

Visible-Light-Driven Radical 1,3-Addition of Selenosulfonates to Vinyldiazo Compounds

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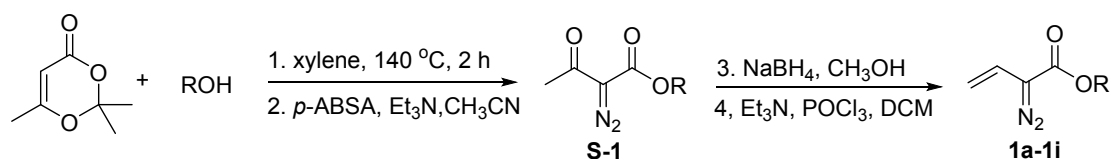
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1. Preparation of alkenyl diazoacetates

All the vinyl diazo compounds used in this work are known compounds. Their preparation and characterization data have been reported in our previous paper.¹ Herein, the procedures for the synthesis of alkenyl diazoacetates **1a-1r** were described.

Method A: Preparation of vinyl diazoacetates **1a-1i**

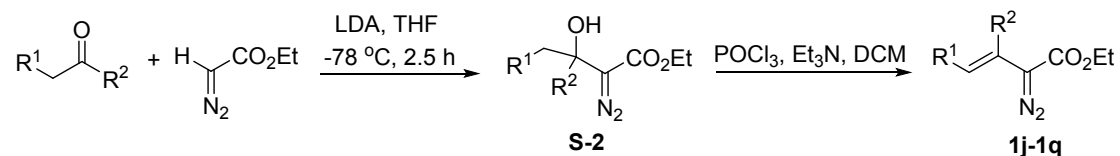


Alcohol (10.0 mmol) and 2,2,6-trimethyl-1,3-dioxene-4-one (12.0 mmol, 1.2 equiv) were dissolved in xylene (2.0 M) and refluxed at 140 °C under argon for 2 h. The solvent was removed from the reaction by vacuum leaving a black oil. The crude mixture was purified by column chromatography (PE/EA = 10:1) to give acetoacetate. Then, acetoacetate was dissolved in MeCN (0.4 M) and cooled to 0 °C. *p*-Acetamidobenzenesulfonyl azide (*p*-ABSA, 1.1 equiv), followed by triethylamine (1.5 equiv) were added and the reaction warmed to rt for 2 h. The pale yellow solid precipitate was filtered and the residue concentrated and purified by column chromatography (PE/EA = 10:1) to give 2-diazo-3-oxobutanoate **S-1**.

The solution of 2-diazo-3-oxobutanoate **S-1** in MeOH (0.6 M) at 0 °C was slowly added NaBH₄ (1.5 equiv). The resulting solution was warmed to room temperature and stirred for 1 h. Then the MeOH was evaporated and the residue was diluted with water and extracted with ethyl acetate and dried over anhydrous Na₂SO₄. After the solvent was evaporated, the crude product was purified by column chromatography (PE/EA = 5:1) to give 2-diazo-3-hydroxybutanoate as a yellow oil. To a solution of 2-diazo-3-hydroxybutanoate and Et₃N (4.0 equiv) in CH₂Cl₂ (0.33 M) at 0 °C was slowly added a solution of POCl₃ (1.5 equiv) in CH₂Cl₂ (1.0 M) over 20 minutes. The resulting solution was warmed to room temperature and stirred for 2 h. The solution

was washed with water and dried over anhydrous NaSO₄. The crude product was purified by flash chromatography (PE/EA = 50:1) to afford vinyldiazoacetate **1a-1i**.

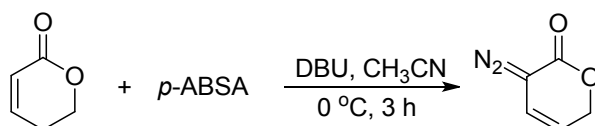
Method B: Preparation of alkenyl diazoacetates **1j-1q**



To a solution of ethyl diazoacetate (12.0 mmol) in anhydrous THF (10.0 mL) was added LDA (12.5 mmol) over 20 min at -78 °C. Then aldehyde or ketone (10 mmol) was added. The resulting solution was stirred at -78 °C for 2.5 h, and then quenched by addition of saturated NH₄Cl (15 mL). The reaction mixture was extracted with Et₂O (3 x 25 mL), and the combined organic layers were washed with saturated NaHCO₃ (20 mL), then brine (25 mL), and dried over anhydrous Na₂SO₄. The solvent was removed in *vacuo* and the crude product was purified by column chromatography (PE/EA = 5:1) to give β-hydroxy-α-diazo ester **S-2** as a yellow oil.

To a solution of **S-2** and Et₃N (4.0 equiv) in CH₂Cl₂ (0.33 M) at 0 °C was slowly added a solution of POCl₃ (1.5 equiv) in CH₂Cl₂ over 20 minutes. The resulting solution was warmed to room temperature and stirred for 2 h. The solution was washed with water and dried over anhydrous Na₂SO₄. The crude product was purified by flash chromatography (PE/EA = 50:1) to afford desired vinyldiazo compound **1j-1q**.

Method C: Preparation of cyclic alkenyl diazo compounds **1r**

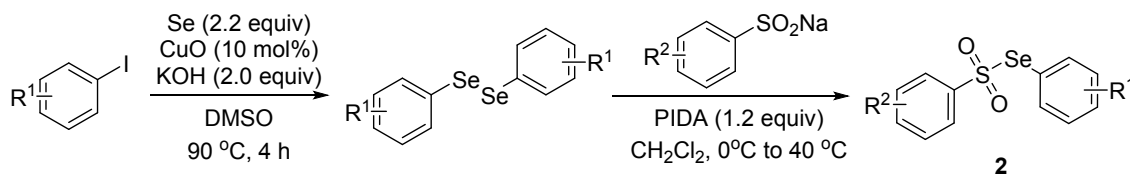


A solution of 3,5-dihydro-pyran-2-one (10 mmol) in acetonitrile (80 mL) was stirred at 0 °C. *p*-ABSA (12 mmol, 1.2 equiv) and DBU (15 mmol, 1.5 equiv) were slowly added to the stirred solution. After 3 h, The mixture was concentrated in *vacuo* and was added saturated NaHCO₃ solution (50 mL), extracted with dichloromethane

(2 x 25 mL). The residue was purified by column chromatography (PE/EA = 5:1) to afford **1q** in 63% yield (781.2 mg) as a red solid.

Caution: all the alkenyl diazoacetates should be stored in a -18 °C freezer.

2. Preparation of selenosulfonates

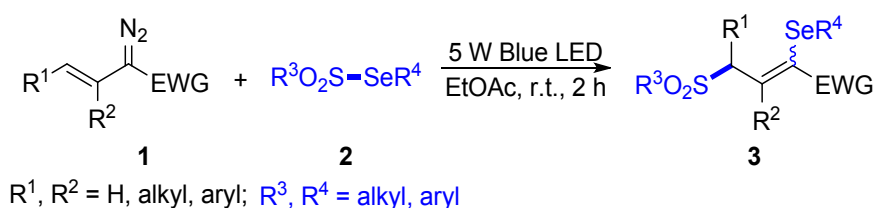


Selenosulfonates were prepared according to the previous reported procedures.²

To a stirred solution of aryl iodides (1.0 equiv) and Se metal (2.0 equiv) in DMSO (0.6 M) was added CuO (10 mol%) followed by KOH (2.0 equiv.) under nitrogen atmosphere. The resulting reaction mixture was stirred at 90 °C for 6 h. After the reaction was complete, the reaction mixture was allowed to cool, extraction with ethyl acetate. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in *vacuo*. The crude product was purified by column chromatography on silica gel (PE:EA =100:1) to afford diselenides.

The CH₂Cl₂ solution of sodium benzenesulfinates (4.0 equiv) and diselenides (1.0 equiv) was cooled at 0 °C. Then [bis(trifluoroacetoxy)iodo]benzene (1.1 equiv) was dissolved in CH₂Cl₂ and added dropwise. The mixture was warmed to 40 °C and stirred for 4 h. After the completion of the reaction, water was added; the organic layer was separated and dried over anhydrous Na₂SO₄. The solvent CH₂Cl₂ was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford compound **2**.

3. General experimental procedure for Radical 1,3-selenosulfonylation

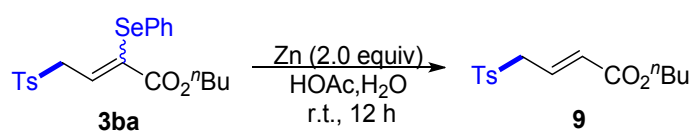


The solution of vinylldiazoacetate **1** (0.20 mmol, 1.0 equiv) and selenosulfonates **2** (0.20 mmol, 1.0 equiv) in EtOAc (1.0 mL) was stirred at room temperature in the open flask under the irradiation of a 5 W blue LED for 2 h. After the removal of solvent in *vacuo*, the residue was purified by column chromatography on silica gel to give product **3**.

For the gram-scale synthesis of **3ba**, the reaction was carried out in a 50 mL round bottom flask using *t*-butyl vinylldiazoacetate **1b** (5 mmol, 0.84 g), TsSePh **2a** (5 mmol, 1.56 g) in 25 mL of EtOAc under the irradiation of a 5 W blue LEDs for 3 h. After the removal of solvent in *vacuo*, the residue was purified by column chromatography on silica gel to give product **3ba** (1.74 g, 77% yield).

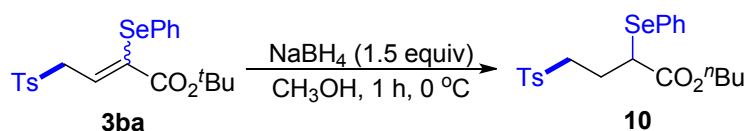
4. Synthetic applications of 3ba

4.1 Reductive deselenization of 3ba by Zn/HOAc



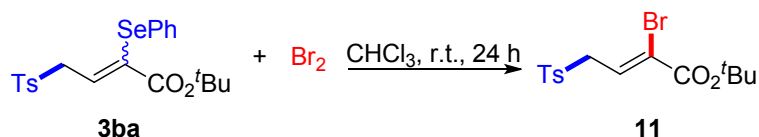
A flame-dried flask was charged with **3ba** (0.20 mmol, 90.4 mg), Zn powder (0.40 mmol, 26.0 mg), HOAc (0.25 mmol) and H₂O (0.25 mmol). The reaction was stirred at ambient temperature for 12 h. Then the solution was diluted with Et₂O, washed with brine, dried over Na₂SO₄. After concentration in *vacuo*, the residue was purified by flash column chromatography (eluent: petroleum ether: ethyl acetate = 10:1) to afford product **9** in 79% yield as a colorless oil (46.8 mg, *E/Z* > 20:1).

4.2 Reduction of 3ba by NaBH₄



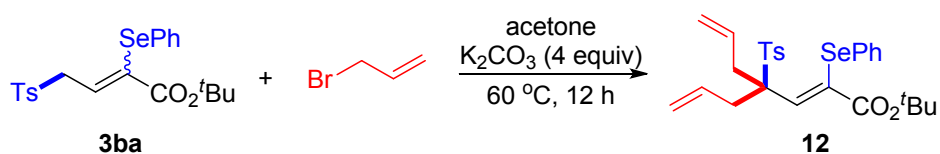
The solution of **3ba** (0.20 mmol, 90.4 mg) in MeOH (1.0 mL) was slowly added NaBH₄ (1.5 equiv, 11.4 mg) at 0 °C and was kept at 0 °C for 1 h. Then the reaction mixture was diluted with Et₂O, washed with brine, dried over Na₂SO₄. After concentration in *vacuo*, the residue was purified by flash column chromatography (eluent: petroleum ether: ethyl acetate = 10:1) to afford product **10** in 83% yield as a colorless oil (75.4 mg).

4.3 Bromination of **3ba** using Br₂.



To a solution of **3ba** (0.20 mmol, 90.4 mg) in CHCl₃ (1.0 mL) was added Br₂ (0.60 mmol, 15.4 μL) using a Microinjector. The reaction mixture was stirred at room temperature, which was quenched by addition of saturated Na₂SO₃ (2 mL) upon the completion of the reaction. Then the reaction mixture was diluted with CH₂Cl₂, washed with brine, dried over Na₂SO₄. After concentration in *vacuo*, the residue was purified by flash column chromatography (eluent: petroleum ether: ethyl acetate = 10:1) to afford product **11** in 78% yield as a colorless oil (58.3 mg, *Z/E* > 20:1).

4.4 Dual allylation substitution of **3ba** using allyl bromide



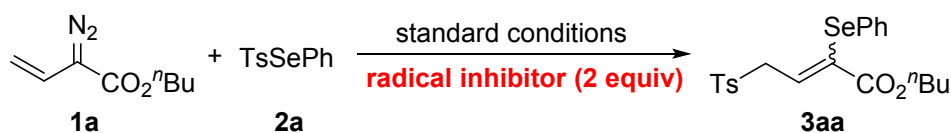
A flame-dried flask was charged with **3ba** (0.20 mmol, 90.4 mg), allyl bromide (0.50 mmol, 60.5 mg), K₂CO₃ (0.80 mmol, 110.4 mg) and acetone (1.0 mL). The reaction was stirred at 60 °C for 12 h. After cooling to room temperature, the solvent was removed in *vacuo*, the residue was purified by flash column chromatography

(eluent: petroleum ether: ethyl acetate = 12:1) to afford **12** in 92% yield as a colorless oil (97.9 mg, *Z/E* > 20:1).

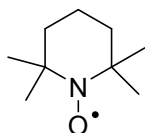
5. Mechanism studies

5.1 Radical inhibition experiments

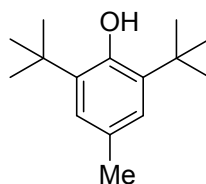
The solution of *n*-butyl vinylldiazoacetate **1a** (0.20 mmol, 1.0 equiv), TsSePh **2a** (0.20 mmol, 1.0 equiv) and radical inhibitor (0.2 mmol, 2.0 equiv.) in EtOAc (1.0 mL) was stirred at room temperature in an open flask under the irradiation of a 5 W blue LED for 2 h. The reaction mixture was diluted with EtOAc and the crude material was examined by GC-MS, it showed that the reaction was completely inhibited and no product of **3aa** was formed



Radical inhibitor:

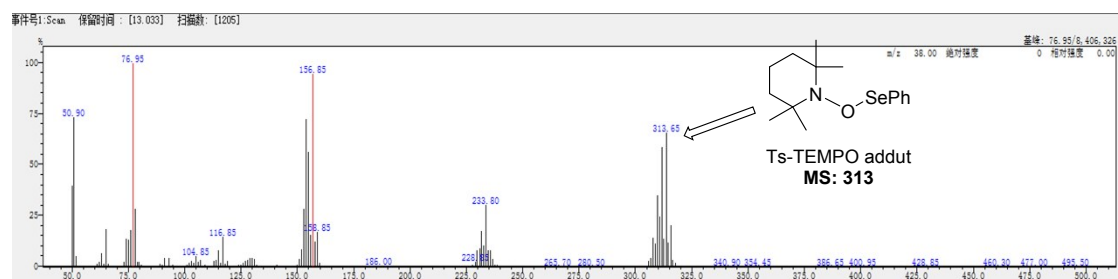


TEMPO
3aa, 0%



BHT
3aa, 0%

The tosyl-TEMPO adduct and phenylselenenyl-TEMPO adduct were detected by GC-MS simultaneously.



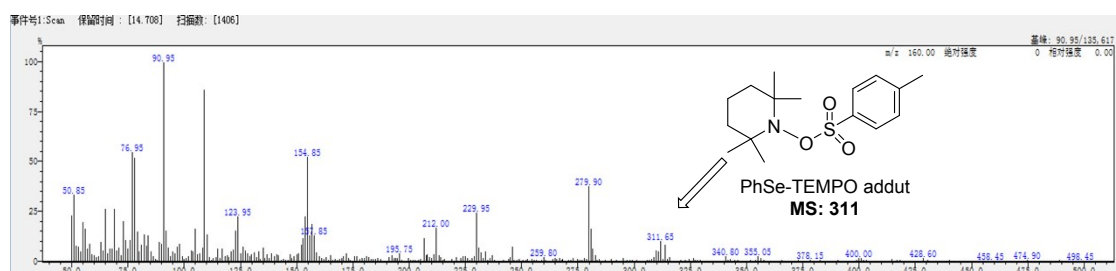


Figure S1 The detection of Ts-TEMPO and PhSe-TEMPO adducts by GC-MS

5.2 Radical clock experiment

The solution of vinyl cyclopropane **5** (0.20 mmol, 1.0 equiv) and selenosulfonates **2a** (0.20 mmol, 1.0 equiv) in EtOAc (1.0 mL) was stirred at room temperature in the open flask under the irradiation of a 5 W blue LED for 2 h. After the removal of solvent in *vacuo*, the residue was purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **6** as white solid (Yield: 91%, 82.9 mg, *Z/E* = 10:1). The radical cyclization product **7** was not detected, indicating the C-Se bond formation is very fast.

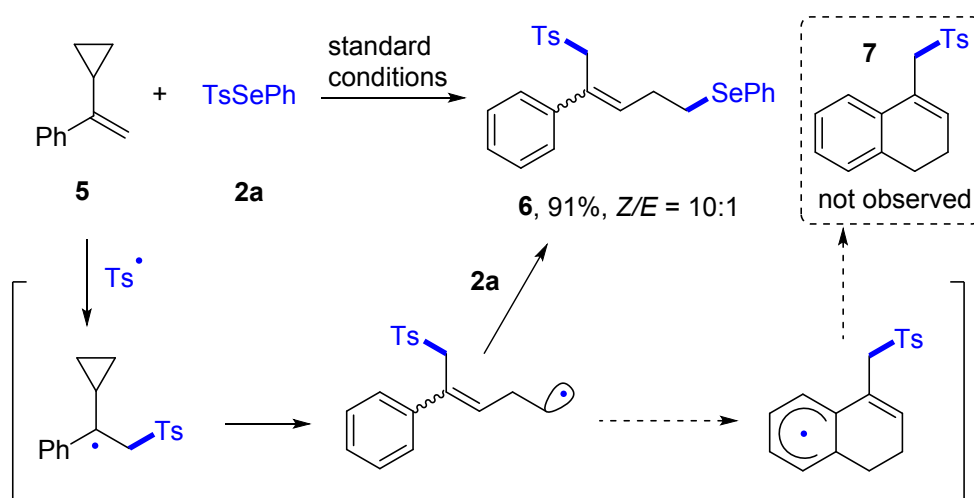


Figure S2 The radical clock experiment using vinyl cyclopropane **5** as the radical acceptor.

5.3 Light on/off experiment

A 5 mL Schlenk tubes were charged with **1a** (0.2 mmol), **2a** (0.2 mmol), EtOAc (1.0 mL), the reaction was alternatively irradiated with a 5 W blue LEDs at room temperature and kept in the dark in 5 min intervals. Aliquots were taken at the start and after each interval, for each sample taken out, 100 μ L of HOAc (1M) added to quench the reaction immediately. Then the solvent was removed with a rotary

evaporator and diluted with CDCl_3 and subjected to ^1H NMR measurements. Yields of **3aa** were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard and the yield at each time point is the average of two parallel reactions.

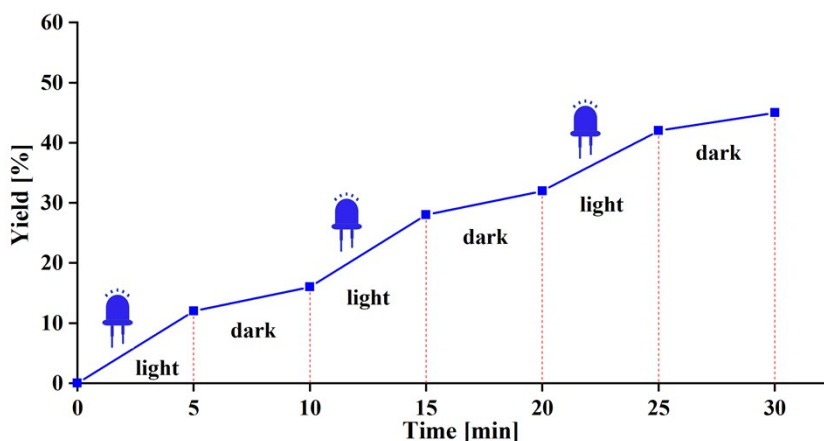
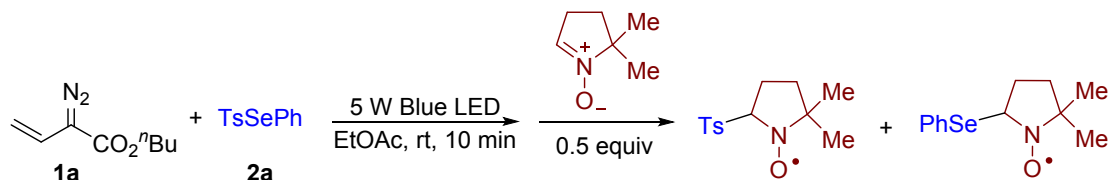


Figure S3 Light on/off experiment

5.4 EPR study



Vinyldiazoacetate **1a** (0.20 mmol, 1.0 equiv) and selenosulfonates **2a** (0.20 mmol, 1.0 equiv) were added in a dried schlenk tube, dissolved in EtOAc (1.0 mL) subsequently. The reaction was irradiated by 5W blue LEDs and stirred at rt for 10 min, 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 11.3 mg, 0.1 mmol) was added, then the solution sample was taken out into a small tube and analyzed by EPR.

EPR spectra was recorded at room temperature on a Bruker ESPA300 spectrometer operated at 9.873 GHz. Typical spectrometer parameters are shown as follows, scan range: 1000 G; center field set: 3510 G; time constant: 40.96 ms; scan time: 20.48 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.0×10^2 .

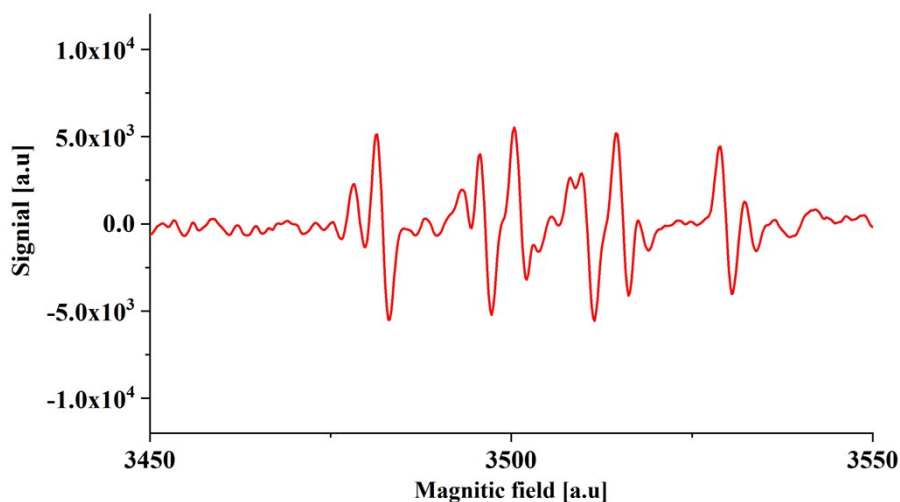


Figure S4. EPR spectrum of the reaction mixture interfered with DMPO

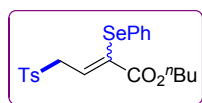
The EPR spectrum is shown in Figure S4, which was compared with the mixed EPR spectra of DMPO-trapped p -MeC₆H₅SO₂• and p -MeC₆H₅S• in CH₂Cl₂ or benzene reported by Maes.³ The signals were quite similar to the Maes's results, indicating the presence of both a phenylselenenyl and a sulfonyl radical.

6. References

1. W. Li, X. Zhou, T. Xiao, Z. Ke and L. Zhou, *CCS Chem.* 2021, **3**, 794.
2. M. R. Mutra, V. S. Kudale, J. Li, W.-H. Tsai and J.-J. Wang, *Green Chem.*, 2020, **22**, 2288.
3. K. Gadde, P. Mampuy, A. Guidetti, H. Y. V. Ching, W. A. Herrebout, S. Van Doorslaer, K. Abbaspour Tehrani and B. U. W. Maes, *ACS Catal.*, 2020, **10**, 8765.

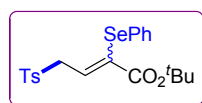
7. Characterization data

(*Z/E*)-butyl 2-(phenylselanyl)-4-tosylbut-2-enoate (**3aa**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3aa** as colorless liquid (**Yield**: 85%, 76.8 mg, *Z/E* = 4:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 – 7.75 (m, 2H), 7.44 – 7.12 (m, 8H), 4.33 (d, $J = 7.7$ Hz, 2H), 4.00 (t, $J = 6.4$ Hz, 2H), 2.46 (s, 3H), 1.45 – 1.36 (m, 2H), 1.23 – 1.11 (m, 2H), 0.82 (t, $J = 7.3$ Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.60 (m, 2H), 7.53 – 7.49 (m, 2H), 7.44 – 7.12 (m, 5H), 5.76 (t, $J = 7.9$ Hz, 1H), 4.38 (d, $J = 8.0$ Hz, 2H), 4.00 (t, $J = 6.4$ Hz, 2H), 2.45 (s, 3H), 1.57 – 1.49 (m, 2H), 1.35 – 1.28 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.7, 164.1 (minor), 145.4, 144.8 (minor), 136.2, 135.7, 135.3, 134.5, 133.1 (minor), 132.0, 130.1, 130.0, (minor) 129.7 (minor), 129.4 (minor), 129.3, 128.6, 127.5, 127.0 (minor), 66.1, 65.8 (minor), 59.9, 57.2 (minor), 30.4, 29.8 (minor), 21.84, 21.78 (minor), 19.2 (minor), 19.0, 13.8 (minor), 13.7. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{NaO}_4\text{SSe}$ 475.0453, Found 475.0447.

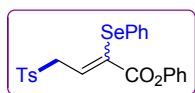
(*Z/E*)-tert-butyl 2-(phenylselanyl)-4-tosylbut-2-enoate (**3ba**)



This compound was prepared according to the general procedure using **1b** (0.20 mmol, 33.6 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ba** as colorless liquid (**Yield**: 85%, 76.8 mg, *Z/E* = 4.5:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 – 7.74 (m, 2H), 7.39 – 7.11 (m, 7H), 7.03 (t, $J = 7.7$ Hz, 1H), 4.29 (d, $J = 7.7$ Hz, 2H), 2.47 (s, 3H), 1.22 (s, 9H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.60 (m, 2H), 7.54 – 7.47 (m, 2H), 7.39 – 7.11 (m, 5H), 5.70 (t, $J = 8.0$ Hz, 1H), 4.36 (d, $J = 7.9$ Hz, 2H), 2.45 (s, 3H), 1.34 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.5, 145.3, 136.5, 136.2, 135.8, 133.3, 132.1, 130.1, 129.9 (minor), 129.8 (minor), 129.2, 128.6, 127.5, 125.7 (minor),

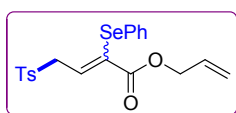
83.4 (minor), 82.5, 59.8, 57.1 (minor), 27.9 (minor), 27.7, 21.85, 21.77 (minor).
HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{24}NaO_4SSe$ 475.0453, Found 475.0449.

(*Z/E*)-phenyl 2-(phenylselanyl)-4-tosylbut-2-enoate (**3ca**)



This compound was prepared according to the general procedure using **1c** (0.20 mmol, 37.6 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ca** as colorless liquid (**Yield**: 83%, 78.4 mg, *Z/E* = 4.5:1). **Major**: 1H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.72 – 7.45 – 7.18 (m, 11H), 6.72 – 6.66 (m, 2H), 4.43 (d, J = 7.8 Hz, 2H), 2.51 (s, 3H). **Minor**: 1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 2H), 7.63 – 7.57 (m, 2H), 7.45 – 7.18 (m, 8H), 6.88 – 6.84 (m, 2H), 6.06 (t, J = 8.1 Hz, 1H), 4.43 (d, J = 7.8 Hz, 2H), 4.7 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 150.7, 145.5, 145.0 (minor), 136.3, 136.0, 135.8, 134.2, 132.6, 130.3, 130.1 (minor), 129.9 (minor), 129.5, 129.5, 128.6, 128.0, 126.5 (minor), 126.2, 121.4 (minor), 121.2, 60.0, 57.3 (minor), 21.9, 21.8 (minor). **HRMS** (ESI) m/z : $[M + Na]^+$ Calcd for $C_{23}H_{20}NaO_4SSe$ 495.0140, Found 495.0135.

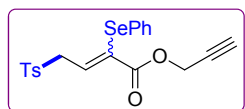
(*Z/E*)-allyl 2-(phenylselanyl)-4-tosylbut-2-enoate (**3da**)



This compound was prepared according to the general procedure using **1d** (0.20 mmol, 30.4 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3da** as colorless liquid (**Yield**: 77%, 67.1 mg, *Z/E* = 4:1). **Major**: 1H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 2H), 7.43 – 7.14 (m, 8H), 5.73 – 5.62 (m, 1H), 5.20 – 5.11 (m, 2H), 4.49 (d, J = 5.4 Hz, 2H), 4.33 (d, J = 7.7 Hz, 2H), 2.46 (s, 3H). **Minor**: 1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 2H), 7.55 – 7.49 (m, 2H), 7.43 – 7.14 (m, 5H), 7.77 (t, J = 8.0 Hz, 1H), 5.73 – 5.62 (m, 1H), 5.32 – 5.20 (m, 2H), 4.49 (d, J = 5.4 Hz, 2H), 4.37 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 163.7 (minor), 145.4, 144.8 (minor), 136.3, 135.7, 134.3, 132.8 (minor), 132.2, 131.4, 131.1 (minor),

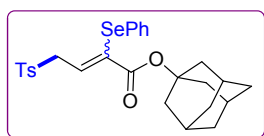
130.2, 130.0 (minor), 129.8 (minor), 129.5 (minor), 129.3, 128.5, 127.7, 127.3 (minor), 119.1 (minor), 118.7, 66.7, 66.4 (minor), 59.9, 57.2 (minor), 29.8 (minor), 21.8. **HRMS** (ESI) m/z : $[M + Na]^+$ Calcd for $C_{20}H_{20}NaO_4SSe$ 459.0140, Found 459.0131.

(*Z/E*)-prop-2-yn-1-yl 2-(phenylselanyl)-4-tosylbut-2-enoate (**3ea**)



This compound was prepared according to the general procedure using **1e** (0.20 mmol, 30.0 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ea** as colorless liquid (**Yield**: 71%, 61.6 mg, *Z/E* = 4:1). **Major**: 1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.40 – 7.16 (m, 8H), 4.60 (d, $J = 2.3$ Hz, 2H), 4.34 (d, $J = 7.8$ Hz, 2H), 2.47 (s, 3H), 2.41 (s, 1H). **Minor**: 1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.54 – 7.51 (m, 2H), 7.40 – 7.16 (m, 5H), 5.84 (t, $J = 8.1$ Hz, 1H), 4.57 (d, $J = 2.3$ Hz, 2H), 4.34 (d, $J = 7.8$ Hz, 2H), 2.49 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 145.5, 144.9 (minor), 136.5, 136.4, 135.7, 133.6, 132.5, 130.2, 130.0 (minor), 129.8 (minor), 129.6 (minor), 129.4, 129.2 (minor), 128.5, 128.2 (minor), 127.8, 77.0 (minor), 76.8, 75.9 (minor), 75.4, 60.0, 57.3 (minor), 53.5, 53.2 (minor), 21.9, 21.8 (minor). **HRMS** (ESI) m/z : $[M + Na]^+$ Calcd for $C_{20}H_{18}NaO_4SSe$ 456.9983, Found 456.9977.

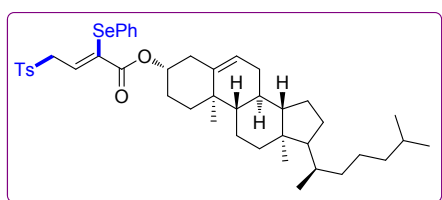
(*Z/E*)-adamantan-1-yl 2-(phenylselanyl)-4-tosylbut-2-enoate (**3fa**)



This compound was prepared according to the general procedure using **1f** (0.20 mmol, 49.2 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 12:1) to give the product **3fa** as colorless liquid (**Yield**: 84%, 89.0 mg, *Z/E* = 4.9:1). **Major**: 1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.45 – 7.11 (m, 7H), 7.06 (t, $J = 7.9$ Hz, 1H), 4.31 (d, $J = 7.8$ Hz, 2H), 2.49 (s, 3H), 2.09 (s, 3H), 1.86 (s, 6H), 1.59 (s, 6H). **Minor**: 1H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.58 – 7.49 (m, 2H), 7.45 – 7.11 (m, 5H),

5.69 (t, $J = 8.1$ Hz, 1H), 4.38 (d, $J = 8.1$ Hz, 2H), 2.49 (s, 3H), 2.17 (s, 3H), 2.00 (s, 6H), 1.65 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.1, 145.3, 136.5, 136.3, 135.8, 133.4, 132.1, 130.2 (minor), 130.1, 129.9 (minor), 129.8 (minor), 129.2, 128.6, 127.4, 82.7, 59.9, 56.4 (minor), 41.2 (minor), 40.9, 36.2, 31.0 (minor), 30.9, 21.9. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{30}\text{NaO}_4\text{SSe}$ 553.0922, Found 553.0917..

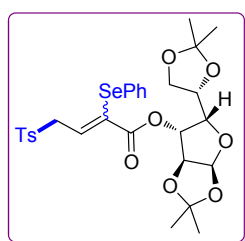
(Z)-(3S,8S,9S,10R,13R,14S)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(phenylselanyl)-4-tosylbut-2-enoate (3ga)



This compound was prepared according to the general procedure using **1g** (0.20 mmol, 96.0 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica

gel (eluent: petroleum ether: ethyl acetate = 15:1) to give the product **3ga** as white solid (Yield: 73%, 111.5 mg, $Z/E = 8:1$). Because this compound is a solid, we further purify it by recrystallization using hexane and EtOAc as the solvent. Only the major *Z*-isomer was obtained after the recrystallization in 71% yield (79 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.84 – 7.72 (m, 2H), 7.43 – 7.33 (m, 2H), 7.28 – 7.04 (m, 6H), 5.27 (d, $J=5.0$, 1H), 4.53 – 4.41 (m, 1H), 4.32 (d, $J=7.7$, 2H), 2.47 (s, 3H), 2.16 – 1.72 (m, 6H), 1.66 – 0.82 (m, 34H), 0.66 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 145.4, 139.5, 135.8, 135.2, 134.5, 132.3, 130.2, 130.0, 129.3, 128.6, 127.6, 122.9, 76.1, 59.9, 56.8, 56.3, 50.1, 42.4, 39.8, 39.7, 37.6, 36.9, 36.7, 36.3, 35.9, 31.99, 31.96, 28.3, 28.1, 27.3, 24.4, 24.0, 22.9, 22.7, 21.9, 21.1, 19.4, 18.8, 12.0. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{44}\text{H}_{60}\text{NaO}_4\text{SSe}$ 787.3270, Found 787.3256.

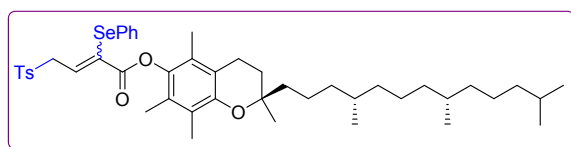
(Z/E)-(3aS,5S,6R,6aS)-5-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 2-(phenylselanyl)-4-tosylbut-2-enoate (3ha)



This compound was prepared according to the general procedure using **1h** (0.20 mmol, 70.8 mg), **2a** (0.20 mmol, 62.4 mg),

EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 5.7:1) to give the product **3ha** as colorless liquid (**Yield**: 71%, 90.6 mg, *Z/E* = 5.7:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 – 7.82 (m, 2H), 7.41 – 7.06 (m, 8H), 5.28 (d, $J = 3.7$ Hz, 1H), 5.16 (d, $J = 3.0$ Hz, 1H), 4.42 (dd, $J = 13.9, 8.1$ Hz, 1H), 4.30 (dd, $J = 13.9, 7.7$ Hz, 1H), 4.25 – 4.08 (m, 1H), 4.08 – 3.91 (m, 3H), 3.70 (d, $J = 3.7$ Hz, 1H), 2.49 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H), 1.18 (s, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.73 – 7.61 (m, 2H), 7.52 – 7.46 (m, 2H), 7.42 – 7.06 (m, 5H), 5.94 (t, $J = 8.1$ Hz, 1H), 5.69 (d, $J = 3.8$ Hz, 1H), 5.16 (d, $J = 3.0$ Hz, 1H), 4.54 (dd, $J = 14.5, 8.5$ Hz, 1H), 4.25 – 4.08 (m, 5H), 4.08 – 3.91 (m, 1H), 2.49 (s, 3H), 1.51 (s, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 1.27 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.5, 145.5, 136.7, 135.7, 133.4, 131.9, 130.2, 130.0 (minor), 129.9 (minor), 129.5, 128.6, 127.7, 112.2, 109.4, 105.0, 82.8, 79.8 (minor), 79.7, 77.7, 77.5, 72.5, 67.5 (minor), 67.2, 59.9, 27.0, 26.7, 26.3 (minor), 26.1, 25.5, 25.3 (minor), 21.9. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{34}\text{NaO}_9\text{SSe}$ 661.0981, Found 661.0969.

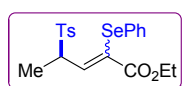
(*Z/E*)-(R)-2,5,7,8-tetramethyl-2-((3R,7R)-3,7,11-trimethyldodecyl)chroman-6-yl 2-(phenylselanyl)-4-tosylbut-2-enoate (3ia**)**



This compound was prepared according to the general procedure using **1i** (0.20 mmol, 104.8 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 15:1) to give the product **3ia** as white solid (**Yield**: 76%, 122.8 mg, *Z/E* = 7.3:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.78 (m, 2H), 7.46 – 7.33 (m, 2H), 7.27 – 7.11 (m, 6H), 4.45 (d, $J = 7.9$ Hz, 2H), 2.62 – 2.49 (m, 2H), 2.49 (s, 3H), 2.05 – 1.99 (m, 3H), 1.91 – 1.71 (m, 4H), 1.70 – 1.61 (m, 6H), 1.58 – 1.48 (m, 4H), 1.44 – 1.22 (m, 12H), 1.16 – 1.01 (m, 4H), 0.88 – 0.82 (m, 14H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 – 7.60 (m, 2H), 7.46 – 7.33 (m, 2H), 7.27 – 7.11 (m, 5H), 5.94 (t, $J = 8.0$ Hz, 1H), 4.45 (d, $J = 7.9$ Hz, 2H), 2.62 – 2.49 (m, 2H), 2.49 (s, 3H), 2.05 – 1.99 (m, 3H), 1.91 – 1.71 (m, 4H), 1.70 –

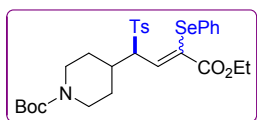
1.61 (m, 6H), 1.58 – 1.48 (m, 4H), 1.44 – 1.22 (m, 12H), 1.16 – 1.01 (m, 4H), 0.88 – 0.82 (m, 14H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.1, 162.8 (minor), 149.9 (minor), 149.7, 145.5, 144.8 (minor), 140.7, 140.1 (minor), 137.8 (minor), 136.9, 136.5, 135.8 (minor), 135.6, 134.2, 133.0, 131.8 (minor), 130.2, 130.1 (minor), 129.8 (minor), 129.4, 129.3 (minor), 128.7, 128.5 (minor), 127.9, 126.5, 124.9 (minor), 124.8, 123.3 (minor), 123.2, 117.6 (minor), 117.5, 75.3 (minor), 75.2, 60.2, 57.4 (minor), 39.5, 37.7, 37.6, 37.5, 37.4, 32.9, 32.8, 31.1, 28.1, 24.9, 24.6, 22.85, 22.76, 21.9, 21.8 (minor), 21.1, 20.71 (minor), 20.65, 19.9, 19.8, 13.0 (minor), 12.7, 12.2 (minor), 11.94 (minor), 11.88, 11.8. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{46}\text{H}_{64}\text{NaO}_5\text{SSe}$ 831.3532, Found 831.3518.

(Z/E)-ethyl 2-(phenylselanyl)-4-tosylpent-2-enoate (3ja)



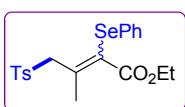
This compound was prepared according to the general procedure using **1j** (0.20 mmol, 30.8 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ja** as colorless liquid (**Yield**: 79%, 69.2 mg, *Z/E* = 1.8:1). **Major**: ^1H NMR (400 MHz, CDCl_3) δ 7.65 – 7.59 (m, 2H), 7.53 – 7.49 (m, 1H), 7.44 – 7.15 (m, 4H), 7.24 – 7.16 (m, 2H), 5.72 (d, $J = 10.5$ Hz, 1H), 5.00 (dq, $J = 10.5, 6.8$ Hz, 1H), 4.11 – 3.99 (m, 2H), 2.46 (s, 3H), 1.40 (d, $J = 6.9$ Hz, 3H), 1.16 (t, $J = 7.2$ Hz, 3H). **Minor**: ^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.67 (m, 1H), 7.53 – 7.49 (m, 1H), 7.44 – 7.15 (m, 4H), 7.24 – 7.16 (m, 2H), 7.72 (d, $J = 10.5$ Hz, 1H), 4.56 (dq, $J = 10.2, 6.9$ Hz, 1H), 4.11 – 3.99 (m, 2H), 2.48 (s, 3H), 1.55 (d, $J = 6.9$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H). **Major**: ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 144.6, 135.7, 134.4, 132.0, 129.8, 129.5, 129.2, 129.09, 129.0, 127.4, 61.8, 60.5, 21.65, 13.84, 13.3. **Minor**: ^{13}C NMR (100 MHz, CDCl_3) δ 164.5, 145.1, 141.7, 137.3, 134.5, 132.6, 131.1, 129.9, 129.13, 128.4, 127.2, 63.7, 62.0, 21.72, 13.77, 13.5. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{NaO}_4\text{SSe}$ 461.0296, Found 461.0287.

