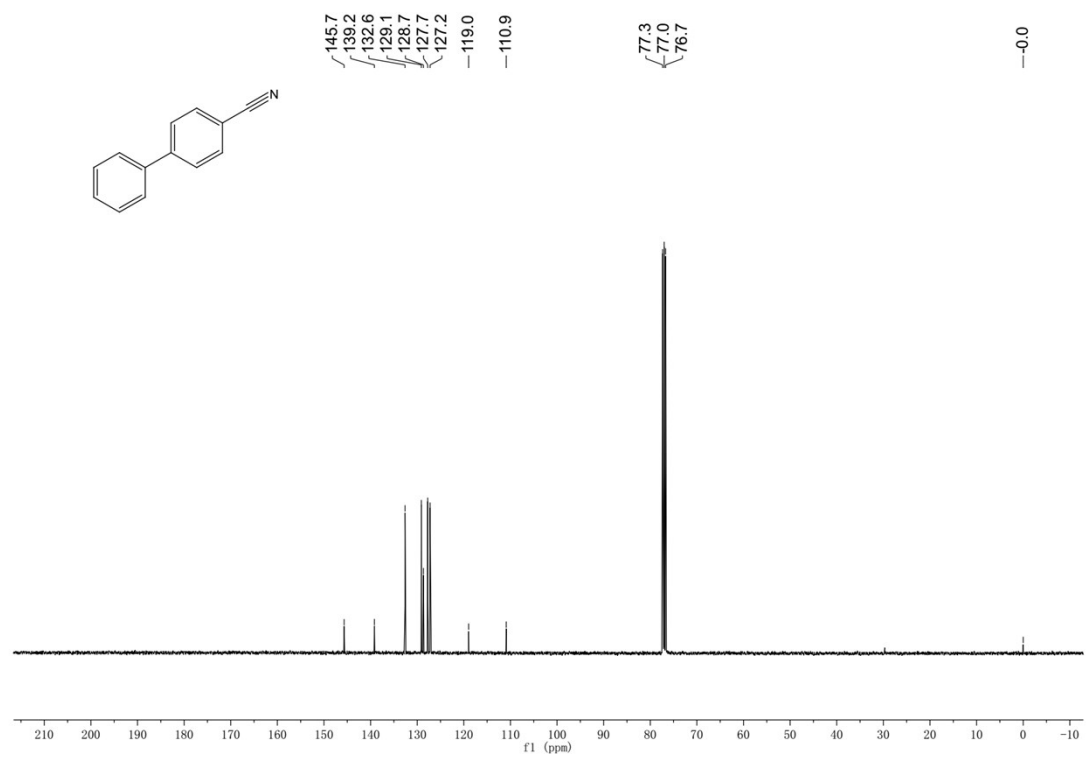
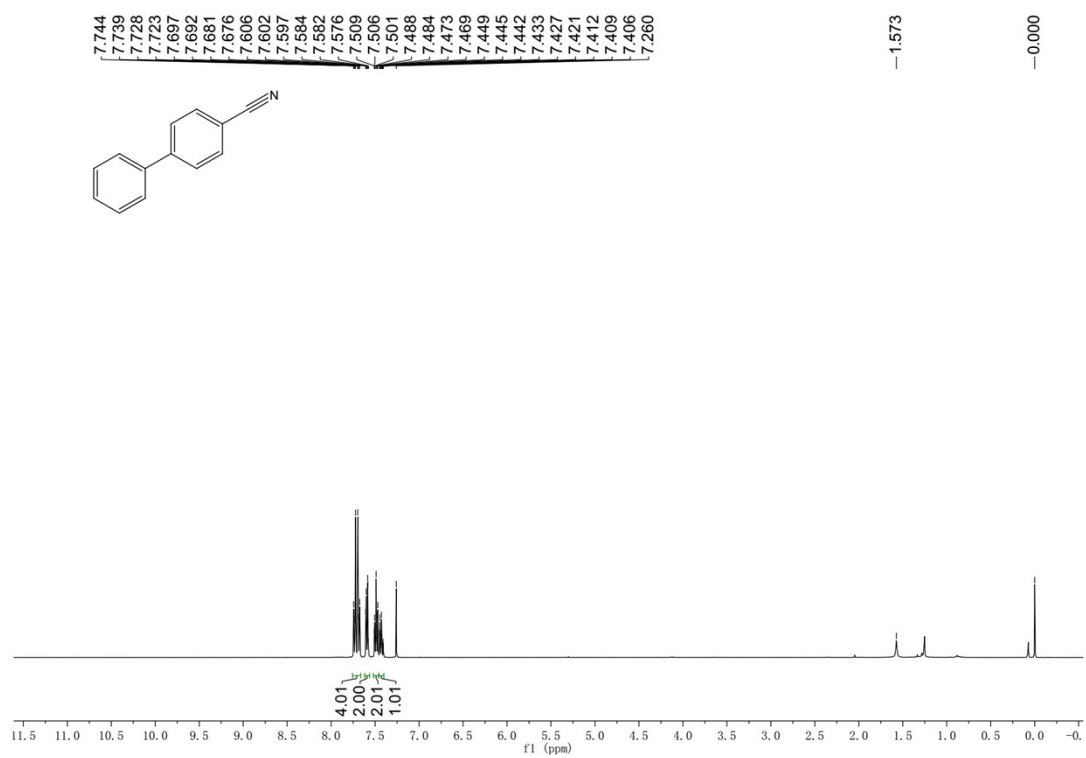
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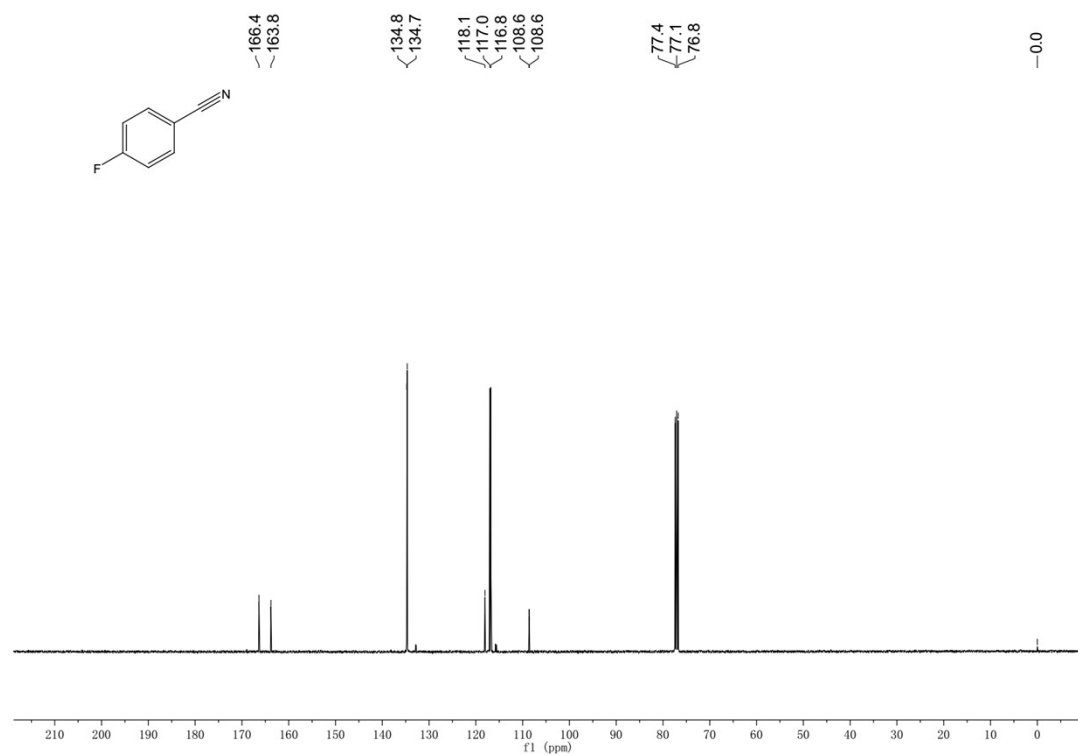
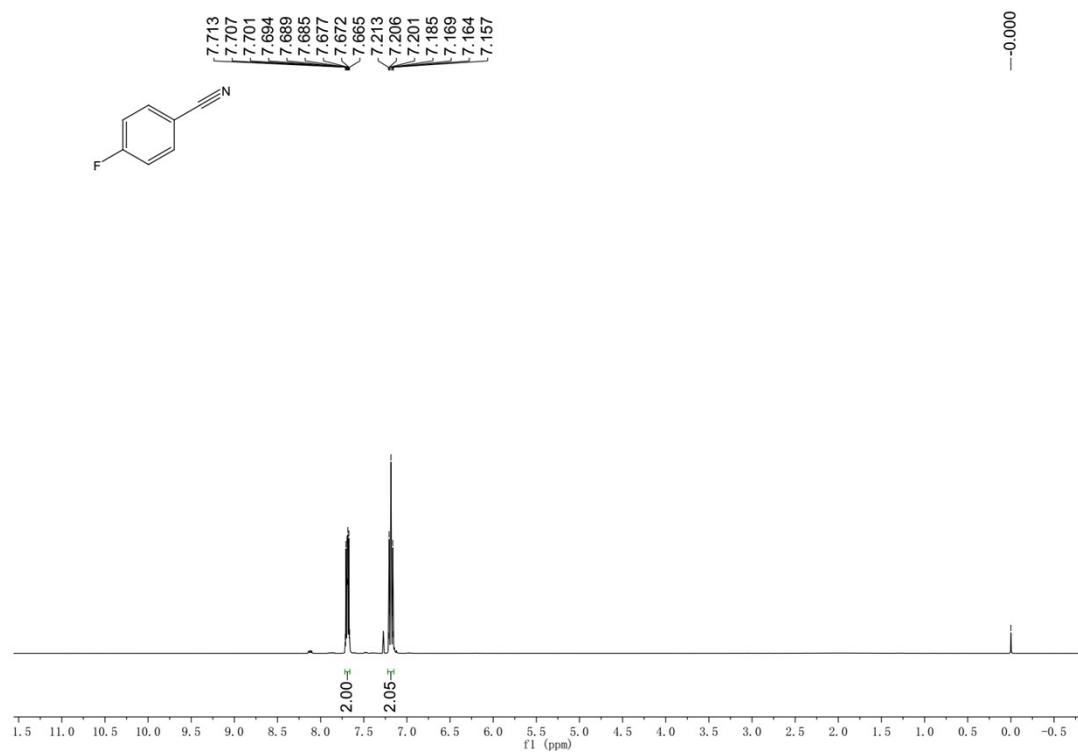
