Electronic Supplementary Information(ESI)

"Triflic Acid Catalyzed Metal-Free Synthesis of (*E*)-2-Cyanoacrylamides and 3-Substituted Azetidine-2,4-diones"

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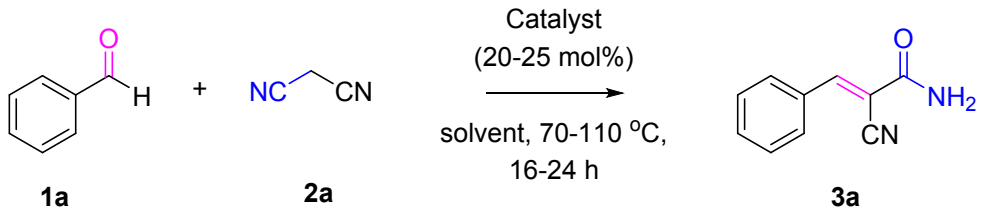
1. General information

Unless otherwise specified, all reactions were carried out under an open atmosphere in solvent at reflux condition and reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. All reagents and solvents were obtained from commercial suppliers and Aldrich, Merck Millipore, Alfa Aesar and Avra Synthesis. Aldehydes were purified either by distillation or washing with $NaHCO_3$ after dissolving in ether, prior to use and all AR grade solvents wereused without further purification.

Petroleum ether of boiling range 60–80 °C was used. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on AC-200, 400, 500 MHz NMR spectrometers. Deuterated solvent $CDCl_3$+CCl_4 (70:30) were used as internal standard and singlet at 96.1 ppm in ^{13}C NMR corresponds to carbon of CCl_4. The septet at 39.51 ppm in ^{13}C NMR corresponds to carbon of DMSO-D_6. HRMS data for all new compounds were recorded using Orbitrap mass analyzer associated with Accela 1250 pump. Purification was done using column chromatography (100-200 mesh). The reactions were monitored by TLC visualized by UV (254 nm) and/or with iodine. Coupling constants are given in hertz (Hz) and the classical abbreviations are used to describe the signal multiplicities.

2. Optimization study

Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

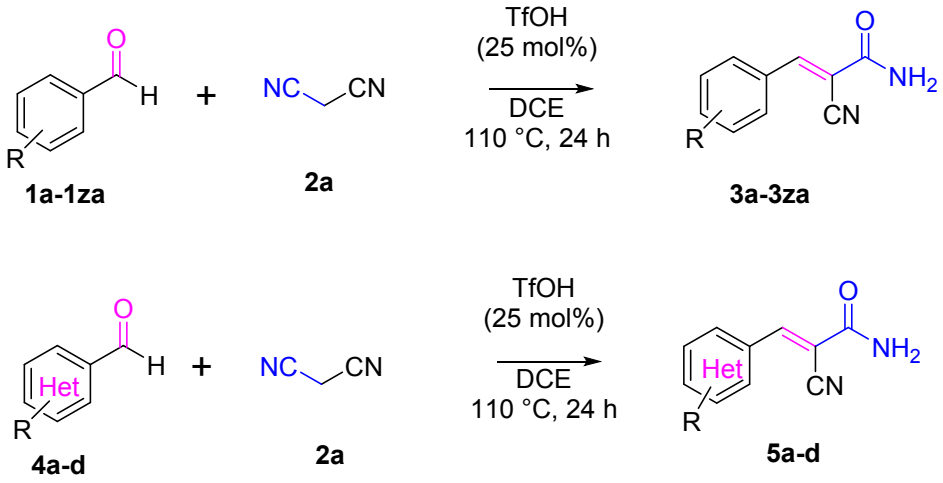
Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	$ZnCl_2$	DCE	110	16	60
2	$FeCl_3$	DCE	110	16	N.R
3	$AlCl_3$	DCE	110	16	N.R
4	$MgCl_2$	DCE	110	16	N.R
5	$TiCl_4$	DCE	110	16	N.R
6	$AgCOCF_3$	DCE	110	16	Trace
7	$BF_3.Et_2O$	DCE	110	16	Trace
8	TFA	DCE	110	16	Trace
9	$(CF_3SO_2)_2O$	DCE	110	16	N.R
10	TFAA	DCE	110	16	53
11	TfOH	DCE	110	24	84
12	TsOH	DCE	110	16	79
13	TfOH	PhMe	110	24	36
14	TfOH	DMSO	110	24	41
15	TfOH	1,4-dioxane	110	24	47
16	TfOH	THF	70	24	31
17	TfOH	MeCN	90	24	70
18	TfOH	EtOH	80	24	46
19	TfOH	IPA	110	24	N.R
20	TfOH	DMF	110	24	N.R
21[c]	TfOH	DCE	110	24	78

[a]**Reaction conditions:** Benzaldehyde **1a**(1 mmol), malononitrile**2a** (1.2 mmol), catalyst (25 mol%), solvent (5 mL), 70-110 ^{0}C for 16-24 h. [b]Isolated yields. [c]Catalyst TfOH (20 mol%), N.R=No reaction.

General procedure for the Optimization of Reaction Conditions

In a 25 mL round bottom flask benzaldehyde **1a**(1 mmol), malanonitrile**2a** (1.2 mmol), catalyst (20-25 mol%) and solvent (5 mL) were added. The round bottom flask was equipped with condenser and the resultant reaction mixture was refluxed at 70-110 °C for 24 h (**Table 1**) and the progress of the reaction was monitored by TLC. Upon completion of the reaction, reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of silica gel and eluted with EtOAc (20 mL). The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified by column chromatography to afford the corresponding compound **3a** in moderate to good yields.

3. General Procedure for the Synthesis of Compound 3a-3zd and 5a-d

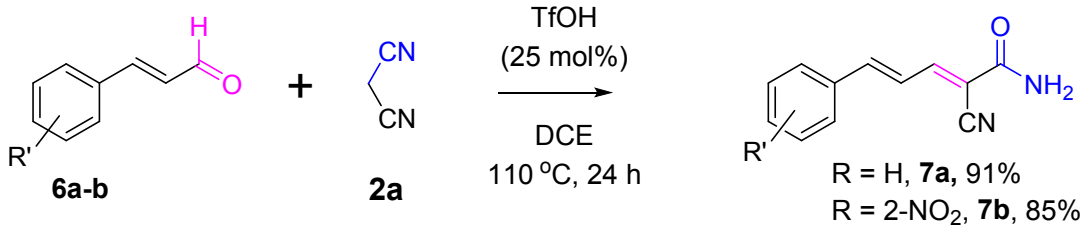


In a 25 mL round bottom flask aldehydes **1a-1za**(1 mmol)**or 4a-d** (1 mmol), malononitrile**2a** (1.2 mmol), catalyst TfOH (25 mol%) and DCE (5 mL) were taken. The round bottom flask was equipped with condenser and the resultant reaction mixture was refluxed at 110 ^{0}C for 24 h and progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (10 mL) and filtered through a pad of silica gel and eluted with EtOAc (20 mL). The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified

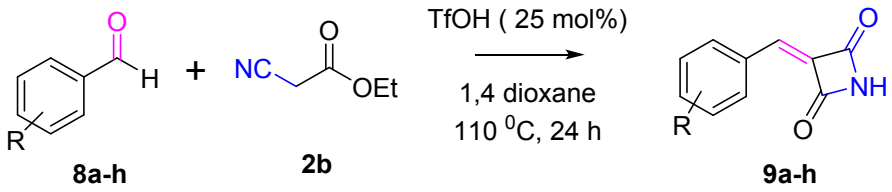
by column chromatography to afford the corresponding (*E*)-2-cyanoacrylamides**3a-3za** and **5a-d** in good to excellent yields.

4. General Procedure for the Synthesis of Compounds 7a and 7b

Compound **7a** and **7b** was prepared by using similar reaction procedure as above used for the synthesis of **3a-3zd** and **5a-d.**

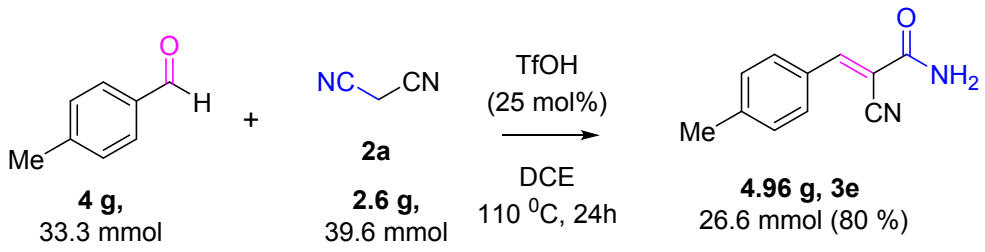


5. General Procedure for the Synthesis of 3-Substituted Azetidine-2,4-diones 9a-h



In a 10 mL round bottom flask equipped with a magnetic stir bar was added the aldehyde **8a-h** (1 mmol), ethyl cyanoacetate **2b(**1.2 mmol), TfOH (25 mol %) and 1,4-dioxane (5 mL). Then the resultant reaction mixture was kept in stirring at 110 °C for 14 h. Upon completion of the reaction, the reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water. The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified by column chromatography to afford the corresponding 3-substituted azetidine-2,4-diones **9a-h**in 75-89% yields.

6. General Procedure for the Gram Scale Synthesis of 3e



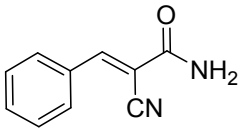
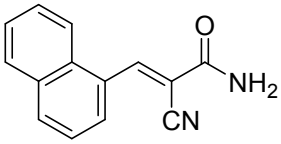
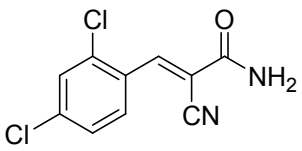
4 g, 33.3 mmol

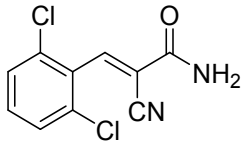
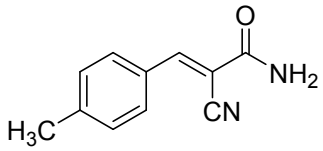
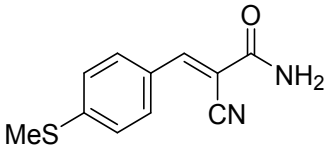
2.6 g, 39.6 mmol

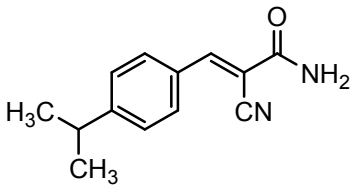
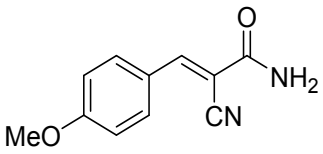
4.96 g, 3e 26.6 mmol (80 %)

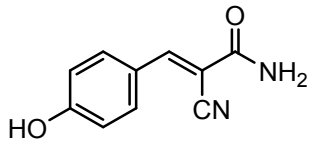
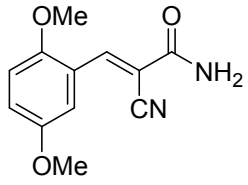
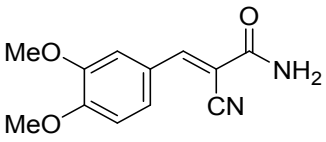
Following the general procedure as described above for the synthesis of (*E*)-2-cyanoacrylamides,a flame-dried flask was charged with 4-methylbenzaldehyde (**4g**, 33.3 mmol), malononitrile**2a** (**2.6g**, 39.6 mmol), catalyst TfOH (**1.25g**, 0.0083 mmol) and 1,4-dioxane (35 mL). The round bottom flask was equipped with condenser and the resultant reaction mixture was refluxed at 110 °C for 24 h. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was dried under vacuum. Then the crude reaction mixture was diluted with ethyl acetate (50 mL) and filtered through a pad of silica gel and eluted with EtOAc (600 mL). The solvent was evaporated and the crude residue was preadsorbed on silica gel and purified by column chromatography with eluted solvent (pet.ether + ethylaceate 65:35) to afford the corresponding (*E*)-2-cyano-3-(p-tolyl)acrylamide derivate **3e** in (**4.96g**, 80%) yield.

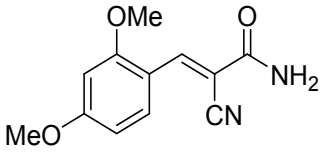
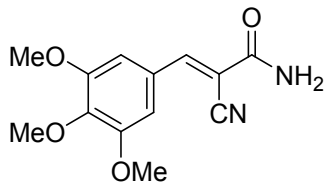
7. Spectral Data:

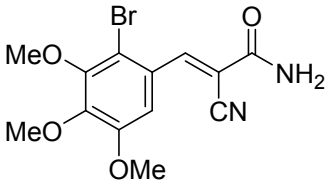
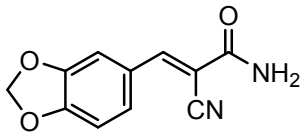
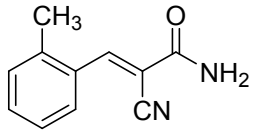
(E)-2-cyano-3-phenylacrylamide (3a)	
	***R*f**: 0.42 (Pet. Ether/EtOAc = 60/40); **Yield:** 136 mg, 84%; White solid; **mp:** 130 ◦C; **^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm: 7.46 (br. s, 3H) 7.78 - 7.95 (m, 2H) 8.06-8.22 (m, 1H);**^{13}C NMR** (50 MHz, DMSO-d_6)δ ppm: 103.1 117.0, 129.2, 130.8, 131.6, 133.1, 154.0, 162.1; **HRMS** (ESI) calculated $[M + H]^+$ for $C_{10}H_9ON_2$: 173.0709; found: 173.0706.
(*E*)-2-cyano-3-(naphthalen-1-yl)acrylamide (3b)	
	***R*f:** 0.38 (Pet. ether / EtOAc = 65/35); **Yield:** 125 mg, 88%; White solid; **mp:** 168 ˚C; **^{1}H NMR** (500 MHz, *DMSO-d_6*) δ ppm: 7.66 (br. s., 3H), 7.86 (br. s., 1H), 8.05 (br. s., 2H), 8.15 (br. s., 2H), 8.20 (br. s., 1H), 8.87 (br. s., 1H); **^{13}C NMR** (101 MHz, *DMSO-d_6*) δ ppm: 111.4, 116.4,123.9, 125.6, 127.1,127.4, 127.7, 129.1,129.6, 131, 132.1, 133.2, 148.7, 162.9;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{14}H_{11}ON_2$: 223.0866; found: 223.0860.
(*E*)-2-cyano-3-(2,4-dichlorophenyl)acrylamide (3c)	
	***R*f :**0.43 (Pet. ether /EtOAc = 60/40); **Yield:** 113 mg, 90%; White solid; **mp:** 125 ˚C; **^{1}H NMR** (200 MHz, DMSO-d_6) δ ppm : 7.5 (dd, *J*= 8.5, 2.0 Hz, 1H), 7.6 (d, *J*=2.1 Hz, 1H), 7.8 (br. s., 2H), 8.0 (d, *J*= 8.7 Hz, 1H), 8.3 (s, 1H); **^{13}C NMR** (50 MHz, DMSO-d_6**)** δ ppm : 110.4, 115.2,

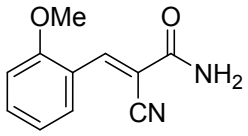
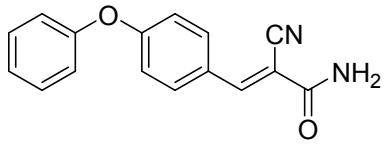
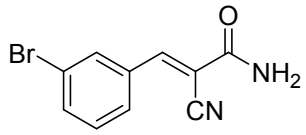
	127.7 , 129.1, 129.5 , 130.3, 135.5, 137.2, 145.7, 161.2; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_7ON_2Cl_2$: 240.9930; found: 240.9928.
(*E*)-2-cyano-3-(2,6-dichlorophenyl)acrylamide (3d)	
	***R*_f:** 0.42 (Pet. ether / EtOAc = 55/45); **Yield:**122 mg, 83%; White solid; **mp :** 125-128 ˚C; **^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm : 7.4-7.5 (m, 4H), 7.8 (br. s., 1H), 7.9 (br. s., 1H), 8.1 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$) δ ppm : 163.1, 161.8, 150.9, 132.7, 122.8, 117.2, 116.0, 100.5, 95.6;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_7ON_2Cl_2$: 240.9930; found: 240.9928.
(*E*)-2-cyano-3-(p-tolyl)acrylamide (3e)	
	***R*_f:** 0.41 (Pet. ether /EtOAc = 70/30); **Yield:** 129 mg, 83%; White solid; **mp:** 136 ˚C; **^{1}H NMR** (200 MHz, $CDCl_3$)δ ppm: 2.4 (s, 3H), 6.4 (br.s., 2H), 7.3 (d, *J*= 8.2 Hz, 2H), 7.9 (d, *J*= 8.2 Hz, 2H), 8.3(s,1H); **^{13}C NMR** (50 MHz, $CDCl_3$)δ ppm: 21.2,105.3, 116.7, 129.2, 129.9, 130.1, 143.0, 150.5, 162.9; **HRMS** (ESI) calculated $[M + H]^+$ for $C_{11}H_{11}ON_2$: 187.0866; found: 187.0862.
(*E*)-2-cyano-3-(4-(methylthio)phenyl)acrylamide (3f)	
	***R*_f:** 0.32 (Pet. ether /EtOAc = 60/40); **Yield:** 108 mg, 75%; White solid; **mp:** 153 ˚C;**^{1}H NMR** (200 MHz, $CDCl_3$)δ ppm: 2.55 (s, 3H), 6.17 (br. s., 1H), 6.33 (br. s., 1H), 7.31 (d, *J*= 8.6 Hz, 2H), 7.88 (d, *J*= 8.6 Hz, 2H), 8.27 (s, 1H);

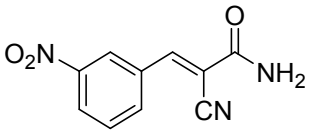
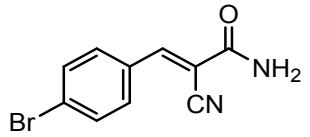
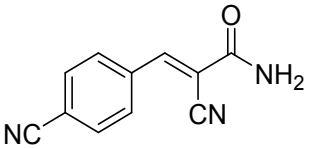
	^{13}C NMR (50 MHz, DMSO-d_6)δ ppm: 13.4, 102.2, 116.0, 124.3, 126.9, 129.7, 144.6, 150.2, 161.6; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}ON_2S$: 219.0587; found: 219.0581.
(*E*)-2-cyano-3-(4-isopropylphenyl)acrylamide (3g)	
	***R*$_f$:** 0.41 (Pet. ether /EtOAc = 65/35); **Yield:** 126 mg, 87%; Yellow solid; **mp:** 136-138 ˚C; **^{1}H NMR** (500 MHz, $CDCl_3$)δ ppm : 0.81 (d, *J*= 6.71 Hz, 7H) 5.67 (br. s., 1H) 5.88 (br. s., 1H) 6.88 (m, *J*= 8.24 Hz, 2H) 7.41 (m, *J*= 8.24 Hz, 2H) 7.81 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$)δ ppm: 23.7, 34.5, 101.8, 117.3, 127.5, 129.4, 131.2, 153.9, 154.9,162.2; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{13}H_{15}ON_2$: 215.1179; found: 215.1177.
(*E*)-2-cyano-3-(4-methoxyphenyl)acrylamide (3h)	
	***R*$_f$:** 0.35 (Pet. ether /EtOAc = 60/40); **Yield:** 99 mg, 64%; White solid; **mp:** 220˚C;**^{1}H NMR** (400 MHz, *DMSO-d_6*) δ ppm: 3.85 (br. s., 3H) 7.13 (d, *J* = 7.32 Hz, 2H) 7.67 (br. s., 1H) 7.80 (br. s., 1H) 7.96 (d, *J* = 7.32 Hz, 2H) 8.11 (br. s., 1H);**^{13}C NMR** (101 MHz, *DMSO-d_6*) δ ppm:55.6, 102.9, 114.83,117.09, 124, 132.47,150.1,162.59, 163.13;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}O_2N_2$: 203.0815; found: 203.0814.
(*E*)-2-cyano-3-(4-hydroxyphenyl)acrylamide (3i)	
	***R*$_f$:** 0.50 (Pet. ether /EtOAc = 70/30); **Yield:** 99 mg, 64%;

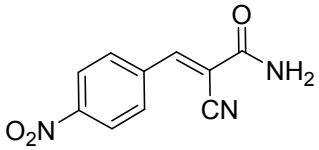
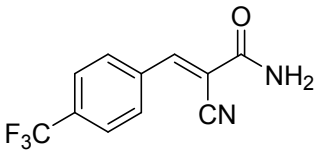
	White solid; **mp:** 242-243˚C; **^{1}H NMR** (200 MHz, DMSO-d_6) δ ppm : 6.85 (m, *J*= 8.7 Hz, 2H) 7.37 (br. s., 2 H) 7.79 (m, *J*= 8.7 Hz, 2H) 8.00 (s, 1H) 10.26 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$)δ ppm : 100.5, 116.0, 117.2, 122.8, 132.7, 150.9, 161.8, 163.1; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_9O_2N_2$: 189.0659; found: 189.0658.
(*E*)-2-cyano-3-(2,5-dimethoxyphenyl)acrylamide (3j)	
	***R*$_f$:** 0.41 (Pet. ether /EtOAc = 60/40); **Yield:** 108 mg, 76%; Yellow; **mp:** 165 ˚C; **^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm : 3.7 (s, 3H), 3.7 (s, 3H), 6.5-6.7 (m, 2H), 6.8 (d, *J*= 9.1 Hz, 1H), 7.0 (dd, *J*= 9.1, 3.0 Hz, 1H), 7.6 (d, *J*= 2.9 Hz, 1H), 8.6 (s, 1H); **^{13}C NMR** (126 MHz, *DMSO-d_6*) δ ppm: 55.5, 56.3, 106.6, 112.8, 113.1, 116.6, 119.8, 120.8, 145.4, 152.7, 152.8, 162.6; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{12}H_{13}O_3N_2$: 233.0921; found: 233.0915.
(*E*)-2-cyano-3-(3,4-dimethoxyphenyl)acrylamide (3k)	
	***R*$_f$:** 0.38 (Pet. ether /EtOAc = 65/35); **Yield:** 103 mg, 74%; White solid; **mp:** 195-196 ˚C; ^{1}H NMR (200 MHz, *DMSO-d_6*) δ ppm 3.81 (3 H, s), 3.86 (3 H, s), 7.14 (1 H, d, *J*=8.6 Hz), 7.56 (1 H, dd, *J*=8.5, 1.9 Hz), 7.66 (1 H, s), 7.68 - 7.89 (2 H, m), 8.06 - 8.19 (1 H, m); **^{13}C NMR** (50 MHz, *DMSO-d_6*) δ ppm :55.4, 55.80, 102.8, 111.8, 112.2, 117.2, 124.4, 125.5, 148.7, 150.6, 152.5, 163.1;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{12}H_{13}O_3N_2$: 233.0921;

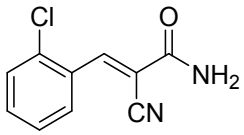
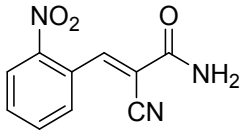
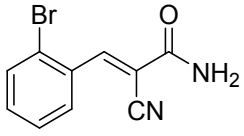
	found: 233.0915.
(*E*)-2-cyano-3-(2,4-dimethoxyphenyl)acrylamide (3l)	
	***R*_f:** 0.39 (Pet. ether /EtOAc = 60/40); **Yield:** 110 mg, 79%; White solid; **mp :** 168-169 ˚C; **^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm : 3.9 (s, 3H) 3.8 (s, 3H) 7.0 (d, *J*= 8.34 Hz, 1H) 7.2-7.5 (m, 3H) 7.6 (d, *J*= 2.02 Hz, 1H) 8.0 (s, 1 H); **^{13}C NMR** (50 MHz, DMSO-d_6) δ ppm : 55.3, 55.5, 95.5, 101.9, 111.0, 111.4, 117.0, 124.4, 126.0, 148.6, 150.9, 152.4, 162.6;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{12}H_{13}O_3N_2$: 233.0921; found: 233.0915.
(*E*)-2-cyano-3-(3,4,5-trimethoxyphenyl)acrylamide (3m)	
	***R*_f:** 0.35 (Pet. ether /EtOAc = 70/30); **Yield:** 113 mg, 85%; White solid; **mp :** 113-114 ˚C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ ppm : 3.77 (s, 3H) 3.88 (s, 3H) 3.89 (s, 3H) 7.03 (d, *J*= 9.05 Hz, 1H) 7.69 (br. s., 1H) 7.85 (br. s 1H) 7.91 (d, *J*= 9.05 Hz, 1H) 8.25 (s, 1H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm:56.3, 60.6, 62.0, 104.4, 108.4, 117.0 , 118.3, 123.7, 141.5, 144.9, 153.6, 157.4, 163.0; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{13}H_{15}O_4N_2$: 263.1026; found: 263.1024.
(*E*)-3-(2-bromo-3,4,5-trimethoxyphenyl)-2-cyanoacrylamide (3n)	
	***R*_f:** 0.39 (Pet. ether /EtOAc =60/40); **Yield:** 111 mg, 89%; Pale Yellow; **mp:** 221 ˚C; **^{1}H NMR**(500 MHz, *DMSO-d_6*) δ ppm: 3.82 (br. s., 3H) 3.86 (br. s., 3H) 3.88 (br. s., 3H)

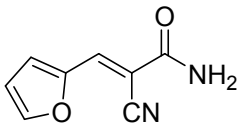
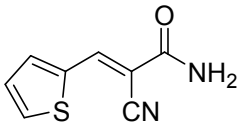
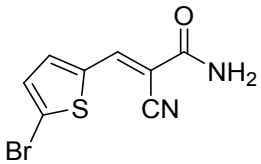
	7.55 (br. s., 1H) 7.87 (br. s., 1H) 8.00 (br. s., 1 H) 8.29 (br. s., 1H);**^{13}C NMR**(126 MHz, *DMSO-d_6*) δ(s) 56.2, 60.9, 109.1,109.6, 111.8, 115.8,127.1, 145.3, 149.3,150.5, 152.3,161.8;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{13}H_{14}O_4N_2Br$: 341.0131; found: 341.0124.
(*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-cyanoacrylamide(3o)	
	***R*$_f$:** 0.38 (Pet. ether /EtOAc = 65/35); **Yield:** 130 mg, 90%; white solid; **mp:** 204-206 ˚C; **^{1}H NMR** (200 MHz, DMSO-*d_6*) δ ppm : 6.1 (s, 2H), 6.9 (d, *J*= 8.2 Hz, 1H), 7.2-7.5 (m, 3H), 7.6 (s, 1H), 8.0 (s, 1H);**^{13}C NMR** (50 MHz, DMSO-*d_6*)δ ppm : 101.8, 102.4, 107.7, 108.4, 116.6, 125.8, 128.1, 148.0, 150.4 , 150.9 , 162.4; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_9O_3N_2$: 217.0608; found: 217.0606.
(*E*)-2-cyano-3-(o-tolyl)acrylamide (3p)	
	***R*$_f$:** 0.42 (Pet. ether /EtOAc = 65/35); **Yield:** 125 mg, 81%; White solid; **mp:** 125-127 ˚C; **^{1}H NMR** (400 MHz, $CDCl_3$)δ ppm : 2.48 (s, 3H) 6.35 (br. s., 1H) 6.41 (br. s., 1H) 7.27-7.47 (m, 4H) 8.07 (d, *J*= 7.78 Hz, 1H) 8.63 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$)δ ppm : 20.0, 104.8, 116.8, 126.7, 128.3, 130.9, 131.1, 132.6, 139.8, 152.1, 161.9; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}ON_2$: 187.0866; found: 187.0862.
(*E*)-2-cyano-3-(2-methoxyphenyl)acrylamide (3q)	

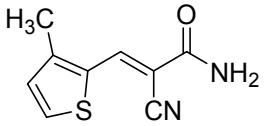
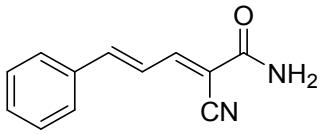
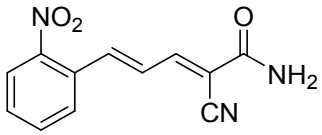
	***R*_f:** 0.35 (Pet. ether /EtOAc = 60/40); **Yield:** 111 mg, 75%; White solid; **mp :** 146-148 ˚C;**^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm : 3.85 (s, 3H), 6.97-7.22 (m, 1H), 7.32-7.50 (m, 3H), 7.53 (br. s., 2H), 8.16 (s, 1H); **^{13}C NMR** (50 MHz, DMSO-d_6)δ ppm : 54.8, 105.7, 114.1, 116.2, 118.1, 122.7, 129.7, 132.8, 150.9, 159.3, 162.0; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_{11}O_2N_2$: 203.0815; found: 203.0814.
(*E*)-2-cyano-3-(4-phenoxyphenyl)acrylamide (3r)	
	***R*_f:** 0.44 (Pet. ether /EtOAc = 60/40); **Yield:** 110 mg, 76%; White solid; **mp :** 112-114 ˚C; **^{1}H NMR** (200 MHz, $CDCl_3$)δ ppm : 6.40 (br. s., 1H) 6.56 (br. s., 1H) 7.01-7.09 (m, 2H) 7.13-7.26 (m, 2H) 7.34 -7.52 (m, 4H) 7.69 (d, *J*= 7.83 Hz, 1H) 8.26 (s, 1H): **^{13}C NMR** (50 MHz, DMSO-d_6)δ ppm : 161.6, 150.6, 133.1, 132.3, 131.2, 128.6, 127.2, 127.1, 126.4, 124.9, 122.8, 118.5, 116.4, 107.2; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{16}H_{13}O_2N_2$: 265.0972; found: 265.0969.
***E*)-3-(3-bromophenyl)-2-cyanoacrylamide (3s)**	
	***R*_f:** 0.4 (Pet. ether /EtOAc = 60/40); **Yield:** 122 mg, 90%; White solid; **mp:** 131-134 ˚C;**^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm : 7.4-7.5 (m, 1H), 7.6-7.8 (m, 3H), 7.9 (d, *J*= 7.8 Hz, 1H), 8.0 (s, 1H), 8.1 (s, 1H); **^{13}C NMR** (50 MHz, DMSO-d_6) δ ppm : 107.9, 115.8, 122.2, 128.6,

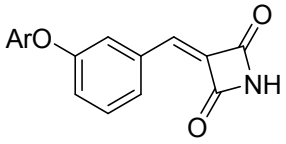
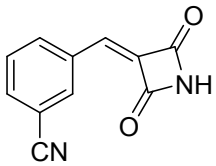
	130.8, 132.2, 134.0, 134.4, 148.8, 162.0;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_8ON_2Br$: 250.9815; found: 250.9808.
***E*)-2-cyano-3-(3-nitrophenyl)acrylamide (3t)**	
	***R*$_f$:** 0.34 (Pet. ether /EtOAc = 65/35);**Yield:** 137 mg, 84%; Brown solid; **mp:** 210-211 ˚C;**^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm : 8.2 (s, 1H), 7.7-7.9 (m, 4H), 7.2 (t, *J*= 8.0 Hz, 1H), 6.8 (s, 1H), 6.9 (s, 1H);**^{13}C NMR** (50 MHz, DMSO-d_6)δ ppm : 160.8, 148.2, 147.4, 134.7, 132.6, 129.6, 125.3, 123.7, 114.9, 107.8; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_8O_3N_3$: 218.0560; found: 218.055
(*E*)-3-(4-bromophenyl)-2-cyanoacrylamide(3u)	
	***R*$_f$:** 0.41 (Pet. ether /EtOAc = 65/35); **Yield:** 121 mg, 89%; White Solid; **mp:** 198 ˚C ;**^{1}H NMR** (500 MHz, *DMSO-d_6*) δ ppm : 7.72 (d, *J*=8.01 Hz, 2 H) 7.77 (br. s., 1 H) 7.82 (d, *J*=8.01 Hz, 2 H) 7.93 (br. s., 1 H) 8.11 (s, 1 H); **^{13}C NMR** (126 MHz, *DMSO-d_6*) δ ppm : 107.51, 116.4, 126.2, 131.2, 131.9, 132.5, 149.7, 162.8; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_8ON_2Br$: 250.9815; found: 250.9808.
(*E*)-2-cyano-3-(4-cyanophenyl)acrylamide (3v)	
	***R*$_f$:** 0.35 (Pet. ether /EtOAc = 60/40); **Yield:** 126 mg, 86%; White solid; **mp:** 146-148 ˚C;**^{1}H NMR** (200 MHz, DMSO-d_6) δ ppm : 7.44 (s, 1H), 7.36 (s, 1H), 7.68-7.85 (m, 2H), 7.96 (d, *J*= 8.5 Hz, 2H), 8.19 (s, 1H);**^{13}C NMR**

