Electronic Supporting Information (ESI) for:

# Unusual DBU-catalyzed decarboxylative formation of allylic thioethers from vinyl cyclic carbonates and thiols

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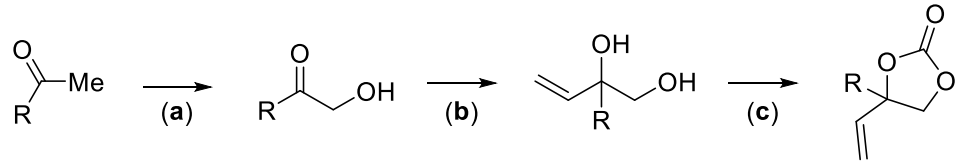
## General Remarks

The thiophenols and applied catalysts were purchased from Aldrich or TCI, and used without further purification. Solvents were dried using an Innovative Technology PURE SOLV solvent purification system. Reactions were monitored by TLC and $^{1}$H NMR. TLC was carried out on 0.25 mm Merck aluminum-backed sheets coated with 60 F254 silica gel. Visualization of the silica plates was achieved using a UV lamp ($\lambda$ = 254 nm) and/or by heating plates that were dipped in a ceric ammonium molybdate stain. Flash chromatography was carried out on Sigma-Aldrich silica gel 60 (70-230 mesh) using the indicated eluent system. $^{1}$H NMR, $^{13}$C NMR, $^{19}$F NMR and related 2D NMR spectra were recorded at room temperature on a Bruker AV-400 or AV-500 spectrometer and referenced to the residual deuterated solvent signals. All reported NMR values are given in parts per million (ppm).

## Typical procedure for the preparation of starting materials

### General procedure for the preparation of vinyl cyclic carbonates



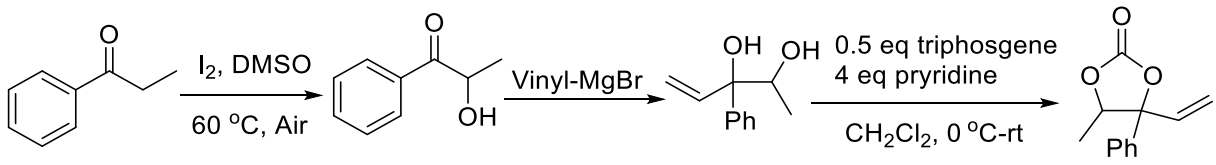

Vinyl carbonate was prepared according to a reported procedure [1]

**Step (a)**: In a round bottom flask, powdered KOH (5.5 equiv.) was added portion-wise to a cold solution of ketone (10 mmol, 1 equiv.) in MeOH (0.6 M). (Diacetoxyiodo)benzene (1.1 equiv.) was subsequently added portion-wise. The resulting mixture was allowed to return to room temperature and stirred at this temperature for 3h. Then, the mixture was concentrated under reduced pressure, the residue was partitioned in $H_2O$ (15 mL) and $Et_2O$ (15 mL). The organic phase was separated, dried over $Na_2SO_4$, filtered and concentrated under reduced pressure. The residue was dissolved in MeOH (20 mL) and 2M HCl (20 mL) was added. The mixture was stirred for 16 hours at room temperature. A saturated aqueous solution of $NaHCO_3$ was added to the mixture until pH 7, the resulting biphasic mixture was diluted with DCM and separated. The organic phase was collected, dried over $Na_2SO_4$, filtered and concentrated. The pure diol was obtained through flash chromatography on silica.

**Step (b)**: To a solution of the respective hydroxy methyl ketone (5 mmol, 1 equiv) in THF (20 mL) was added vinyl magnesium bromide (1.0 M in THF, 2.5 equiv) at 0 °C. The reaction was stirred under an $N_2$ atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous $NH_4Cl$, and extracted with EtOAc. The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated affording the crude product which was directly used in step (c).

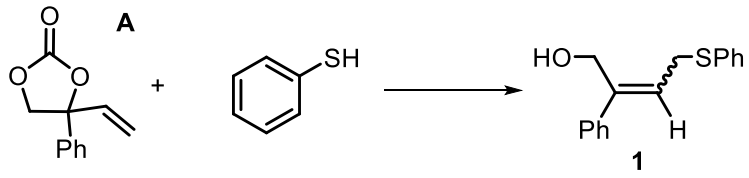
**Step (c)**: To a solution of diol (5 mmol, 1 equiv) and pyridine (20 mmol, 4 equiv) in $CH_2Cl_2$ (20 mL) was added triphosgene (2.5 mmol, 0.5 equiv, 1.0 M in $CH_2Cl_2$) at 0 °C. The reaction was stirred under an $N_2$ atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous $NH_4Cl$, and extracted with $CH_2Cl_2$. The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated. The residue was purified by flash chromatography on silica to afford the corresponding carbonate.

**Procedure for the preparation of other vinyl cyclic carbonates**




This vinyl carbonate was prepared according to a reported procedure:[2] Propiophenone (1.34 g, 10 mmol), $I_2$ (508 mg, 20 mol%), and DMSO (20 mL) and a stirring bar were added to a round-bottom flask under air. The mixture was stirred at 60 °C for 24 h and monitored by TLC. After cooling down to room temperature, the mixture was diluted with ethyl acetate (10 mL) and washed with 0.1 mol/L $Na_2S_2O_3$ (5 mL) aqueous solution, extracted with ethyl acetate (3 × 100 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to get the desired 2-hydroxypropiophenone. The next synthetic step is the same as reported above.

**Table S1.** Additional screening data for the formation of allylic thioether **1**.

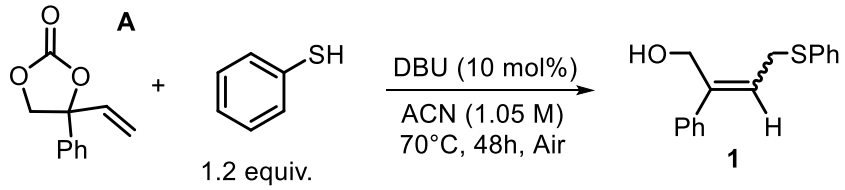



| Entry | Base (mol%) | Solv. | T (° C) | Conv. (%) | *E/Z* | NMR yield (%) |
|---|---|---|---|---|---|---|
| 1 | DABCO (5) | ACN(0.2 ml) | rt | 3 | 0/0 | 0 |
| 2 | DABCO (10) | ACN(0.2 ml) | rt | 3 | 0/3 | 3 |
| 3 | DABCO (20) | ACN(0.2 ml) | rt | 3 | 0/3 | 3 |
| 4 | DABCO (30) | ACN(0.2 ml) | rt | 6 | 3/3 | 6 |
| 5 | DABCO (50) | ACN(0.2 ml) | rt | 9 | 3/6 | 9 |
| 6 | DABCO (50) | ACN(0.2 ml) | 50 | 58 | 15/24 | 39 |
| 7 | TBD (50) | ACN(0.2 ml) | 50 | 79 | 24/33 | 57 |
| 8 | DBU (50) | ACN(0.2 ml) | 50 | 94 | 30/48 | 78 |
| 9 | DMAP (50) | ACN(0.2 ml) | 50 | 29 | 12/15 | 27 |
| 10 | i-$Pr_2Et$ (50) | ACN(0.2 ml) | 50 | 40 | 12/18 | 30 |
| 11 | $NEt_3$ (50) | ACN(0.2 ml) | 50 | 28 | 6/9 | 15 |
| 12 | NMM (50) | ACN(0.2 ml) | 50 | 0 | 0/0 | 0 |
| 13 | NMP (50) | ACN(0.2 ml) | 50 | 0 | 0/0 | 0 |
| 14 | DBU (5) | ACN(0.2 ml) | 50 | 46 | 18/27 | 45 |
| 15 | DBU (10) | ACN(0.2 ml) | 50 | 82 | 27/42 | 69 |
| 16 | DBU (50) | ACN(0.2 ml) | 80 | 100 | 33/33 | 66 |
| 17[a] | DBU (50) | ACN(0.2 ml) | 50 | 100 | 27/45 | 72 |
| 18 | – | ACN(0.2 ml) | 80 | ~0 | 0/0 | 0 |
| **19** | **DBU (10)** | **ACN(0.2 ml)** | **70** | **100** | **30/48** | **78** |
| 20 | DBU (10) | ACN(0.1 ml) | 70 | 100 | 30/48 | 78 |
| 21[a] | DBU (10) | ACN(0.1 ml) | 70 | 100 | 30/45 | 75 |
| 22 | DBU (5) | ACN(0.1 ml) | 70 | 85 | 30/45 | 75 |
| 23 | DBU (10) | ACN(0.1 ml) | 50 | 70 | 21/36 | 57 |
| 24[a] | DBU (10) | ACN(0.1 ml) | 50 | 73 | 21/39 | 60 |
| **25[a]** | **DBU (10)** | **ACN(0.2 ml)** | **70** | **97** | **33/48** | **81(81)[b]** |
| 26[a] | DBU (10) | ACN(0.1 ml) | 70 | 97 | 27/39 | 66 |

[a] Thiophenol (1.2 equiv). [b] In brackets, the isolated yield.

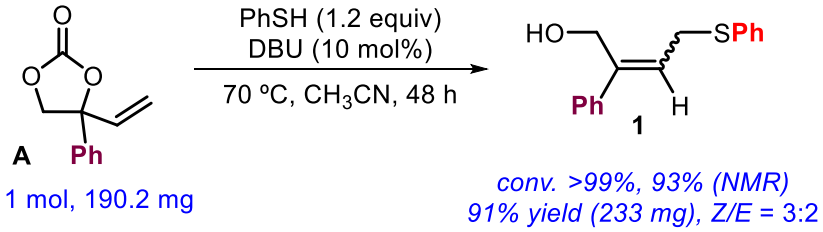
**Procedure**: A screw-capped vial was charged with the vinyl cyclic carbonate **A** (0.1 mmol, 1 equiv), the base catalyst (amount indicated) and thiophenol (0.15 mmol, 1.5 equiv) followed by dry ACN. The reaction was stirred at the corresponding temperature as reported in Table S1. The resulting crude mixture was concentrated under reduced pressure and $^{1}$H NMR was recorded. The NMR yield of **1** was calculated using mesitylene as internal standard.

## General procedure for the preparation of the allylic thioethers

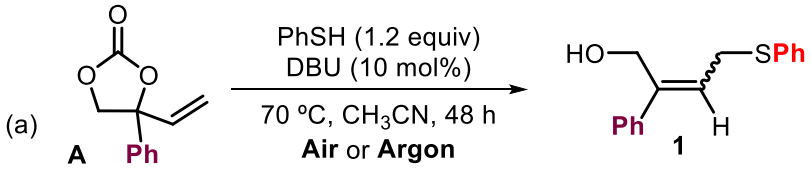



A screw-capped vial was charged with the vinyl cyclic carbonate **A** (0.21 mmol, 1 equiv), DBU (3.2 mg, 0.021 mmol, 10 mol%), thiophenol (26 µL, 0.252 mmol, 1.2 equiv) and dry ACN (0.2 mL). The reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was purified by flash column chromatography on silica gel to afford the corresponding allylic thioether product **1** (hexane:ethyl acetate 5:1) These separation conditions were used for **all** the allylic thioether compounds.

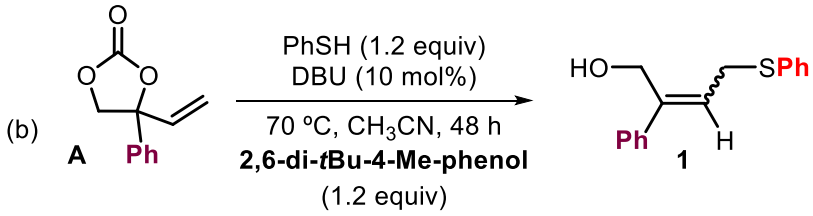
**Scale-up of 1**: A screw-capped vial was charged with **A** (190.2 mg, 1 mmol, 1 equiv), DBU (15 mg, 0.1 mmol, 10 mol%), thiophenol (132 mg, 1.2 mmol, 1.2 equiv) and dry ACN (5 mL). The reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was purified by flash column chromatography on silica gel to afford **1** as colorless oil in 91% yield (282 mg, 0.91 mmol). The *Z/E* ratio was determined by $^1$H NMR to be 3/2.



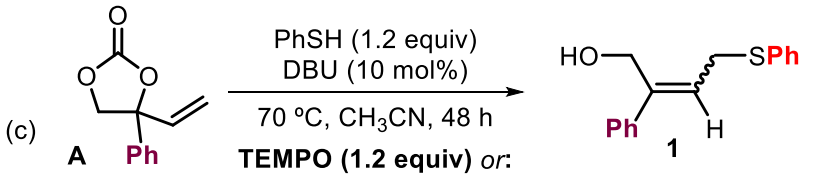
## Control experiments



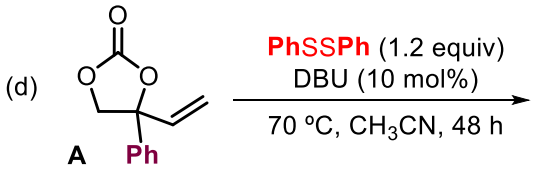

***Both conditions**: conv. >99%, 81% (NMR), E/Z = 3:5*



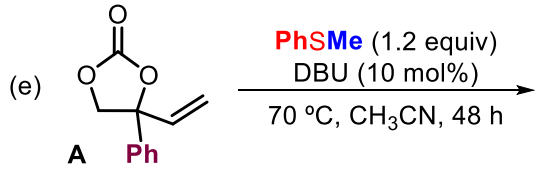

*conv. >99%, 63% (NMR), E/Z = 3:4*



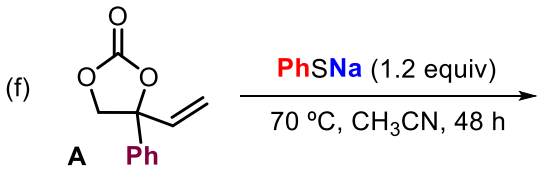

*TEMPO: conv. 28%, 0%*
*Galvinoxyl: conv. 0%, 0%*




*conv. 16%*
*0% (NMR)*

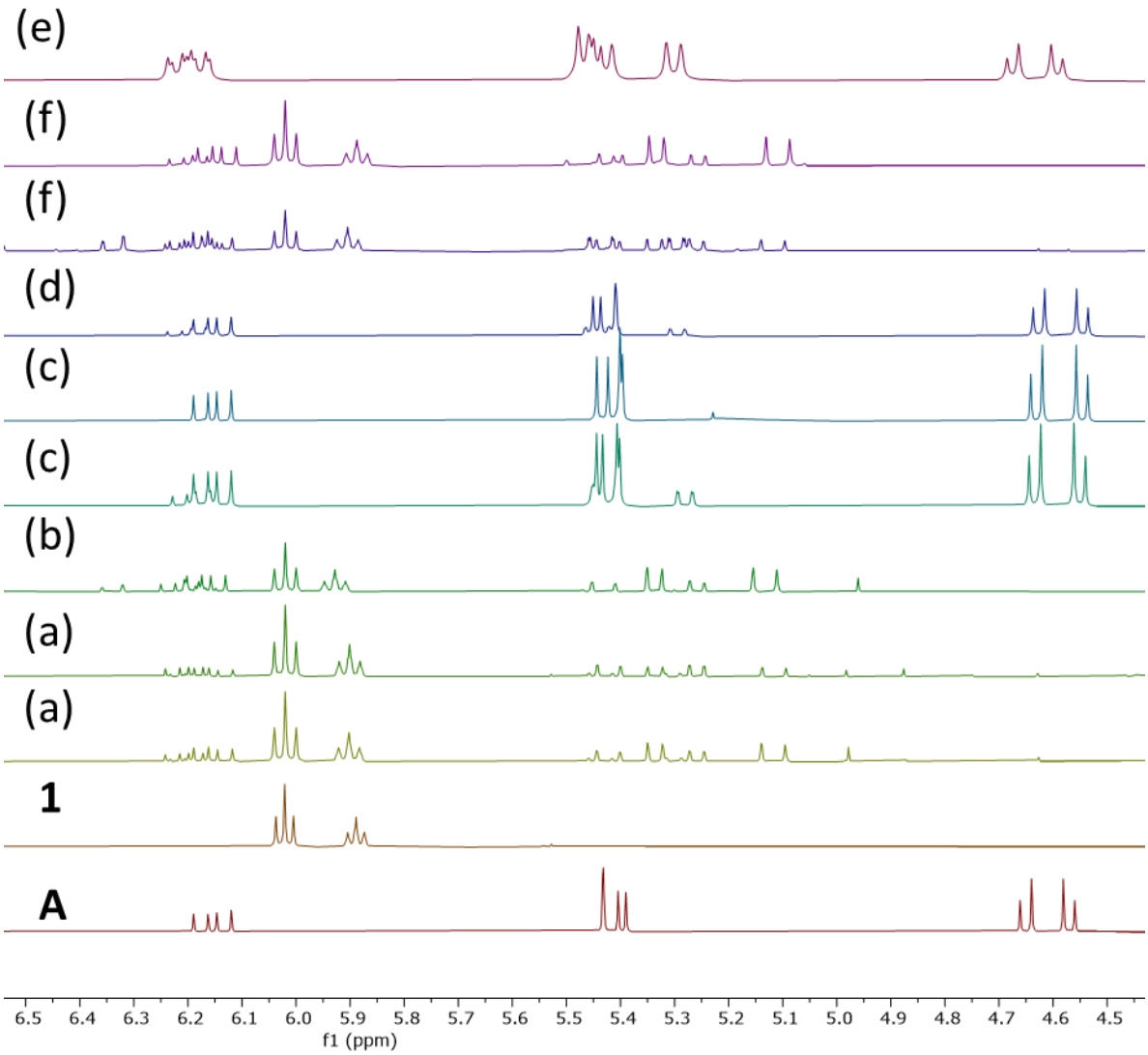



*conv. 2%*
*0% (NMR)*

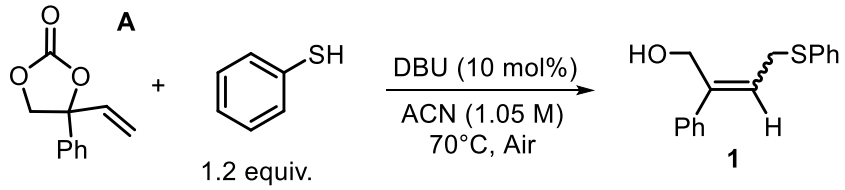



*conv. >99%, 72% (NMR)*
*Z/E = 5:3*

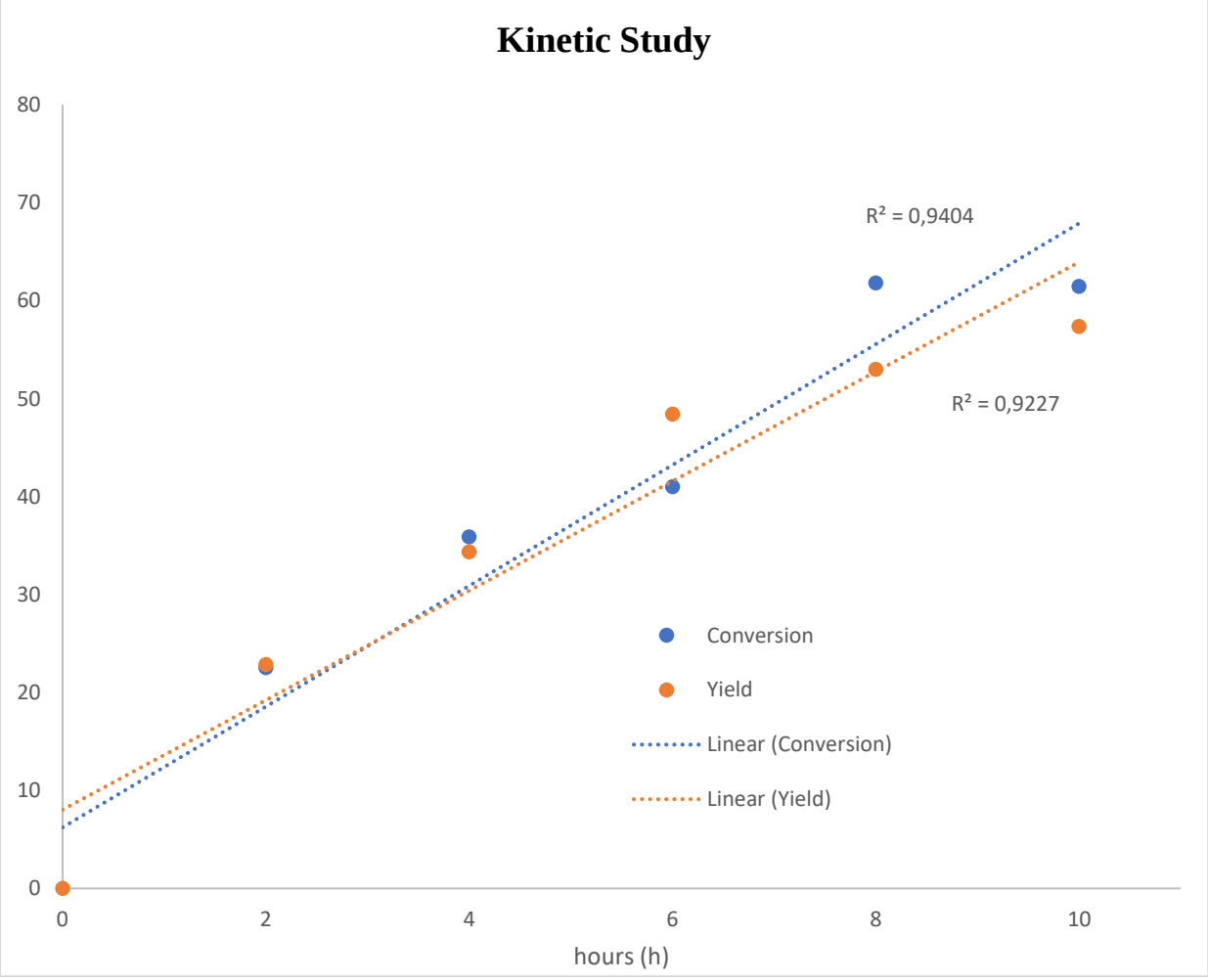
Selected NMR region (4.5-6.5 ppm) for identification of the products of the control experiments:



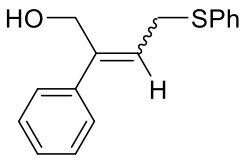
## Kinetic studies




Six screw-capped vials were charged with a solution of the vinyl cyclic carbonate **A** (0.21 mmol, 1 equiv), DBU (3.2 mg, 0.021 mmol, 10 mol%), thiophenol (26 µL, 0.252 mmol, 1.2 equiv) and dry ACN (0.2 mL). The reaction mixtures were stirred at 70 °C and examined by $^1$H NMR at respectively 0, 2, 4, 6, 8 and 10 h of reaction time. The crude products were concentrated under vacuum and conversions and yields were determined by $^1$H NMR using $CH_2Br_2$ as an internal standard.



## Characterization data for the allylic thioethers

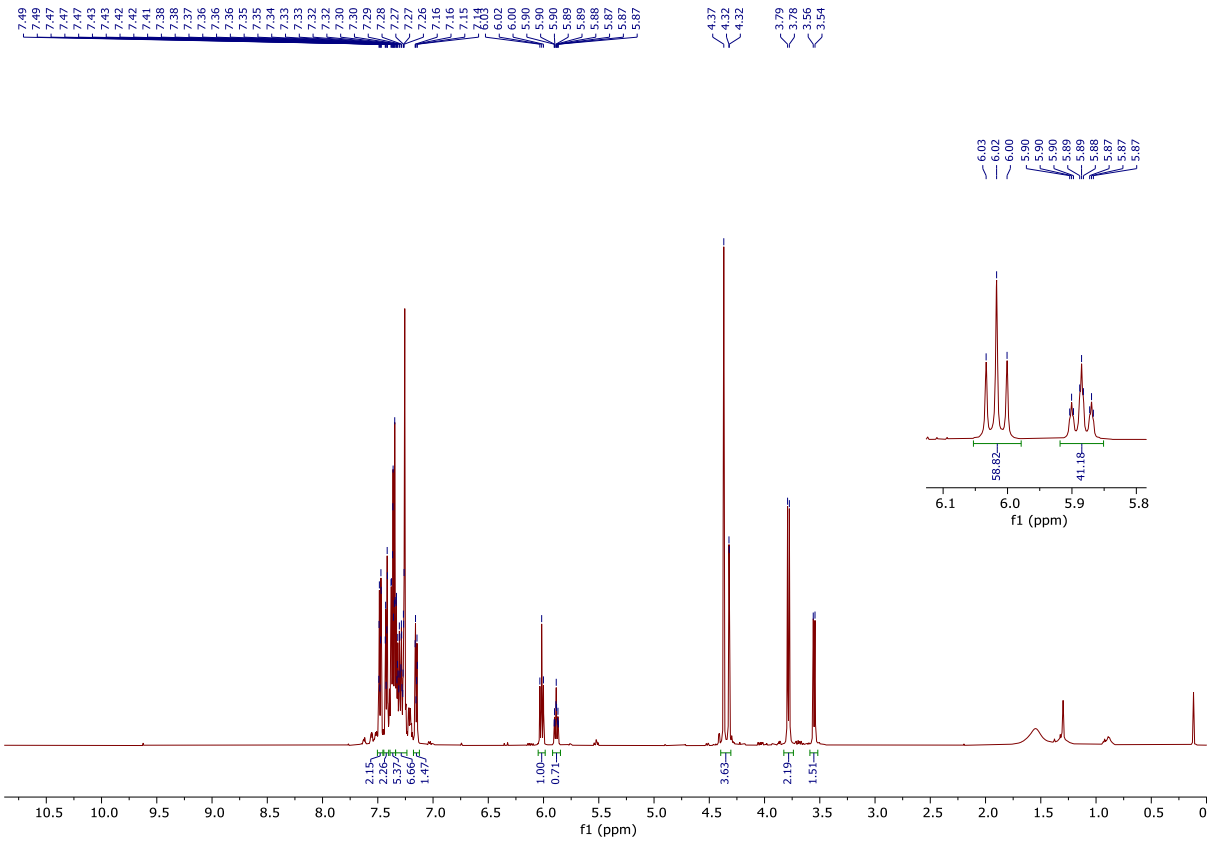



**1**

**2-phenyl-4-(phenylthio)but-2-en-1-ol**

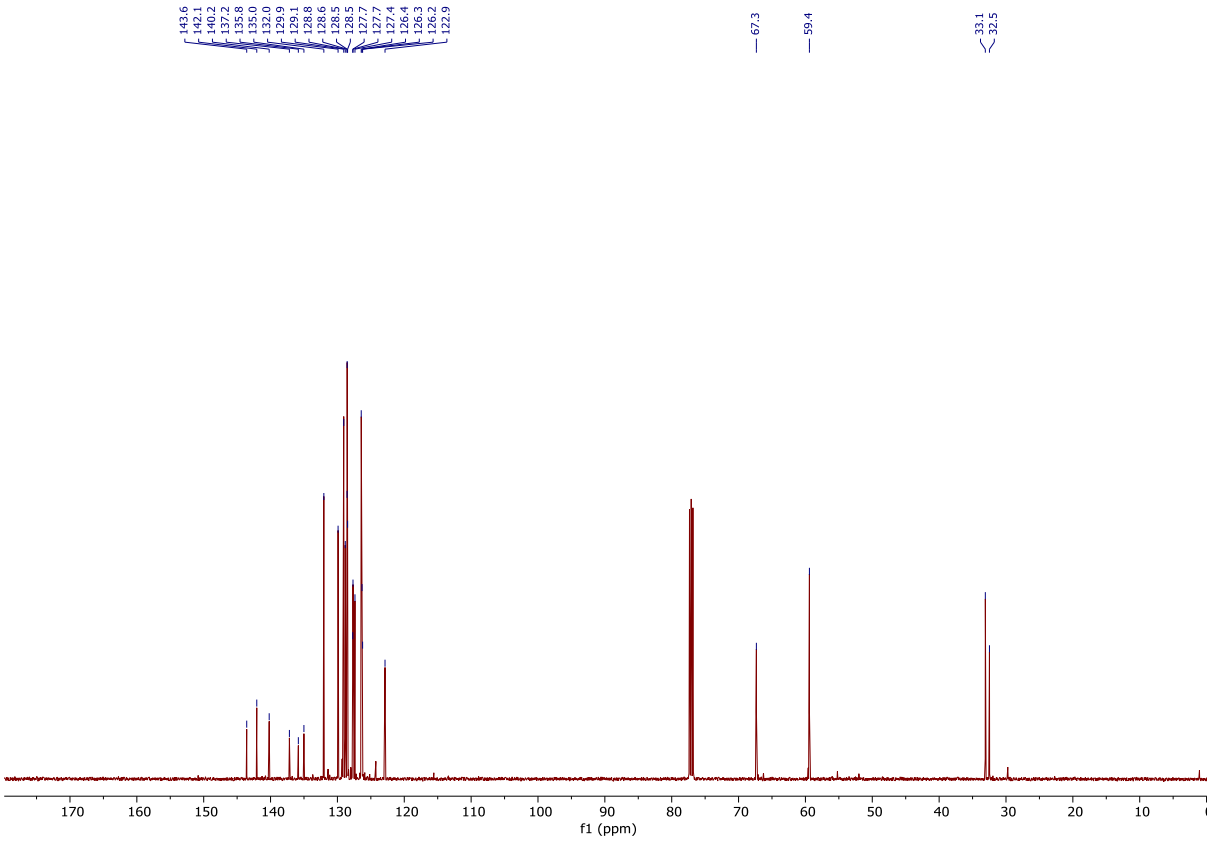
Following the general procedure, product **1** was isolated as an orange oil in 81% yield (43.5 mg, 0.17 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 6/4

$^{1}$H NMR spectrum ($CDCl_3$)



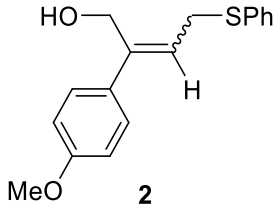

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H, 2H M), 7.43-7.41 (m, 2H, 2H M), 7.38-7.34 (m, 5H, 5H M), 7.33-7.27 (m, 9H, 1H M + 8H m), 7.16-7.14 (m, 2H, 2H m), 6.02 (t, *J* = 8.1 Hz, 1H, 1H M *Z* isomer), 5.89 (tt, *J* = 7.7, 1.4 Hz, 1H, 1H m *E* isomer), 4.37 (s, 2H, 2H M), 4.32 (s, 2H. 2H m), 3.78 (d, *J* = 8.1 Hz, 2H, 2H M), 3.55 (d, *J* = 7.9 Hz, 2H, 2H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.6, 142.1, 140.2, 137.2, 135.8, 135.0, 132.0 (2C), 129.9, 129.1 (2C), 128.8 (2C), 128.6, 128.5, 128.5 (2C), 127.7, 127.7, 127.4, 126.4, 126.3, 126.2, 122.9, 67.3, 59.4, 33.1, 32.5.

