Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Copper–Mediated Intramolecular C-H/N-H Cross–coupling of α-Alkenoyl Ketene N,S-Acetals to Pyrrolone Derivatives

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Experimental procedures and analytical data

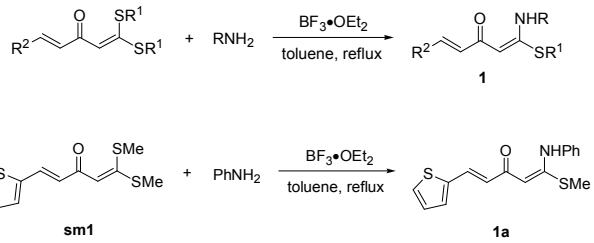
Contents:

1. General considerations

The solvents were dried and distilled prior to use by the literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX–400 spectrometer and all chemical shift values refer to δ_{TMS} = 0.00 ppm or $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the melting points were uncorrected. Analytical TLC plates, Sigma-Aldrich silica gel 60_{F200} were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

2. Experimental procedures

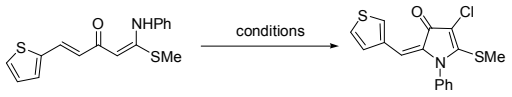
2.1. Preparation of α-alkenoyl ketene N,S-acetals (1)



A typical procedure for the synthesis of 1 – *Synthesis of 1a:* To a stirred solution of ketene S,S-acetal **sm1** (2.56 g, 10 mmol) and aniline (1.0 mL, 11 mmol) in toluene (30 mL) was added $BF_3{\cdot}Et_2O$ (0.13 mL, 1.0 mmol) and then heated to reflux. When TLC monitoring on silica gel indicated complete consumption of acetal **sm1**, the mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 30:1, v/v), affording **1a** (2.13 g, 71%) as a yellow solid.

2.2. Synthesis of pyrrolones 2 and 3 from the reactions of N,S-acetals 1

Table 1 Screening of conditions for the reaction of N,S-acetal **1a**



1a **2a**

Entry	[M]	Base	Solvent (v:v)	Temp. (°C)	Additive	Yield[a] (%)
1	$CuCl_2$	K_3PO_4	DMF	120		77
2	$CuCl_2$	K_3PO_4	DMF	140		73
3	$CuCl_2$	K_3PO_4	DMF	100		79
4	$CuCl_2$	K_3PO_4	DMF/DMSO (7:1)	120		76 (44)[b]
5	$CuCl_2$	K_3PO_4	DMF	80		81
6	$CuCl_2$	K_3PO_4	DMF	60		58
7	$CuCl_2$[e]	K_3PO_4	DMF	80		85
8	$CuCl_2$	K_3PO_4	CH_3CN	80		63
9	$CuCl_2$	K_3PO_4	DMSO	80		71
10	$CuCl_2$	K_3PO_4	DMF/DMSO (7:1)	80		70
11	$CuCl_2$	K_3PO_4	NMP	80		79
12	$CuCl_2$	Li_2CO_3	DMF	80		50
13	$CuCl_2$	Na_2CO_3	DMF	80		72
14	$CuCl_2$	K_2CO_3	DMF	80		76
15	$CuCl_2$	Cs_2CO_3	DMF	80		80
16	$CuCl_2$	K_3PO_4	DMF	80	LiCl	85
17	$CuCl_2$[e]	K_3PO_4	DMF	80	LiCl[f]	90
18	$CuCl_2$[e]	K_3PO_4	DMF	80	LiCl[g]	92
19	**$CuCl_2$[e]**	**K_3PO_4**	**DMF**	**80**	**LiCl**	**96 (86)[b]**
20		K_3PO_4	DMF	80	LiCl	0
21	$CuCl_2$[e]		DMF	80	LiCl	0
22[c]	$CuCl_2$[e]	K_3PO_4	DMF	80	LiCl	85
23[d]	$CuCl_2$[e]	K_3PO_4	DMF	80	LiCl	43
24	$CuCl_2 \cdot 2H_2O$	K_3PO_4	DMF	80	LiCl	65

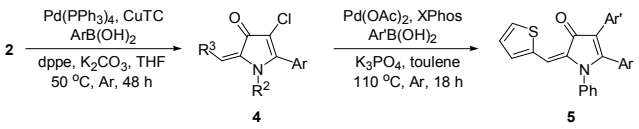
Conditions: **1a** (0.3 mmol), [M] (0.9 mmol), base (0.9 mmol), additive (0.9 mmol), solvent (3 mL), 0.1 MPa Ar, 2 h. [a] Determined by GC analysis with mesitylene as the internal standard. [b] Isolated yield given in parentheses. [c] In air. [d] In 0.1 MPa O_2. [e] 1.2 mmol. [f] 0.3 mmol. [g] 0.6 mmol.

A typical procedure for the synthesis of 2 and 3 – *Synthesis of (E)-2-Benzylidene-4-chloro-5-thiomethyl-1-phenyl-1H-pyrrol-3(2H)-one (2a):* Under an argon atmosphere, a mixture of ketene N,S-acetal **1a** (148 mg, 0.5 mmol), $CuCl_2$ (269 mg, 2.0 mmol), K_3PO_4 (424 mg, 2.0 mmol), and LiCl (64 mg, 1.5 mmol) in 5 mL DMF was stirred at 80 °C for 2 h. After cooled to ambient temperature, the resulting mixture was filtered through a short pad of celite and rinsed with 20 mL AcOEt, and washed with 10% aqueous $NH_3 \cdot H_2O$ (2×10 mL) and brine (10 mL). The organic

phase was dried over anhydrous Na_2SO_4 and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent:petroleum ether (60-90 ^oC)/AcOEt = 20:1, v/v) to afford **2a** as a red solid (144 mg, 86%).

Synthesis of (E)-4-bromo-5-thiomethyl-1-phenyl-2-(thiophen-2-ylmethylene)-1H-pyrrol-3(2H)-one (3a): Under an argon atmosphere, a mixture of ketene N,S-acetal **1a** (151 mg, 0.5 mmol), $CuBr_2$ (335 mg, 1.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), and LiBr (130 mg, 1.5 mmol) in 5 mL DMF was stirred at 80 ^oC for 2 h. After cooled to ambient temperature, the resulting mixture was filtered through a short pad of celite and rinsed with 20 mL AcOEt, and washed with 10% aqueous $NH_3 \cdot H_2O$ (2×10 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 ^oC)/AcOEt = 20:1, v/v) to afford **3a** as a red solid (151 mg, 80%).

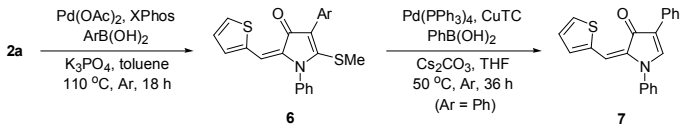
2.3. Functionalization of pyrrolones 2



Synthesis of (E)-4-chloro-1,5-diphenyl-2-(thiophen-2-ylmethylene)-1H-pyrrol-3(2H)-one (4a): Under a nitrogen atmosphere, a mixture of **2a** (200 mg, 0.6 mmol), phenylboronic acid (220 mg, 1.8 mmol), $Pd(PPh_3)_4$ (52 mg, 0.045 mmol), CuTC (229 mg, 1.2 mmol), dppe (18 mg, 0.045 mmol), and K_2CO_3 (176 mg, 0.5 mmol) in 10 mL THF was stirred at 50 ^oC for 48 h. After cooled to ambient temperature, the mixture was filtered through a short pad of celite and rinsed with 10 mL CH_2Cl_2. The combined filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 ^oC)/AcOEt = 30:1, v/v) to afford **4a** as a red solid (188 mg, 86%). **4b** was prepared in a similar fashion.

Synthesis of (E)-4-(4-methoxyphenyl)-1,5-diphenyl-2-(thiophen-2-ylmethylene)

-1H-pyrrol-3(2H)-one (5a): Under a nitrogen atmosphere, a mixture of **4a** (73 mg, 0.2 mmol), 4-methoxyphenylboronic acid (91 mg, 0.6 mmol), $Pd(OAc)_2$ (3 mg, 0.01 mmol), XPhos (10 mg, 0.02 mmol) and K_3PO_4 (85 mg, 0.4 mmol) in 3 mL toluene was stirred at 110 ^oC for 18 h. After cooled to ambient temperature, the resulting mixture was filtered through a short pad of celite and rinsed with 10 mL CH_2Cl_2. The combined filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether (60-90 ^oC)/AcOEt = 30:1, v/v) to afford **5a** as a red solid (80 mg, 92%). **5b** was prepared in a similar fashion.

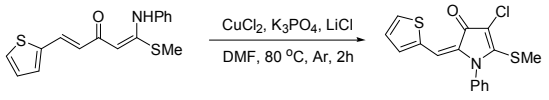


Synthesis of (E)-5-thiomethyl-1,4-diphenyl-2-(thiophen-3-ylmethylene)-1H-pyrrol-3(2H)-one (6a): Under a nitrogen atmosphere, a mixture of **2a** (100 mg, 0.3 mmol), phenylboronic acid (110 mg, 0.9 mmol), $Pd(OAc)_2$ (4 mg, 0.015 mmol), XPhos (15 mg, 0.03 mmol), and K_3PO_4 (128 mg, 0.6 mmol) in 3 mL toluene was stirred at 110 ^oC for 18 h. After cooled to ambient temperature, the resulting mixture was filtered through a short pad of celite and rinsed with 10 mL CH_2Cl_2. The combined filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 ^oC)/AcOEt = 30:1, v/v) to afford **6a** as a red solid (102 mg, 90%). **6b** was prepared in a similar fashion.

Synthesis of (E)-1,4-diphenyl-2-(thiophen-3-ylmethylene)-1H-pyrrol-3(2H)-one (7): Under a nitrogen atmosphere, a mixture of **6a** (100 mg, 0.27 mmol), phenylboronic acid (99 mg, 0.81 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), CuTC (103 mg, 0.54 mmol), and Cs_2CO_3 (176 mg, 0.54 mmol) in 3 mL THF was stirred at 50 ^oC for 48 h. After cooled to ambient temperature, the mixture was filtered through a short pad of celite and rinsed with 10 mL CH_2Cl_2. The combined filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel

column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 30:1, v/v) to afford **7** as a red solid (66 mg, 74%).

2.4. Radical trapping study



1a	radical scavenger	2a
	TEMPO (3 equiv)	0%
	BHT (3 equiv)	0%

Under an argon atmosphere, a mixture of ketene N,S-acetals **1a** (151 mg, 0.5 mmol), $CuCl_2$ (202 mg, 1.5 mmol), K_3PO_4 (318 mg, 1.5 mmol), TEMPO or BHT (2,6-di-*tert*-butyl-4-methylphenol) (1.5 mmol) and LiCl (64 mg, 1.5 mmol) in 5 mL DMF stirred at 80 °C for 2 h. The resultant mixture was cooled to ambient temperature and subject to GC analysis by using mesitylene as the internal standard. The desired product **2a** was not detected from the reaction mixture.

3. X–Ray crystallographic studies

Single crystals for the X–ray diffraction studies for compounds **2a** 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 999801 for **2a**. 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).

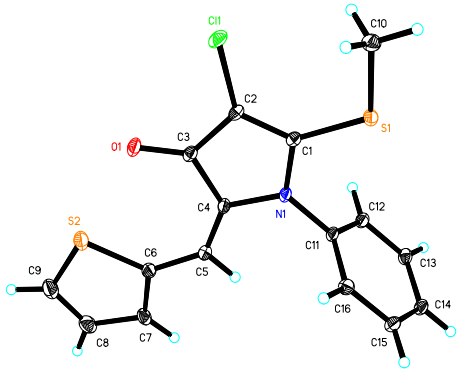
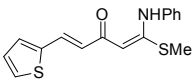


Figure 1 Molecular structure of **2a**.

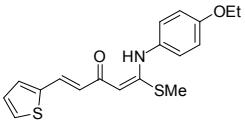
Table 2 Crystal data and structure refinement for **2a**

Empirical formula	$C_{16}H_{12}NOS_2Cl$	
Formula weight	333.84	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	triclinic, P -1	
Unit cell dimensions	a = 7.4568(11) Å	alpha = 110.442(3)°
	b = 10.4808(16) Å	beta = 98.772(4) °
	c = 10.804(3) Å	gamma = 103.159(2)°
Volume	745.1(2) $Å^3$	
Z, Calculated density	2, 1.488 Mg/m^3	
Absorption coefficient	0.533 mm^{-1}	
F(000)	344	
Crystal size	0.150 x 0.130 x 0.080 mm	
Theta range for data collection	2.080 to 30.554°	
Limiting indices	-10<=h<=10, -14<=k<=14, -12<=l<=15	
Reflections collected/unique	7423/4501 [R(int) = 0.0231]	
Completeness to theta = 30.554	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5764	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4501 / 0 / 191	
Goodness-of-fit on F^2	1.071	
Final R indices [I > 2 sigma(I)]	R1 = 0.0399, wR2 = 0.1230	
R indices (all data)	R1 = 0.0480, wR2 = 0.1347	
Largest diff. peak and hole	0.626 and -0.566 $e.Å^{-3}$	

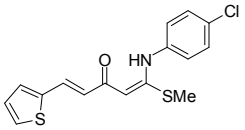
4. Analytical data



(1*E*,4*E*)-1-(Thiomethyl)-1-(phenylamino)-5-(thiophen-2-yl)penta-1,4-dien-3-one (1a)： Yellow solid. M.p.: 93-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.67 (s, 1 H, NH), 7.73 and 6.57 (d each, *J* = 15.4 Hz, 1:1 H, CH=CH), 7.36 and 7.30 (m each, 2:3 H, aromatic CH), 7.23 and 7.03 (t each, 2:1 H, thienyl CH), 5.32 (s, 1 H, CH=C-S), 2.38 (d, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.8 (Cq, C=O), 167.4 (Cq, *C*SMe), 141.2 (Cq, thienyl *C*-CH=CH), 138.3 (Cq, aromatic C-N), 131.2 and 127.4 (thienyl C-*C*H=*C*H), 130.0, 128.0, and 127.0 (thienyl CH), 129.1, 126.3, and 125.0 (aromatic CH), 93.4 (*C*H=C-S), 14.7 (SCH_3). HRMS Calcd for $C_{16}H_{16}NOS_2$ $[M+H]^+$: 302.0668; Found: 302.0677.

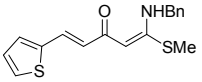


(1*E*,4*E*)-1-(4-Ethoxyphenylamino)-1-(thiomethyl)-5-(thiophen-2-yl)penta-1,4-dien-3-one (1b): Yellow solid. M.p.: 129-131 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.35 (s, 1 H, NH), 7.69 and 6.55 (d each, *J* = 15.4 Hz, 1:1 H, CH=CH), 7.29 (d), 7.21 (d), and 7.0 (m) (1:1:1 H, thienyl CH), 7.18 and 6.87 (d each, *J* = 8.9 Hz, 2:2 H, aromatic CH), 5.27 (s, 1 H, CH=C-S), 4.03 (q, 2 H, O*C*H_2), 2.37 (s, 3 H, SCH_3), 1.41 (t, 3 H, OCH_2*C*H_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.9 (Cq, C=O), 168.6 (Cq, *C*SMe), 157.8 (Cq, aromatic *C*-O), 141.5 (Cq, thienyl *C*-CH=CH), 131.0 and 128.1 (thienyl CH), 129.75 and 127.7 (thienyl C-*C*H=*C*H), 127.1 and 114.9 (aromatic CH), 127.0 (Cq, aromatic C-N), 92.8 (*C*H=C-S), 63.8 (O*C*$H_2$$CH_3$), 14.9 ($OCH_2$*C*$H_3$), 14.7 ($SCH_3$). HRMS Calcd for $C_{18}H_{19}NO_2S_2Na$ $[M+Na]^+$: 368.0755; Found: 368.0760.

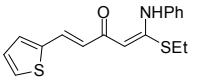


(1*E*,4*E*)-1-(4-Chlorophenylamino)-1-(thiomethyl)-5-(thiophen-2-yl)penta-1,4-dien-3-one (1c): Yellow solid. M.p.: 95-97 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.65 (s, 1 H, NH), 7.71 and 6.55 (d each, *J* = 15.4 Hz, 1:1 H, CH=CH), 7.32, 7.23, and 7.02 (1:1:1 H, thienyl CH), 7.30 and 7.22 (d each, 2:2 H, aromatic CH), 5.32 (s, 1 H, CH=C-S), 2.39 (d, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.0 (Cq, C=O),

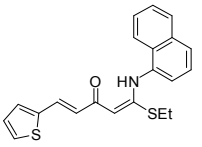
167.1 (Cq, *C*SMe), 141.2 (Cq, thienyl *C*-CH=CH), 137.1 (Cq, aromatic C-N), 131.7(Cq, aromatic *C*-Cl), 131.5 and1 27.1 (thienyl C-*C*H=*C*H), 130.0, 128.1, and 127.2 (thienyl CH), 129.2 and 126.1 (aromatic CH), 93.9 (*C*H=C-S), 14.7 (SCH_3). HRMS Calcd for $C_{16}H_{14}NOS_2ClNa$ $[M+Na]^+$: 358.0103; Found: 358.0108.



(1*E*,4*E*)-1-(Benzylamino)-1-(thiomethyl)-5-(thiophen-2-yl)penta-1,4-dien-3-one (1d): Yellow solid. M.p.: 80-82 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 12.27 (s, 1 H, NH), 7.66 and 6.52 (d each, *J* = 15.4 Hz, 1:1 H, CH=CH), 7.35 and 7.29 (m each, 4:1 H, aromatic CH), 7.27, 7.18, and 7.01 (1:1:1 H, thienyl CH), 5.15 (s, 1 H,CH=C-S), 4.57 (d, 2 H, N-CH_2), 2.41 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.4 (Cq, C=O), 169.5 (Cq, *C*SMe), 141.5 (Cq, thienyl *C*-CH=CH), 137.1 and 127.9 (thienyl C-*C*H=*C*H), 130.4, 129.4, and 127.7 (thienyl CH), 128.8, 127.3, and 126.7 (aromatic CH), 127.8 (Cq, *i*-C of Ph), 91.7 (*C*H=C-S), 48.0 (Ph-*C*H_2), 14.4 (SCH_3). HRMS Calcd for $C_{17}H_{18}NOS_2$ $[M+H]^+$: 316.0824; Found: 316.0834.

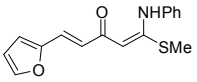


(1*E*,4*E*)-1-(Thioethyl)-1-(phenylamino)-5-(thiophen-2-yl)penta-1,4-dien-3-one (1e)： Yellow solid. M.p.: 123-126 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 13.70 (s, 1 H, NH), 7.71 and 6.55 (d each, *J* = 15.4 Hz, 1:1 H, CH=CH), 7.37, 7.31, and 7.03 (m each, 2:2:1 H, aromatic CH), 7.29 and 7.23 (1:2 H, thienyl CH), 5.38 (s, 1 H, CH=C-S), 2.92 (q, 2 H, SCH_2), 1.35 (t, 3 H, SCH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.9 (Cq, C=O), 166.5 (Cq, *C*SEt), 141.4 (Cq, thienyl *C*-CH=CH), 138.5 (Cq, aromatic C-N), 131.2 and 127.5 (thienyl C-*C*H=*C*H), 129.9, 127.0, and 126.3 (thienyl CH), 129.1, 128.1, and 125.0 (aromatic CH), 94.3 (*C*H=C-S), 26.1 (S$CH_2$$CH_3$), 13.5 ($SCH_2CH_3$). HRMS Calcd for $C_{17}H_{18}NOS_2$ $[M+H]^+$: 316.0824; Found: 316.0830.

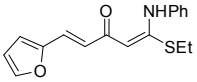


(1*E*,4*E*)-1-(Thioethyl)-1-(naphthalen-1-ylamino)-5-(thiophen-2-yl)penta-1,4-dien-3-one (1f)： Yellow solid. M.p.: 95-98 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 14.17

(d, 1 H, NH), 8.19 (d), 7.78 (d), and 7.46 (t) (1:1:1 H, aromatic CH), 7.85 (m, 2 H, 1 H of aromatic CH and 1 H of CH=CH), 7.55 (m, 3 H, aromatic CH), 7.28 (m) and 7.03 (t) (2:1 H, thienyl CH), 6.69 (d, *J* = 15.4 Hz, 1 H, CH=CH), 5.52 (s, 1 H,CH=C-S), 2.86 (m, 2 H, SCH_2), 1.26 (m, 3 H, $SCH_2\mathit{CH_3}$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.7 (Cq, C=O), 168.0 (Cq, *C*SEt), 141.2 (Cq, thienyl *C*-CH=CH), 134.5 (Cq, naphthyl C-N), 134.1 and 129.2 (Cq, *i*-C of naphthyl), 131.1, 129.7, 128.2, 127.9, 127.3, 127.2, 126.9, 126.8, 126.5, 124.9, 123.3, and 122.75 (aromatic CH), 94.2 (*C*H=C-S), 25.8 (SCH_2CH_3), 13.2 ($SCH_2\mathit{CH_3}$). HRMS Calcd for $C_{21}H_{20}NOS_2$ $[M+H]^+$: 366.0986; Found: 366.0990.

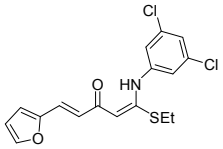


(1*E*,4*E*)-5-(Furan-2-yl)-1-(thiomethyl)-1-(phenylamino)penta-1,4-dien-3-one (1g): Yellow solid. M.p.: 68-70 °C. ^1H NMR (400 MHz, CDCl3) δ 13.74 (s, 1 H, NH), 7.38 (m, 2 H, 1 H of CH=CH, 1 H of furyl CH), 7.29 (m), 7.24 (t), and 7.13 (m) (2:2:1 H, aromatic CH), 6.65 (d, J = 15.5 Hz, 1 H, CH=CH), 6.48 (d) and 6.37 (m, 1:1 H, furyl CH), 5.29 (s, 1 H, CH=C-S), 2.25 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.5 (Cq, C=O), 166.8 (Cq, *C*SMe), 152.0 (Cq, furyl *C*-CH=CH), 143.5, 128.7, and 111.9 (furyl CH), 138.1 (Cq, aromatic C-N), 124.3 and 113.0 (aromatic CH), 125.9 and 124.9 (CH=CH), 93.4 (*C*H=C-S), 14.2 (SCH_3). HRMS Calcd for $C_{16}H_{16}NO_2S$ $[M+H]^+$: 286.0902; Found: 286.0892.

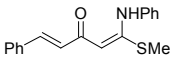


(1*E*,4*E*)-1-(Thioethyl)-5-(furan-2-yl)-1-(phenylamino)penta-1,4-dien-3-one (1h): Yellow solid. M.p.: 81-84 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 13.70 (s, 1 H, NH), 7.45, 6.54, and 6.45 (m each, 1:1:1 H, furyl CH), 7.36 (m, 3 H, 1 H of CH=CH, and 2 H of aromatic CH), 7.30 and 7.22 (m each, 2:1 H, aromatic CH), 6.65 (d, *J* = 15.5 Hz, 1 H, CH=CH), 5.39 (s, 1 H, CH=C-S), 2.91 (q, 2 H, SCH_2), 1.35 (t, 3 H, $SCH_2\mathit{CH_3}$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.4 (Cq, C=O), 165.9 (Cq, *C*SEt), 152.0 (Cq, furyl *C*-CH=CH), 143.5, 125.8, and 112.0 (furyl CH), 138.2 (Cq, aromatic C-N), 128.7, 124.4, and 112.9 (aromatic CH), 126.0 and 124.8 (CH=CH), 94.2

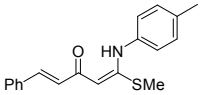
(*C*H=C-S), 25.7 (S*CH*$_2$CH$_3$), 13.1(SCH$_2$*CH*$_3$). HRMS Calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1058; Found: 300.1066.



(1*E*,4*E*)-1-(3,5-Dichlorophenylamino)-1-(thioethyl)-5-(furan-2-yl)penta-1,4-dien-3-one (1i): Yellow solid. M.p.: 90-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.86 (s, 1 H, NH), 7.45(d), 6.56 (d) and 6.45(dd) (*J* = 3.4 Hz, 1.8 Hz, 1:1:1 H, furyl CH), 7.35 and 6.60 (d each, *J* = 15.4 Hz, 1:1 H, CH=CH), 7.21 (d) and 7.16 (t) (2:1 H, aromatic CH), 5.42 (s, 1 H), 2.93 (q, 2 H, S*C*H$_2$), 1.37 (t, 3 H, SCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.9 (Cq, C=O), 165.2 (Cq, *C*SEt), 152.3 (Cq, furyl *C*-CH=CH), 144.1, 125.5, and 112.4 (furyl CH), 141.2 (Cq, aromatic *C*-N), 135.2 (Cq, 2×*C*-Cl), 126.0 and 125.4 (CH=CH), 122.6 and 113.9 (aromatic CH), 96.0 (*C*H=C-S), 26.4 (S*CH*$_2$CH$_3$), 13.5 (SCH$_2$*CH*$_3$). HRMS Calcd for $C_{17}H_{16}NO_2SCl_2$ $[M+H]^+$: 368.0279; Found: 368.0275.

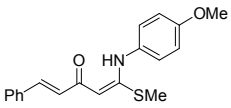


(1*E*,4*E*)-1-(Thiomethyl)-5-phenyl-1-(phenylamino)penta-1,4-dien-3-one (1j): Yellow solid. M.p.: 71-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.74 (s, 1 H, NH), 7.63 and 6.78 (d each, *J* = 15.7 Hz, 1:1 H, CH=CH), 7.58 (d) and 7.34 (m) (2:3 H, aromatic CH), 7.37, 7.31, and 7.23 (m each, 3:1:1 H, aromatic CH), 5.39 (s, 1 H, CH=C-S), 2.38 (d, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, CDCl3) δ 183.3 (Cq, C=O), 167.5 (Cq, *C*SMe), 138.4 and 128.2 (*C*H=*C*H), 138.3 (Cq, aromatic C-N), 129.3 (Cq, *i*-C of Ph), 135.8, 129.0, 128.8, 127.9, 126.3, and 124.9 (aromatic CH), 93.4 (*C*H=C-S), 14.7 (SCH_3). HRMS Calcd for $C_{18}H_{17}NOSNa$ $[M+Na]^+$: 318.0929; Found: 318.0923.

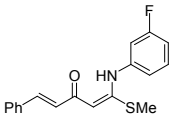


(1*E*,4*E*)-1-(Thiomethyl)-5-phenyl-1-(*p*-tolylamino)penta-1,4-dien-3-one (1k): Yellow solid. M.p.: 87-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.64 (s, 1 H, NH), 7.63 and 6.78 (d each, *J* = 15.7 Hz, 1:1 H, CH=CH), 7.57, 7.37, and 7.33 (m each, 2:2:1 H, aromatic CH), 7.21 and 7.17 (d each, *J* = 8.5 Hz, 2:2 H, aromatic CH), 5.37 (s, 1 H,

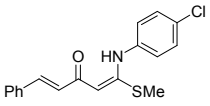
CH=C-S), 2.38 (s, 3 H, C_6H_4-*CH_3*), 2.36 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.2 (Cq, C=O), 167.9 (Cq, *C*SMe), 138.2 and 128.3 (*C*H=*C*H), 136.3 (Cq, aromatic C-N), 135.8 (Cq, *i*-C of Ph), 135.7 (Cq, aromatic *C*-Me), 129.7, 129.2, 128.7, 127.8, and 125.0 (aromatic CH), 93.1 (*C*H=C-S), 21.0 (C_6H_4-*CH_3*), 14.6 (SCH_3). HRMS Calcd for $C_{19}H_{20}NOS$ $[M+H]^+$: 310.1266; Found: 310.1257.



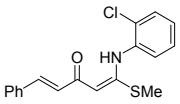
(1*E*,4*E*)-1-(4-Methoxyphenylamino)-1-(thiomethyl)-5-phenylpenta-1,4-dien-3-one (1l): Yellow solid. M.p.: 113-116 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 13.45 (s, 1 H, NH), 7.60 and 6.76 (d each, *J* = 15.7 Hz, 1:1 H, *CH*=*CH*Ph), 7.56, 7.37, and 7.32 (m each, 2:2:1 H, aromatic CH), 7.21 and 6.89 (d each, *J* = 8.8 Hz, 2:2 H, aromatic CH), 5.34 (s, 1 H, CH=C-S), 3.80 (d, 3 H, O*C*H_3), 2.37 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.3 (Cq, C=O), 168.6 (Cq, *C*SMe), 158.4 (Cq, aromatic C-O), 138.2 and 128.4 (*C*H=*C*H), 135.9 (Cq, aromatic *C*-N), 131.1 (Cq, *i*-C of Ph), 129.3, 128.8, 127.9, 127.1, and 114.3 (aromatic CH), 92.8 (*C*H=C-S), 55.5 (C_6H_4-O*CH_3*), 14.6 (SCH_3). HRMS Calcd for $C_{19}H_{20}NO_2S$ $[M+H]^+$: 326.1215; Found: 326.1216.



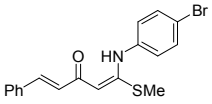
(1*E*,4*E*)-1-(3-Fluorophenylamino)-1-(thiomethyl)-5-phenylpenta-1,4-dien-3-one (1m): Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 13.83 (s, 1 H, NH), 7.62 and 6.76 (d each, *J* = 15.7 Hz, 1:1 H, CH=CH), 7.56, 7.28, and 6.90 (m each, 2:1:1 H, aromatic CH), 7.36 and 7.08 (m each, 3:2 H, aromatic CH), 5.40 (s, 1 H, CH=C-S), 2.40 (d, *J* = 1.8 Hz, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.4 (Cq, C=O), 166.8 (Cq, *C*SMe), 162.8 (d and Cq, *J* = 246.9 Hz, aromatic *C*-F), 140.2 (d and Cq, *J* = 9.9 Hz, aromatic C-N), 138.9 and 129.4 (*C*H=*C*H), 135.6 (Cq, *i*-C of Ph), 130.2 (d, *J* = 9.3 Hz), 128.8, 127.9, 120.1, 112.7 (d, *J* = 21.2 Hz), and 111.6 (d, *J* = 23.9 Hz) (aromatic CH), 94.1 (*C*H=C-S), 14.7 (SCH_3). HRMS Calcd for $C_{18}H_{17}NOSF$ $[M+H]^+$: 314.1015; Found: 314.1016.



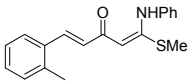
(1*E*,4*E*)-1-(4-Chlorophenylamino)-1-(thiomethyl)-5-phenylpenta-1,4-dien-3-one (1n): Yellow solid. M.p.: 88-91 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.71 (s, 1 H, NH), 7.60 and 6.75 (d each, *J* = 15.7 Hz, 1:1 H, CH=CH), 7.56 and 7.24 (d each, *J* = 8.6 Hz, 2:2 H, aromatic CH), 7.35 (m, 5 H, aromatic CH), 5.39 (d, 1 H, CH=C-S), 2.40 (d, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.5 (Cq, C=O), 167.2 (Cq, *C*SMe), 138.8 and 128.0 (*C*H=*C*H), 137.1, 135.7, and 131.7 (Cq each), 129.5, 129.2, 128.8, 127.9, and 126.1 (aromatic CH), 93.9 (*C*H=C-S), 14.8 (SCH_3). HRMS Calcd for $C_{18}H_{17}NOSCl$ $[M+H]^+$: 330.0719; Found: 330.0728.



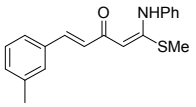
(1*E*,4*E*)-1-(2-Chlorophenylamino)-1-(thiomethyl)-5-phenylpenta-1,4-dien-3-one (1o): Yellow solid. M.p.: 84-88 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.60 (s, 1 H, NH), 7.59 and 6.72 (d each, *J* = 15.7 Hz, 1:1 H, CH=CH), 7.51, 7.29, and 7.32 (m each, 2:1:2 H, aromatic CH), 7.44, 7.41, 7.20, and 7.12 (m each, 1:1:1:1 H, aromatic CH), 5.40 (s, 1 H, CH=C-S), 2.35 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.4 (Cq, C=O), 167.2 (Cq, *C*SMe), 139.1 and 130.2 (*C*H=*C*H), 136.3, 135.8, and 129.7 (Cq each), 129.5, 128.9, 128.0, 127.9, 127.4, 127.0, and 126.9 (aromatic CH), 94.5 (*C*H=C-S), 14.9 (SCH_3). HRMS Calcd for $C_{18}H_{17}NOSCl$ $[M+H]^+$: 330.0719; Found: 330.0725.



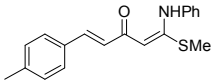
(1*E*,4*E*)-1-(4-Bromophenylamino)-1-(thiomethyl)-5-phenylpenta-1,4-dien-3-one (1p): Yellow solid. M.p.: 101-104 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.73 (s, 1 H, NH), 7.61 and 6.75 (d each, *J* = 15.7 Hz, 1:1 H, CH=CH), 7.56 and 7.35 (m each, 2:3 H, aromatic CH), 7.46 and 7.17 (d each, *J* = 8.7 Hz, 2:2 H, aromatic CH), 5.39 (s, 1 H, CH=C-S), 2.39 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.4 (Cq, C=O), 166.9 (Cq, *C*SMe), 138.8 and 128.0 (*C*H=*C*H), 137.6 (Cq, aromatic C-N), 135.7 (Cq, *i*-C of Ph), 132.1, 129.4, 128.8, 127.9, and 126.3 (aromatic CH), 119.4 (Cq, aromatic C-Br), 93.9 (*C*H=C-S), 14.72 (SCH_3). HRMS Calcd for $C_{18}H_{17}NOSBr$ $[M+H]^+$: 374.0214; Found: 374.0217.



(1*E*,4*E*)-1-(Thiomethyl)-1-(phenylamino)-5-o-tolylpenta-1,4-dien-3-one (1q): Yellow solid. M.p.: 64-67 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.73 (s, 1 H, NH), 7.88 and 6.64 (d each, *J* = 15.6 Hz, 1:1 H, CH=CH), 7.56, 7.30 and 7.26 (m each, 1:2:2 H, aromatic CH), 7.15 (m, 4 H, aromatic CH), 5.33 (s, 1 H, CH=C-S), 2.42 (s, 3 H, SCH_3), 2.30 (m, 3 H, C_6H_4-CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.2 (Cq, C=O), 167.4 (Cq, *C*SMe), 138.3, 137.4, and 134.6 (Cq each), 136.0 and 126.0 (*C*H=*C*H), 130.6, 129.2, 129.0, 128.9, 126.2, 126.1, and 124.7 (aromatic CH), 93.6 (*C*H=C-S), 19.8 (C_6H_4-*C*H_3), 14.6 (SCH_3). HRMS Calcd for $C_{19}H_{20}NOS$ $[M+H]^+$: 310.1260; Found: 310.1268.

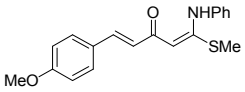


(1*E*,4*E*)-1-(Thiomethyl)-1-(phenylamino)-5-m-tolylpenta-1,4-dien-3-one (1r): Yellow solid. M.p.: 66-69 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.89 (s, 1 H, NH), 7.71 and 6.87 (d each, J = 15.7 Hz, 1:1 H, CH=CH), 7.46, 7.42, and 7.28 (m each, 2:1:1 H, aromatic CH), 7.39, 7.33, and 7.21 (m each, 3:1:1 H, aromatic CH), 5.47 (s, 1 H, CH=C-S), 2.44 (s, 3 H, SCH_3), 2.41 (t, *J* = 2.8 Hz, 3 H, C_6H_4-CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.6 (Cq, C=O), 167.5 (Cq, *C*SMe), 138.8 and 126.4 (*C*H=*C*H), 138.6, 138.5, and 135.9 (Cq each), 130.3, 129.2, 128.8, 128.6, 128.2, 125.3, 125.1 (aromatic CH), 93.5 (*C*H=C-S), 21.5 (C_6H_4-*C*H_3), 14.8 (SCH_3). HRMS Calcd for $C_{19}H_{20}NOS$ $[M+H]^+$: 310.1260; Found: 310.1267.

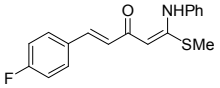


(1*E*,4*E*)-1-(Thiomethyl)-1-(phenylamino)-5-p-tolylpenta-1,4-dien-3-one (1s): Yellow solid. M.p.: 118-121 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.72 (s, 1 H, NH), 7.64 and 6.77 (d each, J = 15.7 Hz, 1:1 H, CH=CH), 7.52 and 7.23 (d each, *J* = 8.0 Hz, 2:2 H, aromatic CH), 7.41, 7.36, and 7.29 (m each, 2:2:1 H, aromatic CH), 5.42 (s, 1 H, CH=C-S), 2.45 (s, 3 H, C_6H_4-CH_3), 2.42 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 183.7 (Cq, C=O), 167.33 (Cq, *C*SMe), 139.7 (Cq, aromatic *C*-Me), 138.7 and 127.3 (*C*H=*C*H),138.6 (Cq, aromatic C-N), 133.1, 129.6, 129.1, 128.0, and 125.1

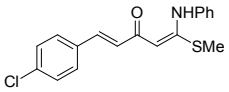
(aromatic CH), 126.3 (Cq, *i*-C of C_6H_4), 93.5 (*C*H=C-S), 21.5 (C_6H_4-*C*H_3), 14.8 (SCH_3). HRMS Calcd for $C_{19}H_{20}NOS$ $[M+H]^+$: 310.1260; Found: 310.1262.



(1*E*,4*E*)-5-(4-Methoxyphenyl)-1-(thiomethyl)-1-(phenylamino)penta-1,4-dien-3-one (1t): Yellow solid. M.p.: 98-100 °C. ^{1}H NMR (400 MHz, CDCl3) δ 13.66 (s, 1 H, NH), 7.57 and 6.64 (d each, J = 15.7 Hz, 1:1 H, CH=CH), 7.51 and 6.89 (d each, J = 8.7 Hz, 2:2 H, aromatic CH),7.36, 7.30, and 7.21 (m each, 2:2:1 H, aromatic CH) 5.35 (s, 1 H, CH=C-S), 3.81 (s, 3 H, OCH_3), 2.38 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, CDCl3) δ 183.8 (Cq, C=O), 167.0 (Cq, *C*SMe), 160.8 (Cq, aromatic C-O), 138.5 (Cq, aromatic C-N), 138.3 and 126.0 (*C*H=*C*H), 129.5, 129.1, 126.2, 124.9, and 114.3 (aromatic CH), 128.5 (Cq, *i*-C of C_6H_4), 93.4 (*C*H=C-S), 55.4 (OCH_3), 14.7 (SCH_3). HRMS Calcd for $C_{19}H_{20}NO_2S$ $[M+Na]^+$: 348.1034; Found: 348.1032.

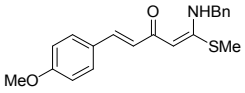


(1*E*,4*E*)-5-(4-Fluorophenyl)-1-(thiomethyl)-1-(phenylamino)penta-1,4-dien-3-one (1u)： Yellow solid. M.p.: 109-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.84 (s, 1 H, NH), 7.61 and 6.71 (d each, J = 15.7 Hz, 1:1 H, CH=CH), 7.52, and 7.04 (d each, *J* = 8.7 Hz, 2:2 H, aromatic CH), 7.35, 7.31, and 7.21 (m each, 2:2:1 H, aromatic CH), 5.39 (s, 1 H,CH=C-S), 2.34 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.6 (Cq, C=O), 167.1 (Cq, *C*SMe), 163.0 (d, *J* = 248.2 Hz, Cq, aromatic C-F), 138.1 and 127.8 (d, *J* = 2.2 Hz, *C*H=*C*H), 136.8 (Cq, aromatic C-N), 131.7 (d, *J* = 3.3 Hz, Cq, *i*-C of C_6H_4), 129.3 (d, *J* = 8.3 Hz, aromatic *C*-C-C-F), 128.8, 125.9, and 124.4 (aromatic CH), 115.5 (d, *J* = 21.6 Hz, aromatic *C*-C-F), 93.2 (*C*H=C-S), 14.3 (SCH_3). HRMS Calcd for $C_{18}H_{17}NOSF$ $[M+H]^+$: 314.1015; Found: 314.1011.

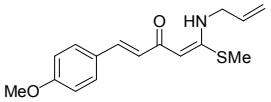


(1*E*,4*E*)-5-(4-Chlorophenyl)-1-(thiomethyl)-1-(phenylamino)penta-1,4-dien-3-one (1v): Yellow solid. M.p.: 104-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.70 (s, 1 H, NH), 7.54 and 6.72 (d each, J = 15.7 Hz, 1:1 H, CH=CH), 7.47, 7.37, and 7.23 (m each, 2:2:1 H, aromatic CH), 7.31 (m, 4 H, aromatic CH), 5.36 (s, 1 H, CH=C-S), 2.39 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.9 (Cq, C=O), 167.9 (Cq,

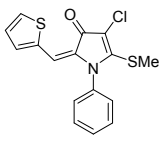
*C*SMe), 138.4 (Cq, aromatic C-N), 137.0 and126.5 (*C*H=*C*H), 135.1 (Cq, aromatic C-Cl), 134.4, 129.1, 129.0, 129.0, and 125.0 (aromatic CH), 128.8 (Cq, *i*-C of C_6H_4), 93.5 (*C*H=C-S), 14.8 (SCH_3). HRMS Calcd for $C_{18}H_{17}NOSCl$ $[M+H]^+$: 330.0719; Found: 330.0723.



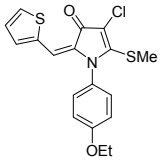
(1*E*,4*E*)-1-(Benzylamino)-5-(4-methoxyphenyl)-1-(thiomethyl)penta-1,4-dien-3-one (1w): Yellow solid. M.p.: 117-119 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1 H, NH), 7.49 (m, 3 H, 1 H of CH=CH and 2 H of aromatic CH), 7.35 and 7.27 (m each, 4:1 H, aromatic CH), 6.88 (d, *J* = 8.8 Hz, 2 H, aromatic CH), 6.59 (d, *J* = 15.7 Hz, 1 H of CH=CH), 5.18 (s, 1 H, CH=C-S), 4.58 (d, 2 H, Ph-*CH_2*), 3.81 (s, 3 H, OCH_3), 2.41 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.3 (Cq, C=O), 169.2 (Cq, *C*SMe), 160.6 (Cq, aromatic C-O), 137.5 and 126.4 (*C*H=*C*H), 137.3 (Cq, aromatic *C*-CH_2), 129.3, 128.9, 127.7, 127.4, and 114.3 (aromatic CH), 128.8 (Cq, *i*-C of C_6H_4), 91.6 (*C*H=C-S), 55.4 (OCH_3), 48.0 (Ph-*CH_2*), 14.4 (SCH_3). HRMS Calcd for $C_{20}H_{22}NOS$ $[M+H]^+$: 340.1366; Found: 340.1378.



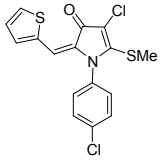
(1*E*,4*E*)-1-(Allylamino)-5-(4-methoxyphenyl)-1-(thiomethyl)penta-1,4-dien-3-one (1x): Yellow liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 11.91 (t, *J* = 5.4 Hz, 1 H, NH), 7.42 and 6.50 (d each, *J* = 15.7 Hz, 1:1 H, *CH*=*CH*-CO), 7.38 and 6.77 (d each, *J* = 8.7 Hz, 2:2 H, aromatic CH), 5.80 (m, 1 H, *CH*=CH_2), 5.23 and 5.12 (m each, 1:1 H, CH=*CH_2*), 5.06 (s, 1 H, CH=C-S), 3.88 (t, *J* = 5.4 Hz, 2 H, NH-*CH_2*), 3.67 (s, 3 H, OCH_3), 2.28 (s, 3 H, SCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7 (Cq, C=O), 168.9 (Cq, *C*SMe), 160.2 (Cq, aromatic C-O), 136.9 and 126.1 (*C*H=*C*H-CO), 132.7 and 116.6 (*C*H=*C*H_2), 128.9 and 113.9 (aromatic CH), 128.3 (Cq, *i*-C of C_6H_4), 91.1 (*C*H=C-S), 55.0 (OCH_3), 45.9 (NH-*CH_2*), 13.9 (SCH_3). HRMS Calcd for $C_{16}H_{20}NO_2S$ $[M+H]^+$: 290.1215; Found: 290.1210.



(*E*)-4-Chloro-5-(thiomethyl)-1-phenyl-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (2a): Red solid. M.p.: 135-138 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d), 7.48 (d), and 7.03 (dd) (1:1:1 H, thienyl CH), 7.52 and 7.29 (3:2 H, aromatic CH), 6.44 (s, 1 H, thienyl-C*H*=C), 2.52 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2 (Cq, C=O), 159.8 (Cq, *C*SMe), 136.4 (Cq, thienyl *C*-CH=C), 136.2, 132.4, and 129.5 (thienyl CH), 136.1 (Cq, aromatic C-N), 134.6 (Cq, CH=*C*-CO), 129.9, 129.8, and 127.4 (aromatic CH), 116.7 (thienyl-*C*H=C), 107.4 (Cq, C-Cl), 16.1 (SCH_3). HRMS Calcd for $C_{16}H_{12}NOS_2Cl$ $[M]^+$: 333.0049; Found: 333.0051.

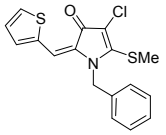


(*E*)-4-Chloro-1-(4-ethoxyphenyl)-5-(thiomethyl)-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (2b): Red solid. M.p.: 182-185 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d), 7.49 (d), and 7.05 (dd) (1:1:1 H, thienyl CH), 7.17 and 7.01 (d each, J = 8.8 Hz, 2:2 H, aromatic CH), 6.42 (s, 1 H, thienyl-C*H*=C), 4.10 (q, 2 H, O*C*H_2), 2.57 (s, 3 H, SCH_3), 1.47 (t, J = 7.0 Hz, 3H, OCH_2CH_3).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.3 (Cq, C=O), 160.3 (Cq, aromatic C-O), 159.7 (Cq, *C*SMe), 136.6 (Cq, thienyl *C*-CH=C), 136.0, 132.3, and 127.4 (thienyl CH), 135.0 (Cq, CH=*C*-CO), 131.0 and 115.5 (aromatic CH), 128.3 (Cq, aromatic C-N), 116.5 (thienyl-*C*H=C), 106.7 (Cq, C-Cl), 64.0 (OCH_2), 16.0 (SCH_3), 14.9 (OCH_2CH_3). HRMS Calcd for $C_{18}H_{17}NO_2S_2Cl$ $[M+H]^+$: 378.0389; Found: 378.0379.

