Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

A new method for synthesizing terminal olefins from esters using Corey-Chaykovsky's reagents

Hucheng Shi, [a] Guoren Yue, [a, b] * Penji Yan, [b] Xiangdong Ji,[b] Yangfei Wei,[b] Hai Song[b] and Xin Jia.[a]

a. School of Chemistry and Chemical Engineering, State Key Laboratory Incubation Base for Green Processing of Chemical Engineering, Shihezi University, Shihezi 832003, China.
b. Key Laboratory of Hexi Corridor Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Hexi University, Zhangye, Gansu 734000, PR China;
.

Table of Contents

1.General

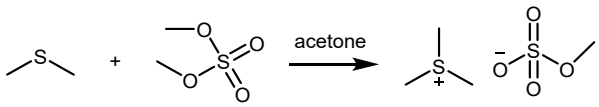
The experiments were conducted under a nitrogen atmosphere. THF was treated by introducing sodium filaments and allowing them to stand overnight. Subsequently, benzophenone was introduced and the solution was refluxed until it exhibited a blue hue. The resulting fractions were gathered to obtain anhydrous THF.

NMR spectra were recorded on Bruker-400 MB instrument using $CDCl_3$ as solvent and Me_4Si as internal standard at room temperature; the chemical shifts δ were measured in ppm with respect to solvent (^1H: $CDCl_3$, δ = 7.28 ppm; $^{13}C\{^1H\}$: CDCl3, δ = 77.00 ppm). Coupling constants (J) were in Hertz. The structures of compounds were ascertained with the aid of 1D NMR and 2D NMR spectroscopy. High resolution and accurate mass measurements were carried out using a Bruker micro TOF-QTM ESI-TOF (electrospray ionization/time of flight). Melting points (mp) were uncorrected and were measured on Hanon MP-100 automated melting point apparatus. Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates; the revelation was viewed by UV lamp (254 nm). Column chromatography was performed by using 300−400 mesh silica gel (Qingdao Haiyang) and a mixture of petroleum ether/ethyl acetate or petroleum ether as an eluent.

Solvents and chemicals for all feedstocks are procured from Adamas-Beta, Aladdin, and Shao Yuan, and are utilized without additional purification unless specified otherwise.

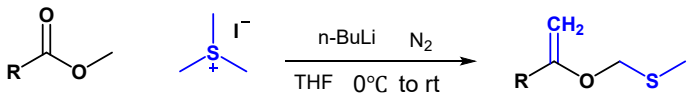
2. Experimental Procedures

2.1 Synthesis of 2c[1]



Experimental procedure: To dimethylsulfate (19 ml, 0.2 mol) in acetone (80 ml) was added dimethylsulfide (15 ml, 0.2 mol.). Stirring was sustained for 5 hours at 20-30°C，The acetone was removed under vacuum and the white solid was washed twice with acetone and dried under vacuum: 28 g of 2c (75% yield) was obtained.

2.2. General procedure for the synthesis of terminal olefins

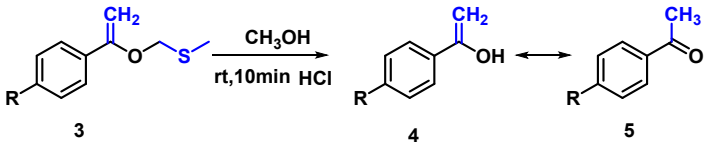


1 2a 3

General reaction procedure: A solution of the sulfonium salt (2 mmol) in anhydrous THF (4 mL) was cooled to 0ºC under nitrogen atmosphere. n-BuLi (1.6 M solution in Hexanes,4 mmol) was added dropwise via syringe, and the reaction mixture allowed while stirring for 0.5 h. A solution of the esters (1 mmol) in anhydrous THF (1 mL) was added dropwise via syringe. The mixture was warmed to rt. After stirring an additional 1h the reaction was quenched with saturated aqueous

NH_4Cl (5 mL) and then diluted with EA (10 mL). The organic layers were separated, the aqueous phase extracted with EA (3X10 mL), and the combined organic layers dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (PE / EA as eluent) provided terminal olefin derivatives.

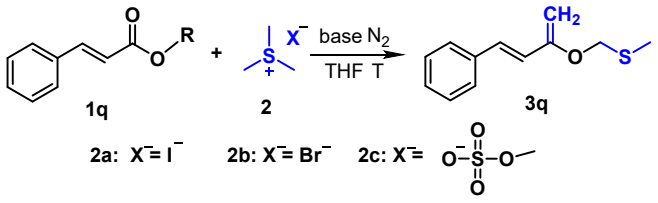
2.3 Derivatization reaction[2]



3 4 5

Experimental procedure: Alkenyl ether 3(0.5mmol) was dissolved in methanol, followed by the gradual addition of 0.5 ml of hydrochloric acid (1 M). After stirring an additional 10 minutes the reaction was quenched with saturated aqueous $NaHCO_3$ (5 mL) and then diluted with EA (10 mL). The organic layers were separated, the aqueous phase extracted with EA (3X10 mL), and the combined organic layers dried over anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography (PE / EA as eluent) provided ketone derivatives.

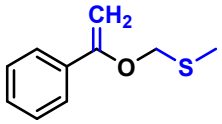
3. Screening of Reaction Conditions [a]



Entry	T(℃)	reagents（equiv.）	base（equiv.）	Yield(%)[b]
1	-30	2a(2)	n-BuLi(2)	--
2	-30	2a(2)	n-BuLi(3)	40
3	**-30**	2a(**2**)	**n-BuLi**(4)	**56**
4	-30	2a(2)	n-BuLi(5)	44
5	-10	2a(2)	n-BuLi(4)	60
6	0	2a(2)	n-BuLi(4)	71
7	**rt**	2a**(2)**	**n-BuL(4)**	**81**
8	60	2a(2)	n-BuLi(4)	14
9[c]	rt	2a(2)	NaH(4)	--
10[c]	rt	2a (2)	t-BuOK(4)	--
11[c]	rt	2a(2)	K_2CO_3(4)	--
12	rt	2b(2)	n-BuLi(4)	80
13	rt	2c(2)	n-BuLi(4)	88

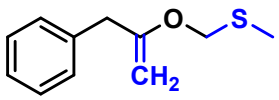
[a]General procedure: To a suspension of compound 2 in anhydrous THF was added the base under nitrogen atmosphere. After the mixture was stirred at certain temperature for 1 hour, 1q was added to the solution. After an additional hour, the reaction was quenched with saturated aqueous ammonium chloride. [b]Isolated yields. [c]Base and 2a were added at the same time.

methyl(((1-phenylvinyl)oxy)methyl)sulfane



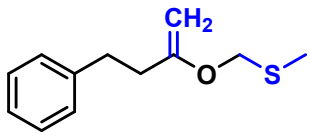
Compound **3a** was prepared from methyl benzoate (50 mg, 0.367 mmol, 1 eq) and trimethyl sulphur iodide (149.89 mg, 0.734 mmol, 2 eq) according to the general reaction procedure. Purification by flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column afforded 47 mg (81% integrated yield), clear liquid, Rf = 0.5 (silica gel, PE/EA = 100:1,v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.63 (m, 2H), 7.42 – 7.32 (m, 3H), 5.08 (s, 2H), 4.86 (d, *J* = 3.1 Hz, 1H), 4.33 (d, *J* = 3.1 Hz, 1H), 2.33 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.51, 136.13, 128.63, 128.17, 125.48, 85.03, 71.98, 15.08. HRMS(ESI) m/z: [M + Na]$^{+}$Calcd of $C_{10}H_{12}OSNa$ 203.0501, Found 203.0504. CAS RN:14439-02-2.

methyl(((3-phenylprop-1-en-2-yl)oxy)methyl)sulfane



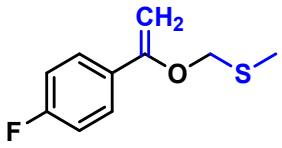
Compound **3b** was prepared from ethyl phenylacetate (50 mg, 0.337 mmol, 1 eq) and trimethyl sulphur iodide (137.89 mg, 0.675 mmol, 2 eq) according to the general reaction procedure. Purification by flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column gave 46 mg (80% integrated yield), clear liquid, Rf = 0.5 (silica gel, PE/EA = 100:1, v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.21 (m, 5H), 4.85 (s, 2H), 4.12 (d, *J* = 2.4 Hz, 1H), 4.06 (d, *J* = 2.4 Hz, 1H), 3.46 (s, 2H), 2.10 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.47, 138.26, 128.91, 128.25, 126.33, 85.15, 71.25, 41.46, 14.71. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{11}H_{14}OSNa$ 217.0657, Found 217.0657. New compound.

methyl(((4-phenylbut-1-en-2-yl)oxy)methyl)sulfane



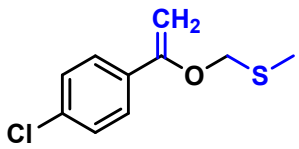
The compound **3c** was synthesized using 50 mg (0.304 mmol, 1 eq) of methyl phenylpropionate and 124.28 mg (0.609 mmol, 2 eq) of trimethyl sulphur iodide, following the standard reaction protocol. The purification process involved flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column, resulting in the isolation of 45 mg of a clear liquid (81% integrated yield) with an Rf value of 0.5 (silica gel, PE/EA= 100:1, v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.21 (m, 6H), 4.88 (s, 2H), 4.07 (d, *J* = 2.4 Hz, 1H), 3.98 (d, *J* = 2.4 Hz, 1H), 2.91 – 2.86 (m, 2H), 2.51 – 2.45 (m, 2H), 2.28 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.99, 141.55, 128.41, 128.31, 125.91, 83.69, 71.22, 36.89, 33.77, 14.99. HRMS(ESI) m/z: [M + Na]$^{+}$ Calcd of $C_{12}H_{16}OSNa$ 231.0814, Found 231.0816. New compound.

(((1-(4-fluorophenyl)vinyl)oxy)methyl)(methyl)sulfane



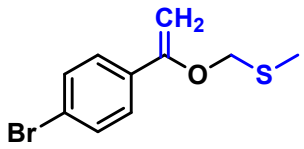
Compound **3d** was synthesized from 50 mg (0.324 mmol, 1 eq) of methyl 4-fluoro-benzoate and 132.39 mg (0.648 mmol, 2 eq) of trimethylsulphur iodide, following the standard reaction protocol. The purification was achieved through flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column, resulting in the isolation of 42 mg of a clear liquid (77% integrated yield) with an Rf value of 0.5 (PE/EA = 100:1, v/v).^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.55 (m, 2H), 7.05 (t, *J* = 8.7 Hz, 2H), 5.05 (s, 2H), 4.77 (d, *J* = 3.3 Hz, 1H), 4.30 (d, *J* = 3.3 Hz, 1H), 2.31 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.28, 161.82, 157.67, 132.30, 132.27, 127.32, 127.24, 84.75, 84.74, 72.08, 15.09. HRMS(ESI) m/z:[M + Na]$^{+}$ Calcd of $C_{10}H_{11}FOSNa$：221.0406, Found 221.0432. New compound.

(((1-(4-chlorophenyl)vinyl)oxy)methyl)(methyl)sulfane



Compound **3e** was synthesized from 50 mg (0.293 mmol, 1 eq) of methyl 4-chloro-benzoate and 119.62 mg (0.586 mmol, 2 eq) of trimethylsulphur iodide, following the standard reaction procedure. Purification through flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 54 mg of a clear liquid (90% combined yield) with an Rf value of 0.5 (silica gel, PE/EA= 100:1,v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.51 (m, 2H), 7.38 – 7.28 (m, 2H), 5.05 (s, 2H), 4.82 (d, *J* = 3.3 Hz, 1H), 4.33 (d, *J* = 3.3 Hz, 1H), 2.31 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.43, 134.58, 134.46, 128.34, 126.75, 85.35, 72.10, 15.11. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{10}H_{11}ClOSNa$ 237.0111, Found 237.0120. CAS RN:14679-93-7.

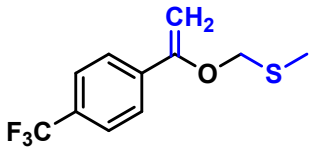
(((1-(4-bromophenyl)vinyl)oxy)methyl)(methyl)sulfane



Compound **3f** was synthesized from 50 mg (0.232 mmol, 1 eq) of methyl 4-bromo-benzoate and 94.90 mg (0.465 mmol, 2 eq) of trimethylsulphur iodide, in accordance with the standard reaction protocol. Subsequent purification via flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 34 mg of a clear liquid (66% combined yield) with an Rf value of 0.5 (silica gel, petroleum ether/ethyl acetate = 100:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.38 (m, 4H), 5.05 (s, 2H), 4.83 (d, *J* = 3.3 Hz, 1H), 4.33 (d, *J* = 3.3 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.49, 135.04, 131.30, 127.05, 122.70, 85.44, 72.11, 15.11. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of

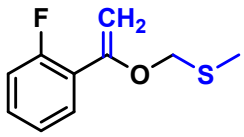
$C_{10}H_{11}BrOSNa$ 280.9606, Found 280.9614. CAS RN:14680-04-7.

methyl(((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)methyl)sulfane



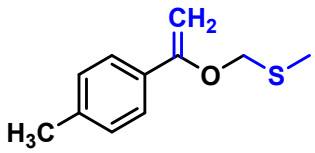
Compound **3g** was synthesized from 50 mg (0.225 mmol, 1 eq) of methyl 4-methyl-benzoate and 99.96 mg (0.450 mmol, 2 eq) of trimethylsulphur iodide, in accordance with the standard reaction protocol. Subsequent purification via flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 48 mg of a clear liquid (80% combined yield) with an Rf value of 0.5 (silica gel, petroleum ether/ethyl acetate = 100:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H), 5.08 (s, 2H), 4.93 (d, J = 3.4 Hz, 1H), 4.43 (d, J = 3.4 Hz, 1H), 2.32 (s, 3H).^{13}C NMR (101 MHz, Chloroform-d) δ 157.10, 139.48, 139.47, 130.68, 130.36, 129.05, 125.86, 125.68, 125.45, 125.20, 125.16, 125.12, 125.08, 86.78, 72.22, 15.07. HRMS(ESI) m/z:[M + H]$^{+}$Calcd of $C_{11}H_{12}F_3OS$ 249.0555, Found 249.0552. New compound.

(((1-(2-fluorophenyl)vinyl)oxy)methyl)(methyl)sulfane



Compound **3h** was synthesized from 50 mg (0.324 mmol, 1 eq) of methyl 2-fluorobenzoate and 132.39 mg (0.648 mmol, 2 eq) of trimethylsulphur iodide, following the prescribed reaction protocol. Subsequent purification via flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 40 mg of a clear liquid (72% combined yield) with an Rf value of 0.5 (silica gel, PE/EA = 100:1,v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (td, *J* = 7.7, 1.9 Hz, 1H), 7.35 – 7.27 (m, 1H), 7.27 – 7.03 (m, 2H), 5.04 (s, 2H), 4.92 – 4.86 (m, 1H), 4.57 (dd, *J* = 2.9, 1.3 Hz, 1H), 2.31 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.30, 158.80, 153.67, 153.64, 129.93, 129.84, 129.16, 129.13, 124.44, 124.32, 123.82, 123.79, 116.14, 115.91, 90.49, 90.41, 71.91, 14.98. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{11}H_{11}FOSNa$ 221.0406, Found 221.0432. New compound.

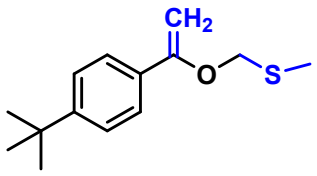
methyl(((1-(p-tolyl)vinyl)oxy)methyl)sulfane



Compound **3i** was synthesized from 50 mg (0.333 mmol, 1 eq) of methyl 4-methyl-benzoate and 135.89 mg (0.666 mmol, 2 eq) of trimethylsulphur iodide according to the standard reaction protocol. Subsequent purification through flash column chromatography (1% ethyl acetate in petroleum ether)

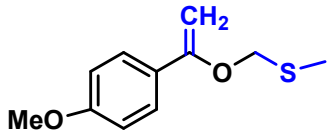
on a silica gel column yielded 22 mg of a clear liquid (44% integrated yield) with an Rf value of 0.5 (silica gel, PE/EA = 100:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 5.06 (s, 2H), 4.80 (d, *J* = 3.0 Hz, 1H), 4.28 (d, *J* = 3.0 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.64, 138.49, 133.36, 128.84, 125.39, 84.31, 71.91, 21.16, 15.02. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{11}H_{14}OSNa$ 217.0657, Found 217.0676. New compound.

(((1-(4-(tert-butyl)phenyl)vinyl)oxy)methyl)(methyl)sulfane



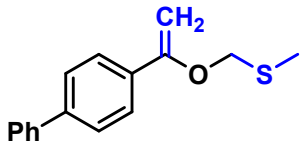
Compound **3j** was derived from 100 mg (0.52 mmol, 1 eq) of methyl 4-tert-butylbenzene-carboxylate and 212.29 mg (1.04 mmol, 2 eq) of trimethyl iodide under the conditions of the standard reaction protocol at 40 °C. Subsequent purification by means of flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 60 mg of a yellow oily liquid (80% combined yield) with an Rf value of 0.5 (silica gel, PE/EA = 100:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 5.06 (s, 2H), 4.80 (d, *J* = 3.0 Hz, 1H), 4.28 (d, *J* = 3.0 Hz, 1H), 2.31 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.50, 151.75, 133.29, 125.19, 125.09, 84.40, 71.85, 34.60, 31.27, 15.04. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{14}H_{20}OSNa$ 259.1127, Found 259.1128. New compound.

(((1-(4-methoxyphenyl)vinyl)oxy)methyl)(methyl)sulfane



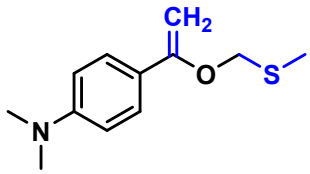
Compound **3k** was synthesized from 100 mg (0.61 mmol, 1 eq) of methyl 4-methoxybenzoate and 245.61 mg (1.2 mmol, 2 eq) of trimethyl iodide at 40 °C in accordance with the standard reaction procedure. Subsequent purification through flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 61 mg of a yellow oily liquid (58% combined yield) with an Rf value of 0.5 (silica gel, PE/EA = 50:1.v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.05 (s, 2H), 4.73 (d, *J* = 3.1 Hz, 1H), 4.22 (d, *J* = 3.1 Hz, 1H), 3.84 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.00, 158.31, 128.76, 126.79, 113.51, 83.44, 71.87, 55.30, 15.10. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{11}H_{14}O_2SNa$ 233.0606, Found 233.0615. New compound.

(((1-([1,1'-biphenyl]-4-yl)vinyl)oxy)methyl)(methyl)sulfane



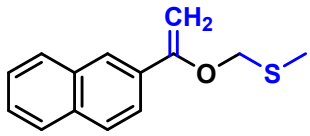
Compound **3l** was synthesized from 80 mg (0.376 mmol, 1 eq) of methyl 4-phenylcarboxylate and 154 mg (0.752 mmol, 2 eq) of trimethyl iodide following the general reaction procedure. Subsequent purification via flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 46 mg of a white solid with a melting point of 108.6 °C (57% integrated yield) and an Rf value of 0.5 (silica gel, p PE/EA = 50:1,v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 – 7.74 (m, 2H), 7.66 – 7.61 (m, 4H), 7.50 (td, *J* = 7.8, 4.9 Hz, 3H), 5.11 (s, 2H), 4.92 (d, *J* = 3.2 Hz, 1H), 4.37 (d, *J* = 3.2 Hz, 1H), 2.35 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.17, 141.42, 140.64, 135.05, 128.83, 127.47, 127.06, 126.91, 125.89, 85.09, 72.03, 15.14. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{16}H_{16}NOSNa$ 279.0921, Found 279.0930. CAS RN:14679-94-8.

N, N-dimethyl-4-(1-((methylthio)methoxy)vinyl)aniline



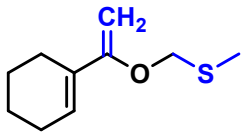
Compound **2m** was derived from 100 mg (0.558 mmol, 1 eq) of methyl p-dimethylaminobenzoate and 227.7 mg (1.116 mmol, 2 eq) of trimethyl iodide at 45 °C, in accordance with the general reaction protocol. Following purification through flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column, a yield of 32 mg (35% combined yield) of yellow oily liquid with an Rf value of 0.2 (silica gel, petroleum ether:ethyl acetate = 40:1) was obtained.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.51 (m, 2H), 6.72 – 6.69 (m, 2H), 5.05 (s, 2H), 4.68 (d, *J* = 2.9 Hz, 1H), 4.16 (d, *J* = 2.9 Hz, 1H), 3.00 (s, 6H), 2.31 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.92, 150.78, 126.41, 124.18, 111.77, 81.94, 71.73, 40.42, 15.05. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{12}H_{17}NOSNa$ 246.0923, Found 246.0950. New compound.

methyl(((1-(naphthalen-2-yl)vinyl)oxy)methyl)sulfane[2]



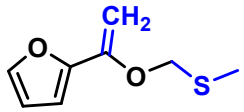
Compound **3n** was synthesized from 50 mg (0.217 mmol, 1 eq) of methyl 1-naphthalenecarboxylate and 102.06 mg (0.537 mmol, 2 eq) of trimethylsulphur iodide in accordance with the general reaction protocol. The purification process involved flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column, resulting in a yield of 36 mg (66% combined yield) of a clear liquid with an Rf value of 0.5 (silica gel, petroleum ether/ethyl acetate = 100:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.35 – 8.10 (m, 1H), 7.96 – 7.84 (m, 2H), 7.63 – 7.45 (m, 4H), 5.11 (s, 2H), 4.70 (d, *J* = 2.4 Hz, 1H), 4.65 (d, *J* = 2.4 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.25, 135.06, 133.64, 131.35, 129.15, 128.24, 127.09, 126.27, 125.89, 125.75, 125.14, 90.57, 72.08, 15.25. HRMS (ESI) m/z:[M + Na]$^{+}$Calcd of C14H14OSNa253.0657, Found 253.0660. CAS RN:14679-95-9.

(((1-(cyclohex-1-en-1-yl)vinyl)oxy)methyl)(methyl)sulfane



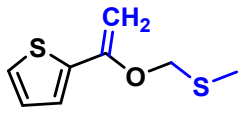
Compound **3o** was synthesized from 100 mg (0.731 mmol, 1 eq) of methyl cyclohex-1-ene-1-carboxylate and 291 mg (2.43 mmol, 2 eq) of trimethyl iodide following the general reaction protocol. Subsequent purification via flash column chromatography (in pure petroleum ether) on a silica gel column yielded 62.8 mg (57.7% combined yield) of a clear oily liquid with an Rf value of 0.5 (silica gel, petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.35 (td, *J* = 3.8, 1.8 Hz, 1H), 4.34 (d, *J* = 2.8 Hz, 1H), 4.08 (d, *J* = 2.8 Hz, 1H), 2.27 (s, 3H), 2.17 (tdd, *J* = 6.7, 4.3, 2.1 Hz, 4H), 1.69 (qd, *J* = 6.3, 2.5 Hz, 2H), 1.61 (tq, *J* = 5.4, 3.2, 2.3 Hz, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.09, 131.65, 125.41, 83.35, 71.46, 25.38, 25.09, 22.67, 22.06, 15.11.HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{10}H_{16}OSNa$207.0814, Found 207.0821. New compound.

2-(1-((methylthio)methoxy)vinyl)furan



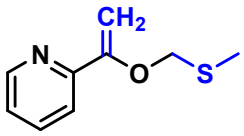
Compound **3p** was synthesized from 50 mg (0.396 mmol, 1 eq) of methyl furan-2-carboxylate and 161.82 mg (0.792 mmol, 2 eq) of trimethylsulphur iodide following the standard reaction protocol. The subsequent purification via flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 40 mg of a clear liquid (69% combined yield) with an Rf value of 0.5 (silica gel, PE/EA = 100:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.53 (dd, *J* = 3.4, 0.9 Hz, 1H), 6.41 (dd, *J* = 3.3, 1.8 Hz, 1H), 5.04 (s, 2H), 4.91 (d, *J* = 3.1 Hz, 1H), 4.32 (d, *J* = 3.0 Hz, 1H), 2.29 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.54, 150.19, 142.37, 111.06, 106.83, 84.35, 71.95, 14.96. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_8H_{10}O_2SNa$ 193.0193, Found 193.0201. New compound.

2-(1-((methylthio)methoxy)vinyl)thiophene



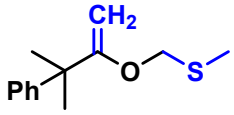
Compound **3q** was synthesized from 50 mg (0.351 mmol, 1 eq) of methyl thiophene-2-carboxylate and 134.54 mg (0.702 mmol, 2 eq) of trimethylsulphur iodide following the standard reaction protocol. The subsequent purification via flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column yielded 37 mg of a clear liquid (66% integrated yield) with an Rf value of 0.5 (silica gel, PE/EA = 100:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 2H), 7.01 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.06 (s, 2H), 4.82 (d, *J* = 3.4 Hz, 1H), 4.27 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.59, 140.08, 127.17, 125.21, 124.06, 84.41, 72.04, 15.01. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_8H_{10}OS_2Na$ 209.0065, Found 209.0082. New compound.

2-(1-((methylthio)methoxy)vinyl)pyridine



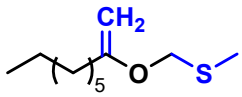
Compound **3r** was synthesized from 50 mg (0.364 mmol, 1 eq) of methyl 2-pyridinecarboxylate and 148 mg (0.728 mmol, 2 eq) of trimethyl iodide following the general reaction protocol. Subsequent purification via flash column chromatography (1% ethyl acetate in petroleum ether) on a silica gel column furnished 42 mg (71% combined yield) of a yellow-green liquid with an Rf value of 0.5 (silica gel, PE/EA = 5:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.70 (dd, *J* = 3.7, 1.4 Hz, 2H), 7.23 (td, *J* = 5.0, 3.2 Hz, 1H), 5.59 (d, *J* = 2.6 Hz, 1H), 5.11 (s, 2H), 4.48 (d, *J* = 2.5 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.13, 153.12, 149.04, 136.50, 123.24, 119.24, 87.52, 72.21, 15.12. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_9H_{10}NOSNa$ 203.0375, Found 203.0513. New compound.

methyl(((3-methyl-3-phenylbut-1-en-2-yl)oxy)methyl)sulfane



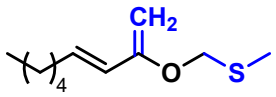
Compound **3s** was synthesized from 100 mg (0.561 mmol, 1 eq) of methyl 2-methyl-2-phenylpropionate and 229 mg (1.12 mmol, 2 eq) of trimethyl iodide following the general reaction protocol. Purification through flash column chromatography (in pure petroleum ether) on a silica gel column yielded 38.6 mg (41.1% combined yield) of a clear oily liquid with an Rf value of 0.5 (silica gel, PE/EA =50:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.38 (m, 2H), 7.31 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.23 – 7.18 (m, 1H), 4.82 (s, 2H), 4.41 (d, *J* = 2.9 Hz, 1H), 4.13 (d, *J* = 3.0 Hz, 1H), 1.93 (s, 3H), 1.52 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.12, 147.58, 127.95, 126.00, 125.81, 82.76, 70.94, 43.77, 27.91, 14.52. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{13}H_{18}OSNa2$ 54.0970, Found 254.0996. New compound.

methyl((non-1-en-2-yloxy)methyl)sulfane



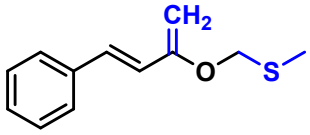
Compound **3t** was synthesized from 100 mg (0.437 mmol, 1 eq) of methyl methyl octanoate and 178 mg (0.875 mmol, 2 eq) of trimethyl iodide following the general reaction protocol. Subsequent purification through flash column chromatography (in pure petroleum ether) on a silica gel column yielded 77.1 mg (60.2% overall yield) of a clear oily liquid with an Rf value of 0.5 (silica gel, petroleum ether). ^{1}H NMR (400 MHz, Chloroform-d) δ 4.83 (s, 2H), 4.02 (d, J = 2.3 Hz, 1H), 3.90 (d, J = 2.3 Hz, 1H), 2.23 (s, 3H), 2.15 – 2.09 (m, 2H), 1.51 (t, J = 7.5 Hz, 2H), 1.29 (d, J = 5.1 Hz, 8H), 0.90 (d, J = 6.5 Hz, 3H). 13C NMR (101 MHz, Chloroform-d) δ 161.95, 82.88, 70.99, 34.99, 31.92, 29.65, 29.36, 27.30, 22.68, 14.89, 14.09. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{11}H_{22}OSNa$ 225.1283, Found 225.1301. New compound.

