Supporting Information

Rhodium-catalyzed enone carbonyl directed C–H activation for synthesis of indanones containing all-carbon quaternary centers

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Experimental procedures and analytical data

Contents: Page

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 400 MHz spectrometer and all chemical shift values refer to $CDCl_3$ (δ (^{1}H), 7.26 ppm; δ (^{13}C), 77.16 ppm). High resolution mass spectra were measured on a Waters GC-TOF CA156 mass spectrometer. All the melting points were measured and uncorrected. X-Ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Analytical TLC plates were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. The starting chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. □*α*-Oxo ketene dithioacetals **1a-n,**[1] **1o**,[2] **1p**,[3] and diazo compounds **2**[4] were prepared by the reported methods.

References

(1) (a) J. He, Z. Man, Y. Shi and C.-Y. Li, Synthesis of *β*-Amino-*α*,*β*-unsaturated Ketone Derivatives via Sequential Rhodium-Catalyzed Sulfur Ylide Formation/Rearrangement, *J. Org. Chem.,* 2015, **80**, 4816; (b) P. Wu, L. Wang, K. Wu and Z. Yu, Brønsted Acid Catalyzed PhSe Transfer versus Radical Aryl Transfer: Linear Codimerization of Styrenes and Internal Olefins, *Org. Lett.,* 2015, **17**, 868; (c) Z. Fu, M. Wang, Y. Dong, J. Liu and Q. Liu, Direct Synthesis of Highly Substituted 2-Cyclohexenones and Sterically Hindered Benzophenones Based on a [5C+1C] Annulation, *J. Org. Chem.,* 2009, **74**, 6105.

(2) X. Zhao, F. Zhang, K. Liu, X. Zhang and H. Lv, Nickel-Catalyzed Chemoselective Asymmetric Hydrogenation of *α*,*β*-Unsaturated Ketoimines: An Efficient Approach to Chiral Allylic Amines, *Org. Lett.,* 2019, **21**, 8966.

(3) S. Zhou, B.-Y. Yan, S.-X. Fan, J.-S. Tian and T.-P. Loh, Regioselective Formal [4+2] Cycloadditions of Enaminones with Diazocarbonyls through Rh^{III}-Catalyzed C–H Bond Functionalization, *Org. Lett.,* 2018, **20**, 3975.

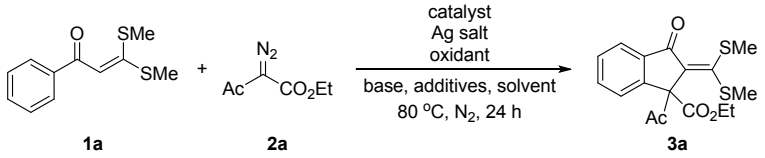
(4) P. Li, X. Xu, J. Chen, H. Yao and A. Lin, Rh(III)-Catalyzed Synthesis of Pyrazolo[1,2-*a*]cinnolines from Pyrazolidinones and Diazo Compounds, *Org. Chem. Front.,* 2018, **5**, 1777.

2. Experimental procedures

2.1 Optimization of the reaction conditions

A mixture of **1a** (44.9 mg, 0.2 mmol), diazo compound **2a** (62.5 mg, 0.4 mmol), catalyst, silver salt, oxidant, and additives in 2 mL solvent was vigorously stirred for 24 h under a nitrogen atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 20:1, v/v) to afford product **3a**.

Table S1. Optimization of the reaction conditions[a]



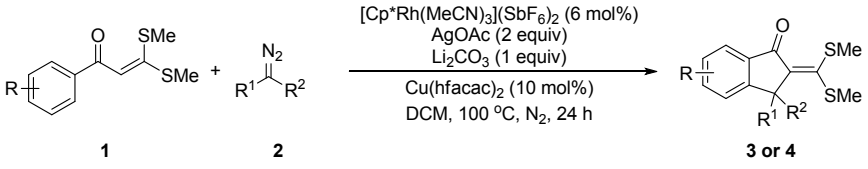
1a **2a** **3a**

entry	catalyst (mol%)	Ag salt (mol%)	oxidant	base	additives (mol%)	solvent	yield (%)[b]
1	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	NaOAc		DCE	19
2	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		DCE	34
3	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	Ag_2CO_3	LiOAc		DCE	27
4	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgTFA	LiOAc		DCE	trace
5	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	$Cu(OAc)_2$	LiOAc		DCE	trace
6	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	$Cu(OAc)_2·H_2O$	LiOAc		DCE	trace
7	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		1,4-dioxane	10
8	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		THF	12
9	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		CH_3CN	8
10	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		toluene	10
11	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		MeOH	trace
12	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		EtOAc	28
13	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		$CHCl_3$	24
14	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	LiOAc		DCM	40
15	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc			DCM	38
16	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Li_2CO_3		DCM	47
17	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Na_2CO_3		DCM	trace
18	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	NaOPiv		DCM	trace
19	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	K_2HPO_4		DCM	trace
20	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	CsOAc		DCM	trace
21	$[Cp^*RhCl_2]_2$ (4)	$AgBF_4$ (16)	AgOAc	Li_2CO_3		DCM	20
22	$[Cp^*RhCl_2]_2$ (4)	AgPF6 (16)	AgOAc	Li_2CO_3		DCM	16
23[c]	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Li_2CO_3		DCM	38
24[d]	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Li_2CO_3		DCM	49

25[e]	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Li_2CO_3		DCM	48
26[f]	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Li_2CO_3		DCM	35
27[e,g]	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Li_2CO_3		DCM	40
28[e,h]	$[Cp^*RhCl_2]_2$ (4)	$AgSbF_6$ (16)	AgOAc	Li_2CO_3		DCM	45
29[e]	$[Cp^*RhCl_2]_2$ (2)	$AgSbF_6$ (8)	AgOAc	Li_2CO_3		DCM	41
30[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3		DCM	64
31[e]	$[Cp^*RhCl_2]_2$ (5)	$AgSbF_6$ (20)	AgOAc	Li_2CO_3		DCM	46
33[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Zn(OAc)_2$	DCM	49
34[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Zn(OTf)_2$	DCM	38
35[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Mg(OTf)_2$	DCM	49
36[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Ni(hfacac)_2$	DCM	62
37[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Cu(hfacac)_2$	DCM	68
38[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Ni(OTf)_2$	DCM	42
39[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$B(OH)_3$	DCM	60
40[e]	$[Cp^*RhCl_2]_2$ (3)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	Trimesic acid	DCM	57
41[e]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6)		AgOAc	Li_2CO_3	$Cu(hfacac)_2$	DCM	70
42[e,i]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6)		AgOAc	Li_2CO_3	$Cu(hfacac)_2$	DCM	74
43[e,j]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6)		AgOAc	Li_2CO_3	$Cu(hfacac)_2$	DCM	75
44[e,j]	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ (6)		AgOAc	Li_2CO_3		DCM	66
45[e,i]	$Cp^*Co(CO)I_2$ (6)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Cu(hfacac)_2$	DCM	n.d.
46[e,i]	$RhCl_3$ (6)	$AgSbF_6$ (12)	AgOAc	Li_2CO_3	$Cu(hfacac)_2$	DCM	n.d.
47[e,i]			AgOAc	Li_2CO_3	$Cu(hfacac)_2$	DCM	n.d.
48[e,i]	$Cp^*Rh(MeCN)_3](SbF_6)_2$ (6)			Li_2CO_3	$Cu(hfacac)_2$	DCM	n.d.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Cp^*RhCl_2]_2$ (4 mol%), $AgSbF_6$ (16 mol%), oxidant (2 equiv), base (2 equiv), and additive (10 mol%) in solvent (2 mL) at 80 °C for 24 h under a nitrogen atmosphere. [b]Yields of isolated products. [c]**2a** (0.6 mmol). [d]Li_2CO_3 (3 equiv). [e]Li_2CO_3 (1 equiv). [f]Li_2CO_3 (0.5 equiv). [g]AgOAc (1 equiv). [h]AgOAc (1.5 equiv). [i]100 °C. [j]120 °C.

2.2 General procedure for the synthesis of indanones 3 and 4



***A typical procedure for the synthesis of 3a*:** A mixture of **1a** (44.9 mg, 0.2 mmol), diazo compound **2a** (62.5 mg, 0.4 mmol), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.0 mg, 0.012 mmol), AgOAc (66.8 mg, 0.4 mmol), Li_2CO_3 (14.8 mg, 0.2 mmol), and $Cu(hfacac)_2$ (9.6 mg, 0.02 mmol) in 2 mL DCM was vigorously stirred at 100 °C for 24 h under a nitrogen atmosphere. After cooling to ambient temperature, all the

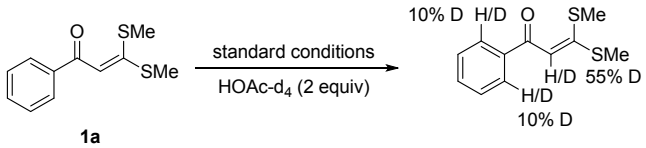
volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 20:1, v/v) to afford product **3a** (52.2 mg, 74%).

A typical procedure for the synthesis of 3g on 1 mmol scale: A mixture of **1g** (238.4 mg, 1 mmol), diazo compound **2a** (312.3 mg, 2 mmol), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (50.9 mg, 0.06 mmol), AgOAc (333.8 mg, 2 mmol), Li_2CO_3 (74.0 mg, 1 mmol), and $Cu(hfacac)_2$ (47.8 mg, 0.1 mmol) in 10 mL DCM was vigorously stirred at 100 °C for 24 h under a nitrogen atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 20:1, v/v) to afford product **3g** (255.5 mg, 70%).

A typical procedure for the synthesis of 3p′: A mixture of **1p** (35.0 mg, 0.2 mmol), diazo compound **2a** (93.7 mg, 0.6 mmol), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.0 mg, 0.012 mmol), AgOAc (66.8 mg, 0.4 mmol), Li_2CO_3 (14.8 mg, 0.2 mmol), and $Cu(hfacac)_2$ (9.6 mg, 0.02 mmol) in 2 mL DCM was vigorously stirred at 100 °C for 24 h under a nitrogen atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 20:1, v/v) to afford product **3p′** (32.6 mg, 44%).

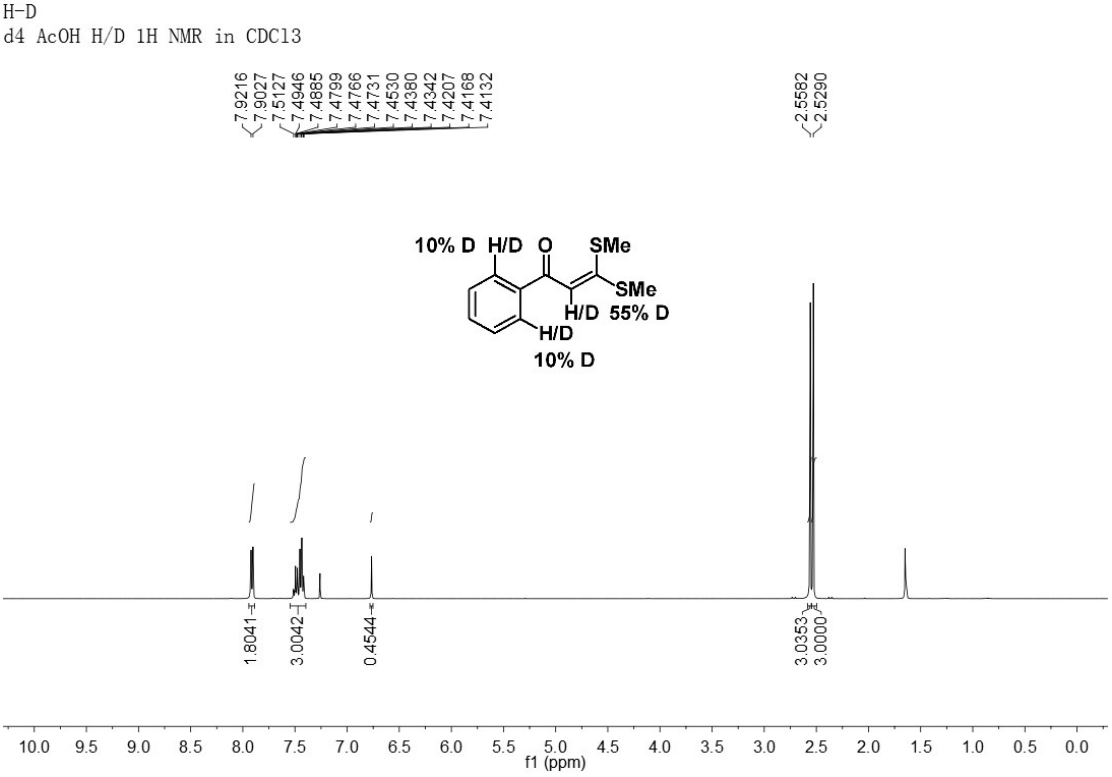
2.3 Mechanistic studies

(a) H/D Exchange experiment

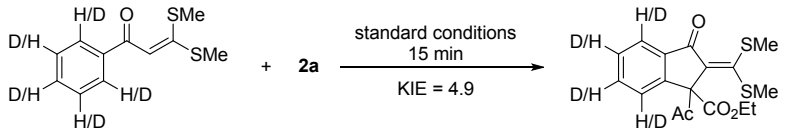


A mixture of **1a** (44.9 mg, 0.2 mmol), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.0 mg, 0.012 mmol), AgOAc (66.8 mg, 0.4 mmol), Li_2CO_3 (14.8 mg, 0.2 mmol), $Cu(hfacac)_2$ (9.6 mg, 0.02 mmol), and HOAc-d_4 (25.6 mg, 0.4 mmol) in 2 mL DCM was vigorously stirred at 100 °C for 24 h under a nitrogen atmosphere. After cooling to ambient

temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 20:1, v/v) to afford product **3a**, which was characterized by ^{1}H NMR spectroscopy



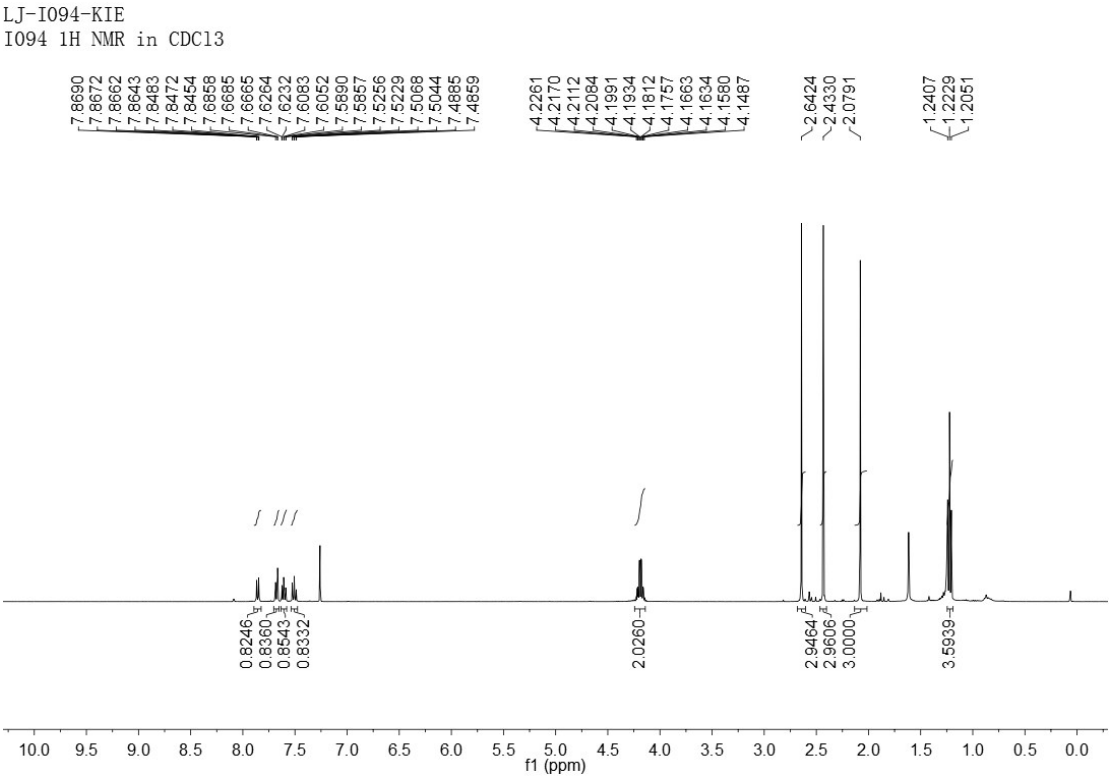
(b) Kinetic isotope effect (KIE) experiments



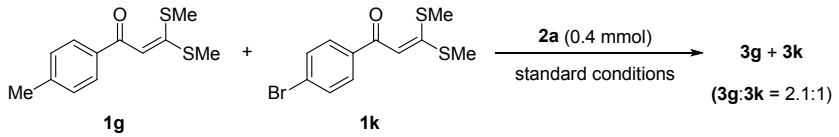
1a, 1a[D] **3a, 3a[D]**

The reactions of benzoyl ketene dithioacetal **1a** and its deuterated form **1a**[D], were carried out in a parallel manner under the optimized conditions. A mixture of **1a** or **1a**[D] (44.9 mg, 0.2 mmol), diazo compound **2a** (62.5 mg, 0.4 mmol), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.0 mg, 0.012 mmol), AgOAc (66.8 mg, 0.4 mmol), Li_2CO_3 (14.8 mg, 0.2 mmol), and $Cu(hfacac)_2$ (9.6 mg, 0.02 mmol) in 2 mL DCM was vigorously stirred at 100 ^{o}C for 15 min under a nitrogen atmosphere. After cooling to ambient temperature, the two reaction solutions were mixed together and

all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 20:1, v/v) to afford the mixture of **3a** and **3a**[D]. The KIE value was determined to be k_H/k_D= 4.9 on the basis of ^{1}H NMR analysis.

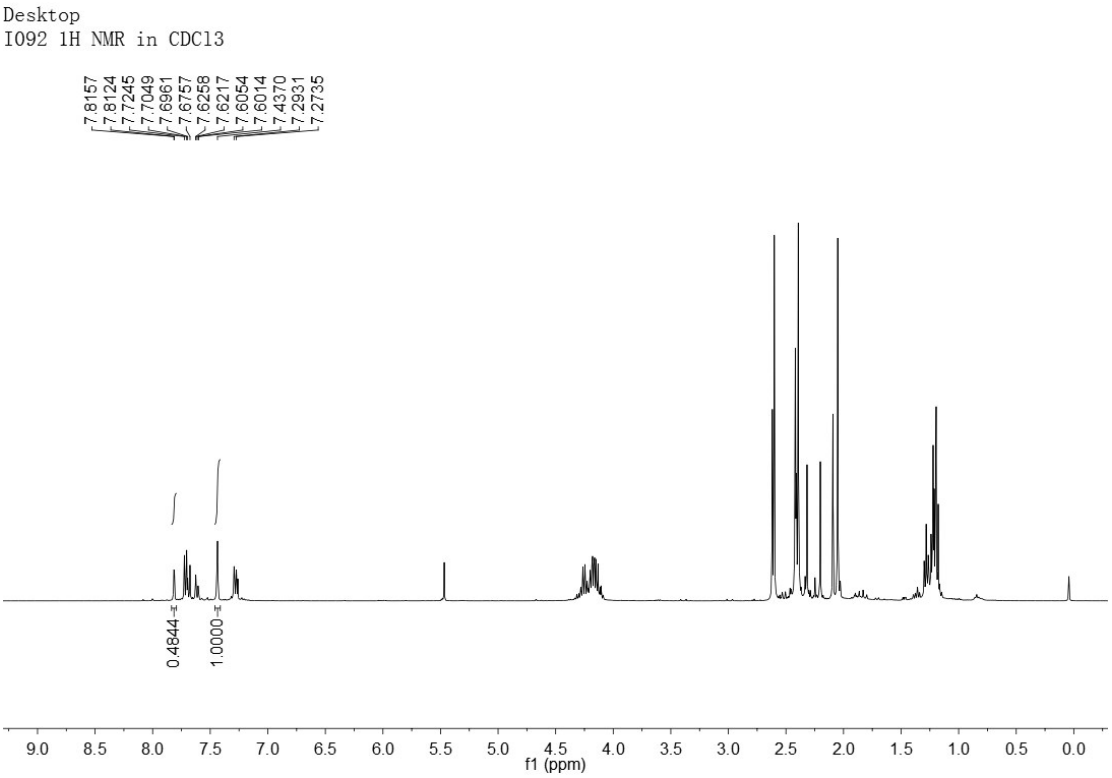


(c) Intermolecular competition reaction



A mixture of **1g** (47.7 mg, 0.2 mmol), **1k** (60.6 mg, 0.2 mmol), diazo compound **2a** (62.5 mg, 0.4 mmol), $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (10.0 mg, 0.012 mmol), AgOAc (66.8 mg, 0.4 mmol), Li_2CO_3 (14.8 mg, 0.2 mmol), and $Cu(hfacac)_2$ (9.6 mg, 0.02 mmol) in 2 mL DCM was vigorously stirred at 100 °C for 24 h under a nitrogen atmosphere. After cooling to ambient temperature, all the volatiles were evaporated under reduced pressure. The resultant residue was purified by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/ethyl acetate = 20:1, v/v) to afford the mixture of **3g** and **3k**. The ratio of 3g and 3k was determined

to be **3g**:**3k** = 1:0.48 on the basis of ^{1}H NMR analysis.