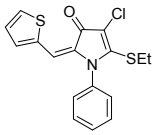


(*E*)-4-Chloro-1-(4-chlorophenyl)-5-(thiomethyl)-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (2c): Red solid. M.p.: 150-153 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53, 7.46 and 7.00 (m each, 1:1:1 H, thienyl CH), 7.46 and 7.20 (d each, J = 8.5 Hz, 2:2 H, aromatic CH), 6.36 (s, 1 H, thienyl-C*H*=C), 2.52 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.2 (Cq, C=O), 159.5 (Cq, *C*SMe), 136.4, 132.7, and 127.5 (thienyl CH), 136.3, 135.6, 134.8 and 134.3 (Cq each), 131.3 and 130.2

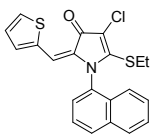
(aromatic CH), 116.7 (thienyl-*C*H=C), 108.1 (Cq, C-Cl), 16.1 (SCH_3). HRMS Calcd for $C_{16}H_{12}NOS_2Cl_2$ $[M+H]^+$: 367.9737; Found: 367.9728.



(*E*)-1-Benzyl-4-chloro-5-(thiomethyl)-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (2d): Red liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d), 7.51 (d), and 7.06 (dd) (1:1:1 H, thienyl CH), 7.35, 7.29, and 7.15 (m each, 2:1:2 H, aromatic CH), 6.75 (s, 1 H, thienyl-C*H*=C), 5.14 (s, 2 H, Ph-CH_2), 2.71 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.6 (Cq, C=O), 159.7 (Cq, *C*SMe), 136.6, 132.7, and 128.0 (thienyl CH), 136.52, 136.51, and 132.0 (Cq each), 129.2, 127.4, and 126.0 (aromatic CH), 116.6 (thienyl-*C*H=C), 107.3 (Cq, C-Cl), 47.4 (Ph-CH_2), 16.7 (SCH_3). HRMS Calcd for $C_{17}H_{15}NOS_2Cl$ $[M+H]^+$: 348.0284; Found: 348.0279.

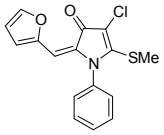


(*E*)-4-Chloro-5-(thioethyl)-1-phenyl-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (2e)： Red solid. M.p.: 151-153 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d), 7.50 (d), and 7.05 (dd) (1:1:1 H, thienyl CH), 7.55 and 7.27 (m each, 3:2 H, aromatic CH), 6.45 (s, 1 H, thienyl-C*H*=C), 3.08 (q, 2 H, SCH_2), 1.25 (t, 3 H, SCH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.3 (Cq, C=O), 158.6 (Cq, *C*SEt), 136.5 (Cq, thienyl *C*-CH=C), 136.3 (Cq, aromatic C-N), 136.2, 132.5, and 129.5 (thienyl CH), 134.7 (Cq, CH=*C*-CO), 130.0, 129.9, and 127.4 (aromatic CH), 116.9 (thienyl-*C*H=C), 108.1 (Cq, C-Cl), 27.4 (SCH_2CH_3), 15.2 (SCH_2CH_3). HRMS Calcd for $C_{17}H_{15}NOS_2Cl$ $[M+H]^+$: 348.0284; Found: 348.0286.

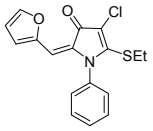


(*E*)-4-Chloro-5-(thioethyl)-1-(naphthalen-1-yl)-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (2f): Red solid. M.p.: 164-166 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 and 7.97 (d each, J = 8.2 Hz, 1:1 H, aromatic CH), 7.60 and 7.55 (t each, J =

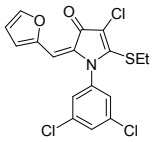
7.8 Hz, 1:1 H, aromatic CH), 7.50, 7.39, and 6.96 (m each, 1:1:1 H, thienyl CH), 7.50 and 7.46 (m each, 1:2 H, aromatic CH), 6.25 (s, 1 H, thienyl-C*H*=C), 3.05 (m, 2 H, SCH_2), 1.18 (m, 3 H, SCH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.2 (Cq, C=O), 159.6 (Cq, *C*SEt), 136.4, 134.6, 134.5, 132.3, and 131.8 (Cq each), 136.3, 132.4, 130.4, 129.0, 128.7, 127.9, 127.3, 127.1, 125.6 and 122.6 (CH each), 116.9 (thienyl-*C*H=C), 107.4 (Cq, C-Cl), 27.1 (SCH_2), 15.1 (SCH_2CH_3). HRMS Calcd for $C_{21}H_{17}NOS_2Cl$ $[M+H]^+$: 398.0440; Found: 398.0451.



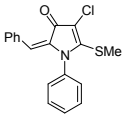
(*E*)-4-Chloro-2-(furan-2-ylmethylene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2g): Red solid. M.p.: 153-156 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.46, 7.47, and 6.55 (m each, 1:1:1 H, furyl CH), 7.55, 7.51, and 7.28 (m each, 1:2:2 H, aromatic CH), 6.19 (s, 1 H, furyl-C*H*=C), 2.54 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.2 (Cq, C=O), 159.8 (Cq, *C*SMe), 150.1 (Cq, furyl *C*-CH=C), 145.3, 118.0, and 113.6 (furyl CH), 136.2 and 134.9 (Cq each), 130.0, 129.8, and 129.5 (aromatic CH), 110.3 (furyl-*C*H=C), 107.7 (Cq, C-Cl), 16.1 (SCH_3). HRMS Calcd for $C_{16}H_{13}NO_2SCl$ $[M+H]^+$: 318.0356; Found: 318.0355.



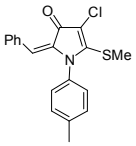
(*E*)-4-Chloro-5-(thioethyl)-2-(furan-2-ylmethylene)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2h): Red solid. M.p.: 151-154 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.50, 7.49, and 6.57 (d each, 1:1:1 H, furyl CH), 7.55 and 7.28 (m each, 3:2 H, aromatic CH), 6.22 (s, 1 H, furyl-C*H*=C), 3.11 (q, 2 H, SCH_2), 1.28 (t, 3 H, SCH_2CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.2 (Cq, C=O), 158.6 (Cq, *C*SEt), 150.1 (Cq, furyl *C*-CH=C), 145.3, 118.1, and 113.6 (furyl CH), 136.3 and 135.0 (Cq each), 129.9, 129.8, and 129.5 (aromatic CH), 110.5 (furyl-*C*H=C), 108.3 (Cq, C-Cl), 27.4 (SCH_2CH_3), 15.2 (SCH_2CH_3). HRMS Calcd for $C_{17}H_{15}NO_2SCl$ $[M+H]^+$: 332.0512; Found: 332.0515.



(*E*)-4-Chloro-1-(3,5-dichlorophenyl)-5-(thioethyl)-2-(furan-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (2i): Red solid. M.p.: 159-162 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d), 7.50 (d), and 6.56 (dd) (1:1:1 H, furyl CH), 7.49 and 7.19 (d each, J = 1.8 Hz, 1:2 H, aromatic CH), 6.17 (s, 1 H, furyl-C*H*=C), 3.17 (q, 2 H, SCH_2), 1.29 (t, 3 H, SCH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.1 (Cq, C=O), 157.7 (Cq, *C*SEt), 149.7 (Cq, furyl *C*-CH=C), 145.8, 118.6, and 113.8 (furyl CH), 138.3 and 134.2 (Cq each), 136.1 (Cq, C-Cl), 129.9 and 128.7 (aromatic CH), 110.7 (furyl-*C*H=C), 110.0 (Cq, O=C-*C*-Cl), 27.6 (SCH_2CH_3), 15.2 (SCH_2CH_3). HRMS Calcd for $C_{17}H_{13}NO_2SCl_3$ $[M+H]^+$: 399.9733; Found: 399.9735.

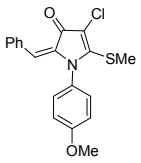


(*E*)-2-Benzylidene-4-chloro-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2j): Red solid. M.p.: 113-115 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 and 7.52 (m each, 2:3 H, aromatic CH), 7.31 and 7.28 (m each, 4:1 H, aromatic CH), 6.14 (s, 1 H, Ph-*CH*=C), 2.54 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.6 (Cq, C=O), 161.7 (Cq, *C*SMe), 138.0, 136.5, and 132.6 (Cq each), 131.3, 130.2, 130.0, 129.9, 129.5, and 128.2 (aromatic CH), 124.8 (Ph-*CH*=C), 107.7 (Cq, C-Cl), 15.9 (SCH_3). HRMS Calcd for $C_{18}H_{15}NOSCl$ $[M+H]^+$: 328.0563; Found: 328.0569.

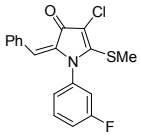


(*E*)-2-Benzylidene-4-chloro-5-(thiomethyl)-1-p-tolyl-1*H*-pyrrol-3(2*H*)-one (2k): Red solid. M.p.: 168-171 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 and 7.17 (d each, J = 8.1 Hz, 2:2 H, aromatic CH), 7.33 and 7.32 (m each, 3:2 H, aromatic CH), 6.14 (s, 1 H, Ph-C*H*=C), 2.57 (s, 3 H, SCH_3), 2.46 (s, 3 H, C_6H_4-CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 161.8 (Cq, *C*SMe), 139.8, 138.1, 133.8, and 132.7 (Cq each), 131.4, 130.6, 130.2, 129.8, and 128.2 (aromatic CH), 124.8 (Ph-

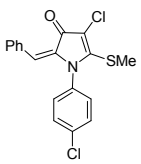
*C*H=C), 107.4 (Cq, C-Cl), 21.4 (C_6H_4-*C*H_3), 16.0 (SCH_3). HRMS Calcd for $C_{19}H_{17}NOSCl$ $[M+H]^+$: 342.0719; Found: 342.0715.



(*E*)-2-Benzylidene-4-chloro-1-(4-methoxyphenyl)-5-(thiomethyl)-1*H*-pyrrol-3(2*H*)-one (2l): Red solid. M.p.: 129-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 and 7.32 (m each, 2:3 H, aromatic CH), 7.20 and 7.02 (d each, *J* = 8.7 Hz, 2:2 H, aromatic CH), 6.12 (s, 1 H, Ph-C*H*=C), 3.88 (s, 3 H, OCH_3), 2.58 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 162.0 (Cq, aromatic C-O), 160.2 (Cq, *C*SMe), 138.3, 132.7, and 128.7 (Cq each), 131.4, 131.2, 130.2, 128.2, and 115.1 (aromatic CH), 124.7 (Ph-*CH*=C), 107.0 (Cq, C-Cl), 55.7 (OCH_3), 15.9 (SCH_3). HRMS Calcd for $C_{19}H_{17}NO_2SCl$ $[M+H]^+$: 358.0669; Found: 358.0663.

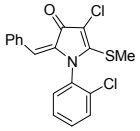


(*E*)-2-Benzylidene-4-chloro-1-(3-fluorophenyl)-5-(thiomethyl)-1*H*-pyrrol-3(2*H*)-one (2m)： Red solid. M.p.: 174-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 and 7.39 (m each, 2:3 H), 7.56 and 7.17 (m each, 1:1 H, aromatic CH), 7.28 (t) and 7.11 (d) (1:1 H, aromatic CH), 6.20 (s, 1 H, Ph-C*H*=C), 2.65 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 163.1 (d, *J* = 250.5 Hz, Cq, C-F), 161.3 (Cq, *C*SMe), 138.1 (d, *J* = 9.5 Hz, Cq, aromatic C-N), 137.7 and 132.4 (Cq each), 131.4, 130.5, and 128.3 (aromatic CH), 131.1 (d, *J* = 9.1 Hz, aromatic *C*-C-C-F), 126.0 (d, *J* = 3.3 Hz, aromatic *C*-C-C-C-F), 125.0 (Ph-*C*H=C), 117.6 (d, *J* = 22.1 Hz, aromatic *C*-C-F), 116.8 (d, *J* = 20.9 Hz, aromatic *C*-C-F), 108.7 (Cq, C-Cl), 16.0 (SCH_3). HRMS Calcd for $C_{18}H_{14}NOSClF$ $[M+H]^+$: 346.0469; Found: 346.0466.

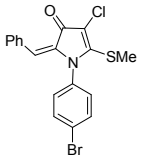


(*E*)-2-Benzylidene-4-chloro-1-(4-chlorophenyl)-5-(thiomethyl)-1*H*-pyrrol-3(2*H*)-one (2n): Red solid. M.p.: 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12,

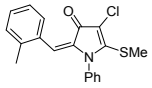
7.37 and 7.35 (m each, 2:2:1 H, aromatic CH), 7.53 and 7.28 (d each, J = 8.6 Hz, 2:2 H, aromatic CH), 6.13 (s, 1 H, Ph-C*H*=C), 2.61 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 161.3 (Cq, *C*SMe), 137.7, 135.5, 135.0, and 132.4 (Cq each), 131.4, 131.3, 130.5, 130.2, and 128.3 (aromatic CH), 124.8 (Ph-*C*H=C), 108.3 (Cq, C-Cl), 16.0 (SCH_3). HRMS Calcd for $C_{18}H_{14}NOSCl_2$ $[M+H]^+$: 362.0173; Found: 362.0173.



(*E*)-2-Benzylidene-4-chloro-1-(2-chlorophenyl)-5-(thiomethyl)-1*H*-pyrrol-3(2*H*)-one (2o): Red solid. M.p.: 133-136 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 and 7.47 (m each, 2:2 H, aromatic CH), 7.59, 7.39, and 7.33 (m each, 1:1:3 H, aromatic CH), 5.95 (s, 1 H, Ph-C*H*=C), 2.63 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.8 (Cq, C=O), 161.5 (Cq, *C*SMe), 136.6, 135.6, 134.1, and 132.6 (Cq each), 132.7, 131.4, 131.3, 131.0, 130.4, 128.3, and 128.2 (aromatic CH), 124.4 (Ph-*C*H=C), 108.6 (Cq, C-Cl), 16.0 (SCH_3). HRMS Calcd for $C_{18}H_{14}NOSCl_2$ $[M+H]^+$: 362.0173; Found: 362.0179.

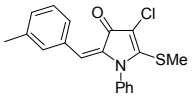


(*E*)-2-Benzylidene-1-(4-bromophenyl)-4-chloro-5-(thiomethyl)-1*H*-pyrrol-3(2*H*)-one (2p): Red solid. M.p.: 182-184 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.09, 7.34 and 7.33 (m each, 2:2:1 H, aromatic CH), 7.66 and 7.18 (d each, J = 8.6 Hz, 2:2 H, aromatic CH), 6.11 (s, 1 H, Ph-C*H*=C), 2.59 (s, 3 H, SCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 161.2 (Cq, *C*SMe), 137.7, 135.6, 132.4, and 123.6 (Cq each), 133.2, 131.7, 131.4, 130.5, and 128.3 (aromatic CH), 124.9 (Ph-*C*H=C), 108.4 (Cq, C-Cl), 16.0 (SCH_3). HRMS Calcd for $C_{18}H_{14}NOSClBr$ $[M+H]^+$: 405.9668; Found: 405.9670.

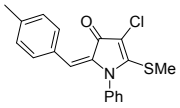


(*E*)-4-Chloro-2-(2-methylbenzylidene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2q): Red solid. M.p.: 120-122 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 and

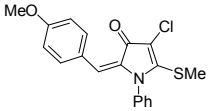
7.20 (m each, 1:2 H, aromatic CH), 7.53 (m, 3 H, aromatic CH), 7.33 and 7.11 (d each, *J* = 6.6 Hz, 2:2 H, aromatic CH), 6.33 (s, 1 H, C_6H_4-C*H*=C), 2.56 (s, 3 H, SCH_3), 2.09 (s, 3 H, C_6H_4-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.9 (Cq, C=O), 162.1 (Cq, *C*SMe), 137.8, 137.5, 136.8, and 131.1 (Cq each), 130.5, 129.93, 129.90, 129.89, 129.8, 129.4, and 121.7 (aromatic CH), 125.6 (C_6H_4-*C*H=C), 108.0 (Cq, C-Cl), 20.0 (C_6H_4-*C*H_3), 15.9 (SCH_3). HRMS Calcd for $C_{19}H_{17}NOSCl$ $[M+H]^+$: 342.0719; Found: 342.0716.



(*E*)-4-Chloro-2-(3-methylbenzylidene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2r): Red solid. M.p.: 111-114 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s) and 7.54 (m) (1:3 H, aromatic CH), 7.87, 7.30, 7.15, and 7.22 (m each, 1:2:1:1 H, aromatic CH), 6.13 (s, 1 H, C_6H_4-C*H*=C), 2.56 (s, 3 H, SCH_3), 2.34 (s, 3 H, C_6H_4-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 161.4 (Cq, *C*SMe), 138.0, 137.9, 136.6, and 132.6 (Cq each), 131.9, 131.3, 130.00, 129.9, 129.5, 128.7, and 128.2 (aromatic CH), 125.3 (C_6H_4-*C*H=C), 107.8 (Cq, C-Cl), 21.4 (C_6H_4-*C*H_3), 16.0 (SCH_3). HRMS Calcd for $C_{19}H_{17}NOSCl$ $[M+H]^+$: 342.0719; Found: 342.0718.

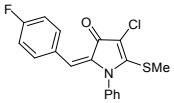


(*E*)-4-Chloro-2-(4-methylbenzylidene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2s): Red solid. M.p.: 157-160 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 and 7.13 (d each, *J* = 8.0 Hz, 2:2 H, aromatic CH), 7.52 and 7.29 (m each, 3:2 H, aromatic CH), 6.13 (s, 1 H, C_6H_4-C*H*=C), 2.53 (s, 3 H, SCH_3), 2.34 (s, 3 H, C_6H_4-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 176.5 (Cq, C=O), 160.9 (Cq, *C*SMe), 141.0, 137.6, 136.6, and 129.9 (Cq each), 131.5, 130.0, 129.8, 129.4, and 129.0 (aromatic CH), 125.4 (C_6H_4-*C*H=C), 107.8 (Cq, C-Cl), 21.7 (C_6H_4-*C*H_3), 15.9 (SCH_3). HRMS Calcd for $C_{19}H_{17}NOSCl$ $[M+H]^+$: 342.0719; Found: 342.0713.

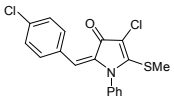


(*E*)-4-Chloro-2-(4-methoxybenzylidene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-

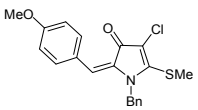
3(2*H*)-one (2t): Red solid. M.p.: 148-151 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 and 6.84 (d each, *J* = 8.9 Hz, 2:2 H, aromatic CH), 7.52 and 7.28 (m each, 3:2 H, aromatic CH), 6.13 (s, 1 H, C_6H_4-C*H*=C), 3.81 (s, 3 H, OCH_3), 2.53 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.4 (Cq, C=O), 161.6 (Cq, *C*SMe), 160.1 (Cq, aromatic C-O), 136.8 and 136.7 (Cq each), 133.8, 130.1, 129.8, 129.4, and 113.8 (aromatic CH), 125.7 (C_6H_4-*C*H=C), 108.0 (Cq, C-Cl), 55.4 (OCH_3), 16.0 (SCH_3). HRMS Calcd for $C_{19}H_{17}NO_2SCl$ $[M+H]^+$: 358.0669; Found: 358.0675.



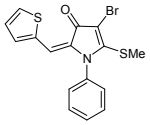
(*E*)-4-Chloro-2-(4-fluorobenzylidene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2u): Red solid. M.p.: 147-150 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 and 7.00 (m each, 2:2 H, aromatic CH), 7.56, 7.52 and 7.30 (m each, 1:2:2 H, aromatic CH), 6.10 (s, 1 H, C_6H_4-C*H*=C), 2.57 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 163.8 (d and Cq, *J* = 252.6 Hz, C-F), 161.8 (Cq, *C*SMe), 137.7 (d and Cq, *J* = 2.4 Hz, *i*-C of C_6H_4), 136.5 (Cq, aromatic C-N), 133.8 (d, *J* = 8.4 Hz, aromatic *C*-C-C-F), 130.1, 130.0, and 129.6 (aromatic CH), 129.0 (d, *J* = 3.3 Hz, C_6H_4-*C*H=C), 123.7, 115.3 (d, *J* = 21.6 Hz, aromatic *C*-C-F), 107.7 (Cq, C-Cl), 15.0 (SCH_3). HRMS Calcd for $C_{18}H_{14}NOSClF$ $[M+H]^+$: 346.0469; Found: 346.0468.



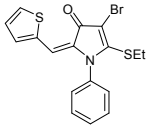
(*E*)-4-Chloro-2-(4-chlorobenzylidene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (2v): Red solid. M.p.: 182-184 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 and 7.27 (d each, *J* = 8.6 Hz, 2:2 H, aromatic CH), 7.52, 7.30, and 7.27 (m each, 3:1:1 H, aromatic CH), 6.05 (s, 1 H, C_6H_4-C*H*=C), 2.57 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.7 (Cq, C=O), 162.1 (Cq, *C*SMe), 138.2, 136.3, 136.1, and 131.2 (Cq each), 132.7, 130.1, 130.0, 129.7, and 128. 5 (aromatic CH), 123.2 (C_6H_4-*C*H=C), 107.6 (Cq, C-Cl), 15.9 (SCH_3). HRMS Calcd for $C_{18}H_{14}NOSCl_2$ $[M+H]^+$: 362.0173; Found: 362.0167.



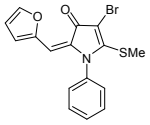
(*E*)-1-Benzyl-4-chloro-2-(4-methoxybenzylidene)-5-(thiomethyl)-1*H*-pyrrol-3(2*H*)-one (2w): Red solid. M.p.: 147-150 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 and 6.86 (d each, J = 8.9 Hz, 2:2 H, aromatic CH), 7.35, 7.29, and 7.17 (m each, 2:1:2 H, aromatic CH), 6.43 (s, 1 H, C_6H_4-C*H*=C), 5.14 (s, 2 H, Ph-CH_2), 3.82 (s, 3 H, OCH_3), 2.71 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.8 (Cq, C=O), 161.8 (Cq, *C*SMe), 160.1 (Cq, aromatic C-O), 136.8, 134.1, and 125.7 (Cq each), 133.8, 129.2, 127.9, 126.1, and 113.8 (aromatic CH), 125.3 (C_6H_4-*C*H=C), 107.8 (Cq, C-Cl), 55.5 (OCH_3), 47.7 (Ph-*C*H_2), 16.6 (SCH_3). HRMS Calcd for $C_{20}H_{19}NO_2SCl$ $[M+H]^+$: 372.0825; Found: 372.0827.



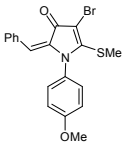
(*E*)-4-Bromo-5-(thiomethyl)-1-phenyl-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (3a): Red solid. M.p.: 123-126 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d), 7.49 (d), and 7.04 (dd) (1:1:1 H thienyl CH), 7.53 and 7.30 (m each, 3:2 H, aromatic CH), 6.46 (s, 1 H, thienyl-C*H*=C), 2.44 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0 (Cq, C=O), 161.4 (Cq, *C*SMe), 136.6, 136.4, and 134.7 (Cq each), 136.3, 132.5, and 127.4 (thienyl CH), 130.0, 129.8, and 129.5 (aromatic CH), 116.9 (thienyl-*C*H=C), 95.4 (Cq, C-Br), 16.8 (SCH_3). HRMS Calcd for $C_{16}H_{13}NOS_2Br$ $[M+H]^+$: 377.9622; Found: 377.9628.



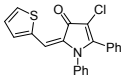
(*E*)-4-Bromo-5-(thioethyl)-1-phenyl-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (3b): Red solid. M.p.: 110-113 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 and 6.95 (m each, 2:1 H, thienyl CH), 7.41 and 7.18 (m each, 3:2 H, aromatic CH), 6.38 (s, 1 H, thienyl-C*H*=C), 2.88 (m, 2 H, SC$H_2$$CH_3$), 1.12 (m, 3 H, SCH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.0 (Cq, C=O), 160.0 (Cq, *C*SEt), 136.5, 136.3, and 134.6 (Cq each), 136.4, 132.5, and 127.3 (thienyl CH), 129.8, 129.7, and 129.4 (aromatic CH), 117.1 (thienyl-*C*H=C), 96.4 (Cq, C-Br), 28.0 (S*C*H_2), 15.1 (SCH_2*C*H_3). HRMS Calcd for $C_{17}H_{15}NOS_2Br$ $[M+H]^+$: 391.9778; Found: 391.9789.



(*E*)-4-Bromo-2-(furan-2-ylmethylene)-5-(thiomethyl)-1-phenyl-1*H*-pyrrol-3(2*H*)-one (3c): Red solid. M.p.: 116-119 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46, 7.46 and 6.54 (m each, 1:1:1 H, furyl CH), 7.52 and 7.28 (m each, 3:2 H, aromatic CH), 6.20 (s, 1 H, furyl-C*H*=C), 2.44 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.9 (Cq, C=O), 161.4 (Cq, *C*SMe), 150.1 (Cq, furyl *C*-CH=C), 145.3, 118.1, and 113.6 (furyl CH), 136.6 and 135.1 (Cq each), 130.0, 129.7, and 129.5 (aromatic CH), 110.4 (furyl-*C*H=C), 95.8 (Cq, C-Br), 16.8 (SCH_3). HRMS Calcd for $C_{16}H_{13}NO_2SBr$ $[M+H]^+$: 361.9850; Found: 361.9854.

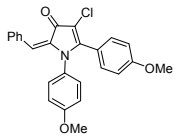


(*E*)-2-Benzylidene-4-bromo-1-(4-methoxyphenyl)-5-(thiomethyl)-1*H*-pyrrol-3(2*H*)-one (3d): Red solid. M.p.: 101-103 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 and 7.32 (m each, 2:3 H, aromatic CH), 7.21 and 7.02 (d each, J = 8.8 Hz, 2:2 H, aromatic CH), 6.14 (s, 1 H, Ph-C*H*=C), 3.88 (s, 3 H, OCH_3), 2.50 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.4 (Cq, C=O), 163.6 (Cq, aromatic C-O), 160.2 (Cq, *C*SMe), 138.4, 132.7, and 129.1 (Cq each), 131.4, 131.1, 130.3, 128.2, and 115.1 (aromatic CH), 124.8 (Ph-*C*H=C), 95.0 (Cq, C-Br), 55.7 (OCH_3), 16.7 (SCH_3). HRMS Calcd for $C_{19}H_{17}NO_2SBr$ $[M+H]^+$: 402.0163; Found: 402.0160.

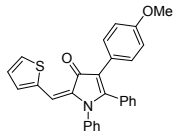


(*E*)-4-Chloro-1,5-diphenyl-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (4a): Red solid. M.p.: 190-193 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s), 7.53 (d) and 7.08 (d) (1:1:1 H, thienyl CH), 7.36 (d, J = 6.0 Hz, 4 H, aromatic CH), 7.30 (t, J = 7.4 Hz, 4 H, aromatic CH), 7.12 (d, J = 7.2 Hz, 2 H, aromatic CH), 6.75 (s, 1 H, thienyl-C*H*=C). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.9 (Cq, C=O), 158.9 (Cq, pyrrolyl *C*-Ph), 137.1 (Cq, thienyl *C*-CH=C), 136.7, 132.8, and 128.5 (thienyl CH), 136.7, 134.5, and 128.4 (Cq each), 130.4, 129.8, 129.7, 129.6, 128.3, and 127.5

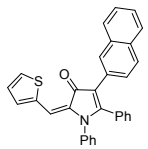
(aromatic CH), 118.6 (thienyl-*C*H=C), 106.3 (Cq, C-Cl). HRMS Calcd for $C_{21}H_{15}NOSCl$ $[M+H]^+$: 364.0563; Found: 364.0560.



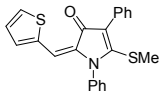
(*E*)-2-Benzylidene-4-chloro-1,5-bis(4-methoxyphenyl)-1*H*-pyrrol-3(2*H*)-one (4b): Red solid. M.p.: 218-220 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 6.6 and 2.7 Hz, 2 H, aromatic CH), 7.35 (m, 5 H, aromatic CH), 7.05, 6.87, and 6.81 (d each, *J* = 8.8 Hz, 2:2:2 H, aromatic CH), 6.38 (s, 1 H, Ph-C*H*=C), 3.80 and 3.78 (s each, 3:3 H, 2×OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 178.5 (Cq, C=O), 161.2 and 160.4 (Cq each, aromatic C-O), 159.2 (Cq, pyrrolyl *C*-C_6H_4-OCH_3), 138.7, 132.9, 130.2, and 120.6 (Cq each), 131.7, 131.4, 130.9, 130.3, 128.2, 114.9, and 113.8 (aromatic CH), 126.4 (Ph-*C*H=C), 106.1 (Cq, C-Cl), 55.6 and 55.4 (2×OCH_3). HRMS Calcd for $C_{25}H_{21}NO_3SCl$ $[M+H]^+$: 418.1210; Found: 418.1212.



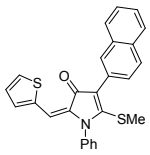
(*E*)-4-(4-Methoxyphenyl)-1,5-diphenyl-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (5a): Red solid. M.p.: 233-235 ^oC. ^1H NMR (400 MHz, CDCl3) δ 7.55 (d), 7.46 (d) and 7.06 (m) (1:1:1 H, thienyl CH), 7.33 (t, J = 7.3 Hz, 2 H, aromatic CH), 7.28, 7.20, and 7.14 (m each, 1:1:6 H, aromatic CH), 7.23 and 6.77 (d each, J = 8.7 Hz, 2:2 H, aromatic CH), 6.70 (s, 1 H, thienyl-C*H*=C), 3.75 (s, 3 H, OCH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.9 (Cq, C=O), 160.4 (Cq, aromatic C-O,), 157.9 (Cq, pyrrolyl *C*-Ph), 137.3 (Cq, thienyl *C*-CH=C), 137.0, 135.9, 130.7, 124.0, and 114.8 (Cq each), 135.7, 131.5, and 128.0 (thienyl CH), 130.5, 130.0, 129.8, 129.5, 129.4, 128.3, 127.1, and 113.6 (aromatic CH), 116.4 (thienyl-*C*H=C), 55.24 (OCH_3). HRMS Calcd for $C_{28}H_{22}NO_2S$ $[M+H]^+$: 436.1371; Found: 436.1373.



(*E*)-4-(Naphthalen-2-yl)-1,5-diphenyl-2-(thiophen-2-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (5b): Red solid. M.p.: 237-239 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s), 7.71 (br), and 7.59 (d) (1:2:1 H, aromatic CH), 7.56 (d), 7.48 (d), and 7.06 (m) (1:1:1 H, thienyl CH), 7.34, 7.28, 7.21, and 7.13 (m each, 4:1:2:6 H, aromatic CH), 6.72 (s, 1 H, thienyl-C*H*=C). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 182.7 (Cq, C=O), 161.2 (Cq, pyrrolyl *C*-Ph), 137.2 (Cq, thienyl *C*-CH=C), 136.9, 135.9, 133.6, 132.0, 130.6, 129.2, and 114.9 (Cq each), 135.9, 131.7, and 128.1 (thienyl CH), 130.1, 129.9, 129.6, 129.5, 128.4, 128.2, 127.7, 127.5, 127.2, 125.6, and 125.4 (aromatic CH), 116.8 (thienyl-*C*H=C). HRMS Calcd for $C_{31}H_{22}NOS$ $[M+H]^+$: 456.1422; Found: 456.1421.

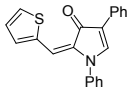


(*E*)-5-(Thiomethyl)-1,4-diphenyl-2-(thiophen-3-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (6a): Red solid. M.p.: 124-127 °C. 1H NMR (400 MHz, CDCl3) δ 7.63 (d) and 7.01 (br) (2:1 H, thienyl CH), 7.50 (m, 4 H, aromatic CH), 7.37 (m, 5 H, aromatic CH), 7.24 (m, 1 H, aromatic CH), 6.48 (s, 1 H, thienyl-C*H*=C), 1.96 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 180.9 (Cq, C=O), 161.2 (Cq, *C*SMe), 136.8 (Cq, thienyl *C*-CH=C), 136.7 (Cq, aromatic C-N), 135.7(Cq, CH=*C*-CO), 131.4 (Cq, aromatic *C*-C), 135.5, 131.4, and 129.0 (thienyl CH), 129.8, 129.7, 129.6, 128.2, 127.1, and 126.7 (aromatic CH), 116.4 (Cq, pyrrolyl *C*-Ph), 115.0 (thienyl-*C*H=C), 16.9 (SCH_3). Calcd for $C_{22}H_{18}NOS_2$ $[M+H]^+$: 376.0830; Found: 376.0829.



(*E*)-5-(Thiomethyl)-4-(naphthalen-2-yl)-1-phenyl-2-(thiophen-3-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (6b): Red solid. M.p.: 201-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1 H, aromatic CH), 7.89 (dd, *J* = 8.7 and 4.4 Hz, 2 H, aromatic CH), 7.84 and 7.59 (m each, 2:2 H, aromatic CH), 7.55 (t) and 7.06 (d) (2:1 H, thienyl CH), 7.47 (m, 3 H, aromatic CH), 7.41 (t, *J* = 1.7 Hz, 1 H, aromatic CH), 7.40 (s, 1 H, aromatic CH), 6.54 (s, 1 H, thienyl-C*H*=C), 2.00 (s, 3 H, SCH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 181.0 (Cq, C=O), 161.6 (Cq, *C*SMe), 136.9, 136.8, 135.8,

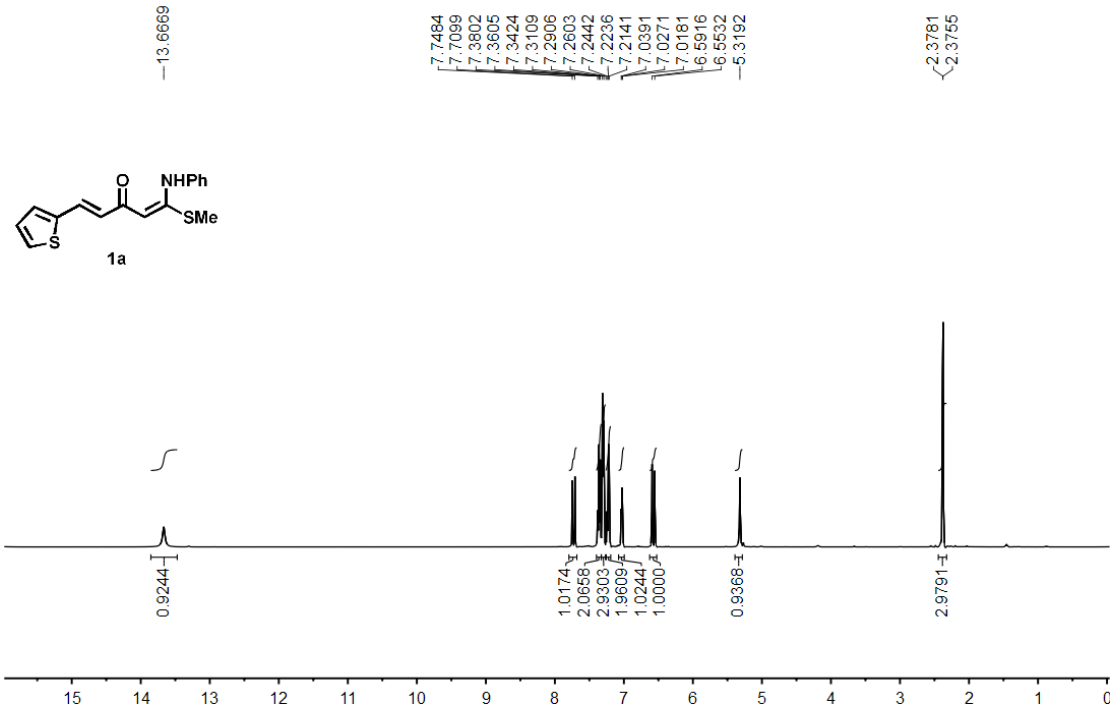
133.6, 132.4, and 129.0 (Cq each), 135.7, 131.6, and 129.2 (thienyl CH), 130.0, 129.9, 128.6, 128.2, 127.8, 127.7, 127.2, 126.0, and 125.7 (aromatic CH), 116.3 (Cq, pyrrolyl *C*-naphthyl), 115.3 (thienyl-*C*H=C), 17.2 (SCH_3). Calcd for $C_{26}H_{20}NOS_2$ $[M+H]^+$: 426.0986; Found: 426.0990.



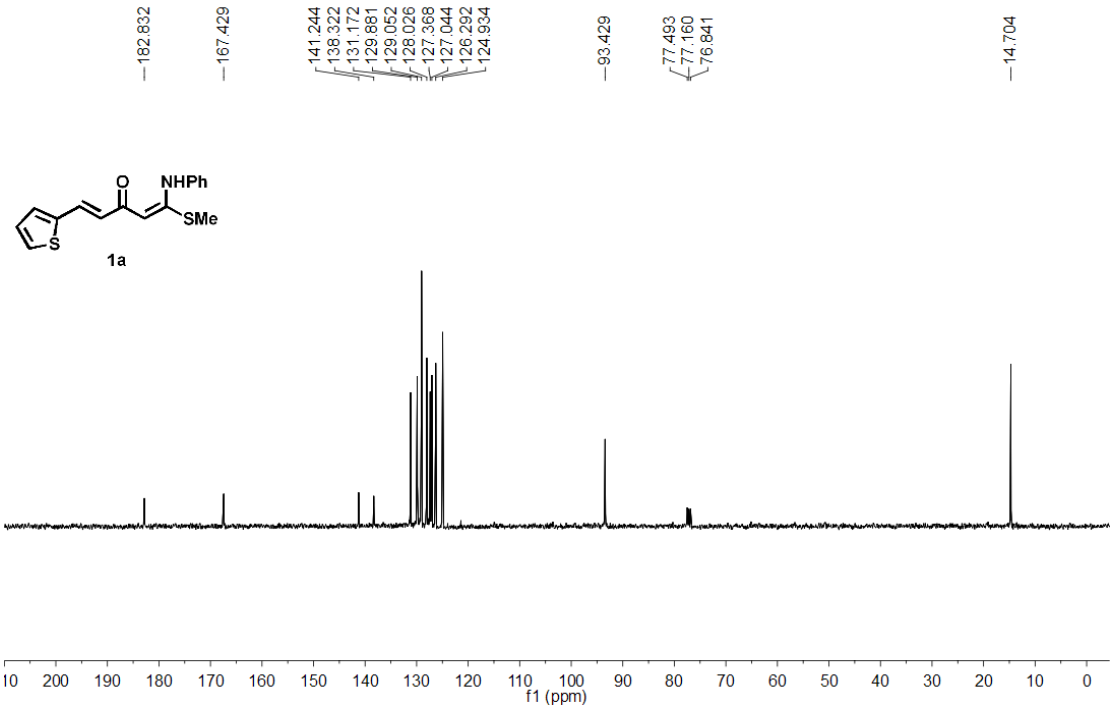
(*E*)-1,4-Diphenyl-2-(thiophen-3-ylmethylene)-1*H*-pyrrol-3(2*H*)-one (7): Red solid. M.p.: 144-147 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1 H, pyrrolyl CH), 7.87 (d, *J* = 7.2 Hz, 2 H, aromatic CH), 7.63 (d) and 7.12 (d) (1:1 H, thienyl CH), 7.55 (m, 3 H, 1 H of thienyl CH and 2 H of aromatic CH), 7.44 and 7.21 (m each, 1:1 H, aromatic CH), 7.37 (m, 4 H, aromatic CH), 7.01 (s, 1 H, thienyl-C*H*=C). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.8 (Cq, C=O), 149.1 (pyrrolyl CH), 138.5 (Cq, thienyl *C*-CH=C), 136.4 (Cq, aromatic *C*-N), 133.8 (Cq, CH=*C*-CO), 131.9 (Cq, aromatic *C*-C), 136.4, 132.3, and 128.0 (thienyl CH), 130.2, 128.7, 127.4, 126.3, 126.2, and 125.3 (aromatic CH), 116.7 (thienyl-*C*H=C), 114.7 (Cq, pyrrolyl *C*-Ph). HRMS Calcd for $C_{22}H_{16}NOS$ $[M+H]^+$: 330.0953; Found: 330.0952.