(Z/E)-tert-butyl 4-(4-ethoxy-4-oxo-3-(phenylselanyl)-1-tosylbut-2-en-1-yl)piperidine-1-carboxylate (3ka)



This compound was prepared according to the general procedure using **1k** (0.20 mmol, 64.6 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 4:1) to give the product **3ka** as colorless liquid (**Yield**: 69%, 83.8 mg, *Z/E* = 1.5:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 – 7.55 (m, 2H), 7.50 – 7.03 (m, 7H), 6.85 (d, $J = 7.6$ Hz, 1H), 4.87 (dd, $J = 11.5, 4.4$ Hz, 1H), 4.27 – 3.78 (m, 4H), 2.87 – 2.57 (m, 3H), 2.44 (s, 3H), 1.94 – 1.71 (m, 2H), 1.46 (s, 9H), 1.39 – 1.21 (m, 2H), 1.08 (t, $J = 7.2$ Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 – 7.65 (m, 2H), 7.50 – 7.03 (m, 7H), 5.75 (d, $J = 11.4$ Hz, 1H), 4.40 (dd, $J = 11.1, 4.1$ Hz, 1H), 4.27 – 3.78 (m, 4H), 2.87 – 2.57 (m, 2H), 2.46 (s, 3H), 2.17– 2.10 (m, 1H), 1.94 – 1.71 (m, 2H), 1.46 (s, 9H), 1.39 – 1.21 (m, 2H), 0.98 (t, $J = 7.1$ Hz, 3H). **Major**: $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 163.9, 154.6, 144.5, 136.0, 135.7, 135.6, 132.0, 129.9, 129.4, 128.6, 127.5, 79.5, 68.2, 61.6, 43.5, 35.8, 28.5, 27.8, 21.65, 13.8. **Minor**: $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.1, 154.6, 145.0, 138.2, 136.0, 134.8, 132.9, 131.2, 129.0, 128.8, 127.1, 79.6, 71.9, 62.0, 43.5, 36.3, 30.8, 28.4, 21.75, 13.7. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{29}\text{H}_{37}\text{NNaO}_6\text{SSe}$ 630.1399, Found 630.1403.

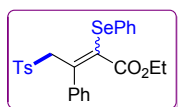
(*Z/E*)-ethyl 3-methyl-2-(phenylselanyl)-4-tosylbut-2-enoate (**3la**)



This compound was prepared according to the general procedure using **1l** (0.20 mmol, 30.8 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3la** as colorless liquid (**Yield**: 81%, 71.0 mg, *Z/E* = 2:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 – 7.69 (m, 2H), 7.43 – 7.17 (m, 7H), 4.42 (s, 2H), 3.67 (q, $J = 7.2$ Hz, 2H), 2.44 (s, 3H), 2.19 (s, 3H), 0.87 (t, $J = 7.1$ Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.75 (m, 2H), 7.43 – 7.17 (m, 7H), 4.32 (s, 2H), 3.91 (q, $J = 7.1$ Hz, 2H), 2.47 (s, 3H), 2.15 (s, 3H), 0.97 (t, $J = 7.0$ Hz, 3H). **Major**: $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 165.8, 144.8, 136.2, 136.0, 133.1, 129.9, 129.3, 128.6, 127.8, 61.9, 61.5, 24.7, 21.8, 13.6. **Minor**: $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.5, 145.3, 135.9, 135.2, 133.5, 130.2, 129.1, 128.8, 128.1, 64.8,

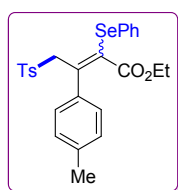
61.4, 22.2, 21.9, 13.8. **HRMS** (ESI) m/z : $[M + Na]^+$ Calcd for $C_{20}H_{22}NaO_4SSe$ 461.0296, Found 461.0287.

(Z/E)-ethyl 3-phenyl-2-(phenylselanyl)-4-tosylbut-2-enoate (3ma)



This compound was prepared according to the general procedure using **1m** (0.20 mmol, 43.2 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ma** as colorless liquid (**Yield**: 68%, 68.0 mg, $Z/E = 1.5:1$). **Major**: 1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.43 – 7.37 (m, 2H), 7.33 – 7.03 (m, 10H), 4.70 (s, 2H), 3.73 (q, $J = 7.2$ Hz, 2H), 2.38 (s, 3H), 0.93 (t, $J = 7.2$ Hz, 3H). **Minor**: 1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.53 – 7.47 (m, 2H), 7.33 – 7.03 (m, 10H), 4.72 (s, 2H), 3.52 (q, $J = 7.1$ Hz, 2H), 2.38 (s, 3H), 0.63 (t, $J = 7.1$ Hz, 3H). **Major**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 144.6, 139.9, 136.4, 135.5, 134.5, 134.1, 129.7, 129.10, 128.7, 128.46, 128.4, 128.3, 128.1, 127.7, 61.9, 61.5, 21.69, 13.6. **Minor**: ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 145.0, 139.5, 136.0, 135.1, 134.8, 133.6, 129.9, 129.14, 128.6, 128.54, 128.46, 128.41, 128.2, 127.9, 65.0, 61.2, 21.71, 13.4. **HRMS** (ESI) m/z : $[M + Na]^+$ Calcd for $C_{25}H_{24}NaO_4SSe$ 523.0453, Found 523.0445.

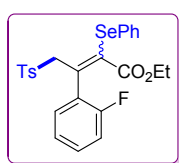
(Z/E)-ethyl 2-(phenylselanyl)-3-(p-tolyl)-4-tosylbut-2-enoate (3na)



This compound was prepared according to the general procedure using **1n** (0.20 mmol, 46.0 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3na** as colorless liquid (**Yield**: 70%, 72.0 mg, $Z/E = 1.3:1$). **Major**: 1H NMR (400 MHz, $CDCl_3$) δ 6.62 – 7.58 (m, 2H), 7.41 – 7.38 (m, 2H), 7.26 – 7.18 (m, 5H), 7.05 – 7.02 (m, 2H), 6.98 – 6.97 (m, 2H), 4.69 (s, 2H), 3.70 (q, $J = 7.1$ Hz, 2H), 2.39 (s, 3H), 2.34 (s, 3H), 0.92 (t, $J = 7.1$ Hz, 3H). **Minor**: 1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.63 (m, 2H), 7.50 – 7.47 (m, 2H), 7.26 – 7.18 (m, 5H), 7.13 – 7.09 (m, 2H), 6.98 – 6.97 (m, 2H), 4.70 (s, 2H), 3.56 (q, $J = 7.1$ Hz, 2H), 2.39 (s, 3H), 2.27 (s, 3H), 0.67 (t, $J =$

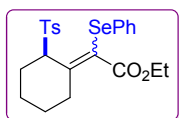
7.1 Hz, 3H). **Major:** ^{13}C NMR (100 MHz, CDCl_3) δ 165.9, 144.5, 138.8, 136.9, 136.4, 135.8, 134.5, 134.3, 129.7, 129.14, 129.05, 128.41, 128.35, 128.03, 127.6, 61.8, 61.1, 21.7, 21.4, 13.6. **Minor:** ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 144.9, 138.3, 136.5, 136.1, 134.6, 134.1, 133.0, 129.8, 129.3, 129.12, 129.05, 128.54, 128.48, 127.98, 61.5, 21.7, 21.3, 13.4. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{26}\text{NaO}_4\text{SSe}$ 537.0609, Found 537.0605.

(Z/E)-ethyl 3-(4-fluorophenyl)-2-(phenylselanyl)-4-tosylbut-2-enoate (3oa)



This compound was prepared according to the general procedure using **1o** (0.20 mmol, 46.8 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3oa** as colorless liquid (**Yield:** 77%, 79.8 mg, $Z/E = 1.2:1$). **Major:** ^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.63 (m, 2H), 7.40 – 7.37 (m, 2H), 7.30 – 7.16 (m, 6H), 7.13 – 6.89 (m, 3H), 4.70 (s, 2H), 3.73 (q, $J = 7.1$ Hz, 2H), 2.40 (s, 3H), 0.91 (t, $J = 7.1$ Hz, 3H). **Minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.75 – 7.69 (m, 2H), 7.51 – 7.45 (m, 2H), 7.40 – 7.37 (m, 6H), 7.30 – 7.16 (m, 3H), 7.13 – 6.89 (m, 2H), 4.70 (s, 2H), 3.54 (q, $J = 7.1$ Hz, 2H), 2.41 (s, 3H), 0.64 (t, $J = 7.1$ Hz, 3H). **Major:** ^{13}C NMR (100 MHz, CDCl_3) δ 165.4, 158.8 (d, $J = 248.0$ Hz), 144.7, 136.4, 136.2, 134.4, 131.00, 130.88, 129.95, 129.8, 129.18, 128.6, 128.4, 124.1 (d, $J = 3.3$ Hz), 116.0 (d, $J = 21.6$ Hz), 61.9, 61.3, 21.7, 13.6. **Minor:** ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 159.0 (d, $J = 247.1$ Hz), 145.1, 137.7, 135.7, 134.5, 131.03, 130.91, 130.32 (d, $J = 8.4$ Hz), 130.01, 129.23, 128.8, 128.5, 124.1 (d, $J = 3.4$ Hz), 115.5 (d, $J = 21.7$ Hz), 64.0, 60.6, 21.8, 13.4. **Major:** ^{19}F NMR (376 MHz, CDCl_3) δ -112.8. **Minor:** ^{19}F NMR (376 MHz, CDCl_3) δ -114.1. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{23}\text{FNaO}_4\text{SSe}$ 541.0359, Found 541.0350.

(Z/E)-ethyl 2-(phenylselanyl)-2-(2-tosylcyclohexylidene)acetate (3pa)

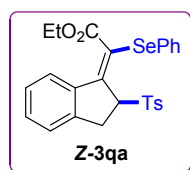


This compound was prepared according to the general procedure using **1p** (0.20 mmol, 38.8 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent:

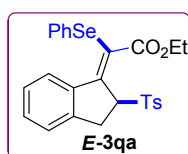
petroleum ether: ethyl acetate = 10:1) to give the product **3pa** as colorless liquid (**Yield**: 63%, 60.2 mg, *Z/E* = 2.1:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 – 7.66 (m, 2H), 7.48 – 7.17 (m, 7H), 4.93 (s, 1H), 4.06 – 3.86 (m, 2H), 3.62 – 3.51 (m, 2H), 2.92 – 2.74 (m, 2H), 2.74 – 2.53 (m, 1H), 2.45 (s, 3H), 2.29 – 2.11 (m, 1H), 1.93 – 1.73 (m, 2H), 0.85 (t, $J = 7.1$ Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.79 (m, 2H) 7.48 – 7.17 (m, 7H), 4.67 (s, 1H), 3.72 – 3.62 (m, 2H), 3.62 – 3.51 (m, 1H), 3.20 – 3.12 (m, 1H), 2.92 – 2.74 (m, 1H), 2.74 – 2.53 (m, 1H), 2.45 (s, 3H), 2.29 – 2.11 (m, 1H), 2.04 – 1.93 (m, 2H), 1.57 – 1.36 (m, 1H), 0.85 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.8 (minor), 166.0, 145.0 (minor), 144.5, 144.0, 141.8 (minor), 135.6, 135.3 (minor), 133.3 (minor), 132.9, 130.1 (minor), 129.9, 129.7, 129.3 (minor), 129.2, 129.1 (minor), 128.9, 127.9 (minor), 127.7, 127.2, 126.8 (minor), 66.6 (minor), 64.2, 61.4, 61.3 (minor), 32.1, 30.7 (minor), 26.9, 26.6 (minor), 21.84 (minor), 21.76, 21.2 (minor), 21.1, 13.9 (minor), 13.5. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{26}\text{NaO}_4\text{SSe}$ 501.0609, Found 501.0601.

ethyl 2-(phenylselanyl)-2-(2-tosyl-2,3-dihydro-1H-inden-1-ylidene)acetate (**3qa**)

This compound was prepared according to the general procedure using **1q** (0.20 mmol, 45.6 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1). **Z-3qa** and **E-3qa** are two isolatable isomers.



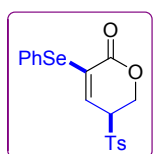
Yellow solid (**Yield**: 49.3%, 50.5 mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 – 7.77 (m, 1H), 7.57 – 7.48 (m, 4H), 7.31 – 7.05 (m, 8H), 5.71 – 5.64 (m, 1H), 3.98 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.80 (dq, $J = 10.7, 7.1$ Hz, 1H), 3.48 – 3.39 (m, 2H), 2.30 (s, 3H), 1.01 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 166.6, 145.7, 144.6, 141.3, 139.2, 134.0, 133.7, 130.1, 129.7, 129.3, 129.3, 129.2, 128.2, 127.4, 126.7, 125.7, 124.7, 68.6, 61.9, 33.5, 21.6, 13.7. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{24}\text{NaO}_4\text{SSe}$ 535.0453, Found 535.0443.



Yellow solid (**Yield**: 24.7%, 25.3mg). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51 – 7.46 (m, 3H), 7.34 – 7.21 (m, 7H), 7.18 – 7.06 (m, 3H),

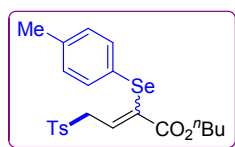
6.23 (s, 1H), 4.10 – 3.99 (m, 2H), 3.71 (d, $J = 20.0$ Hz, 1H), 2.86 (d, $J = 20.0$ Hz, 1H), 2.37 (s, 3H), 1.08 (t, $J = 7.1$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 145.3, 144.9, 142.1, 134.4, 133.5, 133.3, 129.7, 129.7, 129.4, 129.2, 128.0, 127.6, 127.3, 124.3, 73.8, 61.9, 41.0, 21.8, 13.9. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{26}\text{H}_{24}\text{NaO}_4\text{SSe}$ 535.0453, Found 535.0445.

3-(phenylselanyl)-5-tosyl-5,6-dihydro-2H-pyran-2-one (3ra)



This compound was prepared according to the general procedure using **1r** (0.20 mmol, 24.8 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ra** as yellow solid (**Yield**: 63%, 51.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.59 (m, 4H), 7.52 – 7.42 (m, 3H), 7.39 – 7.33 (m, 2H), 6.04 (d, $J = 5.9$ Hz, 1H), 4.89 (d, $J = 12.8$, 1H), 4.56 (dd, $J = 12.8, 5.0$ Hz, 1H), 3.79 (td, $J = 5.5, 2.5$ Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.7, 146.3, 137.2, 135.3, 132.6, 130.4, 130.2, 130.1, 129.5, 127.9, 124.9, 65.8, 61.2, 21.9. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{NaO}_4\text{SSe}$ 430.9827, Found 430.9819.

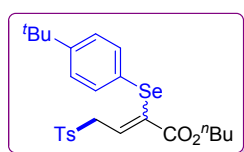
(Z/E)-butyl 2-(p-tolylselanyl)-4-tosylbut-2-enoate (3ab)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2b** (0.20 mmol, 65.2 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ab** as colorless liquid (**Yield**: 85%, 79.2 mg, $Z/E = 4.9:1$). **Major**: ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.77 (m, 2H), 7.41 – 7.36 (m, 2H), 7.13 (t, $J = 7.8$ Hz, 1H), 7.10 – 7.05 (m, 2H), 7.03 – 6.96 (m, 2H), 4.34 (d, $J = 7.8$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 2.49 (s, 3H), 2.31 (s, 3H), 1.50 – 1.37 (m, 2H), 1.33 – 1.16 (m, 2H), 0.86 (t, $J = 7.4$ Hz, 3H). **Minor**: ^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.59 (m, 2H), 7.47 – 7.41 (m, 2H), 7.35 – 7.30 (m, 2H), 7.24 – 7.19 (m, 2H), 5.69 (t, $J = 8.1$ Hz, 1H), 4.39 (d, $J = 8.1$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 2.47 (s, 3H), 2.42 (s, 3H), 1.50 – 1.37 (m, 2H),

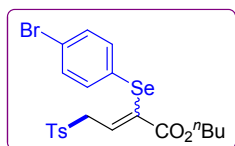
1.33 – 1.16 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.8, 164.2 (minor), 145.3, 144.7 (minor), 137.8, 136.6, 135.7, 134.9 (minor), 134.6, 132.5, 130.9 (minor), 130.14, 130.11, 129.7 (minor), 128.6, 126.0 (minor), 125.8, 66.0, 65.8 (minor), 59.8, 57.1 (minor), 30.5, 21.9, 21.8 (minor), 21.5 (minor), 21.2, 19.2 (minor), 19.1, 13.8. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NaO}_4\text{SSe}$ 489.0609, Found 489.0600.

(*Z/E*)-butyl 2-((4-(tert-butyl)phenyl)selanyl)-4-tosylbut-2-enoate (**3ac**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2c** (0.20 mmol, 73.6 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ac** as colorless liquid (Yield: 86%, 87.4 mg, *Z/E* = 4.3:1). **Major:** ^1H NMR (400 MHz, CDCl_3) δ 7.82 – 7.75 (m, 2H), 7.45 – 7.26 (m, 3H), 7.22 – 7.01 (m, 4H), 4.32 (d, $J = 7.8$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 2.47 (s, 3H), 1.46 – 1.35 (m, 2H), 1.26 (s, 9H), 1.21 – 1.08 (m, 2H), 0.82 (t, $J = 7.4$ Hz, 3H). **Minor:** ^1H NMR (400 MHz, CDCl_3) δ 7.68 – 7.61 (m, 2H), 7.45 – 7.26 (m, 3H), 7.22 – 7.01 (m, 3H), 5.76 (t, $J = 8.1$ Hz, 1H), 4.38 (d, $J = 8.1$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 2.44 (s, 3H), 1.57 – 1.47 (m, 2H), 1.34 (s, 9H), 1.33 – 1.27 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.8, 164.2 (minor), 152.8 (minor), 150.9, 145.3, 144.7 (minor), 136.1, 135.72, 135.67 (minor), 134.8, 134.7, 133.4 (minor), 132.0, 130.1, 129.7 (minor), 128.6, 127.1 (minor), 126.4, 126.0 (minor), 123.3 (minor), 65.9, 65.7 (minor), 59.8, 57.1 (minor), 34.9 (minor), 34.6, 31.3, 30.40 (minor), 30.35, 21.84 (minor), 21.77, 19.2 (minor), 19.0, 13.8 (minor), 13.7. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{NaO}_4\text{SSe}$ 531.1079, Found 531.1068.

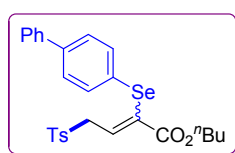
(*Z/E*)-butyl 2-((4-bromophenyl)selanyl)-4-tosylbut-2-enoate (**3ad**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2d** (0.20 mmol, 78.0 mg), EtOAc (1.0 mL) and purified by column chromatography on

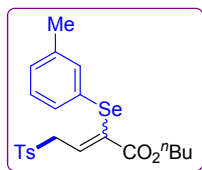
silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ad** as colorless liquid (**Yield**: 82%, 86.9 mg, *Z/E* = 4.9:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 – 7.75 (m, 2H), 7.38 – 7.25 (m, 4H), 7.19 (t, J = 7.9 Hz, 1H), 7.04 – 6.99 (m, 2H), 4.33 (d, J = 7.9 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 2.47 (s, 3H), 1.47 – 1.38 (m, 2H), 1.23 – 1.11 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 – 7.59 (m, 2H), 7.50 – 7.45 (m, 2H), 7.38 – 7.25 (m, 4H), 5.76 (t, J = 7.9 Hz, 1H), 4.39 (d, J = 8.0 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 2.47 (s, 3H), 1.47 – 1.38 (m, 2H), 1.23 – 1.11 (m, 2H), 0.91 (t, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.4, 164.0 (minor), 145.5, 145.0 (minor), 137.6, 136.1, 135.7, 134.1, 133.6, 133.2 (minor), 132.4, 130.2, 129.9 (minor), 128.7 (minor), 128.6, 128.5 (minor), 127.8 (minor), 121.9, 66.2, 66.0 (minor), 60.0, 57.2 (minor), 30.52, 30.47 (minor), 21.9, 21.8 (minor), 19.2 (minor), 19.1, 13.8. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{BrNaO}_4\text{SSe}$ 552.9558, Found 552.9544.

(*Z/E*)-butyl 2-([1,1'-biphenyl]-4-ylselanyl)-4-tosylbut-2-enoate (3ae**)**



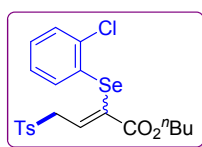
This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2e** (0.20 mmol, 77.6 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ae** as colorless liquid (**Yield**: 75%, 79.2 mg, *Z/E* = 3.8:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.84 – 7.76 (m, 2H), 7.68 – 7.35 (m, 10H), 7.32 – 7.22 (m, 2H), 4.38 (d, J = 7.8 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 2.48 (s, 3H), 1.50 – 1.41 (m, 2H), 1.25 – 1.15 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 – 7.75 (m, 2H), 7.68 – 7.35 (m, 9H), 7.32 – 7.22 (m, 2H), 5.84 (t, J = 8.0 Hz, 1H), 4.43 (d, J = 8.0 Hz, 2H), 4.06 (t, J = 6.6 Hz, 2H), 2.41 (s, 3H), 1.62 – 1.54 (m, 2H), 1.41 – 1.32 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.7, 164.2 (minor), 145.4, 144.8 (minor), 140.6, 140.3, 136.6, 135.7, 135.5, 134.5, 132.4, 130.2, 129.8 (minor), 129.1 (minor), 129.0, 128.7 (minor), 128.6, 128.5 (minor), 128.0, 127.7 (minor), 127.2 (minor), 127.0, 66.1, 65.9 (minor), 60.0, 57.2 (minor), 30.5, 21.9, 21.7 (minor), 19.2 (minor), 19.1, 13.8. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{28}\text{NaO}_4\text{SSe}$ 551.0766, Found 551.0756.

(*Z/E*)-butyl 2-(*o*-tolylselanyl)-4-tosylbut-2-enoate (**3af**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2f** (0.20 mmol, 65.2 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3af** as colorless liquid (**Yield**: 85%, 79.2 mg, *Z/E* = 4:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 – 7.74 (m, 2H), 7.42 – 7.21 (m, 3H), 7.15 (t, J = 7.8 Hz, 1H), 7.09 – 6.98 (m, 2H), 6.90 (d, J = 7.3 Hz, 1H), 4.32 (d, J = 7.8 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 2.46 (s, 3H), 2.26 (s, 3H), 1.46 – 1.37 (m, 2H), 1.25 – 1.11 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.65 – 7.59 (m, 2H), 7.42 – 7.21 (m, 3H), 7.09 – 6.98 (m, 3H), 5.75 (t, J = 8.0 Hz, 1H), 4.37 (d, J = 8.0 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H), 1.57 – 1.49 (m, 2H), 1.36 – 1.25 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.8, 164.1 (minor), 145.3, 144.7 (minor), 139.9 (minor), 139.2, 136.8 (minor), 135.8, 135.1, 134.6, 133.3 (minor), 132.5, 130.3 (minor), 130.1, 129.8 (minor), 129.7 (minor), 129.5 (minor), 129.1, 129.0, 128.6, 128.4, 126.71, 126.69 (minor), 66.0, 65.8 (minor), 59.9, 57.2 (minor), 30.49, 30.47 (minor), 21.84, 21.78 (minor), 21.4 (minor), 21.3, 19.2 (minor), 19.1, 13.78 (minor), 13.75. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{NaO}_4\text{SSe}$ 489.0609, Found 489.0601.

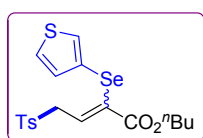
(*Z/E*)-butyl 2-((2-chlorophenyl)selanyl)-4-tosylbut-2-enoate (**3ag**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2g** (0.20 mmol, 69.2 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ag** as colorless liquid (**Yield**: 83%, 80.7 mg, *Z/E* = 5.7:1). **Major**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 – 7.74 (m, 2H), 7.45 – 7.28 (m, 3H), 7.22 – 7.06 (m, 4H), 4.33 (d, J = 7.8 Hz, 2H), 4.03 (t, J = 6.6 Hz, 2H), 2.47 (s, 3H), 1.48 – 1.39 (m, 2H), 1.24 – 1.13 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H). **Minor**: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 – 7.60 (m, 2H),

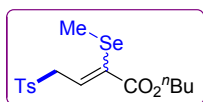
7.45 – 7.28 (m, 3H), 7.22 – 7.06 (m, 3H), 5.74 (t, $J = 8.0$ Hz, 1H), 4.39 (d, $J = 8.0$ Hz, 2H), 4.03 (t, $J = 6.6$ Hz, 2H), 2.46 (s, 3H), 1.58 – 1.50 (m, 2H), 1.38 – 1.29 (m, 2H), 0.92 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 163.9 (minor), 145.5, 145.0 (minor), 137.5, 135.9, 135.7, 134.2, 133.9, 133.4, 130.23 (minor), 130.19, 129.8 (minor), 129.5, 128.6, 128.5 (minor), 127.9, 127.5 (minor), 125.3 (minor), 66.2, 66.0 (minor), 59.9, 57.1 (minor), 30.5, 30.4 (minor), 21.9, 21.8 (minor), 19.2 (minor), 19.1, 13.8 (minor), 13.7. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{23}\text{ClNaO}_4\text{SSe}$ 509.0063, Found 509.0051.

(*Z/E*)-butyl 2-(thiophen-3-ylselanyl)-4-tosylbut-2-enoate (**3ah**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2h** (0.20 mmol, 63.6 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ah** as colorless liquid (Yield: 79%, 72.4 mg, $Z/E = 1:1$). (**Z**): ^1H NMR (400 MHz, CDCl_3) δ 7.79 – 7.69 (m, 3H), 7.40 – 7.23 (m, 3H), 7.15 – 7.11 (m, 1H), 7.09 – 6.87 (m, 1H), 4.33 (d, $J = 7.9$ Hz, 2H), 4.12 – 4.01 (m, 2H), 2.47 (s, 3H), 1.62 – 1.50 (m, 2H), 1.41 – 1.22 (m, 2H), 1.01 – 0.86 (m, 3H). (**E**): ^1H NMR (400 MHz, CDCl_3) δ 7.67 – 7.54 (m, 3H), 7.40 – 7.23 (m, 3H), 7.09 – 6.87 (m, 1H), 5.64 (t, $J = 8.1$ Hz, 1H), 4.39 (d, $J = 8.1$ Hz, 2H), 4.12 – 4.01 (m, 2H), 2.44 (s, 3H), 1.62 – 1.50 (m, 2H), 1.41 – 1.22 (m, 2H), 1.01 – 0.86 (m, 3H). (**Z**): ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 145.5, 139.2, 135.73, 135.49, 134.1, 131.3, 130.2, 128.6, 128.0, 122.2, 66.2, 59.6, 30.5, 21.83, 19.15, 13.77. (**E**): ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 144.8, 136.0, 135.54, 133.9, 133.8, 129.7, 129.1, 128.5, 126.3, 120.2, 65.9, 57.0, 30.4, 21.77, 19.23, 13.80. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{22}\text{NaO}_4\text{S}_2\text{Se}$ 481.0017, Found 481.0008.

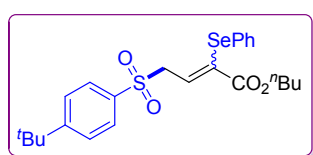
(*Z/E*)-butyl 2-(methylselanyl)-4-tosylbut-2-enoate (**3ai**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2i** (0.20 mmol, 50.0 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum

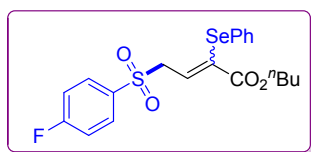
ether: ethyl acetate = 10:1) to give the product **3ai** as colorless liquid (**Yield:** 78%, 60.8 mg, *Z/E* = 2:1). **Major:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 – 7.70 (m, 2H), 7.39 – 7.31 (m, 2H), 7.00 (t, J = 7.9 Hz, 1H), 4.30 (d, J = 7.9 Hz, 2H), 4.20 (t, J = 6.7 Hz, 2H), 2.45 (s, 3H), 1.97 (s, 3H), 1.73 – 1.62 (m, 2H), 1.48 – 1.28 (m, 2H), 1.02 – 0.83 (m, 3H). **Minor:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 – 7.70 (m, 2H), 7.39 – 7.31 (m, 2H), 5.90 (t, J = 8.0 Hz, 1H), 4.48 (d, J = 8.0 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 2.45 (s, 3H), 2.14 (s, 3H), 1.62 – 1.53 (m, 2H), 1.48 – 1.28 (m, 2H), 1.02 – 0.83 (m, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.7, 164.2 (minor), 145.3, 144.9 (minor), 135.7, 134.4 (minor), 134.0, 132.3 (minor), 130.0, 129.8 (minor), 128.6, 128.5 (minor), 123.8, 66.0, 65.7 (minor), 60.0, 57.1 (minor), 30.7, 30.5 (minor), 21.79, 21.76 (minor), 19.3, 19.2 (minor), 13.82, 13.76 (minor), 7.9, 6.6 (minor). **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{22}\text{NaO}_4\text{SSe}$ 413.0296, Found 413.0288.

(*Z/E*)-butyl 4-((4-(tert-butyl)phenyl)sulfonyl)-2-(phenylselanyl)but-2-enoate (3aj)



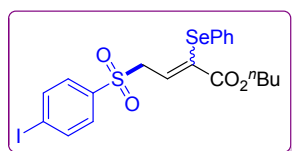
This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2j** (0.20 mmol, 70.8 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3aj** as colorless liquid (**Yield:** 85%, 84.0 mg, *Z/E* = 4:1). **Major:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 – 7.78 (m, 2H), 7.61 – 7.56 (m, 2H), 7.14 – 7.23 (m, 6H), 4.32 (d, J = 7.8 Hz, 2H), 4.08 – 3.89 (m, 2H), 1.45 – 1.39 (m, 2H), 1.36 (s, 9H), 1.23 – 1.13 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H). **Minor:** $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 – 7.63 (m, 2H), 7.55 – 7.48 (m, 2H), 7.43 – 7.23 (m, 3H), 7.14 – 7.23 (m, 2H), 5.75 (t, J = 7.9 Hz, 1H), 4.38 (d, J = 8.0 Hz, 2H), 4.08 – 3.89 (m, 2H), 1.58 – 1.50 (m, 2H), 1.36 (s, 9H), 1.33 – 1.25 (m, 2H), 0.91 (t, J = 7.4 Hz, 2H), 0.83 (t, J = 7.4 Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 164.8, 158.4, 157.8 (minor), 136.4, 135.6, 134.9, 134.8, 132.1, 130.0 (minor), 129.8 (minor), 129.44 (minor), 129.37, 128.4, 128.3 (minor), 127.6, 126.8 (minor), 126.6, 126.2 (minor), 66.0, 65.9 (minor), 59.9, 57.2 (minor), 35.5, 31.2, 30.4, 19.2 (minor), 19.1, 13.77 (minor), 13.75. **HRMS** (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{30}\text{NaO}_4\text{SSe}$ 517.0922, Found 517.0914.

(*Z/E*)-butyl 4-((4-fluorophenyl)sulfonyl)-2-(phenylselanyl)but-2-enoate (**3ak**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2k** (0.20 mmol, 63.2 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ak** as colorless liquid (**Yield**: 82%, 74.8 mg, *Z/E* = 4:1). **Major: ¹H NMR** (400 MHz, CDCl₃) δ 7.98 – 7.90 (m, 2H), 7.31 – 7.11 (m, 8H), 4.37 (d, *J* = 7.8 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 1.48 – 1.38 (m, 2H), 1.25 – 1.14 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **Minor: ¹H NMR** (400 MHz, CDCl₃) δ 7.81 – 7.73 (m, 2H), 7.57 – 7.50 (m, 2H), 7.48 – 7.38 (m, 3H), 7.31 – 7.11 (m, 2H), 5.73 (t, *J* = 8.1 Hz, 1H), 4.42 (d, *J* = 8.1 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 1.62 – 1.50 (m, 2H), 1.38 – 1.30 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 166.3 (d, *J* = 257.2), 164.6, 164.0 (minor), 136.4, 135.0, 134.7, 134.56 (d, *J* = 3.0 Hz), 133.7 (minor), 131.9, 131.5 (d, *J* = 9.8), 131.5 (d, *J* = 9.7) (minor), 130.1 (minor), 129.6 (minor), 129.5 (minor), 129.4, 127.7, 126.8 (minor), 126.3 (minor), 116.9 (d, *J* = 22.7), 116.4 (d, *J* = 22.6) (minor), 66.2, 65.9 (minor), 59.9, 57.1 (minor), 30.4, 19.2 (minor), 19.0, 13.8 (minor), 13.7. **Major: ¹⁹F NMR** (376 MHz, CDCl₃) δ -102.4. **Minor: ¹⁹F NMR** (376 MHz, CDCl₃) δ -103.3. **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₁FN₄SSe 479.0202, Found 479.0192.

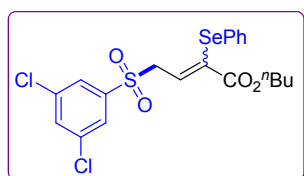
(*Z/E*)-butyl 4-((4-iodophenyl)sulfonyl)-2-(phenylselanyl)but-2-enoate (**3al**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2l** (0.20 mmol, 84.8 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3al** as colorless liquid (**Yield**: 82%, 92.5 mg, *Z/E* = 4:1). **Major: ¹H NMR** (400 MHz, CDCl₃) δ 7.94 – 7.90 (m, 2H), 7.64 – 7.56 (m, 2H), 7.46 – 7.36 (m, 1H), 7.24 – 7.08 (m, 5H), 4.33 (d, *J* = 7.8 Hz, 2H), 4.04 – 3.96 (m, 2H), 1.45 – 1.32 (m, 2H), 1.23 – 1.11 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). **Minor: ¹H NMR** (400 MHz,

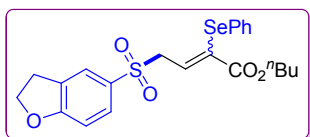
CDCl₃) δ 7.89 – 7.84 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.36 (m, 2H), 7.24 – 7.08 (m, 3H), 5.67 (t, J = 8.1 Hz, 1H), 4.39 (d, J = 8.1 Hz, 2H), 4.04 – 3.96 (m, 2H), 1.61 – 1.49 (m, 2H), 1.32 – 1.25 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 164.0 (minor), 138.8, 138.4, 138.3 (minor), 136.3, 135.0 (minor), 134.4, 132.0, 130.1 (minor), 130.0 (minor), 129.9, 129.6 (minor), 129.5, 129.4 (minor), 127.7, 126.8 (minor), 126.1, 102.5, 101.8 (minor), 66.1, 66.0 (minor), 59.7, 56.9 (minor), 30.5 (minor), 30.4, 19.2 (minor), 19.0, 13.8 (minor), 13.7. **HRMS** (ESI) m/z : [M + Na]⁺ Calcd for C₂₀H₂₁INaO₄SSe 586.9263, Found 586.9254.

(*Z/E*)-butyl 4-((3,5-dichlorophenyl)sulfonyl)-2-(phenylselanyl)but-2-enoate (3am)



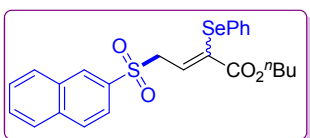
This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2m** (0.20 mmol, 73.2 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3am** as colorless liquid (**Yield**: 86%, 87.0 mg, *Z/E* = 4:1). **Major**: ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.76 (m, 2H), 7.66 – 7.59 (m, 2H), 7.27 – 7.15 (m, 4H), 7.12 (t, J = 7.9 Hz, 1H), 4.34 (d, J = 7.8 Hz, 2H), 4.11 – 3.99 (m, 2H), 1.48 – 1.38 (m, 2H), 1.23 – 1.13 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H). **Minor**: ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.53 (m, 2H), 7.46 – 7.41 (m, 2H), 7.27 – 7.15 (m, 4H), 5.55 (t, J = 8.1 Hz, 1H), 4.43 (d, J = 8.2 Hz, 2H), 4.11 – 3.99 (m, 2H), 1.61 – 1.54 (m, 2H), 1.40 – 1.30 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 163.9 (minor), 141.3, 141.2 (minor), 136.7, 136.6, 136.1 (minor), 135.9 (minor), 135.0 (minor), 134.4, 133.9 (minor), 133.3, 132.0, 130.3 (minor), 129.9 (minor), 129.5, 129.3 (minor), 127.9, 127.1 (minor), 127.0, 124.5, 66.3, 66.1 (minor), 59.6, 56.9 (minor), 30.4, 19.2 (minor), 19.1, 13.8 (minor), 13.7. **HRMS** (ESI) m/z : [M + Na]⁺ Calcd for C₂₀H₂₀Cl₂NaO₄SSe 528.9517, Found 528.9501.

(*Z/E*)-butyl 4-((2,3-dihydrobenzofuran-5-yl)sulfonyl)-2-(phenylselanyl)but-2-enoate (3an)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2n** (0.20 mmol, 68.0 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 7:1) to give the product **3an** as colorless liquid (**Yield**: 80%, 76.8 mg, *Z/E* = 4:1). **Major: ¹H NMR** (400 MHz, CDCl₃) δ 7.73 – 7.67 (m, 2H), 7.27 – 7.08 (m, 6H), 6.90 (d, *J* = 9.2 Hz, 1H), 4.70 (t, *J* = 8.8 Hz, 2H), 4.52 – 4.31 (m, 2H), 4.11 – 3.87 (m, 2H), 3.69 – 2.98 (m, 2H), 1.48 – 1.38 (m, 2H), 1.25 – 1.14 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **Minor: ¹H NMR** (400 MHz, CDCl₃) δ 7.62 – 7.47 (m, 2H), 7.45 – 7.37 (m, 2H), 7.27 – 7.08 (m, 3H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.81 (t, *J* = 8.0 Hz, 1H), 4.70 (t, *J* = 8.8 Hz, 2H), 4.52 – 4.31 (m, 2H), 4.11 – 3.87 (m, 2H), 3.69 – 2.98 (m, 2H), 1.60 – 1.52 (m, 2H), 1.38 – 1.31 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 165.2, 164.7, 136.1, 135.8, 134.2, 131.8, 130.4, 130.3 (minor), 130.0, 129.8 (minor), 129.3, 129.0 (minor), 127.5, 127.4 (minor), 125.8 (minor), 125.7, 110.0, 109.6 (minor), 72.6, 66.0, 65.8 (minor), 60.1, 57.4 (minor), 30.4, 29.0, 19.2 (minor), 19.0, 13.8 (minor), 13.7. **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₂H₂₄NaO₅SSe 503.0402, Found 503.0407.

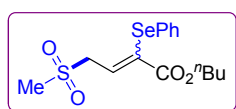
(*Z/E*)-butyl 4-(naphthalen-2-ylsulfonyl)-2-(phenylselanyl)but-2-enoate (**3ao**)



This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2o** (0.20 mmol, 69.6 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1) to give the product **3ao** as colorless liquid (**Yield**: 76%, 74.2 mg, *Z/E* = 4.6:1). **Major: ¹H NMR** (400 MHz, CDCl₃) δ 8.49 (s, 1H), 8.04 – 7.91 (m, 3H), 7.90 – 7.84 (m, 1H), 7.76 – 7.61 (m, 2H), 7.26 – 7.18 (m, 2H), 7.15 – 7.06 (m, 1H), 6.98 – 6.93 (m, 3H), 4.43 (d, *J* = 7.7 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 1.41 – 1.32 (m, 2H), 1.21 – 1.08 (m, 2H), 0.86 – 0.77 (m, 3H). **Minor: ¹H NMR** (400 MHz, CDCl₃) δ 8.34 (s, 1H), 8.04 – 7.91 (m, 3H), 7.76 – 7.61 (m, 2H), 7.47 – 7.41 (m, 1H), 7.26 – 7.18 (m, 2H), 6.98 – 6.93 (m, 3H), 5.76 (t, *J* = 8.1 Hz, 1H), 4.49 (d, *J* = 8.1 Hz, 2H), 3.80 (t, *J* = 6.7 Hz, 2H), 1.41 – 1.32 (m, 2H), 1.21 – 1.08 (m, 2H), 0.86 – 0.77 (m, 3H). **¹³C NMR** (100

MHz, CDCl₃) δ 164.6, 164.0 (minor), 136.2, 135.7, 135.6, 135.5 (minor), 135.4 (minor), 135.1, 134.7, 133.5 (minor), 132.3 (minor), 131.9, 130.6, 130.5 (minor), 130.0, 129.9, 129.72, 129.67, 129.52 (minor), 129.46 (minor), 129.40 (minor), 129.36 (minor), 129.2, 128.2, 128.1 (minor), 128.0, 127.8 (minor), 127.5, 126.8 (minor), 126.6 (minor), 123.2 (minor), 122.9, 66.0, 65.7 (minor), 59.9, 57.1 (minor), 30.4, 30.3 (minor), 19.1 (minor), 19.0, 13.7. **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₂₄H₂₄NaO₄SSe 511.0453, Found 511.0446.

