Supporting Information

Rongalite/Iodine-Mediated C(sp^3)–H Bond Oximation and Thiomethylation Reaction of Methyl Ketones Using Copper Nitrate as the [NO] Reagent: Synthesis of Thiohydroximic Acids

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Table of Contents **page**

1. General.

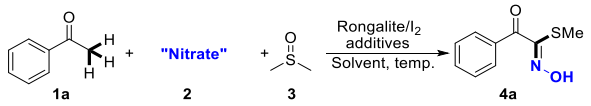
All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). ^{1}H spectra were recorded in $CDCl_3$ or DMSO-d_6 on 400/600 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quadruple), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ or DMSO-d_6 on 100/150 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS or an Agilent 1290 LC/MS with the TOF analyzer. Melting points were determined using XT-4 apparatus and not corrected.

2. General procedure for the synthesis of 4 (4a as an example).

A mixture of acetophenone **1a** (0.3 mmol, 36.0 mg), $Cu(NO_3)_2 \cdot 3H_2O$ **2a** (0.3 mmol, 72.6 mg), rongalite (0.75 mmol, 115.5 mg), I_2 (0.3 mmol, 76.2 mg) and $Na_2S \cdot 9H_2O$ (0.3 mmol, 72.1 mg) in DMSO (2.0 mL) was stirred at 100^{o}C for 3h in a pressure vessel. The resulting mixture was dropped into 50 mL H_2O and extracted with EtOAc 3 times (3 × 50 mL). The organic extract was dried with anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc = 5/1) to afford the product **4a** as yellow solid (43.0 mg, 74%).

3. Optimization of the Reaction Conditions.

Table S1. Optimization of the Reaction Conditions. [a]

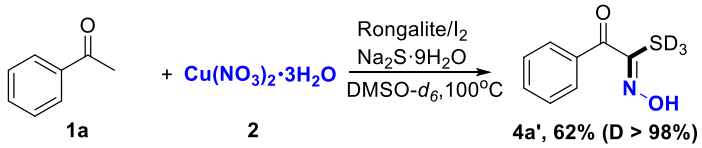


Entry	Rongalite (equiv)	Nitrate	additives	Temp (℃)	Yield (%)
1	2.0	$Cu(NO_3)_2$ $3H_2O$	-	100	45
2	2.0	$Al(NO_3)_3$ $9H_2O$	-	100	9
3	2.0	$Fe(NO_3)_3$ $9H_2O$	-	100	42
4	2.0	$Zn(NO_3)_2$ $6H_2O$	-	100	trace
5	2.0	$Cd(NO_3)_2$ $4H_2O$	-	100	0
6	2.0	$Ce(NH_4)_2(NO_3)_6$	-	100	31
7	2.0	$NaNO_3$	-	100	0
8	2.0	KNO_3	-	100	0
9	2.0	$Cu(NO_3)_2$ $3H_2O$	S	100	23
10	2.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	100	68
11	0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	100	trace
12	1.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	100	65
13	1.5	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	100	62
14	**2.5**	**$Cu(NO_3)_2$ $3H_2O$**	**Na_2S $9H_2O$**	**100**	**74**
15	2.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	80	67
16	2.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	90	70
17	2.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	110	20
18[b]	2.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	100	0
19[c]	2.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	100	42
20[d]	2.0	$Cu(NO_3)_2$ $3H_2O$	Na_2S $9H_2O$	100	69

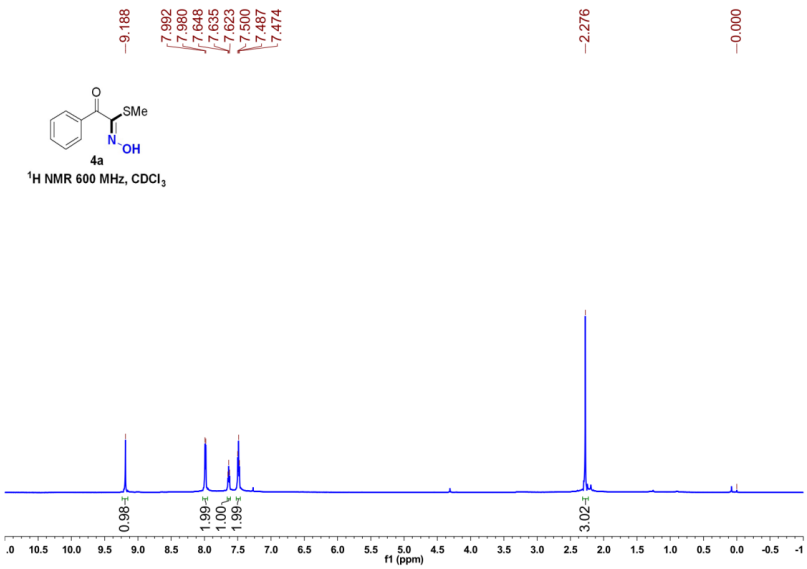
[a]Reaction conditions: **1a** (0.3 mmol), Rongalite, I_2 (0.3 mmol) and nitrate (0.3 mmol) in solvent (2.0 mL) at different temperatures in a sealed vessel. The reaction was performed for 3.0 h. Isolated yields based on **1a**. [b] I_2 (0 mmol) was used. [c] I_2 (0.15 mmol) was used. [d] I_2 (0.45 mmol) was used.

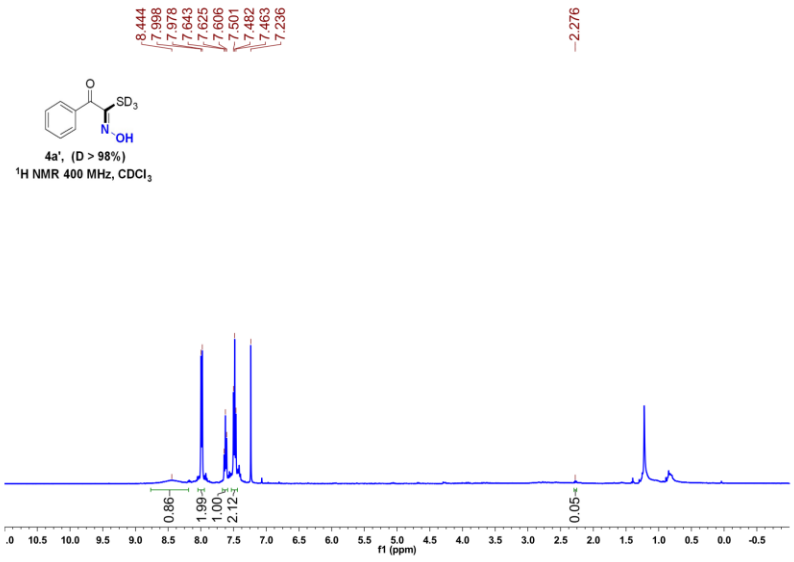
4. Evidence in support of the mechanism

The reaction of **1a** and **2** was performed in DMSO-d_6 under the standard conditions and the deuterated product **4a'** was generated (D > 98%). (Please see below)

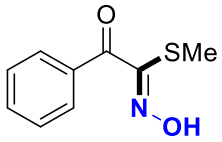


^{1}H NMR spectrum of **4a** and **4a'** were shown as below:



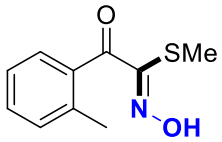


5. Characterization data for target compound.



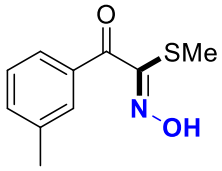
methyl (Z)-*N*-hydroxy-2-oxo-2-phenylethanimidothioate (**4a**):

Yield: 74% (43.0 mg); light yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.19 (s, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.6, 154.6, 135.3, 134.5, 130.4, 128.7, 13.3; HRMS (ESI) m/z calcd for $C_9H_{10}NO_2S^+$ $(M+H)^+$ 196.0427, found 196.0423.



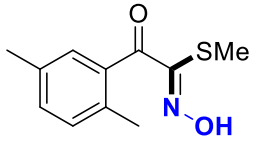
methyl (Z)-*N*-hydroxy-2-oxo-2-(o-tolyl)ethanimidothioate (**4b**):

Yield: 66% (41.2 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (s, 1H), 7.55 (d, *J* = 9.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.19 (m, 2H), 2.45 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.2, 156.0, 139.6, 135.8, 132.6, 131.8, 131.5, 125.7, 21.0, 13.5. HRMS (ESI) m/z calcd for $C_{10}H_{12}NO_2S^+$ $(M+H)^+$ 210.0583, found 210.0582.



methyl (Z)-*N*-hydroxy-2-oxo-2-(m-tolyl)ethanimidothioate (**4c**):

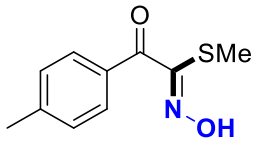
Yield: 69% (43.2 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.8, 154.7, 138.7, 135.5, 135.3, 130.7, 128.7, 127.8, 21.3, 13.3. HRMS (ESI) m/z calcd for $C_{10}H_{12}NO_2S^+$ $(M+H)^+$ 210.0583, found 210.0580.



methyl (Z)-2-(2,5-dimethylphenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4d**):

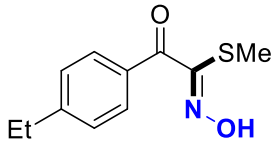
Yield: 60% (40.1 mg); light yellow solid; mp: 96.9–99.1°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 7.34 (s, 1H), 7.19 – 7.16 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H), 2.27

(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.3, 156.1, 136.5, 135.7, 135.4, 133.5, 131.8, 131.7, 20.8, 20.6, 13.5. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO_2S^+$ $(M+H)^+$ 224.0740, found 224.0739.



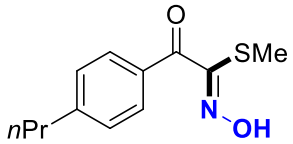
methyl (Z)-*N*-hydroxy-2-oxo-2-(p-tolyl)ethanimidothioate (**4e**):

Yield: 72% (45.1 mg); light yellow solid; mp: 66.7–69.5°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.18 (s, 1H), 7.91 – 7.89 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.2, 154.7, 145.8, 132.8, 130.5, 129.5, 21.8, 13.2. The data are in agreement with those previously reported in the literature.[1]



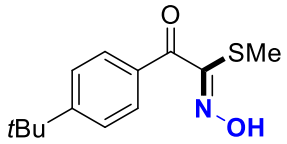
methyl (Z)-2-(4-ethylphenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4f**):

Yield: 70% (46.7 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.2, 154.8, 151.9, 133.2, 130.7, 128.4, 29.1, 15.0, 13.3. HRMS (ESI) m/z calcd for $C_{11}H_{14}NO_2S$ $(M+H)^+$ 224.0740, found 224.0739.



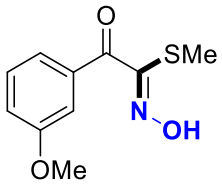
methyl (Z)-*N*-hydroxy-2-oxo-2-(4-propylphenyl)ethanimidothioate (**4g**):

Yield: 65% (46.1 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 1.65 – 1.55 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.2, 154.8, 150.4, 133.2, 130.6, 128.9, 38.2, 24.1, 13.7, 13.3. HRMS (ESI) m/z calcd for $C_{12}H_{16}NO_2S$ $(M+H)^+$ 238.0896, found 238.0896.



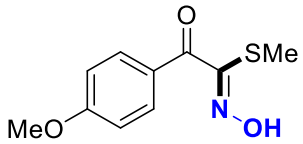
methyl (Z)-2-(4-(tert-butyl)phenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4h**):

Yield: 77% (57.8 mg); light yellow solid; mp: 97.5–98.1°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 2.22 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.2, 158.6, 154.8, 132.9, 130.4, 125.8, 35.3, 31.0, 13.3. HRMS (ESI) m/z calcd for $C_{13}H_{18}NO_2S$ $(M+H)^+$ 252.1053, found 252.1051.



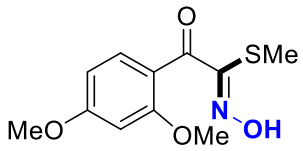
methyl (Z)-*N*-hydroxy-2-(3-methoxyphenyl)-2-oxoethanimidothioate (**4i**):

Yield: 76% (51.1 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.78 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 8.50 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.20 – 7.17 (m, 1H), 3.86 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.4, 159.7, 154.6, 136.5, 129.8, 123.6, 121.5, 113.5, 55.5, 13.3; HRMS (ESI) m/z calcd for $C_{10}H_{12}NO_3S^+$ $(M+H)^+$ 226.0532, found 226.0533.



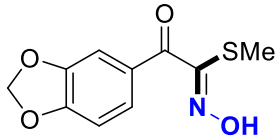
methyl (Z)-*N*-hydroxy-2-(4-methoxyphenyl)-2-oxoethanimidothioate (**4j**):

Yield: 68% (45.8 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.33 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.0, 164.7, 154.6, 132.9, 128.1, 114.1, 55.6, 13.1; HRMS (ESI) m/z calcd for $C_{10}H_{12}NO_3S^+$ $(M+H)^+$ 226.0532, found 226.0531.



methyl (Z)-2-(2,4-dimethoxyphenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4k**):

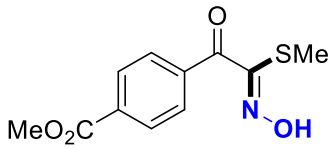
Yield: 62% (47.3 mg); white solid, mp: 138.9–141.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.8 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 6.46 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.4, 165.7, 161.8, 157.0, 133.7, 119.7, 105.7, 98.7, 56.0, 55.7, 13.3; HRMS (ESI) m/z calcd for $C_{11}H_{14}NO_4S^+$ $(M+H)^+$ 256.0638, found 256.0635.



methyl (Z)-2-(benzo[d][1,3]dioxol-5-yl)-*N*-hydroxy-2-oxoethanimidothioate (**4l**):

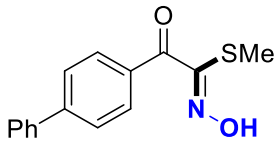
Yield: 71% (50.8 mg); white solid, mp: 142.7–145.5 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.27 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 2H), 2.18 (s,

3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 185.1, 152.9, 151.6, 148.1, 130.0, 128.2, 108.3, 108.2, 102.6, 12.5; HRMS (ESI) m/z calcd for $C_{10}H_{10}NO_4S^+$ $(M+H)^+$ 240.0325, found 240.0320.



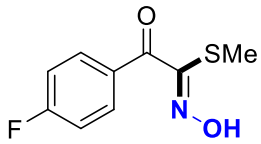
methyl (Z)-4-(2-(hydroxyimino)-2-(methylthio)acetyl)benzoate (**4m**):

Yield: 80% (60.6 mg); light yellow solid; mp: 97.9–100.1°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.71 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 187.0, 165.5, 152.0, 139.6, 133.7, 130.4, 129.3, 52.6, 12.8; HRMS (ESI) m/z calcd for $C_{11}H_{12}NO_4S^+$ $(M+H)^+$ 254.0482, found 254.0481.



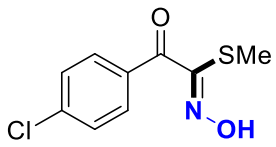
methyl (Z)-2-([1,1'-biphenyl]-4-yl)-*N*-hydroxy-2-oxoethanimidothioate (**4n**):

Yield: 66% (53.5 mg); light yellow solid; mp: 203.1–206.3°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.34 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.2, 154.7, 147.1, 139.3, 133.9, 131.0, 128.9, 128.5, 127.3, 127.2(6), 13.3. The data are in agreement with those previously reported in the literature.[1]



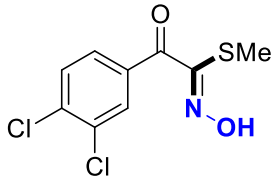
methyl (Z)-2-(4-fluorophenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4o**):

Yield: 73% (46.5 mg); light yellow solid; mp: 65.8–67.3°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.37 (s, 1H), 8.04 – 8.01 (m, 2H), 7.15 (t, *J* = 8.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.1, 166.3 (d, *J* = 257.0 Hz), 154.5, 133.3 (d, *J* = 9.6 Hz), 131.6, 116.0 (d, *J* = 22.1 Hz), 13.3; HRMS (ESI) m/z calcd for $C_9H_9FNO_2S^+$ $(M+H)^+$ 214.0333, found 214.0332.



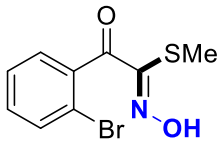
methyl (Z)-2-(4-chlorophenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4p**):

Yield: 70% (48.1 mg); light yellow solid; mp: 60.2–62.5°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.23 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.4, 154.5, 141.2, 133.6, 131.7, 129.1, 13.3 The data are in agreement with those previously reported in the literature.[1]



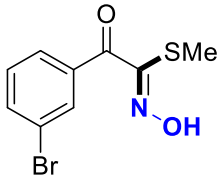
methyl (Z)-2-(3,4-dichlorophenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4q**):

Yield: 58% (45.6 mg); light yellow solid; mp: 99.6–102.3°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.81 (s, 1H), 8.06 (s, 1H), 7.84 (d, *J* = 1.2 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 185.1, 152.0, 136.7, 136.2, 132.0, 131.4, 131.0, 130.1, 12.9; HRMS (ESI) m/z calcd for $C_9H_8Cl_2NO_2S^+$ $(M+H)^+$ 263.9647, found 263.9647.



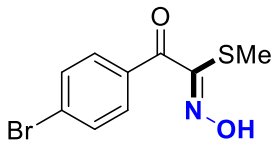
methyl (Z)-2-(2-bromophenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4r**):

Yield: 71% (58.0 mg); light yellow solid; mp: 118.3–123.6°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.91 (s, 1H), 7.53 (s, 1H), 7.38 – 7.32 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 189.7, 152.6, 140.6, 132.6, 132.1, 129.8, 127.6, 119.1, 13.3; HRMS (ESI) m/z calcd for $C_9H_9BrNO_2S^+$ $(M+H)^+$ 273.9532, found 273.9532.



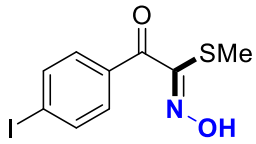
methyl (Z)-2-(3-bromophenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4s**):

Yield: 75% (61.2 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.22 (s, 1H), 8.10 (d, *J* =1.6 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.3, 154.3, 137.2, 137.0, 133.0, 130.2, 129.1, 122.9, 13.4; HRMS (ESI) m/z calcd for $C_9H_9BrNO_2S^+$ $(M+H)^+$ 273.9532, found 273.9531.



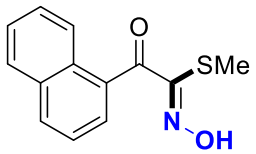
methyl (Z)-2-(4-bromophenyl)-*N*-hydroxy-2-oxoethanimidothioate (**4t**):

Yield: 70% (57.2 mg); light yellow solid; mp: 88.3–90.6℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.92 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.6, 154.5, 134.1, 132.1, 131.8, 130.1, 13.4; HRMS (ESI) m/z calcd for $C_9H_9BrNO_2S^+$ $(M+H)^+$ 273.9532, found 273.9536.



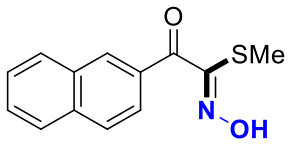
methyl (Z)-*N*-hydroxy-2-(4-iodophenyl)-2-oxoethanimidothioate (**4u**):

Yield: 56% (53.8 mg); light yellow solid; mp: 108.7–121.3℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.55 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 187.1, 152.2, 138.2, 135.5, 132.1, 103.8, 13.2; HRMS (ESI) m/z calcd for $C_9H_9INO_2S^+$ $(M+H)^+$ 321.9393, found 321.9395.



methyl (Z)-*N*-hydroxy-2-(naphthalen-1-yl)-2-oxoethanimidothioate (**4v**):

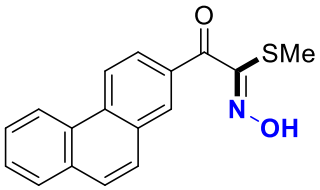
Yield: 79% (57.8 mg); light yellow solid; mp: 129.7–131.4℃ ; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.59 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.70 – 7.61 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 189.8, 153.9, 134.2, 133.3, 133.2, 131.3, 130.1, 128.8, 128.3, 126.7, 124.8, 124.7, 13.0; HRMS (ESI) m/z calcd for $C_{13}H_{12}NO_2S^+$ $(M+H)^+$ 246.0583, found 246.0582.



methyl (Z)-*N*-hydroxy-2-(naphthalen-2-yl)-2-oxoethanimidothioate (**4w**):

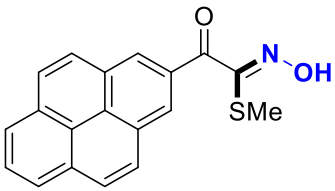
Yield: 76% (55.6 mg); light yellow oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 12.51 (s, 1H), 8.56 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (150 MHz,

DMSO-d_6) δ = 187.2, 152.0, 135.5, 133.3, 133.1, 131.9, 129.9, 129.4, 128.7, 127.8, 127.3, 124.4, 12.7; HRMS (ESI) m/z calcd for $C_{13}H_{12}NO_2S^+$ $(M+H)^+$ 246.0583, found 246.0585.



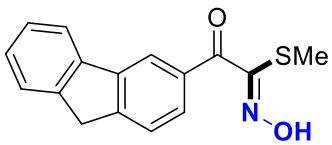
methyl (Z)-*N*-hydroxy-2-oxo-2-(phenanthren-2-yl)ethanimidothioate (**4x**):

Yield: 59% (52.2 mg); white solid; mp: 202.8–205.4°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.59 (s, 1H), 8.99 (d, *J* = 8.8 Hz, 1H), 8.91 – 8.89 (m, 1H), 8.59 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.06 – 8.03 (m, 2H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.77 – 7.75 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 187.0, 152.1, 133.7, 133.4, 132.8, 132.4, 130.9, 129.1, 128.7, 128.4, 128.1, 127.5, 127.3, 126.4, 123.9, 123.8, 12.8. The data are in agreement with those previously reported in the literature.[1]



methyl (Z)-*N*-hydroxy-2-oxo-2-(pyren-2-yl)ethanimidothioate (**4y**):

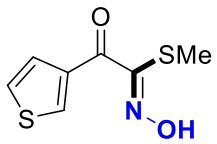
Yield: 62% (59.2 mg); white solid; mp: 225.2–227.6°C; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 12.61 (s, 1H), 8.70 (d, *J* = 9.0 Hz, 1H), 8.43 – 8.33 (m, 6H), 8.25 (d, *J* = 9.0 Hz, 1H), 8.16 (t, *J* = 7.8 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 190.0, 154.2, 133.8, 130.9, 130.6, 130.1, 130.0, 129.9, 129.6, 129.3, 127.2, 127.0, 126.6, 124.1, 123.9, 123.8, 123.3, 13.1; HRMS (ESI) m/z calcd for $C_{19}H_{14}NO_2S^+$ $(M+H)^+$ 320.0740, found 320.0738.



methyl (Z)-2-(9H-fluoren-3-yl)-*N*-hydroxy-2-oxoethanimidothioate (**4z**):

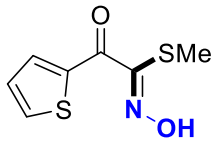
Yield: 61% (51.5 mg); white solid; mp: 142.1–144.0°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.83 (s, 1H), 8.17 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.83 (m, 2H), 7.59 (d, *J* = 6.6 Hz, 1H), 7.43 – 7.39 (m, 2H), 3.94 (s, 2H), 2.29 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.3, 155.0, 148.0, 144.8, 143.4, 140.0, 133.6, 130.0, 128.5, 127.1, 127.0, 125.3 121.2, 119.9, 36.8, 13.3; HRMS (ESI)

m/z calcd for $C_{16}H_{14}NO_2S^+$ $(M+H)^+$ 284.0740, found 284.0739.



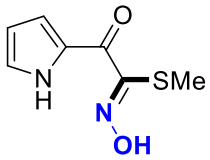
methyl (Z)-*N*-hydroxy-2-oxo-2-(thiophen-3-yl)ethanimidothioate (**4aa**):

Yield: 65% (39.1 mg); light yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 9.00 (s, 1H), 8.25 (s, 1H), 7.64 (d, *J* = 4.8 Hz, 1H), 7.36 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 179.7, 155.3, 140.0, 137.5, 127.7, 126.8, 13.5; HRMS (ESI) m/z calcd for $C_7H_8NO_2S_2^+$ $(M+H)^+$ 201.9991, found 201.9992.



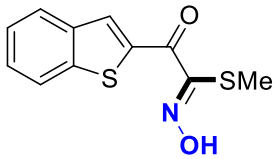
methyl (Z)-*N*-hydroxy-2-oxo-2-(thiophen-2-yl)ethanimidothioate (**4ab**):

Yield: 68% (40.9 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.40 (s, 1H), 7.89 (s, 1H), 7.79, (d, *J* = 4.0 Hz, 1H), 7.17 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.2, 154.6, 141.4, 137.1, 137.0, 128.6, 13.6; HRMS (ESI) m/z calcd for $C_7H_8NO_2S_2^+$ $(M+H)^+$ 201.9991, found 201.9991.



methyl (Z)-*N*-hydroxy-2-oxo-2-(1H-pyrrol-2-yl)ethanimidothioate (**4ac**):

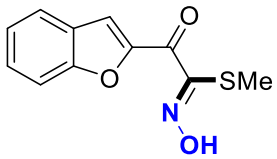
Yield: 48% (26.5 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.03 (s, 1H), 9.30 (s, 1H), 7.04 – 7.02 (m, 1H), 6.94 – 6.92 (m, 1H), 6.25 – 6.23 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 154.8, 130.6, 128.0, 122.8, 112.0, 13.5. HRMS (ESI) m/z calcd for $C_7H_8N_2O_2SNa^+$ $(M+Na)^+$ 207.0199, found 207.0199.



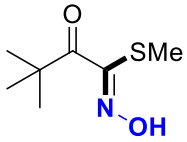
methyl (Z)-2-(benzo[b]thiophen-2-yl)-*N*-hydroxy-2-oxoethanimidothioate (**4ad**):

Yield: 62% (46.5 mg); white solid; mp: 138.7–141.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.57 (s, 1H), 8.08 (s, 1H), 7.82 (dd, *J* = 14.4, 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H),

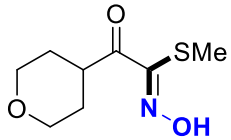
2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 179.8, 154.4, 143.7, 141.2, 138.8, 135.0, 128.3, 126.7, 125.3, 122.9, 13.7. The data are in agreement with those previously reported in the literature.[1]



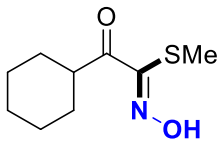
methyl (Z)-2-(benzofuran-2-yl)-*N*-hydroxy-2-oxoethanimidothioate (**4ae**):
Yield: 57% (40.1 mg); light yellow solid; mp: 179.3–181.9°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (s, 1H), 7.64 (d, *J* = 10.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 175.1, 156.6, 154.3, 150.7, 129.5, 126.8, 124.2, 123.9, 120.3, 112.6, 13.7. The data are in agreement with those previously reported in the literature.[1]



methyl (Z)-*N*-hydroxy-3,3-dimethyl-2-oxobutanimidothioate (**4af**):
Yield: 46% (24.1 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (s, 1H), 2.18 (s, 3H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 201.4, 154.3, 45.0, 26.4, 13.9; HRMS (ESI) m/z calcd for $C_7H_{17}N_2O_2S^+$ $(M+NH_4)^+$ 193.1005, found 193.1008.

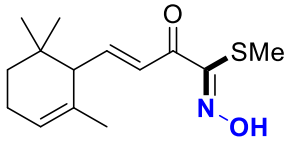


methyl (Z)-*N*-hydroxy-2-oxo-2-(tetrahydro-2*H*-pyran-4-yl)ethanimidothioate (**4ag**):
Yield: 33% (20.1 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (s, 1H), 3.96 (d, *J* = 11.6 Hz, 2H), 3.44–3.34 (m, 3H), 2.39 (s, 3H), 1.71–1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.5, 153.8, 67.1, 44.0, 28.1, 14.3; HRMS (ESI) m/z calcd for $C_8H_{14}NO_3S^+$ $(M+H)^+$ 204.0689, found 204.0690.



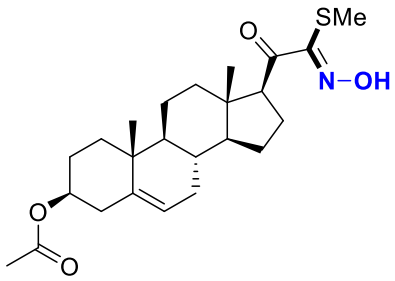
methyl (Z)-2-cyclohexyl-N-hydroxy-2-oxoethanimidothioate (**4ah**):

Yield: 50% (30.1 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (s, 1H), 3.09 – 3.03 (m, 1H), 2.35 (s, 3H), 1.81 – 1.72 (m, 4H), 1.34 – 1.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.5, 154.8, 47.3, 28.3, 25.8, 25.5, 14.2; HRMS (ESI) m/z calcd for $C_9H_{16}NO_2S^+$ $(M+H)^+$ 202.0896, found 202.0898.



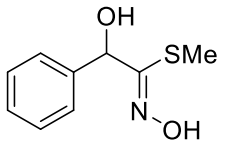
methyl (1Z,3E)-*N*-hydroxy-2-oxo-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-enimidothioate (**4ai**):

Yield: 61% (48.7 mg); light yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.93 (s, 1H), 6.93 – 6.88 (m, 1H), 6.57 (d, *J* =15.6 Hz, 1H), 5.52 (s, 1H), 2.44 (s, 3H), 2.35 (d, *J* = 10.2 Hz, 1H), 2.05 (s, 2H), 1.56 (s, 3H), 1.49 – 1.44 (m, 1H), 1.23 – 1.20 (m, 1H), 0.93 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ= 184.6, 154.9, 153.7, 131.3 127.9, 123.1, 54.5, 32.7, 31.0, 27.7, 26.8, 23.0, 22.8, 14.0; HRMS (ESI) m/z calcd for $C_{14}H_{21}NO_2SK^+$ $(M+K)^+$ 306.0925, found 306.0924.



