

## Supporting Information

### Rhodium-catalyzed regioselective addition of thioacids to terminal allenes: Enantioselective access to branched allylic thioesters

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## General remarks

**Chemicals** were purchased from commercial suppliers and used as received.

**Dried solvents** were used for reactions. Solvents employed for work-up and column chromatography were purchased in technical grade quality and distilled before use.

**Column Chromatography** was performed using silica gel 60 (0.04 - 0.063 mm, 230 - 240 mesh ASTM) from Macherey-Nagel GmbH & Co. TLC (Thin Layer Chromatography) was performed on aluminum plates pre-coated with silica gel (MERCK, 60 F254), which were visualized by UV fluorescence ( $\lambda_{\text{max}} = 254 \text{ nm}$ ) and/or by staining with 1% w/v  $\text{KMnO}_4$  in 0.5 M aqueous  $\text{K}_2\text{CO}_3$  solution.

**NMR** spectra were recorded on a Bruker Avance spectrometer (300, 400 or 500 MHz for  $^1\text{H}$  and 75, 100.6 or 126 MHz for  $^{13}\text{C}$  nucleus). All  $^1\text{H}$  NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm. All  $^{13}\text{C}$  NMR spectra were reported in ppm relative to residual  $\text{CHCl}_3$  (77.16 ppm) and were obtained with  $^1\text{H}$ -decoupling.

**HRMS** (High Resolution Mass Spectra) was measured on a THERMO SCIENTIFIC Advantage and a THERMO SCIENTIFIC Exactive instrument equipped with an APCI source in the positive-ion mode.

**Chiral HPLC** was performed on a MERCK HITACHI HPLC apparatus (pump: L-7100, UV detector: D-7400, oven: L-7360; columns: AD-3R, OD-3, OJ-3R and OJ-H).

**Optical Rotation** of chiral compounds was determined on a PERKIN-ELMER PE 241 apparatus and converted to the specific optical rotation with the following formula:

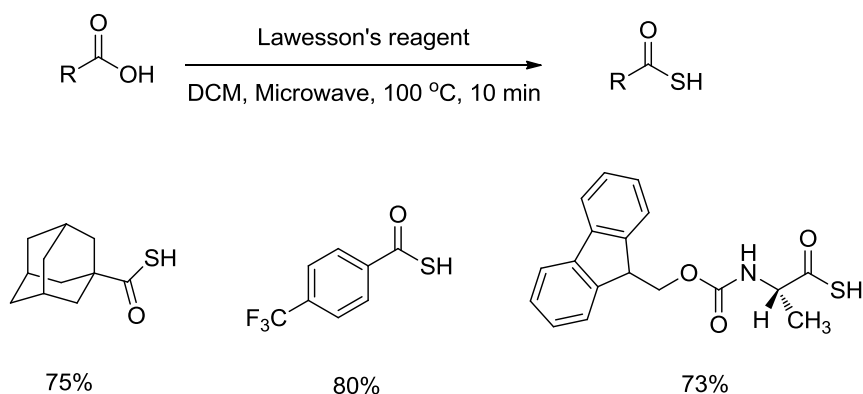
$$[\alpha]_D^T = \frac{\alpha \cdot 100}{c \cdot d}$$

$\alpha$ : measured value; c: concentration in g/100 mL; d: length of the cuvette in dm; T: temperature in  $^{\circ}\text{C}$ .

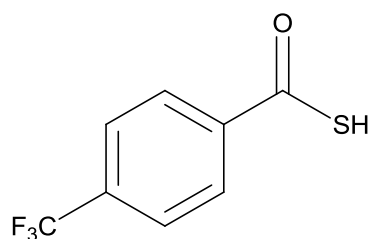
## Synthesis of starting materials

### a) Thioacids

Thiobenzoic acid and thioacetic acid were purchased from Th. Geyer and ABCR chemical companies, respectively and were used as received. Adamantane-1-carbothioic S-acid, 4-(trifluoromethyl)benzothioic S-acid, and (S)-2-(((9H-fluoren-9-yl)methoxy)carbonyl)amino)propanethioic S-acid were prepared according to the procedure reported by Danishefsky *et al.*<sup>1</sup> (General procedure A). Spectroscopic data for known compounds are in agreement with the literature<sup>1</sup>.

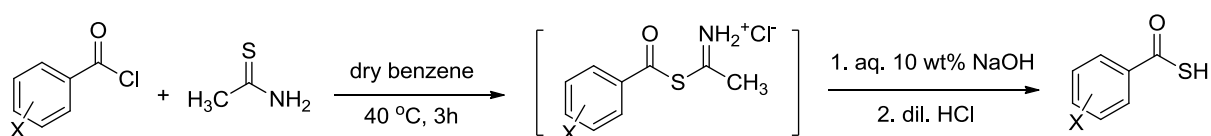


**General procedure A:** Lawson's reagent (2.2 mmol, 0.55 equivalent), carboxylic acid (4 mmol), and  $\text{CH}_2\text{Cl}_2$  (16 mL) were added to a sealed tube (for microwave reaction) and the mixture was irradiated by microwave (100 °C, 10 min). After completion of the reaction, the mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (25 mL) and the organic phase was washed by 1N HCl aqueous solution (2\*20 mL) and brine (20 mL). The organic phase was dried over anhydrous  $\text{MgSO}_4$ , filtered, and evaporated under reduced pressure to give an oily residue. Purification was carried out using flash column chromatography under  $\text{N}_2$  atmosphere ( $\text{SiO}_2$ , degassed EtOAc/*n*-pentane: 1/3).



*4-(trifluoromethyl)benzothioic S-acid:*  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.01 (dt,  $J = 7.9, 0.8$  Hz, 2H), 7.79 – 7.70 (m, 2H), 4.70 (s, 1H) ppm;  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$  189.2, 139.3, 134.9 (q,  $J = 32.7$  Hz), 128.3, 126.0 (q,  $J = 3.7$  Hz), 124.9 (q,  $^1J_{\text{C-F}} = 273$  Hz) ppm;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.24 ppm; HRMS (ESI) calcd for  $\text{C}_8\text{H}_6\text{F}_3\text{OS}$   $[\text{M}+\text{H}]^+$ : 207.0091; found: 217.0087.

**4-Methoxybenzothioic S-acid** and **3-methylbenzothioic S-acid** were prepared according to the reported procedure by Takido *et al.* with a slight modification (General procedure B).<sup>2</sup> Spectroscopic data for known compounds are in agreement with the literature.<sup>2</sup>

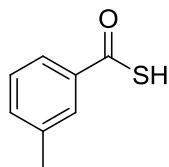


X = 3-Me (69%), 4-MeO (77%)

### General procedure B

A mixture of thioacetamide (2.25 g, 30 mmol) and acyl chloride (30 mmol) in dry benzene (50 mL) was stirred at 40 °C for 3 hours under argon or nitrogen atmosphere. Then, 10% (w/w) sodium hydroxide aqueous solution (50 g) was added to the reaction mixture, and the whole was stirred at room temperature for 30 minutes. The aqueous layer was separated,

washed with benzene (20 mL), and then acidified with 10% aqueous HCl under ice cooling. The acidic aqueous mixture was extracted with benzene / ether = 1 / 1 (100 mL x 2). The combined organic layers were washed with water and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness *in vacuo* to give a residue, which was purified by column chromatography (silica gel, hexanes / ethyl acetate = 4 / 1) to give pure thioacid **4**.

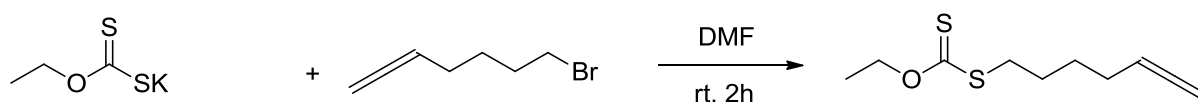


*3-methylbenzothioic S-acid*: <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.60 (m, 2H), 7.46 – 7.31 (m, 2H), 4.48 (brs, 1H), 2.41 (s, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.3, 138.7, 136.7, 134.7, 128.6, 128.3, 125.2, 21.30 ppm; HRMS (ESI) calcd for C<sub>8</sub>H<sub>9</sub>OS [M+H]<sup>+</sup>: 153.0374; found: 153.0373.

## b) Allenes

All known allenes were prepared according to literature procedures.<sup>3-5</sup> New allenes were prepared according to the following procedures:

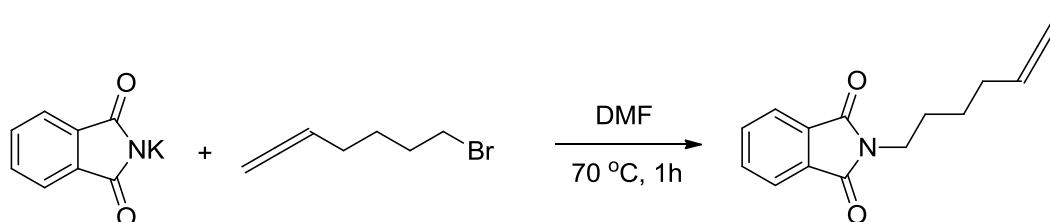
*Synthesis of O-ethyl S-hepta-5,6-dien-1-yl carbonodithioate*:



In a round bottom flask containing a magnet stirrer bar, potassium *O*-ethyl carbonodithioate (7.5 mmol), 7-bromohepta-1,2-diene (5 mmol), and DMF (15 mL) were added and the mixture was stirred at rt for 1h. Then, the solvent was evaporated under reduced pressure and the residue was dissolved in DCM (50 mL). The mixture was filtered through a plug of silica gel (5 cm × 5 cm, aided by house vacuum). Removal of all volatiles by rotary evaporation afforded the pure product in quantitative yield.

*O-ethyl S-hepta-5,6-dien-1-yl carbonodithioate*: Viscous oil; (*R*<sub>f</sub> = 0.26, CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane = 1/4); <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 5.10–5.05 (m, 1H), 4.68–4.62 (m, 4H), 3.12 (t, *J* = 7.3 Hz, 2H), 2.05 – 2.01 (m, 2H), 1.76 – 1.70 (m, 2H), 1.58 – 1.42 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 2H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 215.2, 208.7, 89.5, 75.0, 69.8, 35.7, 28.3, 27.9, 27.7, 13.9 ppm; HRMS (ESI) calcd for C<sub>10</sub>H<sub>16</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 217.0721; found: 217.0715.

*Synthesis of 2-(hepta-5,6-dien-1-yl)isoindoline-1,3-dione*:



In a round bottom flask containing a magnet stirrer bar, potassium phthalimide (7.5 mmol), 7-bromohepta-1,2-diene (5 mmol), and DMF (15 mL) were added and the mixture was stirred at

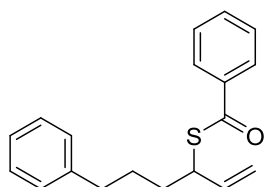
70 °C for 1h. Then, the solvent was evaporated under reduced pressure and the residue was dissolved in DCM (50 mL). The mixture was filtered through a plug of silica gel (5 cm × 5 cm, aided by house vacuum). Removal of all volatiles by rotary evaporation afforded the pure product in quantitative yield.

*2-(hepta-5,6-dien-1-yl)isoindoline-1,3-dione*: Viscous oil; ( $R_f = 0.7$ , EtOAc/*n*-pentane = 1/4);  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.90 – 7.78 (m, 2H), 7.70 (dd,  $J = 5.4, 3.1$  Hz, 2H), 5.10 – 5.07 (m, 1H), 4.66 – 4.62 (m, 2H), 3.69 (t,  $J = 7.2$  Hz, 2H), 2.07 – 2.00 (m, 2H), 1.81 – 1.69 (m, 2H), 1.55 – 1.40 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  208.6, 168.4, 133.9, 132.3, 123.22, 89.51, 74.9, 37.9, 28.1, 27.8, 26.3 ppm; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_2$   $[\text{M}+\text{H}]^+$ : 242.1181; found: 242.1174.

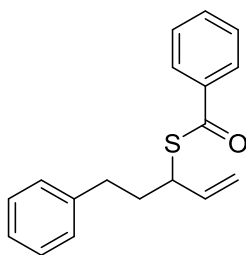
## Synthesis and Characterization of thioesters

### *General Procedure for the Synthesis of Allylic thioesters*

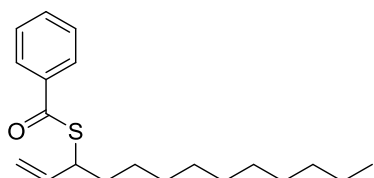
A screw-cap Schlenk tube was flame-dried under vacuum, backfilled with argon, and cooled to r.t. using a standard Schlenk line apparatus. The Schlenk tube was charged with  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (3 mg, 0.006 mmol, 4 mol%) and (+)-DIOP (6 mg, 0.012 mmol, 8 mol %) or (*R*)-Xyl-Binap (for cyclopentyl and cyclohexyl allene, 8.8 mg, 0.012 mmol, 8 mol%). The tube was placed on the Schlenk line to evacuate and backfilled with argon three times. MeCN (1 mL, 0.15 M) was added under a flow of argon, and the mixture was stirred for 15 minutes. Then, TFA (20 mol %), allene (0.225 mmol, 1.5 equiv) and thioacid (0.15 mmol, 1 equiv) were added respectively under a flow of argon. Then the tube was sealed by a screw cap and the resulting mixture was stirred at rt (23 °C) for 16 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel as described for each compound.



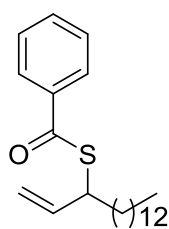
*S*-(6-phenylhex-1-en-3-yl) benzothioate (**3a**): Purification was carried out using column chromatography ( $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2$ /*n*-pentane=1/10;  $R_f = 0.15$ ), colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.06 – 7.84 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.41 (m, 2H), 7.32 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 5.86 (ddd,  $J = 17.0, 10.2, 8.1$  Hz, 1H), 5.33 (dt,  $J = 17.0, 1.2$  Hz, 1H), 5.14 (ddd,  $J = 10.1, 1.4, 0.8$  Hz, 1H), 4.34 (m, 1H), 2.76 – 2.59 (m, 2H), 1.91 – 1.72 (m, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.1, 142.1, 137.8, 137.3, 133.4, 128.6, 128.5, 128.4, 127.3, 125.9, 116.5, 46.5, 35.6, 33.9, 28.9 ppm; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{21}\text{OS}$   $[\text{M}+\text{H}]^+$ : 297.1313; found: 297.1309; HPLC (CHIRALCEL OD-3, *n*-heptane/*i*PrOH = 99.5:0.5, 0.5 mL/min)  $t_R = 11.17$  min (major),  $t_R = 13.44$  min (minor), 87.2% ee;  $[\alpha]_D^{25} = -35.79$  ( $c = 0.38$ ,  $\text{CH}_2\text{Cl}_2$ ).



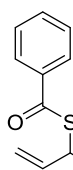
*S*-(5-phenylpent-1-en-3-yl) benzothioate (**3b**): Purification was carried out using column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.15), colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.90 (m, 2H), 7.63 – 7.51 (m, 1H), 7.50 – 7.38 (m, 2H), 7.33 – 7.23 (m, 2H), 7.23 – 7.14 (m, 3H), 5.92 (ddd, *J* = 17.0, 10.2, 8.1 Hz, 1H), 5.36 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.18 (ddd, *J* = 10.2, 1.3, 0.8 Hz, 1H), 4.42 – 4.22 (m, 1H), 2.84 – 2.72 (m, 2H), 2.15 – 2.03 (m, 2H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.9, 141.4, 137.6, 137.3, 133.4, 128.6, 128.5, 128.5, 127.3, 126.1, 116.8, 46.3, 36.0, 33.5 ppm; HRMS (ESI) calcd for C<sub>18</sub>H<sub>22</sub>ONS [M+NH<sub>4</sub>]<sup>+</sup>: 300.1422; found: 300.1415; HPLC (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 20:80, 0.5 mL/min) t<sub>R</sub> = 14.72 min (major), t<sub>R</sub> = 17.65 min (minor), 85.4% ee; [α]<sub>D</sub><sup>25</sup> = -26.99 (c = 0.452, CH<sub>2</sub>Cl<sub>2</sub>).



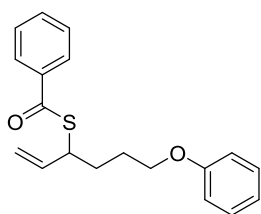
*S*-tridec-1-en-3-yl benzothioate (**3c**): Purification was carried out using column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/15; R<sub>f</sub> = 0.27), colorless viscous oil; <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.60 – 7.46 (m, 1H), 7.48 – 7.36 (m, 2H), 5.85 (ddd, *J* = 17.0, 10.2, 8.2 Hz, 1H), 5.32 (dt, *J* = 17.0, 1.3 Hz, 1H), 5.12 (dt, *J* = 10.1, 1.0 Hz, 1H), 4.33 – 4.11 (m, 1H), 1.79 – 1.72 (m, 2H), 1.47 – 1.38 (m, 2H), 1.36 – 1.22 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 191.2, 138.0, 137.4, 133.3, 128.6, 127.3, 116.3, 46.7, 34.3, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 27.2, 22.7, 14.2 ppm; HRMS (ESI) calcd for C<sub>20</sub>H<sub>31</sub>OS [M+H]<sup>+</sup>: 319.2096; found: 319.2093; HPLC (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 10:90, 0.7 mL/min) t<sub>R</sub> = 21.27 min (major), t<sub>R</sub> = 33.27 min (minor), 86.8% ee; [α]<sub>D</sub><sup>25</sup> = -32.23 (c = 0.512, CH<sub>2</sub>Cl<sub>2</sub>).



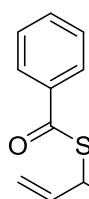
*S*-hexadec-1-en-3-yl benzothioate (**3d**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.23), colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.90 (m, 2H), 7.66 – 7.52 (m, 1H), 7.52 – 7.35 (m, 2H), 5.85 (ddd, *J* = 17.0, 10.2, 8.1 Hz, 1H), 5.32 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.22 – 5.03 (m, 1H), 4.27 – 4.29 (m, 1H), 1.85 – 1.65 (m, 2H), 1.49 – 1.39 (m, 2H), 1.27 – 1.23 (m, 20H), 0.99 – 0.72 (t, *J* = 6.7 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.2, 138.0, 137.4, 133.3, 128.6, 127.3, 116.2, 46.7, 34.3, 32.0, 29.8, 29.74, 29.74, 29.72, 29.66, 29.57, 29.44, 29.40, 27.2, 22.8, 14.2 ppm; HRMS (ESI) calcd for C<sub>23</sub>H<sub>37</sub>OS [M+H]<sup>+</sup>: 361.2565; found: 361.2559; HPLC (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 5:95, 0.7 mL/min) t<sub>R</sub> = 25.95 min (major), t<sub>R</sub> = 47.87 min (minor), 86.3% ee; [α]<sub>D</sub><sup>25</sup> = -28.82 (c = 0.628, CH<sub>2</sub>Cl<sub>2</sub>).



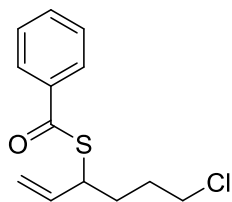
*S*-(6-cyanohept-1-en-3-yl) benzothioate (**3e**): Purification was carried out using column chromatography [SiO<sub>2</sub>; EtOAc/*n*-pentane=1/10; R<sub>f</sub> = 0.20]; colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.89 (m, 2H), 7.67 – 7.55 (m, 1H), 7.53 – 7.43 (m, 2H), 5.87 (ddd, *J* = 17.0, 10.2, 8.1 Hz, 1H), 5.35 (dt, *J* = 17.0, 1.1 Hz, 1H), 5.19 (dt, *J* = 10.2, 1.0 Hz, 1H), 4.42 – 4.19 (m, 1H), 2.41 – 2.43 (m, 2H), 2.03 – 1.90 (m, 2H), 1.90 – 1.78 (m, 2H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.8, 136.9, 136.8, 133.6, 128.7, 127.4, 119.3, 117.3, 45.5, 33.4, 23.2, 16.9 ppm; HRMS (ESI) calcd for C<sub>14</sub>H<sub>16</sub>NOS [M+H]<sup>+</sup>: 246.0953; found: 246.0947; HPLC (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 20:80, 0.5 mL/min) t<sub>R</sub> = 9.13 min (major), t<sub>R</sub> = 10.55 min (minor), 83.2% ee; [α]<sub>D</sub><sup>25</sup> = -37.30 (c = 0.252, CH<sub>2</sub>Cl<sub>2</sub>).



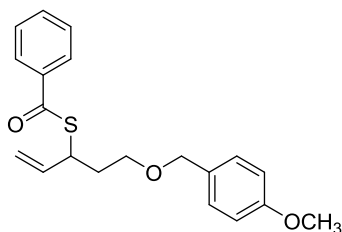
*S*-(6-phenoxyhept-1-en-3-yl) benzothioate (**3f**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=2/8; R<sub>f</sub> = 0.25), colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.91 (m, 2H), 7.66 – 7.54 (m, 1H), 7.52 – 7.42 (m, 2H), 7.30 – 7.26 (m, 2H), 7.02 – 6.78 (m, 3H), 5.90 (ddd, *J* = 17.0, 10.2, 8.1 Hz, 1H), 5.36 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.16 (ddd, *J* = 10.2, 0.9 Hz, 1H), 4.36 – 4.38 (m, 1H), 3.98 – 4.01 (m, 2H), 2.06 – 1.88 (m, 4H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.0, 159.0, 137.6, 137.3, 133.4, 129.5, 128.7, 127.4, 120.7, 116.7, 114.6, 67.4, 46.3, 30.9, 27.1 ppm; HRMS (ESI) calcd for C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>S [M+H]<sup>+</sup>: 313.1262; found: 313.1258; HPLC (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 20:80, 0.5 mL/min) t<sub>R</sub> = 24.66 min (minor), t<sub>R</sub> = 30.90 min (major), 86% ee; [α]<sub>D</sub><sup>25</sup> = -30.00 (c = 0.10, CH<sub>2</sub>Cl<sub>2</sub>).



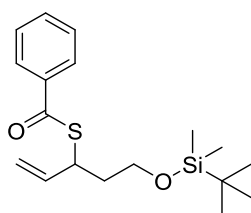
*S*-(7-bromohept-1-en-3-yl) benzothioate (**3g**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.48 (CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane= 3/7)]; colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.83 (m, 2H), 7.62 – 7.50 (m, 1H), 7.50 – 7.33 (m, 2H), 5.86 (ddd, *J* = 17.0, 10.2, 8.2 Hz, 1H), 5.34 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.15 (ddd, *J* = 10.2, 1.3, 0.8 Hz, 1H), 4.30 – 4.27 (m, 1H), 3.41 (t, *J* = 6.8 Hz, 2H), 1.96 – 1.87 (m, 2H), 1.84 – 1.77 (m, 2H), 1.65 – 1.56 (m, 2H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.0, 137.4, 137.2, 133.4, 128.7, 127.3, 116.7, 46.3, 33.5, 33.4, 32.4, 25.8 ppm; HRMS (ESI) calcd for C<sub>14</sub>H<sub>18</sub>BrOS [M+H]<sup>+</sup>: 313.0262; found: 313.0258; HPLC (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 20:80, 0.5 mL/min) t<sub>R</sub> = 18.95 min (major), t<sub>R</sub> = 23.19 min (minor), 87.6% ee; [α]<sub>D</sub><sup>25</sup> = -30.08 (c = 0.266, CH<sub>2</sub>Cl<sub>2</sub>).



*S*-(6-chlorohex-1-en-3-yl) benzothioate (**3h**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.57 (CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane= 2/8)]; colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.87 (m, 2H), 7.64 – 7.53 (m, 1H), 7.53 – 7.40 (m, 2H), 5.87 (ddd, *J* = 17.0, 10.2, 8.0 Hz, 1H), 5.35 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.17 (dt, *J* = 10.2, 1.0 Hz, 1H), 4.30 (m, 1H), 3.69 – 3.49 (m, 2H), 2.03 – 1.88 (m, 4H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.9, 137.3, 137.2, 133.5, 128.7, 127.4, 116.9, 45.8, 44.6, 31.7, 30.2 ppm; HRMS (ESI) calcd for C<sub>13</sub>H<sub>16</sub>ClOS [M+H]<sup>+</sup>: 255.0610; found: 255.0609; **HPLC** (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 20:80, 0.5 mL/min) t<sub>R</sub> = 11.95 min (major), t<sub>R</sub> = 14.05 min (minor), 80.8% ee; [α]<sub>D</sub><sup>25</sup> = -16.07 (c = 0.112, CH<sub>2</sub>Cl<sub>2</sub>).

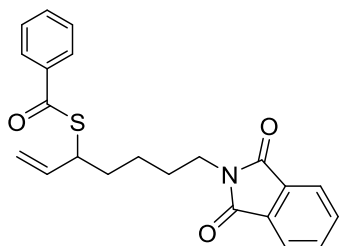


*S*-(5-((4-methoxybenzyl)oxy)pent-1-en-3-yl) benzothioate (**3i**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=7/3; R<sub>f</sub> = 0.33), colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.80 (m, 2H), 7.63 – 7.51 (m, 1H), 7.51 – 7.38 (m, 2H), 7.34 – 7.22 (m, 2H), 6.95 – 6.80 (m, 2H), 5.89 (ddd, *J* = 17.0, 10.2, 8.1 Hz, 1H), 5.33 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.12 (ddd, *J* = 10.2, 1.3, 0.9 Hz, 1H), 4.56 – 4.33 (m, 3H), 3.78 (s, 3H), 3.64 – 3.52 (m, 2H), 2.16 – 2.04 (m, 2H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.8, 159.3, 137.6, 137.3, 133.3, 130.5, 129.4, 128.6, 127.3, 116.5, 113.9, 72.7, 67.2, 55.3, 43.6, 34.1 ppm; HRMS (ESI) calcd for C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>NaS [M+Na]<sup>+</sup>: 365.1187; found: 365.1181; **HPLC** (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 20:80, 0.5 mL/min) t<sub>R</sub> = 17.65 min (major), t<sub>R</sub> = 21.31 min (minor), 88.6% ee; [α]<sub>D</sub><sup>25</sup> = -44.62 (c = 0.39, CH<sub>2</sub>Cl<sub>2</sub>).



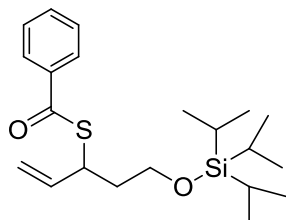
*S*-(5-((tert-butyl dimethylsilyl)oxy)pent-1-en-3-yl) benzothioate (**3j**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=2/8; R<sub>f</sub> = 0.45 (CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane= 3/7)], colorless viscous oil; <sup>1</sup>H NMR (300 MHz, Chloroform-*d*) δ 7.97 – 7.76 (m, 2H), 7.63 – 7.46 (m, 1H), 7.46 – 7.31 (m, 2H), 5.84 (ddd, *J* = 17.0, 10.1, 8.1 Hz, 1H), 5.29 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.07 (ddd, *J* = 10.1, 1.3, 0.8 Hz, 1H), 4.45 – 4.23 (m, 1H), 3.68 (td, *J* = 6.4, 1.9 Hz, 2H), 2.00 – 1.88 (m, 2H), 0.85 (s, 9H), 0.00 (s, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 190.8, 137.8, 137.4, 133.3, 128.6, 127.3, 116.3, 60.5, 43.3, 36.8, 26.0, 18.3, -5.25 ppm; HRMS (ESI) calcd for C<sub>18</sub>H<sub>29</sub>O<sub>2</sub>SSi [M+H]<sup>+</sup>: 337.1658; found: 337.1654; **HPLC** (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 10:90, 0.7 mL/min) t<sub>R</sub> = 8.48 min (major), t<sub>R</sub> = 13.83 min (minor), 89.8% ee; [α]<sub>D</sub><sup>25</sup> = -43.00 (c = 0.40, CH<sub>2</sub>Cl<sub>2</sub>).





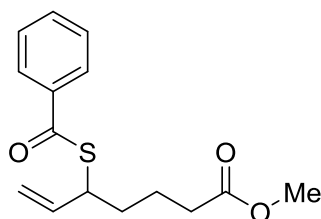
*S*-(7-(1,3-dioxisoindolin-2-yl)hept-1-en-3-yl) benzothioate

**(3k)**: Purification was carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=2/8 to 8/2;  $R_f = 0.56$  ( $\text{CH}_2\text{Cl}_2$ )]; colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.96 – 7.88 (m, 2H), 7.87 – 7.79 (m, 2H), 7.75 – 7.68 (m, 2H), 7.60 – 7.52 (m, 1H), 7.48 – 7.39 (m, 2H), 5.84 (ddd,  $J = 17.0, 10.2, 8.2$  Hz, 1H), 5.31 (dt,  $J = 17.0, 1.2$  Hz, 1H), 5.11 (ddd,  $J = 10.2, 1.3, 0.8$  Hz, 1H), 4.26 (m, 1H), 3.72 – 3.66 (m, 2H), 1.88 – 1.78 (m, 2H), 1.78 – 1.71 (m, 2H), 1.57 – 1.46 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.9, 168.4, 137.6, 137.3, 133.9, 133.3, 132.3, 128.6, 127.3, 123.2, 116.6, 46.3, 37.8, 33.8, 28.3, 24.4 ppm; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{21}\text{O}_3\text{NNaS}$  [ $\text{M}+\text{Na}$ ] $^+$ : 402.1140; found: 402.1137; **HPLC** (ChiralPAK OJ-3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 35:65$ , 1.0 mL/min)  $t_R = 8.53$  min (major),  $t_R = 10.06$  min (minor), 85.6% ee;  $[\alpha]_D^{25} = -23.04$  ( $c = 0.382$ ,  $\text{CH}_2\text{Cl}_2$ ).



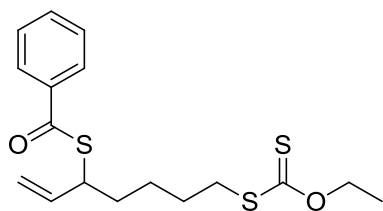
*S*-(5-((triisopropylsilyl)oxy)pent-1-en-3-yl) benzothioate (**3l**):

Purification was carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=1/10;  $R_f = 0.28$  ( $\text{CH}_2\text{Cl}_2/n$ -pentane= 1/4)]; colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.01 – 7.90 (m, 2H), 7.61 – 7.52 (m, 1H), 7.50 – 7.40 (m, 2H), 5.91 (ddd,  $J = 17.0, 10.2, 8.1$  Hz, 1H), 5.35 (dt,  $J = 17.0, 1.2$  Hz, 1H), 5.13 (ddd,  $J = 10.2, 1.4, 0.8$  Hz, 1H), 4.46 (m, 1H), 3.82 (td,  $J = 6.5, 3.1$  Hz, 2H), 2.03 (dt,  $J = 7.4, 6.5$  Hz, 2H), 1.11 – 1.03 (m, 21H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8, 137.8, 137.4, 133.3, 128.6, 127.3, 116.3, 60.8, 43.4, 37.1, 18.1, 12.1 ppm; HRMS (ESI) calcd for  $\text{C}_{21}\text{H}_{35}\text{O}_2\text{SSi}$  [ $\text{M}+\text{H}$ ] $^+$ : 379.2127; found: 379.2119;  $[\alpha]_D^{25} = -34.73$  ( $c = 0.55$ ,  $\text{CH}_2\text{Cl}_2$ ).



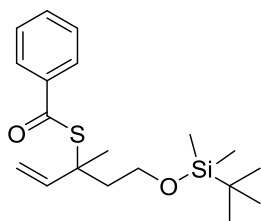
*Methyl 5-(benzoylthio)hept-6-enoate* (**3m**): Purification was

carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=1/1;  $R_f = 0.25$ ], colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.04 – 7.85 (m, 2H), 7.64 – 7.51 (m, 1H), 7.51 – 7.37 (m, 2H), 5.85 (ddd,  $J = 17.0, 10.2, 8.1$  Hz, 1H), 5.34 (dt,  $J = 17.0, 1.2$  Hz, 1H), 5.15 (ddd,  $J = 10.2, 1.2, 0.8$  Hz, 1H), 4.27 – 4.29 (m, 1H), 3.67 (s, 3H), 2.43 – 2.34 (m, 2H), 1.88 – 1.74 (m, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.9, 173.7, 137.4, 137.2, 133.4, 128.6, 127.3, 116.8, 51.6, 46.2, 33.7, 33.7, 22.6 ppm; HRMS (ESI) calcd for  $\text{C}_{15}\text{H}_{19}\text{O}_3\text{S}$  [ $\text{M}+\text{H}$ ] $^+$ : 279.1055; found: 279.1051; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 20:80$ , 0.5 mL/min)  $t_R = 10.39$  min (major),  $t_R = 12.43$  min (minor), 87% ee;  $[\alpha]_D^{25} = -32.80$  ( $c = 0.25$ ,  $\text{CH}_2\text{Cl}_2$ ).



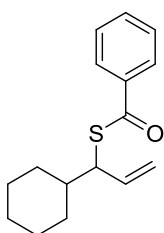
*S*-(7-((ethoxycarbonothioyl)thio)hept-1-en-3-yl)

**benzothioate (3n):** Purification was carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=1/8 to 1/1;  $R_f = 0.26$  ( $\text{CH}_2\text{Cl}_2/n$ -pentane= 2/8)]; colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.98 – 7.92 (m, 2H), 7.65 – 7.53 (m, 1H), 7.50 – 7.38 (m, 2H), 5.85 (ddd,  $J = 17.0, 10.2, 8.2$  Hz, 1H), 5.33 (dt,  $J = 17.0, 1.2$  Hz, 1H), 5.14 (ddd,  $J = 10.2, 1.3, 0.8$  Hz, 1H), 4.65 (q,  $J = 7.1$  Hz, 2H), 4.28 (m, 1H), 3.22 – 3.07 (m, 2H), 1.86 – 1.70 (m, 4H), 1.62 – 1.51 (m, 2H), 1.41 (t,  $J = 7.1$  Hz, 3H) ppm; HRMS (ESI) calcd for  $\text{C}_{17}\text{H}_{23}\text{O}_2\text{S}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 355.0860; found: 355.0852; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 20:80$ , 0.5 mL/min)  $t_R = 24.13$  min (major),  $t_R = 29.51$  min (minor), 87.2% ee;  $[\alpha]_D^{25} = -23.08$  ( $c = 0.208$ ,  $\text{CH}_2\text{Cl}_2$ ).

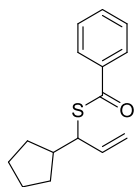


*S*-(5-((tert-butyldimethylsilyl)oxy)-3-methylpent-1-en-3-yl) benzothioate

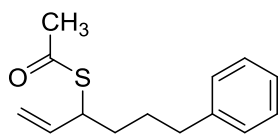
**(3o):** Purification was carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=2/8;  $R_f = 0.46$  ( $\text{CH}_2\text{Cl}_2/n$ -pentane=3/7)]; colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.99 – 7.85 (m, 2H), 7.61 – 7.49 (m, 1H), 7.49 – 7.37 (m, 2H), 6.20 (dd,  $J = 17.4, 10.7$  Hz, 1H), 5.26 (dd,  $J = 17.3, 0.8$  Hz, 1H), 5.16 (dd,  $J = 10.6, 0.7$  Hz, 1H), 3.76 (dd,  $J = 7.3, 6.7$  Hz, 2H), 2.44 – 2.10 (m, 2H), 1.69 (s, 3H), 0.89 (s, 9H), 0.05 (s, 6H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.6, 142.1, 138.1, 133.1, 128.5, 127.1, 113.8, 59.9, 53.9, 42.3, 26.0, 24.3, 18.3, -5.22 ppm; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{31}\text{O}_2\text{SSi}$  [ $\text{M}+\text{H}$ ] $^+$ : 351.1814; found: 351.1809; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 20:80$ , 0.7 mL/min)  $t_R = 9.21$  min (major),  $t_R = 11.27$  min (minor), 9.4% ee.



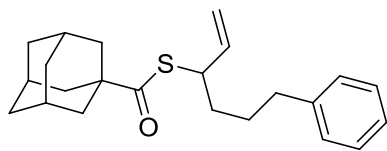
***S*-(1-cyclohexylallyl) benzothioate (3p):** Purification was carried out using column chromatography ( $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=1/10;  $R_f = 0.18$ ), colorless viscous oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.88 (m, 2H), 7.50-7.45 (m, 1H), 7.39-7.33 (m, 2H), 5.78 (ddd, 1H,  $J = 16.9, 10.1, 8.9$  Hz), 5.26 (ddd,  $J = 16.9, 1.6, 0.87$  Hz, 1H), 5.03 (ddd,  $J = 10.1, 1.5, 0.7$  Hz), 4.15 (dd,  $J = 9.0, 6.2$  Hz), 1.85-1.54 (m, 6H), 1.24-0.99 (m, 5H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.0, 137.6, 136.6, 133.2, 128.6, 127.4, 116.9, 53.0, 41.9, 30.7, 30.6, 26.4, 26.3 ppm; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{21}\text{OS}$  [ $\text{M}+\text{H}$ ] $^+$ : 261.1313; found: 261.1313; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 20:80$ , 0.5 mL/min)  $t_R = 34.58$  min (major),  $t_R = 40.32$  min (minor), 88.6% ee;  $[\alpha]_D^{25} = 21.43$  ( $c = 0.126$ ,  $\text{CH}_2\text{Cl}_2$ ).