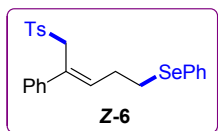
(Z/E)-butyl 4-(methylsulfonyl)-2-(phenylselanyl)but-2-enoate (3ap)



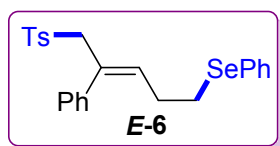
This compound was prepared according to the general procedure using **1a** (0.20 mmol, 33.6 mg), **2p** (0.20 mmol, 47.2 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 8:1) to give the product **3ap** as colorless liquid (**Yield**: 79%, 59.4 mg, *Z/E* = 4:1). **Major**: ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.38 (m, 3H), 7.30 – 7.25 (m, 3H), 4.25 – 4.16 (m, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.88 (s, 3H), 1.50 – 1.35 (m, 2H), 1.28 – 1.17 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H). **Minor**: ¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.56 (m, 2H), 7.43 – 7.38 (m, 1H), 7.30 – 7.25 (m, 2H), 5.89 (t, *J* = 8.3 Hz, 1H), 4.25 – 4.16 (m, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.83 (s, 3H), 1.50 – 1.35 (m, 2H), 1.28 – 1.17 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 136.1, 134.9, 134.8, 132.2, 130.2 (minor), 129.6, 127.9, 127.1 (minor), 66.3, 66.2 (minor), 58.3, 56.0 (minor), 40.8, 40.1 (minor), 30.5, 29.8 (minor), 19.2 (minor), 19.1, 13.7. **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₁₅H₂₀NaO₄SSe 399.0140, Found 399.0140.

Phenyl(4-phenyl-5-tosylpent-3-en-1-yl)selane (6)

This compound was prepared according to the general procedure using **5** (0.20 mmol, 28.8 mg), **2a** (0.20 mmol, 62.4 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 10:1). **Z-6** and **E-6** are two isolatable isomers.



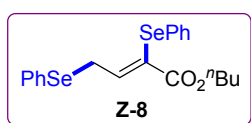
White solid (**Yield:** 83%, 75.4 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.59 – 7.46 (m, 4H), 7.30 – 7.24 (m, 3H), 7.21 – 7.10 (m, 7H), 5.99 (t, *J* = 7.4 Hz, 1H), 4.23 (s, 2H), 2.90 (t, *J* = 7.1 Hz, 2H), 2.47 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 144.6, 140.7, 136.5, 136.1, 132.9, 129.9, 129.6, 129.4, 129.2, 128.5, 128.3, 127.3, 127.1, 126.6, 57.9, 30.0, 26.6, 21.6. **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₄H₂₄NaO₂SSe 479.0554, Found 479.0563.



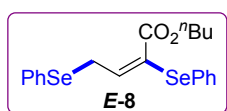
White solid (**Yield:** 8%, 7.5 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.67 – 7.61 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.17 (m, 8H), 7.03 – 6.98 (m, 2H), 5.65 (t, *J* = 7.4 Hz, 1H), 4.08 (s, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.43 – 2.35 (m, 5H). **¹³C NMR** (100 MHz, CDCl₃) δ 144.6, 138.2, 136.6, 136.0, 132.8, 130.1, 129.9, 129.7, 129.2, 128.7, 128.6, 128.3, 127.5, 127.0, 65.1, 30.0, 26.8, 21.7. **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₄H₂₄NaO₂SSe 479.0554, Found 479.0561.

Butyl 2,4-bis(phenylselanyl)but-2-enoate (**8**)

This compound was prepared according to the general procedure using **1a** (0.20 mmol, 45.6 mg), **diphenyl diselenide** (0.20 mmol, 62.6 mg), EtOAc (1.0 mL) and purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate = 50:1). **Z-8** and **E-8** are two isolatable isomers.



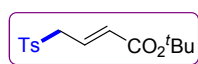
Colorless liquid (**Yield:** 59%, 53.6 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.62 – 7.58 (m, 2H), 7.49 (t, *J* = 8.2 Hz, 1H), 7.34 – 7.18 (m, 8H), 4.04 (t, *J* = 6.5 Hz, 2H), 3.94 (d, *J* = 8.2 Hz, 2H), 1.49 – 1.41 (m, 2H), 1.26 – 1.15 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 165.5, 147.4, 134.7, 131.2, 130.9, 129.2, 129.1, 128.2, 128.1, 126.8, 126.1, 65.6, 30.4, 28.7, 19.0, 13.7. **HRMS** (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₂NaO₂Se₂ 476.9842, Found 476.9836.



Colorless liquid (**Yield:** 17%, 15.4 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.49 – 7.41 (m, 4H), 7.32 – 7.19 (m, 6H), 6.22 (t, *J* = 8.7 Hz, 1H), 4.01 (t, *J* = 6.6 Hz, 2H), 3.95 (d, *J* = 8.6 Hz, 2H),

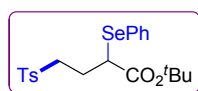
1.56 – 1.47 (m, 2H), 1.35 – 1.22 (m, 2H), 0.89 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.3, 141.5, 134.9, 134.7, 129.6, 129.1, 128.9, 128.8, 128.4, 127.8, 124.9, 65.4, 30.6, 27.2, 19.3, 13.8. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{NaO}_2\text{Se}_2$ 476.9842, Found 476.9835

(E)-tert-butyl 4-tosylbut-2-enoate (9)



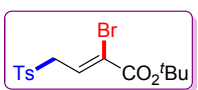
^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.72 (m, 2H), 7.40 – 7.33 (m, 2H), 6.65 (dt, $J = 15.5, 7.8$ Hz, 1H), 5.80 (d, $J = 15.6$ Hz, 1H), 3.88 (d, $J = 7.7$ Hz, 2H), 2.46 (s, 3H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 145.4, 135.5, 131.8, 131.5, 130.1, 128.5, 81.4, 59.4, 28.2, 21.8. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{20}\text{NaO}_4\text{S}$ 319.0975, Found 319.0971.

tert-butyl 2-(phenylselanyl)-4-tosylbutanoate (10)



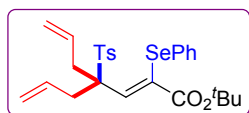
^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.70 (m, 2H), 7.53 – 7.49 (m, 2H), 7.37 – 7.23 (m, 5H), 3.57 (t, $J = 7.4$ Hz, 1H), 3.32 – 3.13 (m, 2H), 2.45 (s, 3H), 2.24 – 2.00 (m, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 144.9, 136.0, 135.7, 130.1, 129.2, 128.8, 128.2, 127.3, 81.9, 54.5, 42.6, 27.9, 25.2, 21.7. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{26}\text{NaO}_4\text{SSe}$ 477.0609, Found 477.0603.

(Z)-tert-butyl 2-bromo-4-tosylbut-2-enoate (11)



^1H NMR (400 MHz, CDCl_3) δ 7.78 – 7.75 (m, 2H), 7.37 – 7.33 (m, 2H), 7.16 (t, $J = 7.7$ Hz, 1H), 4.12 (d, $J = 7.7$ Hz, 2H), 2.46 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 145.4, 135.5, 130.0, 129.9, 128.3, 125.4, 83.9, 59.5, 27.9, 21.7. HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{BrNaO}_4\text{S}$ 397.0080, Found 397.0086.

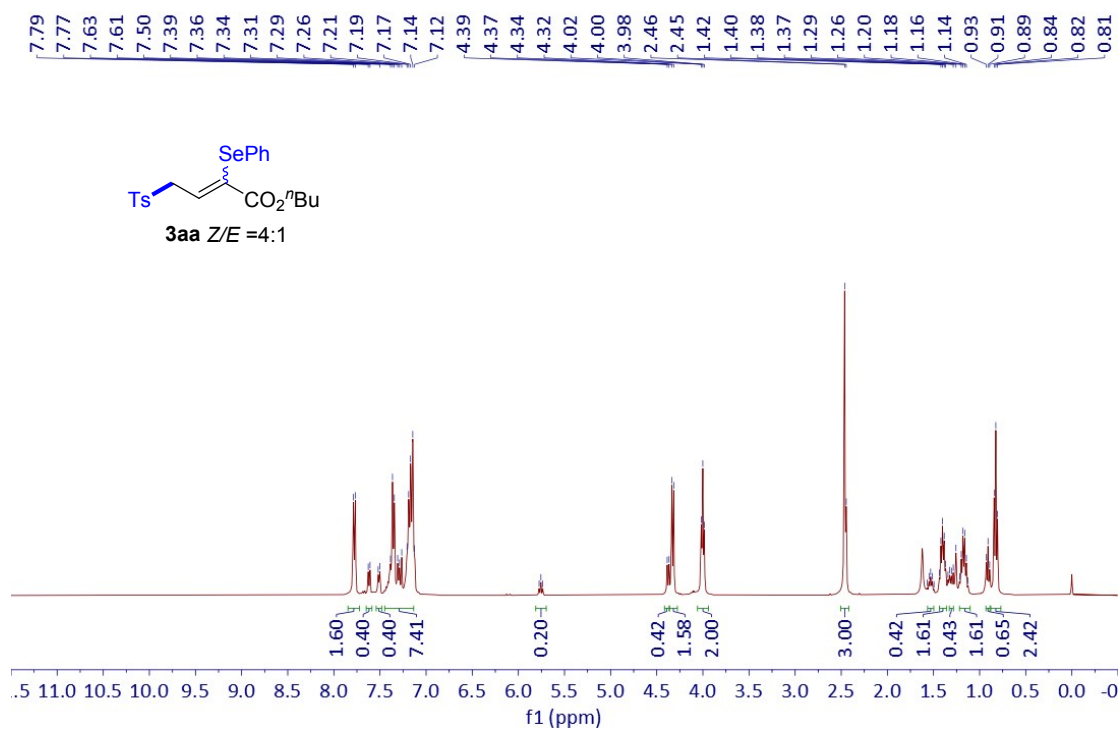
(Z)-tert-butyl 4-allyl-2-(phenylselanyl)-4-tosylhepta-2,6-dienoate (12)



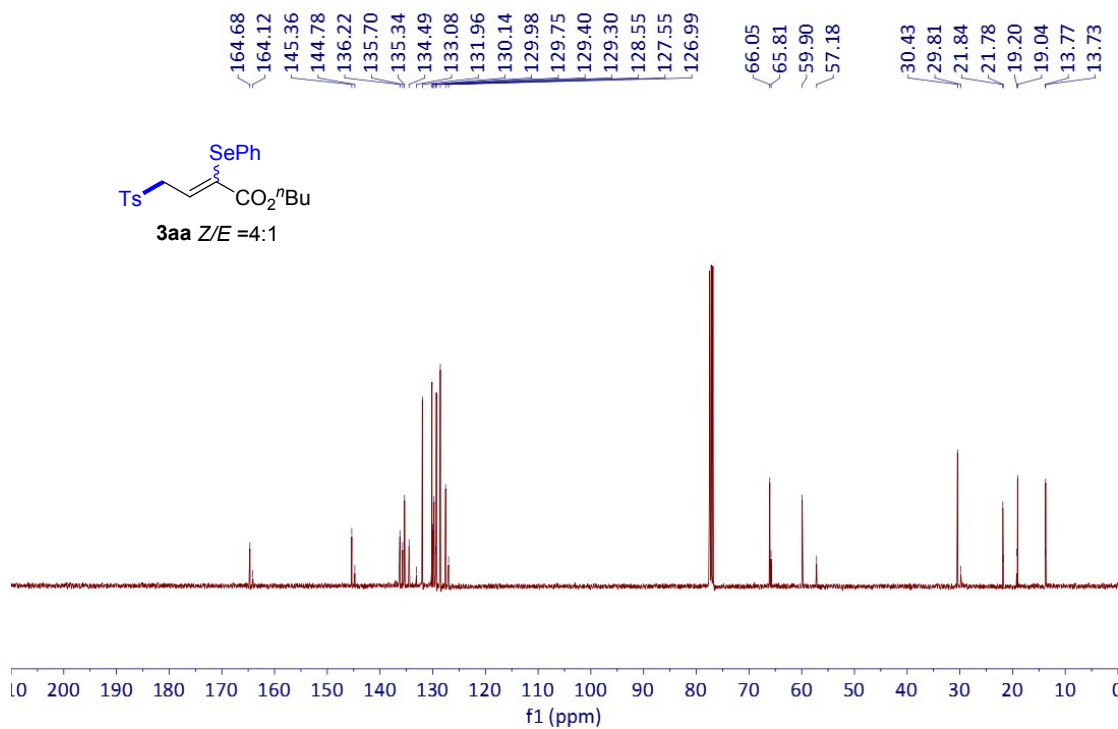
^1H NMR (400 MHz, CDCl_3) δ 7.83 (s, 1H), 7.73 – 7.67 (m, 2H), 7.38 – 7.32 (m, 2H), 7.25 – 7.13 (m, 5H), 5.72 – 5.57 (m, 2H), 5.10 – 4.99 (m, 4H), 2.80 – 2.60 (m, 4H), 2.39 (s, 9H). ^{13}C

NMR (100 MHz, CDCl₃) δ = 171.7, 156.0, 144.3, 136.2, 133.8, 132.5, 131.5, 130.0, 129.5, 129.3, 129.0, 127.5, 119.5, 82.3, 53.2, 41.2, 28.1, 21.7. **HRMS** (ESI) m/z: [M + Na]⁺ Calcd for C₂₇H₃₂NaO₄SSe 555.1079, Found 555.1071.

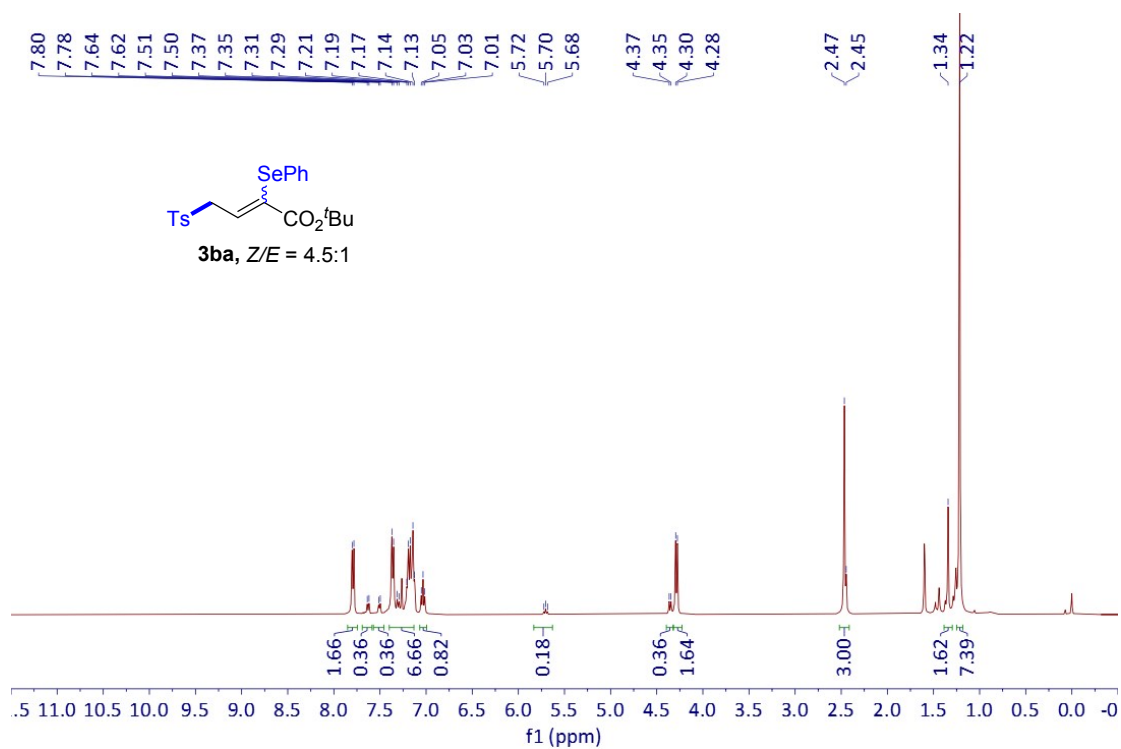
8. Copies of ^1H , ^{13}C NMR spectra of products



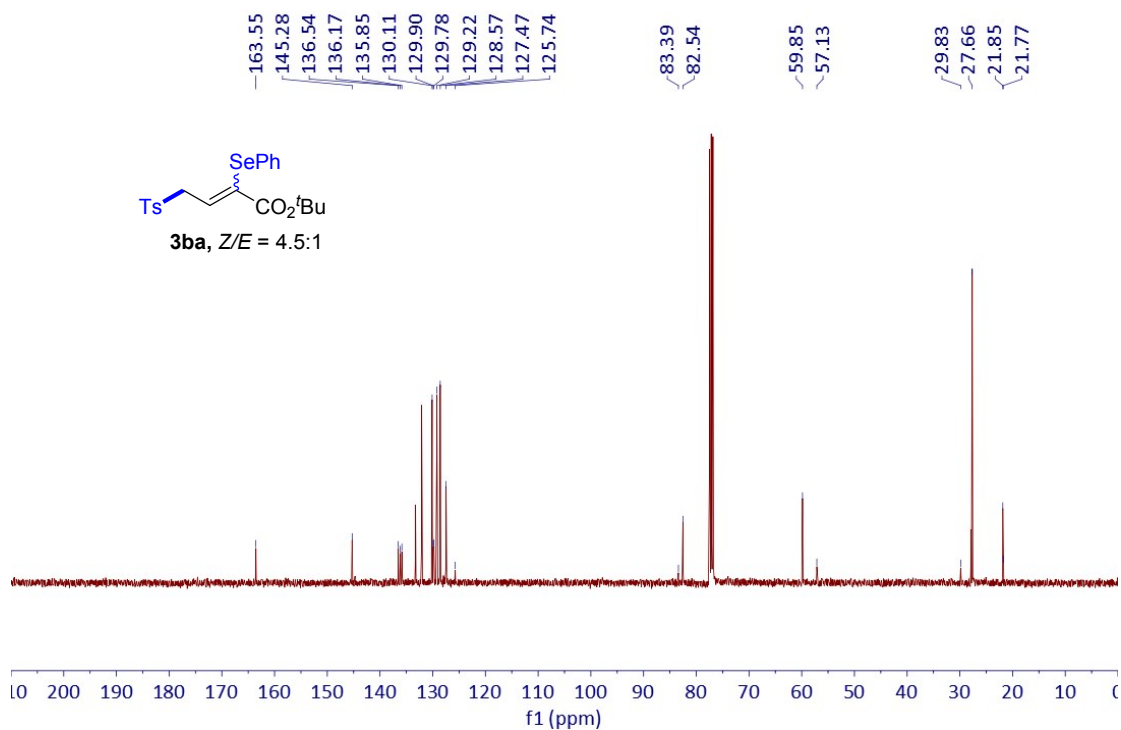
^1H NMR of **3aa** (400 Hz, CDCl_3)



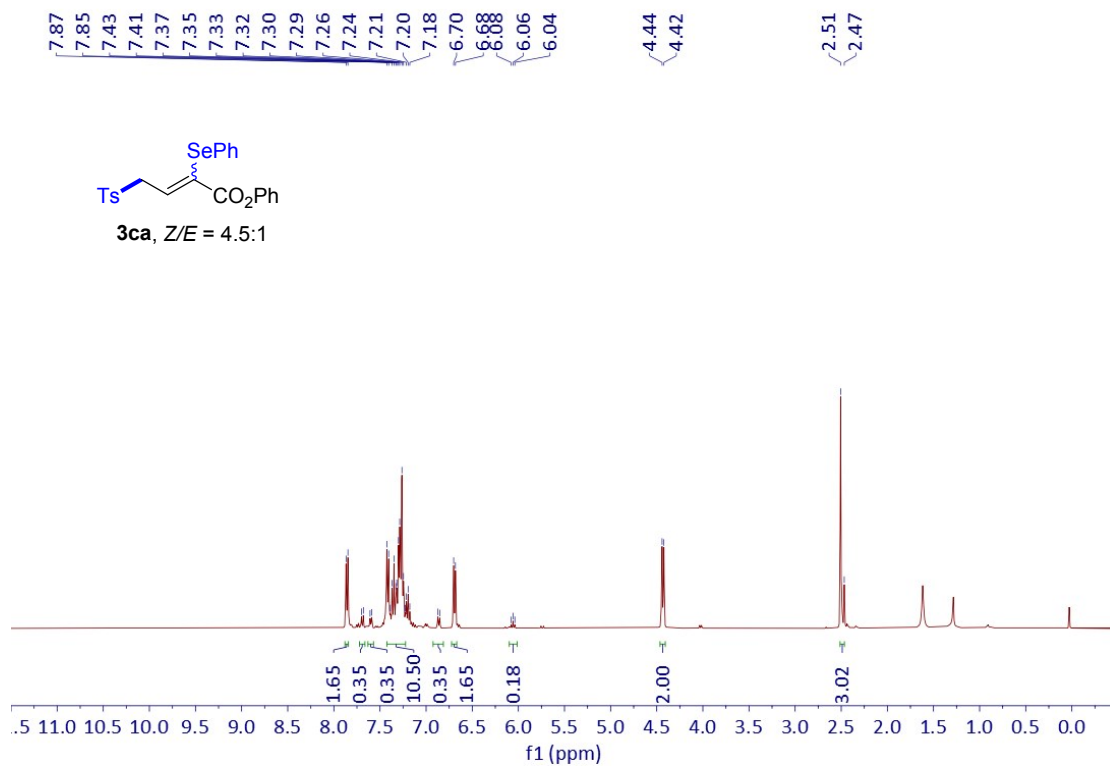
^{13}C NMR of **3aa** (100 Hz, CDCl_3)



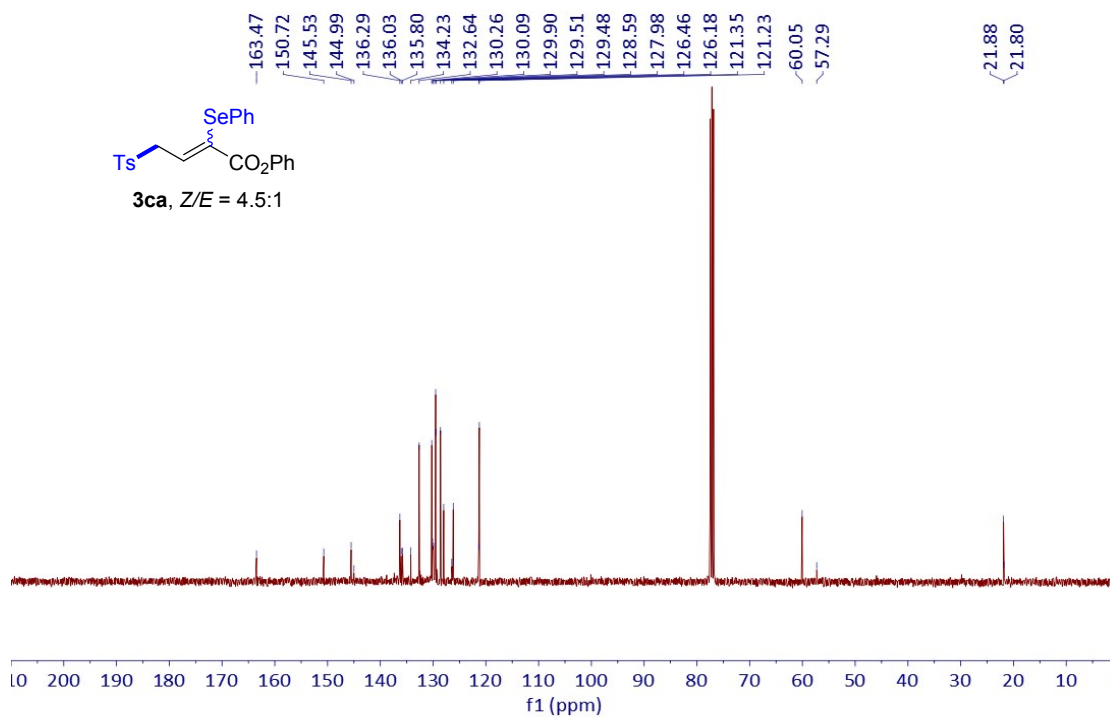
^1H NMR of **3ba** (400 Hz, CDCl_3)



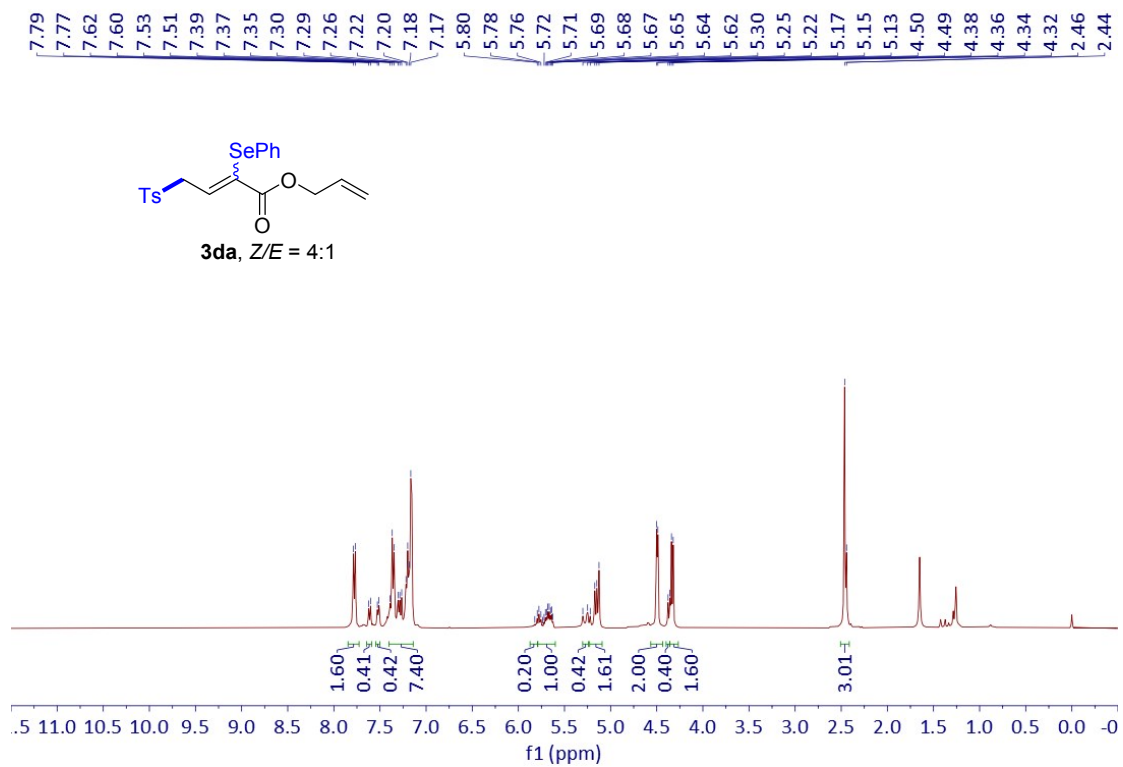
^{13}C NMR of **3ba** (100 Hz, CDCl_3)



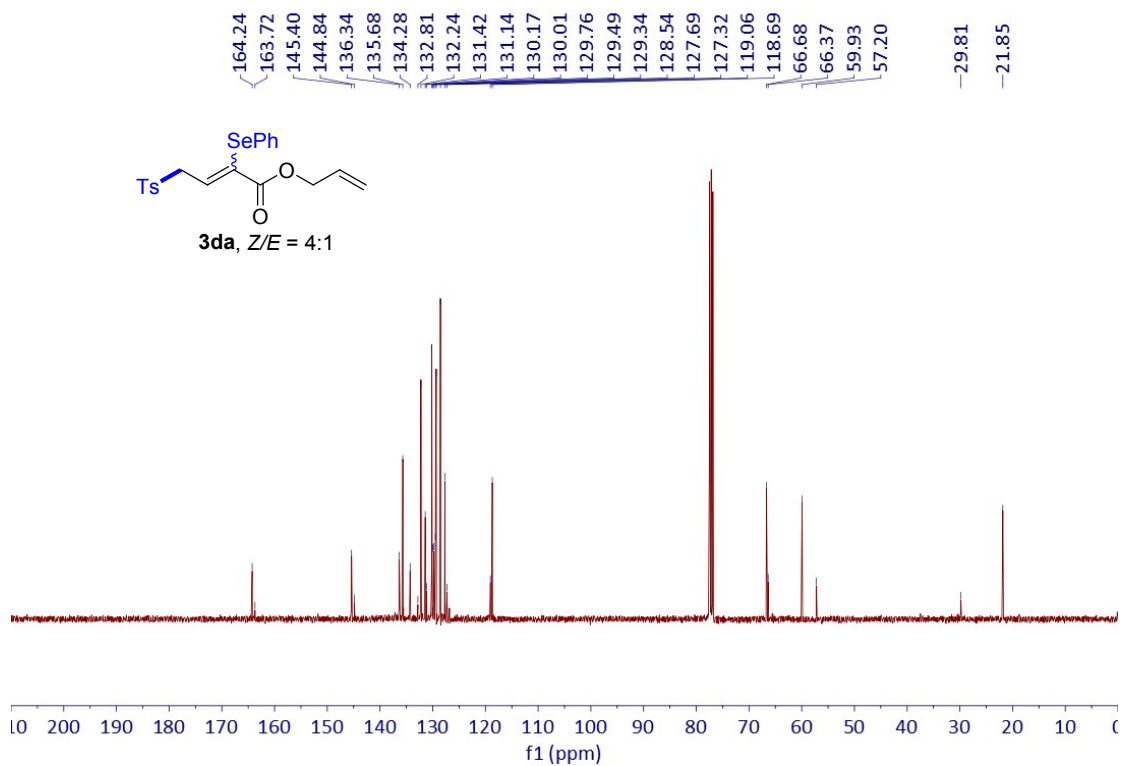
¹H NMR of **3ca** (400 Hz, CDCl₃)



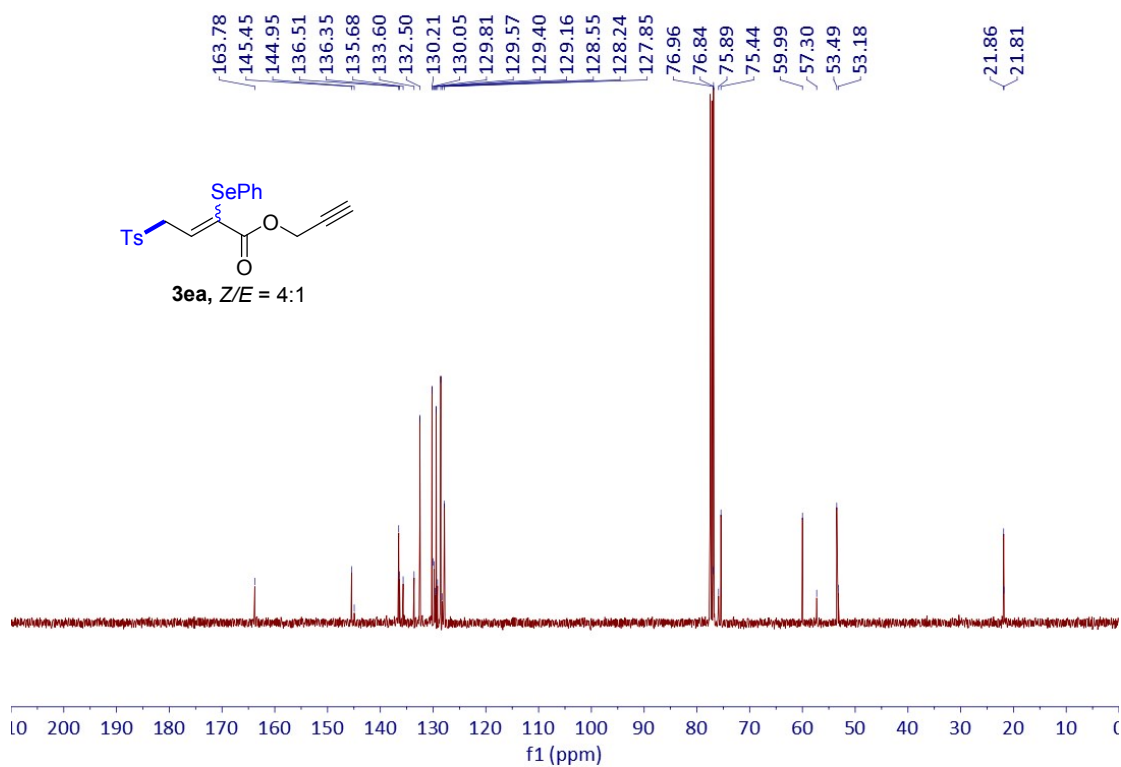
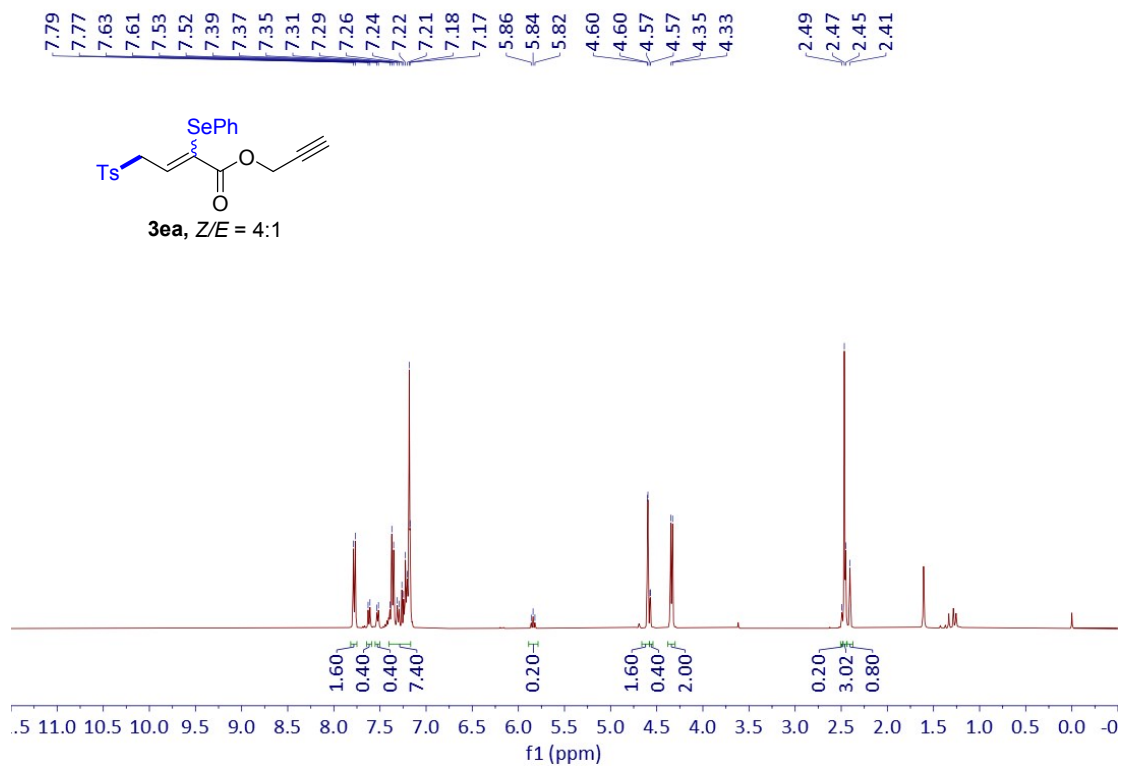
¹³C NMR of **3ca** (100 Hz, CDCl₃)

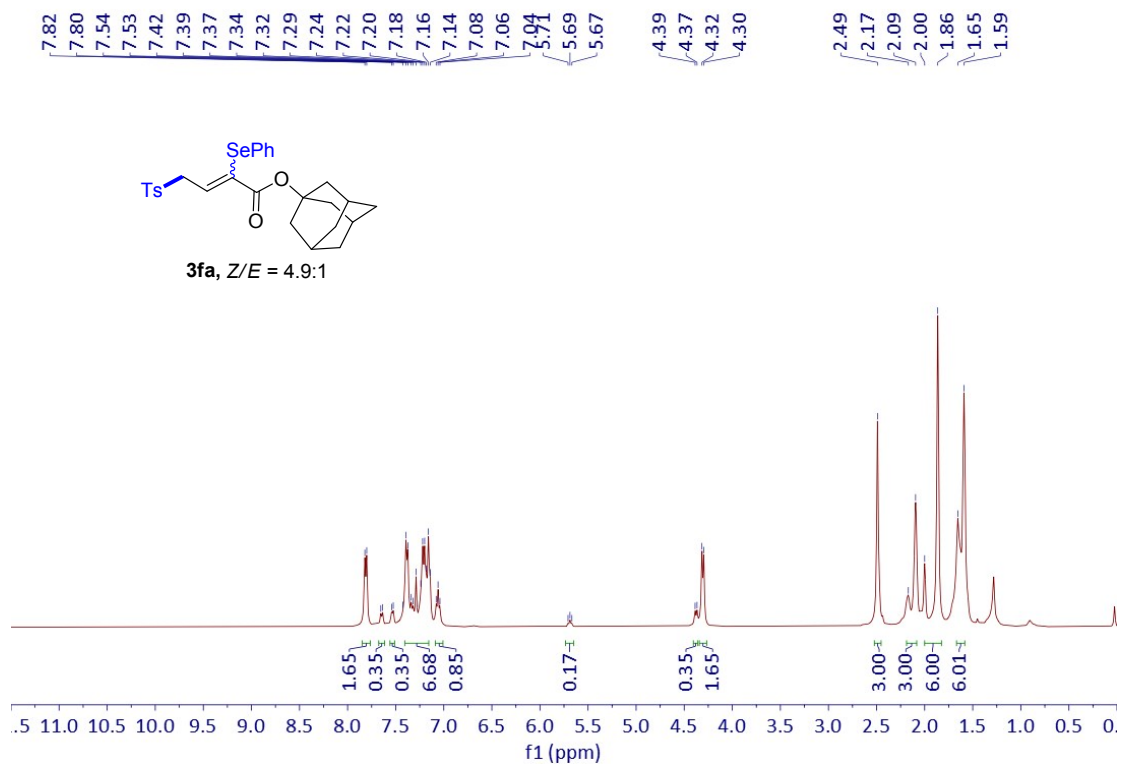


¹H NMR of **3da** (400 Hz, CDCl₃)

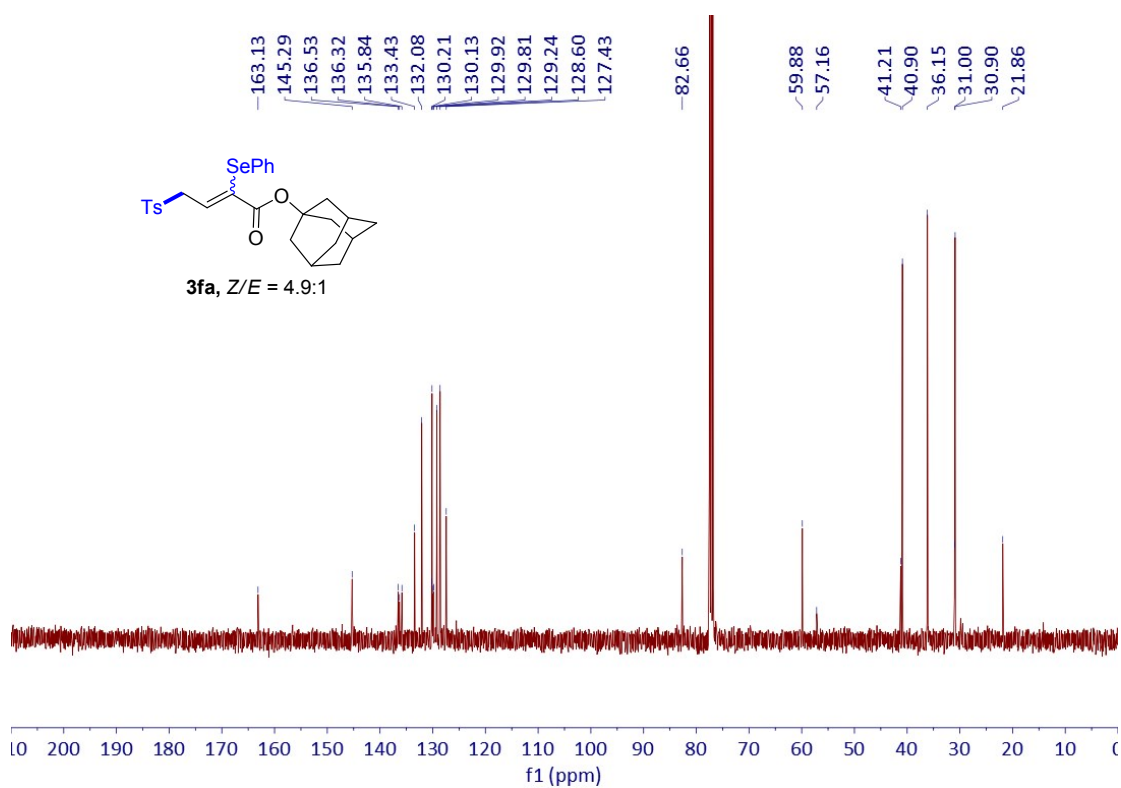


¹³C NMR of **3da** (100 Hz, CDCl₃)