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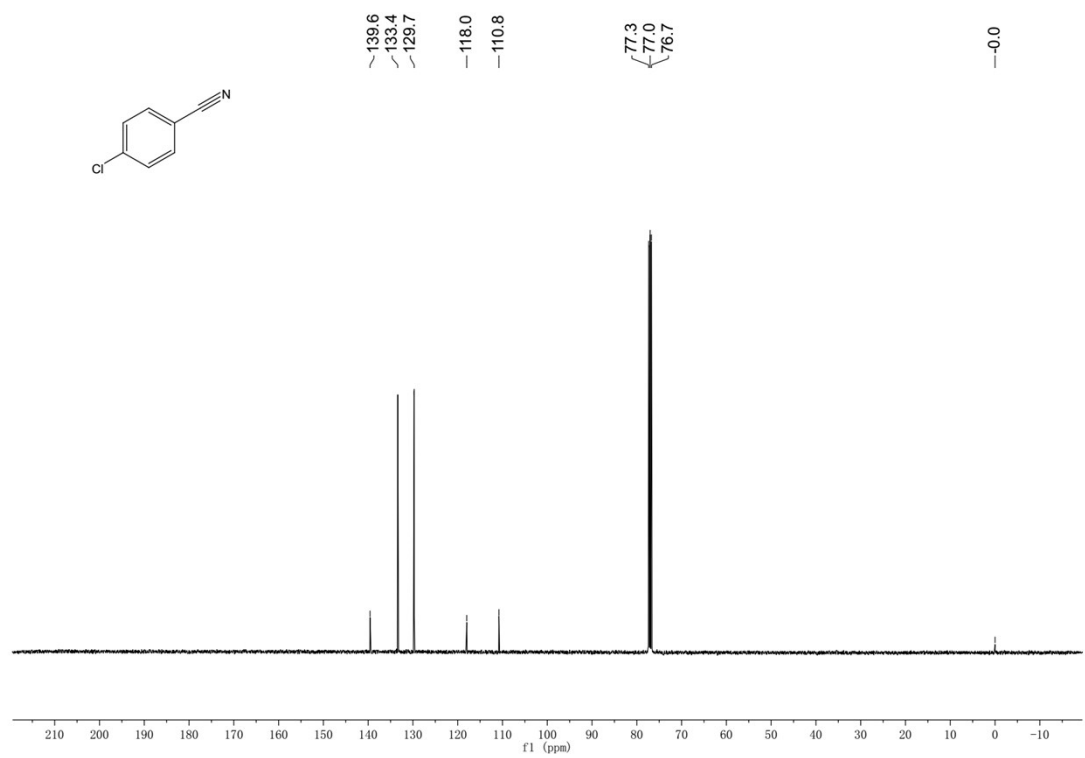
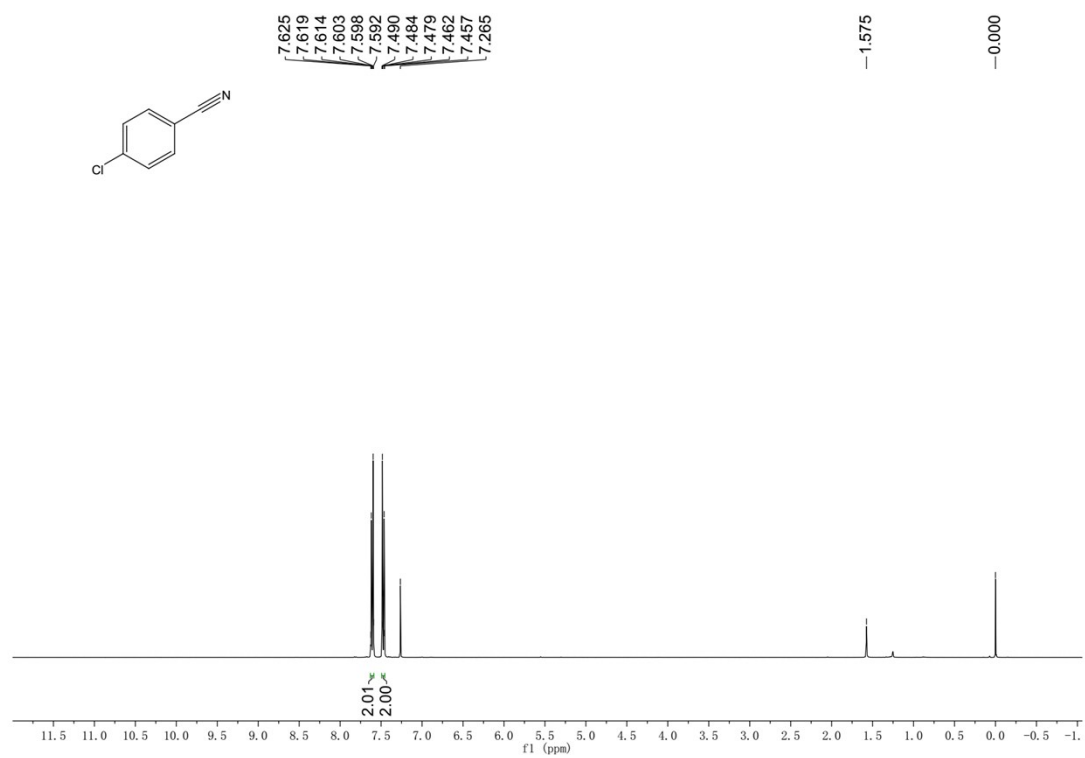
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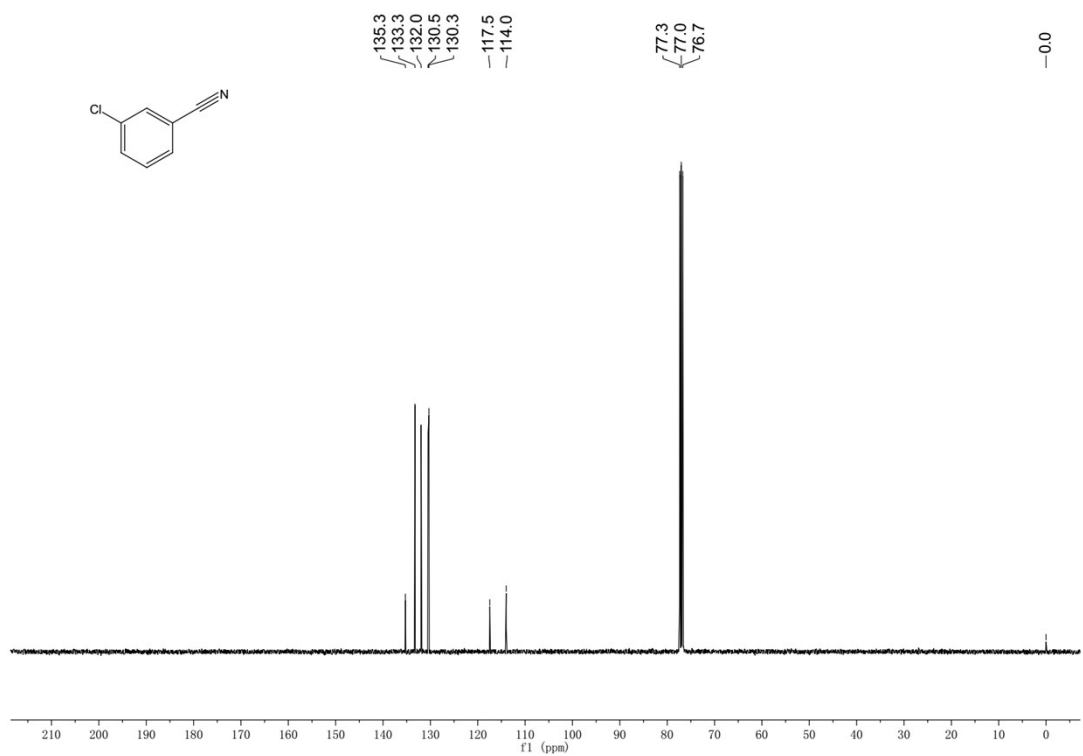
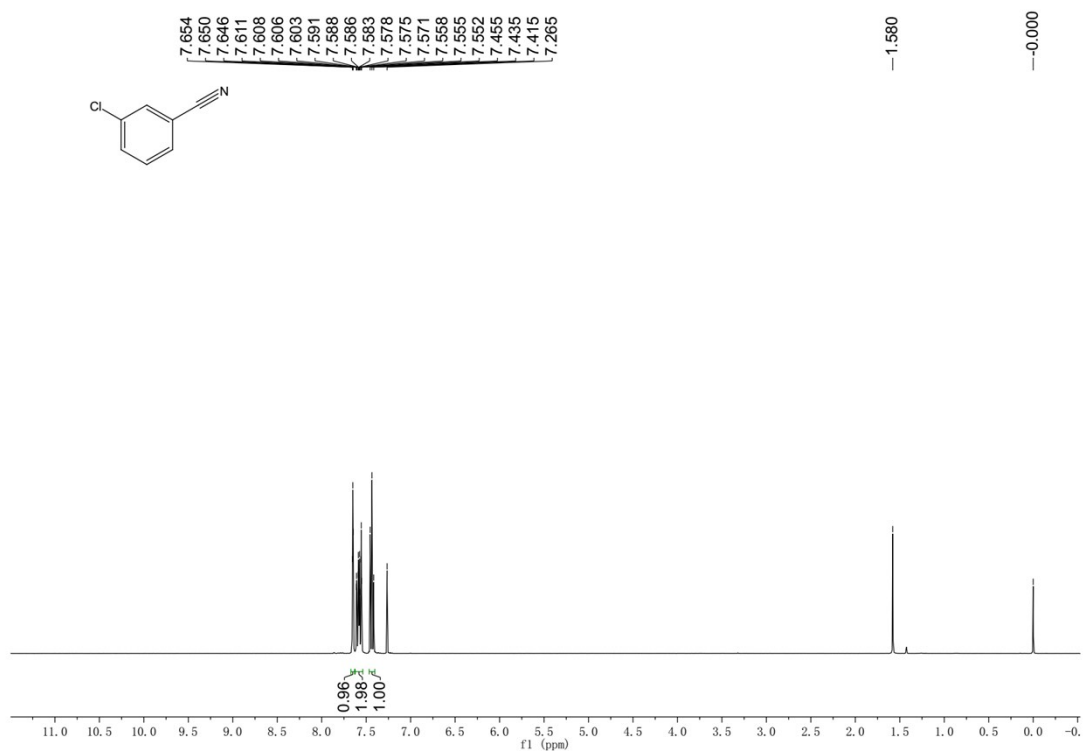