The spectral data correspond to the literature.[3]

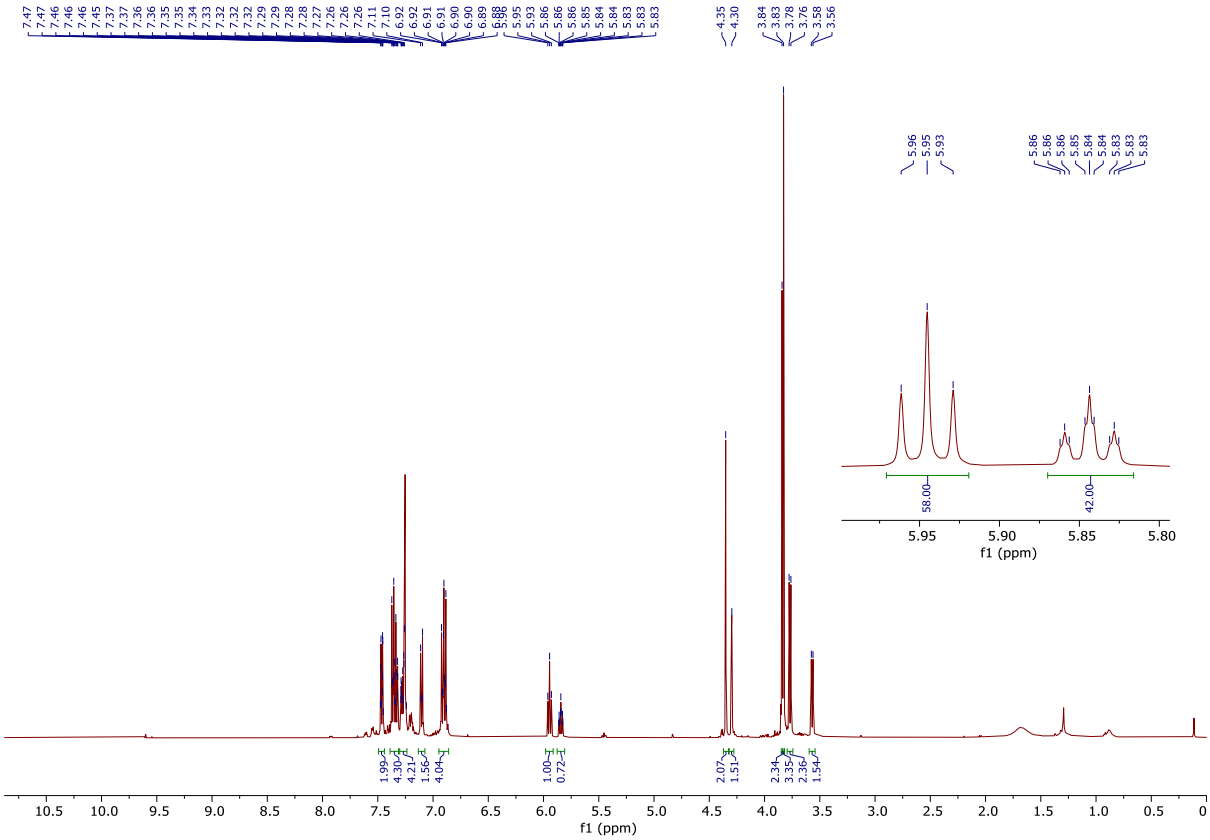



**2**

**2-(4-methoxyphenyl)-4-(phenylthio)but-2-en-1-ol**

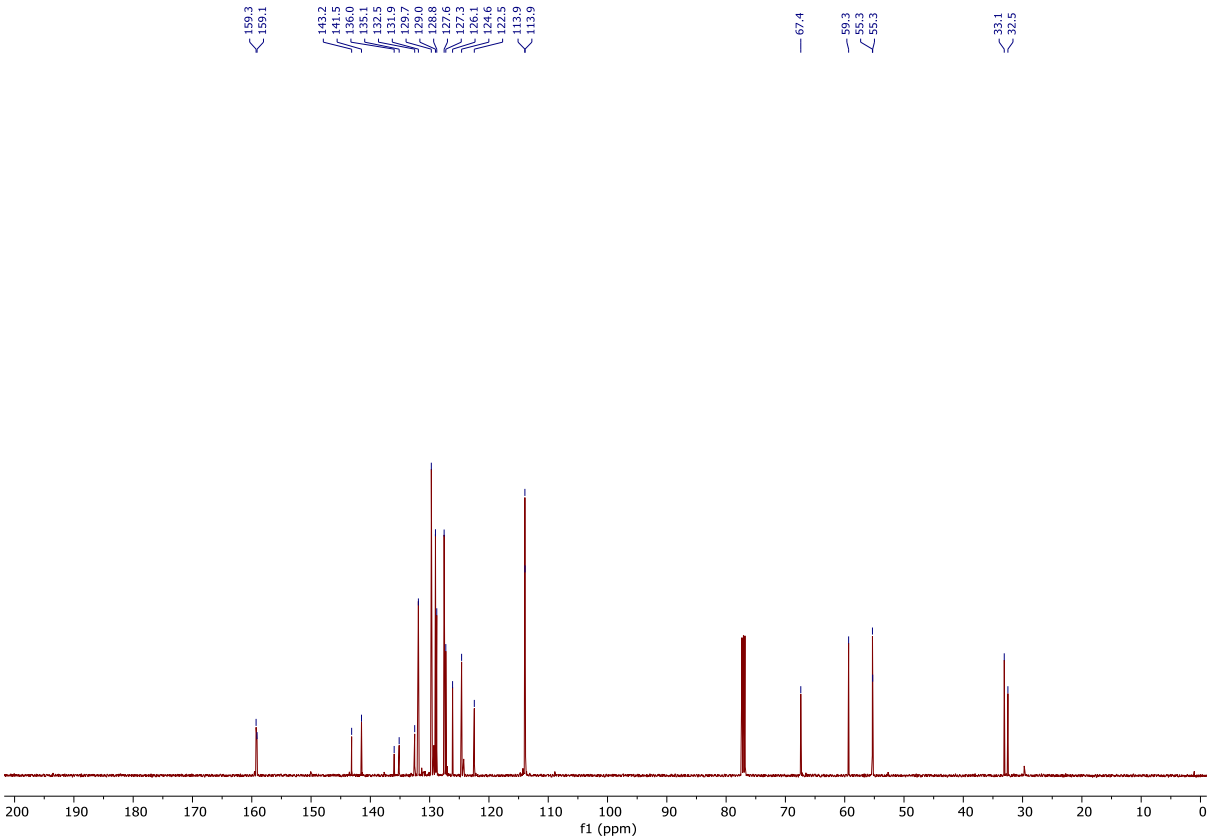
Following the general procedure, product **2** was isolated as a brown oil in 71% yield (37.0 mg, 0.13 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 6/4

$^{1}$H NMR spectrum ($CDCl_3$)



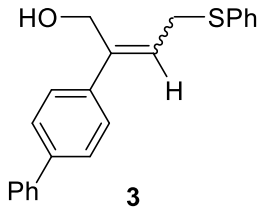

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H, 2H M), 7.37-7.32 (m, 4H, 4H M), 7.29-7.26 (m, 5H, 1H M + 4H m), 7.11-7.10 (m, 2H, 2H m), 6.92-6.88 (m, 5H, 3 H m + 2H M), 5.95 (t, *J* = 8.1 Hz, 1H, 1H M *Z* isomer), 5.84 (tt, *J* = 7.7, 1.4 Hz, 1H, 1H *E* isomer), 4.35 (s, 2H M), 4.30 (s, 2H m), 3.84 (s, 3H m), 3.83 (s, 3H M), 3.77 (d, *J* = 8.1 Hz, 2H M), 3.57 (d, *J* = 7.6 Hz, 2H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.3, 159.1, 143.2, 141.5, 136.0, 135.1, 132.5, 131.9 (2C), 129.7 (3C), 129.0 (2C), 128.8 (2C), 127.6 (2C), 127.3 (2C), 126.1, 124.6, 122.5, 113.9 (3C), 113.9 (2C), 67.4, 59.3, 55.3, 55.3, 33.1, 32.5.

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{17}H_{18}NaO_2S$, $[M + Na]^+$: 309.0920, found: 309.0921.

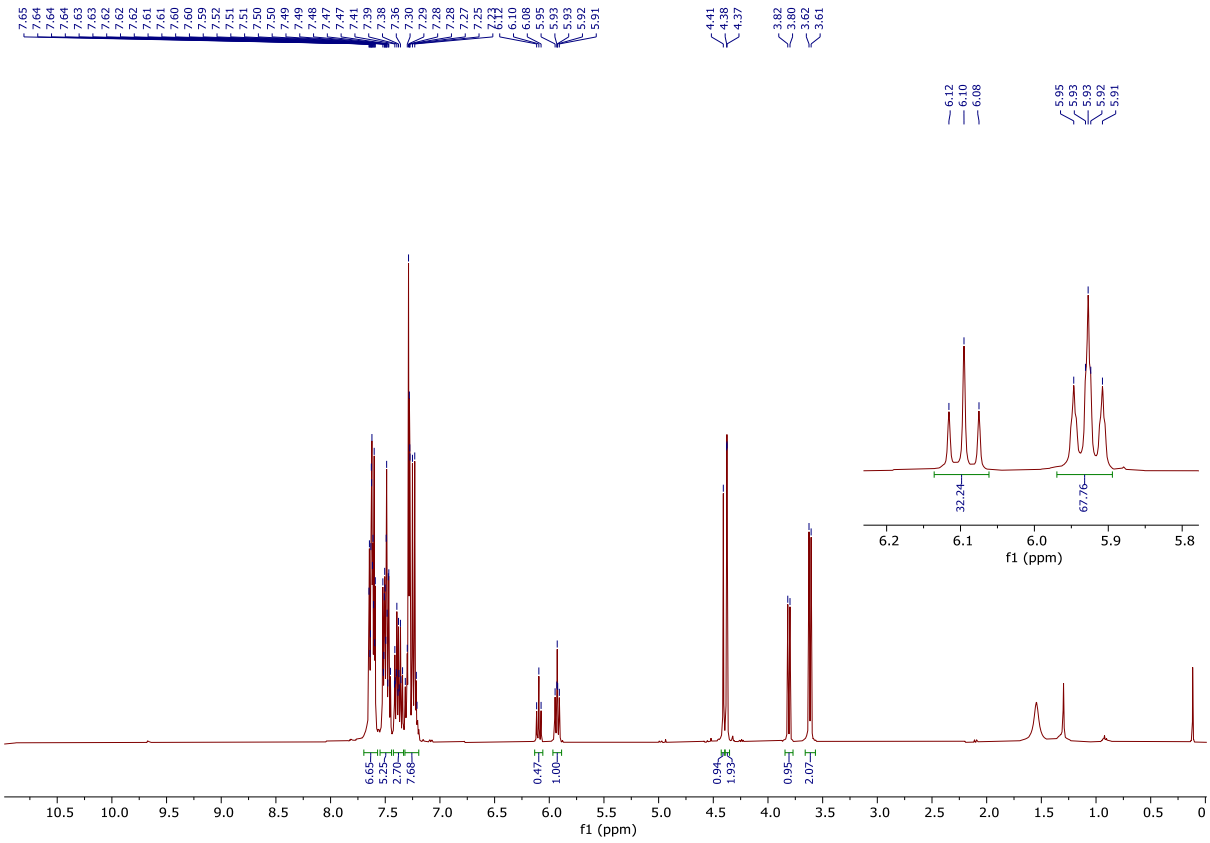



**3**

**2-([1,1'-biphenyl]-4-yl)-4-(phenylthio)but-2-en-1-ol**

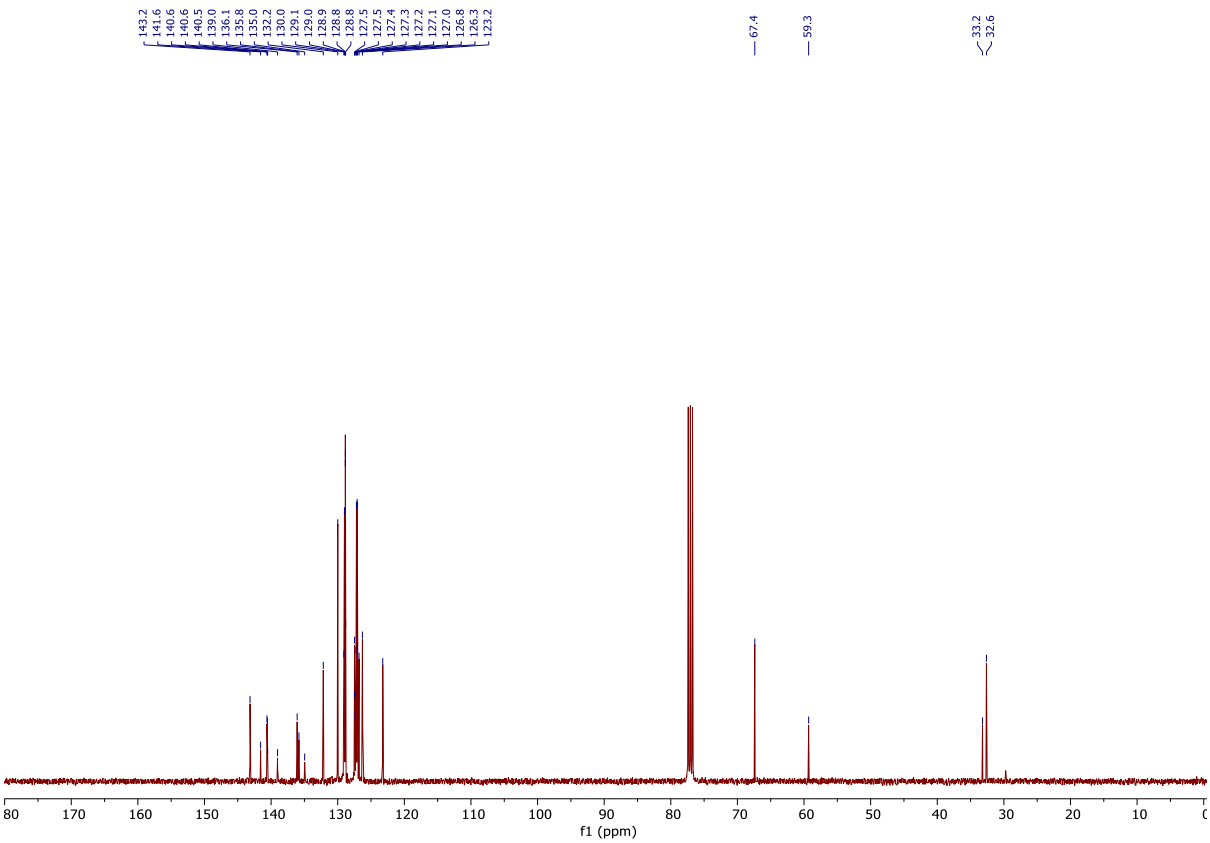
Following the general procedure, product **3** was isolated as a white solid in 47% yield (23.4 mg, 0.07 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 3:7

$^{1}$H NMR spectrum ($CDCl_3$)



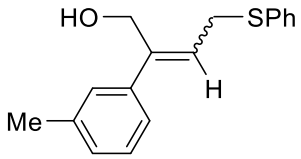

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.65-7.59 (m, 8H), 7.52-7.45 (m, 6H), 7.42-7.34 (m, 4H), 7.29-7.23 (m, 10H), 6.10 (t, *J* = 8.0 Hz, 1H, 1H m *Z* isomer), 5.93 (tt, *J* = 7.8, 1.5 Hz, 1H, 1H m *E* isomer), 4.41 (s, 2H, 2H m), 4.38 (s, 2H, 2H M), 3.81 (d, *J* = 8.1 Hz, 2H, 2H m), 3.62 (d, *J* = 7.8 Hz, 2H, 2H M).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.2, 141.6, 140.6, 140.6, 140.6, 140.5, 139.0, 136.1, 135.8, 135.0, 132.2, 130.0, 129.1, 129.0, 128.9, 128.8, 128.8, 127.5, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.8, 126.3, 126.3, 123.2, 67.4, 59.3, 33.2, 32.6.

The spectral data correspond to the literature.[3]

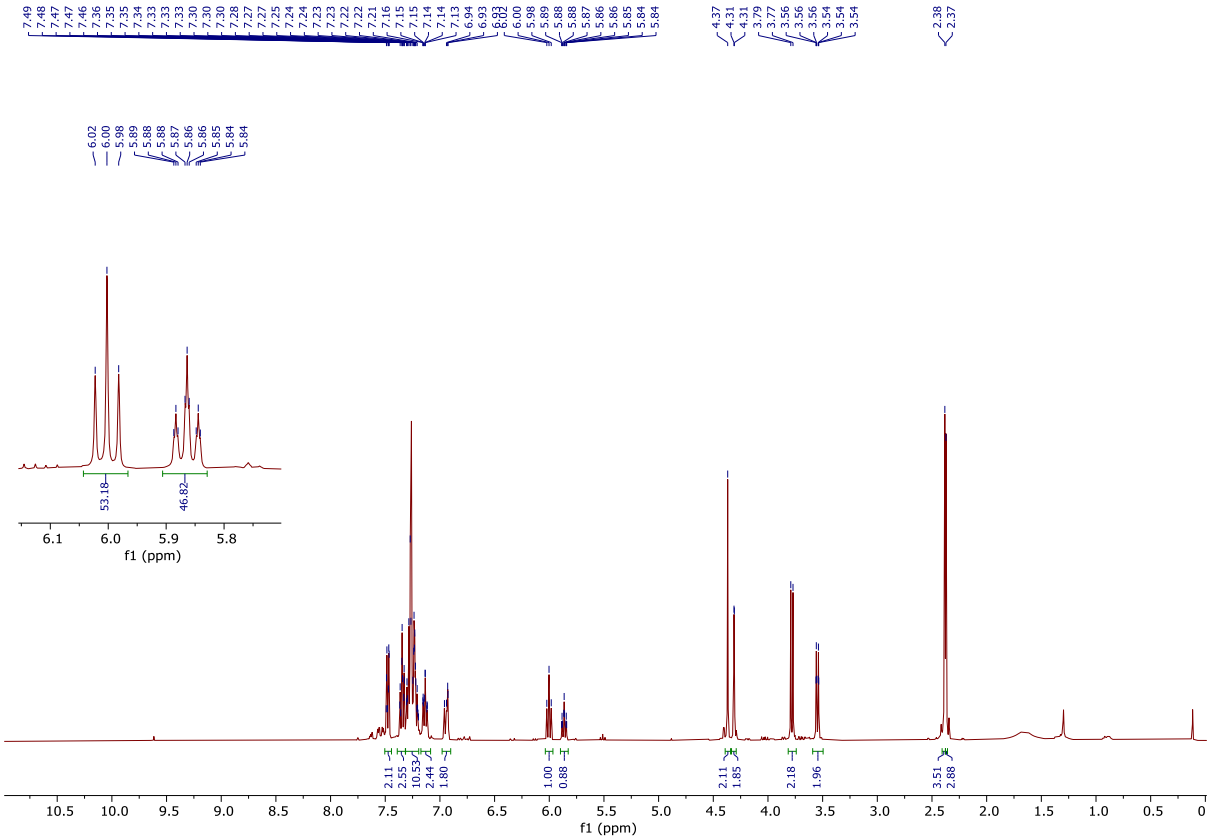



**4**

**4-(phenylthio)-2-(*m*-tolyl)but-2-en-1-ol**

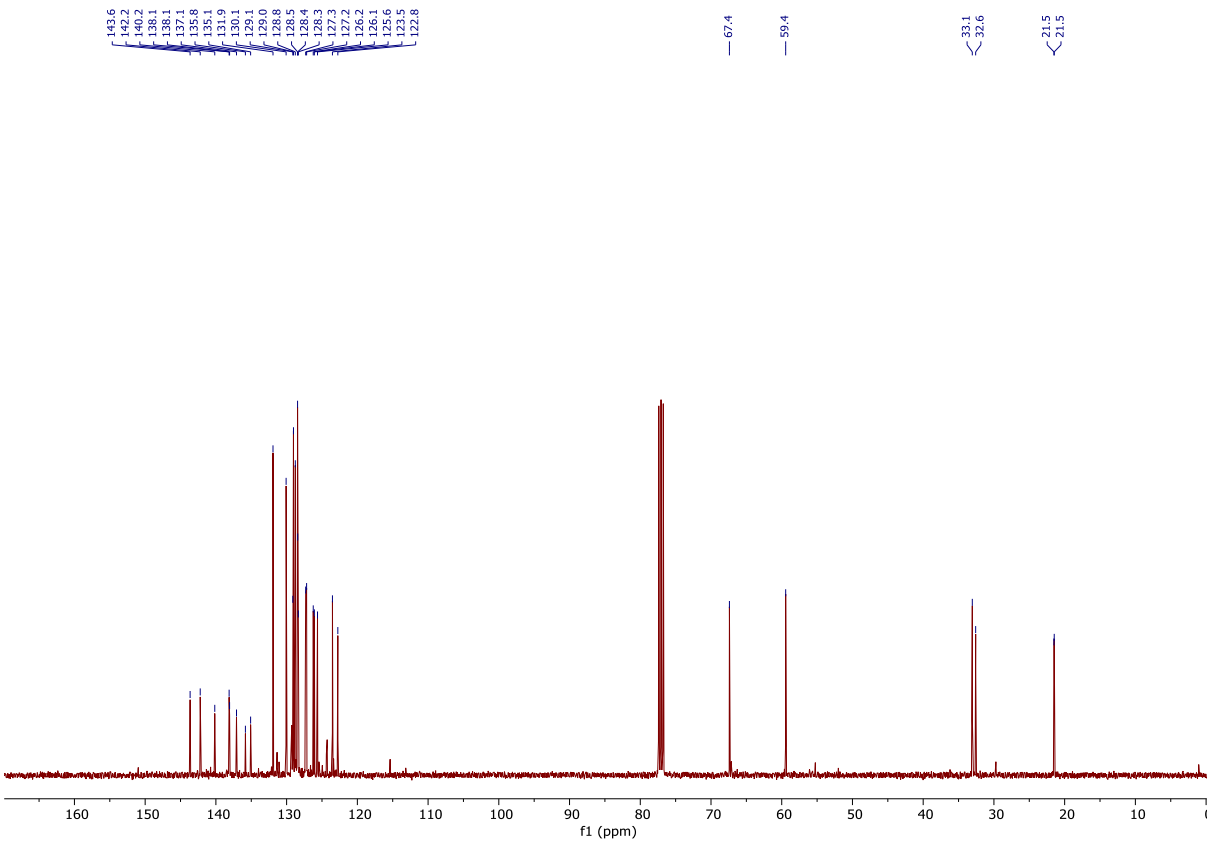
Following the general procedure, product **4** was isolated as an orange oil in 80% yield (42.3 mg, 0.16 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 1:1

$^{1}$H NMR spectrum ($CDCl_3$)



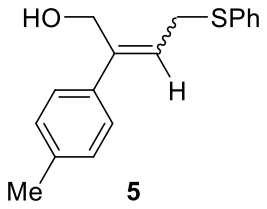

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.37-7.33 (m, 2H), 7.30-7.20 (m, 10H), 7.16-7.12 (m, 2H), 6.96-6.93 (m, 2H), 6.00 (t, *J* = 8.1 Hz, 1H, 1H M *Z* isomer), 5.86 (tt, *J* = 7.7, 1.4 Hz, 1H, 1H m *E* isomer), 4.37 (s, 2H, 2H M), 4.31 (s, 2H, 2H m), 3.78 (d, *J* = 8.1 Hz, 1H, 1H M), 3.55 (dt, *J* = 7.7, 1.0 Hz, 1H, 1H m), 2.38 (s, 3H, 3H M), 2.37 (s, 3H, 3H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.6, 142.2, 140.2, 138.1, 138.1, 137.1, 135.8, 135.1, 131.9, 130.1, 129.1, 129.0, 128.8, 128.5, 128.3, 127.3, 127.2, 126.2, 126.1, 125.6, 123.5, 122.8, 67.4, 59.4, 33.1, 32.6, 21.5, 21.5.

HRMS (ESI+, MeOH): *m/z* calcd for $C_{17}H_{18}NaOS$, $[M + Na]^+$: 293.0971, found: 293.0973.

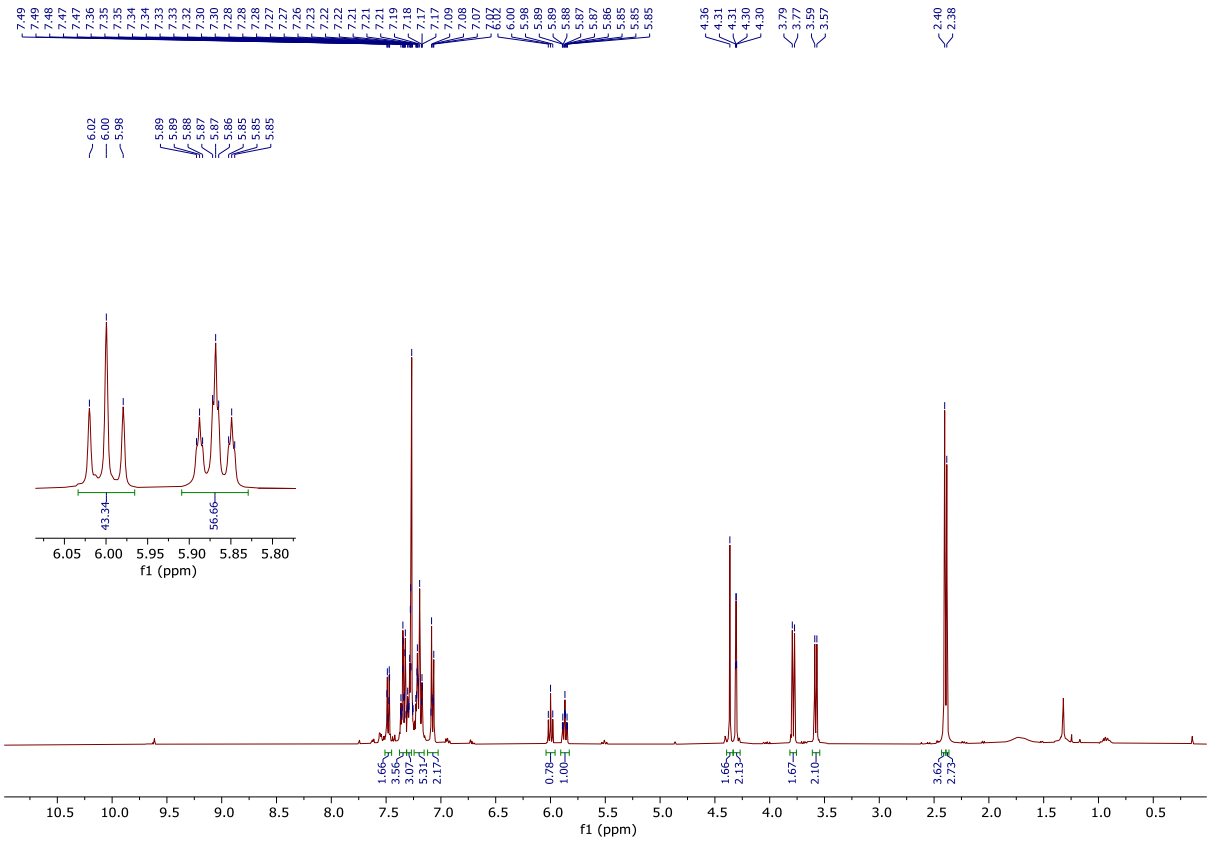



**5**

**4-(phenylthio)-2-(*p*-tolyl)but-2-en-1-ol**

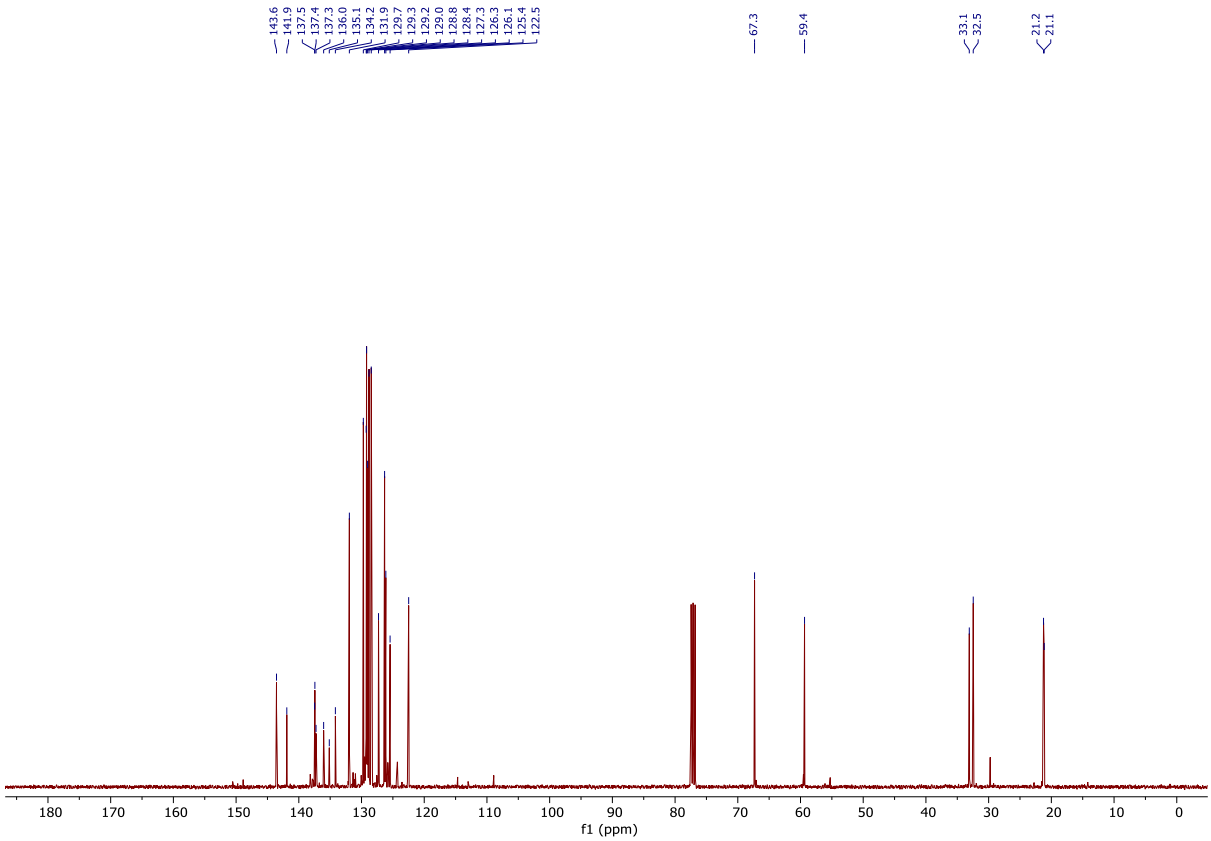
Following the general procedure, product **5** was isolated as an orange oil in 82% yield (43.4 mg, 0.16 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 4:6

$^{1}$H NMR spectrum ($CDCl_3$)



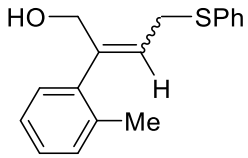

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.37-7.32 (m, 4H), 7.31-7.25 (m, 4H), 7.23-7.17 (m, 6H), 7.09-7.07 (m, 2H), 6.00 (t, *J* = 8.1 Hz, 1H, 1H m *Z* isomer), 5.87 (tt, *J* = 7.7, 1.5 Hz, 1H. 1H *E* isomer), 4.36 (s, 2H, 2H m), 4.31 (d, *J* = 1.3 Hz, 2H, 2H M), 3.78 (d, *J* = 8.1 Hz, 2H, 2H m), 3.58 (d, *J* = 7.7 Hz, 2H, 2H M), 2.40 (s, 3H, 3H M), 2.38 (s, 3H, 3H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.6, 141.9, 137.5, 137.4, 137.3, 136.0, 135.1, 134.2, 131.9 (2C), 129.7 (2C), 129.3 (2C), 129.2 (2C), 129.0 (2C), 128.8 (2C), 128.4 (2C), 127.3, 126.3 (2C), 126.1, 125.5, 122.5, 67.3, 59.4, 33.1, 32.5, 21.3, 21.1.

