Supporting Information

Diastereoselective Synthesis of β - Hydroxy Allylic Tertiary Sulfides via Nickel/Photoredox Cooperative Catalysis

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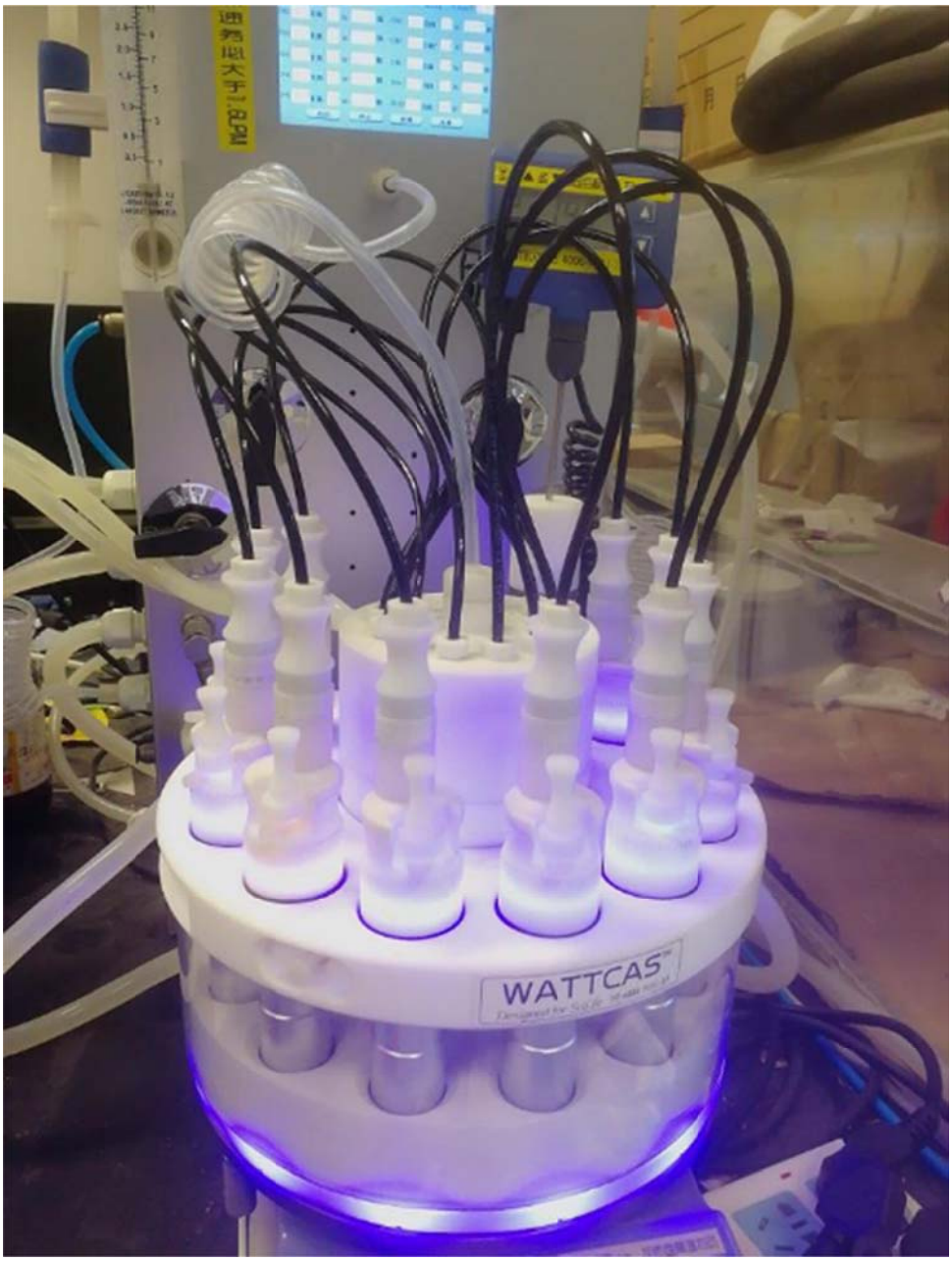
S1 General Information

Unless otherwise noted, all reactions of substrates preparation were conducted in flame-dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin-layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde, or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L) with a 10W LED. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 400 M and 500 M spectrometer. Chemical shifts in ^{1}H NMR spectra were reported in parts per million (ppm) on the δ = scale from an internal standard of residual $CDCl_3$ (7.26 ppm). Data for ^{1}H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of $CDCl_3$ (77.00 ppm). ESI mass spectra were obtained from an HPLC-Q-Tof mass spectrometer using acetonitrile as the mobile phase. The fluorescence emission spectra were collected on an Edinburg FLS1000. Chemicals were purchased from commercial suppliers. Unless stated otherwise, all the substrates and solvents were purified dried according to standard methods prior use.

S2 Reaction Set-Up and Light Source

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP-TEC-1020L).

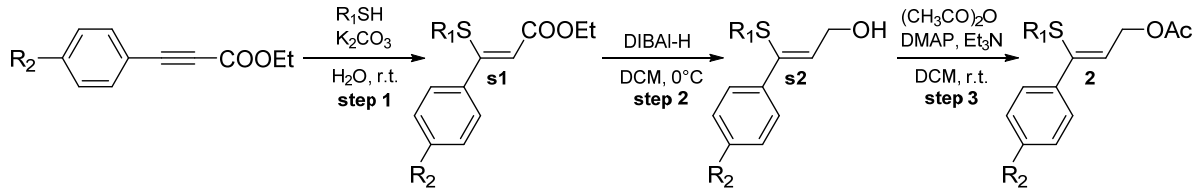


Emission spectra of the 10 W blue LED lamp (maximum emission at λ = 455 nm). Wavelength: 450-455 nm Quartz glass was used as reaction vessel. Distance between the light source and quartz tube was approximately 0.5 cm and no filter was used for the reaction.

S3 Synthesis of Substrates

1a-1x were obtained from commercial sources.

S3.1 Synthesis of allyl substrates



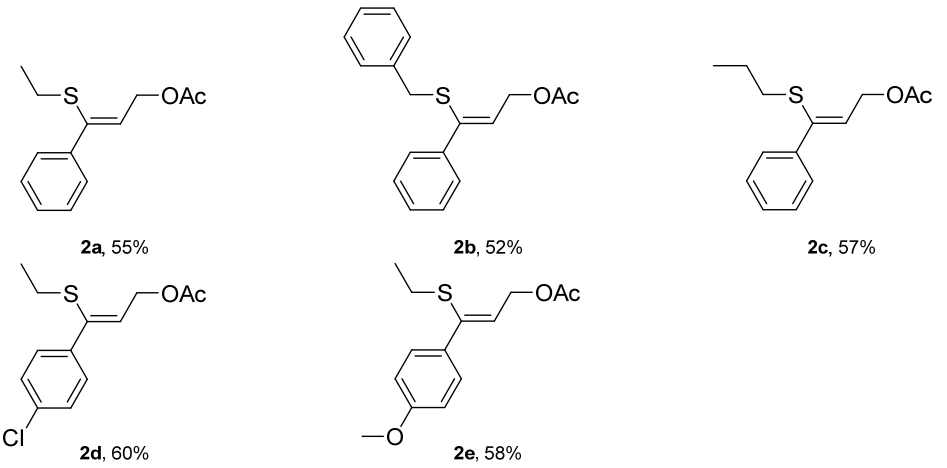


Table S1 Synthesis of allyl substrates

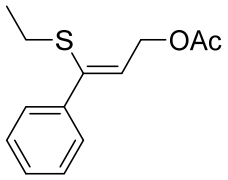
Step 1. A round-bottom flask equipped with a magnetic stir bar was charged with K_2CO_3 (28.7 mmol, 1.0 equiv.) and water (70 mL, 0.4 M), followed by ethyl phenylpropiolate (28.7 mmol, 1.0 equiv.) and ethanethiol (28.7 mmol, 1.0 equiv.). The mixture was stirred vigorously at room temperature for 24 h and monitored by TLC until complete consumption of the starting material.[1] The saturated Na_2CO_3 was added into the system, followed by extraction with EA for three times. The organic layers were combined and washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified via silica gel column chromatography to obtain **s1** (72%) as yellow liquid.

Step 2. A double-neck flask equipped with a magnetic stir bar and **s1** (20.7 mmol, 1.0 equiv.) was purged with N_2 three times. DCM (50 mL, 0.4 M) was added under N_2 protection, and the mixture was stirred at 0°C for 15 min. DIBAl-H (51.7 mmol, 2.5 equiv.) was then added dropwise under N_2 protection.[2] The mixture was stirred at 0°C and monitored by TLC. After approximately 2 h, the reaction was complete, and HCl (1M) was added dropwise slowly at 0°C. Vigorous gas evolution was observed during the quenching, and the mixture turned into a gelatinous mass. Upon further addition of HCl with continued stirring, the mixture reverted to a clear solution, followed by extraction with DCM for three times. The organic layers were combined, dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue containing the unstable intermediate **s2** was used directly in the next step without complete removal of the DCM.

Step 3. A round-bottom flask equipped with a magnetic stir bar and containing the intermediate **s2** (20.7 mmol, 1.0 equiv.) in DCM was added sequentially DMAP (2.1 mmol, 0.1 equiv.), Et_3N (41.4 mmol, 2.0 equiv.) and $(CH_3CO)_2O$ (31.1 mmol, 1.5 equiv.).[3] The mixture was stirred at room

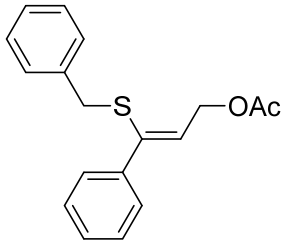
temperature and monitored by TLC. After approximately 2 h, the reaction was complete. The mixture was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to obtain **2**.

(Z)-3-(ethylthio)-3-phenylallyl acetate（2a）



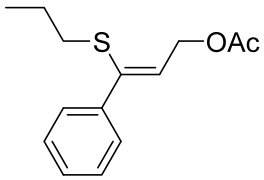
Purified by silica gel flash colum chromatograph (EA/PE = 1/100) to give **2a** as yellow liquid.
Rf = 0.5 (EA/PE = 1/10).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 6.8 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.06 (t, *J* = 6.4 Hz, 1H), 4.97 (d, *J* = 6.4 Hz, 2H), 2.39 (q, *J* = 7.2 Hz, 2H), 2.09 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 140.9, 138.9, 128.3, 128.2, 128.1, 127.9, 62.5, 26.2, 20.9, 14.9 .
HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{13}H_{16}O_2SNa$, 259.0763, found: 259.0760.

(Z)-3-(benzylthio)-3-phenylallyl acetate（2b）



Purified by silica gel flash colum chromatograph (EA/PE = 1/100) to give **2b** as yellow liquid.
Rf = 0.5 (EA/PE = 1/10).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.29 – 7.22 (m, 3H), 7.08 (d, *J* = 7.1 Hz, 2H), 6.11 (t, *J* = 6.5 Hz, 1H), 4.85 (d, *J* = 6.5 Hz, 2H), 3.65 (s, 2H), 2.09 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7 , 140.4 , 138.8 , 137.8 , 129.0 , 128.6 , 128.4 , 128.3 , 128.1 , 128.0 , 126.8 , 62.4 , 36.8 , 20.8 .
HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{18}H_{18}O_2SNa$, 321.0920, found: 321.0922.

(Z)-3-phenyl-3-(propylthio)allyl acetate（2c）



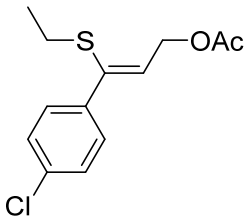
Purified by silica gel flash colum chromatograph (EA/PE = 1/100) to give **2c** as yellow liquid.
Rf = 0.5 (EA/PE = 1/10).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.34 – 7.27 (m, 3H), 6.02 (t, *J* = 6.4 Hz, 1H), 4.96 (d, *J* = 6.5 Hz, 2H), 2.33 (t, 2H), 2.05 (s, 3H), 1.38 (h, *J* = 7.3 Hz, 2H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5 , 141.1 , 138.8 , 128.1 , 128.0 , 127.8 , 127.7 , 62.3 , 33.9 , 22.9 , 20.7 , 12.8 .

HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{14}H_{18}O_2SNa$, 273.0920, found: 273.0923.

(Z)-3-(4-chlorophenyl)-3-(ethylthio)allyl acetate（2d）



Purified by silica gel flash colum chromatograph (EA/PE = 1/100) to give **2d** as yellow liquid.

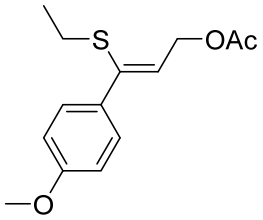
Rf = 0.5 (EA/PE = 1/10).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 6.04 (t, *J* = 6.2 Hz, 1H), 4.93 (d, *J* = 6.4 Hz, 2H), 2.35 (q, *J* = 7.3 Hz, 2H), 2.07 (s, 3H), 1.04 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8 , 139.6 , 137.4 , 134.0 , 129.1 , 128.8 , 128.5 , 62.4 , 26.2 , 20.9 , 14.9 .

HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{13}H_{15}ClO_2SNa$, 293.0373, found: 293.0376.

(Z)-3-(ethylthio)-3-(4-methoxyphenyl)allyl acetate（2e）



Purified by silica gel flash colum chromatograph (EA/PE = 1/100) to give **2e** as yellow liquid.

Rf = 0.3 (EA/PE = 1/10).

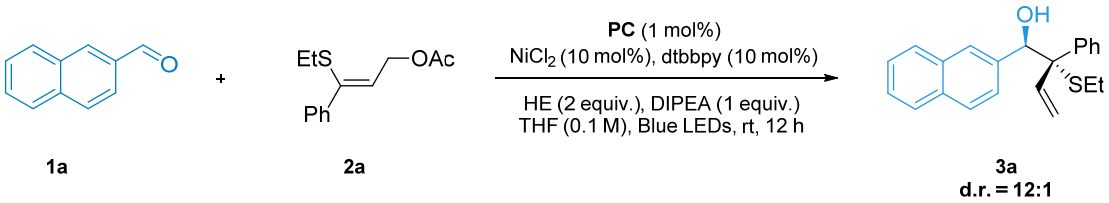
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.00 (t, *J* = 6.5 Hz, 1H), 4.95 (d, *J* = 6.6 Hz, 2H), 3.81 (s, 3H), 2.39 (q, *J* = 7.3 Hz, 2H), 2.09 (s, 3H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9 , 159.6 , 140.7 , 131.3 , 129.1 , 126.7 , 113.7 , 62.6 , 55.2 , 26.2 , 21.0 , 15.0 .

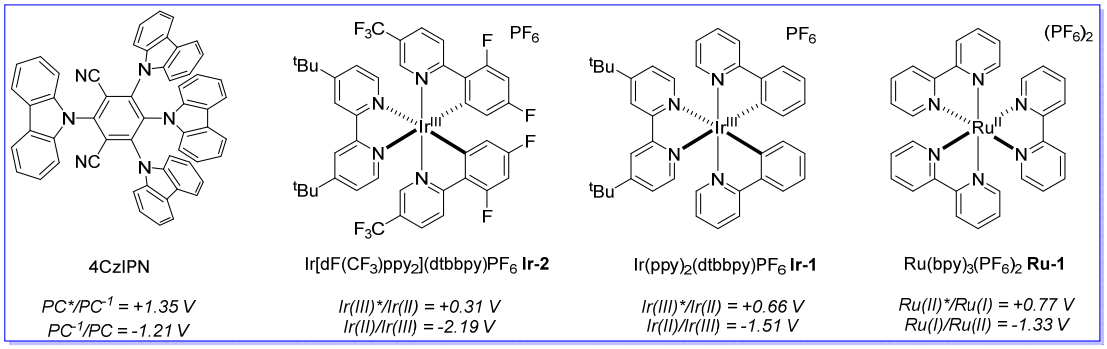
HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{14}H_{18}O_3SNa$, 289.0869, found: 289.0872.

S4 Detailed Optimizations of Conditions

Table S2 Screening of Photocatalysts[a,b,c]



1a **2a** **3a**
d.r. = 12:1



4CzIPN
PC/PC^{-1} = +1.35 V*
PC^{-1}/PC = -1.21 V

Ir[dF(CF$_3$)ppy$_2$](dtbbpy)PF$_6$ **Ir-2**
Ir(III)/Ir(II) = +0.31 V*
Ir(II)/Ir(III) = -2.19 V

Ir(ppy)$_2$(dtbbpy)PF$_6$ **Ir-1**
Ir(III)/Ir(II) = +0.66 V*
Ir(II)/Ir(III) = -1.51 V

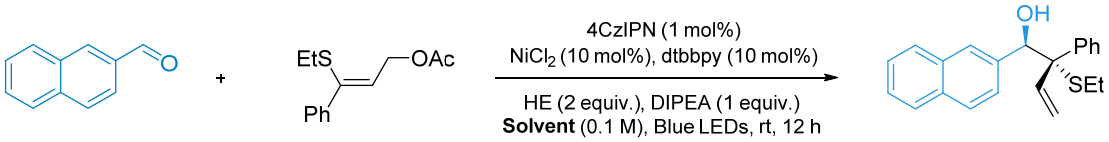
Ru(bpy)$_3$(PF$_6$)$_2$ **Ru-1**
Ru(II)/Ru(I) = +0.77 V*
Ru(I)/Ru(II) = -1.33 V

Entry	Photocatalysts	Yield (%)	d.r.
1	4CzIPN	85	12:1
2	Ir[dF(CF$_3$)ppy$_2$](dtbbpy)PF$_6$ **Ir-2**	64	12:1
3	Ir(ppy)$_2$(dtbbpy)PF$_6$ **Ir-1**	49	12:1
4	Ru(bpy)$_3$(PF$_6$)$_2$ **Ru-1**	0	-

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), 12 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [c] The diastereoselectivity was determined by ^{1}H NMR.

Based on the hard–soft acid–base (HSAB) theory, sulfur atoms in sulfides are typical soft bases. Conventional nucleophilic allylation mostly relies on noble metal catalysts (Pd, Ir, Rh) whose active species are classic soft acids. Sulfur will form stable, irreversible coordination bonds with these metals, causing severe catalyst poisoning and deactivation, which is the core reason why conventional methods fail to realize this transformation. In contrast, the catalytically active species of nickel are borderline acids in the HSAB classification, which have much weaker binding affinity toward soft sulfur donors. The weak and reversible S–Ni coordination will not cause irreversible catalyst poisoning, enabling our nickel-based system to inherently circumvent this limitation and achieve the desired allylation efficiently.

Table S3 Screening of Solvents[a,b,c]



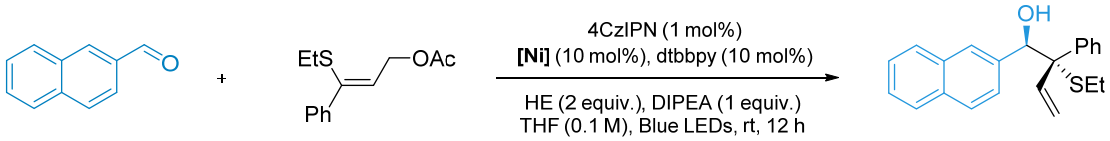
1a **2a** **3a**
d.r. = 12:1

Entry	Solvents	Yield (%)	d.r.
1	THF	85	12:1
2	MeCN	47	12:1
3	1,4-Dioxane	60	12:1
4	Et_2O	61	2:1

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), 12 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [c] The diastereoselectivity was determined by ^{1}H NMR.

We speculate that the reduced diastereoselectivity in diethyl ether arises from its weaker solvation ability compared with the cyclic ethers THF and 1,4-dioxane. Polar cyclic ethers may better stabilize the stereoselective transition state of the reaction, while acyclic diethyl ether with lower polarity cannot provide sufficient stabilization, resulting in decreased diastereoselectivity.

Table S4 Screening of Nickel salts[a,b,c]

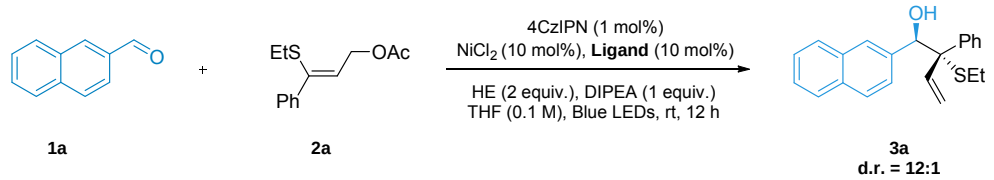


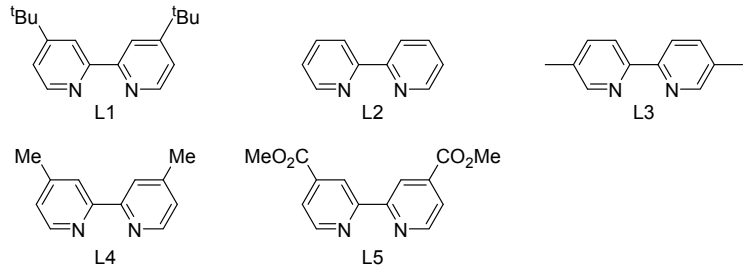
1a **2a** **3a**
d.r. = 12:1

Entry	Nickel salts	Yield (%)	d.r.
1	$NiCl_2$	85	12:1
2	$NiBr_2$	73	12:1
3	NiF_2	0	-
4	$Ni(OTf)_2$	50	12:1
5	$Ni(COD)_2$	0	-
6	$Ni(OH)_2$	0	-
7	$NiCO_3$	0	-

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), 12 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [c] The diastereoselectivity was determined by ^{1}H NMR.

Table S5 Screening of Ligands[a,b,c]



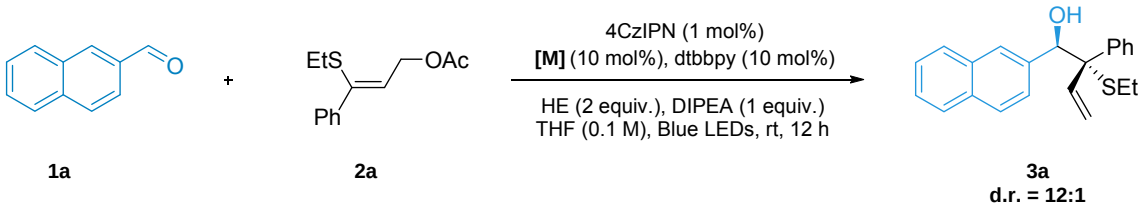


Entry	Ligands	Yield (%)	d.r.
1	L1	85	12:1
2	L2	75	10:1
3	L3	51	4:1
4	L4	53	5:1
5	L5	28	3:1

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), 12 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [c] The diastereoselectivity was determined by ^{1}H NMR.

We hypothesize that the significant difference in diastereoselectivity among L1, L2 and L4 may be attributed to the combined electronic and steric effects of the ligands. The electron-donating ability and steric bulk of the ligand substituents may follow the order L1 > L4 > L2. We speculate that stronger electron donation from L1 may elevate the electron density of the Ni center, enhancing the nucleophilicity of the allyl-nickel intermediate and amplifying the energy difference between diastereomeric transition states. Meanwhile, the bulky substituents of L1 may form a congested coordination sphere around Ni, which may restrict aldehyde addition to the sterically favorable anti-pathway, thus delivering the highest diastereoselectivity.

Table S6 Screening of Metals[a,b,c]

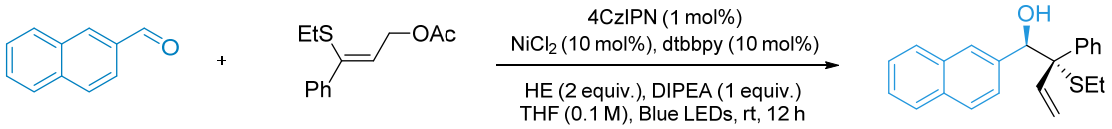


1a **2a** **3a**
d.r. = 12:1

Entry	Metals	Yield (%)	d.r.
1	$NiCl_2$	85	12:1
2	$CoBr_2$	0	-
3	$CoCl_2$	0	-
4	$CrCl_2$	0	-
5	Cp_2TiCl_2	0	-

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), 12 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [c] The diastereoselectivity was determined by ^{1}H NMR.

Table S7 Control experiments[a,b,c]

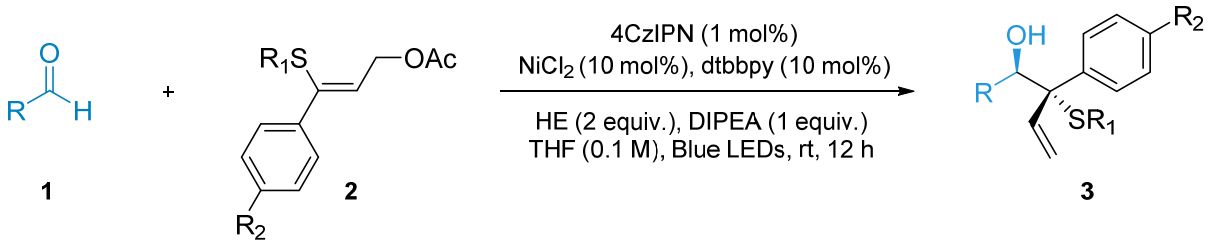


1a **2a** **3a**
d.r. = 12:1

Entry	Conditions	Yield (%)	d.r.
1	As show	85	12:1
2	No $NiCl_2$	0	-
3	No dtbbpy	0	-
4	No 4CzIPN	22	12:1
5	No HE	38	3:1
6	No DIPEA	70	12:1
7	No light	0	-
8	No 4CzIPN and DIPEA	11	12:1
9	No 4CzIPN and HE	0	-
10	No HE and DIPEA	0	-

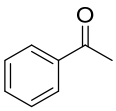
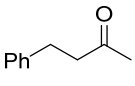
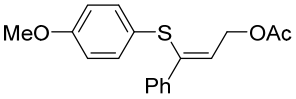
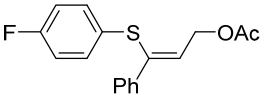
[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), 12 h. [b] Yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [c] The diastereoselectivity was determined by ^{1}H NMR.

S5 General Procedure



An oven-dried Schlenk tube containing a stir bar was charged under nitrogen with $NiCl_2$ (0.02 mmol, 10 mol%), dtbbpy (0.02 mmol, 10 mol%) and THF (0.1 M). The above mixture was stirred in N_2-filled glovebox for 2 h till clear. Subsequently, 4CzIPN (0.002 mmol, 1 mol%), HE (0.4 mmol, 2.0 equiv.), DIPEA (0.2 mmol, 1.0 equiv.), corresponding **1** (0.2 mmol, 1.0 equiv.) and **2** (0.6 mmol, 3.0 equiv.) were added. The reaction mixture was then stirred at room temperate under blue LEDs irradiation (10 W, 450 nm) for 12 h. After completing, the reaction mixture was purified by silica gel column chromatography (PE/EA) and refined by semipre HPLC (PE/EA) to afford the corresponding compounds.

non-reactive substrates.

			
0%	0%	0%	0%

S6 Stern-Volmer Luminescence Quenching Analysis

All samples used in the luminescence quenching-based screening studies were prepared under oxygen free conditions. The photosensitizer 4CzIPN and potential quenchers were weighed into vials and placed inside a glovebox under a positive pressure of nitrogen. THF was degassed by nitrogen sparging for one hour and also placed inside along with micropipettes and their tips, cuvettes, empty vials, waste containers and parafilm. SternVolmer luminescence quenching studies were carried out using 1.0×10^{-5} M solution of 4CzIPN and equal concentrations of HE and allyl substrate (**2a**) and DIPEA and $Ni(dtbbpy)Cl_2$ in degassed and dried THF at room temperature under an nitrogen atmosphere. The samples were prepared in screw-top 4.5 cm quartz cuvettes, equipped with PTFE stopper, and sealed with parafilm inside a nitrogen-filled glovebox. The solutions were irradiated at 396 nm and the luminescence was measured at 518 nm. The ratio of I_0/I was plotted as a function of the quencher concentration (I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed emission intensity of the photocatalyst with added quencher). The results verify that HE exhibits the highest quenching efficiency toward the photosensitizer 4CzIPN.

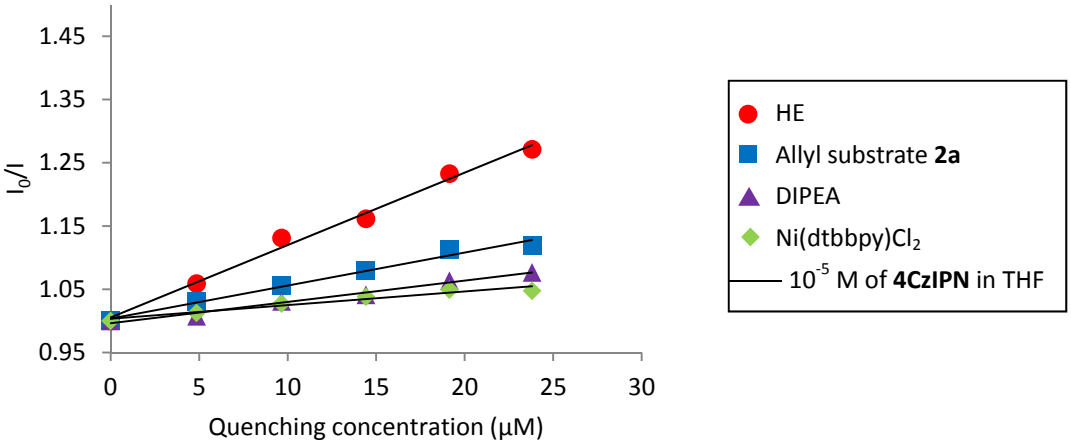
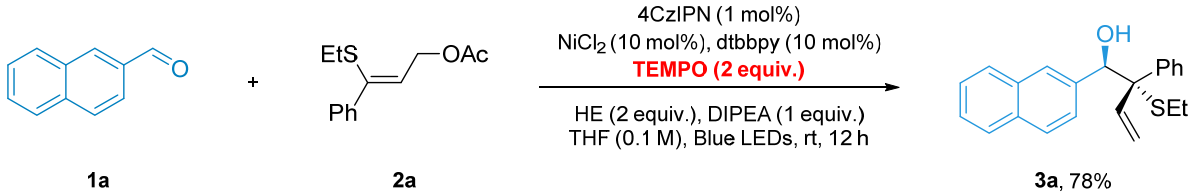


Figure S1. 4CzIPN emission quenching by HE, **2a**, DIPEA, $Ni(dtbbpy)Cl_2$

S7 Mechanistic Studies



1a **2a** **3a**, 78%

An oven-dried Schlenk tube containing a stir bar was charged under nitrogen with $NiCl_2$ (0.01 mmol, 10 mol%), dtbbpy (0.01 mmol, 10 mol%) and THF (0.1 M). the above mixture was stirred in N_2-filled glovebox for 2h. Subsequently, 4CzIPN (0.001 mmol, 1 mol%), HE (0.2 mmol, 2equiv.) and DIPEA (0.1 mmol, 1 equiv.), corresponding **1a** (0.1 mmol, 1 equiv.), **2a** (0.3 mmol, 3 equiv.) and radical inhibitor (TEMPO, 2 equiv.) were added. The reaction mixture was then stirred at room temperate under blue LEDs irradiation (10 W, 450 nm). After 12 h, the reaction mixture was filtered through a short layer of silica gel and the filtrate was concentrated in vacuo. The results of ^1H NMR and HRMS showed that the reaction was not inhibited.