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21

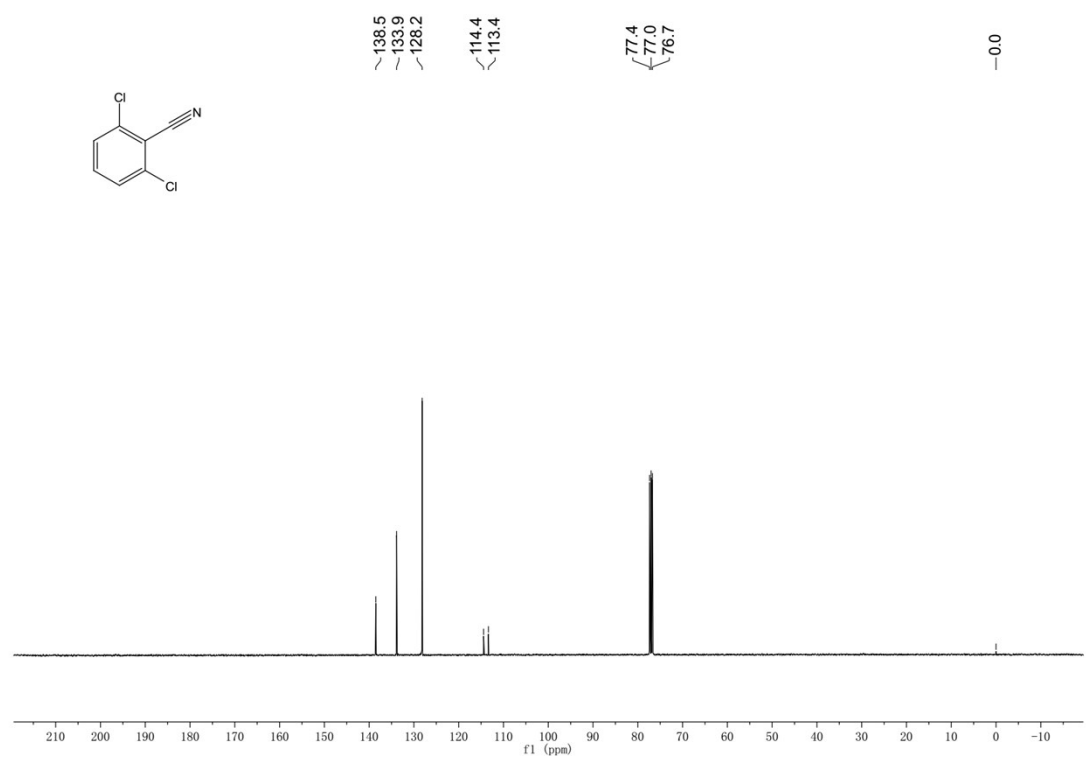
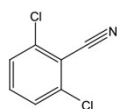
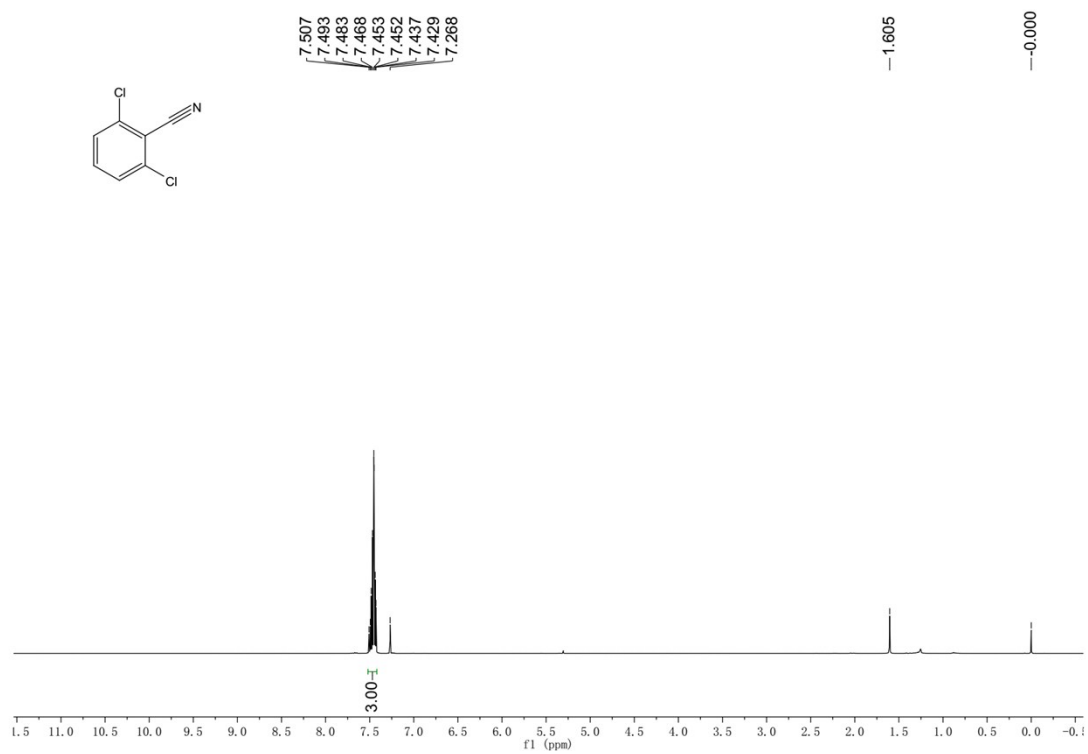
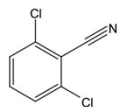