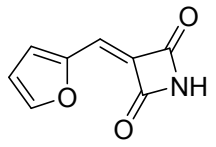
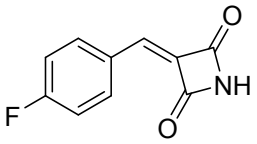
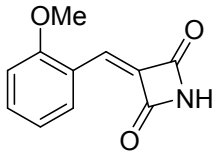
	(50 MHz, $CDCl_3$)δ ppm : 110.0, 113.8, 115.8, 118.2, 130.3, 133.0, 136.3, 148.7, 162; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_8ON_3$: 198.0662; found: 198.0658.
(*E*)-2-cyano-3-(4-nitrophenyl)acrylamide (3w)	
	***R*_f:** 0.41 (Pet. ether /EtOAc = 60/40); **Yield:** 131 mg, 91%; Yellow solid; **mp:** 198-200 ˚C; **^{1}H NMR** (400 MHz, DMSO-d_6)δ ppm : 7.91 (br. s., 1H) 8.06 (br. s., 1H) 8.12 (m, *J*= 8.80 Hz, 2H) 8.29 (s, 1H) 8.38 (m, *J*=8.80 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$)δ ppm : 110.7, 115.8, 124.2, 131.0, 138.1, 148.3, 148.8, 162.1; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_8O_3N_3$: 218.0560; found: 218.0556.
(*E*)-2-cyano-3-(4-(trifluoromethyl)phenyl)acrylamide (3x)	
	***R*_f:** 0.39 (Pet. ether /EtOAc = 70/30); **Yield:** 127, 92%; Light Brown; **mp:** 172 ˚C; **^{1}H NMR** (200 MHz, $CDCl_3$)δ ppm : 6.53 (br. s., 2H), 7.76 (d, *J*= 8.3 Hz, 3H), 8.04 (d, *J*= 8.2 Hz, 2H), 8.38 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$)δ ppm : 106.0, 116.2 , 120.6 , 126.1 - 126.3 (q, *J*=3.66 and 7.32 Hz), 130.7, 134.3, 134.6, 152.1, 161.5; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_8ON_2F_3$: 241.0583; found: 241.0577.
(*E*)-3-(2-chlorophenyl)-2-cyanoacrylamide (3y)	
	***R*_f:** 0.41 (Pet. ether /EtOAc = 65/35); **Yield:** 133 mg, 91%; off white solid; **mp:** 143 ˚C ; **^{1}H NMR** (500 MHz, *METHANOL-d_4*) δ ppm 7.4 (1 H, br. s.), 7.5 - 7.6 (3 H,

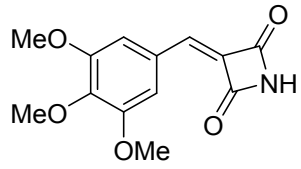
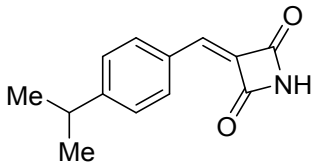
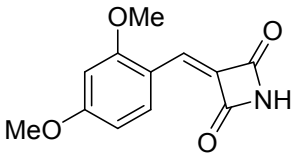
	m), 7.8 (1 H, d, *J*=7.2 Hz), 8.1 (1 H, d, *J*=7.6 Hz), 8.5 (1 H, s); ^{13}C NMR (126 MHz, *METHANOL-d*$_4$) δ ppm; 100.8, 106.9, 119.08, 121.27, 121.8, 124.9, 127.1, 140.07, 154.8, 159.5; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_8ON_3$: 198.0662; found: 198.0658.
(*E*)-2-cyano-3-(2-nitrophenyl)acrylamide (3z)	
	***R*$_f$:** 0.43 (Pet. ether /EtOAc = 60/40); **Yield:** 135 mg, 94%; White solid; **mp:** 168-169 ˚C; ^{1}H NMR (200 MHz, *DMSO-d*$_6$) δ ppm 7.5 - 7.9 (2 H, m), 7.9 - 7.9 (2 H, m), 8.0 (1 H, br. s.), 8.3 (1 H, d, *J*=8.0 Hz), 8.7 (1 H, s)^{13}C NMR (50 MHz, *DMSO-d*$_6$) δ ppm: 108.7, 114.7, 125.1, 128.4, 130.6, 132.3, 134.7, 147.2, 154.1, 162.4;**HRMS** (ESI) calculated $[M+H]^+$ for $_0H_8O_3N_3$: 218.0560; found: 218.0555.
(*E*)-3-(2-bromophenyl)-2-cyanoacrylamide (3za)	
	***R*$_f$:** 0.4 (Pet. ether /EtOAc = 65/35); **Yield:** 126 mg, 93%; White solid; **mp:** 178 ˚C; **^{1}H NMR** (200 MHz, $CDCl_3$)δ ppm : 6.17 (br. s., 1H), 6.37 (br. s., 1H), 7.36 - 7.52 (m, 3H), 7.67-7.75 (m, 1H), 8.09 (dd, *J*= 7.6, 1.8 Hz, 1H); **^{13}C NMR** (50 MHz, DMSO-*d*$_6$)δ ppm : 108.2, 114.5, 124.2, 126.7, 128.5, 131.0, 131.8, 132.1, 149.4, 160.4; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_8ON_2Br$: 250.9815; found: 250.9808.
(*E*)-2-cyano-3-(furan-2-yl)acrylamide (5a)	

	***R*_f:** 0.35 (Pet. ether /EtOAc = 60/40); **Yield:** 150 mg, 89%; Yellow solid; **mp:** 148-150 ˚C; **^{1}H NMR** (500 MHz, $CDCl_3$)δ ppm : 6.49-6.55 (m, 1H), 6.60 (br. s., 1H), 6.70 (br. s., 1H), 7.13 (d, *J*= 3.4 Hz, 1H), 7.63 (s, 1H), 7.93 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$)δ ppm : 99.8 , 113.2 , 116.4 , 120.5 , 137.4 , 147.3 , 148.8 , 161.8; **HRMS** (ESI) calculated $[M+H]^+$ for $C_8H_7O_2N_2$: 163.0502; found: 163.0501.
(*E*)-2-cyano-3-(thiophen-2-yl)acrylamide (5b)	
	***R*_f:** 0.39 (Pet. ether /EtOAc = 70/30); **Yield:** 138 mg, 87%; Dark Brown; **mp:** 221 ˚C; **^{1}H NMR** (200 MHz, DMSO-d_6) δ ppm : 7.10-7.32 (m, 1H), 7.59 (br. s., 2H), 7.78 (br. s., 1H), 7.83-8.00 (m, 1H), 8.33 (s, 1H); **^{13}C NMR** (50 MHz, DMSO-d_6)δ ppm : 102.1, 116.7, 128.6, 134.9, 135.8, 137.8, 143.6, 162.6; **HRMS** (ESI) calculated $[M+H]^+$ for $C_8H_7ON_2S$: 179.0274; found:179.0270.
(*E*)-3-(5-bromothiophen-2-yl)-2-cyanoacrylamide (5c)	
	***R*_f:** 0.35 (Pet. ether /EtOAc =65/35); **Yield:** 117 mg, 94%; Pale Yellow; **mp:** 168 ˚C; **^{1}H NMR** (200 MHz, $CDCl_3$)δ ppm : 6.01 (br. s., 1H), 6.24 (br. s., 1H), 7.19 (d, *J*= 4.0 Hz, 1H), 7.41-7.60 (m, 1H), 8.31 (s, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$)δ ppm : 103.02, 117.70., 121.70, 132.34 137.93, 139.16, 143.45, 162.67; **HRMS** (ESI) calculated $[M + H]^+$ for $C_8H_6ON_2BrS$: 258.9358; found: 258.9349.

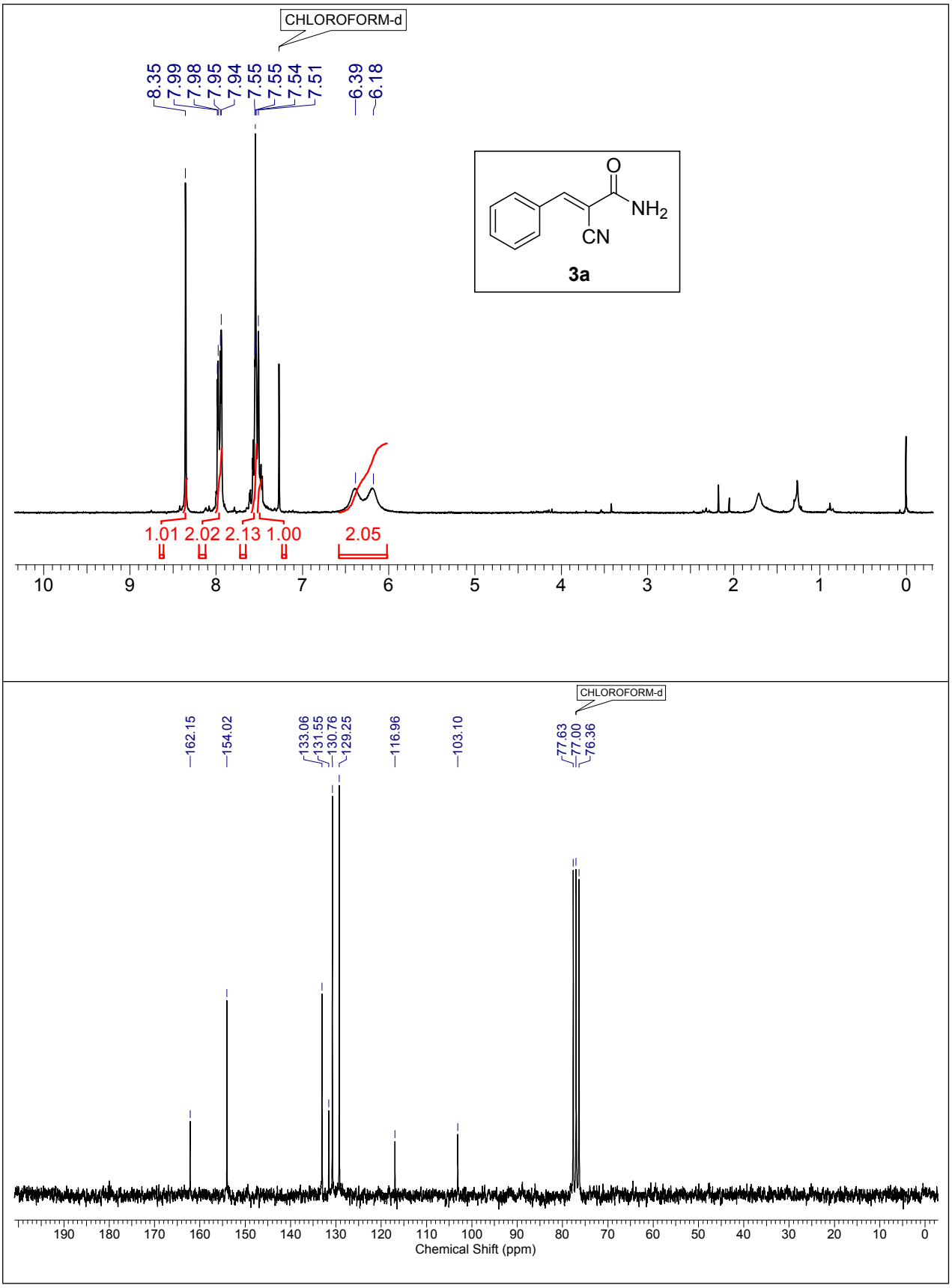
(*E*)-2-cyano-3-(3-methylthiophen-2-yl)acrylamide (5d)	
	***R*$_f$**: 0.36 (Pet. ether /EtOAc = 60/40); **Yield:** 128 mg, 84%; Dark Brown; **mp:** 155 ˚C; **^{1}H NMR** (200 MHz, $CDCl_3$)δ ppm : 2.47 (s, 3H), 5.91-6.46 (m, 2H), 7.02 (d, *J*= 5.2 Hz, 1H), 7.66 (d, *J*= 4.8 Hz, 1H), 8.53 (d, *J*= 0.9 Hz, 1H); **^{13}C NMR** (50 MHz, $CDCl_3$)δ ppm : 102.6, 116.6, 121.2, 131.9, 137.5, 138.7, 142.9, 162.2; **HRMS** (ESI) calculated $[M+H]^+$ for $C_9H_9ON_2S$: 193.0430; found: 193.0426.
(2*E*,4*E*)-2-cyano-5-phenylpenta-2,4-dienamide (7a)	
	***R*$_f$:** 0.30 (Pet. ether /EtOAc = 50/50); **Yield:**136 mg, 91%; Orange solid; **mp:** 150-152 ˚C; **^{1}H NMR** (400 MHz, DMSO-d_6)δ ppm : 7.96-8.03 (m, 1H) 7.60-7.62 (m, 2H) 7.40-7.50 (m, 5H) 7.30-7.34 (m, 1H) 7.15-7.21 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$)δ ppm : 167.4, 156.5, 151.6, 150.9, 139.9, 135.4, 135.1, 133.9, 133.0, 128.1, 120.4, 112.7, 100.8;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{12}H_{11}ON_2$: 199.0866; found: 199.0865.
(2*E*,4*E*)-2-cyano-5-(2-nitrophenyl)penta-2,4-dienamide (7b)	
	***R*$_f$:** 0.32 (Pet. ether /EtOAc = 60/40); **Yield:** 116 mg, 85%; White solid; **mp:** 207-209 ˚C; **^{1}H NMR** (200 MHz, DMSO-d_6)δ ppm : 7.1 (dd, *J*= 15.1, 11.3 Hz, 1H), 7.2-7.8 (m, 5H), 7.9 (d, *J*= 6.7 Hz, 1H), 8.0 (d, *J*= 8.7 Hz, 2H);**^{13}C NMR** (50 MHz, DMSO-d_6)δppm : 110.3,114.7,

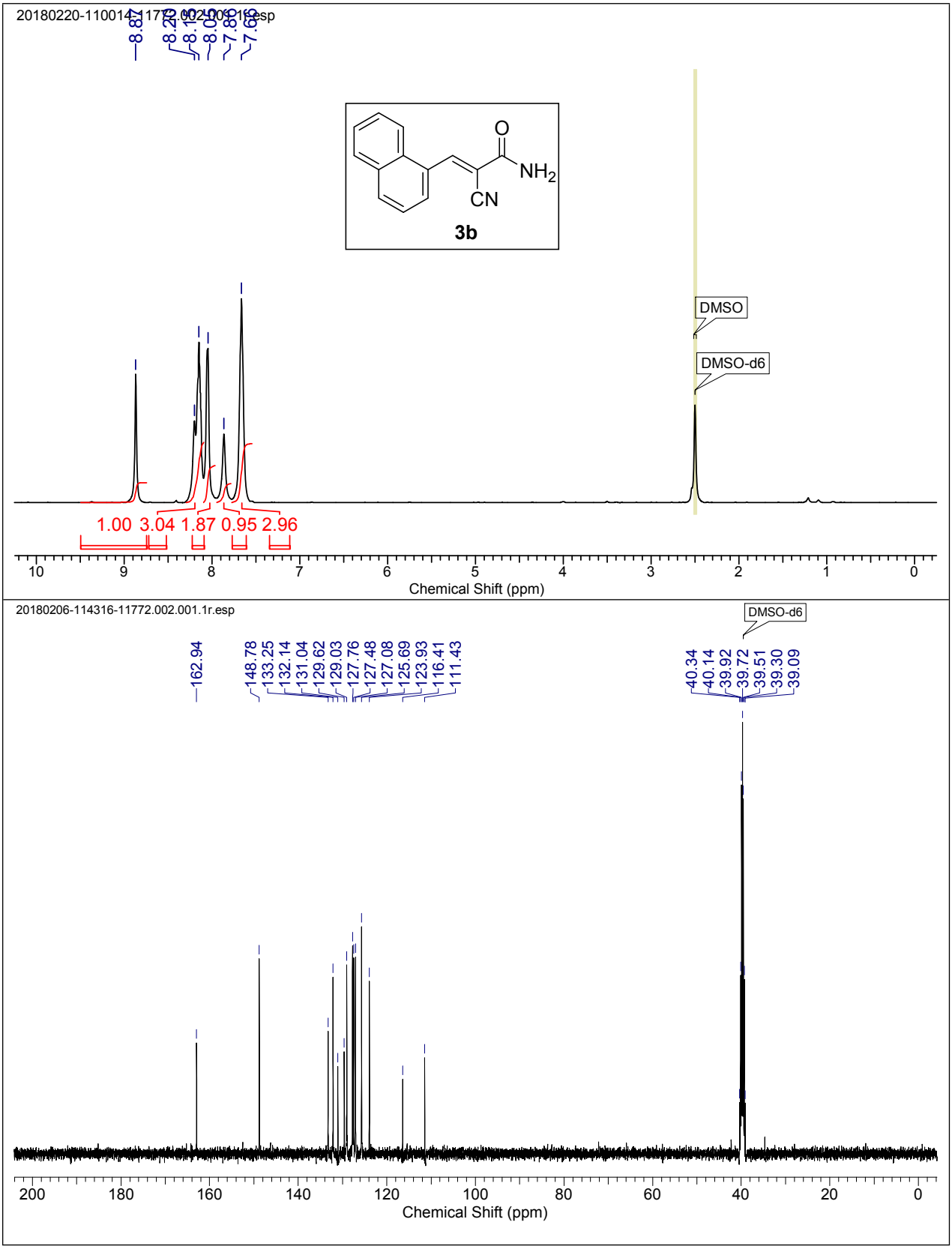
	124.5,127.2, 128.7, 129.9, 130.4, 133.5, 140.2, 147.9, 149.8, 162.0; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{12}H_{10}O_3N_3$: 244.0717; found: 244.0717.
3-(3-phenoxybenzylidene)azetidine-2,4-dione (9a)	
	***R*_f:** 0.32 (Pet. ether /EtOAc = 60/40); **Yield:** 119 mg, 89%; White solid; **mp:** 207-209 ˚C; **^{1}H NMR** (500 MHz, *CHLOROFORM-d*) δ ppm: 6.94 - 7.02 (m, 2H), 7.07 - 7.17 (m, 2H), 7.29 - 7.36 (m, 2H), 7.40 (t, *J*= 8.12 Hz, 1H), 7.46 (s, 1H), 7.68 (d, *J*= 7.70 Hz, 1H), 8.10 (s, 1 H), 9.41 (br. s., 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm : 163.8, 158.0, 156.0, 153.6, 133.2, 130.5, 130.0, 125.0, 124.1, 122.7, 120.2, 119.4, 115.5, 104.9;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{16}H_{12}NO_3$: 266.0812, found: 266.0810.
3-((2,4-dioxoazetidin-3-ylidene)methyl)benzonitrile (9b)	
	***R*_f:** 0.4 (Pet. ether / EtOAc = 50/50); **Yield:** 122 mg, 81%; White solid; **mp:** 170˚C; **^{1}H NMR** (500 MHz, *CHLOROFORM-d*) δ ppm : 7.58 (t, *J*=8.01 Hz, 1H), 7.74 (d, *J*=7.63 Hz, 1H), 8.08 (s, 1H), 8.12 (s, 1H), 8.16 (d, *J*=8.01 Hz, 1H);**^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm: 163.0, 151.3, 135.3, 133.9, 133.8, 132.8, 130.2, 117.4, 115.0, 113.7, 107.2;**HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_7N_2O_2$: 198.1820, found: 198.1818.
3-(furan-2-ylmethylene)azetidine-2,4-dione (9c)	

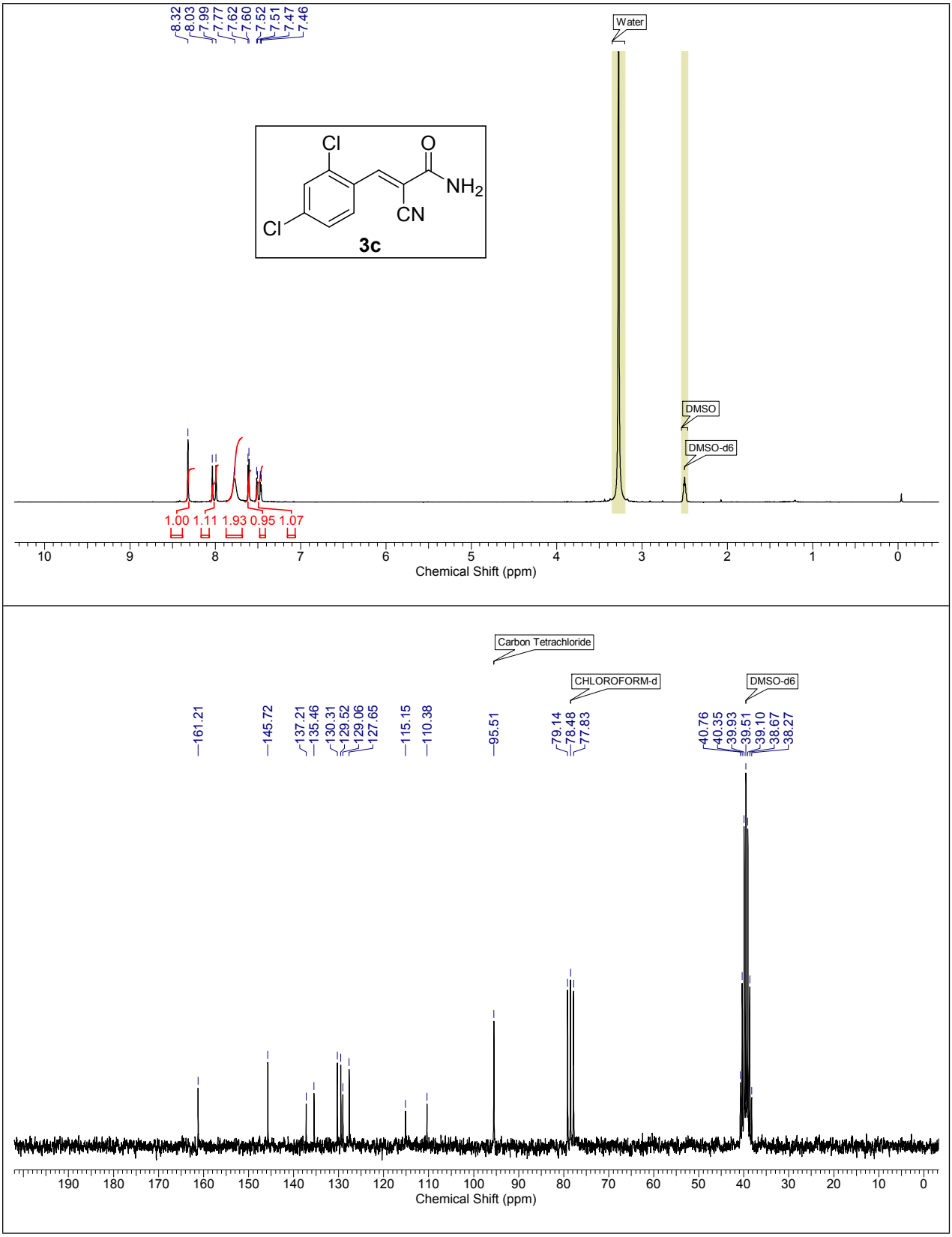
	***R*f:** 0.34 (Pet. ether /EtOAc = 60/40); **Yield:** 145 mg, 86%; White solid; **mp:** 146-148˚C; **^{1}H NMR** (500 MHz, *DMSO-d*$_6$) δ ppm: 6.62 (br. s., 1H), 7.29 (br. s., 1H), 7.77 (br. s., 1H), 7.90 (br. s., 1H); **^{13}C NMR** (125 MHz, DMSO-*d*$_6$) δ ppm : 162.6, 147.1, 137.7, 120.4, 114.5, 112.6, 98.3;**HRMS** (ESI) calculated $[M+H]^+$ for $C_8H_6NO_3$: 163.1310, found: 163.1312.
3-(4-fluorobenzylidene)azetidine-2,4-dione (9d)	
	***R*f:** 0.32 (Pet. ether /EtOAc = 60/40); **Yield:** 121 mg, 79%; White solid; **mp:** 160-164˚C; **^{1}H NMR** (500 MHz, *DMSO-d*$_6$) δ ppm: 7.09 (t, *J*=8.58 Hz, 2H), 7.85 - 7.95 (m, 2H), 8.08 (s, 1H), 8.48 (br. s., 1H);**^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm : 165.7, 163.6, 152.2, 132.9, 132.9, 127.8, 116.2, 116.0, 115.6, 103.7; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{10}H_7NO_2F$: 192.0455, found: 192.0456.
3-(2-methoxybenzylidene)azetidine-2,4-dione (9e)	
	***R*f:** 0.31 (Pet. ether /EtOAc = 60/40); **Yield:** 120 mg, 87%; White solid; **mp:** 176-178˚C; **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ ppm : 8.62 (1H, s), 8.17 (1H, d, *J*=7.3 Hz), 7.42 (1H, t, *J*= 7.6 Hz), 6.83-7.04 (2H, m), 3.81 (3H, s);**^{13}C NMR** (101 MHz, $CDCl_3$) δ ppm : 163.9, 158.5, 148.7, 134.2, 128.6, 120.3, 115.8, 110.7, 102.8, 55.2; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{11}H_9NO_3Na$: 226.0475, found: 226.0478.
3-(3,4,5-trimethoxybenzylidene)azetidine-2,4-dione (9f)	
	***R*f:** 0.35 (Pet. ether / EtOAc = 70/30); **Yield:** 107 mg, 80%; White solid; **mp:** 210˚C; **^{1}H NMR** (500 MHz,

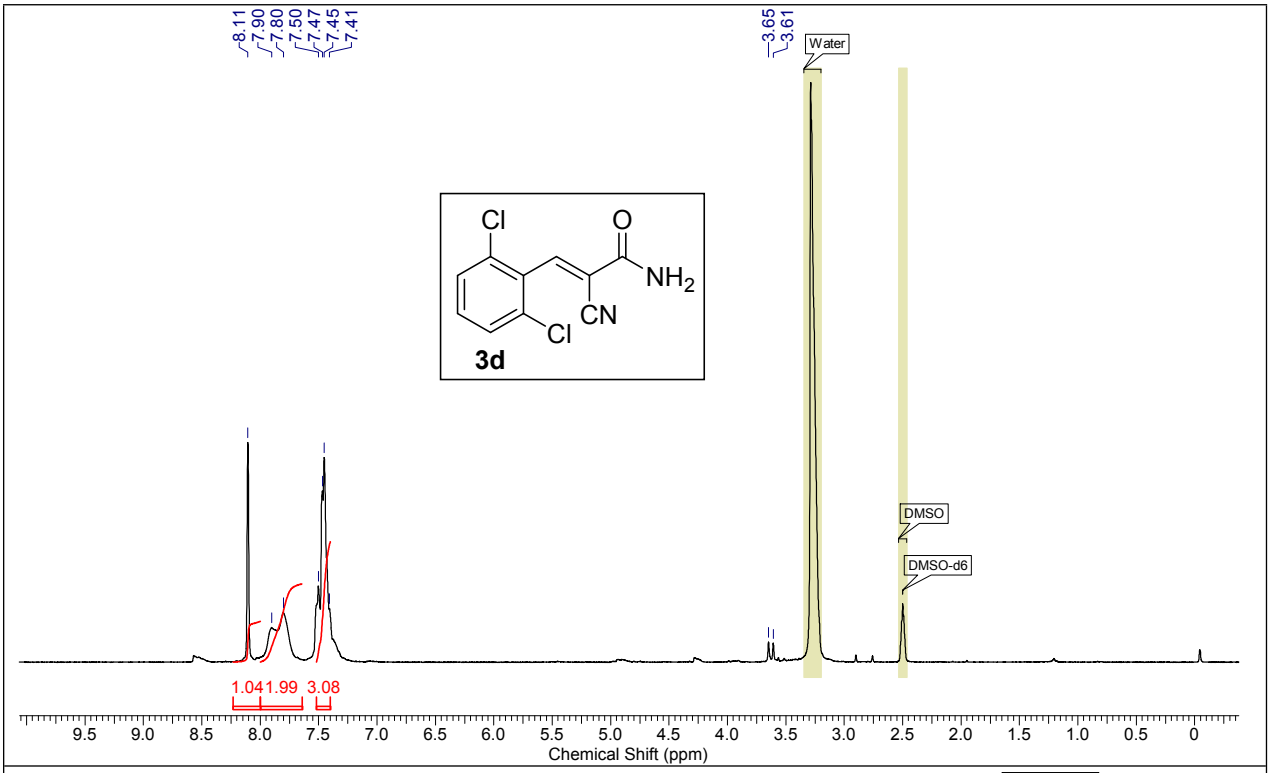
	*CHLOROFORM-d*) δ ppm: 3.77 - 3.87 (m, 9H), 7.14 - 7.27 (m, 2H), 8.02 (br. s., 1H);**^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 164.0, 153.9, 152.9, 142.1, 126.5, 116.1, 108.2, 102.1, 60.7, 55.9, 40.0; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{13}H_{13}NO_5Na$: 286.0686, found: 286.0690.
3-(4-isopropylbenzylidene)azetidine-2,4-dione (9g)	
	***R*$_f$:** 0.37 (Pet. ether /EtOAc = 60/40); **Yield:** 108 mg, 75%; White solid; **mp:** 246˚C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm : 8.30 (1H, s), 7.99 (2H, m, *J*=7.9 Hz), 7.40 (2H, m, *J*= 7.9 Hz), 2.94-3.07 (1H, m), 1.26-1.31 (7H, m);**^{13}C NMR** (50 MHz, $CDCl_3$) δ ppm : **^{13}C NMR** (101 MHz, *CHLOROFORM-d*) δ ppm: 163.5, 154.5, 154.3, 131.0, 129.3, 127.4, 116.3, 102.6, 33.7, 23.4; **HRMS** (ESI) calculated $[M+H]^+$ for $C_{13}H_{14}NO_2$: 216.1019, found: 216.1022.
3-(2,4-dimethoxybenzylidene)azetidine-2,4-dione (9h)	
	***R*$_f$:** 0.3 (Pet. ether /EtOAc = 60/40); **Yield:** 117 mg, 84%; White solid; **mp:** 216˚C; **^{1}H NMR** (200 MHz, *DMSO-d*$_6$) δ ppm: 3.68 (s, 7 H), 6.26 (d, *J*=2.27 Hz, 1 H), 6.38 (d, *J*=6.44 Hz, 1 H), 8.14 (d, *J*=8.84 Hz, 1 H), 8.43 (s, 1 H); **^{13}C NMR** (126 MHz, *DMSO-d*$_6$) δ ppm: 164.99, 164.49 , 160.70, 147.60, 130.22, 116.65, 113.37, 105.67, 98.51, 97.43, 56.31, 55.17; **HRMS**:(ESI) calculated $[M+H]^+$ for $C_{12}H_{12}NO_4$: 234.0761, found: 234.0766.

