Supporting Information for

Copper-Mediated Intramolecular Oxidative C–H/C–H Cross-Coupling of α-Oxo Ketene *N,S*-Acetals for Indole Synthesis

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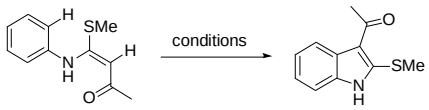
1. Optimization of the Reaction Conditions

Table S1. Screening of Conditions for the Reaction of 1a



1a **2a**

Entry	[Cu]	Base	Solvent (v:v)	Temp. (^oC)	Yield[a] (%)
1	$CuCl_2$	K_2CO_3	DMF	120	76 (72)[b]
2[c]	$CuCl_2$	K_2CO_3	DMF	120	61
3[d]	$CuCl_2$	K_2CO_3	DMF	120	6
4	$CuCl_2$	K_2CO_3	DMSO	120	31
5	$CuCl_2$	K_2CO_3	THF	120	6
6	$CuCl_2$[e]	K_2CO_3	DMF	120	52
7	$CuCl_2$[f]	K_2CO_3	DMF	120	7
8[d]	$CuCl_2$[f]	K_2CO_3	DMF	120	0
9[g]	$CuCl_2$[f]	K_2CO_3	DMF	120	0
10[h]	$CuCl_2$[f]	K_2CO_3	DMF	120	31
11[i]	$CuCl_2$[j]	K_2CO_3	DMF	130	0
12	$CuCl_2$[k]	K_2CO_3	DMF	130	91
13	$CuCl_2{\cdot}2H_2O$	K_2CO_3	DMF	120	68 (55)[b]
14	$CuBr_2$	K_2CO_3	DMF	120	75
15	$CuBr_2$[k]	K_2CO_3	DMF	120	93
16	$CuCl_2$	K_2CO_3	DMF	140	80
17	$CuCl_2$	K_2CO_3	*o*-xylene	140	26
18	$CuCl_2$	K_2CO_3	1,4-dioxane	140	18
19	$CuCl_2$	K_2CO_3	DMF/DMSO (3:1)	120	75
20	$CuCl_2$	K_2CO_3	DMF/DMSO (5:1)	120	83
21	$CuCl_2$	K_2CO_3	DMF/DMSO (7:1)	120	88
22	$CuCl_2$	K_2CO_3	DMF/DMSO (9:1)	120	81
23	$CuCl_2$	K_2CO_3	DMF/DMSO (11:1)	120	82
24	$CuCl_2$	Li_2CO_3	DMF	120	94 (84)[b]
25	$CuCl_2$	Na_2CO_3	DMF	120	84
26	$CuCl_2$	Cs_2CO_3	DMF	120	66
27	$CuCl_2$	Na_2CO_3	DMF/DMSO (7:1)	120	80
28	$CuCl_2$	Li_2CO_3	DMF/DMSO (5:1)	120	85
29	$CuCl_2$	Li_2CO_3	DMF/DMSO (7:1)	120	87
30	$CuCl_2$	Li_2CO_3	DMF/DMSO (9:1)	120	86
31	$CuCl_2$	Li_2CO_3	DMF/DMSO (11:1)	120	91
32	$CuCl_2$	Li_2CO_3	toluene	140	10
33	$CuCl_2$	Li_2CO_3	$ClCH_2CH_2Cl$	140	69
34	$CuCl_2$		DMF	140	52
35	$CuCl_2$	K_3PO_4	DMF	140	86
36	$CuCl_2$	K_3PO_4	DMF/DMSO (7:1)	140	96 (94)[b]
37	$CuCO_3$	LiCl	DMF	140	8
38	**$CuCl_2$**	**K_3PO_4**	**DMF/DMSO (7:1)**	**120**	**97 (94)[b]**
39	$CuCl_2$	K_3PO_4	DMF/DMSO (7:1)	100	81
40[c]	$CuCl_2$	K_3PO_4	DMF/DMSO (7:1)	120	68
41[d]	$CuCl_2$	K_3PO_4	DMF/DMSO (7:1)	120	7
42	$CuCl_2$	K_3PO_4[e]	DMF/DMSO (7:1)	120	83
43	$CuCl_2$	K_3PO_4[l]	DMF/DMSO (7:1)	120	73
44	$CuCl_2$[e]	K_3PO_4	DMF/DMSO (7:1)	120	52
45	$CuCl_2$[l]	K_3PO_4	DMF/DMSO (7:1)	120	6
46	$CuCl_2$	K_3PO_4	DMF/DMSO (20:1)	120	94

47	$CuCl_2 \cdot 2H_2O$	K_3PO_4	DMF/DMSO (7:1)	120	76
48	$CuBr_2$	K_3PO_4	DMF/DMSO (7:1)	120	95

Conditions: **1a** (0.2 mmol), [Cu] (0.6 mmol), base (0.6 mmol), solvent (2 mL), 0.1 MPa Ar, 0.5 h. [a] Determined by GC analysis with mesitylene as the internal standard. [b] Isolated yield given in parentheses. [c] In air. [d] In 0.1 MPa O_2. [e] 2 equiv. [f] 0.2 equiv. [g] with 2 equiv BQ. [h] with 2 equiv DDQ. [i] with 2 equiv $K_2S_2O_8$. [j] 0.5 equiv. [k] 4 equiv. [l] 1 equiv.

2. X-Ray Crystallographic Studies

Single crystals for the X-ray diffraction studies for compounds **2d**, **2x**, and **3b** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on *F*2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 999743 for **2d**, CCDC 999802 for **2x**, and CCDC 999742 for **3b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

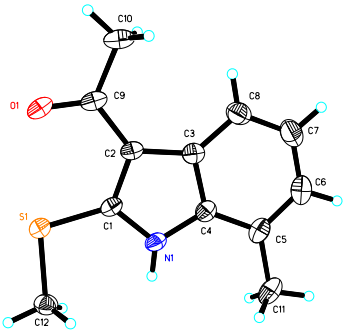


Table S2. Crystal data and structure refinement for 2d

Empirical formula	$C_{12}H_{13}NOS$	
Formula weight	219.29	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P2(1)/n	
Unit cell dimensions	a = 5.262(6) Å	alpha = 90°
	b = 16.416(19) Å	beta = 99.99(2) °
	c = 13.074(15) Å	gamma = 90°
Volume	1112(2) $Å^3$	
Z, Calculated density	4, 1.310 Mg/m^3	
Absorption coefficient	0.263 mm^{-1}	
F(000)	464	
Crystal size	0.212 x 0.156 x 0.123 mm	
Theta range for data collection	2.01 to 26.00°	
Limiting indices	-6<=h<=6, -20<=k<=20, -16<=l<=14	
Reflections collected/unique	6383 / 2183 [R(int) = 0.0734]	
Completeness to theta = 26.00	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	1.00000 and 0.37703	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2183 / 0 / 144	
Goodness-of-fit on F^2	1.067	
Final R indices [I > 2 sigma(I)]	R1 = 0.0537, wR2 = 0.1344	
R indices (all data)	R1 = 0.0598, wR2 = 0.1403	
Largest diff. peak and hole	0.335 and -0.311 $e.Å^{-3}$	

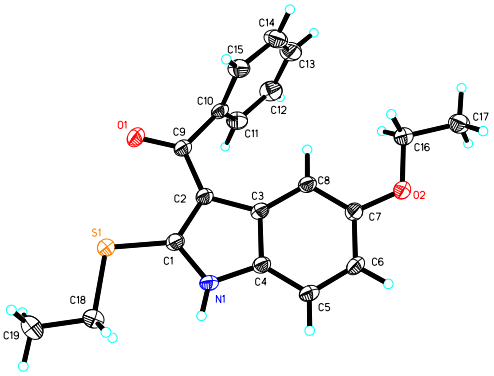


Table S3. Crystal data and structure refinement for 2x

Empirical formula	$C_{19}H_{19}NO_2S$	
Formula weight	325.41	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic, Pbca	
Unit cell dimensions	a = 14.0334(9) Å	alpha = 90°
	b = 10.0587(7) Å	beta = 90 °
	c = 23.4532(15) Å	gamma = 90°
Volume	3310.6(4) $Å^3$	
Z, Calculated density	8, 1.306 Mg/m^3	
Absorption coefficient	0.205 mm^{-1}	
F(000)	1376.0	

Crystal size	0.231 x 0.175 x 0.101 mm
Theta range for data collection	1.74 to 26.00°
Limiting indices	-17<=h<=16, -12<=k<=10, -28<=l<=28
Reflections collected/unique	18897 / 3259 [R(int) = 0.0418]
Completeness to theta = 26.00	100.0 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.66890
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3259 / 0 / 214
Goodness-of-fit on F^2	1.056
Final R indices [I > 2 sigma(I)]	R1 = 0.0365, wR2 = 0.0975
R indices (all data)	R1 = 0.0476, wR2 = 0.1043
Largest diff. peak and hole	0.240 and -0.188 e.Å^{-3}

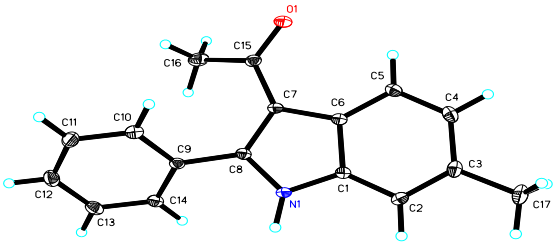
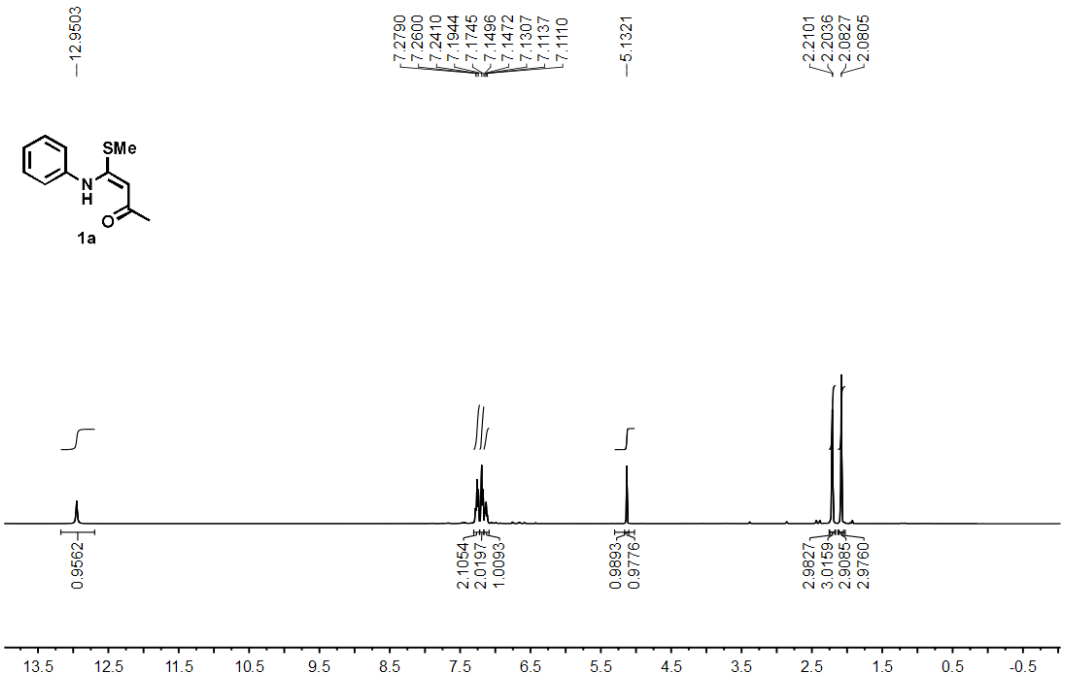


Table S4. Crystal data and structure refinement for 3b

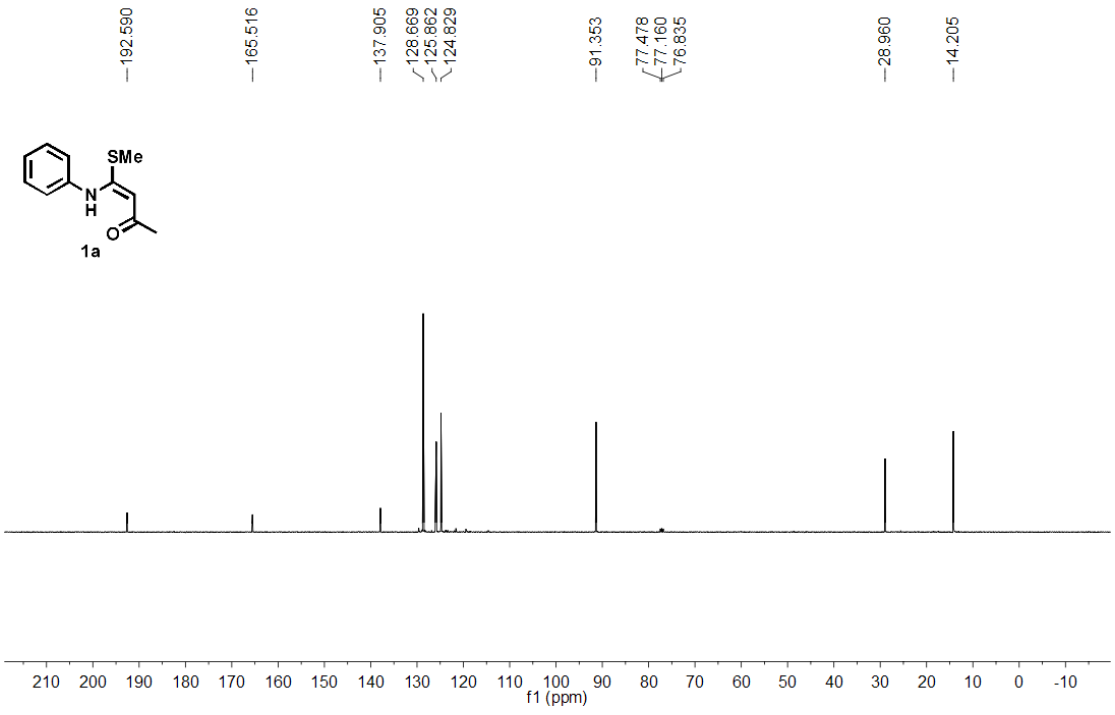
Empirical formula	$C_{17}H_{15}NO$	
Formula weight	249.30	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	monoclinic, P 21/c	
Unit cell dimensions	a = 14.094(3) Å	alpha = 90°
	b = 7.3935(15) Å	beta = 90.653(4) °
	c = 12.576(3) Å	gamma = 90°
Volume	1310.4(5) Å^3	
Z, Calculated density	4, 1.264 Mg/m^3	
Absorption coefficient	0.078mm^{-1}	
F(000)	528	
Crystal size	0.250 x 0.150 x 0.150 mm	
Theta range for data collection	1.445 to 30.583°	
Limiting indices	-20<=h<=19, -10<=k<=10, -17<=l<=15	
Reflections collected/unique	12603 / 4009 [R(int) = 0.0571]	
Completeness to theta = 30.554	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6728 and 0.7461	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4009 / 0 / 178	
Goodness-of-fit on F^2	1.155	
Final R indices [I > 2 sigma(I)]	R1 = 0.0539, wR2 = 0.1076	
R indices (all data)	R1 = 0.0987, wR2 = 0.1207	
Largest diff. peak and hole	0.289 and -0.356 e.Å^{-3}	

3. Copies of NMR Spectra for Known Compounds

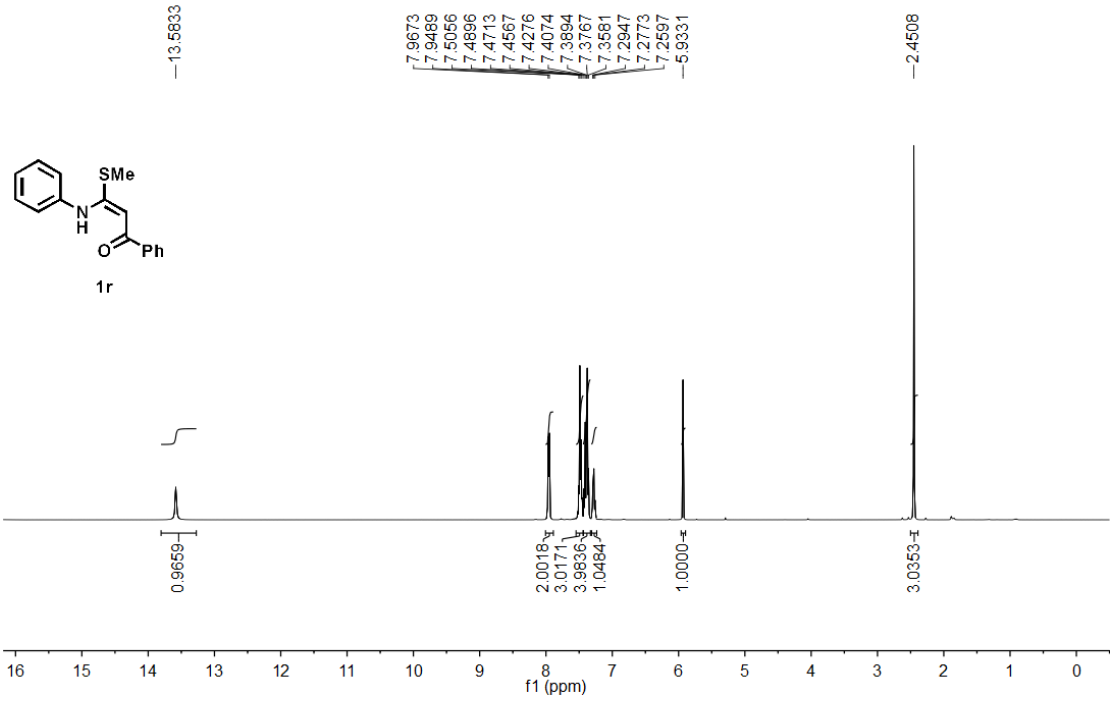
hf95
1H NMR (hf95 in CDCl3)



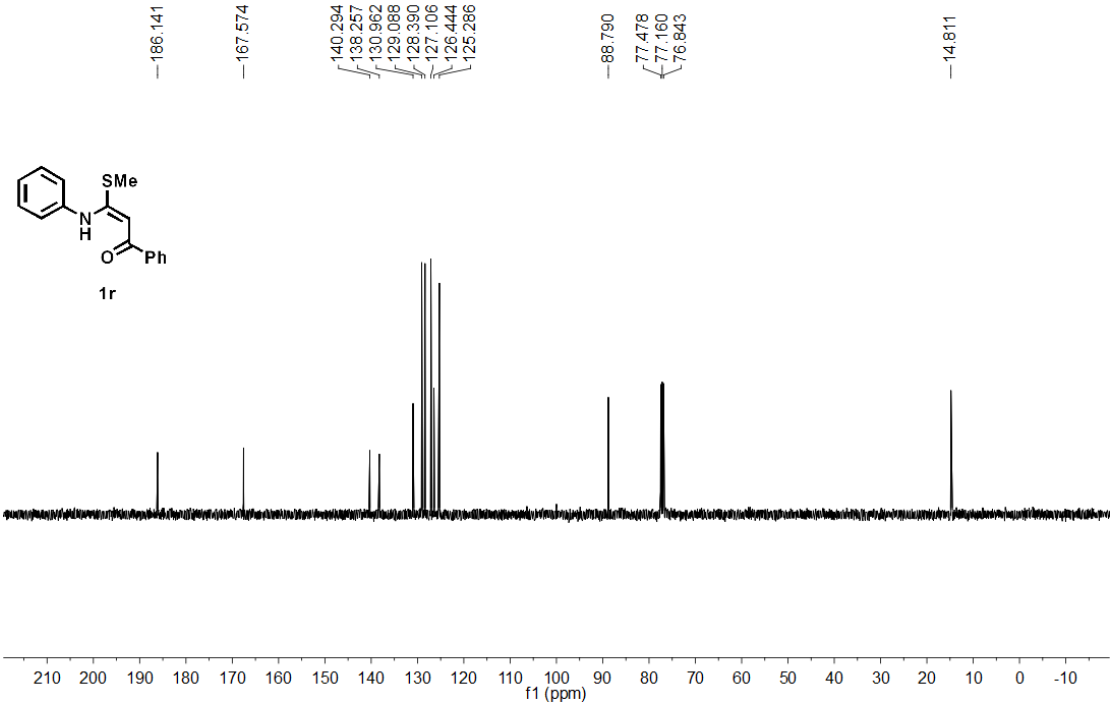
hf95
13C NMR (hf95 in CDCl3)



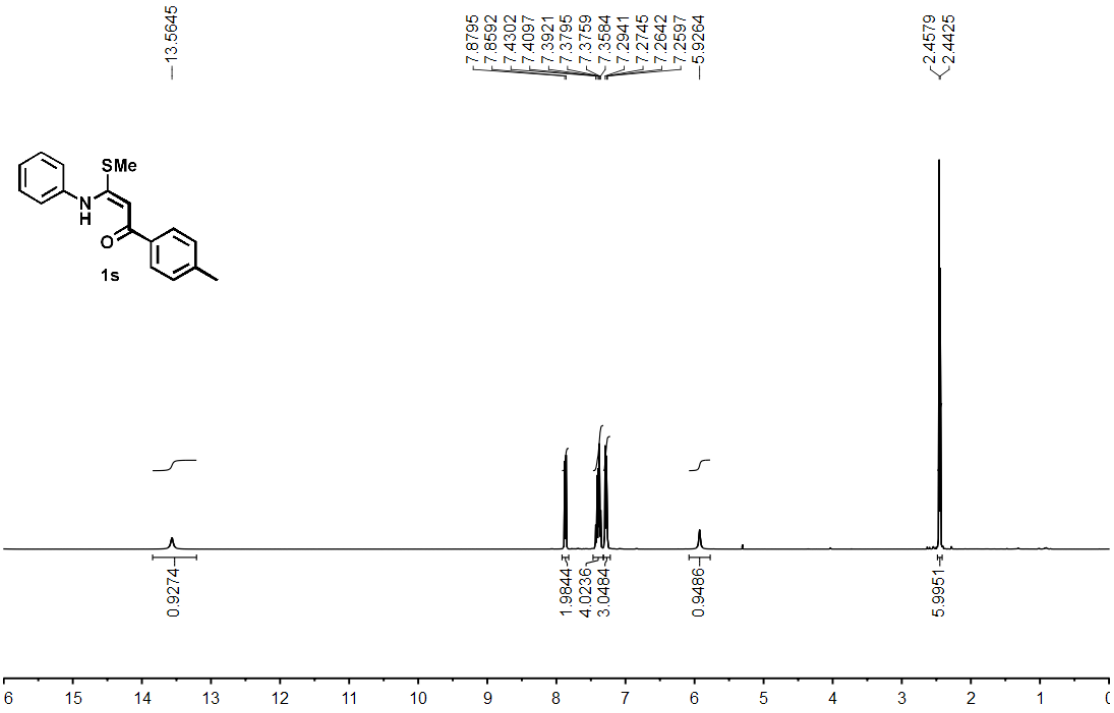
HF171
1H NMR IN CDCl3



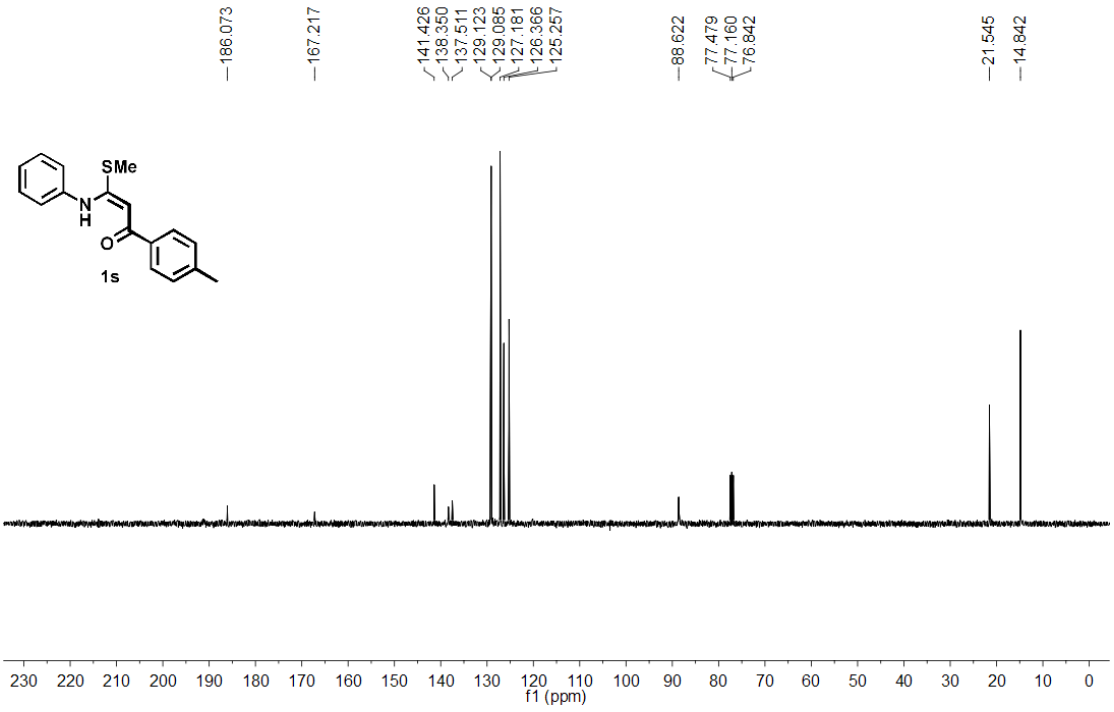
HF171
13C NMR IN CDCl3



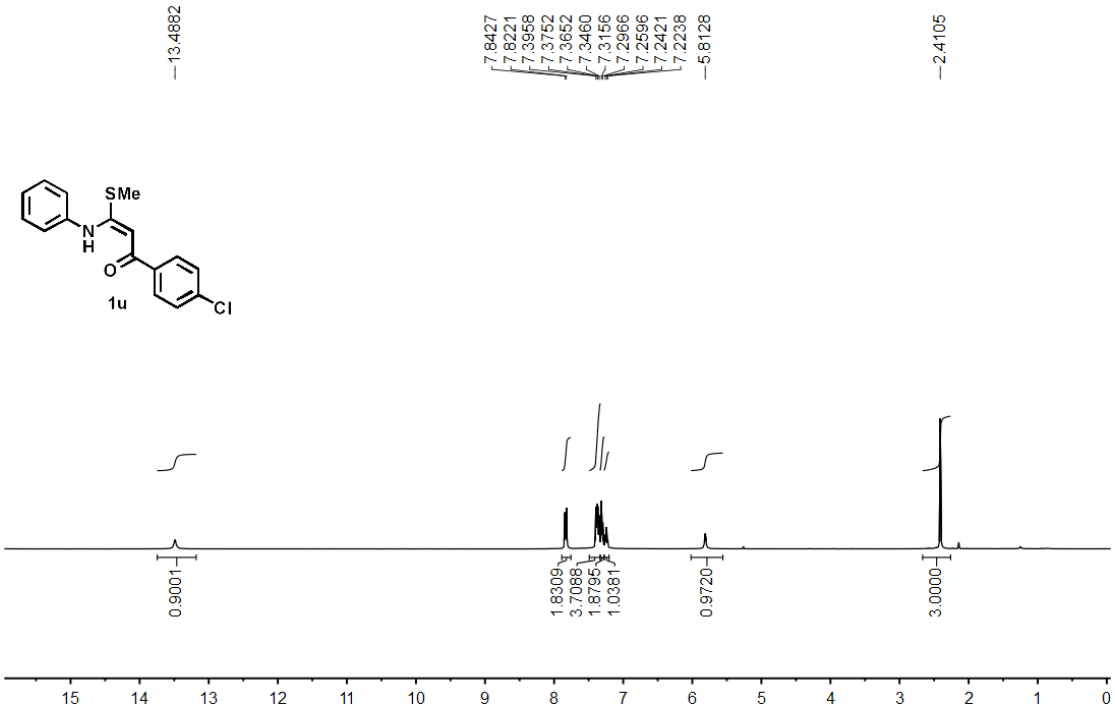
hf257-1
1H NMR hf257 in CDCl3



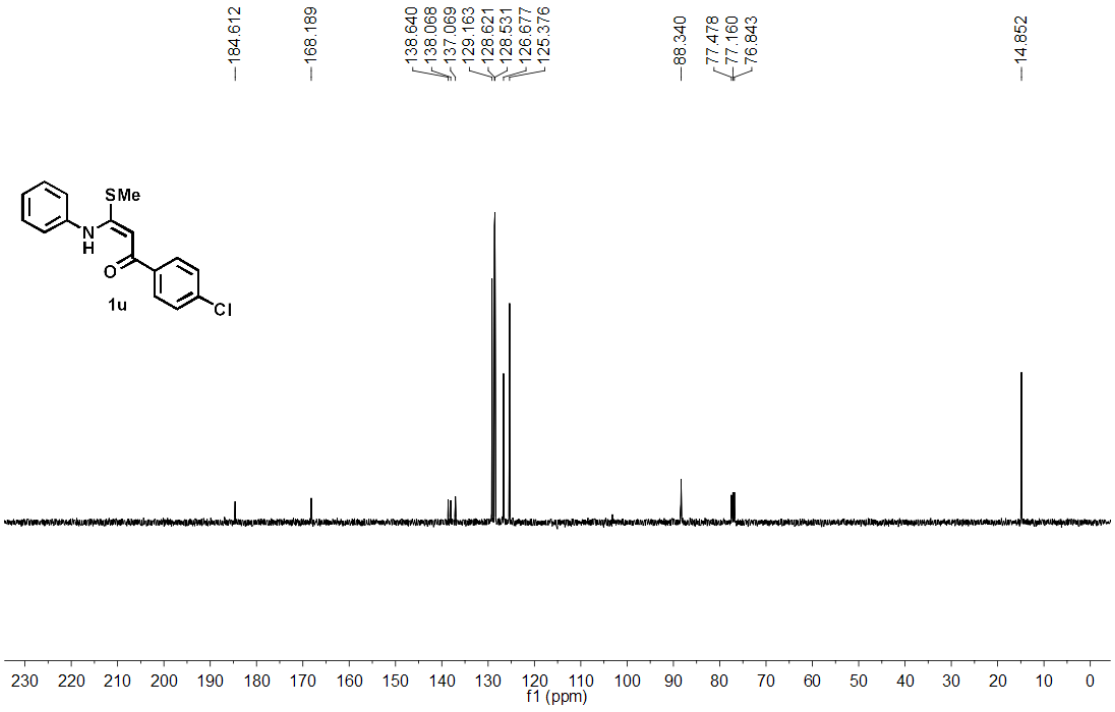
hf257-1
13C NMR hf257 CDCl3



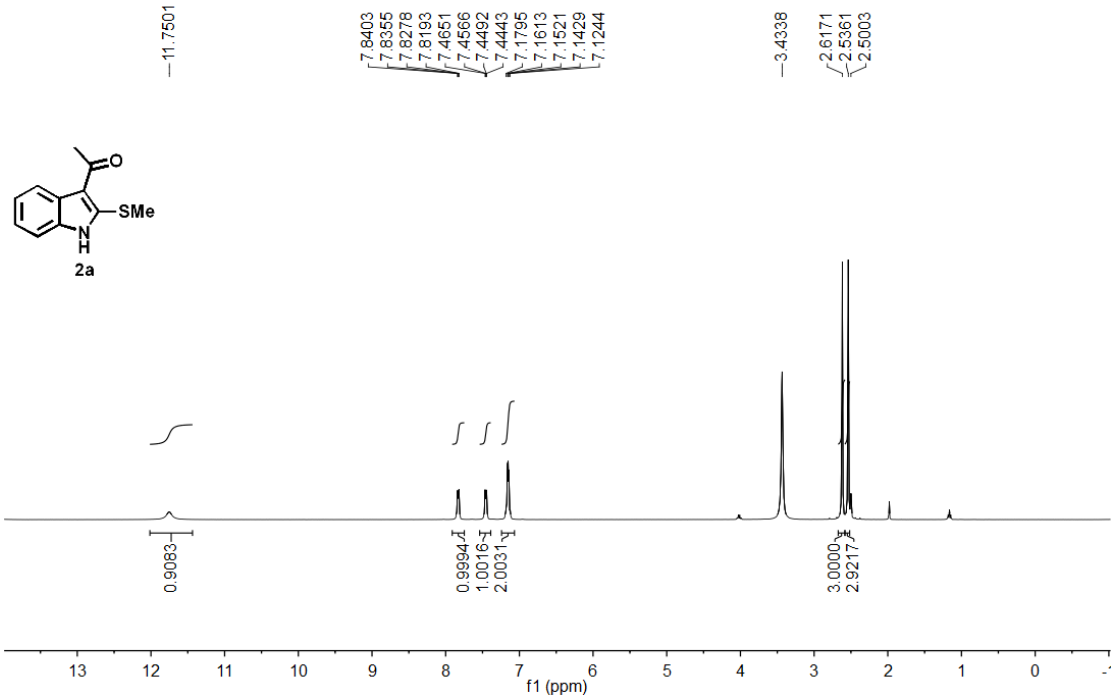
hf261
1H NMR hf261 in CDCl3



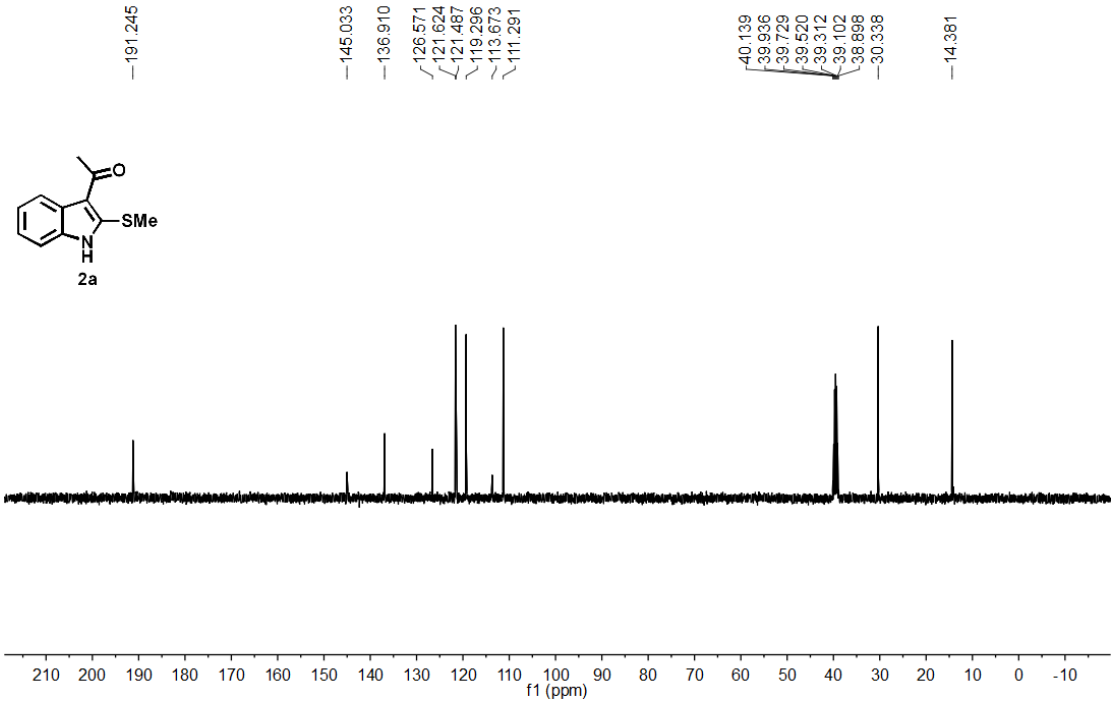
hf261
13C NMR hf261 CDCl3

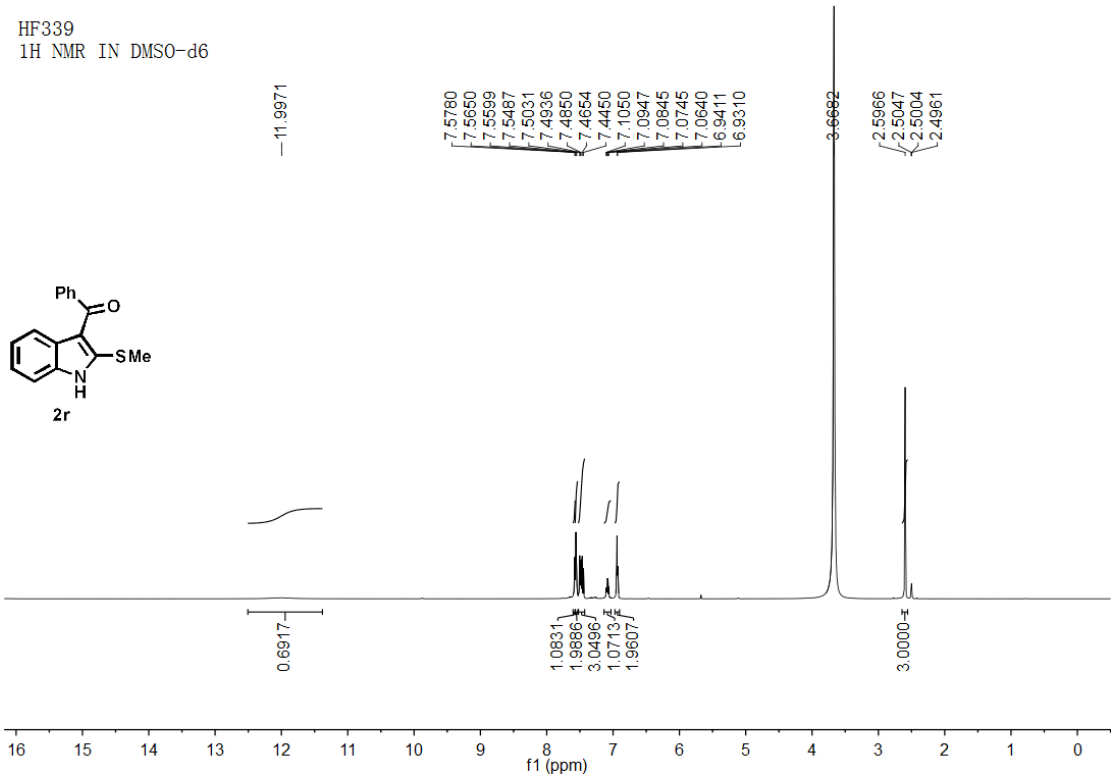


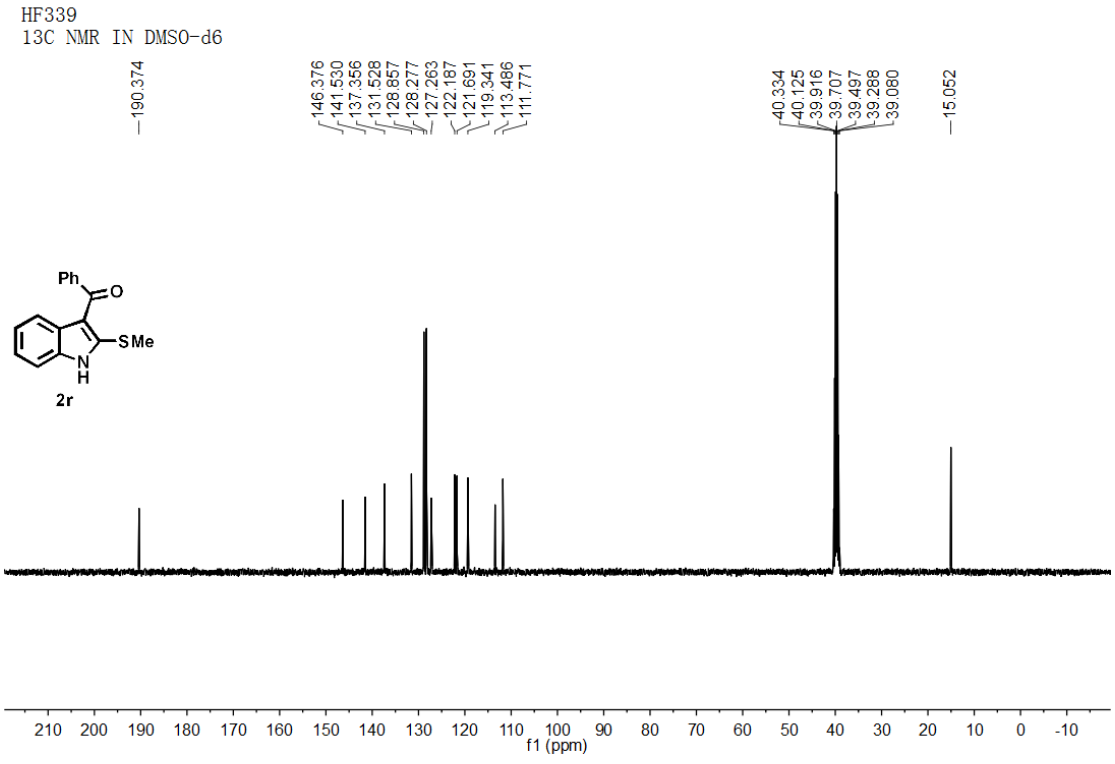
HF106
1H NMR IN DMSO-d6



HF106
13C NMR IN DMSO-d6

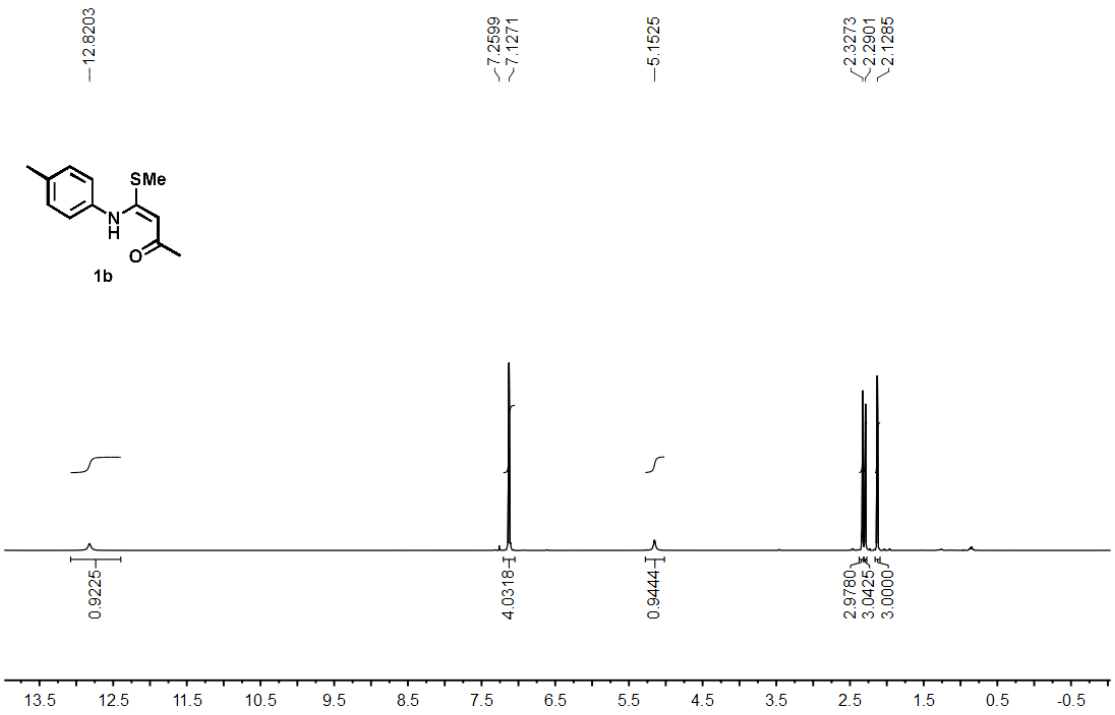



HF339
1H NMR IN DMSO-d6
11.9971
7.5780
7.5650
7.5599
7.5487
7.5031
7.4936
7.4850
7.4654
7.4450
7.1050
7.0947
7.0845
7.0745
7.0640
6.9411
6.9310
3.6682
2.5966
2.5047
2.5004
2.4961
Ph
O
SMe
N
H
2r
0.6917
1.0831
1.9886
3.0496
1.0713
1.9607
3.0000
f1 (ppm)

