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Supporting Information

Facile Synthesis of Cyanofurans via Michael-Addition/Cyclization of Ene-Yne-Ketones with Trimethylsilyl Cyanide

Yue Yu, Yang Chen, Wanqing Wu* and Huanfeng Jiang*

Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

E-mail: cewuwq@scut.edu.cn, jianghf@scut.edu.cn

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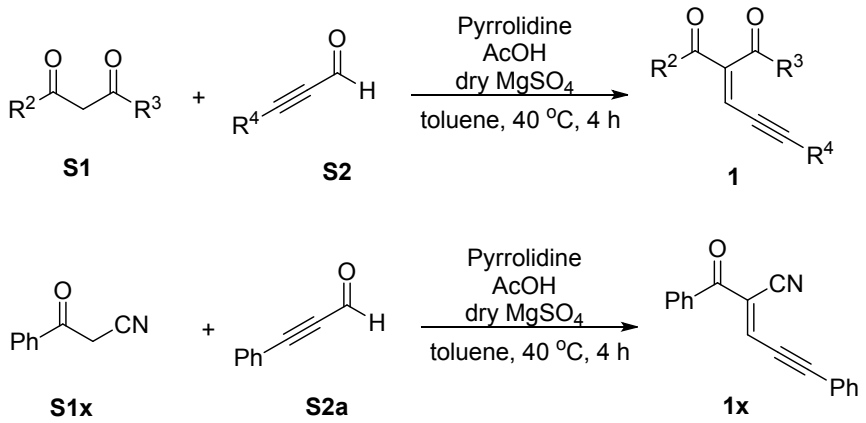
A. General Methods

^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument.

B. General Procedure for the Preparation of 1 and 3

General Procedure for the Preparation of 1

To a 25 mL round bottom flask, the mixture of 1,3-diketones **S1** (5 mmol), AcOH (0.2 equiv), piperidine (0.1 equiv) and dry $MgSO_4$ (1 equiv) was added to a solution of propiolaldehyde **S2** (1.2 equiv) in toluene. The reaction was carried out at 40 ^{o}C stirring for 4 h and monitored by TLC. After the completion of the reaction, the reaction mixture was filtered through *celite* and removal of the solvent by rotary evaporation to give the crude product. The ene-yne-ketones **1** was purified by chromatography on silica gel with the appropriate mixture of PE and EA in 60-90% yields (Z/E mixture, **1x** was isolated in 42% yield).



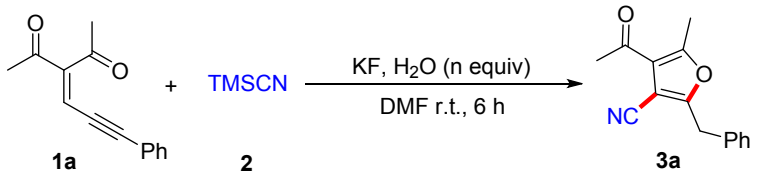
General Procedure for the Preparation of 3

In a test tube, a mixture of ene-yne-ketone **1** (0.4 mmol), trimethylsilyl cyanide **2** (0.6 mmol) and KF (0.6 mmol) was stirred in DMF (2 mL). Then H_2O (2.0 mmol) was added by using a microliter syringe. The mixture was allowed to stir at room temperature for 6 h. After completion of the reaction (monitored by

TLC), water (10 mL) was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were then dried over $MgSO_4$, filtered, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give products **3**.

C. Optimization of the Reaction Conditions

Table S1. Screening of the Amount of Water for Reaction[a]

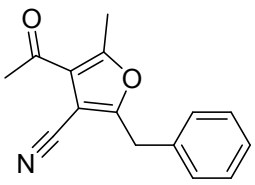


Entry	n (equiv)	Yield of **3a**[b] (%)
1	0	21
2	1	47
3	3	86
4	5	94
5	10	94

[a] Reaction conditions: All reactions were performed with **1a** (0.1 mmol), **2** (0.15 mmol), KF (0.15 mmol) and 1.0 mL DMF at room temperature for 6 h unless otherwise noted. [b] Yields were analyzed by GC-MS using *n*-dodecane as an internal standard.

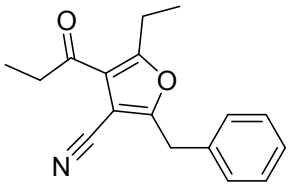
D. Analytical data

4-Acetyl-2-benzyl-5-methylfuran-3-carbonitrile (3a)



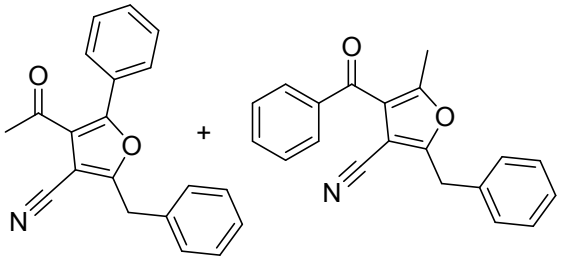
Yellow solid (87.1 mg, 91%) mp 60.2-61.0 ^{o}C; IR (KBr): 2922, 2230, 1675, 1244 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.24 (m, 5H), 4.09 (s, 2H), 2.54 (d, J = 1.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 191.7, 162.2, 158.7, 135.0, 128.9, 128.6, 127.4, 120.9, 113.6, 93.9, 33.5, 29.8, 14.3; MS (EI, 70 eV) *m*/*z*: 239.24, 224.21, 196.21, 91.18; HRMS ESI (m/z): calcd for $C_{15}H_{13}NNaO_2$ $[M + Na]^+$: 262.0838, found: 262.0837.

2-Benzyl-5-ethyl-4-propionylfuran-3-carbonitrile (3b)



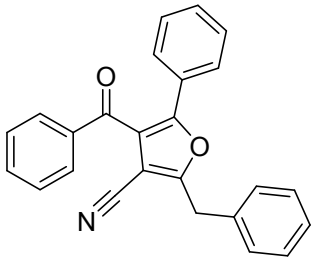
Yellow oil (93.0 mg, 87%); IR (KBr): 2974, 2231, 1680, 929 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.29-7.25 (m, 3H), 4.11 (s, 2H), 2.93 (dq, J = 19.5, 7.3 Hz, 4H), 1.19 (dt, J = 12.5, 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 194.9, 163.5, 162.2, 135.1, 128.9, 128.6, 127.4, 119.7, 113.9, 93.6, 35.2, 33.6, 21.6, 11.7, 7.5; MS (EI, 70 eV) *m*/*z*: 267.30, 238.25, 182.22, 91.14; HRMS ESI (m/z): calcd for $C_{17}H_{17}NNaO_2$ $[M + Na]^+$: 290.1151, found: 290.1153.

4-Acetyl-2-benzyl-5-phenylfuran-3-carbonitrile and 4-Benzoyl-2-benzyl-5-methylfuran-3 -carbonitrile (3c and 3c')



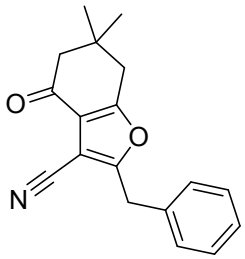
Yellow oil (101.2 mg, 84%); IR (KBr): 3052, 2232, 1662, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.26 (m, 10H), 4.17 (d, J = 25.4 Hz, 2H), 2.37 (d, J = 49.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 192.0, 188.9, 163.1, 162.3, 157.4, 156.6, 137.4, 135.0, 134.8, 133.3, 130.6, 129.1, 128.9, 128.9, 128.9, 128.6, 128.6, 128.5, 128.5, 128.2, 127.4, 127.3, 95.4, 95.3, 33.6, 33.5, 29.9, 13.9; MS (EI, 70 eV) *m*/*z*: 301.30, 286.27, 105.16, 77.16; HRMS ESI (m/z): calcd for $C_{20}H_{15}NNaO_2$ $[M + Na]^+$: 324.0995, found: 324.0998.

4-Benzoyl-2-benzyl-5-phenylfuran-3-carbonitrile (3d)



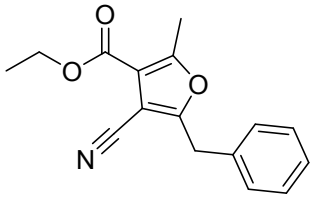
Yellow solid (119.2 mg, 82%), mp 105.6-106.6 °C; IR (KBr): 2995, 2231, 1763, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.53-7.48 (m, 1H), 7.43 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.38-7.21 (m, 10H), 4.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 189.2, 162.7, 154.7, 136.3, 134.9, 133.8, 129.8, 129.8, 129.0, 128.8, 128.6, 128.5, 127.9, 127.5, 127.5, 120.3, 112.2, 97.2, 33.8; MS (EI, 70 eV) *m/z*: 363.37, 286.30, 105.16, 77.18; HRMS ESI (m/z): calcd for $C_{25}H_{17}NNaO_2$ $[M + Na]^+$: 386.1151, found: 386.1150.

2-Benzyl-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-3-carbonitrile (3e)



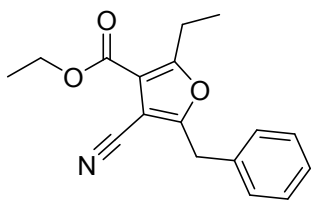
Brown oil (86.0 mg, 77%); IR (KBr): 2951, 2234, 1682, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 15.0, 7.0 Hz, 5H), 4.11 (d, *J* = 7.2 Hz, 2H), 2.69 (d, *J* = 7.1 Hz, 2H), 2.37 (d, *J* = 7.1 Hz, 2H), 1.12 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 191.1, 165.6, 164.2, 134.9, 129.0, 128.7, 127.5, 118.8, 112.2, 91.4, 51.7, 37.0, 35.1, 33.7, 28.5; MS (EI, 70 eV) *m/z*: 279.33, 223.25, 195.25, 91.18; HRMS ESI (m/z): calcd for $C_{18}H_{17}NNaO_2$ $[M + Na]^+$: 302.1151, found: 302.1153.

Ethyl 5-Benzyl-4-cyano-2-methylfuran-3-carboxylate (3f)



Yellow oil (97.1 mg, 90%); IR (KBr): 2984, 2235, 1718, 1090 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.24 (m, 5H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.08 (s, 2H), 2.53 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 162.0, 161.6, 159.5, 135.2, 128.9, 128.6, 127.3, 113.1, 112.9, 94.9, 61.0, 33.5, 14.0, 13.5; MS (EI, 70 eV) *m/z*: 269.69, 240.23, 223.23, 195.23; HRMS ESI (m/z): calcd for $C_{16}H_{15}NNaO_3$ $[M + Na]^+$: 292.0944, found: 292.0943.

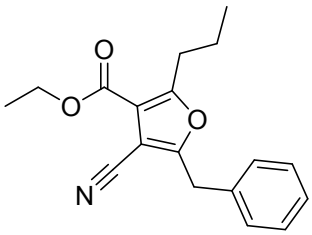
Ethyl 5-Benzyl-4-cyano-2-ethylfuran-3-carboxylate (3g)



Yellow oil (96.3 mg, 85%); IR (KBr): 2981, 2236, 1720, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 2.97 (q, *J* = 7.6 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 164.2, 161.9, 161.5, 135.2, 128.8, 128.5,

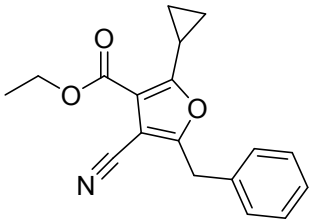
127.2, 112.8, 112.2, 94.8, 33.5, 20.9, 13.9, 11.8; MS (EI, 70 eV) *m/z*: 283.30, 254.24, 176.19, 91.17; HRMS ESI (m/z): calcd for $C_{17}H_{17}NNaO_3$ $[M + Na]^+$: 306.1101, found: 306.1101.

Ethyl 5-Benzyl-4-cyano-2-propylfuran-3-carboxylate (3h)



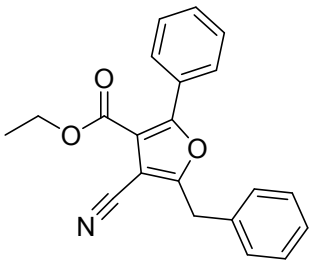
Yellow oil (92.8 mg, 78%); IR (KBr): 2966, 2236, 1719, 1101 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.18 (m, 5H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 3.01-2.83 (m, 2H), 1.74-1.56 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 163.3, 161.9, 161.5, 135.2, 128.8, 128.5, 127.2, 112.9, 112.9, 94.8, 60.9, 33.5, 29.1, 21.1, 13.9, 13.5; MS (EI, 70 eV) *m/z*: 297.29, 268.25, 250.24, 190.20; HRMS ESI (m/z): calcd for $C_{18}H19NNaO_3$ $[M + Na]^+$: 320.1257, found: 320.1256.

Ethyl 5-Benzyl-4-cyano-2-cyclopropylfuran-3-carboxylate (3i)



Yellow solid (92.1 mg, 78%), mp 76.3-77.6 °C; IR (KBr): 2990, 2235, 1716, 1052 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.17 (m, 5H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 2H), 2.82-2.66 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.09-0.97 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 163.6, 161.9, 160.5, 135.1, 128.8, 128.4, 127.2, 112.8, 112.2, 95.1, 60.9, 33.3, 14.0, 9.0, 8.9; MS (EI, 70 eV) *m/z*: 295.31, 249.27, 144.18, 91.16; HRMS ESI (m/z): calcd for $C_{18}H_{17}NNaO_3$ $[M + Na]^+$: 318.1101, found: 318.1102.

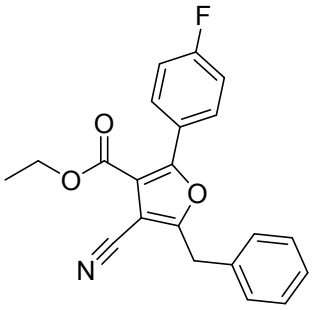
Ethyl 5-Benzyl-4-cyano-2-phenylfuran-3-carboxylate (3j)



Yellow solid (123.3 mg, 93%), mp 76.9-77.6 °C; IR (KBr): 2984, 2236, 2721, 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.46-7.37 (m, 3H), 7.37-7.19 (m, 5H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.15 (s, 2H), 1.36 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 162.5, 161.0, 157.3, 134.8, 130.2, 128.8, 128.5, 128.4, 128.0, 127.8, 127.2, 113.0, 112.6, 96.7, 61.3, 33.4, 13.7; MS (EI, 70 eV) *m/z*: 331.32, 302.25, 286.27, 105.14; HRMS ESI (m/z): calcd for $C_{21}H_{17}NNaO_3$ $[M + Na]^+$: 354.1101, found: 354.1102.

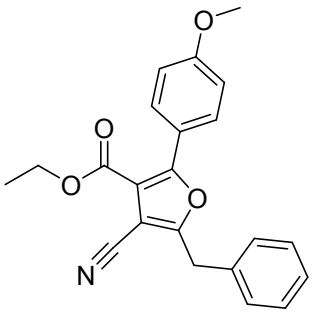
Ethyl 5-Benzyl-4-cyano-2-(4-fluorophenyl)furan-3-carboxylate (3k)

White solid (122.9 mg, 88%), mp 114.9-115.6 °C; IR (KBr): 2987, 2235, 1718, 1224 cm^{-1}; ^1H NMR (400



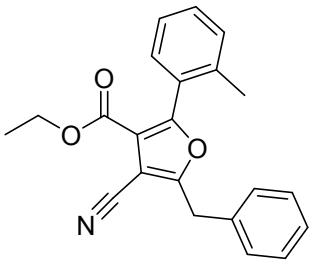
MHz, $CDCl_3$) δ 7.99-7.86 (m, 2H), 7.40-7.26 (m, 5H), 7.15-7.08 (m, 2H), 4.37 (q, J = 7.1 Hz, 2H), 4.20 (s, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.7 (J = 250.5 Hz), 162.6, 161.1, 156.6, 134.9, 130.8 (J = 8.6 Hz), 128.9, 128.6, 127.4, 124.1 (J = 3.4 Hz), 115.3 (J = 21.9 Hz), 112.9, 112.7, 96.8, 61.6, 33.6, 13.8; ^{19}F NMR ($CDCl_3$) δ ppm 108.8; MS (EI, 70 eV) *m*/*z*: 349.28, 320.21, 304.25, 123.15,; HRMS ESI (m/z): calcd for $C_{21}H_{16}FNNaO_3$ $[M + Na]^+$: 372.1006, found: 372.1006.

Ethyl 5-Benzyl-4-cyano-2-(4-methoxyphenyl)furan-3-carboxylate (3l)



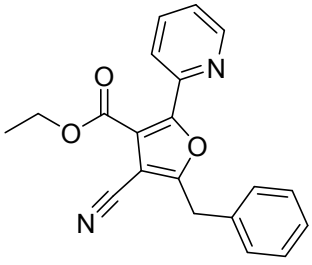
Yellow solid (109.9 mg, 76%), mp 77.1-78.2 ^{o}C; IR (KBr): 2979, 2234, 1717, 1240 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 9.0 Hz, 2H), 7.37-7.24 (m, 5H), 6.93 (d, J = 9.0 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 4.16 (s, 2H), 3.82 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.0, 161.3, 161.1, 157.8, 135.1, 130.2, 128.9, 128.6, 127.3, 120.4, 113.6, 113.0, 111.6, 96.7, 61.33, 55.3, 33.6, 13.9; MS (EI, 70 eV) *m*/*z*: 361.36, 333.32, 316.31, 135.18; HRMS ESI (m/z): calcd for $C_{22}H_{19}NNaO_4$ $[M + Na]^+$: 384.1206, found: 384.1204.

Ethyl 5-Benzyl-4-cyano-2-(*o*-tolyl)furan-3-carboxylate (3m)



Yellow oil (113.3mg, 82%); IR (KBr): 2982, 2236, 1721, 1096 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 2H), 7.35-7.21 (m, 7H), 4.34 (q, J = 7.1 Hz, 2H), 4.16 (s, 2H), 2.37 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.4, 161.1, 157.6, 137.8, 134.9, 131.0, 129.0, 128.8, 128.5, 128.0, 127.7, 127.3, 125.7, 112.9, 112.7, 96.8, 61.3, 33.5, 21.3, 13.8; MS (EI, 70 eV) *m*/*z*: 345.35, 316.28, 119.17, 91.18; HRMS ESI (m/z): calcd for $C_{22}H_{19}NNaO_3$ $[M + Na]^+$: 368.1257, found: 368.1258.

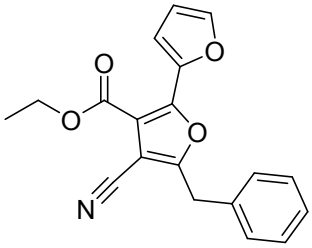
Ethyl 5-Benzyl-4-cyano-2-(pyridin-2-yl)furan-3-carboxylate (3n)



Brown oil (90.4 mg, 68%); IR (KBr): 2984, 2236, 1722, 1234 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79-8.68 (m, 1H), 8.01 (dt, J = 8.0, 1.0 Hz, 1H), 7.77 (td,

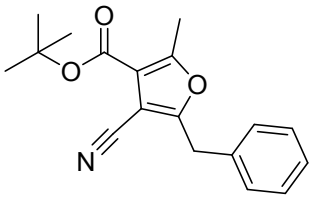
J = 7.8, 1.8 Hz, 1H), 7.37-7.30 (m, 5H), 7.28-7.24 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.24 (s, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 163.7, 160.9, 155.0, 149.6, 146.5, 136.3, 134.7, 128.9, 128.7, 127.4, 124.6, 124.3, 115.7, 112.3, 96.8, 61.7, 33.7, 13.8; MS (EI, 70 eV) *m*/*z*: 332.29, 260.27, 169.16, 78.15; HRMS ESI (m/z): calcd for $C_{20}H_{16}N_2NaO_3$ $[M + Na]^+$: 355.1053, found: 355.1052.

Ethyl 5-Benzyl-4-cyano-[2,2'-bifuran]-3-carboxylate (3o)



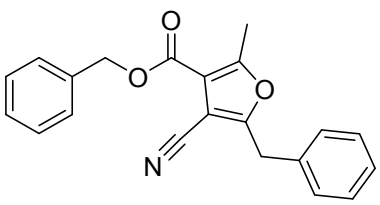
Brown solid (97.7 mg, 76%), mp 99.2-100.3 ^{o}C; IR (KBr): 2987, 2237, 1759, 1240 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.50 (m, 2H), 7.37-7.30 (m, 4H), 7.29-7.23 (m, 1H), 6.53 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.17 (s, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.4, 160.5, 148.8, 144.5, 142.6, 134.8, 128.9, 128.6, 127.4, 115.2, 112.5, 112.1, 111.2, 96.4, 61.4, 33.5, 13.9; MS (EI, 70 eV) *m*/*z*: 321.26, 276.23, 219.21, 91.18; HRMS ESI (m/z): calcd for $C_{19}H_{15}NNaO_4$ $[M + Na]^+$: 344.0893, found: 344.0890.

tert-Butyl 5-Benzyl-4-cyano-2-methylfuran-3-carboxylate (3p)



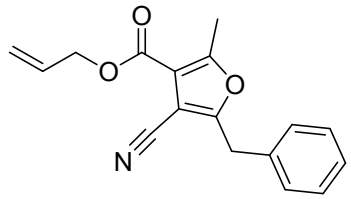
Yellow oil (93.9 mg, 79%); IR (KBr): 2982, 2236, 1713, 1243 cm^{-1}; ^{1}H NMR NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (m, 5H), 4.07 (s, 2H), 2.51 (s, 3H), 1.58 (s, 9H)); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.6, 160.8, 158.9, 135.3, 128.8, 128.6, 127.2, 114.2, 113.0, 95.1, 82.3, 33.5, 28.0, 13.4; MS (EI, 70 eV) *m*/*z*: 297.29, 241.22, 224.23, 195.21; HRMS ESI (m/z): calcd for $C_{18}H_{19}NNaO_3$ $[M + Na]^+$: 320.1257, found: 320.1253.

Benzyl 5-Benzyl-4-cyano-2-methylfuran-3-carboxylate (3q)



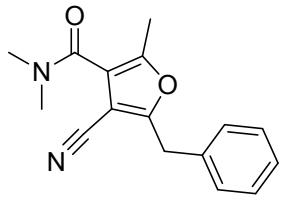
Yellow oil (120.6 mg, 91%); IR (KBr): 2934, 2235, 1719, 1240 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.42 (m, 2H), 7.41-7.18 (m, 8H), 5.34 (s, 2H), 4.07 (s, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.1, 161.4, 159.9, 135.4, 135.1, 128.9, 128.6, 128.9, 128.3, 128.3, 127.4, 113.0, 112.9, 94.9, 66.6, 33.5, 13.7; MS (EI, 70 eV) *m*/*z*: 331.33, 224.22, 107.20, 91.18; HRMS ESI (m/z): calcd for $C_{21}H_{17}NNaO_3$ $[M + Na]^+$: 354.1101, found: 354.1100.

Allyl 5-Benzyl-4-cyano-2-methylfuran-3-carboxylate (3r)



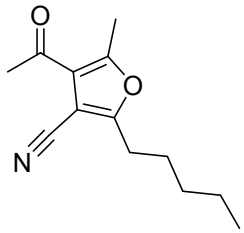
Yellow oil (90.0 mg, 80%); IR (KBr): 2932, 2236, 1720, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 10.5, 8.1, 5.9 Hz, 5H), 6.09-5.91 (m, 1H), 5.45 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.29 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.79 (dt, *J* = 5.6, 1.4 Hz, 2H), 4.08 (s, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 162.1, 161.3, 159.8, 135.1, 131.5, 128.9, 128.6, 127.3, 118.6, 112.9, 112.8, 94.8, 65.5, 33.5, 13.6; MS (EI, 70 eV) *m*/*z*: 281.27, 240.25, 224.23, 91.17; HRMS ESI (m/z): calcd for $C_{17}H_{15}NNaO_3$ $[M + Na]^+$: 304.0944, found: 304.0940.

5-Benzyl-4-cyano-*N*,*N*,2-trimethylfuran-3-carboxamide (3s)



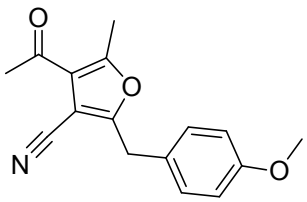
Brown oil (65.5 mg, 61%); IR (KBr): 2925, 2231, 1635, 1062 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 5H), 4.07 (s, 2H), 3.07 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 163.2, 161.7, 152.8, 135.2, 128.9, 128.7, 127.4, 116.8, 113.0, 94.3, 38.6, 33.7, 12.7; MS (EI, 70 eV) *m*/*z*: 268.30, 224.24, 182.22, 91.17; HRMS ESI (m/z): calcd for $C_{16}H_{16}N_2NaO_2$ $[M + Na]^+$: 291.1104, found: 291.1102.

4-Acetyl-5-methyl-2-pentylfuran-3-carbonitrile (3t)



Brown oil (56.1 mg, 64%); IR (KBr): 2941, 2231, 1680, 1411 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.74 (t, *J* = 7.5 Hz, 2H), 2.51 (d, *J* = 9.2 Hz, 6H), 1.73-1.60 (m, 2H), 1.36-1.24 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 191.9, 164.6, 158.0, 120.7, 113.8, 93.2, 30.9, 29.7, 27.2, 27.1, 22.0, 14.2, 13.7; MS (EI, 70 eV) *m*/*z*: 219.28, 204.23, 182.22, 91.17; HRMS ESI (m/z): calcd for $C_{13}H_{17}NNaO_2$ $[M + Na]^+$: 242.1151, found: 242.1152.

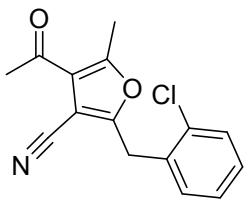
4-Acetyl-2-(4-methoxybenzyl)-5-methylfuran-3-carbonitrile (3u)



Yellow oil (82.9 mg, 77%); IR (KBr): 2929, 2231, 1676, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.15 (m, 2H), 6.90-6.83 (m, 2H), 4.03 (s, 2H), 3.78

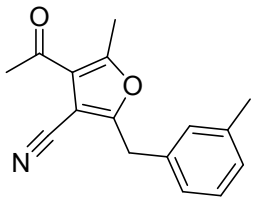
(s, 3H), 2.53 (d, J = 2.9 Hz, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 191.8, 162.8, 158.9, 158.7, 128.7, 127.0, 120.9, 114.3, 113.7, 93.6, 55.2, 32.7, 29.8, 14.3; MS (EI, 70 eV) *m*/*z*: 269.29, 254.26, 226.27, 108.18; HRMS ESI (m/z): calcd for $C_{16}H_{15}NNaO_3$ $[M + Na]^+$: 292.0944, found:292.0944.

4-Acetyl-2-(2-chlorobenzyl)-5-methylfuran-3-carbonitrile (3v)



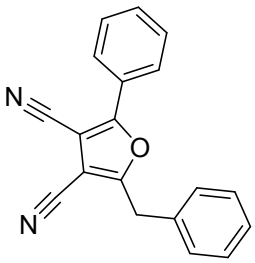
White solid (87.4 mg, 80%), mp 97.5-98.0 °C; IR (KBr): 2988, 2231, 1675, 1243 cm^{-1}; ^{1}HMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 1H), 7.30-7.23 (m, 3H), 4.25 (s, 2H), 2.62-2.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 191.8, 160.5, 158.9, 134.1, 132.6, 130.9, 129.8, 129.0, 127.2, 121.0, 113.3, 94.7, 31.4, 29.8, 14.4; MS (EI, 70 eV) *m*/*z*: 273.24, 258.21, 238.29, 216.29; HRMS ESI (m/z): calcd for $C_{15}H_{12}NClNaO_2$ $[M + Na]^+$: 296.0449, found: 296.0448.

4-Acetyl-5-methyl-2-(3-methylbenzyl)furan-3-carbonitrile (3w)



White solid (83.1 mg, 82%), mp 76.2-77.4 °C; IR (KBr): 2923, 2231, 1677, 1083 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, J = 14.8, 7.0 Hz, 1H), 7.11 (t, J = 6.9 Hz, 3H), 4.08 (s, 2H), 2.57 (d, J = 4.3 Hz, 6H), 2.37 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 191.9, 162.4, 158.8, 138.7, 134.9, 129.3, 128.8, 128.2, 125.6, 120.9, 113.7, 33.5, 29.8, 21.3, 14.4; MS (EI, 70 eV) *m*/*z*: 253.29, 238.26, 210.26, 161.17; HRMS ESI (m/z): calcd for $C_{16}H_{15}NNaO_2$ $[M + Na]^+$: 276.0995, found: 276.0997.