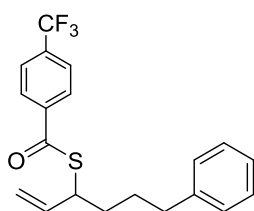
*S*-(1-cyclopentylallyl) benzothioate (**3q**): Purification was carried out using column chromatography (SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.2), colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.58 – 7.52 (m, 1H), 7.47 – 7.40 (m, 2H), 5.86 (ddd, *J* = 16.9, 10.1, 8.7 Hz, 1H), 5.33 (ddd, *J* = 16.9, 1.5, 0.9 Hz, 1H), 5.09 (ddd, *J* = 10.1, 1.5, 0.7 Hz, 1H), 4.37 – 4.12 (m, 1H), 2.28 – 2.17 (m, 1H), 1.89 – 1.75 (m, 2H), 1.69 – 1.54 (m, 4H), 1.43 – 1.32 (m, 2H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.1, 137.6, 137.5, 133.2, 128.6, 127.3, 116.4, 52.0, 43.4, 30.8, 30.8, 25.7, 25.5 ppm; HRMS (ESI) calcd for C<sub>15</sub>H<sub>19</sub>OS [M+H]<sup>+</sup>: 247.1157; found: 247.1152; HPLC (ChiralPAK AD3R, H<sub>2</sub>O/CH<sub>3</sub>CN = 20:80, 0.5 mL/min) t<sub>R</sub> = 24.08 min (major), t<sub>R</sub> = 28.08 min (minor), 83.3% ee; [α]<sub>D</sub><sup>25</sup> = 44.44 (c = 0.234, CH<sub>2</sub>Cl<sub>2</sub>).



*S*-(6-phenylhex-1-en-3-yl) ethanethioate (**4a**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.5 (CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane= 3/7)]; colorless oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.24 (m, 2H), 7.24 – 7.09 (m, 3H), 5.75 (ddd, *J* = 17.0, 10.2, 8.2 Hz, 1H), 5.22 (dt, *J* = 17.0, 1.2 Hz, 1H), 5.07 (ddd, *J* = 10.2, 1.3, 0.8 Hz, 1H), 4.09 (m, 1H), 2.72 – 2.53 (m, 2H), 2.31 (s, 3H), 1.72 – 1.68 (m, 4H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 194.8, 142.1, 137.7, 128.5, 128.4, 125.9, 116.2, 46.5, 35.5, 33.7, 30.8, 28.9 ppm; HRMS (ESI) calcd for C<sub>14</sub>H<sub>22</sub>ONS [M+NH<sub>4</sub>]<sup>+</sup>: 252.1422; found: 252.1417; [α]<sub>D</sub><sup>25</sup> = -28.45 (c = 0.232, CH<sub>2</sub>Cl<sub>2</sub>).

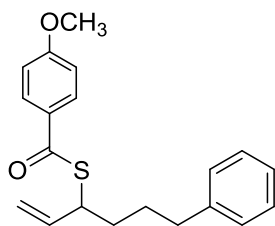


(3*r*,5*r*,7*r*)-*S*-(6-phenylhex-1-en-3-yl) adamantane-1-carbothioate (**4b**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.33 (CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane= 2/8)]; colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.24 (m, 2H), 7.23 – 7.11 (m, 3H), 5.74 (ddd, *J* = 17.0, 10.1, 8.1 Hz, 1H), 5.20 (dt, *J* = 17.0, 1.3 Hz, 1H), 5.05 (ddd, *J* = 10.2, 1.4, 0.8 Hz, 1H), 4.17 – 3.82 (m, 1H), 2.65 – 2.57 (m, 2H), 2.08 – 2.02 (m, 4H), 1.92 – 1.89 (m, 6H), 1.74 – 1.67 (m, 9H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 205.5, 142.2, 138.1, 128.5, 128.4, 125.8, 115.9, 48.7, 45.2, 39.4, 36.6, 35.6, 33.9, 28.9, 28.3 ppm; HRMS (ESI) calcd for C<sub>23</sub>H<sub>31</sub>OS [M+H]<sup>+</sup>: 355.2096; found: 355.2092; HPLC (ChiralPAK OJ-H, heptane/EtOH = 99:1, 0.5 mL/min) t<sub>R</sub> = 11.64 min (major), t<sub>R</sub> = 13.96 min (minor), 92% ee; [α]<sub>D</sub><sup>25</sup> = -21.64 (c = 0.268, CH<sub>2</sub>Cl<sub>2</sub>).

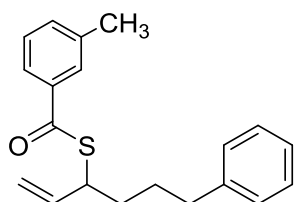


*S*-(6-phenylhex-1-en-3-yl) 4-(trifluoromethyl)benzothioate (**4c**): Purification was carried out using column chromatography [SiO<sub>2</sub>; CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane=1/10; R<sub>f</sub> = 0.55 (CH<sub>2</sub>Cl<sub>2</sub>/*n*-pentane= 2/8)]; colorless viscous oil; <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ

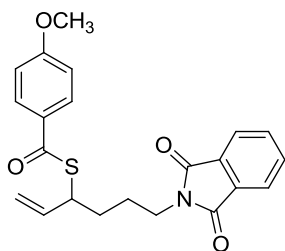
8.16 – 7.98 (m, 2H), 7.79 – 7.63 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.12 (m, 3H), 5.84 (ddd,  $J = 17.0, 10.2, 8.2$  Hz, 1H), 5.33 (dt,  $J = 16.9, 1.1$  Hz, 1H), 5.15 (ddd,  $J = 10.1, 1.3, 0.8$  Hz, 1H), 4.34 (m, 1H), 2.75 – 2.63 (m, 2H), 1.88 – 1.71 (m, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  190.1, 141.9, 140.1 (d,  $J = 1.2$  Hz), 137.3, 134.8 (q,  $J = 32.7$  Hz), 128.5, 128.4, 127.7, 125.9, 125.8 (q,  $J = 3.7$  Hz), 124.9 (q,  $^1J_{\text{C-F}} = 273$  Hz), 116.9, 46.9, 35.6, 33.8, 28.9 ppm;  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.12 ppm; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{20}\text{F}_3\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 365.1187; found: 365.1179; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 10:90$ , 0.7 mL/min)  $t_R = 9.73$  min (major),  $t_R = 14.90$  min (minor), 84.6% ee;  $[\alpha]_{\text{D}}^{25} = -23.08$  ( $c = 0.364$ ,  $\text{CH}_2\text{Cl}_2$ ).



*S*-(6-phenylhex-1-en-3-yl) 4-methoxybenzothioate (**4d**): Purification was carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=1/10;  $R_f = 0.36$  ( $\text{CH}_2\text{Cl}_2/n$ -pentane= 3/7)]; colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J = 9.0$  Hz, 2H), 7.34 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 6.96 – 6.90 (m, 2H), 5.84 (ddd,  $J = 17.0, 10.1, 8.1$  Hz, 1H), 5.29 (dt,  $J = 17.0, 1.2$  Hz, 1H), 5.11 (ddd,  $J = 10.2, 1.3, 0.8$  Hz, 1H), 4.40 – 4.22 (m, 1H), 3.86 (s, 3H), 2.68 – 2.64 (m, 2H), 1.85 – 1.73 (m, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  189.6, 163.8, 142.2, 138.0, 130.2, 129.5, 128.5, 128.4, 125.8, 116.3, 113.8, 55.6, 46.3, 35.6, 33.9, 28.9 ppm; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{23}\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 327.1419; found: 327.1418; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 10:90$ , 0.7 mL/min)  $t_R = 11.81$  min (major),  $t_R = 16.33$  min (minor), 79.8% ee;  $[\alpha]_{\text{D}}^{25} = -20.13$  ( $c = 0.154$ ,  $\text{CH}_2\text{Cl}_2$ ).

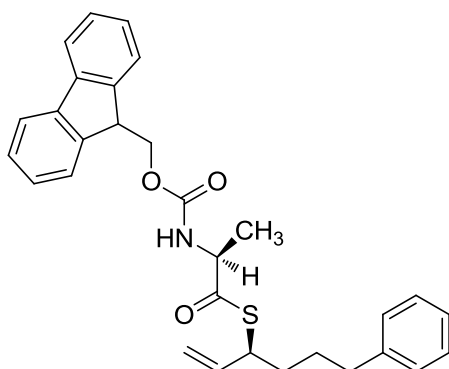


*S*-(6-phenylhex-1-en-3-yl) 3-methylbenzothioate (**4e**): Purification was carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -pentane=1/10;  $R_f = 0.46$  ( $\text{CH}_2\text{Cl}_2/n$ -pentane= 2/8)]; colorless viscous oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.75 (dd,  $J = 6.6, 1.6$  Hz, 2H), 7.43 – 7.23 (m, 5H), 7.18 (dt,  $J = 6.4, 1.4$  Hz, 3H), 5.84 (ddd,  $J = 17.0, 10.2, 8.1$  Hz, 1H), 5.31 (dt,  $J = 17.1, 1.3$  Hz, 1H), 5.12 (dt,  $J = 10.3, 1.1$  Hz, 1H), 4.31 (m, 1H), 2.66 (t,  $J = 7.3$  Hz, 2H), 2.40 (s, 3H), 1.86 – 1.72 (m, 4H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.2, 142.1, 138.5, 137.8, 137.3, 134.1, 128.5, 128.5, 128.4, 127.8, 125.9, 124.5, 116.4, 46.4, 35.6, 33.9, 28.9, 21.4 ppm; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{23}\text{OS}$   $[\text{M}+\text{H}]^+$ : 311.1470; found: 311.1467; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 20:80$ , 0.5 mL/min)  $t_R = 18.45$  min (major),  $t_R = 26.28$  min (minor), 85.2% ee;  $[\alpha]_{\text{D}}^{25} = -27.00$  ( $c = 0.2$ ,  $\text{CH}_2\text{Cl}_2$ ).



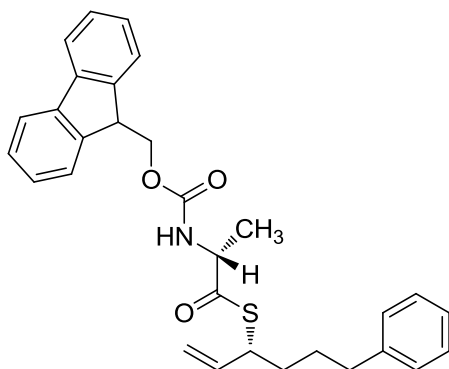
*S*-(6-(1,3-dioxisoindolin-2-yl)hex-1-en-3-yl) 4-methoxybenzothioate (**4f**): Purification was carried out using column chromatography [ $\text{SiO}_2$ ;  $\text{CH}_2\text{Cl}_2/n$ -

pentane=4/6;  $R_f = 0.21$  ( $\text{CH}_2\text{Cl}_2/n\text{-pentane} = 4/6$ ); white gummy solid;  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.92 – 7.87 (m, 2H), 7.83 (dd,  $J = 5.4, 3.1$  Hz, 2H), 7.70 (dd,  $J = 5.5, 3.0$  Hz, 2H), 6.90 (d,  $J = 9.1$  Hz, 2H), 5.83 (ddd,  $J = 17.0, 10.2, 8.2$  Hz, 1H), 5.31 (dt,  $J = 17.0, 1.1$  Hz, 1H), 5.12 (dt,  $J = 10.2, 1.0$  Hz, 1H), 4.38 – 4.19 (m, 1H), 3.85 (s, 3H), 3.77 – 3.69 (m, 2H), 1.85 – 1.81 (m, 4H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  189.3, 168.4, 163.3, 137.5, 133.9, 132.2, 130.0, 129.5, 123.3, 116.6, 113.8, 55.5, 45.9, 37.7, 31.7, 26.4 ppm; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{21}\text{NO}_4\text{S}$   $[\text{M}+\text{Na}]^+$ : 418.1089; found: 418.1084; **HPLC** (ChiralPAK AD3R,  $\text{H}_2\text{O}/\text{CH}_3\text{CN} = 25:75$ , 0.5 mL/min)  $t_R = 18.04$  min (major),  $t_R = 22.03$  min (minor), 90.3% ee;  $[\alpha]_D^{25} = 15.5$  ( $c = 0.375$ ,  $\text{CH}_2\text{Cl}_2$ ).

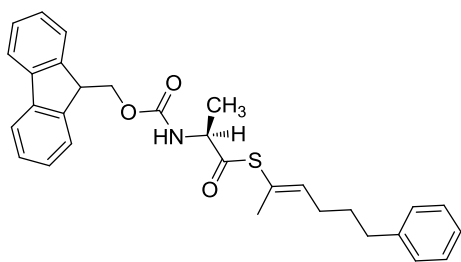


(*S*)-*S*-((*S*)-6-phenylhex-1-en-3-yl) 2-(((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)propanethioate (**6a**):

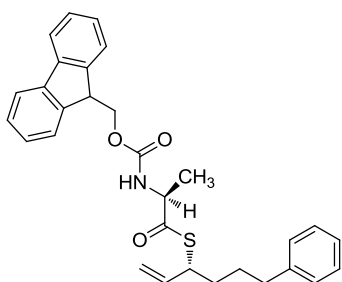
Purification was carried out using plate chromatography ( $\text{SiO}_2$ ;  $\text{EtOAc}/n\text{-pentane} = 1/5$ ;  $R_f = 0.45$ ); White solid; m.p. 100-103 °C;  $^1\text{H NMR}$  (500 MHz, Chloroform-*d*)  $\delta$  7.80 – 7.75 (m, 2H), 7.61 (t,  $J = 7.5$  Hz, 2H), 7.42 – 7.38 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 5.72 (ddd,  $J = 16.9, 10.2, 8.3$  Hz, 1H), 5.31 – 5.17 (m, 2H), 5.08 (d,  $J = 10.2$  Hz, 1H), 4.53 – 4.34 (m, 3H), 4.24 (t,  $J = 6.7$  Hz, 1H), 4.07 (d,  $J = 7.6$  Hz, 1H), 2.63 – 2.60 (m, 2H), 1.73 – 1.69 (m, 4H), 1.42 (d,  $J = 7.4$  Hz, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  200.1, 155.5, 143.9, 141.9, 141.4, 137.3, 128.4, 128.4, 127.8, 127.2, 125.9, 125.1, 120.1, 116.7, 67.2, 56.8, 47.3, 46.5, 35.5, 33.6, 28.9, 19.2 ppm; HRMS (ESI) calcd for  $\text{C}_{30}\text{H}_{32}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 486.2103; found: 486.2103;  $[\alpha]_D^{25} = -28.2$  ( $c = 0.425$ ,  $\text{CH}_2\text{Cl}_2$ ).



The opposite enantiomer of **6a** was synthesized according to the general procedure by using Fmoc-D-alanine thioacid and (-)-DIOP. (*R*)-*S*-((*R*)-6-phenylhex-1-en-3-yl) 2-(((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)propanethioate: Purification was carried out using plate chromatography ( $\text{SiO}_2$ ;  $\text{EtOAc}/n\text{-pentane} = 1/5$ ;  $R_f = 0.45$ ); White solid; m.p. 98-101 °C;  $[\alpha]_D^{25} = +27.8$  ( $c = 0.60$ ,  $\text{CH}_2\text{Cl}_2$ ).

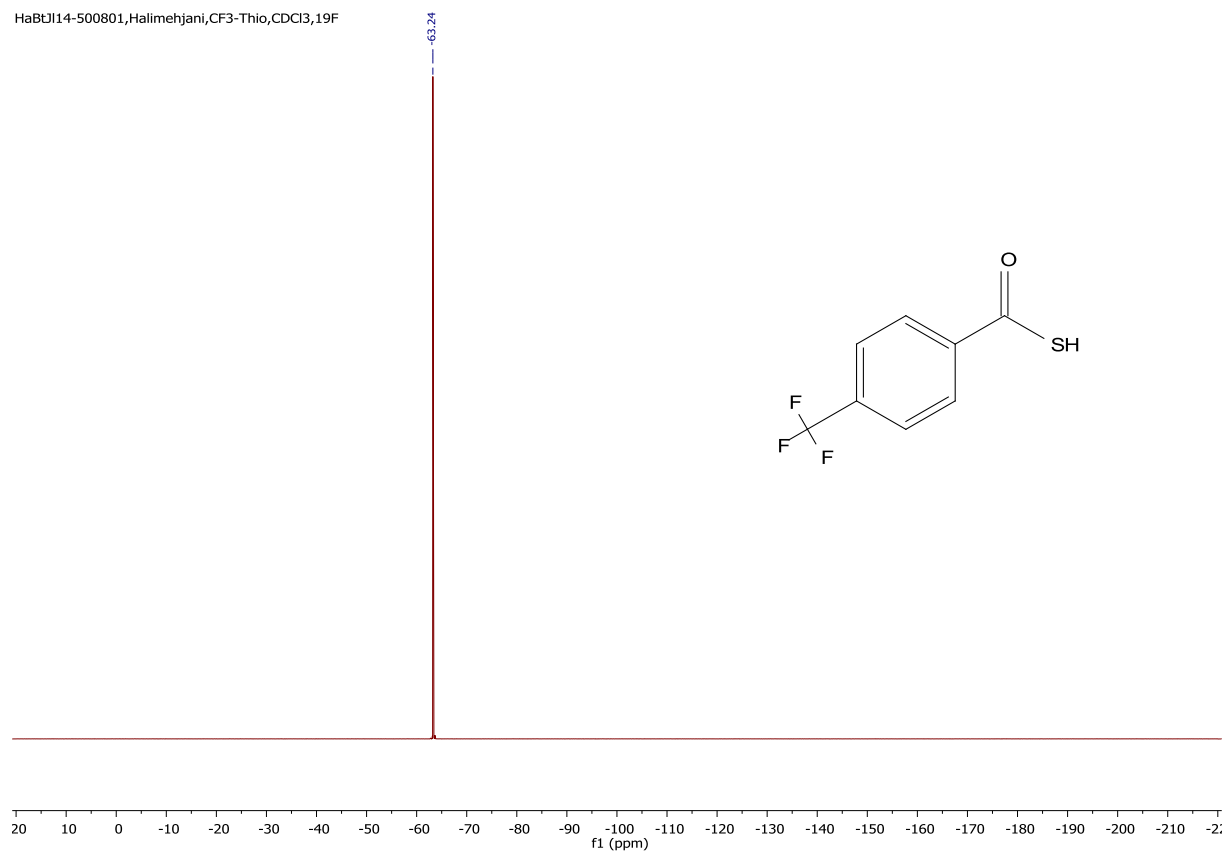


(*S,E*)-*S*-(6-phenylhex-2-en-2-yl) 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)propanethioate (Markovnikov product): Purification was carried out using column chromatography (SiO<sub>2</sub>; EtOAc/*n*-pentane=1/5; R<sub>f</sub> = 0.50); colorless viscous oil; <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.77 (dt, *J* = 7.5, 0.9 Hz, 2H), 7.63 (t, *J* = 8.0 Hz, 2H), 7.42 – 7.38 (m, 2H), 7.34 – 7.26 (m, 4H), 7.22 – 7.17 (m, 3H), 5.67 (d, *J* = 8.6 Hz, 1H), 5.17 (t, *J* = 8.0 Hz, 1H), 4.64 (m, 1H), 4.47 – 4.42 (m, 1H), 4.35 (dd, *J* = 10.6, 7.4 Hz, 1H), 4.25 (t, *J* = 7.2 Hz, 1H), 2.70 – 2.65 (m, 2H), 2.13 – 2.07 (m, 2H), 1.87 (s, 3H), 1.75 – 1.70 (m, 2H), 1.50 (d, *J* = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 221.5, 155.4, 149.3, 144.0, 143.9, 142.1, 141.3, 128.5, 127.8, 127.1, 125.2, 125.2, 120.0, 118.7, 67.1, 57.4, 47.3, 35.1, 30.9, 25.9, 21.1, 14.4 ppm; HRMS (ESI) calcd for C<sub>30</sub>H<sub>32</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 486.2103; found: 486.2103.



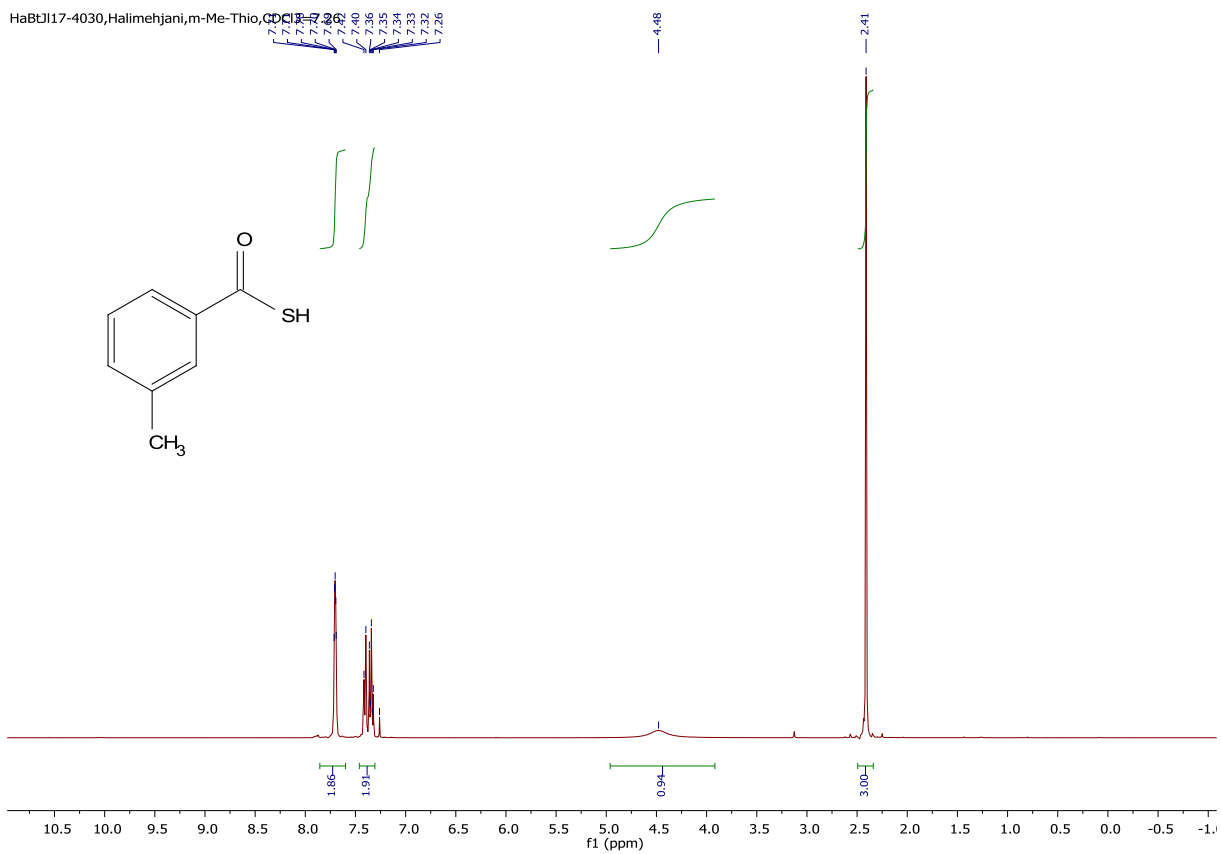
(*S*)-*S*-((*R*)-6-phenylhex-1-en-3-yl) 2-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)propanethioate (**6b**): Purification was carried out using plate chromatography (SiO<sub>2</sub>; EtOAc/*n*-pentane=1/5; R<sub>f</sub> = 0.43); gummy solid; <sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 7.70 – 7.67 (m, 2H), 7.53 (t, *J* = 6.2 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.09 – 7.06 (m, 3H), 5.65 (ddd, *J* = 16.9, 10.2, 8.3 Hz, 1H), 5.18 – 5.11 (m, 2H), 4.99 (d, *J* = 11.2 Hz, 1H), 4.43 – 4.24 (m, 3H), 4.15 (t, *J* = 7.1 Hz, 1H), 4.01-3.98 (m, 1H), 2.46 – 2.53 (m, 2H), 1.61 – 1.63 (m, 4H), 1.32 (d, *J* = 7.3 Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 200.2, 155.5, 143.7, 142.0, 141.3, 137.2, 128.4, 128.3, 127.8, 127.1, 125.8, 125.1, 120.0, 116.7, 67.2, 56.8, 47.2, 46.3, 35.5, 33.7, 28.8, 19.1 ppm; HRMS (ESI) calcd for C<sub>30</sub>H<sub>32</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 486.2103; found: 486.2103; [α]<sub>D</sub><sup>25</sup> = -5.8 (c = 0.59, CH<sub>2</sub>Cl<sub>2</sub>).



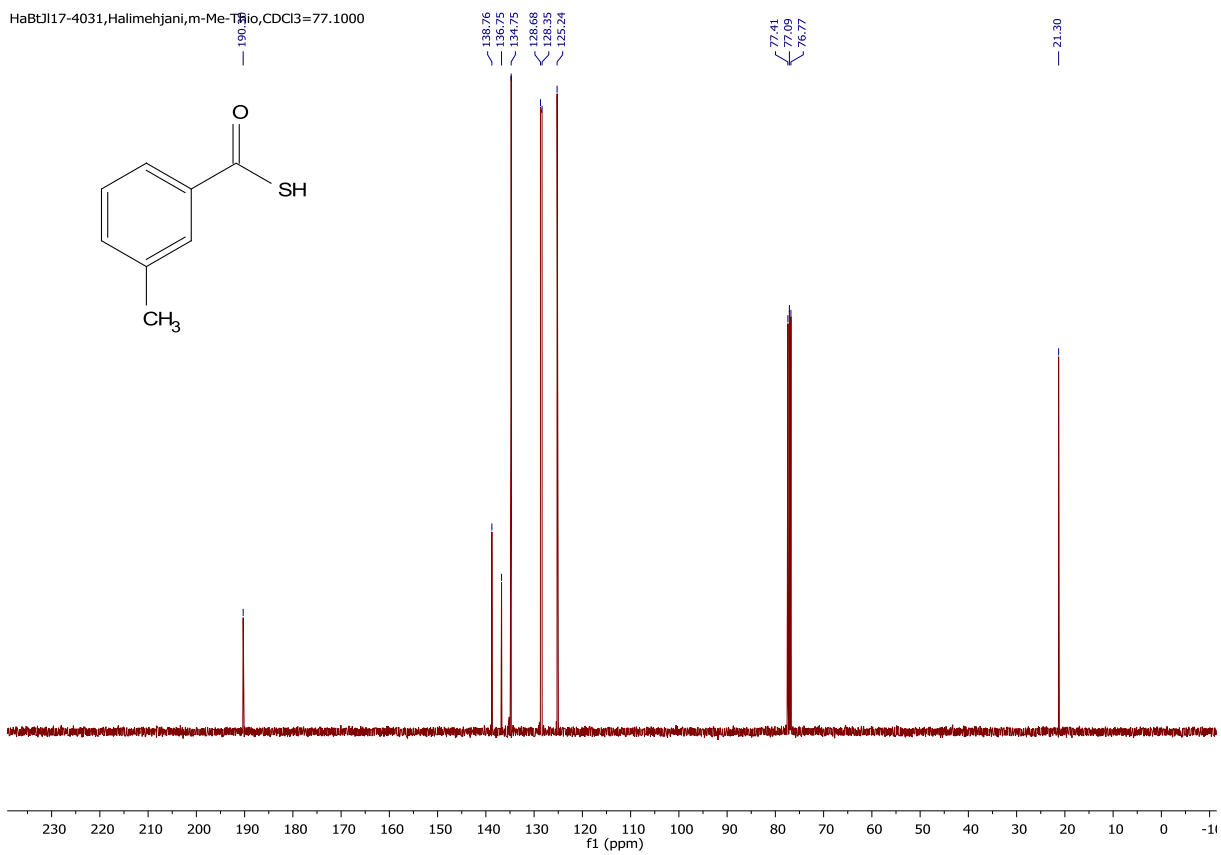




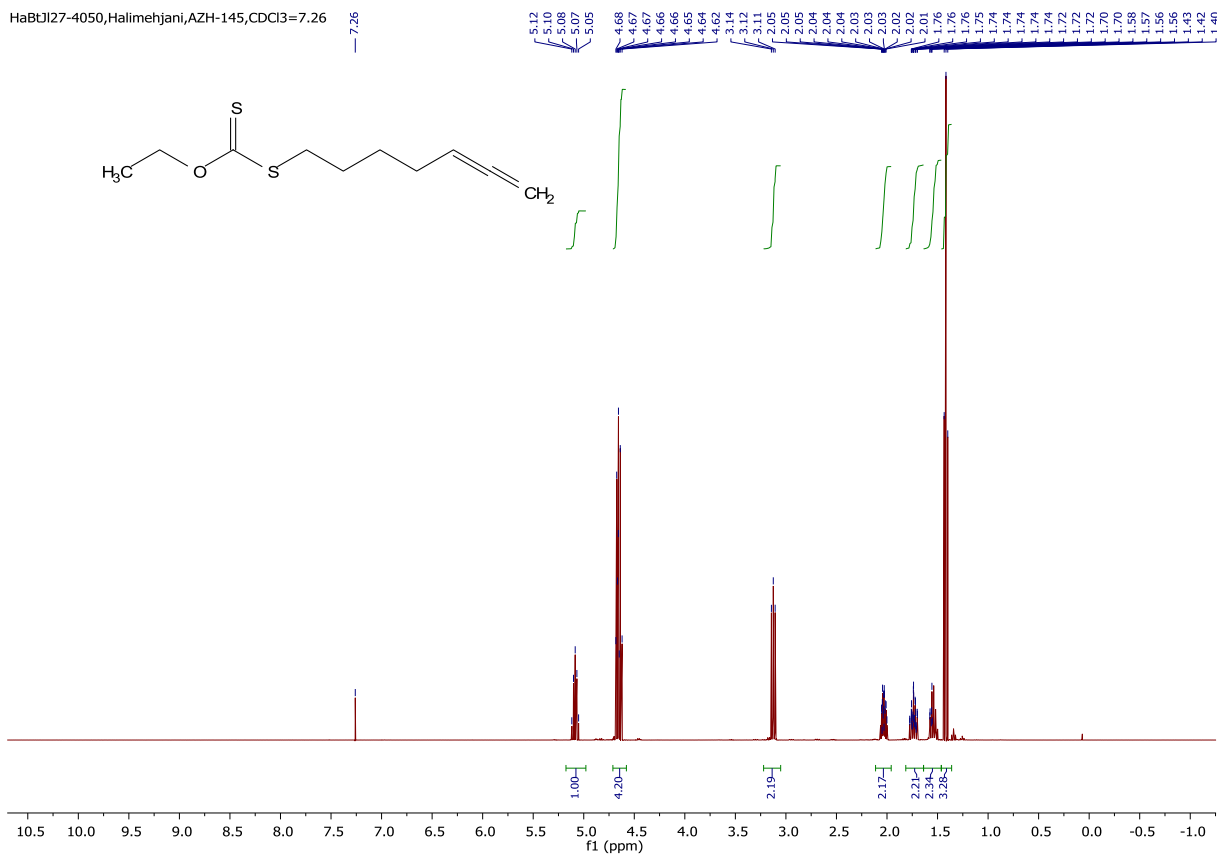
HaBJ17-4030, Halimehjani, m-Me-Thio, CDCl<sub>3</sub>



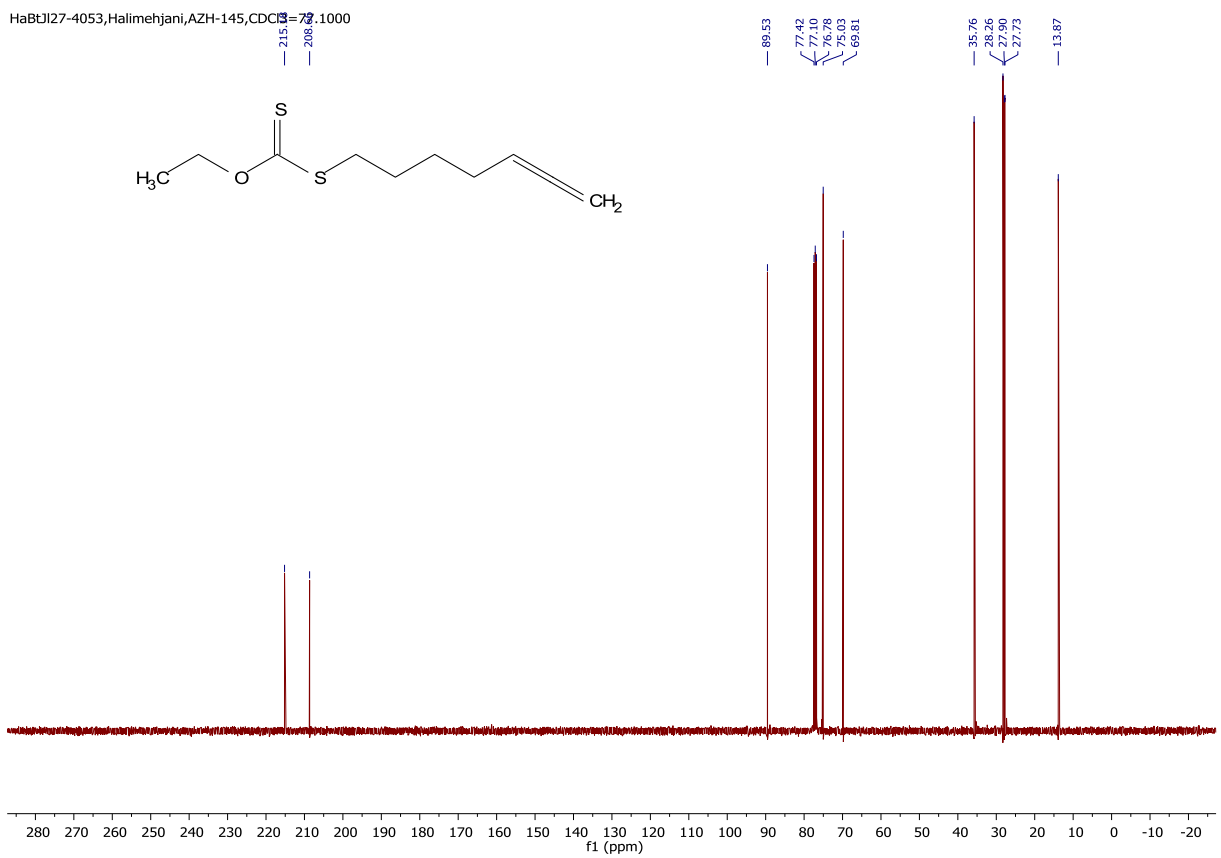
HaBJ17-4031, Halimehjani, m-Me-Thio, CDCl<sub>3</sub> = 77.1000



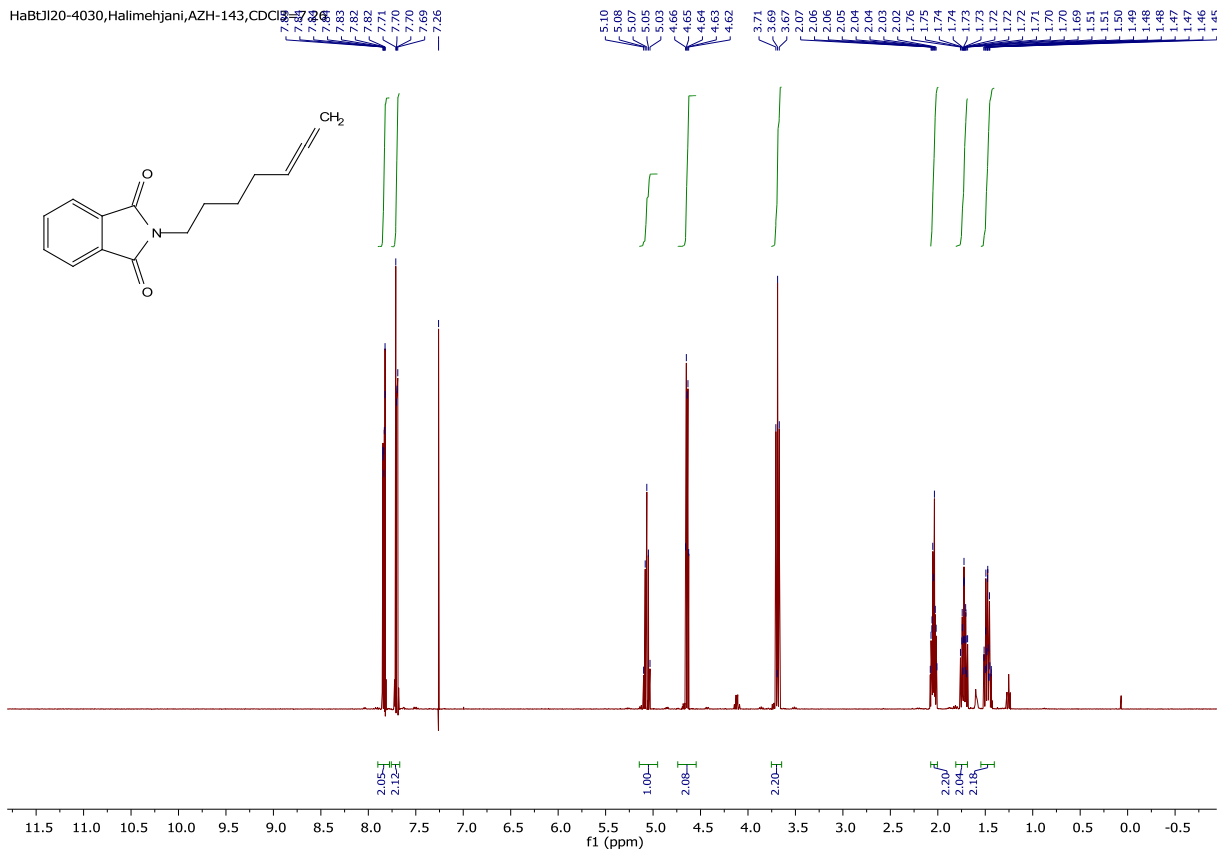
HaBJI27-4050, Halimehjeni, AZH-145, CDCl3 = 7.26