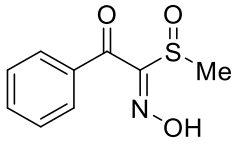
(3S,8S,9S,10R,13S,14S,17S)-17-((Z)-2-(hydroxyimino)-2-(methylthio)acetyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl acetate (**4aj**):

Yield: 55% (71.1 mg); light yellow solid; mp: 181.4–185.6℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.82 (s, 1H), 5.31 (d, *J* = 4.8 Hz, 1H), 4.58 – 4.50 (m, 1H), 3.37 (t, *J* = 8.8 Hz, 1H), 2.41 (s, 3H), 2.29 – 2.14 (m, 3H), 1.97 (s, 3H), 1.80 – 1.72 (m, 3H), 1.65 – 1.32 (m, 9H), 1.23–1.02 (m, 4H), 0.94 (s, 3H), 0.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 196.8, 171.0, 155.2, 139.6, 122.3, 74.0, 58.5, 56.9, 49.9, 45.4, 38.8, 38.0 37.0, 36.6, 31.9, 31.7, 27.7, 24.6, 22.8, 21.4, 21.0, 19.3, 14.3, 13.9. HRMS (ESI) m/z calcd for $C_{24}H_{35}NO_4SNa^+$ $(M+Na)^+$ 456.2179, found 456.2173.



methyl (Z)-*N*,2-dihydroxy-2-phenylethanimidothioate (**6a**):

Yield: 72% (28.4 mg); light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.33 (m, 5H), 5.97 (s, 2H), 5.58 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.9, 138.9, 128.8, 128.5, 126.8, 73.8, 12.8. HRMS (ESI) m/z calcd for $C_9H_{12}NO_2S^+$ $(M+H)^+$ 198.0583; found 198.0583.



(Z)-2-(hydroxyimino)-2-(methylsulfinyl)-1-phenylethan-1-one (**6b**):

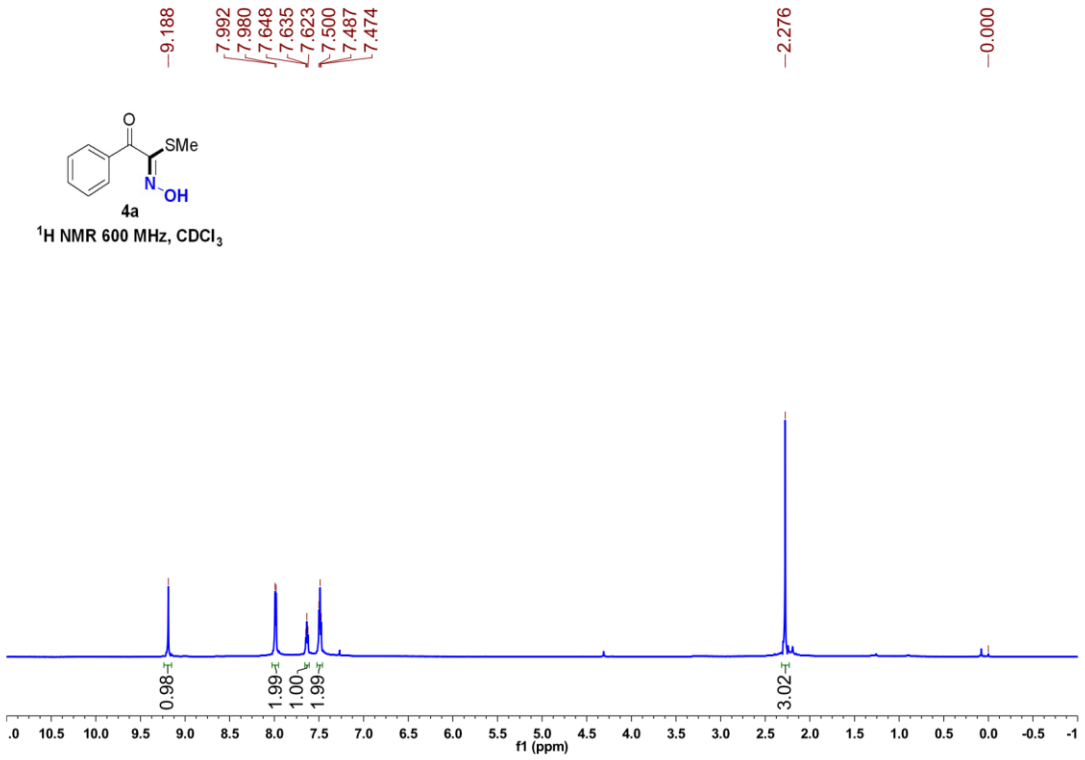
Yield: 80% (33.6 mg); white soild; mp: 125.1–127.8℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.31 (s, 1H), 7.98 – 7.61 (m, 5H), 3.06 (s, 3H). The data are in agreement with those previously reported in the literature.[2]

References:

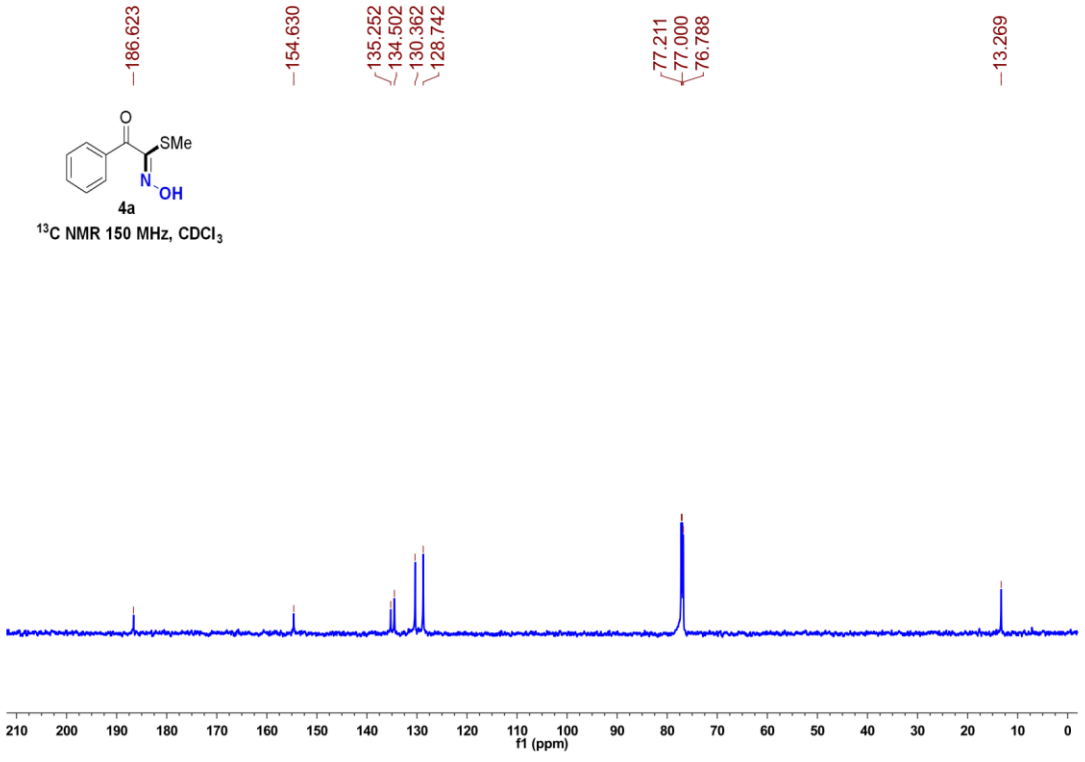
(1) Dighe, S. U.; Mukhopadhyay, S.; Priyanka, K.; Batra, S. Metal-Free Oxidative Nitration of A-Carbon of Carbonyls Leads to One-Pot Synthesis of Thiohydroximic Acids from Acetophenones. *Org. Lett.* **2016**, *18*, 4190-4193.

(2) Otsuji, Y.; Tsujii, Y.; Yoshida, A.; Imoto, E. The Nitrosation of β-Keto Sulfoxides. *Bulletin of the Chemical Society of Japan* **1971**, *44*, 219-223.

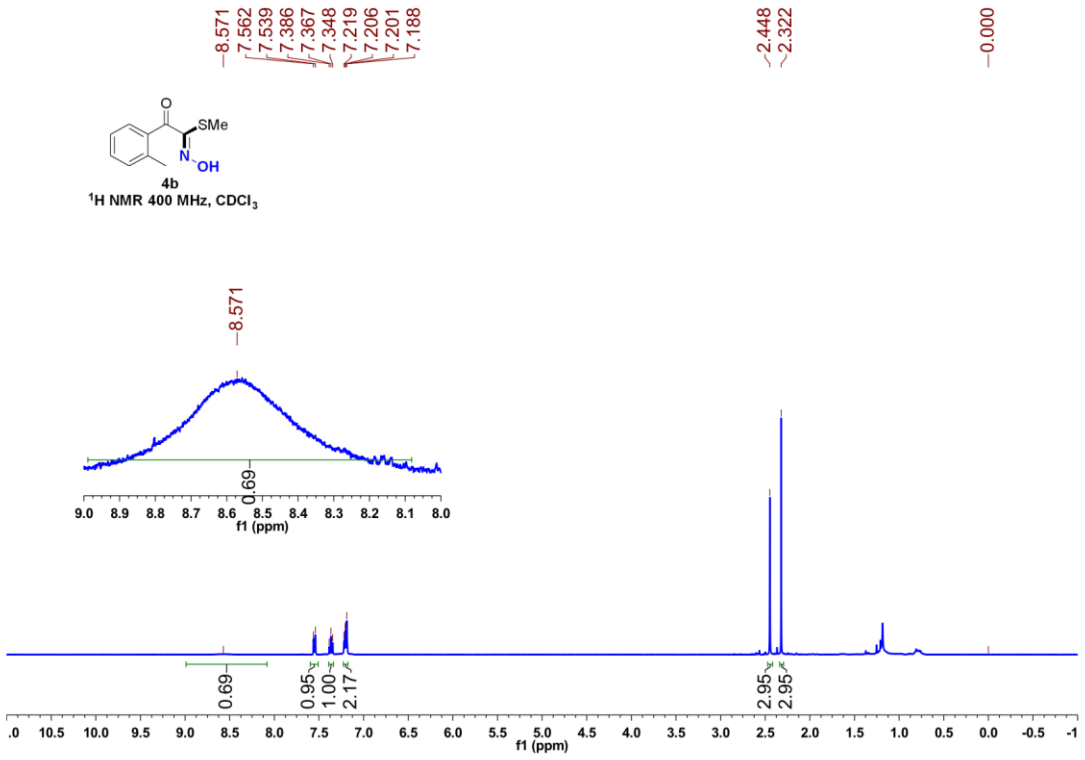
6. Copies of ^{1}H NMR, ^{13}C NMR



^{1}H NMR 600 MHz, $CDCl_3$



^{13}C NMR 150 MHz, $CDCl_3$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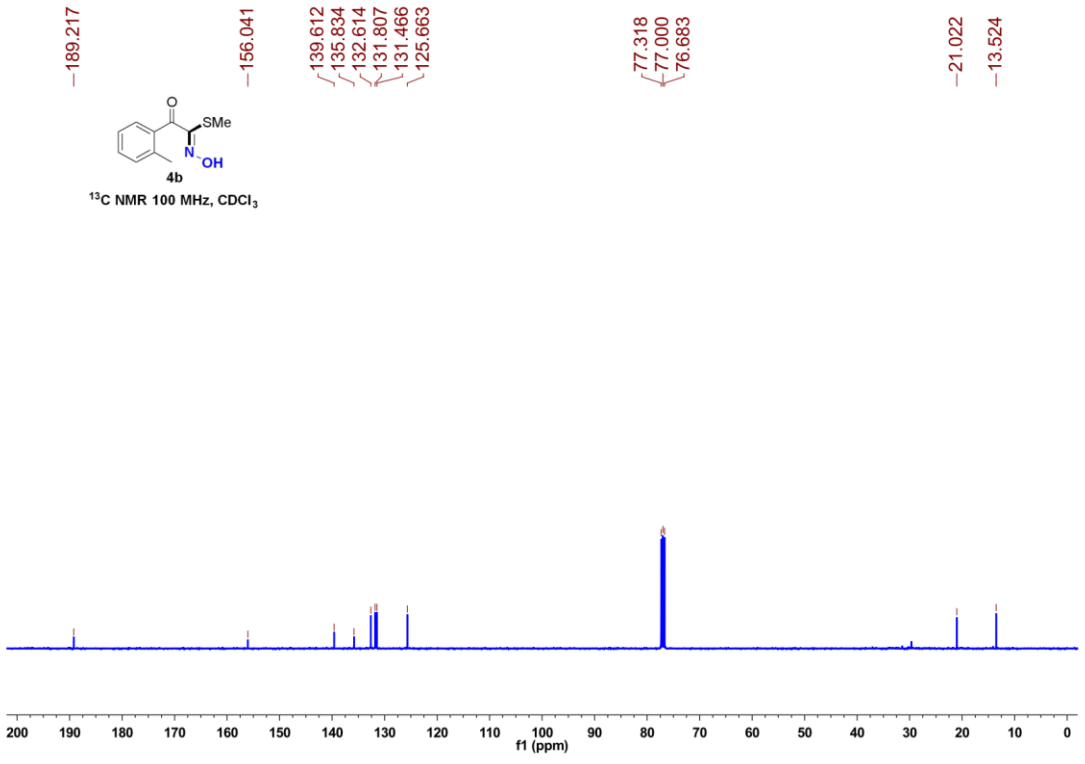
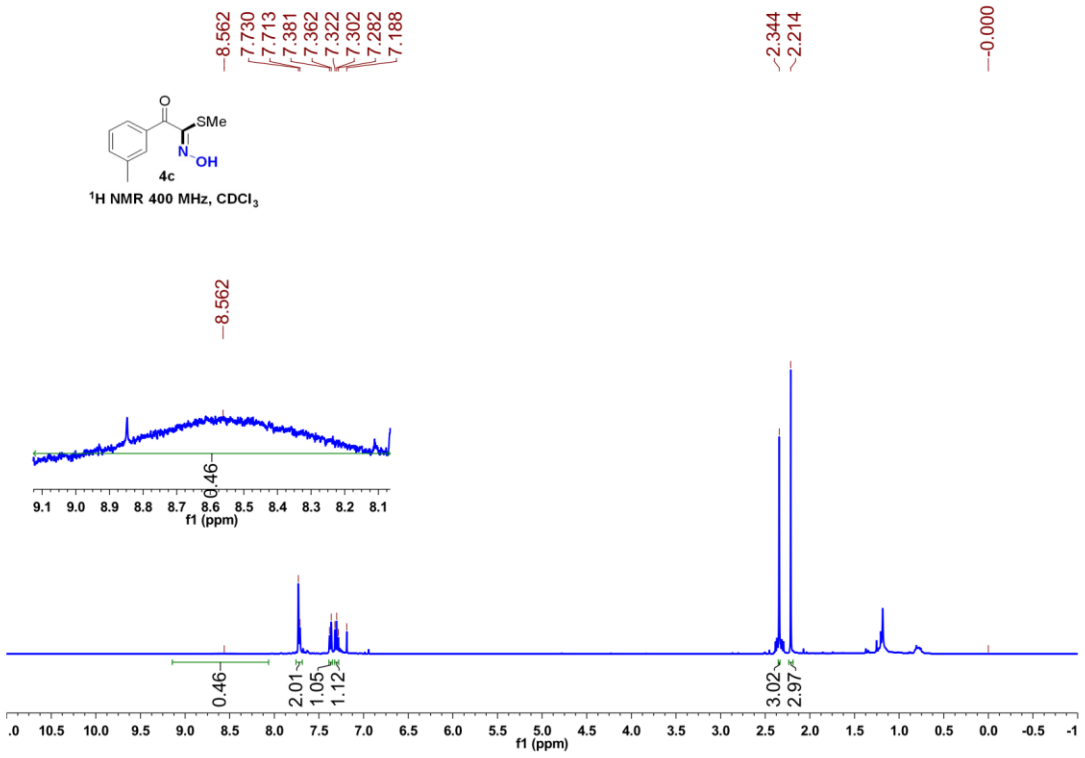
7.539
7.386
7.367
7.348
7.219
7.206
7.201
7.188
2.448
2.322
0.000
SMe
N
OH
4b
1H NMR 400 MHz, CDCl3
0.69
f1 (ppm)
0.69
0.95
1.00
2.17
2.95
2.95
f1 (ppm)