S8 Mechanistic Studies

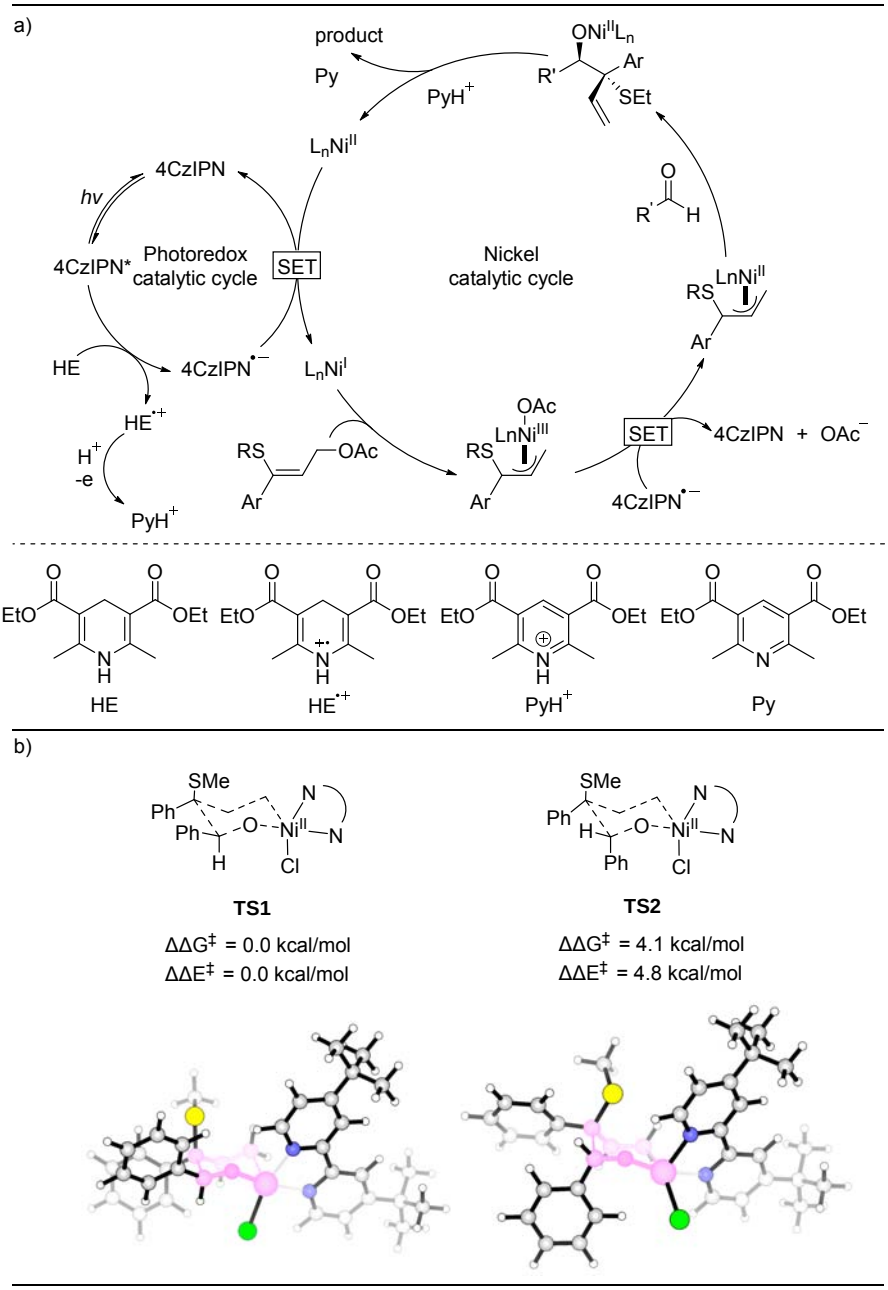


Figure S2. a) Proposed mechanism; b) Two stereo-determining transition states calculated at the (U)M06-D3/6-311+G(d,p) (SDD for Ni)/SMD(THF)//(U)M06-L-D3/6-31G(d) (SDD for Ni) level at 298.15 K. The six-membered rings of the chair-like transition states are labeled in pink.

S9 Single crystal X-ray diffraction data

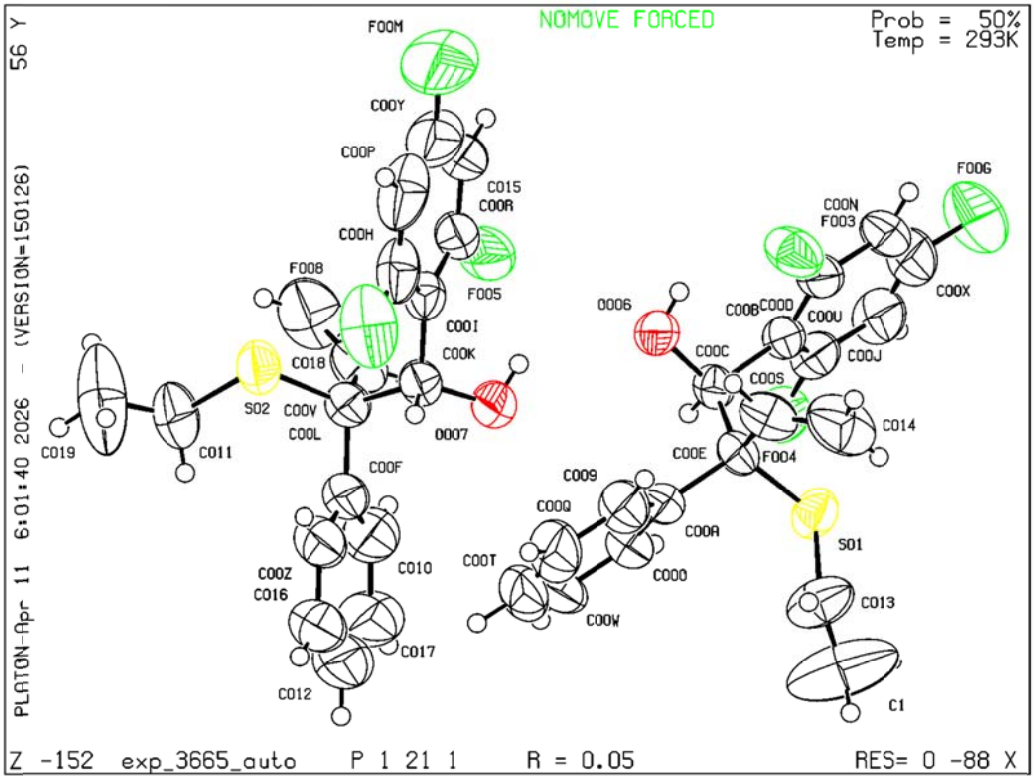


Figure S3. X-ray crystallographic analysis of **3y** (CCDC: 2545520).

Table S8 Crystal imformation of product **3y** (CCDC no. 2545520)

Identification code	**exp_3665_auto**
Empirical formula	$C_{18}H_{17}F_3OS$
Formula weight	338.38
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.1812(2)
b/Å	21.2592(6)
c/Å	11.2046(3)
α/°	90
β/°	91.832(2)
γ/°	90
Volume/Å^3	1709.69(8)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	1.965
F(000)	704.0
Crystal size/mm^3	0.5 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.894 to 135.958
Index ranges	$-6 \le h \le 8$, $-25 \le k \le 23$, $-13 \le l \le 13$
Reflections collected	8401
Independent reflections	4540 [R_{int} = 0.0384, R_{sigma} = 0.0513]
Data/restraints/parameters	4540/79/420
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	R_1 = 0.0460, wR_2 = 0.1266
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1359
Largest diff. peak/hole / e Å^{-3}	0.22/-0.20
Flack parameter	-0.016(14)

S10 Computational Details

DFT calculations of the two transition states were performed in the Gaussian 16 program.[4] Geometry optimizations were performed using the pure functional M06-L (with Grimme's D3 dispersion correction) in the gas phase, with the Pople basis set 6-31G(d).[5-7] Pseudopotential basis set SDD was applied for the nickel atom.[8] Single point energy calculations were then performed using the hybrid functional M06 (with Grimme's D3 dispersion correction) with the SMD solvation model (solvent is set to tetrahydrofuran), with the Pople basis set 6-311+G(d,p).[9-10]

Gibbs free energy calculations were performed using the Goodvibes program with Grimme's quasi-harmonic entropic correction at 298.15 K.[11-12]

The 3D structures in the main text are generated using the CYLview20 program.[13]

S11 Cartesian Coordinates

TS1

Imaginary Frequency: -302.73 cm^{-1}

0 3 (0 denotes the net charge; 3 denotes the multiplicity)

Ni	-2.42299200	-0.09797100	1.34846600
C	-0.77005600	0.66847000	0.02027500
C	-1.01155700	-0.31902500	-0.90464400
C	-1.92136600	-0.27503700	-2.02012300
C	-3.65701900	-0.67684300	-1.11767500
O	-3.74891300	0.10282000	-0.08273900
H	-0.53226900	-1.28214400	-0.72083200
H	-1.09930500	1.68976600	-0.16922600
H	0.03368300	0.53270600	0.74298600
C	-4.67562900	-0.50632200	-2.18666000
C	-4.91654000	-1.53517100	-3.10502100
C	-5.41641900	0.67704900	-2.28821100
C	-5.85934700	-1.37475700	-4.11460800
C	-6.36130400	0.83618600	-3.29394400
C	-6.58169500	-0.18769100	-4.21464400
H	-6.93078600	1.76217400	-3.36254600
H	-3.38351000	-1.72932100	-0.93210600
C	-1.77513200	-1.37606300	-3.01606200
C	-1.91589800	-1.17847100	-4.39556900
C	-1.58475100	-2.69347000	-2.55852000
C	-1.84985600	-2.24731200	-5.28493800
H	-2.11106200	-0.17377000	-4.76715100
C	-1.52057800	-3.75905200	-3.44885000
H	-1.52611200	-2.89158200	-1.48659200
C	-1.64903200	-3.54360900	-4.82004200
H	-1.38252000	-4.76840400	-3.06364000
H	-5.23657800	1.46730000	-1.56155400
H	-4.35634100	-2.46622000	-3.02154900
H	-1.96504200	-2.06150200	-6.35214300
H	-1.60242200	-4.37935100	-5.51626200
C	-2.25153600	2.34544400	3.03010700
C	-2.37573600	3.67770100	3.41209500
C	-3.14678600	4.56881600	2.65839200
C	-3.76428800	4.05095500	1.51766300
C	-3.59572200	2.71192300	1.18481700
C	-1.44073500	1.35214400	3.75842600
C	-0.80992700	1.61208000	4.97090000
C	-0.04309000	0.62905500	5.60497300
C	0.04511800	-0.60520700	4.95827800
C	-0.61918600	-0.80704000	3.75370200

H	-1.85714700	4.03435500	4.29994000
H	-4.37344500	4.67722600	0.87234700
H	-4.03550100	2.26092300	0.29638900
H	-0.92269100	2.58914700	5.43677900
H	0.61914700	-1.42427300	5.38204500
H	-0.60189200	-1.76112800	3.22622100
N	-2.86644200	1.87384400	1.92480600
N	-1.34515800	0.14343100	3.15988200
C	-3.26879300	6.02422400	3.09254700
C	0.63324000	0.93152100	6.93619900
C	-1.87018100	6.65558900	3.12532200
H	-1.20359900	6.13960600	3.82694200
H	-1.93591700	7.70372100	3.44249000
H	-1.39768400	6.63124500	2.13595800
C	-3.88191600	6.07657900	4.49865900
H	-4.88291900	5.62896000	4.51525500
H	-3.97194200	7.11741500	4.83338900
H	-3.26596400	5.54528700	5.23435400
C	-4.14990700	6.83294800	2.14267900
H	-5.17209300	6.43781700	2.09498500
H	-3.74426400	6.85316600	1.12374200
H	-4.21528700	7.87050900	2.48997800
C	-0.44317600	1.29060000	7.97002900
H	-1.02404100	2.17055200	7.66810800
H	0.02221700	1.51744900	8.93723800
H	-1.14562300	0.46185500	8.11939400
C	1.58333300	2.12347200	6.75795700
H	2.36576900	1.90444800	6.02133500
H	2.07346700	2.36167300	7.71002300
H	1.05356400	3.02433300	6.42529500
C	1.43396800	-0.26105500	7.45512100
H	2.23179800	-0.55271300	6.76099900
H	0.79786800	-1.13718600	7.63085800
H	1.90737400	-0.00336100	8.40952900
Cl	-2.21148700	-2.39269700	1.36156800
H	-7.32125700	-0.06250700	-5.00424300
H	-6.03209700	-2.18235000	-4.82441400
S	-2.23553900	1.39285100	-2.65788800
C	-0.55797700	1.84321700	-3.17873700
H	-0.60157400	2.84809300	-3.61013800
H	-0.18550000	1.14829100	-3.94043700
H	0.13471500	1.84994200	-2.32883800

TS2

Imaginary Frequency: -319.73 cm^{-1}

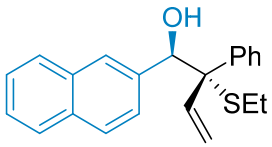
0 3 (0 denotes the net charge; 3 denotes the multiplicity)

Ni	1.84961400	-1.37894300	-1.11138400
C	0.27689600	-2.17043300	-2.68857100
C	-0.94573400	-1.88903200	-2.14089200
C	-1.54261400	-0.59761200	-1.97897300
C	-0.68282700	-0.11361000	-0.20650300
O	0.58156200	-0.02069300	-0.45219800
H	-1.43496000	-2.69848100	-1.59188700
H	0.73288100	-1.47479200	-3.39508600
H	0.60848800	-3.20647200	-2.73647900
C	-1.21493500	-1.11436200	0.75701300
C	-2.51158600	-0.97212400	1.26757000
C	-0.44792000	-2.21061600	1.16781500
C	-3.04334200	-1.92199300	2.13251300
C	-0.97792800	-3.15836700	2.03706000
C	-2.28064500	-3.02392700	2.51415000
H	-0.36091600	-3.99649200	2.35743900
C	-3.00428000	-0.47723900	-1.76169300
C	-3.59397800	0.78757700	-1.58428000
C	-3.84146600	-1.59898500	-1.64315900
C	-4.94156000	0.92190600	-1.27435200
H	-2.96647400	1.67282100	-1.68707900
C	-5.18952900	-1.46453200	-1.32727500
H	-3.43848800	-2.59803000	-1.79519300
C	-5.74998700	-0.20513900	-1.13486800
H	-5.80701900	-2.35701900	-1.23576900
H	0.59258000	-2.29338700	0.85182200
H	-3.10969400	-0.10967000	0.97308100
H	-5.36310700	1.91684400	-1.13727900
H	-6.80572800	-0.10153100	-0.89112100
C	3.75955300	-0.42580600	-3.11092800
C	4.42271800	0.44281700	-3.97121300
C	4.13153200	1.81095700	-3.96963500
C	3.15545100	2.24249100	-3.06968400
C	2.51689600	1.32394200	-2.24439900
C	4.02276000	-1.87376300	-3.03788100
C	5.06320000	-2.50728300	-3.71237000
C	5.27656300	-3.88107500	-3.57170900
C	4.40196400	-4.56590800	-2.72404900
C	3.39032300	-3.87109200	-2.07431300
H	5.17047900	0.05201200	-4.65859300
H	2.87198400	3.28883400	-3.00337200
H	1.73475300	1.60380400	-1.54142700
H	5.73049100	-1.92103200	-4.34120800

H	4.50383300	-5.63299500	-2.54926400
H	2.71180000	-4.37105000	-1.38390000
N	2.80852500	0.02284400	-2.26378300
N	3.19083000	-2.56352500	-2.23052300
C	4.86584600	2.74494700	-4.92367000
C	6.42707900	-4.55331800	-4.31069000
C	4.60464900	2.29143900	-6.36655500
H	4.95676500	1.26822900	-6.54508000
H	5.12968600	2.94885600	-7.07071400
H	3.53519800	2.32334700	-6.60759000
C	6.37130300	2.67416600	-4.63386400
H	6.59539800	2.98683700	-3.60697200
H	6.91960700	3.33566100	-5.31613900
H	6.76704200	1.66005500	-4.76762500
C	4.40468500	4.19326500	-4.77453700
H	4.58987900	4.58075400	-3.76522300
H	3.33565400	4.30731300	-4.99255900
H	4.95302300	4.83183800	-5.47677300
C	7.74851300	-3.91300200	-3.86384200
H	7.77813100	-2.83890200	-4.08289600
H	8.59121900	-4.38087000	-4.38789000
H	7.90828500	-4.03760800	-2.78628100
C	6.24483400	-4.34222400	-5.81983100
H	5.30689100	-4.78595700	-6.17530600
H	7.06990700	-4.81146500	-6.36995100
H	6.23334300	-3.27838900	-6.08627400
C	6.48928100	-6.05319100	-4.02909000
H	5.57404900	-6.56851000	-4.34614100
H	6.64862900	-6.26411700	-2.96450700
H	7.32478000	-6.50015600	-4.58008700
H	-1.22467400	0.85065700	-0.17043000
Cl	3.16003200	-1.80245400	0.70823400
H	-2.69365400	-3.76606100	3.19581400
H	-4.05725300	-1.79821500	2.51065200
S	-0.79199600	0.73111500	-2.96673900
C	-1.78510700	0.57211400	-4.47389600
H	-1.42798700	1.32061100	-5.18776700
H	-2.84643700	0.75575000	-4.26904700
H	-1.66974300	-0.42374300	-4.91652800

S12 Characterization data of Products

2-(ethylthio)-1-(naphthalen-2-yl)-2-phenylbut-3-en-1-ol (3a)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3a** as colorless oil (57 mg, 85%, d.r. = 12:1).

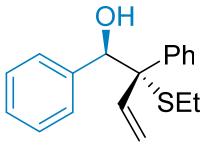
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H), 7.75 – 7.68 (m, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.53 (s, 1H), 7.45 – 7.42 (m, 4H), 7.28 (d, *J* = 4.9 Hz, 3H), 7.11 (d, *J* = 8.5 Hz, 1H), 6.42 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.45 (d, *J* = 10.8 Hz, 1H), 5.29 (dd, *J* = 10.7, 7.5 Hz, 2H), 2.86 (s, 1H), 2.28 (dq, *J* = 11.5, 7.6 Hz, 1H), 2.13 (dq, *J* = 11.4, 7.6 Hz, 1H), 1.12 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 136.5, 136.4, 133.0, 132.4, 129.7, 128.1, 127.9, 127.7, 127.5, 127.3, 126.4, 126.2, 125.9, 125.7, 117.9, 79.5, 65.6, 23.9, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{22}H_{21}S$, 317.1358, found: 317.1357.

2-(ethylthio)-1,2-diphenylbut-3-en-1-ol (3b)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3b** as colorless oil (52 mg, 92%, d.r. > 20:1).

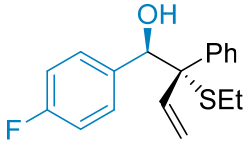
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.9 Hz, 2H), 7.30 (q, *J* = 7.0 Hz, 3H), 7.25 – 7.14 (m, 3H), 7.07 (d, *J* = 7.1 Hz, 2H), 6.38 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.46 (d, *J* = 10.8 Hz, 1H), 5.30 (d, *J* = 17.4 Hz, 1H), 5.15 (d, *J* = 3.5 Hz, 1H), 2.74 (d, *J* = 3.6 Hz, 1H), 2.27 (dq, *J* = 11.6, 7.6 Hz, 1H), 2.12 (dq, *J* = 11.5, 7.4 Hz, 1H), 1.13 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.9, 136.4, 129.6, 128.3, 127.8, 127.8, 127.2, 127.1, 117.8, 79.4, 65.4, 23.8, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{18}H_{19}S$, 267.1202, found: 267.1200.

2-(ethylthio)-1-(4-fluorophenyl)-2-phenylbut-3-en-1-ol (3c)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3c** as colorless oil (50 mg, 83%, d.r. > 20:1).

R_f = 0.4 (EA/PE = 1/10)

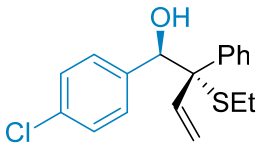
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 6.7, 2H), 7.29 (d, *J* = 8.2 Hz, 4H), 7.25 – 7.11 (m, 1H), 6.99 – 6.87 (m, 2H), 6.31 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.45 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.09 (d, *J* = 3.4 Hz, 1H), 2.75 (d, *J* = 3.4 Hz, 1H), 2.25 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.09 (dq, *J* = 11.6, 7.4 Hz, 1H), 1.11 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.8, 136.1, 130.2, 130.0, 129.5, 128.4(d, *J* = 241.4 Hz), 128.0, 127.5, 121.8, 118.1, 78.7, 65.2, 23.9, 13.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -114.56.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{18}H_{18}FS$, 285.1108, found: 285.1107.

1-(4-chlorophenyl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3d)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3d** as colorless oil (48 mg, 75%, d.r. > 20:1).

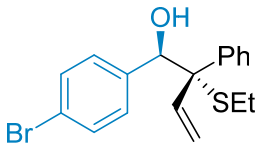
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.9 Hz, 2H), 7.34 – 7.22 (m, 3H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.32 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.45 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 17.3 Hz, 1H), 5.10 (d, *J* = 3.4 Hz, 1H), 2.75 (d, *J* = 3.4 Hz, 1H), 2.25 (dq, *J* = 11.4, 7.5 Hz, 1H), 2.10 (dq, *J* = 11.5, 7.5 Hz, 1H), 1.11 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.3, 136.2, 133.6, 129.6, 129.5, 128.0, 127.4, 127.3, 118.1, 78.7, 65.3, 23.9, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{18}H_{18}ClS$, 301.0812, found: 301.0810.

1-(4-bromophenyl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3e)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3e** as colorless oil (44 mg, 60%, d.r. > 20:1).

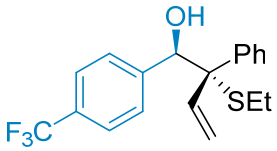
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 7.07 (d, *J* = 6.8 Hz, 2H), 6.38 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.46 (d, *J* = 10.8 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.15 (d, *J* = 3.3 Hz, 1H), 2.74 (d, *J* = 3.5 Hz, 1H), 2.27 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.12 (dq, *J* = 11.6, 7.5 Hz, 1H), 1.13 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.8, 136.4, 129.6, 128.3, 127.8, 127.8, 127.3, 127.1, 117.8, 79.4, 65.4, 23.8, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{18}H_{18}BrS$, 345.0307, found: 345.0307.

2-(ethylthio)-2-phenyl-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (3f)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3f** as a white solid (55 mg, 78%, d.r. > 20:1).

R_f = 0.4 (EA/PE = 1/10)

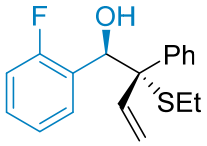
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.0 Hz, 4H), 7.35 – 7.24 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.33 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.46 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 17.4 Hz, 1H), 5.18 (d, *J* = 3.5 Hz, 1H), 2.83 (d, *J* = 3.4 Hz, 1H), 2.26 (dq, *J* = 11.4, 7.5 Hz, 1H), 2.11 (dq, *J* = 11.4, 7.5 Hz, 1H), 1.11 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.6, 136.0, 129.8 (d, *J* = 26.3 Hz), 129.4, 128.6, 128.1, 127.6, 124.1 (d, *J* = 218.2 Hz), 124.0 (q, *J* = 3.0 Hz), 118.3, 78.7, 65.2, 23.9, 13.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.48.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{19}H_{18}F_3S$, 335.1076, found: 335.1074.

2-(ethylthio)-1-(2-fluorophenyl)-2-phenylbut-3-en-1-ol (3g)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3g** as colorless oil (48 mg, 79%, d.r. > 20:1).

R_f = 0.4 (EA/PE = 1/10)

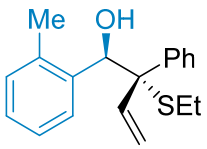
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.33 – 7.22 (m, 3H), 7.25 – 7.15 (m, 1H), 6.98 – 6.85 (m, 3H), 6.32 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.53 (d, *J* = 4.0 Hz, 1H), 5.45 (d, *J* = 10.8 Hz, 1H), 5.32 (d, *J* = 17.4 Hz, 1H), 2.81 (d, *J* = 4.0 Hz, 1H), 2.34 – 2.26 (m, 1H), 2.25 – 2.17 (m, 1H), 1.13 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2 (d, *J* = 197.6 Hz), 138.4, 136.2 (d, *J* = 1.7 Hz), 130.2 (d, *J* = 2.8 Hz), 129.7, 129.3 (d, *J* = 6.9 Hz), 127.7, 127.4, 126.3 (d, *J* = 9.5 Hz), 123.0 (d, *J* = 2.8 Hz), 117.9, 114.6 (d, *J* = 18.6 Hz), 71.4, 65.4, 23.7, 13.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -115.08.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{18}H_{18}FS$, 285.1108, found: 285.1107.

2-(ethylthio)-2-phenyl-1-(o-tolyl)but-3-en-1-ol (3h)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3h** as colorless oil (45 mg, 76%, d.r. > 20:1).

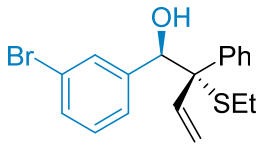
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.26 (m, 3H), 7.24 – 7.14 (m, 2H), 7.14 – 7.05 (m, 2H), 6.42 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.58 (d, *J* = 2.3 Hz, 1H), 5.55 (d, *J* = 2.0 Hz, 1H), 5.46 (d, *J* = 3.3 Hz, 1H), 2.51 (d, *J* = 3.2 Hz, 1H), 2.27 (s, 3H), 2.23 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.05 (dq, *J* = 11.5, 7.5 Hz, 1H), 1.10 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 137.5, 136.6, 136.4, 129.9, 129.4, 128.7, 127.9, 127.8, 127.2, 125.1, 118.4, 74.8, 65.4, 23.9, 20.2, 13.7.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{19}H_{21}S$, 281.1358, found: 281.1358.

1-(3-bromophenyl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3i)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3i** as colorless oil (54 mg, 74%, d.r. = 5:1).

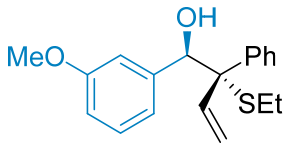
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.31 (dt, *J* = 15.1, 7.4 Hz, 4H), 7.13 (s, 1H), 7.04 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.32 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.47 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 17.3 Hz, 1H), 5.08 (d, *J* = 3.4 Hz, 1H), 2.79 (d, *J* = 3.4 Hz, 1H), 2.24 (dq, *J* = 11.4, 7.4 Hz, 1H), 2.11 (dq, *J* = 11.2, 7.4 Hz, 1H), 1.12 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 138.6, 136.0, 131.4, 130.8, 129.5, 128.5, 128.0, 127.5, 126.9, 121.2, 118.2, 78.6, 65.2, 23.9, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{18}H_{18}BrS$, 345.0307, found: 345.0304.

2-(ethylthio)-1-(3-methoxyphenyl)-2-phenylbut-3-en-1-ol (3j)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3j** as colorless oil (48 mg, 76%, d.r. > 20:1).

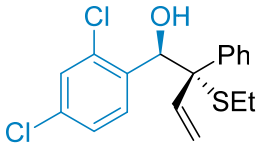
R_f = 0.3 (EA/PE = 1/10)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.12 – 7.08 (m, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.46 (s, 1H), 6.34 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 5.30 (d, *J* = 17.4 Hz, 1H), 5.08 (s, 1H), 3.61 (s, 3H), 2.78 (s, 1H), 2.31 – 2.23 (m, 1H), 2.17 – 2.10 (m, 1H), 1.13 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5 , 140.4 , 139.0 , 136.6 , 129.7 , 128.0 , 127.8 , 127.3 , 120.8 , 117.7 , 114.0 , 113.3 , 79.1 , 65.4 , 55.0 , 23.9 , 13.6 .

HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{19}H_{22}O_2SNa$, 337.1233, found: 337.1228.

1-(2,4-dichlorophenyl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3k)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3k** as colorless oil (54 mg, 77%, d.r. = 13:1).

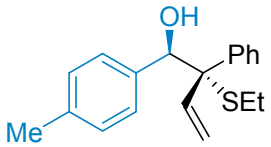
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.3 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.35 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.67 (d, *J* = 3.2 Hz, 1H), 5.52 (d, *J* = 10.8 Hz, 1H), 5.45 (d, *J* = 17.2 Hz, 1H), 2.77 (d, *J* = 3.2 Hz, 1H), 2.29 (dq, *J* = 11.5, 7.5 Hz, 1H), 2.17 (dq, *J* = 11.5, 7.4 Hz, 1H), 1.11 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 135.9, 135.4, 134.7, 134.1, 131.7, 129.6, 128.6, 127.9, 127.5, 126.2, 118.7, 73.6, 65.4, 23.9, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{18}H_{17}Cl_2S$, 335.0423, found: 335.0419.

2-(ethylthio)-2-phenyl-1-(p-tolyl)but-3-en-1-ol (3l)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3l** as colorless oil (48 mg, 80%, d.r. > 20:1).

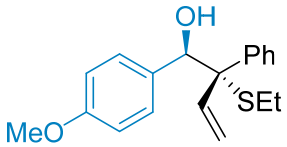
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.34 – 7.22 (m, 3H), 6.96 (dd, *J* = 21.4, 8.0 Hz, 4H), 6.37 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.11 (d, *J* = 3.4 Hz, 1H), 2.63 (d, *J* = 3.5 Hz, 1H), 2.29 (s, 3H), 2.23 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.08 (dq, *J* = 11.6, 7.5 Hz, 1H), 1.10 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 137.5, 136.4, 135.9, 129.6, 128.2, 127.9, 127.8, 127.2, 117.8, 79.4, 65.3, 23.8, 21.2, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{19}H_{21}S$, 281.1358, found: 281.1358.

2-(ethylthio)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-ol (3m)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3m** as colorless oil (47 mg, 75%, d.r. > 20:1).

R_f = 0.4 (EA/PE = 1/10)

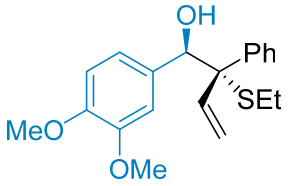
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.9 Hz, 2H), 7.34 – 7.21 (m, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.35 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 17.4

Hz, 1H), 5.09 (d, *J* = 3.3 Hz, 1H), 3.76 (s, 3H), 2.64 (d, *J* = 3.3 Hz, 1H), 2.24 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.09 (dq, *J* = 11.5, 7.5 Hz, 1H), 1.10 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 159.2, 139.2, 136.5, 131.0, 129.6, 129.5, 127.8, 127.2, 117.8, 112.5, 79.1, 65.5, 55.1, 23.9, 13.6.

HRMS-ESI$^+$ (m/z) [M−OH]$^+$ calculated for $C_{19}H_{21}OS$, 297.1308, found: 297.1307.

1-(3,4-dimethoxyphenyl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3n)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3n** as white solid (50 mg, 73%, d.r. > 20:1).

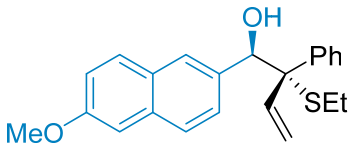
R$_f$ = 0.3 (EA/PE = 1/4)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.30 – 7.27 (m, 3H), 6.77 – 6.68 (m, 2H), 6.32 (dd, *J* = 17.4, 10.8 Hz, 1H), 6.26 (d, *J* = 1.4 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 5.31 (d, *J* = 17.5 Hz, 1H), 5.03(s, 1H), 3.83 (s, 3H), 3.56 (s, 3H), 2.88 (s, 1H), 2.30 (dq, *J* = 11.5, 7.5 Hz, 1H), 2.16 (dq, *J* = 11.6, 7.5 Hz, 1H), 1.14 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 148.4 , 147.6 , 139.0 , 136.8 , 131.2 , 129.8 , 127.8 , 127.2 , 120.7 , 117.6 , 111.3 , 109.5 , 78.8 , 65.7 , 55.7 , 55.4 , 23.8 , 13.6 .

HRMS-ESI$^+$ (m/z) [M+Na]$^+$ calculated for $C_{20}H_{24}O_3SNa$, 367.1338, found: 337.1334.

2-(ethylthio)-1-(6-methoxynaphthalen-2-yl)-2-phenylbut-3-en-1-ol (3o)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3o** as colorless oil (56 mg, 77%, d.r. > 20:1).

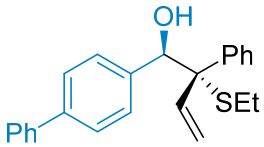
R$_f$ = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.43 (s, 1H), 7.28 (m, 3H), 7.13 – 7.05 (m, 3H), 6.41 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.44 (d, *J* = 10.9 Hz, 1H), 5.33 – 5.23 (m, 2H), 3.90 (s, 3H), 2.82 (d, *J* = 3.4 Hz, 1H), 2.27 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.13 (dq, *J* = 11.6, 7.6 Hz, 1H), 1.12 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 157.7, 139.1, 136.5, 134.2, 134.1, 129.7, 129.6, 127.9, 127.8, 127.5, 127.3, 126.8, 125.3, 118.6, 117.8, 105.5, 79.5, 65.6, 55.3, 23.9, 13.6.

HRMS-ESI$^+$ (m/z) [M−OH]$^+$ calculated for $C_{23}H_{23}OS$, 347.1464, found: 347.1461.

1-([1,1'-biphenyl]-4-yl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3p)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3p** as colorless oil (61 mg, 85%, d.r. = 6:1).