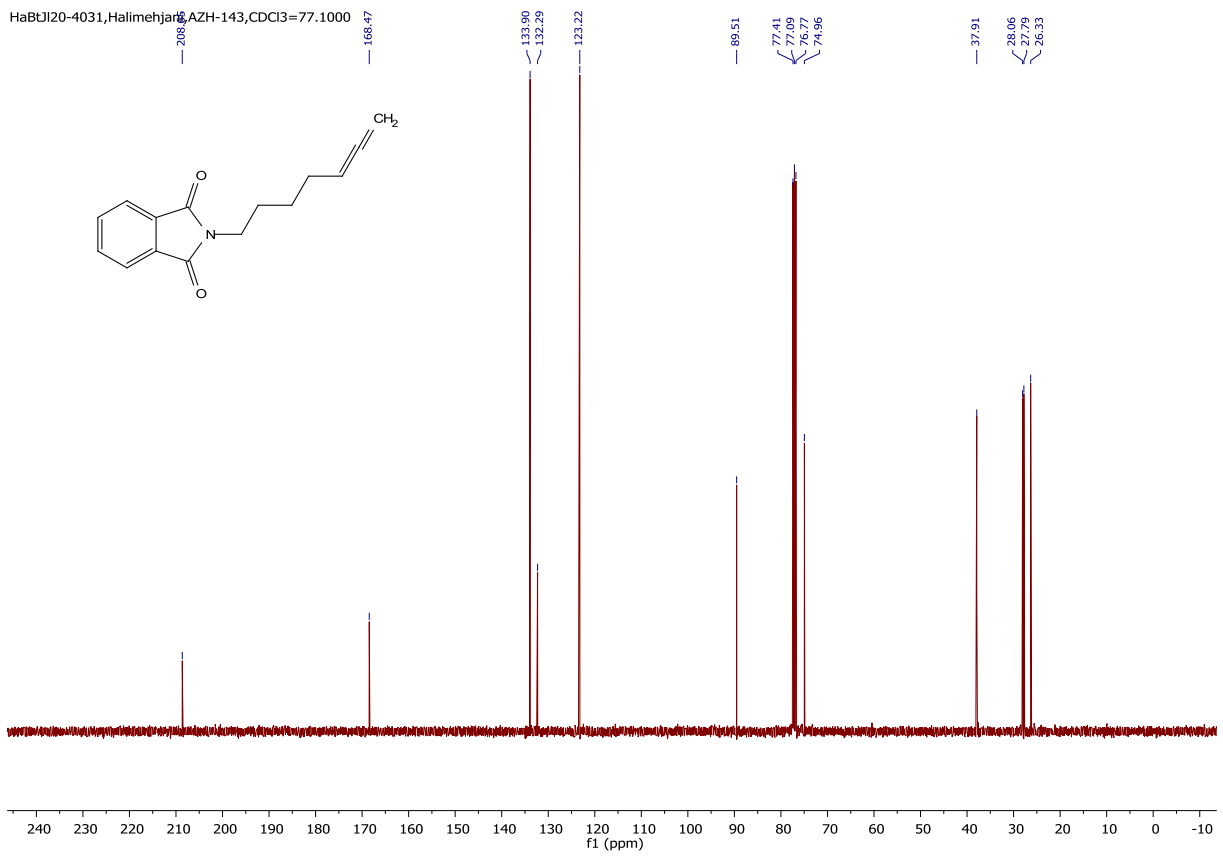
HaBJI27-4053, Halimehjeni, AZH-145, CDCl3 = 7.1000

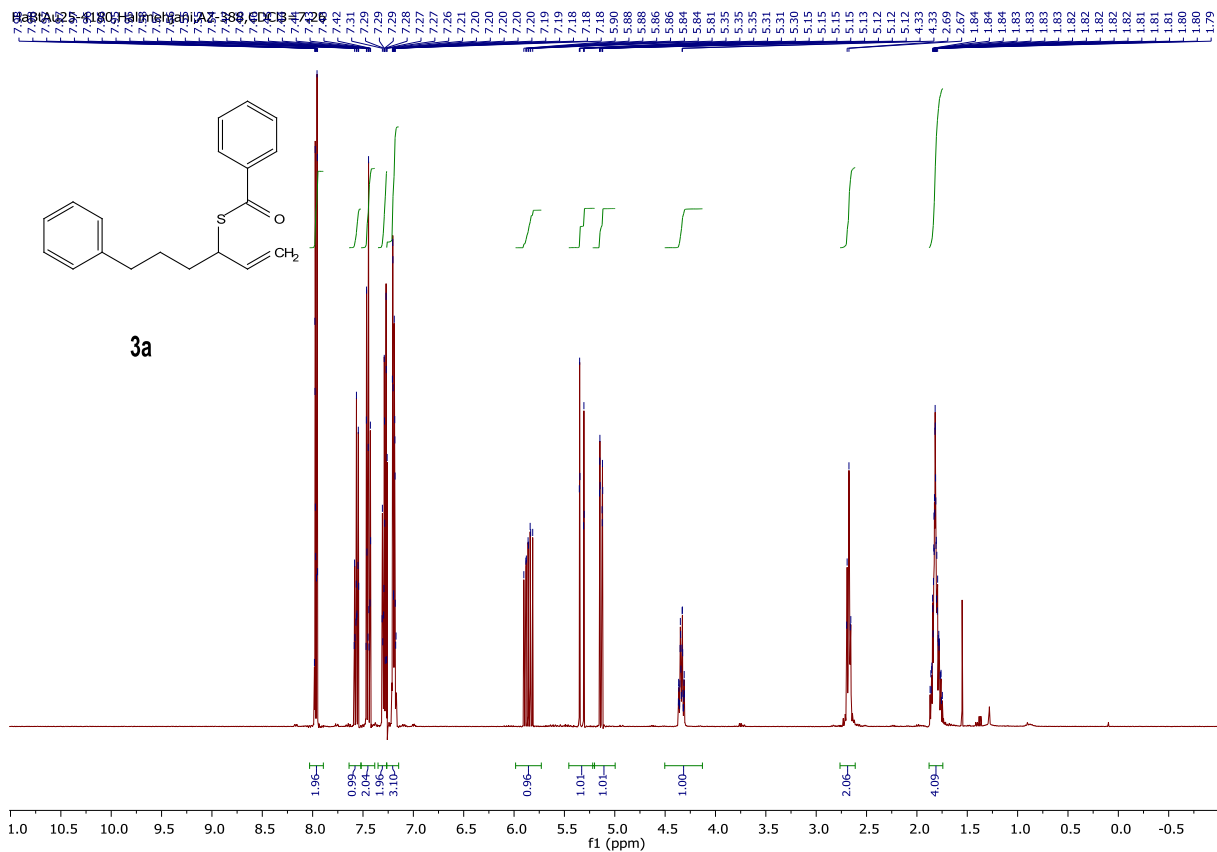


HaBUJ20-4030, Halimehjani, AZH-143, CDCl<sub>3</sub>

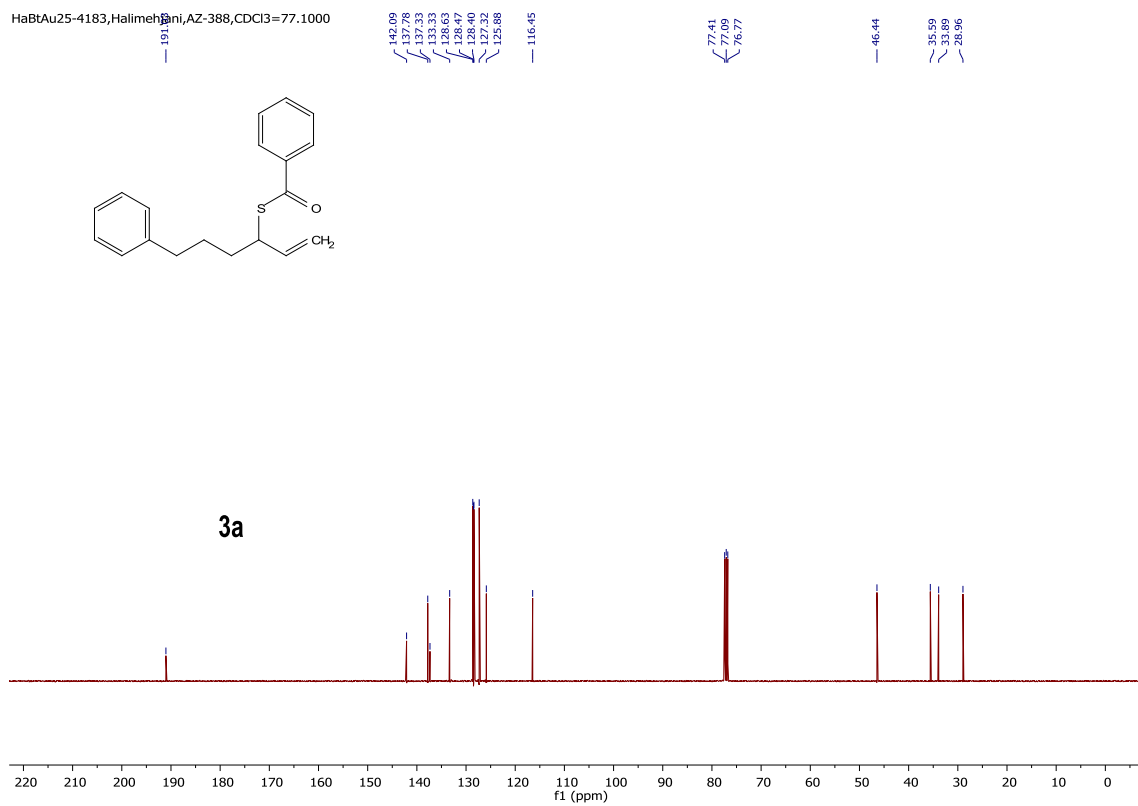


HaBUJ20-4031, Halimehjani, AZH-143, CDCl<sub>3</sub>=77.1000

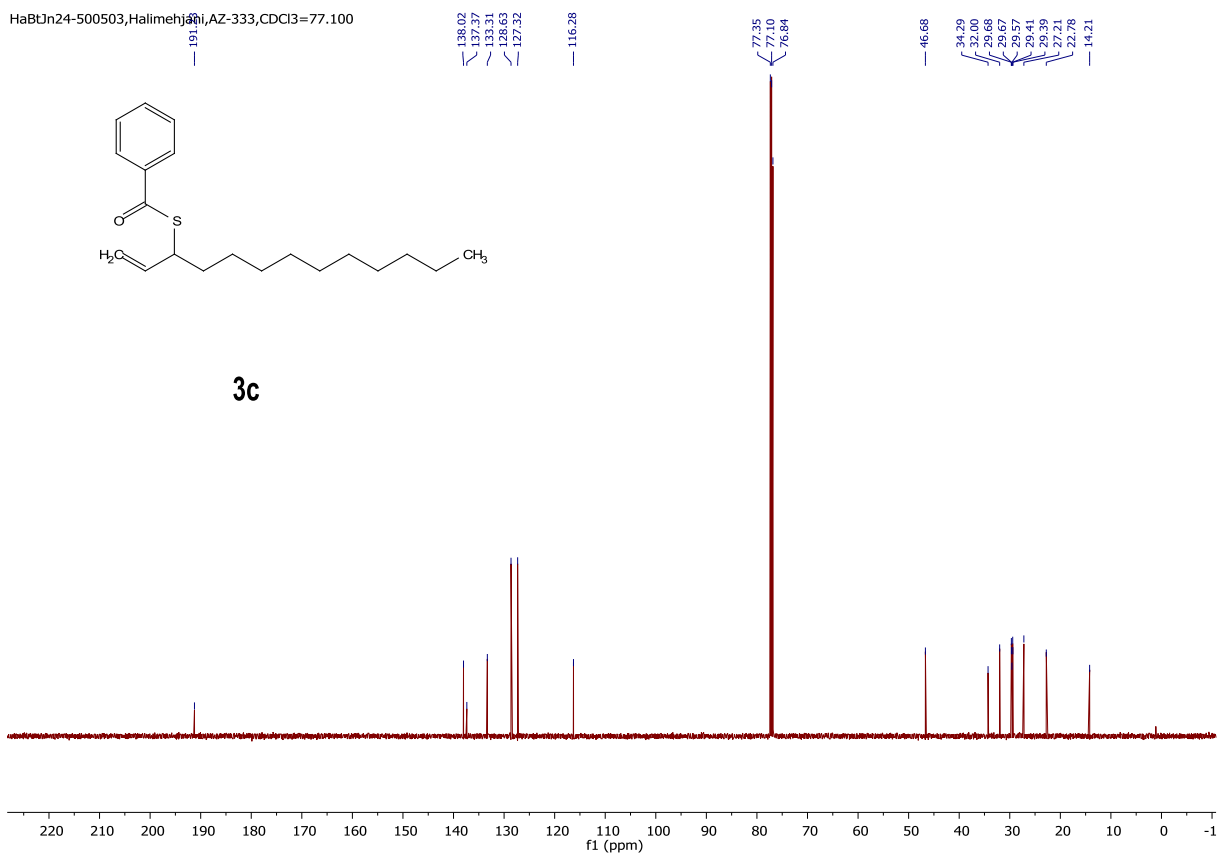
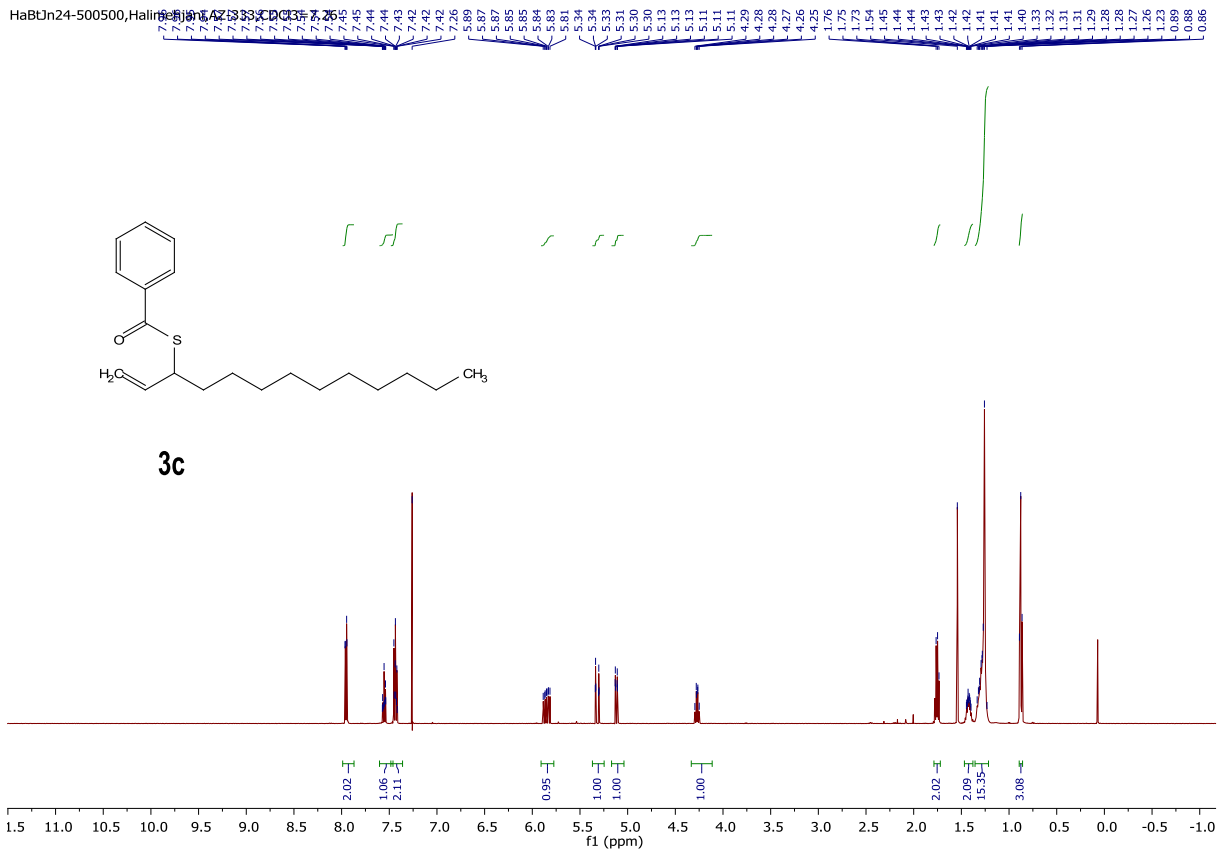




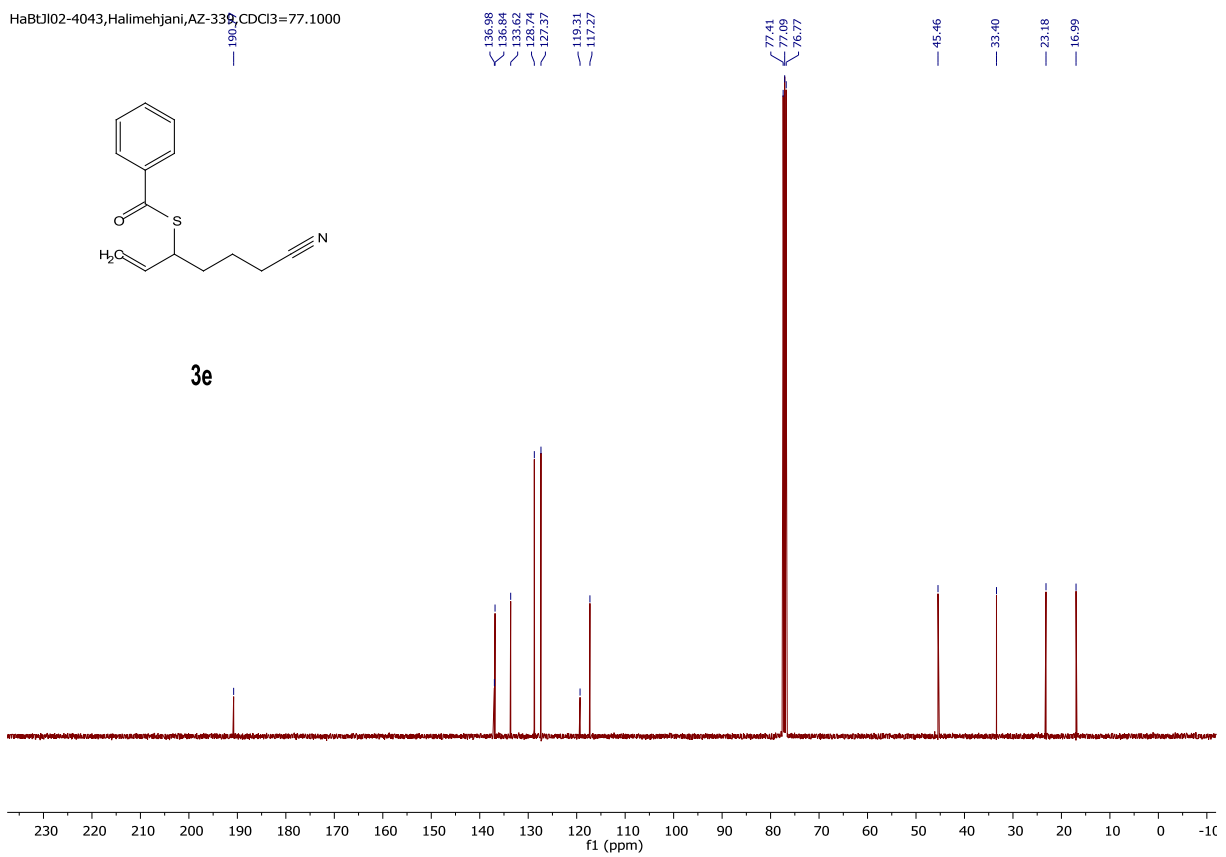
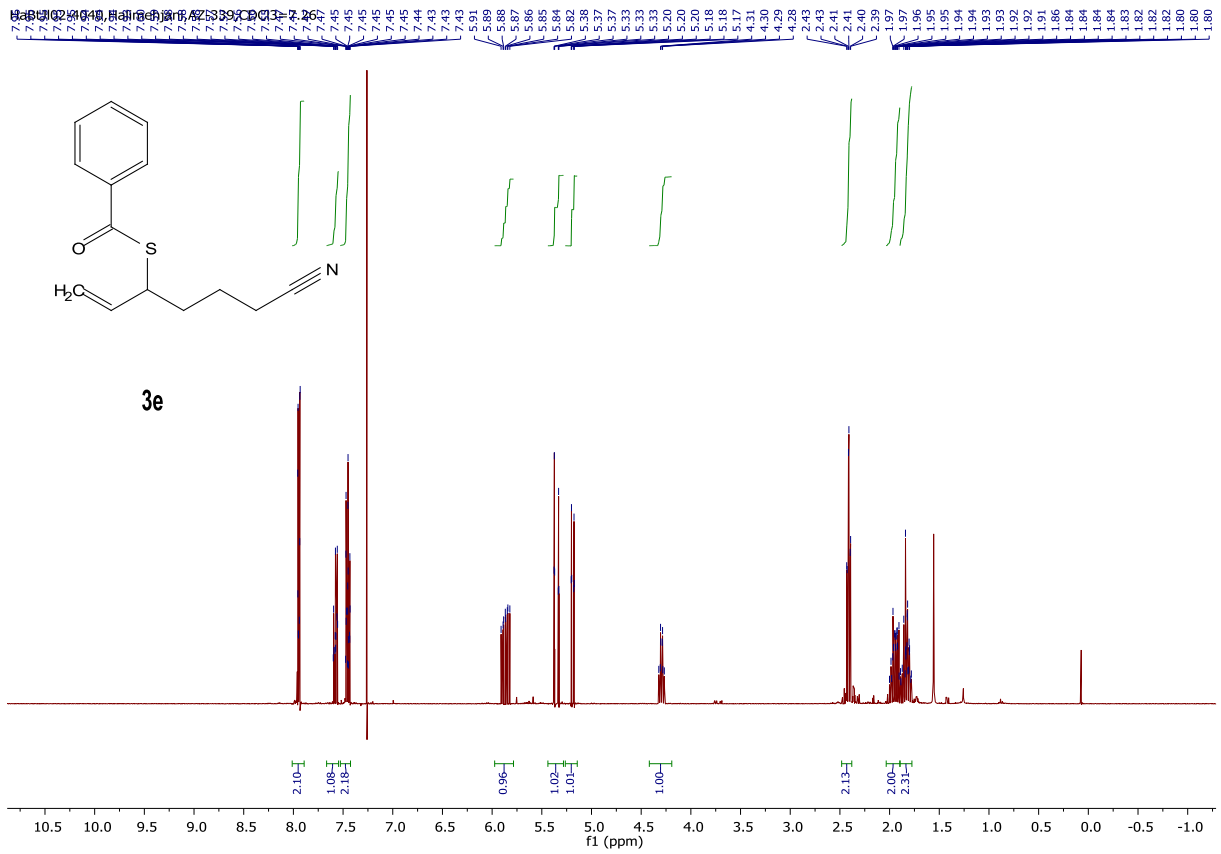
HaBtAu25-4183, Halimethani, AZ-388, CDCl<sub>3</sub>=77.1000



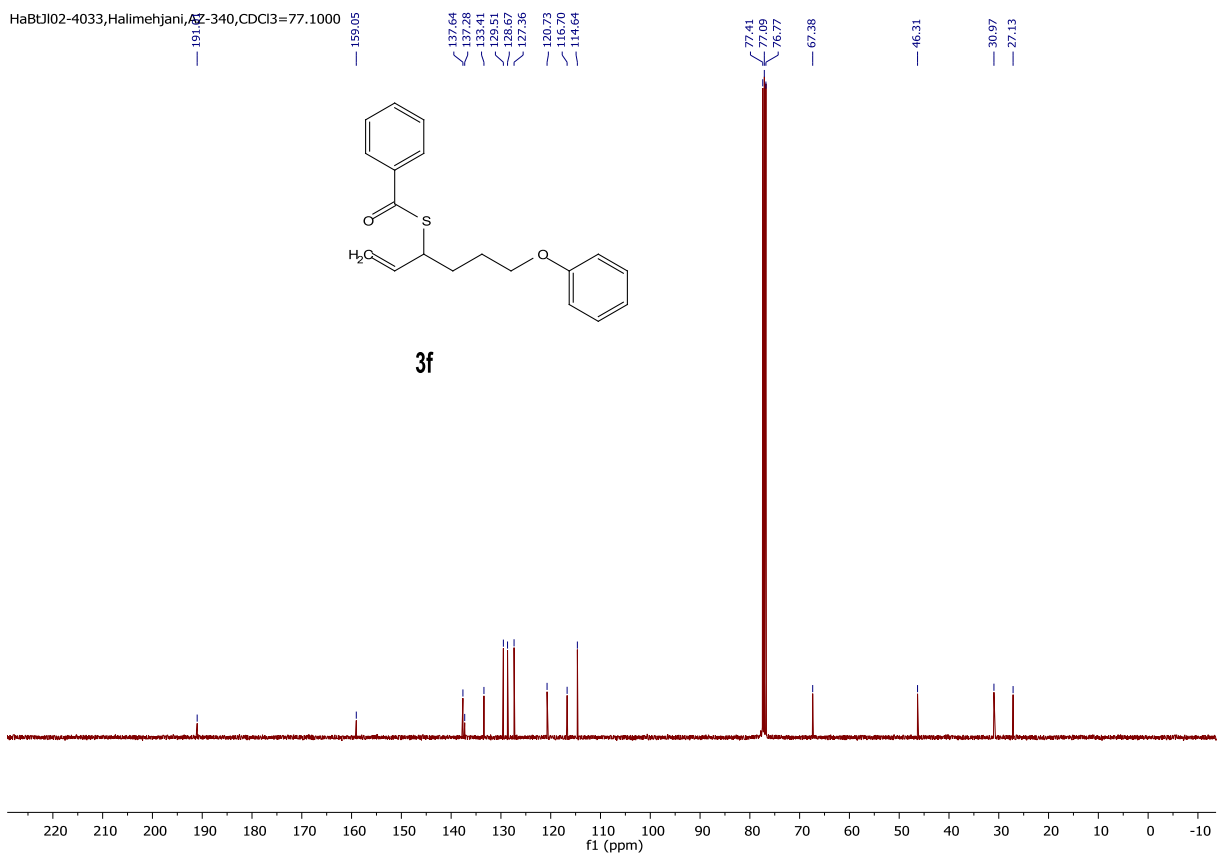
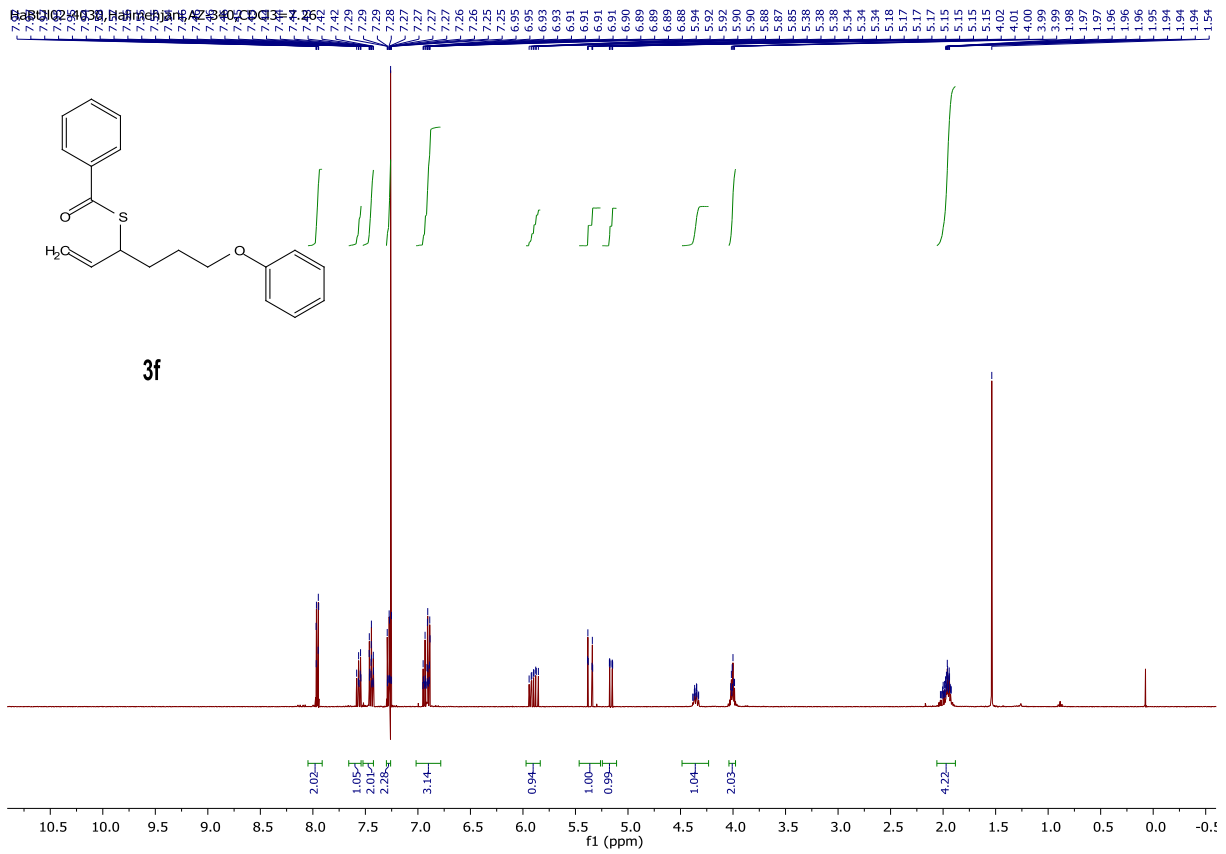


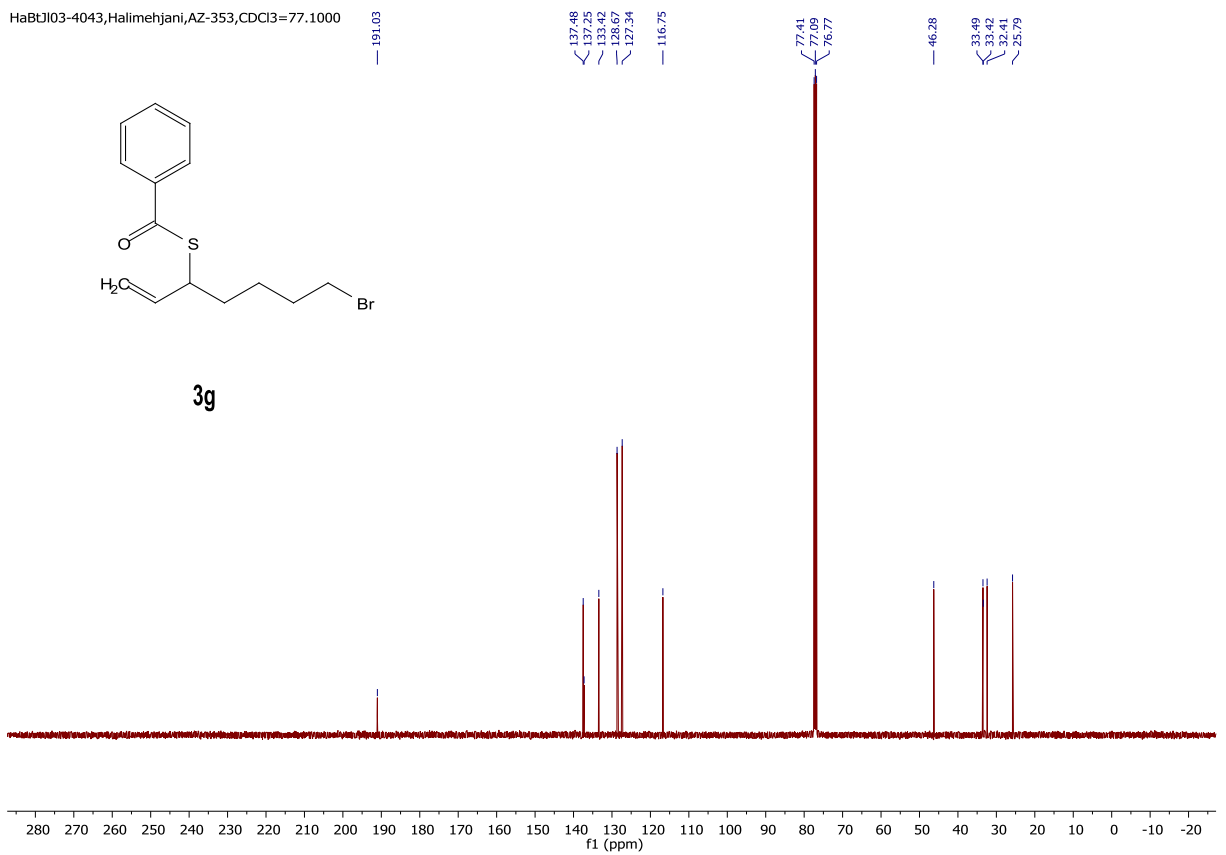
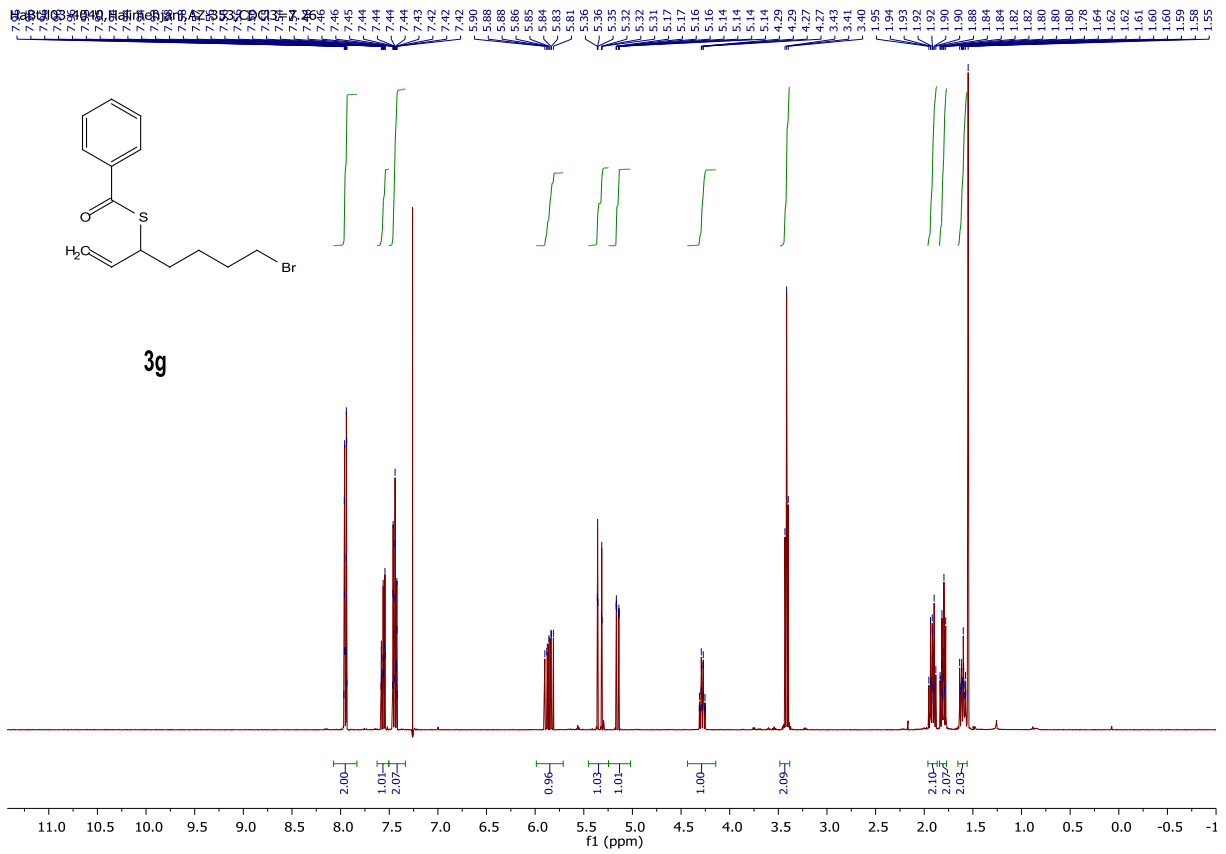


