# Supporting Information

# Rhodium-catalyzed Directed C-H Cyanation of Arenes with *N*-Cyano-*N*-phenyl-*p*-toluenesulfonamide

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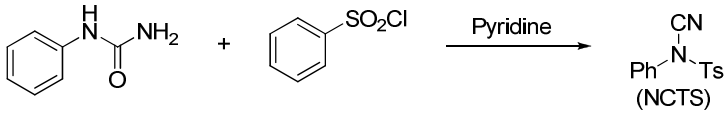
## I. General Remark:

All solvents were obtained from commercial suppliers and used without further purification. Aromatic ring were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted[1]. $[RhCp^*(CH_3CN)_3](SbF_6)_2$ was prepared according to the literature[2]. Analytical TLC was done on pre-coated silica gel plates. Column chromatography was conducted with 300-400 mesh silica gel. $^1H$ NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts of $^1H$ NMR spectra were reported in parts per million relative to tetramethylsilane ($\delta$ = 0). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). $^{13}C$ NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane ($\delta$ = 0). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

## II. General Procedure for the Preparation of Starting Materials

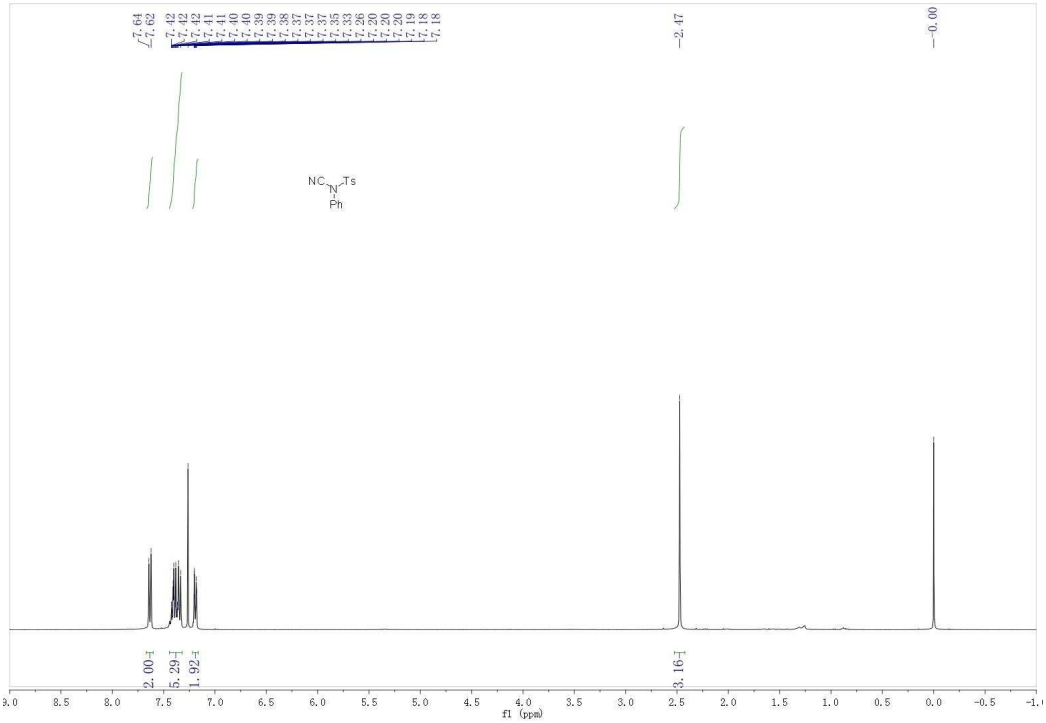
### A. Synthesis of *N*-cyano-*N* -phenyl-*p*-methylbenzenesulfonamide (NCTS)[3]:

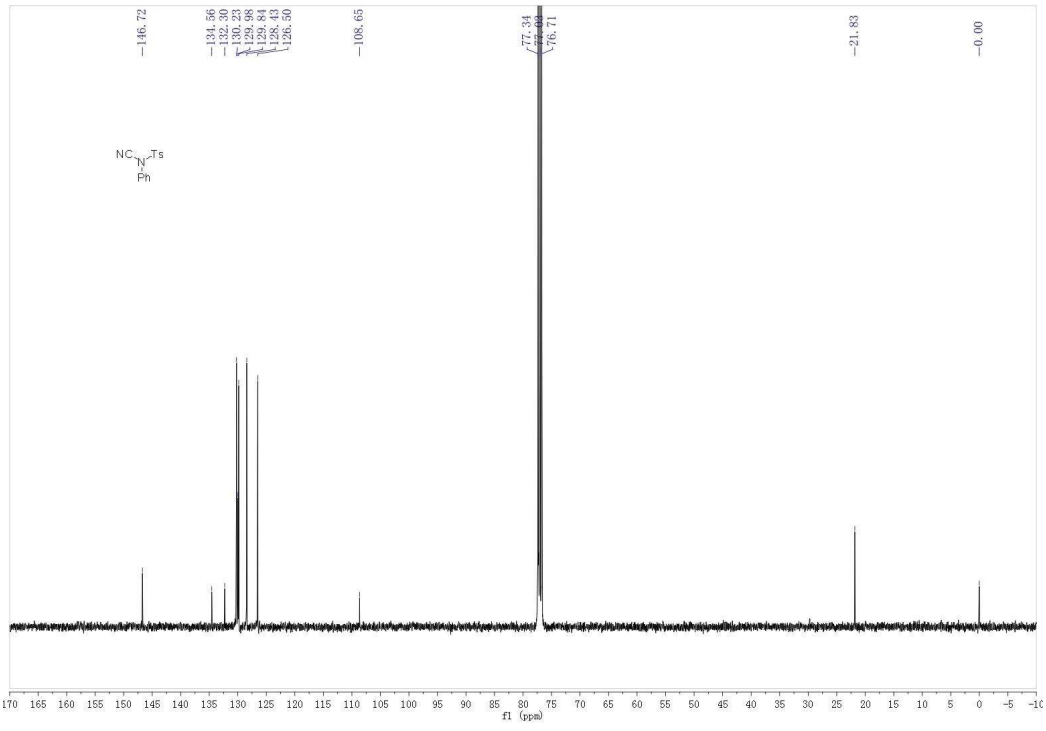



Dry 500 mL Schlenk flask was charged with phenylurea (20.41g, 150mmol) and dissolved by addition of pyridine (100 mL). *p*-Toluenesulfonyl chloride (71.25g, 375 mmol) was added over 3 min at room temperature. The reaction mixture was stirred for additional 20 min and poured into to ice-cooled water (1000 mL) with Vigorous stirring. Precipitate formed during stirring was filtered and washed with water. Precipitated product was further purified by column chromatography using Petroleum ether: ethyl acetate (10:1) as eluent to yield *N*-cyano-*N*-phenyl-4-methylbenzenesulfonamide(NCTS) as colorless solid (41 g, 71%).

$^1H$ NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4, 2H), 7.46 – 7.32 (m, 5H), 7.21 – 7.17 (m, 2H), 2.47 (s, 3H).

$^{13}C$ NMR (101 MHz, $CDCl_3$) δ 146.72, 134.56, 132.30, 130.23, 129.98, 129.84, 128.43, 126.50, 108.65, 21.83. Spectral data matched those previously reported.

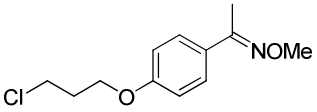



## B. General procedure for the preparation of O-methyl oximes[4].

The parent ketone (1.0 equiv.) was dissolved in EtOH (0.50 – 0.80 M) and methoxylammonium chloride (1.5-5 equiv.) was added. The reaction mixture was stirred at room temperature for 10 min and then sodium hydrogencarbonate was gradully added until the medium became neutral.

Stirring was continued for further 4h and $CH_2Cl_2$ was added to the reaction flask, followed by the same volume of distilled water. After being vigorously shaken, the organic layer was separated and washed with a dilute aqueous solution of sodium hydroxide, and with distilled water until neutral. The dried solution was filtered and the solvent evaporated. The crude product was purified in a chromatographic column using hexane–acetone (50 : 1-2 : 1) as eluent.

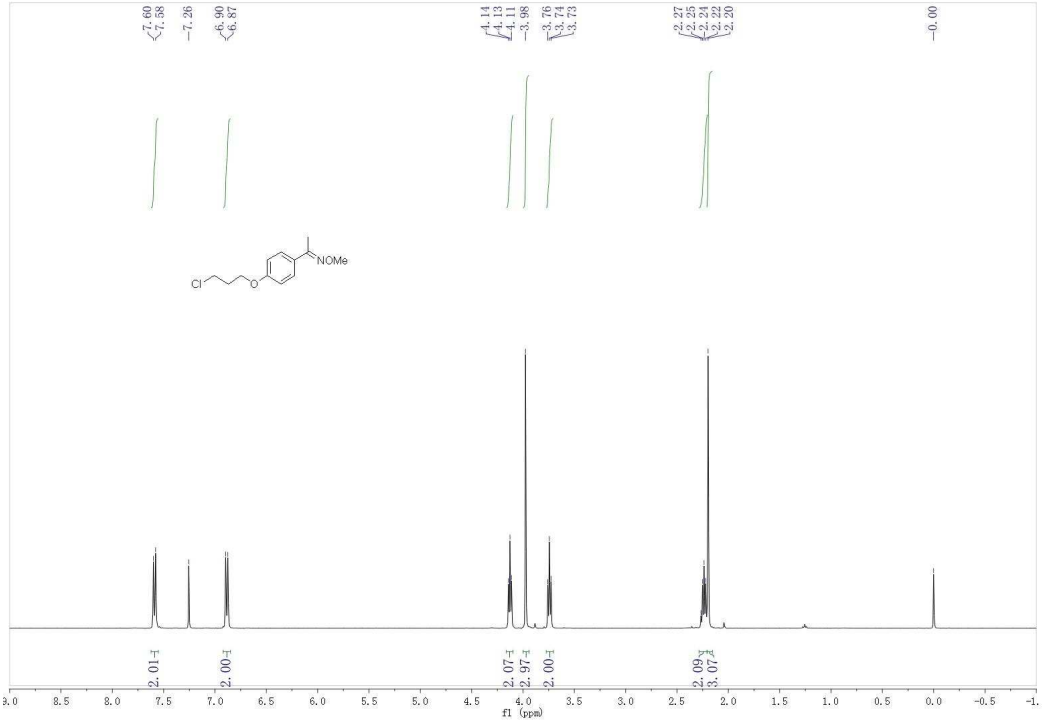


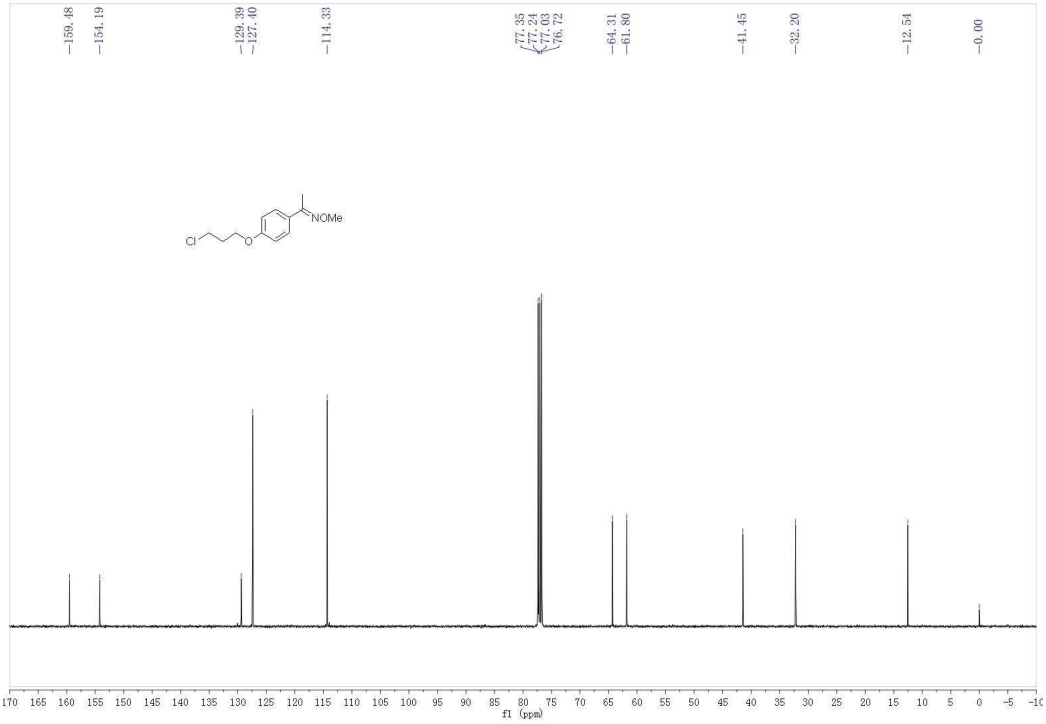

**1-(4-(3-chloropropoxy)phenyl)ethanone O-methyl oxime**

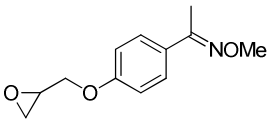
White solid.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6, 2H), 6.89 (d, *J* = 8.6, 2H), 4.13 (t, *J* = 5.8, 2H), 3.98 (s, 2H), 3.74 (t, *J* = 6.3, 2H), 2.24 (dd, *J* = 12.2, 6.1, 1H), 2.20 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.48, 154.19, 129.39, 127.40, 114.33, 64.31, 61.80, 41.45, 32.20, 12.54.





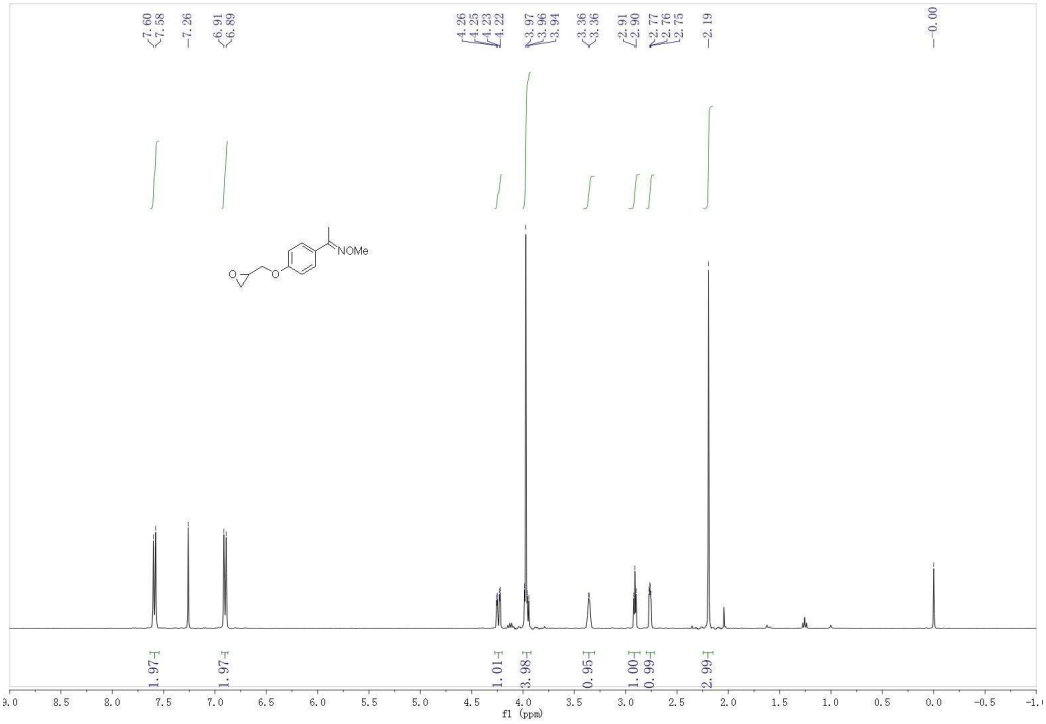



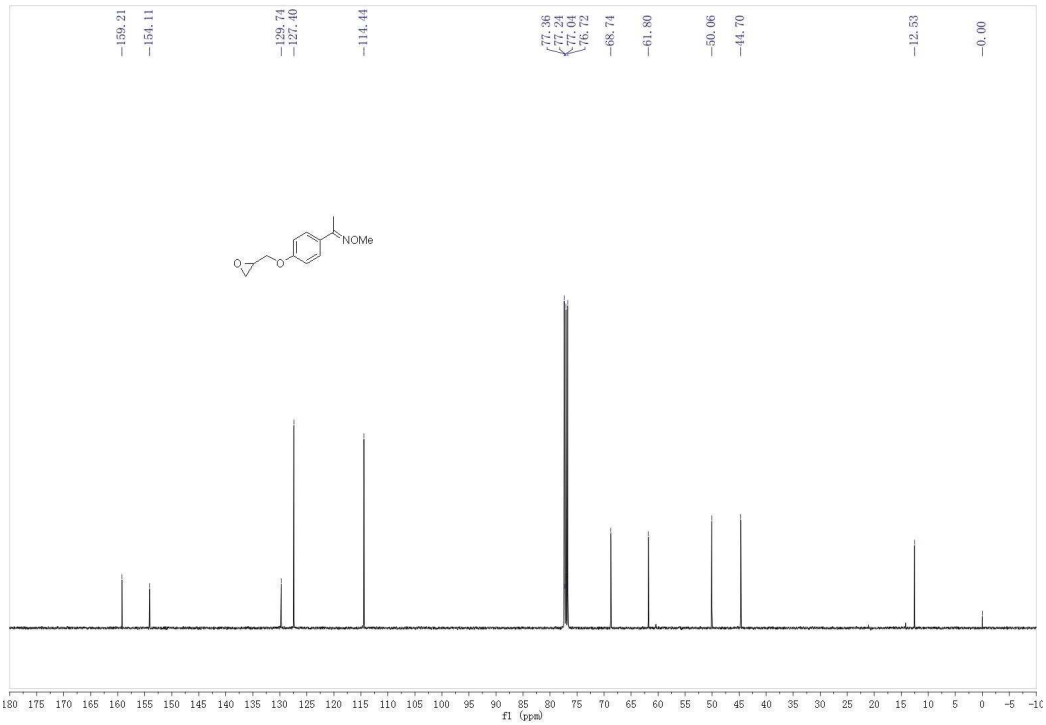

**1-(4-(oxiran-2-ylmethoxy)phenyl)ethanone O-methyl oxime**

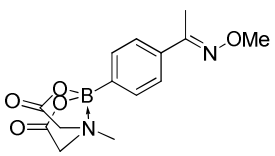
White solid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8, 2H), 6.90 (d, *J* = 8.8, 2H), 4.24 (dd, *J* = 11.0, 3.0, 1H), 4.03 – 3.90 (m, 4H), 3.36 (d, *J* = 1.5, 1H), 2.91 (t, *J* = 4.5, 1H), 2.76 (dd, *J* = 4.5, 2.7, 1H), 2.19 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.21, 154.11, 129.74, 127.40, 114.44, 68.74, 61.80, 50.06, 44.70, 12.53.



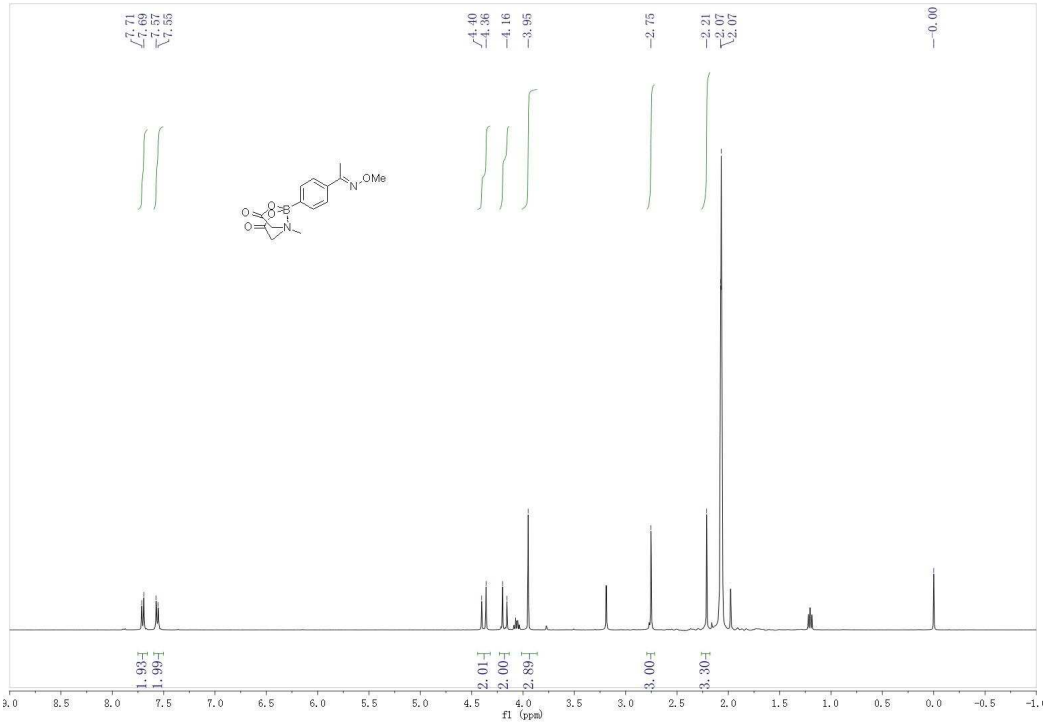



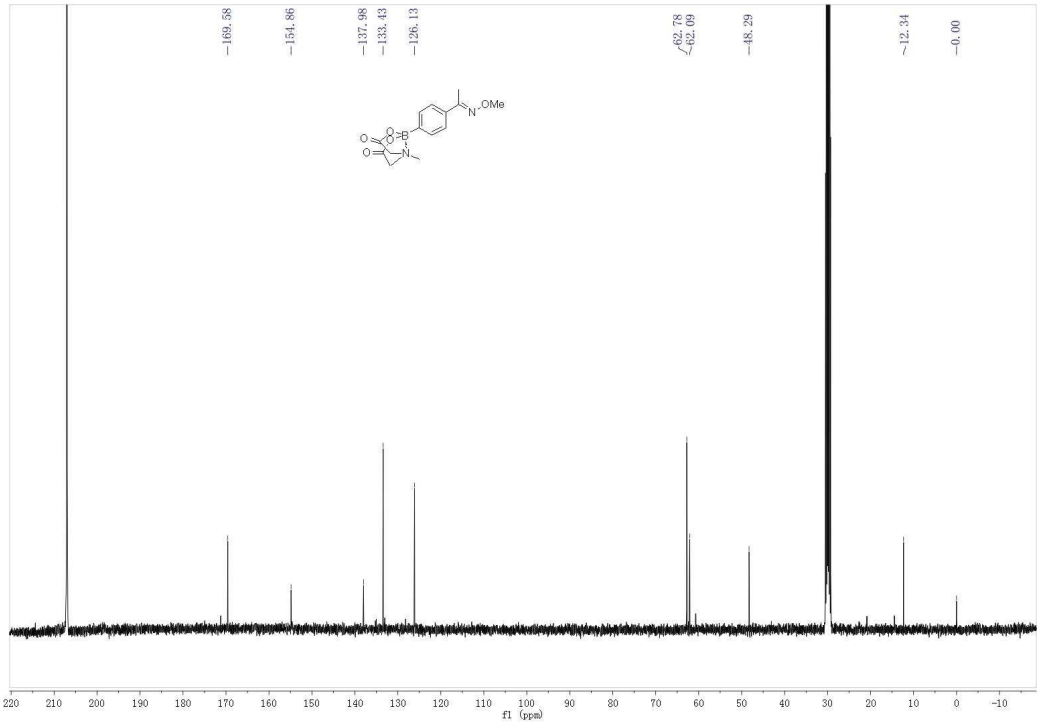

**2-(4-(1-(methoxyimino)ethyl)phenyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione**

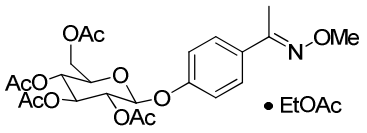
White solid.

$^{1}$H NMR (400 MHz, Acetone) δ 7.70 (d, *J* = 8.0, 2H), 7.56 (d, *J* = 8.0, 2H), 4.38 (d, *J* = 17.1, 2H), 4.18 (d, *J* = 17.1, 2H), 3.95 (s, 3H), 2.75 (s, 3H), 2.21 (s, 3H).

$^{13}$C NMR (101 MHz, Acetone) δ 169.58, 154.86, 137.98, 133.43, 126.13, 62.78, 62.09, 48.29, 12.34.



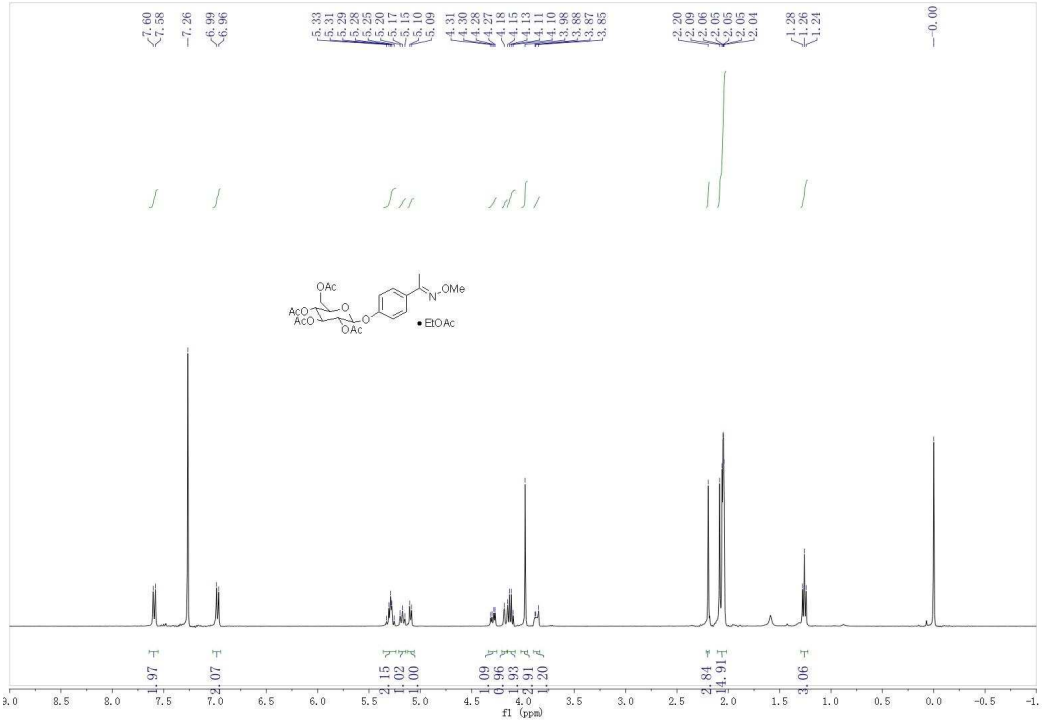


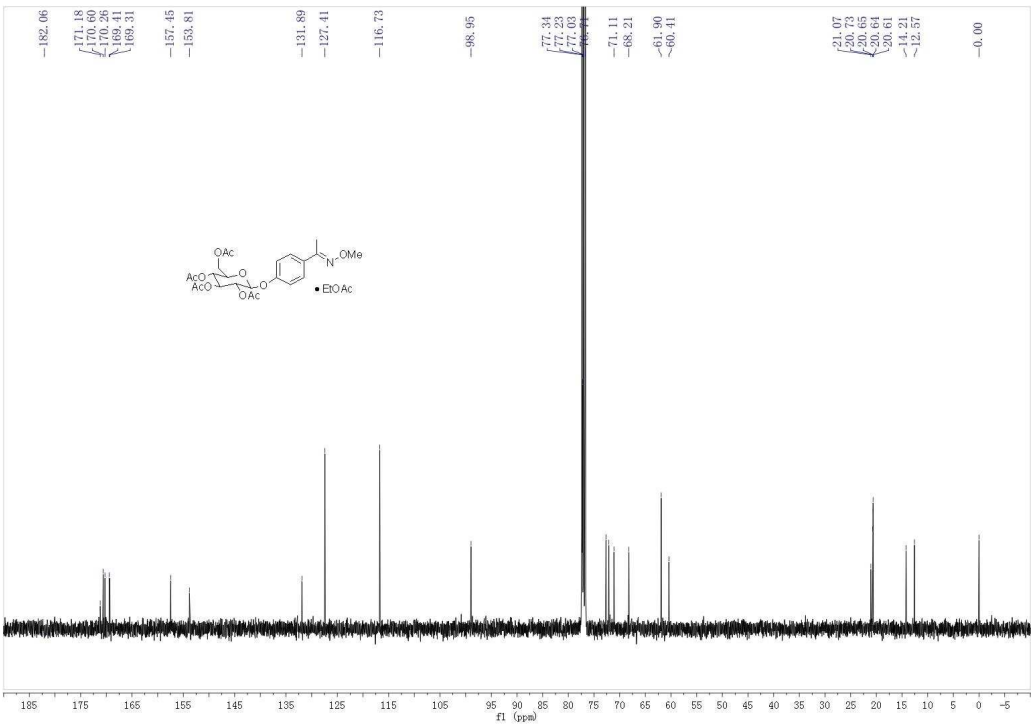

**(2R,3S,4R,5S,6S)-2-(acetoxymethyl)-6-(4-((E)-1-(methoxyimino)ethyl)phenoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate with ethyl acetate (1:1)**

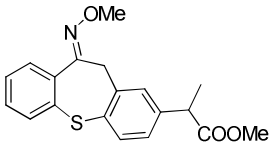
White solid.

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.7, 2H), 6.98 (d, *J* = 8.7, 2H), 5.29 (p, *J* = 9.1, 2H), 5.17 (t, *J* = 9.2, 1H), 5.09 (d, *J* = 7.1, 1H), 4.29 (dd, *J* = 12.3, 5.2, 1H), 4.17 (d, *J* = 13.2, 1H), 4.12 (q, *J* =7.2, 2H), 3.98 (s, 3H), 3.91 – 3.84 (m, 1H), 2.09 (s, 3H), 2.07 – 2.01 (m, 15H), 1.26(t, *J*=7.2, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 182.06, 171.18, 170.60, 170.26, 169.41, 169.31, 157.45, 153.81, 131.89, 127.41, 116.73, 98.95, 72.66, 72.11, 71.11, 68.21, 61.90, 60.41, 21.07, 20.73, 20.65, 20.64, 20.61, 14.21, 12.57.





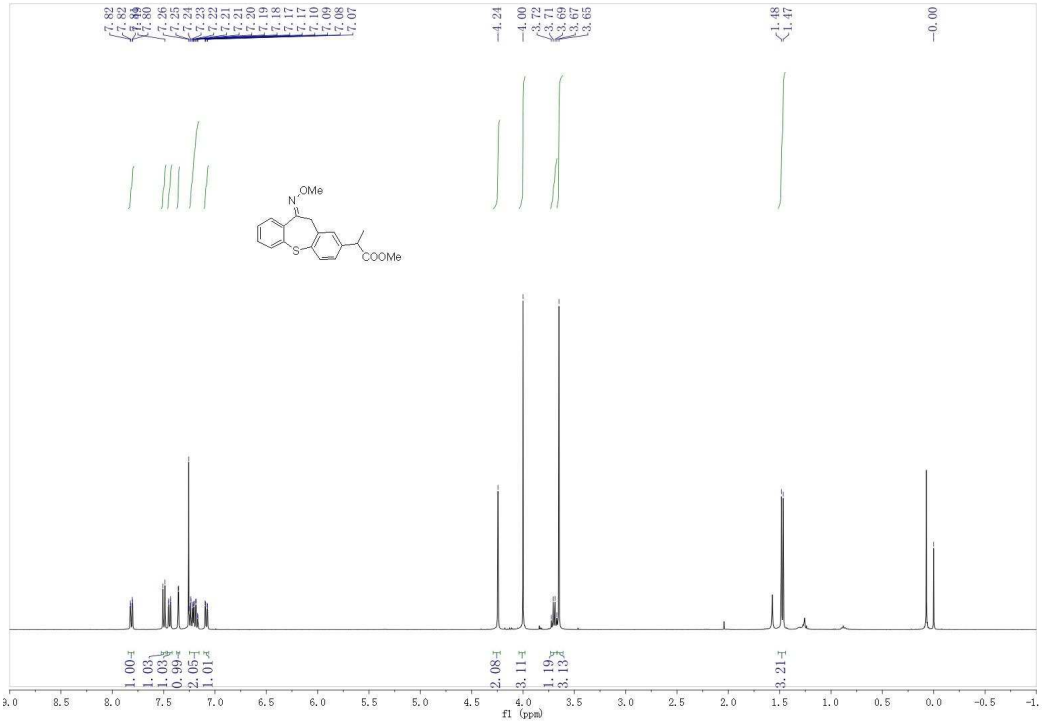

**(E)-methyl 2-(10-(methoxyimino)-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (5)**

Thick oil.