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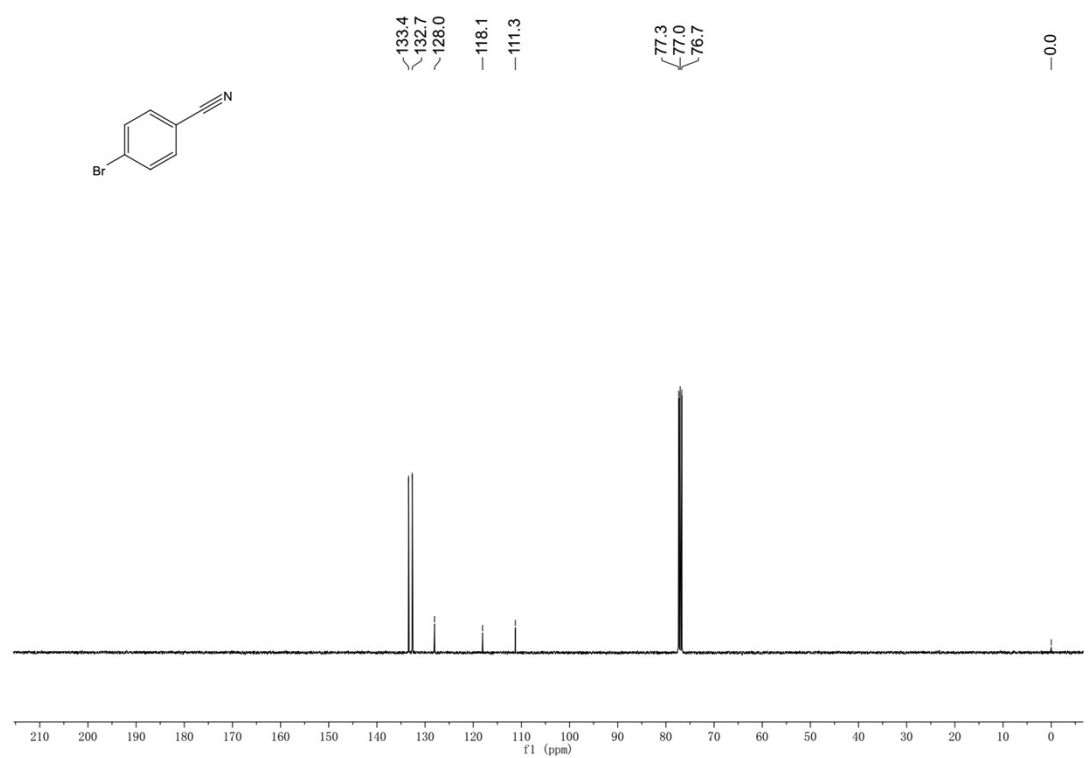
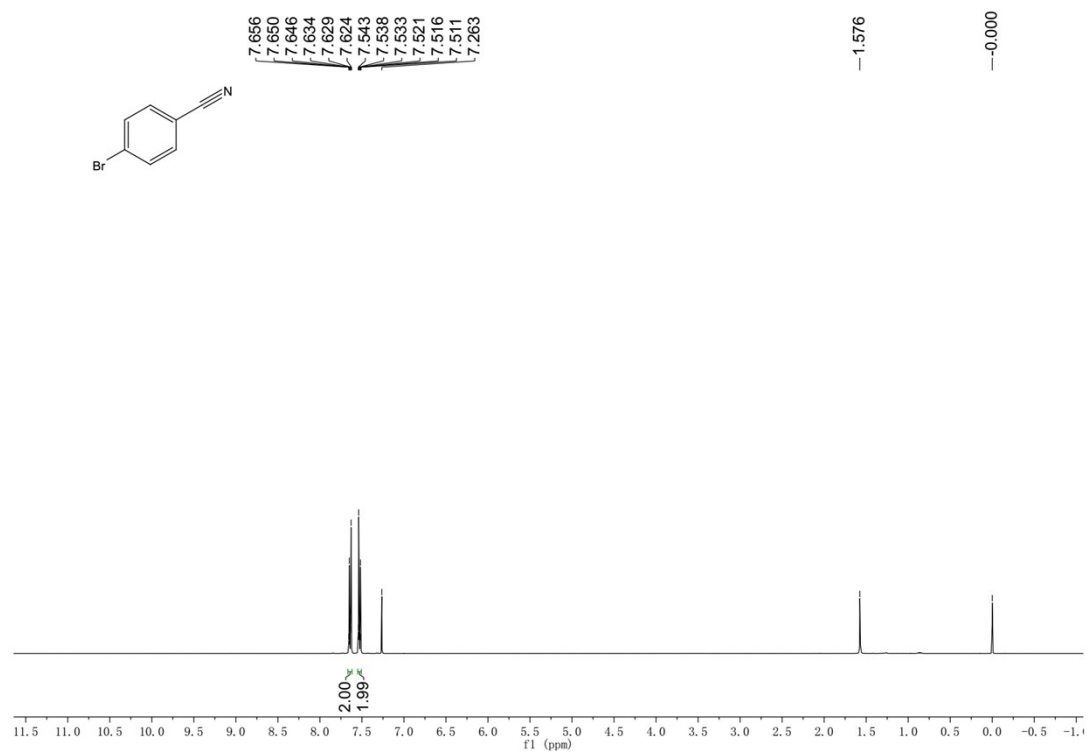




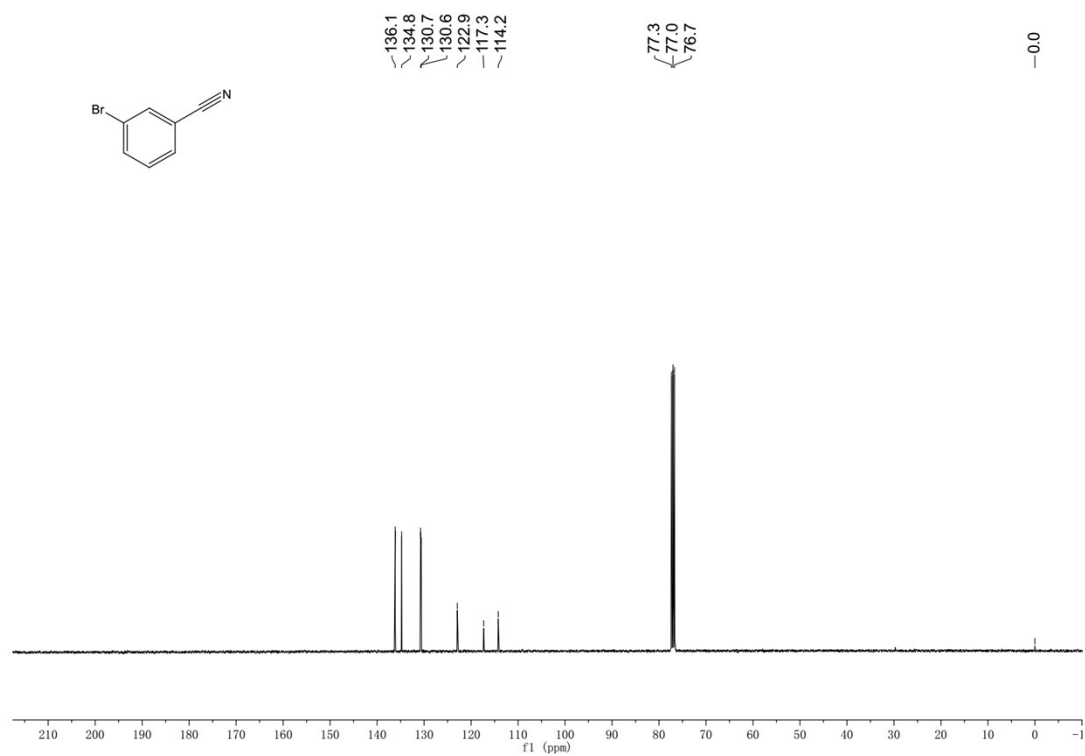
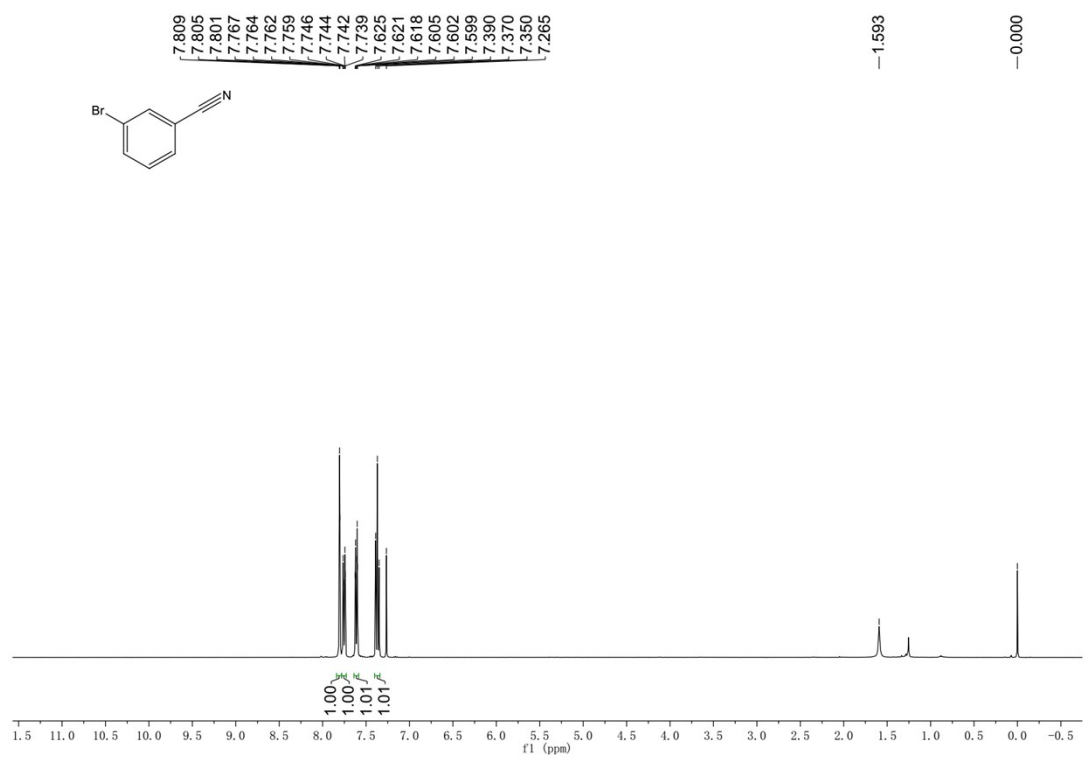
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