Supplementary Information

Deacetylative Cyanation: A Cyanide-Free Route to Thiocyanates and Cyanamides

Si Yeon Kim[a] and Hee Nam Lim[a]*

[a]Department of Chemistry, Yeungnam University, 280 Daehak-Ro, Gyeongsan, Gyeongbuk, 38541, Republic of Korea

*E-mail: heenam@yu.ac.kr

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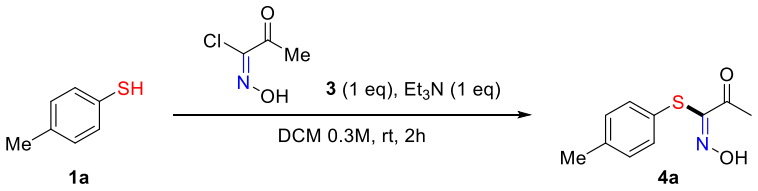
1. Materials and Methods

Common solvents including Dichloromethane (CH_2Cl_2), Tetrahydrofuran (THF), Acetonitrile (CH_3CN) and Chloroform ($CHCl_3$), etc. were directly used after purchase from TCI chemicals without further purification. Thin layer chromatography (TLC) analysis was run on silica gel plates. Most of spots were visualized by exposure to ultraviolet (UV) light (254 nm). Some spots that were invisible to ultraviolet (UV) used PMA stain solution. NMR and HRMS spectra were recorded using Bruker DPX 300, VNMR 600 MHz (either on 300 or 600 MHz for ^1H, 565 MHz for ^{19}F NMR, and either on 75 or 150 MHz for ^{13}C) and Vanquish UHPLC High Resolution Mass System with ion trap (orbitrap) mass analyzer [Ionization mode: ESI] at Core Research Support Center for Natural Products and Medical Materials at Yeungnam University. High-resolution mass spectra were reported for the molecular ion $[M+Na]^+$ or $[M+H]^+$. Chemical shifts for proton NMR spectra are reported in parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-d, to the quintet at 2.50 ppm for dimethylsulfoxide-d_6, and quintet at 2.05 ppm for acetone-d_6. Chemical shifts for carbon NMR spectra are reported in 77.16 ppm with the center line of triplet for chloroform-d and in 39.52 ppm with the center line of the septet for dimethylsulfoxide-d_6. Data for ^1H NMR were presented as following: chemical shifts (δ, ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and integration. The chemical shifts of peaks found were reported for ^{13}C NMR spectra. Infrared spectra were recorded with a Nicole iS10 FTIR Spectrometer.

[Cautions: DAST (N,N-diethylaminosulfur trifluoride) should be stored in the fridge, and the reactions using this reagent are recommended to run under 50 °C. Due to its explosive and exothermic nature above 90 °C, the bulk synthesis using this reagent is not recommended at elevated temperatures. Use DAST under a fume hood and avoid contact with water. For small-scale reactions (up to 1 mmol) described in this paper, a normal round bottom flask can be used without noticeable glass etching problems, likely due to the short reaction time. However, for large-scale reactions, it is recommended to use Teflon bottles instead of common glassware]

2. Table S1. Reaction Optimization for Synthesis of 4a

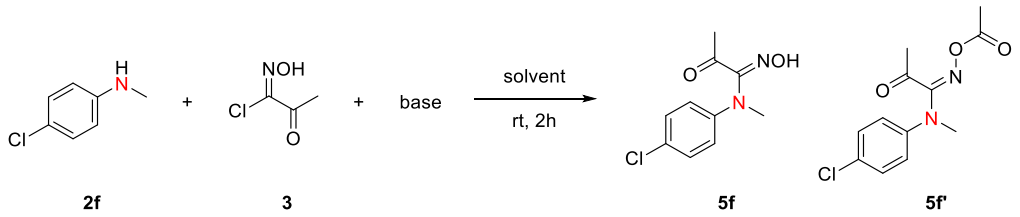


Base screening in DCM as solvent

Entry	Reaction Conditions	Yield (%)[a]	
		1a	4a
1	**triethylamine**	**8**	**85**
2	1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	20	<5
3	*N*,*N*-diisopropylethylamine (DIPEA)	15	84
4	1,4-diazabicyclo[2.2.2]octane (DABCO)	12	75
5	K_2CO_3	33	52
6	NaOH	22	41
7	NaH	23	28

[a]NMR yields with 1,3,5-trimethoxybenzene as internal standard.

3. Table S2. Optimization for synthesis of 5



2f **3** **5f** **5f'**

S2-1. Solvent screening

Entry	conditions				Yield (%)[a]		
	2f (eqiv)	**3** (eqiv)	**base** (eqiv)	**solvent**	**2f**	**5f**	**5f'**
1	1	1	Et_3N (1.0 eq)	DMF	70	12	12
2	1	1	Et_3N (1.0 eq)	CH_3CN	72	6	13
3	1	1	Et_3N (1.0 eq)	Toluene	65	7	25
4	1	1	Et_3N (1.0 eq)	TBME	61	12	22
5	1	1	Et_3N (1.0 eq)	DCM	65	9	22
6	1	1	Et_3N (1.0 eq)	THF	58	16	20

[a]NMR yields with 1,3,5-trimethoxybenzene as internal standard.

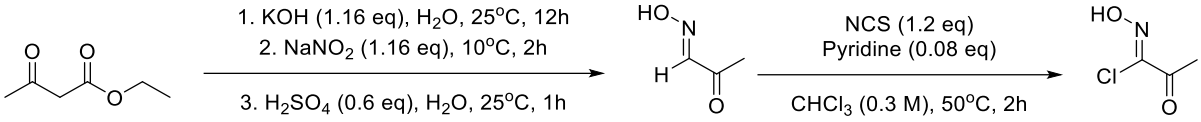
S2-2. Base screening

Entry	conditions				Yield (%)[a]		
	2f (eqiv)	**3** (eqiv)	**base** (eqiv)	**solvent**	**2f**	**5f**[a]	**5f'**
1	1	2	Et_3N (1.0 eq)	THF	10	55	15
2	1	2	Et_3N (2.0 eq)	THF	18	31	44
3	1	2	DBU (1.0 eq)	THF	67	<3	<3
4	1	2	DIPEA (1.0 eq)	THF	31	38	20
5	1	2	K_2CO_3 (1.0 eq)	THF	0	82	<5
6	1	2	K_2CO_3 (1.0 eq)	MeOH	<5	79	10
7	**1**	**2**	**K_2CO_3 (2.0 eq)**	**MeOH**	**<1**	**88 (75)**[b]	**0**

[a]NMR yields with 1,3,5-trimethoxybenzene as internal standard. [b]Isolated yield

4. Experimental Procedures

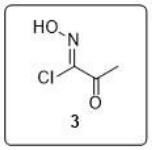
4. 1) Procedure for synthesis of *N*-hydroxy-2-oxopropanimidoyl chloride (3)[1]



3

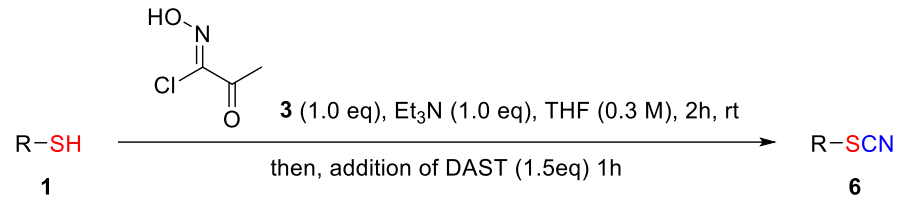
Step 1: KOH (5.15 g, 91.7 mmol) was charged in water (50.0 mL) and stirred for 10-15 min at room temperature and then cooled to 0 °C. Ethyl acetoacetate (10.0 mL, 79.1 mmol) was added dropwise. The resulting mixture was allowed to reach 25 °C and stirred for 12 h. It was then cooled to 10 °C, and the sodium nitrite (6.38 g, 92.5 mmol) was added portion wise. After 2 h, an aqueous solution of sulfuric acid (2.53 mL, 47.4 mmol, in 10.0 mL water) was added over while maintaining the temperature at 0 °C. Upon completion of the addition, the resulting mixture was stirred for 1 h at room temperature. The mixture was next extracted with ethyl acetate (6 x 100 mL). The combined organic solution was dried over $MgSO_4$, filtered, and concentrated to afford (E)-2-oxopropanal oxime (5.87 g, 67.4 mmol, 88% yield) as a white solid.

Step 2: (E)-2-oxopropanal oxime (3.13 g, 35.9 mmol) was dissolved in $CHCl_3$ (120 mL) in the presence of a catalytic amount of pyridine (0.23 mL, 2.9 mmol); the reaction mixture was stirred at 50 °C, then stepwise added with portions of N-chlorosuccinimide (NCS) (5.76g, 43.1 mmol). The reaction mixture was kept stirring at 50 °C for 2 h, and the reaction was monitored by TLC. Then, it was quenched with ice water (200 mL) and extracted with diethyl ether (250 mL). The combined organic solution was washed with ice water (3 X 200 mL), dried over $MgSO_4$, filtered, concentrated and recrystallized (Hex:EtOAc = 20:1, 135 mL) to afford N-hydroxy-2-oxopropanimidoyl chloride **3** (2.86g, 66%) as white solid.

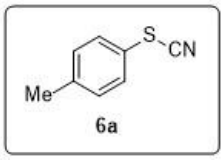


N-hydroxy-2-oxopropanimidoyl chloride (3);[1] R_f = 0.6 (He:EtOAc = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (br s, 1H), 2.51 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 140.5, 26.0.

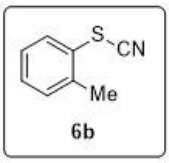
4. 2) General procedure for preparation of thiocyanates 6a–6n



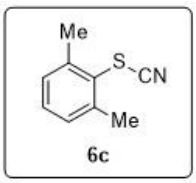
To a stirred solution of **3** (122 mg, 1.0 mmol) in THF (3 mL) was added **1** (1.0 mmol) and triethylamine (0.14 mL, 1.0 mmol) at 0 ºC. Then, reaction mixture was warmed to room temperature. Upon full conversion of **3**, (diethylamino)sulfur trifluoride (DAST, 0.20 mL, 1.5 mmol) was added to the reaction mixture. After 1 h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n (15 mL) and extracted with diethyl ether (10 X 2 mL). The organic solution was dried over $MgSO_4$, filtered, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 20:1 or 10:1) to afford **6**.



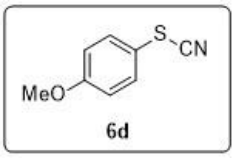
1-methyl-4-thiocyanatobenzene (6a);[2] The title compound was prepared according to the general procedure; 199 mg, 80%; yellow solid; R_f = 0.7 (Hex:EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 2.38 (s, 3H). IR (neat) ν_{max} 3025, 2922, 2156, 1493, 1450 cm^{-1}.



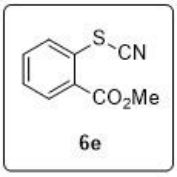
1-methyl-2-thiocyanatobenzene (6b);[2] The title compound was prepared according to the general procedure; 127 mg, 85%; yellow oil R_f = 0.5 (Hex:EtOAc = 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7. Hz, 1H), 7.30–7.26 (m, 2H), 2.48 (s, 3H). IR (neat) ν_{max} 3063, 2984, 2924, 2843, 2157, 1473 cm^{-1}.



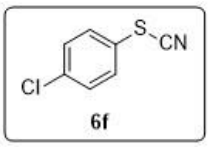
1,3-dimethyl-2-thiocyanatobenzene (6c);[2] The title compound was prepared according to the general procedure; 122 mg, 75%; white solid; R_f = 0.6 (Hex:EtOAc = 10:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.7, 7.4 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 2.60 (s, 6H). IR (neat) ν_{max} 2952, 2916, 2151, 1463, 1034 cm^{-1}.



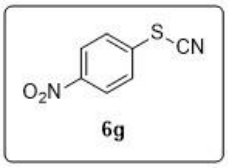
1-methoxy-4-thiocyanatobenzene (6d);[2] The title compound was prepared according to the general procedure; 119 mg, 72%; yellow solid; R_f = 0.6 (Hex:EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H). IR (neat) ν_{max} 2918, 2852, 2155, 1591, 1495 cm^{-1}.



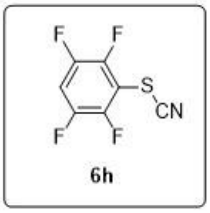
Methyl 2-thiocyanatobenzoate (6e);[2] The title compound was prepared according to the general procedure; 137 mg, 71%; white solid; R_f = 0.5 (Hex:EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H), 7.91 (dd, *J* = 8.2 Hz, 0.7 Hz, 1H), 7.64 (m, 1H), 7.41 (m, 1H), 3.96 (s, 3H). IR (neat) ν_{max} 2961, 2911, 2153, 1698, 1309 cm^{-1}.



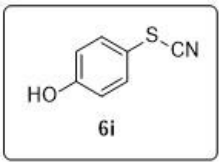
1-chloro-4-thiocyanatobenzene (6f);[2] The title compound was prepared according to the general procedure; 129 mg, 76%; yellow solid; R_f = 0.7 (Hex:EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.42 (m, 2H). IR (neat) ν_{max} 3085, 2924, 2849, 2159, 1476, 1391 cm^{-1}.



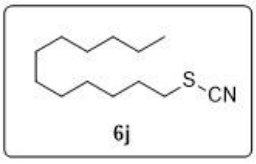
1-nitro-4-thiocyanatobenzene (6g);[2] The title compound was prepared according to the general procedure; 117 mg, 65%; white solid; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (m, 2H), 7.67 (m, 2H). IR (neat) ν_{max} 3104, 2920, 2846, 2163, 1578, 1343 cm^{-1}.



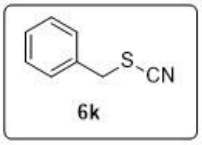
1,2,4,5-tetrafluoro-3-thiocyanatobenzene (6h);[2] The title compound was prepared according to the general procedure; 108 mg, 52%; yellow oil; R_f = 0.4 (Hex:EtOAc = 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35–7.29 (m, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -130.20 (m), -134.76 (m). IR (neat) ν_{max} 3076, 2926, 2167, 1501, 1239 cm^{-1}.



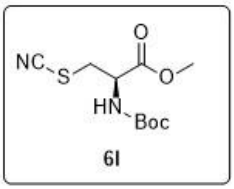
4-thiocyanatophenol (6i);[2] The title compound was prepared according to the general procedure; 70 mg, 46%; yellow oil; R_f = 0.2 (Hex:EtOAc = 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 2H), 6.89 (m, 2H). IR (neat) ν_{max} 3365, 2917, 2852, 2159, 1584, 1496 cm^{-1}.



1-thiocyanatododecane (6j);[2] The title compound was prepared according to the general procedure; 161 mg, 71%; yellow oil; R_f = 0.5 (Hex:EtOAc = 20:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.94 (t, *J* = 7.2 Hz, 2H), 1.84–1.79 (m, 2H), 1.46-1.41 (m, 2H), 1.32–1.26 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 3H). IR (neat) ν_{max} 2925, 2854, 2155, 1789, 1466, 1173 cm^{-1}.

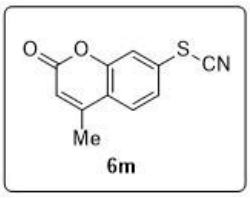


(Thiocyanatomethyl)benzene (6k);[2] The title compound was prepared according to the general procedure; 112 mg, 75%; yellow oil; R_f = 0.5 (Hex:EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.36 (m, 5H), 4.17 (s, 2H). IR (neat) ν_{max} 3063, 3032, 2153, 1495, 1455, 1245 cm^{-1}.



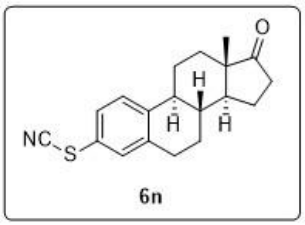
6l

Methyl N-(tert-butoxycarbonyl)-S-cyano-L-cysteinate (6l);[3] The title compound was prepared according to the general procedure; 141 mg, 54%; yellow solid; R_f = 0.4 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.52 (br d, *J* = 3.8 Hz , 1H), 4.68 (m, 1H), 3.84 (s, 3H), 3.53 (dd, *J* = 13.9, 4.0 Hz, 1H), 3.44 (dd, *J* = 13.9, 3.7 Hz), 1.45 (s, 9H). IR (neat) ν_{max} 3369, 2979, 2156, 1715, 1511 cm^{-1}.



6m

4-methyl-7-thiocyanato-2H-chromen-2-one (6m);[4] The title compound was prepared according to the general procedure; 185 mg, 85%; white solid; R_f = 0.2 (Hex:EtOAc = 3:1); ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.49 (s, 1H), 2.44 (d, *J* = 1.1 Hz, 3H). IR (neat) ν_{max} 2916, 2863, 2163, 1749, 1602, 1392 cm^{-1}.

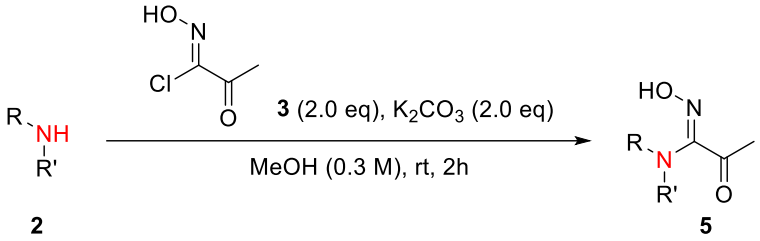


6n

(8R,9S,13S,14S)-13-methyl-3-thiocyanato-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phen anthren-17-one (6n); 206 mg, 66%; white solid; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.3 Hz, 1H), 7.30–7.27 (m, 2H), 2.94-2.91 (m, 2H), 2.51 (m, 1H), 2.40 (m, 1H), 2.29 (m, 1H), 2.15 (m, 1H), 2.09–2.03 (m, 2H), 1.97 (m, 1H), 1.61–1.59 (m, 2H), 1.55-1.43 (m, 4H), 0.92 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 220.6, 142.1, 139.3, 131.0, 127.9, 127.5, 121.1, 111.1, 50.5, 48.0, 44.3, 37.9, 35.9 31.6, 29.3, 26.2, 25.7, 21.7, 13.9. IR (neat) ν_{max} 2931, 2863, 2155, 1738, 1484, 1008 cm^{-1}. HRMS[ESI] calcd for $C_{19}H_{21}ONNaS$ $[M+Na]^+$ 334.1242, found 324.1227.

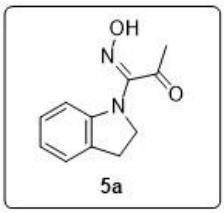
4. 3) General Procedure for the synthesis of 5a–5g

General Procedure for the synthesis of 5a–5g

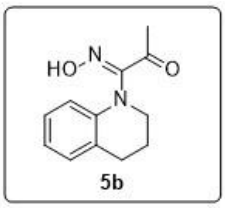


2 5

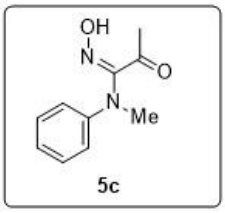
To a stirred solution of **2a**–**g** (2.5 mmol) in MeOH (8 mL) was added **3** (5 mmol) and K_2CO_3 (5 mmol) at room temperature. After 2 h, the reaction mixture was concentrated under reduced pressure to remove the MeOH. Then, it was neutralized with sat. NH_4Cl sol'n (20 mL) and extracted with ethyl acetate (15 mL X 3). Then, the organic solution was dried over $MgSO_4$, filtered, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 or 3:1) to afford **5a**–**g**.



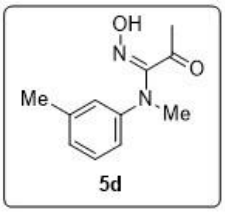
(E)-1-(hydroxyimino)-1-(indolin-1-yl)propan-2-one (5a); The title compound was prepared according to the general procedure; 475 mg, 93%; yellow solid; R_f = 0.4 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (br s, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.4, 1H), 6.27 (d, *J* = 7.9 Hz, 1H), 4.04 (t, *J* = 8.4 Hz, 2H), 3.16 (t, *J* = 8.4 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.0, 149.2, 145.5, 130.0, 126.8, 124.9, 120.9, 111.9, 52.0, 29.5, 27.3. IR (neat) ν_{max} 3320, 3031, 2898, 1698, 1592, 1487 cm^{-1}. HRMS[ESI] calcd for $C_{11}H_{13}O_2N_2$ $[M+H]^+$ 205.0972, found 205.0968.



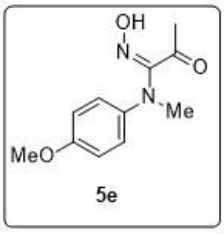
(Z)-1-(3,4-dihydroquinolin-1(2H)-yl)-1-(hydroxyimino)propan-2-one (5b); The title compound was prepared according to the general procedure; 442 mg, 81%; yellow solid; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (br s, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.97 (m, 1H), 6.80 (m, 1H), 6.20 (d, *J* = 8.0 Hz, 1H), 3.49–3.47 (m, 2H), 2.87 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.05-2.03 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.3, 152.1, 140.6, 129.9, 126.7, 124.2, 120.6, 116.0, 47.9, 27.11, 27.09, 22.3. IR (neat) ν_{max} 3331, 2933, 2876, 1763, 1701, 1579, 1495 cm^{-1}. HRMS[ESI] calcd for $C_{12}H_{15}O_2N_2$ $[M+H]^+$ 219.1128, found 219.1126.



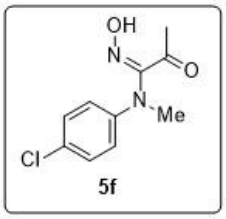
(Z)-N'-hydroxy-N-methyl-2-oxo-N-phenylpropanimidamide (5c); The title compound was prepared according to the general procedure; 404 mg, 84%; yellow solid; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (br s, 1H), 7.26–7.24 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 2H), 3.18 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.4, 152.5, 145.3, 129.3, 121.2, 115.6, 36.6, 27.0. IR (neat) ν_{max} 3330, 2923, 1759, 1701, 1593, 1497 cm^{-1}. HRMS[ESI] calcd for $C_{10}H_{13}O_2N_2$ $[M+H]^+$ 193.0972, found 193.0969.



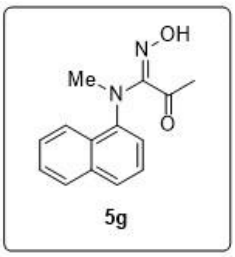
(Z)-N'-hydroxy-N-methyl-2-oxo-N-(m-tolyl)propanimidamide (5d); The title compound was prepared according to the general procedure; 490 mg, 95%; yellow oil; R_f = 0.4 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (br s, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 7.1 Hz, 1H), 6.53–6.50 (m, 2H), 3.16 (s, 3H), 2.42 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.4, 152.7, 145.3, 139.2, 129.1, 122.3, 116.2, 112.9, 36.7, 27.1, 21.8. IR (neat) ν_{max} 3331, 3023, 2919, 1763, 1701, 1583 cm^{-1}. HRMS[ESI] calcd for $C_{11}H_{15}O_2N_2$ $[M+H]^+$ 207.1128, found 207.1126.



(Z)-N'-hydroxy-N-(4-methoxyphenyl)-N-methyl-2-oxopropanimidamide (5e); The title compound was prepared according to the general procedure; 517 mg, 93%; yellow solid; R_f = 0.4 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers, ratio 25:1) δ 8.15 (br s, 1H), 6.83–6.80 (m, 2H), 6.73–6.70 (m, 2H), 3.76 (s, 3H), 3.17 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.7, 154.9, 152.9, 139.3, 118.0, 114.7, 55.7, 37.5, 27.2. IR (neat) ν_{max} 3416, 1692, 1633, 1511, 1245 cm^{-1}. HRMS[ESI] calcd for $C_{11}H_{15}O_3N_2$ $[M+H]^+$ 223.1077, found 223.1075.

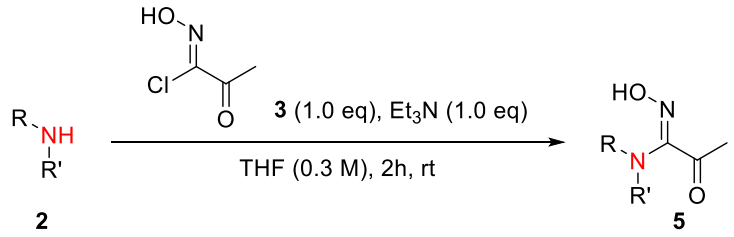


(Z)-N-(4-chlorophenyl)-N'-hydroxy-N-methyl-2-oxopropanimidamide (5f); The title compound was prepared according to the general procedure; 425 mg, 75%; yellow solid; R_f = 0.4 (Hex:EtOAc = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (br s, 1H), 7.18 (m, 2H), 6.60 (m, 2H), 3.14 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.1, 152.0, 144.1, 129.1, 126.0, 116.7, 36.8, 27.0. IR (neat) ν_{max} 3320, 2917, 2227, 1693, 1592, 1117 cm^{-1}. HRMS[ESI] calcd for $C_{10}H_{12}O_2N_2Cl$ $[M+H]^+$ 227.0582, found 227.0578.

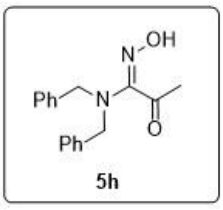


(E)-N'-hydroxy-N-methyl-N-(naphthalen-1-yl)-2-oxopropanimidamide (5g); The title compound was prepared according to the general procedure; 503 mg, 83%; yellow oil. R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (m, 1H), 7.86 (m, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.52–7.42 (m, 3H), 7.32 (dd, J = 7.4, 1.0 Hz, 1H), 3.47 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.2, 152.9, 143.8, 134.6, 129.5, 128.7, 126.3, 126.1, 125.8, 122.7, 120.7, 40.9, 27.5. IR (neat) ν_{max} 3331, 3052, 1698, 1594, 1351, 1082 cm^{-1}. HRMS[ESI] calcd for $C_{14}H_{15}O_2N_2$ $[M+H]^+$ 243.1128, found 243.1126.