The spectral data correspond to the literature.[3]

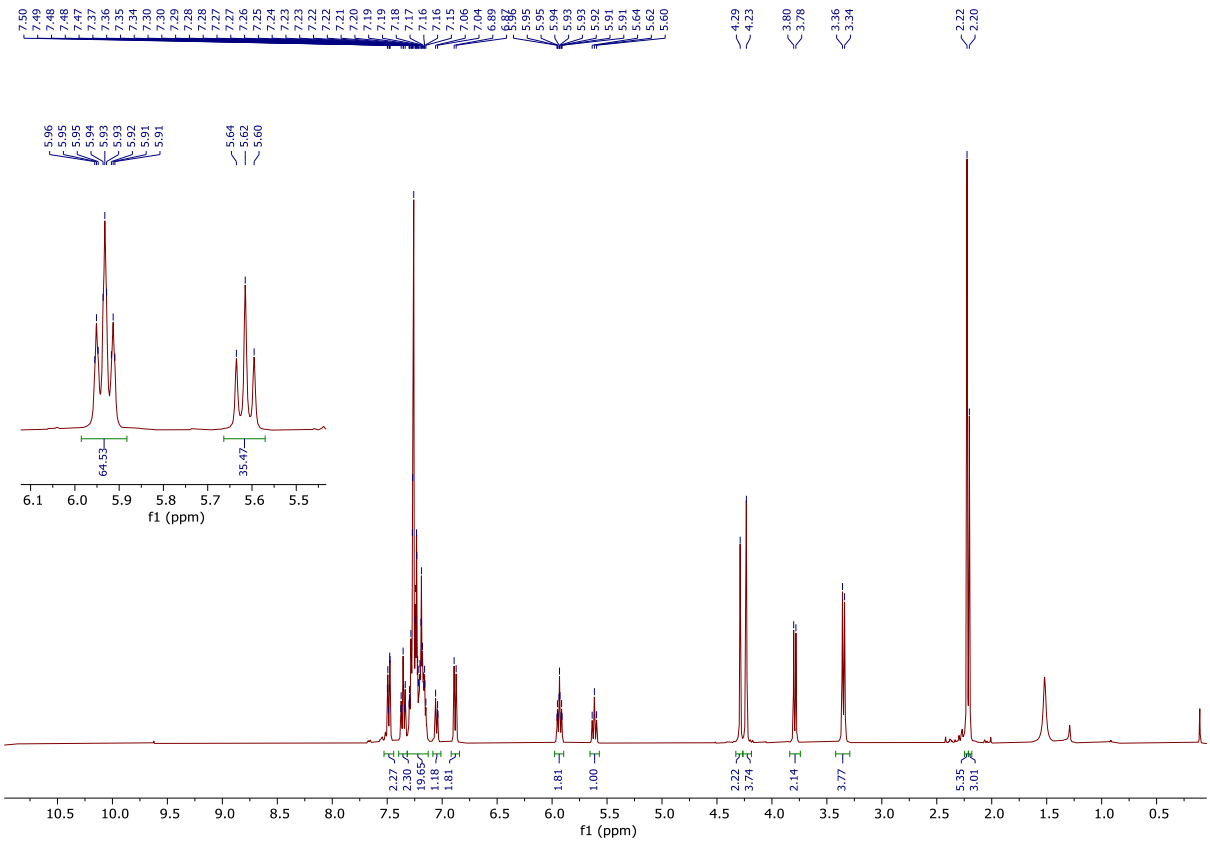



**6**

**4-(phenylthio)-2-(*o*-tolyl)but-2-en-1-ol**

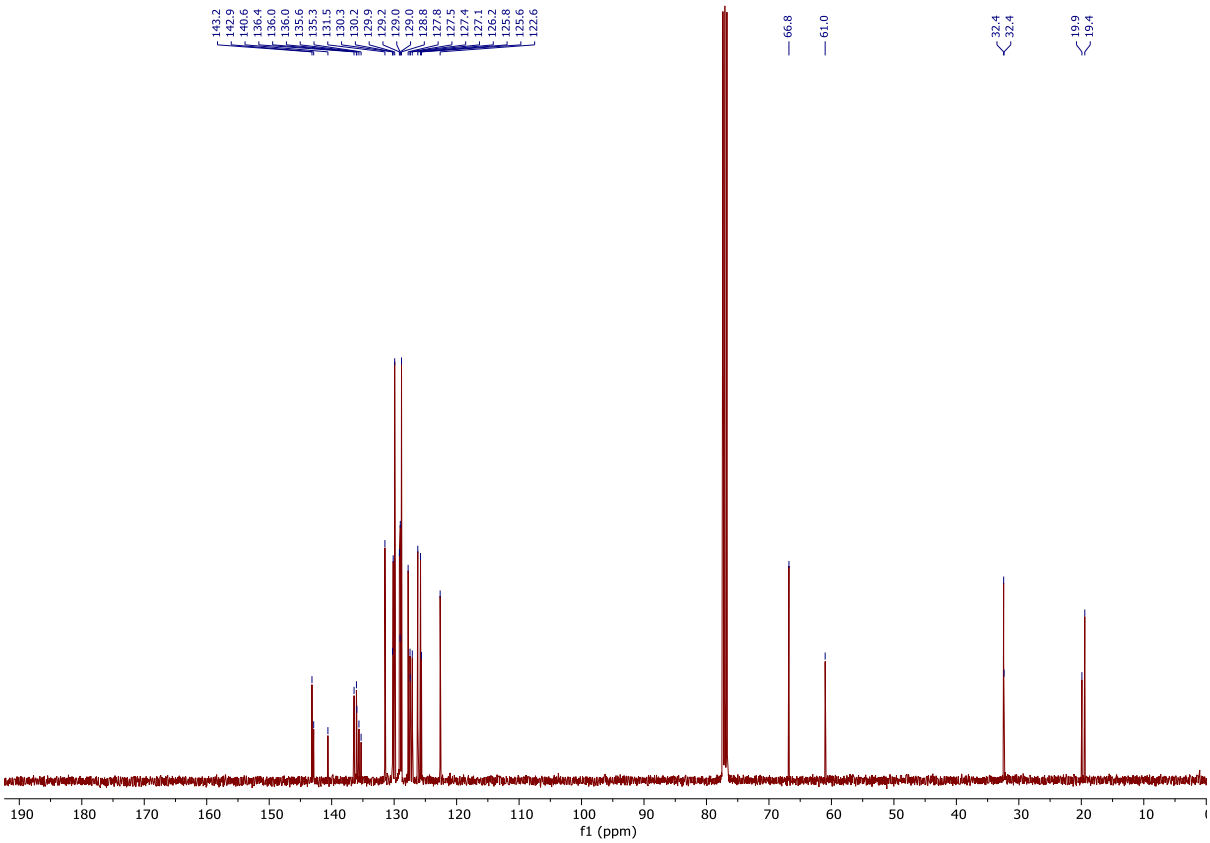
Following the general procedure, product **6** was isolated as a yellow oil in 91% yield (48.2 mg, 0.18 mmol). *Z/E* ratio was determined by $^1$H NMR to be 4:7

$^1$H NMR spectrum ($CDCl_3$)



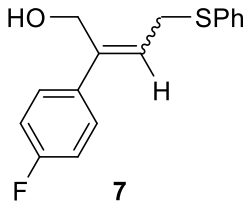
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.38-7.34 (m, 2H), 7.30-7.15 (m, 10H), 7.06-7.04 (m, 2H), 6.89-6.87 (m, 2H), 5.93 (tt, *J* = 7.5, 1.6 Hz, 1H, 1H M, *E* isomer,), 5.62 (t, *J* = 8.0 Hz, 1H, 1H M *Z* isomer), 4.29 (s, 2H, 2H m), 4.23 (s, 2H, 2H M), 3.79 (d, *J* = 8.0 Hz, 2H, 2H m), 3.35 (d, *J* = 7.6 Hz, 2H, 2H M), 2.22 (s, 3H, 3H M), 2.20 (s, 3H, 3H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.2, 142.9, 140.6, 136.4, 136.0, 135.9, 135.6, 135.3, 131.5, 130.3, 130.2 (2C), 129.9 (2C), 129.2, 129.1, 129.0 (2C), 128.8 (2C), 127.8, 127.5, 127.4, 127.1, 126.2, 125.8, 125.6, 122.6, 66.8, 61.0, 32.4, 32.4, 19.9, 19.4.

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{17}H_{18}NaOS$, $[M + Na]^+$: 293.0971, found: 293.0981.

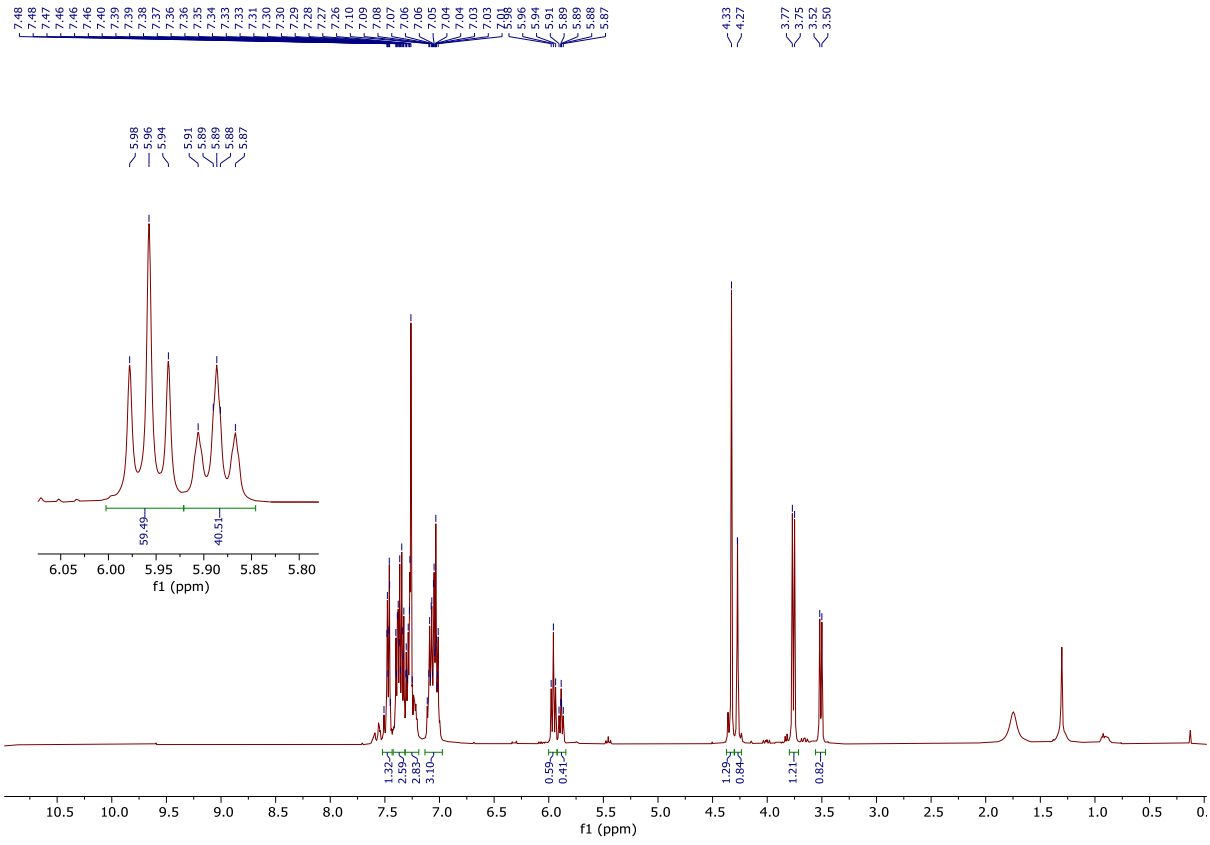



**7**

**2-(4-fluorophenyl)-4-(phenylthio)but-2-en-1-ol**

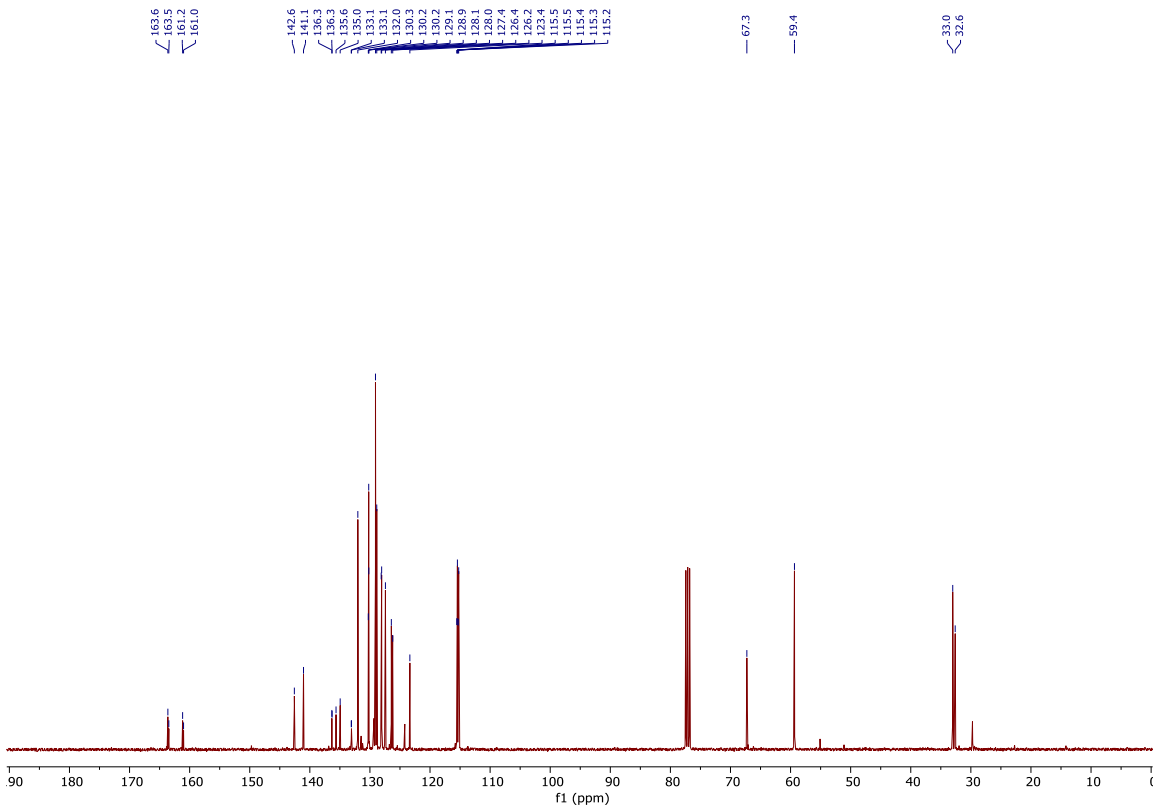
Following the general procedure, product **7** was isolated as a white solid in 67% yield (35.2 mg, 0.13 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 6:4

$^{1}$H NMR spectrum ($CDCl_3$)




**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.40-7.33 (m, 6H), 7.31-7.25 (m, 4H), 7.11-7.01 (m, 6H), 5.96 (t, *J* = 8.1 Hz, 1H, 1H *Z* isomer), 5.89 (tt, *J* = 7.8, 1.5 Hz, 1H, 1H *E* isomer), 4.33 (s, 2H, 2H M), 4.27 (s, 2H, 2H m), 3.76 (d, *J* = 8.1 Hz, 2H, 2H M), 3.51 (d, *J* = 7.8 Hz, 2H, 2H m).

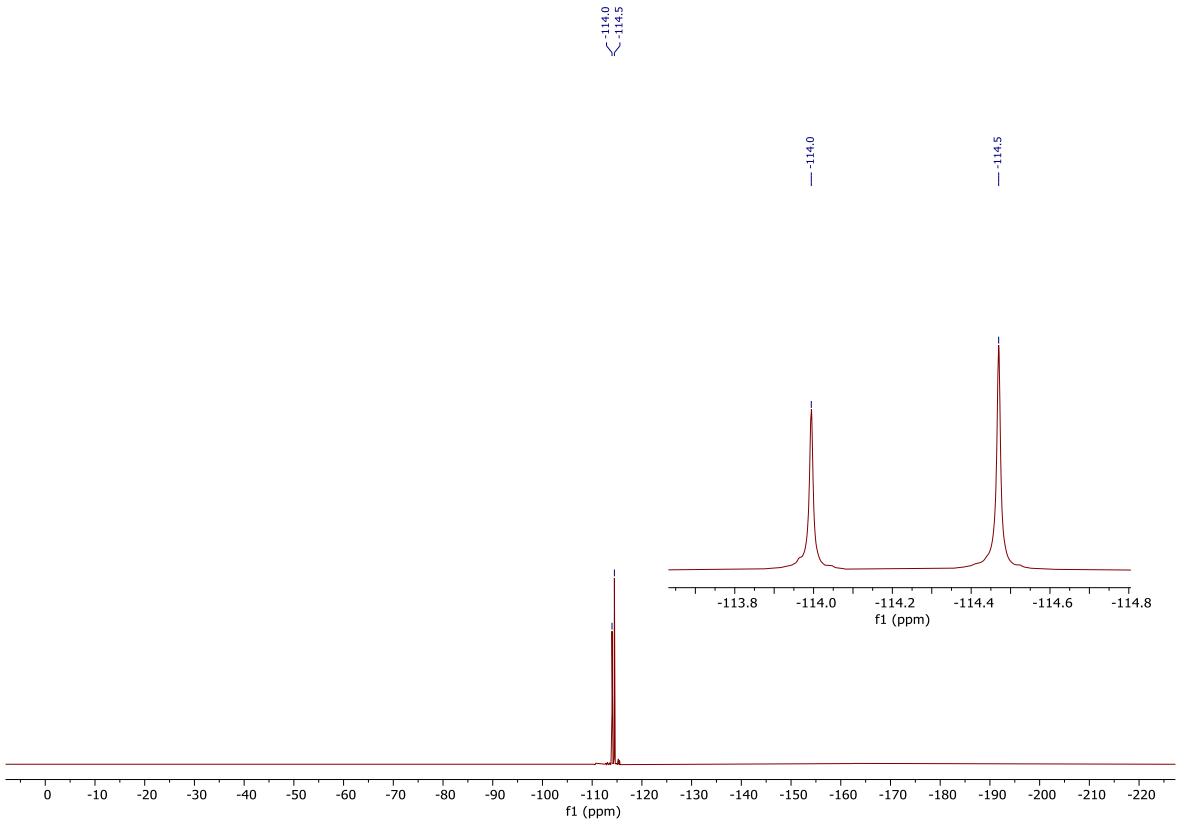
$^{13}$C NMR spectrum ($CDCl_3$)



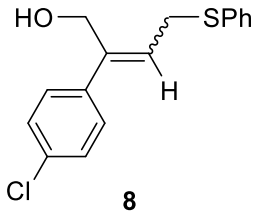

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 247.0 Hz), 162.2 (d, *J* = 246.7 Hz), 142.6, 141.1, 136.3 (d, *J* = 3.3 Hz), 135.6, 135.0, 133.1 (d, *J* = 3.3 Hz), 132.0 (2C), 130.2 (2C), 130.2 (d, *J* = 8.0 Hz, 2C), 129.1 (2C), 128.9 (2C), 128.1 (d, *J* = 7.9 Hz, 2C), 127.4, 126.4, 126.2, 124.4, 115.3 (d, *J* = 21.4 Hz, 2C), 115.4 (d, *J* = 21.2 Hz, 2C), 67.3, 59.4, 33.0, 32.6.

The spectral data correspond to the literature.[3]

$^{19}$F NMR spectrum ($CDCl_3$)




**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -114.0, -114.5.

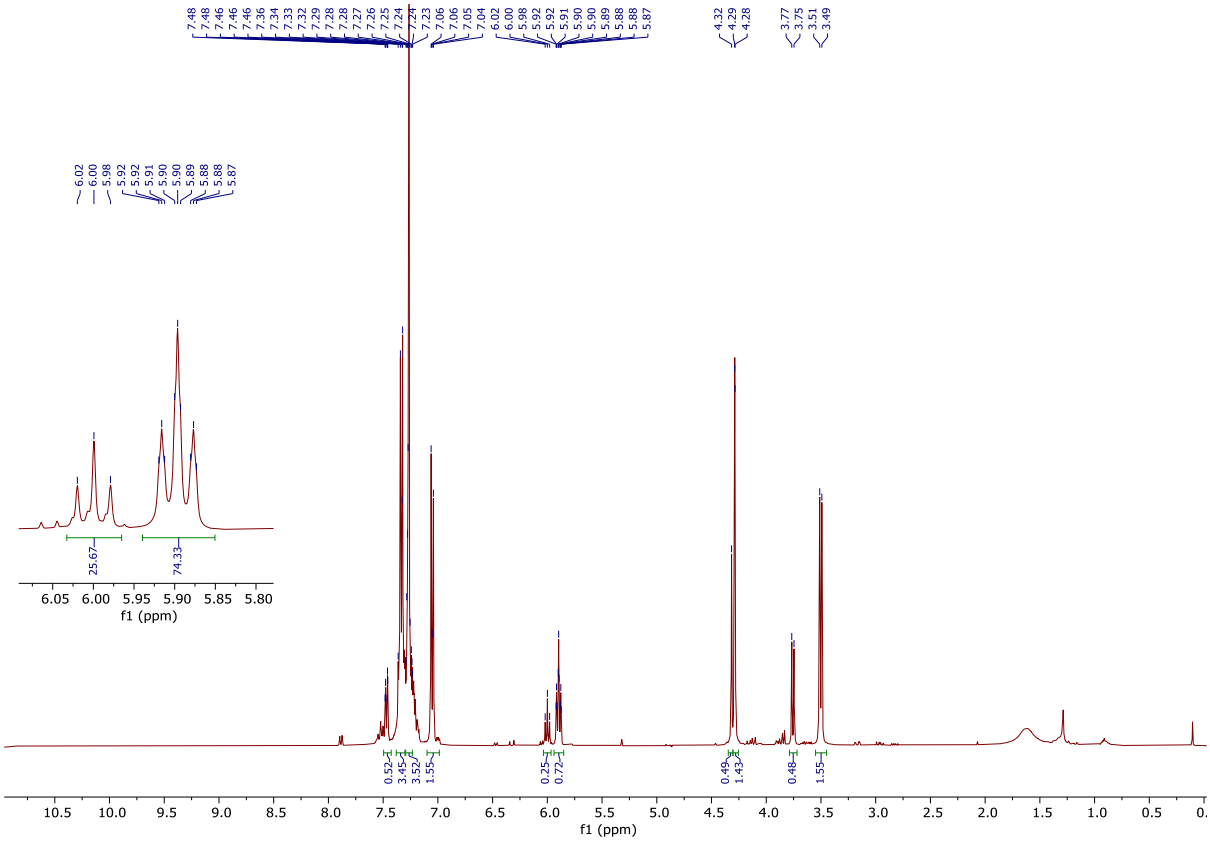



**8**

**2-(4-chlorophenyl)-4-(phenylthio)but-2-en-1-ol**

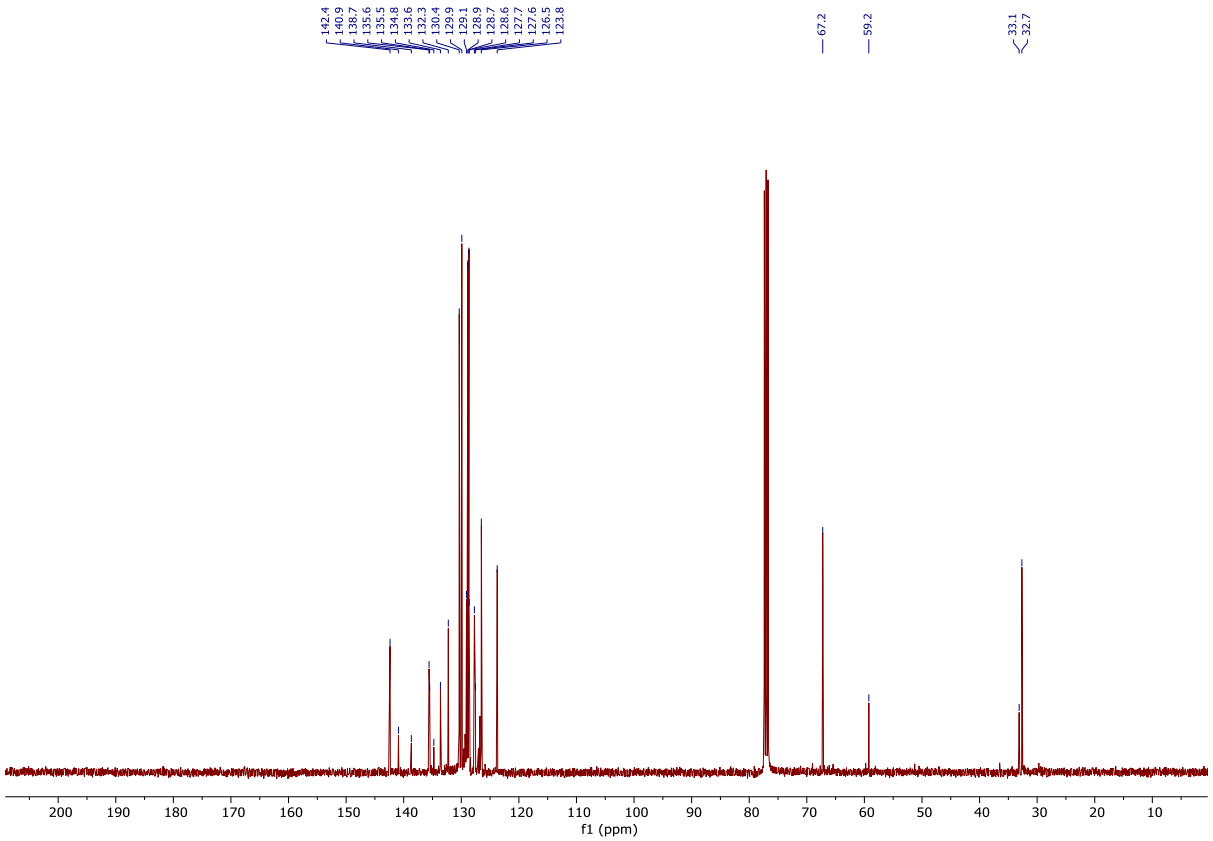
Following the general procedure, product **8** was isolated as a yellow oil in 45% yield (23.2 mg, 0.08 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 3:7

$^{1}$H NMR spectrum ($CDCl_3$)



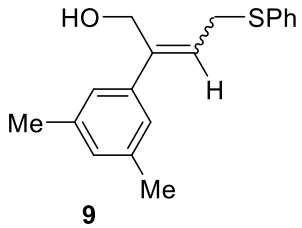

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.36-7.32 (m, 6H), 7.29-7.23 (m, 6H), 7.06-7.04 (m, 4H), 6.00 (t, *J* = 8.2 Hz, 1H, 1H m *Z* isomer), 5.90 (tt, *J* = 7.8, 1.4 Hz, 1H, 1H M *E* isomer), 4.32 (s, 2H, 2H m), 4.29 (s, 2H, 2H M), 3.76 (d, *J* = 8.1 Hz, 2H, 2H m), 3.50 (d, *J* = 7.8 Hz, 2H, 2H M).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.4, 140.9, 138.7, 135.6, 135.5, 134.8, 133.6, 132.3, 130.4 (2C), 129.9 (2C), 129.1 (2C), 128.9 (2C), 128.7 (2C), 128.6 (2C), 127.7, 127.6, 126.5 (2C), 123.8 (2C), 67.2, 59.2, 33.1, 32.7.

HRMS (APCI+, MeOH): *m/z* calcd for $C_{16}H_{14}ClOS$, $[M-H]^+$: 289.0448, found: 289.0444.