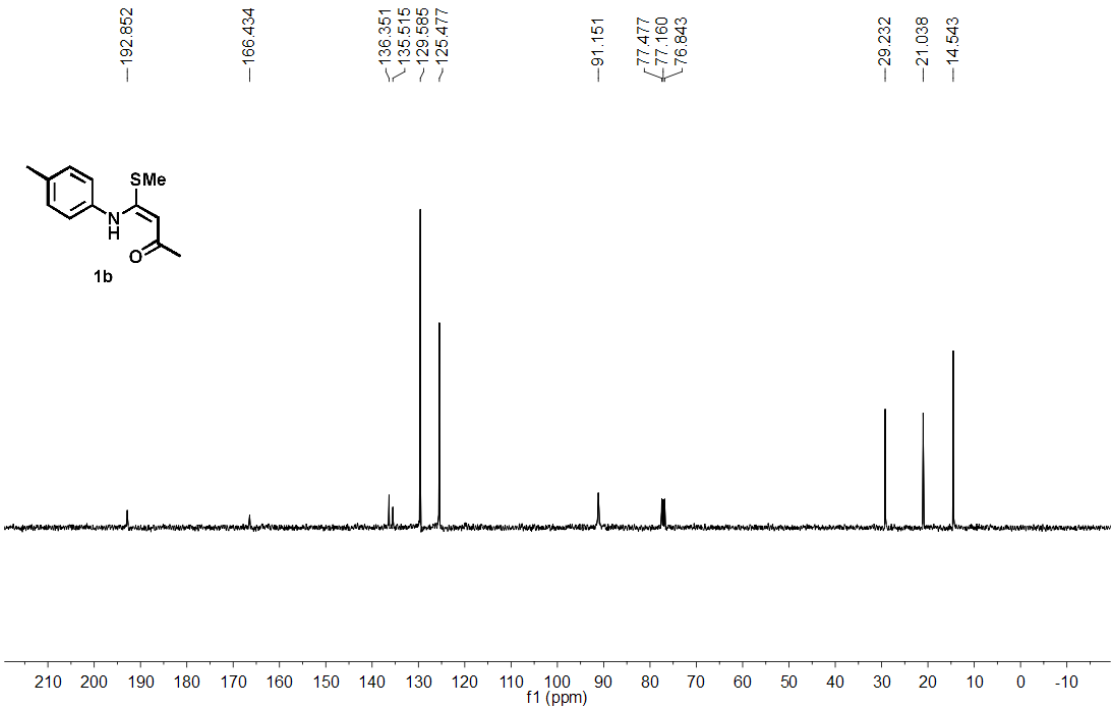

HF339
13C NMR IN DMSO-d6
190.374
146.376
141.530
137.356
131.528
128.857
128.277
127.263
122.187
121.691
119.341
113.486
111.771
40.334
40.125
39.916
39.707
39.497
39.288
39.080
15.052
Ph
O
SMe
N
H
2r
f1 (ppm)

4. Copies of NMR Spectra for New Compounds

hf191
1H NMR (hf191 in CDCl3)



hf191
13C NMR (hf191 in CDCl3)



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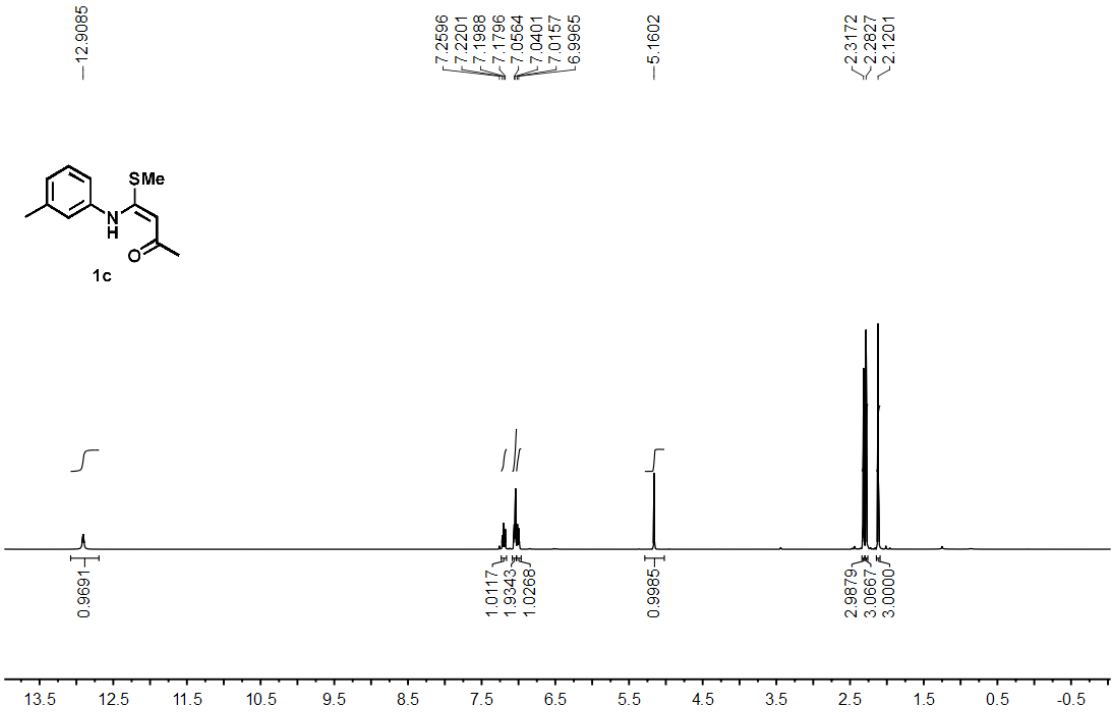
1H NMR (hf209 in CDCl3)



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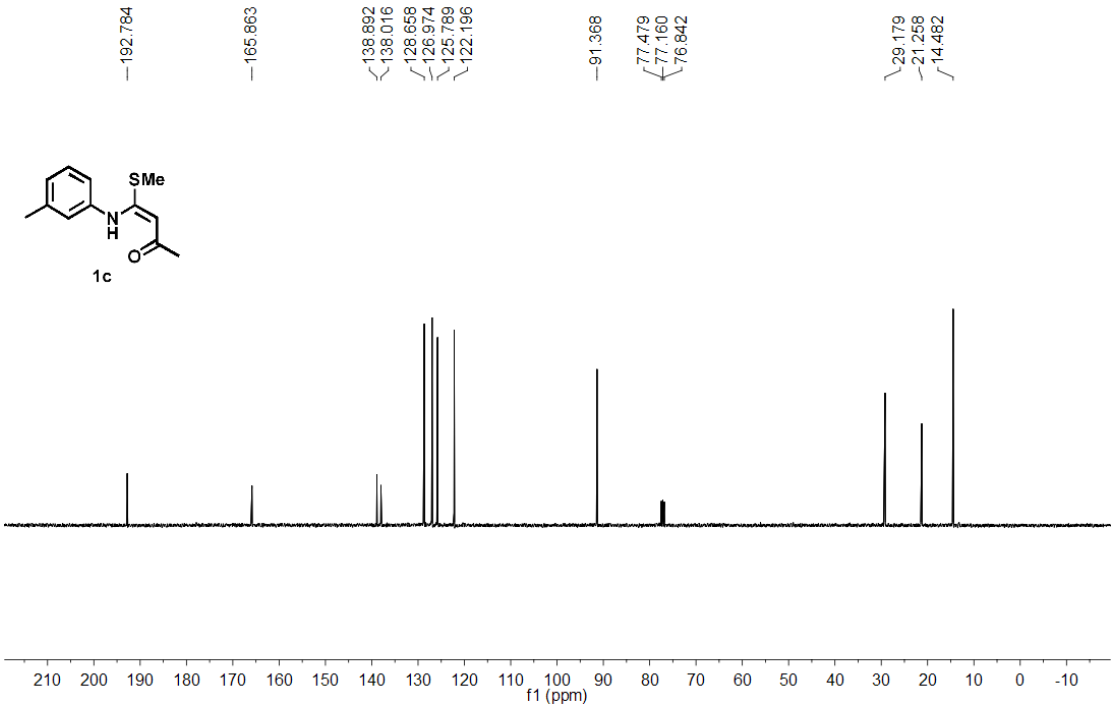
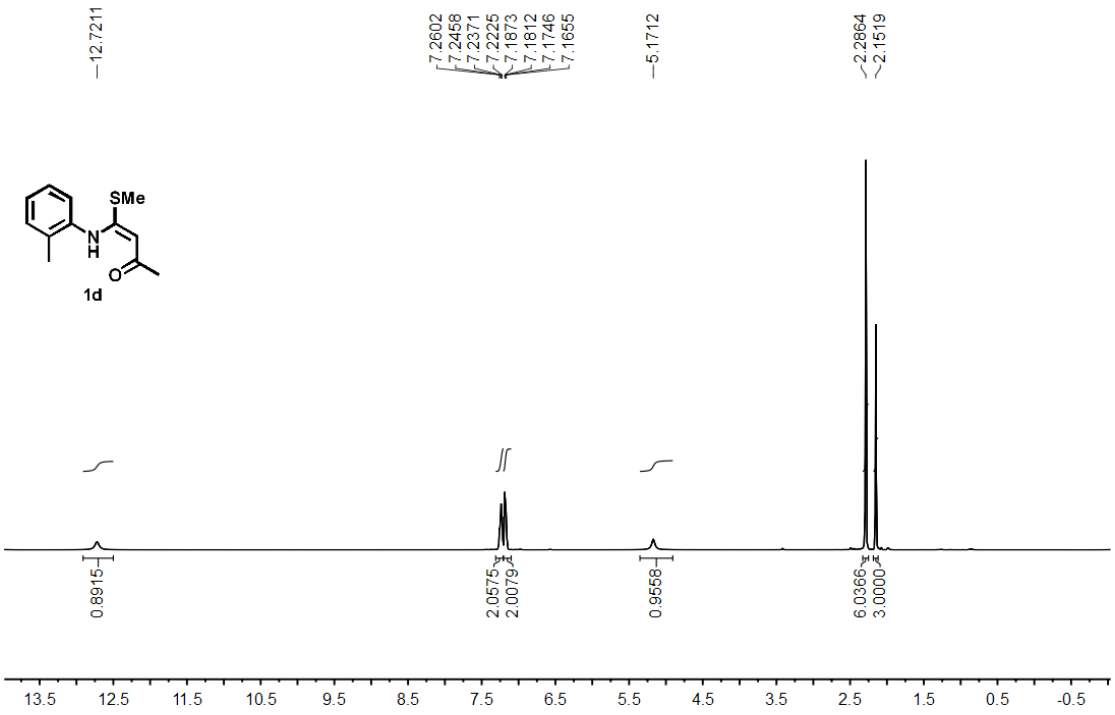
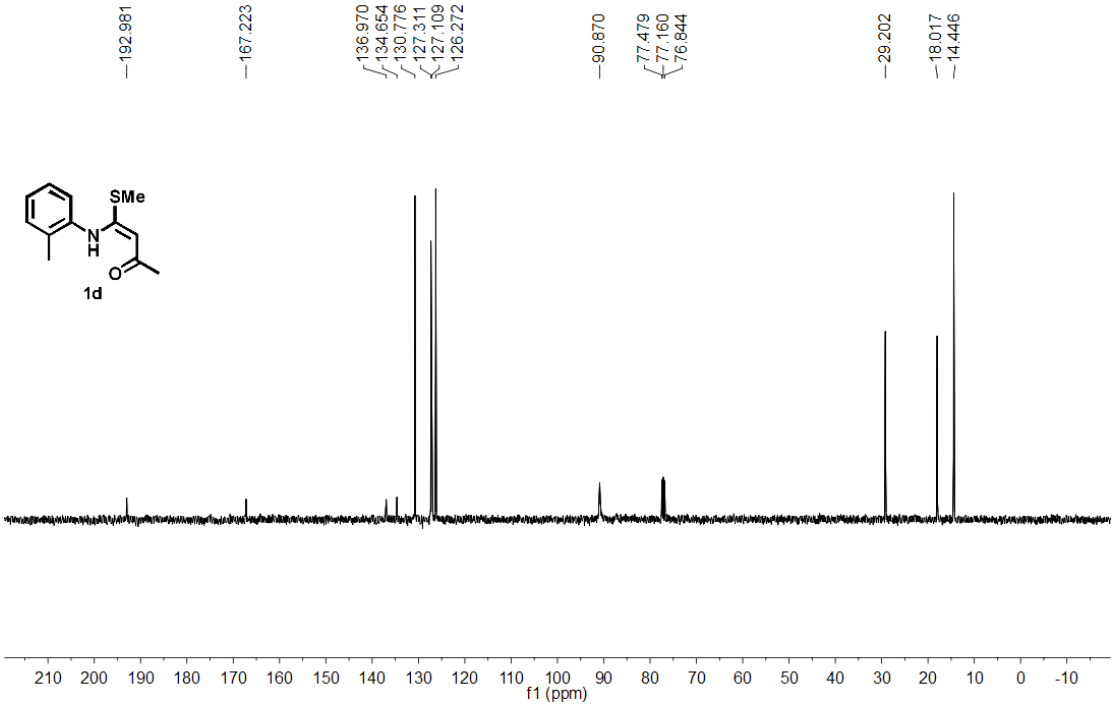
13C NMR (hf209 in CDCl3)



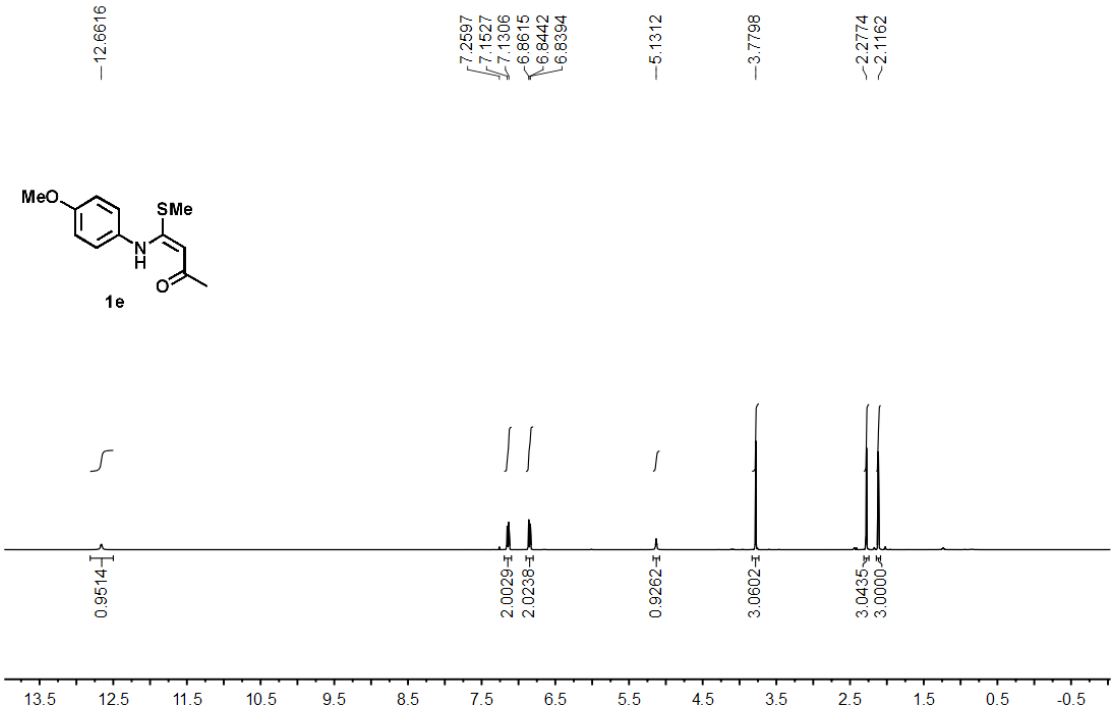
hf192
1H NMR (hf192 in CDCl3)



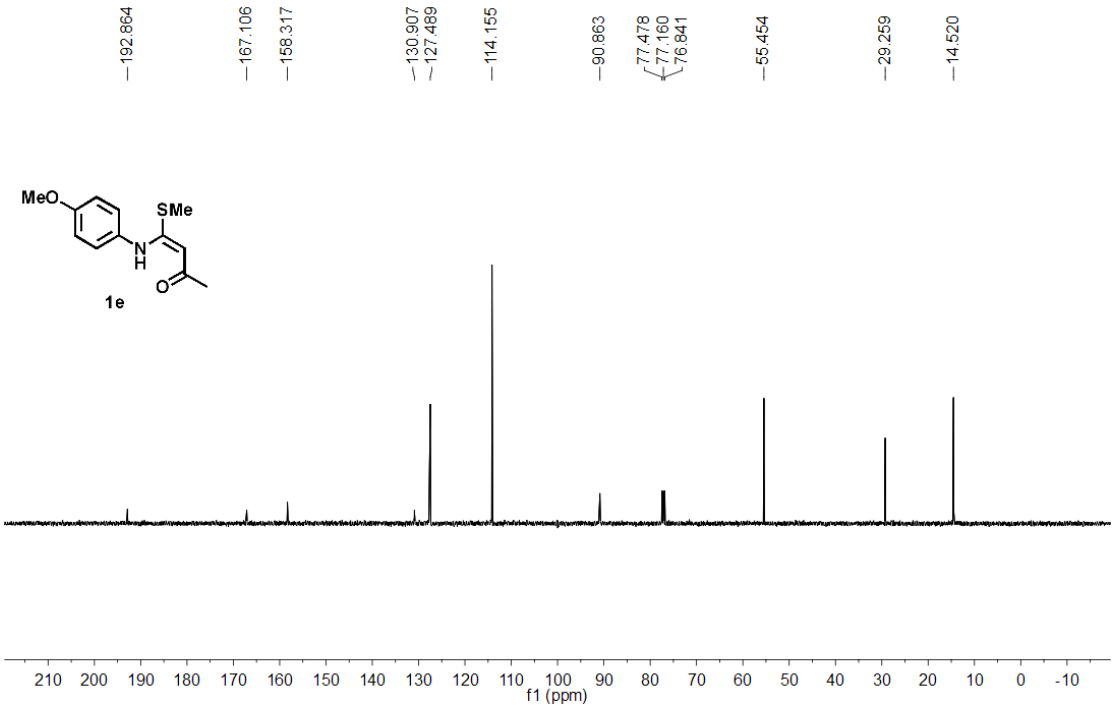
hf192
13C NMR (hf192 in CDCl3)



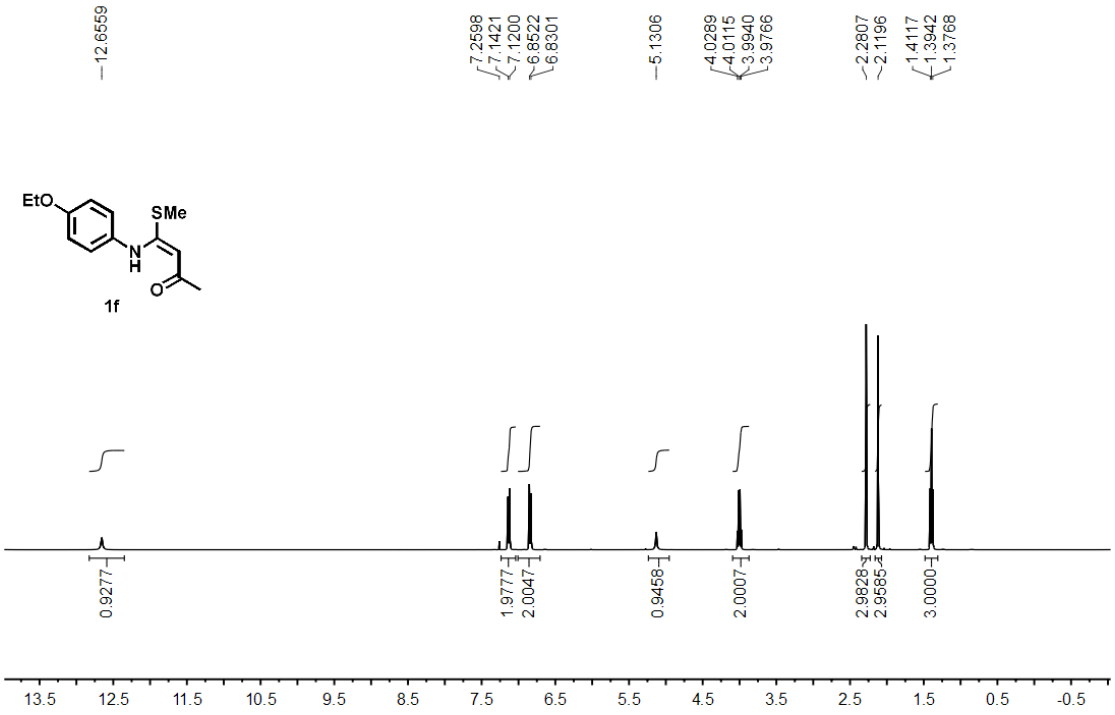
hf208
1H NMR (hf208 in CDCl3)



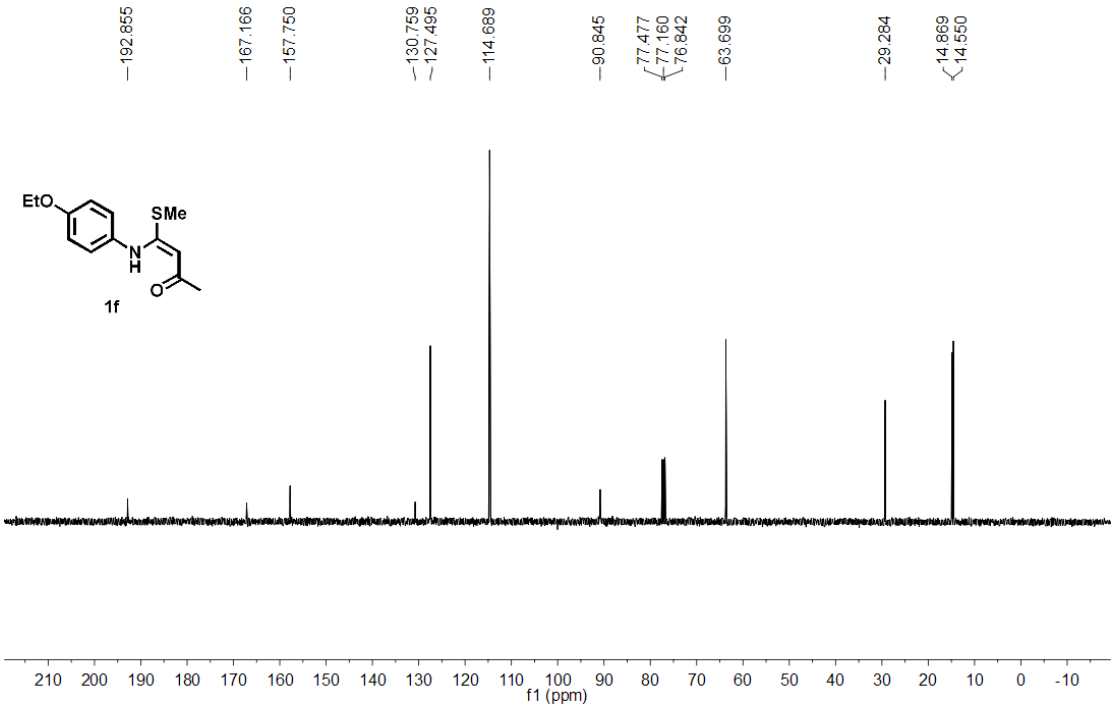
hf208
13C NMR (hf208 in CDCl3)



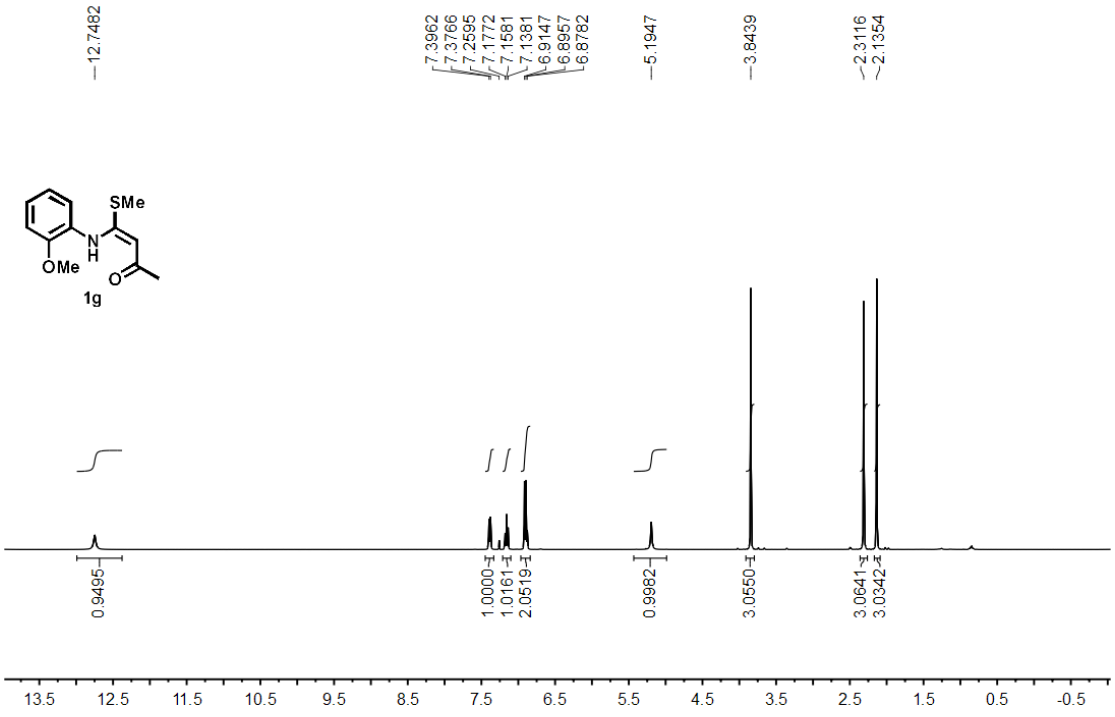
hf188-2
1H NMR (hf188-2 in CDCl3)



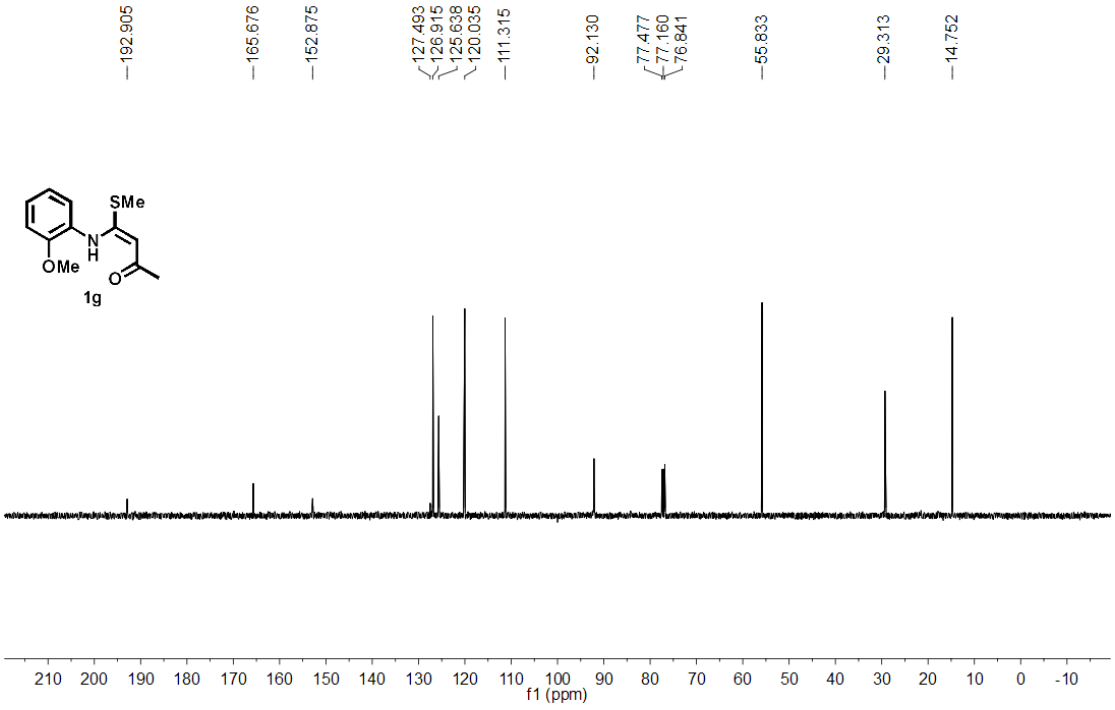
hf188-2
13C NMR (hf188-2 in CDCl3)



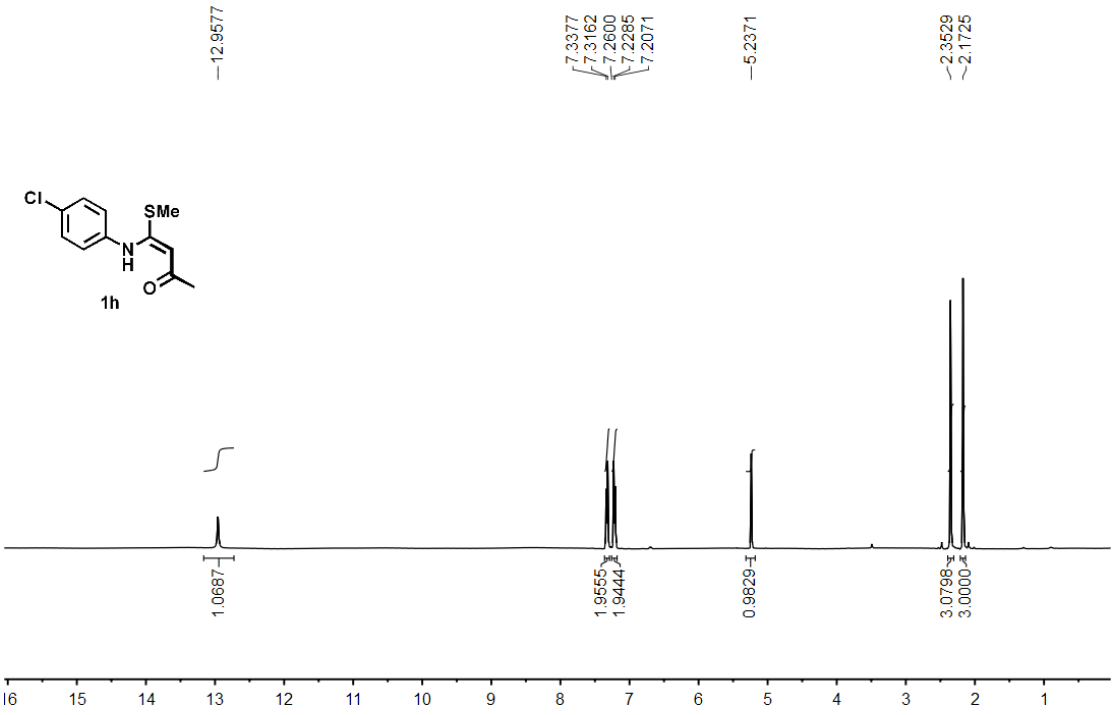
hf219
1H NMR (hf219 in CDCl3)