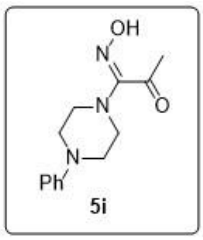
General Procedure for the synthesis of 5h–5k



To a stirred solution of **3** (304 mg, 2.5 mmol) in THF (8 mL) was added **2h**–**k** (2.5 mmol) and triethylamine (0.35 mL, 2.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 2 h. Then, the reaction mixture was diluted with water (20 mL) and extracted with ethyl acetate (15 mL X 3). The organic solution was dried over $MgSO_4$, filtered, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 or 3:1) to afford **5h–k**.

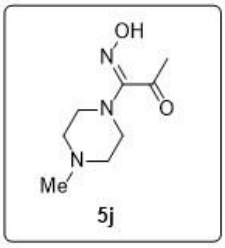


(Z)-N,N-dibenzyl-N'-hydroxy-2-oxopropanimidamide (5h); The title compound was prepared according to the general procedure; 522 mg, 74%; white solid; R_f = 0.6 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$, mixture of isomers, ratio 1:0.8) δ 7.35–7.25 (m, 18H), 4.28 (s, 4H), 4.26 (s, 3.2H), 2.38 (s, 2.4H), 2.10 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.8, 195.9, 160.0, 154.2, 137.6, 136.1, 128.9, 128.7, 128.6, 128.0, 127.9, 127.7, 54.8, 50.9, 31.1, 27.0. IR (neat) ν_{max} 3331, 3063, 3029, 1699, 1614, 1357 cm^{-1}. HRMS[ESI] calcd for $C_{17}H_{19}O_2N_2$ $[M+H]^+$ 283.1441, found 283.1437.

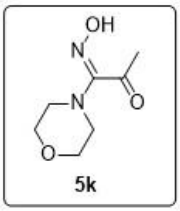


(E)-1-(hydroxyimino)-1-(4-phenylpiperazin-1-yl)propan-2-one (5i); The title compound was prepared according to the general procedure; 389 mg, 63%; white solid; R_f = 0.4 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (br s, 1H), 7.29–7.27 (m, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 3.43 (m, 4H), 3.24 (m, 4H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.6, 153.1, 151.5, 129.3, 120.4, 116.7, 50.2, 48.3, 27.4. IR (neat) ν_{max} 3299, 3234, 2842, 1697, 1636, 1263, 1152 cm^{-1}. HRMS[ESI] calcd for $C_{13}H_{18}O_2N_3$ $[M+H]^+$ 248.1394, found 248.1390.

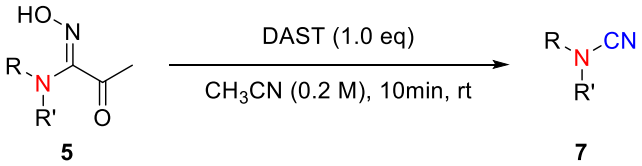
(E)-1-(hydroxyimino)-1-(piperidin-1-yl)propan-2-one (5j); The title compound was prepared according to the general procedure and purified with 5% MeOH in DCM; 310 mg, 67%; yellow solide; R_f = 0.4 (10% MeOH in DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.65 (br s, 1H), 3.36 (m, 4H), 2.53 (m, 4H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.3, 152.3, 55.5, 47.6, 46.2, 27.4. IR (neat) ν_{max} 3142, 2946, 2814, 1694, 1450, 1352 cm^{-1}. HRMS[ESI] calcd for $C_8H_{16}O_2N_3$ $[M+H]^+$ 186.1237, found 186.1235.



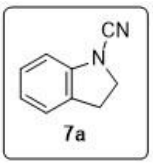
(E)-1-(hydroxyimino)-1-morpholinopropan-2-one (5k); The title compound was prepared according to the general procedure; 280 mg, 65%; white solid; R_f = 0.3 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (br s, 1H), 3.74–3.72 (m, 4H), 3.31–3.29 (m, 4H), 2.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 152.0, 67.5, 48.6, 27.5. IR (neat) ν_{max} 3300, 2964, 2859, 1698, 1614, 1260 cm^{-1}. HRMS[ESI] calcd for $C_7H_{13}O_3N_2$ $[M+H]^+$ 173.0921, found 173.0920.



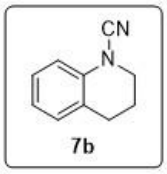
4. 4) General Procedure for the synthesis of 7a–7k



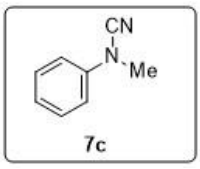
To a stirred solution of **5** (0.3 mmol) in CH_3CN (1 mL) was added (diethylamino)sulfur trifluoride (DAST, 0.04 mL, 0.3 mmol) at room temperature. After 10 min, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n (20 mL) and extracted with ethyl acetate (10 mL X 2). Then, the organic solution was dried over $MgSO_4$, filtered, concentrated, and subjected to silica gel column chromatography (Het:EtOAc = 5:1 or 3:1) to afford **7a–k.**



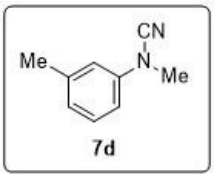
Indoline-1-carbonitrile (7a);[5] The title compound was prepared according to the general procedure; 31 mg, 72%; white solid; R_f = 0.4 (Hex:EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.01–6.97 (m, 2H), 4.05 (t, *J* = 8.6 Hz, 2H), 3.20 (t, *J* = 8.5 Hz, 2H). IR (neat) ν_{max} 3053, 2968, 2918, 2222, 1732, 1489 cm^{-1}.



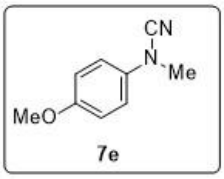
3,4-dihydroquinoline-1(2H)-carbonitrile (7b);[5] The title compound was prepared according to the general procedure; 36 mg, 76%; yellow oil; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22–7.17 (m, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.97 (m, 1H), 3.75 (t, *J* = 5.7 Hz, 2H), 2.80 (t, *J* = 6.3 Hz, 2H), 2.04 (quint, *J* = 6.2 Hz, 2H). IR (neat) ν_{max} 2940, 2889, 2216, 1588, 1496 cm^{-1}.



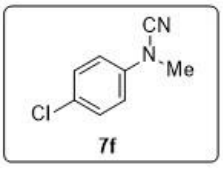
N-methyl-N-phenylcyanamide (7c);[5] The title compound was prepared according to the general procedure; 30 mg, 75%; yellow oil; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40–7.37 (m, 2H), 7.12–7.09 (m, 3H), 3.34 (s, 3H). IR (neat) ν_{max} 3046, 2920, 2222, 1599, 1499, 1113 cm^{-1}.



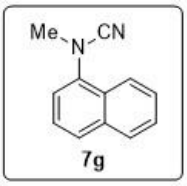
N-methyl-N-(m-tolyl)cyanamide (7d); The title compound was prepared according to the general procedure; 29 mg, 67%; white oil; R_f = 0.5 (Hex:EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (t, *J* = 4.4 Hz, 1H), 6.92–6.86 (m, 3H), 3.32 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.4, 140.0, 129.5, 124.3, 115.8 114.4, 112.0, 36.9, 21.7. IR (neat) ν_{max} 2918, 2846, 2222, 1606, 1477 cm^{-1}. HRMS[ESI] calcd for $C_9H_{11}N_2$ $[M+H]^+$ 147.0917, found 147.0915.



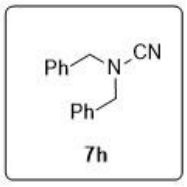
N-(4-methoxyphenyl)-N-methylcyanamide (7e); The title compound was prepared according to the general procedure; 44 mg, 91%; white solid; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03–6.99 (m, 2H), 6.91–6.89 (m, 2H), 3.78 (s, 3H), 3.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.1, 133.9, 116.6, 114.99, 114.96, 55.7, 37.4. IR (neat) ν_{max} 2961, 2836, 2221, 1512, 1116, 1035 cm^{-1}. HRMS[ESI] calcd for $C_9H_{11}ON_2$ $[M+H]^+$ 163.0866, found 163.0864.



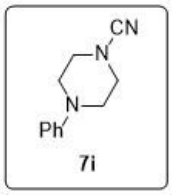
N-(4-chlorophenyl)-N-methylcyanamide (7f);[6] The title compound was prepared according to the general procedure; 37 mg, 75%; yellow solid; R_f = 0.5 (Hex:EtOAc = 5:1); ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.46–7.44 (m, 2H), 7.19–7.17 (m, 2H), 3.40 (s, 3H). IR (neat) ν_{max} 2924, 2227, 1495, 1336, 1119 cm^{-1}.



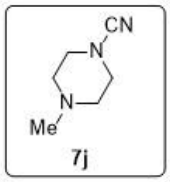
N-methyl-N-(naphthalen-1-yl)cyanamide (7g); The title compound was prepared according to the general procedure; 35 mg, 64%; yellow solid; R_f = 0.2 (Hex:EtOAc = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (m, 1H), 7.91 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.82 (dd, *J* = 6.6, 2.5 Hz, 1H), 7.63 (m, 1H), 7.58 (m, 1H), 7.54–7.47 (m, 2H), 3.45 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 134.8, 128.8, 128.4, 128.1, 127.3, 126.9, 125.6, 122.2, 121.2, 117.3, 42.4. IR (neat) ν_{max} 2916, 2215, 1596, 1575, 1395 cm^{-1}. HRMS[ESI] calcd for $C_{12}H_{11}N_2$ $[M+H]^+$ 183.0917, found 183.0916.



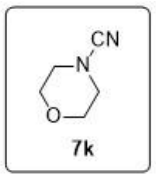
N,N-dibenzylcyanamide (7h);[7] The title compound was prepared according to the general procedure; 35 mg, 53%; white solid; R_f = 0.3 (Hex:EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41–7.35 (m, 6H), 7.31 (d, *J* = 6.8 Hz, 4H), 4.12 (s, 4H). IR (neat) ν_{max} 3031, 2921, 2208, 1496, 1454 cm^{-1}.



4-phenylpiperazine-1-carbonitrile (7i);[5] The title compound was prepared according to the general procedure; 34 mg, 60%; white oil; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.3, 7.6 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 3.41-3.39 (m, 4H), 3.25–3.23 (m, 4H). IR (neat) ν_{max} 2917, 2828, 2213, 1598, 1495 cm^{-1}.



Piperidine-1-carbonitrile (7j);[8] The title compound was prepared according to the general procedure; 12 mg, 33%; yellow solide; R_f = 0.7 (10% MeOH in DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.27–3.24 (m, 4H), 2.48–2.45 (m, 4H), 2.31 (s, 3H). IR (neat) ν_{max} 2924, 2851, 2221, 1469, 1374 cm^{-1}.



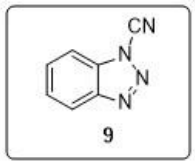
Morpholine-4-carbonitrile (7k);[7] The title compound was prepared according to the general procedure; 12 mg, 35%; white solid; R_f = 0.5 (Hex:EtOAc = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75–3.74 (m, 4H), 3.25–3.24 (m, 4H). IR (neat) ν_{max} 2968, 2922, 2860, 2215, 1454, 1262 cm^{-1}.

4.5) Procedure for preparation of 9

The known compounds **8** were prepared by the known procedures and not characterized.[9]

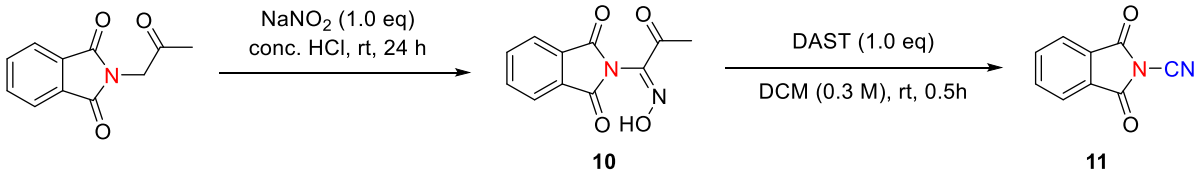
8 **9**

To a stirred solution of **8** (204 mg, 1 mmol) in DCM (3.3 mL) was added (diethylamino)sulfur trifluoride (DAST, 0.13 mL, 1 mmol) at room temperature. After 2h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n (40 mL) and extracted with ethyl acetate (20 mL X 2). Then, the organic solution was dried over $MgSO_4$, filtered, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 10:1) to afford **9**.



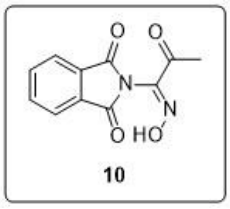
1H-benzo[d][1,2,3]triazole-1-carbonitrile (9);[10] 79 mg, 55%; white solid; R_f = 0.6 (Hex : EtOAc = 3:1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.3 Hz, 2H), 7.80–7.78 (m, 2H), 7.61 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 132.9, 131.8, 127.0, 121.7, 109.7, 103.9. IR (neat) ν_{max} 3096, 2917, 2254, 1484, 1454 cm^{-1}.

4.6) Procedure for preparation of 11

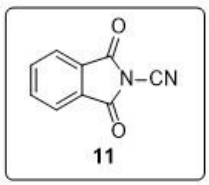


Step 1: A 40 mL vial was charged with 2-(2-oxopropyl)isoindoline-1,3-dione (1.22 g, 6.0 mmol) and conc. HCl (12 mL). Then, sodium nitrite (1.04 g, 15 mmol) was added to the reaction mixture at room temperature, and the vial was capped. After stirring for 24 h, the reaction mixture was poured onto ice water, and the resulting white solid was filtered, dried, and purified by silica gel column chromatography (Hex:EtOAc = 5:1 to 1:1) to afford **10**.

Step 2: To a stirred solution of **8** (232 mg, 1 mmol) in DCM (3.3 mL) was added (diethylamino)sulfur trifluoride (DAST, 0.13 mL, 1 mmol) at room temperature. After 2h, the reaction mixture was quenched with sat. $NaHCO_3$ sol'n (40 mL) and extracted with ethyl acetate (20 mL X 2). Then, the organic solution was dried over $MgSO_4$, filtered, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 5:1 to 1:1) to afford **11**.

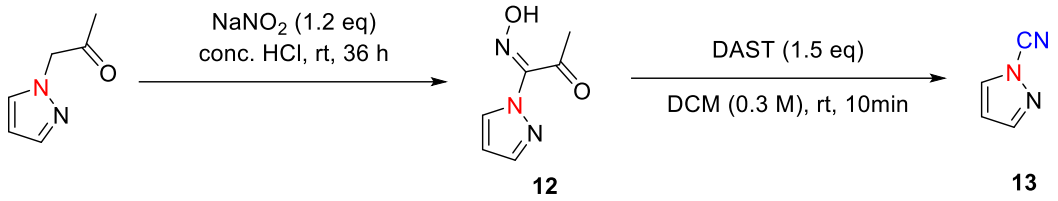


(Z)-2-(1-(hydroxyimino)-2-oxopropyl)isoindoline-1,3-dione (10); 390mg, 28%; white solid ; R_f = 0.5 (Hex:EtOAc = 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.21 (br s, 1H), 7.94-7.91 (m, 2H), 7.80-7.77 (m, 2H), 2.55 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.5, 168.1, 165.1, 141.5, 134.8, 134.6, 132.7, 132.1, 124.3, 123.8, 25.6. IR (neat) ν_{max} 3289, 3031, 2929, 1774, 1715, 1417 cm^{-1}. HRMS[ESI] calcd for $C_{11}H_8O_4N_2Na$ $[M+Na]^+$ 255.0376, found 255.0368.



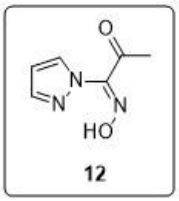
1,3-dioxoisoindoline-2-carbonitrile (11);[11] 103mg, 60%; white solid; R_f = 0.4 (Hex:EtOAc = 2:1); ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.10–8.06 (m, 2H), 8.04–7.99 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.6, 136.3, 130.8, 125.0, 102.9. IR (neat) ν_{max} 2919, 2846, 2252, 1749, 1353 cm^{-1}.

4.7) Procedure for preparation of 13

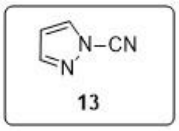


Step 1: To a stirred suspension of 1-(1H-pyrazol-1-yl)propan-2-one (3.32 g, 26.7 mmol) in conc. HCl (64.1 mL) was added sodium nitrite (2.21 g, 32.1 mmol) at room temperature. After stirring for 36 h, the reaction mixture was neutralized with 2M NaOH until pH becomes to 6-7 and extracted with ethyl acetate (100 mL X 3). Then, the organic solution was dried over $MgSO_4$, filtered, concentrated, and subjected to silica gel column chromatography (Hex:EtOAc = 3:1) to afford **12**.

Step 2: To a stirred solution of **12** (153 mg, 1.0 mmol) in DCM (3.3 mL) was added (diethylamino)sulfur trifluoride (DAST, 0.79 mL, 6.0 mmol) at room temperature. After 10min, the reaction mixture was diluted with diethyl ether (30 mL). Then, the organic solution was washed with 1N HCl sol'n (20 mL) and then neutralized with sat. $NaHCO_3$ sol'n (40 mL). Then, the organic solution was dried over $MgSO_4$, filtered, concentrated to afford **13** in analytically pure form. Its separation by column chromatography was unsuccessful due to hydrolysis of **13** into 1H-pyrazole-1-carboxamide.

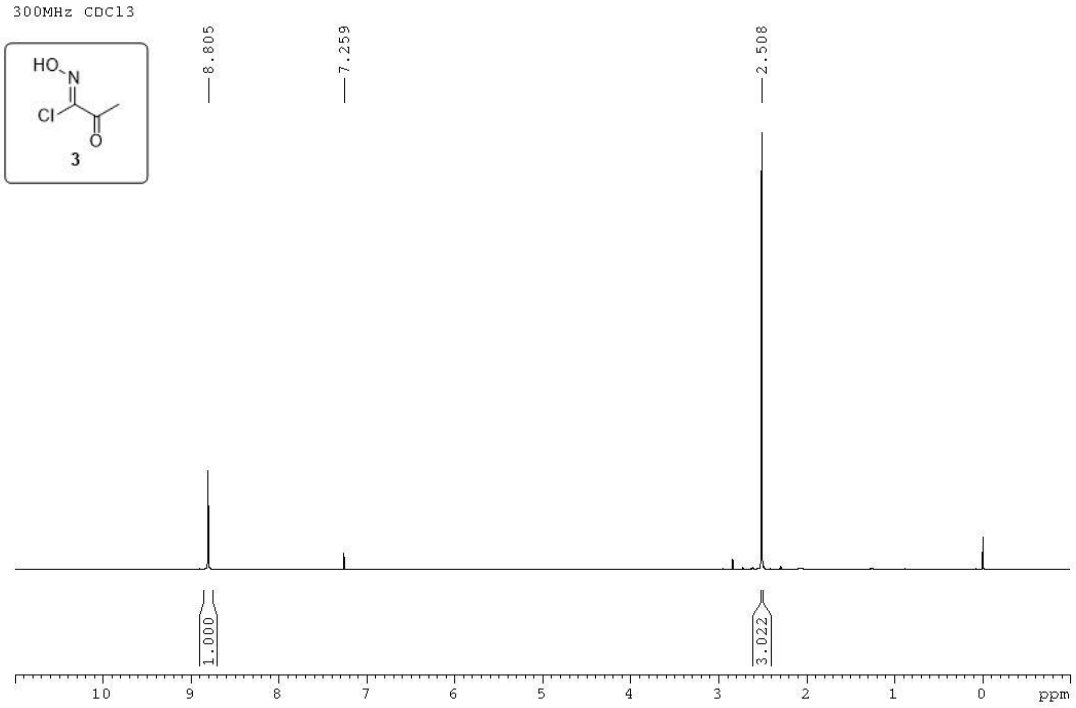


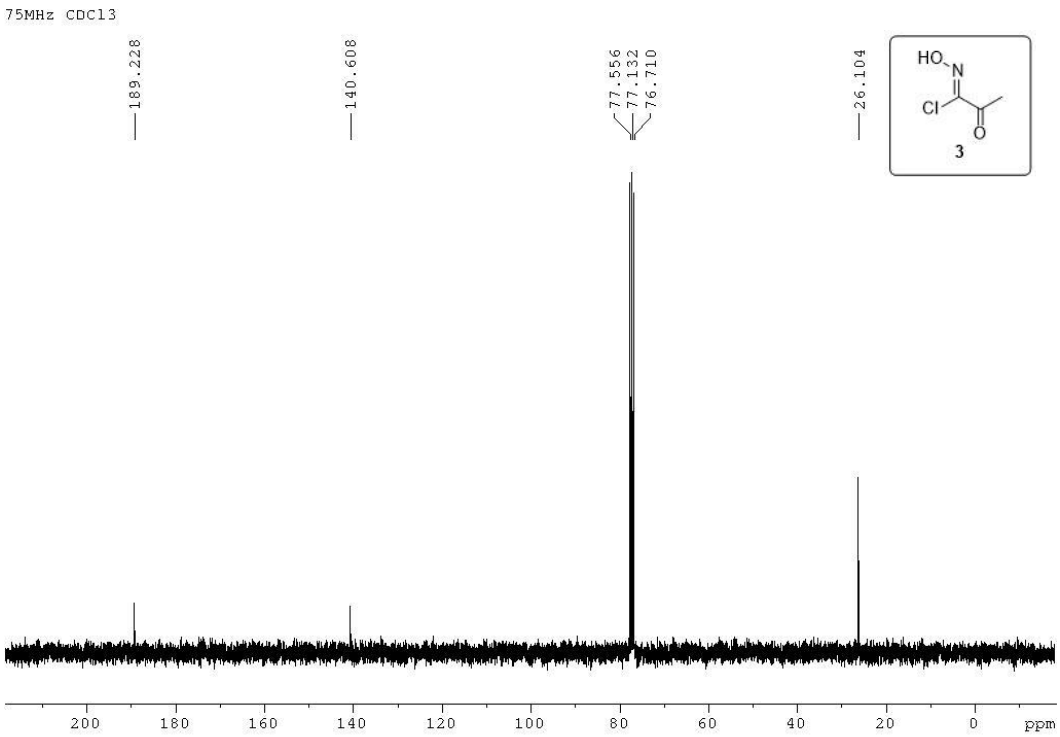
(E)-1-(hydroxyimino)-1-(1H-pyrazol-1-yl)propan-2-one (12); 2.45g, 60%; white solid; R_f = 0.3 (Hex:EtOAc = 3:1); ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.0 (br s), 7.93 (d, J = 2.5 Hz, 1H), 7.69 (d, J = 1.6 Hz, 1H), 6.45 (dd, J = 2.3, 1.9 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 191.3, 144.3, 140.3, 132.6, 106.1, 26.4. IR (neat) ν_{max} 3386, 3042, 1704, 1521, 1410, 1333 cm^{-1}. HRMS[ESI] calcd for $C_6H_8O_2N_3$ $[M+H]^+$ 154.0611, found 154.0608.

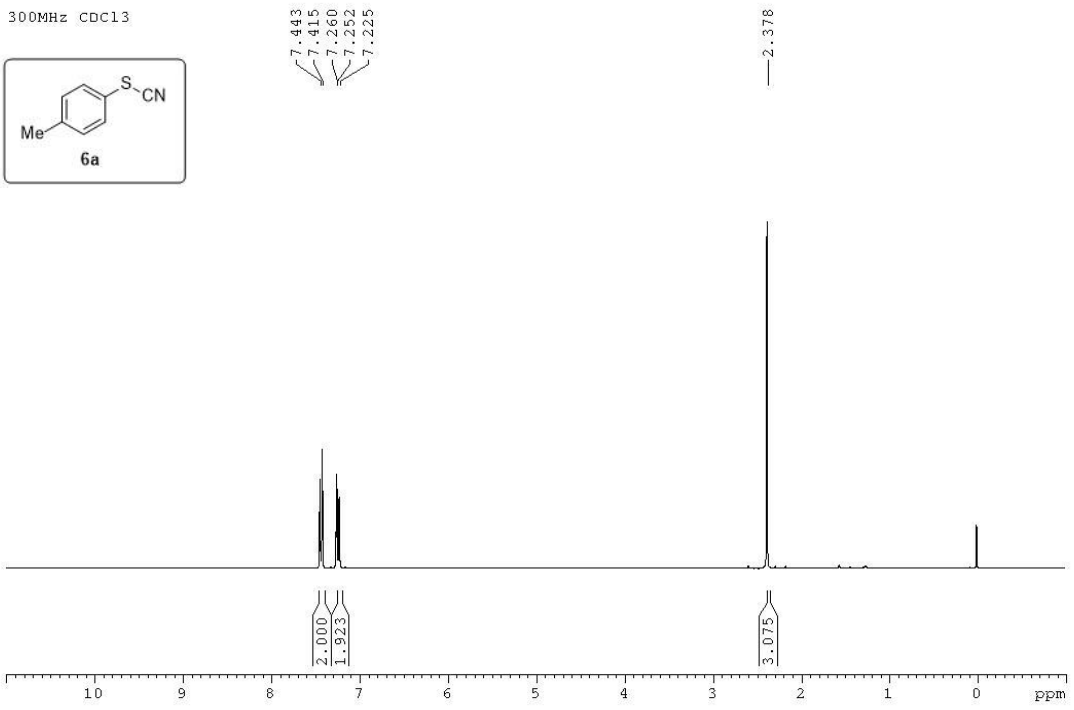


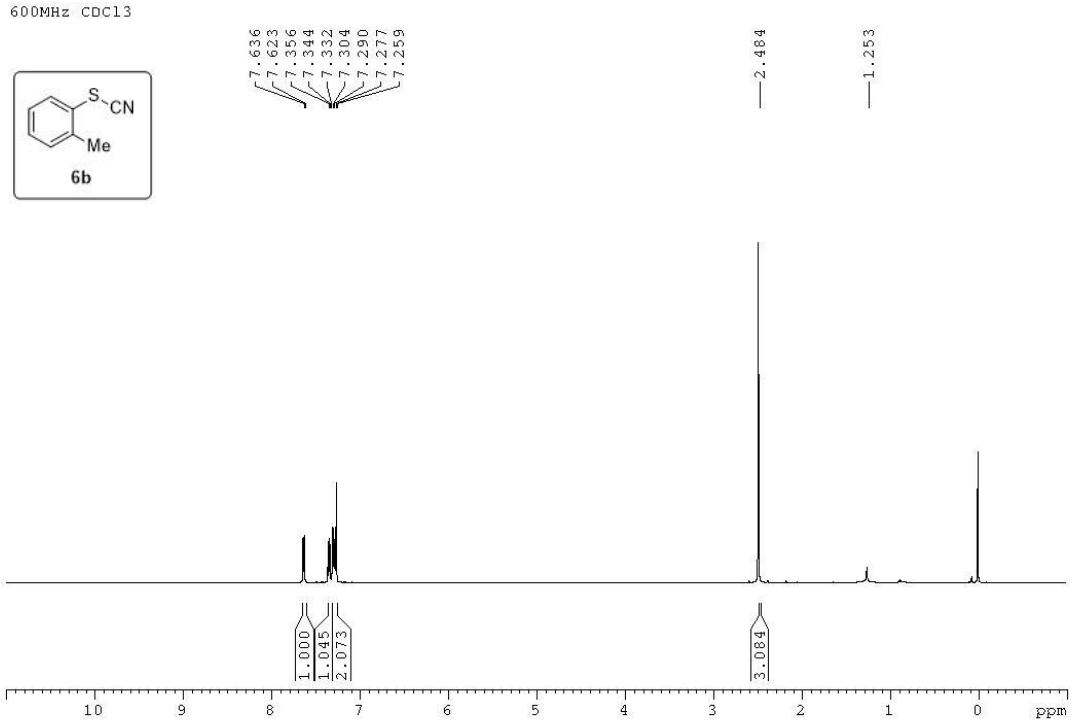
1H-pyrazole-1-carbonitrile (13); 79 mg, 85%; yellow oil; R_f = 0.5 (Hex:EtOAc = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 2.8 Hz, 1H), 7.83 (d, J = 1.4 Hz, 1H), 6.50 (dd, J = 2.7, 1.8 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.9, 134.7, 109.7, 106.8. IR (neat) ν_{max} 3133, 2918, 2261, 1390 cm^{-1}. HRMS[ESI] calcd for $C_4H_4N_3$ $[M+H]^+$ 94.0400, found 94.0401.