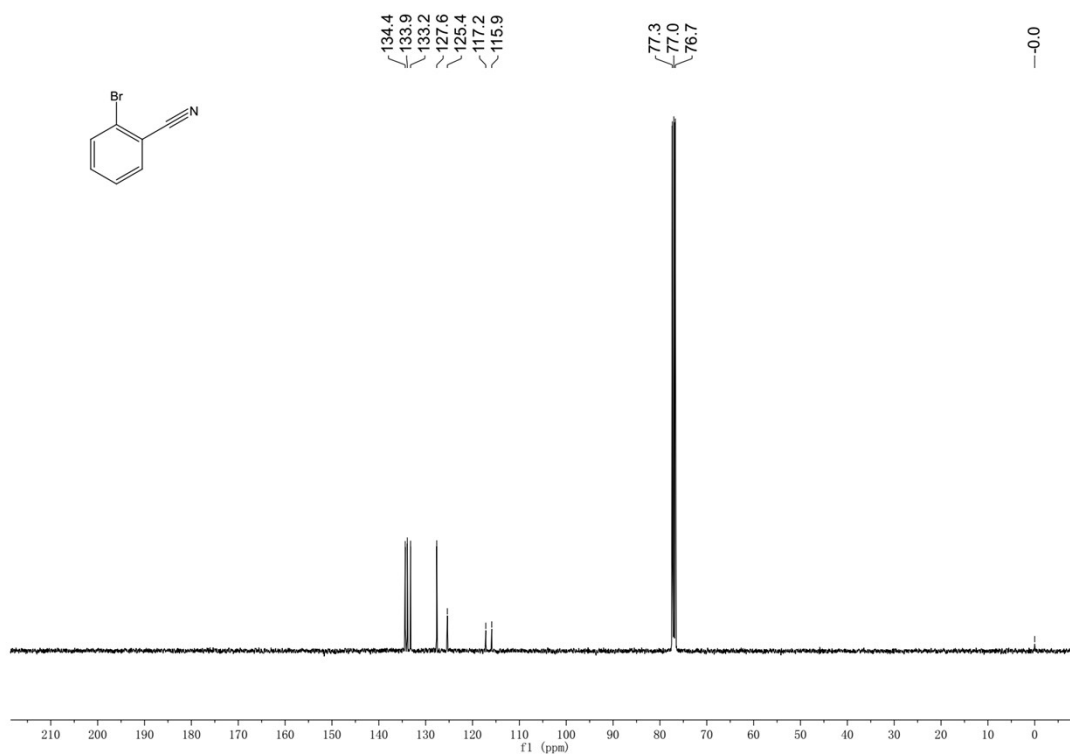
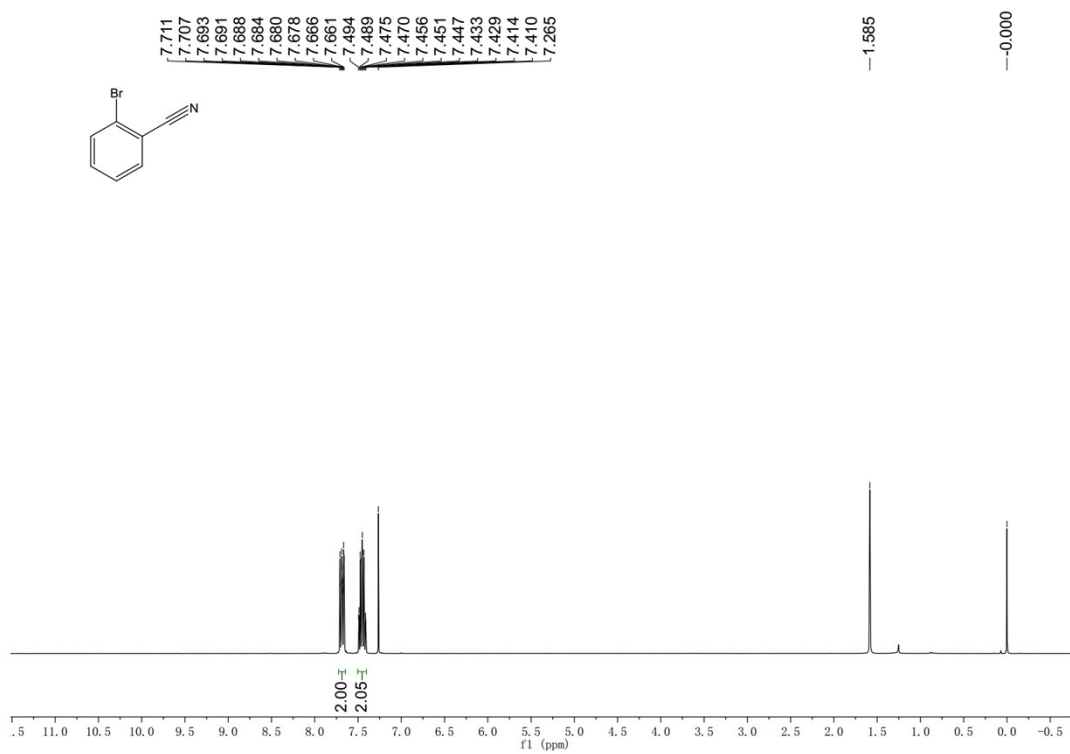
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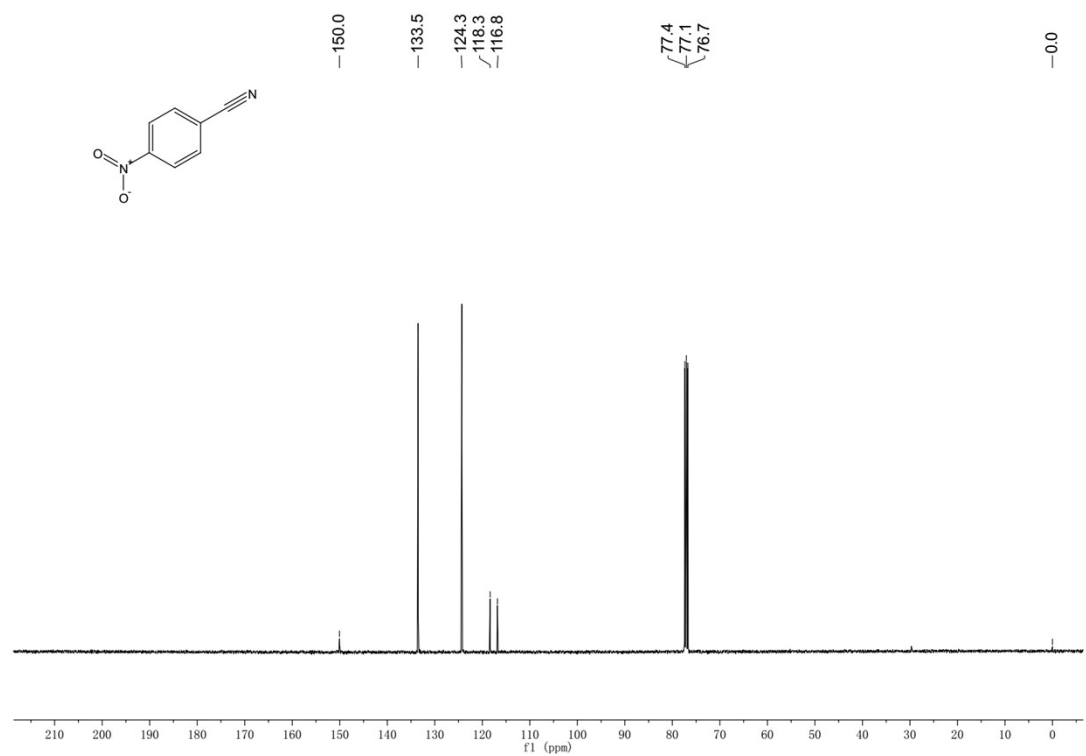
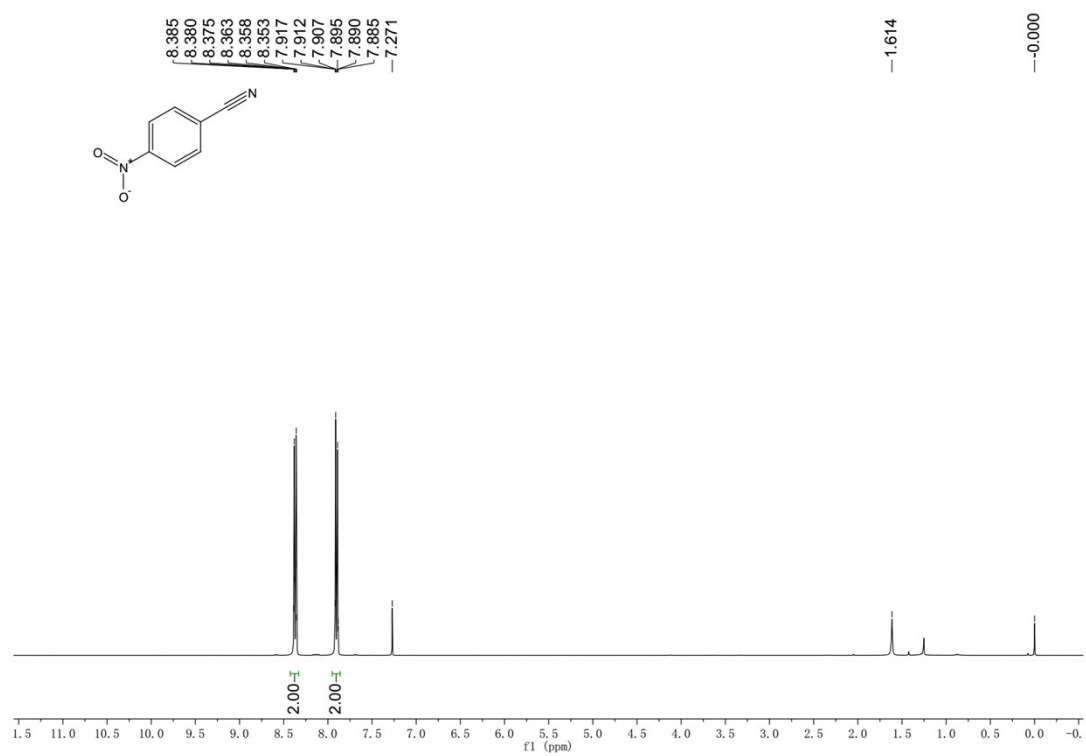