Methyl((nona-1,3-dien-2-yloxy)methyl)sulfane



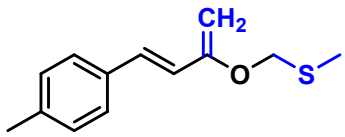
Compound **3u** was prepared from methyl methyl octenoate (100 mg, 0.441 mmol, 1 eq) and trimethyl iodide (180.31 mg, 0.882 mmol, 2 eq) according to the general reaction procedure. Purification by flash column chromatography (pure petroleum ether) on a silica gel column afforded 60.2 g (47% overall yield), clear oily liquid, Rf=0.5 (silica gel, petroleum ether). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.13 (dt, J = 15.6, 7.0 Hz, 1H), 5.87 (dt, J = 15.5, 1.5 Hz, 1H), 4.94 (s, 2H), 4.20 (d, J = 2.3 Hz, 1H), 4.11 (d, J = 2.3 Hz, 1H), 2.27 (s, 3H), 2.11 (qd, J = 7.1, 1.4 Hz, 2H), 1.35 – 1.28 (m, 6H), 0.91 (d, J = 1.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 157.00, 131.94, 125.82, 86.93, 71.39, 32.28, 31.44, 28.72, 22.51, 15.03, 14.01. HRMS(ESI) m/z:[M + Na]$^{+}$Calcd of $C_{14}H_{14}OSNa$ 223.1127, Found 253.0660. New compound.

(E)-methyl(((4-phenylbuta-1,3-dien-2-yl)oxy)methyl)sulfane



Compound **3v** was synthesized from 50 mg (0.283 mmol, 1 eq) of ethyl cinnamate and 115.81 mg (0.566 mmol, 2 eq) of trimethyl iodide following the standard reaction protocol. Purification via flash column chromatography (using 1% ethyl acetate in petroleum ether) on a silica gel column yielded 42 mg (81% combined yield) of a yellow-green liquid with an Rf value of 0.5 (silica gel, PE/EA = 50:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.01 (d, *J* = 15.9 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 5.04 (s, 2H), 4.47 (d, *J* = 2.5 Hz, 1H), 4.35 (d, *J* = 2.5 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.88, 136.67, 129.01, 128.63, 127.86, 126.77, 124.56, 90.00, 71.66, 15.14. (DEPT-135) ^{13}C NMR (101 MHz, Chloroform-*d*) δ 129.00, 128.64, 127.87, 126.78, 124.55. HRMS(ESI) m/z: [M + Na]$^{+}$Calcd of $C_{12}H_{14}OSNa$ 229.0657, Found 229.0668. New compound.

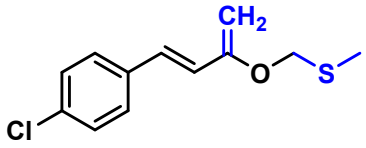
(E)-methyl(((4-(p-tolyl)buta-1,3-dien-2-yl)oxy)methyl)sulfane



Compound **3w** was synthesized from 50 mg (0.262 mmol, 1 eq) of ethyl 4-methylcinnamate and 107.27 mg (0.524 mmol, 2 eq) of trimethyl iodide following the standard reaction procedure. The subsequent purification through flash column chromatography (employing 1% ethyl acetate in petroleum ether) on a silica gel column resulted in the isolation of 35 mg (70% combined yield) of a yellow-green liquid with an Rf value of 0.5 (silica gel, PE/EA = 50:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.34 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.99 (d, *J* = 15.9 Hz, 1H), 6.54 (d, *J* = 15.9 Hz, 1H), 5.03 (s, 2H), 4.44 (d, *J* = 2.4 Hz, 1H), 4.33 (d, *J* = 2.4 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.11,

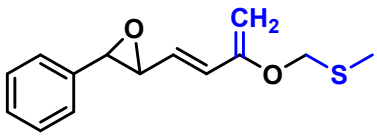
137.75, 133.92, 129.35, 128.98, 126.70, 123.61, 89.48, 71.68, 21.23, 15.09. HRMS(ESI) m/z: $[M + Na]^+$ Calcd of $C_{13}H_{16}OSNa$ 243.0814, Found 243.0818. New compound.

(E)-(((4-(4-chlorophenyl)buta-1,3-dien-2-yl)oxy)methyl)(methyl)sulfane



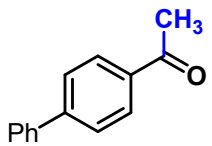
Compound 3x was synthesized from 50 mg (0.262 mmol, 1 eq) of ethyl 4-chlorocinnamate and 107.27 mg (0.524 mmol, 2 eq) of trimethyl iodide following the established reaction protocol. The subsequent purification through flash column chromatography (using 1% ethyl acetate in petroleum ether) on a silica gel column resulted in the isolation of 46 mg (80% combined yield) of a yellow-green liquid with an Rf value of 0.5 (silica gel, PE/EA = 50:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.26 (m, 4H), 6.94 (d, *J* = 15.9 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 5.02 (s, 2H), 4.46 (d, *J* = 2.5 Hz, 1H), 4.36 (d, *J* = 2.5 Hz, 1H), 2.32 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.68, 135.22, 133.47, 128.79, 127.90, 127.73, 125.17, 90.43, 71.76, 15.11. HRMS(ESI) m/z: $[M + Na]^+$ Calcd of $C_{12}H_{13}ClOSNa$ 263.0627, Found 253.0660. New compound.

(E)-2-(3-((methylthio)methoxy)buta-1,3-dien-1-yl)-3-phenyloxirane



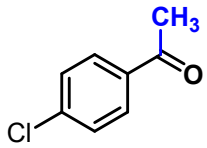
Compound 3y was synthesized from 50 mg (0.229 mmol, 1 eq) of methyl 2-pyridinecarboxylate and 93 mg (0.458 mmol, 2 eq) of trimethyl iodide following the established reaction protocol. The subsequent purification through flash column chromatography (using 1% ethyl acetate in petroleum ether) on a silica gel column resulted in the isolation of 32 mg (66% combined yield) of a yellow-green liquid with an Rf value of 0.5 (silica gel, PE/EA = 50:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.25 (m, 6H), 6.29 (d, *J* = 15.5 Hz, 1H), 6.04 (d, *J* = 7.5 Hz, 1H), 4.97 (s, 2H), 4.37 (d, *J* = 2.6 Hz, 1H), 4.30 (d, *J* = 2.5 Hz, 1H), 3.84 (d, *J* = 1.9 Hz, 1H), 3.43 (dd, *J* = 7.5, 2.0 Hz, 1H), 2.29 (s, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.74, 136.99, 130.03, 128.52, 128.25, 128.10, 126.97, 125.45, 90.16, 71.64, 62.22, 60.82, 15.09. ^{13}C NMR(DEPT-135)(101 MHz, Chloroform-*d*) δ 130.06, 128.54, 128.27, 128.12, 126.96, 126.50, 125.46, 62.27, 60.82. HRMS(ESI) m/z:$[M + Na]^+$Calcd of $C_{14}H_{16}NO_2SNa$ 271.0871, Found 271.0868. New compound.

1-([1,1'-biphenyl]-4-yl)ethan-1-one[4]



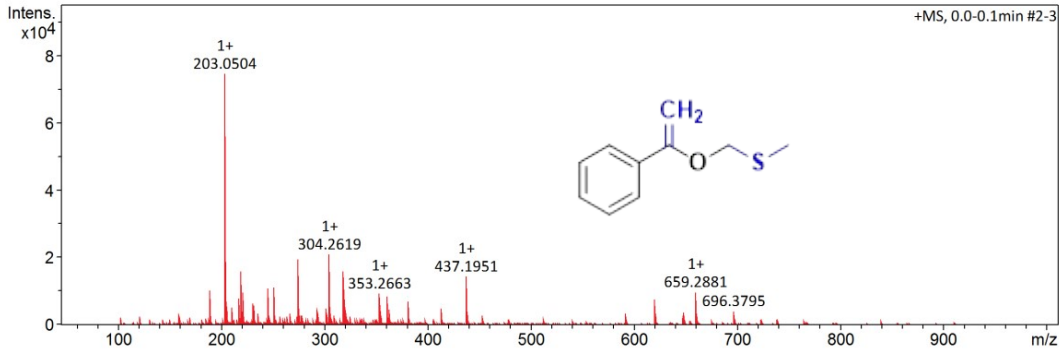
Compound **5l** was synthesized from 150 mg (0.58 mmol) of **3l** using the established reaction protocol. Following purification via flash column chromatography on a silica gel column (PE/EA=40:1 v/v), 115 mg (98% overall yield) of a white solid with an Rf value of 0.5 and a melting point of 194-198 °C was isolated. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.04 (m, 2H), 7.73 – 7.64 (m, 4H), 7.53 – 7.41 (m, 3H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.70, 145.79, 139.90, 135.90, 128.96, 128.92, 128.24, 127.28, 127.23, 26.64. White crystal, mp 194–198 ℃.CAS RN：92-91-1.

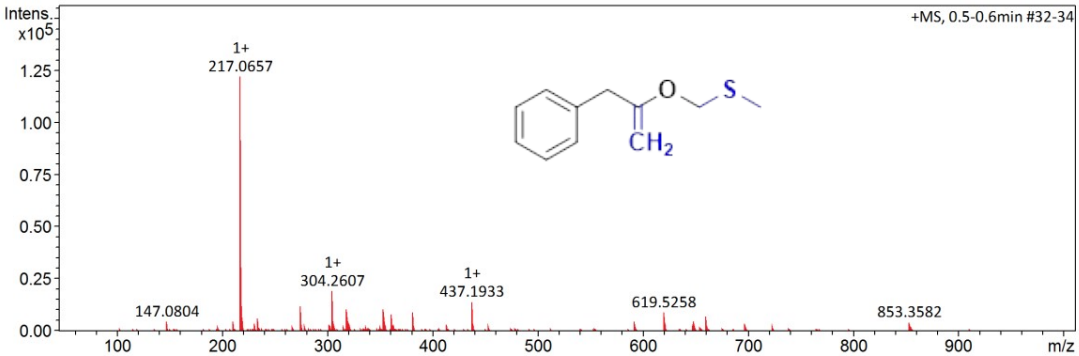
1-(4-chlorophenyl)ethan-1-one[5]

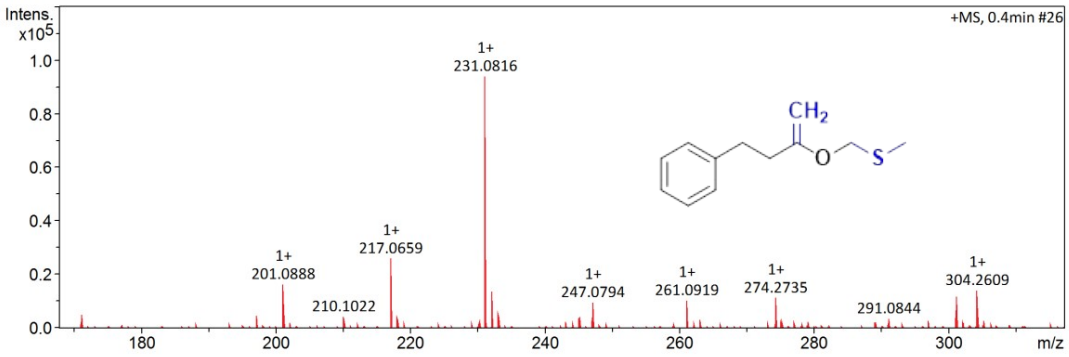


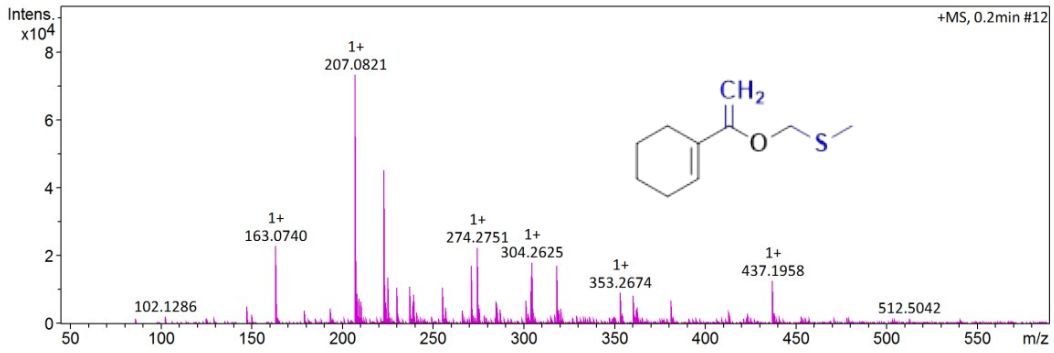
Compound **5e** was synthesized from 100 mg (0.58 mmol) of **3e** using the established reaction protocol. Following purification via flash column chromatography on a silica gel column (PE/EA=40:1 v/v), 70.5 mg (98% overall yield) of transparent liquid with an Rf value of 0.5. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.88 (m, 2H), 7.44 – 7.41 (m, 2H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.73, 139.53, 135.45,129.71, 128.86, 26.49. CAS RN: 92-91-1.

4.HRMS

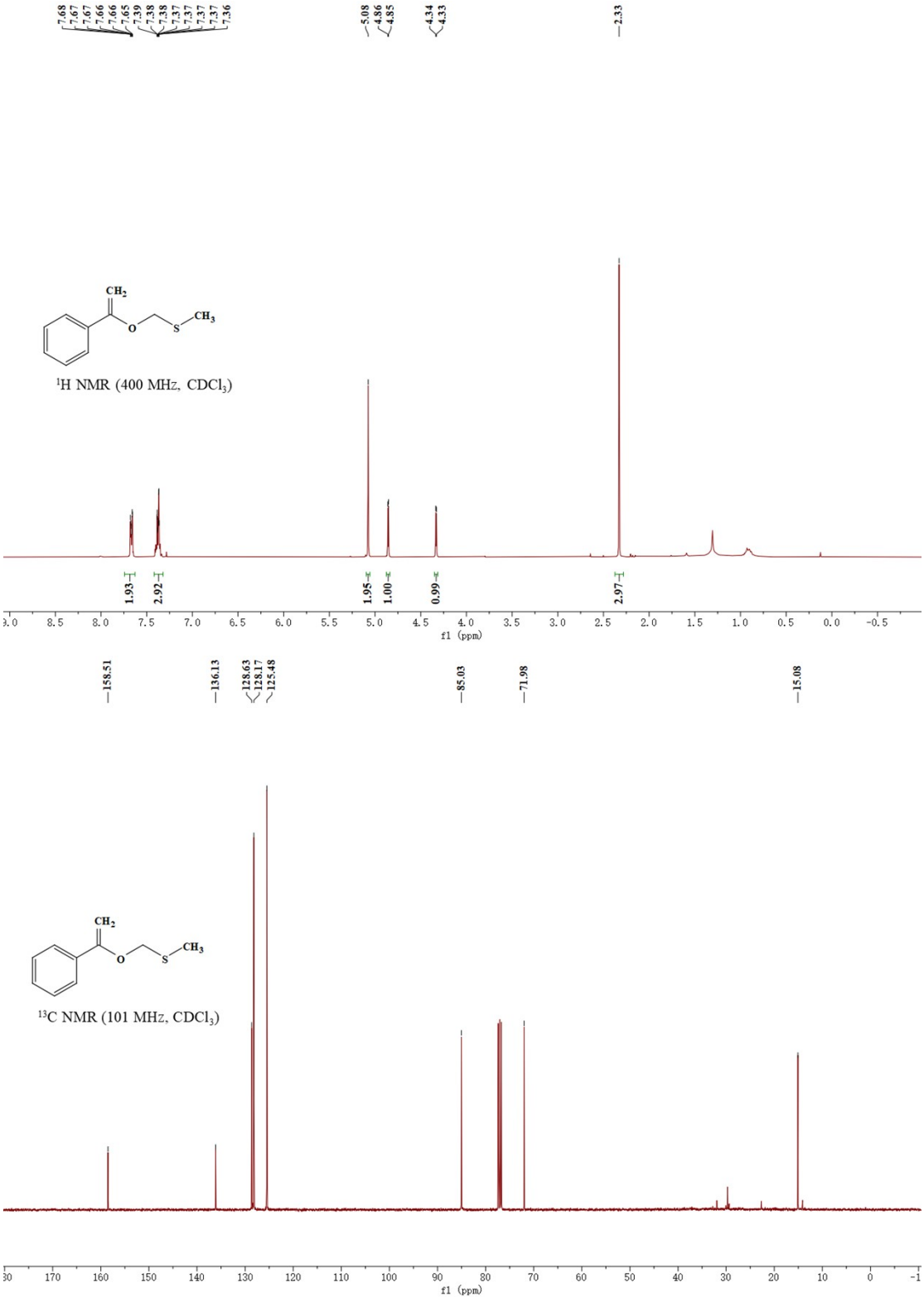


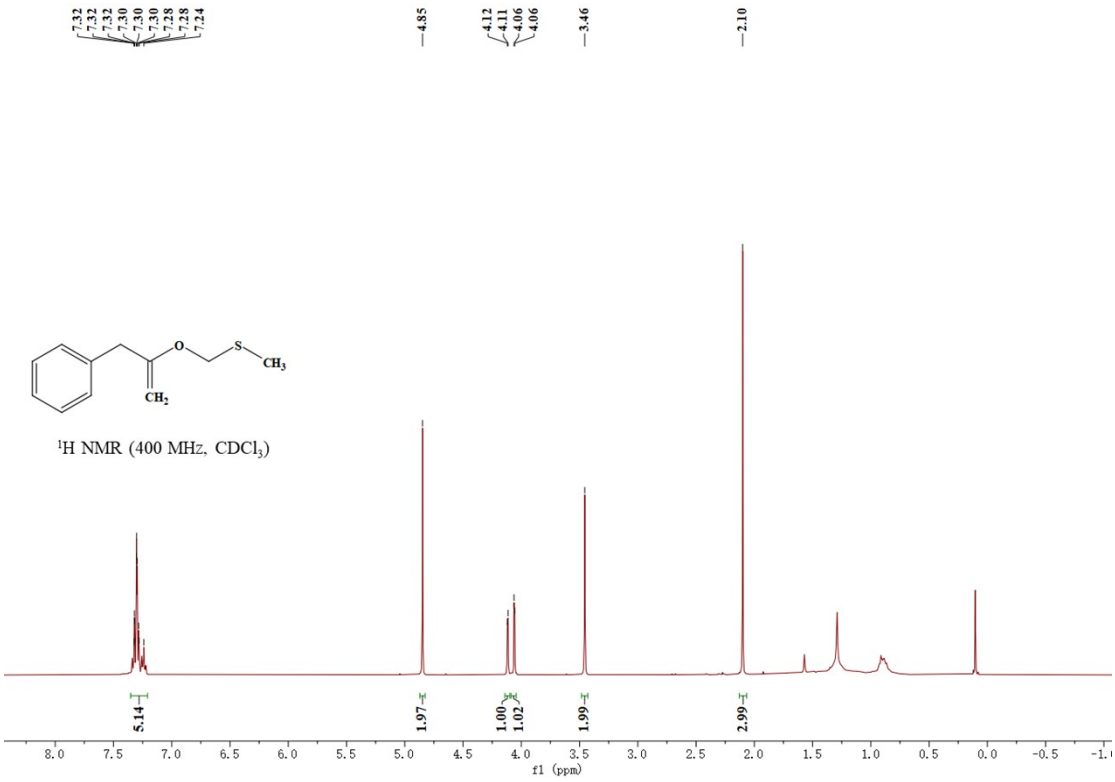


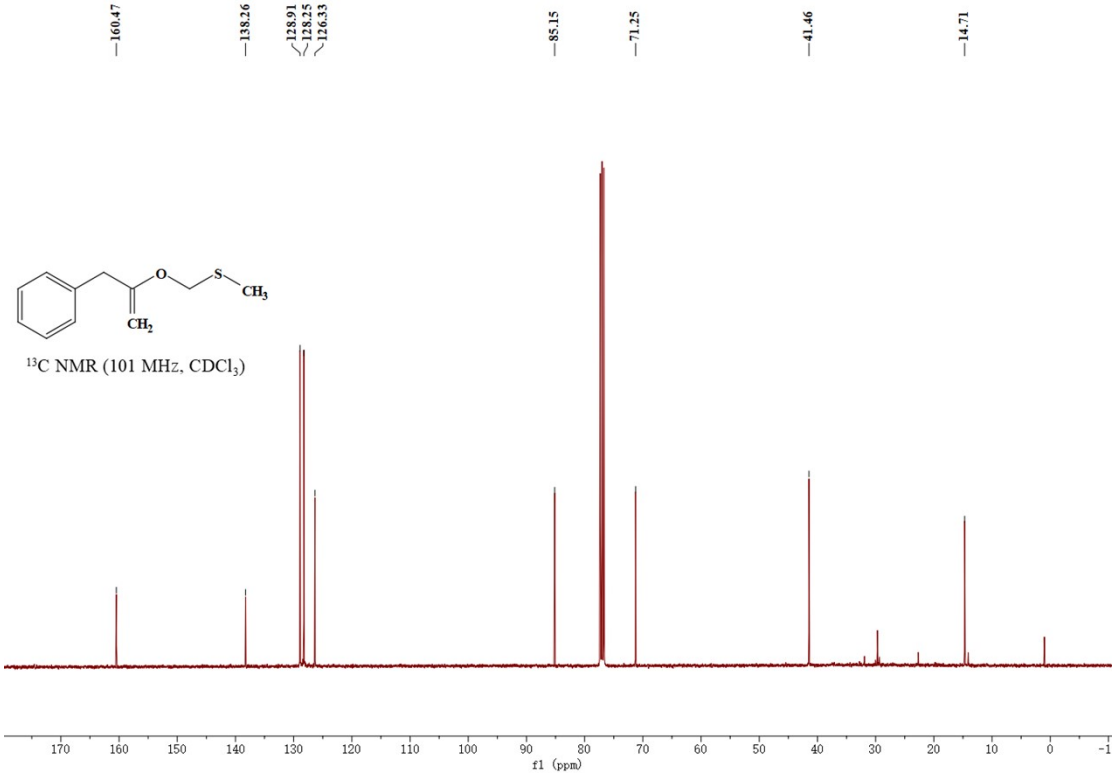

Intens.
x10^5
+MS, 0.4min #26
1+
231.0816
1+
217.0659
1+
201.0888
210.1022
1+
247.0794
1+
261.0919
1+
274.2735
291.0844
1+
304.2609
CH2
O
S
m/z

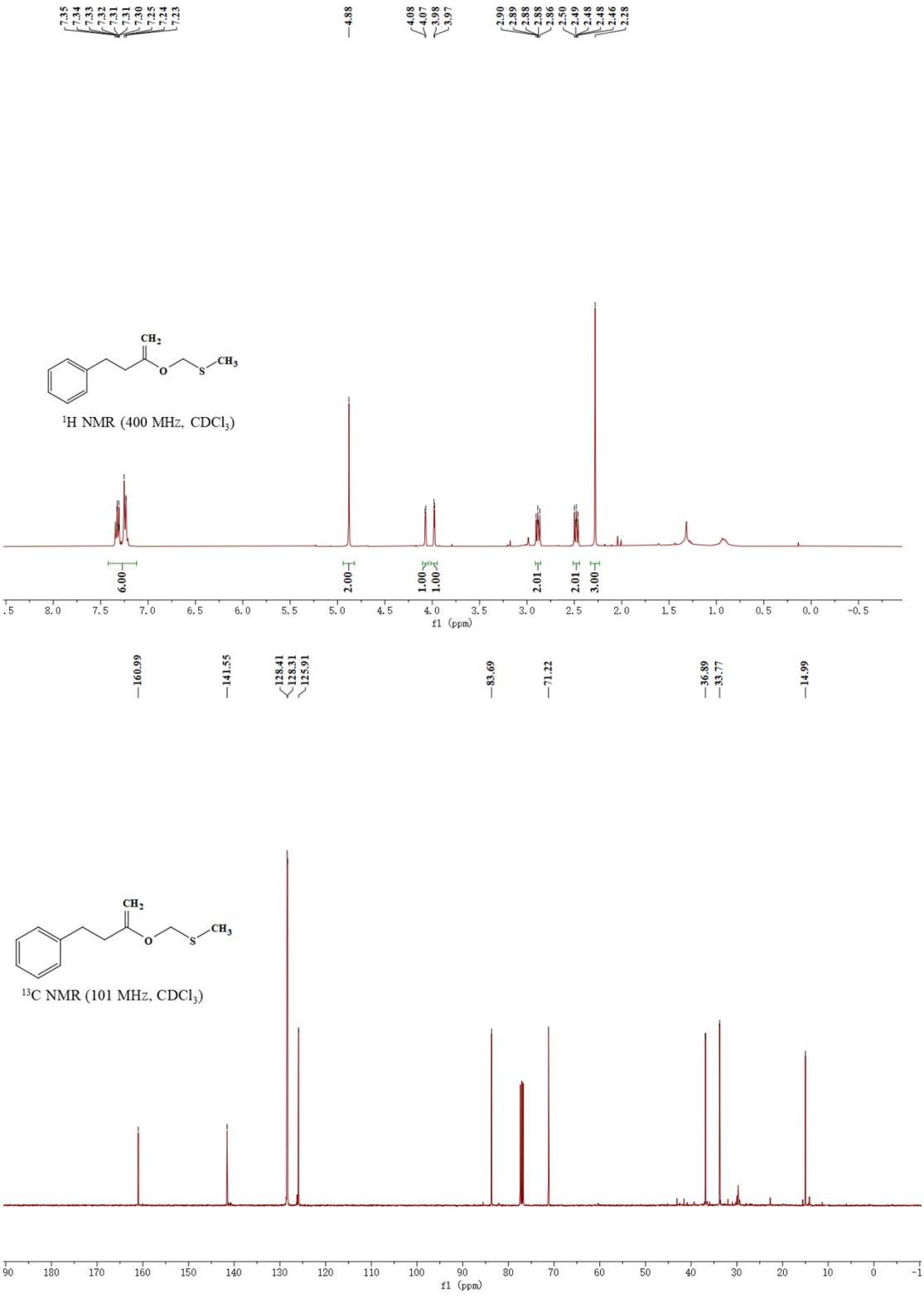

Intens.
x10^4
+MS, 0.2min #12
1+
207.0821
1+
163.0740
1+
274.2751
1+
304.2625
1+
353.2674
1+
437.1958
102.1286
512.5042
CH2
O
S
m/z