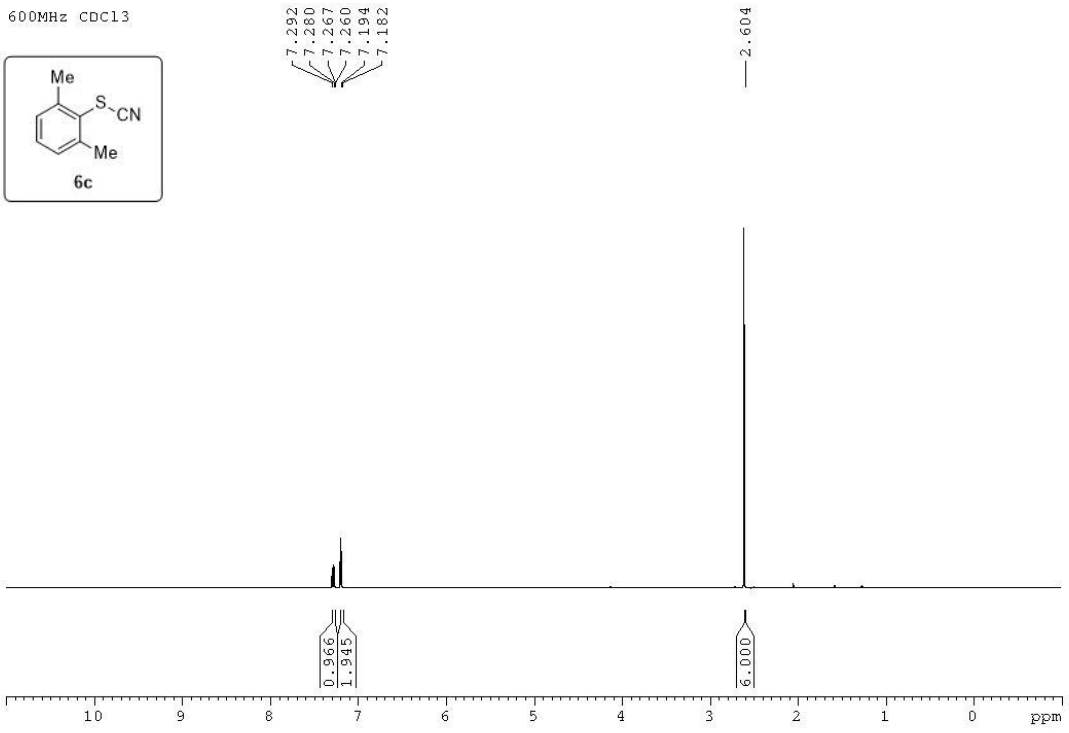
5. ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR

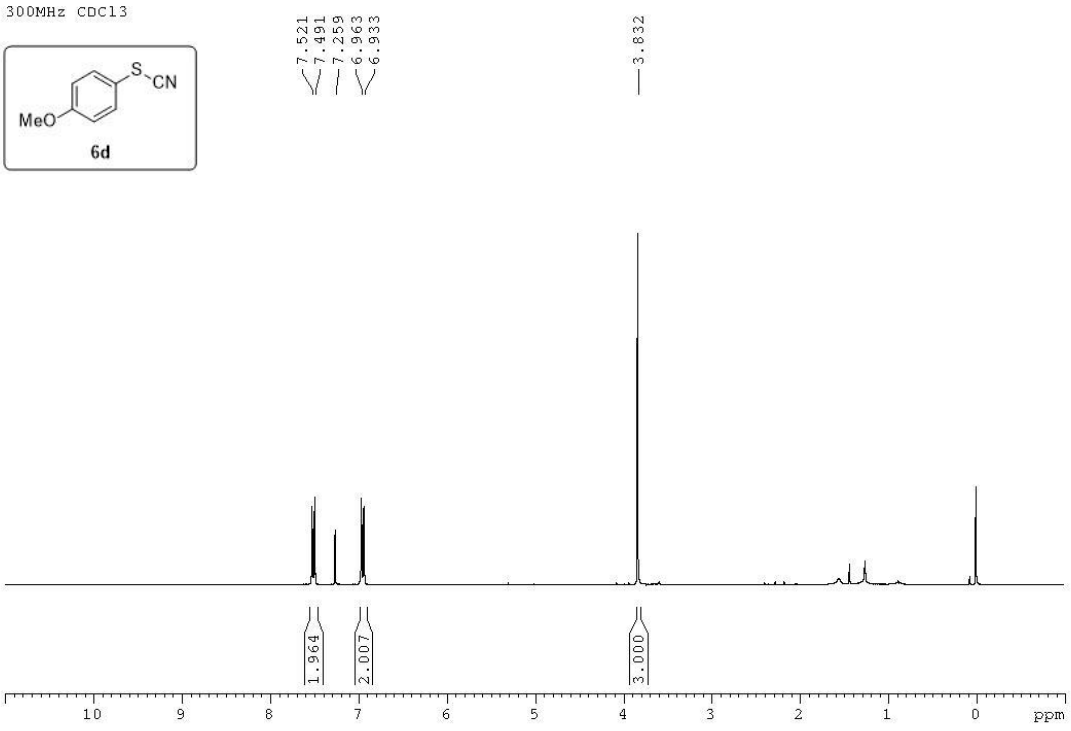


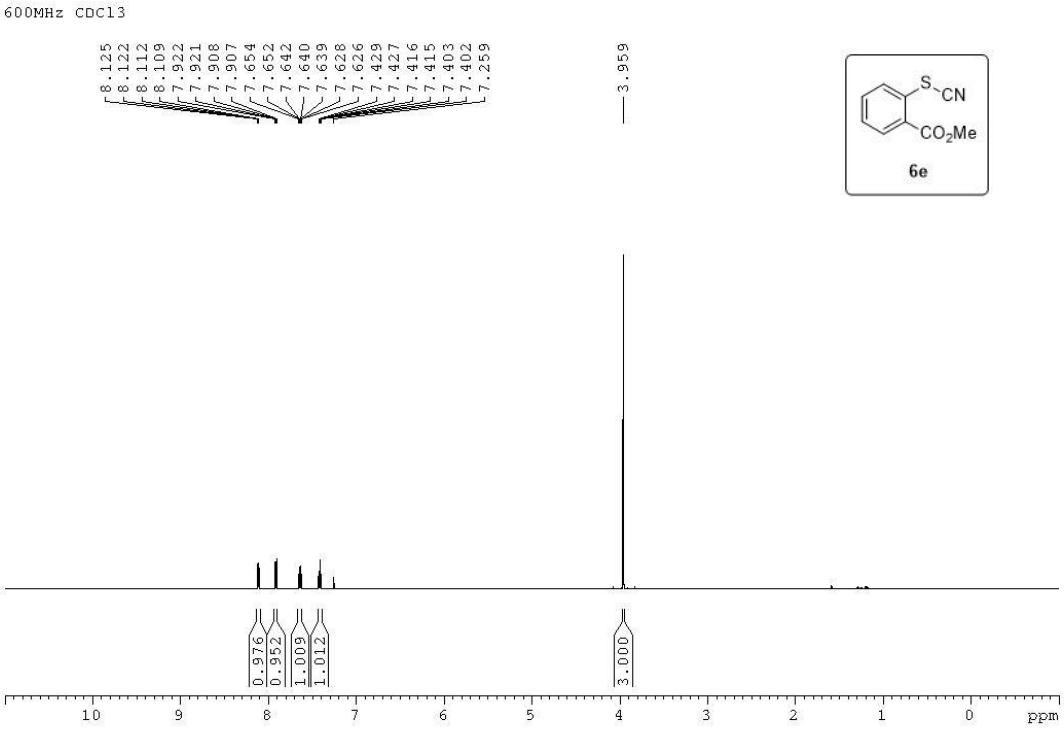


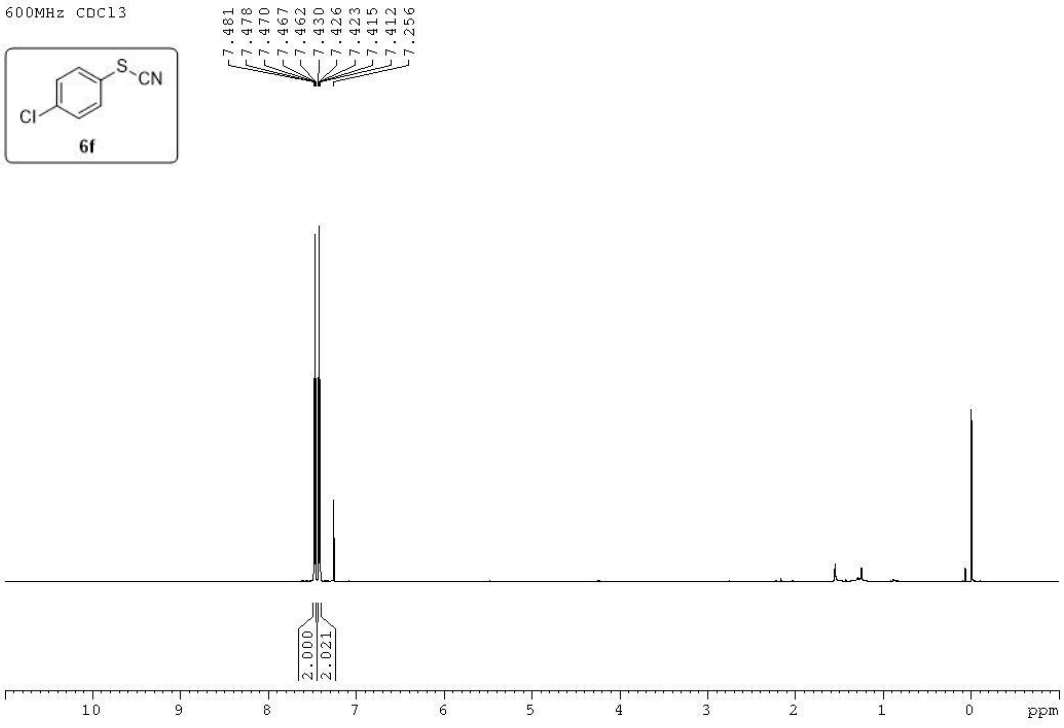

300MHz CDCl3
7.443
7.415
7.260
7.252
7.225
2.378
S
CN
Me
6a
2.000
1.923
3.075
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
7.636
7.623
7.356
7.344
7.332
7.304
7.290
7.277
7.259
2.484
1.253
S
CN
Me
6b
1.000
1.045
2.073
3.084
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
Me
S
CN
Me
6c
7.292
7.280
7.267
7.260
7.194
7.182
2.604
0.966
1.945
6.000
10
9
8
7
6
5
4
3
2
1
0
ppm


300MHz CDCl3
S
CN
MeO
6d
7.521
7.491
7.259
6.963
6.933
3.832
1.964
2.007
3.000
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
8.125
8.122
8.112
8.109
7.922
7.921
7.908
7.907
7.654
7.652
7.642
7.640
7.639
7.628
7.626
7.429
7.427
7.416
7.415
7.403
7.402
7.259
3.959
S
CN
CO2Me
6e
0.976
0.952
1.009
1.012
3.000
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
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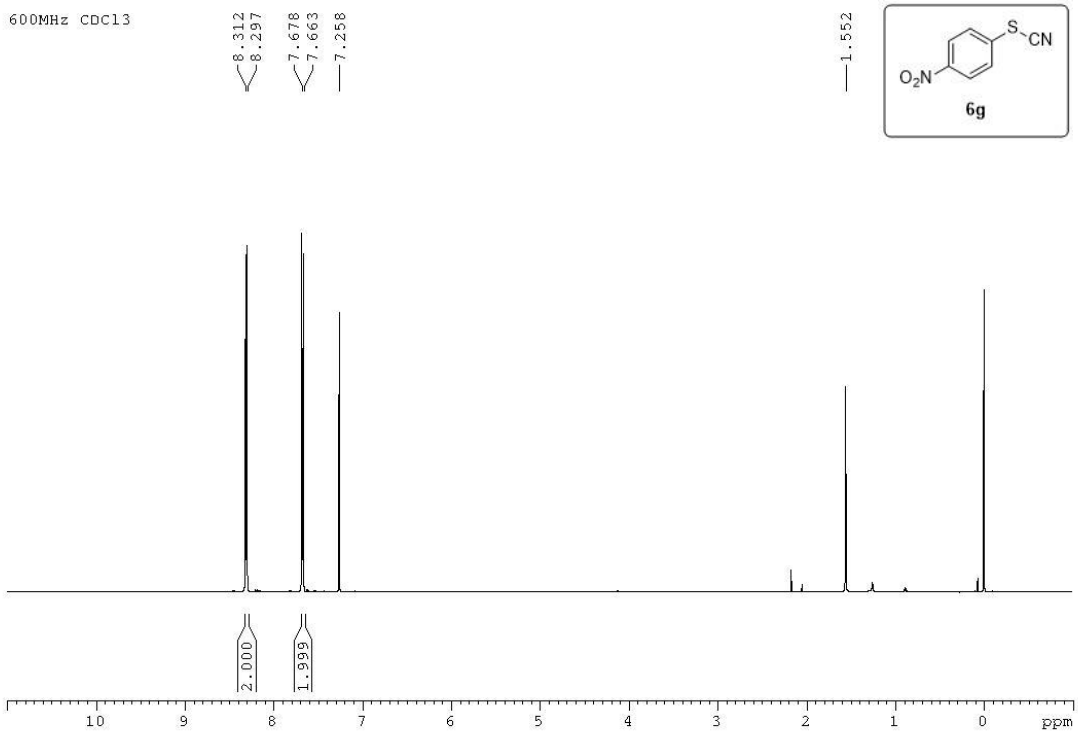
7.478
7.470
7.467
7.462
7.430
7.426
7.423
7.415
7.412
7.256
S
CN
Cl
6f
2.000
2.021
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
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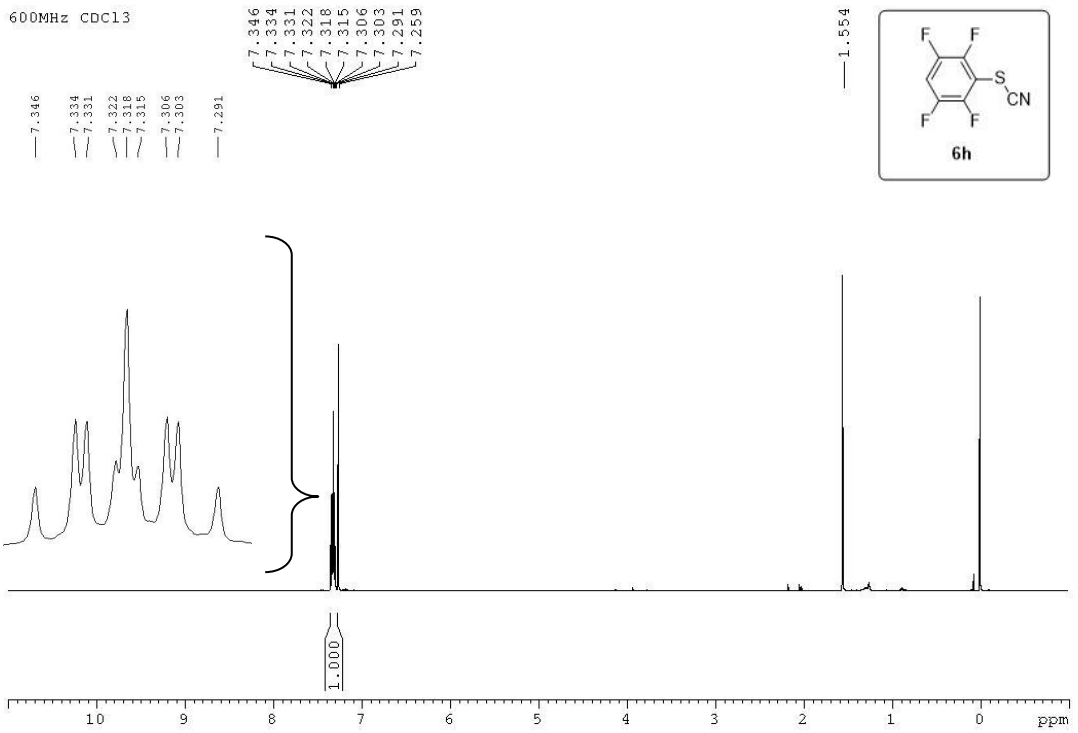
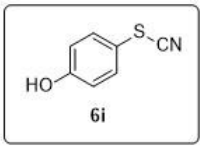
8.297
7.678
7.663
7.258
1.552
6g
2.000
1.999
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
7.346
7.334
7.331
7.322
7.318
7.315
7.306
7.303
7.291
7.259
1.554
6h
1.000
10
9
8
7
6
5
4
3
2
1
0
ppm