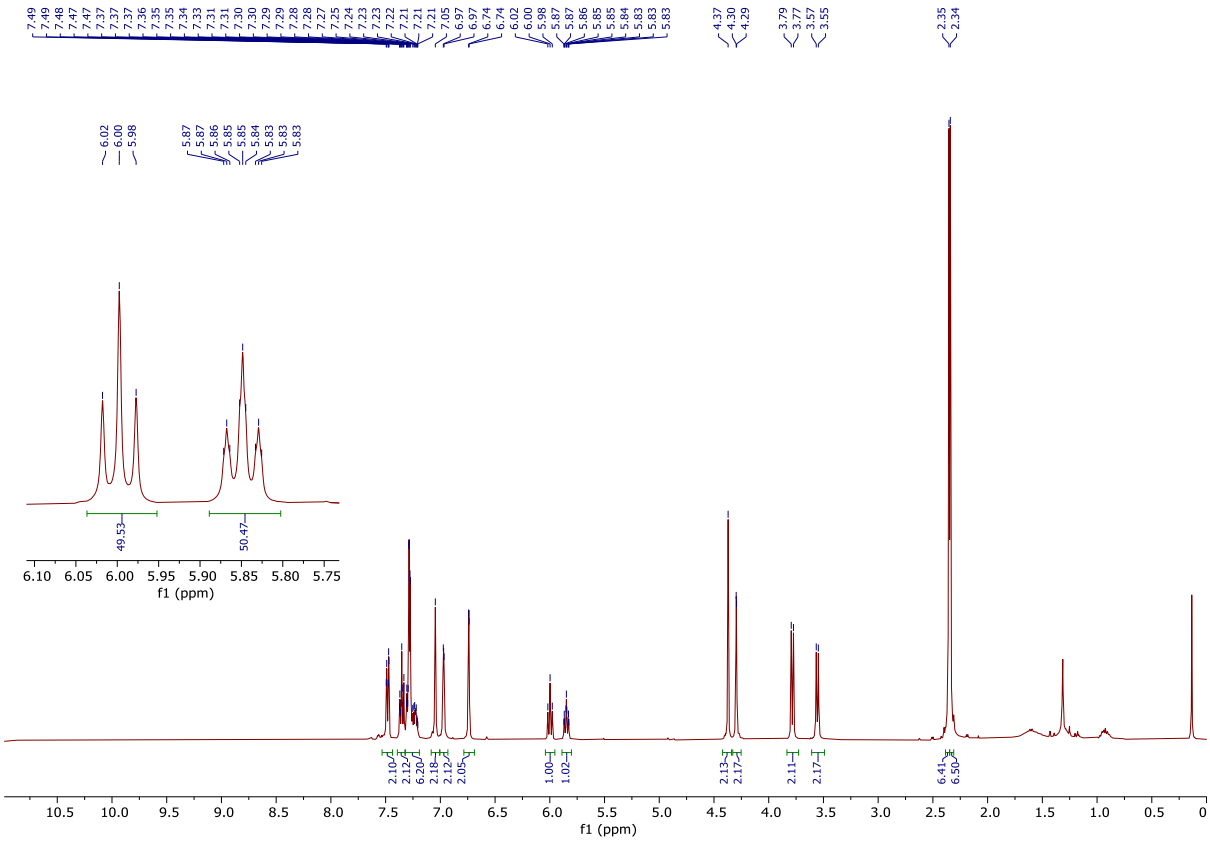



**9**

**2-(3,5-dimethylphenyl)-4-(phenylthio)but-2-en-1-ol**

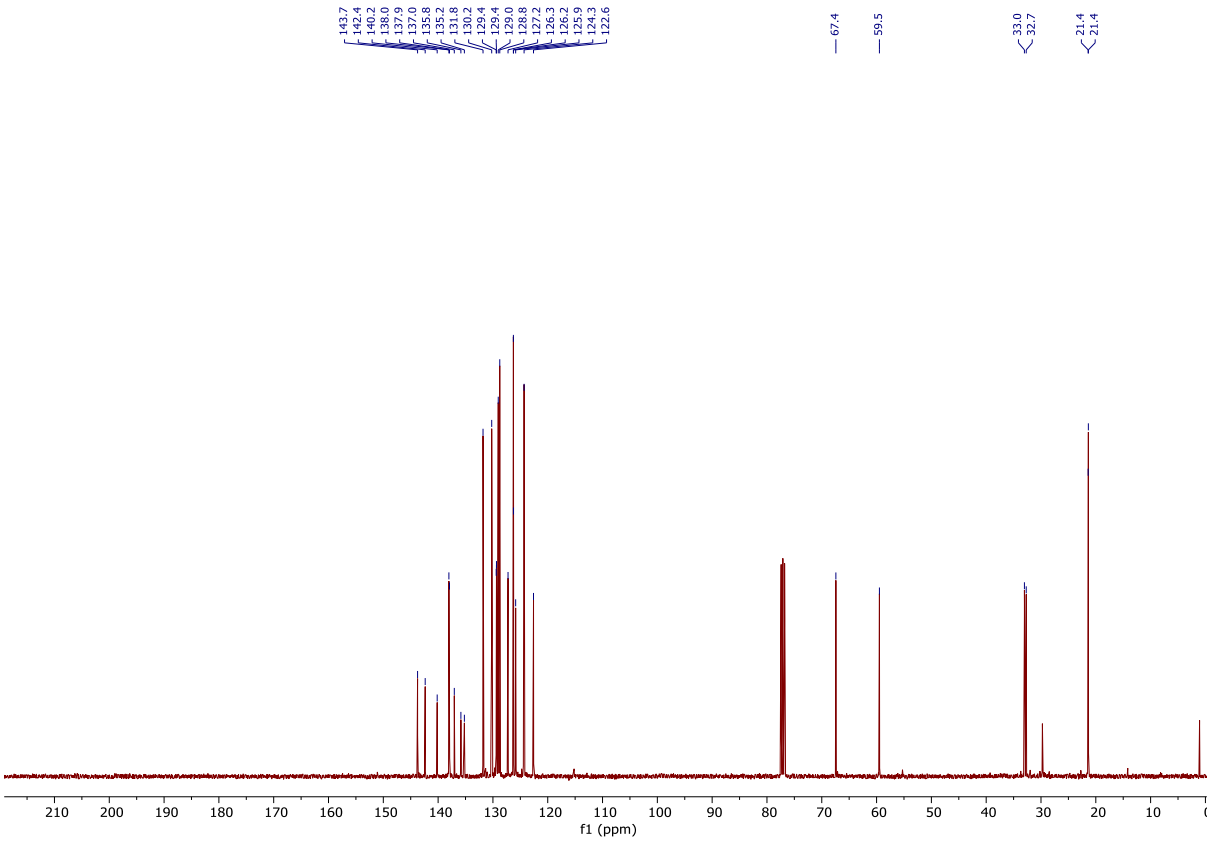
Following the general procedure, product **9** was isolated as an orange oil in 55% yield (28.7 mg, 0.10 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 1:1

$^{1}$H NMR spectrum ($CDCl_3$)



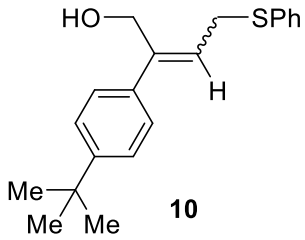

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.37-7.33 (m, 2H), 7.31-7.21 (m, 6H), 7.05 (s, 2H), 6.97 (s, 2H), 6.74-6.74 (m, 2H), 6.00 (t, *J* = 8.1 Hz, 1H, 1H *Z* isomer), 5.85 (tt, *J* = 7.7, 1.5 Hz, 1H, 1H *E* isomer), 4.37 (s, 2H), 4.30 (s, 2H), 3.78 (d, *J* = 8.1 Hz, 2H), 3.56 (d, *J* = 7.7 Hz, 2H), 2.35 (s, 6H), 2.34 (s, 6H).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.8, 142.4, 140.2, 138.0 (2C), 137.9 (2C), 137.1, 135.8, 135.2, 131.8 (2C), 130.2 (2C), 129.4, 129.3, 129.0 (2C), 128.8 (2C), 127.2, 126.3 (2C), 126.2, 125.9, 124.3 (2C), 122.6, 67.4, 59.5, 33.0, 32.7, 21.4, 21.3.

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{18}H_{20}NaOS$, $[M + Na]^+$: 307.1127, found: 307.1141.

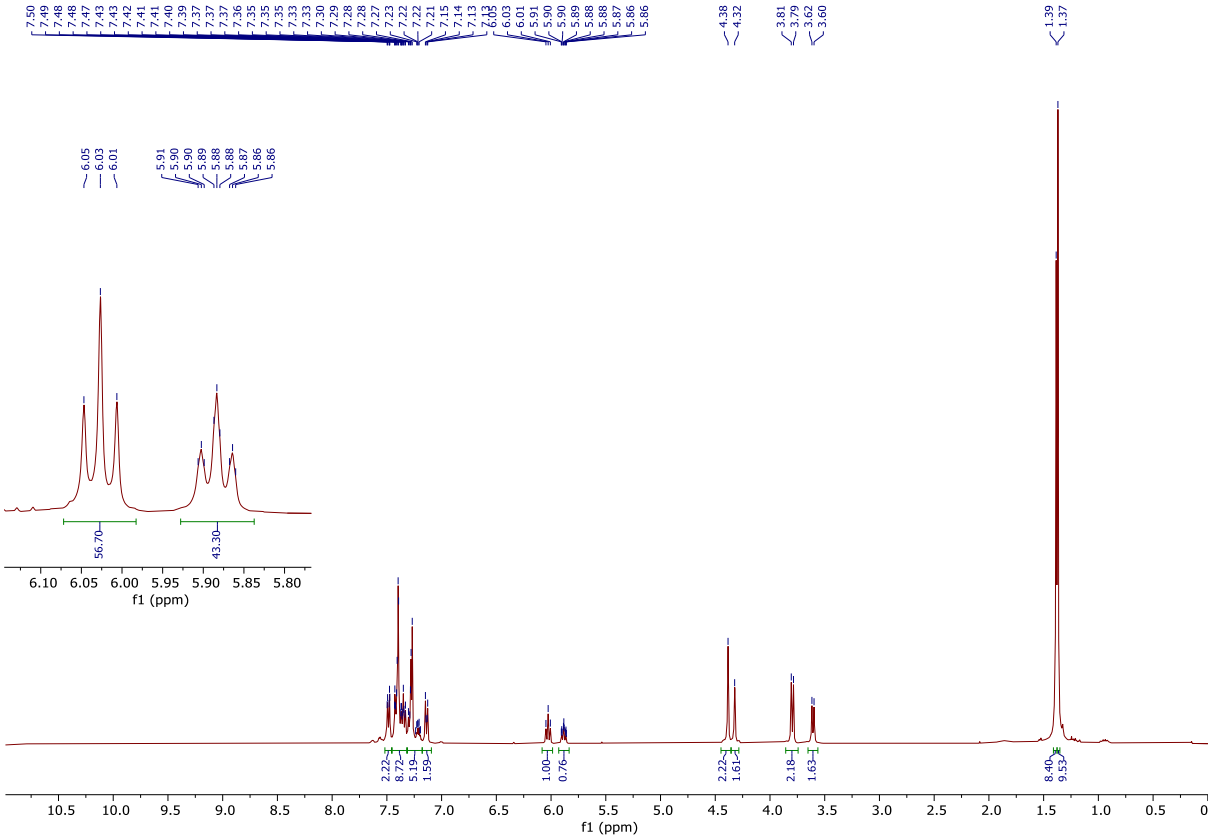



**10**

**2-(4-(*tert*-butyl)phenyl)-4-(phenylthio)but-2-en-1-ol**

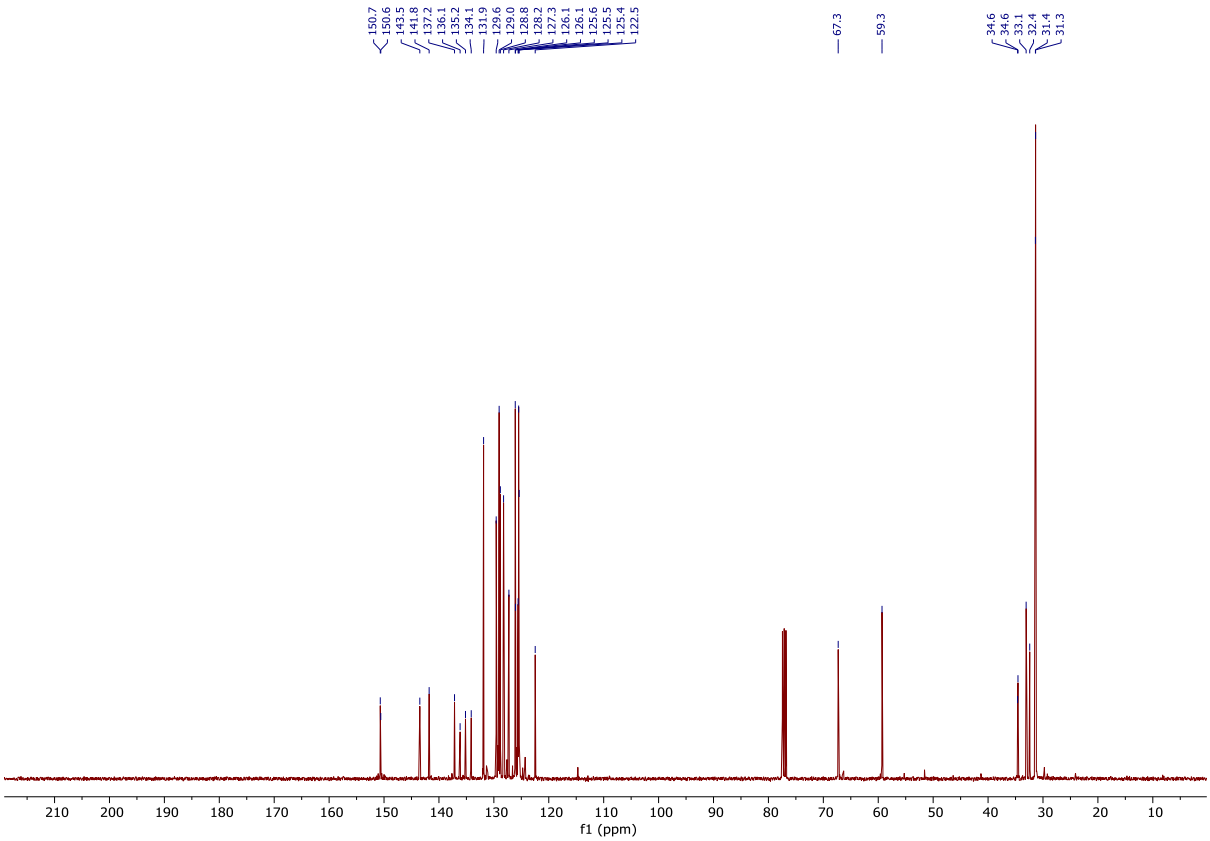
Following the general procedure, product **10** was isolated as an orange oil in 53% yield (26.9 mg, 0.09 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 6:4

$^{1}$H NMR spectrum ($CDCl_3$)



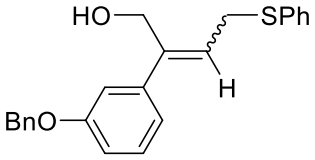

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.47 (m, 2H), 7.43-7.33 (m, 8H), 7.30-7.19 (m, 6H), 7.15-7.13 (m, 2H), 6.03 (t, *J* = 8.1 Hz, 1H, 1H M *Z* isomer), 5.88 (tt, *J* = 7.8, 1.6 Hz, 1H, 1H m *E* isomer), 4.38 (s, 2H M), 4.32 (s, 2H m), 3.80 (d, *J* = 8.1 Hz, 2H, 2H M), 3.61 (d, *J* = 7.7 Hz, 2H, 2H m), 1.39 (s, 9H, 9 H m), 1.37(s, 9H, 9H M).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 150.7, 150.6, 143.5, 141.8, 137.2, 136.2, 135.2, 134.1, 131.9 (2C), 129.6 (2C), 129.0 (2C), 128.8 (2C), 128.2 (2C), 127.3, 126.1 (2C), 126.1, 125.6, 125.5 (2C), 125.4 (2C), 122.5, 67.3, 59.3, 34.6, 34.5, 33.1, 32.4, 31.4 (*t*Bu), 31.3 (*t*Bu).

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{20}H_{24}NaOS$, $[M + Na]^+$: 335.1440, found: 335.1443.

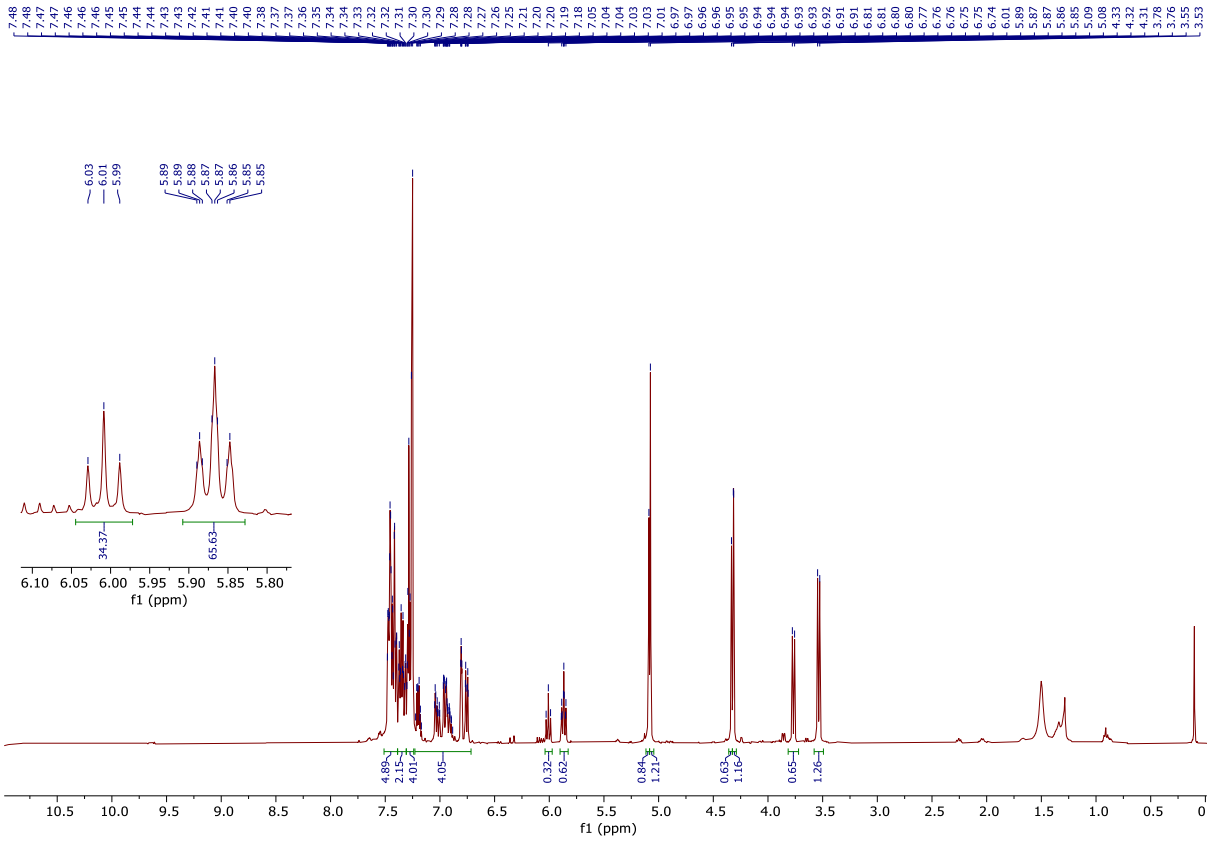



**11**

**2-(3-(benzyloxy)phenyl)-4-(phenylthio)but-2-en-1-ol**

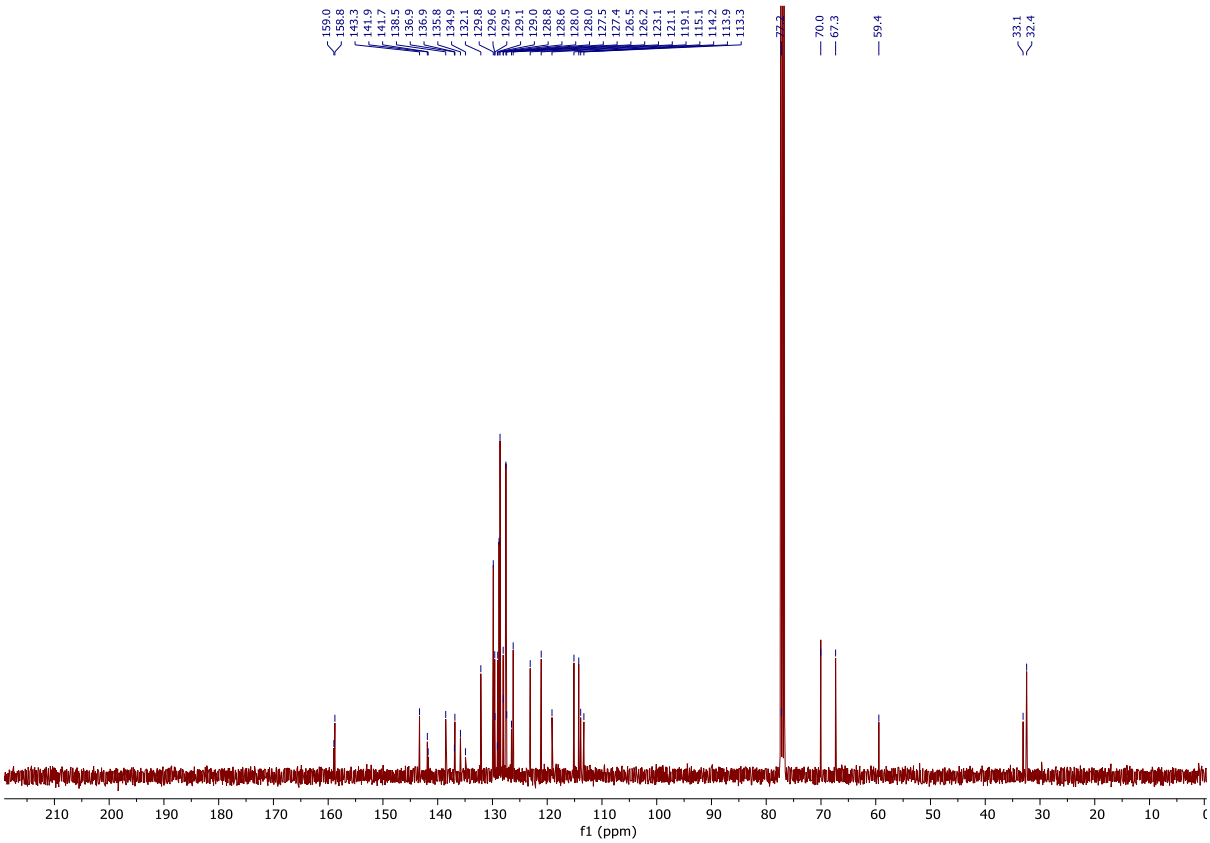
Following the general procedure, product **11** was isolated as a yellow oil in 64% yield (31.3 mg, 0.09 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 3:7

$^{1}$H NMR spectrum ($CDCl_3$)



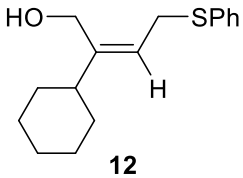

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 10H), 7.38-7.31 (m, 4H), 7.30-7.25 (m, 6H), 7.22-6.74 (m, 8H), 6.01 (t, *J* = 8.1 Hz, 1H, 1H m *Z* isomer), 5.87 (tt, *J* = 7.8, 1.4 Hz, 1H. 1H M *E* isomer), 5.09 (s, 2H, 2H m), 5.08 (s, 2H, 2H M) 4.33 (s, 2H, 2H m), 4.31 (s, 2H, 2H M), 3.77 (d, *J* = 8.2 Hz, 2H, 2H m), 3.54 (d, *J* = 7.9 Hz, 2H, 2H M).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.0, 158.8, 143.3, 141.9, 141.7, 138.5, 137.0, 136.9, 135.9, 132.1, 129.8 (2C), 129.6, 129.5, 129.1, 129.0, 128.8 (2C), 128.6 (3C), 128.0, 128.0, 127.5 (2C), 127.4, 126.5, 126.2, 123.1, 121.1, 119.1, 115.1, 114.2, 113.9, 113.3, 77.2, 70.0, 67.3, 59.4, 33.1, 32.4.

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{23}H_{22}NaO_2S$, $[M + Na]^+$: 385.1233, found: 385.1233.

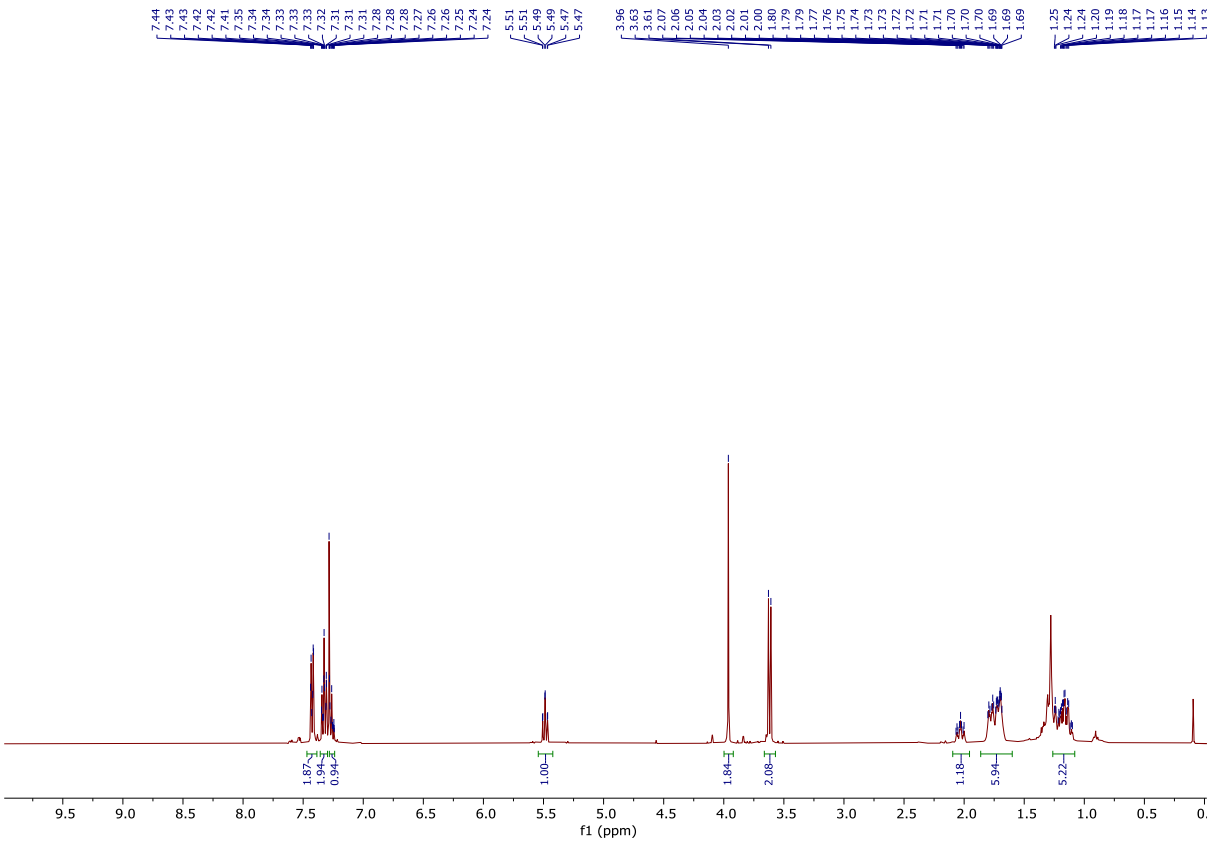



**12**

**(*Z*)-2-cyclohexyl-4-(phenylthio)but-2-en-1-ol**

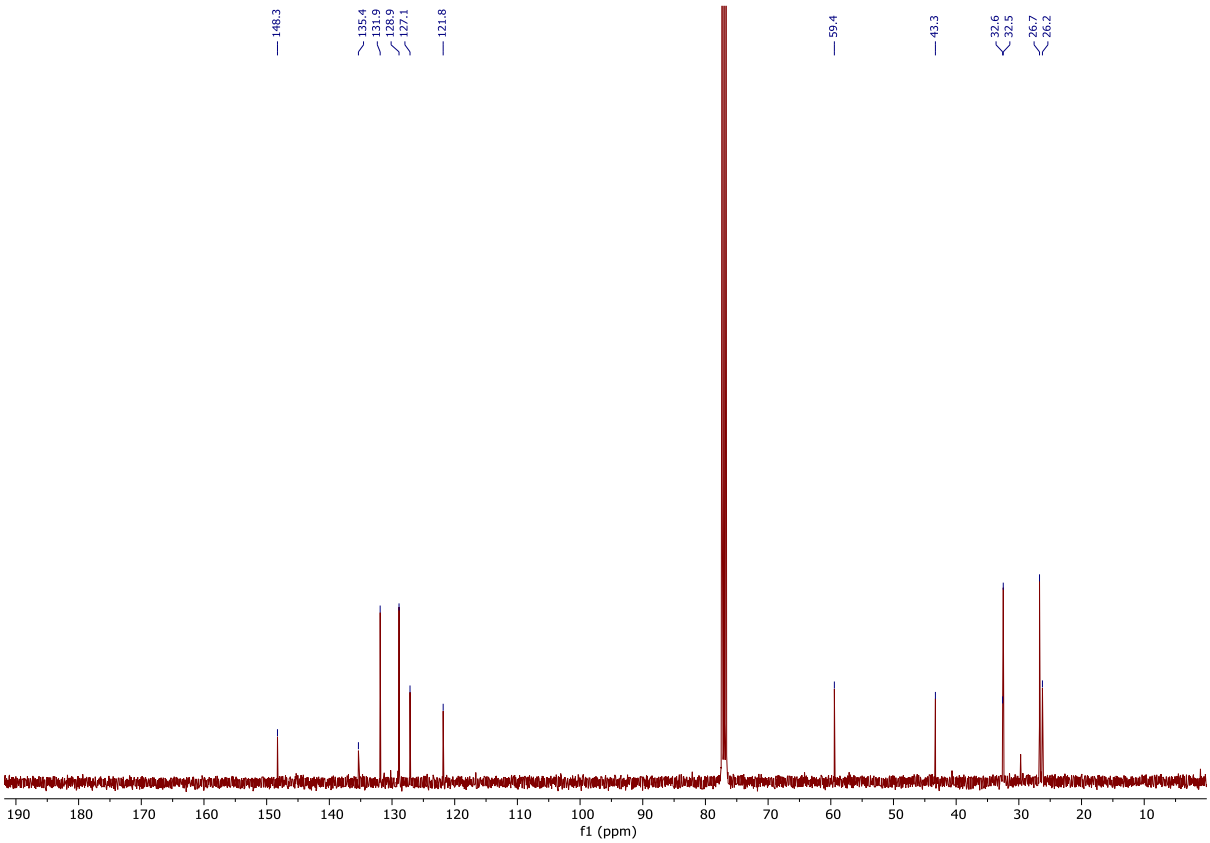
Following the general procedure, product **12** was isolated as a colorless oil in 53% yield (28.3 mg, 0.11 mmol). *Z/E* ratio was determined by $^{1}$H NMR of the crude to be 9:1. Note that only the *Z* isomer has been isolated.

$^{1}$H NMR spectrum ($CDCl_3$)



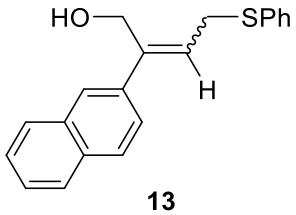

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.24 (m, 1H), 5.49 (td, *J* = 8.0, 1.0 Hz, 1 H), 3.96 (s, 2H), 3.62 (d, *J* = 8.0 Hz, 2 H), 2.07-2.00 (m, 1 H), 1.80-1.69 (m, 6H), 1.25-1.10 (m, 5H).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 148.3, 135.4, 131.9 (2C), 128.9 (2C), 127.1, 121.8, 59.4, 43.3, 32.6 (2C), 32.5 (2C), 26.7 (2C), 26.2 (2C).