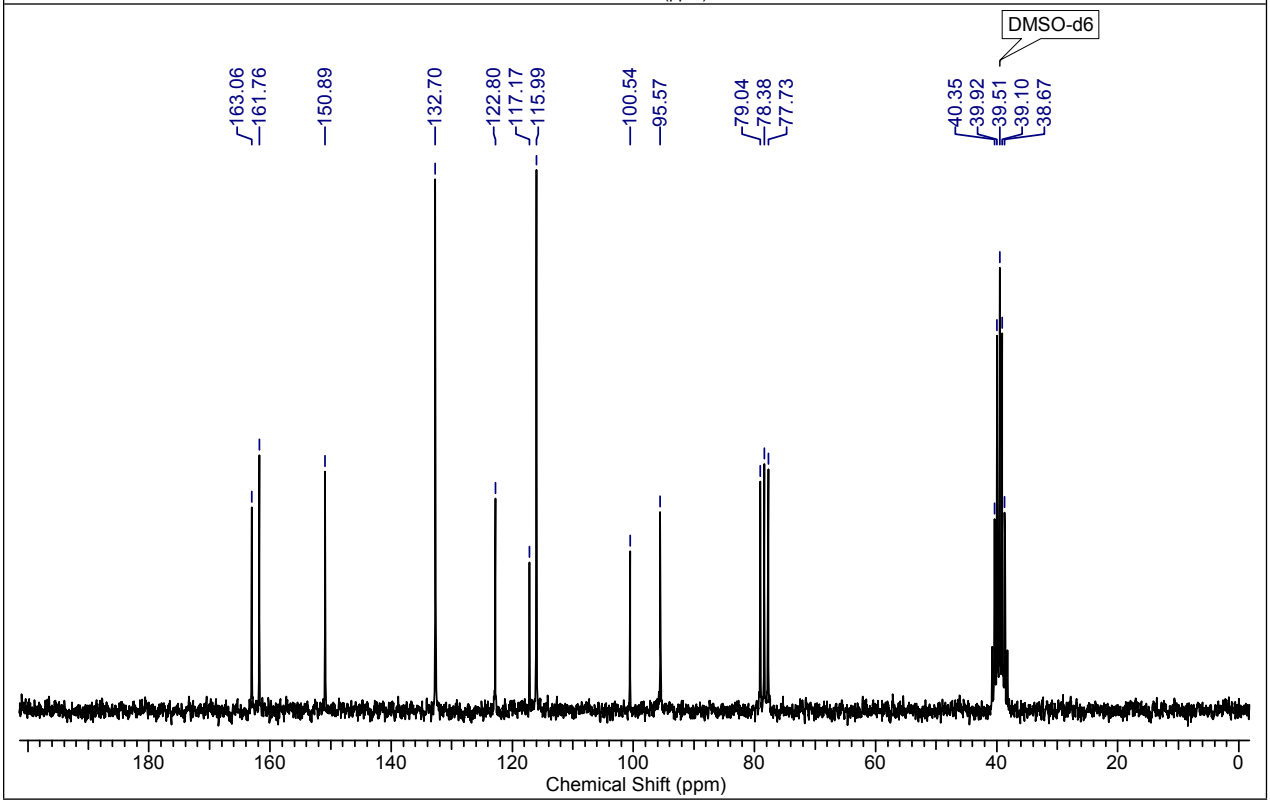
8. ^{1}H and ^{13}C-NMR Spectras

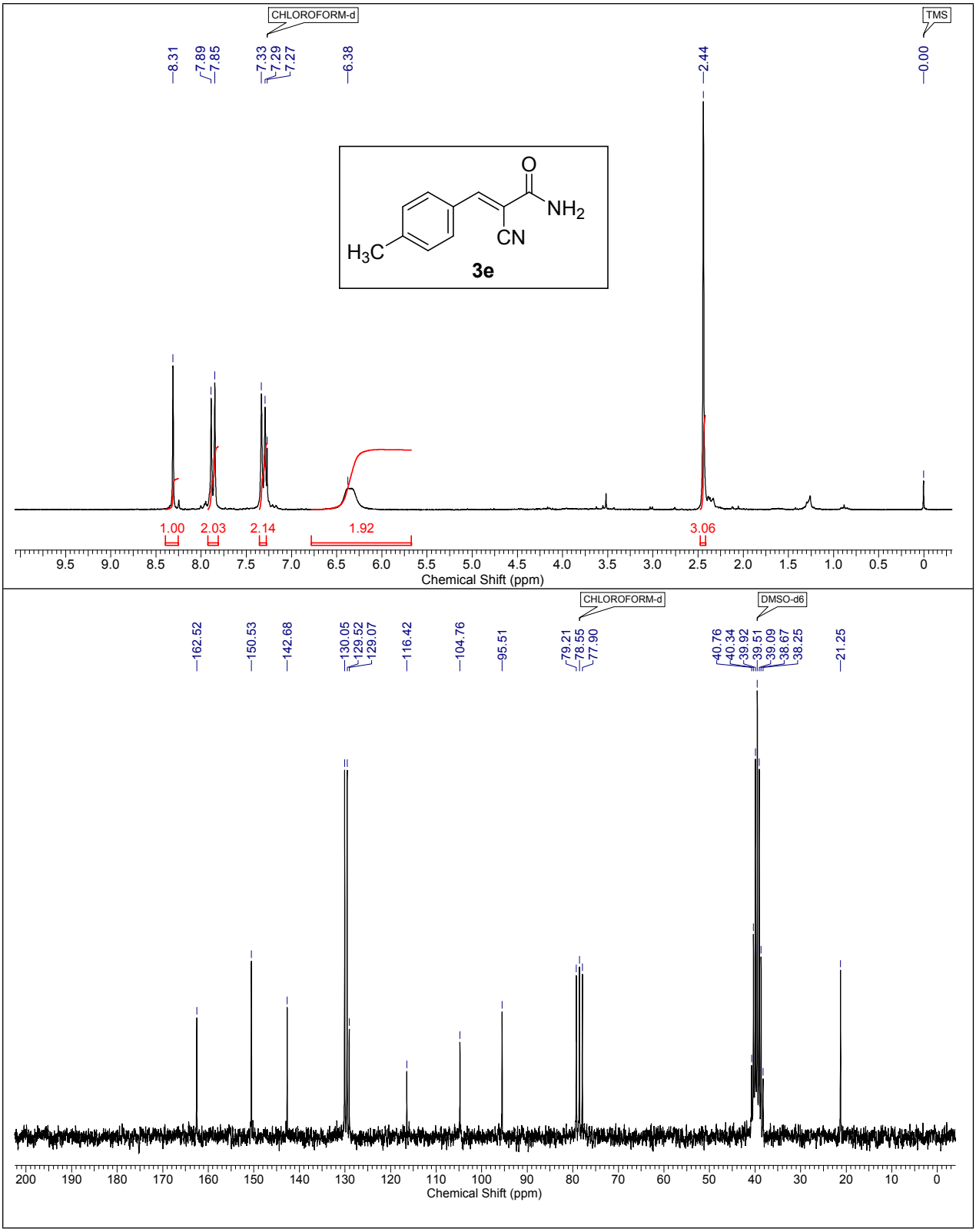


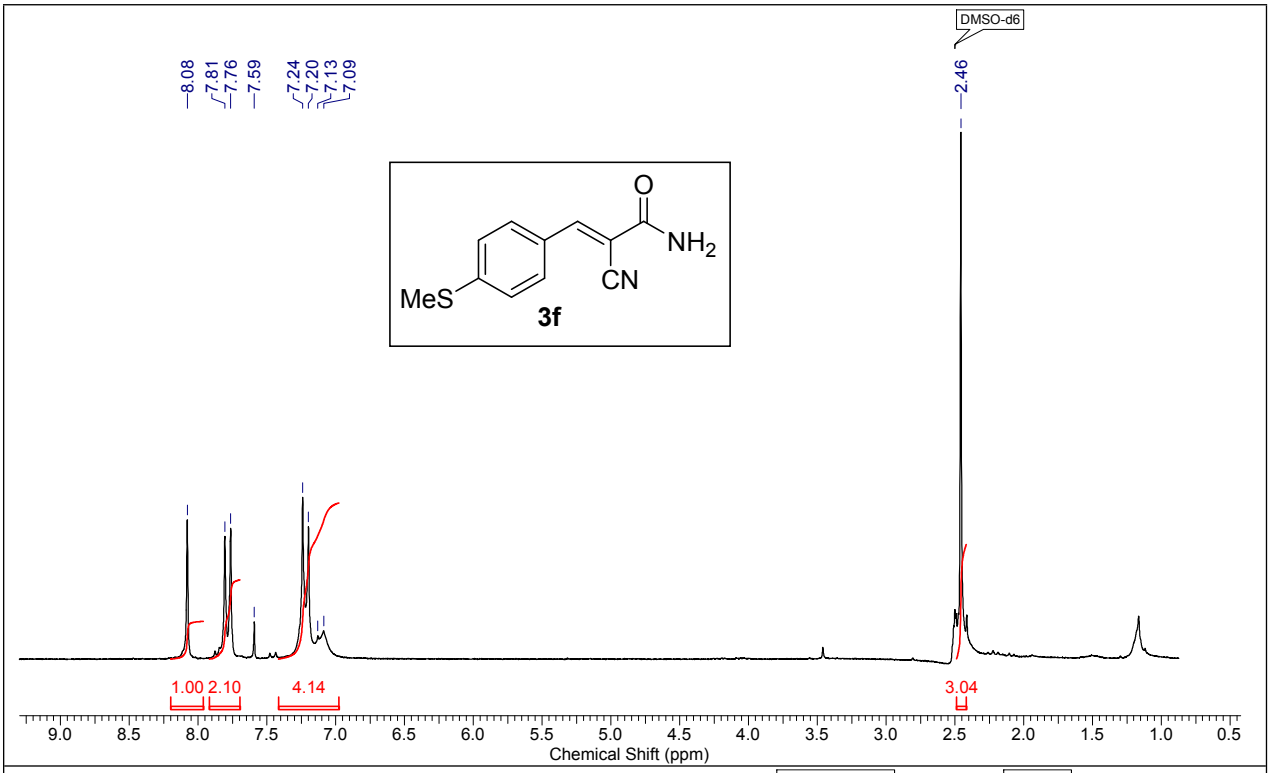

20180220-110014-11772.002.001.1r.esp
8.87
8.26
8.12
8.00
7.86
7.66
O
NH2
CN
3b
DMSO
DMSO-d6
1.00 3.04 1.87 0.95 2.96
Chemical Shift (ppm)
20180206-114316-11772.002.001.1r.esp
DMSO-d6
162.94
148.78
133.25
132.14
131.04
129.62
129.03
127.76
127.48
127.08
125.69
123.93
116.41
111.43
40.34
40.14
39.92
39.72
39.51
39.30
39.09
Chemical Shift (ppm)

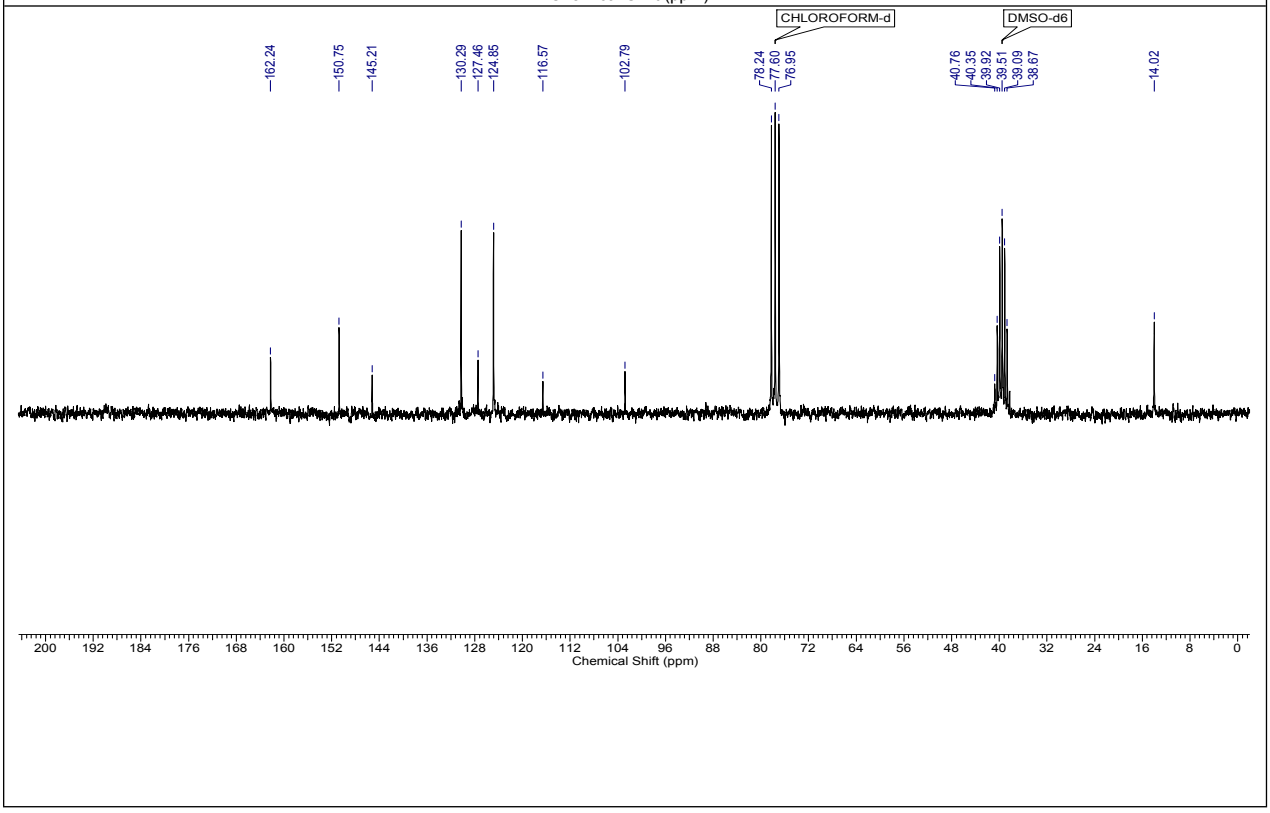

8.32
8.03
7.99
7.77
7.62
7.60
7.52
7.51
7.47
7.46
Water
DMSO
DMSO-d6
Cl
O
NH2
CN
Cl
3c
1.00 1.11 1.93 0.95 1.07
Chemical Shift (ppm)
Carbon Tetrachloride
CHLOROFORM-d
DMSO-d6
161.21
145.72
137.21
135.46
130.31
129.52
129.06
127.65
115.15
110.38
95.51
79.14
78.48
77.83
40.76
40.35
39.93
39.51
39.10
38.67
38.27
Chemical Shift (ppm)

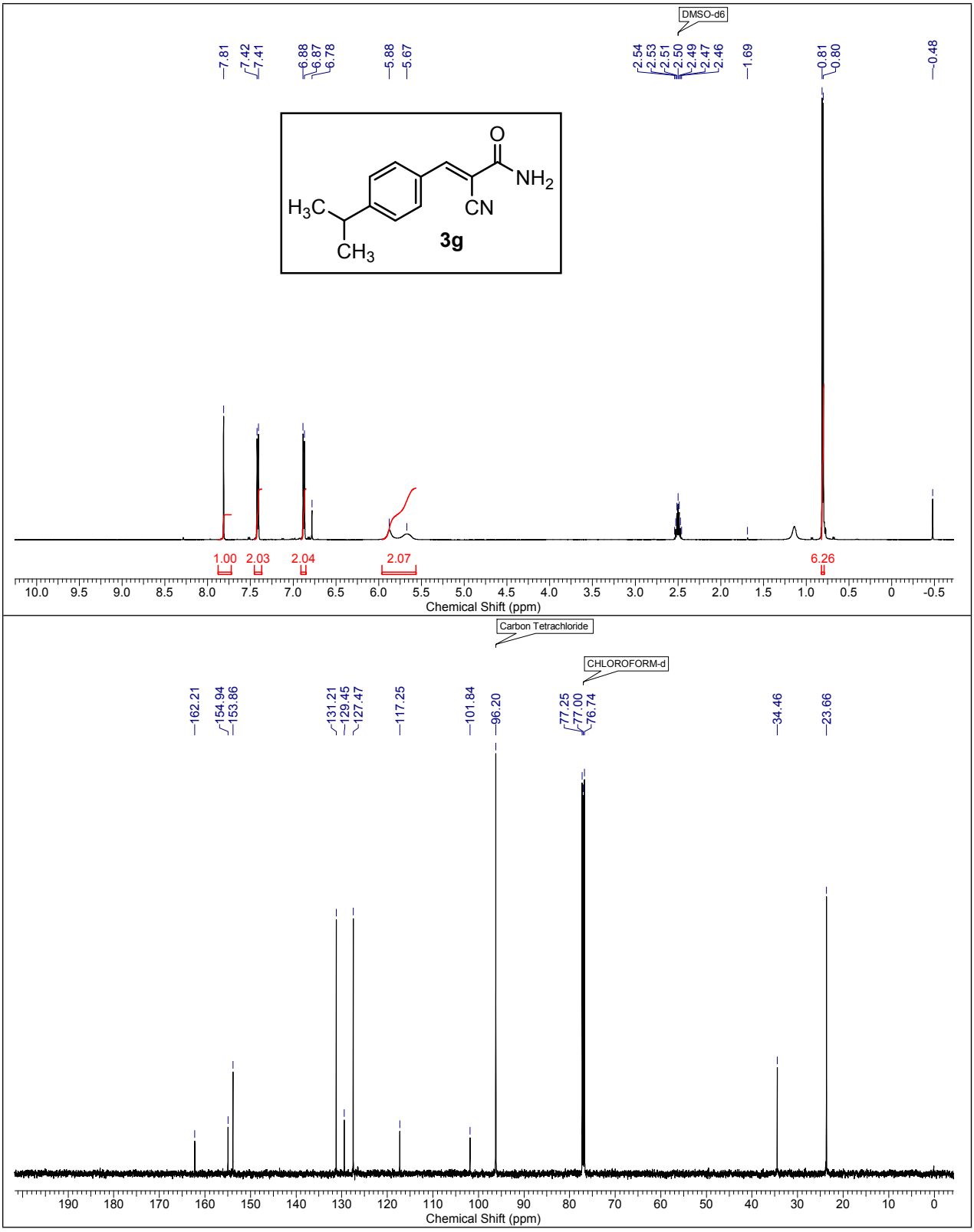

8.11
7.90
7.80
7.50
7.47
7.45
7.41
3.65
3.61
Water
DMSO
DMSO-d6
Cl
O
NH2
CN
Cl
3d
1.04 1.99 3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

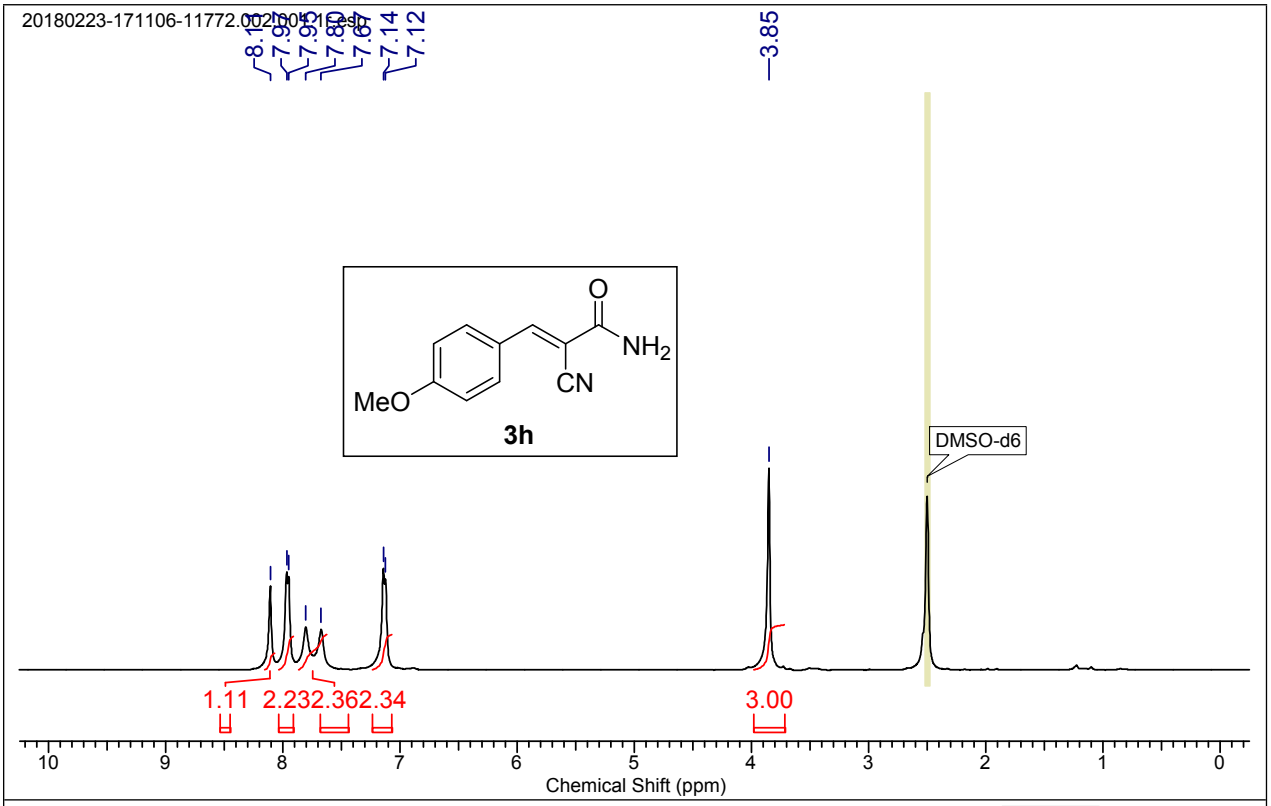

DMSO-d6
163.06
161.76
150.89
132.70
122.80
117.17
115.99
100.54
95.57
79.04
78.38
77.73
40.35
39.92
39.51
39.10
38.67
180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

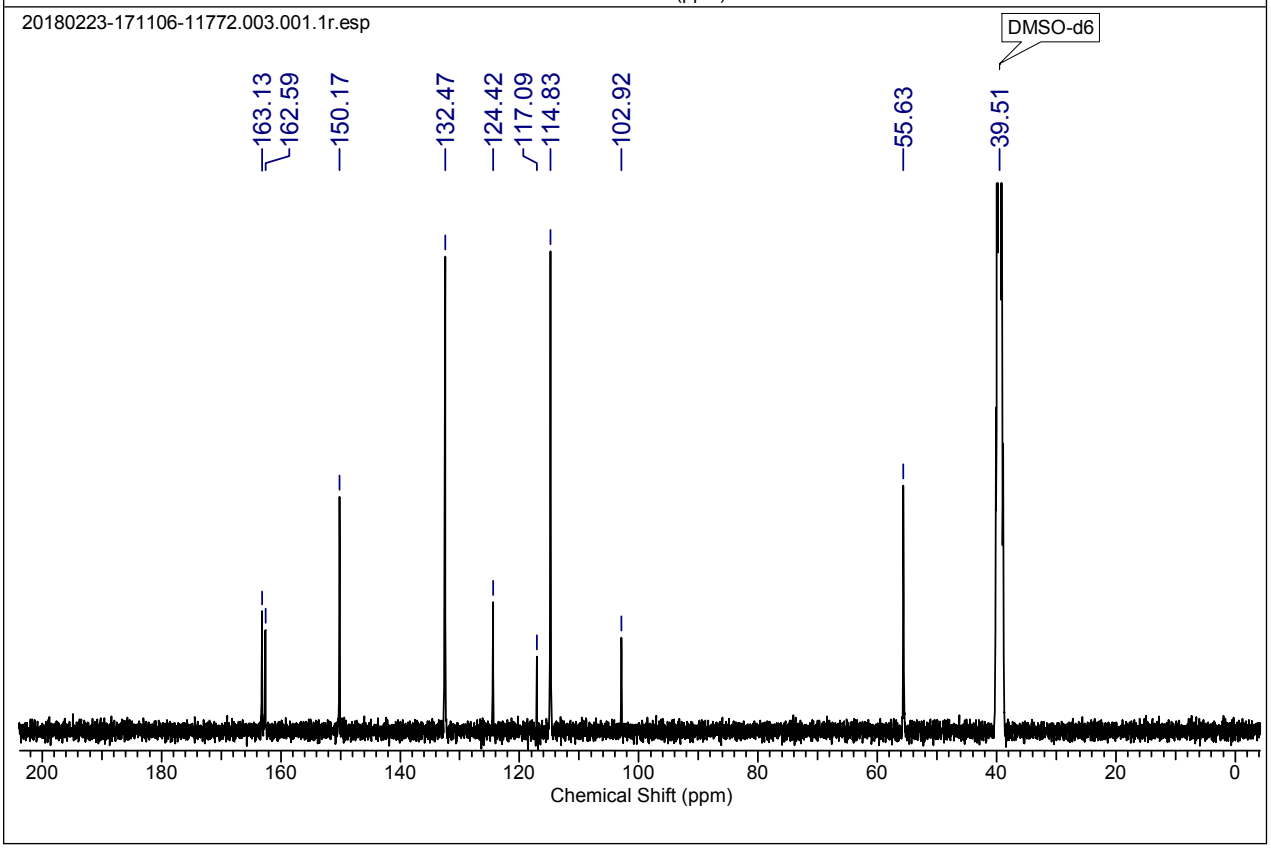

CHLOROFORM-d
TMS
8.31
7.89
7.85
7.33
7.29
7.27
6.38
2.44
0.00
O
NH2
CN
H3C
3e
1.00
2.03
2.14
1.92
3.06
Chemical Shift (ppm)
CHLOROFORM-d
DMSO-d6
162.52
150.53
142.68
130.05
129.52
129.07
116.42
104.76
95.51
79.21
78.55
77.90
40.76
40.34
39.92
39.51
39.09
38.67
38.25
21.25
Chemical Shift (ppm)

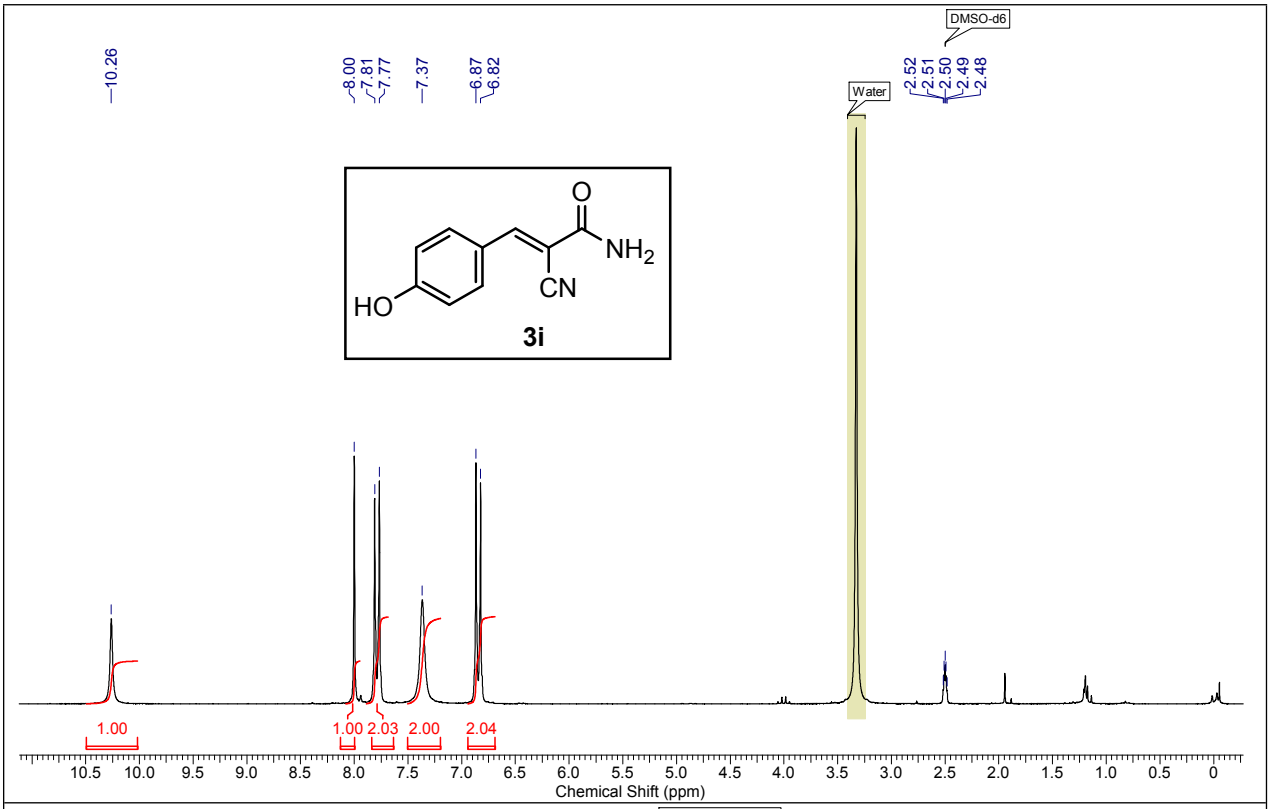

DMSO-d6
8.08
7.81
7.76
7.59
7.24
7.20
7.13
7.09
2.46
O
NH2
CN
MeS
3f
1.00
2.10
4.14
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

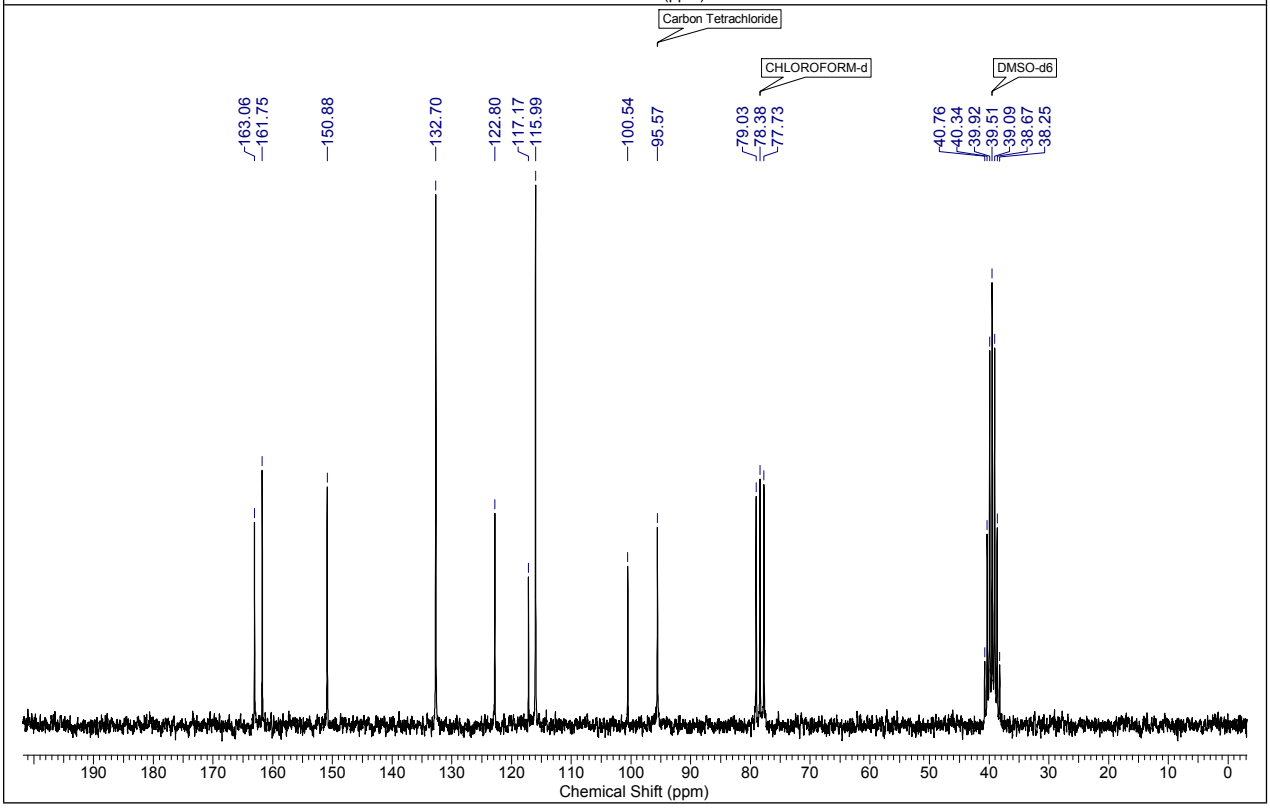

CHLOROFORM-d
DMSO-d6
162.24
150.75
145.21
130.29
127.46
124.85
116.57
102.79
78.24
77.60
76.95
40.76
40.35
39.92
39.51
39.09
38.67
14.02
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

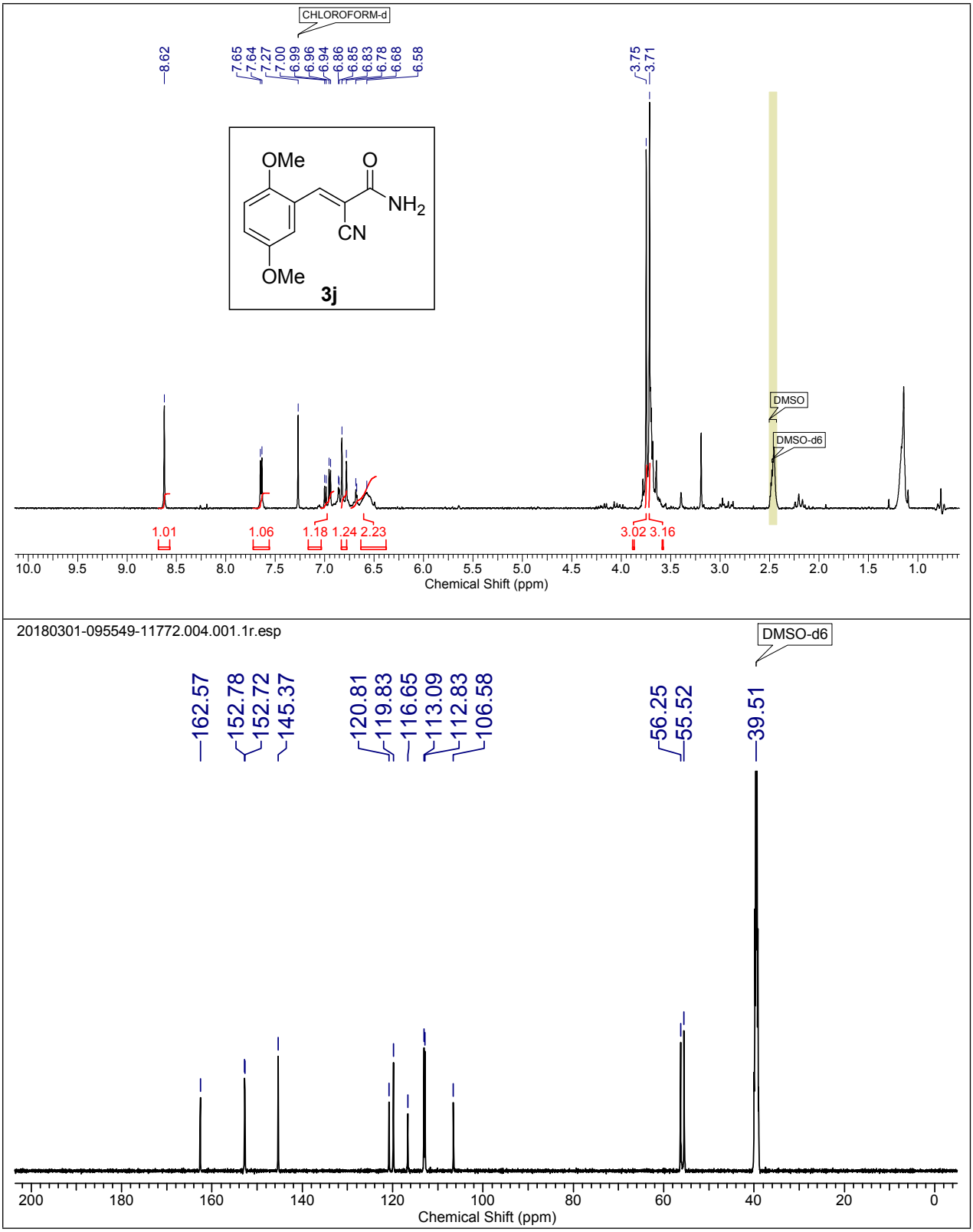

DMSO-d6
7.81
7.42
7.41
6.88
6.87
6.78
5.88
5.67
2.54
2.53
2.51
2.50
2.49
2.47
2.46
1.69
0.81
0.80
0.48
O
NH2
H3C
CN
CH3
3g
1.00
2.03
2.04
2.07
6.26
Chemical Shift (ppm)
Carbon Tetrachloride
CHLOROFORM-d
162.21
154.94
153.86
131.21
129.45
127.47
117.25
101.84
96.20
77.25
77.00
76.74
34.46
23.66
Chemical Shift (ppm)