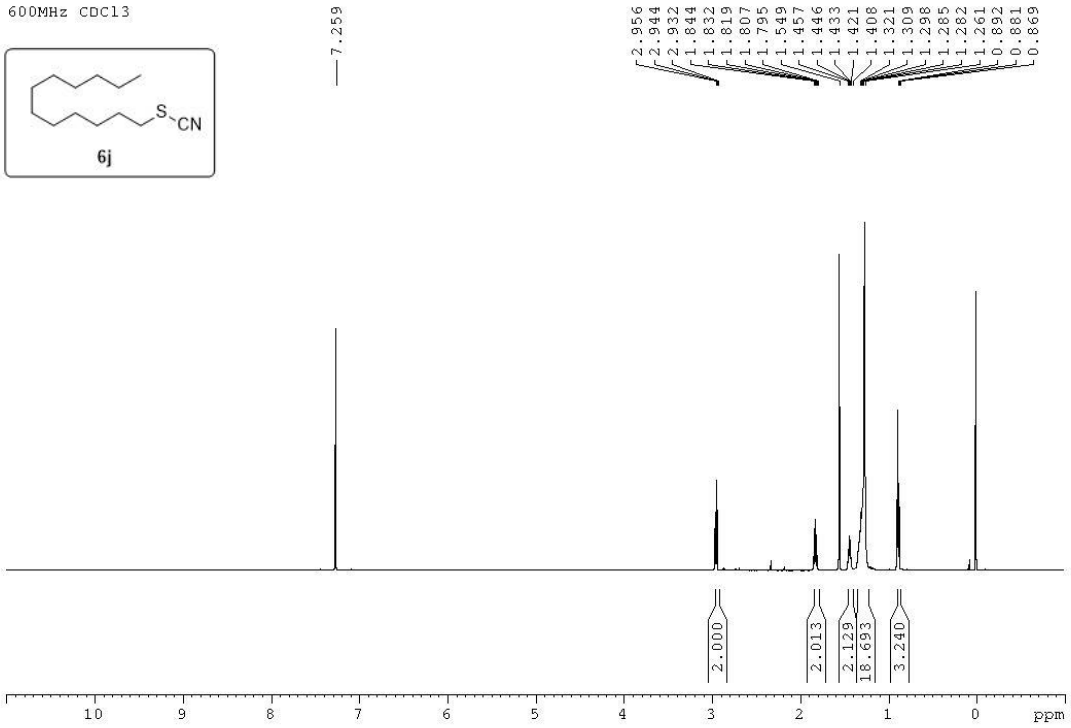
565MHz CDCl3

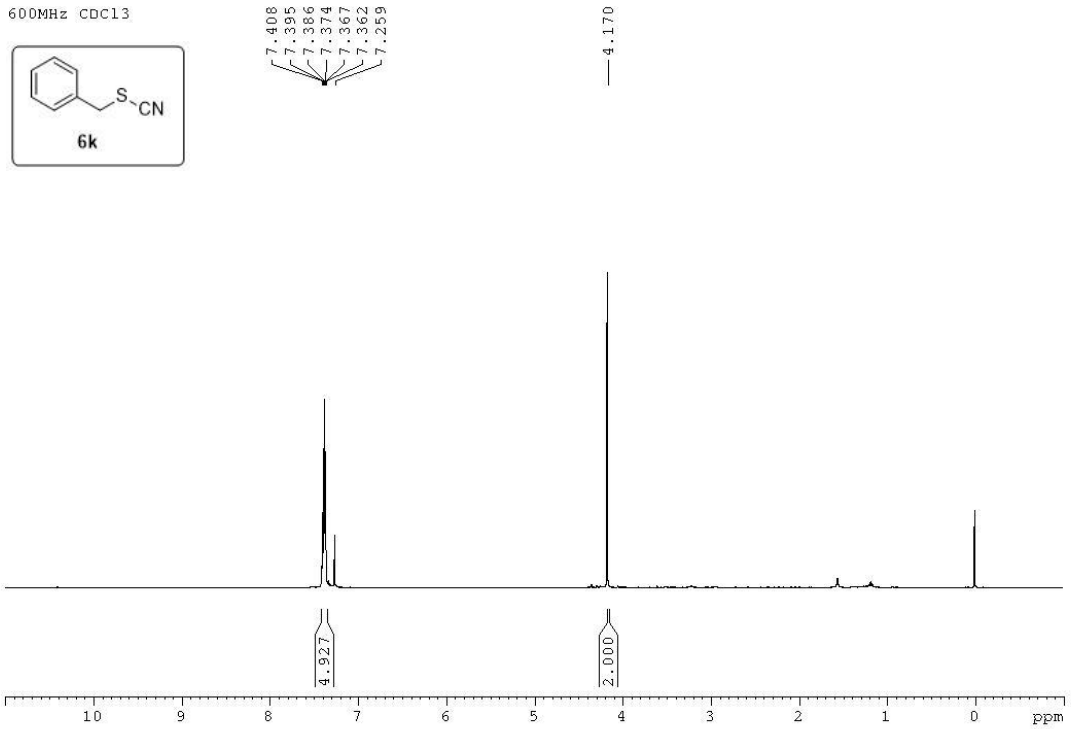
6h

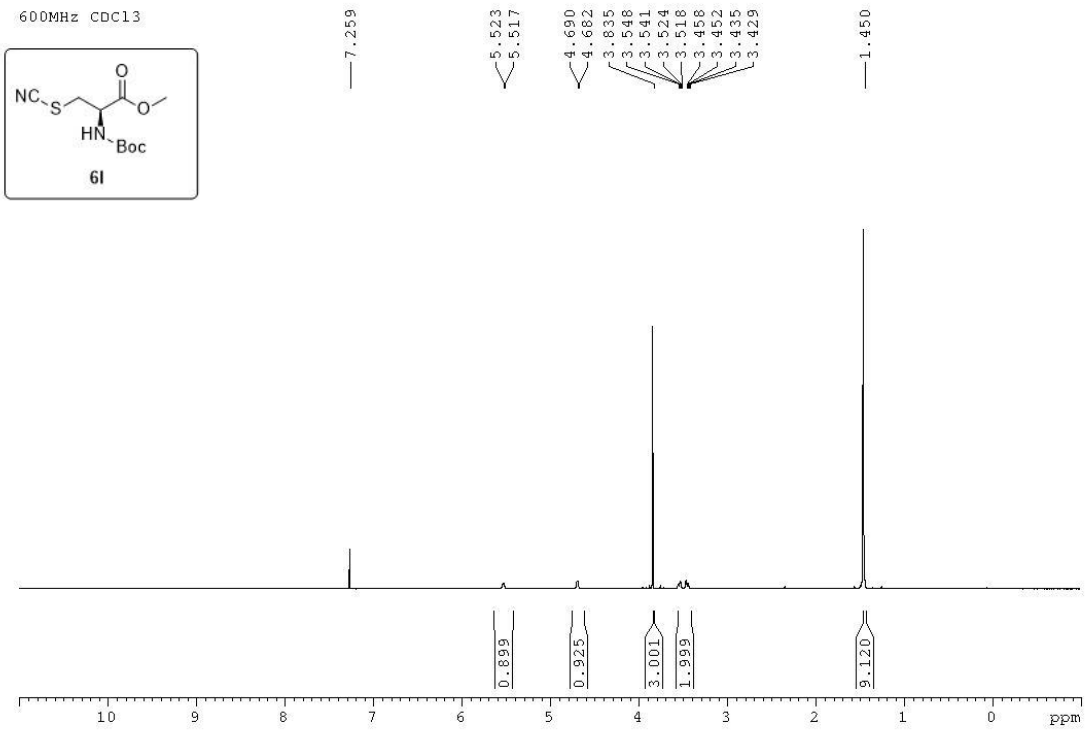
300MHz CDCl3

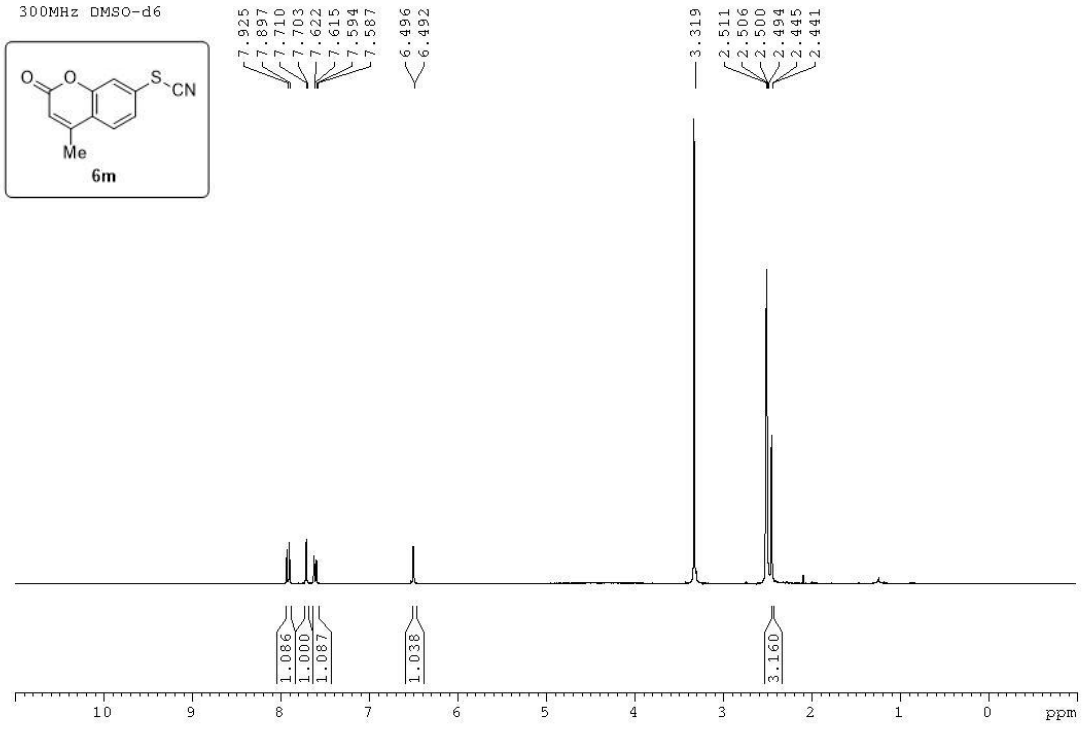


6i

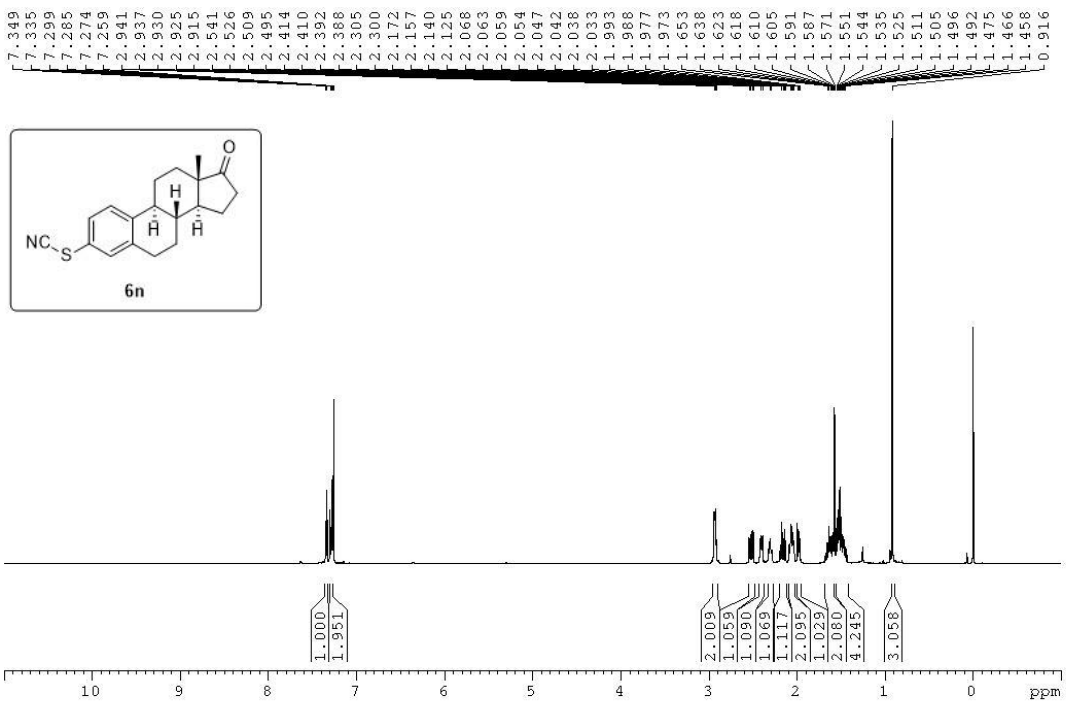

600MHz CDCl3
6j
7.259
2.956
2.944
2.932
1.844
1.832
1.819
1.807
1.795
1.549
1.457
1.446
1.433
1.421
1.408
1.321
1.309
1.298
1.285
1.282
1.261
0.892
0.881
0.869
2.000
2.013
2.129
18.693
3.240
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
6k
7.408
7.395
7.386
7.374
7.367
7.362
7.259
4.170
4.927
2.000
10
9
8
7
6
5
4
3
2
1
0
ppm

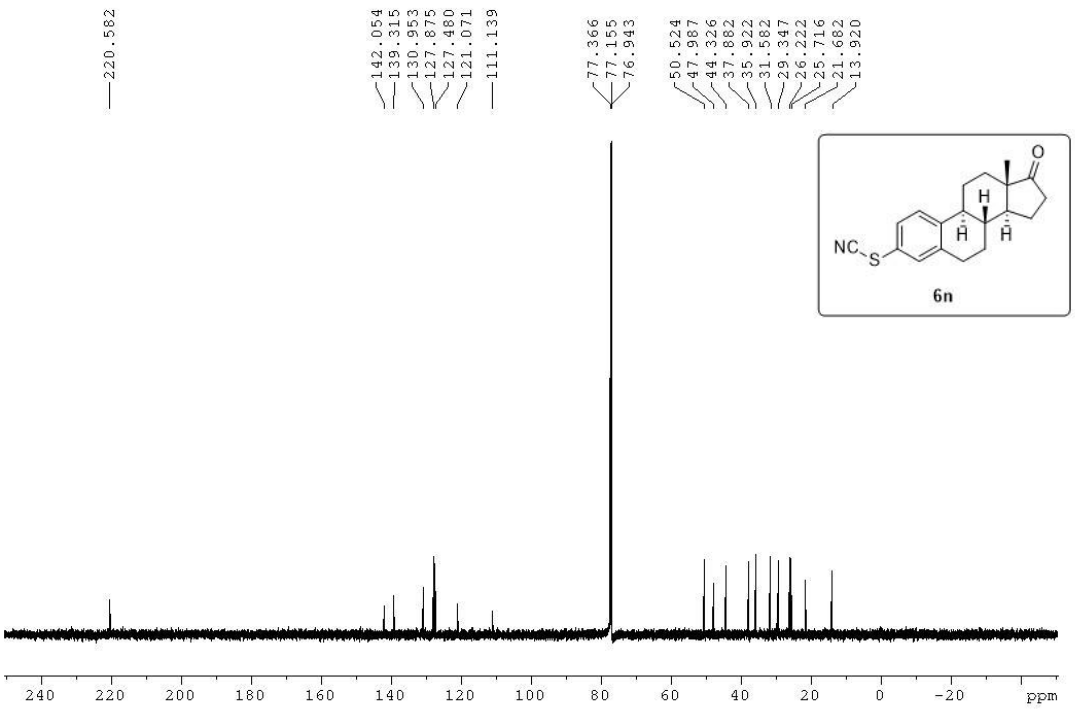

600MHz CDCl3
NC
S
O
O
HN
Boc
6l
7.259
5.523
5.517
4.690
4.682
3.835
3.548
3.541
3.524
3.518
3.458
3.452
3.435
3.429
1.450
0.899
0.925
3.001
1.999
9.120
10
9
8
7
6
5
4
3
2
1
0
ppm

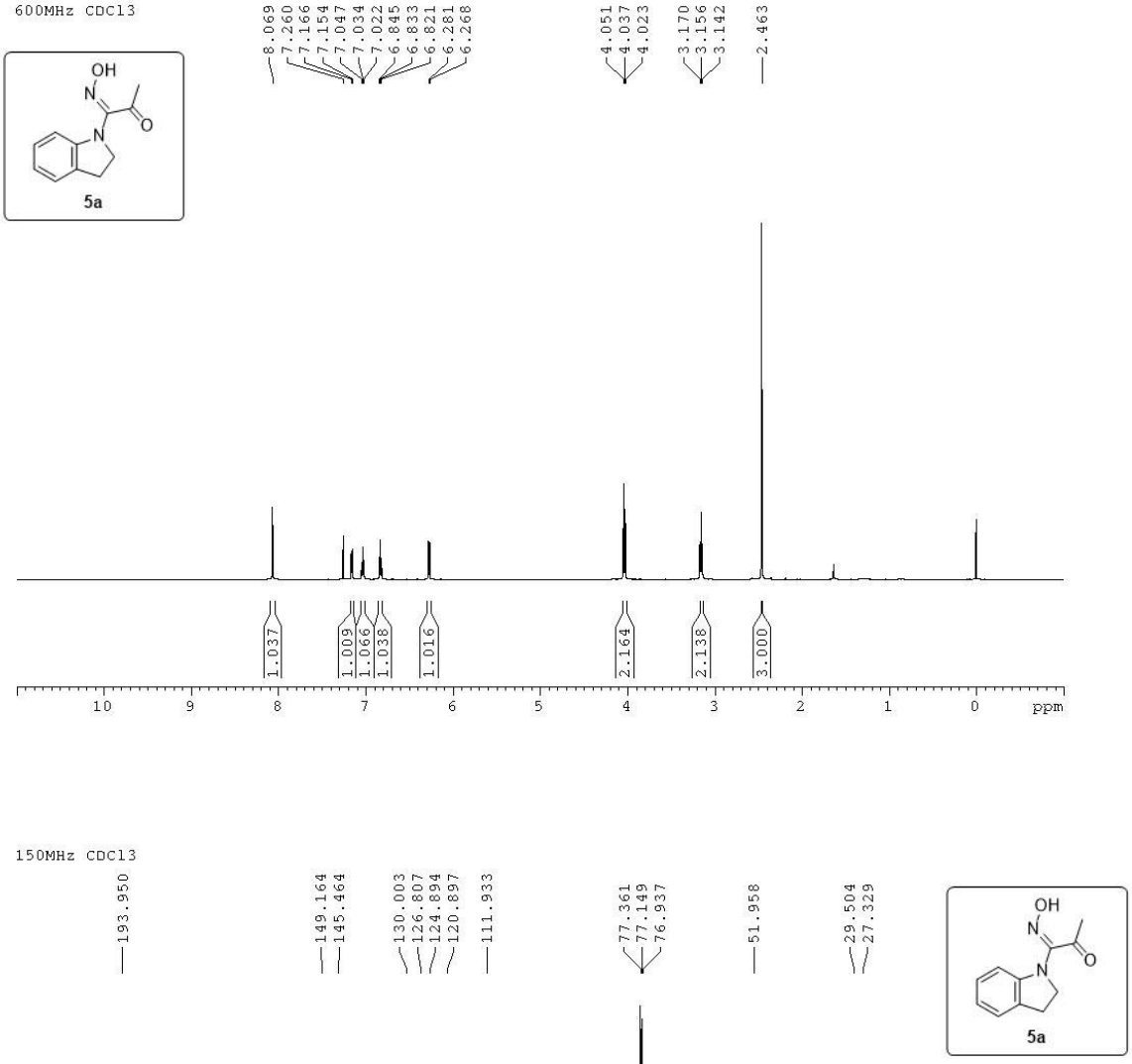

300MHz DMSO-d6
O
O
S
CN
Me
6m
7.925
7.897
7.710
7.703
7.622
7.615
7.594
7.587
6.496
6.492
3.319
2.511
2.506
2.500
2.494
2.445
2.441
1.086
1.000
1.087
1.038
3.160
10
9
8
7
6
5
4
3
2
1
0
ppm

600MHz CDCl3

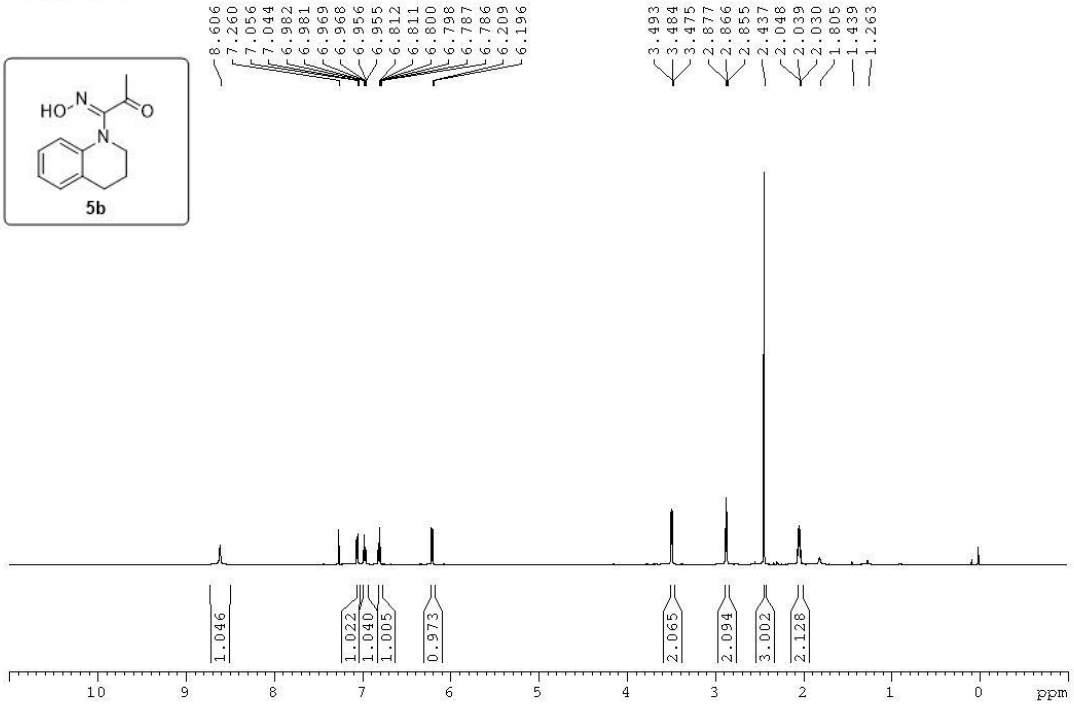


150MHz CDCl3

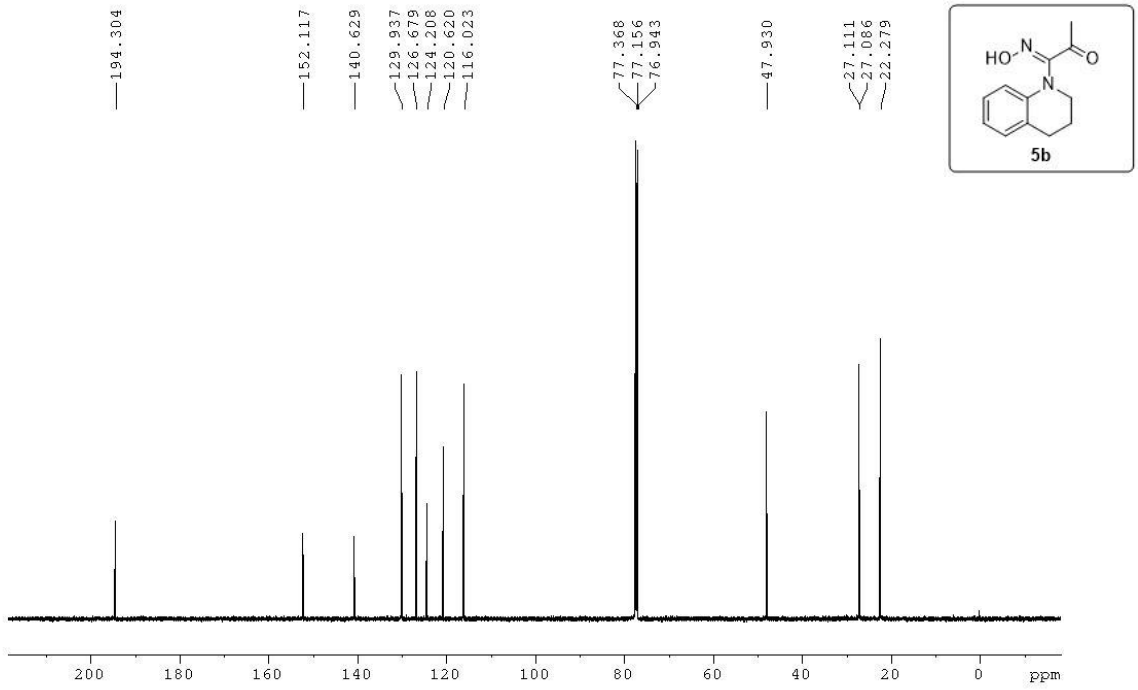


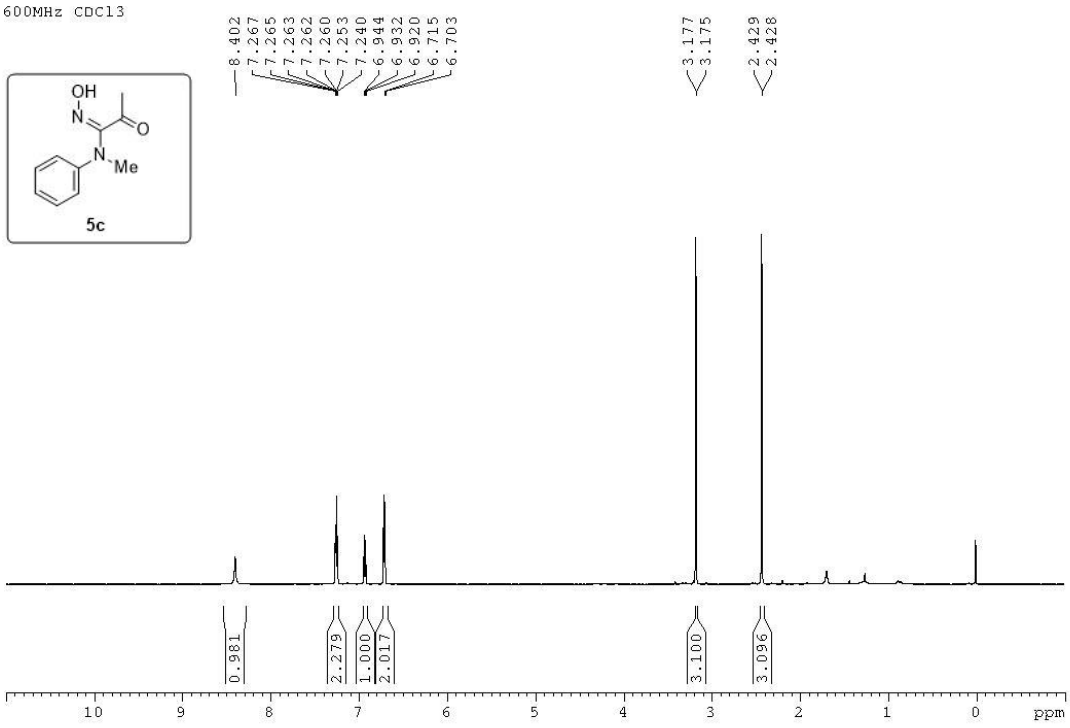

600MHz CDCl3
8.069
7.260
7.166
7.154
7.047
7.034
7.022
6.845
6.833
6.821
6.281
6.268
4.051
4.037
4.023
3.170
3.156
3.142
2.463
OH
N
O
N
5a
1.037
1.009
1.066
1.038
1.016
2.164
2.138
3.000
10
9
8
7
6
5
4
3
2
1
0
ppm
150MHz CDCl3
193.950
149.164
145.464
130.003
126.807
124.894
120.897
111.933
77.361
77.149
76.937
51.958
29.504
27.329
OH
N
O
N
5a
200
180
160
140
120
100
80
60
40
20
0
ppm

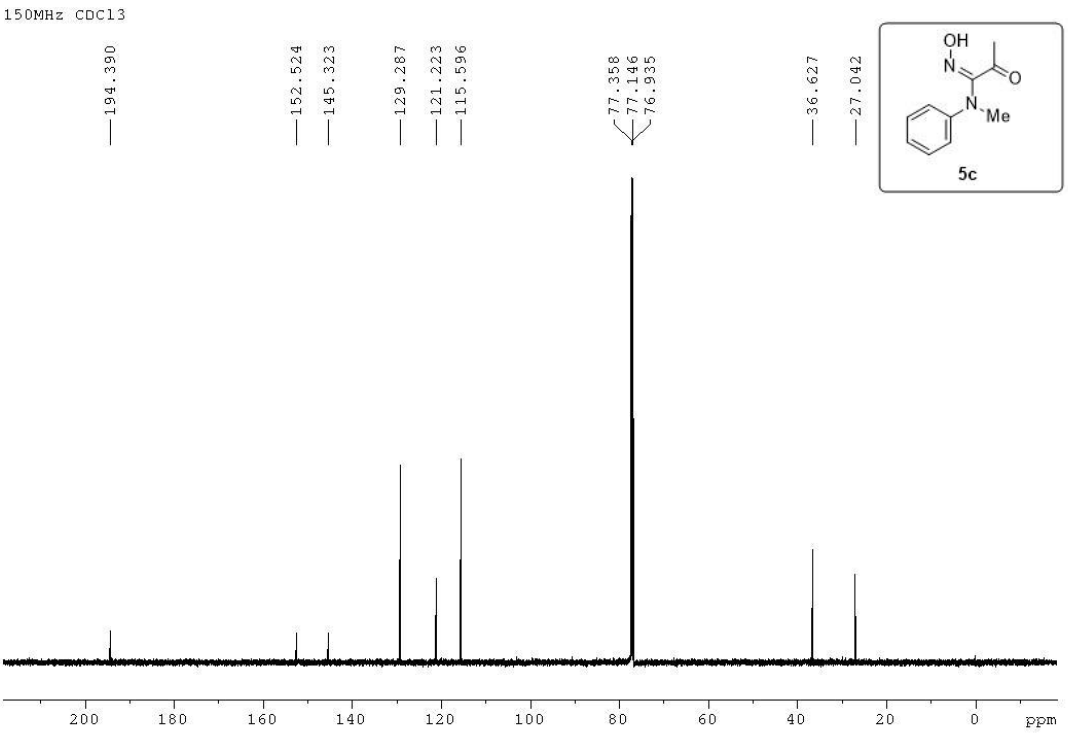
600MHz CDCl3

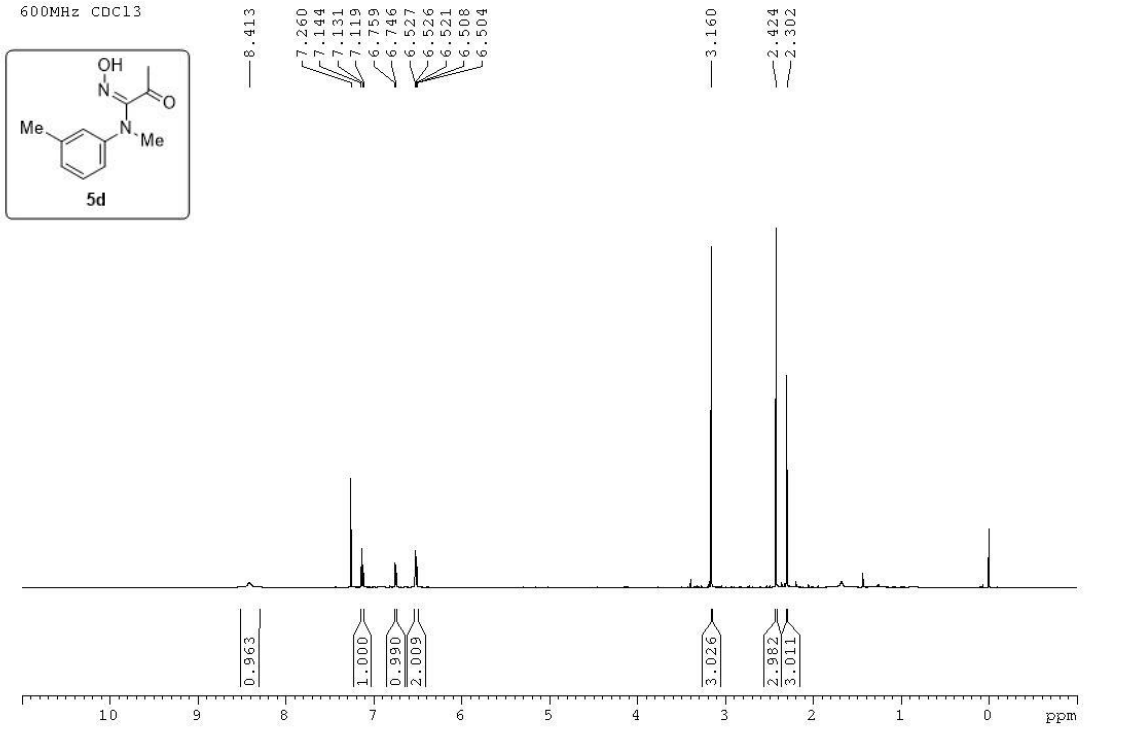


150MHz CDCl3




600MHz CDCl3
8.402
7.267
7.265
7.263
7.262
7.260
7.253
7.240
6.944
6.932
6.920
6.715
6.703
3.177
3.175
2.429
2.428
OH
N
O
N
Me
5c
0.981
2.279
1.000
2.017
3.100
3.096
10
9
8
7
6
5
4
3
2
1
0
ppm