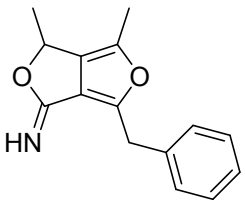
2-Benzyl-5-phenylfuran-3,4-dicarbonitrile (3x)



White solid (60.3 mg, 53%), mp 122.3-124.3 °C; IR (KBr): 2920, 2230, 2762, 1242 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.87 (m, 2H), 7.52-7.47 (m, 3H), 7.35 (dt, J = 11.8, 8.1 Hz, 5H), 4.20 (s, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.8, 159.9, 134.0, 131.4, 129.3, 129.2, 128.7, 127.9, 126.3, 125.7, 111.7, 110.4, 97.5, 92.5, 33.9; MS (EI, 70 eV) *m*/*z*: 284.30, 225.30, 105.18, 77.18; HRMS ESI (m/z):

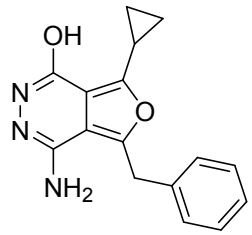
calcd for $C_{19}H_{12}N_2NaO$ $[M + Na]^+$: 307.0842, found: 307.0843.

6-Benzyl-3,4-dimethylfuro[3,4-*c*]furan-1(3*H*)-imine (4)



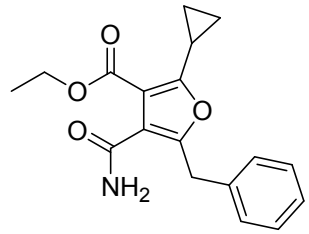
Yellow oil (33.4 mg, 69%); IR (KBr): 2921, 2230, 1579, 1075, 710cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.15 (m, 5H), 4.84 (q, J = 6.6 Hz, 1H), 4.03 (s, 2H), 2.58 (s, 1H), 2.24 (s, 3H), 1.53 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.7, 147.9, 135.8, 128.7, 128.7, 127.1, 123.4, 114.0, 93.3, 62.4, 33.7, 23.5, 11.8; MS (EI, 70 eV) *m*/*z*: 241.27, 226.25, 148.16, 91.17; HRMS ESI (m/z): calcd for $C_{15}H_{15}NNaO_2$ $[M + Na]^+$: 264.0995, found: 264.0998.

4-Amino-5-benzyl-7-cyclopropylfuro[3,4-*d*]pyridazin-1-ol (5)



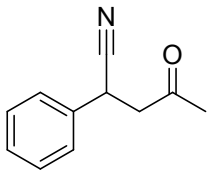
Yellow solid (28.1 mg, 45%), mp 268.3-269.5 ^{o}C; IR (KBr): 3320, 2232, 1598, 1049, 714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.25 (m, 3H), 7.20 (d, J = 7.0 Hz, 2H), 3.79 (d, J = 192.0 Hz, 4H), 2.76-2.62 (m, 1H), 1.26 (s, 1H), 1.09-0.91 (m, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.5, 160.9, 151.7, 146.3, 134.9, 128.9, 128.5, 127.5, 113.4, 92.8, 33.7, 9.0, 8.7; MS (EI, 70 eV) *m*/*z*: 281.28, 250.26, 180.22, 91.18; HRMS ESI (m/z): calcd for $C_{16}H_{16}N_3O_2$ $[M + H]^+$: 282.1237, found: 282.1241.

Ethyl 5-Benzyl-4-carbamoyl-2-cyclopropylfuran-3-carboxylate (6)



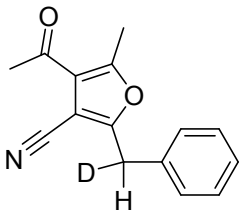
White solid (45.1 mg, 72%), mp 128.0-128.9 ^{o}C; IR (KBr): 3320, 1664, 1413, 1086, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.25 (d, J = 4.4 Hz, 4H), 7.18 (dq, J = 8.7, 4.2 Hz, 1H), 5.72 (s, 1H), 4.50-4.23 (m, 4H), 2.68-2.49 (m, 1H), 1.37 (t, J = 7.1 Hz, 3H), 1.09-0.87 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.1, 164.9, 162.7, 158.6, 137.6, 128.8, 128.3, 126.3, 115.0, 110.6, 61.2, 33.5, 14.1, 9.9, 8.6; MS (EI, 70 eV) *m*/*z*: 313.29, 296.29, 250.23, 222.23; HRMS ESI (m/z): calcd for $C_{18}H_{19}NNaO_4$ $[M + Na]^+$: 336.1206, found: 336.1210.

4-Oxo-2-phenylpentanenitrile (8)



Yellow oil (58.2 mg, 84%); IR (KBr): 3027, 2932, 2235, 1715, 1362 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 4.34 (dd, J = 7.9, 6.1 Hz, 1H), 3.07 (ddd, J = 24.1, 18.0, 7.0 Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 203.0, 135.0, 129.2, 128.3, 127.3, 120.3, 48.7, 31.5, 29.9; MS (EI, 70 eV) *m*/*z*: 173.25, 130.19, 103.19, 77.18; HRMS ESI (m/z): calcd for $C_{11}H_{11}NNaO$ $[M + Na]^+$: 196.0733, found: 196.0731.

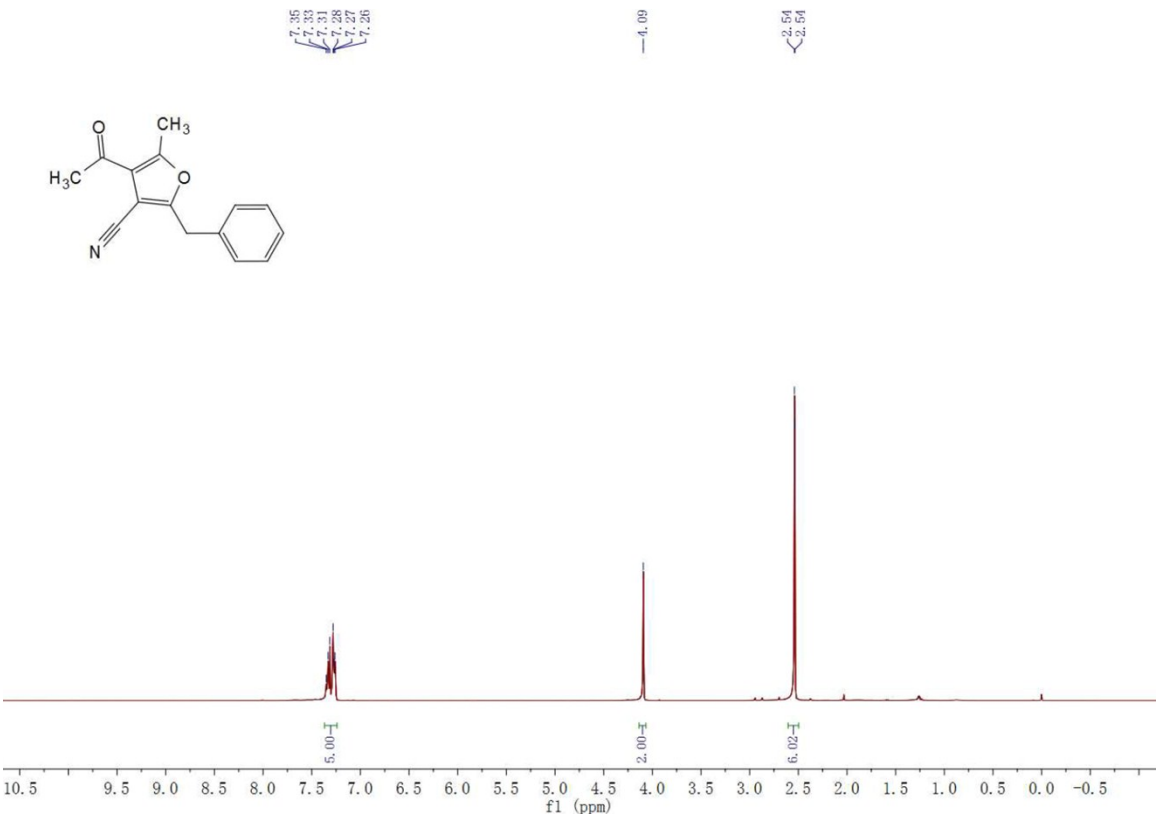
D_1-3a

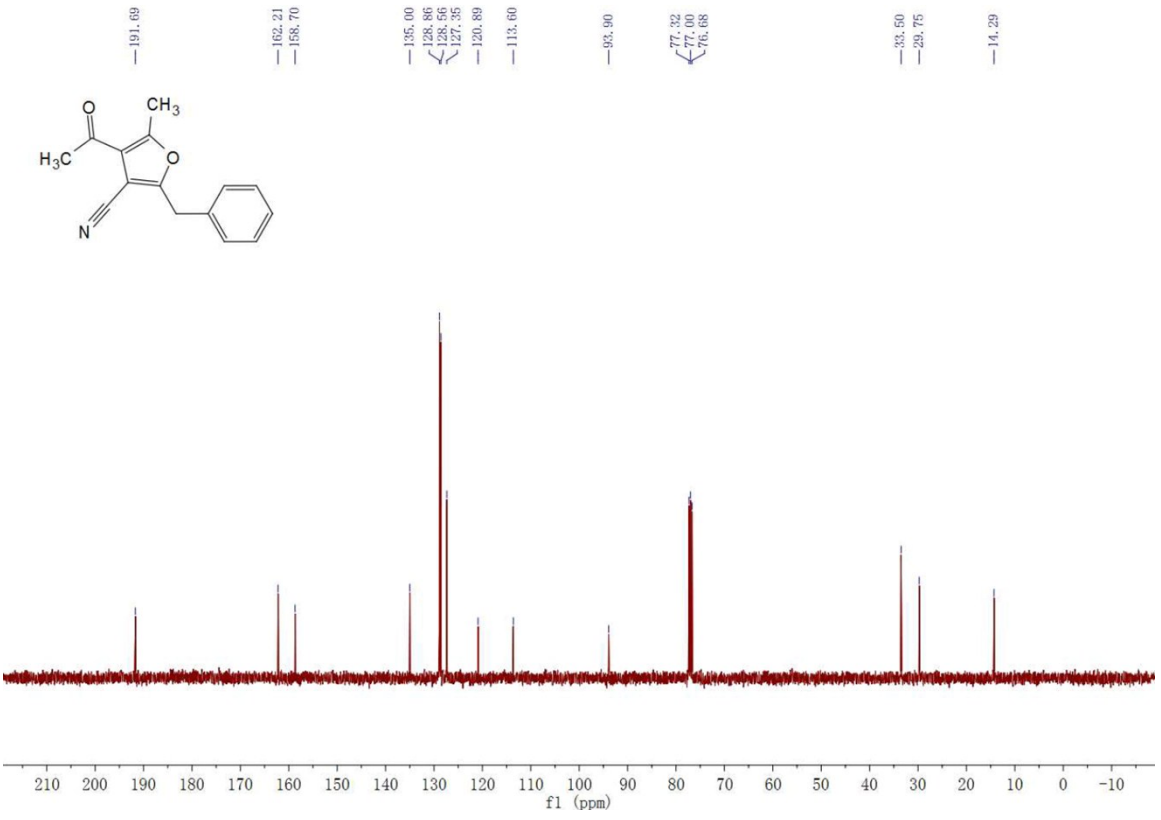


Yellow oil (75.0 mg, 78%); IR (KBr): 2923, 2231, 1675, 1410 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.21 (m, 5H), 4.09 (d, J = 6.8 Hz, 1.15H), 2.54 (d, J = 3.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 191.8, 162.3, 158.8, 135.0 (J = 3.9 Hz), 128.9, 128.6, 127.4, 120.9, 113.9, 93.9 (J = 1.1 Hz), 33.6, 29.8, 14.4; MS (EI, 70 eV) *m*/*z*: 240.29, 225.26, 197.24, 92.26; HRMS ESI (m/z): calcd for $C_{15}H_{12}DNNaO_2$ $[M + Na]^+$: 263.0901, found: 263.0896.

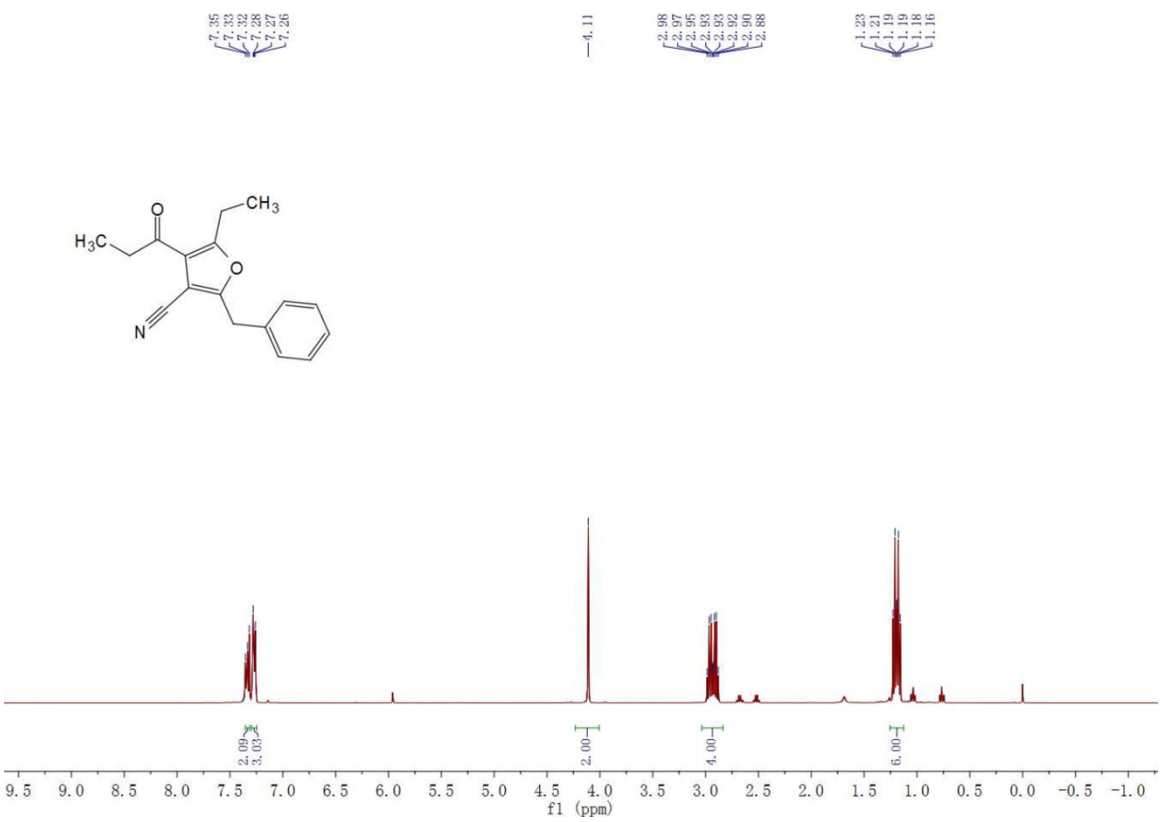
E. NMR Spectra

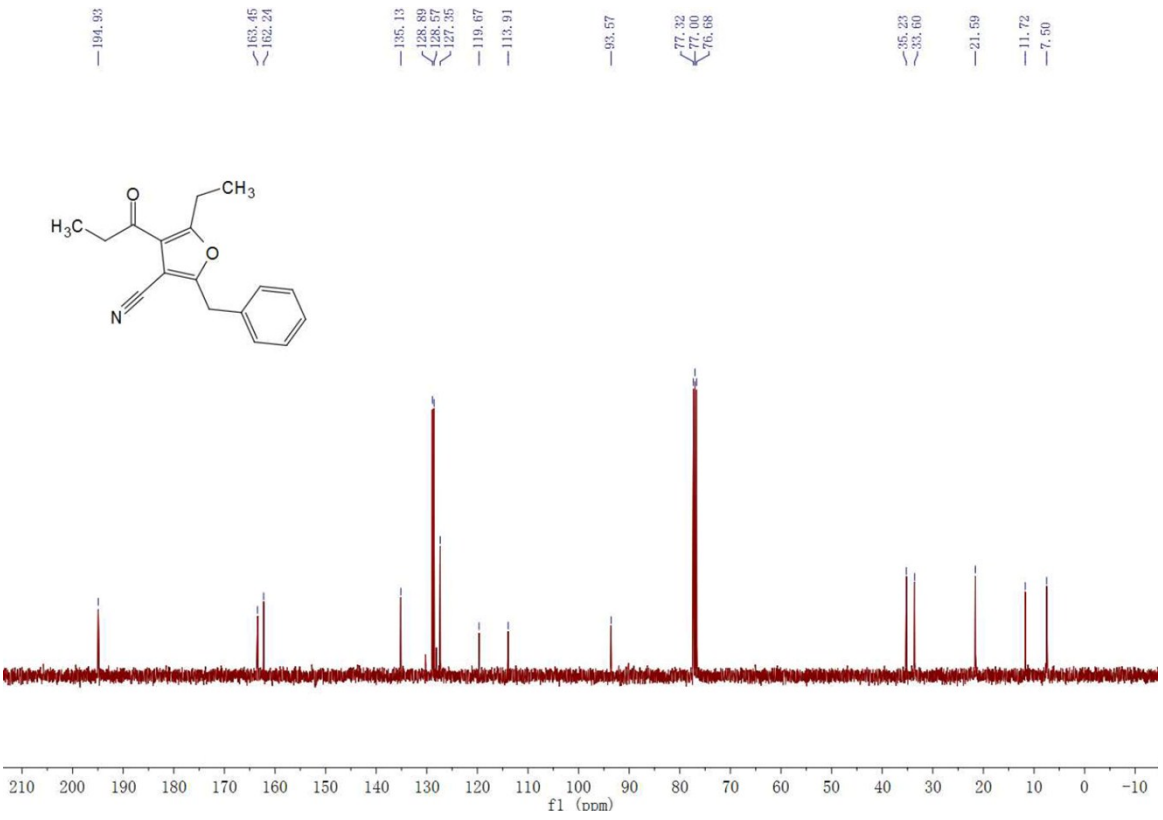
3a


7.35
7.33
7.31
7.28
7.27
7.26
4.09
2.54
2.54
O
CH3
H3C
O
N
5.00
2.00
6.02
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

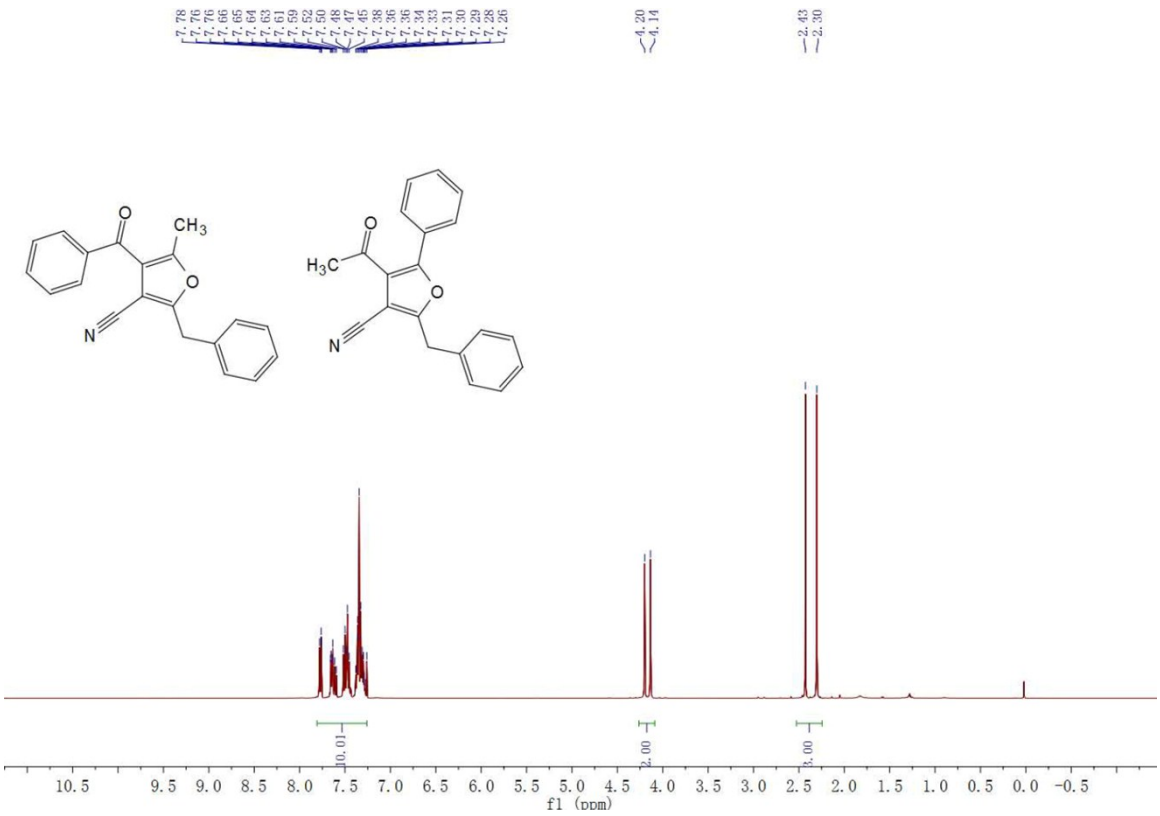

191.69
162.21
158.70
135.00
128.86
128.56
127.35
120.89
113.60
93.90
77.32
77.00
76.68
33.50
29.75
14.29
O
CH3
H3C
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

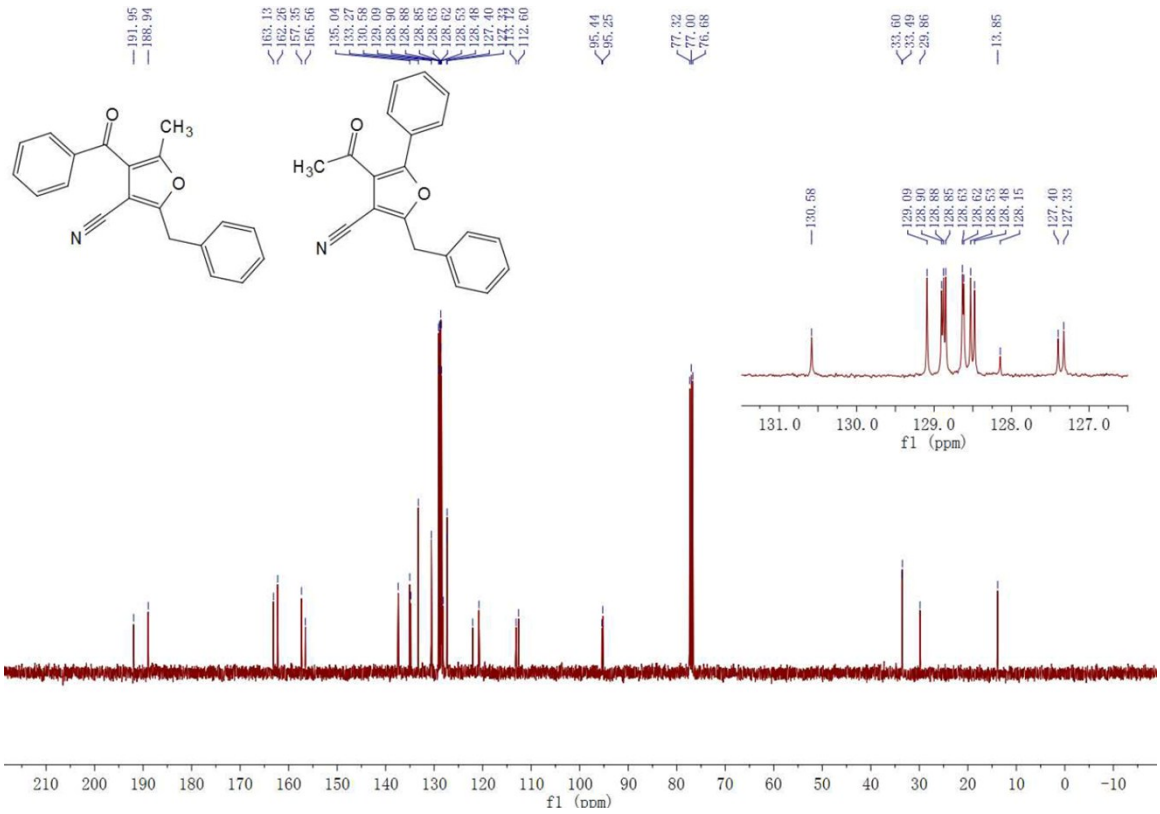
3b


7.35
7.33
7.32
7.28
7.27
7.26
4.11
2.98
2.97
2.95
2.93
2.93
2.92
2.90
2.88
1.23
1.21
1.19
1.19
1.18
1.16
O
CH3
H3C
O
N
2.09
3.03
2.00
4.00
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


194.93
163.45
162.24
135.13
128.89
128.57
127.35
119.67
113.91
93.57
77.32
77.00
76.68
35.23
33.60
21.59
11.72
7.50
O
CH3
H3C
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3c