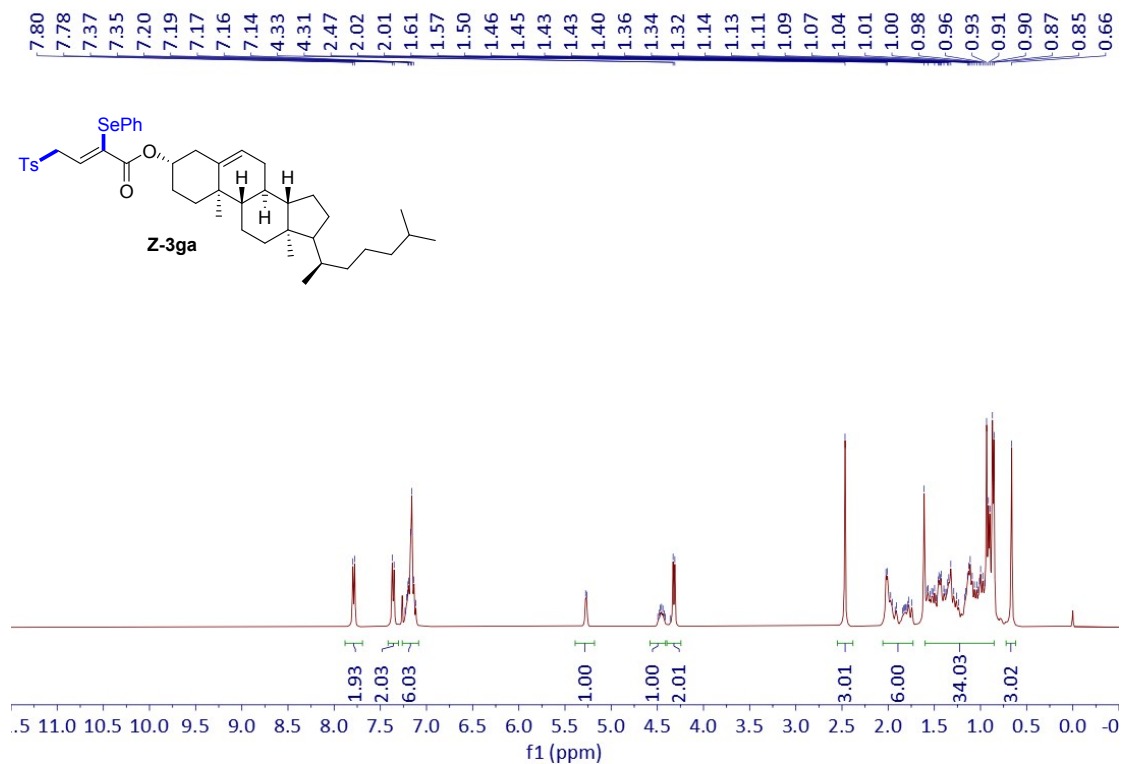




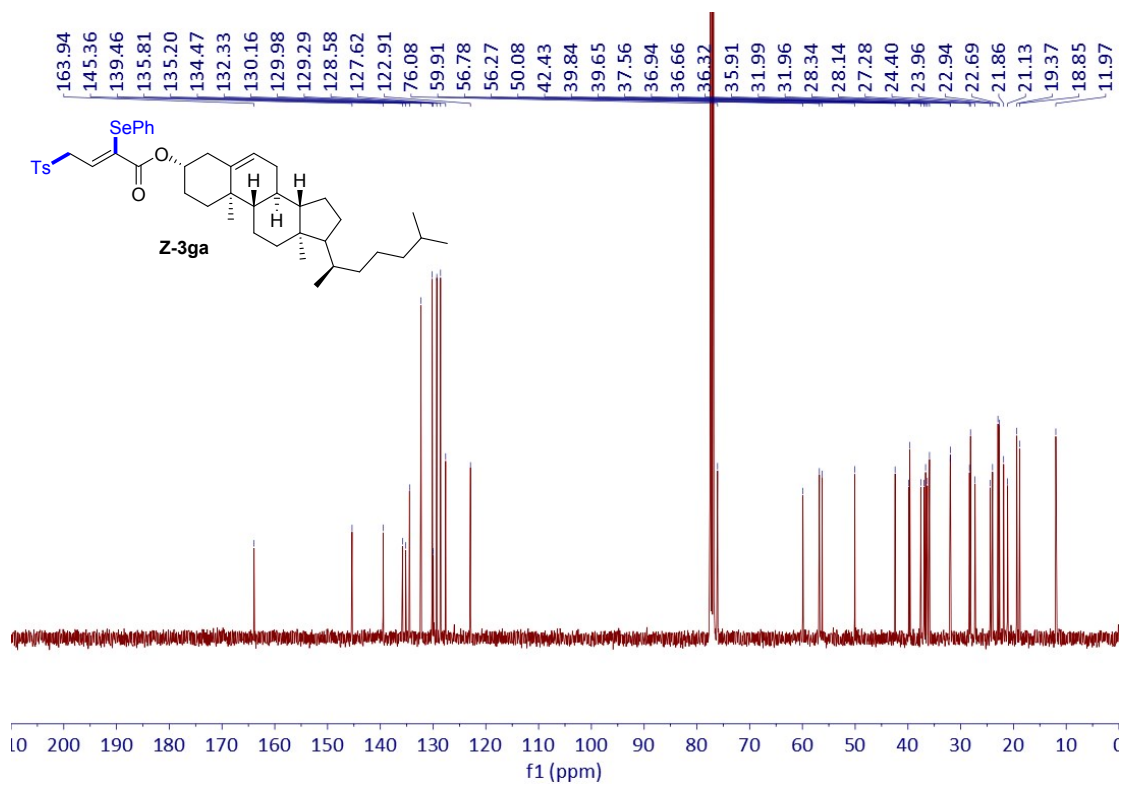
¹H NMR of 3fa (400 Hz, CDCl₃)



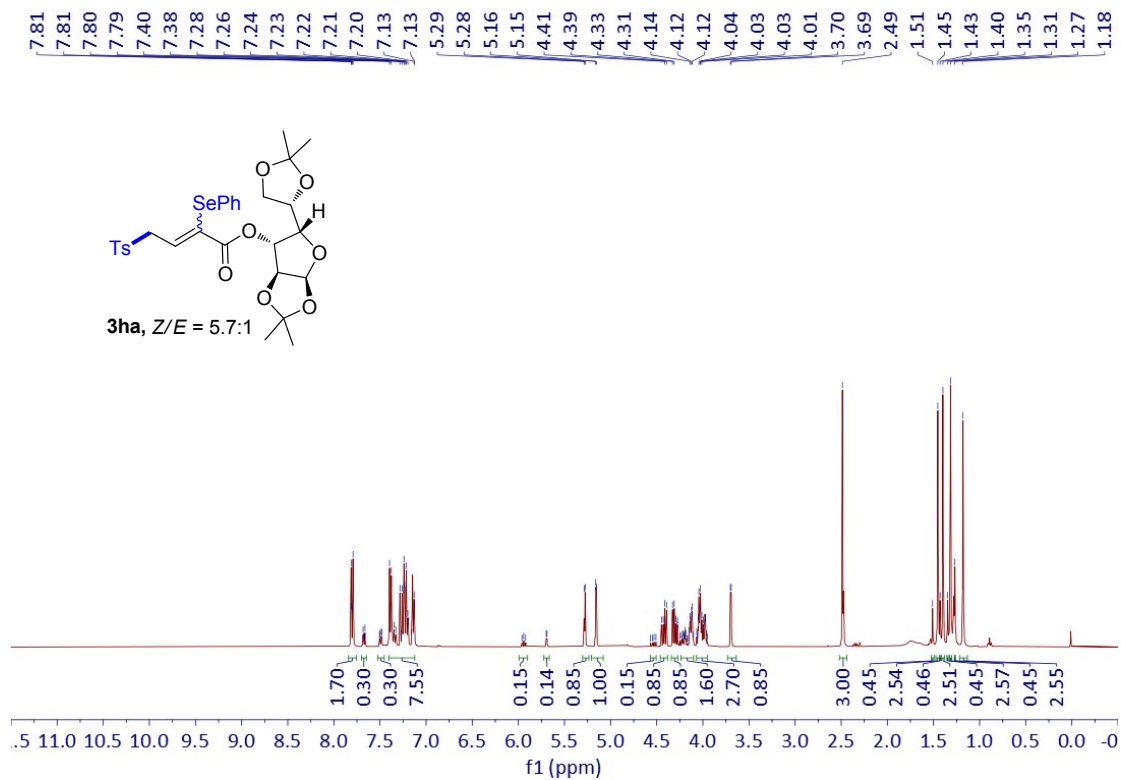
¹³C NMR of 3fa (100 Hz, CDCl₃)



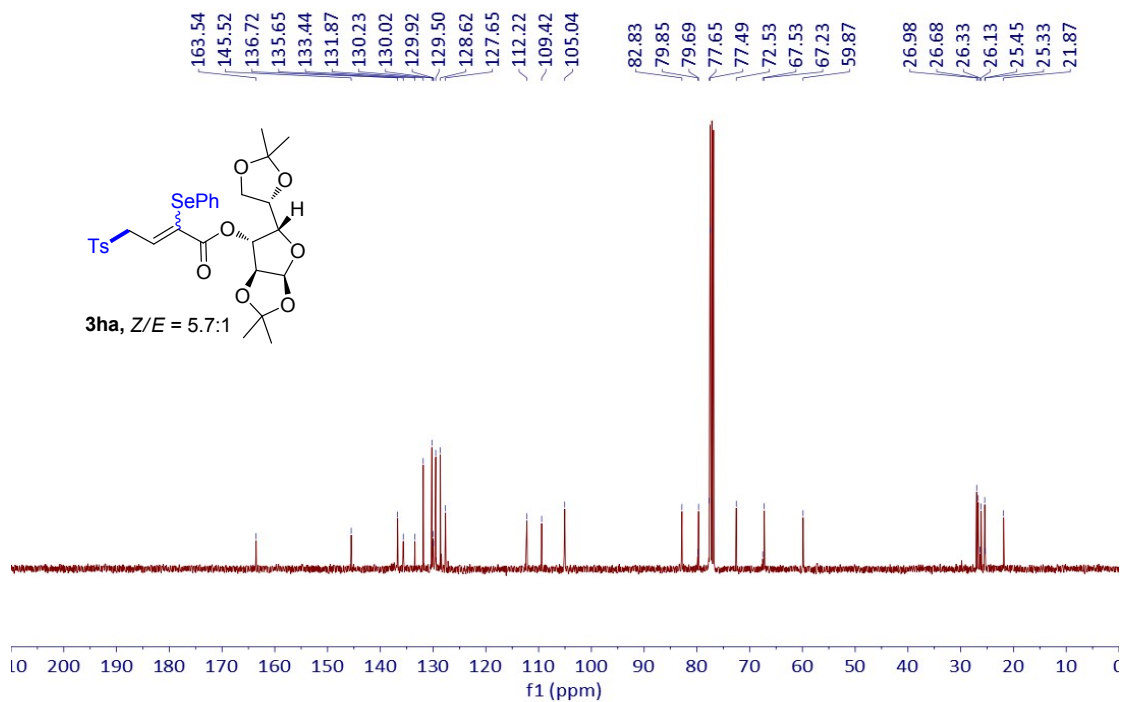
^1H NMR of **3ga** (400 Hz, CDCl_3)



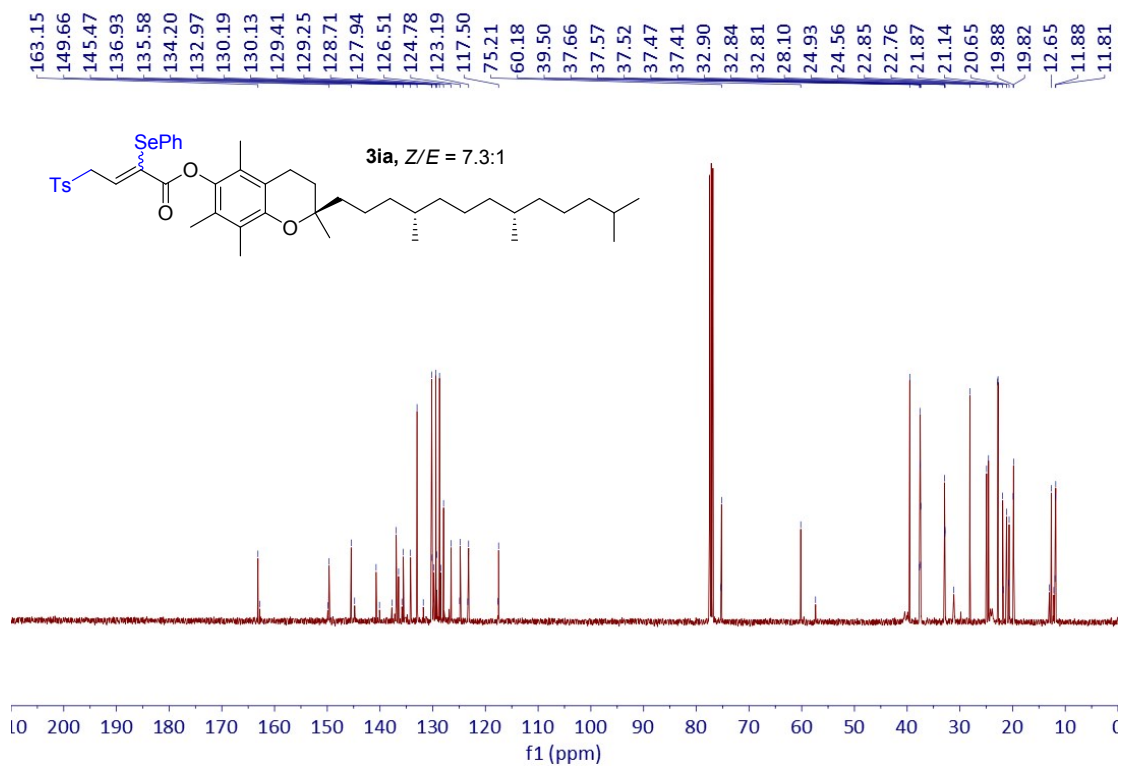
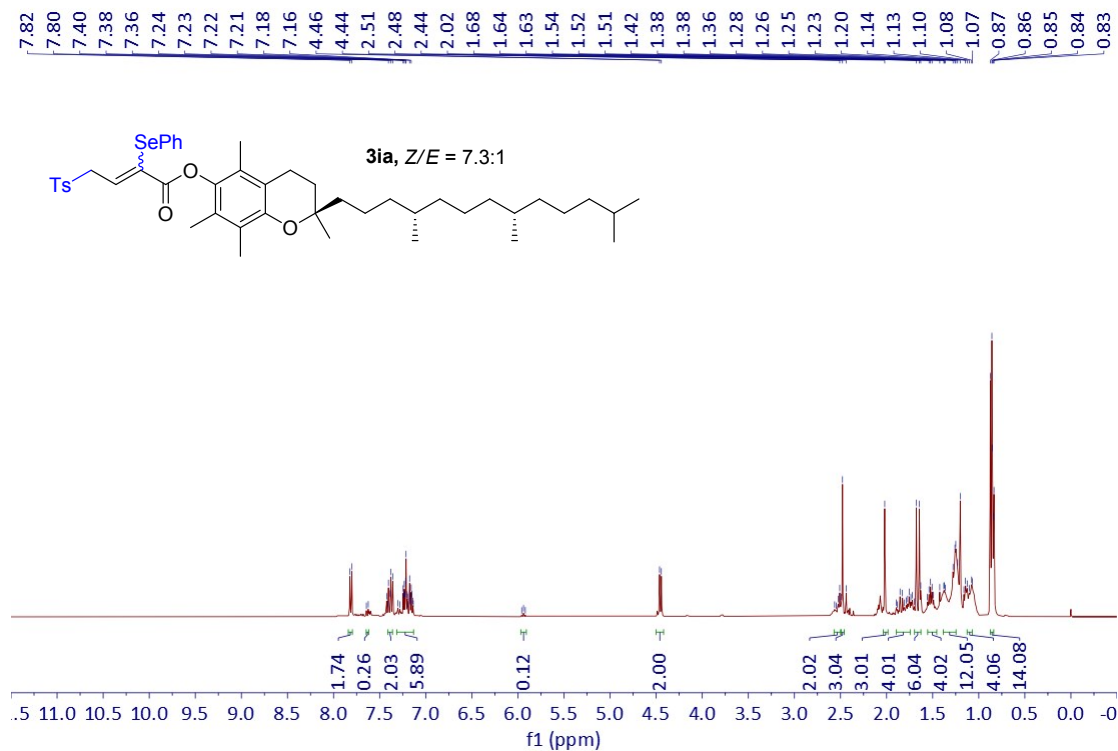
^{13}C NMR of **3ga** (400 Hz, CDCl_3)

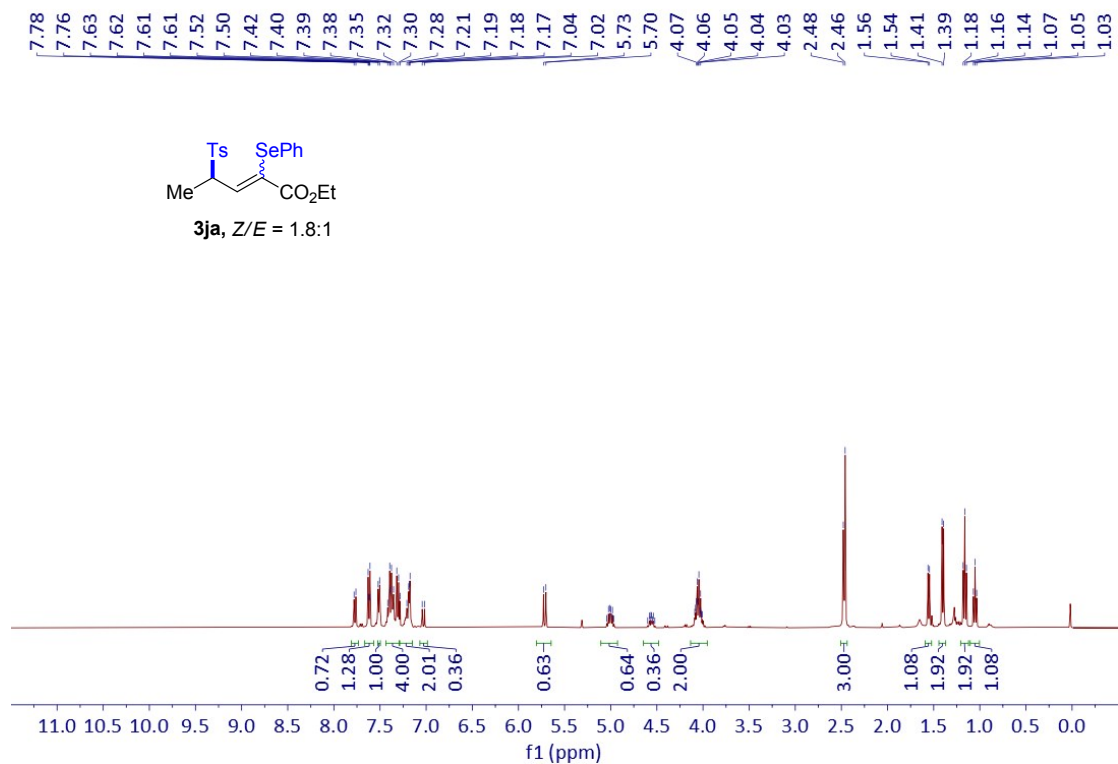


¹H NMR of **3ha** (400 Hz, CDCl₃)

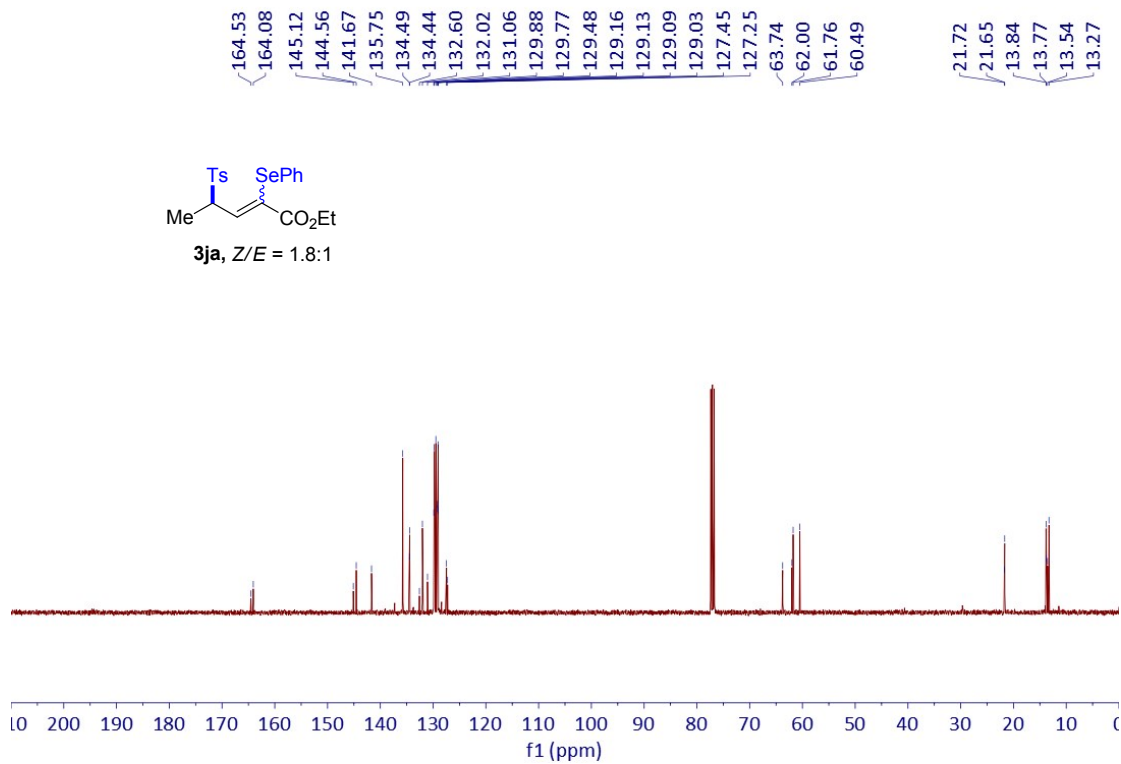


¹³C NMR of **3ha** (100 Hz, CDCl₃)

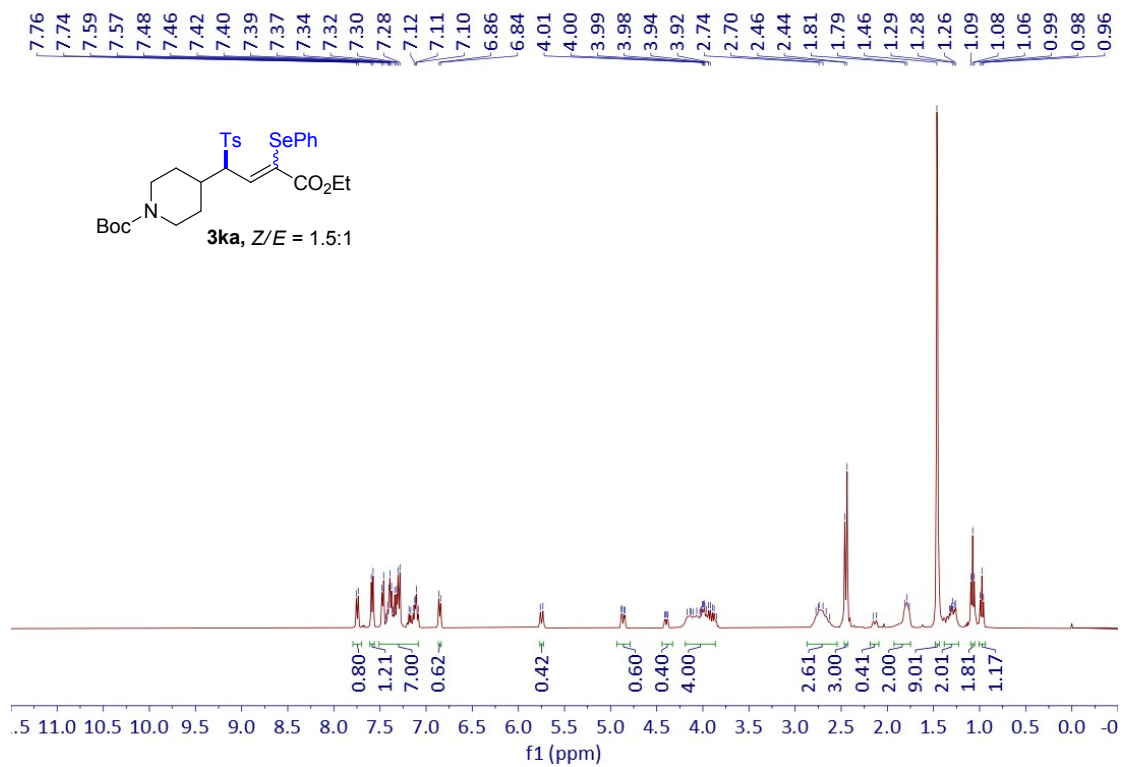




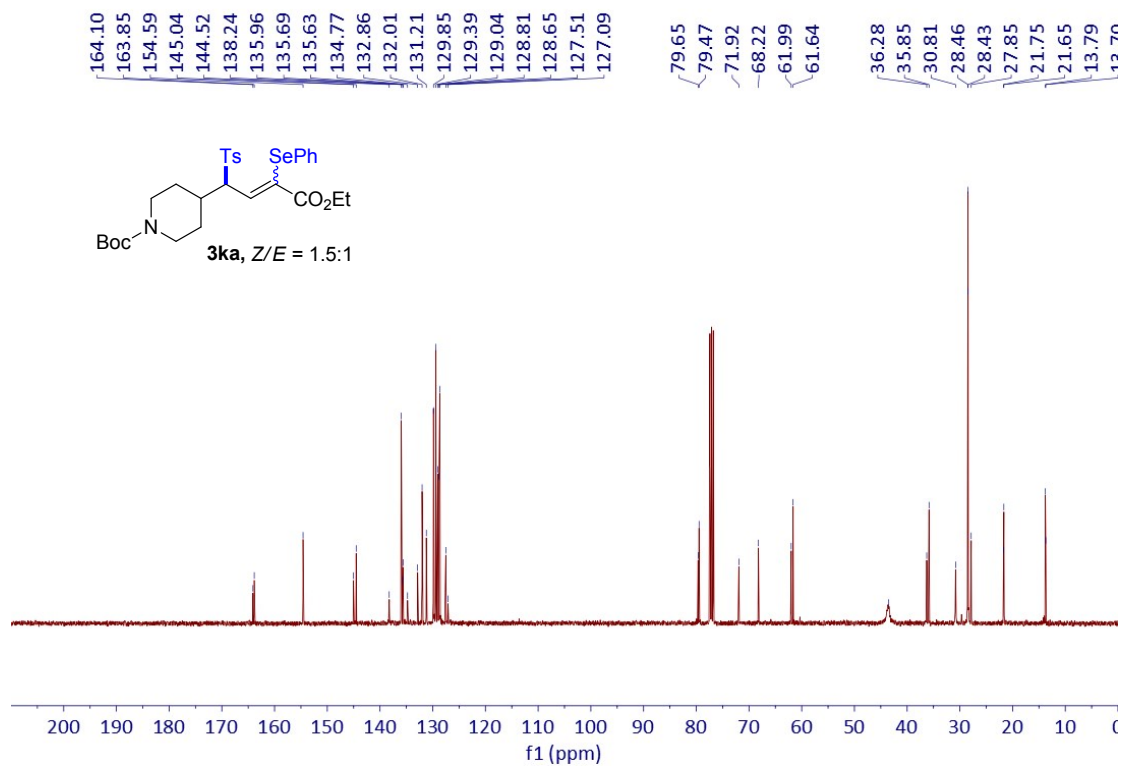
¹H NMR of **3ja** (400 Hz, CDCl₃)



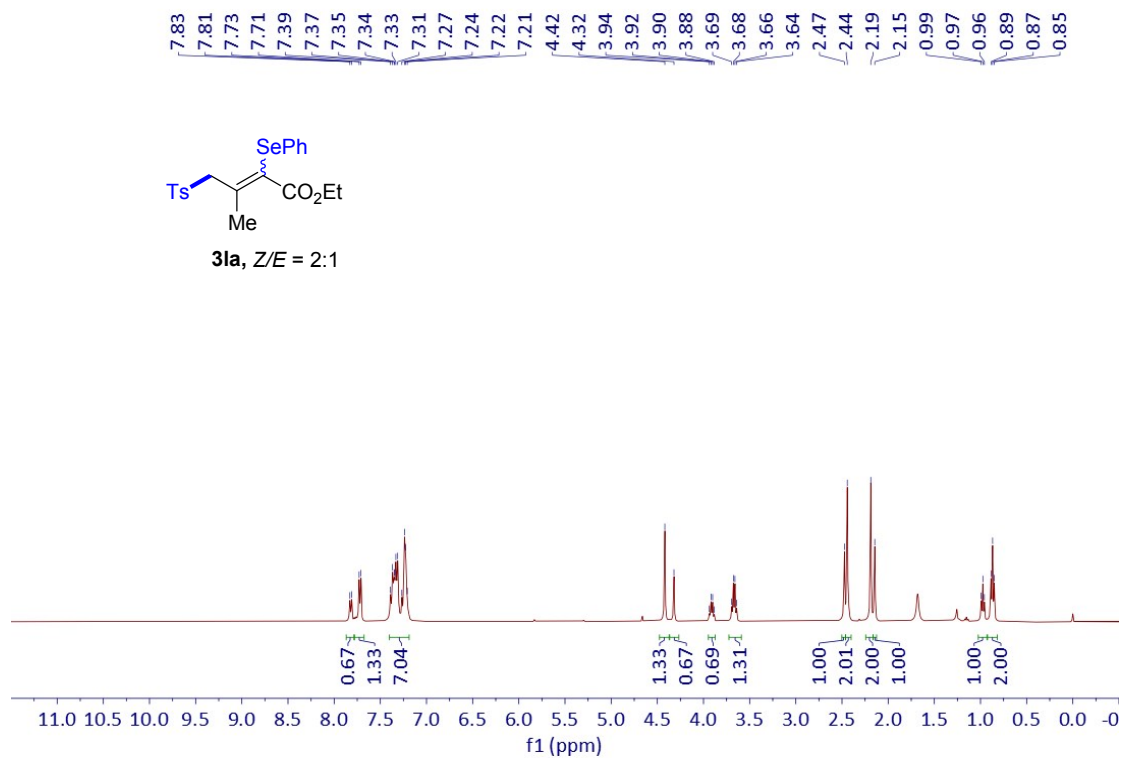
¹³C NMR of **3ja** (100 Hz, CDCl₃)



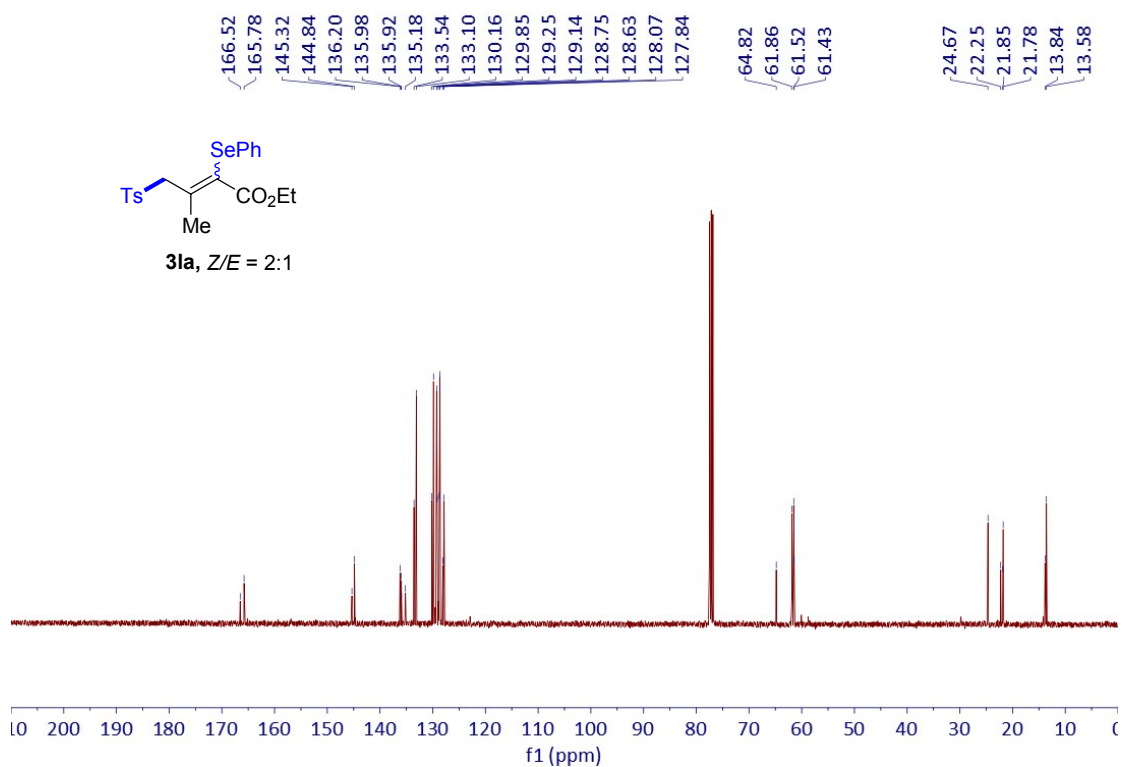
¹H NMR of **3ka** (400 Hz, CDCl₃)



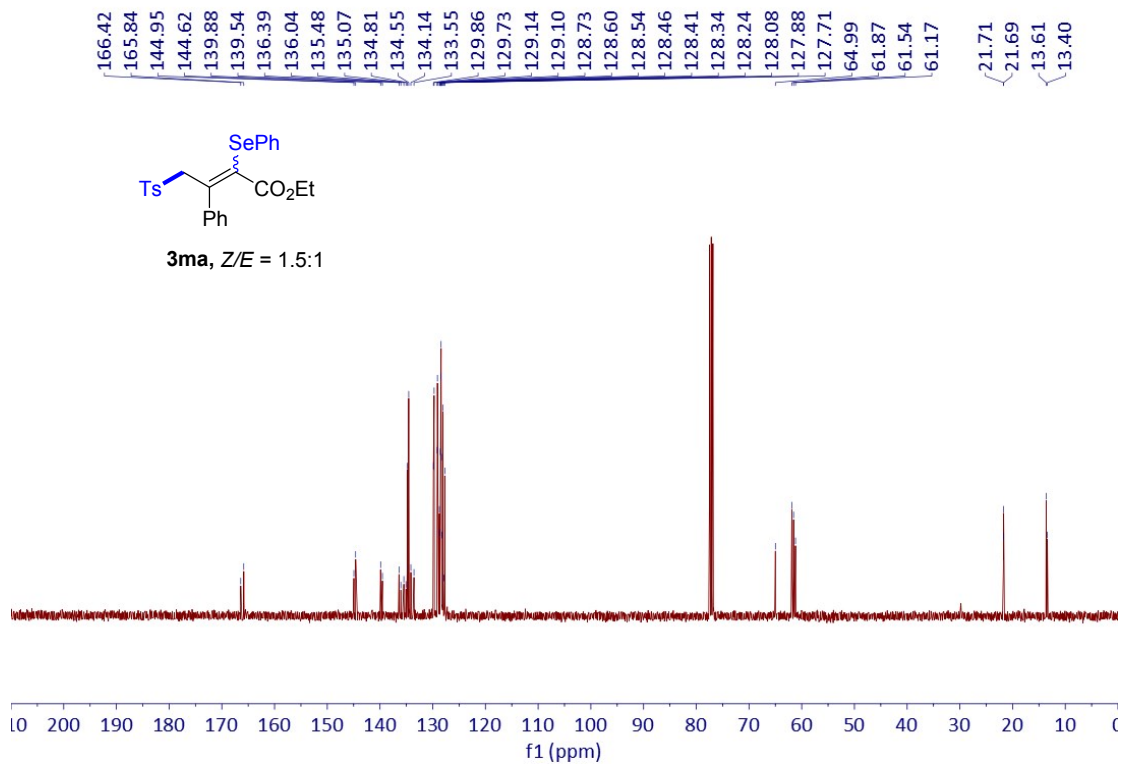
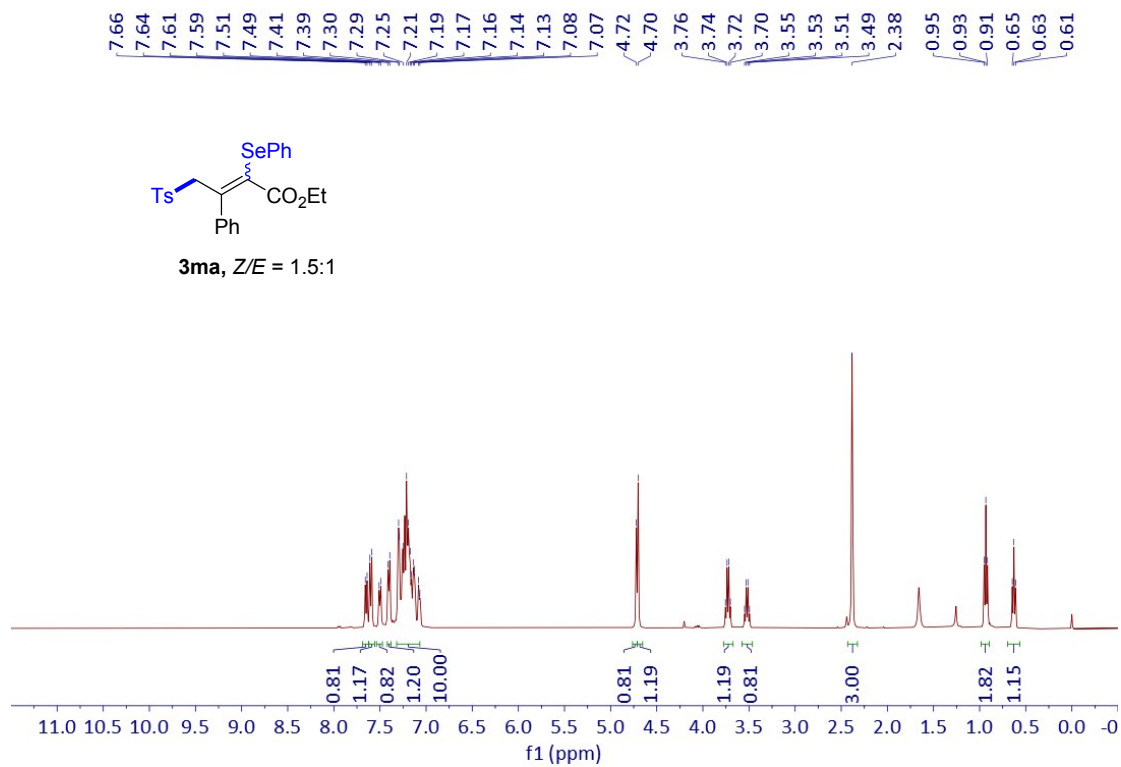
¹³C NMR of **3ka** (100 Hz, CDCl₃)

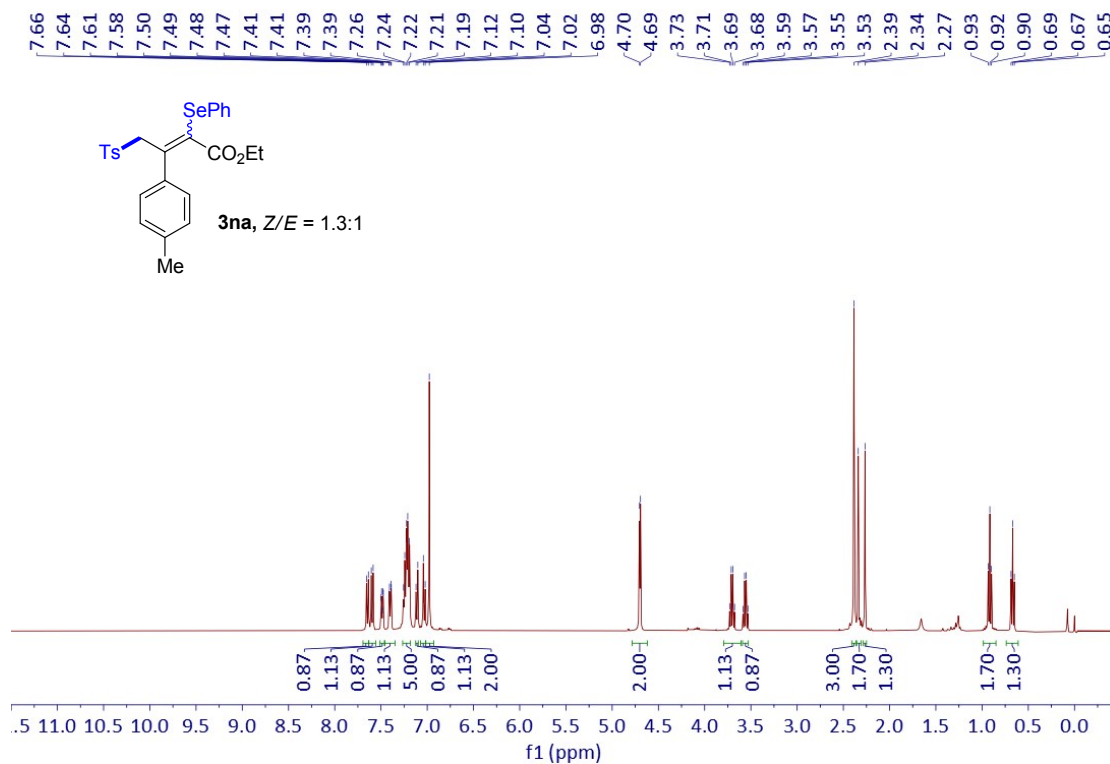


¹H NMR of **3la** (400 Hz, CDCl₃)