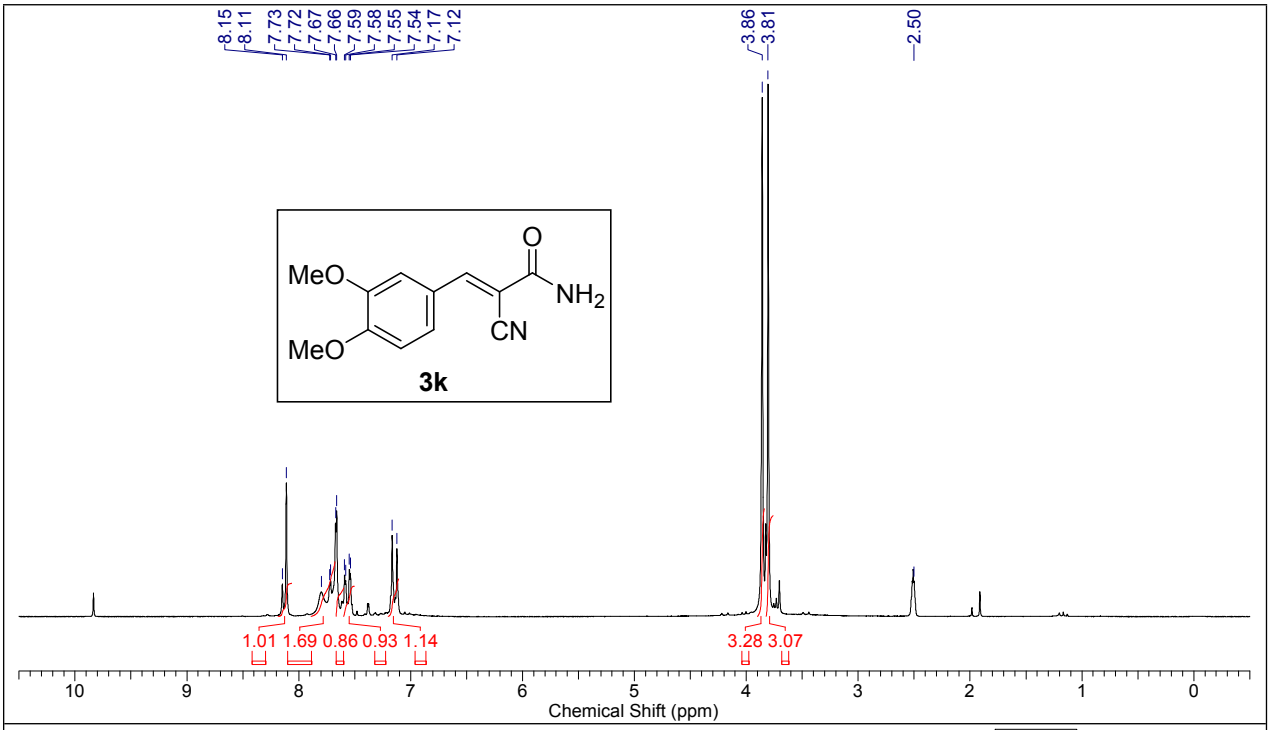

8.12
7.99
7.97
7.88
7.87
7.14
7.12
3.85
O
NH2
CN
MeO
3h
DMSO-d6
1.11
2.23
2.36
2.34
3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

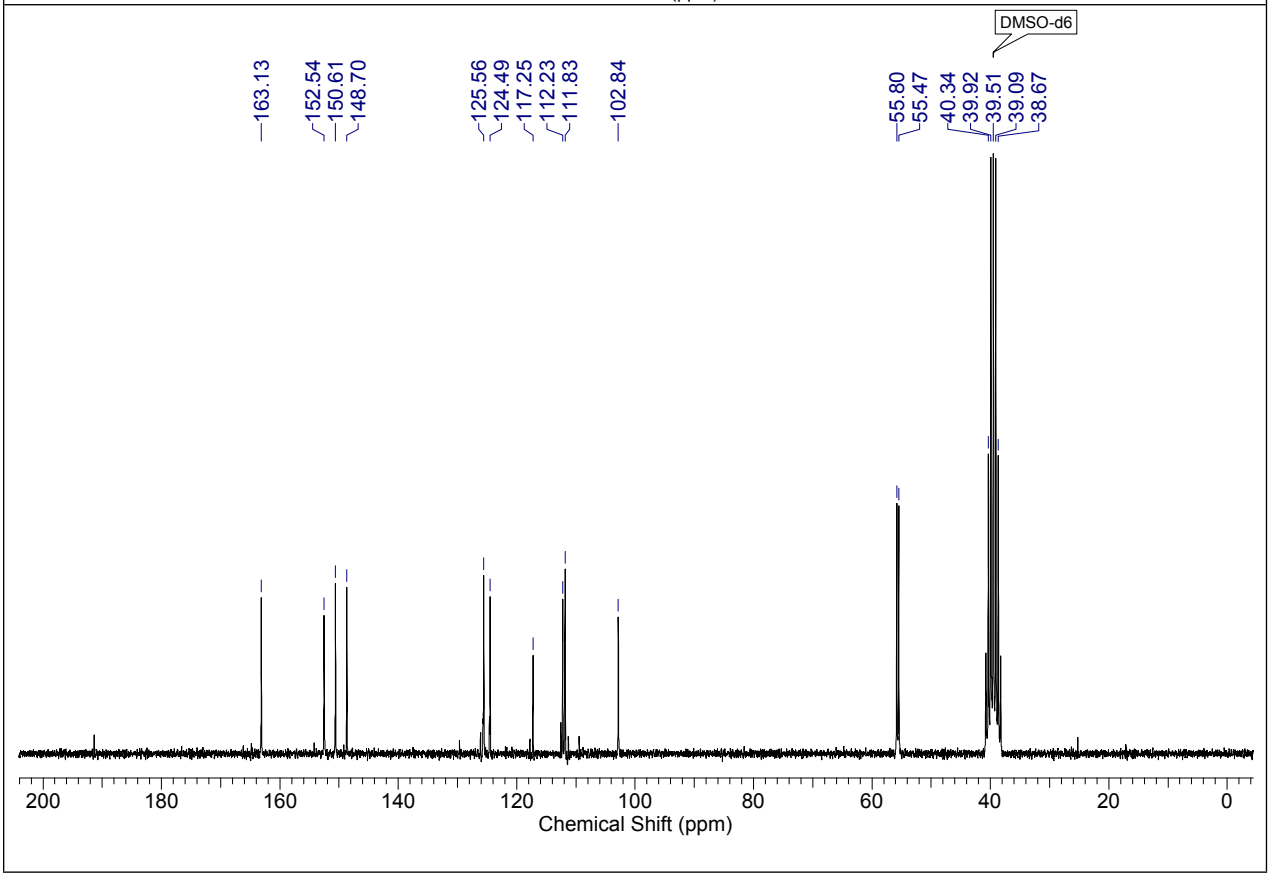

20180223-171106-11772.003.001.1r.esp
DMSO-d6
163.13
162.59
150.17
132.47
124.42
117.09
114.83
102.92
55.63
39.51
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

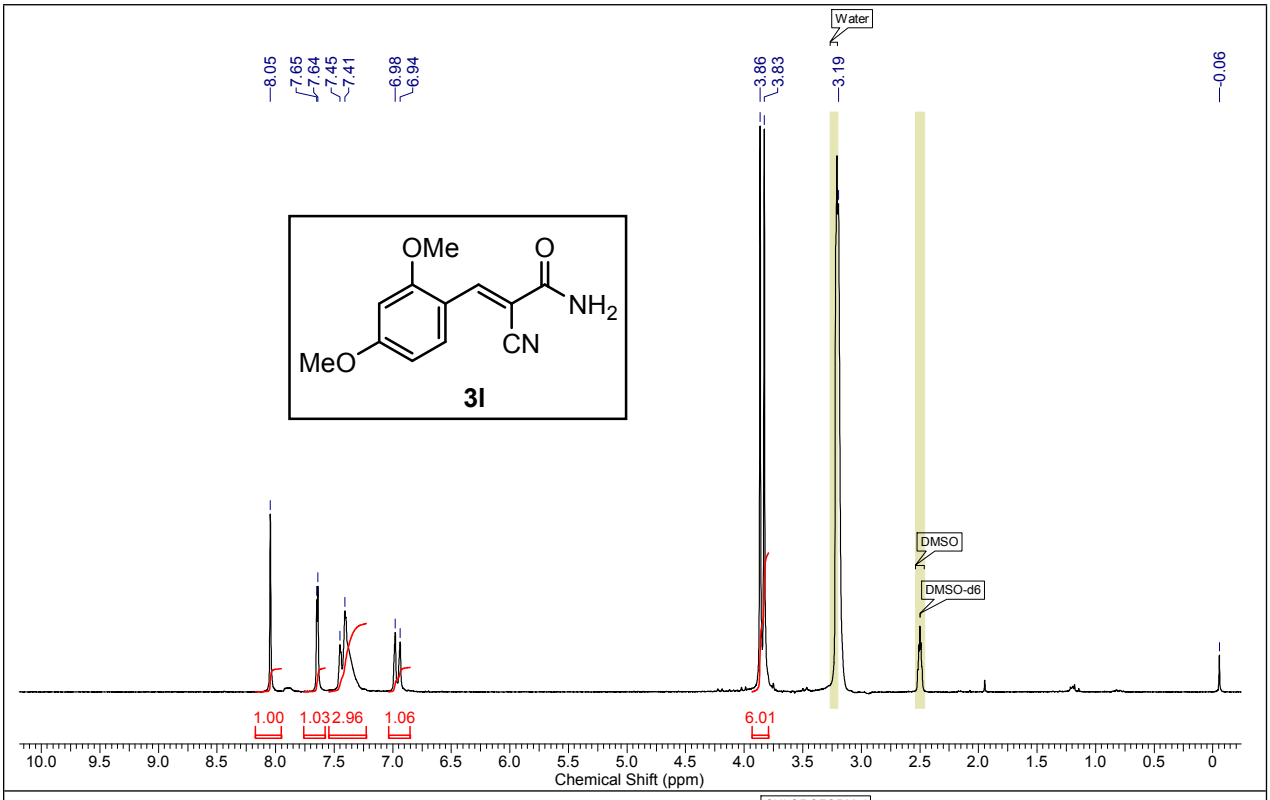

DMSO-d6
Water
10.26
8.00
7.81
7.77
7.37
6.87
6.82
2.52
2.51
2.50
2.49
2.48
O
NH2
CN
HO
3i
1.00
1.00
2.03
2.00
2.04
Chemical Shift (ppm)

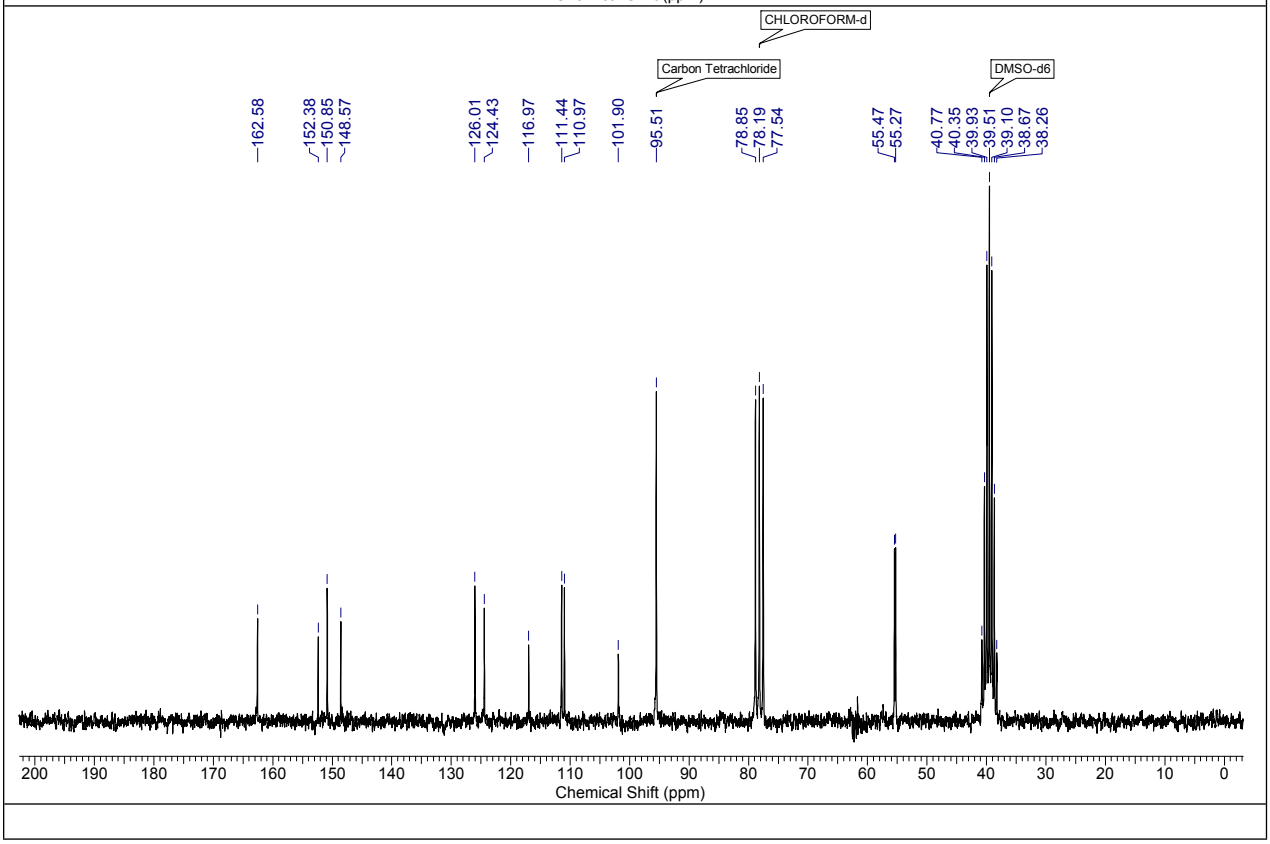

Carbon Tetrachloride
CHLOROFORM-d
DMSO-d6
163.06
161.75
150.88
132.70
122.80
117.17
115.99
100.54
95.57
79.03
78.38
77.73
40.76
40.34
39.92
39.51
39.09
38.67
38.25
Chemical Shift (ppm)

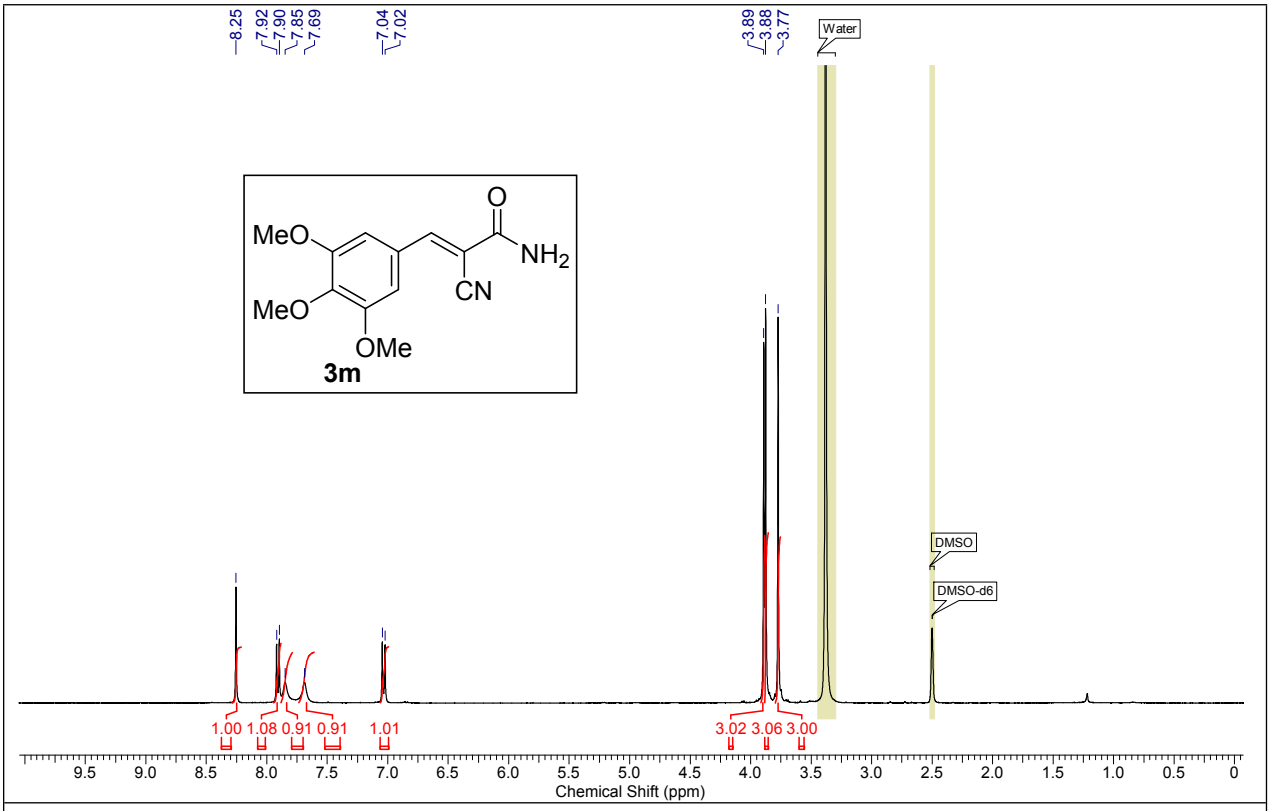

CHLOROFORM-d
8.62
7.65
7.64
7.27
7.00
6.99
6.96
6.94
6.86
6.85
6.83
6.78
6.68
6.58
3.75
3.71
OMe
O
NH2
CN
OMe
3j
DMSO
DMSO-d6
1.01
1.06
1.18
1.24
2.23
3.02
3.16
Chemical Shift (ppm)
20180301-095549-11772.004.001.1r.esp
DMSO-d6
162.57
152.78
152.72
145.37
120.81
119.83
116.65
113.09
112.83
106.58
56.25
55.52
39.51
Chemical Shift (ppm)

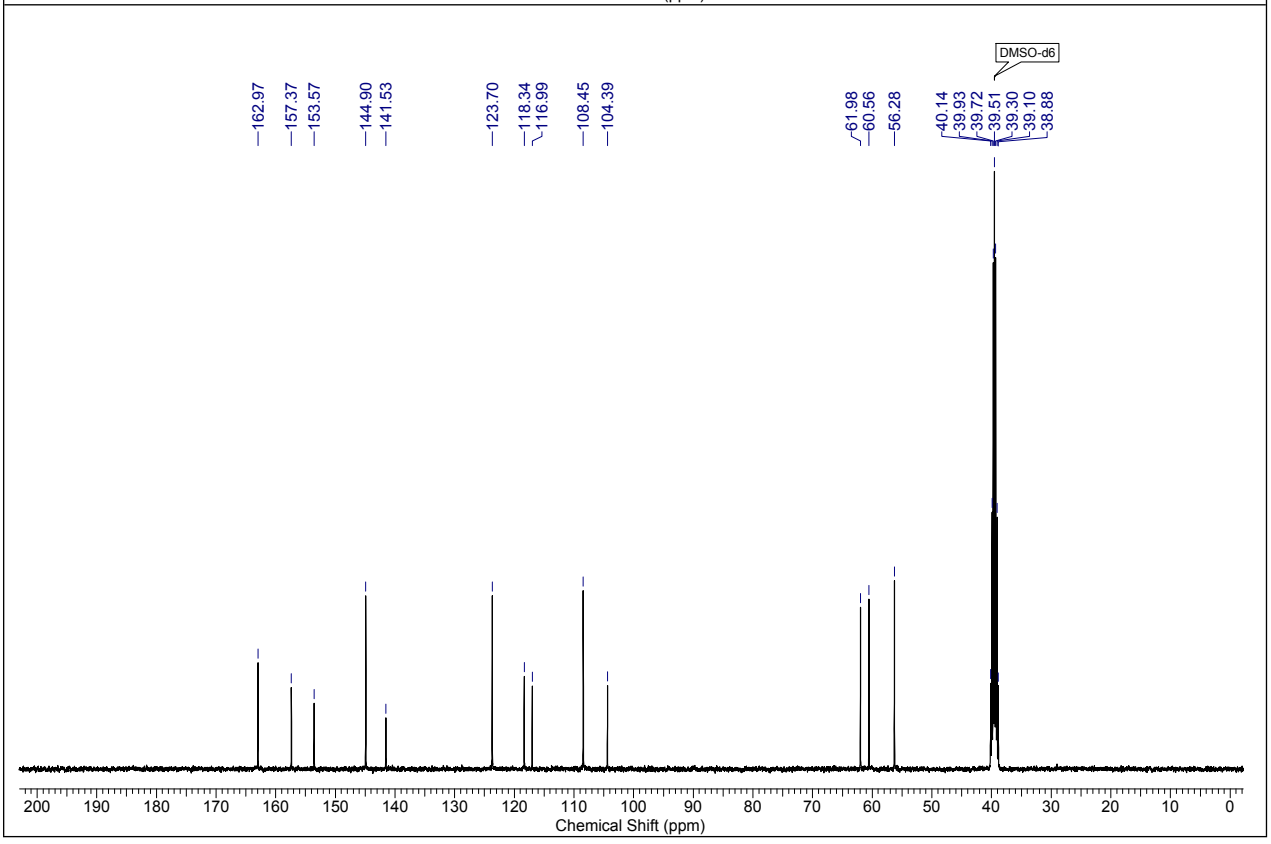

8.15
8.11
7.73
7.72
7.67
7.66
7.59
7.58
7.55
7.54
7.17
7.12
3.86
3.81
2.50
MeO
MeO
O
NH2
CN
3k
1.01 1.69 0.86 0.93 1.14
3.28 3.07
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

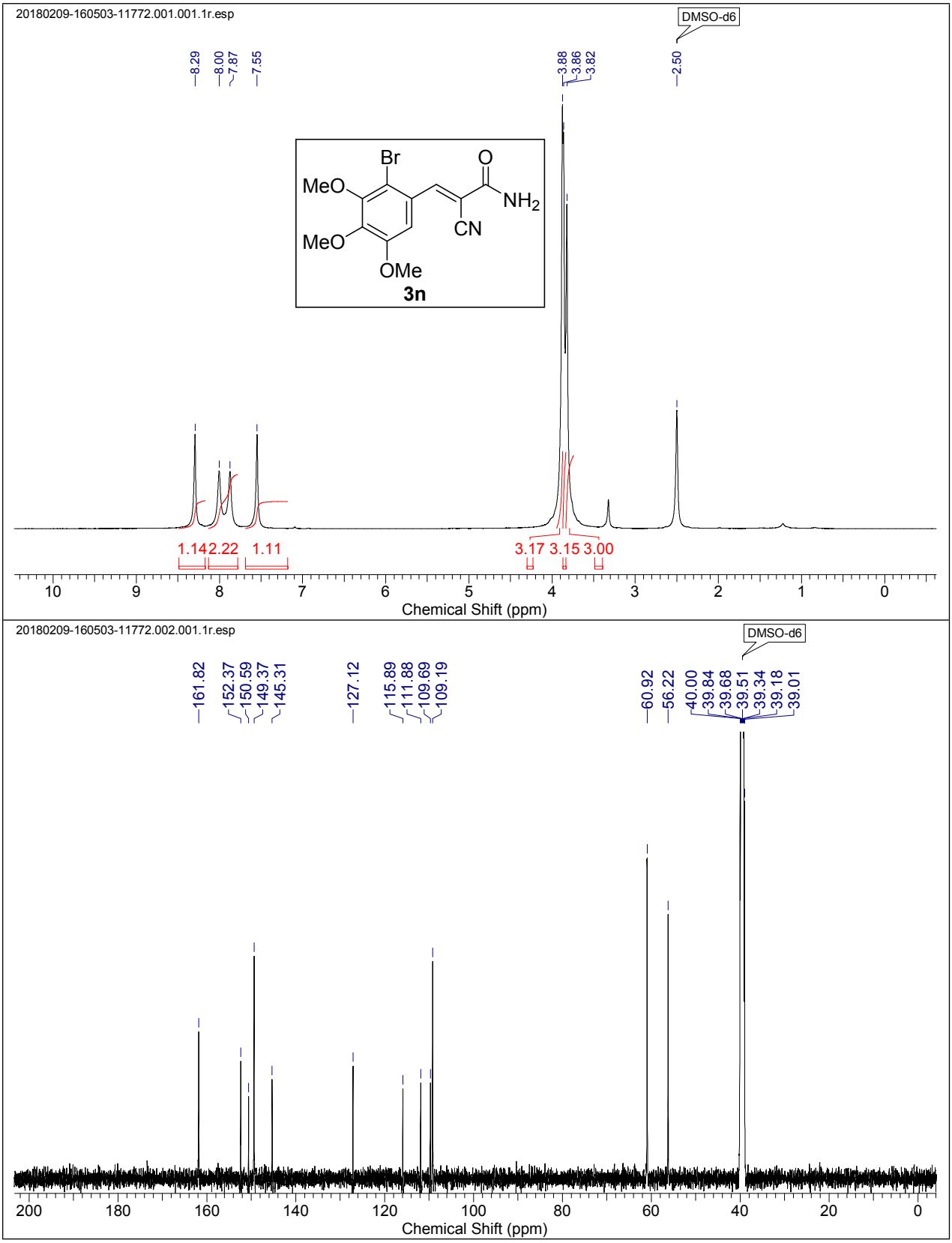

DMSO-d6
163.13
152.54
150.61
148.70
125.56
124.49
117.25
112.23
111.83
102.84
55.80
55.47
40.34
39.92
39.51
39.09
38.67
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

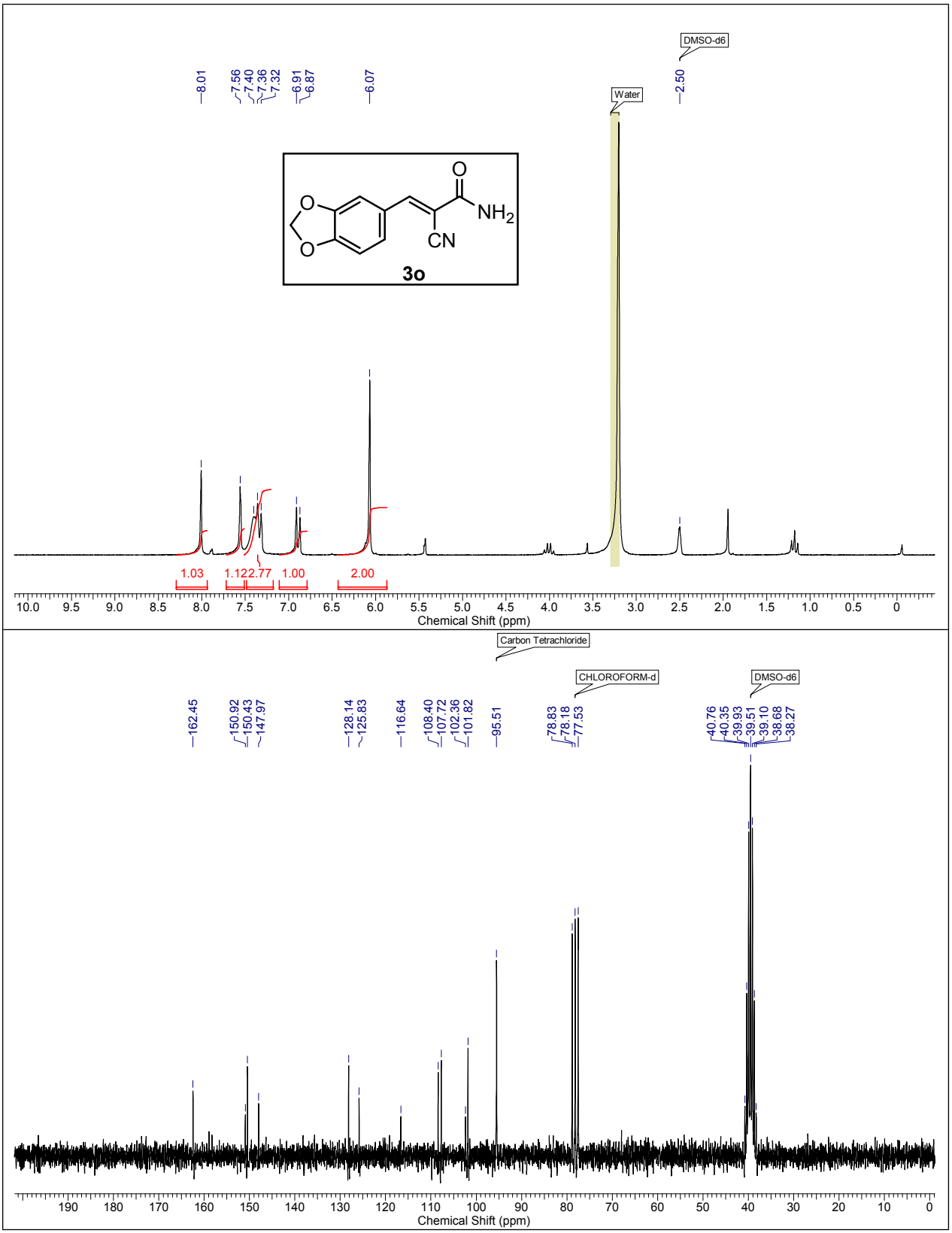

Water
8.05
7.65
7.64
7.45
7.41
6.98
6.94
3.86
3.83
3.19
0.06
OMe
O
NH2
CN
MeO
3l
DMSO
DMSO-d6
1.00
1.03
2.96
1.06
6.01
Chemical Shift (ppm)

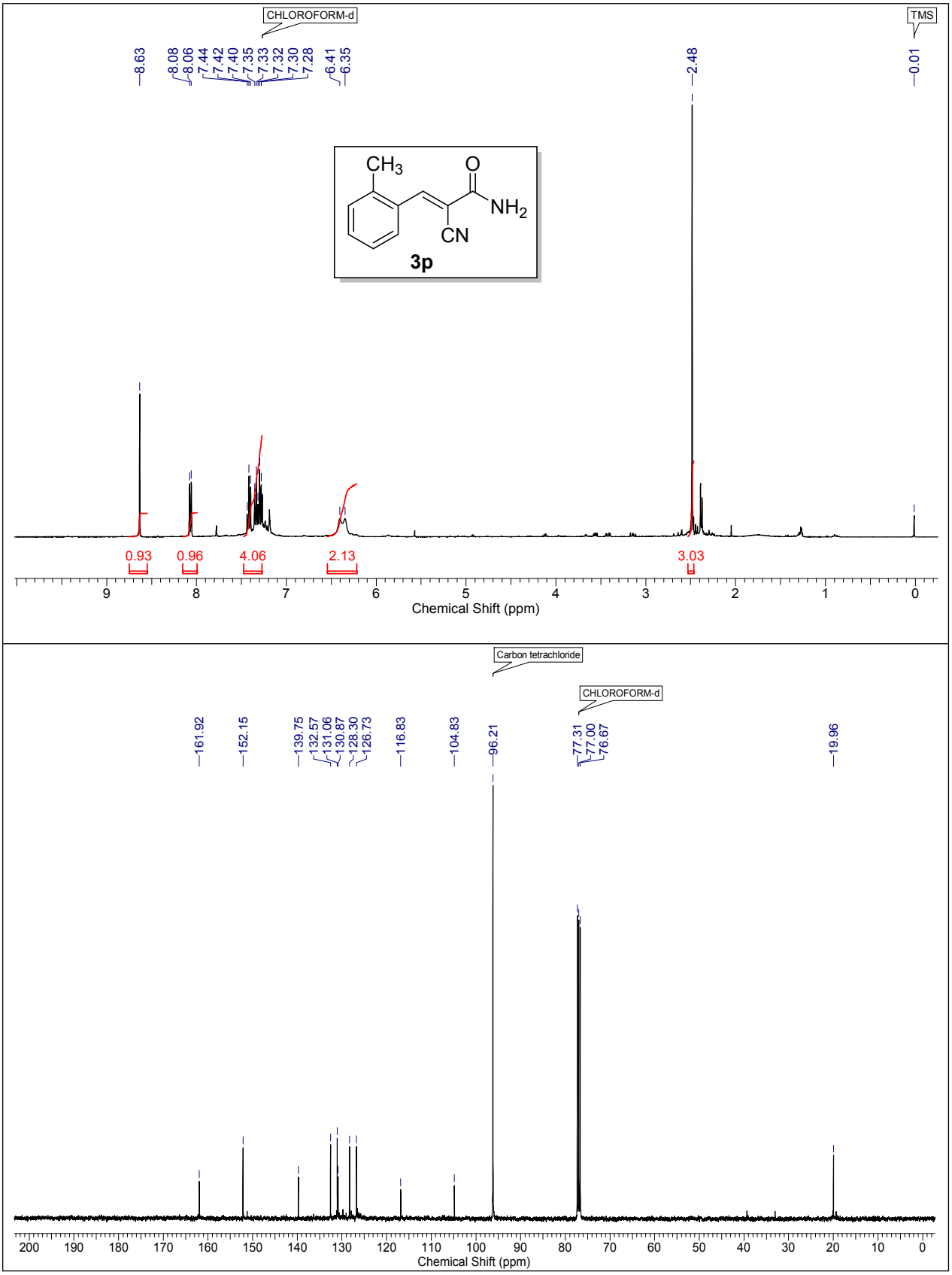

CHLOROFORM-d
Carbon Tetrachloride
DMSO-d6
162.58
152.38
150.85
148.57
126.01
124.43
116.97
111.44
110.97
101.90
95.51
78.85
78.19
77.54
55.47
55.27
40.77
40.35
39.93
39.51
39.10
38.67
38.26
Chemical Shift (ppm)

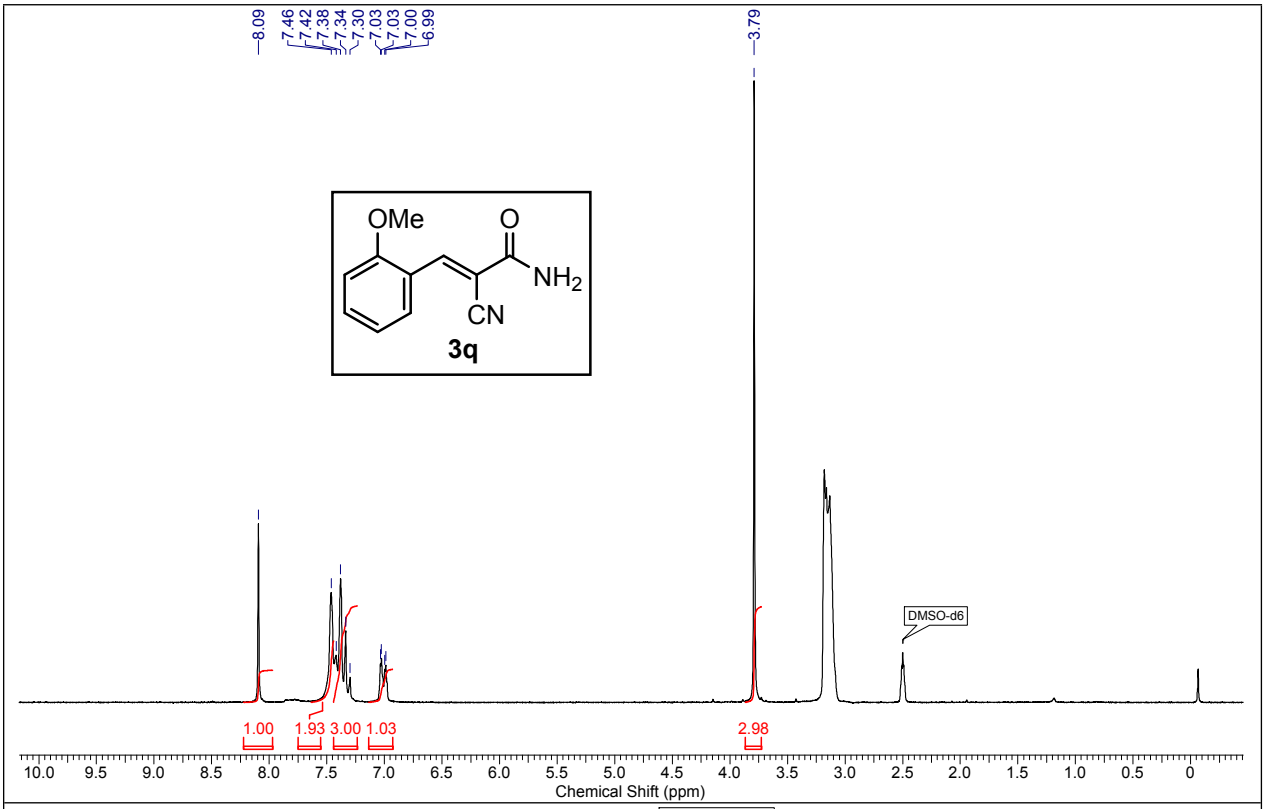

8.25
7.92
7.90
7.85
7.69
7.04
7.02
3.89
3.88
3.77
Water
DMSO
DMSO-d6
MeO
MeO
OMe
O
NH2
CN
3m
1.00 1.08 0.91 0.91 1.01
3.02 3.06 3.00
Chemical Shift (ppm)