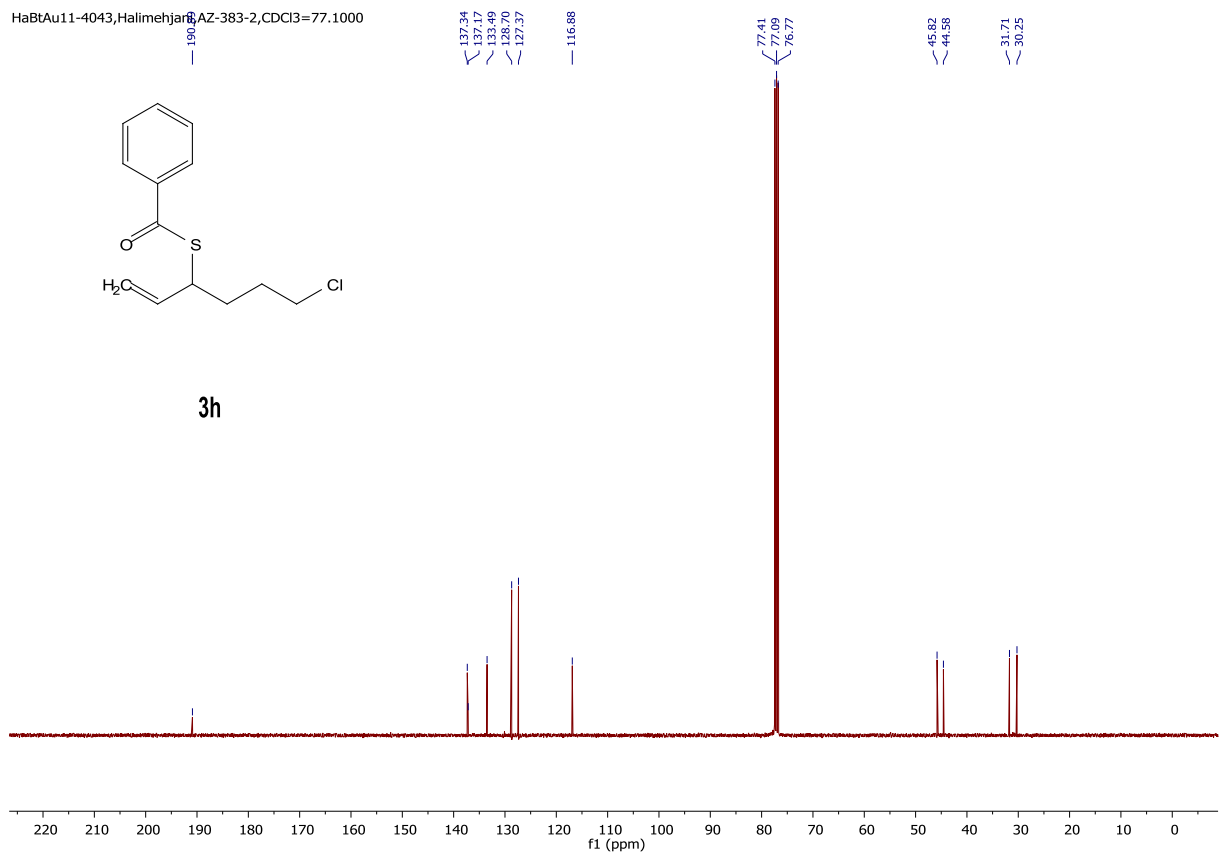
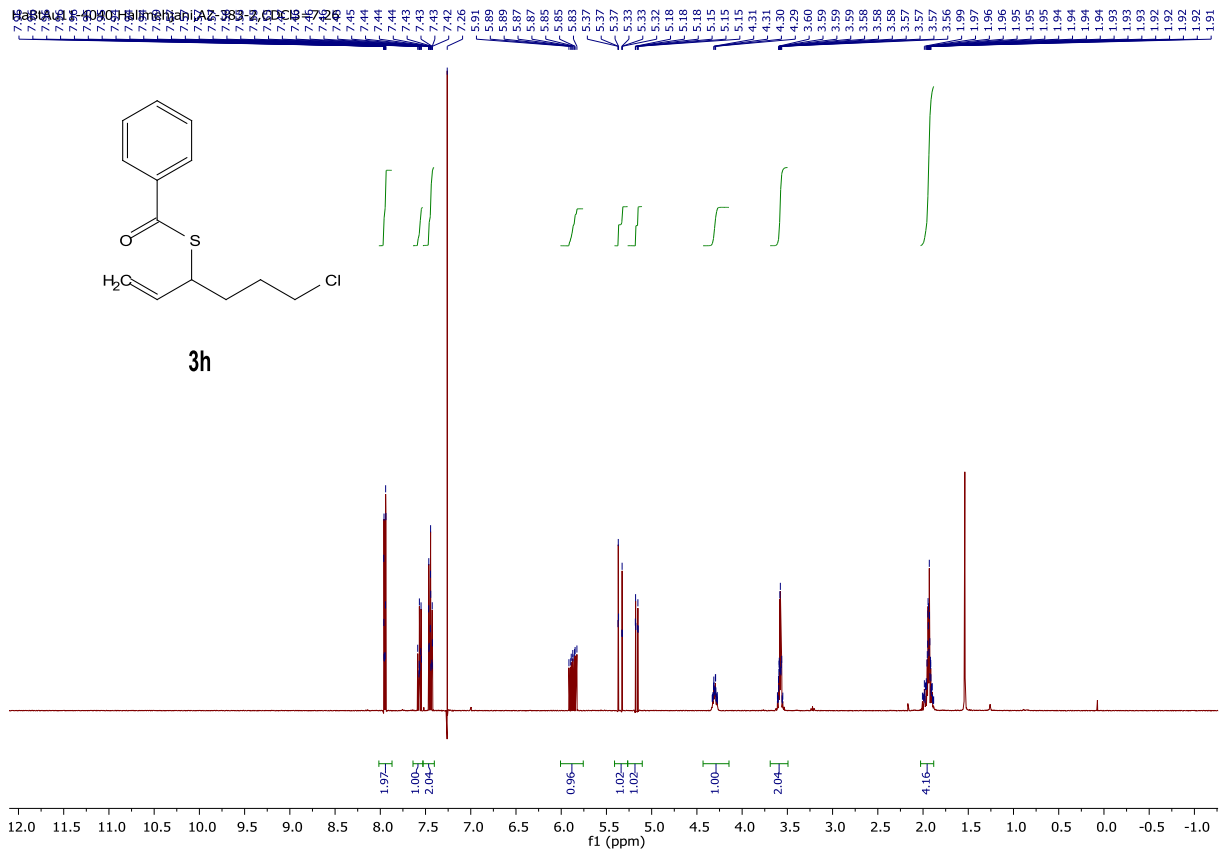


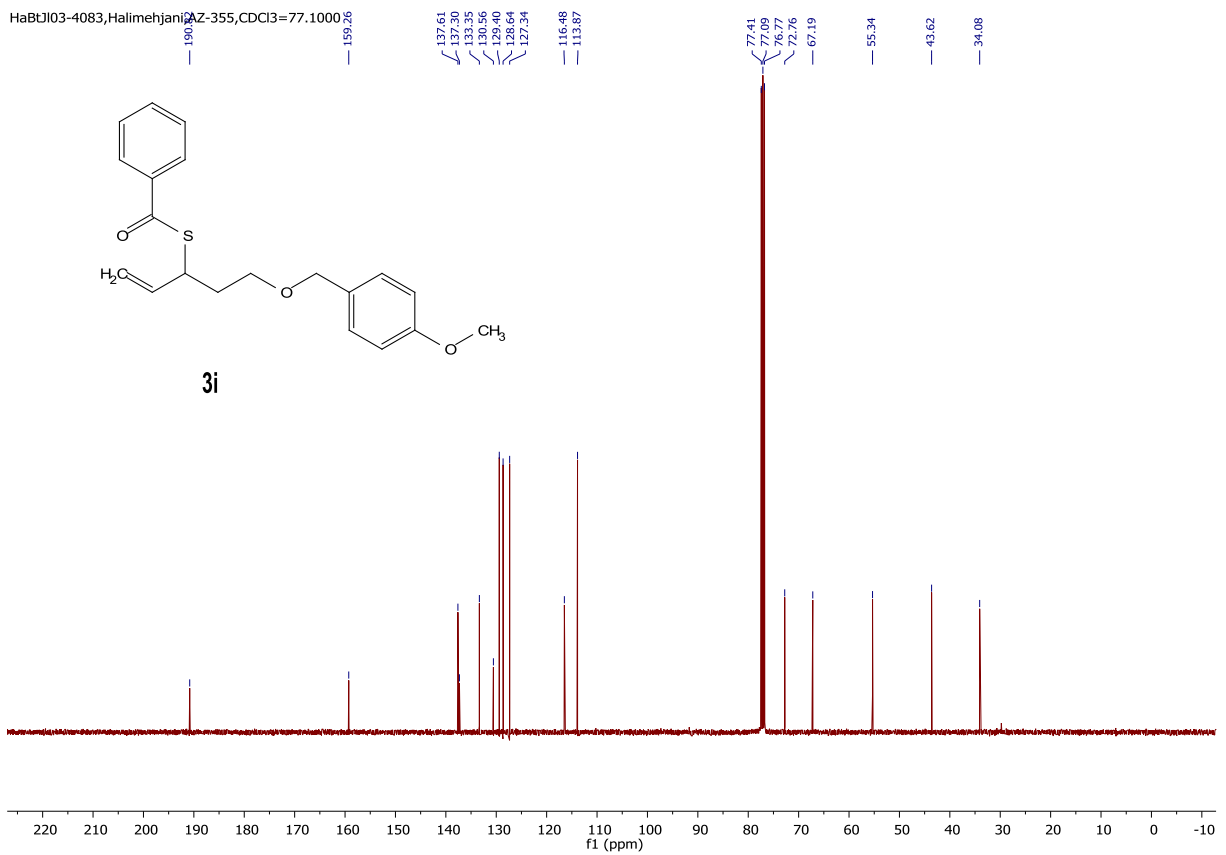
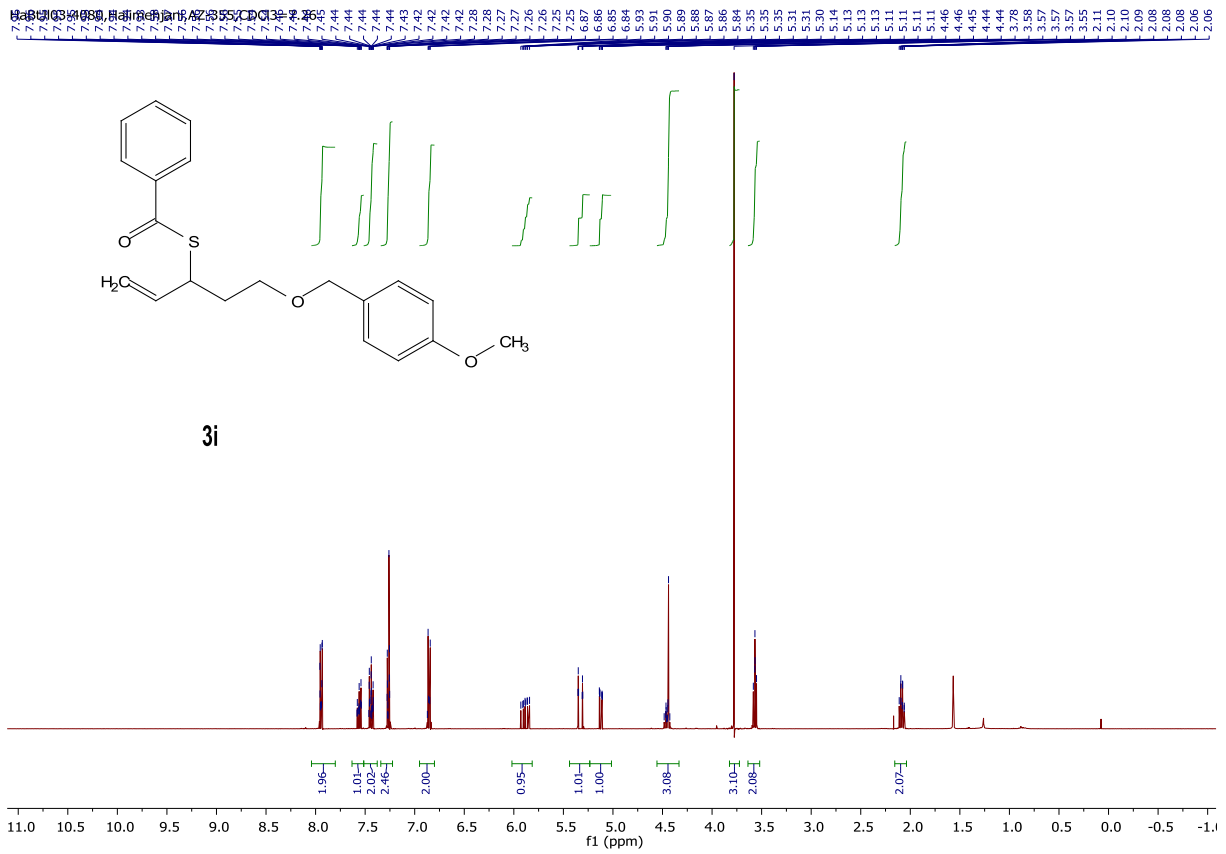


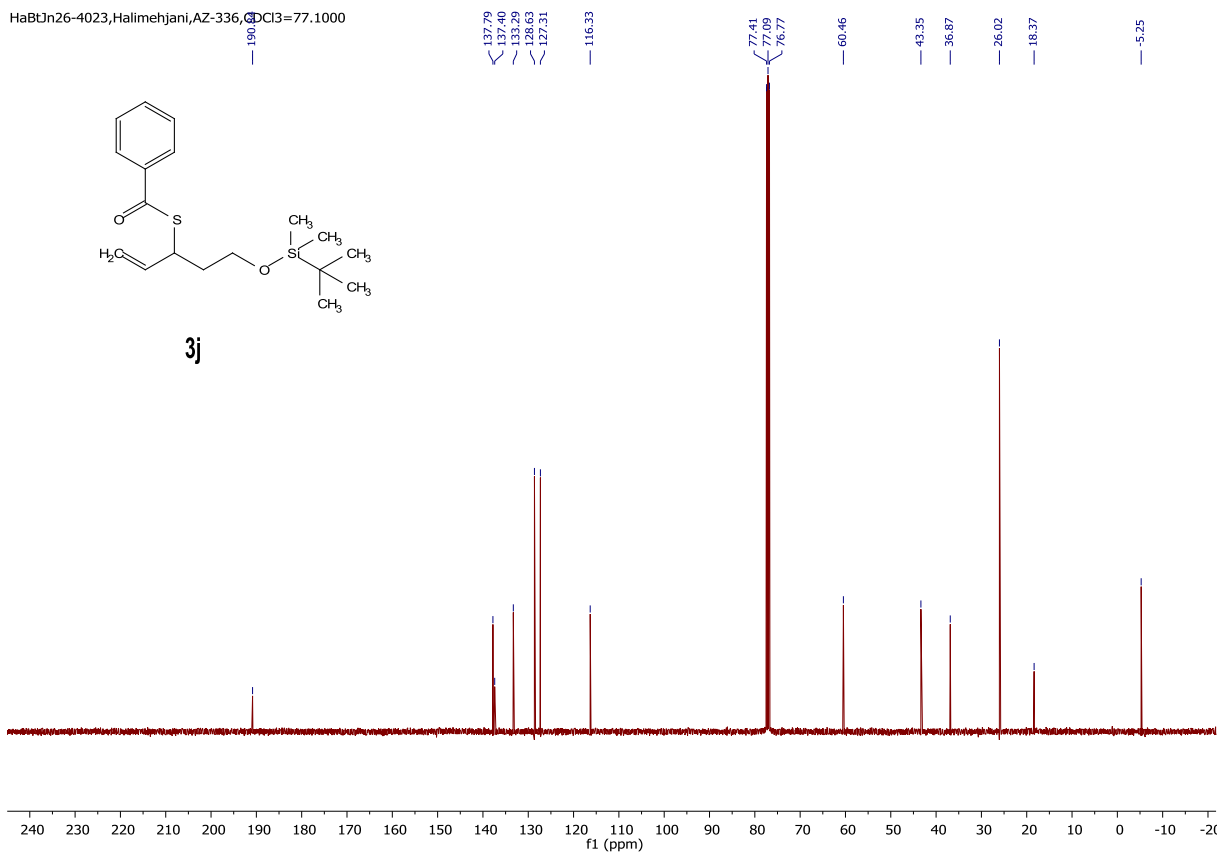
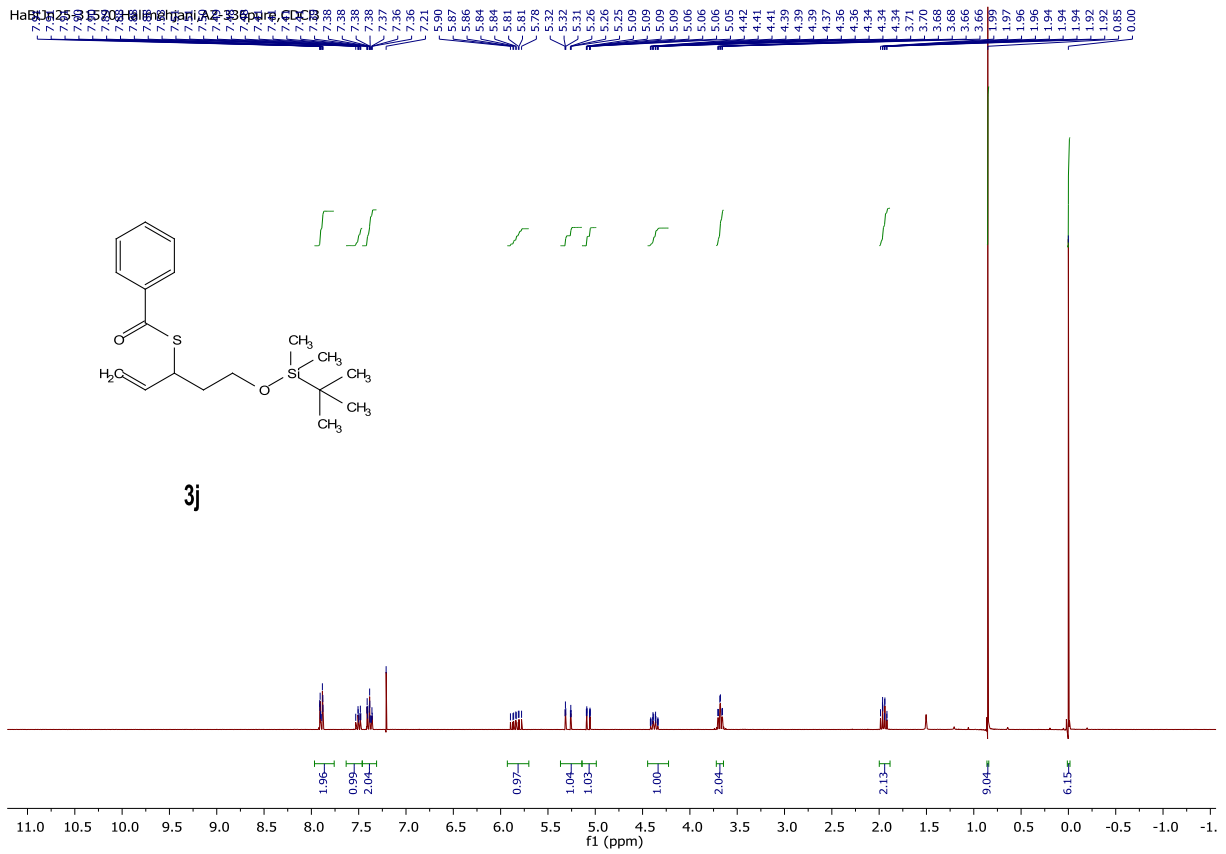


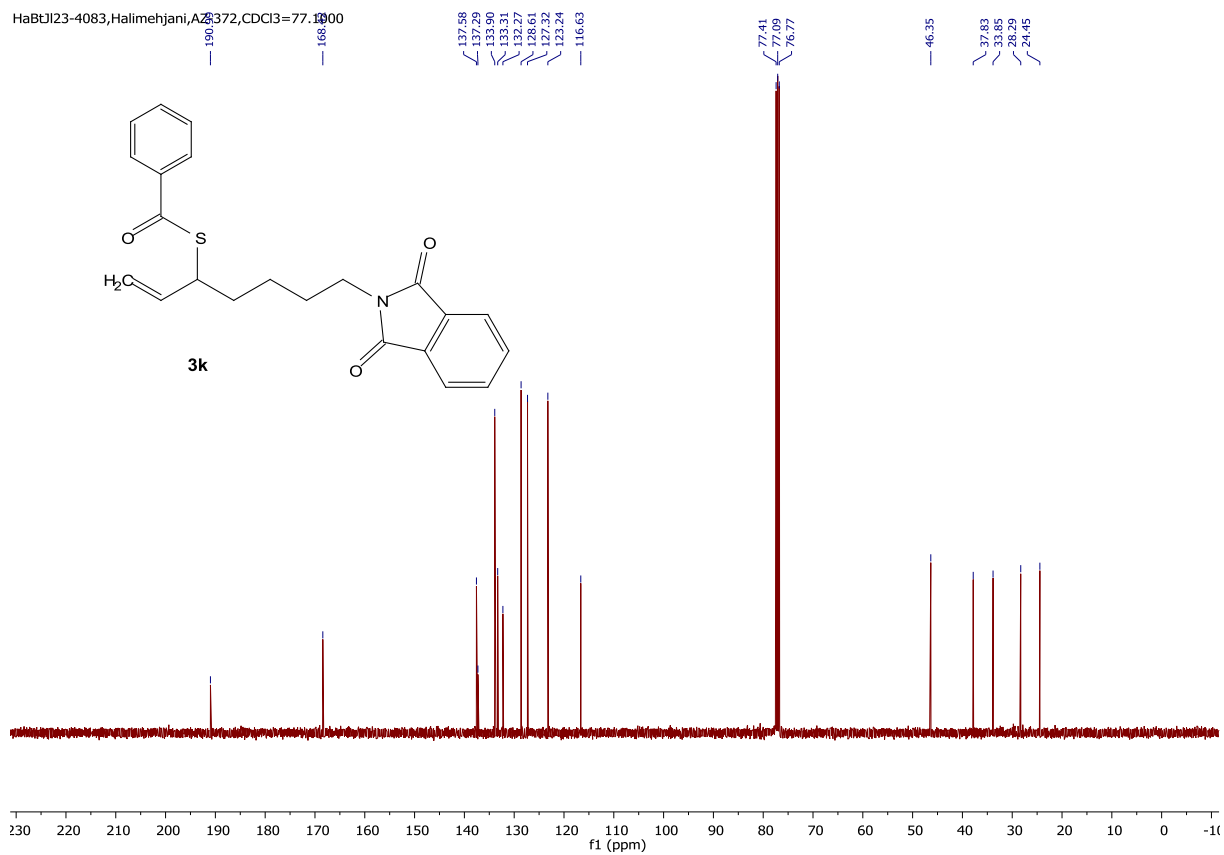
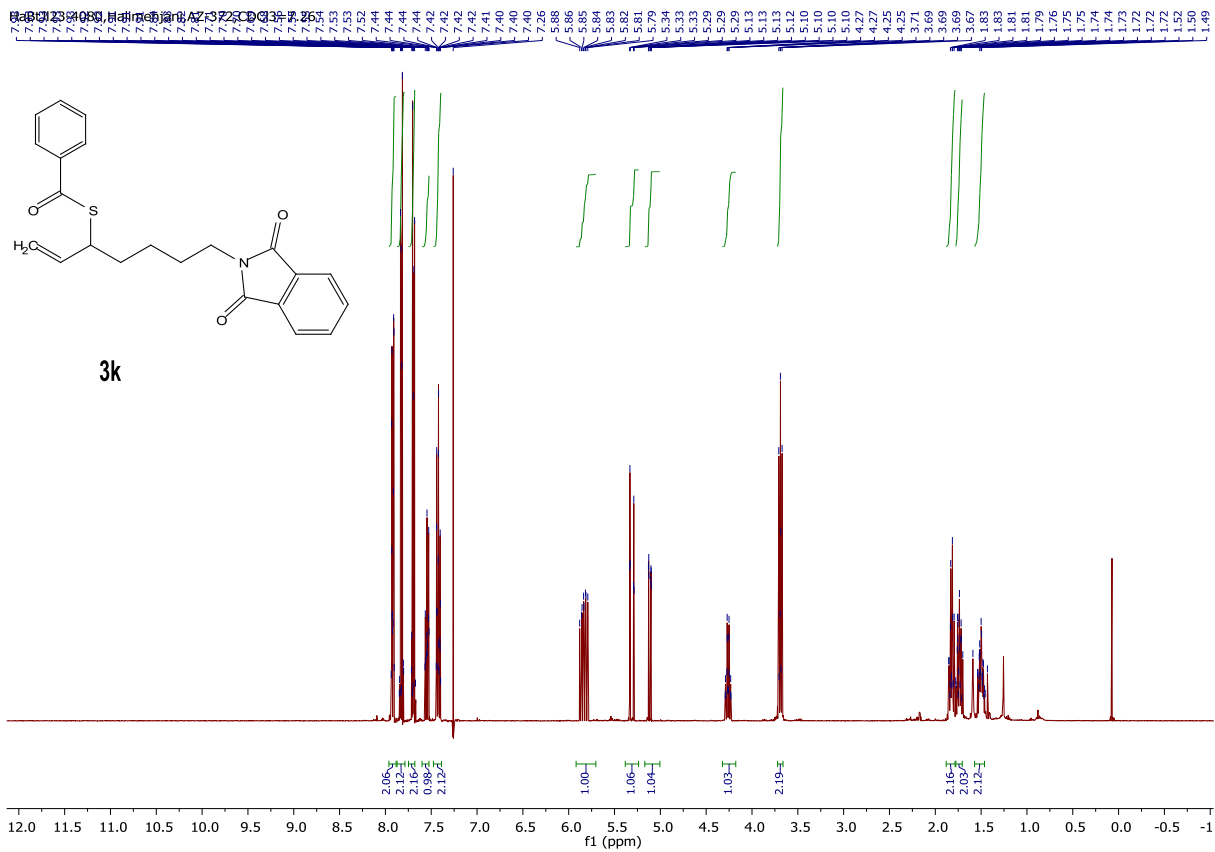


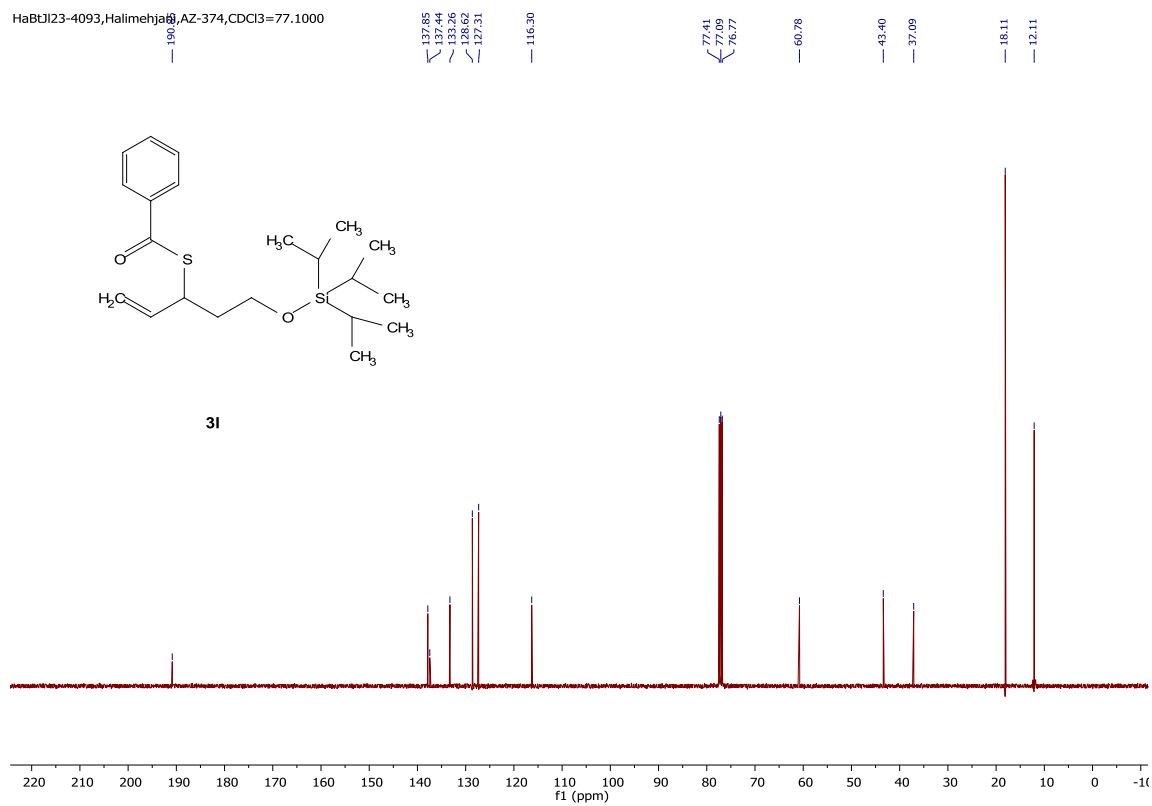
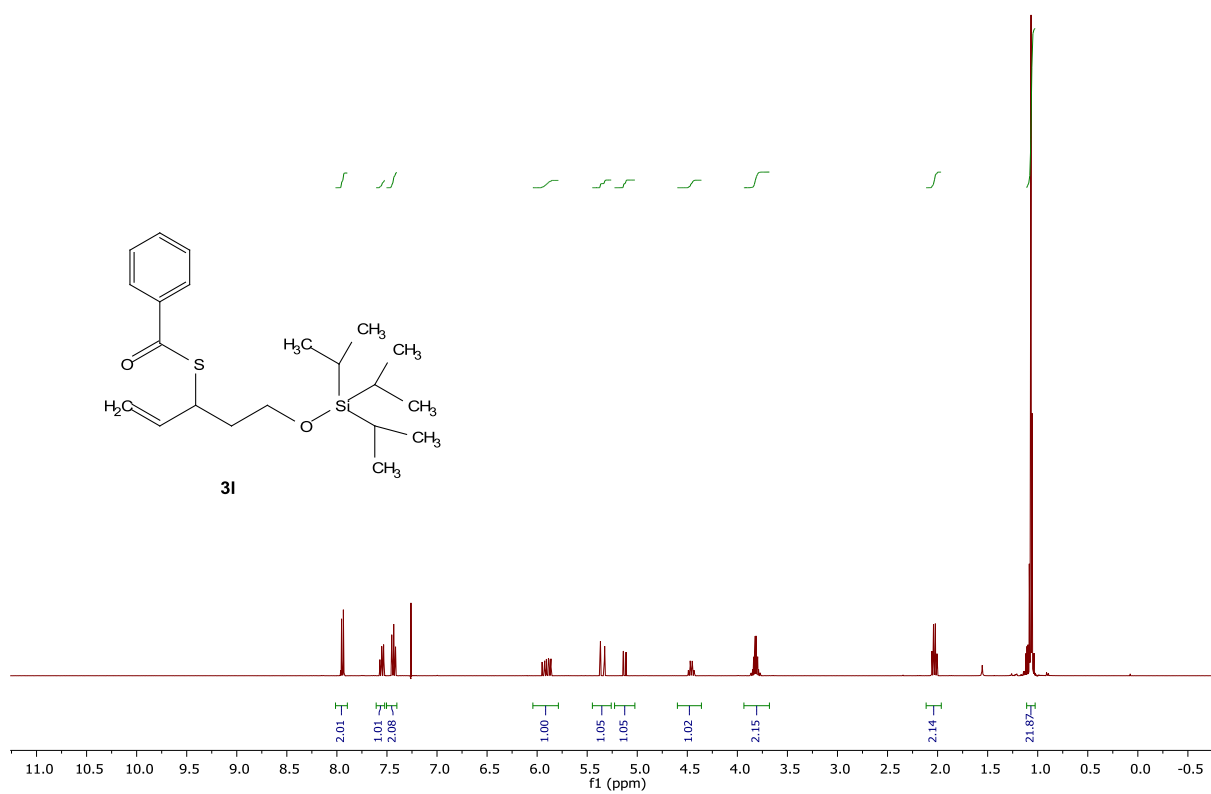


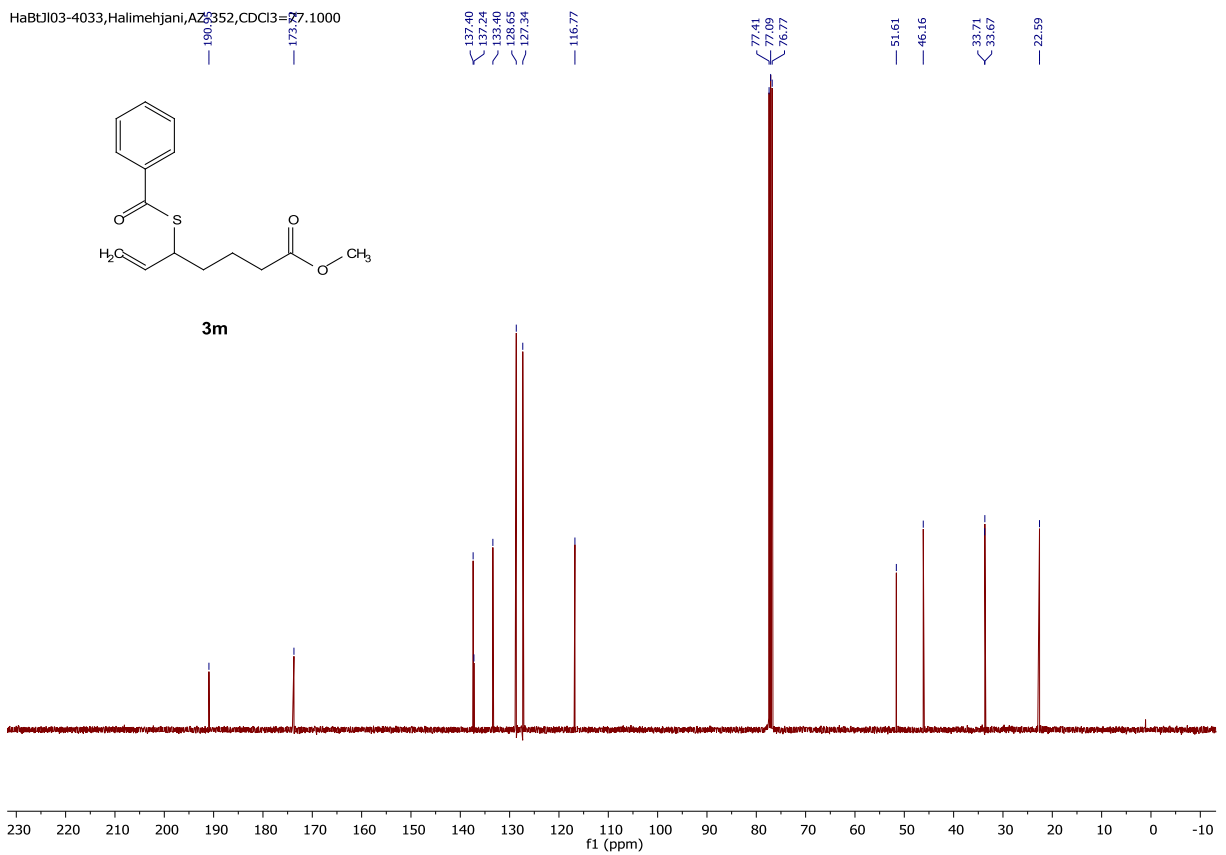
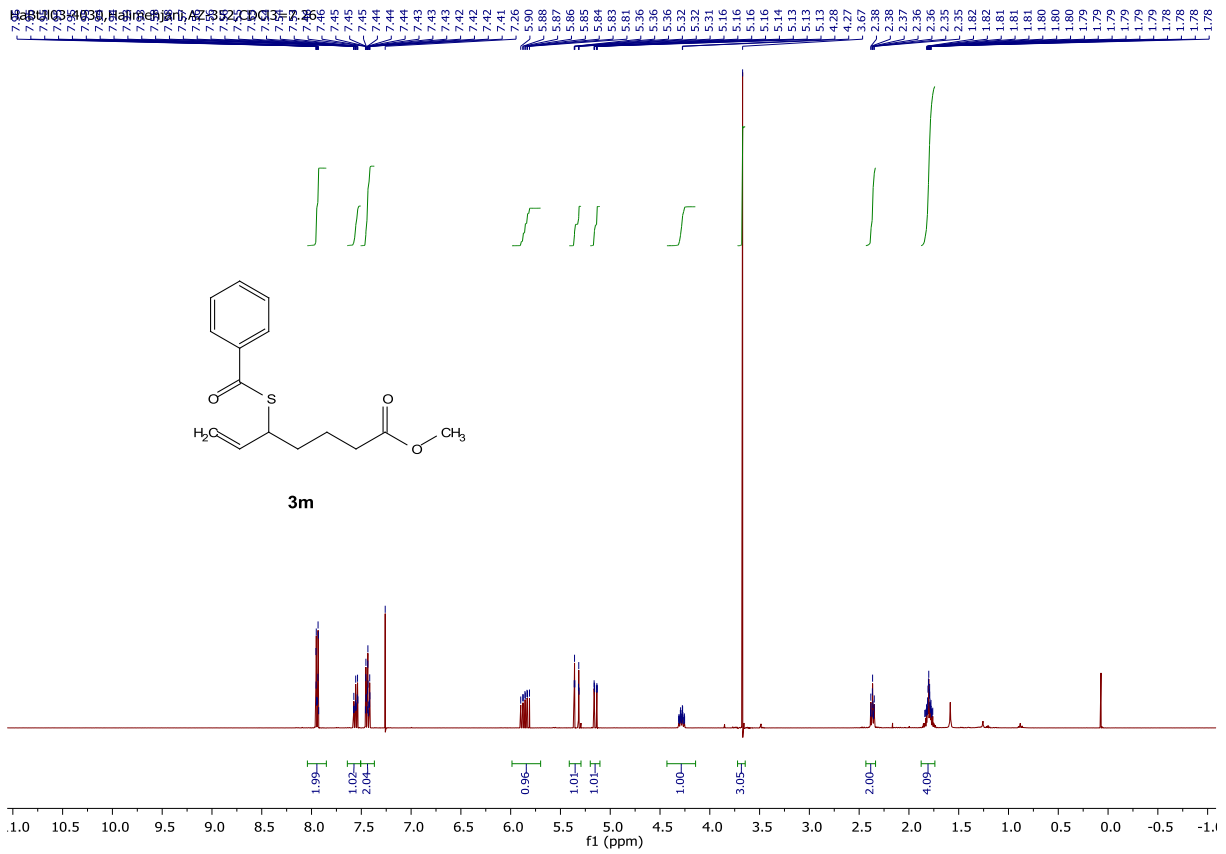