5. Copies of NMR spectra for new compounds

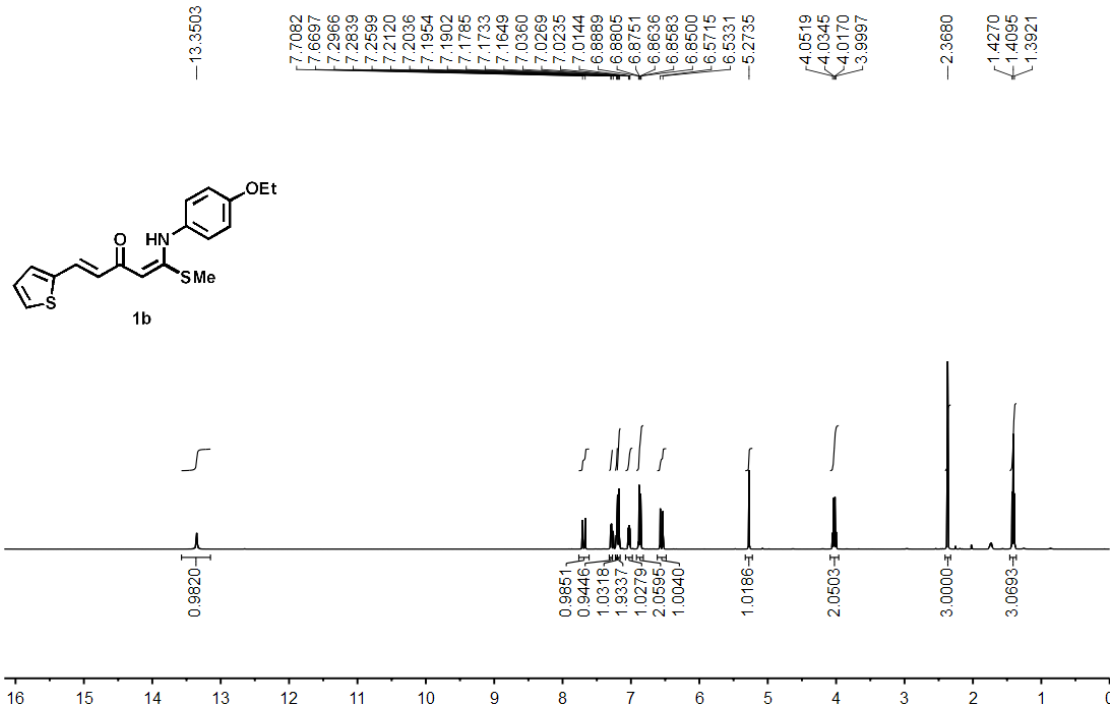
HF275
1H NMR IN CDC13



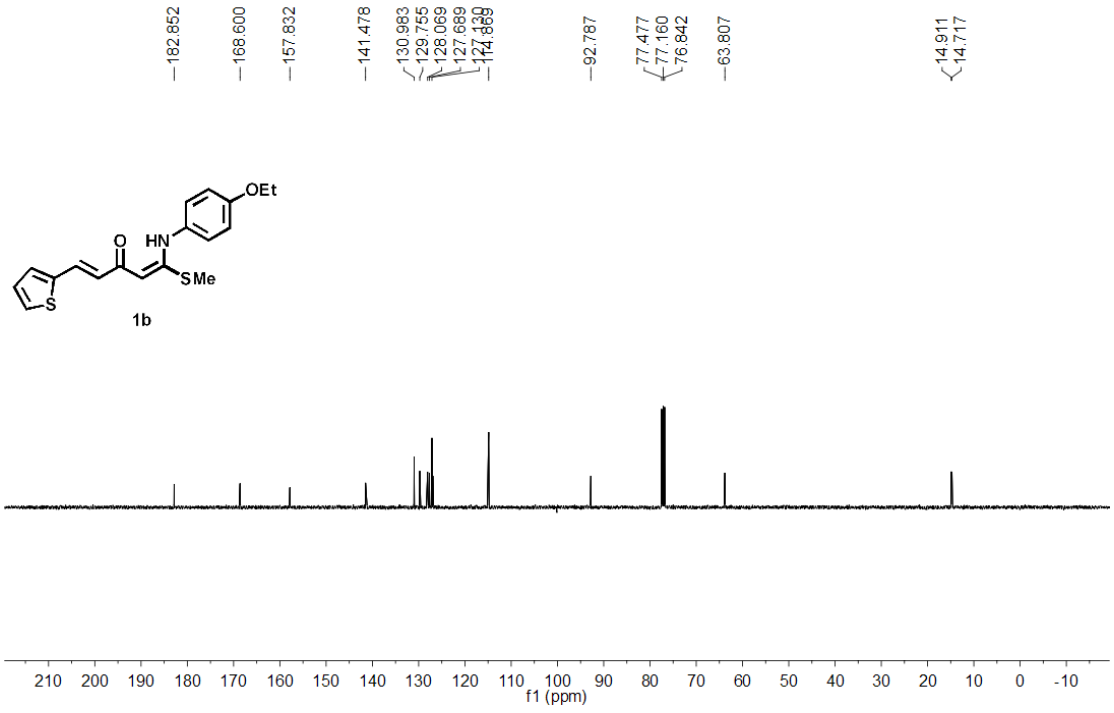
HF275
13C NMR IN CDC13



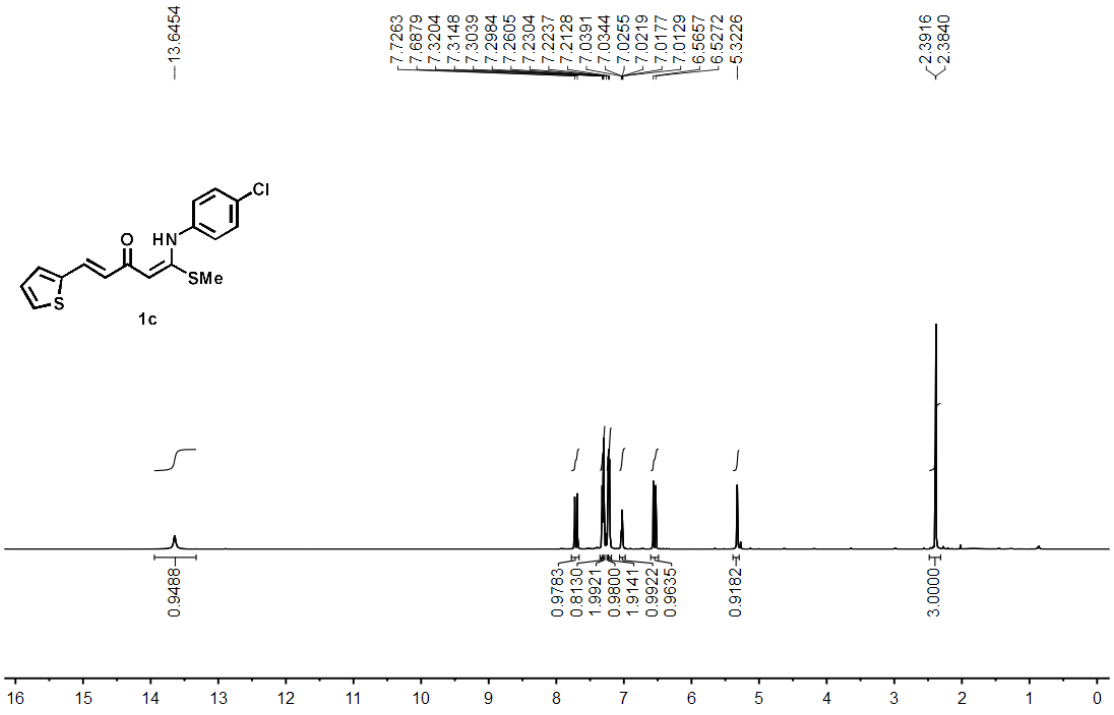
HF368
1H NMR IN CDCl3



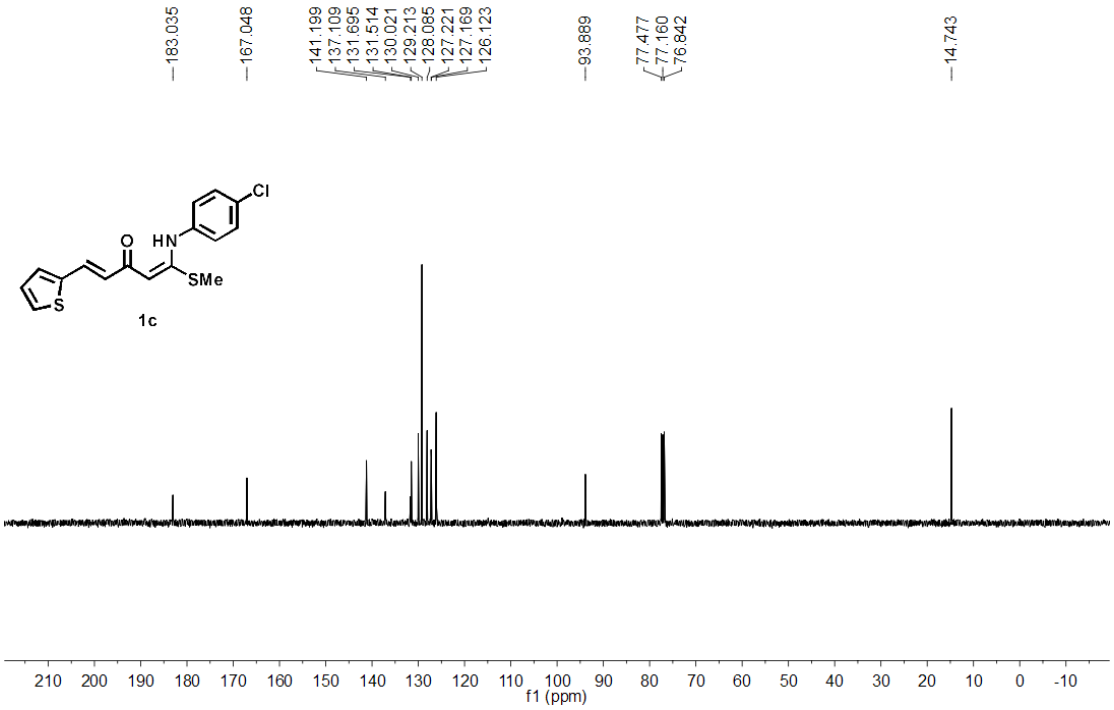
HF368
13C NMR IN CDCl3



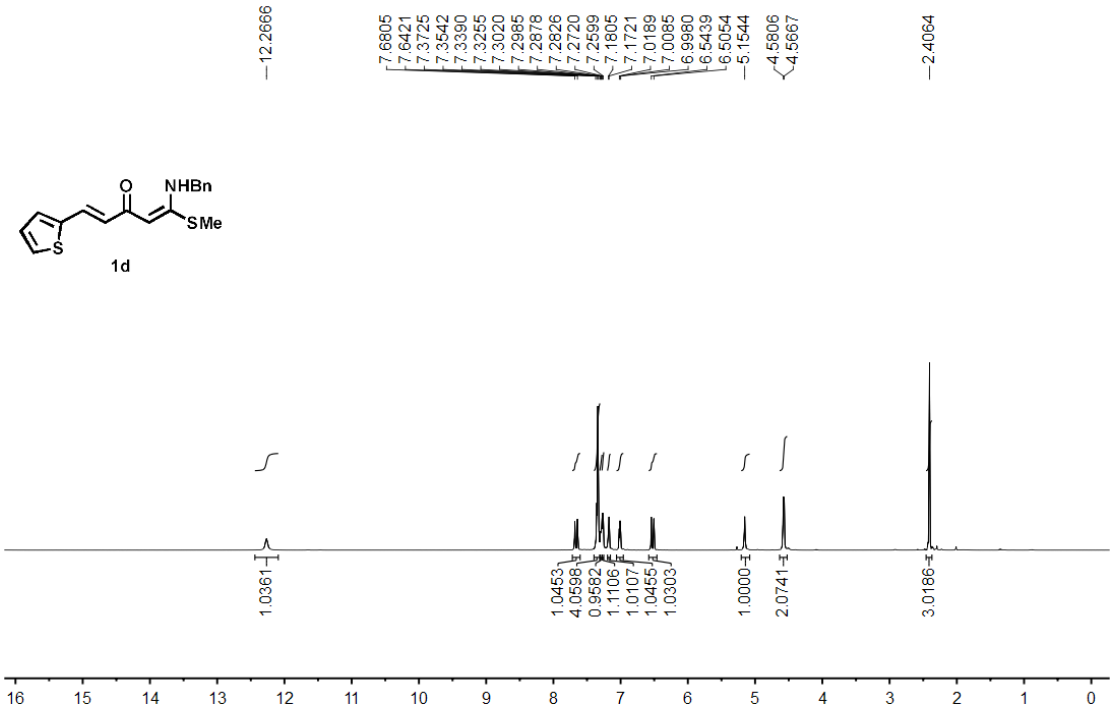
HF369-P
1H NMR IN CDC13



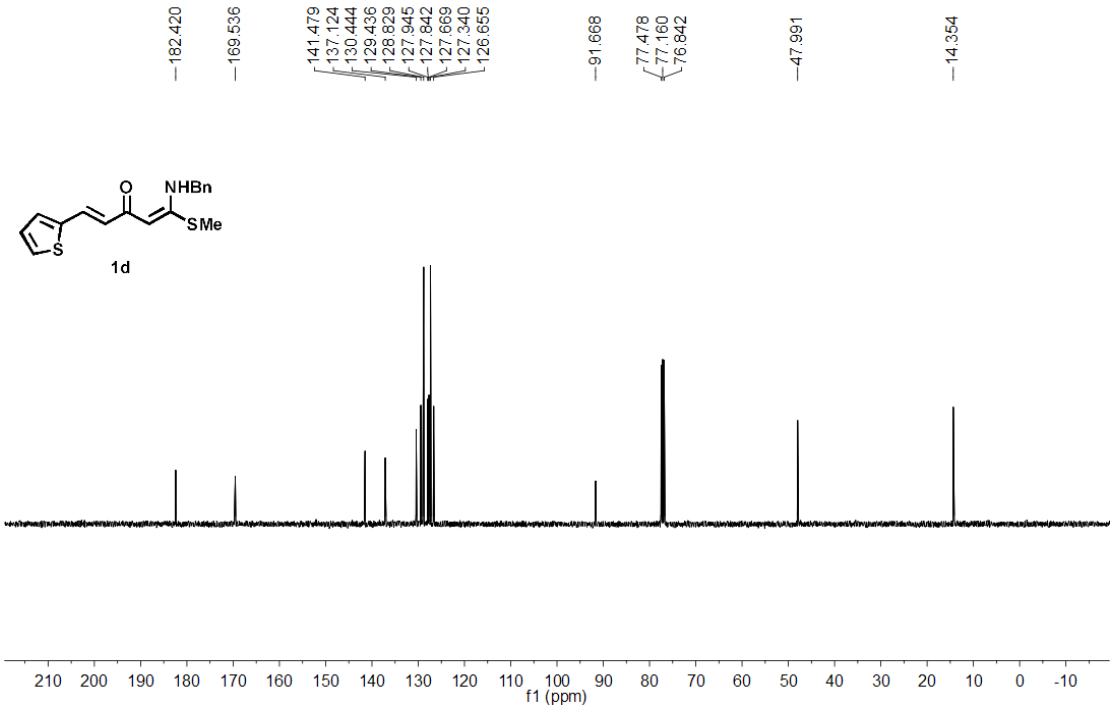
HF369-P
13C NMR IN CDC13



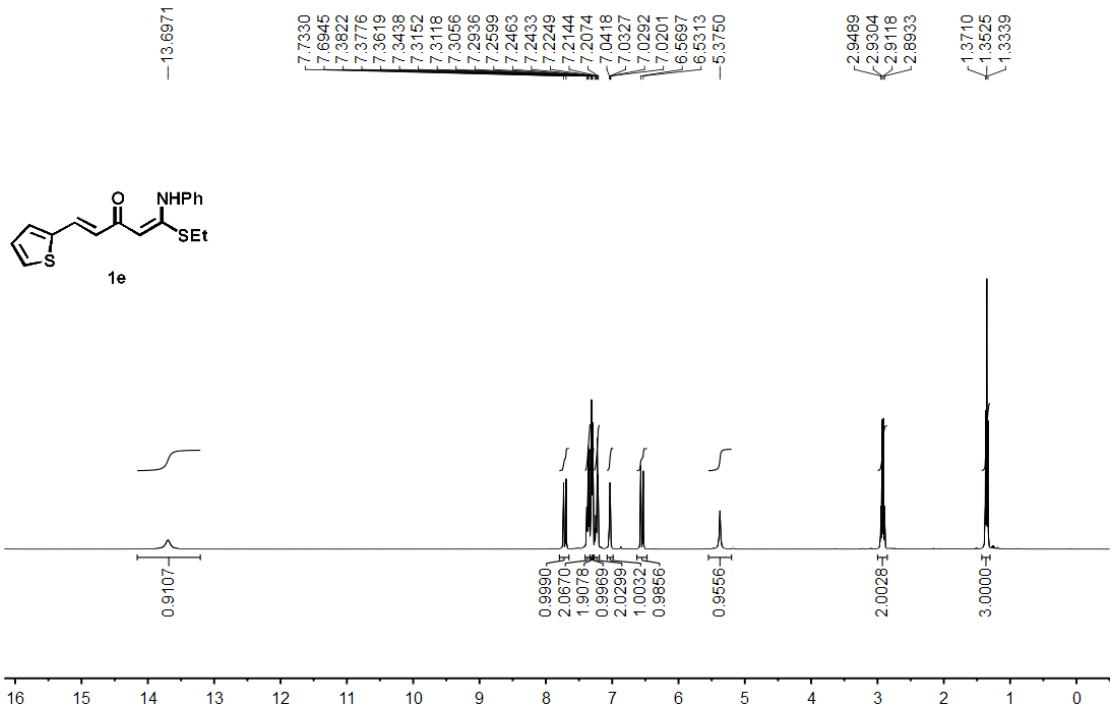
hf404
1H NMR IN CDCl3



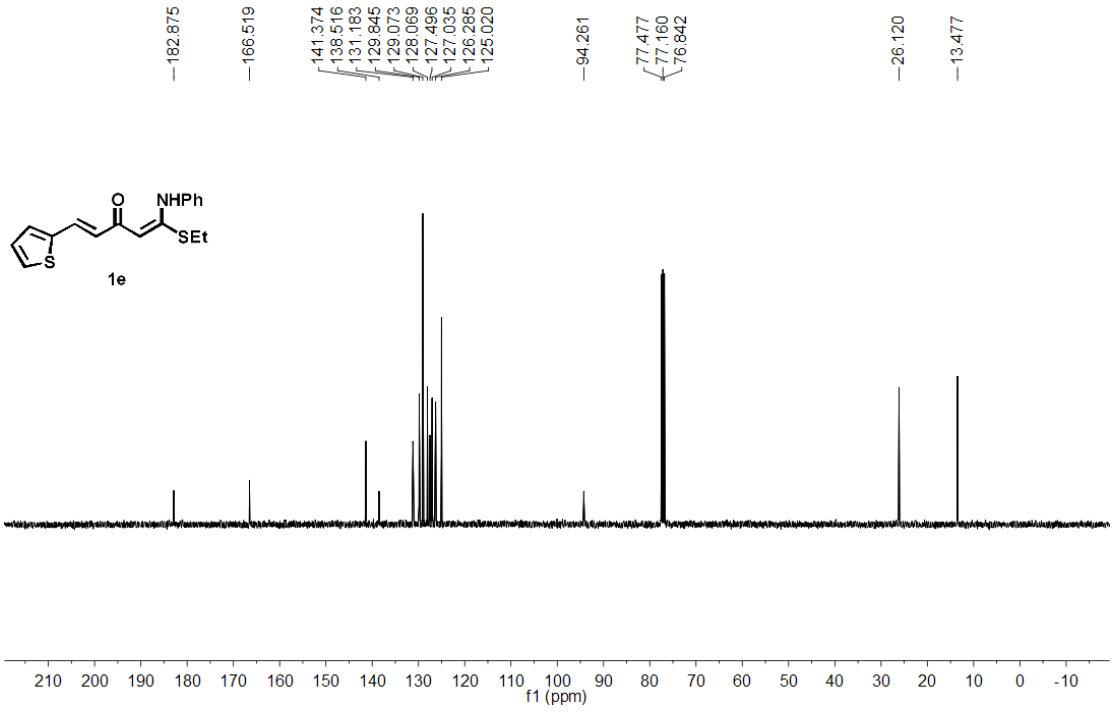
hf404
13C NMR IN CDCl3



HF423-P
1H NMR IN CDCl3

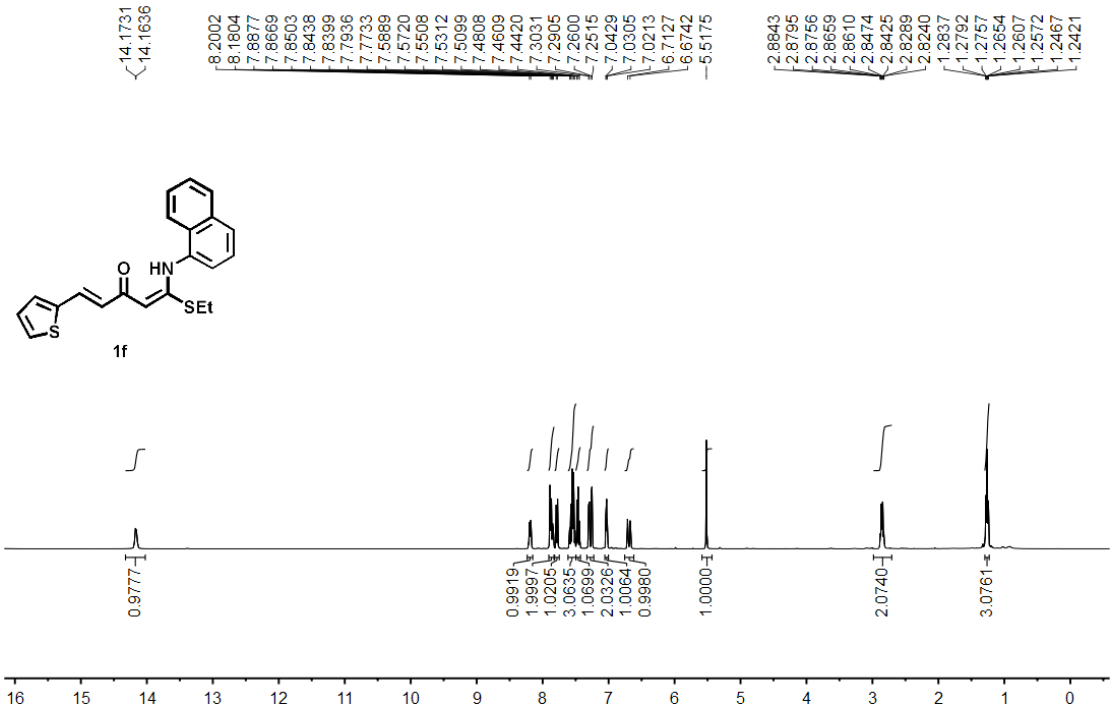


HF423-P
13C NMR IN CDCl3



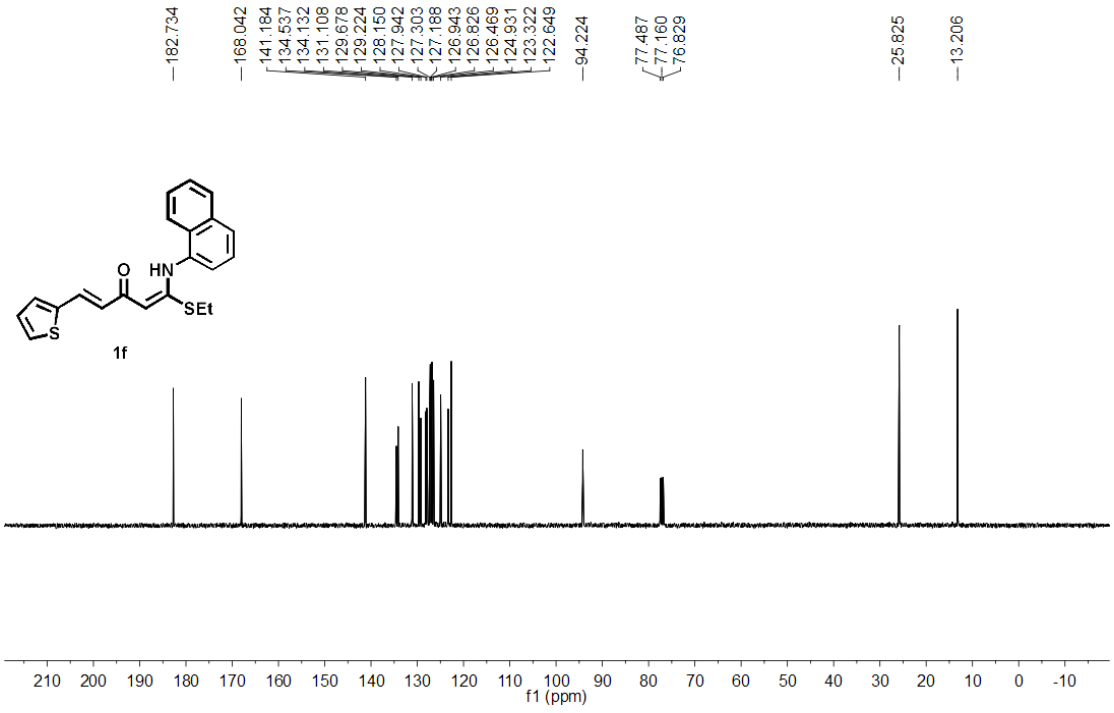
HF431

HF431 in CDCl3 1H NMR

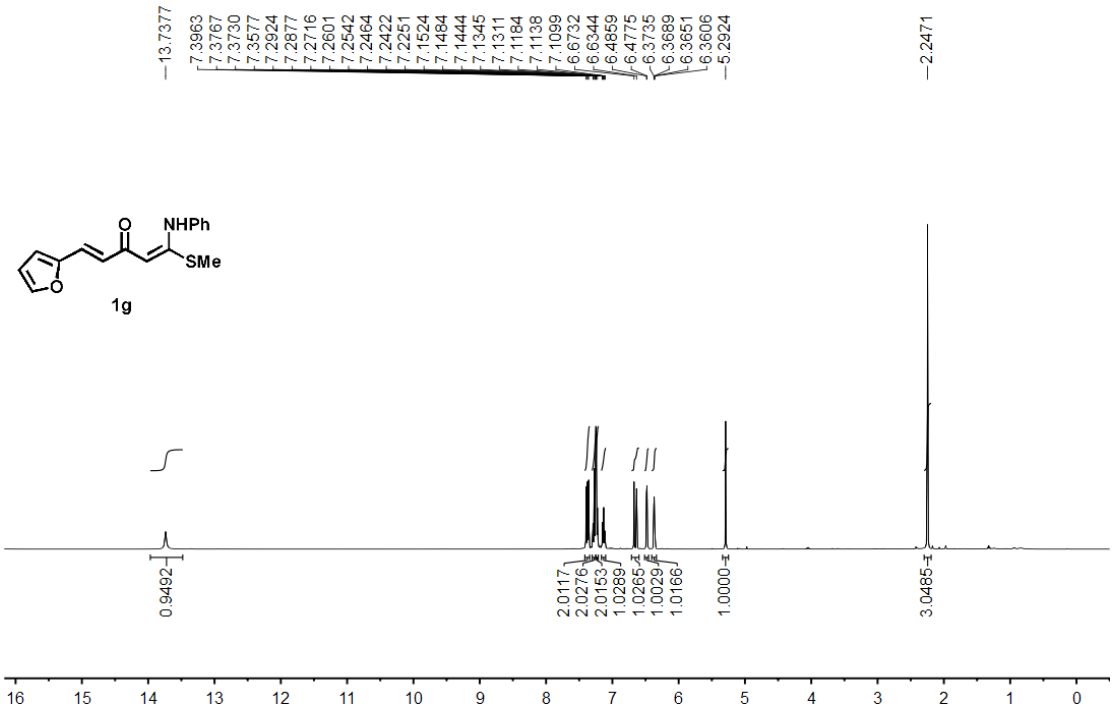


HF431

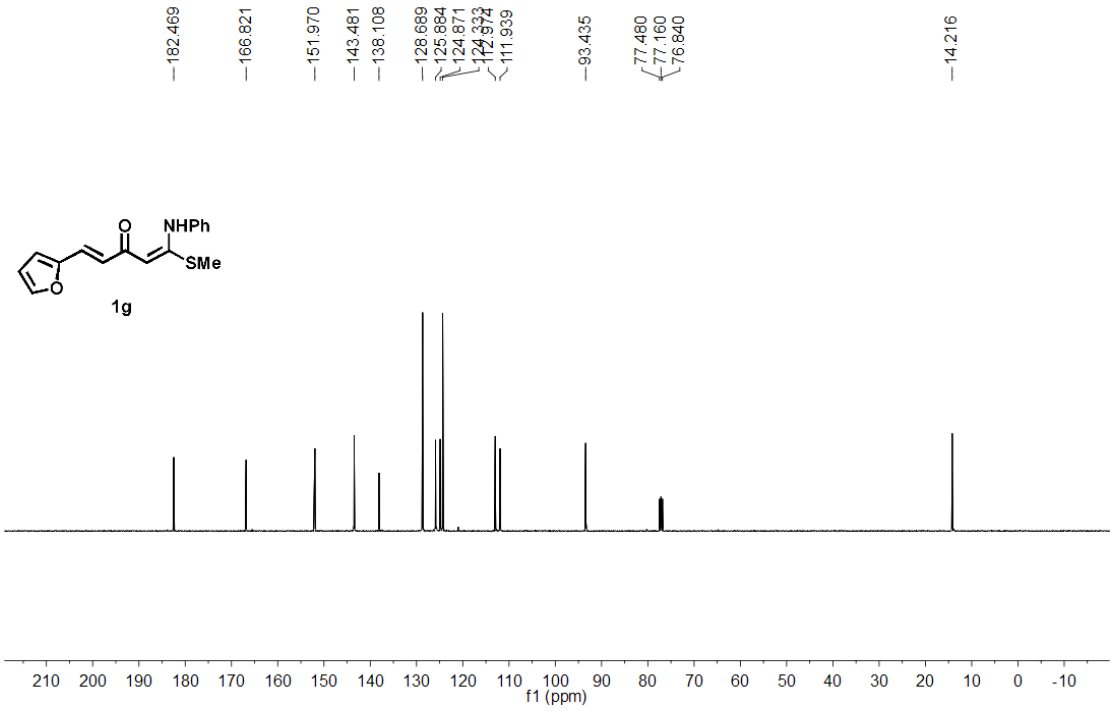
HF431 in CDCl3 13C NMR



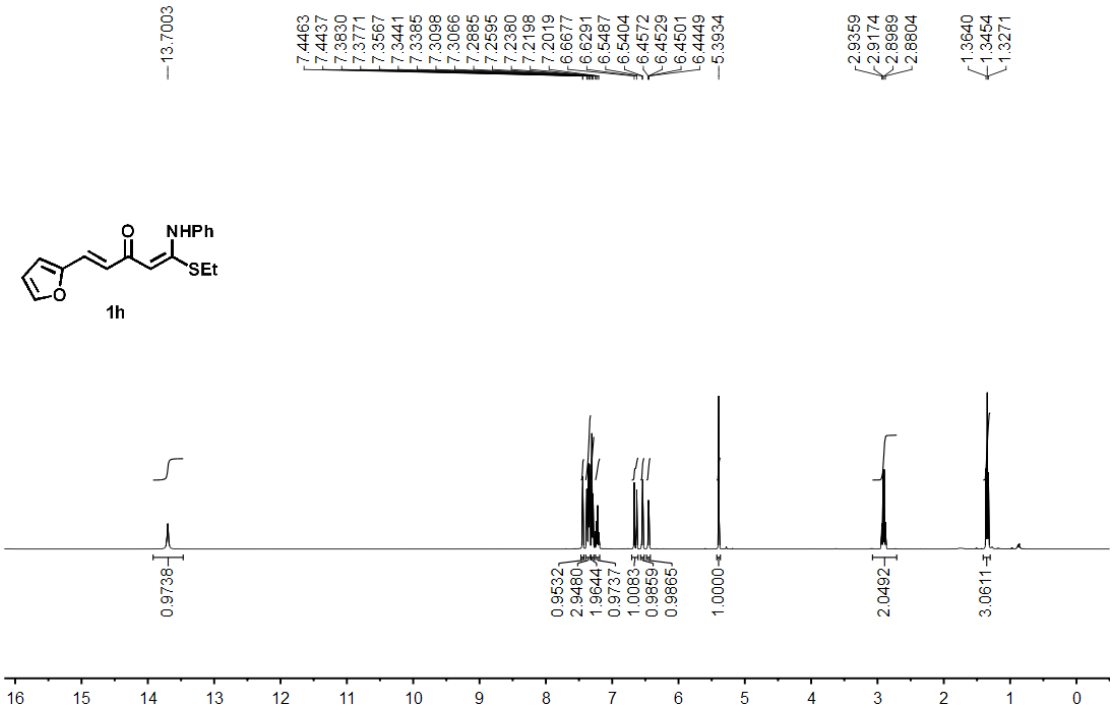
HF453
HF453 in CDC13 1H NMR



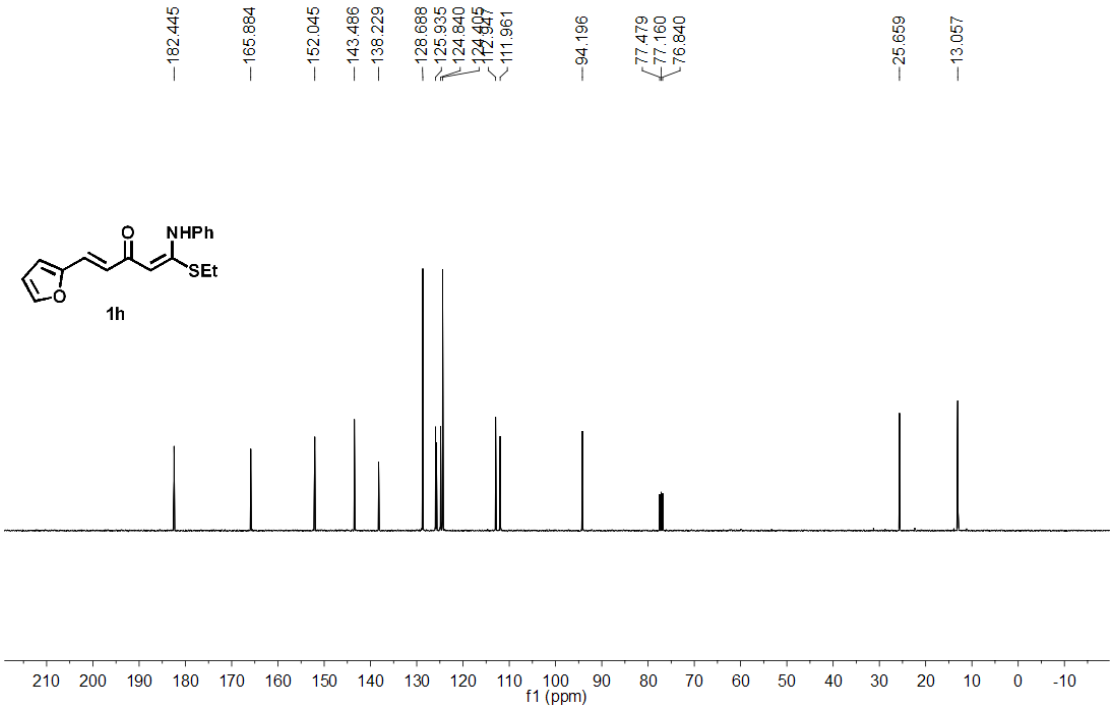
HF453
HF453 in CDC13 13C NMR



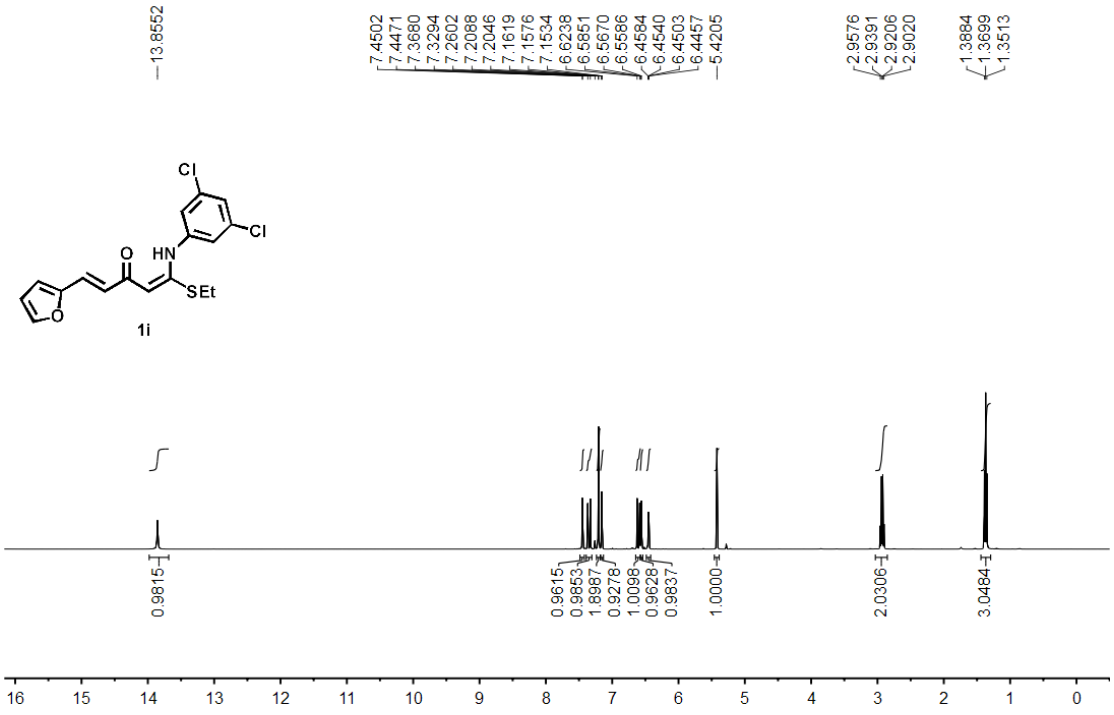
hf451
1H NMR IN CDCl3



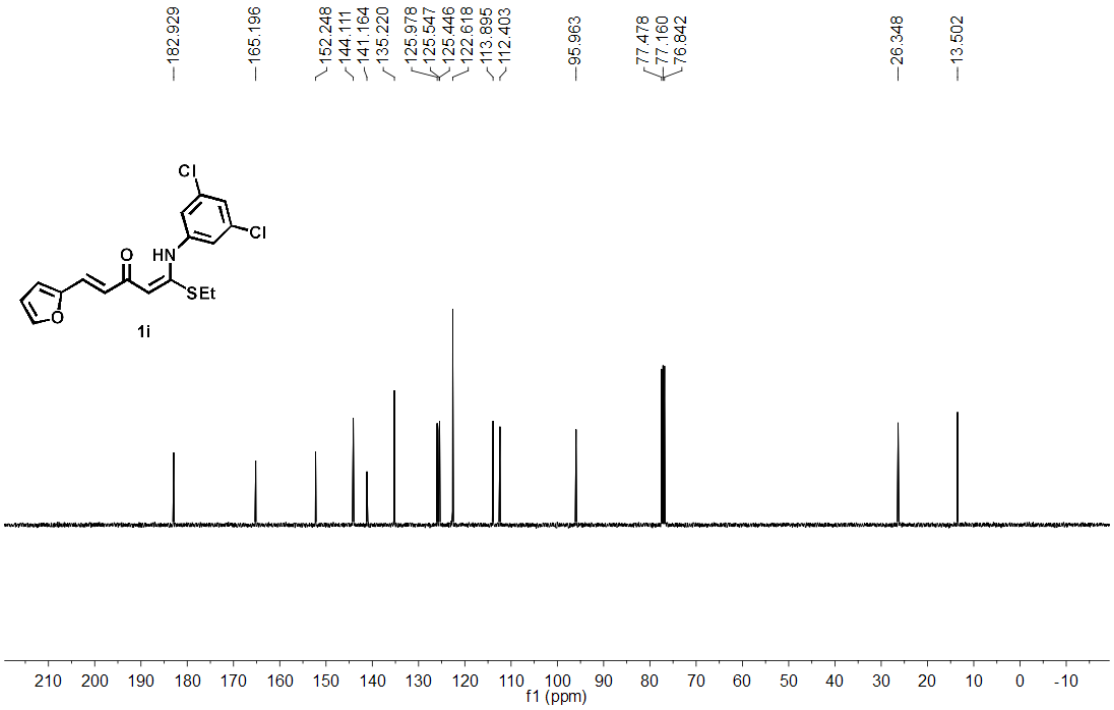
hf451
13C NMR IN CDCl3