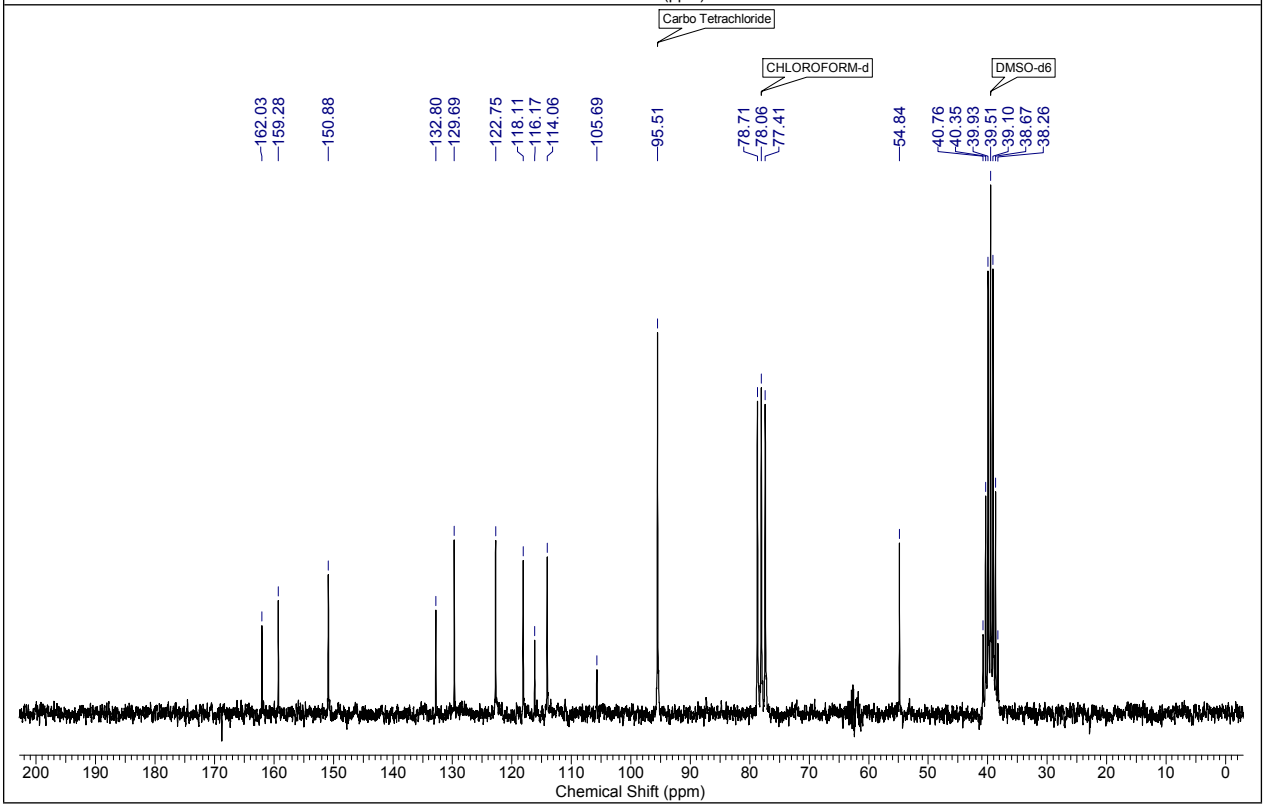

DMSO-d6
162.97
157.37
153.57
144.90
141.53
123.70
118.34
116.99
108.45
104.39
61.98
60.56
56.28
40.14
39.93
39.72
39.51
39.30
39.10
38.88
Chemical Shift (ppm)

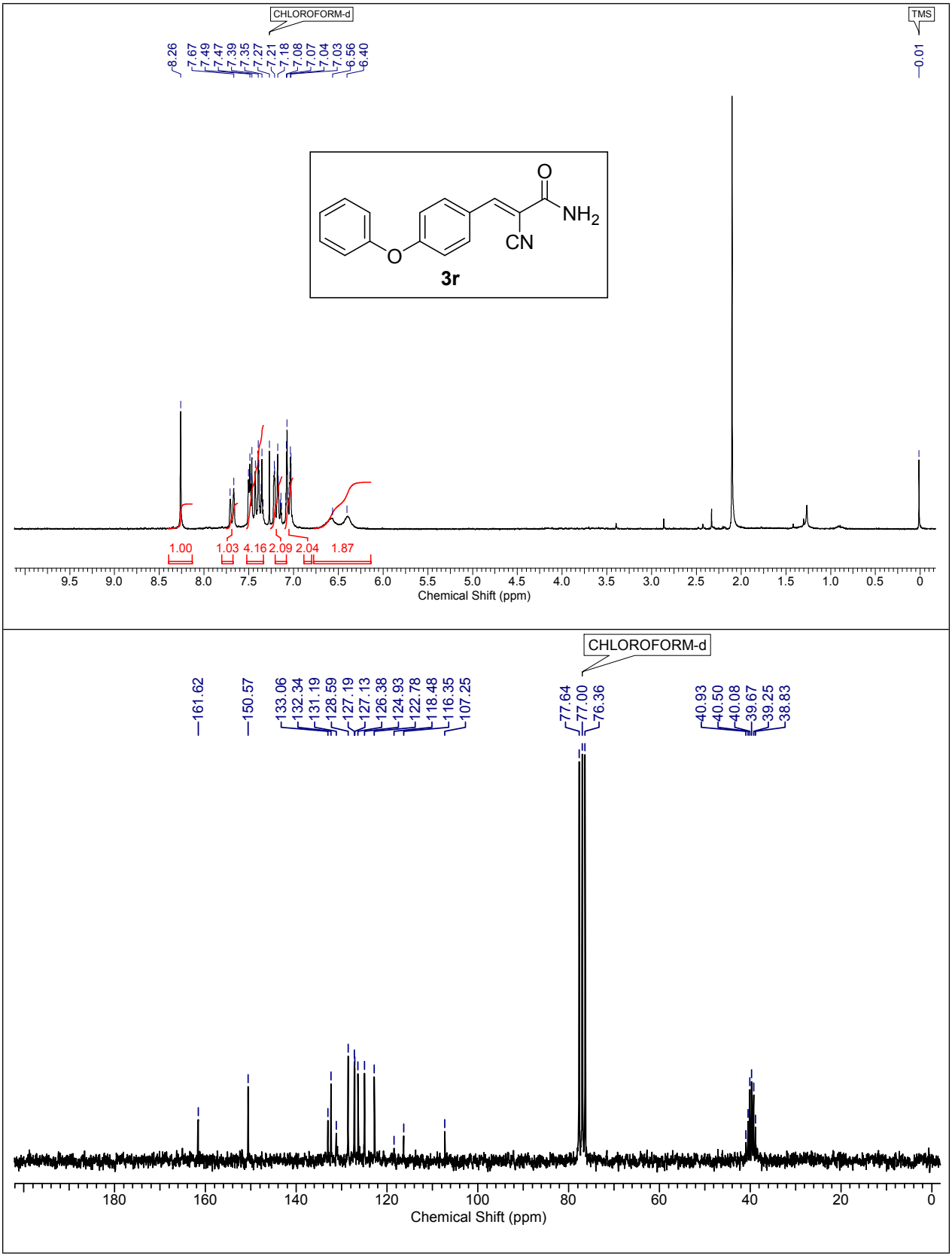

20180209-160503-11772.001.001.1r.esp
DMSO-d6
8.29
8.00
7.87
7.55
3.88
3.86
3.82
2.50
Br
O
MeO
NH2
CN
MeO
OMe
3n
1.14 2.22 1.11
3.17 3.15 3.00
Chemical Shift (ppm)
20180209-160503-11772.002.001.1r.esp
DMSO-d6
161.82
152.37
150.59
149.37
145.31
127.12
115.89
111.88
109.69
109.19
60.92
56.22
40.00
39.84
39.68
39.51
39.34
39.18
39.01
Chemical Shift (ppm)

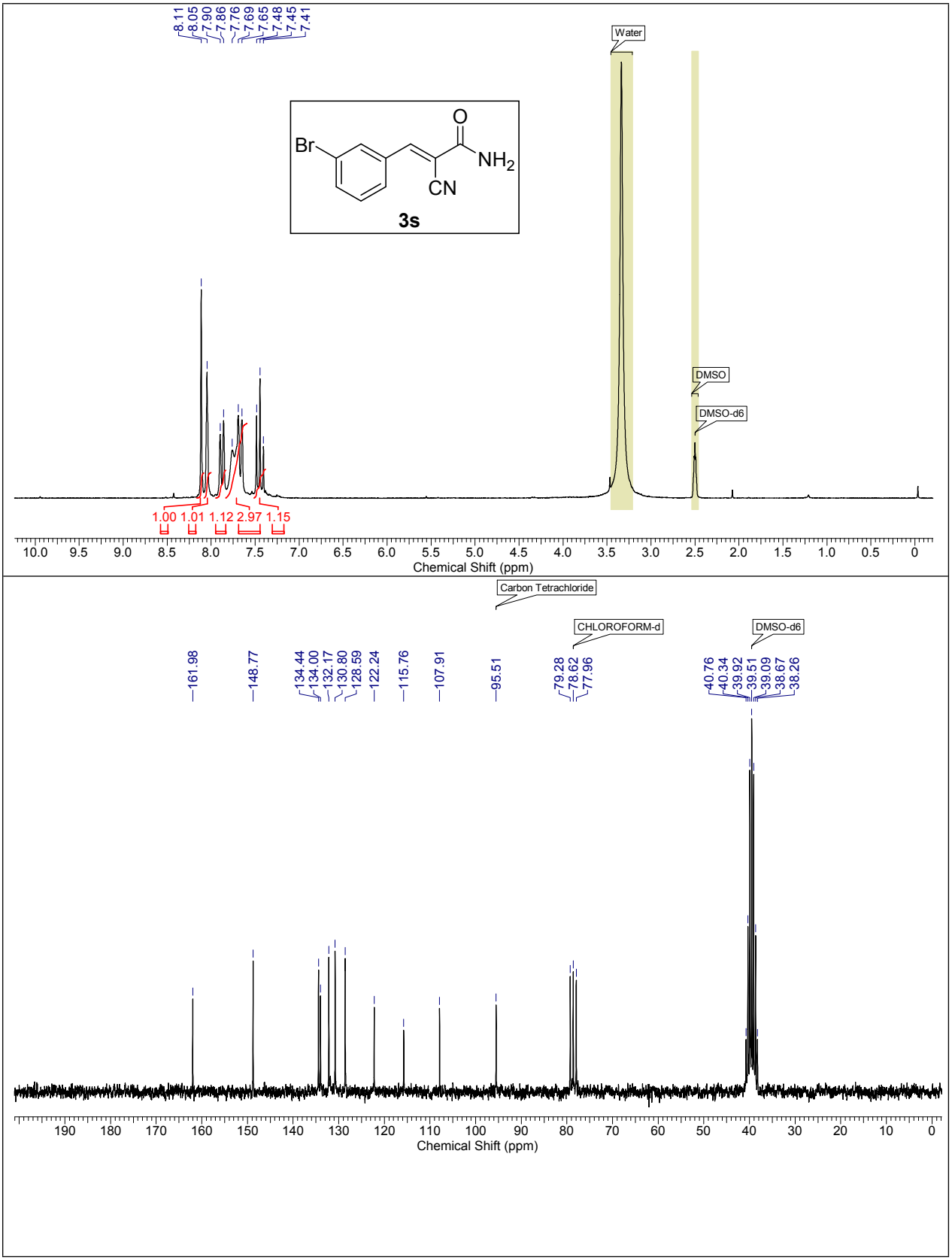

DMSO-d6
Water
8.01
7.56
7.40
7.36
7.32
6.91
6.87
6.07
2.50
O
O
O
NH2
CN
3o
1.03
1.12
2.77
1.00
2.00
Chemical Shift (ppm)
Carbon Tetrachloride
CHLOROFORM-d
DMSO-d6
162.45
150.92
150.43
147.97
128.14
125.83
116.64
108.40
107.72
102.36
101.82
95.51
78.83
78.18
77.53
40.76
40.35
39.93
39.51
39.10
38.68
38.27
Chemical Shift (ppm)

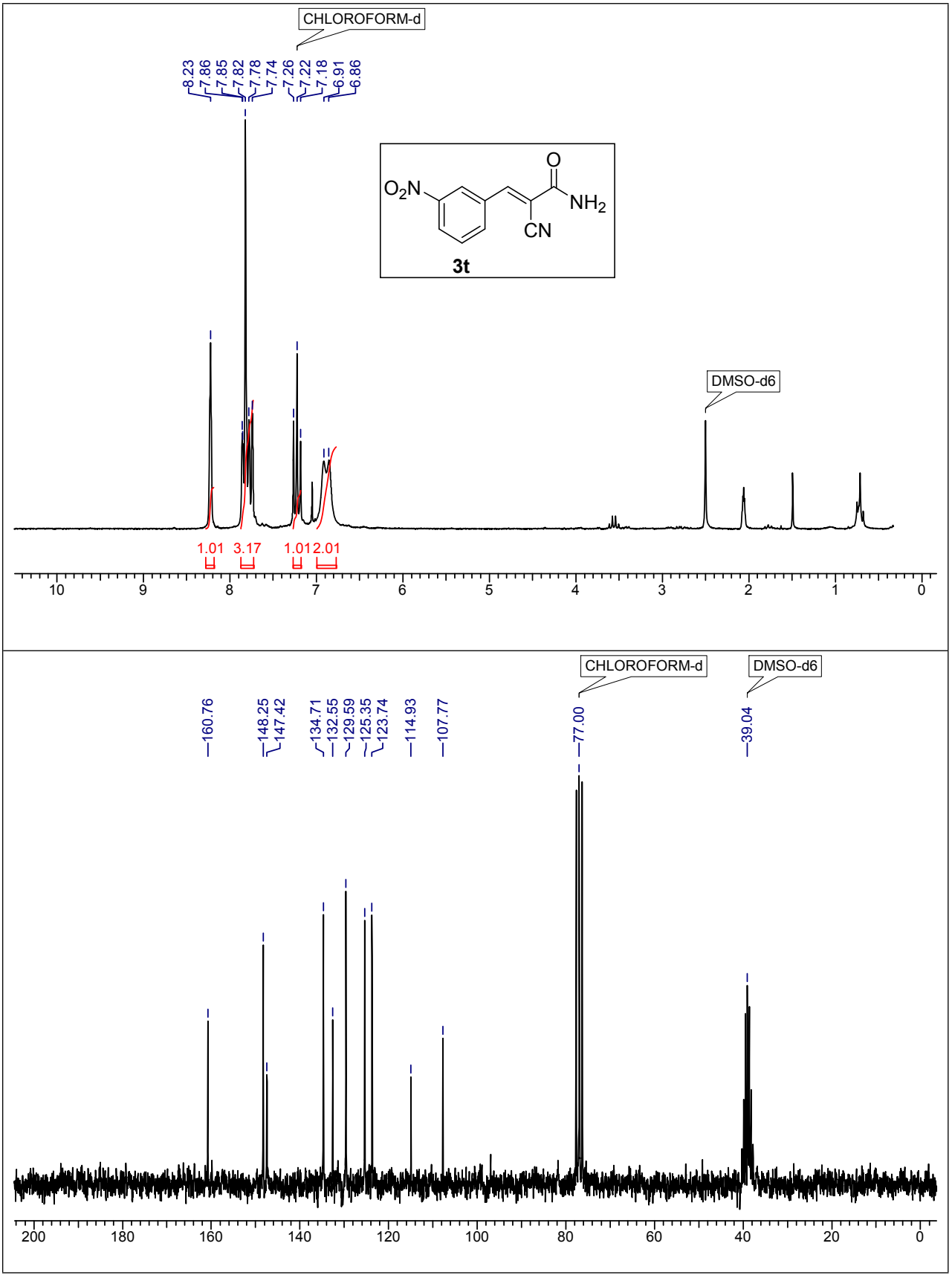

CHLOROFORM-d
TMS
8.63
8.08
8.06
7.44
7.42
7.40
7.35
7.33
7.32
7.30
7.28
6.41
6.35
2.48
0.01
CH3
O
NH2
CN
3p
0.93
0.96
4.06
2.13
3.03
Chemical Shift (ppm)
Carbon tetrachloride
CHLOROFORM-d
161.92
152.15
139.75
132.57
131.06
130.87
128.30
126.73
116.83
104.83
96.21
77.31
77.00
76.67
19.96
Chemical Shift (ppm)

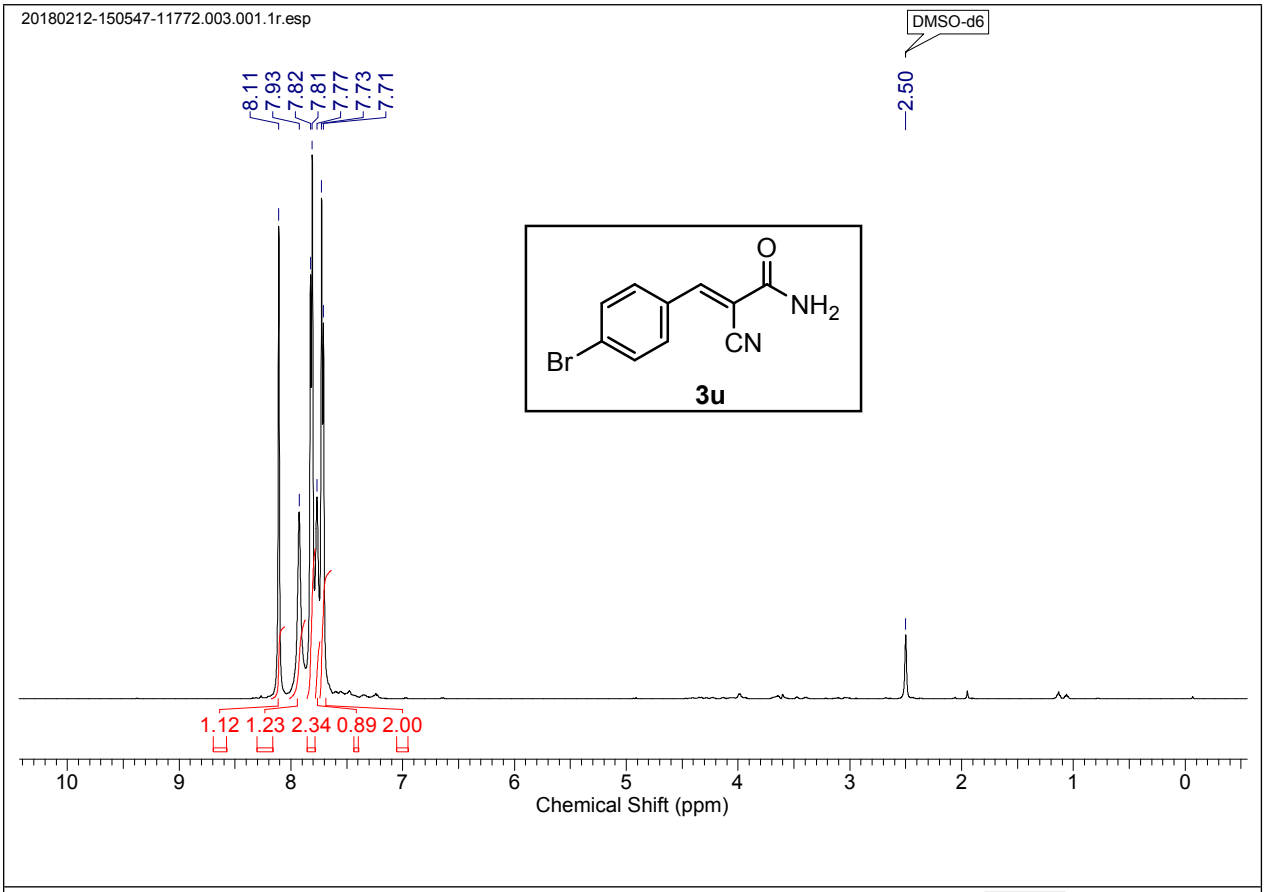

8.09
7.46
7.42
7.38
7.34
7.30
7.03
7.03
7.00
6.99
3.79
OMe
O
NH2
CN
3q
DMSO-d6
1.00
1.93
3.00
1.03
2.98
Chemical Shift (ppm)

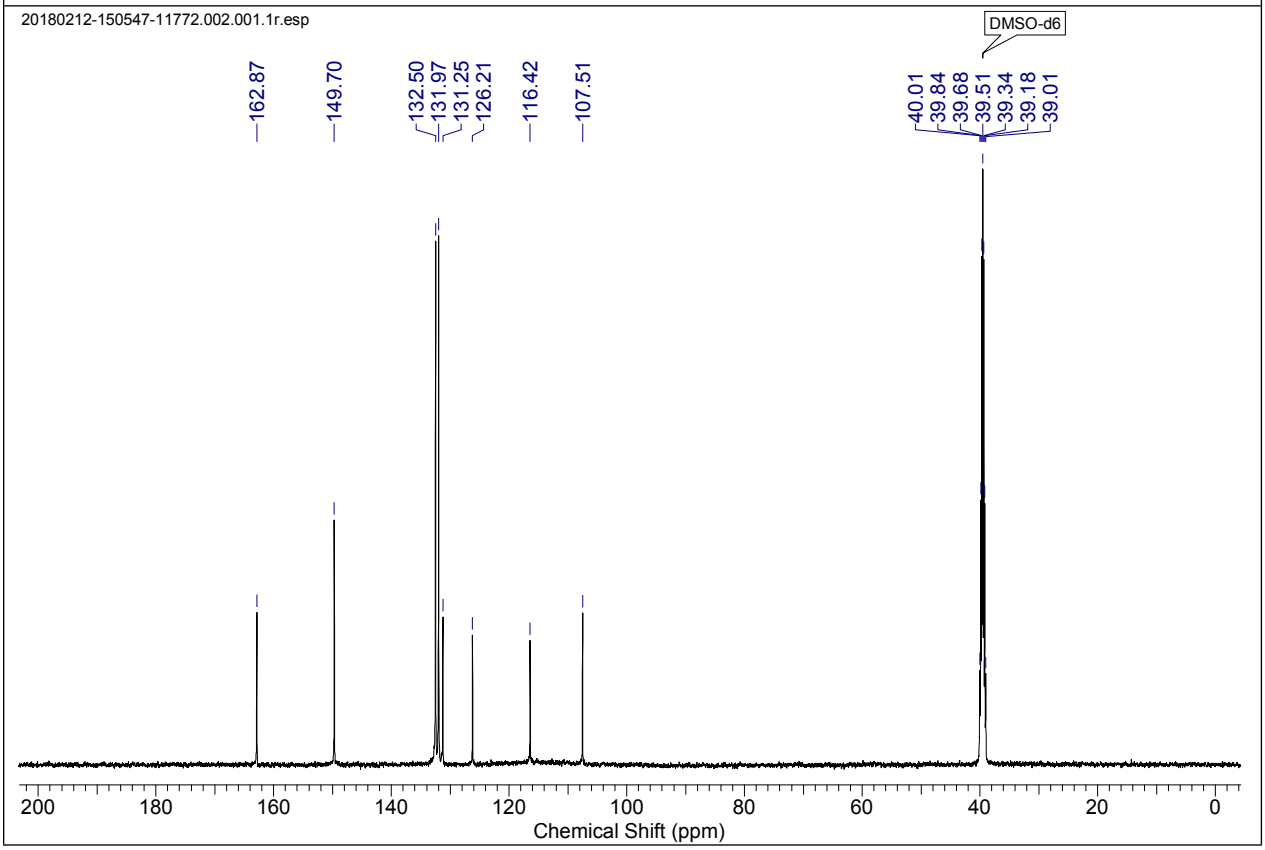

Carbo Tetrachloride
CHLOROFORM-d
DMSO-d6
162.03
159.28
150.88
132.80
129.69
122.75
118.11
116.17
114.06
105.69
95.51
78.71
78.06
77.41
54.84
40.76
40.35
39.93
39.51
39.10
38.67
38.26
Chemical Shift (ppm)

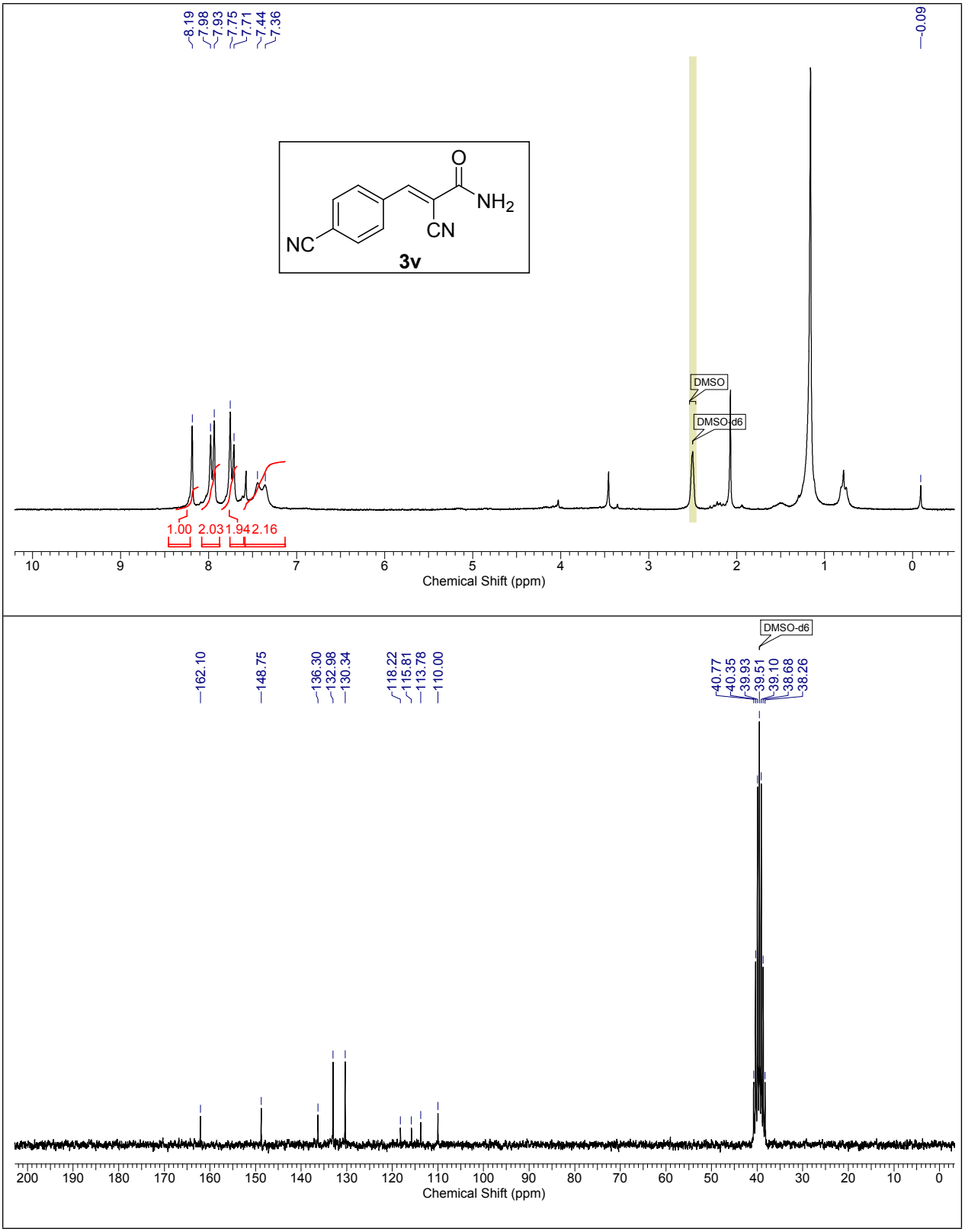

CHLOROFORM-d
TMS
8.26
7.67
7.49
7.47
7.39
7.35
7.27
7.21
7.18
7.08
7.07
7.04
7.03
6.56
6.40
0.01
O
NH2
CN
O
3r
1.00
1.03
4.16
2.09
2.04
1.87
Chemical Shift (ppm)
CHLOROFORM-d
161.62
150.57
133.06
132.34
131.19
128.59
127.19
127.13
126.38
124.93
122.78
118.48
116.35
107.25
77.64
77.00
76.36
40.93
40.50
40.08
39.67
39.25
38.83
Chemical Shift (ppm)

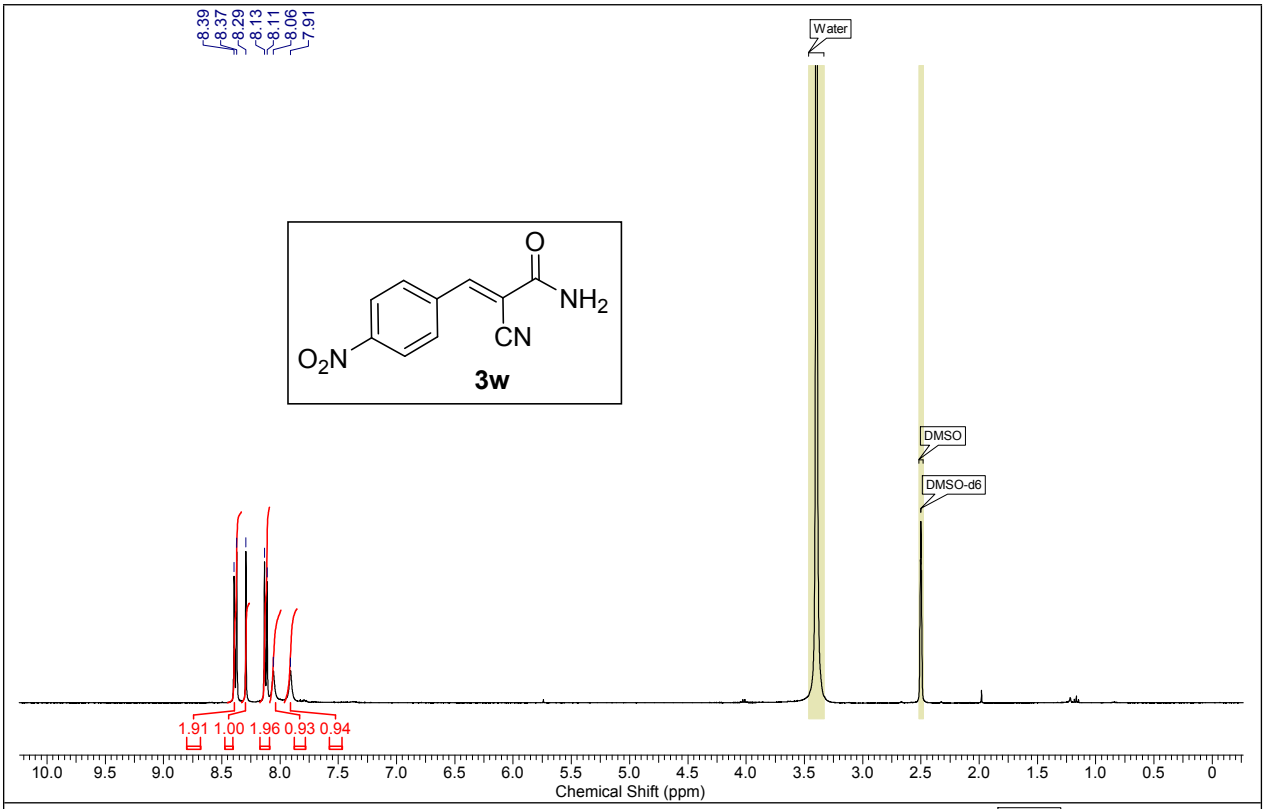

8.11
8.05
7.90
7.86
7.76
7.69
7.65
7.48
7.45
7.41
Water
DMSO
DMSO-d6
Br
O
NH2
CN
3s
1.00 1.01 1.12 2.97 1.15
Chemical Shift (ppm)
Carbon Tetrachloride
CHLOROFORM-d
DMSO-d6
161.98
148.77
134.44
134.00
132.17
130.80
128.59
122.24
115.76
107.91
95.51
79.28
78.62
77.96
40.76
40.34
39.92
39.51
39.09
38.67
38.26
Chemical Shift (ppm)