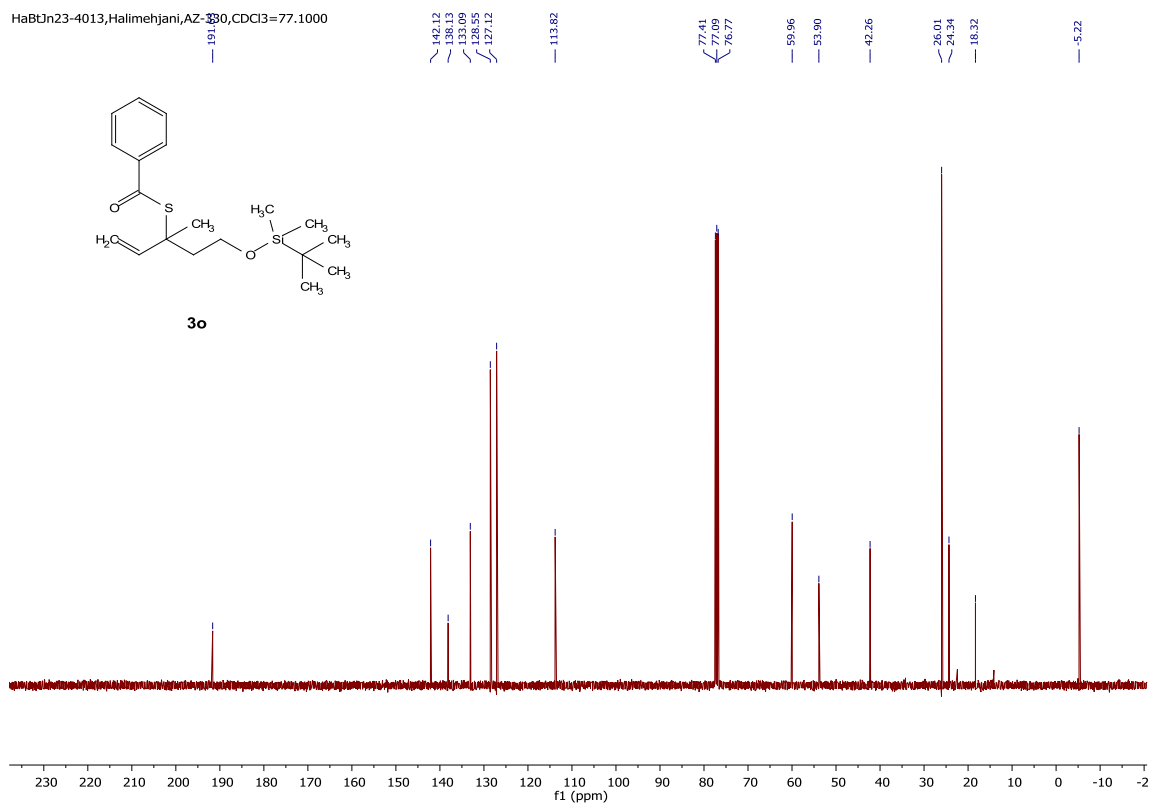
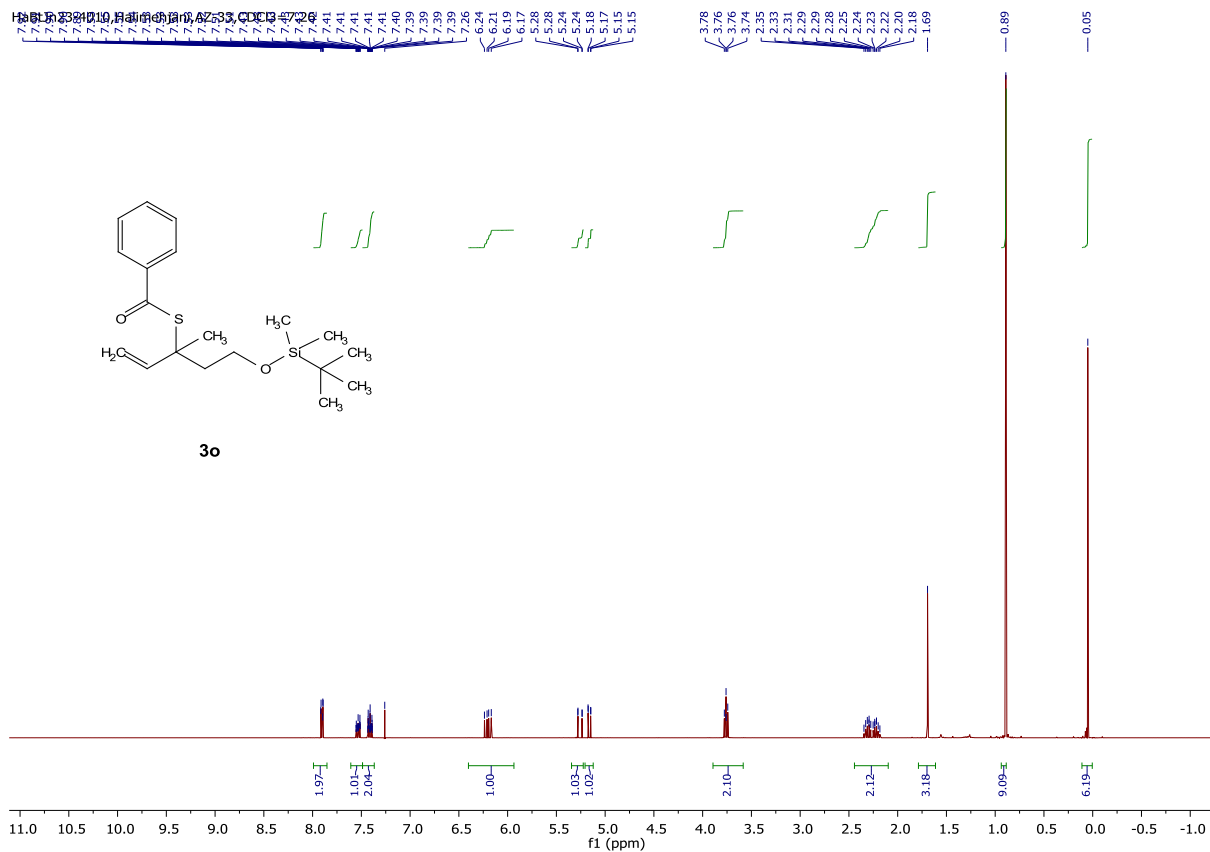


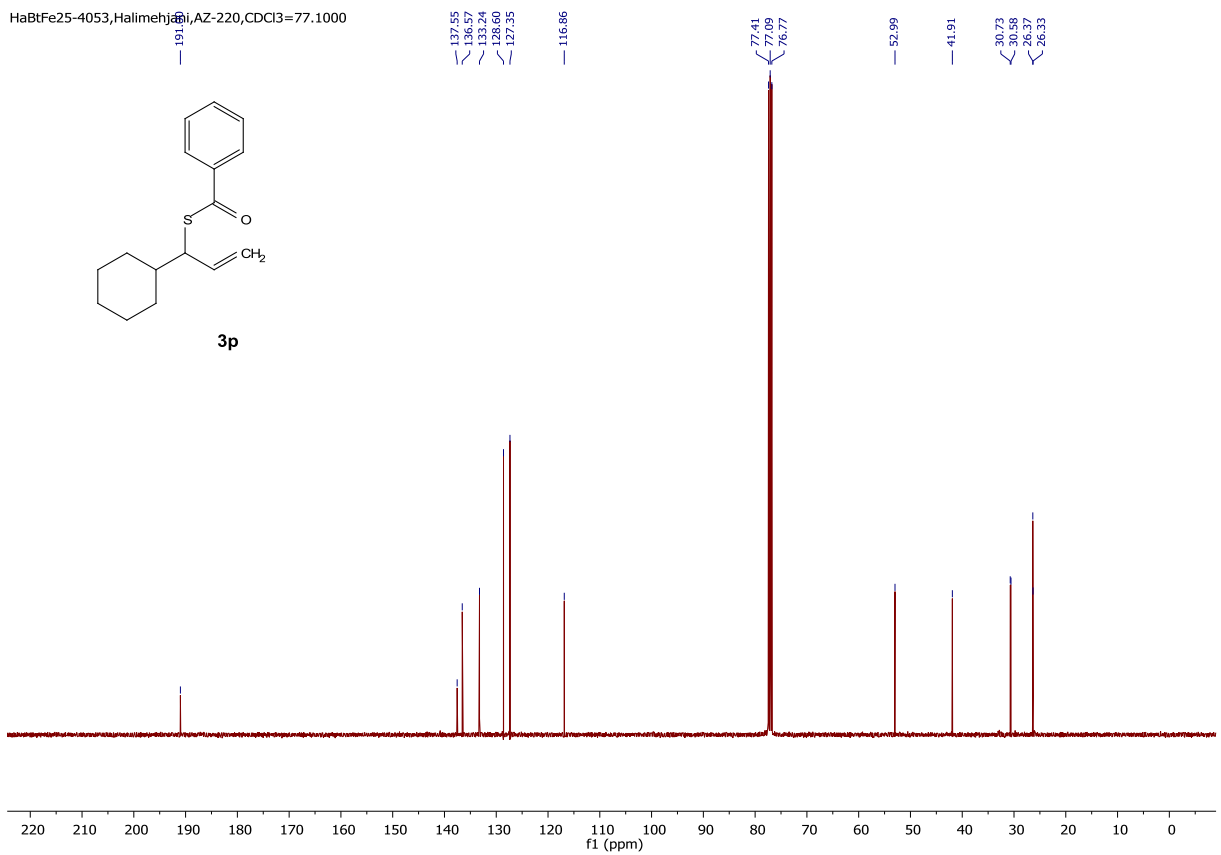
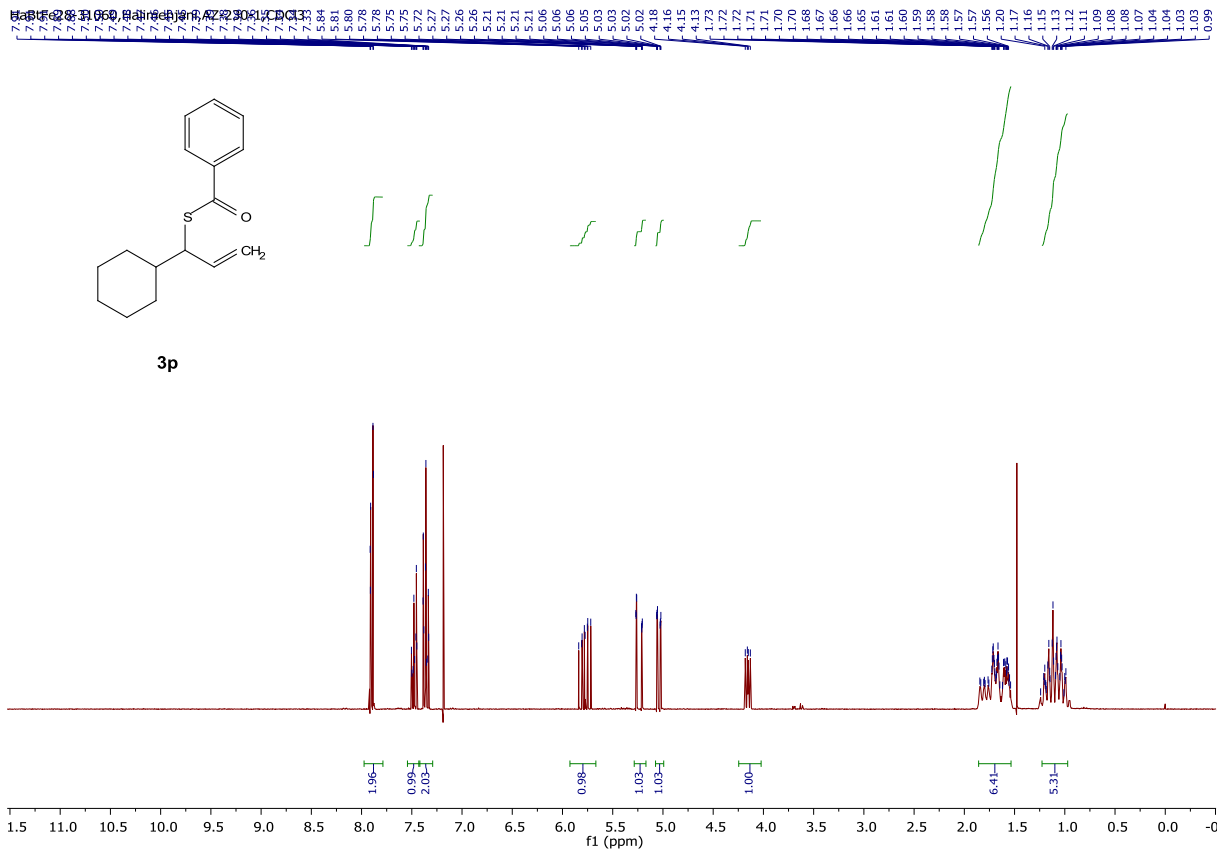


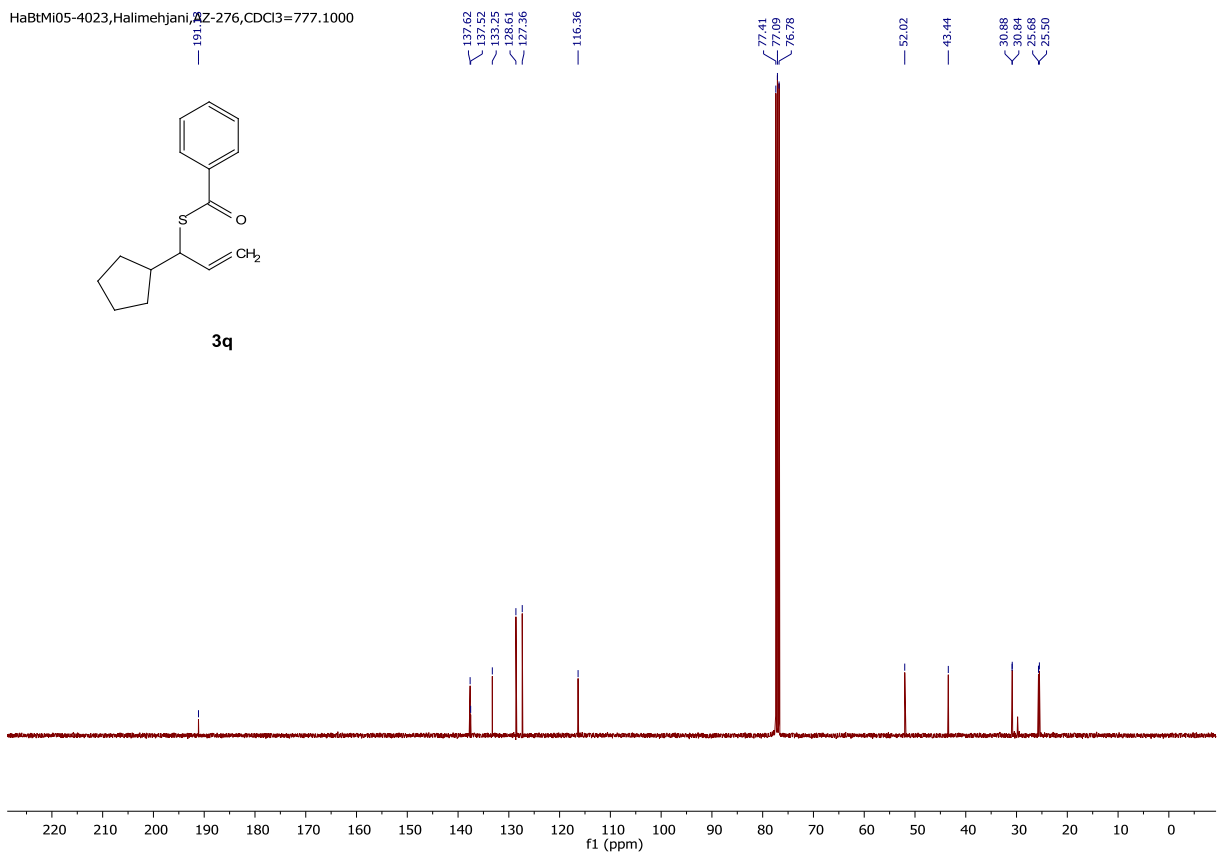
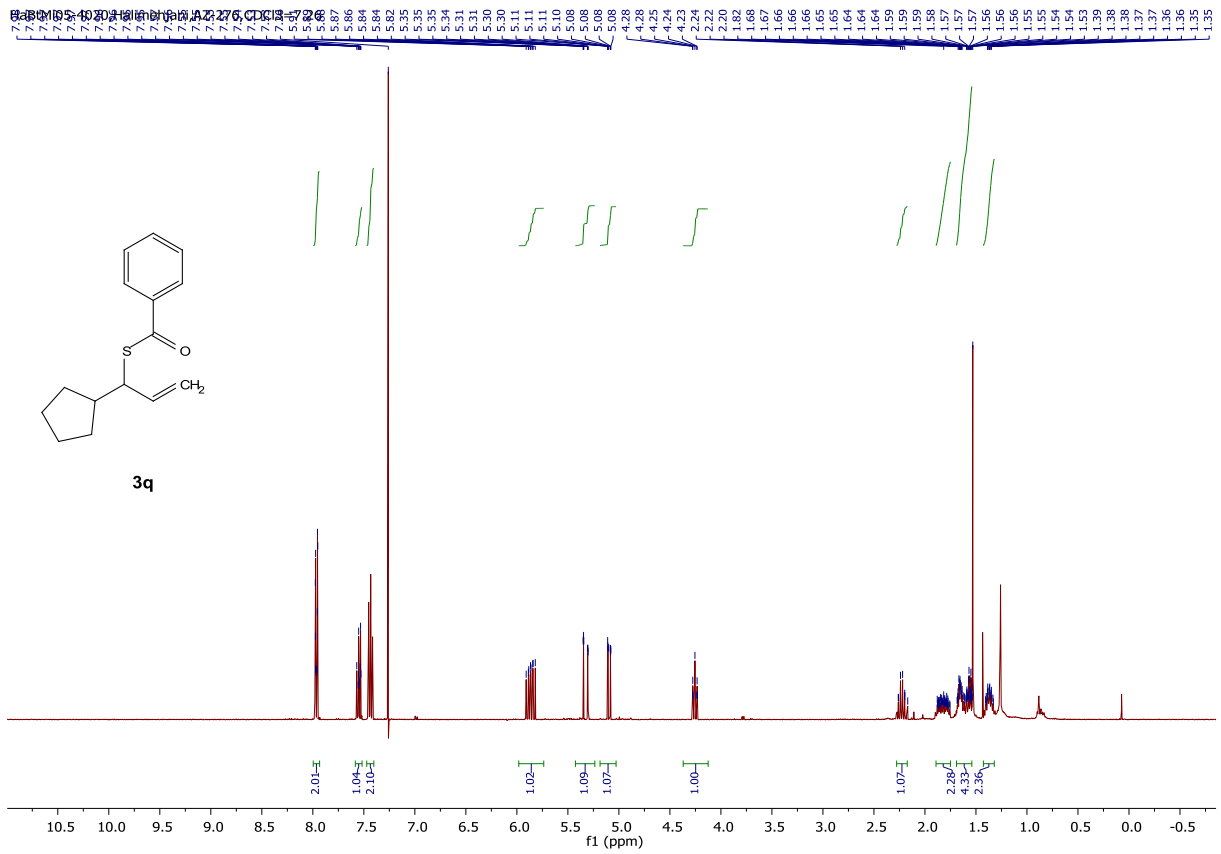


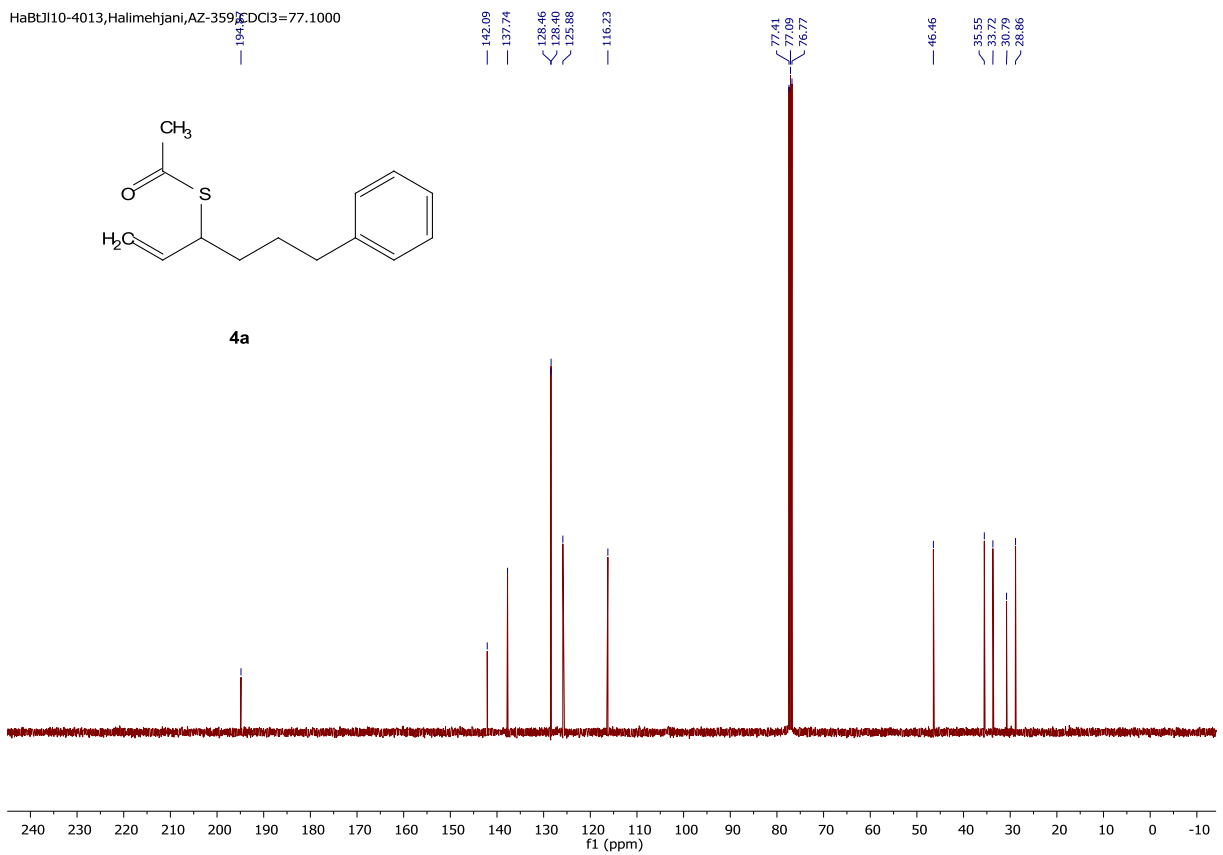
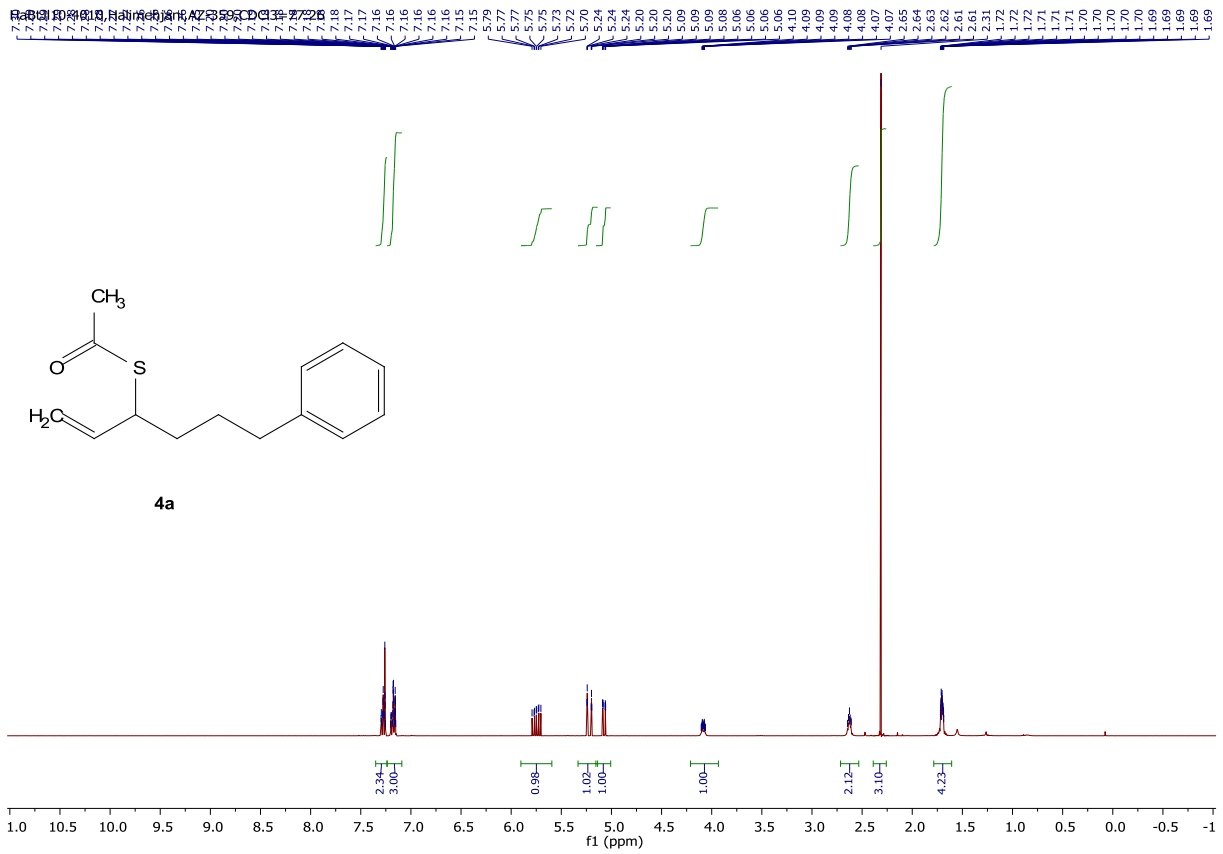


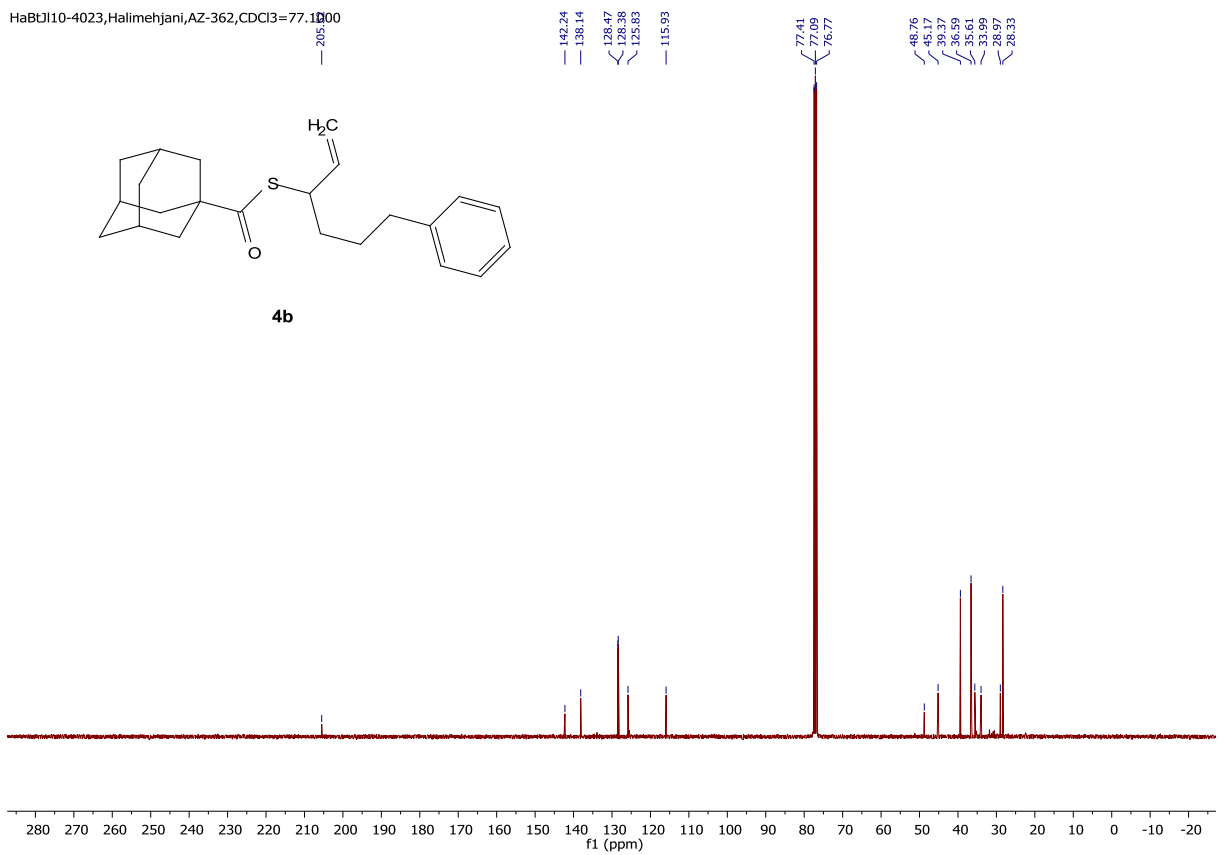
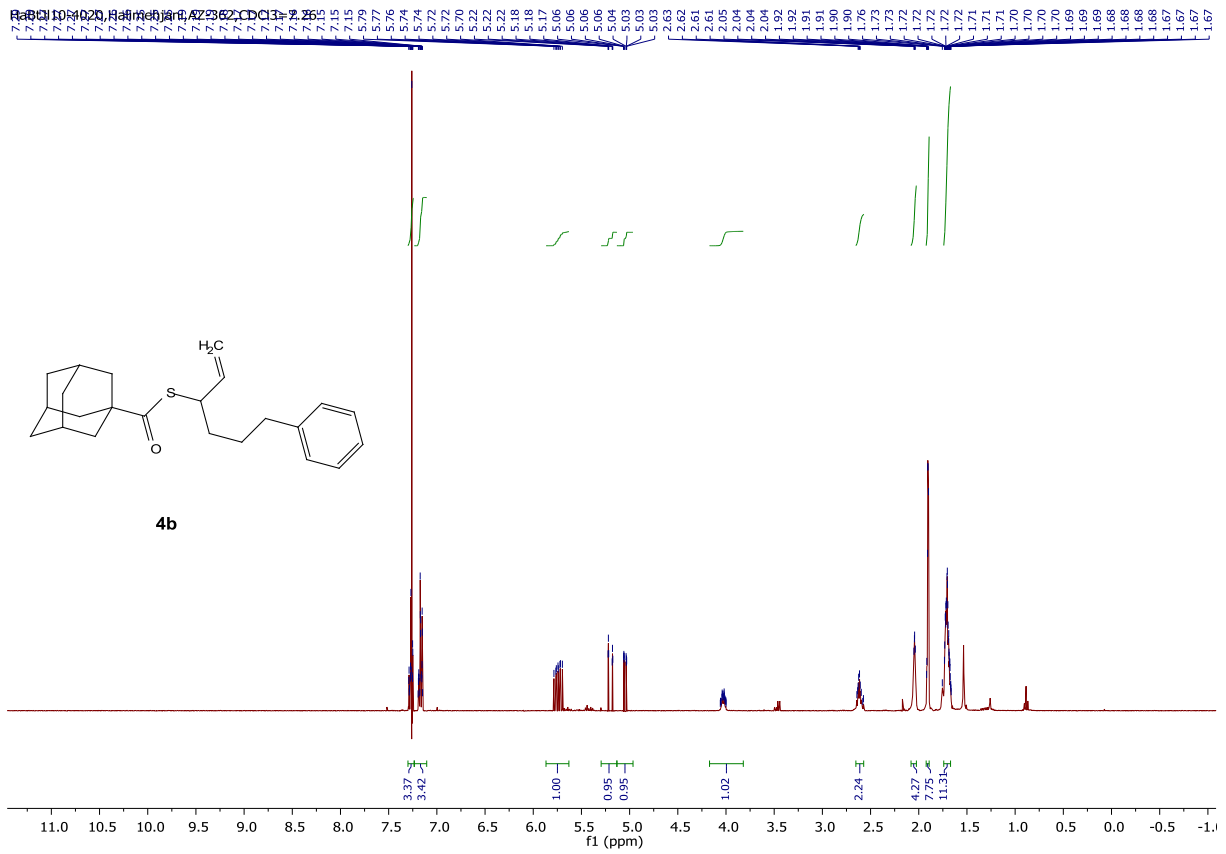