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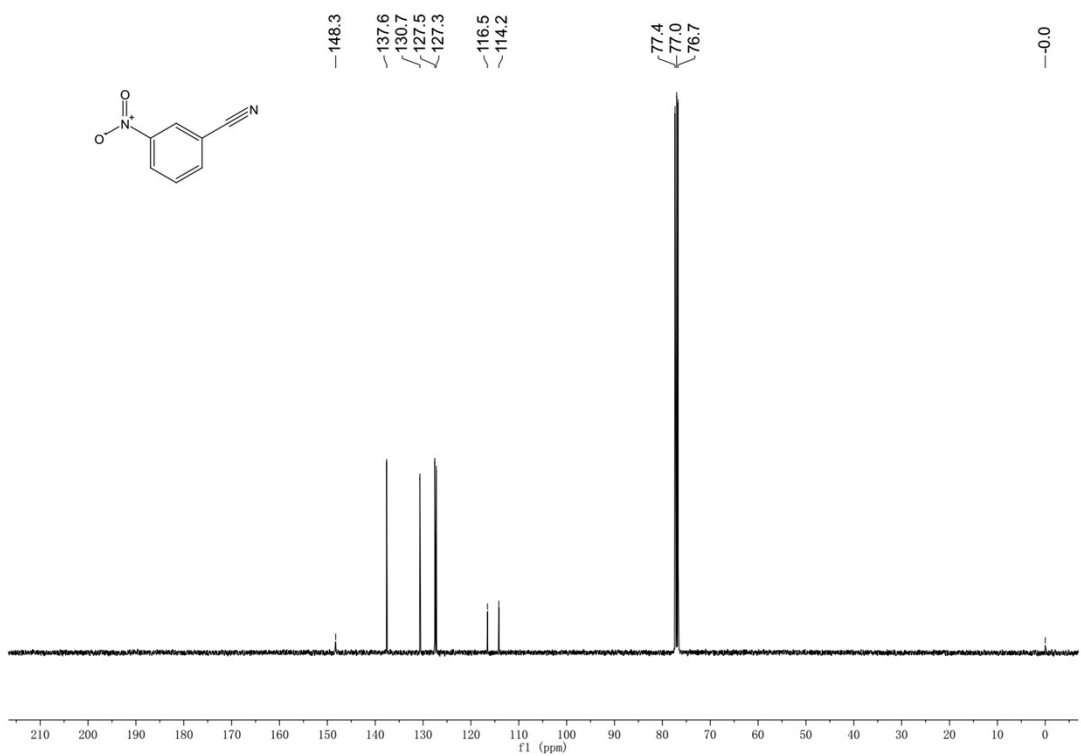
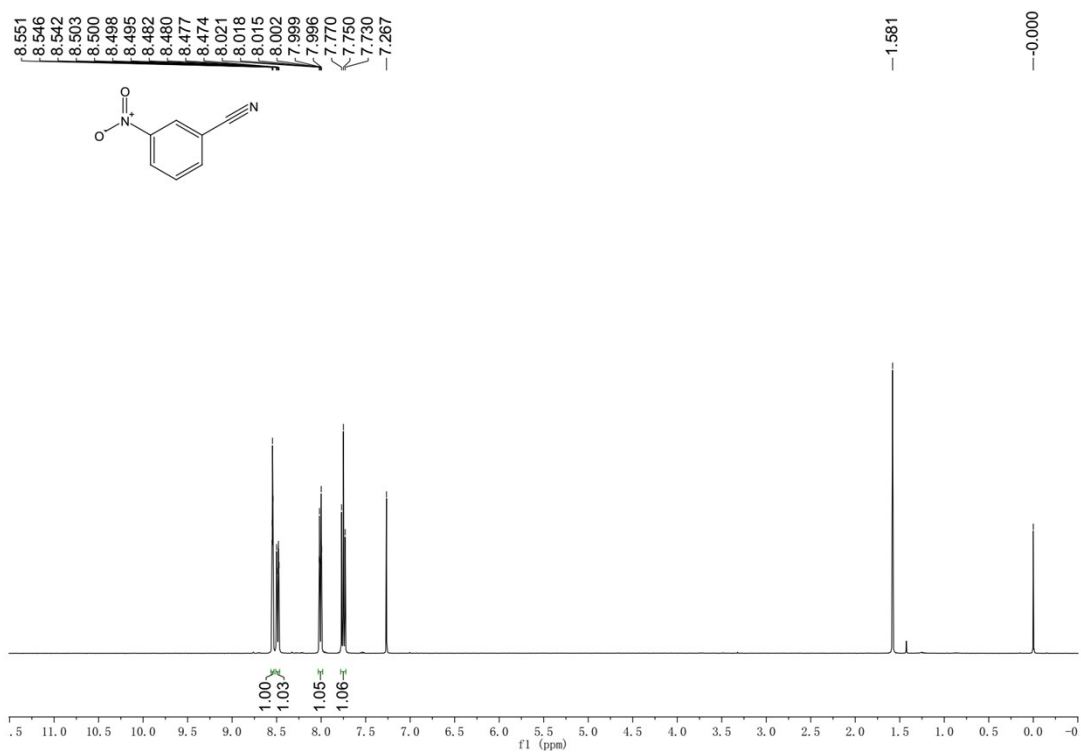
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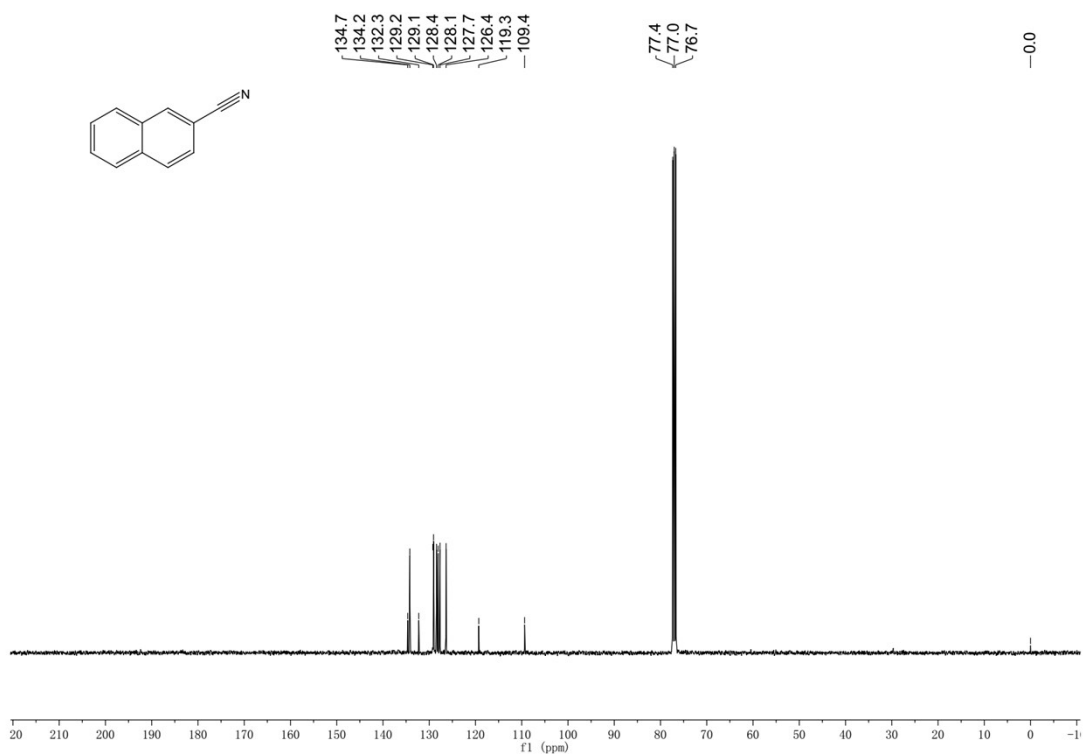
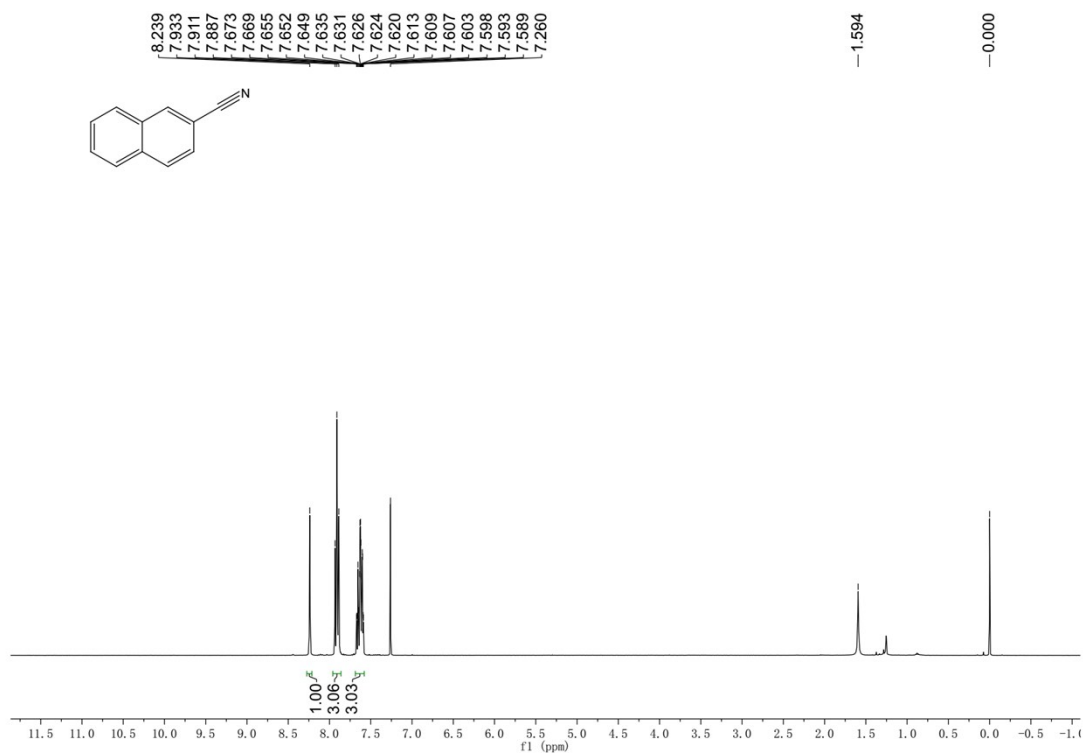