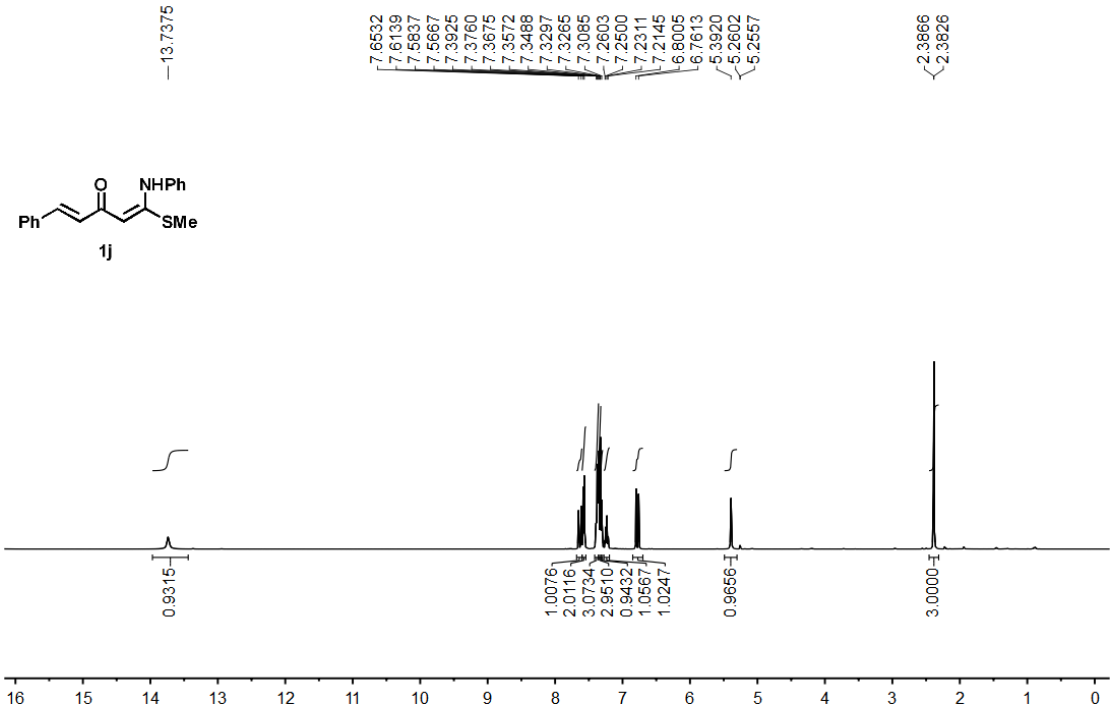
hf452-P
1H NMR IN CDCl3



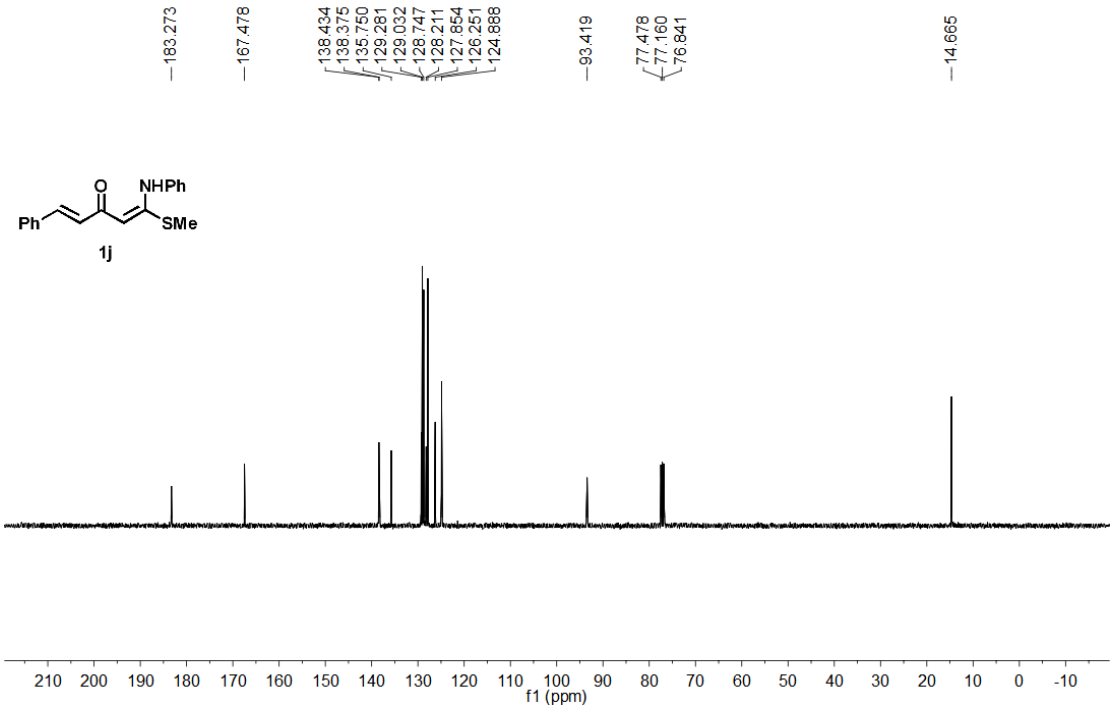
hf452-P
13C NMR IN CDCl3



HF276-P
1H NMR IN CDCl3

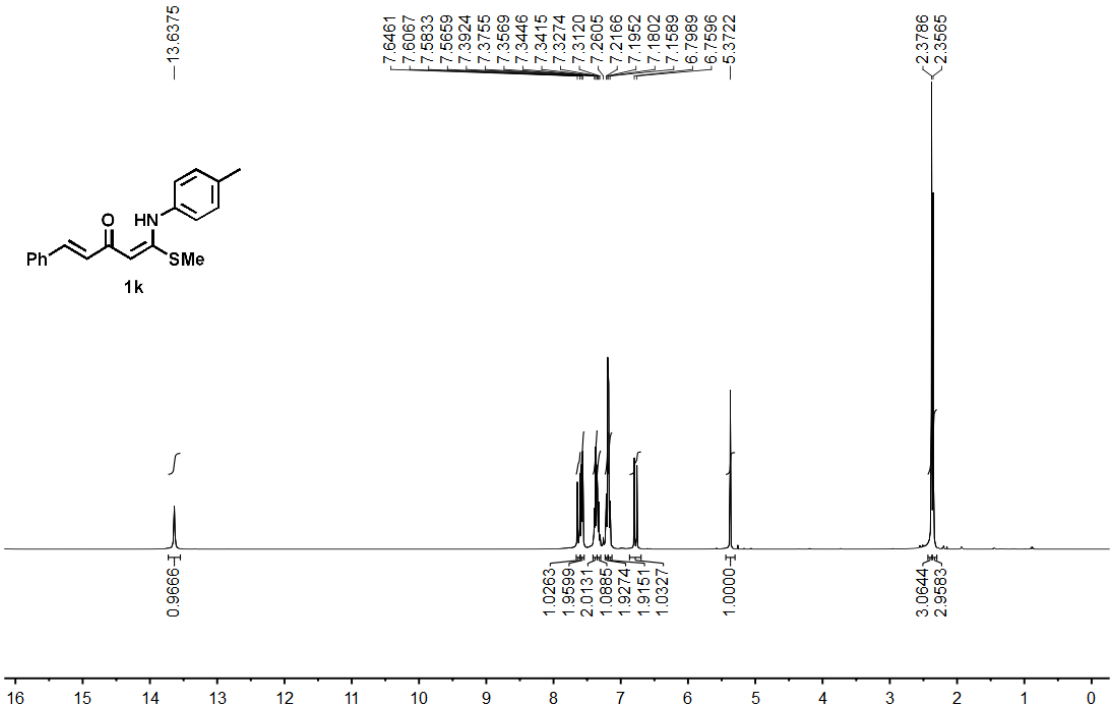


HF276-P
13C NMR IN CDCl3



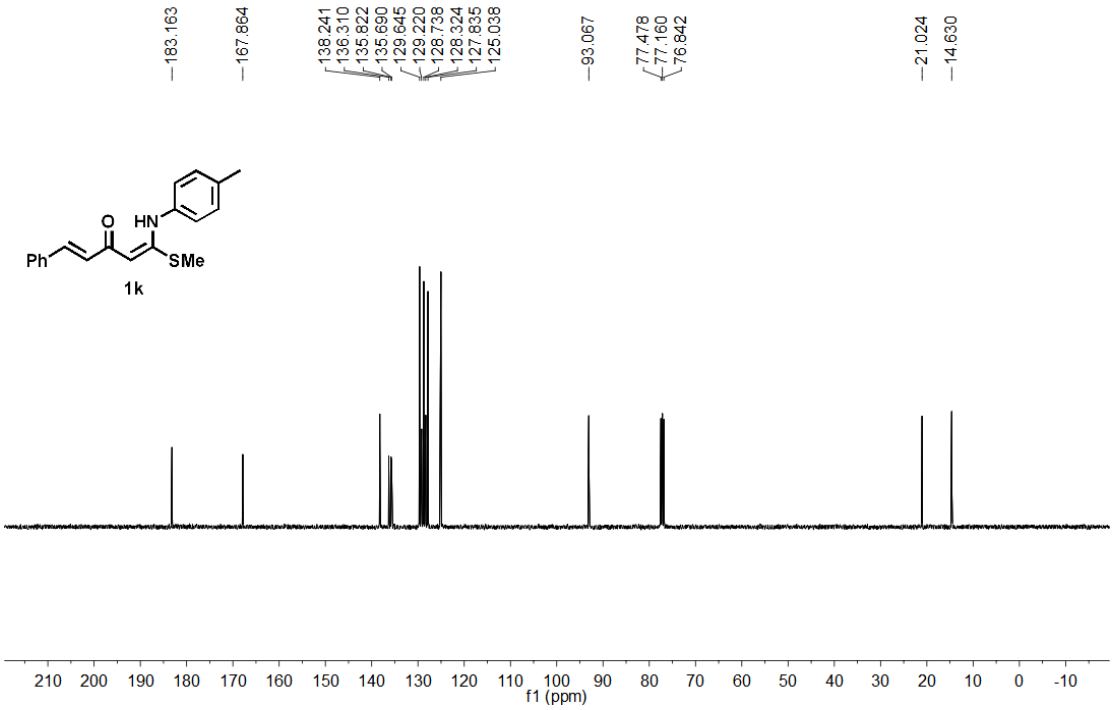
HF463

HF463 in CDC13 1H NMR

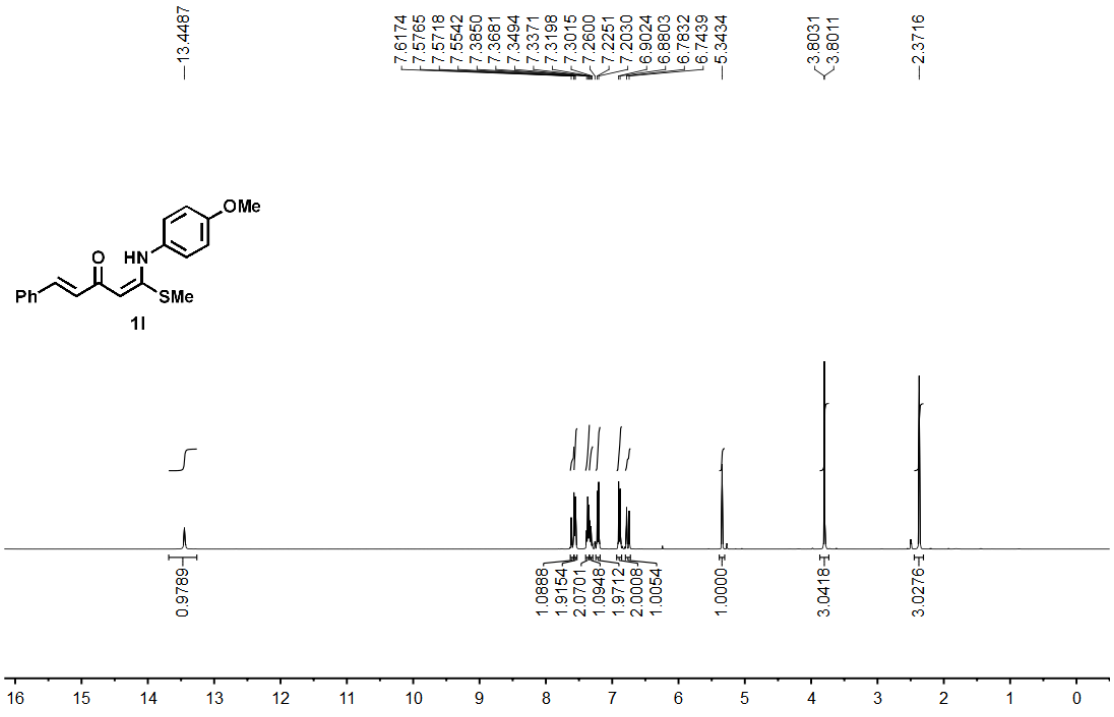


HF463

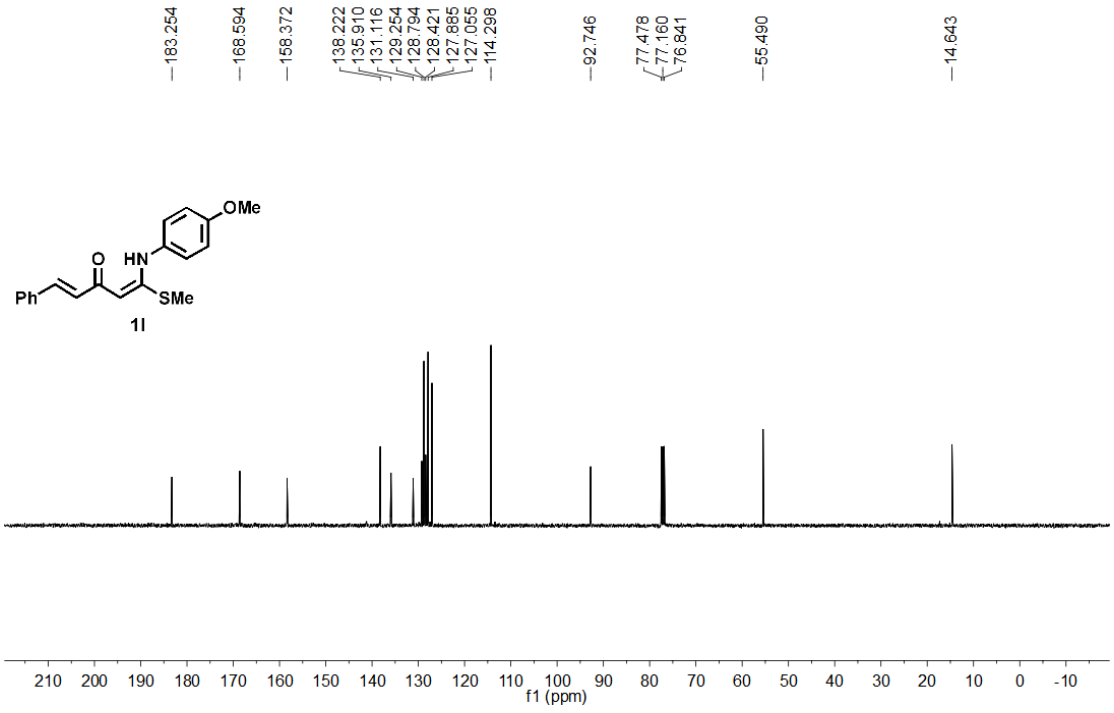
HF463 in CDC13 13C NMR



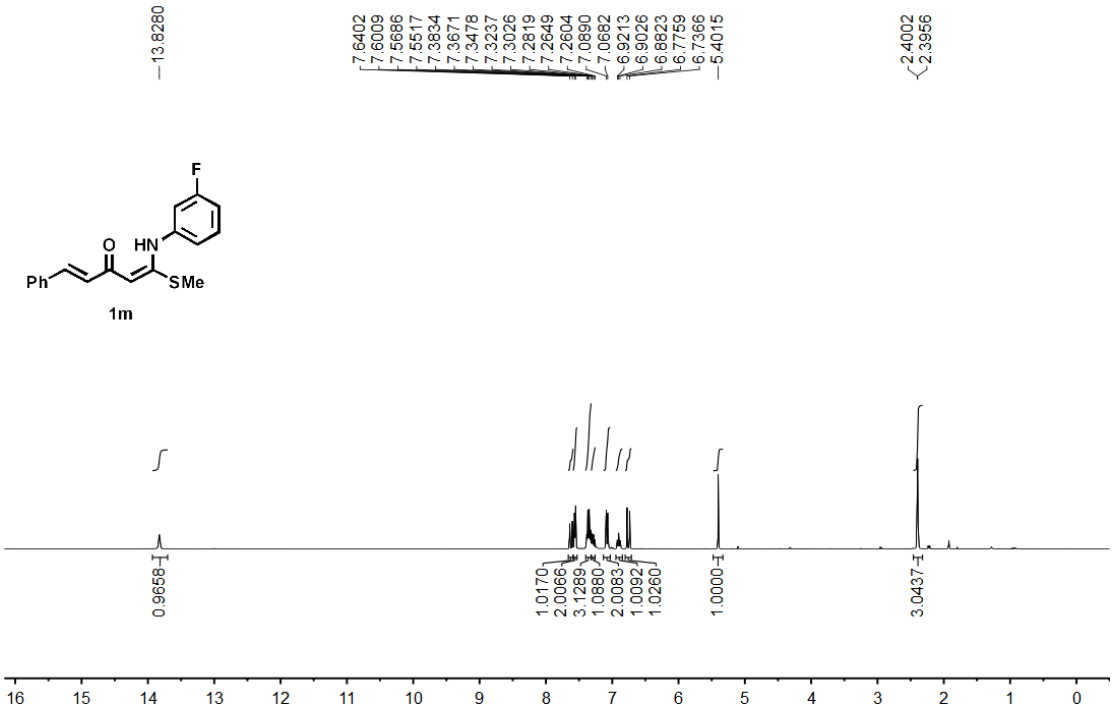
HF462-P
1H NMR IN CDCl3



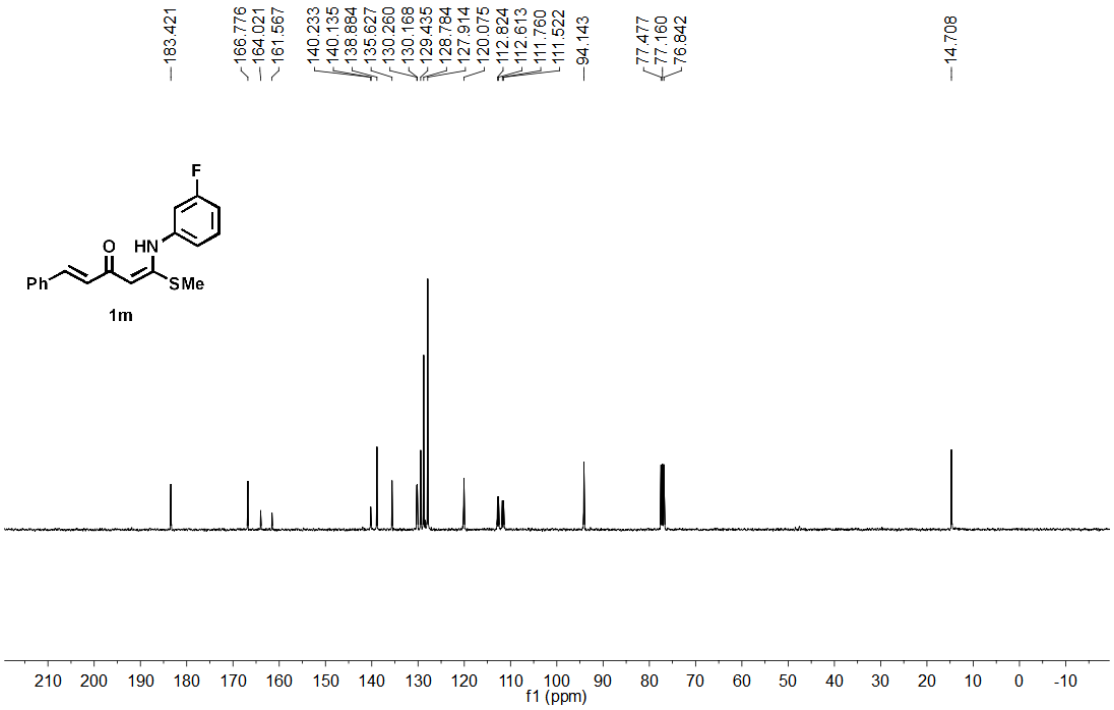
HF462-P
13C NMR IN CDCl3



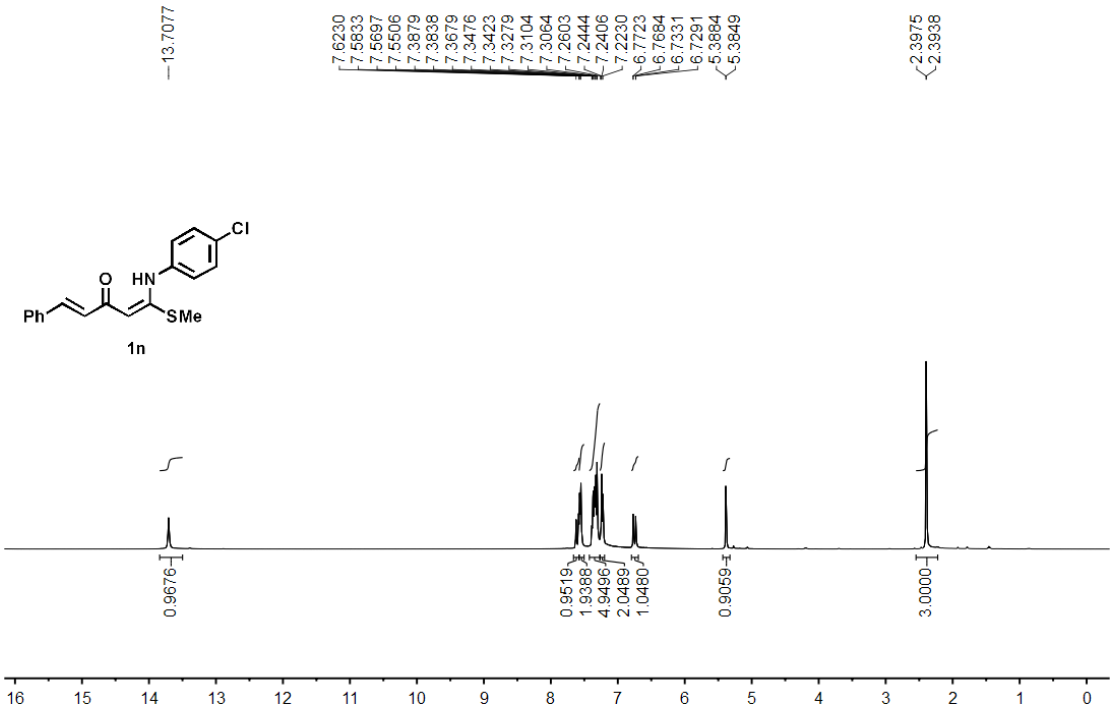
HF499
1H NMR IN CDCl3



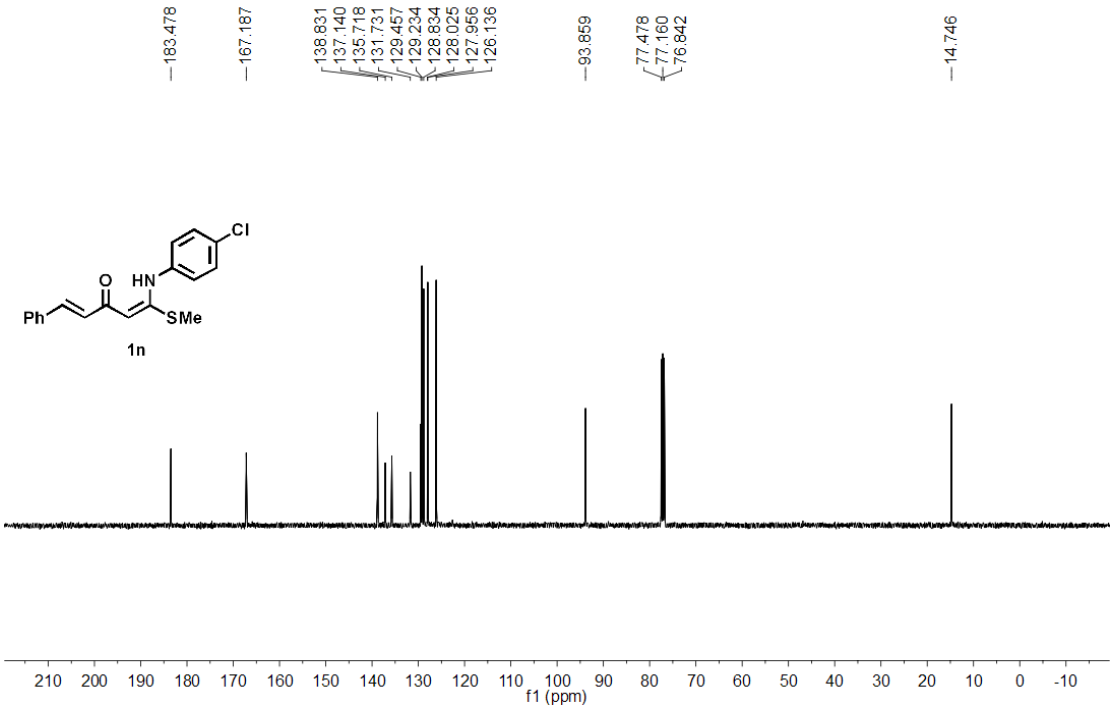
HF499
13C NMR IN CDCl3



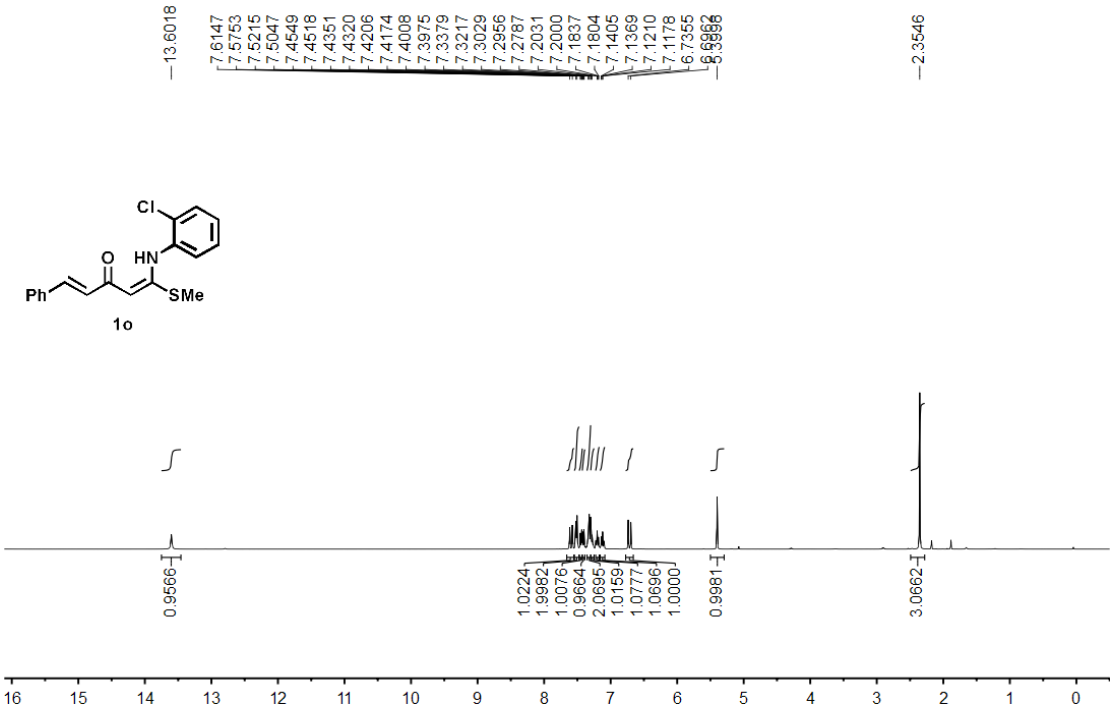
hf461-p
1H NMR IN CDCl3



hf461-p
13C NMR IN CDCl3



HF500
1H NMR IN CDCl3



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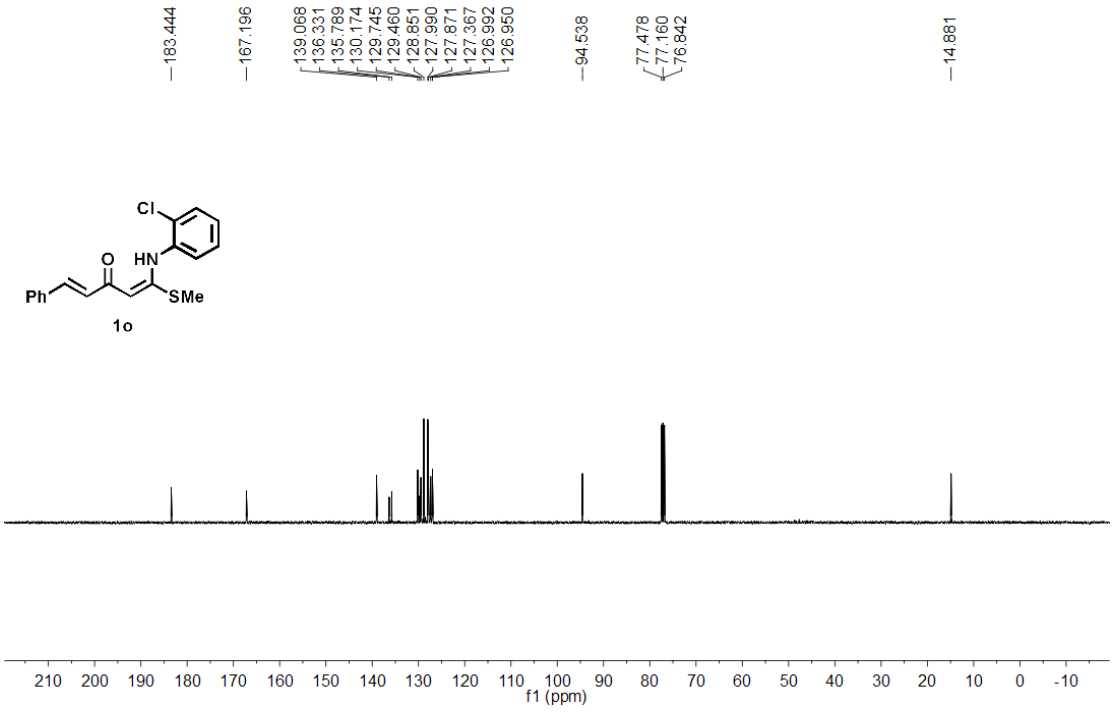
HF500
13C NMR IN CDCl3



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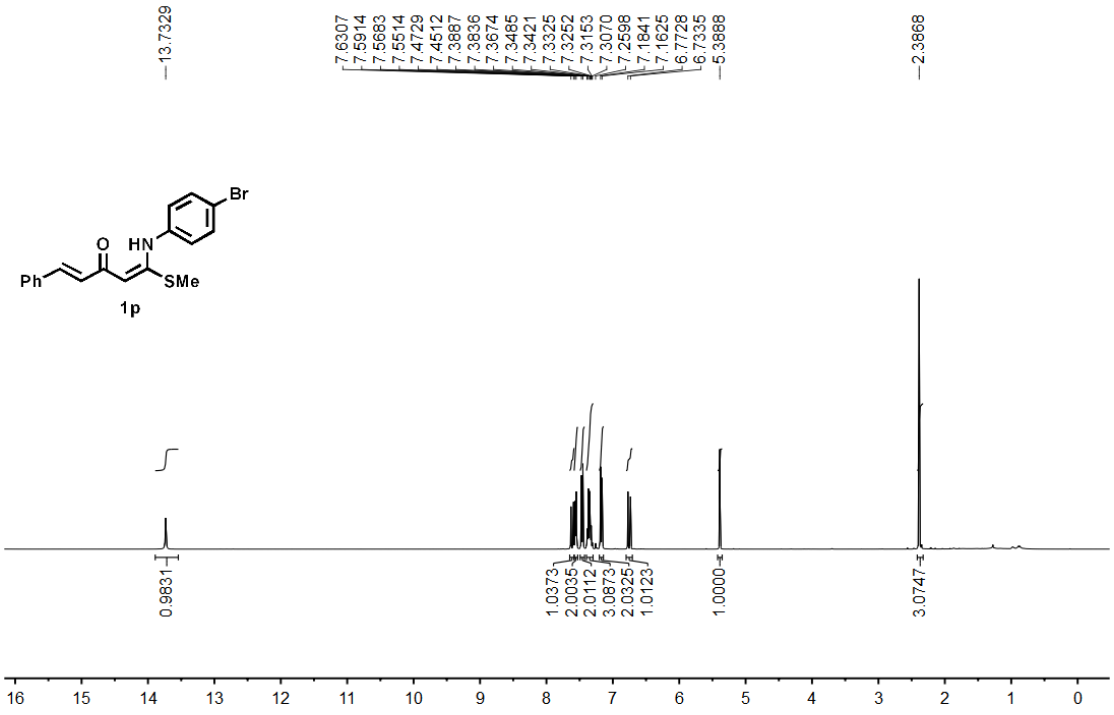
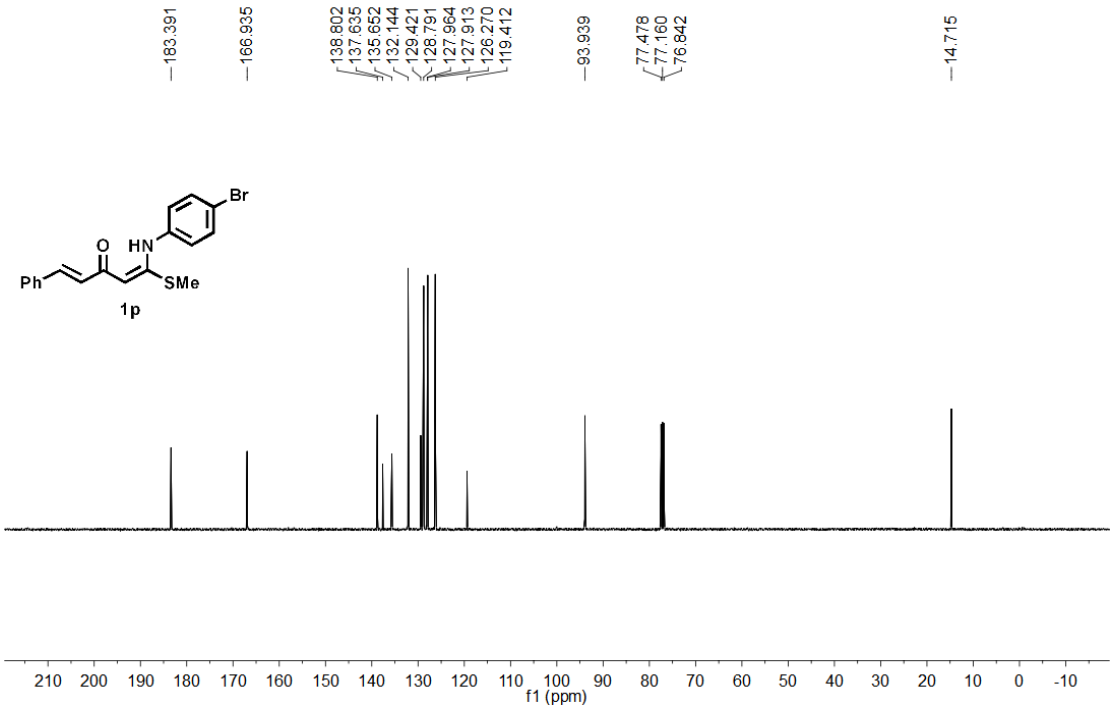
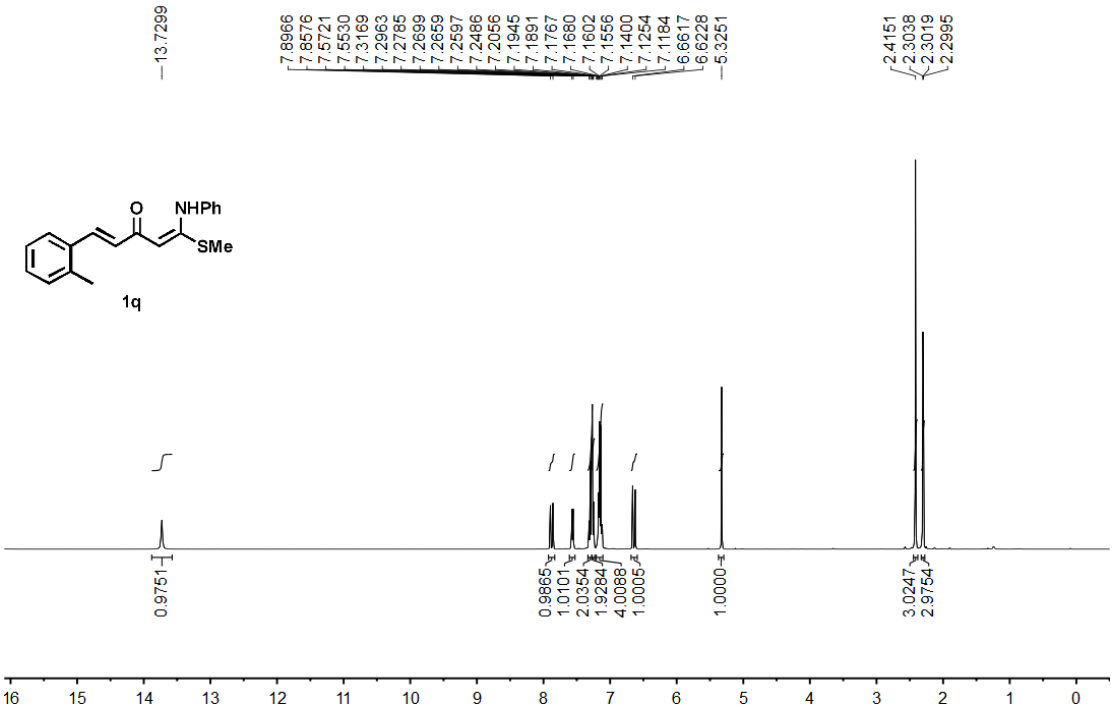
hf460
1H NMR IN CDCl3