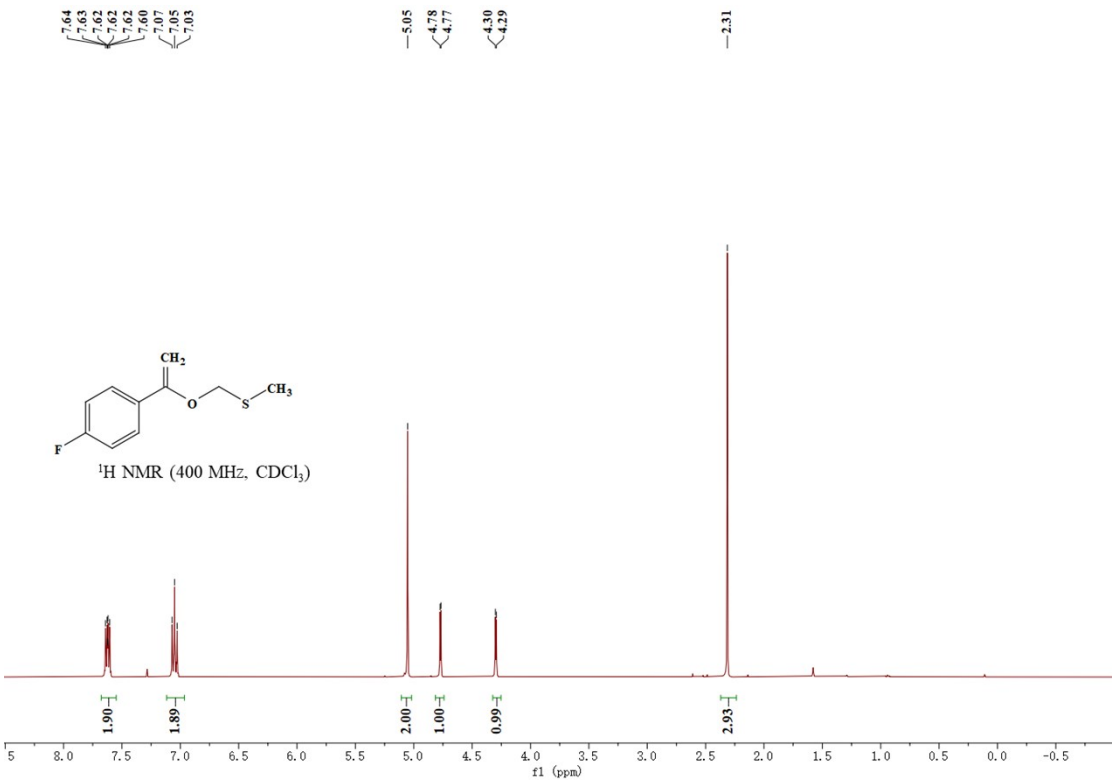
5.^{1}H and ^{13}C NMR Spectrogram

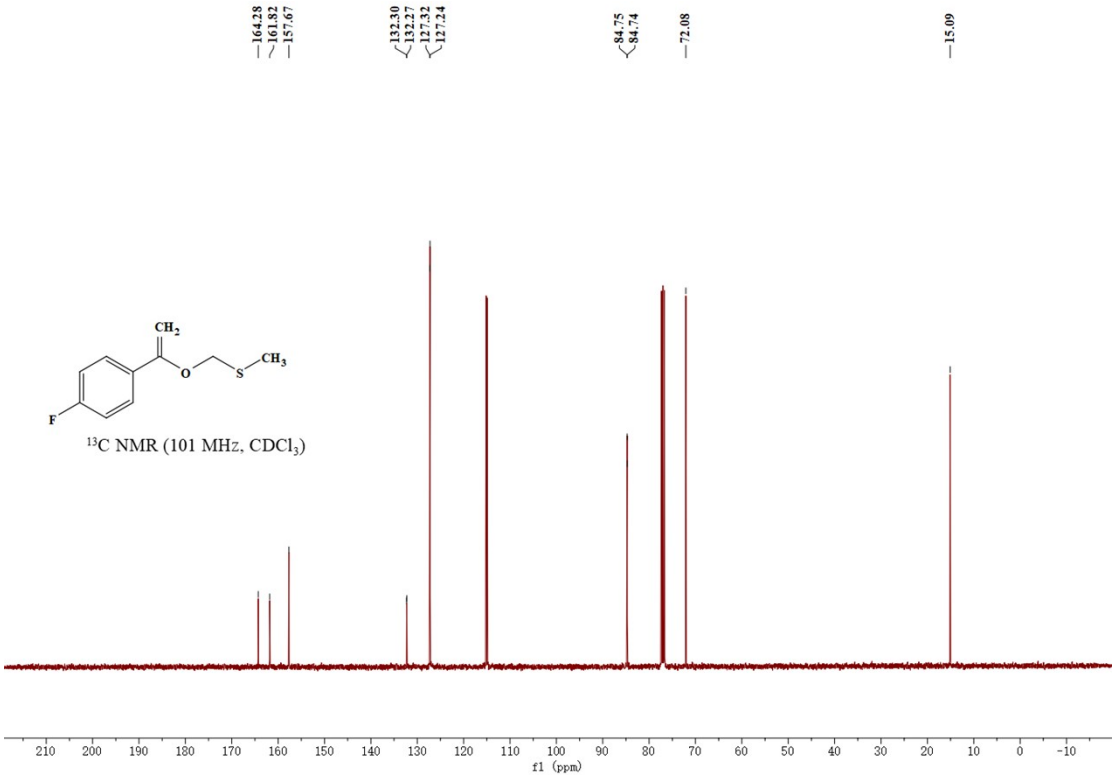


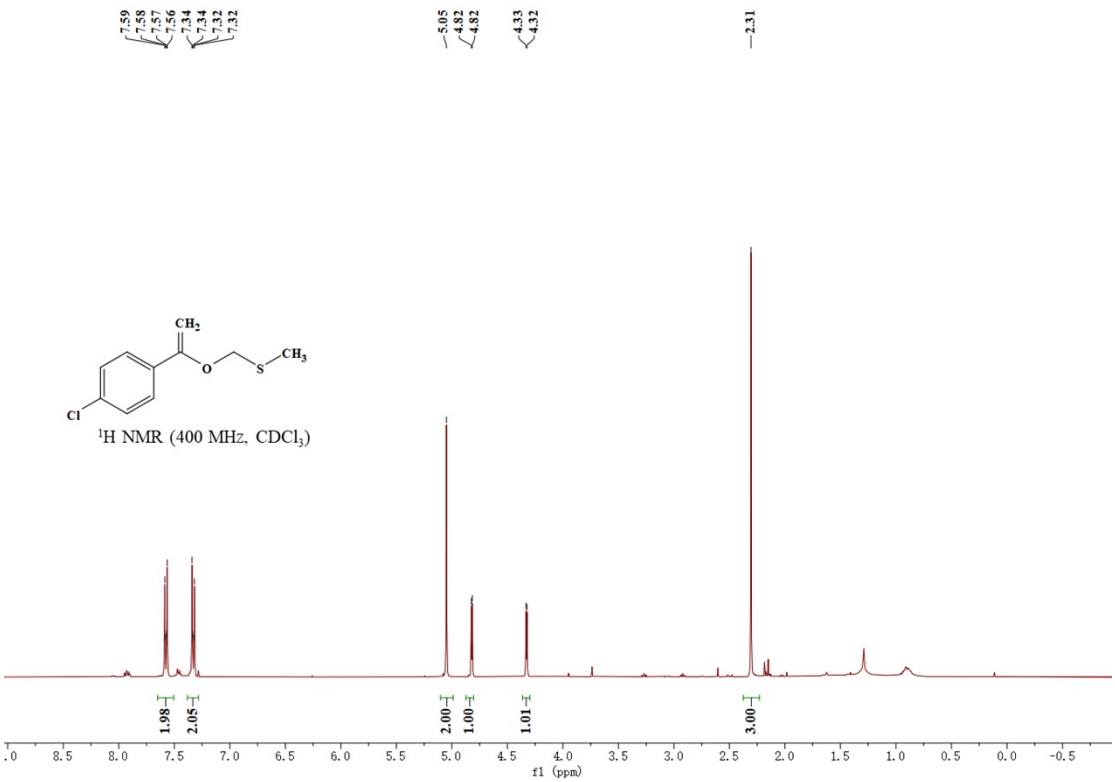

7.32
7.32
7.32
7.30
7.30
7.28
7.28
7.24
4.85
4.12
4.11
4.06
4.06
3.46
2.10
O
S
CH3
CH2
1H NMR (400 MHz, CDCl3)
5.14
1.97
1.00
1.02
1.99
2.99
f1 (ppm)

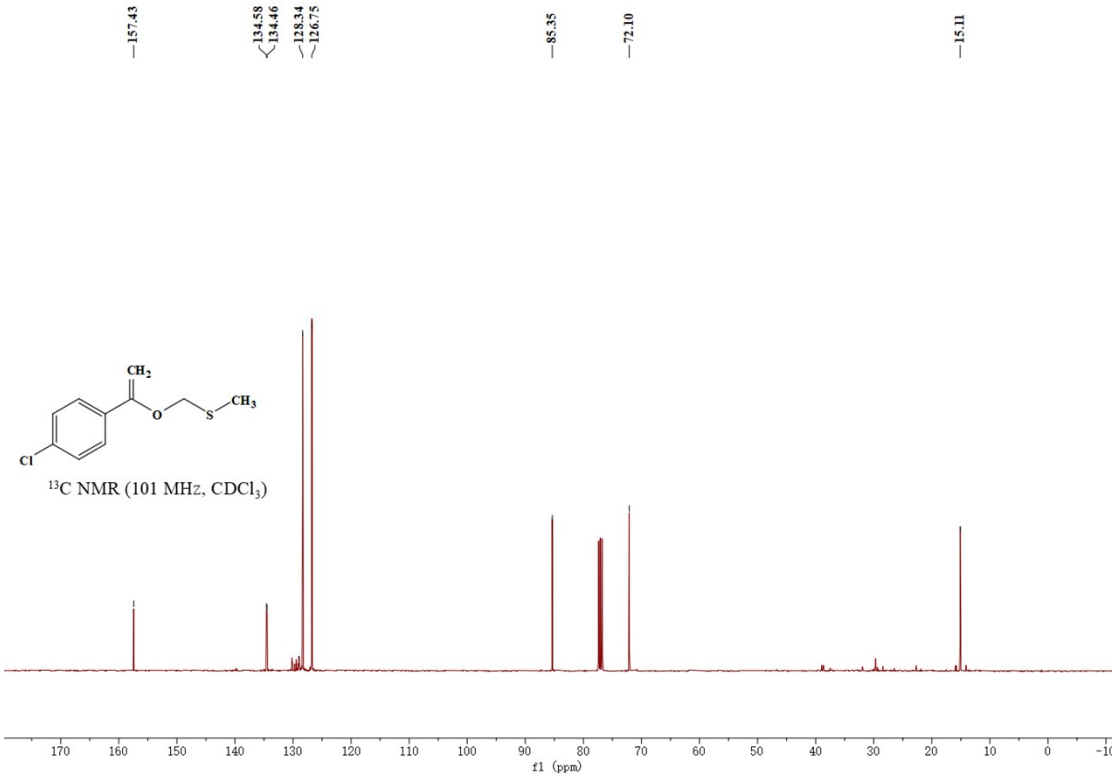

160.47
138.26
128.91
128.25
126.33
85.15
71.25
41.46
14.71
O
S
CH3
CH2
13C NMR (101 MHz, CDCl3)
f1 (ppm)

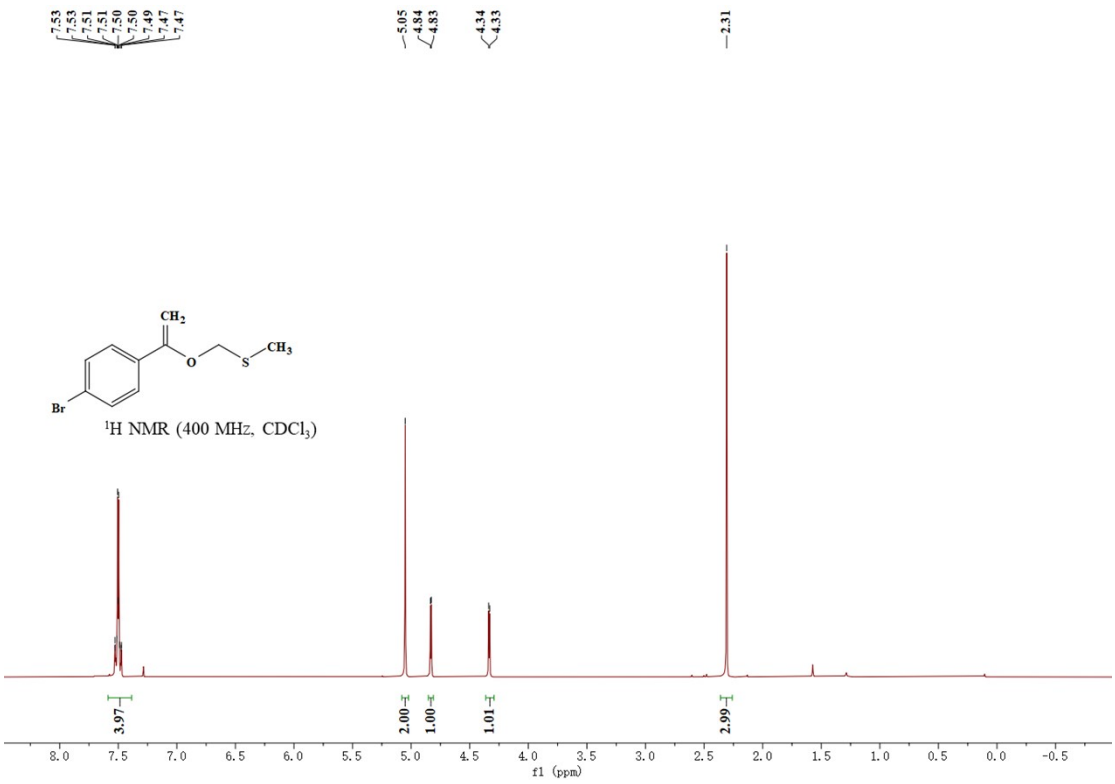

7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.25
7.24
7.23
4.88
4.08
4.07
3.98
3.97
2.90
2.89
2.88
2.88
2.86
2.50
2.49
2.48
2.48
2.46
2.28
CH2
O
S
CH3
1H NMR (400 MHz, CDCl3)
6.00
2.00
1.00
1.00
2.01
2.01
3.00
f1 (ppm)
160.99
141.55
128.41
128.31
125.91
83.69
71.22
36.89
33.77
14.99
13C NMR (101 MHz, CDCl3)
f1 (ppm)

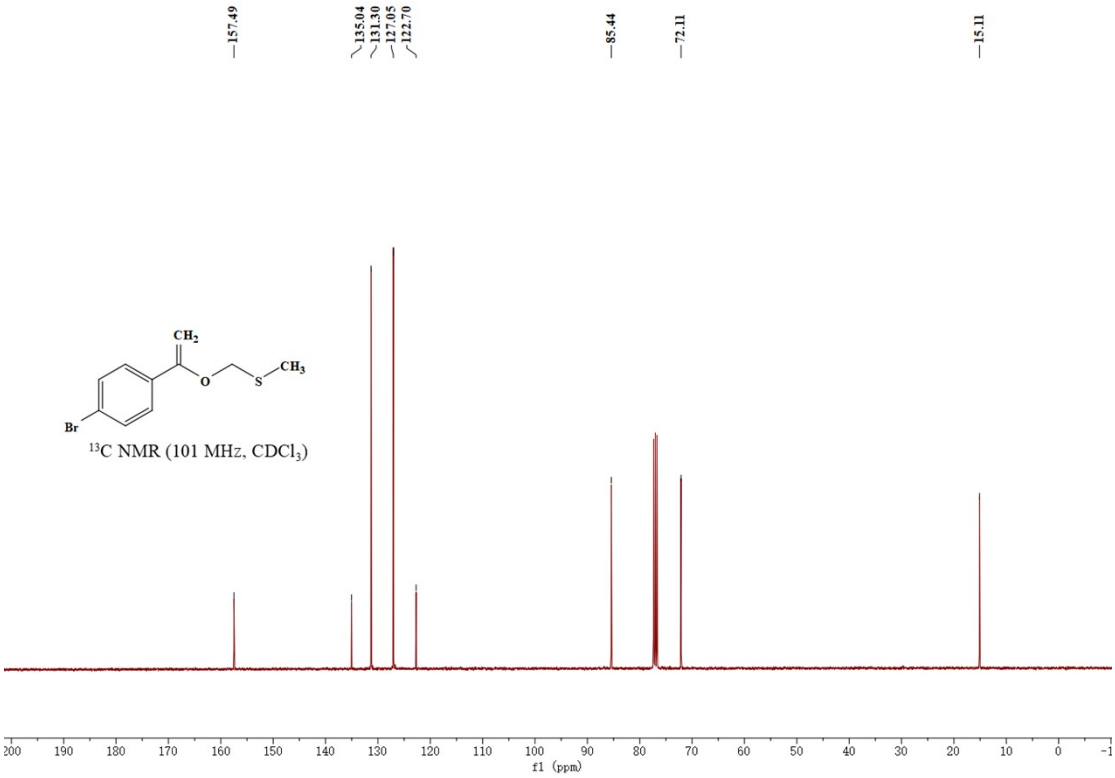

7.64
7.63
7.62
7.62
7.62
7.60
7.07
7.05
7.03
5.05
4.78
4.77
4.30
4.29
2.31
CH2
O
S
CH3
F
1H NMR (400 MHz, CDCl3)
1.90
1.89
2.00
1.00
0.99
2.93
f1 (ppm)

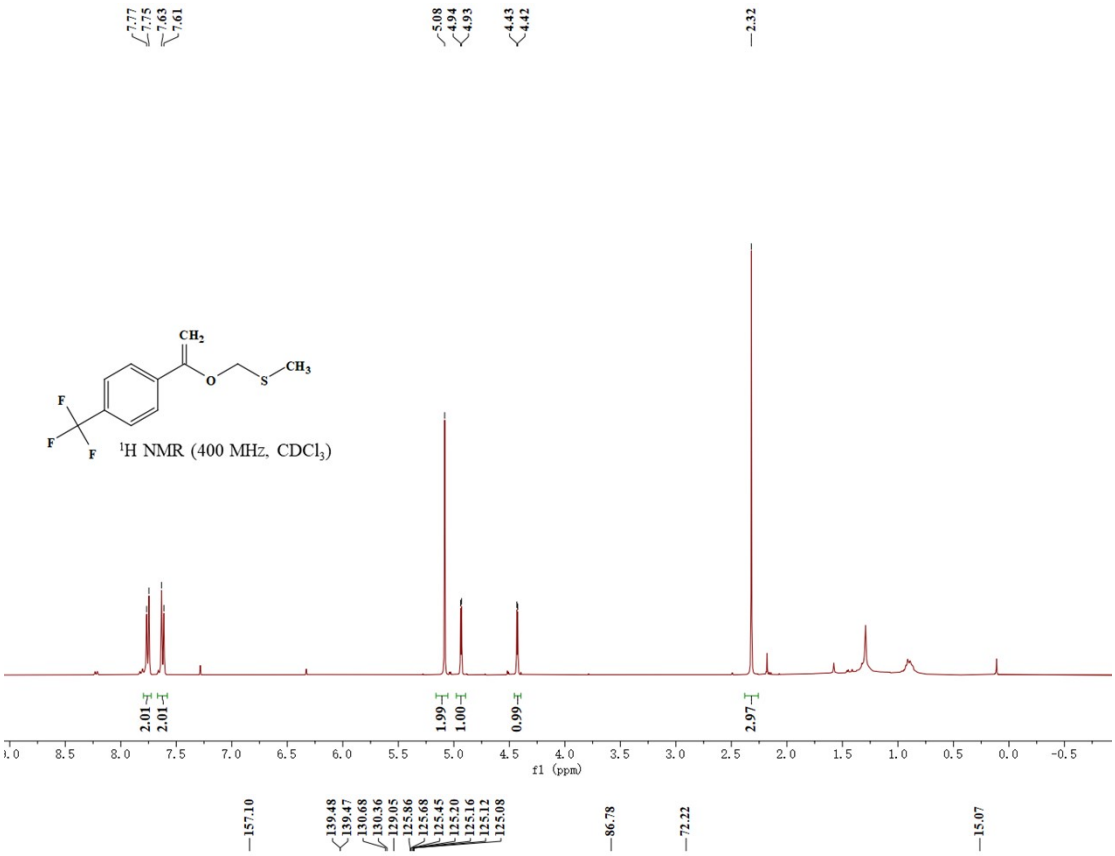

164.28
161.82
157.67
132.30
132.27
127.32
127.24
84.75
84.74
72.08
15.09
CH2
O
S
CH3
F
13C NMR (101 MHz, CDCl3)
f1 (ppm)

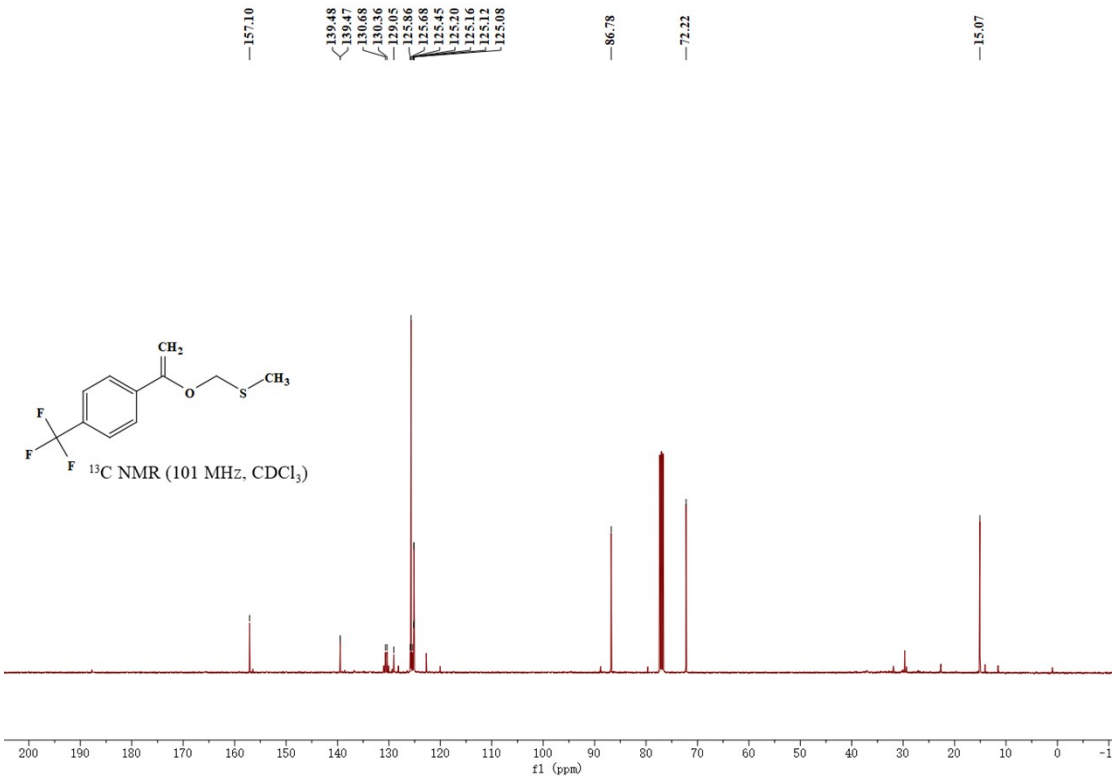

7.59
7.58
7.57
7.56
7.34
7.34
7.32
7.32
5.05
4.82
4.82
4.33
4.32
2.31
CH2
O
S
CH3
Cl
1H NMR (400 MHz, CDCl3)
1.98
2.05
2.00
1.00
1.01
3.00
f1 (ppm)

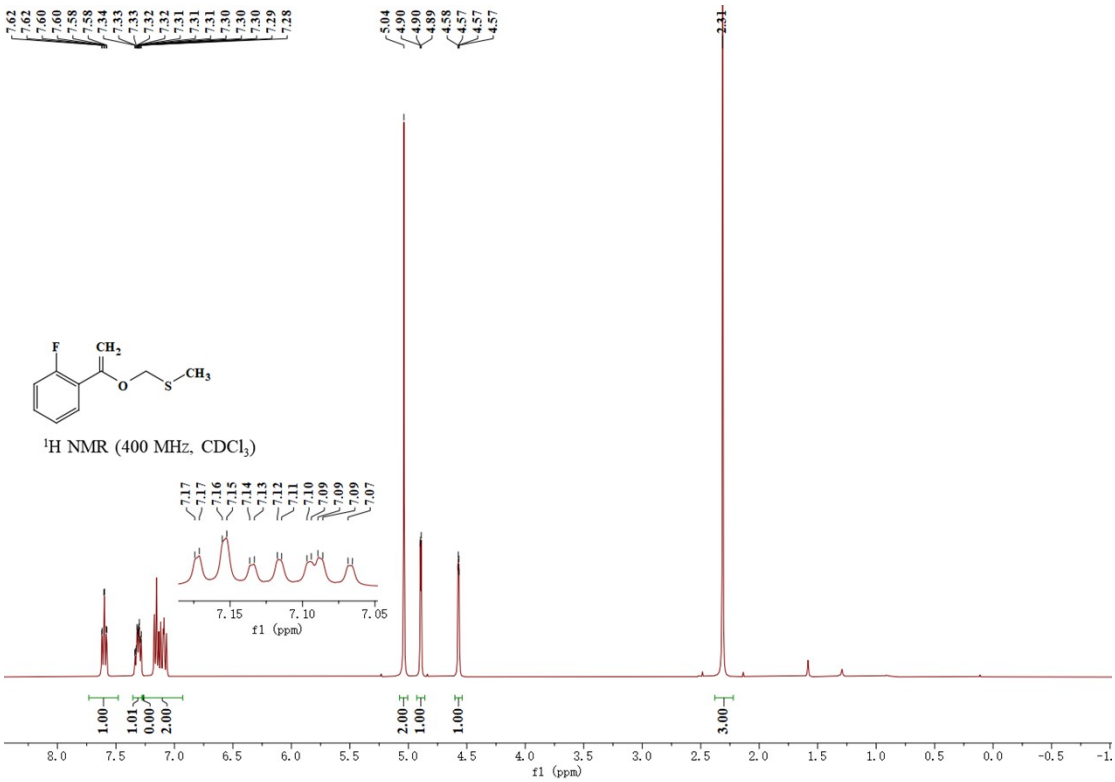

157.43
134.58
134.46
128.34
126.75
85.35
72.10
15.11
CH2
O
S
CH3
Cl
13C NMR (101 MHz, CDCl3)
f1 (ppm)