The spectral data correspond to the literature.[3]

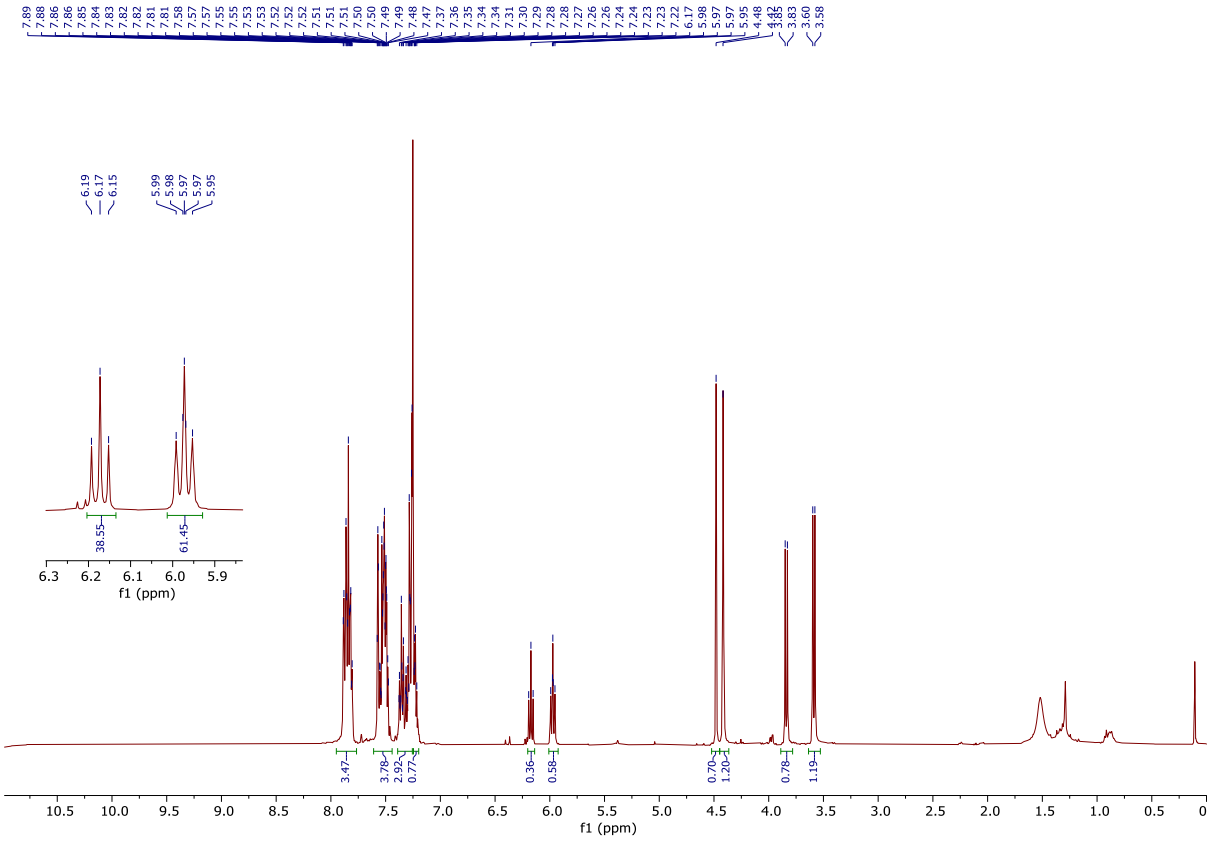



**13**

**2-(naphthalen-2-yl)-4-(phenylthio)but-2-en-1-ol**

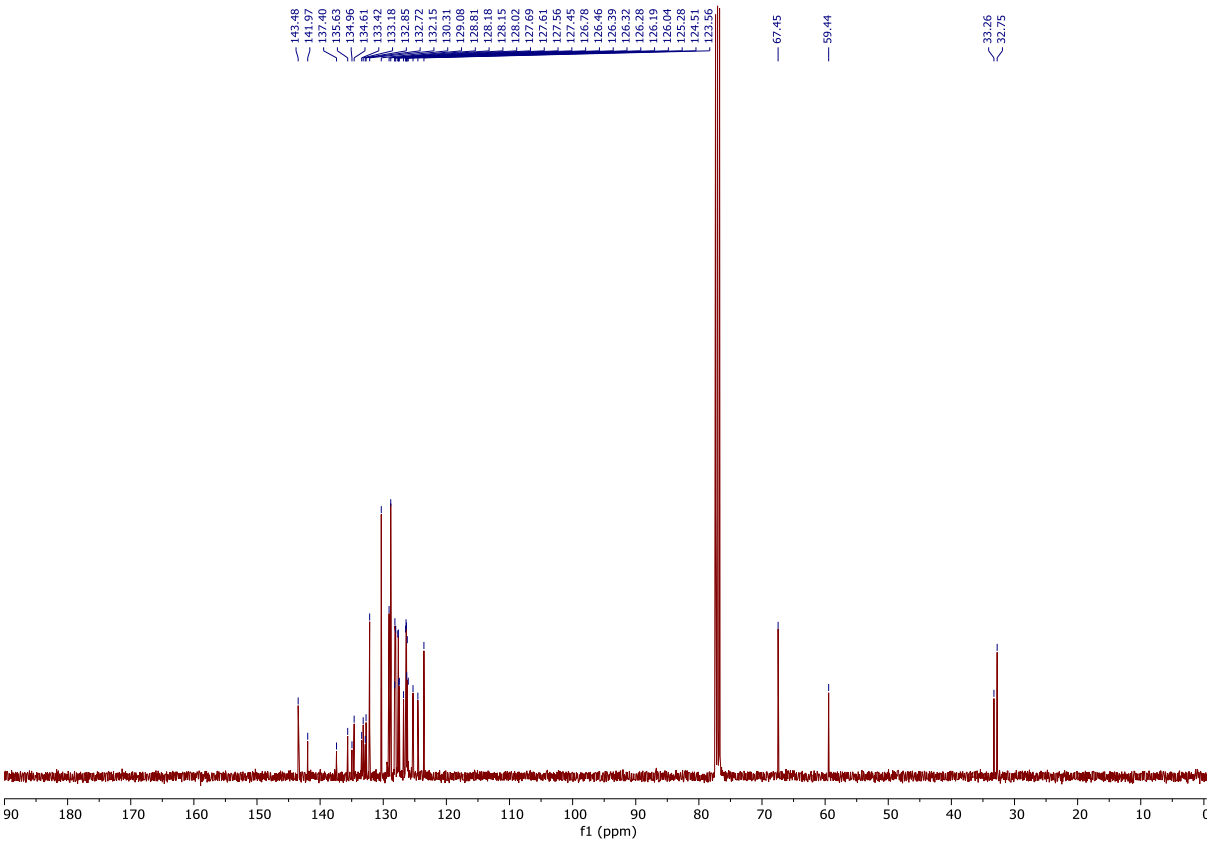
Following the general procedure, product **13** was isolated as a yellow oil in 51% yield (26.0 mg, 0.085 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 4:6

$^{1}$H NMR spectrum ($CDCl_3$)



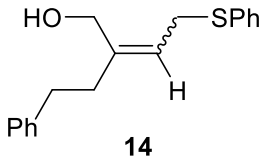

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.81 (m, 8H), 7.58-7.47 (m, 8H), 7.38-7.26 (m, 6H), 7.24-7.22 (m, 2H), 6.17 (t, *J* = 8.1 Hz, 1H, 1 H m *Z* isomer), 5.97 (tt, *J* = 7.7, 1.4 Hz, 1H, 1H M *E* isomer), 4.48 (s, 2H., 2H m), 4.42 (s, 2H, 2H M), 3.84 (d, *J* = 8.1 Hz, 2H, 2H m), 3.59 (d, *J* = 7.7 Hz, 2H, 2H M).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.5, 142.0, 137.4, 135.6, 135.0, 134.6, 133.4, 133.2, 132.9, 132.7, 132.2 (2C), 130.3 (2C), 129.1 (2C), 128.8 (2C), 128.2, 128.2, 128.1, 128.0, 127.7, 127.6, 127.6, 127.5, 126.8, 126.5, 126.4, 126.3, 126.3, 126.2, 126.0, 125.3, 124.5, 123.6, 67.5, 59.4, 33.3, 32.8.

The spectral data correspond to the literature.[3]

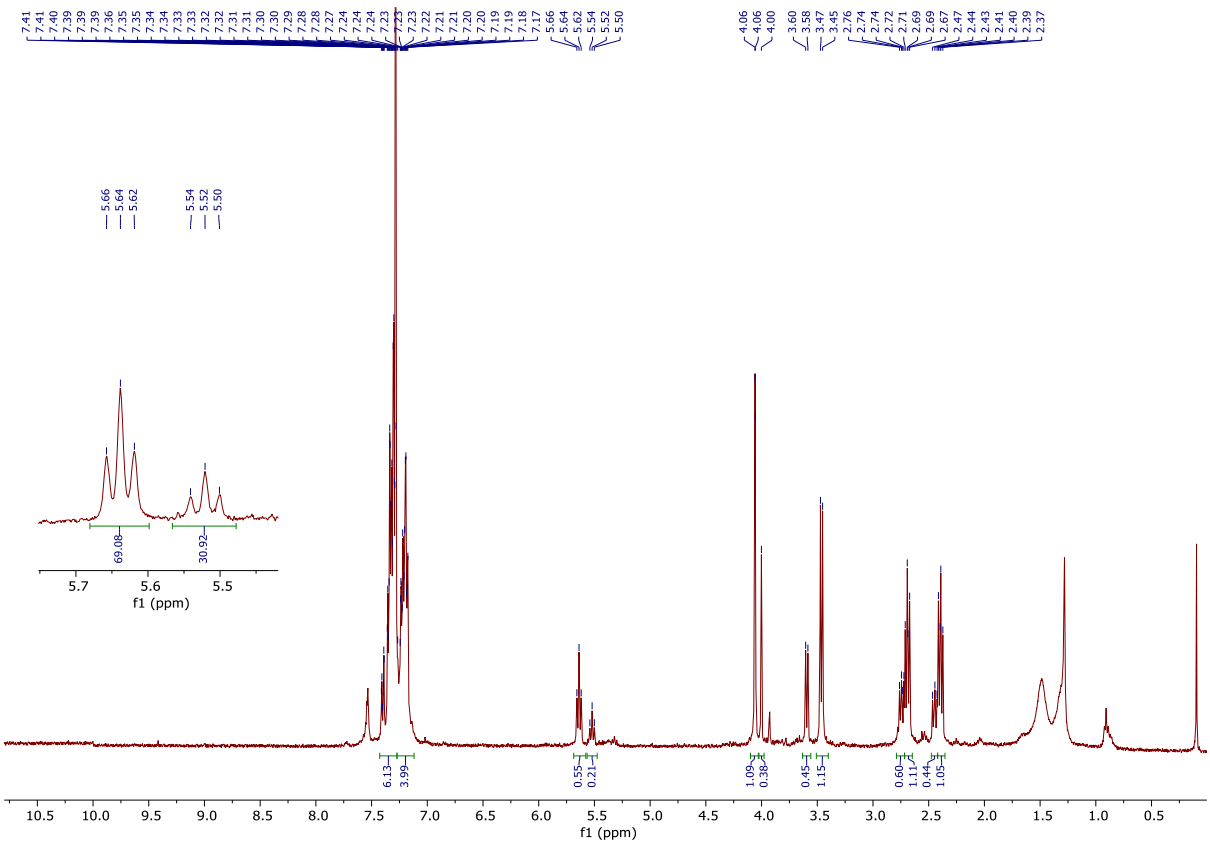



**14**

**2-phenethyl-4-(phenylthio)but-2-en-1-ol**

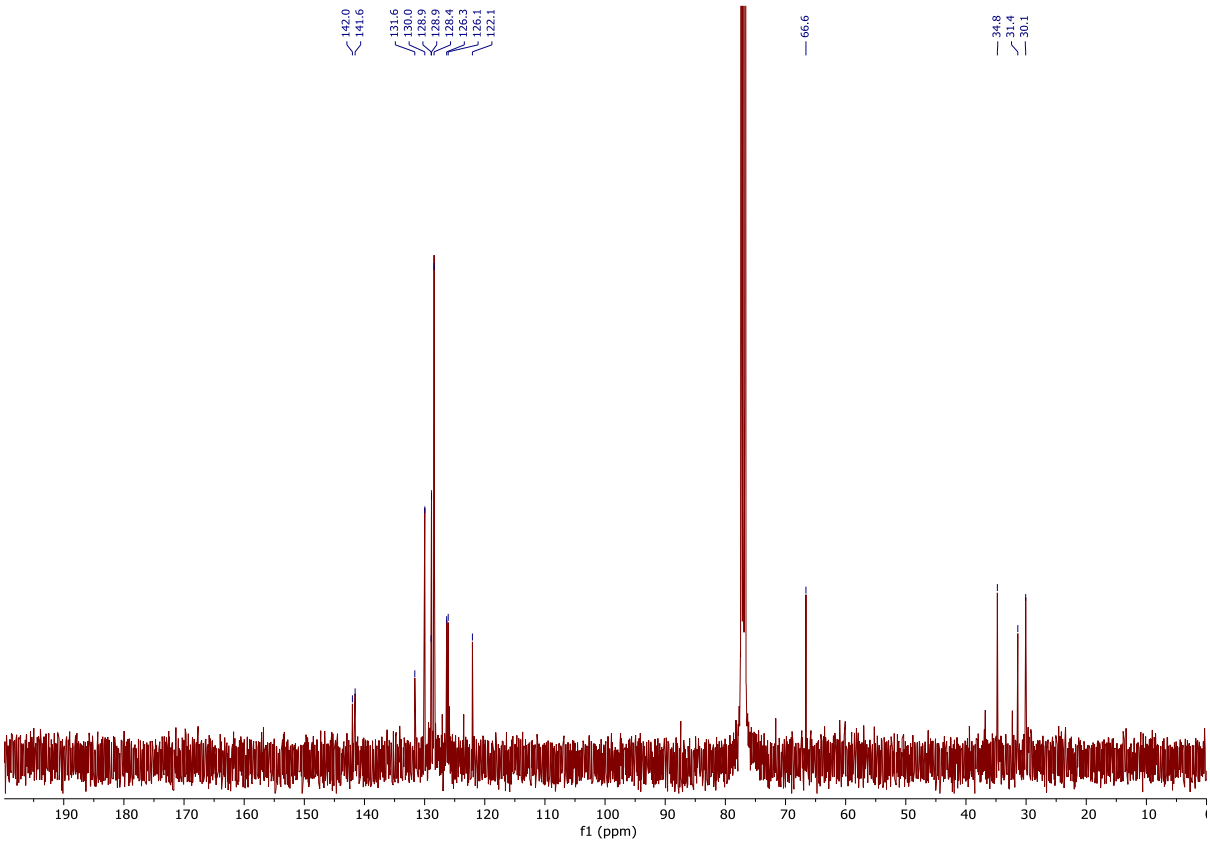
Following the general procedure, product **14** was isolated as a yellow oil in 90% yield (46.8 mg, 0.16 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 3:7

$^{1}$H NMR spectrum ($CDCl_3$)



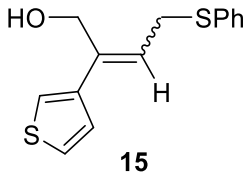

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 10H), 7.24-7.17 (m, 10H), 5.64 (t, *J* = 7.7 Hz, 1H, 1H *E* M isomer), 5.52 (t, *J* = 8.0 Hz, 1H, 1H m *Z* isomer), 4.06 (s, 2H, 2H M), 4.00 (s, 2H, 2H m), 3.59 (d, *J* = 8.0 Hz, 2H, 2H m), 3.46 (d, *J* = 7.7 Hz, 2H, 2H M), 2.76-2.72 (m, 2H, 2H m), 2.71-2.67 (m, 2H, 2H M), 2.47-2.43 (m, 2H, 2H m), 2.41-2.37 (m, 2H, 2H M).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.0, 141.6, 131.6, 130.0, 128.9, 128.9, 128.4, 126.3, 126.1, 122.1, 66.6, 34.8, 31.4, 30.1. (Only the *E* isomer identified)

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{18}H_{20}NaOS$, $[M+Na]^+$: 307.1127, found: 307.1134.

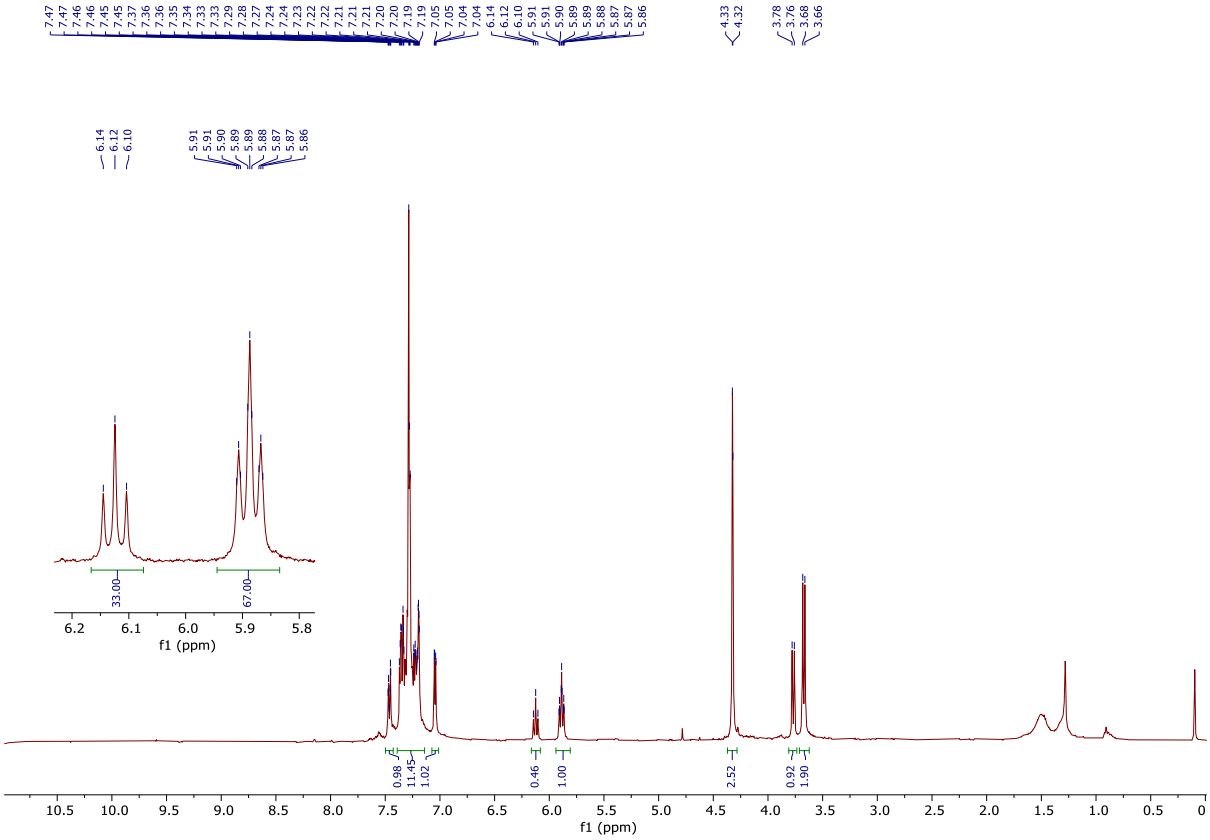



**15**

**4-(phenylthio)-2-(thiophen-3-yl)but-2-en-1-ol**

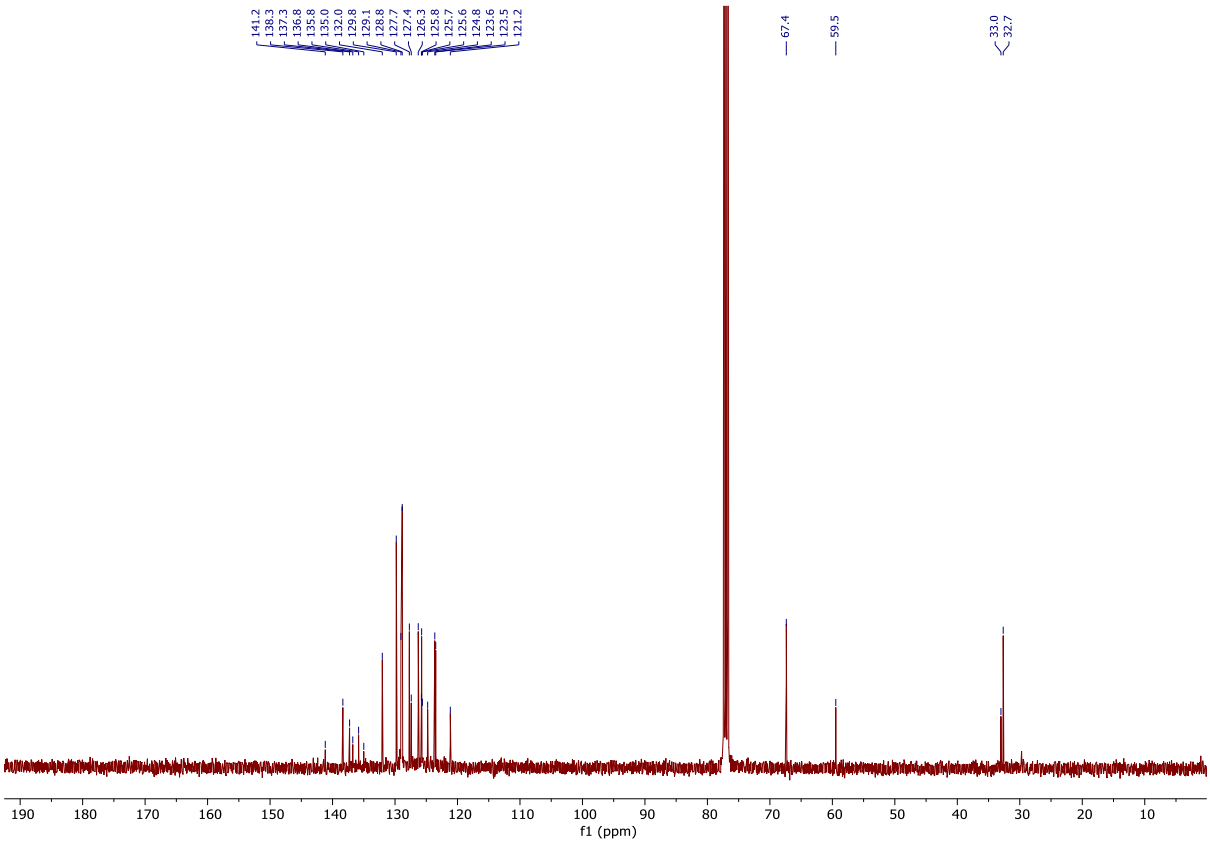
Following the general procedure, product **15** was isolated as an orange oil in 56% yield (30.0 mg, 0.11 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 3:7

$^{1}$H NMR spectrum ($CDCl_3$)



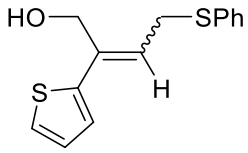

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.37-7.19 (m, 12H), 7.05-7.04 (m, 2H), 6.12 (t, *J* = 8.2 Hz, 1H, 1H m *Z* isomer), 5.90 (t, *J* = 7.9, 1.4 Hz, 1H, 1H M *E* isomer), 4.33 (s, 2H), 4.32 (s, 2H), 3.77 (d, *J* = 8.2 Hz, 2H), 3.67 (d, *J* = 7.8 Hz, 2H).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.2, 138.4, 137.3, 136.8, 135.8, 135.0, 132.0, 129.8 (2C), 129.1 (2C), 128.8 (2C), 127.7, 127.4, 126.3 (2C), 125.8, 125.7, 125.6, 124.8, 123.6, 123.5, 121.2, 67.4, 59.5, 33.0, 32.7.

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{14}H_{14}NaOS_2$, $[M + Na]^+$: 285.0378, found: 285.0380.

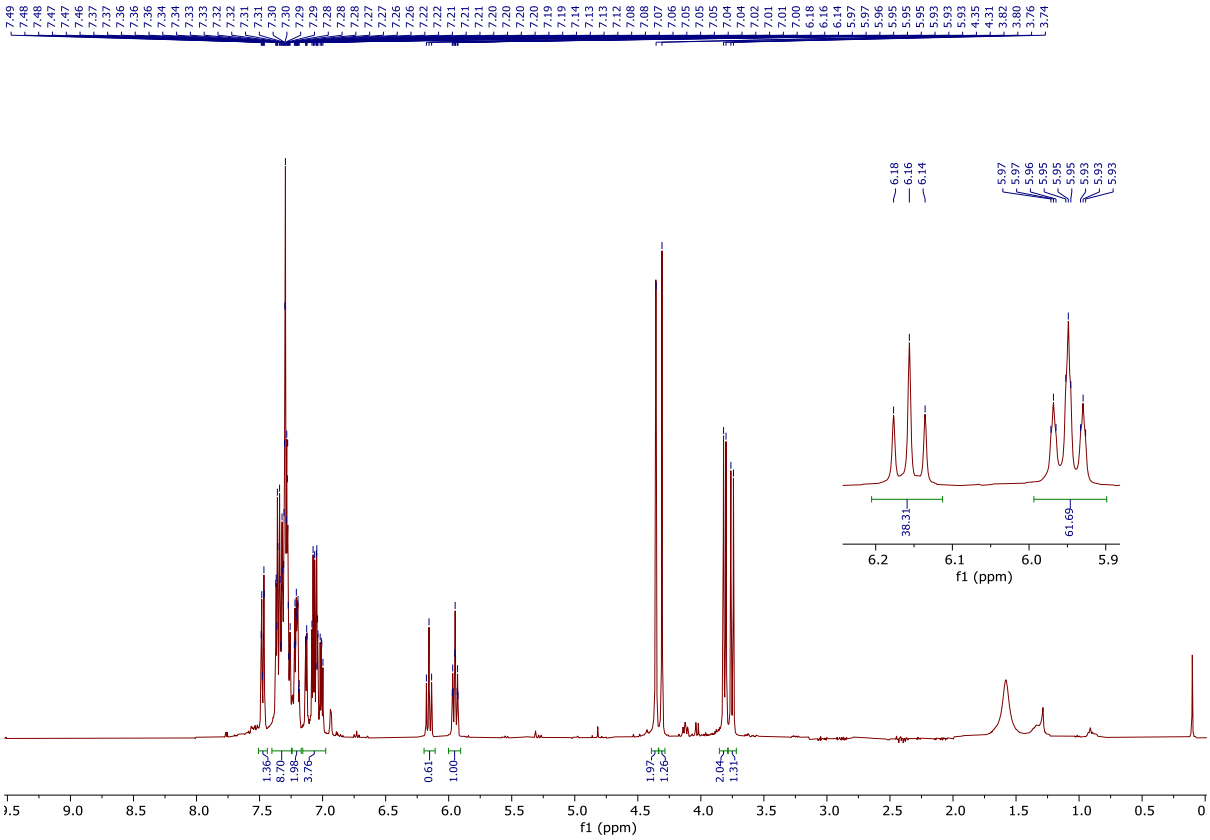



**16**

**4-(phenylthio)-2-(thiophen-2-yl)but-2-en-1-ol**

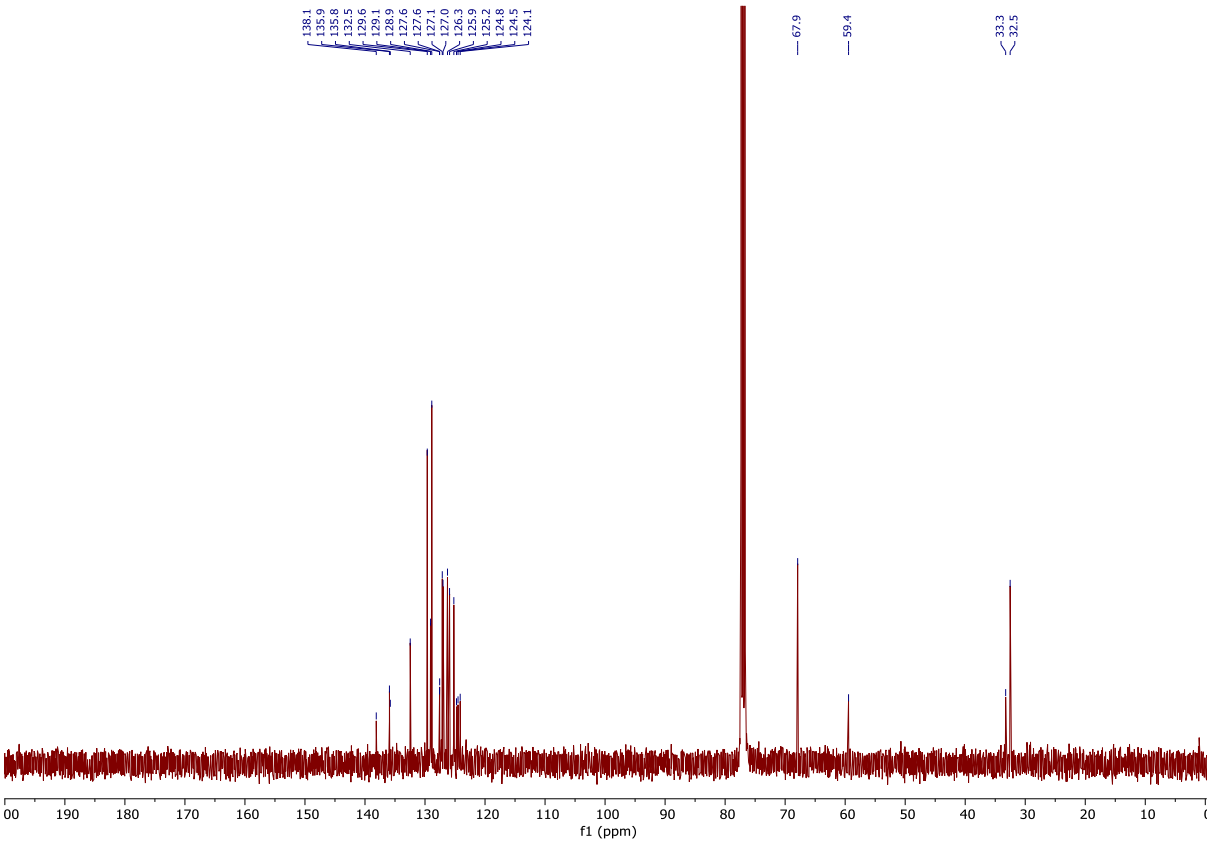
Following the general procedure, product **16** was isolated as a yellow oil in 60% yield (32.1 mg, 0.12 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 4:6

$^{1}$H NMR spectrum ($CDCl_3$)



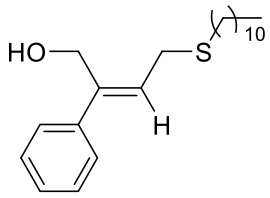

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.37-7.26 (m, 8H), 7.22-7.19 (m, 2H), 7.14-7.00 (m, 4H), 6.16 (t, *J* = 8.2 Hz, 1H, 1H m, *Z* isomer), 5.95 (tt, *J* = 7.7, 1.3 Hz, 1H, 1H m, *E* isomer), 4.35 (s, 2H, 2H M), 4.31 (s, 2H, 2H m), 3.81 (d, *J* = 7.8 Hz, 2H, 2H M), 3.75 (d, *J* = 8.2 Hz, 2H, 2H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.1 (2C), 135.9 (2C), 135.8 (2C), 132.5, 129.6, 129.1, 128.9, 127.6, 127.6, 127.1, 127.0, 126.3, 125.9, 125.2, 124.8, 124.5, 124.1, 67.9, 59.4, 33.3, 32.5.

HRMS (APCI+, MeOH): *m/z* calcd for $C_{14}H_{15}OS_2$, $[M+H]^+$: 263.0559, found: 263.0555.