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 1.7, 1H), 7.50 (d, *J* = 7.9, 1H), 7.44 (dd, *J* = 7.7, 1.4, 1H), 7.36 (d, *J* = 1.9, 1H), 7.25 – 7.15 (m, 2H), 7.08 (dd, *J* = 7.9, 2.0, 1H), 4.24 (s, 2H), 4.00 (s, 3H), 3.70 (q, *J* = 7.2, 1H), 3.65 (s, 3H), 1.47 (d, *J* = 7.2, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.59, 153.56, 141.51, 140.36, 134.87, 134.64, 133.74, 131.41, 130.10, 129.06, 128.94, 128.85, 126.67, 126.11, 62.00, 52.11, 45.06, 34.07, 18.50.

HRMS calcd for $C_{19}H_{19}NO_3S$ ($[M+1]^+$): 342.1159; found: 342.1157.


7.82
7.82
7.80
7.26
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3.72
3.71
3.69
3.67
3.65
1.48
1.47
0.00
OMe
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S
COOMe
1.00
1.03
1.03
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1.01
2.08
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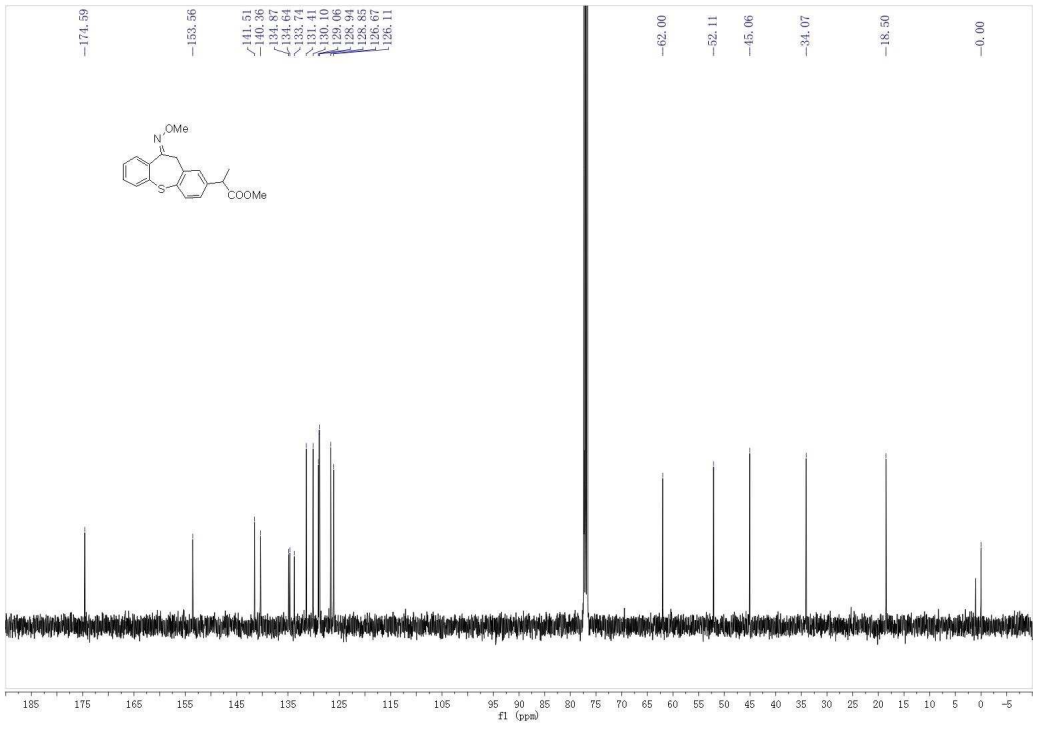
f1 (ppm)


174.59
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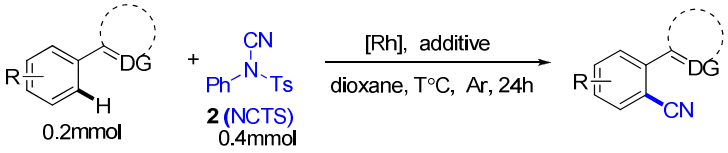
126.67
126.11
62.00
52.11
45.06
34.07
18.50
0.00
OMe
N
S
COOMe
f1 (ppm)

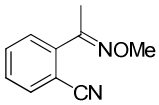
## III. General Procedure for Rhodium-Catalyzed C-H Cyanation and NMR Spectra of Products.

### A. General Procedure for Rhodium-Catalyzed C-H Cyanation




A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (5 mol%), $Ag_2CO_3$ (20 mol%), *N*-cyano-*N*-phenyl-*p*-methylbenzene sulfonamide **2** (0.4 mmol). The tube was evacuated and backfilled with argon for three times. Then aryl ketone *O*-methyl oxime *or* other aryl substrates (0.2 mmol) (0.2mol) in dioxane (1 mL) was added. After addition of all substrates, the reaction mixture was stirred and heated at 120°C for 24h. Then reaction was cooled to room temperature. Solvent and volatile reagents were removed by rotary evaporation and the residue was purified by flash column chromatography on silica gel to give the target product.

### B. NMR Spectra of Products:



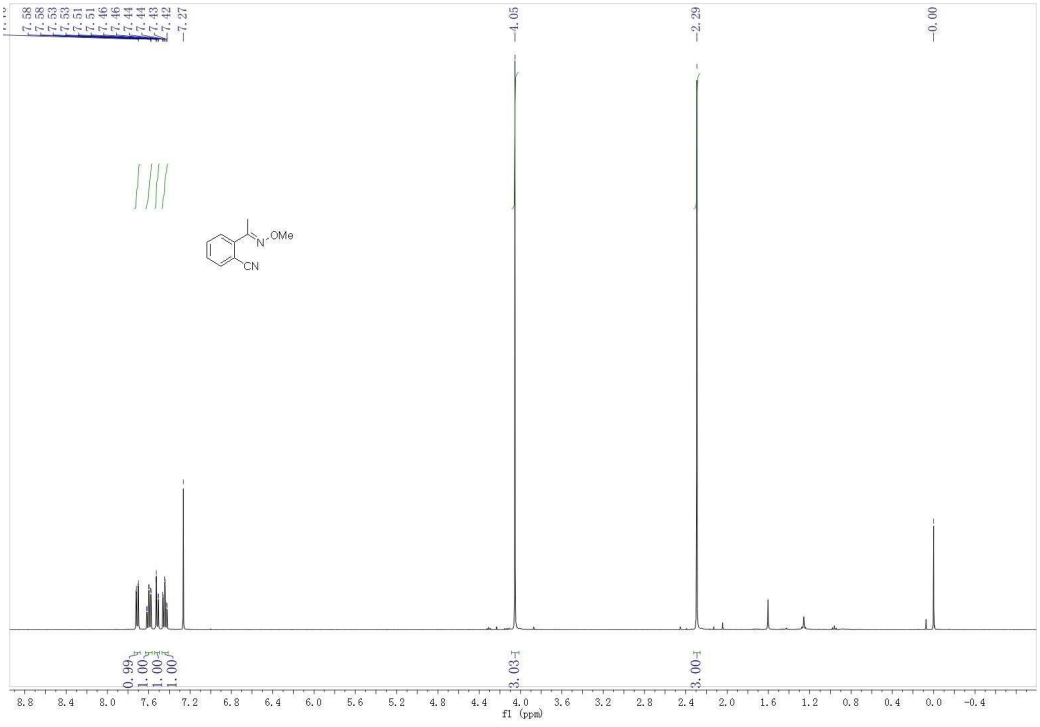

**2-(1-(methoxyimino)ethyl)benzonitrile (3a)**

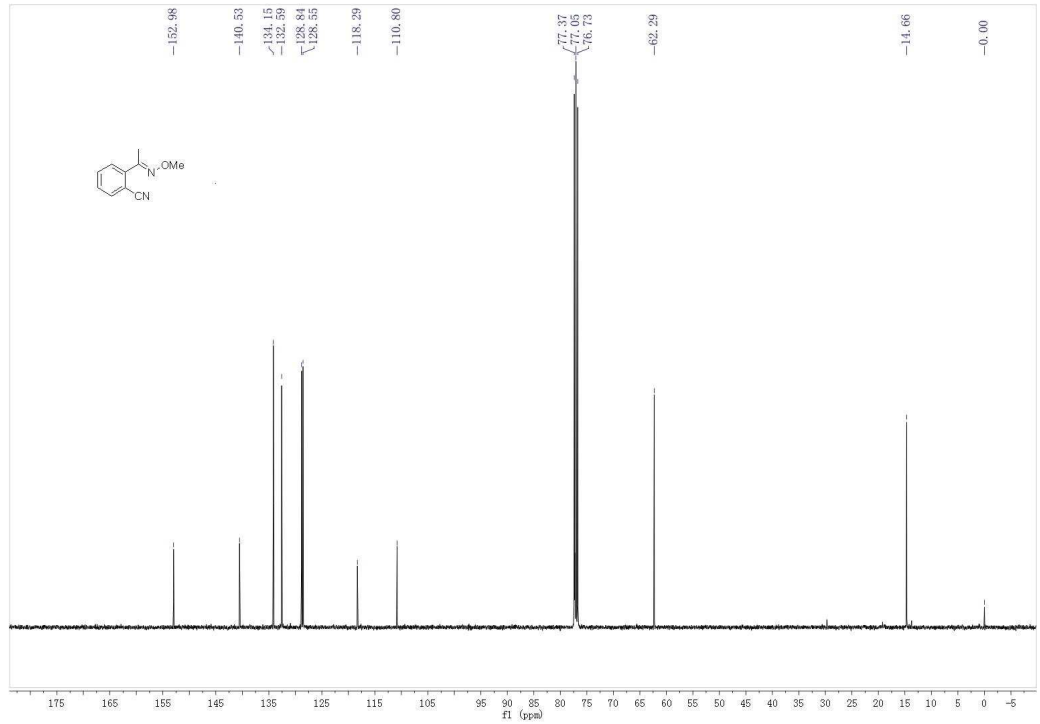
This compound was obtained in 86% (30 mg) yield as thick oil by following the general procedure (PE : EA=30 : 1).

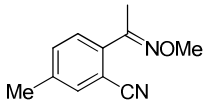
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.0, 1H), 7.63 – 7.56 ((td, *J* = 7.7, 1.0, 1H), 7.52 (dd, *J* = 7.8, 0.9, 1H), 7.44 (td, *J* = 7.6, 1.0, 1H), 4.05 (s, 3H), 2.29 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.98, 140.53, 134.15, 132.59, 128.84, 128.55, 118.29, 110.80, 62.29, 14.66.

HRMS calcd for $C_{10}H_{10}N_2O$ ($[M]^+$): 174.0793; found: 174.0791.



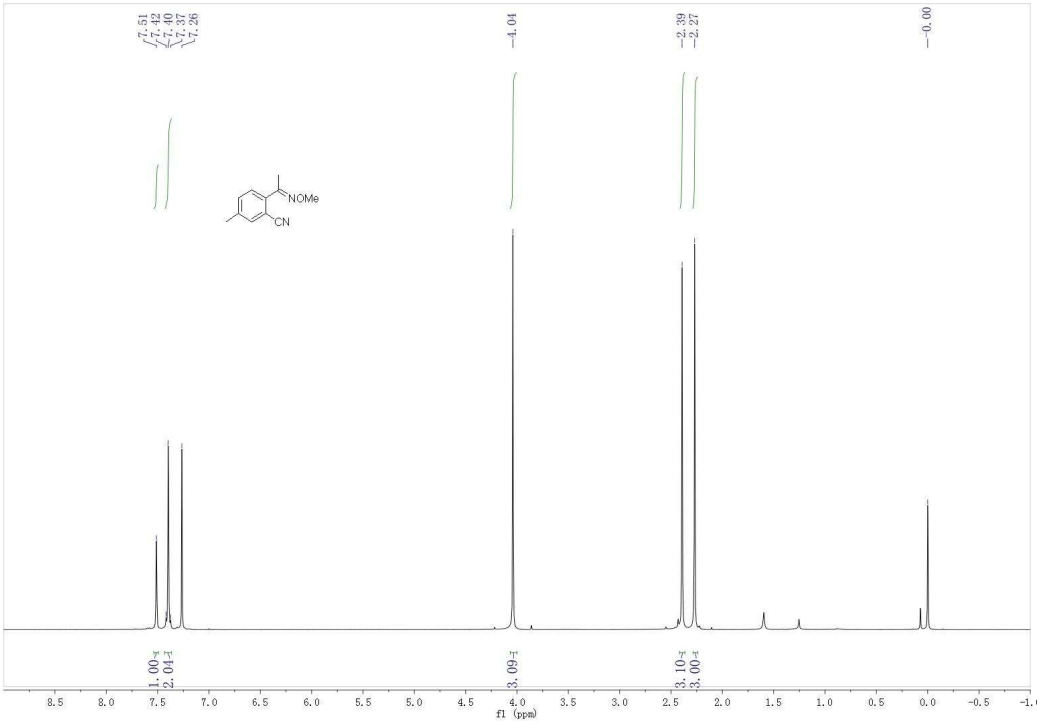

**2-(1-(methoxyimino)ethyl)-5-methylbenzonitrile (3b)**

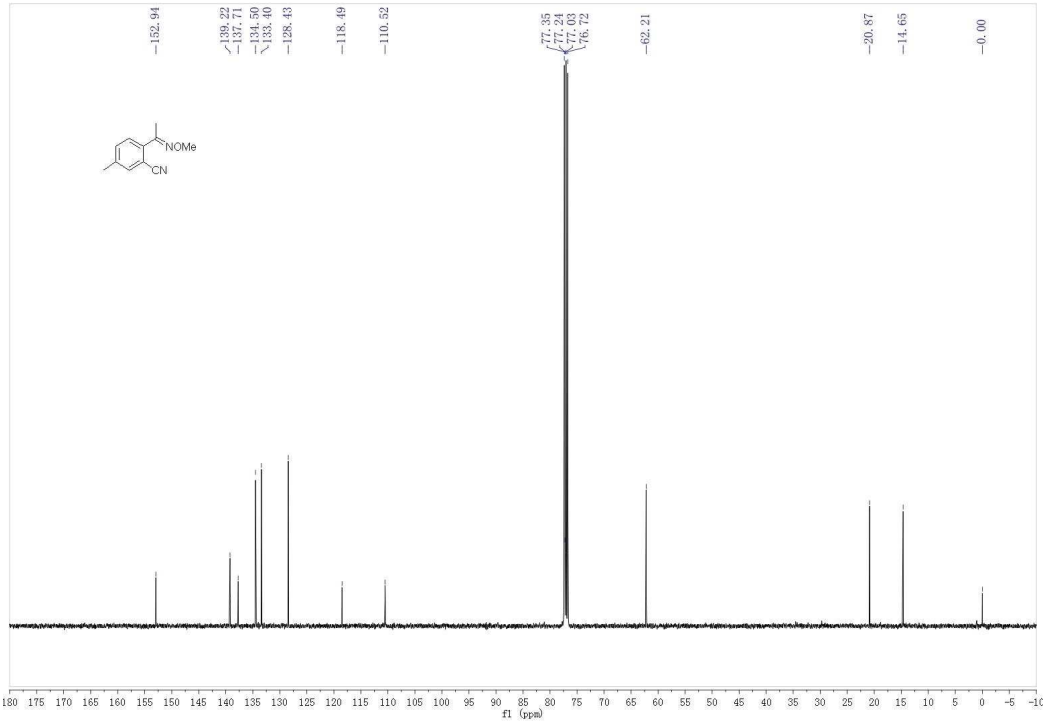
This compound was obtained in 79% (30mg) yield as thick oil by following the general procedure (PE : EA=30 : 1).

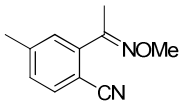
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.42 – 7.37 (m, 2H), 4.04 (s, 3H), 2.39 (s, 3H), 2.27 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.94, 139.22, 137.71, 134.50, 133.40, 128.43, 118.49, 110.52, 62.21, 20.87, 14.65.

HRMS calcd for $C_{11}H_{12}N_2O$ ([M]$^+$): 188.0950; found: 188.0953.





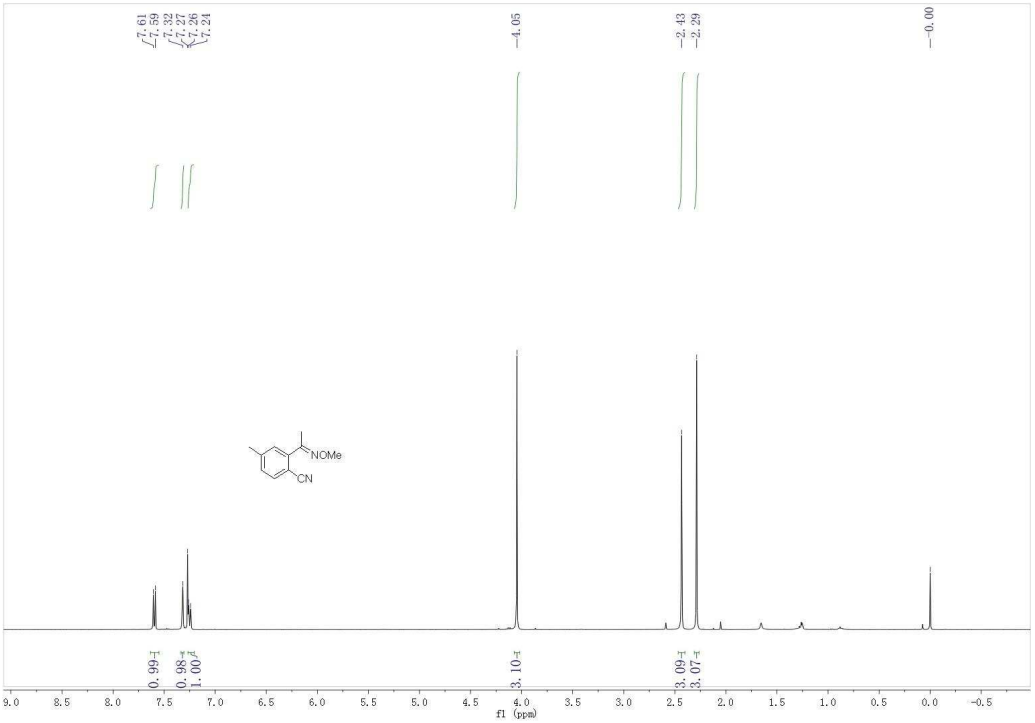

**2-(1-(methoxyimino)ethyl)-4-methylbenzonitrile (3c)**

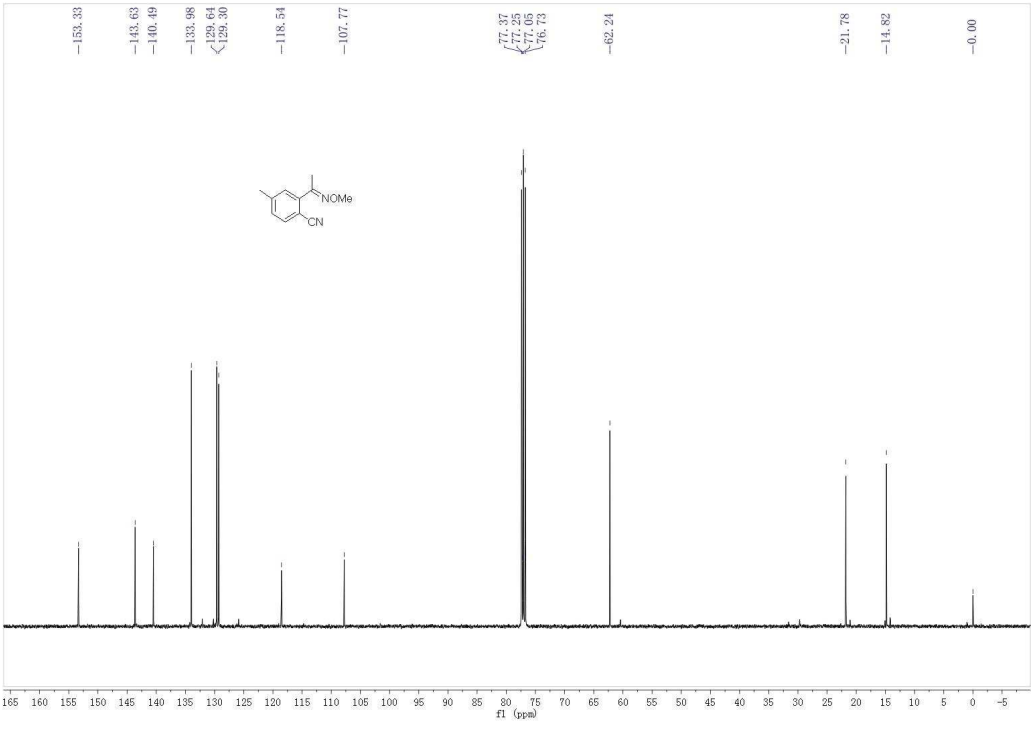
This compound was obtained in 94% (36mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

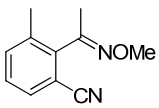
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9, 1H), 7.32 (s, 1H), 7.25 (d, *J* = 8.0, 1H), 4.05 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.33, 143.63, 140.49, 133.98, 129.64, 129.30, 118.54, 107.77, 62.24, 21.78, 14.82.

HRMS calcd for $C_{11}H_{12}N_2O$ ($[M]^+$): 188.0950; found: 188.0951.




**2-(1-(methoxyimino)ethyl)-3-methylbenzonitrile (3d)**

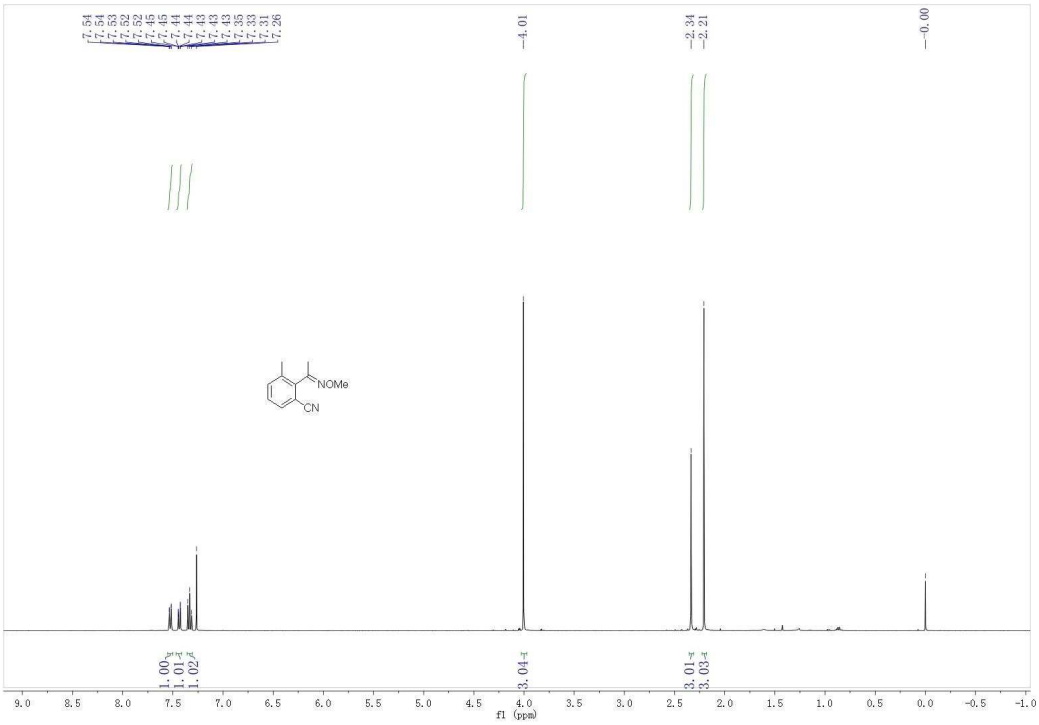
This compound was obtained in 40% (15mg) yield as thick oil by following the general procedure

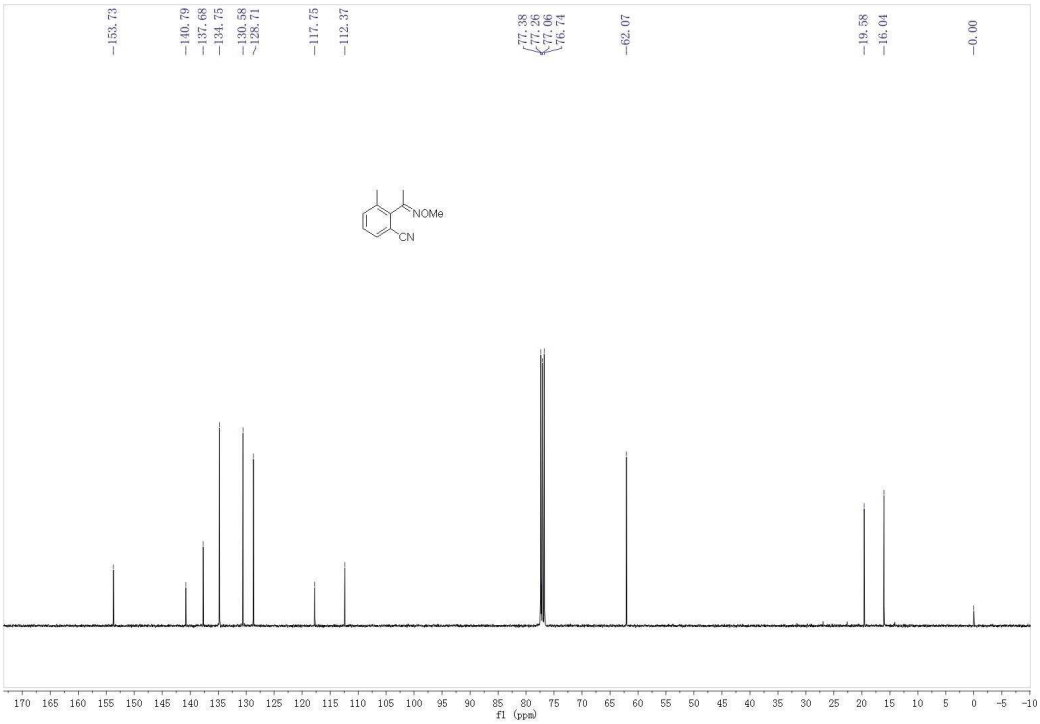
(PE : EA=30 : 1)

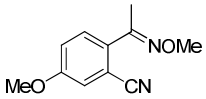
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 1H), 7.46 – 7.42 (m, 1H), 7.33 (t, *J* = 7.7, 1H), 4.01 (s, 3H), 2.34 (s, 3H), 2.21 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.73, 140.79, 137.68, 134.75, 130.58, 128.71, 117.75, 112.37, 62.07, 19.58, 16.04.

HRMS calcd for $C_{11}H_{12}N_2O$ ([M]$^+$): 188.0950; found: 188.0955.





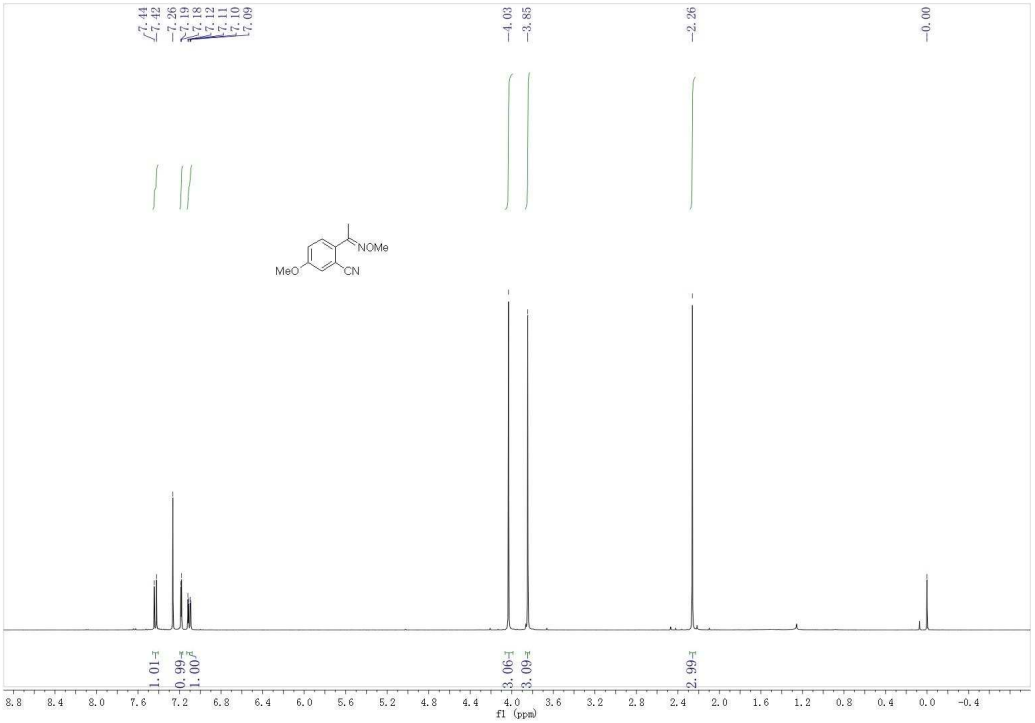

**5-methoxy-2-(1-(methoxyimino)ethyl)benzonitrile (3e)**

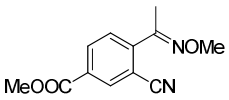
This compound was obtained in 80% (33 mg) yield as thick oil by following the general procedure (PE : EA=10 : 1)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7, 1H), 7.18 (d, *J* = 2.7, 1H), 7.11 (dd, *J* = 8.7, 2.7, 1H), 4.03 (s, 3H), 3.85 (s, 3H), 2.26 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.53, 152.65, 132.99, 129.92, 118.93, 118.74, 118.23, 111.60, 62.15, 55.74, 14.66.

HRMS calcd for $C_{11}H_{12}N_2O_2$ ($[M]^+$): 204.0899; found: 204.0911.



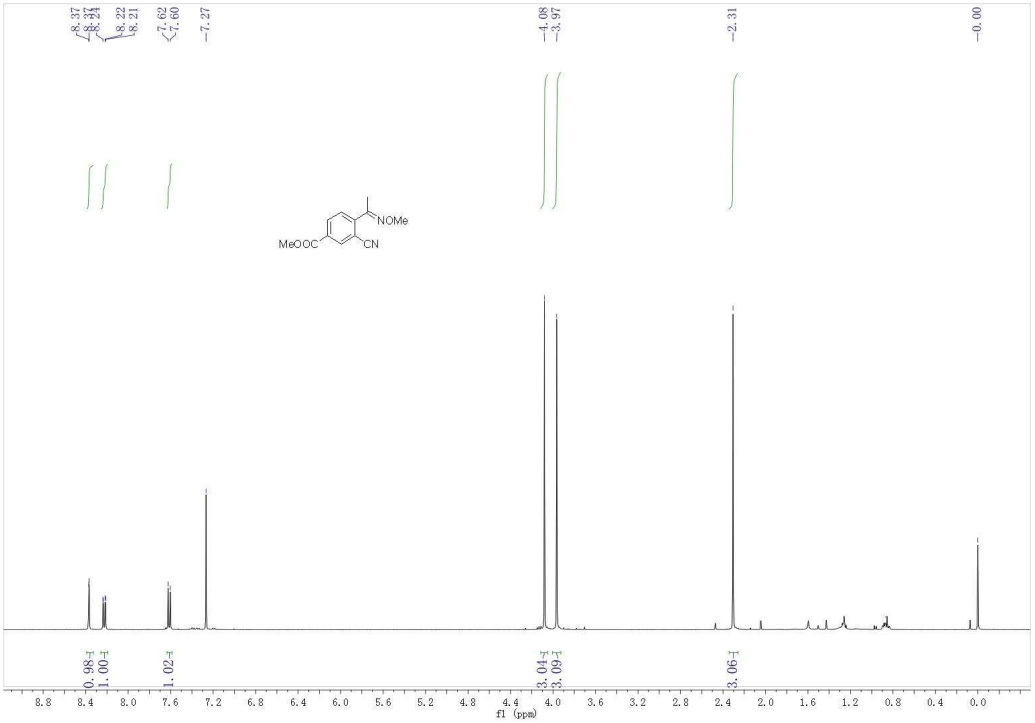

**Methyl 3-cyano-4-(1-(methoxyimino)ethyl)benzoate (3f)**

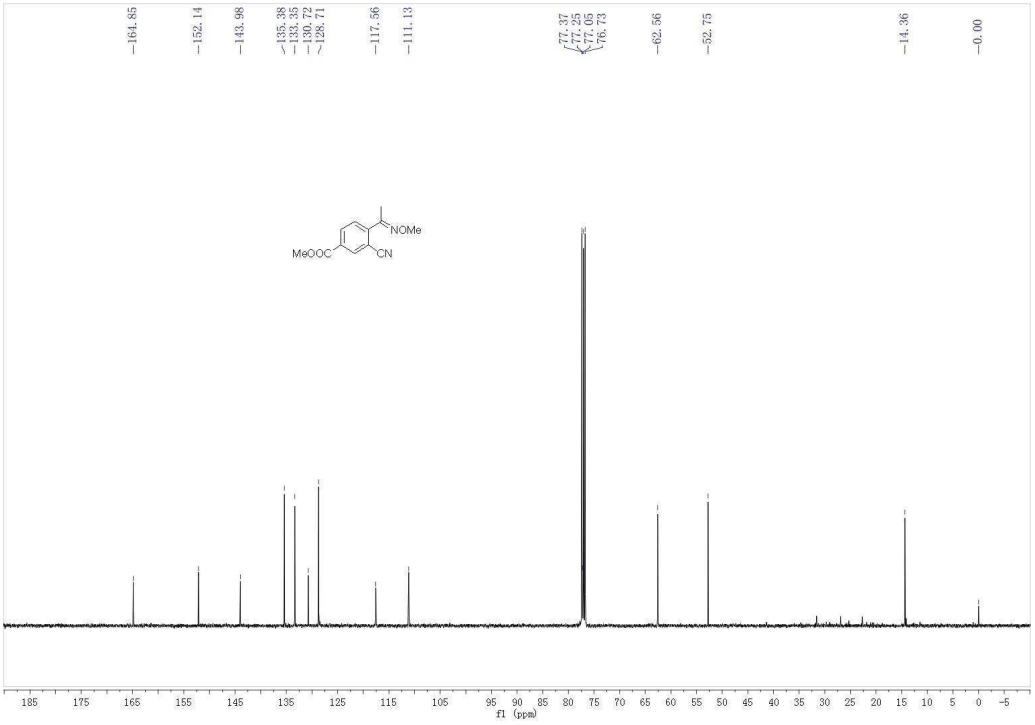
This compound was obtained in 74% (34mg) yield as white solid by following the general procedure (PE : EA=10 : 1)

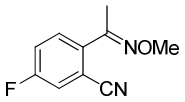
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.5, 1H), 8.23 (dd, *J* = 8.3, 1.5, 1H), 7.61 (d, *J* = 8.3, 1H), 4.08 (s, 3H), 3.97 (s, 3H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.85, 152.14, 143.98, 135.38, 133.35, 130.72, 128.71, 117.56, 111.13, 62.56, 52.75, 14.36.