150MHz CDCl3
194.390
152.524
145.323
129.287
121.223
115.596
77.358
77.146
76.935
36.627
27.042
OH
N
O
N
Me
5c
200
180
160
140
120
100
80
60
40
20
0
ppm


600MHz CDCl3
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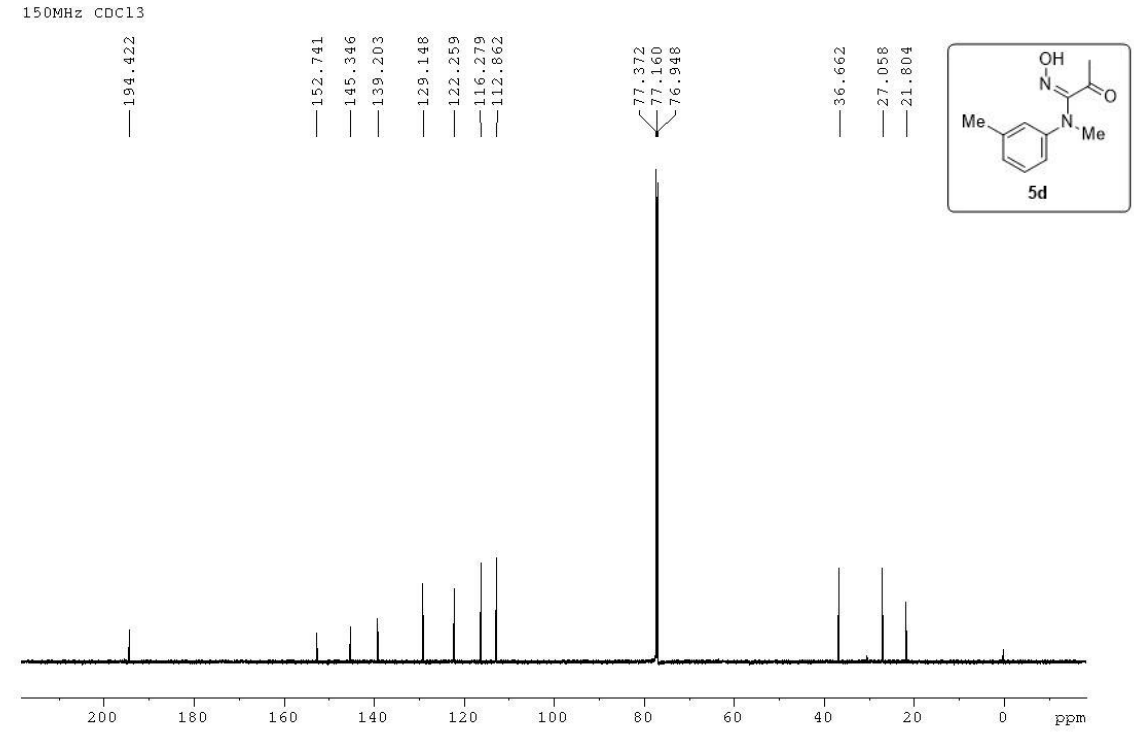
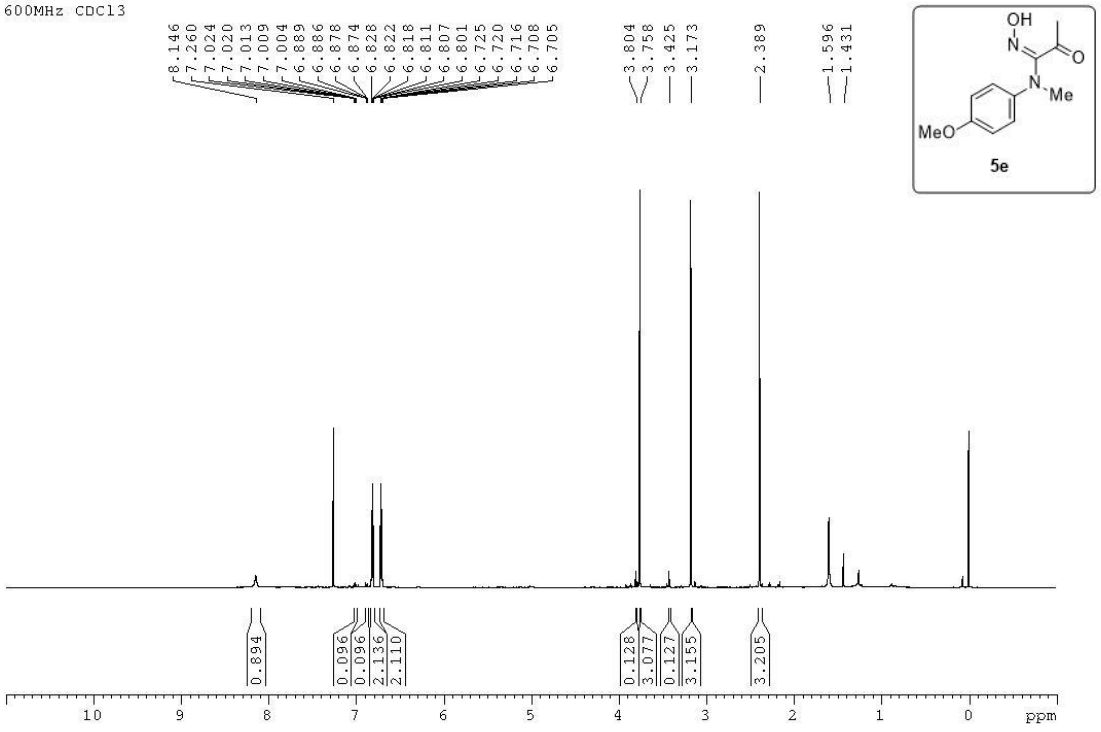
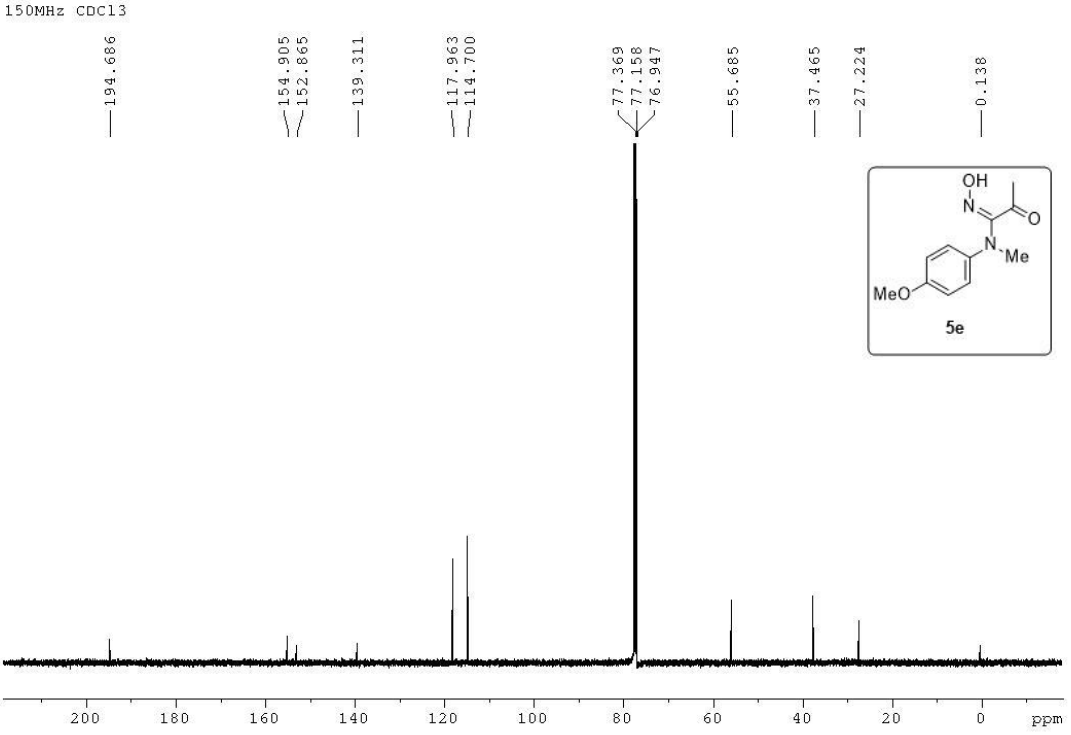
7.260
7.144
7.131
7.119
6.759
6.746
6.527
6.526
6.521
6.508
6.504
3.160
2.424
2.302
OH
N
O
Me
N
Me
5d
0.963
1.000
0.990
2.009
3.026
2.982
3.011
10
9
8
7
6
5
4
3
2
1
0
ppm


150MHz CDCl3
194.422
152.741
145.346
139.203
129.148
122.259
116.279
112.862
77.372
77.160
76.948
36.662
27.058
21.804
OH
N
O
Me
N
Me
5d
200
180
160
140
120
100
80
60
40
20
0
ppm


600MHz CDCl3
8.146
7.260
7.024
7.020
7.013
7.009
7.004
6.889
6.886
6.878
6.874
6.828
6.822
6.818
6.811
6.807
6.801
6.725
6.720
6.716
6.708
6.705
3.804
3.758
3.425
3.173
2.389
1.596
1.431
OH
N
O
N
Me
MeO
5e
0.894
0.096
0.096
2.136
2.110
0.128
3.077
0.127
3.155
3.205
10
9
8
7
6
5
4
3
2
1
0
ppm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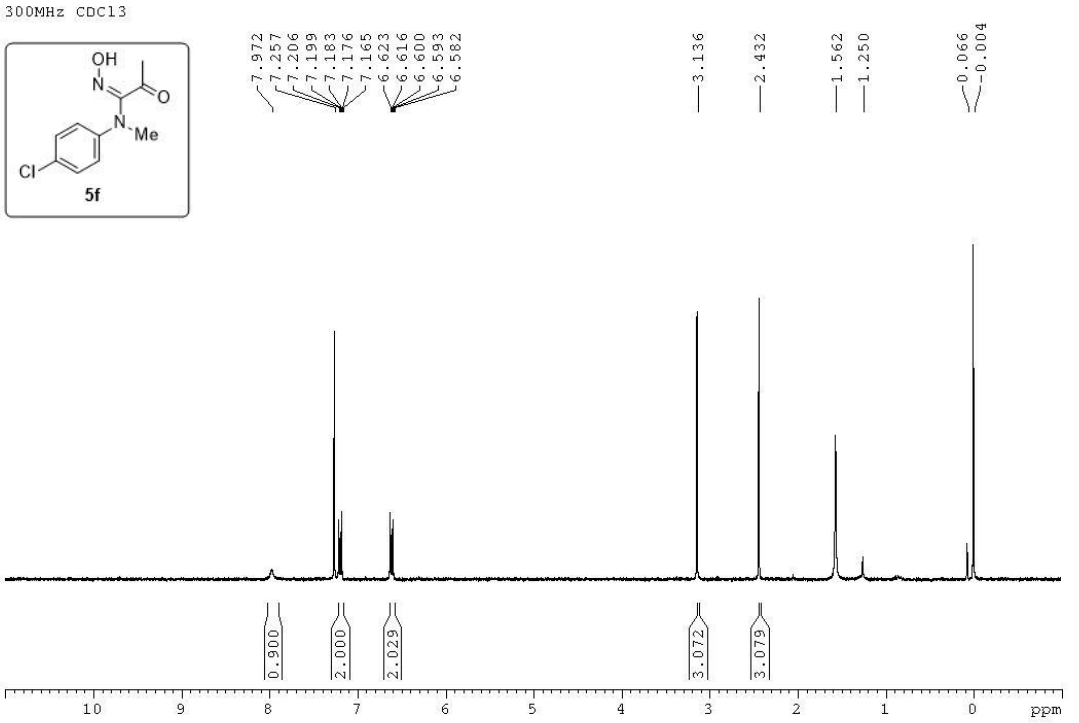
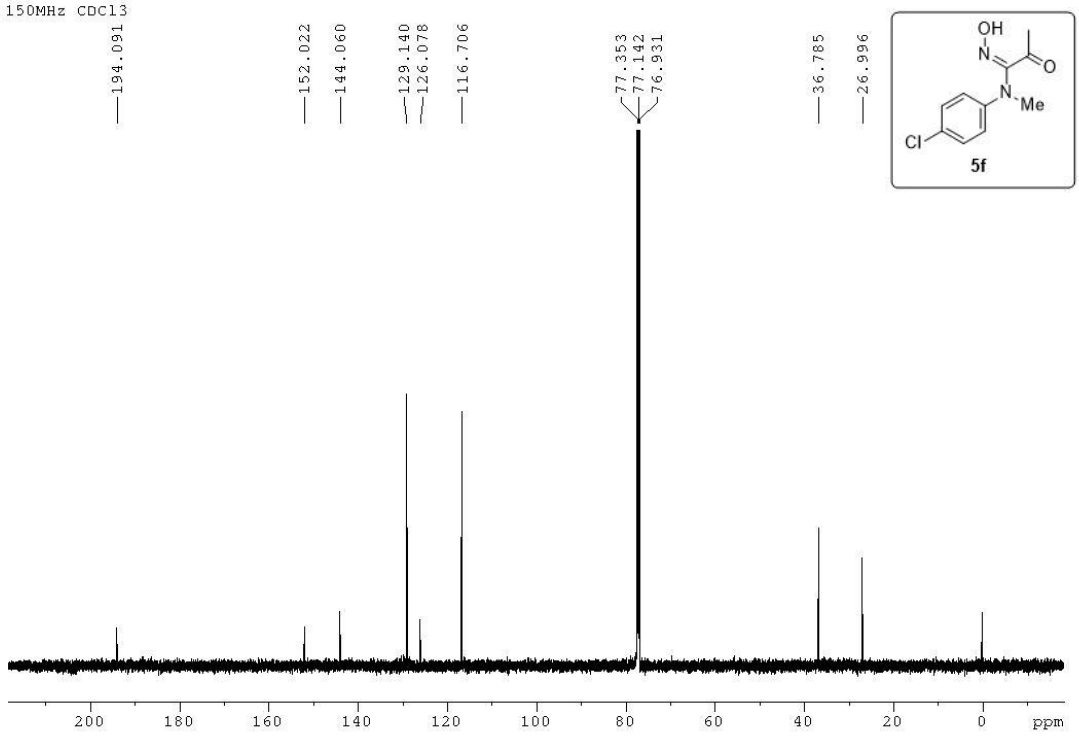
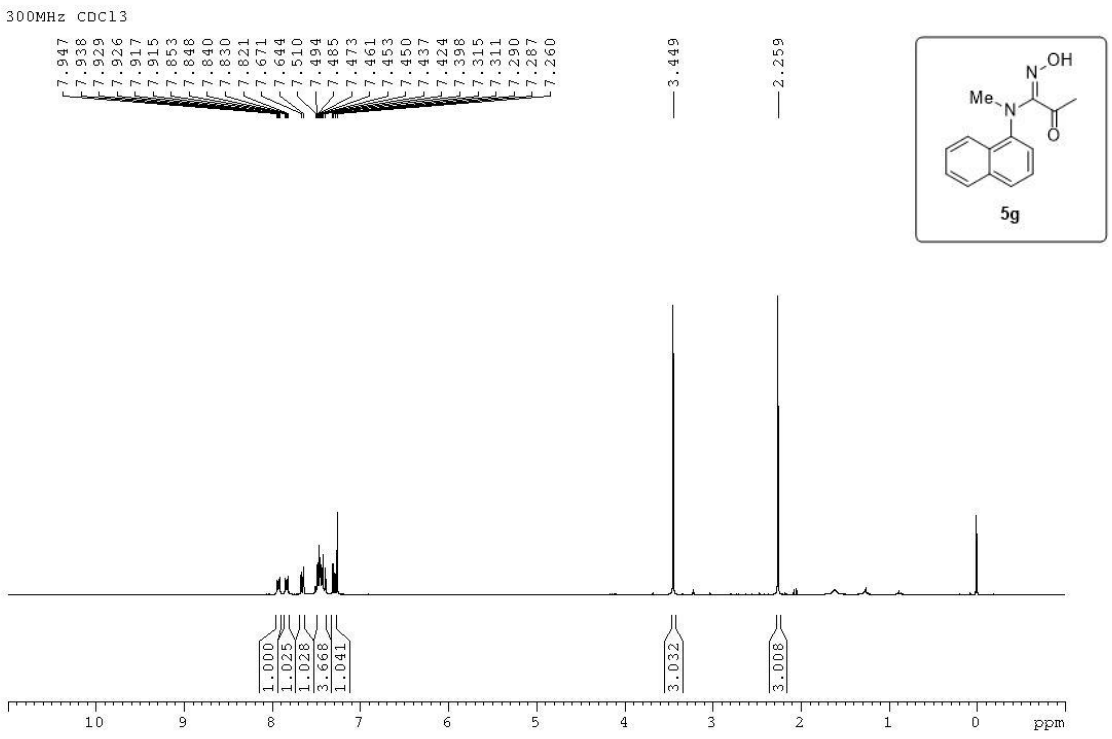
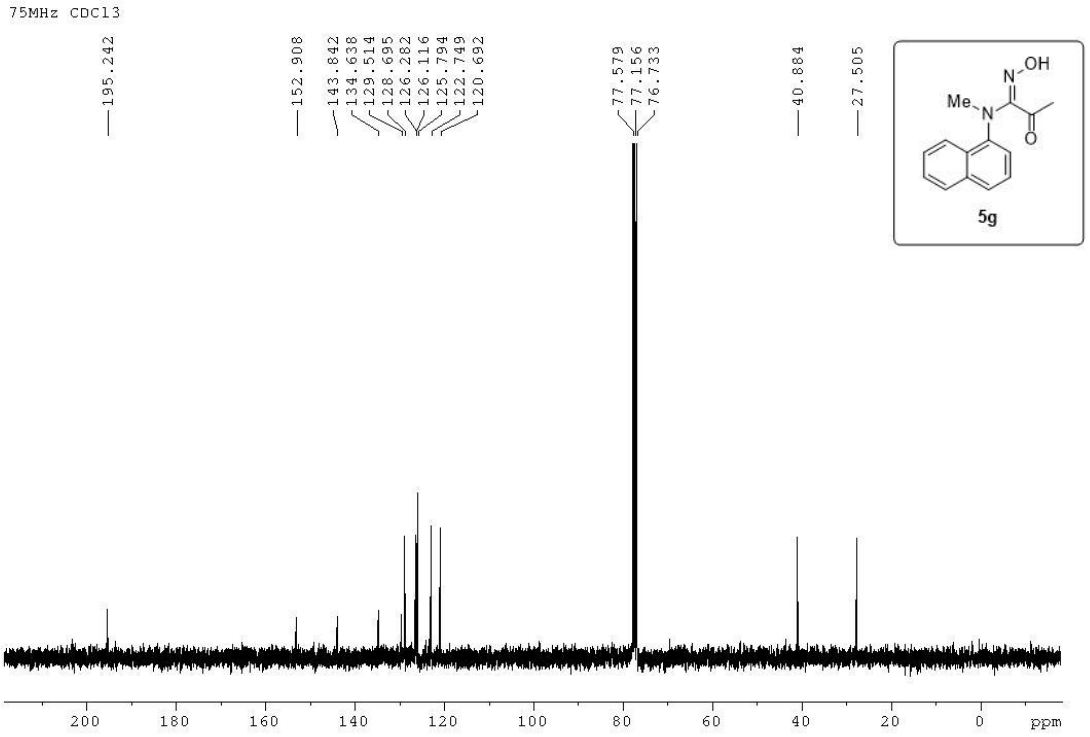
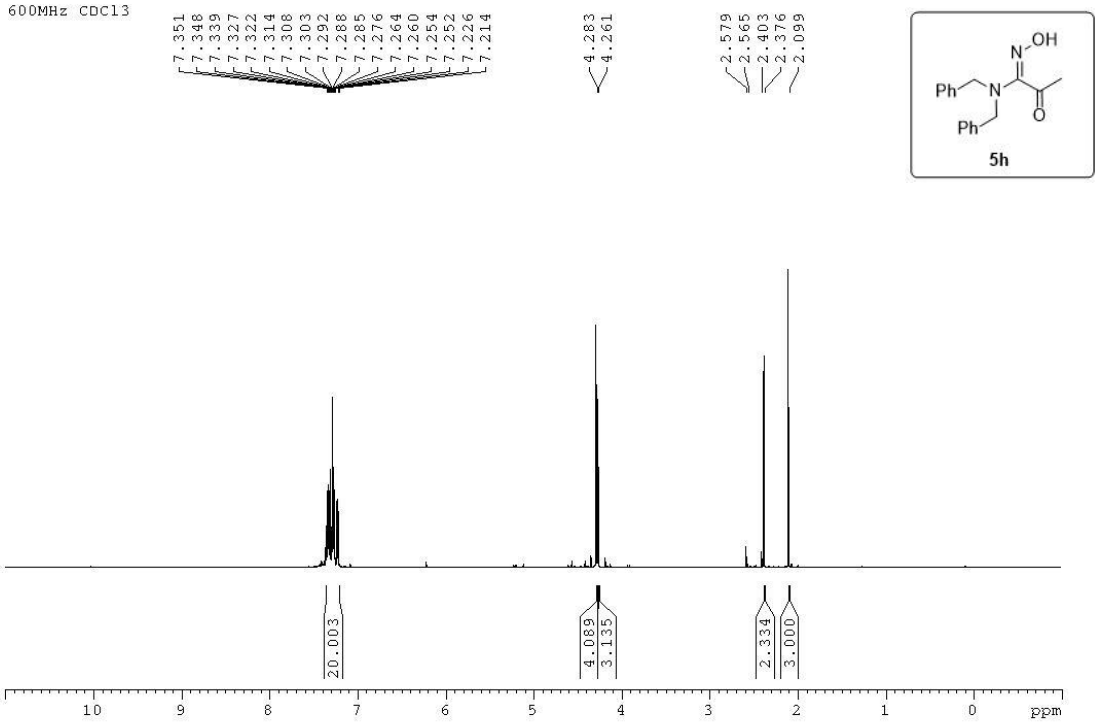
154.905
152.865
139.311
117.963
114.700
77.369
77.158
76.947
55.685
37.465
27.224
0.138
OH
N
O
N
Me
MeO
5e
200
180
160
140
120
100
80
60
40
20
0
ppm

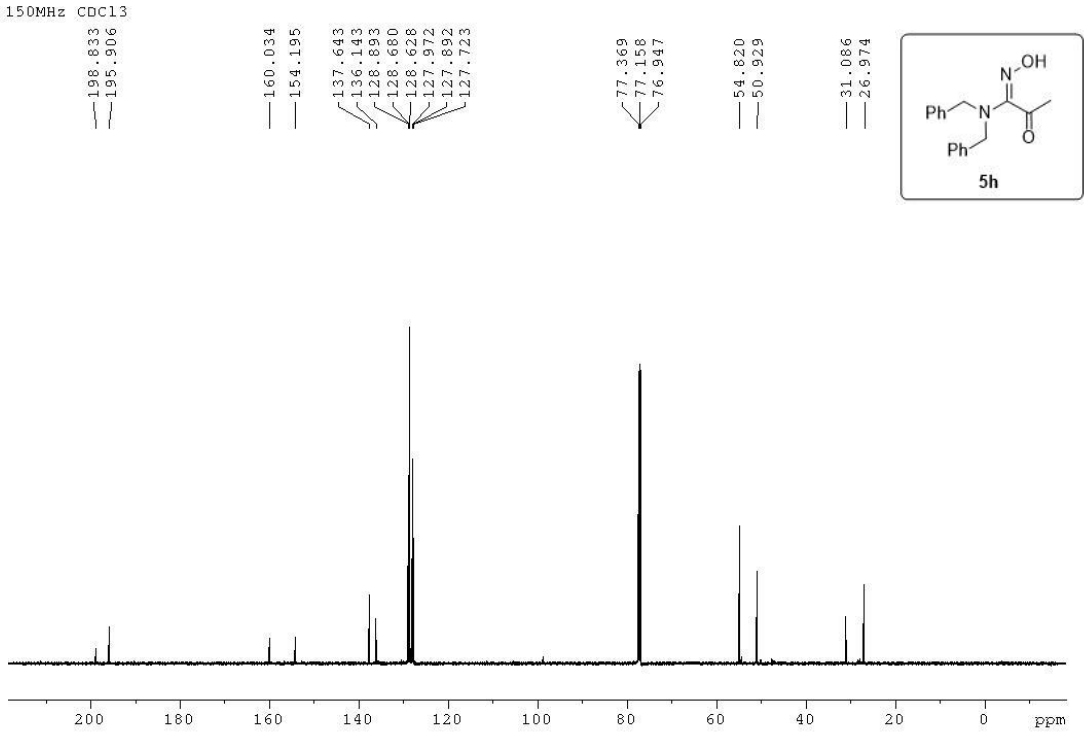

300MHz CDCl3
OH
N
O
N
Me
Cl
5f
7.972
7.257
7.206
7.199
7.183
7.176
7.165
6.623
6.616
6.600
6.593
6.582
3.136
2.432
1.562
1.250
0.066
-0.004
0.900
2.000
2.029
3.072
3.079
10
9
8
7
6
5
4
3
2
1
0
ppm