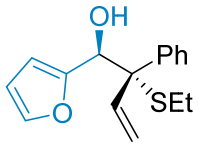
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.43 (t, *J* = 8.1 Hz, 4H), 7.37 – 7.25 (m, 4H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.41 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.48 (d, *J* = 10.8 Hz, 1H), 5.33 (d, *J* = 17.4 Hz, 1H), 5.18 (d, *J* = 3.4 Hz, 1H), 2.79 (d, *J* = 3.4 Hz, 1H), 2.29 (dq, *J* = 11.6, 7.4 Hz, 1H), 2.14 (dq, *J* = 11.3, 7.4 Hz, 1H), 1.14 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.5, 139.1, 138.0, 136.4, 129.6, 128.8, 128.7, 127.9, 127.3, 127.2, 127.0, 125.8, 117.9, 79.2, 65.4, 23.9, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{24}H_{23}S$, 343.1515, found: 343.1517.

2-(ethylthio)-1-(furan-2-yl)-2-phenylbut-3-en-1-ol (3q)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3q** as colorless oil (39 mg, 71%, d.r. > 20:1).

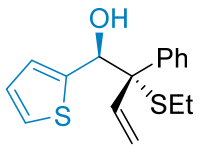
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.33 – 7.28 (m, 4H), 6.33 (dd, *J* = 17.5, 10.9 Hz, 1H), 6.23 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.92 (d, *J* = 3.3 Hz, 1H), 5.46 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 5.4 Hz, 1H), 2.86 (d, *J* = 5.4 Hz, 1H), 2.34 – 2.21 (m, 2H), 1.15 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 141.4, 139.0, 136.9, 129.2, 127.8, 127.4, 117.5, 110.2, 108.5, 72.9, 64.4, 23.9, 13.7.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{16}H_{17}OS$, 257.0995, found: 257.0993.

2-(ethylthio)-2-phenyl-1-(thiophen-2-yl)but-3-en-1-ol (3r)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3r** as colorless oil (38 mg, 66%, d.r. > 20:1).

R_f = 0.4 (EA/PE = 1/10)

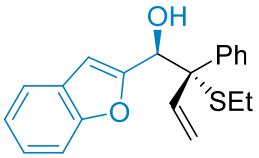
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.25 (m, 3H), 7.15 (d, *J* = 4.9 Hz, 1H), 6.85 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.77 (d, *J* = 3.5 Hz, 1H), 6.38 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.51 (d, *J* =

10.8 Hz, 1H), 5.43 (d, *J* = 4.2 Hz, 1H), 5.34 (d, *J* = 17.3 Hz, 1H), 3.01 (d, *J* = 4.2 Hz, 1H), 2.32 (dq, *J* = 11.6, 7.6 Hz, 1H), 2.21 (dq, *J* = 11.6, 7.5 Hz, 1H), 1.15 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 139.1, 136.8, 129.4, 128.0, 127.5, 126.3, 125.7, 125.2, 118.3, 75.4, 65.2, 24.1, 13.8.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{16}H_{17}S_2$, 273.0766, found: 273.0764.

1-(benzofuran-2-yl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3s)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3s** as colorless oil (49 mg, 76%, d.r. = 10:1).

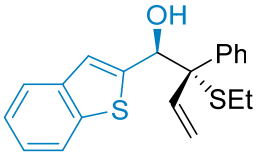
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 6.4 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 3H), 7.25 – 7.13 (m, 2H), 6.40 (dd, *J* = 17.5, 10.9 Hz, 1H), 6.31 (s, 1H), 5.49 (d, *J* = 10.9 Hz, 1H), 5.31 (dd, *J* = 10.4, 4.8 Hz, 2H), 3.04 (d, *J* = 5.5 Hz, 1H), 2.39 – 2.24 (m, 2H), 1.17 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 154.2, 138.7, 136.8, 129.2, 127.9, 127.9, 127.5, 124.0, 122.6, 121.0, 117.7, 111.1, 105.4, 73.2, 64.4, 24.0, 13.7.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{20}H_{19}OS$, 307.1151, found: 307.1148.

1-(benzo[b]thiophen-2-yl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3t)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3t** as colorless oil (54 mg, 80%, d.r. > 20:1).

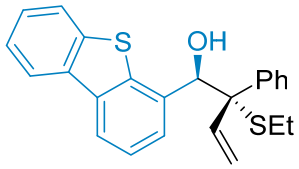
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 1H), 7.64 (d, *J* = 6.9 Hz, 1H), 7.56 (d, *J* = 6.6 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.01 (s, 1H), 6.43 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.53 (d, *J* = 10.8 Hz, 1H), 5.48 (d, *J* = 4.4 Hz, 1H), 5.36 (d, *J* = 17.4 Hz, 1H), 3.13 (d, *J* = 4.4 Hz, 1H), 2.34 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.23 (dq, *J* = 11.6, 7.5 Hz, 1H), 1.16 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.8, 138.9, 138.8, 136.8, 129.4, 128.1, 127.6, 124.0, 123.9, 123.4, 123.1, 122.0, 118.4, 75.8, 65.1, 24.2, 13.8.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{20}H_{19}S_2$, 323.0923, found: 323.0920.

1-(dibenzo[b,d]thiophen-4-yl)-2-(ethylthio)-2-phenylbut-3-en-1-ol (3u)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3u** as colorless oil (64 mg, 82%, d.r. > 20:1).

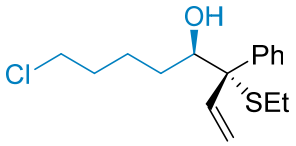
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.55 (d, *J* = 9.1 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.30 (q, *J* = 7.8 Hz, 4H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.49 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.51 (d, *J* = 2.6 Hz, 1H), 5.49 – 5.37 (m, 2H), 2.92 (d, *J* = 2.8 Hz, 1H), 2.27 (dq, *J* = 11.8, 7.6 Hz, 1H), 2.17 (dq, *J* = 11.8, 7.5 Hz, 1H), 1.10 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 139.5, 139.1, 136.1, 135.6, 135.4, 134.0, 129.6, 127.9, 127.4, 127.0, 126.6, 124.2, 123.7, 122.3, 121.4, 121.2, 118.6, 78.8, 65.9, 24.1, 13.6.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{24}H_{21}S_2$, 373.1079, found: 373.1076.

8-chloro-3-(ethylthio)-3-phenyloct-1-en-4-ol (3v)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3v** as colorless oil (42 mg, 71%, d.r. > 20:1).

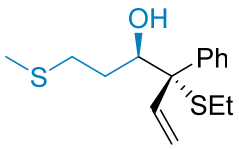
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 1H), 6.21 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.44 (d, *J* = 11.0 Hz, 1H), 5.22 (d, *J* = 17.6 Hz, 1H), 4.00 (dd, *J* = 9.8, 4.0 Hz, 1H), 3.48 (t, *J* = 6.5 Hz, 2H), 2.36 (d, *J* = 4.0 Hz, 1H), 2.30 (dq, *J* = 11.7, 7.4 Hz, 1H), 2.16 (dq, *J* = 11.6, 7.5 Hz, 1H), 1.80 – 1.62 (m, 3H), 1.56 – 1.41 (m, 2H), 1.14 (t, *J* = 7.6 Hz, 3H), 1.10 – 1.02 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.5, 128.8, 128.2, 127.3, 116.5, 74.9, 64.5, 44.9, 32.4, 31.5, 24.3, 23.7, 13.8.

HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{16}H_{22}ClS$, 281.1125, found: 281.1123.

4-(ethylthio)-1-(methylthio)-4-phenylhex-5-en-3-ol (3w)

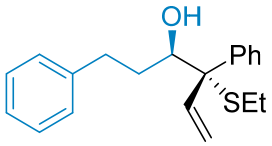


Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3w** as colorless oil (42 mg, 74%, d.r. > 20:1).

R_f = 0.4 (EA/PE = 1/10)

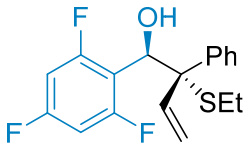
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 6.21 (dd, *J* = 17.7, 11.0 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 17.6 Hz, 1H), 4.24 (dd, *J* = 9.7, 3.6 Hz, 1H), 2.70 – 2.54 (m, 2H), 2.53 (d, *J* = 3.7 Hz, 1H), 2.33 (dq, *J* = 11.6, 7.5 Hz, 1H), 2.21 (dq, *J* = 11.8, 7.5 Hz, 1H), 2.03 (s, 3H), 1.79 (dt, *J* = 14.7, 8.0 Hz, 1H), 1.37 – 1.28 (m, 1H), 1.15 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 137.5, 128.7, 128.1, 127.3, 116.5, 73.0, 64.1, 31.5, 31.3, 23.7, 15.4, 13.8.
HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{15}H_{21}S_2$, 265.1079, found: 265.1077.

4-(ethylthio)-1,4-diphenylhex-5-en-3-ol (3x)



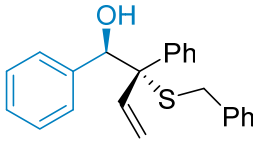
Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/20) to give **3x** as colorless oil (52 mg, 83%, d.r. > 20:1).
R_f = 0.4 (EA/PE = 1/10)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 3H), 7.23 – 7.13 (m, 3H), 6.19 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.39 (d, *J* = 11.0 Hz, 1H), 5.08 (d, *J* = 17.6 Hz, 1H), 4.03 (dd, *J* = 10.0, 3.8 Hz, 1H), 2.88 (ddd, *J* = 14.0, 9.5, 4.8 Hz, 1H), 2.65 (dt, *J* = 13.7, 8.2 Hz, 1H), 2.45 (d, *J* = 4.0 Hz, 1H), 2.30 (dq, *J* = 11.7, 7.5 Hz, 1H), 2.17 (dq, *J* = 11.6, 7.5 Hz, 1H), 1.86 (dt, *J* = 14.5, 8.6 Hz, 1H), 1.38 (dtd, *J* = 14.3, 9.6, 4.8 Hz, 1H), 1.16 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 139.5, 137.5, 128.8, 128.6, 128.3, 128.1, 127.3, 125.8, 116.2, 73.8, 64.4, 34.0, 32.9, 23.6, 13.9.
HRMS-ESI$^+$ (m/z) $[M-OH]^+$ calculated for $C_{20}H_{23}S$, 295.1515, found: 295.1512.

2-(ethylthio)-2-phenyl-1-(2,4,6-trifluorophenyl)but-3-en-1-ol (3y)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/50) to give **3y** as yellow soild (47 mg, 70%, d.r. > 20:1).
R_f = 0.4 (EA/PE = 1/10)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.35 – 7.27 (m, 3H), 6.55 (t, *J* = 9.1 Hz, 2H), 6.31 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.54 (d, *J* = 9.6 Hz, 1H), 5.44 (d, *J* = 10.8 Hz, 1H), 5.20 (d, *J* = 17.3 Hz, 1H), 2.84 (d, *J* = 10.1 Hz, 1H), 2.16 – 2.10 (m, 2H), 1.08 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (t, *J* = 16.3 Hz), 162.6 – 162.2 (m), 161.2 (t, *J* = 16.3 Hz), 160.7 – 160.2 (m), 138.1 , 135.9 , 129.8 , 128.2 , 127.6 , 118.1 , 112.4 (td, *J* = 15.8, 4.6 Hz), 100.5 (t, *J* = 28.4 Hz), 73.1 , 65.6 , 24.1 , 13.4 .
^{19}F NMR (377 MHz, $CDCl_3$) δ -105.11 , -108.24 (t, *J* = 7.0 Hz)
HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{18}H_{17}F_3OSNa$, 361.0844, found: 361.0840.

2-(benzylthio)-1,2-diphenylbut-3-en-1-ol (3ab)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/50) to give **3ab** as colorless oil (50 mg, 72%, d.r. > 20:1).

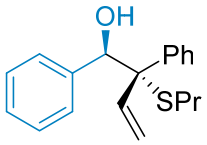
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.26 (m, 5H), 7.24 – 7.14 (m, 6H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.46 (dd, *J* = 17.3, 10.8 Hz, 1H), 5.54 (d, *J* = 10.8 Hz, 1H), 5.41 (d, *J* = 17.4 Hz, 1H), 5.18 (s, 1H), 3.45 (d, *J* = 11.6 Hz, 1H), 3.25 (d, *J* = 11.5 Hz, 1H), 2.64 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.8 , 138.7 , 137.1 , 136.1 , 129.6 , 129.1 , 128.5 , 128.3 , 128.0 , 127.9 , 127.4 , 127.1 , 127.1 , 118.2 , 79.6 , 66.1 , 34.8 .

HRMS-ESI$^+$ (m/z) $[M+H]^+$ calculated for $C_{23}H_{23}OS$, 347.1464, found: 347.1466.

1,2-diphenyl-2-(propylthio)but-3-en-1-ol (3ac)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/50) to give **3ac** as colorless oil (42 mg, 70%, d.r. > 20:1).

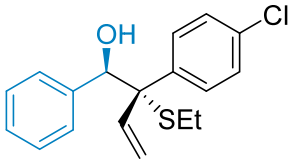
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.31 – 7.26 (m, 3H), 7.23 – 7.14 (m, 3H), 7.03 (d, *J* = 7.4 Hz, 2H), 6.34 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.44 (d, *J* = 10.6 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 5.12 (s, 1H), 2.76 (s, 1H), 2.25 – 2.19 (m, 1H), 2.12 – 2.06 (m, 1H), 1.53 – 1.44 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9 , 138.9 , 136.5 , 129.7 , 128.3 , 127.8 , 127.3 , 127.1 , 117.8 , 79.3 , 65.3 , 31.8 , 22.2 , 13.8 .

HRMS-ESI$^+$ (m/z) $[M+H]^+$ calculated for $C_{19}H_{23}OS$, 299.1464, found: 299.1467.

2-(4-chlorophenyl)-2-(ethylthio)-1-phenylbut-3-en-1-ol (3ad)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/50) to give **3ad** as colorless oil (49 mg, 77%, d.r. > 20:1).

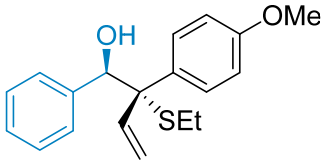
R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.29 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.44 (d, *J* = 10.7 Hz, 1H), 5.23 (d, *J* = 17.4 Hz, 1H), 5.06 (s, 1H), 2.73 (s, 1H), 2.30 – 2.21 (m, 1H), 2.15 – 2.07 (m, 1H), 1.13 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6 , 137.4 , 136.2 , 133.1 , 131.2 , 128.2 , 128.0 , 127.8 , 127.2 , 117.9 , 79.3 , 65.0 , 23.9 , 13.5 .

HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{18}H_{19}ClOSNa$, 341.0737, found: 341.0742.

2-(ethylthio)-2-(4-methoxyphenyl)-1-phenylbut-3-en-1-ol (3ae)



Prepared according to the general procedure and purified by silica gel flash colum chromatograph (EA/PE = 1/50) to give **3ae** as colorless oil (47 mg, 75%, d.r. > 20:1).

R_f = 0.4 (EA/PE = 1/10)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.04 (d, *J* = 7.1 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.31 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.41 (d, *J* = 10.7 Hz, 1H), 5.26 (d, *J* = 17.3 Hz, 1H), 5.07 (s, 1H), 3.81 (s, 3H), 2.70 (s, 1H), 2.28 – 2.21 (m, 1H), 2.14 – 2.07 (m, 1H), 1.12 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6 , 138.9 , 136.6 , 130.8 , 130.7 , 128.4 , 127.8 , 127.1 , 117.6 , 113.1 , 79.5 , 65.0 , 55.2 , 23.8 , 13.6 .

HRMS-ESI$^+$ (m/z) $[M+Na]^+$ calculated for $C_{19}H_{22}O_2SNa$, 337.1232, found: 337.1235.

S13 References

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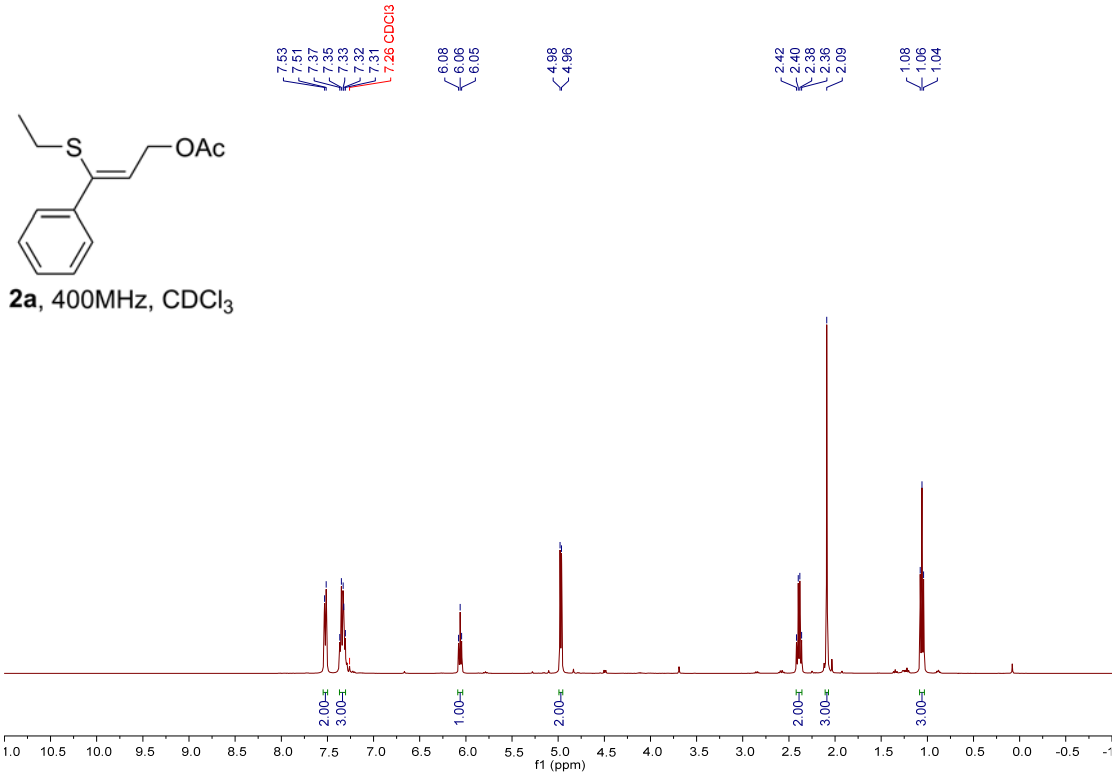
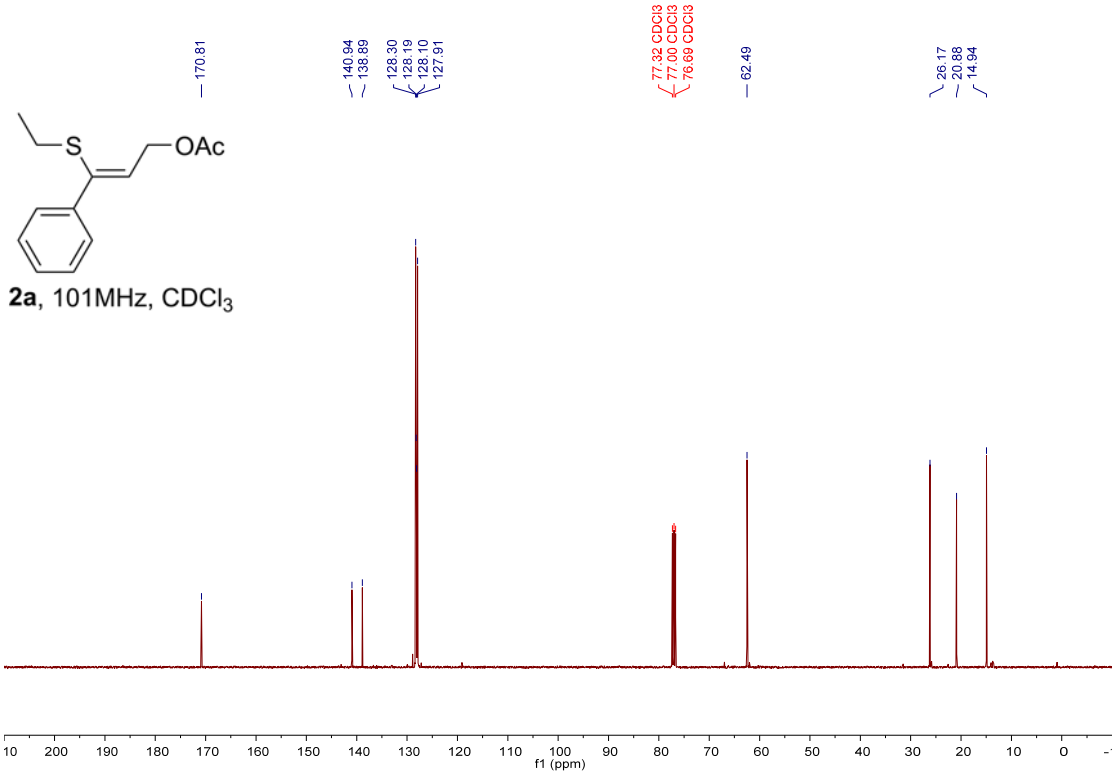
S14 Spectra of Compounds