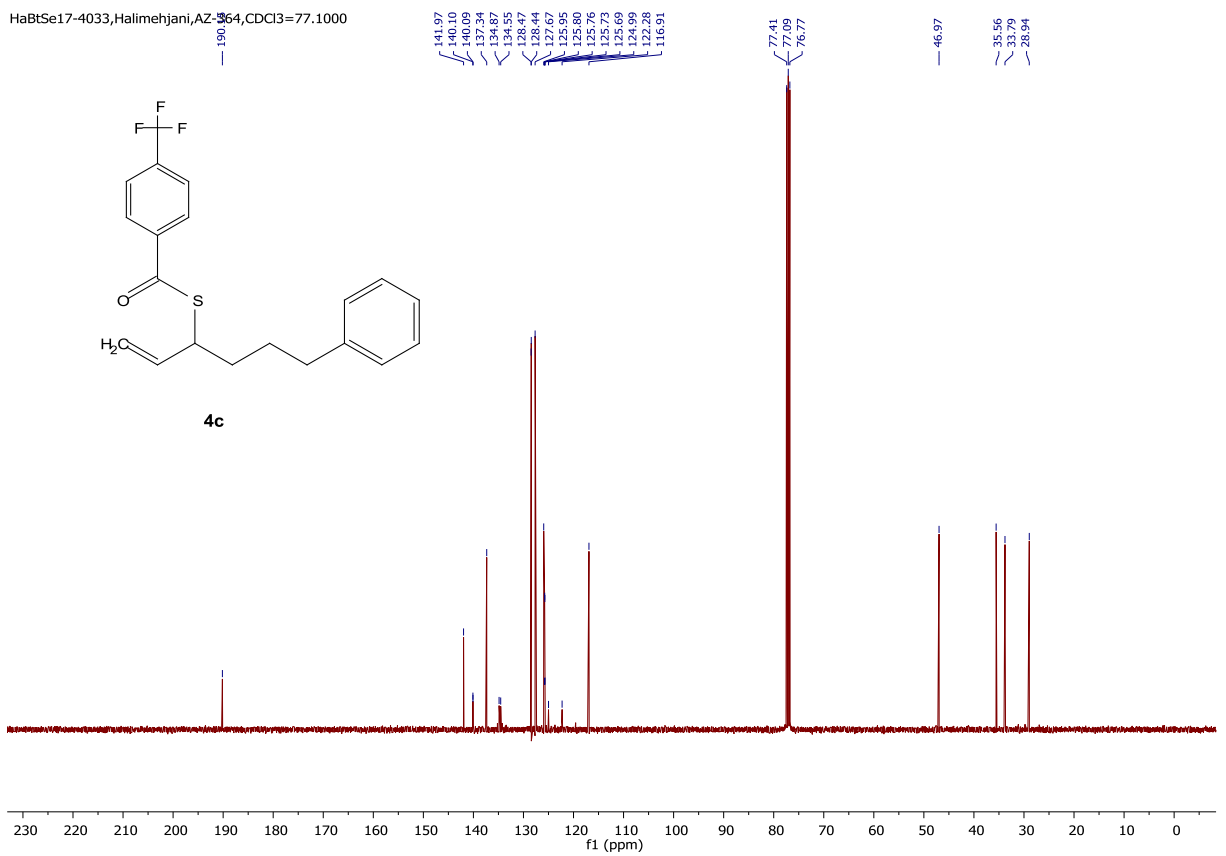
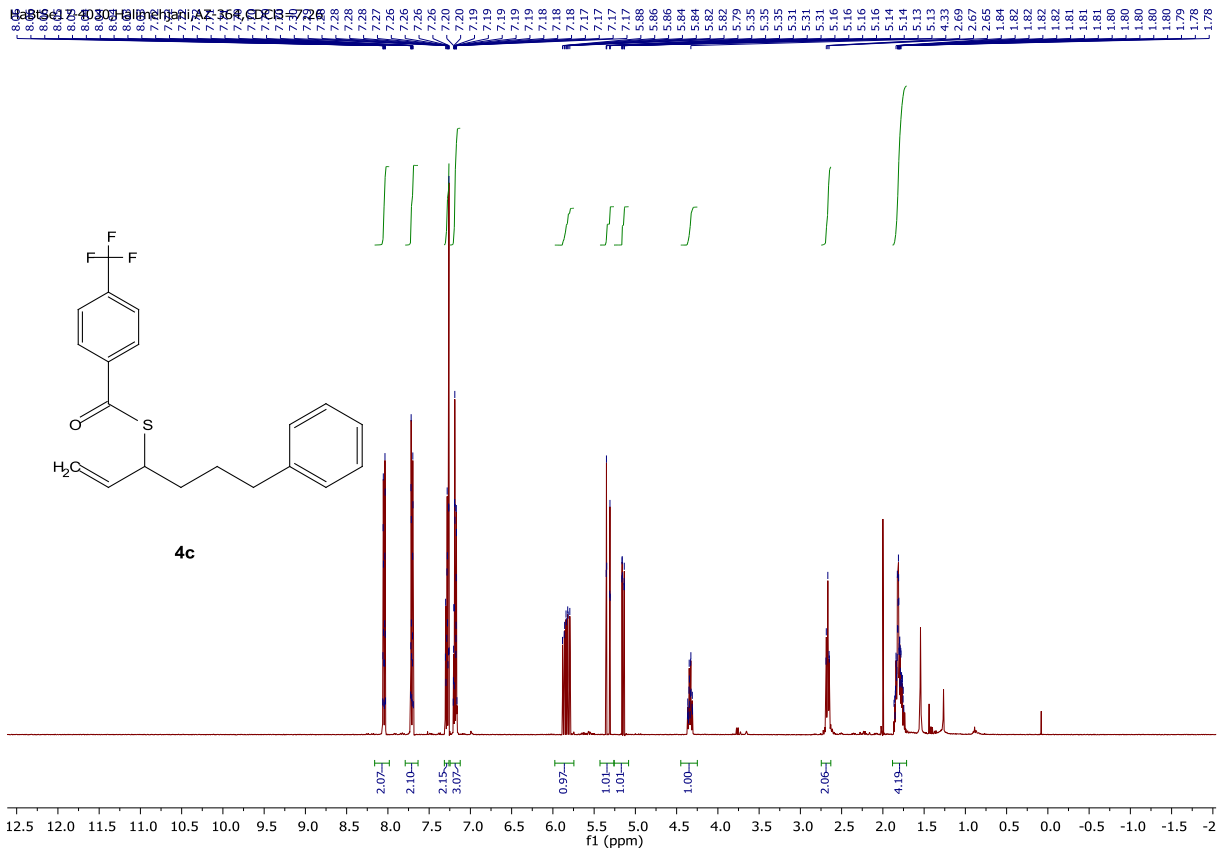




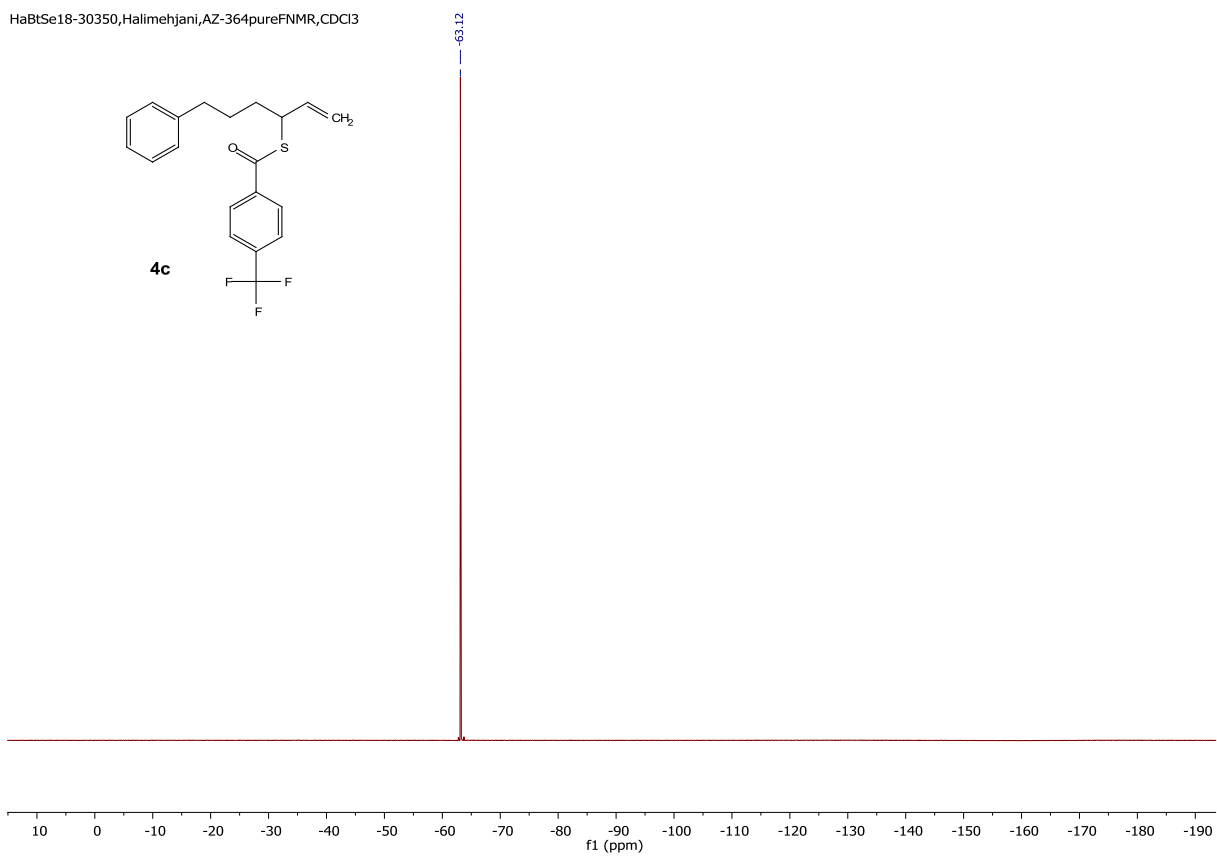
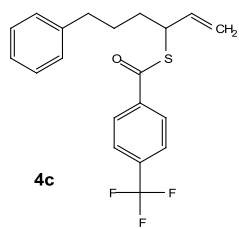








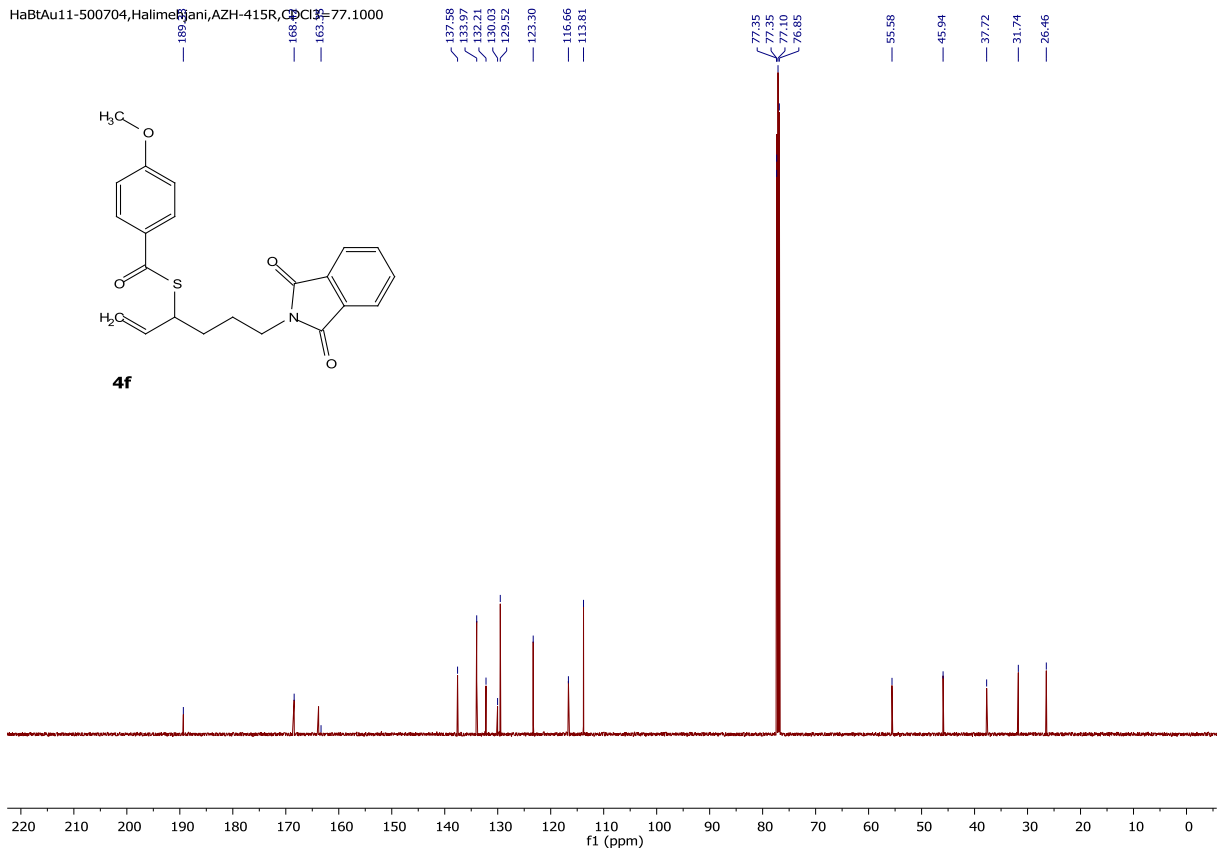
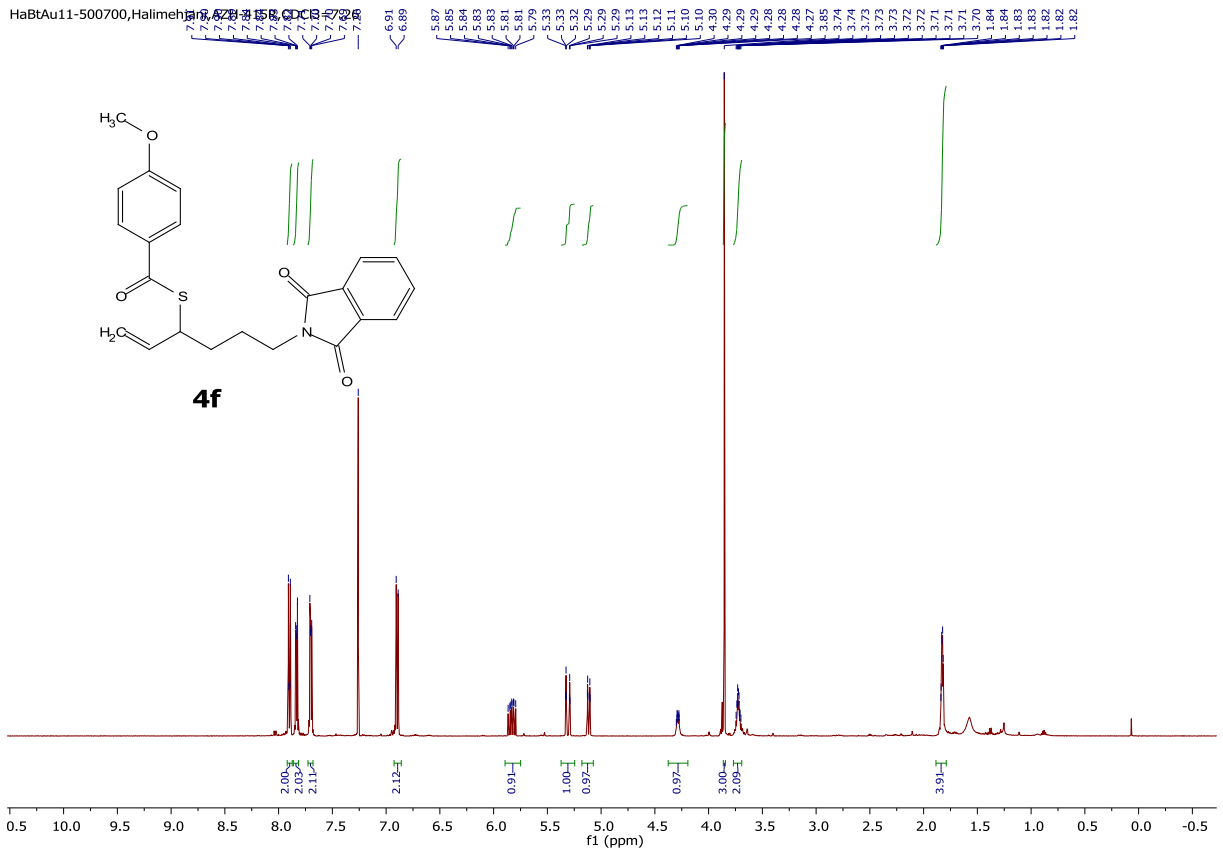
HaBtSe18-30350, Halimehjani, AZ-364 pure FNMR, CDCl<sub>3</sub>

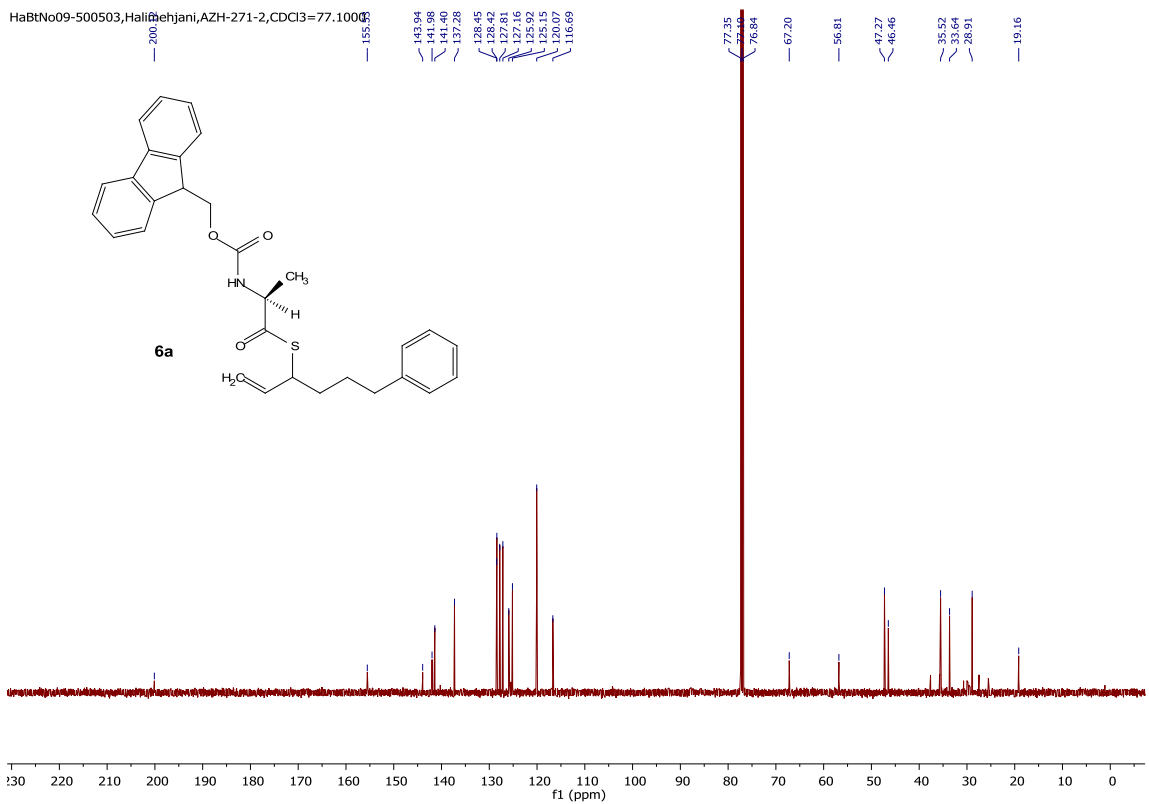
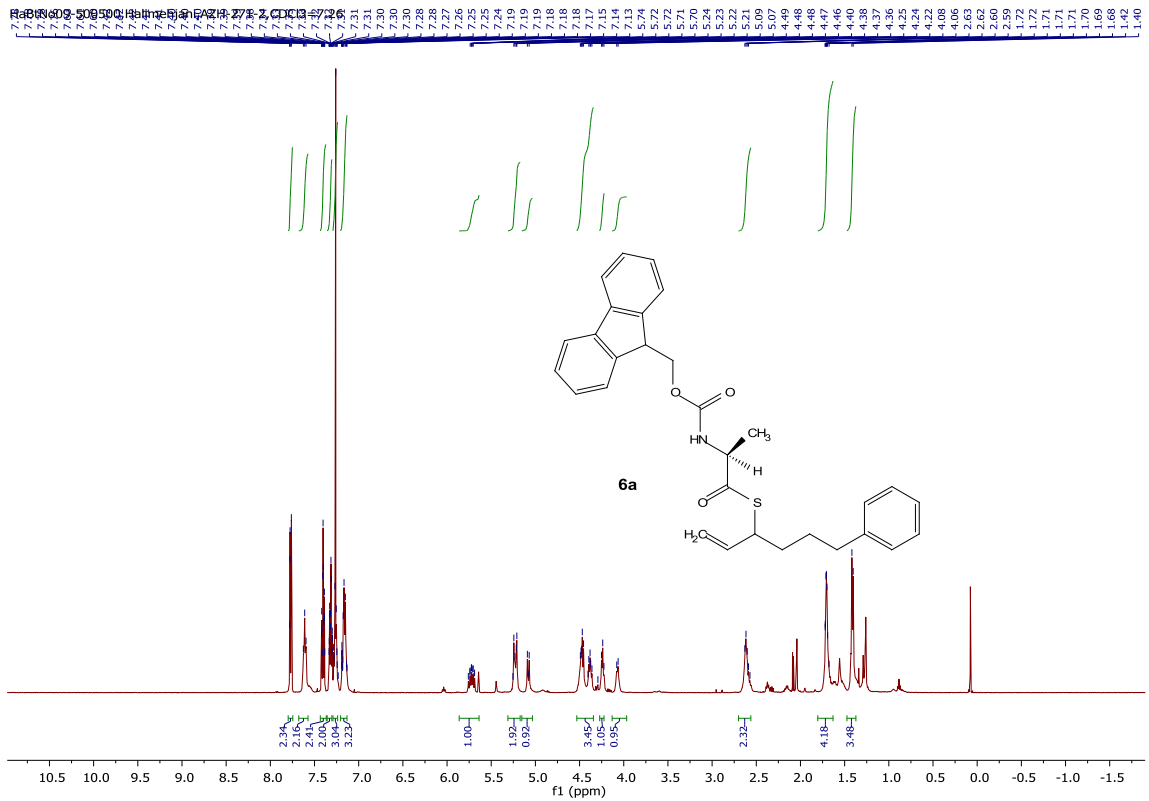


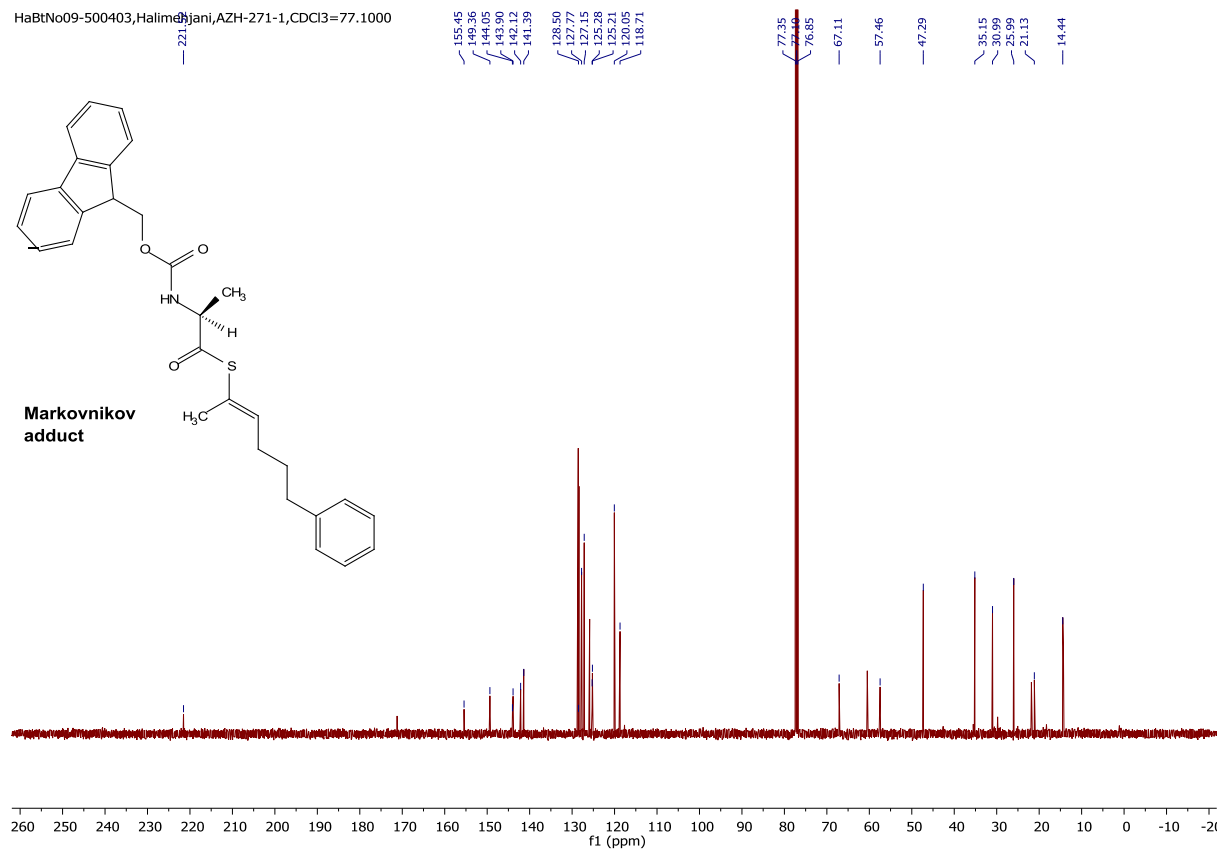
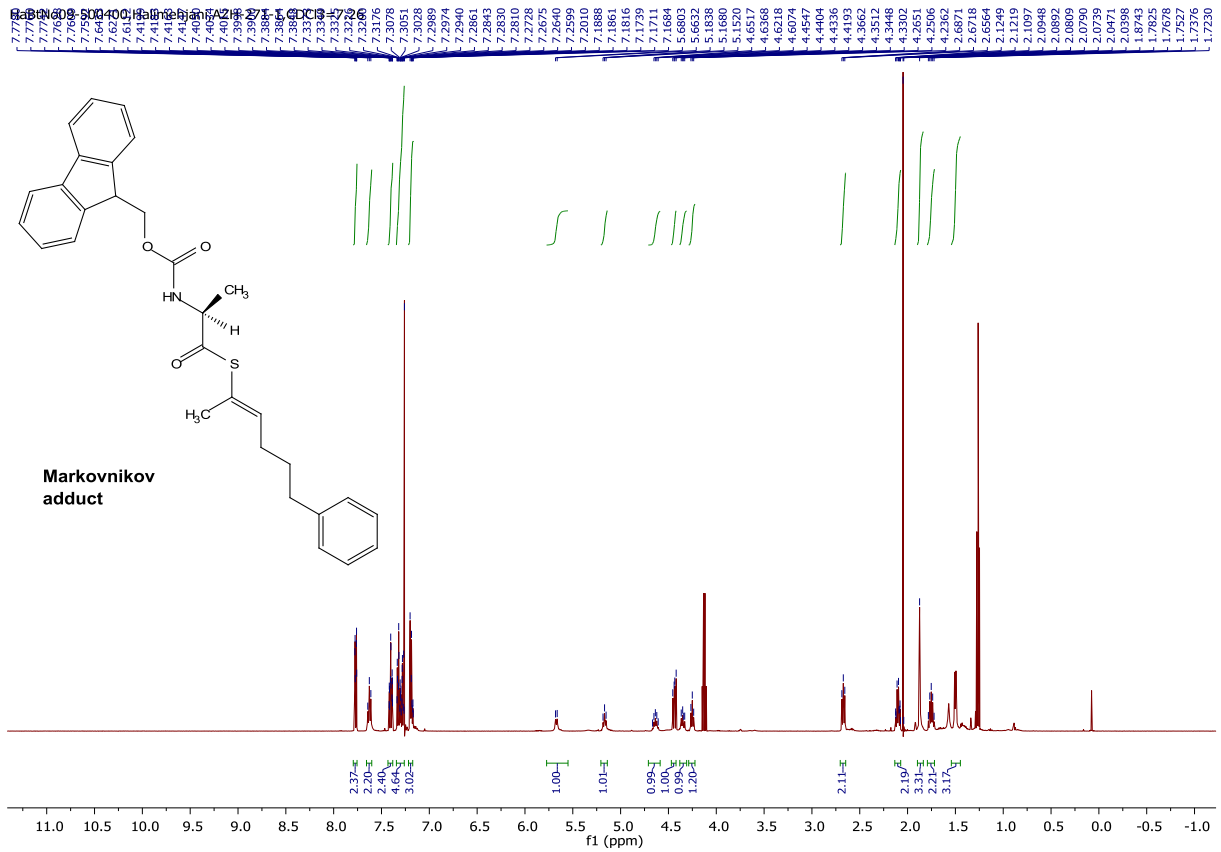


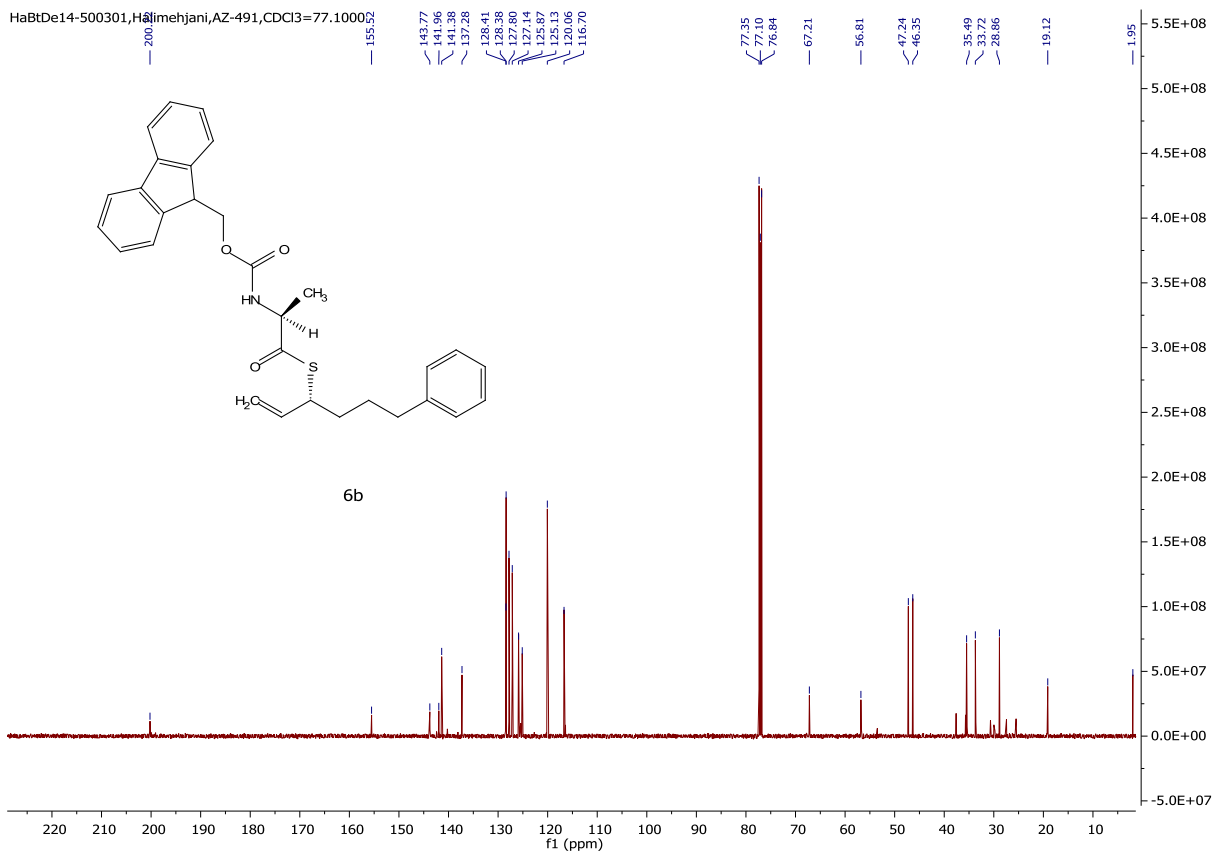
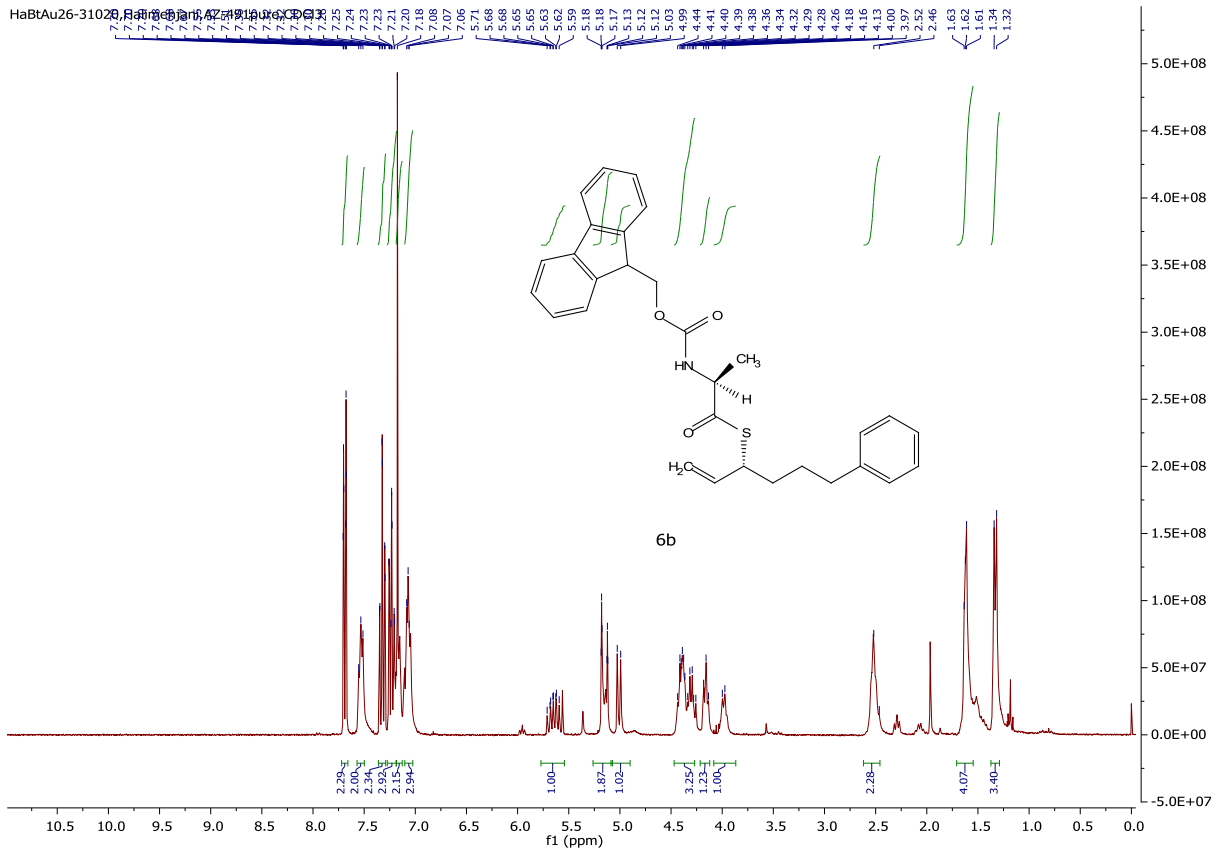




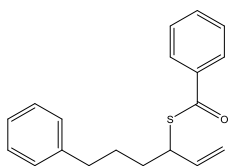




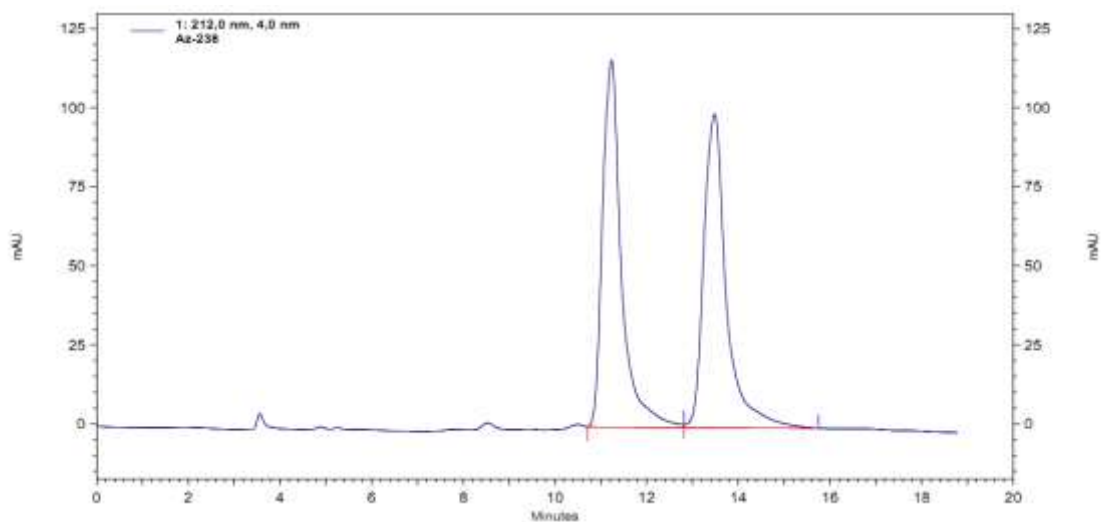




## HPLC data

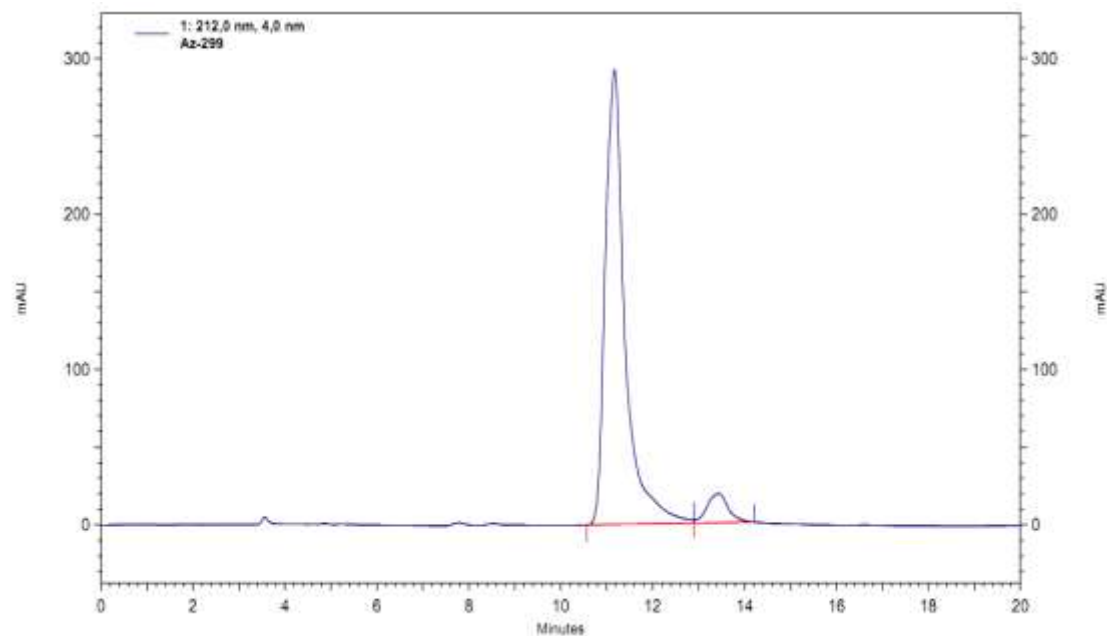


*S*-(6-phenylhex-1-en-3-yl) benzothioate (**3a**)