HRMS calcd for $C_{12}H_{12}N_2O_3$ ($[M]^+$): 232.0848; found: 232.0809.



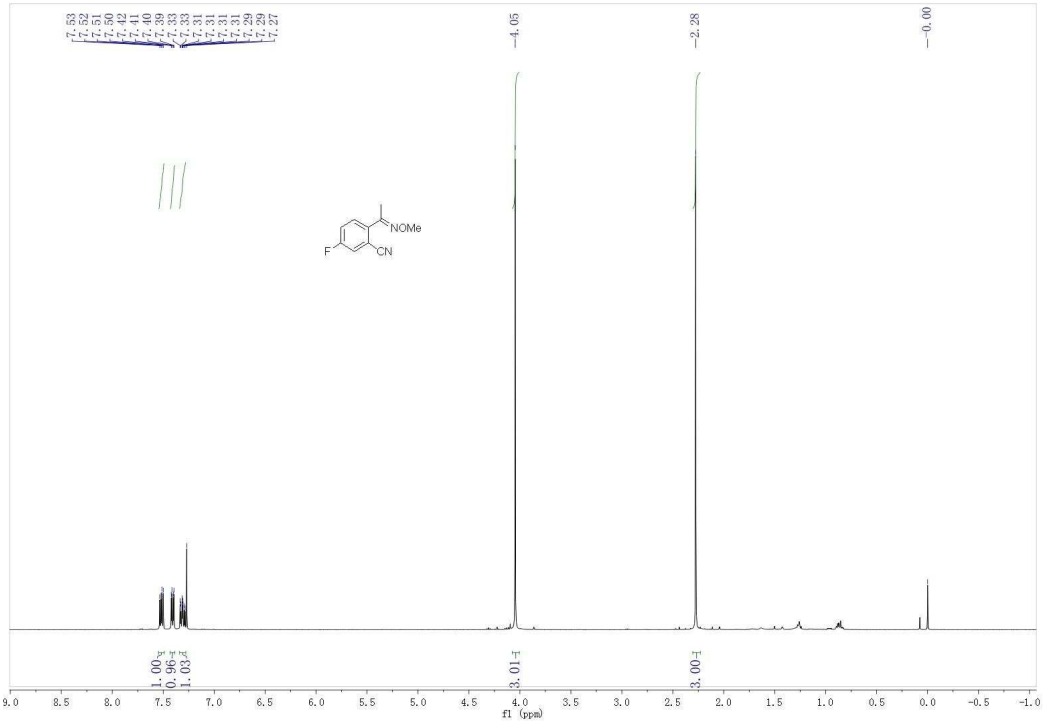

**5-fluoro-2-(1-(methoxyimino)ethyl)benzonitrile (3g)**

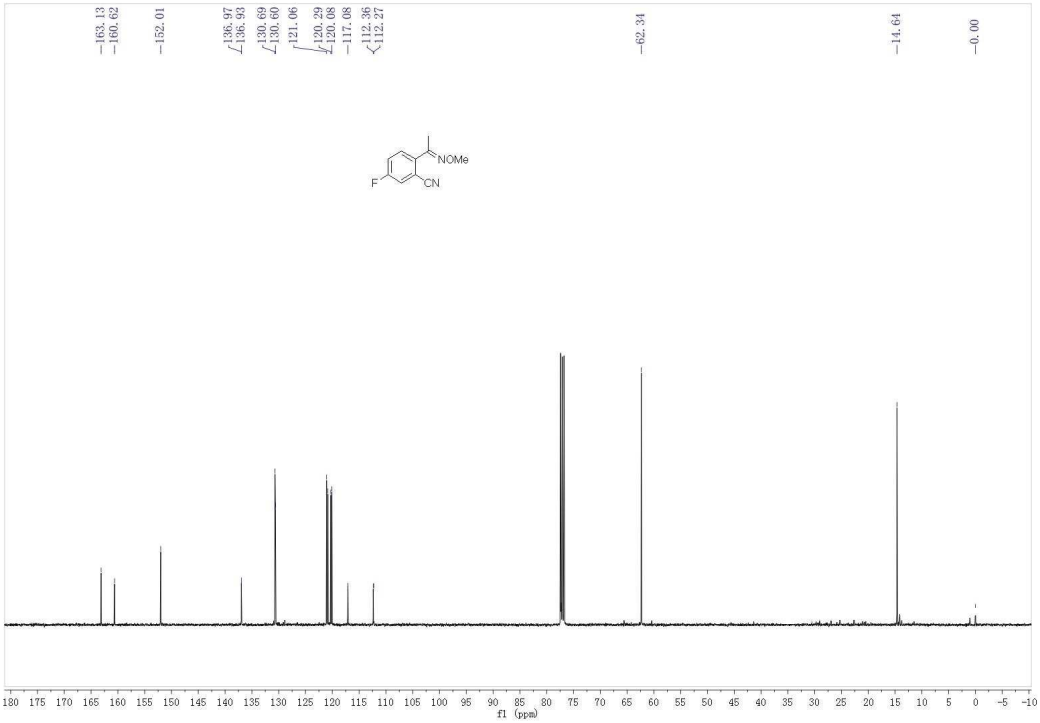
This compound was obtained in 81% (31mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

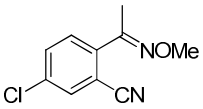
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.7, 5.3, 1H), 7.41 (dd, *J* = 8.0, 2.7, 1H), 7.31 (ddd, *J* = 8.7, 8.0 , 2.7, 1H), 4.05 (s, 3H), 2.28 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.87 (d, *J* = 252.2), 152.01, 136.95 (d, *J* = 3.7), 130.65 (d, *J* = 8.4), 120.94 (d, *J* = 24.8), 120.18 (d, *J* = 21.3), 117.08 (d, *J* = 2.7), 112.31 (d, *J* = 9.4), 62.34, 14.62.

HRMS calcd for $C_{10}H_9FN_2O$ ([M]$^+$): 192.0699; found: 192.0726.





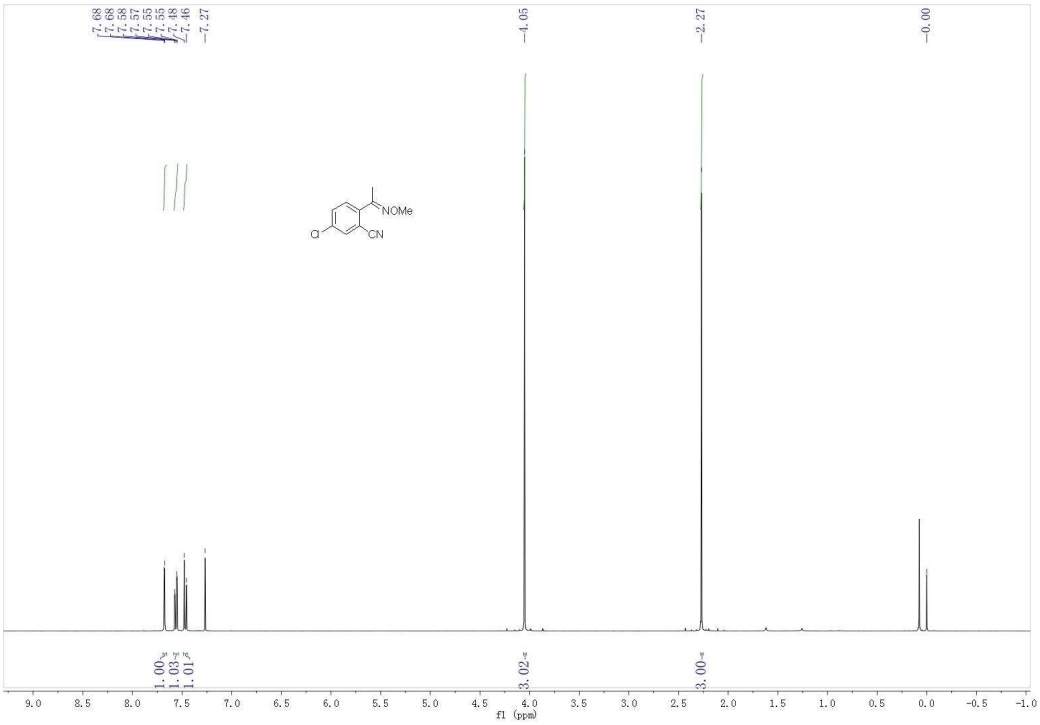

**5-chloro-2-(1-(methoxyimino)ethyl)benzonitrile (3h)**

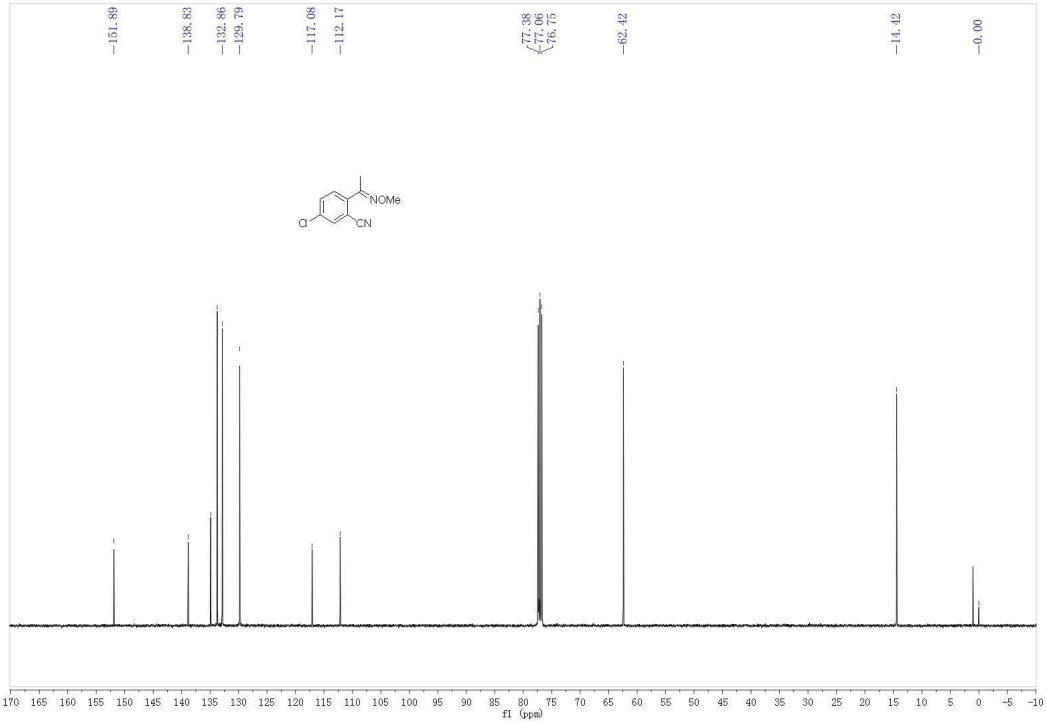
This compound was obtained in 70% (29mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

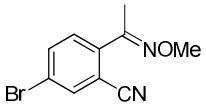
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.0, 1H), 7.56 (dd, *J* = 8.5, 2.0, 1H), 7.47 (d, *J* = 8.5, 1H), 4.05 (s, 3H), 2.27 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.89, 138.83, 134.89, 133.74, 132.86, 129.79, 117.08, 112.17, 62.42, 14.42.

HRMS calcd for $C_{10}H_9ClN_2O$ ($[M]^+$): 208.0403; found: 208.0425.





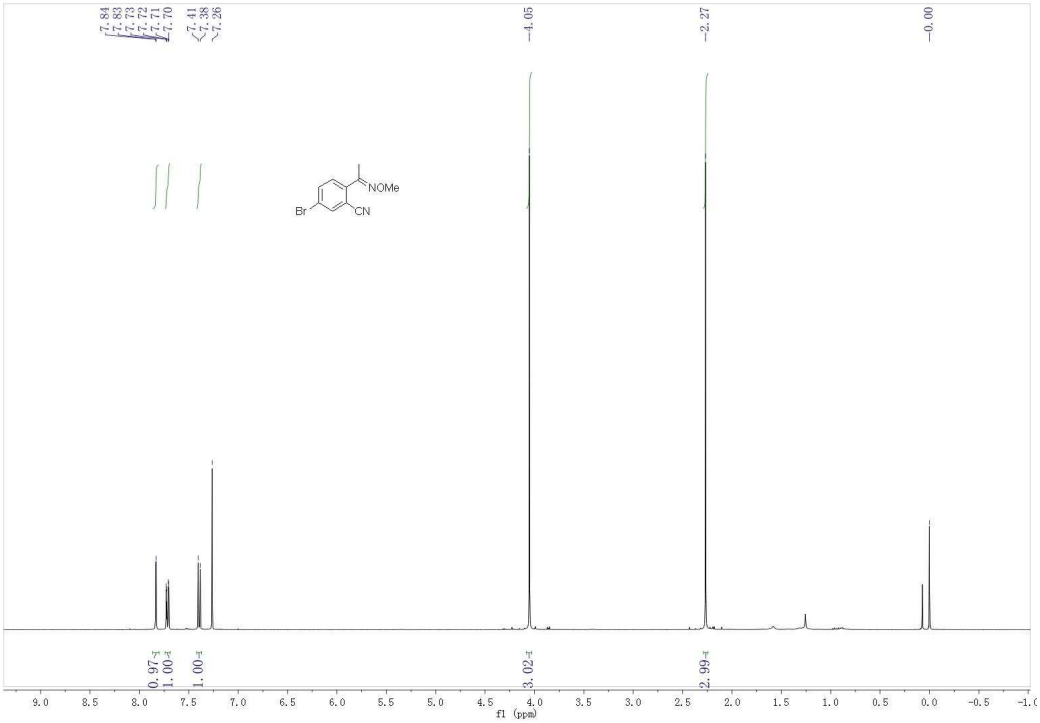

**5-bromo-2-(1-(methoxyimino)ethyl)benzonitrile (3i)**

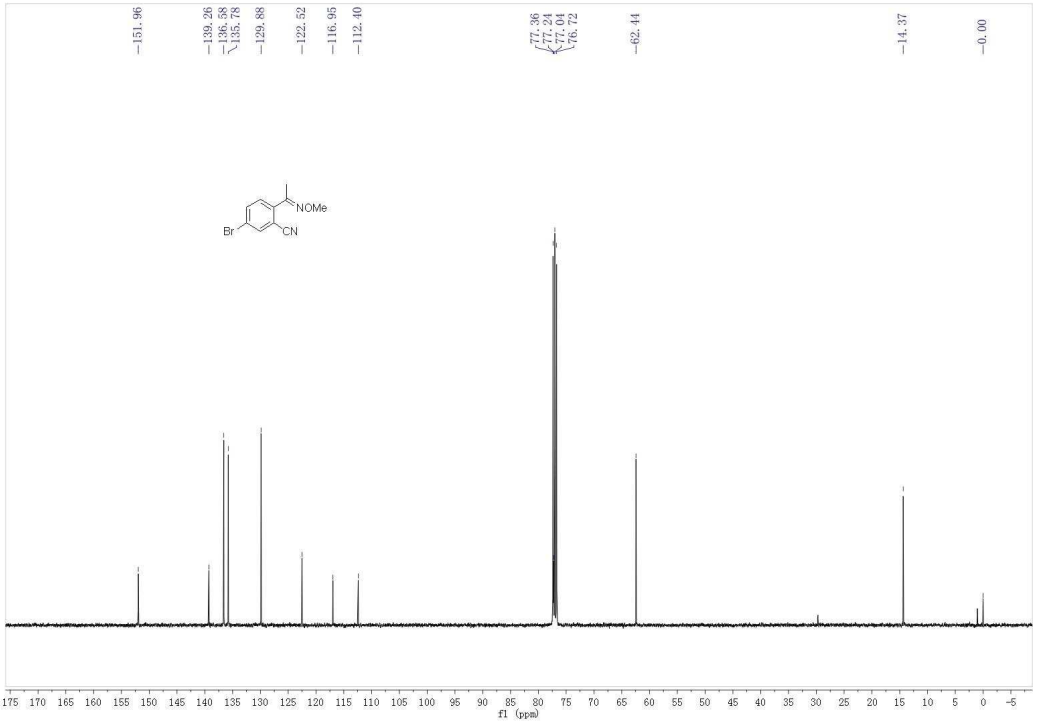
This compound was obtained in 82% (41mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

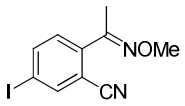
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.0, 1H), 7.72 (dd, *J* = 8.5, 2.0, 1H), 7.39 (d, *J* = 8.5, 1H), 4.05 (s, 3H), 2.27 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.96, 139.26, 136.58, 135.78, 129.88, 122.52, 116.95, 112.40, 62.44, 14.37.

HRMS calcd for $C_{10}H_9BrN_2O$ ($[M]^+$): 251.9898; found: 251.9911.



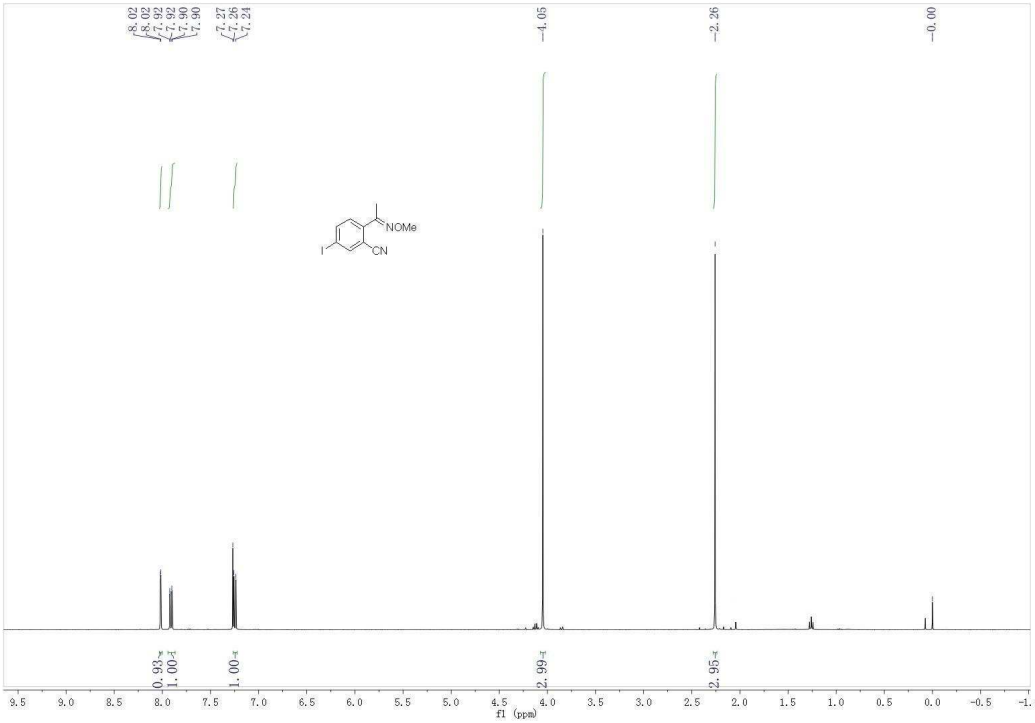

**5-iodo-2-(1-(methoxyimino)ethyl)benzonitrile (3j)**

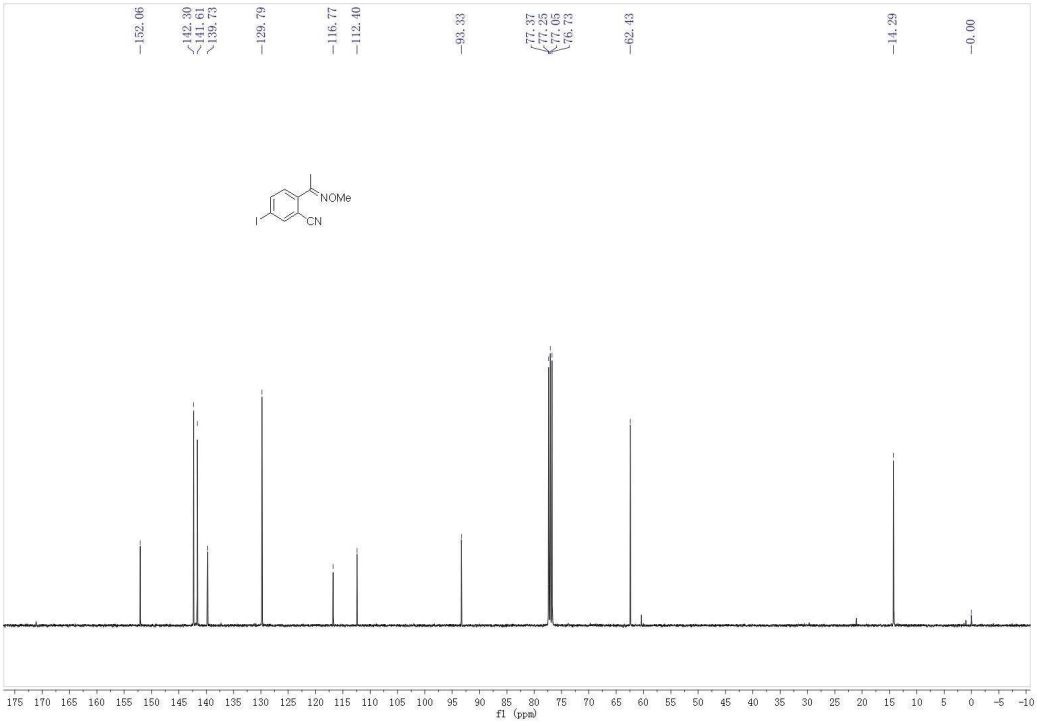
This compound was obtained in 67% (40 mg)yield as white solid by following the general procedure (PE : EA=30 : 1)

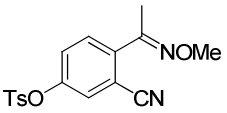
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, $J$ = 1.8, 1H), 7.91 (dd, $J$ = 8.4, 1.8, 1H), 7.25 (d, $J$ = 8.4, 1H), 4.05 (s, 3H), 2.26 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.06, 142.30, 141.61, 139.73, 129.79, 116.77, 112.40, 93.33, 62.43, 14.29.

HRMS calcd for $C_{10}H_9IN_2O$ ($[M]^+$): 299.9760; found: 299.9762.





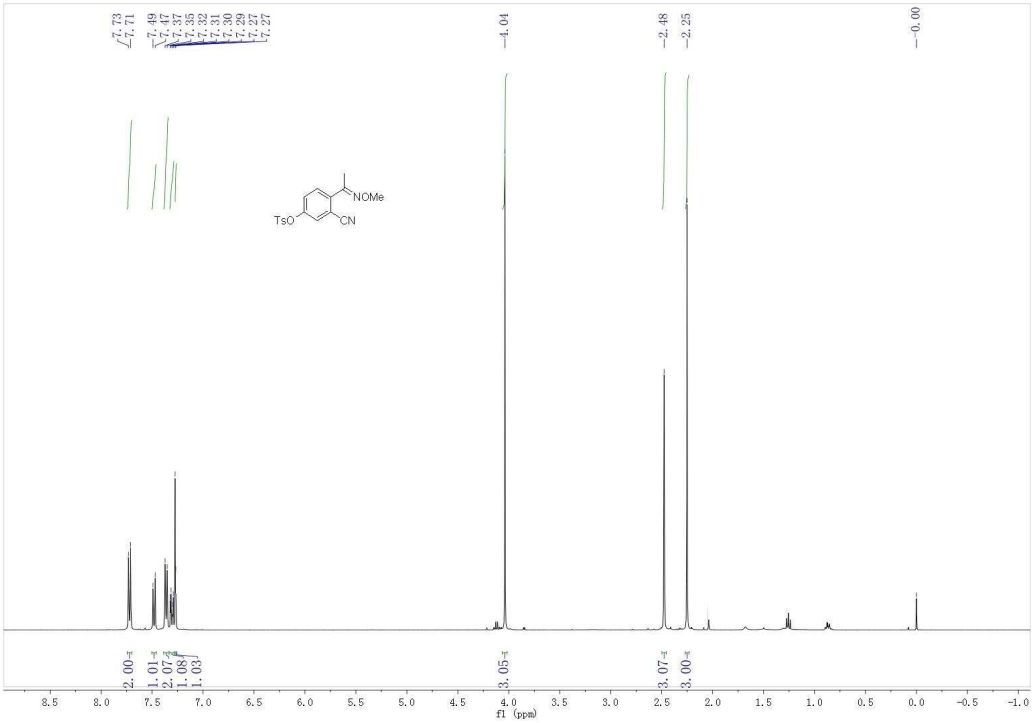

**3-cyano-4-(1-(methoxyimino)ethyl)phenyl 4-methylbenzenesulfonate (3k)**

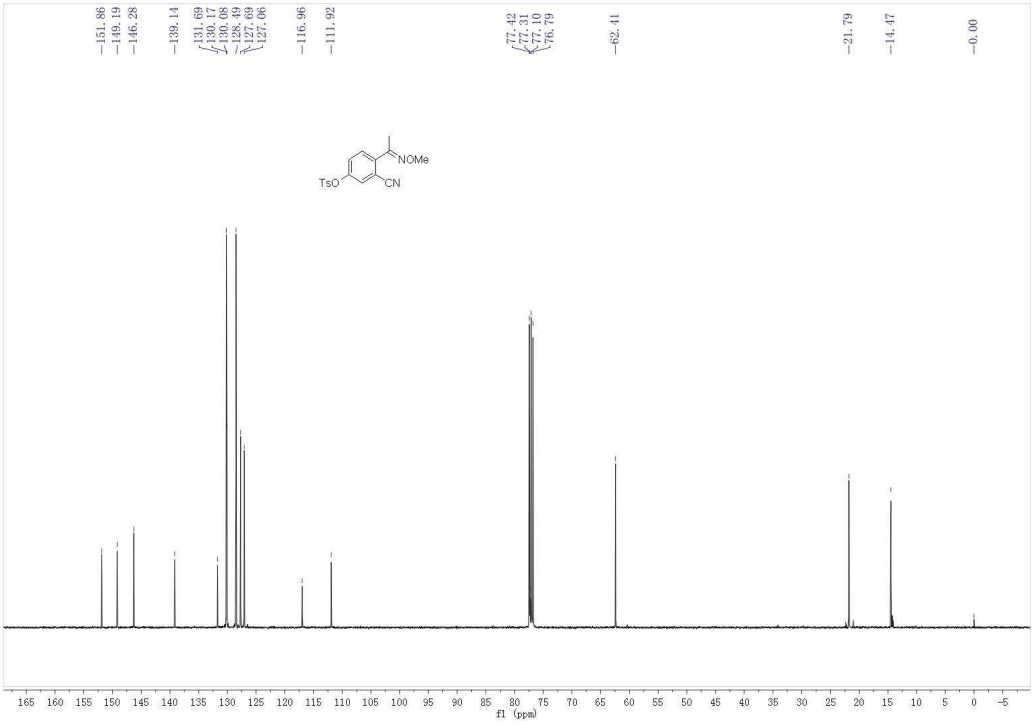
This compound was obtained in 73% (50mg) yield as white solid by following the general procedure (PE : EA=10 : 1)

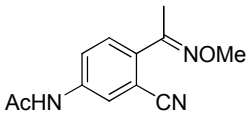
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2, 2H), 7.48 (d, *J* = 8.6, 1H), 7.36 (d, *J* = 8.2, 2H), 7.31 (dd, *J* = 8.6, 2.5, 1H), 7.27 (d, *J* = 2.5, 1H), 4.04 (s, 3H), 2.48 (s, 3H), 2.25 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.86, 149.19, 146.28, 139.14, 131.69, 130.17, 130.08, 128.49, 127.69, 127.06, 116.96, 111.92, 62.41, 21.79, 14.47.

HRMS calcd for $C_{17}H_{16}N_2O_4S$ ($[M]^+$): 344.0831; found: 344.0841.





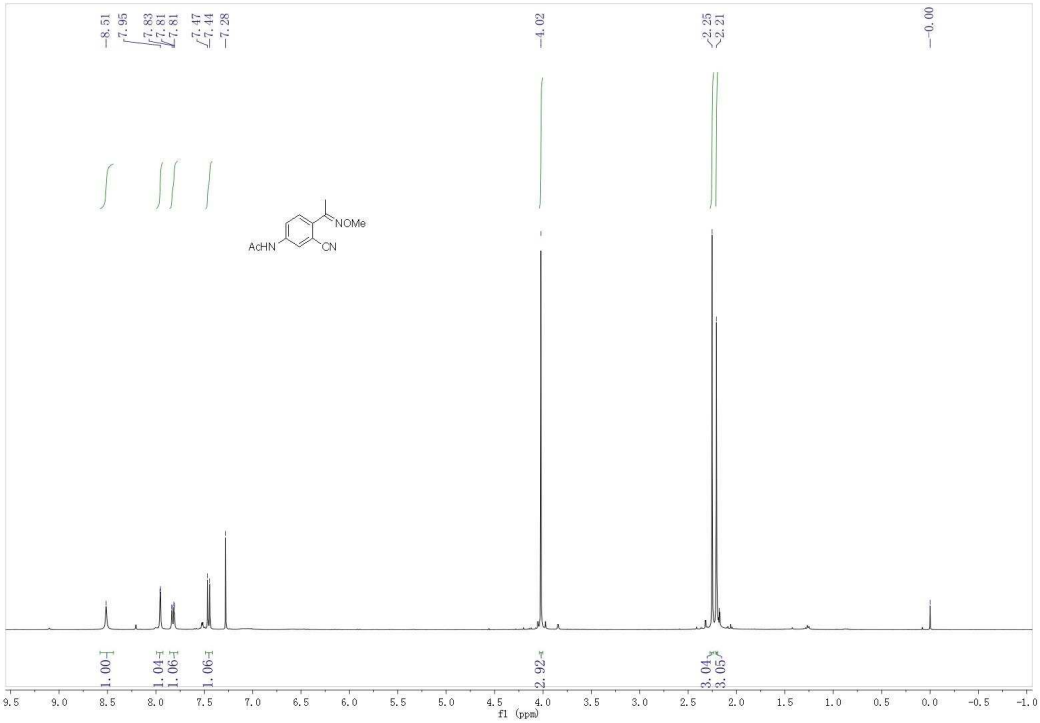

**N-(3-cyano-4-(1-(methoxyimino)ethyl)phenyl)acetamide (3l)**

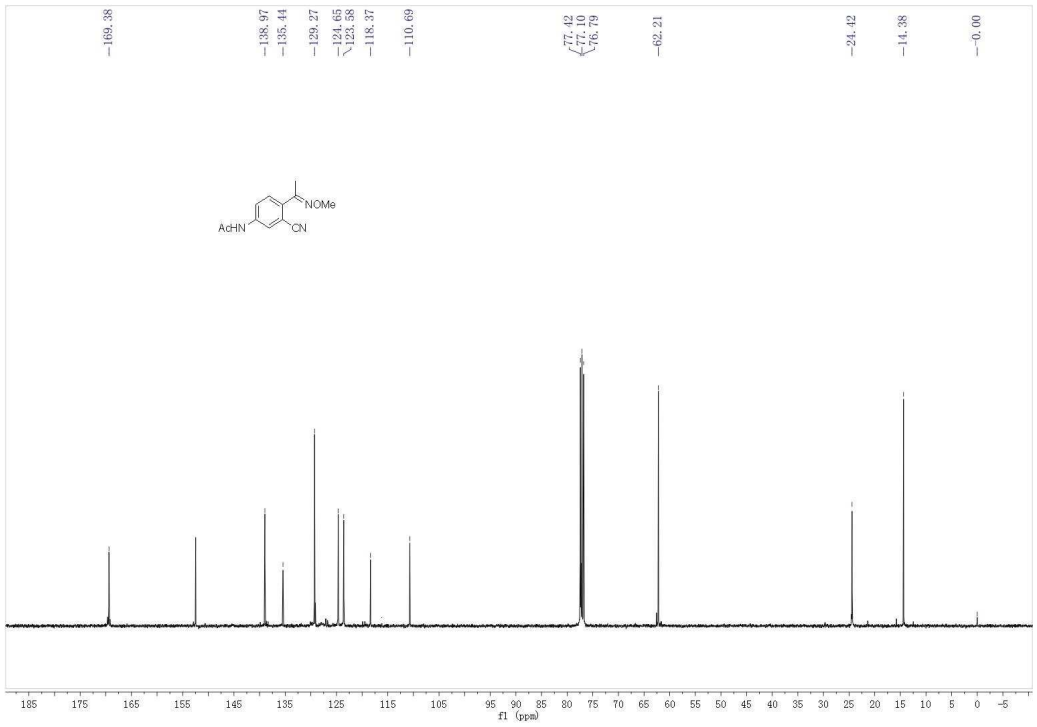
This compound was obtained in 72% (33mg) yield as white solid by following the general procedure (PE : EA=3 : 1)

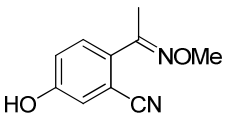
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.96 (d, *J* = 2.1, 1H), 7.82 (dd, *J* = 8.6, 2.1, 1H), 7.45 (d, *J* = 8.6, 1H), 4.02 (s, 3H), 2.25 (s, 3H), 2.21 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 169.38, 152.47, 138.97, 135.44, 129.27, 124.65, 123.58, 118.37, 110.69, 62.21, 24.42, 14.38.