189.217
156.041
139.612
135.834
132.614
131.807
131.466
125.663
77.318
77.000
76.683
21.022
13.524
SMe
N
OH
4b
13C NMR 100 MHz, CDCl3
f1 (ppm)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7.713
7.381
7.362
7.322
7.302
7.282
7.188
2.344
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N
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4c
1H NMR 400 MHz, CDCl3
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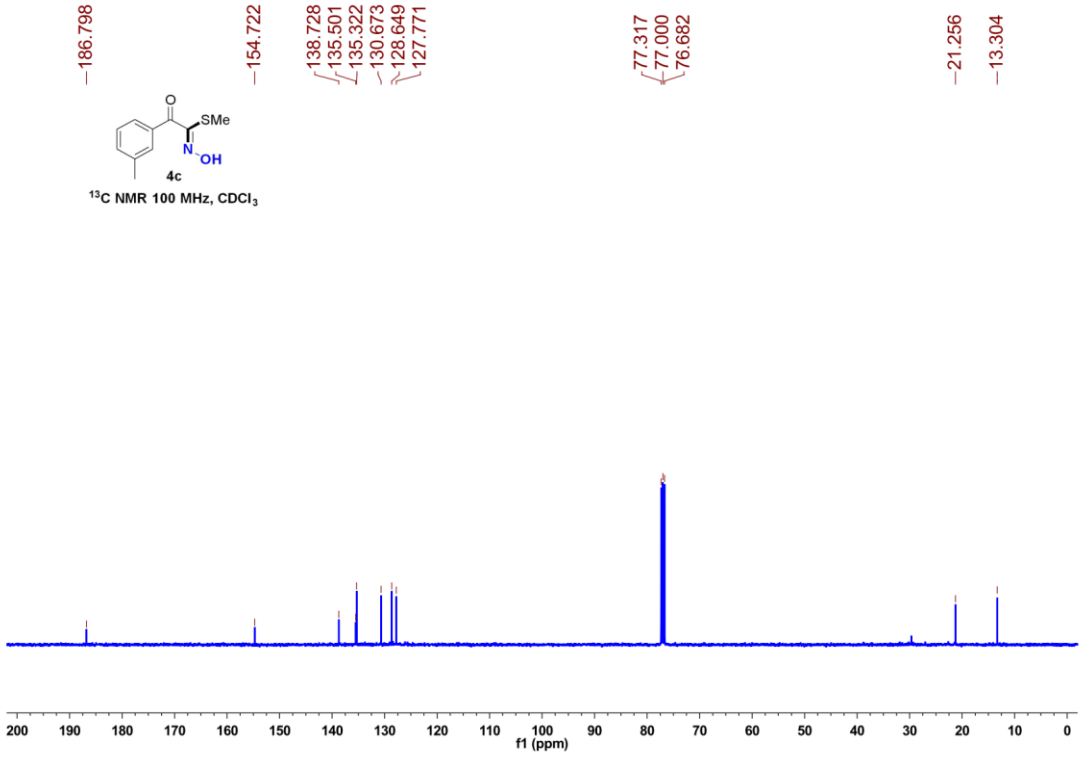
2.01
1.05
1.12
3.02
2.97
f1 (ppm)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138.728
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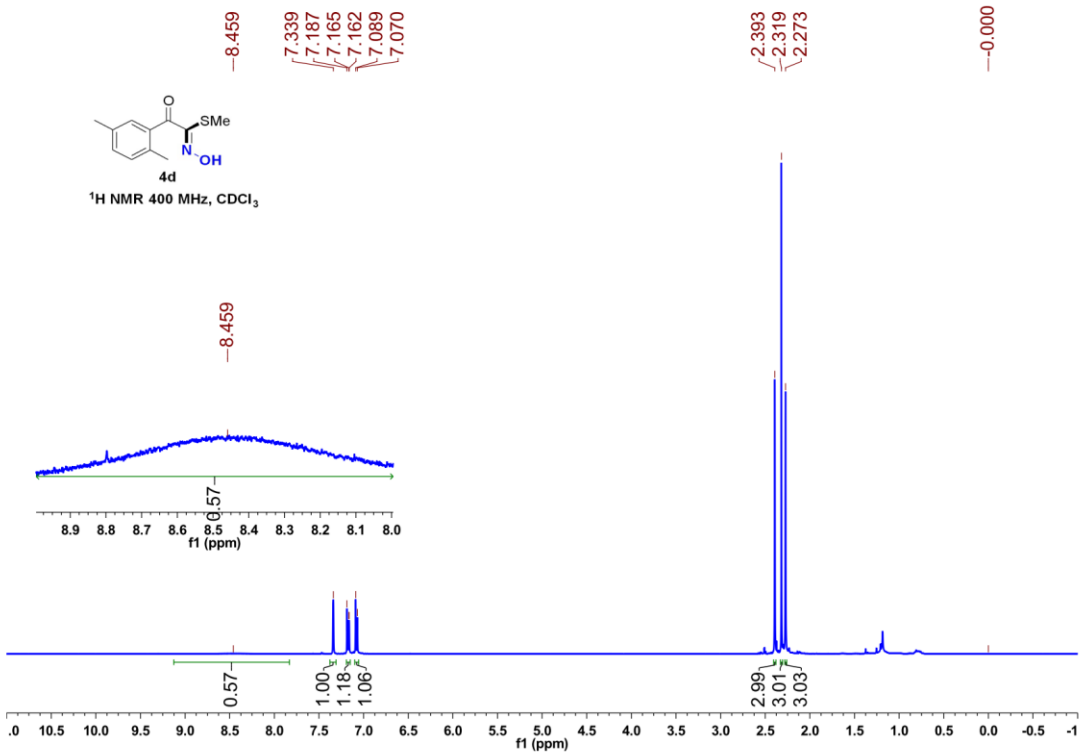
21.256
13.304
SMe
N
OH
4c
13C NMR 100 MHz, CDCl3
f1 (ppm)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7.339
7.187
7.165
7.162
7.089
7.070
2.393
2.319
2.273
0.000
SMe
N
OH
4d
1H NMR 400 MHz, CDCl3
0.57
f1 (ppm)
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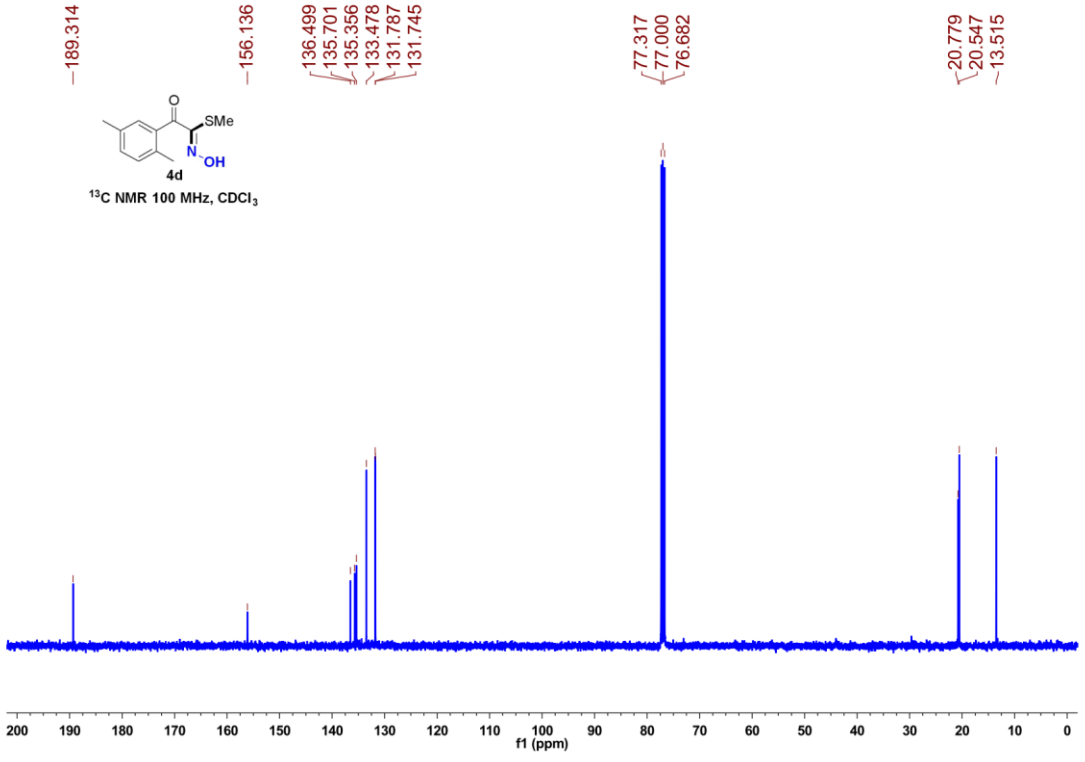
1.18
1.06
2.99
3.01
3.03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156.136
136.499
135.701
135.356
133.478
131.787
131.745
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77.000
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20.779
20.547
13.515
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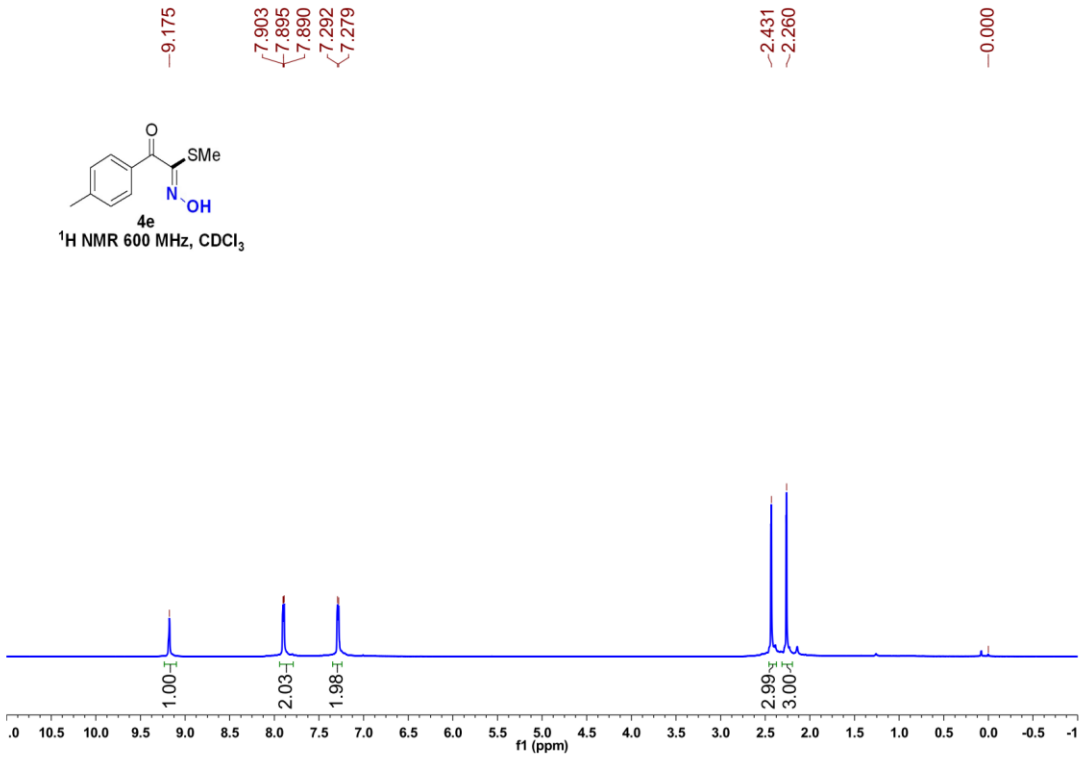
N
OH
4d
13C NMR 100 MHz, CDCl3
f1 (ppm)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7.895
7.890
7.292
7.279
2.431
2.260
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N
OH
4e
1H NMR 600 MHz, CDCl3
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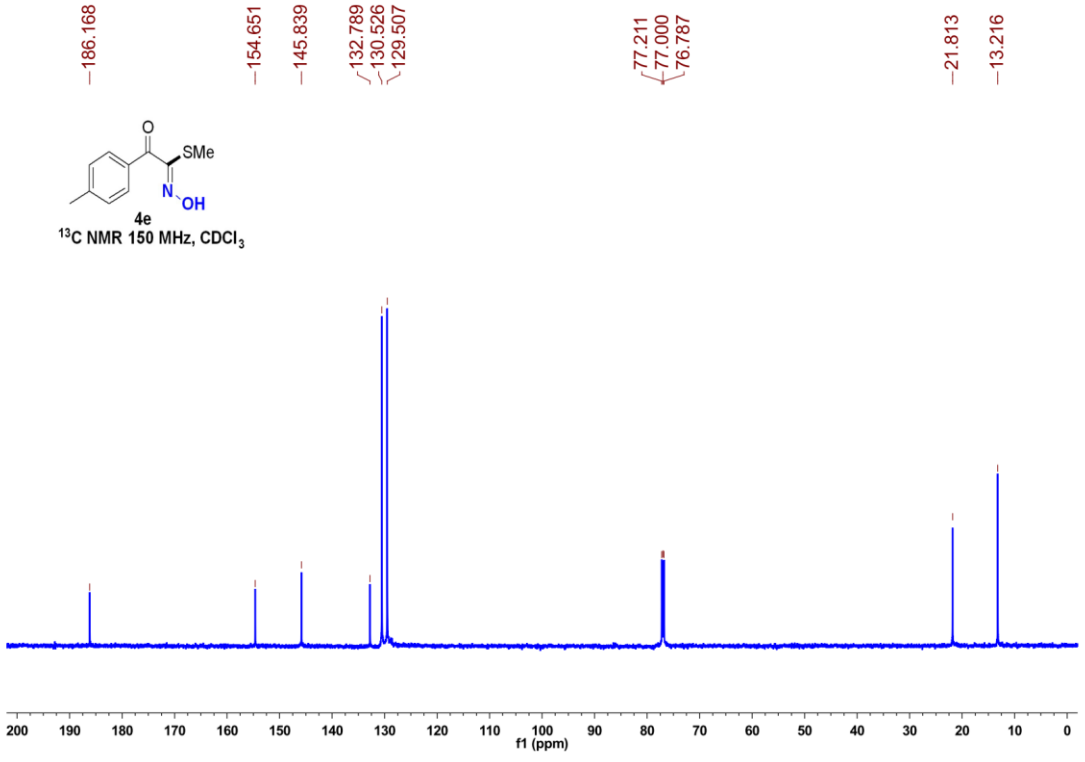
1.98
2.99
3.00
f1 (ppm)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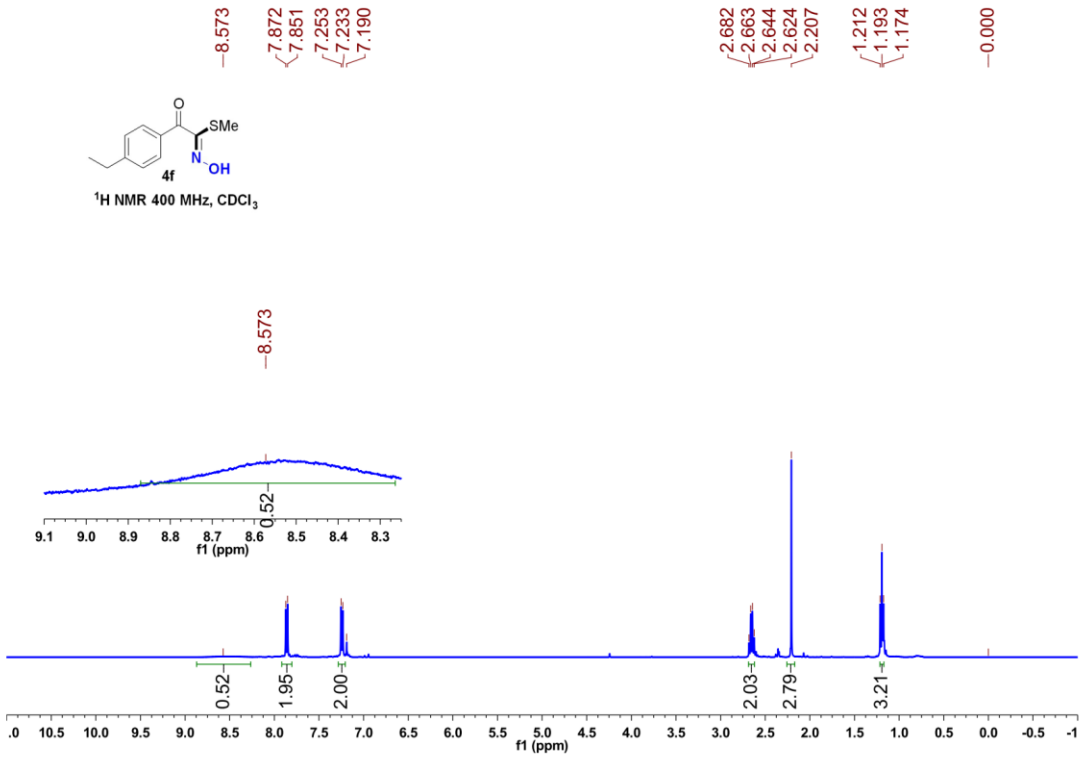
N
OH
4e
13C NMR 150 MHz, CDCl3
f1 (ppm)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7.253
7.233
7.190
2.682
2.663
2.644
2.624
2.207
1.212
1.193
1.174
0.000
SMe
N
OH
4f
1H NMR 400 MHz, CDCl3
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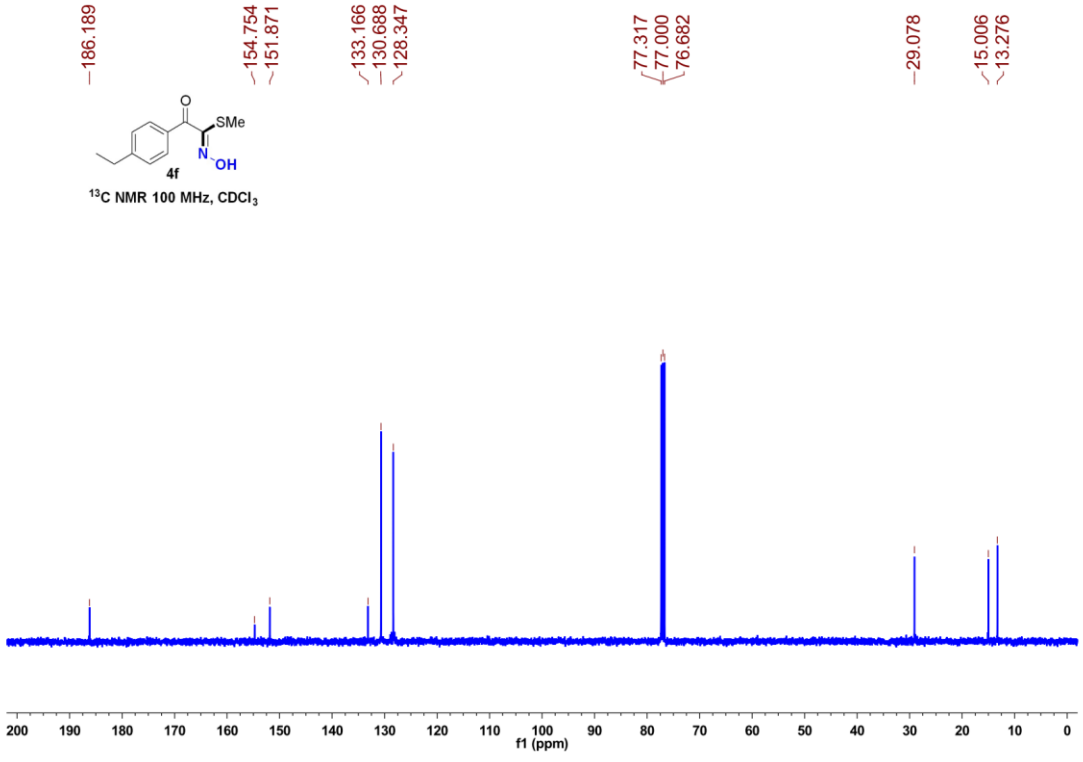
f1 (ppm)
0.52
1.95
2.00
2.03
2.79
3.21
f1 (ppm)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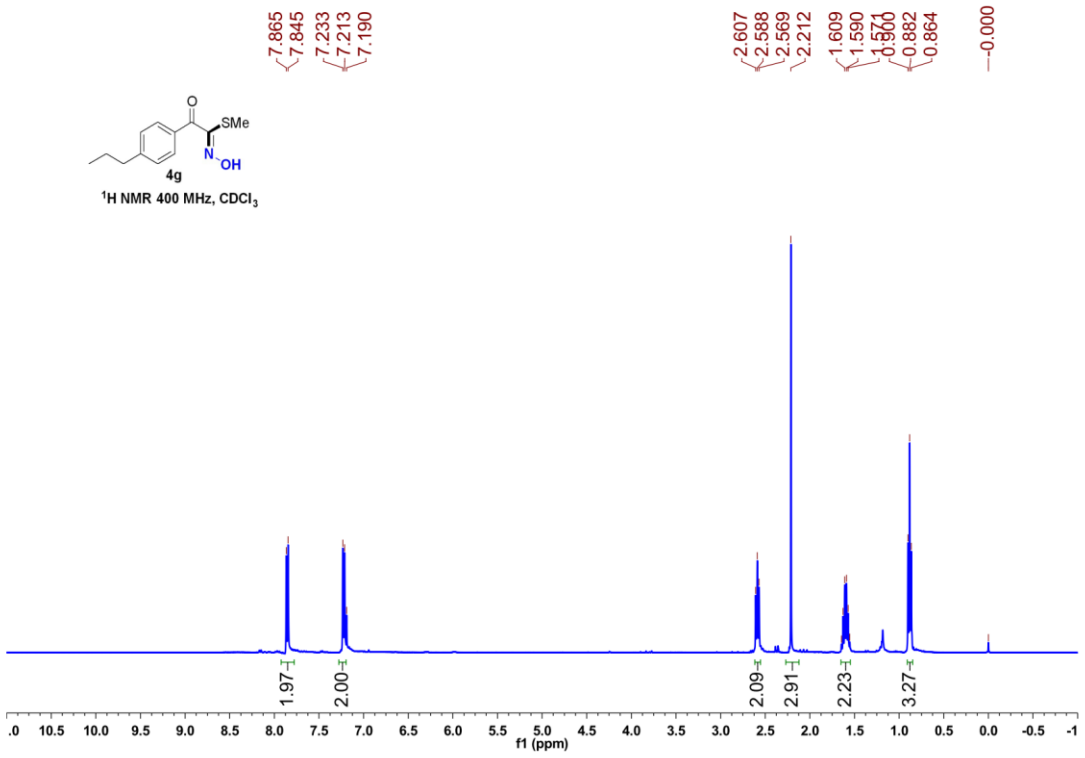
OH
4f
13C NMR 100 MHz, CDCl3
f1 (ppm)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7.233
7.213
7.190
2.607
2.588
2.569
2.212
1.609
1.590
1.571
0.900
0.882
0.864
0.000
SMe
N
OH
4g
1H NMR 400 MHz, CDCl3
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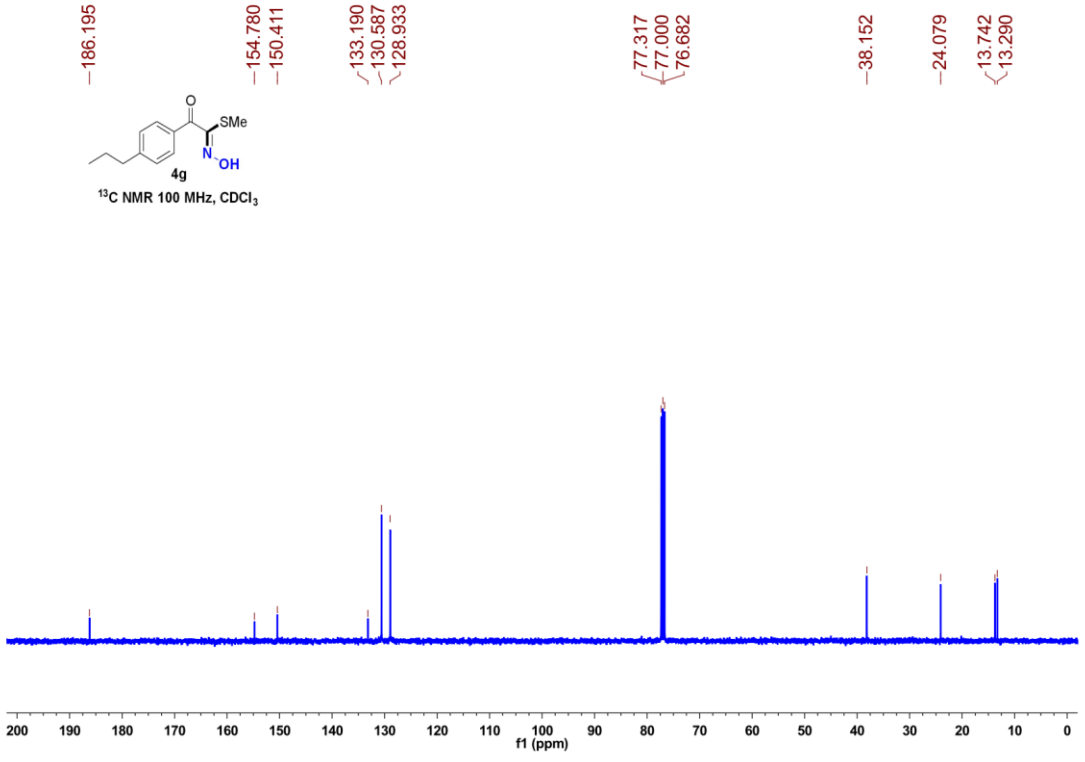
2.00
2.09
2.91
2.23
3.27
f1 (ppm)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150.411
133.190
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77.000
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13.290
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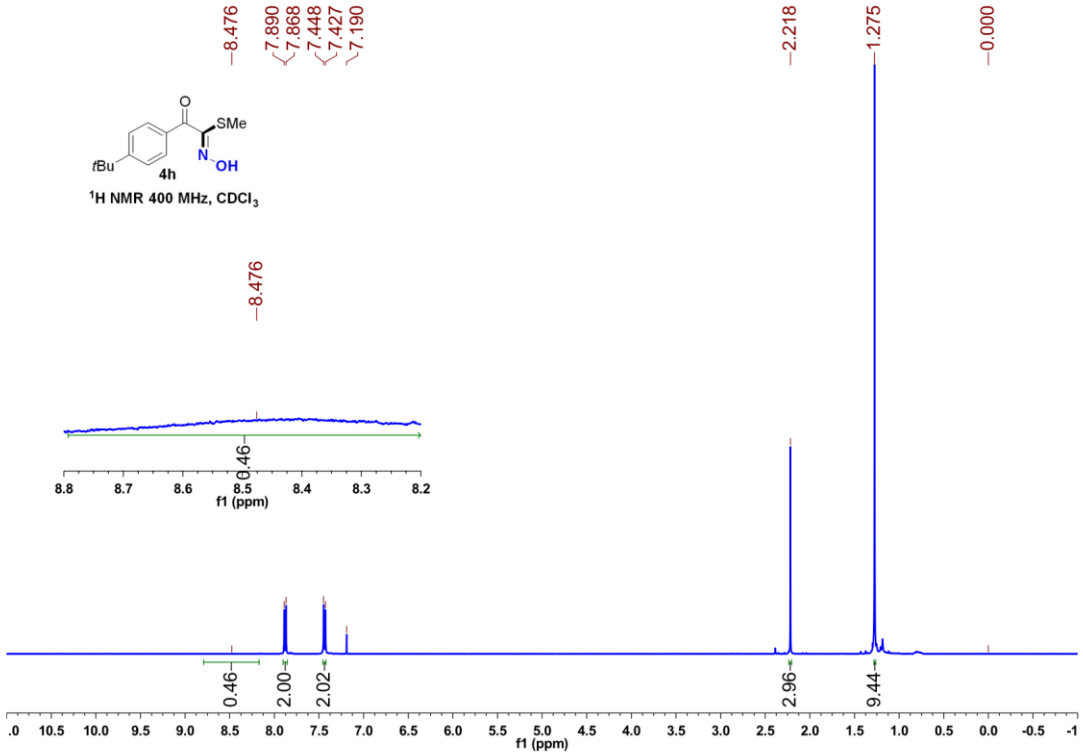
OH
4g
13C NMR 100 MHz, CDCl3
f1 (ppm)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7.190
2.218
1.275
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tBu
4h
1H NMR 400 MHz, CDCl3
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f1 (ppm)
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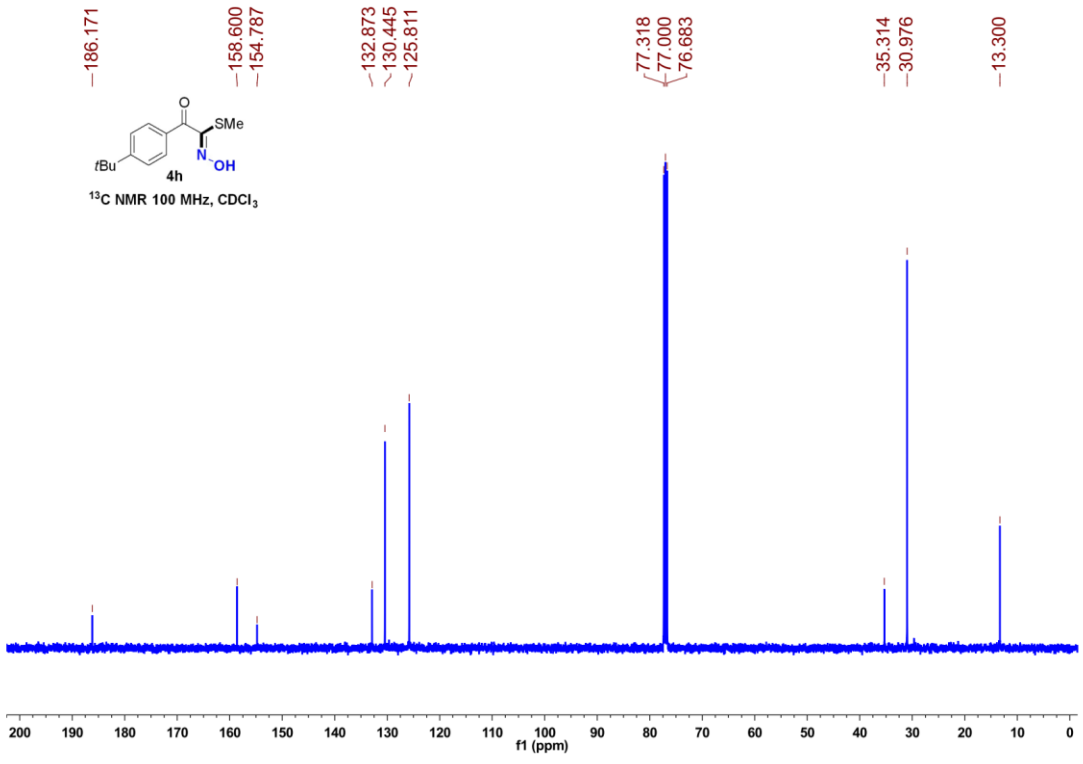
2.02
2.96
9.44
f1 (ppm)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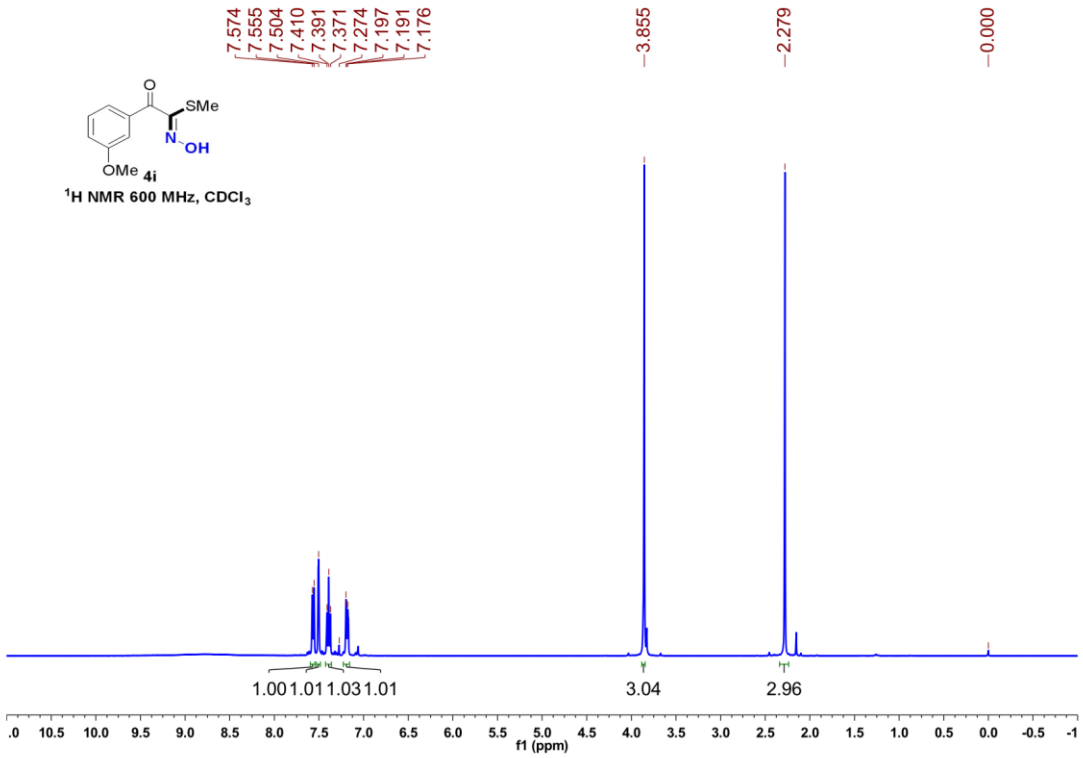
OH
tBu
4h
13C NMR 100 MHz, CDCl3
f1 (ppm)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7.371
7.274
7.197
7.191
7.176
3.855
2.279
0.000
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N
OH
OMe
4i
1H NMR 600 MHz, CDCl3
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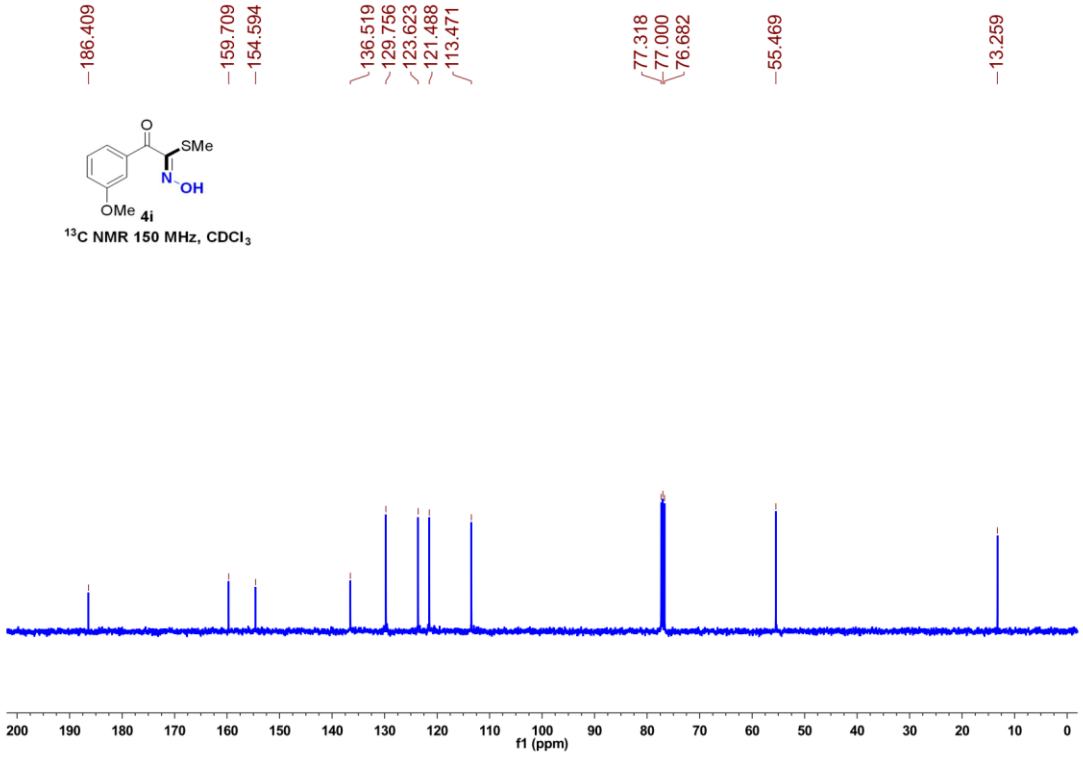
3.04
2.96
f1 (ppm)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OMe
4i
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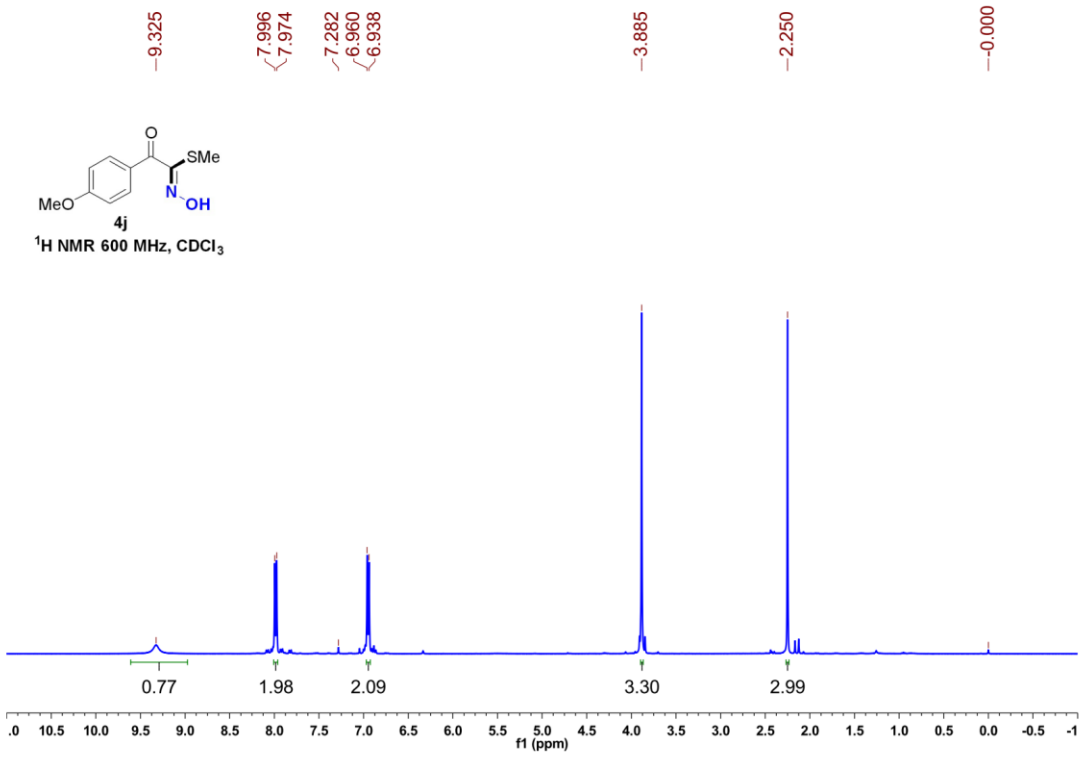
f1 (ppm)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6.960
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2.250
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4j
1H NMR 600 MHz, CDCl3
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3.30
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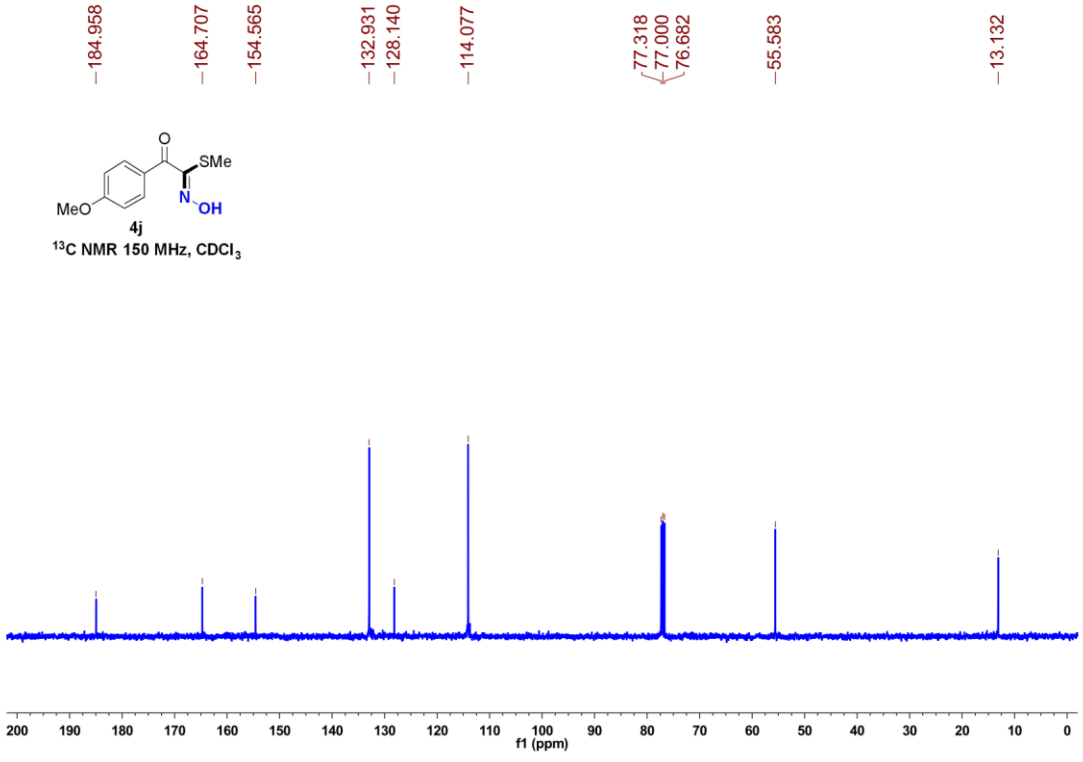
f1 (ppm)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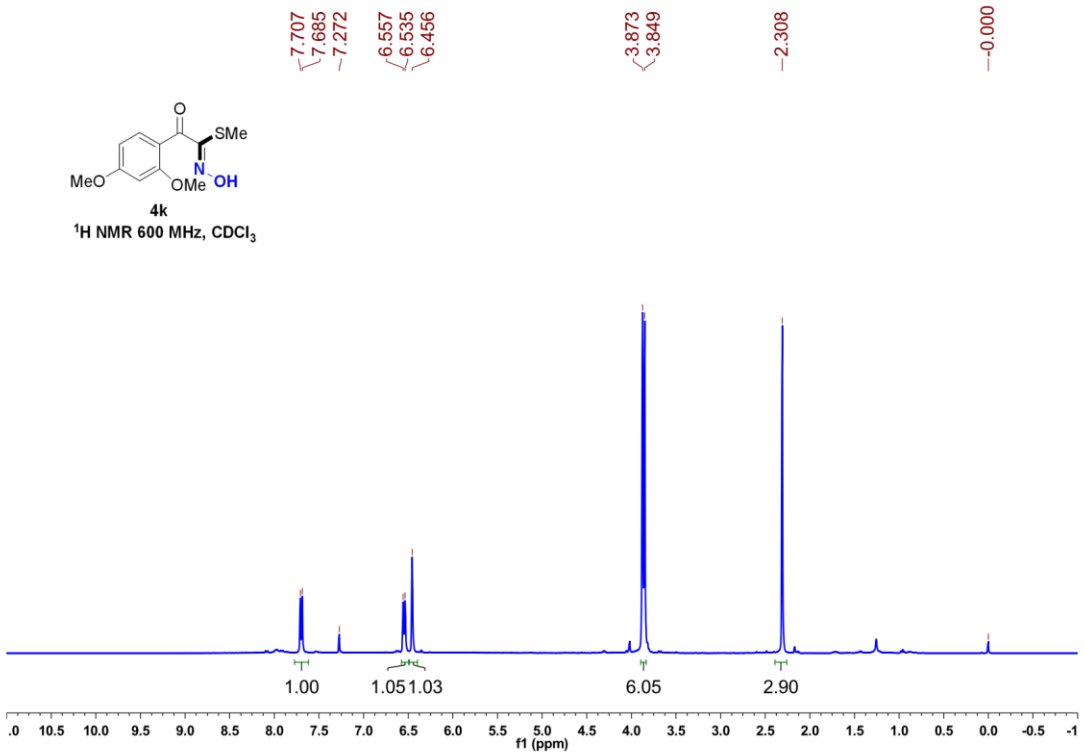
MeO
4j
13C NMR 150 MHz, CDCl3
f1 (ppm)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6.535
6.456
3.873
3.849
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0.000
O
SMe
N
OH
MeO
OMe
4k
1H NMR 600 MHz, CDCl3
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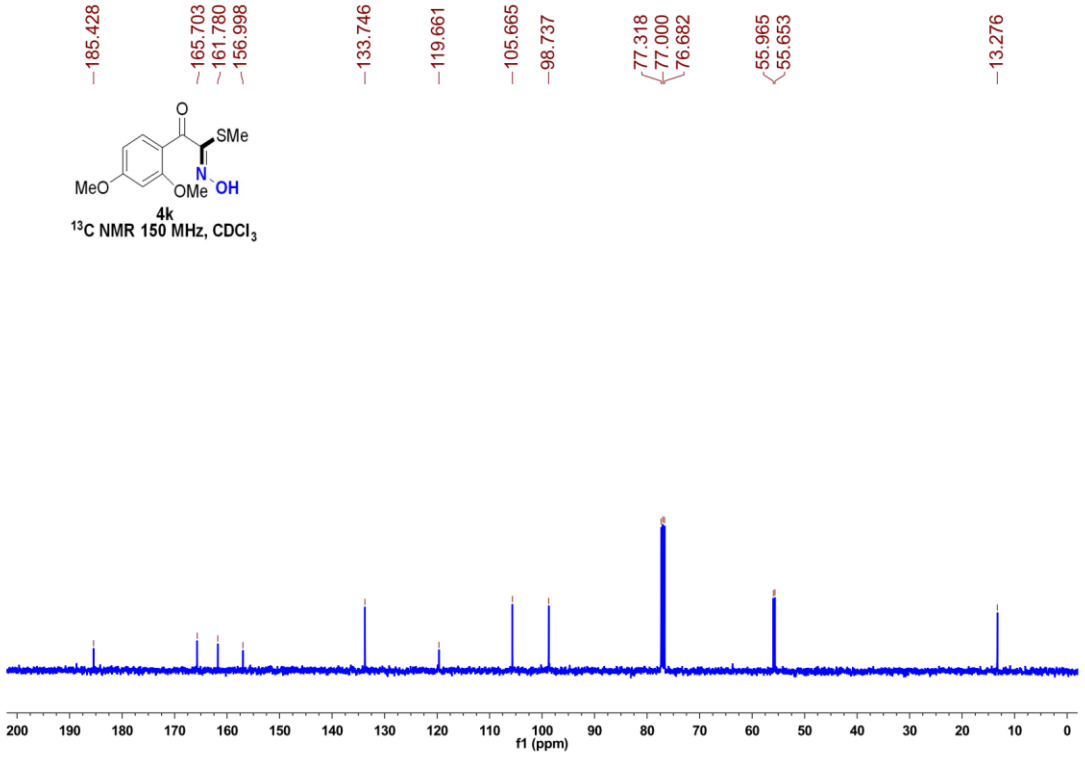
1.05
1.03
6.05
2.90
f1 (ppm)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77.000
76.682
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N
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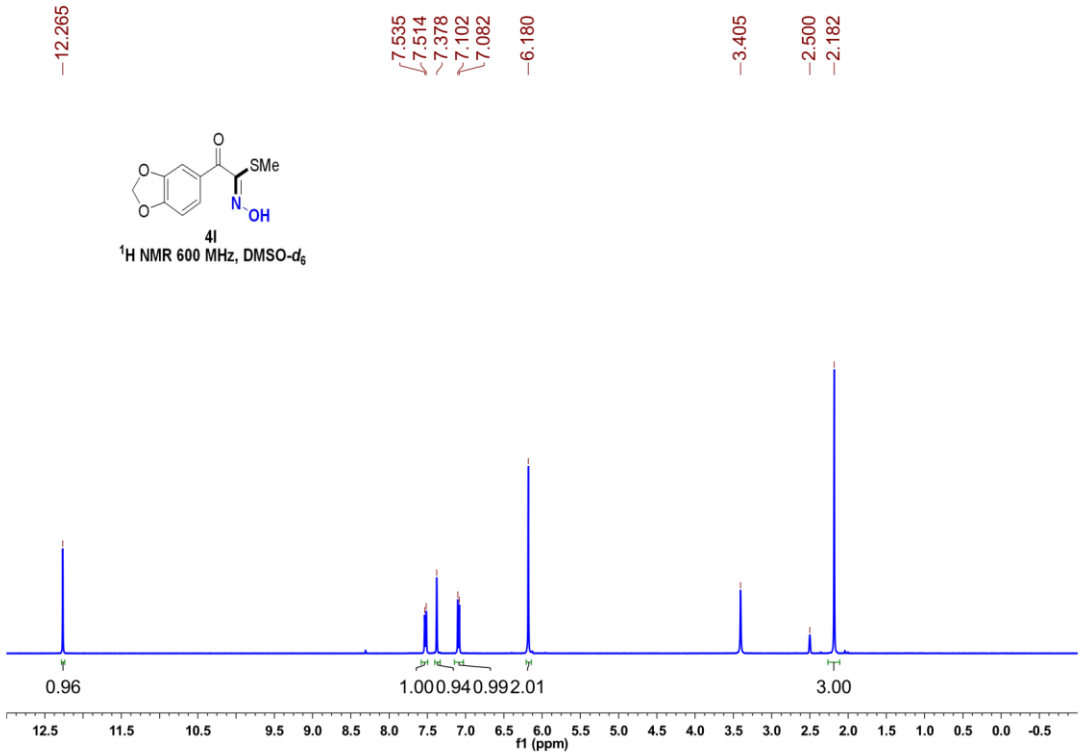
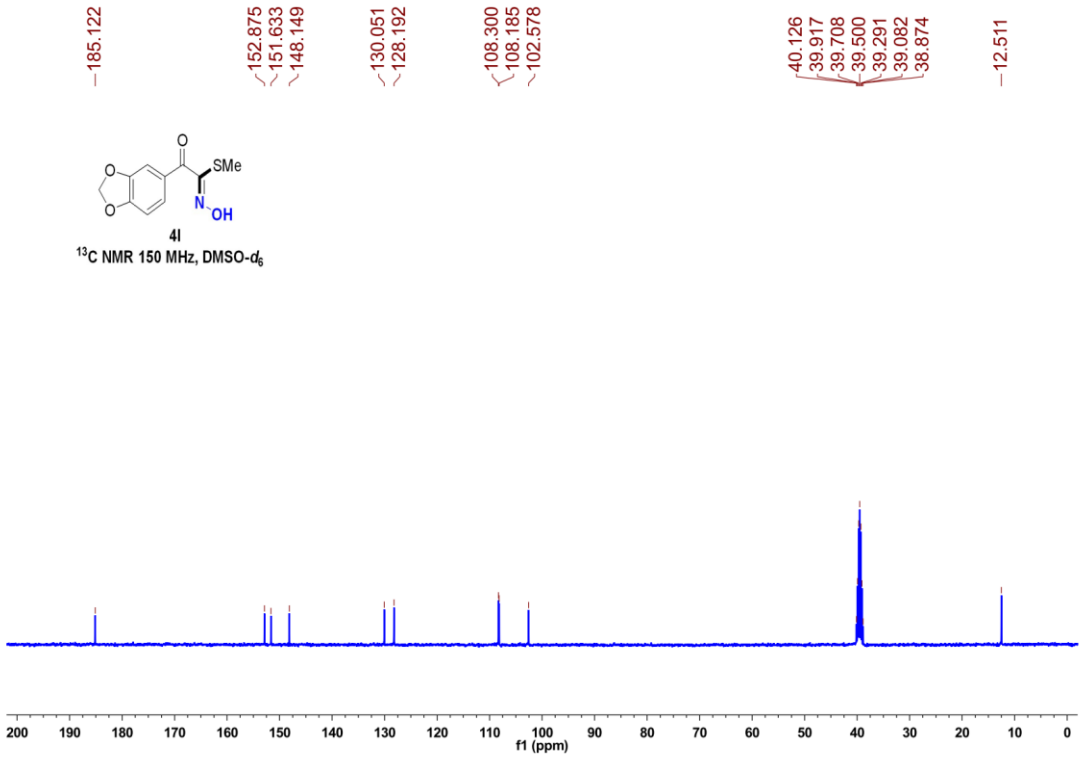
MeO
OMe
4k
13C NMR 150 MHz, CDCl3
f1 (ppm)