7.78
7.76
7.76
7.66
7.65
7.64
7.63
7.61
7.59
7.52
7.50
7.48
7.47
7.45
7.38
7.36
7.36
7.34
7.33
7.31
7.30
7.29
7.28
7.26
4.20
4.14
2.43
2.30
O
CH3
O
N
H3C
10.01
2.00
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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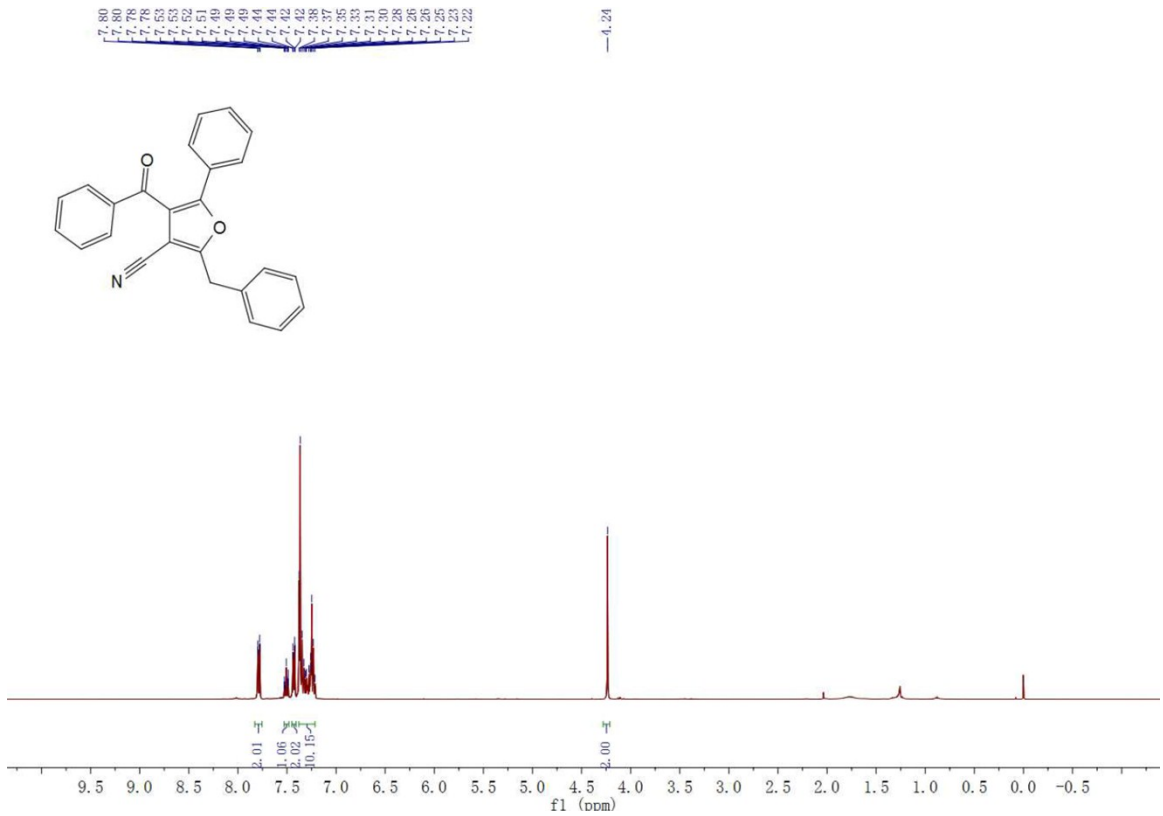
162.26
157.35
156.56
135.04
133.27
130.58
129.09
128.90
128.88
128.85
128.63
128.62
128.53
128.48
127.40
112.60
95.44
95.25
77.32
77.00
76.68
33.60
33.49
29.86
13.85
O
CH3
O
N
H3C
130.58
129.09
128.90
128.88
128.85
128.63
128.62
128.53
128.48
128.15
127.40
127.33
131.0 130.0 129.0 128.0 127.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3d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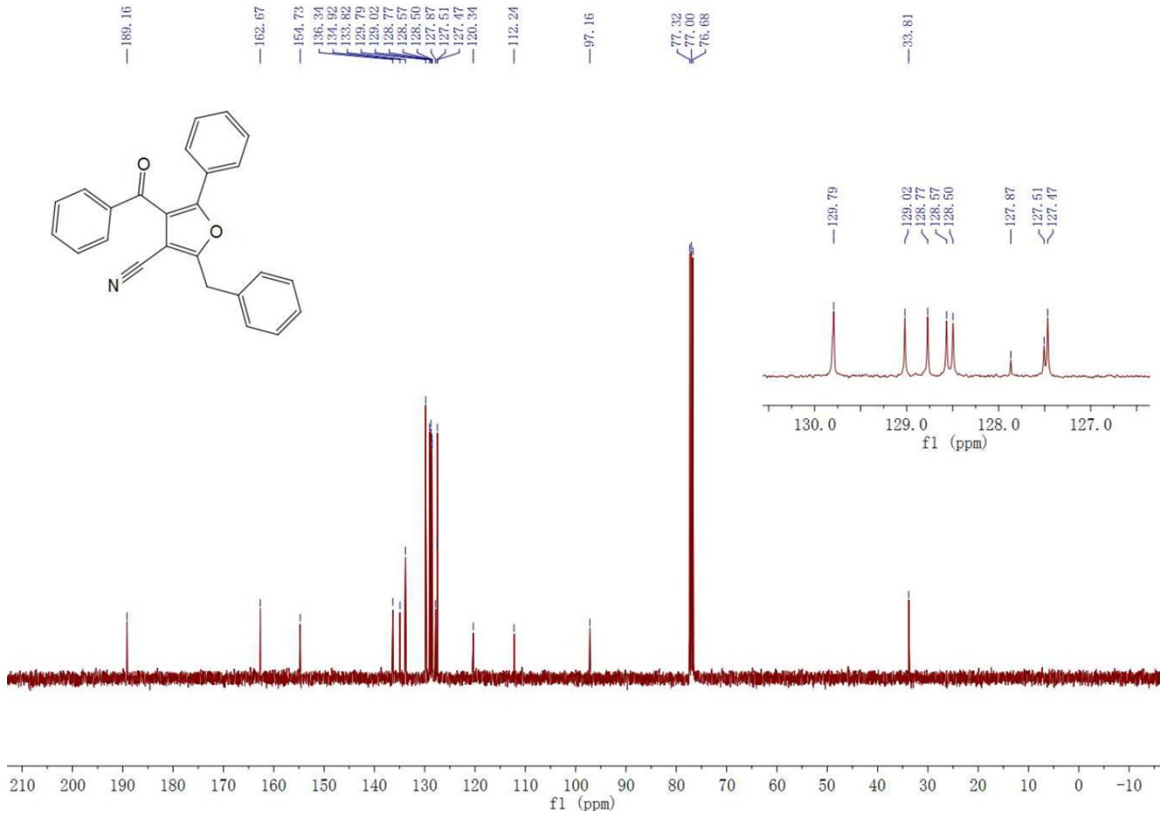
7.80
7.78
7.78
7.53
7.52
7.51
7.49
7.49
7.49
7.44
7.44
7.42
7.42
7.38
7.37
7.35
7.33
7.31
7.30
7.28
7.26
7.26
7.25
7.23
7.22
4.24
O
O
N
2.01
1.06
2.02
10.15
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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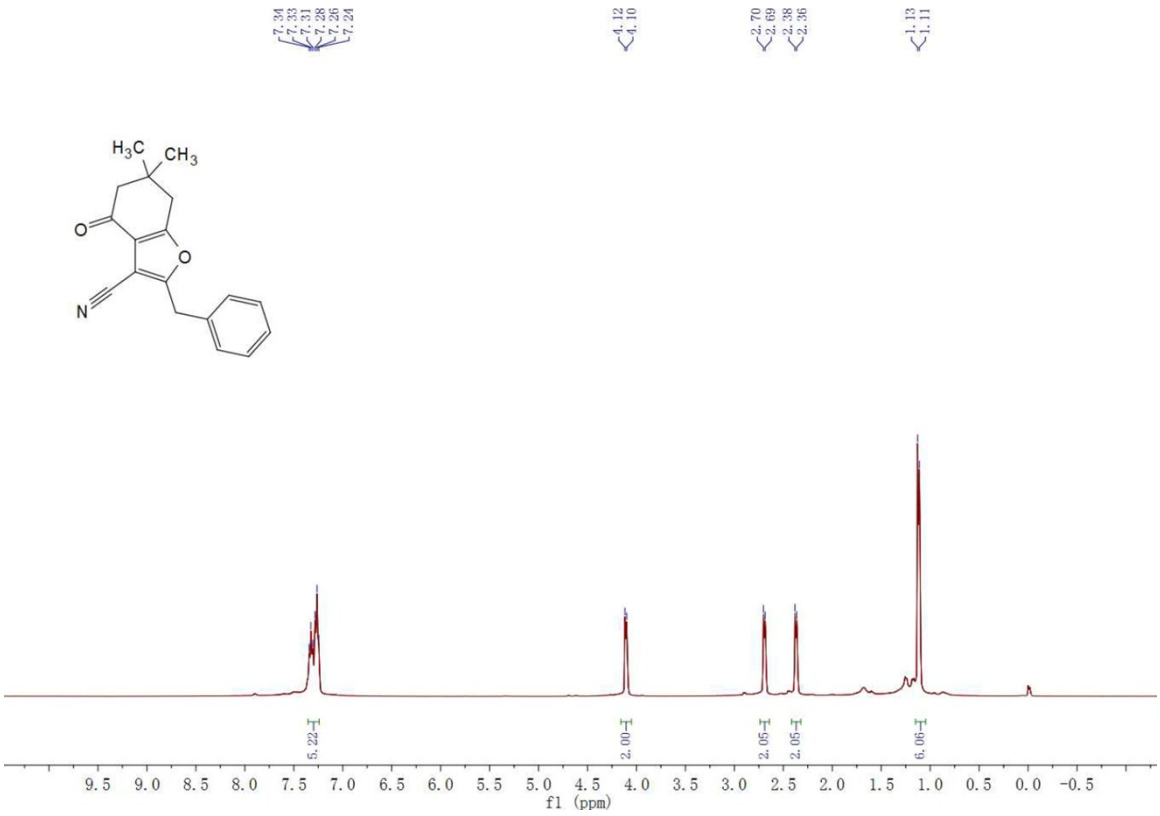
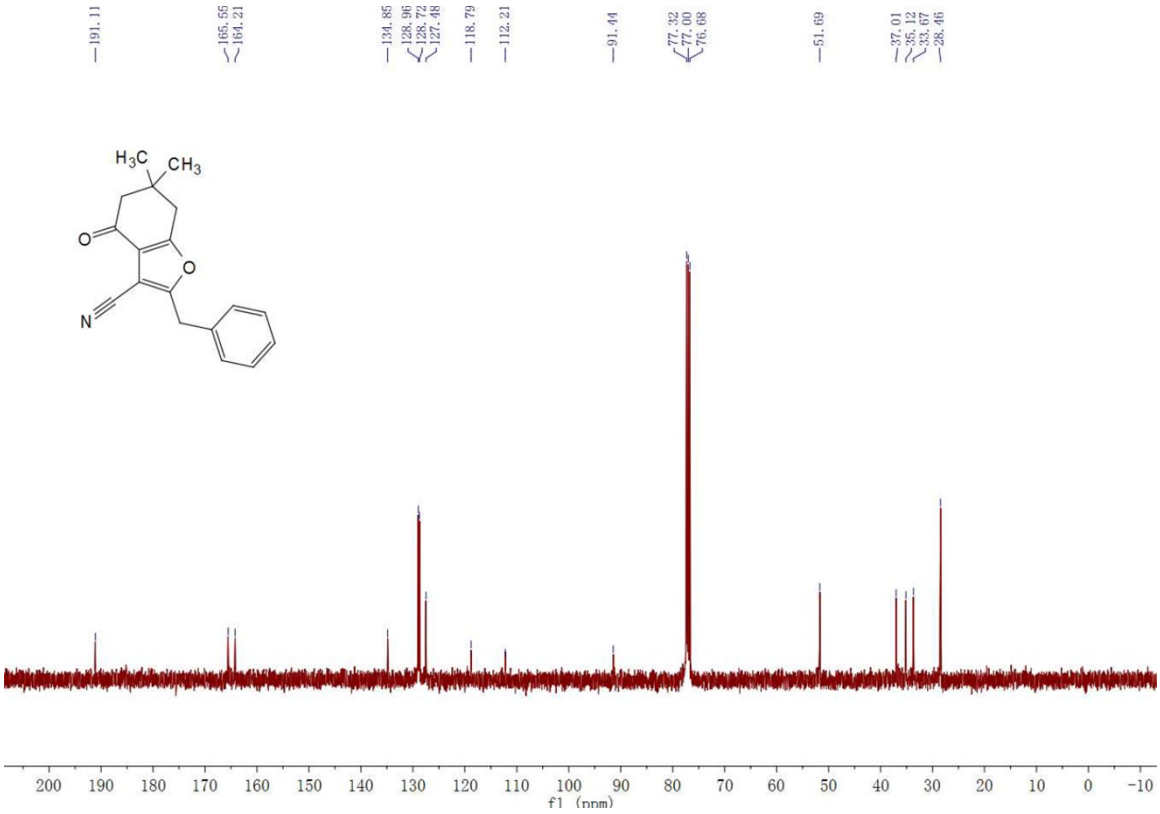
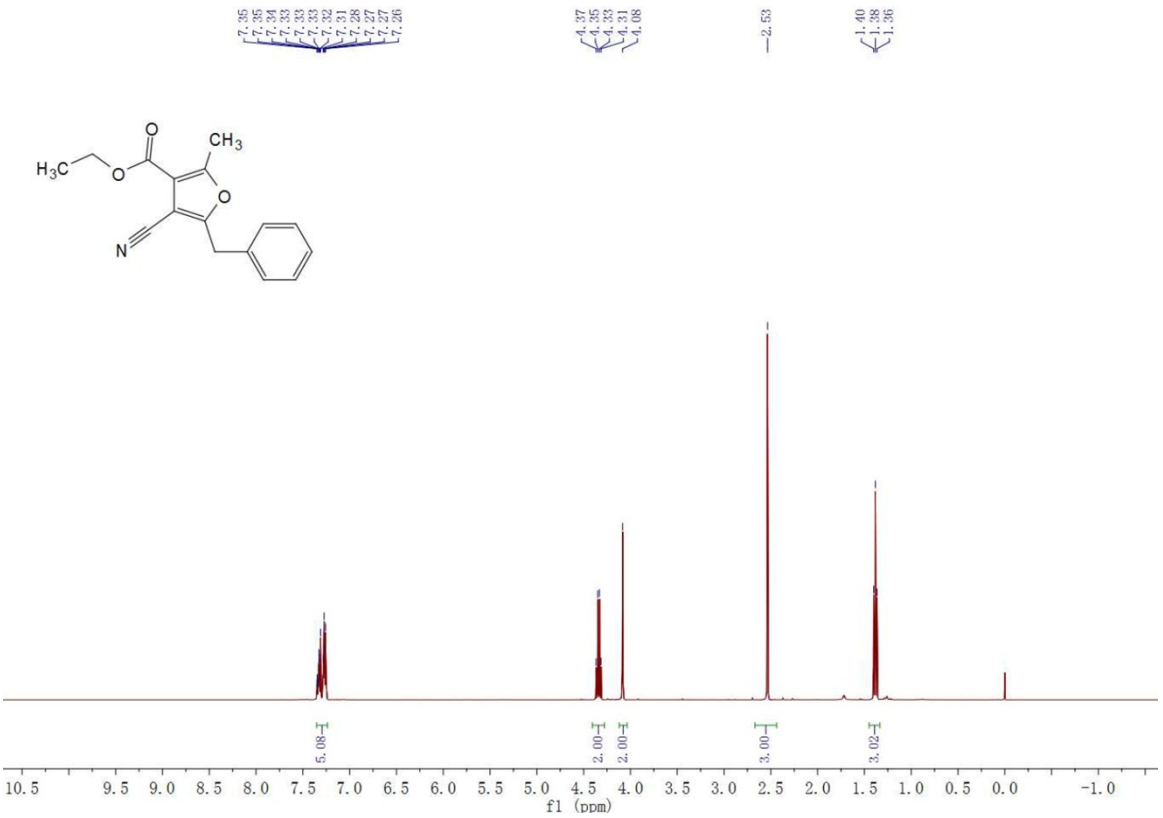
162.67
154.73
136.34
134.92
133.62
129.79
129.02
128.77
128.57
128.50
127.87
127.51
127.47
120.34
112.24
97.16
77.32
77.00
76.68
33.81
O
O
N
129.79
129.02
128.77
128.57
128.50
127.87
127.51
127.47
130.0
129.0
128.0
127.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3e


7.34
7.33
7.31
7.28
7.26
7.24
4.12
4.10
2.70
2.69
2.38
2.36
1.13
1.11
H3C
CH3
O
O
N
5.22
2.00
2.05
2.05
6.06
f1 (ppm)


191.11
165.56
164.21
134.85
128.96
128.72
127.48
118.79
112.21
91.44
77.32
77.00
76.68
51.69
37.01
35.12
33.67
28.46
H3C
CH3
O
O
N
f1 (ppm)

3f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7.34
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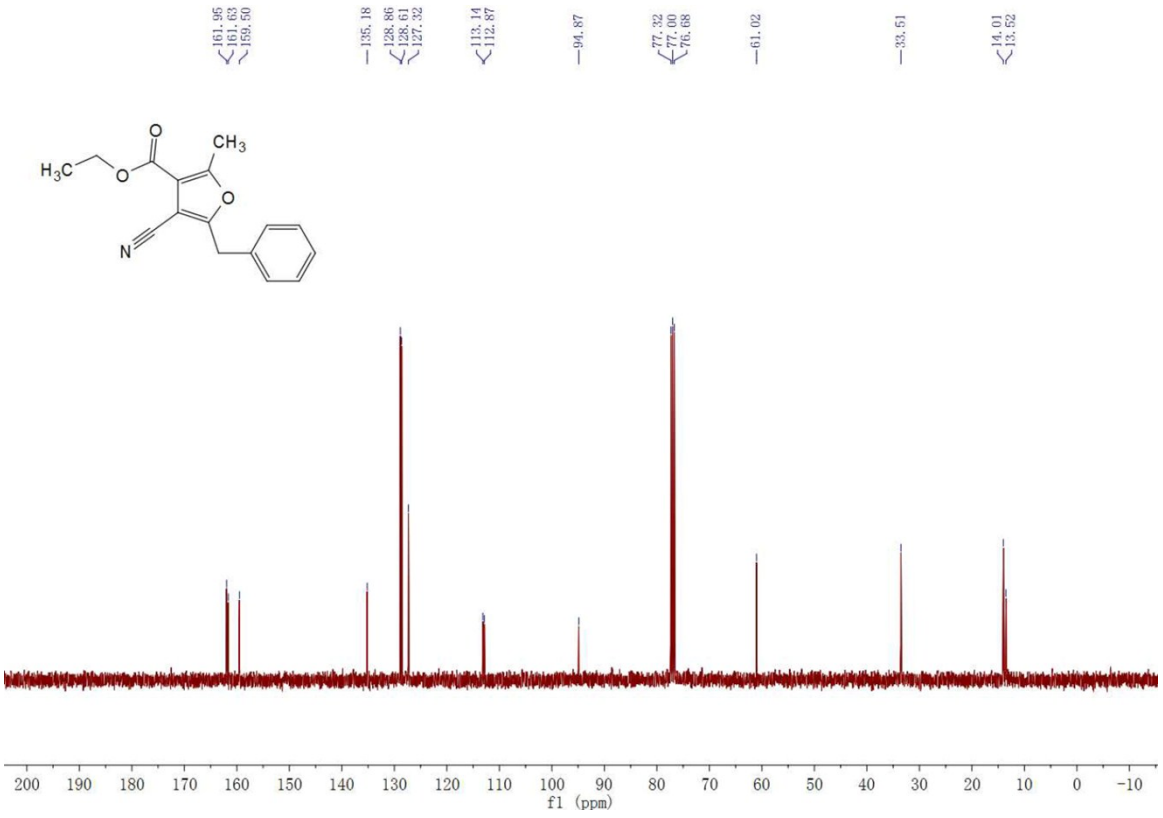
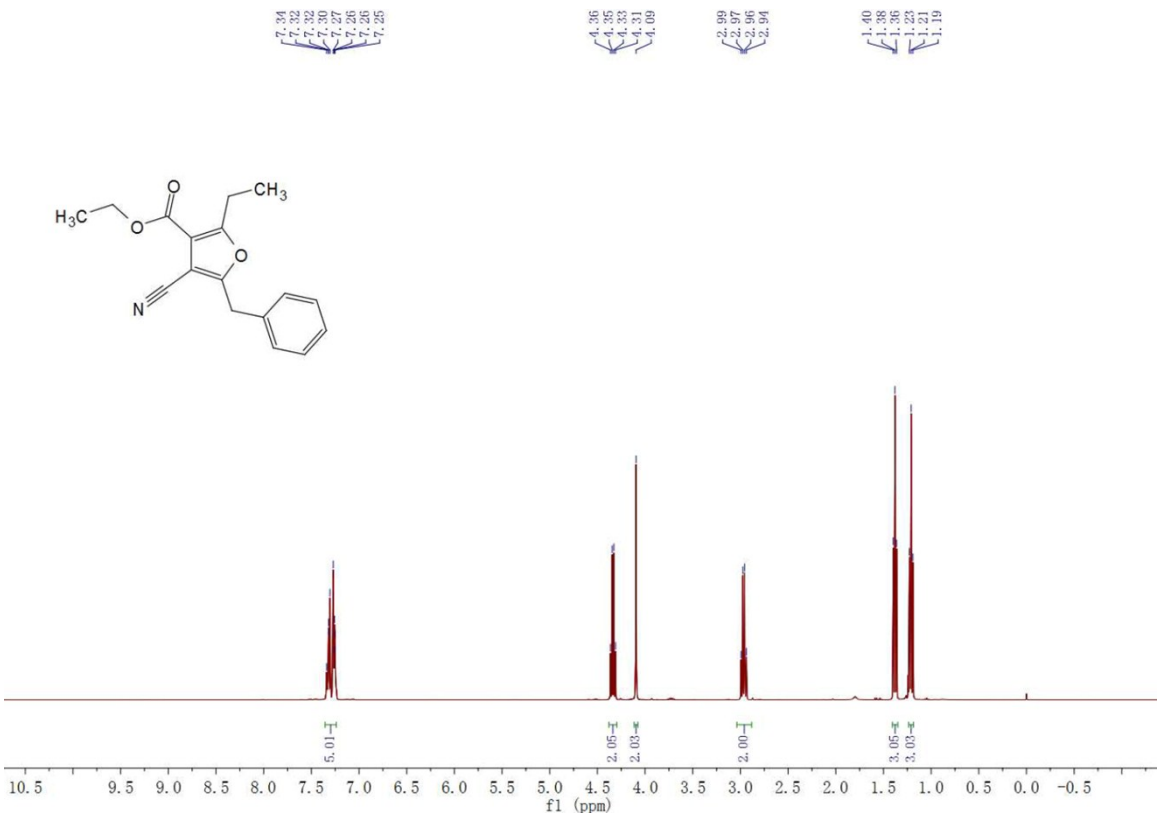
7.32
7.31
7.28
7.27
7.27
7.26
4.37
4.35
4.33
4.31
4.08
2.53
1.40
1.38
1.36
O
CH3
H3C
O
O
N
5.08
2.00
2.00
3.00
3.02
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)


161.95
161.63
159.50
135.18
128.86
128.61
127.32
113.14
112.87
94.87
77.32
77.00
76.68
61.02
33.51
14.01
13.52
O
CH3
H3C
O
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3g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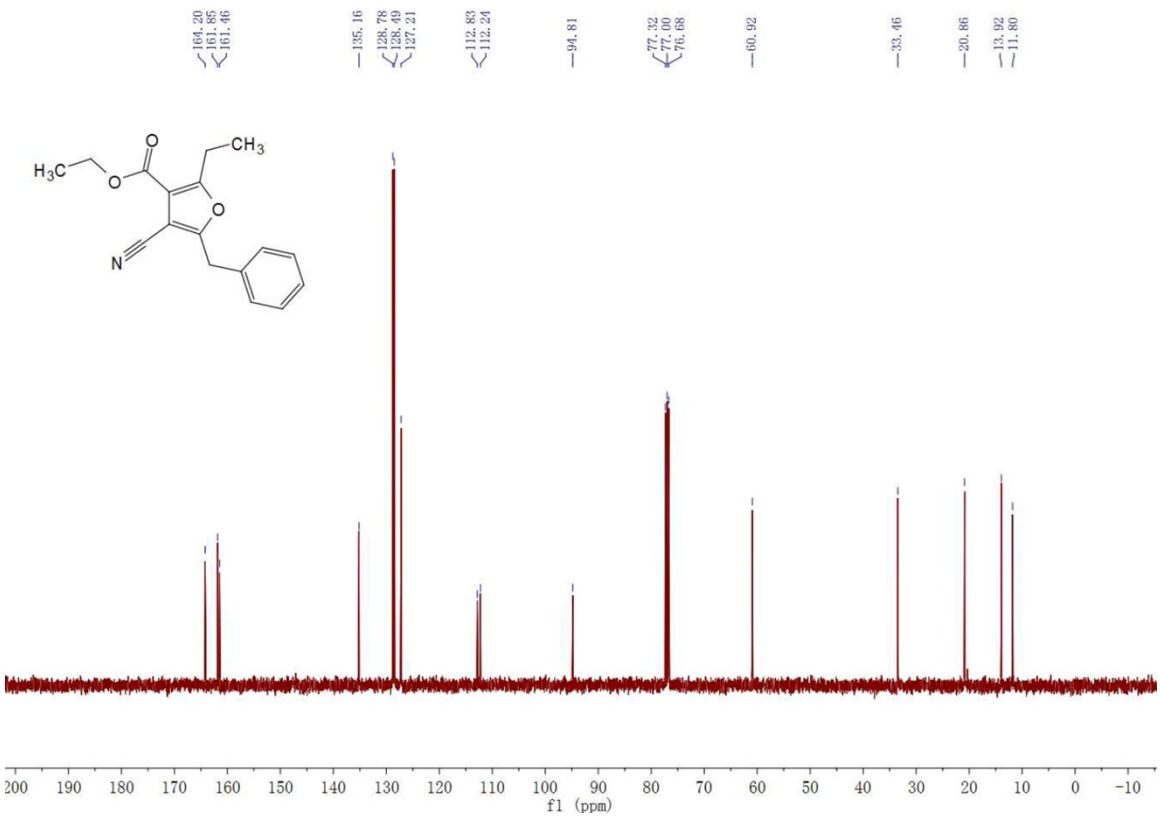
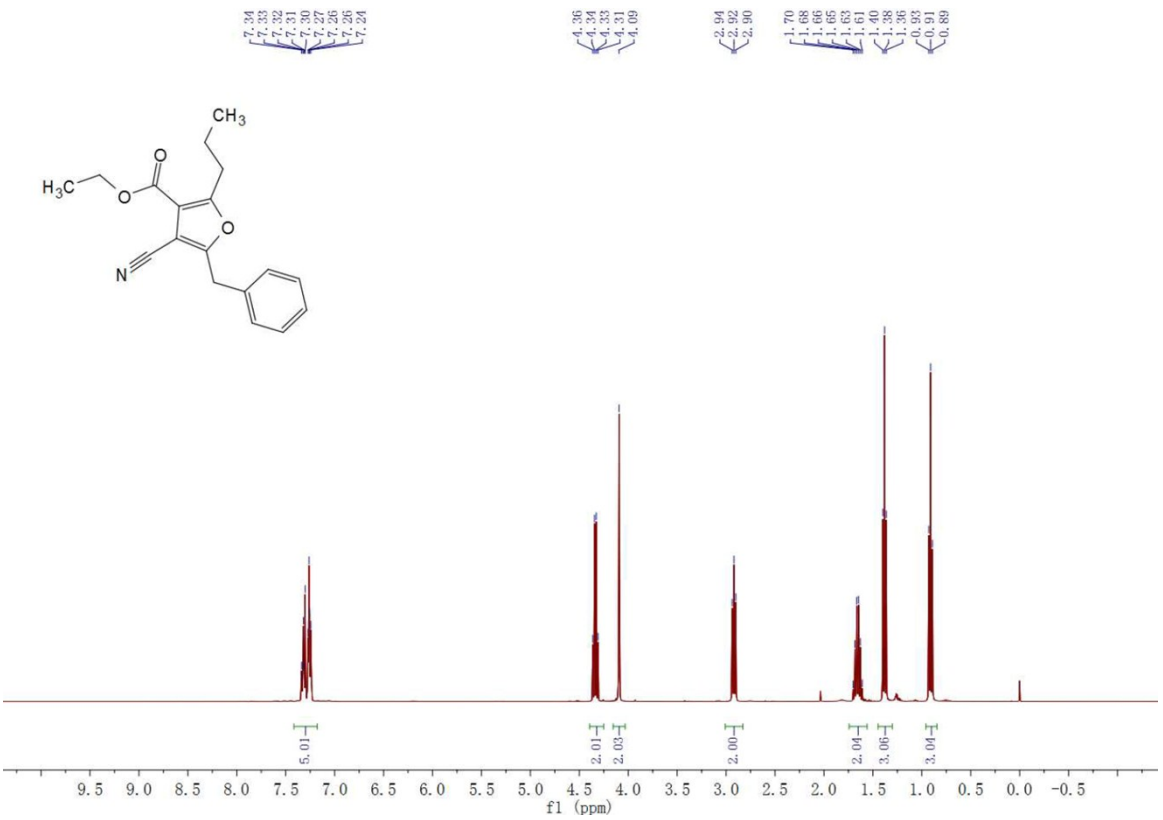
7.32
7.32
7.30
7.27
7.26
7.26
7.25
4.36
4.35
4.33
4.31
4.09
2.99
2.97
2.96
2.94
1.40
1.38
1.36
1.23
1.21
1.19
O
CH3
H3C
O
O
N
5.01
2.05
2.03
2.00
3.05
3.03
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