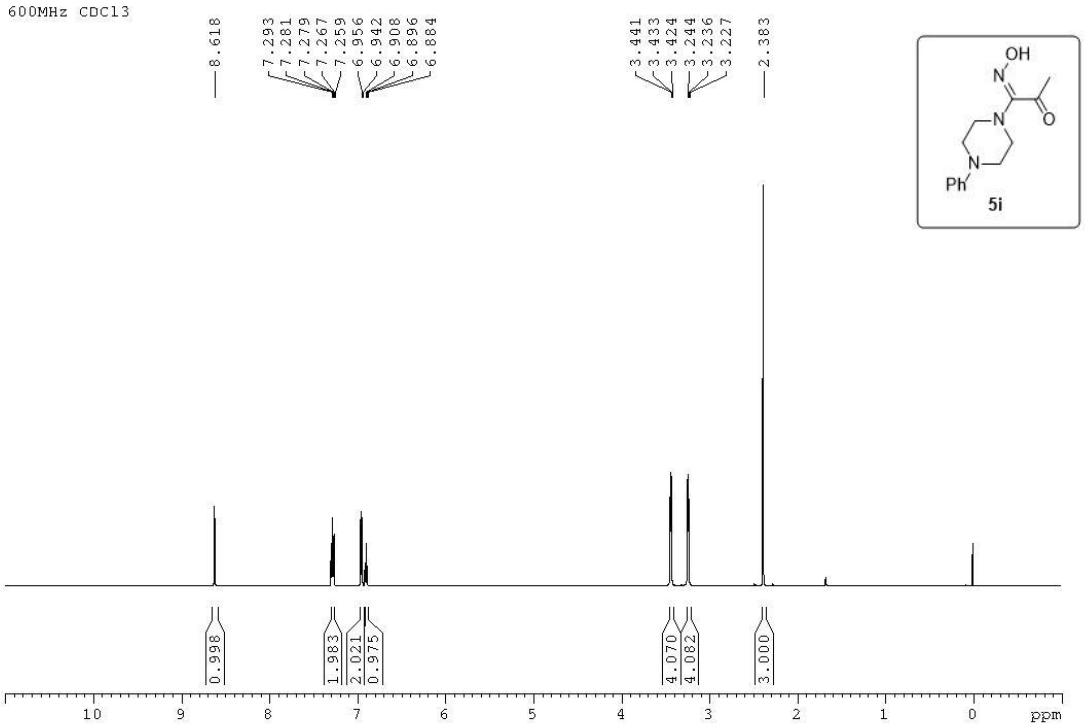

150MHz CDCl3
194.091
152.022
144.060
129.140
126.078
116.706
77.353
77.142
76.931
36.785
26.996
OH
N
O
N
Me
Cl
5f
200
180
160
140
120
100
80
60
40
20
0
ppm

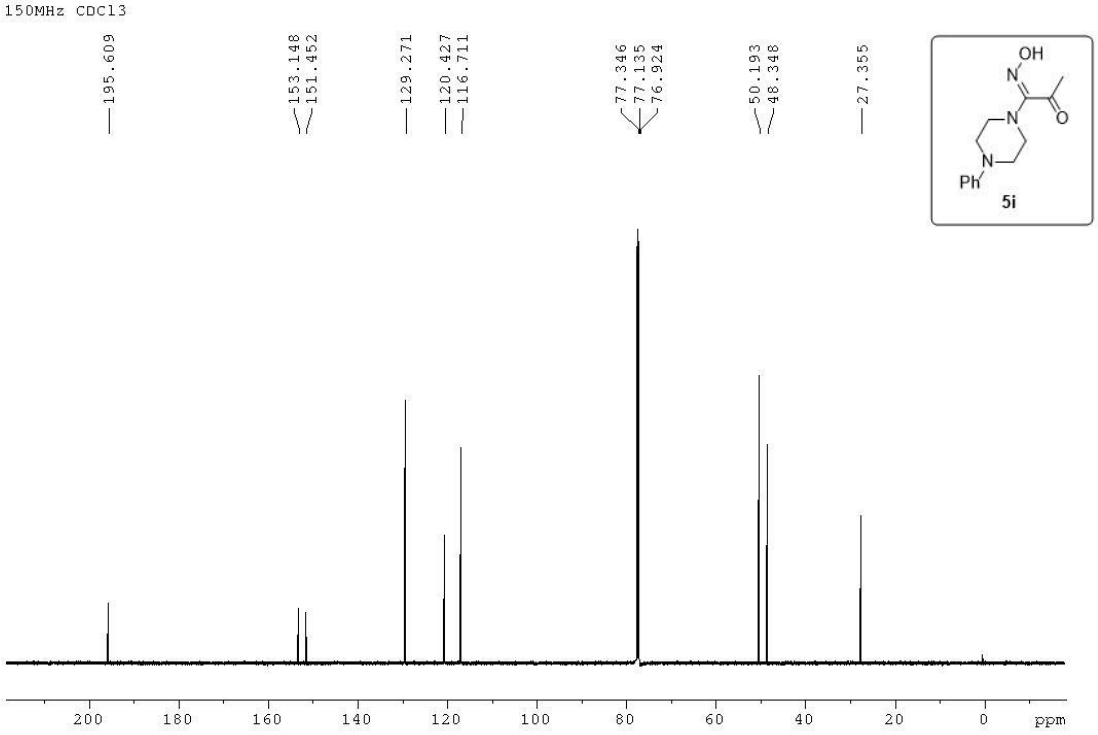

300MHz CDCl3
7.947
7.938
7.929
7.926
7.917
7.915
7.853
7.848
7.840
7.830
7.821
7.671
7.644
7.510
7.494
7.485
7.473
7.461
7.453
7.450
7.437
7.424
7.398
7.315
7.311
7.290
7.287
7.260
3.449
2.259
1.000
1.025
1.028
3.668
1.041
3.032
3.008
10
9
8
7
6
5
4
3
2
1
0
ppm
Me
N
OH
O
5g

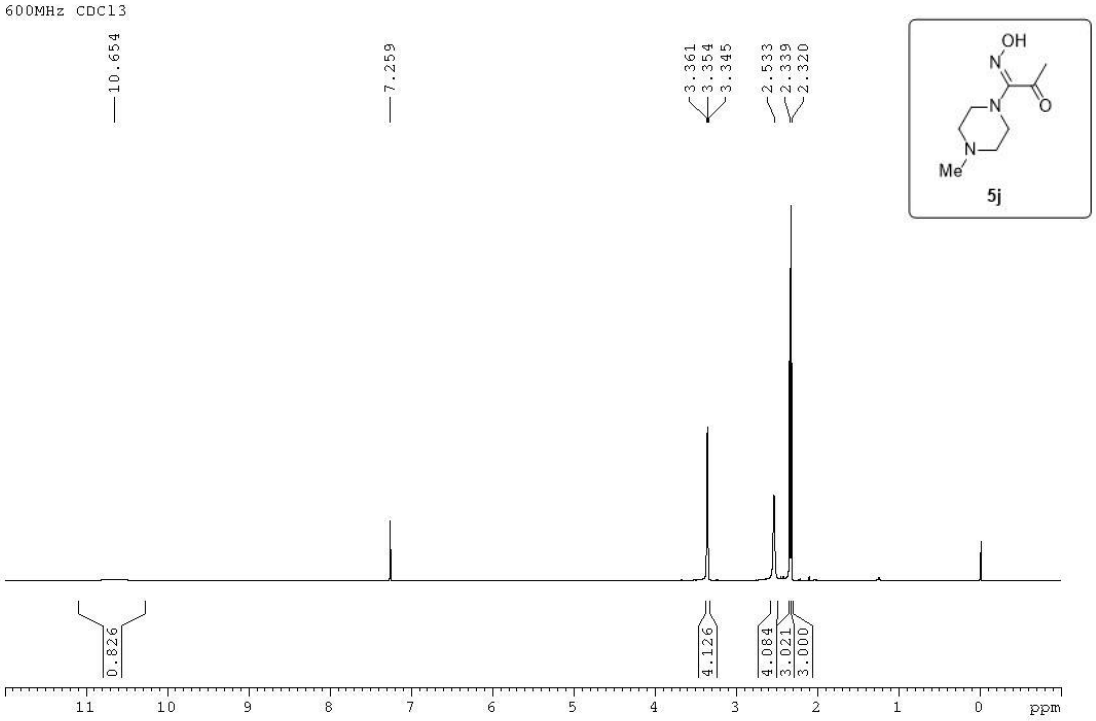

75MHz CDCl3
195.242
152.908
143.842
134.638
129.514
128.695
126.282
126.116
125.794
122.749
120.692
77.579
77.156
76.733
40.884
27.505
200
180
160
140
120
100
80
60
40
20
0
ppm
Me
N
OH
O
5g

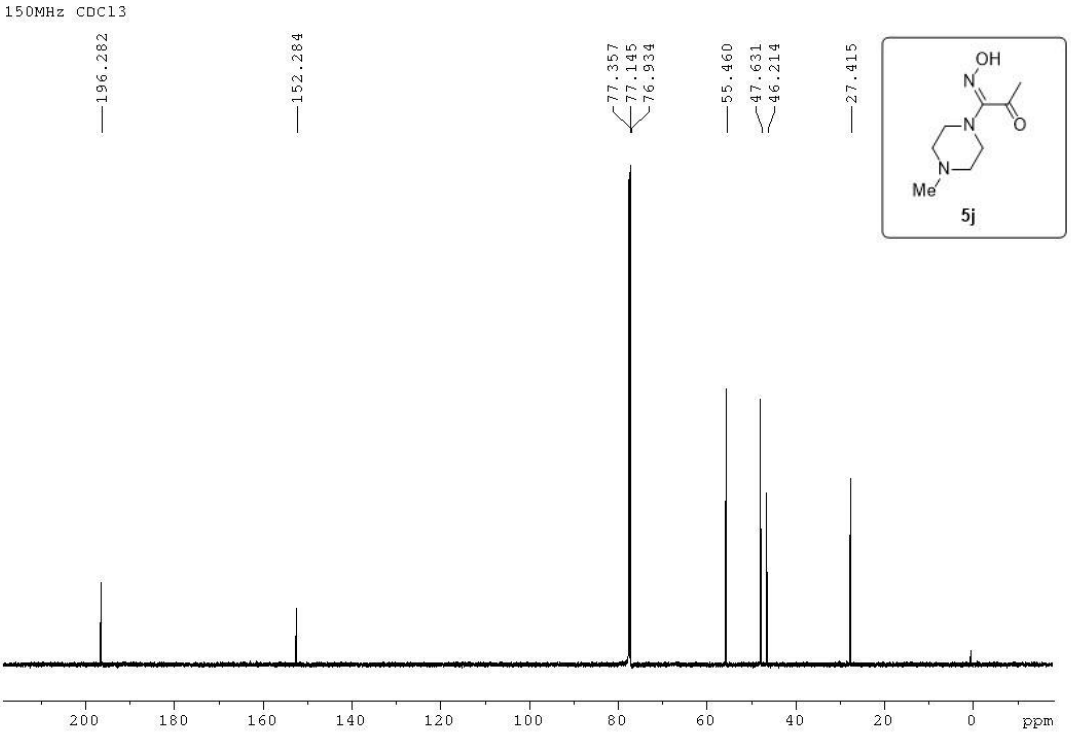

600MHz CDCl3
7.351
7.348
7.339
7.327
7.322
7.314
7.308
7.303
7.292
7.288
7.285
7.276
7.264
7.260
7.254
7.252
7.226
7.214
4.283
4.261
2.579
2.565
2.403
2.376
2.099
Ph
N
OH
O
Ph
5h
20.003
4.089
3.135
2.334
3.000
10
9
8
7
6
5
4
3
2
1
0
ppm

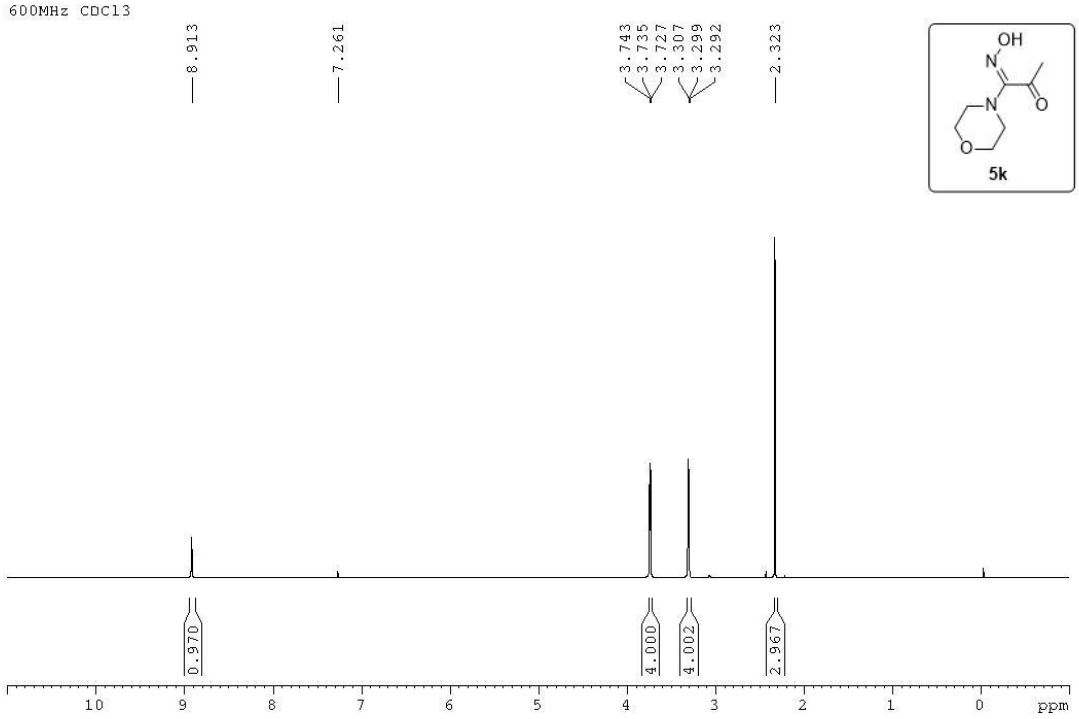

150MHz CDCl3
198.833
195.906
160.034
154.195
137.643
136.143
128.893
128.680
128.628
127.972
127.892
127.723
77.369
77.158
76.947
54.820
50.929
31.086
26.974
Ph
N
OH
O
Ph
5h
200
180
160
140
120
100
80
60
40
20
0
ppm

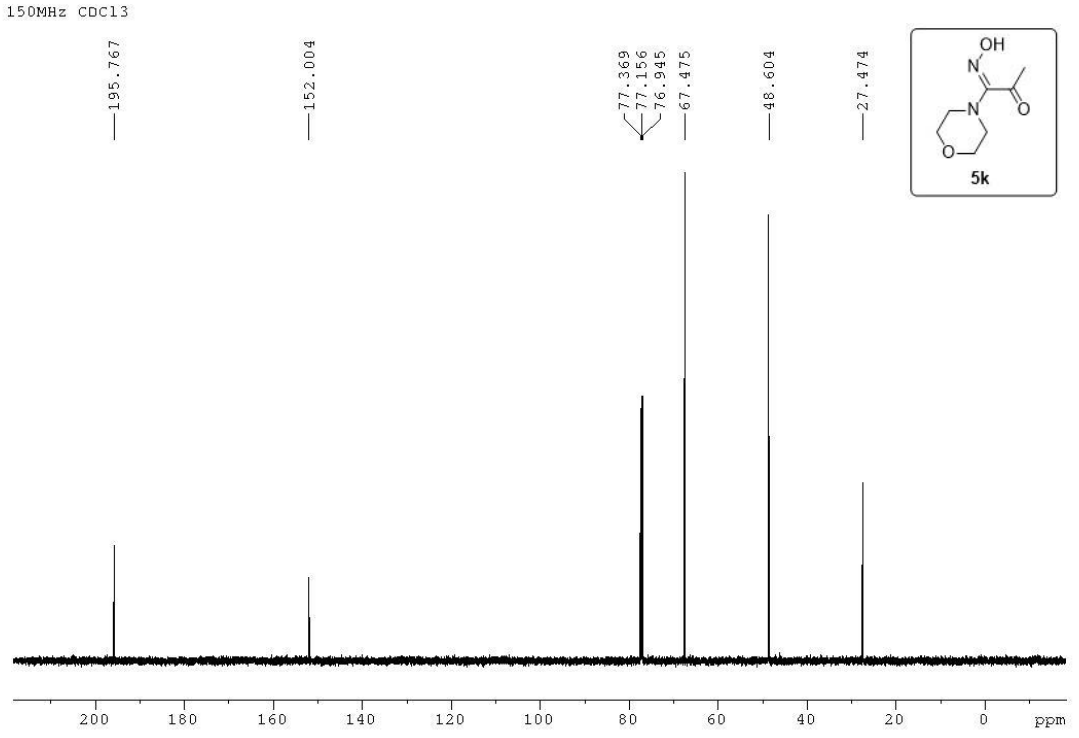

600MHz CDCl3
8.618
7.293
7.281
7.279
7.267
7.259
6.956
6.942
6.908
6.896
6.884
3.441
3.433
3.424
3.244
3.236
3.227
2.383
0.998
1.983
2.021
0.975
4.070
4.082
3.000
10
9
8
7
6
5
4
3
2
1
0
ppm
OH
N
O
N
N
Ph
5i


150MHz CDCl3
195.609
153.148
151.452
129.271
120.427
116.711
77.346
77.135
76.924
50.193
48.348
27.355
200
180
160
140
120
100
80
60
40
20
0
ppm
OH
N
O
N
N
Ph
5i


600MHz CDCl3
10.654
7.259
3.361
3.354
3.345
2.533
2.339
2.320
OH
N
N
O
N
Me
5j
0.826
4.126
4.084
3.021
3.000
11
10
9
8
7
6
5
4
3
2
1
0
ppm


150MHz CDCl3
196.282
152.284
77.357
77.145
76.934
55.460
47.631
46.214
27.415
OH
N
N
O
N
Me
5j
200
180
160
140
120
100
80
60
40
20
0
ppm


600MHz CDCl3
8.913
7.261
3.743
3.735
3.727
3.307
3.299
3.292
2.323
0.970
4.000
4.002
2.967
10
9
8
7
6
5
4
3
2
1
0
ppm
OH
N
O
N
O
5k


150MHz CDCl3
195.767
152.004
77.369
77.156
76.945
67.475
48.604
27.474
200
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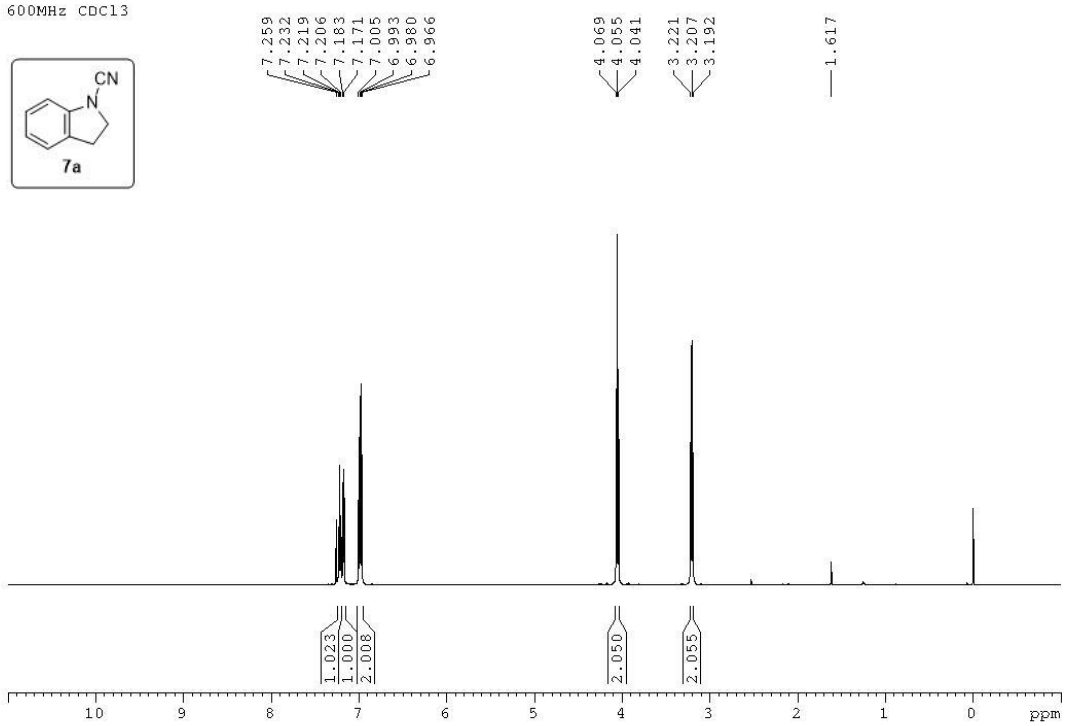
160
140
120
100
80
60
40
20
0
ppm
OH
N
O
N
O
5k


600MHz CDCl3
7.259
7.232
7.219
7.206
7.183
7.171
7.005
6.993
6.980
6.966
4.069
4.055
4.041
3.221
3.207
3.192
1.617
CN
N
7a
1.023
1.000
2.008
2.050
2.055
10
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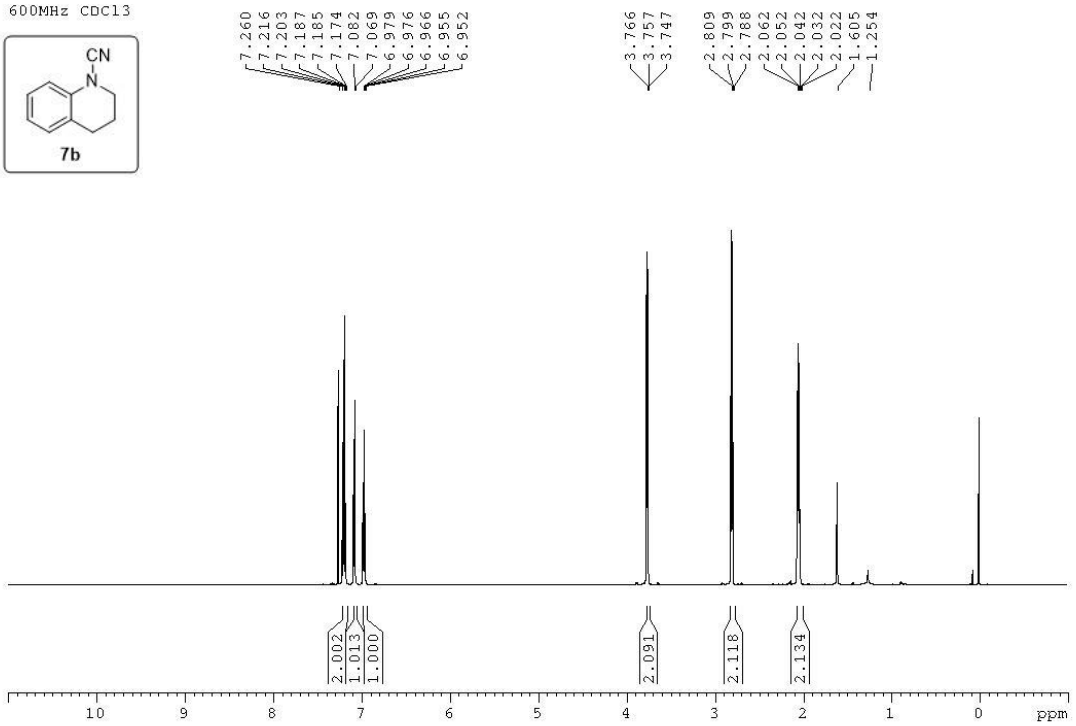
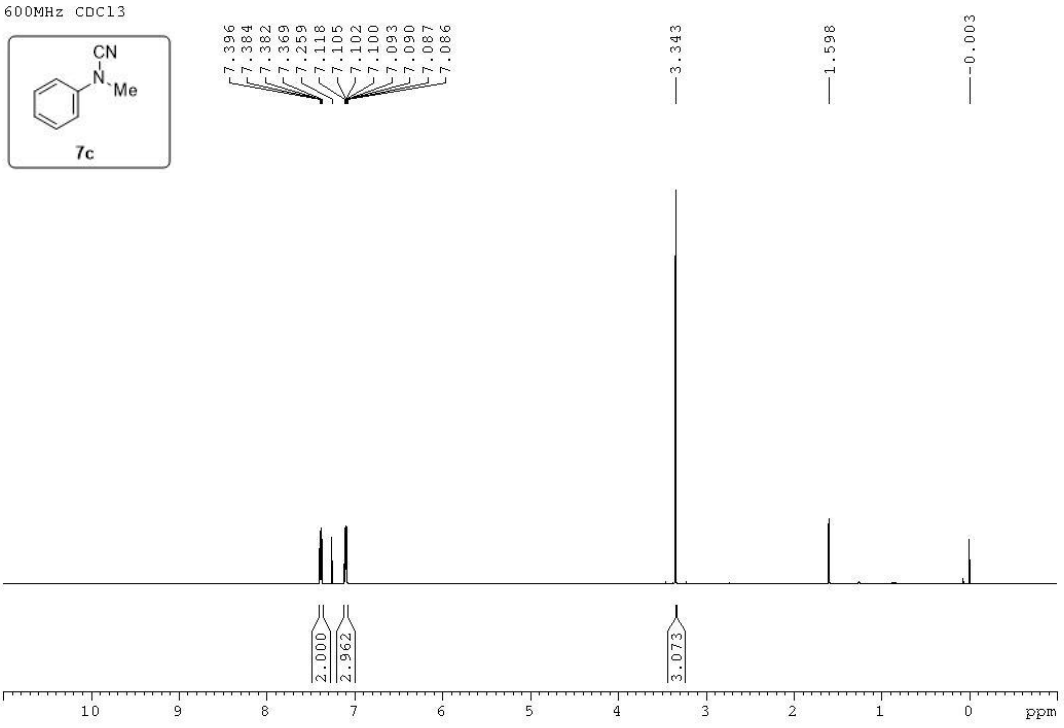
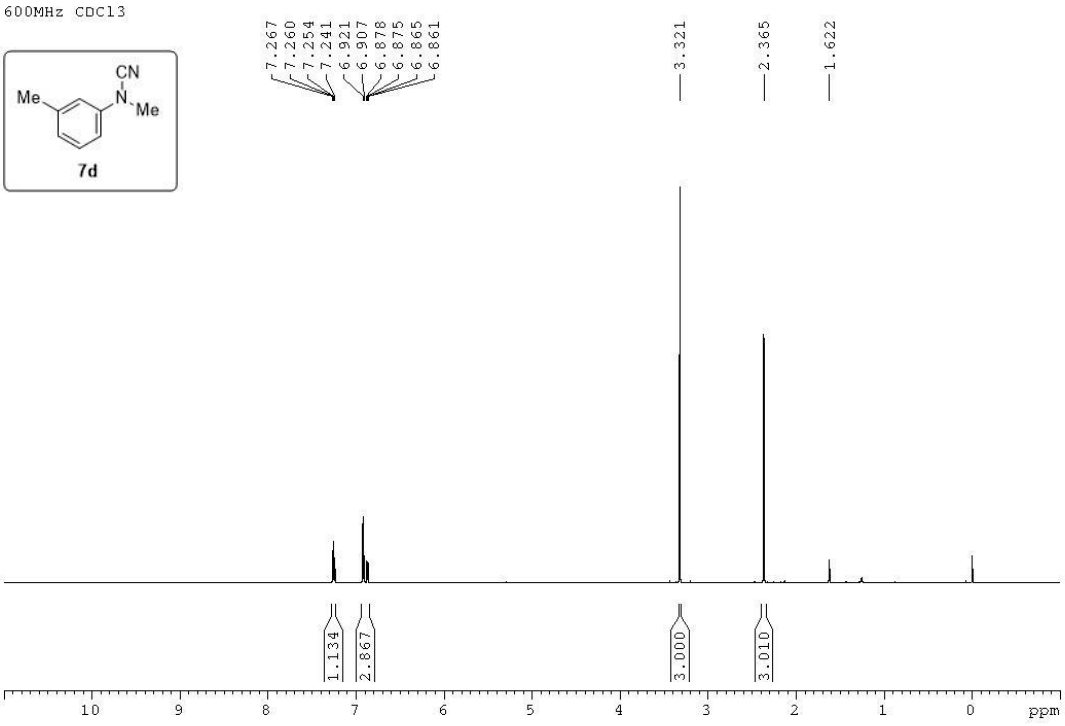
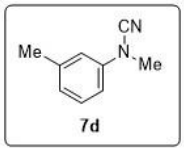
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
7.260
7.216
7.203
7.187
7.185
7.174
7.082
7.069
6.979
6.976
6.966
6.955
6.952
3.766
3.757
3.747
2.809
2.799
2.788
2.062
2.052
2.042
2.032
2.022
1.605
1.254
CN
N
7b
2.002
1.013
1.000
2.091
2.118
2.134
10
9
8
7
6
5
4
3
2
1
0
ppm