HRMS calcd for $C_{12}H_{13}N_3O_2$ ([M]$^+$): 231.1008; found: 230.1028.




**5-hydroxy-2-(1-(methoxyimino)ethyl)benzonitrile (3m)**

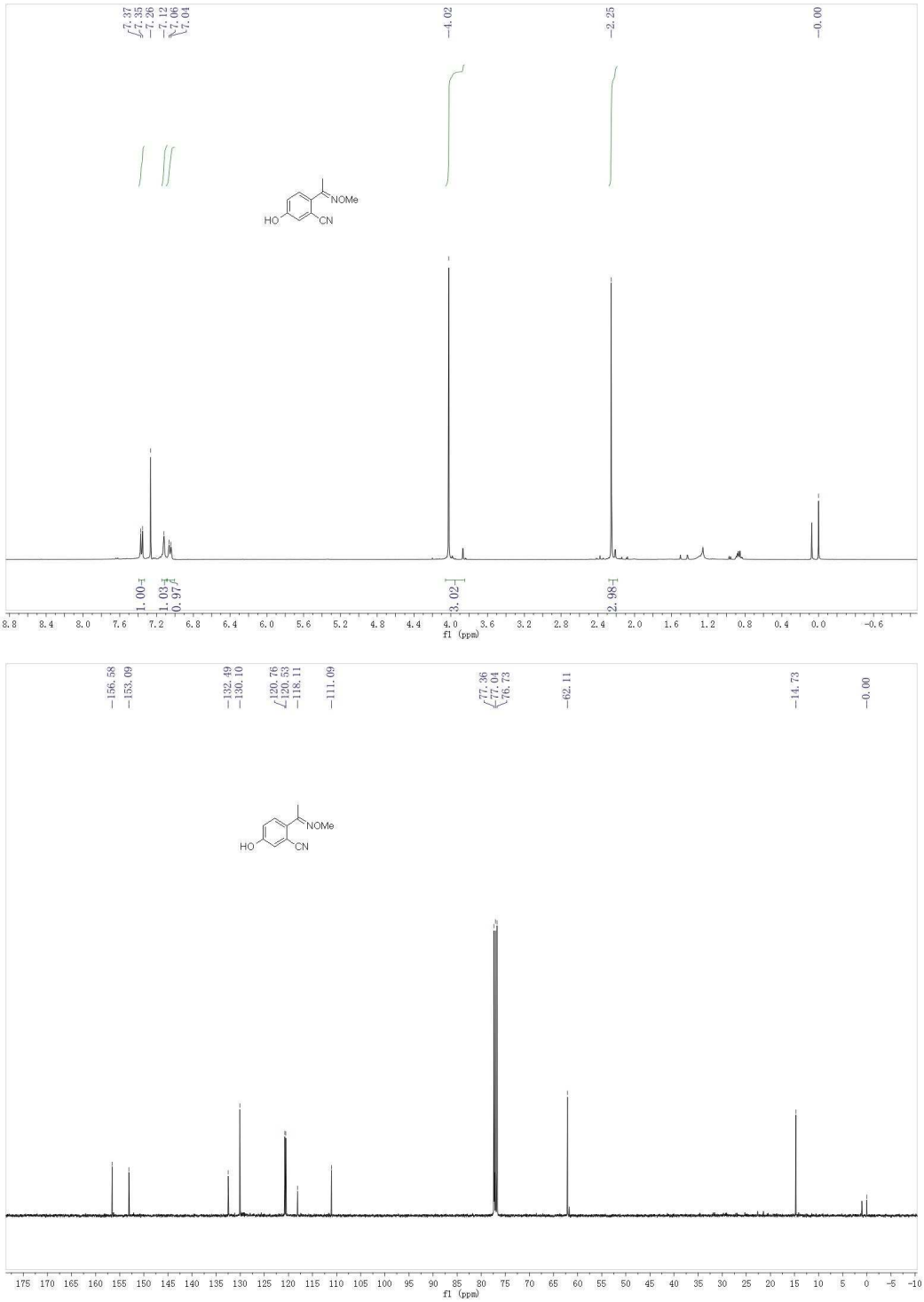
This compound was obtained in 53% (20mg) yield as white solid by following the general

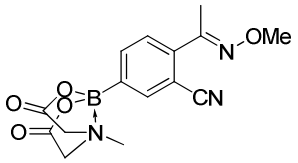
procedure (PE : EA=5 : 1)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.5, 1H), 7.12 (s, 1H), 7.05 (d, *J* = 8.4, 1H), 4.02 (s, 3H), 2.25 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.58, 153.09, 132.49, 130.10, 120.76, 120.53, 118.11, 111.09, 62.11, 14.73.

HRMS calcd for $C_{10}H_{10}N_2O_2$ ($[M]^+$): 190.0742; found: 190.0753.





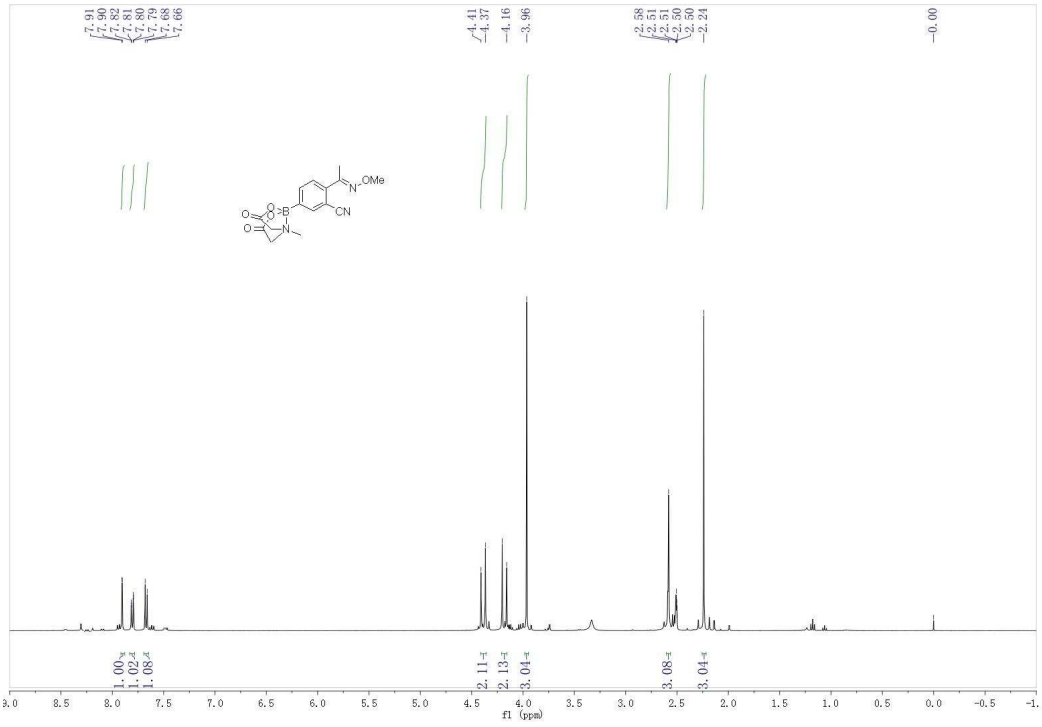
**(E)-2-(1-(methoxyimino)ethyl)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)benzonitrile (3n)**

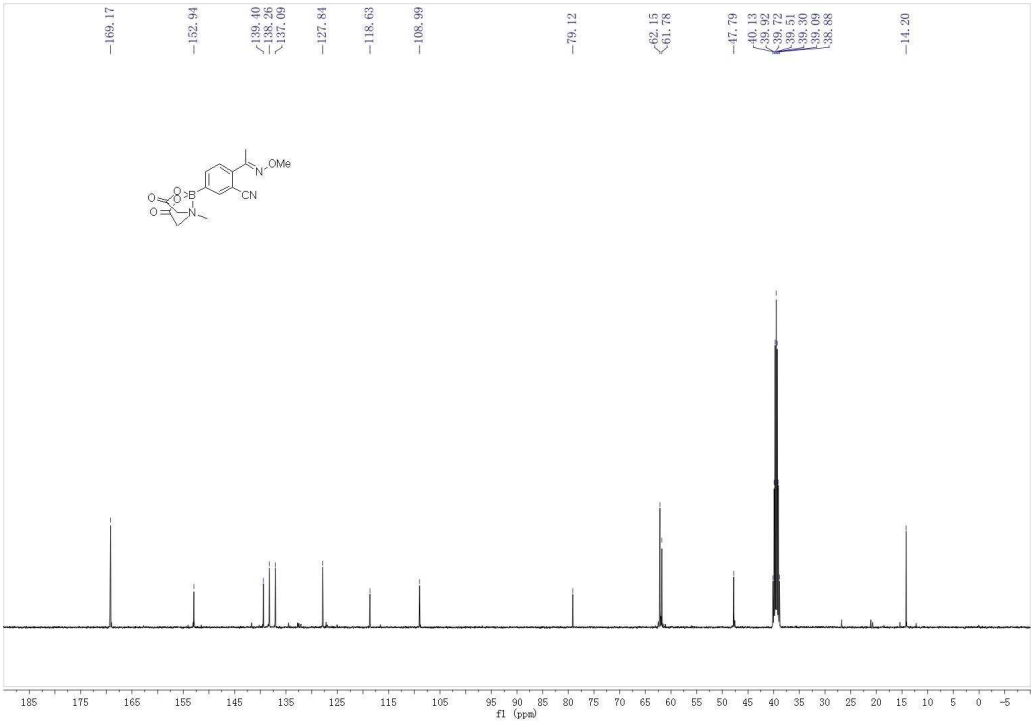
This compound was obtained in 64% (42mg) yield as white solid by following the general procedure (PE : EA=1 : 2)

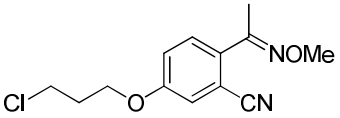
$^{1}$H NMR (400 MHz, DMSO) δ 7.90 (d, *J* = 1.2, 1H), 7.80 (dd, *J* = 7.9, 1.2, 1H), 7.67 (d, *J* = 7.9, 1H), 4.39 (d, *J* = 17.2, 2H), 4.18 (d, *J* = 17.2, 2H), 3.96 (s, 3H), 2.58 (s, 3H), 2.24 (s, 3H).

$^{13}$C NMR (101 MHz, DMSO) δ 169.17, 152.94, 139.40, 138.26, 137.09, 127.84, 118.63, 108.99, 79.12, 62.15, 61.78, 47.79, 14.20.

HRMS calcd for $C_{15}H_{16}BN_3O_5$ ([M+1]$^{+}$): 330.1256; found: 330.1249.





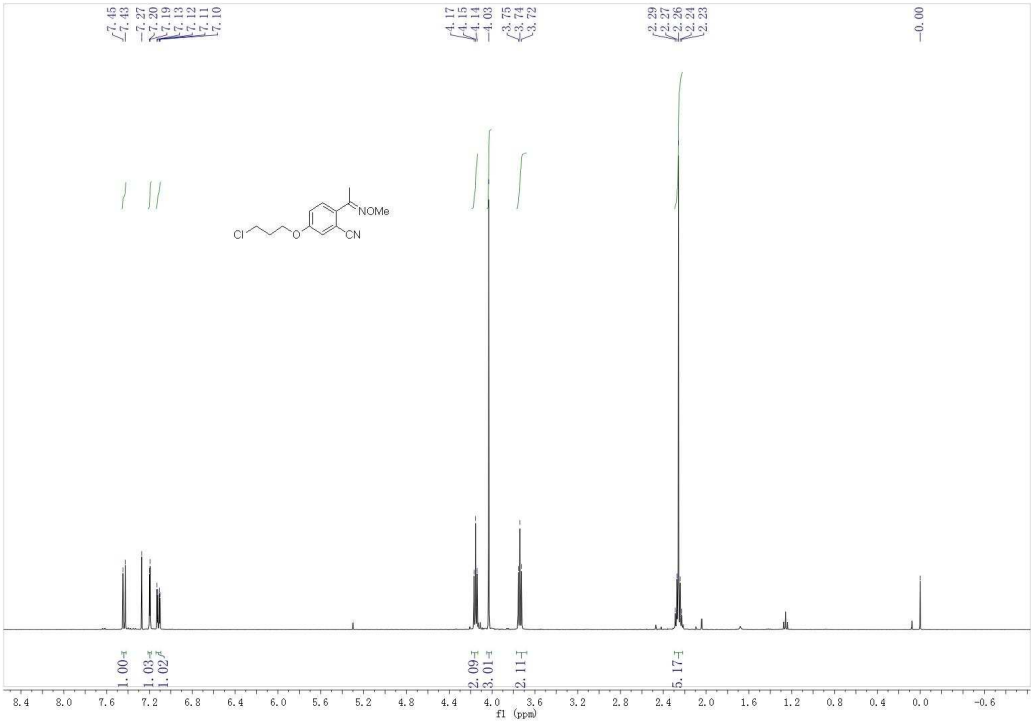

**5-(3-chloropropoxy)-2-(1-(methoxyimino)ethyl)benzonitrile (3o)**

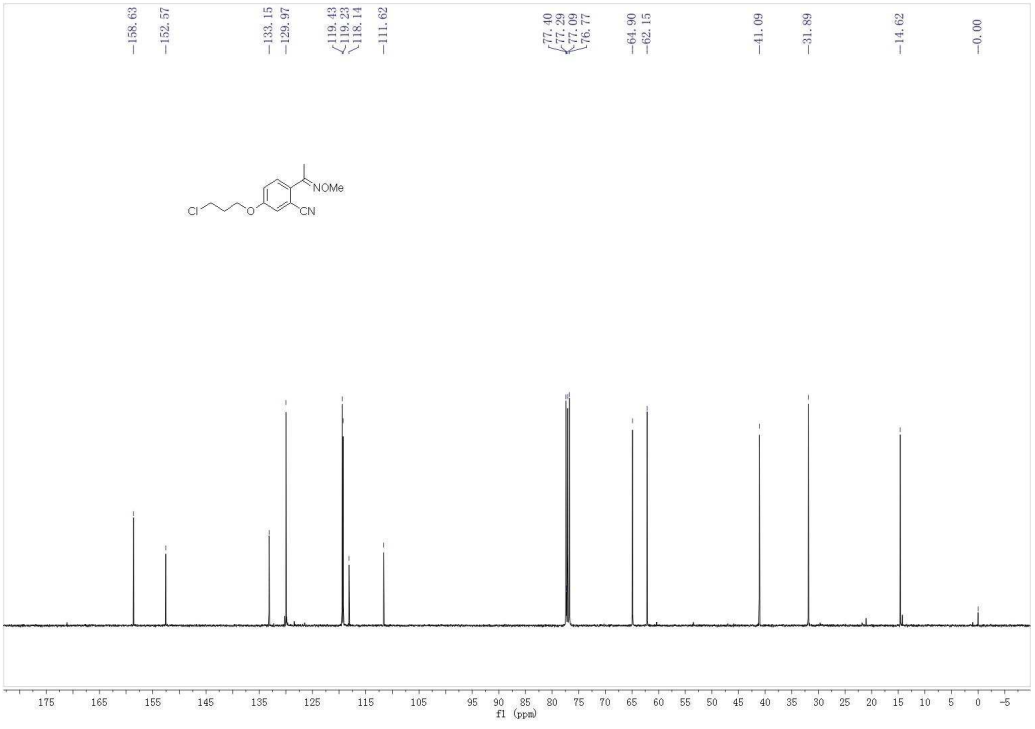
This compound was obtained in 79% (42mg) yield as white solid by following the general procedure (PE : EA=10 : 1)

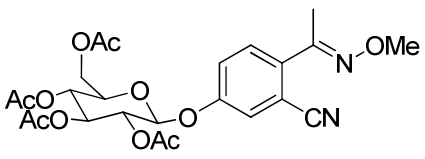
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7, 1H), 7.20 (d, *J* = 2.7, 1H), 7.12 (dd, *J* = 8.7, 2.7, 1H), 4.15 (t, *J* = 5.9, 2H), 4.03 (s, 3H), 3.74 (t, *J* = 6.0, 2H), 2.30 – 2.22 (m, 5H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.63, 152.57, 133.15, 129.97, 119.43, 119.23, 118.14, 111.62, 64.90, 62.15, 41.09, 31.89, 14.62.

HRMS calcd for $C_{13}H_{15}ClN_2O_2$ ($[M]^+$): 266.0822; found: 266.0793.




**2-(acetoxymethyl)-6-(3-cyano-4-(1-(methoxyimino)ethyl)phenoxy)tetrahydro-2H-pyran-3,4,5**

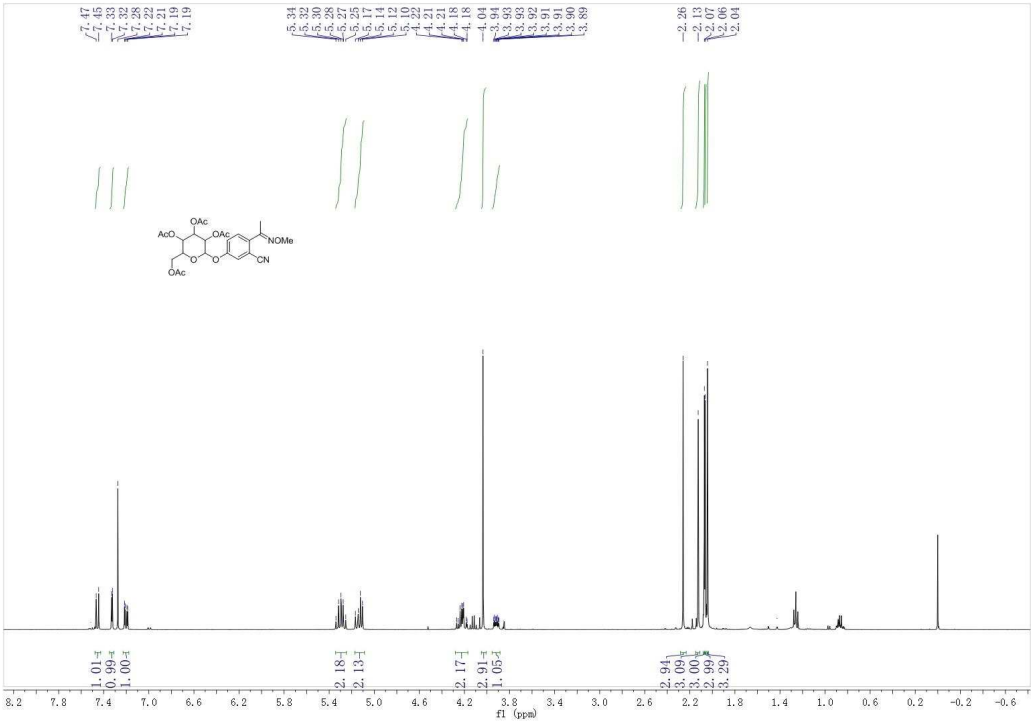
**-triyl triacetate (3p)**

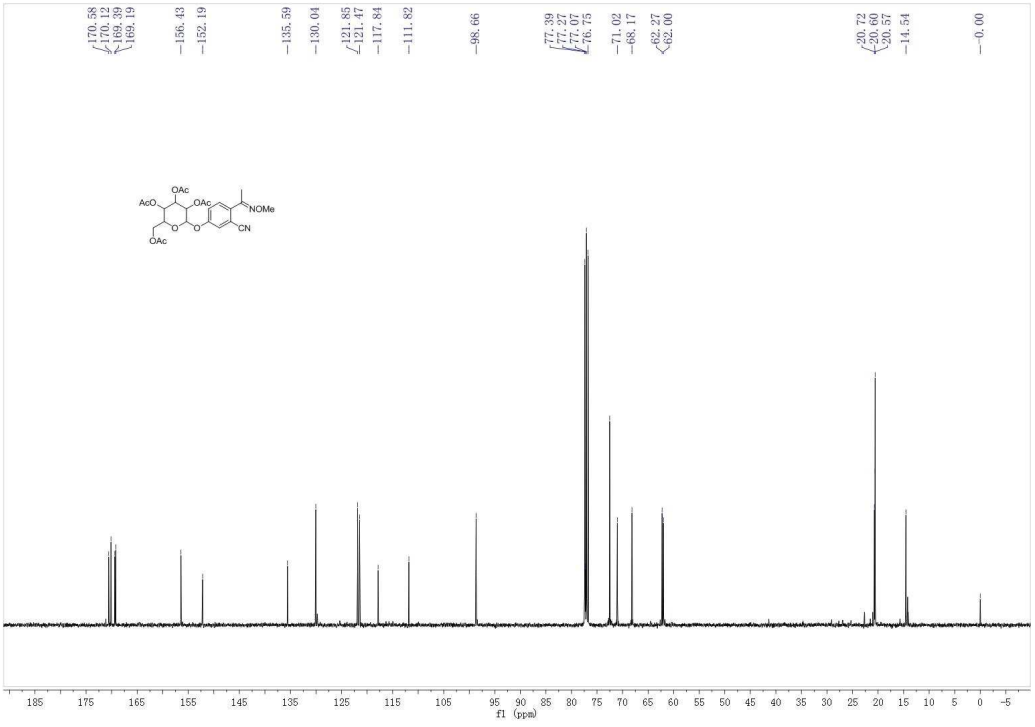
This compound was obtained in 69% (72mg) yield as white solid by following the general procedure (PE : EA=1 : 1)

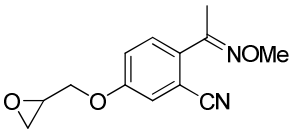
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.7, 1H), 7.33 (d, *J* = 2.6, 1H), 7.20 (dd, *J* = 8.7, 2.6, 1H), 5.35 – 5.23 (m, 2H), 5.13 (dd, *J* = 16.5, 8.7, 2H), 4.22 (qd, *J* = 12.3, 4.2, 2H), 4.04 (s, 3H), 3.92 (ddd, *J* = 10.0, 5.8, 2.6, 1H), 2.26 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.58, 170.12, 169.39, 169.19, 156.43, 152.19, 135.59, 130.04, 121.85, 121.47, 117.84, 111.82, 98.66, 72.53, 71.02, 68.17, 62.27, 62.00, 20.72, 20.60, 20.57, 14.54.

HRMS calcd for $C_{24}H_{28}N_2O_{11}$ ($[M+1]^+$): 521.1766; found: 521.1752.





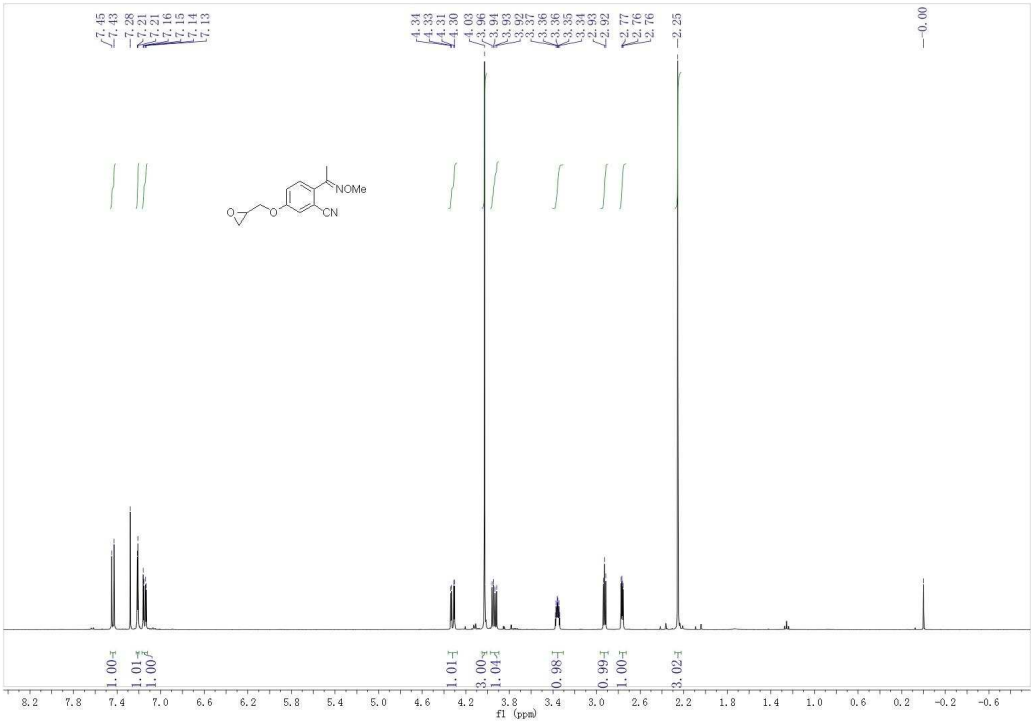

**2-(1-(methoxyimino)ethyl)-5-(oxiran-2-ylmethoxy)benzonitrile (3q)**

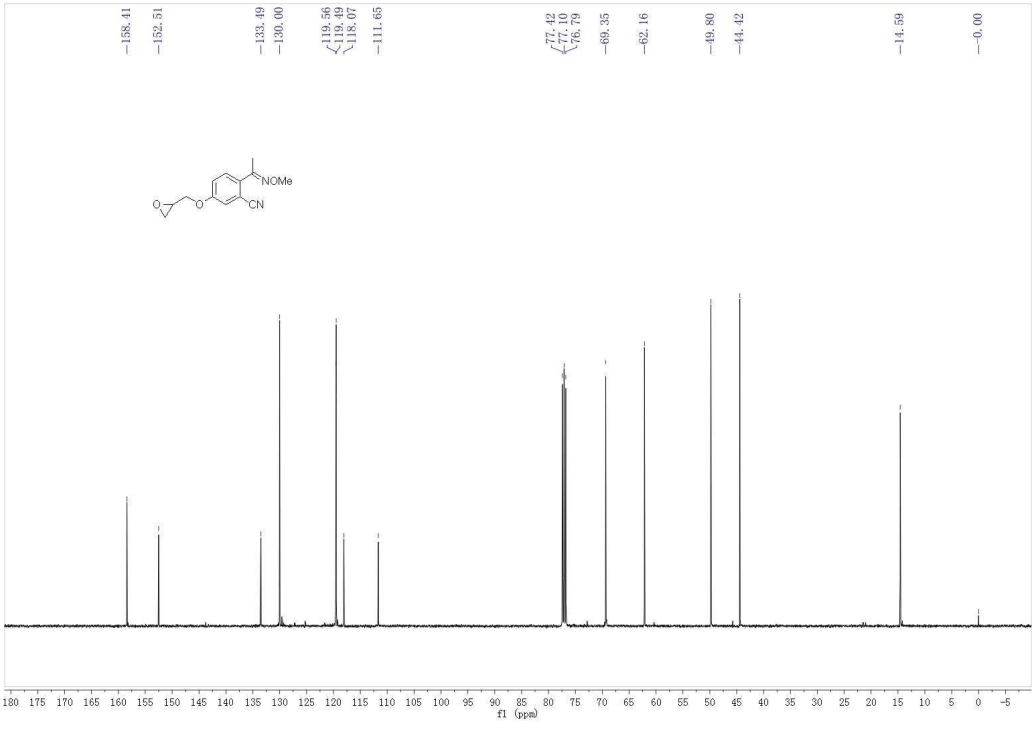
This compound was obtained in 80% (39.4mg) yield as white solid by following the general procedure (PE : EA=5 : 1)

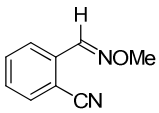
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7, 1H), 7.21 (d, *J* = 2.7, 1H), 7.15 (dd, *J* = 8.7, 2.7, 1H), 4.32 (dd, *J* = 11.1, 2.6, 1H), 4.03 (s, 3H), 3.94 (dd, *J* = 11.1, 6.0, 1H), 3.42 – 3.31 (m, 1H), 2.97 – 2.84 (m, 1H), 2.77 (dd, *J* = 4.8, 2.6, 1H), 2.25 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.41, 152.51, 133.49, 130.00, 119.56, 119.49, 118.07, 111.65, 69.35, 62.16, 49.80, 44.42, 14.59.

HRMS calcd for $C_{13}H_{14}N_2O_3$ ($[M+1]^+$): 247.1077; found: 247.1070



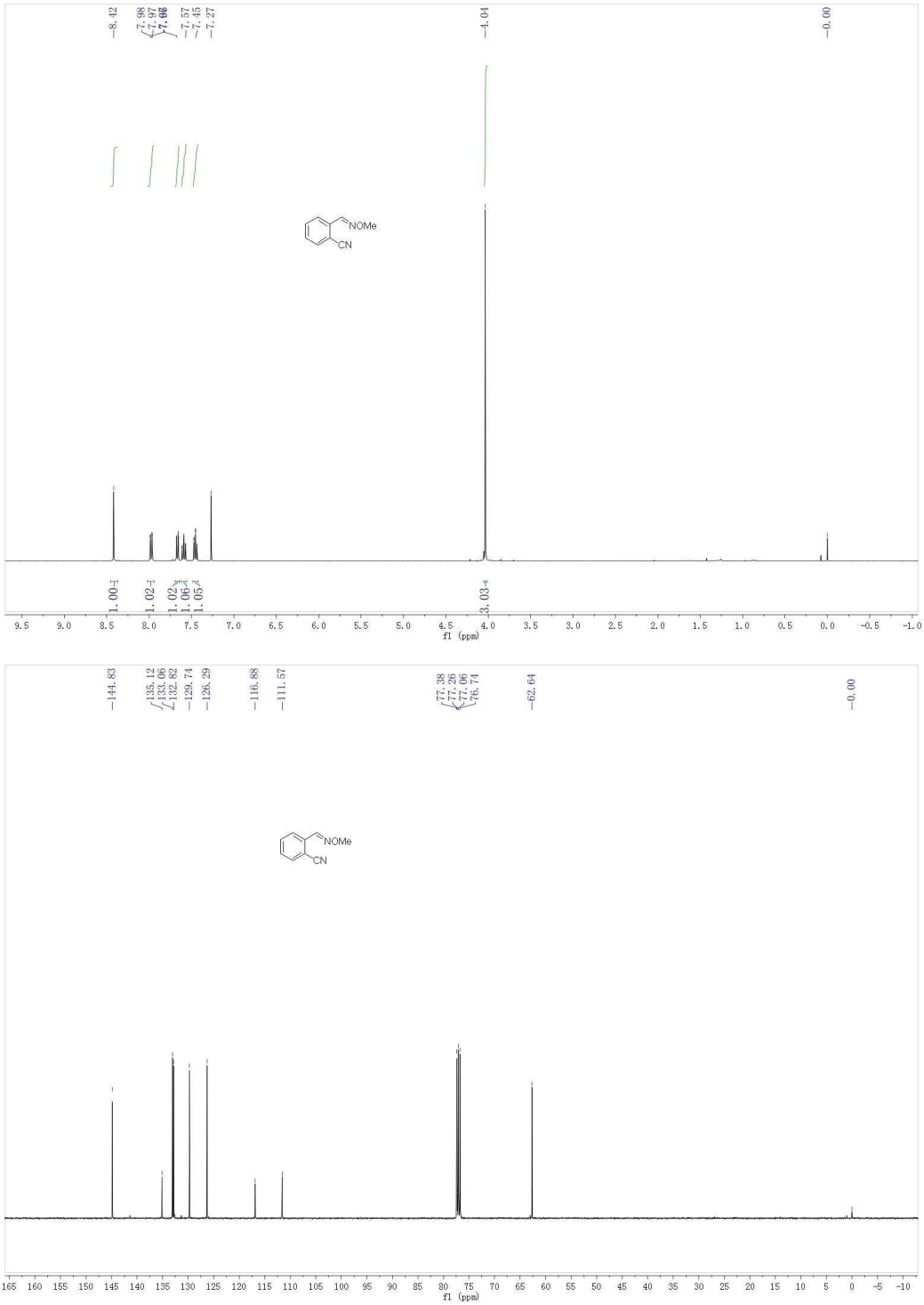

**2-((methoxyimino)methyl)benzonitrile (3r)**

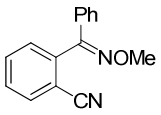
This compound was obtained in 69% (22mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.01 – 7.92 (m, 1H), 7.74 – 7.62 (m, 1H), 7.63 – 7.56 (m, 1H), 7.45 (td, *J* = 7.6, 1.2, 1H), 4.04 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.83, 135.12, 133.06, 132.82, 129.74, 126.29, 116.88, 111.57, 62.64.