164.20
161.85
161.46
135.16
128.78
128.49
127.21
112.83
112.24
94.81
77.32
77.00
76.68
60.92
33.46
20.86
13.92
11.80
O
CH3
H3C
O
O
N
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3h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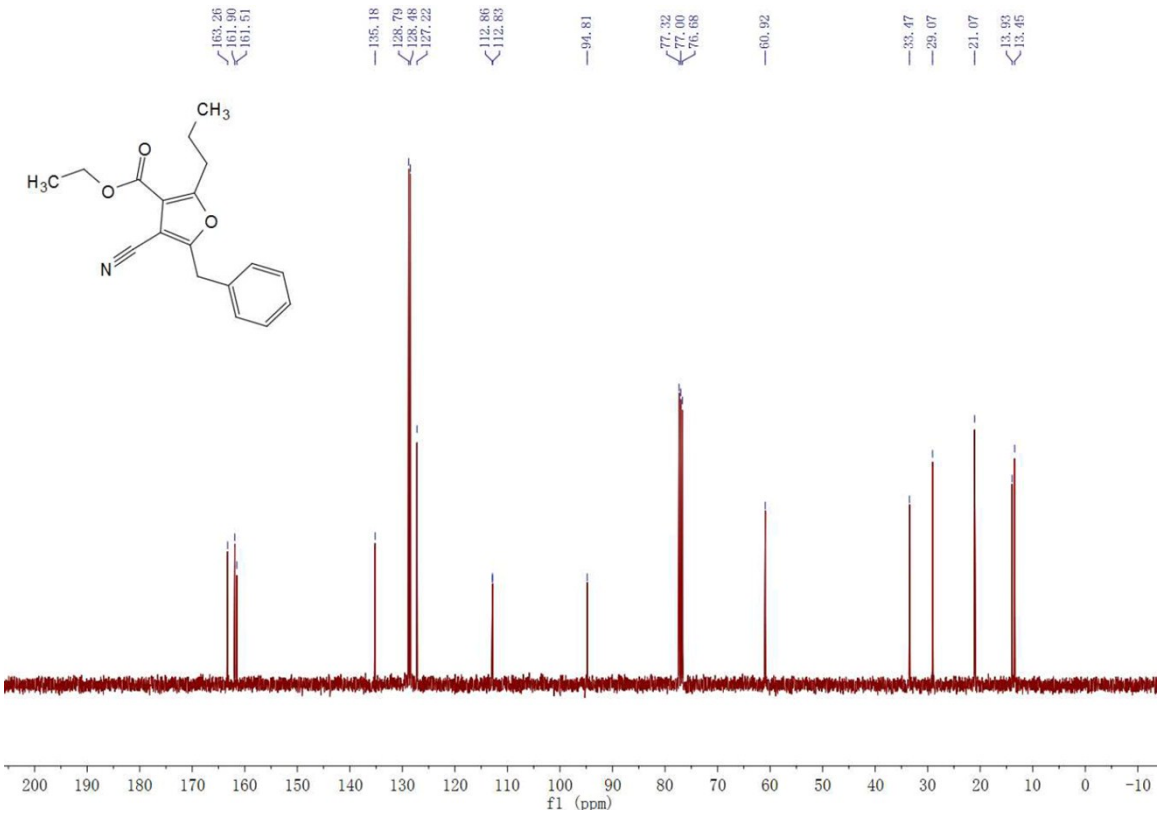
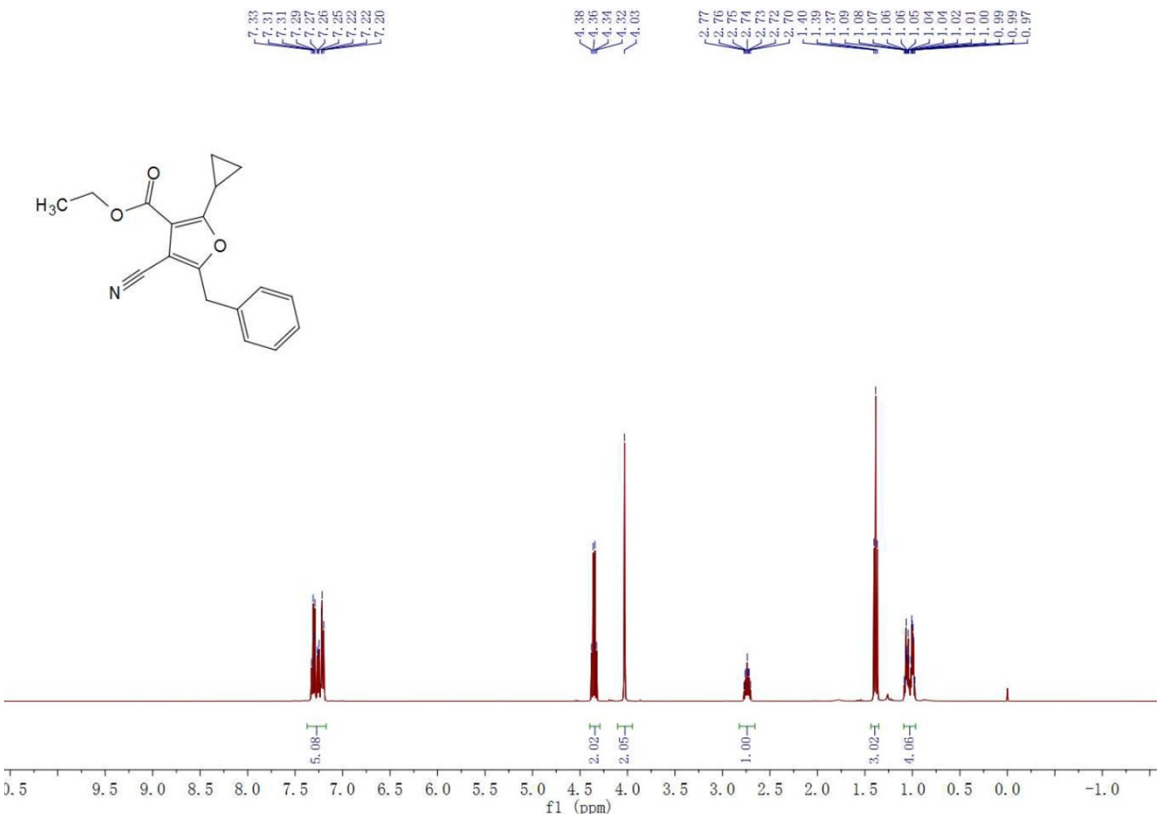
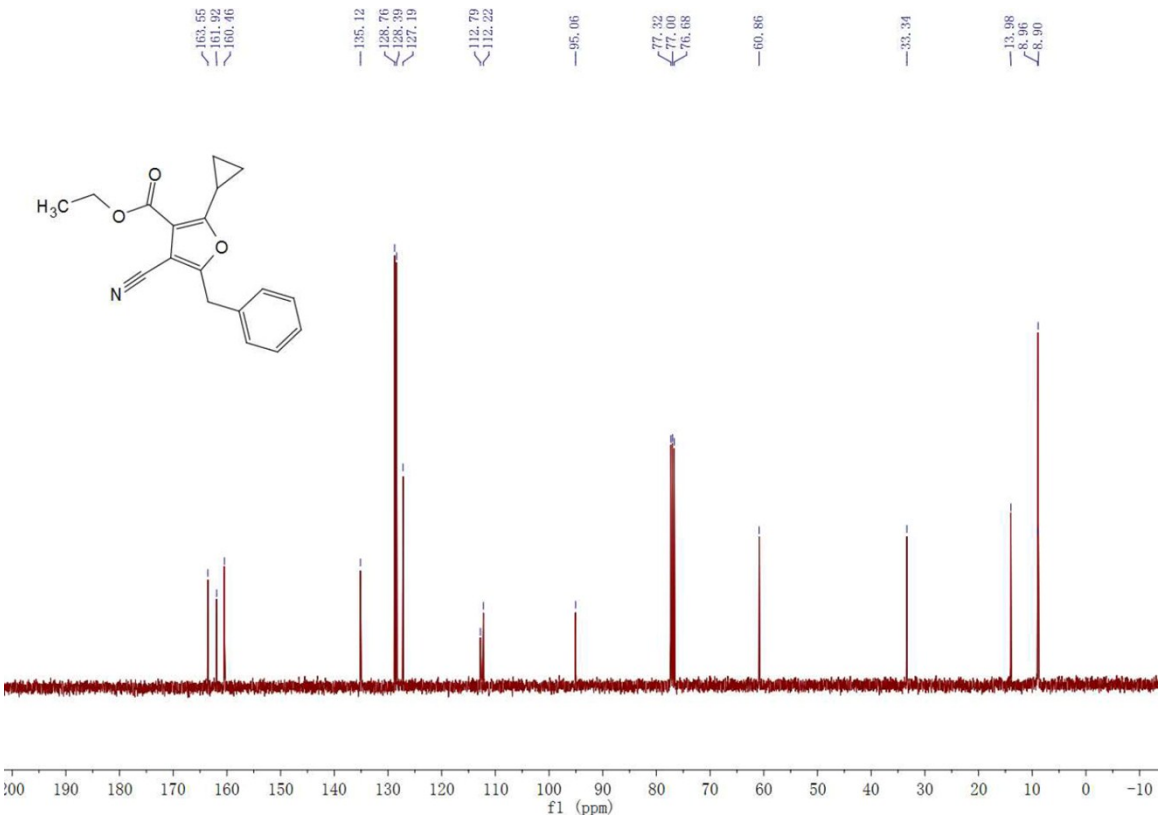
7.33
7.32
7.31
7.30
7.27
7.26
7.26
7.24
4.36
4.34
4.33
4.31
4.09
2.94
2.92
2.90
1.70
1.68
1.66
1.65
1.63
1.61
1.40
1.38
1.36
0.93
0.91
0.89
CH3
O
H3C
O
O
N
5.01
2.01
2.03
2.00
2.04
3.06
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.26
161.90
161.51
135.18
128.79
128.48
127.22
112.86
112.83
94.81
77.32
77.00
76.68
60.92
33.47
29.07
21.07
13.93
13.45
CH3
O
H3C
O
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3i


7.33
7.31
7.31
7.29
7.27
7.26
7.25
7.22
7.22
7.20
4.38
4.36
4.34
4.32
4.03
2.77
2.76
2.75
2.74
2.73
2.72
2.70
2.40
1.39
1.37
1.09
1.08
1.07
1.06
1.06
1.05
1.04
1.04
1.02
1.01
1.00
0.99
0.99
0.97
H3C
O
O
O
N
5.08
2.02
2.05
1.00
3.02
4.06
f1 (ppm)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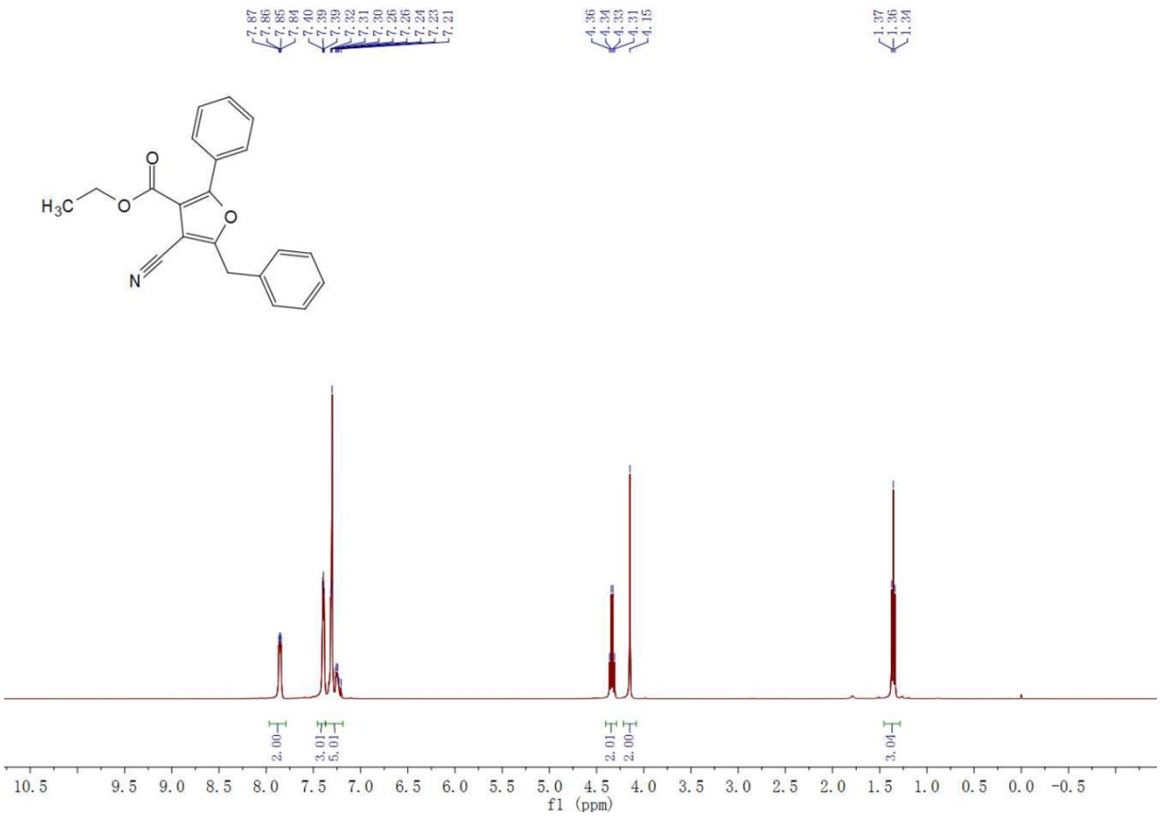
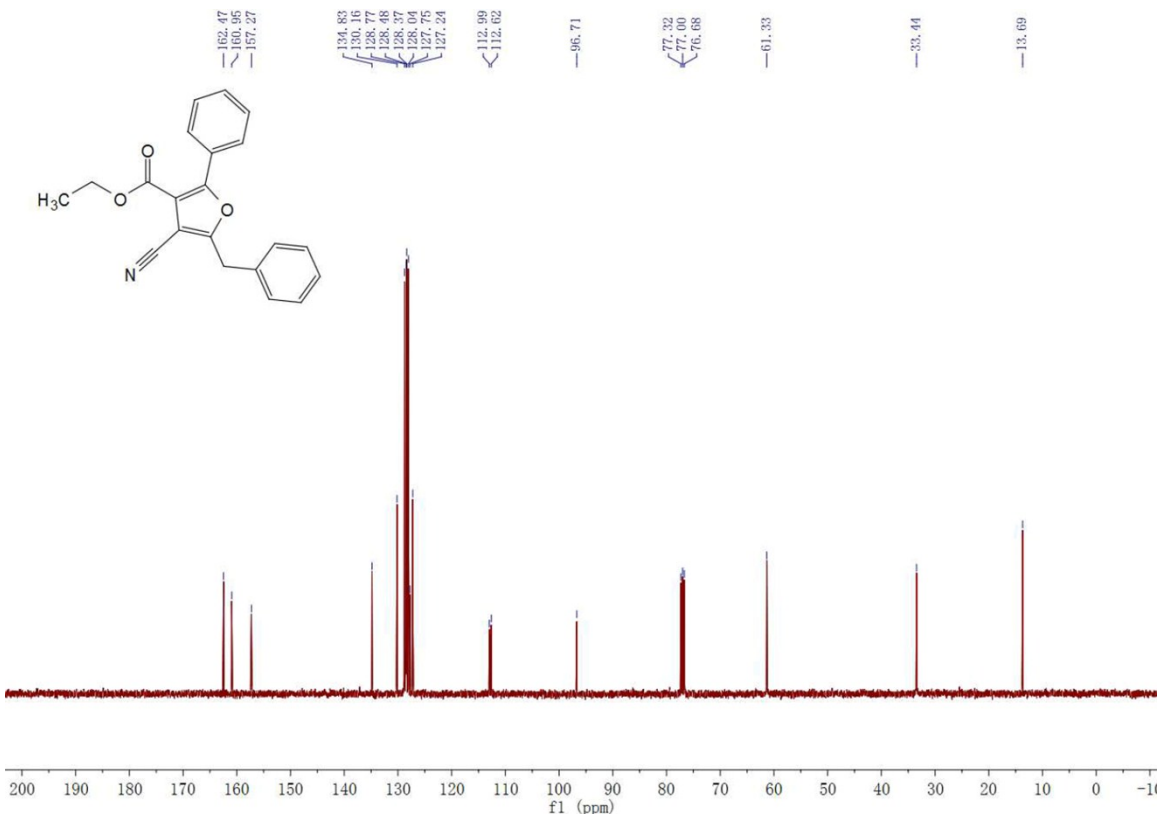
161.92
160.46
135.12
128.76
128.39
127.19
112.79
112.22
95.06
77.32
77.00
76.68
60.86
33.34
13.98
8.96
8.90
H3C
O
O
O
N
f1 (ppm)

3j


7.87
7.86
7.85
7.84
7.40
7.39
7.39
7.32
7.31
7.30
7.26
7.26
7.24
7.23
7.21
4.36
4.34
4.33
4.31
4.15
1.37
1.36
1.34
H3C
O
O
O
N
2.00
3.01
5.01
2.01
2.00
3.04
f1 (ppm)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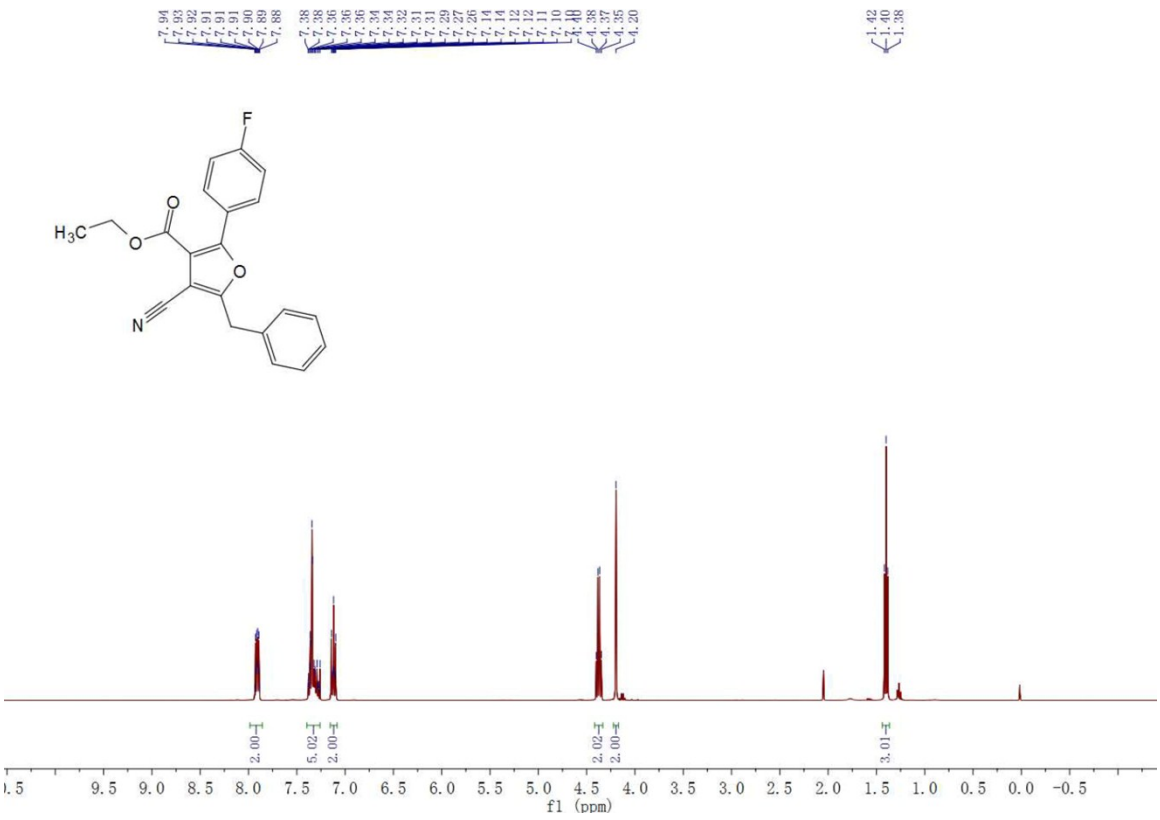
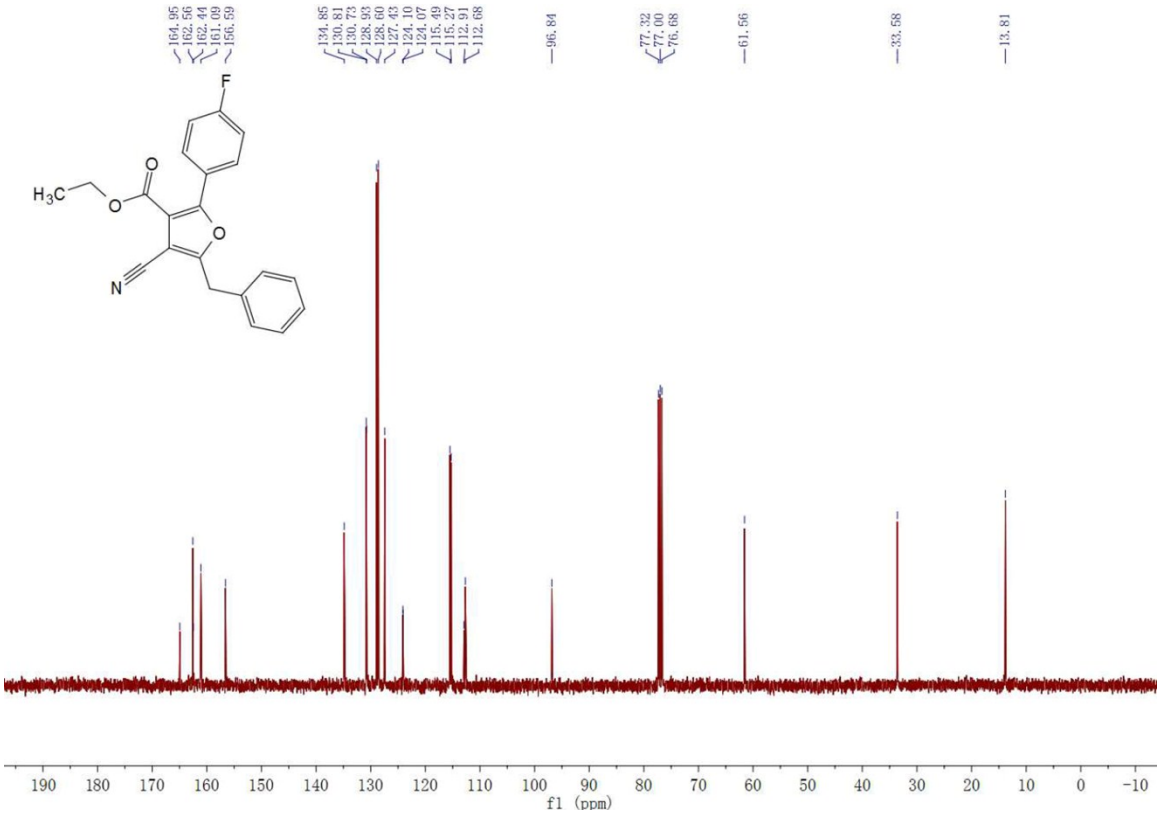
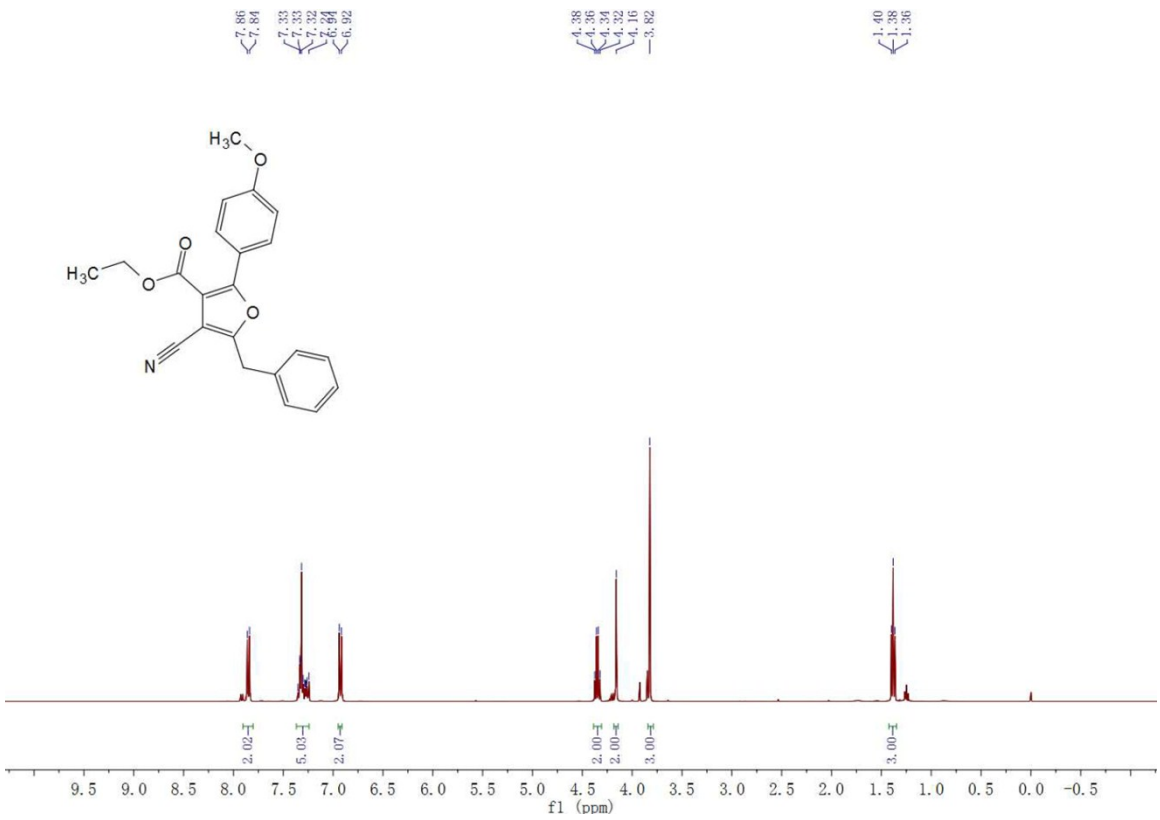
160.95
157.27
134.83
130.16
128.77
128.48
128.37
128.04
127.75
127.24
112.99
112.62
96.71
77.32
77.00
76.68
61.33
33.44
13.69
H3C
O
O
O
N
f1 (ppm)