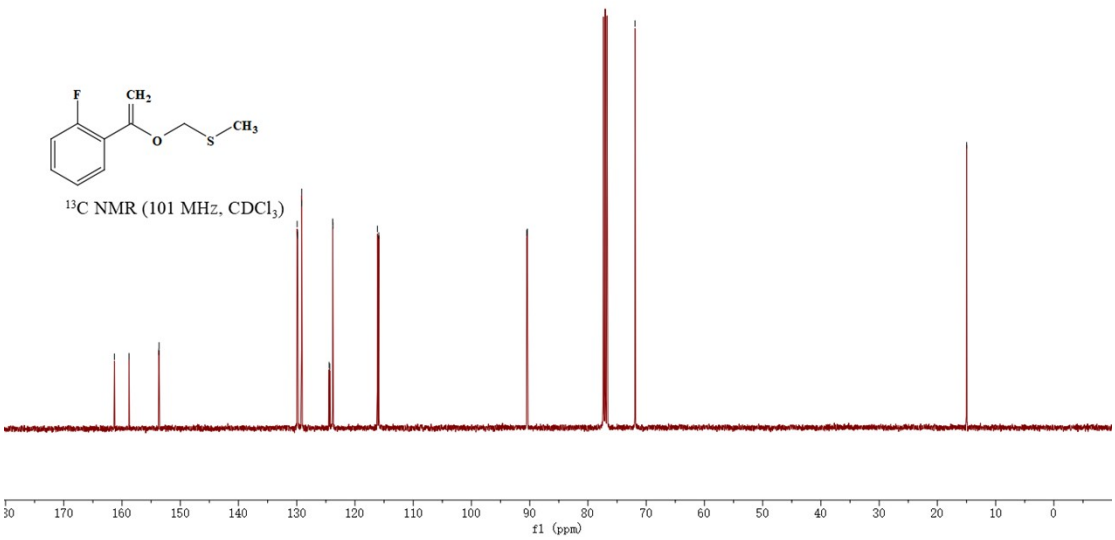

7.53
7.53
7.51
7.51
7.50
7.50
7.49
7.47
7.47
5.05
4.84
4.83
4.34
4.33
2.31
CH2
O
S
CH3
Br
1H NMR (400 MHz, CDCl3)
3.97
2.00
1.00
1.01
2.99
f1 (ppm)

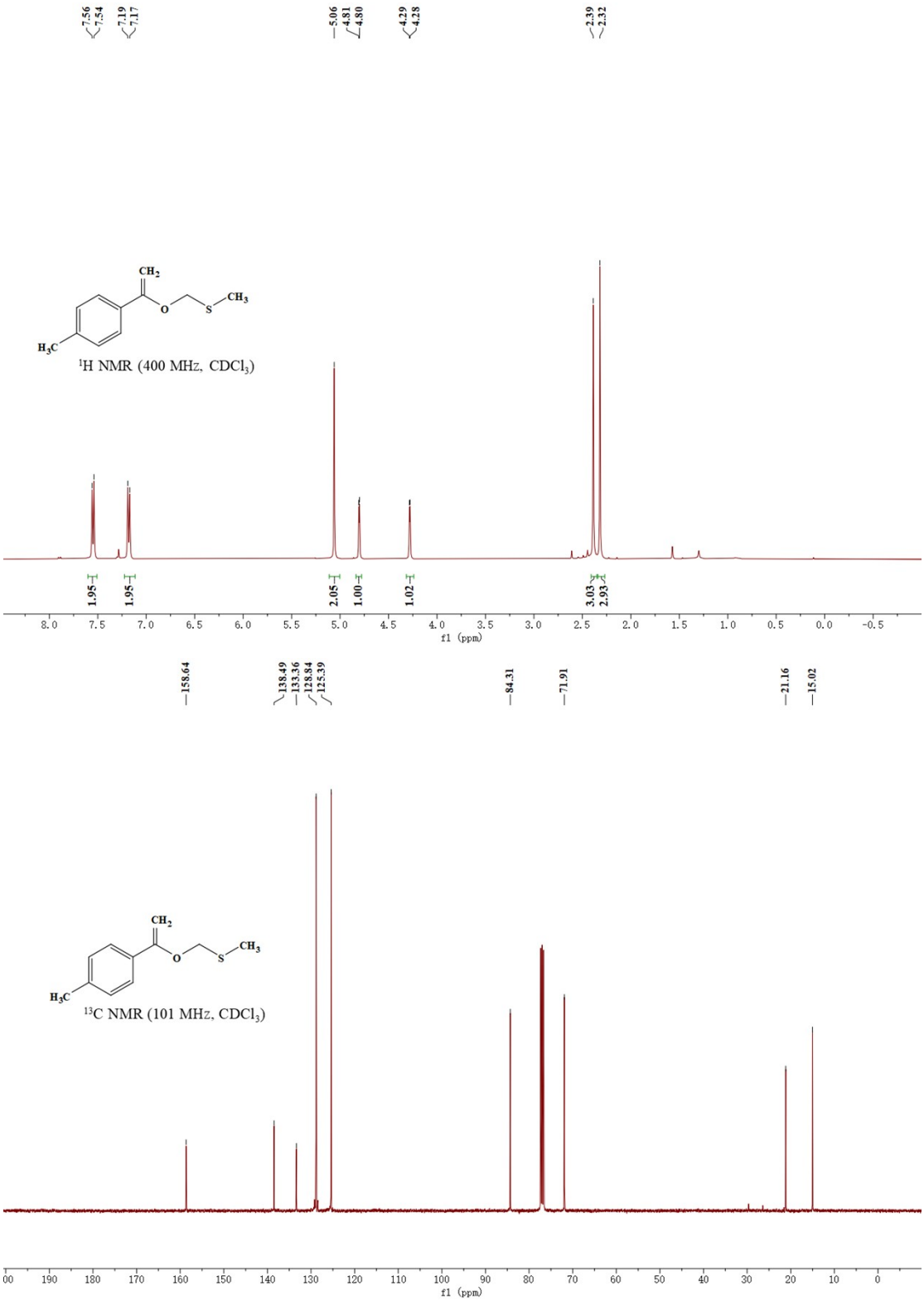

157.49
135.04
131.30
127.05
122.70
85.44
72.11
15.11
CH2
O
S
CH3
Br
13C NMR (101 MHz, CDCl3)
f1 (ppm)

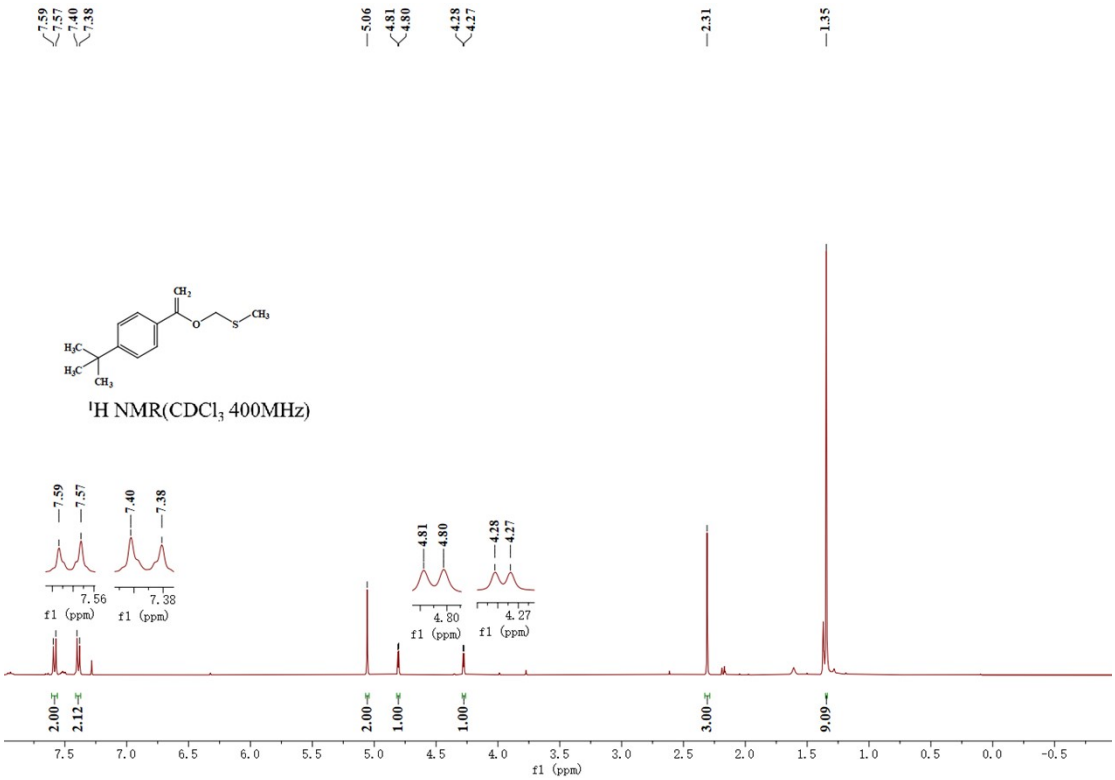

7.77
7.75
7.63
7.61
5.08
4.94
4.93
4.43
4.42
2.32
CH2
O
S
CH3
F
F
F
1H NMR (400 MHz, CDCl3)
2.01
2.01
1.99
1.00
0.99
2.97
f1 (ppm)

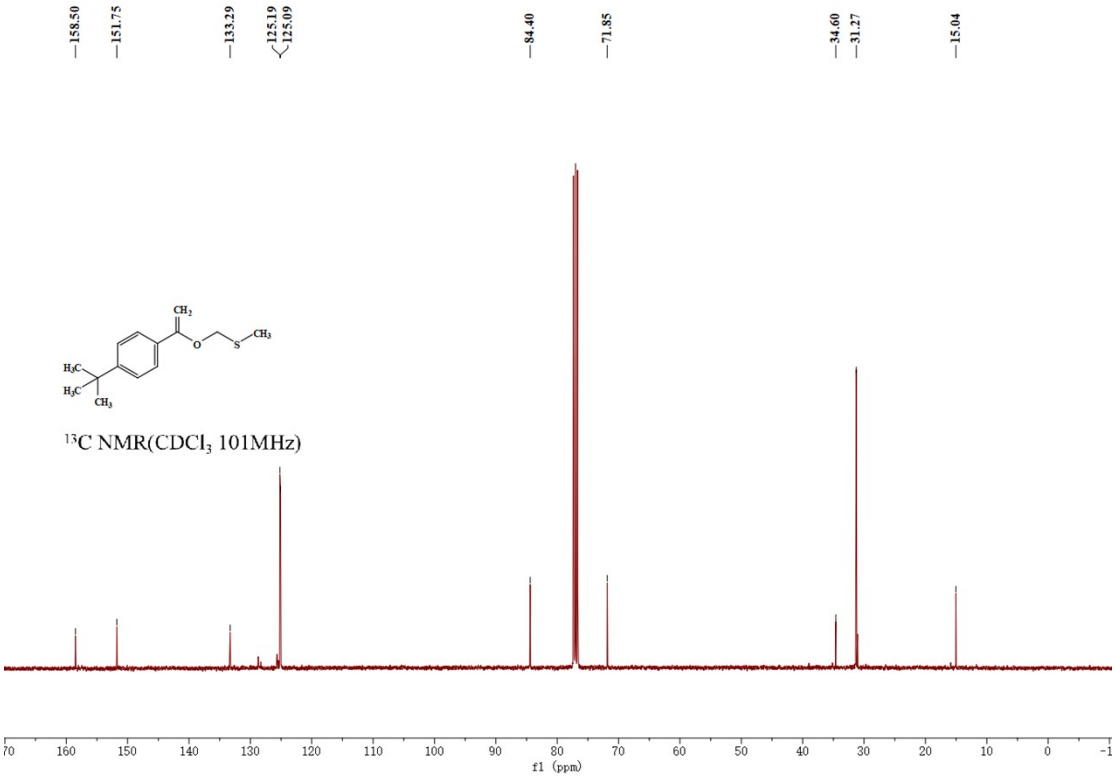

157.10
139.48
139.47
130.68
130.36
129.05
125.86
125.63
125.45
125.20
125.16
125.12
125.08
86.78
72.22
15.07
CH2
O
S
CH3
F
F
F
13C NMR (101 MHz, CDCl3)
f1 (ppm)

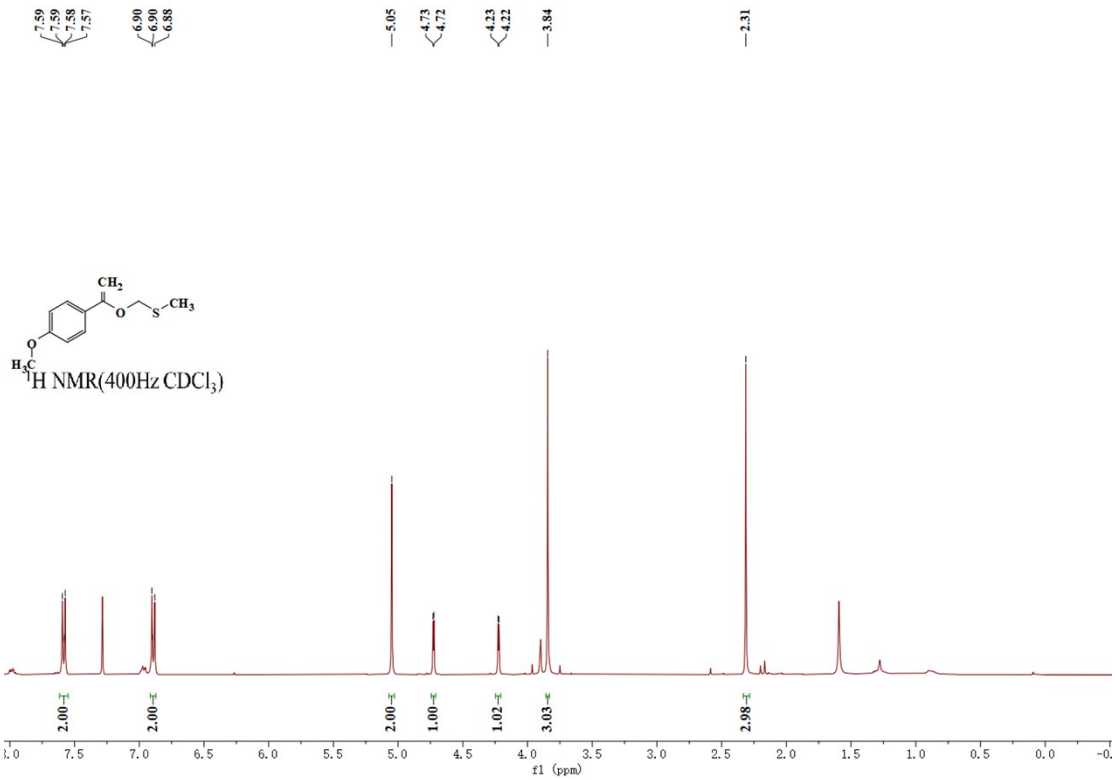

F
CH2
O
S
CH3
1H NMR (400 MHz, CDCl3)
f1 (ppm)

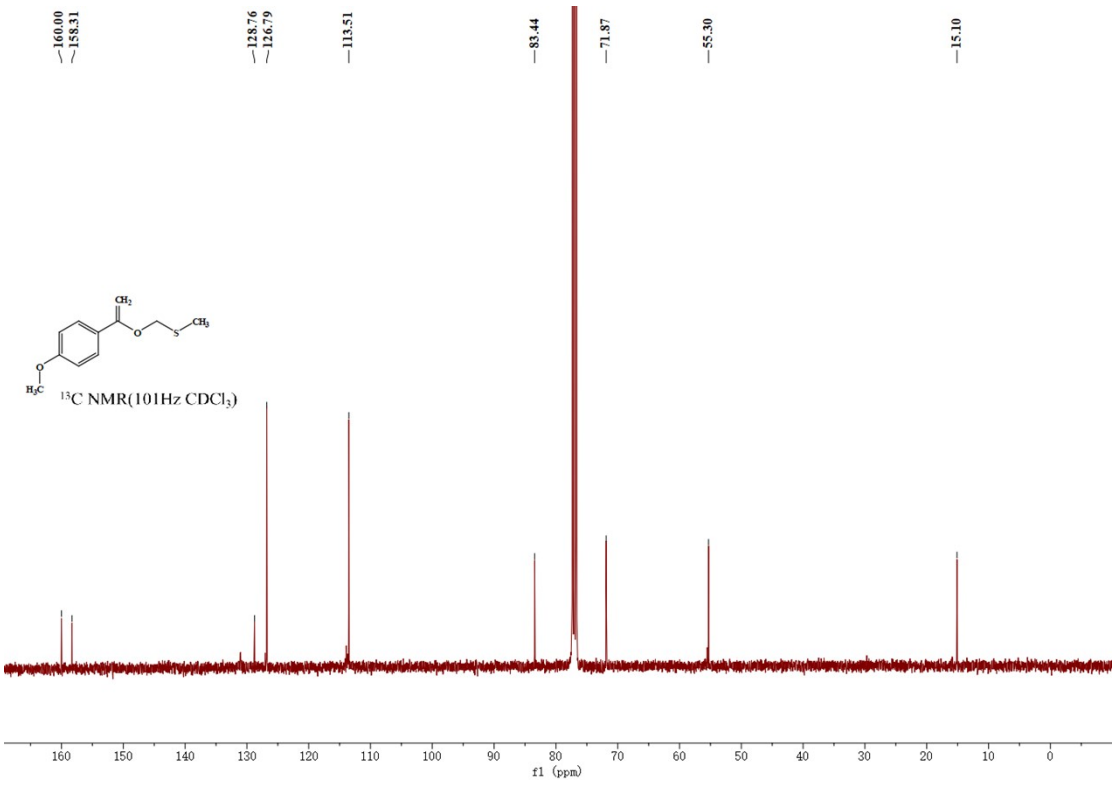

F
CH2
O
S
CH3
13C NMR (101 MHz, CDCl3)
f1 (ppm)

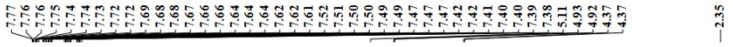

7.56
7.54
7.19
7.17
5.06
4.81
4.80
4.29
4.28
2.39
2.32
CH2
O
S
CH3
H3C
1H NMR (400 MHz, CDCl3)
1.95
1.95
2.05
1.00
1.02
3.03
2.93
f1 (ppm)
158.64
138.49
133.36
128.84
125.39
84.31
71.91
21.16
15.02
13C NMR (101 MHz, CDCl3)

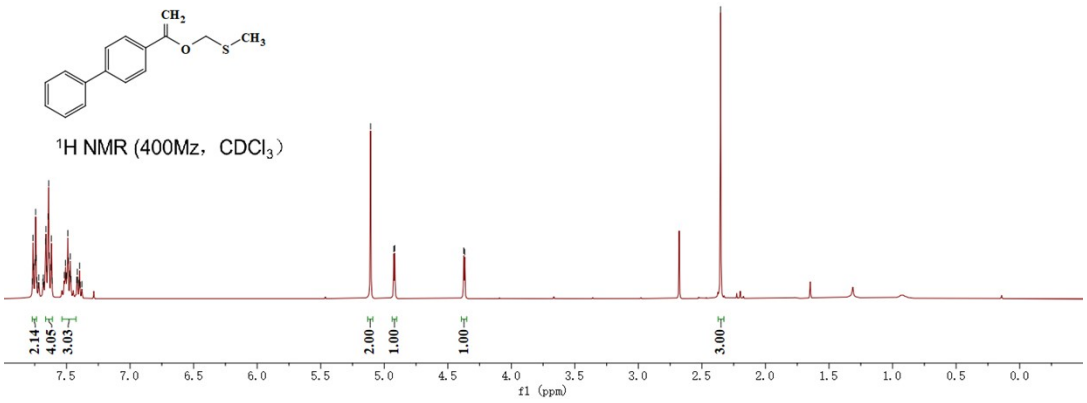

7.59
7.57
7.40
7.38
5.06
4.81
4.80
4.28
4.27
2.31
1.35
CH2
O
S
CH3
H3C
H3C
CH3
1H NMR(CDCl3 400MHz)
7.56
7.38
4.80
4.27
f1 (ppm)
2.00
2.12
2.00
1.00
1.00
3.00
9.09
f1 (ppm)

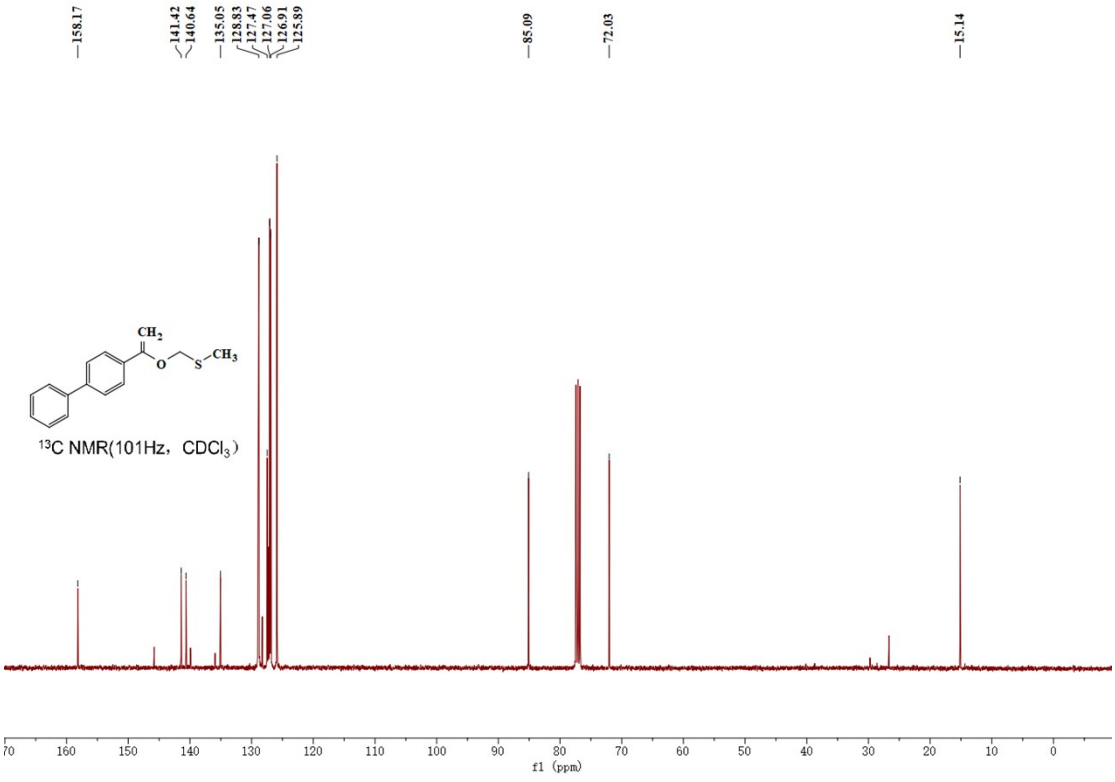

158.50
151.75
133.29
125.19
125.09
84.40
71.85
34.60
31.27
15.04
CH2
O
S
CH3
H3C
H3C
CH3
13C NMR(CDCl3 101MHz)
f1 (ppm)

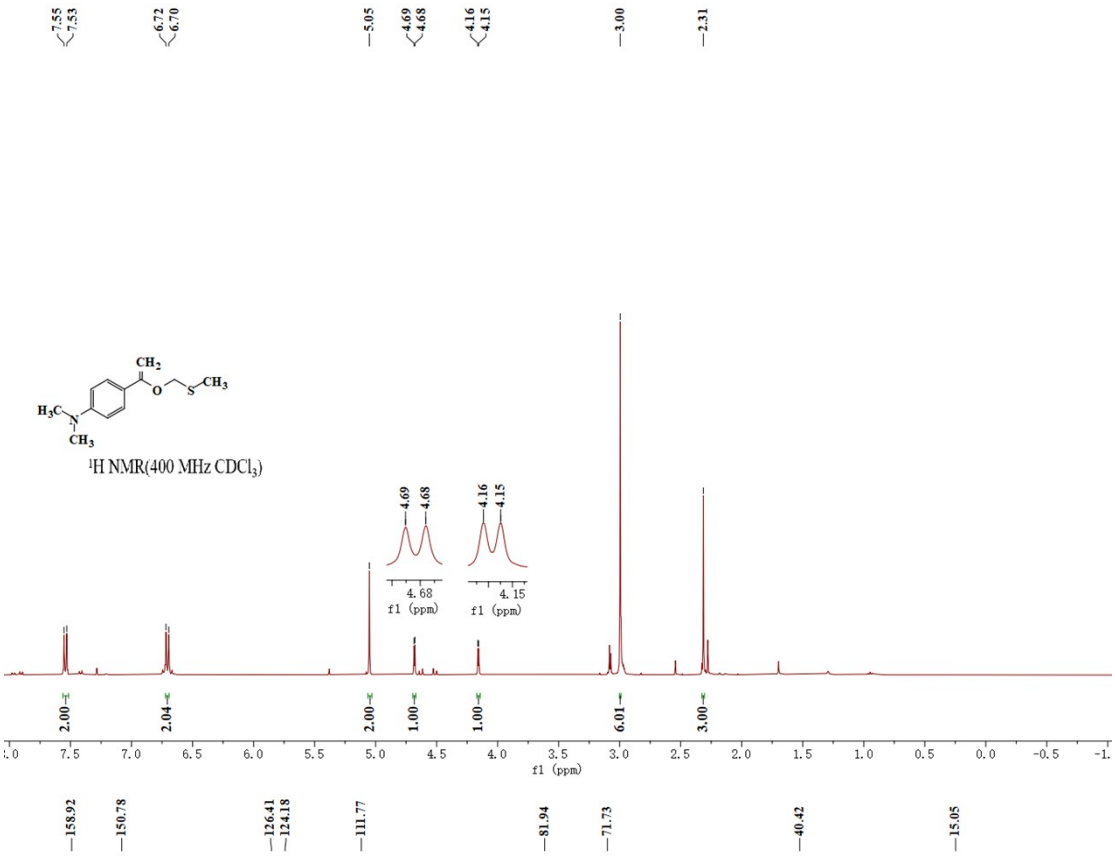

7.59
7.59
7.58
7.57
6.90
6.90
6.88
5.05
4.73
4.72
4.23
4.22
3.84
2.31
^{1}H NMR(400Hz CDCl$_3$)
2.00
2.00
2.00
1.00
1.02
3.03
2.98
f1 (ppm)

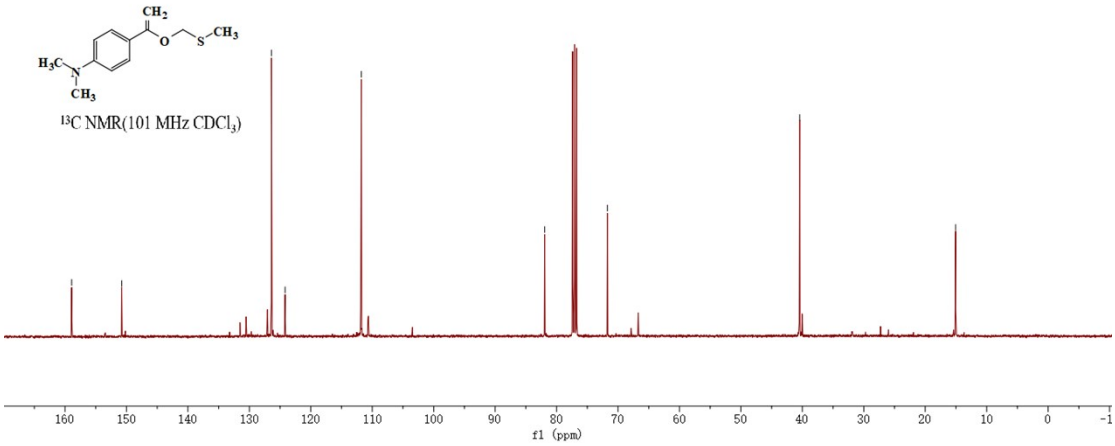

160.00
158.31
128.76
126.79
113.51
83.44
71.87
55.30
15.10
^{13}C NMR(101Hz CDCl$_3$)
f1 (ppm)