HRMS calcd for $C_9H_8N_2O$ ([M]$^+$): 160.0637; found: 160.0645.





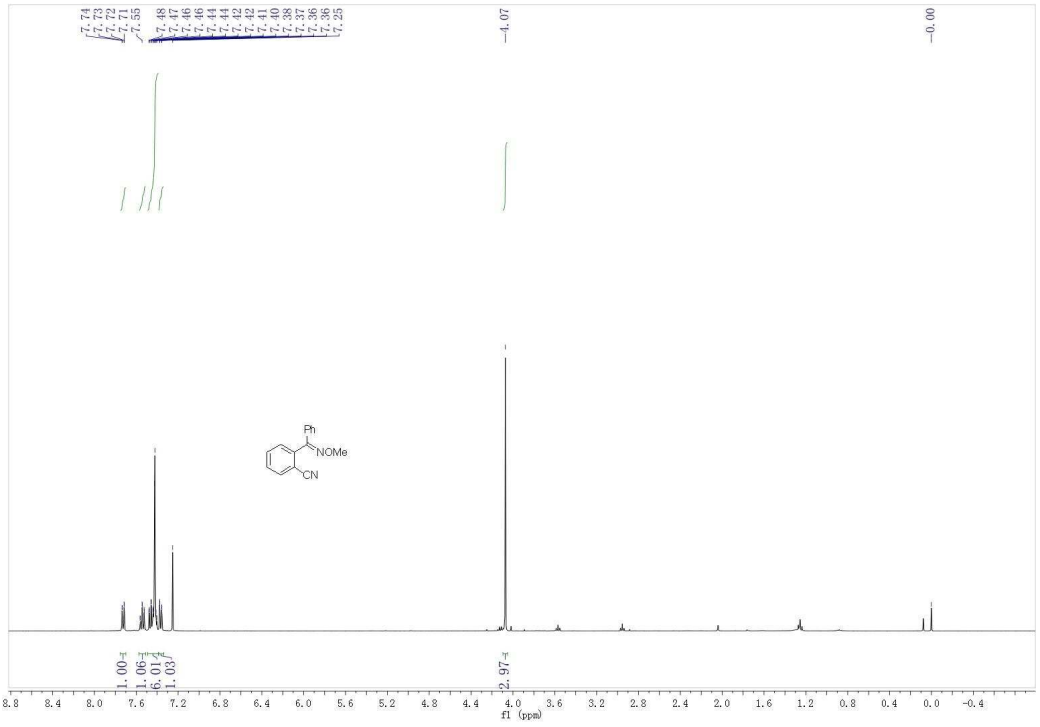

**2-((methoxyimino)(phenyl)methyl)benzonitrile (3s)**

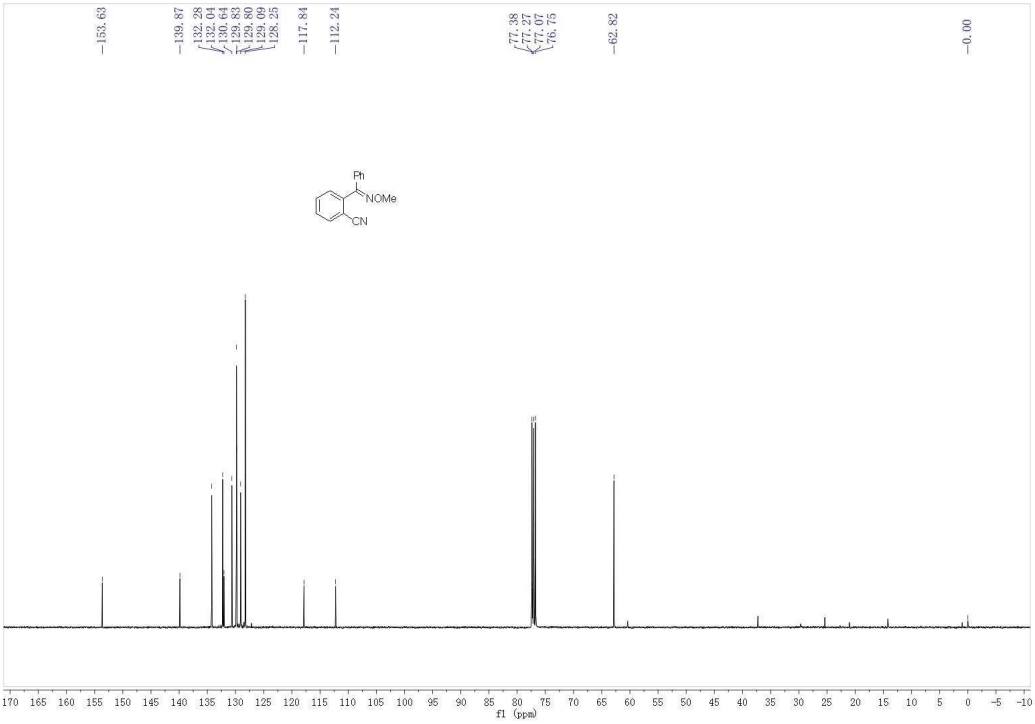
This compound was obtained in 57% (27mg) yield as white solid by following the general procedure (PE : EA=30 : 1)

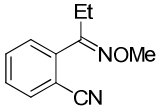
1H NMR (400 MHz, CDCl3) δ 7.73 (dd, J = 7.7, 1.2, 1H), 7.54 (td, J = 7.7, 1.4, 1H), 7.49 – 7.39 (m, 6H), 7.37 (dd, J = 7.7, 1.0, 1H), 4.07 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 153.63, 139.87, 134.22, 132.28, 132.04, 130.64, 129.83, 129.80, 129.09, 128.25, 117.84, 112.24, 62.82.

HRMS calcd for $C_{15}H_{12}N_2O$ ([M]$^+$): 236.0950; found: 236.0951.





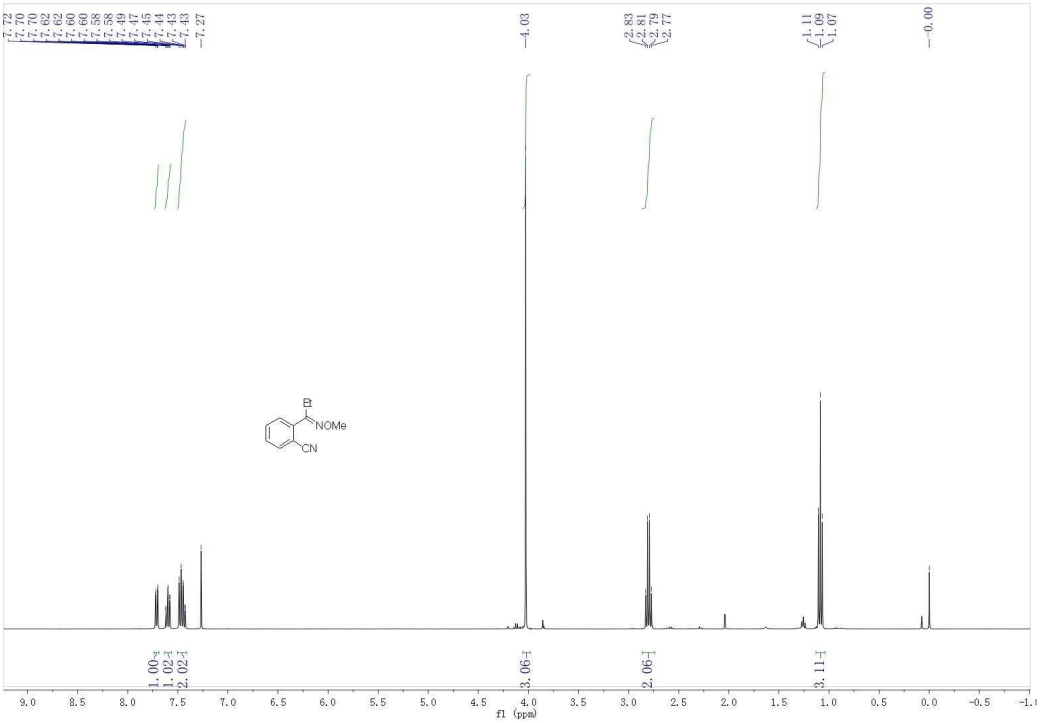

**2-(1-(methoxyimino)propyl)benzonitrile (3t)**

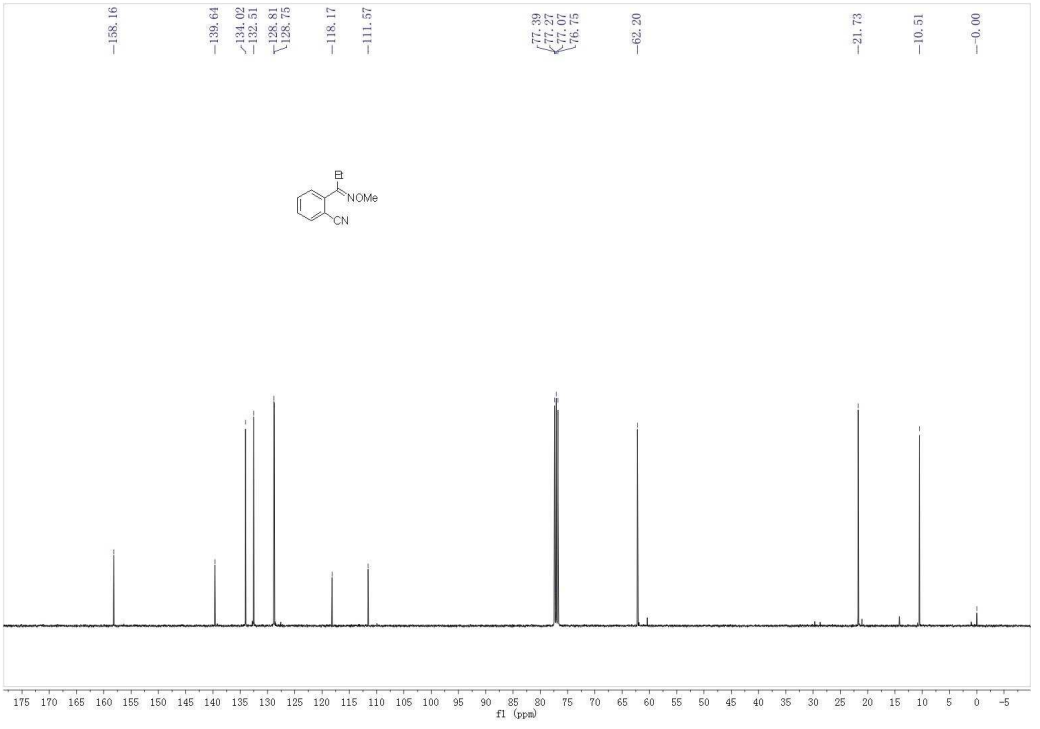
This compound was obtained in 81% (31mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

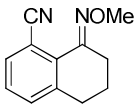
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 7.7, 1.3, 1H), 7.60 (td, *J* = 7.7, 1.3, 1H), 7.51 – 7.39 (m, 2H), 4.03 (s, 3H), 2.80 (q, *J* = 7.6, 2H), 1.09 (t, *J* = 7.6, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 158.16, 139.64, 134.02, 132.51, 128.81, 128.75, 118.17, 111.57, 62.20, 21.73, 10.51.

HRMS calcd for $C_{11}H_{12}N_2O$ ($[M]^+$): 188.0950; found: 188.0948.




**8-(methoxyimino)-5,6,7,8-tetrahydronaphthalene-1-carbonitrile (3u)**

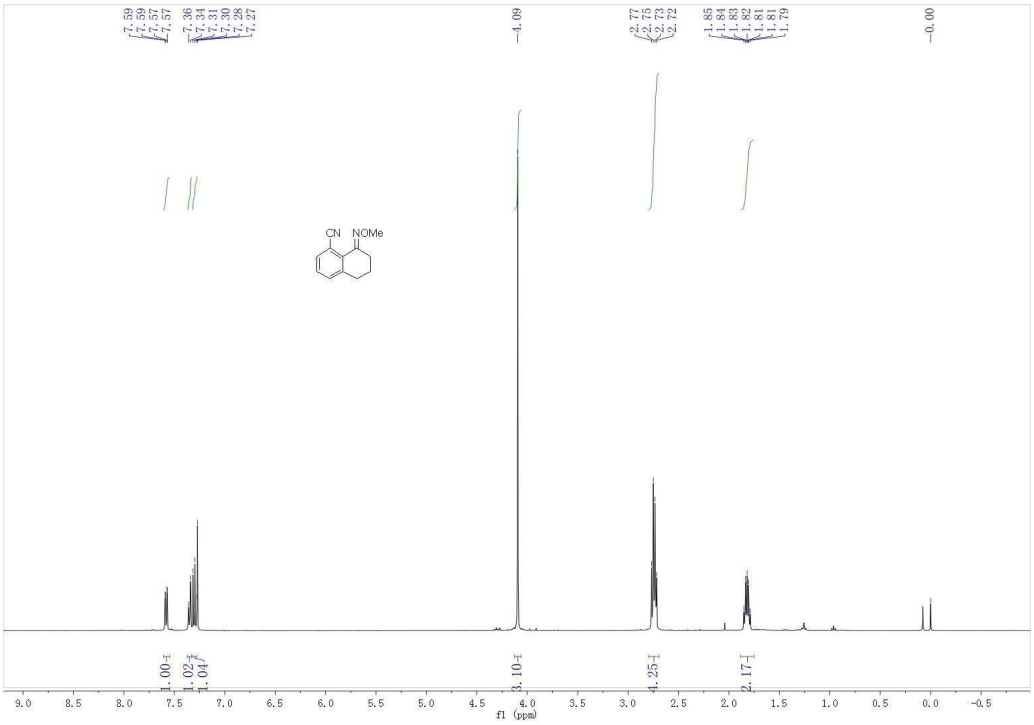
This compound was obtained in 78% (31 mg) yield as thick oil by following the general procedure

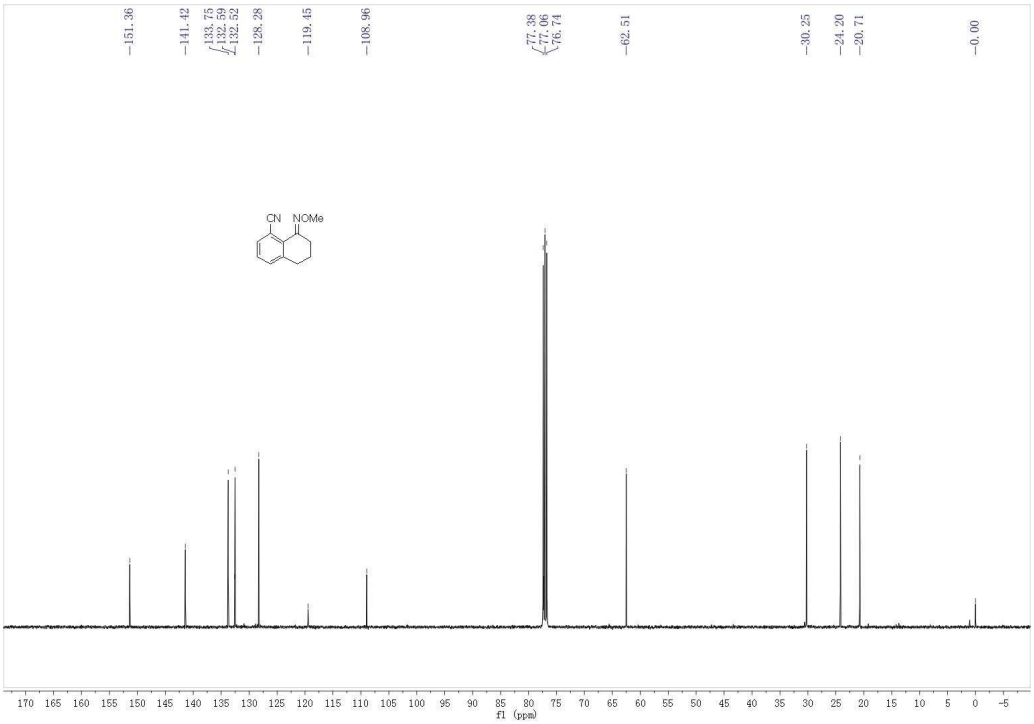
(PE : EA=30 : 1)

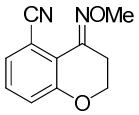
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.6, 1.2, 1H), 7.35 (d, *J* = 7.0, 1H), 7.30 (t, *J* = 7.6, 1H), 4.09 (s, 3H), 2.74 (dd, *J* = 13.3, 6.6, 4H), 1.89 – 1.75 (m, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 151.36, 141.42, 133.75, 132.59, 132.52, 128.28, 119.45, 108.96, 62.51, 30.25, 24.20, 20.71.

HRMS calcd for $C_{12}H_{12}N_2O$ ($[M]^+$): 200.0950; found: 200.0958.





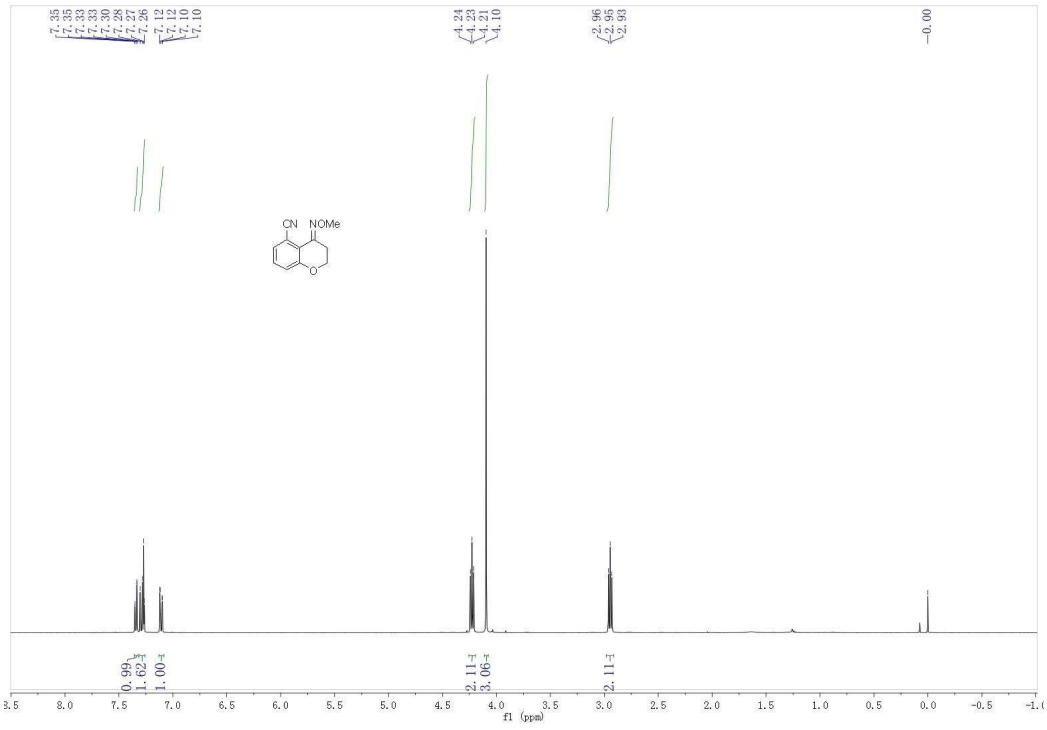

**4-(methoxyimino)chroman-5-carbonitrile (3v)**

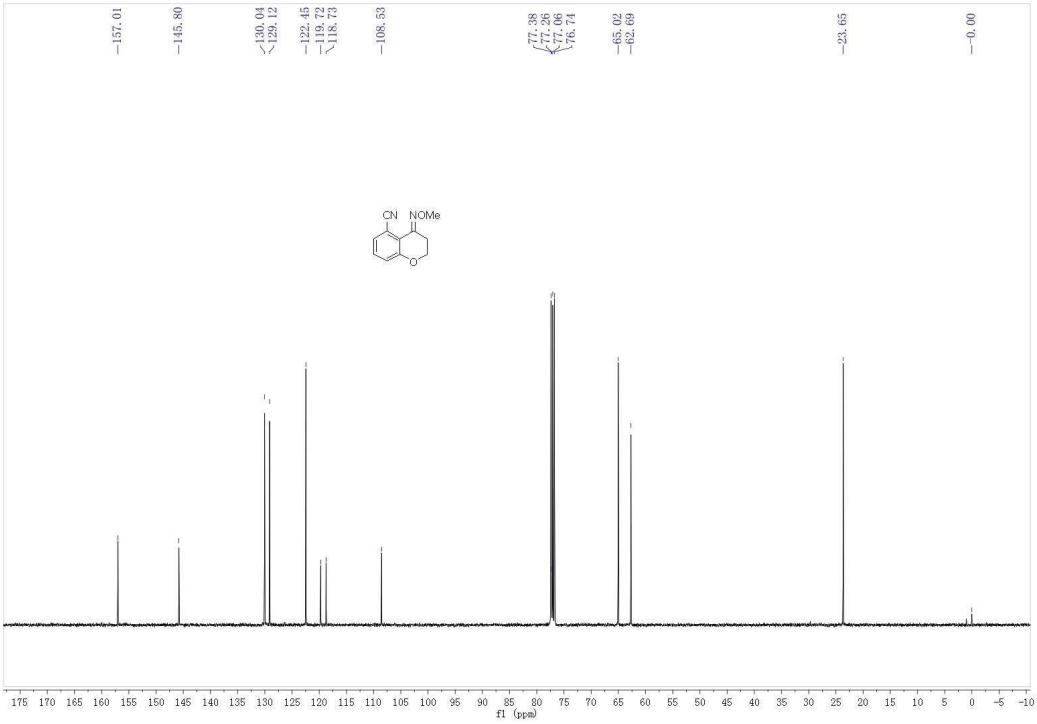
This compound was obtained in 82% (33mg) yield as white solid by following the general procedure (PE : EA=10 : 1)

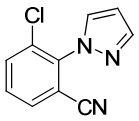
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.6, 1.4, 1H), 7.28 (t, *J* = 8.2, 2H), 7.11 (dd, *J* = 8.2, 1.4, 1H), 4.23 (t, *J* = 6.3, 2H), 4.10 (s, 3H), 2.95 (t, *J* = 6.3, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.01, 145.80, 130.04, 129.12, 122.45, 119.72, 118.73, 108.53, 65.02, 62.69, 23.65.

HRMS calcd for $C_{11}H_{10}N_2O_2$ ($[M]^+$): 202.0742; found: 202.0742.





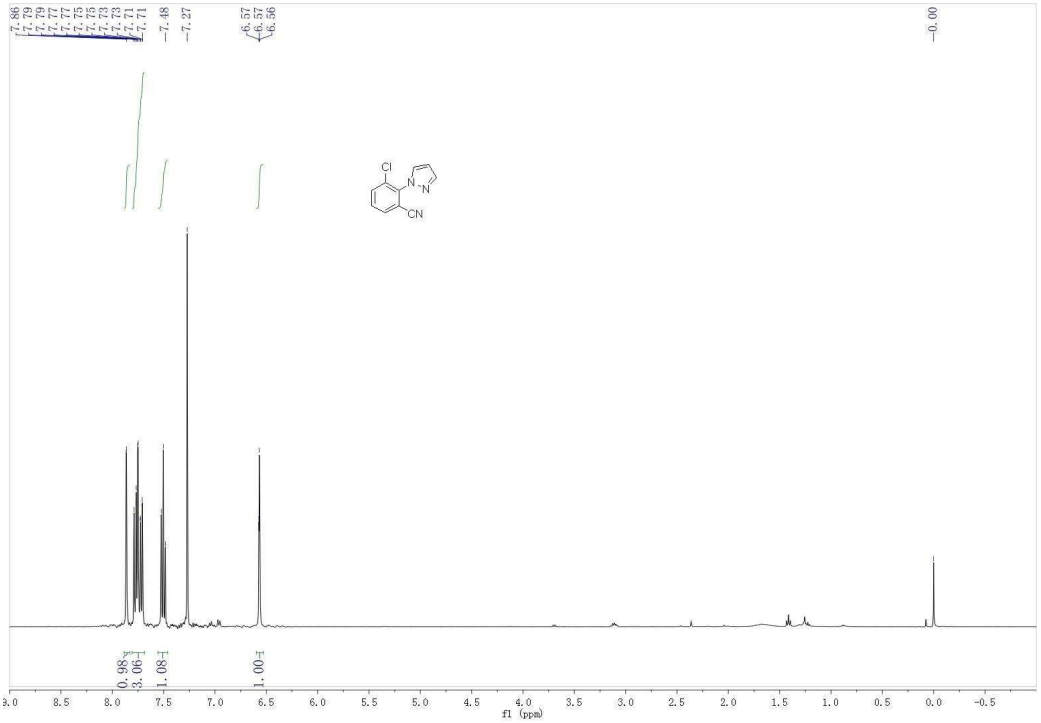

**3-chloro-2-(1H-pyrazol-1-yl)benzonitrile (3w)**

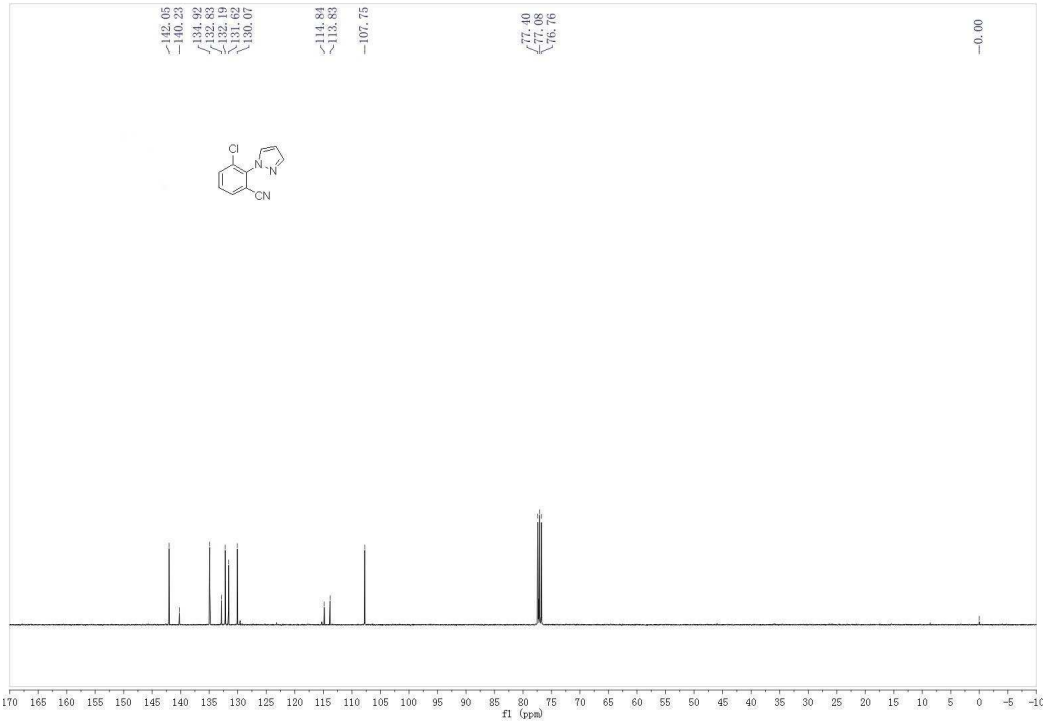
This compound was obtained in 84% (34mg) yield as thick oil by following the general procedure (PE : EA=15 : 1)

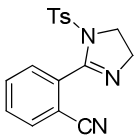
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.5, 1H), 7.80 – 7.68 (m, 3H), 7.50 (t, *J* = 8.0, 1H), 6.57 (t, *J* = 2.1, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.05, 140.23, 134.92, 132.83, 132.19, 131.62, 130.07, 114.84, 113.83, 107.75.

HRMS calcd for $C_{10}H_6ClN_3$ ($[M]^+$): 203.0250; found: 203.0240.



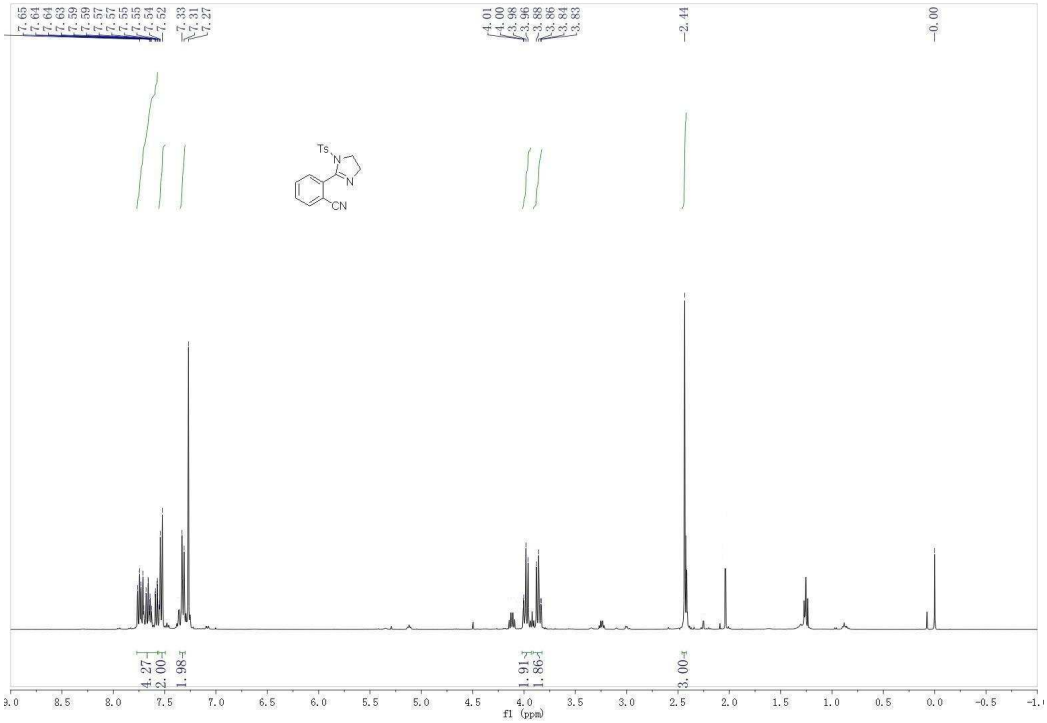

**2-(1-tosyl-4,5-dihydro-1H-imidazol-2-yl)benzonitrile (3x)**

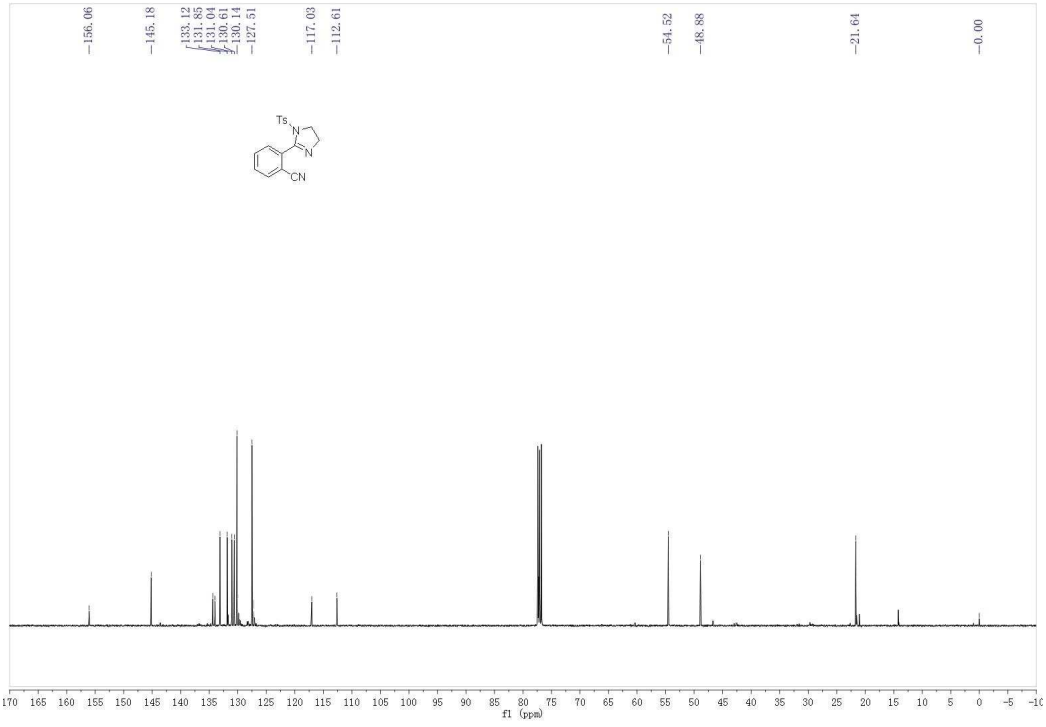
This compound was obtained in 58% (38mg) yield as white solid by following the general procedure (PE : EA=5 : 1)

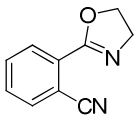
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.55 (m, 4H), 7.53 (d, *J* = 8.3, 2H), 7.32 (d, *J* = 8.3, 2H), 3.99 (dd, *J* = 13.6, 5.0, 2H), 3.85 (dd, *J* = 13.6, 5.0, 2H), 2.44 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 156.06, 145.18, 134.38, 134.00, 133.12, 131.85, 131.04, 130.61, 130.14, 127.51, 117.03, 112.61, 54.52, 48.88, 21.64.