3k





3l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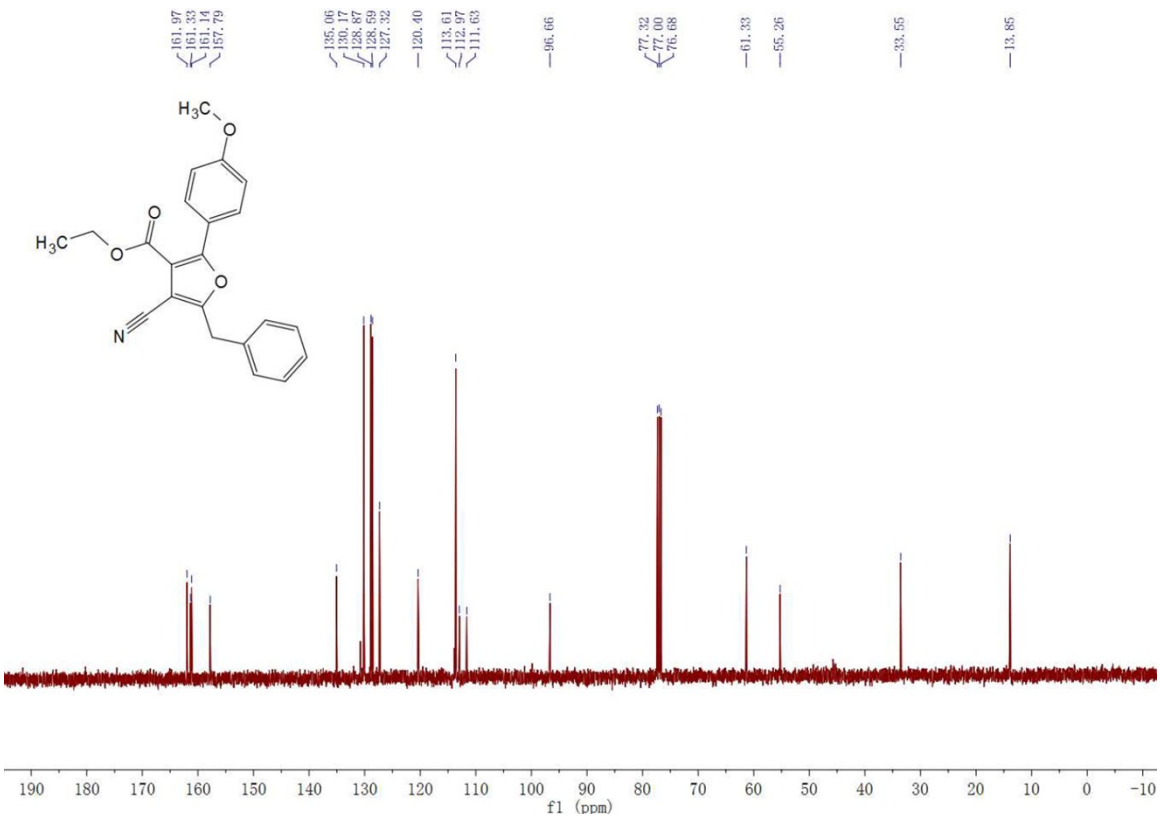
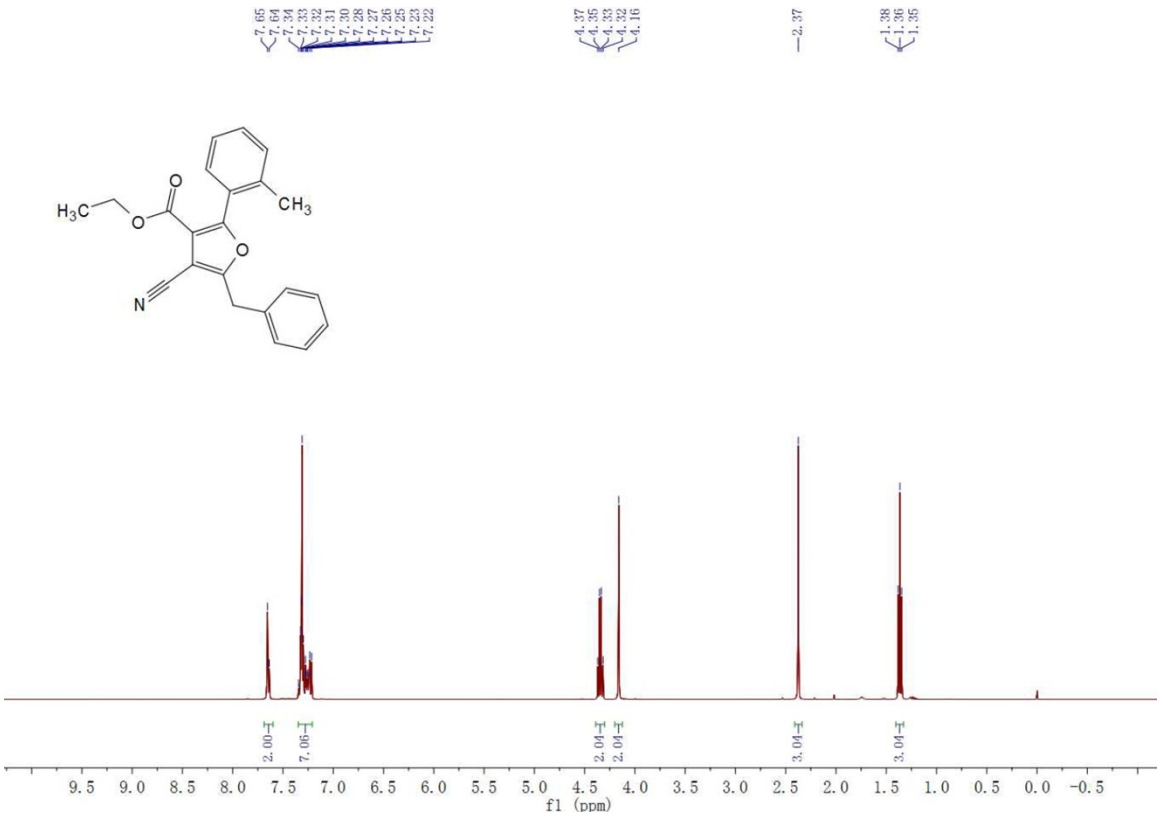
7.84
7.33
7.33
7.32
7.24
6.94
6.92
4.38
4.36
4.34
4.32
4.16
3.82
1.40
1.38
1.36
H3C
O
H3C
O
O
O
N
2.02
5.03
2.07
2.00
2.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


161.97
161.33
161.14
157.79
135.06
130.17
128.87
128.59
127.32
120.40
113.61
112.97
111.63
96.66
77.32
77.00
76.68
61.33
55.26
33.55
13.85
H3C
O
H3C
O
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3m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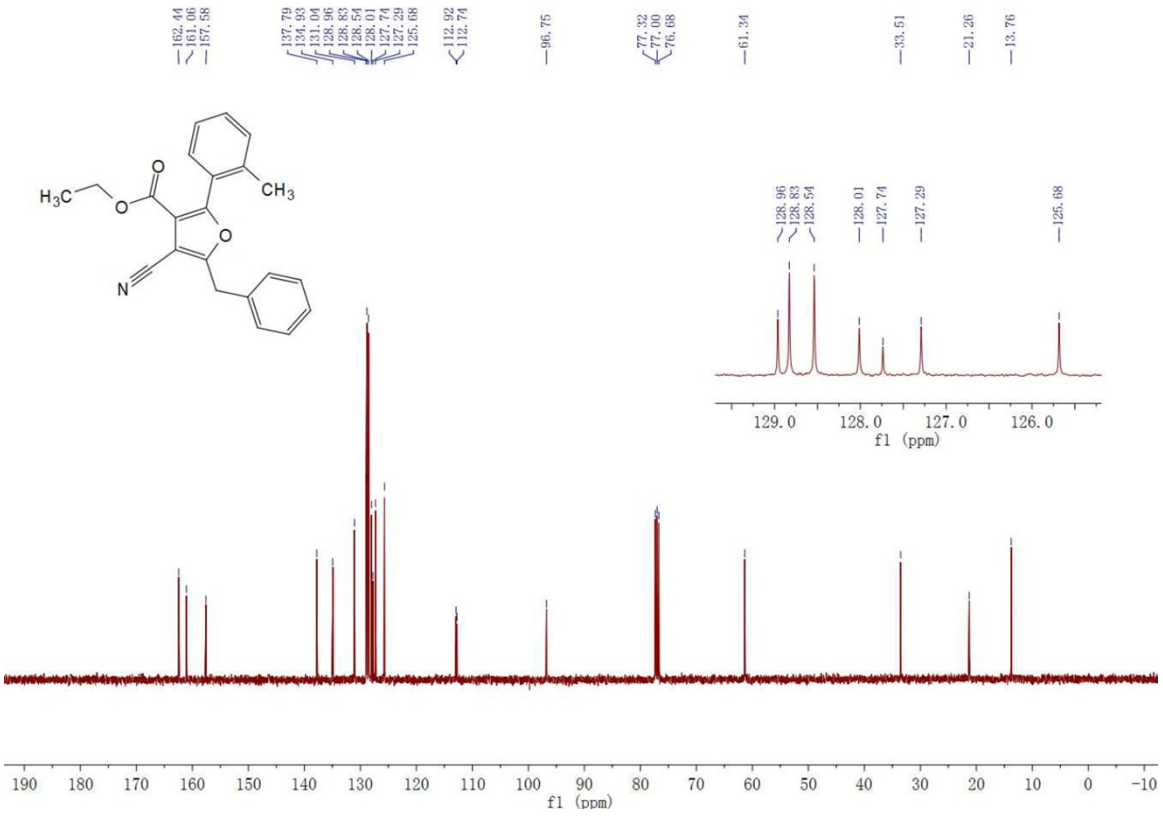
7.31
7.30
7.28
7.27
7.26
7.25
7.23
7.22
4.37
4.35
4.33
4.32
4.16
2.37
1.38
1.36
1.35
H3C
O
O
CH3
O
N
2.00
7.06
2.04
2.04
3.04
3.04
f1 (ppm)


162.44
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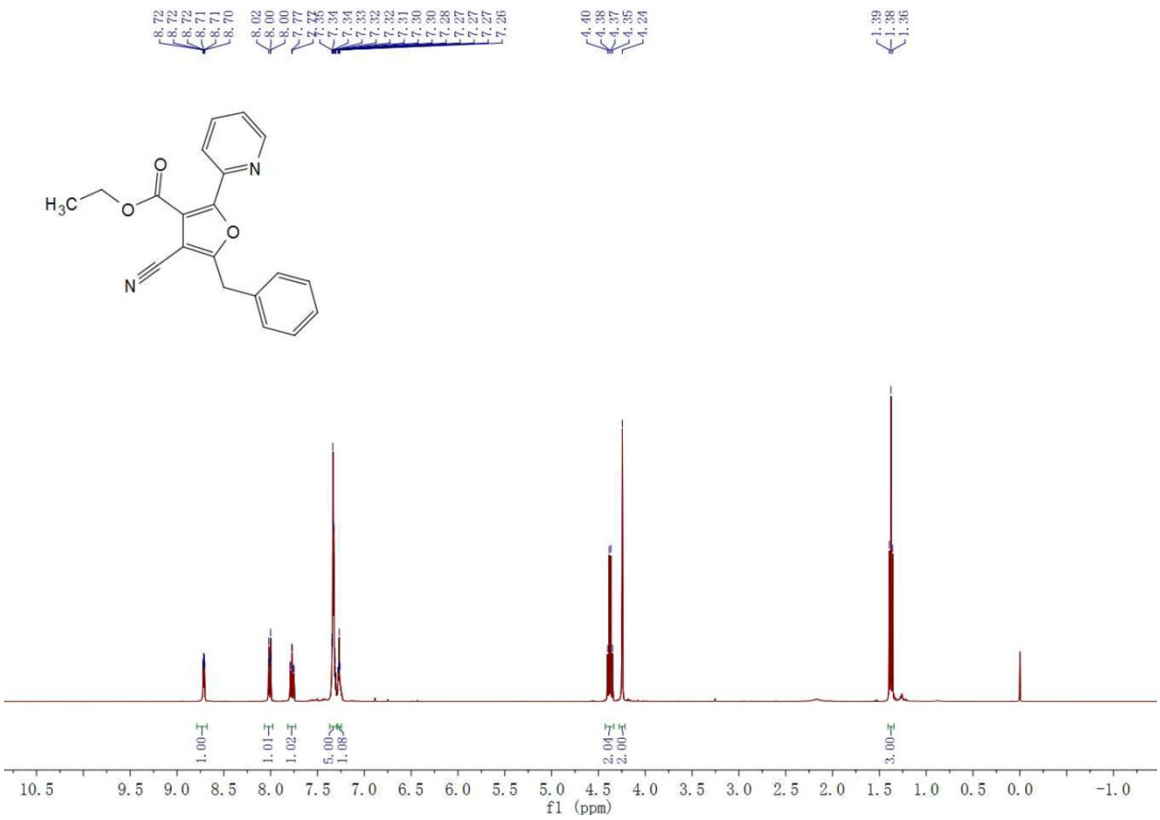
131.04
128.96
128.83
128.54
128.01
127.74
127.29
125.68
112.92
112.74
96.75
77.32
77.00
76.68
61.34
33.51
21.26
13.76
H3C
O
O
CH3
O
N
128.96
128.83
128.54
128.01
127.74
127.29
125.68
129.0
128.0
127.0
126.0
f1 (ppm)
f1 (ppm)

3n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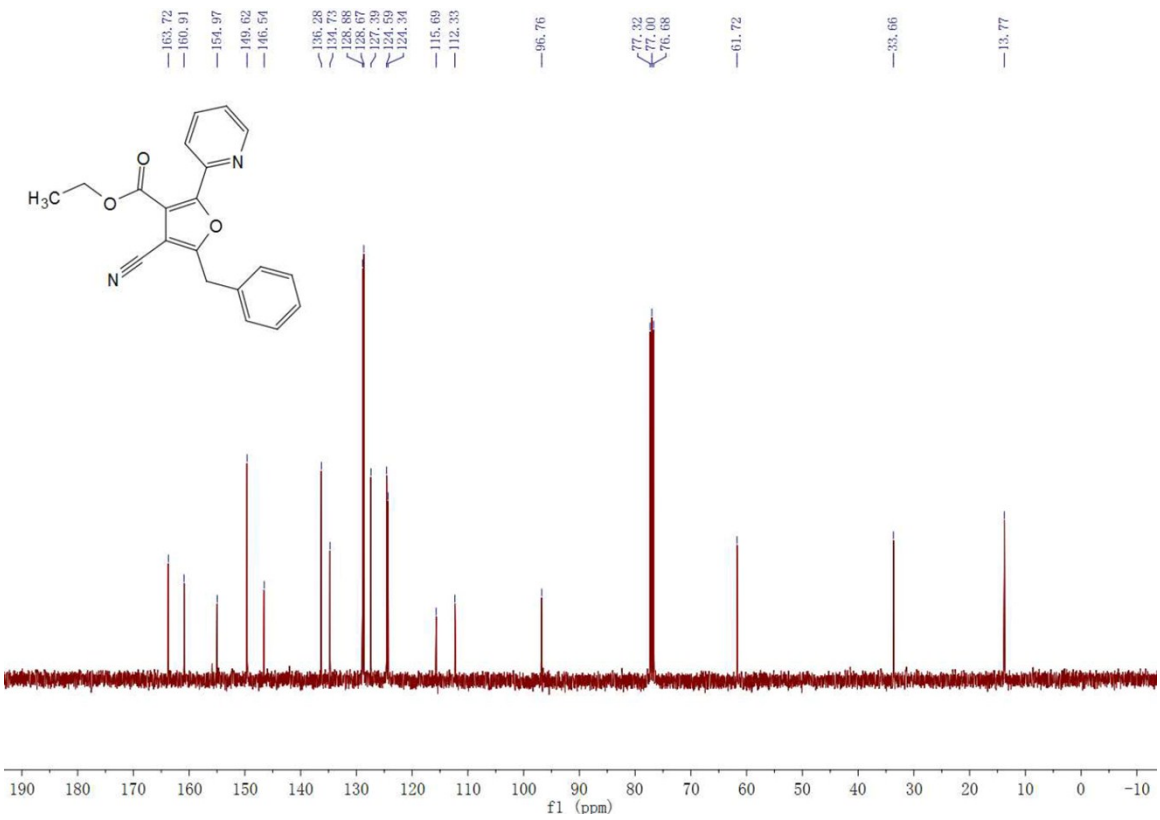
8.72
8.72
8.71
8.71
8.70
8.02
8.00
8.00
7.77
7.75
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.28
7.27
7.27
7.27
7.26
4.40
4.38
4.37
4.35
4.24
1.39
1.38
1.36
O
N
H3C
O
O
N
1.00
1.01
1.02
5.00
1.08
2.04
2.00
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)


163.72
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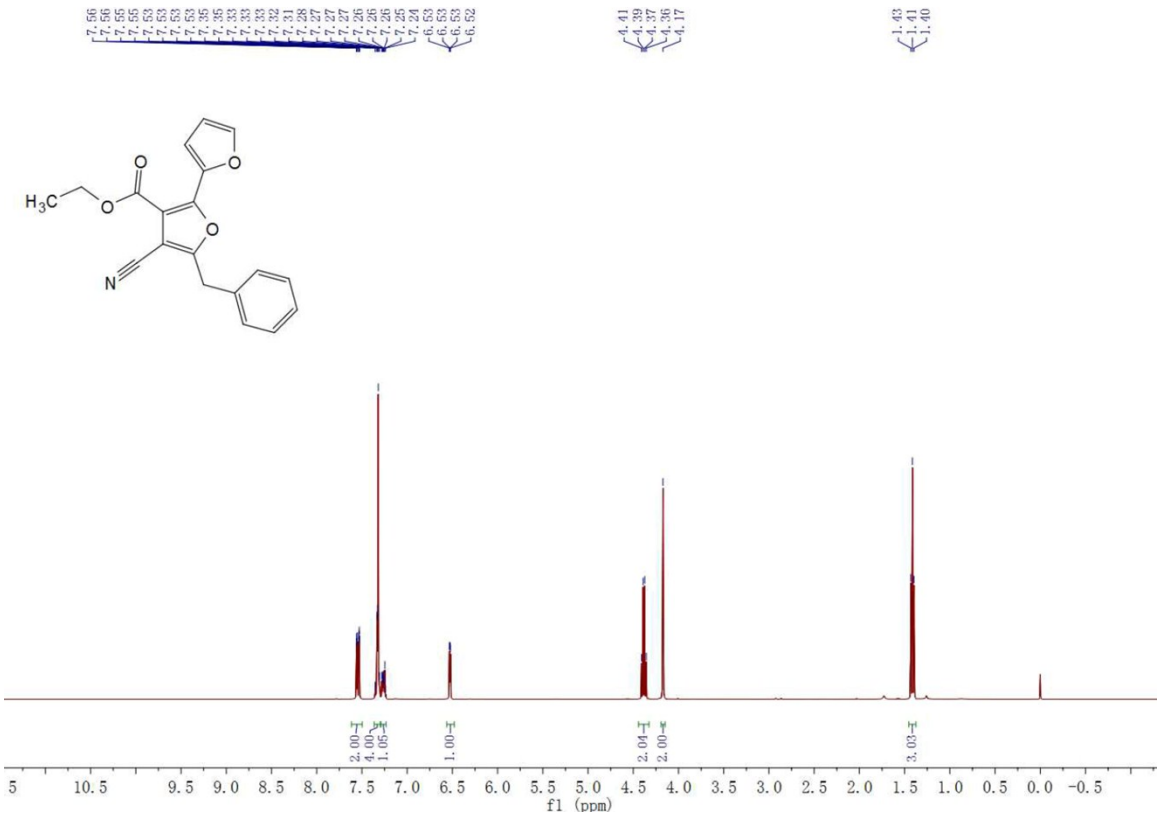
154.97
149.62
146.54
136.28
134.73
128.88
128.67
127.39
124.59
124.34
115.69
112.33
96.76
77.32
77.00
76.68
61.72
33.66
13.77
O
N
H3C
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3o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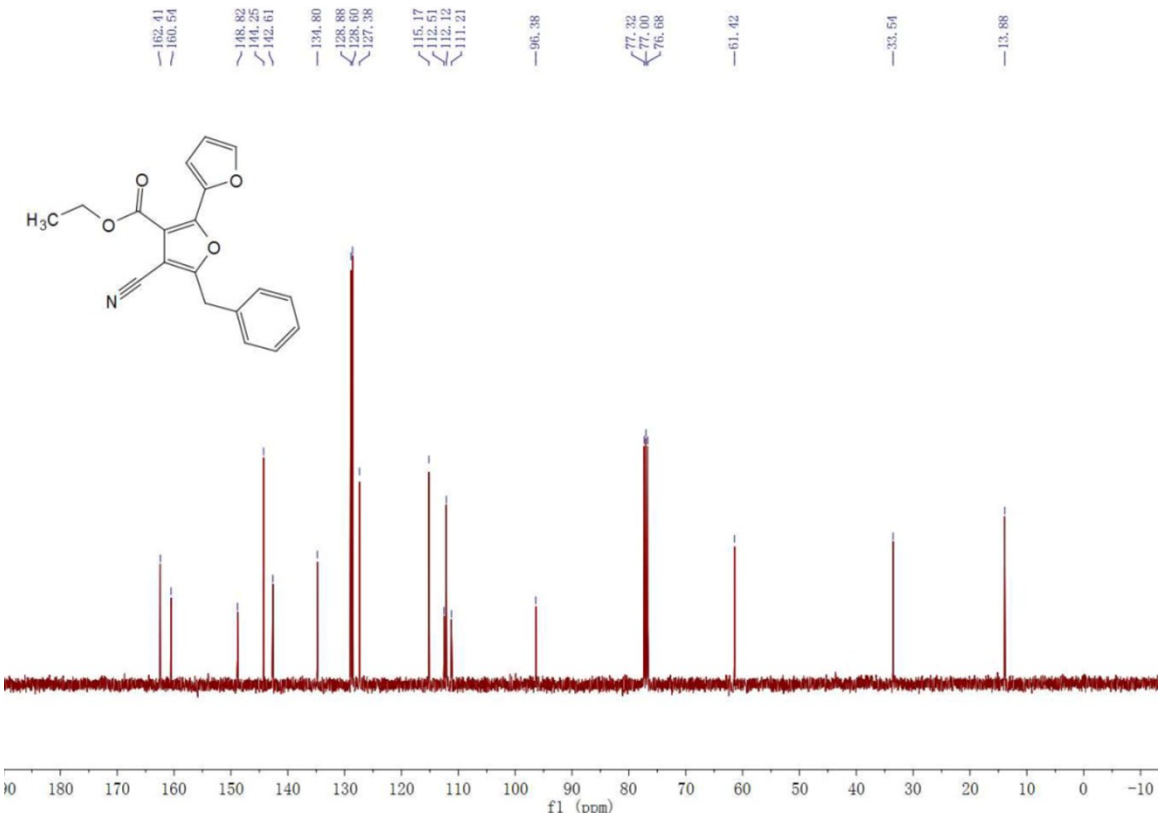
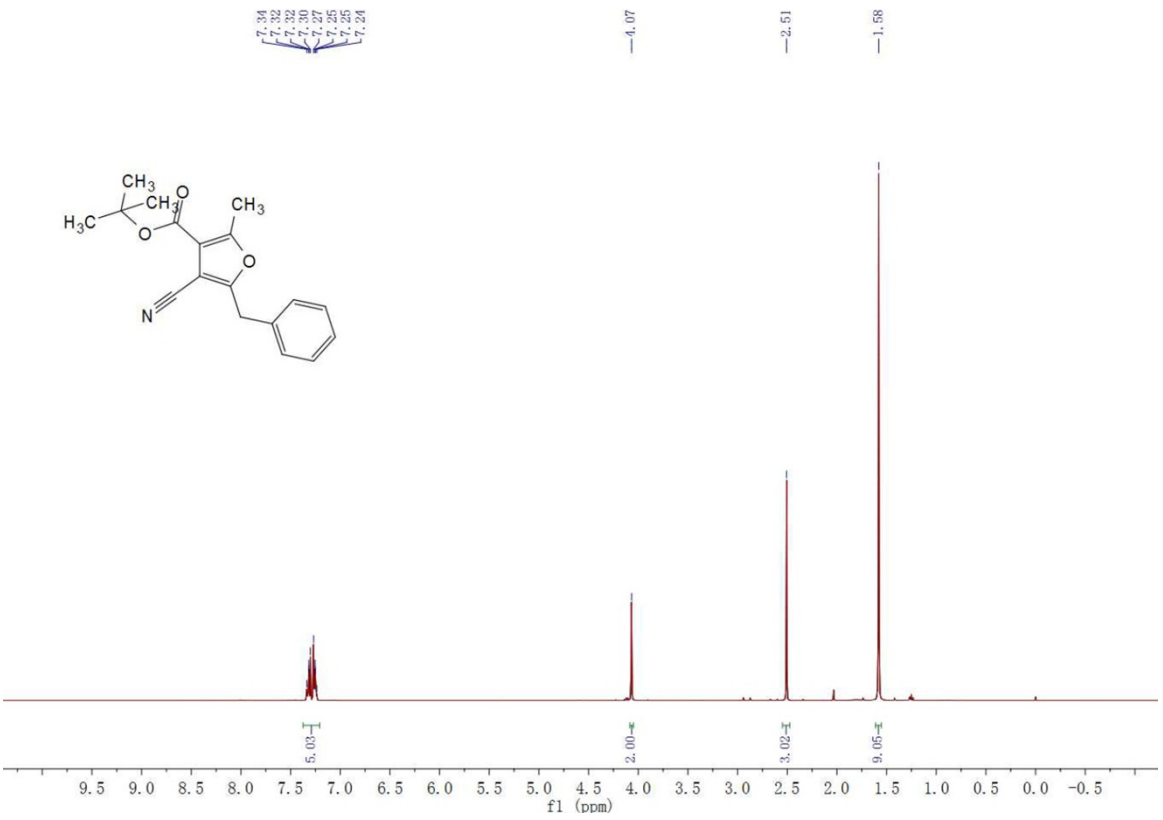
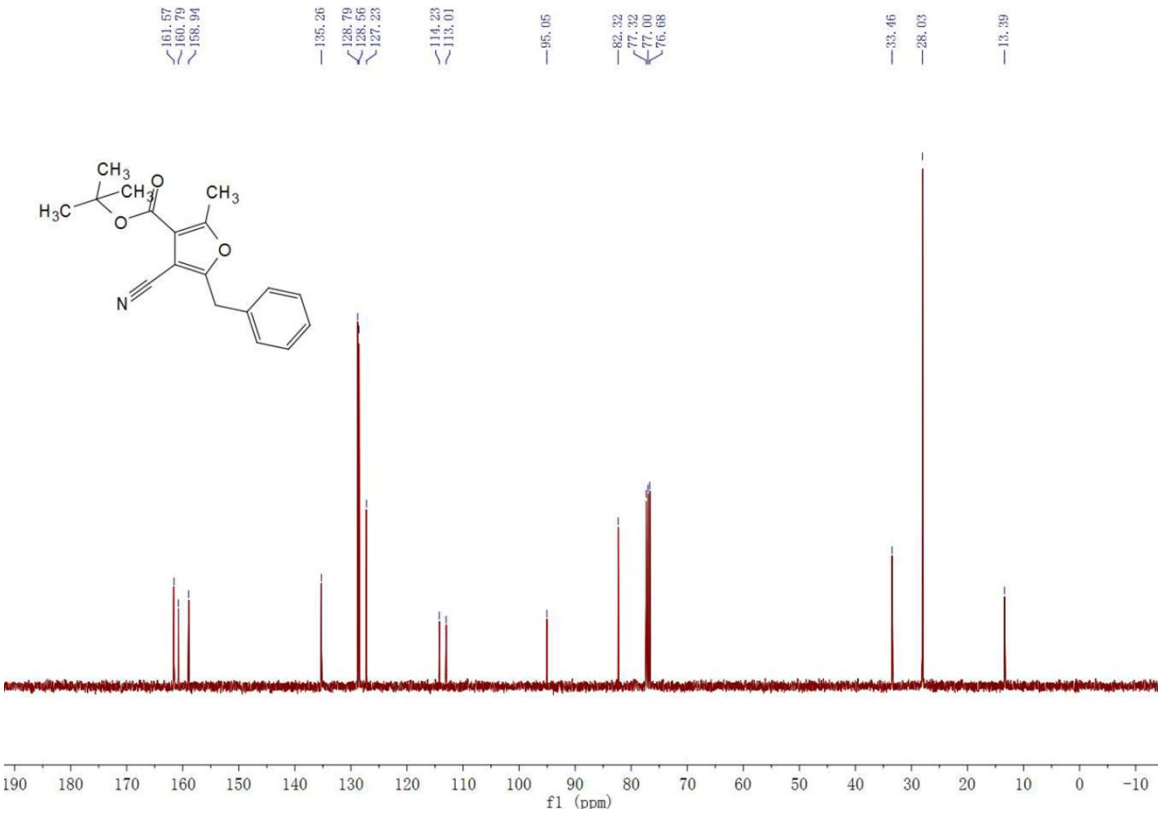
7.56
7.55
7.55
7.53
7.53
7.53
7.53
7.35
7.35
7.33
7.33
7.32
7.31
7.28
7.27
7.27
7.27
7.26
7.26
7.26
7.25
7.24
6.53
6.53
6.52
4.41
4.39
4.37
4.36
4.17
1.43
1.41
1.40
O
O
O
O
N
H3C
2.00
4.00
1.05
1.00
2.04
2.00
3.03
f1 (ppm)