3. X-Ray crystallographic studies

The X–ray diffraction analysis for compound **3h** and **3p′** 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 2052734 for compound **3h** and 2052735 for **3p′**. 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).

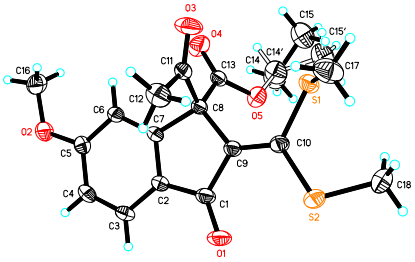


Figure S1. Molecular structure of compound **3h**.

Table S2. Crystal Data and Structure Refinement for Compound 3h

Identification code	LZQ-94	
Empirical formula	$C_{18}H_{20}O_5S_2$	
Formula weight	380.46	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6038(8) Å	α=94.108(9)°.
	b = 9.8764(10) Å	β=103.211(8)°.
	c = 11.2269(12) Å	γ =95.986(8)°.
Volume	919.19(16) $Å^3$	
Z	2	
Density (calculated)	1.375 Mg/m^3	
Absorption coefficient	0.315 mm^{-1}	
F(000)	400	
Crystal size	0.170 x 0.150 x 0.120 mm^3	
Theta range for data collection	3.013 to 25.998°.	
Index ranges	-10<=h<=10, -11<=k<=12, -13<=l<=13	
Reflections collected	7376	
Independent reflections	3608 [R(int) = 0.0253]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.8179	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3608 / 38 / 250	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1162	
R indices (all data)	R1 = 0.0756, wR2 = 0.1372	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.394 and -0.321 $e.Å^{-3}$	

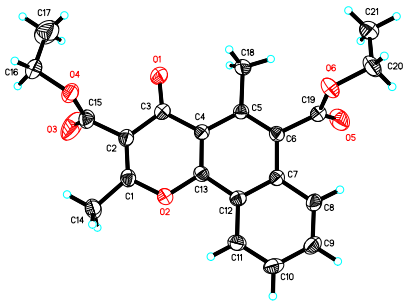
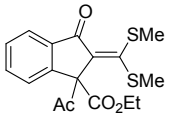


Figure S2. Molecular structure of compound **3p′**.

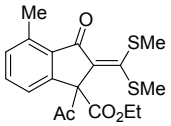
Table S3. Crystal Data and Structure Refinement for Compound 3p′

Identification code	2020611-1	
Empirical formula	$C_{21}H_{20}O_6$	
Formula weight	368.37	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.3893(7) Å	α=90.188(9)°.
	b = 10.2769(14) Å	β=101.277(8)°.
	c = 12.0917(11) Å	γ=91.828(9)°.
Volume	900.01(17) $Å^3$	
Z	2	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	0.100 mm^{-1}	
F(000)	388	
Crystal size	0.200 x 0.160 x 0.130 mm^3	
Theta range for data collection	2.995 to 25.498°.	
Index ranges	-8<=h<=8, -12<=k<=12, -14<=l<=14	
Reflections collected	5899	
Independent reflections	3337 [R(int) = 0.0191]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.815	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3337 / 0 / 249	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1235	
R indices (all data)	R1 = 0.0772, wR2 = 0.1481	
Extinction coefficient	0.040(5)	
Largest diff. peak and hole	0.186 and -0.166 $e.Å^{-3}$	

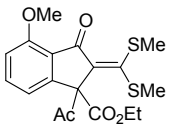
4. Analytical data



Ethyl 1-acetyl-2-(bis(methylthio)methylene)-3-oxo-2,3-dihydro-1*H*-indene-1-carboxylate (**3a**): Following the general procedure, pure **3a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 52.2 mg, 74% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.60 (td, *J* = 7.5 and 1.3 Hz, 1H), 7.49 (td, *J* = 7.5 and 1.0 Hz, 1H), 4.22–4.13 (m, 2H), 2.63 (s, 3H), 2.42 (s, 3H), 2.07 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CDCl3) δ 200.2, 188.4, 167.8, 160.4, 144.9, 139.0, 135.3, 134.4, 129.9, 125.7, 124.6, 72.5, 62.3, 26.7, 18.8, 18.3, 14.0. HRMS Calcd for $C_{17}H_{18}O_4S_2$ $[M+H]^+$: 351.0719; Found: 351.0720.

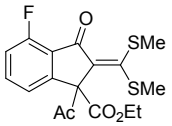


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-4-methyl-3-oxo-2,3-dihydro-1*H*-indene-1-carboxylate (**3b**): Following the general procedure, pure **3b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 33.0 mg, 45% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.24 (m, 1H), 4.24–4.12 (m, 2H), 2.72 (s, 3H), 2.63 (s, 3H), 2.40 (s, 3H), 2.10 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.3, 190.0, 168.1, 158.5, 145.6, 139.8, 136.4, 136.1, 133.8, 132.0, 123.1, 71.9, 62.3, 26.8, 18.8, 18.4, 17.9, 14.1. HRMS Calcd for $C_{18}H_{20}O_4S_2$ $[M+H]^+$: 365.0876; Found: 365.0869.

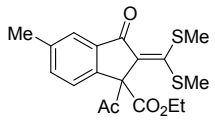


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-4-methoxy-3-oxo-2,3-dihydro-1*H*-indene-1-carboxylate (**3c**): Following the general procedure, pure **3c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 42.8 mg, 56% yield, yellow solid, m.p.: 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 1H), 7.22–7.17 (m, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 4.20–4.10 (m, 2H), 3.96 (s, 3H), 2.59 (s, 3H), 2.39 (s,

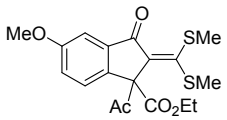
3H), 2.05 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.9, 186.7, 167.8, 158.6, 158.1, 146.9, 135.9, 135.5, 126.9, 117.4, 111.8, 71.7, 62.2, 56.1, 26.6, 18.7, 18.1, 14.0. HRMS Calcd for $C_{18}H_{20}O_5S_2$ $[M+H]^+$: 381.0825; Found: 381.0831.



Ethyl 1-acetyl-2-(bis(methylthio)methylene)-4-fluoro-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3d**): Following the general procedure, pure **3d** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 40.2 mg, 54% yield, yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.45 (m, 1H), 7.13 (t, J = 8.6 Hz, 1H), 4.19 (m, 2H), 2.64 (s, 3H), 2.43 (s, 3H), 2.12 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, CDCl3) δ 199.6, 185.0, 167.5, 161.3, 159.4 (d, J = 263.0 Hz), 146.5 (d, J = 2.8 Hz), 135.9 (d, J = 8.2 Hz), 134.5, 126.6 (d, J = 13.3 Hz), 121.6 (d, J = 4.2 Hz), 117.1 (d, J = 19.0 Hz), 72.3, 62.5, 26.8, 18.9, 18.4, 14.0. HRMS Calcd for $C_{17}H_{17}O_4FS_2$ $[M+H]^+$: 369.0625; Found: 369.0628.

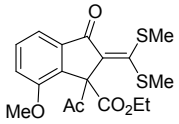


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-5-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3e**): Following the general procedure, pure **3e** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 55.0 mg, 75% yield, yellow solid, m.p.: 67-68 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.40 (dd, J = 7.9, 0.9 Hz, 1H), 4.21 – 4.11 (m, 2H), 2.62 (s, 3H), 2.41 (d, 6H), 2.05 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.3, 188.5, 168.0, 159.8, 142.3, 140.3, 139.2, 135.7, 135.6, 125.4, 124.6, 72.2, 62.2, 26.5, 21.4, 18.7, 18.2, 14.0. HRMS Calcd for $C_{18}H_{20}O_4S_2$ $[M+H]^+$: 365.0876; Found: 365.0870.

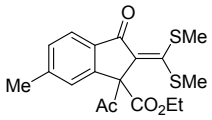


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-5-methoxy-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3f**): Following the general procedure, pure **3f** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 32.2 mg,

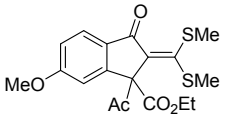
42% yield, yellow solid, m.p.: 131-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.5 Hz, 1H), 7.28 (d, *J* = 2.6 Hz, 1H), 7.16 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.23 – 4.13 (m, 2H), 3.86 (s, 3H), 2.63 (s, 3H), 2.42 (s, 3H), 2.05 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.5, 188.3, 168.1, 161.3, 160.3, 140.6, 137.5, 135.7, 126.8, 123.2, 106.3, 71.9, 62.2, 55.9, 26.4, 18.8, 18.3, 14.1. HRMS Calcd for $C_{18}H_{20}O_5S_2$ [M+H]$^+$: 381.0825; Found: 381.0826.



Ethyl 1-acetyl-2-(bis(methylthio)methylene)-7-methoxy-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3f'**): Following the general procedure, pure **3f'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 25.6 mg, 34% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 4.6 Hz, 2H), 7.05 (m, 1H), 4.19 – 4.06 (m, 2H), 3.86 (s, 3H), 2.57 (s, 3H), 2.47 (s, 3H), 2.36 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 201.8, 188.5, 168.6, 157.9, 156.1, 140.8, 137.6, 134.8, 131.1, 116.4, 116.1, 70.1, 61.7, 55.8, 29.0, 18.7, 18.1, 14.0. HRMS Calcd for $C_{18}H_{20}O_5S_2$ [M+H]$^+$: 381.0825; Found: 381.0830.

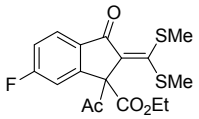


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3g**): Following the general procedure, pure **3g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 57.1 mg, 78% yield, yellow solid, m.p.: 98-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 0.5 Hz, 1H), 7.29 (dd, *J* = 7.8, 0.7 Hz, 1H), 4.25 – 4.08 (m, 2H), 2.61 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H), 2.06 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.2, 188.2, 167.9, 159.1, 145.9, 145.3, 136.9, 135.9, 131.0, 125.9, 124.5, 72.2, 62.2, 26.9, 22.3, 18.7, 18.2, 14.0. HRMS Calcd for $C_{18}H_{20}O_4S_2$ [M+H]$^+$: 365.0876; Found: 365.0875.

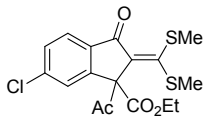


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-6-methoxy-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3h**): Following the general procedure, pure **3h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 61.2 mg,

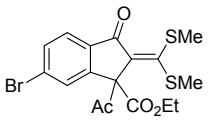
80% yield, yellow solid, m.p.: 129-130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 2.2 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.3 Hz, 1H), 4.18 (m, 2H), 3.87 (s, 3H), 2.61 (s, 3H), 2.40 (s, 3H), 2.04 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.1, 187.3, 167.6, 165.0, 158.0, 147.5, 135.9, 132.5, 126.3, 117.7, 109.2, 72.2, 62.3, 56.0, 26.5, 18.6, 18.1, 14.1. HRMS Calcd for $C_{18}H_{20}O_5S_2$ [M+H]$^+$: 381.0825; Found: 381.0829.



Benzyl 5-(*tert*-butyl)-1-methyl-2-oxo-1a,2,7,7a-tetrahydro-1*H*-cyclopropa[*b*]naphthalene-1-carboxylate (**3i**): Following the general procedure, pure **3i** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 52.1 mg, 71% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.19 (td, *J* = 8.6, 2.3 Hz, 1H), 4.20 (m, 2H), 2.63 (s, 3H), 2.42 (s, 3H), 2.09 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 200.0, 186.7, 167.4, 166.4 (d, *J* = 254.9 Hz), 160.7, 147.3 (d, *J* = 10.1 Hz), 135.4 (d, *J* = 1.9 Hz), 134.9, 126.8 (d, *J* = 10.0 Hz), 118.0 (d, *J* = 23.5 Hz), 113.0 (d, *J* = 24.1 Hz), 72.3, 62.6, 26.7, 18.8, 18.3, 14.0. HRMS Calcd for $C_{17}H_{17}O_4FS_2$ [M+H]$^+$: 369.0625; Found: 369.0621.

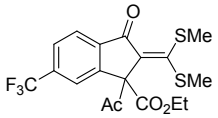


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-6-chloro-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3j**): Following the general procedure, pure **3j** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 56.0 mg, 73% yield, yellow solid, m.p.: 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 1.5 Hz, 1H), 7.46 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.20 (m, 2H), 2.63 (s, 3H), 2.42 (s, 3H), 2.10 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.6, 186.9, 167.4, 161.4, 146.1, 140.6, 137.5, 134.8, 130.5, 126.1, 125.7, 72.2, 62.6, 26.8, 18.8, 18.3, 14.0. HRMS Calcd for $C_{17}H_{17}O_4S_2Cl$ [M+H]$^+$: 385.0330; Found: 385.0339.

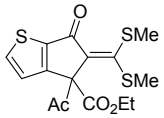


Ethyl 1-acetyl-2-(bis(methylthio)methylene)-6-bromo-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**3k**): Following the general procedure, pure **3k** was obtained by column

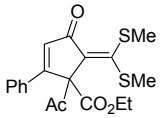
chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 61.2 mg, 71% yield, yellow solid, m.p.: 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.4 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.63 (dd, *J* = 8.1, 1.6 Hz, 1H), 4.26 – 4.15 (m, 2H), 2.64 (s, 3H), 2.43 (s, 3H), 2.11 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, CDCl3) δ 199.7, 187.1, 167.4, 161.5, 146.2, 137.9, 134.7, 133.4, 129.3, 129.1, 125.8, 72.2, 62.6, 26.8, 18.9, 18.4, 14.1. HRMS Calcd for $C_{17}H_{17}O_4S_2Br$ [M+H]$^+$: 428.9824; Found: 428.9823.



Ethyl 1-acetyl-2-(bis(methylthio)methylene)-3-oxo-6-(trifluoromethyl)-2,3-dihydro-1H-indene-1-carboxylate (**3l**): Following the general procedure, pure **3l** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 57.2 mg, 68% yield, yellow solid, m.p.: 106-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 1H), 4.29 – 4.16 (m, 2H), 2.67 (s, 3H), 2.46 (s, 3H), 2.12 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.7, 186.9, 167.2, 163.5, 145.1, 141.6, 135.6 (q, *J* = 32.5 Hz), 134.4, 127.0 (q, *J* = 3.6 Hz), 125.0, 123.5 (q, *J* = 271.6 Hz), 123.3 (q, *J* = 4.0 Hz), 72.6, 62.4, 26.8, 19.1, 18.6, 14.0. HRMS Calcd for $C_{18}H_{17}O_4F_3S_2$ [M+H]$^+$: 419.0593; Found: 419.0596.

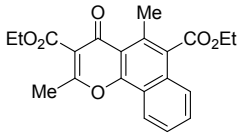


Ethyl 4-acetyl-5-(bis(methylthio)methylene)-6-oxo-5,6-dihydro-4H-cyclopenta[b]thiophene-4-carboxylate (**3m**): Following the general procedure, pure **3m** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 41.2 mg, 58% yield, yellow solid, m.p.: 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 4.8 Hz, 1H), 7.17 (d, *J* = 4.8 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.60 (s, 3H), 2.39 (s, 3H), 2.11 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.3, 181.1, 167.1, 158.4, 155.5, 145.1, 138.5, 137.7, 123.4, 71.3, 62.4, 26.4, 18.7, 18.1, 14.1. HRMS Calcd for $C_{15}H_{16}O_4S_3$ [M+H]$^+$: 357.0283; Found: 357.0281.

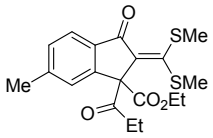


Ethyl 1-acetyl-5-(bis(methylthio)methylene)-4-oxo-2-phenylcyclopent-2-enecarboxylate

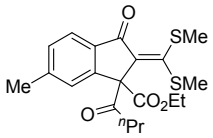
(**3n**): Following the general procedure, pure **3n** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 31.2 mg, 41% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H), 7.45 – 7.34 (m, 3H), 6.91 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 2.41 (s, 3H), 2.17 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.4, 190.7, 167.1, 162.7, 155.7, 135.4, 134.6, 131.9, 131.1, 128.9, 128.3, 74.0, 62.0, 27.0, 18.5, 18.2, 13.9. HRMS Calcd for $C_{19}H_{20}O_4S_2$ [M+H]$^{+}$: 377.0876; Found: 377.0880.



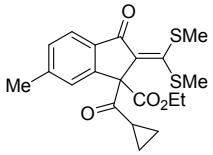
Diethyl 2,5-dimethyl-4-oxo-4H-benzo[h]chromene-3,6-dicarboxylate (**3p'**): Following the general procedure, pure **3p'** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 32.6 mg, 44% yield, red solid, m.p.: 150-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.61 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.88 (s, 3H), 2.58 (s, 3H), 1.43 (m, 6H).. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 169.3, 165.1, 163.7, 154.7, 132.8, 131.7, 130.9, 130.2, 126.9, 124.6, 122.5, 122.4, 121.0, 118.2, 62.0, 61.9, 19.7, 18.9, 14.4, 14.3. HRMS Calcd for $C_{21}H_{20}O_6$ [M+H]$^{+}$: 369.1333; Found: 369.1341.



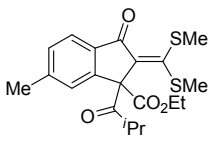
Ethyl 2-(bis(methylthio)methylene)-6-methyl-3-oxo-1-propionyl-2,3-dihydro-1H-indene-1-carboxylate (**4a**): Following the general procedure, pure **4a** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 63.3 mg, 83% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 4.25 – 4.09 (m, 2H), 2.60 (s, 3H), 2.53 – 2.35 (m, 7H), 2.23 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 203.3, 188.2 167.9, 159.0, 145.7, 145.5, 136.8, 135.9, 130.9, 125.9, 124.3, 72.1, 62.2, 31.8, 22.3, 18.7, 18.2, 14.0, 8.5. HRMS Calcd for $C_{19}H_{22}O_4S_2$ [M+H]$^{+}$: 379.1032; Found: 379.1028.



Ethyl 2-(bis(methylthio)methylene)-1-butyryl-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**4b**): Following the general procedure, pure **4b** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 56.2 mg, 72% yield, yellow solid, m.p.: 88-89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 4.25 – 4.07 (m, 2H), 2.60 (s, 3H), 2.48 – 2.30 (m, 7H), 2.15 (m, 1H), 1.55 – 1.36 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.3, 188.2, 167.8, 159.2, 145.7, 145.4, 136.8, 135.7, 130.9, 126.0, 124.3, 72.1, 62.1, 40.2, 22.3, 18.7, 18.2, 17.6, 14.0, 13.5. HRMS Calcd for $C_{20}H_{24}O_4S_2$ $[M+H]^+$: 393.1189; Found: 393.1191.

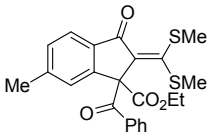


Ethyl 2-(bis(methylthio)methylene)-1-(cyclopropanecarbonyl)-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**4c**): Following the general procedure, pure **4c** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 57.2 mg, 73% yield, yellow solid, m.p.: 138-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.30 – 7.24 (m, 1H), 4.22 – 4.08 (m, 2H), 2.60 (s, 3H), 2.39 (m, 6H), 1.71 – 1.59 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.07 – 0.91 (m, 2H), 0.79 (m, 1H), 0.69 – 0.57 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 202.4, 188.4, 167.5, 159.9, 145.6, 145.4, 136.9, 135.3, 130.9, 126.5, 124.1, 72.3, 62.1, 22.3, 19.0, 18.1, 17.9, 14.0, 12.9, 12.4. HRMS Calcd for $C_{20}H_{22}O_4S_2$ $[M+H]^+$: 391.1032; Found: 391.1034.

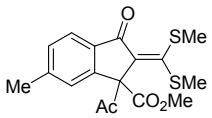


Ethyl 2-(bis(methylthio)methylene)-1-isobutyryl-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**4d**): Following the general procedure, pure **4d** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 55.0 mg, 70% yield, yellow solid, m.p.: 84-85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ. 7.75 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 4.24 – 4.12 (m, 2H), 2.67 (m, 1H), 2.61 (s, 3H), 2.42 (d, 6H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR

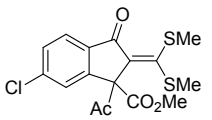
(100 MHz, $CDCl_3$) δ 206.1, 188.2, 167.9, 160.2, 145.5, 145.0, 137.2, 134.6, 131.0, 126.2, 124.5, 72.1, 62.1, 37.0, 22.3, 21.8, 20.9, 18.9, 18.4, 14.1. HRMS Calcd for $C_{20}H_{24}O_4S_2$ $[M+H]^+$: 393.1189; Found: 393.1192.



Ethyl 1-benzoyl-2-(bis(methylthio)methylene)-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**4e**): Following the general procedure, pure **4e** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 56.2 mg, 66% yield, yellow solid, m.p.: 114-115 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.28 (m, 5H), 7.18 (t, *J* = 7.7 Hz, 2H), 4.26 – 4.13 (m, 2H), 2.46 (s, 3H), 2.36 (s, 3H), 1.65 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.5, 188.5, 167.6, 159.7, 146.0, 145.8, 136.8, 135.7, 135.1, 132.6, 130.9, 128.7, 128.2, 127.4, 124.4, 72.1, 62.7, 22.3, 18.3, 17.8, 14.0. HRMS Calcd for $C_{23}H_{22}O_4S_2$ $[M+H]^+$: 427.1032; Found: 427.1028.