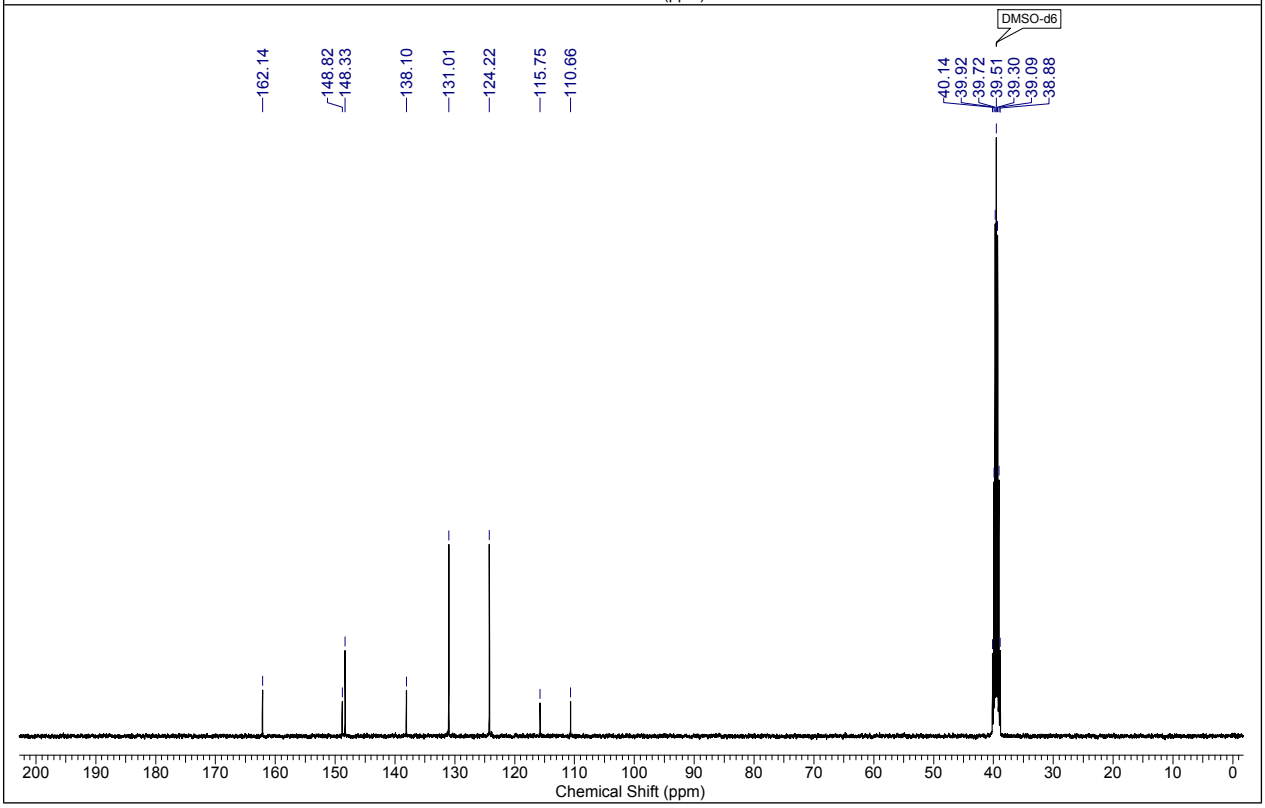

CHLOROFORM-d
8.23
7.86
7.85
7.82
7.78
7.74
7.26
7.22
7.18
6.91
6.86
O
O_2N
NH_2
CN
3t
DMSO-d6
1.01
3.17
1.01
2.01
10
9
8
7
6
5
4
3
2
1
0
CHLOROFORM-d
DMSO-d6
160.76
148.25
147.42
134.71
132.55
129.59
125.35
123.74
114.93
107.77
77.00
39.04
200
180
160
140
120
100
80
60
40
20
0

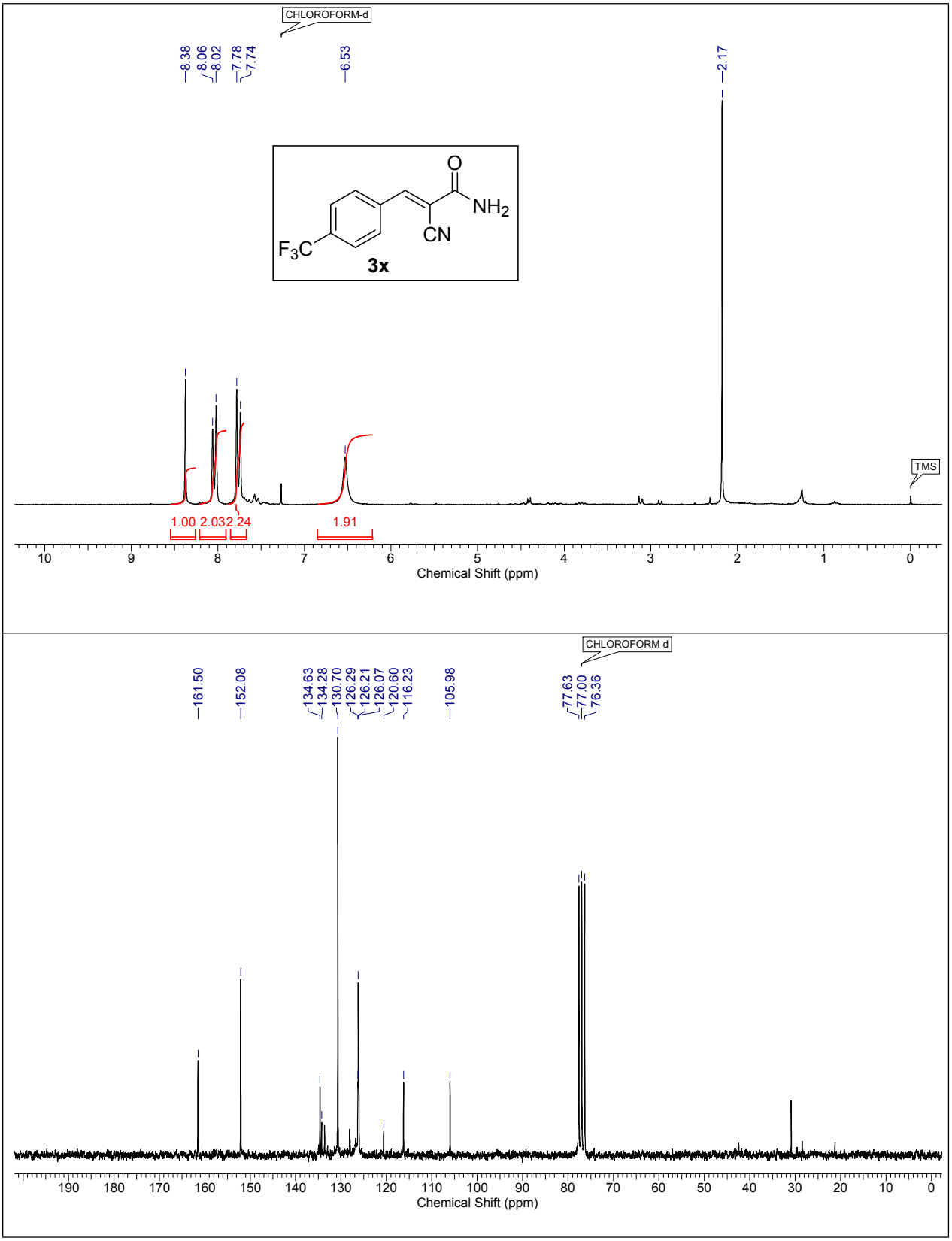

20180212-150547-11772.003.001.1r.esp
DMSO-d6
8.11
7.93
7.82
7.81
7.77
7.73
7.71
2.50
O
NH2
CN
Br
3u
1.12 1.23 2.34 0.89 2.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

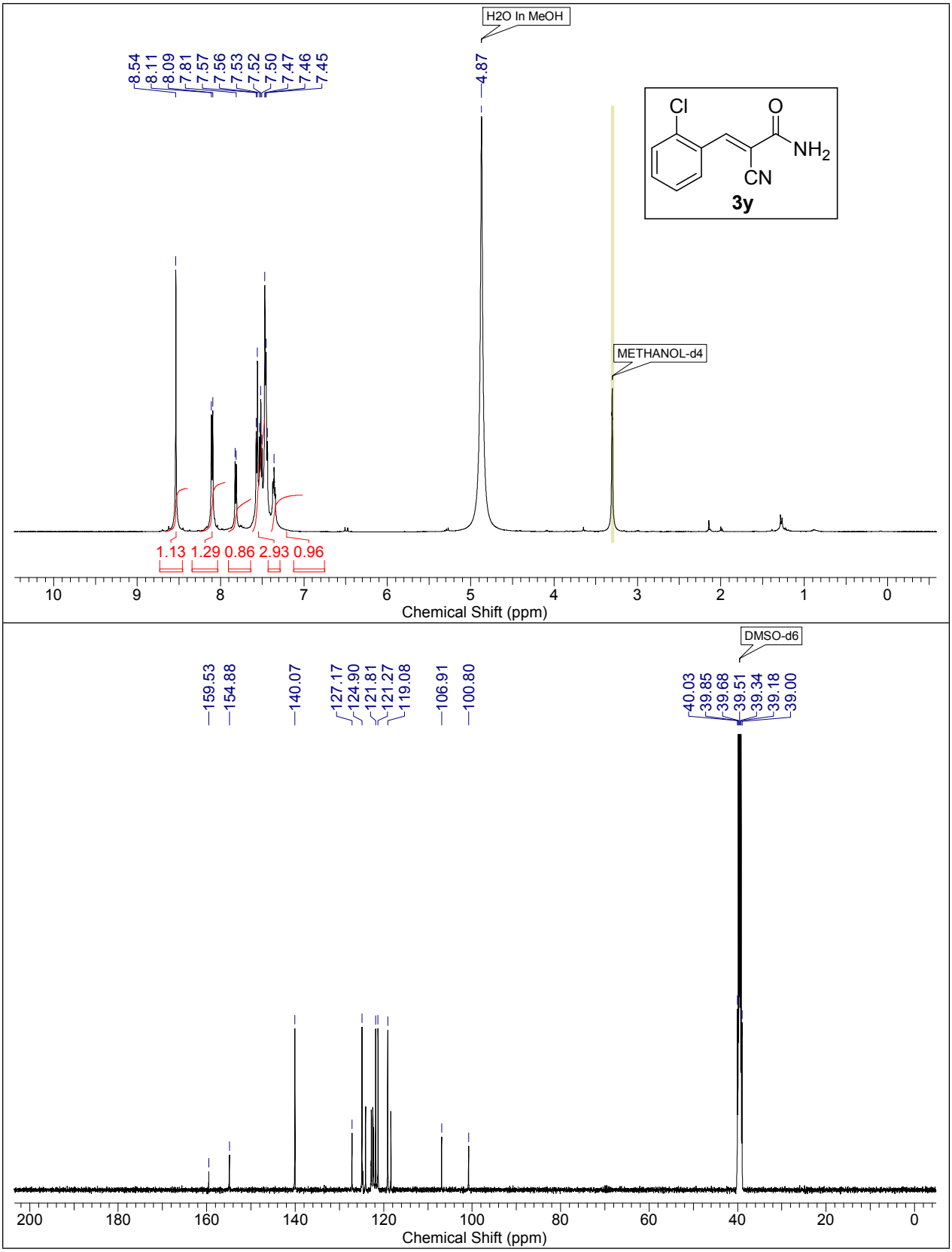

20180212-150547-11772.002.001.1r.esp
DMSO-d6
162.87
149.70
132.50
131.97
131.25
126.21
116.42
107.51
40.01
39.84
39.68
39.51
39.34
39.18
39.01
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

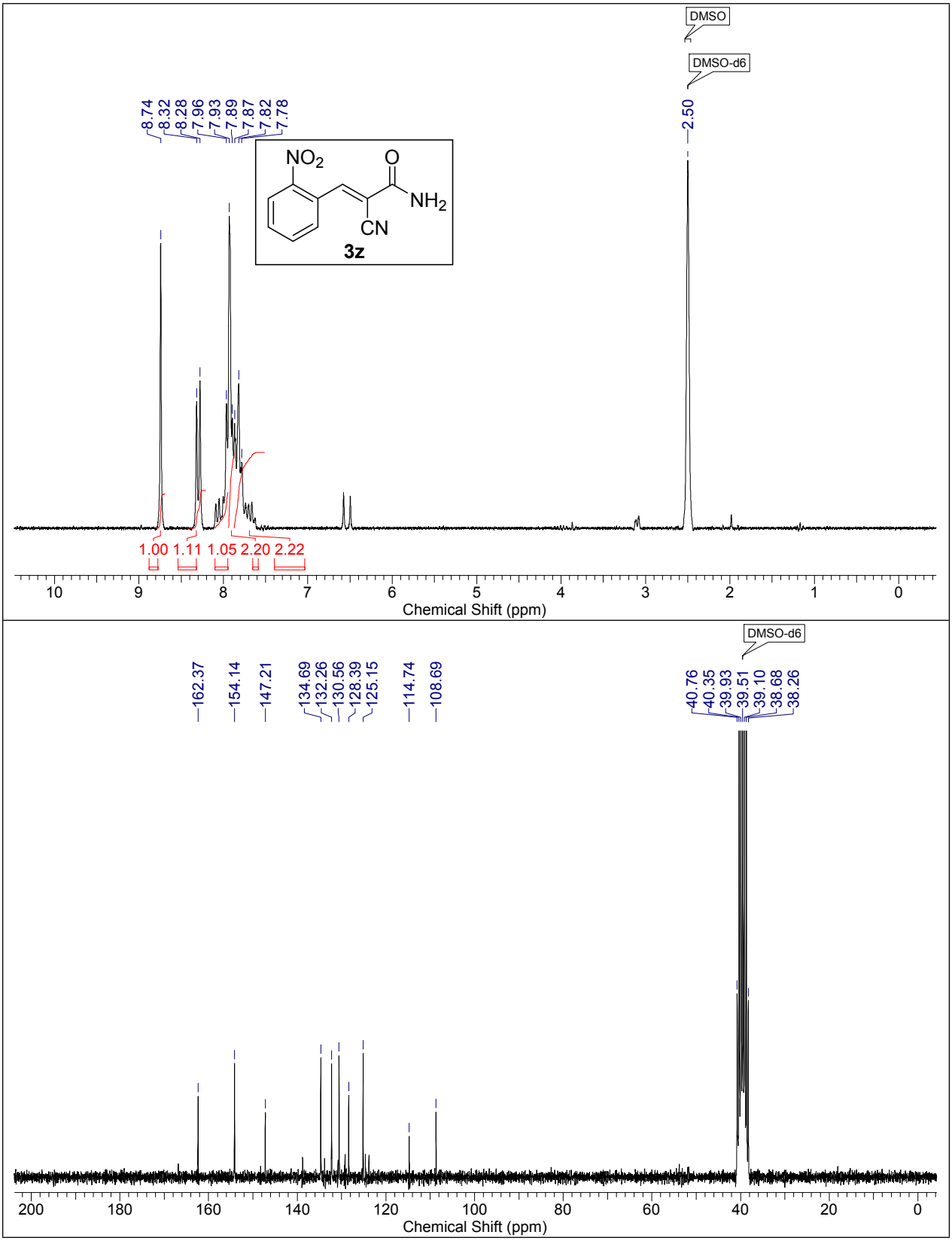

8.19
7.98
7.93
7.75
7.71
7.44
7.36
0.09
O
NH2
CN
NC
3v
DMSO
DMSO-d6
1.00 2.03 1.94 2.16
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
DMSO-d6
162.10
148.75
136.30
132.98
130.34
118.22
115.81
113.78
110.00
40.77
40.35
39.93
39.51
39.10
38.68
38.26
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

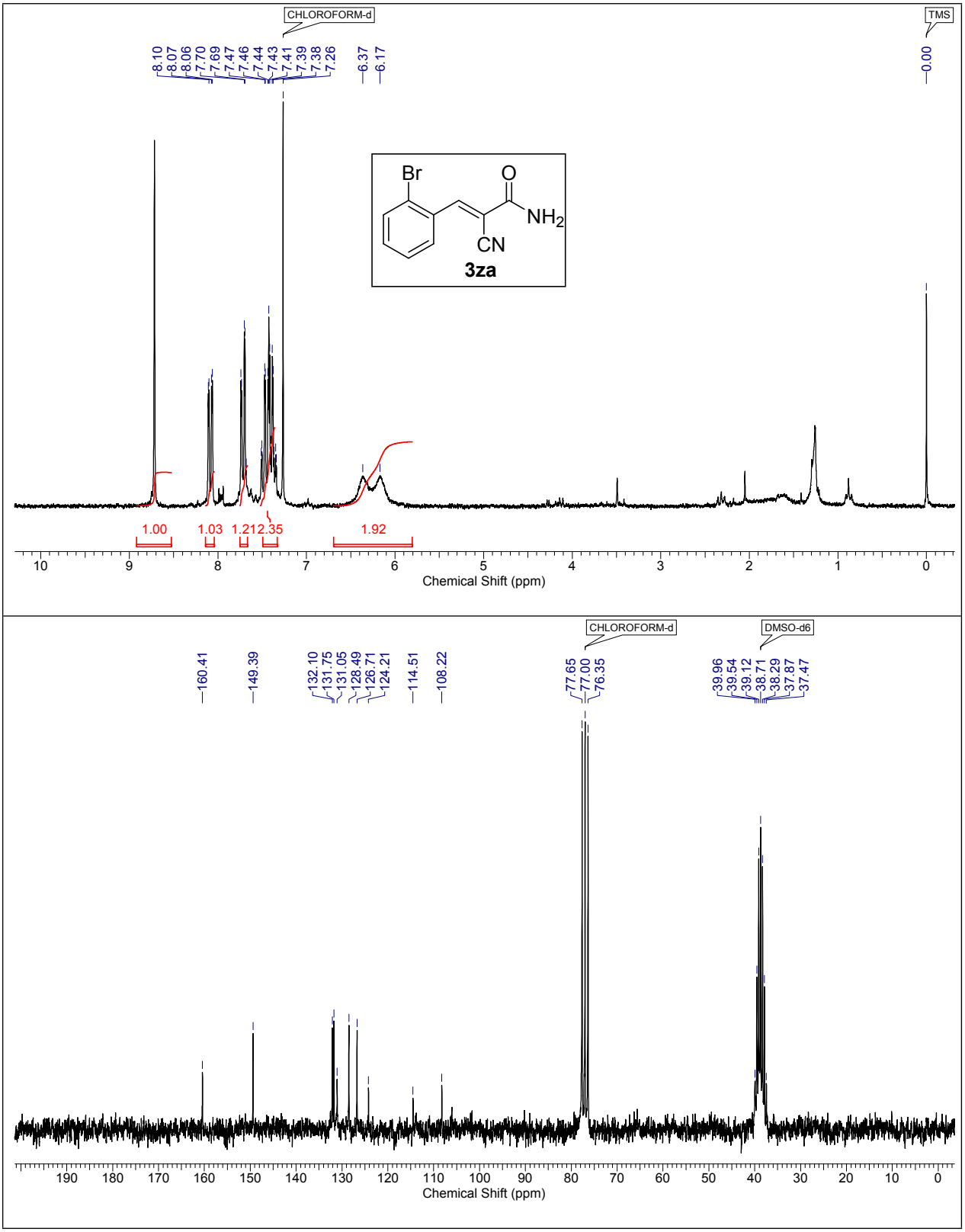

8.39
8.37
8.29
8.13
8.11
8.06
7.91
Water
DMSO
DMSO-d6
O
NH2
CN
O2N
3w
1.91 1.00 1.96 0.93 0.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

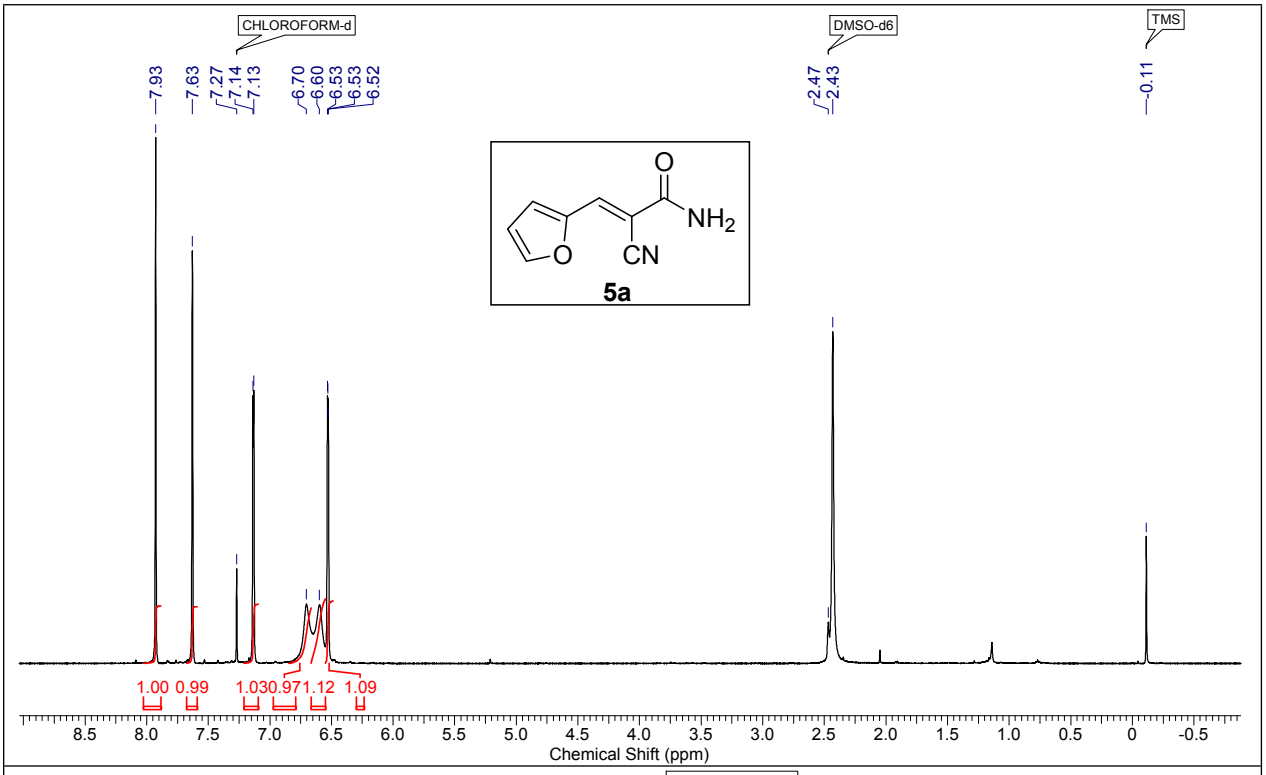

DMSO-d6
162.14
148.82
148.33
138.10
131.01
124.22
115.75
110.66
40.14
39.92
39.72
39.51
39.30
39.09
38.88
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

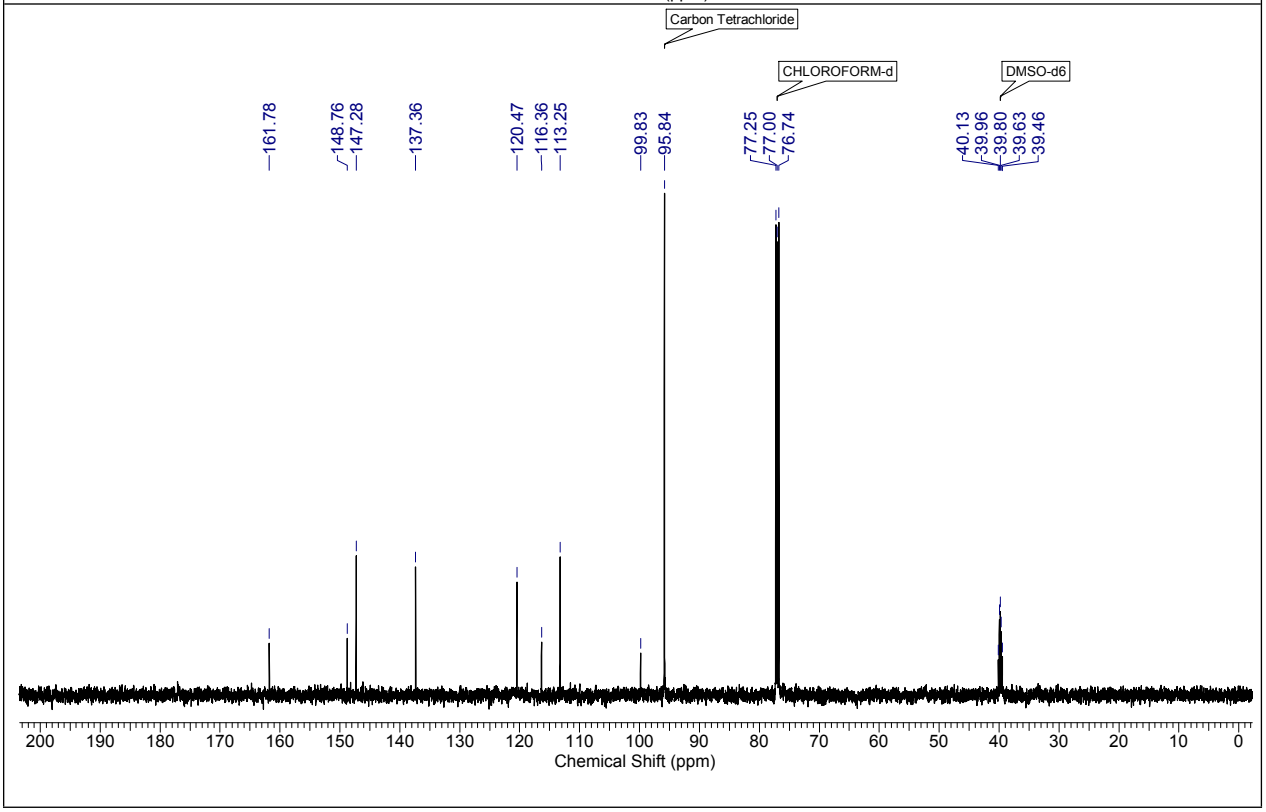

CHLOROFORM-d
8.38
8.06
8.02
7.78
7.74
6.53
2.17
O
NH2
CN
F3C
3x
TMS
1.00
2.03
2.24
1.91
Chemical Shift (ppm)
CHLOROFORM-d
161.50
152.08
134.63
134.28
130.70
126.29
126.21
126.07
120.60
116.23
105.98
77.63
77.00
76.36
Chemical Shift (ppm)

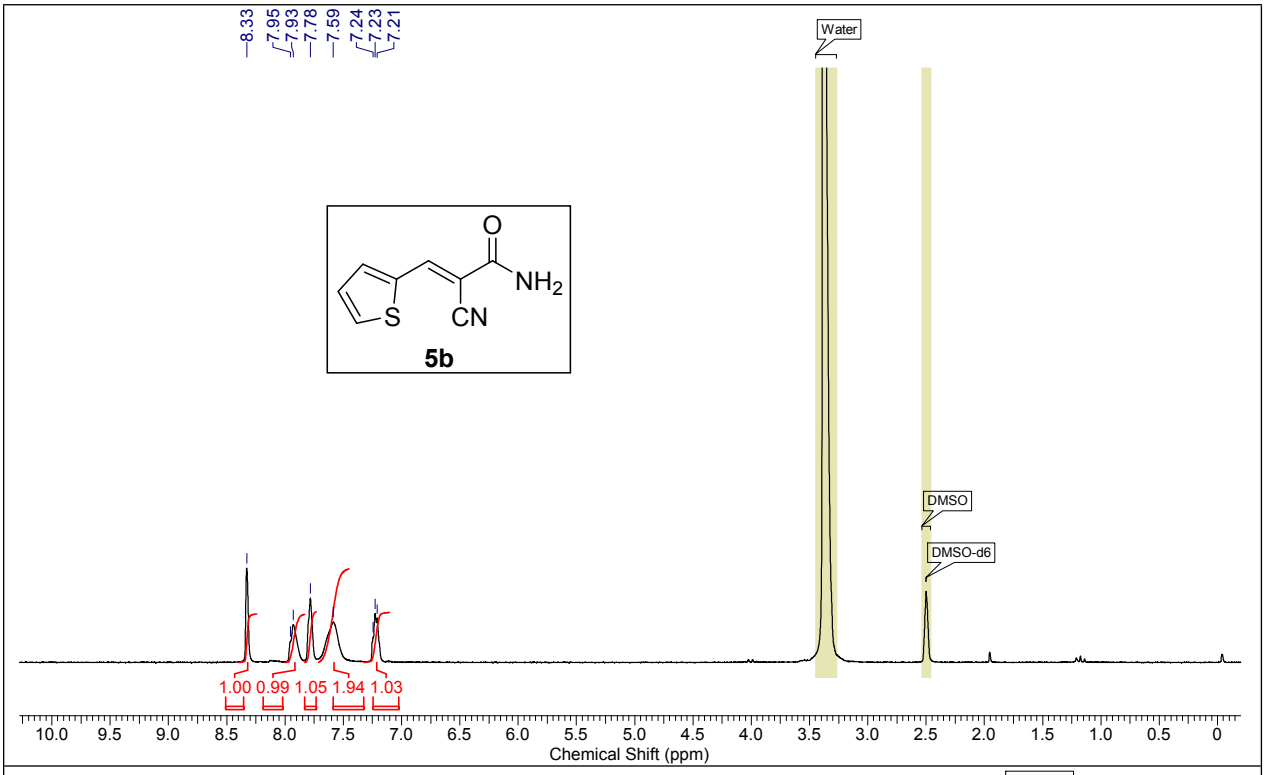

H2O In MeOH
8.54
8.11
8.09
7.81
7.57
7.56
7.53
7.52
7.50
7.47
7.46
7.45
4.87
Cl
O
NH2
CN
3y
METHANOL-d4
1.13 1.29 0.86 2.93 0.96
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
DMSO-d6
159.53
154.88
140.07
127.17
124.90
121.81
121.27
119.08
106.91
100.80
40.03
39.85
39.68
39.51
39.34
39.18
39.00
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

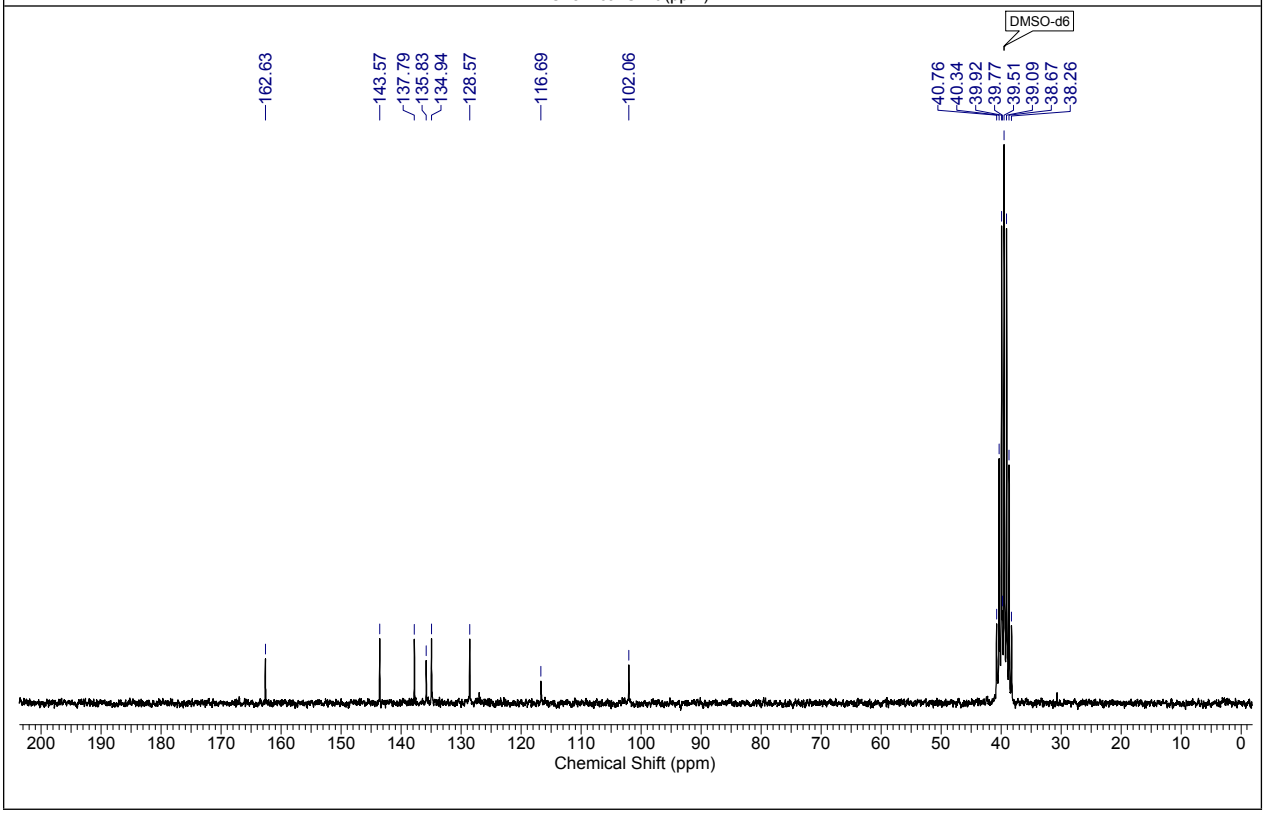

DMSO
DMSO-d6
8.74
8.32
8.28
7.96
7.93
7.89
7.87
7.82
7.78
2.50
NO2
O
NH2
CN
3z
1.00 1.11 1.05 2.20 2.22
Chemical Shift (ppm)
DMSO-d6
162.37
154.14
147.21
134.69
132.26
130.56
128.39
125.15
114.74
108.69
40.76
40.35
39.93
39.51
39.10
38.68
38.26
Chemical Shift (ppm)