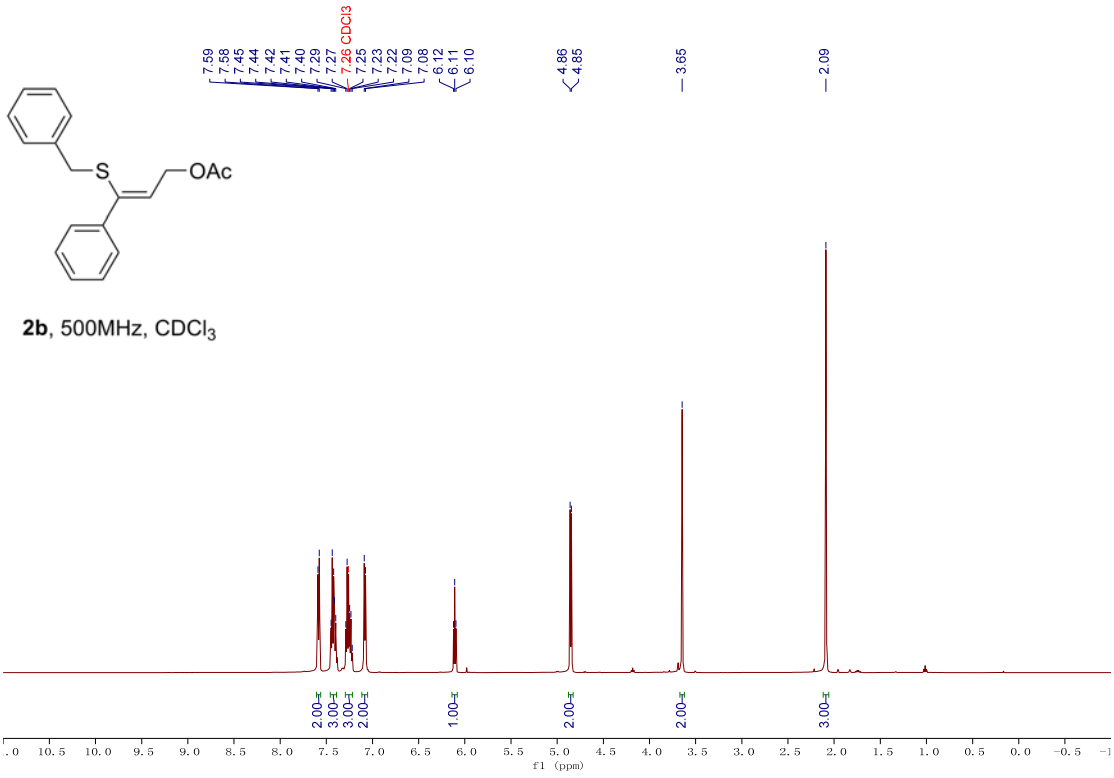
S14.1 Spectra of substrates



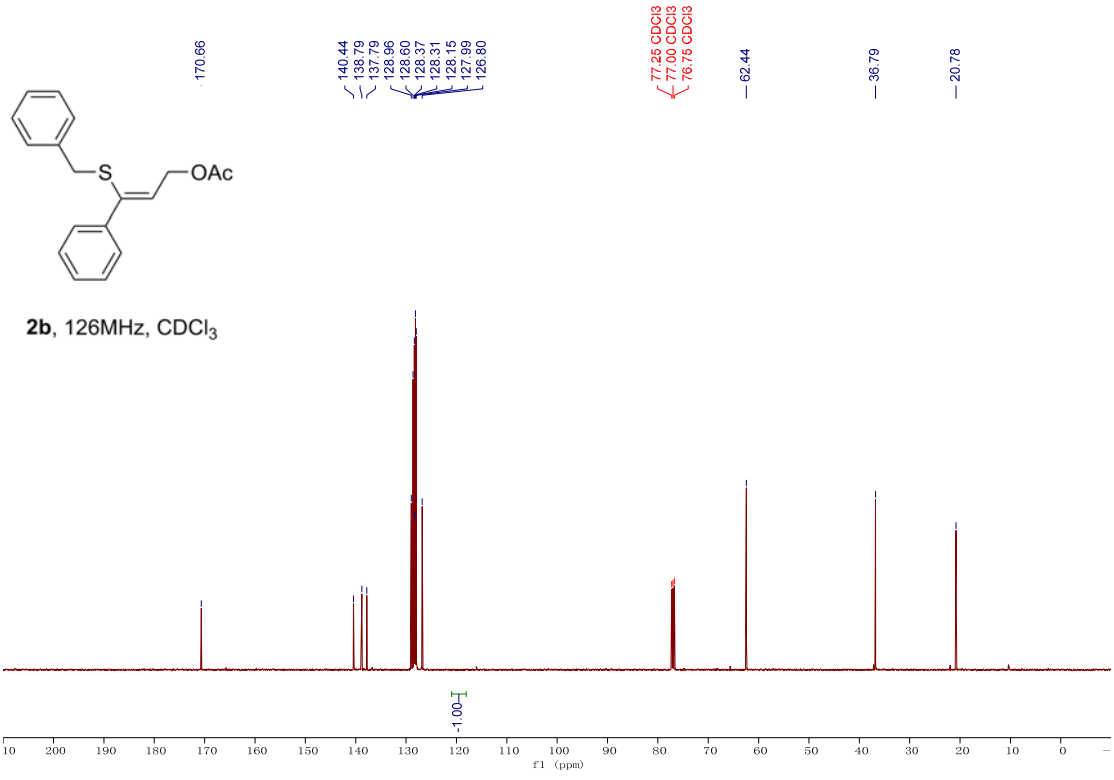
2a, 400MHz, $CDCl_3$



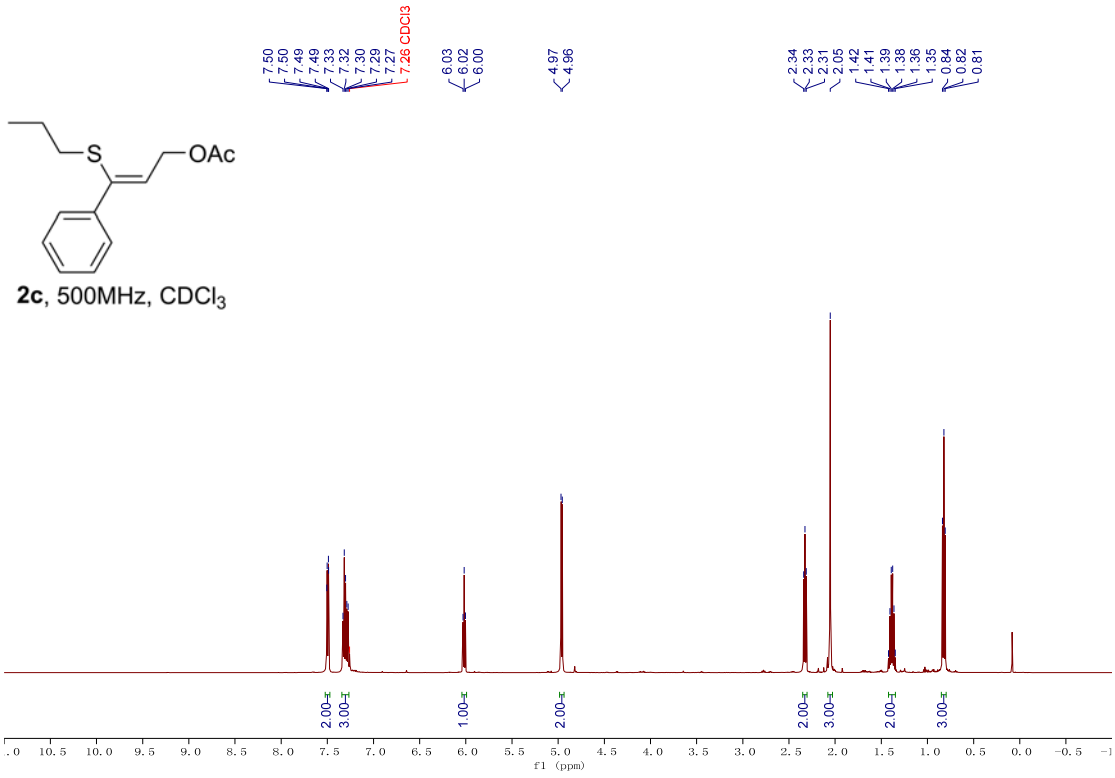
2a, 101MHz, $CDCl_3$

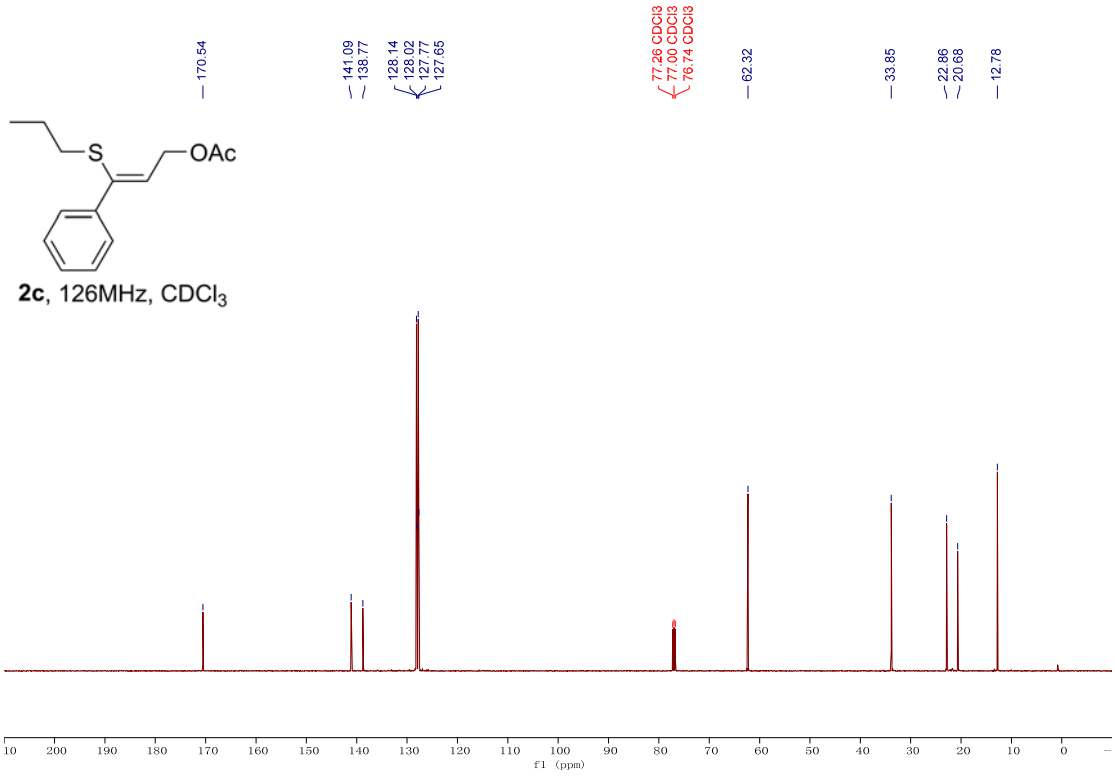


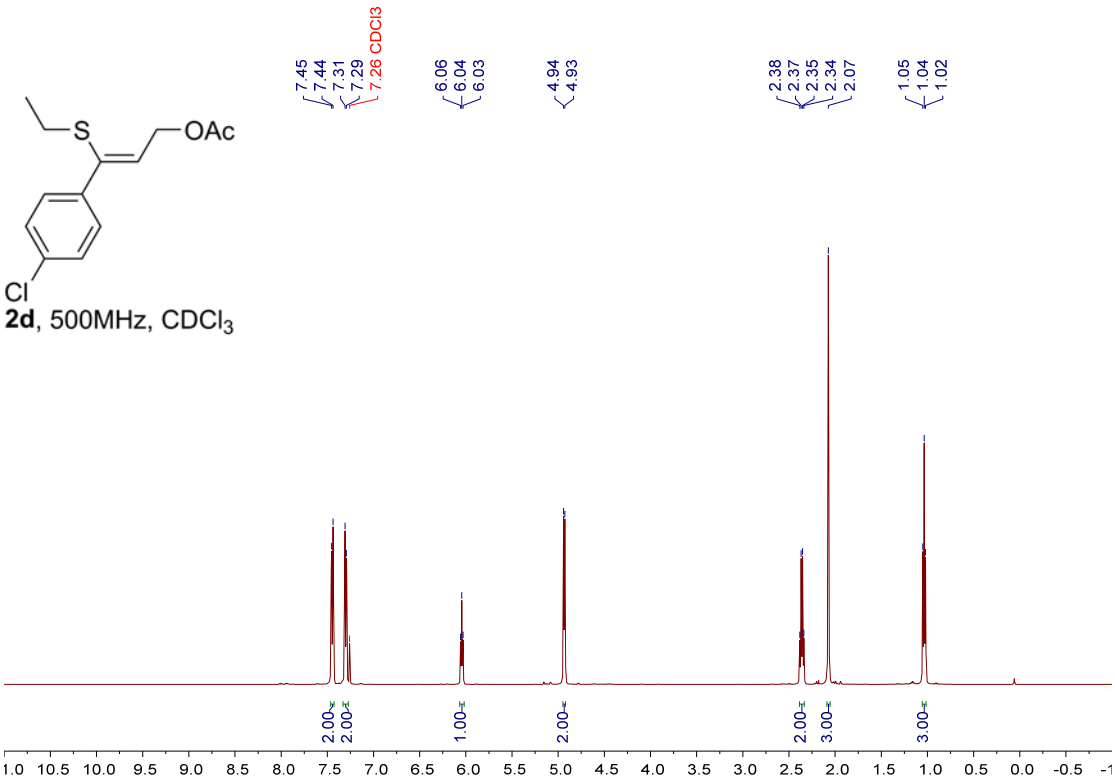
2b, 500MHz, $CDCl_3$

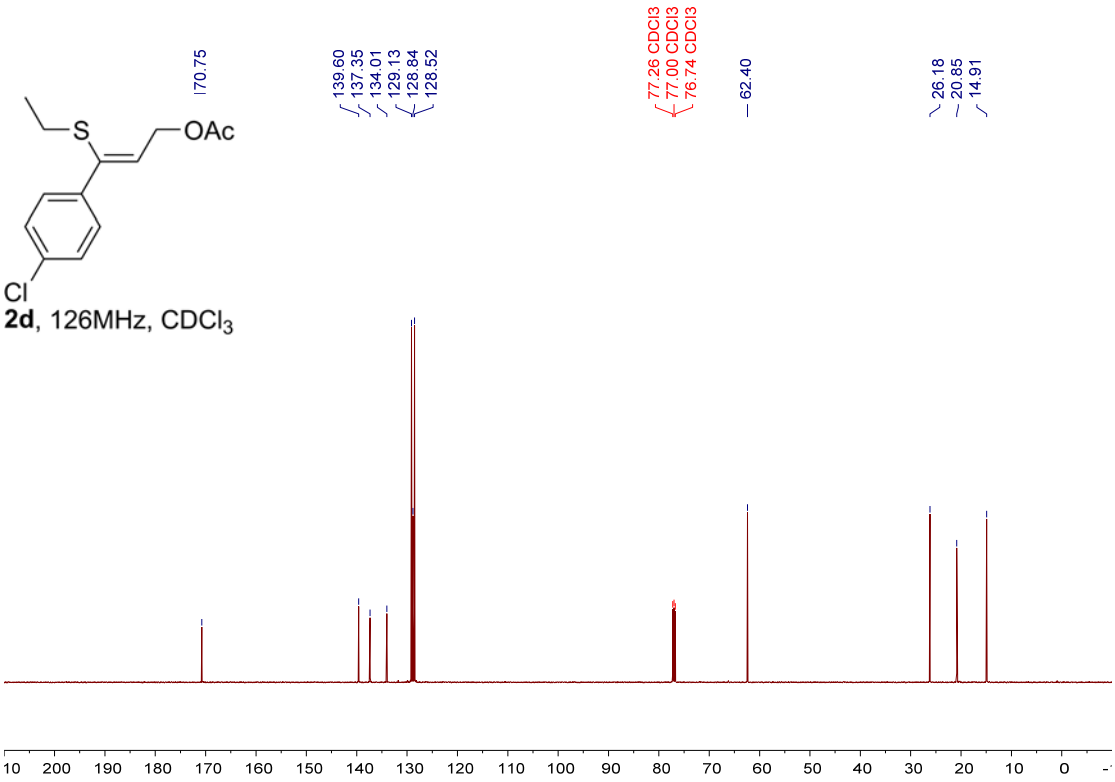


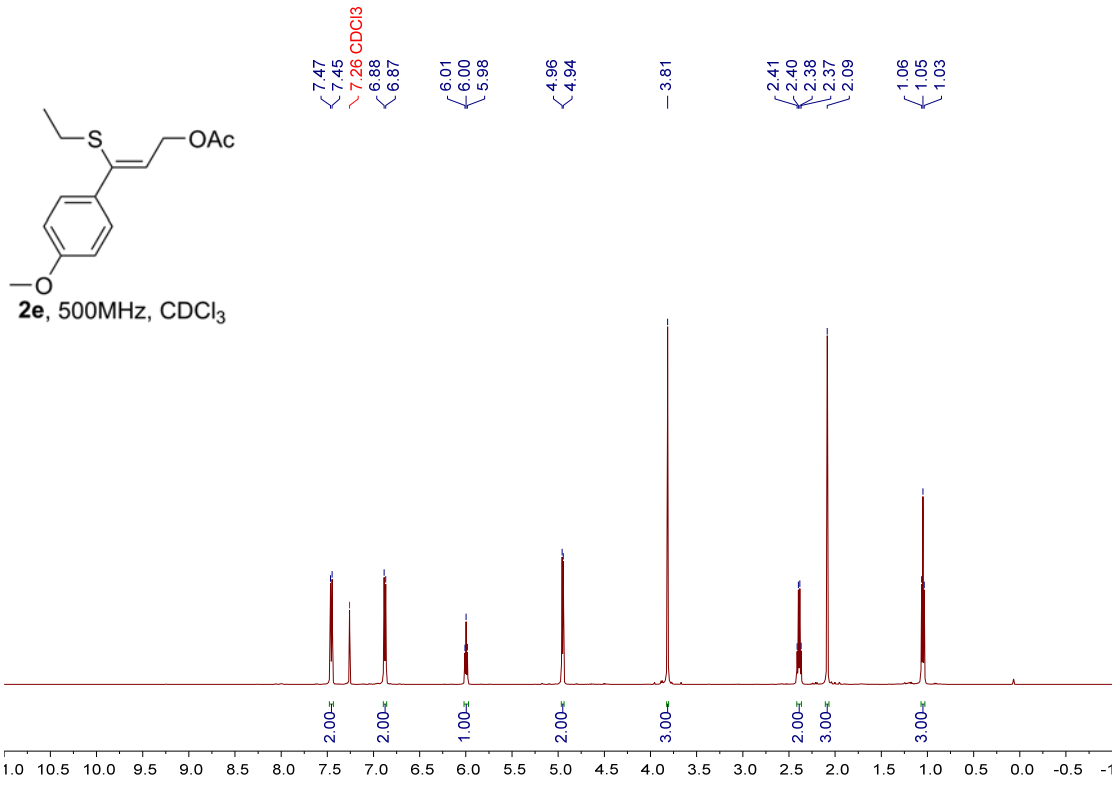
2b, 126MHz, $CDCl_3$

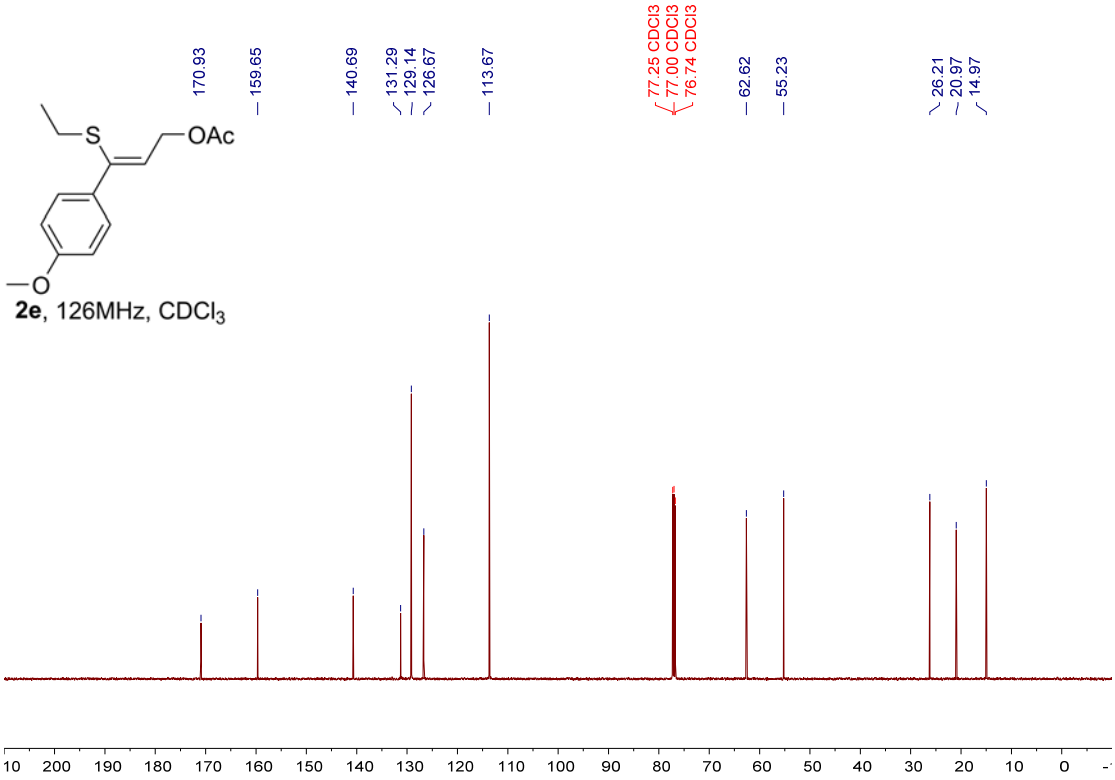

7.50
7.50
7.49
7.49
7.33
7.32
7.30
7.29
7.27
7.26 CDCl3
6.03
6.02
6.00
4.97
4.96
2.34
2.33
2.31
2.05
1.42
1.41
1.39
1.38
1.36
1.35
0.84
0.82
0.81
S
OAc
2c, 500MHz, CDCl3
2.00
3.00
1.00
2.00
2.00
3.00
2.00
3.00
f1 (ppm)


170.54
141.09
138.77
128.14
128.02
127.77
127.65
77.26 CDCl3
77.00 CDCl3
76.74 CDCl3
62.32
33.85
22.86
20.68
12.78
S
OAc
2c, 126MHz, CDCl3
f1 (ppm)

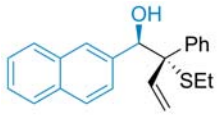

7.45
7.44
7.31
7.29
7.26 CDCl3
6.06
6.04
6.03
4.94
4.93
2.38
2.37
2.35
2.34
2.07
1.05
1.04
1.02
S
OAc
Cl
2d, 500MHz, CDCl3
2.00
2.00
1.00
2.00
2.00
3.00
3.00


170.75
139.60
137.35
134.01
129.13
128.84
128.52
77.26 CDCl3
77.00 CDCl3
76.74 CDCl3
62.40
26.18
20.85
14.91
S
OAc
Cl
2d, 126MHz, CDCl3

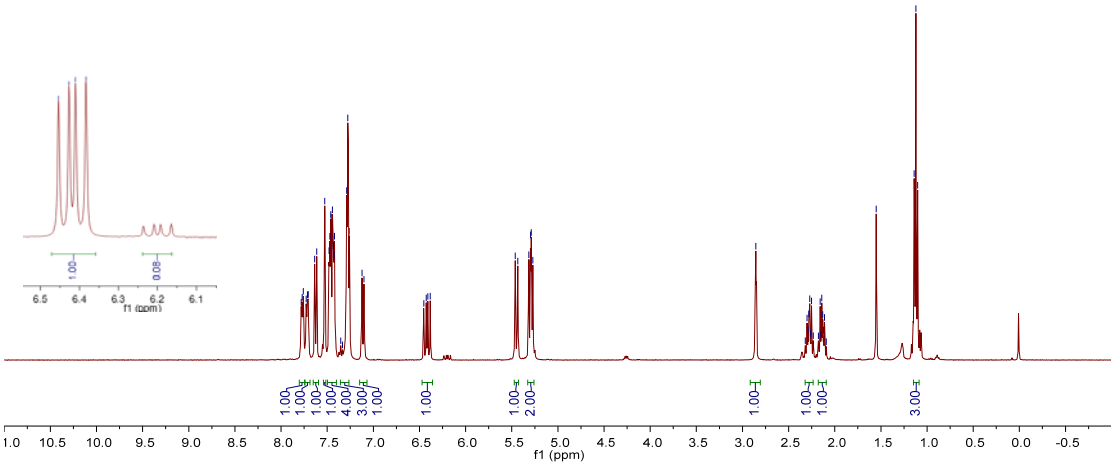

7.47
7.45
7.26 CDCl3
6.88
6.87
6.01
6.00
5.98
4.96
4.94
3.81
2.41
2.40
2.38
2.37
2.09
1.06
1.05
1.03
S
OAc
O
2e, 500MHz, CDCl3
2.00
2.00
1.00
2.00
3.00
2.00
3.00
3.00

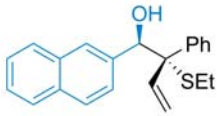

170.93
159.65
140.69
131.29
129.14
126.67
113.67
77.25 CDCl3
77.00 CDCl3
76.74 CDCl3
62.62
55.23
26.21
20.97
14.97
S
OAc
O
2e, 126MHz, CDCl3

S14.2 Spectra of products

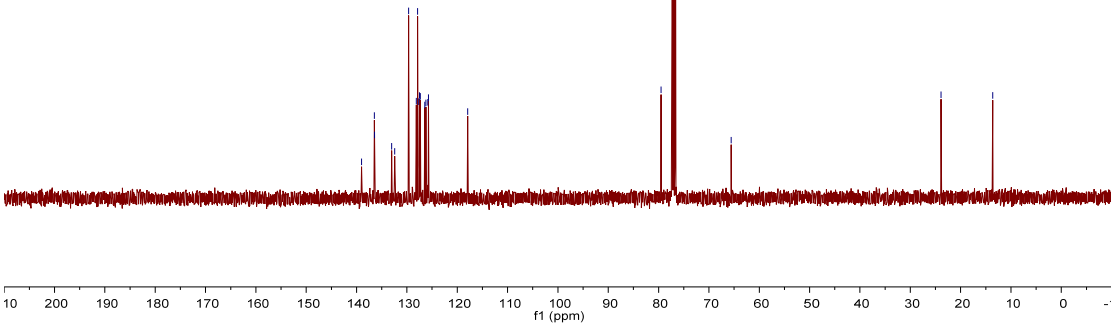


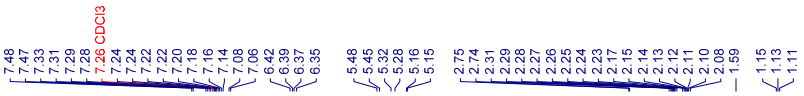
3a, 400 MHz, $CDCl_3$

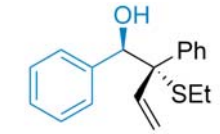




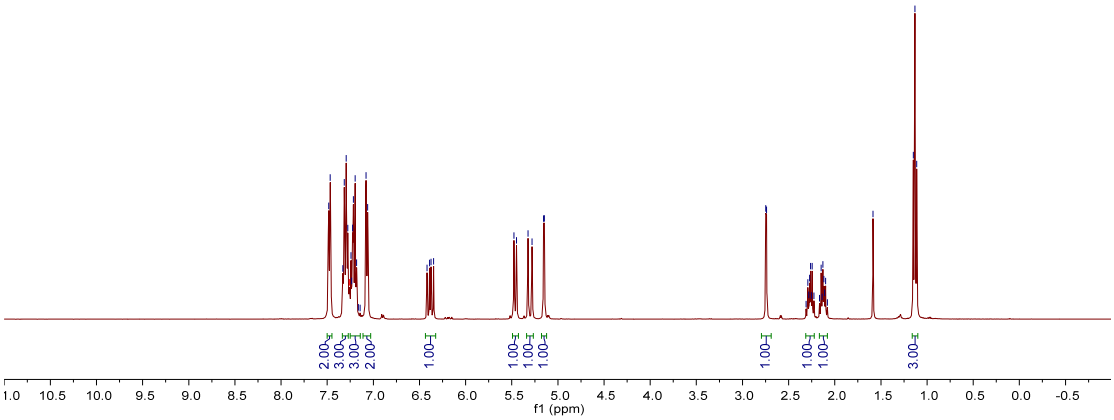
3a, 101 MHz, $CDCl_3$

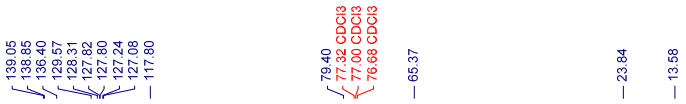


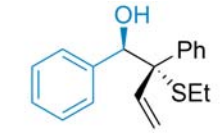




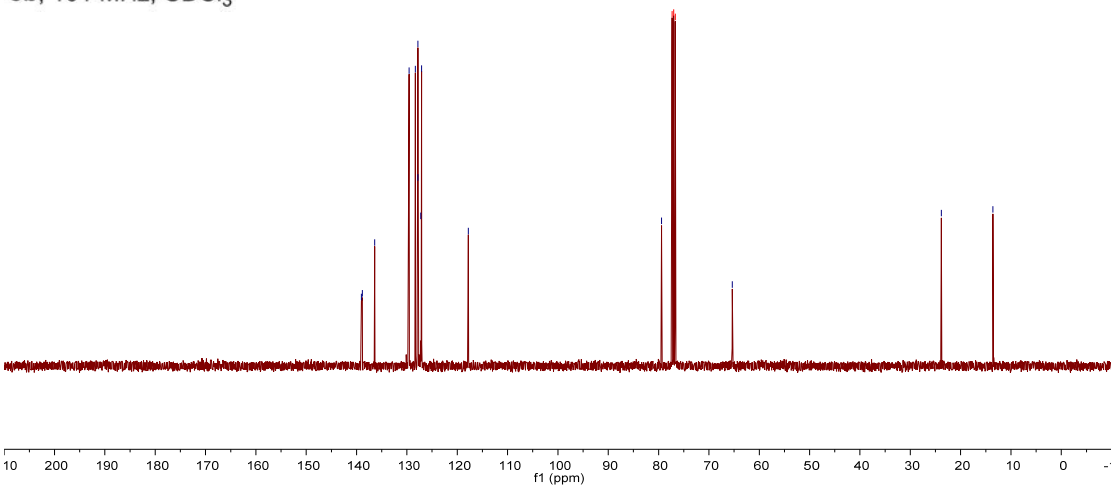
3b, 400 MHz, $CDCl_3$

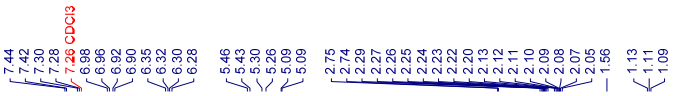


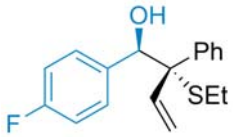




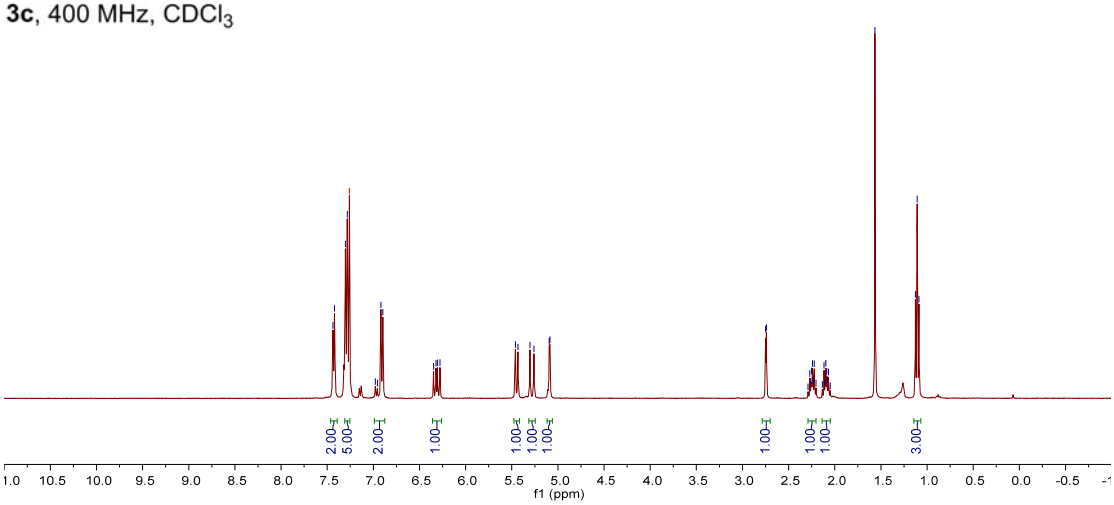
3b, 101 MHz, $CDCl_3$

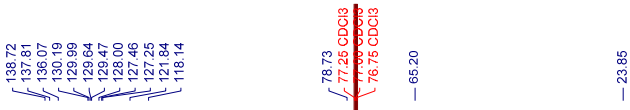


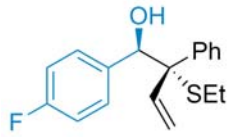




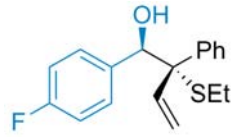
3c, 400 MHz, $CDCl_3$



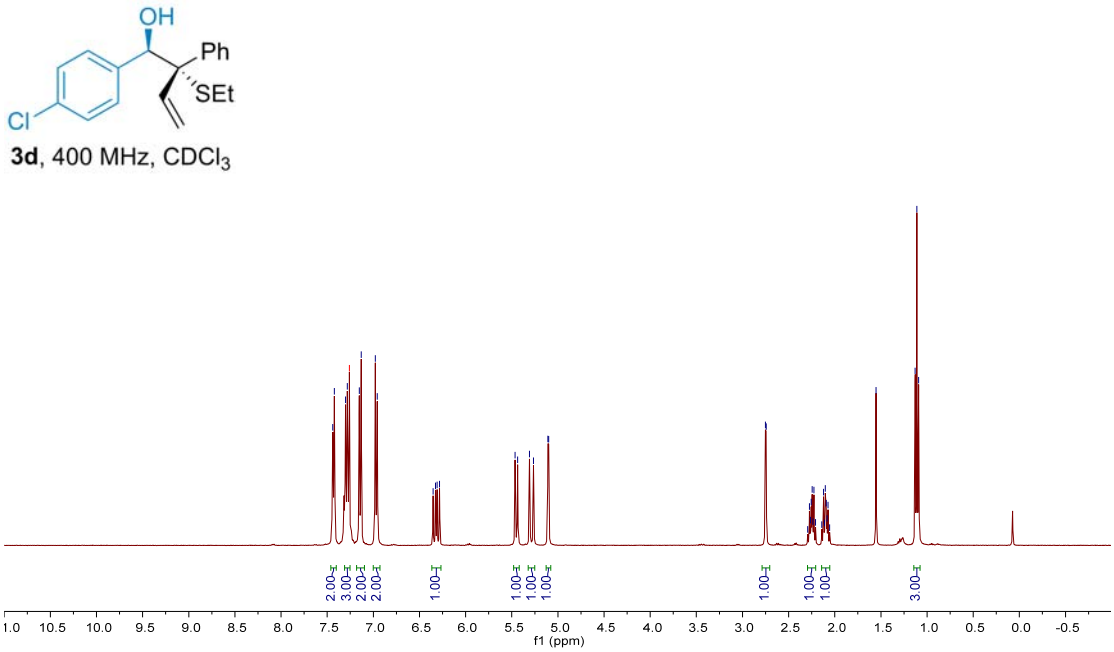




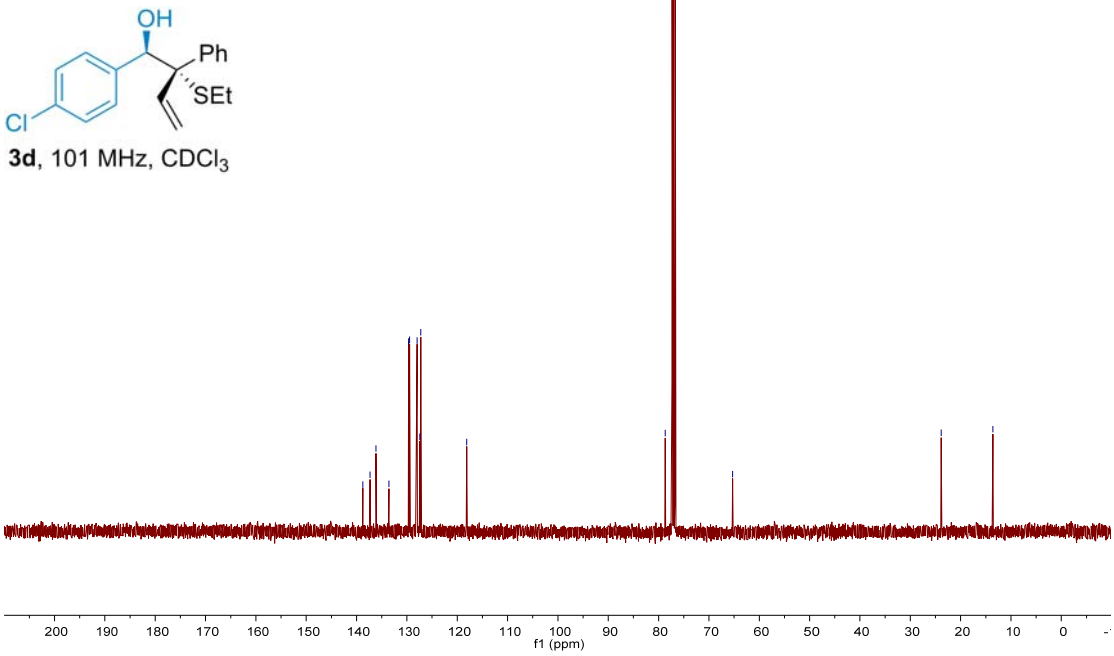
3c, 101 MHz, $CDCl_3$



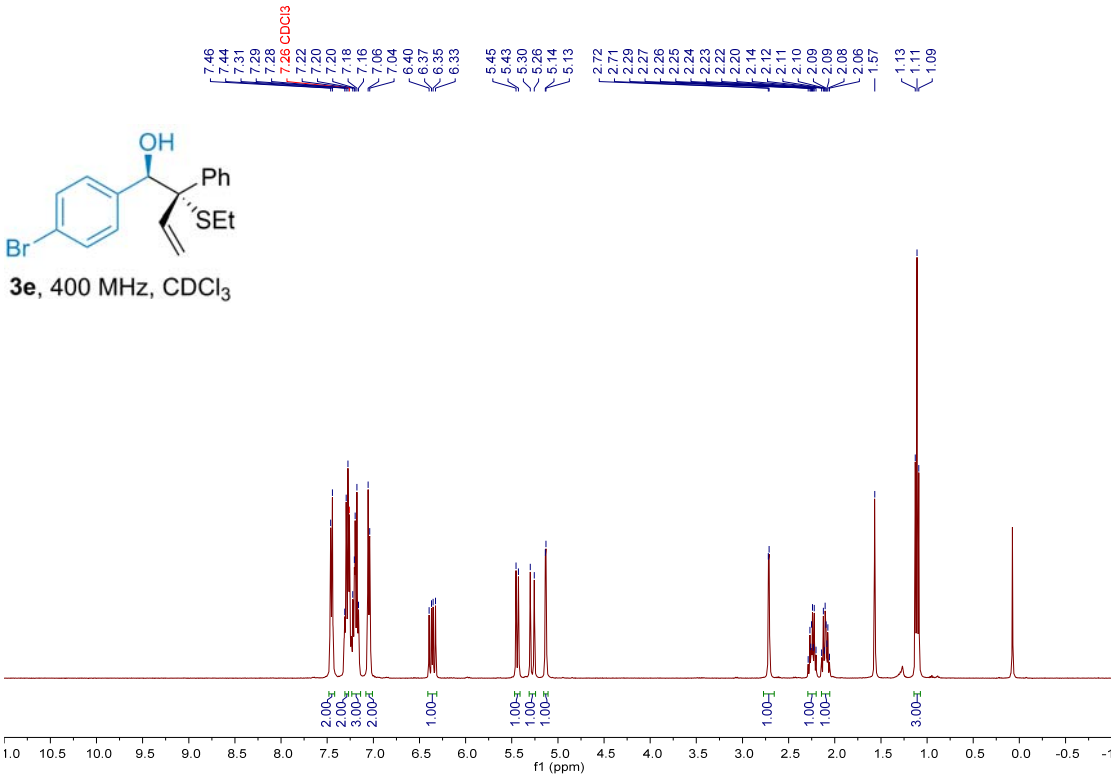
3c, 377 MHz, $CDCl_3$

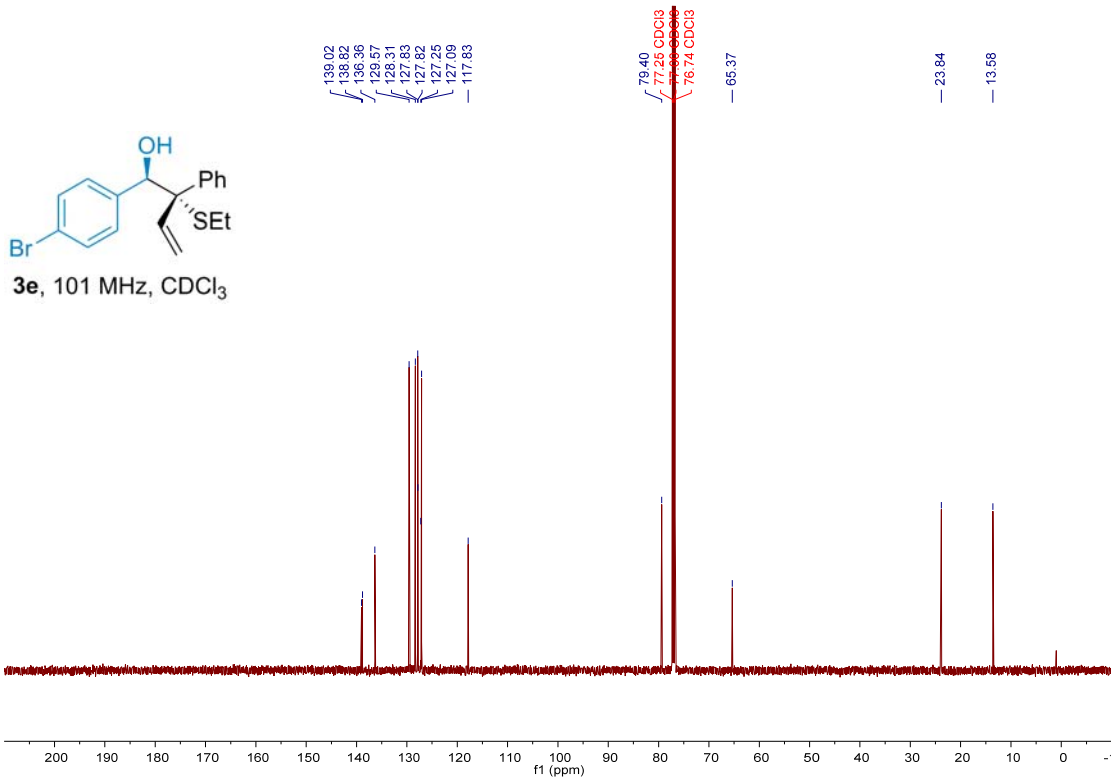


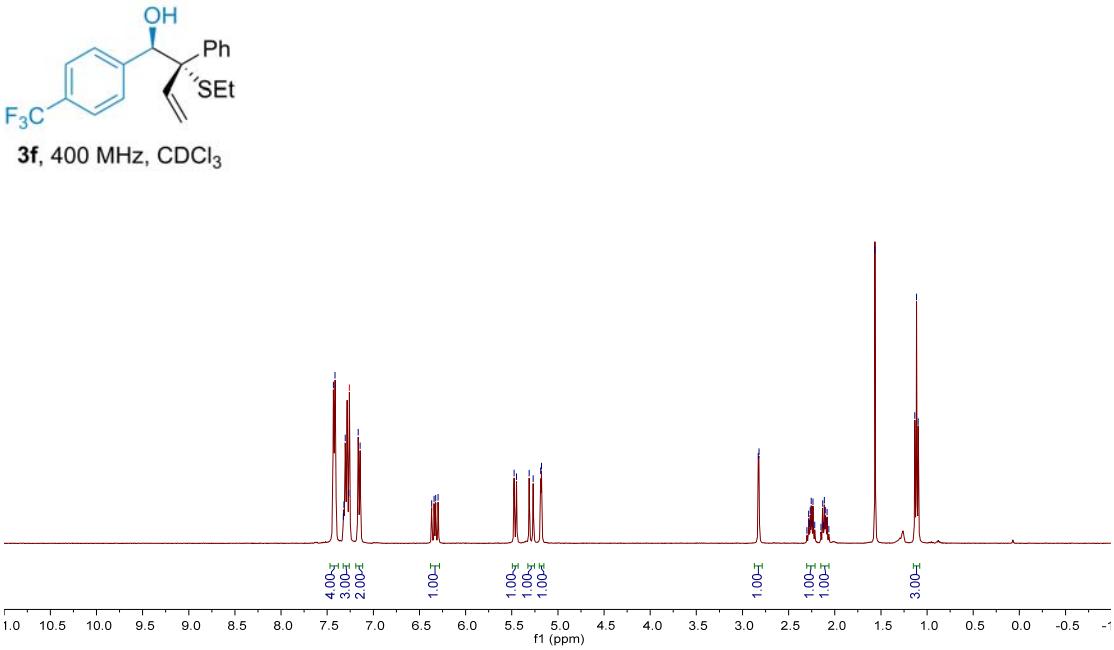
3d, 400 MHz, $CDCl_3$



3d, 101 MHz, $CDCl_3$


7.46
7.44
7.31
7.29
7.28
7.26 CDCl3
7.22
7.20
7.20
7.18
7.16
7.06
7.04
6.40
6.37
6.35
6.33
5.45
5.43
5.30
5.26
5.14
5.13
2.72
2.71
2.29
2.27
2.26
2.25
2.24
2.23
2.22
2.20
2.14
2.12
2.11
2.10
2.09
2.09
2.08
2.06
1.57
1.13
1.11
1.09
OH
Ph
SEt
Br
3e, 400 MHz, CDCl3
2.00
2.00
3.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)