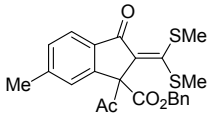


Methyl 1-acetyl-2-(bis(methylthio)methylene)-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**4f**): Following the general procedure, pure **4f** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 57.4 mg, 82% yield, yellow solid, m.p.: 110-111 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 3.69 (s, 3H), 2.60 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H), 2.03 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.0, 188.0, 168.4, 159.1, 145.9, 145.0, 136.8, 135.7, 131.1, 125.8, 124.4, 72.0, 53.1, 26.5, 22.3, 18.6, 18.0. HRMS Calcd for $C_{17}H_{18}O_4S_2$ $[M+H]^+$: 351.0719; Found: 351.0722.

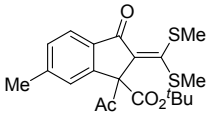


Methyl 1-acetyl-2-(bis(methylthio)methylene)-6-chloro-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**4g**): Following the general procedure, pure **4g** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 55.3 mg, 74% yield, yellow solid, m.p.: 106-107 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz,

1H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.47 (dd, *J* = 8.2, 1.8 Hz, 1H), 3.74 (s, 3H), 2.64 (s, 3H), 2.42 (s, 3H), 2.09 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 199.5, 186.8, 167.9, 161.5, 145.9, 140.7, 137.5, 134.6, 130.7, 126.1, 125.7, 72.1, 53.4, 26.7, 18.9, 18.3. HRMS Calcd for $C_{16}H_{15}O_4S_2Cl$ $[M+H]^+$: 371.0173; Found: 371.0174.



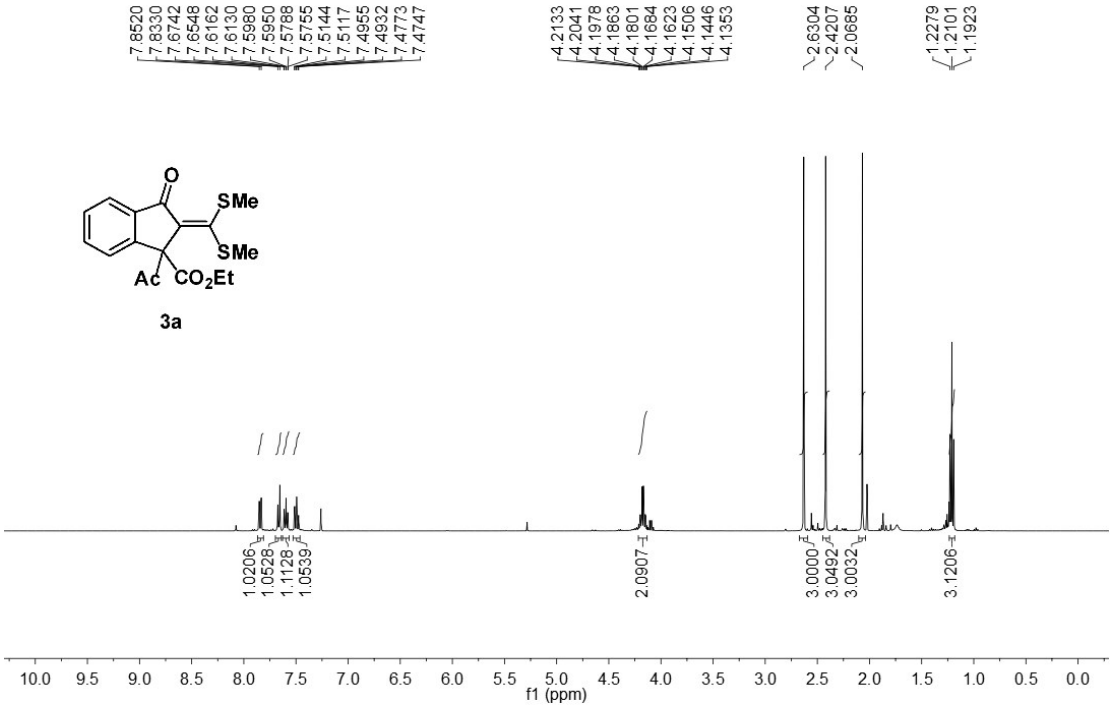
Benzyl 1-acetyl-2-(bis(methylthio)methylene)-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate (**4h**): Following the general procedure, pure **4h** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 62.1 mg, 73% yield, yellow solid, m.p.: 80-81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.39 (s, 1H), 7.27 (m, 4H), 7.21 (m, 2H), 5.18 (d, *J* = 12.4 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 2.55 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H), 2.05 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 200.0, 187.9, 167.6, 159.3, 145.8, 144.9, 136.8, 135.5, 135.2, 131.0, 128.4, 128.3, 128.1, 125.9, 124.4, 72.1, 67.7, 26.6, 22.2, 18.5, 18.1. HRMS Calcd for $C_{23}H_{22}O_4S_2$ $[M+H]^+$: 427.1032; Found: 427.1033.



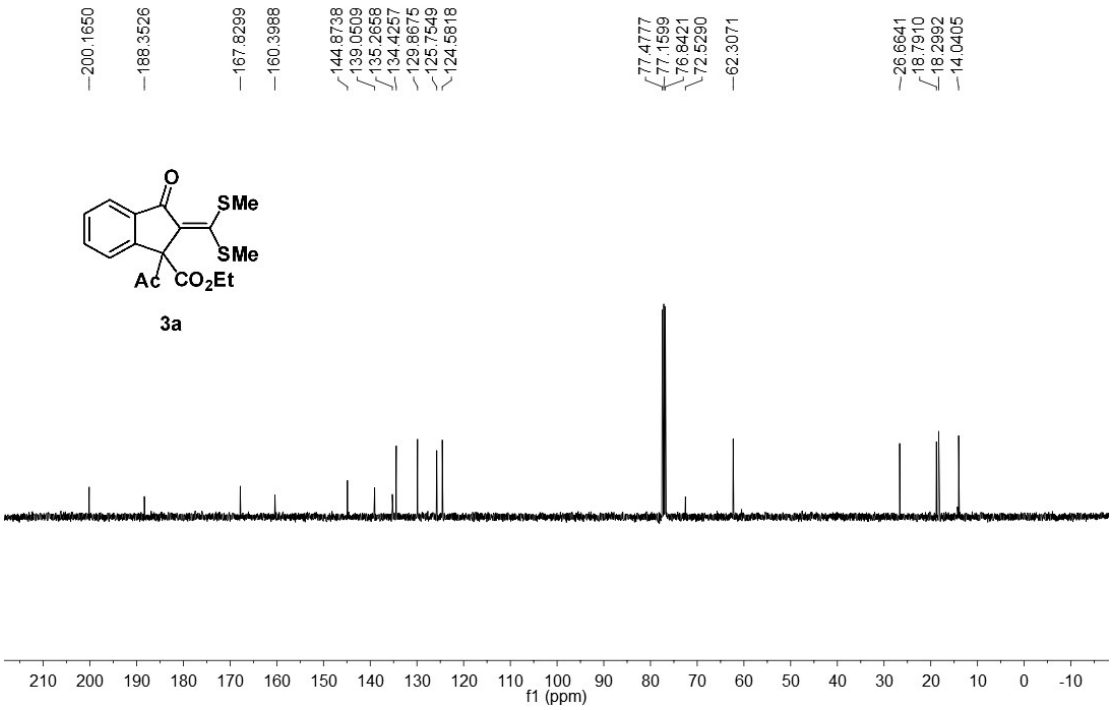
***tert*-Butyl 1-acetyl-2-(bis(methylthio)methylene)-6-methyl-3-oxo-2,3-dihydro-1H-indene-1-carboxylate** (**4i**): Following the general procedure, pure **4i** was obtained by column chromatography on silica gel (eluent: petroleum ether (60−90 °C)/EtOAc = 20:1, v/v). 36.3 mg, 46% yield, yellow solid, m.p.: 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 2.62 (s, 3H), 2.43 (s, 3H), 2.41 (s, 3H), 2.06 (s, 3H), 1.42 (s, 9H).. $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl3) δ 200.7, 188.4, 166.6, 158.6, 145.8, 145.6, 136.8, 136.5, 130.8, 126.0, 124.4, 83.0, 73.1, 27.9, 26.9, 22.4, 18.6, 18.2. HRMS Calcd for $C_{20}H_{24}O_4S_2$ $[M+H]^+$: 393.1189; Found: 393.1188.

5. Copies of NMR spectra

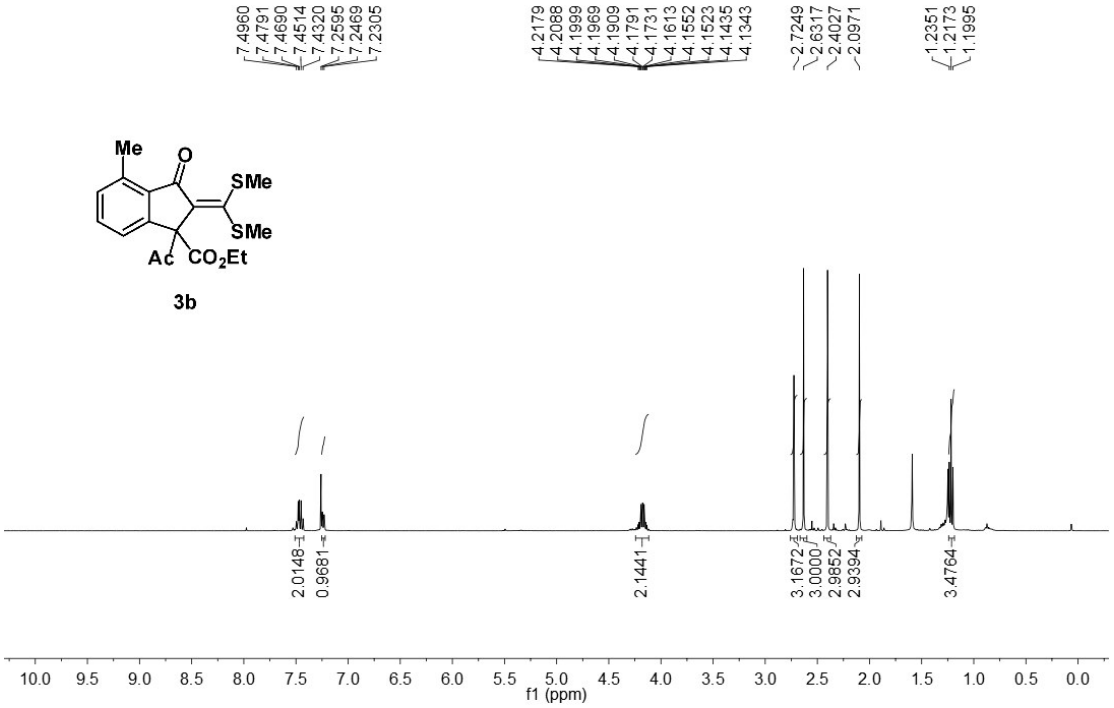
I045
I045 1H NMR in CDCl3



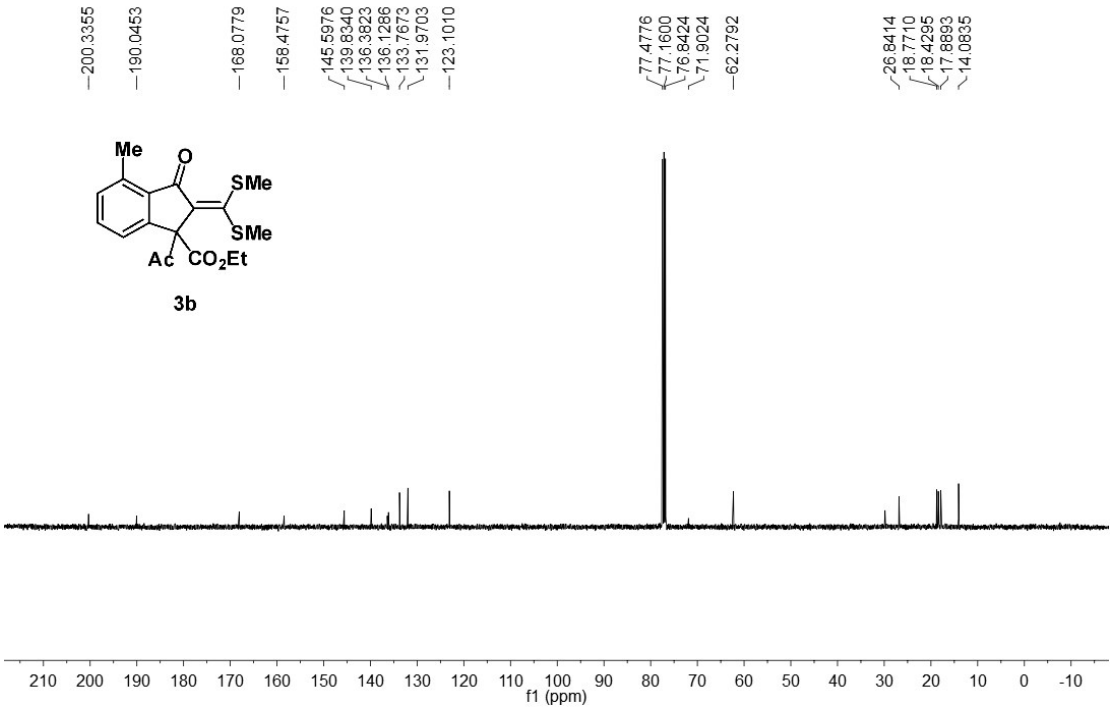
I045
I045 13C NMR in CDCl3



IO43
IO43 1H NMR in CDCl3



IO43
IO43 13C NMR in CDCl3



IO44
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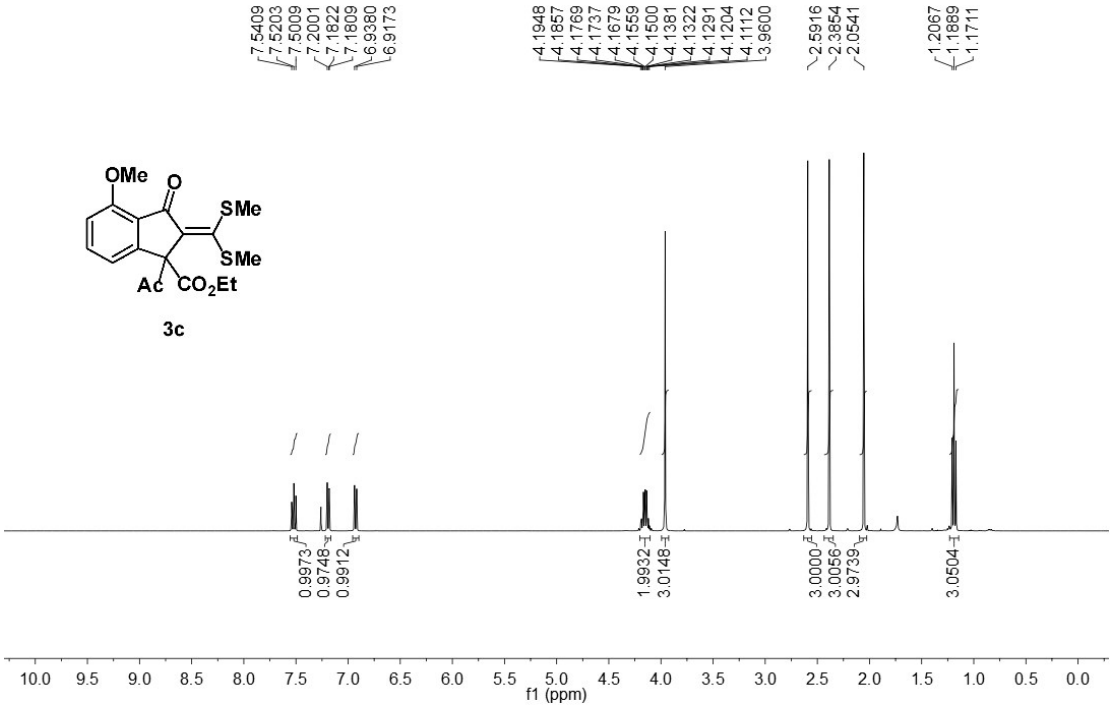
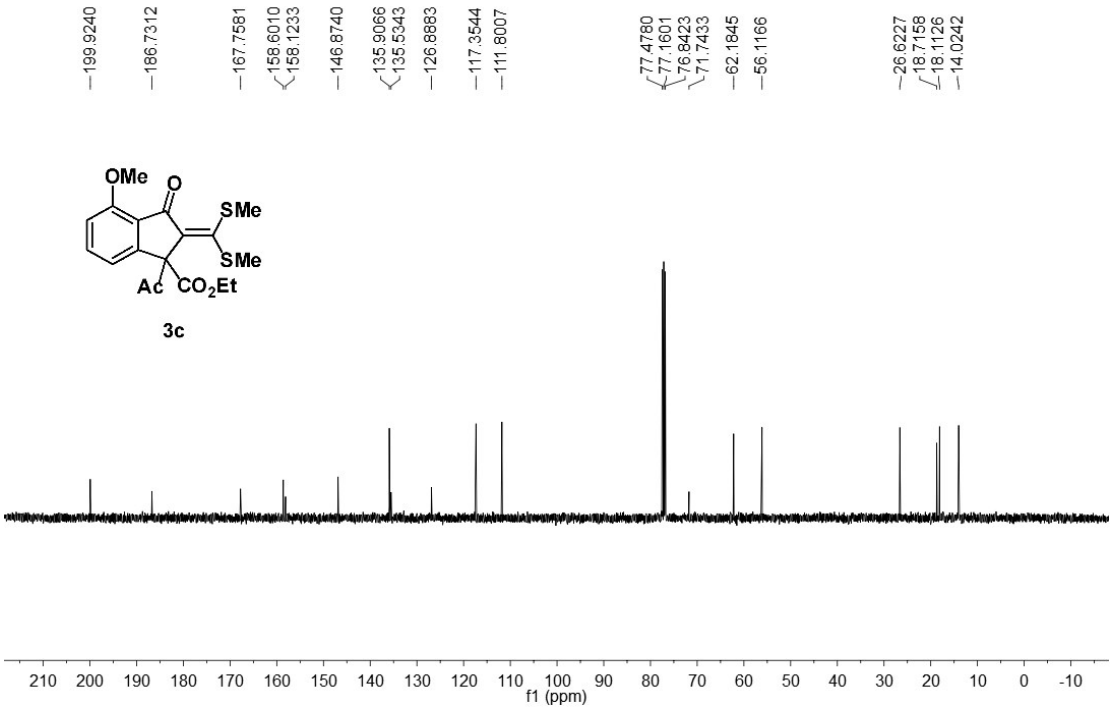
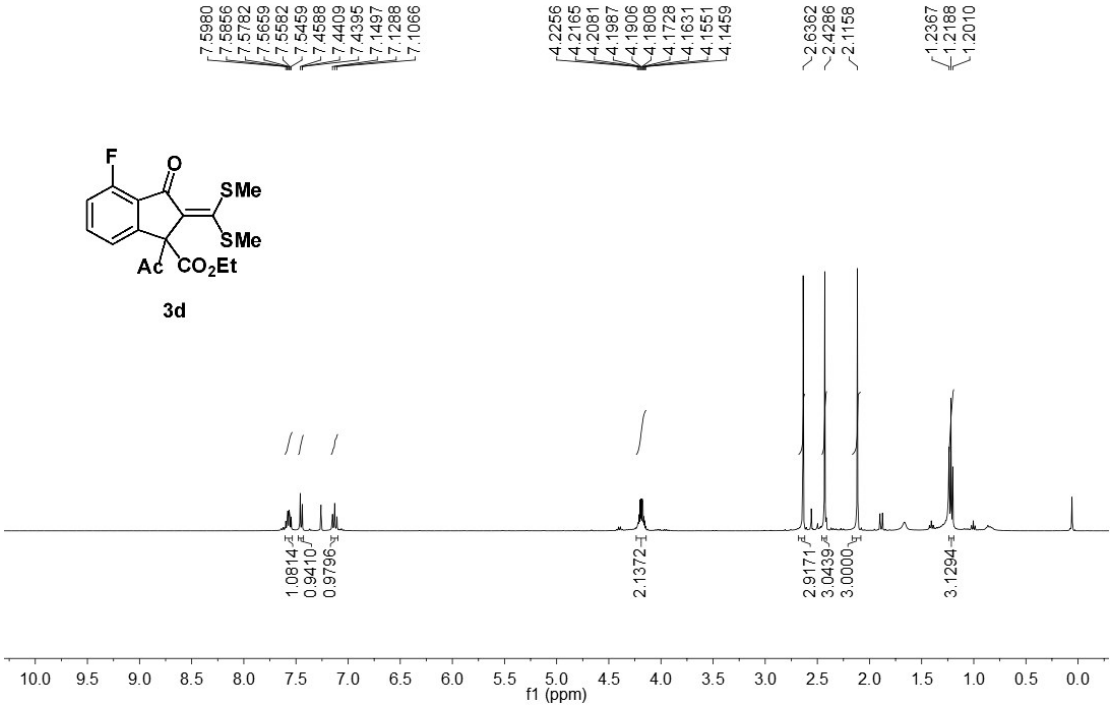