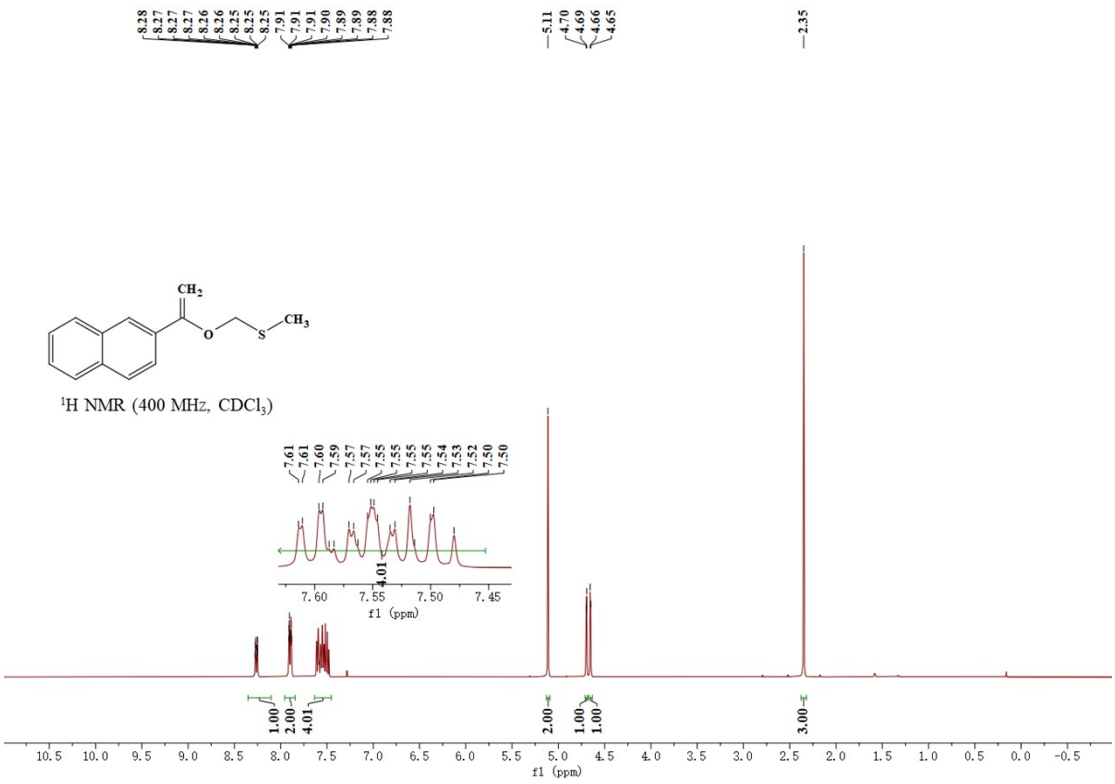

7.77
7.76
7.76
7.75
7.74
7.74
7.73
7.72
7.72
7.69
7.68
7.68
7.67
7.66
7.66
7.64
7.64
7.64
7.62
7.62
7.61
7.52
7.51
7.50
7.50
7.49
7.49
7.47
7.47
7.47
7.42
7.42
7.41
7.40
7.40
7.39
7.38
5.11
4.93
4.92
4.37
4.37
2.35

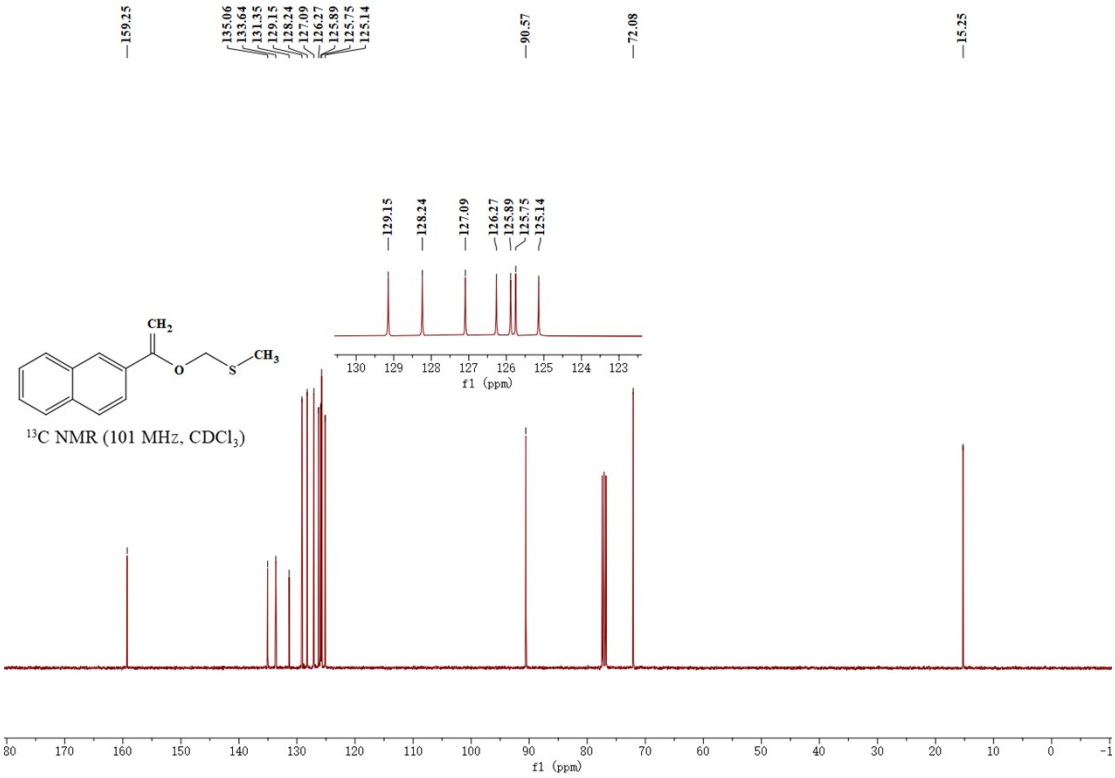

CH2
O
S
CH3
1H NMR (400Mz, CDCl3)
2.14
4.05
3.03
2.00
1.00
1.00
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

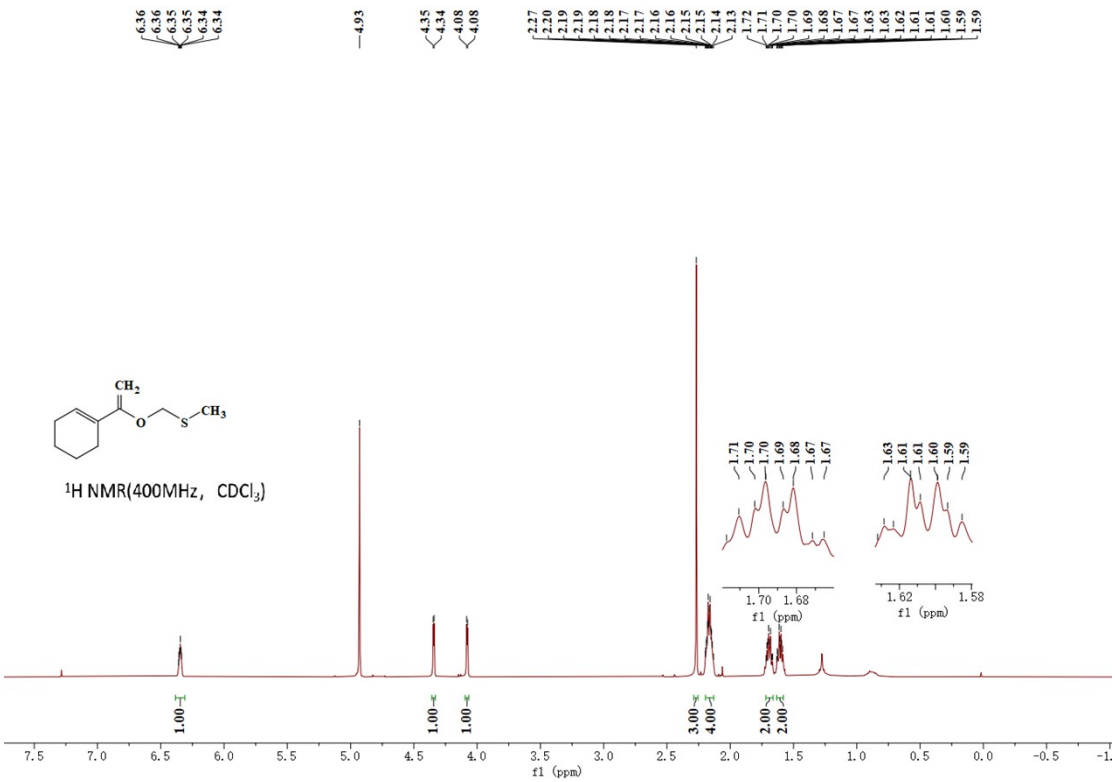

158.17
141.42
140.64
135.05
128.83
127.47
127.06
126.91
125.89
85.09
72.03
15.14
CH2
O
S
CH3
13C NMR(101Hz, CDCl3)
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

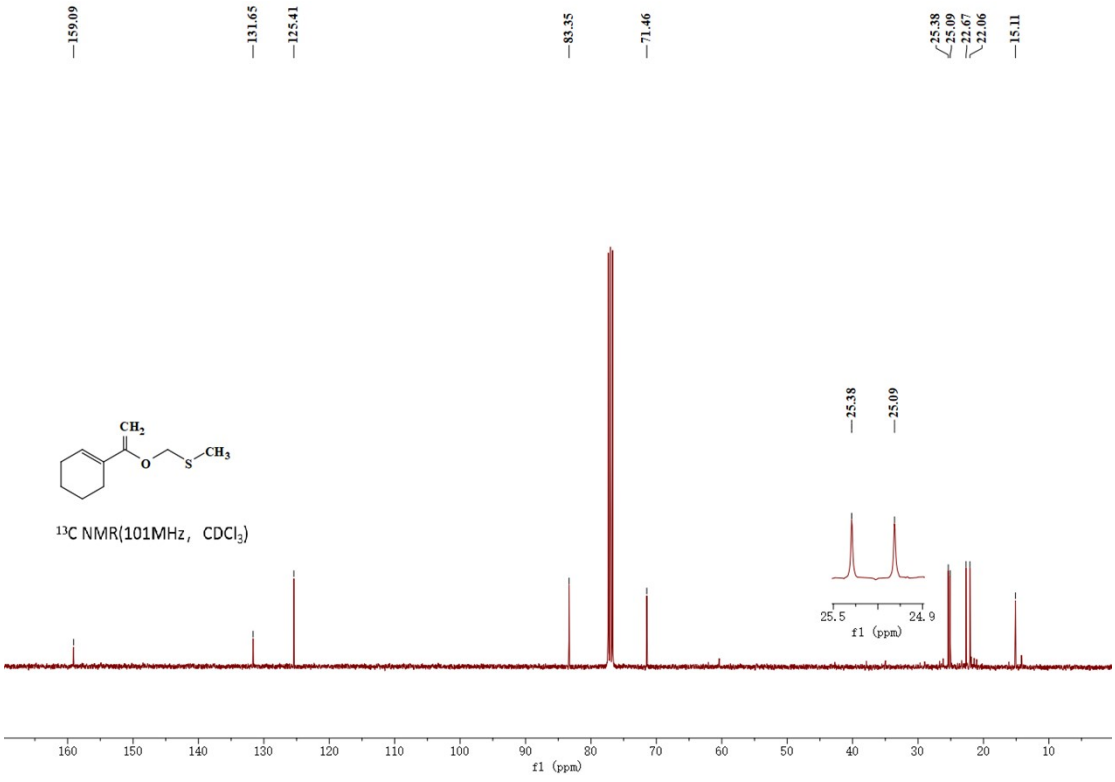

7.55
7.53
6.72
6.70
5.05
4.69
4.68
4.16
4.15
3.00
2.31
CH2
O
S
CH3
H3C
N
CH3
1H NMR(400 MHz CDCl3)
4.68
f1 (ppm)
4.15
f1 (ppm)
2.00
2.04
2.00
1.00
1.00
6.01
3.00
f1 (ppm)

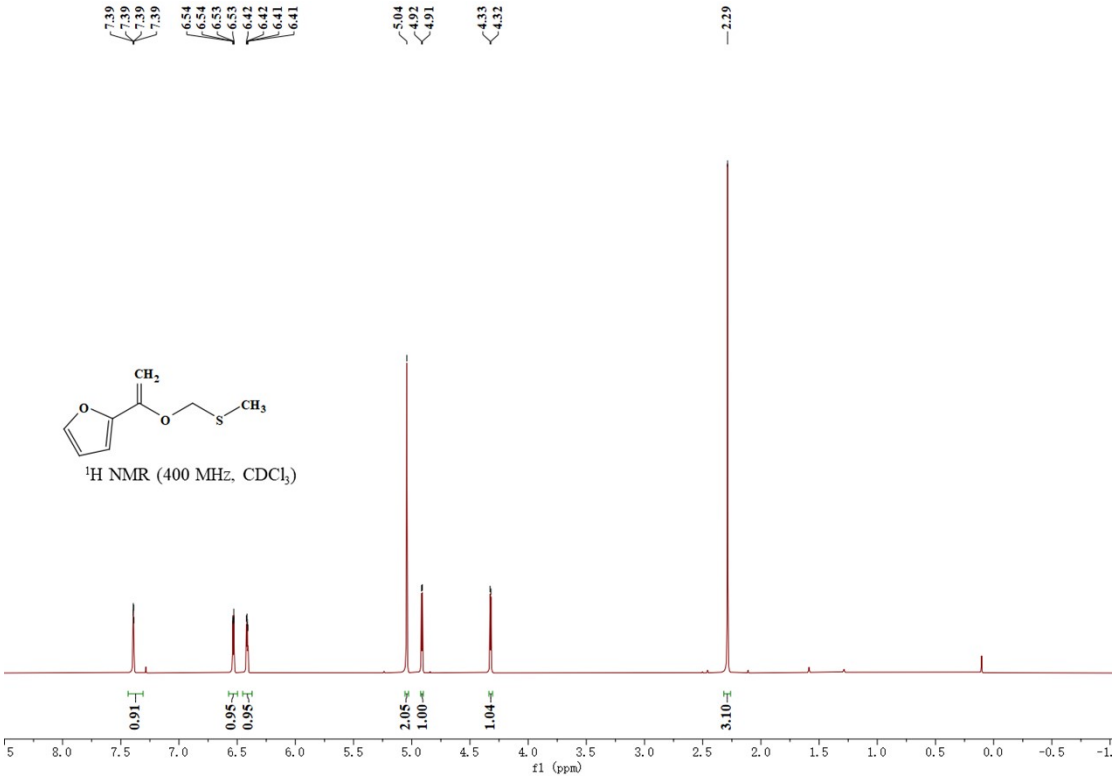

158.92
150.78
126.41
124.18
111.77
81.94
71.73
40.42
15.05
CH2
O
S
CH3
H3C
N
CH3
13C NMR(101 MHz CDCl3)
f1 (ppm)


8.28
8.27
8.27
8.27
8.26
8.26
8.25
8.25
8.25
7.91
7.91
7.91
7.90
7.89
7.89
7.88
7.88
5.11
4.70
4.69
4.66
4.65
2.35
CH2
O
S
CH3
1H NMR (400 MHz, CDCl3)
7.61
7.61
7.60
7.59
7.57
7.57
7.55
7.55
7.55
7.55
7.54
7.53
7.52
7.50
7.50
4.01
7.60
7.55
7.50
7.45
f1 (ppm)
1.00
2.00
4.01
2.00
1.00
1.00
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

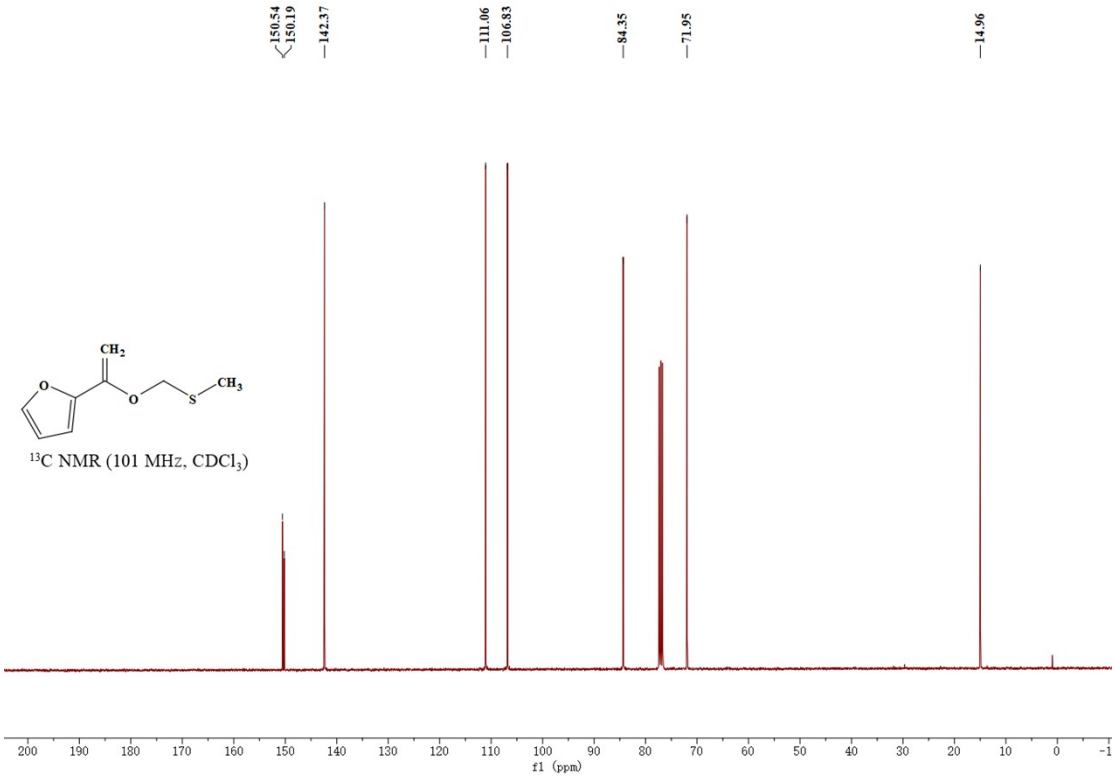

159.25
135.06
133.64
131.35
129.15
128.24
127.09
126.27
125.89
125.75
125.14
90.57
72.08
15.25
129.15
128.24
127.09
126.27
125.89
125.75
125.14
CH2
O
S
CH3
13C NMR (101 MHz, CDCl3)
130
129
128
127
126
125
124
123
f1 (ppm)
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


6.36
6.36
6.35
6.35
6.34
6.34
4.93
4.35
4.34
4.08
4.08
2.27
2.20
2.19
2.19
2.18
2.18
2.17
2.17
2.16
2.16
2.15
2.15
2.14
2.13
1.72
1.71
1.70
1.70
1.69
1.68
1.67
1.67
1.63
1.63
1.62
1.61
1.61
1.60
1.59
1.59
CH2
O
S
CH3
1H NMR(400MHz, CDCl3)
1.71
1.70
1.70
1.69
1.68
1.67
1.67
1.63
1.61
1.61
1.60
1.59
1.59
1.70 1.68
f1 (ppm)
1.62 1.58
f1 (ppm)
1.00
1.00
1.00
3.00
4.00
2.00
2.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

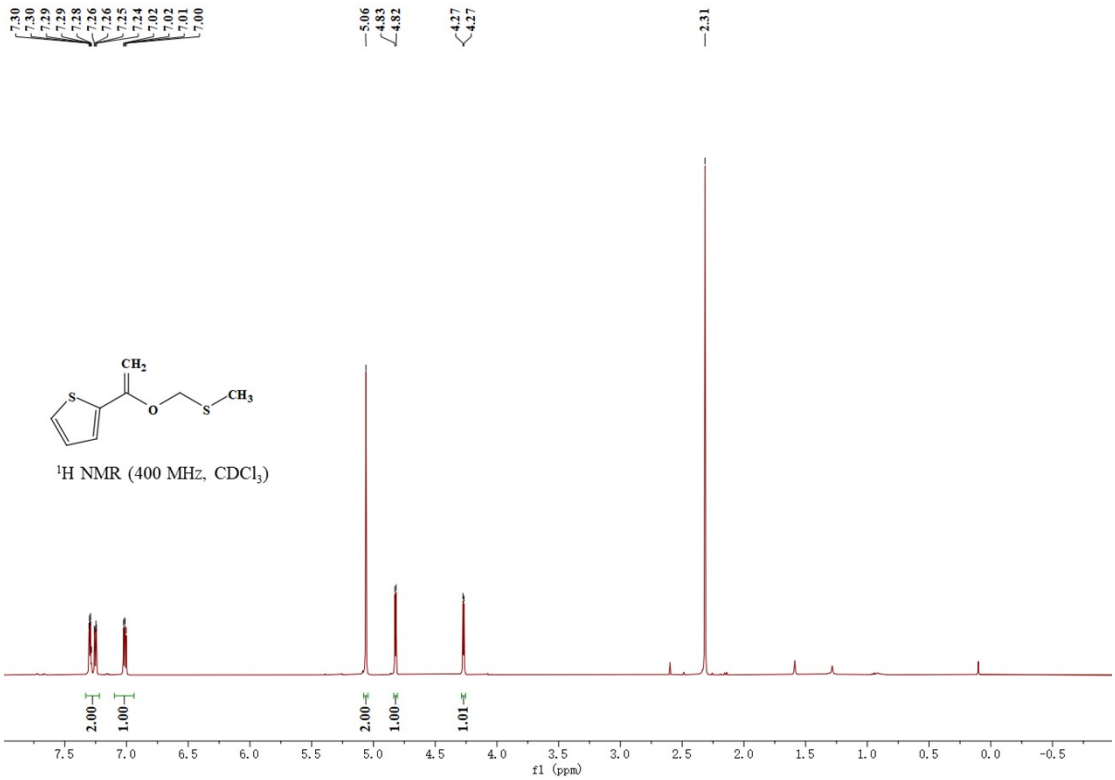

159.09
131.65
125.41
83.35
71.46
25.38
25.09
22.67
22.06
15.11
CH2
O
S
CH3
13C NMR(101MHz, CDCl3)
25.38
25.09
25.5 24.9
f1 (ppm)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

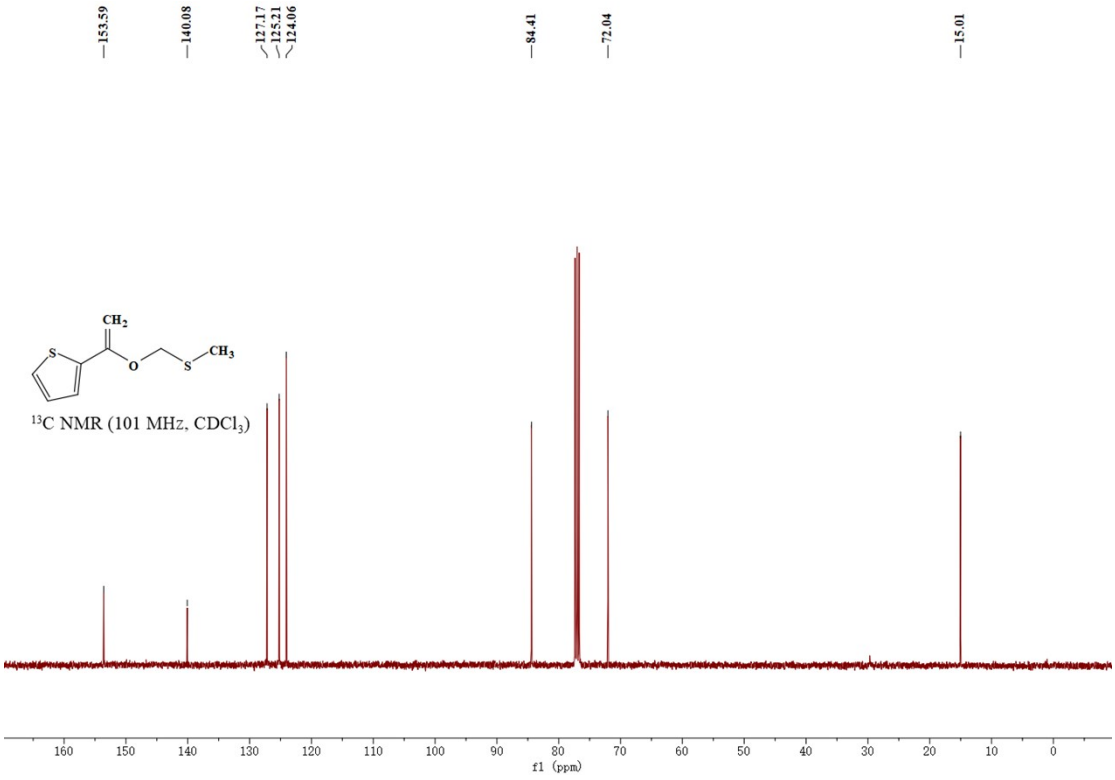


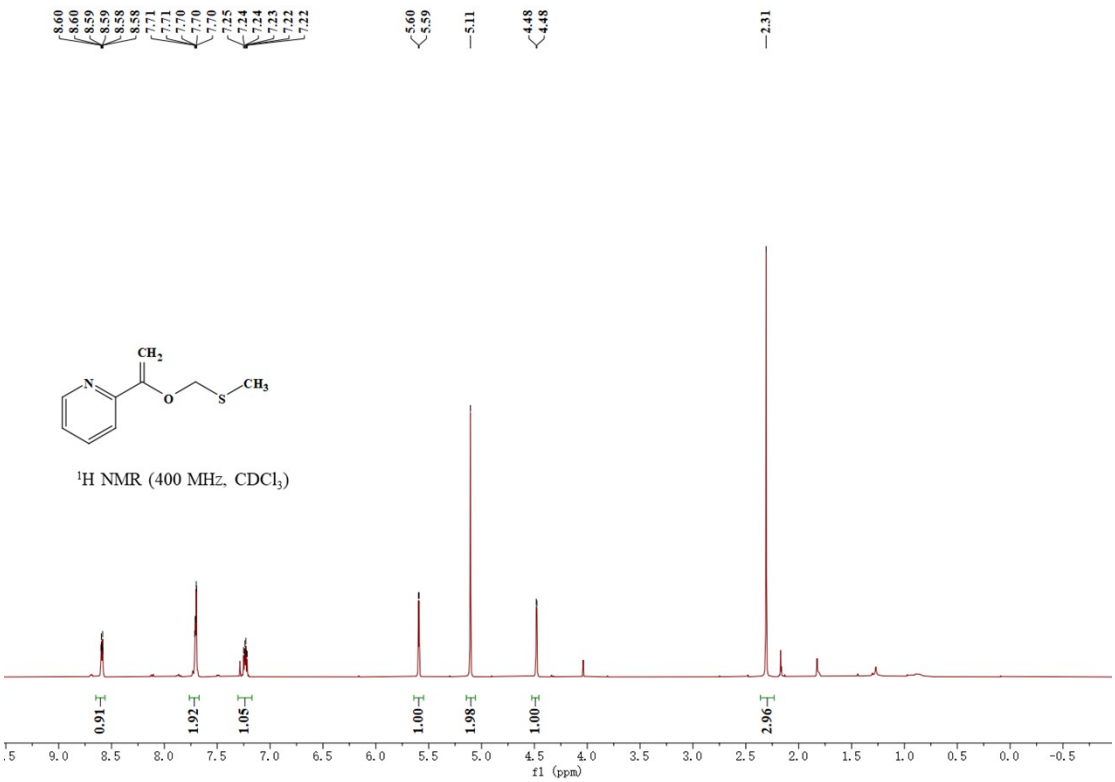
^{1}H NMR (400 MHz, $CDCl_3$)