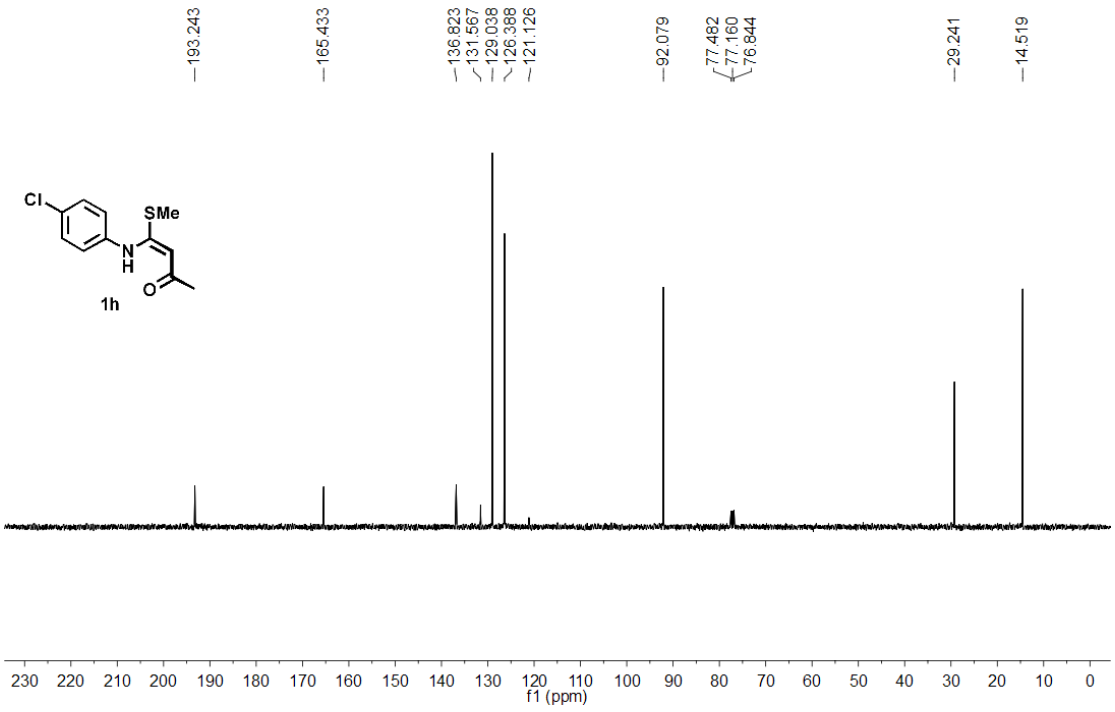
hf219
13C NMR (hf219 in CDCl3)



hf300
1H NMR hf300 in CDCl3

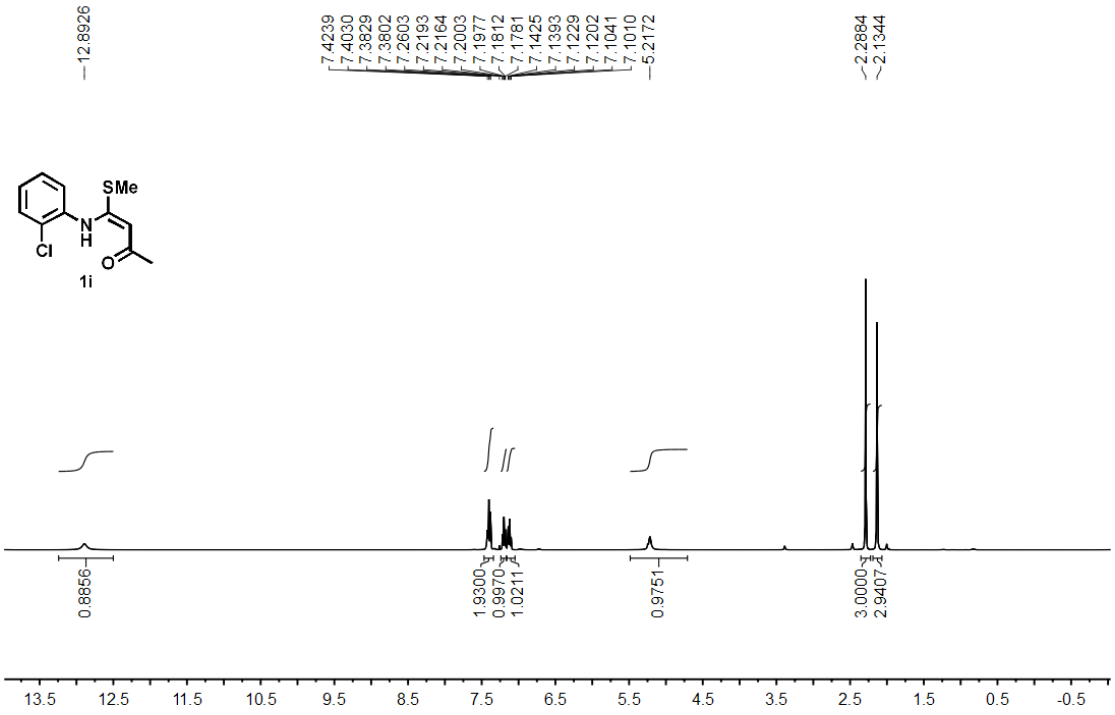


hf300
13C NMR hf300 CDCl3



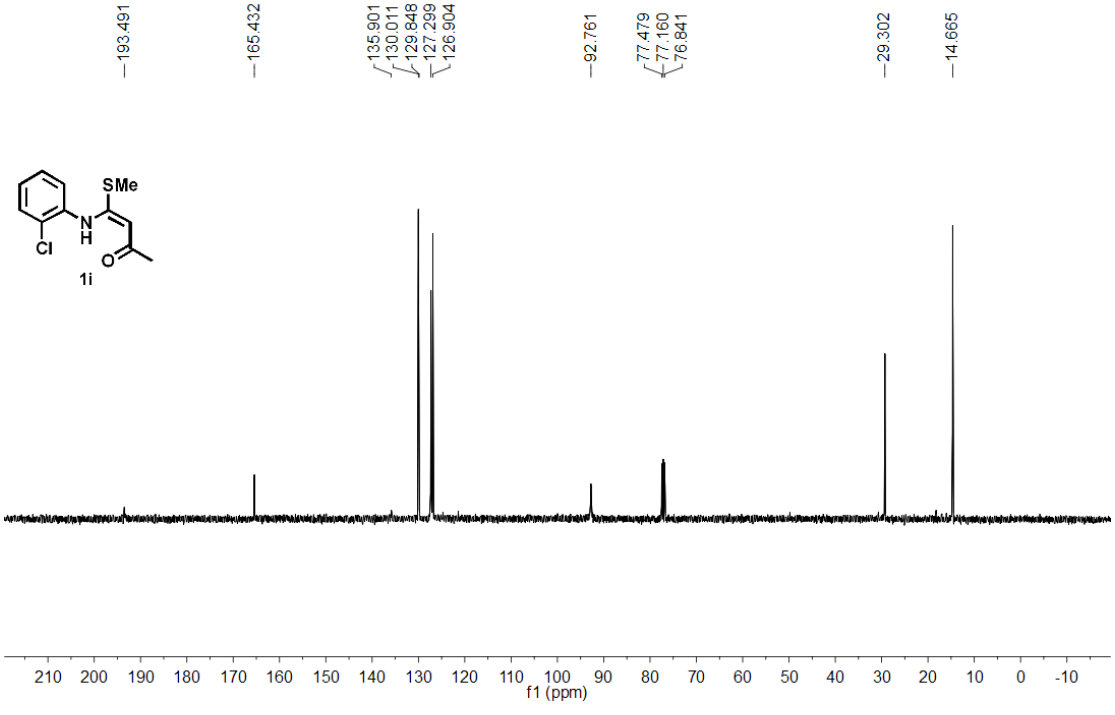
hf196-1

1H NMR (hf196-1 in CDCl3)

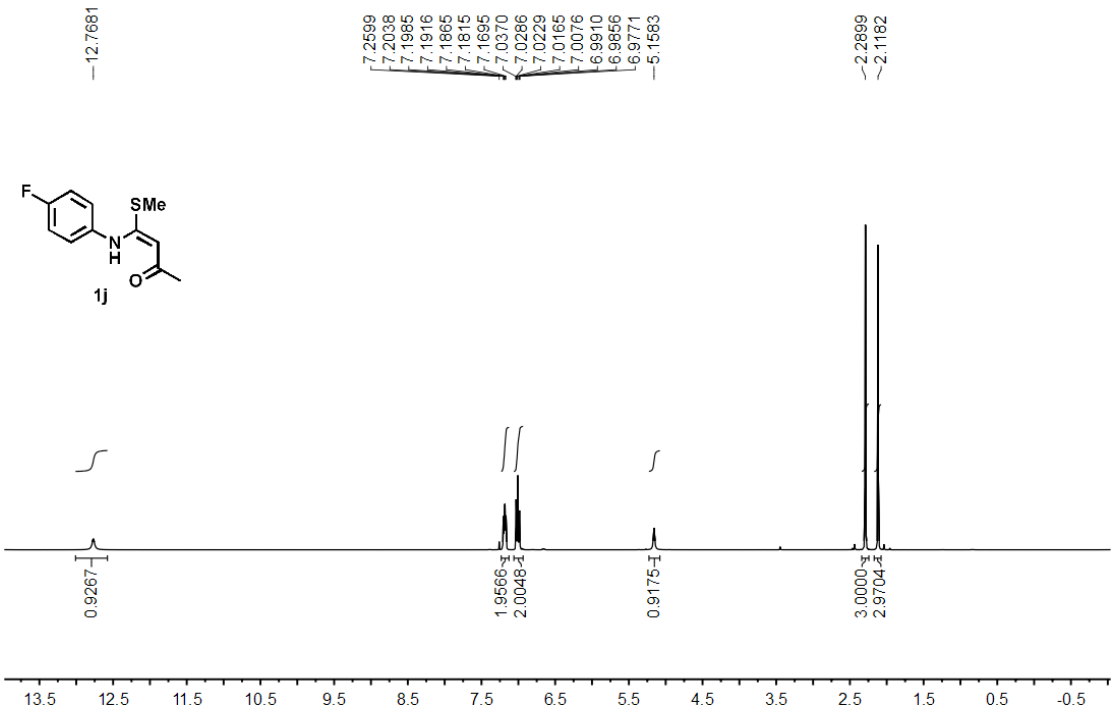


hf196

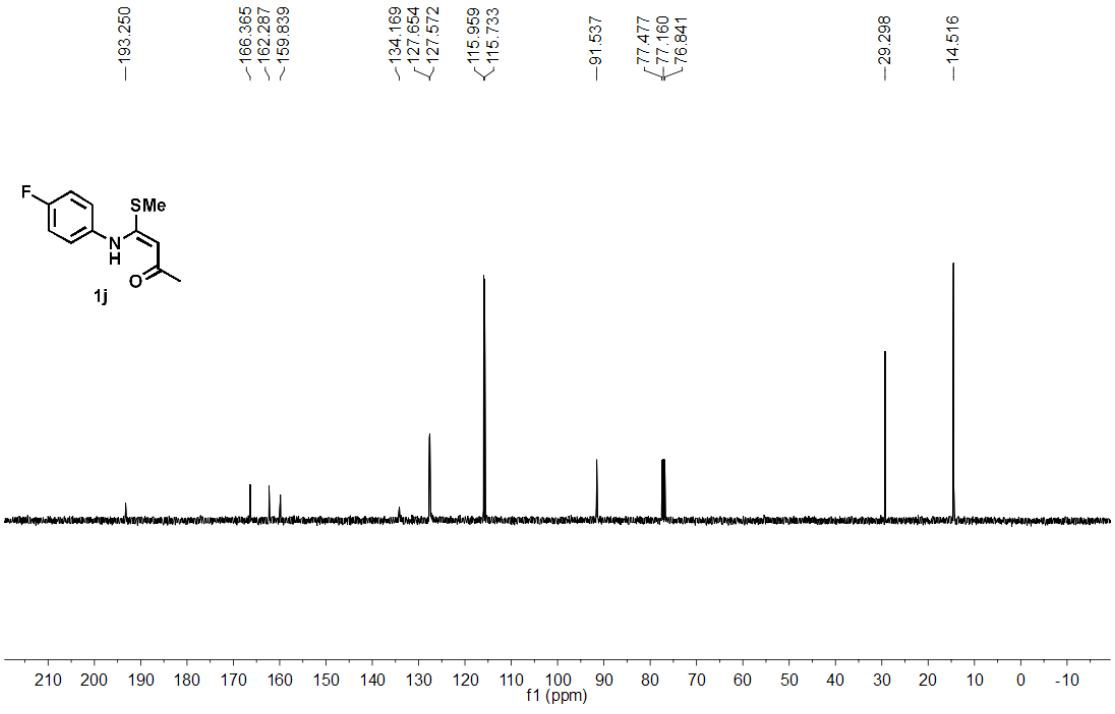
13C NMR (hf196 in CDCl3)



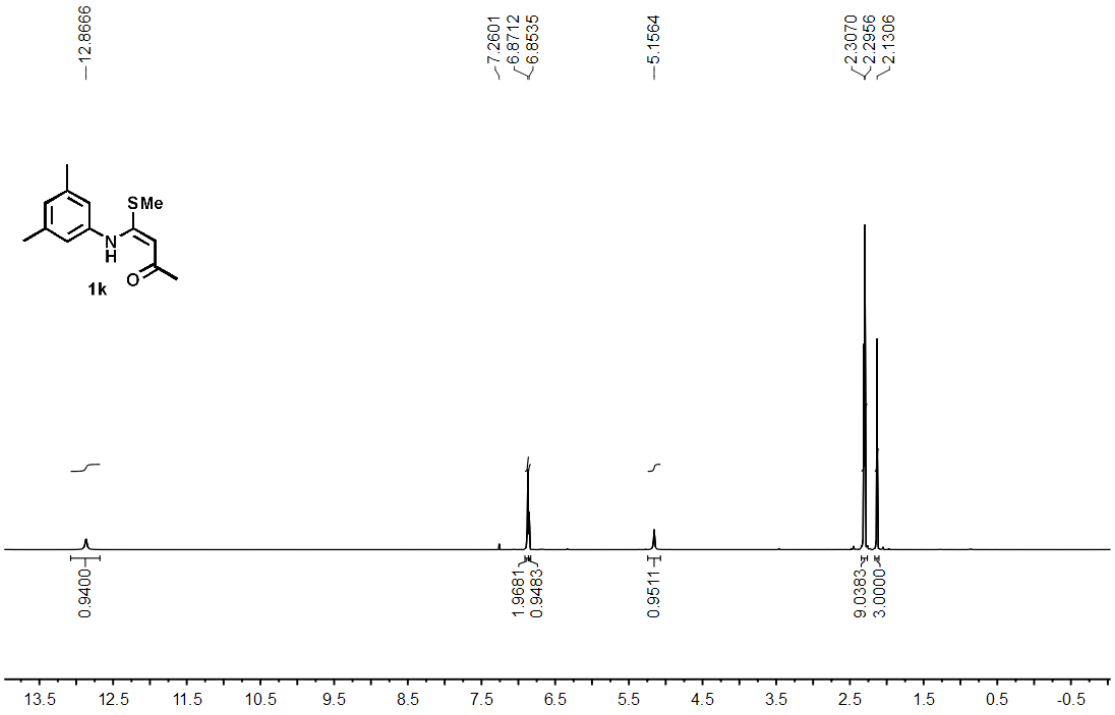
hf218
1H NMR (hf218 in CDCl3)



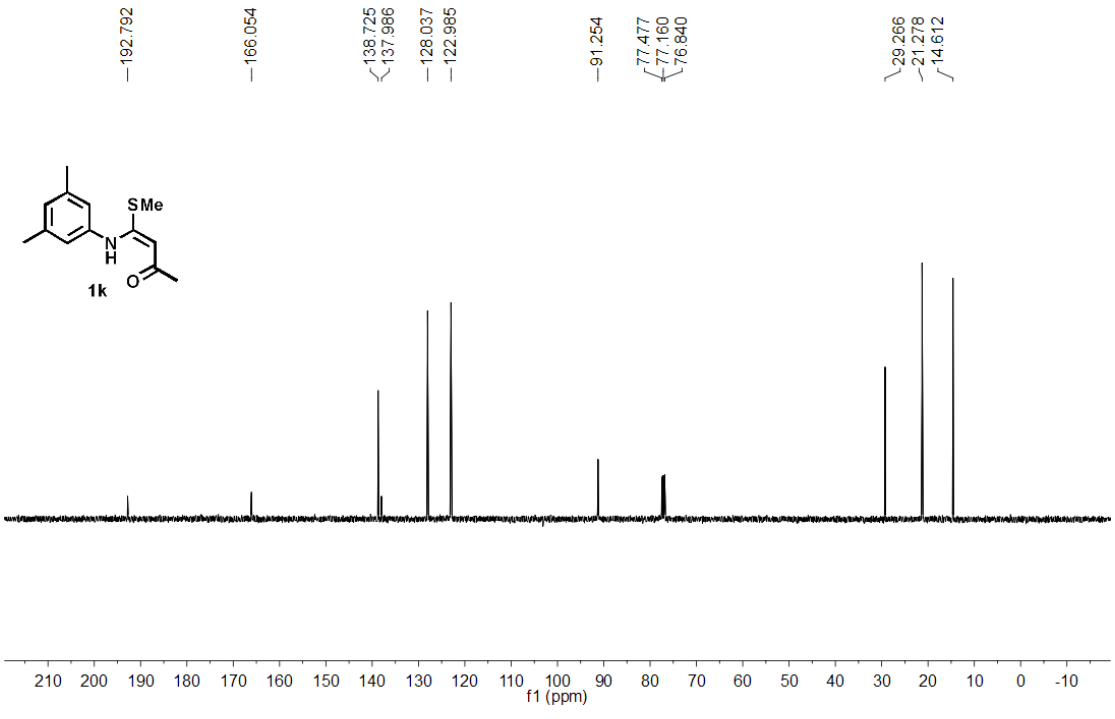
hf218
13C NMR (hf218 in CDCl3)



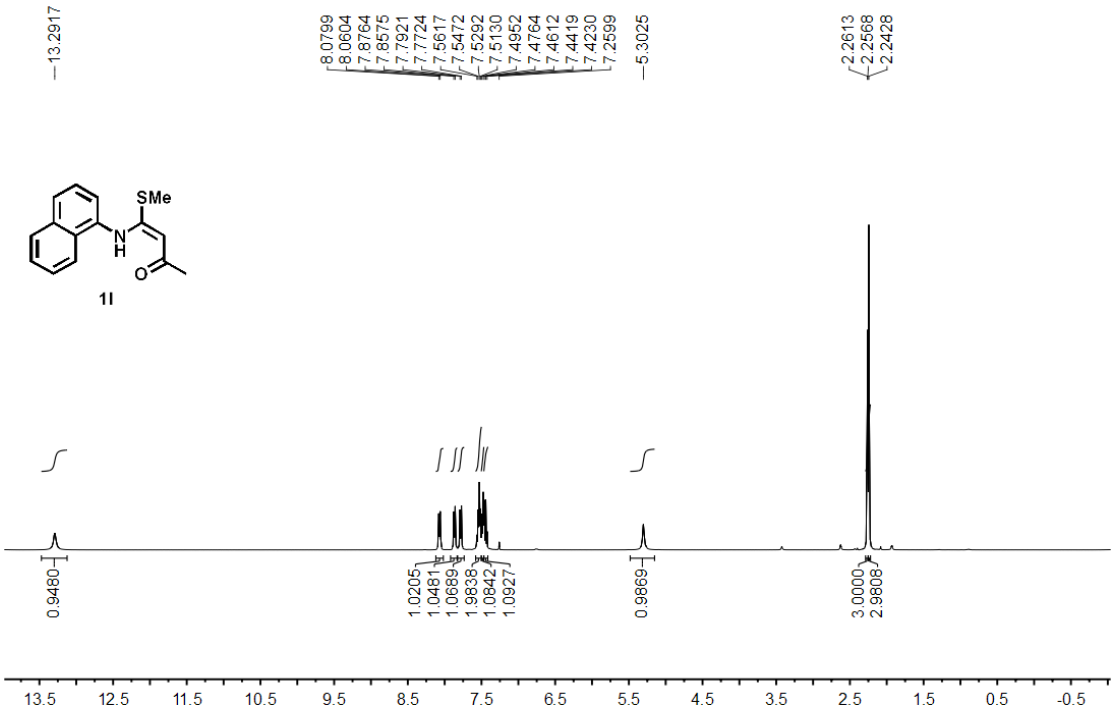
hf216
1H NMR (hf216 in CDCl3)



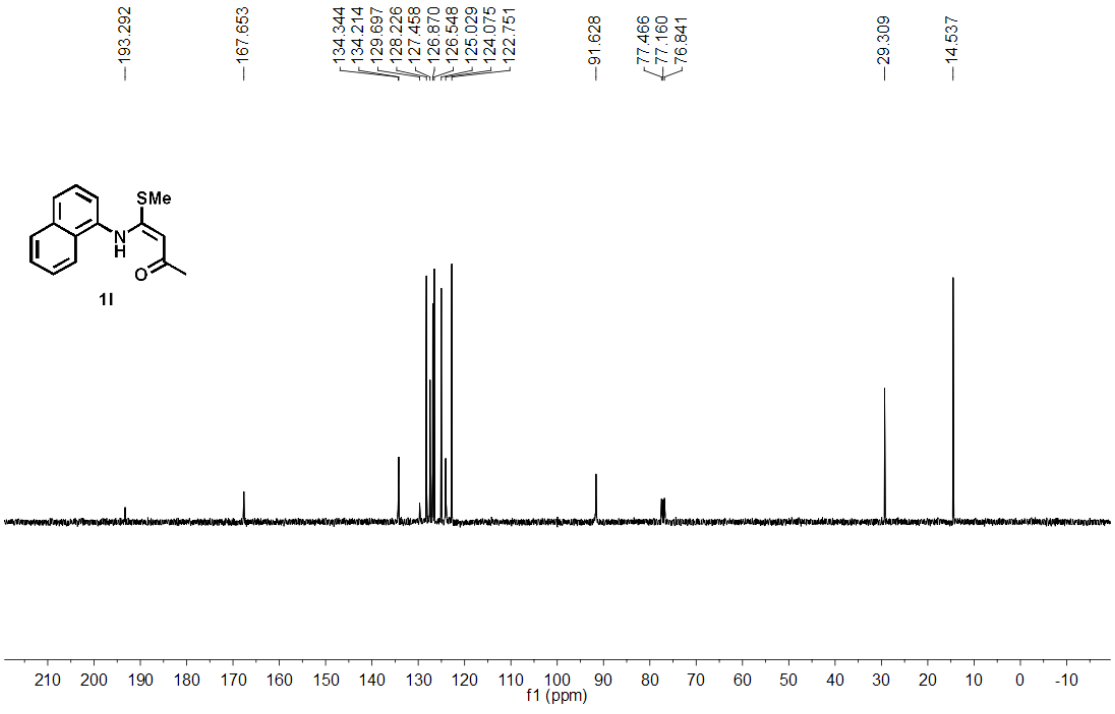
hf216
13C NMR (hf216 in CDCl3)



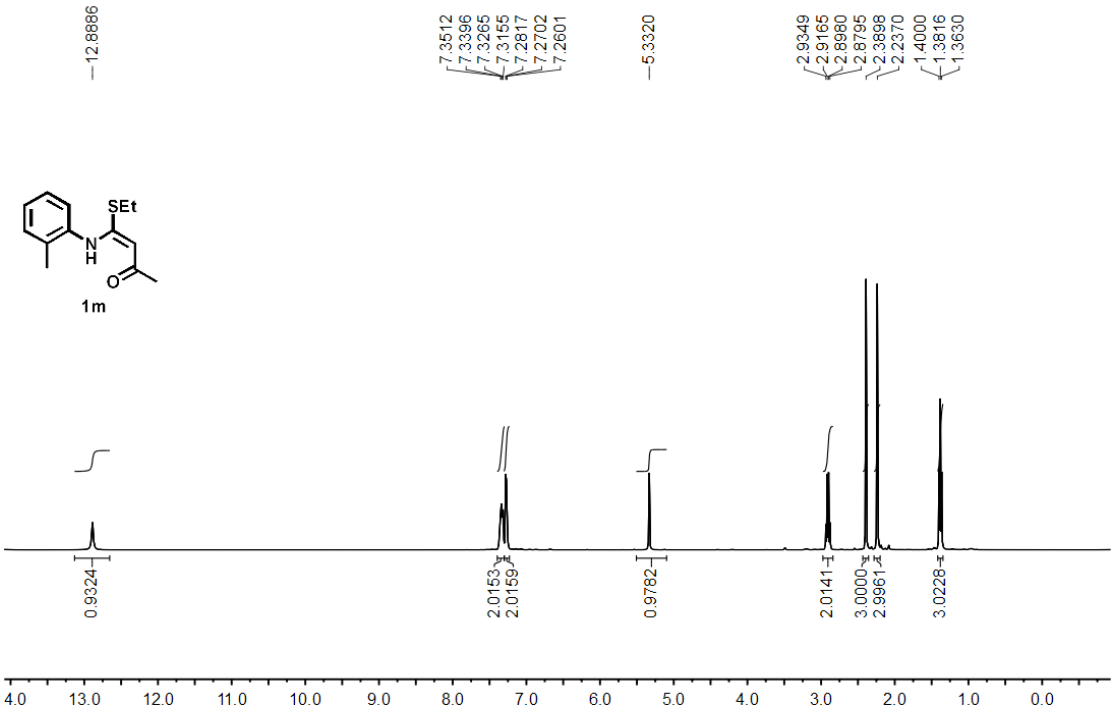
hf231
1H NMR (hf231 in CDCl3)



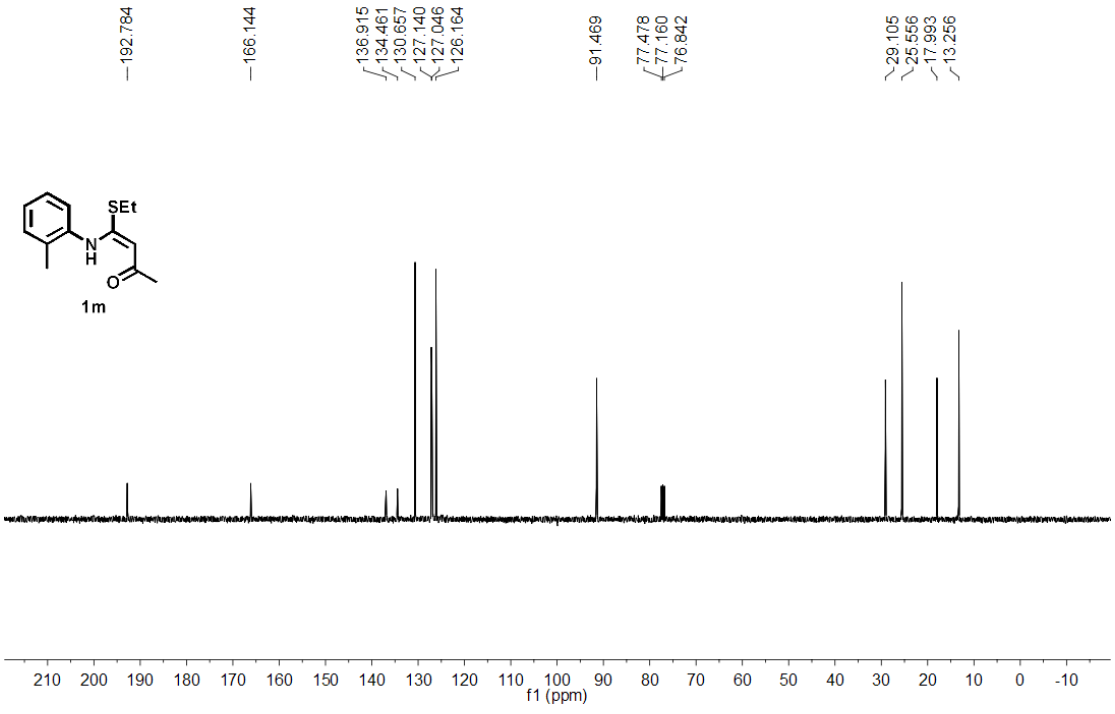
hf231
13C NMR (hf231 in CDCl3)



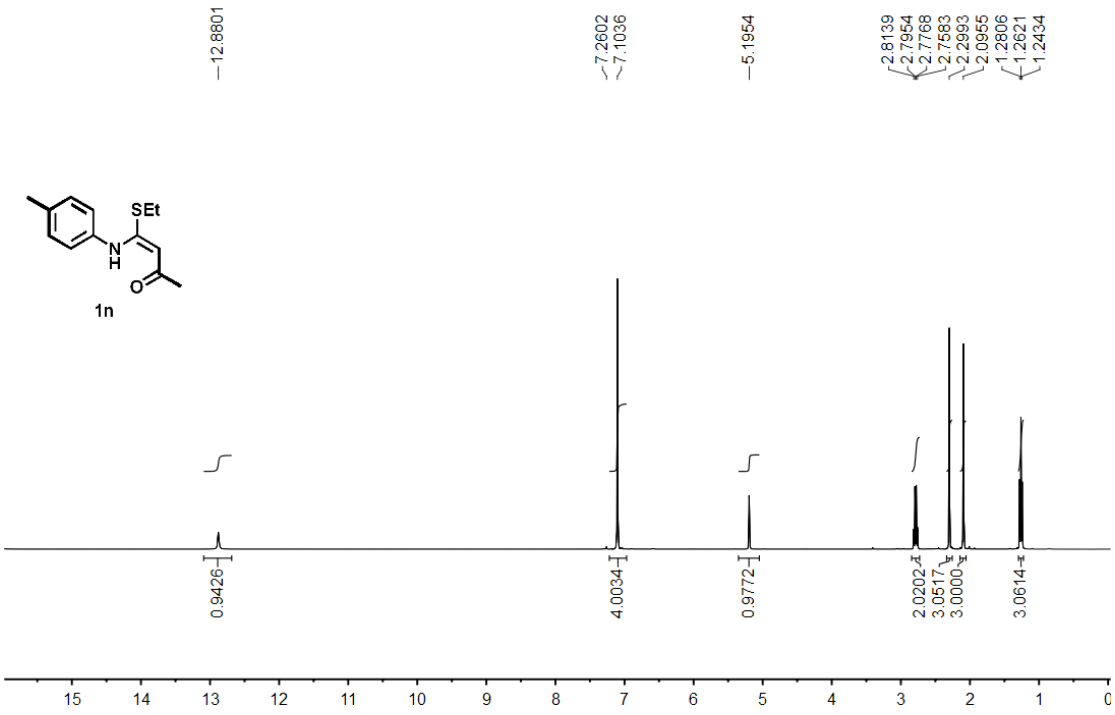
hf156
1H NMR (hf156 in CDCl3)



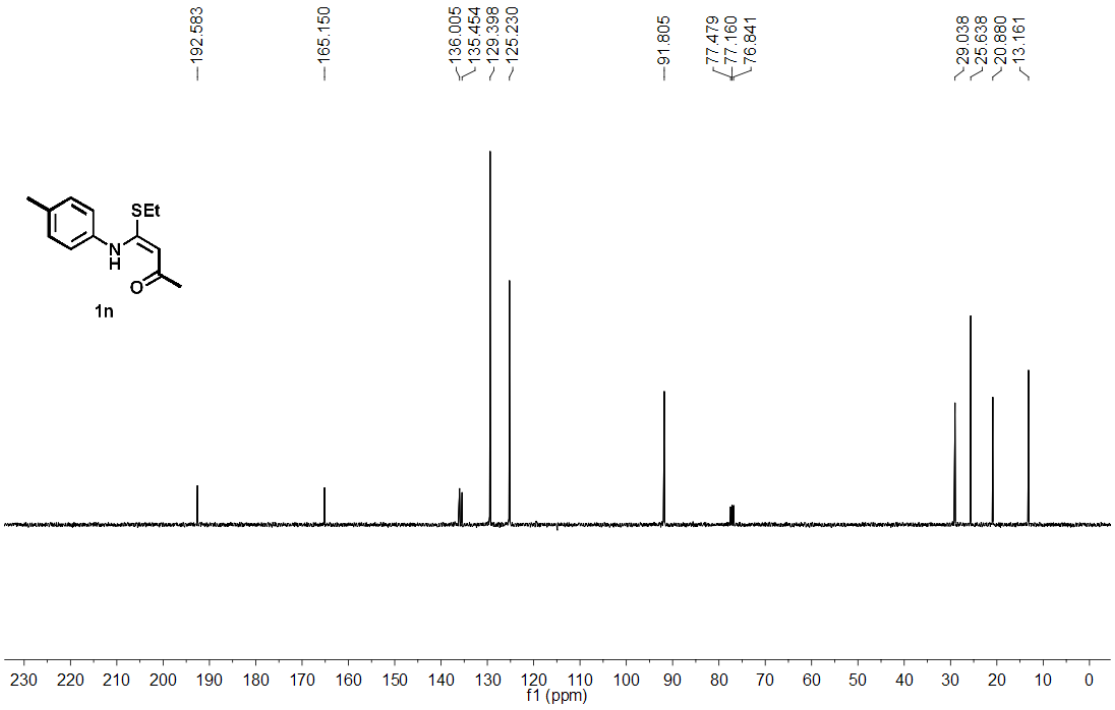
hf156
13C NMR (hf156 in CDCl3)



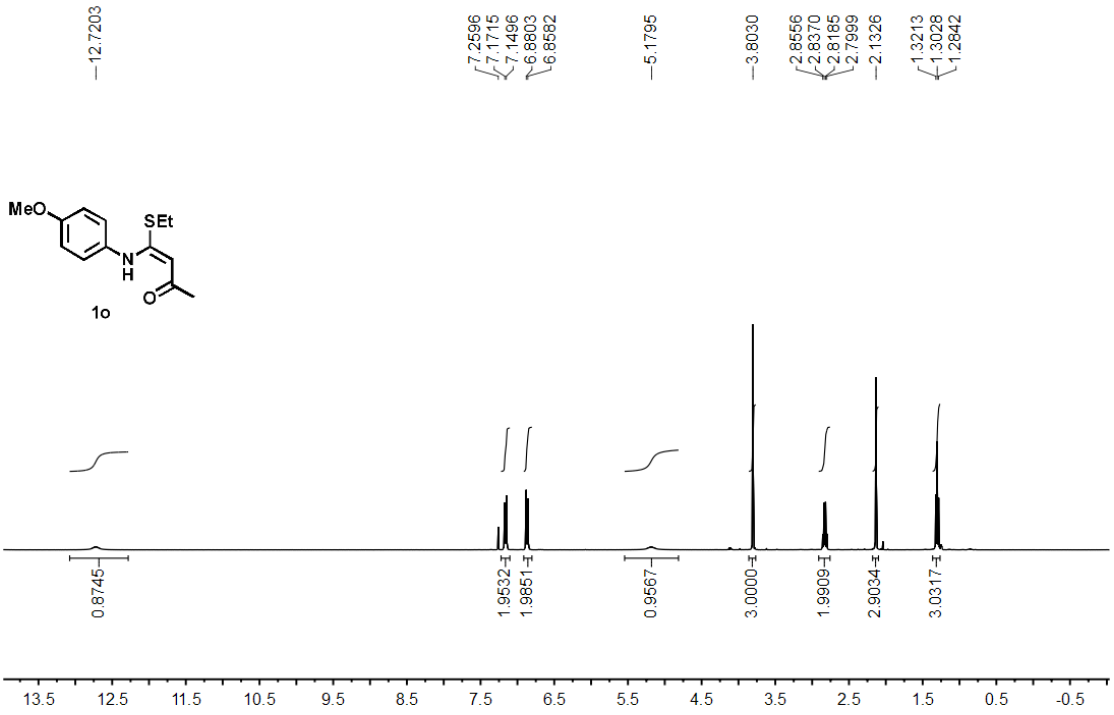
hf302
1H NMR hf302 in CDCl3



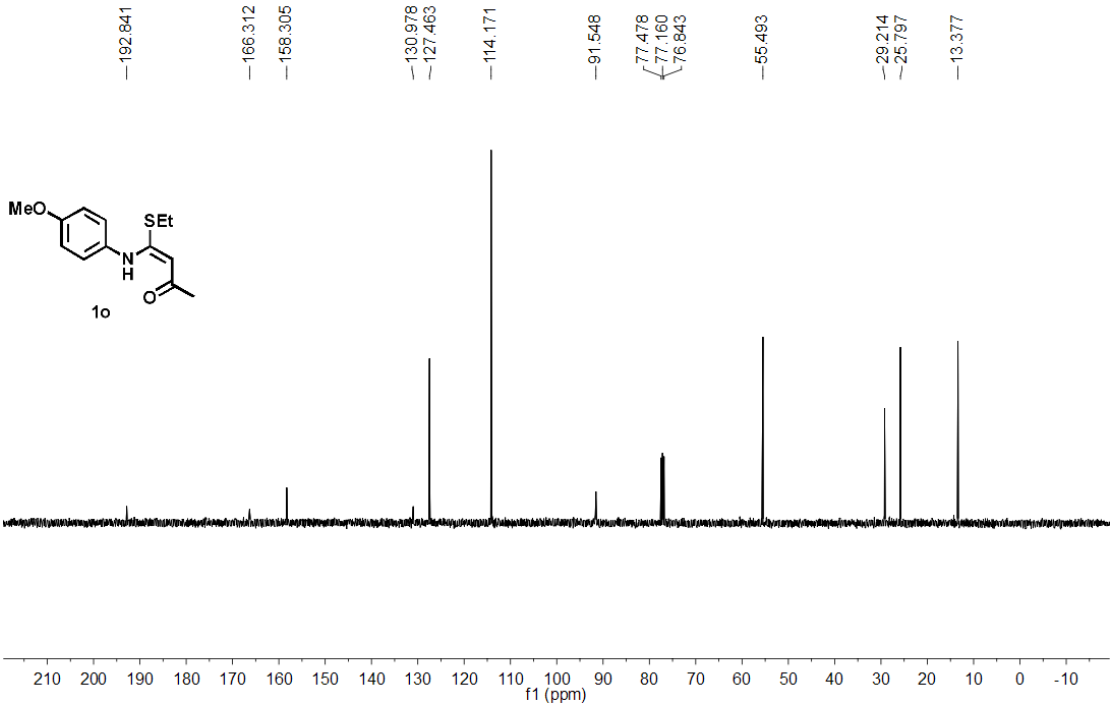
hf302
13C NMR hf302 CDCl3



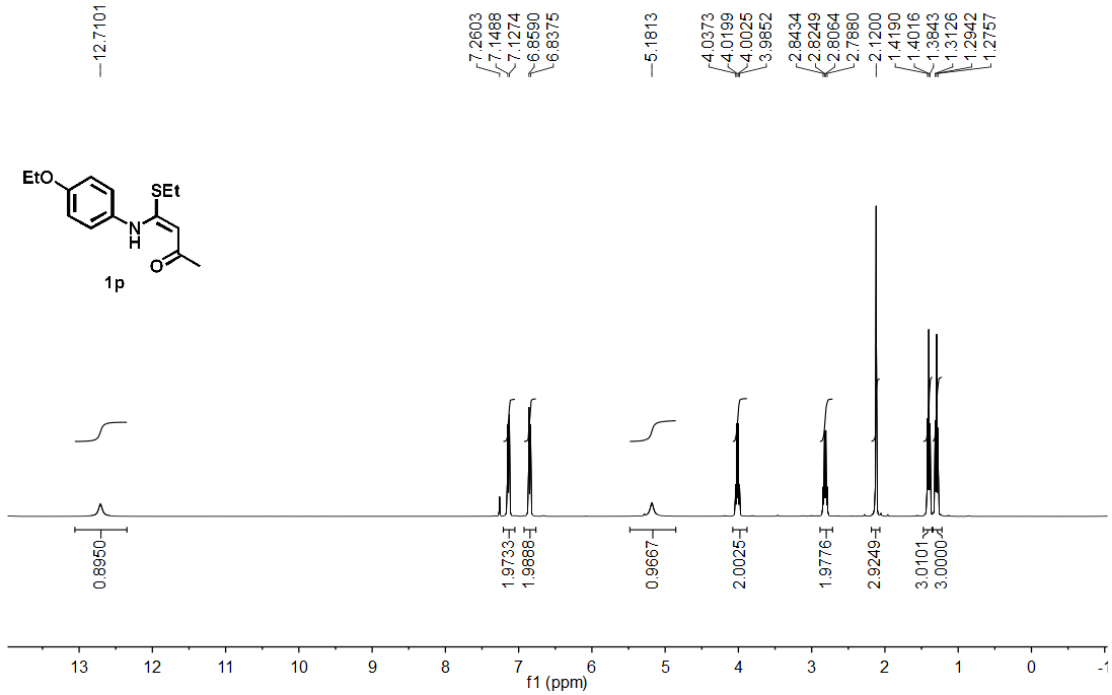
hf163-1
1H NMR (hf163 in CDCl3)