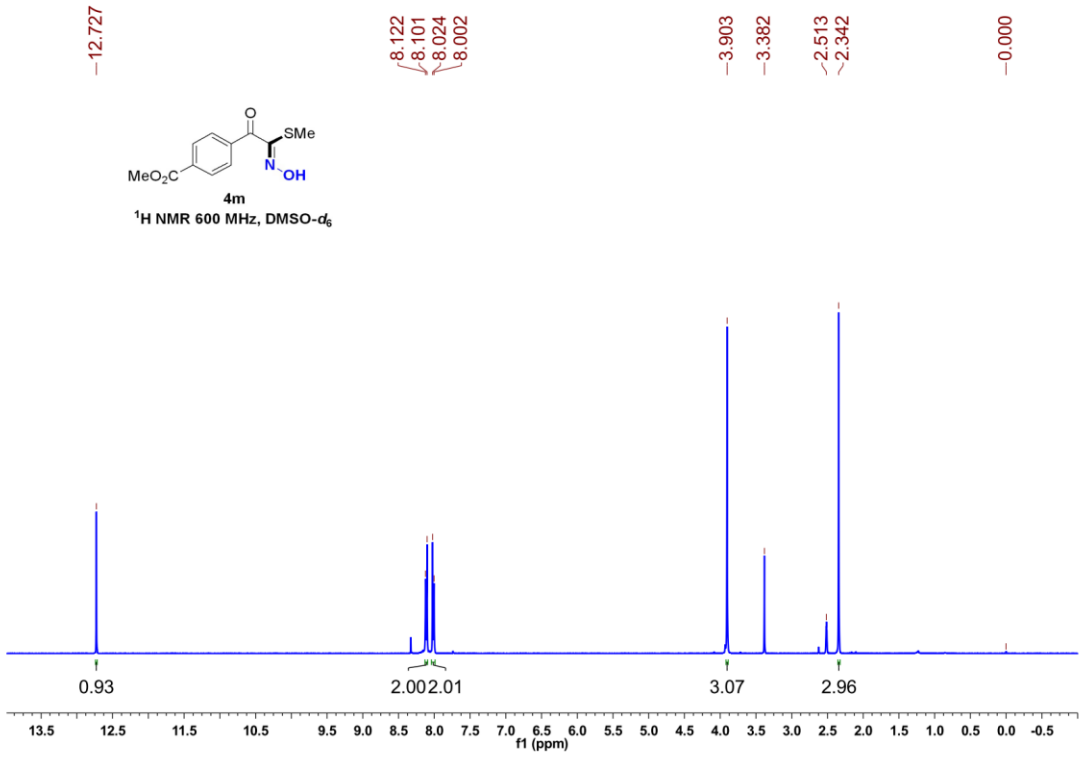
4l

^{1}H NMR 600 MHz, DMSO-d_6



4l

^{13}C NMR 150 MHz, DMSO-d_6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8.122
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8.002
3.903
3.382
2.513
2.342
0.000
SMe
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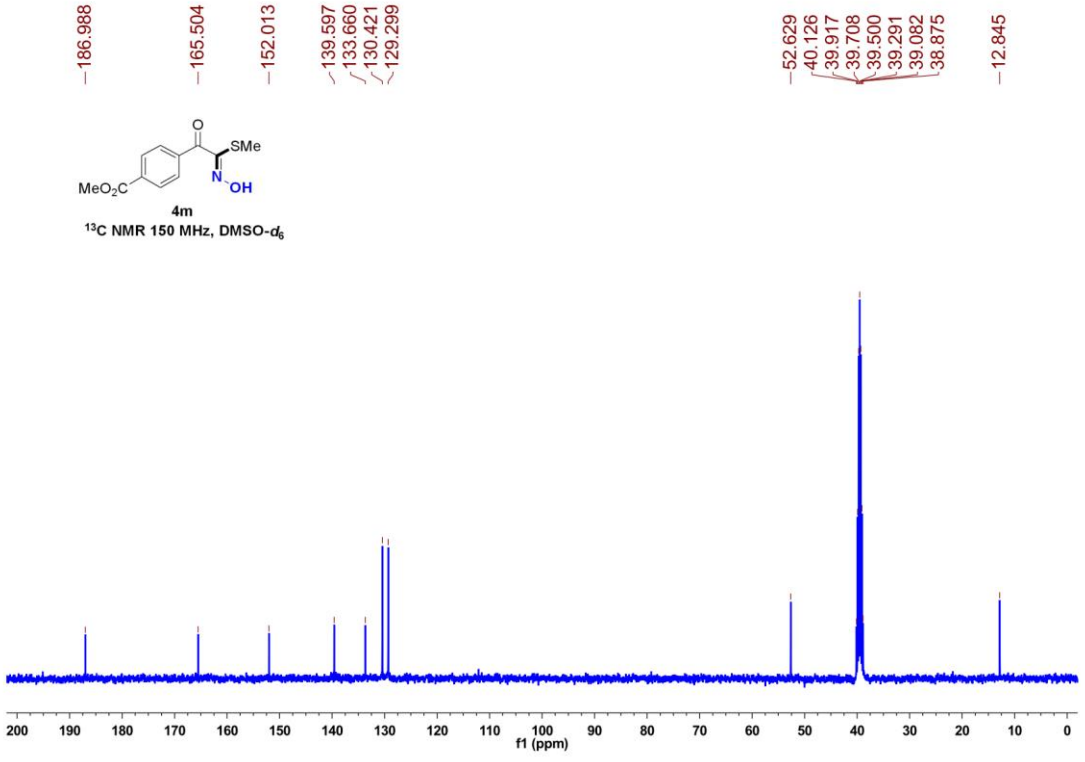
OH
MeO2C
4m
1H NMR 600 MHz, DMSO-d6
0.93
2.00
2.01
3.07
2.96
f1 (ppm)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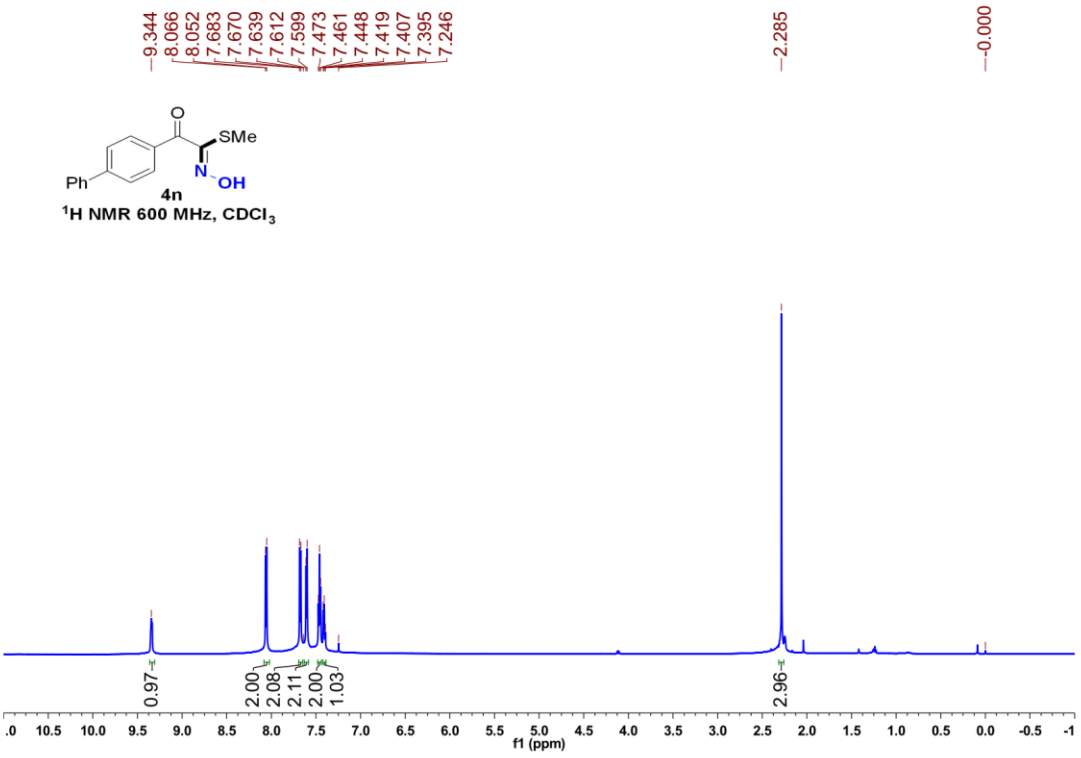
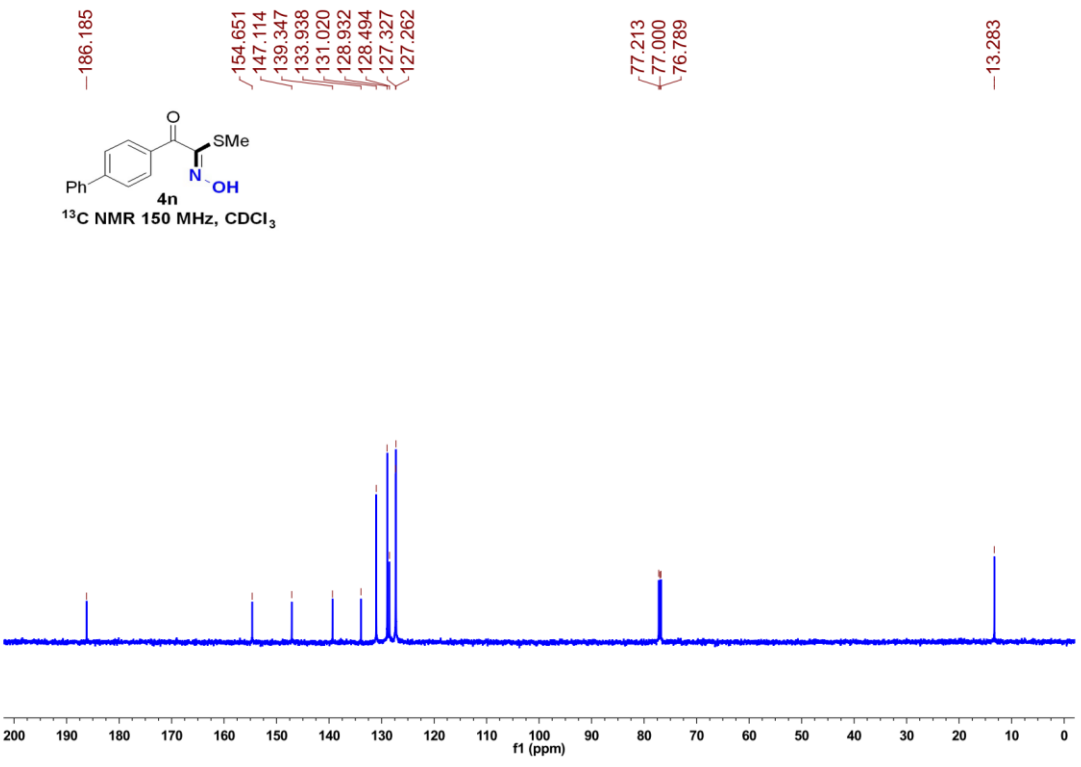
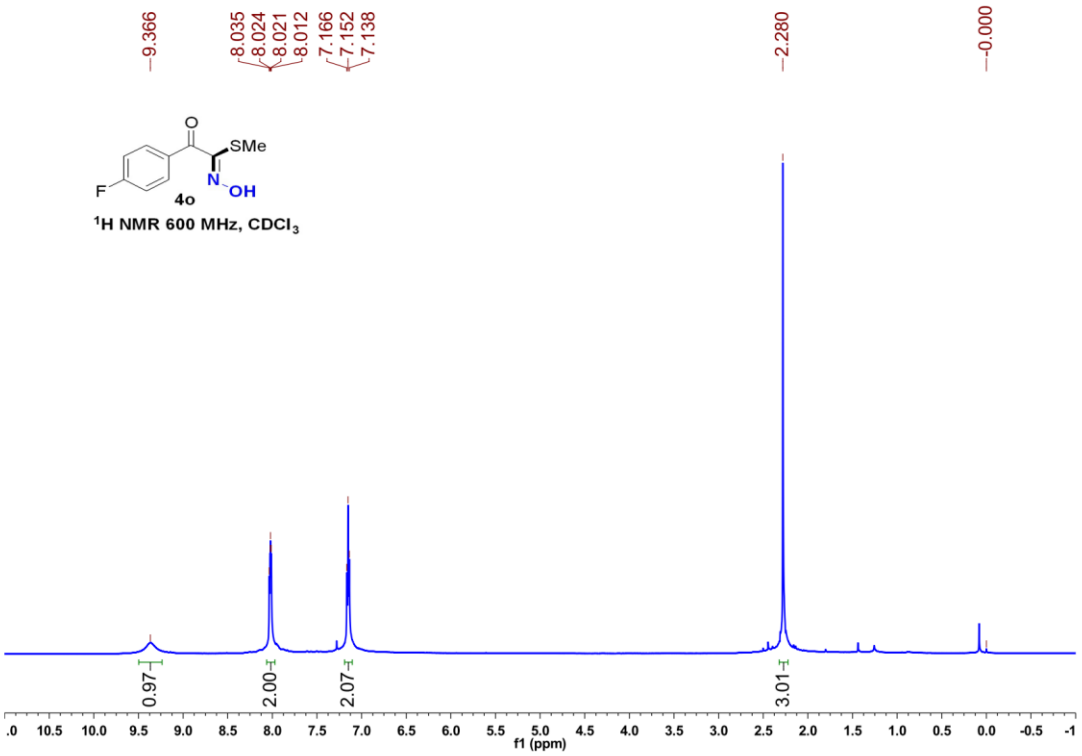
MeO2C
4m
13C NMR 150 MHz, DMSO-d6
f1 (ppm)



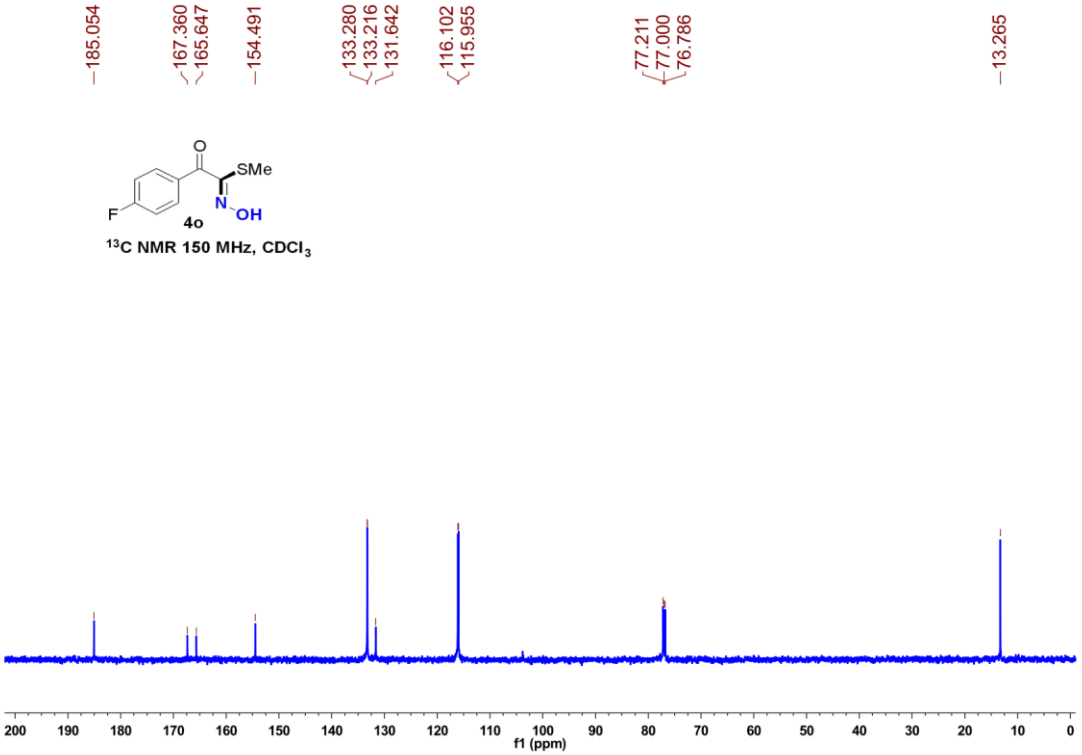
^{1}H NMR 600 MHz, $CDCl_3$



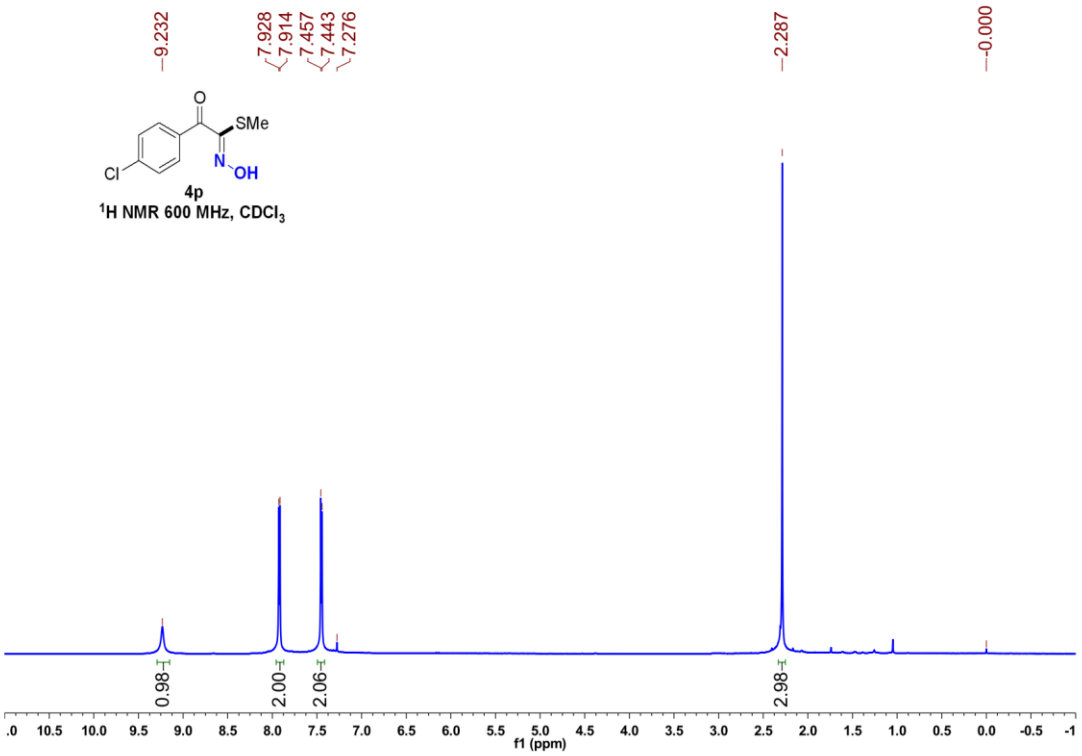
^{13}C NMR 150 MHz, $CDCl_3$



^{1}H NMR 600 MHz, $CDCl_3$



^{13}C NMR 150 MHz, $CDCl_3$


9.232
7.928
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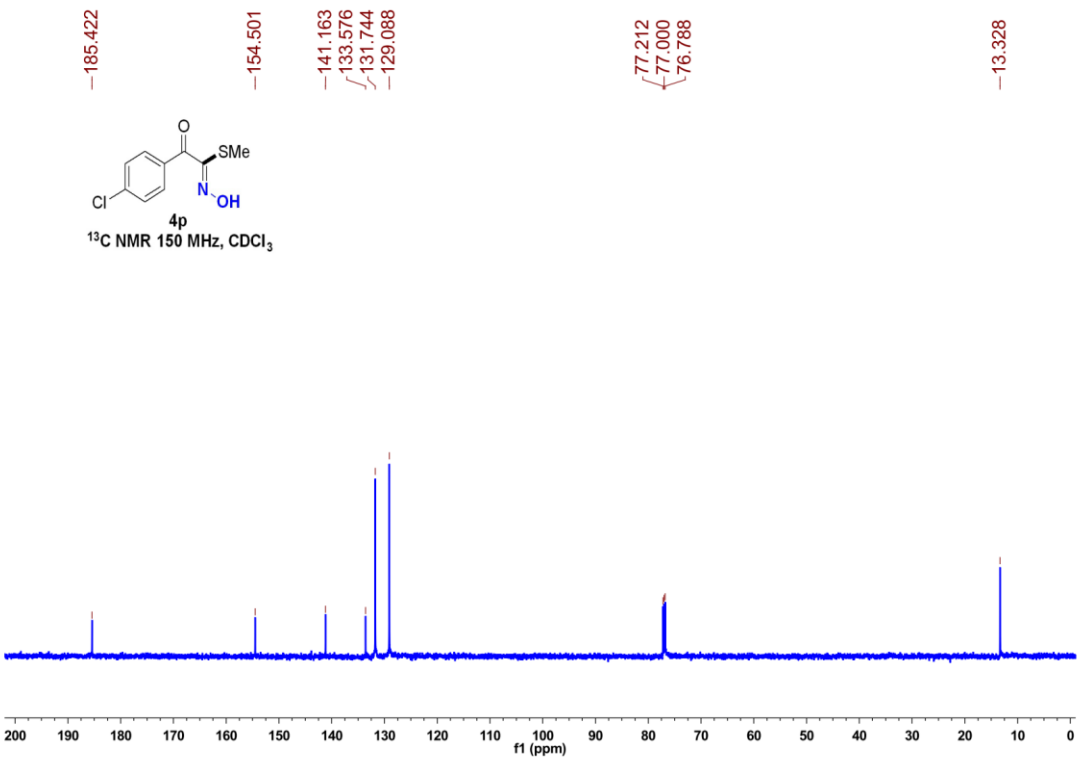
7.457
7.443
7.276
2.287
0.000
SMe
N
OH
Cl
4p
^{1}H NMR 600 MHz, CDCl$_3$
0.98
2.00
2.06
2.98
f1 (ppm)