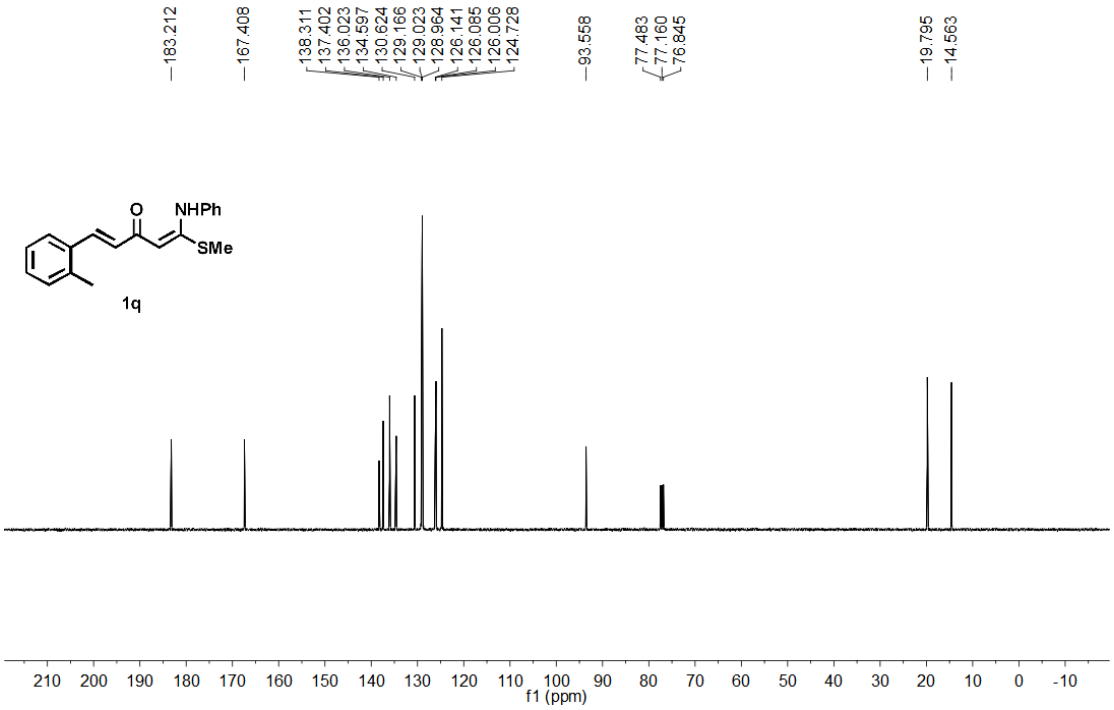
hf460
13C NMR IN CDCl3



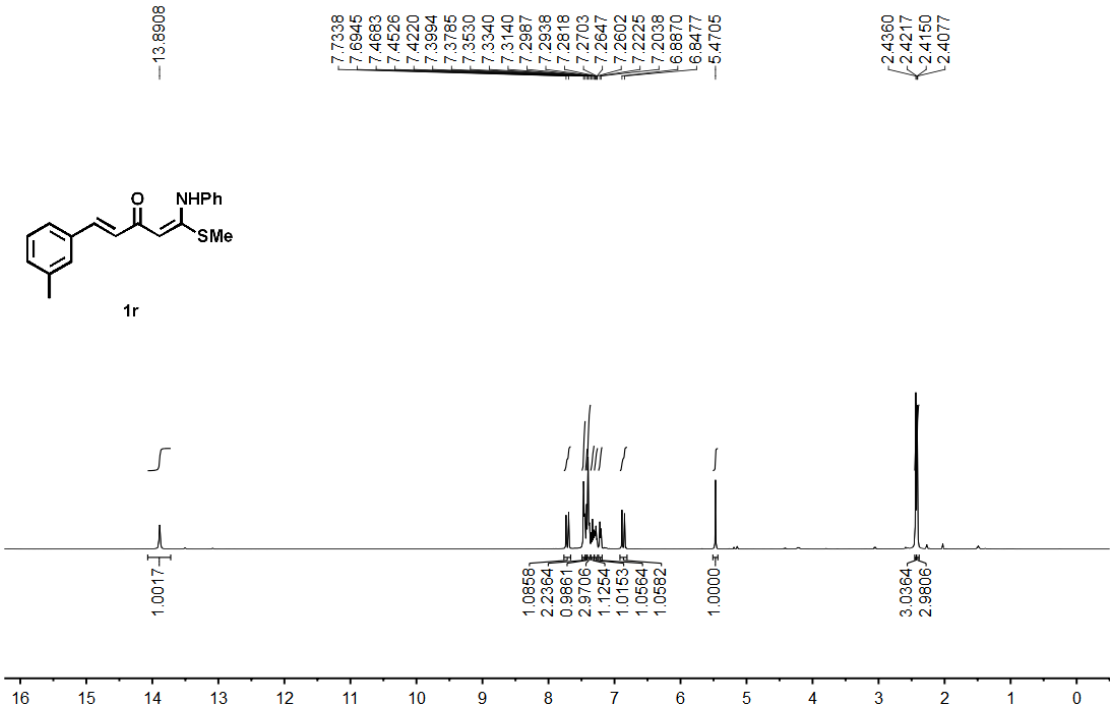
HF498
1H NMR IN CDCl3



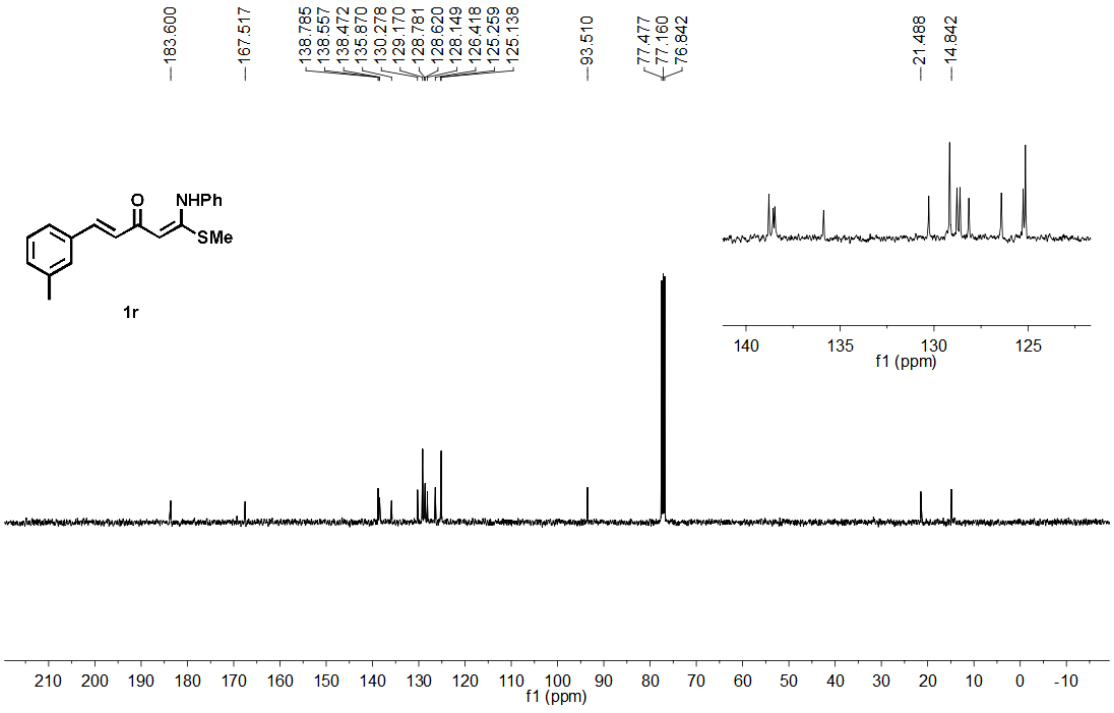
HF498
13C NMR IN CDCl3



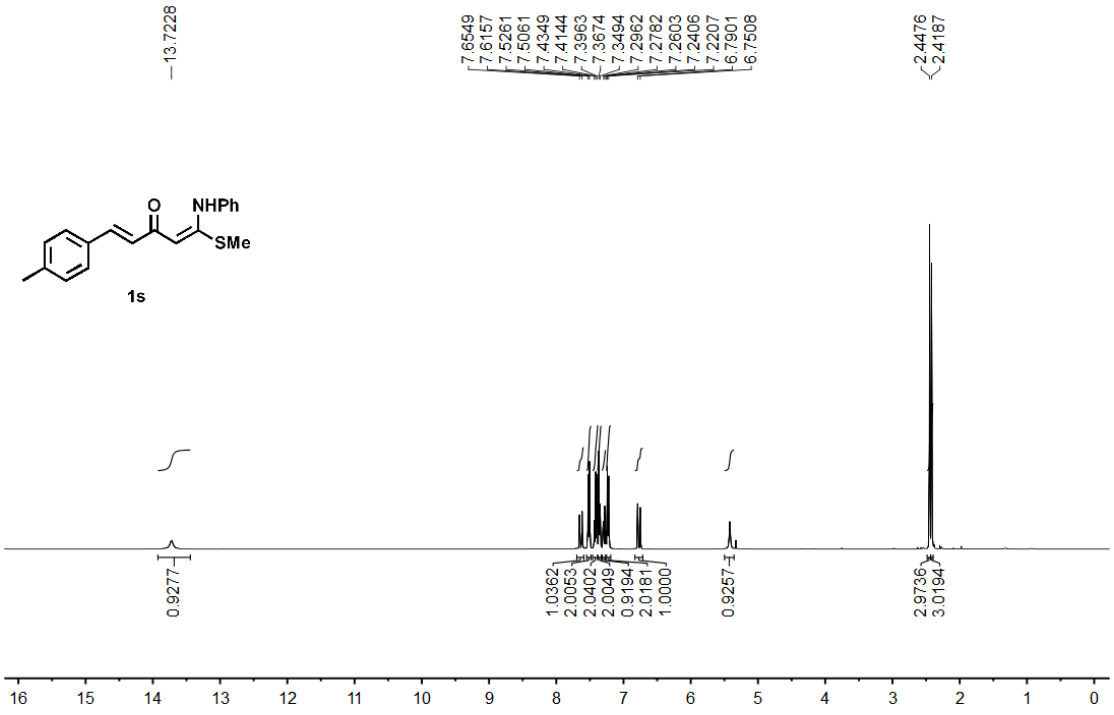
HF497
1H NMR IN CDCl3



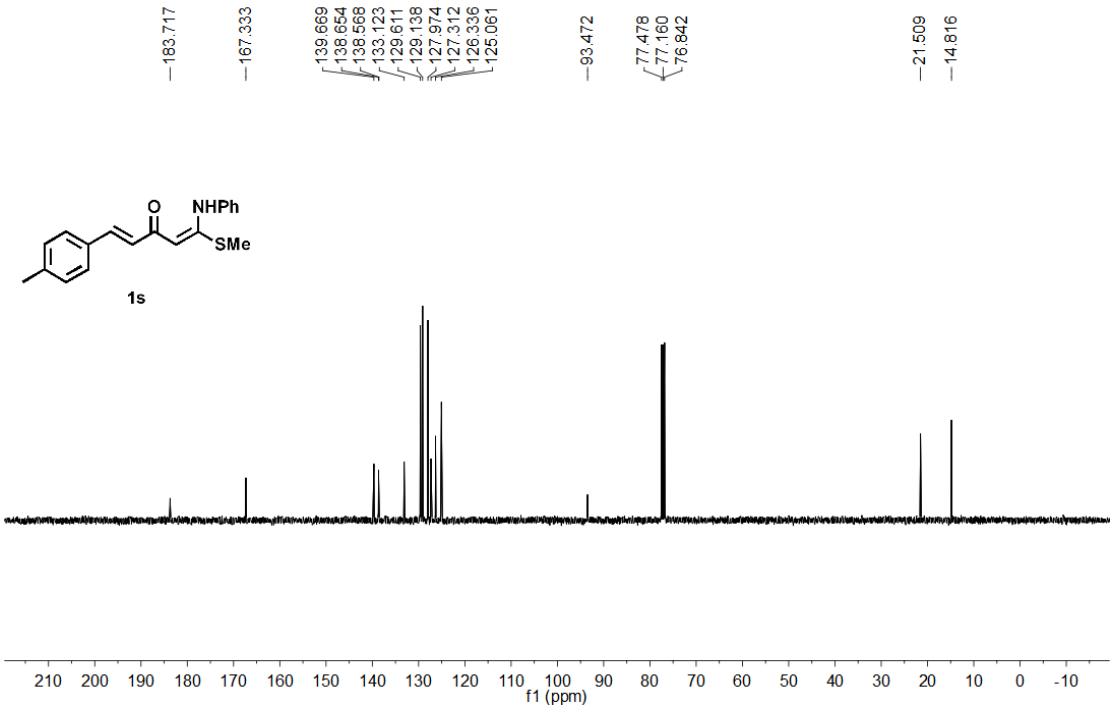
HF497
13C NMR IN CDCl3



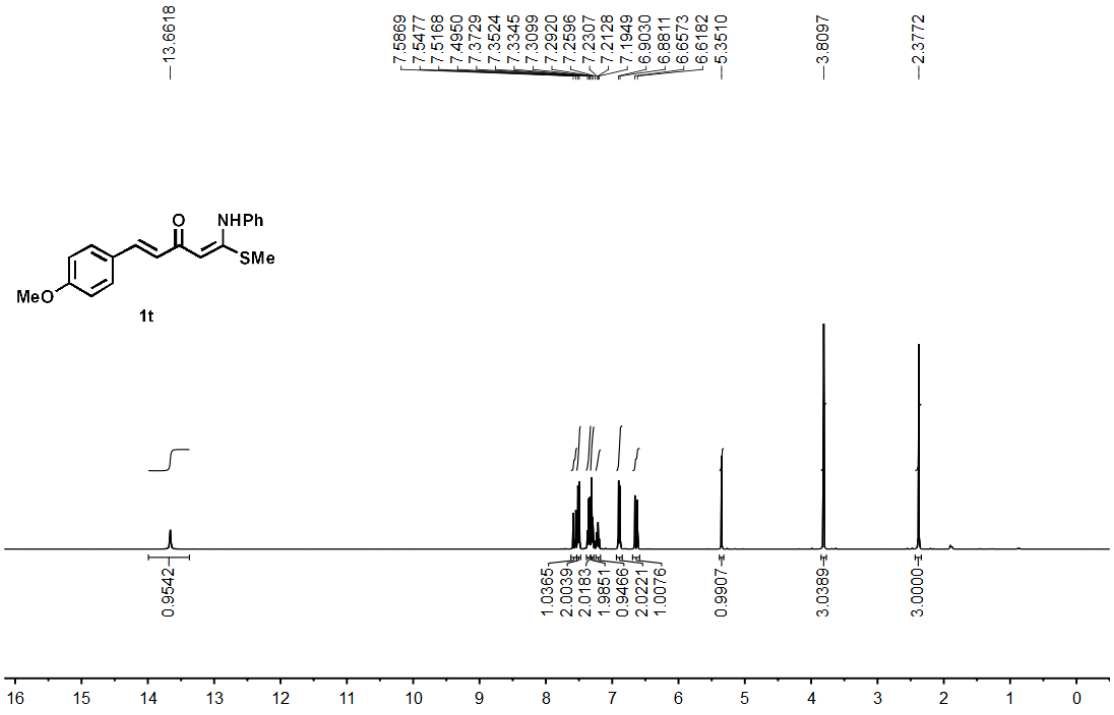
HF403
1H NMR IN CDCl3



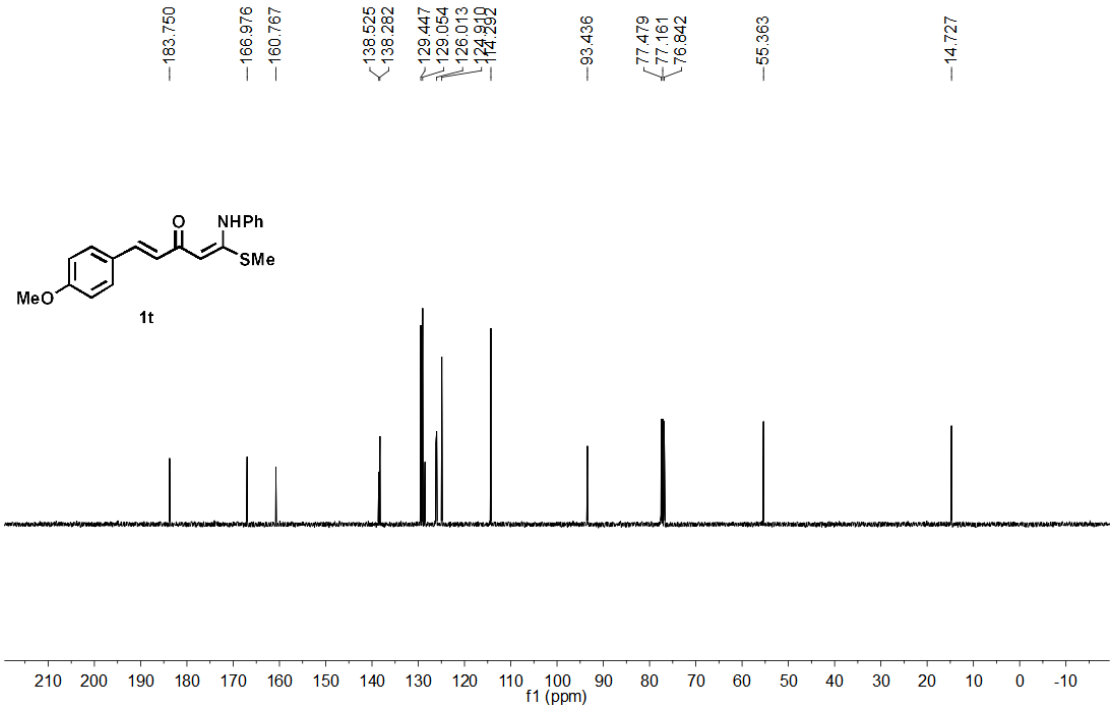
HF403
13C NMR IN CDCl3



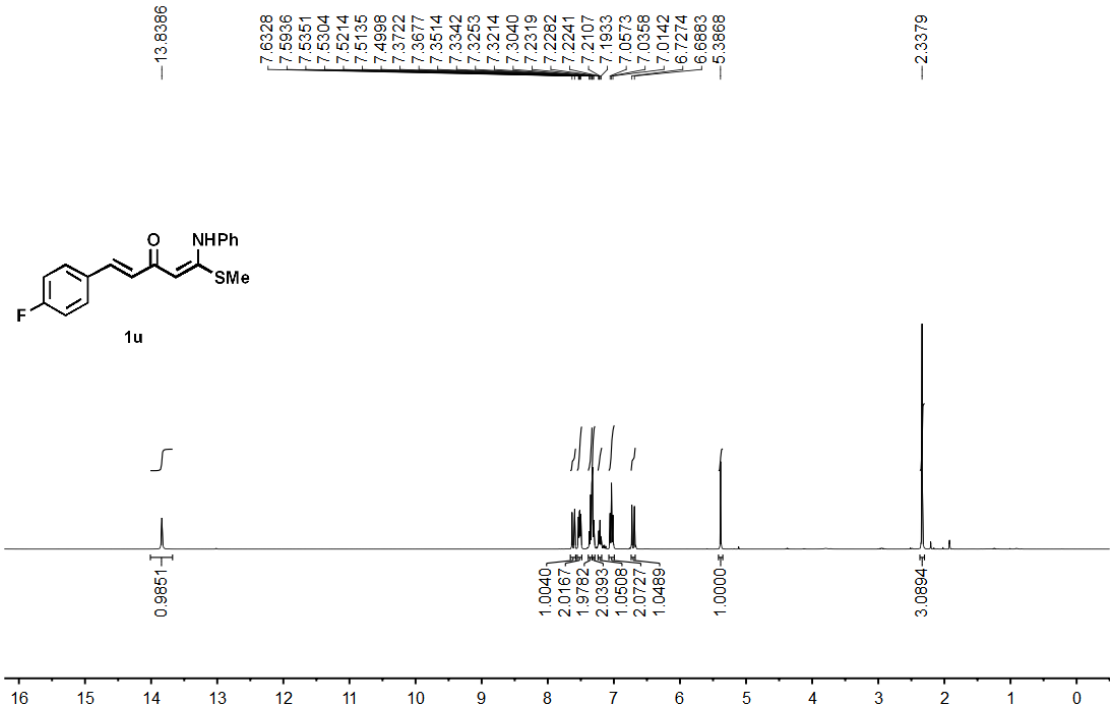
HF363
1H NMR IN CDCl3



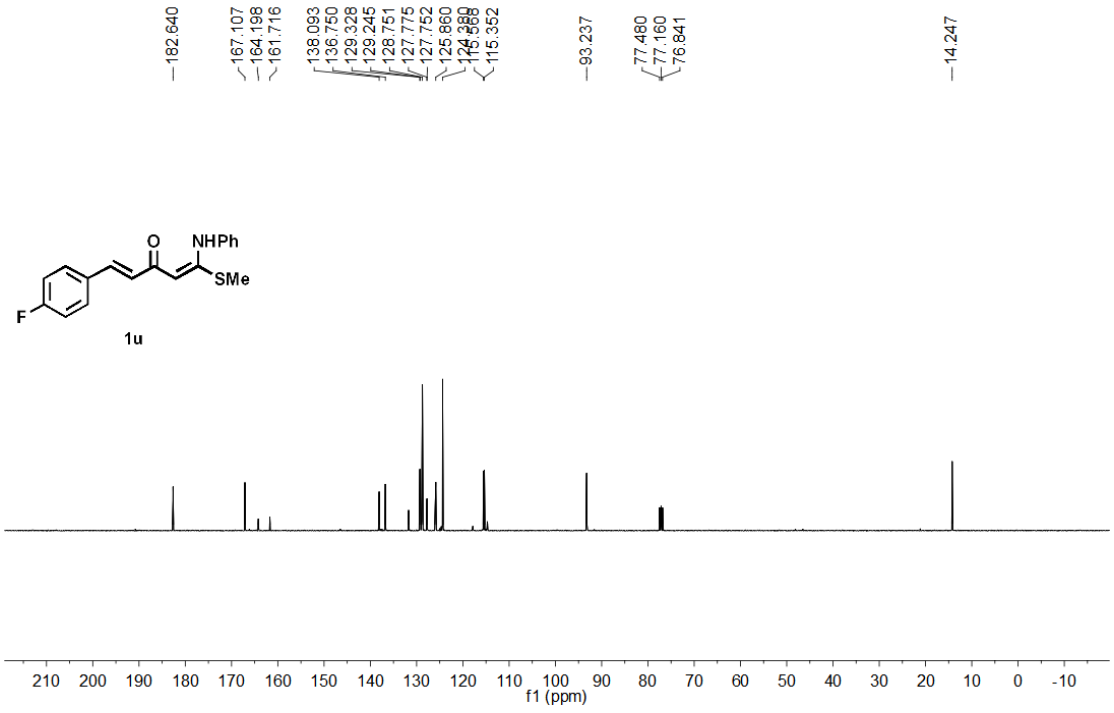
HF363
13C NMR IN CDCl3



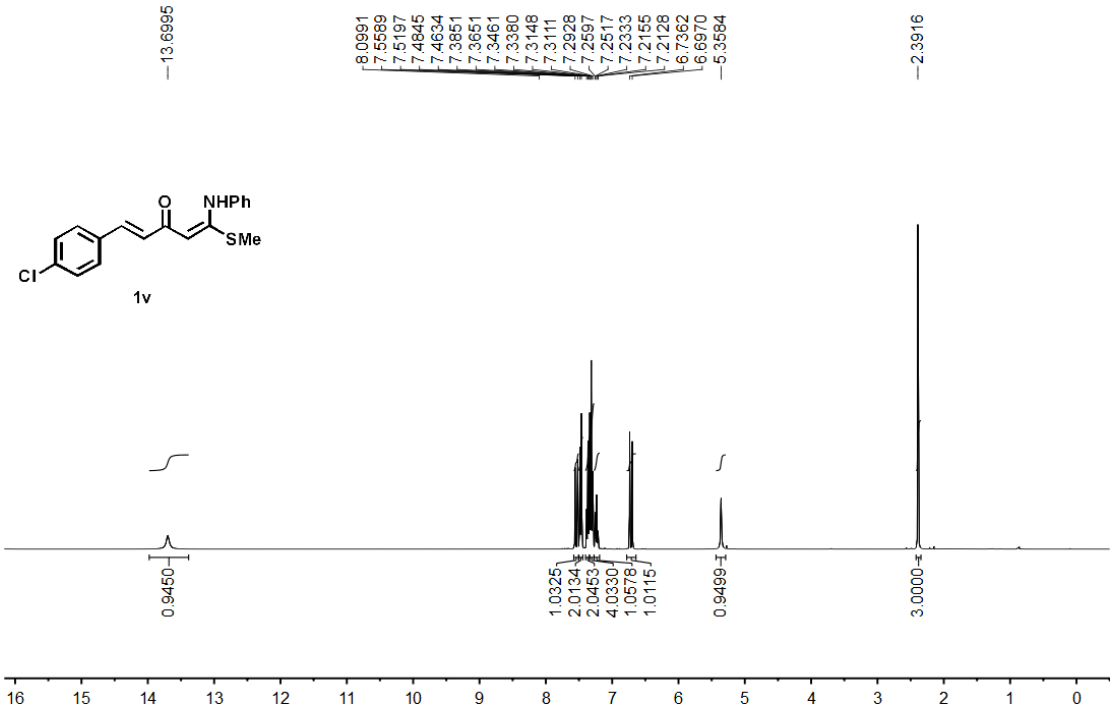
HF439
1H NMR IN CDCl3



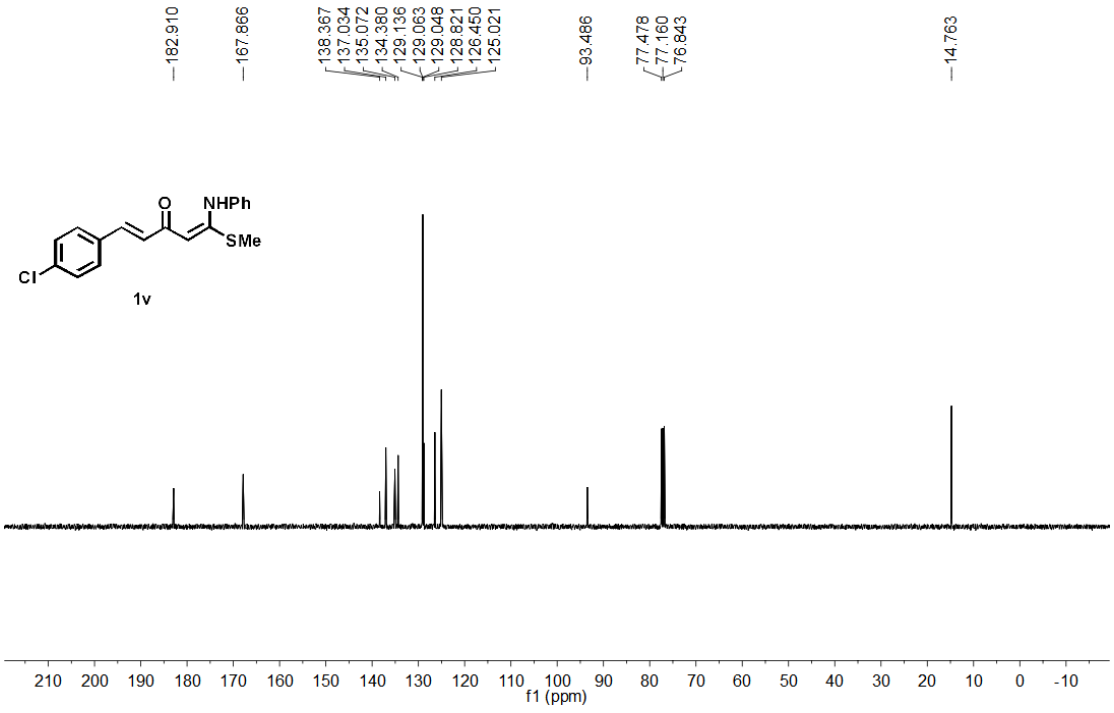
HF439
13C NMR IN CDCl3



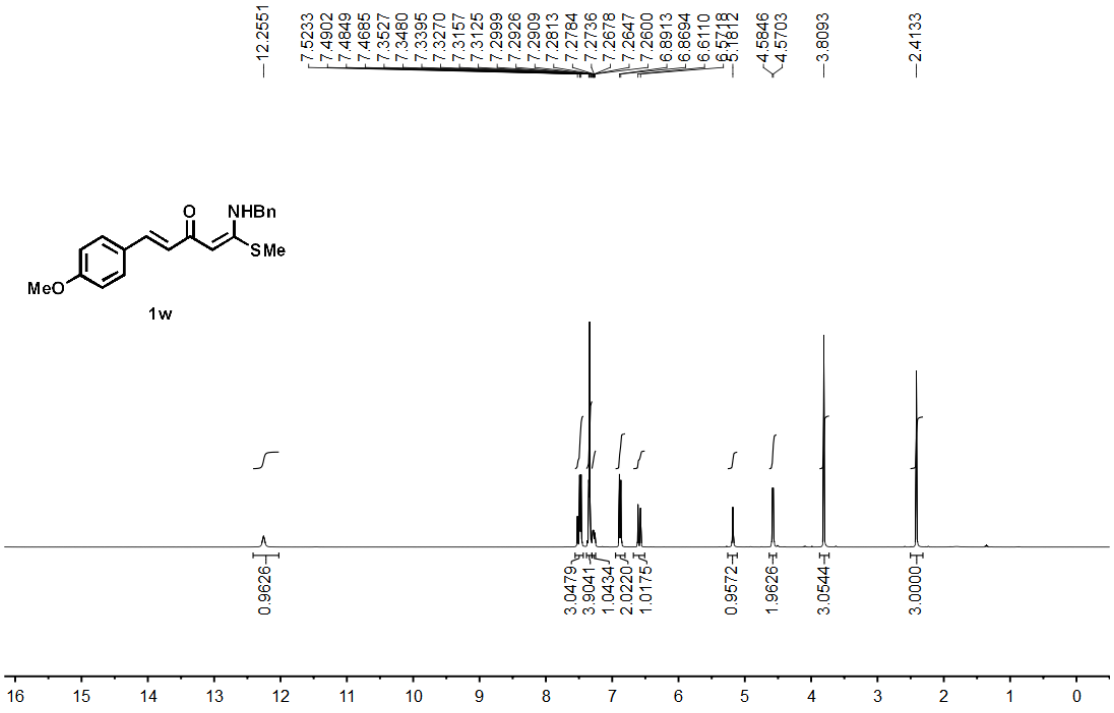
HF409
1H NMR IN CDCl3



HF409
13C NMR IN CDCl3

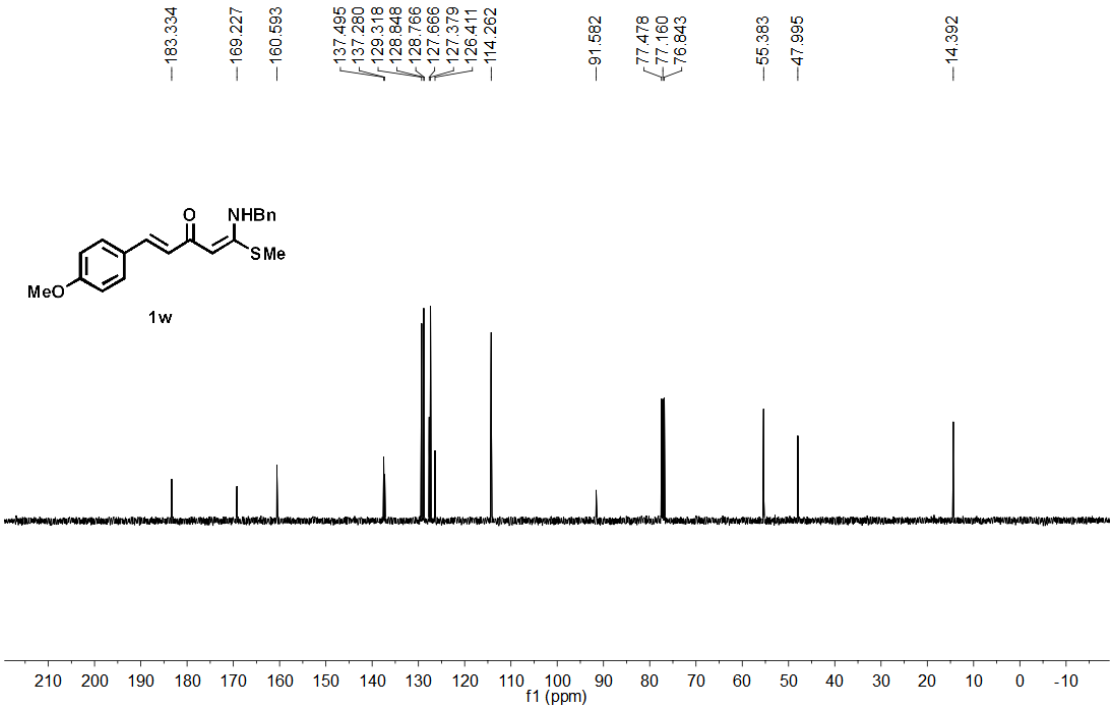


hf393
1H NMR IN CDCl3



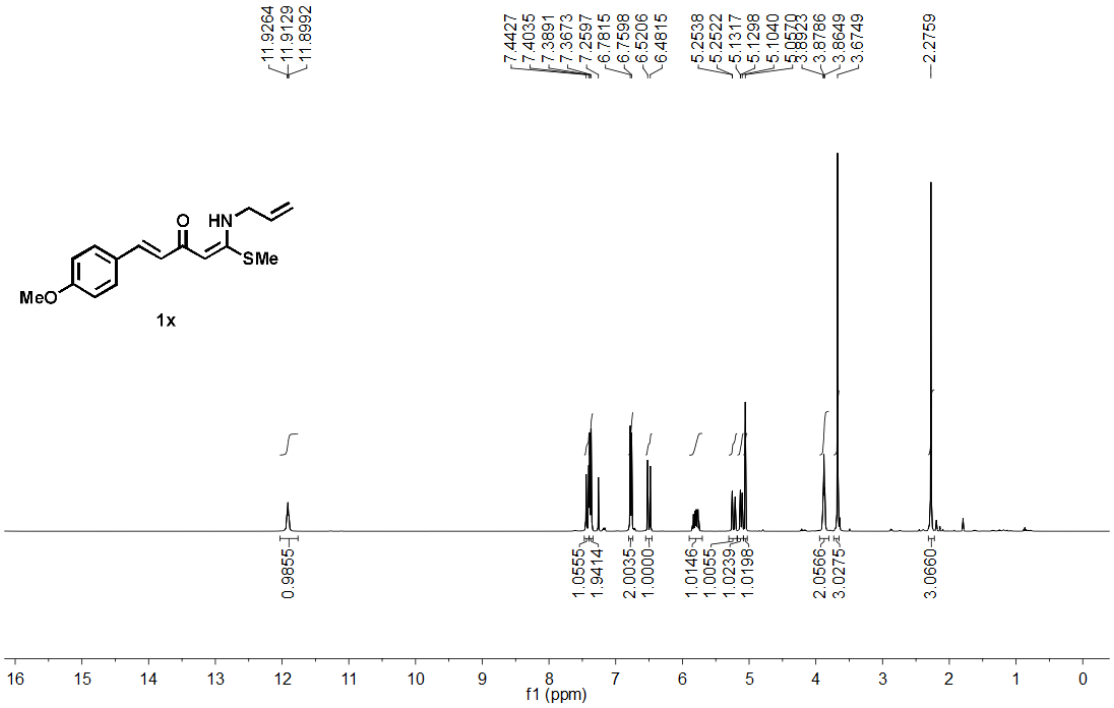
1w

hf393
13C NMR IN CDCl3

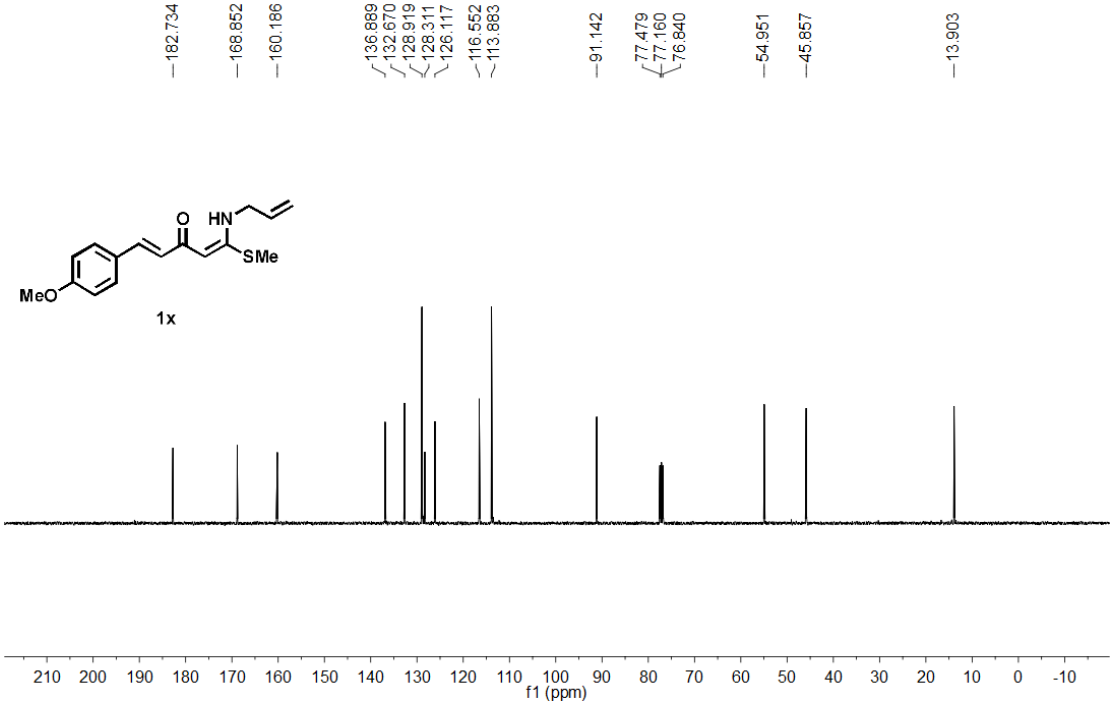


1w

HF614-2
1H NMR IN CDCl3

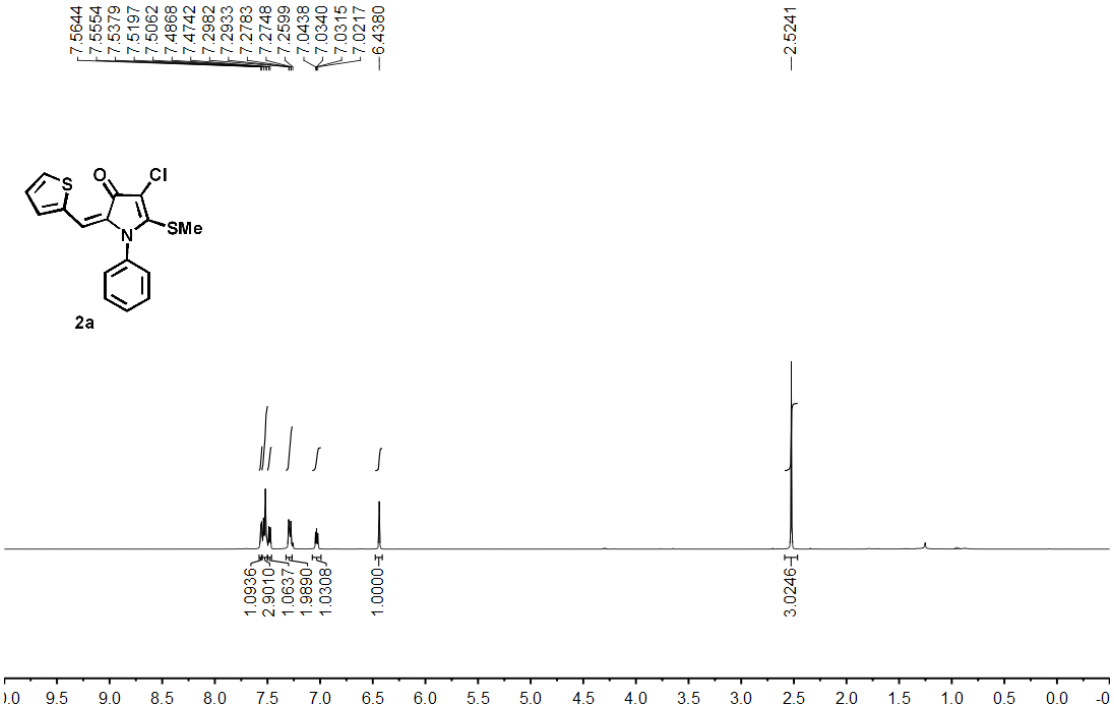


HF614-2
13C NMR IN CDCl3



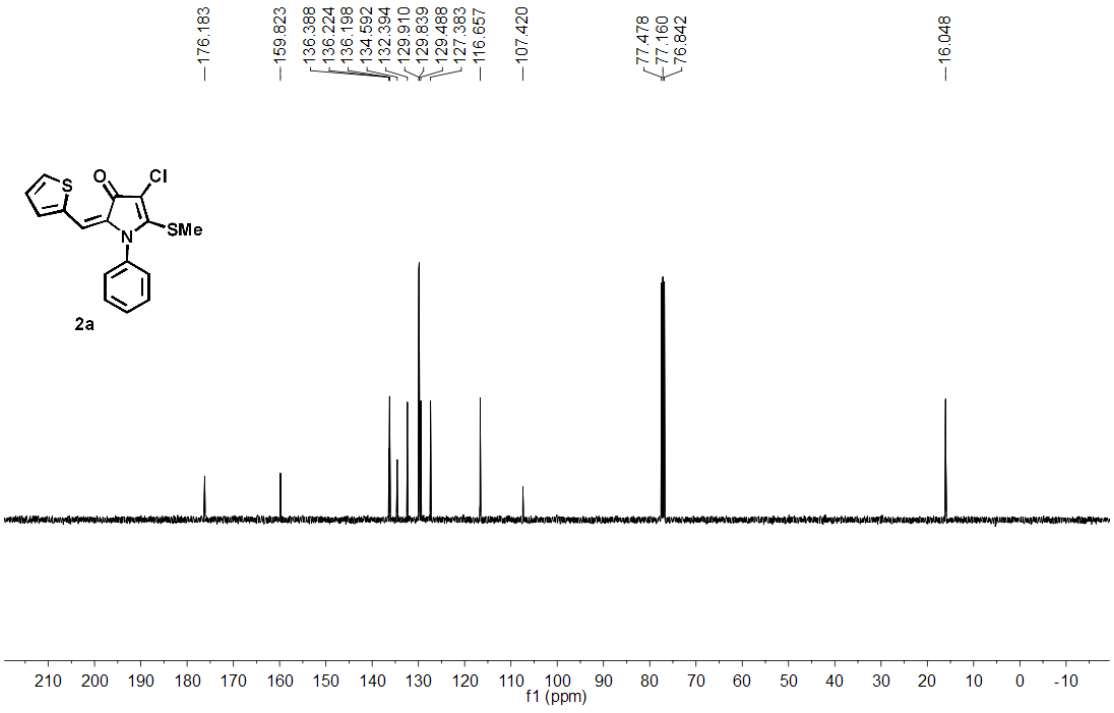
HF468

HF468 in CDC13 1H NMR

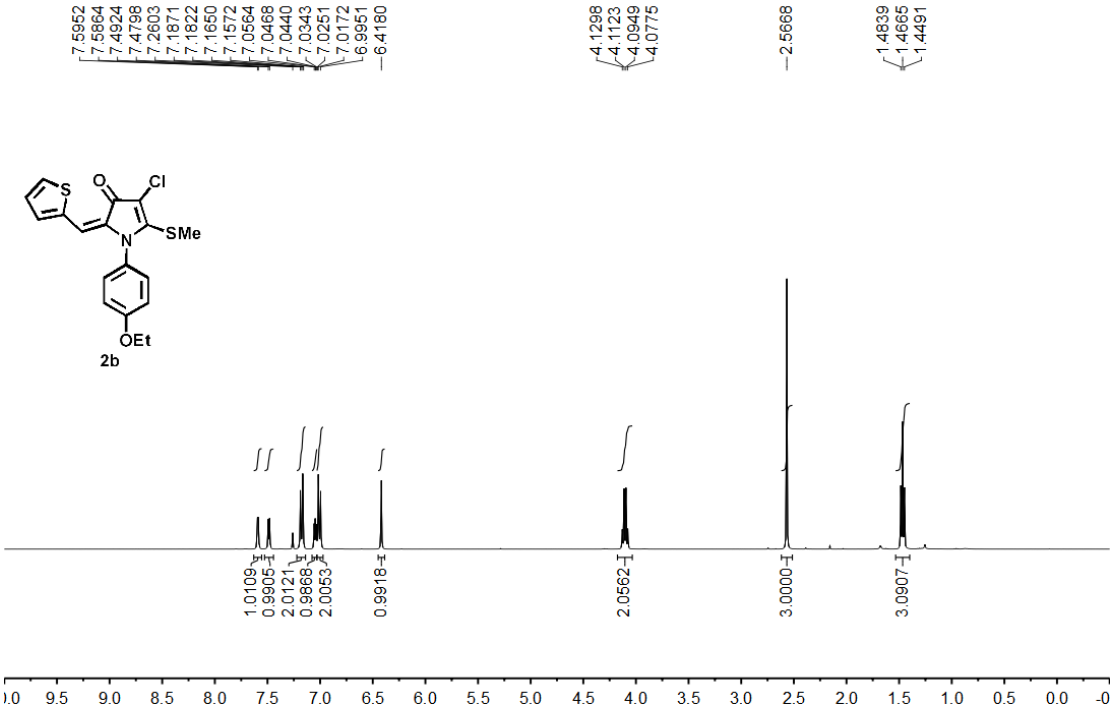


HF468

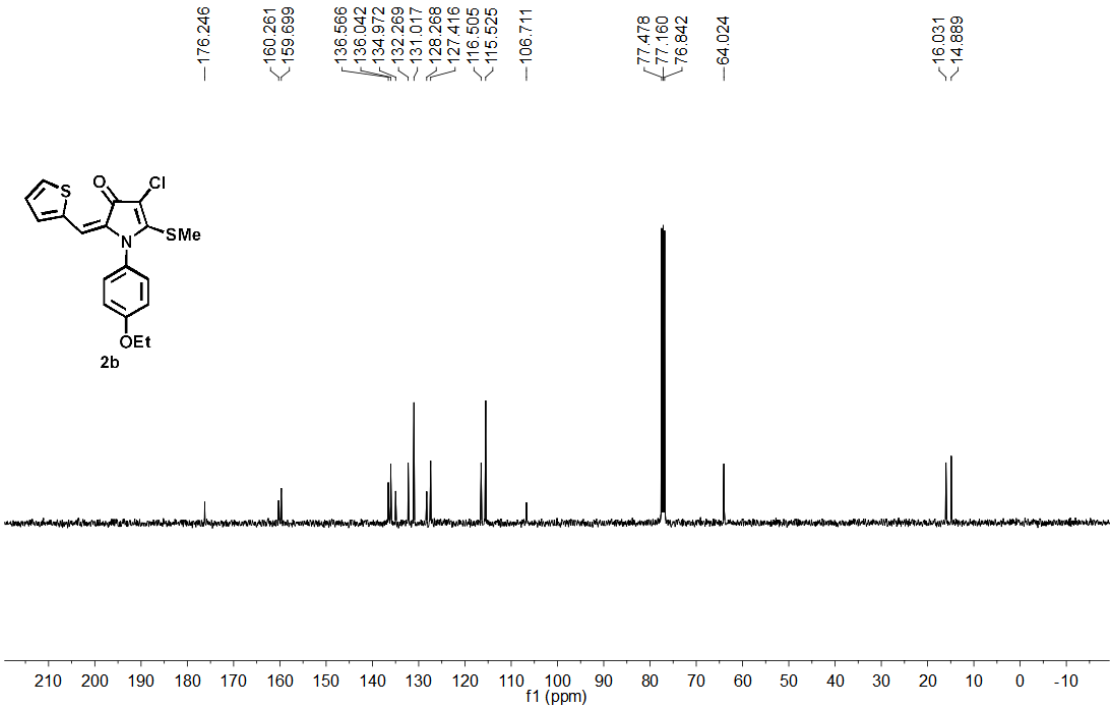
HF468 in CDC13 13C NMR



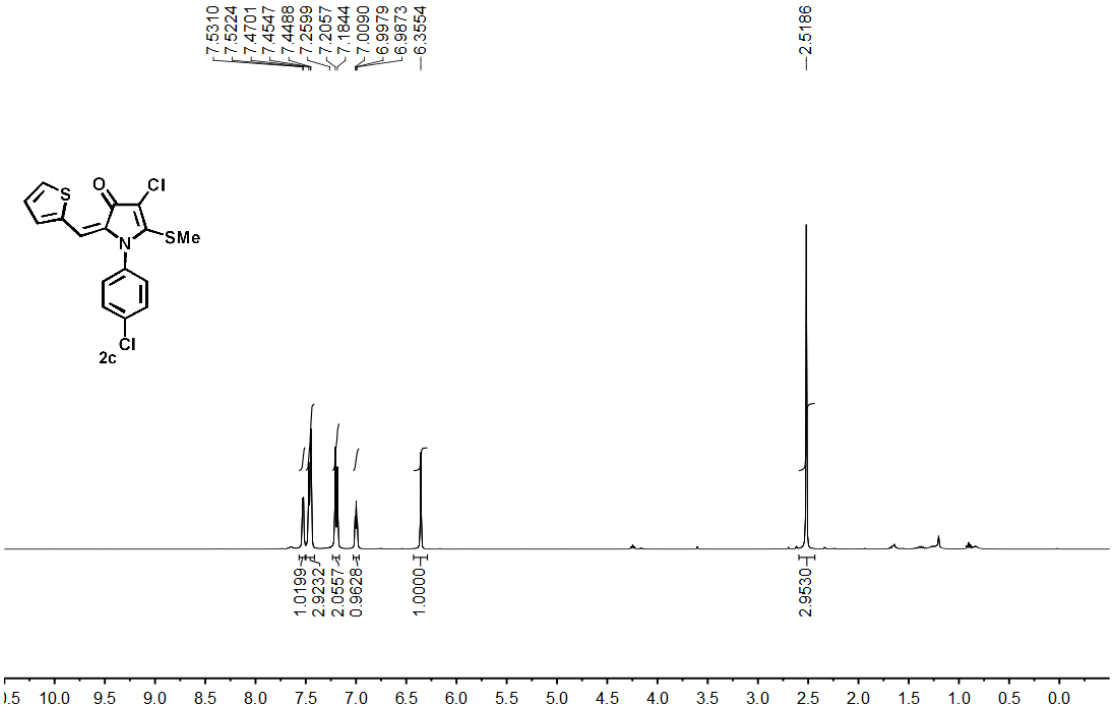
HF443
1H NMR IN CDCl3



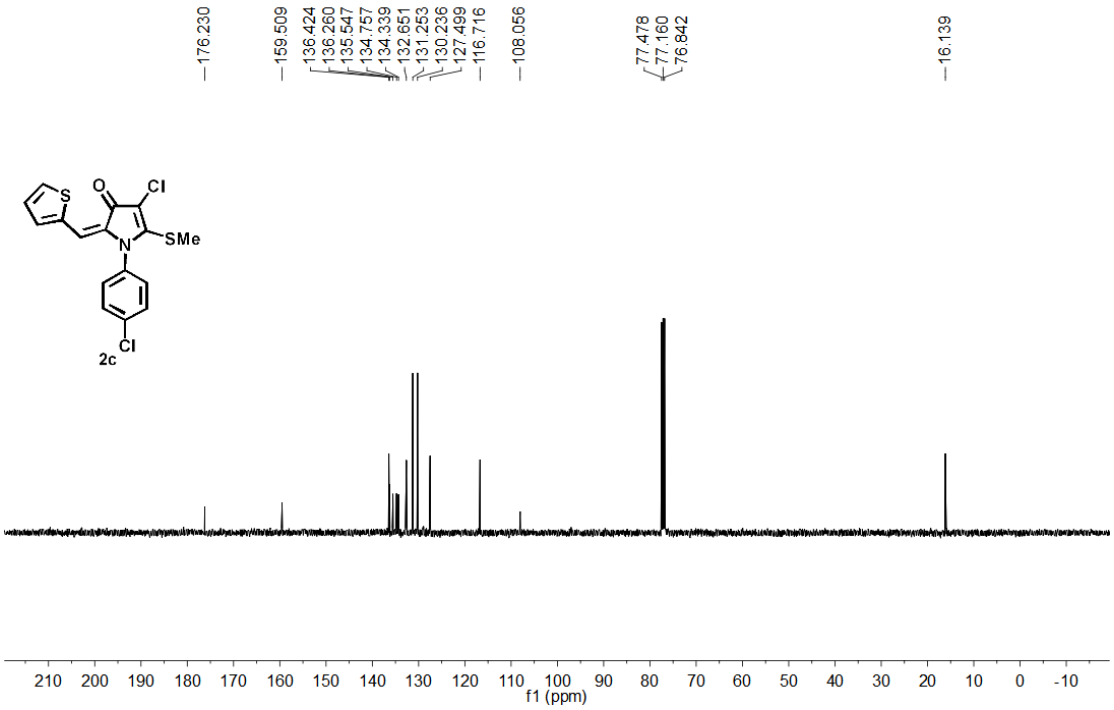
HF443