600MHz CDCl3
CN
N
Me
7c
7.396
7.384
7.382
7.369
7.259
7.118
7.105
7.102
7.100
7.093
7.090
7.087
7.086
3.343
1.598
0.003
2.000
2.962
3.073
10
9
8
7
6
5
4
3
2
1
0
ppm

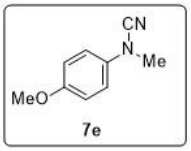

600MHz CDCl3
CN
N
Me
Me
7d
7.267
7.260
7.254
7.241
6.921
6.907
6.878
6.875
6.865
6.861
3.321
2.365
1.622
1.134
2.867
3.000
3.010
10
9
8
7
6
5
4
3
2
1
0
ppm

150MHz CDCl3



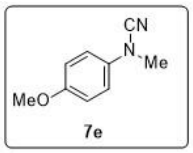
7d

600MHz CDCl3



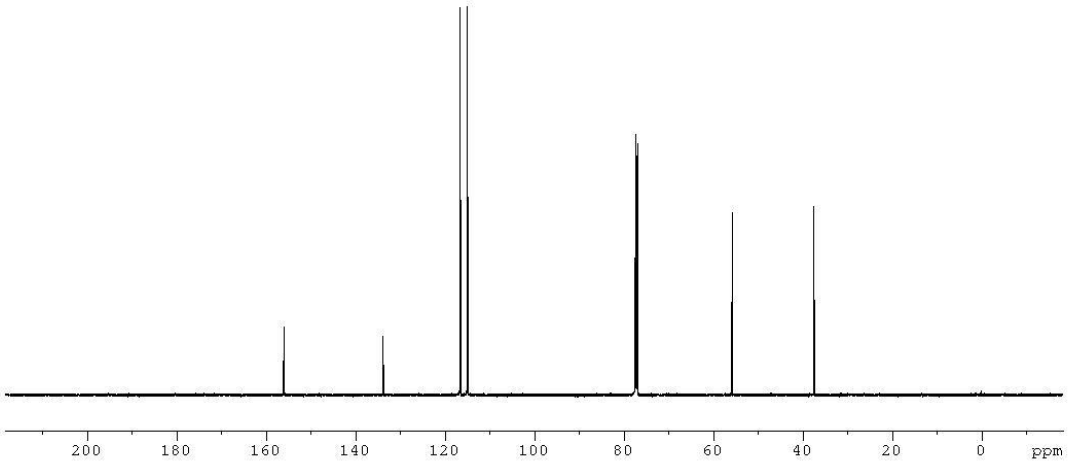
7e

150MHz CDCl3

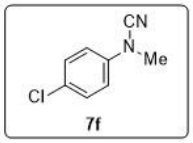


7e

156.060
133.886
116.619
114.990
114.958
77.365
77.153
76.941
55.705
37.420

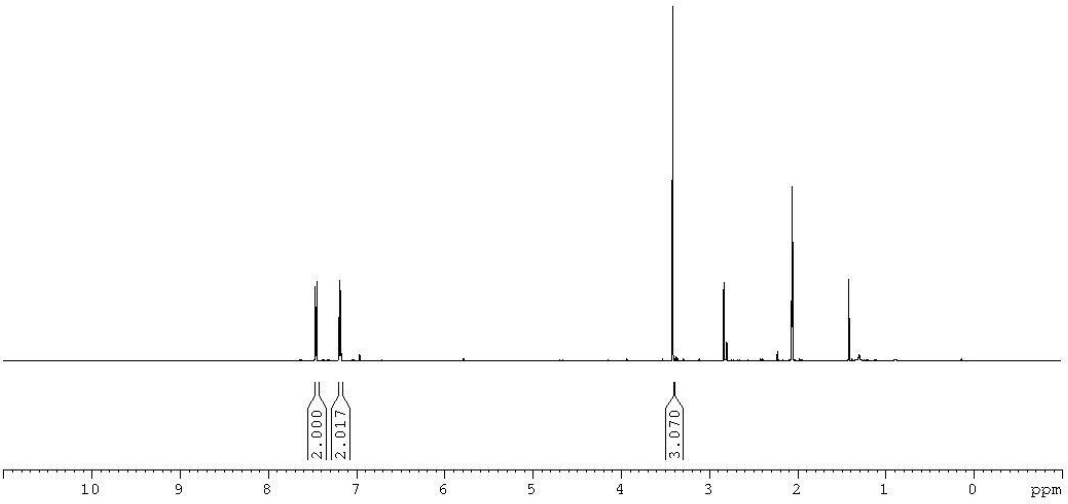


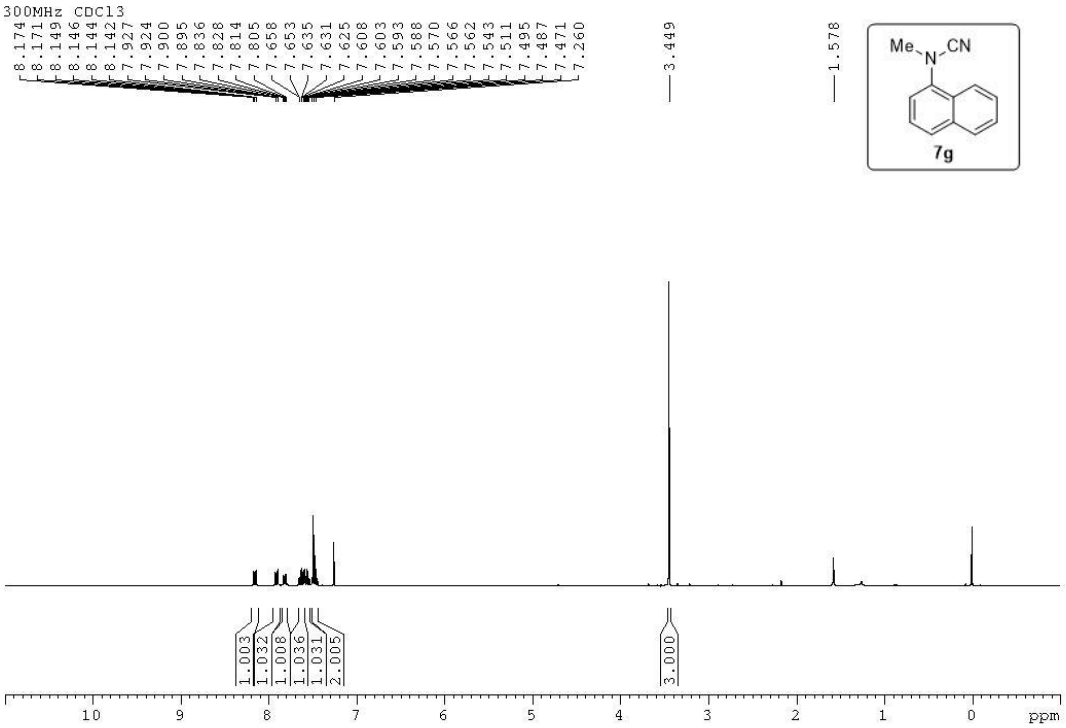
600MHz Acetone-d6

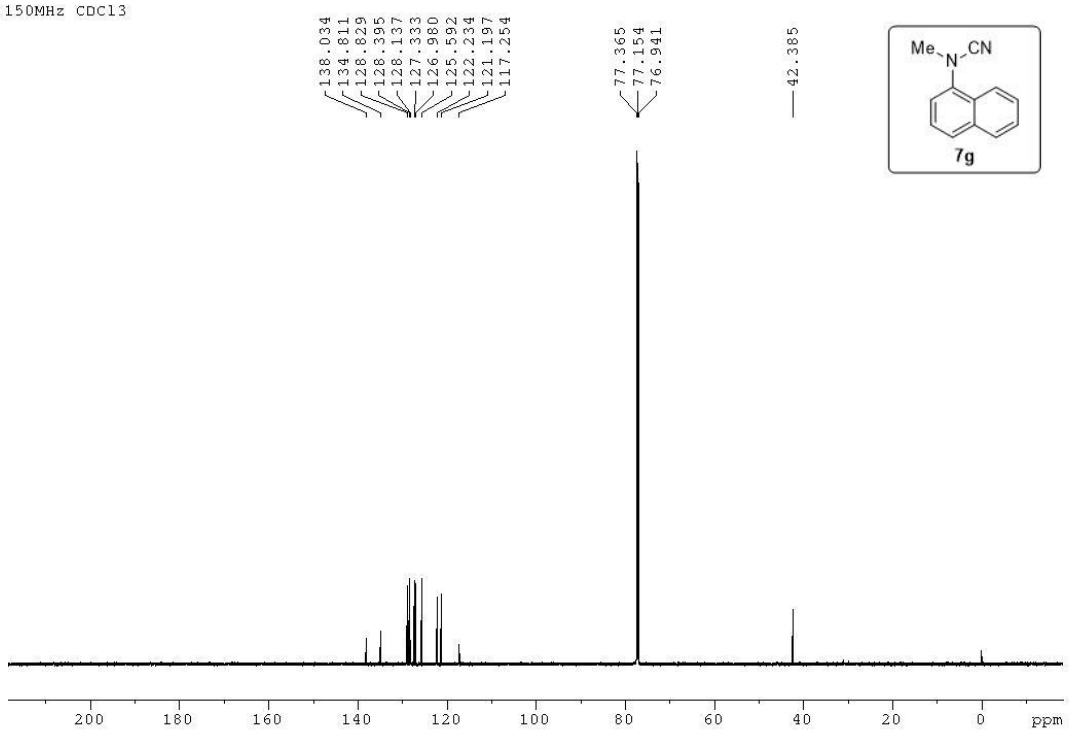


7f

7.457
7.442
7.184
7.169
3.403
2.824
2.791
2.057
2.053
2.049
2.046
2.042




300MHz CDCl3
8.174
8.171
8.149
8.146
8.144
8.142
7.927
7.924
7.900
7.895
7.836
7.828
7.814
7.805
7.658
7.653
7.635
7.631
7.625
7.608
7.603
7.593
7.588
7.570
7.566
7.562
7.543
7.511
7.495
7.487
7.471
7.260
3.449
1.578
Me
N
CN
7g
1.003
1.032
1.008
1.036
1.031
2.005
3.000
10
9
8
7
6
5
4
3
2
1
0
ppm


150MHz CDCl3
138.034
134.811
128.829
128.395
128.137
127.333
126.980
125.592
122.234
121.197
117.254
77.365
77.154
76.941
42.385
Me
N
CN
7g
200
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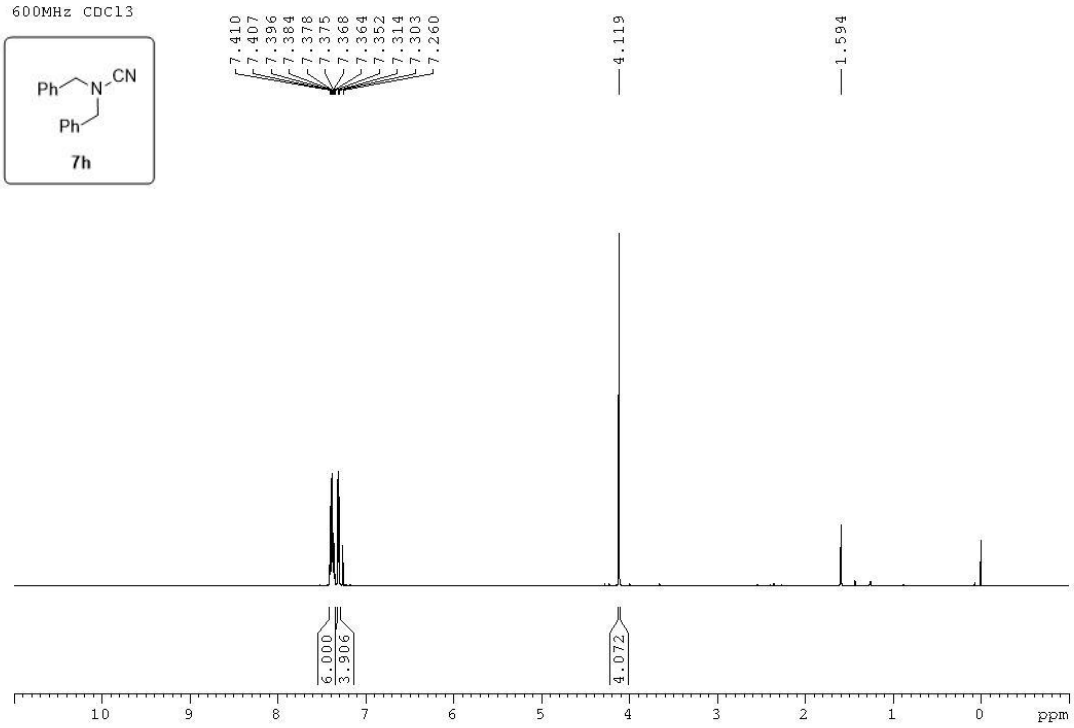
160
140
120
100
80
60
40
20
0
ppm


600MHz CDCl3
7h
7.410
7.407
7.396
7.384
7.378
7.375
7.368
7.364
7.352
7.314
7.303
7.260
4.119
1.594
6.000
3.906
4.072
10
9
8
7
6
5
4
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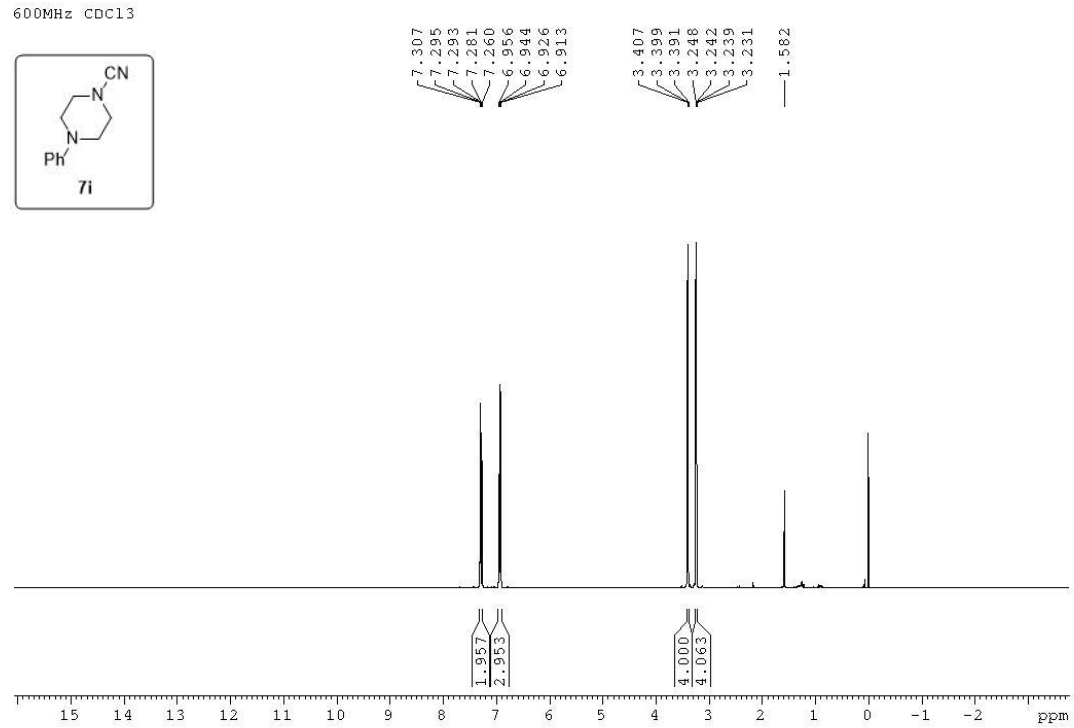
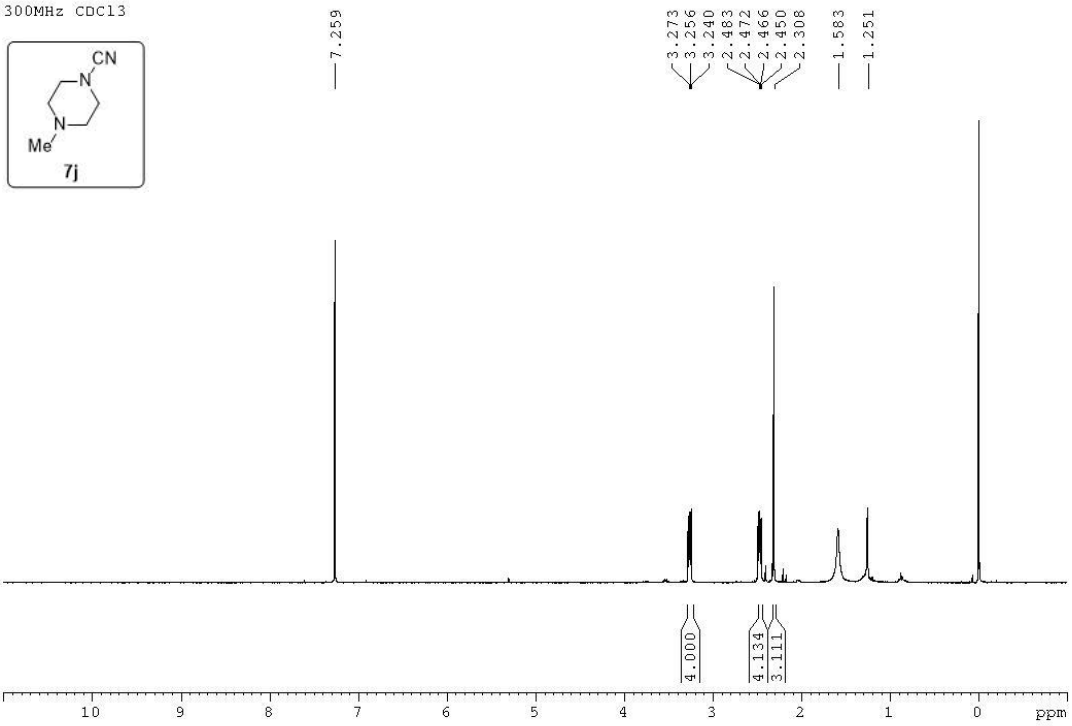
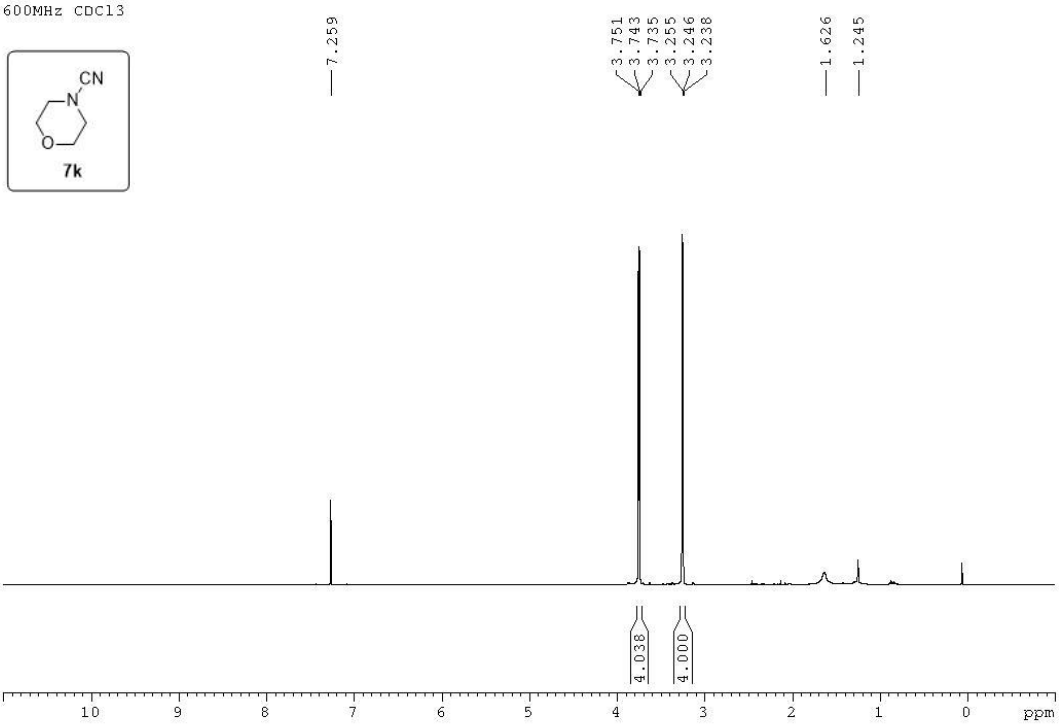
0
ppm


600MHz CDCl3
7i
7.307
7.295
7.293
7.281
7.260
6.956
6.944
6.926
6.913
3.407
3.399
3.391
3.248
3.242
3.239
3.231
1.582
1.957
2.953
4.000
4.063
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
ppm