185.422
154.501
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133.576
131.744
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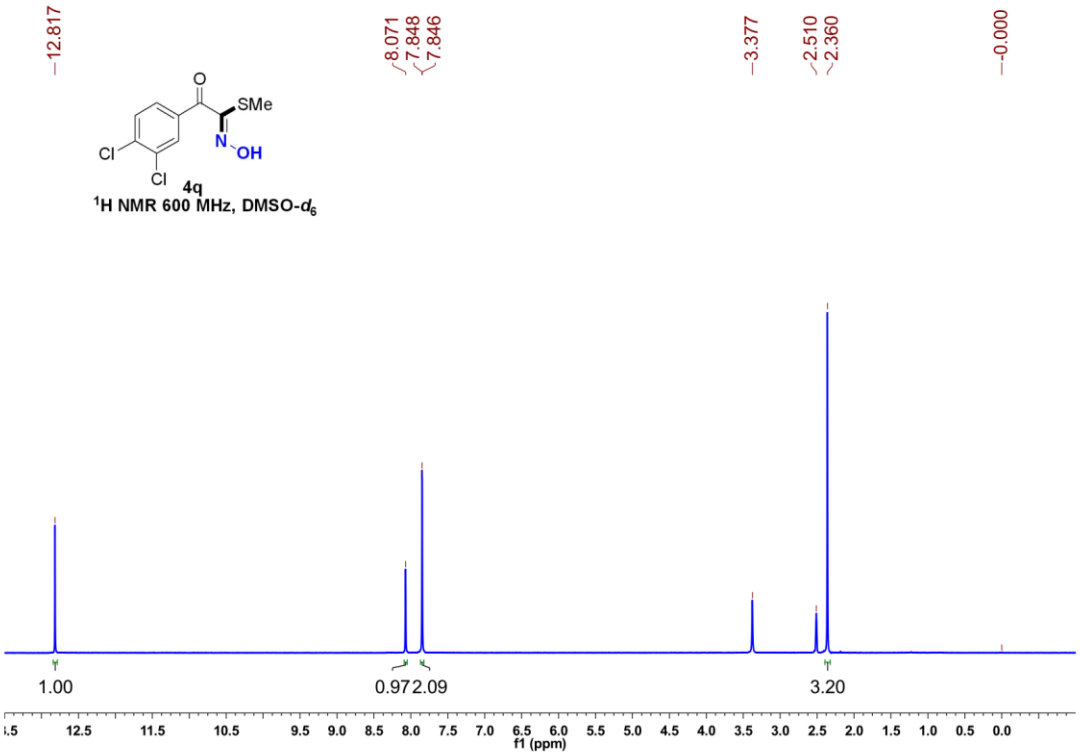
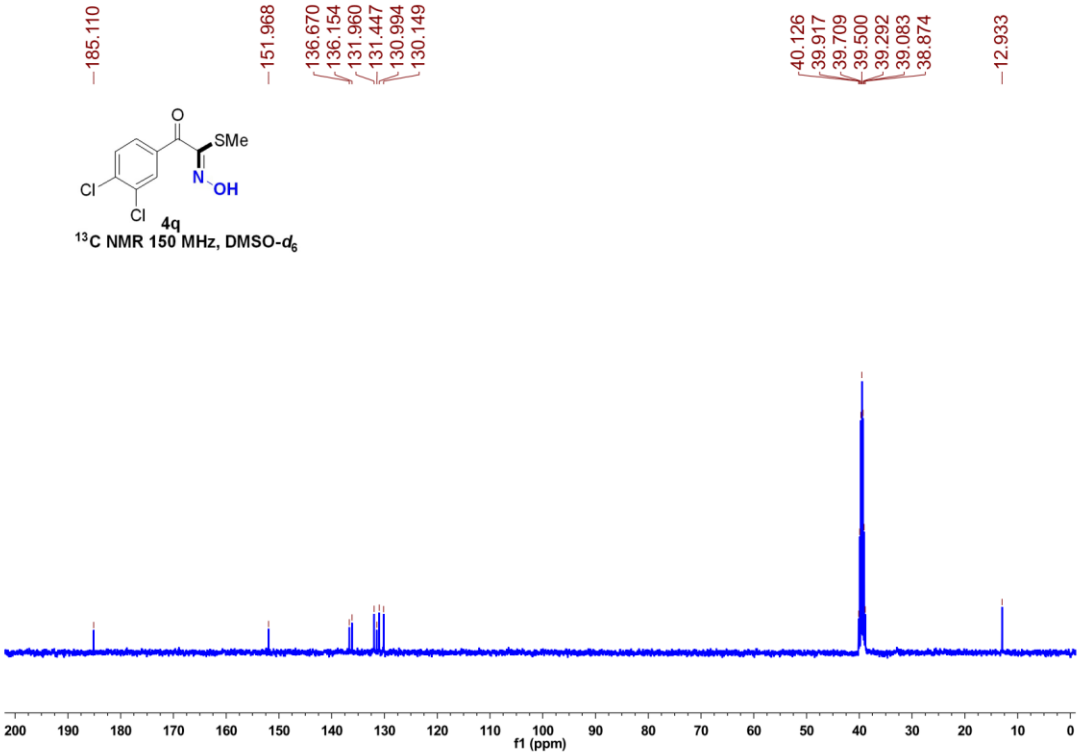
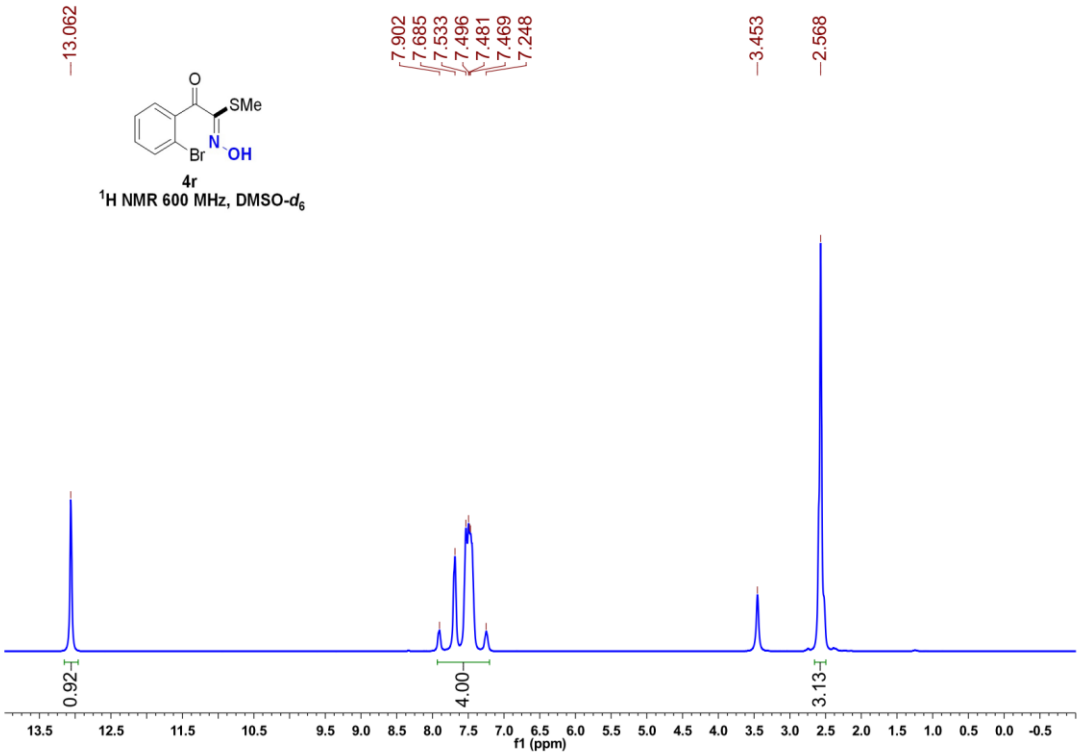
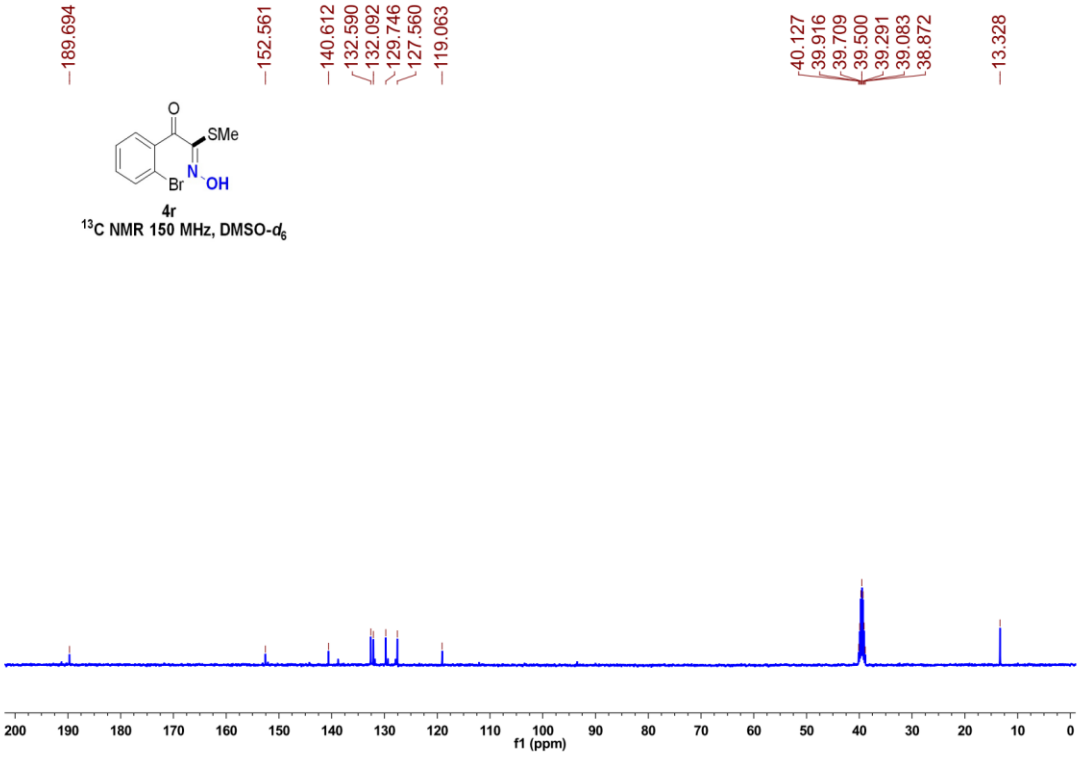
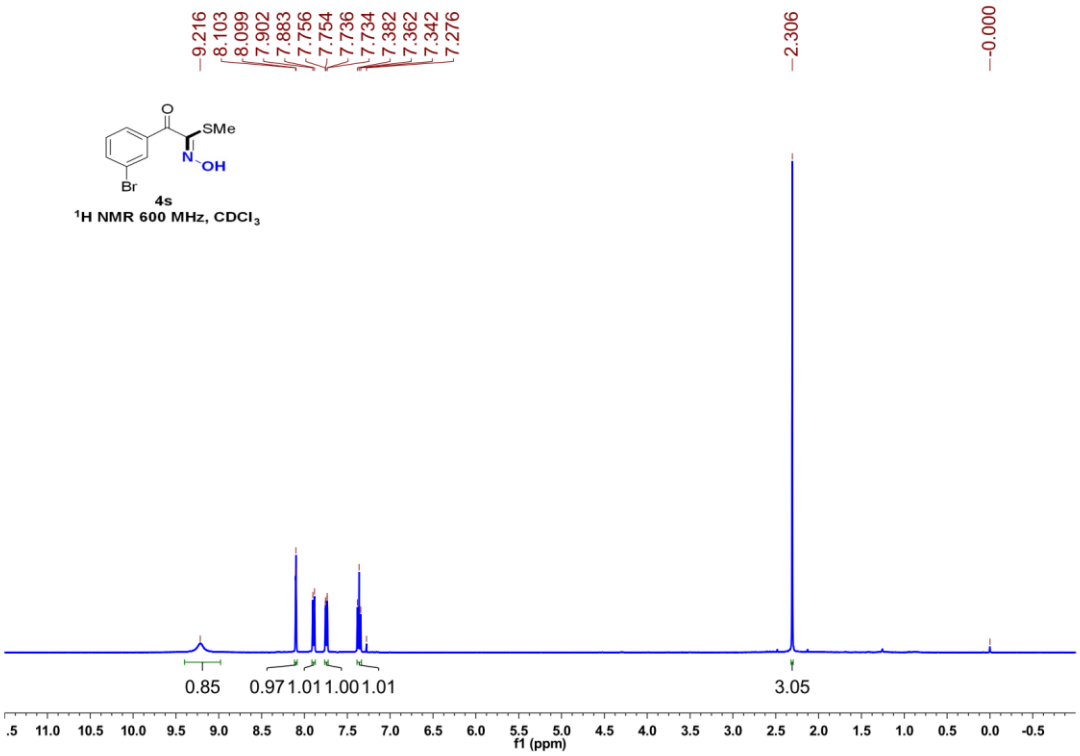
76.788
13.328
SMe
N
OH
Cl
4p
^{13}C NMR 150 MHz, CDCl$_3$
f1 (ppm)

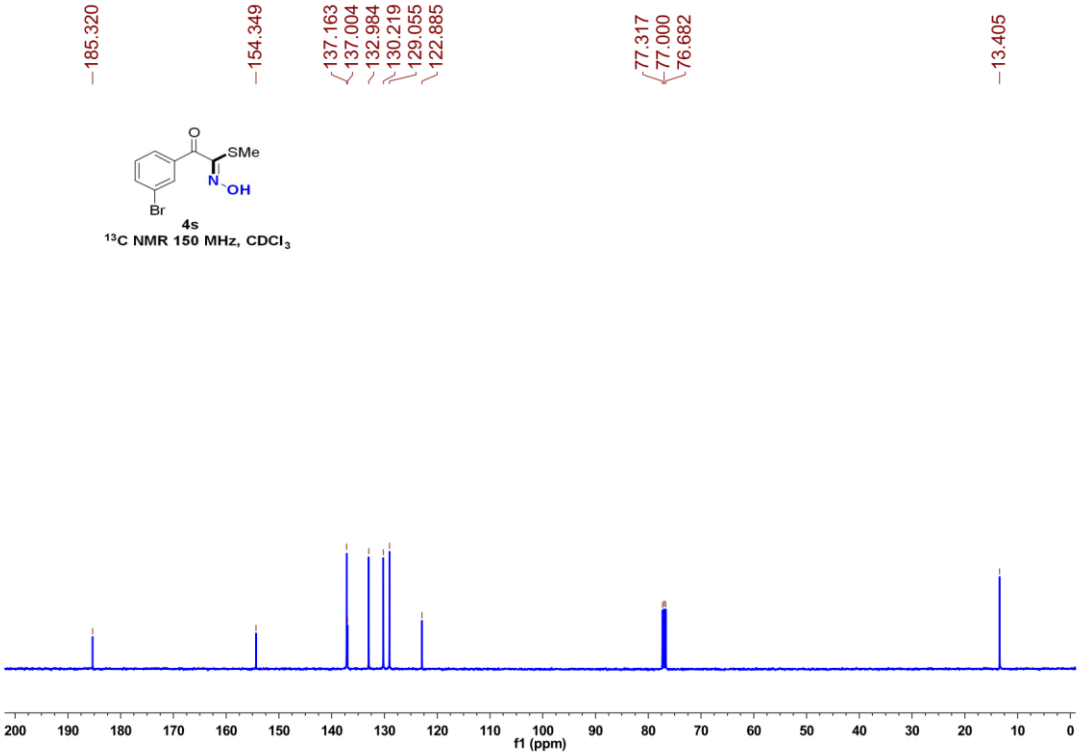

12.817
8.071
7.848
7.846
3.377
2.510
2.360
0.000
O
SMe
N
OH
Cl
Cl
4q
1H NMR 600 MHz, DMSO-d6
1.00
0.97
2.09
3.20
f1 (ppm)

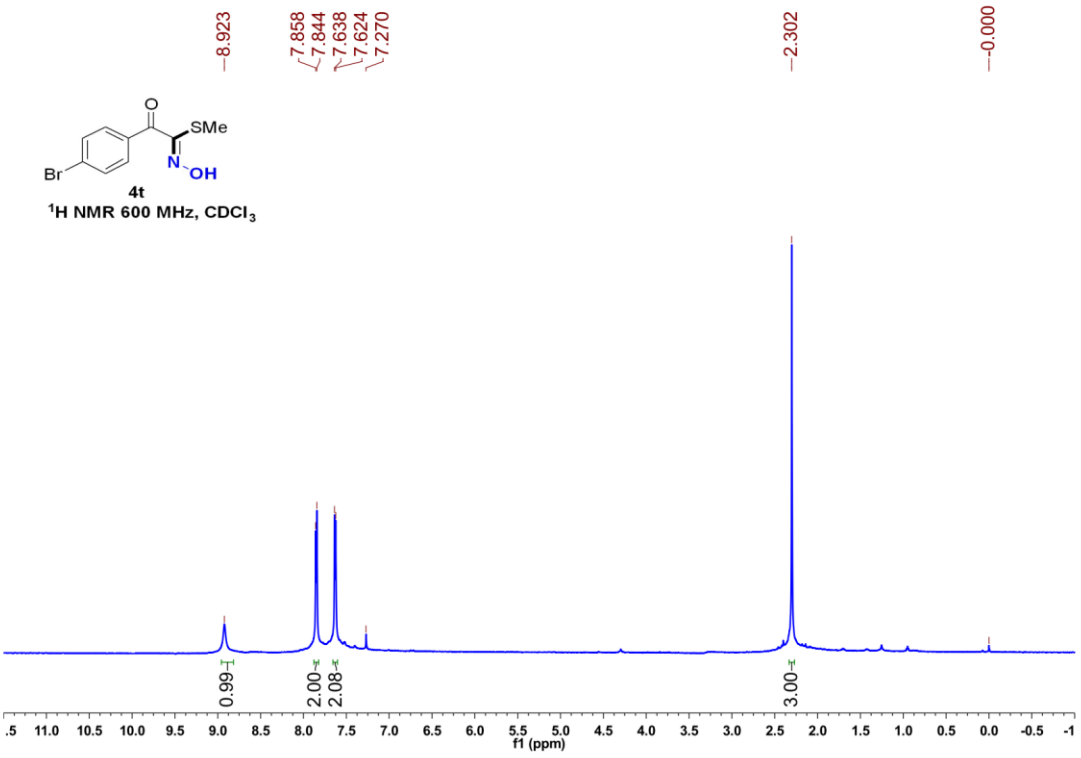

185.110
151.968
136.670
136.154
131.960
131.447
130.994
130.149
40.126
39.917
39.709
39.500
39.292
39.083
38.874
12.933
O
SMe
N
OH
Cl
Cl
4q
13C NMR 150 MHz, DMSO-d6
f1 (ppm)

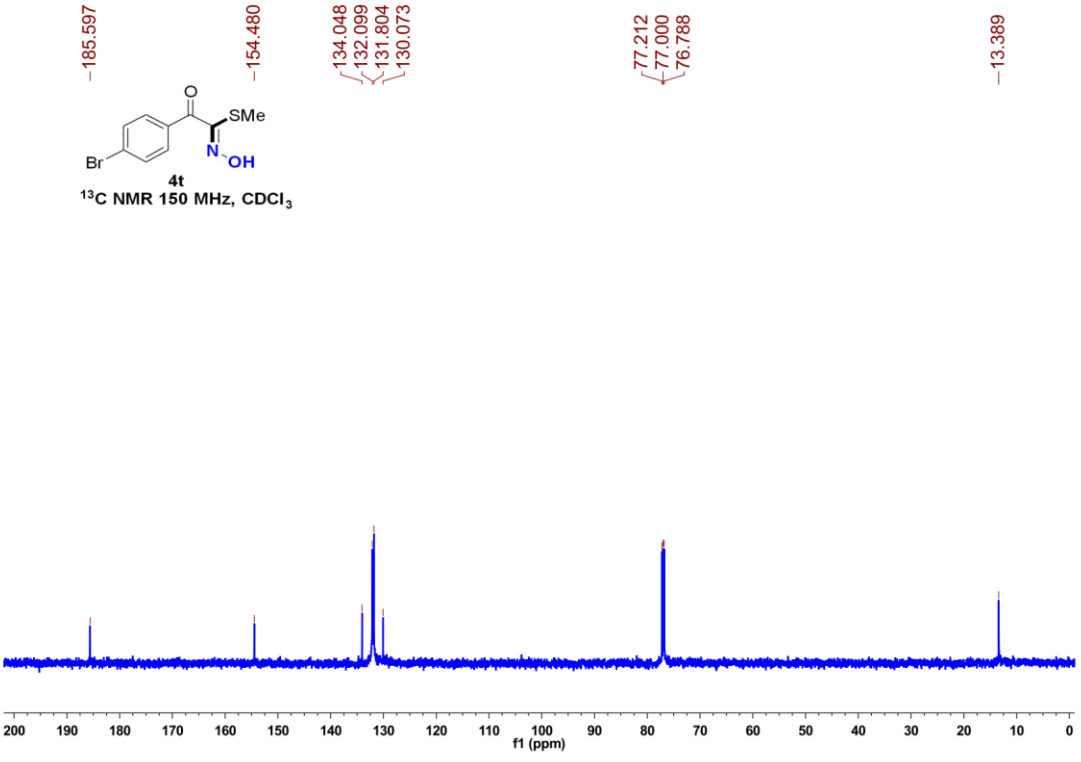

13.062
7.902
7.685
7.533
7.496
7.481
7.469
7.248
3.453
2.568
O
SMe
N
OH
Br
4r
^{1}H NMR 600 MHz, DMSO-d_6
0.92
4.00
3.13
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

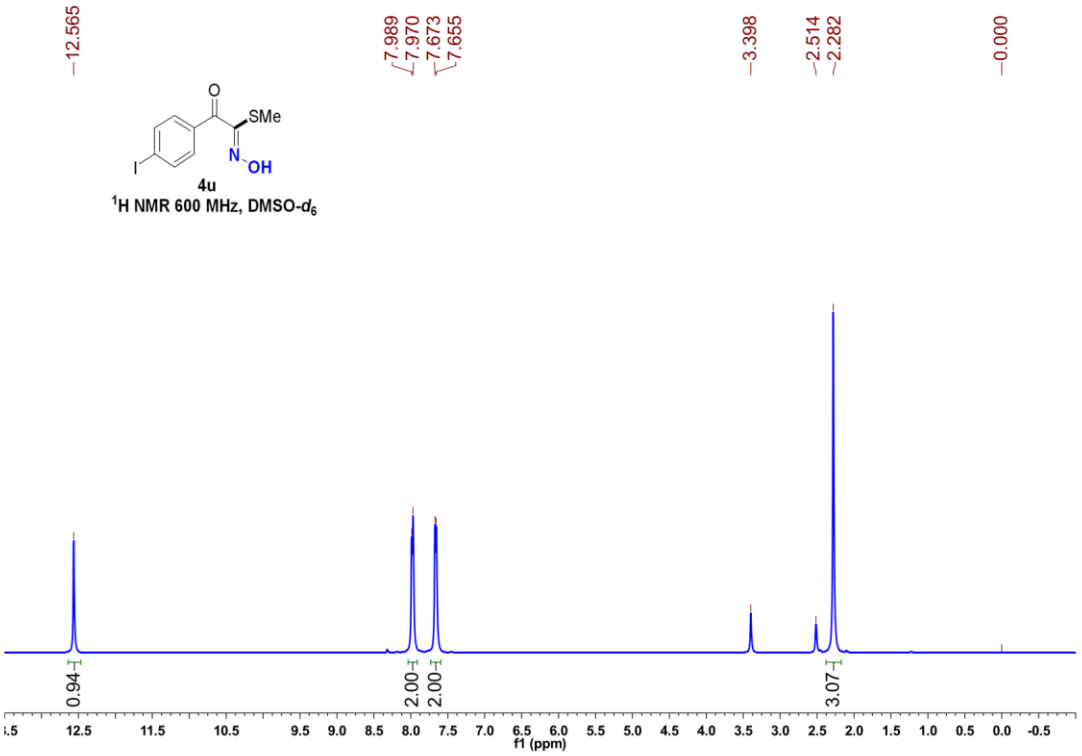

189.694
152.561
140.612
132.590
132.092
129.746
127.560
119.063
40.127
39.916
39.709
39.500
39.291
39.083
38.872
13.328
O
SMe
N
OH
Br
4r
^{13}C NMR 150 MHz, DMSO-d_6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

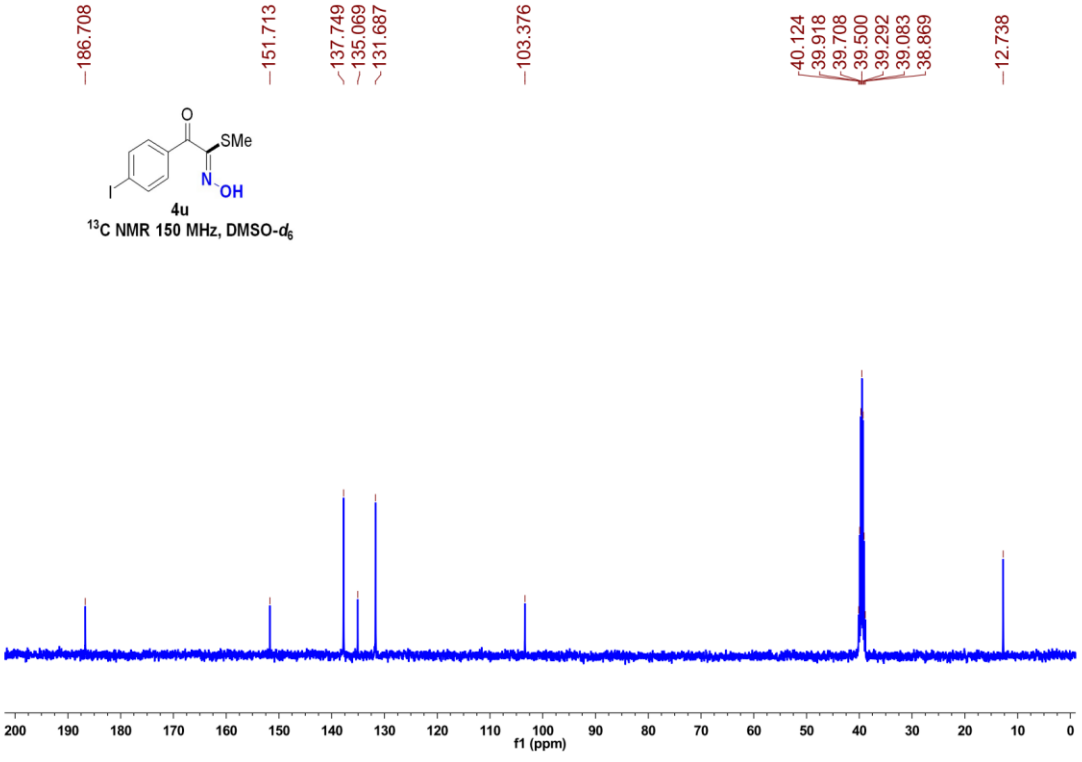

9.216
8.103
8.099
7.902
7.883
7.756
7.754
7.736
7.734
7.382
7.362
7.342
7.276
2.306
0.000
SMe
N
OH
Br
4s
^{1}H NMR 600 MHz, CDCl$_3$
0.85
0.97
1.01
1.00
1.01
3.05
f1 (ppm)

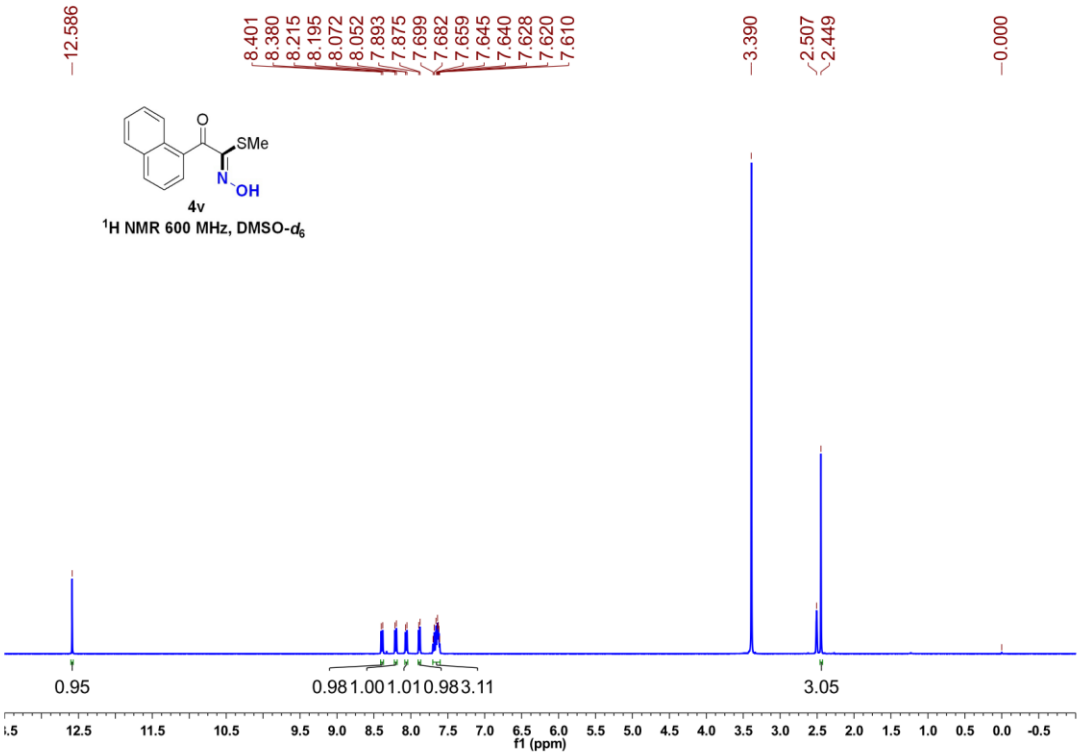

185.320
154.349
137.163
137.004
132.984
130.219
129.055
122.885
77.317
77.000
76.682
13.405
SMe
N
OH
Br
4s
^{13}C NMR 150 MHz, CDCl$_3$
f1 (ppm)