HRMS calcd for $C_{17}H_{15}N_3O_2S$ ([M]$^+$): 325.0885; found: 325.0888.





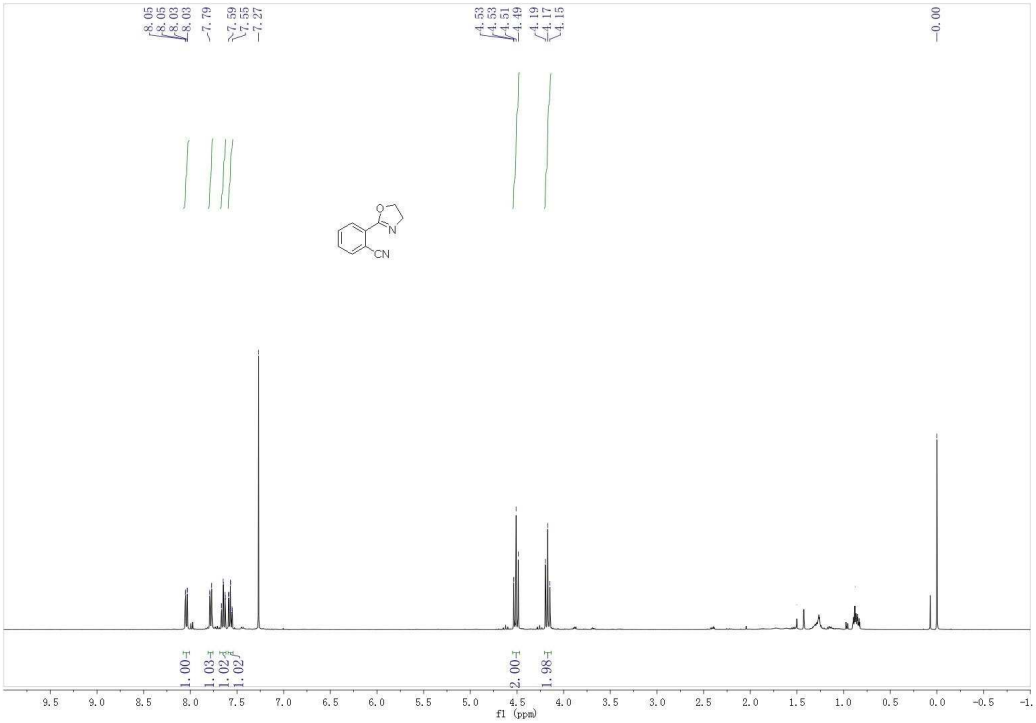

**2-(4,5-dihydrooxazol-2-yl)benzonitrile (3y)**

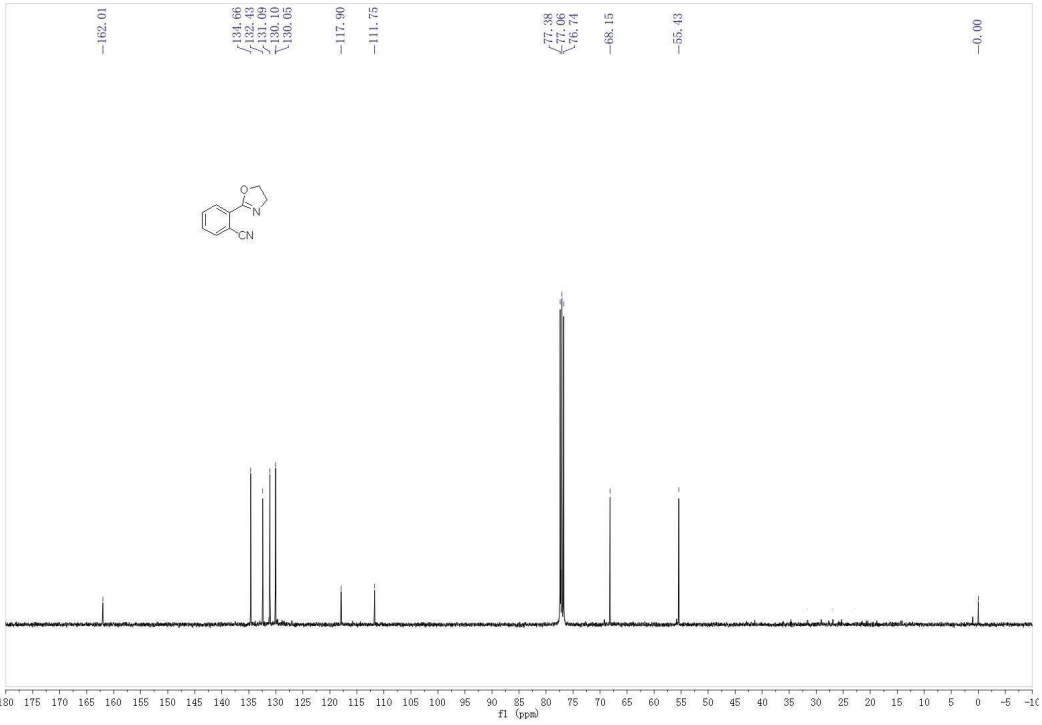
This compound was obtained in 76% (26mg) yield as white solid by following the general procedure (PE : EA=10 : 1)

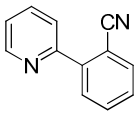
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.7, 1.0, 1H), 7.78 (dd, *J* = 7.7, 1.1, 1H), 7.65 (td, *J* = 7.7, 1.4, 1H), 7.57 (td, *J* = 7.7, 1.4, 1H), 4.52 (dd, *J* =9.6, 2H), 4.17 (t, *J* = 9.6, 2H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.01, 134.66, 132.43, 131.09, 130.10, 130.05, 117.90, 111.75, 68.15, 55.43.

HRMS calcd for $C_{10}H_8N_2O$ ($[M]^+$): 172.0637; found: 172.0629.



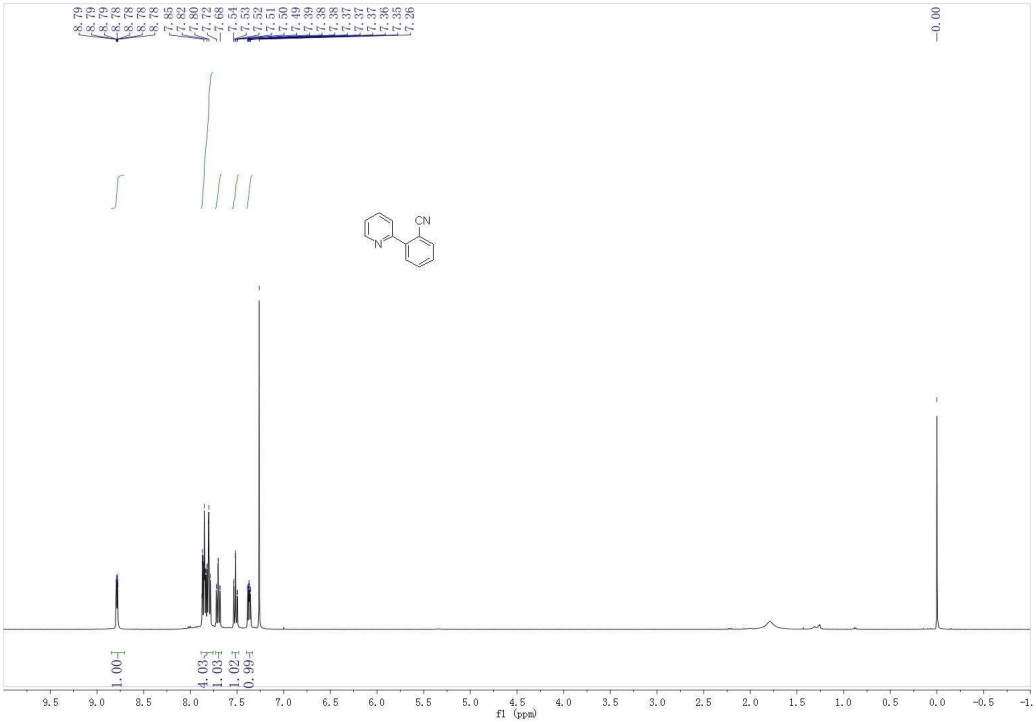

**2-(pyridin-2-yl)benzonitrile (3z)**

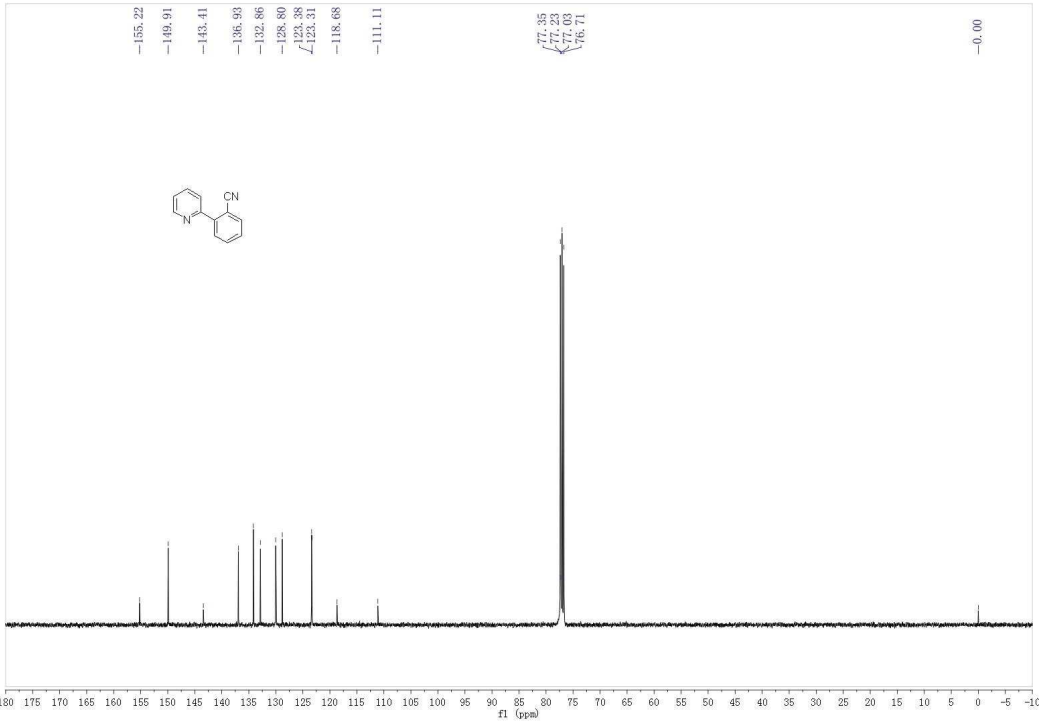
This compound was obtained in 64% (23mg) yield as white solid by following the general

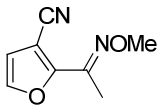
procedure (PE : EA=10 : 1)

$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.82 – 8.76 (m, 1H), 7.91 – 7.77 (m, 4H), 7.70 (td, *J* = 7.7, 1.3, 1H), 7.52 (td, *J* = 7.6, 1.2, 1H), 7.37 (ddd, *J* = 7.4, 4.9, 1.2, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.22, 149.91, 143.41, 136.93, 134.15, 132.86, 130.03, 128.80, 123.38, 123.31, 118.68, 111.11. Spectral data matched those previously reported





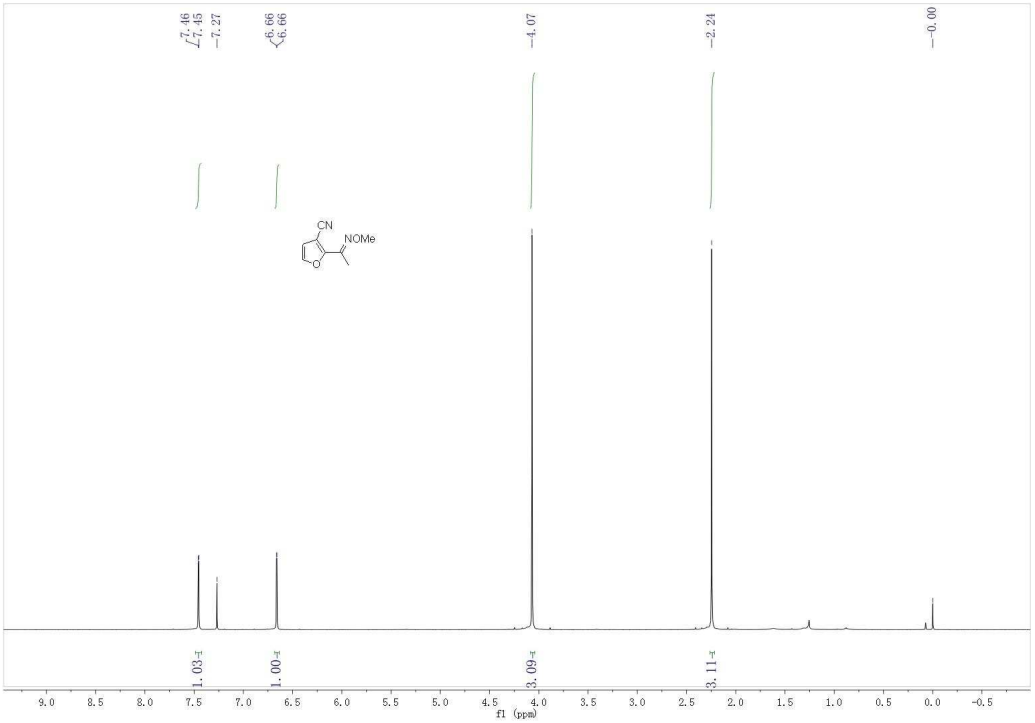

**2-(1-(methoxyimino)ethyl)furan-3-carbonitrile (4a)**

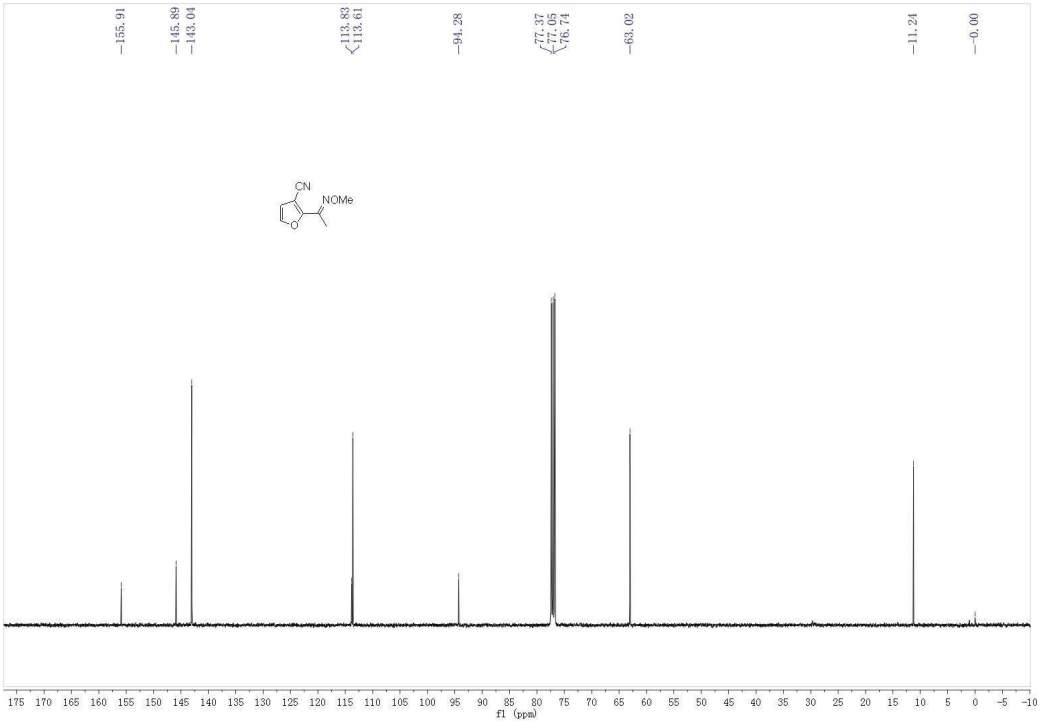
This compound was obtained in 67% (22mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

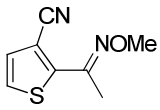
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, $J$ = 2.0, 1H), 6.66 (d, $J$ = 2.0, 1H), 4.07 (s, 3H), 2.24 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 155.91, 145.89, 143.04, 113.83, 113.61, 94.28, 63.02, 11.24.

HRMS calcd for $C_8H_8N_2O_2$ ($[M]^+$): 164.0586; found: 164.0577.





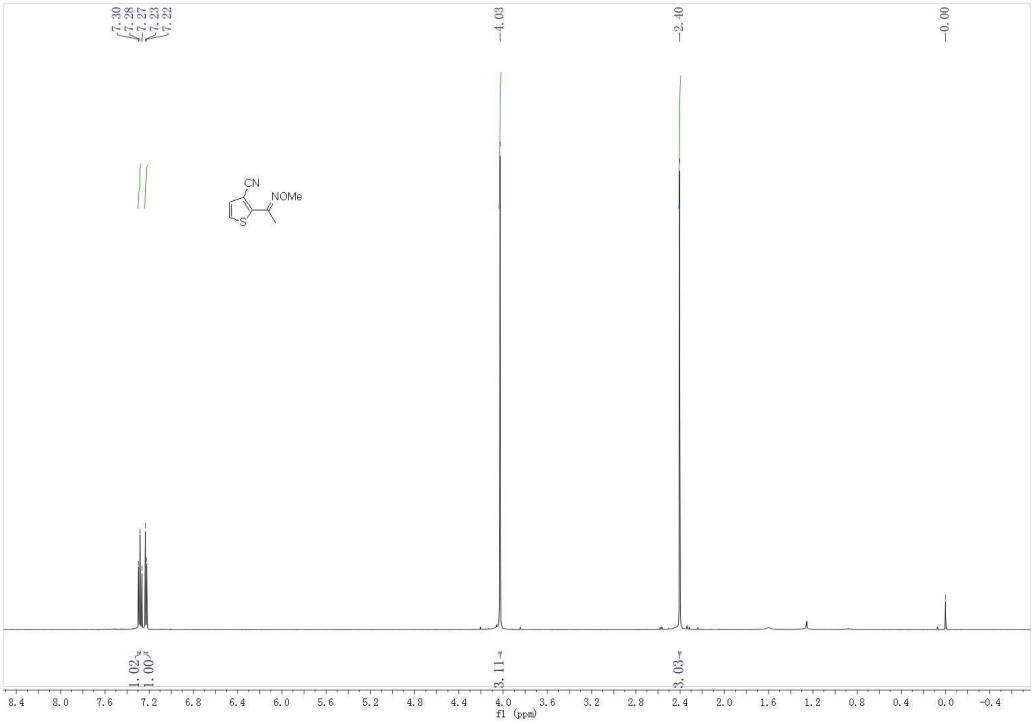

**2-(1-(methoxyimino)ethyl)thiophene-3-carbonitrile (4b)**

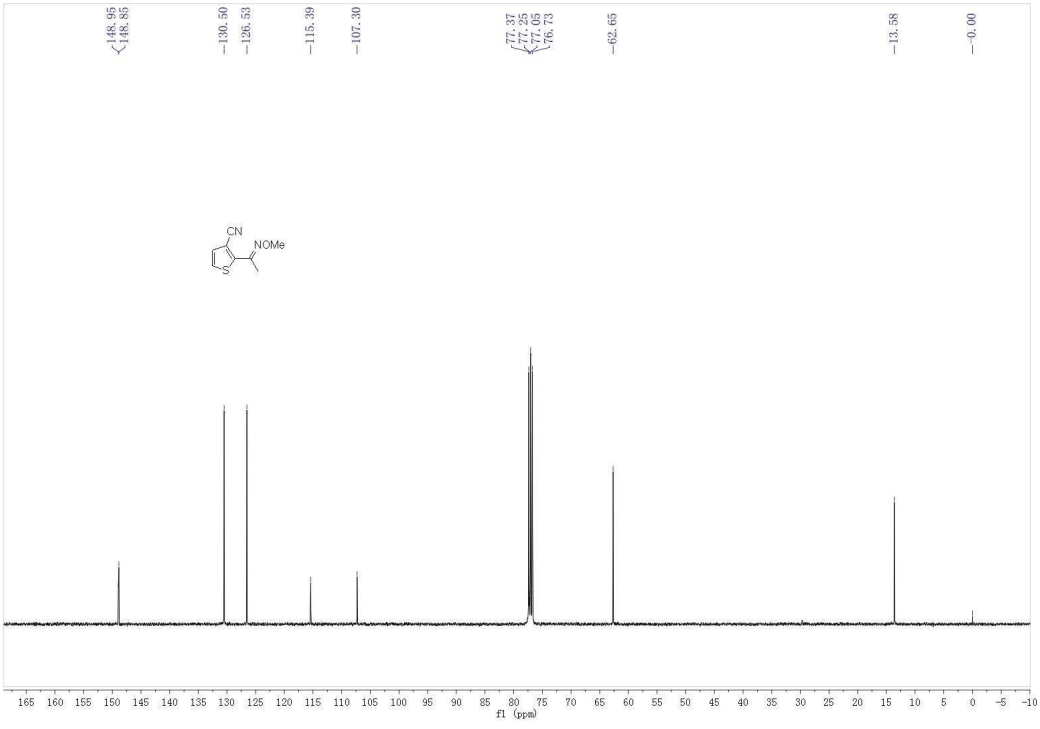
This compound was obtained in 63% (23mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

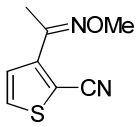
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 5.3, 1H), 7.23 (d, *J* = 5.3, 1H), 4.03 (s, 3H), 2.40 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 148.95, 148.85, 130.50, 126.53, 115.39, 107.30, 62.65, 13.58.

HRMS calcd for $C_8H_8N_2OS$ ($[M]^+$): 180.0357; found: 180.0354.



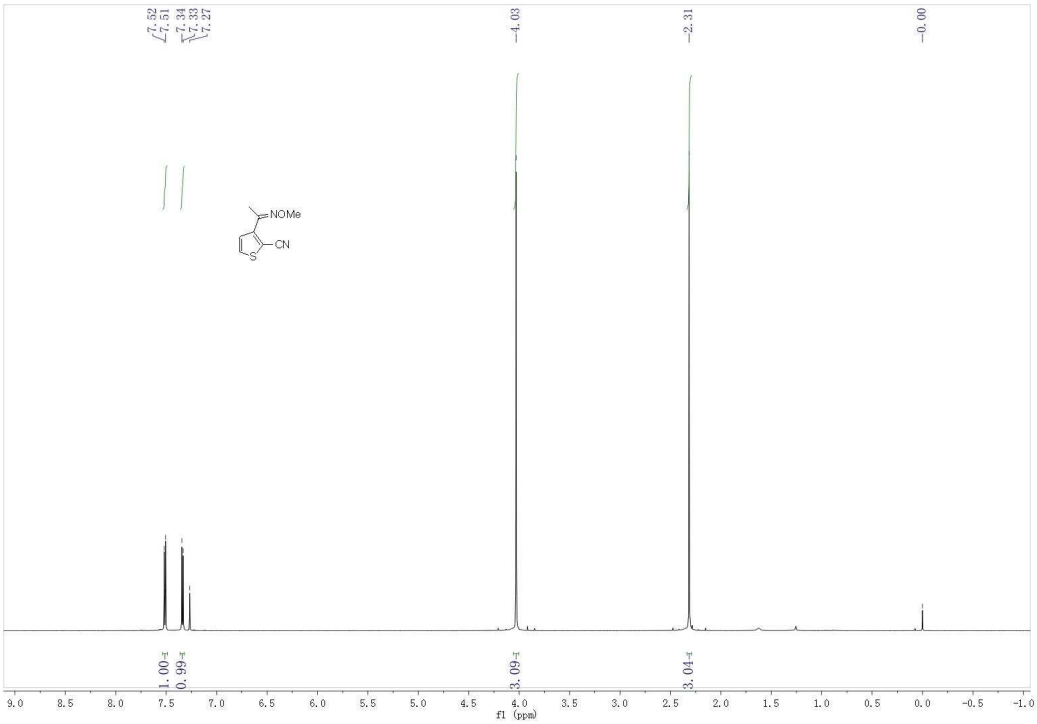

**3-(1-(methoxyimino)ethyl)thiophene-2-carbonitrile (4c)**

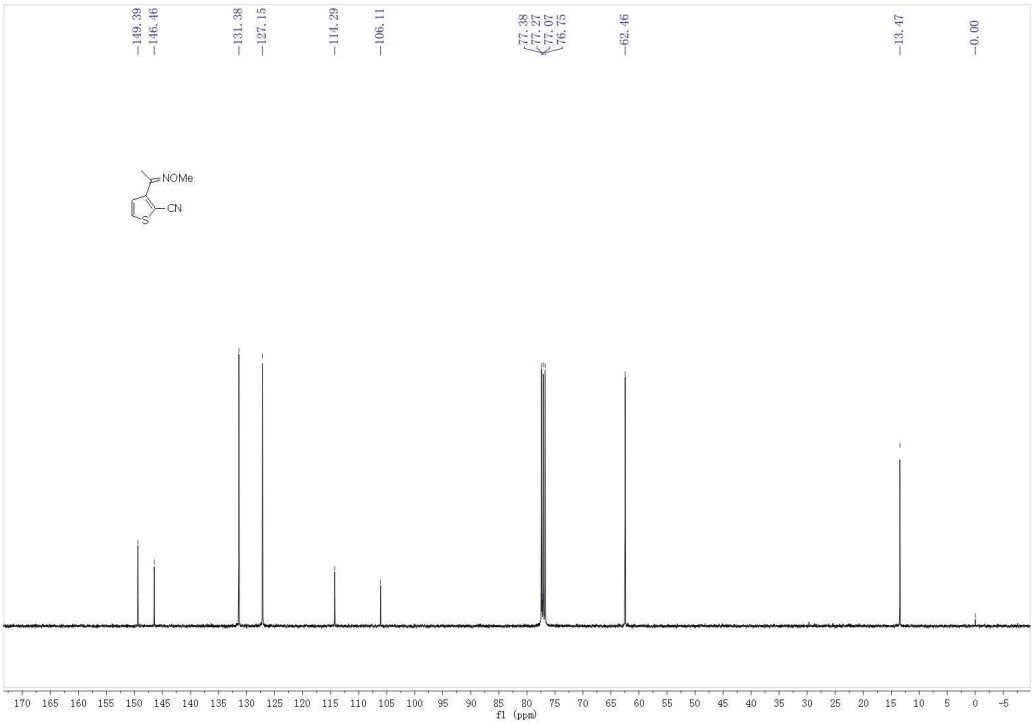
This compound was obtained in 72% (26mg) yield as thick oil by following the general procedure (PE : EA=30 : 1)

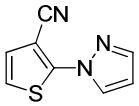
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, $J$ = 5.3, 1H), 7.34 (d, $J$ = 5.3, 1H), 4.03 (s, 3H), 2.31 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.39, 146.46, 131.38, 127.15, 114.29, 106.11, 62.46, 13.47.

HRMS calcd for $C_8H_8N_2OS$ ($[M]^+$): 180.0357; found: 180.0349.





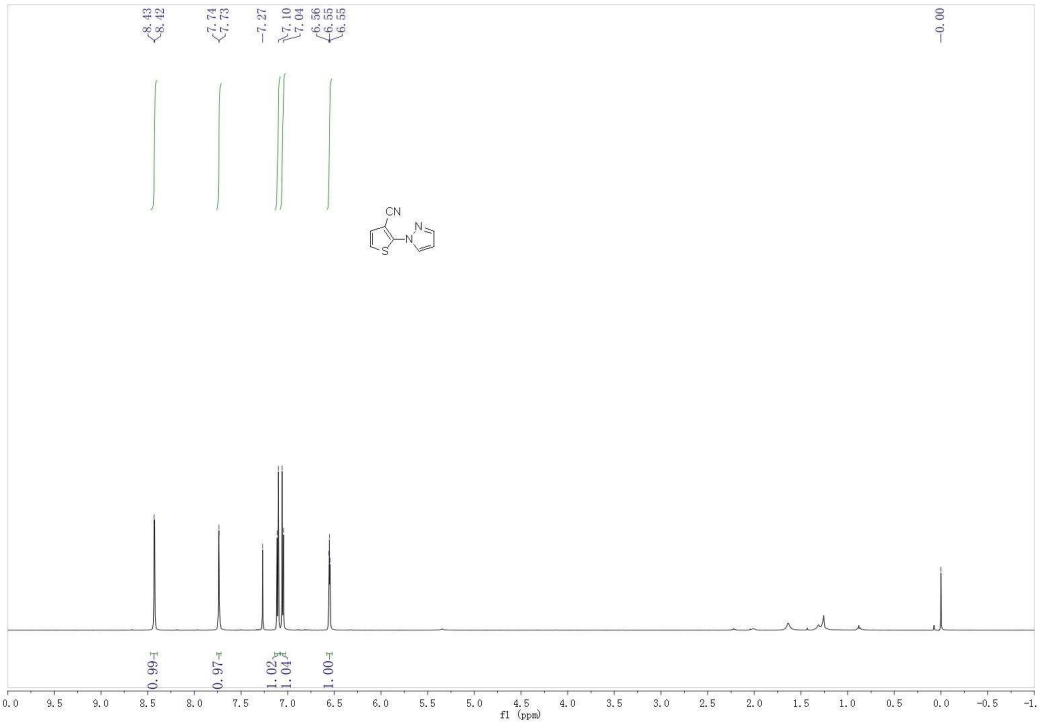
**2-(1H-pyrazol-1-yl)thiophene-3-carbonitrile (4d)**

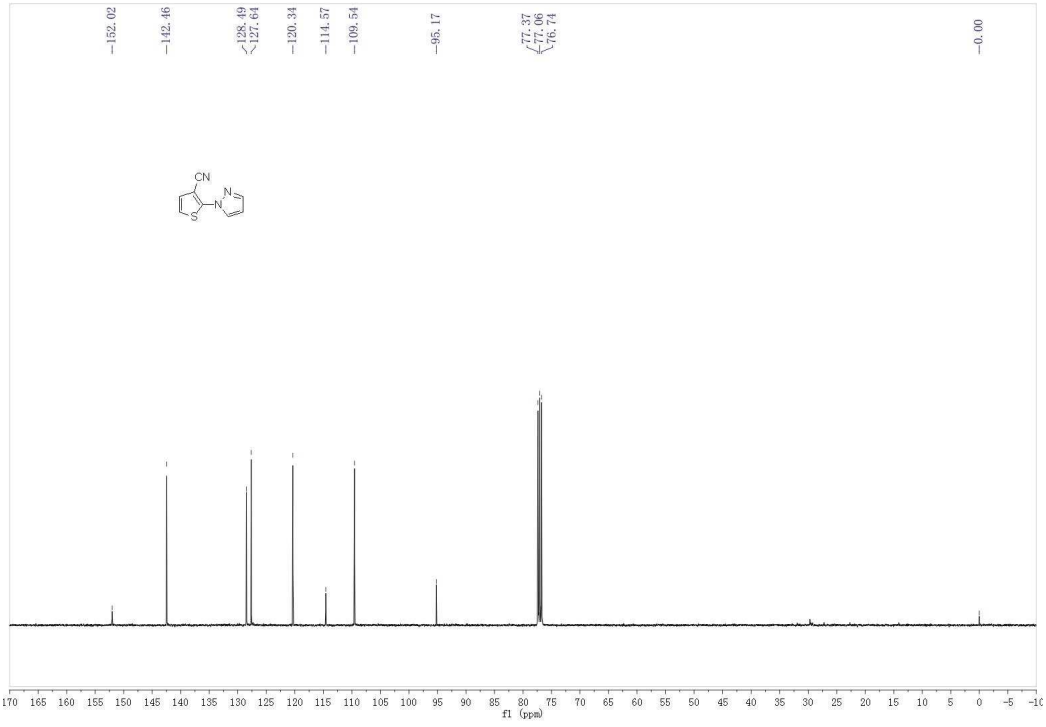
This compound was obtained in 85% (30mg) yield as thick oil by following the general procedure (PE : EA=10 : 1)

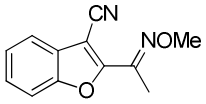
$^1$H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.6, 1H), 7.74 (d, *J* = 1.6, 1H), 7.11 (d, *J* = 5.7, 1H), 7.05 (d, *J* = 5.7, 1H), 6.58 – 6.50 (m, 1H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 152.02, 142.46, 128.49, 127.64, 120.34, 114.57, 109.54, 95.17.