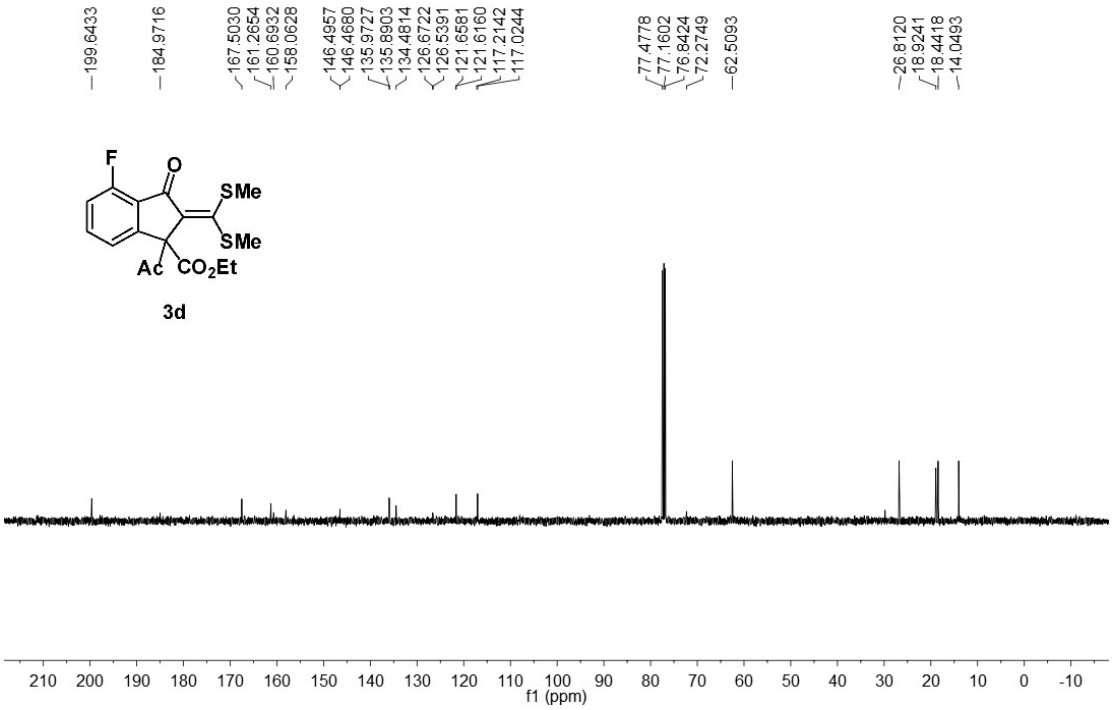
IO44
IO44 13C NMR in CDCl3



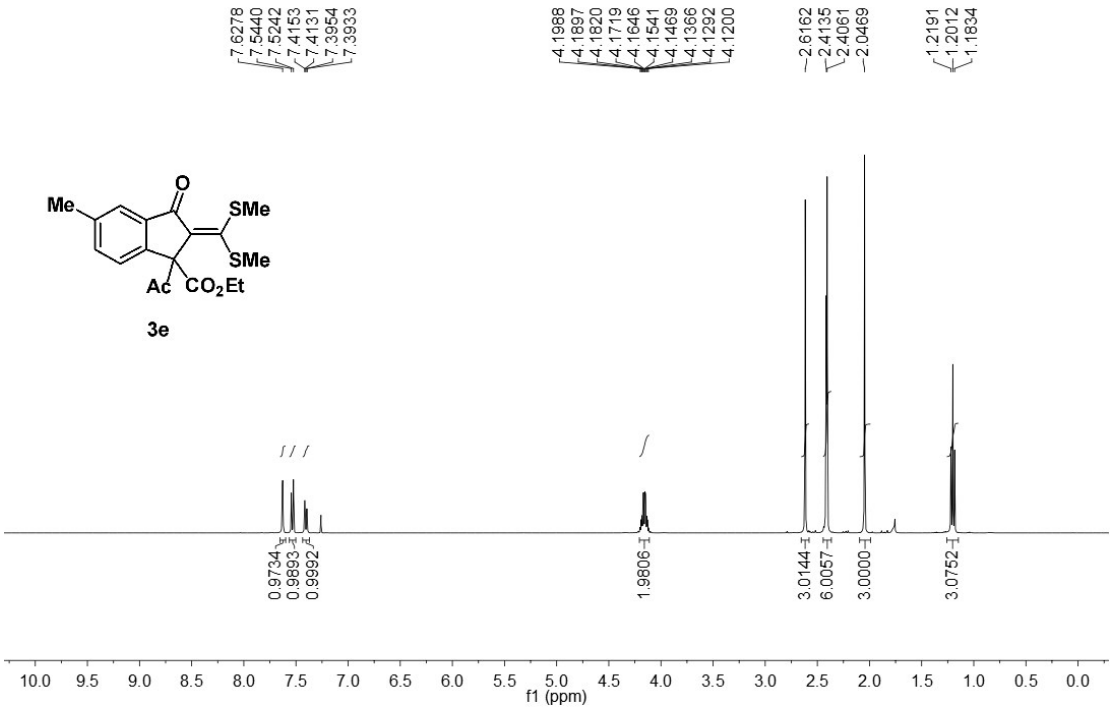
2020630-1-F
1H NMR 2020630-1-F in CDCl3



2020630-1-F
13C NMR 2020630-1-F in CDCl3



I049
I049 1H NMR in CDCl3



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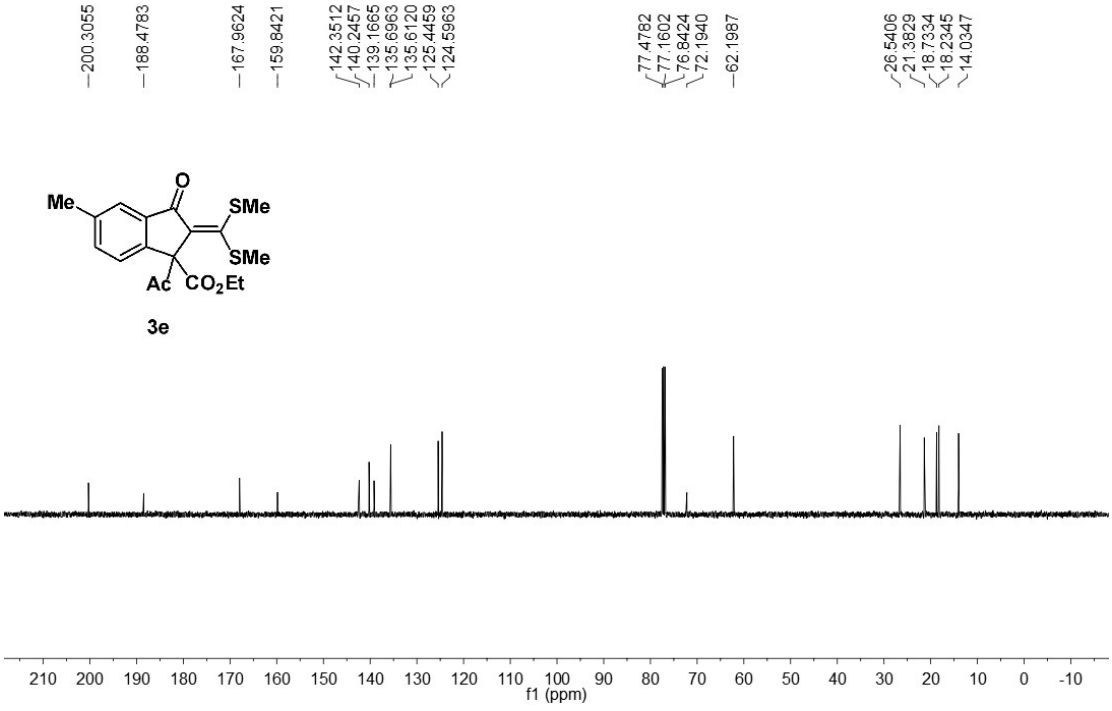
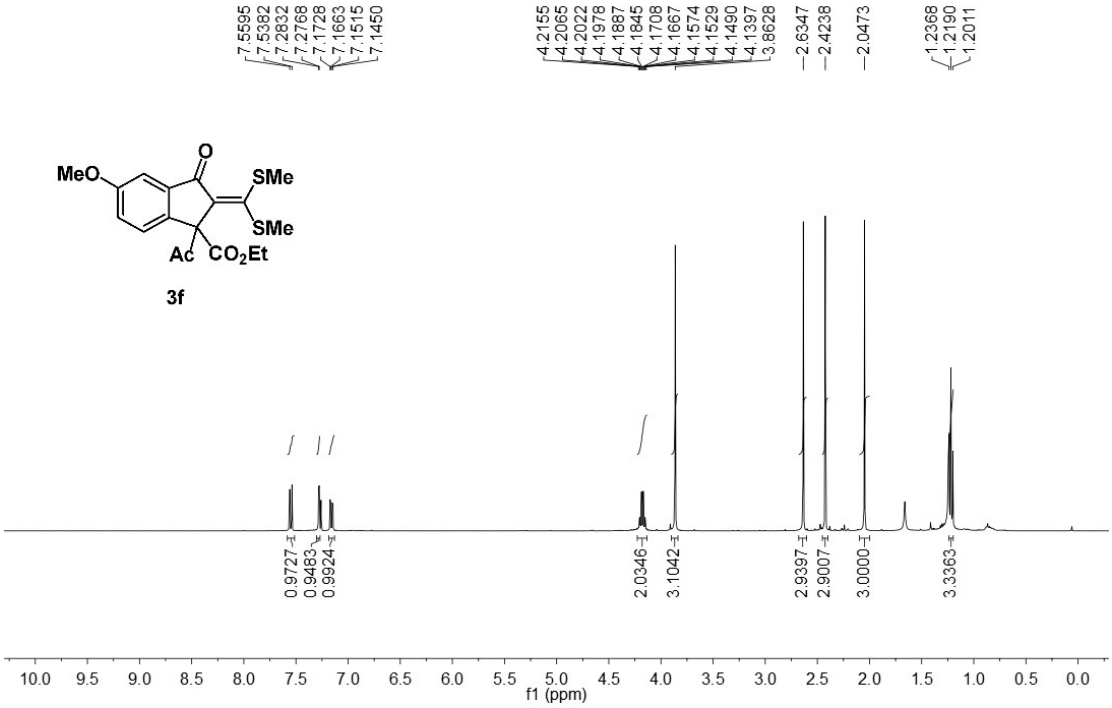
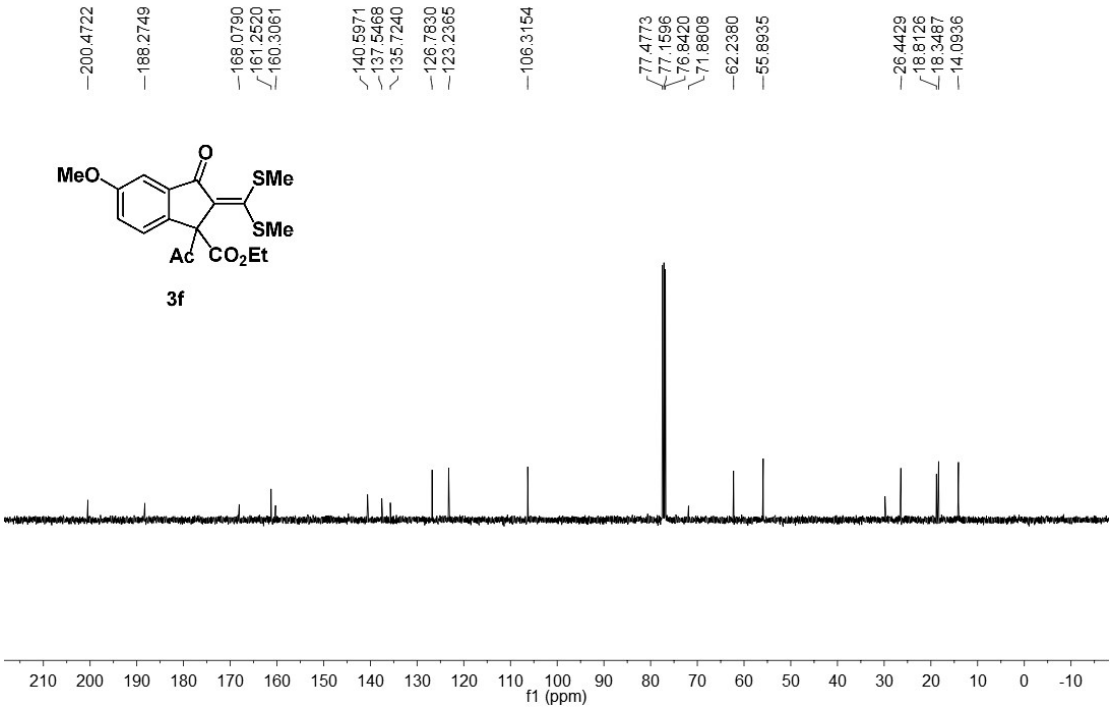


I050P1
I050P1 1H NMR in CDCl3



I050P1
I050P1 13C NMR in CDCl3



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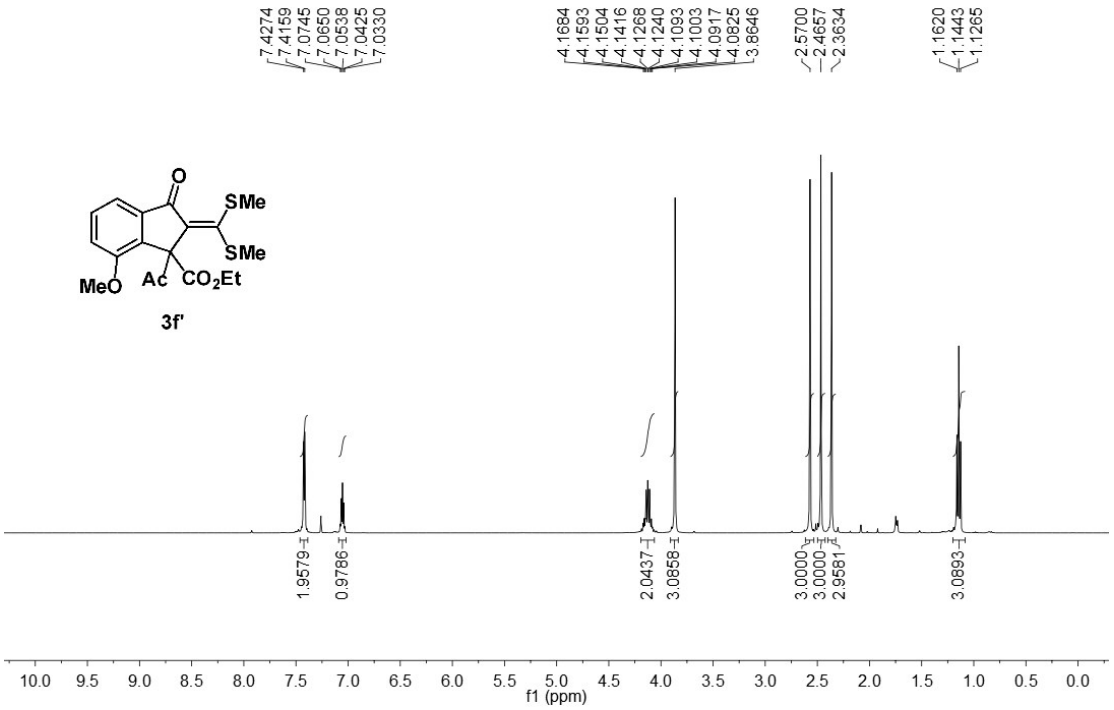
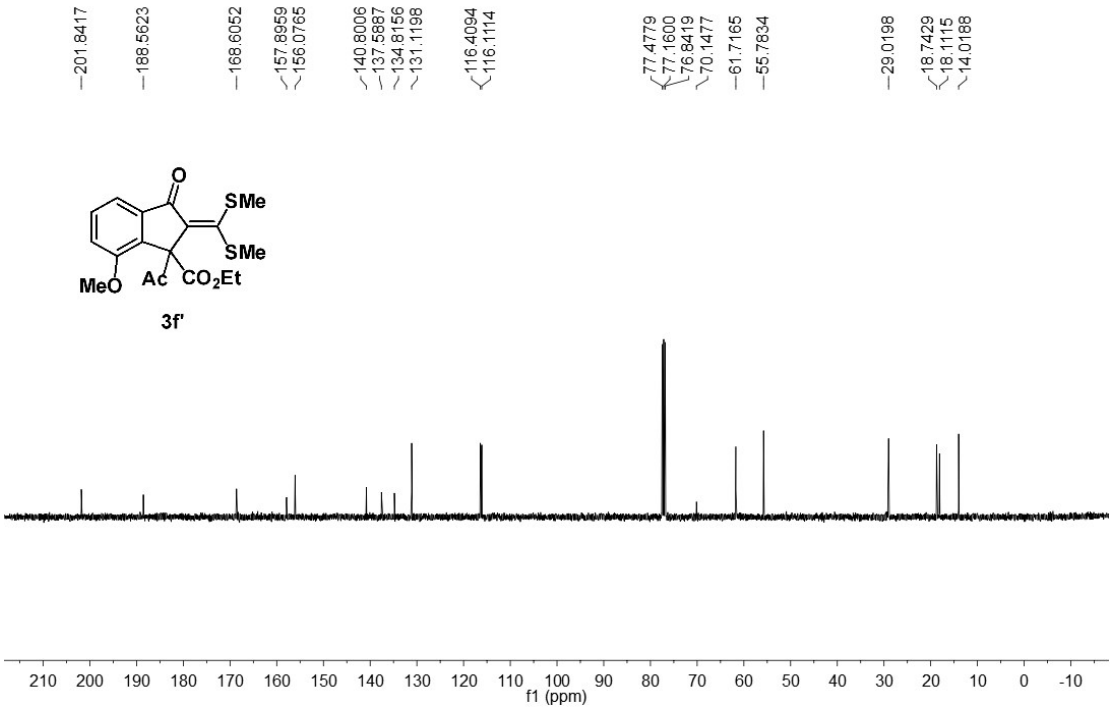
I050 P2 1H NMR in CDCl3



I050P2
I050 P2 13C NMR in CDCl3



0725_NMR
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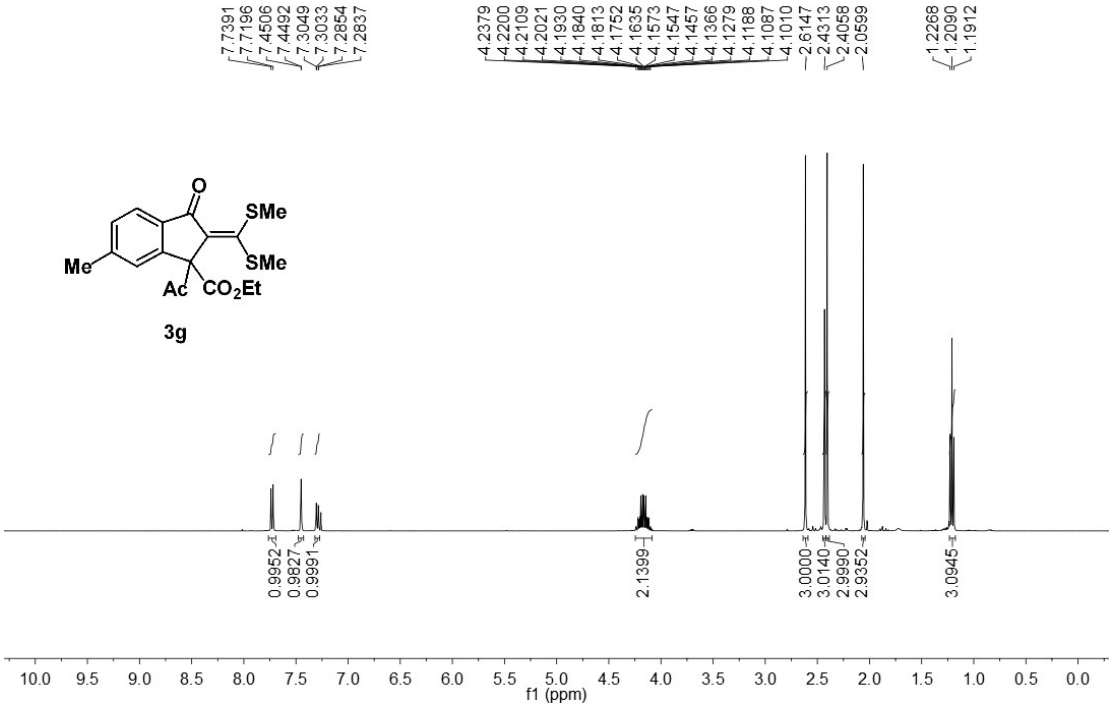