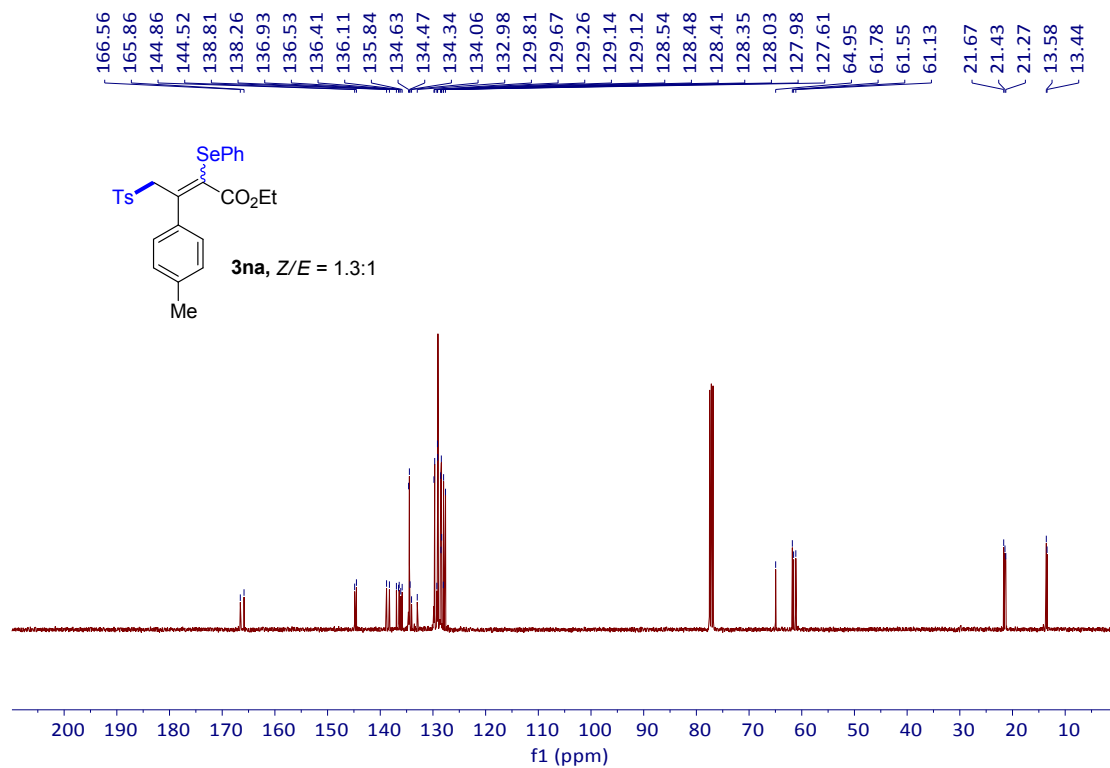


¹³C NMR of **3la** (100 Hz, CDCl₃)

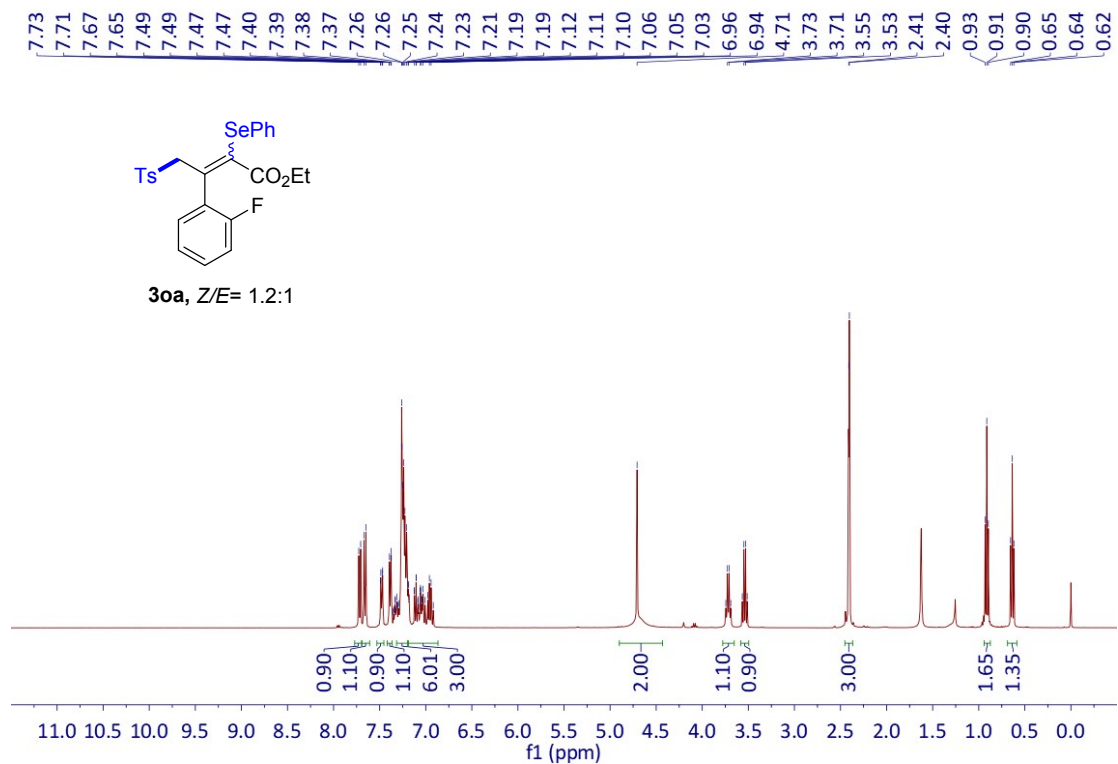




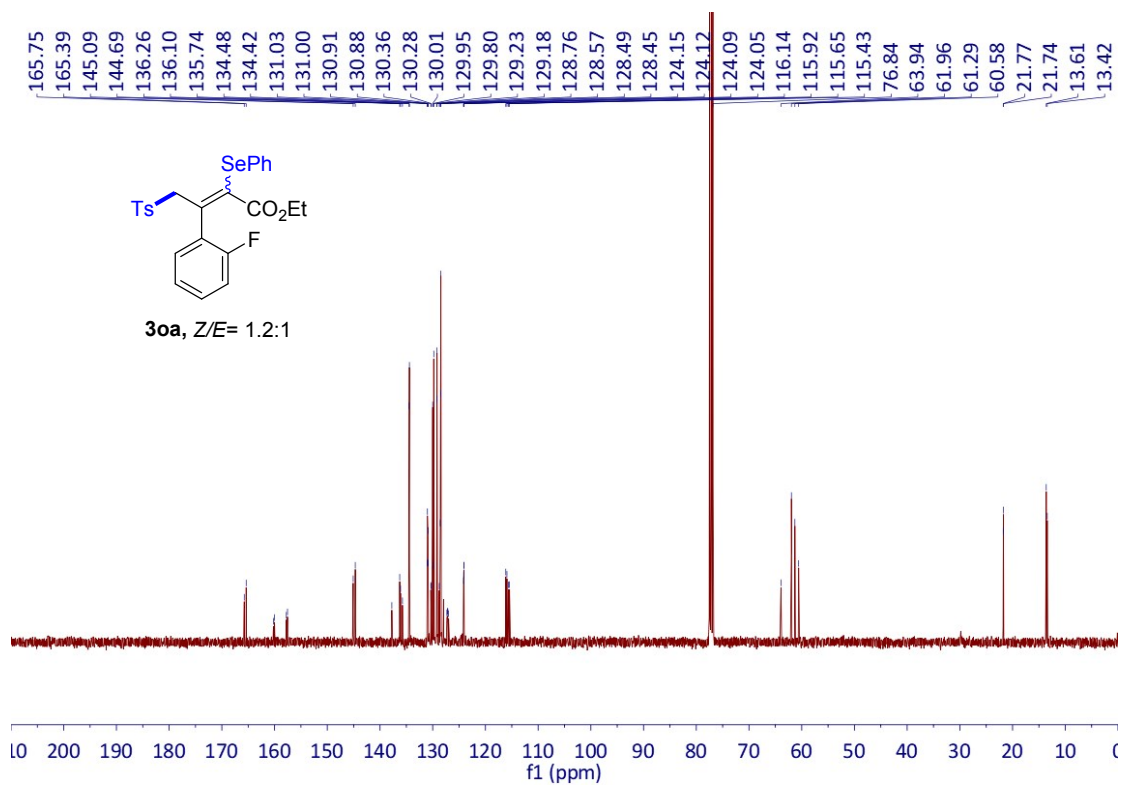
¹H NMR of **3na** (400 Hz, CDCl₃)



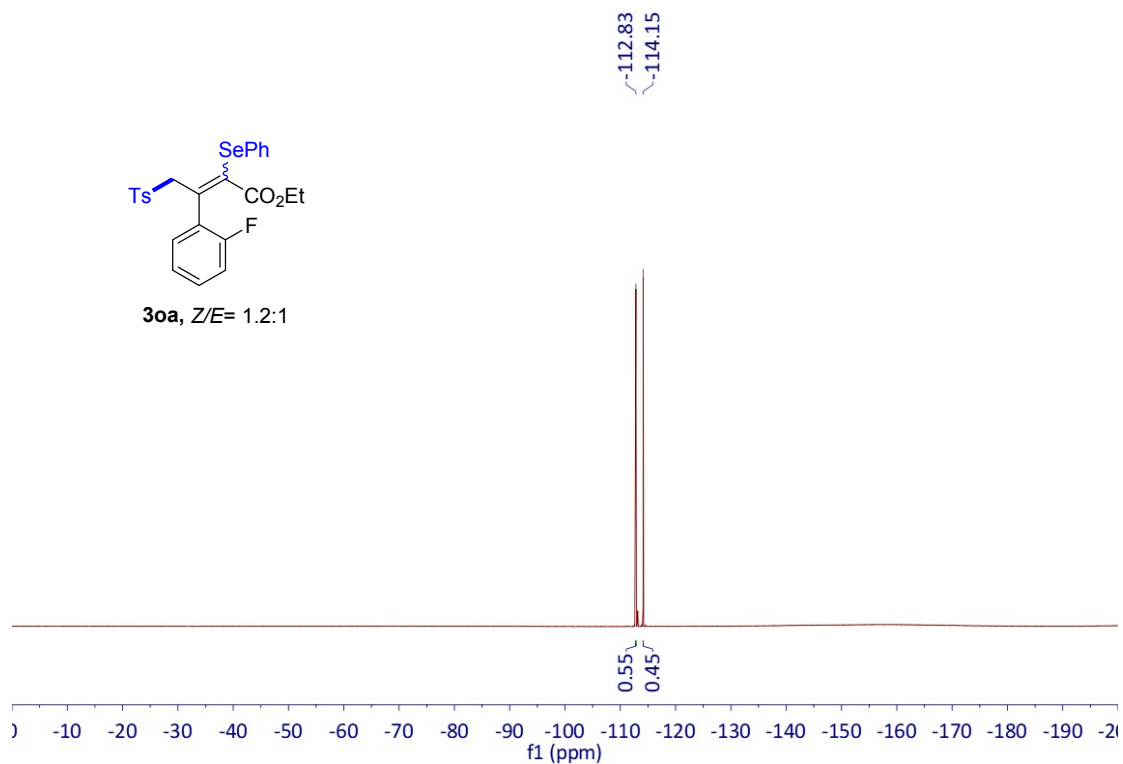
¹³C NMR of **3na** (100 Hz, CDCl₃)



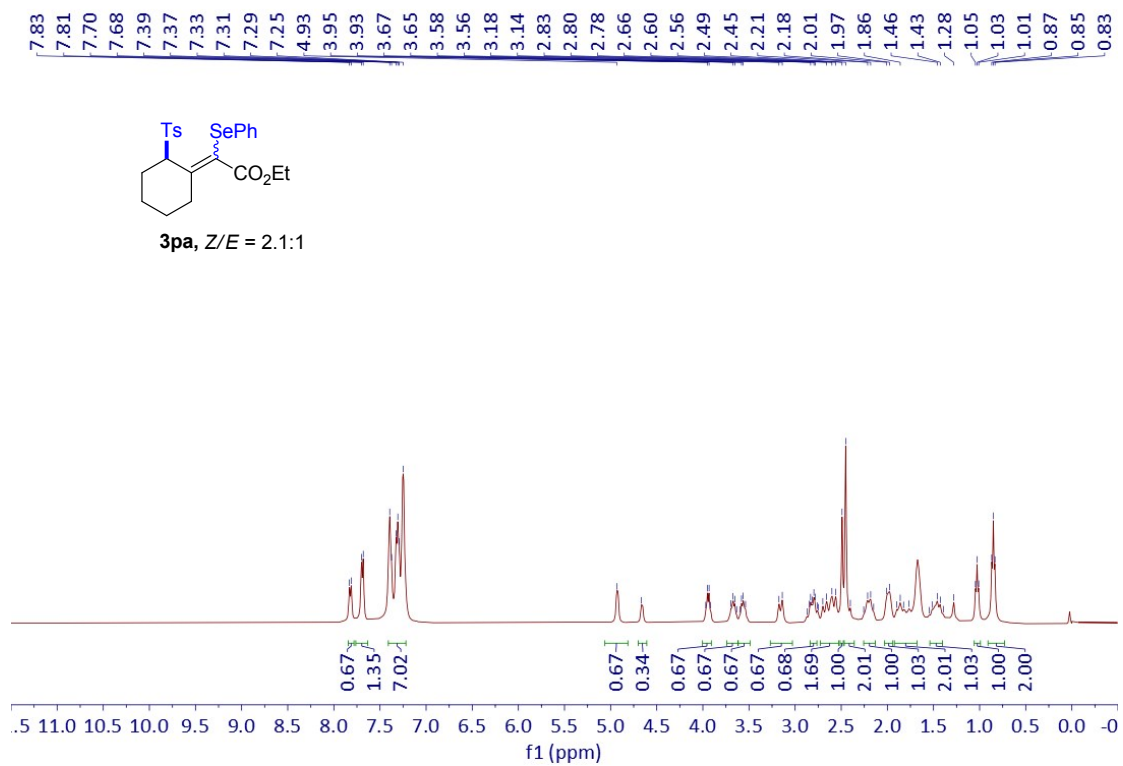
¹H NMR of **3oa** (400 Hz, CDCl₃)



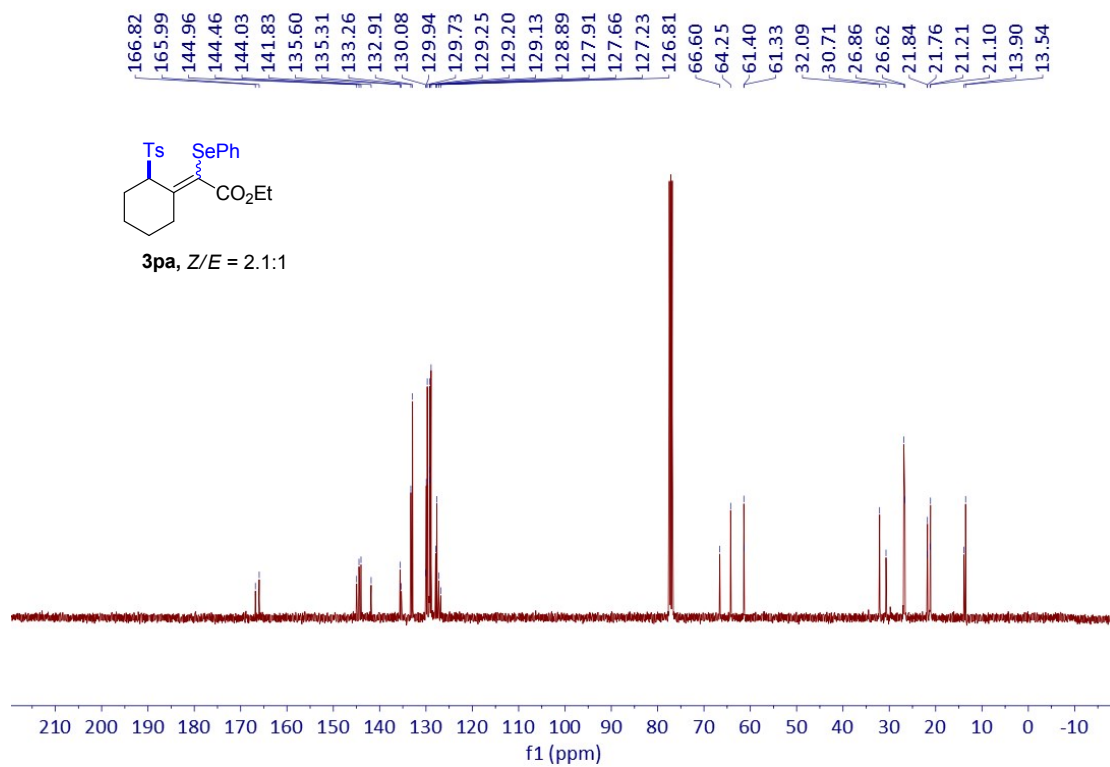
¹³C NMR of **3oa** (100 Hz, CDCl₃)



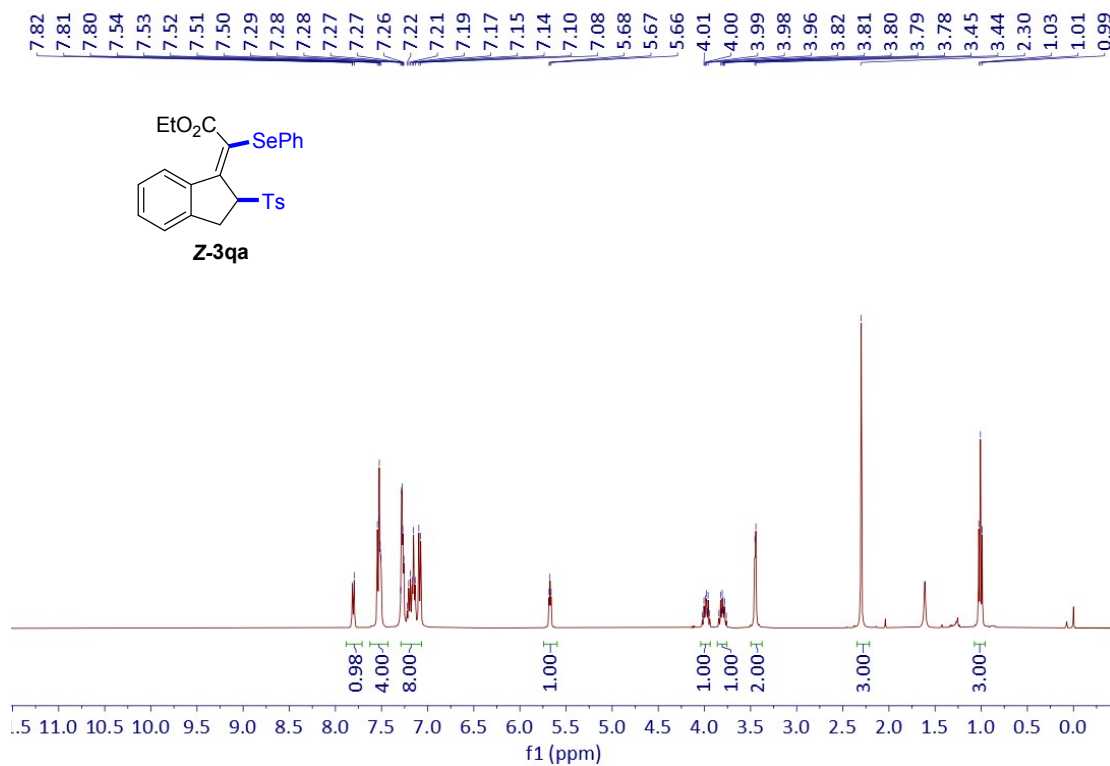
^{19}F NMR of **30a** (376 Hz, CDCl_3)



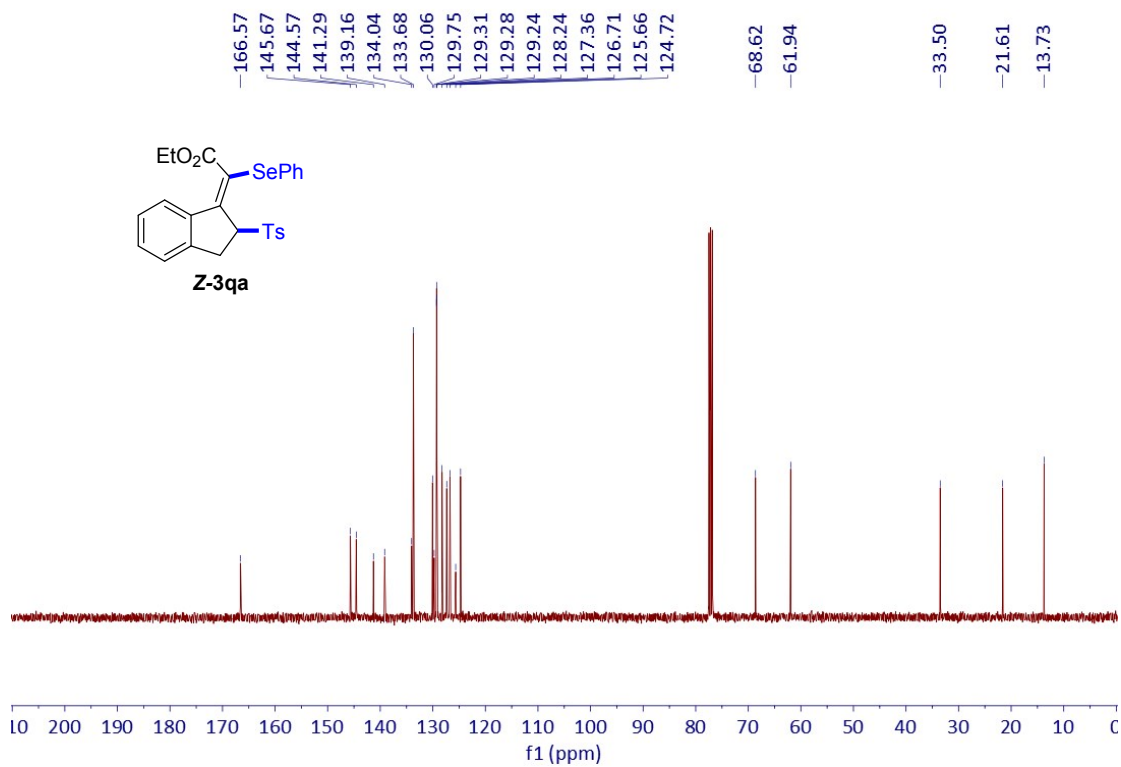
^1H NMR of **3pa** (400 Hz, CDCl_3)



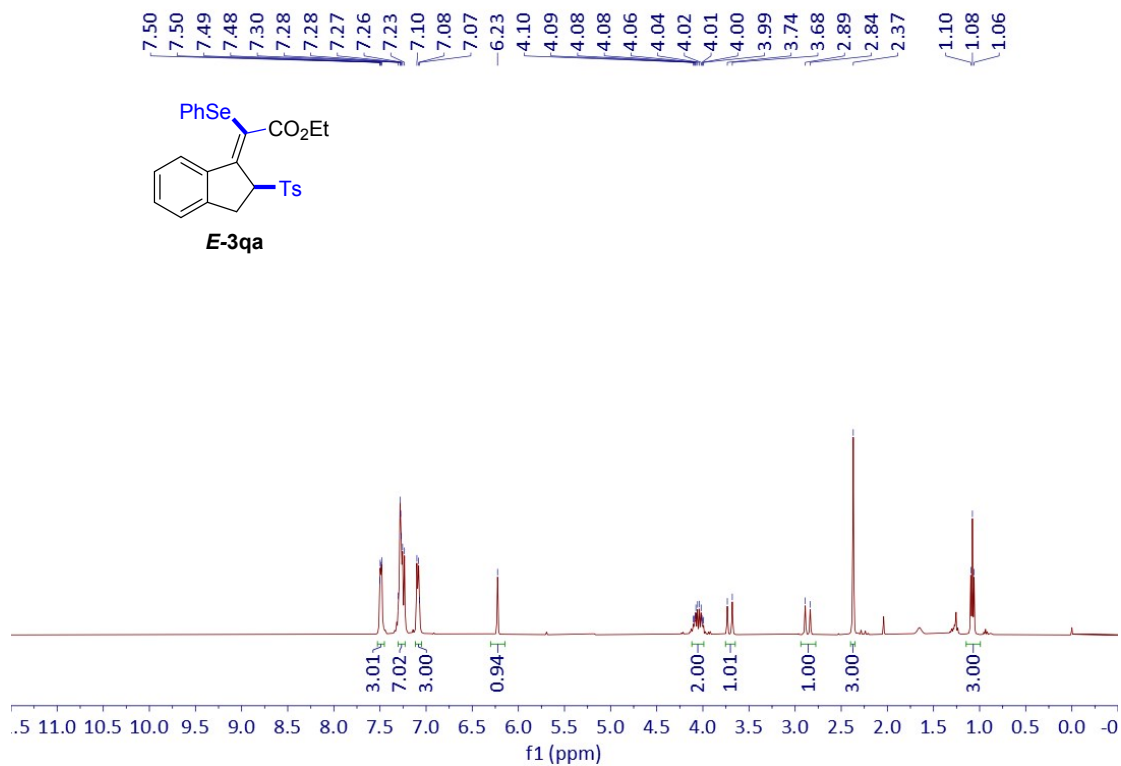
¹³C NMR of **3pa** (100 Hz, CDCl₃)



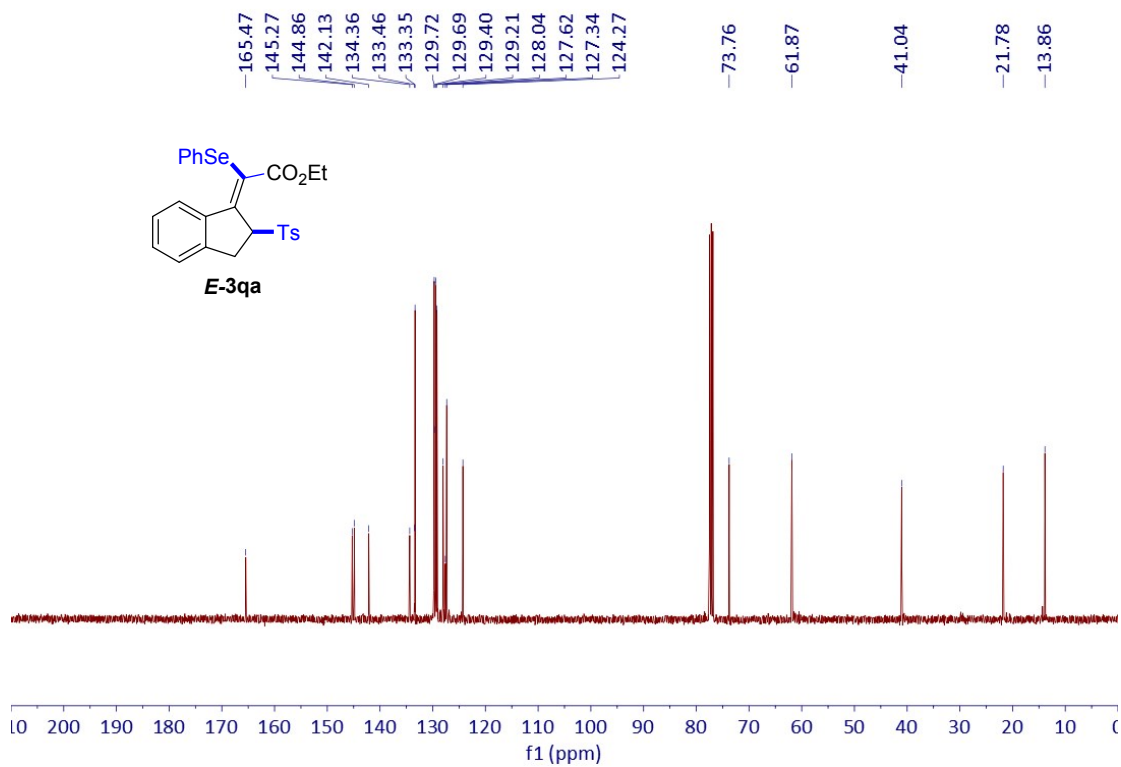
¹H NMR of **Z-3qa** (400 Hz, CDCl₃)



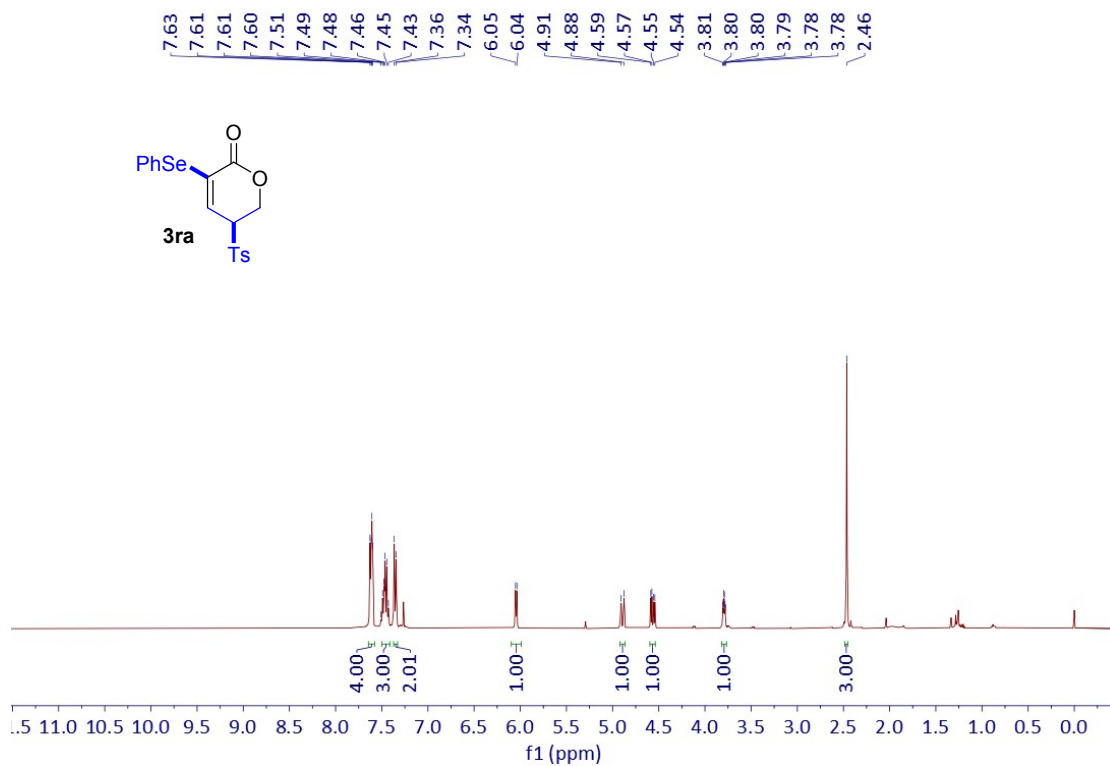
¹³C NMR of **Z-3qa** (100 Hz, CDCl₃)



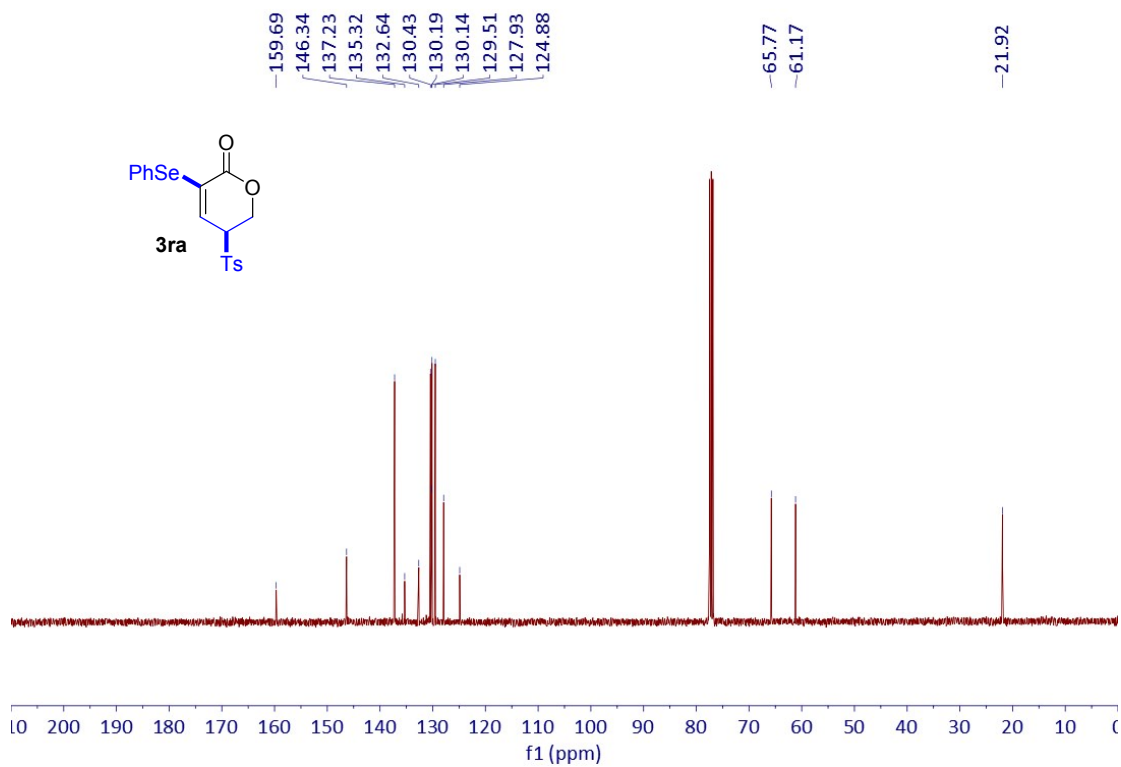
¹H NMR of **E-3qa** (400 Hz, CDCl₃)



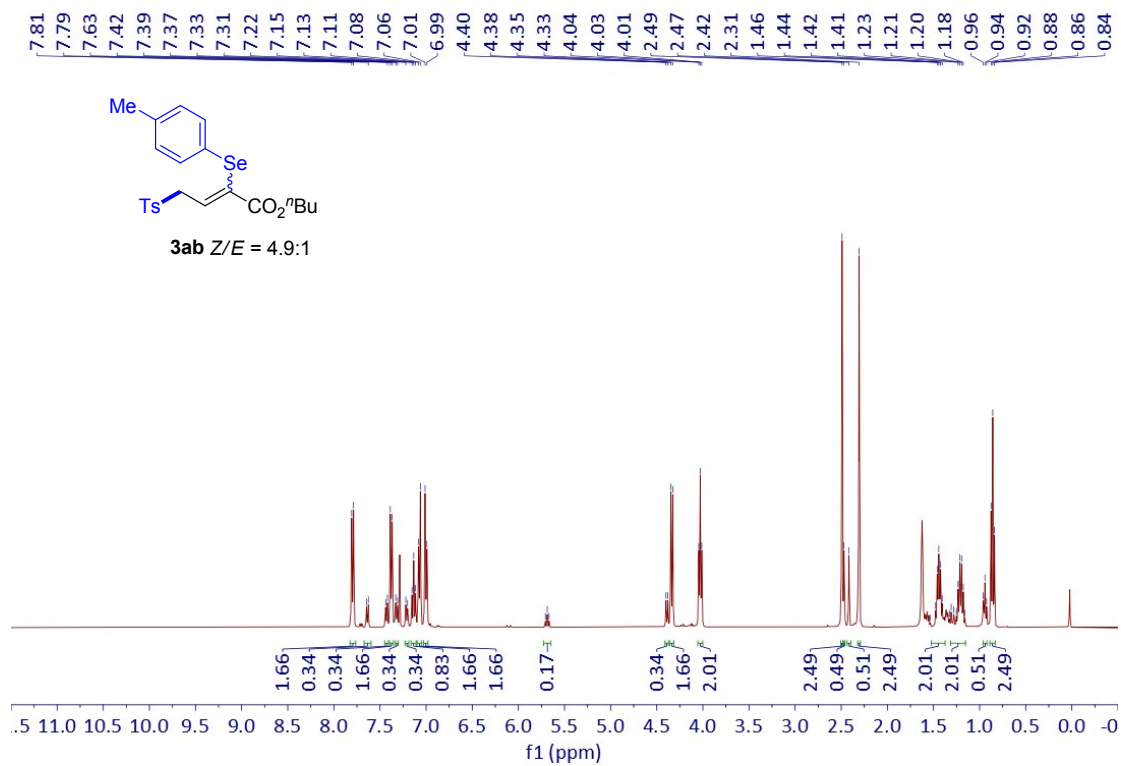
¹³C NMR of **E-3qa** (100 Hz, CDCl₃)



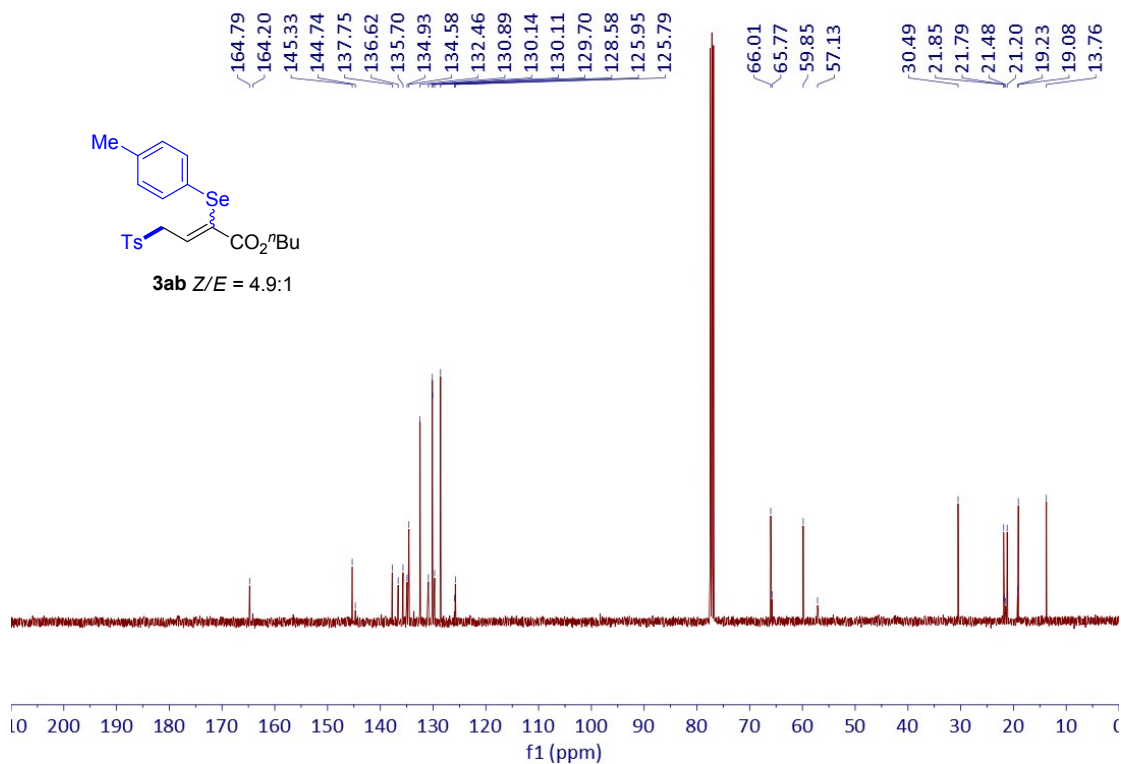
¹H NMR of **3ra** (400 Hz, CDCl₃)



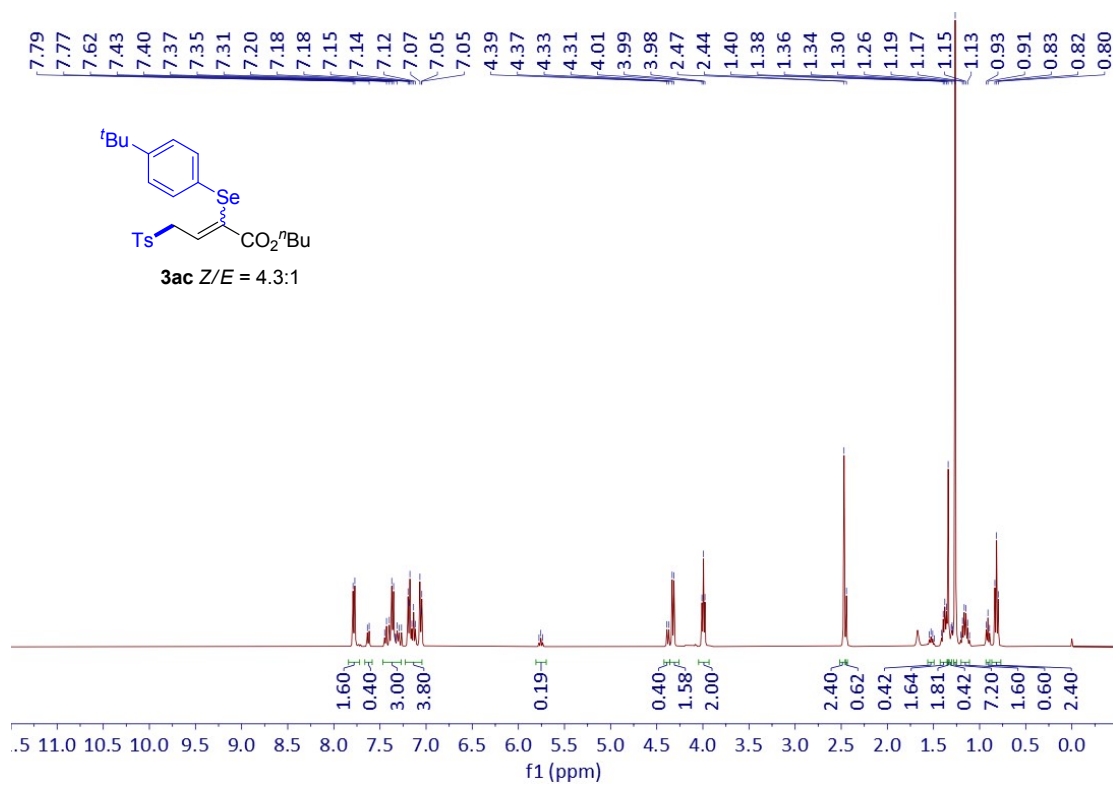
¹³C NMR of **3ra** (100 Hz, CDCl₃)