300MHz CDCl3
CN
N
N
Me
7j
7.259
3.273
3.256
3.240
2.483
2.472
2.466
2.450
2.308
1.583
1.251
4.000
4.134
3.111
10
9
8
7
6
5
4
3
2
1
0
ppm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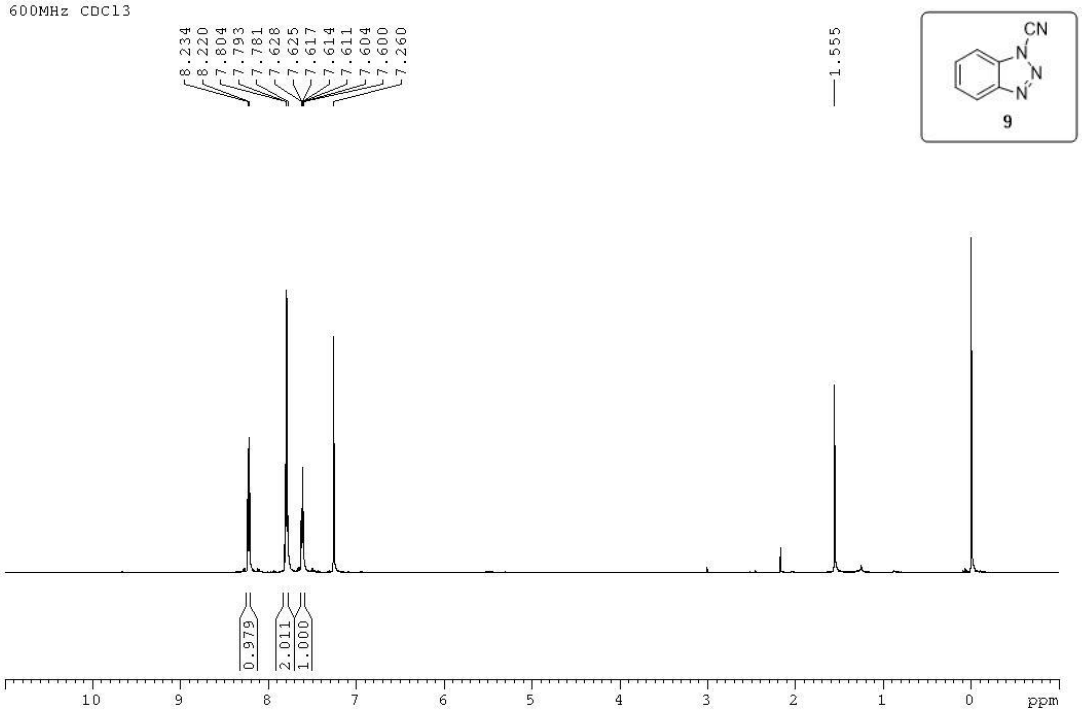
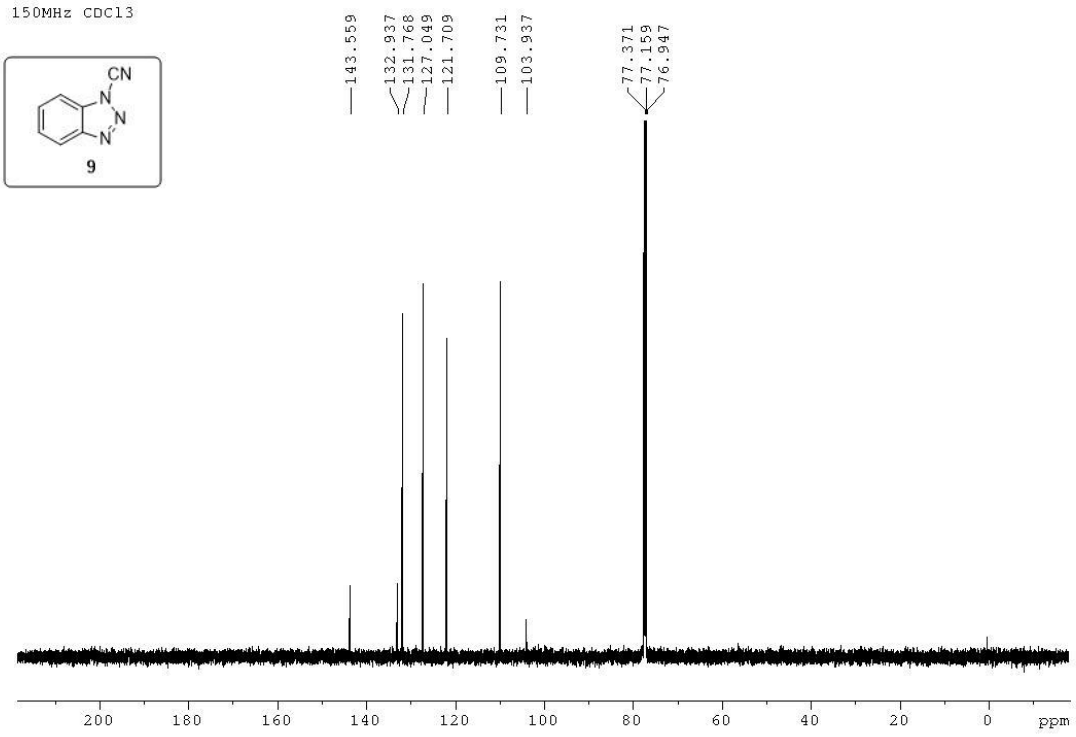
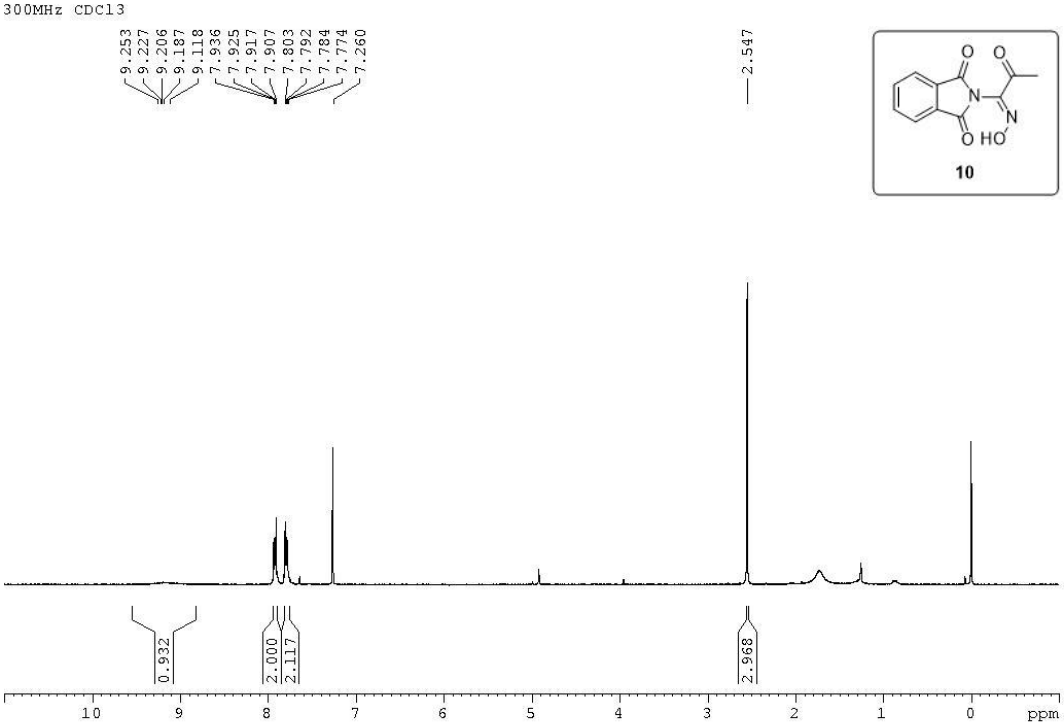
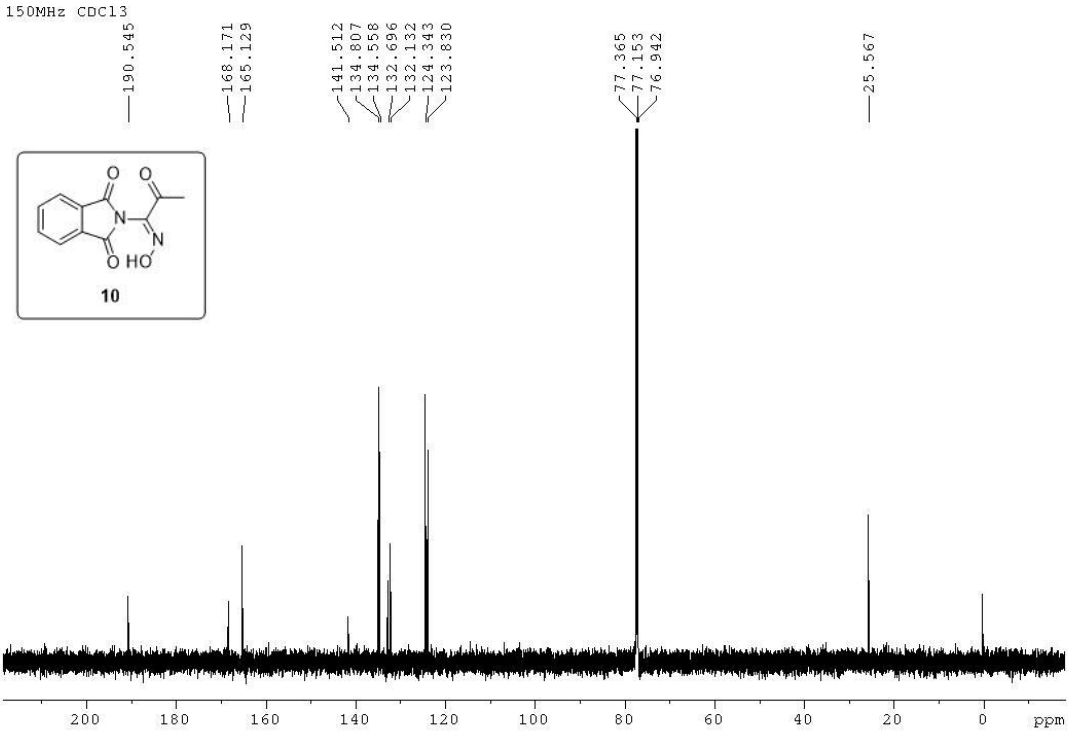
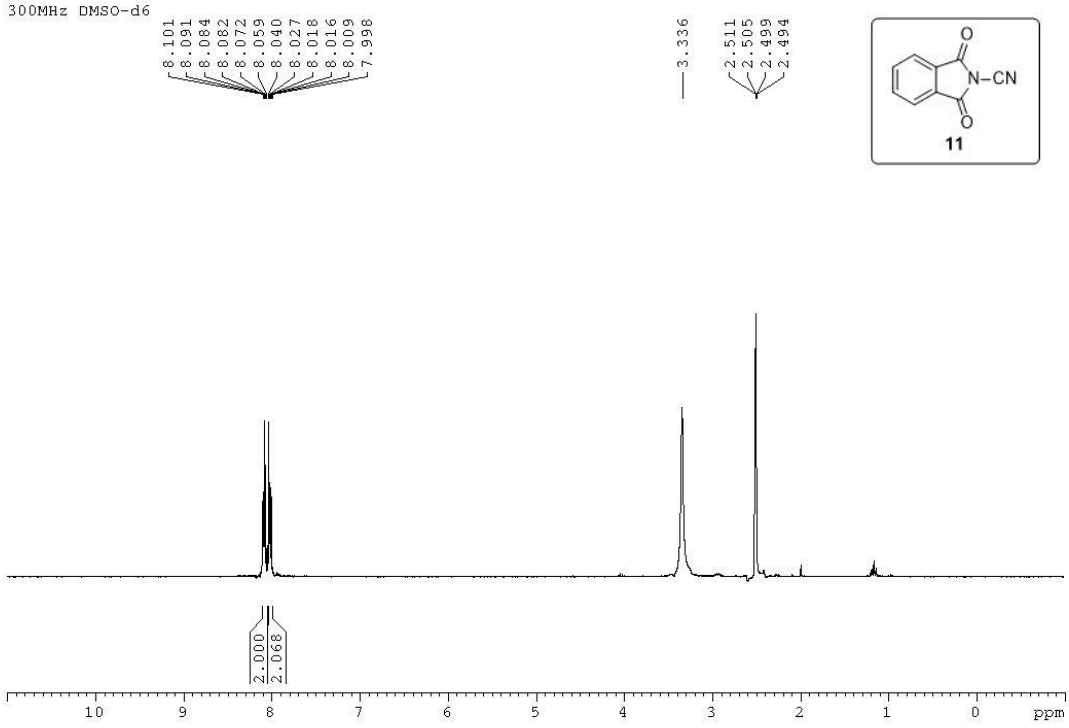
CN
N
O
7k
7.259
3.751
3.743
3.735
3.255
3.246
3.238
1.626
1.245
4.038
4.000
10
9
8
7
6
5
4
3
2
1
0
ppm

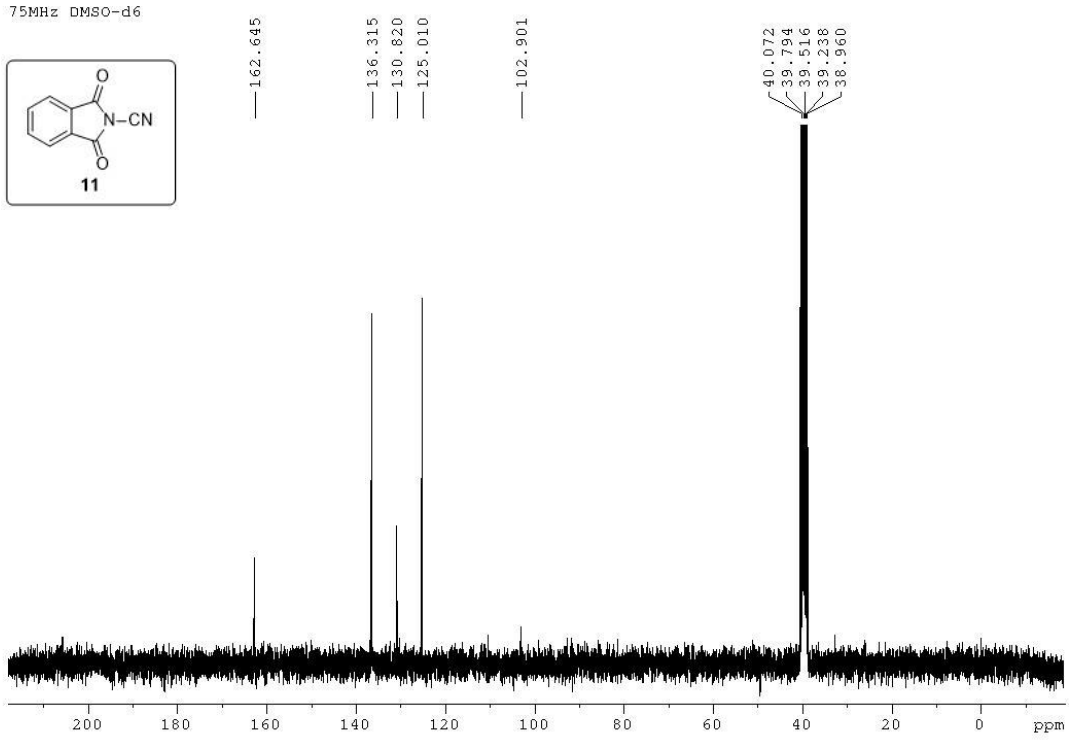

600MHz CDCl3
8.234
8.220
7.804
7.793
7.781
7.628
7.625
7.617
7.614
7.611
7.604
7.600
7.260
1.555
CN
N
N
N
9
0.979
2.011
1.000
10
9
8
7
6
5
4
3
2
1
0
ppm

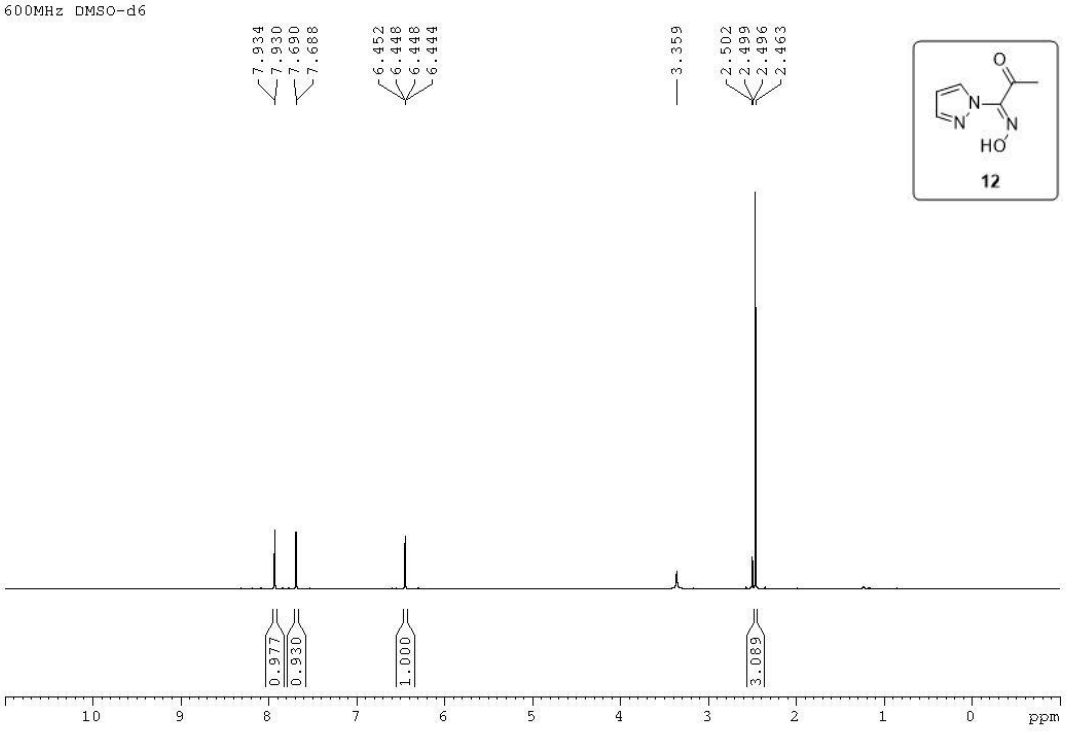

150MHz CDCl3
CN
N
N
N
9
143.559
132.937
131.768
127.049
121.709
109.731
103.937
77.371
77.159
76.947
200
180
160
140
120
100
80
60
40
20
0
ppm

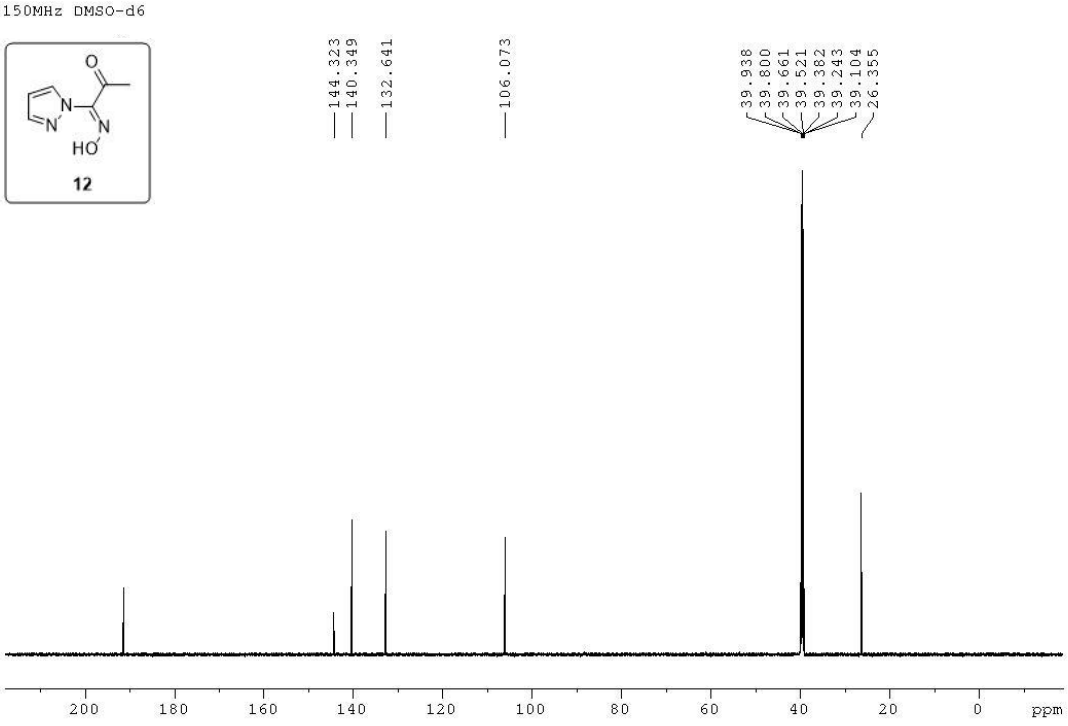

300MHz CDCl3
9.253
9.227
9.206
9.187
9.118
7.936
7.925
7.917
7.907
7.803
7.792
7.784
7.774
7.260
2.547
10
0.932
2.000
2.117
2.968
10
9
8
7
6
5
4
3
2
1
0
ppm

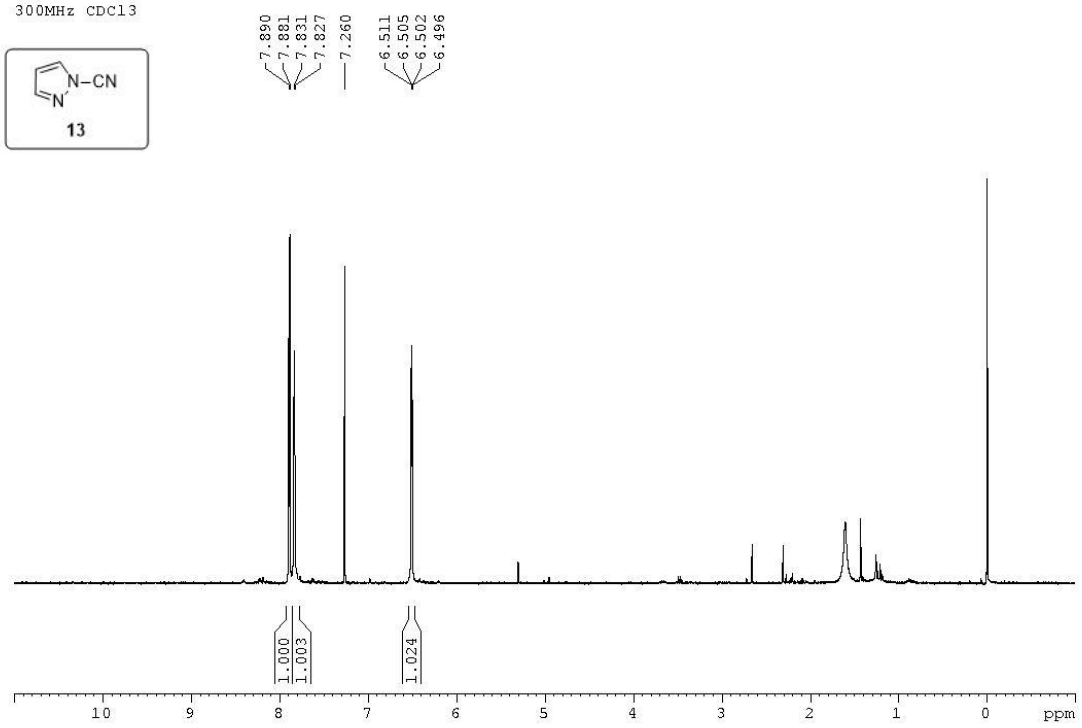

150MHz CDCl3
190.545
168.171
165.129
141.512
134.807
134.558
132.696
132.132
124.343
123.830
77.365
77.153
76.942
25.567
10
200
180
160
140
120
100
80
60
40
20
0
ppm

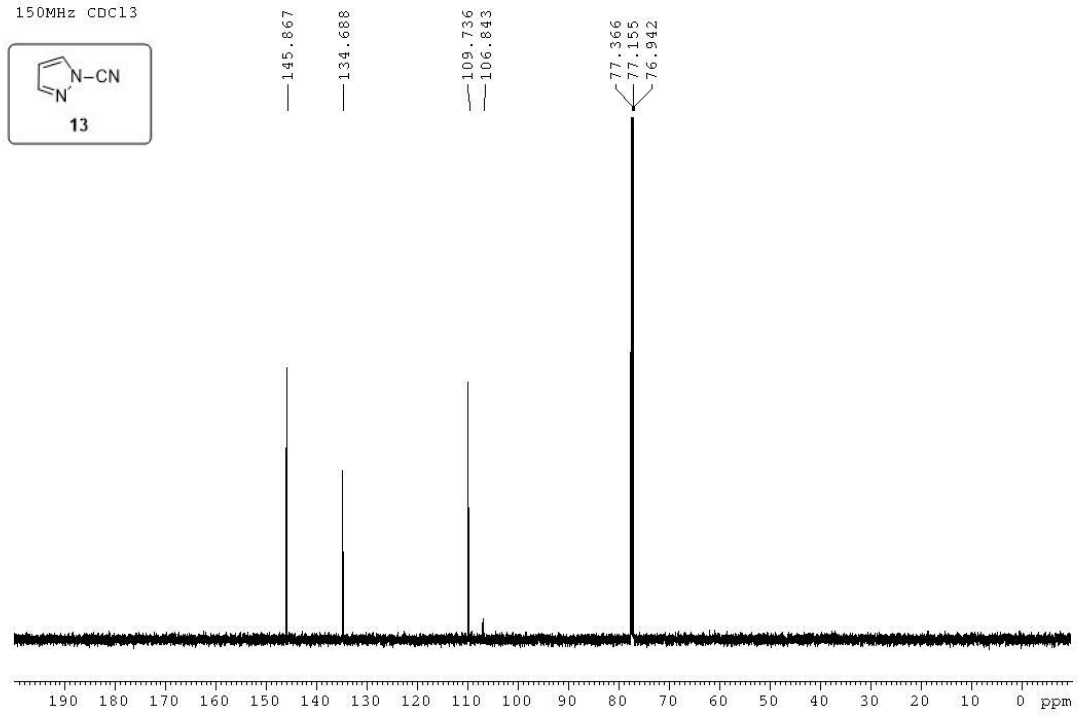

300MHz DMSO-d6
8.101
8.091
8.084
8.082
8.072
8.059
8.040
8.027
8.018
8.016
8.009
7.998
3.336
2.511
2.505
2.499
2.494
N–CN
11
2.000
2.068
10
9
8
7
6
5
4
3
2
1
0
ppm


75MHz DMSO-d6
162.645
136.315
130.820
125.010
102.901
40.072
39.794
39.516
39.238
38.960
N–CN
11
200
180
160
140
120
100
80
60
40
20
0
ppm


600MHz DMSO-d6
7.934
7.930
7.690
7.688
6.452
6.448
6.448
6.444
3.359
2.502
2.499
2.496
2.463
12
0.977
0.930
1.000
3.089
10
9
8
7
6
5
4
3
2
1
0
ppm


150MHz DMSO-d6
12
144.323
140.349
132.641
106.073
39.938
39.800
39.661
39.521
39.382
39.243
39.104
26.355
200
180
160
140
120
100
80
60
40
20
0
ppm


300MHz CDCl3
N–CN
13
7.890
7.881
7.831
7.827
7.260
6.511
6.505
6.502
6.496
1.000
1.003
1.024
10
9
8
7
6
5
4
3
2
1
0
ppm


150MHz CDCl3
N–CN
13
145.867
134.688
109.736
106.843
77.366
77.155
76.942
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

6. References

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