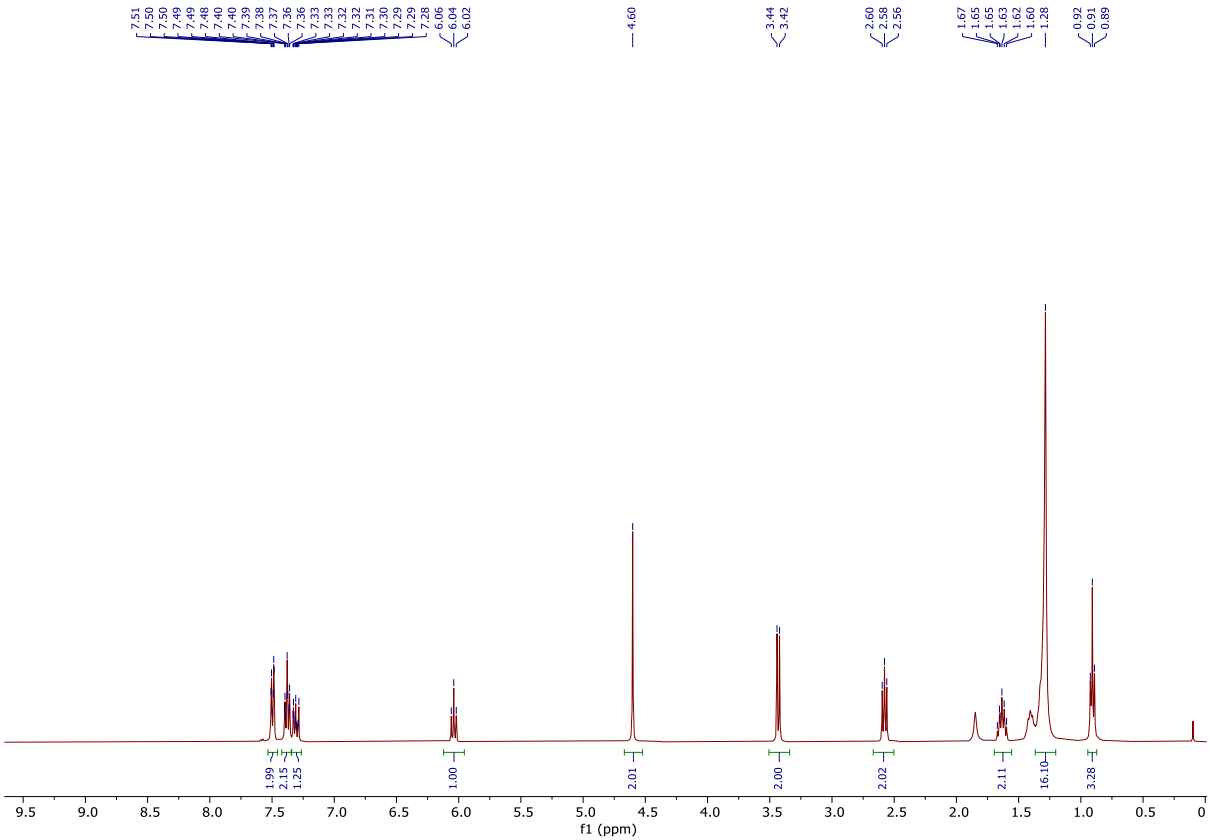



**17**

**(*Z*)-4-(decylthio)-2-phenylbut-2-en-1-ol**

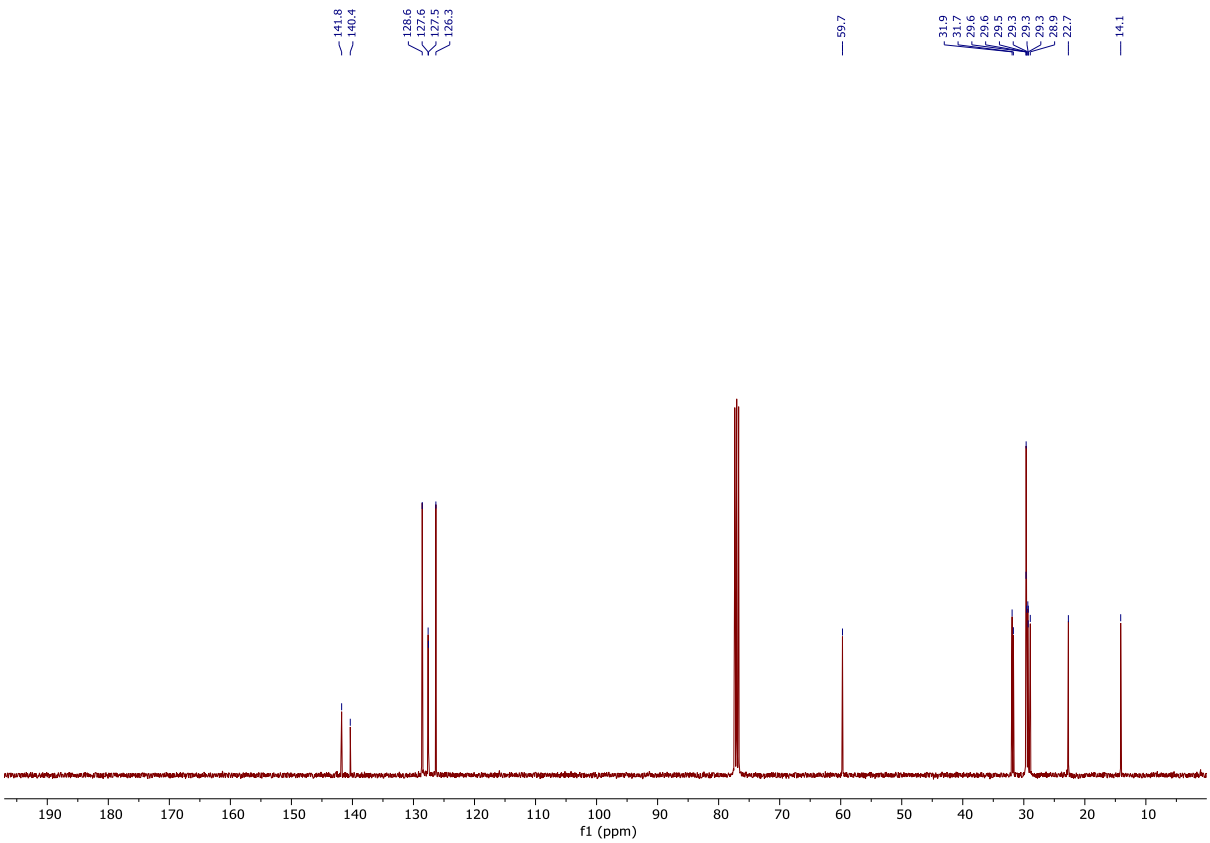
Following the general procedure, product **17** was isolated as a yellow oil in 16% yield (7.0 mg, 0.034 mmol). *Z/E* ratio was determined by $^1$H NMR to be 6:4. Note that only the *Z* isomer was isolated.

$^1$H NMR spectrum ($CDCl_3$)



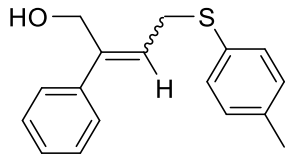

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.40-7.36 (m, 2H), 7.33-7.28 (m, 1H), 6.04 (t, *J* = 8.0 Hz, 1H, *Z* isomer), 4.60 (s, 2H), 3.43 (d, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 1.67-1.60 (m, 2H), 1.28 (m, 16H), 0.91 (t, *J* = 6.7 Hz, 3H).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.8, 140.4, 128.6 (2C), 127.6, 127.5, 126.3 (2C), 59.7, 31.9, 31.7, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 28.9, 22.7, 14.1.

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{21}H_{34}NaOS$, $[M+Na]^+$: 357.2223, found: 357.2230.

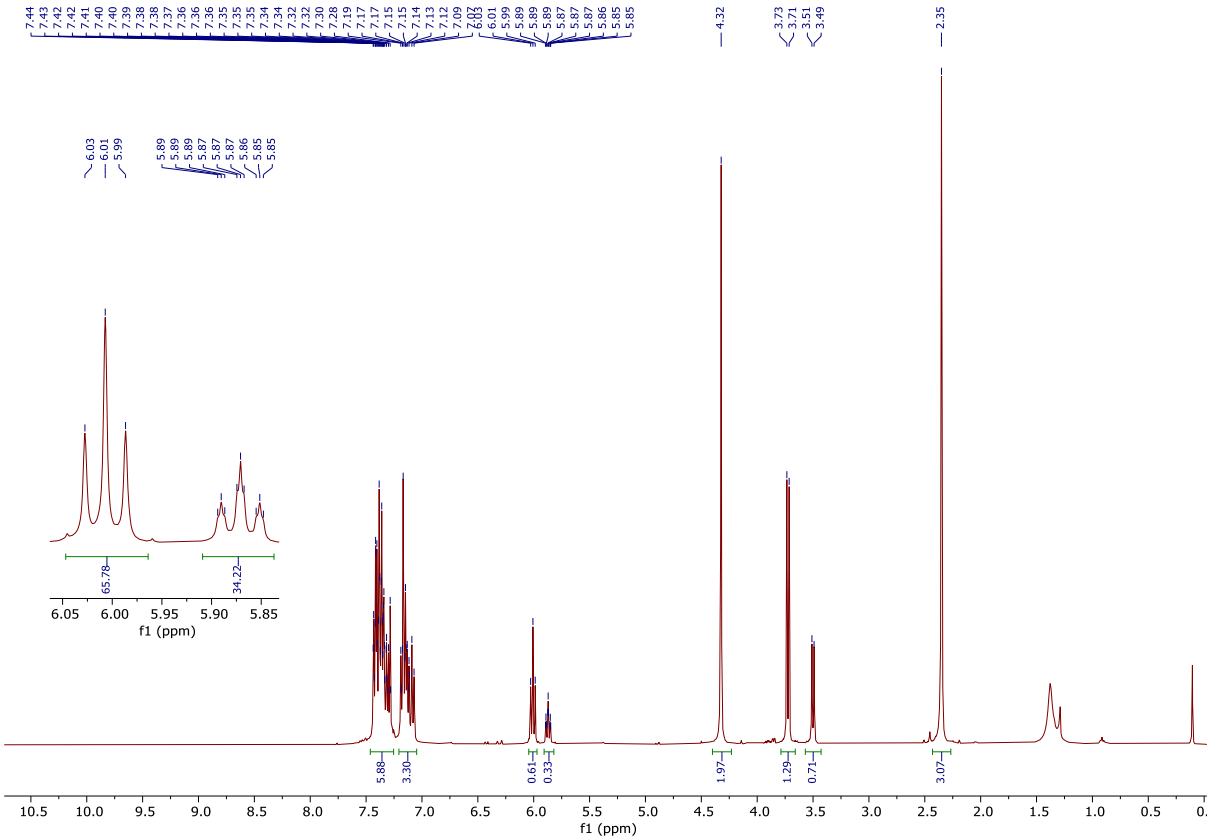



**18**

**2-phenyl-4-(*p*-tolylthio)but-2-en-1-ol**

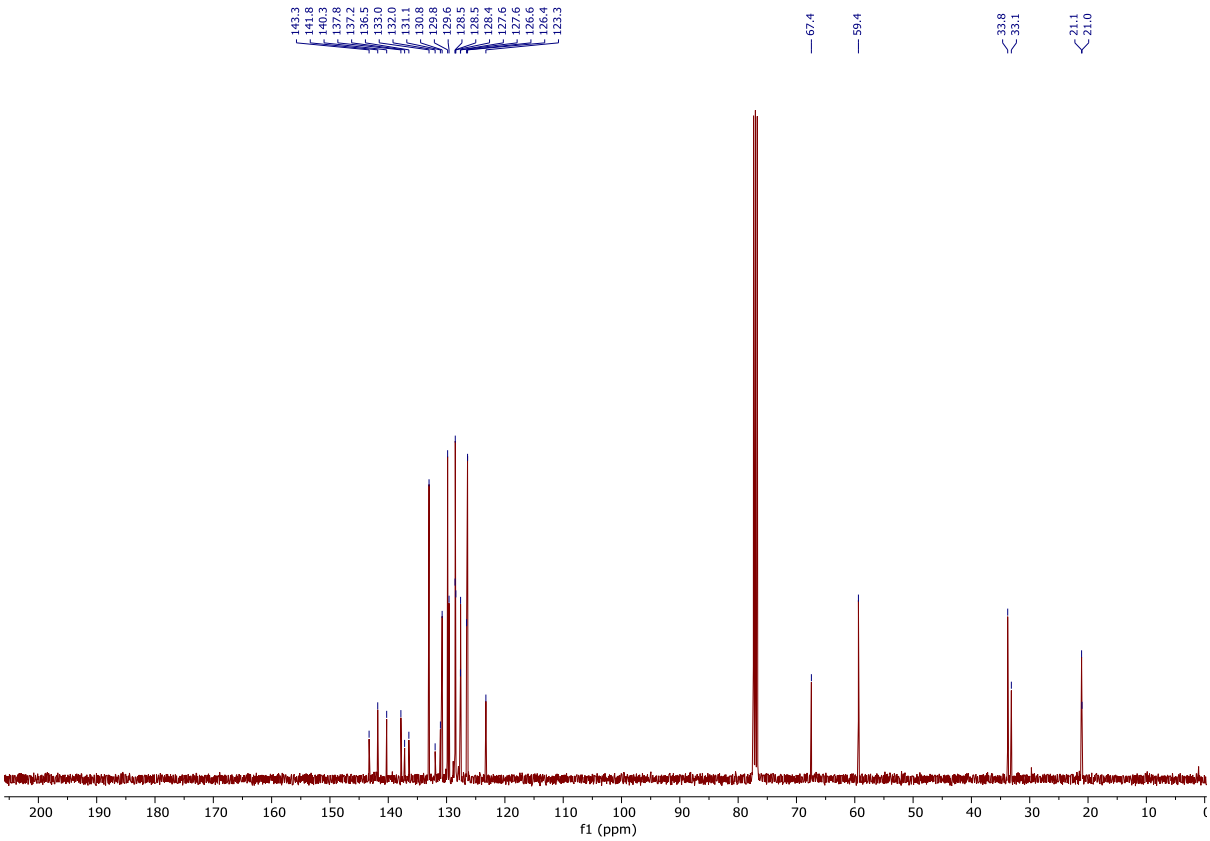
Following the general procedure, product **18** was isolated as a yellow oil in 80% yield (45.4 mg, 0.17 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 7:4

$^{1}$H NMR spectrum ($CDCl_3$)



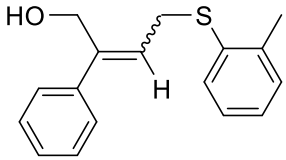

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.28 (m, 12H), 7.19-7.07 (m, 6H), 6.01 (t, *J* = 8.2 Hz, 1H, 1H M, *Z* isomer), 5.87 (tt, *J* = 7.8, 1.4 Hz, 1H, 1H m, *E* isomer), 4.32 (s, 4H, 2H M + 2H m), 3.72 (d, *J* = 8.2 Hz, 2H, 2H M), 3.50 (d, *J* = 7.6 Hz, 2H, 2H m), 2.35 (s, 6H, 3H M + 3H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.3, 141.8, 140.3, 137.8, 137.2, 136.5, 133.0 (2C), 132.0, 131.1, 130.8 (2C), 129.8 (2C), 129.6 (2C), 128.5 (2C), 128.5 (2C), 128.4 (2C), 127.6, 127.6, 126.6, 126.4 (2C), 123.3, 67.4, 59.4, 33.8, 33.2, 21.1, 21.0.

The spectral data correspond to the literature.[3]

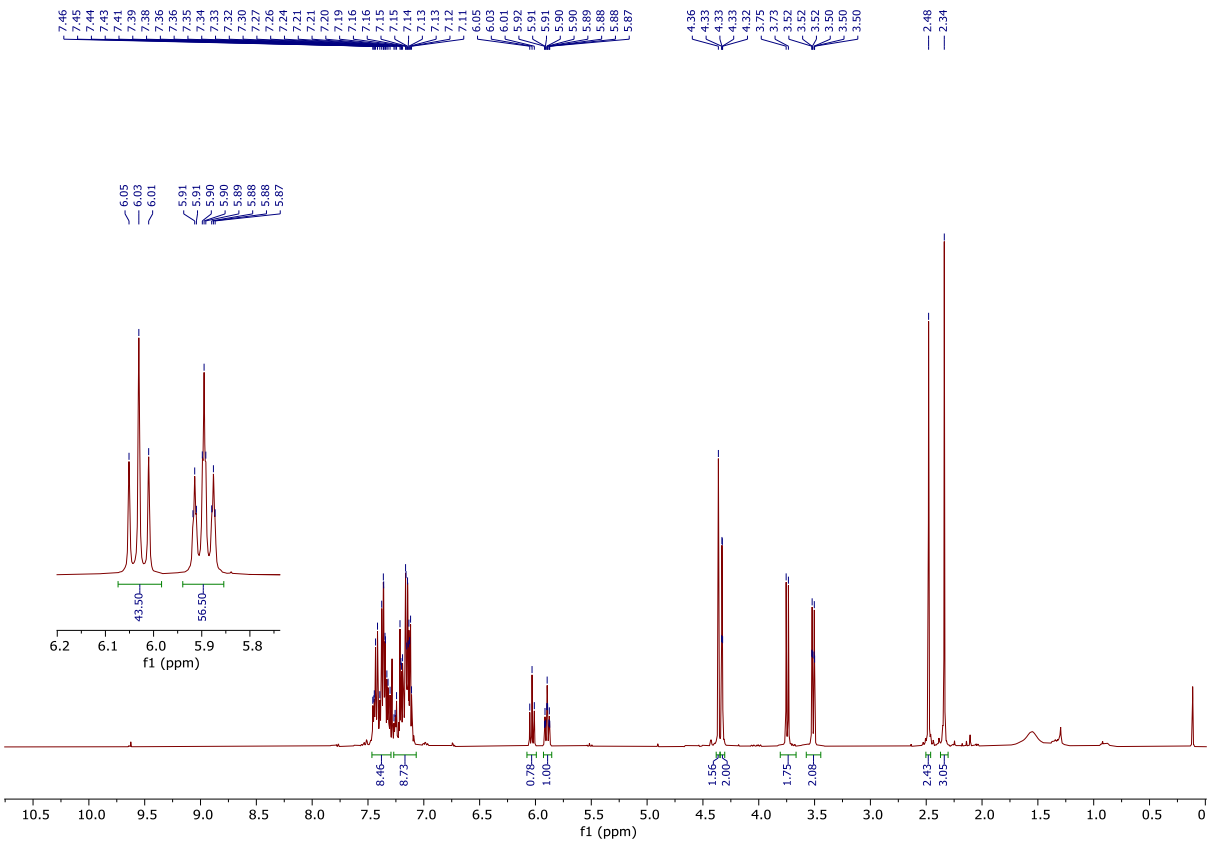



**19**

**2-phenyl-4-(*o*-tolylthio)but-2-en-1-ol**

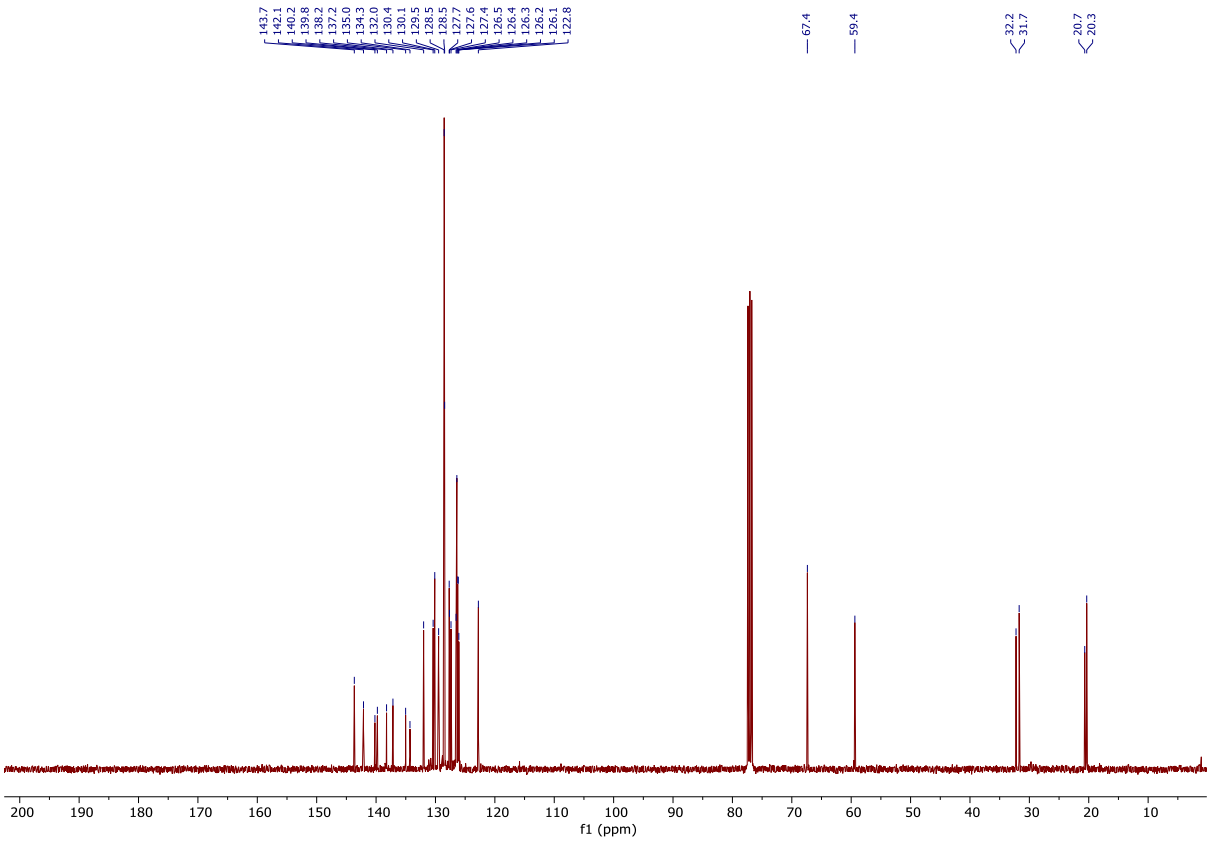
Following the general procedure, product **19** was isolated as a yellow oil in 72% yield (40.8 mg, 0.15 mmol). *Z/E* ratio was determined by $^1$H NMR to be 4:6

$^1$H NMR spectrum ($CDCl_3$)



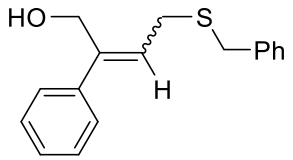

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.30 (m, 8H), 7.27-7.11 (m, 10H), 6.03 (t, *J* = 8.2 Hz, 1 H, 1H m, *Z* isomer), 5.90 (tt, *J* = 7.8, 1.4 Hz, 1 H, 1H M, *E* isomer), 4.36 (s, 2H, 2H m), 4.33 (q, *J* = 1.1 Hz, 2H, 2H M), 3.74 (d, *J* = 8.2 Hz, 2H, 2H m), 3.51 (dt, *J* = 7.8, 1.0 Hz, 2H, 2H M), 2.48 (s, 3H, 3H m), 2.34 (s, 3H, 3H M).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.7, 142.1, 140.2, 139.8, 138.2, 137.2, 135.0, 134.3, 132.0, 130.4, 130.1, 129.5, 128.5 (4C), 128.5 (2C), 127.7, 127.6, 127.4, 126.5, 126.4 (2C), 126.3, 126.2, 126.1, 122.8, 67.4, 59.4, 32.2, 31.7, 20.7, 20.3.

The spectral data correspond to the literature.[3]

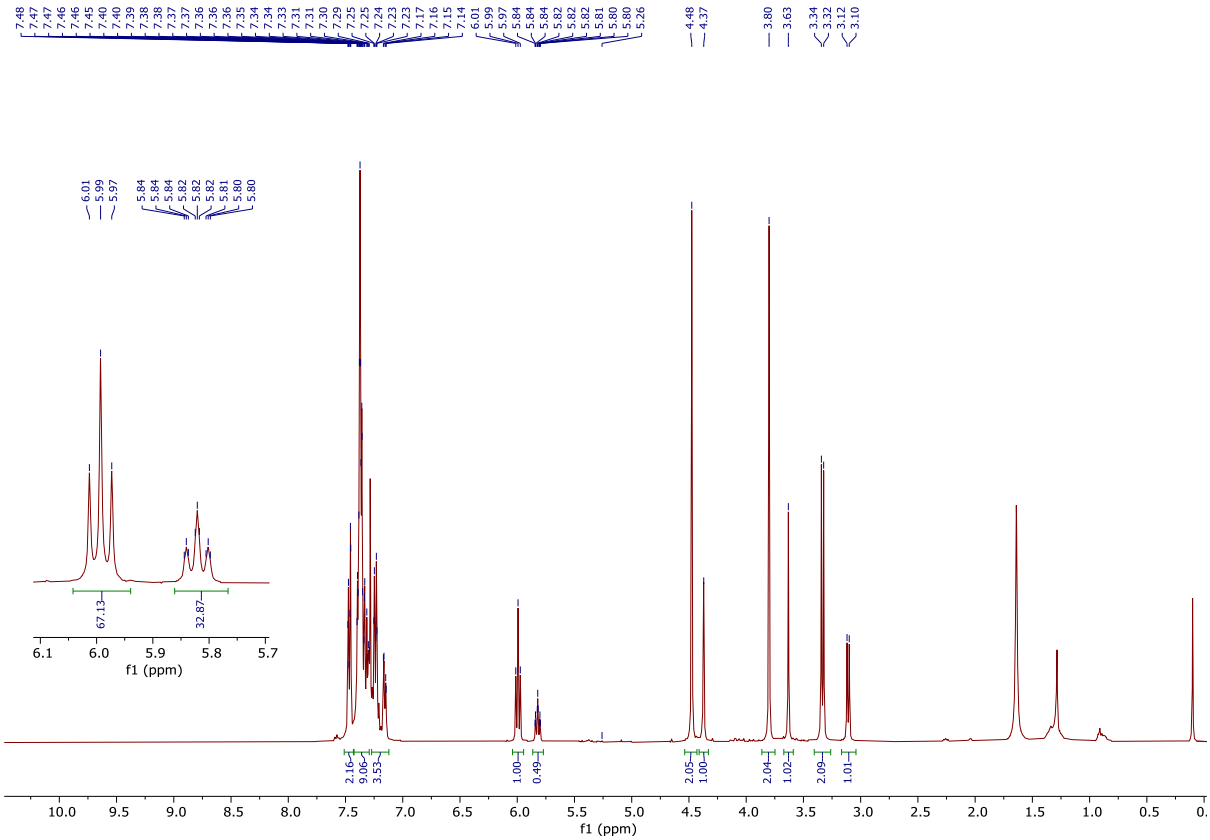



**20**

**4-(benzylthio)-2-phenylbut-2-en-1-ol**

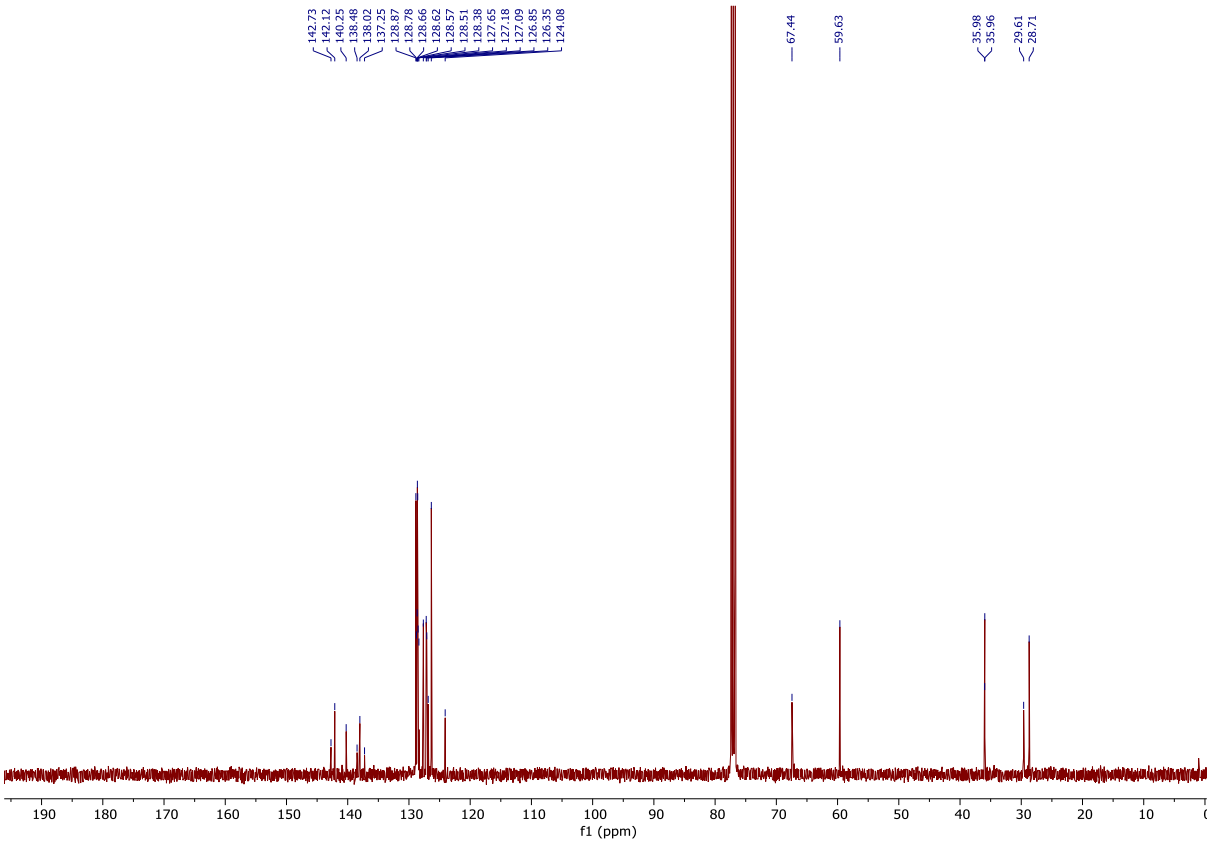
Following the general procedure, product **20** was isolated as a yellow oil in 79% yield (44.8 mg, 0.17 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 7:3

$^{1}$H NMR spectrum ($CDCl_3$)



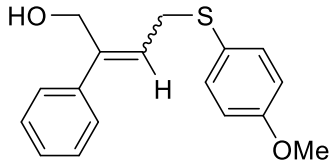

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 4H), 7.40-7.29 (m, 12H), 7.25-7.14 (m, 4H), 5.99 (t, *J* = 8.0 Hz, 1 H, 1H M, *Z* isomer ), 5.82 (tt, *J* = 7.8, 1.5 Hz, 1H, 1H m, *E* isomer), 4.48 (s, 2H, 2H M), 4.37 (s, 2H, 2H m), 3.80 (s, 2H, 2H M), 3.63 (s, 2H, 2H m), 3.33 (d, *J* = 8.0 Hz, 2H, 2H M), 3.11 (d, *J* = 7.8 Hz, 2H, 2H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 142.7, 142.1, 140.3, 138.5, 138.0, 137.3, 128.9 (2C), 128.8 (2C), 128.7 (2C), 128.6 (2C), 128.6 (2C), 128.5 (2C), 128.4, 127.7 (2C), 127.6, 127.2, 127.1, 126.9, 126.3 (2C), 124.1, 67.4, 59.6, 36.0, 35.9, 29.6, 28.7.