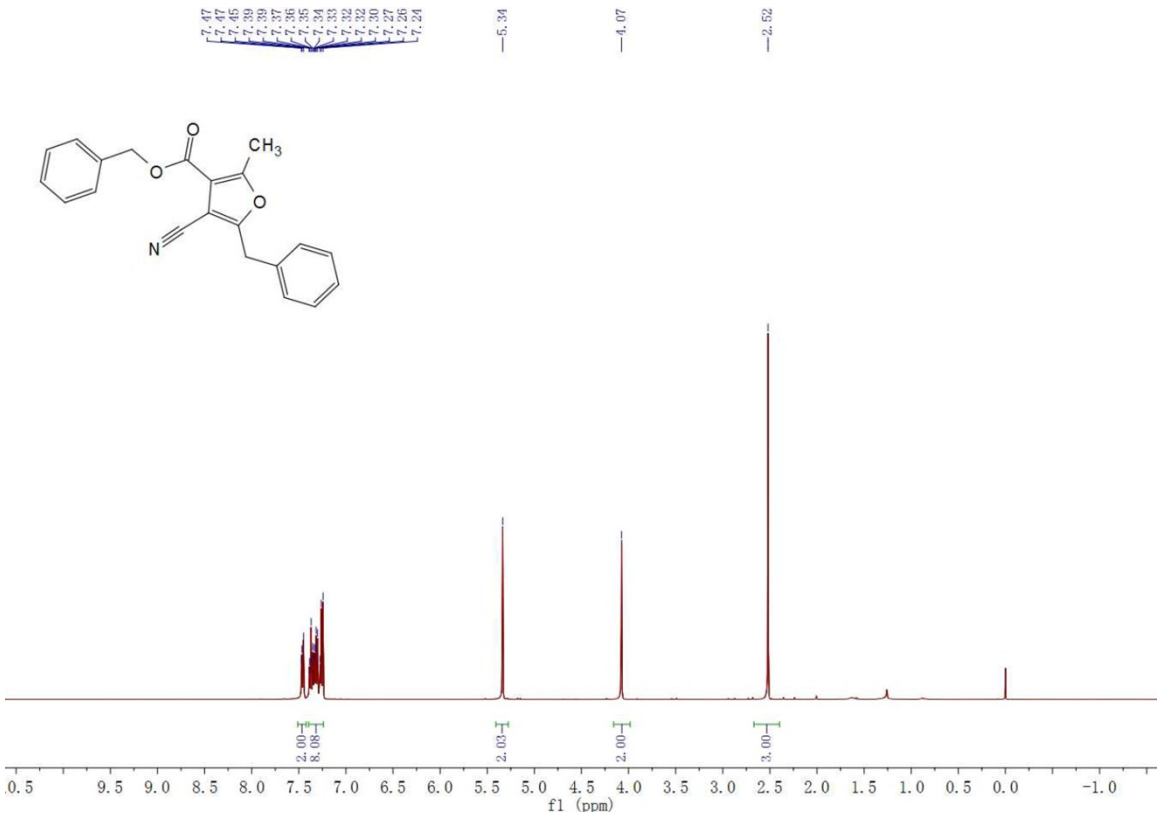

162.41
160.54
148.82
144.25
142.61
134.80
128.88
128.60
127.38
115.17
112.51
112.12
111.21
96.38
77.32
77.00
76.68
61.42
33.54
13.88
O
O
O
O
N
H3C
f1 (ppm)

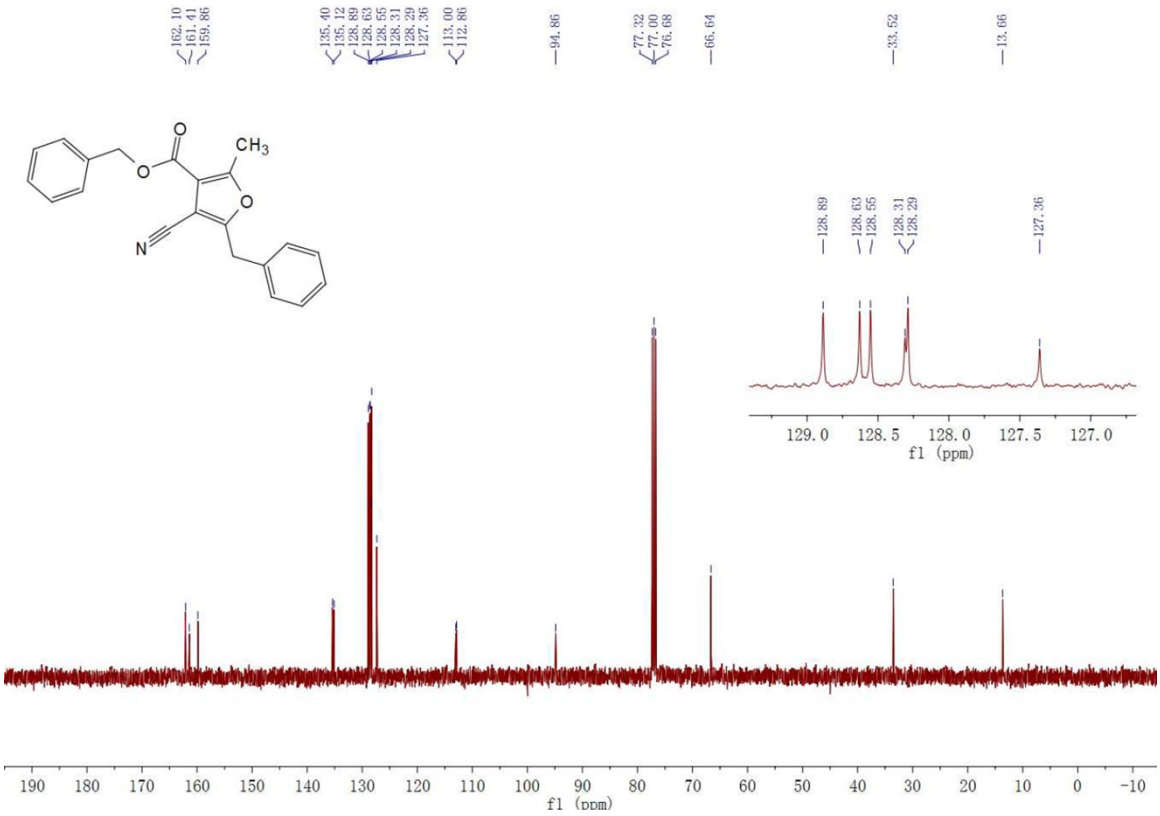
3p


7.34
7.32
7.32
7.30
7.27
7.25
7.25
7.24
4.07
2.51
1.58
CH3
CH3
CH3
H3C
O
O
O
N
5.03
2.00
3.02
9.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

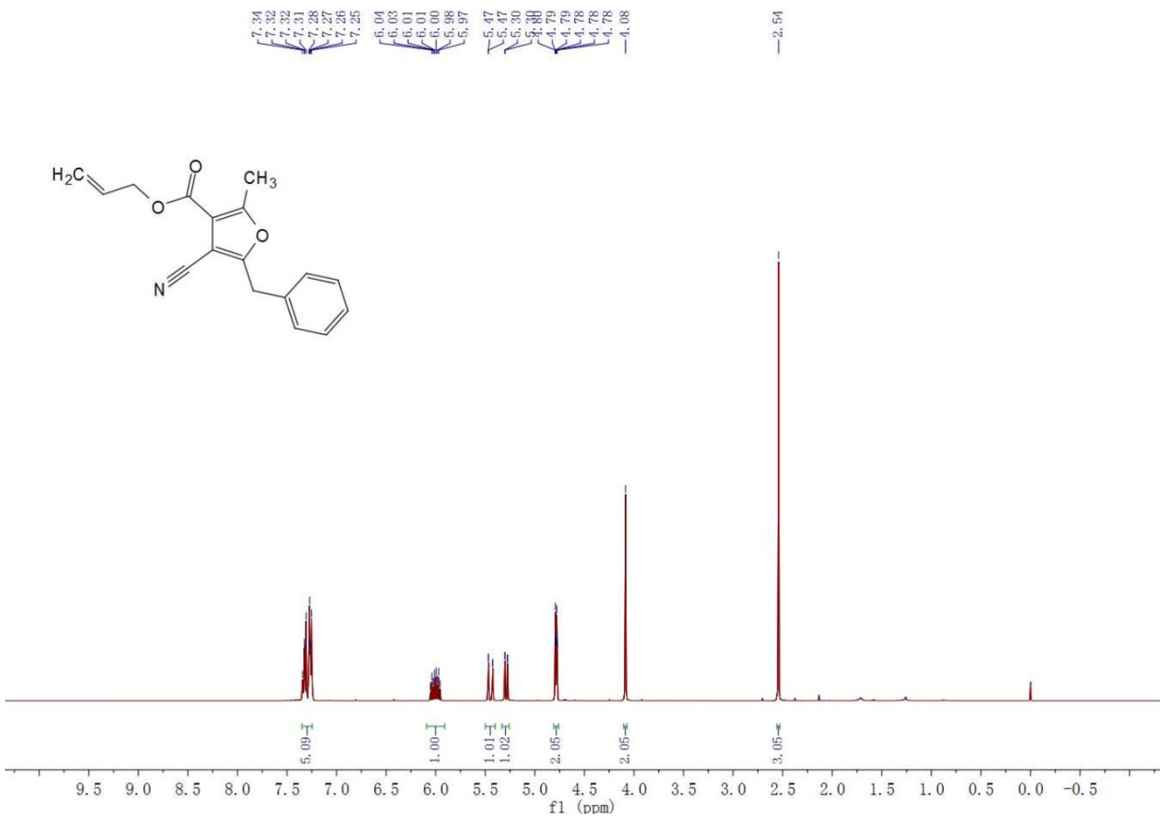

161.57
160.79
158.94
135.26
128.79
128.56
127.23
114.23
113.01
95.05
82.32
77.32
77.00
76.68
33.46
28.03
13.39
CH3
CH3
CH3
H3C
O
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

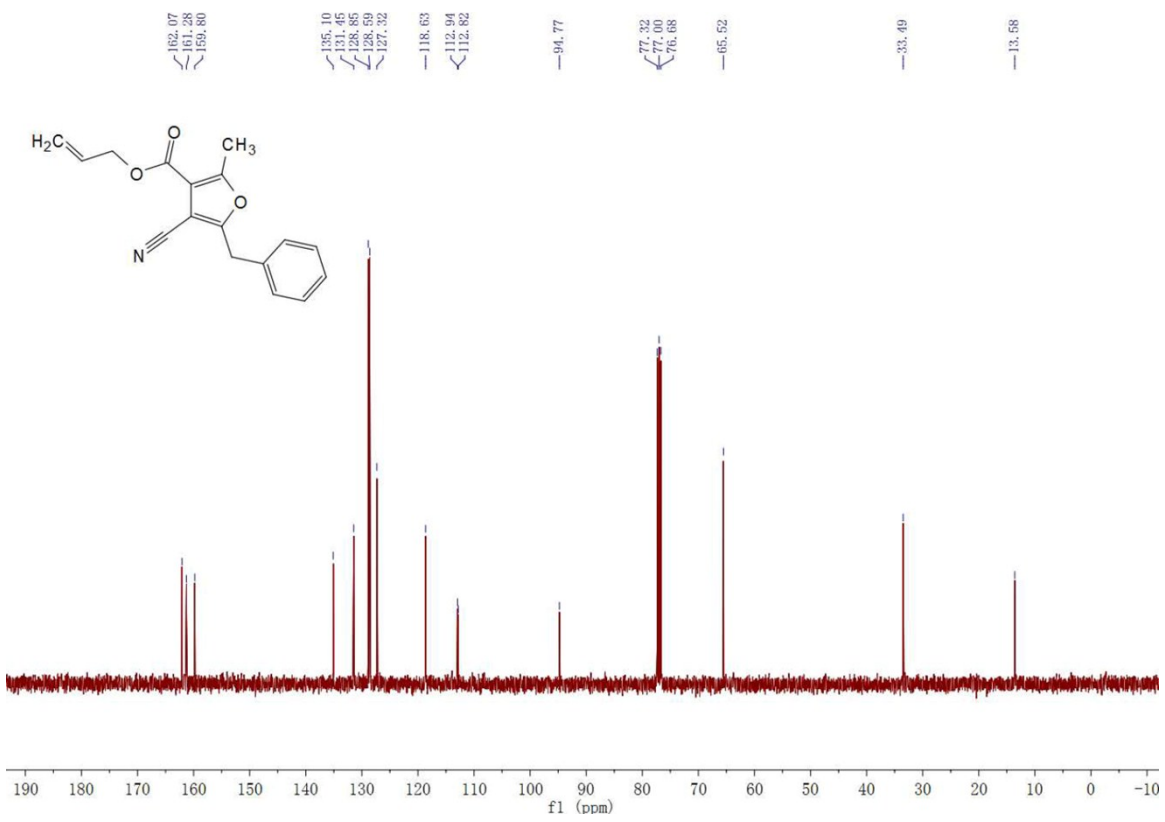
3q


7.47
7.47
7.45
7.39
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.32
7.30
7.27
7.26
7.24
5.34
4.07
2.52
CH3
O
O
O
N
2.00
8.08
2.03
2.00
3.00
f1 (ppm)

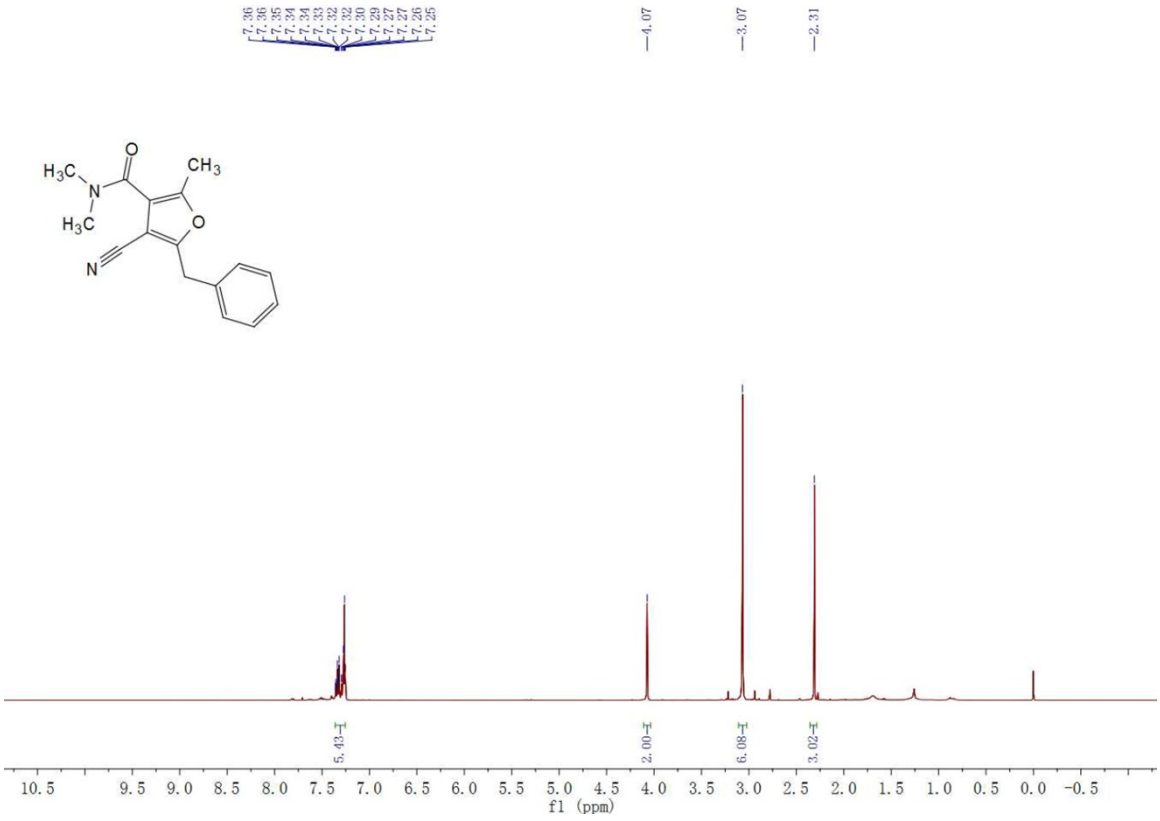

162.10
161.41
159.86
135.40
135.12
128.89
128.63
128.55
128.31
128.29
127.36
113.00
112.86
94.86
77.32
77.00
76.68
66.64
33.52
13.66
CH3
O
O
O
N
128.89
128.63
128.55
128.31
128.29
127.36
f1 (ppm)

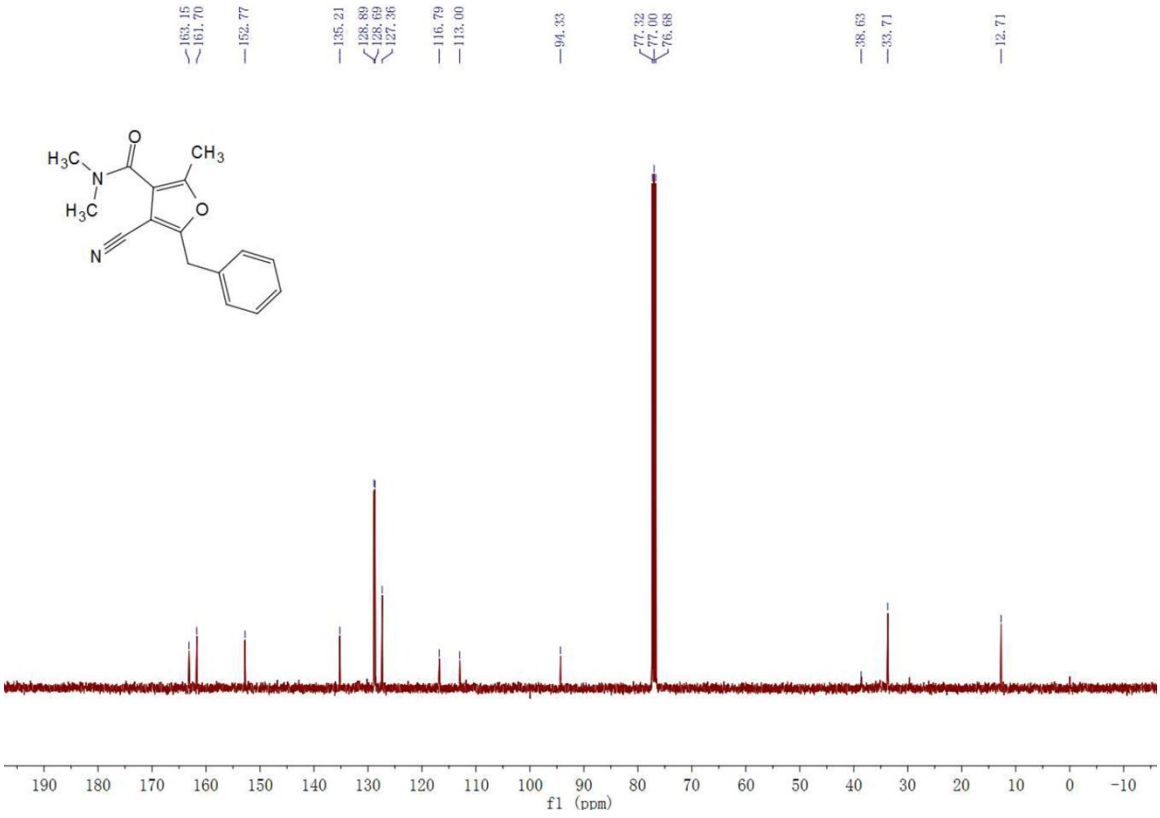
3r


7.34
7.32
7.32
7.31
7.28
7.27
7.26
7.25
6.04
6.03
6.01
6.01
6.00
5.98
5.97
5.47
5.47
5.30
4.79
4.79
4.78
4.78
4.78
4.08
2.54
H2C
O
CH3
O
O
N
5.09
1.00
1.01
1.02
2.05
2.05
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

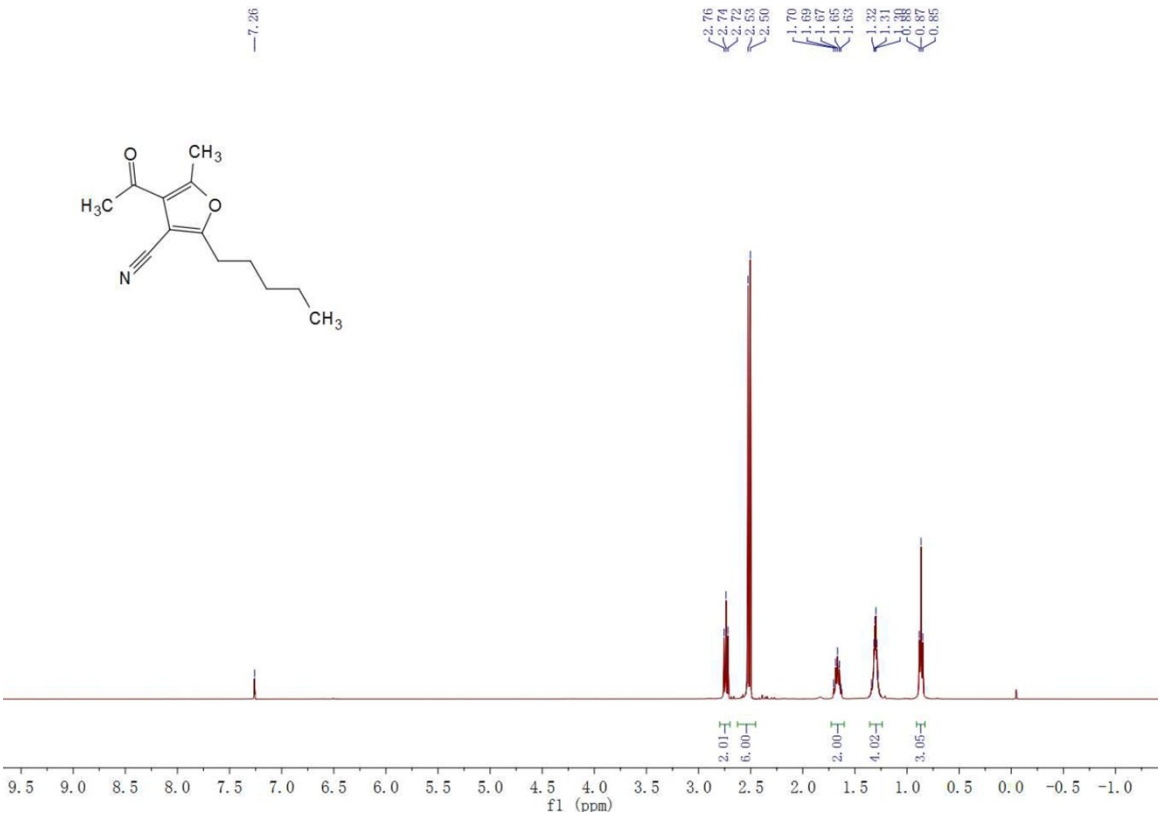

162.07
161.28
159.80
135.10
131.45
128.85
128.59
127.32
118.63
112.94
112.82
94.77
77.32
77.00
76.68
65.52
33.49
13.58
H2C
O
CH3
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

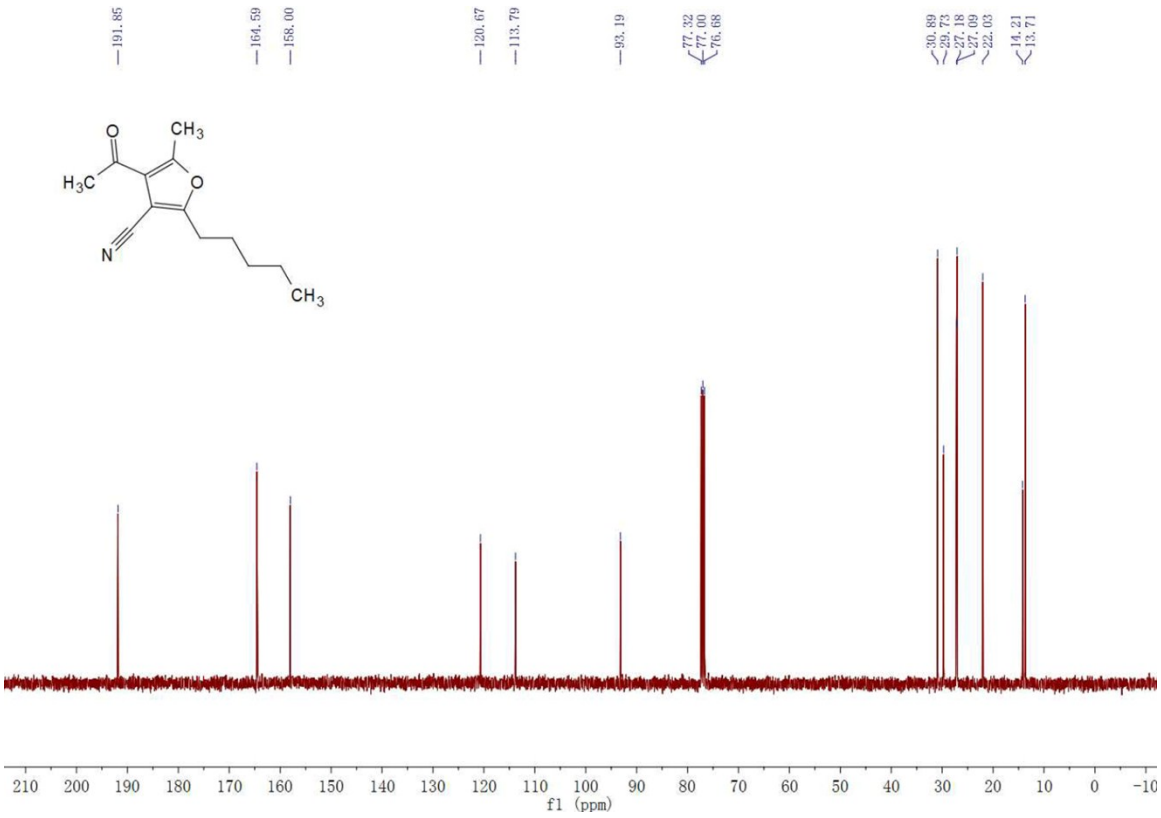
3s


7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.30
7.29
7.27
7.27
7.26
7.25
4.07
3.07
2.31
5.43
2.00
6.08
3.02
f1 (ppm)

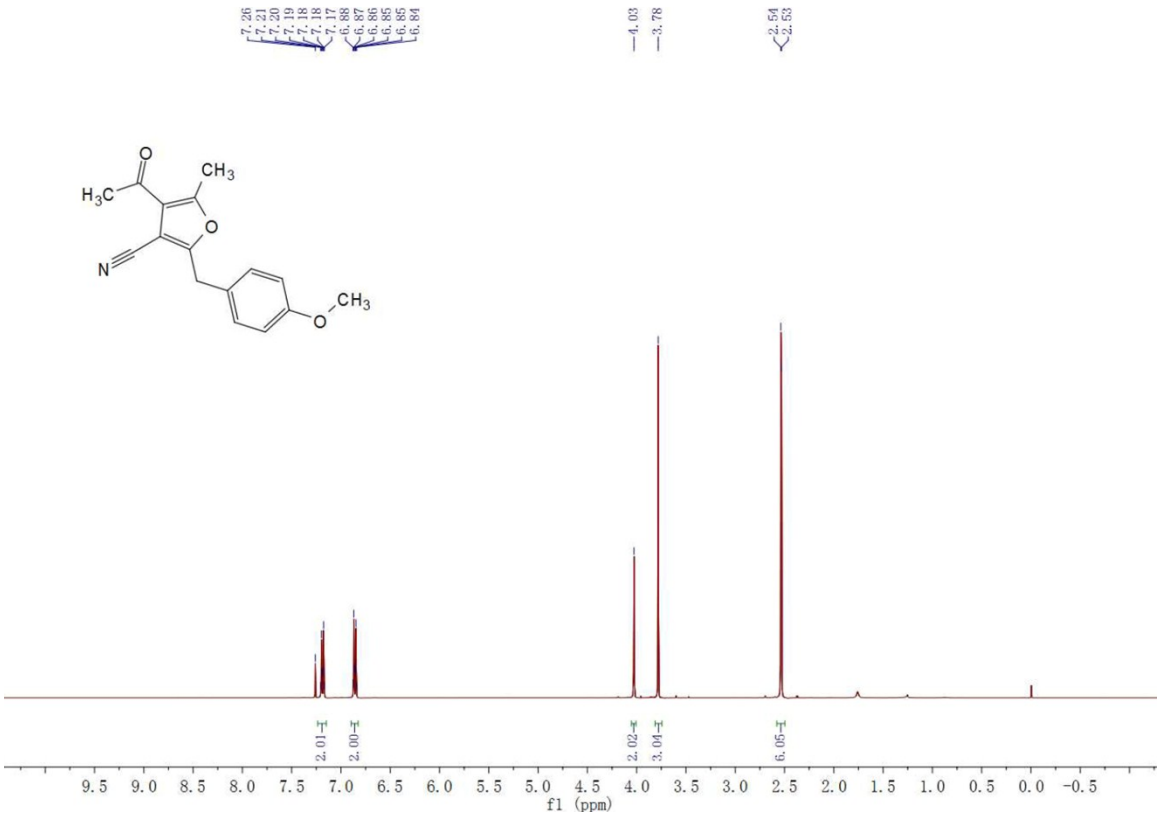

163.15
161.70
152.77
135.21
128.89
128.69
127.36
116.79
113.00
94.33
77.32
77.00
76.68
38.63
33.71
12.71
f1 (ppm)