0725_NMR
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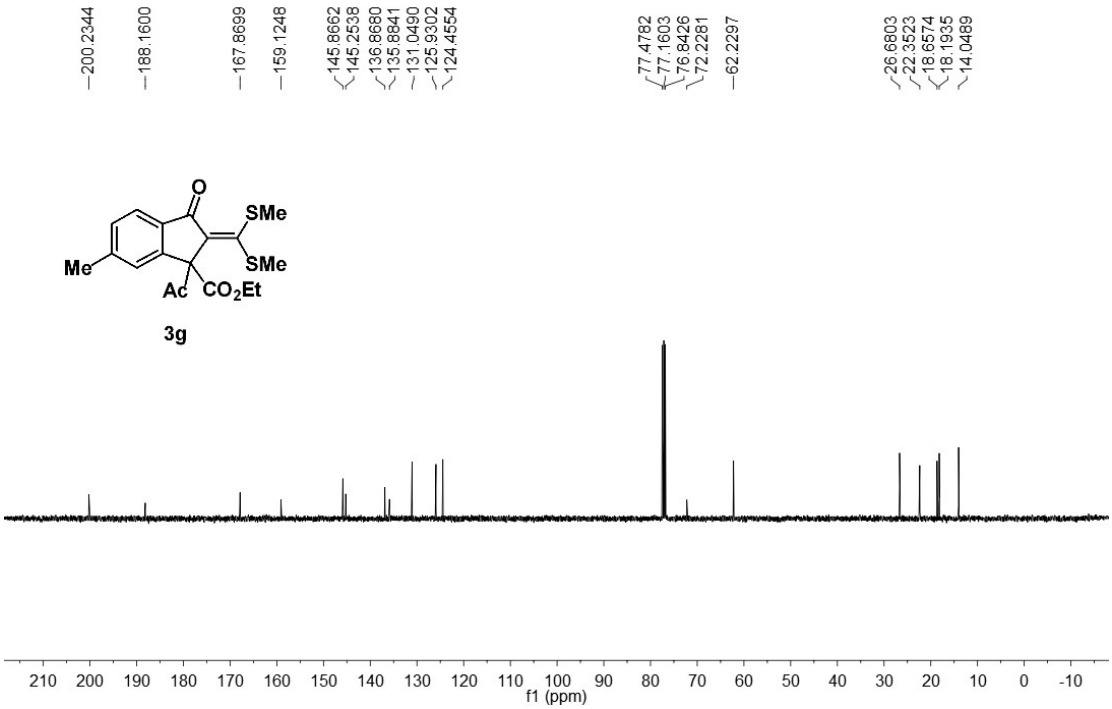
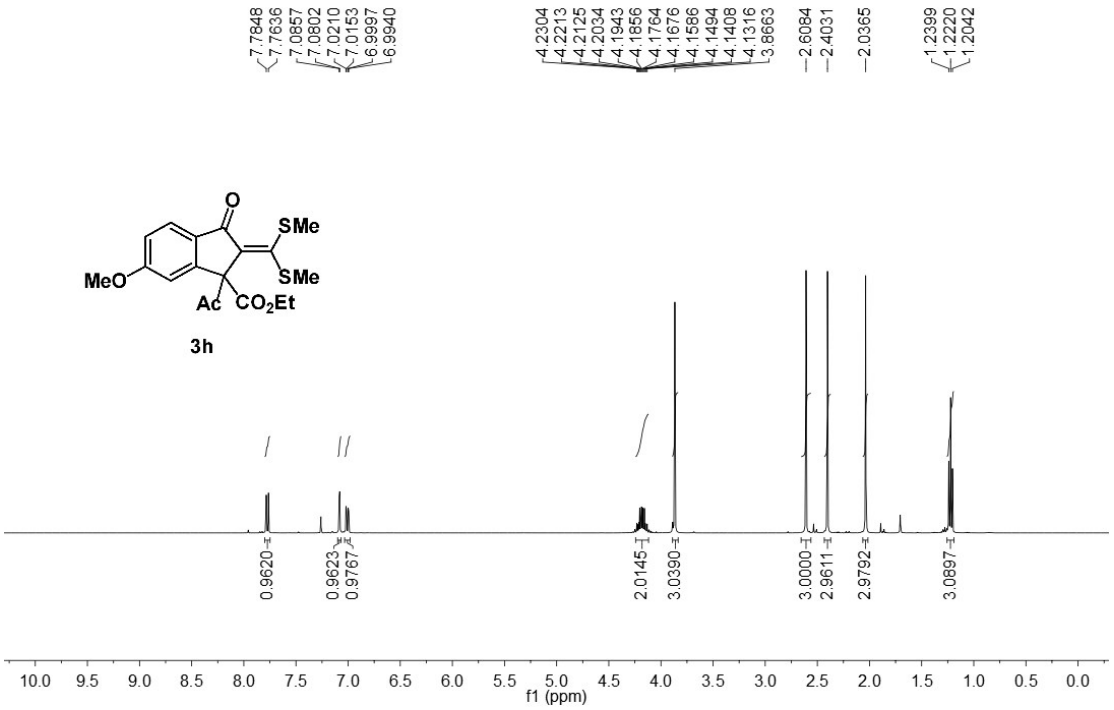
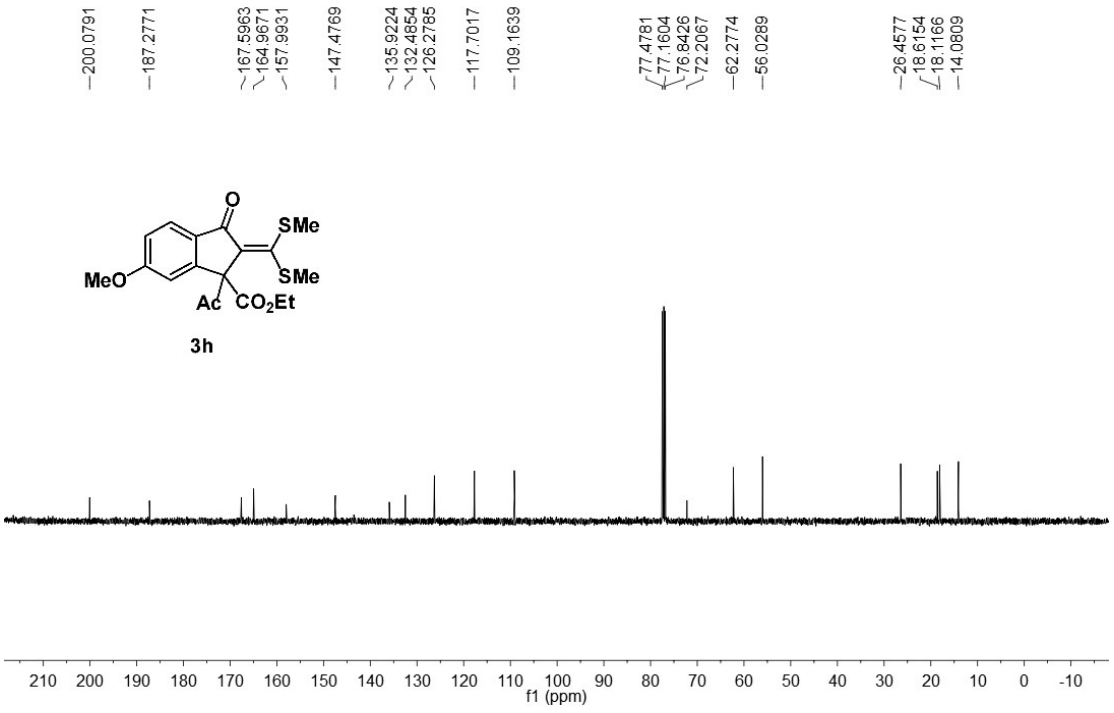