The spectral data correspond to the literature.[3]

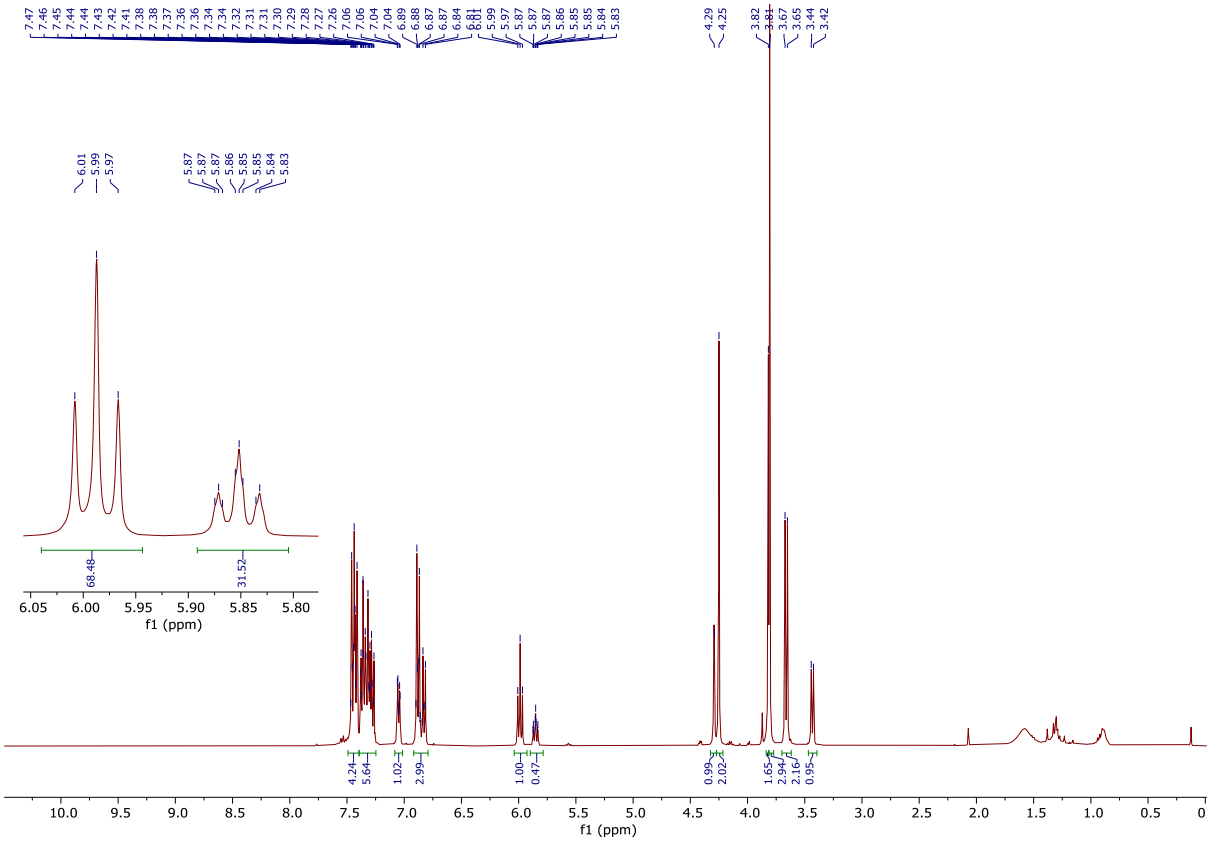



**21**

**4-((4-methoxyphenyl)thio)-2-phenylbut-2-en-1-ol**

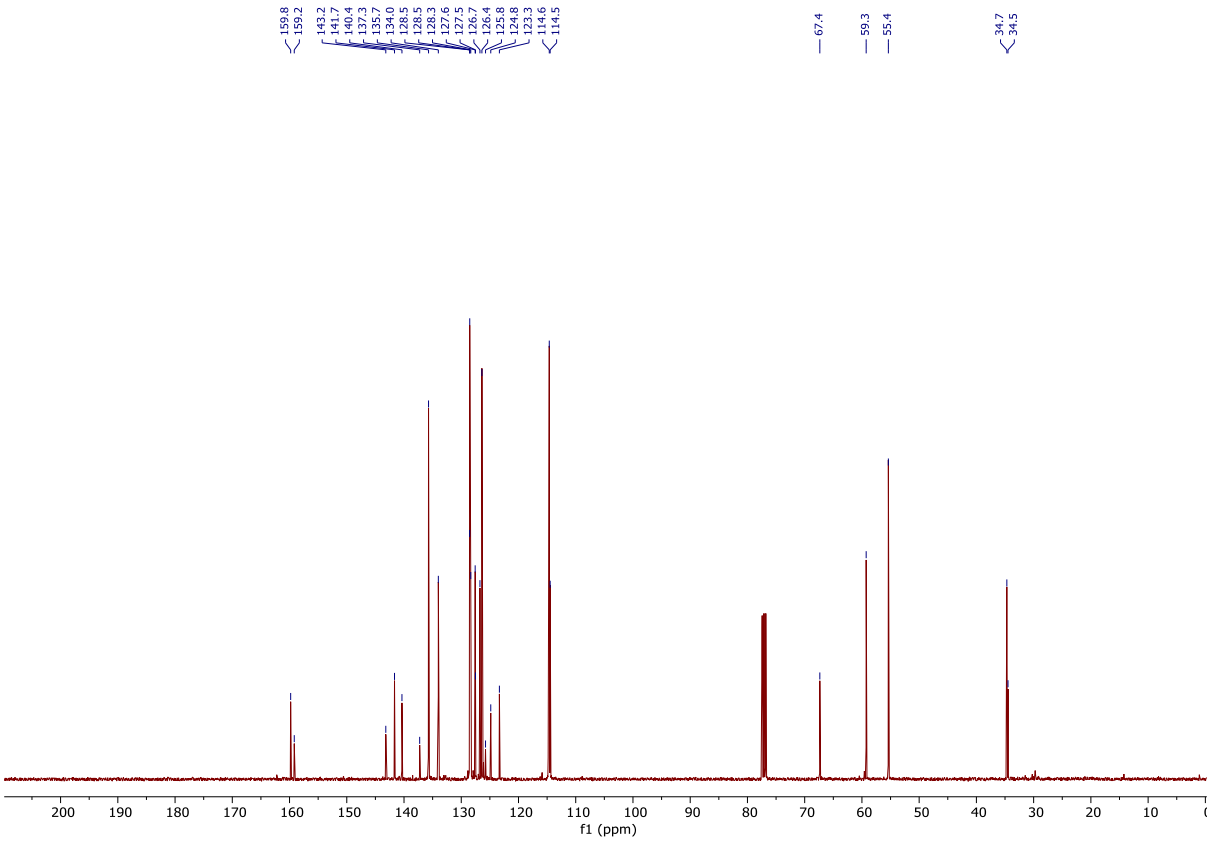
Following the general procedure, product **21** was isolated as a yellow oil in 68% yield (40.8 mg, 0.14 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 7:3

$^{1}$H NMR spectrum ($CDCl_3$)



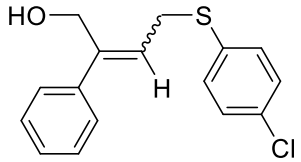

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.41 (m, 6H), 7.38-7.26 (m, 6H), 7.06-7.04 (m, 2H), 6.90-6.81 (m, 4H), 5.99 (t, *J* = 8.2 Hz, 1H, 1H M, *Z* isomer), 5.85 (tt, *J* = 7.8, 1.4 Hz, 1H, 1H m, *E* isomer), 4.29 (s, 2H, 2H m), 4.25 (s, 2H, 2H M), 3.82 (s, 3H, 3H m), 3.81 (s, 3H, 3H M), 3.66 (d, *J* = 8.2 Hz, 2H, 2H M), 3.43 (d, *J* = 7.7 Hz, 2H, 2H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.8, 159.2, 143.2, 141.7, 140.4, 137.3, 135.7 (2C), 134.0 (2C), 128.5 (2C), 128.5 (2C), 128.3 (2C), 127.6 (2C), 127.5, 126.7 (2C), 126.4 (2C), 125.8, 124.9, 123.3, 114.6, 114.5, 67.4, 59.3, 55.4 (2C), 34.7, 34.5.

The spectral data correspond to the literature.[3]

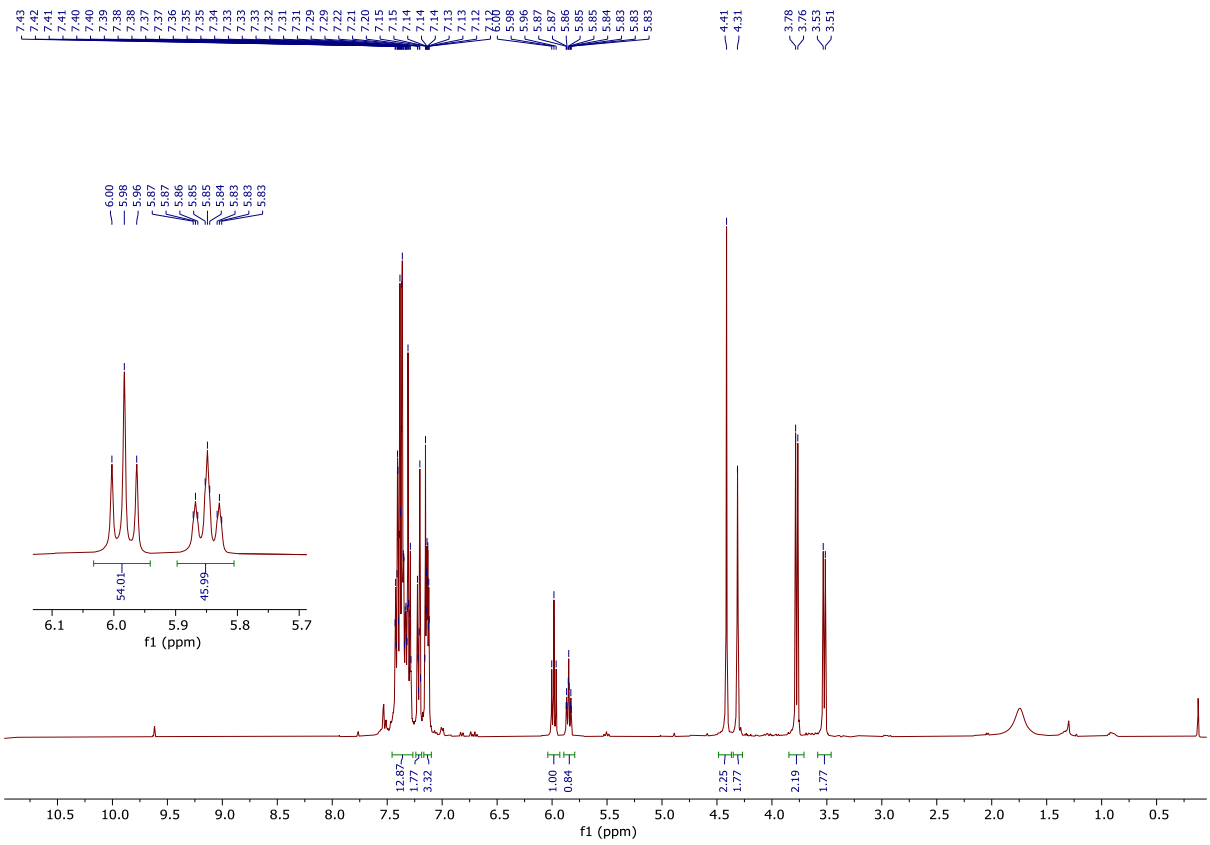



**22**

**4-((4-chlorophenyl)thio)-2-phenylbut-2-en-1-ol**

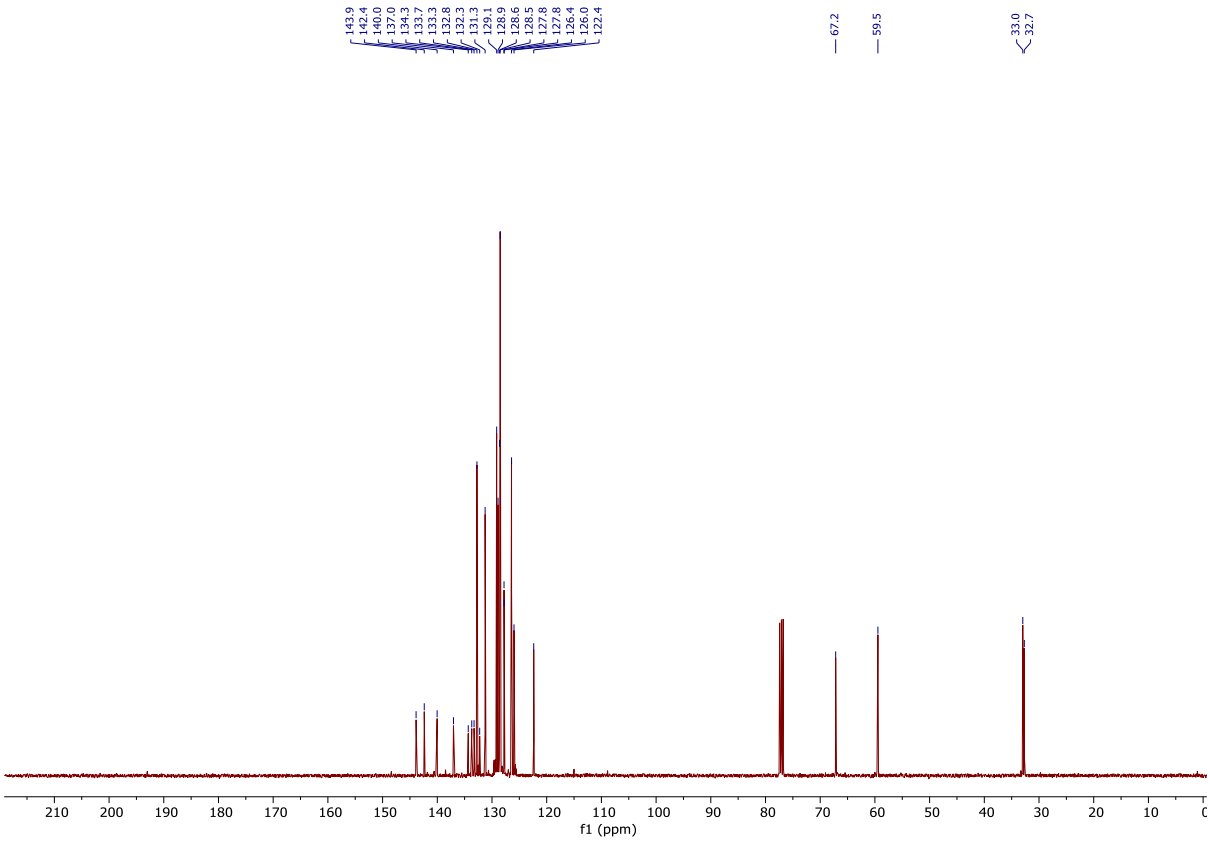
Following the general procedure, product **22** was isolated as a yellow oil in 82% yield (49.9 mg, 0.17 mmol). *Z/E* ratio was determined by $^1$H NMR to be 1:1

$^1$H NMR spectrum ($CDCl_3$)



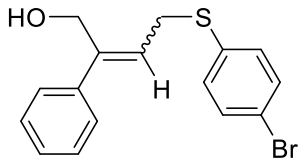

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.28 (m, 12H), 7.22-7.20 (m, 2H), 7.16-7.12 (m, 4H), 5.98 (t, *J* = 8.0 Hz, 1 H, 1H M, *Z* isomer), 5.85 (tt, *J* = 7.7, 1.5 Hz, 1H, 1H m, *E* isomer), 4.41 (s, 2H, 2H M), 4.31 (s, 2H, 2H m), 3.77 (d, *J* = 8.1 Hz, 2H, 2H M), 3.52 (d, *J* = 7.7 Hz, 2H, 2H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.9, 142.4, 140.0, 137.0, 134.3, 133.7, 133.3, 132.8 (2C), 132.3, 131.3 (2C), 129.1, (2C) 128.9 (2C), 128.6 (2C), 128.5 (4C), 127.8, 127.8, 126.4 (2C), 126.0, 122.4, 67.2, 59.5, 33.0, 32.7.

HRMS (APCI+, MeOH): *m*/*z* calcd for $C_{16}H_{14}ClS$, $[M–CH_3OH]^+$: 273.0499, found: 273.0495.

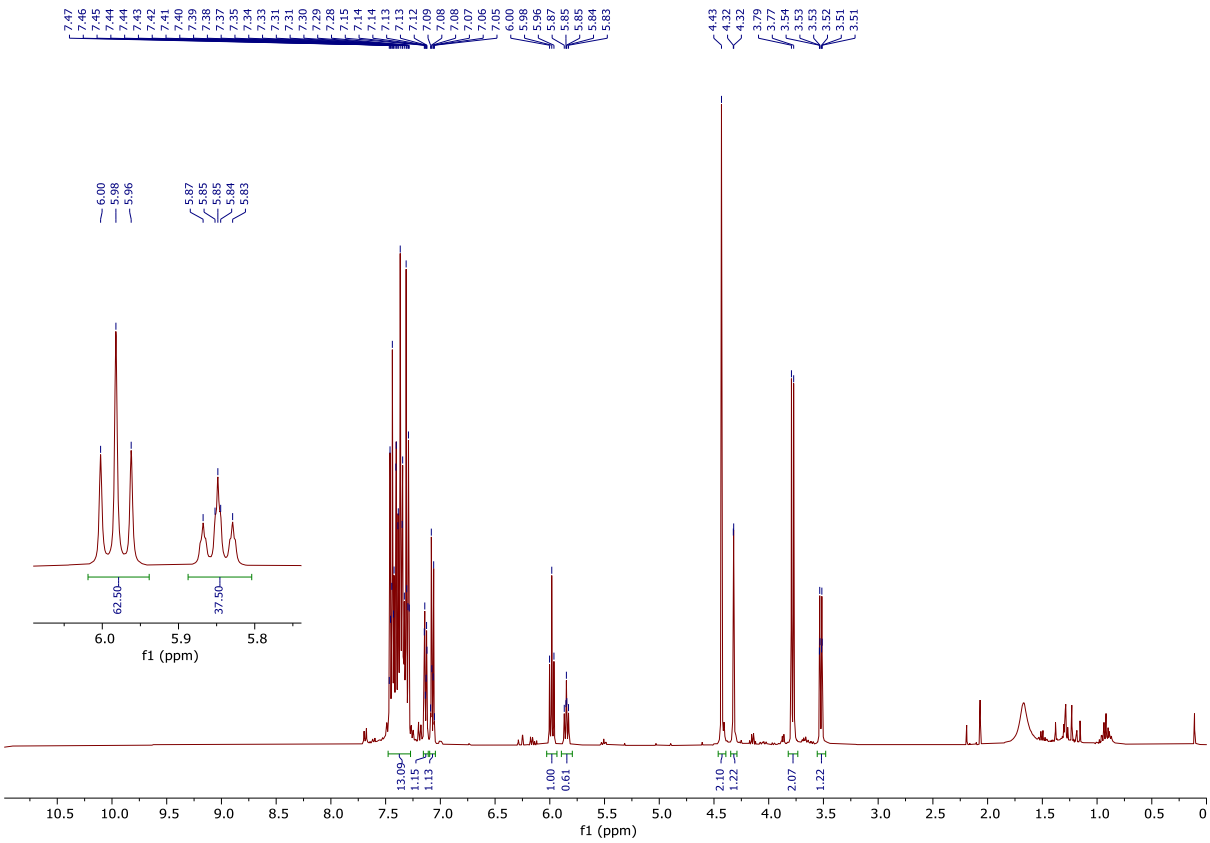



**23**

**4-((4-bromophenyl)thio)-2-phenylbut-2-en-1-ol**

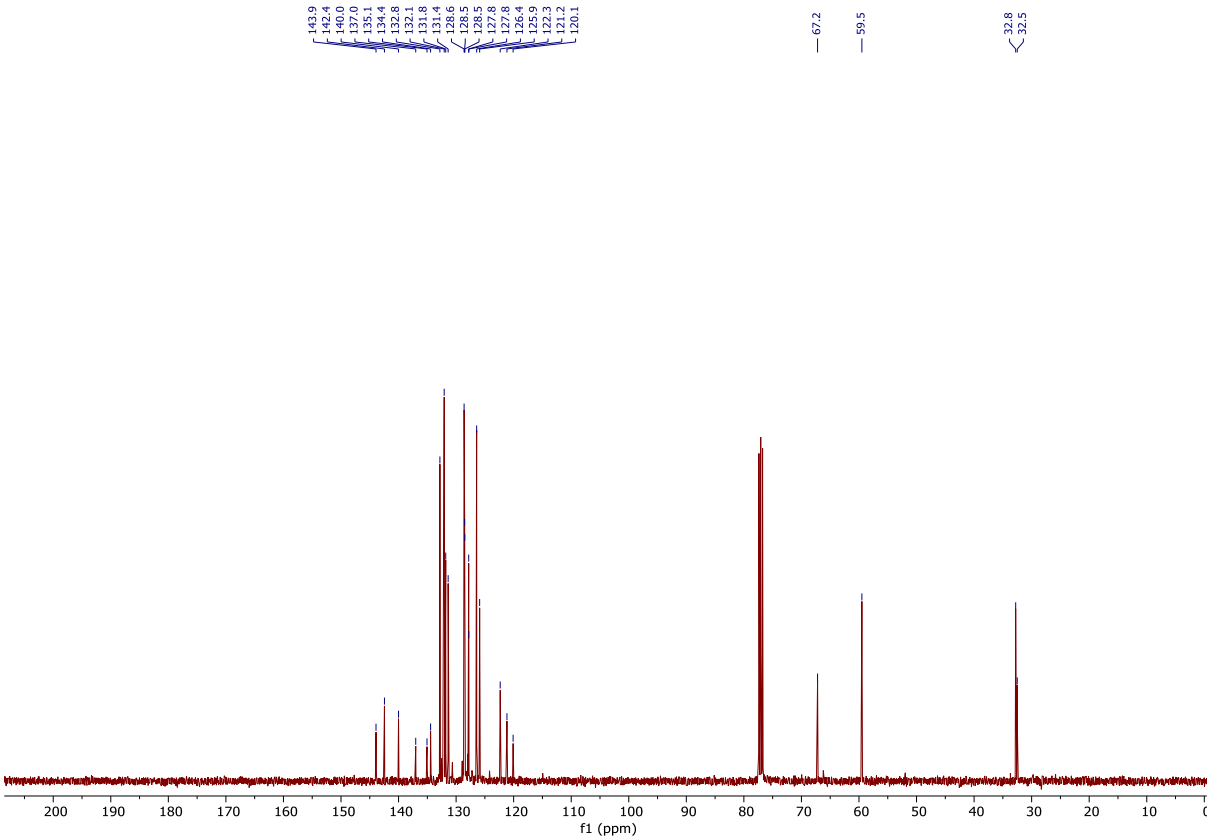
Following the general procedure, product **23** was isolated as a yellow oil in 71% yield (49.8 mg, 0.15 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 6:4

$^{1}$H NMR spectrum ($CDCl_3$)



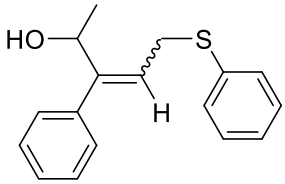

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.28 (m, 14H), 7.15-7.12 (m, 2H), 7.09-7.05 (m, 2H), 5.98 (t, *J* = 8.0 Hz, 1H, 1H M, *Z* isomer), 5.85 (tt, *J* = 7.7, 1.5 Hz, 1H, 1H m, *E* isomer), 4.43 (s, 2H, 2H M), 4.32 (m, 2H, 2H m), 3.78 (d, *J* = 8.1 Hz, 2H, 2H M), 3.52 (dt, *J* = 7.7, 1.0 Hz, 2H, 2H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.9, 142.5, 140.0, 137.0, 135.1, 134.4, 132.8 (2C), 132.1 (2C), 131.8 (2C), 131.4 (2C), 128.6 (2C), 128.5 (2C), 128.5 (2C), 127.8, 127.8, 126.4 (2C), 125.9, 122.3, 121.2, 120.1, 67.2, 59.5, 32.8, 32.5.

The spectral data correspond to the literature.[3]

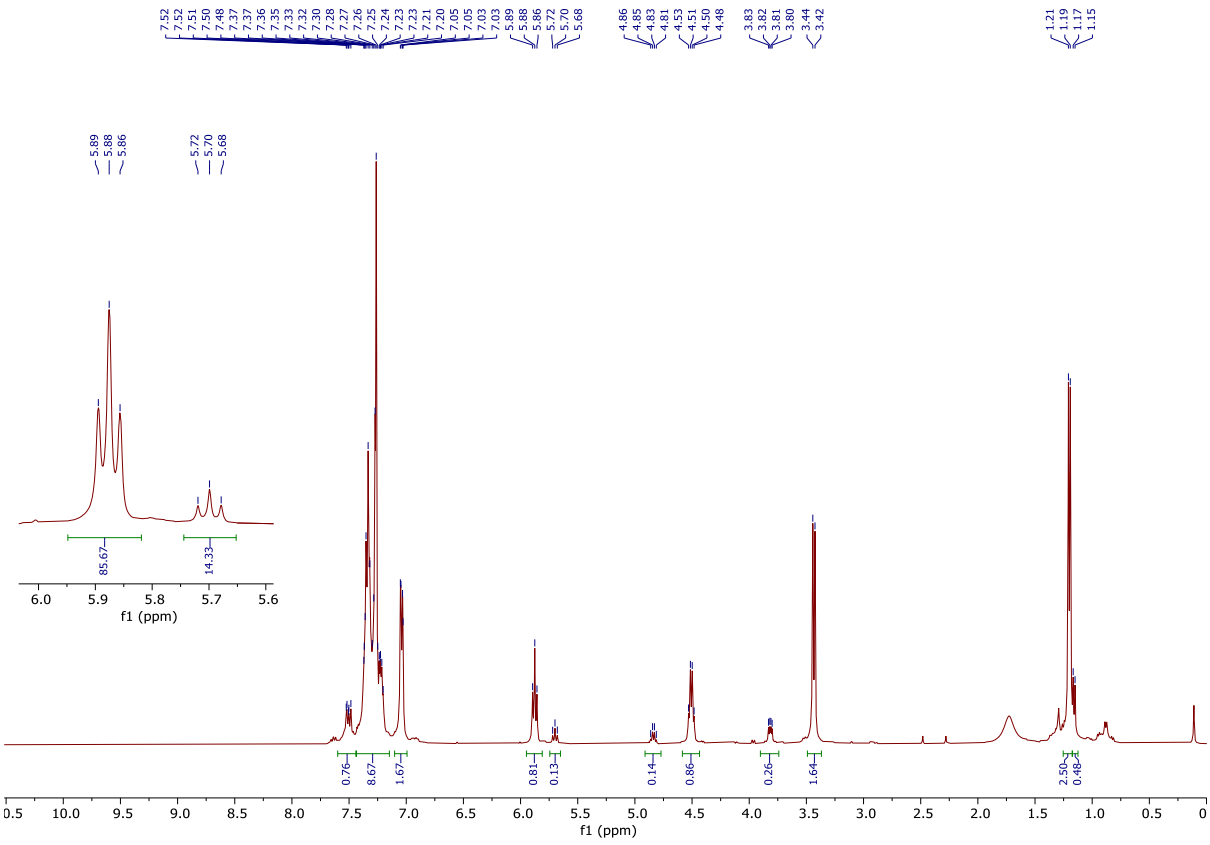



**24**

**3-phenyl-5-(phenylthio)pent-3-en-2-ol**

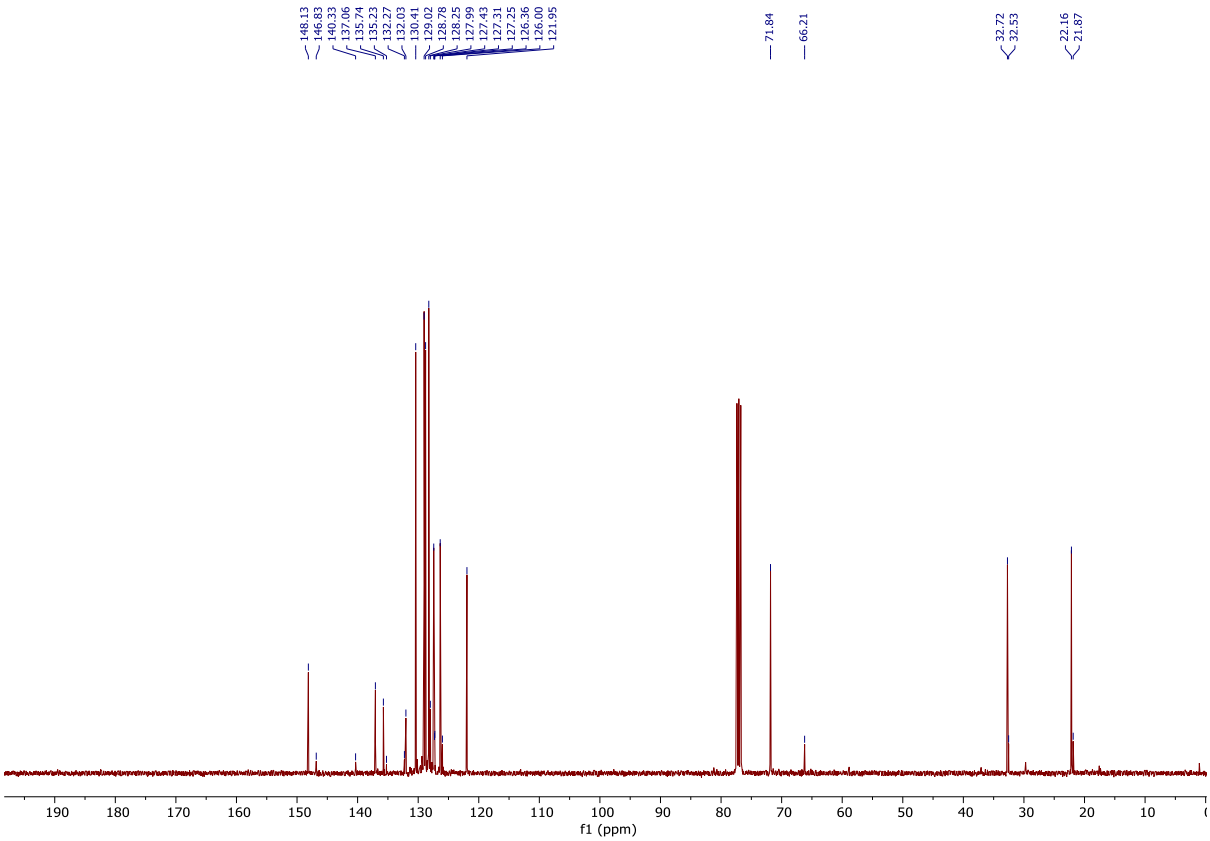
Following the general procedure, product **24** was isolated as a gray oil in 64% yield (33.9 mg, 0.13 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 2:9

$^{1}$H NMR spectrum ($CDCl_3$)



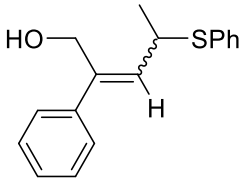

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.37-7.20 (m, 14H), 7.05-7.03 (m, 4H), 5.88 (t, *J* = 7.6 Hz, 1H, 1H M, *E* isomer), 5.70 (t, *J* = 8.2 Hz, 1H, 1H m, *Z* isomer), 4.84 (q, *J* = 6.6 Hz, 1H, 1H m), 4.51 (q, *J* = 6.4 Hz, 1H, 1H M), 3.81 (dd, *J* = 8.1, 4.3 Hz, 2H, 2H m), 3.43 (d, *J* = 7.7 Hz, 2H, 2H M), 1.20 (d, *J* = 6.4 Hz, 3H, 3H M), 1.16 (d, *J* = 6.5 Hz, 3H, 3H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 148.1, 146.8, 140.3, 137.1, 135.7, 135.2, 132.3, 132.0 (2C), 130.4 (2C), 129.0 (2C), 128.8 (2C), 128.3 (2C), 128.2 (2C), 128.0 (2C), 127.4, 127.3 (2C), 127.2, 126.4, 126.0, 122.0, 71.8, 66.2, 32.7, 32.5, 22.2, 21.9.

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{17}H_{18}NaOS$, $[M + Na]^+$: 293.0971, found: 293.0973.