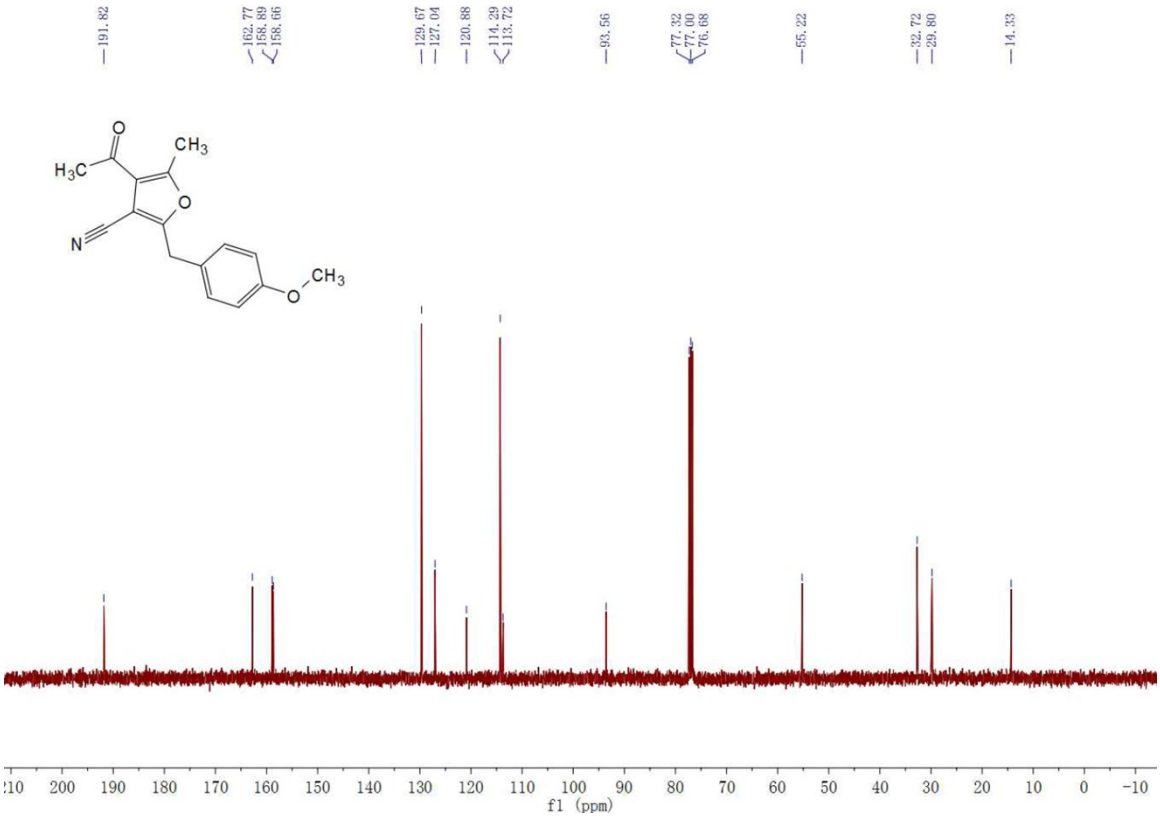
3t


7.26
2.76
2.74
2.72
2.53
2.50
1.70
1.69
1.67
1.65
1.63
1.32
1.31
0.88
0.87
0.85
O
CH3
H3C
O
N
CH3
2.01
6.00
2.00
4.02
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

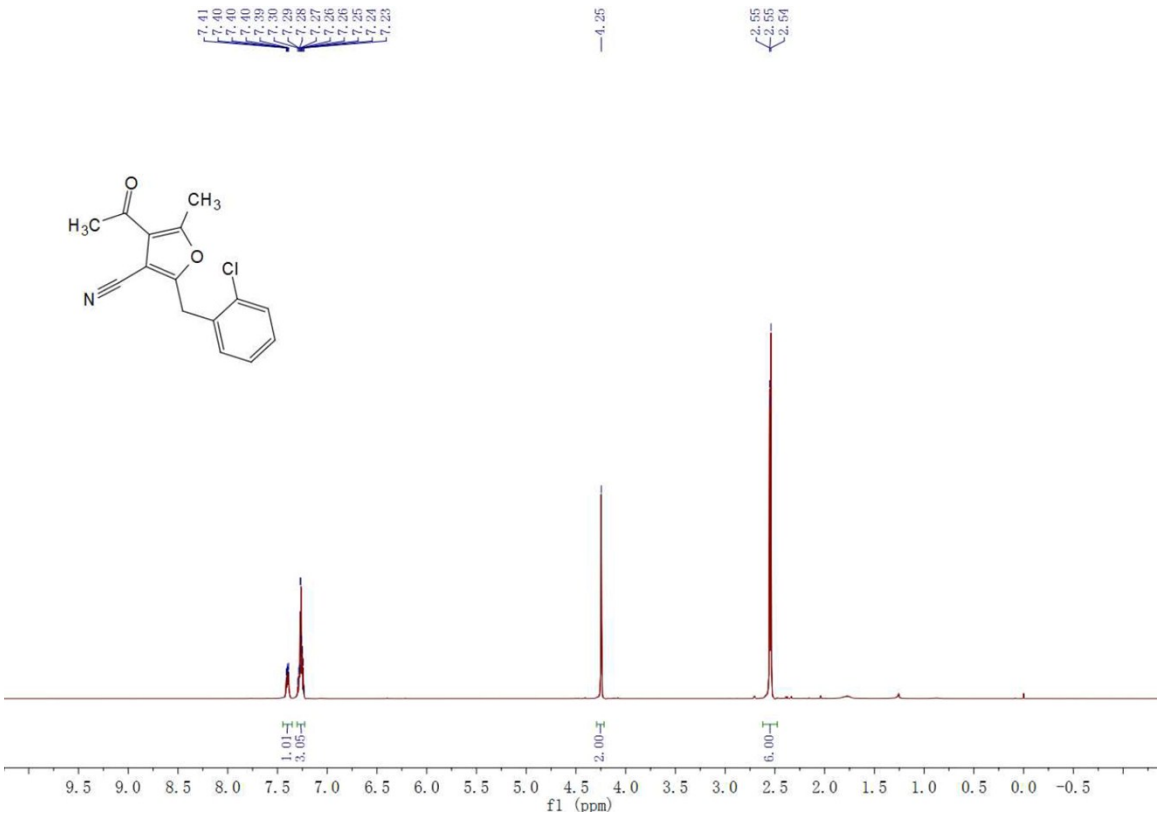

191.85
164.59
158.00
120.67
113.79
93.19
77.32
77.00
76.68
30.89
29.73
27.18
27.09
22.03
14.21
13.71
O
CH3
H3C
O
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

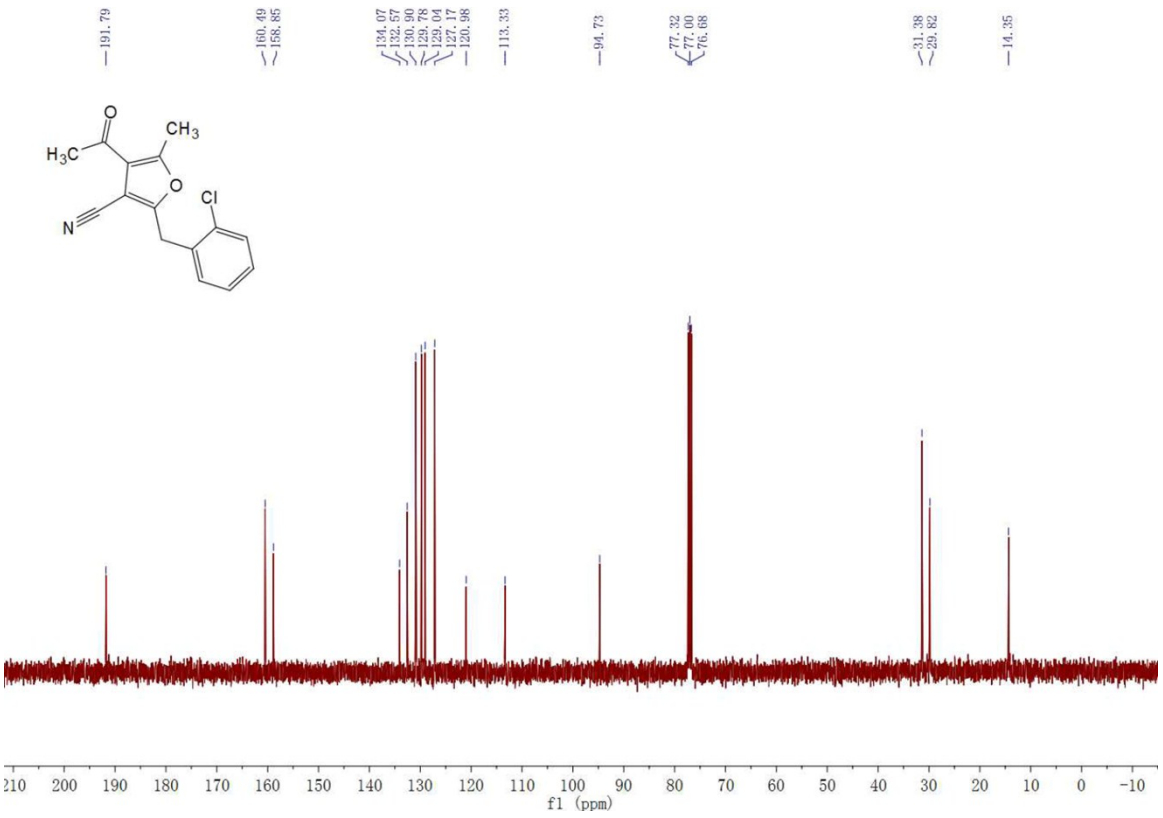
3u


7.26
7.21
7.20
7.19
7.18
7.18
7.17
6.88
6.87
6.86
6.85
6.85
6.84
4.03
3.78
2.54
2.53
O
CH3
H3C
O
N
CH3
O
2.01
2.00
2.02
3.04
6.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

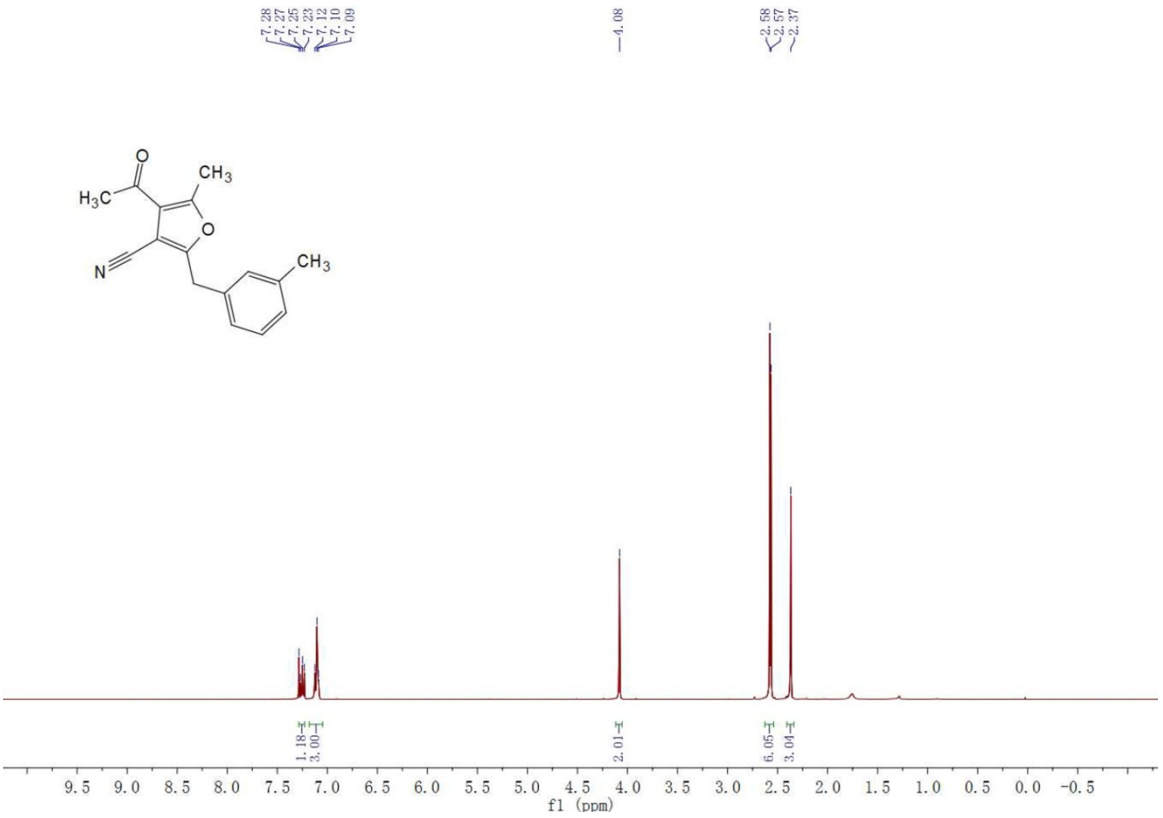

191.82
162.77
158.89
158.66
129.67
127.04
120.88
114.29
113.72
93.56
77.32
77.00
76.68
55.22
32.72
29.80
14.33
O
CH3
H3C
O
N
CH3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

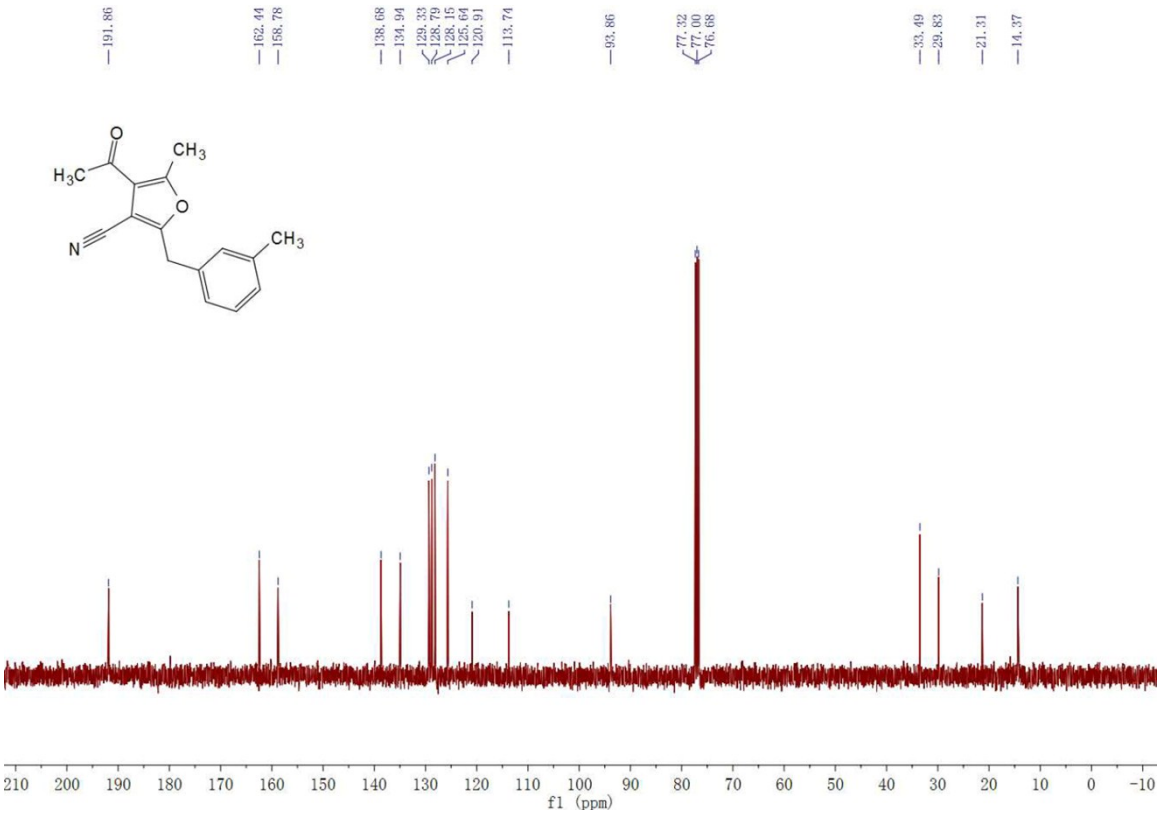
3v


7.41
7.40
7.40
7.40
7.39
7.30
7.29
7.28
7.27
7.26
7.26
7.25
7.24
7.23
4.25
2.55
2.55
2.54
O
CH3
H3C
O
Cl
N
1.01
3.05
2.00
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

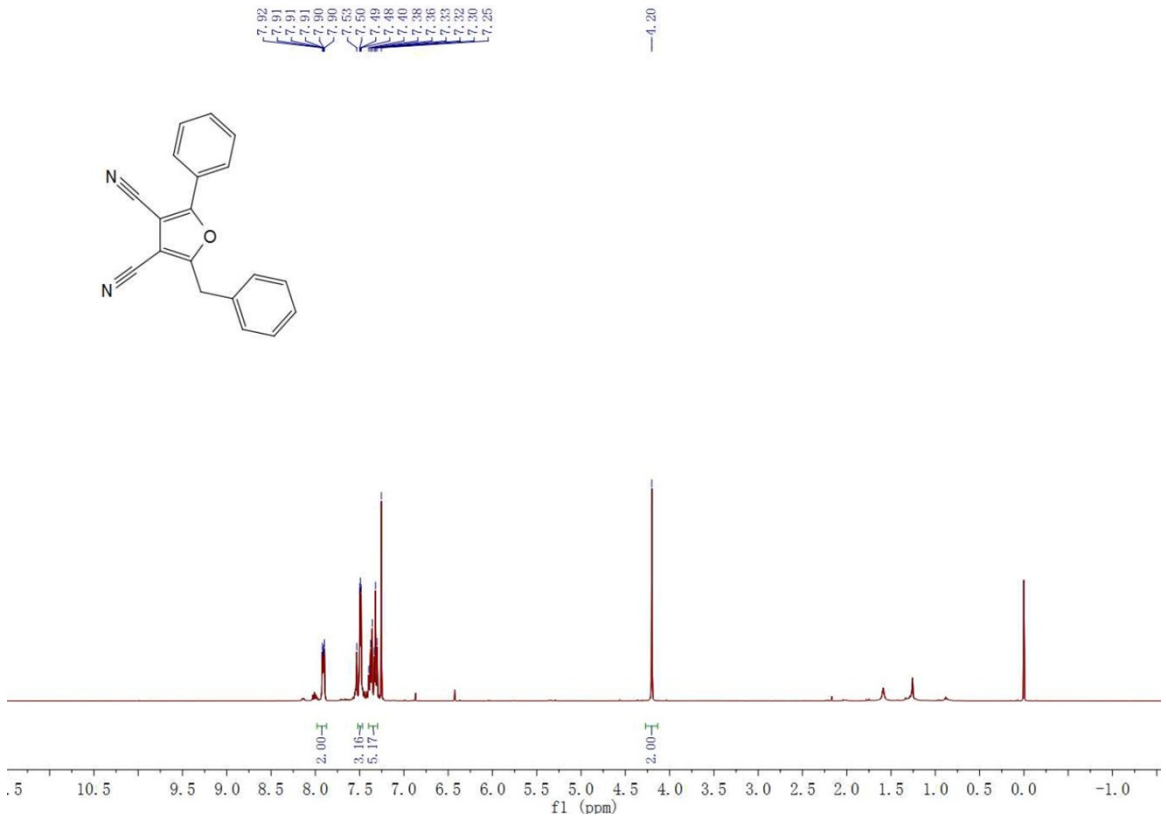

191.79
160.49
158.85
134.07
132.57
130.90
129.78
129.04
127.17
120.98
113.33
94.73
77.32
77.00
76.68
31.38
29.82
14.35
O
CH3
H3C
O
Cl
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

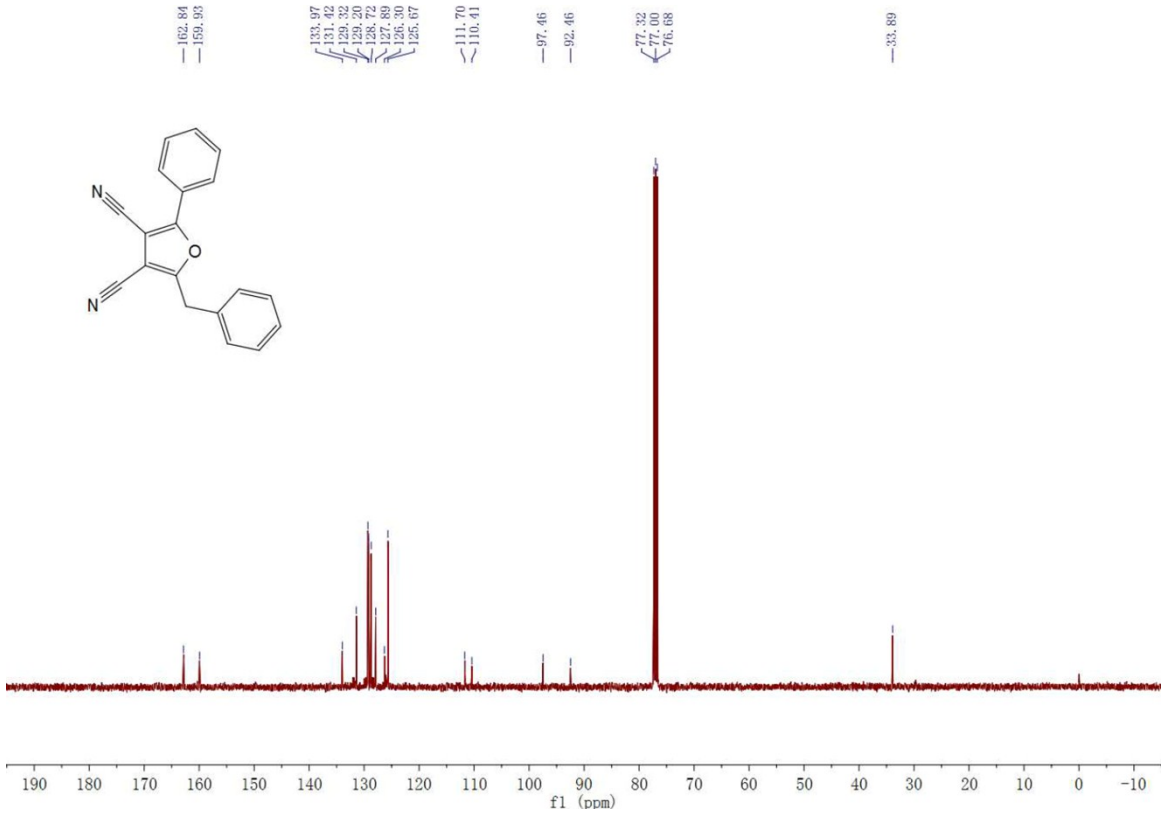
3w


7.28
7.27
7.25
7.23
7.12
7.10
7.09
4.08
2.58
2.57
2.37
O
H3C
CH3
O
N
CH3
1.18
3.00
2.01
6.05
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

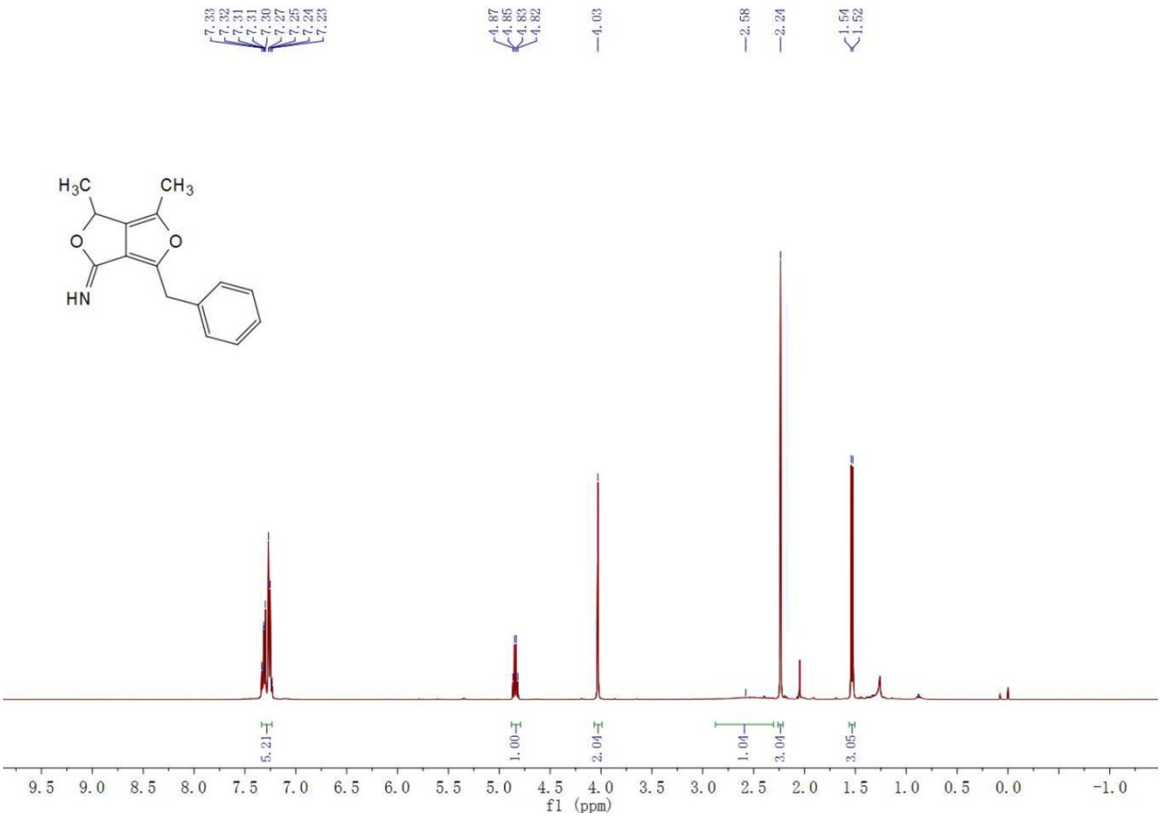

191.86
162.44
158.78
138.68
134.94
129.33
128.79
128.15
125.64
120.91
113.74
93.86
77.32
77.00
76.68
33.49
29.83
21.31
14.37
O
H3C
CH3
O
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

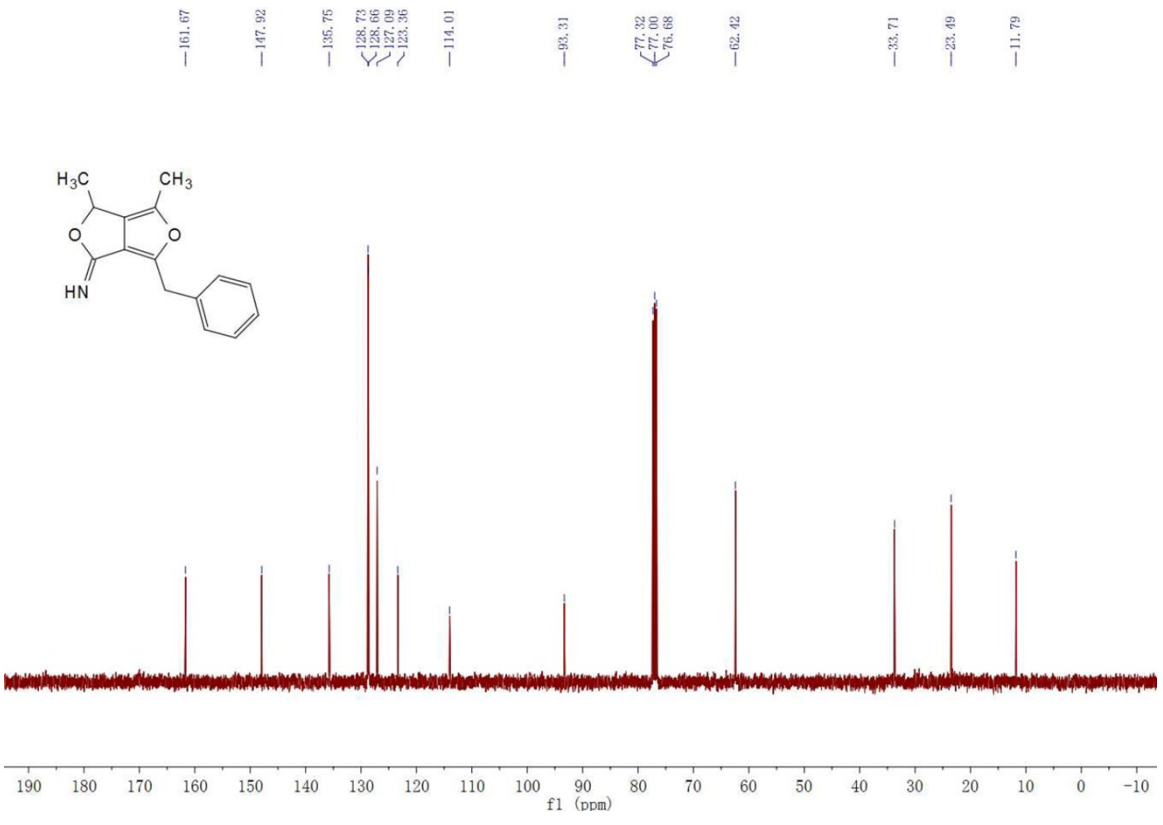
3x


7.92
7.91
7.91
7.91
7.90
7.90
7.53
7.50
7.49
7.48
7.40
7.38
7.36
7.33
7.32
7.30
7.25
4.20
N
N
O
2.00
3.16
3.17
2.00
f1 (ppm)