HRMS calcd for $C_8H_5N_3S$ ($[M]^+$): 175.0204; found: 175.0200.





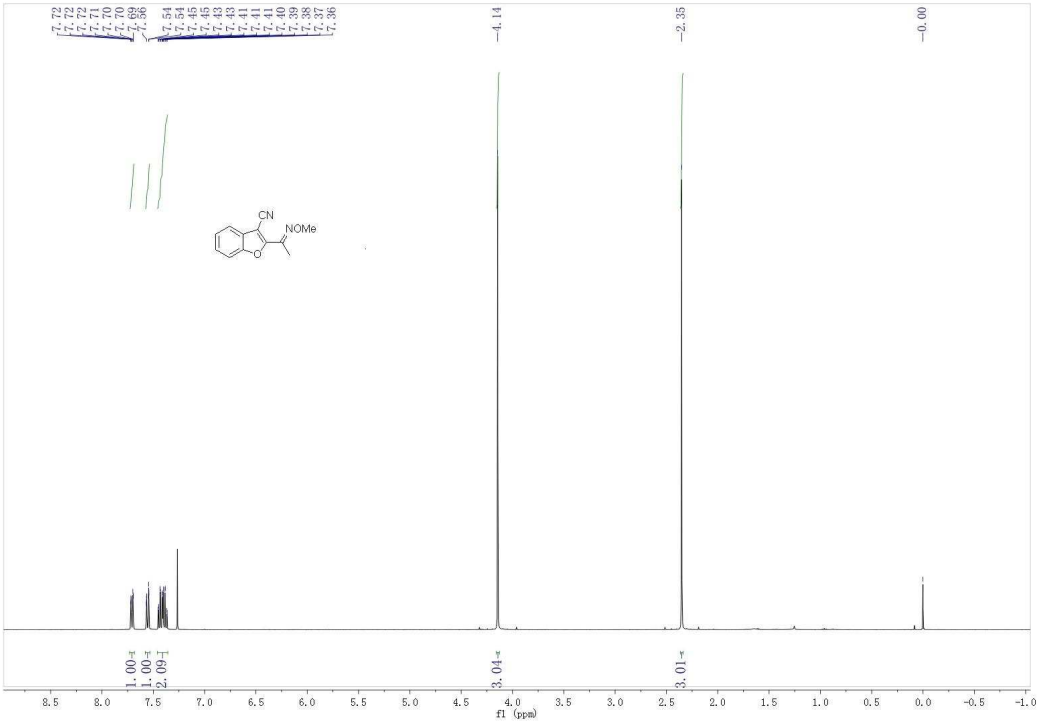

**2-(1-(methoxyimino)ethyl)benzofuran-3-carbonitrile (4e)**

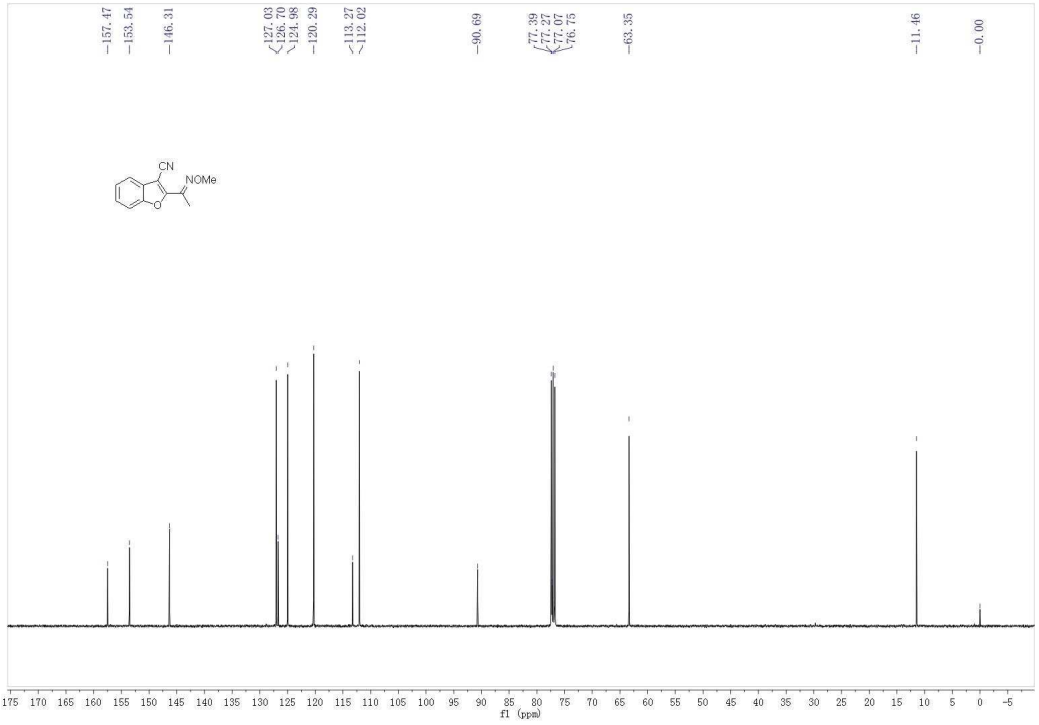
This compound was obtained in 75% (32mg) yield as thick oil by following the general procedure (PE : EA=20 : 1)

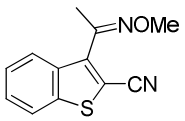
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 1H), 7.59 – 7.49 (m, 1H), 7.41 (m, 2H), 4.14 (s, 3H), 2.35 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 157.47, 153.54, 146.31, 127.03, 126.70, 124.98, 120.29, 113.27, 112.02, 90.69, 63.35, 11.46.

HRMS calcd for $C_{12}H_{10}N_2O_2$ ($[M]^+$): 214.0742; found: 214.0732.




**3-(1-(methoxyimino)ethyl)benzo[b]thiophene-2-carbonitrile (4f)**

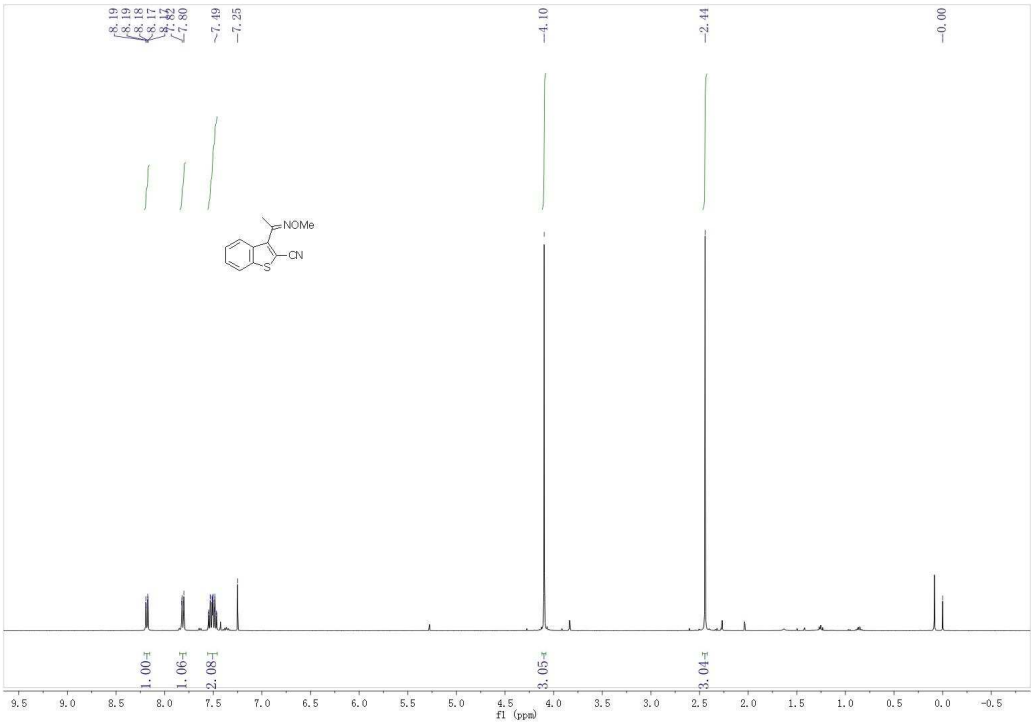
This compound was obtained in 87% (40mg) yield as thick oil by following the general procedure

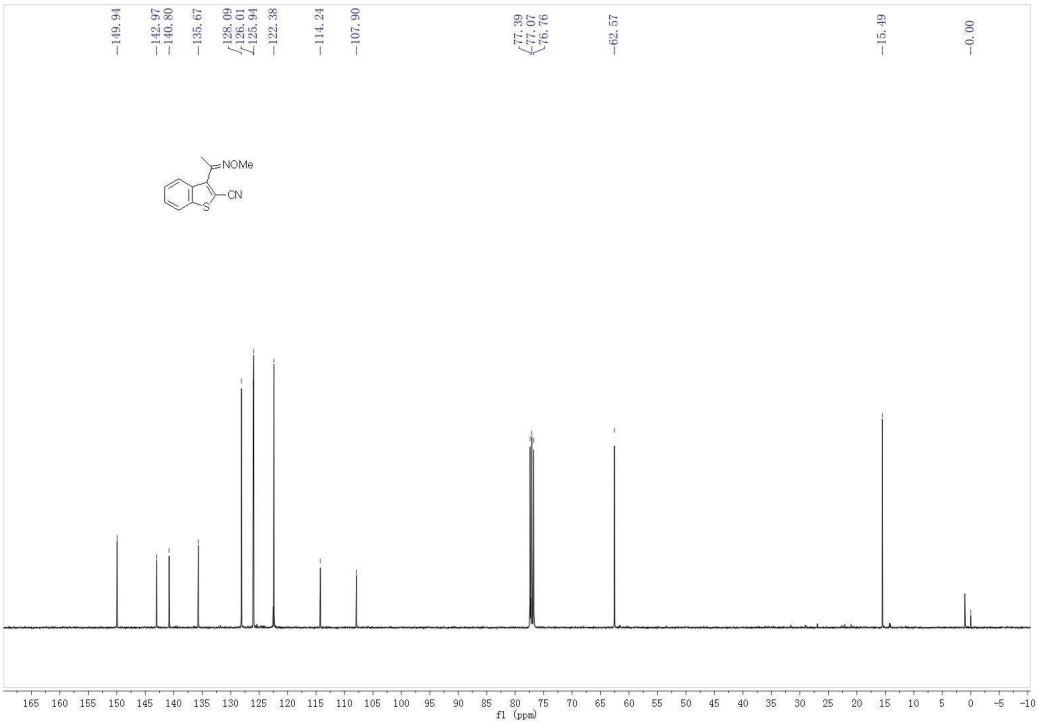
(PE : EA=30 : 1)

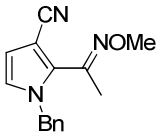
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.15 (m, 1H), 7.84 – 7.78 (m, 1H), 7.51 (m, 2H), 4.10 (s, 3H), 2.44 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 149.94, 142.97, 140.80, 135.67, 128.09, 126.01, 125.94, 122.38, 114.24, 107.90, 62.57, 15.49.

HRMS calcd for $C_{12}H_{10}N_2OS$ ($[M]^+$): 230.0514; found: 230.0513.





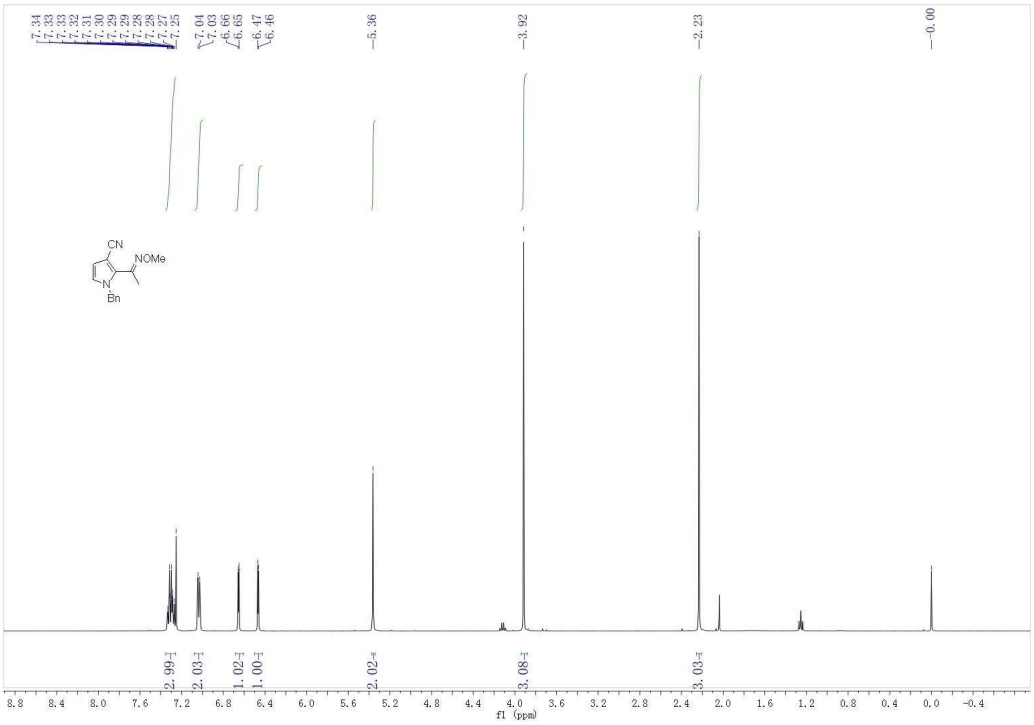

**1-benzyl-2-(1-(methoxyimino)ethyl)-1H-pyrrole-3-carbonitrile (4g)**

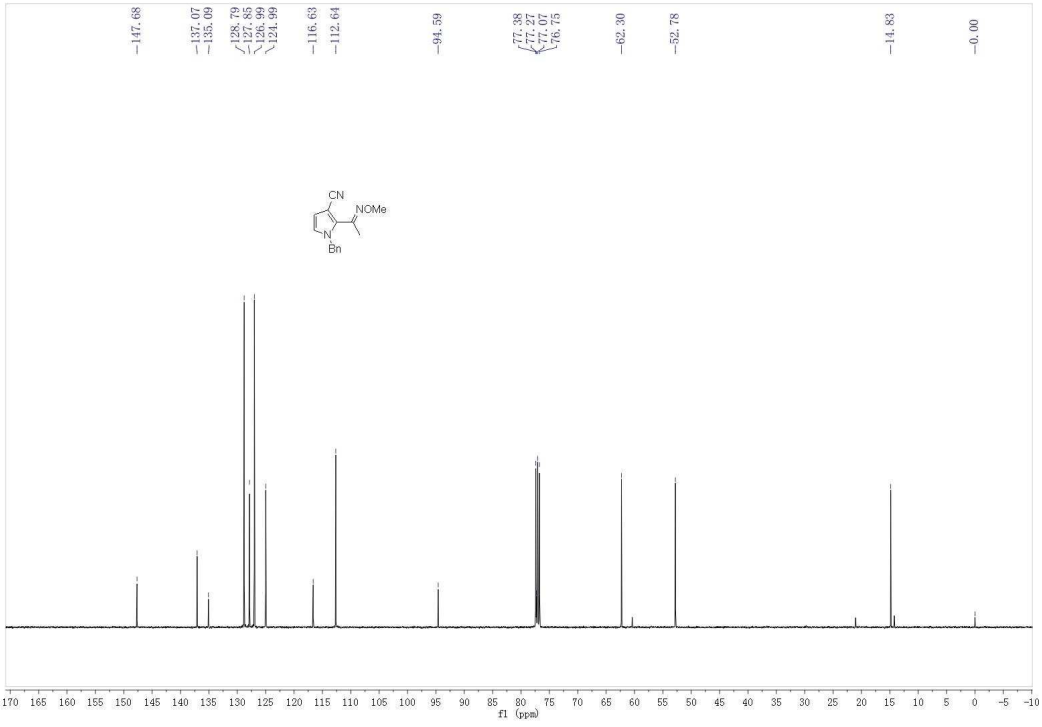
This compound was obtained in 82% (41.5mg) yield as white solid by following the general procedure (PE : EA=10 : 1)

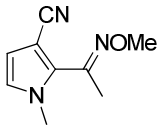
$^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 3H), 7.07 – 7.00 (m, 2H), 6.65 (d, *J* = 3.0, 1H), 6.47 (d, *J* = 3.0, 1H), 5.36 (s, 2H), 3.92 (s, 3H), 2.23 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.68, 137.07, 135.09, 128.79, 127.85, 126.99, 124.99, 116.63, 112.64, 94.59, 62.30, 52.78, 14.83.

HRMS calcd for $C_{15}H_{15}N_3O$ ($[M]^+$): 253.1215; found: 253.1213.





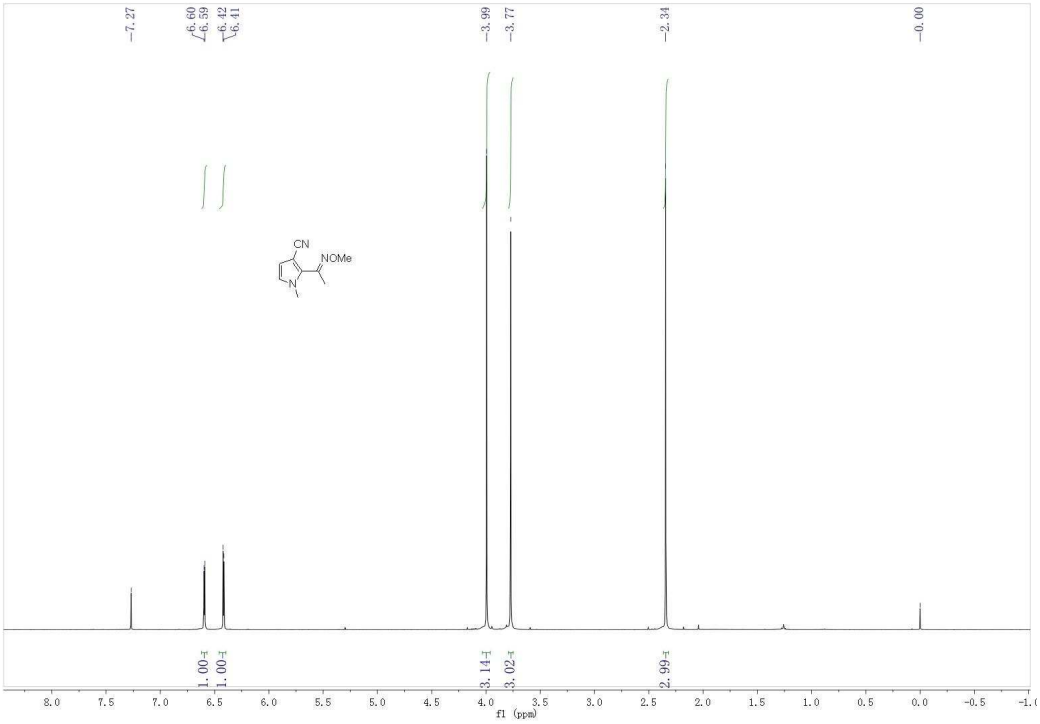

**2-(1-(methoxyimino)ethyl)-1-methyl-1H-pyrrole-3-carbonitrile (4h)**

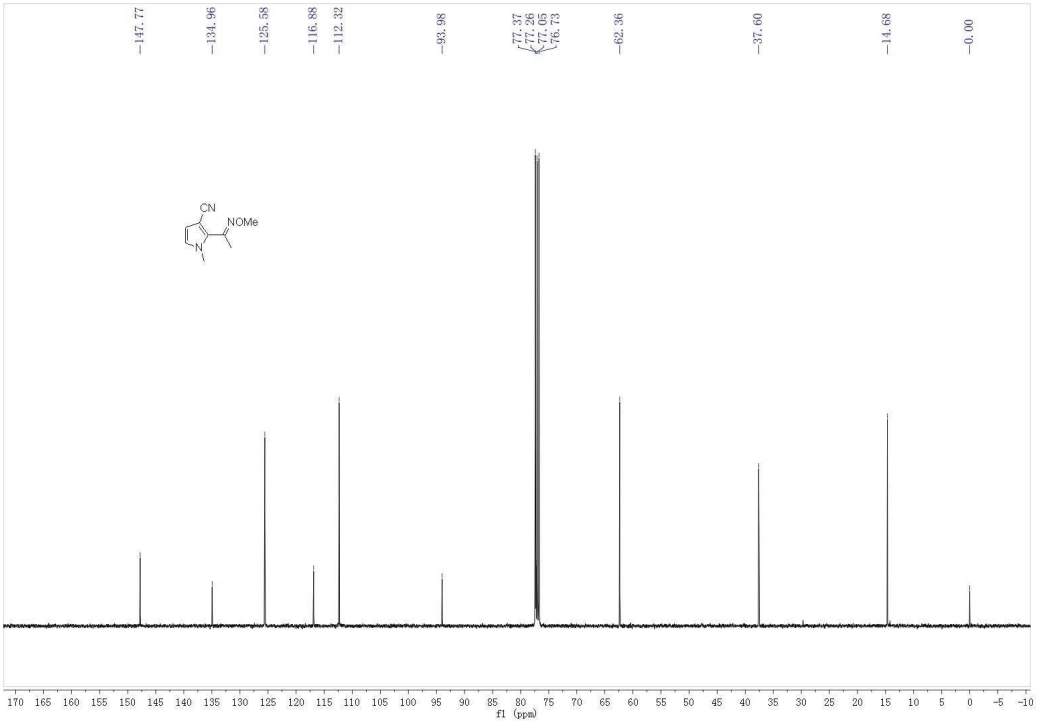
This compound was obtained in 71% (25mg) yield as thick oil by following the general procedure (PE : EA=10 : 1)

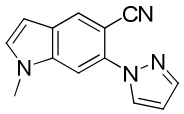
$^1$H NMR (400 MHz, $CDCl_3$) δ 6.59 (d, *J* = 2.9, 1H), 6.42 (d, *J* = 2.9, 1H), 3.99 (s, 3H), 3.77 (s, 3H), 2.34 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 147.77, 134.96, 125.58, 116.88, 112.32, 93.98, 62.36, 37.60, 14.68.

HRMS calcd for $C_9H_{11}N_3O$ ($[M]^+$): 177.0902; found: 177.0898.




**1-methyl-6-(1H-pyrazol-1-yl)-1H-indole-5-carbonitrile (4j)**

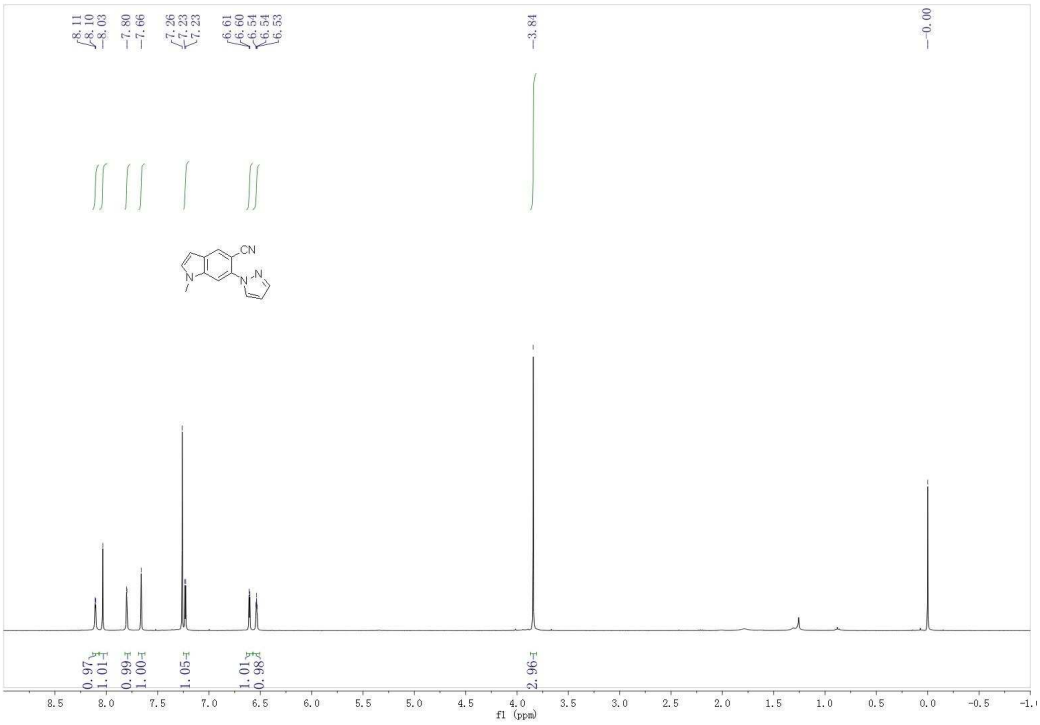
This compound was obtained in 74% (33mg) yield as white solid by following the general

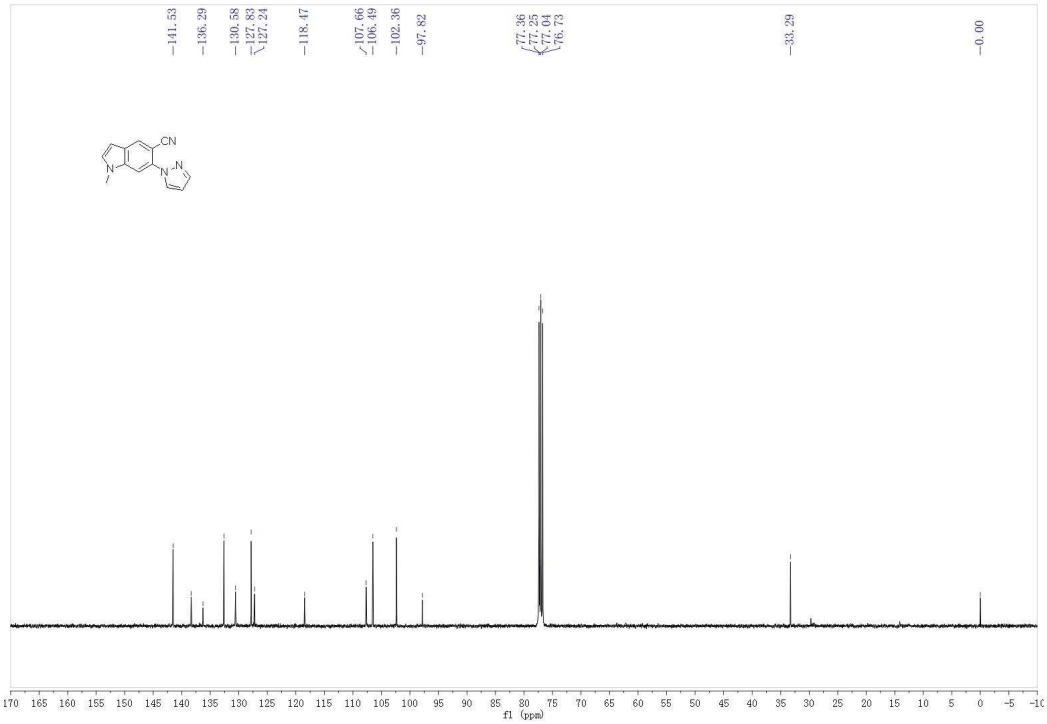
procedure (PE : EA=5 : 1)

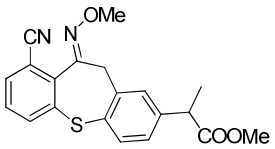
$^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.2, 1H), 8.03 (s, 1H), 7.80 (d, *J* = 1.6, 1H), 7.66 (s, 1H), 7.27 – 7.15 (m, 1H), 6.61 (d, *J* = 3.1, 1H), 6.56 – 6.46 (m, 1H), 3.84 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 141.53, 138.35, 136.29, 132.61, 130.58, 127.83, 127.24, 118.47, 107.66, 106.49, 102.36, 97.82, 33.29.

HRMS calcd for $C_{13}H_{10}N_4$ ($[M]^+$): 222.0905; found: 222.0901.





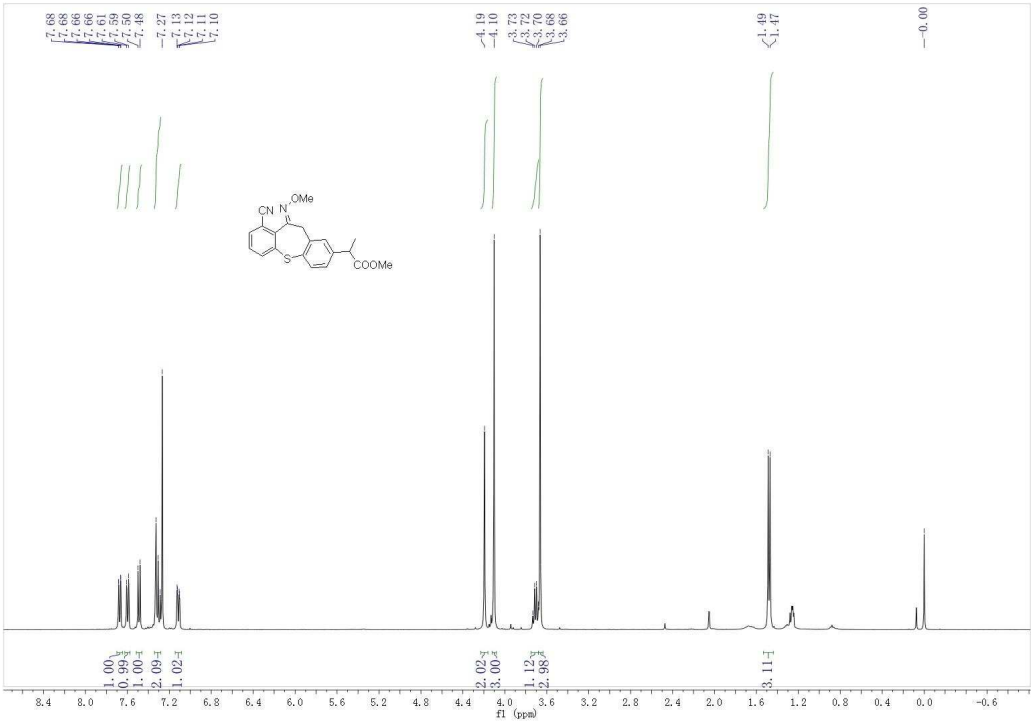

**(E)-methyl 2-(9-cyano-10-(methoxyimino)-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate (6)**

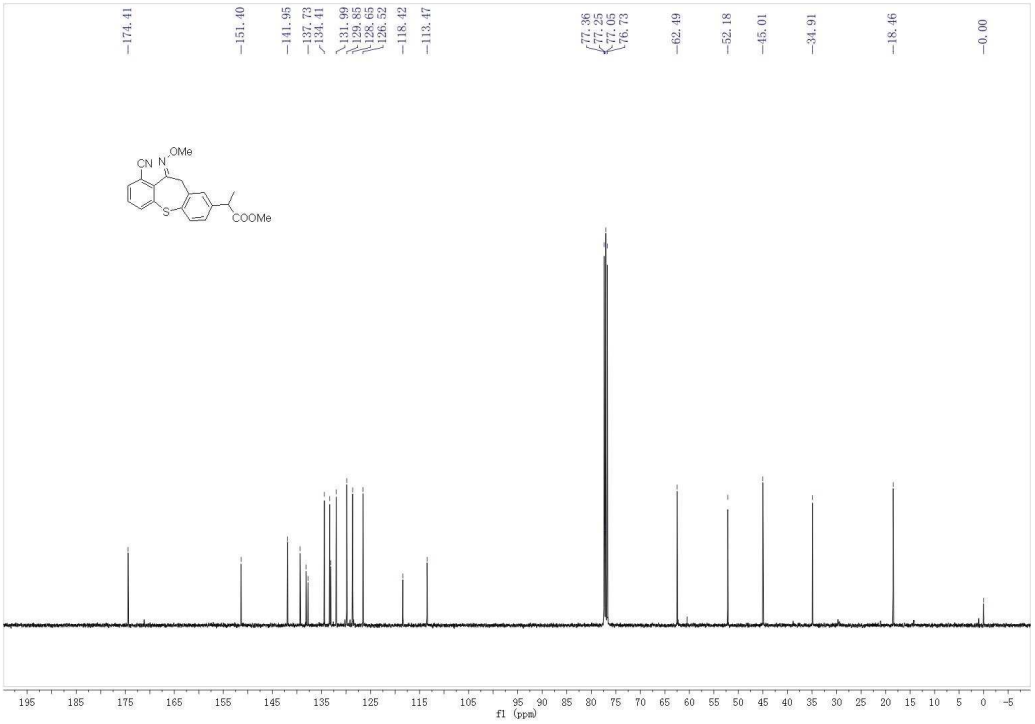
This compound was obtained in 74% (54.2mg) yield as white solid by following the general procedure (PE : EA=10 : 1)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.9, 0.8, 1H), 7.60 (d, *J* = 7.7, 1H), 7.49 (d, *J* = 7.9, 1H), 7.36 – 7.28 (m, 2H), 7.11 (dd, *J* = 7.9, 1.7, 1H), 4.19 (s, 2H), 4.10 (s, 3H), 3.71 (q, *J* = 14.4, 7.2, 1H), 3.66 (s, 3H), 1.48 (d, *J* = 7.2, 3H).