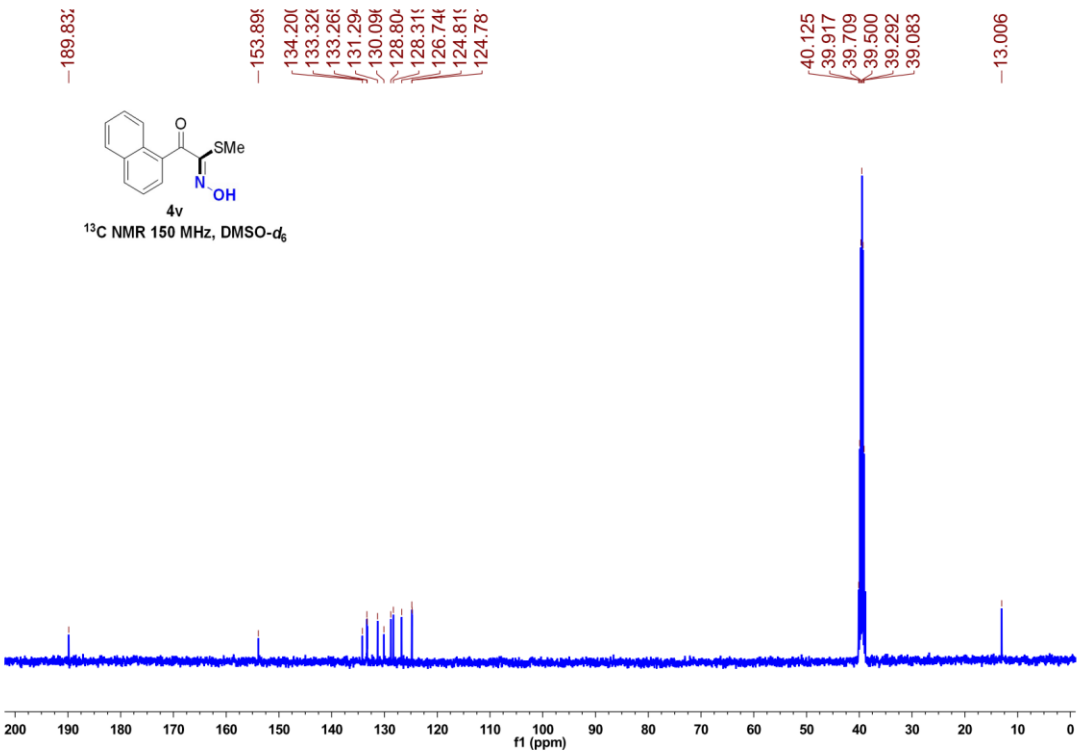

8.923
7.858
7.844
7.638
7.624
7.270
2.302
0.000
SMe
N
OH
Br
4t
^{1}H NMR 600 MHz, CDCl$_3$
0.99
2.00
2.08
3.00
f1 (ppm)

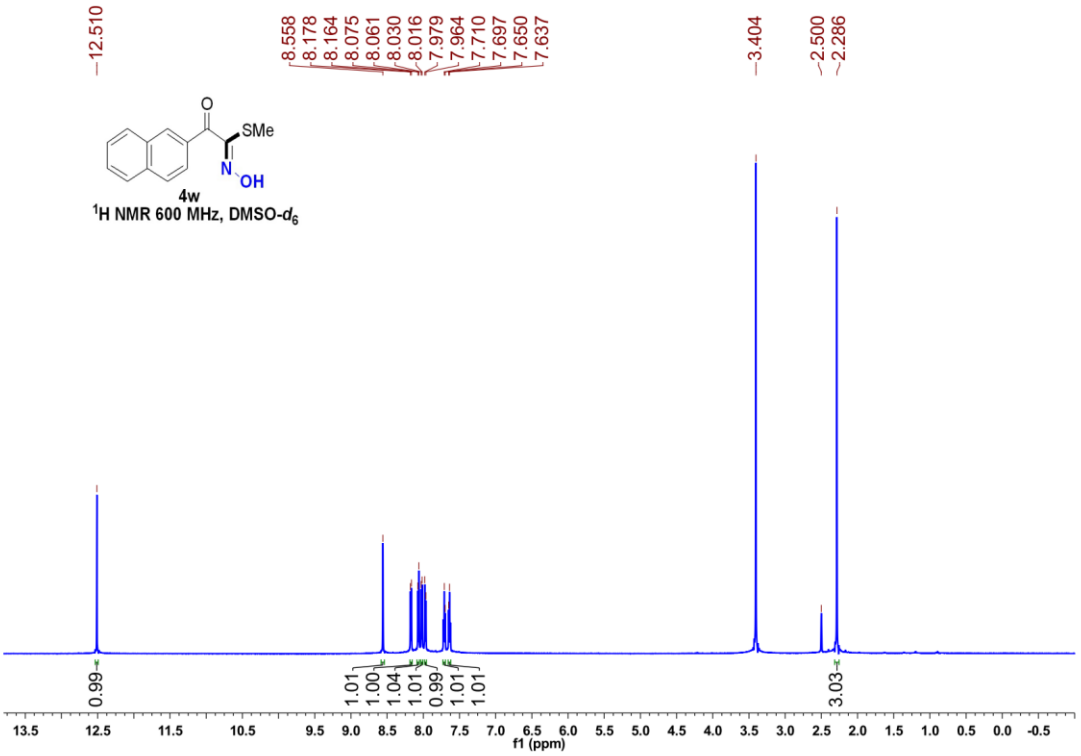

185.597
154.480
134.048
132.099
131.804
130.073
77.212
77.000
76.788
13.389
SMe
N
OH
Br
4t
^{13}C NMR 150 MHz, CDCl$_3$
f1 (ppm)

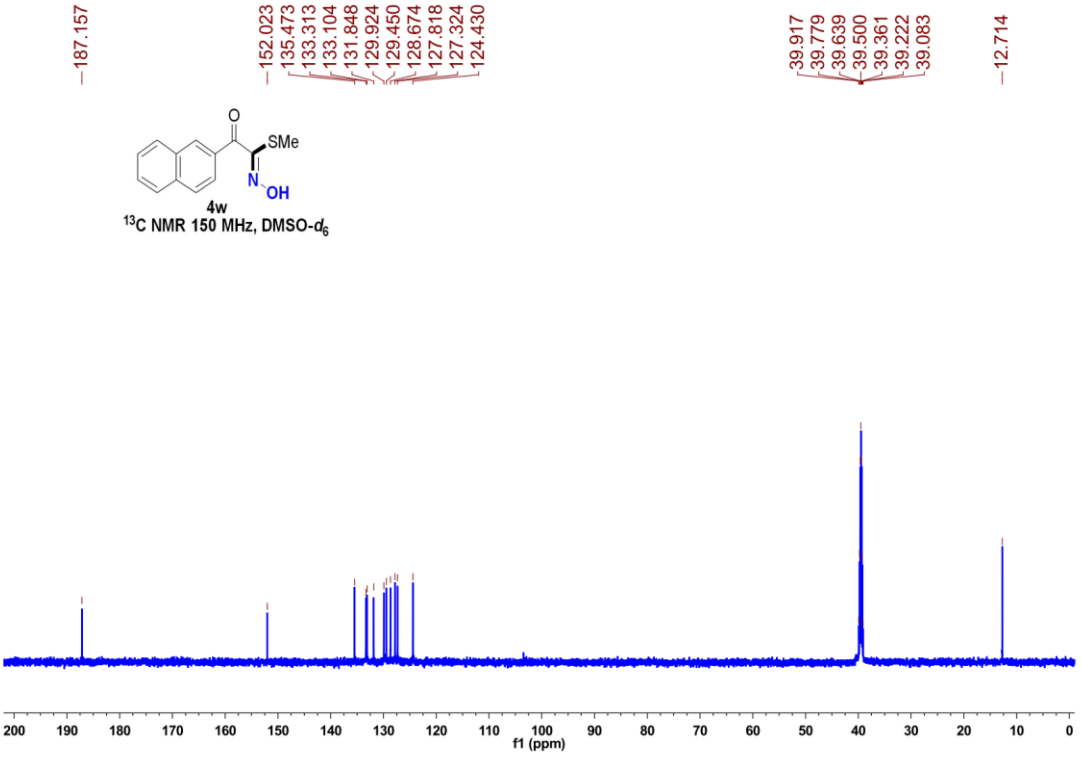

12.565
7.989
7.970
7.673
7.655
3.398
2.514
2.282
0.000
O
SMe
N
OH
I
4u
^{1}H NMR 600 MHz, DMSO-d_6
0.94
2.00
2.00
3.07
f1 (ppm)

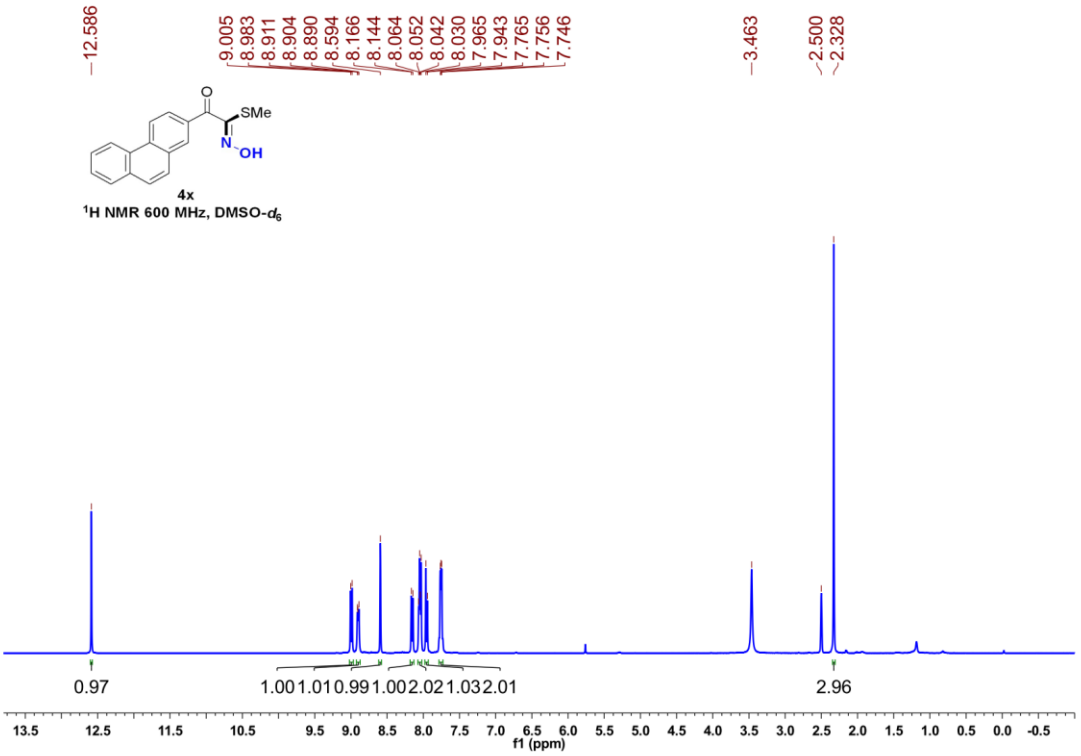

186.708
151.713
137.749
135.069
131.687
103.376
40.124
39.918
39.708
39.500
39.292
39.083
38.869
12.738
O
SMe
N
OH
I
4u
^{13}C NMR 150 MHz, DMSO-d_6
f1 (ppm)

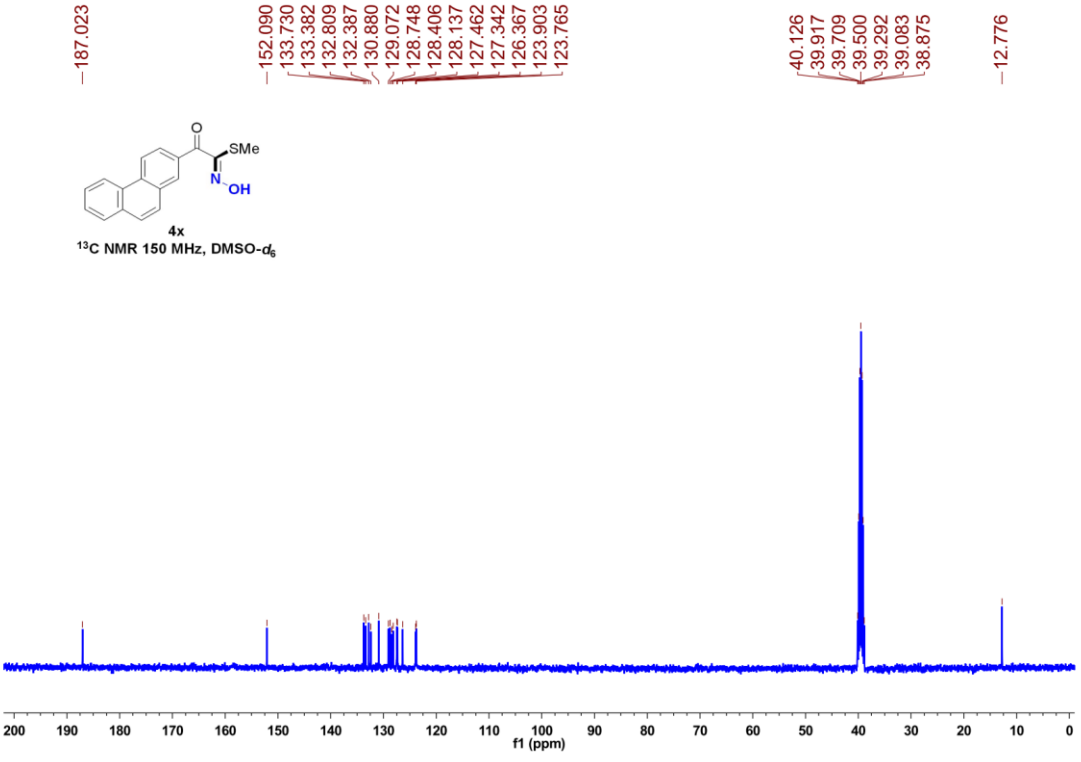

12.586
8.401
8.380
8.215
8.195
8.072
8.052
7.893
7.875
7.699
7.682
7.659
7.645
7.640
7.628
7.620
7.610
3.390
2.507
2.449
0.000
SMe
N
OH
4v
1H NMR 600 MHz, DMSO-d6
0.95
0.98
1.00
1.01
0.98
3.11
3.05
f1 (ppm)

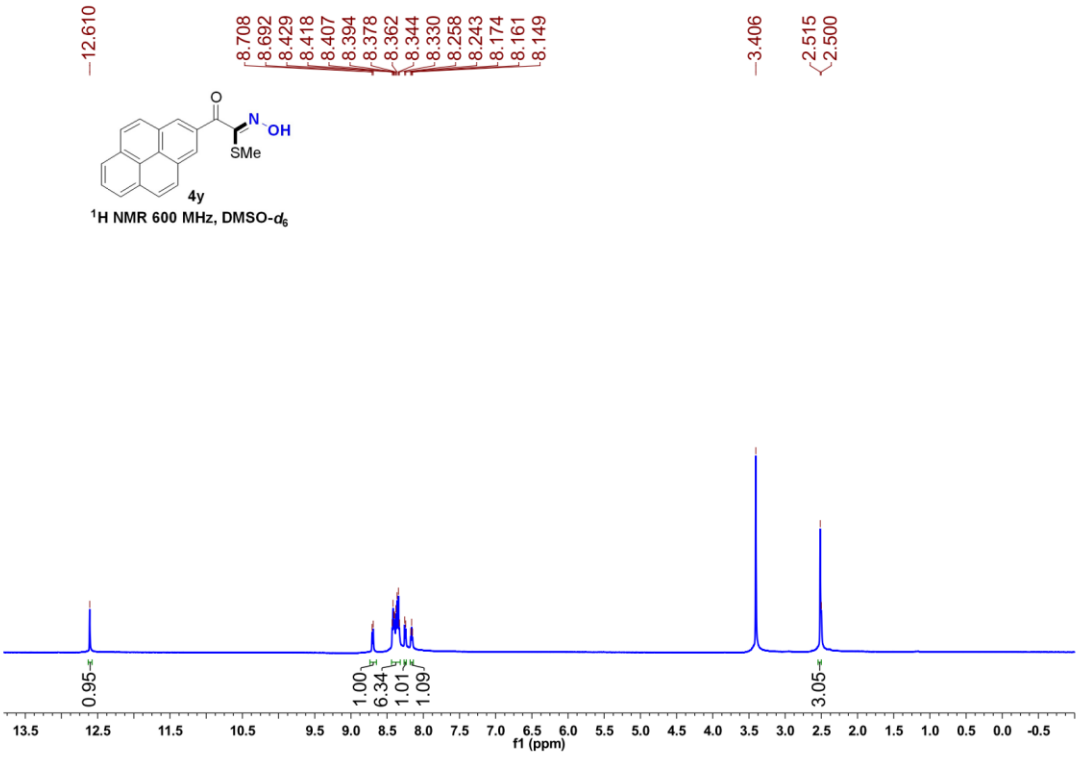

189.83
153.89
134.20
133.32
133.26
131.29
130.09
128.80
128.31
126.74
124.81
124.78
40.125
39.917
39.709
39.500
39.292
39.083
13.006
SMe
N
OH
4v
13C NMR 150 MHz, DMSO-d6
f1 (ppm)

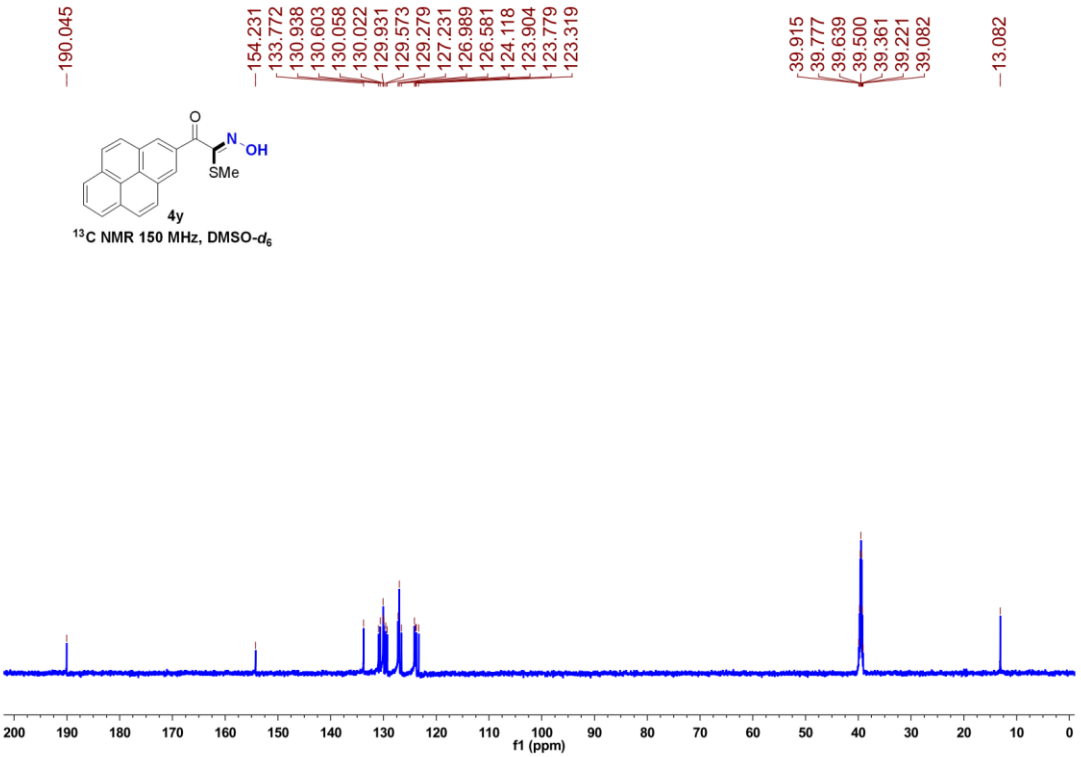

12.510
8.558
8.178
8.164
8.075
8.061
8.030
8.016
7.979
7.964
7.710
7.697
7.650
7.637
3.404
2.500
2.286
SMe
N
OH
4w
1H NMR 600 MHz, DMSO-d6
0.99
1.01
1.00
1.04
1.01
0.99
1.01
1.01
3.03
f1 (ppm)

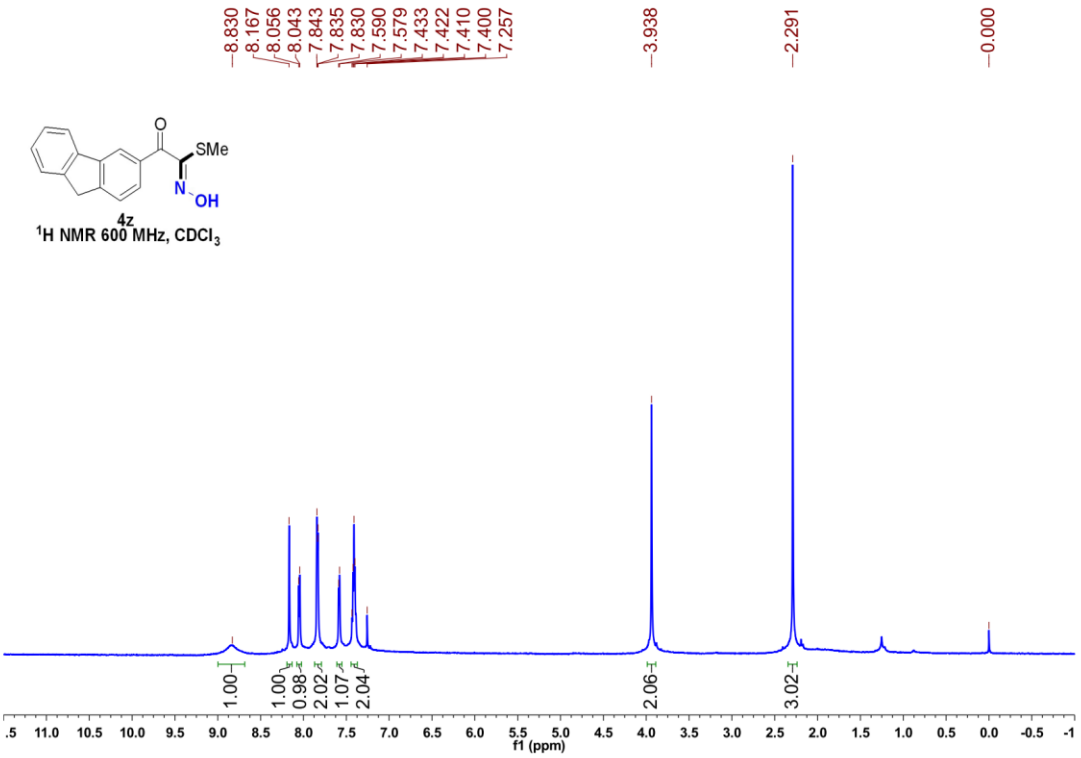

187.157
152.023
135.473
133.313
133.104
131.848
129.924
129.450
128.674
127.818
127.324
124.430
39.917
39.779
39.639
39.500
39.361
39.222
39.083
12.714
SMe
N
OH
4w
13C NMR 150 MHz, DMSO-d6
f1 (ppm)

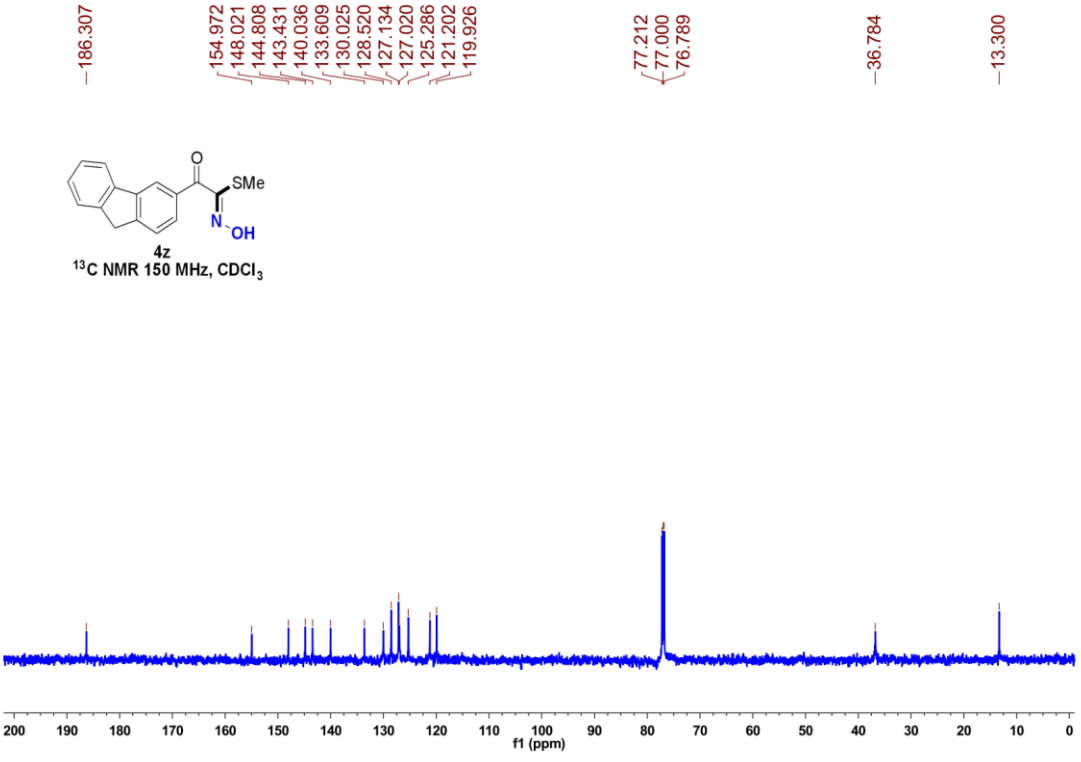

12.586
9.005
8.983
8.911
8.904
8.890
8.594
8.166
8.144
8.064
8.052
8.042
8.030
7.965
7.943
7.765
7.756
7.746
3.463
2.500
2.328
SMe
N
OH
4x
1H NMR 600 MHz, DMSO-d6
0.97
1.00
1.01
0.99
1.00
2.02
1.03
2.01
2.96
f1 (ppm)

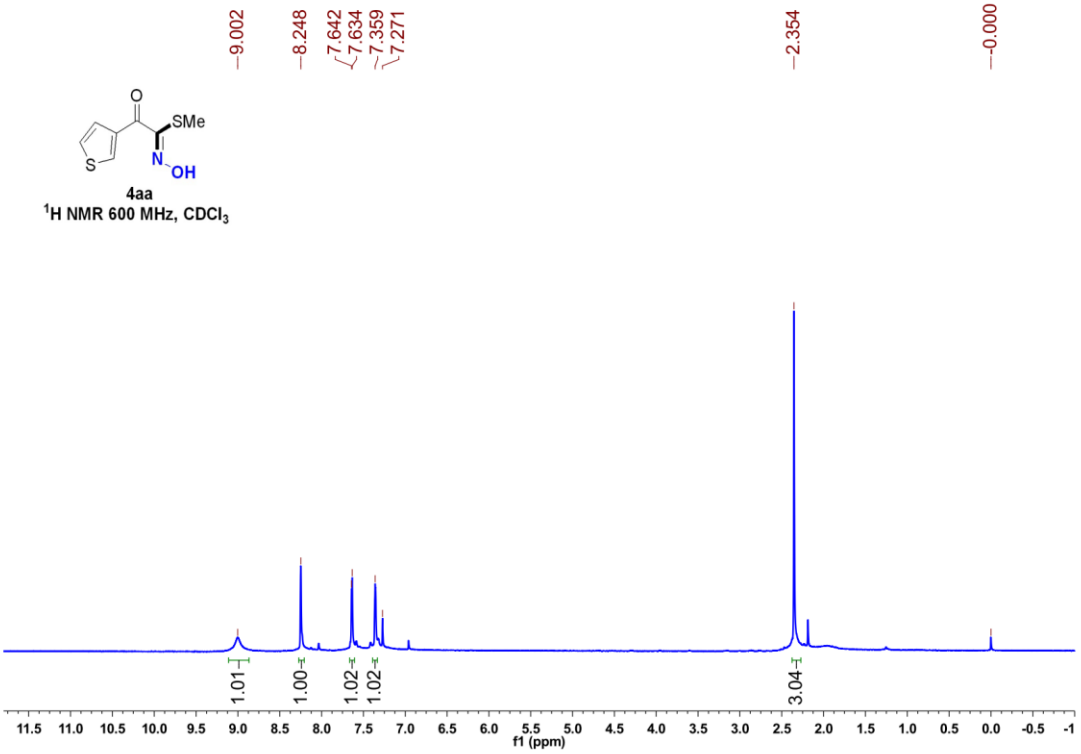

187.023
152.090
133.730
133.382
132.809
132.387
130.880
129.072
128.748
128.406
128.137
127.462
127.342
126.367
123.903
123.765
40.126
39.917
39.709
39.500
39.292
39.083
38.875
12.776
SMe
N
OH
4x
13C NMR 150 MHz, DMSO-d6
f1 (ppm)

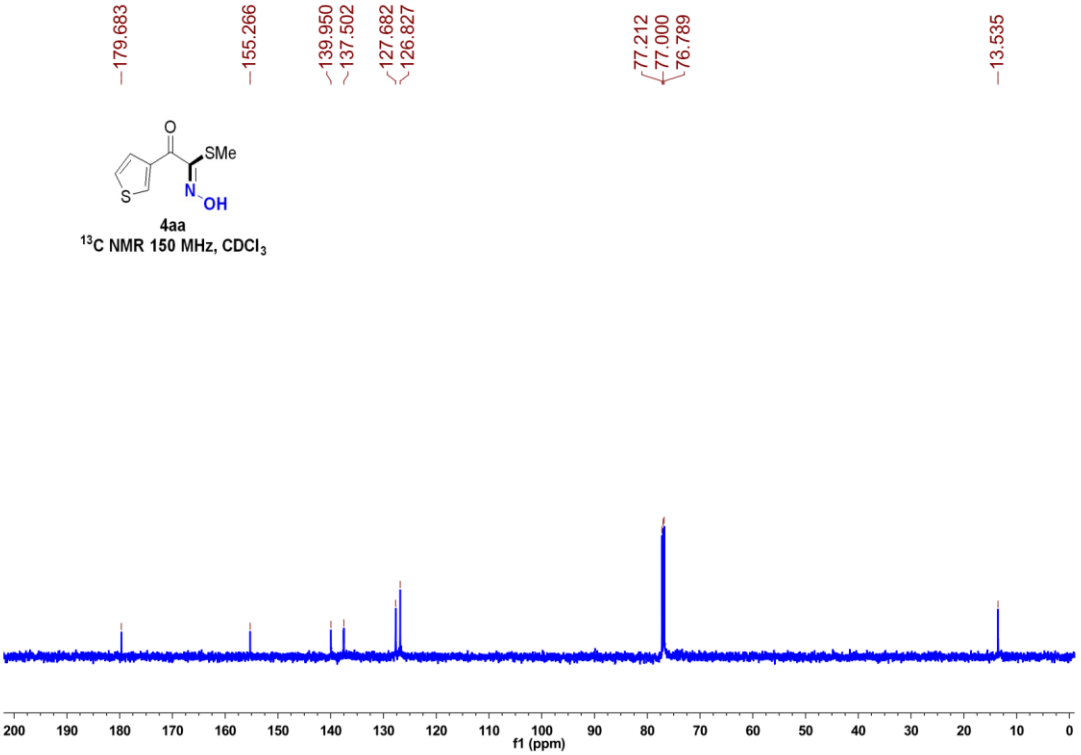

12.610
8.708
8.692
8.429
8.418
8.407
8.394
8.378
8.362
8.344
8.330
8.258
8.243
8.174
8.161
8.149
3.406
2.515
2.500
O
N
OH
SMe
4y
1H NMR 600 MHz, DMSO-d6
0.95
1.00
6.34
1.01
1.09
3.05
f1 (ppm)