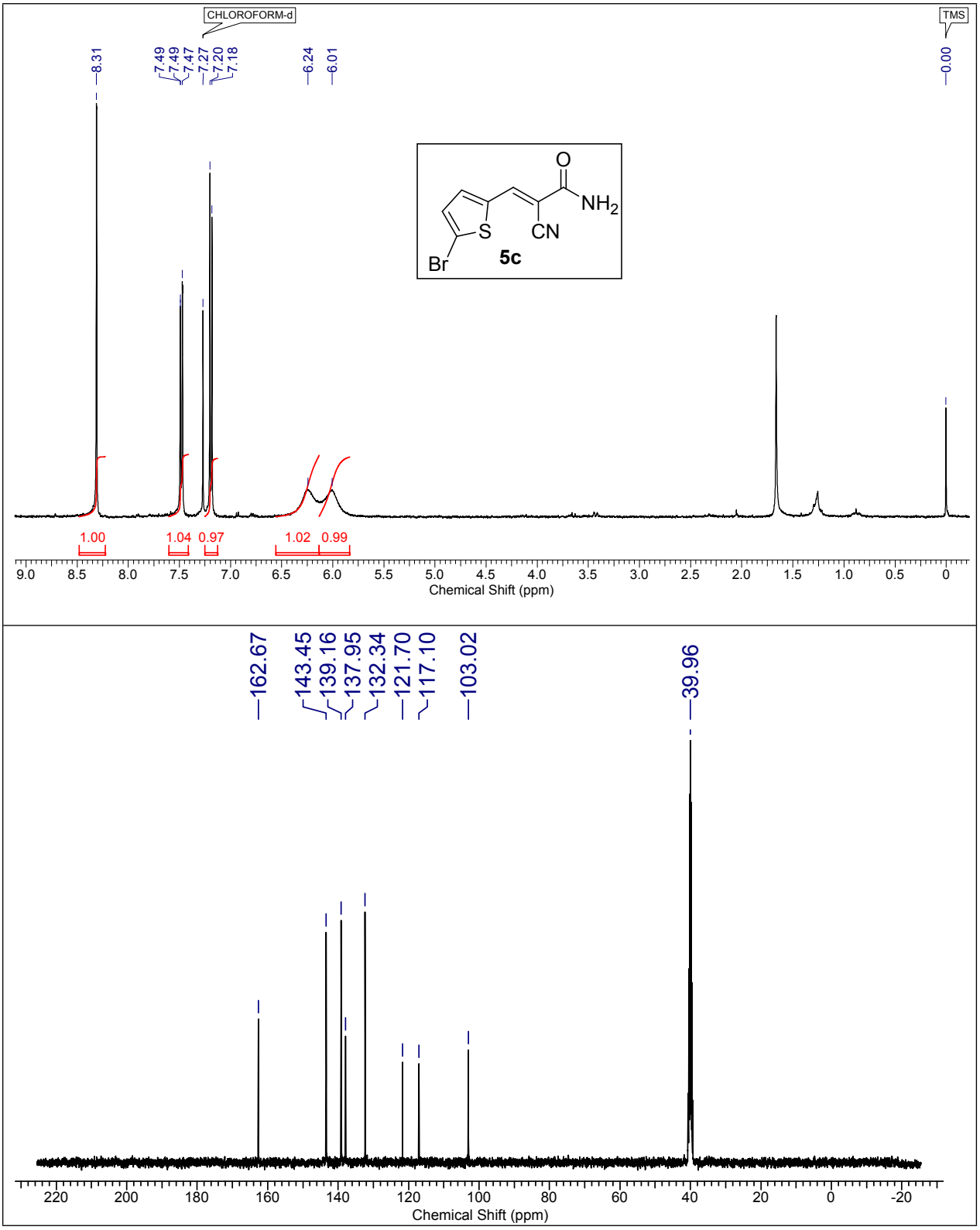

CHLOROFORM-d
TMS
8.10
8.07
8.06
7.70
7.69
7.47
7.46
7.44
7.43
7.41
7.39
7.38
7.26
6.37
6.17
0.00
Br
O
NH2
CN
3za
1.00
1.03
1.21
2.35
1.92
Chemical Shift (ppm)
CHLOROFORM-d
DMSO-d6
160.41
149.39
132.10
131.75
131.05
128.49
126.71
124.21
114.51
108.22
77.65
77.00
76.35
39.96
39.54
39.12
38.71
38.29
37.87
37.47
Chemical Shift (ppm)

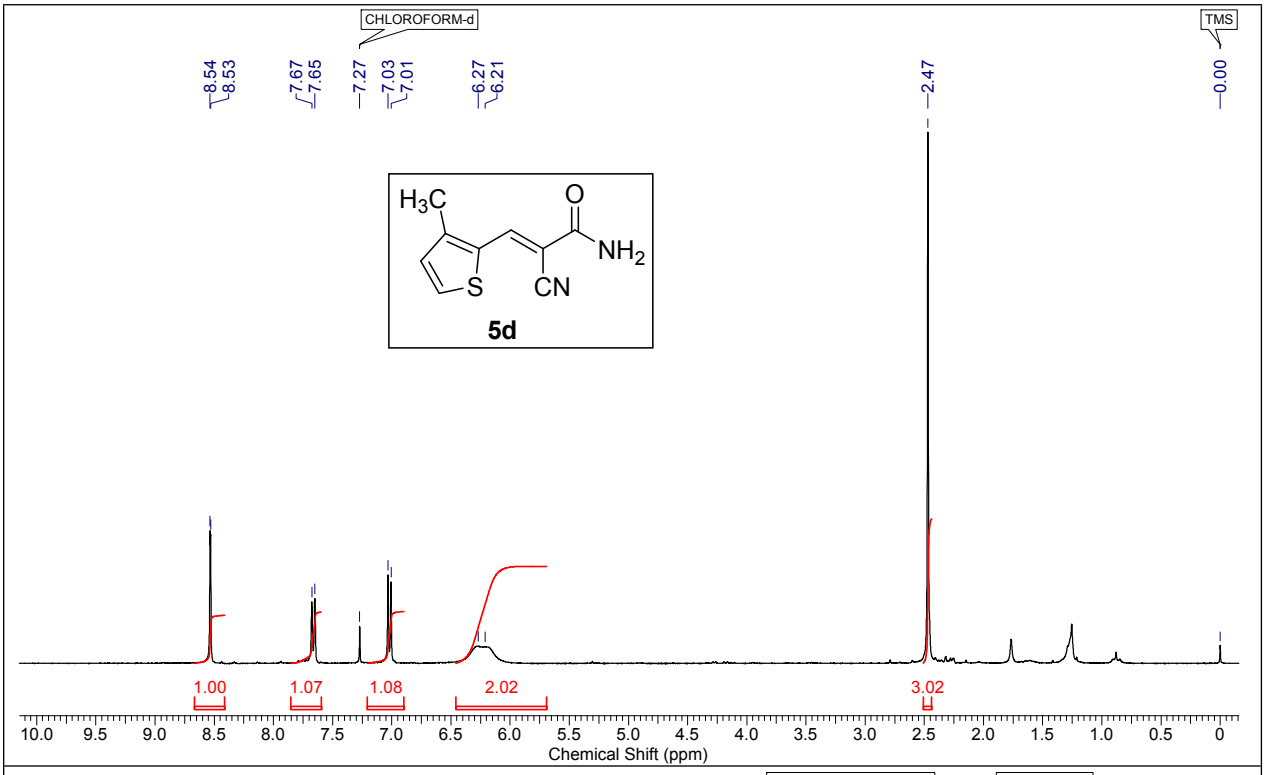

CHLOROFORM-d
DMSO-d6
TMS
7.93
7.63
7.27
7.14
7.13
6.70
6.60
6.53
6.53
6.52
2.47
2.43
0.11
O
NH2
O
CN
5a
1.00 0.99 1.03 0.97 1.12 1.09
Chemical Shift (ppm)

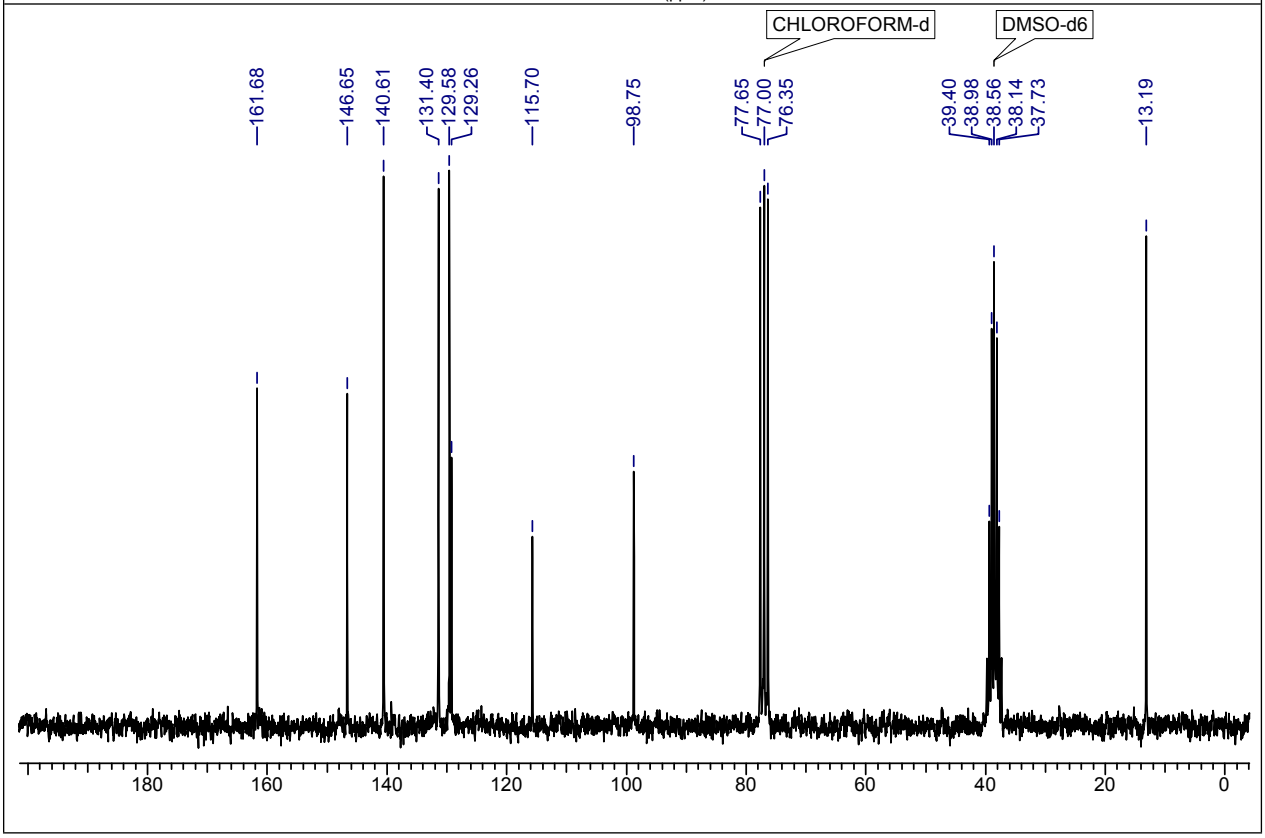

Carbon Tetrachloride
CHLOROFORM-d
DMSO-d6
161.78
148.76
147.28
137.36
120.47
116.36
113.25
99.83
95.84
77.25
77.00
76.74
40.13
39.96
39.80
39.63
39.46
Chemical Shift (ppm)

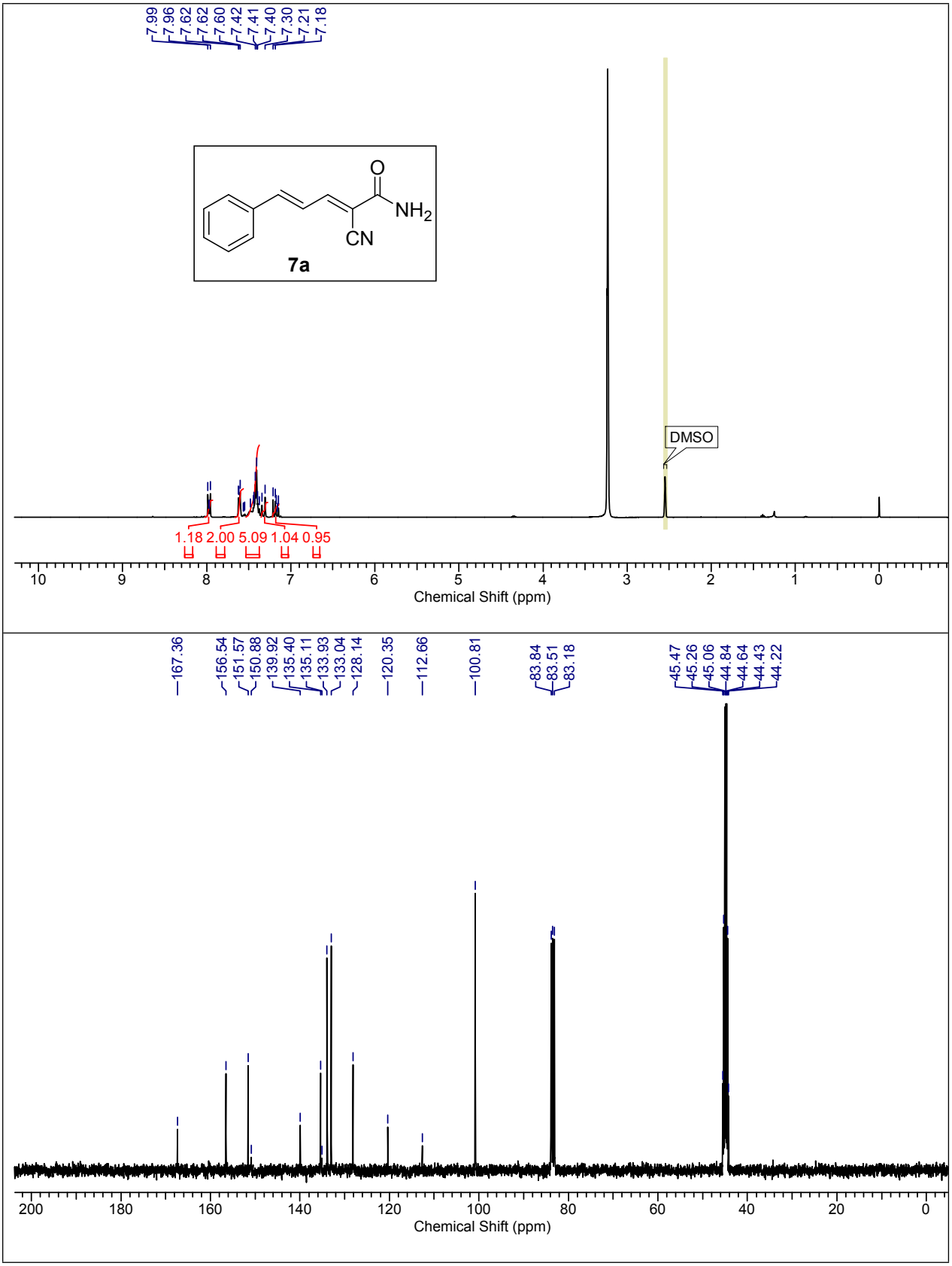

8.33
7.95
7.93
7.78
7.59
7.24
7.23
7.21
Water
DMSO
DMSO-d6
O
NH2
S
CN
5b
1.00 0.99 1.05 1.94 1.03
Chemical Shift (ppm)

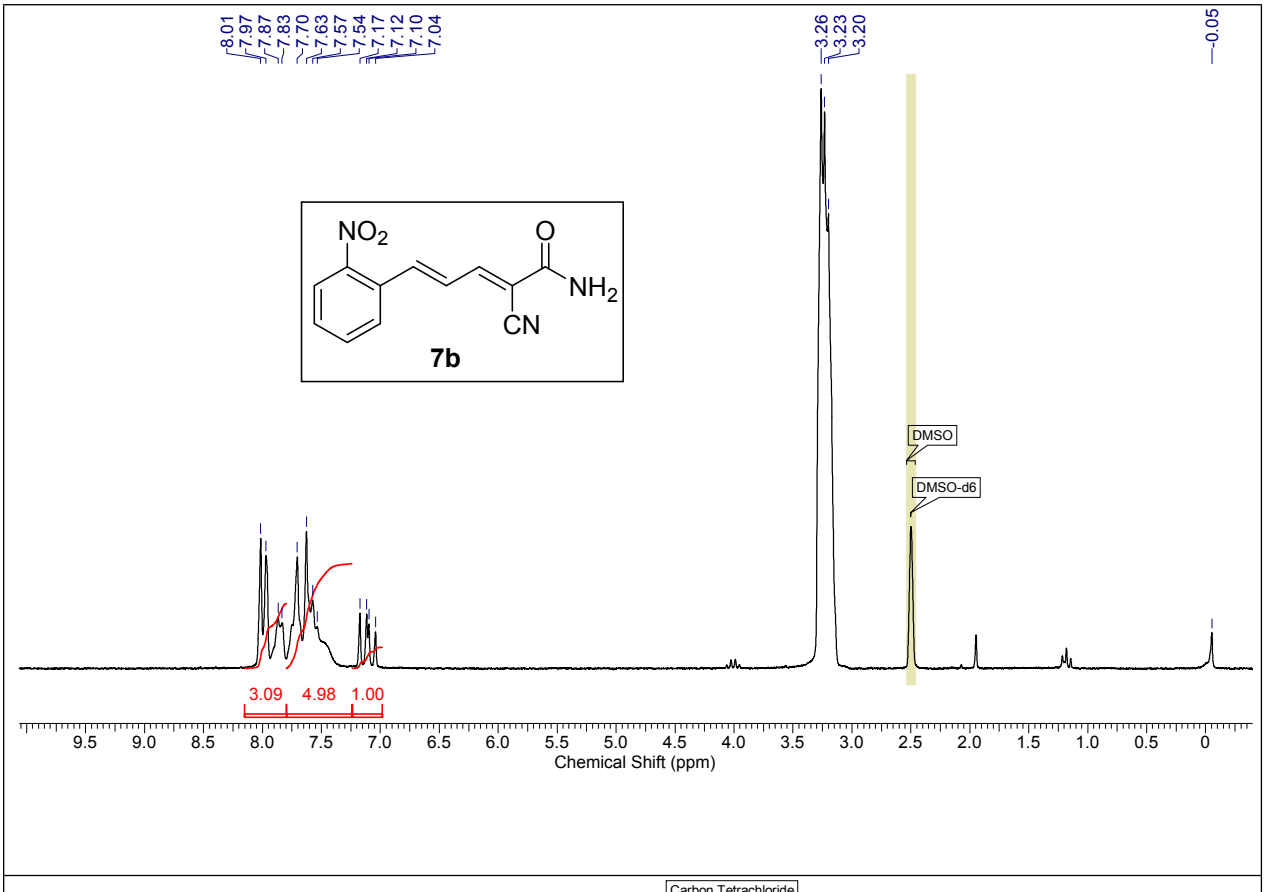

DMSO-d6
162.63
143.57
137.79
135.83
134.94
128.57
116.69
102.06
40.76
40.34
39.92
39.77
39.51
39.09
38.67
38.26
Chemical Shift (ppm)

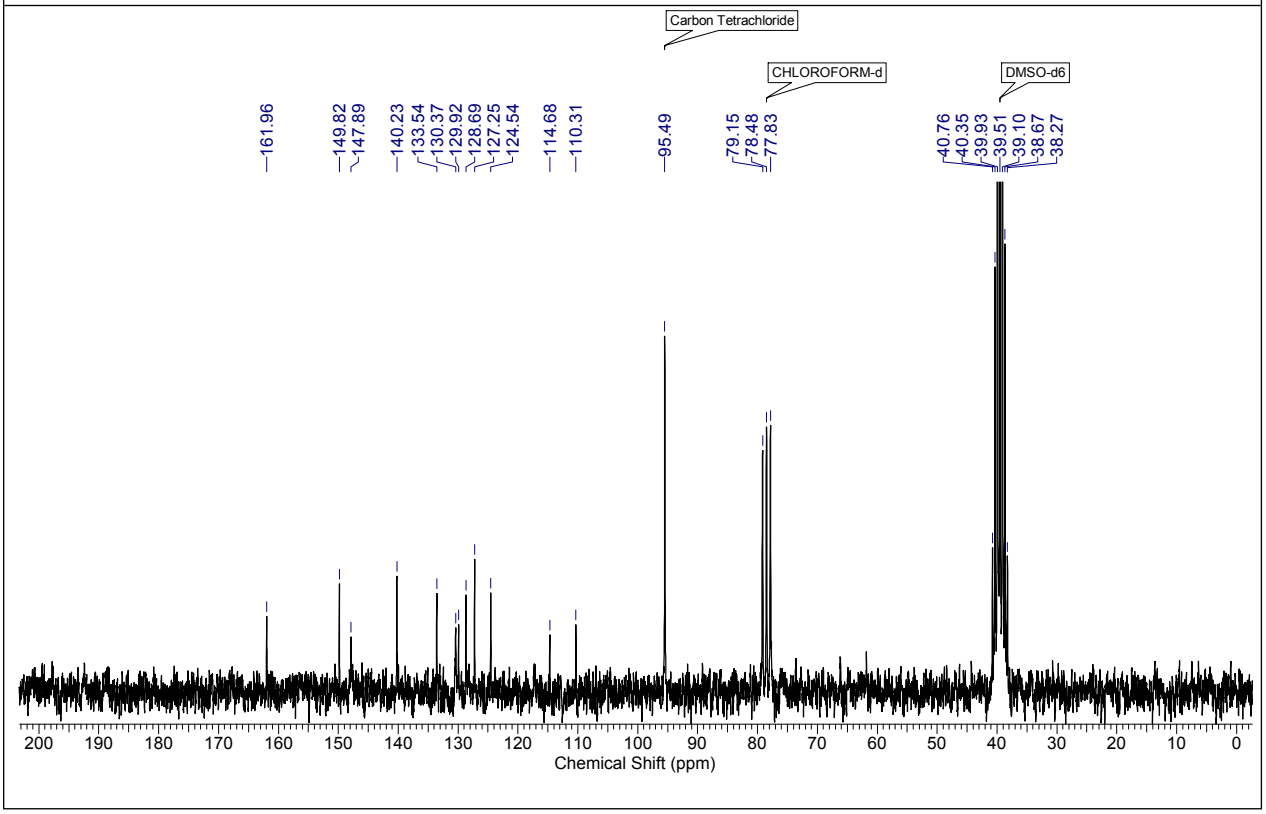

CHLOROFORM-d
TMS
8.31
7.49
7.49
7.47
7.27
7.20
7.18
6.24
6.01
0.00
O
NH2
S
CN
Br
5c
1.00
1.04
0.97
1.02
0.99
Chemical Shift (ppm)
162.67
143.45
139.16
137.95
132.34
121.70
117.10
103.02
39.96
Chemical Shift (ppm)

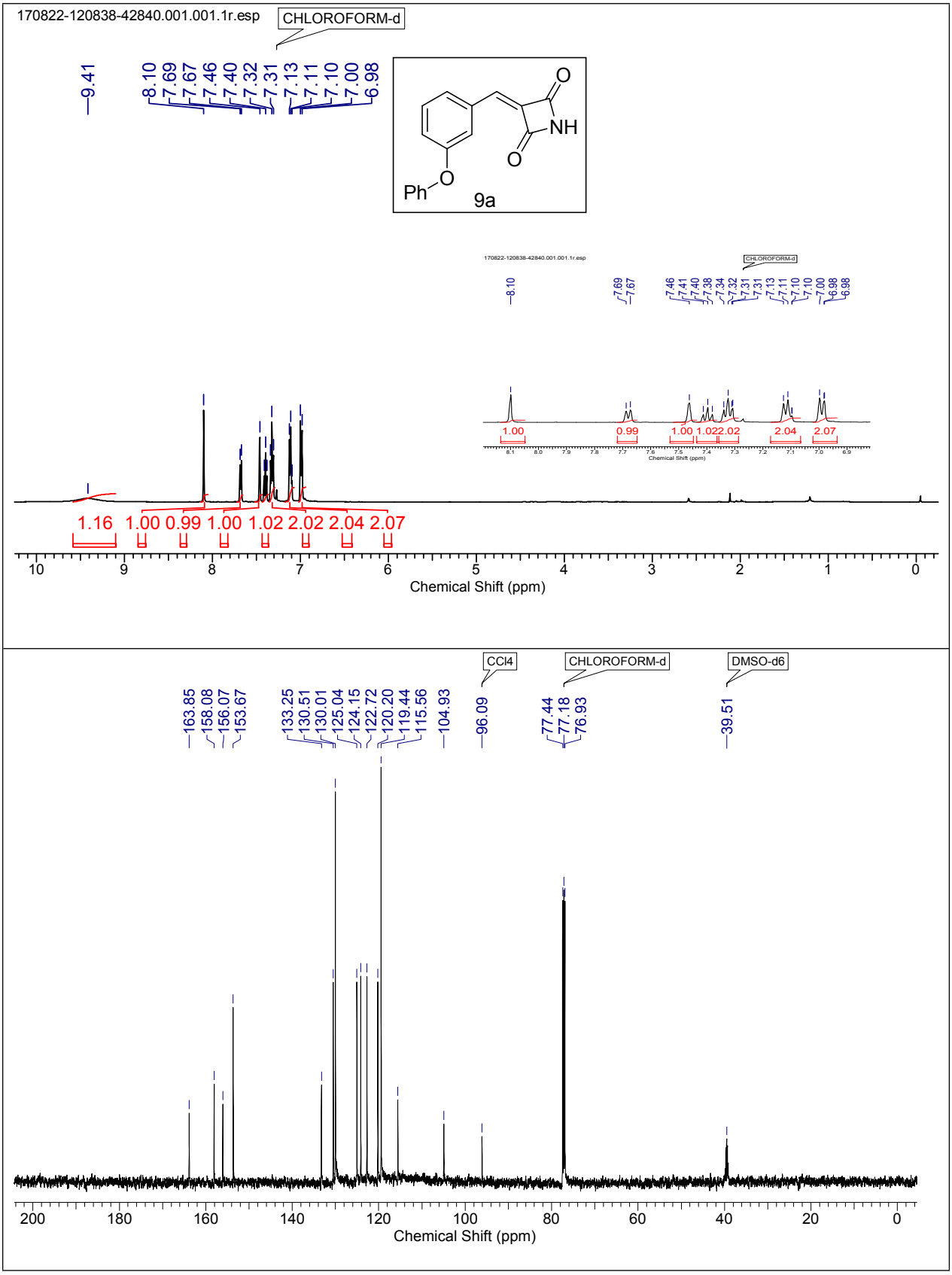

CHLOROFORM-d
TMS
8.54
8.53
7.67
7.65
7.27
7.03
7.01
6.27
6.21
2.47
0.00
H3C
O
NH2
S
CN
5d
1.00
1.07
1.08
2.02
3.02
Chemical Shift (ppm)

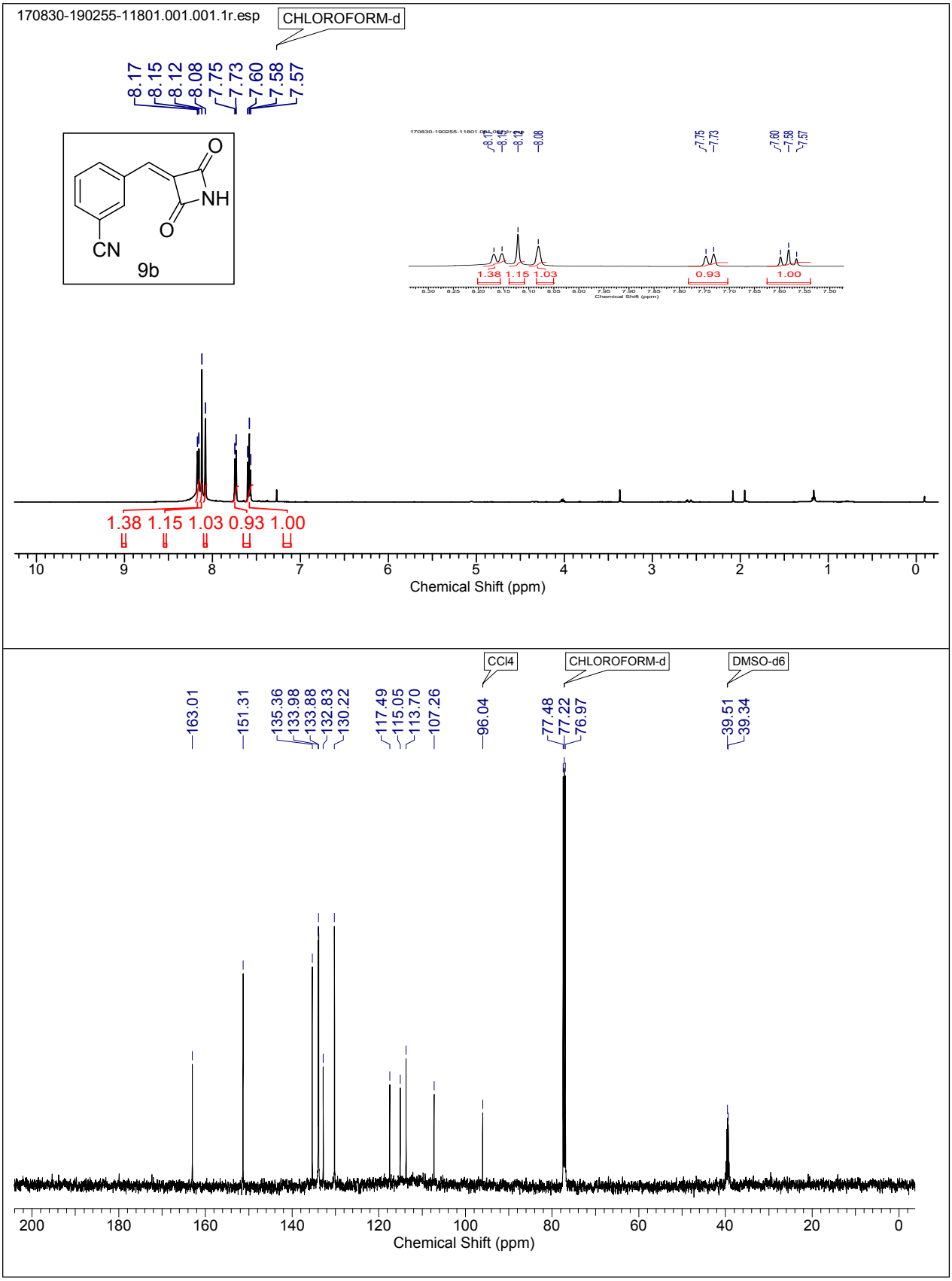

CHLOROFORM-d
DMSO-d6
161.68
146.65
140.61
131.40
129.58
129.26
115.70
98.75
77.65
77.00
76.35
39.40
38.98
38.56
38.14
37.73
13.19

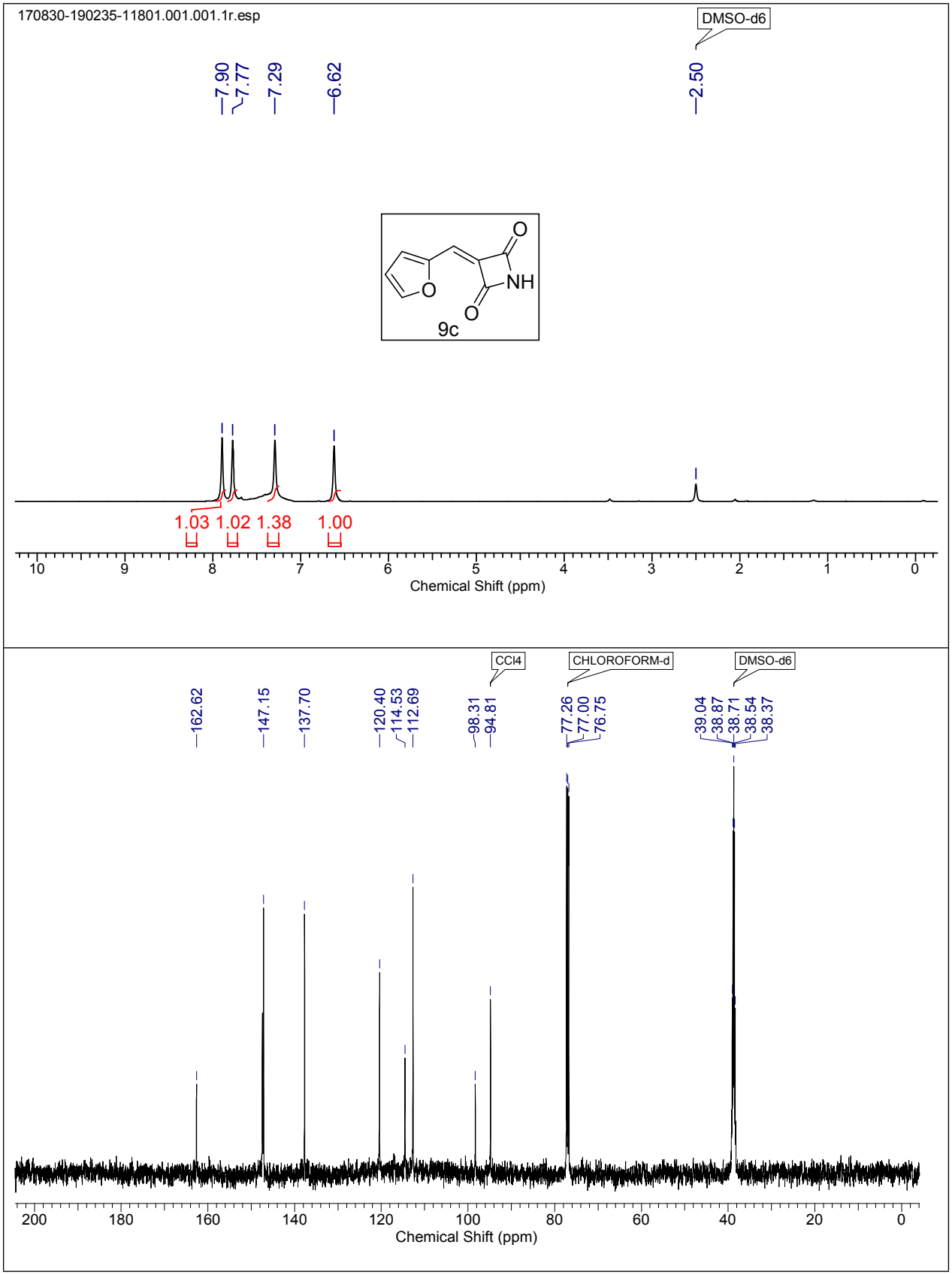

7.99
7.96
7.62
7.62
7.60
7.42
7.41
7.40
7.30
7.21
7.18
O
NH2
CN
7a
DMSO
1.18 2.00 5.09 1.04 0.95
Chemical Shift (ppm)
167.36
156.54
151.57
150.88
139.92
135.40
135.11
133.93
133.04
128.14
120.35
112.66
100.81
83.84
83.51
83.18
45.47
45.26
45.06
44.84
44.64
44.43
44.22
Chemical Shift (ppm)