13C NMR IN CDCl3



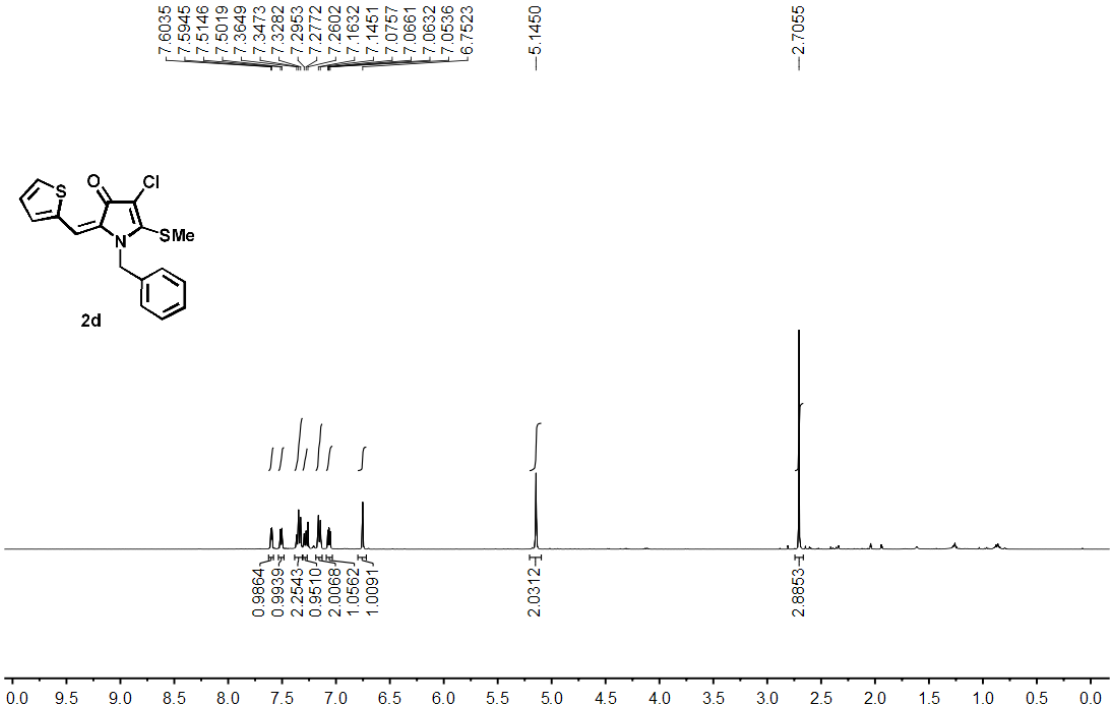
HF444-P
HF444-P in CDCl3 1H NMR



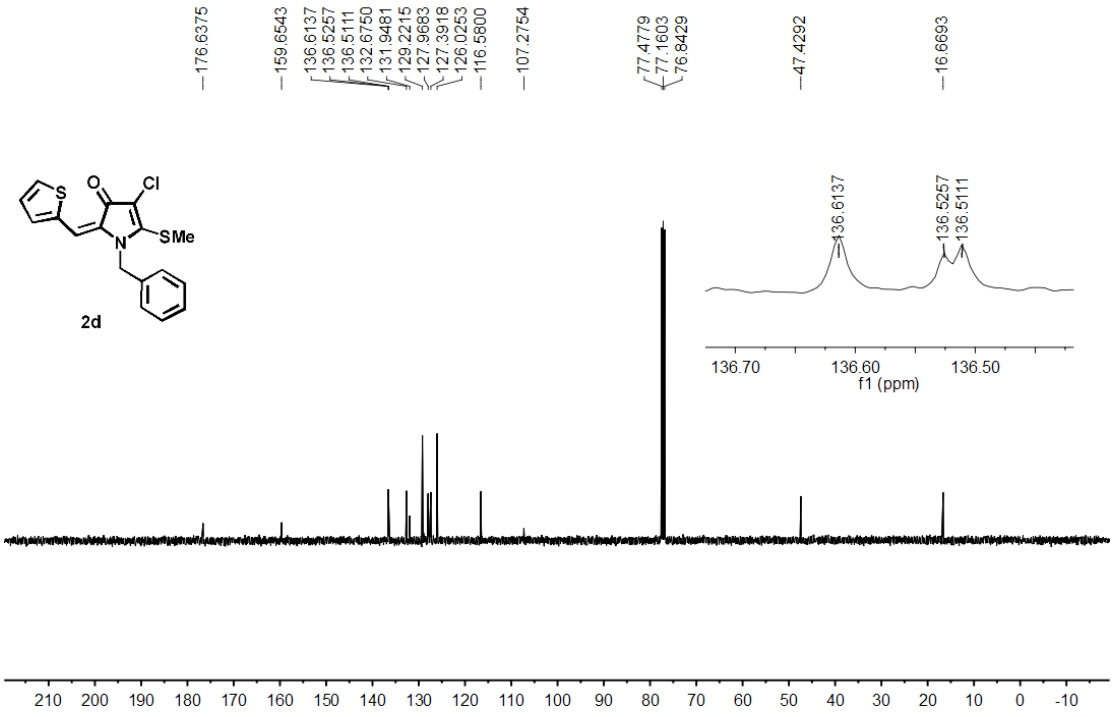
HF444-P
HF444-P in CDCl3 13C NMR



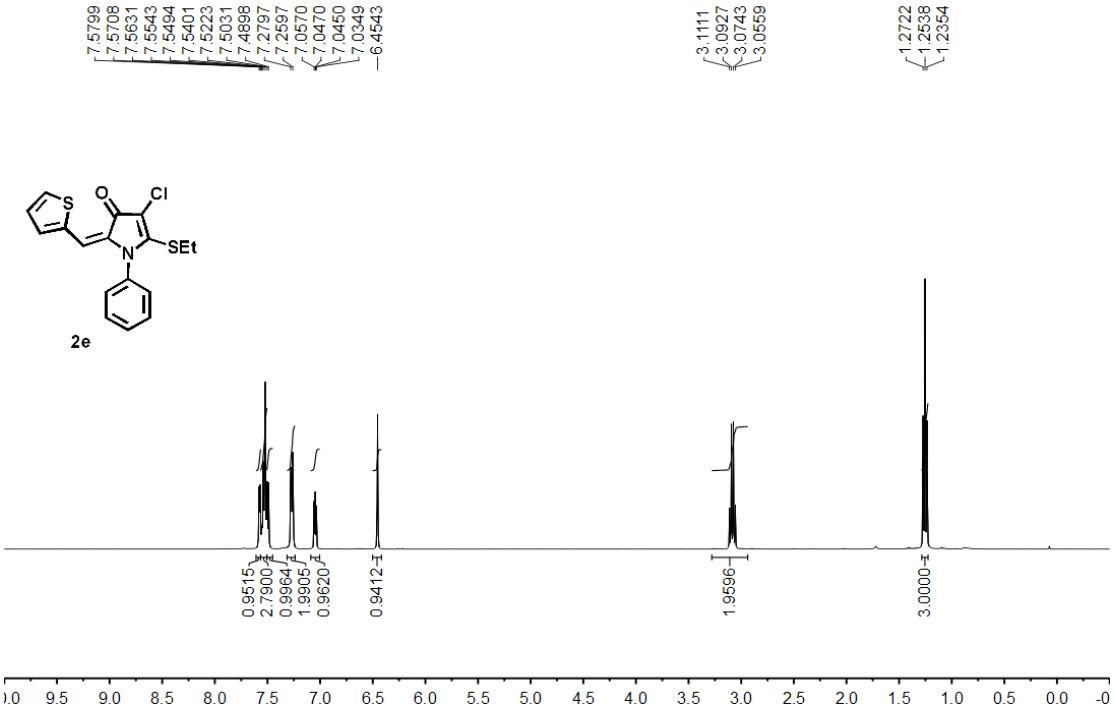
HF438
1H NMR IN CDC13



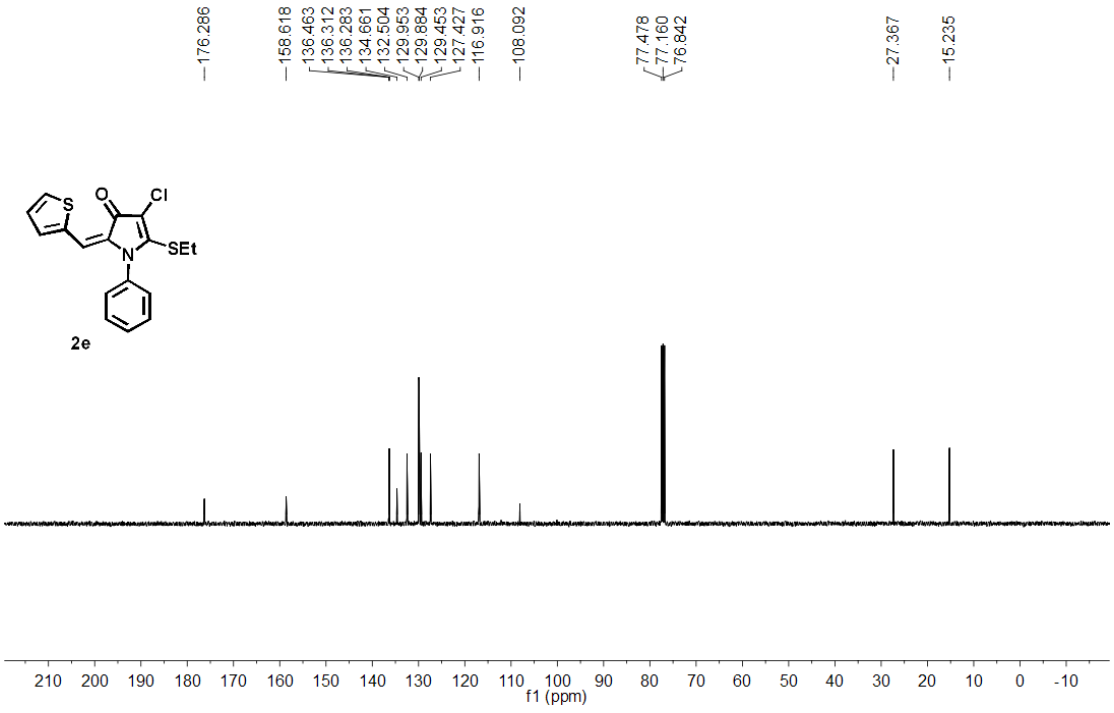
HF438
13C NMR IN CDC13



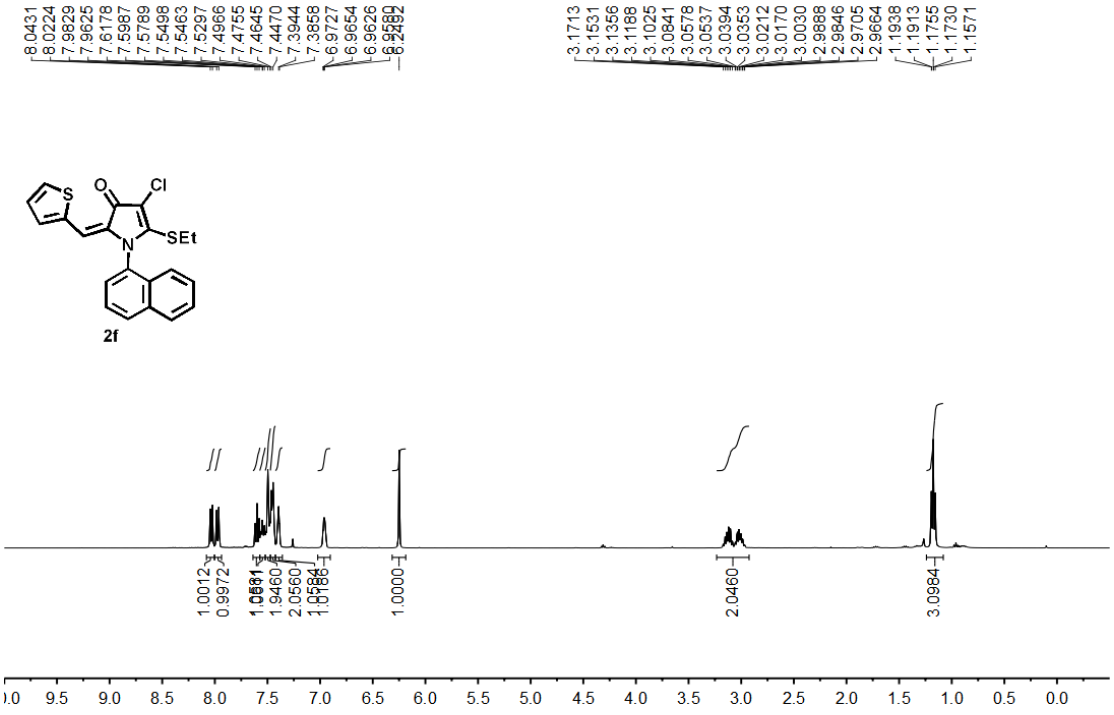
HF437-P
1H NMR IN CDCl3



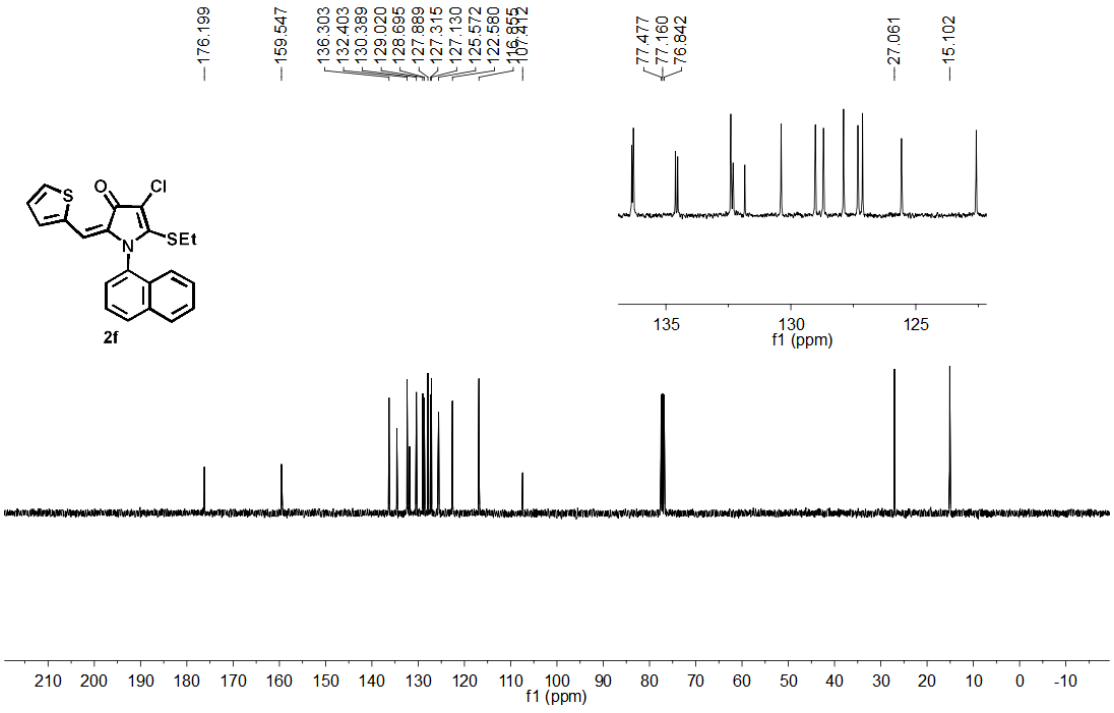
HF437-P
13C NMR IN CDCl3



HF471-P
1H NMR IN CDCl3

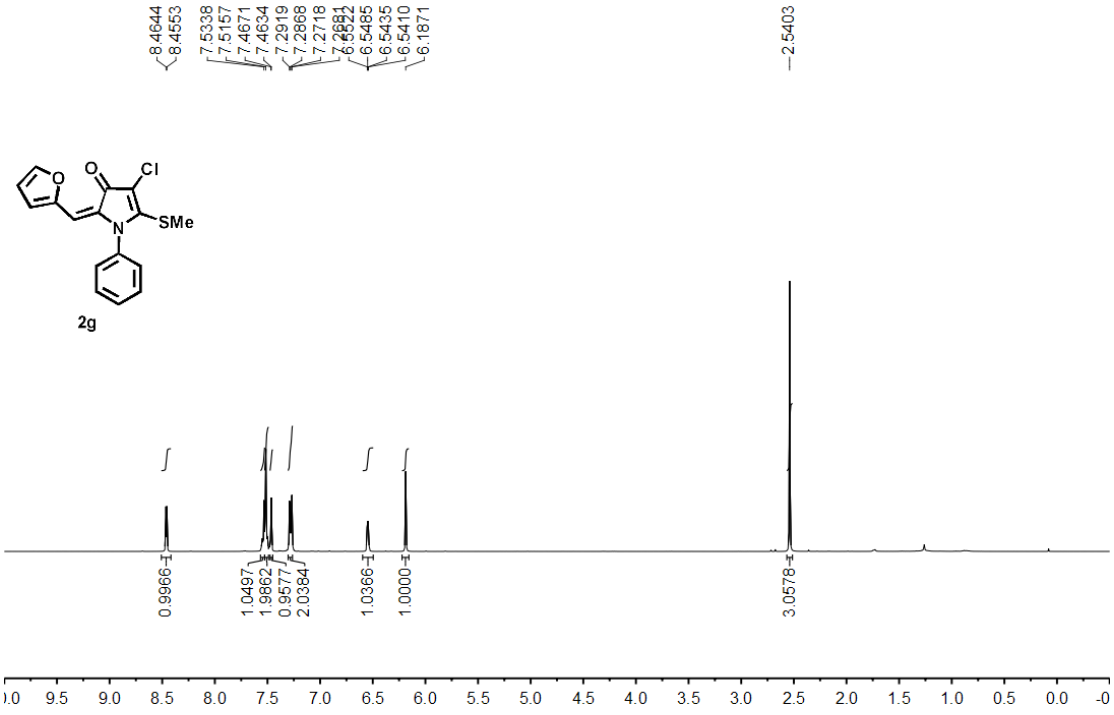


HF471-P
13C NMR IN CDCl3



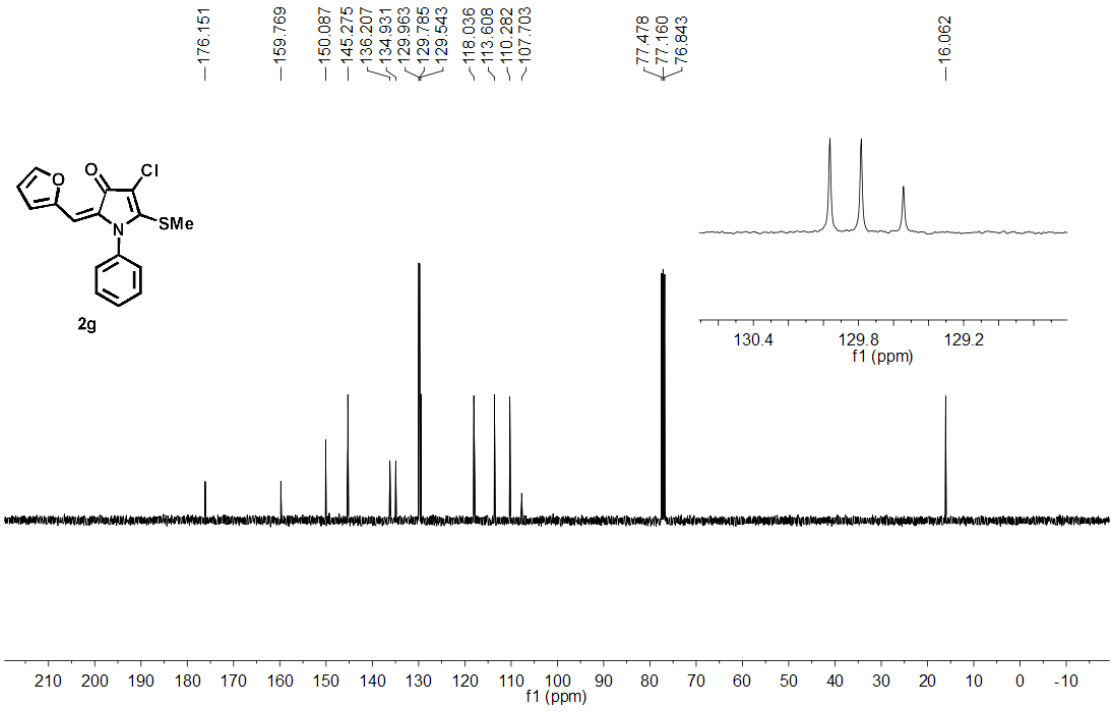
HF481

HF481 in CDC13 1H NMR

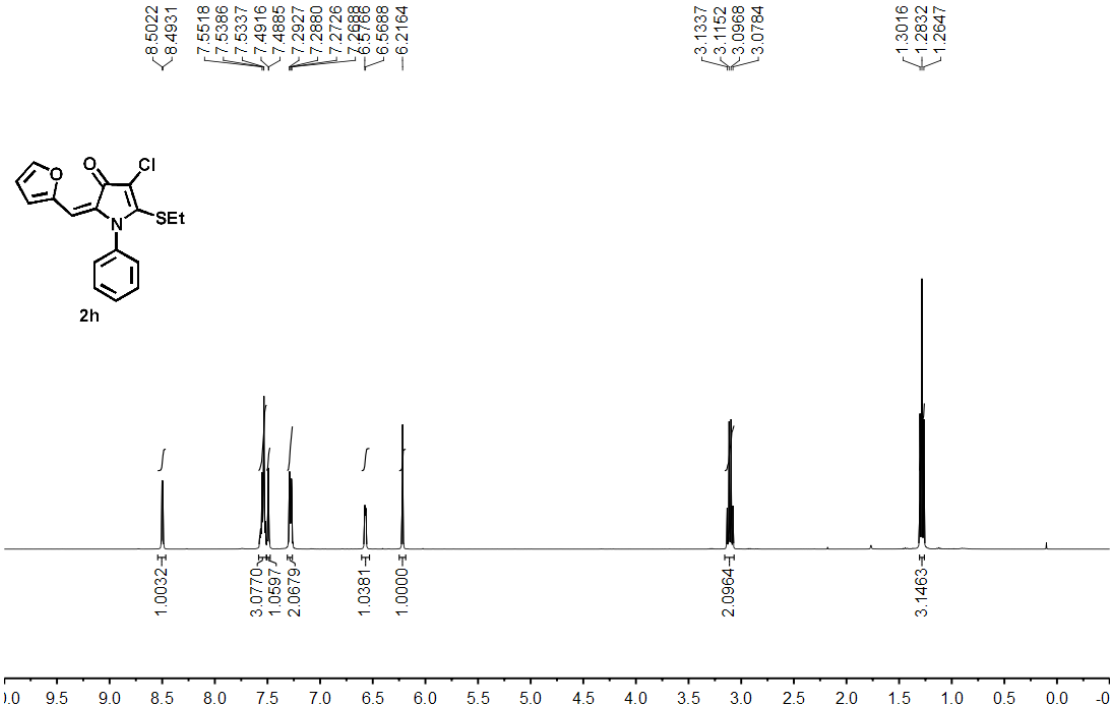


HF481

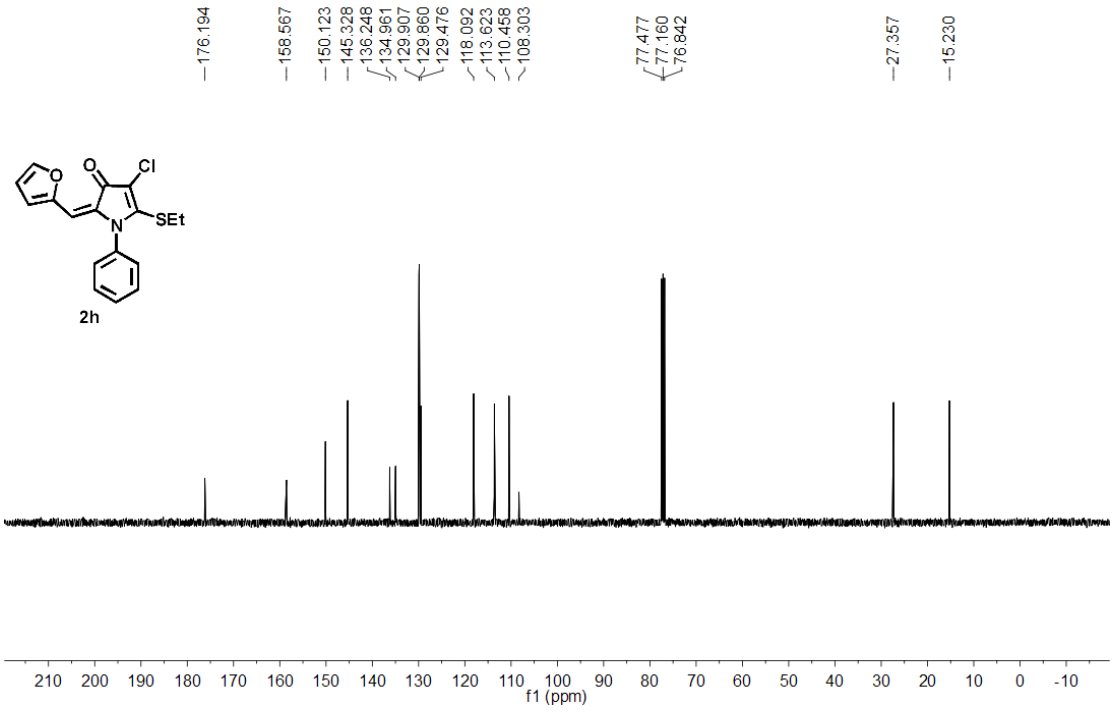
HF481 in CDC13 13C NMR



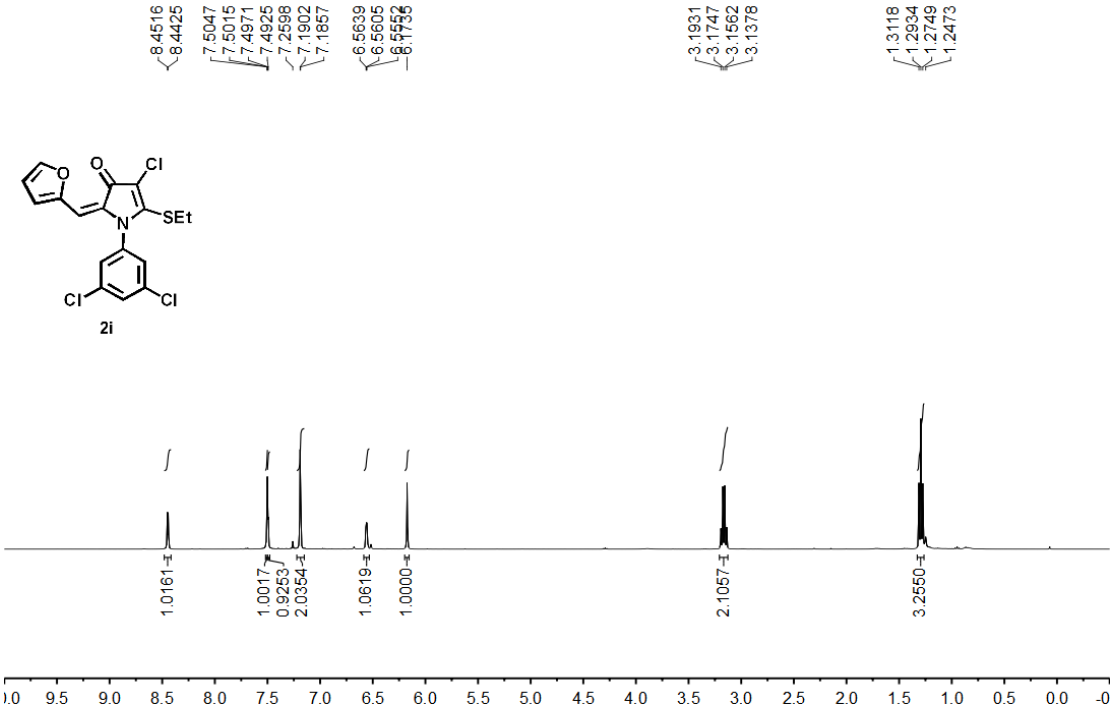
HF486
HF486 in CDCl3 1H NMR



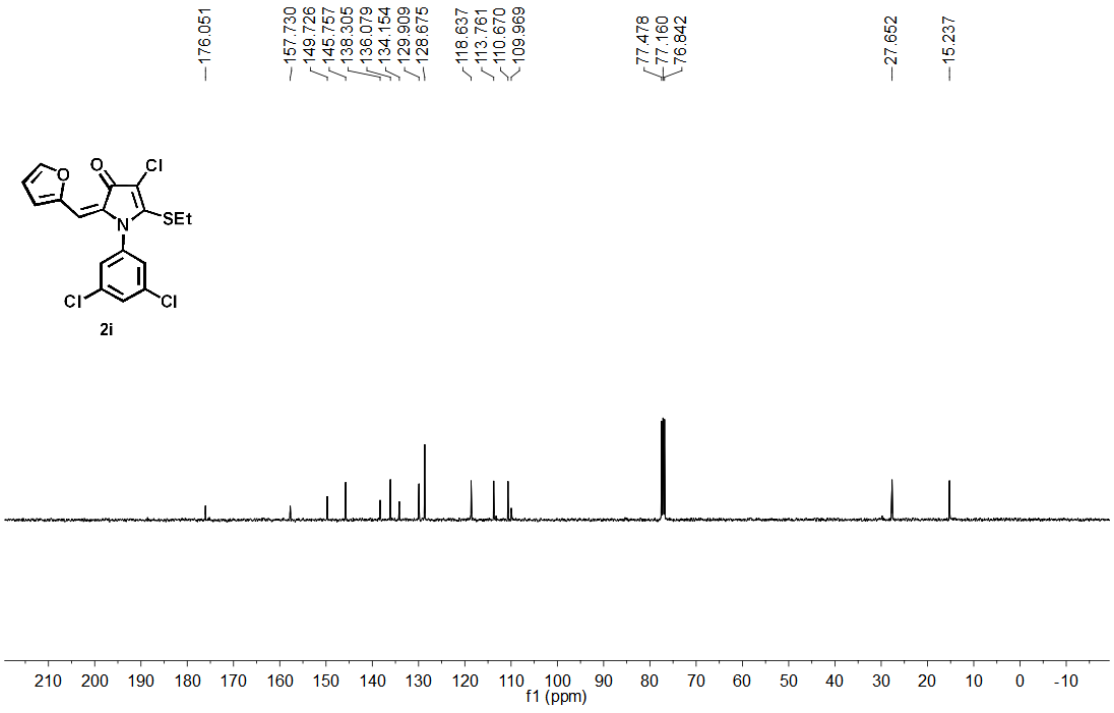
HF486
13C NMR IN CDCl3



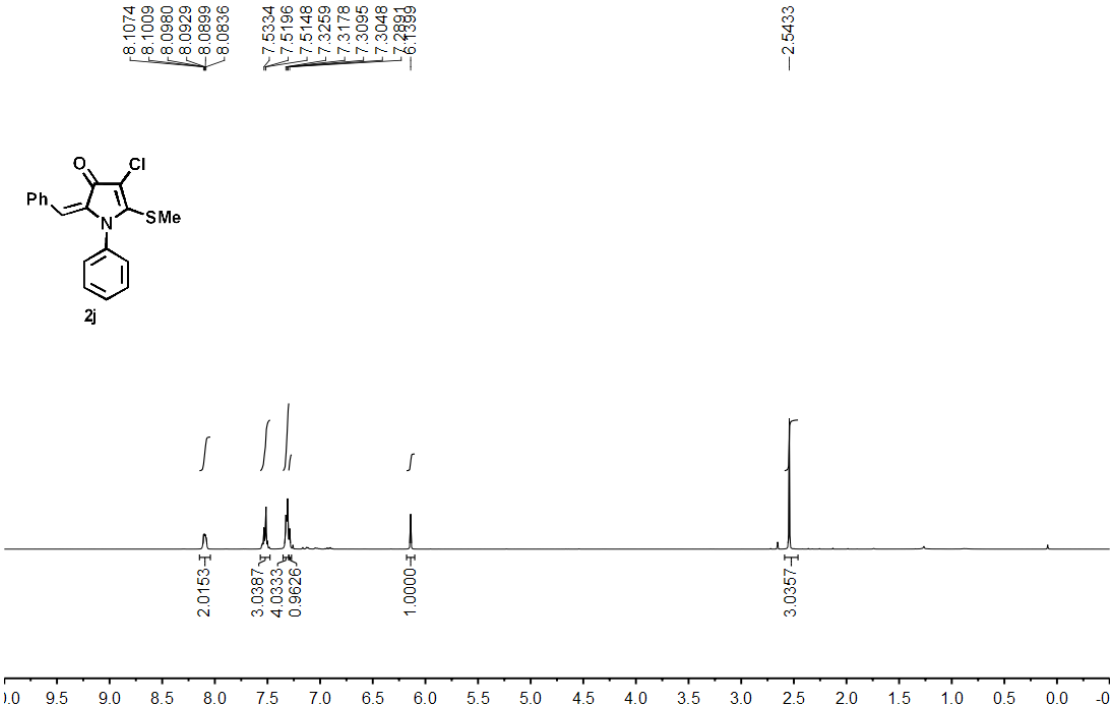
HF487
HF487 in CDC13 1H NMR



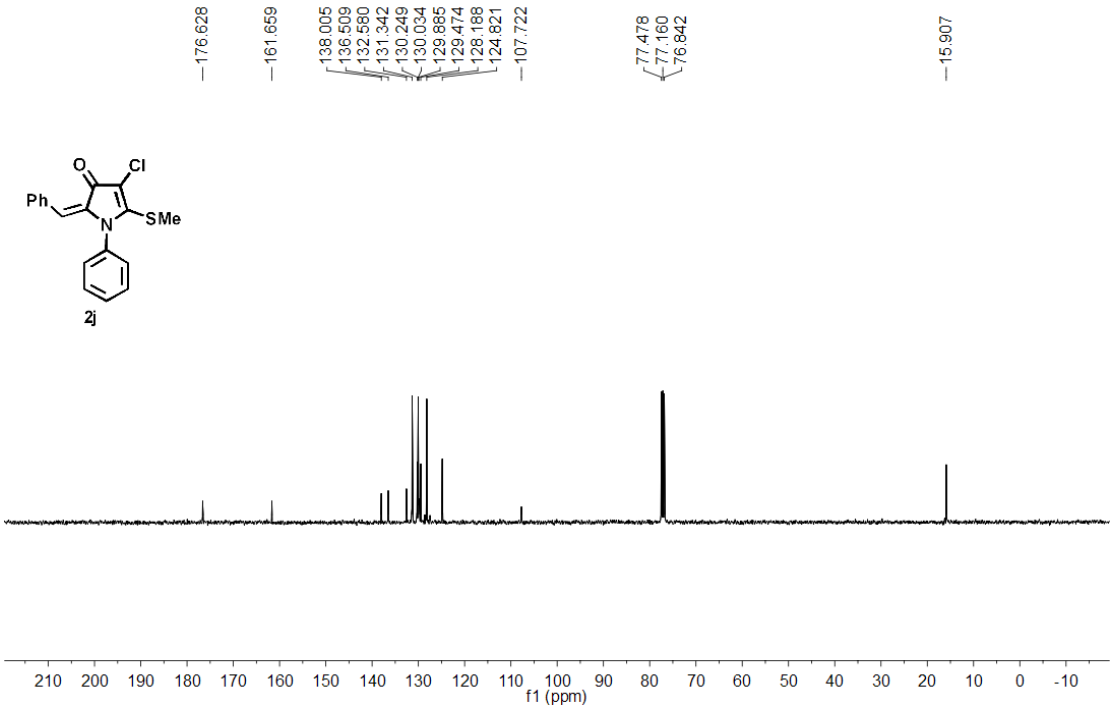
HF487
13C NMR IN CDC13



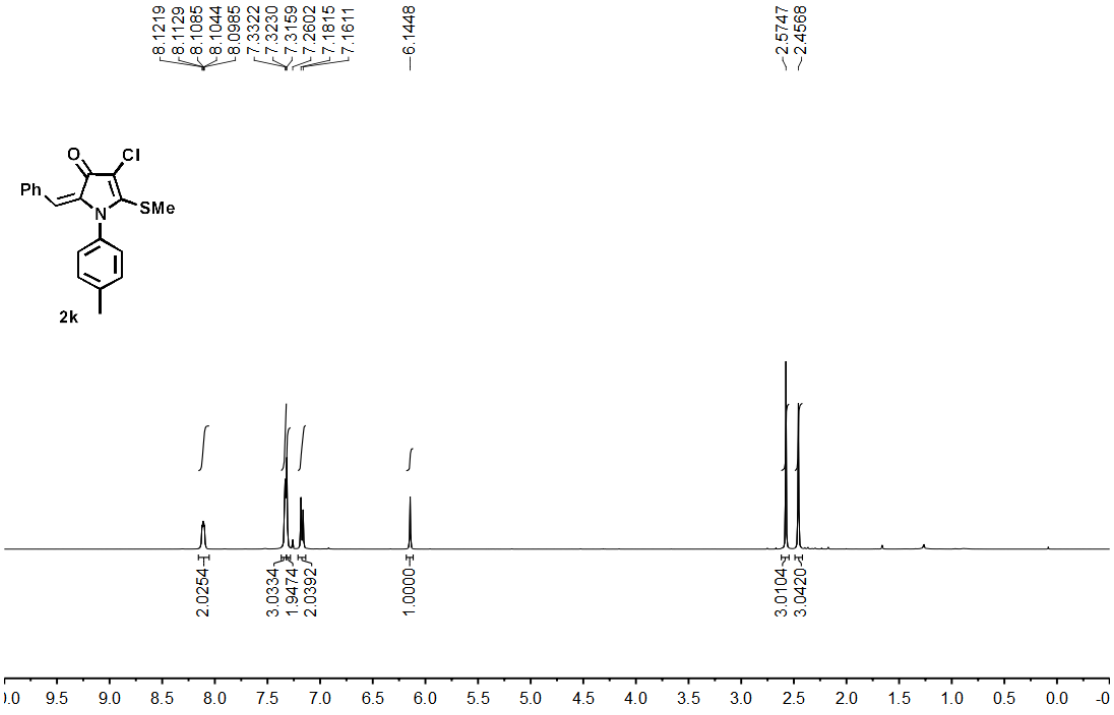
HF480
1H NMR IN CDCl3



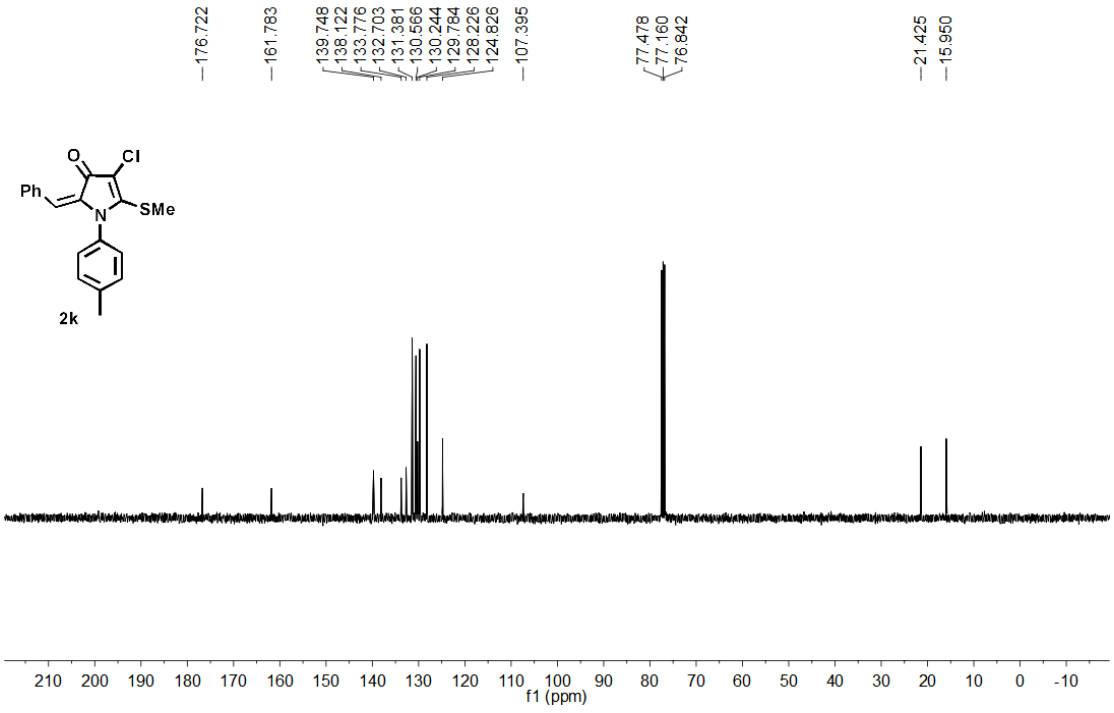
HF480
13C NMR IN CDCl3



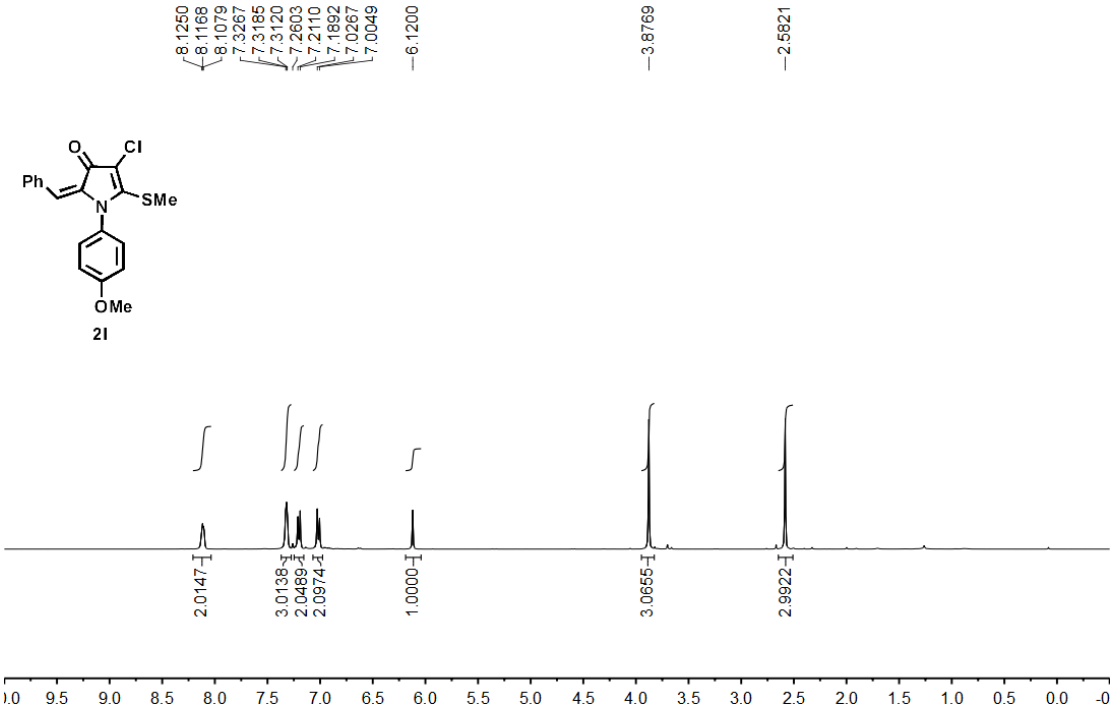
HF493
1H NMR IN CDCl3



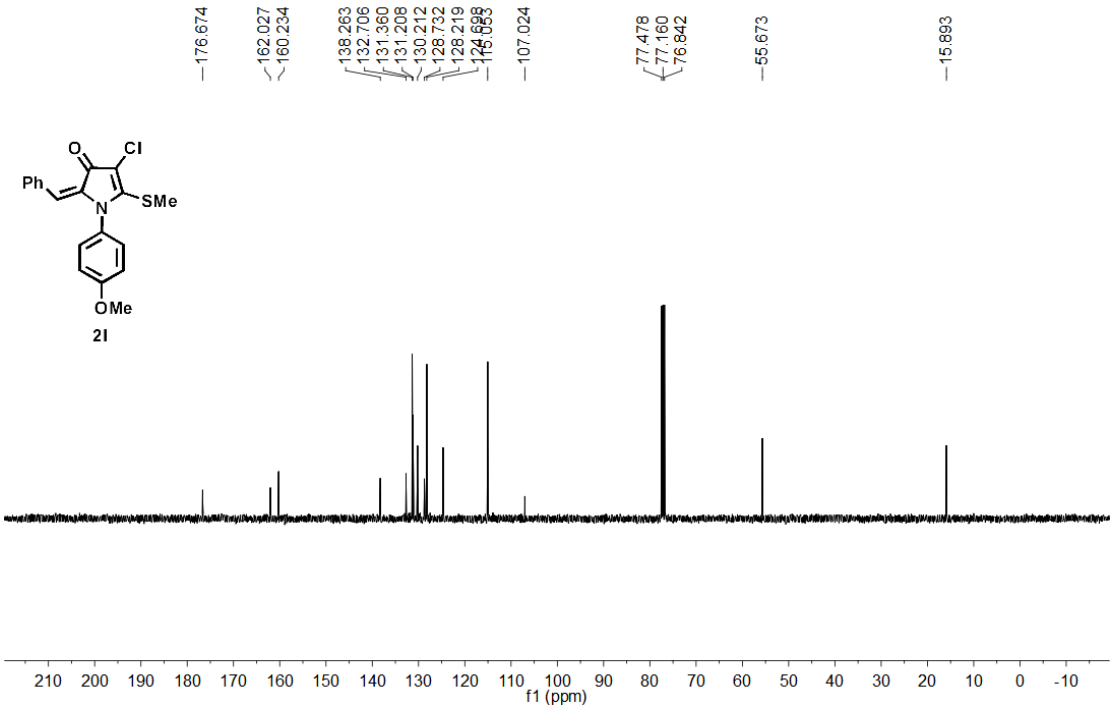
HF493
13C NMR IN CDCl3



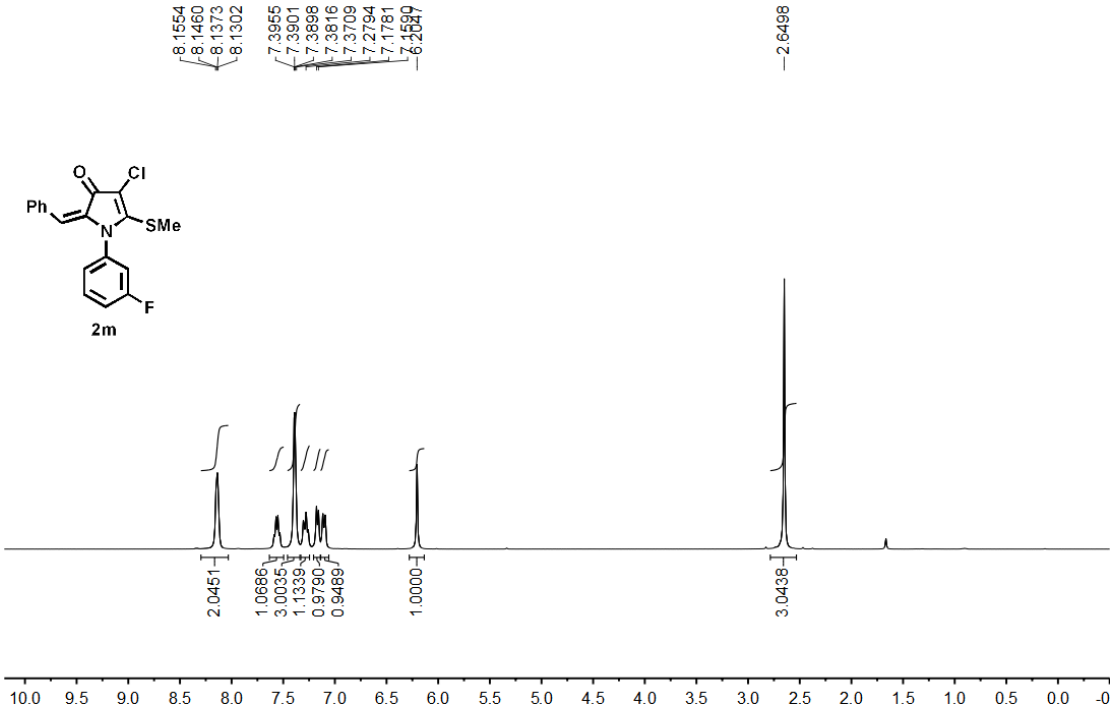
HF494
1H NMR IN CDCl3



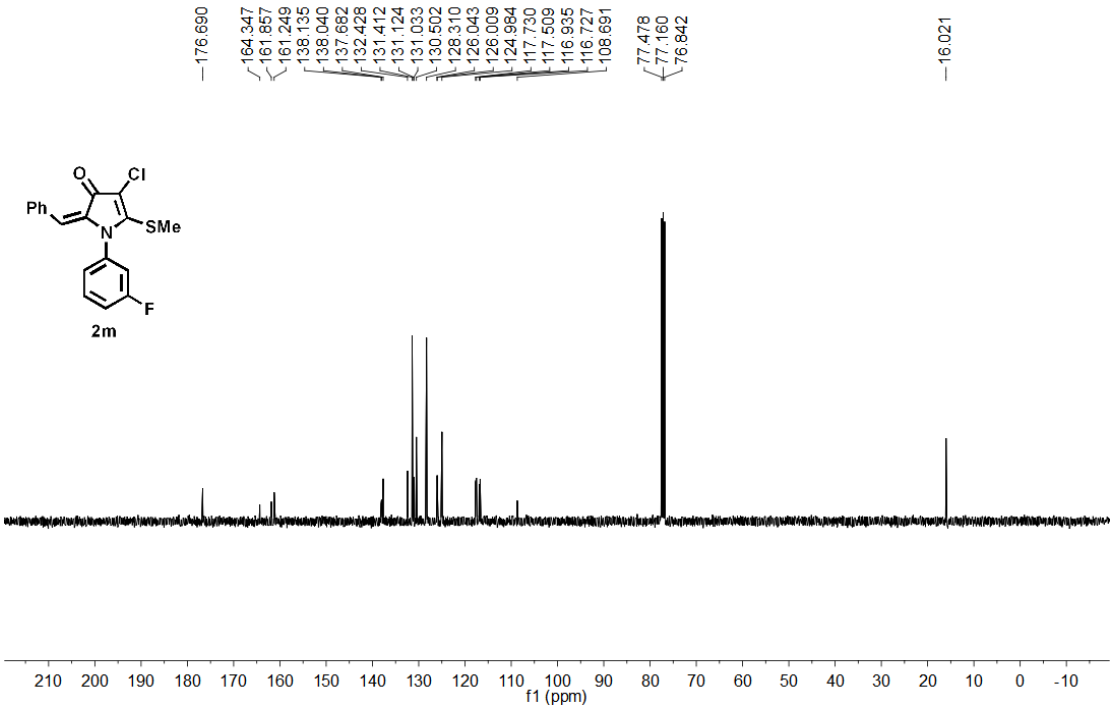
HF494
13C NMR IN CDCl3