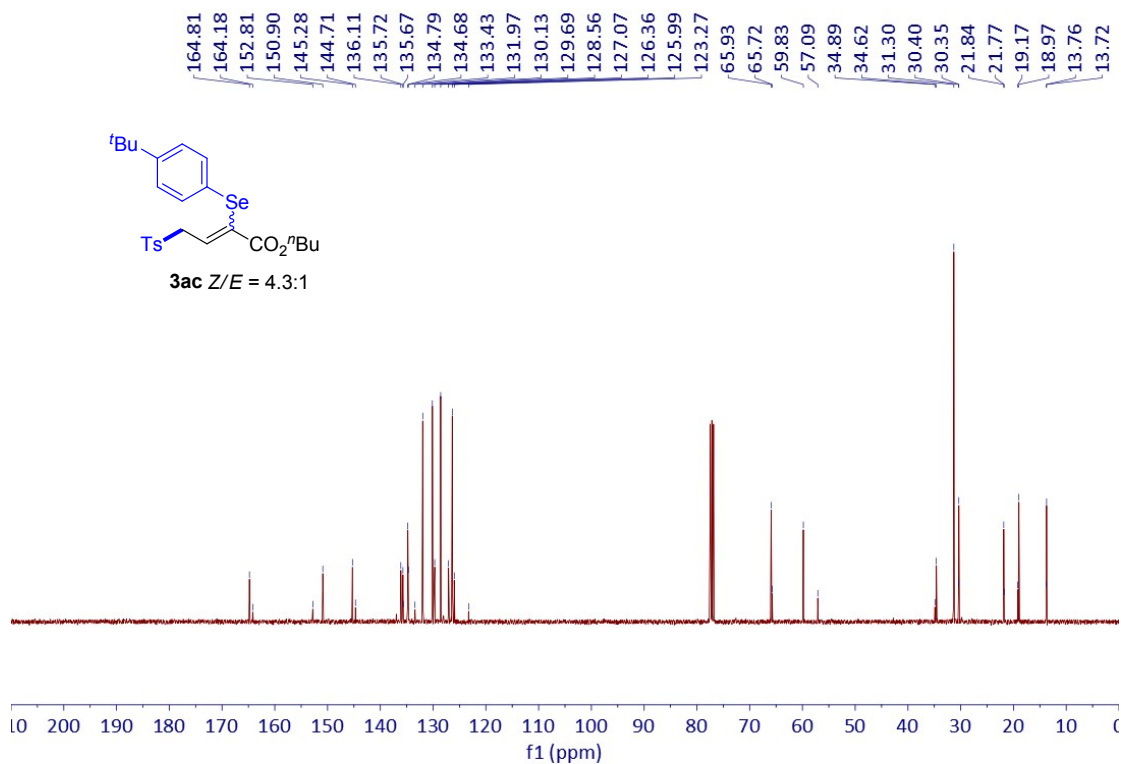
¹H NMR of **3ab** (400 Hz, CDCl₃)



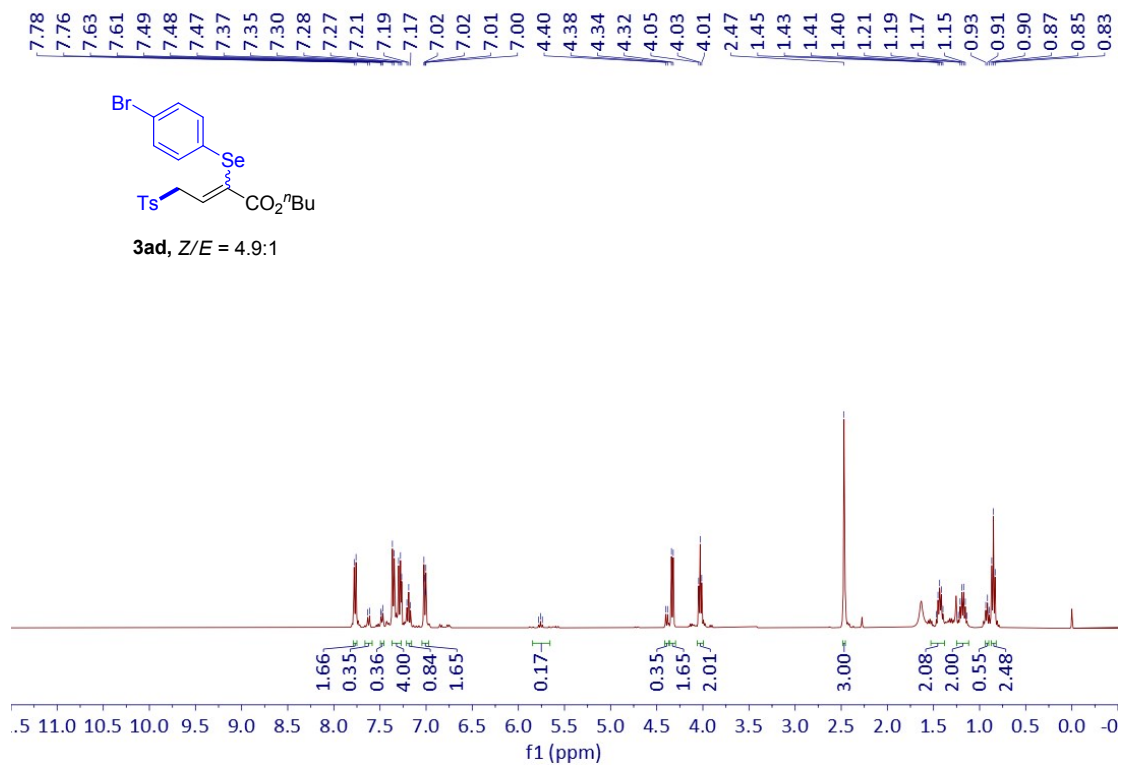
^{13}C NMR of **3ab** (100 Hz, CDCl_3)



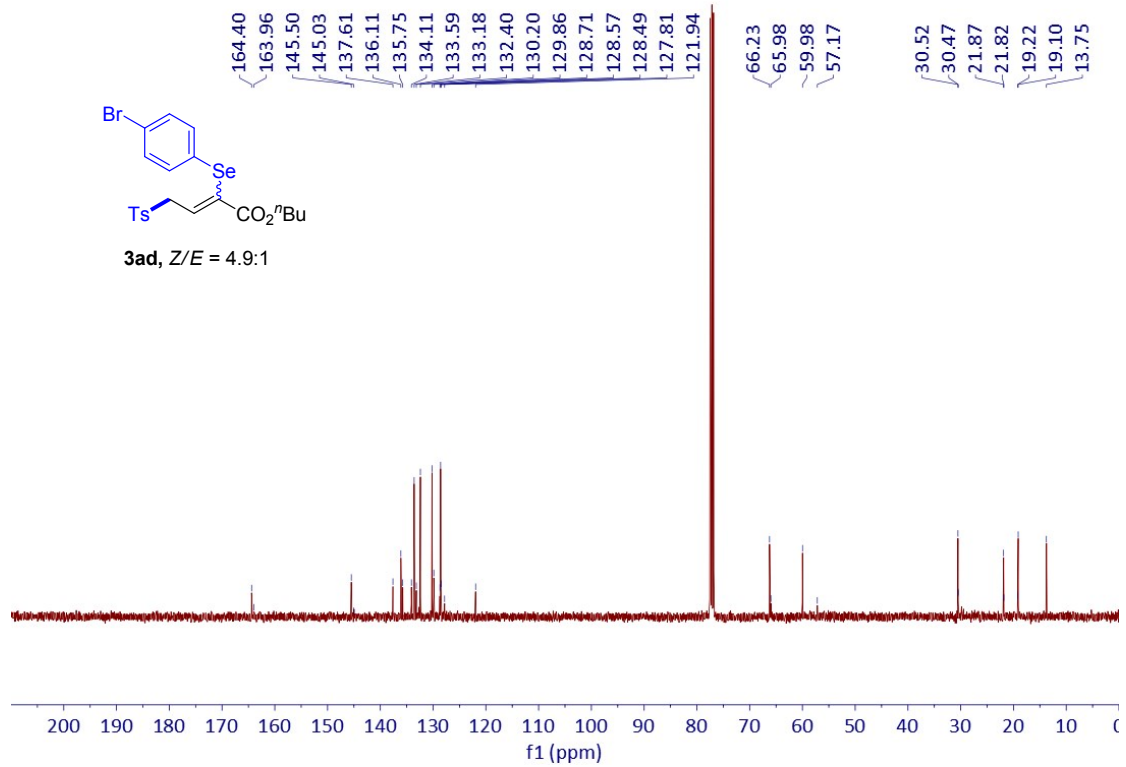
^1H NMR of **3ac** (400 Hz, CDCl_3)



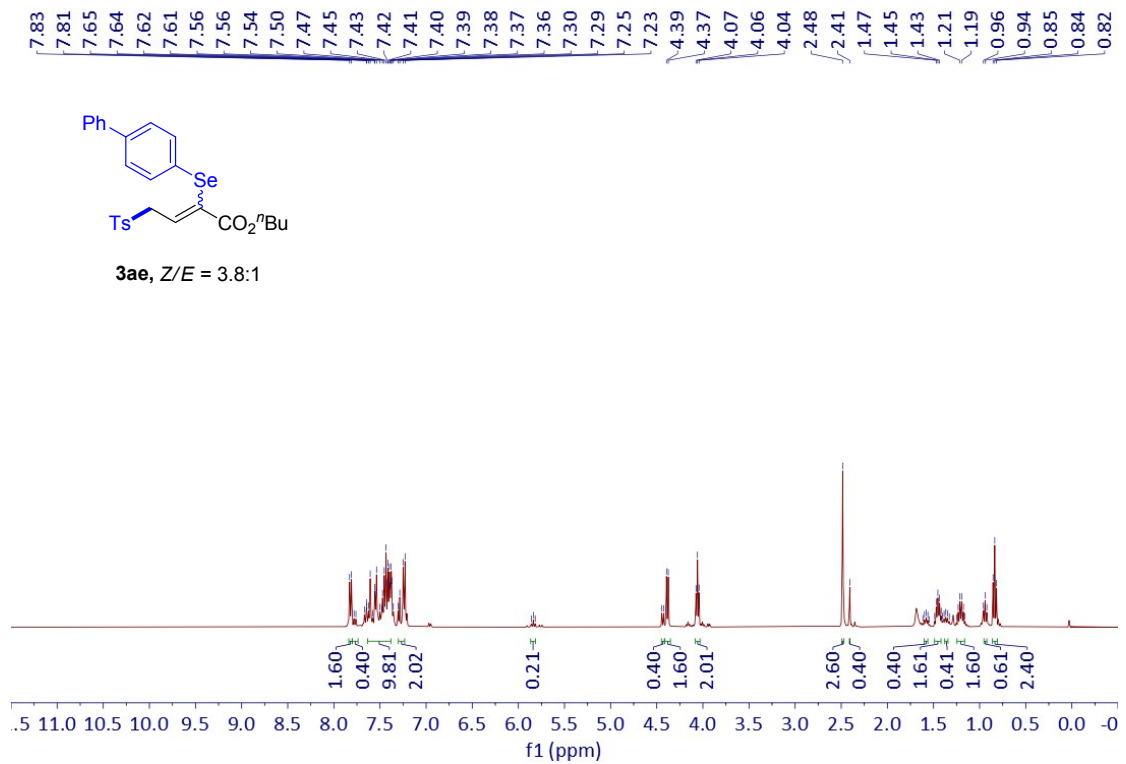
^{13}C NMR of **3ac** (100 Hz, CDCl_3)



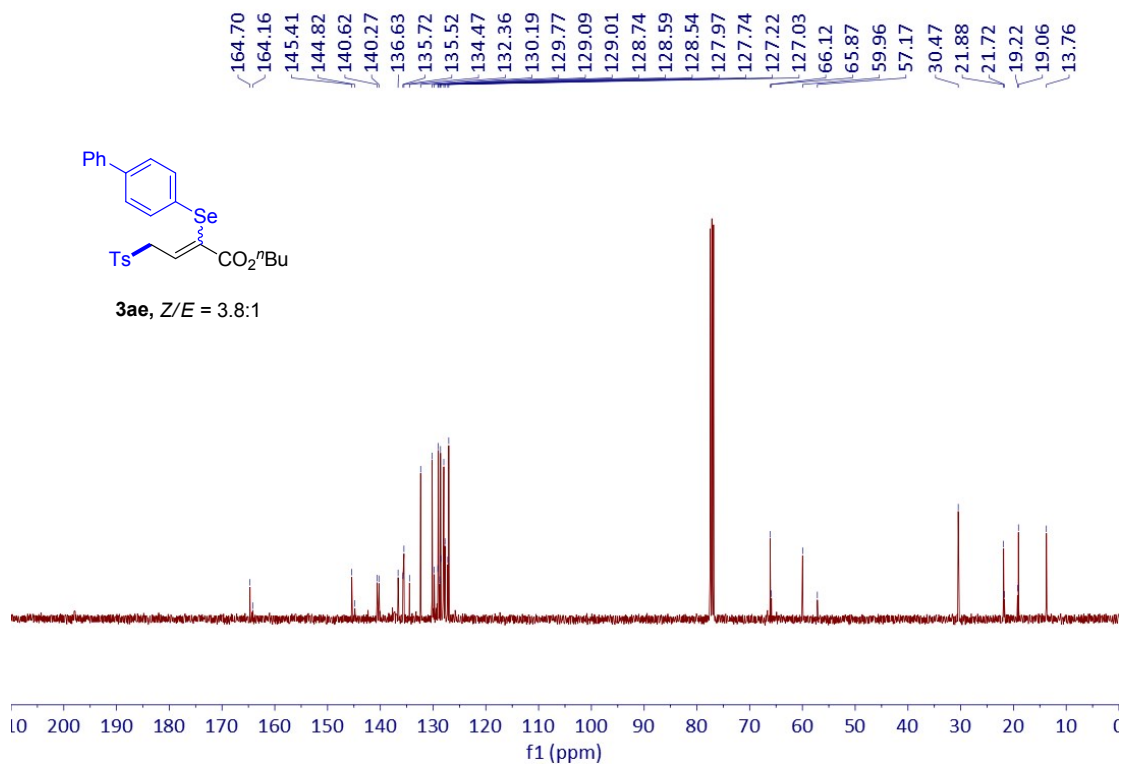
^1H NMR of **3ad** (400 Hz, CDCl_3)



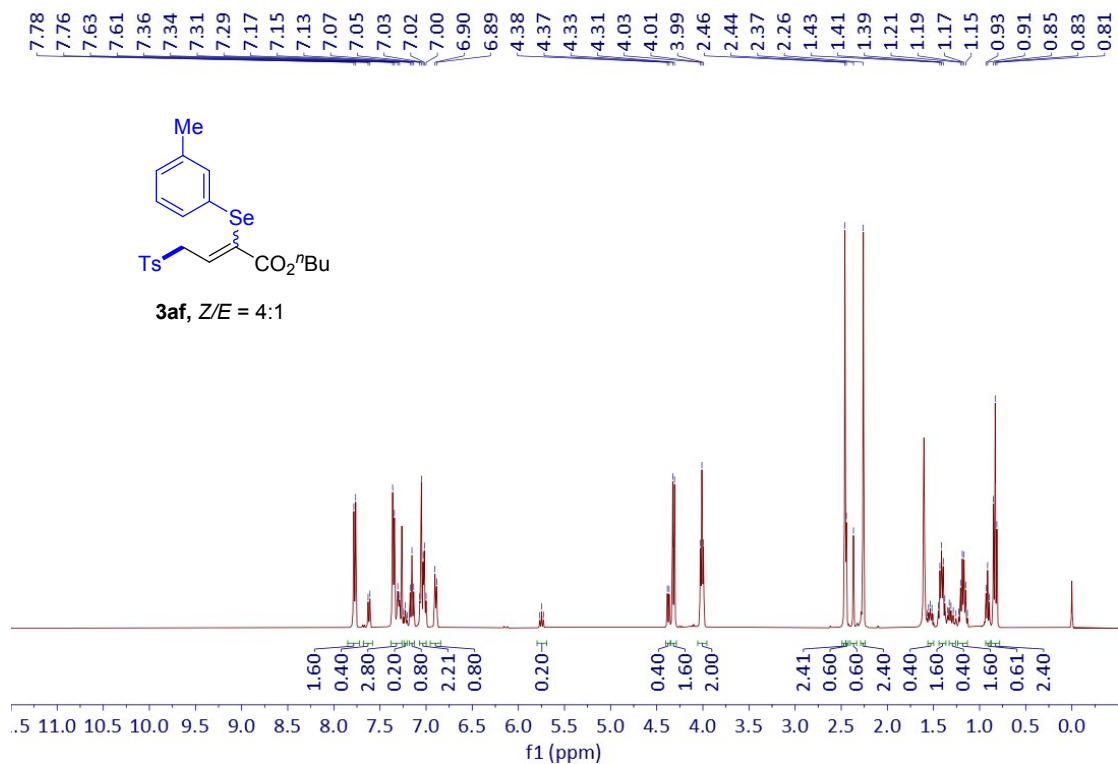
^{13}C NMR of **3ad** (100 Hz, CDCl_3)



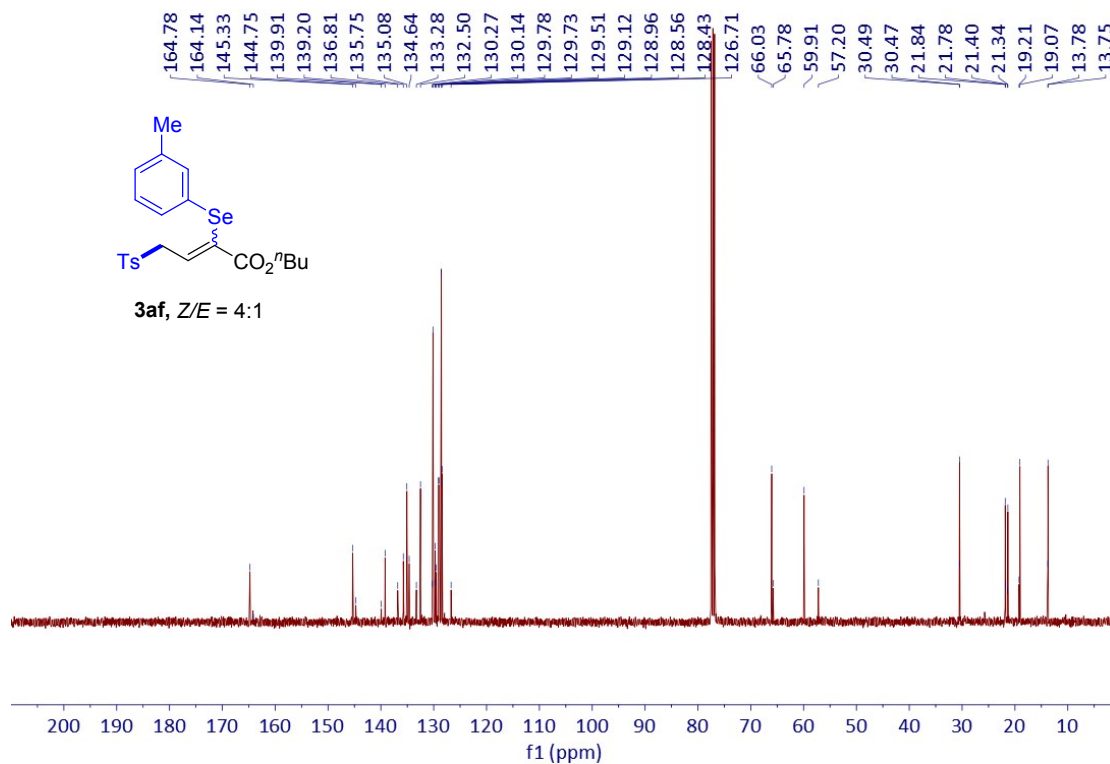
^1H NMR of **3ae** (400 Hz, CDCl_3)



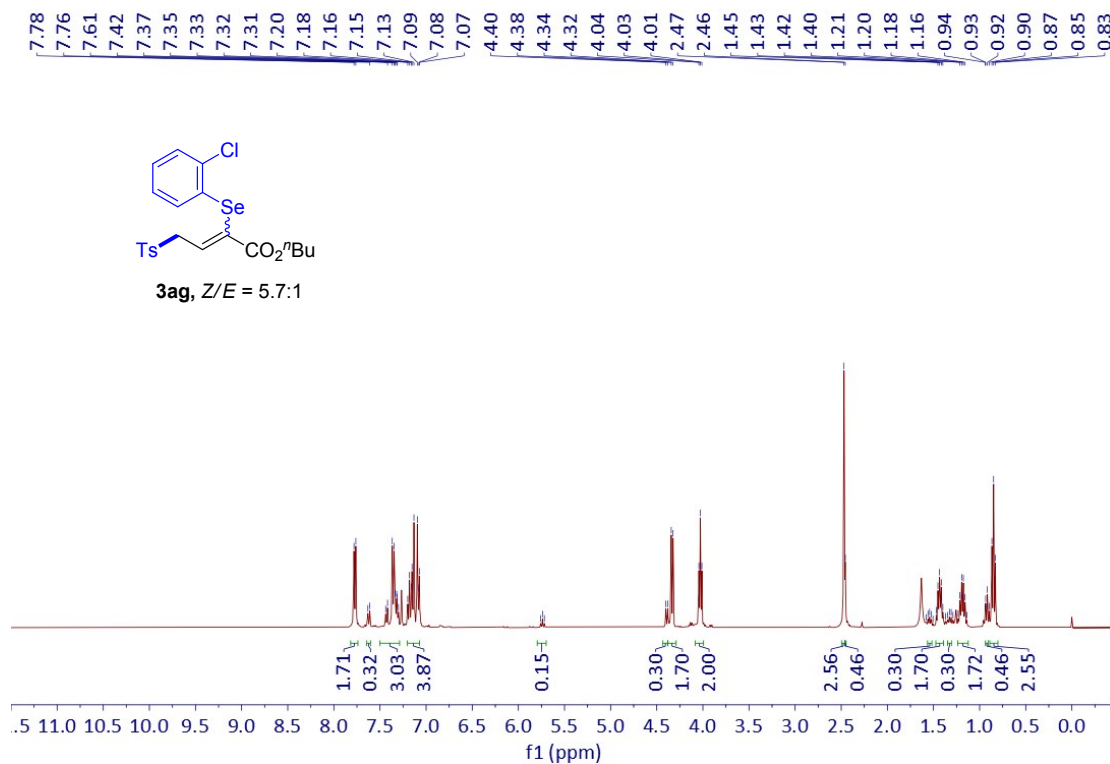
^{13}C NMR of **3ae** (100 Hz, CDCl_3)



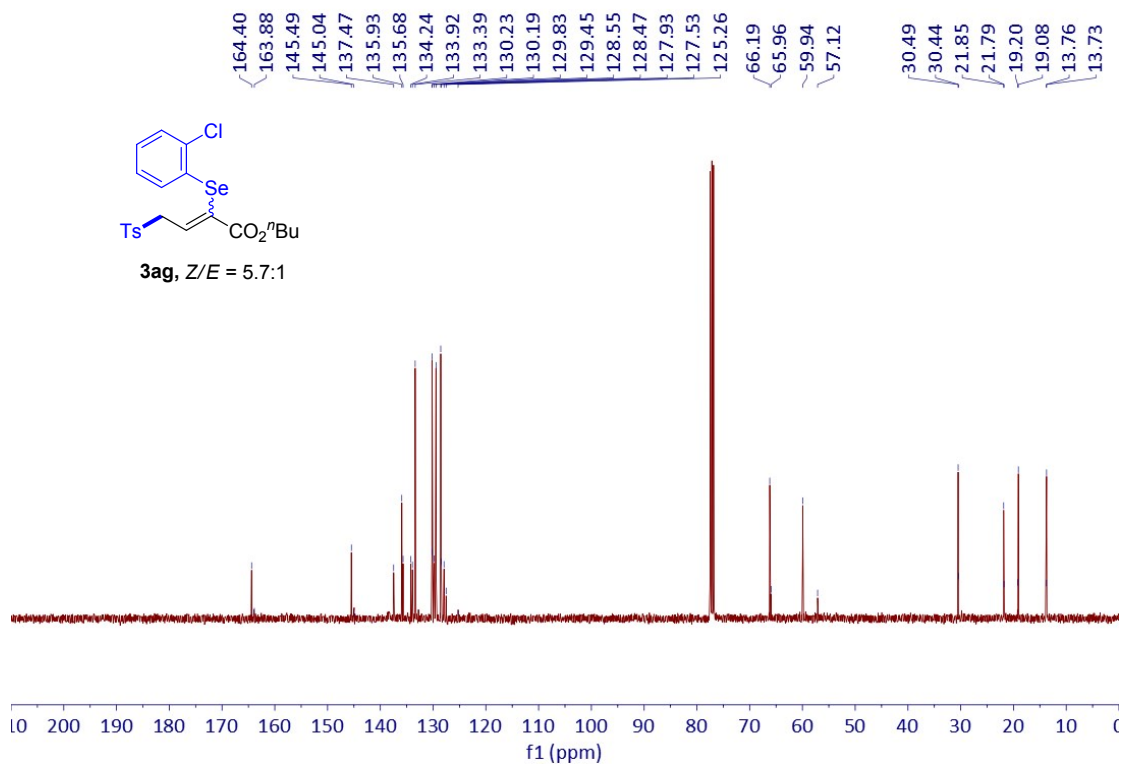
^1H NMR of **3af** (400 Hz, CDCl_3)



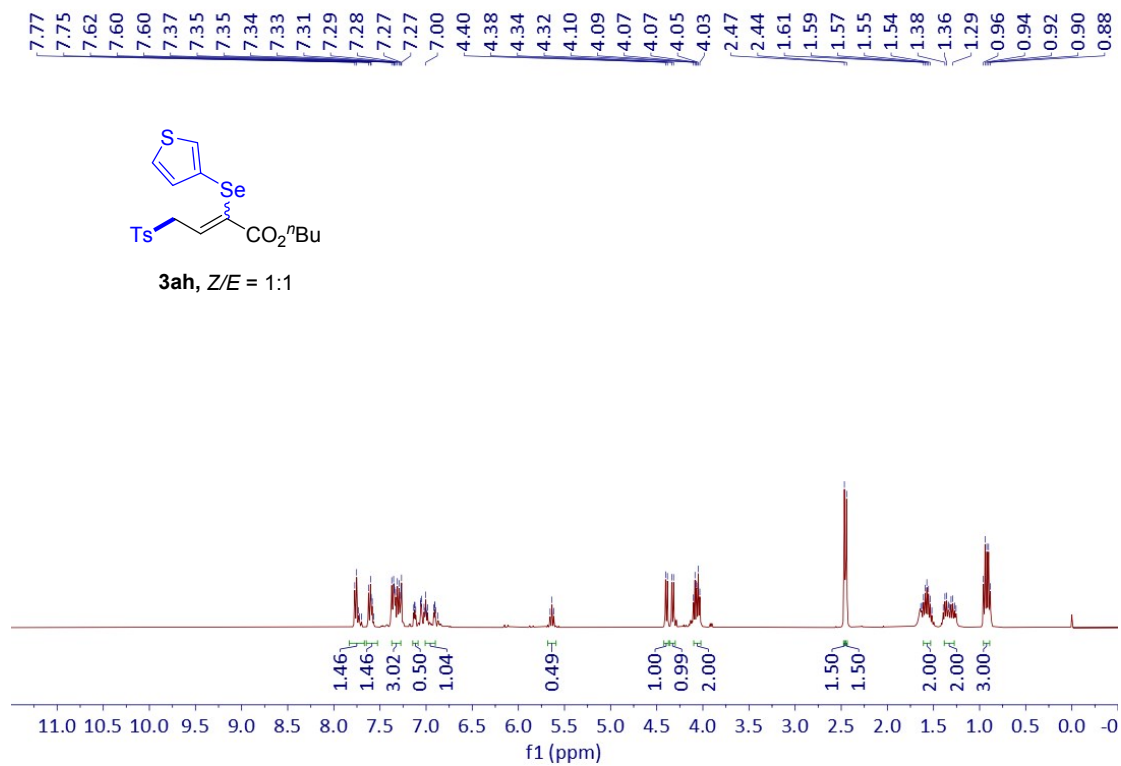
¹³C NMR of **3af** (100 Hz, CDCl₃)



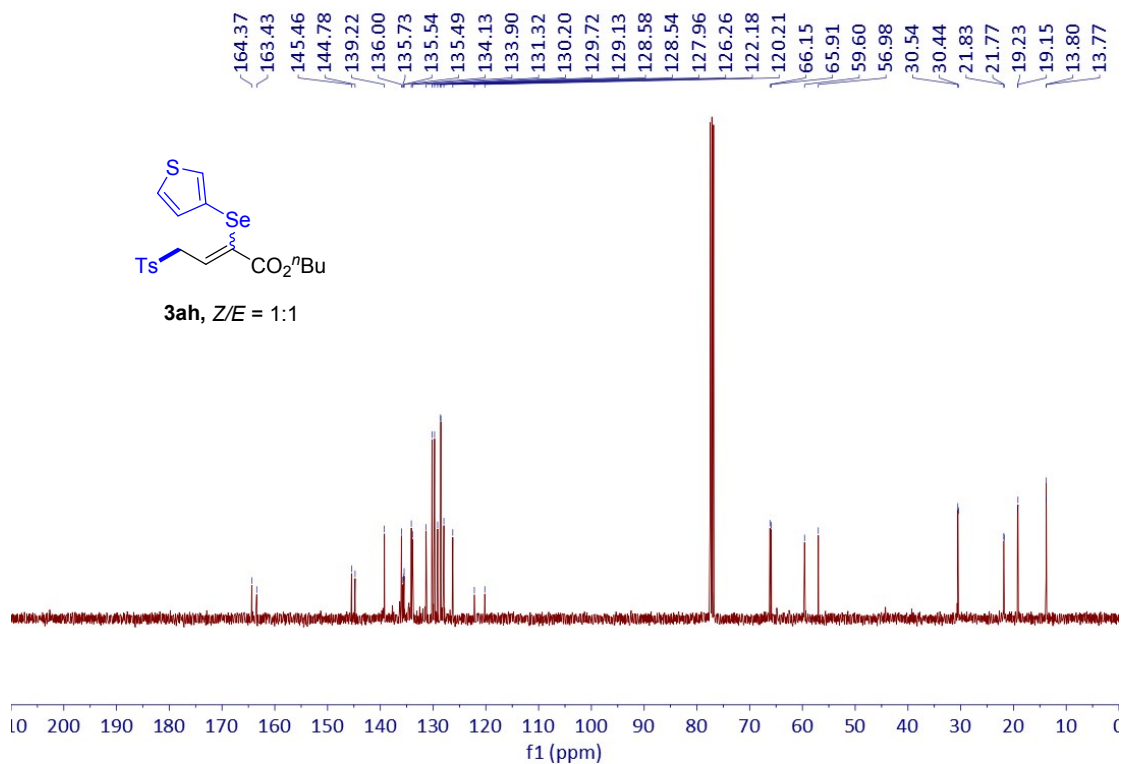
¹H NMR of **3ag** (400 Hz, CDCl₃)



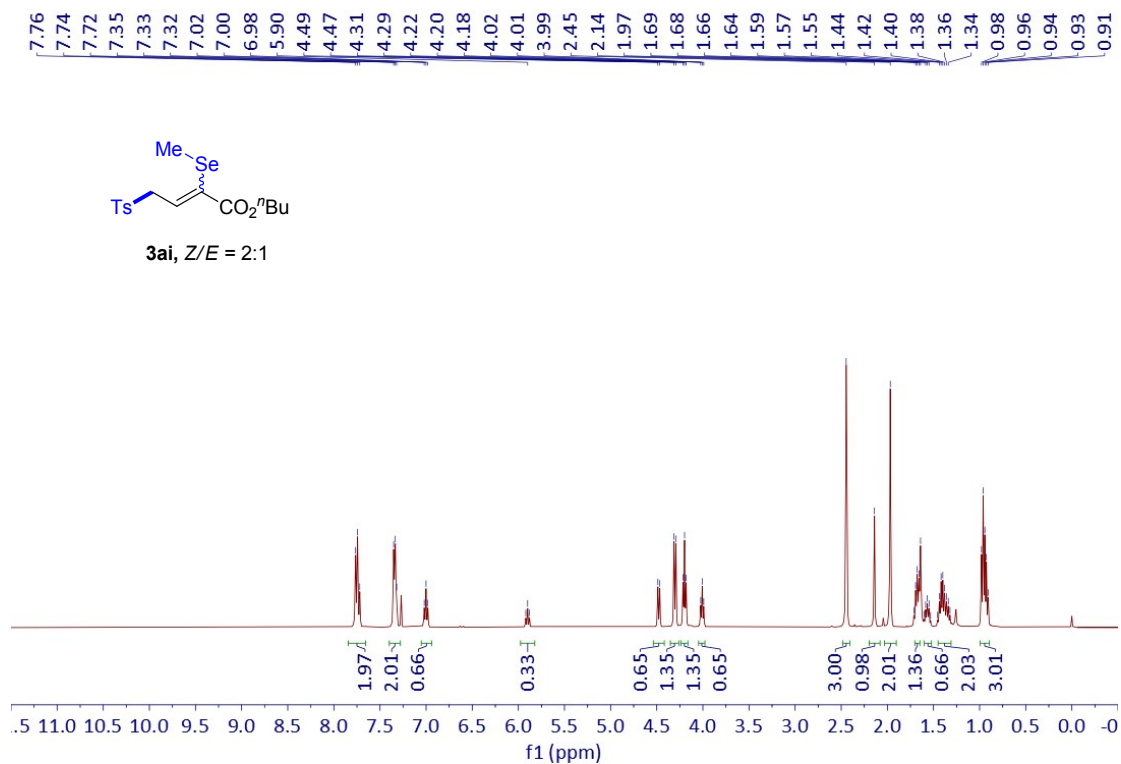
¹³C NMR of **3ag** (100 Hz, CDCl₃)



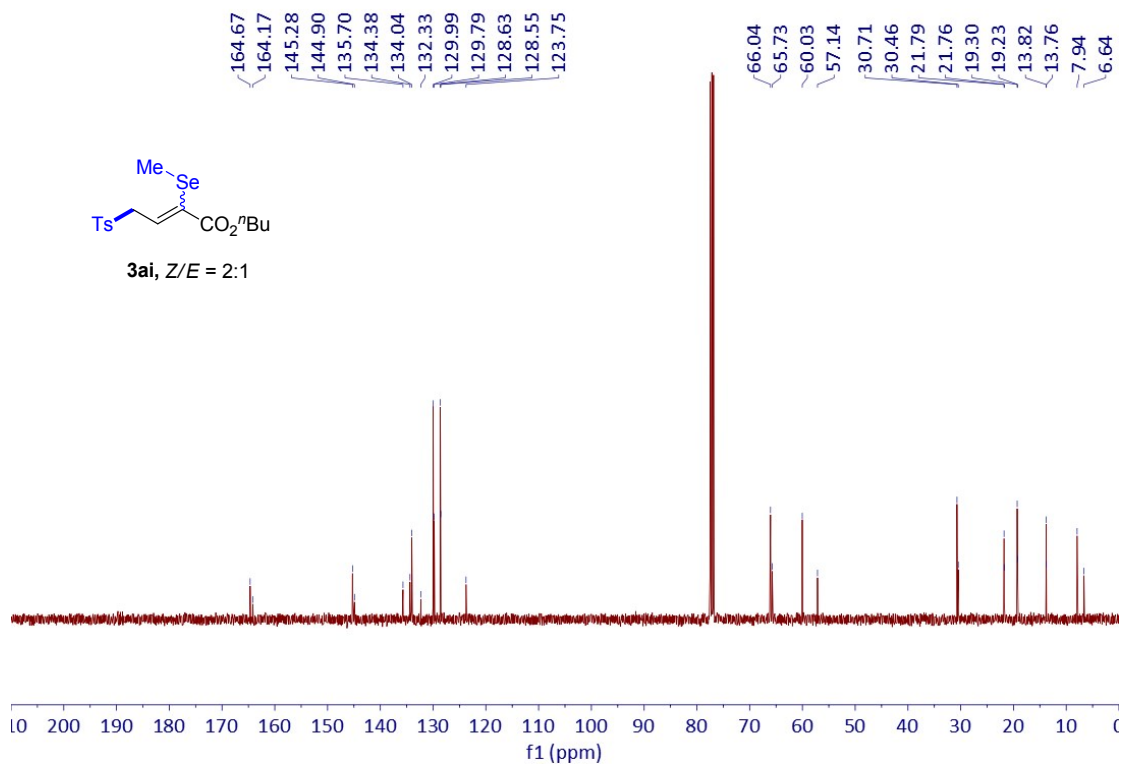
¹H NMR of **3ah** (400 Hz, CDCl₃)



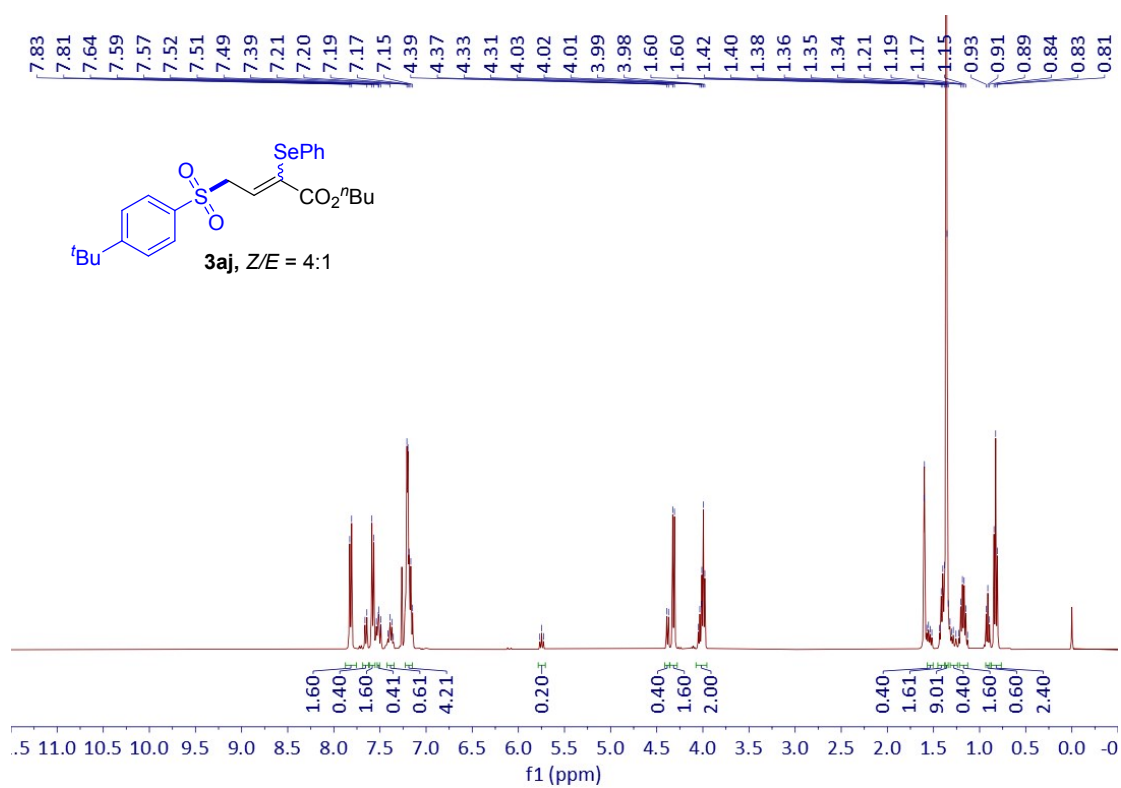
^{13}C NMR of **3ah** (100 Hz, CDCl_3)



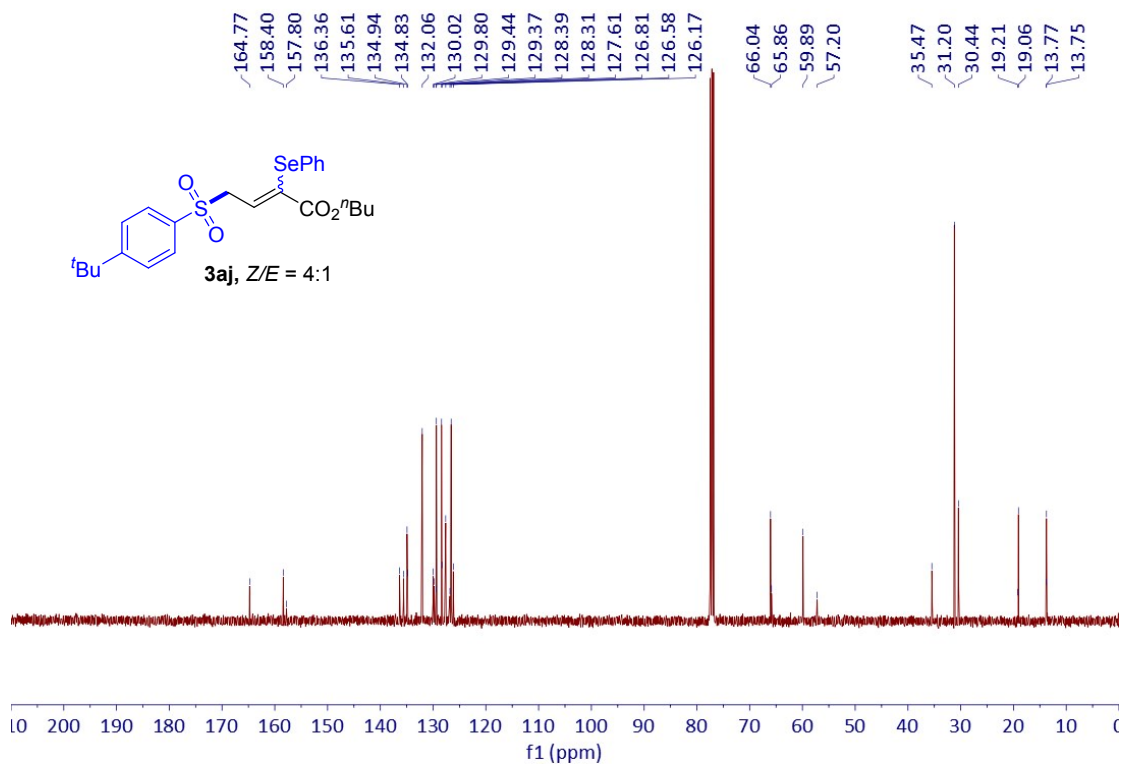
^1H NMR of **3ai** (400 Hz, CDCl_3)