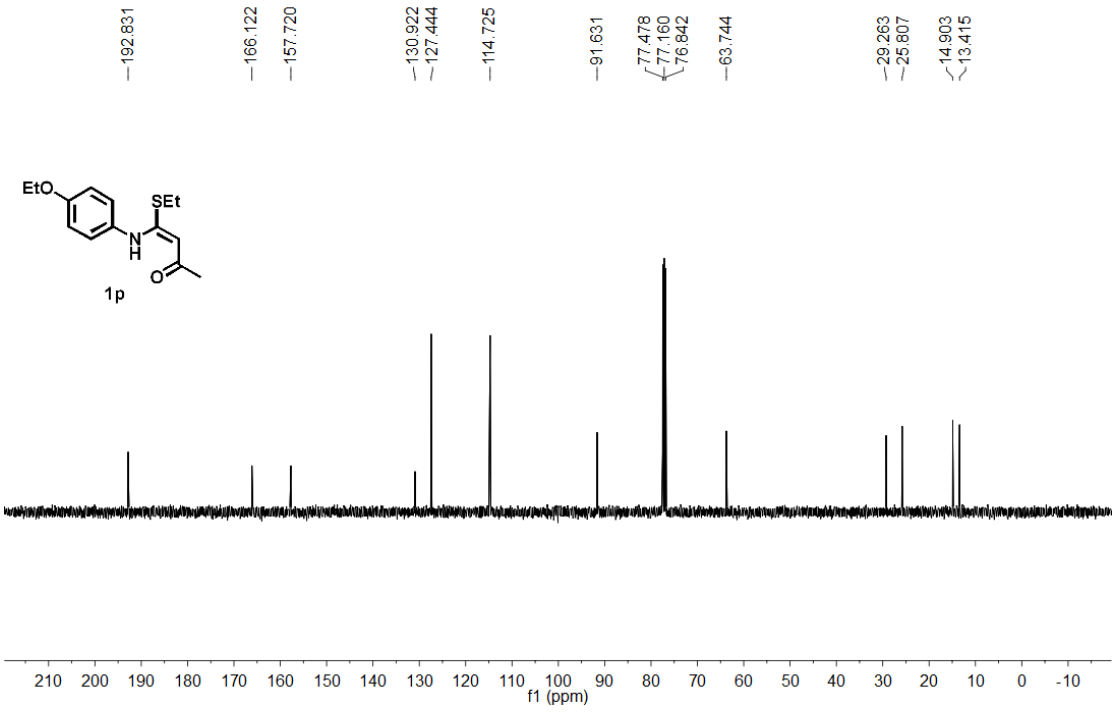
hf163-1
13C NMR (hf163 in CDCl3)



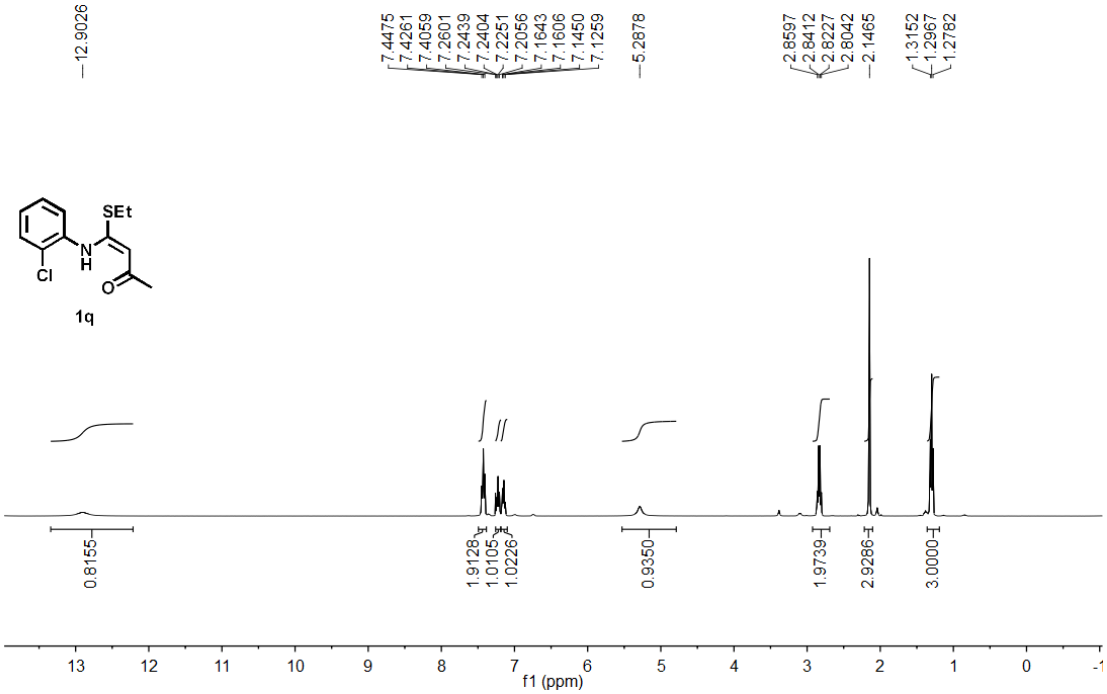
HF134
1H NMR IN CDC13



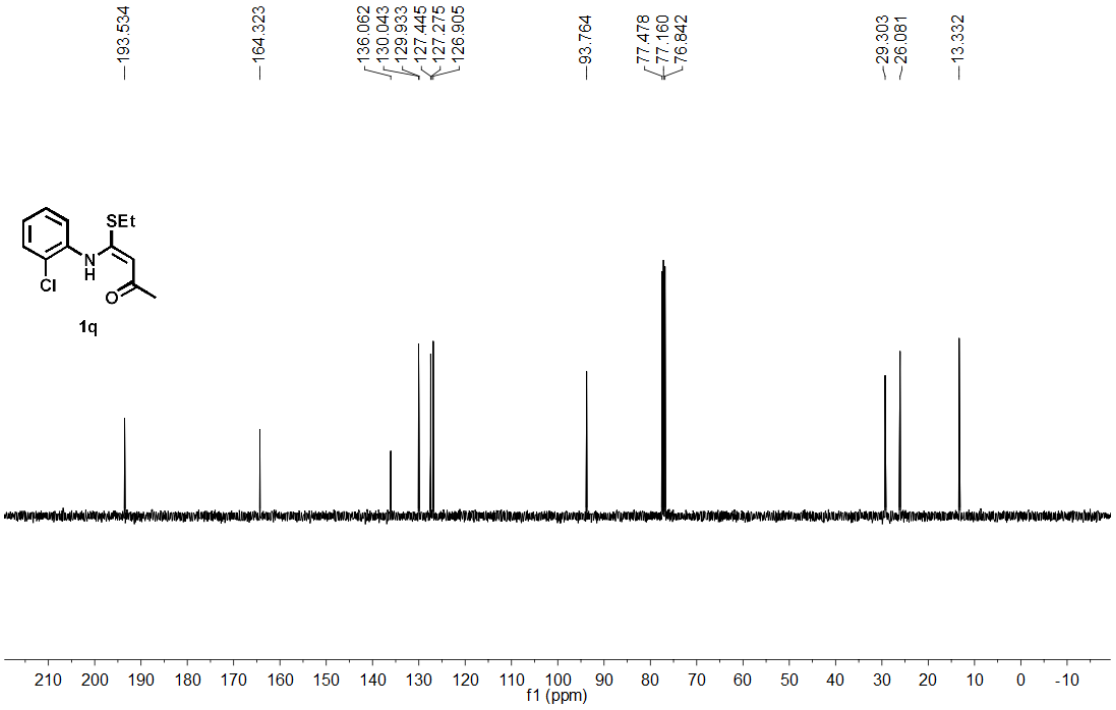
HF134
13C NMR IN CDC13



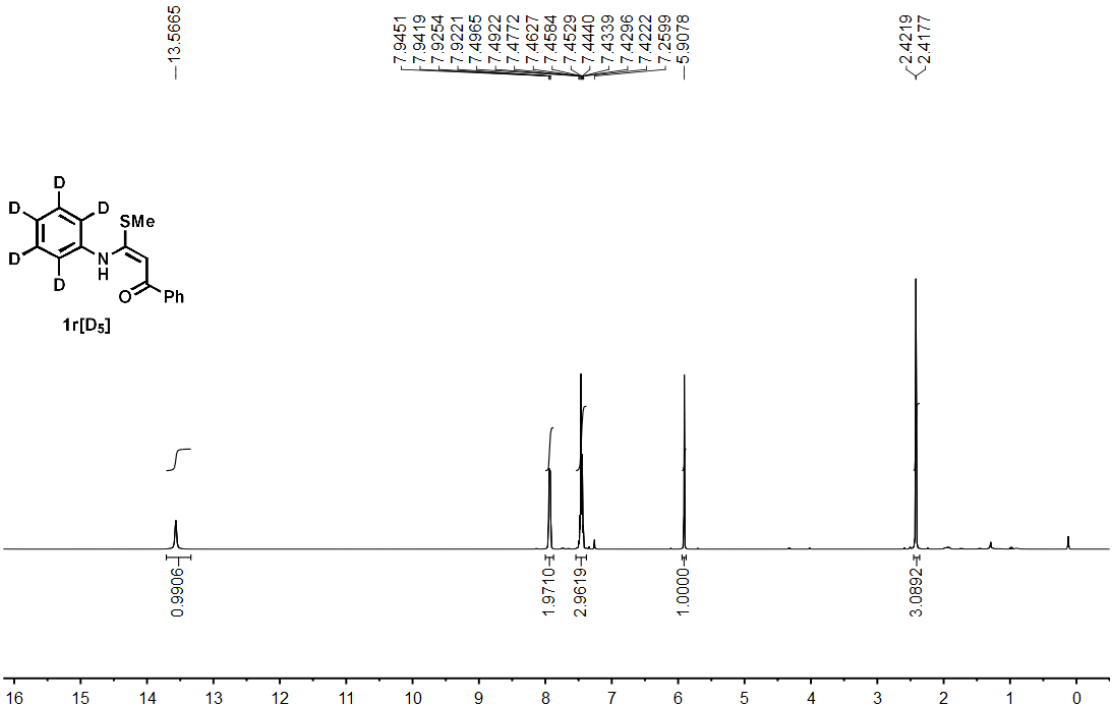
HF158
1H NMR IN CDCl3



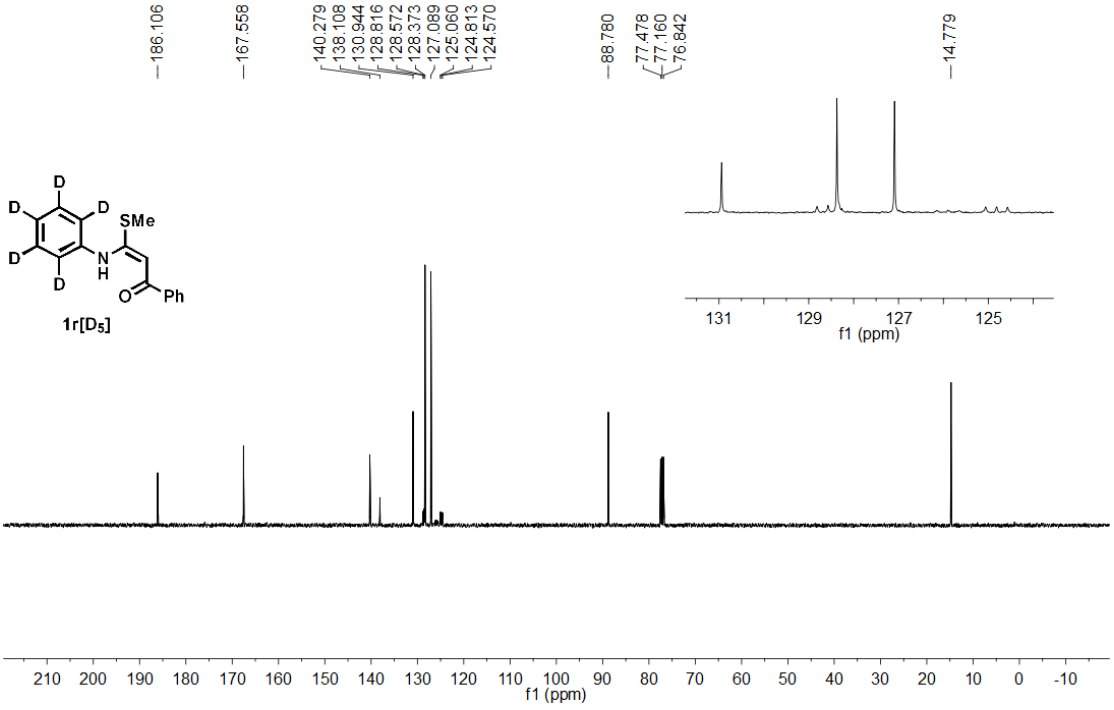
HF158
13C NMR IN CDCl3



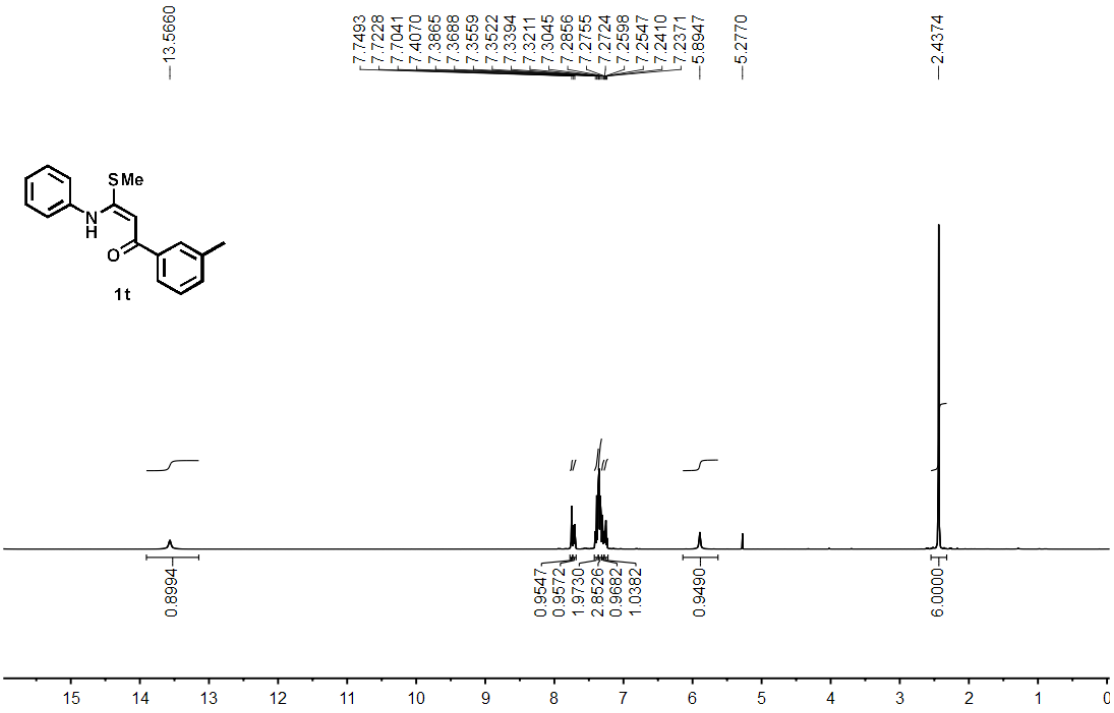
HF358
1H NMR IN CDCl3



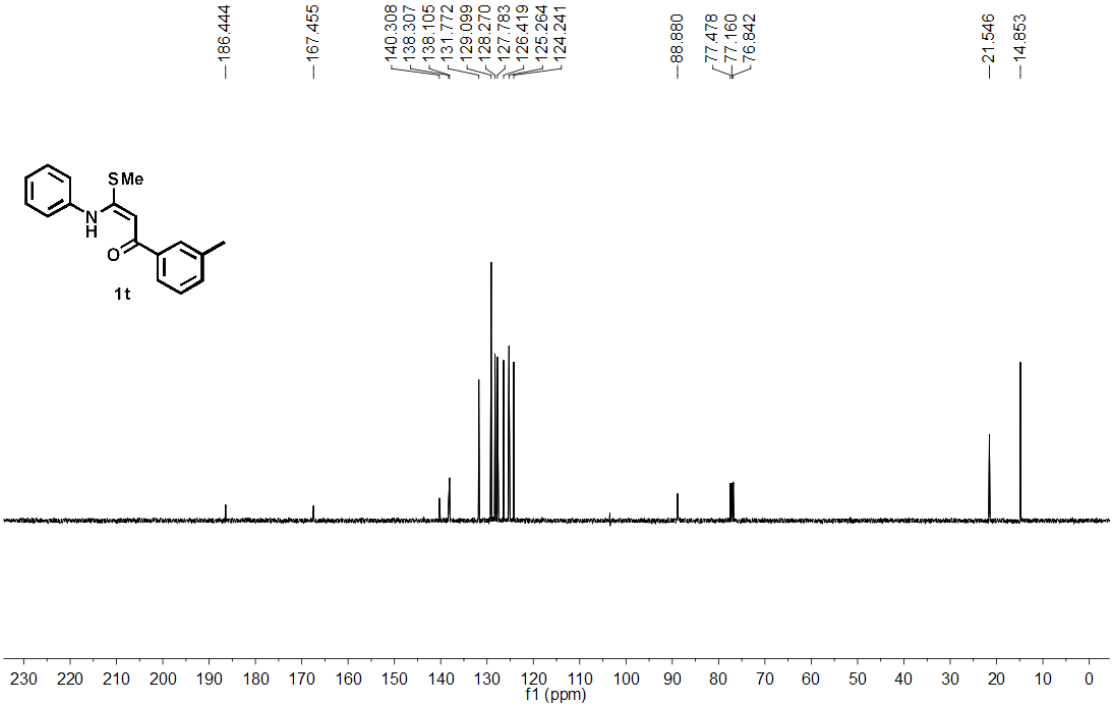
HF358
13C NMR IN CDCl3



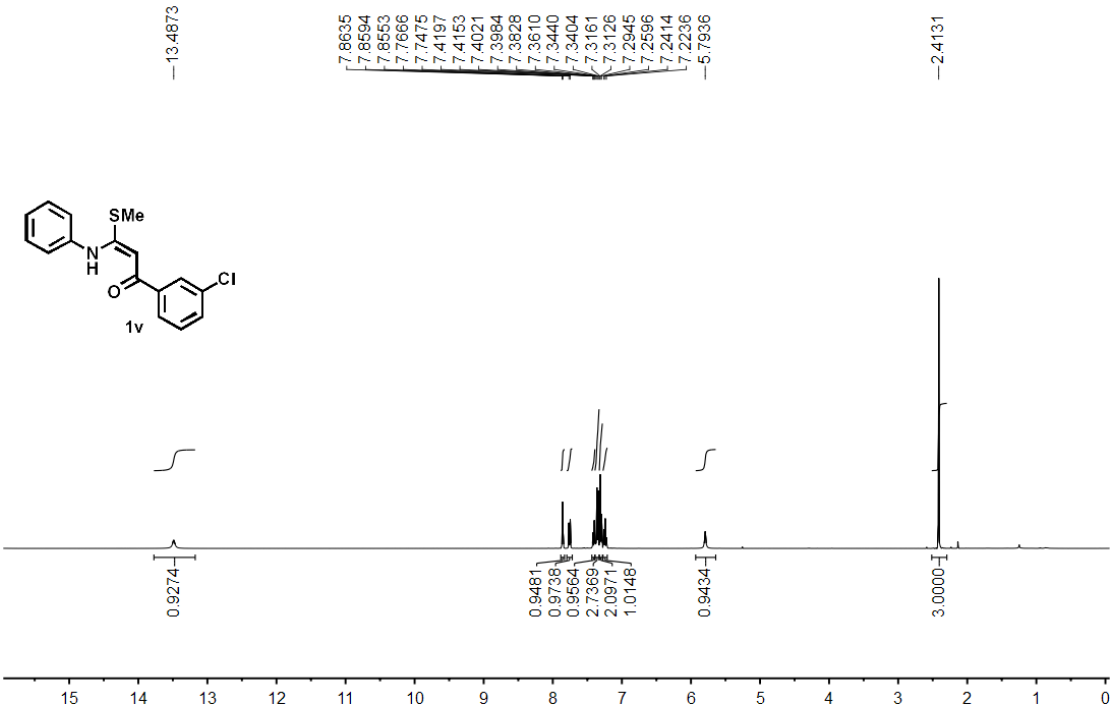
hf258
1H NMR hf258 in CDCl3



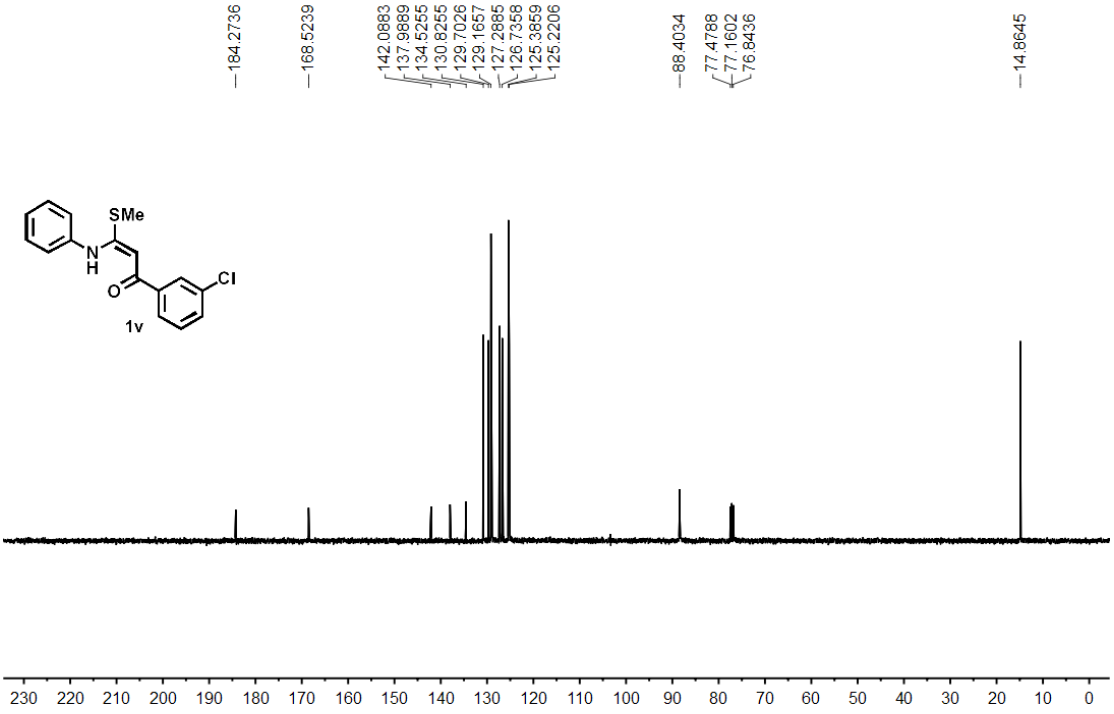
hf258
13C NMR hf258 CDCl3



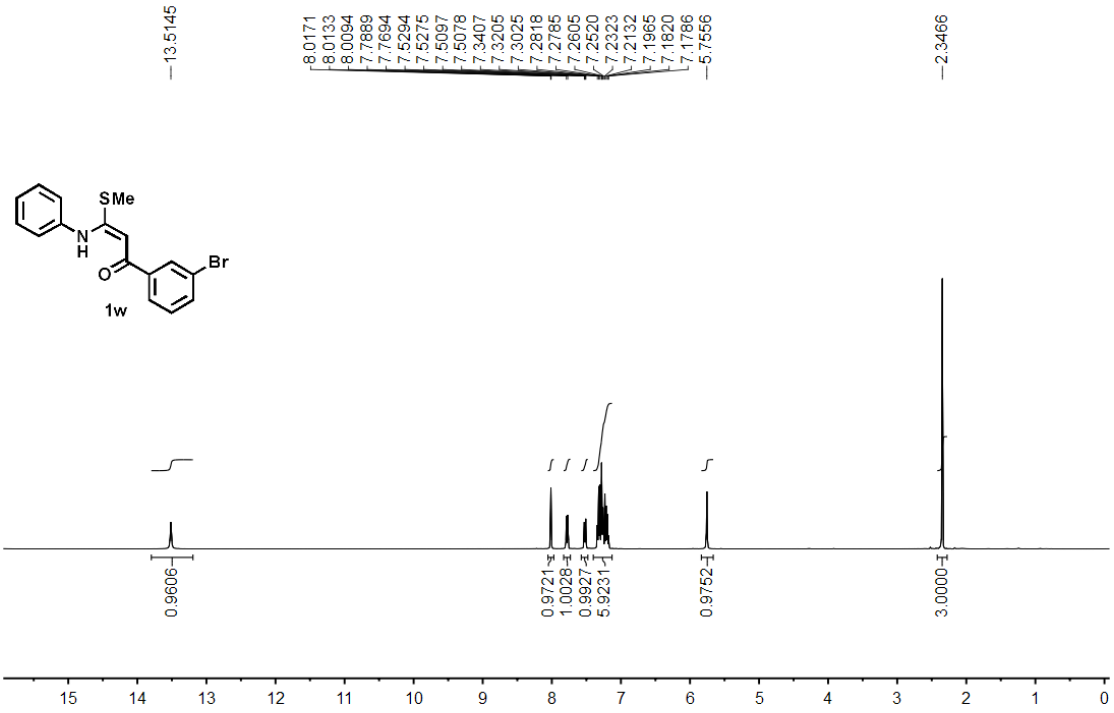
hf262
1H NMR hf262 in CDCl3



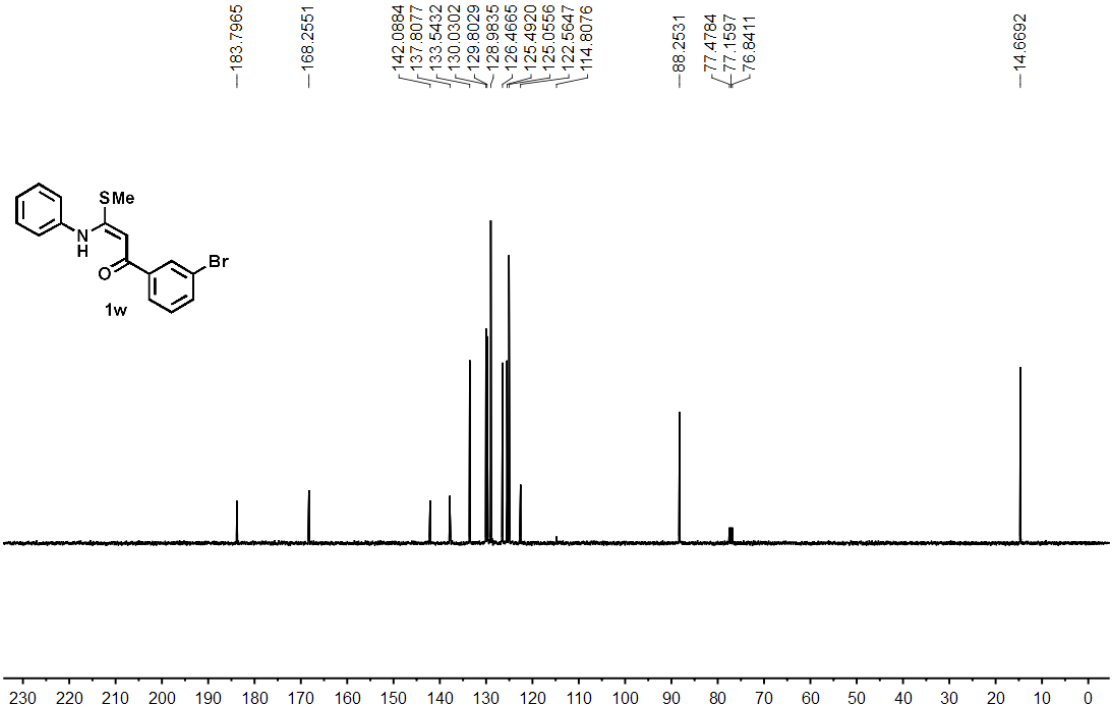
hf262
13C NMR hf262 CDCl3



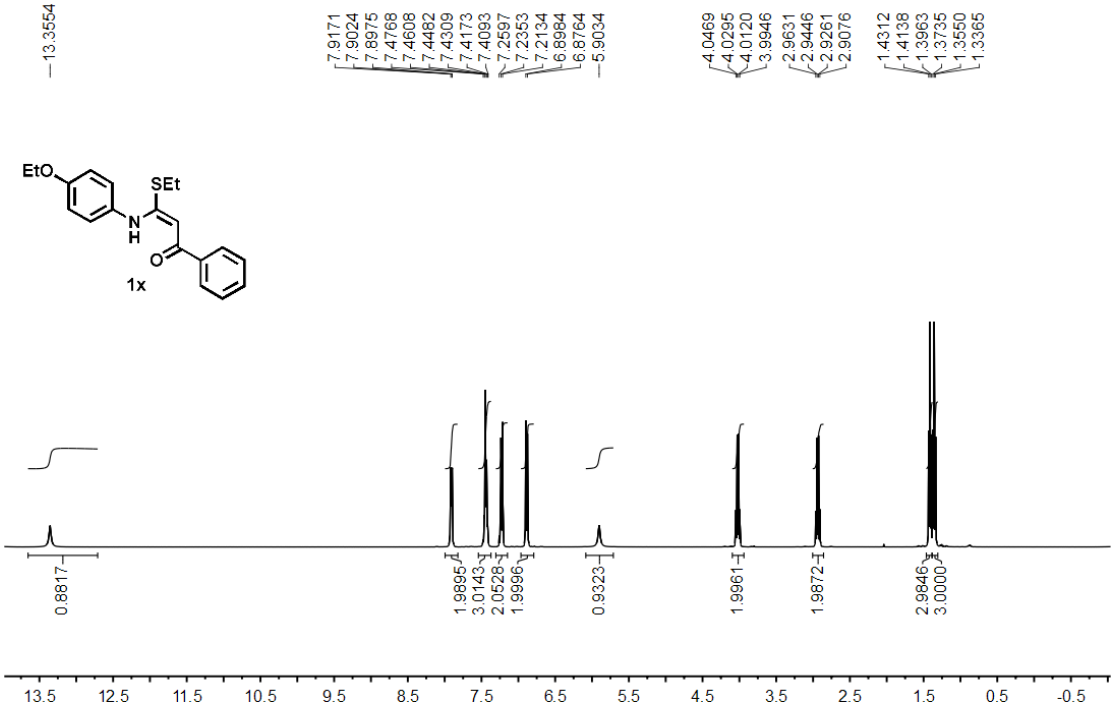
hf294-2
1H NMR hf294-2 in CDCl3



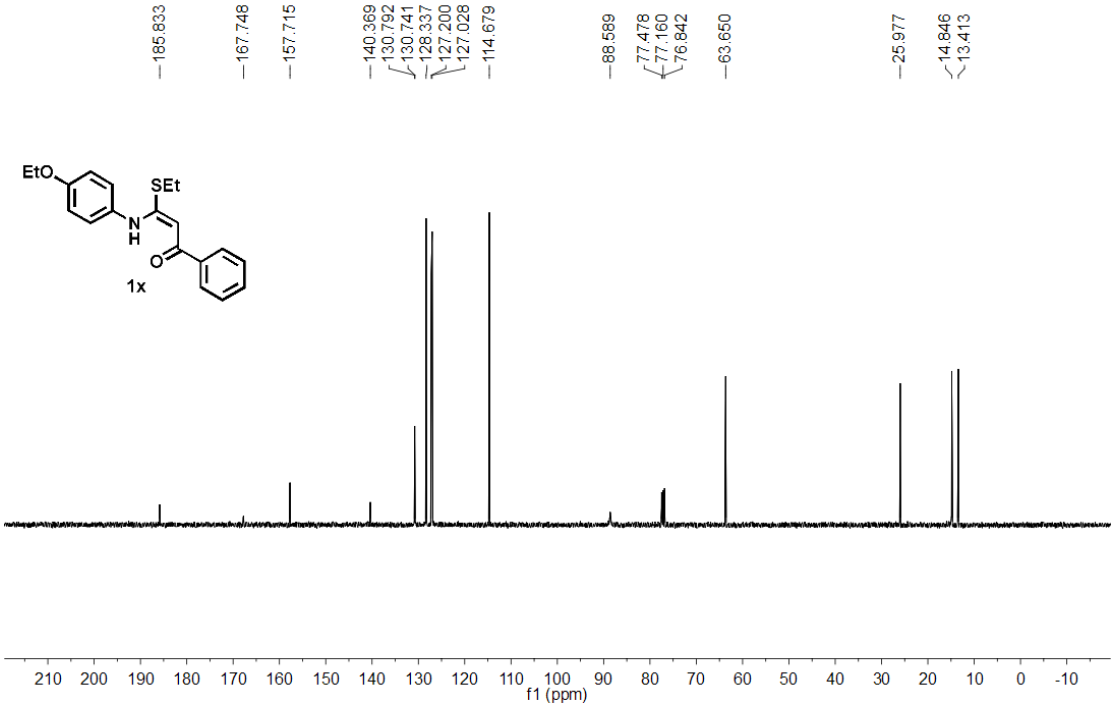
hf294-2
13C NMR hf294-2 CDCl3



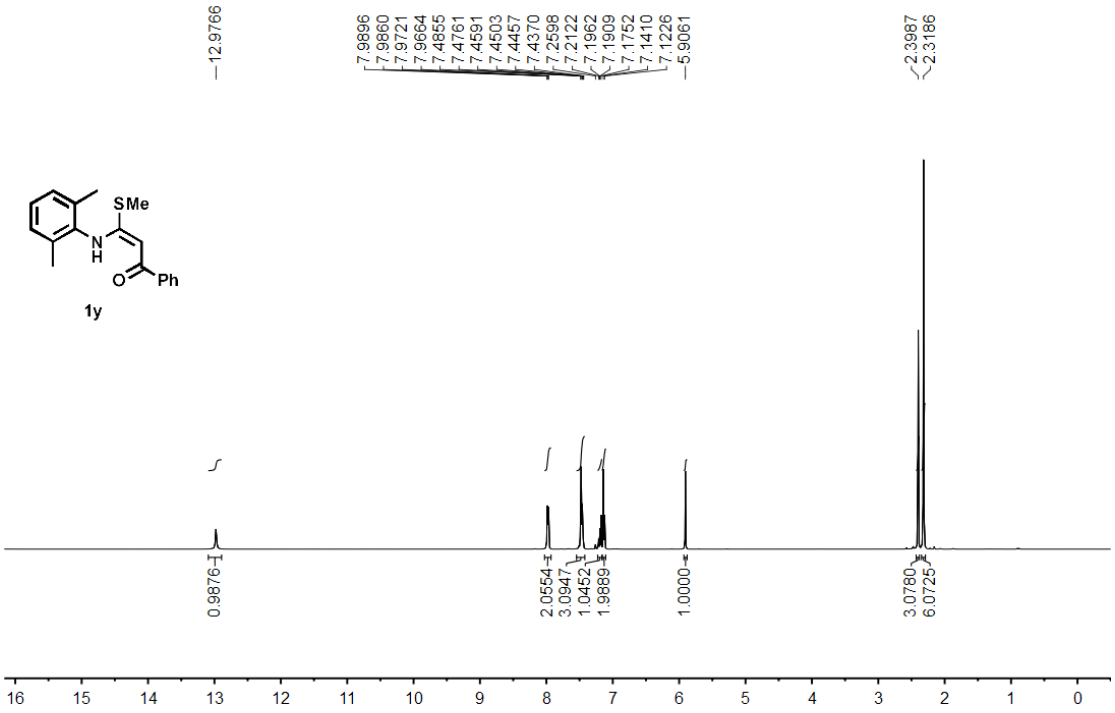
hf141
1H NMR (hf141in CDCl3)



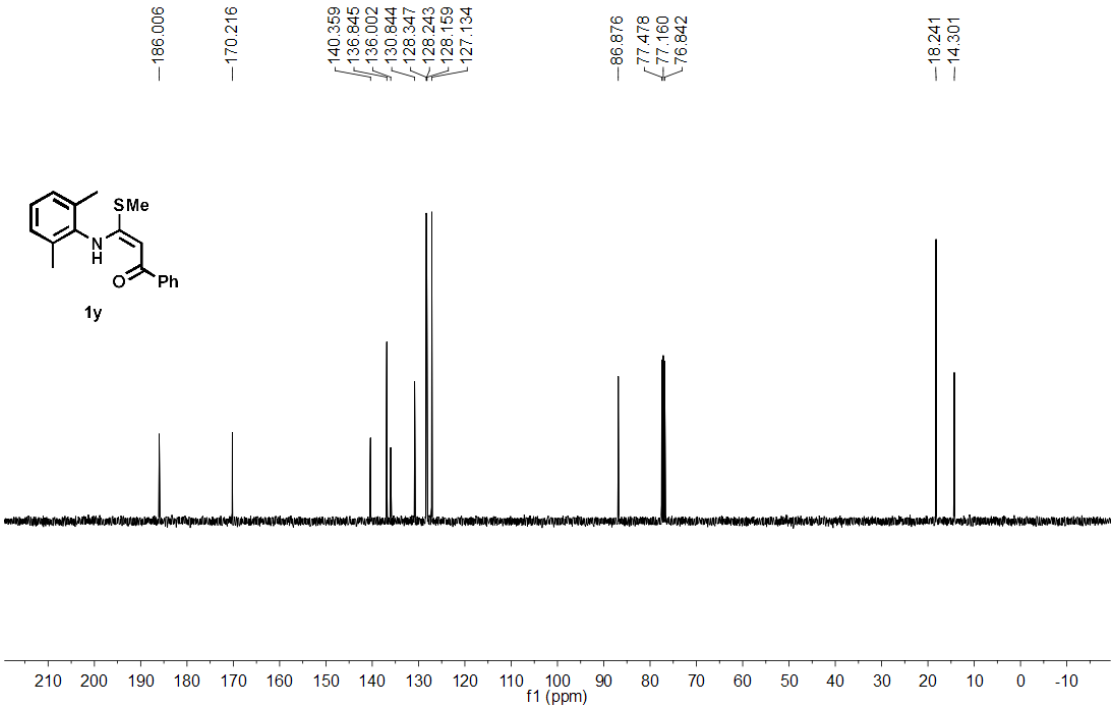
hf141
13C NMR (hf141 in CDCl3)