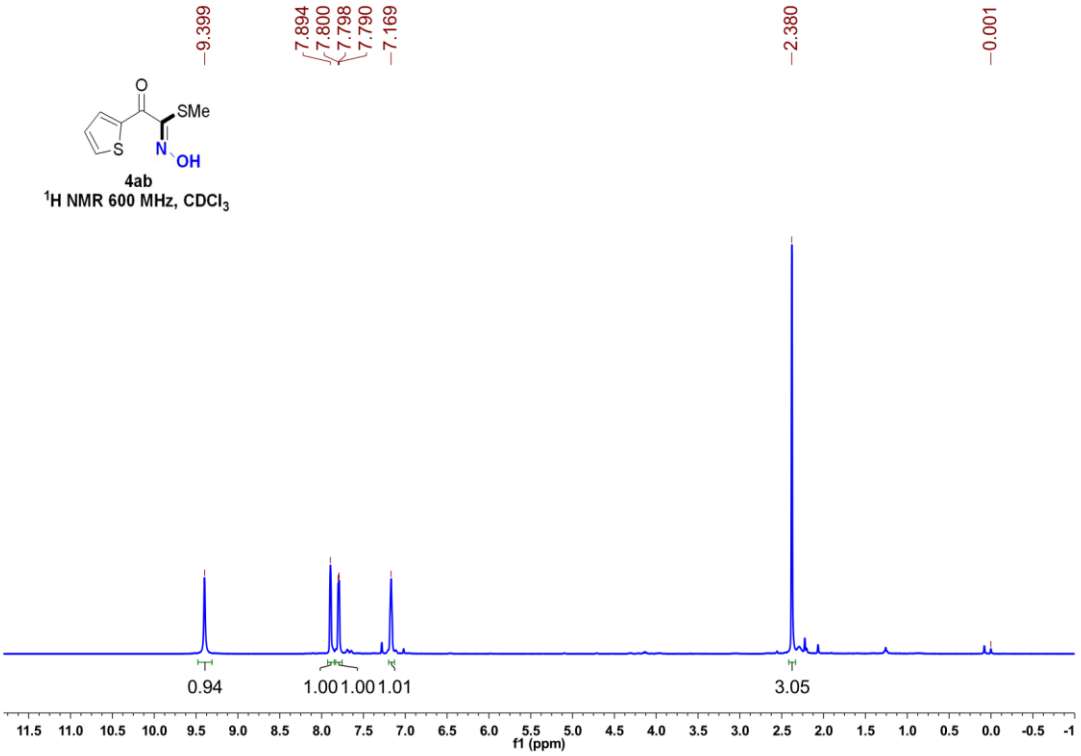

190.045
154.231
133.772
130.938
130.603
130.058
130.022
129.931
129.573
129.279
127.231
126.989
126.581
124.118
123.904
123.779
123.319
39.915
39.777
39.639
39.500
39.361
39.221
39.082
13.082
O
N
OH
SMe
4y
13C NMR 150 MHz, DMSO-d6
f1 (ppm)

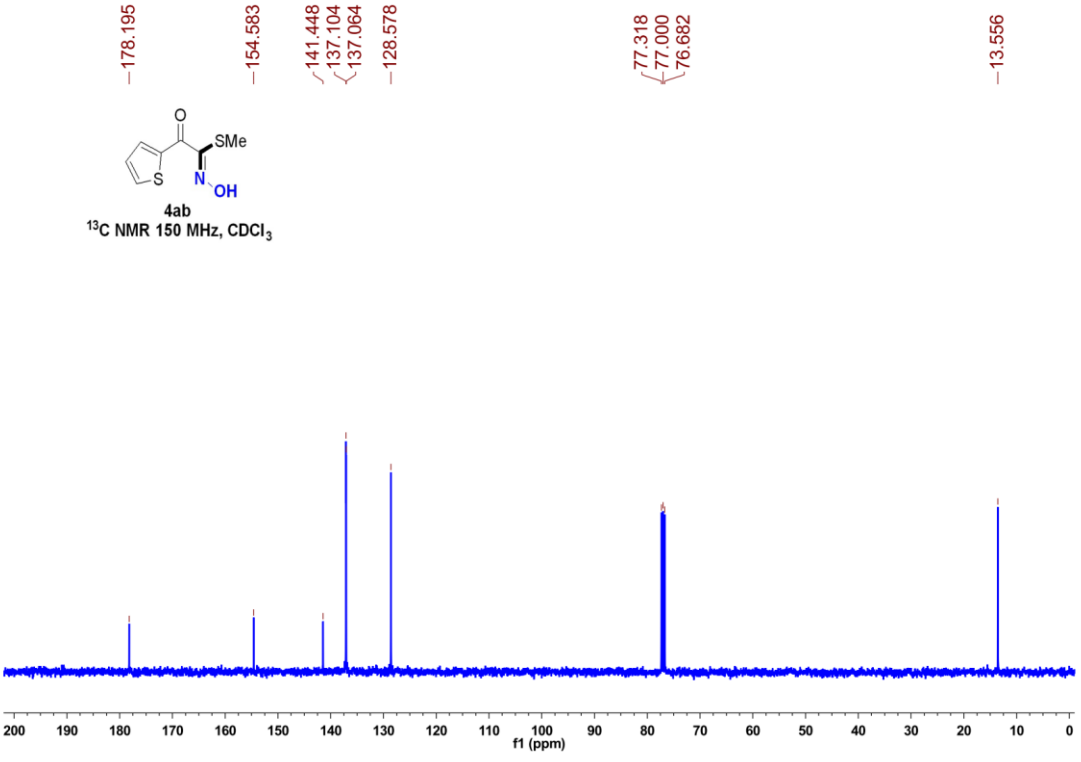

8.830
8.167
8.056
8.043
7.843
7.835
7.830
7.590
7.579
7.433
7.422
7.410
7.400
7.257
3.938
2.291
0.000
SMe
N
OH
4z
1H NMR 600 MHz, CDCl3
1.00
1.00
0.98
2.02
1.07
2.04
2.06
3.02
f1 (ppm)

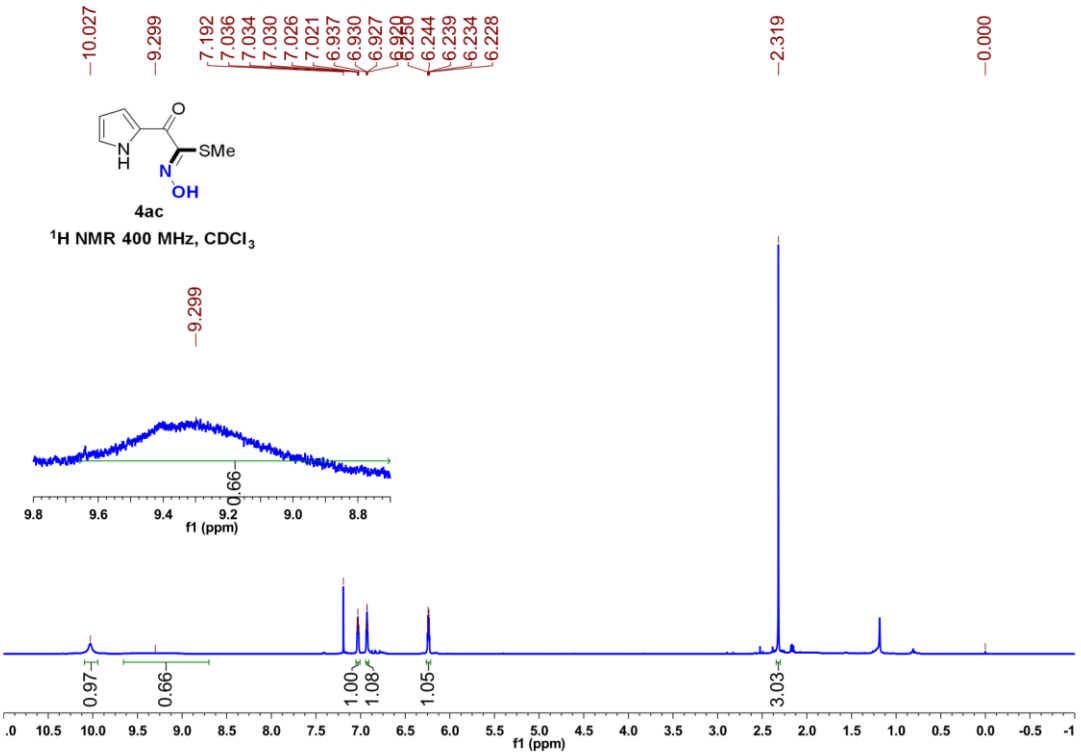

186.307
154.972
148.021
144.808
143.431
140.036
133.609
130.025
128.520
127.134
127.020
125.286
121.202
119.926
77.212
77.000
76.789
36.784
13.300
SMe
N
OH
4z
13C NMR 150 MHz, CDCl3
f1 (ppm)

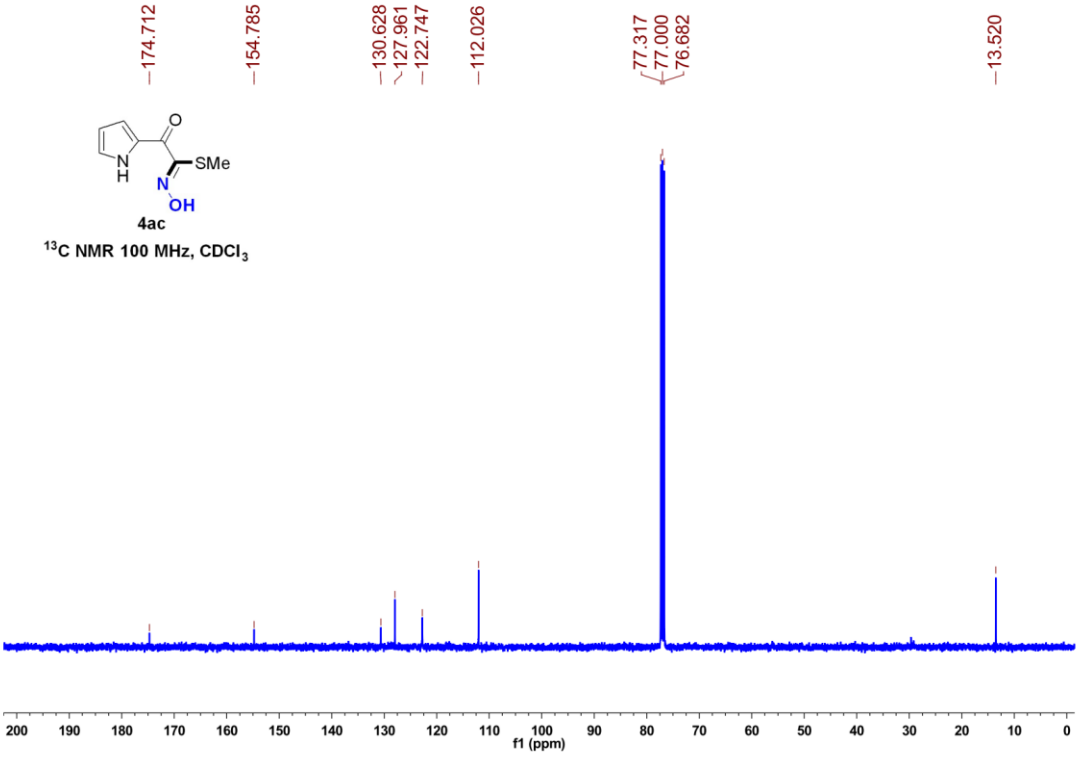

9.002
8.248
7.642
7.634
7.359
7.271
2.354
0.000
SMe
N
OH
S
4aa
1H NMR 600 MHz, CDCl3
1.01
1.00
1.02
1.02
3.04
f1 (ppm)

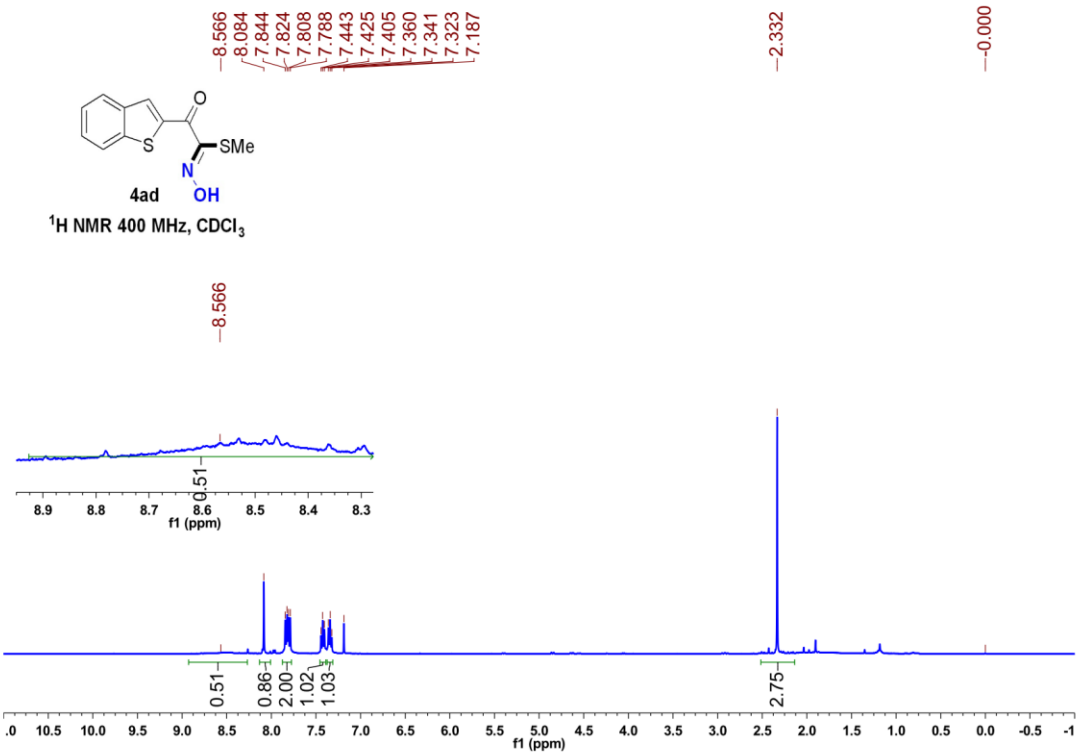

179.683
155.266
139.950
137.502
127.682
126.827
77.212
77.000
76.789
13.535
SMe
N
OH
S
4aa
13C NMR 150 MHz, CDCl3
f1 (ppm)

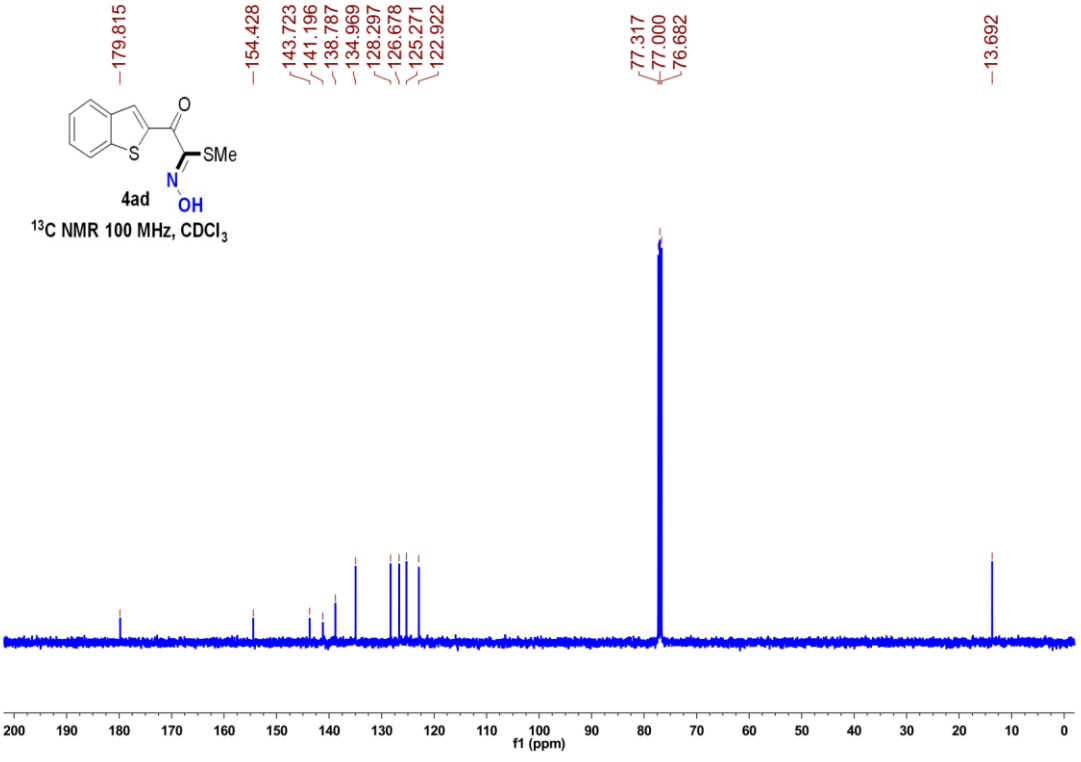

9.399
7.894
7.800
7.798
7.790
7.169
2.380
0.001
SMe
N
OH
S
O
4ab
1H NMR 600 MHz, CDCl3
0.94
1.00
1.00
1.01
3.05
f1 (ppm)

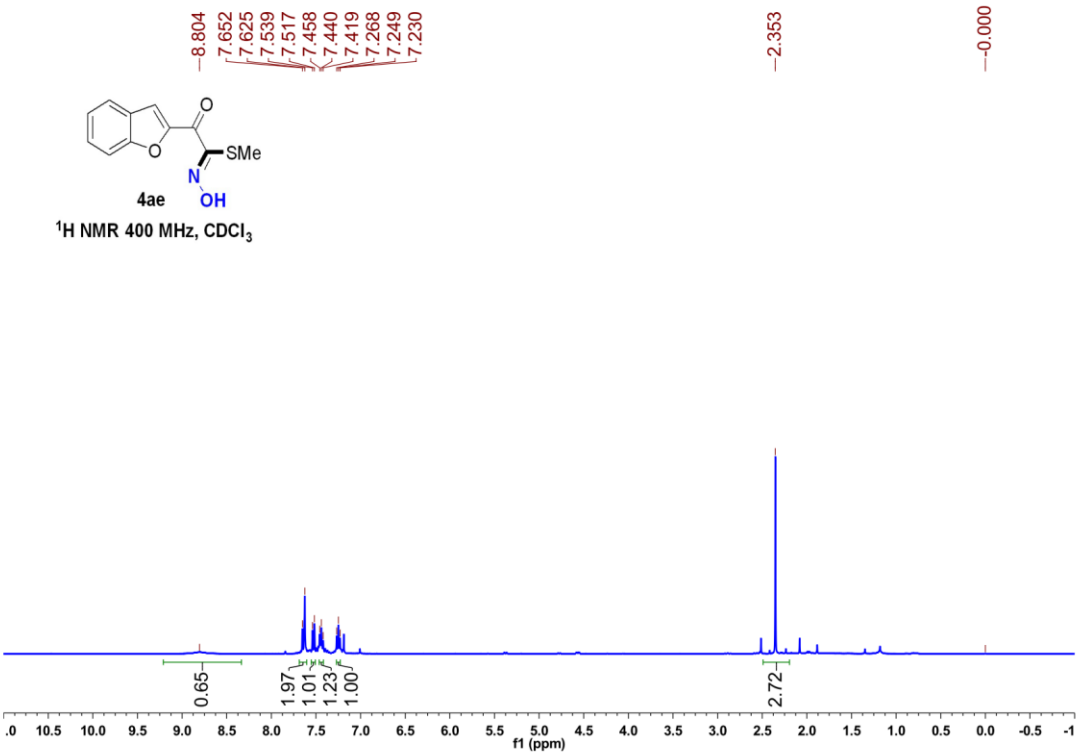

178.195
154.583
141.448
137.104
137.064
128.578
77.318
77.000
76.682
13.556
SMe
N
OH
S
O
4ab
13C NMR 150 MHz, CDCl3
f1 (ppm)


10.027
9.299
7.192
7.036
7.034
7.030
7.026
7.021
6.937
6.930
6.927
6.920
6.250
6.244
6.239
6.234
6.228
2.319
0.000
SMe
N
OH
4ac
1H NMR 400 MHz, CDCl3
9.299
0.66
9.8 9.6 9.4 9.2 9.0 8.8
f1 (ppm)
0.97
0.66
1.00
1.08
1.05
3.03
.0 10.5 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 0.0 -0.5 -1
f1 (ppm)

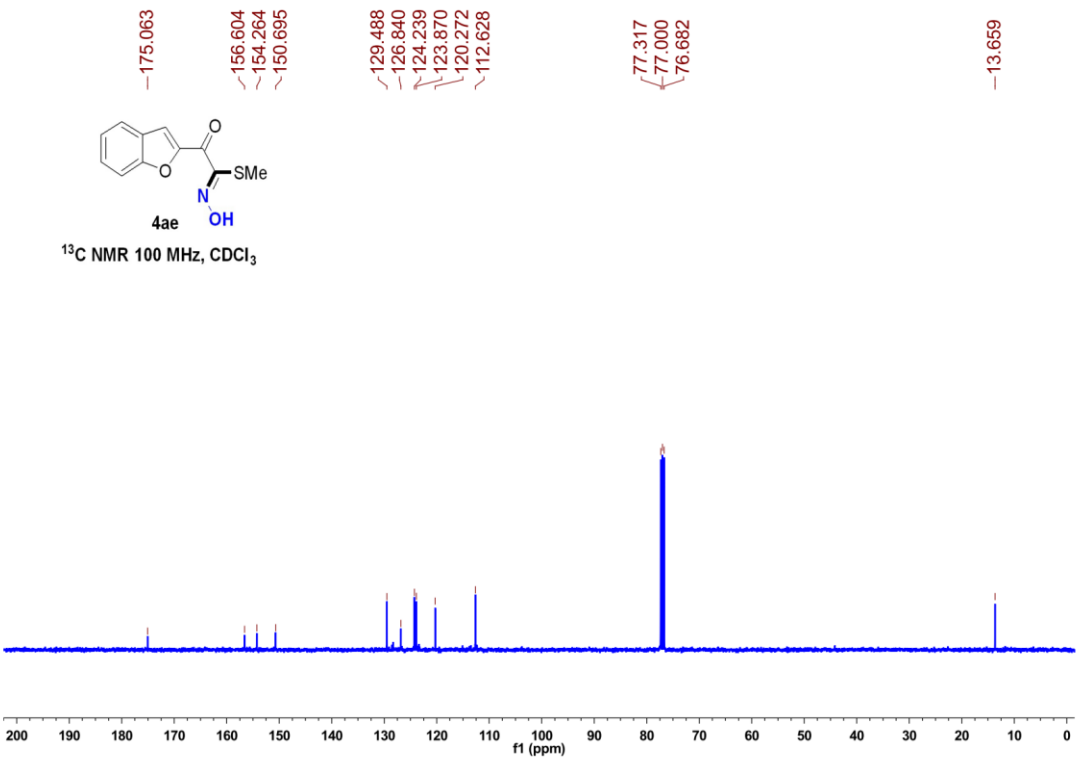

174.712
154.785
130.628
127.961
122.747
112.026
77.317
77.000
76.682
13.520
SMe
N
OH
4ac
13C NMR 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.566
8.084
7.844
7.824
7.808
7.788
7.443
7.425
7.405
7.360
7.341
7.323
7.187
2.332
0.000
O
S
SMe
N
OH
4ad
1H NMR 400 MHz, CDCl3
8.566
0.51
f1 (ppm)
0.51
0.86
2.00
1.02
1.03
2.75
f1 (ppm)

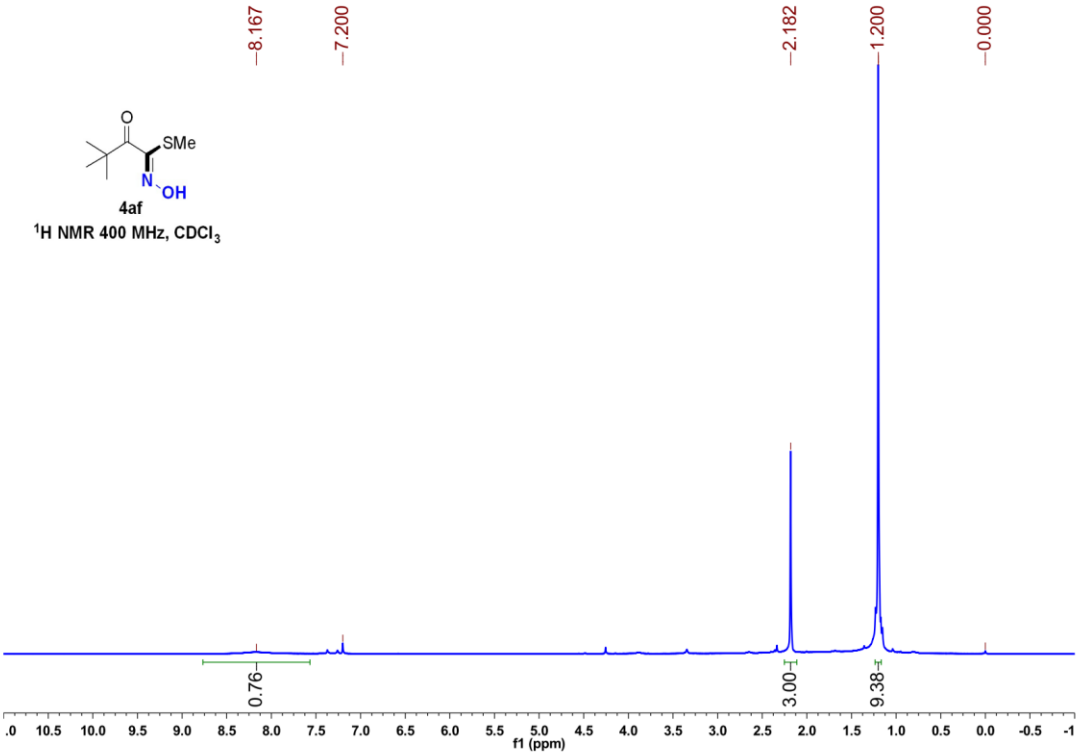

179.815
154.428
143.723
141.196
138.787
134.969
128.297
126.678
125.271
122.922
77.317
77.000
76.682
13.692
O
S
SMe
N
OH
4ad
13C NMR 100 MHz, CDCl3
f1 (ppm)