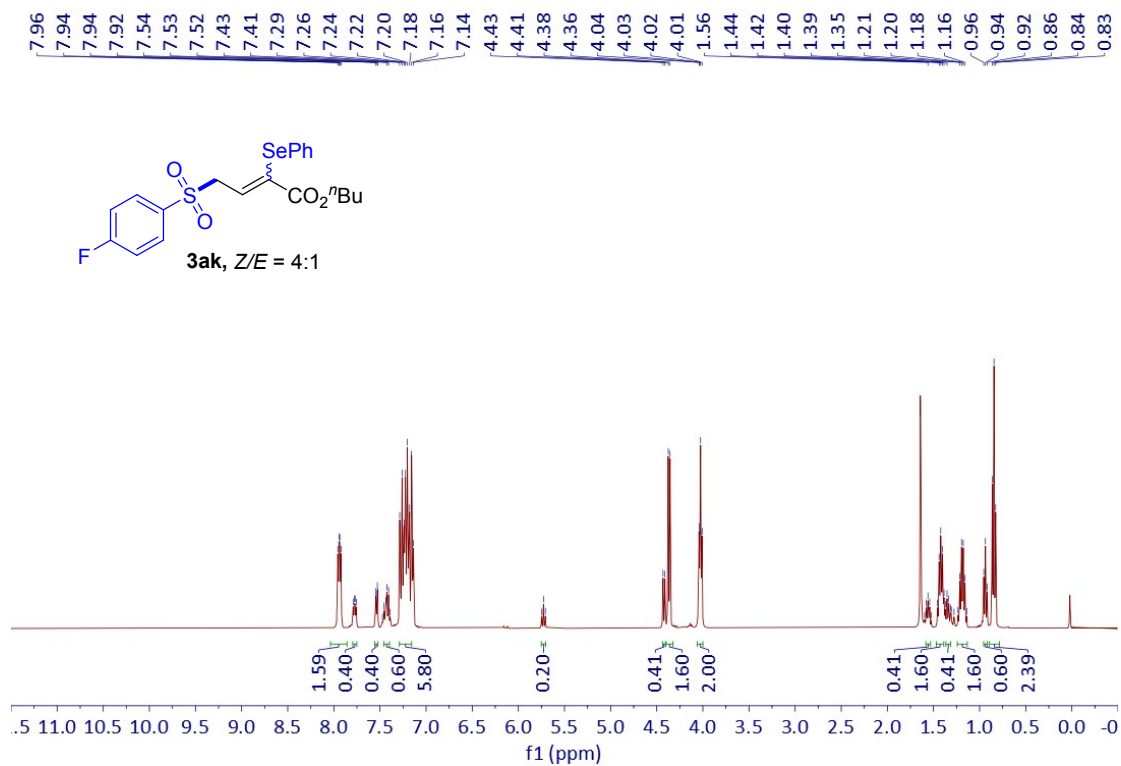
¹³C NMR of **3ai** (100 Hz, CDCl₃)



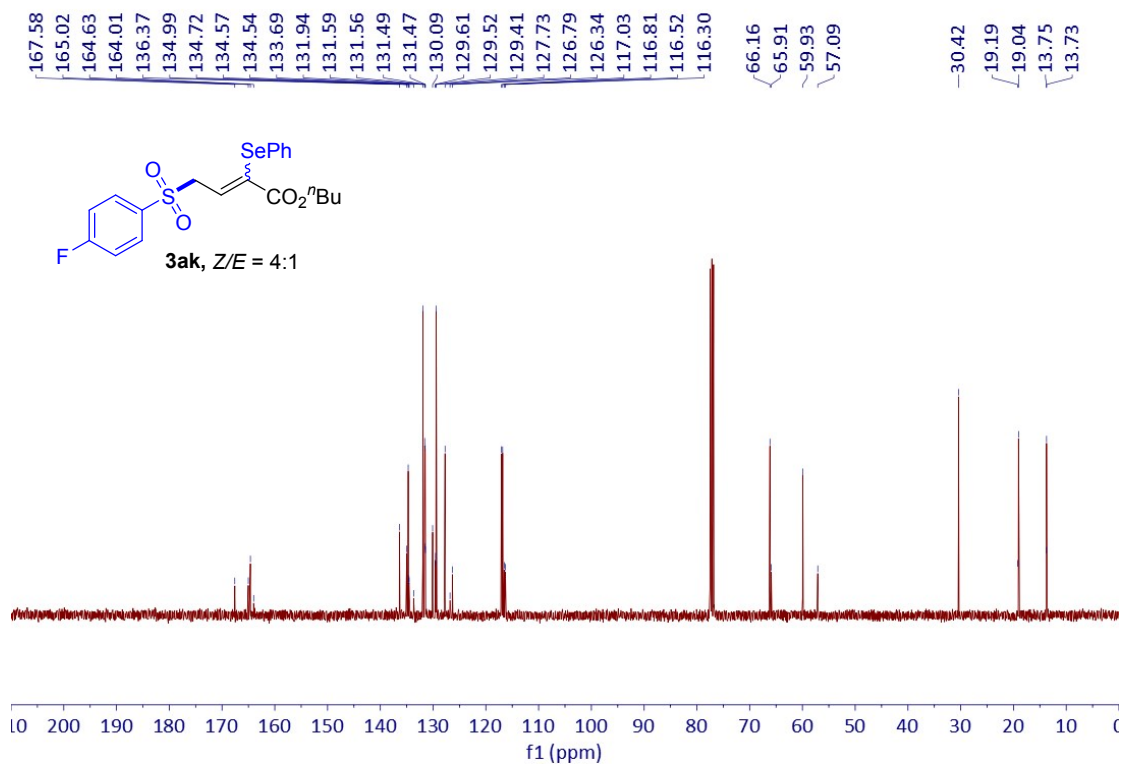
¹H NMR of **3aj** (400 Hz, CDCl₃)



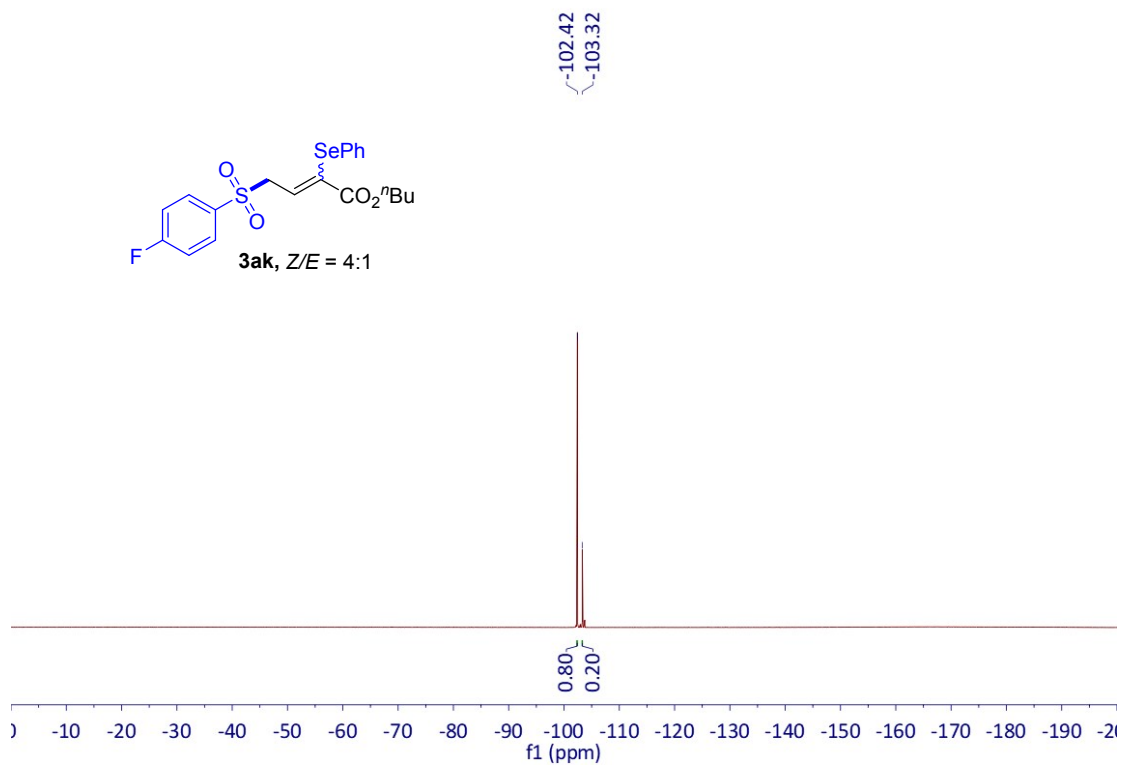
^{13}C NMR of **3aj** (100 Hz, CDCl_3)



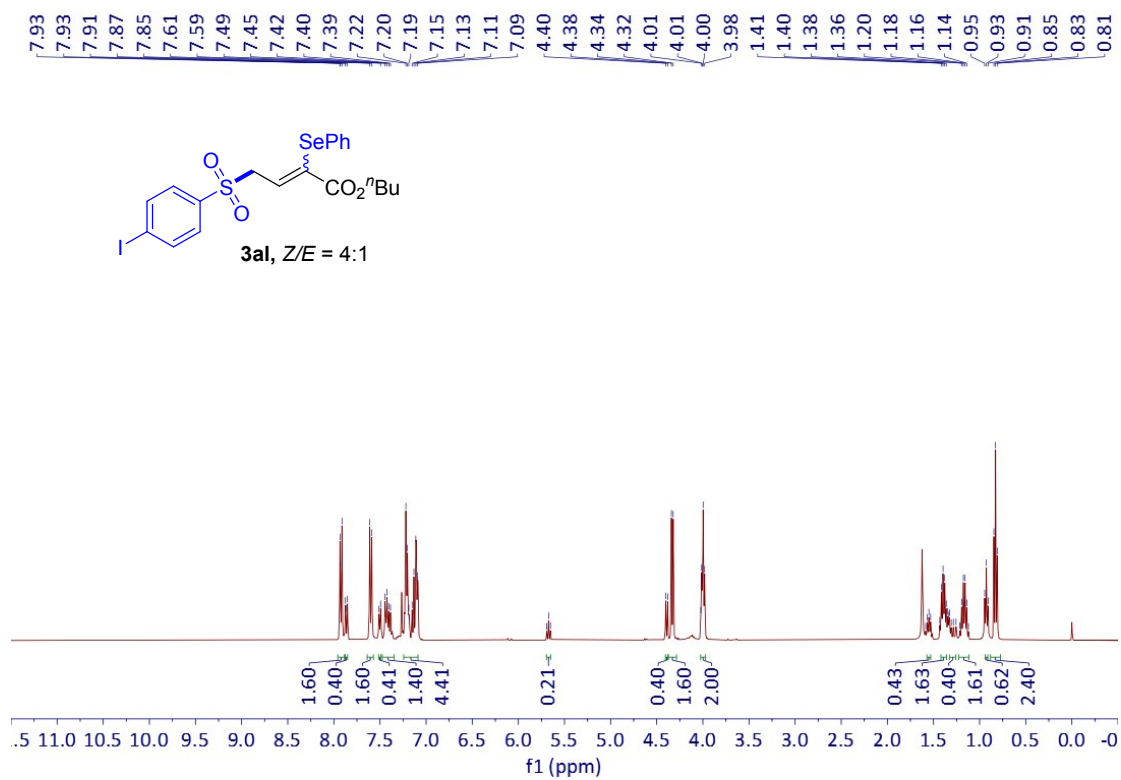
^1H NMR of **3ak** (400 Hz, CDCl_3)



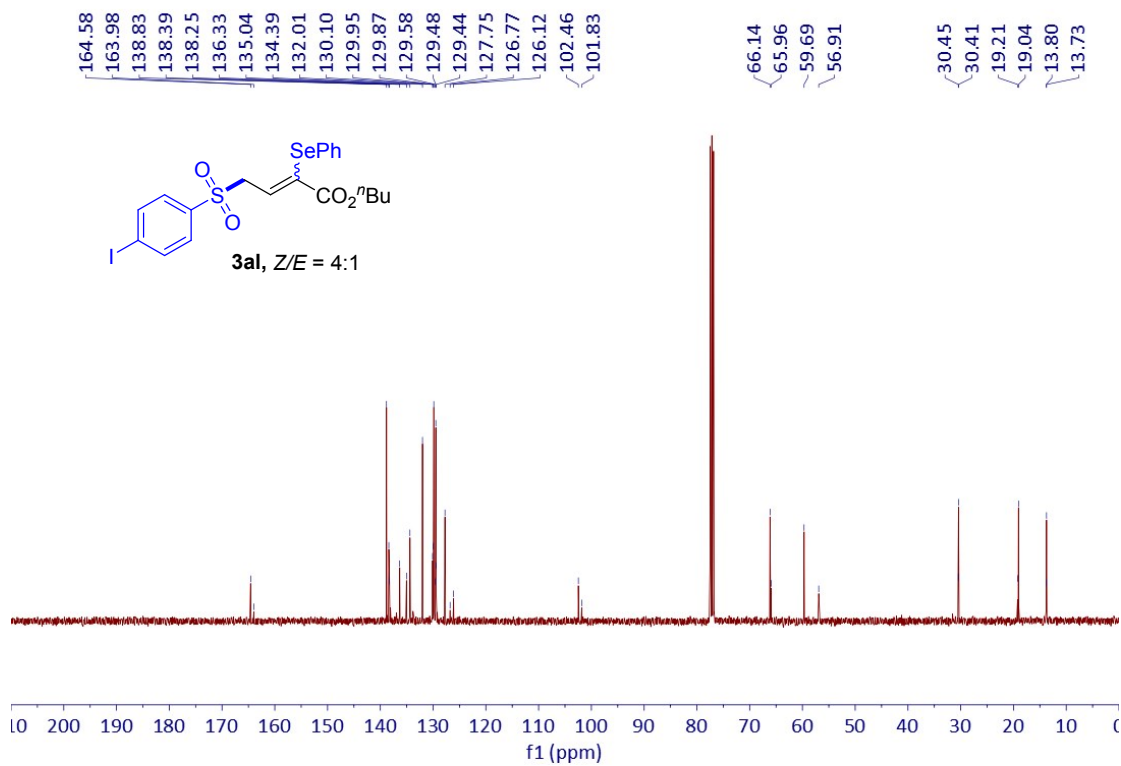
^{13}C NMR of **3ak** (100 Hz, CDCl_3)



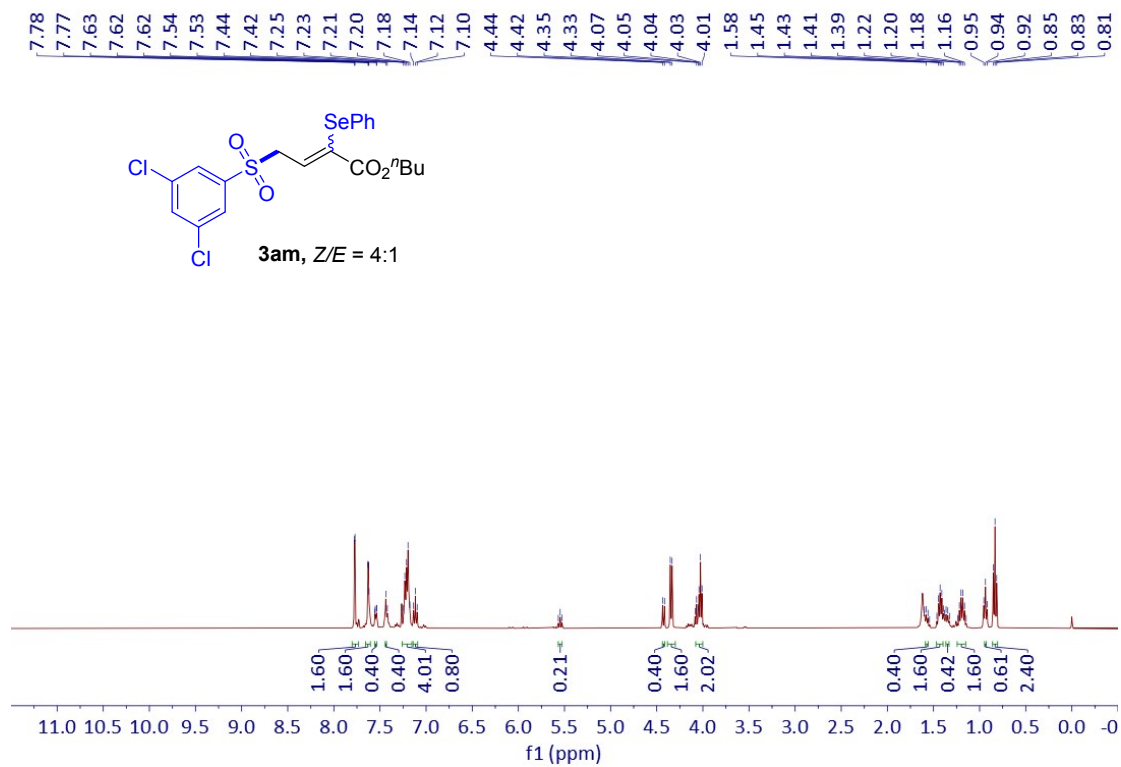
^{19}F NMR of **3ak** (376 Hz, CDCl_3)



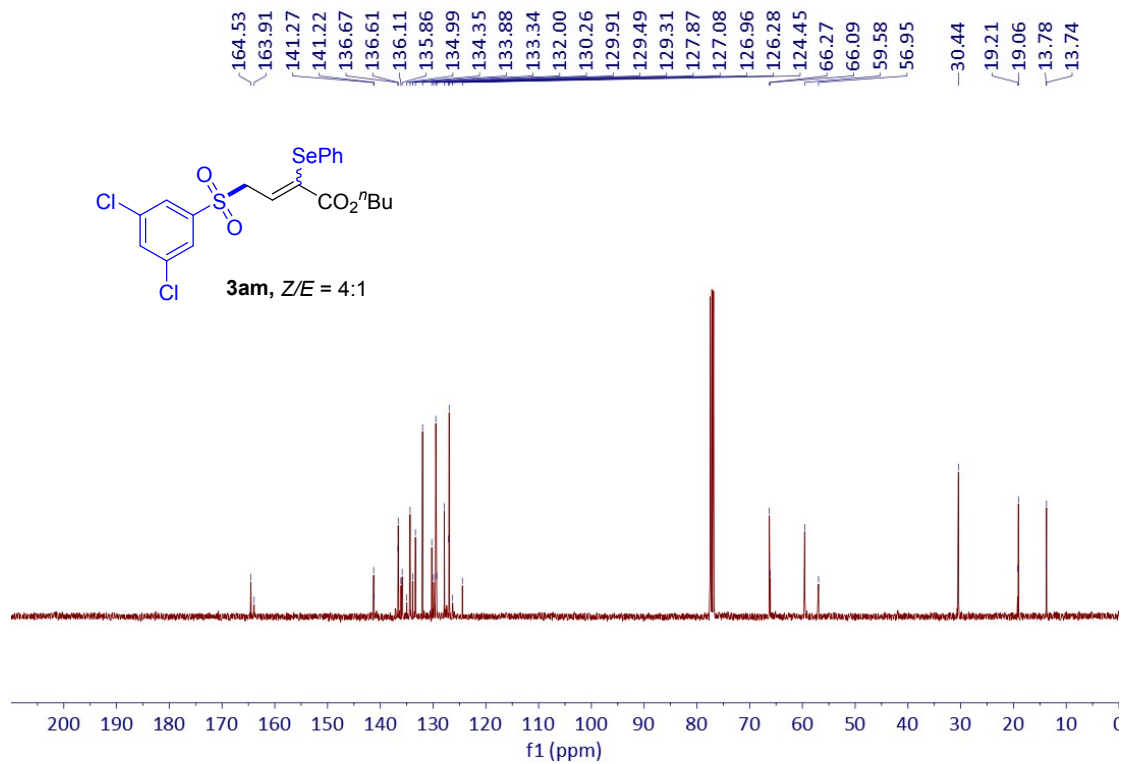
¹H NMR of **3al** (400 Hz, CDCl₃)



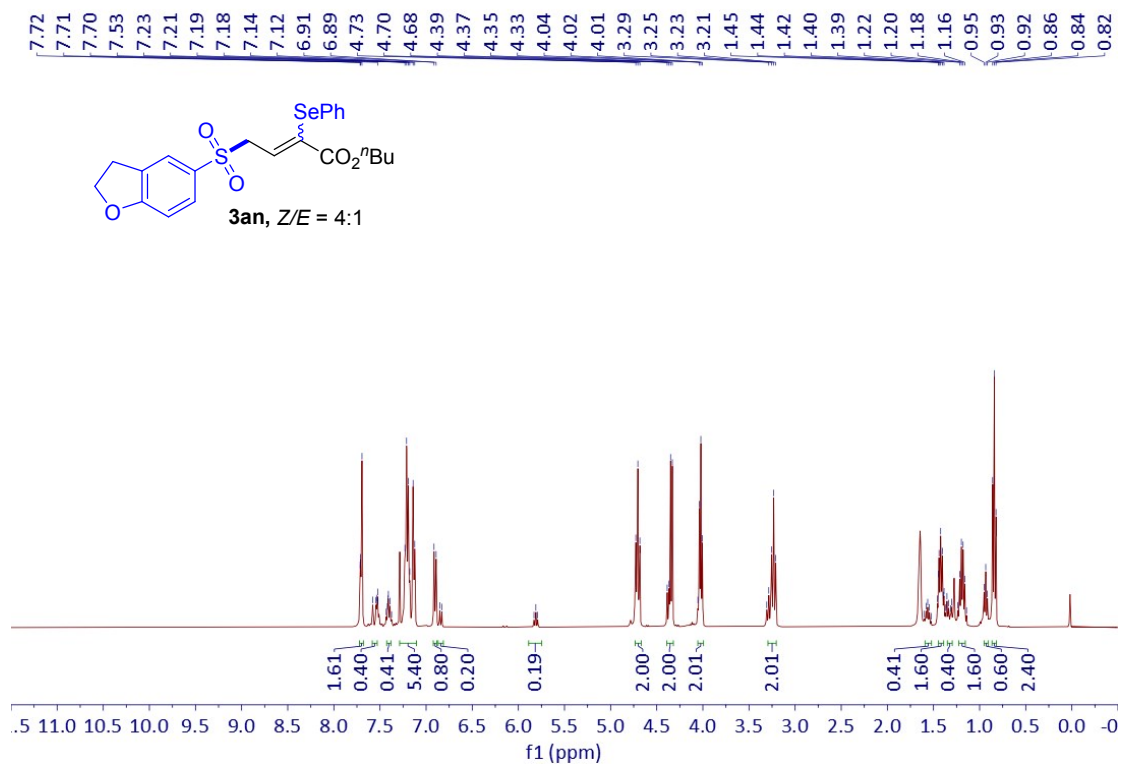
¹³C NMR of **3al** (100 Hz, CDCl₃)



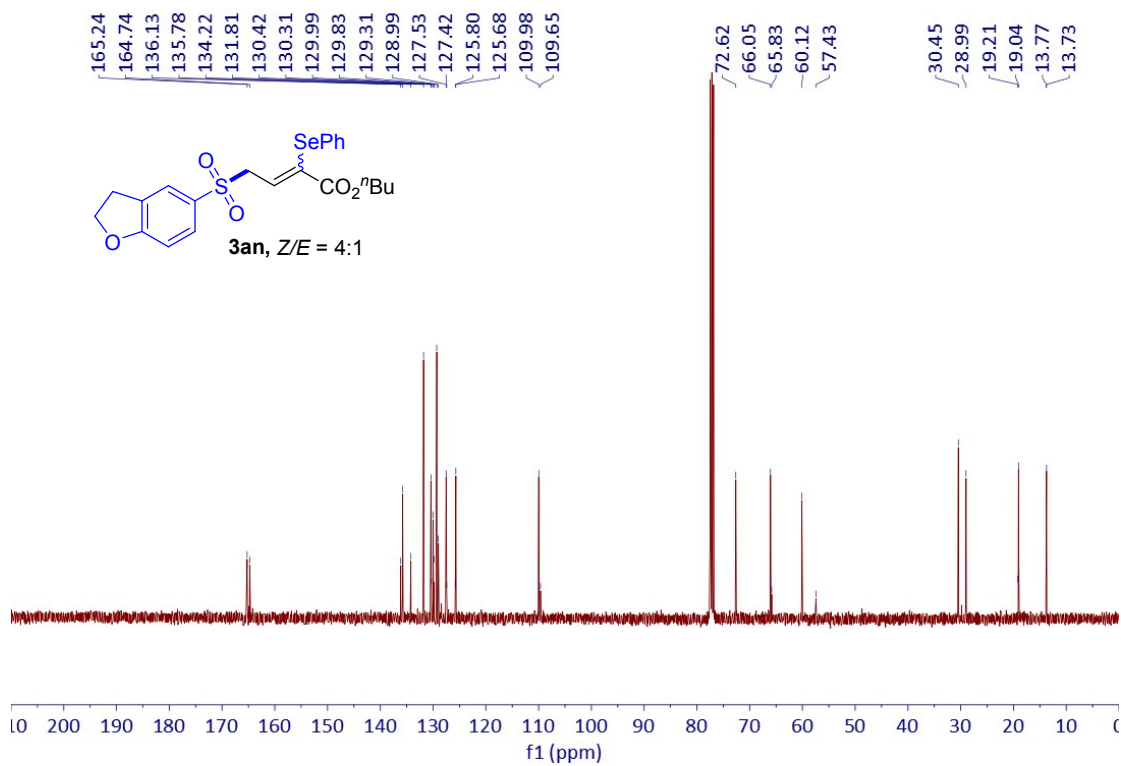
¹H NMR of **3am** (400 Hz, CDCl₃)



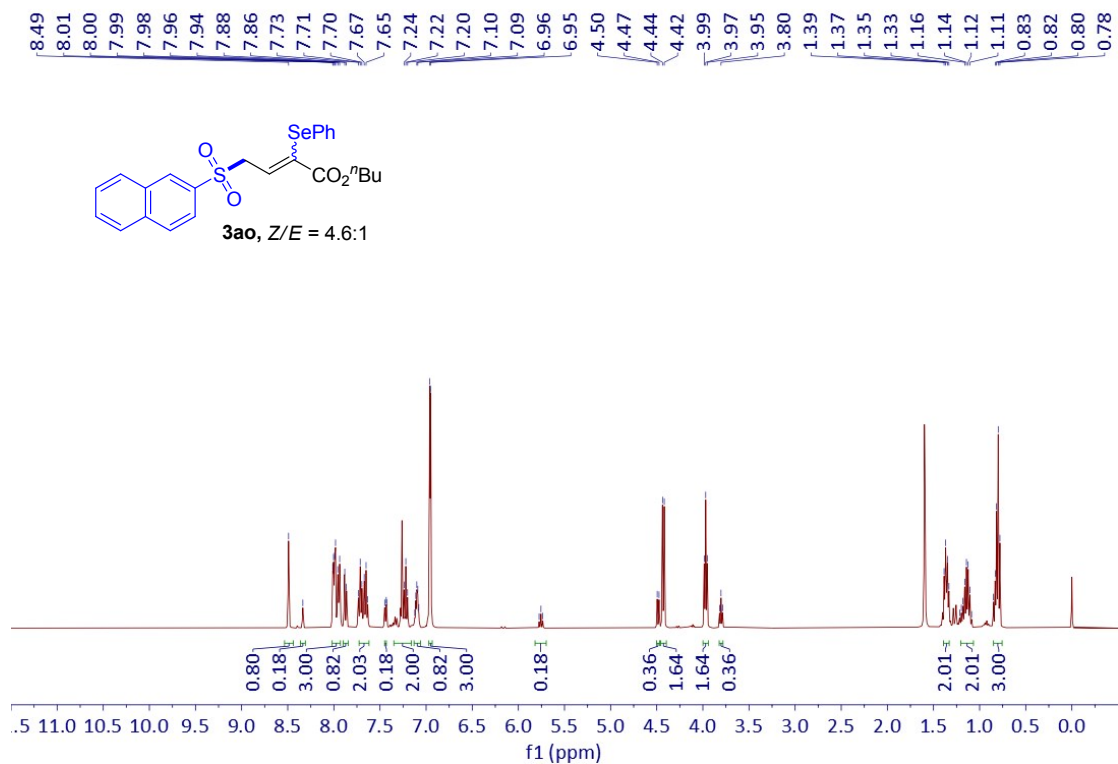
¹³C NMR of **3am** (100 Hz, CDCl₃)



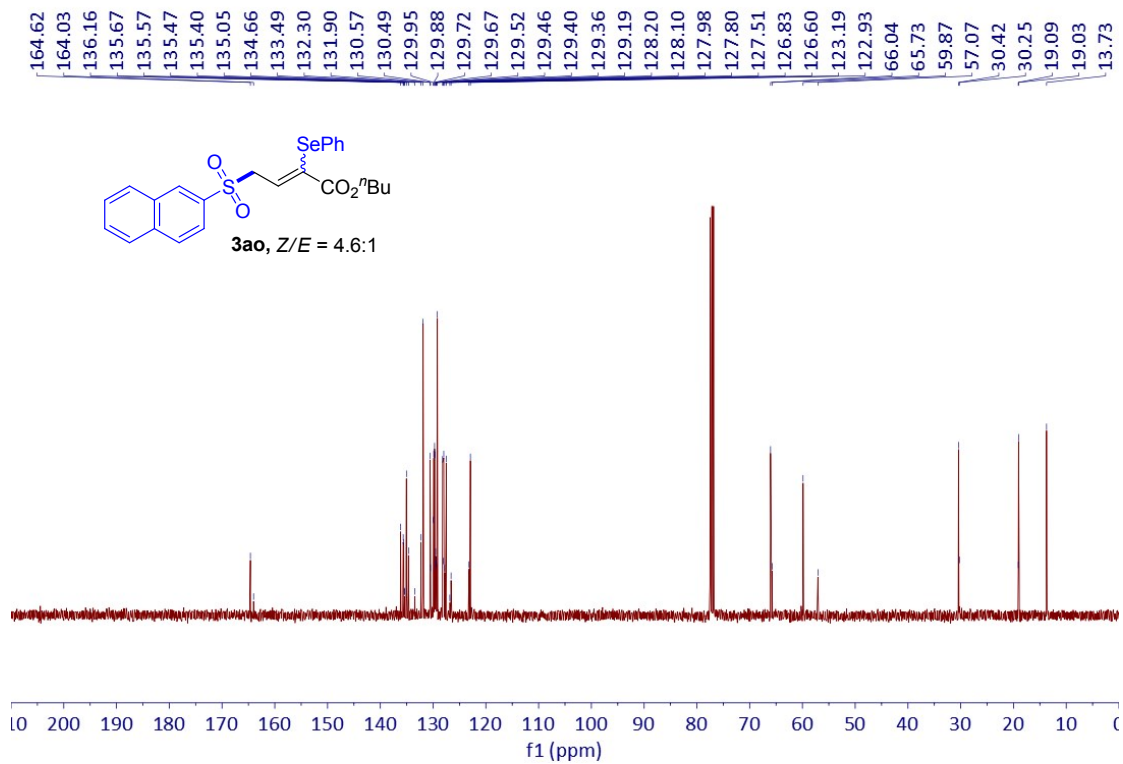
^1H NMR of **3an** (400 Hz, CDCl_3)



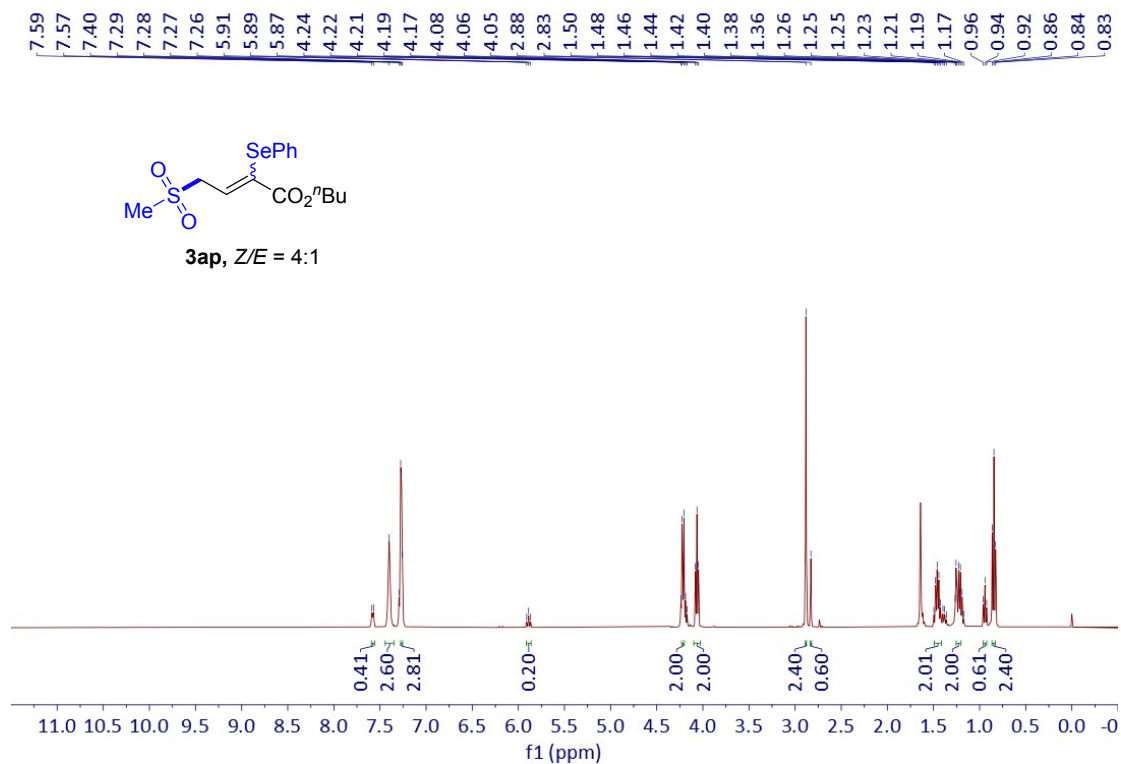
^{13}C NMR of **3an** (100 Hz, CDCl_3)



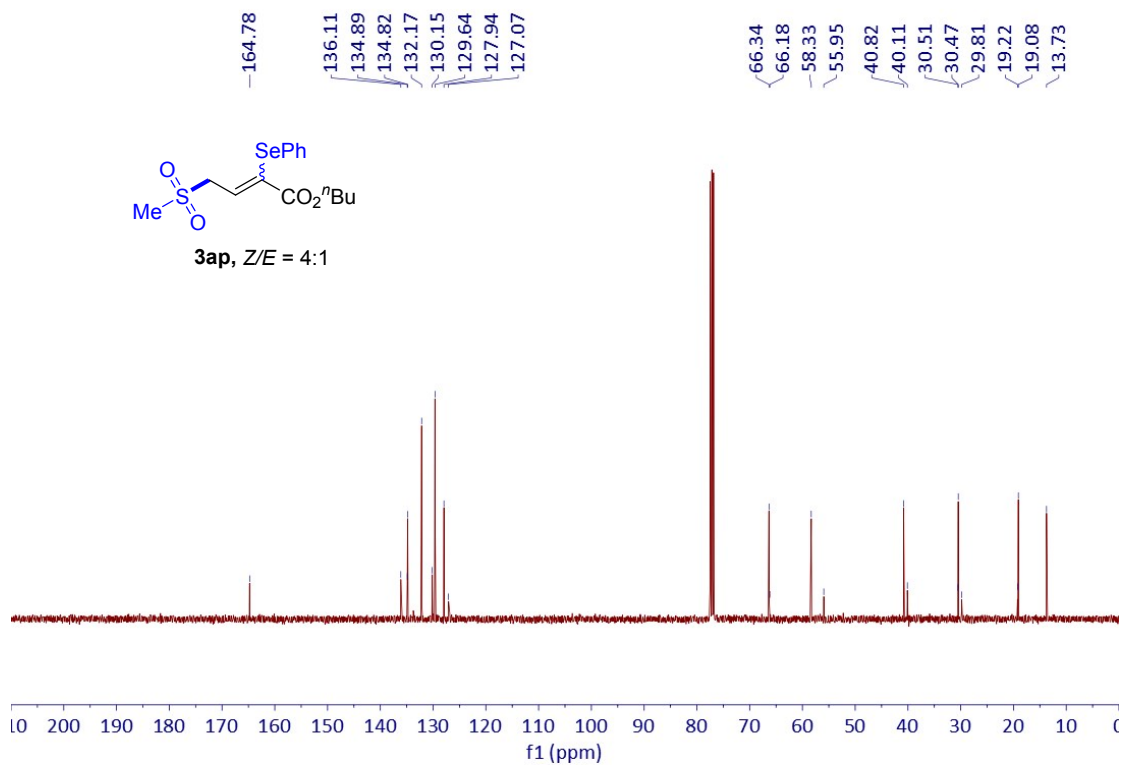
¹H NMR of **3ao** (400 Hz, CDCl₃)



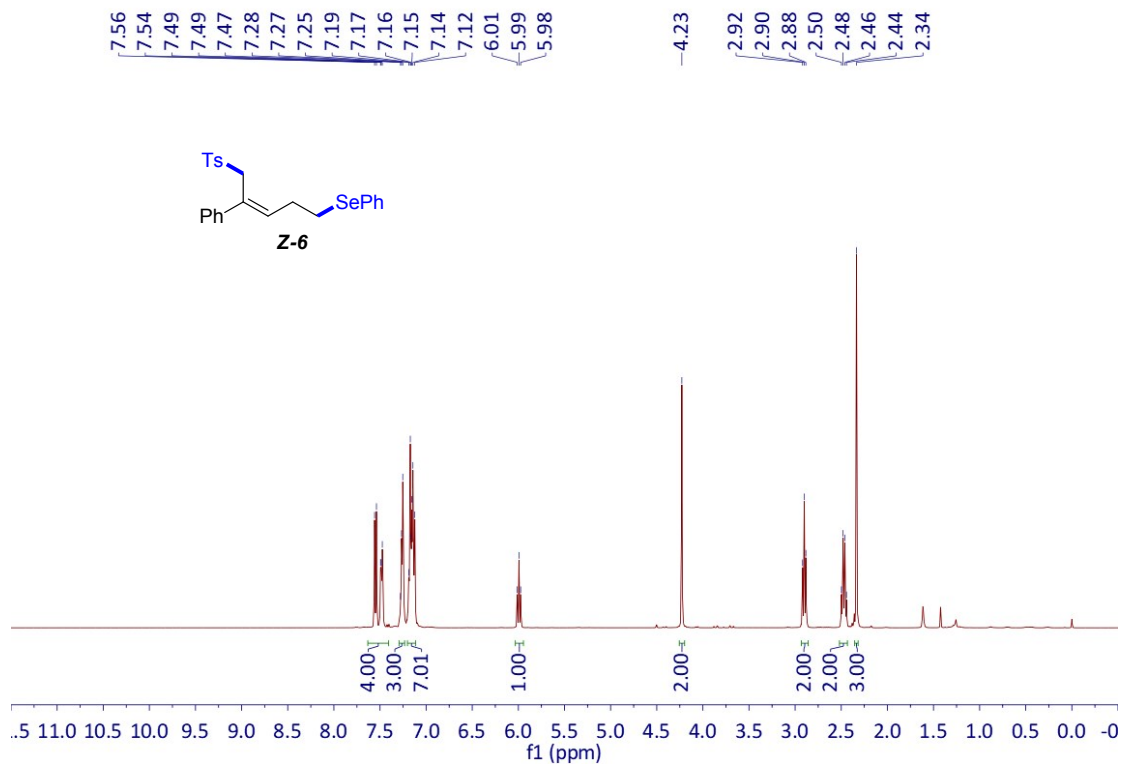
¹³C NMR of **3ao** (100 Hz, CDCl₃)