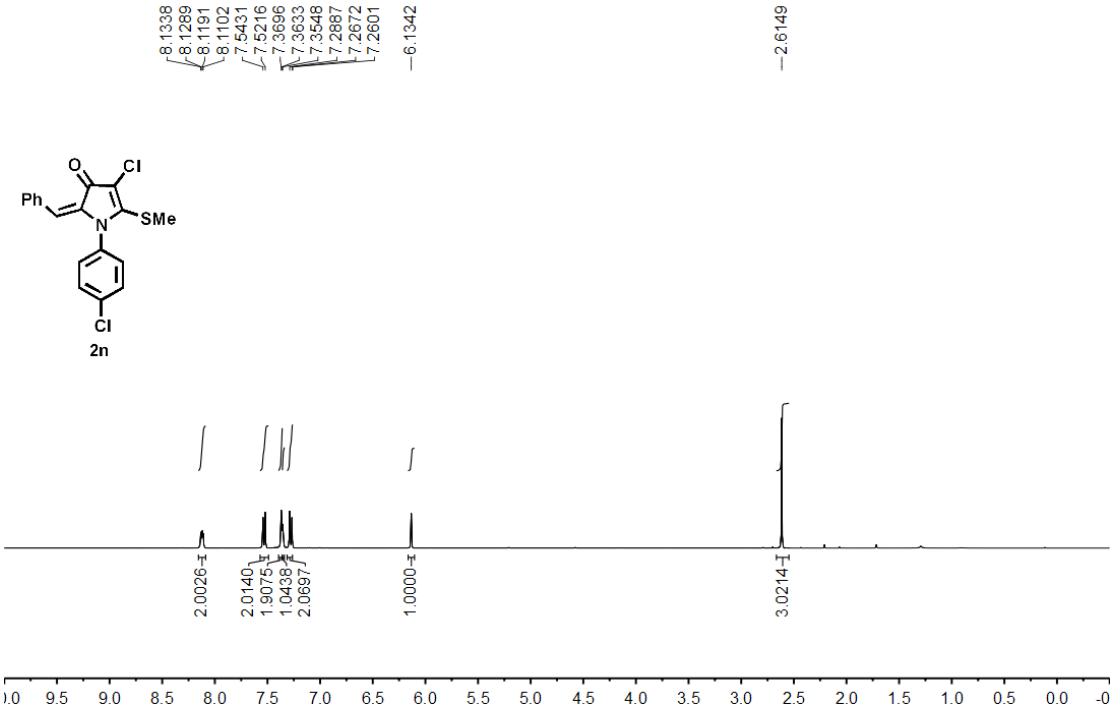
HF513
1H NMR IN CDCl3



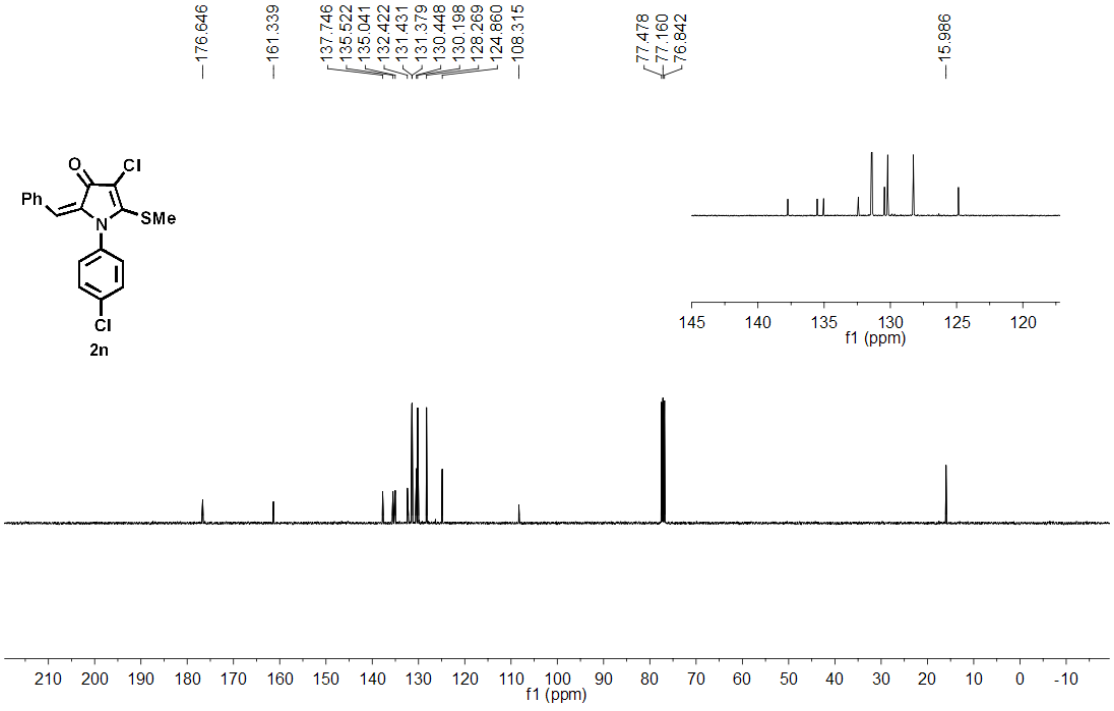
HF513
13C NMR IN CDCl3



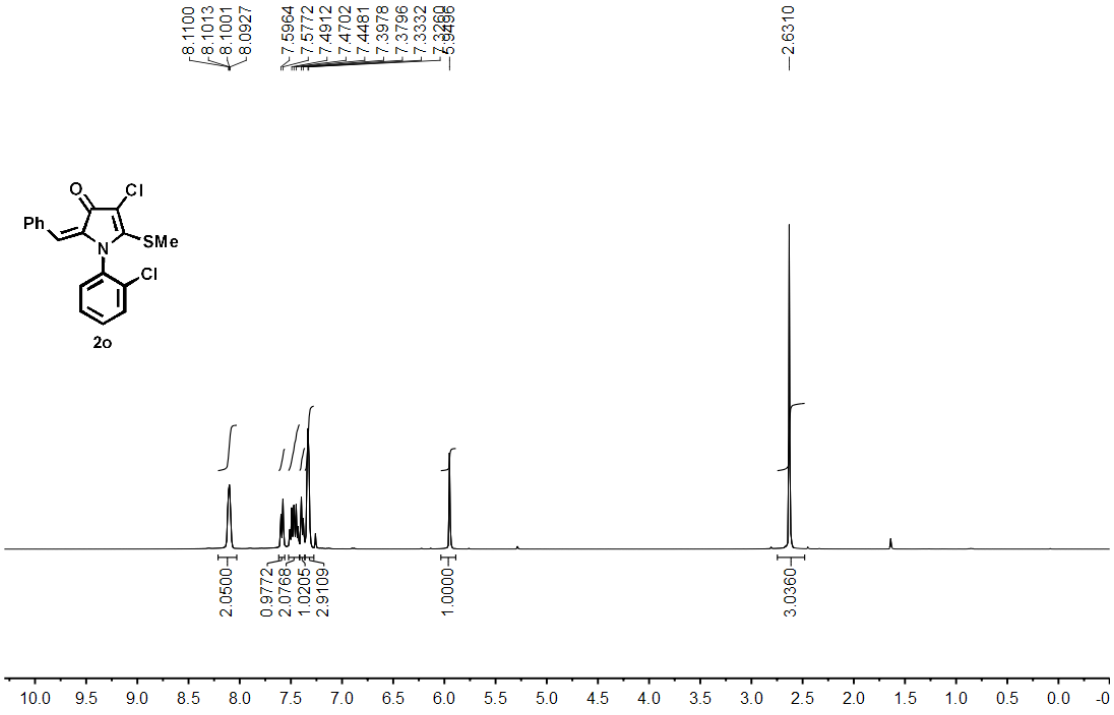
HF495
1H NMR IN CDCl3



HF495
13C NMR IN CDCl3

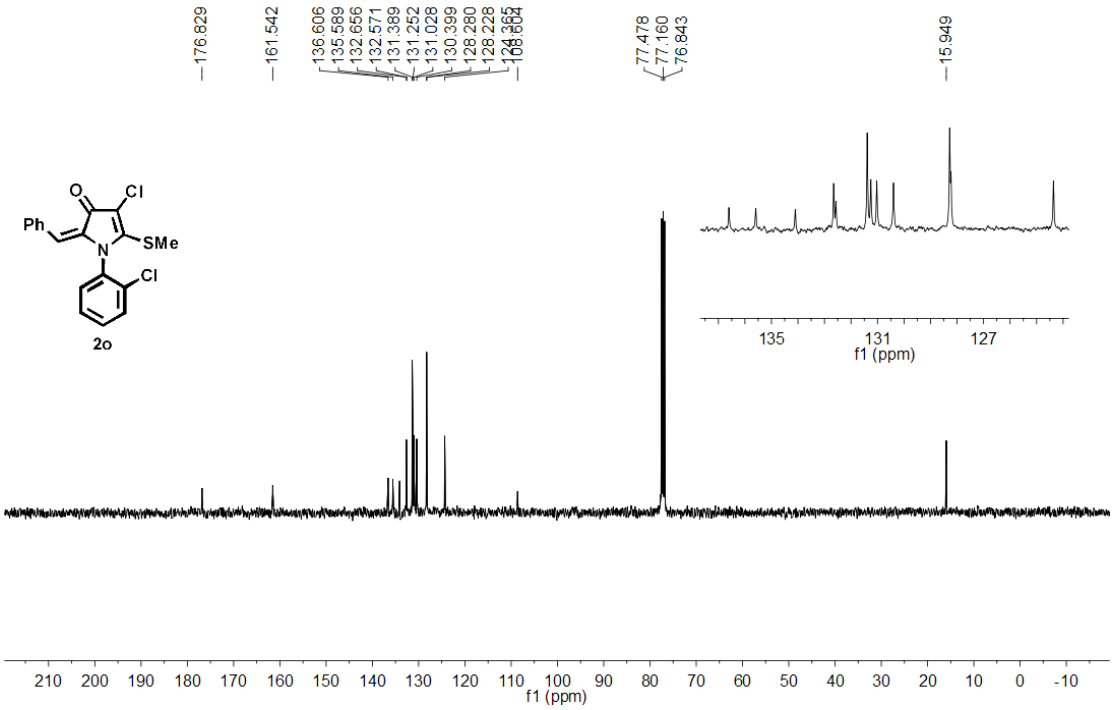


HF512
1H NMR IN CDCl3



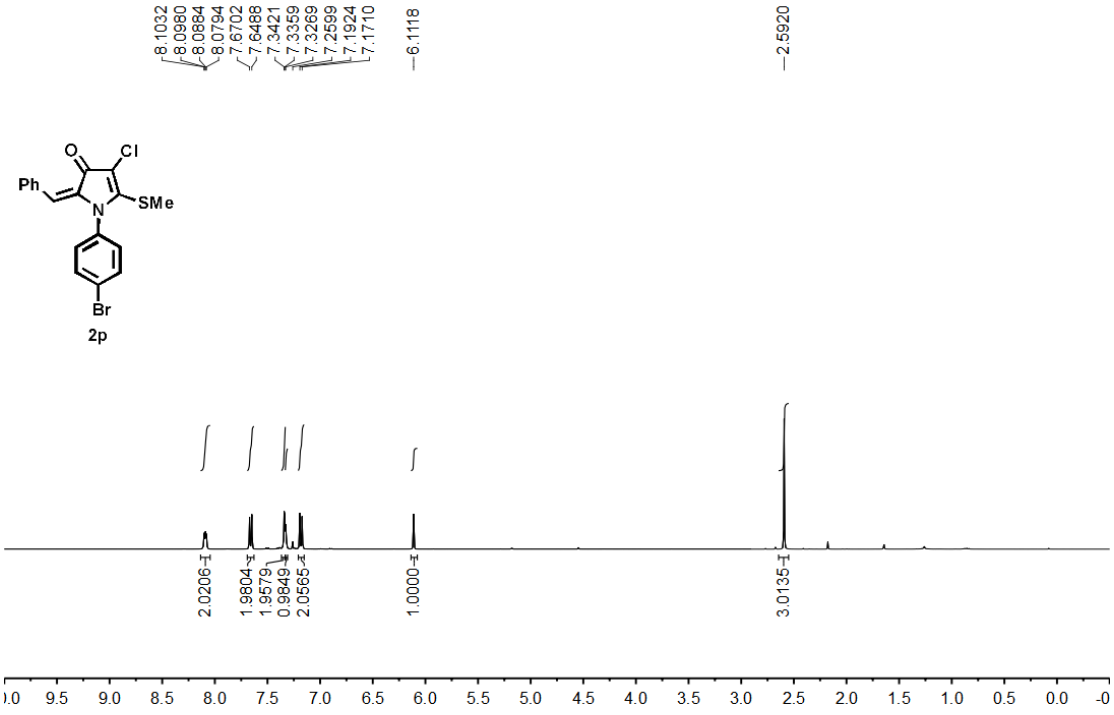
2o

HF512
13C NMR IN CDCl3

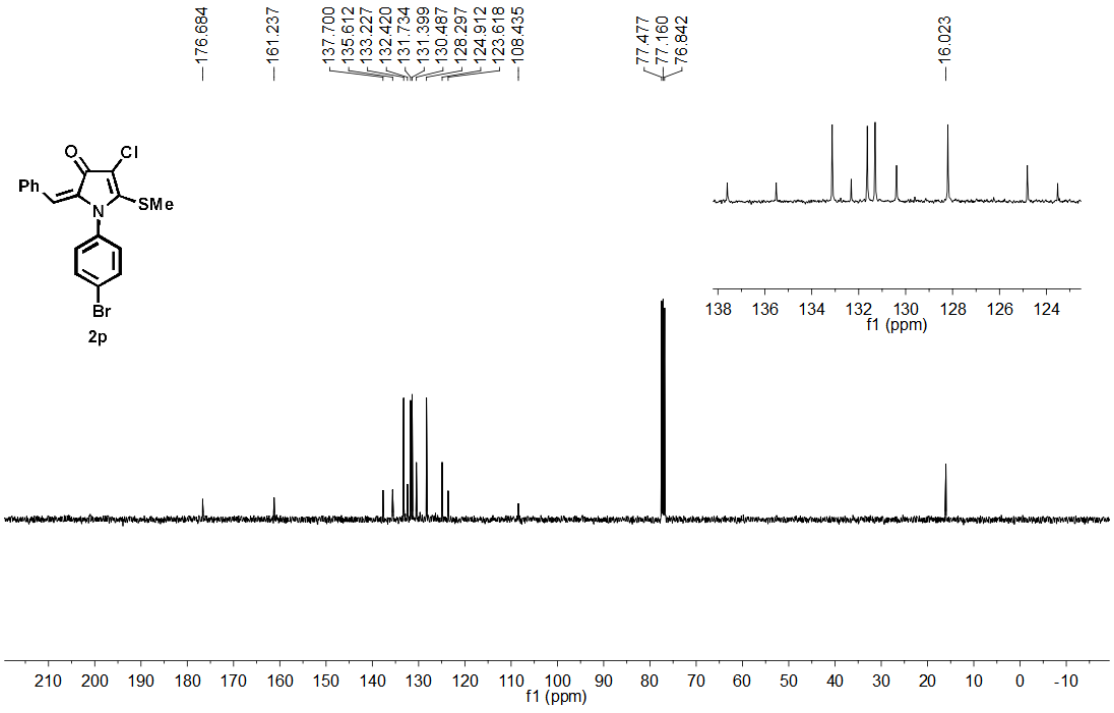


2o

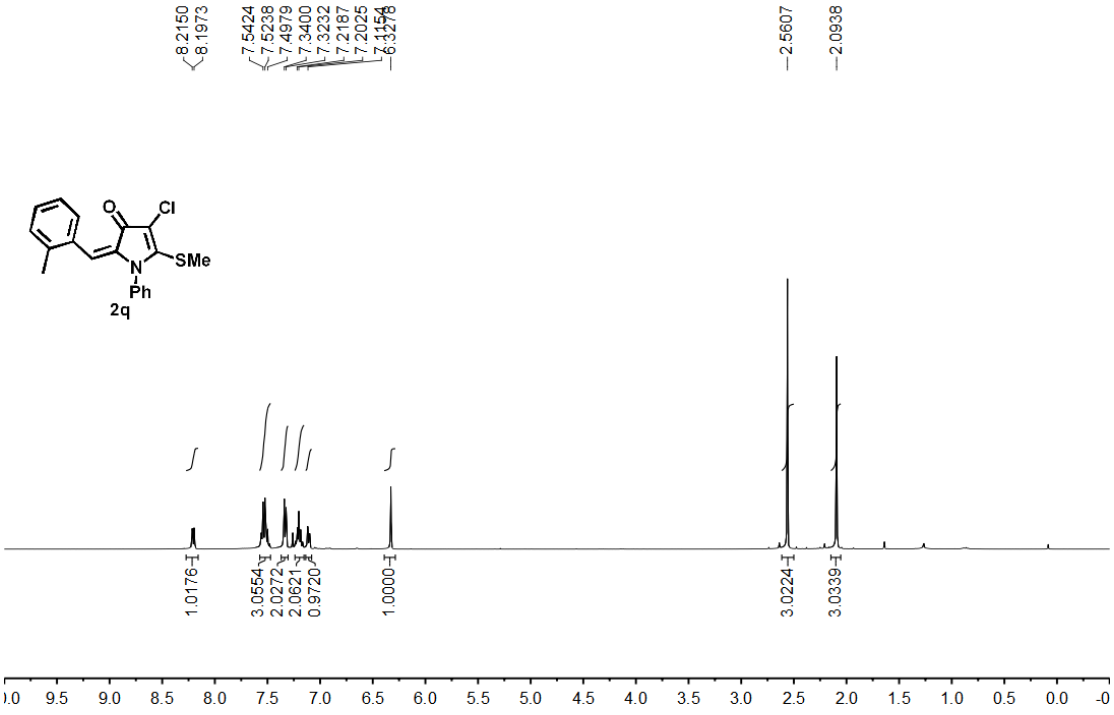
HF496
1H NMR IN CDCl3



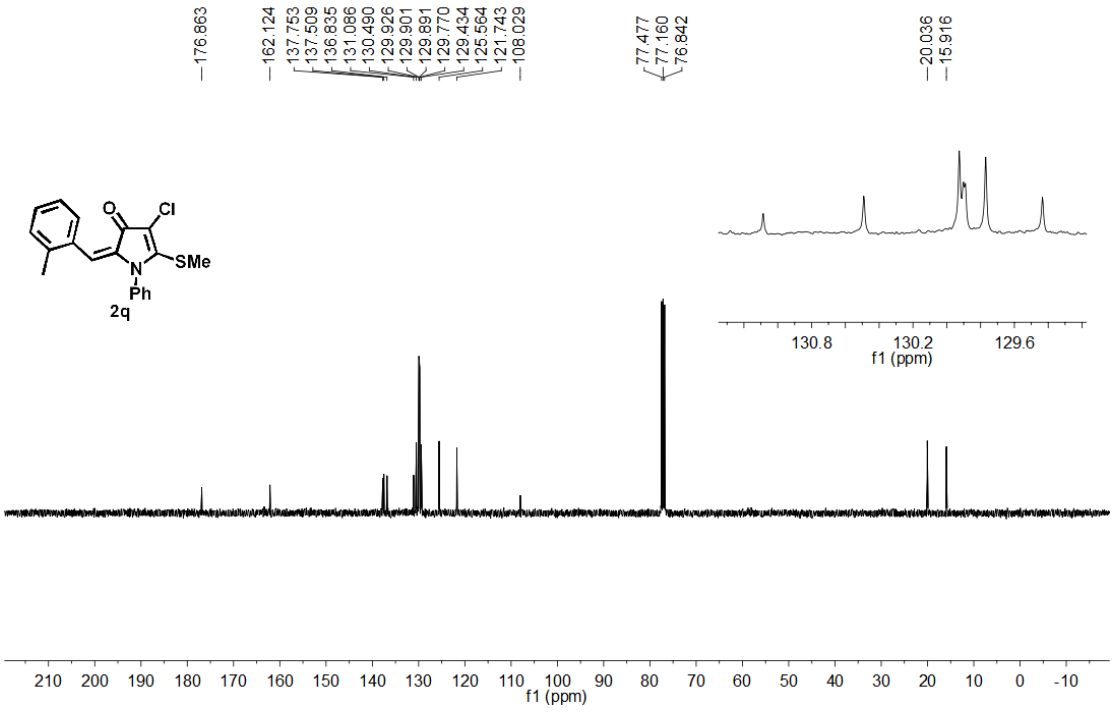
HF496
13C NMR IN CDCl3



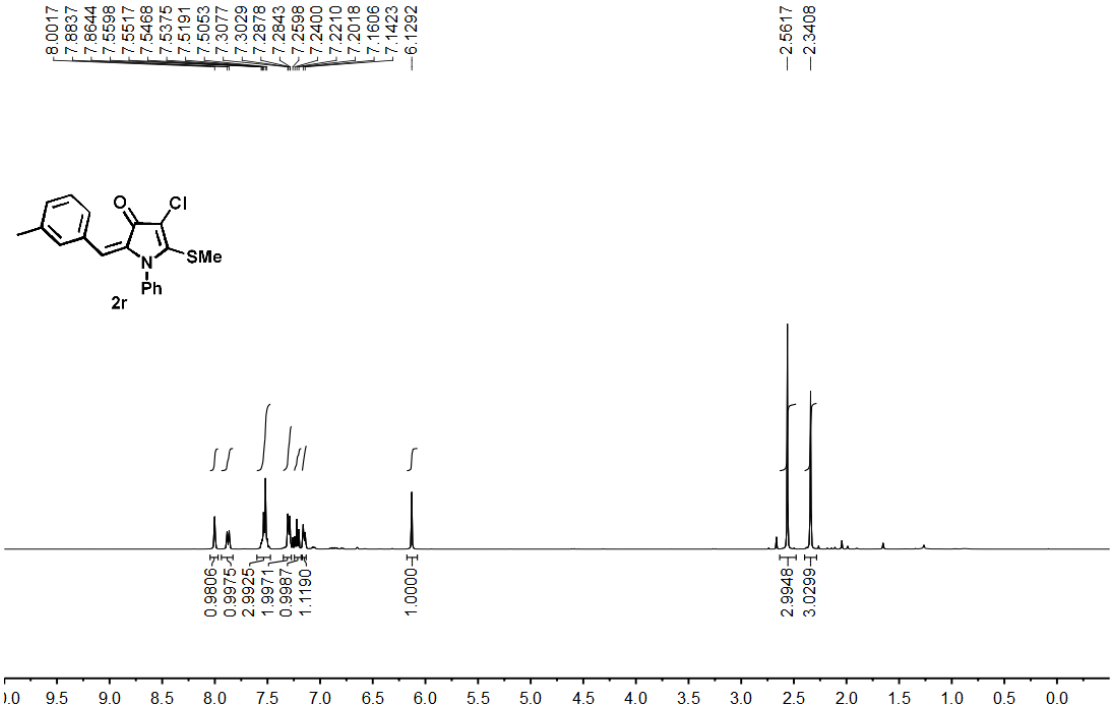
HF510
1H NMR IN CDCl3



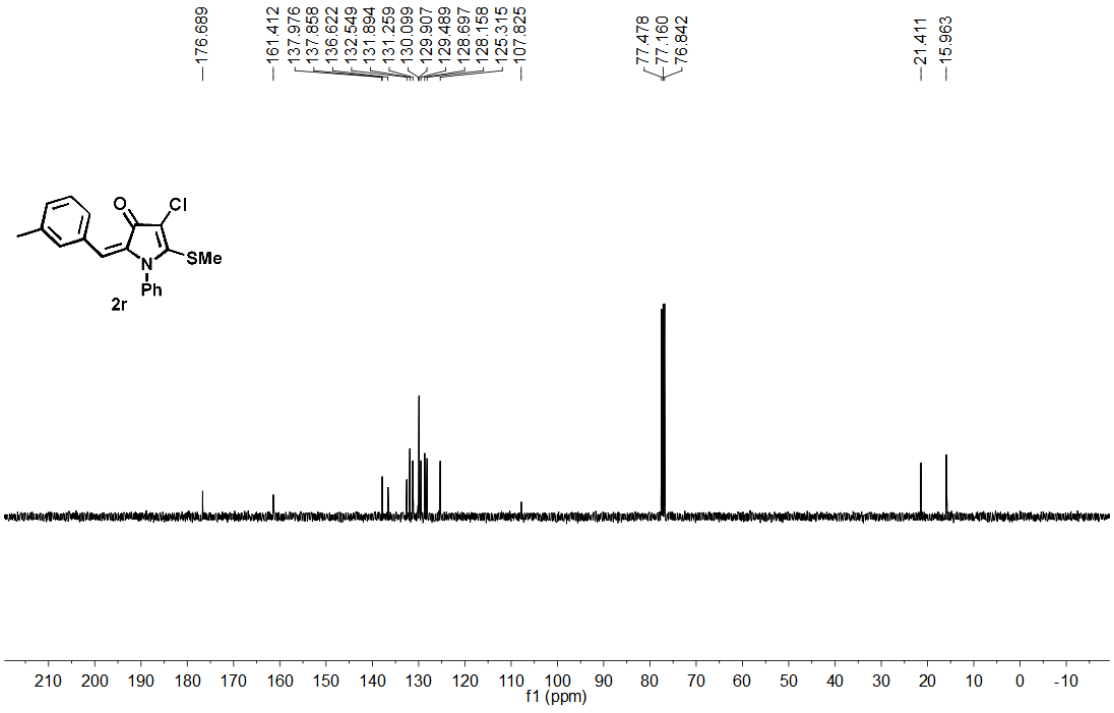
HF510
13C NMR IN CDCl3



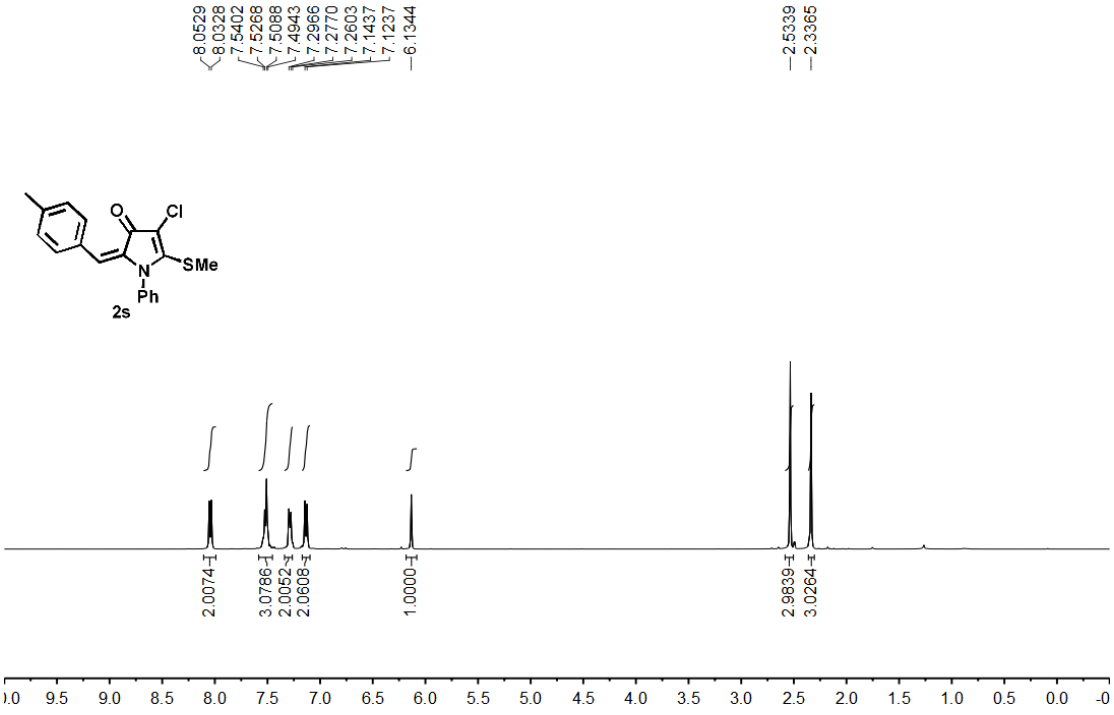
HF511
1H NMR IN CDCl3



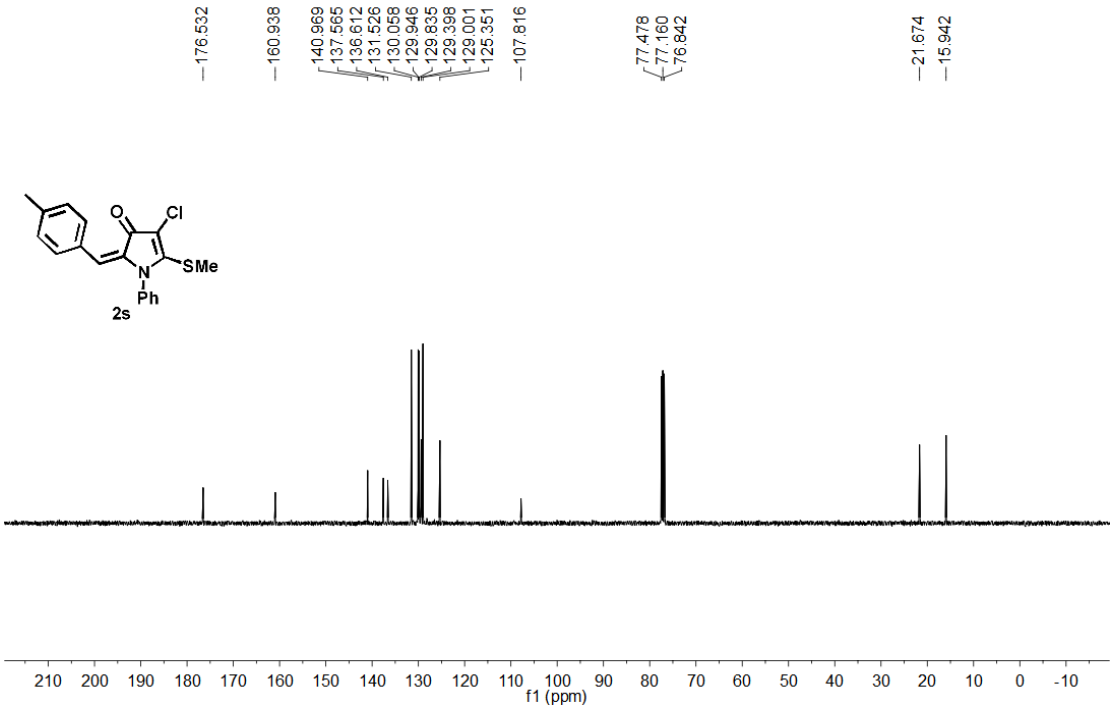
HF511
13C NMR IN CDCl3



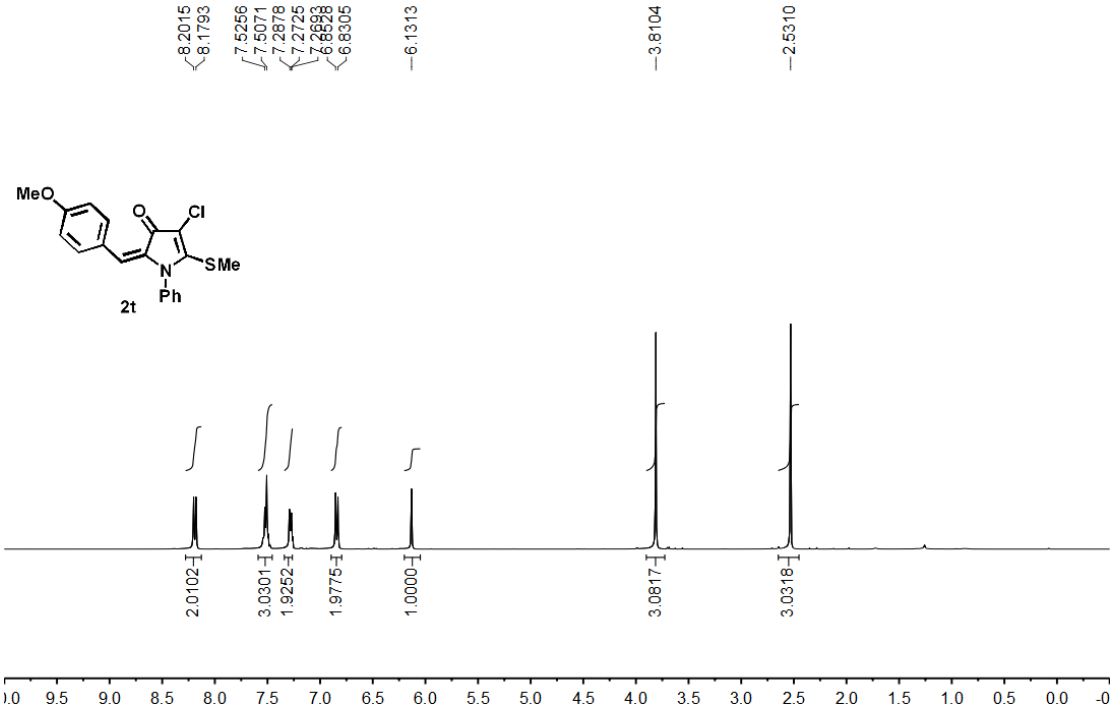
HF474
1H NMR IN CDC13



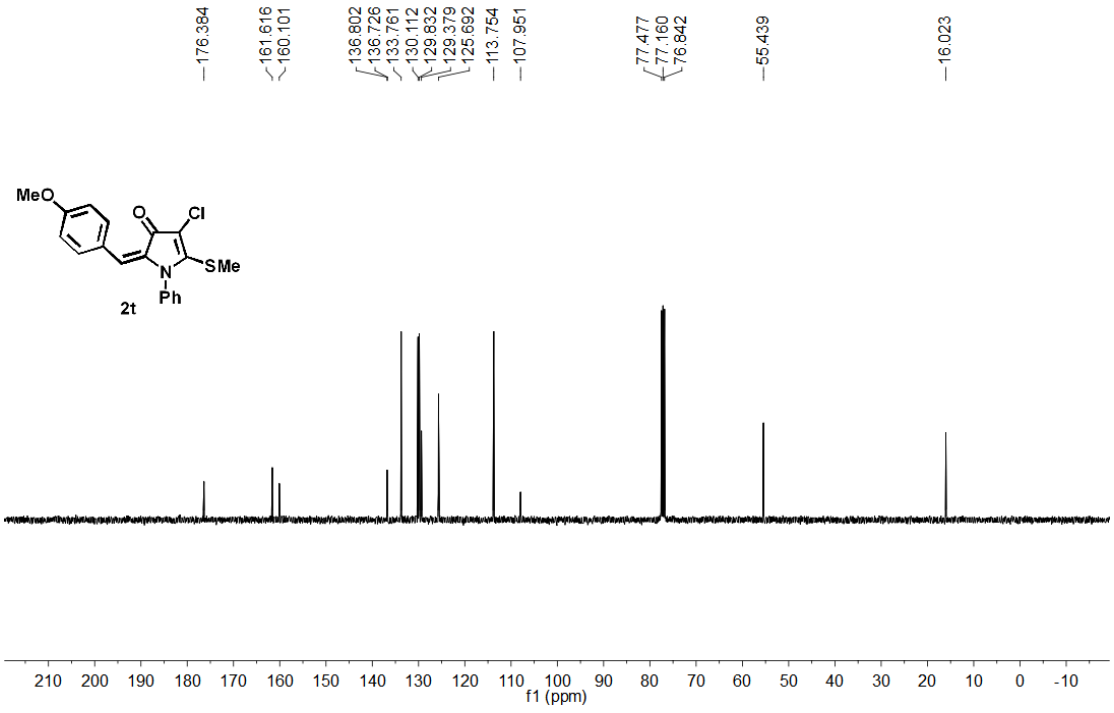
HF474
13C NMR IN CDC13



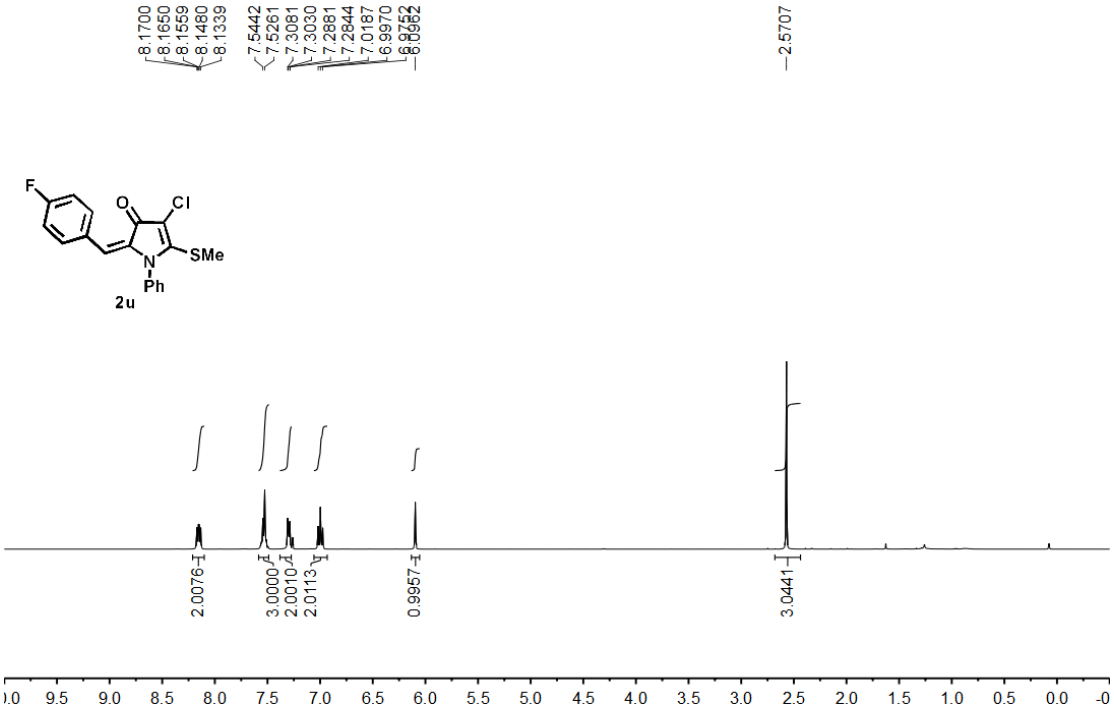
HF473
1H NMR IN CDC13



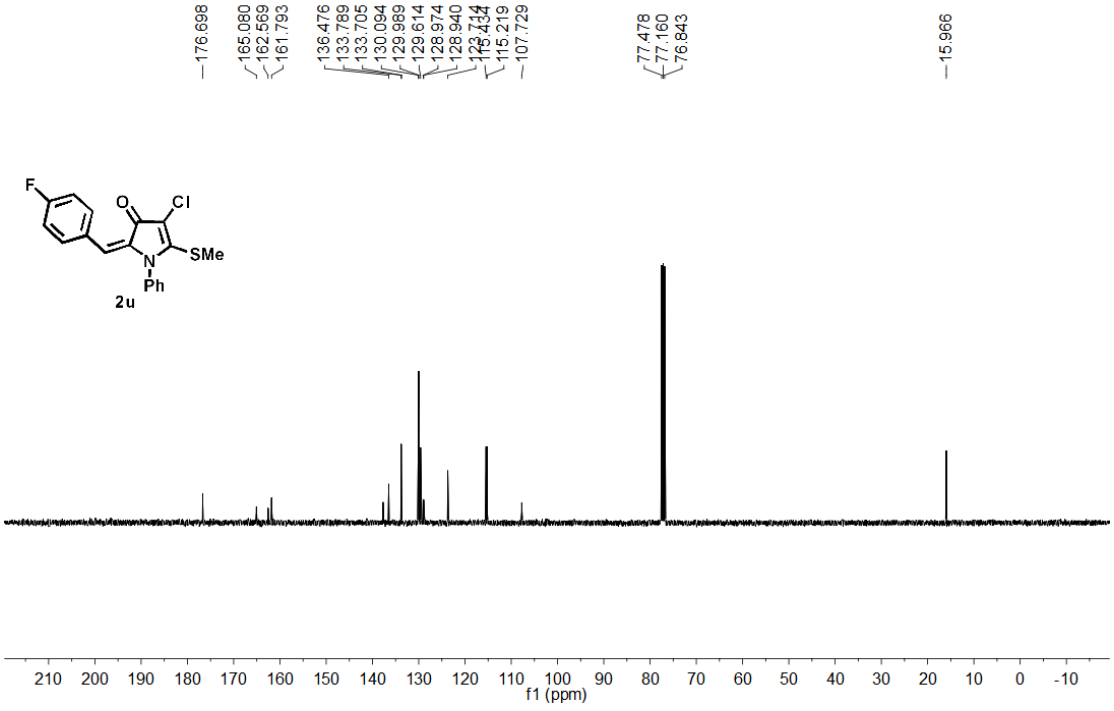
HF473
13C NMR IN CDC13



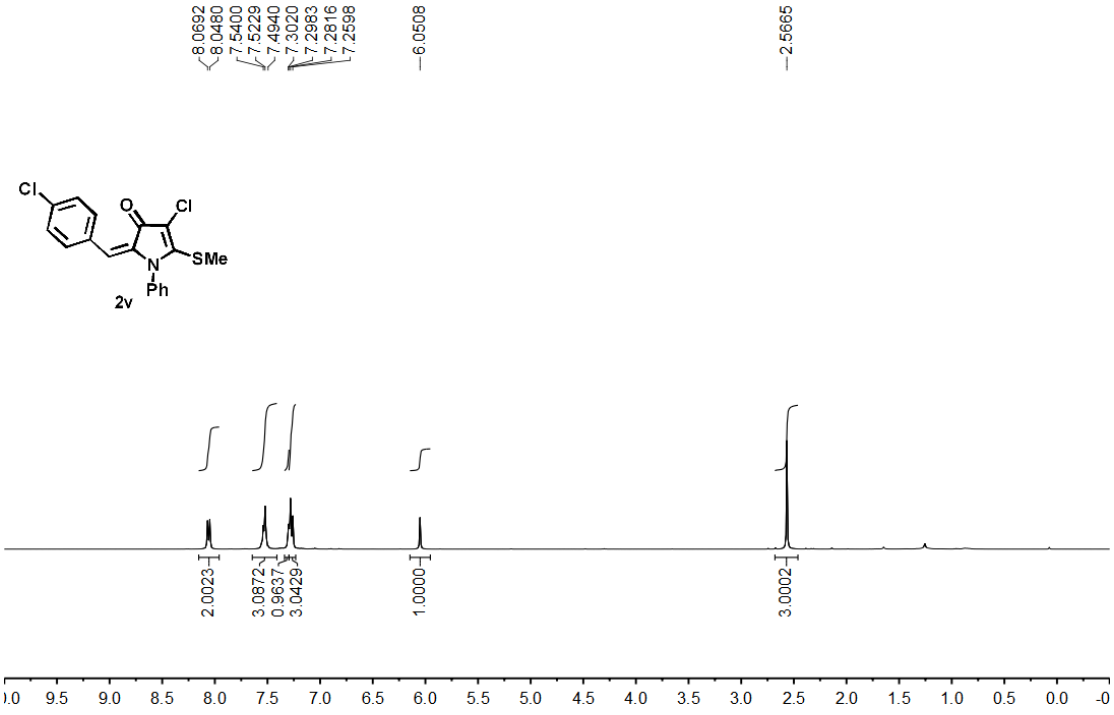
HF488-P
1H NMR IN CDCl3



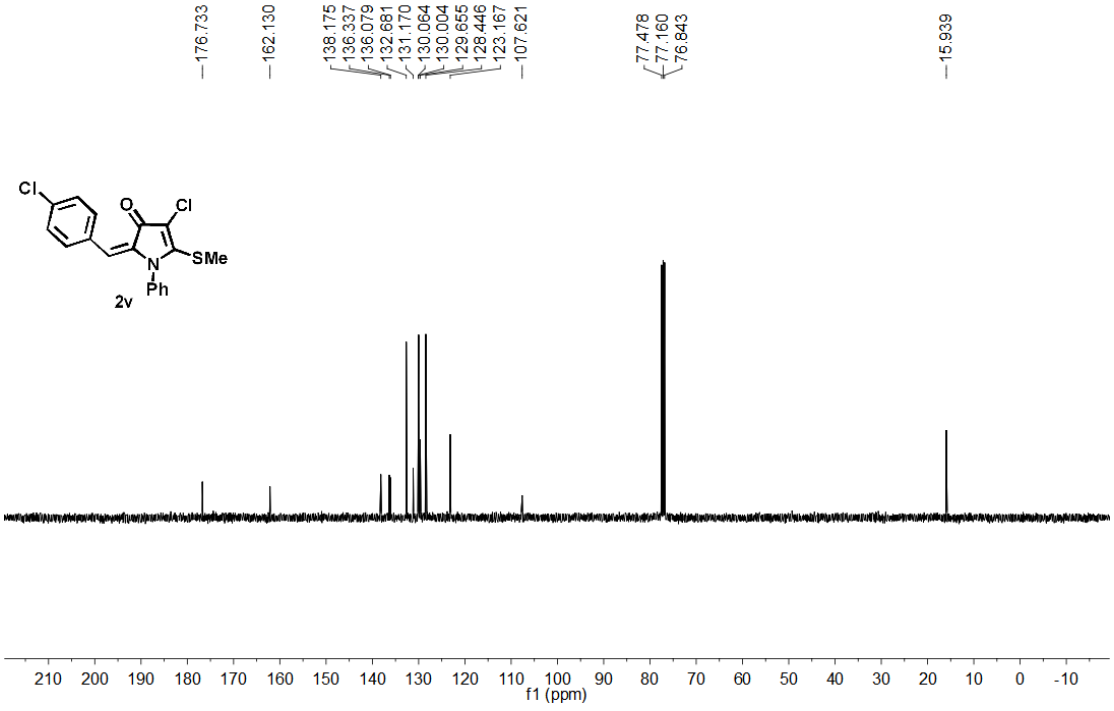
HF488-P
13C NMR IN CDCl3



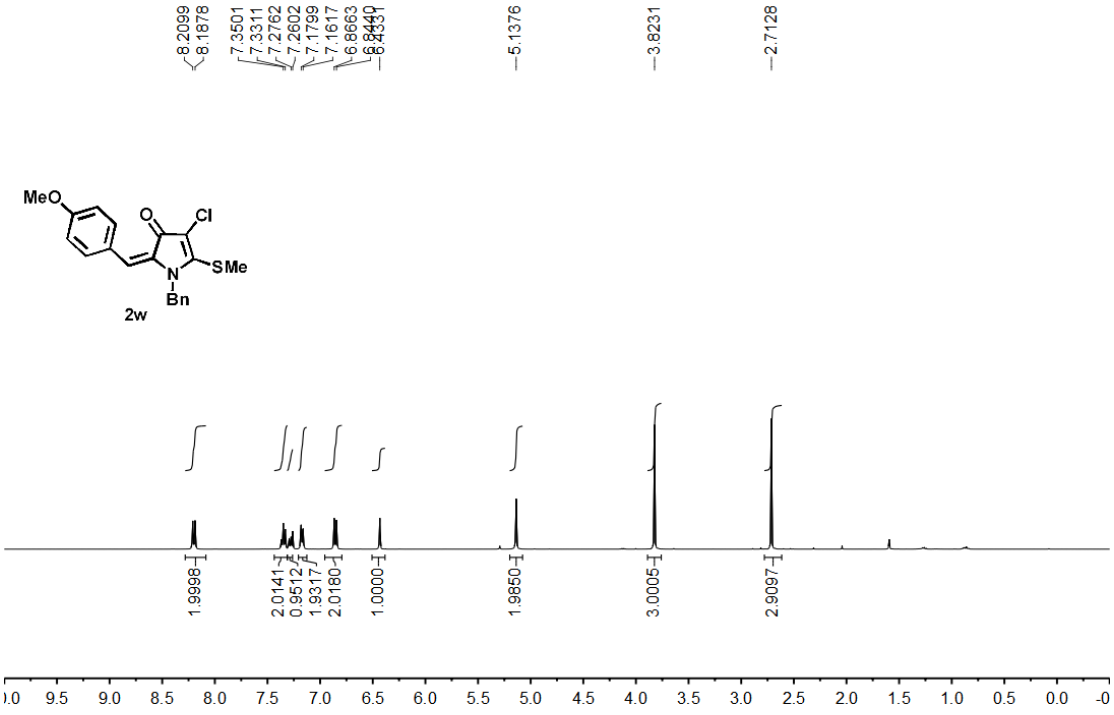
HF489
1H NMR IN CDCl3



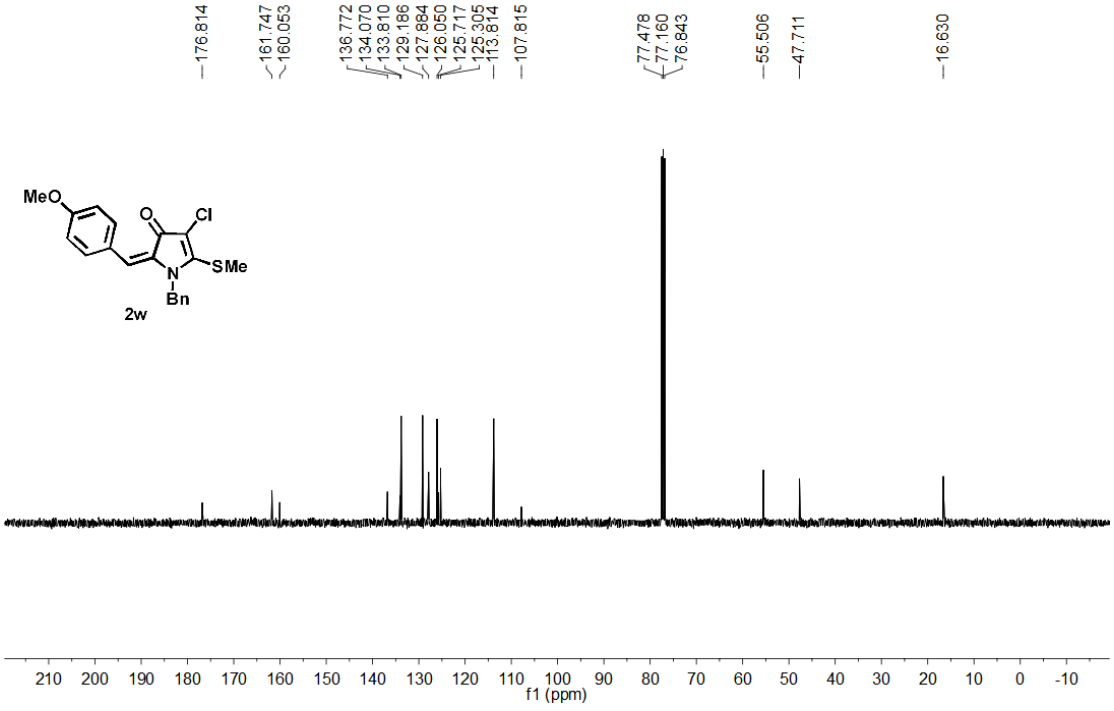
HF489
13C NMR IN CDCl3



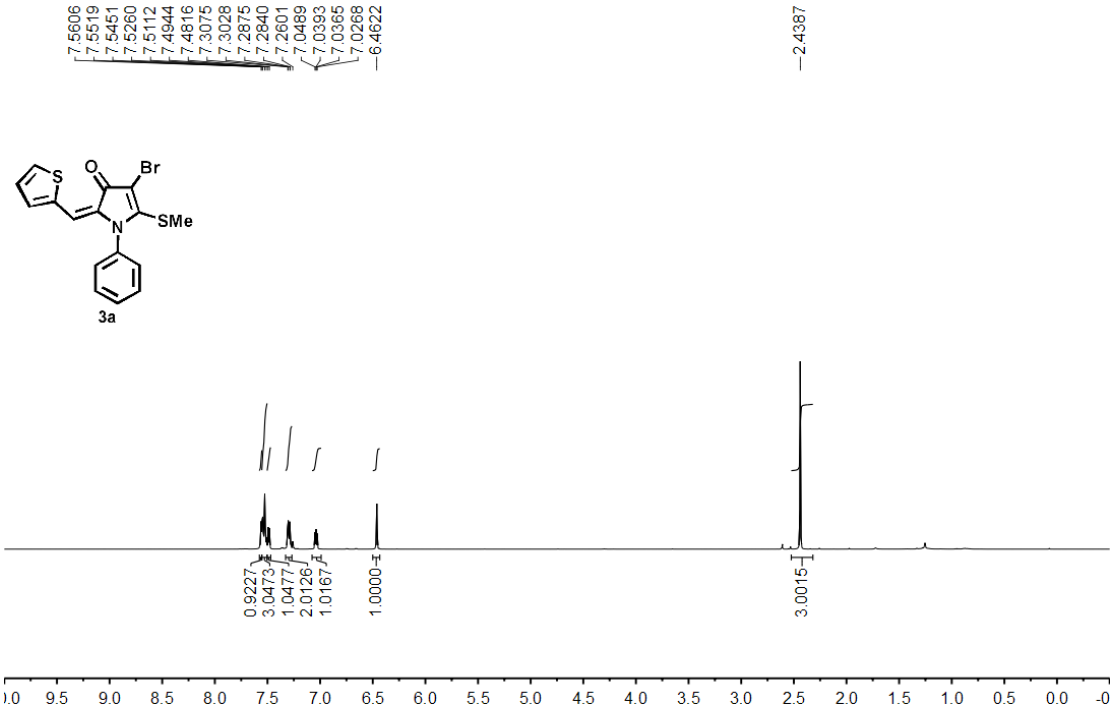
HF491
1H NMR IN CDCl3