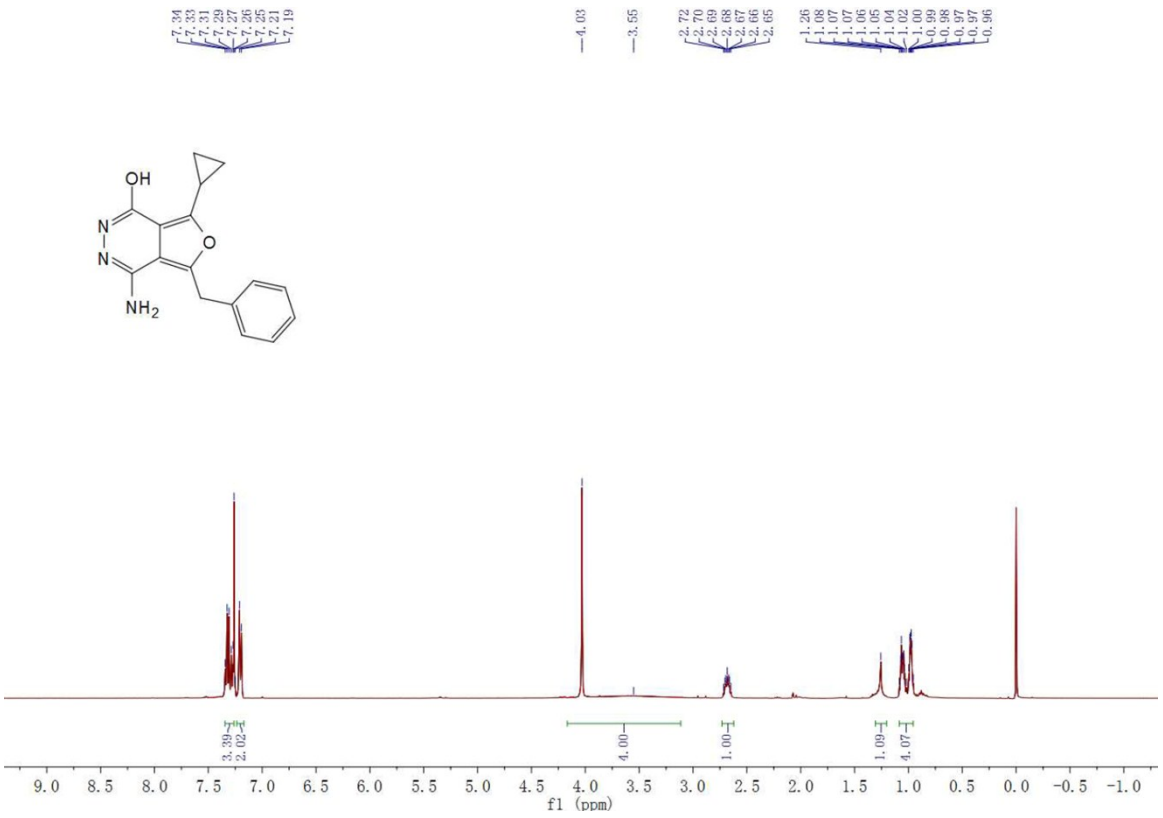

162.84
159.93
133.97
131.42
129.32
129.20
128.72
127.89
126.30
125.67
111.70
110.41
97.46
92.46
77.32
77.00
76.68
33.89
N
N
O
f1 (ppm)

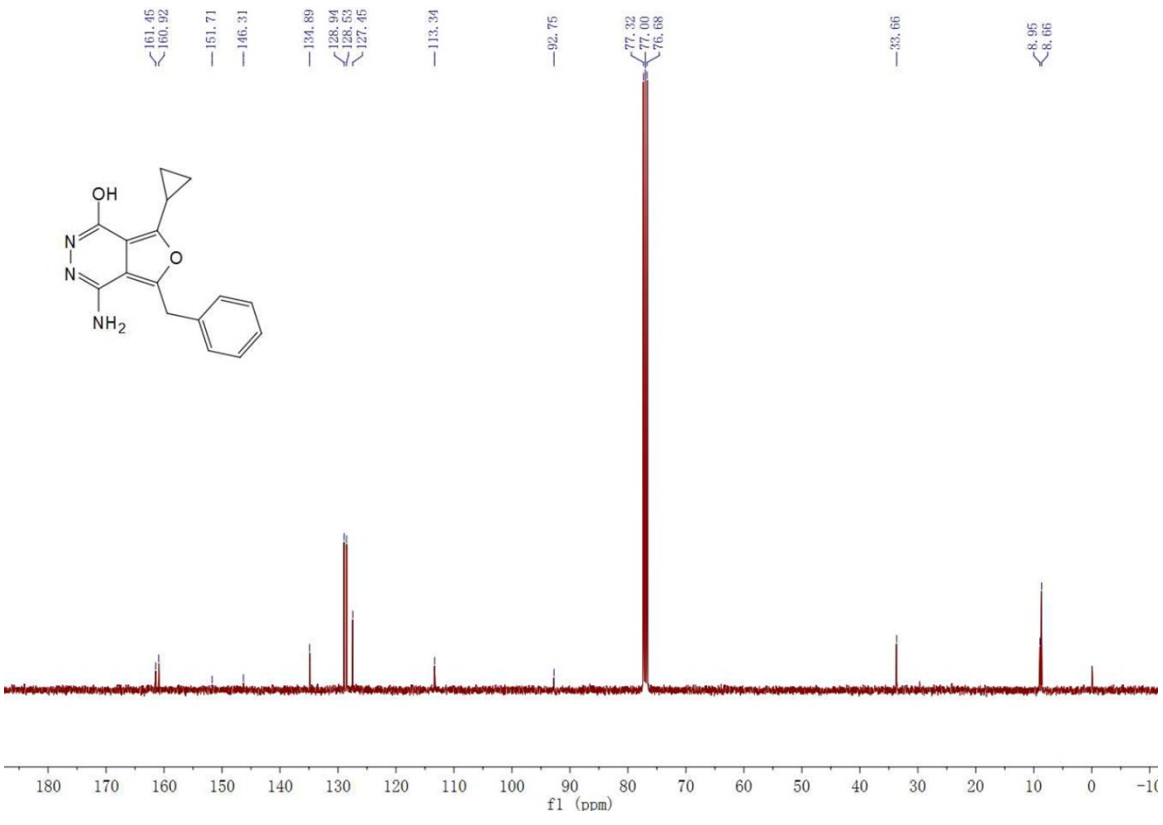
4


7.33
7.32
7.31
7.30
7.27
7.25
7.24
7.23
4.87
4.85
4.83
4.82
4.03
2.58
2.24
1.54
1.52
H3C
CH3
O
O
HN
5.21
1.00
2.04
1.04
3.04
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

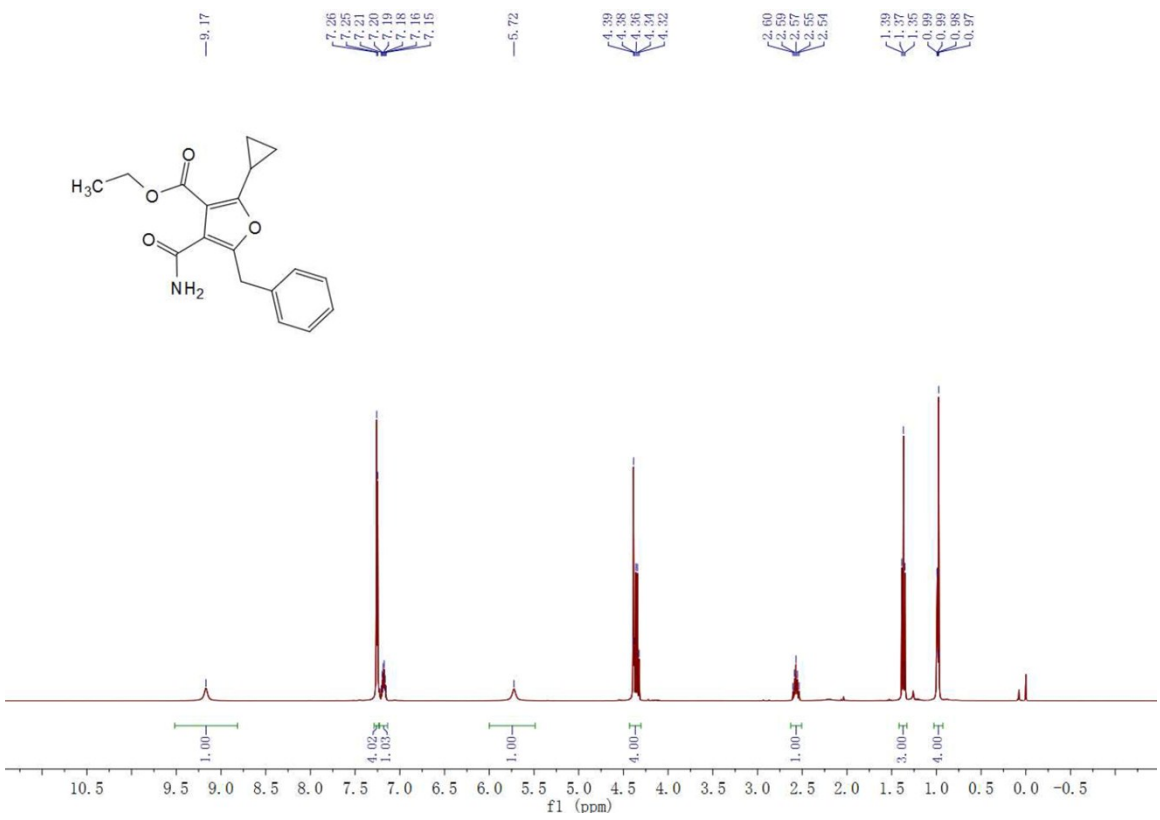

161.67
147.92
135.75
128.73
128.66
127.09
123.36
114.01
93.31
77.32
77.00
76.68
62.42
33.71
23.49
11.79
H3C
CH3
O
O
HN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

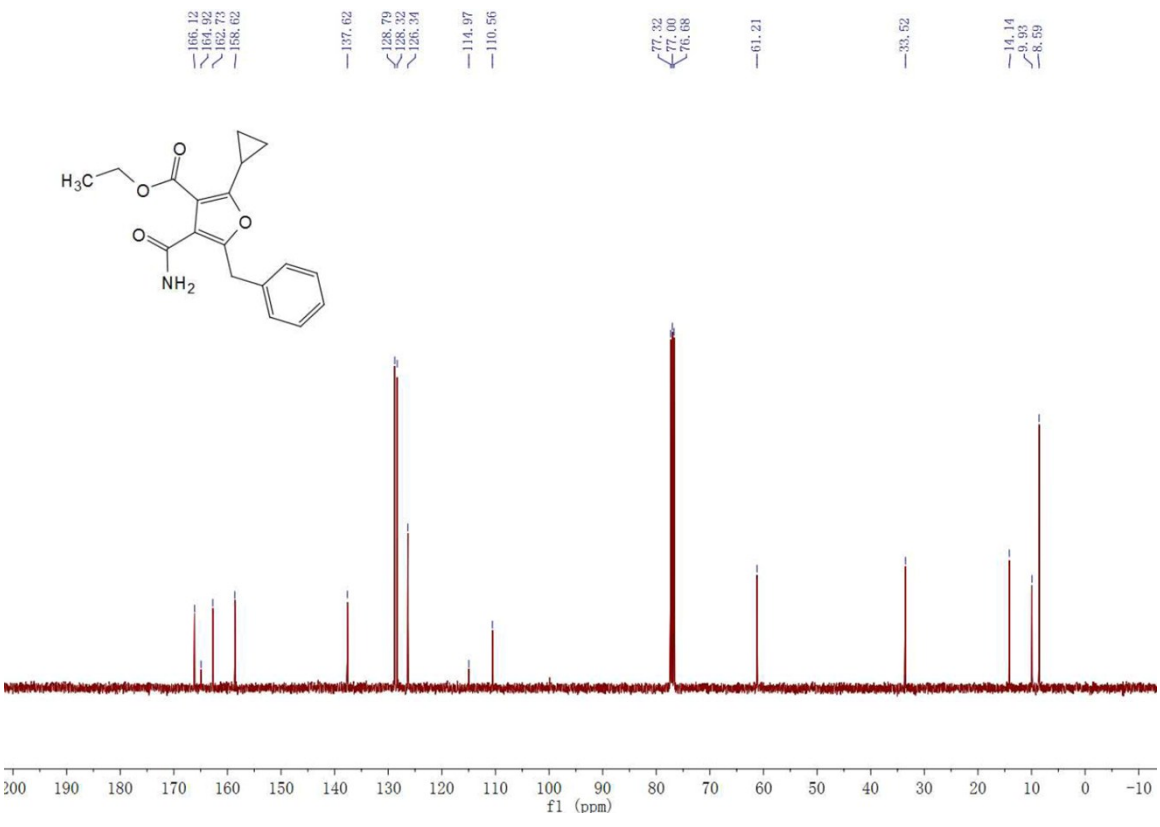
5


7.34
7.33
7.31
7.29
7.27
7.26
7.25
7.21
7.19
4.03
3.55
2.72
2.70
2.69
2.68
2.67
2.66
2.65
1.26
1.08
1.07
1.07
1.06
1.05
1.04
1.02
1.00
0.99
0.98
0.97
0.97
0.96
OH
N
N
O
NH2
3.39
2.02
4.00
1.00
1.09
4.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

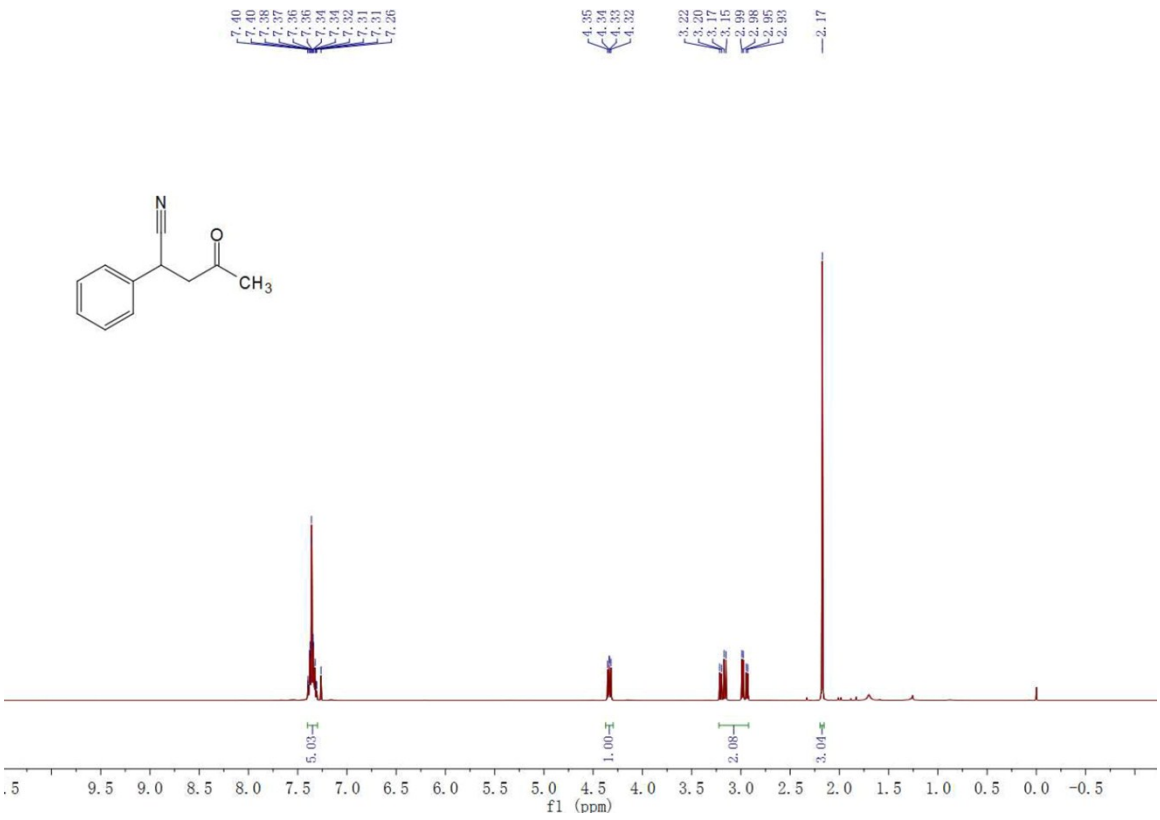

161.45
160.92
151.71
146.31
134.89
128.94
128.53
127.45
113.34
92.75
77.32
77.00
76.68
33.66
8.95
8.66
OH
N
N
O
NH2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

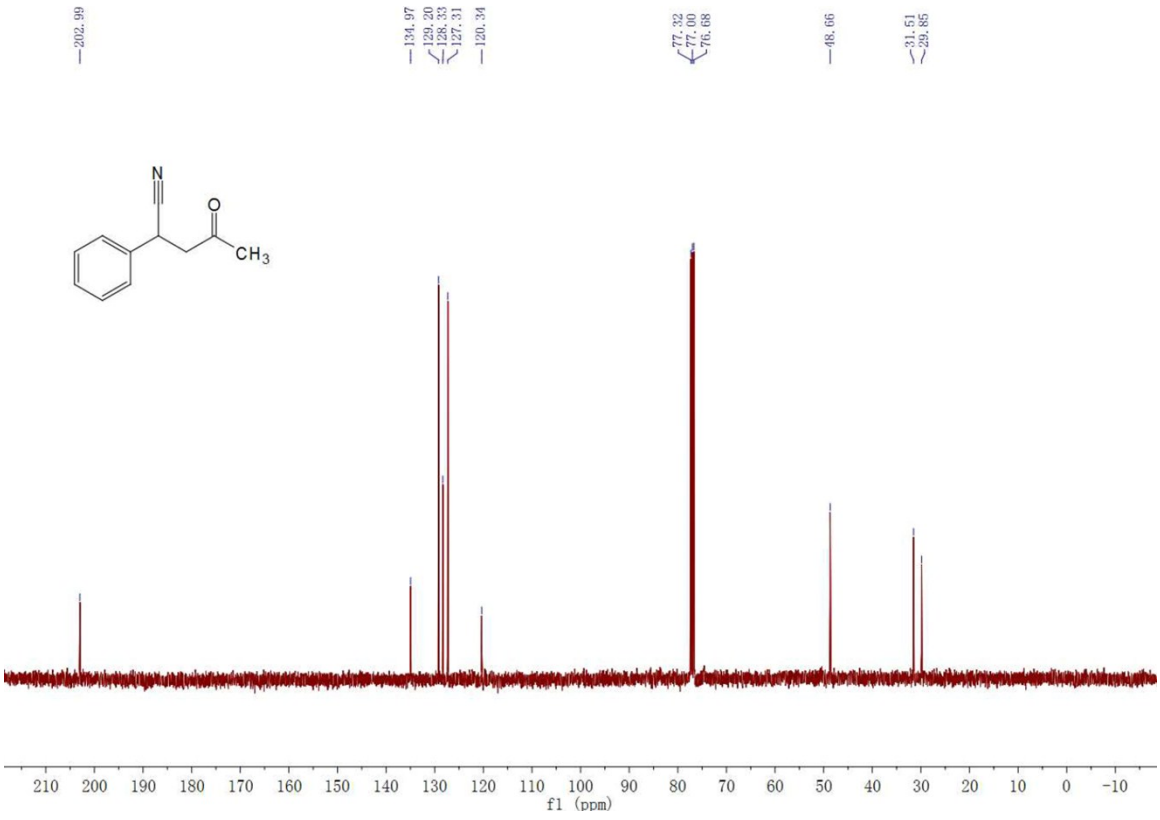
6


9.17
7.26
7.25
7.21
7.20
7.19
7.18
7.16
7.15
5.72
4.39
4.38
4.36
4.34
4.32
2.60
2.59
2.57
2.55
2.54
1.39
1.37
1.35
0.99
0.99
0.98
0.97
H3C
O
O
O
O
NH2
1.00
4.02
1.03
1.00
4.00
1.00
3.00
4.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

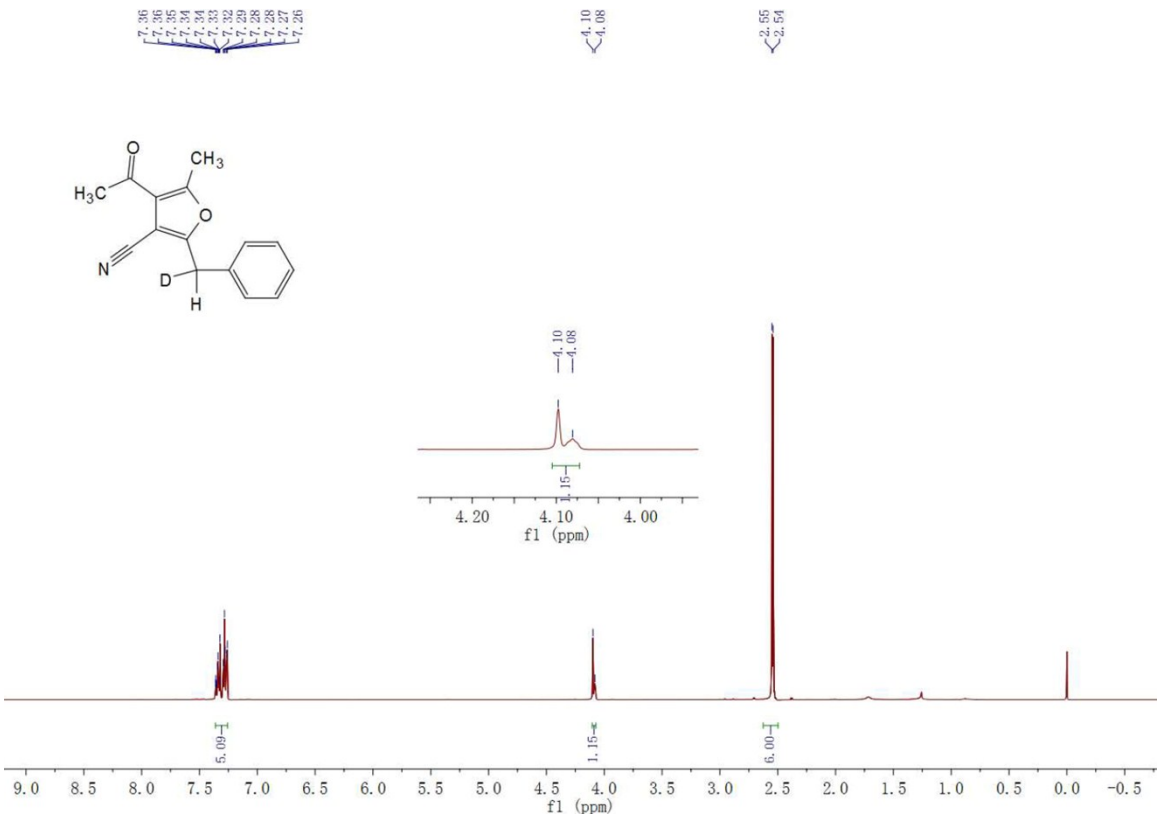

166.12
164.92
162.73
158.62
137.62
128.79
128.32
126.34
114.97
110.56
77.32
77.00
76.68
61.21
33.52
14.14
9.93
8.59
H3C
O
O
O
O
NH2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

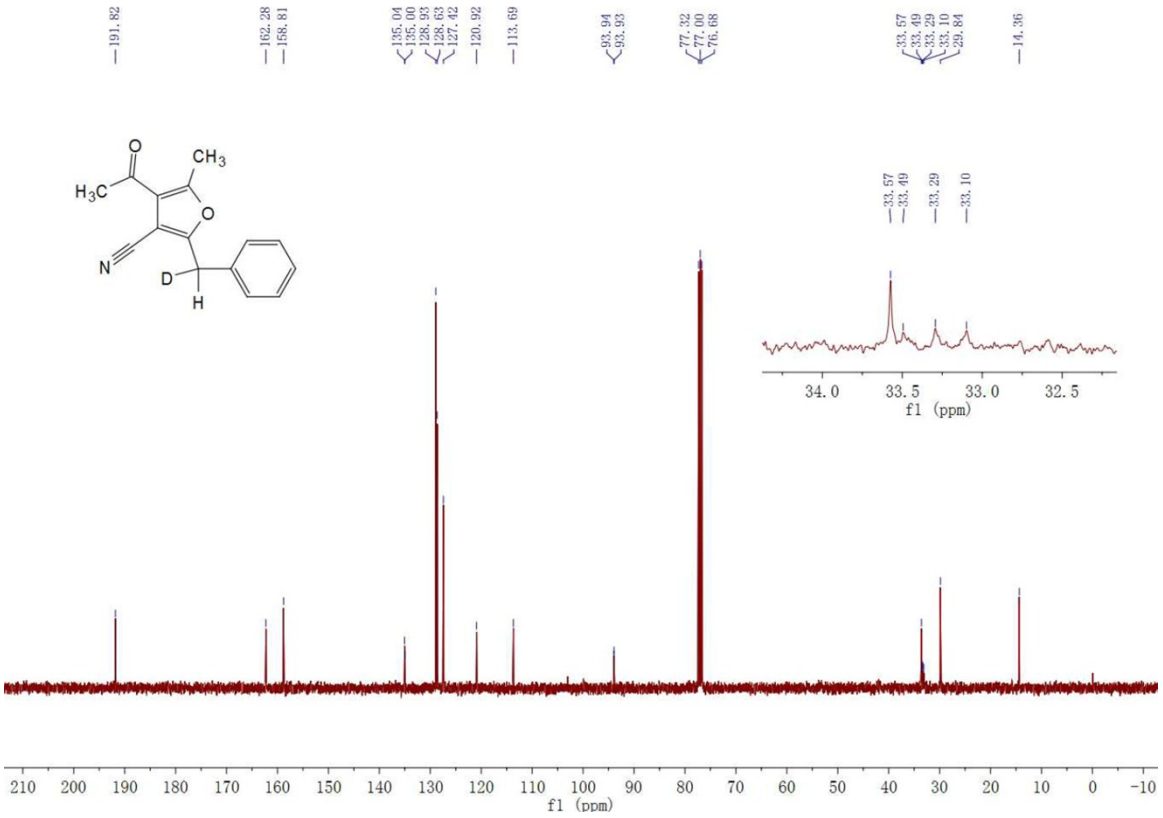
8


7.40
7.40
7.38
7.37
7.36
7.36
7.34
7.34
7.32
7.31
7.31
7.26
4.35
4.34
4.33
4.32
3.22
3.20
3.17
3.15
2.99
2.98
2.95
2.93
2.17
N
O
CH3
5.03
1.00
2.08
3.04
f1 (ppm)


202.99
134.97
129.20
128.33
127.31
120.34
77.32
77.00
76.68
48.66
31.51
29.85
N
O
CH3
f1 (ppm)

D_1-3a


7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.29
7.28
7.28
7.27
7.26
4.10
4.08
2.55
2.54
O
CH3
H3C
O
N
D
H
4.10
4.08
1.15
4.20
4.10
4.00
f1 (ppm)
5.09
1.15
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


191.82
162.28
158.81
135.04
135.00
128.93
128.63
127.42
120.92
113.69
93.94
93.93
77.32
77.00
76.68
33.57
33.49
33.29
33.10
29.84
14.36
O
CH3
H3C
O
N
D
H
33.57
33.49
33.29
33.10
34.0
33.5
33.0
32.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)