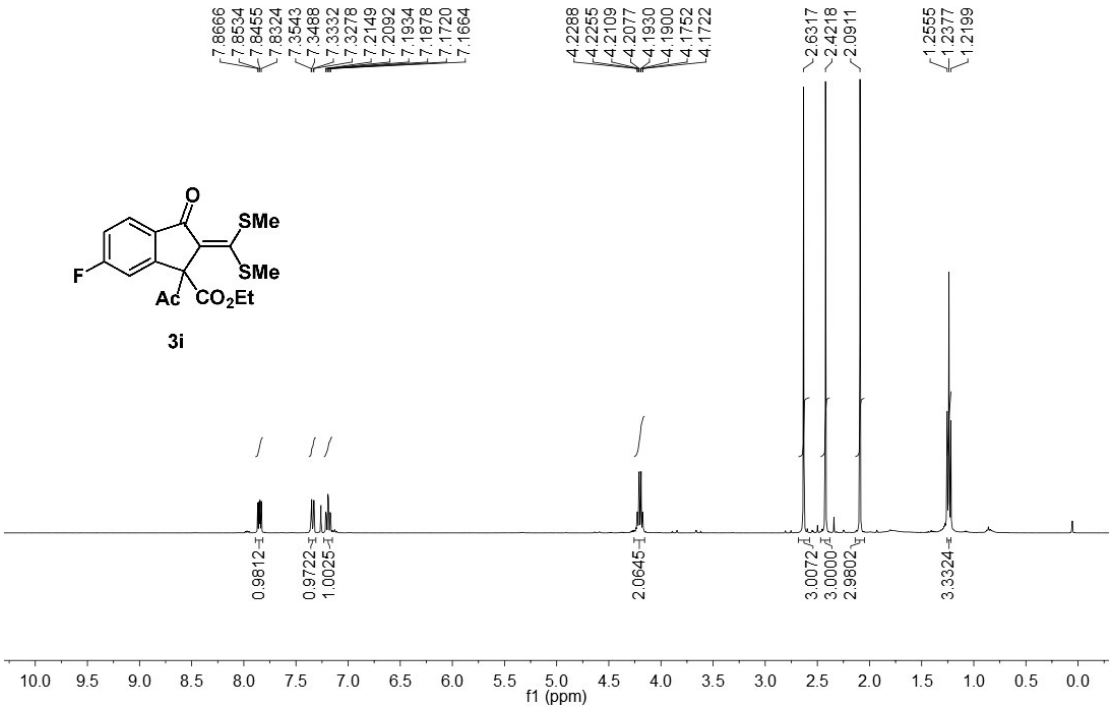
I023
I023 1H NMR in CDCl3



I023
I023 13C NMR in CDCl3

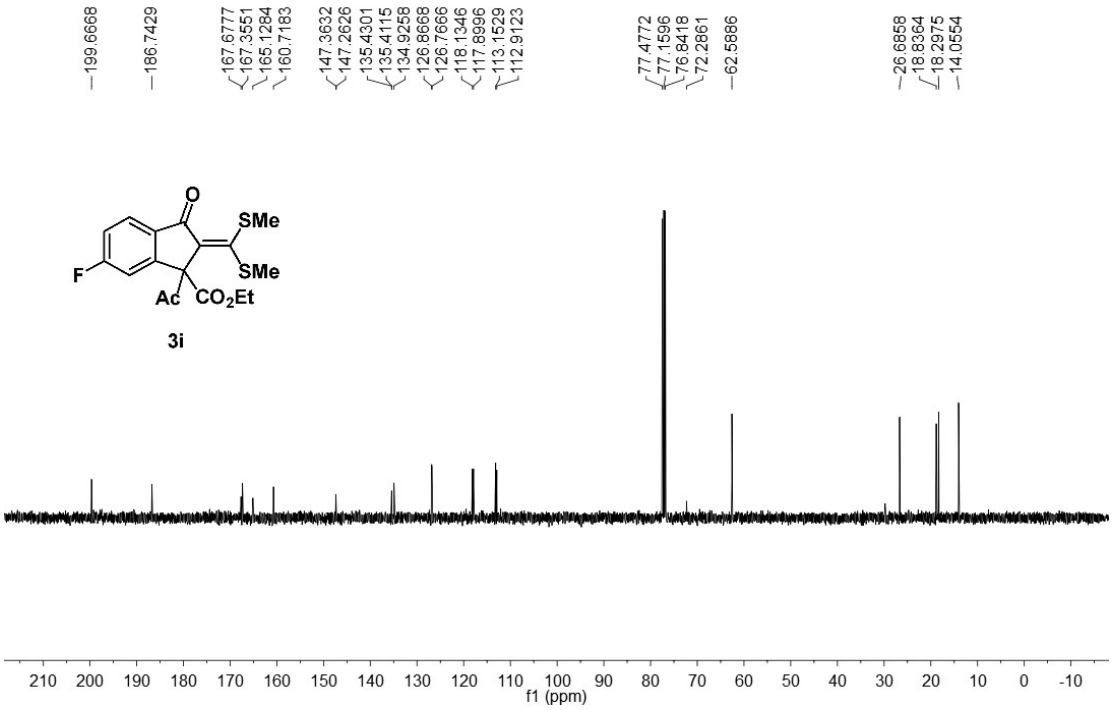


I047
I047 1H NMR in CDCl3



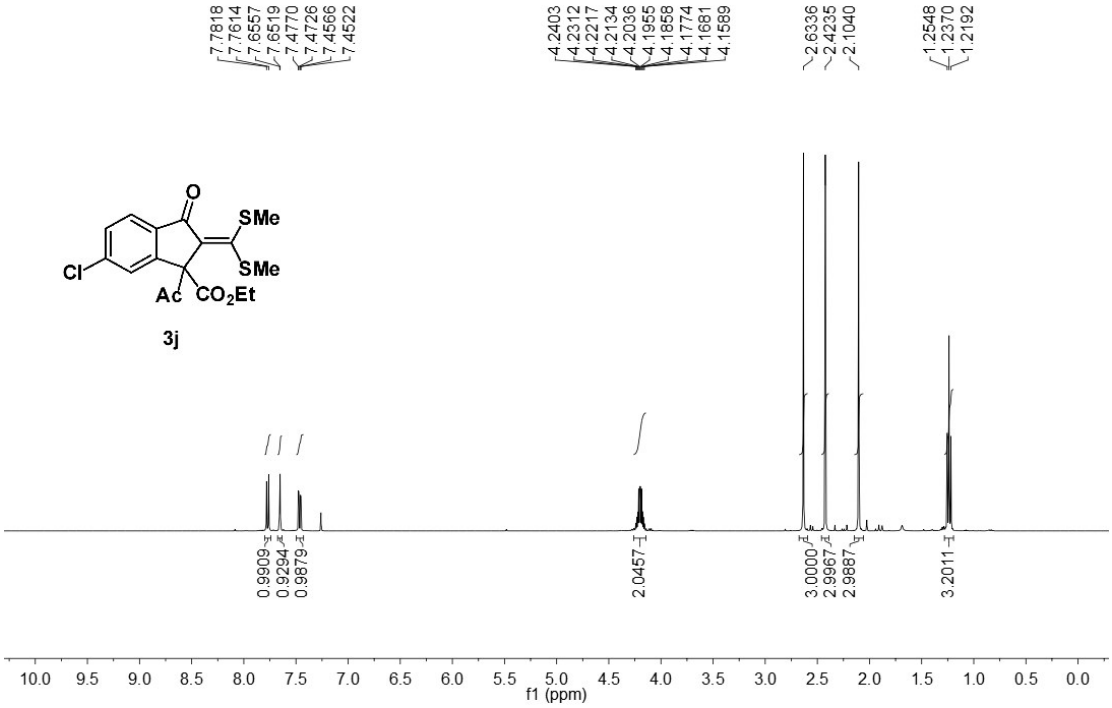
3i

I047
I047 13C NMR in CDCl3

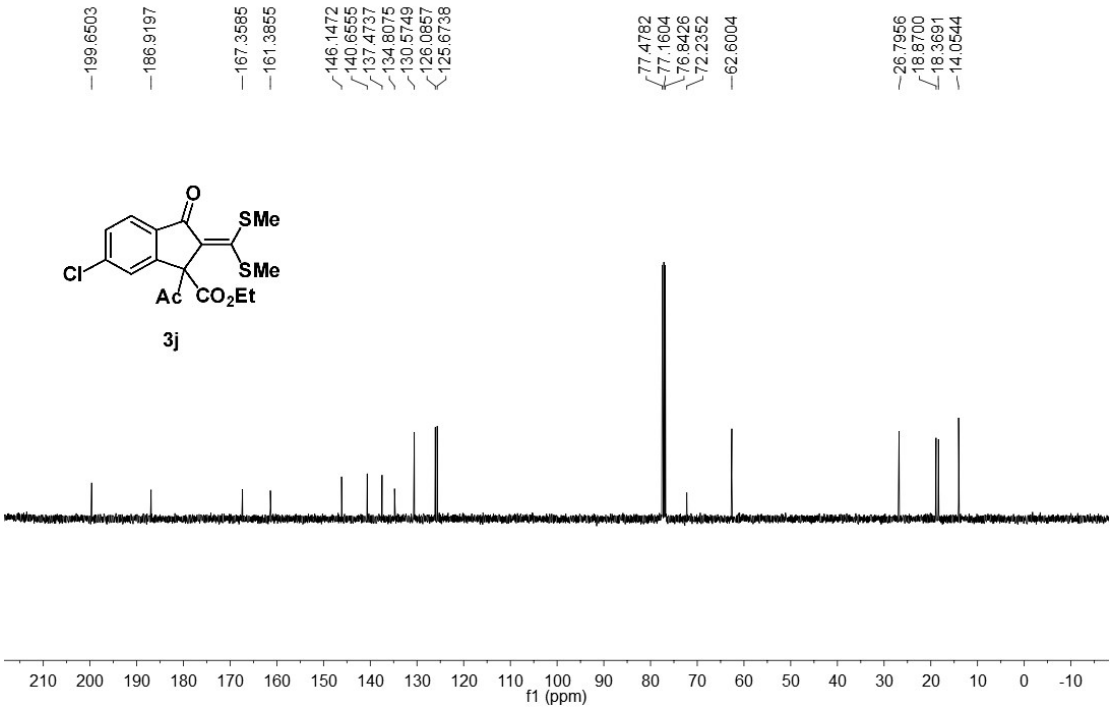


3i

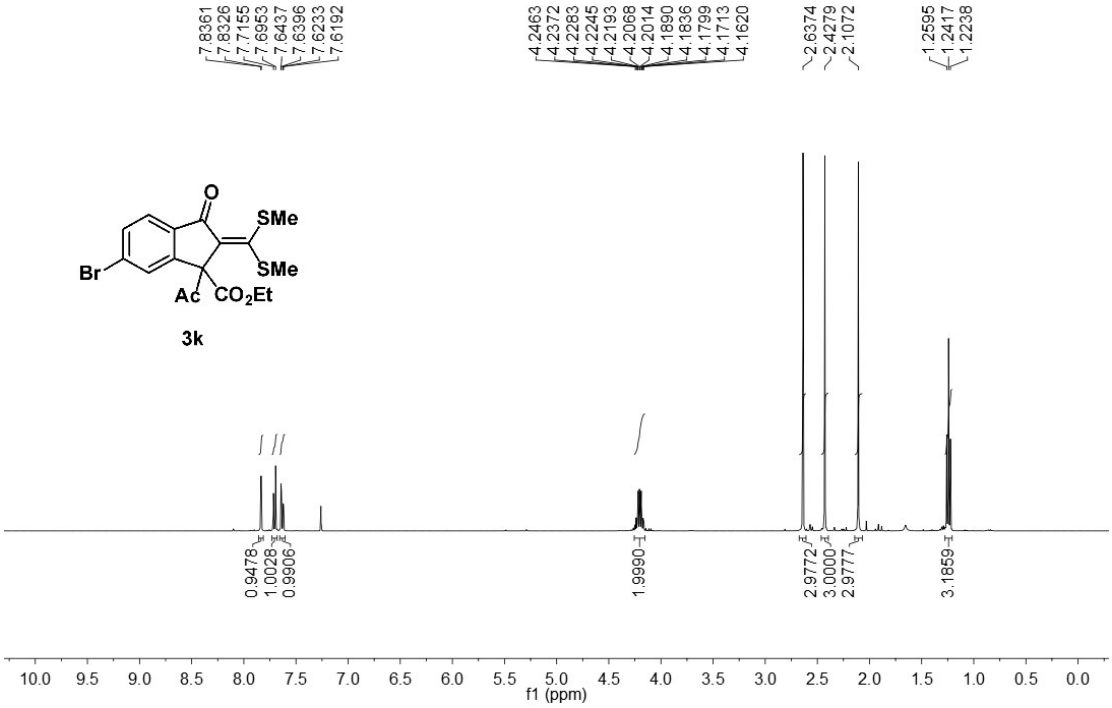
I041
I041 1H NMR in CDCl3



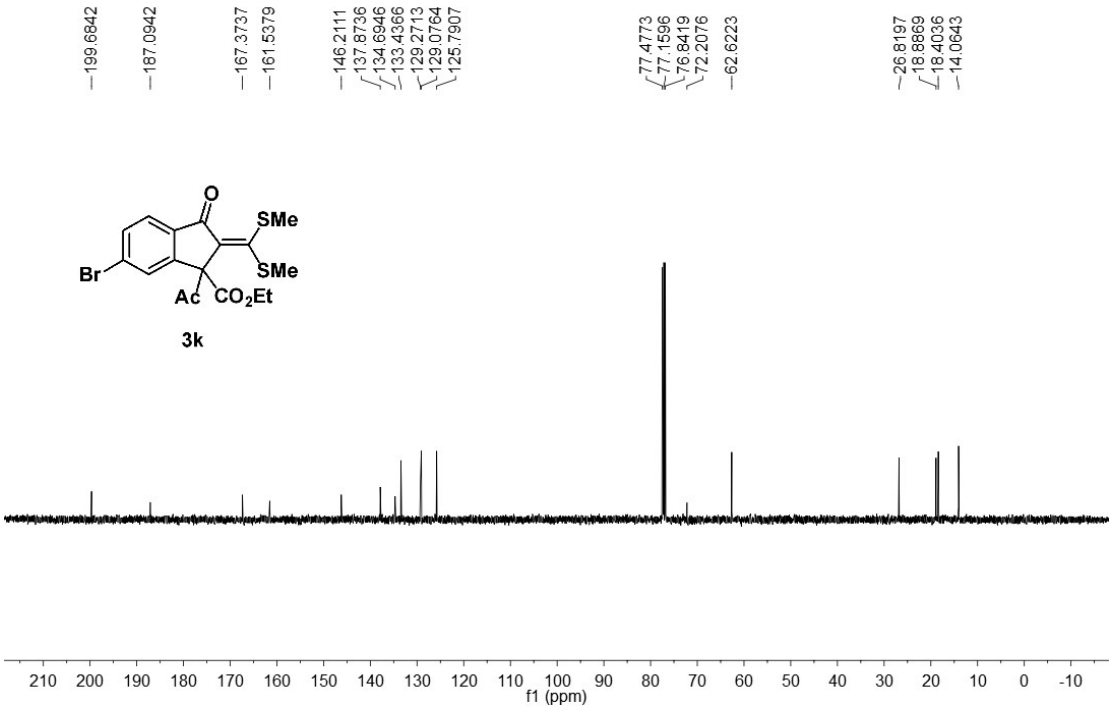
I041
I041 13C NMR in CDCl3



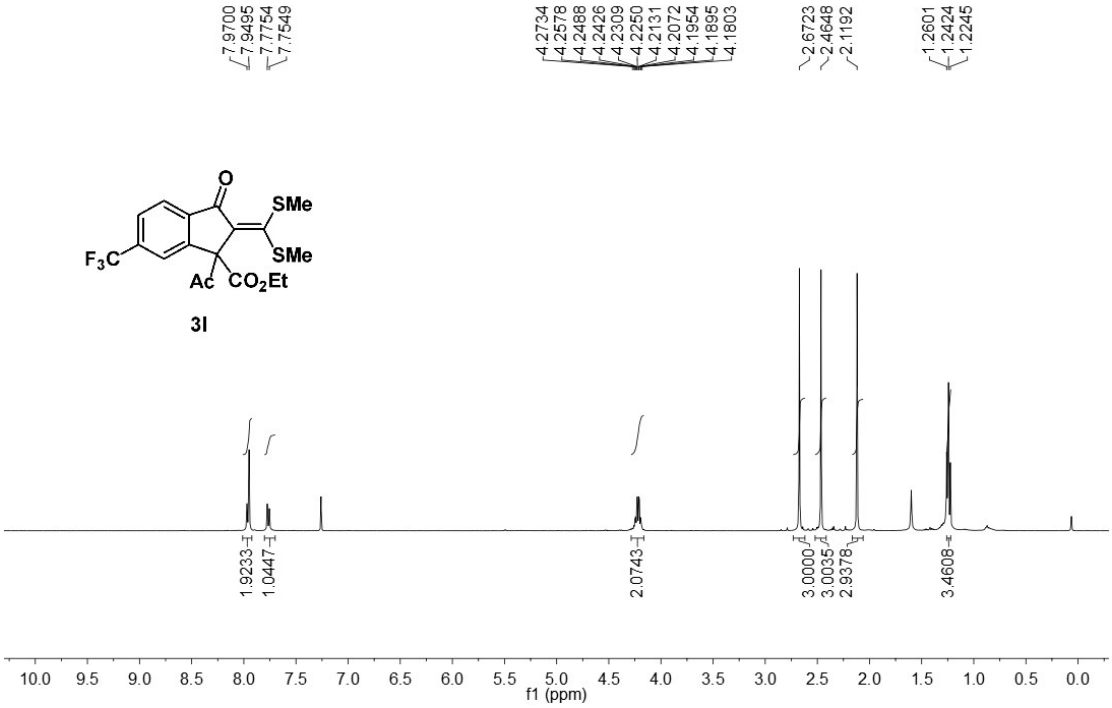
I039
I039 1H NMR in CDCl3



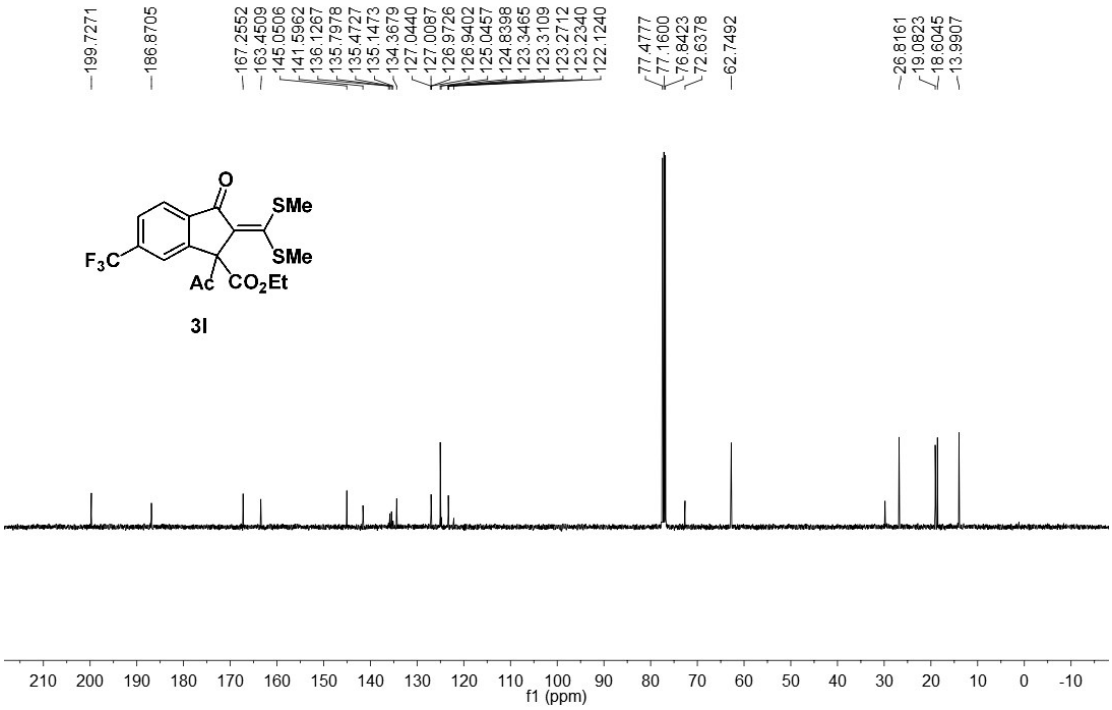
I039
I039 13C NMR in CDCl3



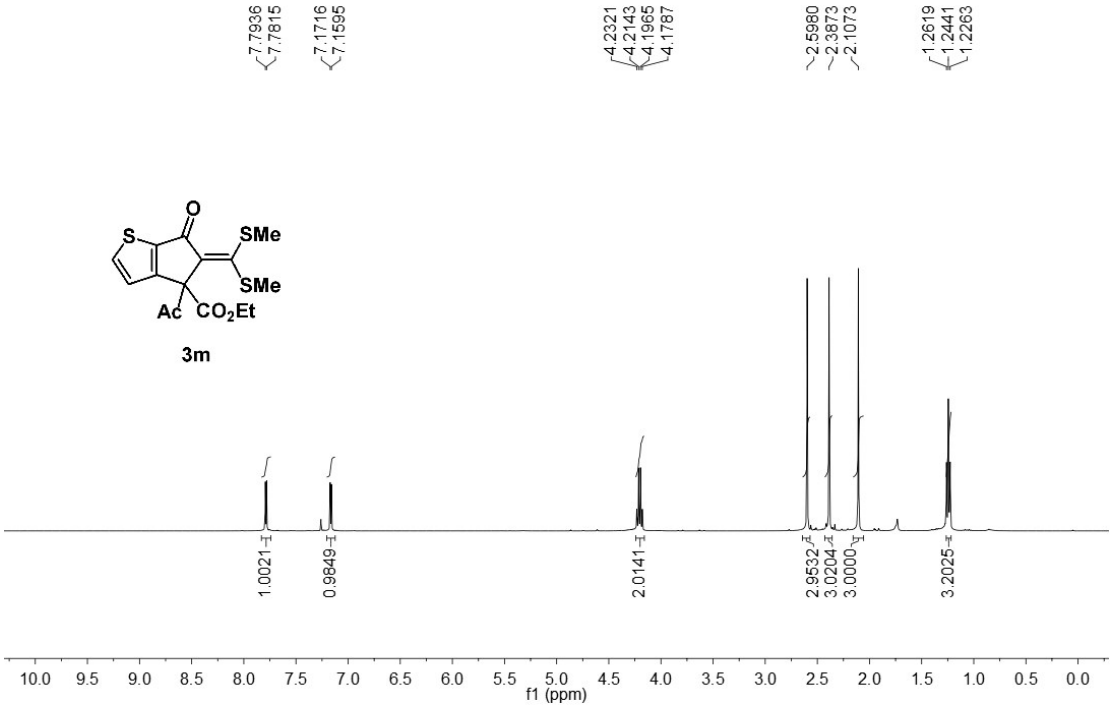
I048
I048 1H NMR in CDCl3



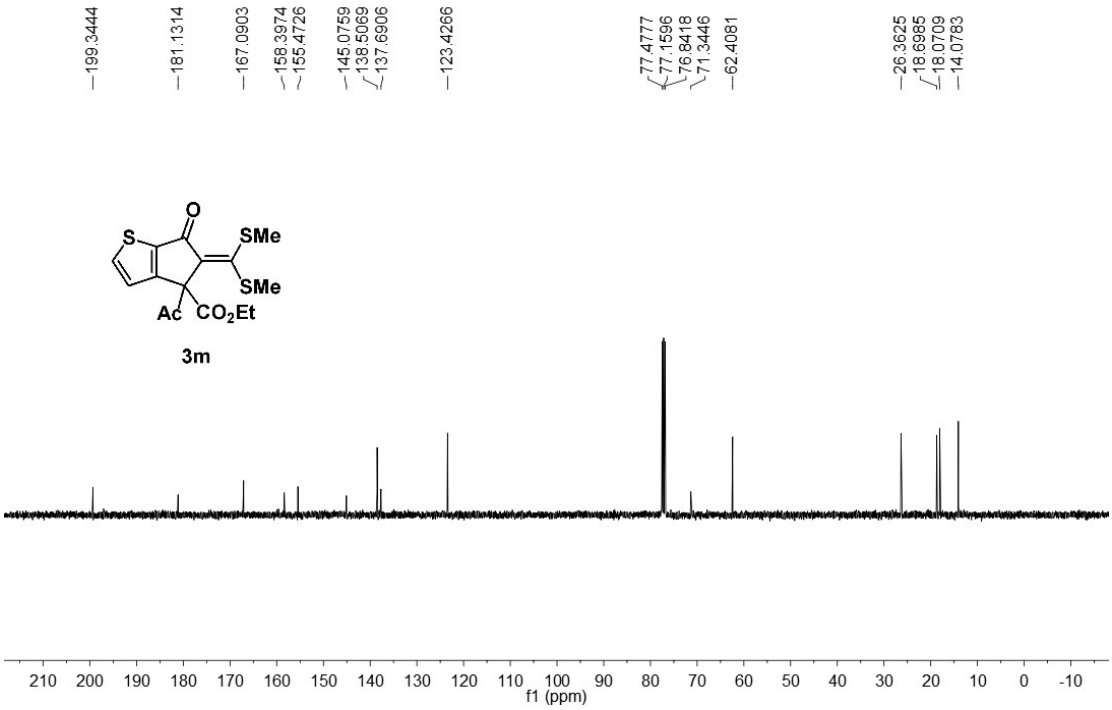
I048
I048 13C NMR in CDCl3



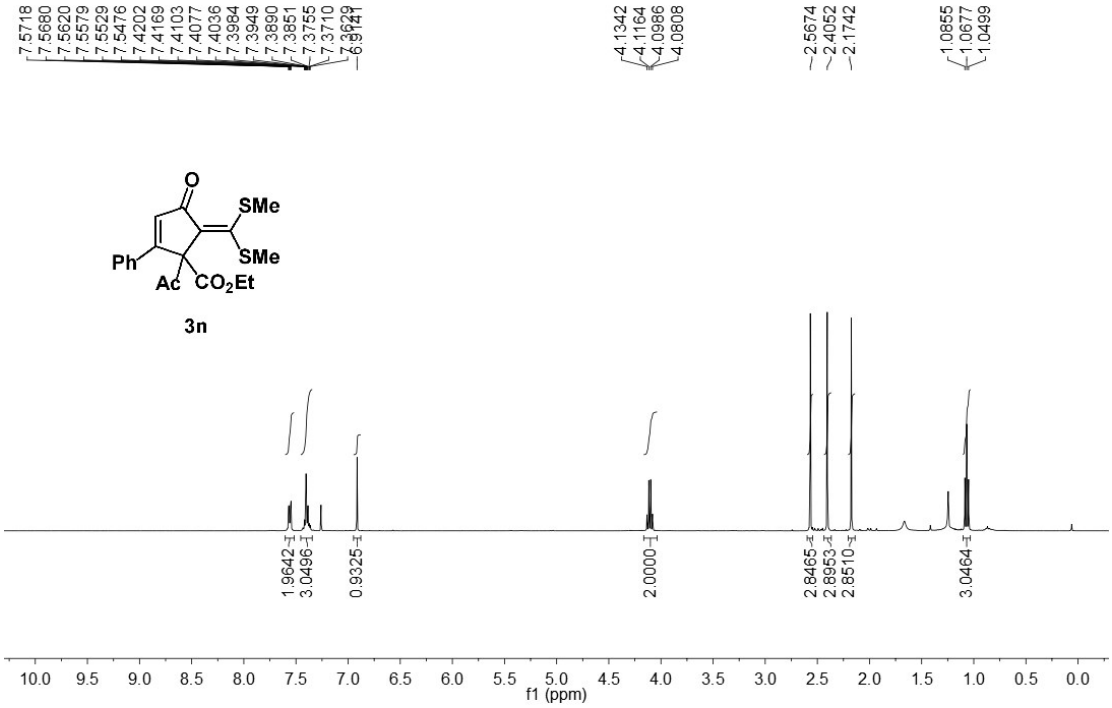
I052