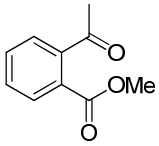
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.41, 151.40, 141.95, 139.36, 138.13, 137.73, 134.41, 133.33, 133.09, 131.99, 129.85, 128.65, 126.52, 118.42, 113.47, 62.49, 52.18, 45.01, 34.91, 18.46.

HRMS calcd for $C_{20}H_{18}N_2O_3S$ ([M+1]$^+$): 367.1111; found: 367.1111.




174.41
151.40
141.95
137.73
134.41
131.99
129.85
128.65
126.52
118.42
113.47
77.36
77.25
77.05
76.73
62.49
52.18
45.01
34.91
18.46
0.00
CN
N
OMe
S
COOMe
f1 (ppm)

## IV. Conversion of Benzonitrile :

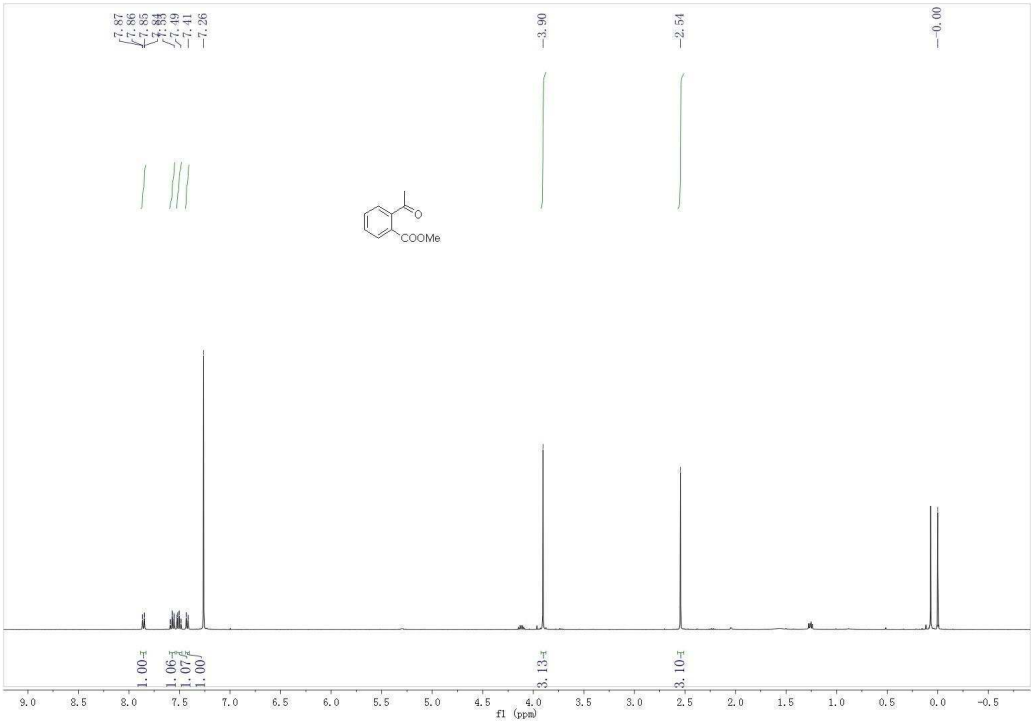


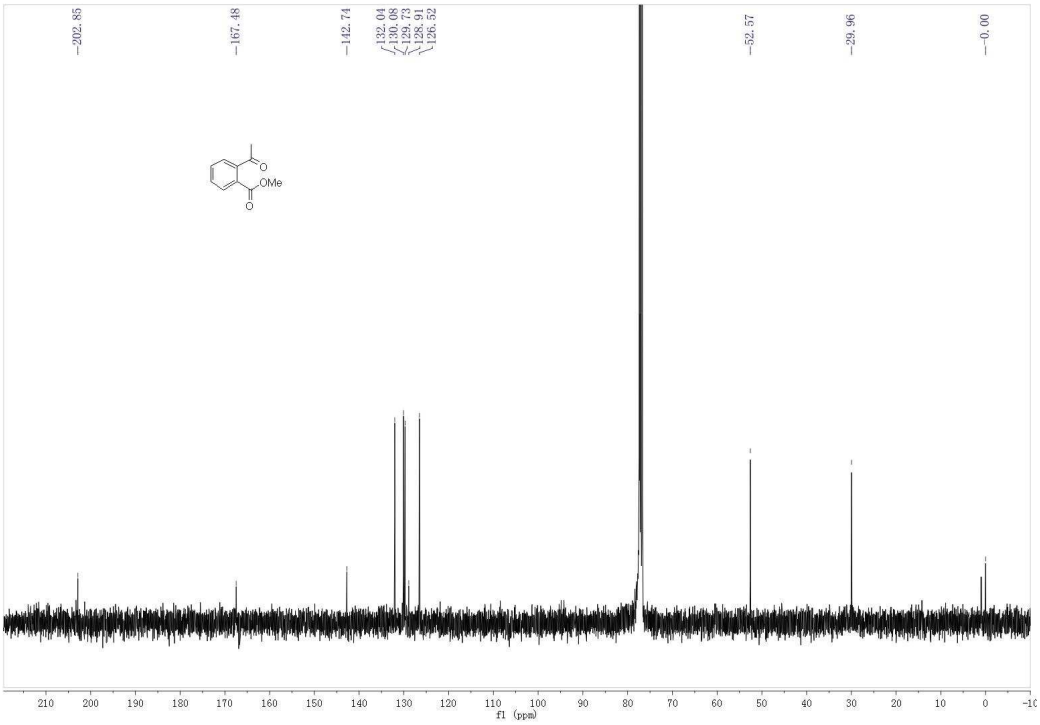

**Synthesis of (E)-methyl 2-(1-(methoxyimino)ethyl)benzoate (7).**

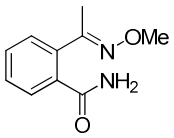
The hydrolysis of (E)-2-(1-(methoxyimino)ethyl)benzonitrile was performed by a modified literature procedure[5]. In a 10 mL round bottom flask containing a stirbar, (*E*)-2-(1-(methoxy-imino)ethyl)benzonitrile (34.8mg, 0.2 mmol) and AcOH (0.5 mL) was added to form a homogenous solution. $H_2O$ (1 mL) and $H_2SO_4$ (1 mL) were added to create a heterogenous solution. the reaction was heated to 120 °C for 5 h. After cooling to room temperature, NaOH (2M) was added dropwise at 0°C until pH=14. The suspension was diluted with $H_2O$ until all the solids dissolved. The solution was then washed with EtOAc (3 x 5 mL). HCl (concentrated) was added dropwise until the pH=1. The suspension was then extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine, dried with $Na_2SO_4$, filtered, and concentrated. The combied crude product was dissolved in MeOH(1ml)，two drops of $H_2SO_4$ added. Then the reaction was maintained at room temperature for 5 h. The suspension was then extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated. The product obtained is a thick oil (18 mg, 48%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.6, 1.0, 1H), 7.57 (td, *J* = 7.5, 1.4, 1H), 7.50 (td, *J* = 7.6, 1.4, 1H), 7.42 (dd, *J* = 7.5, 1.0, 1H), 3.90 (s, 3H), 2.54 (s, 3H).

δ$^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.85, 167.48, 142.74, 132.04, 130.08, 129.73, 128.91, 126.52, 52.57, 29.96. Spectral data matched those previously reported.





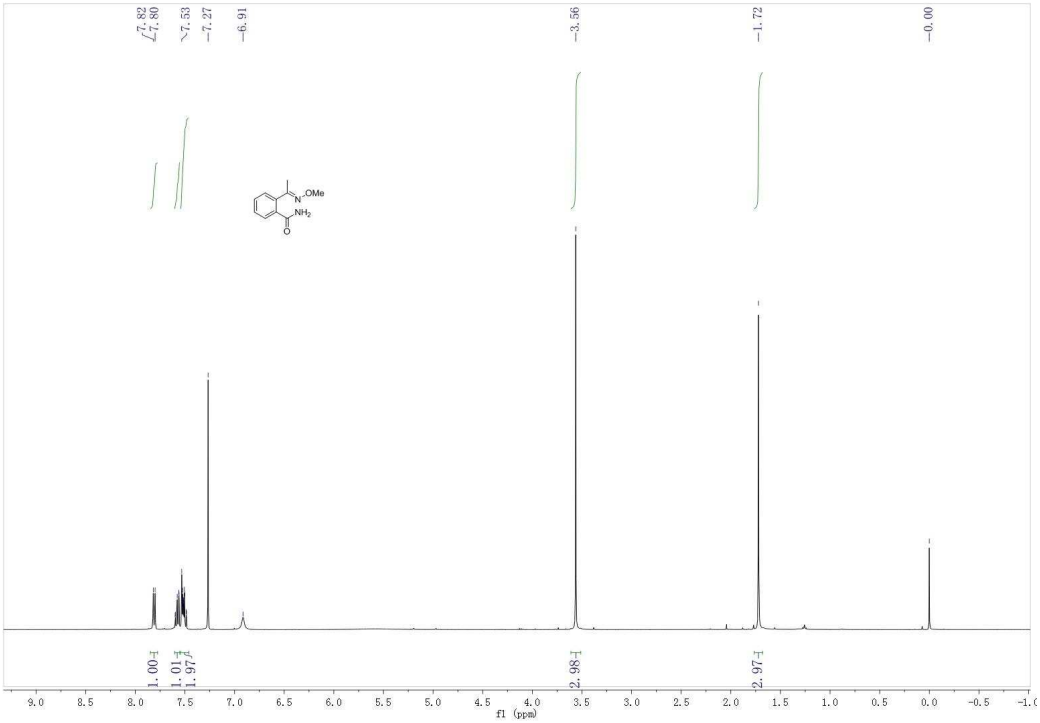



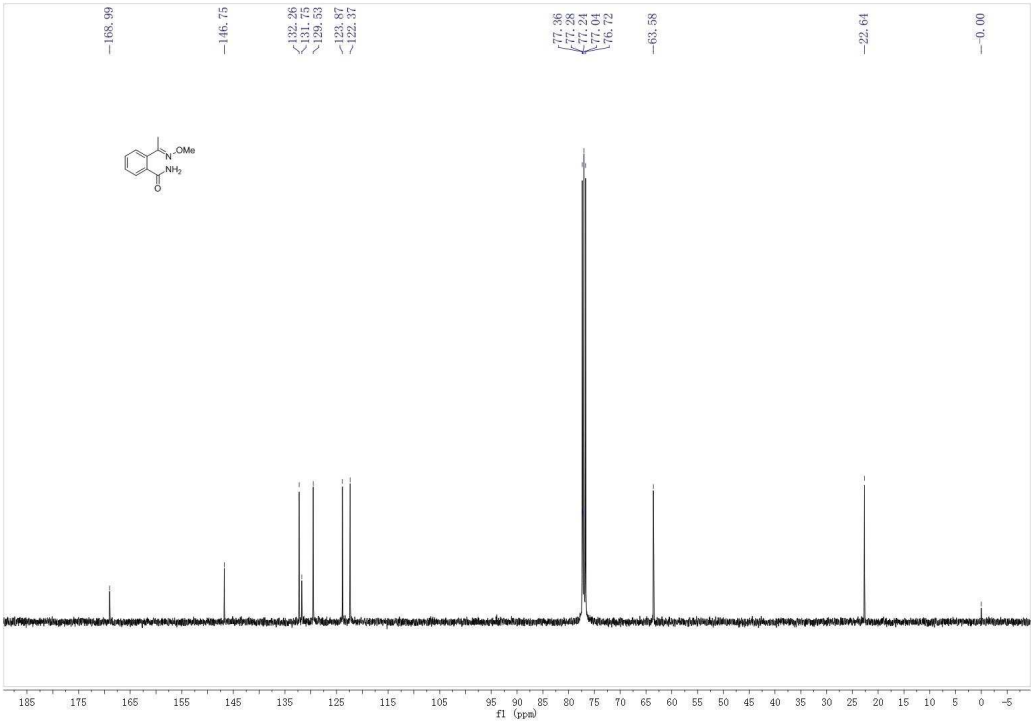

**Synthesis of (E)-2-(1-(methoxyimino)ethyl)benzamide (8).**

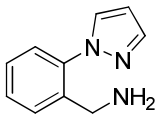
The hydrolysis of (E)-2-(1-(methoxyimino)ethyl)benzonitrile was performed by a modified literature procedure[5]. To a 10 mL vial, (*E*)-2-(1-(methoxyimino)ethyl)benzonitrile (34.8mg, 0.2 mmol) was dissolved in t-BuOH (0.5 mL). Solid KOH (168 mg, 3.75 mmol) was added. The reaction was heated at 60 ºC for 4 h. The reaction was cooled to room temperature and extracted with EtOAc (3 x 10 ml). The combined organic layers were dried with $Na_2SO_4$, filtered, concentrated under reduced pressure. The product obtained is a white solid (30 mg, 78%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4, 1H), 7.62 – 7.55 (m, 1H), 7.54 – 7.47 (m, 2H), 6.91 (s, 1H), 3.56 (s, 3H), 1.72 (s, 3H).

$^{13}$C NMR (101 MHz, $CDCl_3$) δ 168.99, 146.75, 132.26, 131.75, 129.53, 123.87, 122.37, 76.72, 63.58, 22.64.



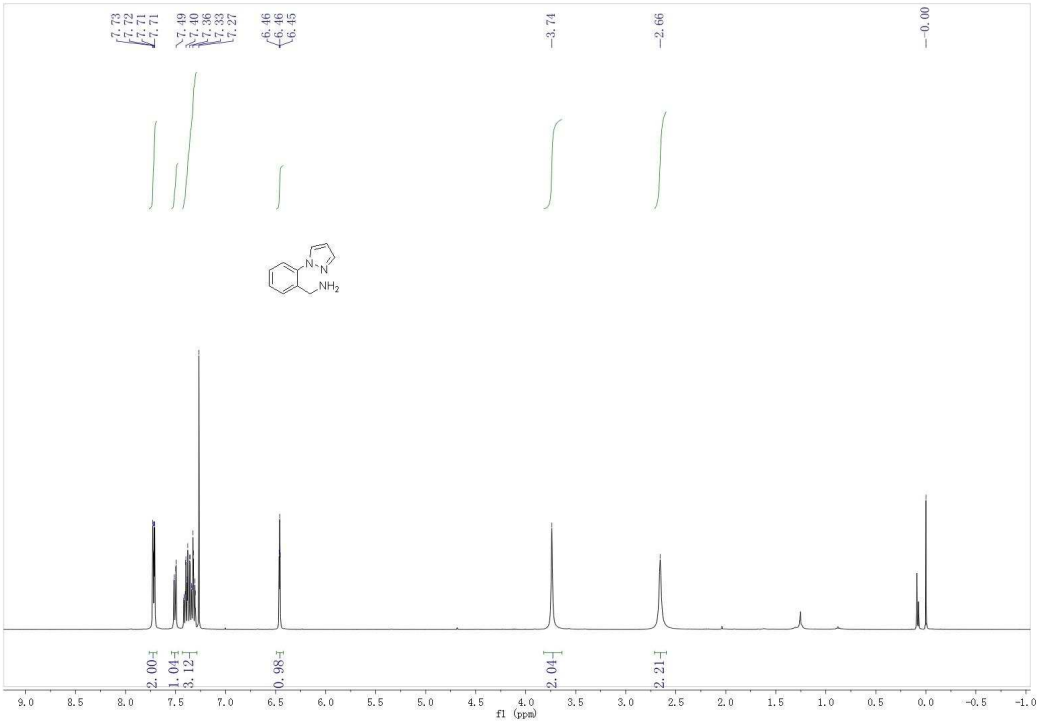

**Synthesis of (2-(1H-pyrazol-1-yl)phenyl)methanamine (9).**

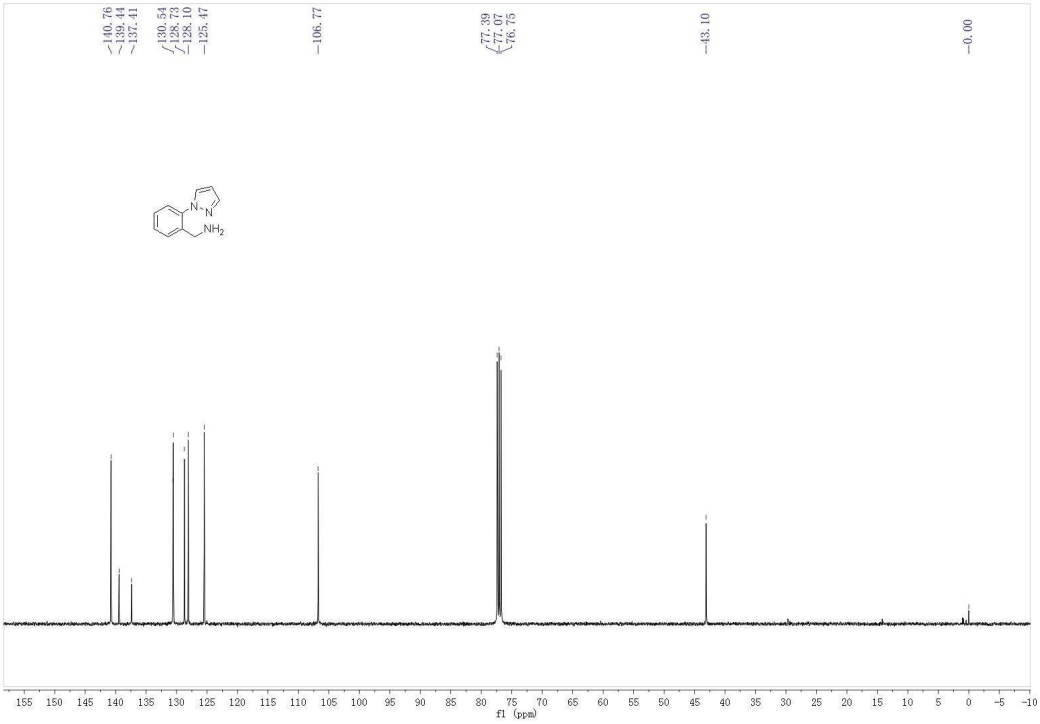
To a solution of 2-(1H-pyrazol-1-yl)benzonitrile (0.2 mmol) in THF (2 mL) was added lithium

aluminum hydride (1.0 M in THF, 0.25 mmol) dropwise. After being stirred for 1 h, diluted with THF and quenched with water (100 µL), NaOH (15% in water, 100µL). The reaction mixture was stirred at room temperature for 1 h, then dried ($Na_2SO_4$). After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography on silica gel . The product obtained is a thick oil (29 mg, 84%).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 6.1, 2.0, 2H), 7.51 (dd, *J* = 7.4, 1.6, 1H), 7.44 – 7.29 (m, 3H), 6.46 (t, *J* = 2.1, 1H), 3.74 (s, 2H), 2.66 (s, 2H).

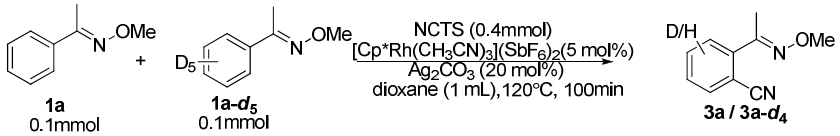
$^{13}$C NMR (101 MHz, $CDCl_3$) δ 140.76, 139.44, 137.41, 130.58, 130.54, 128.73, 128.10, 125.47, 106.77, 43.10. Spectral data matched those previously reported



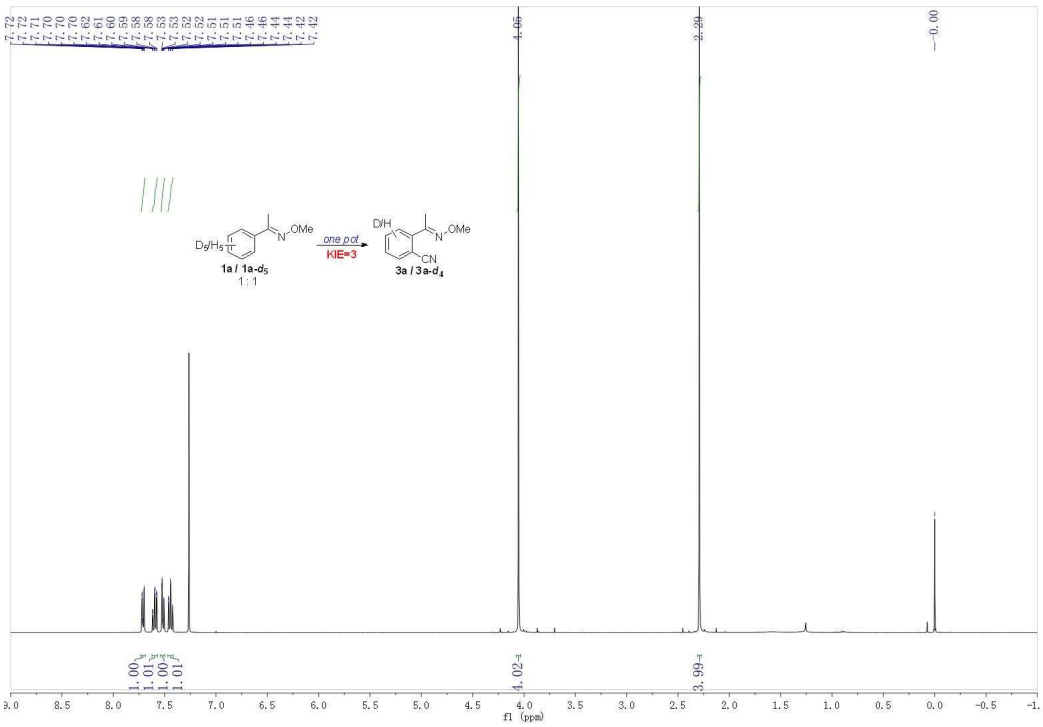



# V. Mechanistic Studies and NMR Spectra：

## KIE intermolecular competition experiment




A 10 mL-vial equipped with a magnetic stirrer was charged with $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$(5 mol%), $Ag_2CO_3$ (20 mol%), **1a** (0.1 mmol), **1a-*d*$_5$** (0.1 mmol) , *N*-cyano-*N* -phenyl-4-Methylbenz -enesulfonamide **2** (0.4 mmol) and dioxane (1 mL). The mixture was stirred and heated at 120°C for 100 min. The reaction was cooled down quickly in ice bath then purified by flash column chromatography to give the desired product. This KIE value was determined by $^1$H NMR analysis. (KIE≈3.0) was obtained.


7.72
7.72
7.71
7.70
7.70
7.70
7.62
7.61
7.60
7.59
7.58
7.58
7.53
7.52
7.52
7.51
7.51
7.46
7.46
7.44
7.44
7.42
7.42
4.05
2.29
0.00
OMe
D/H
one pot
KIE=3
CN
1a / 1a-d5
1 : 1
3a / 3a-d4
1.00
1.01
1.00
1.01
4.02
3.99
f1 (ppm)

## VI. X-ray Crystal data of 3q:

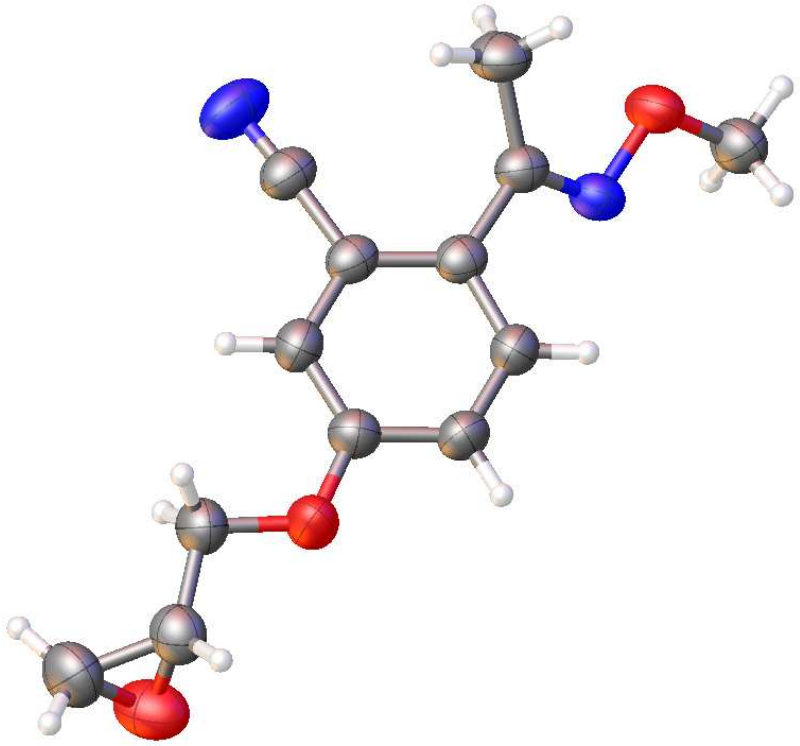


**Table 1 Crystal data and structure refinement for gtj130123**

| | |
|---|---|
| Identification code | gtj130123 |
| Empirical formula | $C_{13}H_{14}N_2O_3$ |
| Formula weight | 246.26 |
| Temperature/K | 290(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.4072(2) |
| b/Å | 13.2641(2) |
| c/Å | 7.61960(10) |
| α /° | 90.00 |
| β /° | 96.3700(10) |
| γ /° | 90.00 |
| Volume/Å$^3$ | 1246.22(3) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.313 |
| m/mm$^{-1}$ | 0.782 |

| | |
|---|---|
| F(000) | 520.0 |
| Crystal size/$mm^3$ | 0.36 × 0.32 × 0.24 |
| 2Θ range for data collection | 7.16 to 125.3° |
| Index ranges | -14 ≤ h ≤ 14, -6 ≤ k ≤ 15, -8 ≤ l ≤ 8 |
| Reflections collected | 4696 |
| Independent reflections | 1963[R(int) = 0.0155] |
| Data/restraints/parameters | 1963/0/165 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0397, $wR_2$ = 0.1056 |
| Final R indexes [all data] | $R_1$ = 0.0444, $wR_2$ = 0.1102 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.18/-0.15 |

**Table 2 Fractional Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$×$10^3$) for gtj130123. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| O3 | 3606.8(8) | 5481.2(9) | -120.0(16) | 60.5(3) |
| O2 | -1950.9(9) | 7389.2(9) | 1716.9(18) | 66.5(4) |
| O1 | -4241.5(10) | 8235.8(12) | 237.7(18) | 80.2(4) |
| N2 | 2512.9(10) | 5740.9(10) | -40.9(17) | 51.4(4) |
| N1 | 2084.6(14) | 9314.0(13) | 252(2) | 76.9(5) |
| C10 | 2429.6(12) | 6538.3(12) | 886.0(19) | 46.9(4) |
| C6 | 907.9(12) | 7810.4(11) | 1028.7(19) | 46.3(4) |
| C5 | -171.7(13) | 8038.1(12) | 1242(2) | 51.0(4) |
| C11 | 1586.2(13) | 8642.4(13) | 628(2) | 53.8(4) |
| C12 | 3643.0(14) | 4574.5(13) | -1118(2) | 61.3(5) |
| C15 | 3381.3(13) | 7104.7(14) | 1788(2) | 60.9(5) |
| C8 | 537.8(12) | 6064.5(12) | 1334(2) | 49.7(4) |
| C7 | 1288.5(12) | 6820.1(11) | 1083.4(18) | 45.0(4) |
| C1 | -4287.3(16) | 9089.6(17) | 1354(3) | 78.8(6) |
| C9 | -523.7(12) | 6275.8(12) | 1534(2) | 52.8(4) |
| C4 | -887.3(12) | 7269.8(12) | 1498(2) | 50.6(4) |
| C3 | -2385.3(14) | 8381.8(13) | 1756(3) | 61.3(5) |
| C2 | -3567.8(14) | 8272.1(14) | 1875(2) | 61.4(5) |

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for gtj130123. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| O3 | 38.9(6) | 62.6(7) | 79.7(8) | -12.5(6) | 5.8(5) | -0.7(5) |
| O2 | 46.8(7) | 48.9(7) | 105.4(10) | 0.6(6) | 15.9(6) | 1.7(5) |
| O1 | 61.8(8) | 99.8(11) | 77.8(9) | -22.6(8) | 2.4(6) | 0.7(7) |
| N2 | 37.6(7) | 56.0(8) | 60.6(8) | -1.4(6) | 4.9(6) | -1.0(6) |
| N1 | 85.4(12) | 66.4(10) | 77.5(11) | 7.3(8) | 2.7(8) | -28.9(9) |
| C10 | 43.7(8) | 49.6(9) | 46.9(8) | 0.4(7) | 3.1(6) | -5.0(7) |
| C6 | 47.8(9) | 45.7(8) | 44.7(8) | -1.2(6) | 1.7(6) | -7.2(7) |
| C5 | 52.7(9) | 41.0(8) | 58.7(9) | -1.1(7) | 3.9(7) | -1.0(7) |
| C11 | 56.7(10) | 50(1) | 53.7(9) | -1.1(7) | 2.1(7) | -9.3(8) |
| C12 | 50.7(10) | 58.9(10) | 74.6(11) | -8.4(8) | 7.6(8) | 3.5(8) |
| C15 | 49.0(9) | 68.2(11) | 63.9(10) | -9.9(8) | -1.5(7) | -7.1(8) |
| C8 | 47.7(9) | 41.9(8) | 59.0(9) | 1.6(7) | 3.6(7) | -1.4(6) |
| C7 | 45.0(8) | 46.6(8) | 42.5(8) | -1.4(6) | 1.1(6) | -3.8(6) |
| C1 | 64.6(12) | 73.2(13) | 99.8(15) | -6.4(11) | 14.7(10) | 13.6(10) |
| C9 | 46.8(9) | 44.1(9) | 67.3(10) | 2.2(7) | 6.1(7) | -6.1(7) |
| C4 | 43.2(8) | 49.2(9) | 59.6(9) | -0.6(7) | 6.0(7) | -1.4(7) |
| C3 | 55.2(10) | 49.3(10) | 78.7(12) | -5.0(8) | 4.6(8) | 4.3(8) |
| C2 | 60.6(11) | 59.9(11) | 64.4(11) | -5.4(8) | 10.0(8) | 5.8(8) |

Table 4 Bond Lengths for gtj130123.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O3 | N2 | 1.4081(16) | C6 | C5 | 1.400(2) |
| O3 | C12 | 1.426(2) | C6 | C11 | 1.441(2) |
| O2 | C4 | 1.3576(19) | C6 | C7 | 1.395(2) |
| O2 | C3 | 1.424(2) | C5 | C4 | 1.380(2) |
| O1 | C1 | 1.421(2) | C8 | C7 | 1.396(2) |
| O1 | C2 | 1.423(2) | C8 | C9 | 1.371(2) |
| N2 | C10 | 1.282(2) | C1 | C2 | 1.432(3) |
| N1 | C11 | 1.139(2) | C9 | C4 | 1.393(2) |
| C10 | C15 | 1.500(2) | C3 | C2 | 1.487(2) |
| C10 | C7 | 1.488(2) | | | |

Table 5 Bond Angles for gtj130123.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N2 | O3 | C12 | 108.45(11) | C6 | C7 | C10 | 123.80(13) |
| C4 | O2 | C3 | 119.06(13) | C6 | C7 | C8 | 116.84(14) |
| C1 | O1 | C2 | 60.47(12) | C8 | C7 | C10 | 119.36(14) |
| C10 | N2 | O3 | 111.24(12) | O1 | C1 | C2 | 59.84(12) |
| N2 | C10 | C15 | 123.91(14) | C8 | C9 | C4 | 120.29(15) |
| N2 | C10 | C7 | 113.49(13) | O2 | C4 | C5 | 125.50(14) |
| C7 | C10 | C15 | 122.50(14) | O2 | C4 | C9 | 115.17(13) |
| C5 | C6 | C11 | 116.63(14) | C5 | C4 | C9 | 119.33(15) |
| C7 | C6 | C5 | 121.65(14) | O2 | C3 | C2 | 106.80(14) |
| C7 | C6 | C11 | 121.58(14) | O1 | C2 | C1 | 59.68(12) |
| C4 | C5 | C6 | 119.74(14) | O1 | C2 | C3 | 115.93(15) |
| N1 | C11 | C6 | 176.78(18) | C1 | C2 | C3 | 119.85(18) |
| C9 | C8 | C7 | 122.14(15) | | | | |

Table 6 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for gtj130123.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H5 | -406 | 8705 | 1211 | 61 |
| H12A | 4383 | 4367 | -1130 | 92 |
| H12B | 3323 | 4691 | -2306 | 92 |
| H12C | 3247 | 4055 | -589 | 92 |
| H15A | 3127 | 7664 | 2426 | 91 |
| H15B | 3823 | 7348 | 920 | 91 |
| H15C | 3803 | 6664 | 2593 | 91 |
| H8 | 765 | 5396 | 1367 | 60 |
| H1A | -4925 | 9170 | 1970 | 95 |
| H1B | -3971 | 9714 | 991 | 95 |
| H9 | -1003 | 5753 | 1693 | 63 |
| H3A | -2262 | 8746 | 692 | 74 |
| H3B | -2043 | 8749 | 2769 | 74 |
| H2 | -3776 | 7834 | 2817 | 74 |

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