139.02
138.82
136.36
129.57
128.31
127.83
127.82
127.25
127.09
117.83
79.40
77.25 CDCl3
76.74 CDCl3
65.37
23.84
13.58
OH
Ph
SEt
Br
3e, 101 MHz, CDCl3
f1 (ppm)


OH
Ph
SEt
F3C
3f, 400 MHz, CDCl3
7.43
7.41
7.33
7.32
7.30
7.27
7.26 CDCl3
7.16
7.14
6.37
6.34
6.33
6.30
5.48
5.45
5.31
5.27
5.19
5.18
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2.30
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1.13
1.11
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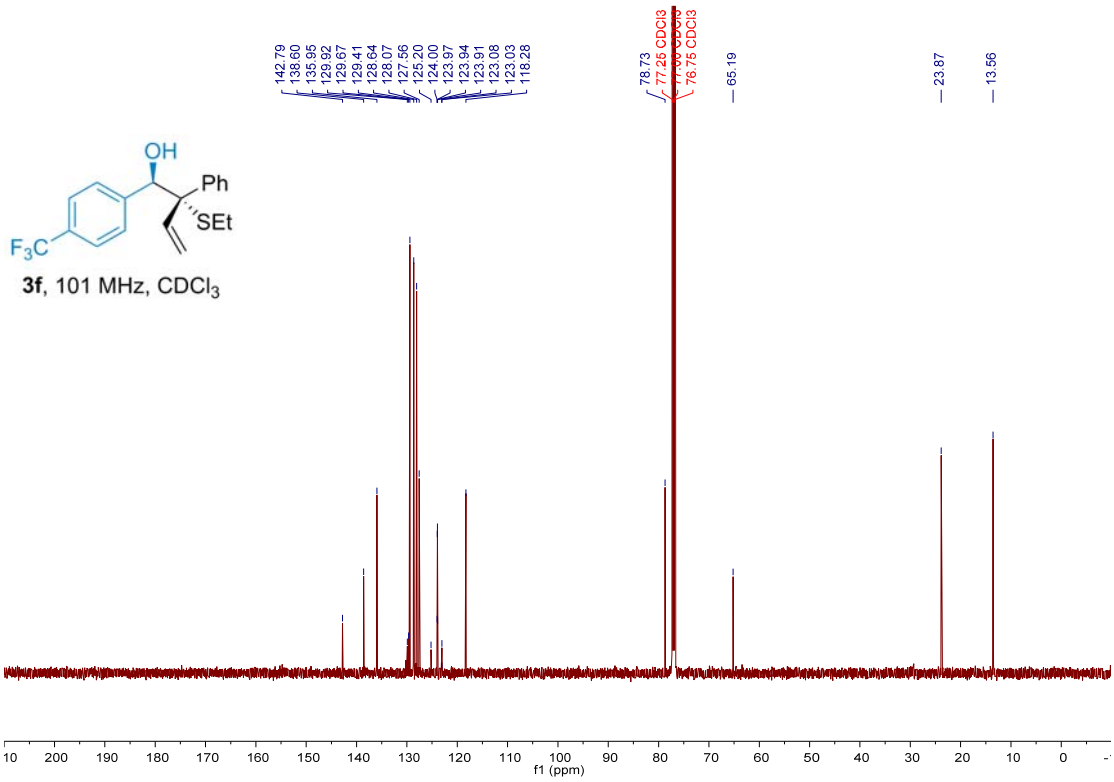
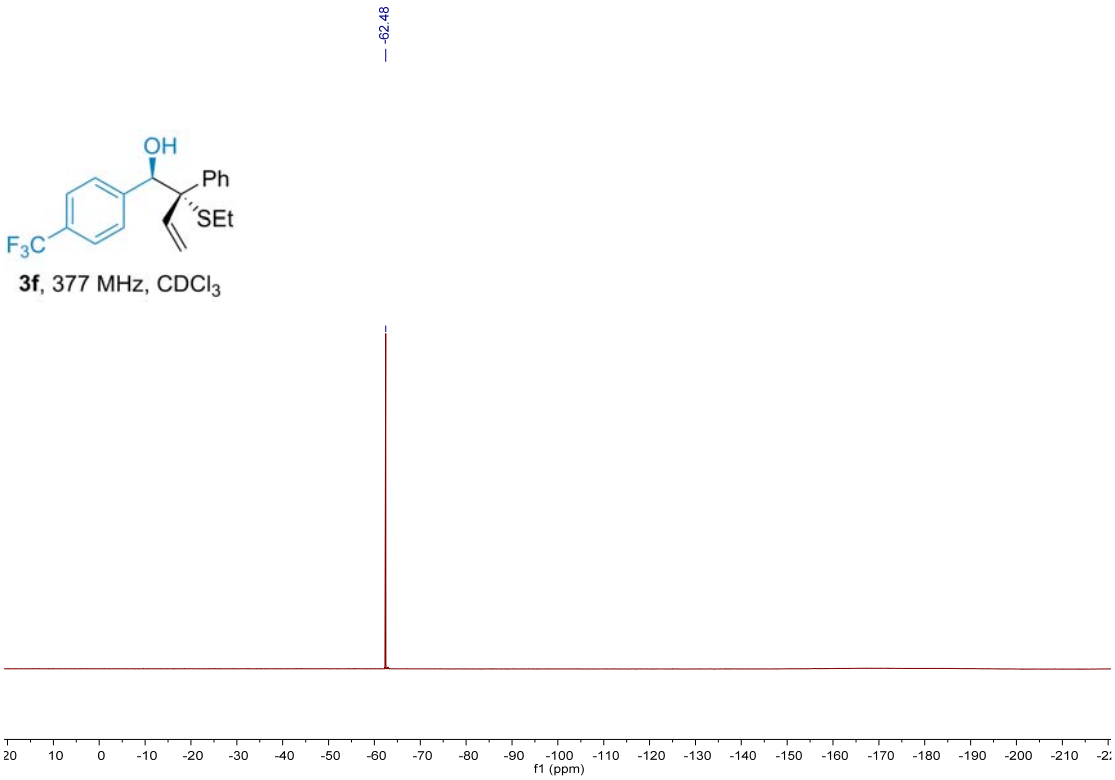
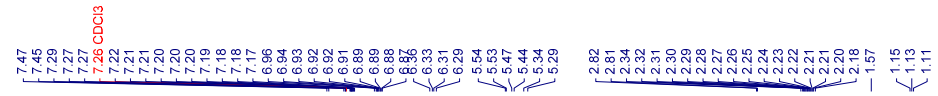
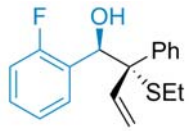
1.00
1.00
1.00
3.00
f1 (ppm)

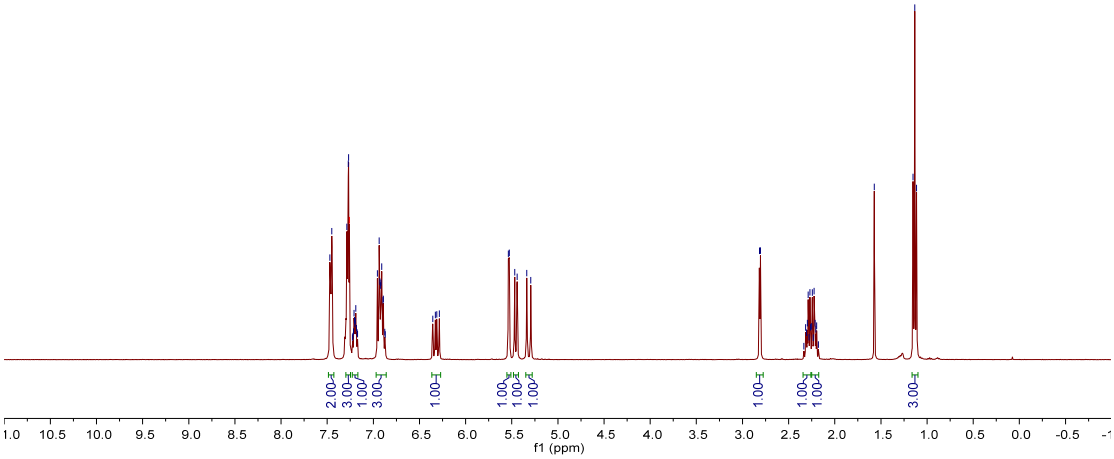

OH
Ph
SEt
F3C
3f, 101 MHz, CDCl3
142.79
138.60
135.95
129.92
129.67
129.41
128.64
128.07
127.56
125.20
124.00
123.97
123.94
123.91
123.08
123.03
118.28
78.73
77.25 CDCl3
76.75 CDCl3
65.19
23.87
13.56
f1 (ppm)

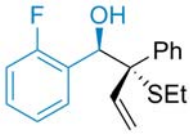

-62.48
OH
Ph
SEt
F3C
3f, 377 MHz, CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



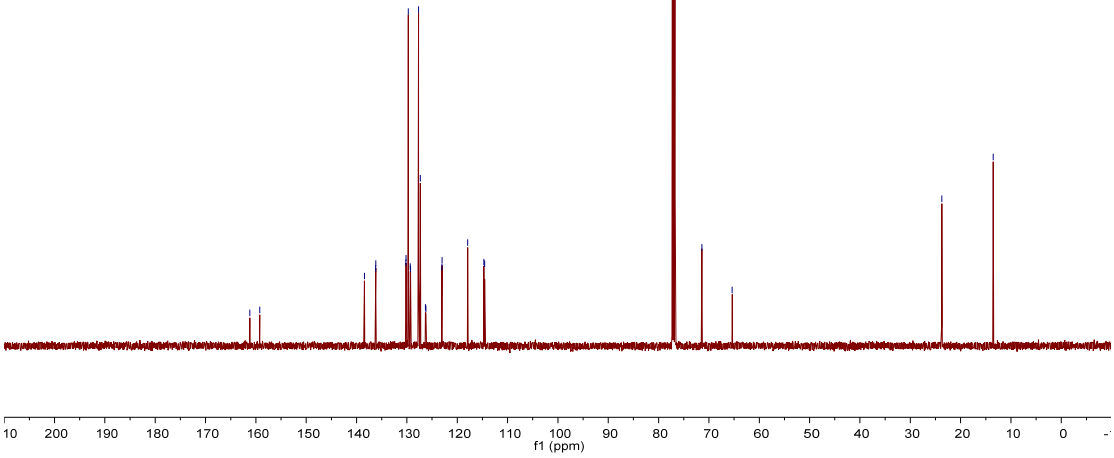


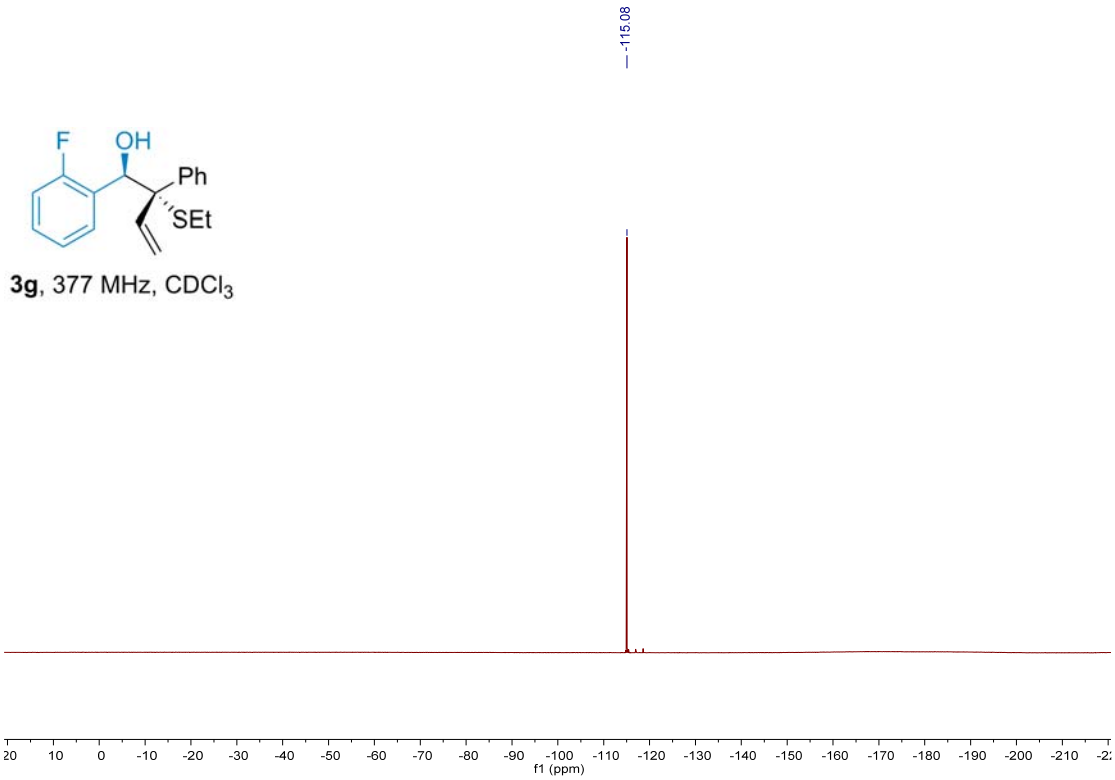
3g, 400 MHz, $CDCl_3$



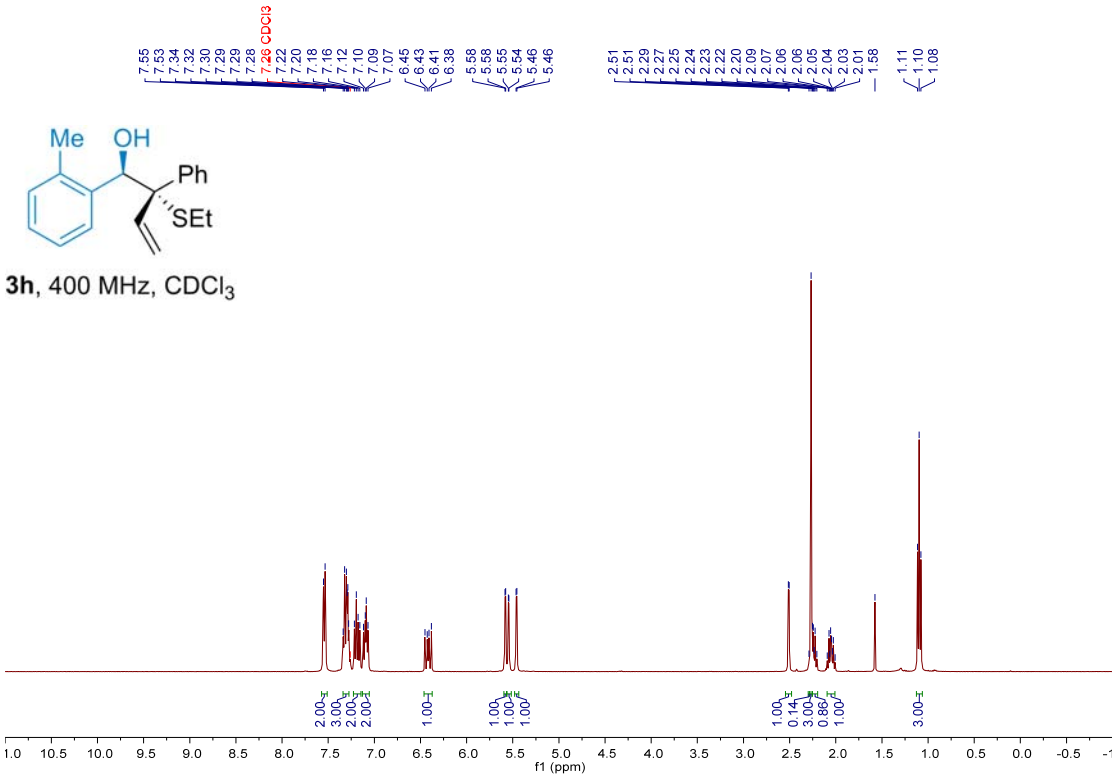


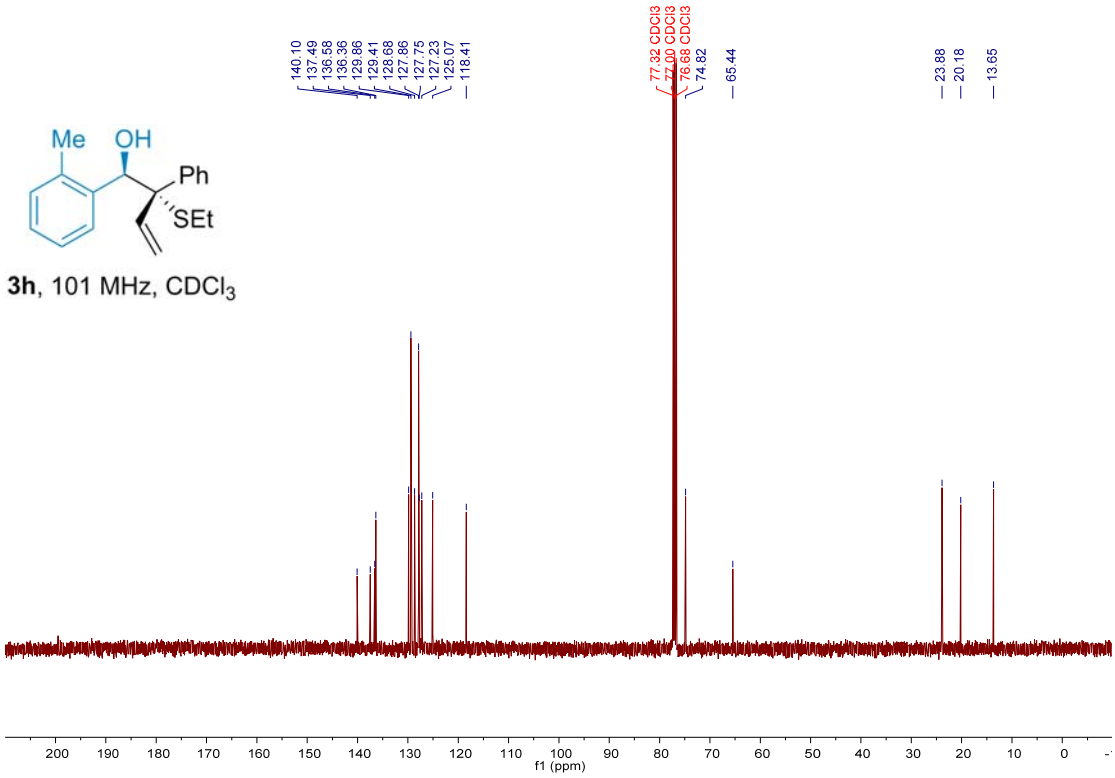
3g, 101 MHz, $CDCl_3$

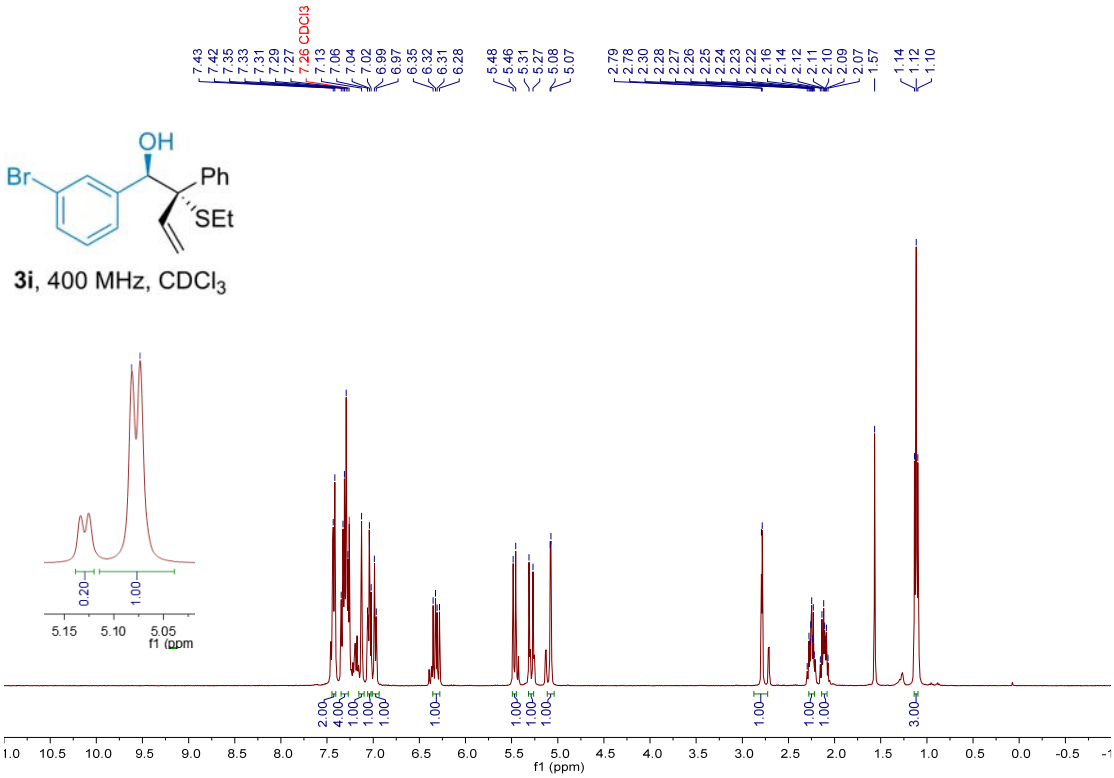


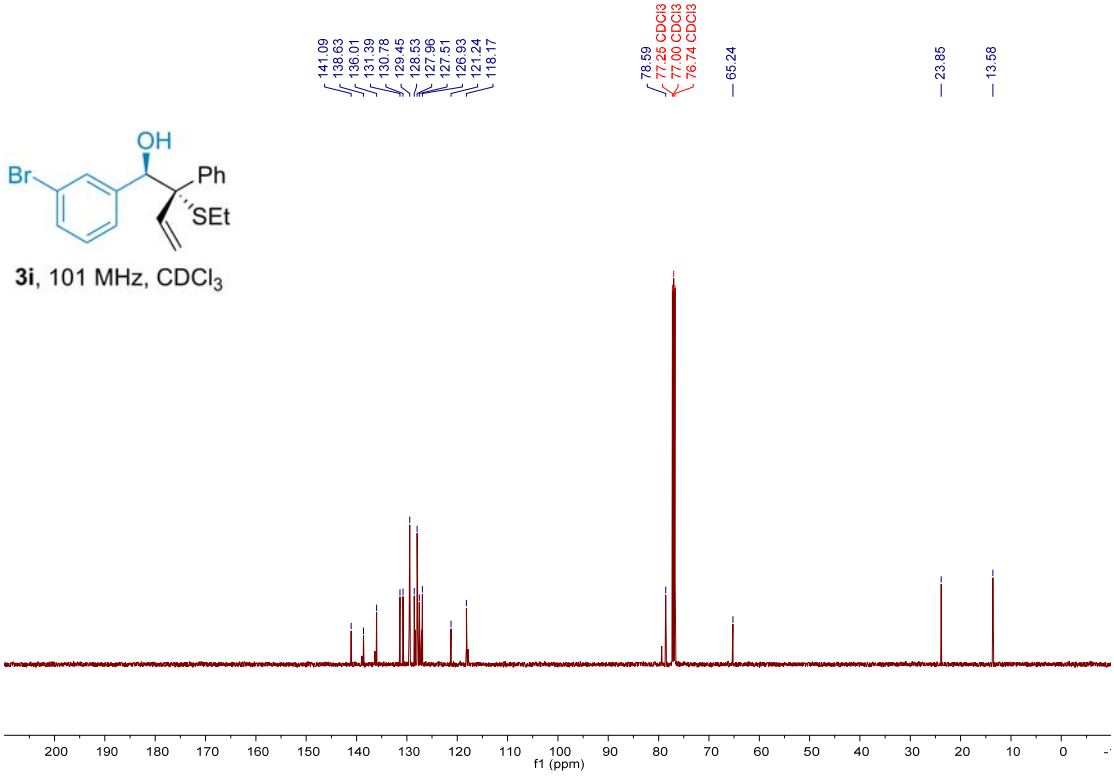


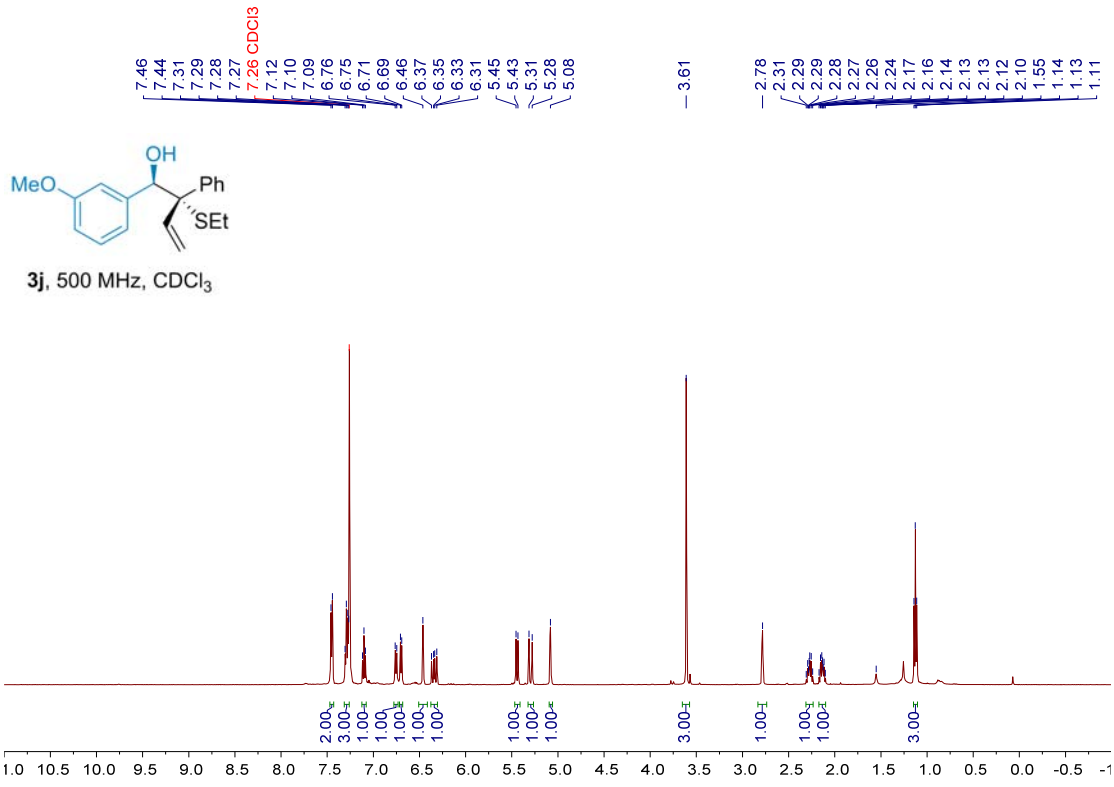
3g, 377 MHz, $CDCl_3$


7.55
7.53
7.34
7.32
7.30
7.29
7.29
7.28
7.26 CDCl3
7.22
7.20
7.18
7.16
7.12
7.10
7.09
7.07
6.45
6.43
6.41
6.38
5.58
5.58
5.55
5.54
5.46
5.46
2.51
2.51
2.29
2.27
2.25
2.24
2.23
2.22
2.20
2.09
2.07
2.06
2.06
2.05
2.04
2.03
2.01
1.58
1.11
1.10
1.08
Me
OH
Ph
SEt
3h, 400 MHz, CDCl3
2.00
3.00
2.00
2.00
1.00
1.00
1.00
1.00
1.00
0.14
3.00
0.86
1.00
3.00
f1 (ppm)

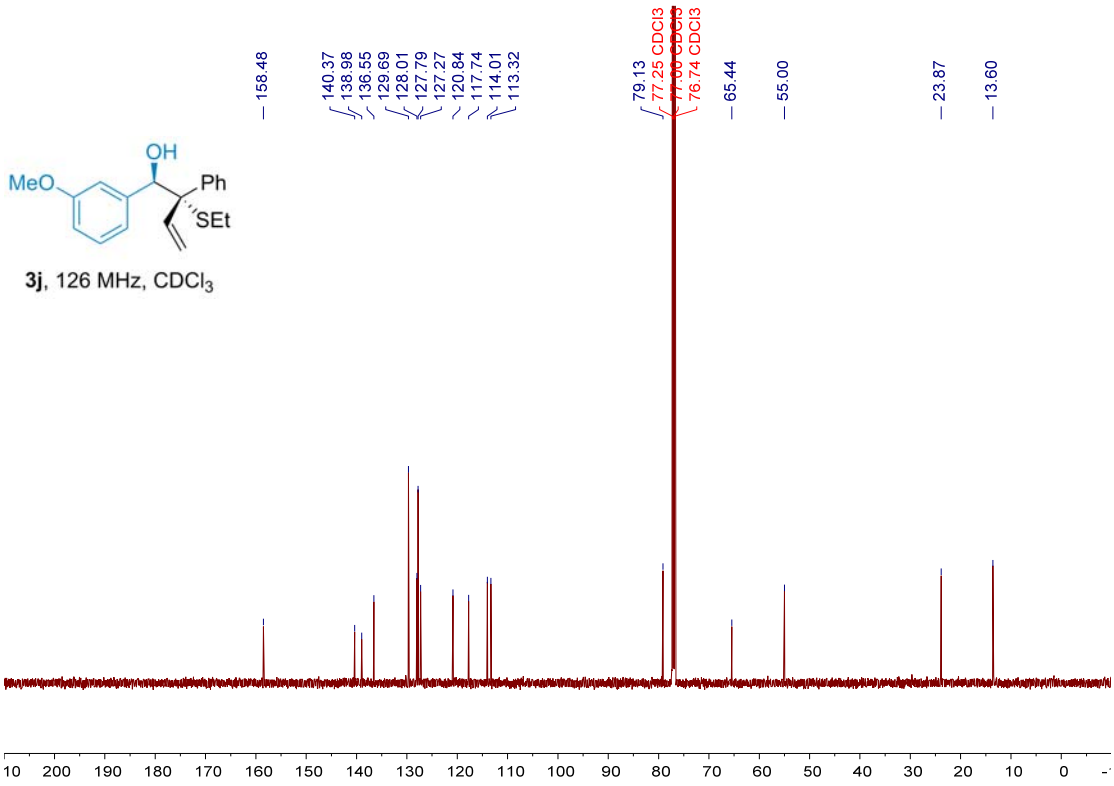

140.10
137.49
136.58
136.36
129.86
129.41
128.68
127.86
127.75
127.23
125.07
118.41
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
74.82
65.44
23.88
20.18
13.65
Me
OH
Ph
SEt
3h, 101 MHz, CDCl3
f1 (ppm)