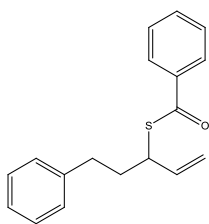
1: 212,0 nm, 4,0 nm  
Results

Peak Number	Retention Time	Area Percent	Area
1	11,236	49,566	447775274
2	13,486	50,434	455615964
Totals			903391238

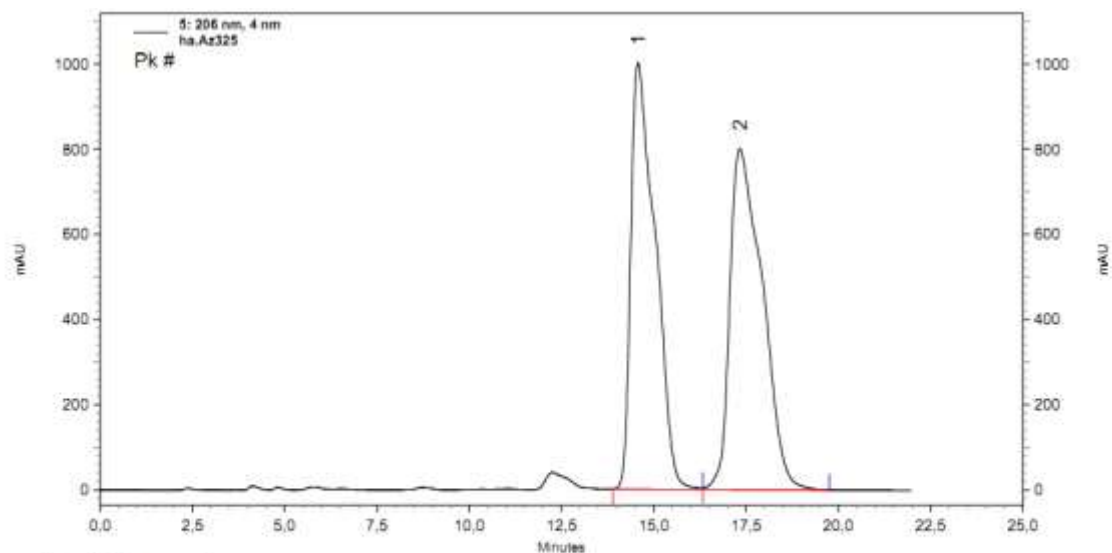


1: 212,0 nm, 4,0 nm  
Results

Peak Number	Retention Time	Area Percent	Area
1	11,172	93,580	1171863077
2	13,439	6,420	80393843
Totals			1252256920

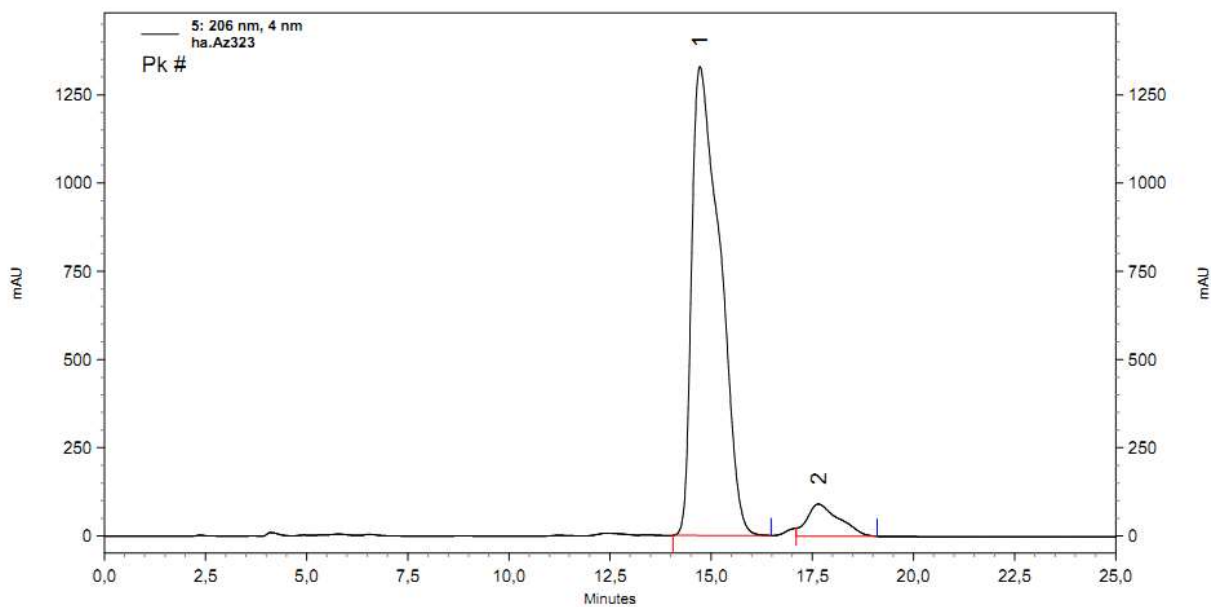


S-(5-phenylpent-1-en-3-yl) benzothioate (**3b**)



5: 206 nm, 4 nm Results

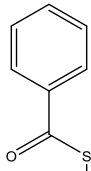
Pk #	Retention Time	Area Percent	Lambda Max
1	14,573	48,459	197
2	17,333	51,541	197



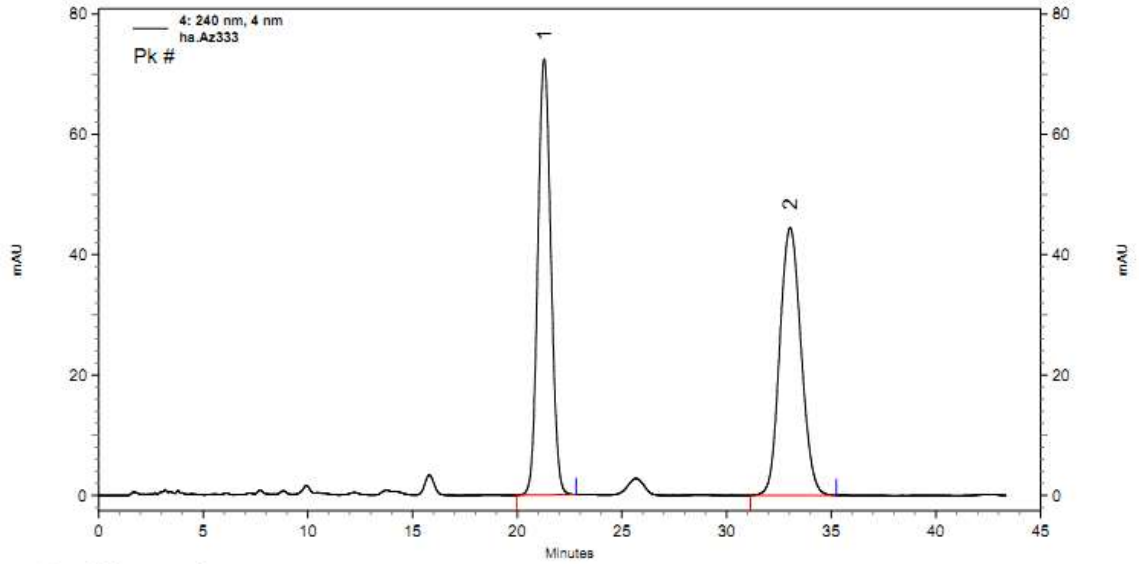
5: 206 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	14,720	92,731	199
2	17,653	7,269	194



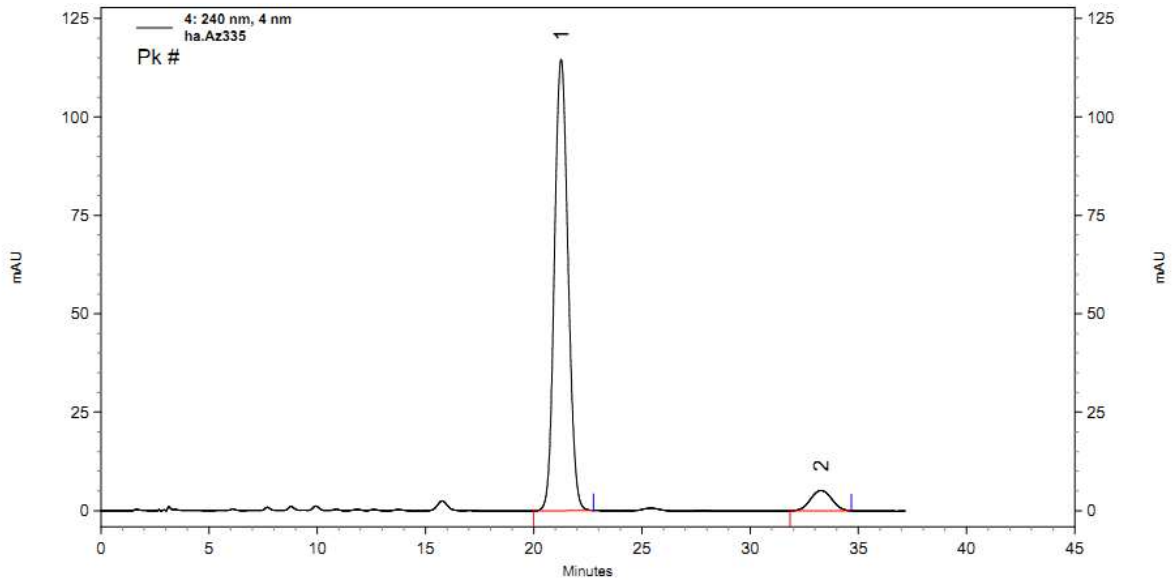


S-tridec-1-en-3-yl benzothioate (**3c**)



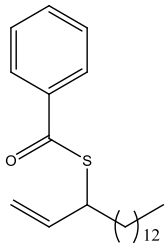
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	21,287	50,052	198
2	33,040	49,948	198

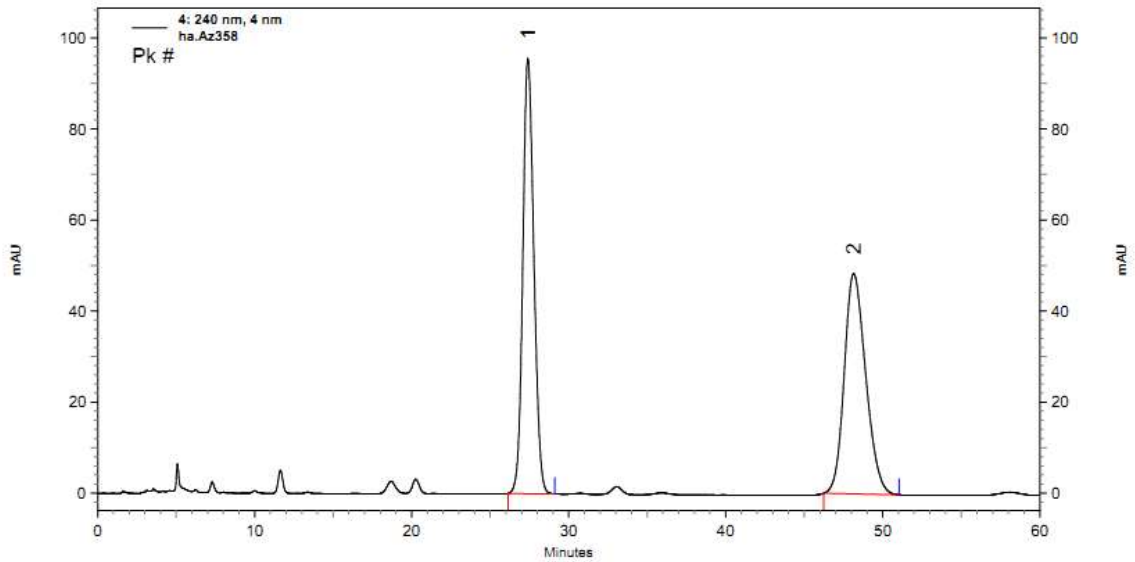


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	21,267	93,405	198
2	33,273	6,595	198

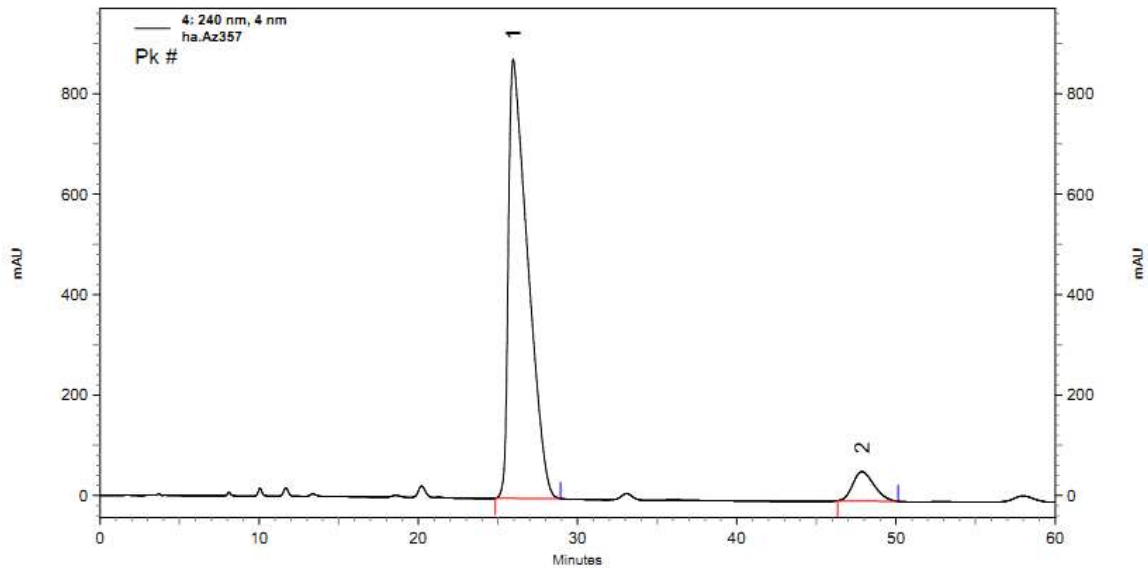


*S*-hexadec-1-en-3-yl benzothioate (**3d**):



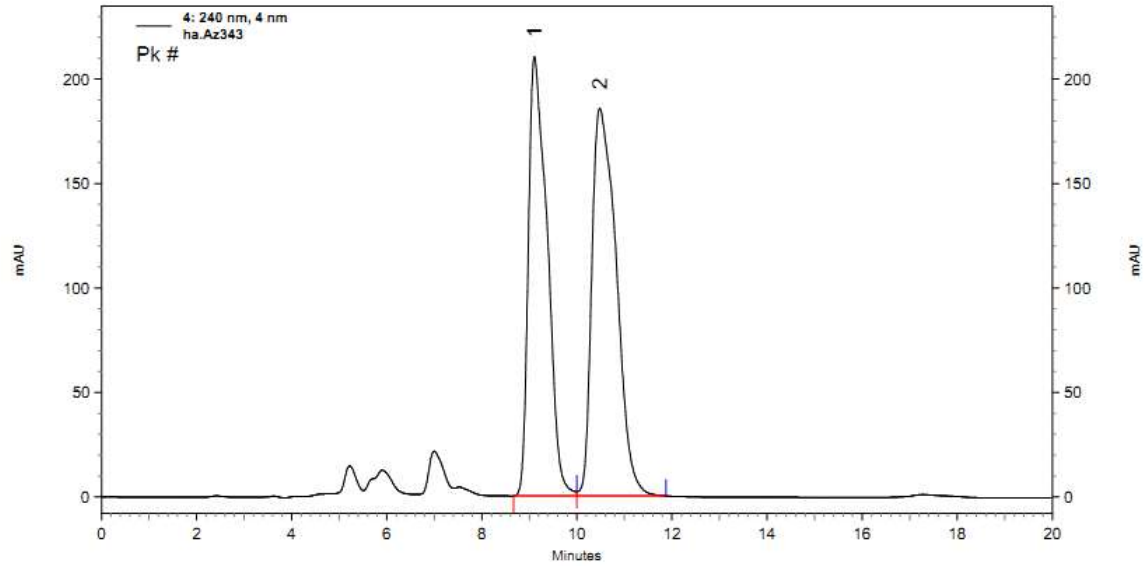
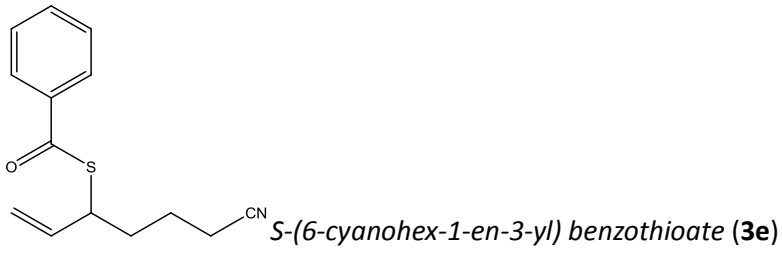
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	27,400	50,311	198
2	48,147	49,689	198



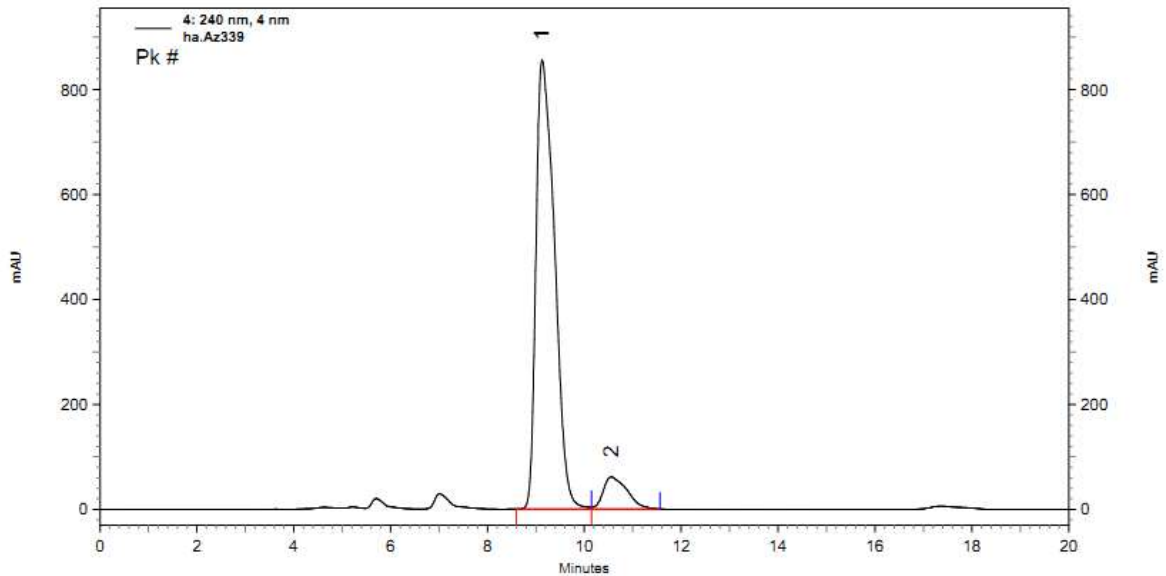
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	25,953	93,135	199
2	47,867	6,865	198



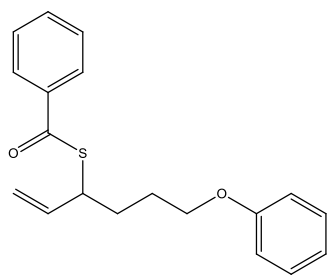
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9,107	46,623	198
2	10,480	53,377	198

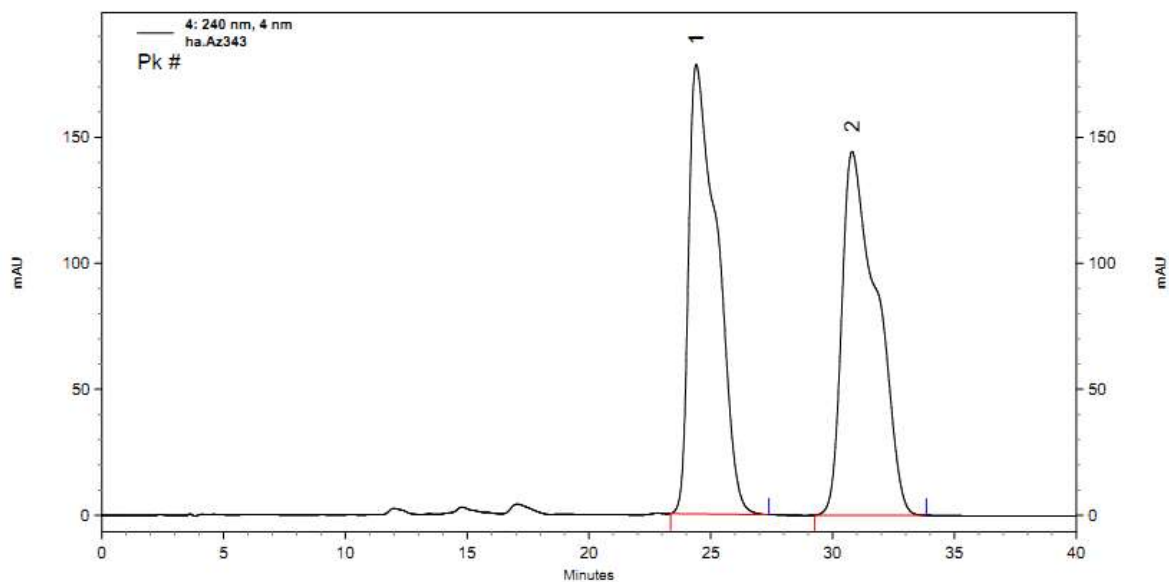


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9,127	91,578	199
2	10,553	8,422	198

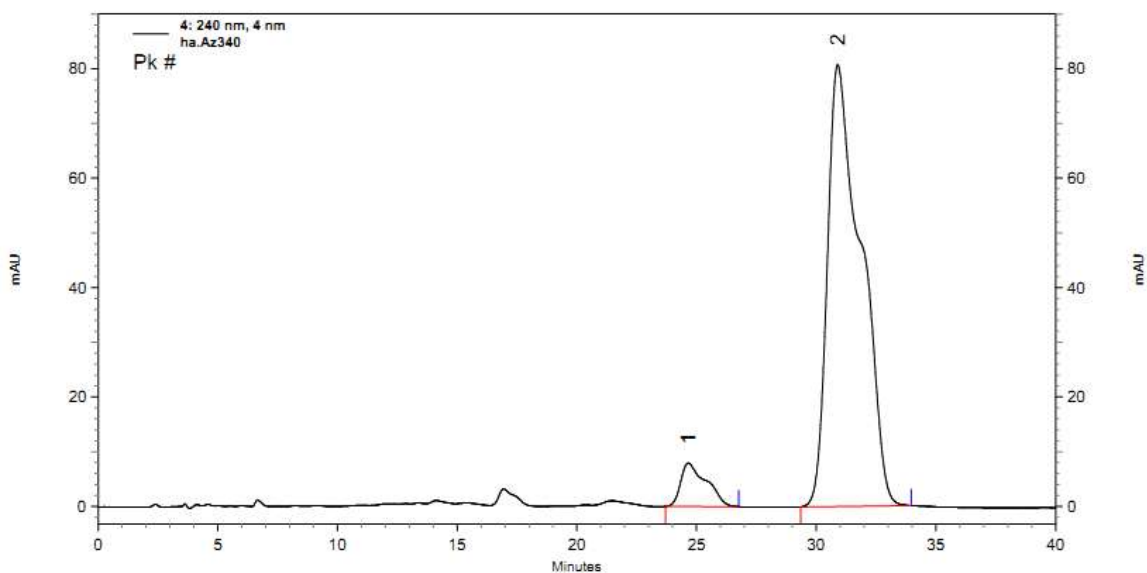


*S*-(6-phenoxyhex-1-en-3-yl) benzothioate (**3f**)



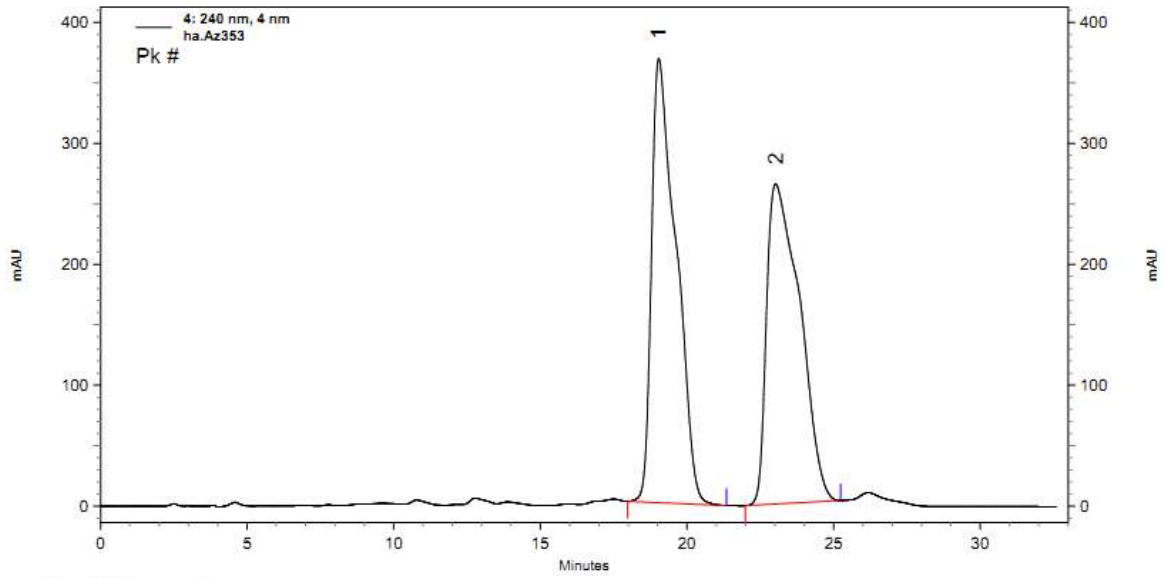
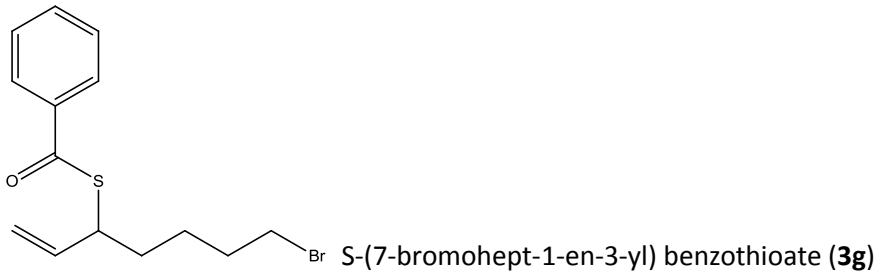
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24,407	50,051	196
2	30,800	49,949	196



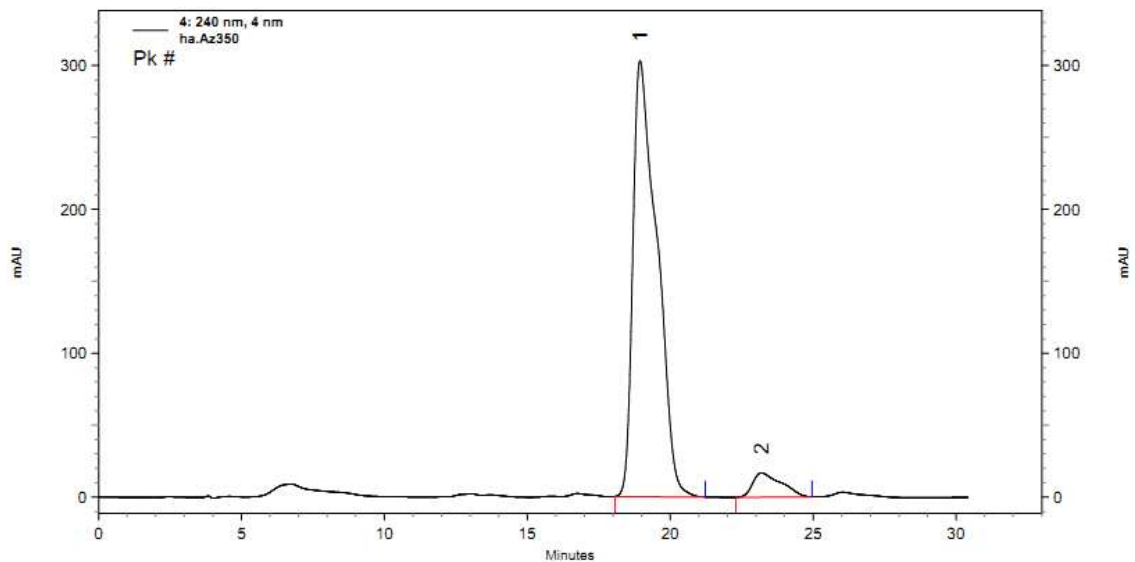
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24,660	7,017	195
2	30,900	92,983	195



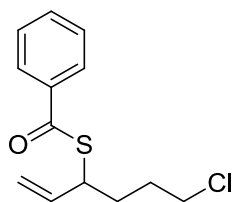
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	19,040	50,711	198
2	23,027	49,289	198

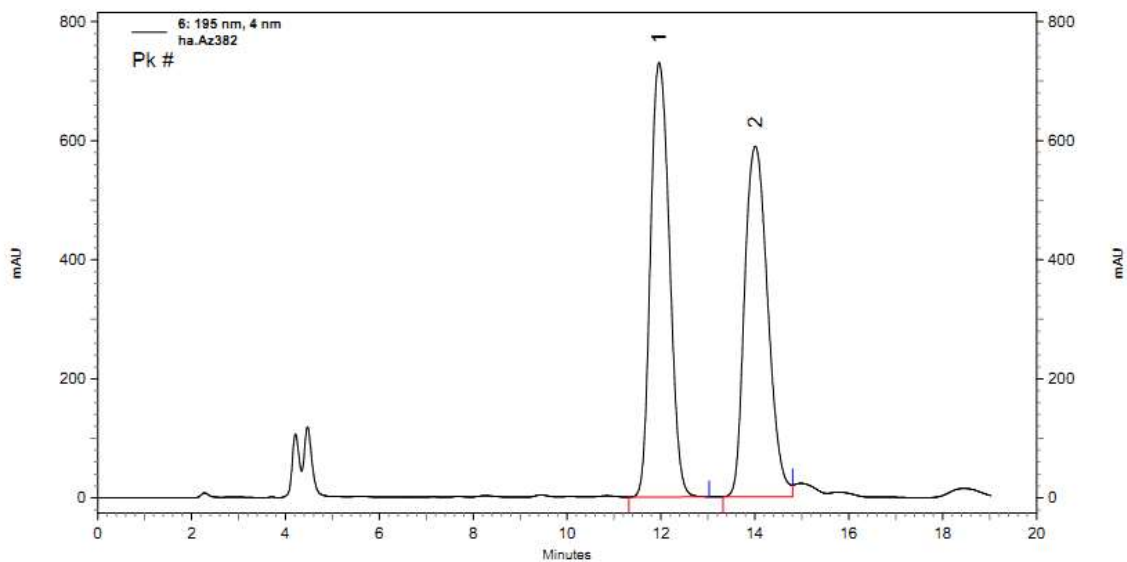


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18,947	93,809	198
2	23,193	6,191	198

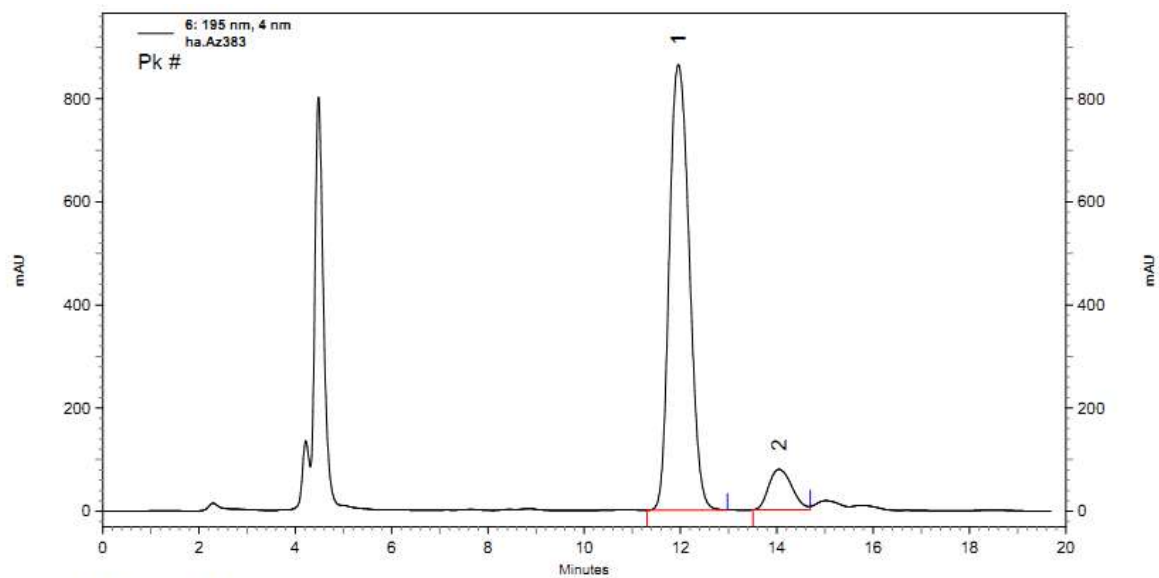


*S*-(6-chlorohex-1-en-3-yl) benzothioate (**3h**):



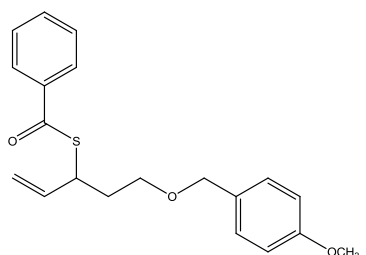
6: 195 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	11,960	50,327	198
2	14,007	49,673	198

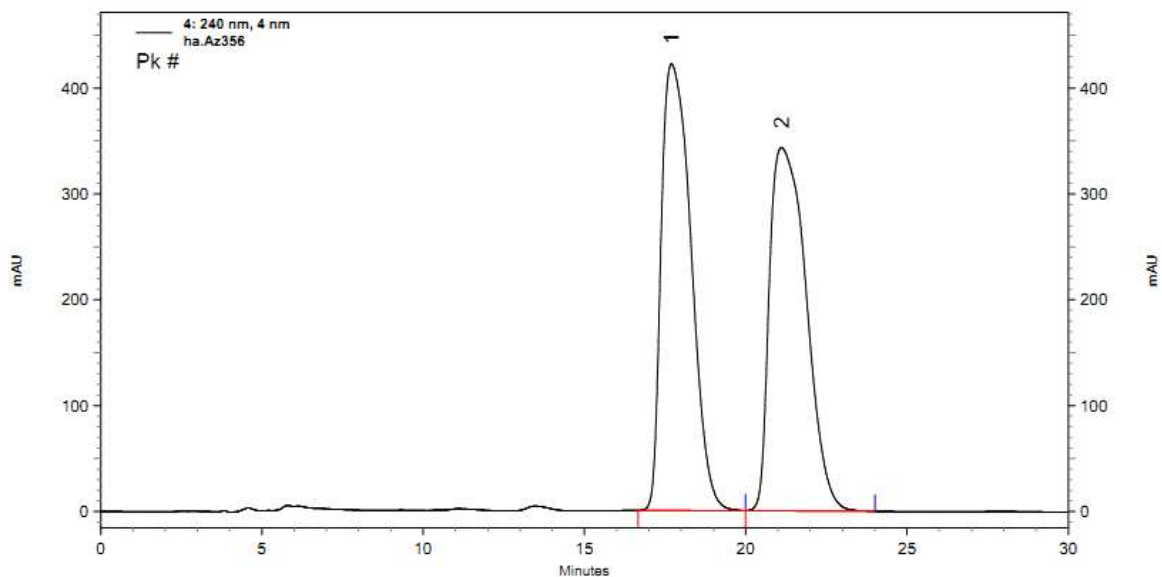


6: 195 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	11,953	90,388	199
2	14,047	9,612	198