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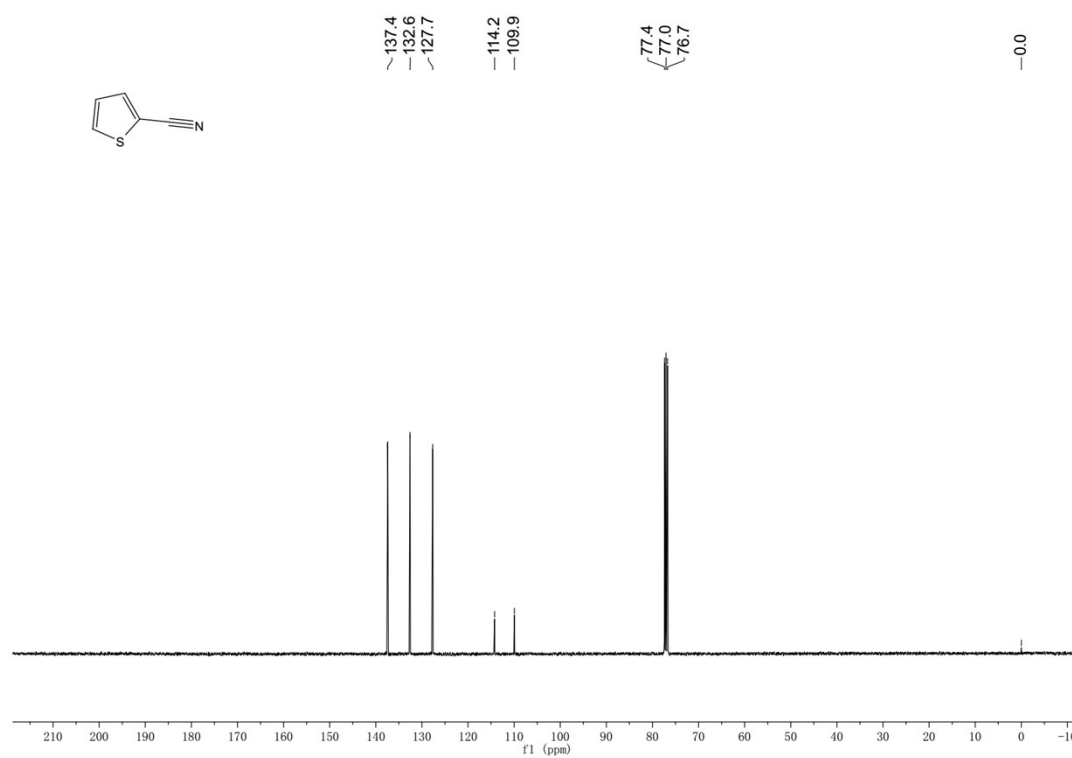
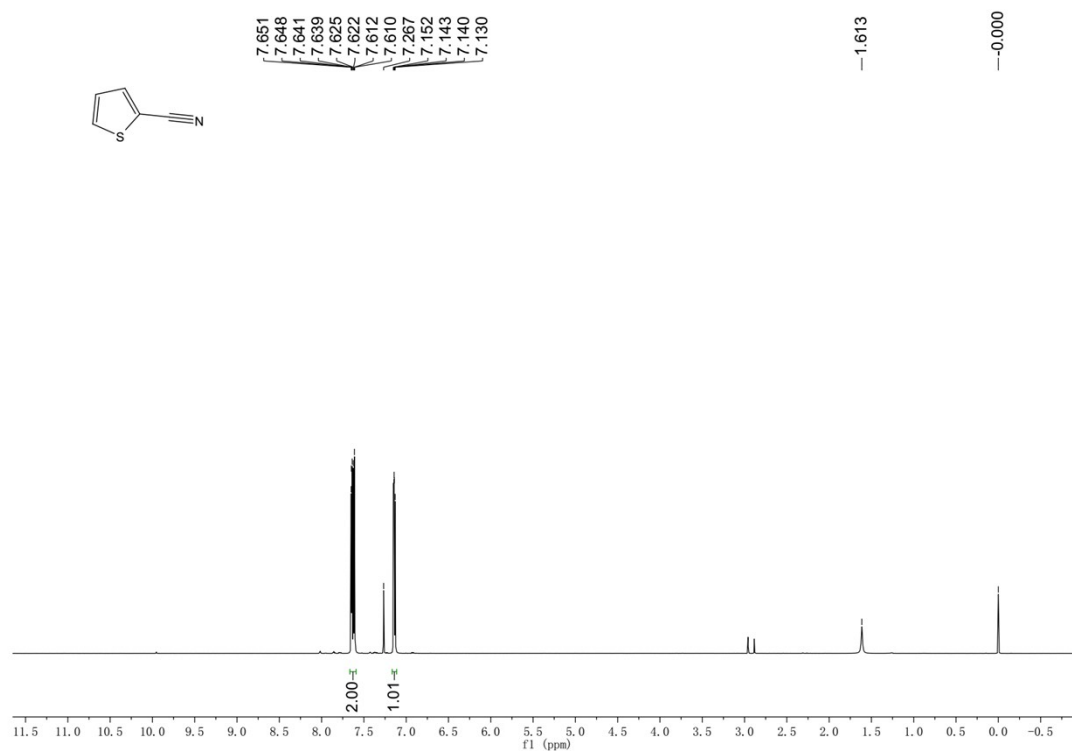
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2t

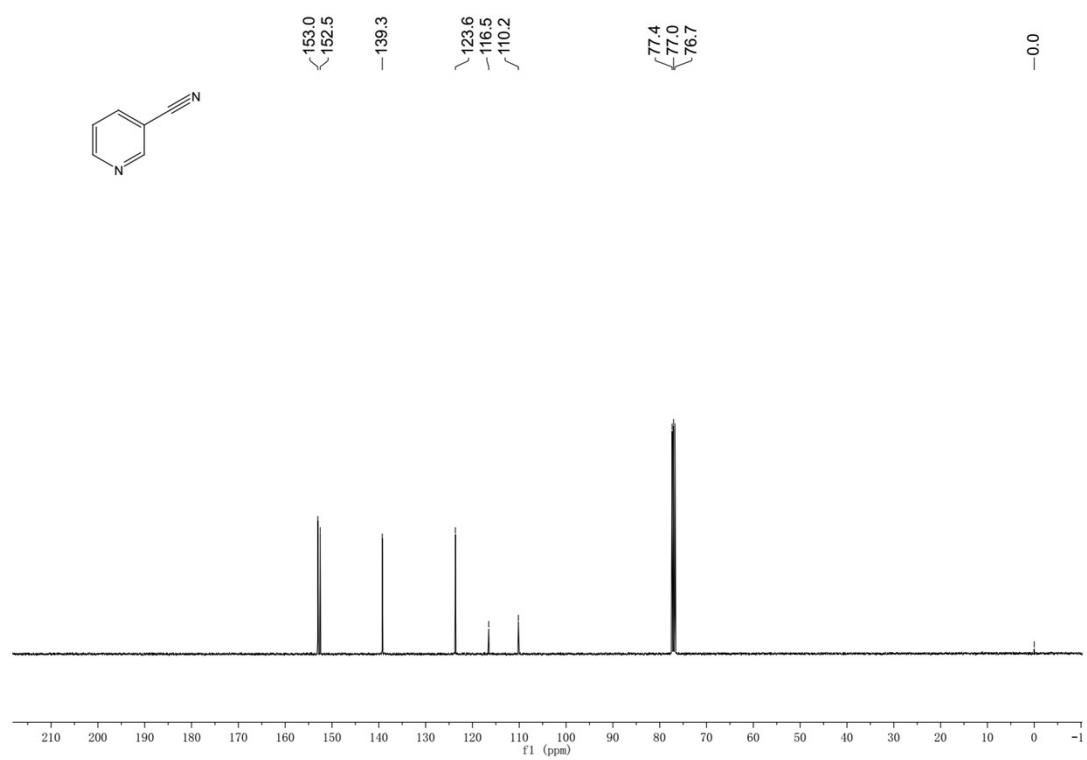