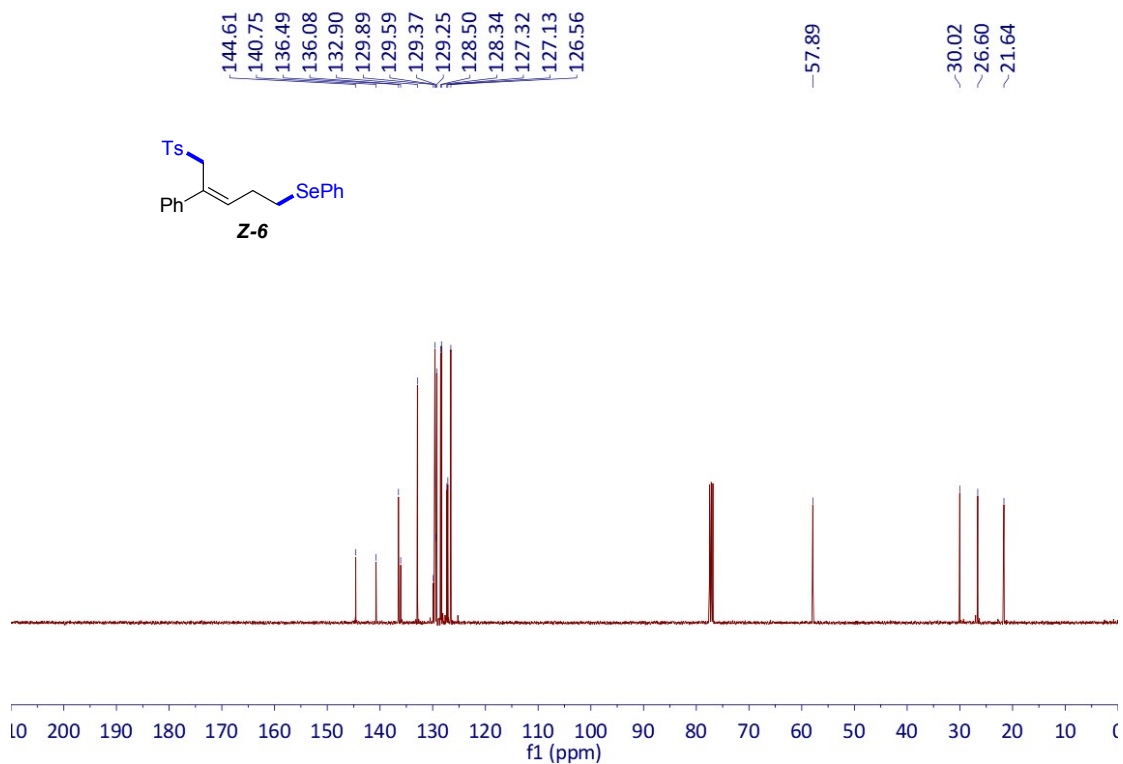
^1H NMR of **3ap** (400 Hz, CDCl_3)



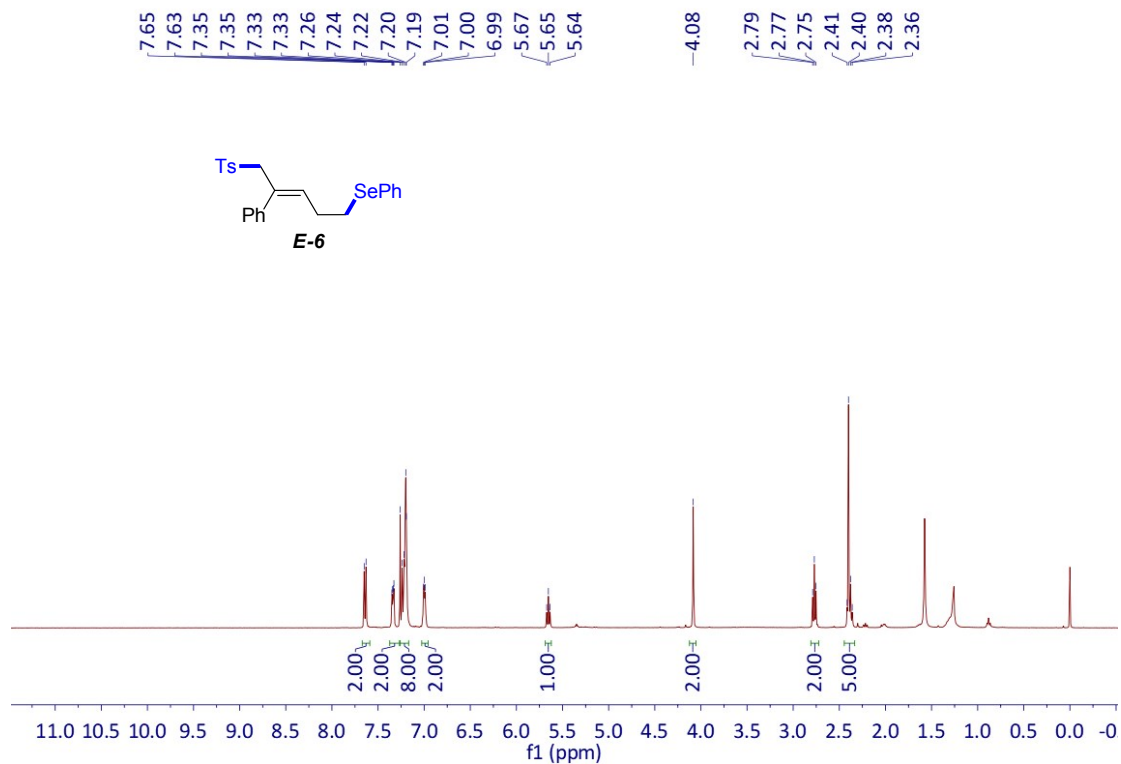
^{13}C NMR of **3ap** (100 Hz, CDCl_3)



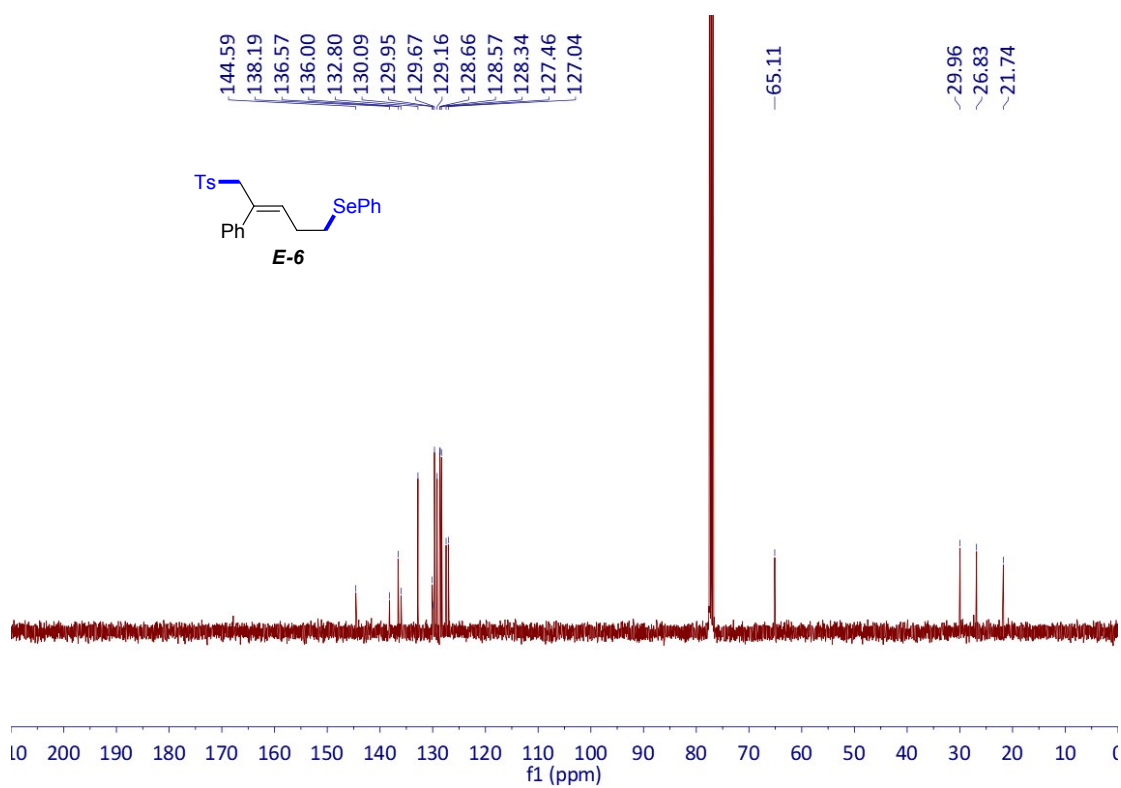
¹H NMR of **Z-6** (400 Hz, CDCl₃)



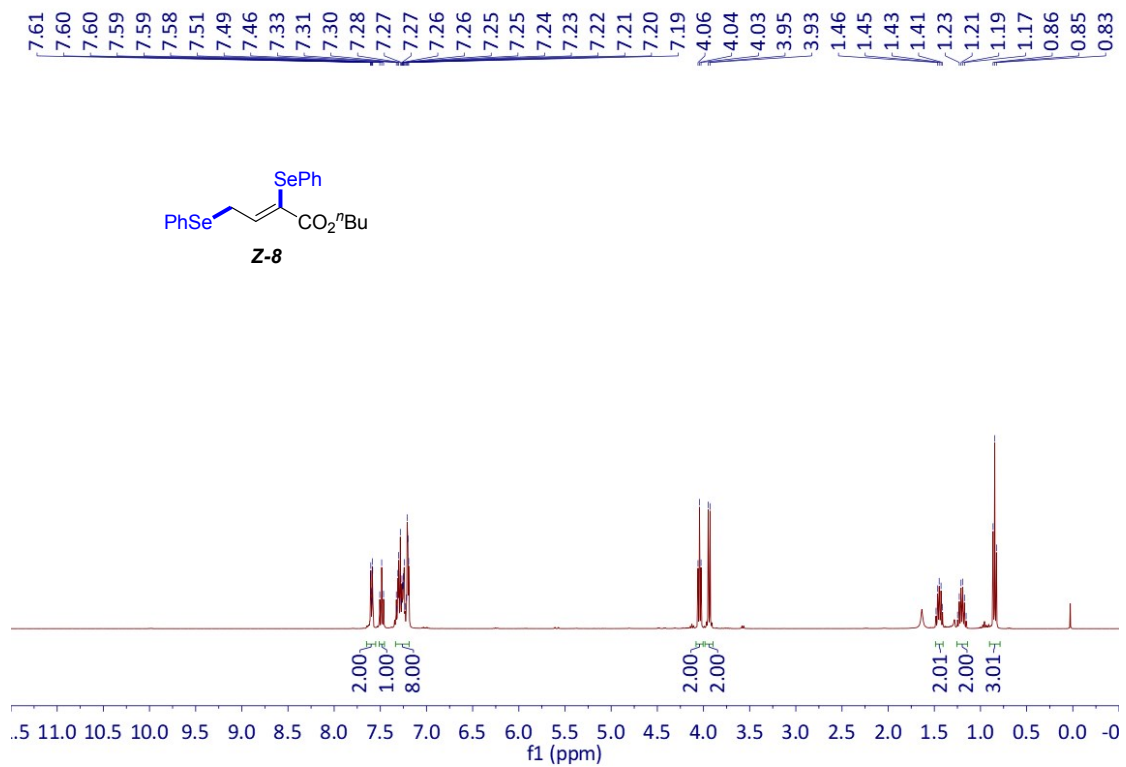
¹³C NMR of **Z-6** (100 Hz, CDCl₃)



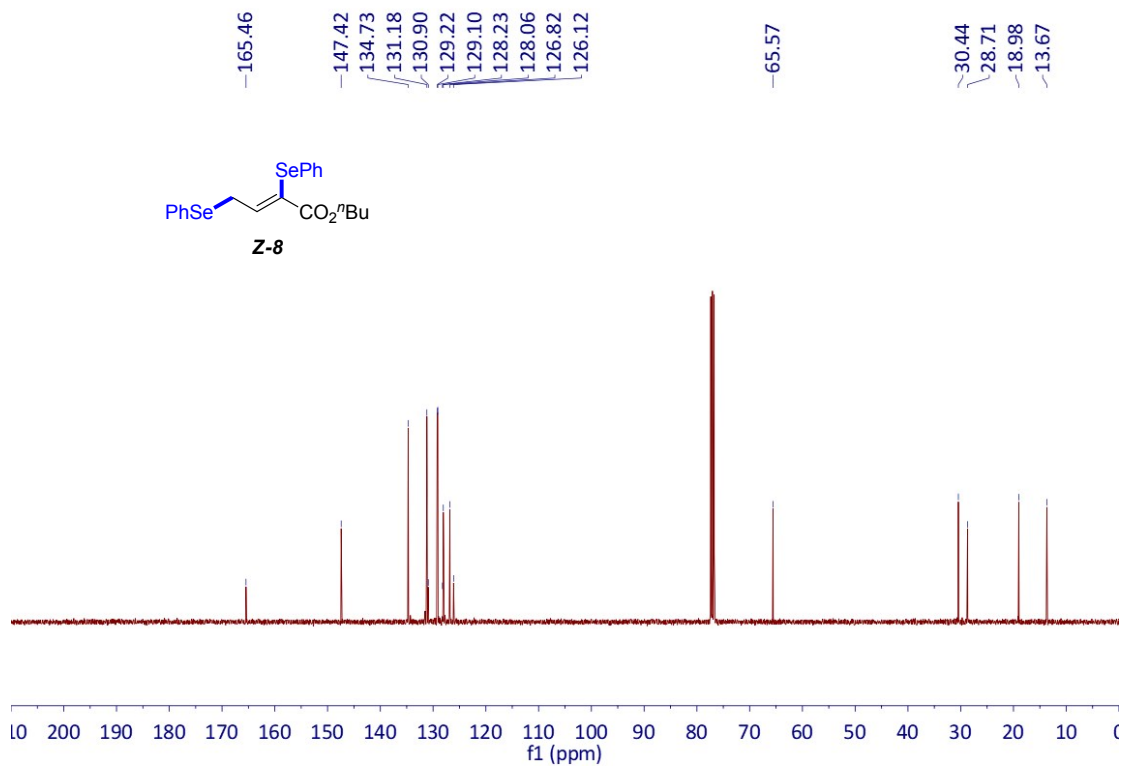
¹H NMR of *E-6* (400 Hz, CDCl₃)



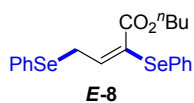
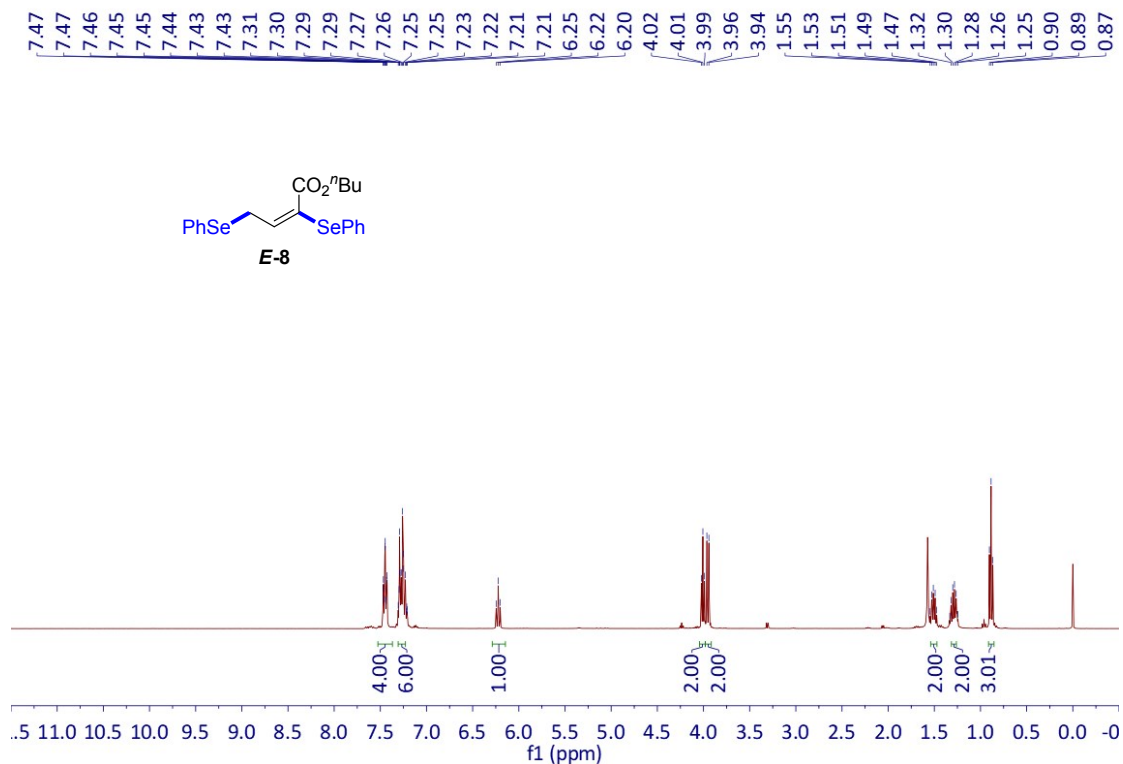
¹³C NMR of *E-6* (100 Hz, CDCl₃)



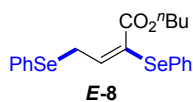
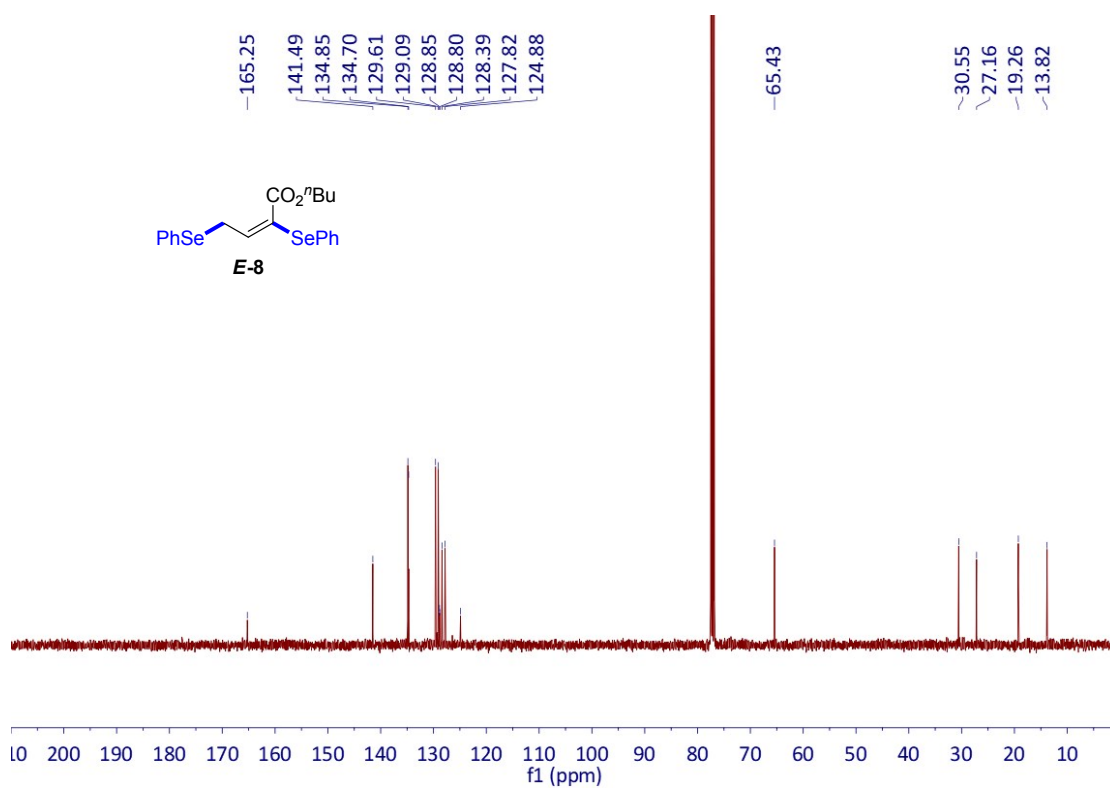
¹H NMR of **Z-8** (400 Hz, CDCl₃)



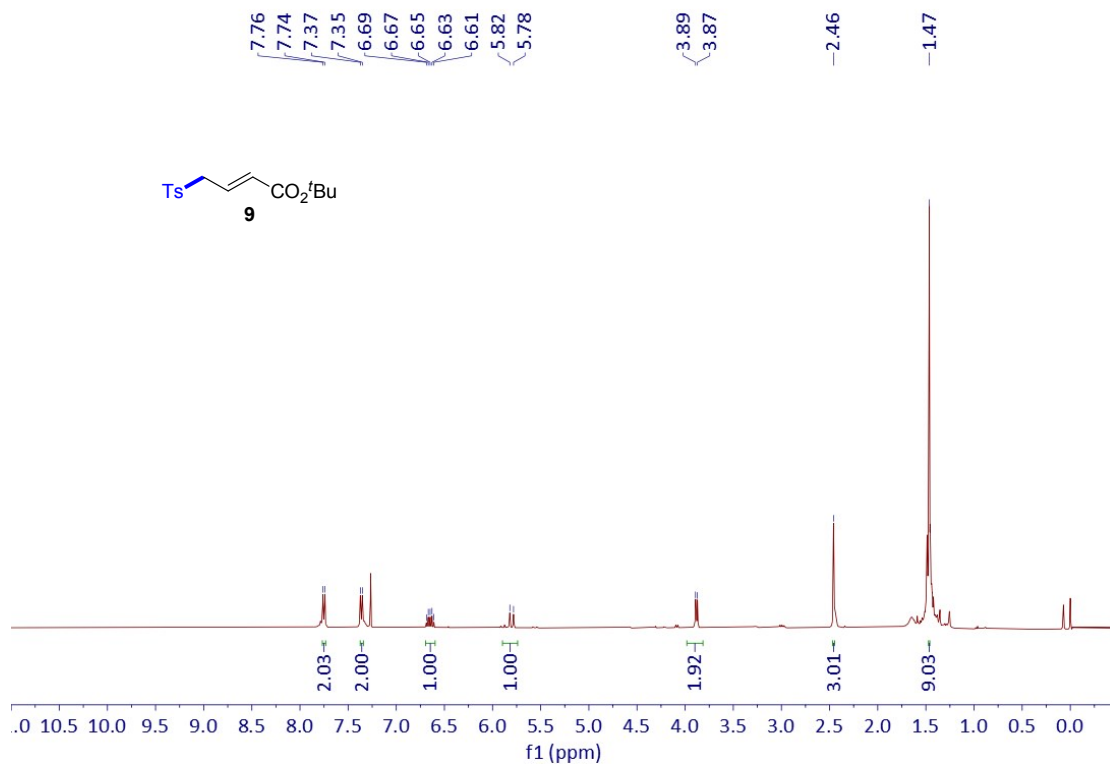
¹³C NMR of **Z-8** (100 Hz, CDCl₃)



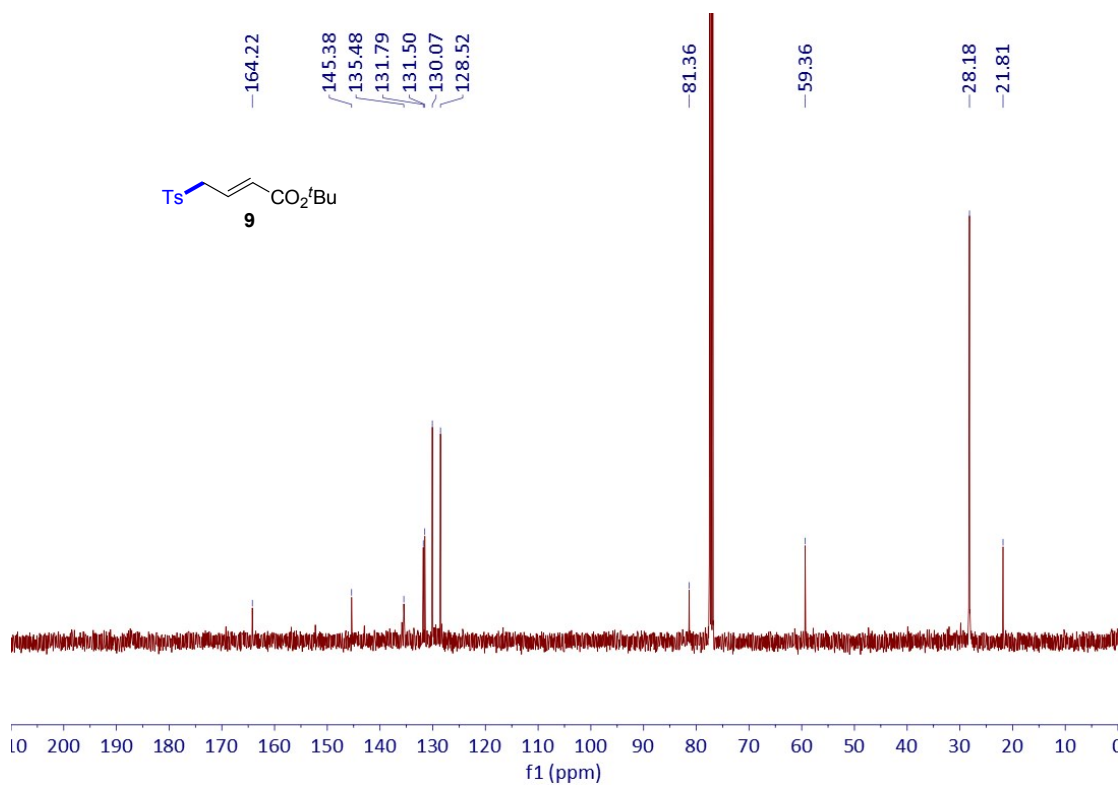
¹H NMR of *E-8* (400 Hz, CDCl₃)



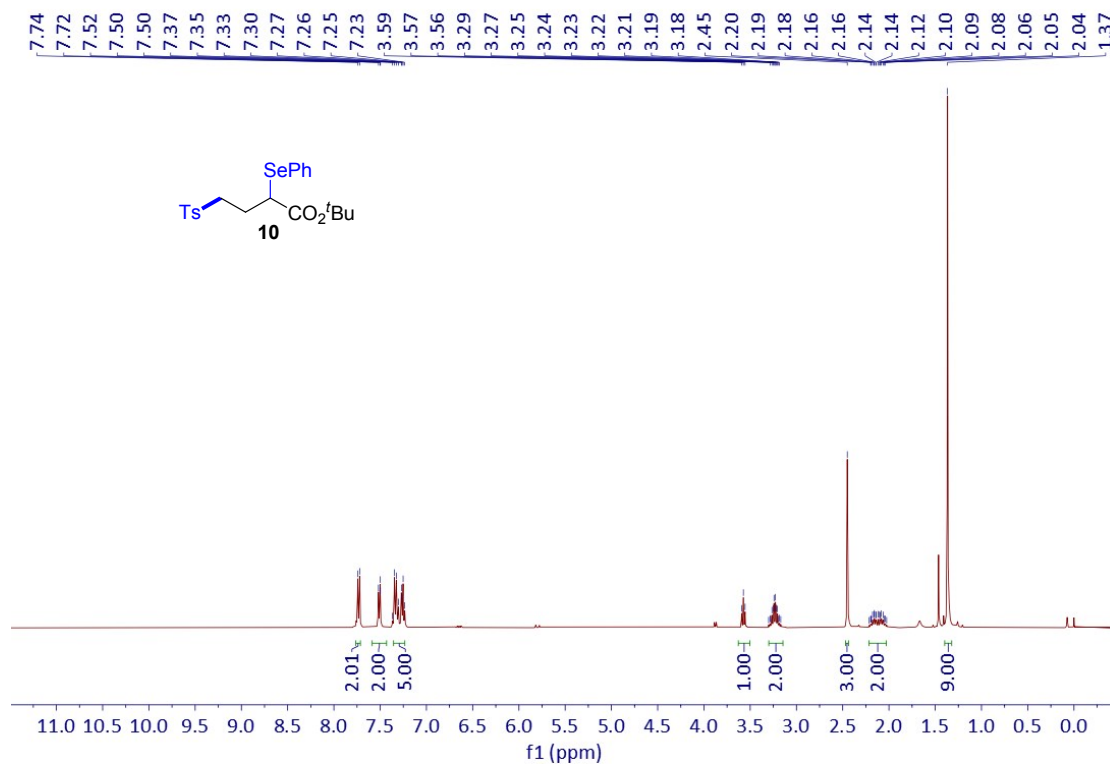
¹³C NMR of *E-8* (100 Hz, CDCl₃)



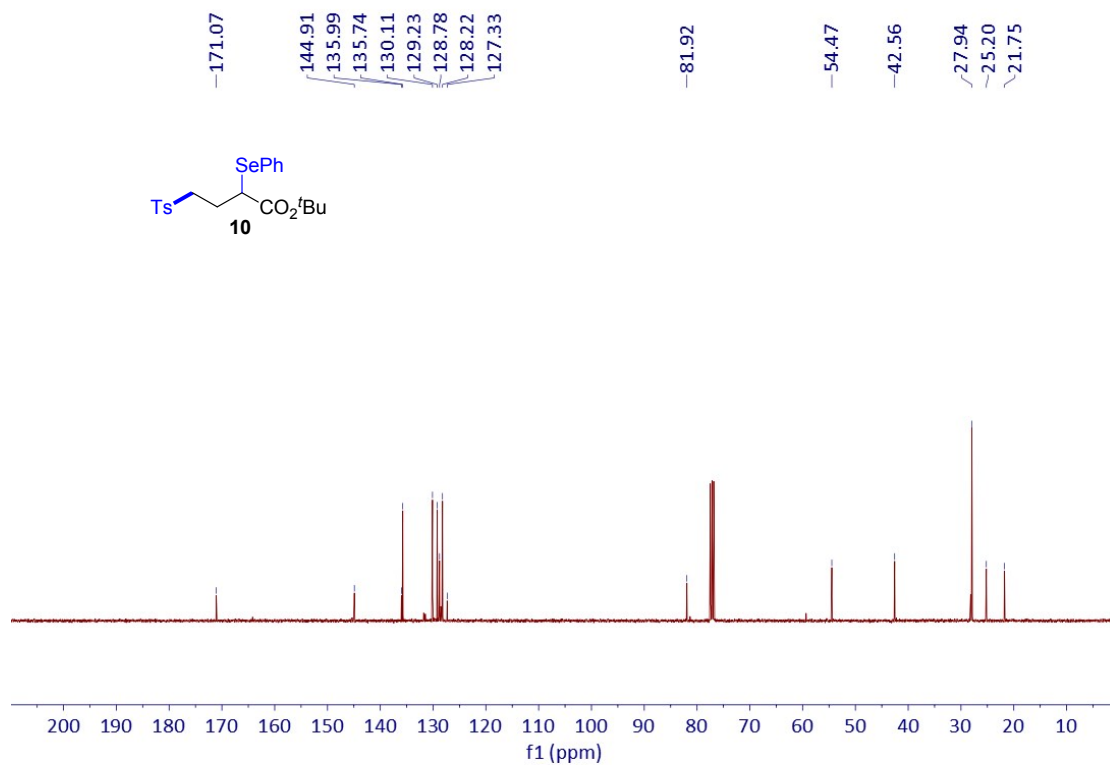
^1H NMR of **9** (400 Hz, CDCl_3)



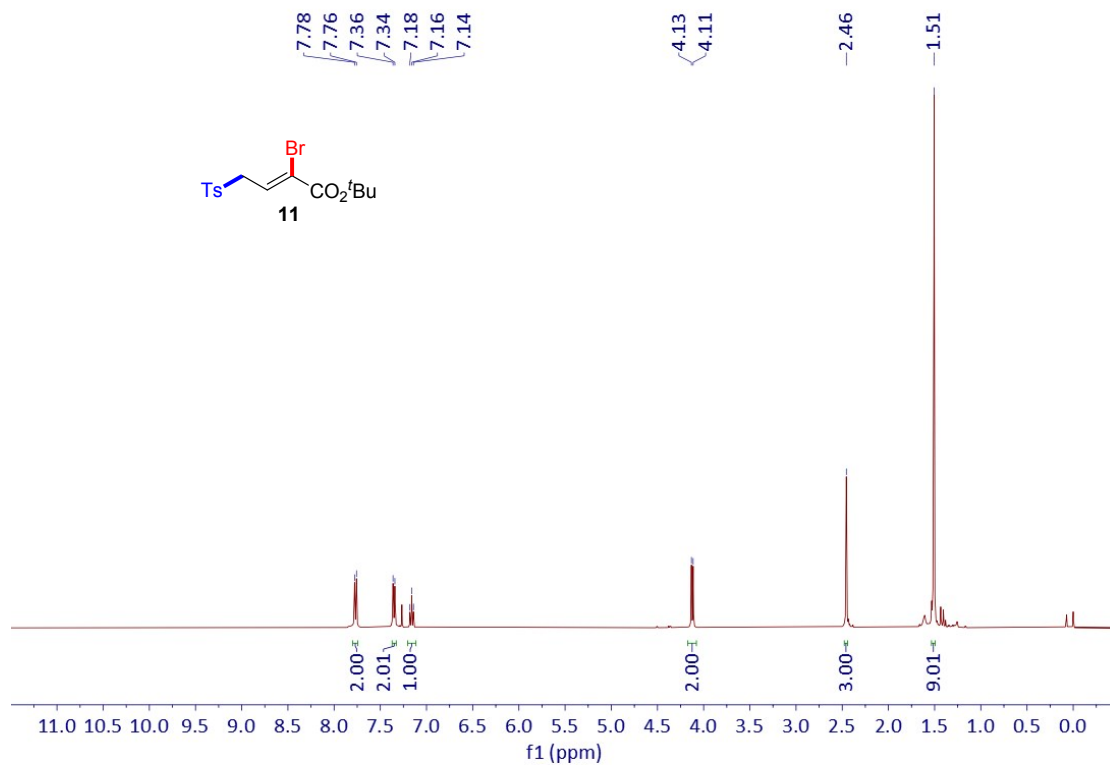
^{13}C NMR of **9** (100 Hz, CDCl_3)



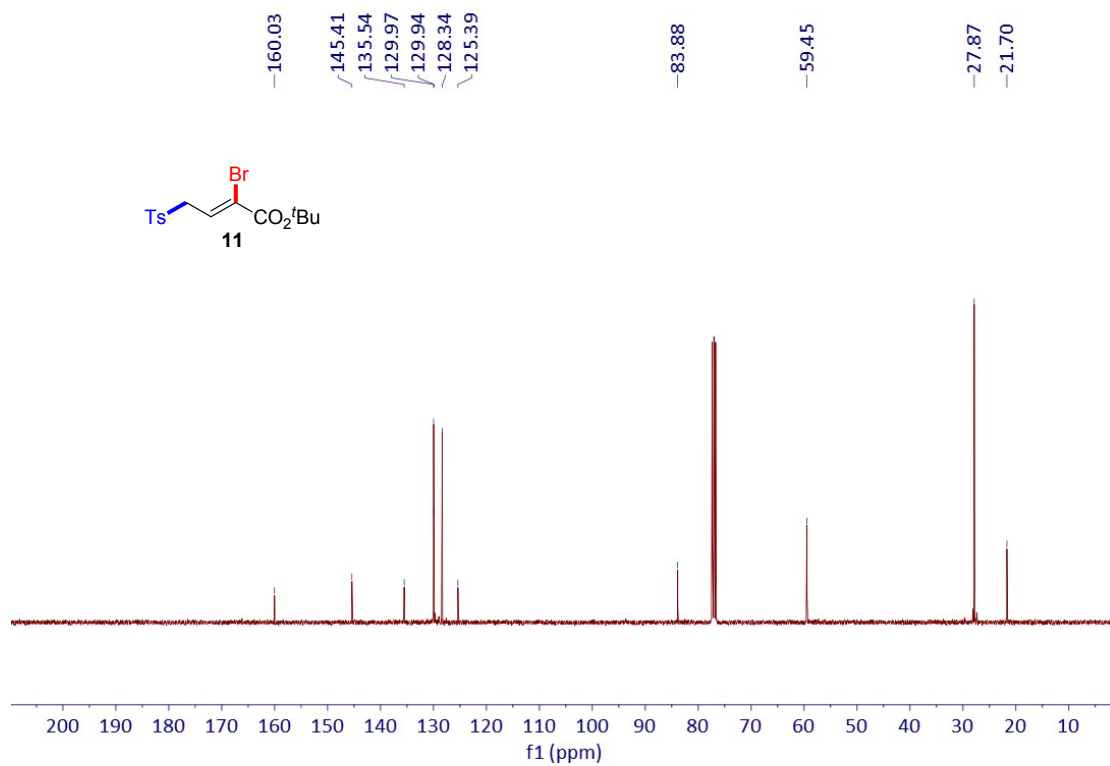
¹H NMR of **10** (400 Hz, CDCl₃)



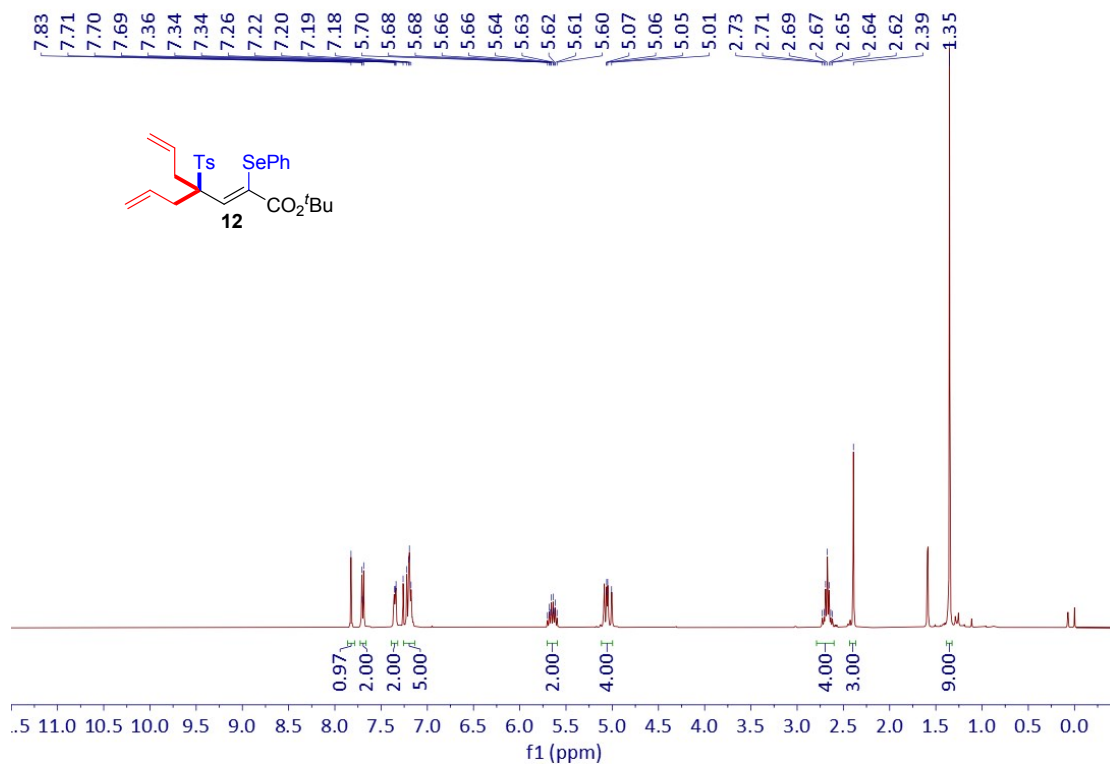
¹³C NMR of **10** (100 Hz, CDCl₃)



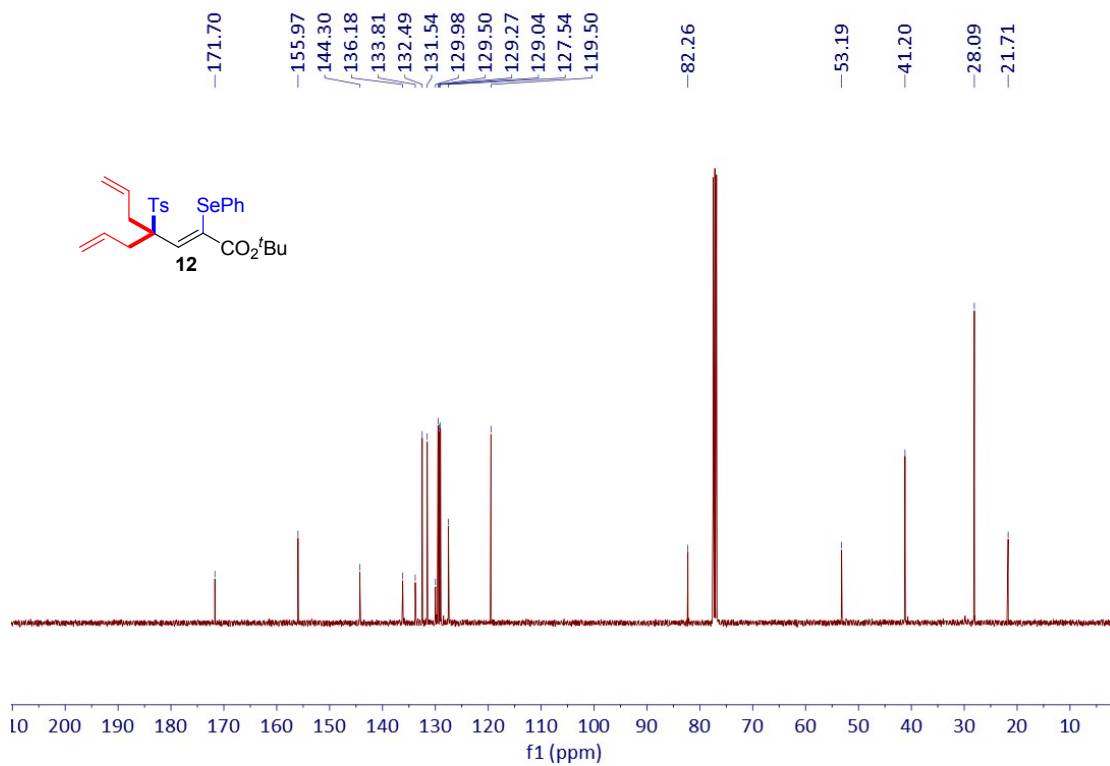
^1H NMR of **11** (400 Hz, CDCl_3)



^{13}C NMR of **11** (100 Hz, CDCl_3)



¹H NMR of **12** (400 Hz, CDCl₃)



¹³C NMR of **12** (100 Hz, CDCl₃)