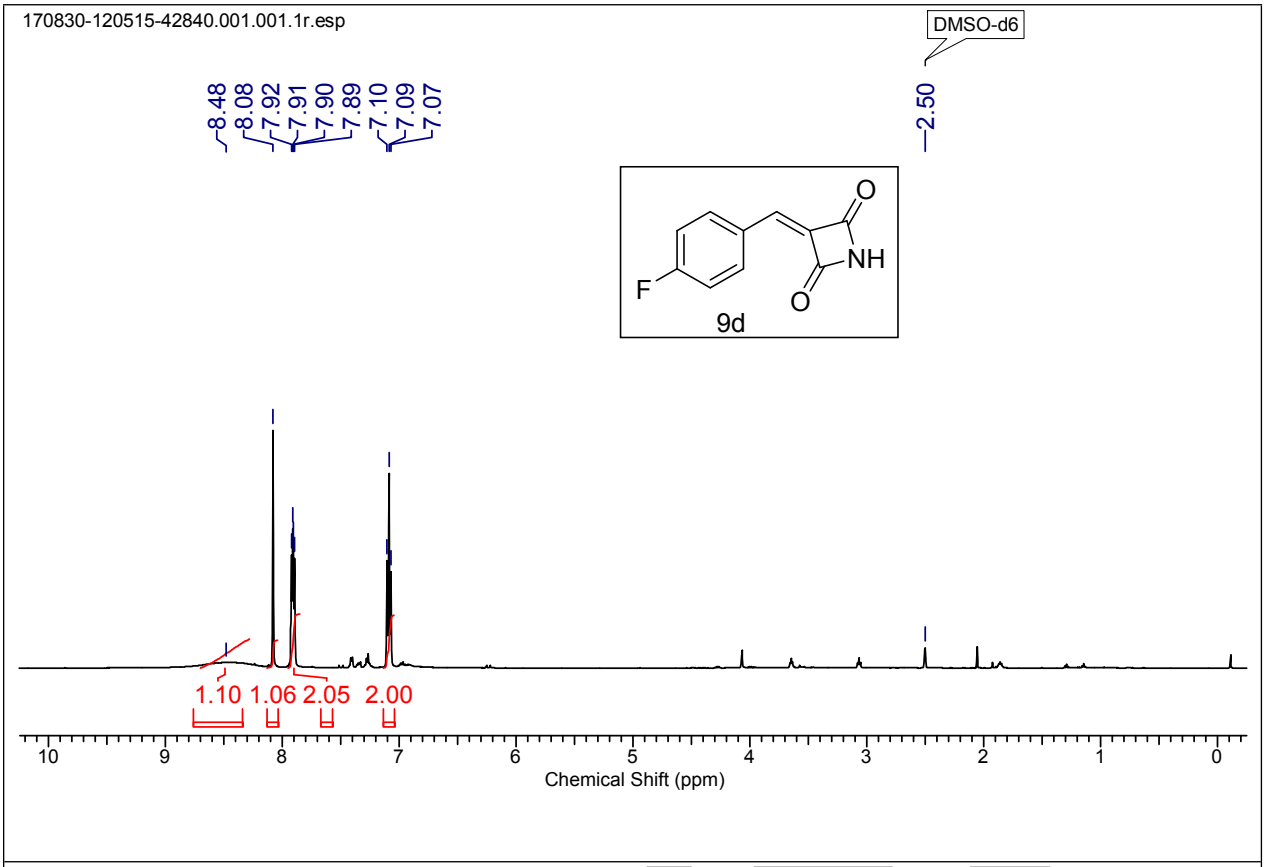

8.01
7.97
7.87
7.83
7.70
7.63
7.57
7.54
7.17
7.12
7.10
7.04
3.26
3.23
3.20
0.05
NO2
O
NH2
CN
7b
DMSO
DMSO-d6
3.09
4.98
1.00
Chemical Shift (ppm)

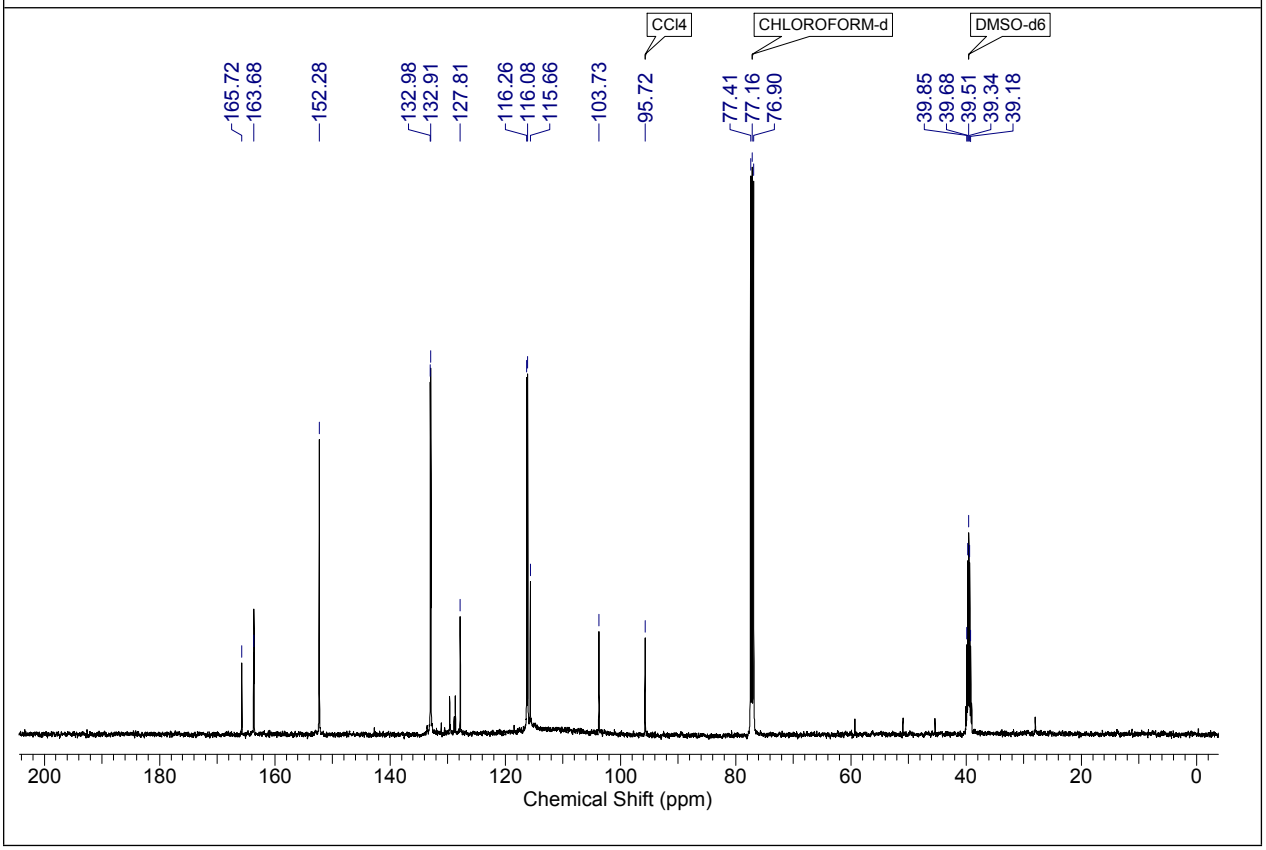

Carbon Tetrachloride
CHLOROFORM-d
DMSO-d6
161.96
149.82
147.89
140.23
133.54
130.37
129.92
128.69
127.25
124.54
114.68
110.31
95.49
79.15
78.48
77.83
40.76
40.35
39.93
39.51
39.10
38.67
38.27
Chemical Shift (ppm)

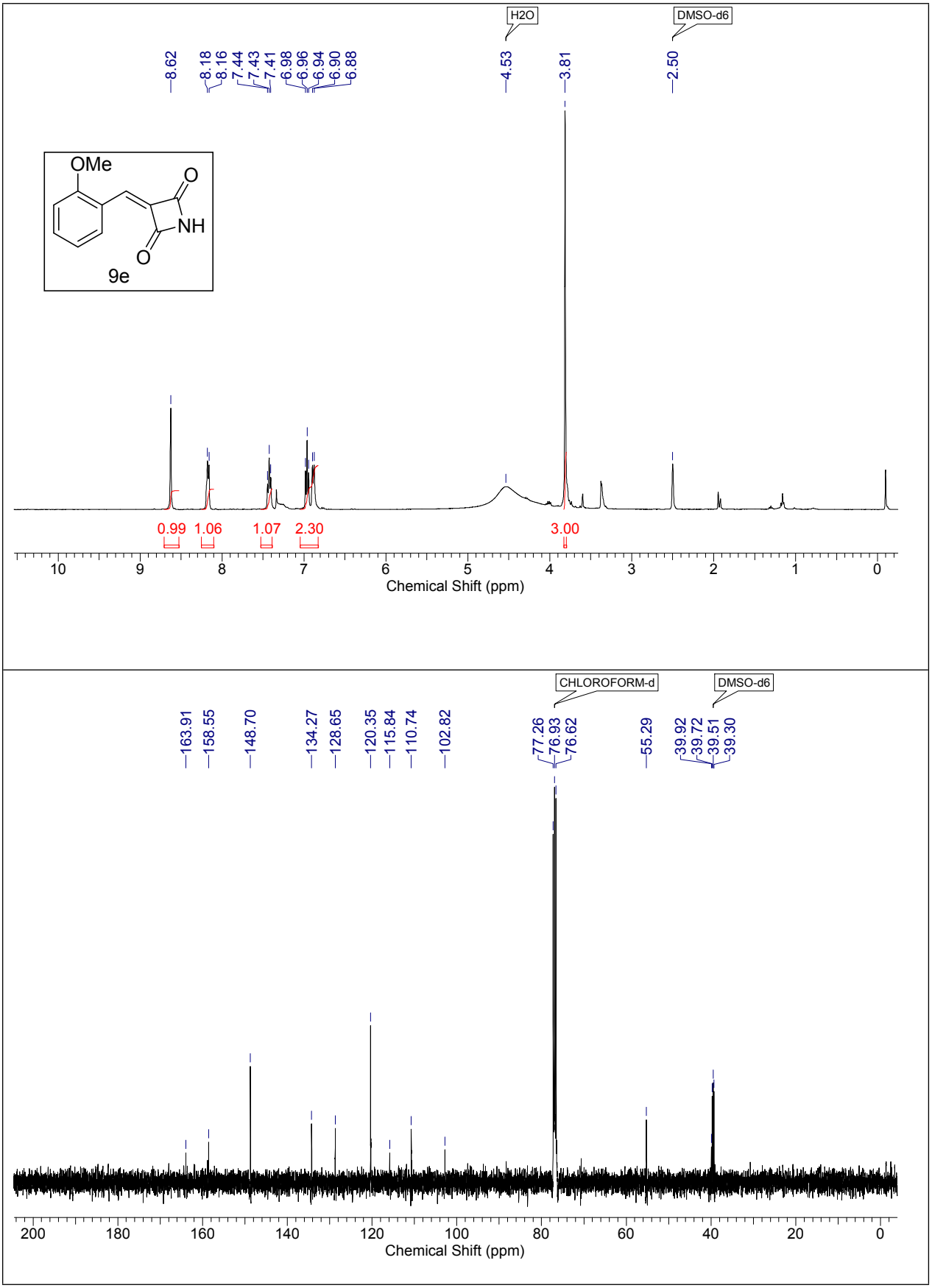

170822-120838-42840.001.001.1r.esp
CHLOROFORM-d
9.41
8.10
7.69
7.67
7.46
7.40
7.32
7.31
7.13
7.11
7.10
7.00
6.98
O
NH
O
Ph
O
9a
1.16 1.00 0.99 1.00 1.02 2.02 2.04 2.07
Chemical Shift (ppm)
CCl4
CHLOROFORM-d
DMSO-d6
163.85
158.08
156.07
153.67
133.25
130.51
130.01
125.04
124.15
122.72
120.20
119.44
115.56
104.93
96.09
77.44
77.18
76.93
39.51
Chemical Shift (ppm)

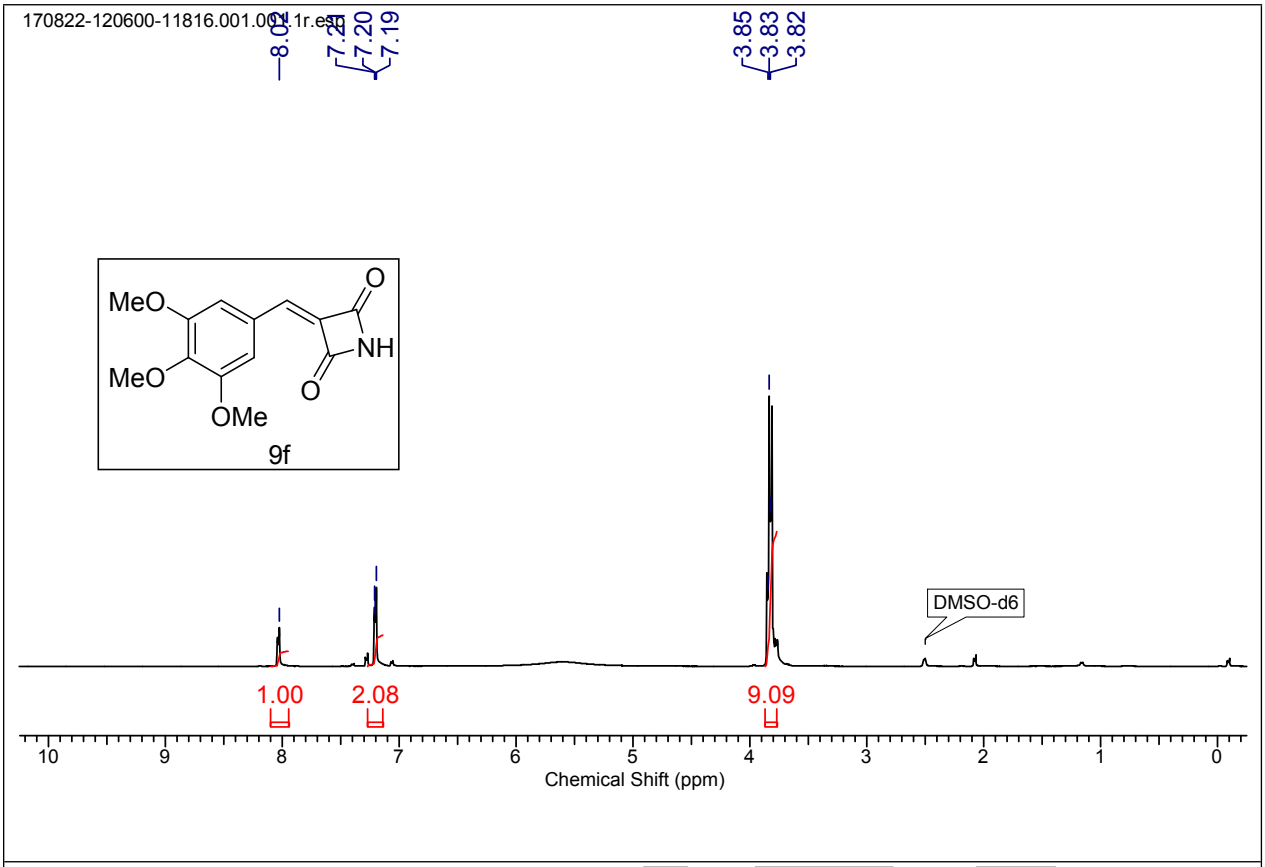

170830-190255-11801.001.001.1r.esp
CHLOROFORM-d
8.17
8.15
8.12
8.08
7.75
7.73
7.60
7.58
7.57
O
NH
O
CN
9b
1.38 1.15 1.03 0.93 1.00
Chemical Shift (ppm)
CCl4
CHLOROFORM-d
DMSO-d6
163.01
151.31
135.36
133.98
133.88
132.83
130.22
117.49
115.05
113.70
107.26
96.04
77.48
77.22
76.97
39.51
39.34
Chemical Shift (ppm)

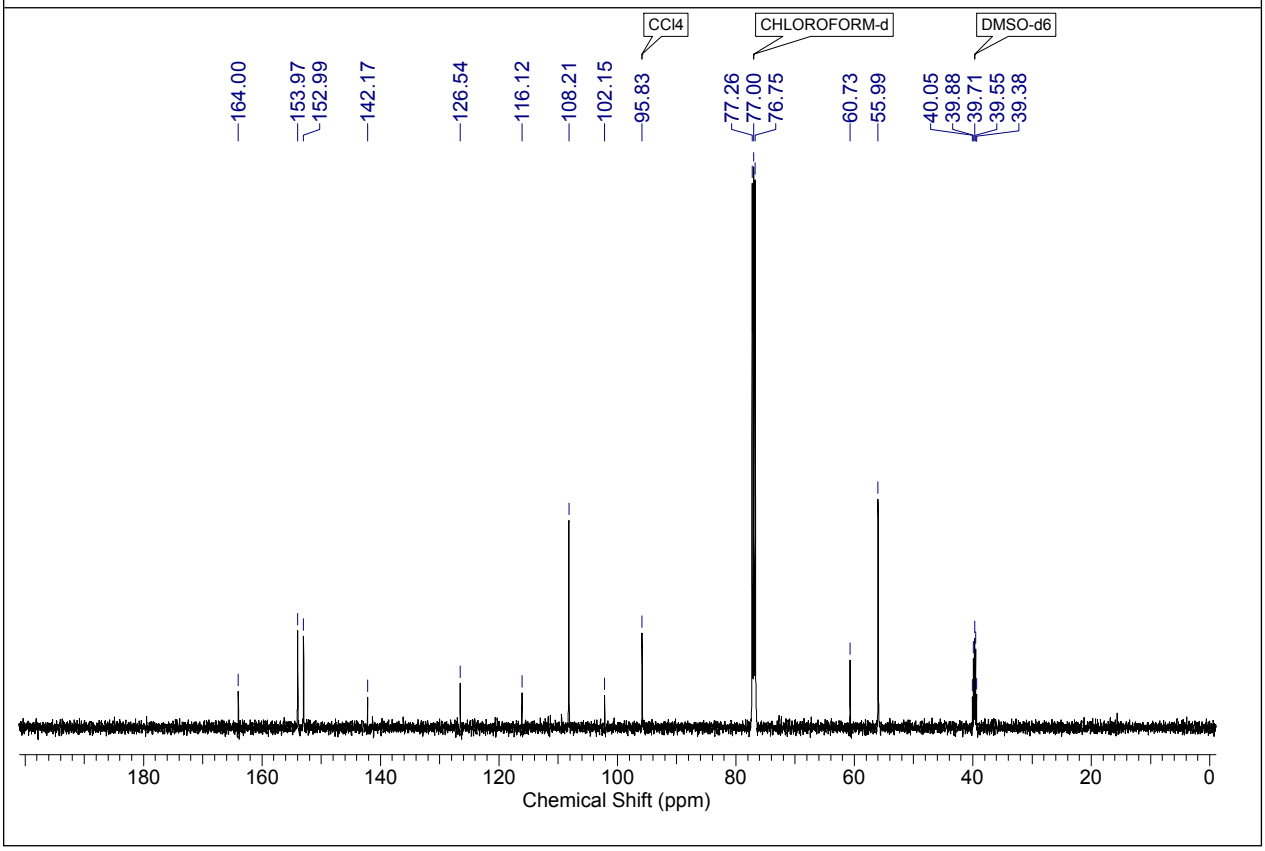

170830-190235-11801.001.001.1r.esp
DMSO-d6
7.90
7.77
7.29
6.62
2.50
O
NH
O
O
9c
1.03 1.02 1.38 1.00
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
CCl4
CHLOROFORM-d
DMSO-d6
162.62
147.15
137.70
120.40
114.53
112.69
98.31
94.81
77.26
77.00
76.75
39.04
38.87
38.71
38.54
38.37
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

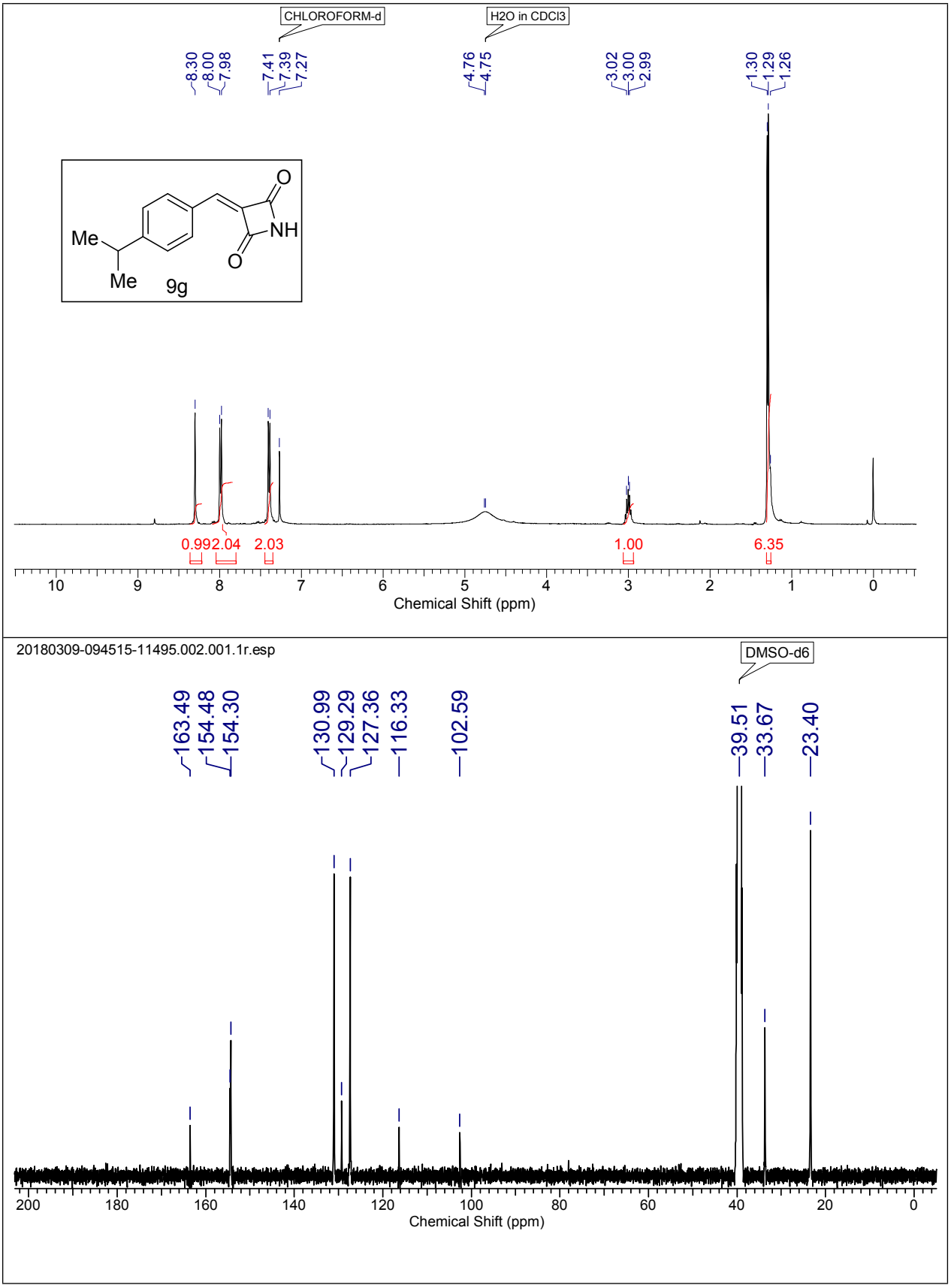

170830-120515-42840.001.001.1r.esp
DMSO-d6
8.48
8.08
7.92
7.91
7.90
7.89
7.10
7.09
7.07
2.50
O
NH
O
F
9d
1.10
1.06
2.05
2.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

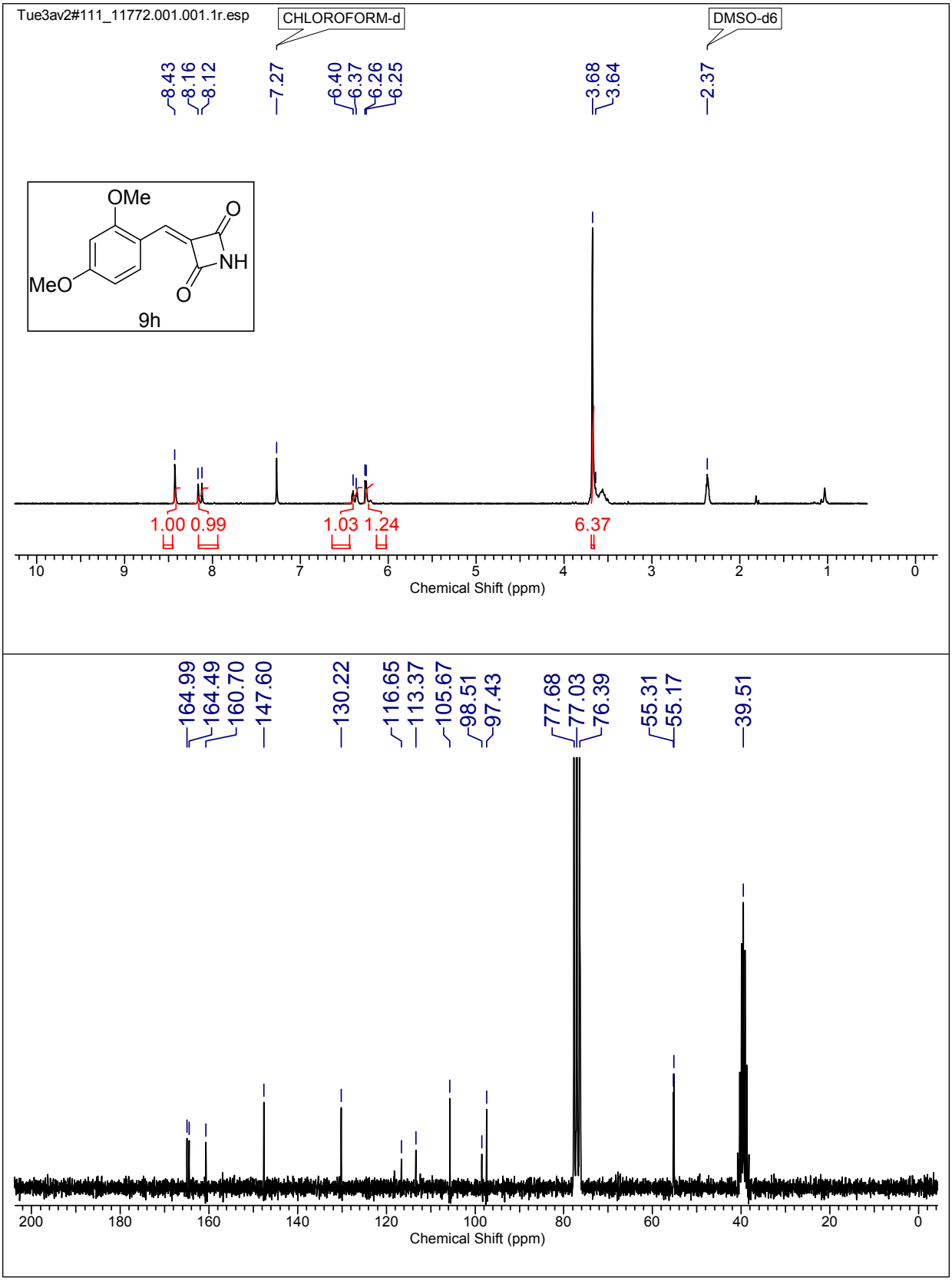

CCl4
CHLOROFORM-d
DMSO-d6
165.72
163.68
152.28
132.98
132.91
127.81
116.26
116.08
115.66
103.73
95.72
77.41
77.16
76.90
39.85
39.68
39.51
39.34
39.18
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

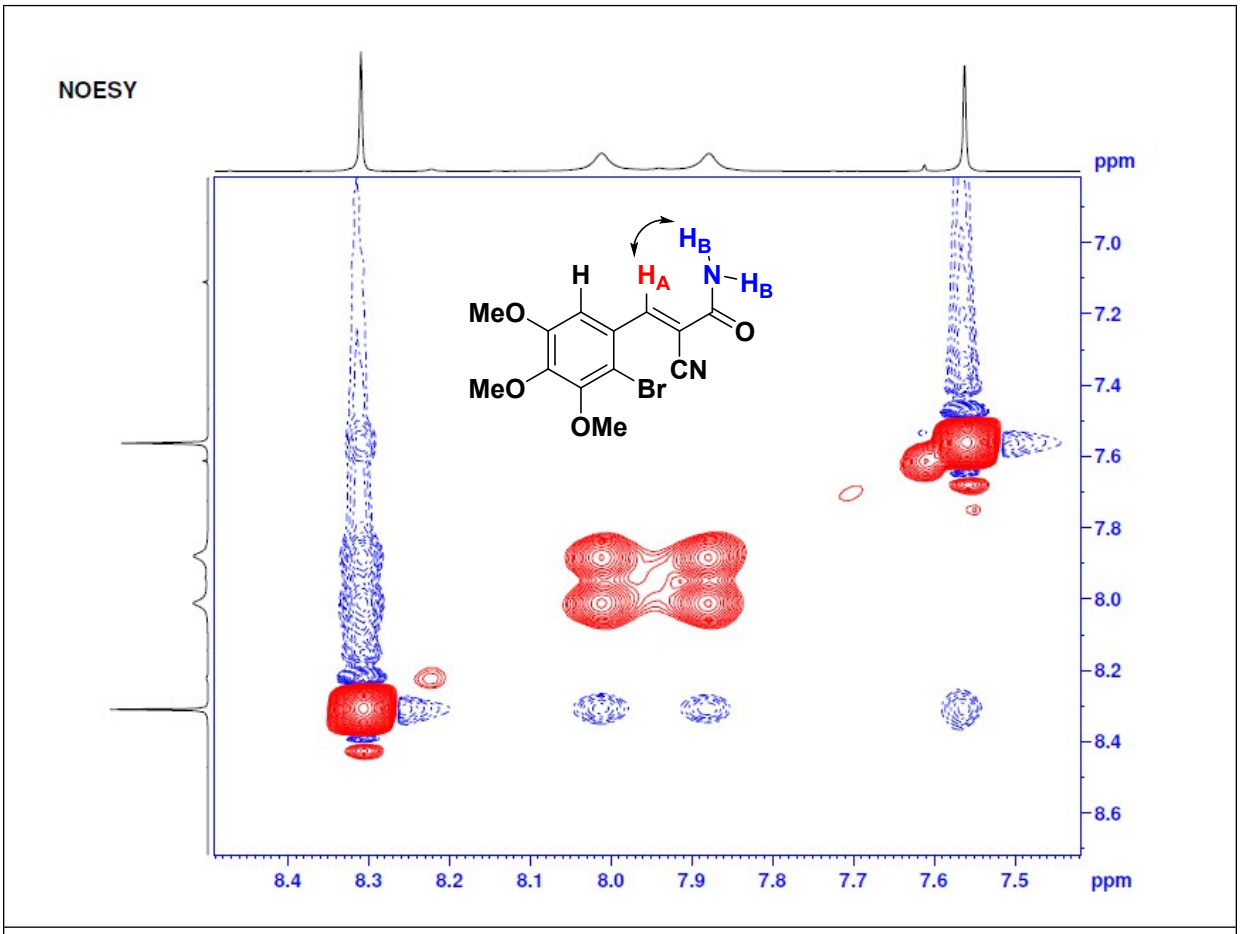

H2O
DMSO-d6
8.62
8.18
8.16
7.44
7.43
7.41
6.98
6.96
6.94
6.90
6.88
4.53
3.81
2.50
OMe
O
NH
O
9e
0.99
1.06
1.07
2.30
3.00
Chemical Shift (ppm)
CHLOROFORM-d
DMSO-d6
163.91
158.55
148.70
134.27
128.65
120.35
115.84
110.74
102.82
77.26
76.93
76.62
55.29
39.92
39.72
39.51
39.30
Chemical Shift (ppm)


170822-120600-11816.001.001.1r.esp
8.01
7.21
7.20
7.19
3.85
3.83
3.82
MeO
MeO
OMe
O
NH
O
9f
DMSO-d6
1.00
2.08
9.09
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


CCl4
CHLOROFORM-d
DMSO-d6
164.00
153.97
152.99
142.17
126.54
116.12
108.21
102.15
95.83
77.26
77.00
76.75
60.73
55.99
40.05
39.88
39.71
39.55
39.38
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


CHLOROFORM-d
H2O in CDCl3
8.30
8.00
7.98
7.41
7.39
7.27
4.76
4.75
3.02
3.00
2.99
1.30
1.29
1.26
O
NH
O
Me
Me
9g
0.99
2.04
2.03
1.00
6.35
Chemical Shift (ppm)
20180309-094515-11495.002.001.1r.esp
DMSO-d6
163.49
154.48
154.30
130.99
129.29
127.36
116.33
102.59
39.51
33.67
23.40
Chemical Shift (ppm)


Tue3av2#111_11772.001.001.1r.esp
CHLOROFORM-d
DMSO-d6
8.43
8.16
8.12
7.27
6.40
6.37
6.26
6.25
3.68
3.64
2.37
OMe
MeO
O
NH
O
9h
1.00
0.99
1.03
1.24
6.37
Chemical Shift (ppm)
164.99
164.49
160.70
147.60
130.22
116.65
113.37
105.67
98.51
97.43
77.68
77.03
76.39
55.31
55.17
39.51
Chemical Shift (ppm)



NOESY Analysis of 3n