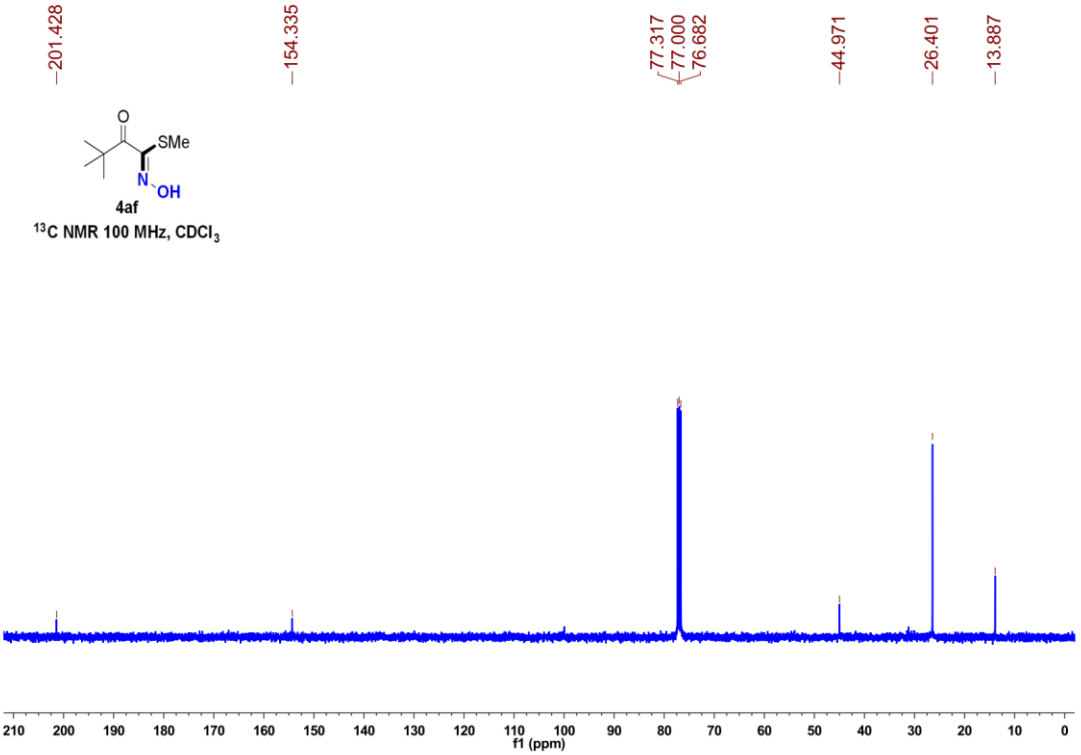


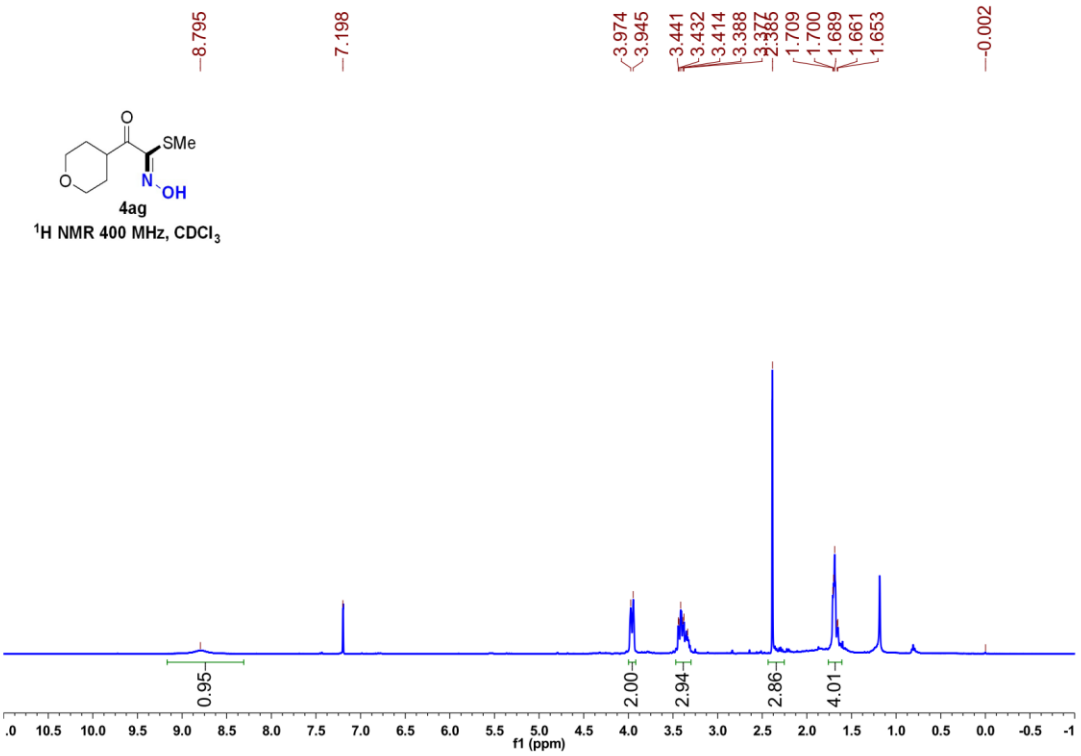
^{1}H NMR 400 MHz, $CDCl_3$

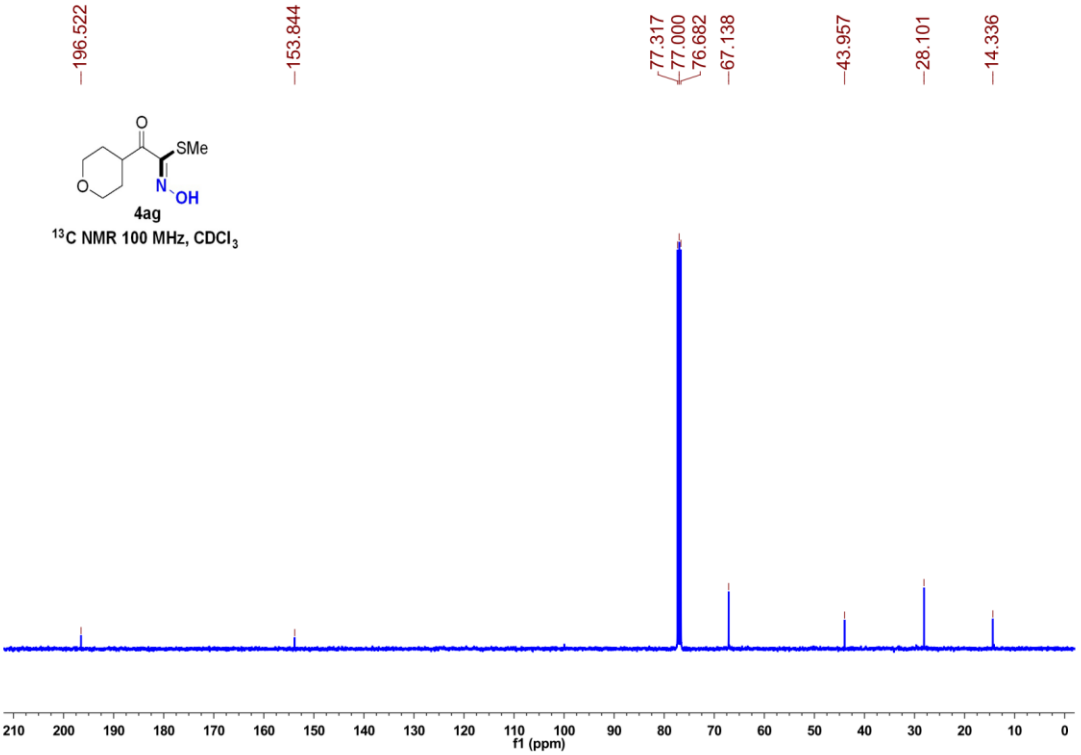


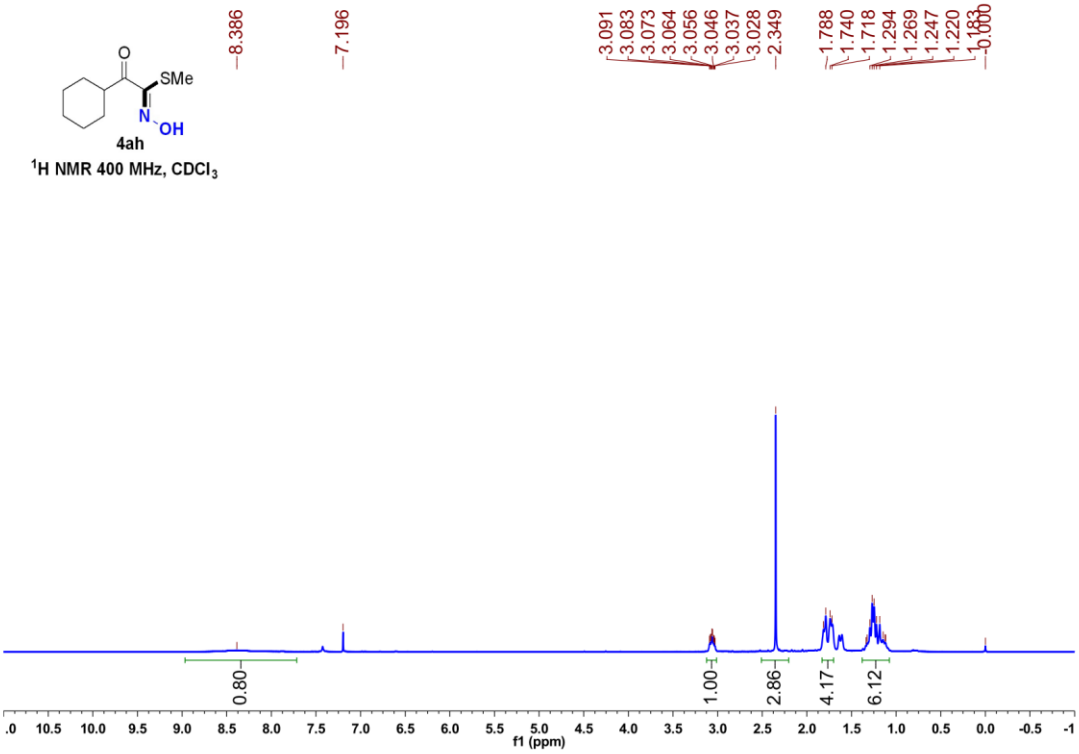
^{13}C NMR 100 MHz, $CDCl_3$


8.167
7.200
2.182
1.200
0.000
SMe
N
OH
4af
^{1}H NMR 400 MHz, CDCl$_3$
0.76
3.00
9.38
f1 (ppm)

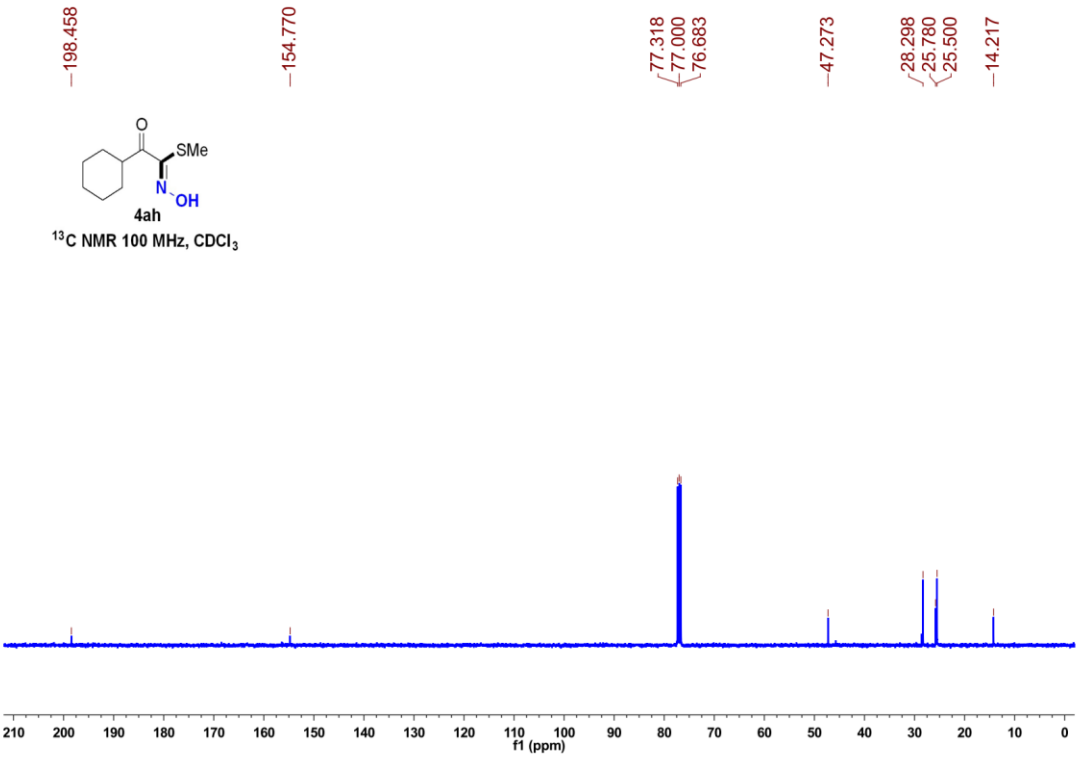

201.428
154.335
77.317
77.000
76.682
44.971
26.401
13.887
SMe
N
OH
4af
^{13}C NMR 100 MHz, CDCl$_3$
f1 (ppm)


8.795
7.198
3.974
3.945
3.441
3.432
3.414
3.388
2.385
1.709
1.700
1.689
1.661
1.653
0.002
SMe
N
OH
4ag
^{1}H NMR 400 MHz, CDCl$_3$
0.95
2.00
2.94
2.86
4.01
f1 (ppm)

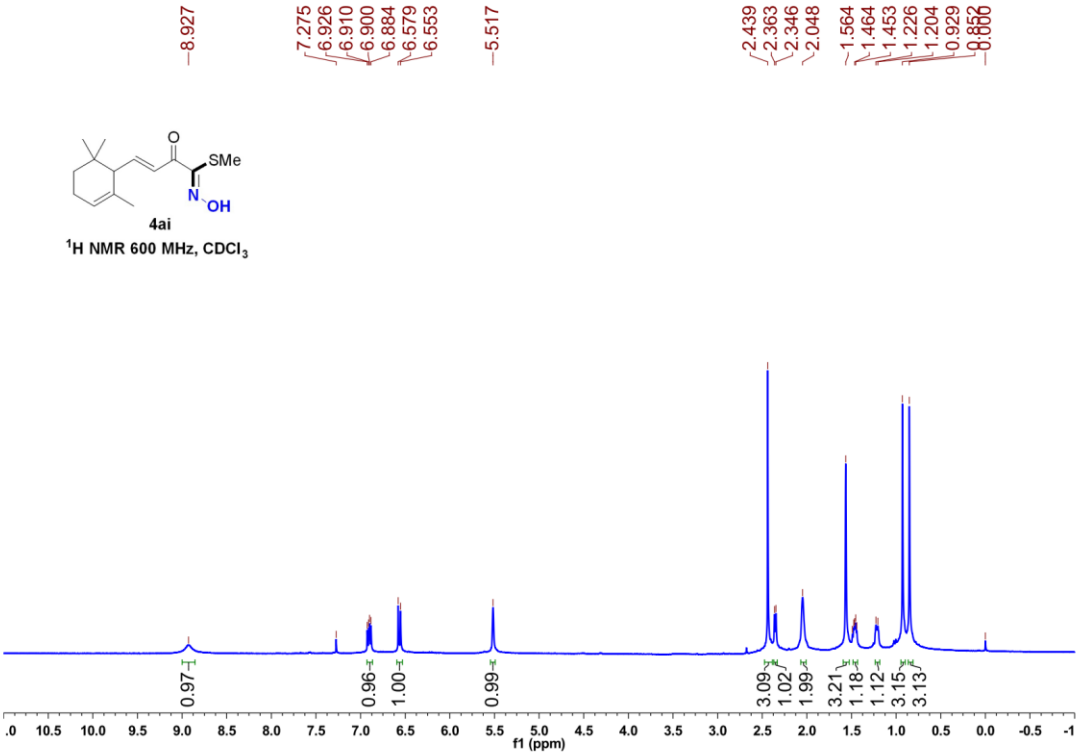

196.522
153.844
77.317
77.000
76.682
67.138
43.957
28.101
14.336
SMe
N
OH
4ag
^{13}C NMR 100 MHz, CDCl$_3$
f1 (ppm)

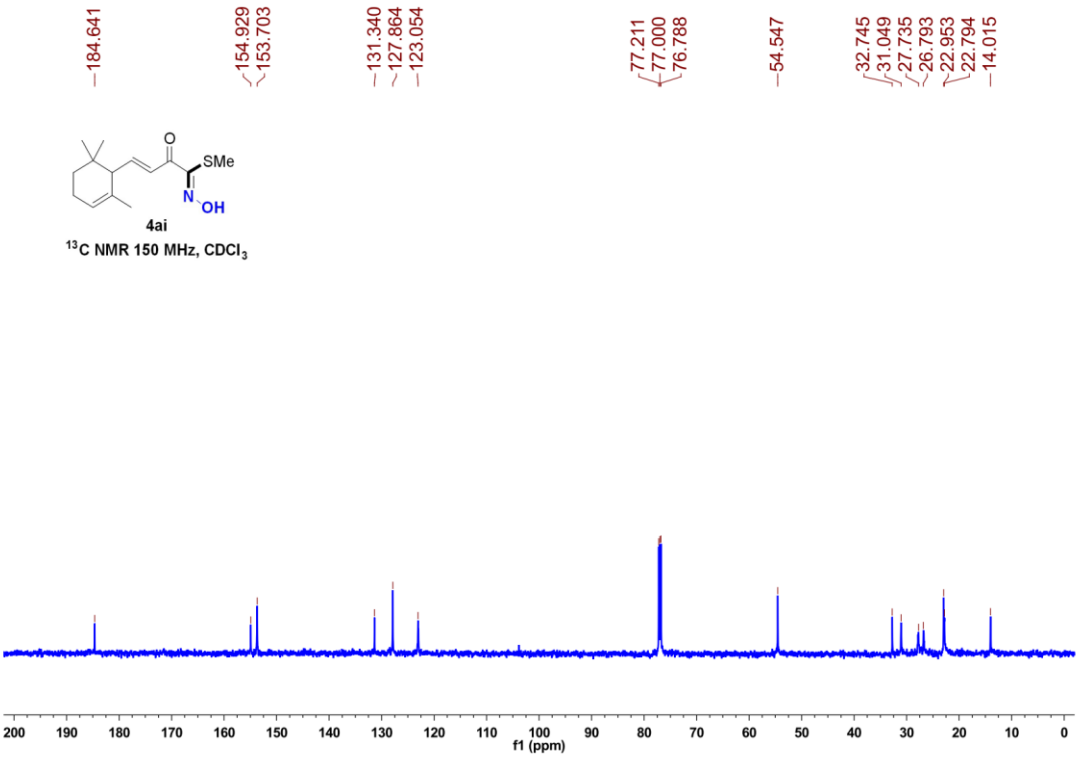


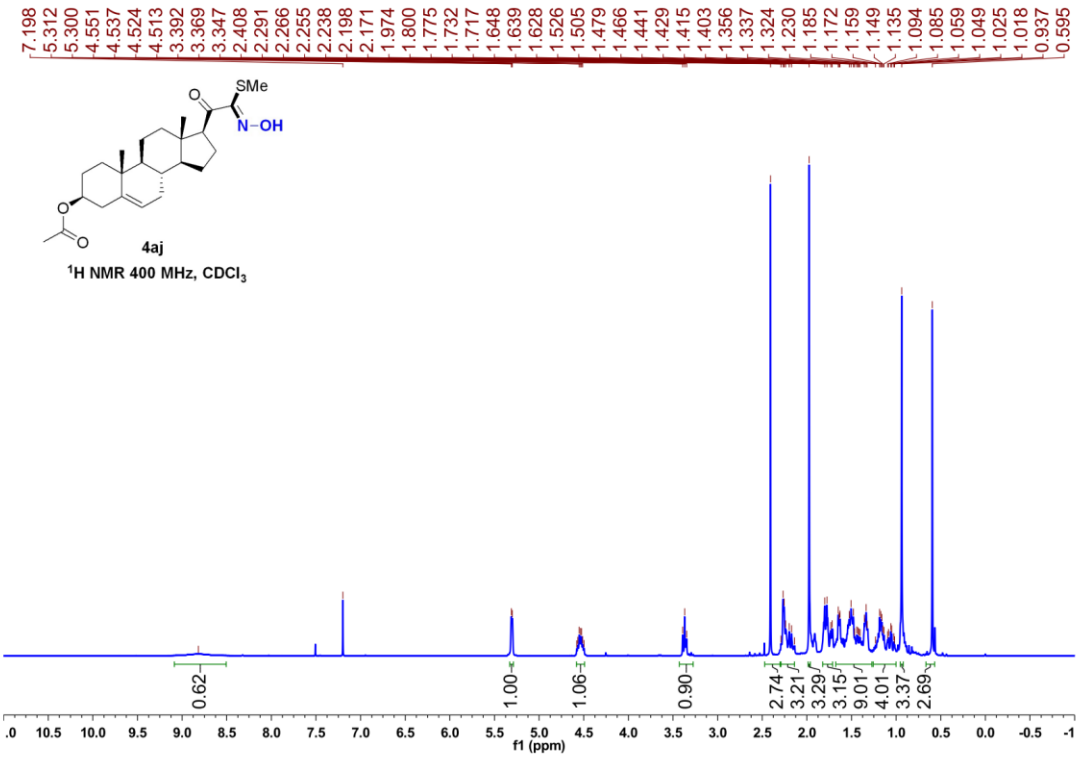
^{1}H NMR 400 MHz, $CDCl_3$

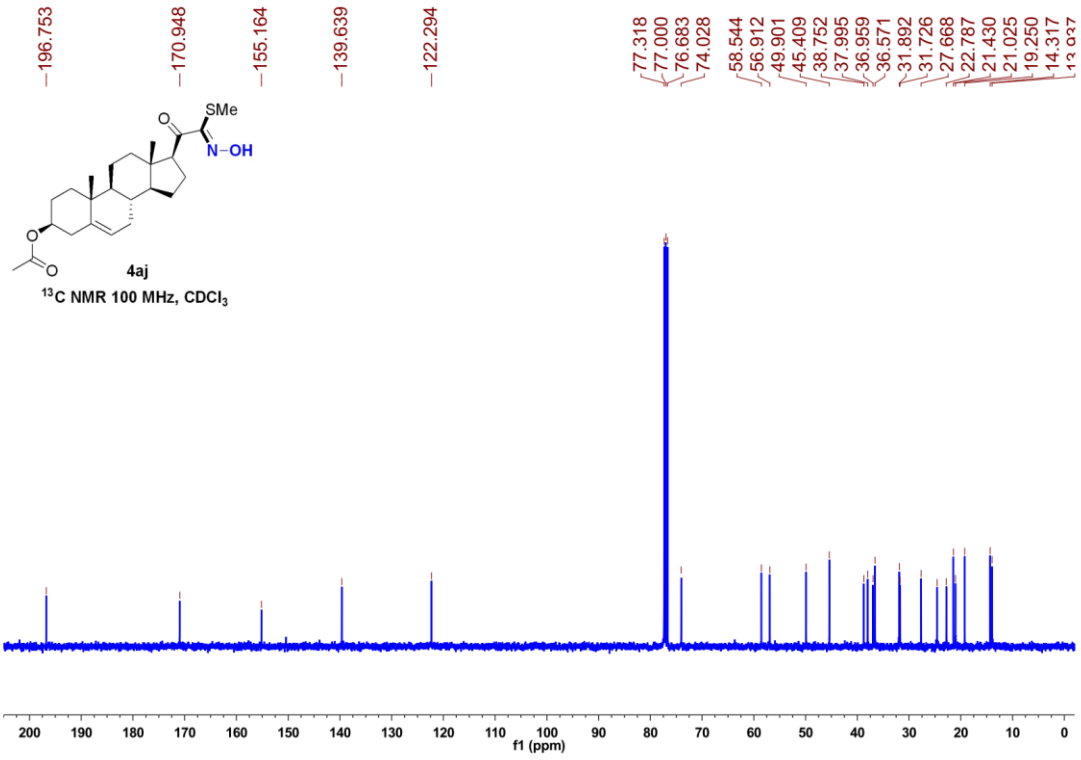


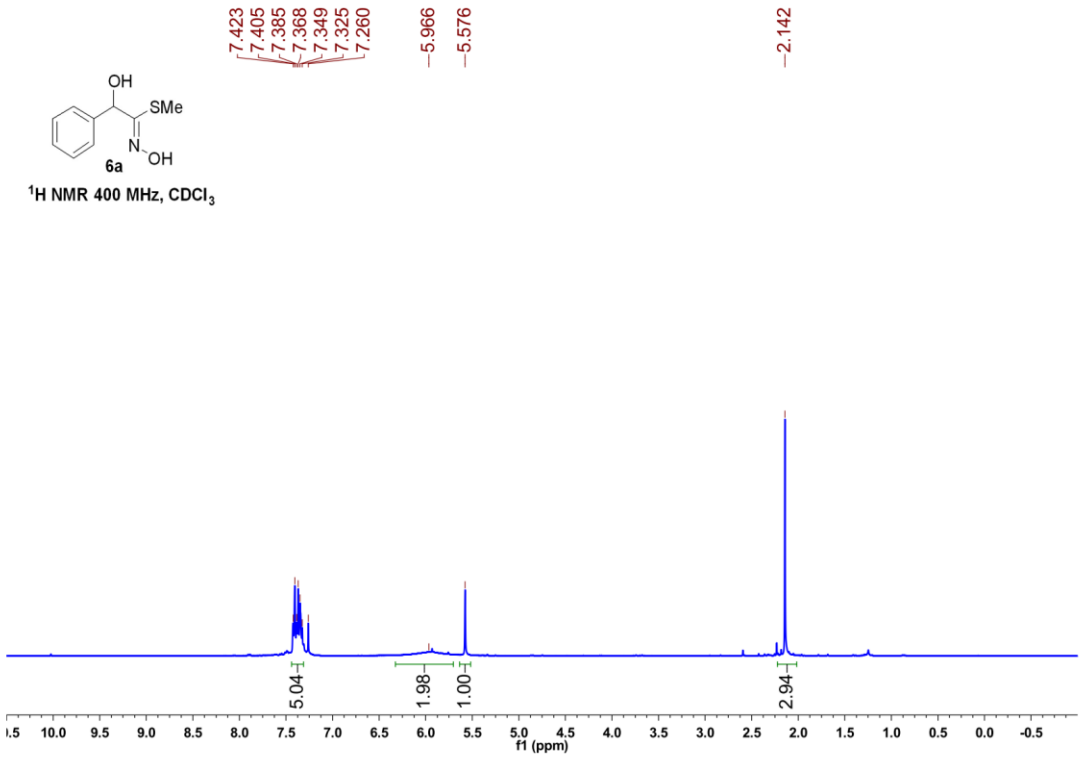
^{13}C NMR 100 MHz, $CDCl_3$


8.927
7.275
6.926
6.910
6.900
6.884
6.579
6.553
5.517
2.439
2.363
2.346
2.048
1.564
1.464
1.453
1.226
1.204
0.929
SMe
N
OH
4ai
1H NMR 600 MHz, CDCl3
0.97
0.96
1.00
0.99
3.09
1.02
1.99
3.21
1.18
1.12
3.15
3.13
f1 (ppm)

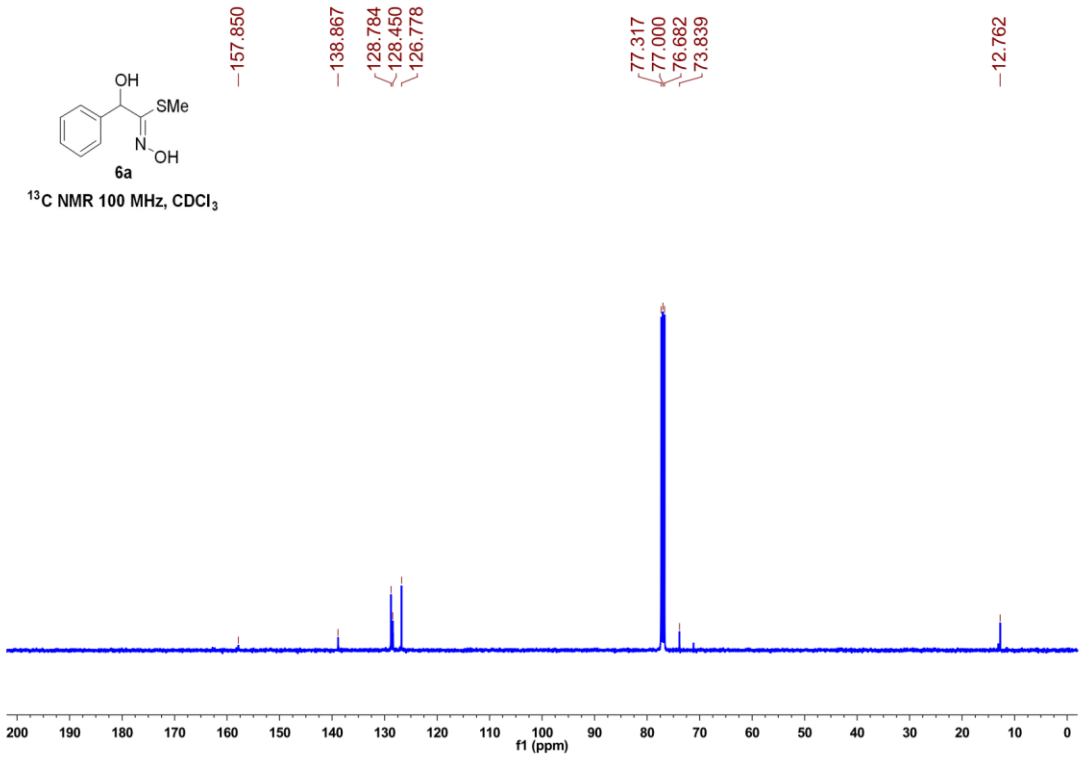

184.641
154.929
153.703
131.340
127.864
123.054
77.211
77.000
76.788
54.547
32.745
31.049
27.735
26.793
22.953
22.794
14.015
SMe
N
OH
4ai
13C NMR 150 MHz, CDCl3
f1 (ppm)


7.198
5.312
5.300
4.551
4.537
4.524
4.513
3.392
3.369
3.347
2.408
2.291
2.266
2.255
2.238
2.198
2.171
1.974
1.800
1.775
1.732
1.717
1.648
1.639
1.628
1.526
1.505
1.479
1.466
1.441
1.429
1.415
1.403
1.356
1.337
1.324
1.230
1.185
1.172
1.159
1.149
1.135
1.094
1.085
1.059
1.049
1.025
1.018
0.937
0.595
SMe
N–OH
4aj
^{1}H NMR 400 MHz, CDCl$_3$
0.62
1.00
1.06
0.90
2.74
3.21
3.29
3.15
9.01
4.01
3.37
2.69
f1 (ppm)

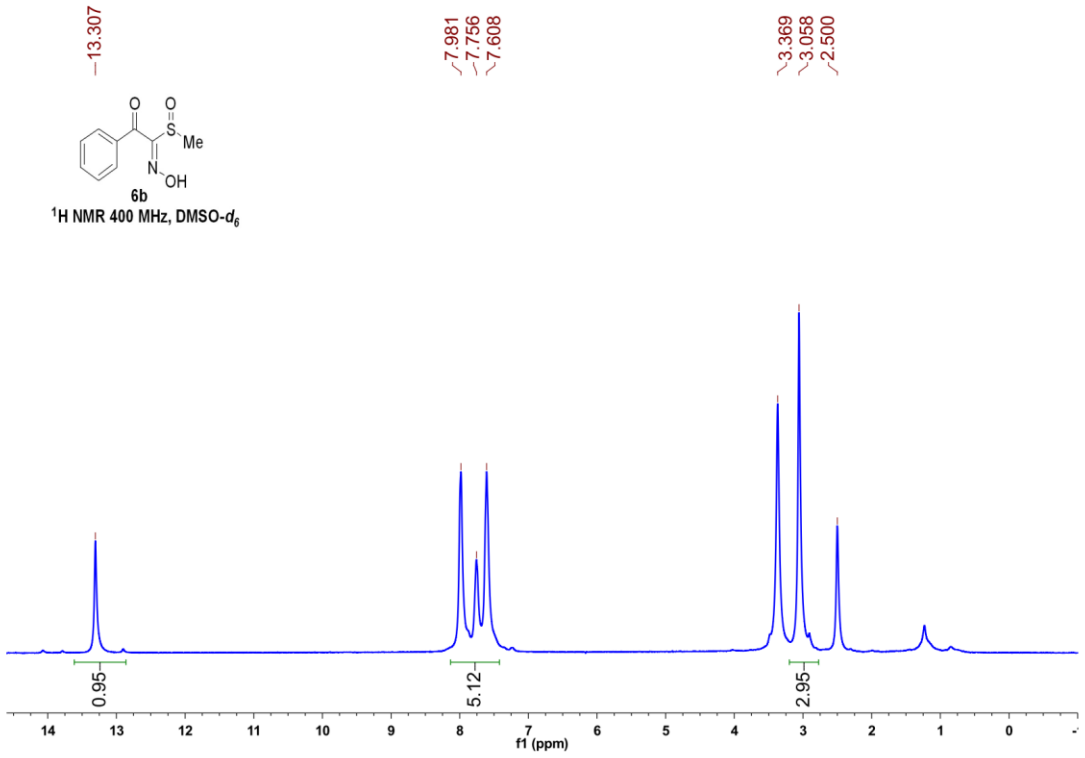

196.753
170.948
155.164
139.639
122.294
77.318
77.000
76.683
74.028
58.544
56.912
49.901
45.409
38.752
37.995
36.959
36.571
31.892
31.726
27.668
22.787
21.430
21.025
19.250
14.317
SMe
N–OH
4aj
^{13}C NMR 100 MHz, CDCl$_3$
f1 (ppm)



^{1}H NMR 400 MHz, $CDCl_3$



^{13}C NMR 100 MHz, $CDCl_3$



^{1}H NMR 400 MHz, DMSO-d_6