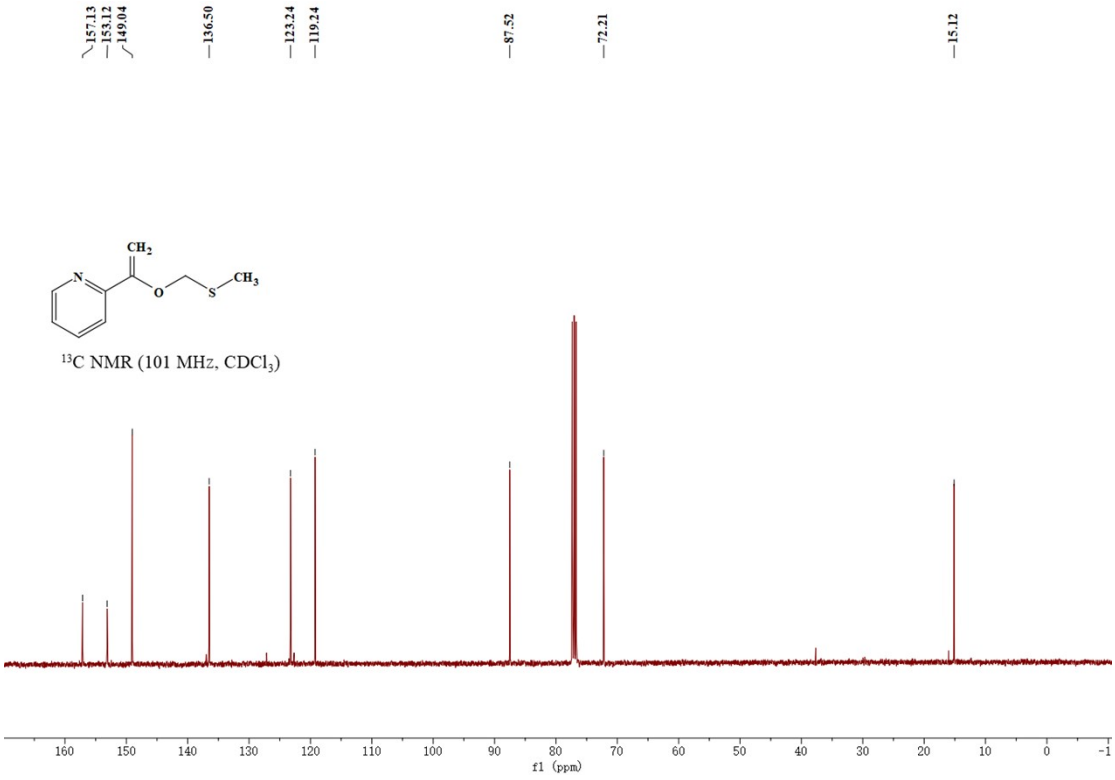


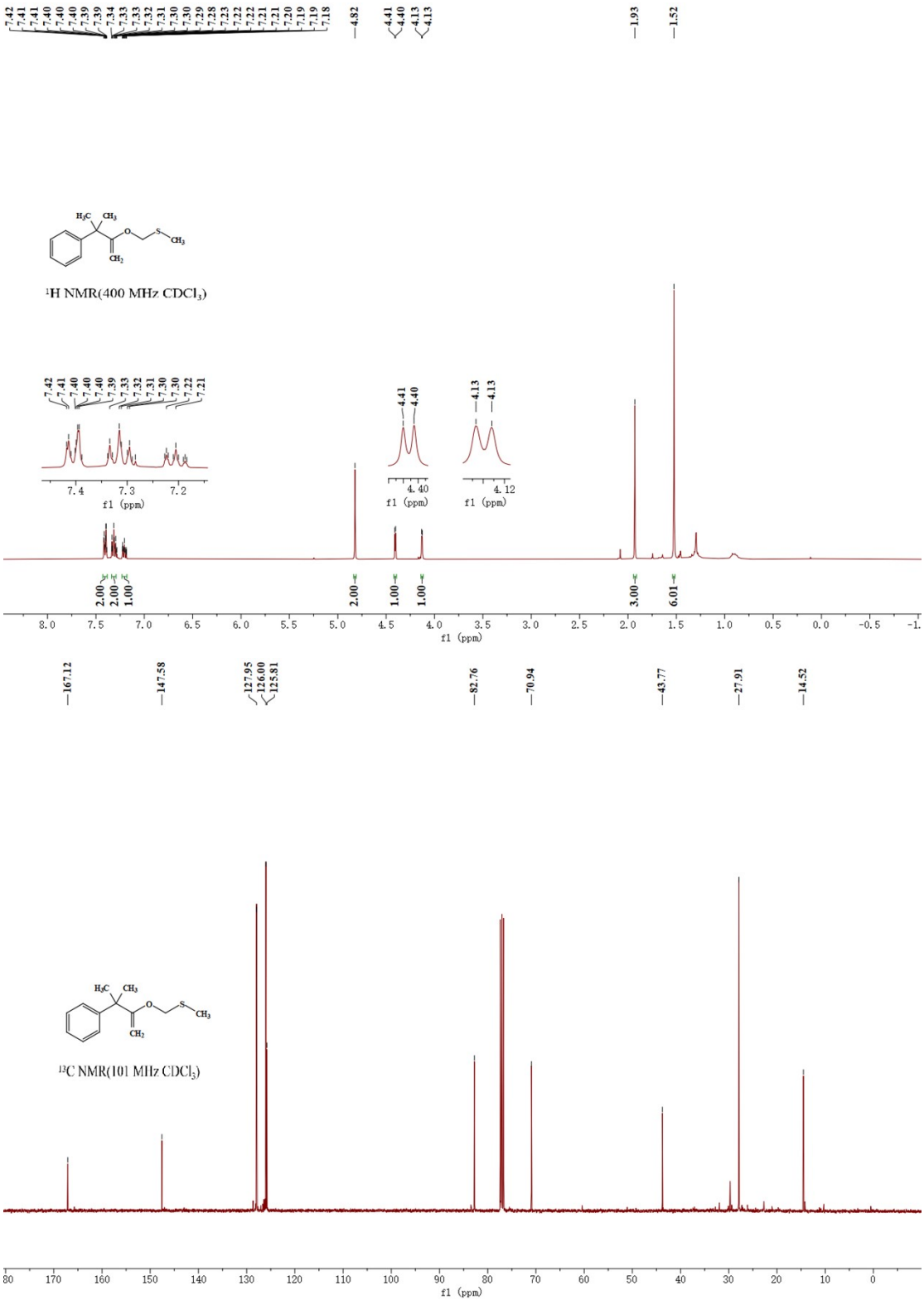
^{13}C NMR (101 MHz, $CDCl_3$)

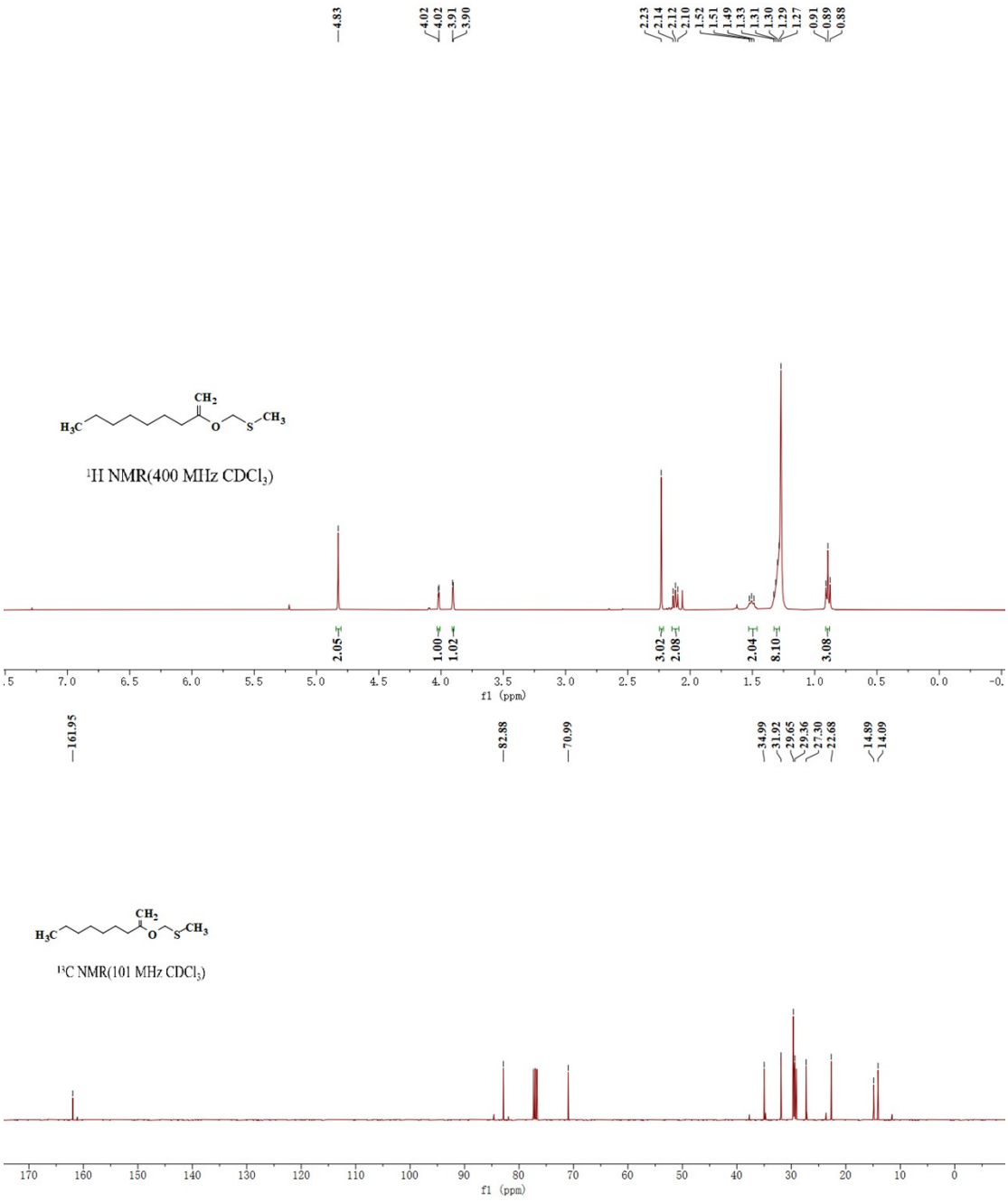

7.30
7.30
7.29
7.29
7.28
7.26
7.26
7.25
7.24
7.02
7.02
7.01
7.00
5.06
4.83
4.82
4.27
4.27
2.31
CH2
S
O
S
CH3
1H NMR (400 MHz, CDCl3)
2.00
1.00
2.00
1.00
1.01
f1 (ppm)

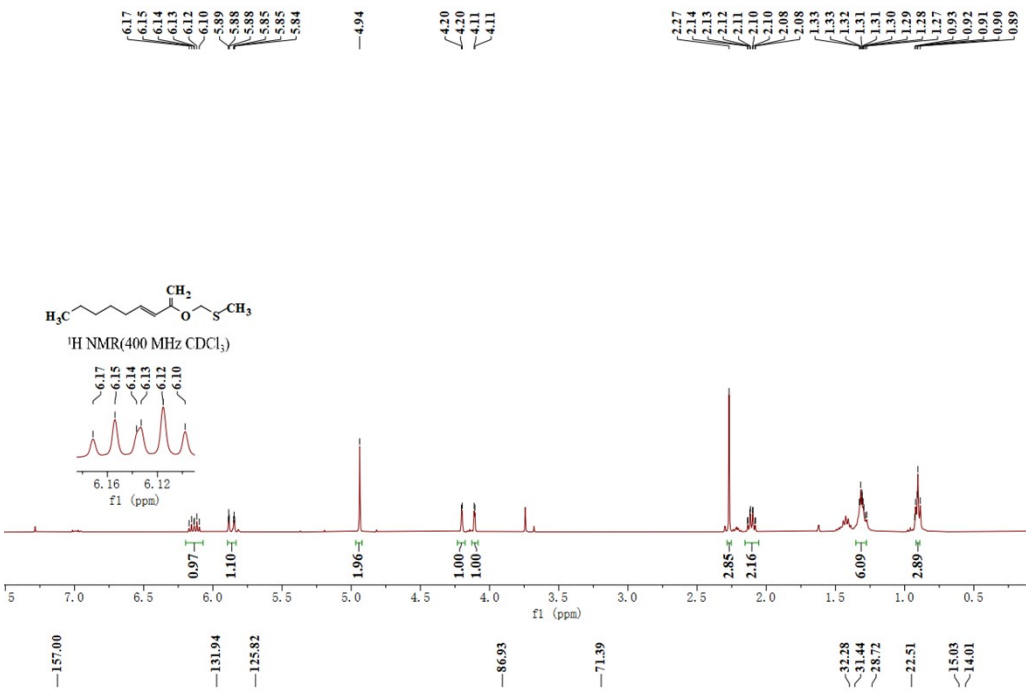

153.59
140.08
127.17
125.21
124.06
84.41
72.04
15.01
CH2
S
O
S
CH3
13C NMR (101 MHz, CDCl3)
f1 (ppm)

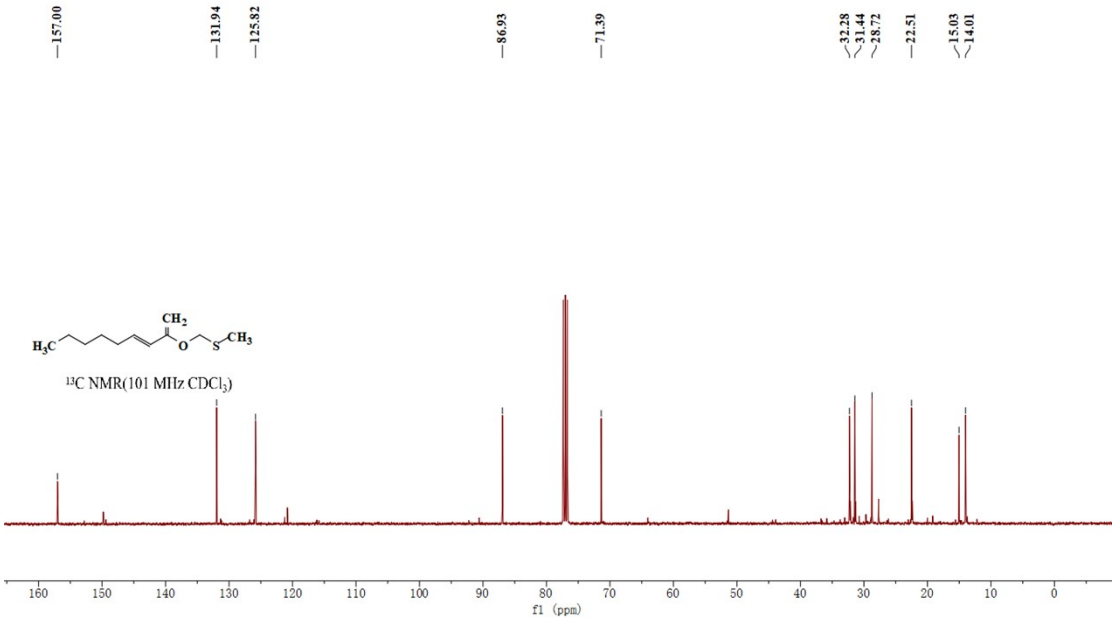

8.60
8.60
8.59
8.59
8.58
8.58
7.71
7.71
7.70
7.70
7.70
7.70
7.25
7.24
7.24
7.23
7.22
7.22
5.60
5.59
5.11
4.48
4.48
2.31
CH2
N
O
S
CH3
1H NMR (400 MHz, CDCl3)
0.91
1.92
1.05
1.00
1.98
1.00
2.96
f1 (ppm)

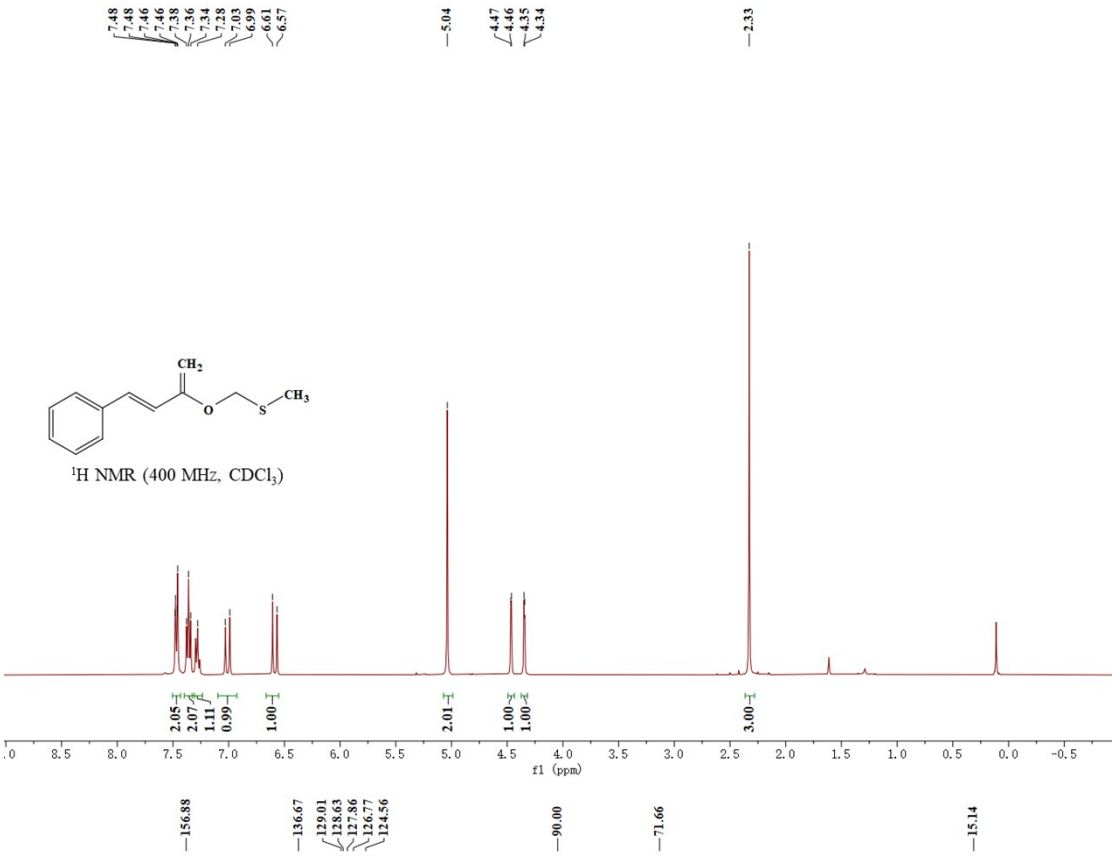

157.13
153.12
149.04
136.50
123.24
119.24
87.52
72.21
15.12
CH2
N
O
S
CH3
13C NMR (101 MHz, CDCl3)
f1 (ppm)

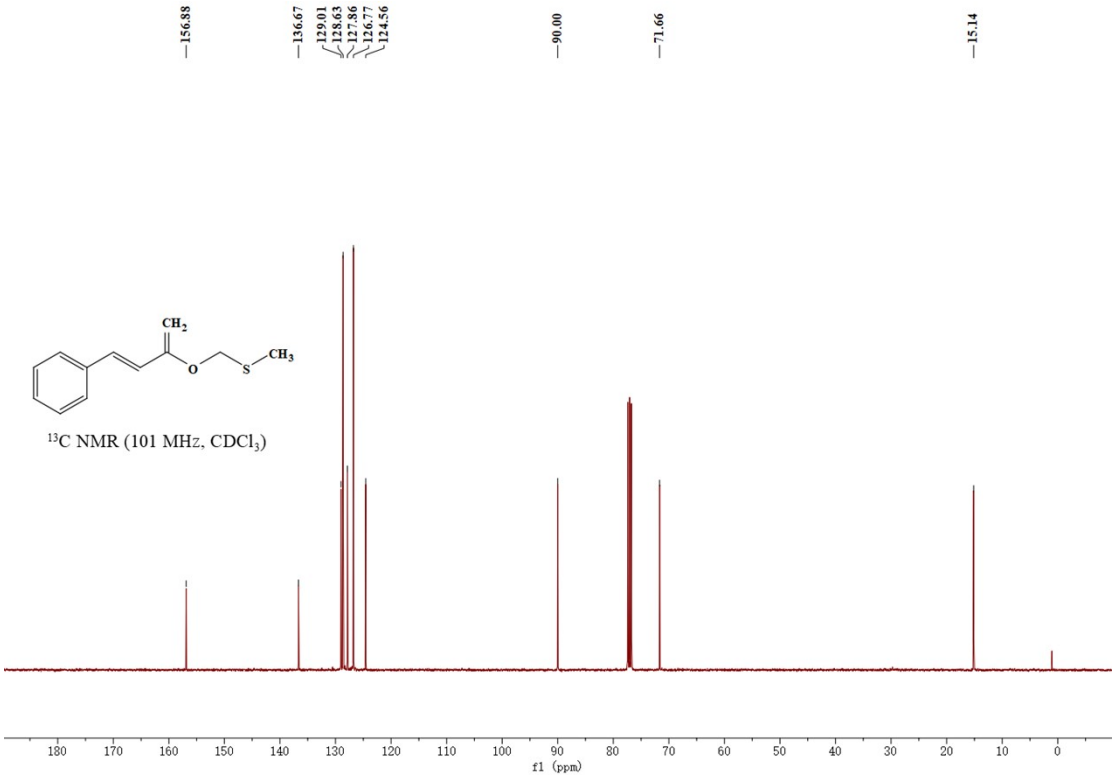

7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.28 7.23 7.22 7.22 7.21 7.21 7.20 7.19 7.19 7.18
4.82
4.41 4.40 4.13 4.13
1.93
1.52
H3C CH3
O
S
CH3
CH2
1H NMR(400 MHz CDCl3)
7.42 7.41 7.40 7.40 7.40 7.39 7.33 7.32 7.31 7.30 7.30 7.22 7.21
7.4 7.3 7.2
f1 (ppm)
4.41 4.40
4.40
f1 (ppm)
4.13 4.13
4.12
f1 (ppm)
2.00 2.00 1.00 2.00 1.00 1.00 3.00 6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)
167.12
147.58
127.95 126.00 125.81
82.76
70.94
43.77
27.91
14.52
H3C CH3
O
S
CH3
CH2
13C NMR(101 MHz CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

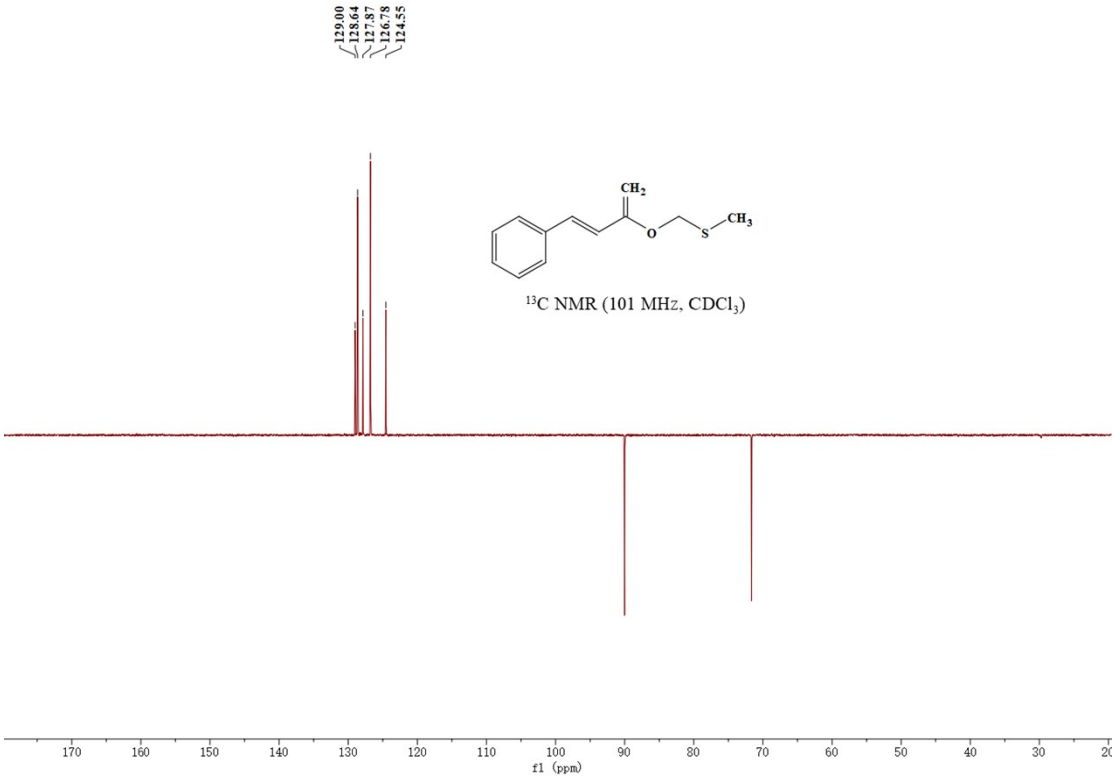

4.83
4.02
4.02
3.91
3.90
2.23
2.14
2.12
2.10
1.52
1.51
1.49
1.33
1.31
1.30
1.29
1.27
0.91
0.89
0.88
CH2
H3C
O
S
CH3
1H NMR(400 MHz CDCl3)
2.05
1.00
1.02
3.02
2.08
2.04
8.10
3.08
f1 (ppm)
161.95
82.88
70.99
34.99
31.92
29.65
29.36
27.30
22.68
14.89
14.09
13C NMR(101 MHz CDCl3)

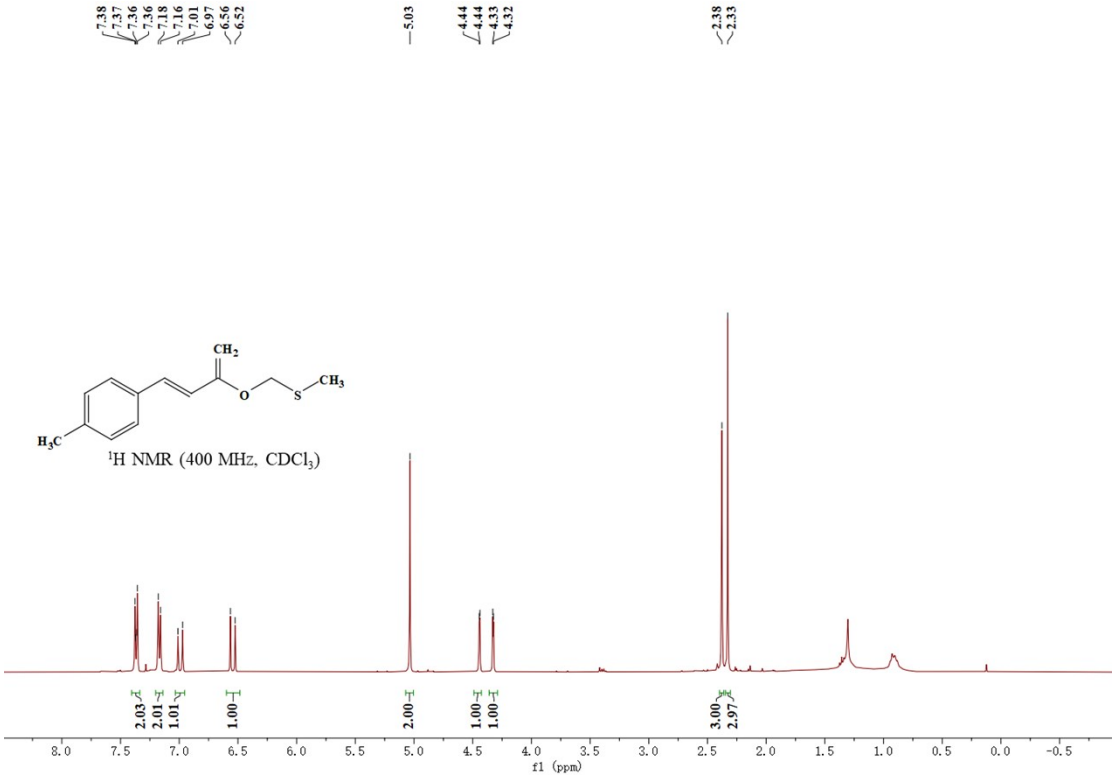

6.17
6.15
6.14
6.13
6.12
6.10
5.89
5.88
5.88
5.85
5.85
5.84
4.94
4.20
4.20
4.11
4.11
2.27
2.14
2.13
2.12
2.11
2.10
2.10
2.08
2.08
1.33
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.27
0.93
0.92
0.91
0.90
0.89
CH2
H3C
O
S
CH3
1H NMR(400 MHz CDCl3)
6.17
6.15
6.14
6.13
6.12
6.10
6.16
6.12
f1 (ppm)
0.97
1.10
1.96
1.00
1.00
2.85
2.16
6.09
2.89
5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