7.43
7.42
7.35
7.33
7.31
7.29
7.27
7.26 CDCl3
7.13
7.06
7.04
7.02
6.99
6.97
6.35
6.32
6.31
6.28
5.48
5.46
5.31
5.27
5.08
5.07
2.79
2.78
2.30
2.28
2.27
2.26
2.25
2.24
2.23
2.22
2.16
2.14
2.12
2.11
2.10
2.09
2.07
1.57
1.14
1.12
1.10
OH
Br
Ph
SEt
3i, 400 MHz, CDCl3
0.20
1.00
5.15
5.10
5.05
f1 (ppm)
2.00
4.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

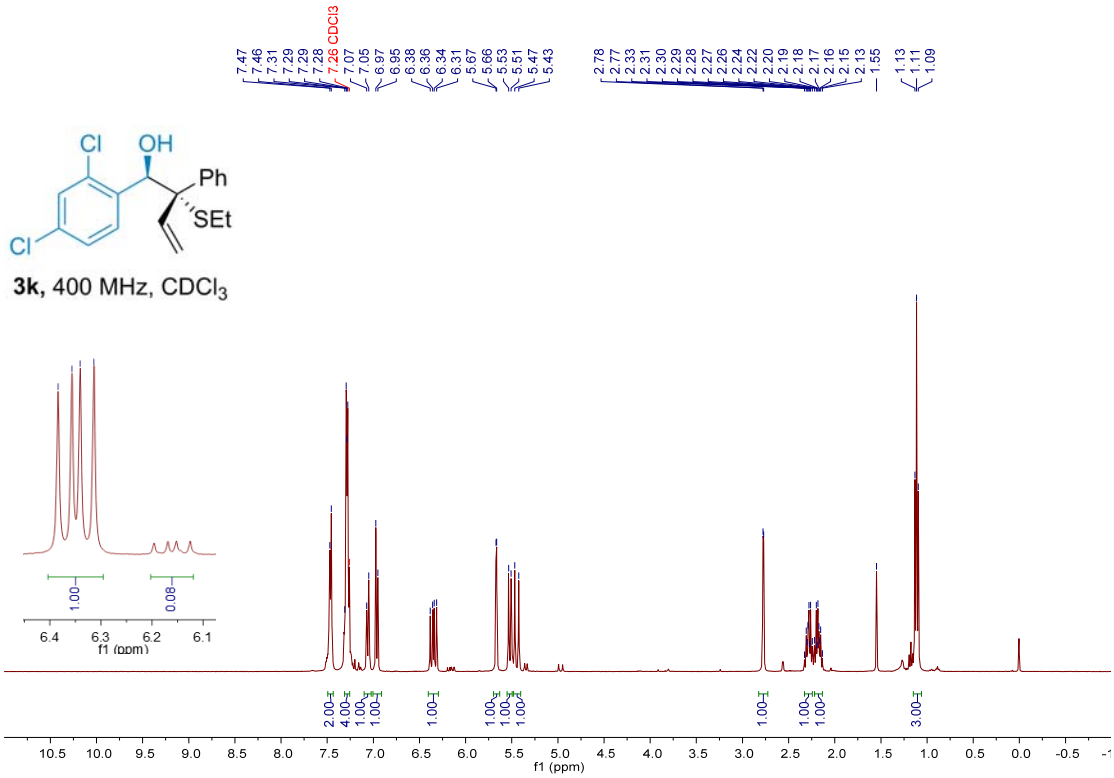

141.09
138.63
136.01
131.39
130.78
129.45
128.53
127.96
127.51
126.93
121.24
118.17
78.59
77.25 CDCl3
77.00 CDCl3
76.74 CDCl3
65.24
23.85
13.58
OH
Br
Ph
SEt
3i, 101 MHz, CDCl3
f1 (ppm)

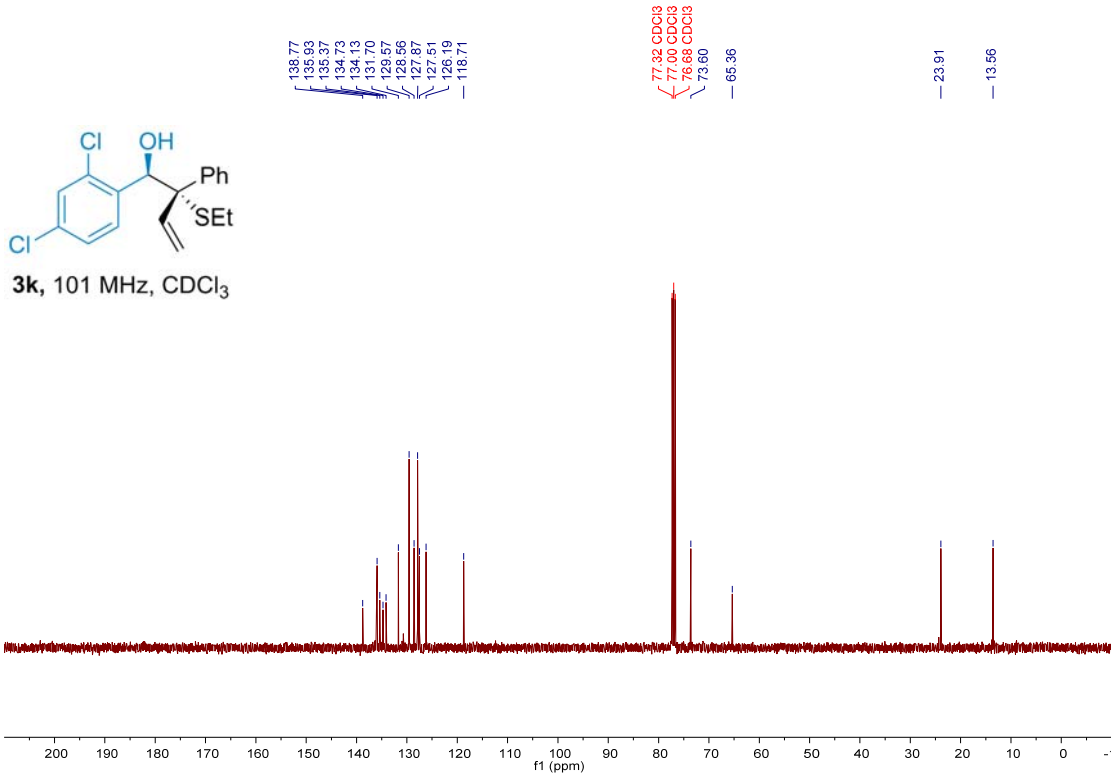


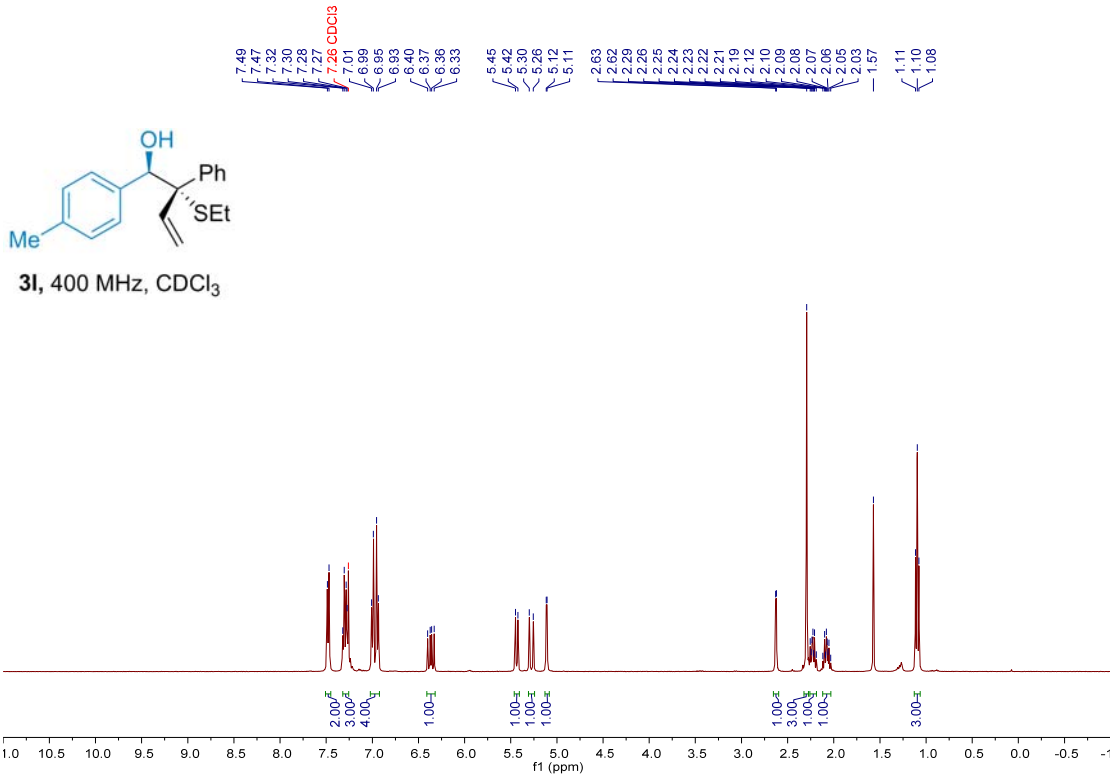
3j, 500 MHz, $CDCl_3$



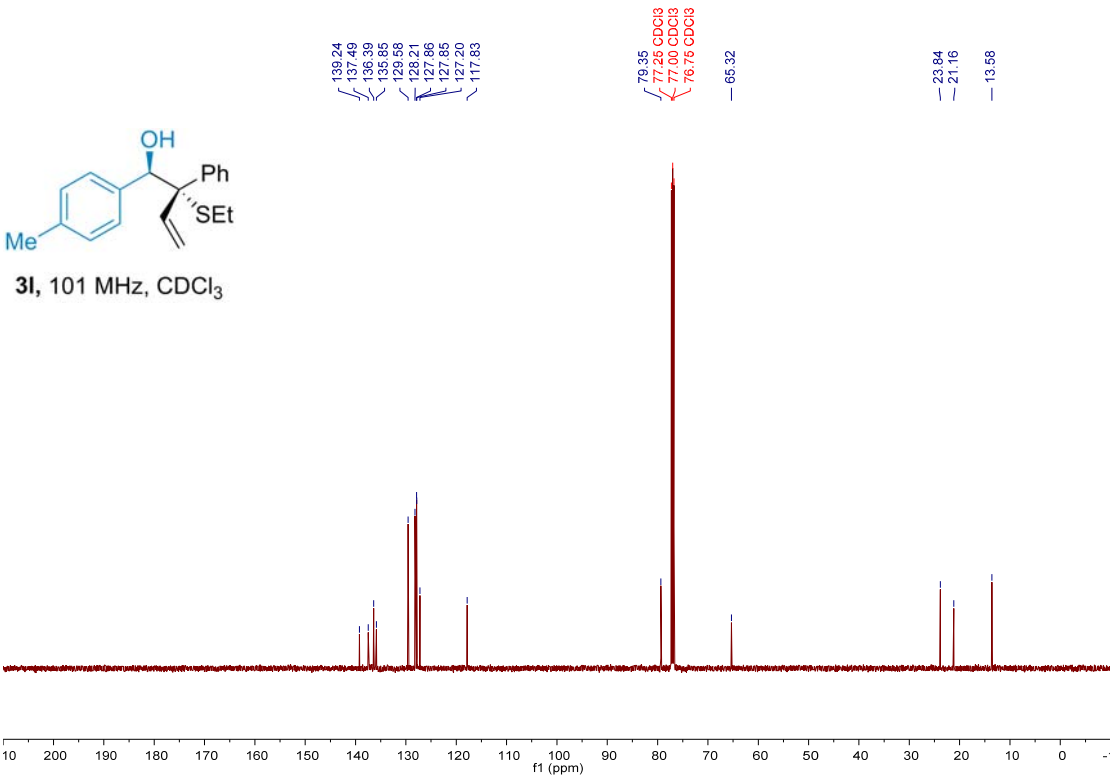
3j, 126 MHz, $CDCl_3$


7.47
7.46
7.31
7.29
7.29
7.28
7.26 CDCl3
7.07
7.05
6.97
6.95
6.38
6.36
6.34
6.31
5.67
5.66
5.53
5.51
5.47
5.43
2.78
2.77
2.33
2.31
2.30
2.29
2.28
2.27
2.26
2.24
2.22
2.20
2.19
2.18
2.17
2.16
2.15
2.13
1.55
1.13
1.11
1.09
Cl
OH
Ph
SEt
Cl
3k, 400 MHz, CDCl3
1.00
0.08
6.4
6.3
6.2
6.1
f1 (ppm)
2.00
4.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
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)

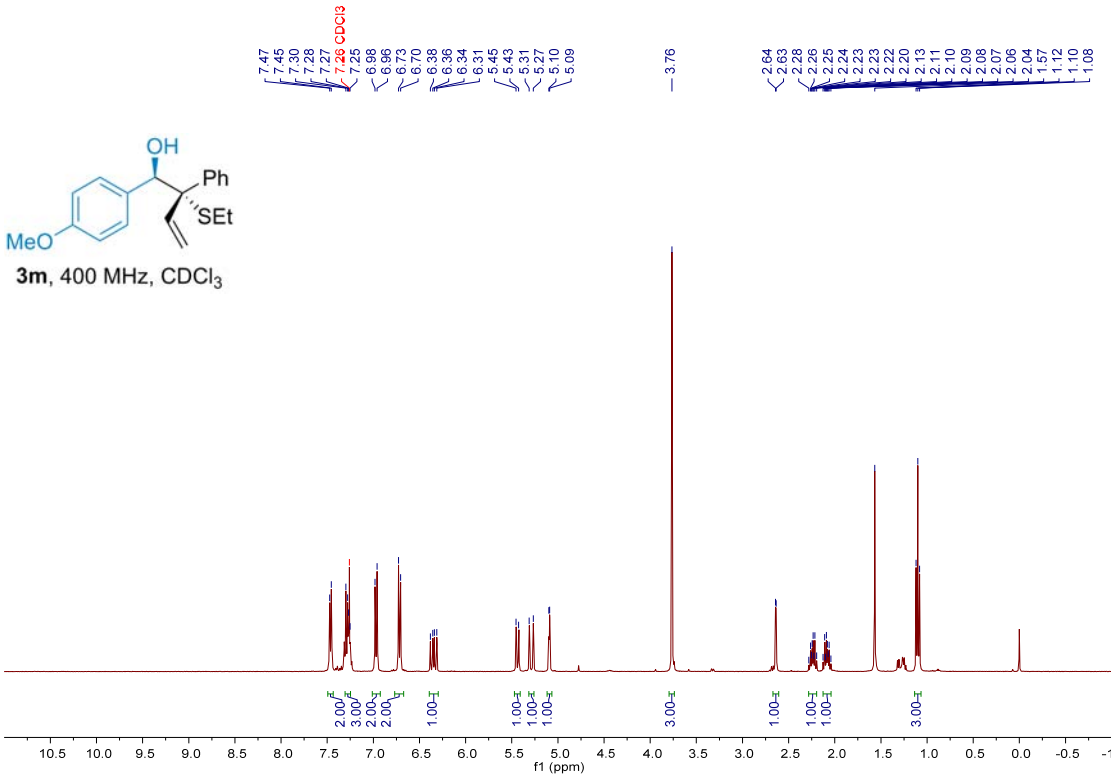

138.77
135.93
135.37
134.73
134.13
131.70
129.57
128.56
127.87
127.51
126.19
118.71
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.60
65.36
23.91
13.56
Cl
OH
Ph
SEt
Cl
3k, 101 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

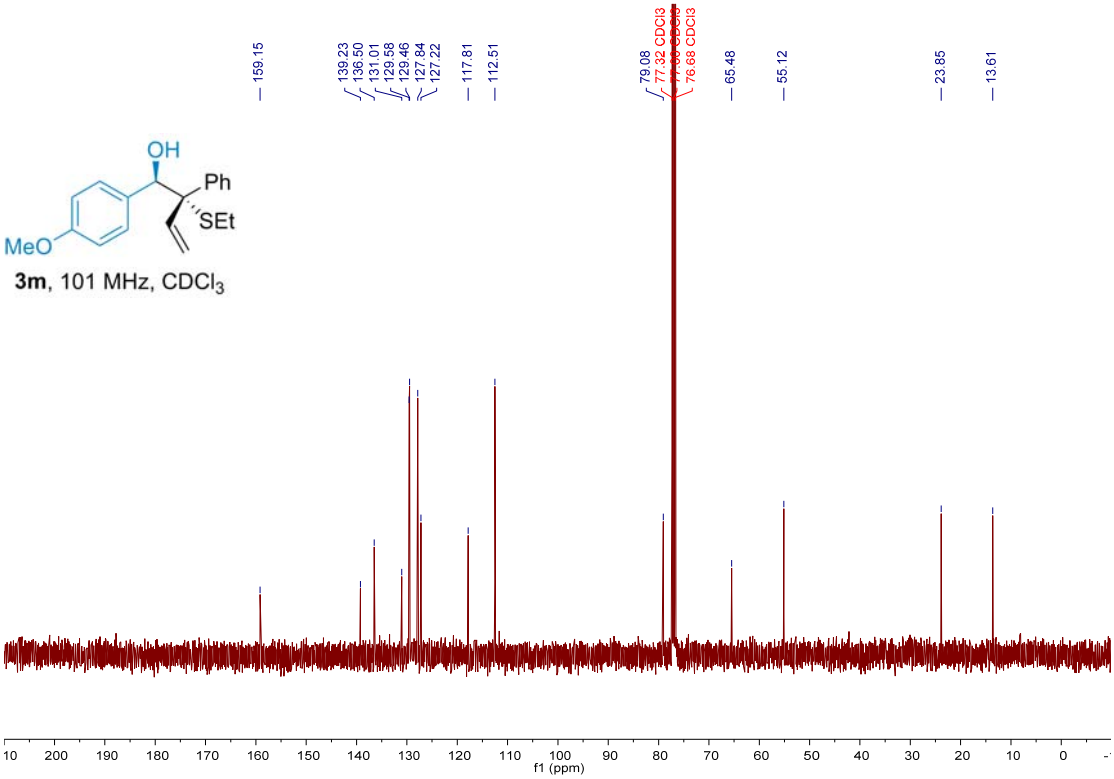


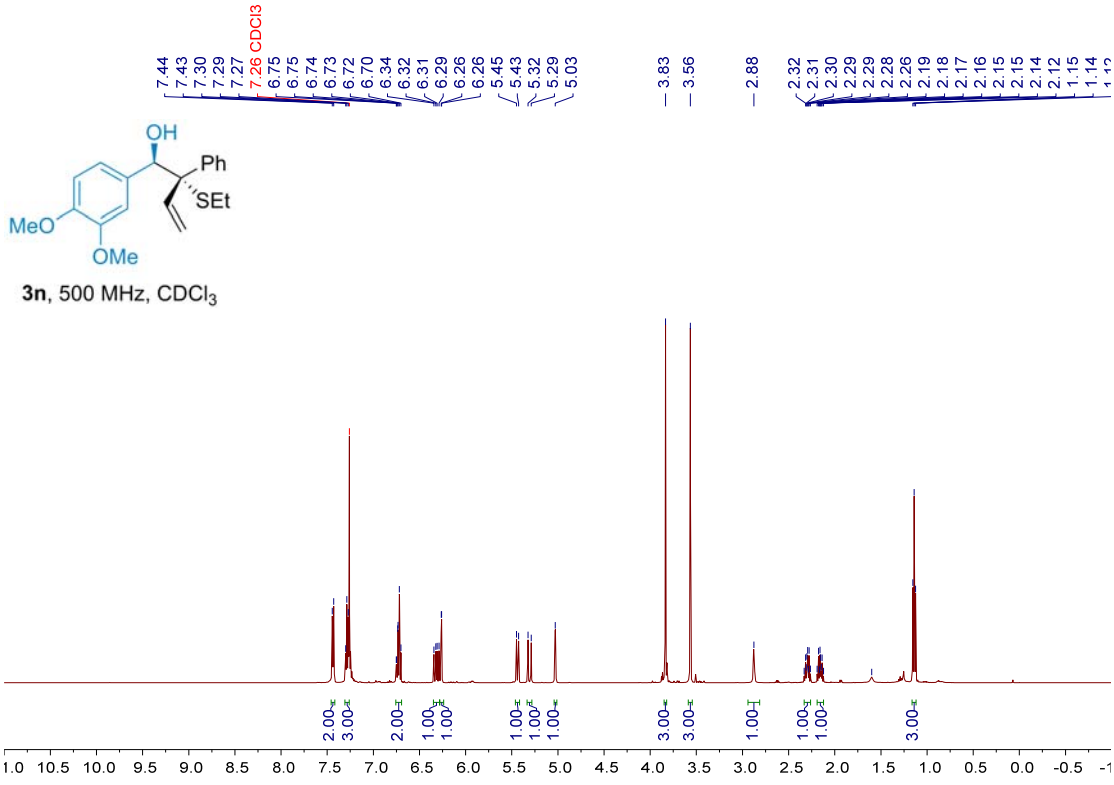
3l, 400 MHz, $CDCl_3$



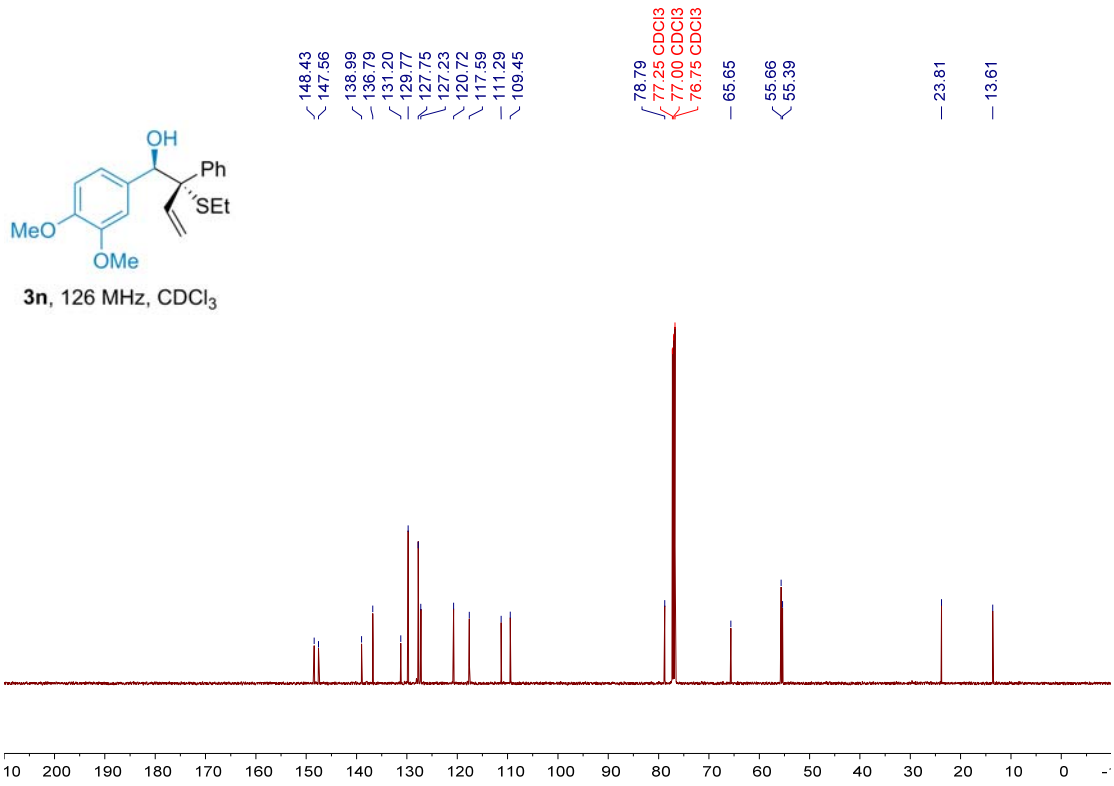
3l, 101 MHz, $CDCl_3$


OH
Ph
SEt
MeO
3m, 400 MHz, CDCl3
f1 (ppm)

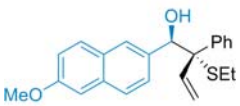

OH
Ph
SEt
MeO
3m, 101 MHz, CDCl3
f1 (ppm)