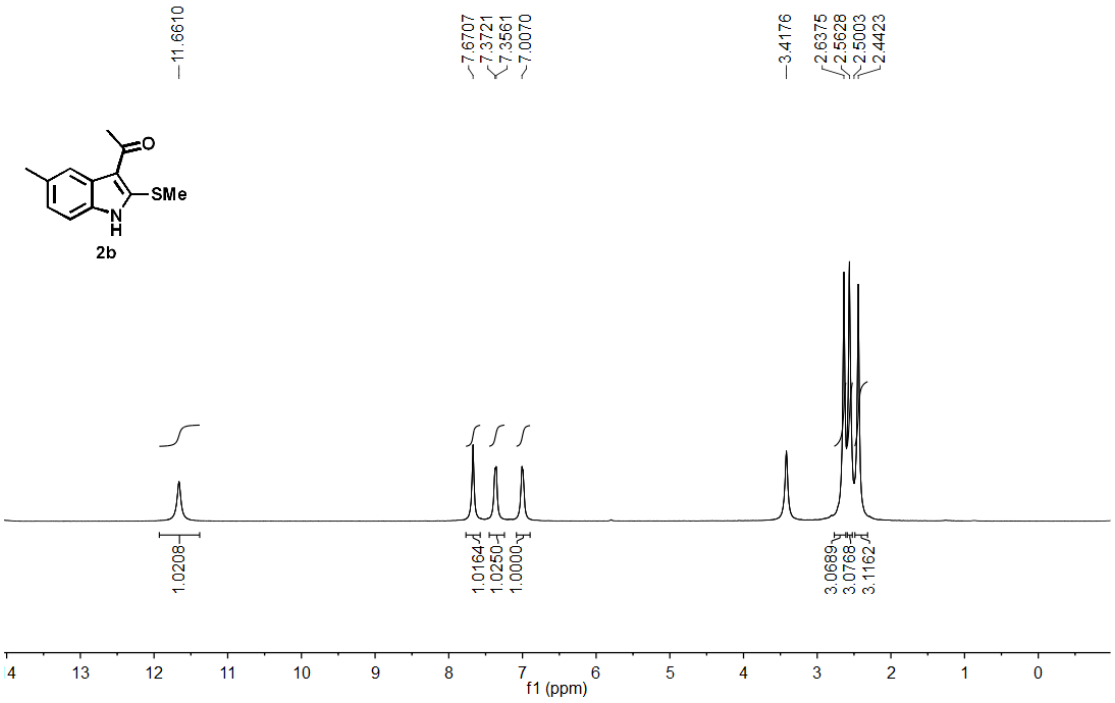
HF546
1H NMR IN CDCl3



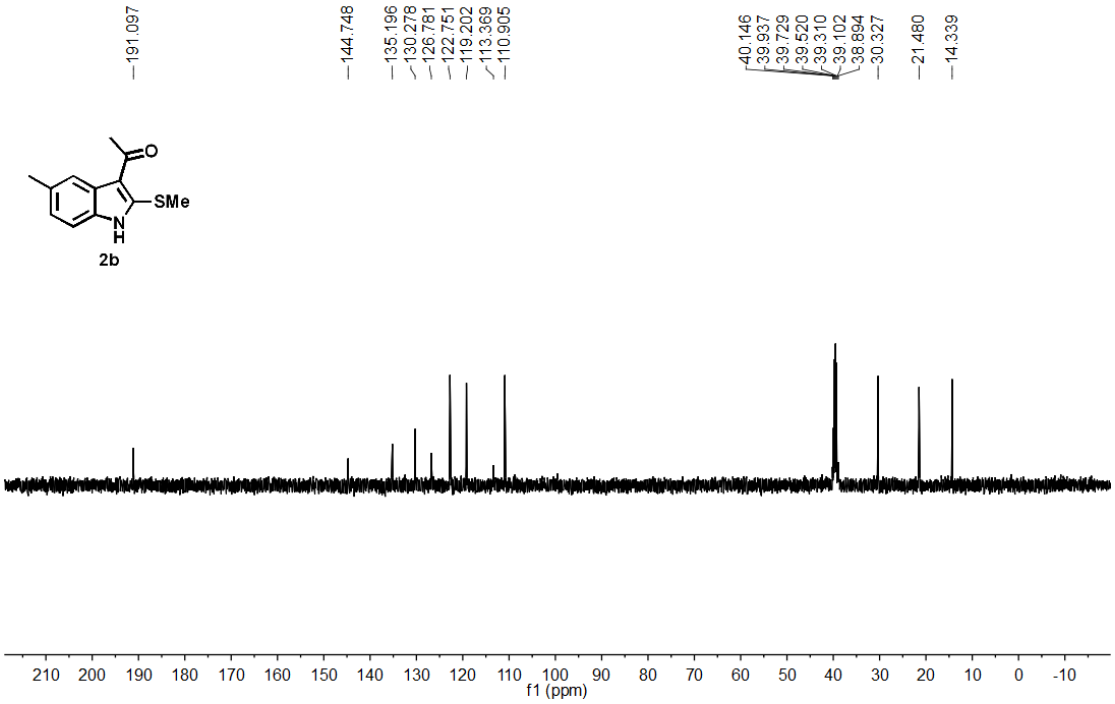
HF546
13C NMR IN CDCl3



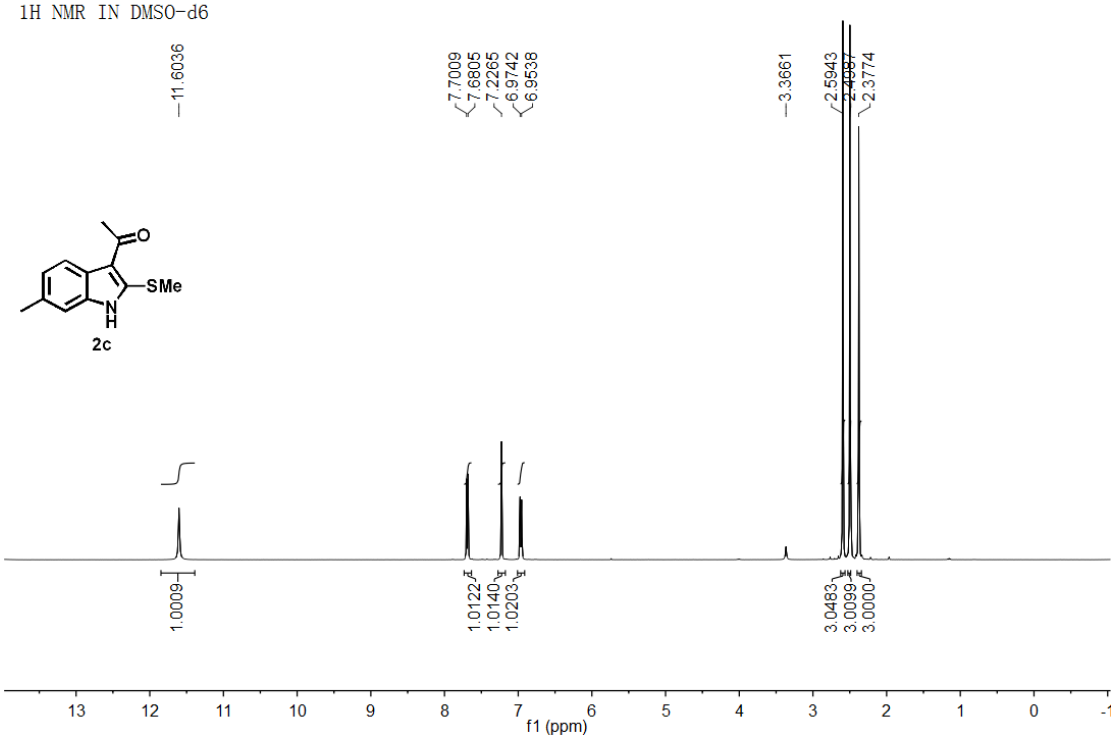
HF199
1H NMR IN DMSO-d6



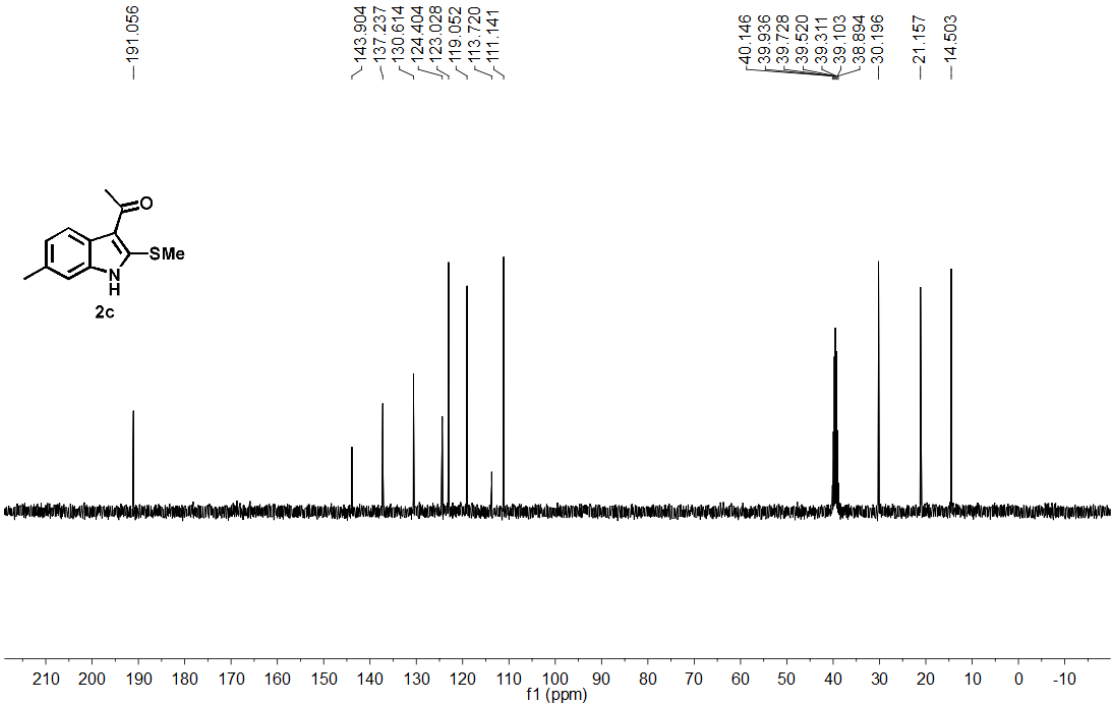
HF199
13C NMR IN DMSO-d6



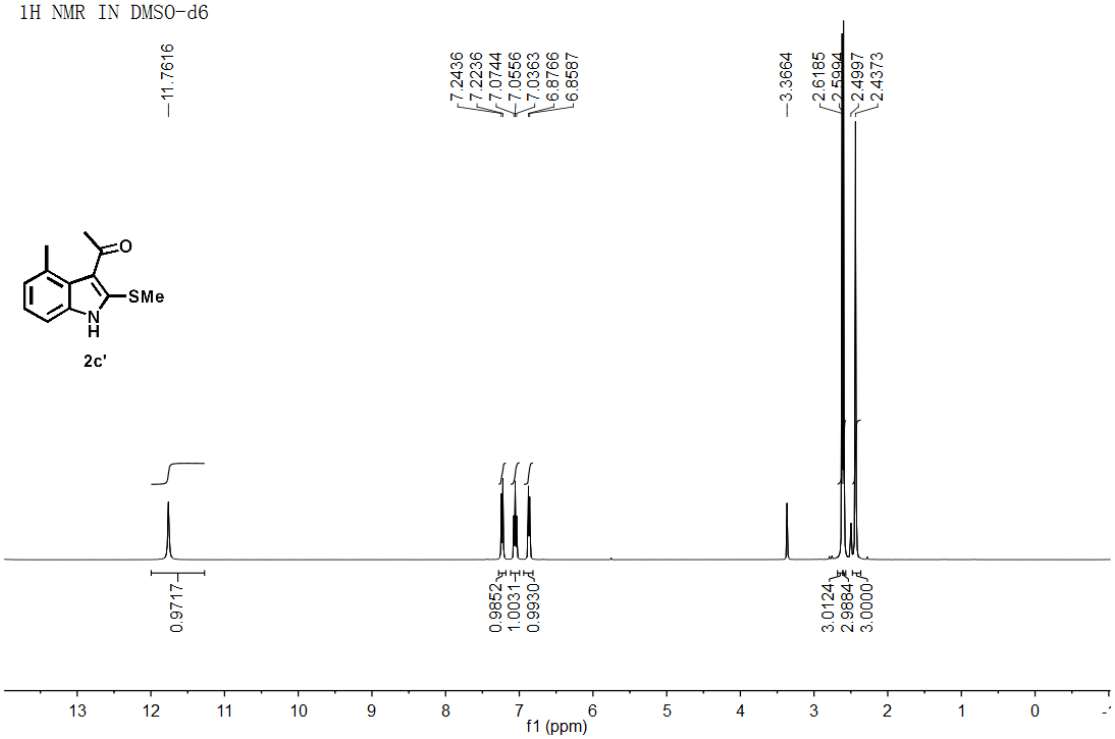
HF223
1H NMR IN DMSO-d6



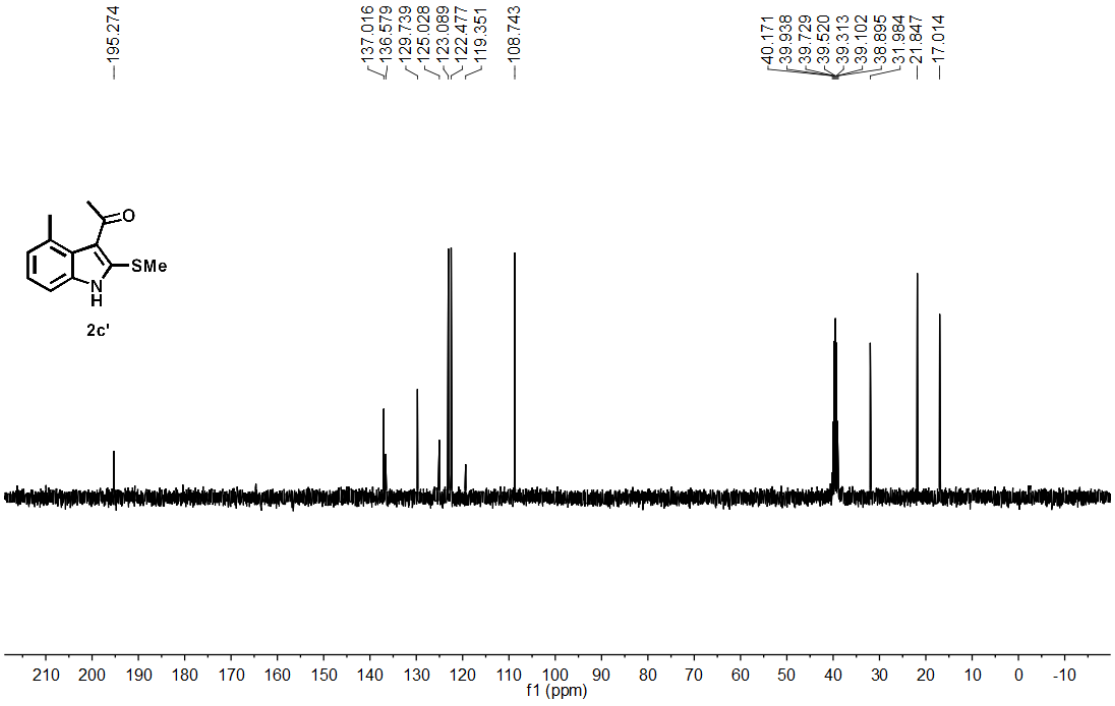
HF223
13C NMR IN DMSO-d6



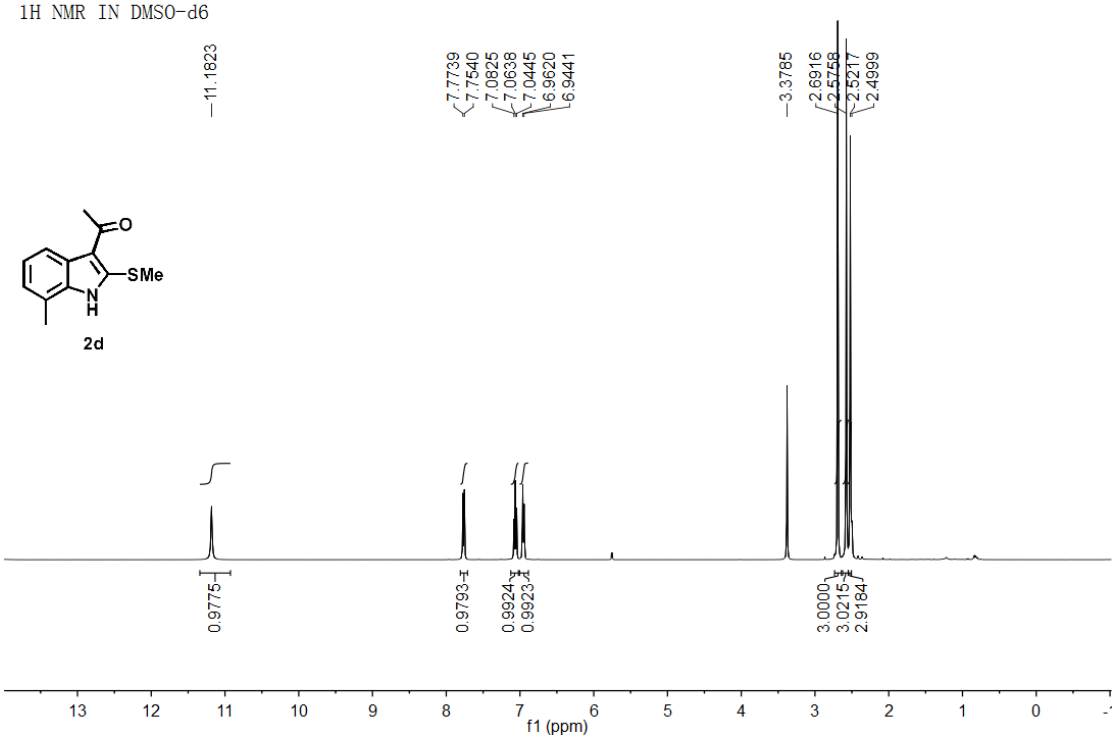
HF223-1
1H NMR IN DMSO-d6



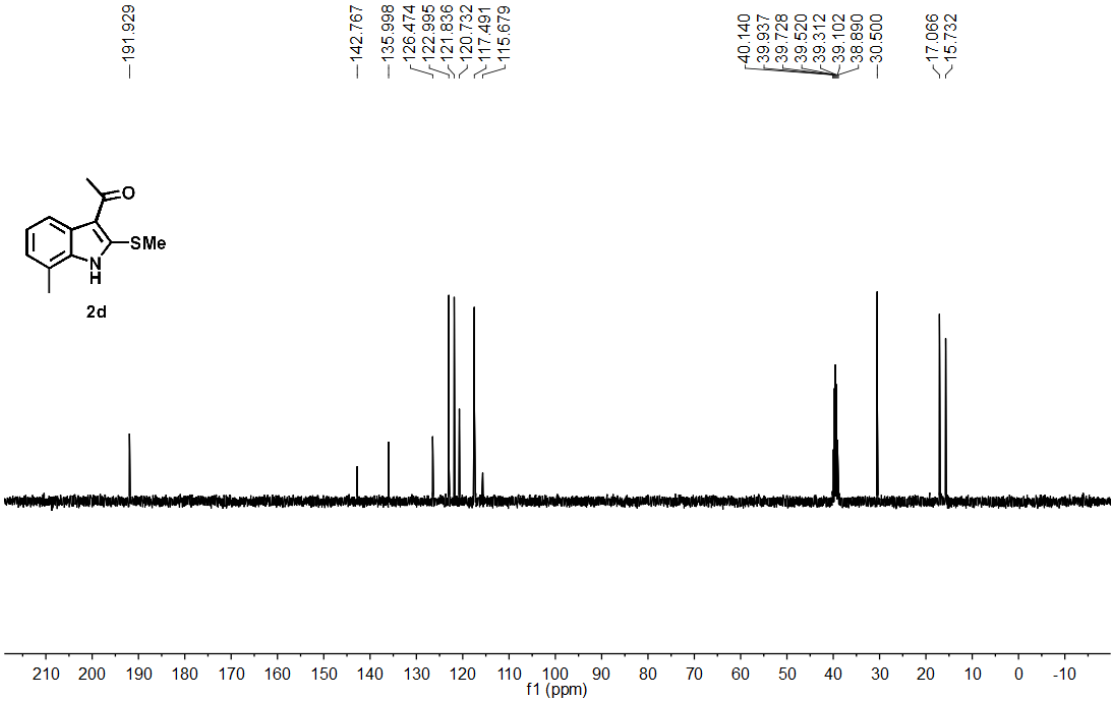
HF223-1
13C NMR IN DMSO-d6



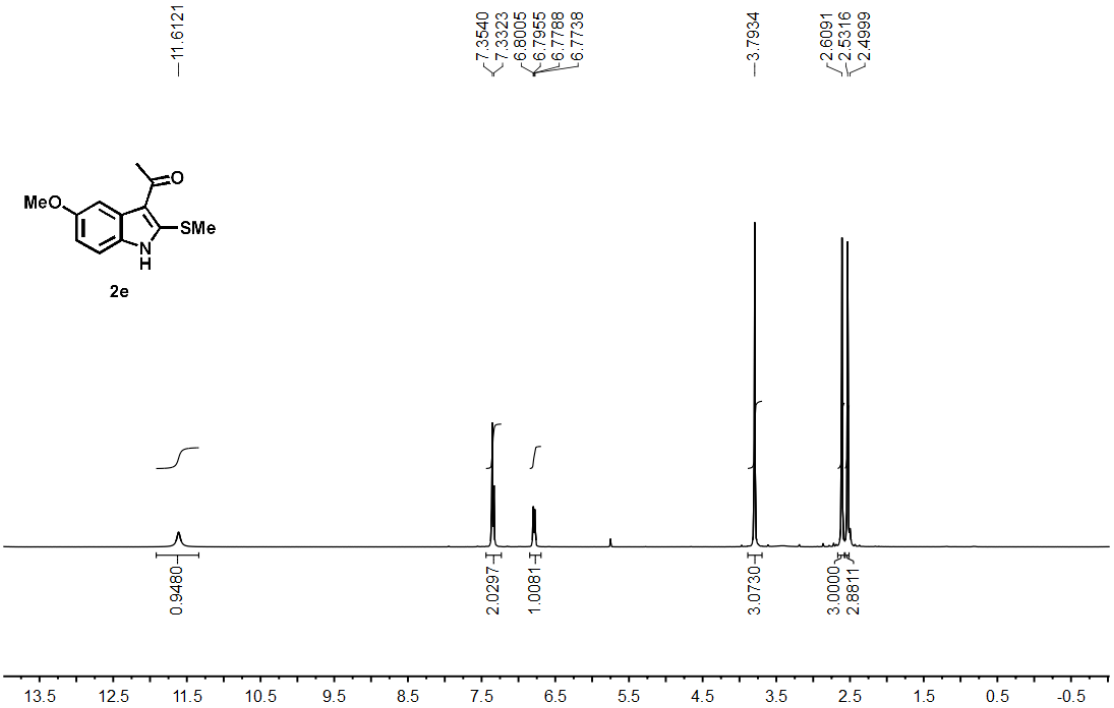
HF198
1H NMR IN DMSO-d6



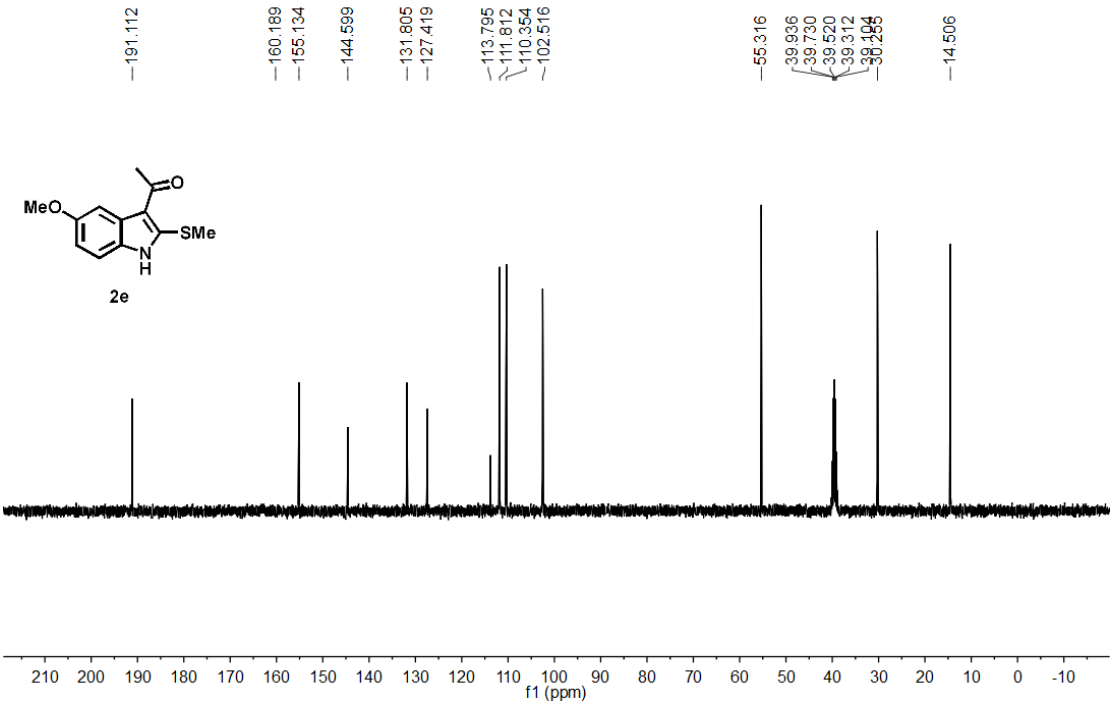
HF198
13C NMR IN DMSO-d6



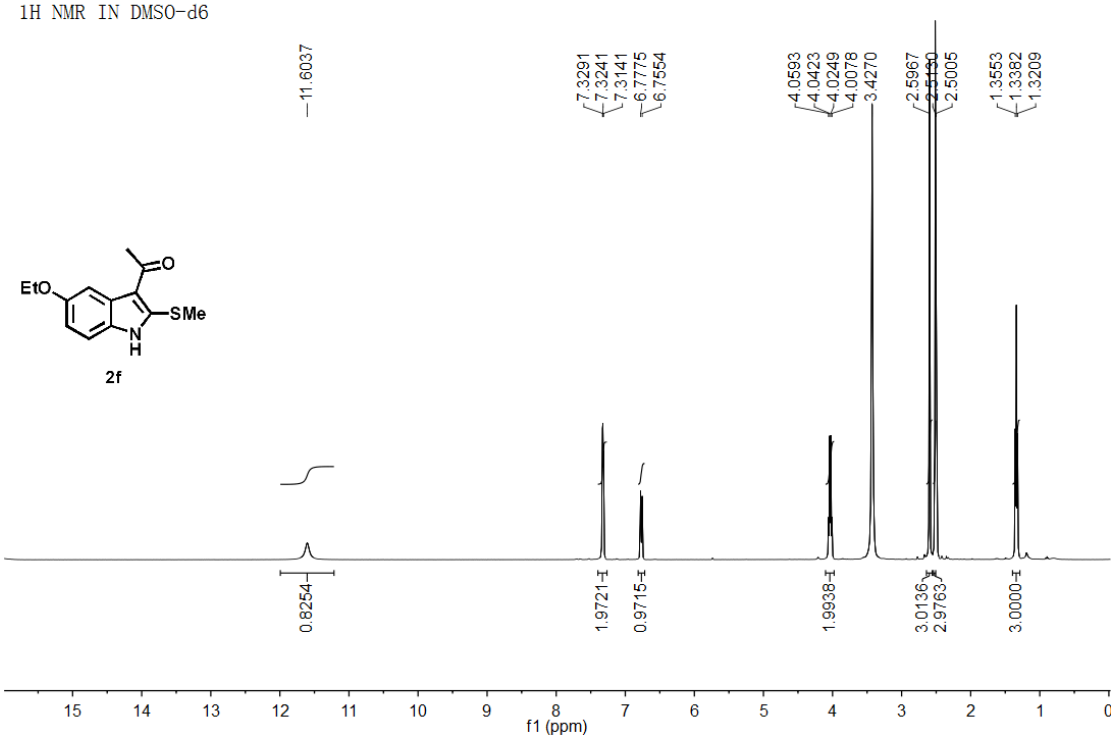
HF222
1H NMR IN DMSO-d6



HF222
13C NMR IN DMSO-d6

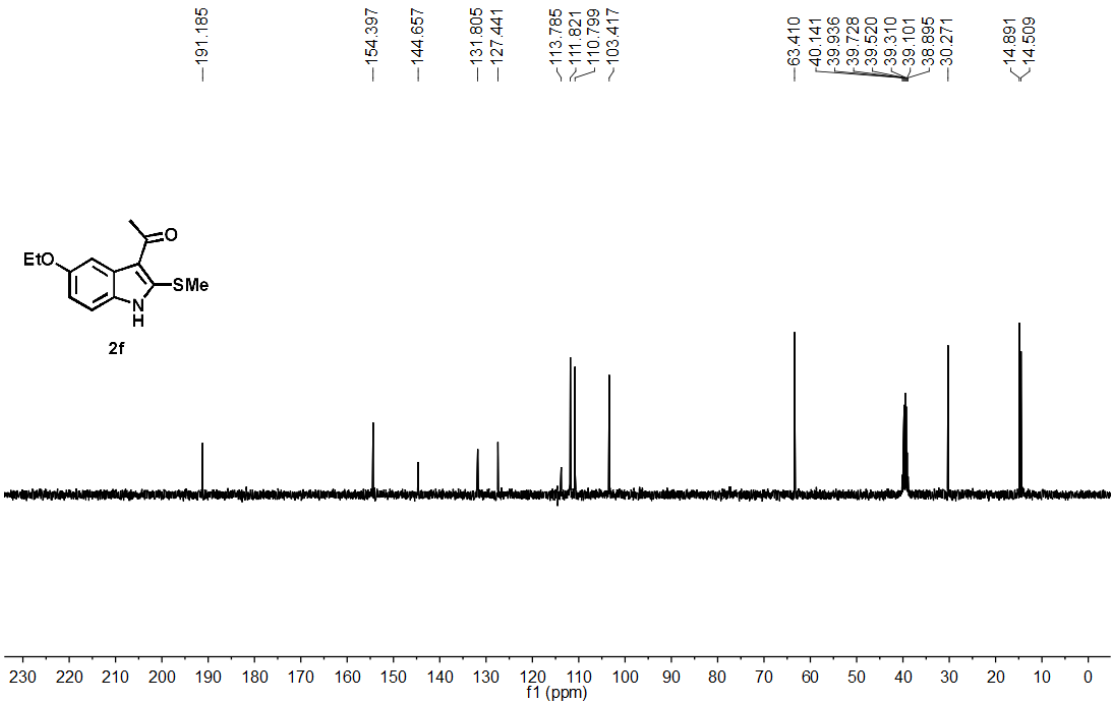


HF221
1H NMR IN DMSO-d6



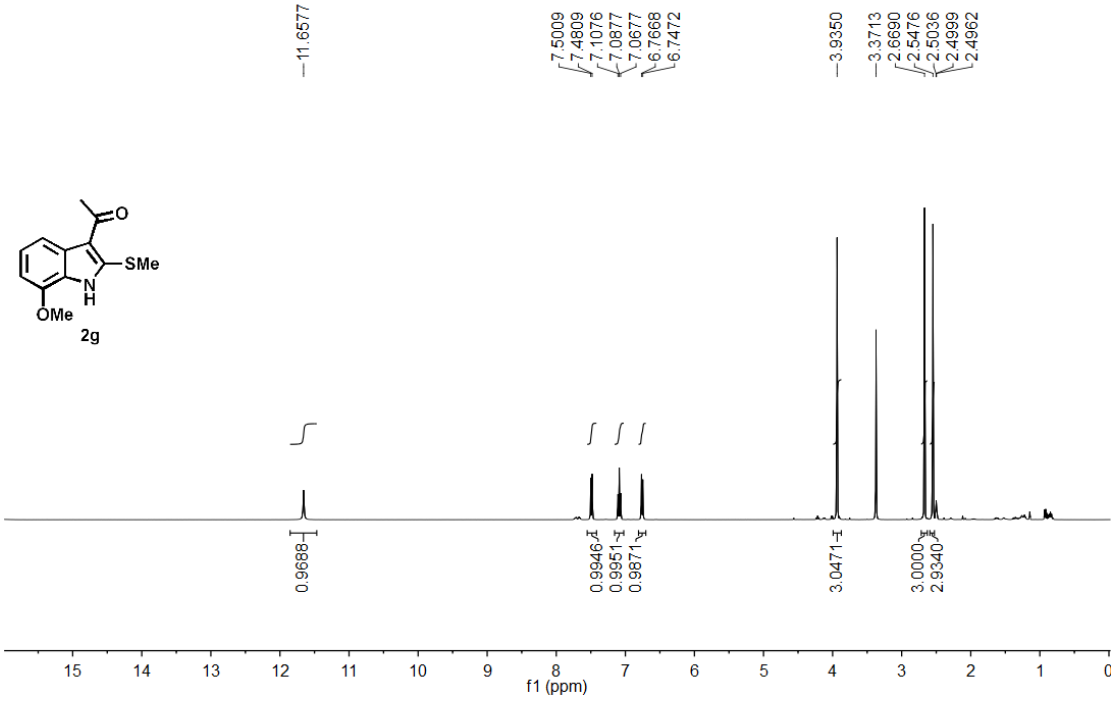
2f

HF221
13C NMR IN DMSO-d6

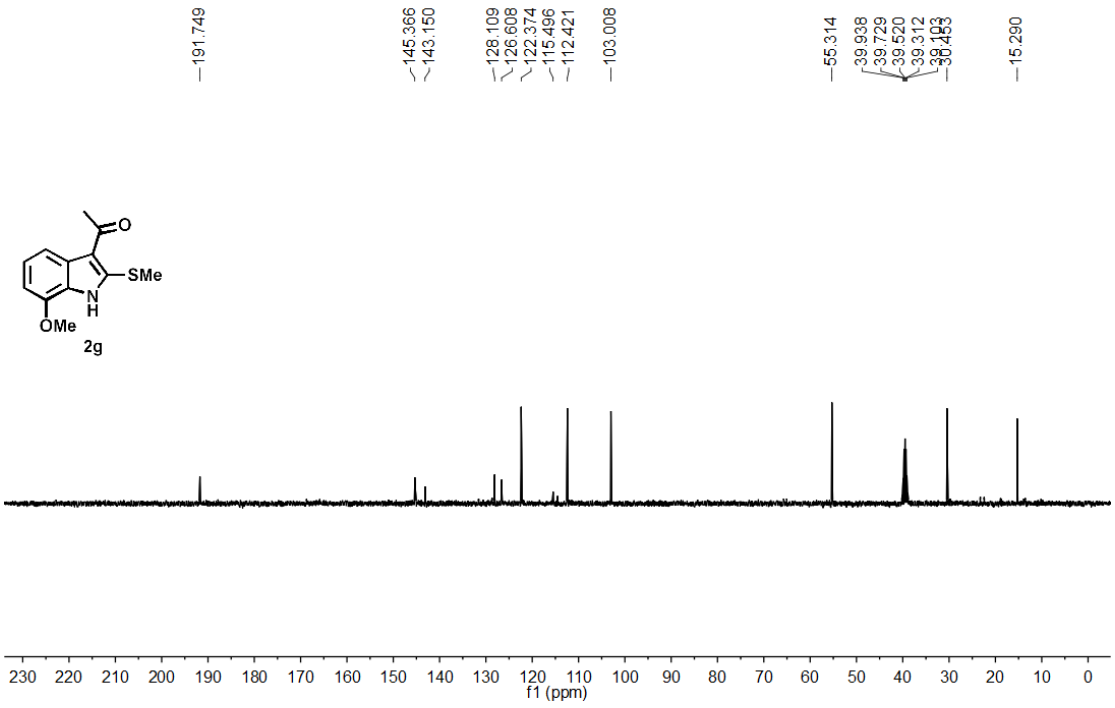


2f

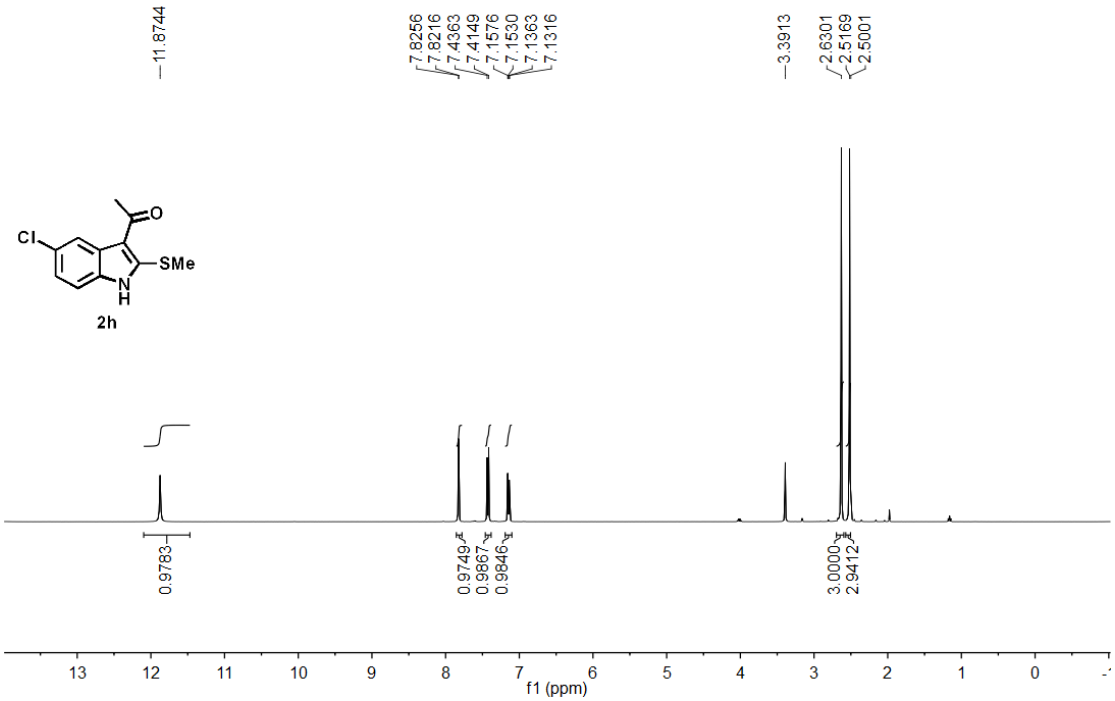
HF247
1H NMR IN DMSO-d6