I052 1H NMR in CDCl3



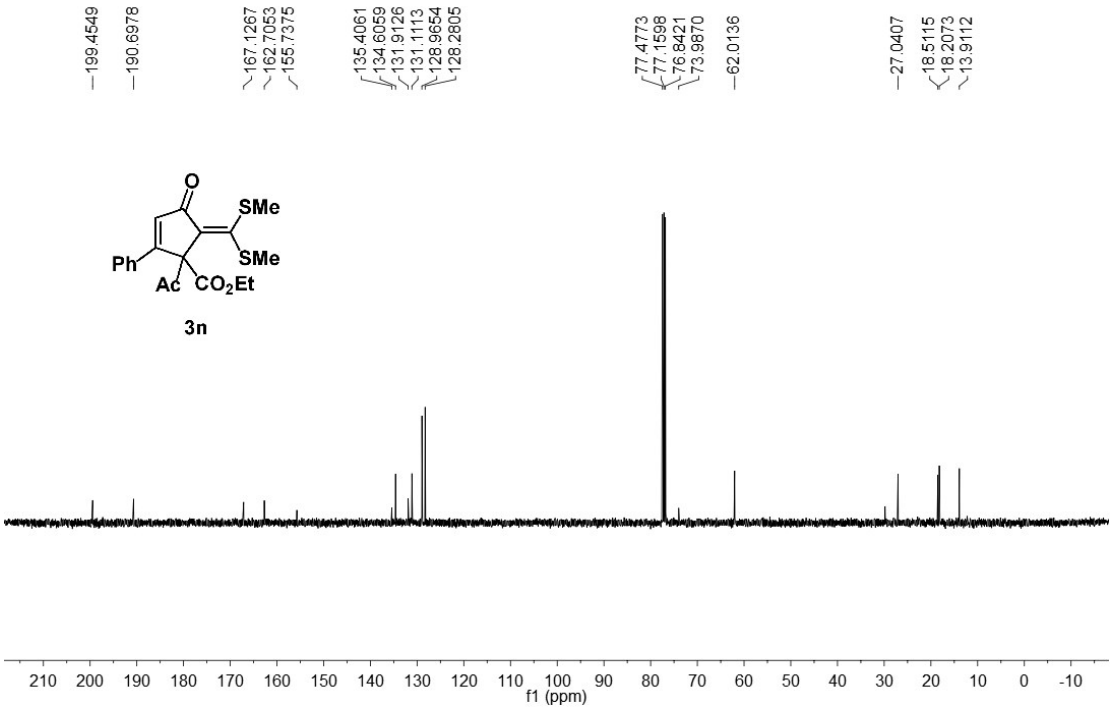
I052
I052 13C NMR in CDCl3



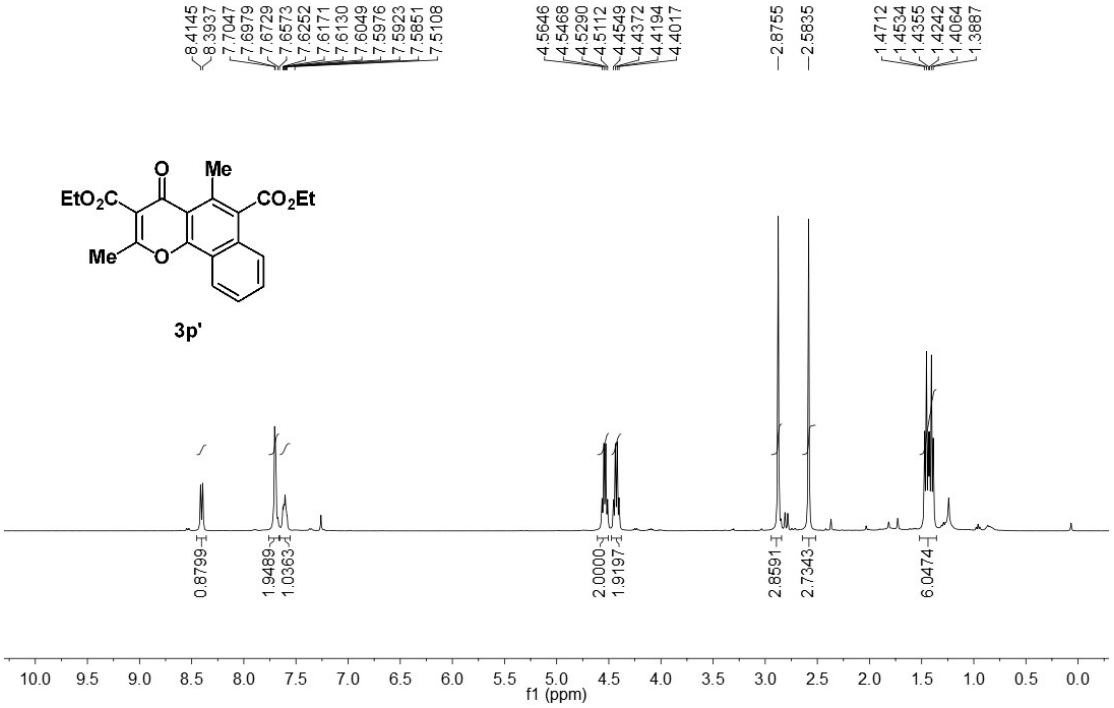
I085
I085 1H NMR in CDCl3



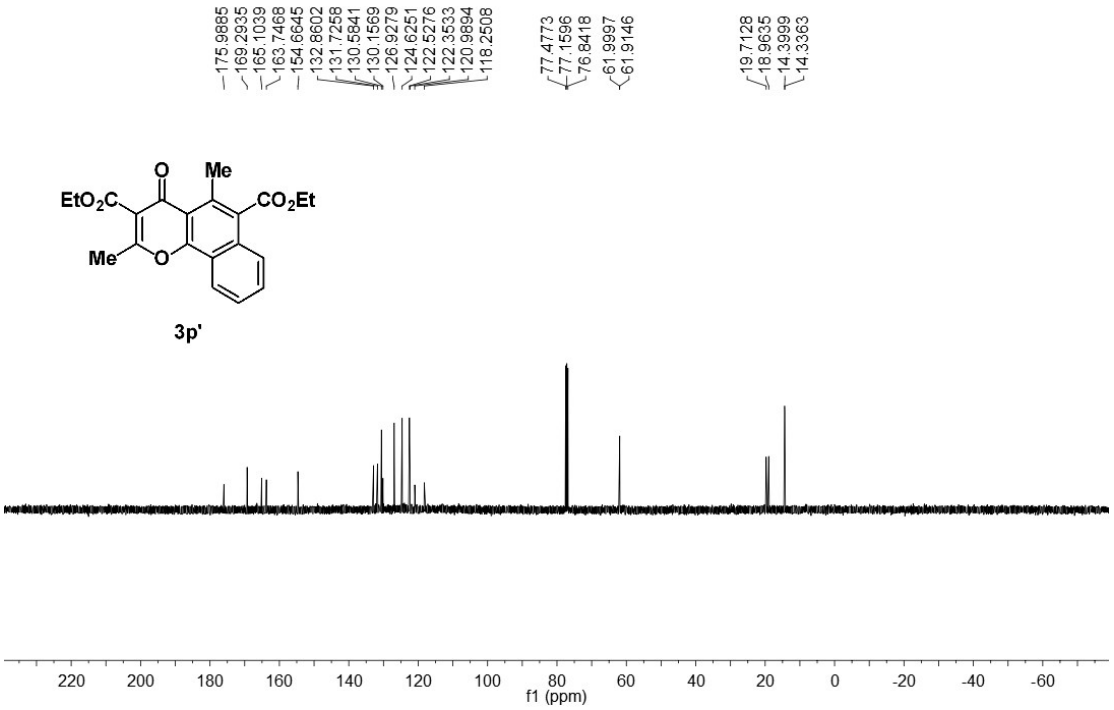
I085
I085 13C NMR in CDCl3



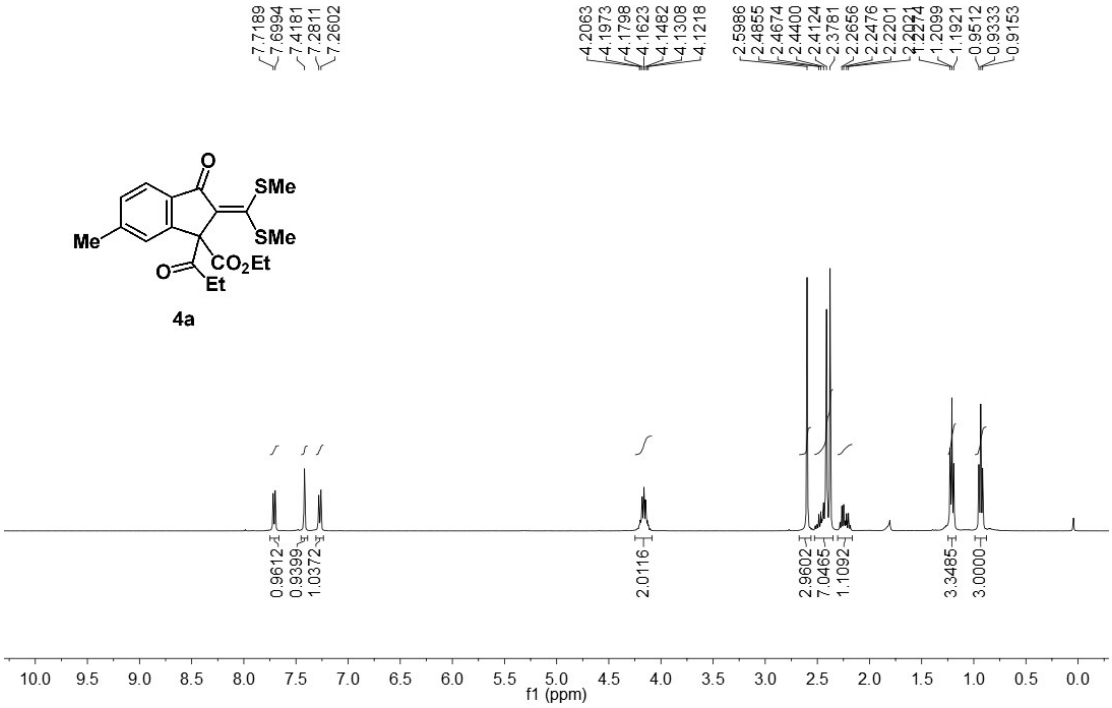
LJ-I025
LJ-I025-P2 1H NMR



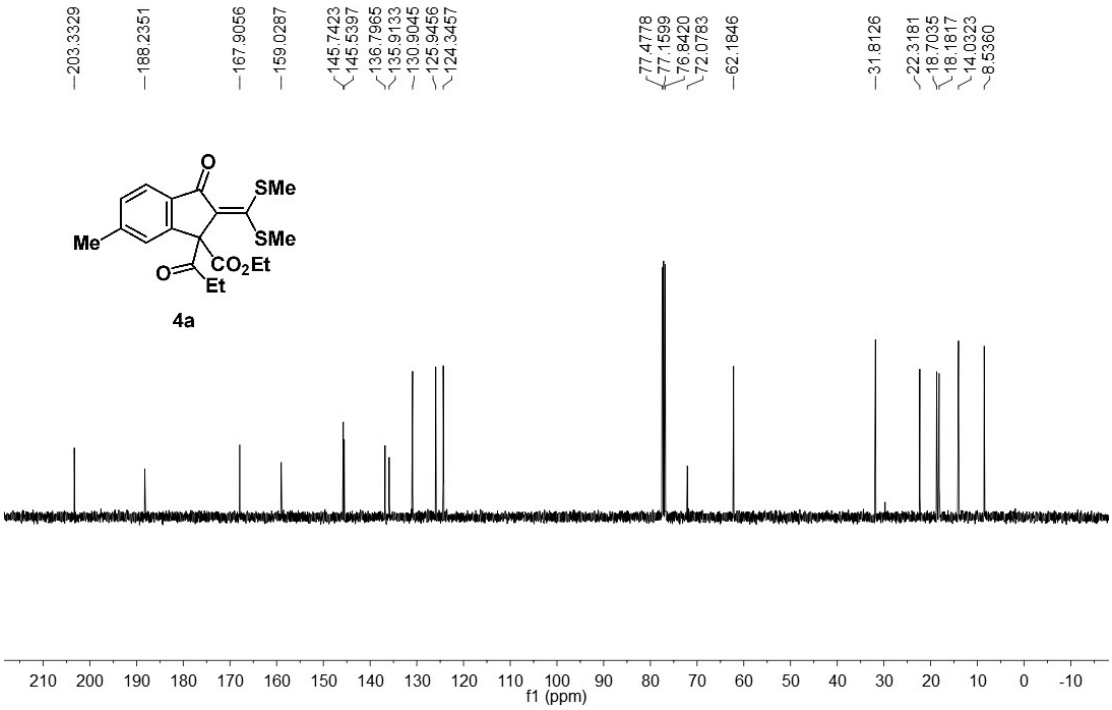
LJ-I025
LJ-i025-p2 13C NMR



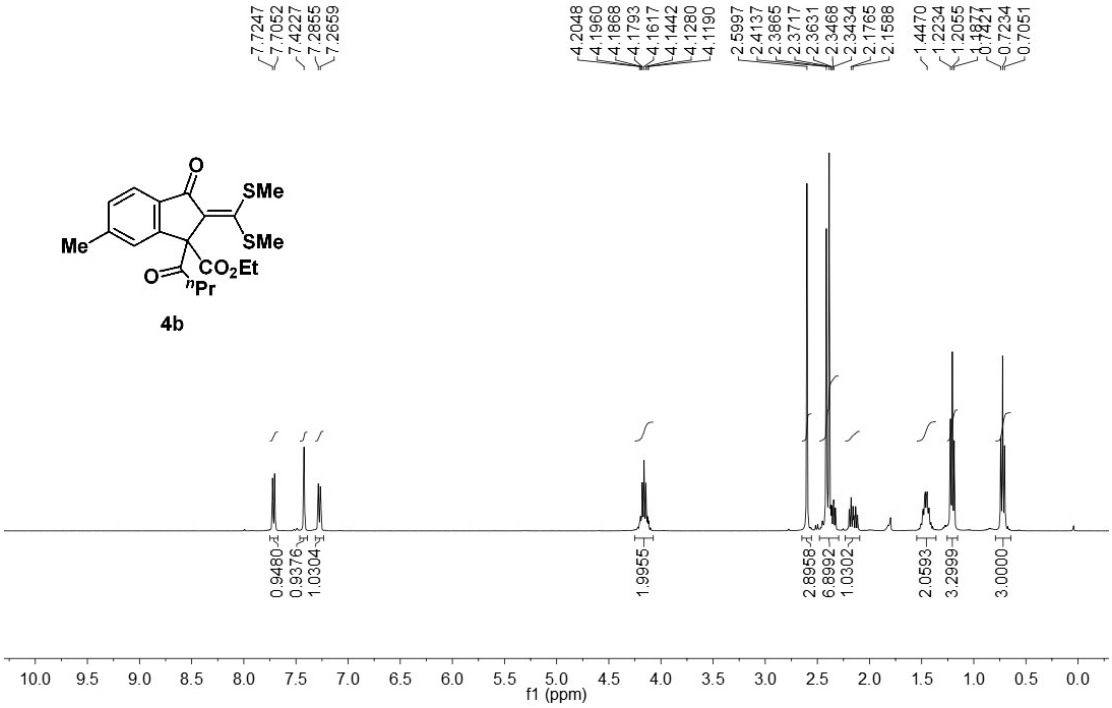
I063
I063 1H NMR in CDCl3



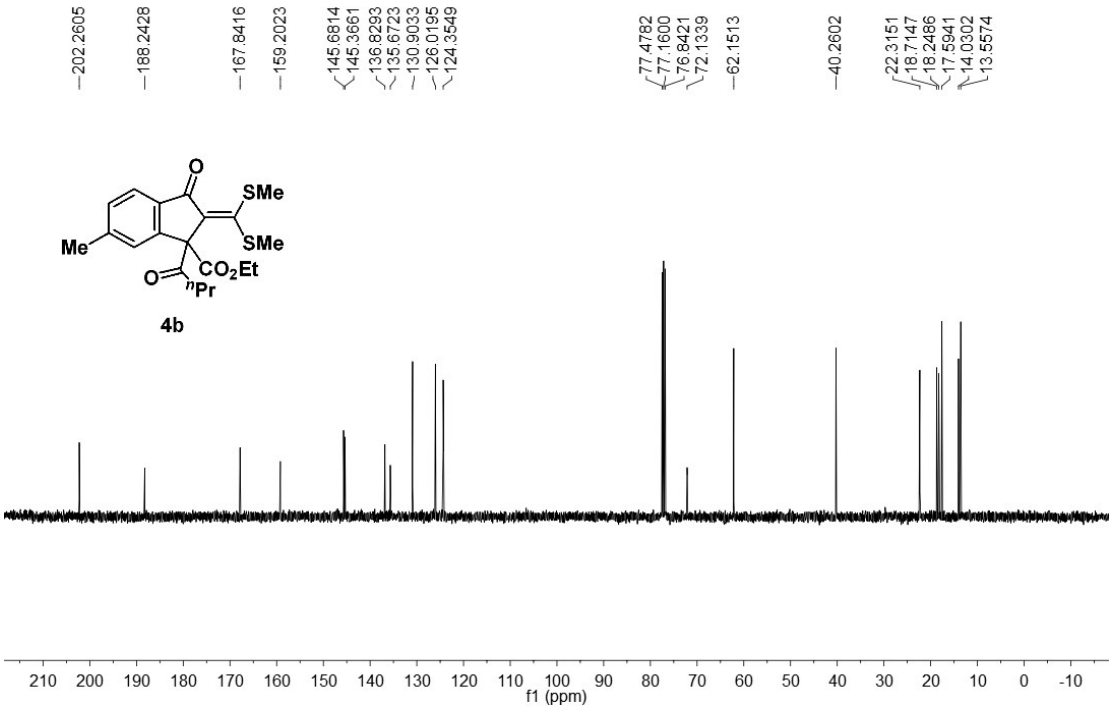
I063
I063 13C NMR in CDCl3



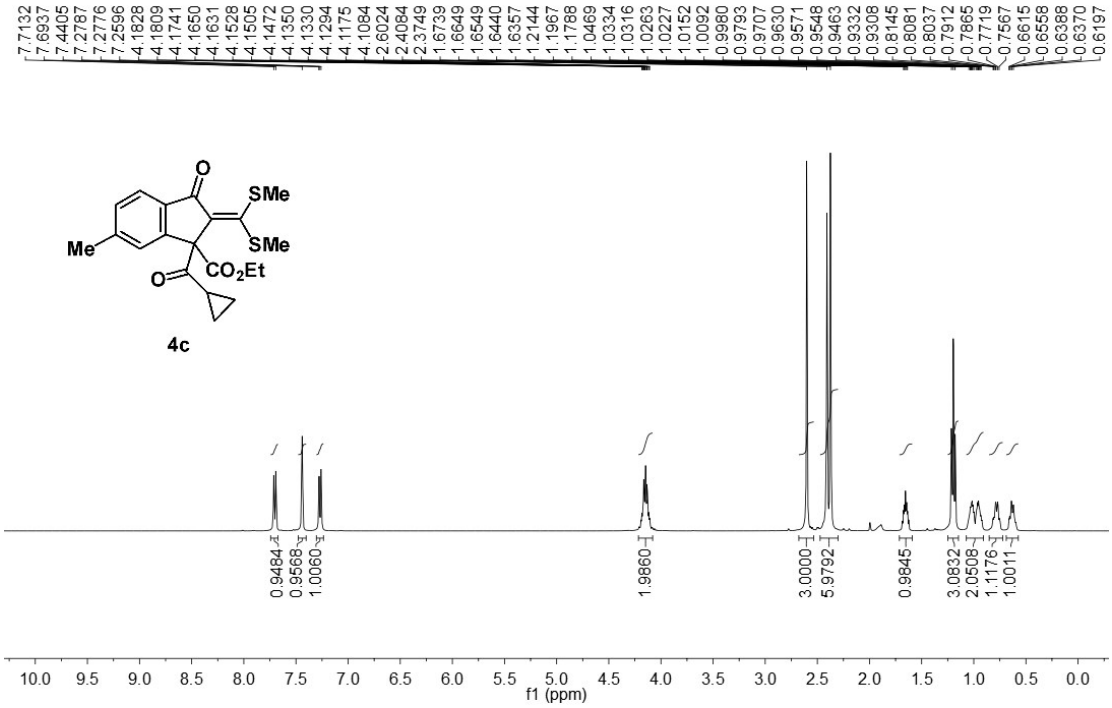
IO70
IO70 1H NMR in CDCl3



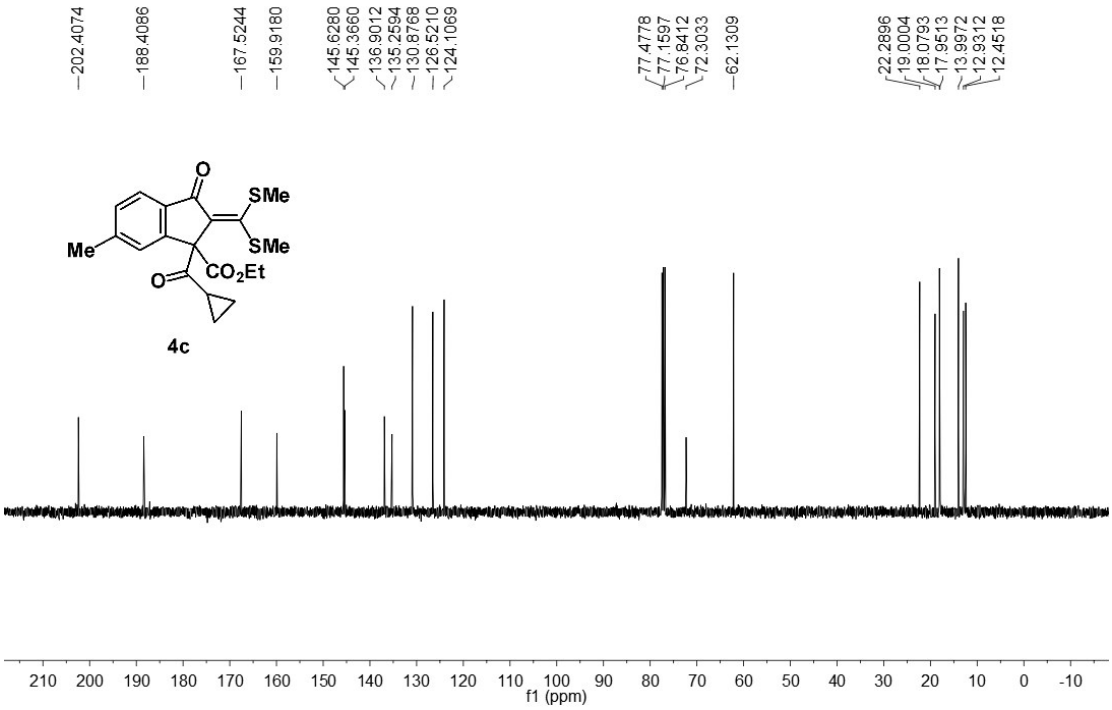
IO70
IO70 13C NMR in CDCl3



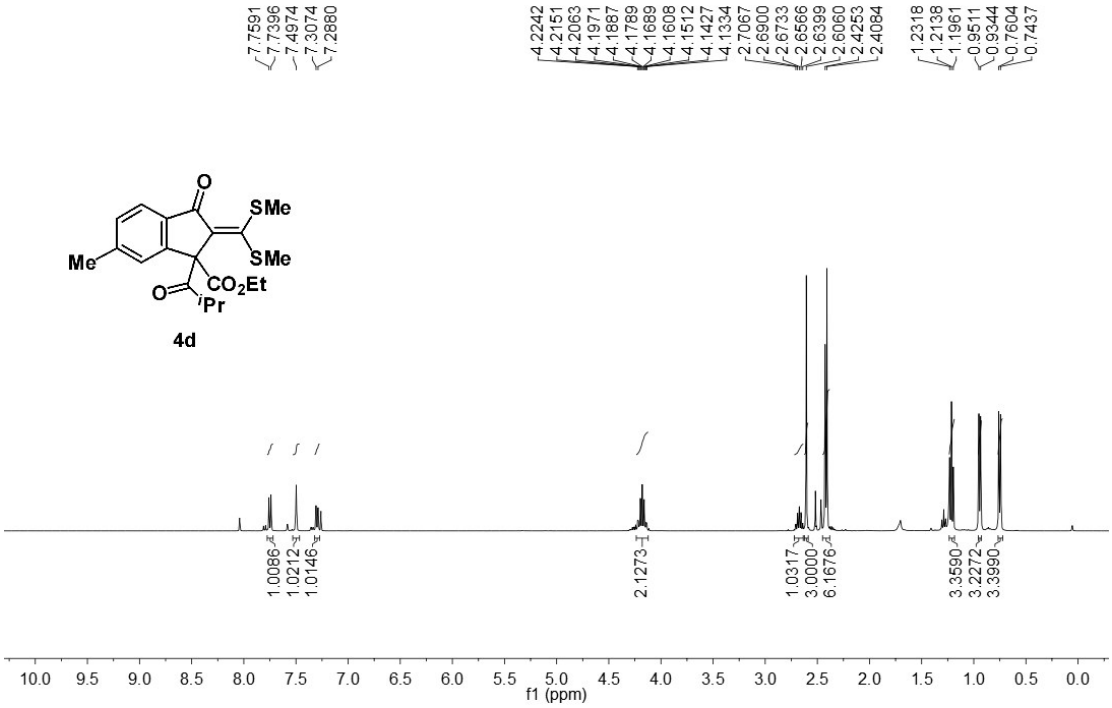
IO78
IO78 1H NMR in CDCl3



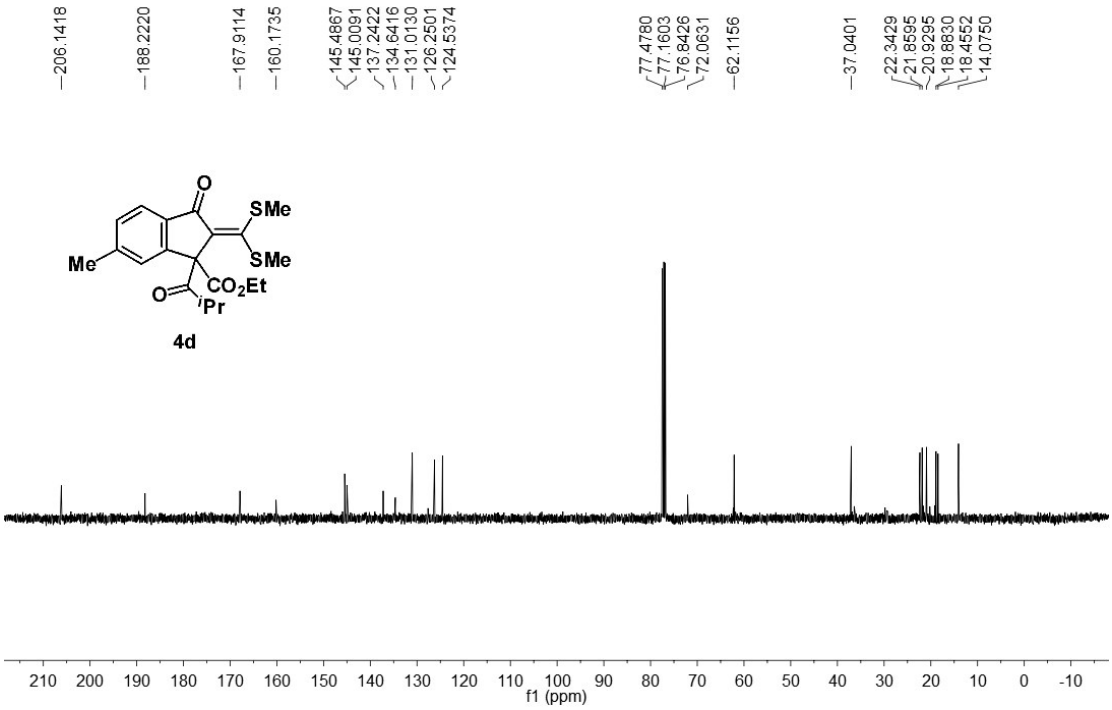