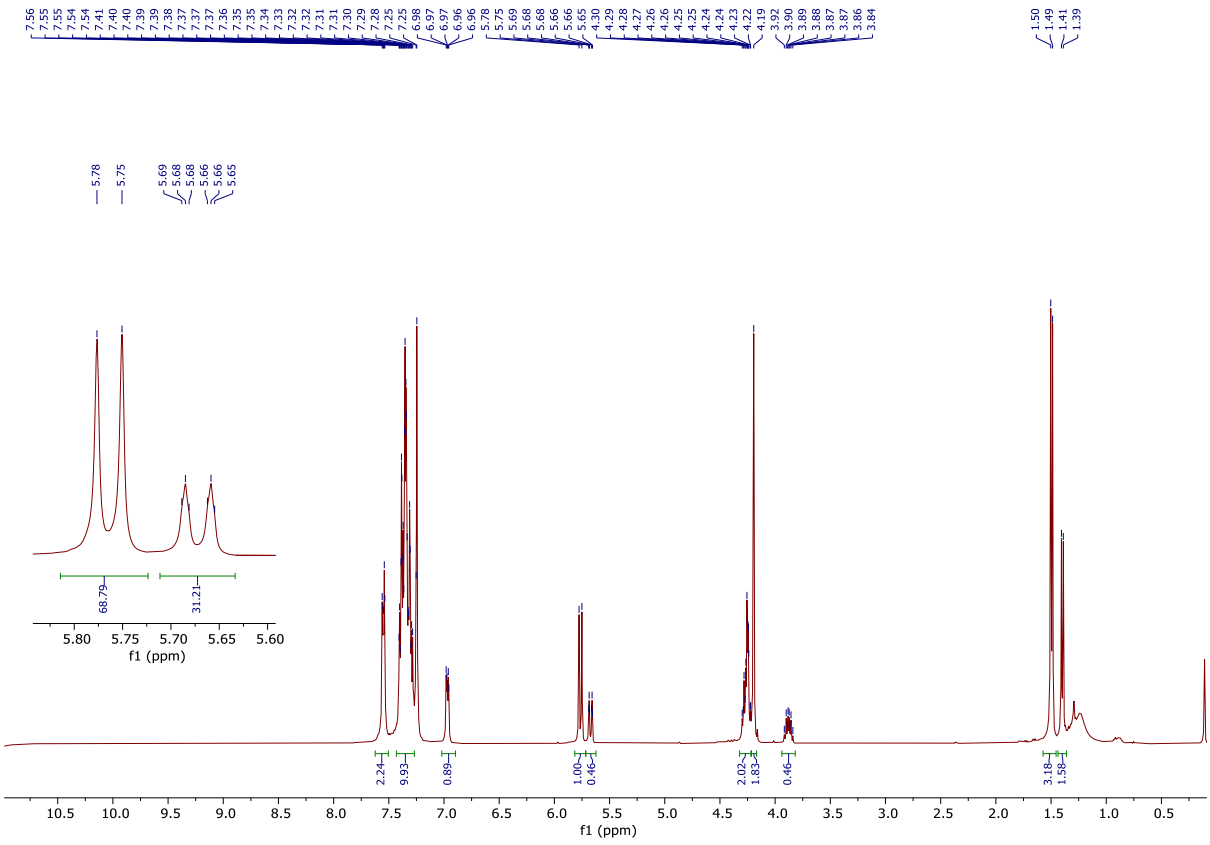



**25**

**2-phenyl-4-(phenylthio)pent-2-en-1-ol**

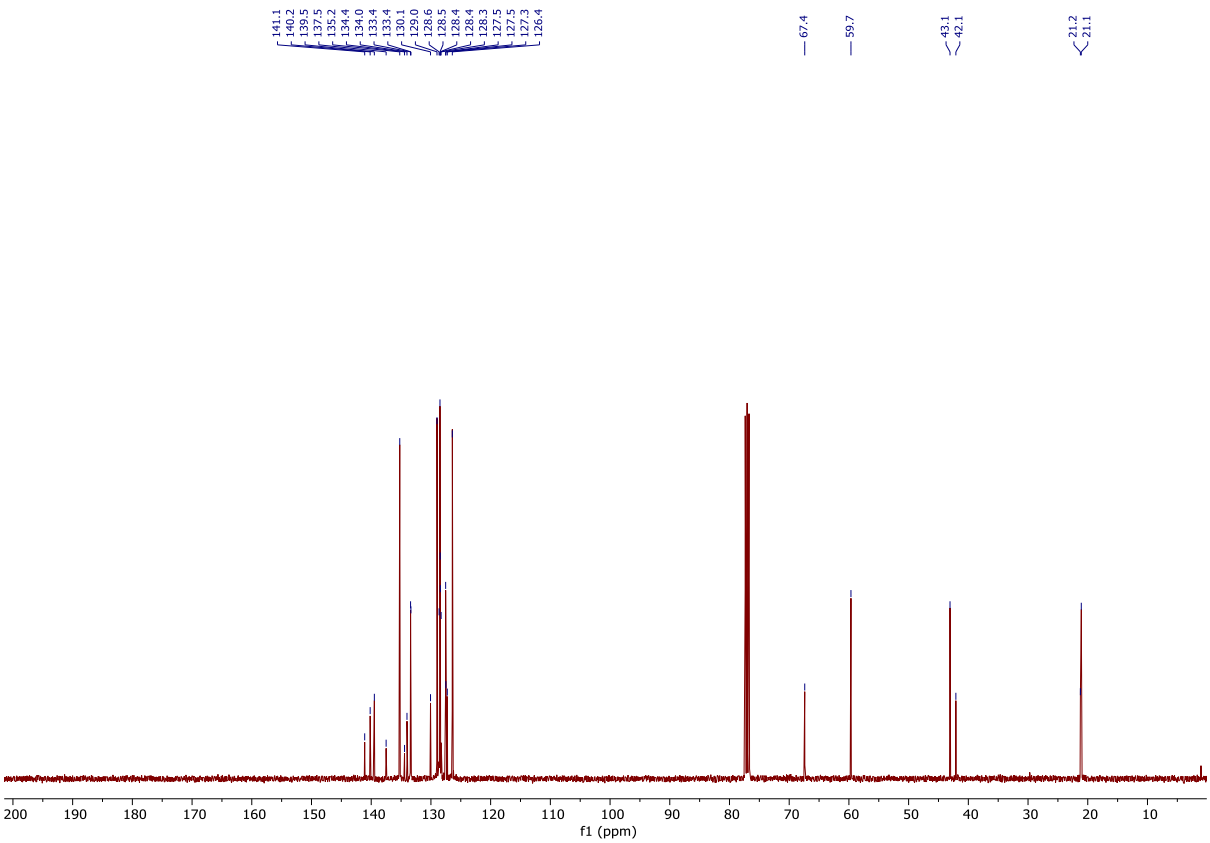
Following the general procedure, product **25** was isolated as a yellow oil in 63% yield (33.3 mg, 0.12 mmol). *Z/E* ratio was determined by $^{1}$H NMR to be 7:3

$^{1}$H NMR spectrum ($CDCl_3$)



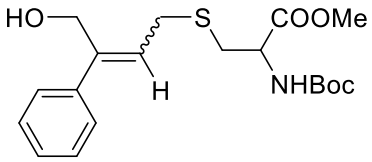

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 4H), 7.41-7.25 (m, 14H), 6.98-6.96 (m, 2H), 5.76 (d, *J* = 10.4 Hz, 1H, 1H M, *Z* isomer), 5.67 (dt, *J* = 10.6, 1.5 Hz, 1H, 1H m, *E* isomer), 4.30 – 4.22 (m, 2H, 2H M), 4.18 (m, 3H, 1H M + 2H m), 3.88 (dq, *J* = 10.5, 6.8 Hz, 1H, 1H m), 1.49 (d, *J* = 6.6 Hz, 3H, 3H M), 1.40 (d, *J* = 6.8 Hz, 3H, 3H m).

$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.1, 140.2, 139.5, 137.5, 135.2 (2C), 134.4, 134.0, 133.4 (2C), 133.4 (2C), 130.1, 129.0 (2C), 128.6, 128.5 (2C), 128.4 (2C), 128.4, 128.3, 127.5 (2C), 127.5, 127.3, 126.4 (2C), 67.4, 59.7, 43.1, 42.1, 21.2, 21.1.

HRMS (ESI+, MeOH): *m/z* calcd for $C_{17}H_{18}NaOS$, $[M + Na]^+$: 293.0971, found: 293.0970.

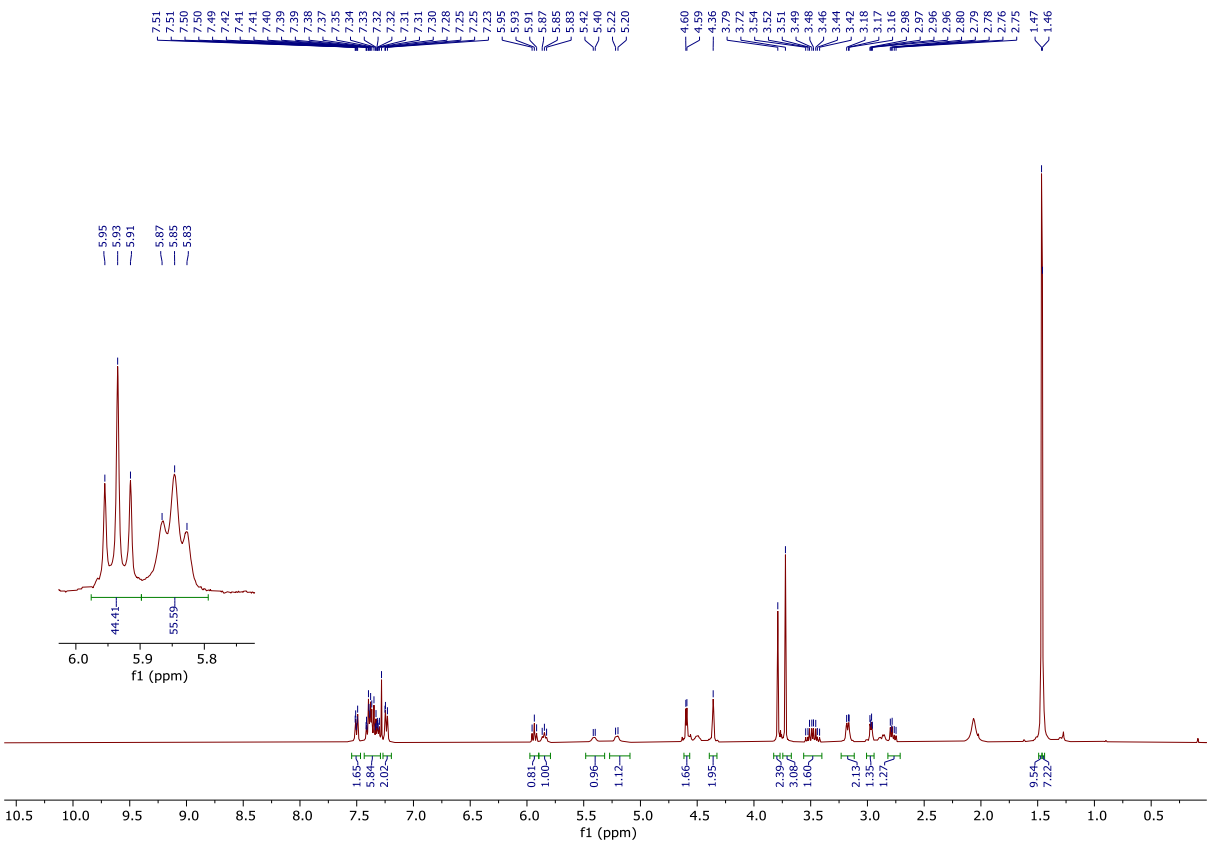



**26**

**Methyl-*N*-(*tert*-butoxycarbonyl)-*S*-(4-hydroxy-3-phenylbut-2-en-1-yl)cysteinate**

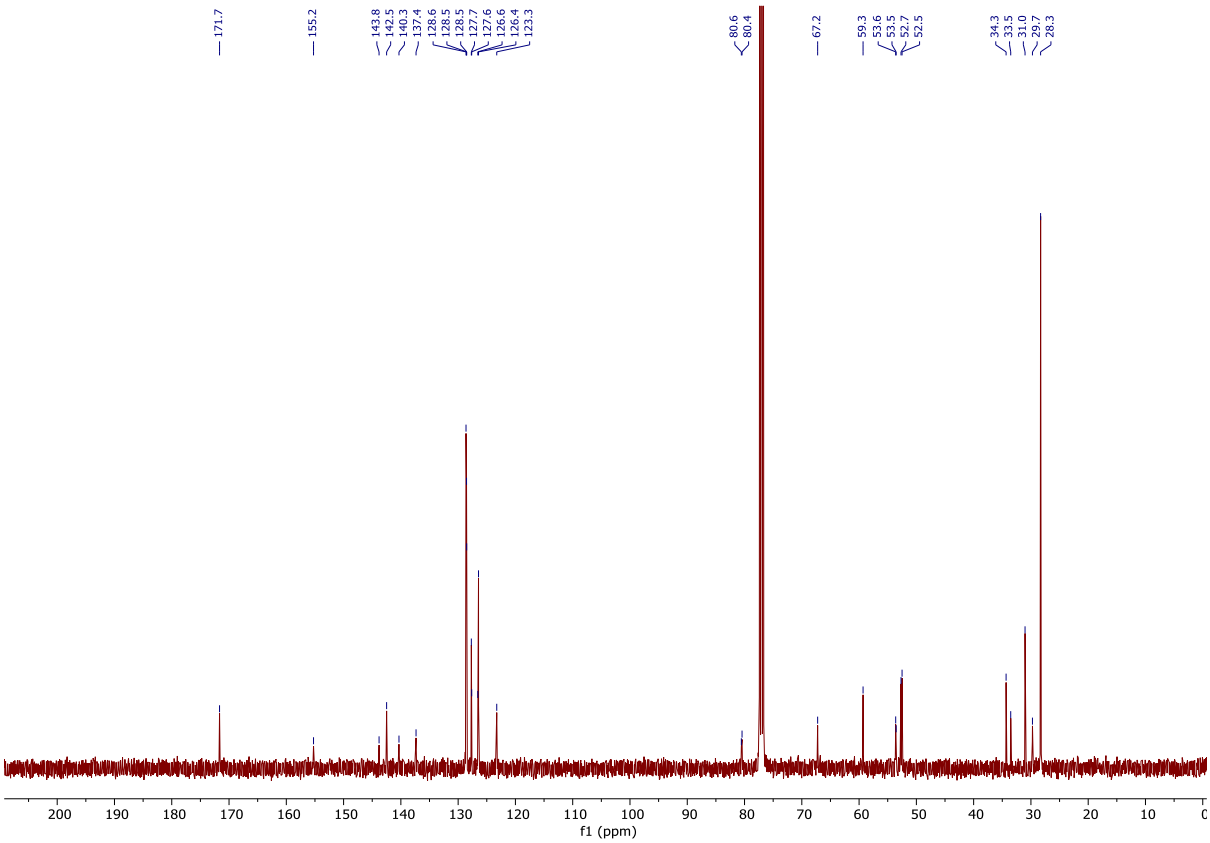
Following the general procedure, product **26** was isolated as a yellow oil in 26% yield (20.8 mg, 0.05 mmol). *Z/E* ratio was determined by $^1$H NMR to be 4:6

$^1$H NMR spectrum ($CDCl_3$)




**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.42-7.30 (m, 6H), 7.25-7.23 (m, 2H), 5.93 (t, *J* = 8.0 Hz, 1H, 1H M, *Z* isomer), 5.85 (t, *J* = 7.8 Hz, 1H, 1H m, *E* isomer), 5.41 (d, *J* = 7.0 Hz, 1H, 1H m), 5.21 (d, *J* = 8.6 Hz, 1H, 1H M), 4.60 (d, *J* = 3.7 Hz, 2H, 2H m), 4.36 (s, 2H, 2H M), 3.79 (s, 3H, 3H m), 3.72 (s, 3H, 3H M), 3.48 (qd, *J* = 13.6, 8.0 Hz, 2H, 2H m), 3.18 – 3.16 (m, 2H, 2H M), 2.97 (dd, *J* = 5.8, 2.8 Hz, 2H, 2H M), 2.77 (dd, *J* = 13.8, 6.4 Hz, 2H, 2H m), 1.47 (s, 9H, 9H M), 1.46 (s, 9H, 9H m).

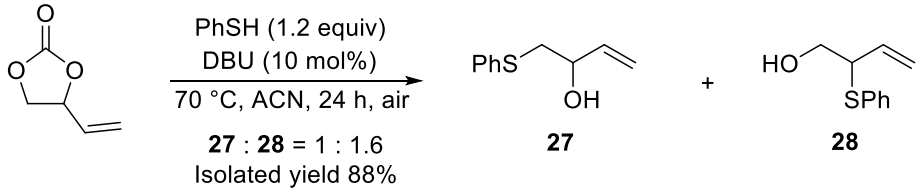
$^{13}$C NMR spectrum ($CDCl_3$)



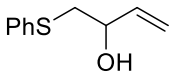

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 171.7 (2C=O), 155.2, 143.8, 142.5 (2Cq), 140.3, 137.4, 128.6 (2C), 128.5 (2C), 128.5 (2C), 127.7, 127.6, 126.6, 126.4 (2C), 123.3, 80.6, 80.4, 67.2, 59.3, 53.6, 53.5, 52.7, 52.5, 34.3, 33.5, 31.0, 29.7, 28.3 (2*t*Bu).

HRMS (ESI+, MeOH): *m*/*z* calcd for $C_{19}H_{27}NNaO_5S$, $[M + Na]^+$: 404.1502, found: 404.1514.

## Reaction with an unsubstituted vinyl carbonate



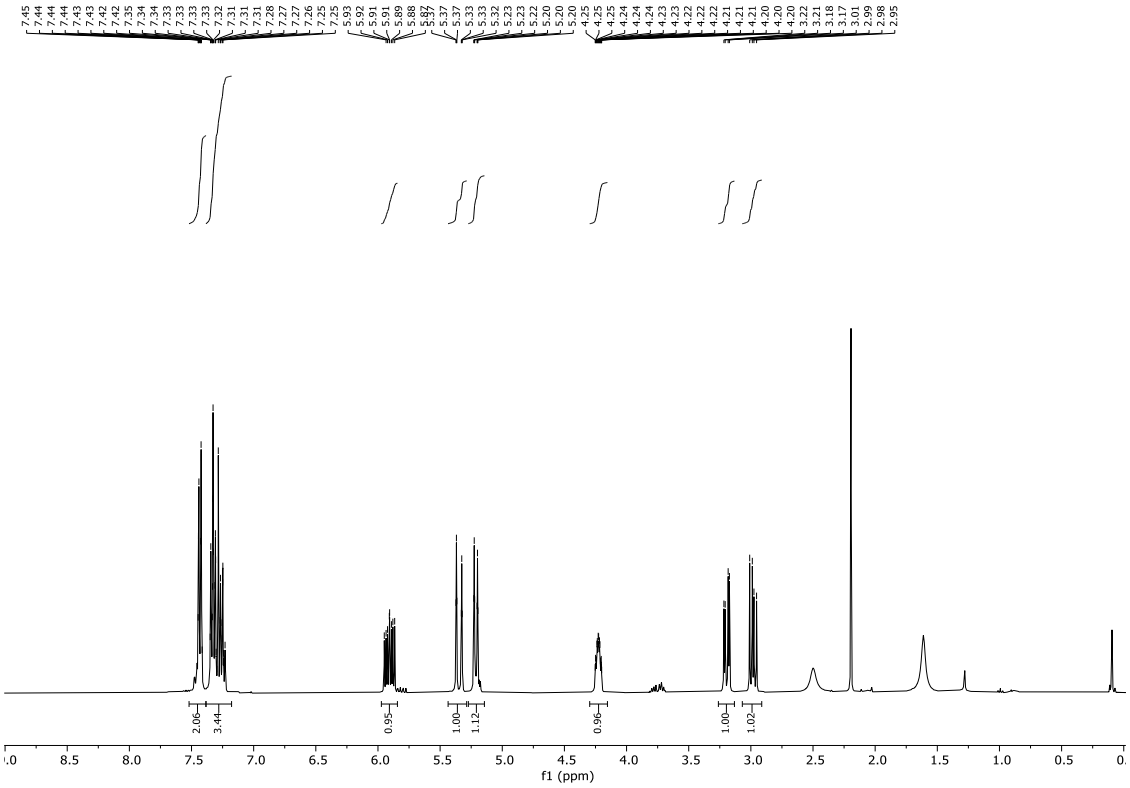

A screw-capped vial was charged with the vinyl cyclic carbonate (19 μL, 0.21 mmol, 1 equiv), DBU (3.2 mg, 0.021 mmol, 10 mol%), thiophenol (26 μL, 0.252 mmol, 1.2 equiv) and dry ACN (0.2 mL). The reaction mixture was stirred at 70 $^{o}$C for 24 h, and then purified by flash column chromatography on silica gel (hexane:ethyl acetate 5:1) to afford **27** and **28** in 88% combined yield as a separable mixture of products in 1:1.6 ratio (note: ratio determined from the crude mixture by $^{1}$H NMR).



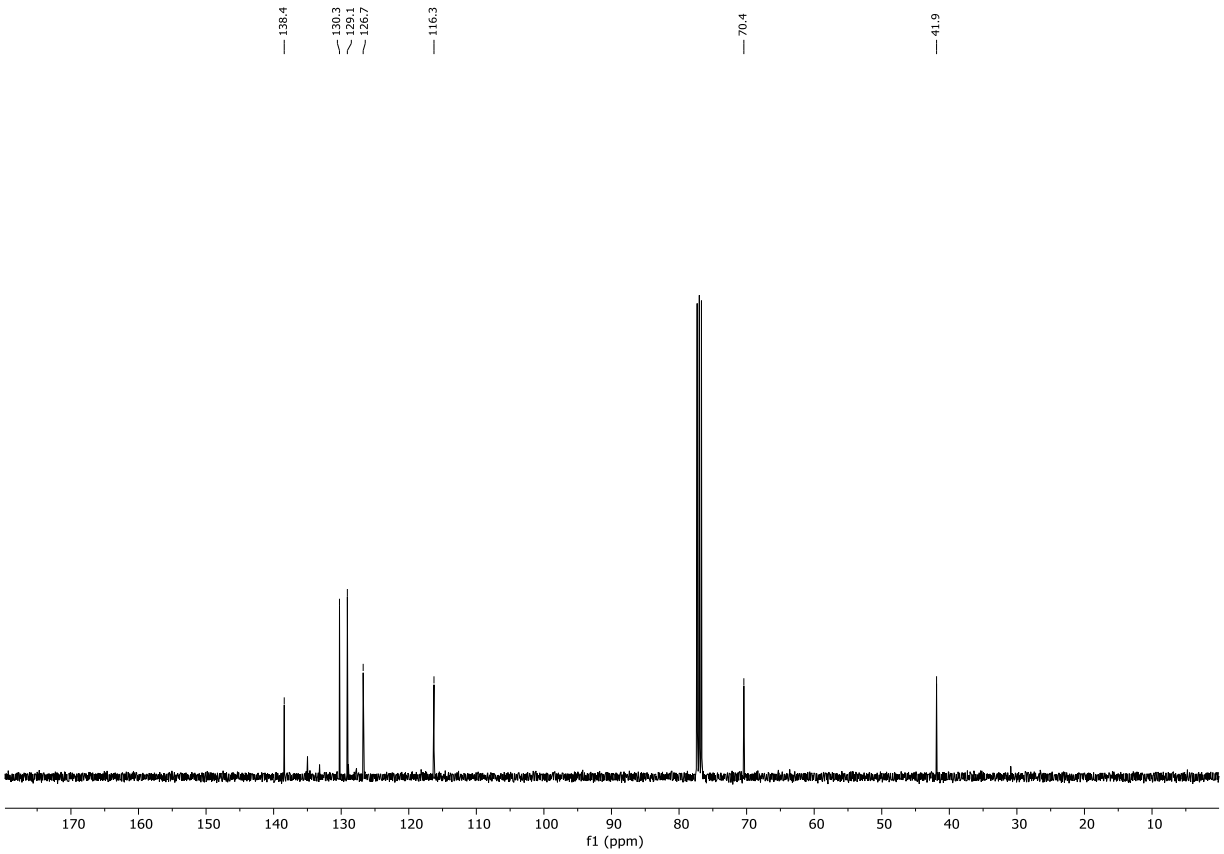

**27**

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.35 – 7.23 (m, 3H), 5.91 (ddd, *J* = 17.3, 10.5, 5.8 Hz, 1H), 5.35 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.21 (dt, *J* = 10.5, 1.3 Hz, 1H), 4.23 (dddt, *J* = 8.5, 5.5, 4.1, 1.3 Hz, 1H), 3.19 (dd, *J* = 13.7, 4.1 Hz, 1H), 2.98 (dd, *J* = 13.7, 8.5 Hz, 1H).

$^1$H NMR spectrum ($CDCl_3$)

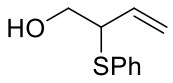


$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.4, 130.3, 129.1, 126.7, 116.3, 70.4, 41.9.

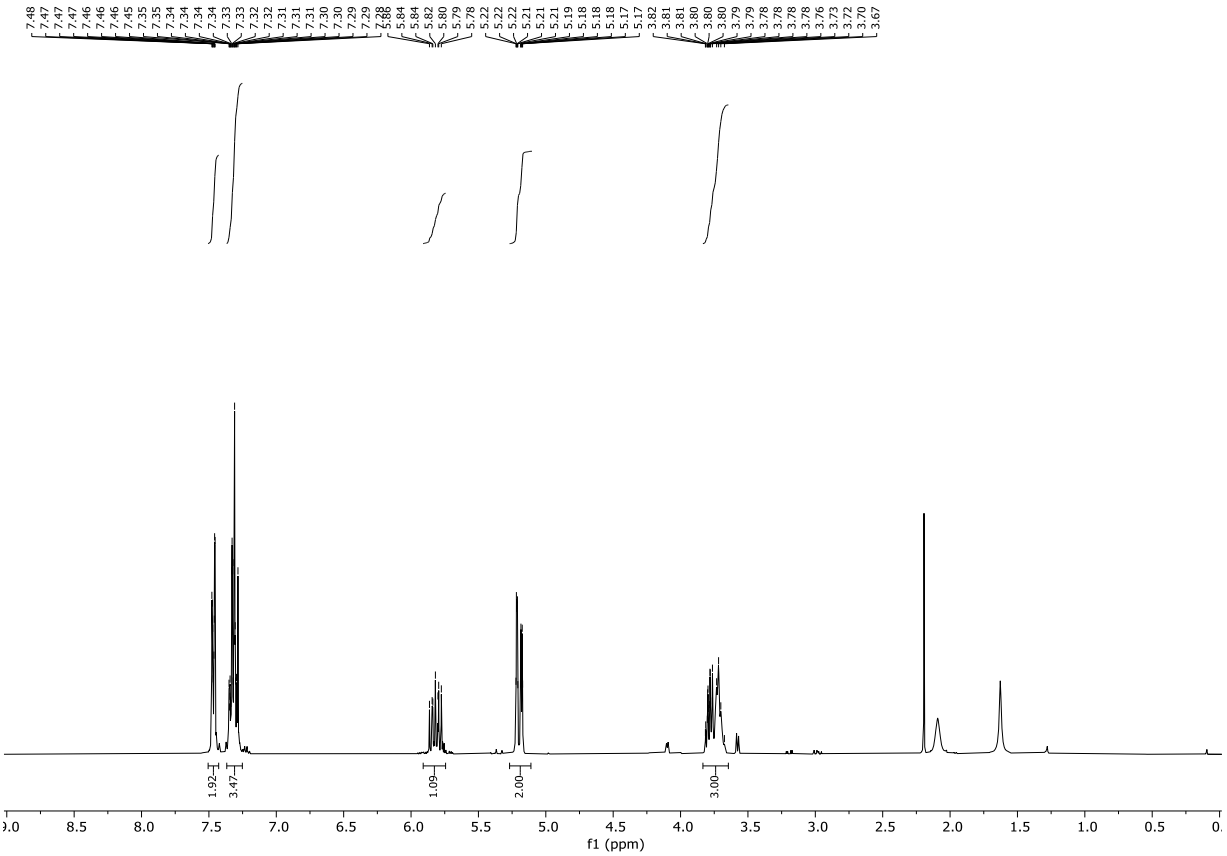
HRMS (ESI+, MeOH, mixture of **27** and **28**): *m/z* calcd for $C_{10}H_{12}NaOS$, $[M + Na]^+$: 209.0501, found: 209.0499.



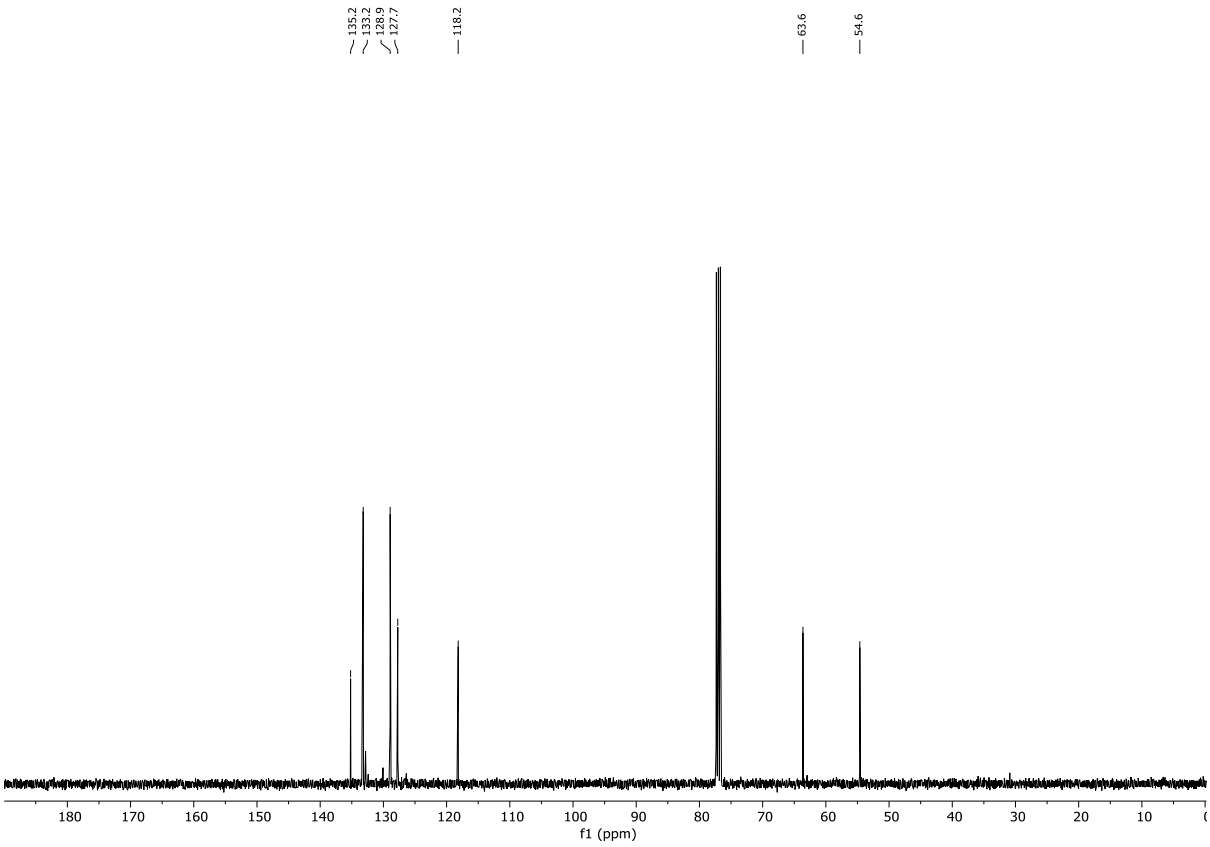

**28**

$^1$H NMR spectrum ($CDCl_3$)

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.35 – 7.29 (m, 3H), 5.82 (ddd, *J* = 17.6, 10.0, 7.9 Hz, 1H), 5.20 (ddt, *J* = 14.1, 4.1, 1.1 Hz, 2H), 3.82 – 3.67 (m, 3H).



$^{13}$C NMR spectrum ($CDCl_3$)




**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 135.2, 133.2, 128.9, 127.7, 118.2, 63.6, 54.6.

HRMS (ESI+, MeOH, mixture of **27** and **28**): *m/z* calcd for $C_{10}H_{12}NaOS$, $[M + Na]^+$: 209.0501, found: 209.0499.

## References:


1 A. Khan, R. Zheng, Y. Kan, J. Ye, J. Xing and Y. J. Zhang, *Angew. Chem. Int. Ed.*, 2014, **53**, 6439

2 Y. F. Liang, K. Wu, S. Song, X. Y. Li, X. Q. Huang and N. Jiao, *Org. Lett.*, 2015, **17**, 876.

3 J. E. Gómez, K. Guo and A. W. Kleij, *Org. Lett.*, 2016, **18**, 6042.