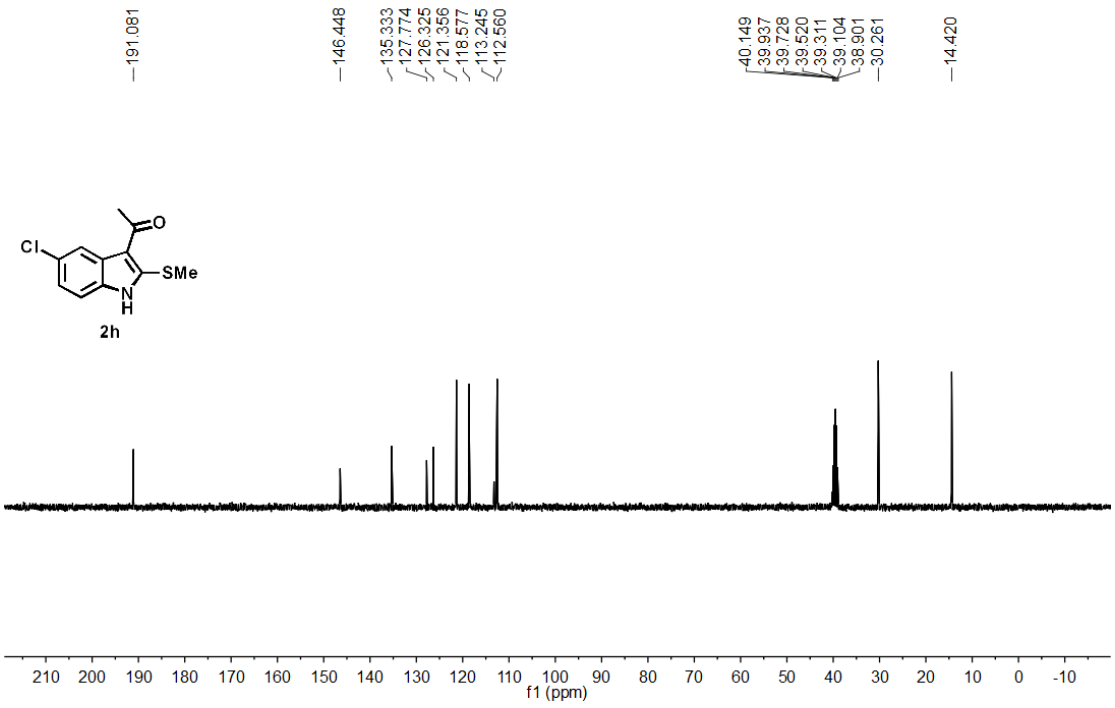
HF247
13C NMR IN DMSO-d6



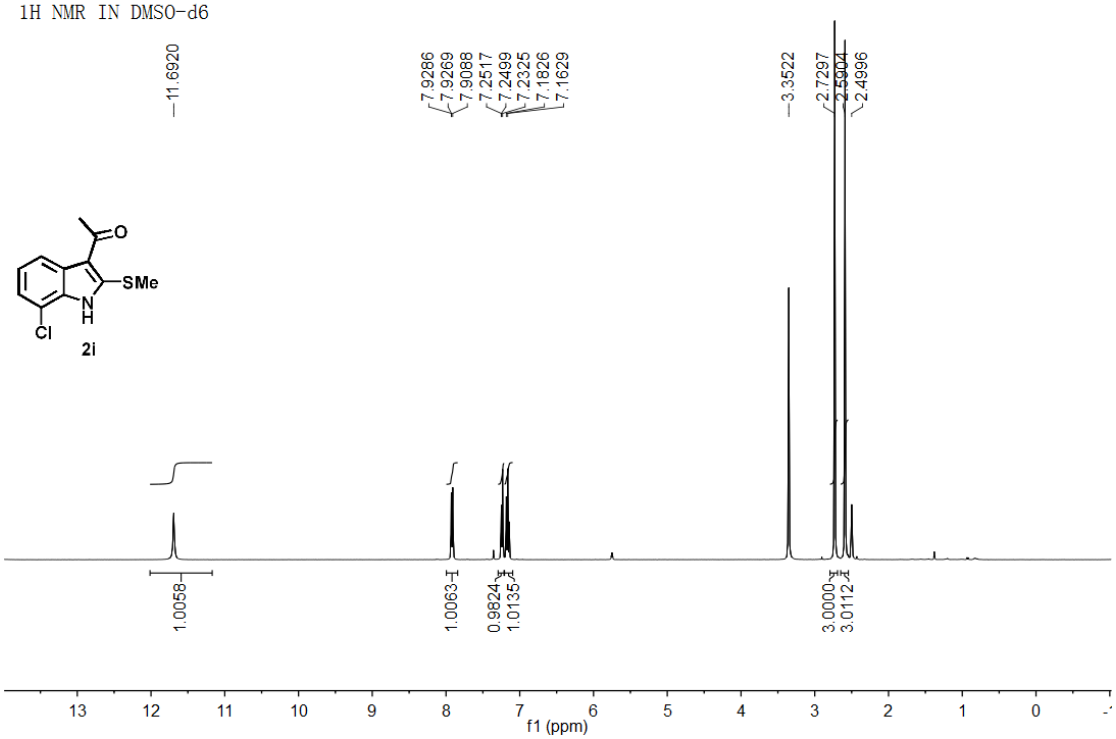
HF228
1H NMR IN DMSO-d6



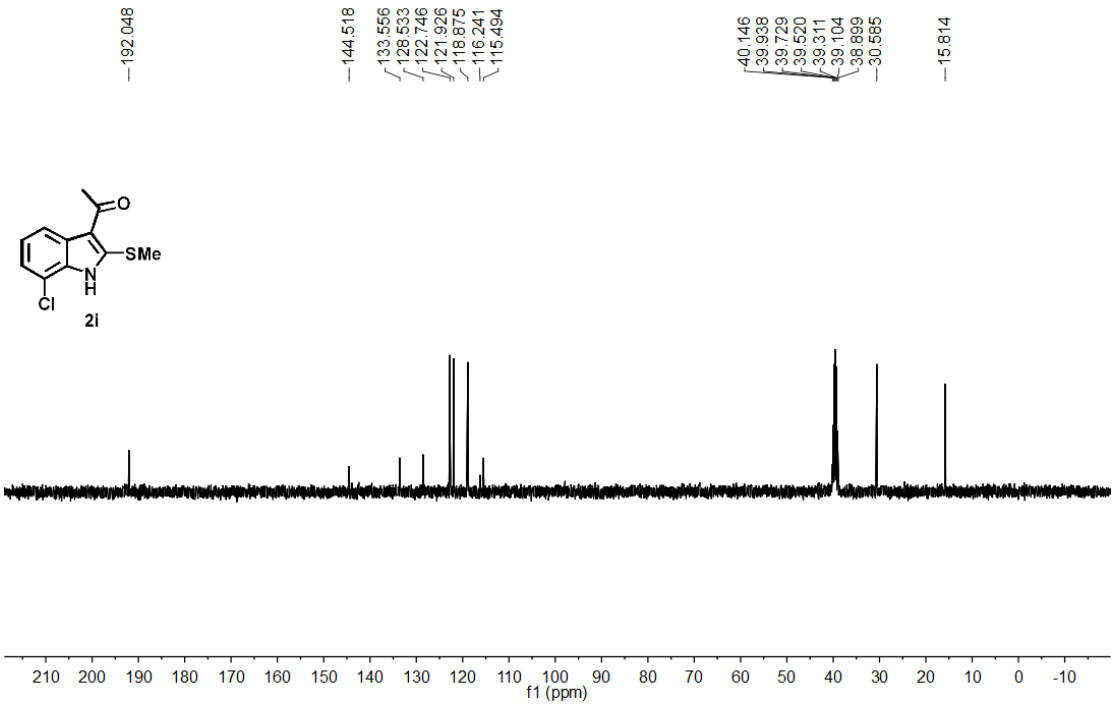
HF228
13C NMR IN DMSO-d6



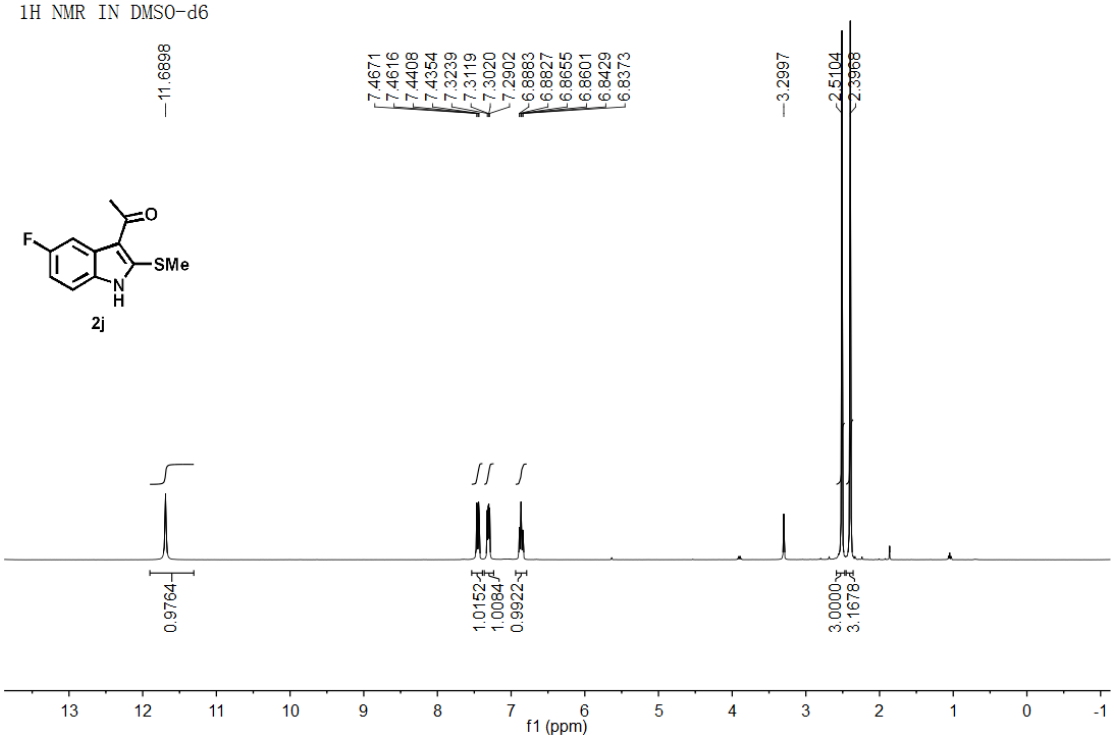
HF220
1H NMR IN DMSO-d6



HF220
13C NMR IN DMSO-d6

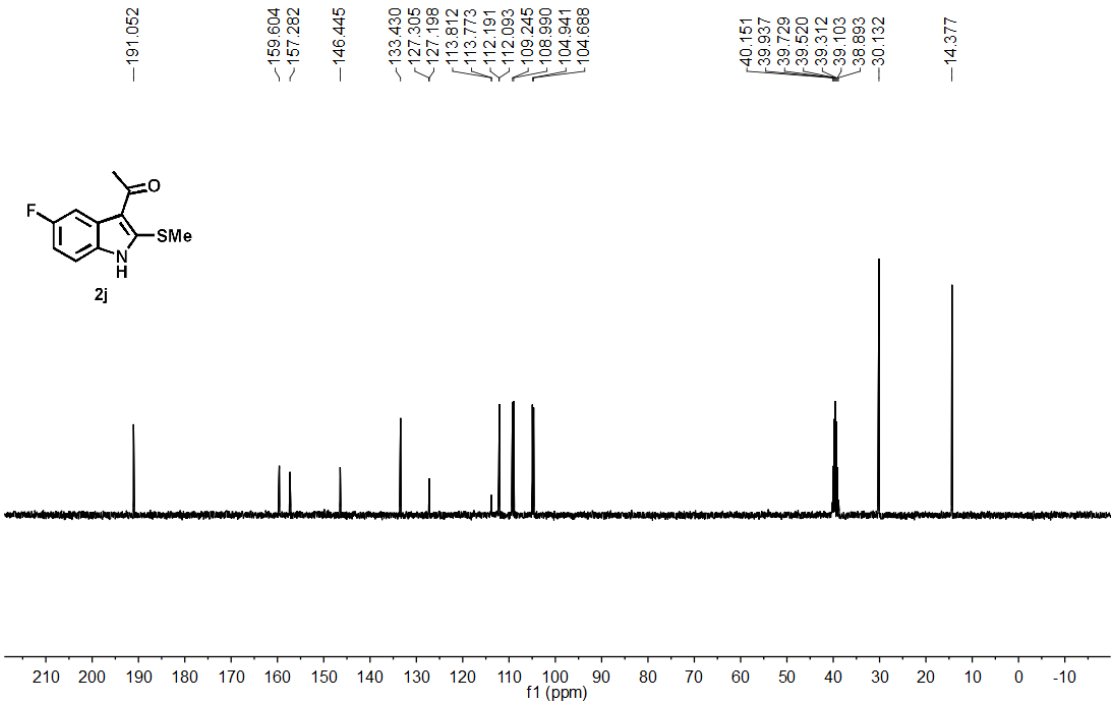


HF226
1H NMR IN DMSO-d6



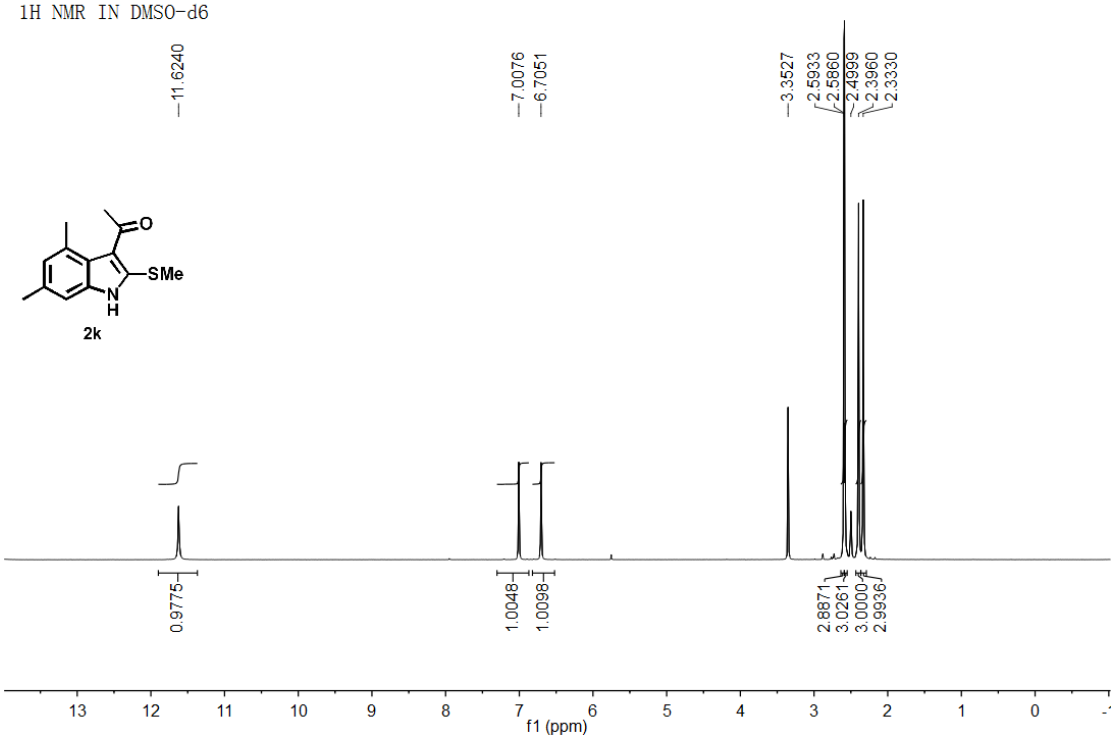
2j

HF226
13C NMR IN DMSO-d6

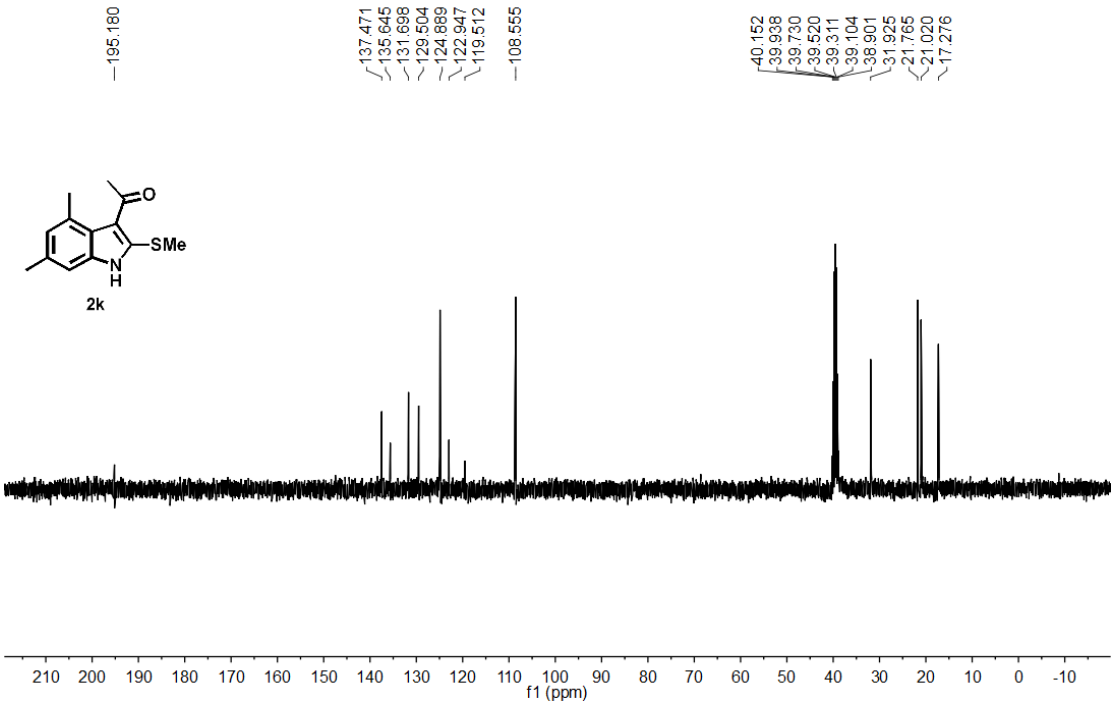


2j

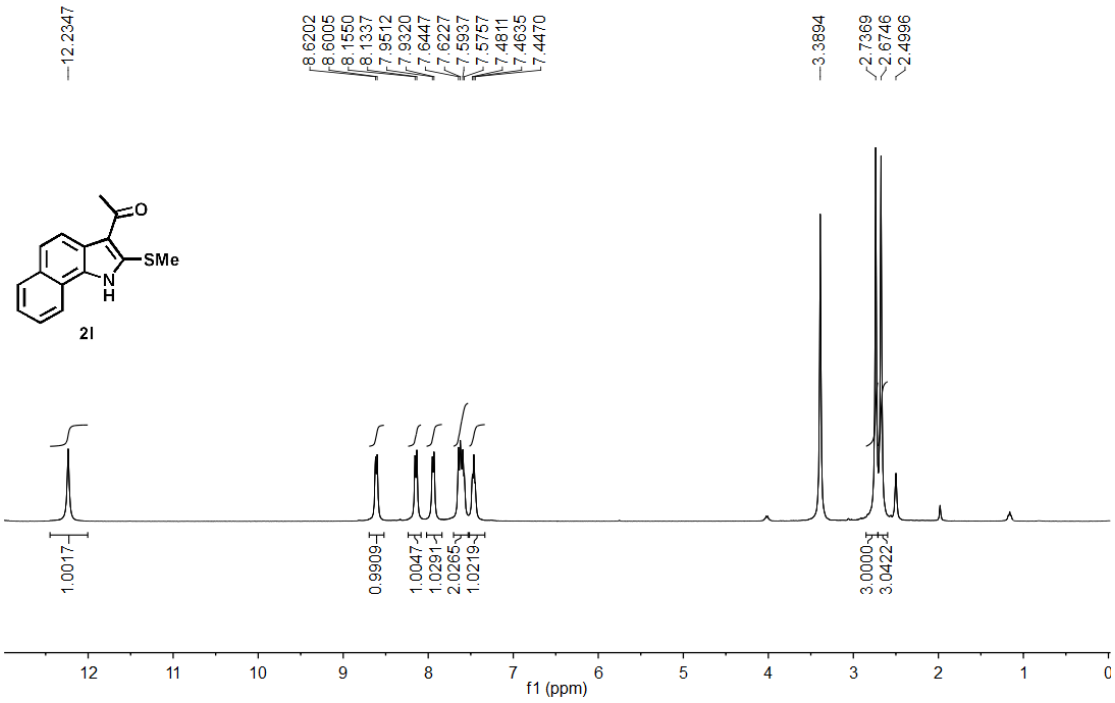
HF225
1H NMR IN DMSO-d6



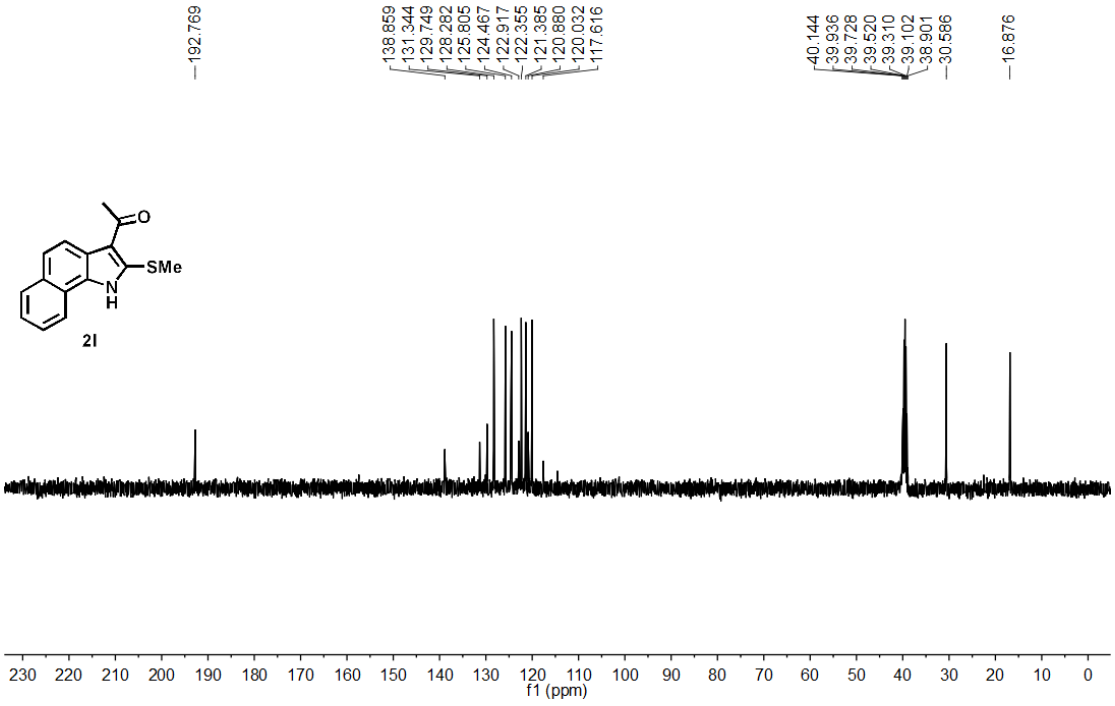
HF225
13C NMR IN DMSO-d6



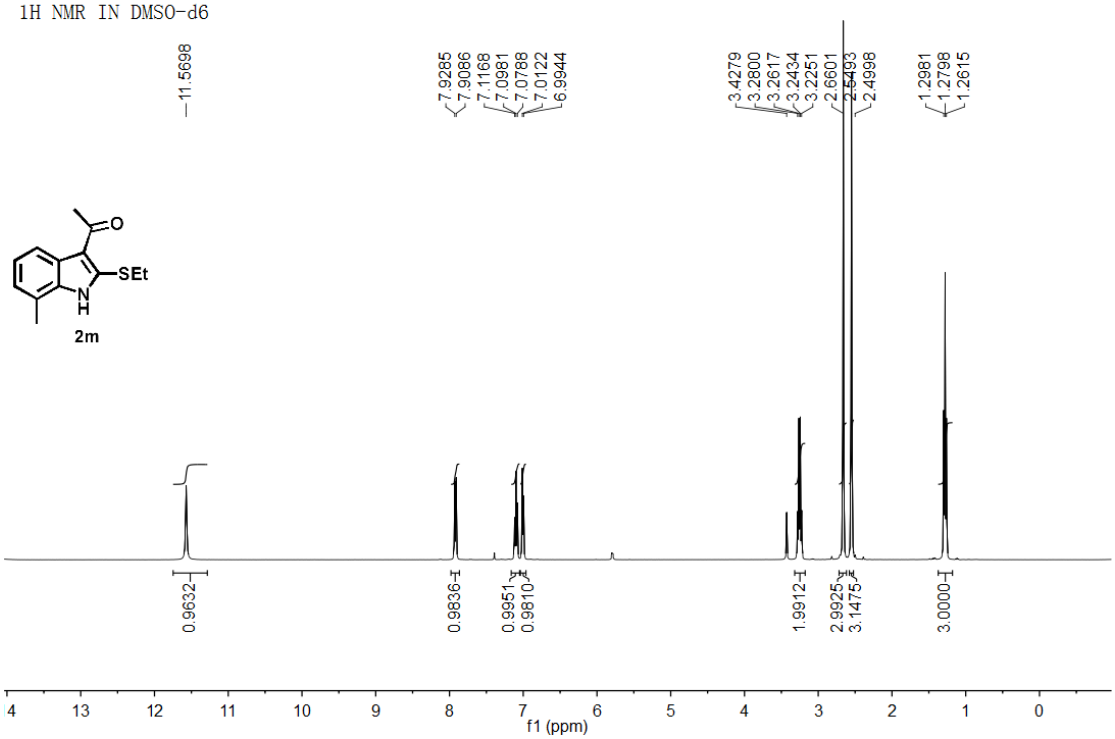
HF241
1H NMR IN DMSO-d6



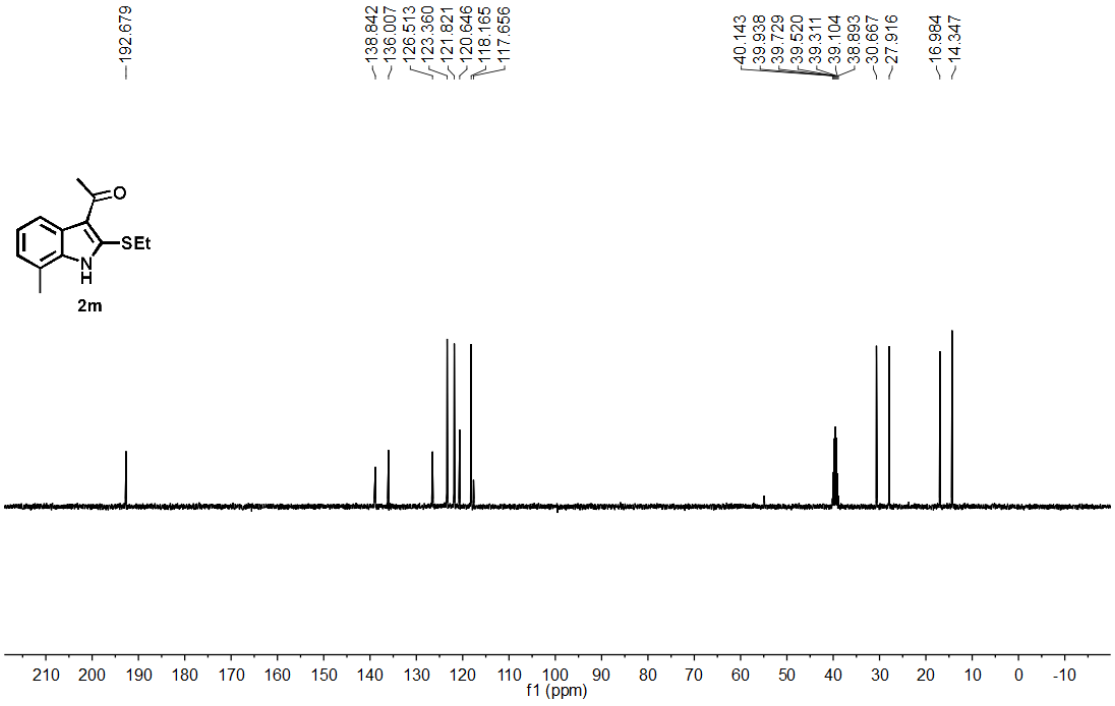
HF241
13C NMR IN DMSO-d6



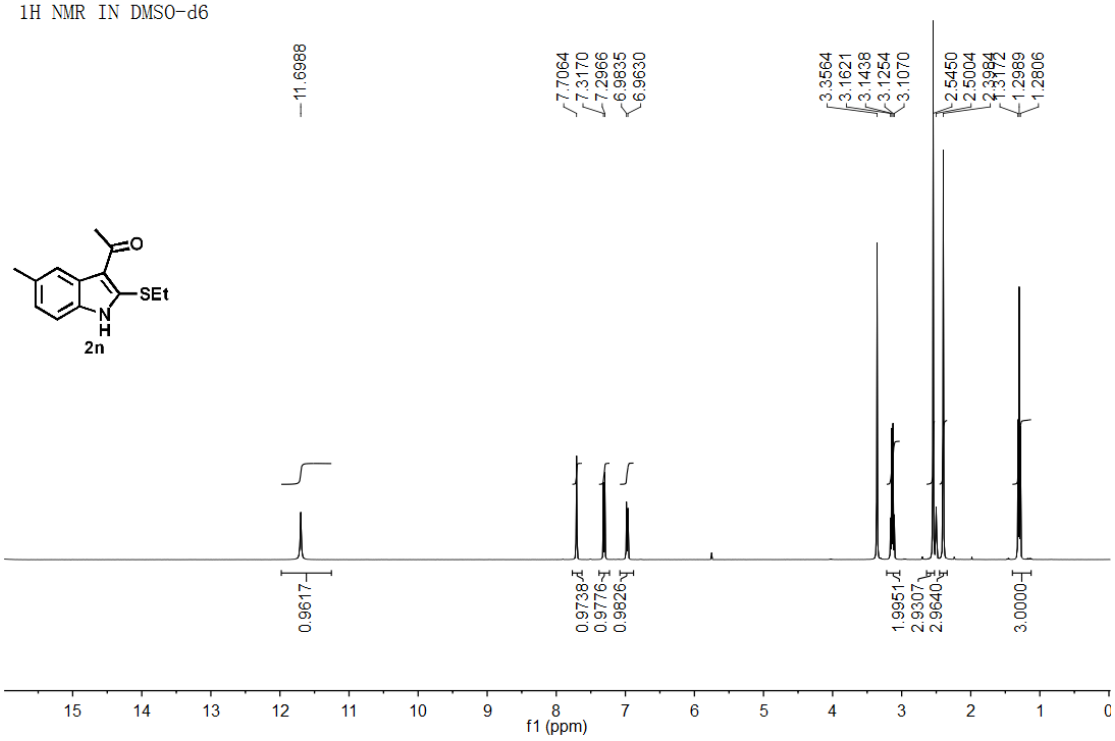
HF205
1H NMR IN DMSO-d6



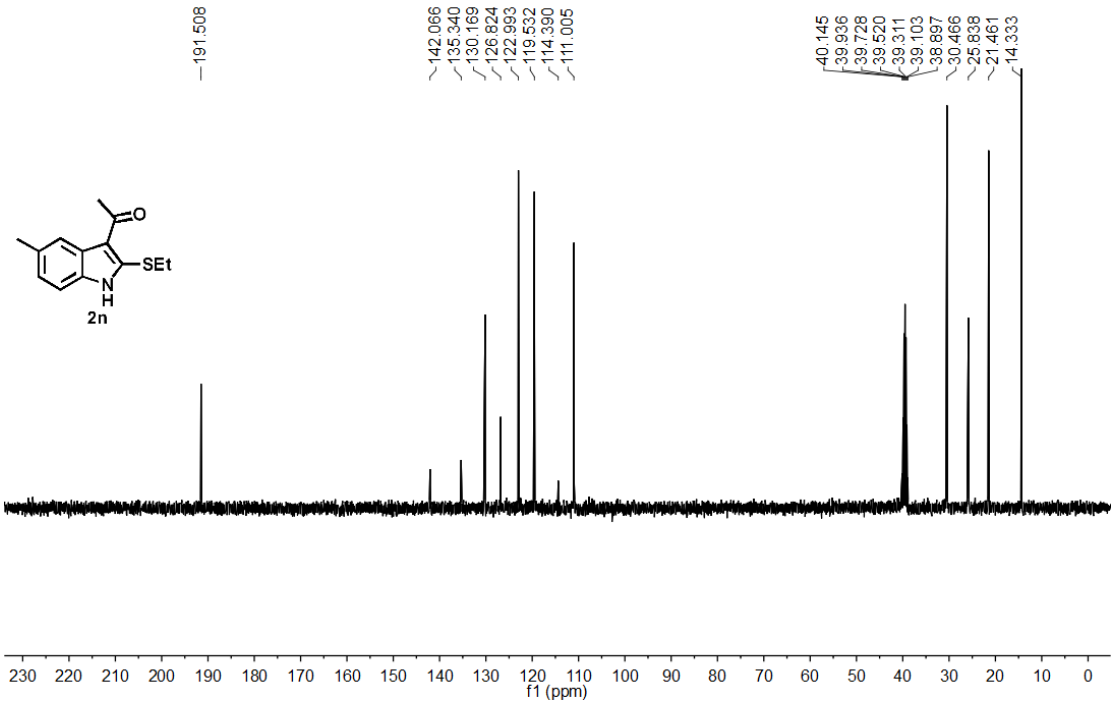
HF205
13C NMR IN DMSO-d6



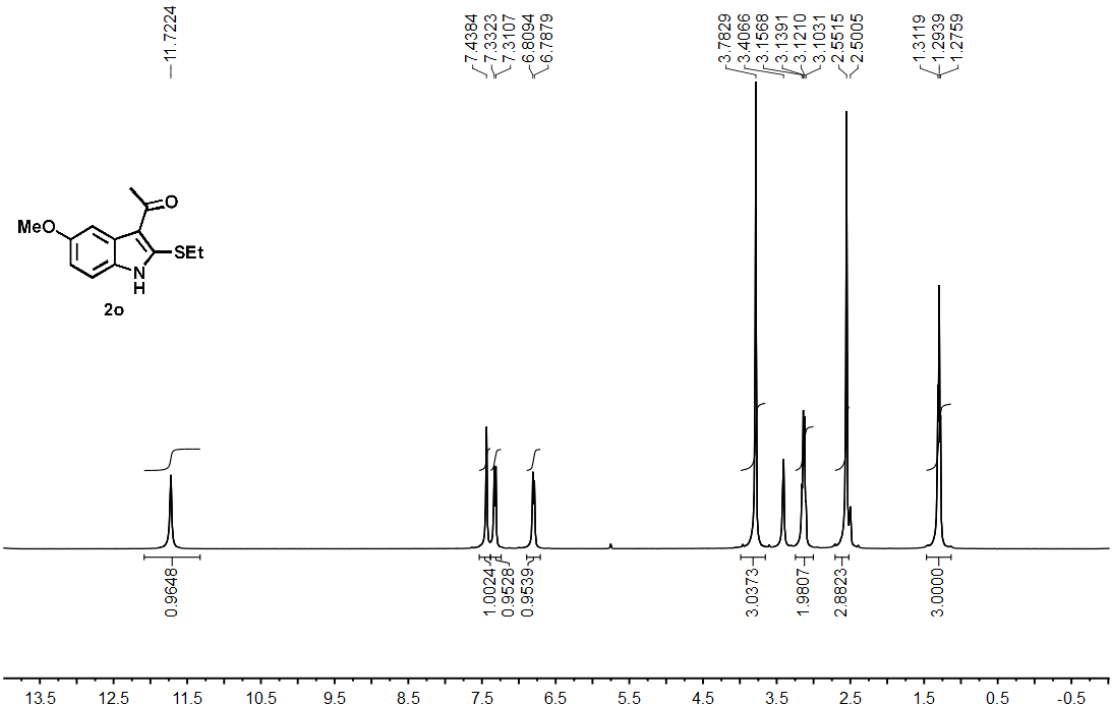
HF259
1H NMR IN DMSO-d6



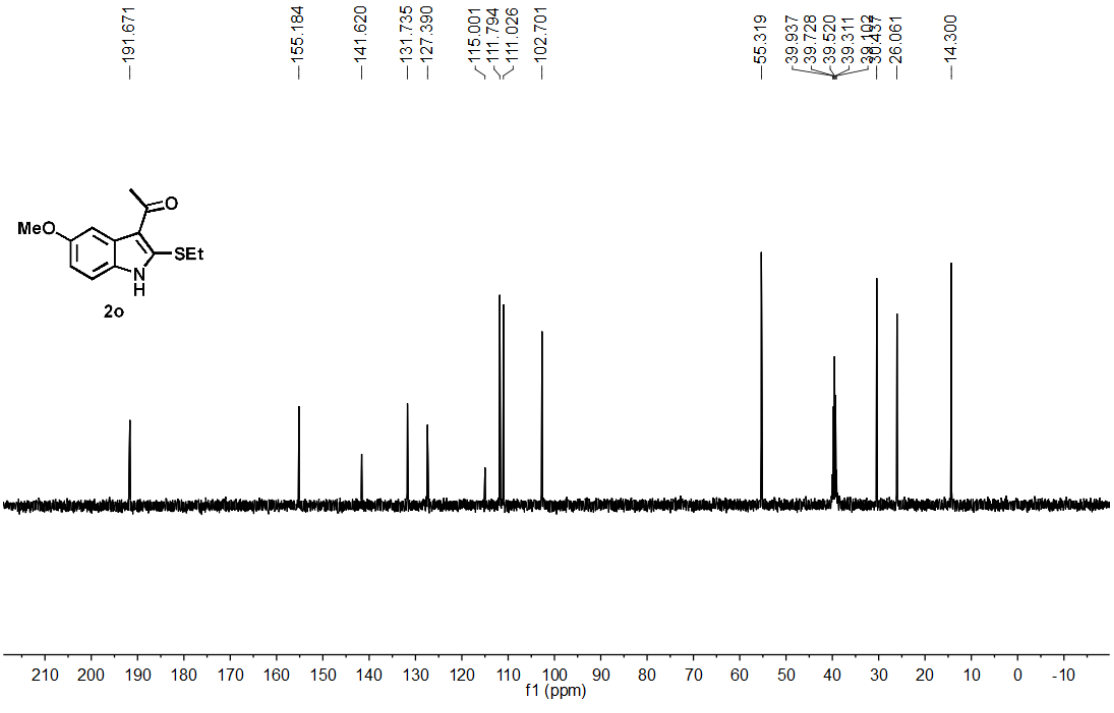
HF259
13C NMR IN DMSO-d6



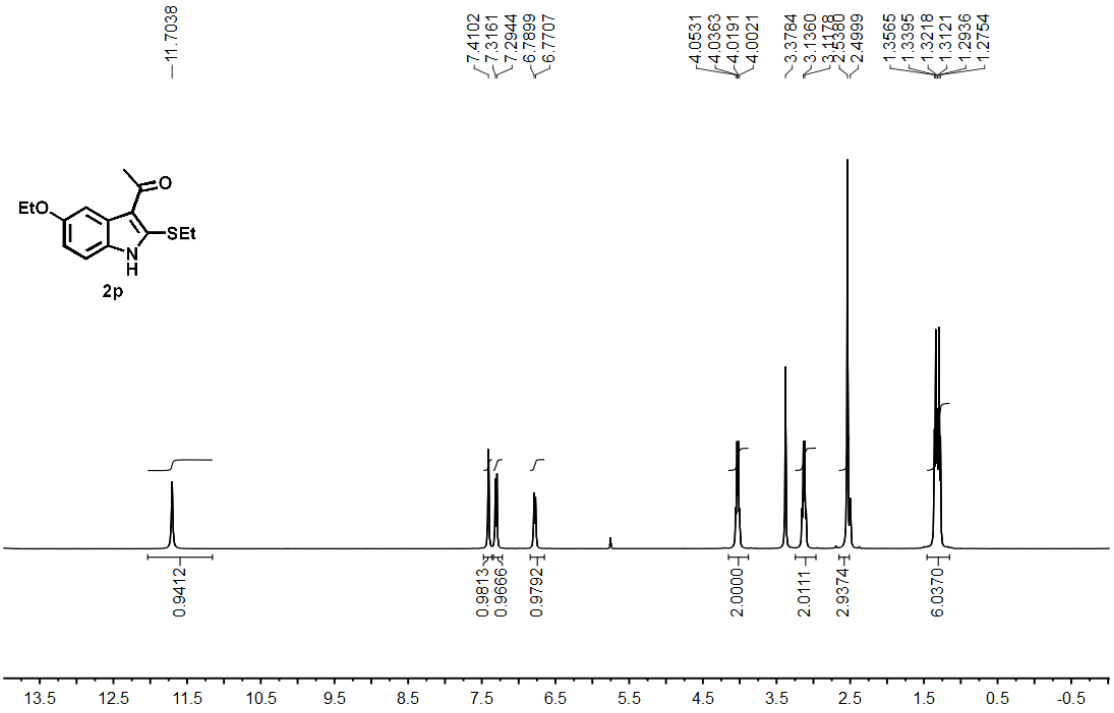