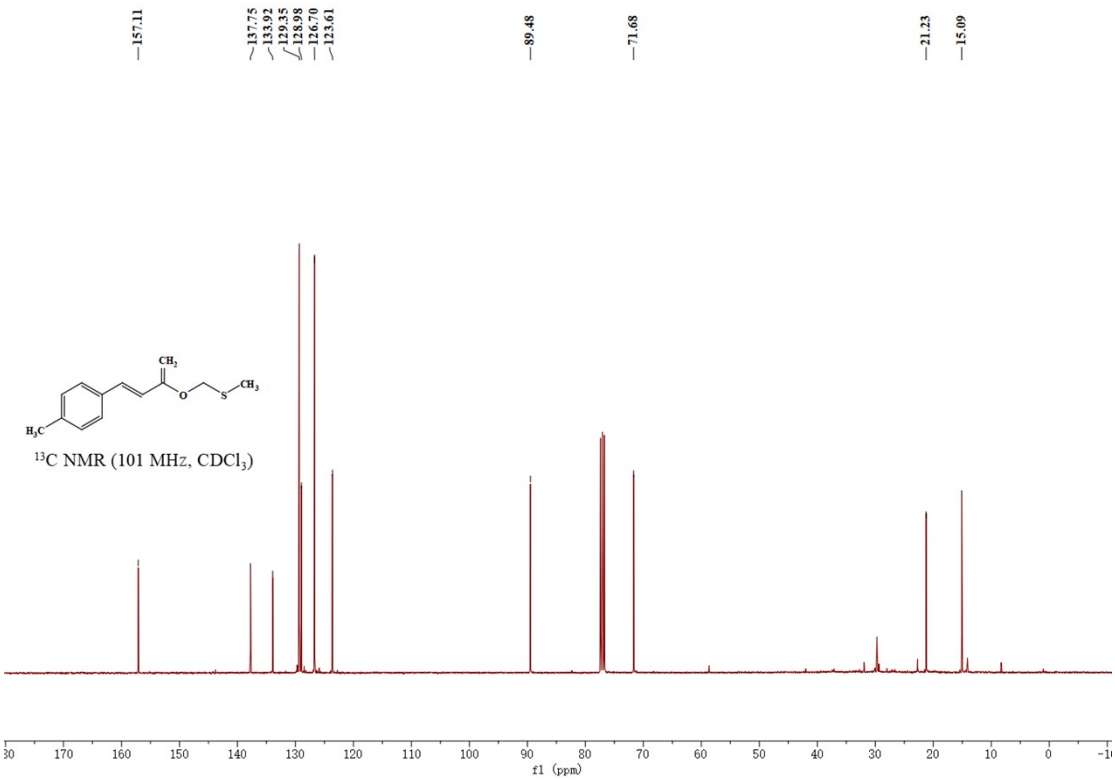

157.00
131.94
125.82
86.93
71.39
32.28
31.44
28.72
22.51
15.03
14.01
CH2
H3C
O
S
CH3
13C NMR(101 MHz CDCl3)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

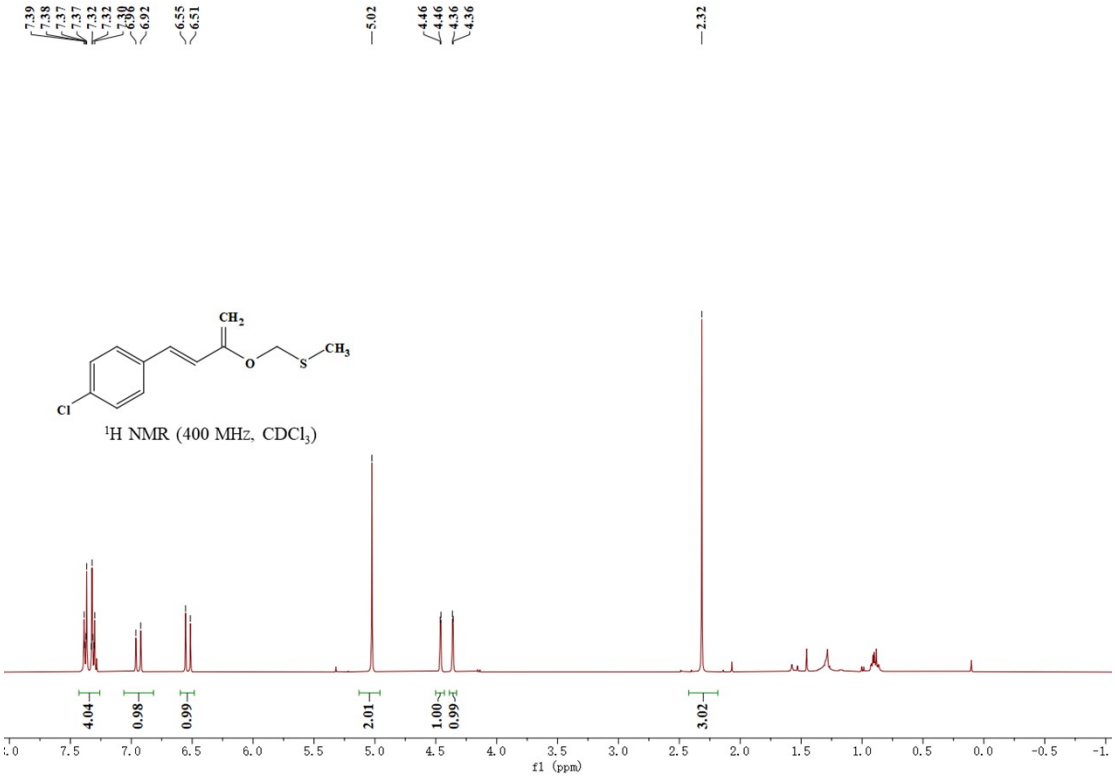

7.48
7.48
7.46
7.46
7.38
7.36
7.34
7.28
7.03
6.99
6.61
6.57
5.04
4.47
4.46
4.35
4.34
2.33
CH2
O
S
CH3
1H NMR (400 MHz, CDCl3)
2.05
2.07
1.11
0.99
1.00
2.01
1.00
1.00
3.00
f1 (ppm)

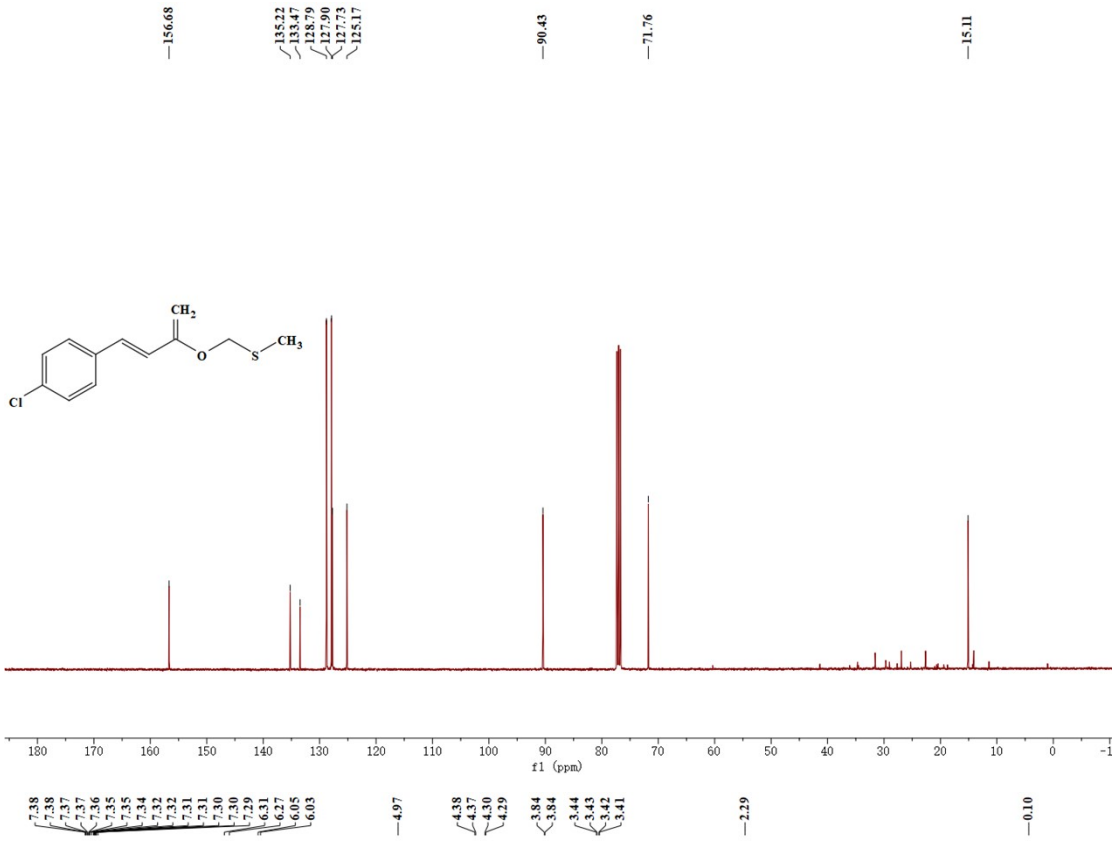

156.88
136.67
129.01
128.63
127.86
126.77
124.56
90.00
71.66
15.14
CH2
O
S
CH3
13C NMR (101 MHz, CDCl3)
f1 (ppm)

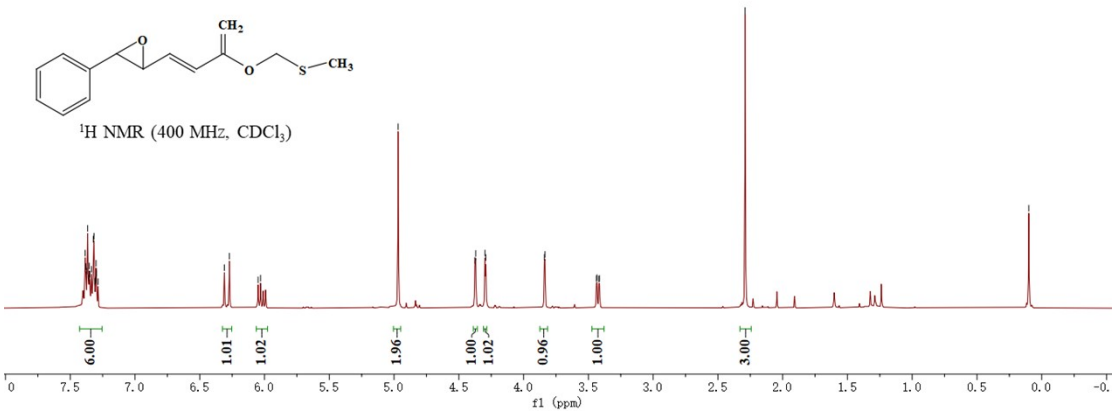

129.00
128.64
127.87
126.78
124.55
CH2
O
S
CH3
13C NMR (101 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

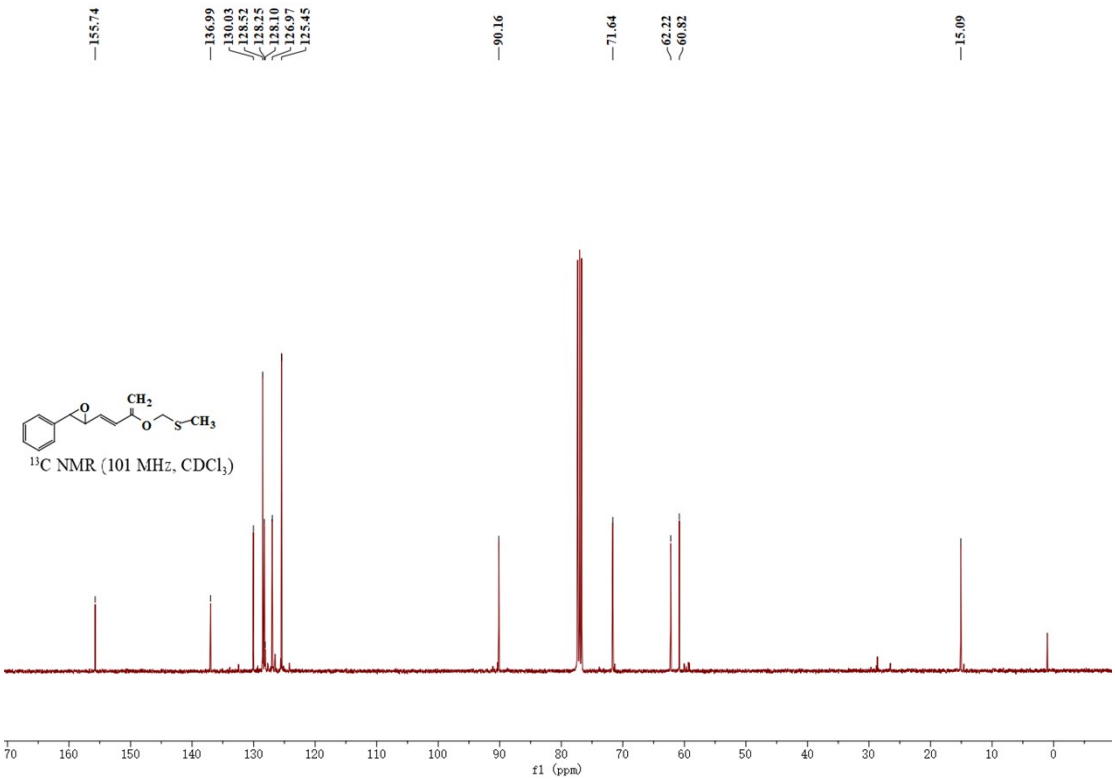

7.38
7.37
7.36
7.36
7.18
7.16
7.01
6.97
6.56
6.52
5.03
4.44
4.44
4.33
4.32
2.38
2.33
CH2
O
S
CH3
H3C
1H NMR (400 MHz, CDCl3)
2.03
2.01
1.01
1.00
2.00
1.00
1.00
3.00
2.97
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

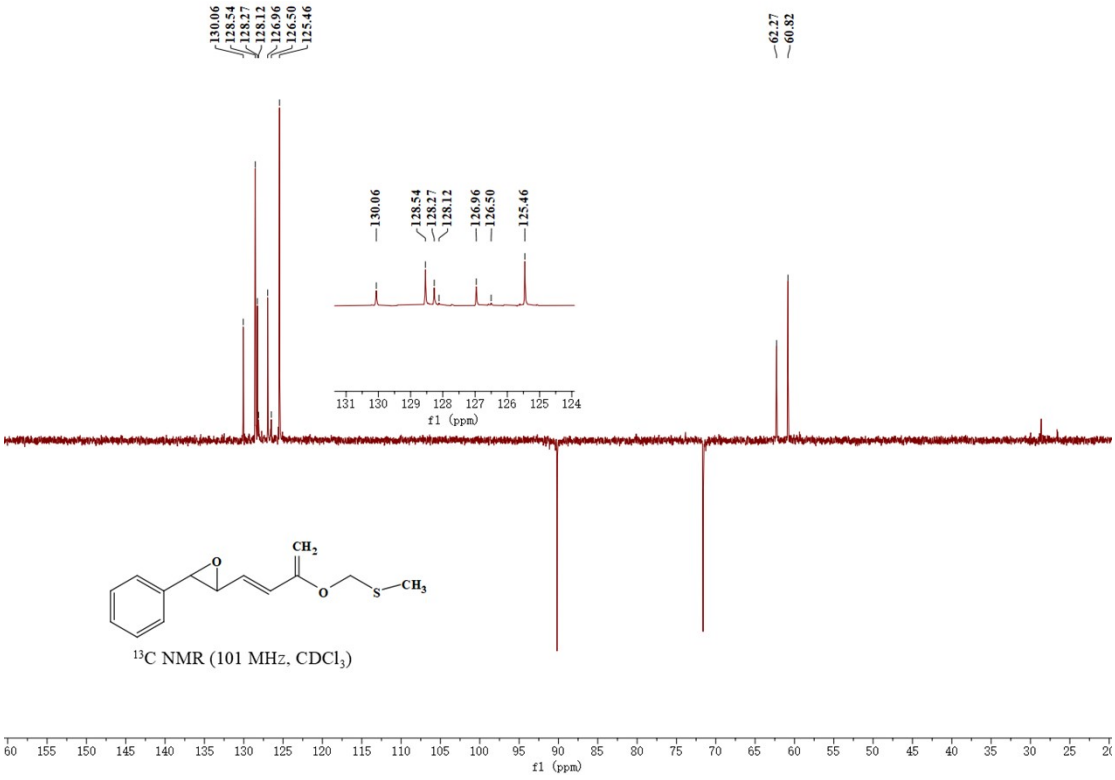

157.11
137.75
133.92
129.35
128.98
126.70
123.61
89.48
71.68
21.23
15.09
CH2
O
S
CH3
H3C
13C NMR (101 MHz, CDCl3)
f1 (ppm)

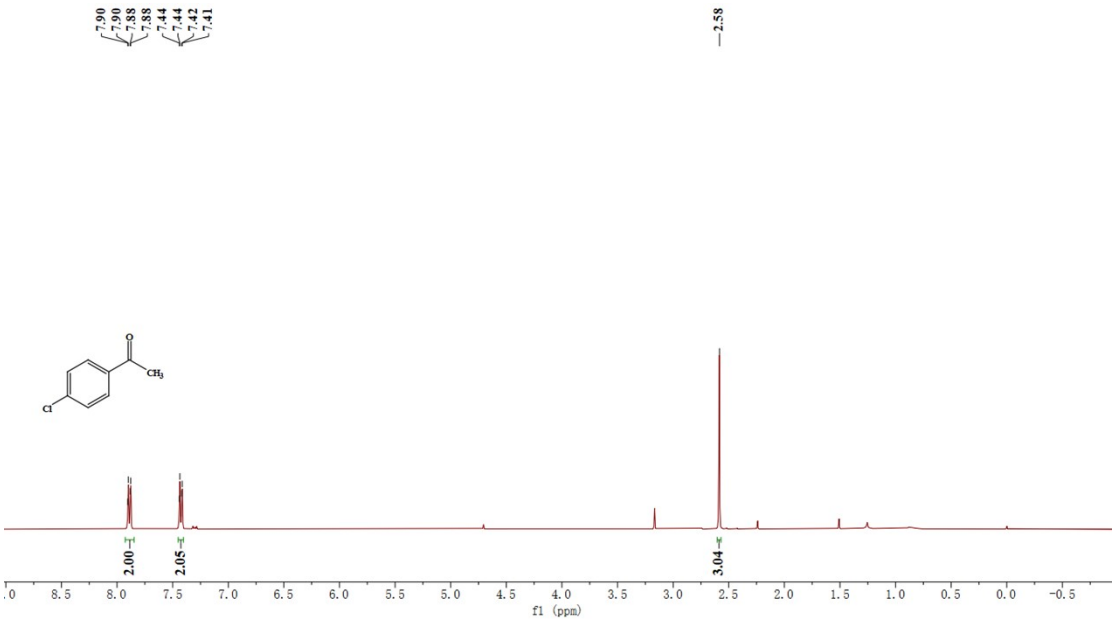

7.39
7.38
7.37
7.37
7.32
7.32
6.98
6.92
6.55
6.51
5.02
4.46
4.46
4.36
4.36
2.32
CH2
O
S
CH3
Cl
1H NMR (400 MHz, CDCl3)
4.04
0.98
0.99
2.01
1.00
0.99
3.02
f1 (ppm)

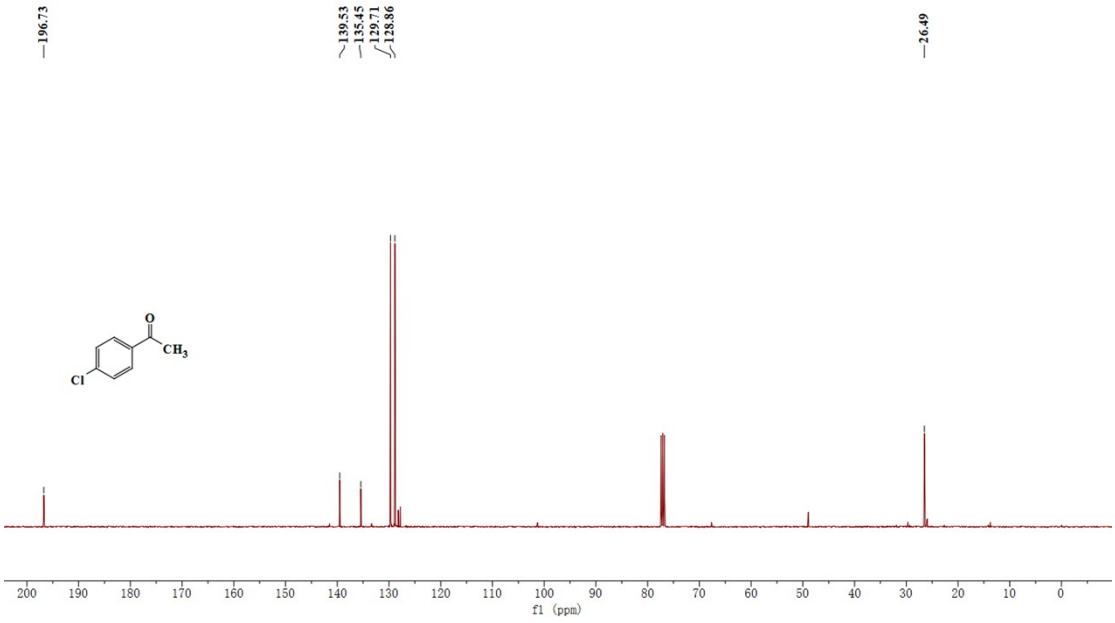

156.68
135.22
133.47
128.79
127.90
127.73
125.17
90.43
71.76
15.11
CH2
O
S
CH3
Cl
f1 (ppm)
7.38
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.32
7.32
7.31
7.31
7.30
7.30
7.29
6.31
6.27
6.05
6.03
4.97
4.38
4.37
4.30
4.29
3.84
3.84
3.44
3.43
3.42
3.41
2.29
0.10

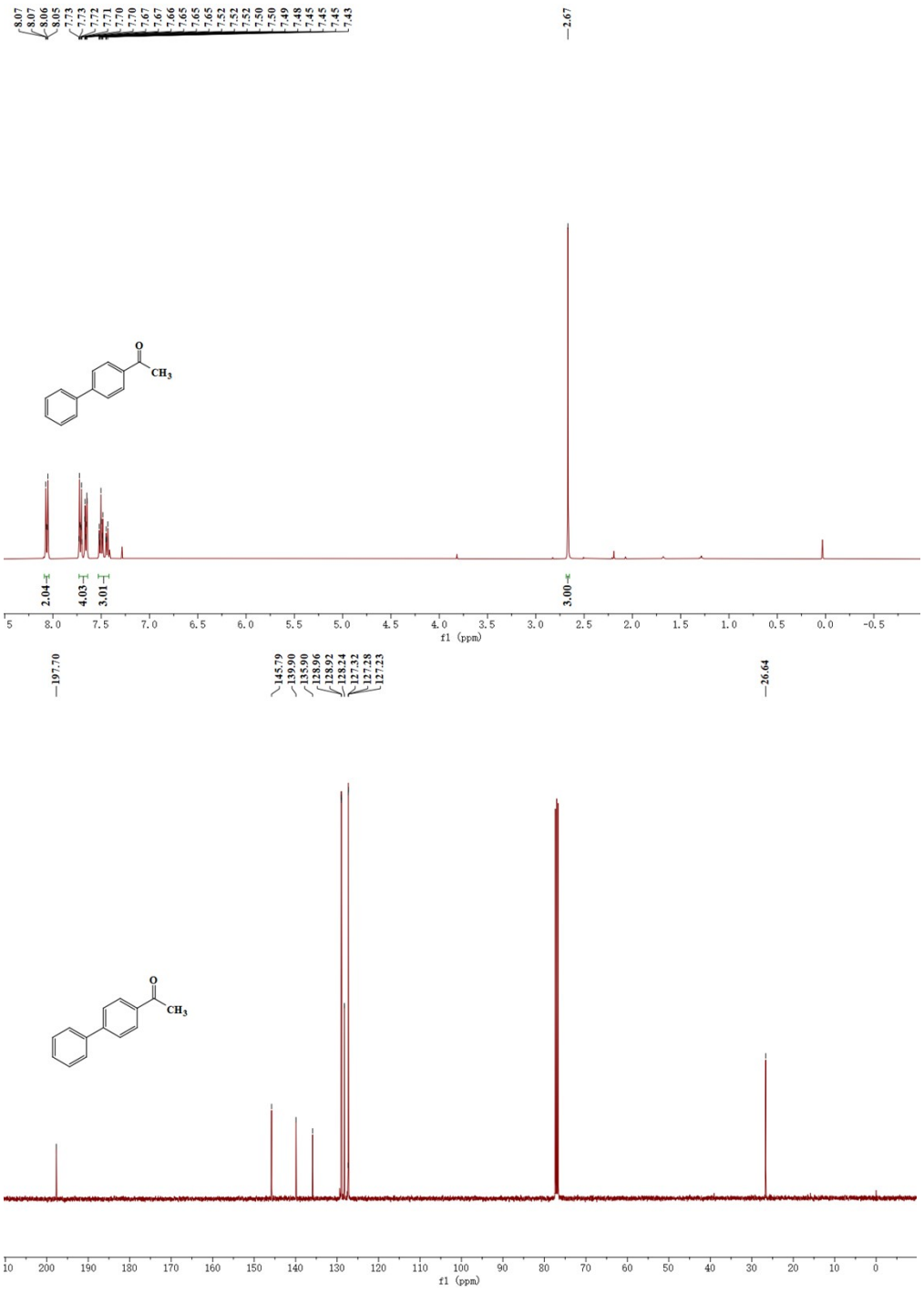

CH2
O
O
S
CH3
1H NMR (400 MHz, CDCl3)
6.00
1.01
1.02
1.96
1.00
1.02
0.96
1.00
3.00
f1 (ppm)


155.74
136.99
130.03
128.52
128.25
128.10
126.97
125.45
90.16
71.64
62.22
60.82
15.09
CH2
O
O
S
CH3
13C NMR (101 MHz, CDCl3)
f1 (ppm)


130.06
128.54
128.27
128.12
126.96
126.50
125.46
62.27
60.82
f1 (ppm)
CH2
O
O
S
CH3
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.90
7.90
7.88
7.88
7.44
7.44
7.42
7.41
2.58
O
CH3
Cl
2.00
2.05
3.04
f1 (ppm)


196.73
139.53
135.45
129.71
128.86
26.49
O
CH3
Cl
f1 (ppm)


8.07
8.07
8.06
8.05
7.73
7.73
7.72
7.71
7.70
7.70
7.67
7.67
7.66
7.65
7.65
7.65
7.52
7.52
7.52
7.50
7.50
7.49
7.48
7.45
7.45
7.45
7.43
2.67
O
CH3
2.04
4.03
3.01
3.00
f1 (ppm)
197.70
145.79
139.90
135.90
128.96
128.92
128.24
127.32
127.28
127.23
26.64
O
CH3
f1 (ppm)

6 Density Functional Theory Calculations

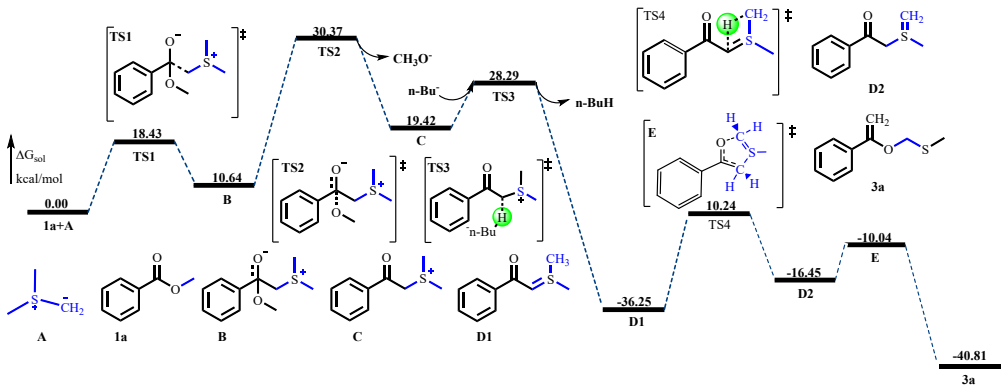


Figure 1. DFT calculations of free energy surfaces before conversion of R1+R2 into intermediates of PC at the M062X(D3)/6-31G (d) level using the SMD solvation model and THF as the solvent.