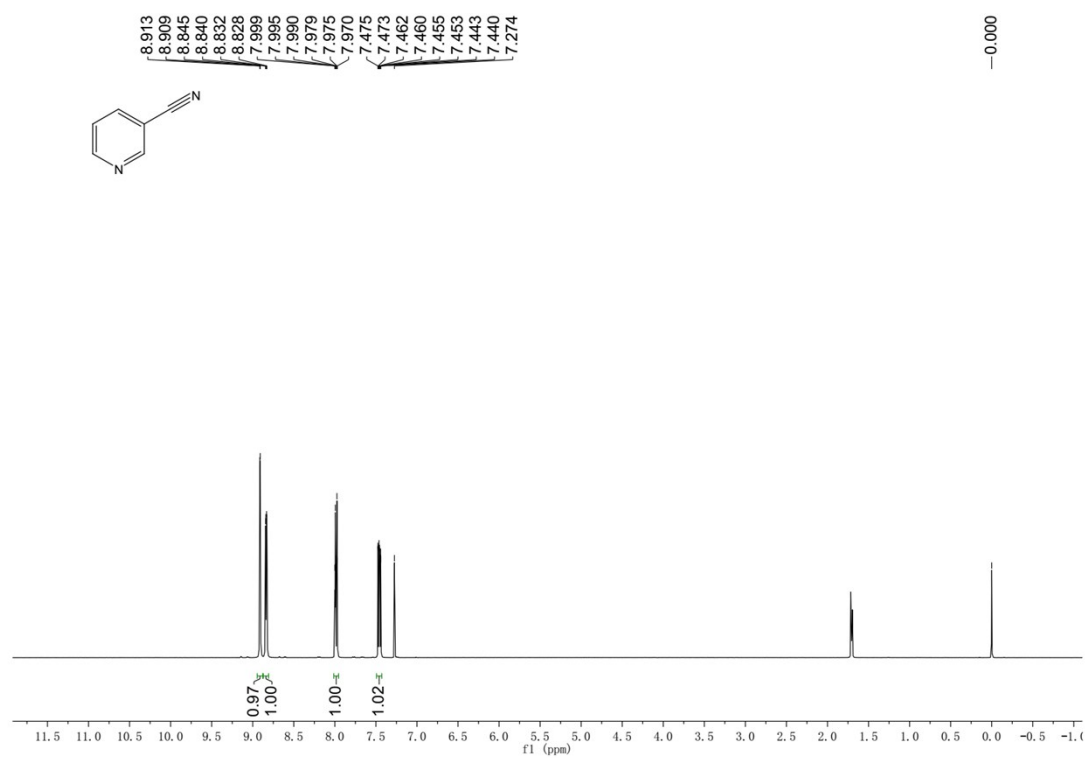


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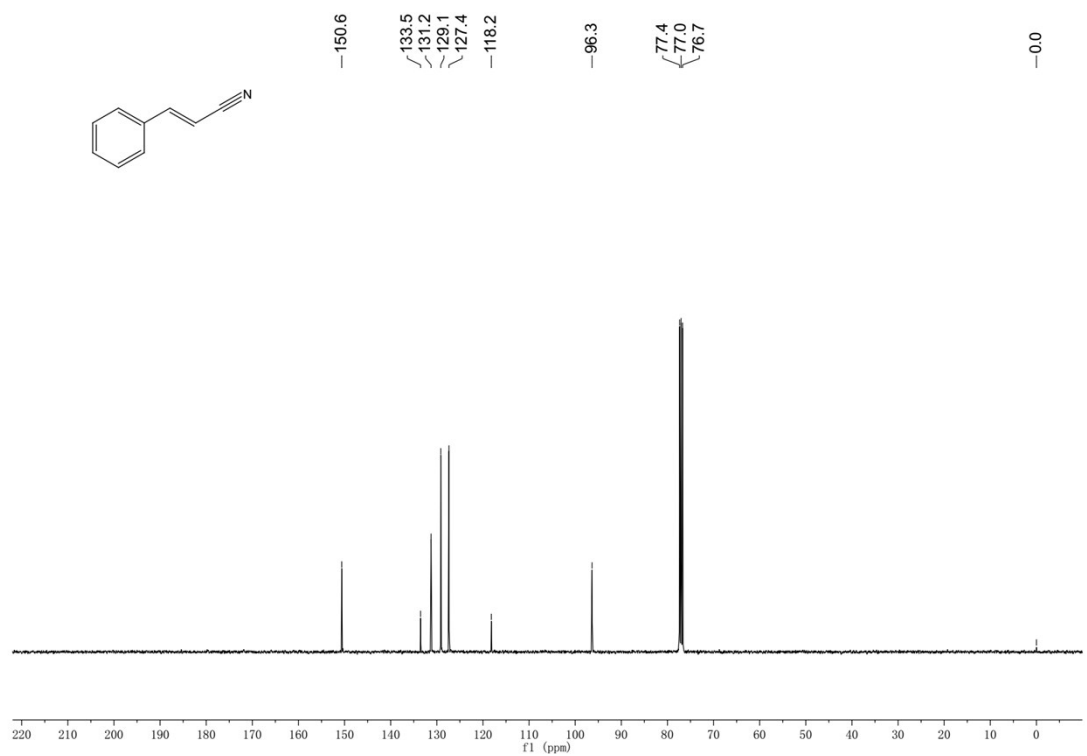
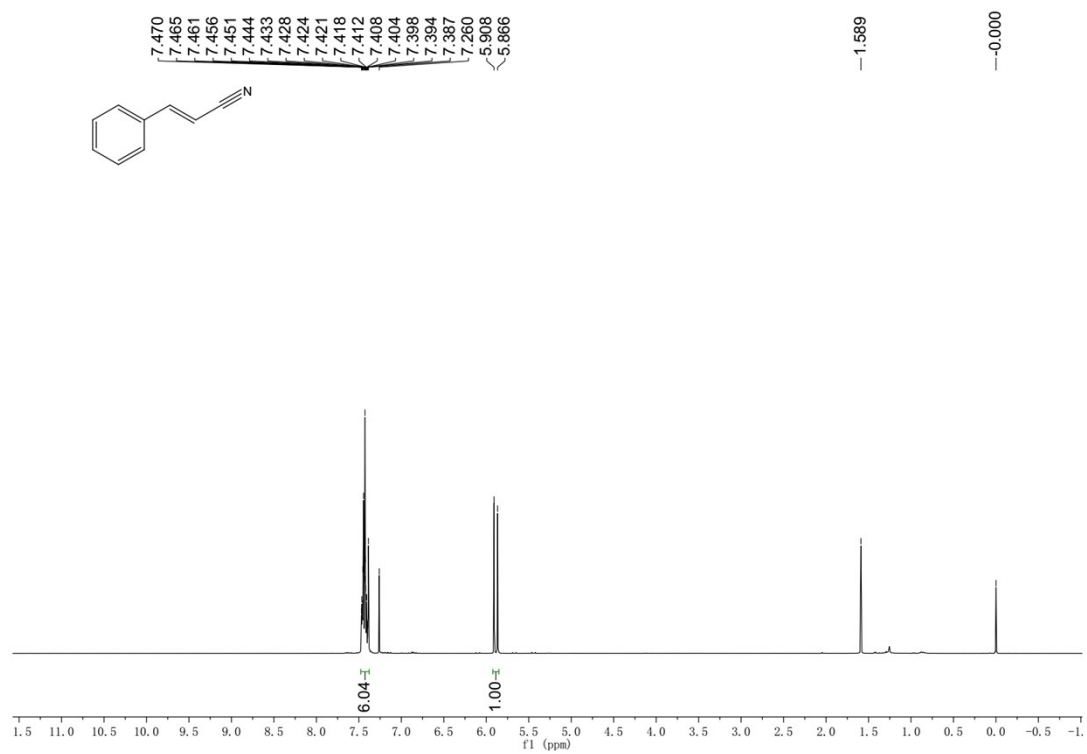




2v



2w



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