HF203
1H NMR IN DMSO-d6



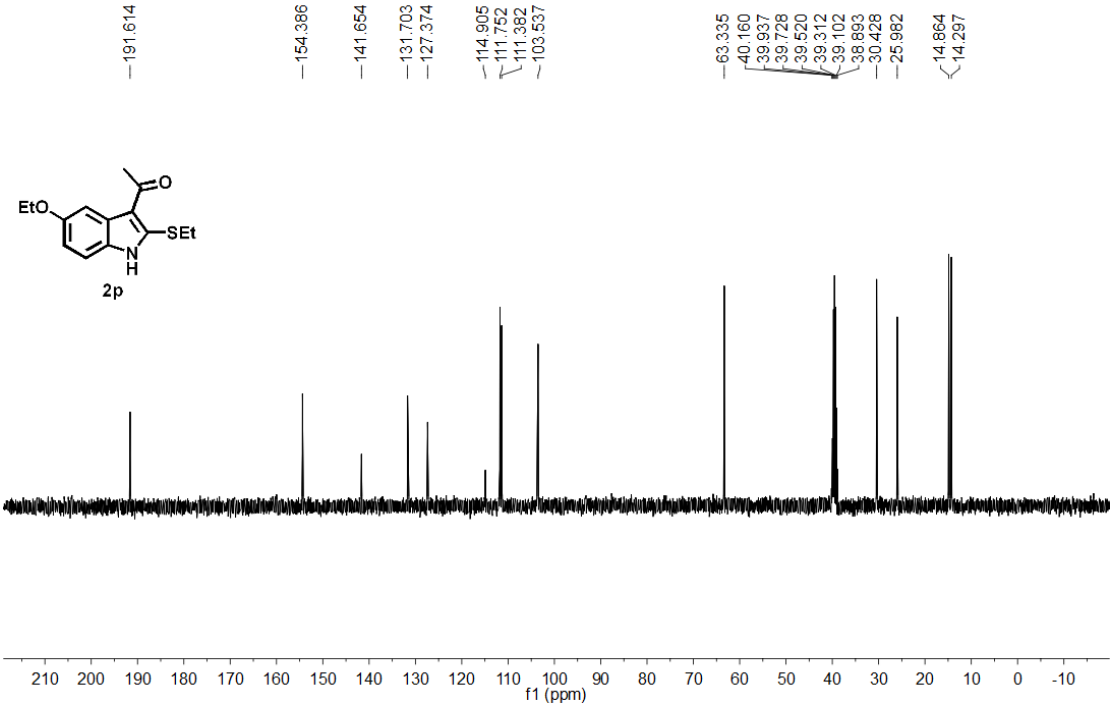
HF203
13C NMR IN DMSO-d6



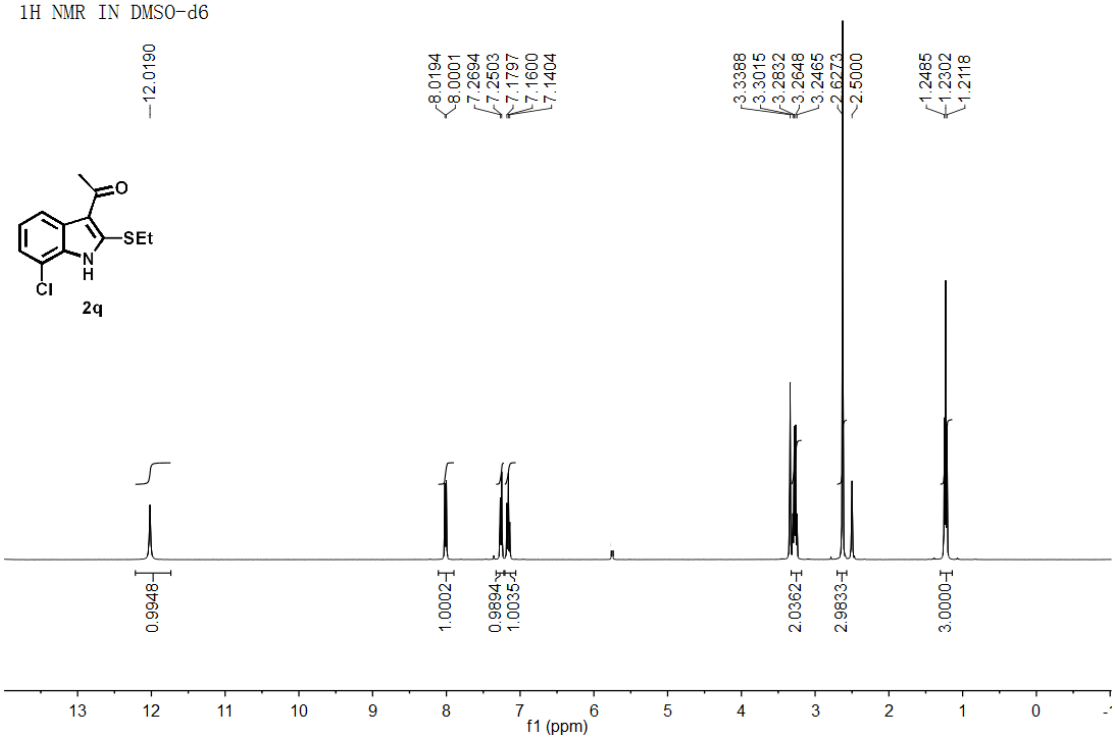
HF200
1H NMR IN DMSO-d6



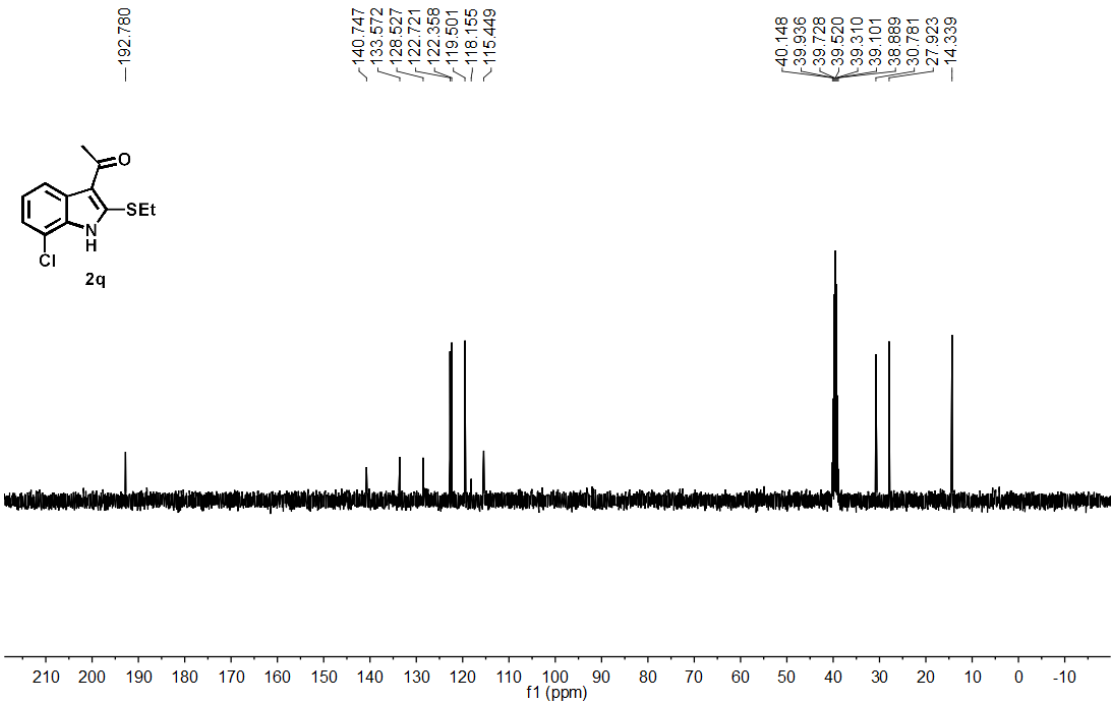
HF200
13C NMR IN DMSO-d6



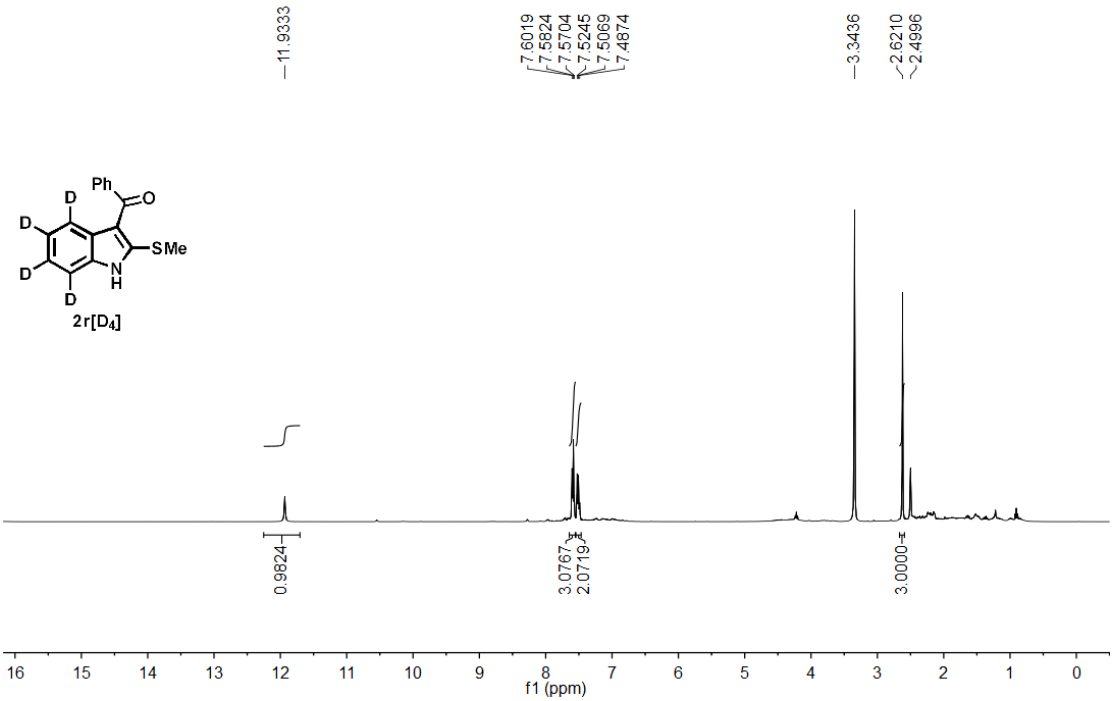
HF204
1H NMR IN DMSO-d6



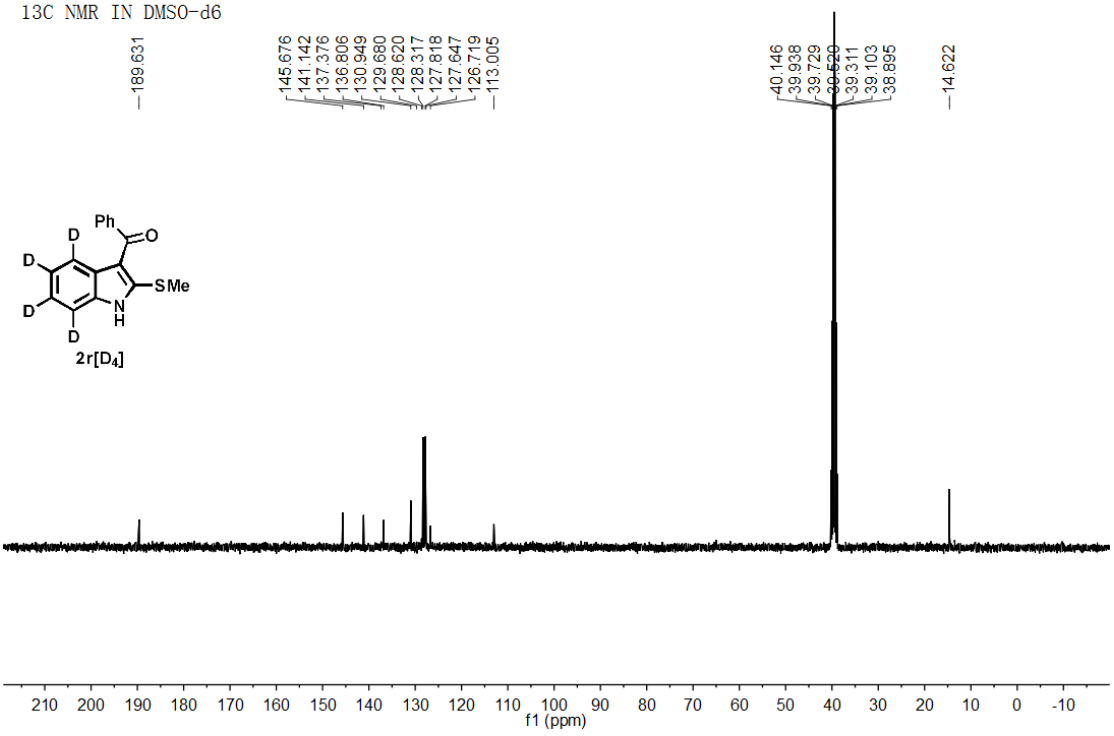
HF204
13C NMR IN DMSO-d6



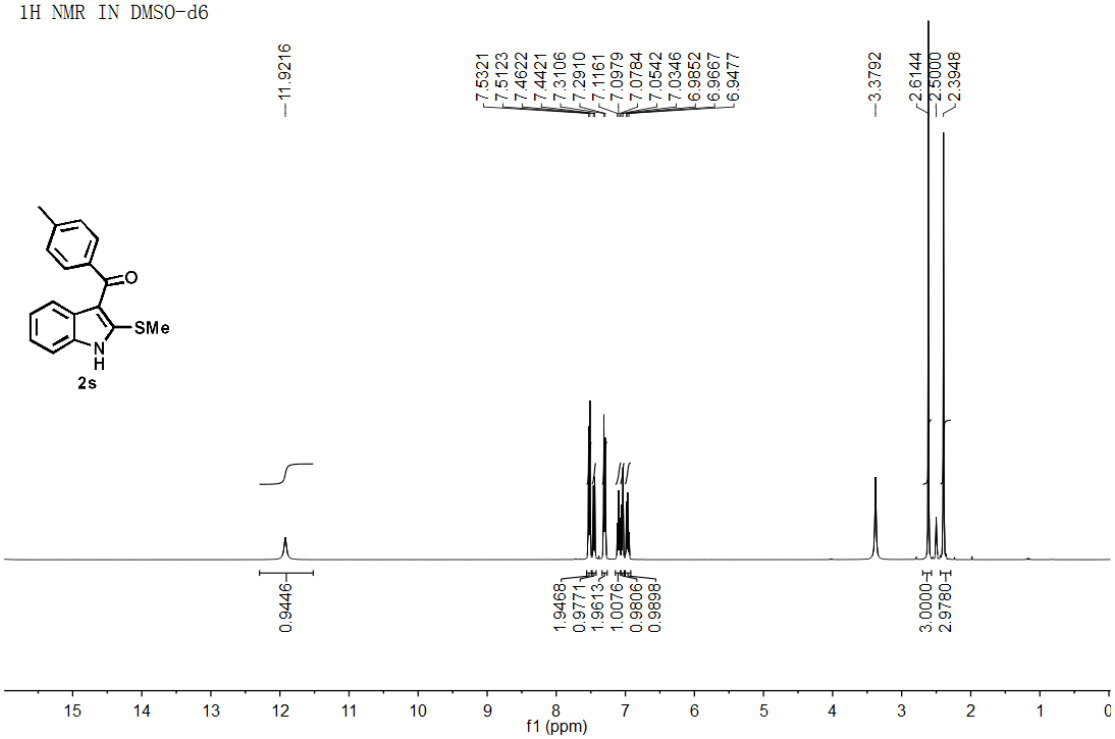
HF341
1H NMR IN DMSO-d6



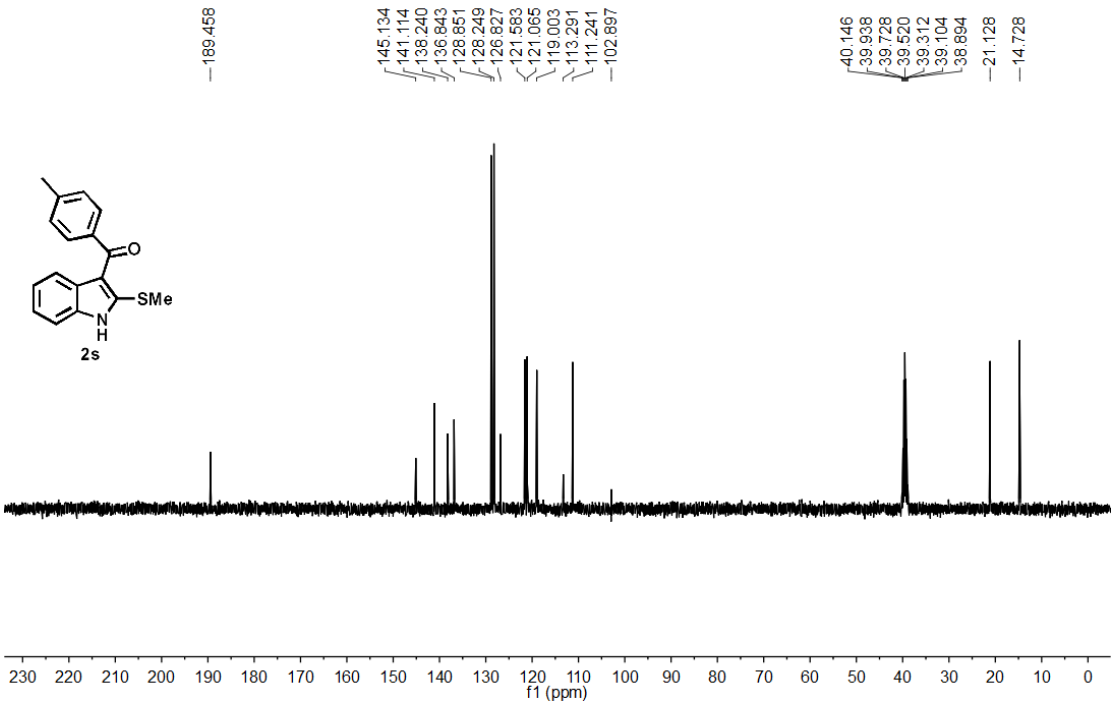
HF341
13C NMR IN DMSO-d6



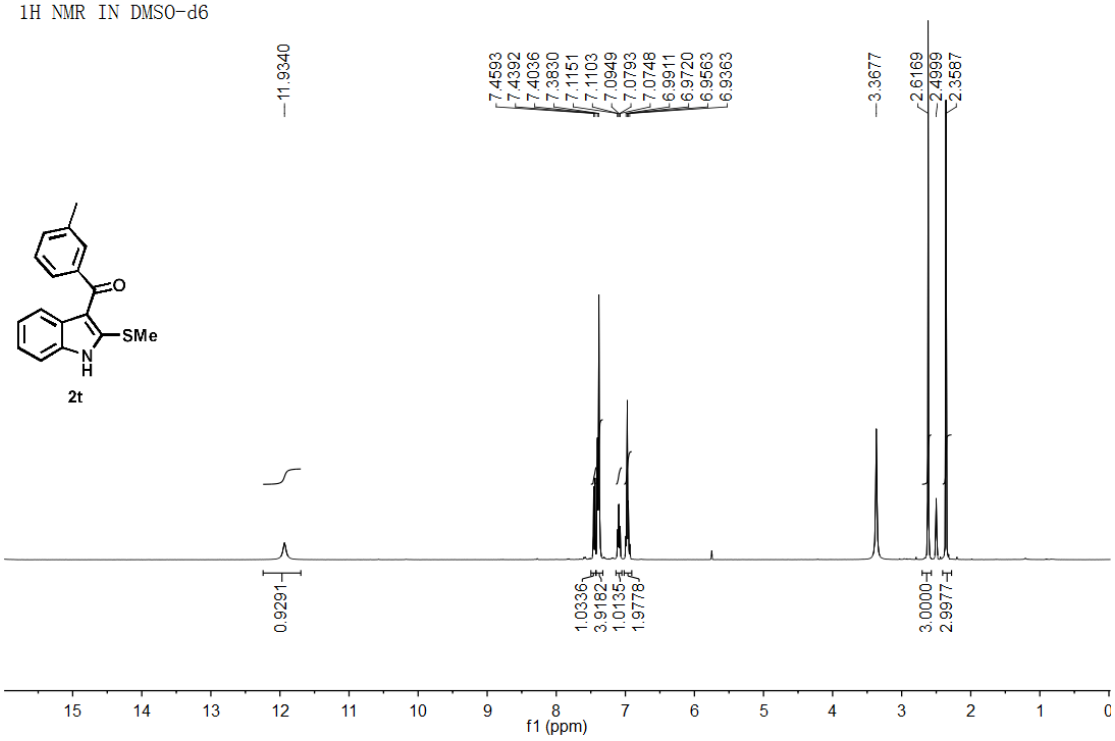
HF267
1H NMR IN DMSO-d6



HF267
13C NMR IN DMSO-d6

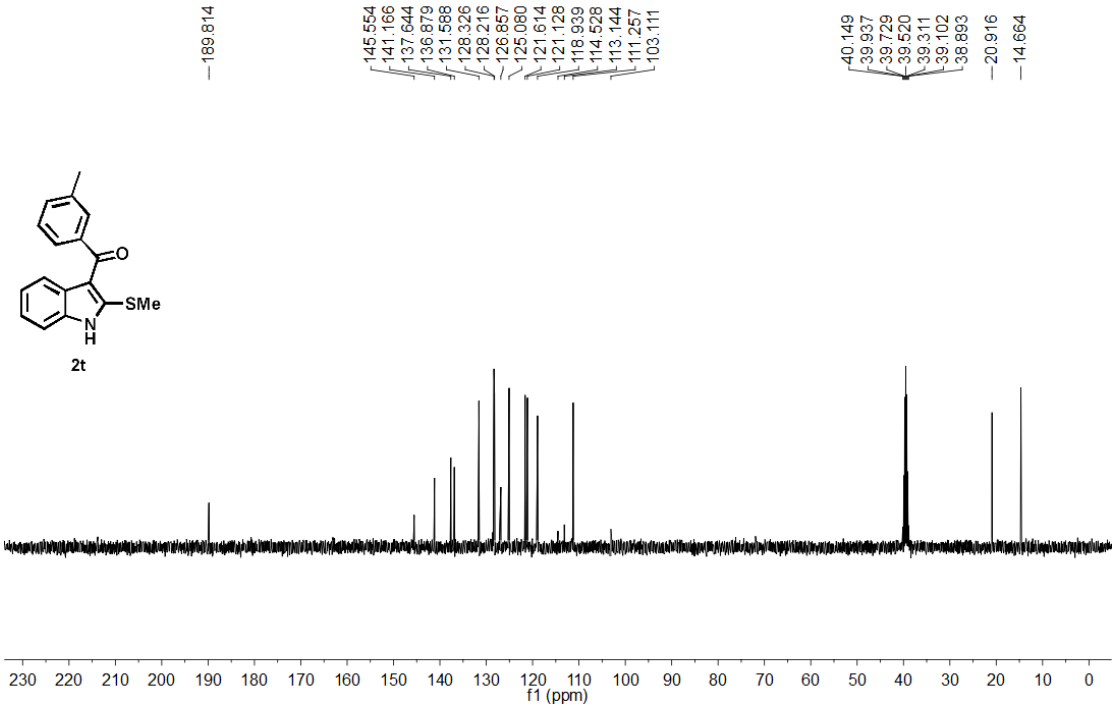


HF268
1H NMR IN DMSO-d6



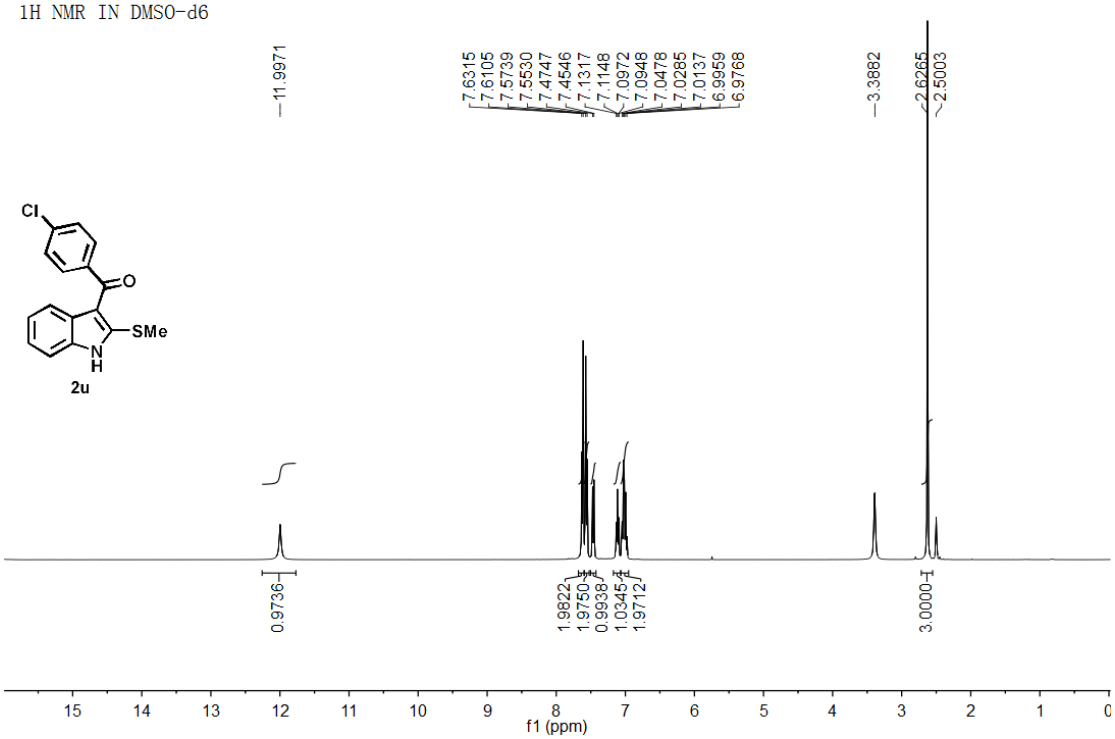
2t

HF268
13C NMR IN DMSO-d6

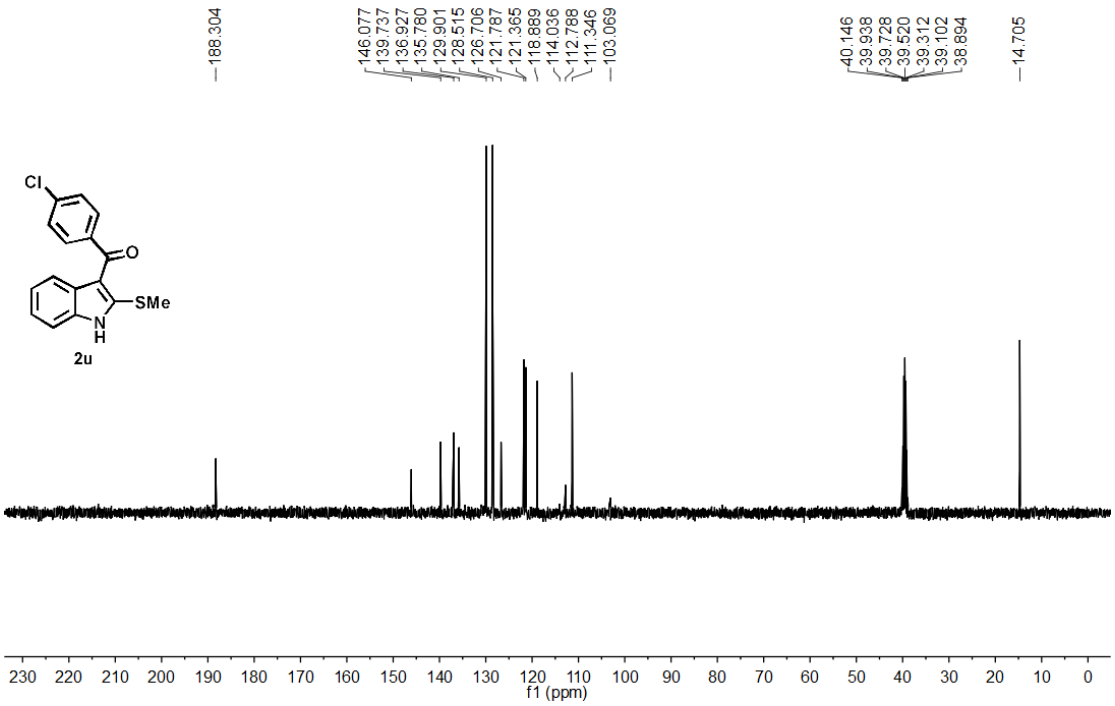


2t

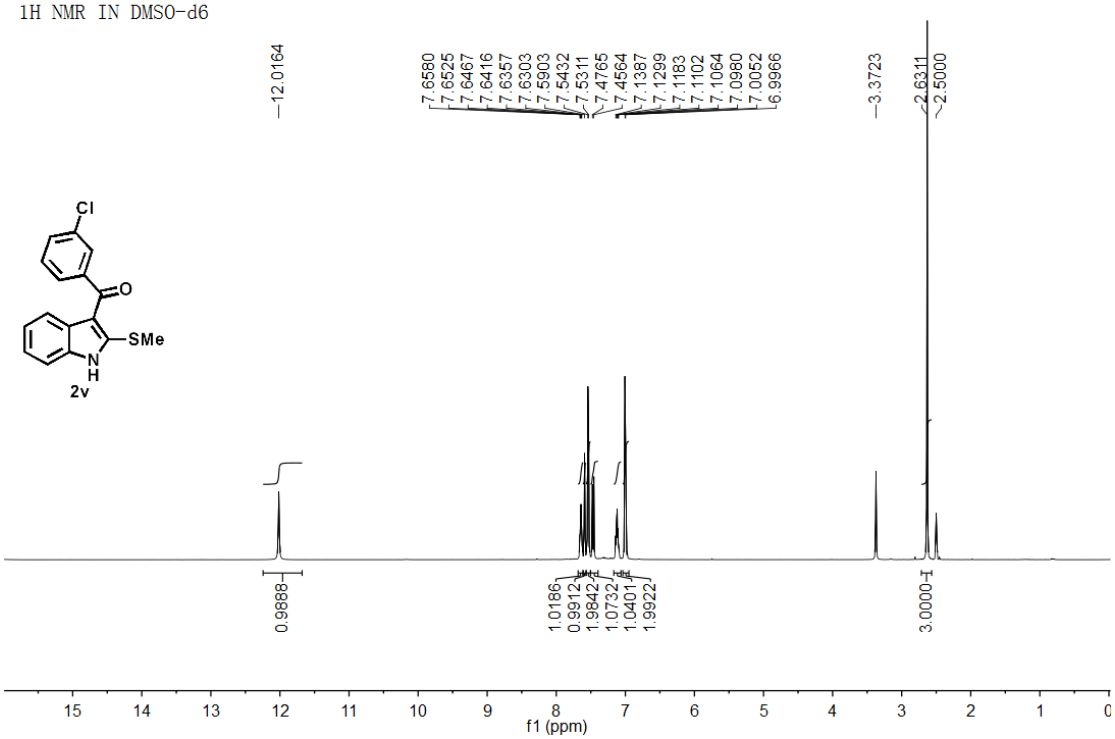
HF269
1H NMR IN DMSO-d6



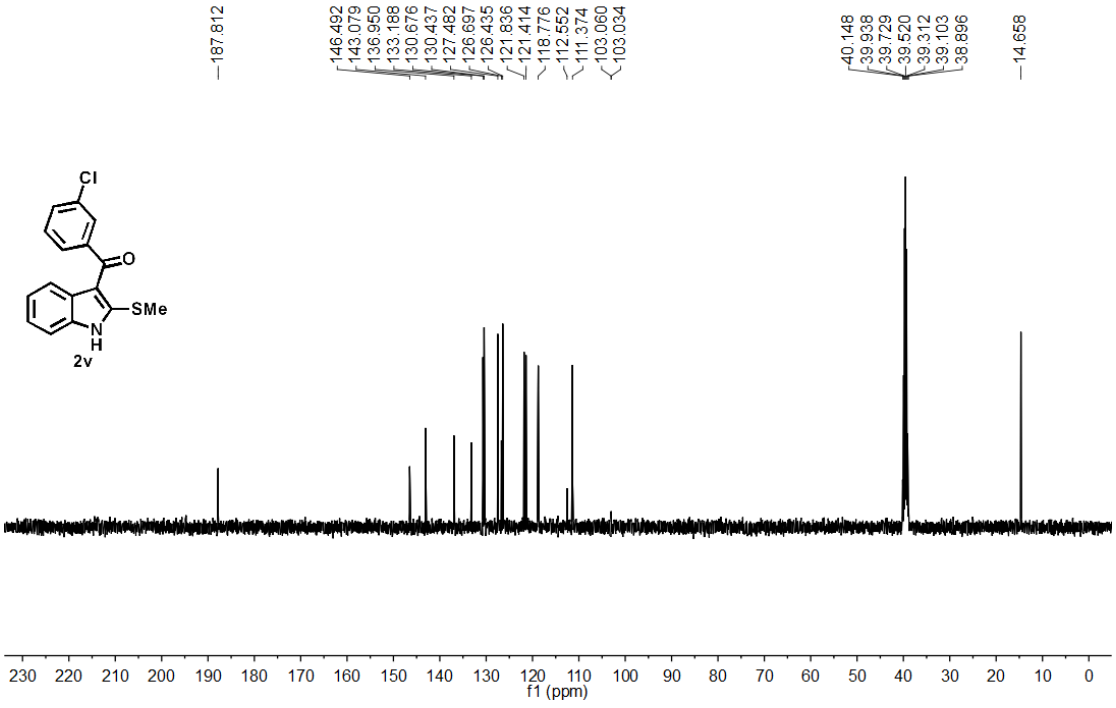
HF269
13C NMR IN DMSO-d6



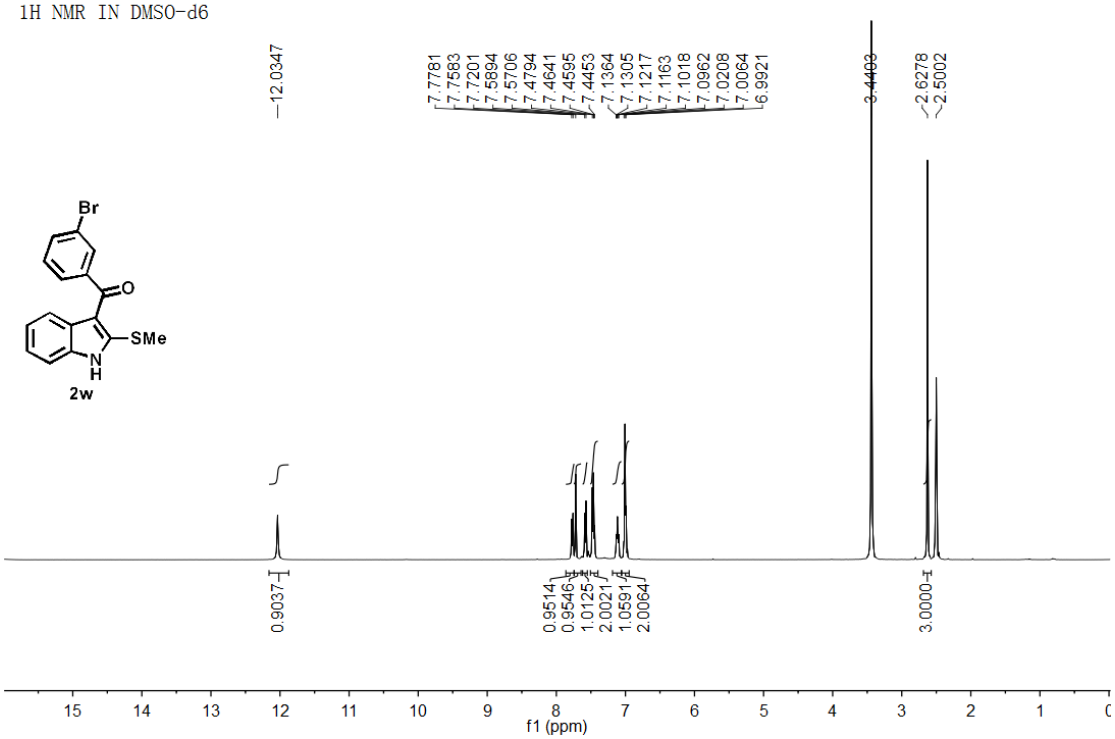
HF270
1H NMR IN DMSO-d6



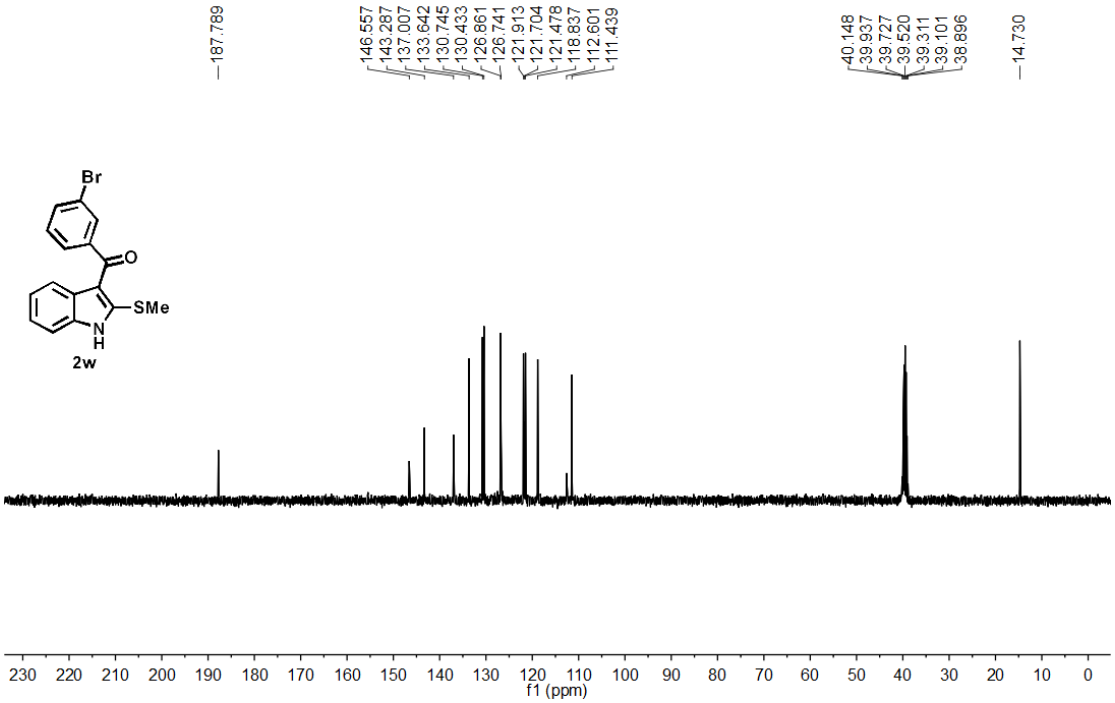
HF270