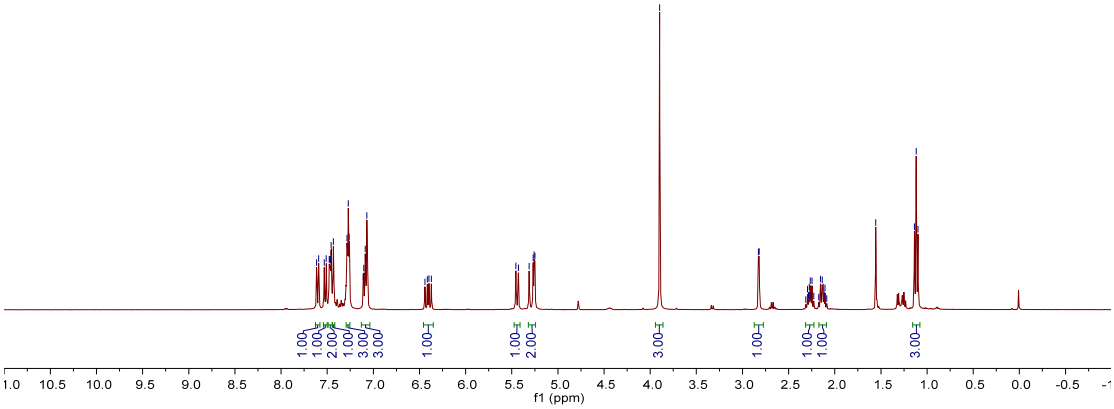
3n, 500 MHz, $CDCl_3$

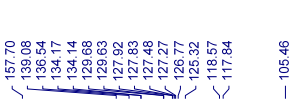


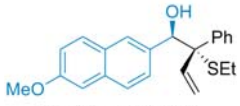
3n, 126 MHz, $CDCl_3$



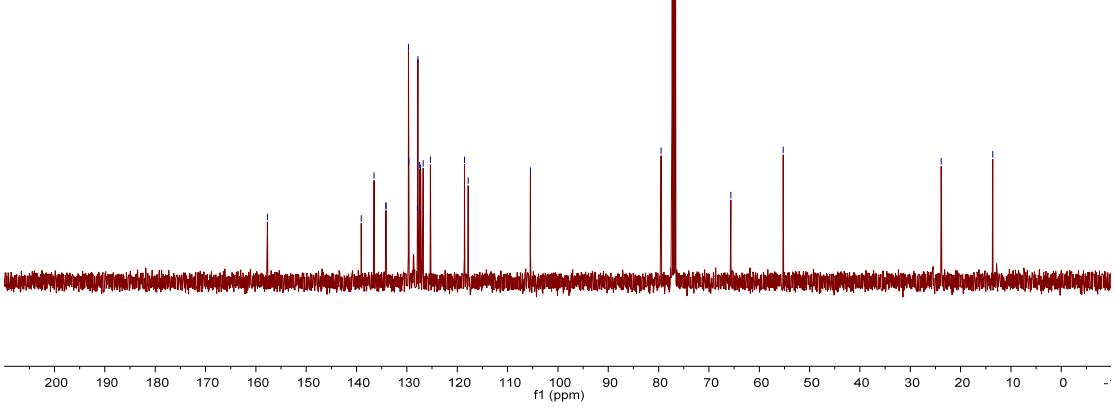
3o, 400 MHz, $CDCl_3$

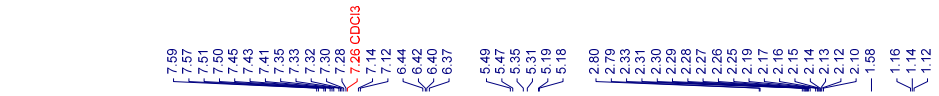


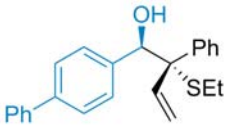




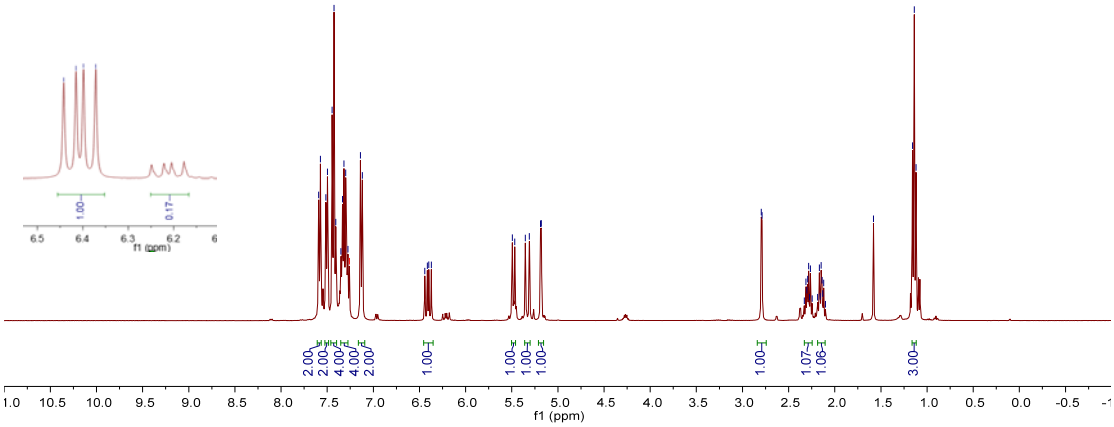
3o, 101 MHz, $CDCl_3$

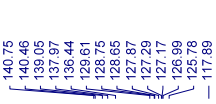


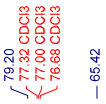


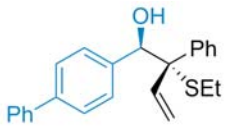


3p, 400 MHz, $CDCl_3$

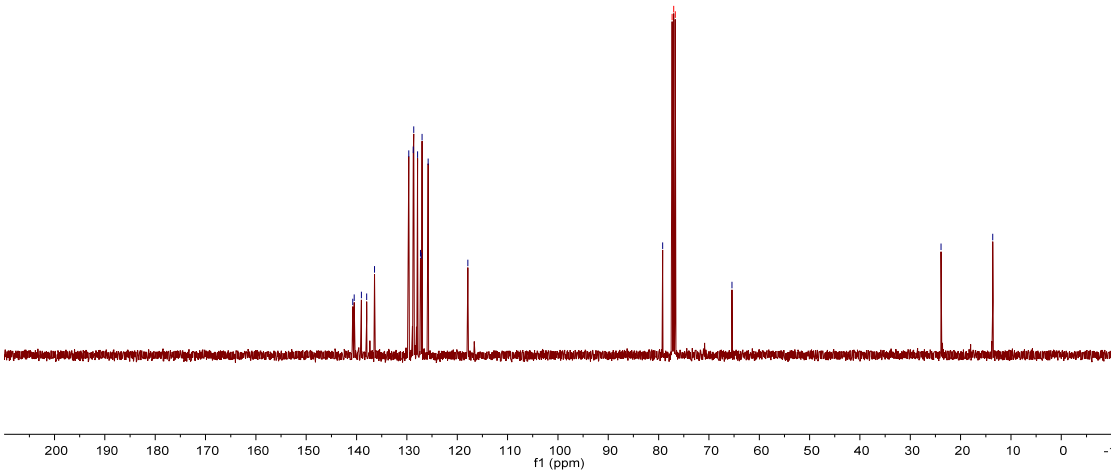


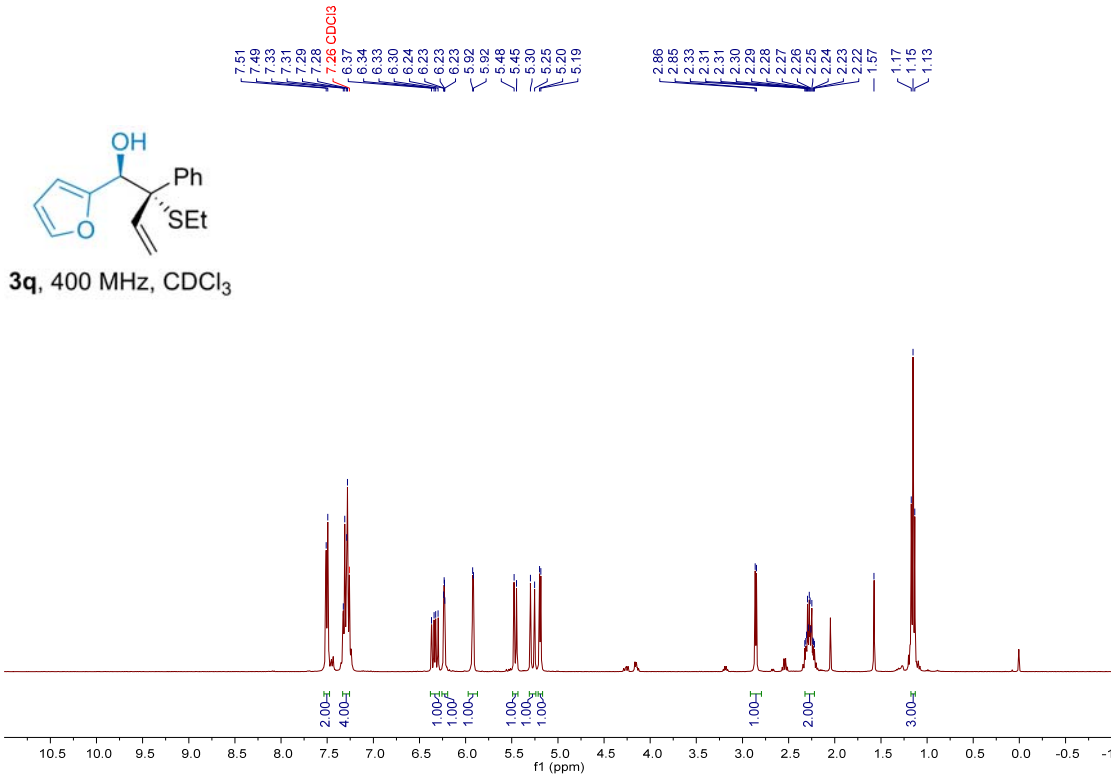


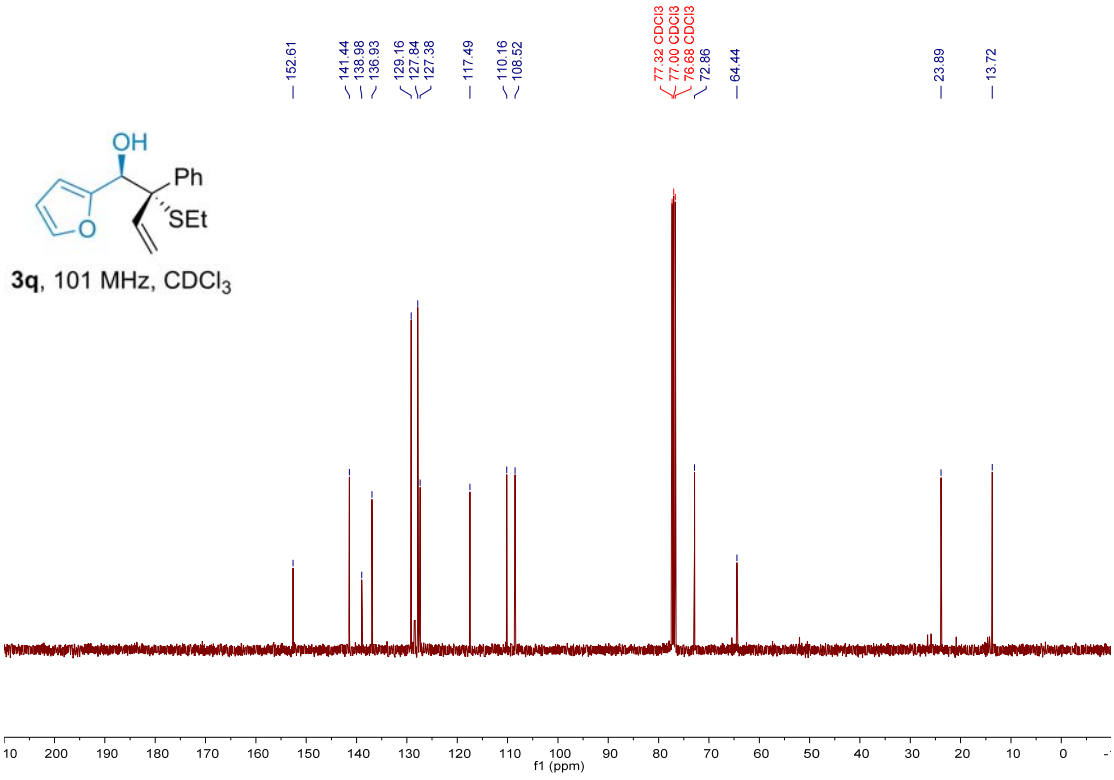


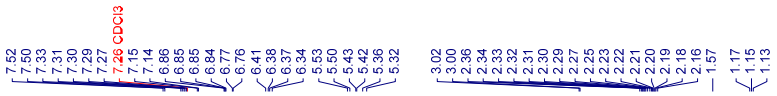


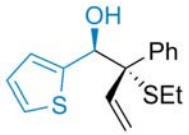
3p, 101 MHz, $CDCl_3$



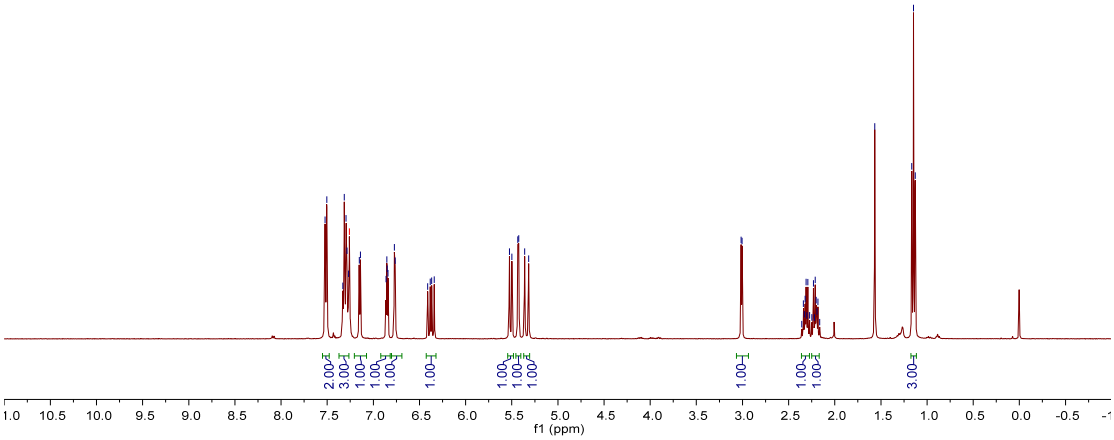

7.51
7.49
7.33
7.31
7.29
7.28
7.26 CDCl3
6.37
6.34
6.33
6.30
6.24
6.23
6.23
5.92
5.48
5.45
5.30
5.25
5.20
5.19
2.86
2.85
2.33
2.31
2.31
2.30
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.22
1.57
1.17
1.15
1.13
OH
Ph
SEt
O
3q, 400 MHz, CDCl3
2.00
4.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
10.5 10.0 9.5 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)

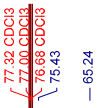

152.61
141.44
138.98
136.93
129.16
127.84
127.38
117.49
110.16
108.52
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
72.86
64.44
23.89
13.72
OH
Ph
SEt
O
3q, 101 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

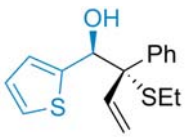




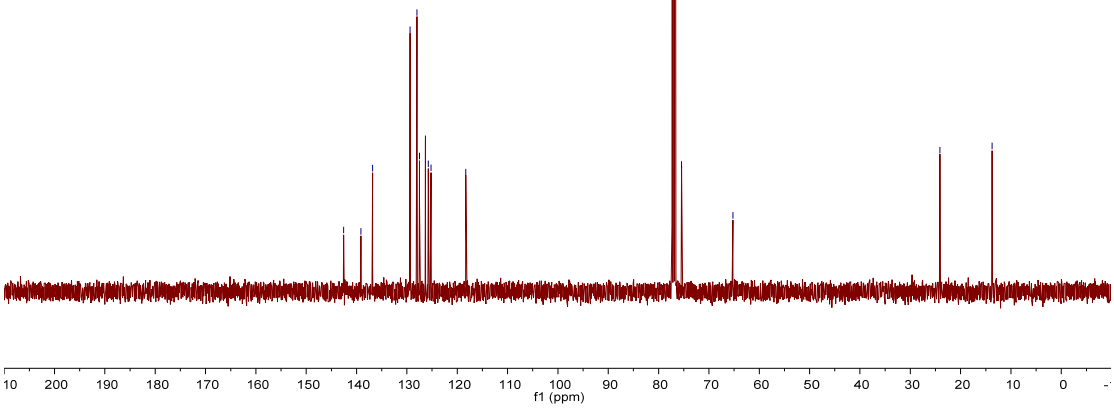
3r, 400 MHz, $CDCl_3$

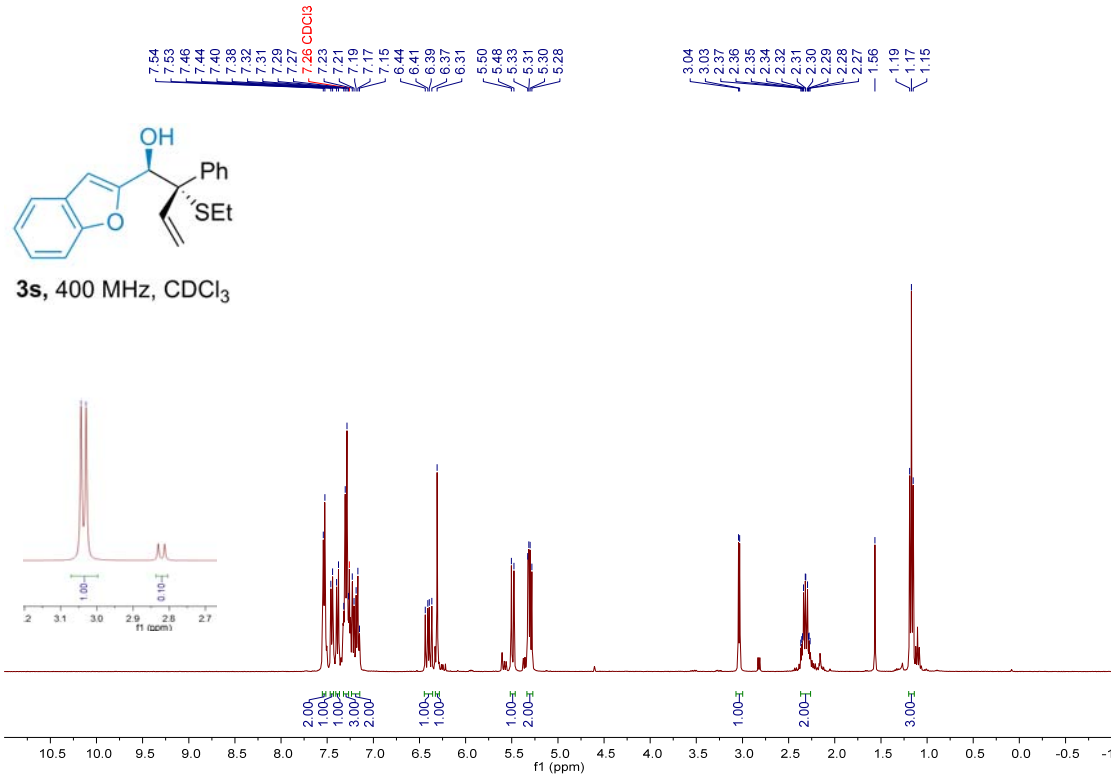


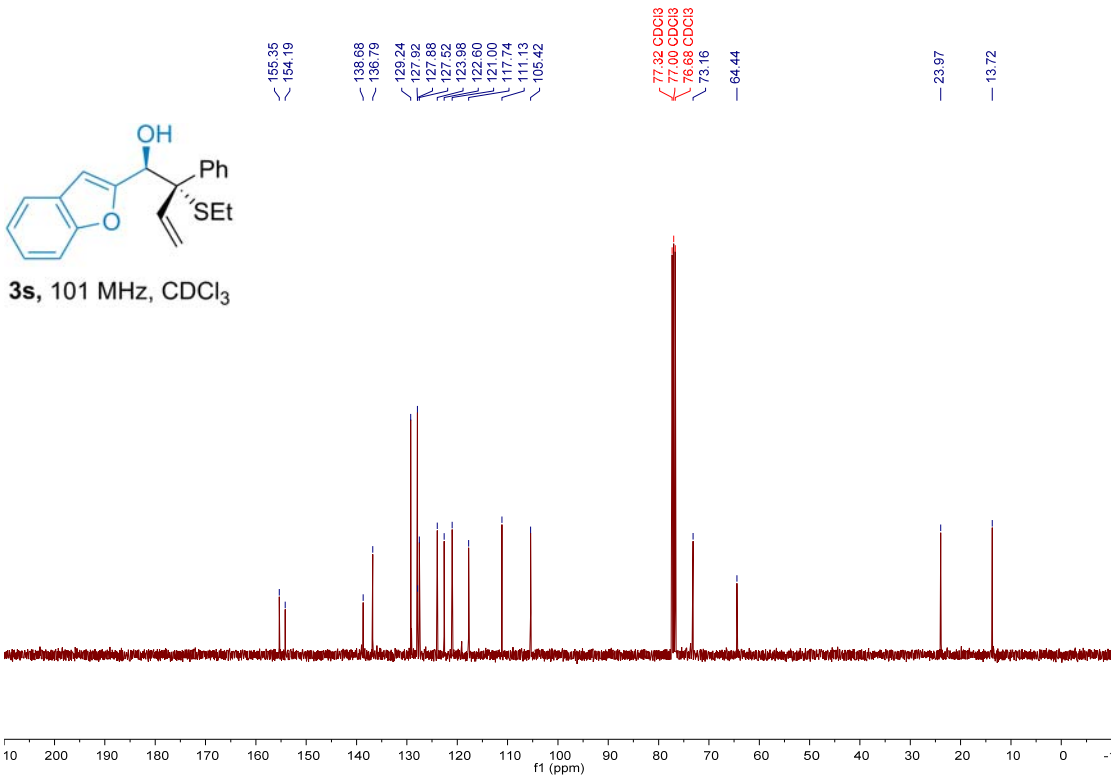


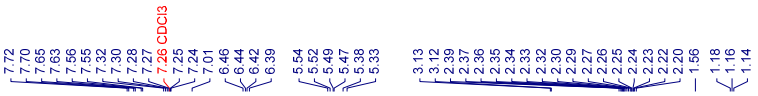


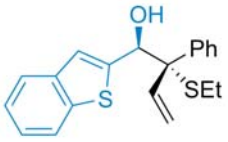
3r, 101 MHz, $CDCl_3$



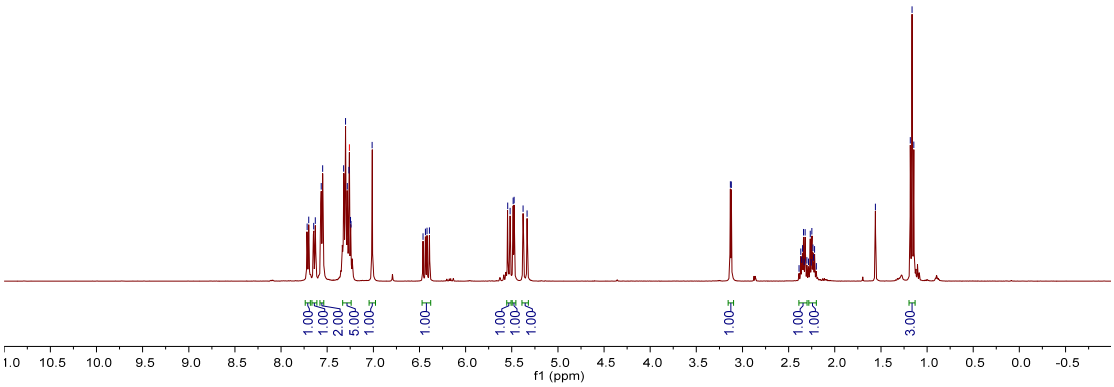

7.54
7.53
7.46
7.44
7.40
7.38
7.32
7.31
7.29
7.27
7.26 CDCl3
7.23
7.21
7.19
7.17
7.15
6.44
6.41
6.39
6.37
6.31
5.50
5.48
5.33
5.31
5.30
5.28
3.04
3.03
2.37
2.36
2.35
2.34
2.32
2.31
2.30
2.29
2.28
2.27
1.56
1.19
1.17
1.15
OH
Ph
SEt
O
3s, 400 MHz, CDCl3
2.00
1.00
1.00
3.00
2.00
1.00
1.00
1.00
2.00
1.00
2.00
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)

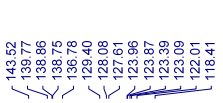

155.35
154.19
138.68
136.79
129.24
127.92
127.88
127.52
123.98
122.60
121.00
117.74
111.13
105.42
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.16
64.44
23.97
13.72
OH
Ph
SEt
O
3s, 101 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