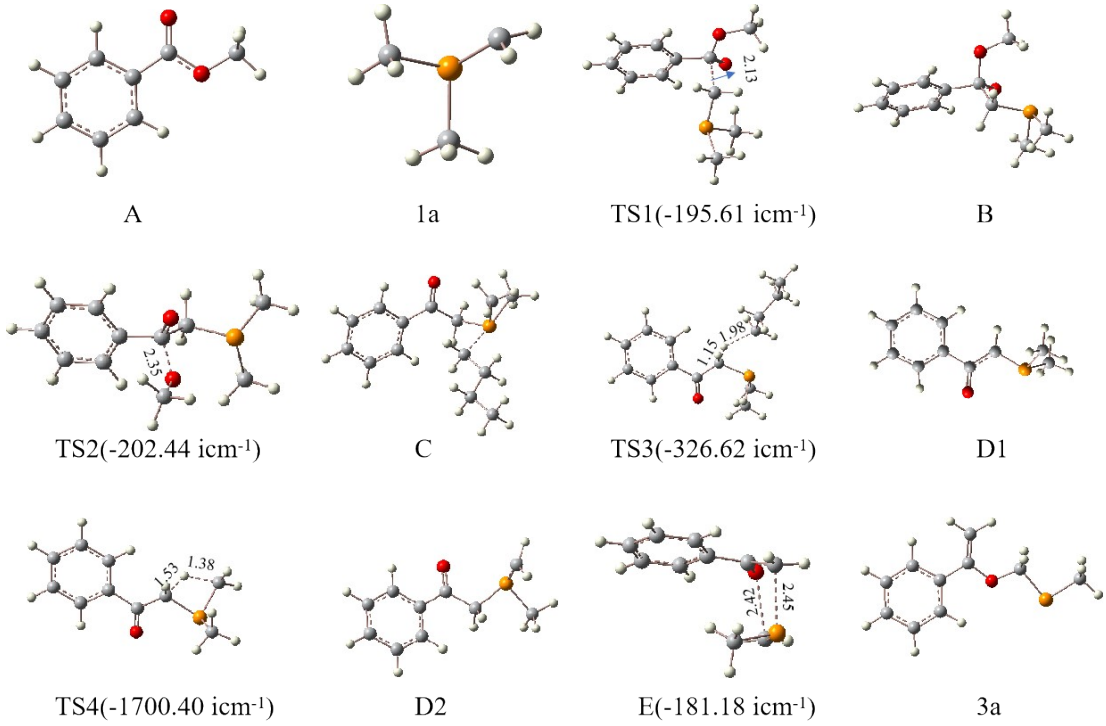


Figure 2. Transition state structures of PCs generated at the M062X(D3)/6-31G (d) level (distances in Å) starting from R1 and R2 transitions using the SMD solvation model and THF as the solvent (distances in Å). The parameter in parentheses is the unique imaginary frequency of the transition state.

To investigate this interesting reaction, we performed density functional theory (DFT) calculations to gain more mechanistic insights (Figure 2). The results showed that the formation of the transition state TS3 was the rate-determining step due to the high energy barrier. Under normal conditions, elevating the temperature proved to be advantageous for the advancement of the reaction, aligning with our experimental findings. In addition, an excess of n-BuLi was important for the reaction to proceed properly. The crucial factor in the generation of the product was the proton transfer of the transition

state TS4, which was an extremely energetic step. Followed by the rearrangement of the intermediate E to produced the final product 3a**.** Transition state structures of PCs generated at the M062X(D3)/6-31G (d) level (distances in Å) starting from R1 and R2 transitions using the SMD solvation model and THF as the solvent (distances in Å). The parameter in parentheses is the unique imaginary frequency of the transition state (Figure 2).

Table 2 The gibbs energies of all optimized stationary points in solvent[a]

Structure	Gsol/Def2svp	Gsol/Def2TZVP	ΔGsol	ΔGsol (kcal/mol) = ΔGsol(Hartree)*627.51
A	0.072079	-517.0244251	-516.95	
3a	0.110242	-459.7971632	-459.69	
TS1	0.203662	-976.8135583	-976.61	0.0293710420
B	0.206262	-976.8285743	-976.62	0.0169550450
TS2	0.207964	-984.2661003	-984.06	0.0483978490
C	0.277231	-1019.437811	-1019.16	0.0309475950
TS3	0.274422	-1019.42086	-1019.15	0.0450898850
D1	0.156201	-861.1920769	-861.04	-0.0577682630
TS4	0.149069	-861.1108616	-860.96	0.0163151030
D3	0.155815	-861.1950091	-861.04	-0.0610863880
D2	0.153654	-861.1579802	-861.00	-0.0262184870
E	0.154291	-861.1483922	-860.99	-0.0159935320
3a	0.155343	-861.1984918	-861.04	-0.0650411150
C4H9	0.087431	-157.7245343	-157.64	

[a]Gibbs free energy conversion of R1 and R3 to PC1 at the M06-2X(D3)/6-31G (d) level using the SMD solvation model and DMF as solvent

7 Cartesian Coordinates Calculated by DFT

Table 2. Standard orientation, imaginary frequencies, thermodynamic energies and single-point energies of All Stationary Points

1a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.473793	-1.016594	0.000031
2	6	0	-1.097212	-1.219045	0.000064
3	6	0	-0.226291	-0.123314	0.000013
4	6	0	-0.743329	1.177976	-0.000066
5	6	0	-2.121580	1.376854	-0.000015
6	6	0	-2.986815	0.281784	0.000005
7	1	0	-3.151303	-1.873981	0.000019
8	1	0	-0.675166	-2.226248	0.000201
9	1	0	-0.060793	2.029207	-0.000138
10	1	0	-2.524060	2.392796	0.000030
11	1	0	-4.068190	0.441516	-0.000010
12	6	0	1.236788	-0.393597	-0.000036
13	8	0	1.724141	-1.499486	-0.000114
14	8	0	1.963726	0.724070	0.000025
15	6	0	3.372985	0.558144	0.000069
16	1	0	3.704874	0.009946	-0.894358
17	1	0	3.802382	1.567164	0.000233
18	1	0	3.704798	0.009672	0.894350

Freq calculation at PBE0-D3BJ/def2svp-smd(tetrahydrofuran) level

0 imaginary frequencies

Zero-point Energies= -459.151901

Thermal Energies= -459.143156

Thermal Enthalpies= -459.142211

Thermal Free Energies= -459.186295

3a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.870345	1.712514	0.221767
2	6	0	1.631410	1.075680	0.245703
3	6	0	1.534639	-0.306263	0.026495
4	6	0	2.707456	-1.030225	-0.235814
5	6	0	3.943709	-0.391624	-0.258090
6	6	0	4.031482	0.982326	-0.027528
7	1	0	2.927283	2.789463	0.399983
8	1	0	0.723142	1.647849	0.440668

9	1	0	2.653128	-2.100898	-0.444000
10	1	0	4.846405	-0.970855	-0.468540
11	1	0	5.002988	1.482579	-0.049308
12	6	0	0.210883	-0.968796	0.073467
13	8	0	-0.788859	-0.073049	-0.101648
14	16	0	-3.150891	0.953694	-0.160486
15	6	0	-4.746016	0.134922	0.034404
16	1	0	-4.914444	-0.615638	-0.753432
17	1	0	-4.840871	-0.338580	1.023901
18	1	0	-5.516813	0.913704	-0.055220
19	6	0	-2.106806	-0.519167	0.017535
20	1	0	-2.353361	-1.253664	-0.771649
21	1	0	-2.279811	-0.990057	1.003186
22	6	0	0.019084	-2.283272	0.284512
23	1	0	0.872703	-2.937955	0.457811
24	1	0	-0.972335	-2.737225	0.302850

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

0 imaginary frequencies

Zero-point Energies= -860.365857

Thermal Energies= -860.353578

Thermal Enthalpies= -860.352634

Thermal Free Energies= -860.406606

A

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.152981	0.047489	-0.448869
2	6	0	-1.636414	0.269628	0.297887
3	1	0	-1.613315	0.434377	1.384062
4	1	0	-2.267460	0.953834	-0.280432
5	6	0	0.494849	-1.510962	0.185968
6	1	0	-0.181798	-2.300782	-0.165478
7	1	0	1.510464	-1.674421	-0.202335
8	1	0	0.503127	-1.485595	1.285794
9	6	0	1.178246	1.121888	0.210022
10	1	0	1.238414	1.007005	1.302773
11	1	0	2.140571	0.869242	-0.260702
12	1	0	0.897607	2.153200	-0.045049

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

0 imaginary frequencies

Zero-point Energies= -516.642822

Thermal Energies= -516.636476

Thermal Enthalpies= -516.635531

Thermal Free Energies= -516.671562

B

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.340441	-1.264283	-0.672537
2	6	0	-2.030791	-0.841329	-0.903842
3	6	0	-1.436096	0.113952	-0.080958
4	6	0	-2.171985	0.650435	0.981389
5	6	0	-3.479744	0.227993	1.218937
6	6	0	-4.067914	-0.732592	0.392748
7	1	0	-3.798707	-2.010094	-1.328636
8	1	0	-1.432905	-1.224775	-1.734487
9	1	0	-1.717720	1.415702	1.615715
10	1	0	-4.048132	0.654483	2.050494
11	1	0	-5.094086	-1.061859	0.577797
12	6	0	0.018114	0.520602	-0.363014
13	8	0	0.531191	0.057216	-1.473945
14	8	0	-0.034936	1.979598	-0.264466
15	6	0	1.111967	2.626484	-0.708525
16	1	0	1.468544	2.204506	-1.664211
17	1	0	0.871173	3.691908	-0.855718
18	1	0	1.952272	2.580791	0.019795
19	16	0	2.483951	-0.334620	-0.005133
20	6	0	0.910525	0.004983	0.821121
21	1	0	0.553618	-0.948439	1.237961
22	1	0	1.103960	0.710992	1.644186
23	6	0	2.325370	-2.027580	-0.570707
24	1	0	1.560255	-1.990762	-1.353760
25	1	0	3.300310	-2.336226	-0.973684
26	1	0	2.026162	-2.675021	0.265321
27	6	0	3.538124	-0.611497	1.441097
28	1	0	3.088581	-1.335282	2.135097
29	1	0	4.509854	-0.977884	1.081416
30	1	0	3.680791	0.358369	1.937890

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

0 imaginary frequencies

Zero-point Energies= -975.805661

Thermal Energies= -975.790421

Thermal Enthalpies= -975.789477

Thermal Free Energies= -975.848418

C

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.026834	0.860593	0.988008
2	6	0	3.017495	-0.090896	1.060755
3	6	0	2.125723	-0.271147	-0.008408
4	6	0	2.270669	0.520738	-1.156173
5	6	0	3.285755	1.472221	-1.229893
6	6	0	4.162900	1.644876	-0.160087
7	1	0	4.713300	0.994307	1.827682
8	1	0	2.895080	-0.715836	1.947628
9	1	0	1.595369	0.405180	-2.005167
10	1	0	3.390187	2.083743	-2.129231
11	1	0	4.956686	2.393982	-0.220081
12	6	0	1.073000	-1.316574	0.149665
13	8	0	1.036582	-2.007991	1.150443
14	16	0	-1.676855	-1.320315	-0.436066
15	6	0	0.066561	-1.557756	-0.953589
16	1	0	0.178158	-2.599830	-1.280776
17	1	0	0.187102	-0.894482	-1.816035
18	6	0	-1.983507	-1.589672	1.324557
19	1	0	-1.091084	-2.055537	1.762481
20	1	0	-2.185893	-0.631684	1.816390
21	1	0	-2.839203	-2.271545	1.408998
22	6	0	-2.015845	-3.323700	-0.720031
23	1	0	-1.419829	-4.007192	-0.090524
24	1	0	-3.089650	-3.494542	-0.533459
25	1	0	-1.811776	-3.532208	-1.784078
26	6	0	-3.759261	3.623056	0.231140
27	1	0	-3.640270	4.714857	0.318214
28	1	0	-4.342435	3.283052	1.103234
29	1	0	-4.368830	3.426614	-0.666654
30	6	0	-2.417246	2.913157	0.153321
31	1	0	-1.841068	3.299872	-0.706419
32	1	0	-1.816062	3.155133	1.048054
33	6	0	-2.536339	1.396493	0.029192
34	1	0	-3.146130	1.157900	-0.864098
35	1	0	-3.127181	1.023167	0.888104

36	6	0	-1.219935	0.656508	-0.065116
37	1	0	-0.590788	0.815024	0.830053
38	1	0	-0.649472	1.011613	-0.940839

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

0 imaginary frequencies

Zero-point Energies= -1018.302142

Thermal Energies= -1018.283176

Thermal Enthalpies= -1018.282232

Thermal Free Energies= -1018.352216

D1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.758797	0.754906	-0.000004
2	6	0	2.416415	1.124709	-0.000008
3	6	0	1.400946	0.160603	-0.000002
4	6	0	1.765216	-1.192772	0.000010
5	6	0	3.108226	-1.567110	0.000015
6	6	0	4.109869	-0.595662	0.000008
7	1	0	4.536990	1.523142	-0.000009
8	1	0	2.110405	2.173160	-0.000017
9	1	0	1.003004	-1.974281	0.000016
10	1	0	3.374497	-2.627495	0.000024
11	1	0	5.162229	-0.891868	0.000012
12	6	0	-0.026791	0.672966	-0.000008
13	8	0	-0.207002	1.898517	-0.000025
14	16	0	-2.659321	0.272046	-0.000012
15	6	0	-1.058439	-0.299512	0.000013
16	1	0	-3.051278	-0.150032	-2.294063
17	1	0	-0.913975	-1.380062	0.000042
18	6	0	-3.498243	-0.545927	1.372401
19	1	0	-3.051305	-0.149890	2.294062
20	1	0	-4.568733	-0.297250	1.335505
21	1	0	-3.347291	-1.633017	1.310353
22	6	0	-3.498229	-0.546010	-1.372383
23	1	0	-3.347281	-1.633097	-1.310264
24	1	0	-4.568719	-0.297327	-1.335515

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

1 imaginary frequencies (-535.95)

Zero-point Energies= -860.353261

Thermal Energies= -860.341700

Thermal Enthalpies= -860.340756

Thermal Free Energies= -860.391578

D2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.704107	-0.819660	-0.000597
2	6	0	2.362489	-1.145234	-0.160539
3	6	0	1.377645	-0.148610	-0.103645
4	6	0	1.760700	1.182698	0.110182
5	6	0	3.106177	1.508157	0.266952
6	6	0	4.077864	0.509112	0.213638
7	1	0	4.465105	-1.602835	-0.042837
8	1	0	2.048172	-2.177044	-0.331311
9	1	0	1.012997	1.977125	0.153268
10	1	0	3.397499	2.548154	0.432598
11	1	0	5.132696	0.766661	0.339419
12	6	0	-0.043947	-0.563119	-0.294427
13	8	0	-0.335349	-1.713543	-0.539362
14	16	0	-2.775337	-0.215218	-0.135079
15	6	0	-1.105341	0.513000	-0.204929
16	1	0	-1.036418	1.164796	-1.092214
17	1	0	-0.977675	1.141328	0.689832
18	6	0	-3.659789	1.338902	-0.525258
19	1	0	-3.417102	1.673379	-1.545385
20	1	0	-4.729610	1.099154	-0.453334
21	1	0	-3.400732	2.115743	0.209304
22	6	0	-3.021507	-0.712076	1.432266
23	1	0	-3.082331	0.052171	2.215825
24	1	0	-3.674805	-1.585816	1.499142

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

0 imaginary frequencies

Zero-point Energies= -860.314585

Thermal Energies= -860.301973

Thermal Enthalpies= -860.301029

Thermal Free Energies= -860.354333

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	2.517881	-1.607088	1.031297
2	6	0	1.493839	-0.670610	1.165492
3	6	0	1.272306	0.287473	0.172634
4	6	0	2.106886	0.310593	-0.950609
5	6	0	3.134352	-0.621569	-1.083034
6	6	0	3.340963	-1.586867	-0.095004
7	1	0	2.679969	-2.353247	1.814124
8	1	0	0.850300	-0.658642	2.048243
9	1	0	1.941744	1.067720	-1.719576
10	1	0	3.782425	-0.594074	-1.963477
11	1	0	4.146359	-2.318456	-0.201592
12	6	0	0.132790	1.259629	0.365498
13	8	0	-0.398949	1.401813	1.473805
14	8	0	0.300082	2.345155	-0.467922
15	6	0	-0.595939	3.400537	-0.251726
16	1	0	-0.545664	3.774115	0.783357
17	1	0	-0.319566	4.204802	-0.947923
18	1	0	-1.639788	3.098090	-0.452347
19	16	0	-1.738138	-1.227138	-0.182999
20	6	0	-1.214568	0.237783	-0.931252
21	1	0	-0.612159	-0.013643	-1.812802
22	1	0	-2.059167	0.905883	-1.157906
23	6	0	-3.124249	-1.965355	-1.088853
24	1	0	-2.727863	-2.323775	-2.049023
25	1	0	-3.514810	-2.814231	-0.507167
26	1	0	-3.904702	-1.208434	-1.252368
27	6	0	-2.600903	-0.637623	1.274050
28	1	0	-3.511039	-0.100335	0.970757
29	1	0	-2.847750	-1.499779	1.907954
30	1	0	-1.897297	0.051052	1.769693

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

1 imaginary frequencies (-195.61 icm-1)

Zero-point Energies= -975.792721

Thermal Energies= -975.777402

Thermal Enthalpies= -975.776458

Thermal Free Energies= -975.835968

TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	3.653299	-0.956544	0.619785
2	6	0	2.326686	-0.730544	0.988371
3	6	0	1.438452	-0.105230	0.112555
4	6	0	1.901150	0.304459	-1.142912
5	6	0	3.226432	0.082711	-1.517101
6	6	0	4.105985	-0.552530	-0.637103
7	1	0	4.340702	-1.445812	1.316195
8	1	0	1.933649	-1.013103	1.968653
9	1	0	1.214592	0.820587	-1.819109
10	1	0	3.580064	0.412932	-2.498235
11	1	0	5.145396	-0.725352	-0.929645
12	6	0	-0.020394	0.093309	0.582233
13	8	0	-0.229463	-0.040066	1.834141
14	8	0	-0.458681	1.433190	0.011937
15	6	0	-0.099172	2.512153	0.818598
16	1	0	0.700676	2.241520	1.528506
17	1	0	0.254367	3.347338	0.187604
18	1	0	-0.949395	2.881095	1.424753
19	16	0	-2.604540	-0.240217	0.111974
20	6	0	-0.942251	-0.820754	-0.285947
21	1	0	-0.869053	-1.854969	0.076239
22	1	0	-0.816661	-0.783183	-1.378836
23	6	0	-3.595801	-1.730060	-0.046037
24	1	0	-3.343872	-2.375165	0.807055
25	1	0	-4.654237	-1.440404	0.014980
26	1	0	-3.385371	-2.240884	-0.995616
27	6	0	-3.076619	0.638488	-1.378477
28	1	0	-2.358293	1.463823	-1.459731
29	1	0	-3.025889	-0.026796	-2.251096
30	1	0	-4.095480	1.024094	-1.235721

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

1 imaginary frequencies (-202.44 icm-1)

Zero-point Energies= -975.801259

Thermal Energies= -975.786448

Thermal Enthalpies= -975.785504

Thermal Free Energies= -975.844100

TS3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.693788	-0.793386	-0.070627

2	6	0	3.693658	0.172369	-0.083263
3	6	0	2.343211	-0.199045	-0.004225
4	6	0	2.012742	-1.560596	0.075922
5	6	0	3.016181	-2.526281	0.084036
6	6	0	4.356981	-2.146131	0.013781
7	1	0	5.743072	-0.492915	-0.128361
8	1	0	3.934903	1.235138	-0.153085
9	1	0	0.968762	-1.877644	0.117774
10	1	0	2.749119	-3.584359	0.141669
11	1	0	5.141963	-2.906758	0.021578
12	6	0	1.322077	0.889094	-0.019054
13	8	0	1.646849	2.047959	-0.252813
14	16	0	-1.389123	1.680304	0.289609
15	6	0	-0.077808	0.459029	0.211211
16	1	0	-0.202190	-0.178645	1.098376
17	1	0	-0.596526	-0.094785	-0.651813
18	6	0	-1.168587	2.677485	-1.190540
19	1	0	-1.224691	1.988947	-2.040520
20	1	0	-2.013922	3.379476	-1.219700
21	1	0	-0.206509	3.199615	-1.148336
22	6	0	-0.706010	2.857286	1.513985
23	1	0	0.306127	3.181652	1.239730
24	1	0	-1.399306	3.709336	1.558395
25	1	0	-0.706899	2.341429	2.484908
26	6	0	-4.664701	-2.805466	0.792586
27	1	0	-5.628944	-3.308416	0.613422
28	1	0	-4.757817	-2.240646	1.735820
29	1	0	-3.908667	-3.591878	0.957579
30	6	0	-4.271035	-1.893818	-0.359590
31	1	0	-4.214448	-2.478260	-1.296019
32	1	0	-5.063891	-1.141827	-0.526804
33	6	0	-2.939410	-1.164211	-0.150508
34	1	0	-2.161933	-1.933404	0.037504
35	1	0	-3.017449	-0.608991	0.812042
36	6	0	-2.479435	-0.226679	-1.243273
37	1	0	-3.285060	0.479715	-1.528025
38	1	0	-2.194433	-0.783225	-2.160020

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

1 imaginary frequencies (-326.62 icm-1)

Zero-point Energies= -1018.291576

Thermal Energies= -1018.272653

Thermal Enthalpies= -1018.271709

Thermal Free Energies= -1018.340731

TS4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.724547	0.782472	0.029888
2	6	0	2.388356	1.155069	-0.080126
3	6	0	1.373790	0.189984	-0.046358
4	6	0	1.722666	-1.160828	0.088549
5	6	0	3.060754	-1.534662	0.194667
6	6	0	4.063624	-0.564772	0.168320
7	1	0	4.507839	1.544616	0.006041
8	1	0	2.098599	2.201891	-0.194755
9	1	0	0.948254	-1.931025	0.095665
10	1	0	3.323030	-2.591013	0.294323
11	1	0	5.112706	-0.860228	0.252687
12	6	0	-0.046321	0.664220	-0.162449
13	8	0	-0.284919	1.834366	-0.440072
14	16	0	-2.775730	0.230909	-0.172568
15	6	0	-1.087290	-0.344945	0.000653
16	1	0	-1.586356	-1.092187	-1.047191
17	1	0	-0.985526	-1.057499	0.830803
18	6	0	-3.502539	0.083250	1.465970
19	1	0	-3.086383	0.878662	2.100853
20	1	0	-4.588033	0.222516	1.365495
21	1	0	-3.279591	-0.907406	1.886796
22	6	0	-3.114421	-1.215195	-1.148991
23	1	0	-3.350992	-2.069290	-0.491807
24	1	0	-3.921512	-1.036060	-1.877978

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

1 imaginary frequencies (-1700.40 icm-1)

Zero-point Energies= -860.279561

Thermal Energies= -860.267460

Thermal Enthalpies= -860.266516

Thermal Free Energies= -860.318955

E

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.744196	0.926575	0.963793

2	6	0	1.498806	1.165892	0.387640
3	6	0	0.947934	0.266638	-0.535788
4	6	0	1.688220	-0.871890	-0.885897
5	6	0	2.935707	-1.111382	-0.313447
6	6	0	3.466687	-0.215940	0.616851
7	1	0	3.156784	1.636369	1.686046
8	1	0	0.919127	2.058153	0.634710
9	1	0	1.294431	-1.575277	-1.623109
10	1	0	3.501314	-2.002412	-0.598919
11	1	0	4.445598	-0.405720	1.064920
12	6	0	-0.411316	0.578090	-1.095390
13	8	0	-0.922176	1.695824	-0.840291
14	16	0	-2.591838	-0.530478	0.322055
15	6	0	-1.184430	-0.445971	-1.677721
16	1	0	-0.781000	-1.440489	-1.886406
17	1	0	-2.060046	-0.143369	-2.256883
18	6	0	-1.417002	-1.482513	1.296734
19	1	0	-0.485991	-0.916109	1.429040
20	1	0	-1.872438	-1.707380	2.271149
21	1	0	-1.214440	-2.414040	0.751827
22	6	0	-2.459894	0.996530	0.893671
23	1	0	-1.685587	1.283470	1.606757
24	1	0	-3.224386	1.711681	0.587645

Freq calculation at PBE0-D3BJ/def2svp- smd(tetrahydrofuran) level

1 imaginary frequencies (-181.18 icm-1)

Zero-point Energies= -860.314811

Thermal Energies= -860.303056

Thermal Enthalpies= -860.302111

Thermal Free Energies= -860.353272

REFERENCES

(1) Paul Mosset & René Grée (1985) Trimethylsulfonium Methylsulfate, A Simple and Efficient Epoxidizing Agent, Synthetic Communications, 15:8, 749-757, DOI: 10.1080/00397918508063867

(2) Nagaki, A., Takabayashi, N., Moriwaki, Y. and Yoshida, J.-i. (2012), Flash Generation of a Highly Reactive Pd Catalyst for Suzuki–Miyaura Coupling by Using a Flow Microreactor. Chem. Eur. J., 18: 11871-11875. https://doi.org/10.1002/chem.201201579

(3) Saravanselvi, C., Somasundaram, N., Vijaikumar, S. et al. Deoximation on irradiated TiO2: regeneration of ketones from ketoximes. Photochem Photobiol Sci 1, 607–608 (2002). https://doi.org/10.1039/b203721c