13C NMR IN DMSO-d6



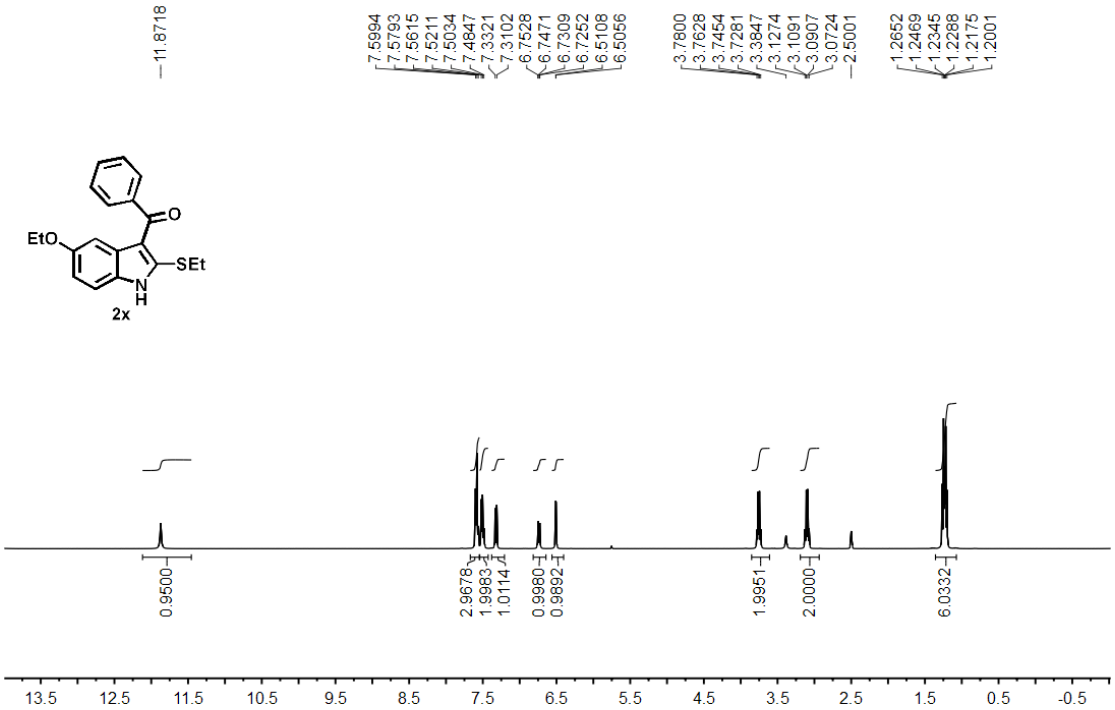
HF297
1H NMR IN DMSO-d6



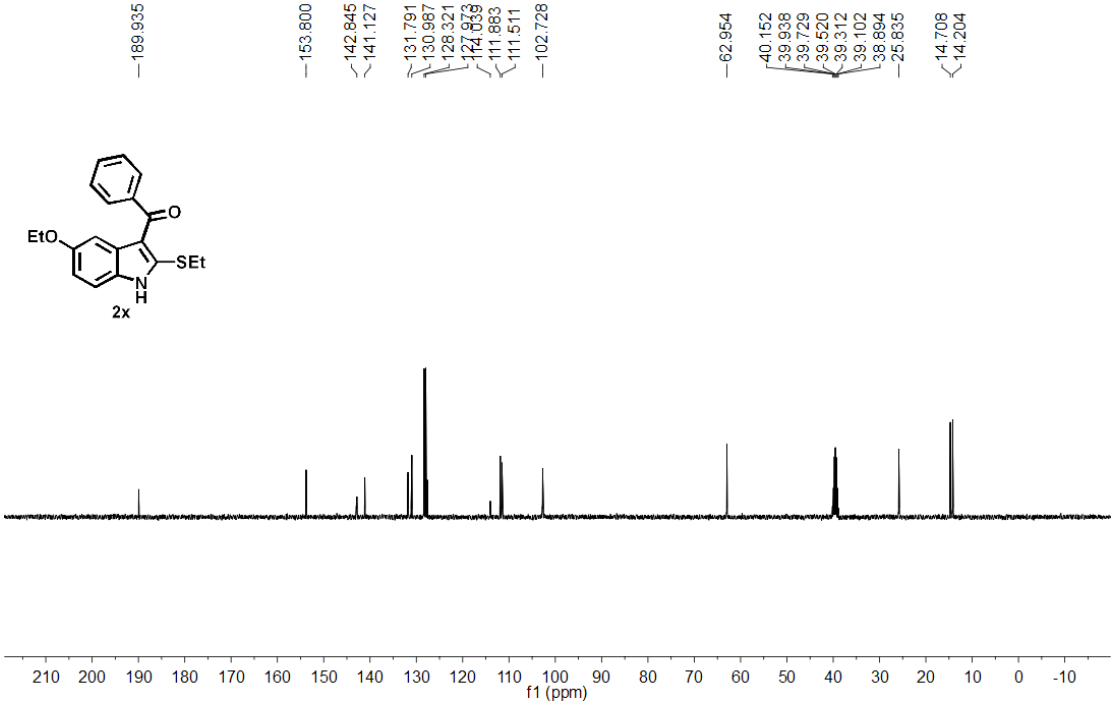
HF297
13C NMR IN DMSO-d6



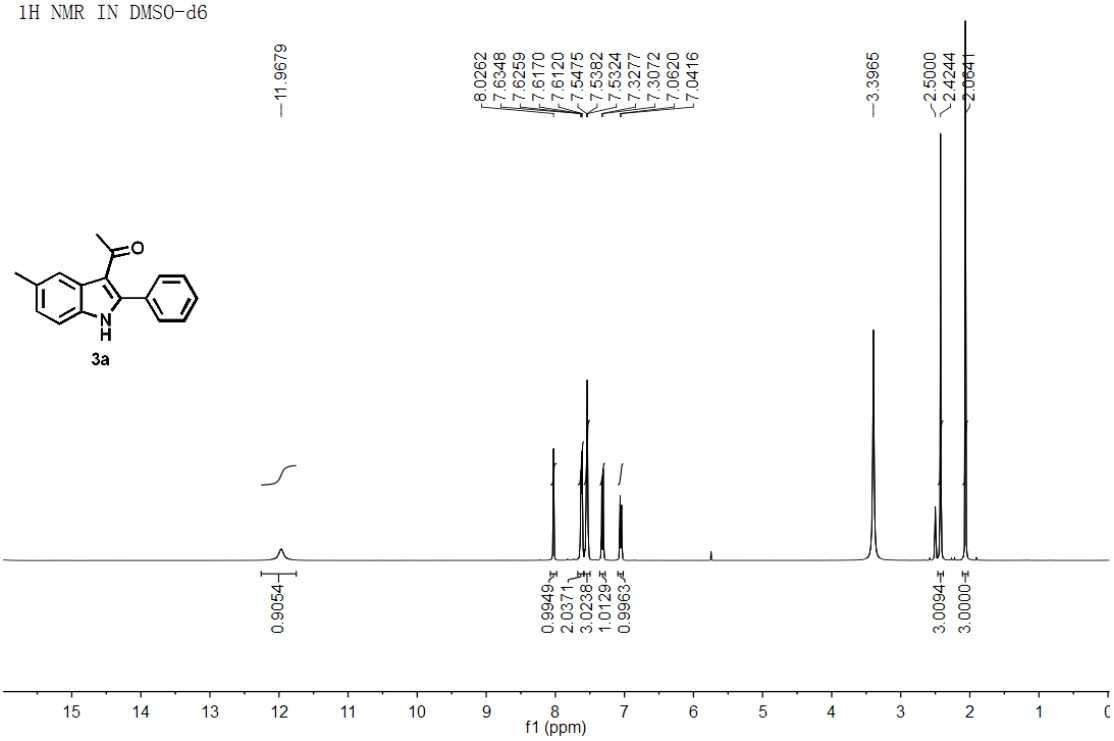
HF201
1H NMR IN DMSO-D6



HF201
13C NMR IN DMSO-D6

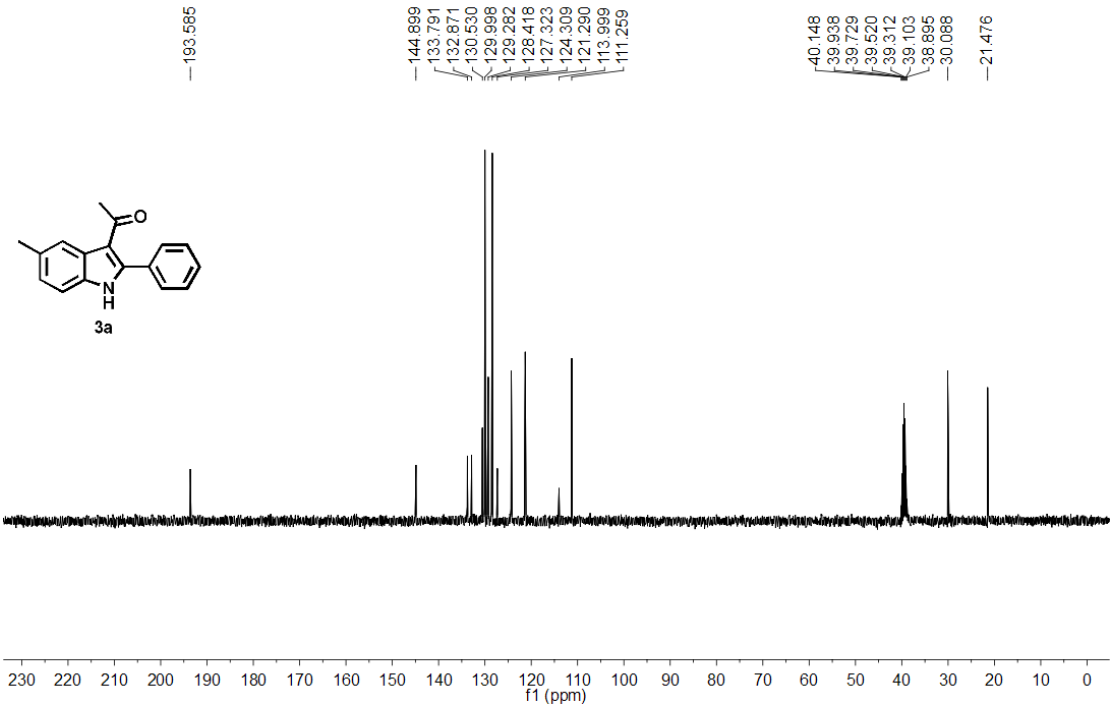


HF315
1H NMR IN DMSO-d6



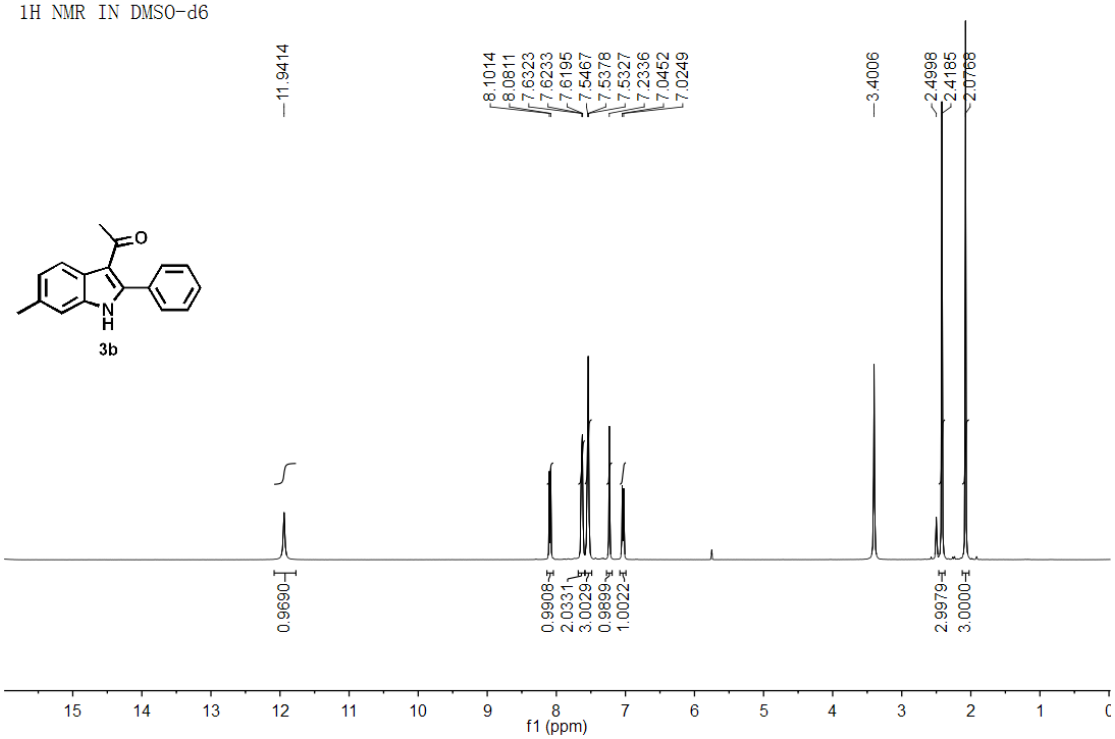
3a

HF315
13C NMR IN DMSO-d6



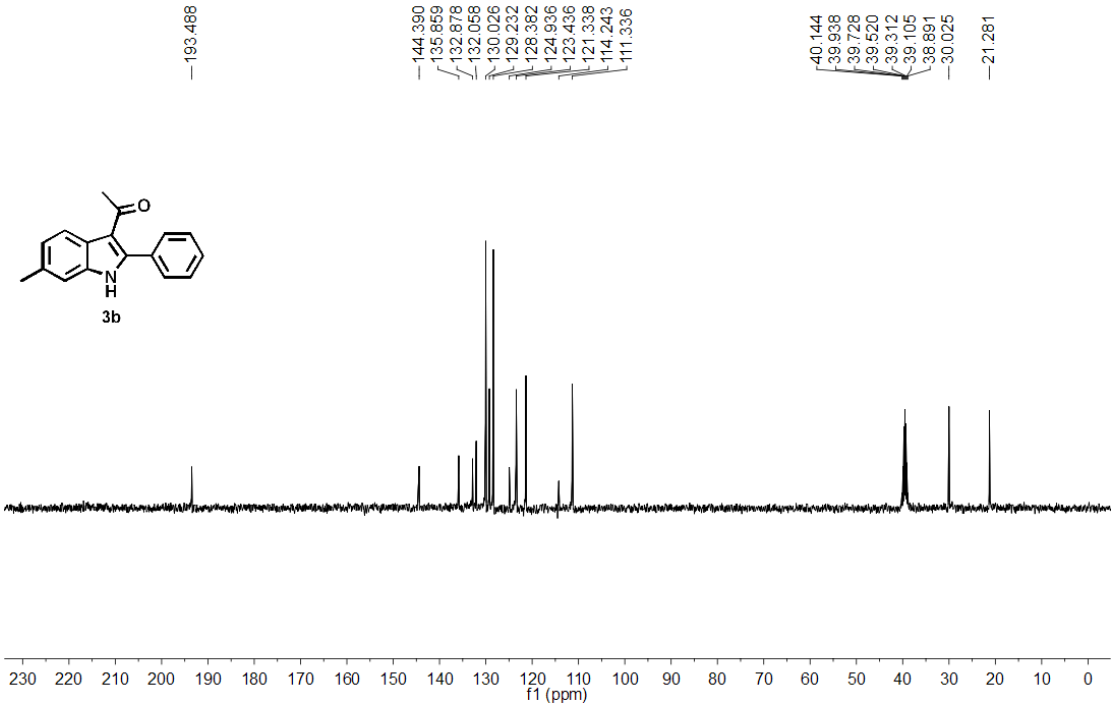
3a

HF313
1H NMR IN DMSO-d6



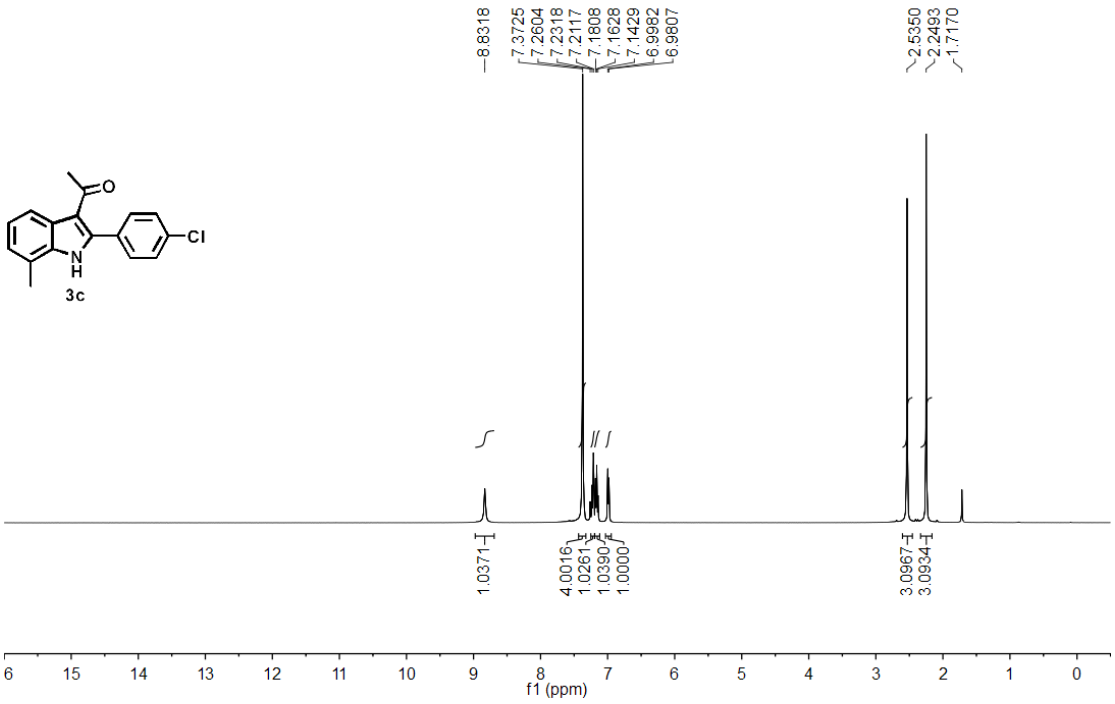
3b

HF313
13C NMR IN DMSO-d6

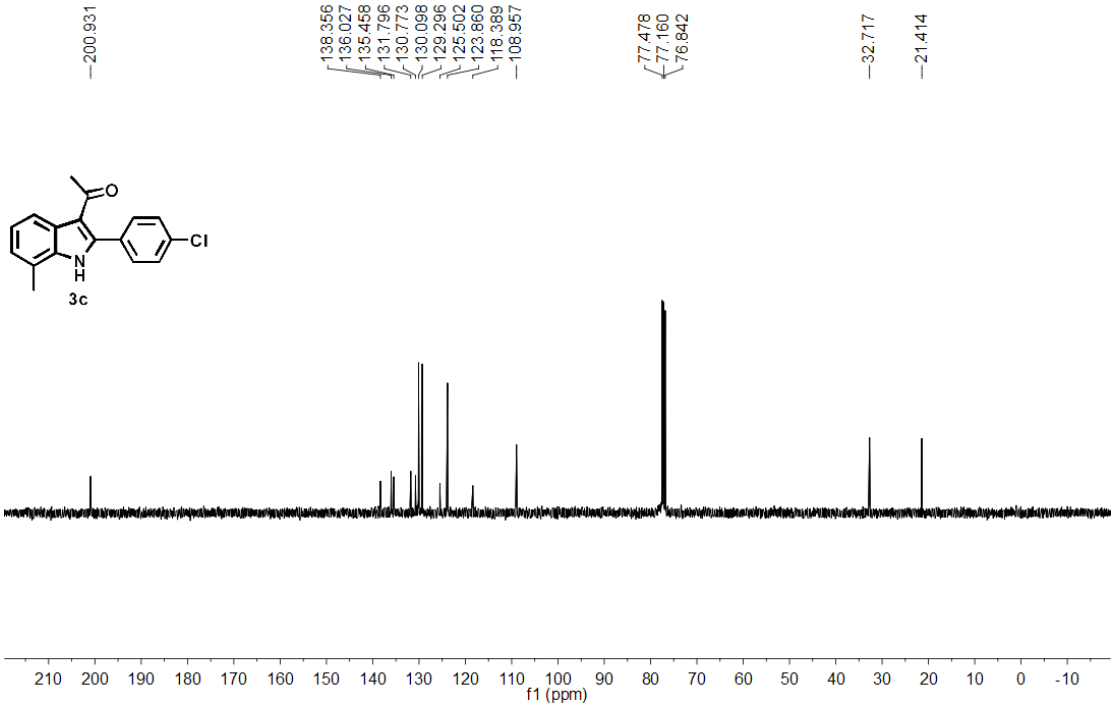


3b

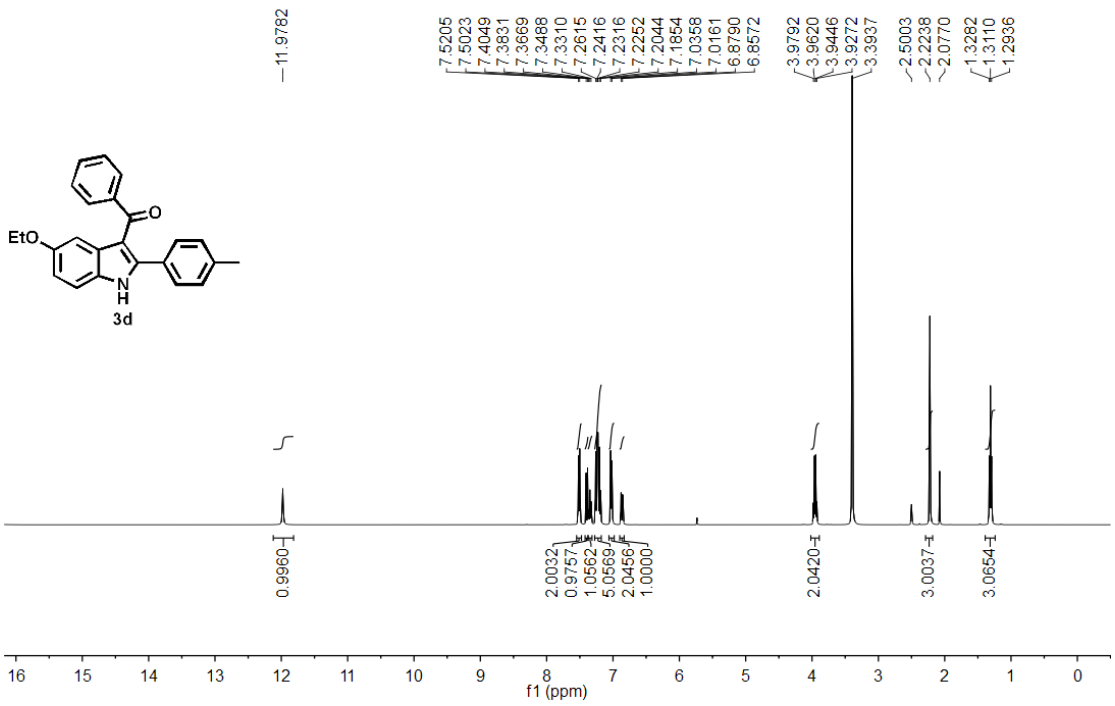
HF569
1H NMR IN CDC13



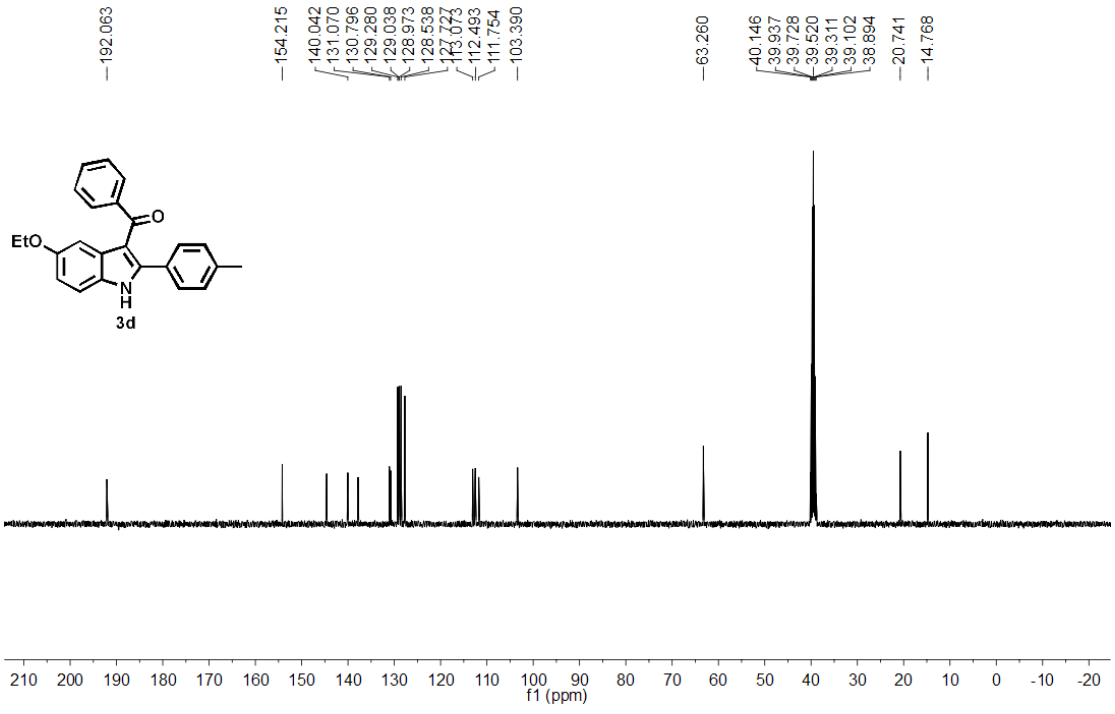
HF569
13CNMR IN CDC13



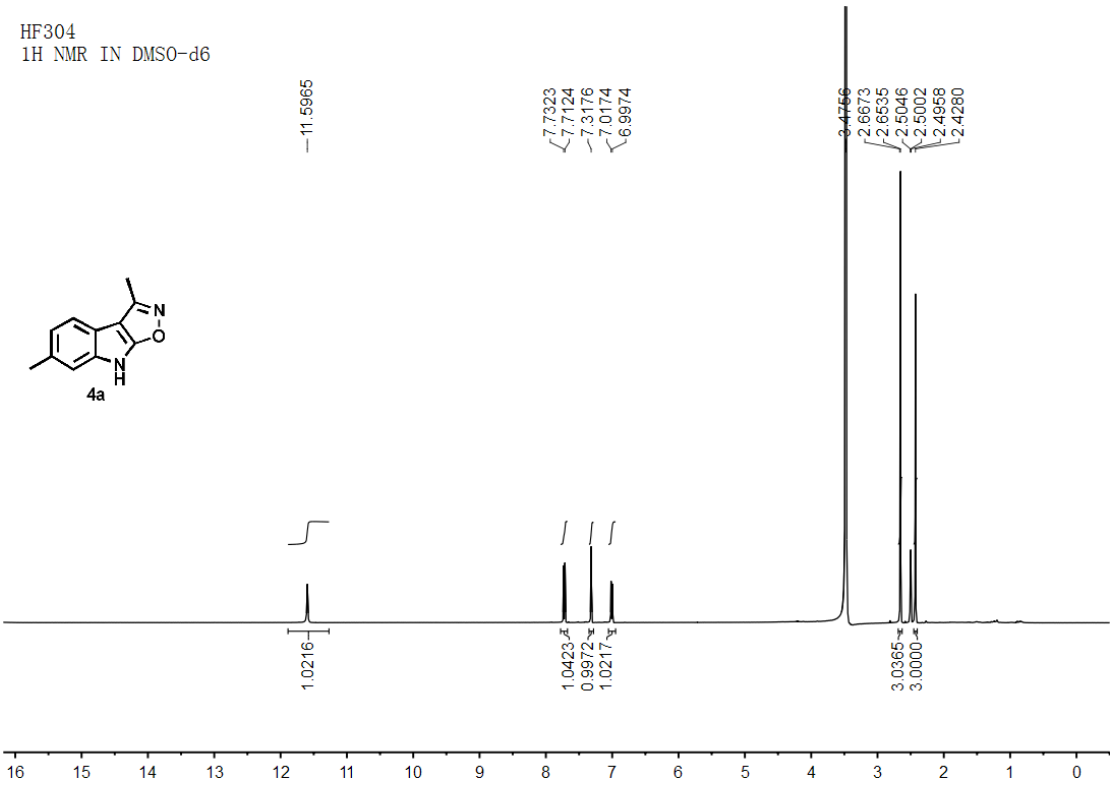
HF406
1H NMR IN DMSO-d6



HF406
13C NMR IN DMSO-d6

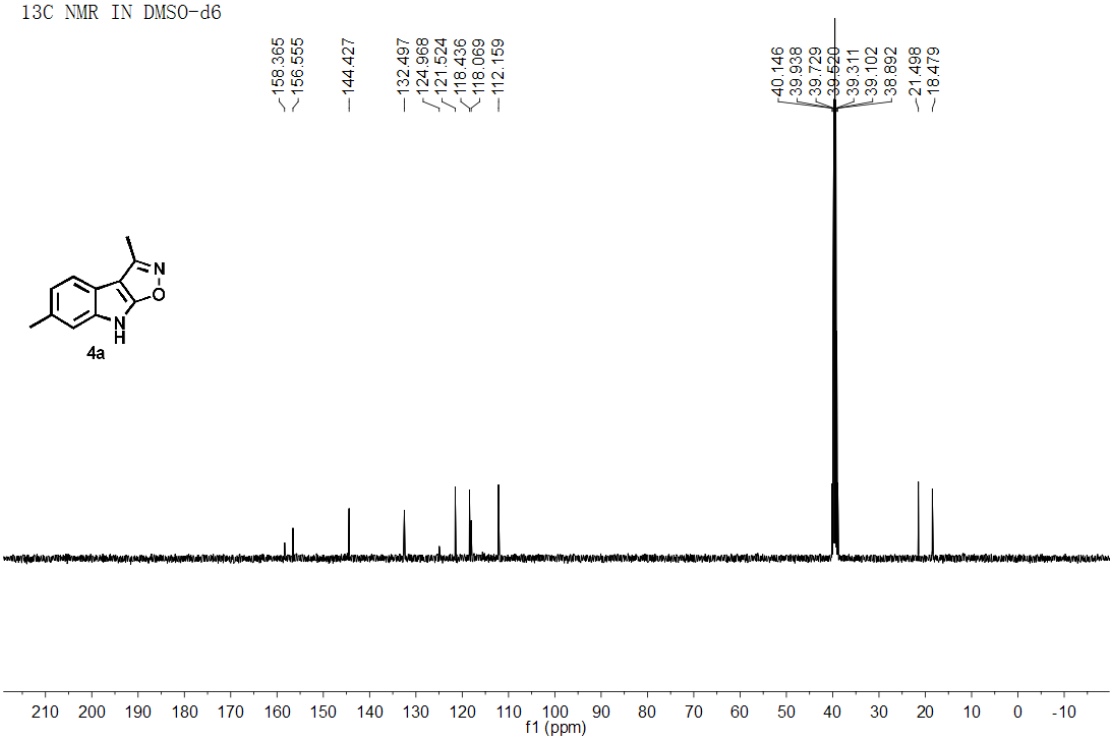


HF304
1H NMR IN DMSO-d6



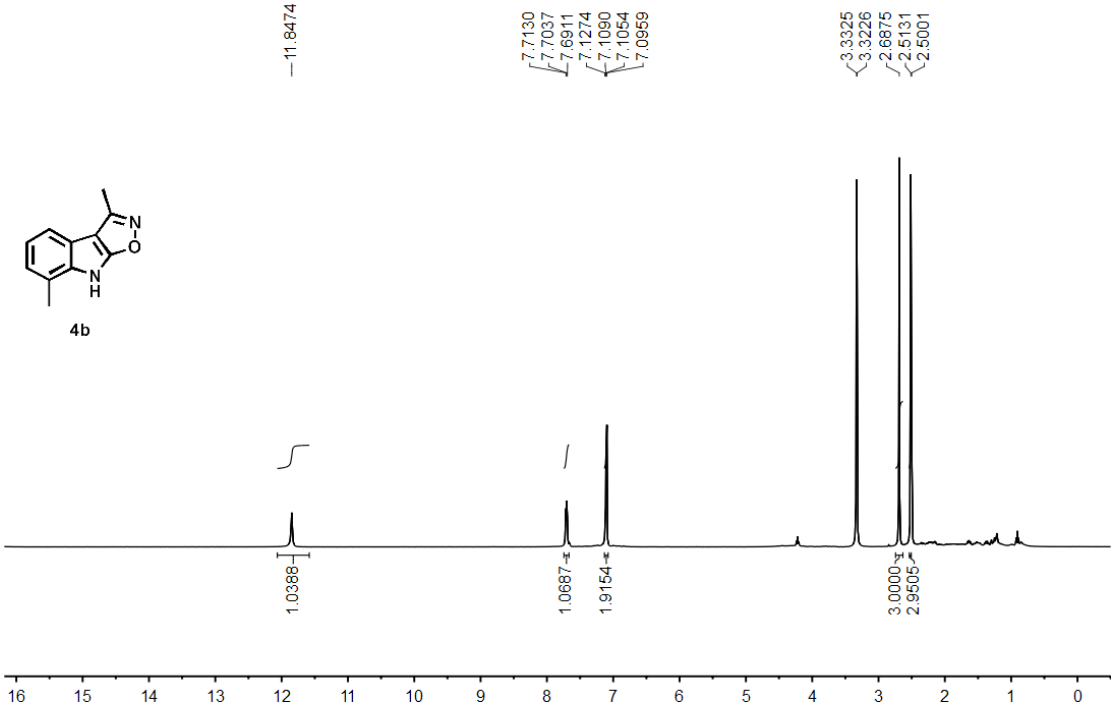
4a

HF304
13C NMR IN DMSO-d6



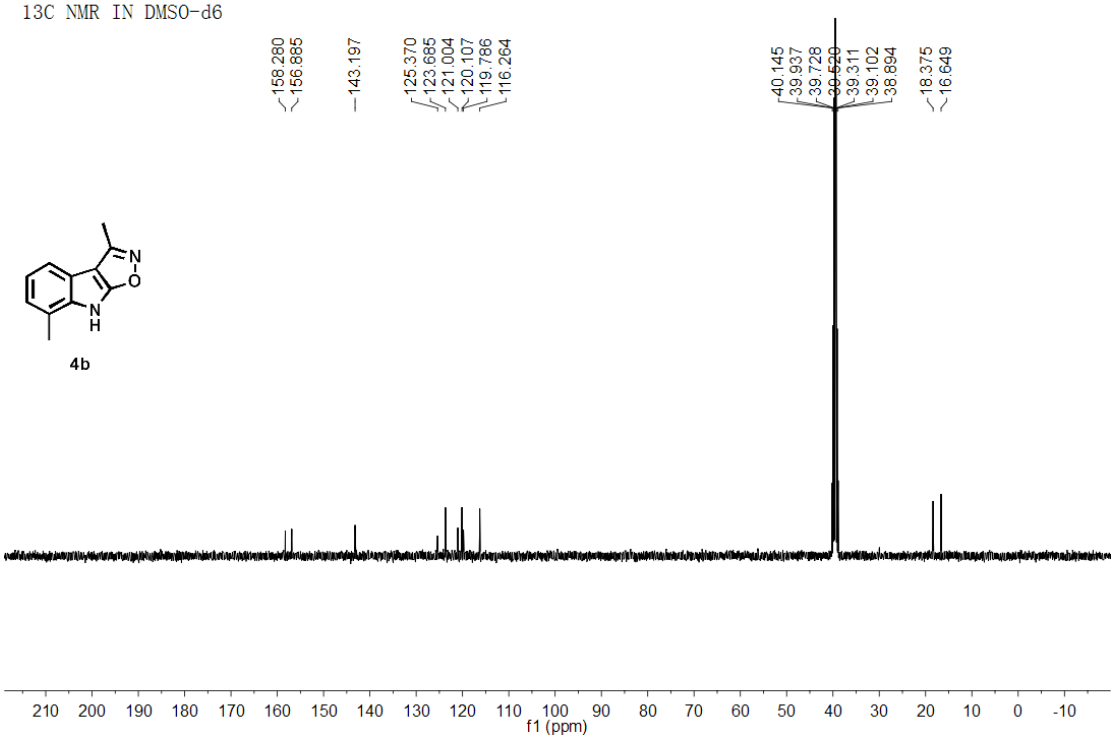
4a

HF296
1H NMR IN DMSO-d6



4b

HF296
13C NMR IN DMSO-d6



4b