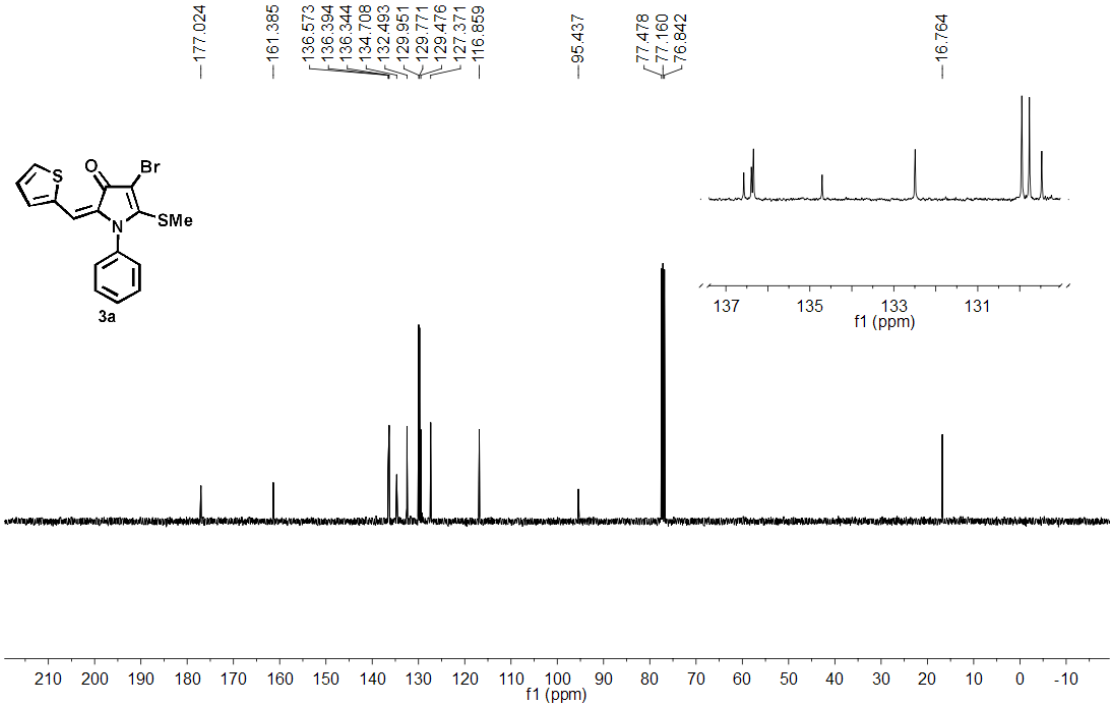
HF491
13C NMR IN CDCl3



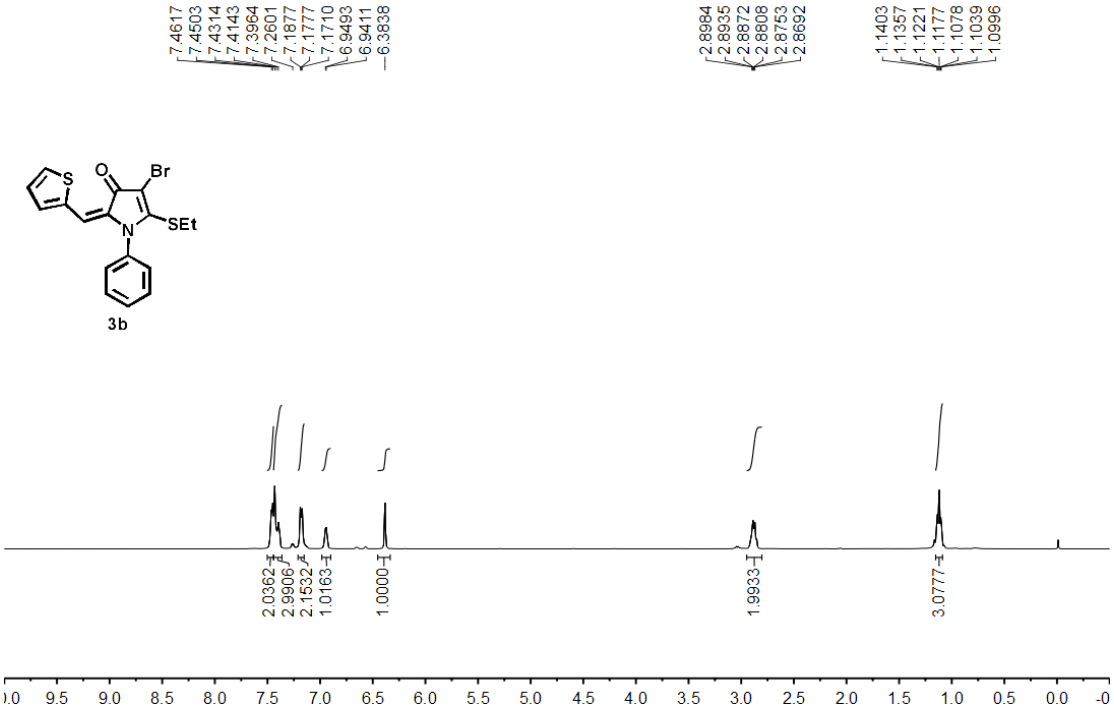
hf470
1H NMR IN CDCl3



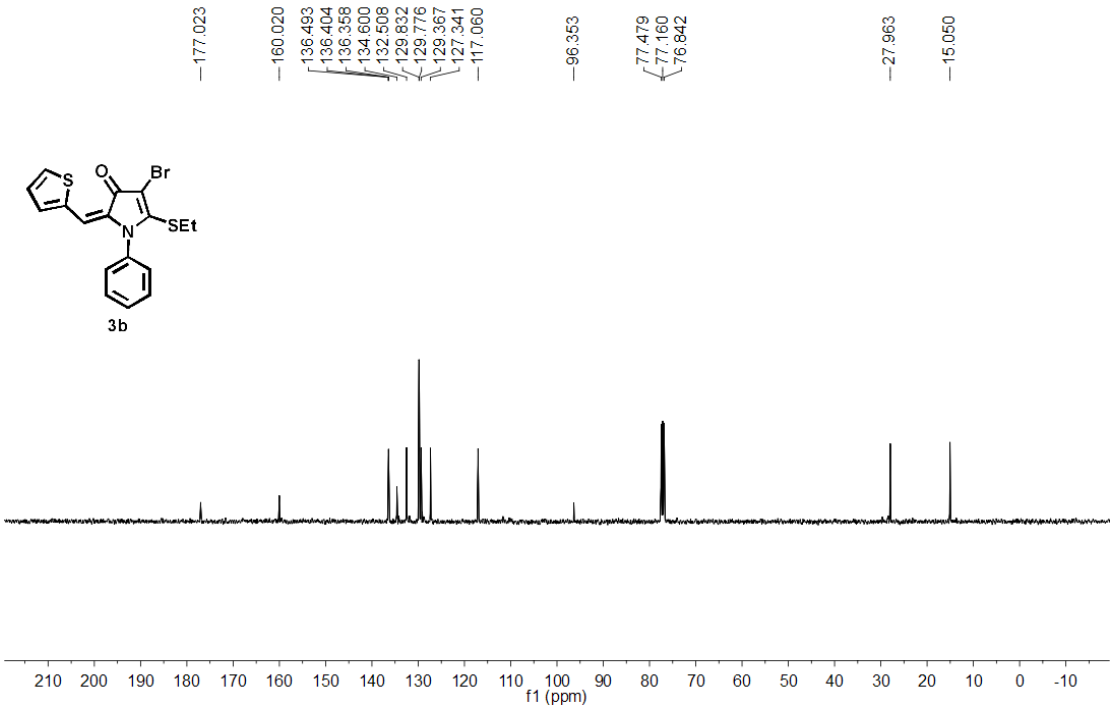
hf470
13C NMR IN CDCl3



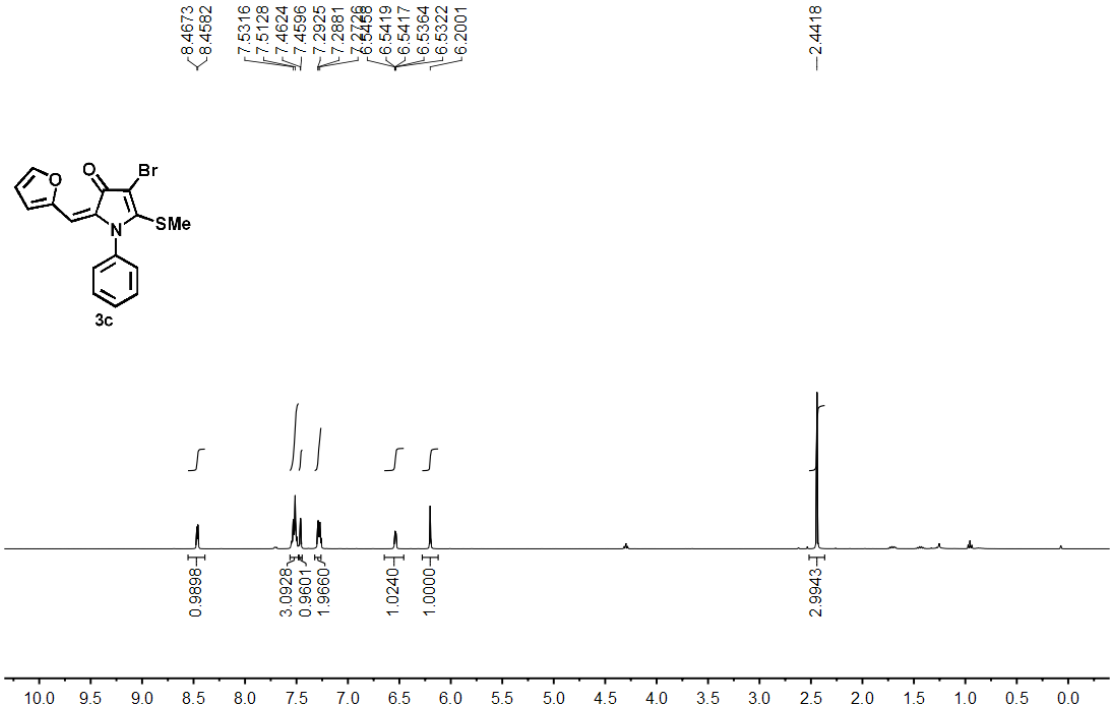
HF484
1H NMR IN CDCl3



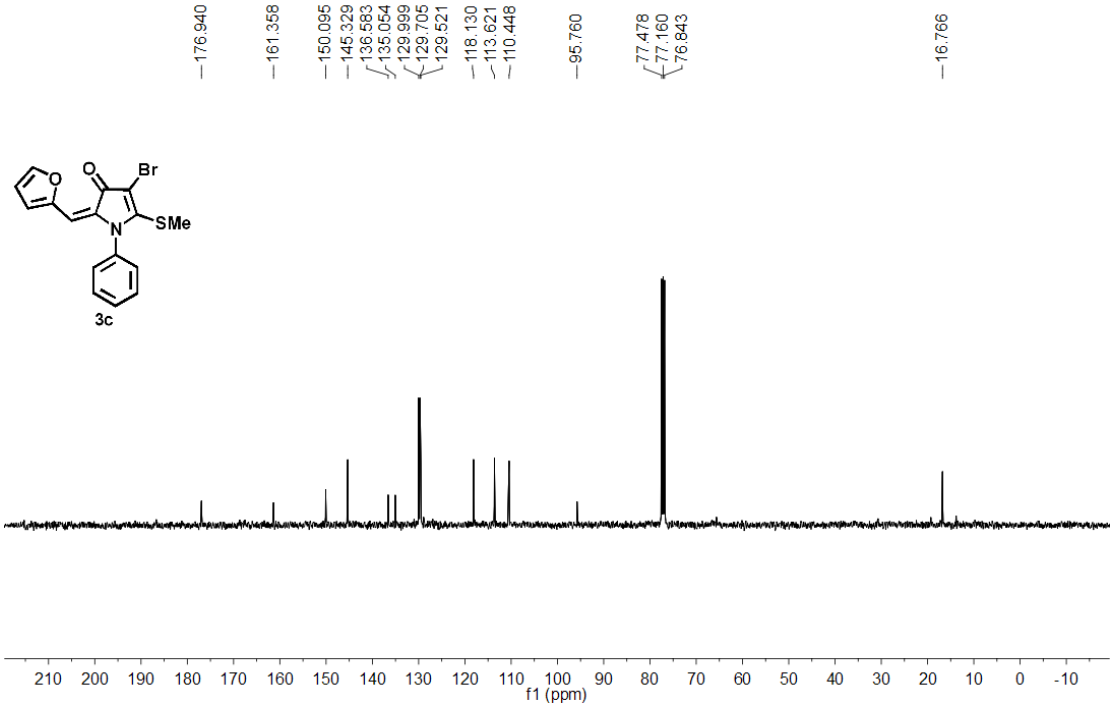
HF484
13C NMR IN CDCl3



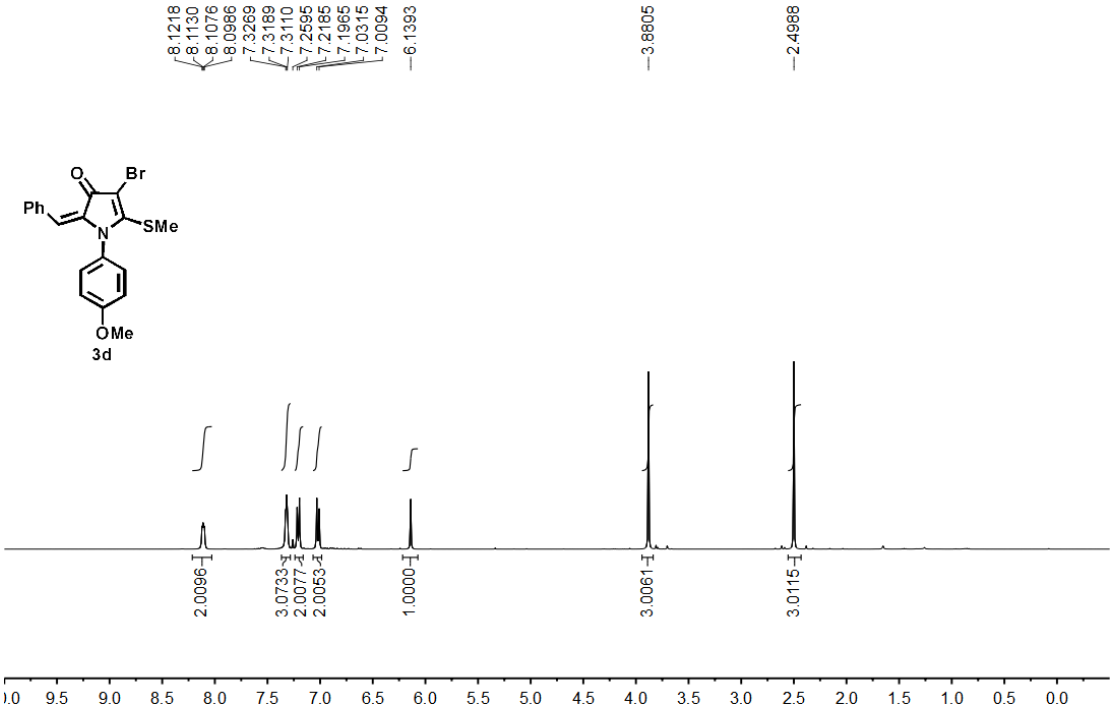
HF482
1H NMR IN CDCl3



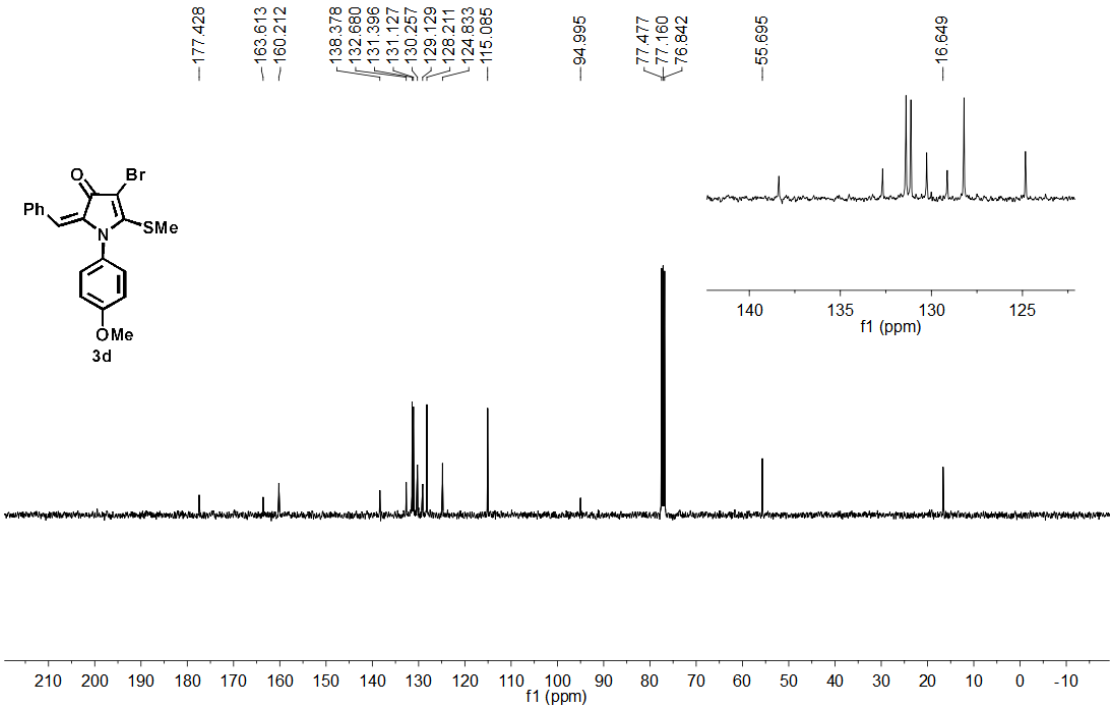
HF482
13C NMR IN CDCl3



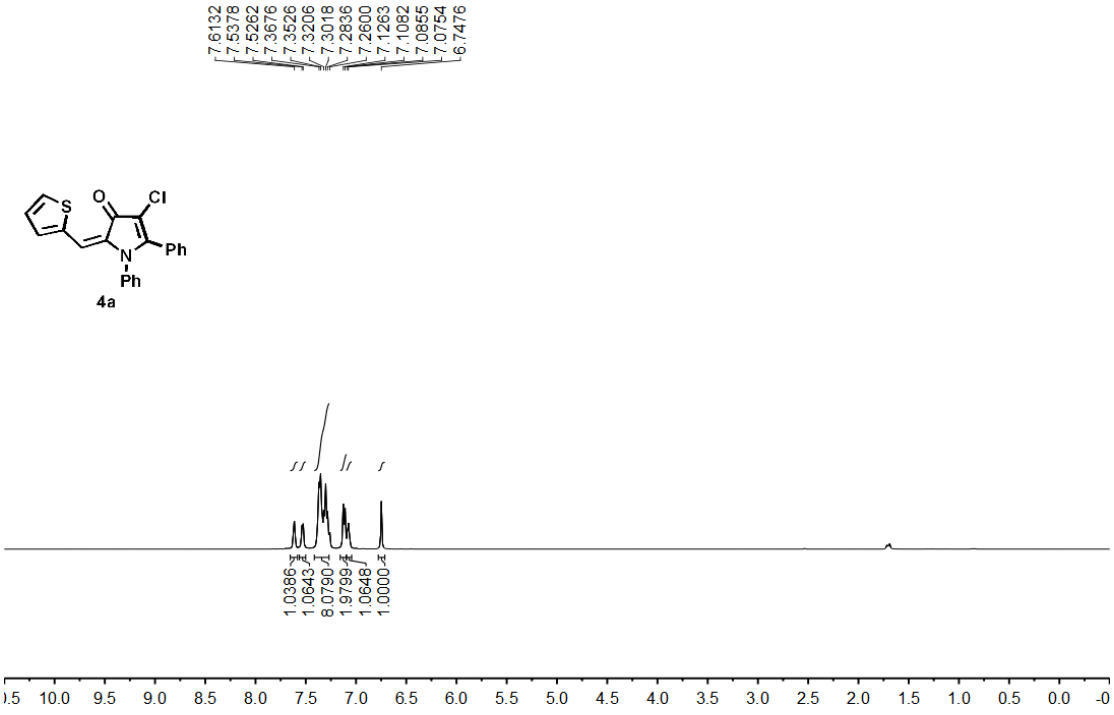
HF509
1H NMR IN CDC13



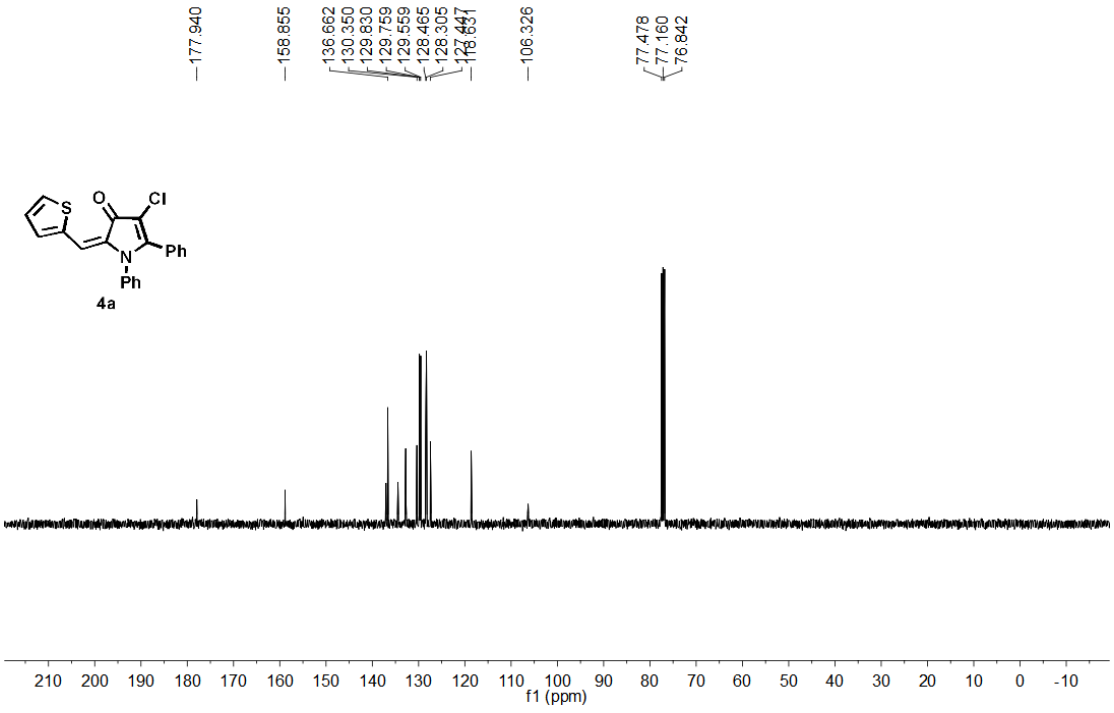
HF509
13C NMR IN CDC13



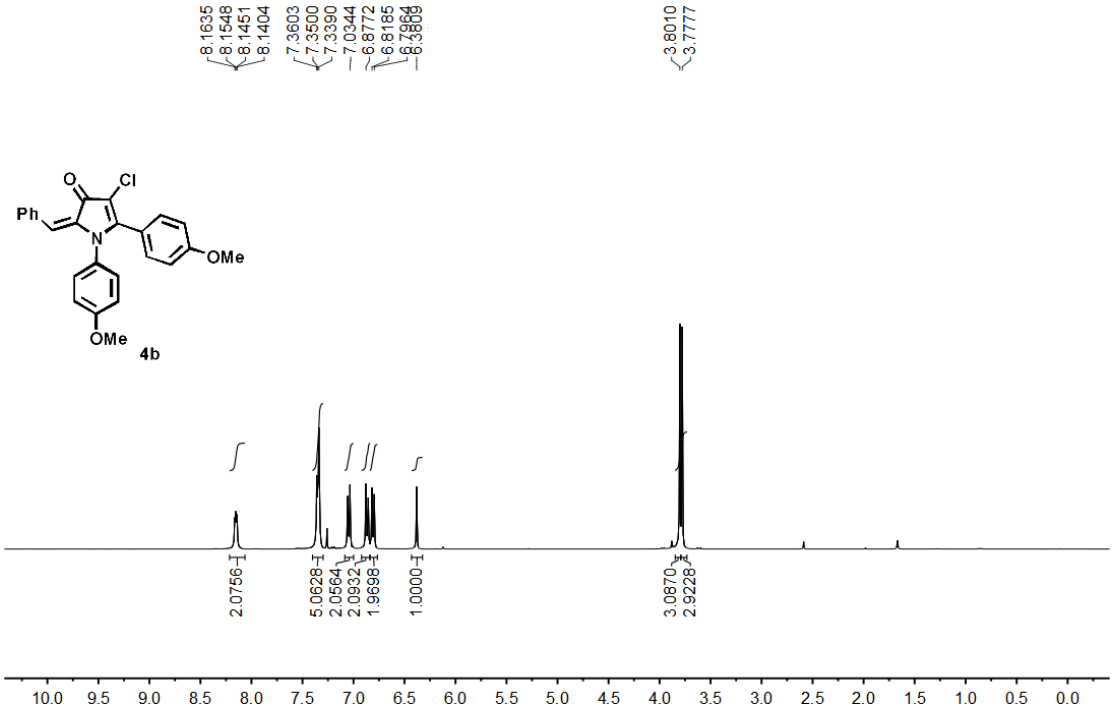
HF590
1H NMR IN CDC13



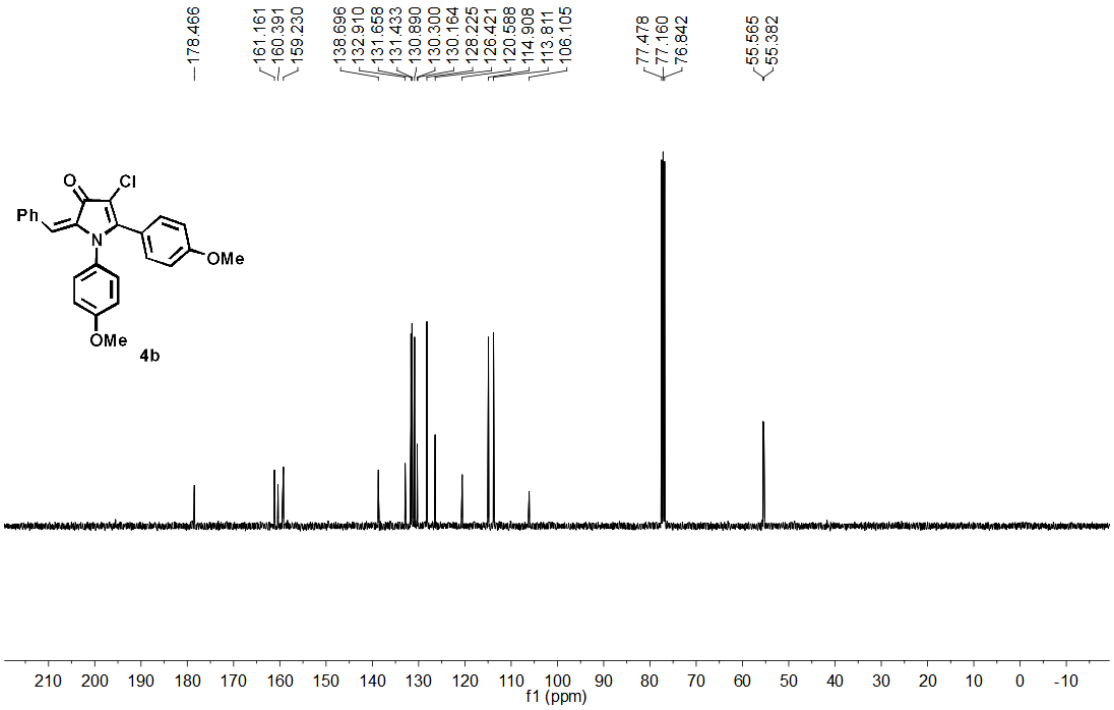
HF590
13C NMR IN CDC13



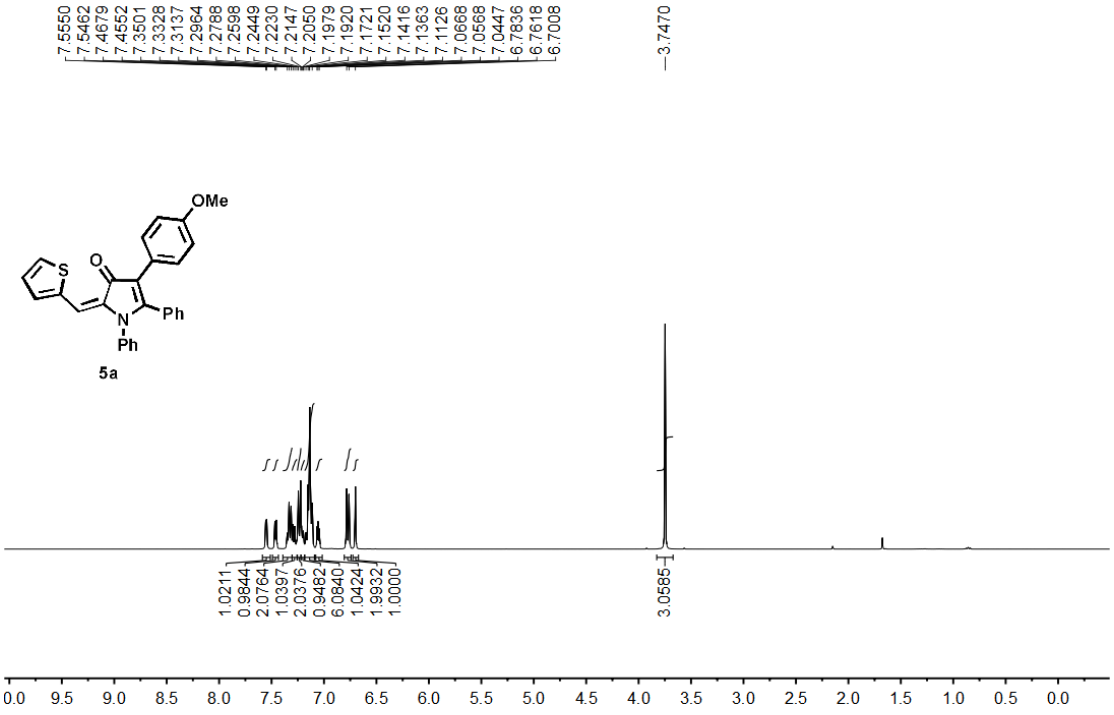
HF587
1H NMR IN CDC13



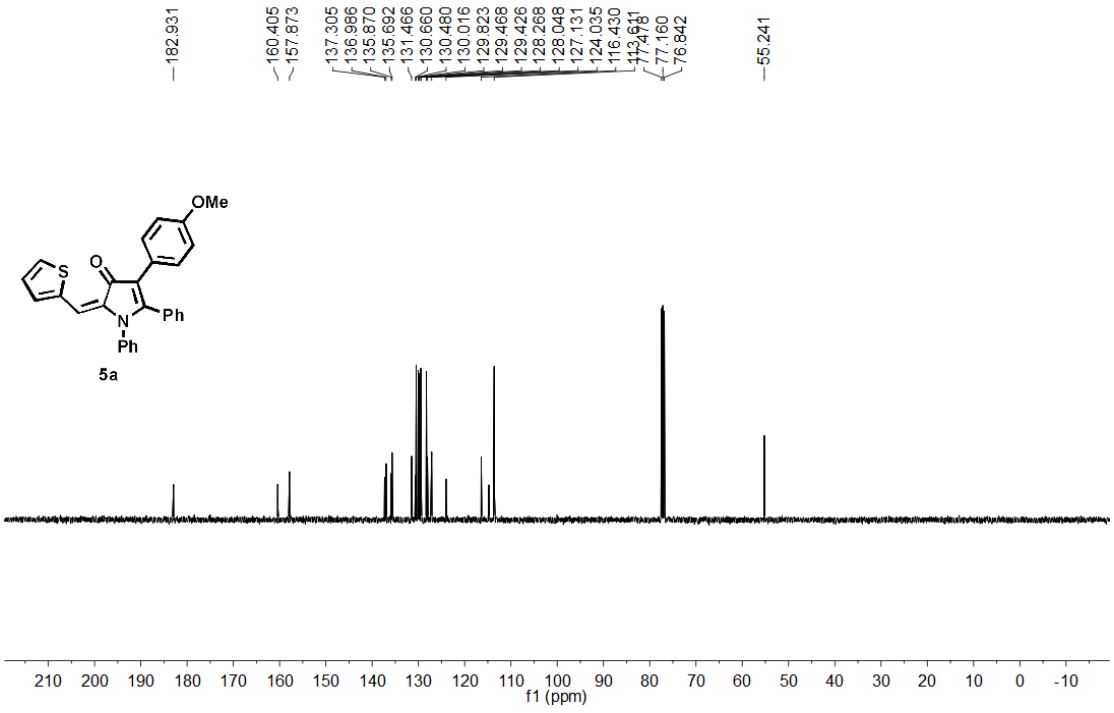
HF587
13C NMR IN CDC13



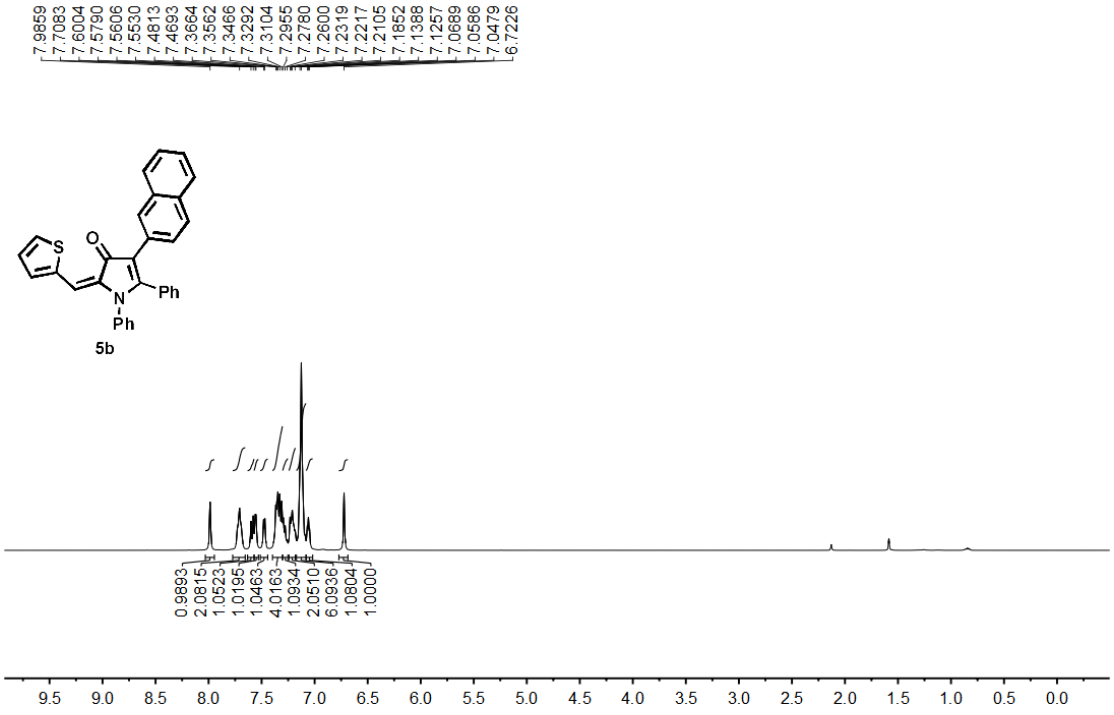
HF595
1H NMR in CDCl3



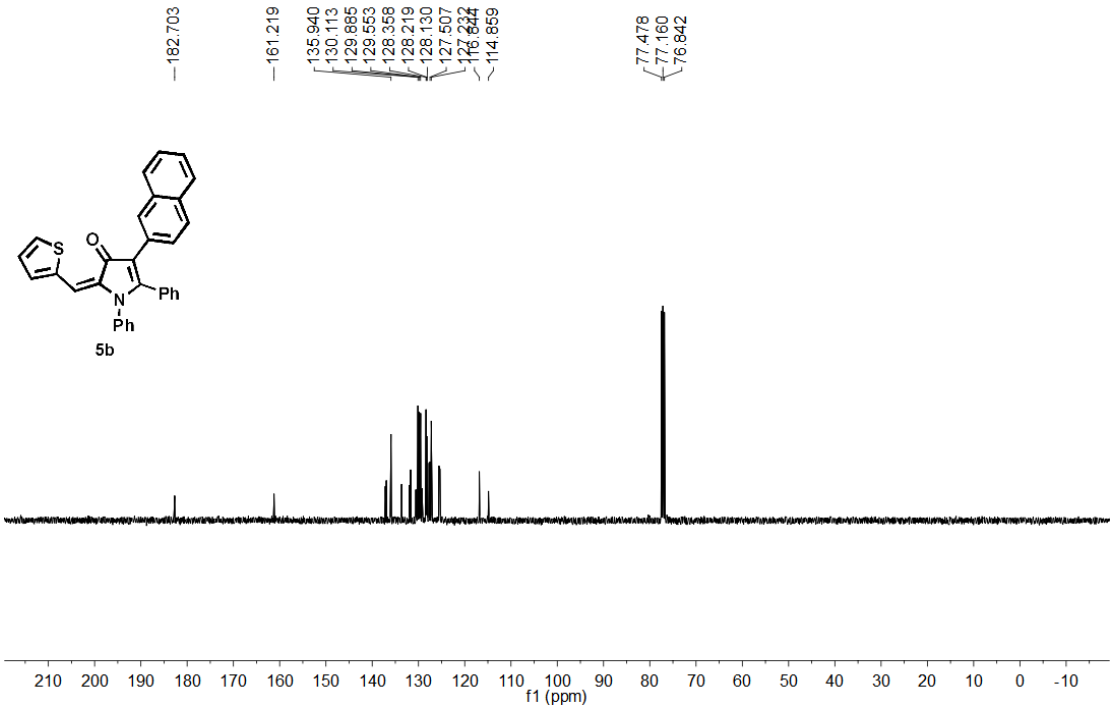
HF595
13C NMR in CDCl3



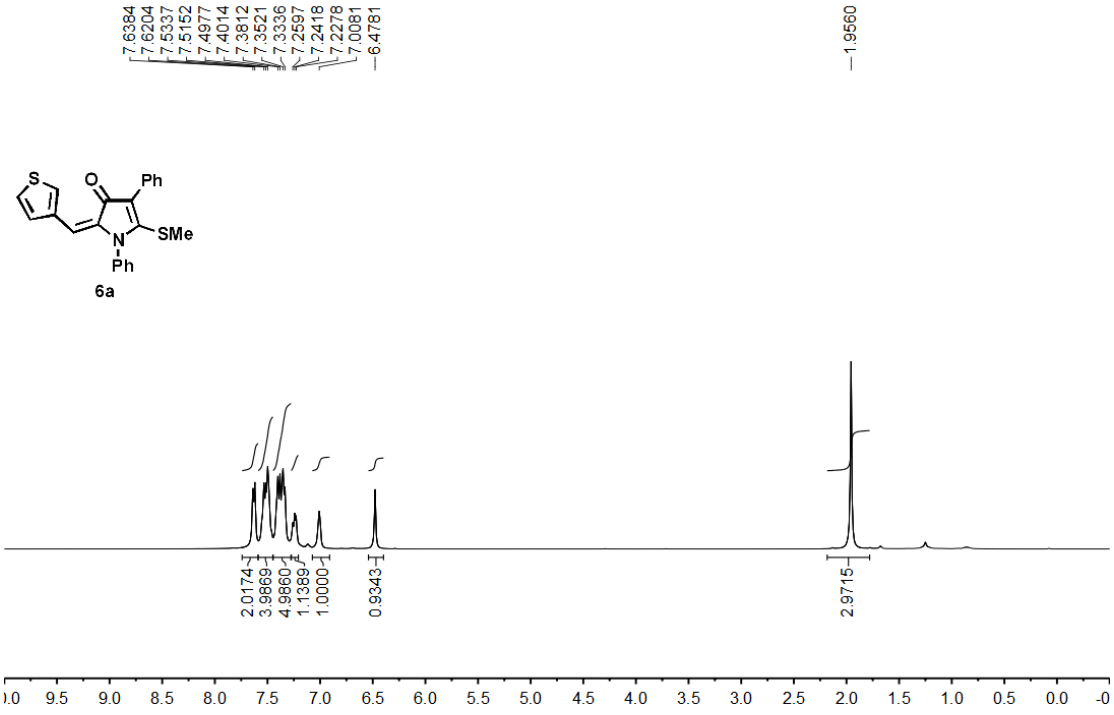
HF594
1H NMR in CDCl3



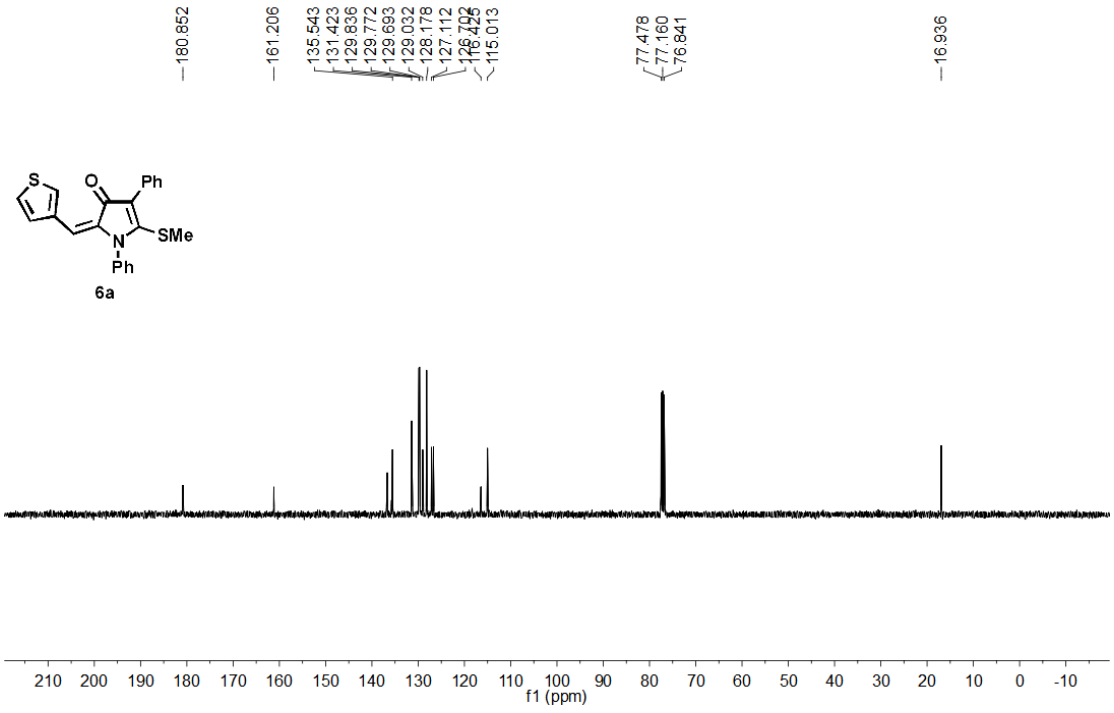
HF594
13C NMR in CDCl3



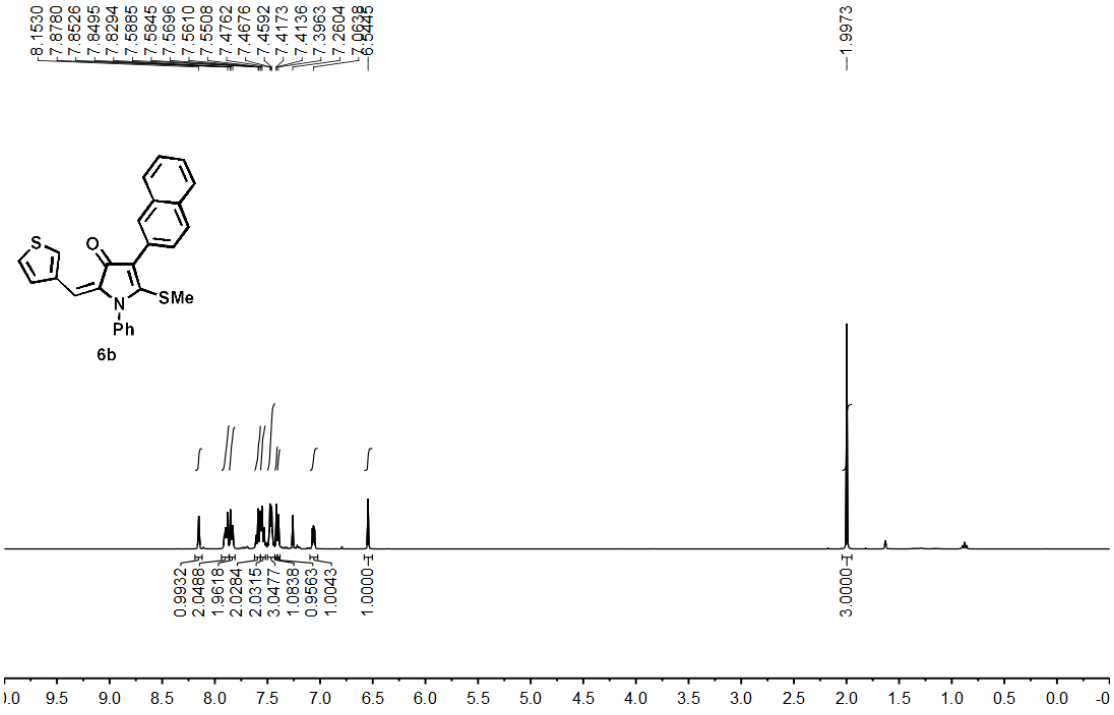
HF555
1H NMR IN CDC13



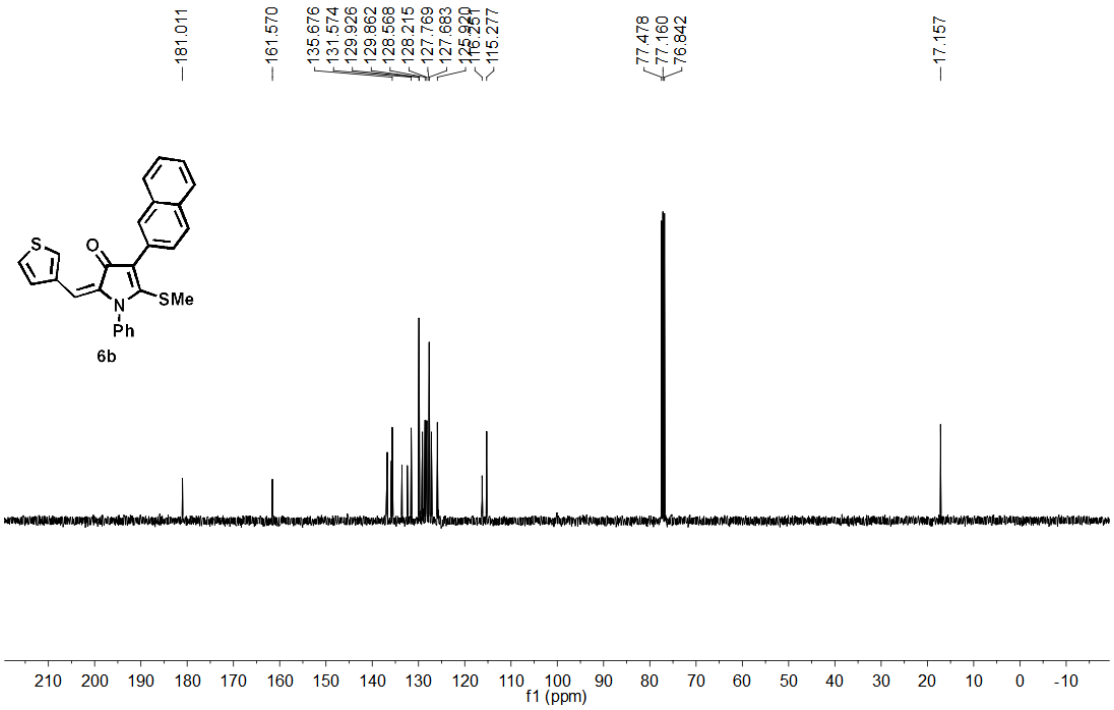
HF555
13C NMR IN CDC13



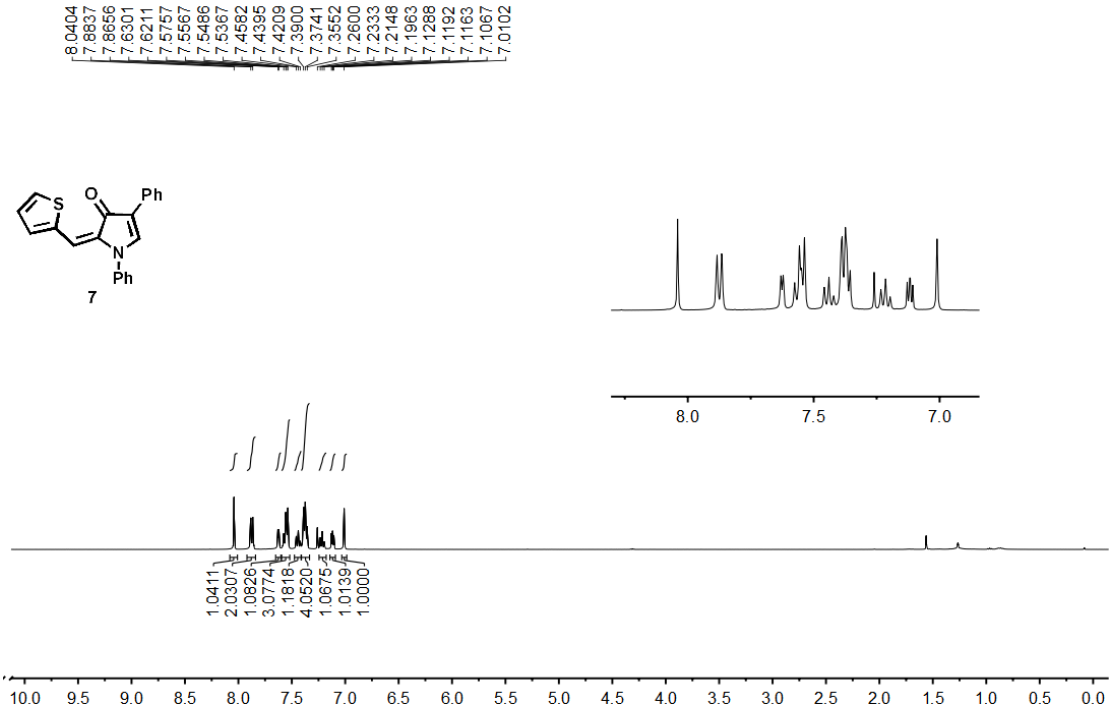
HF572
1H NMR IN CDC13



HF572
13C NMR IN CDC13



HF556
1H NMR IN CDCl3



HF556
13C NMR IN CDCl3