IO78
IO78 13C NMR in CDCl3



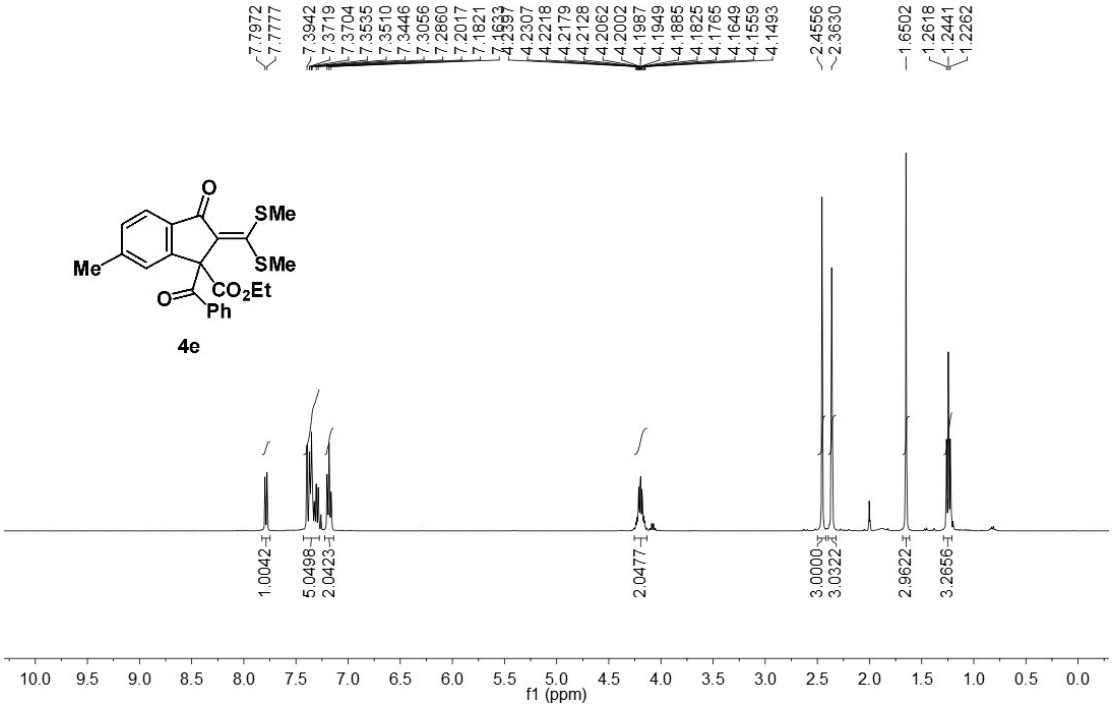
IO82
IO82 1H NMR in CDCl3



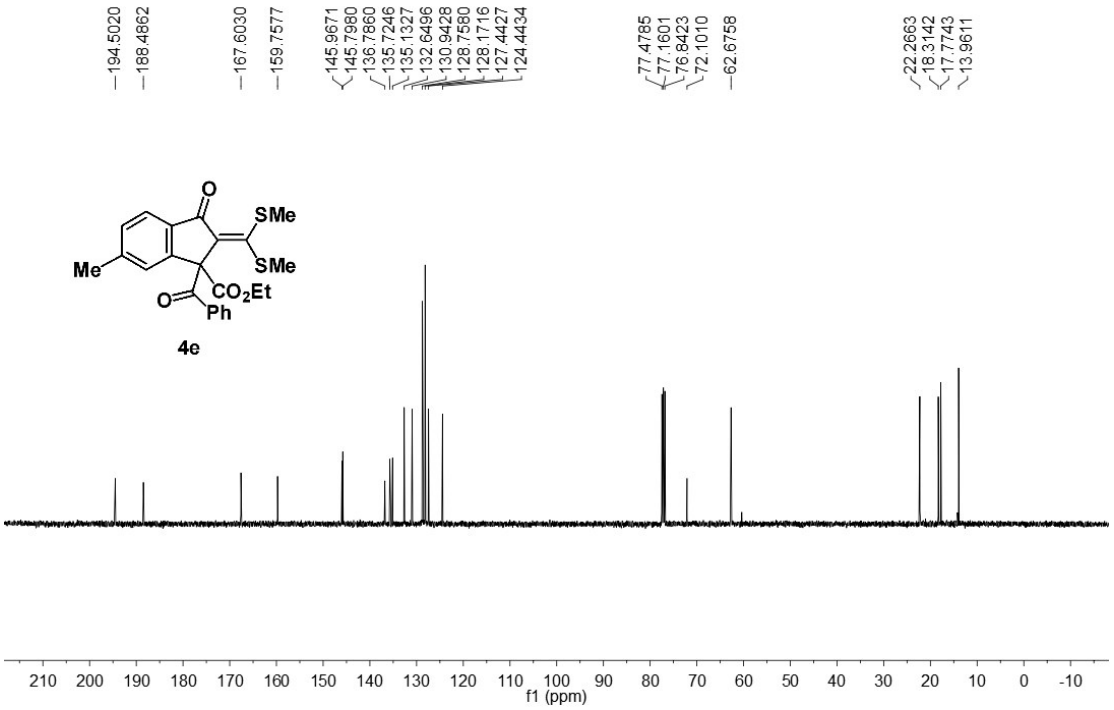
IO82
IO82 13C NMR in CDCl3



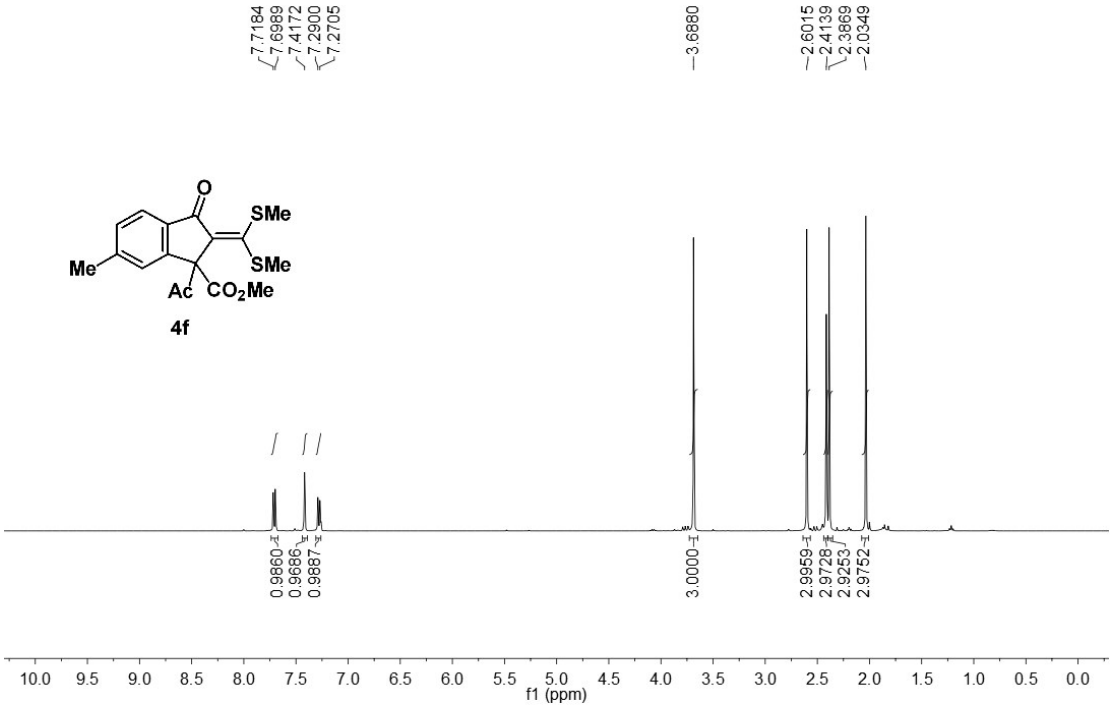
I067
I067 1H NMR in CDCl3



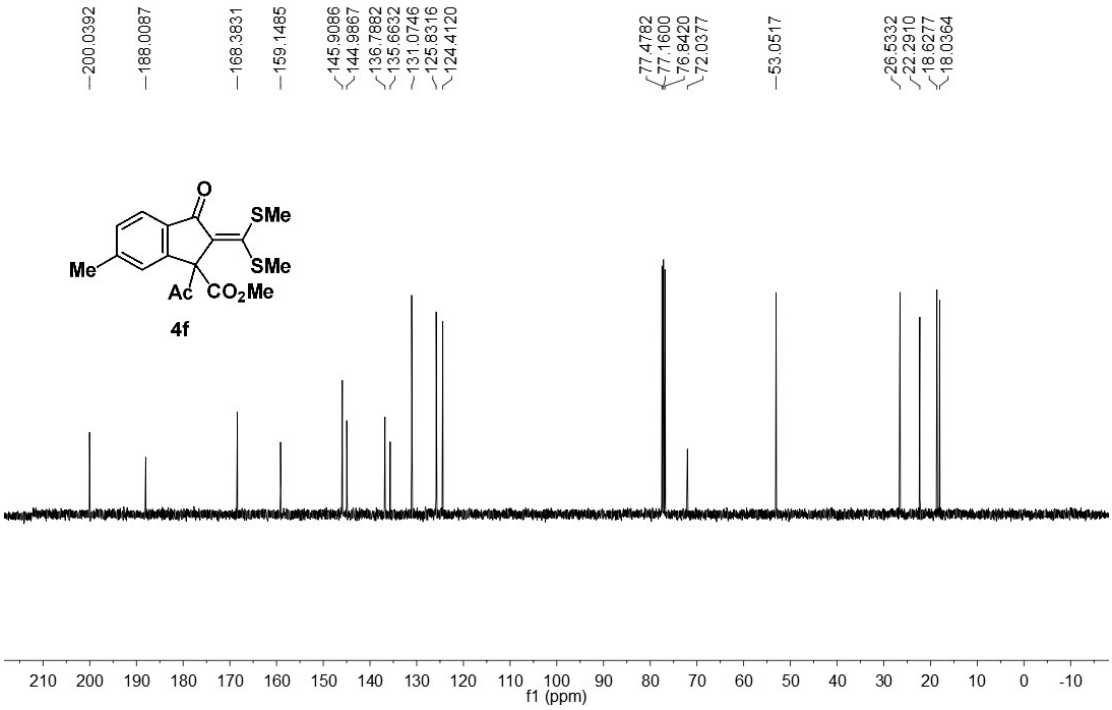
I067
I067 13C NMR in CDCl3



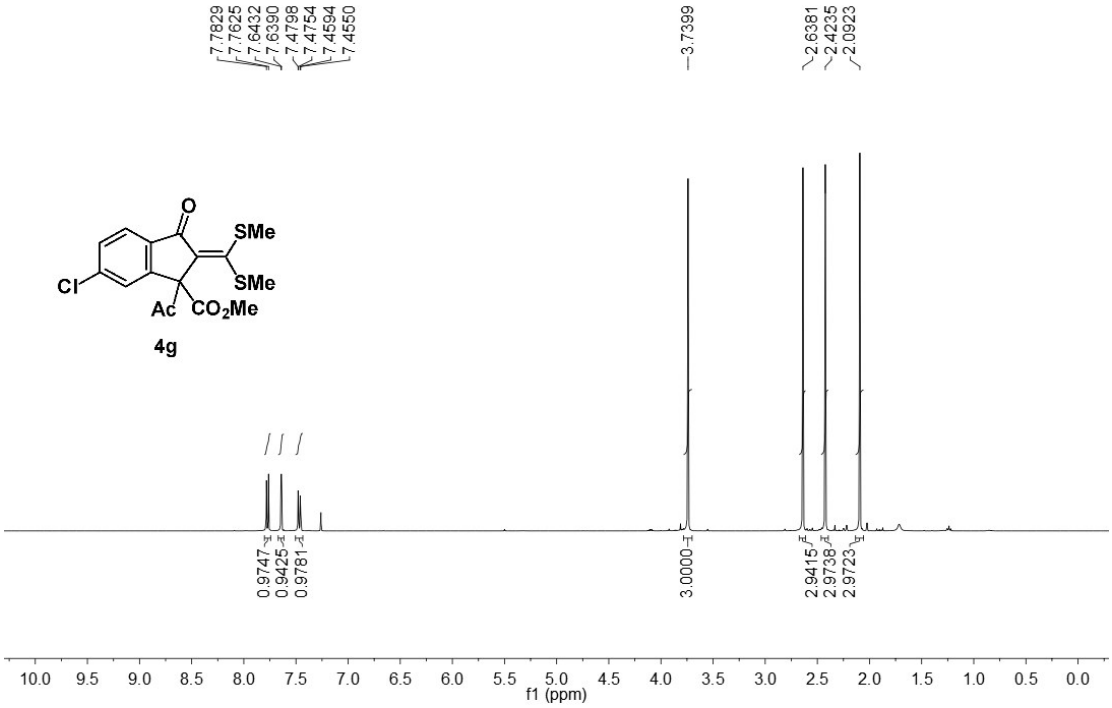
I062
I062 1H NMR in CDCl3



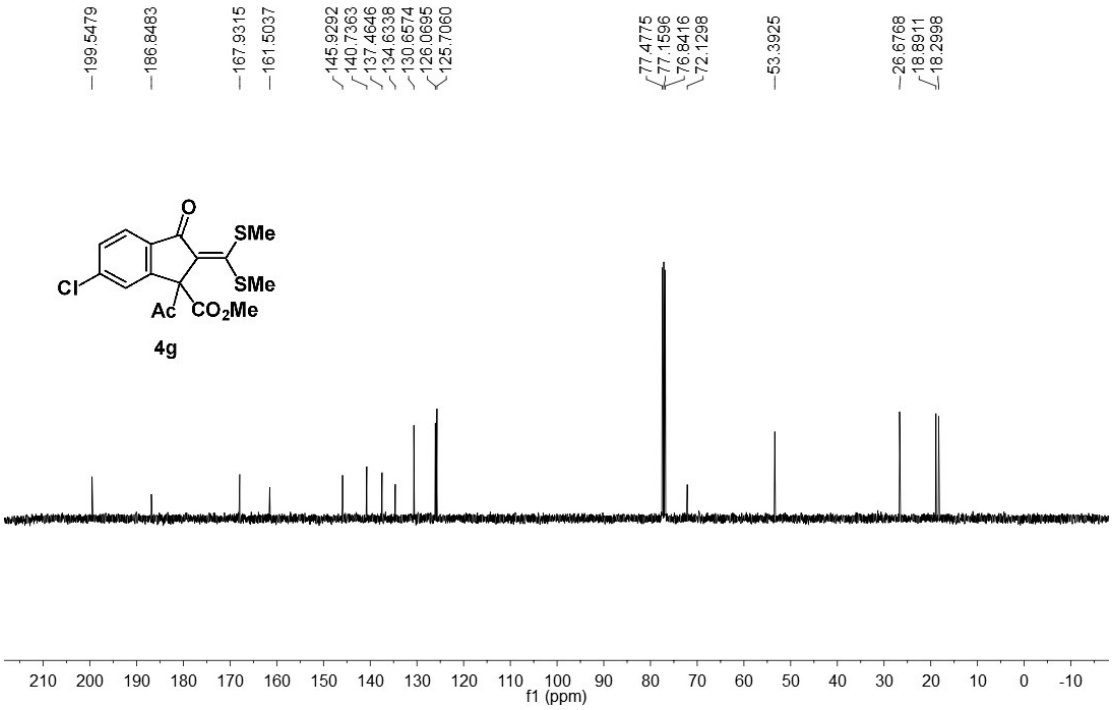
I062
I062 13C NMR in CDCl3



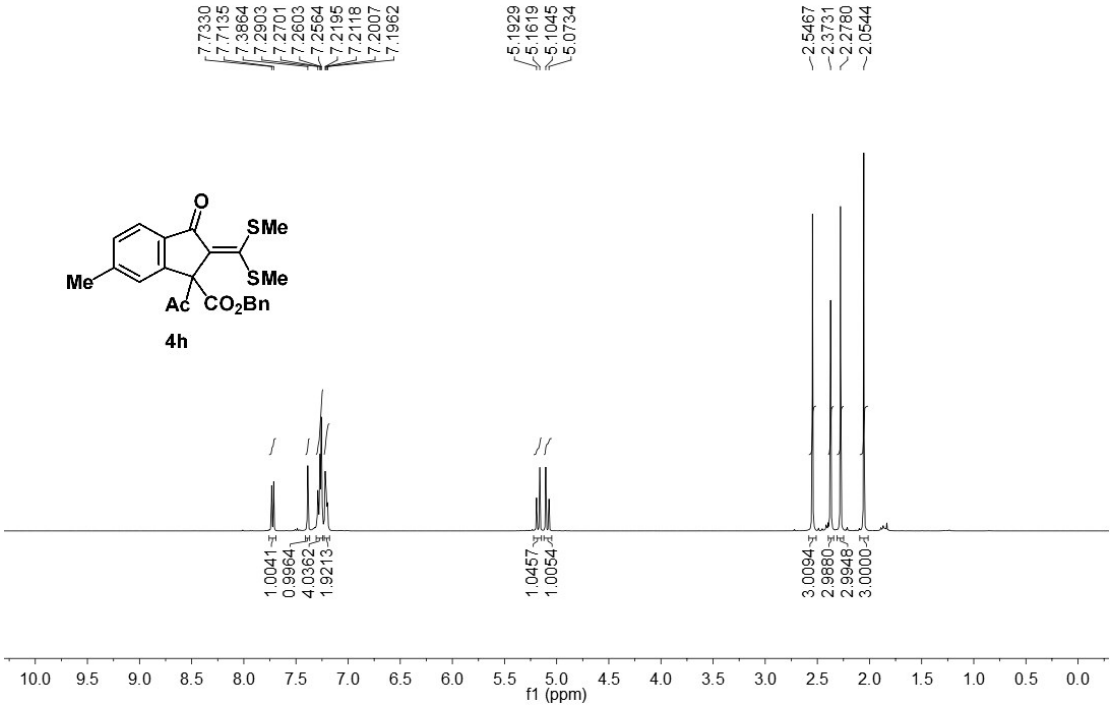
I056
I056 1H NMR in CDCl3



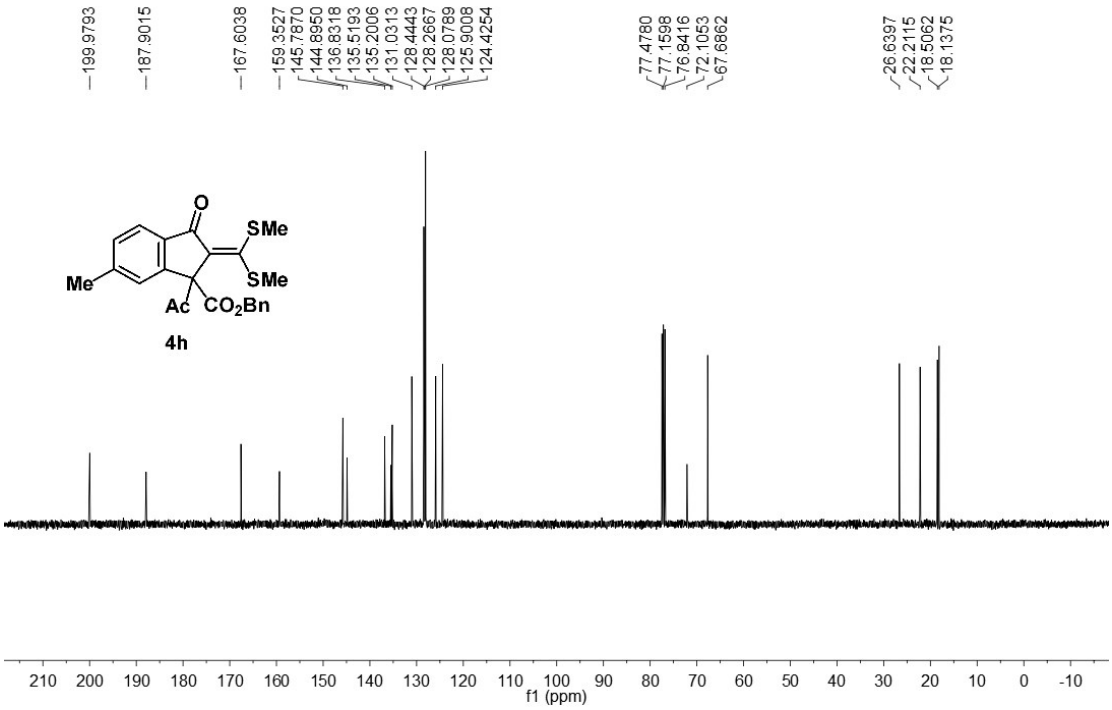
I056
I056 13C NMR in CDCl3



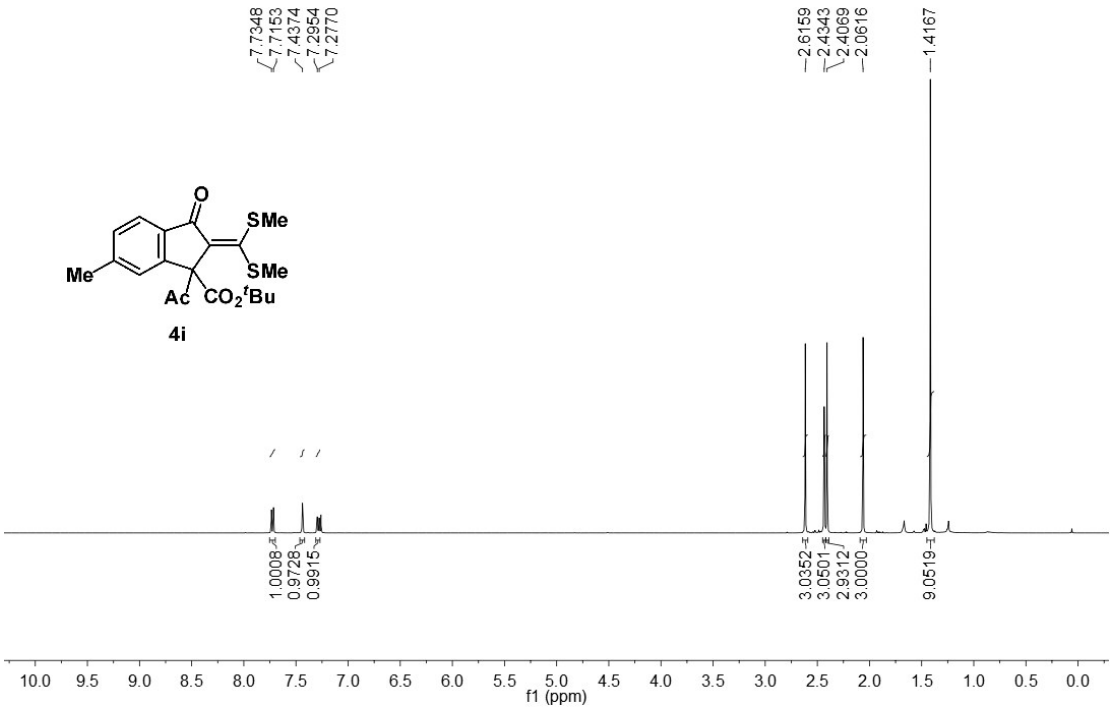
I066
I066 1H NMR in CDCl3



I066
I066 13C NMR in CDCl3



I071
I071 1H NMR in CDCl3



I071
I071 13C NMR in CDCl3