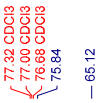


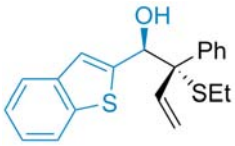


3t, 400 MHz, $CDCl_3$

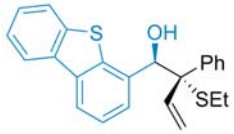




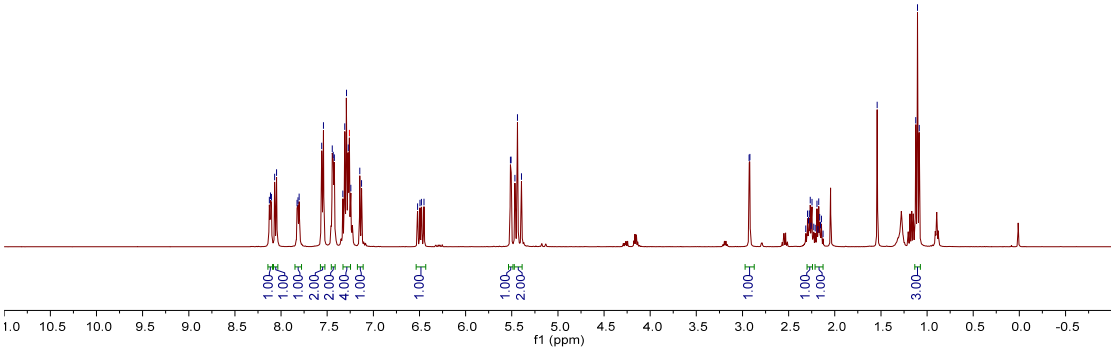


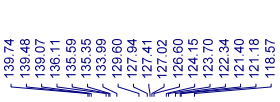


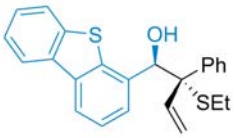
3t, 101 MHz, $CDCl_3$



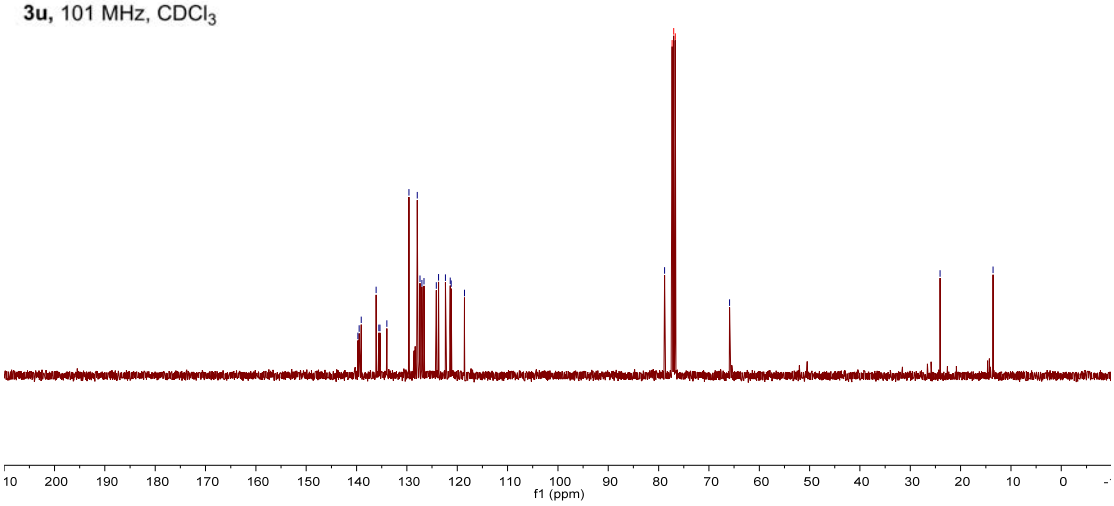
3u, 400 MHz, $CDCl_3$

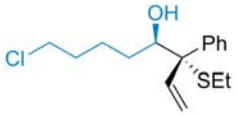




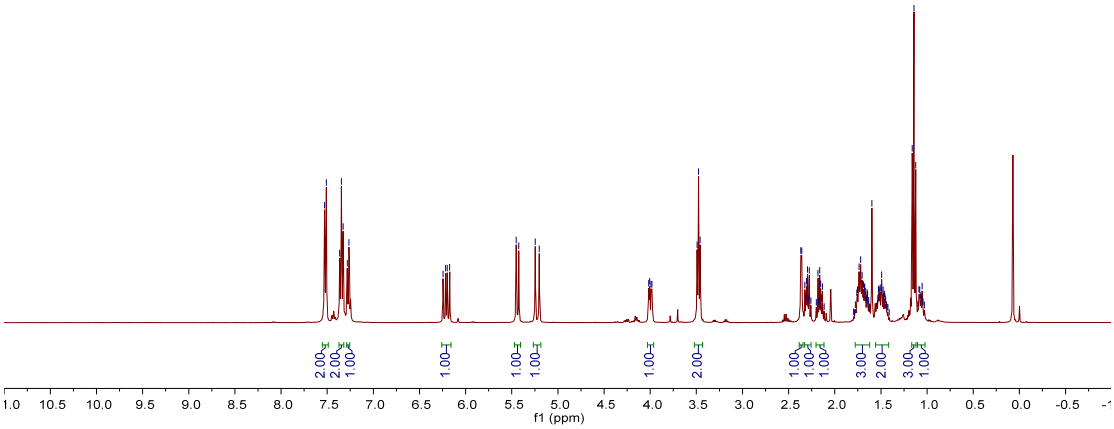


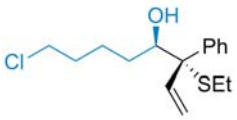
3u, 101 MHz, $CDCl_3$



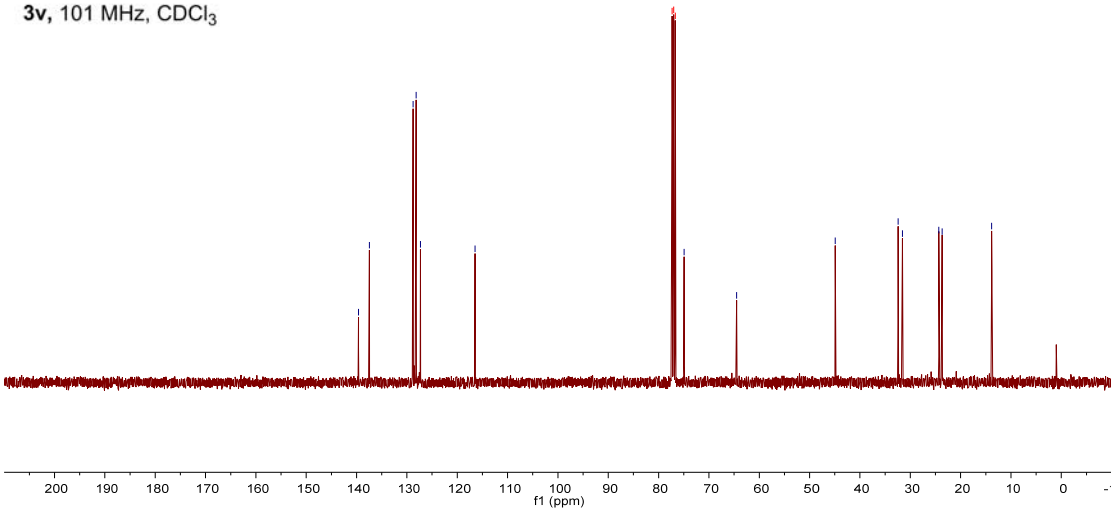


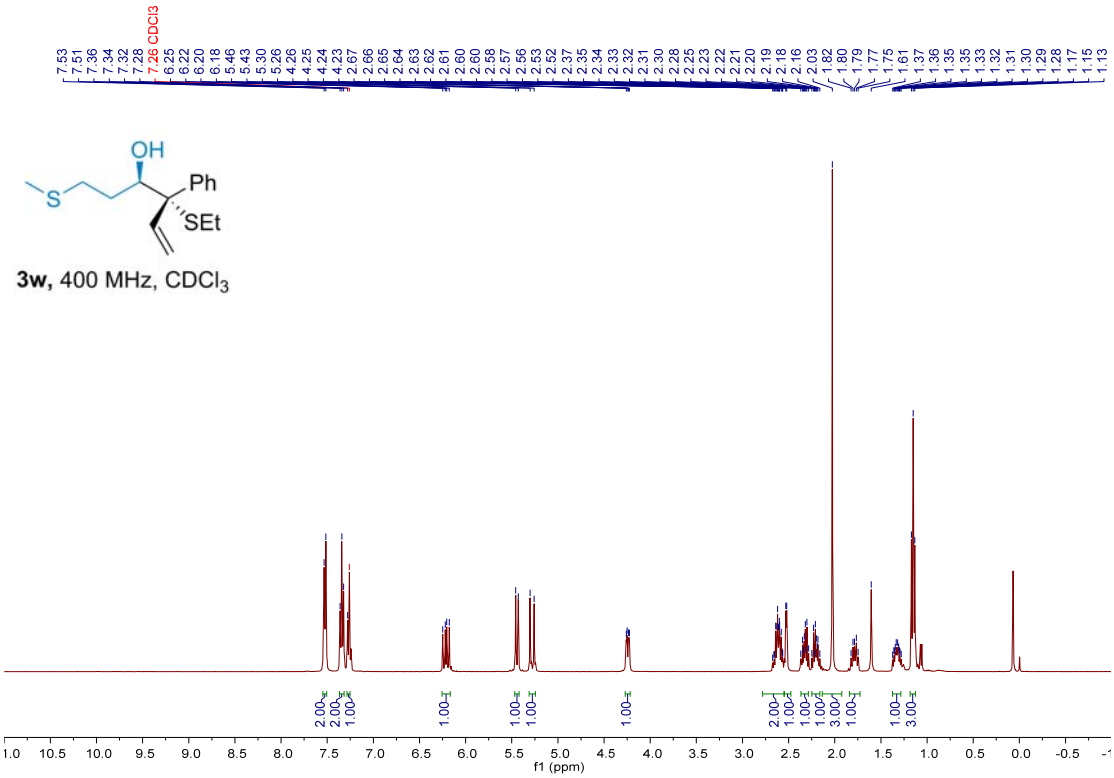
3v, 400 MHz, $CDCl_3$

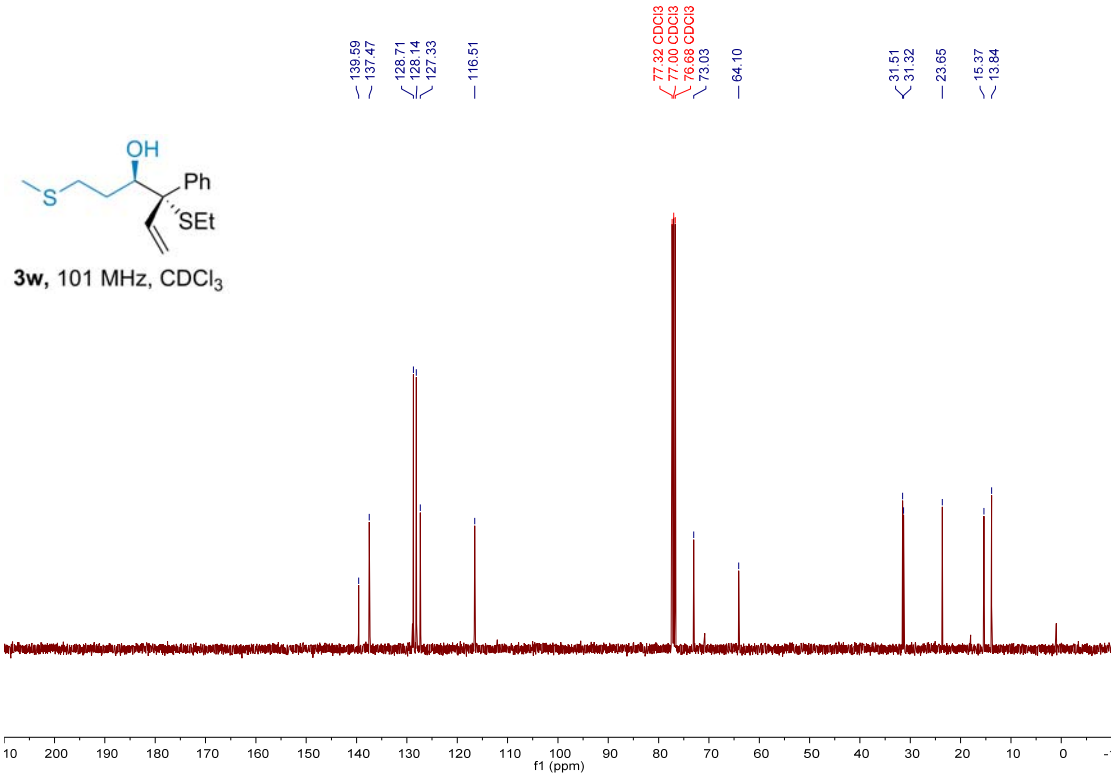


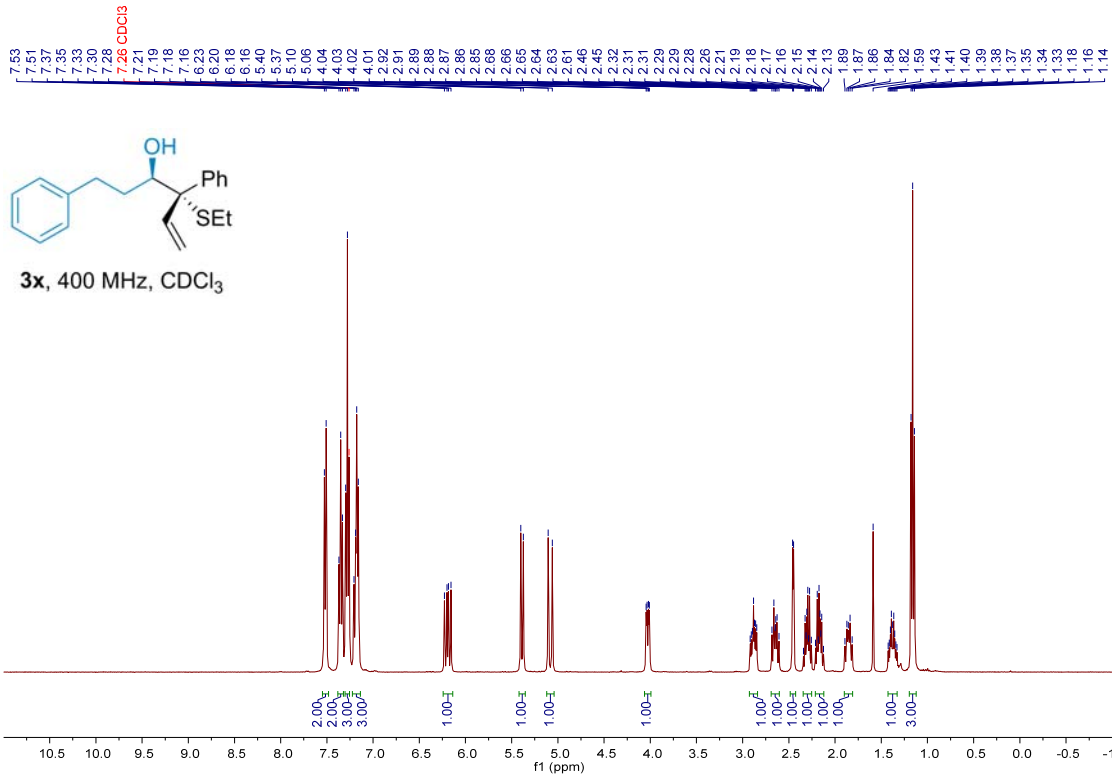


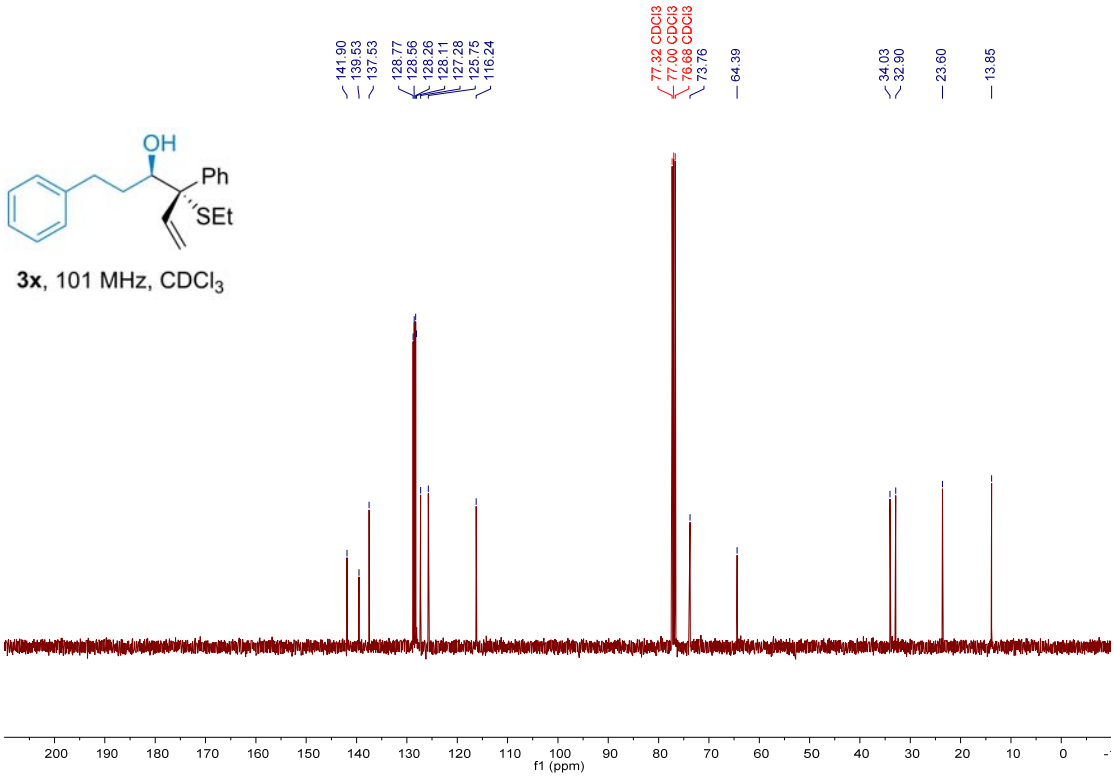
3v, 101 MHz, $CDCl_3$

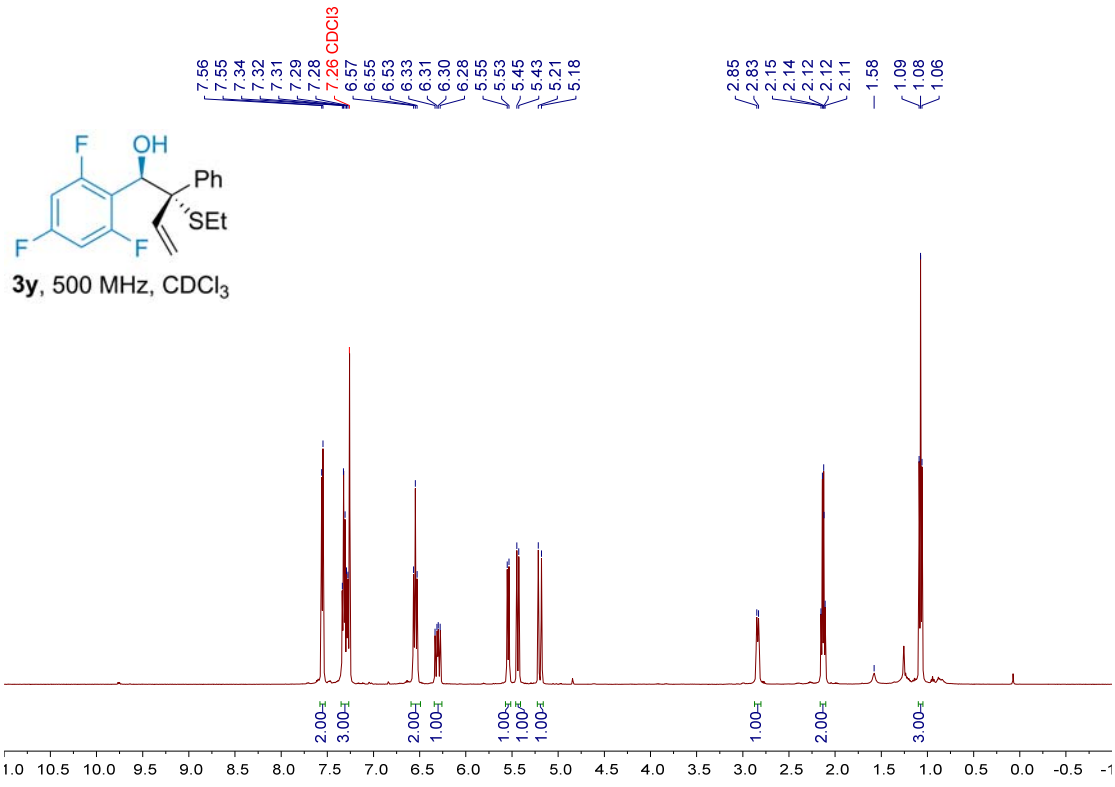


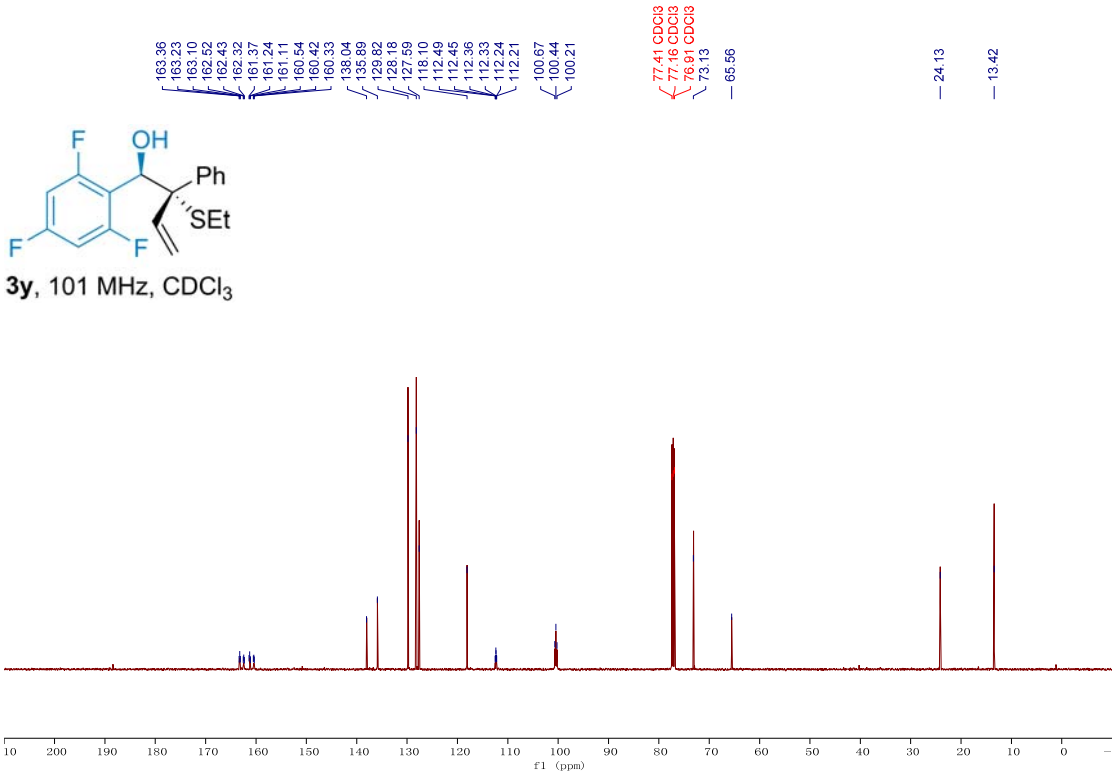

7.53
7.51
7.36
7.34
7.32
7.28
7.26 CDCl3
6.25
6.22
6.20
6.18
5.46
5.43
5.30
5.26
4.26
4.25
4.24
4.23
2.67
2.66
2.65
2.64
2.63
2.62
2.61
2.60
2.60
2.58
2.57
2.56
2.53
2.52
2.37
2.35
2.34
2.33
2.32
2.31
2.30
2.28
2.25
2.23
2.22
2.21
2.20
2.19
2.18
2.16
2.03
1.82
1.80
1.79
1.77
1.75
1.61
1.37
1.36
1.35
1.35
1.33
1.32
1.31
1.30
1.29
1.28
1.17
1.15
1.13
OH
Ph
SEt
S
3w, 400 MHz, CDCl3
2.00
2.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
3.00
1.00
1.00
3.00
f1 (ppm)

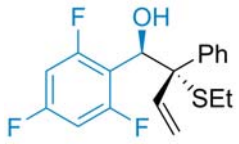

139.59
137.47
128.71
128.14
127.33
116.51
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
73.03
64.10
31.51
31.32
23.65
15.37
13.84
OH
Ph
SEt
S
3w, 101 MHz, CDCl3
f1 (ppm)


OH
Ph
SEt
3x, 400 MHz, CDCl3
f1 (ppm)

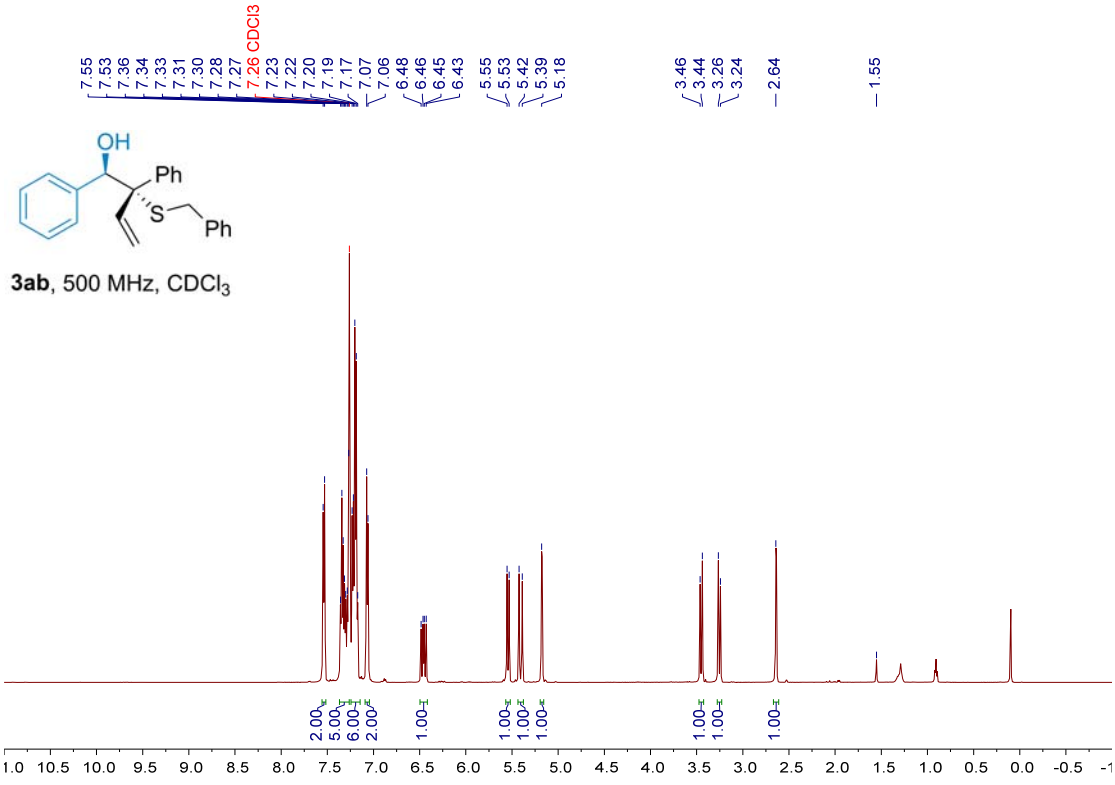

OH
Ph
SEt
3x, 101 MHz, CDCl3
f1 (ppm)


7.56
7.55
7.34
7.32
7.31
7.29
7.28
7.26 CDCl3
6.57
6.55
6.53
6.33
6.31
6.30
6.28
5.55
5.53
5.45
5.43
5.21
5.18
2.85
2.83
2.15
2.14
2.12
2.12
2.11
1.58
1.09
1.08
1.06
F
OH
Ph
SEt
F
F
3y, 500 MHz, CDCl3
2.00
3.00
2.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1

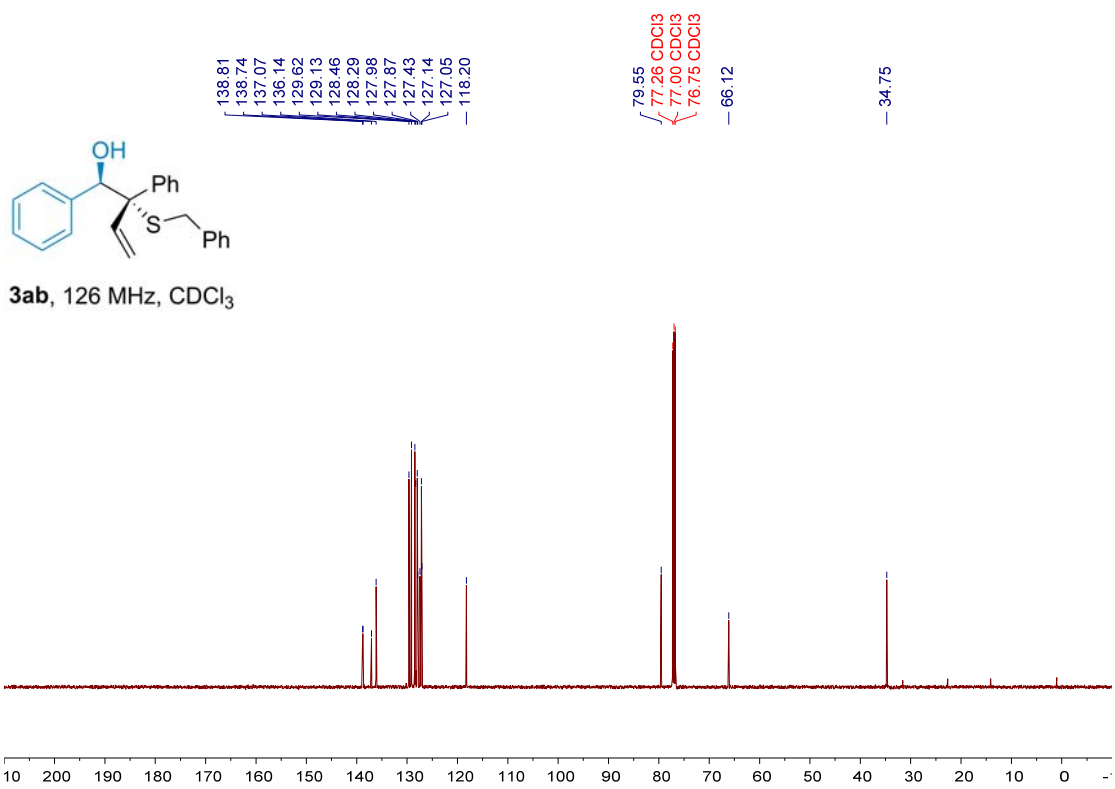

163.36
163.23
163.10
162.52
162.43
162.32
161.37
161.24
161.11
160.54
160.42
160.33
138.04
135.89
129.82
128.18
127.59
118.10
112.49
112.45
112.36
112.33
112.24
112.21
100.67
100.44
100.21
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
73.13
65.56
24.13
13.42
F
OH
Ph
SEt
F
F
3y, 101 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



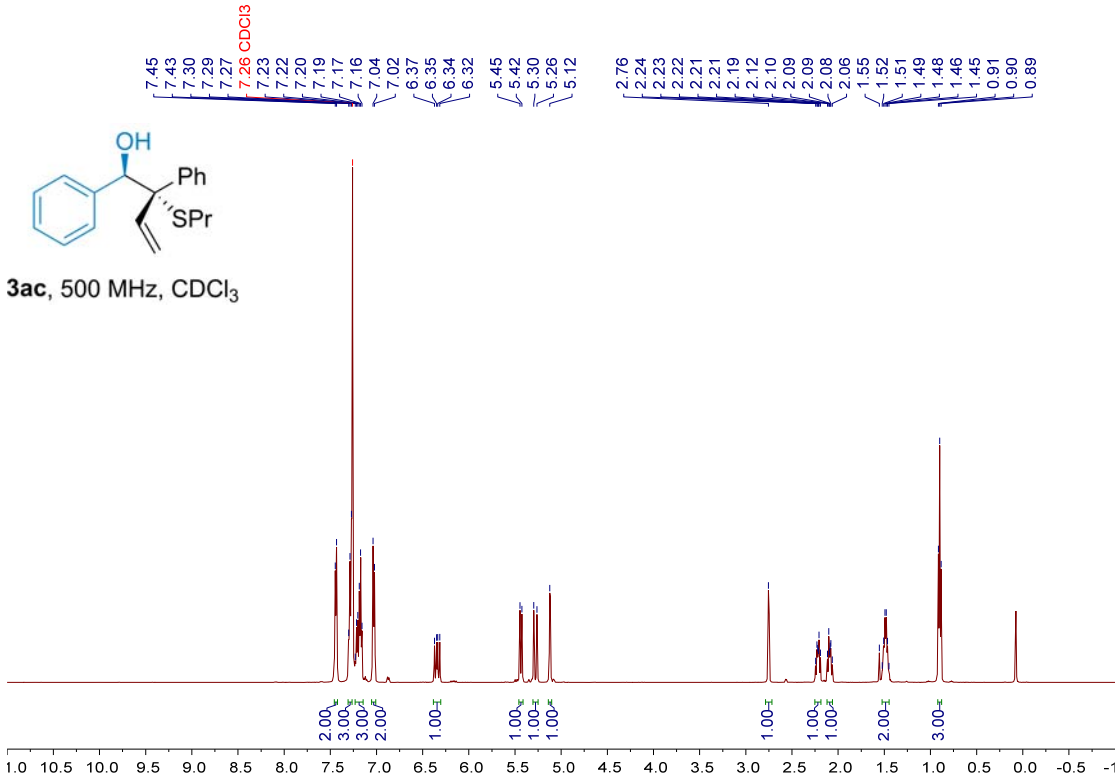
3y, 377 MHz, $CDCl_3$



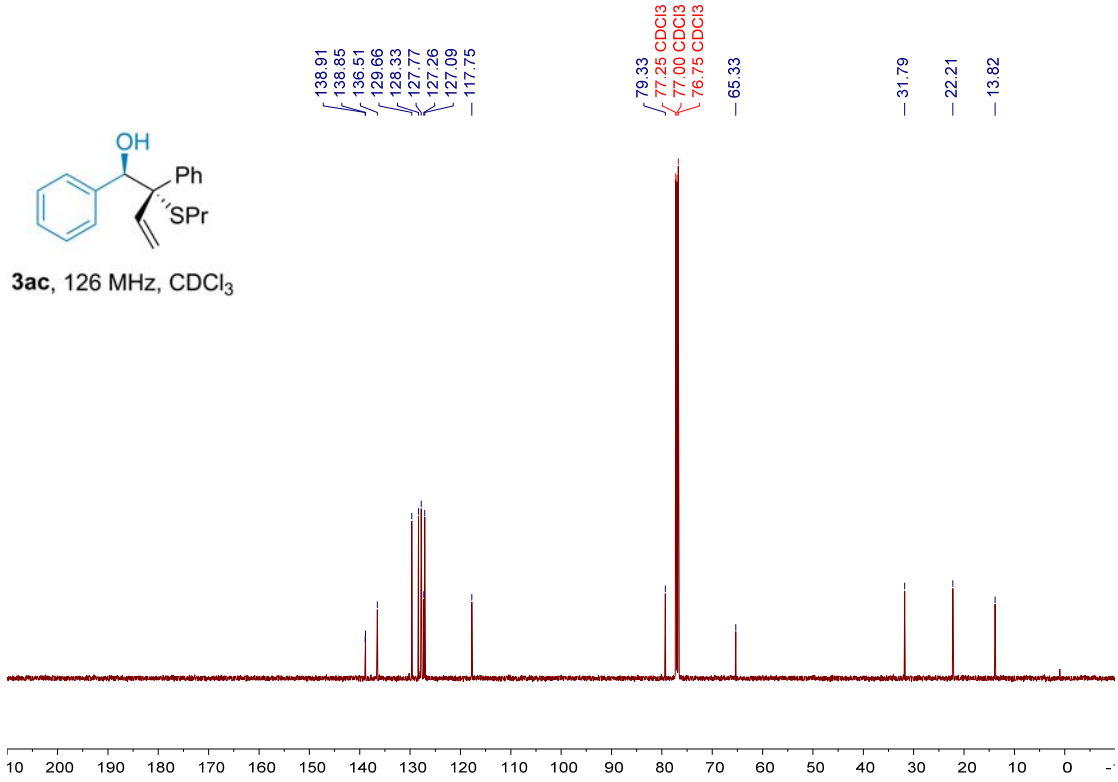
3ab, 500 MHz, $CDCl_3$



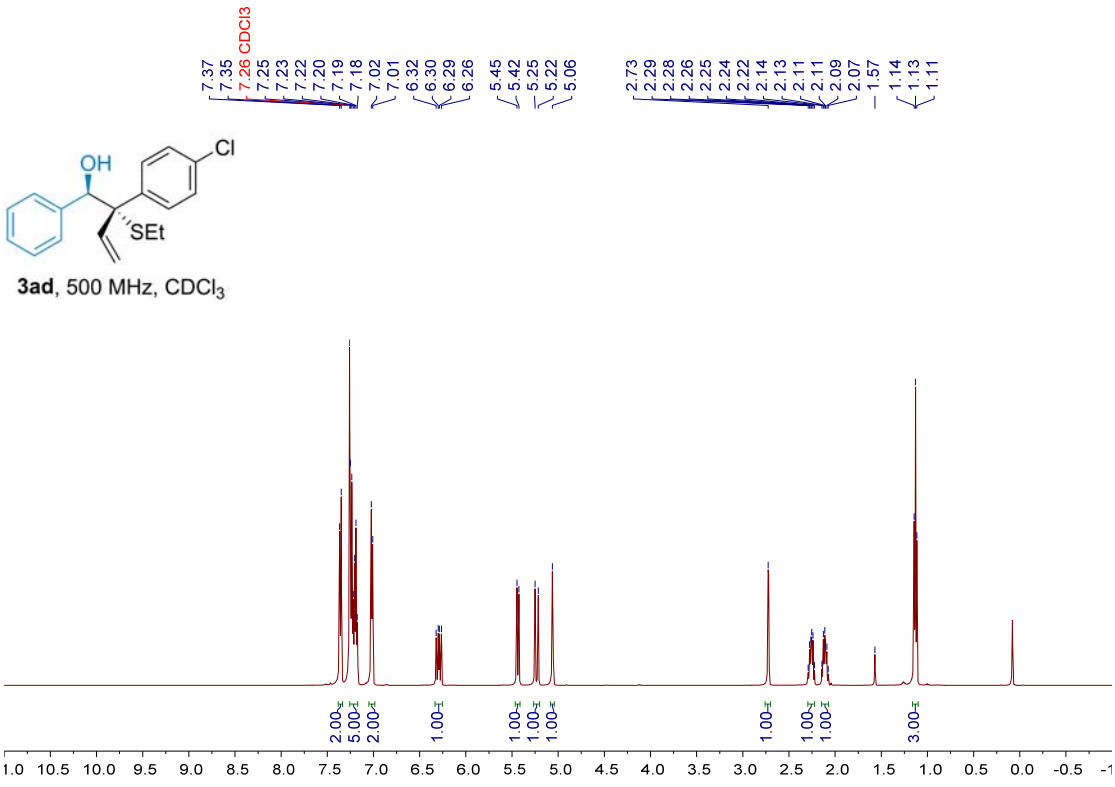
3ab, 126 MHz, $CDCl_3$



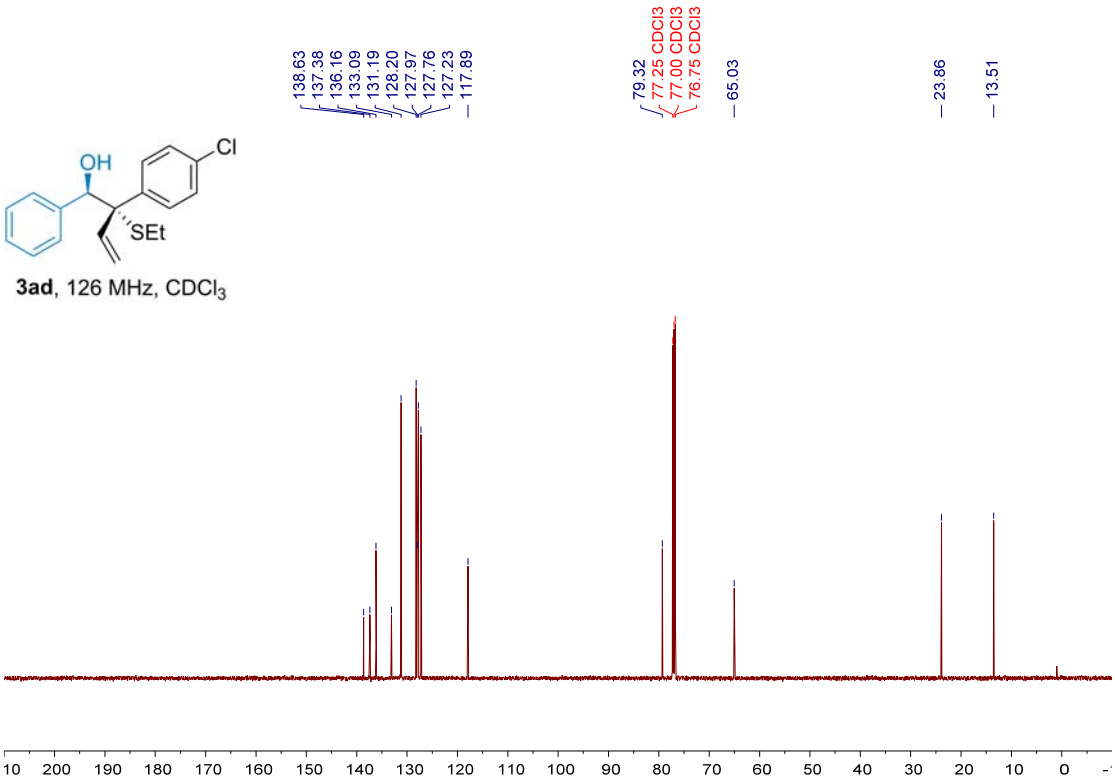
3ac, 500 MHz, $CDCl_3$



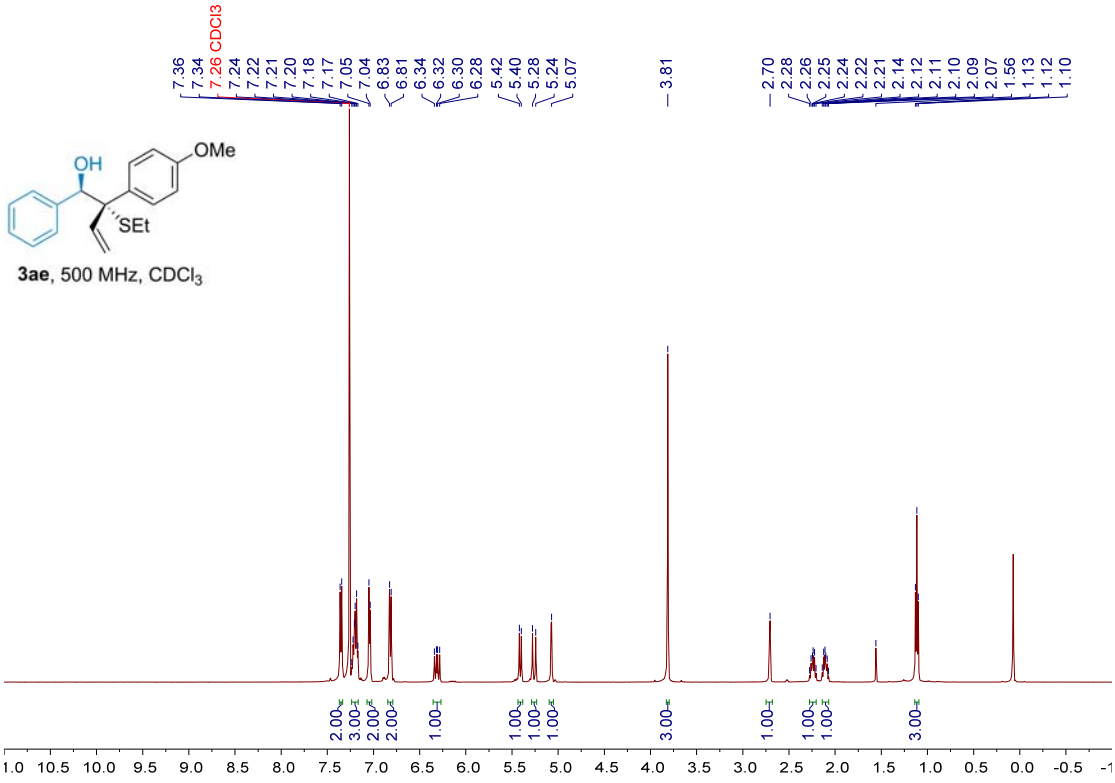
3ac, 126 MHz, $CDCl_3$



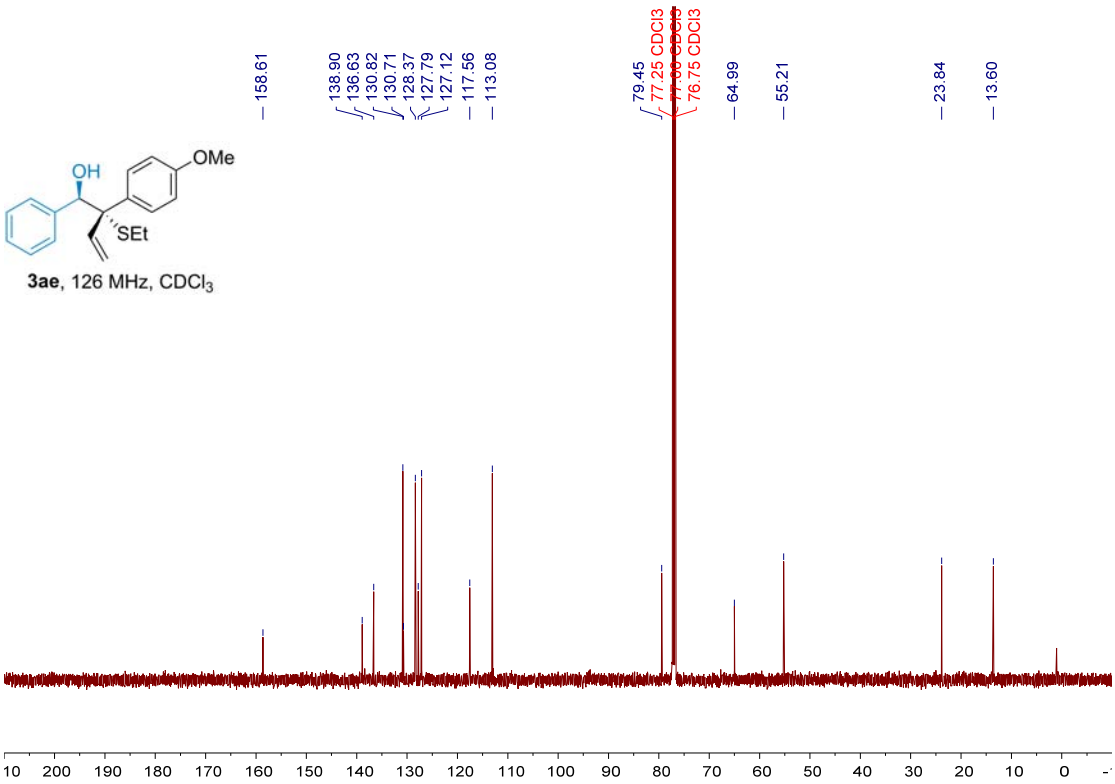
3ad, 500 MHz, $CDCl_3$



3ad, 126 MHz, $CDCl_3$



3ae, 500 MHz, $CDCl_3$



3ae, 126 MHz, $CDCl_3$