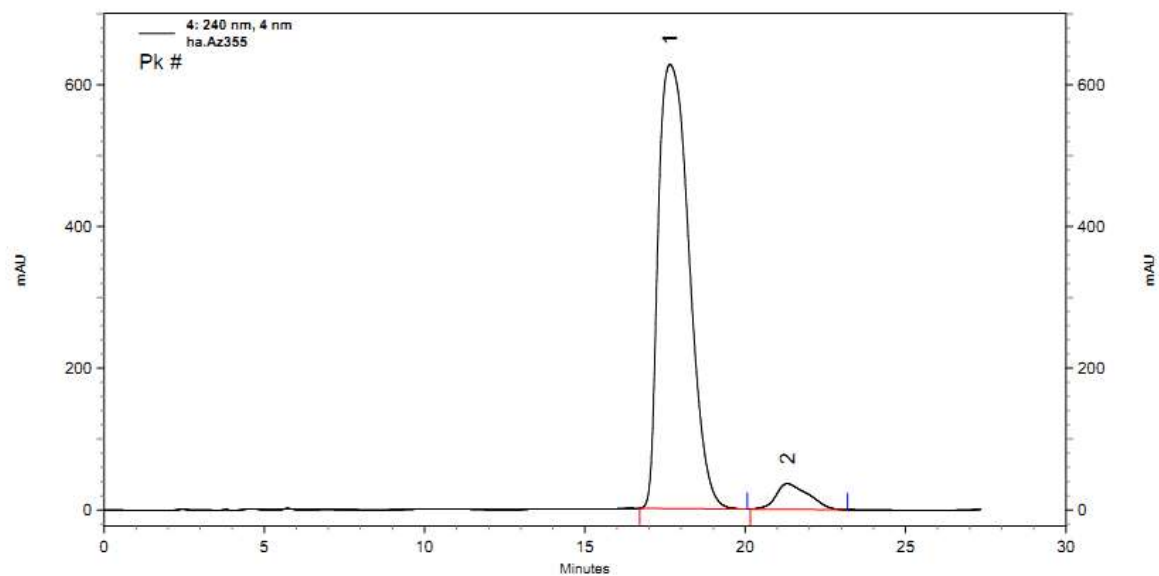


*S*-(5-((4-methoxybenzyl)oxy)pent-1-en-3-yl) benzothioate (**3i**):



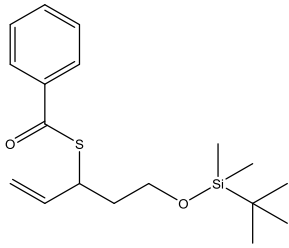
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	17,700	49,997	198
2	21,107	50,003	198

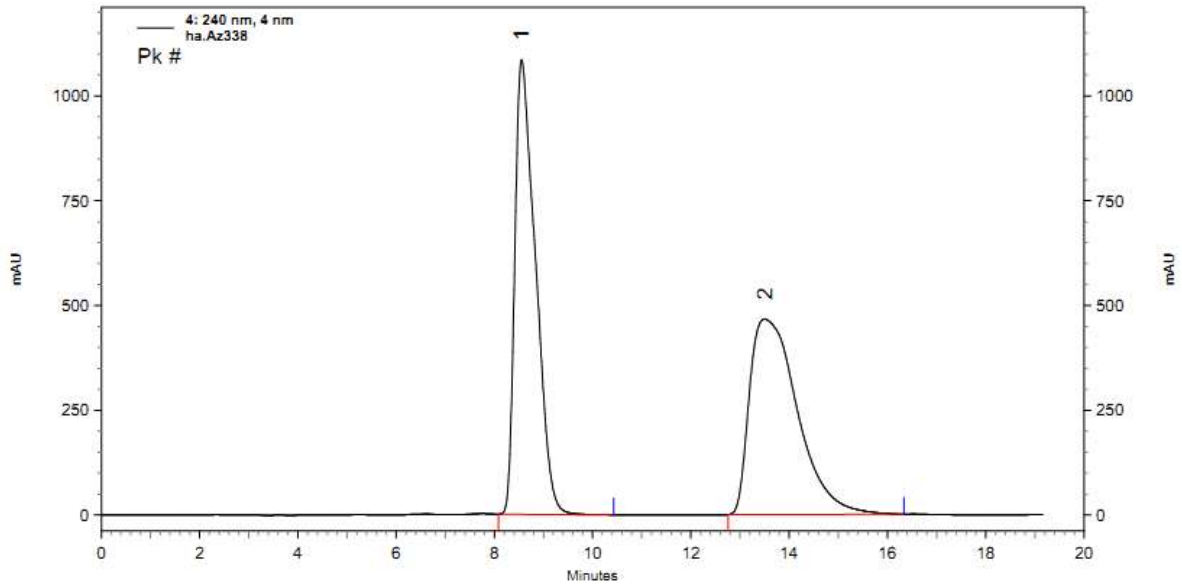


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	17,653	94,309	199
2	21,313	5,691	196

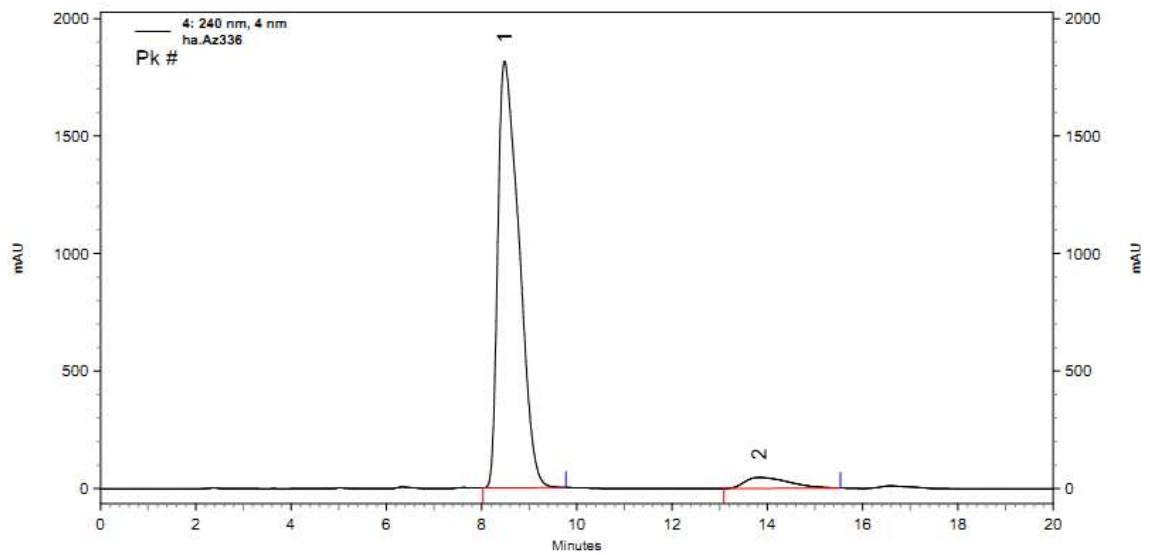


*S*-(5-((*tert*-butyldimethylsilyl)oxy)pent-1-en-3-yl) benzothioate (**3j**):



4: 240 nm, 4 nm Results

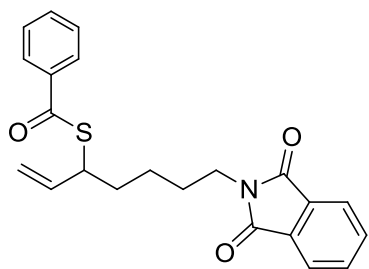
Pk #	Retention Time	Area Percent	Lambda Max
1	8,553	50,018	199
2	13,500	49,982	198



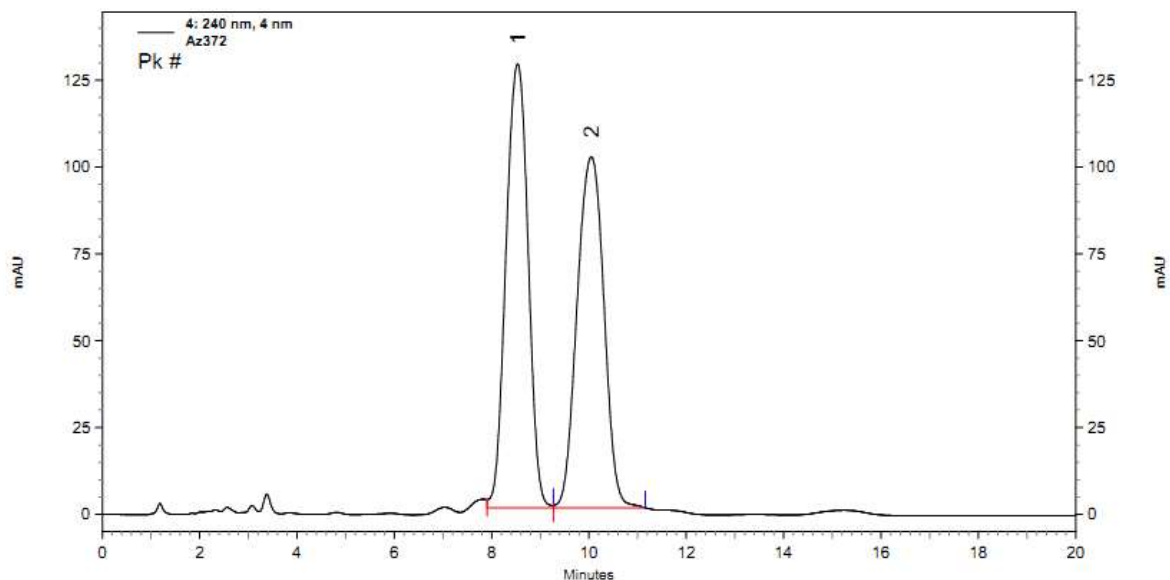
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8,480	94,884	200
2	13,833	5,116	198



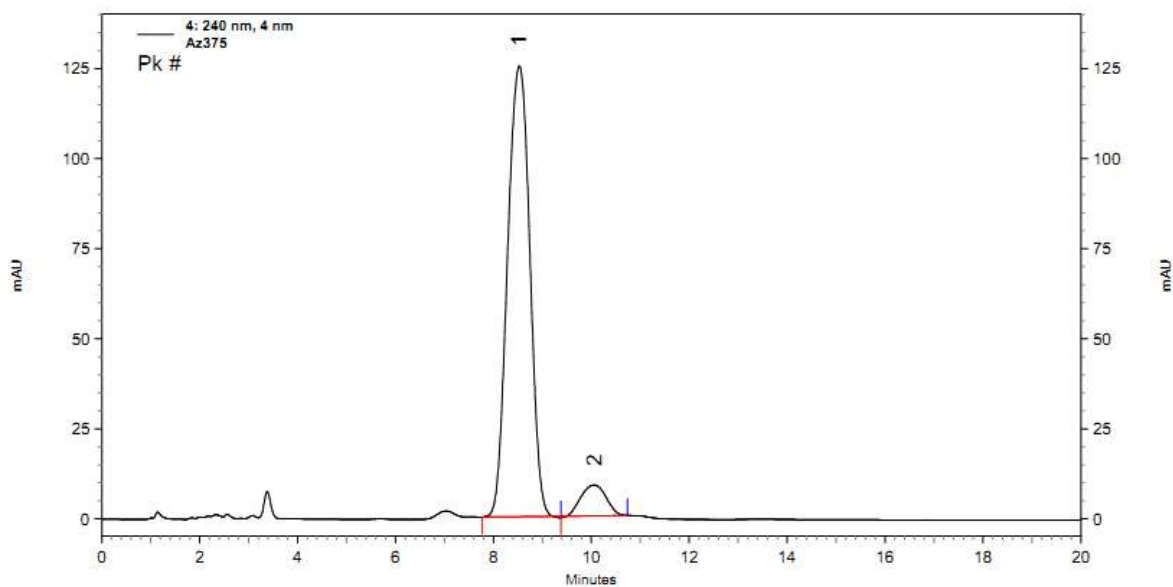


*S*-(7-(1,3-dioxisoindolin-2-yl)hept-1-en-3-yl) benzothioate (**3k**):



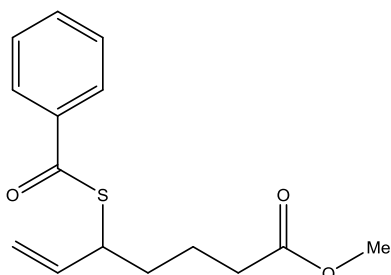
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8,533	51,038	220
2	10,047	48,962	220

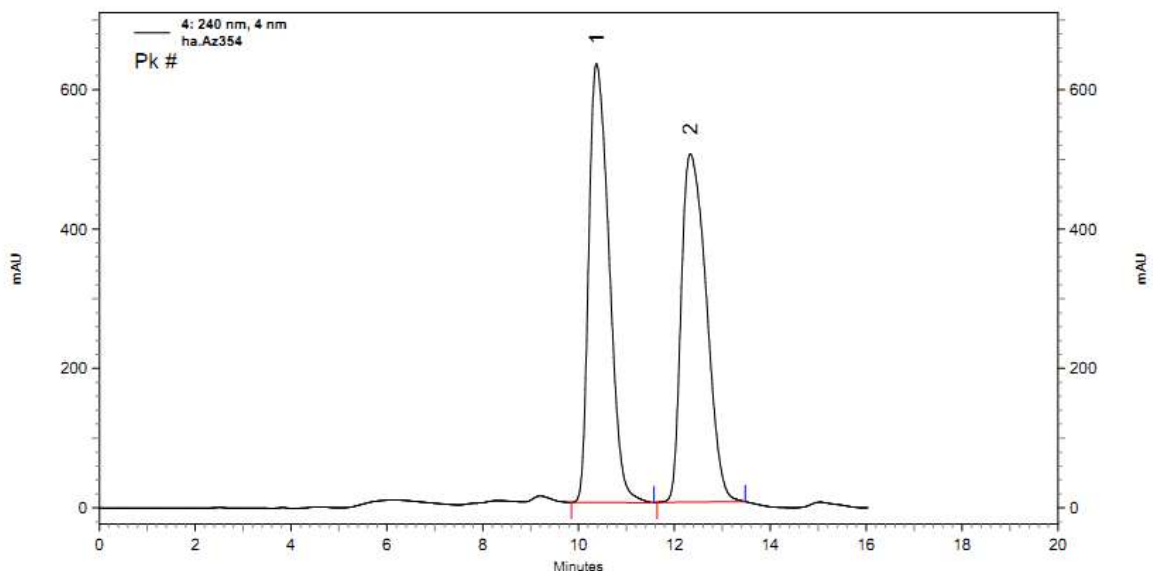


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	8,527	92,789	220
2	10,060	7,211	220

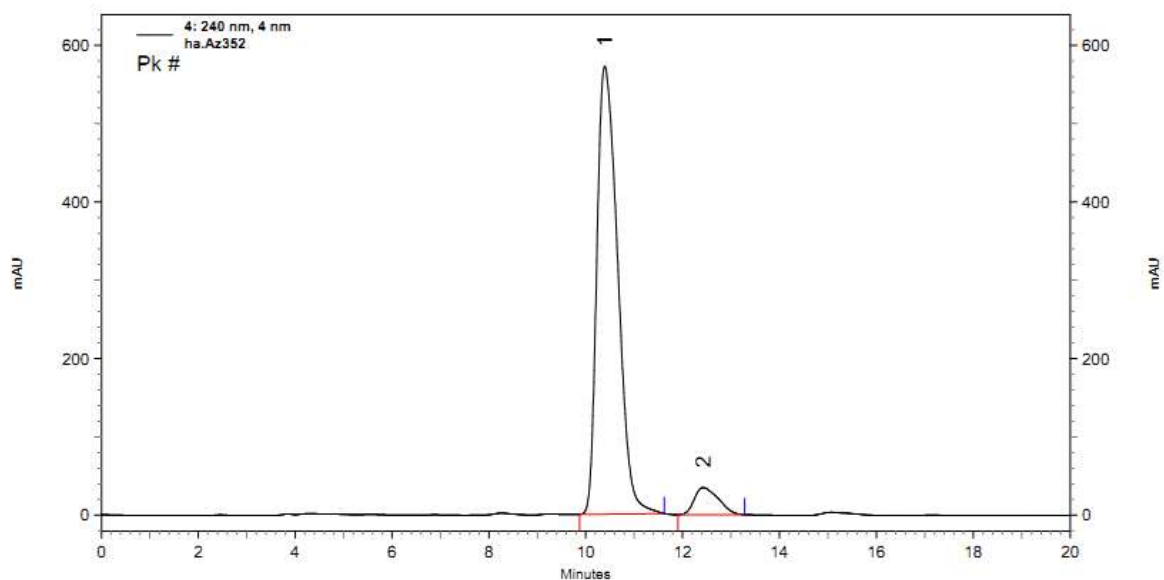


Methyl 5-(benzoylthio)hept-6-enoate (**3m**):



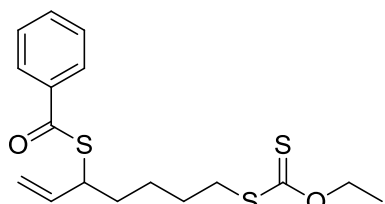
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10,373	50,487	199
2	12,333	49,513	199

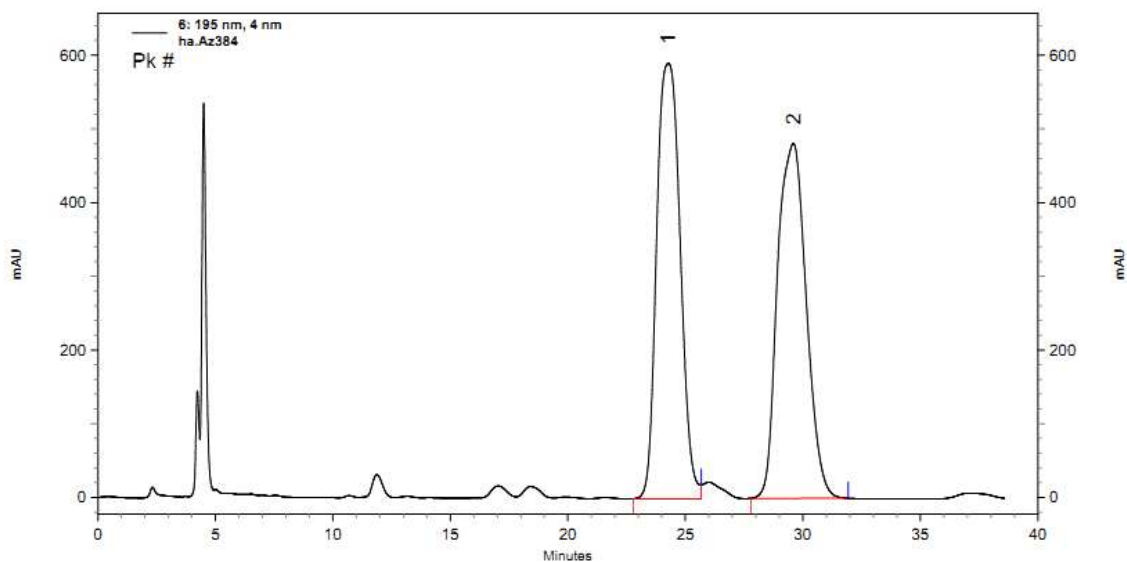


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	10,393	93,471	199
2	12,427	6,529	198

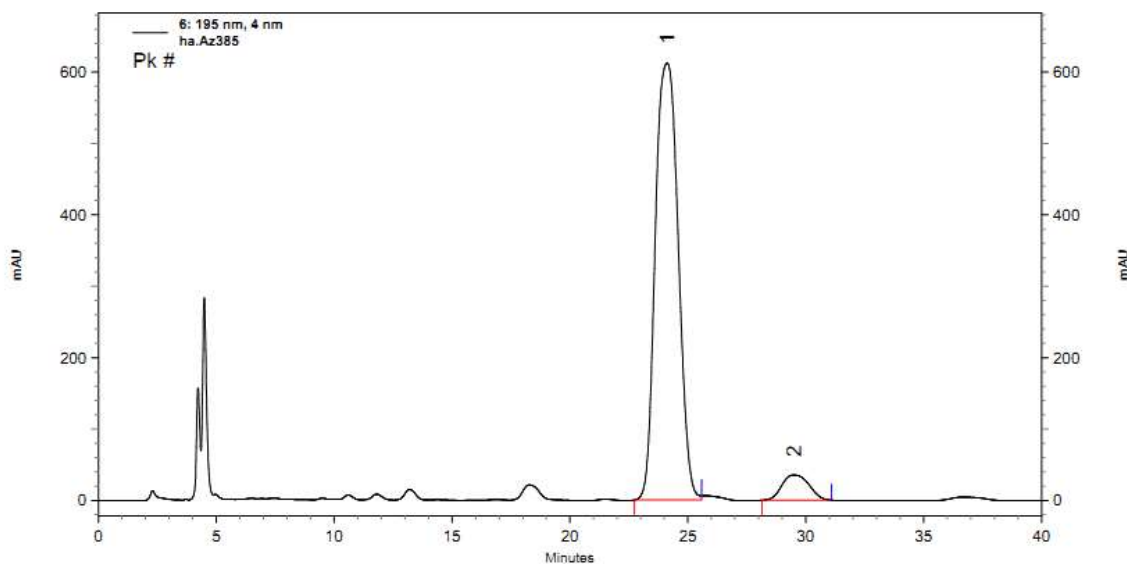


*S*-(7-((ethoxycarbonothioyl)thio)hept-1-en-3-yl) benzothioate (**3n**)



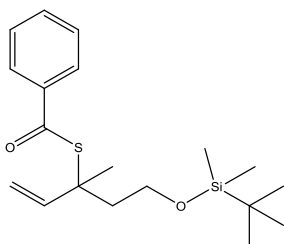
6: 195 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24,273	50,167	199
2	29,600	49,833	199

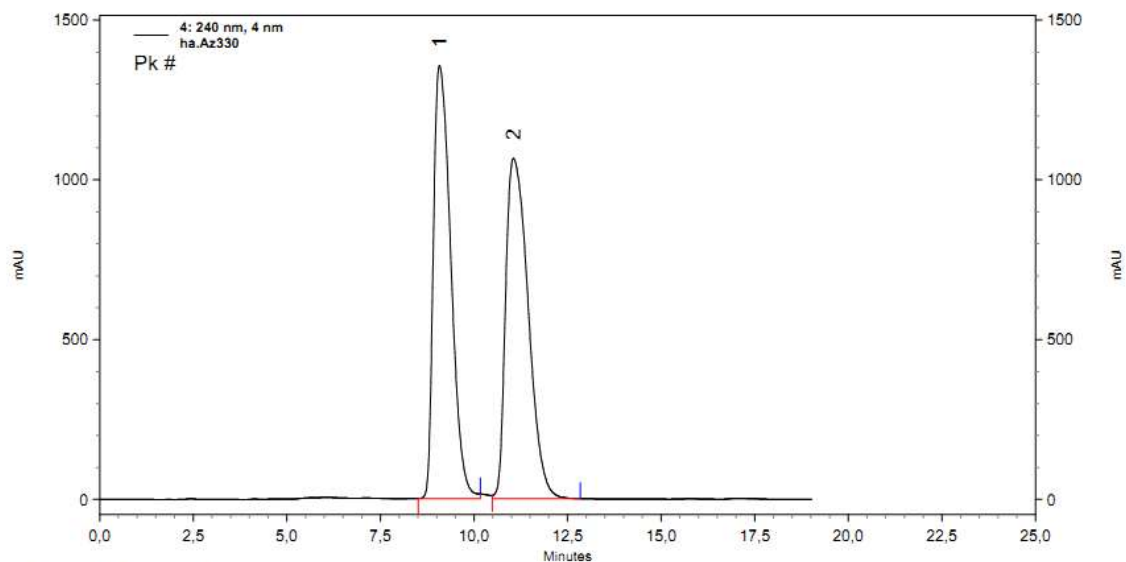


6: 195 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24,127	93,603	199
2	29,507	6,397	198

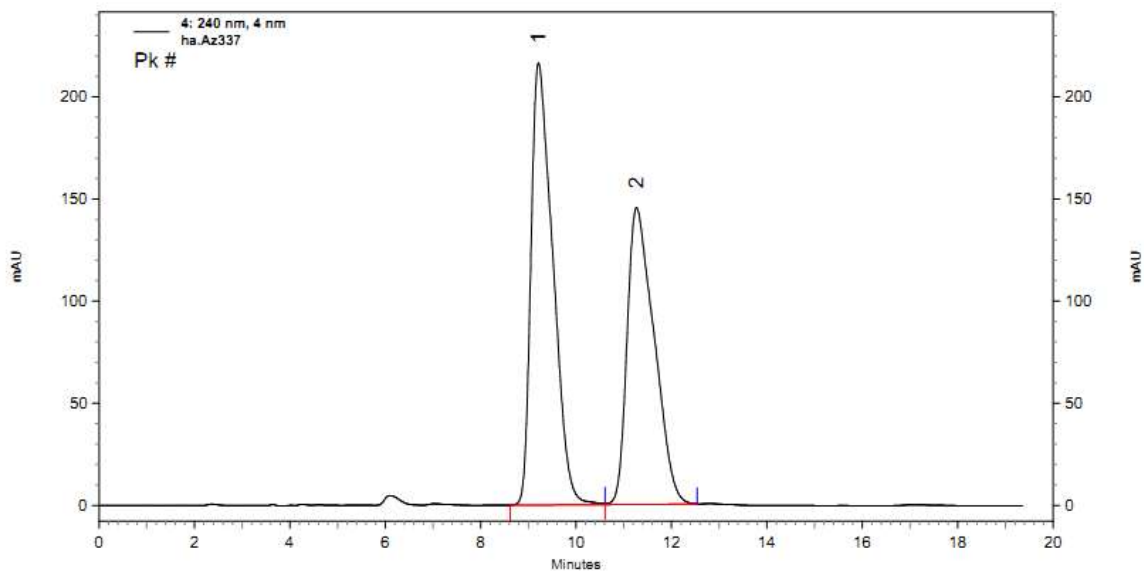


S-(5-((tert-butyldimethylsilyloxy)-3-methylpent-1-en-3-yl) benzothioate (**30**):



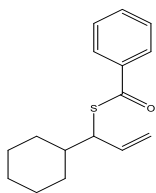
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9,080	49,548	200
2	11,053	50,452	200

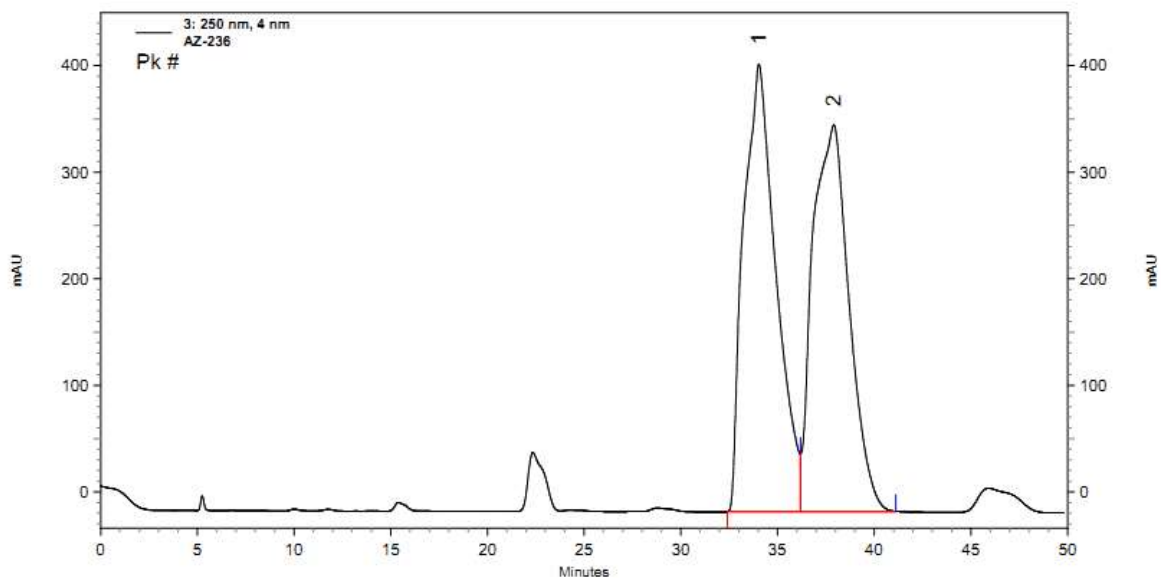


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9,213	54,691	198
2	11,267	45,309	198

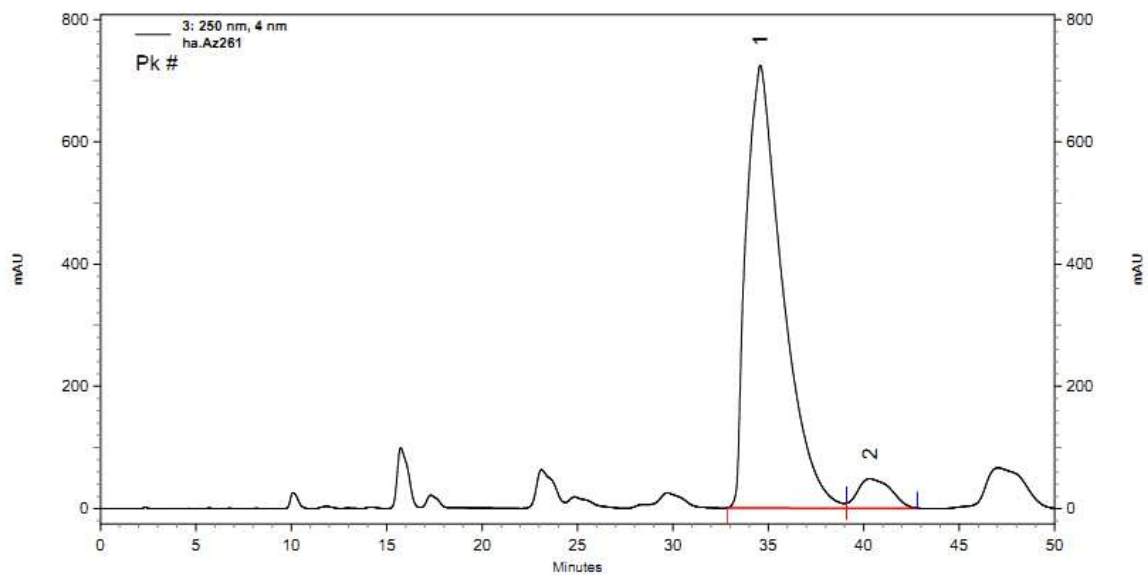


*S*-(1-cyclohexylallyl) benzothioate (**3p**)



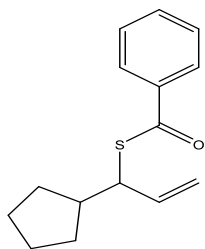
3: 250 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	34,040	50,767	199
2	37,913	49,233	199

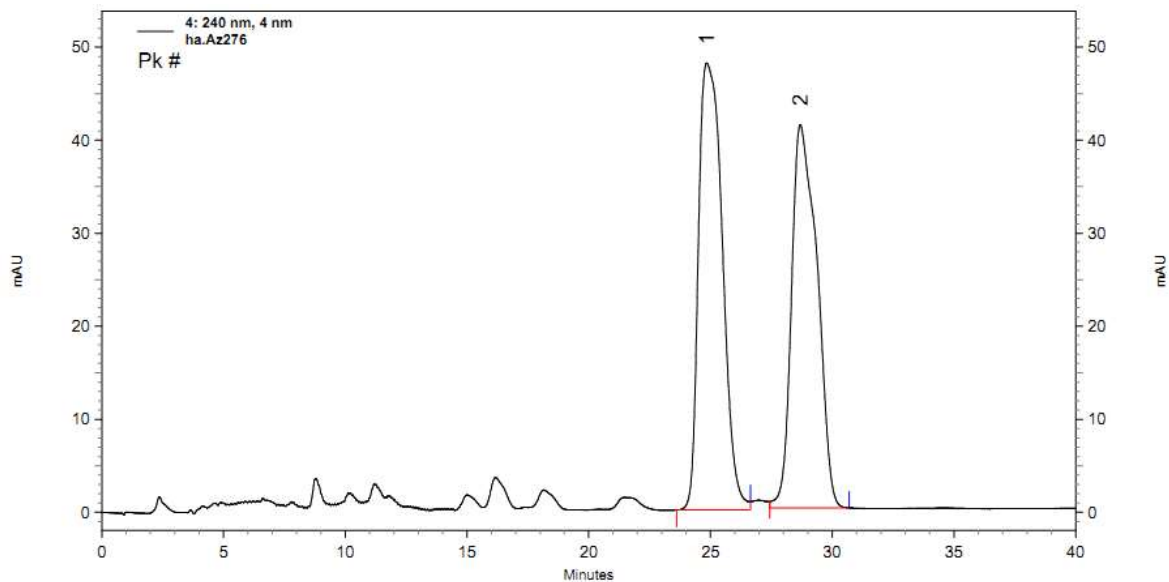


3: 250 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	34,580	94,292	200
2	40,320	5,708	199

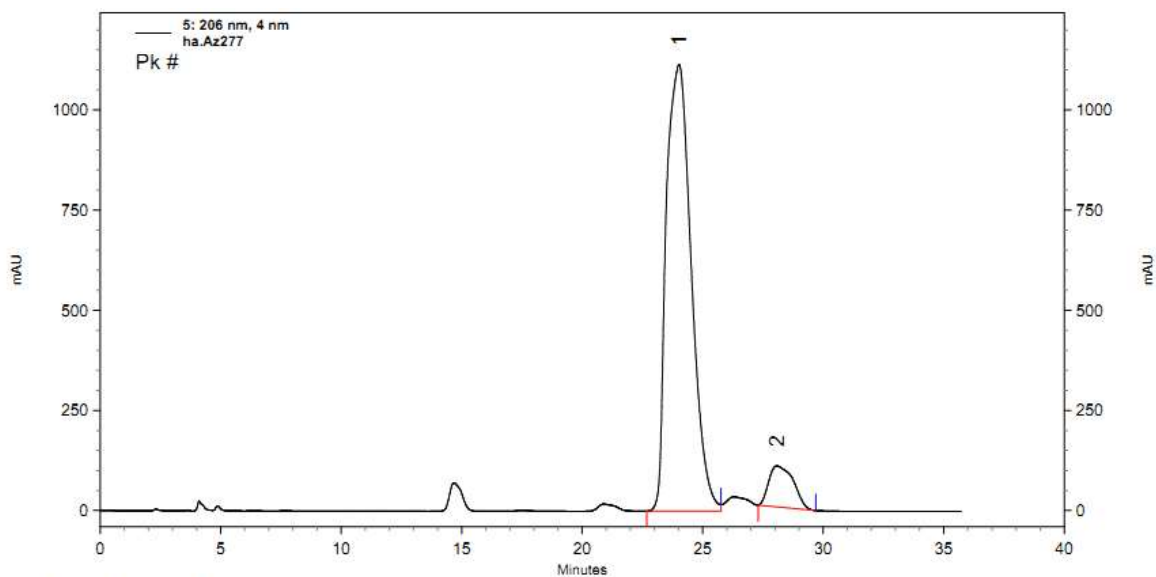


S-(1-cyclopentylallyl) benzothioate (**3q**)



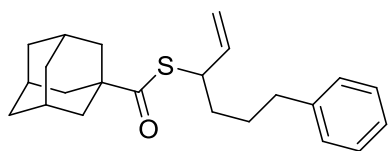
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24,840	52,268	199
2	28,687	47,732	199



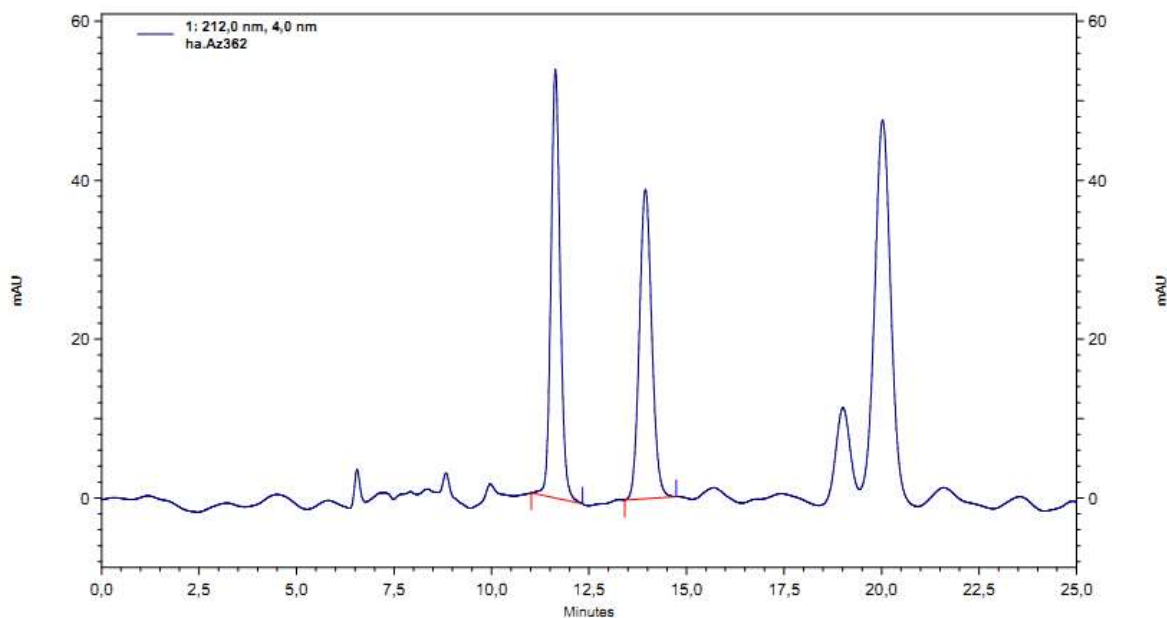
5: 206 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	24,020	91,652	200
2	28,080	8,348	199



(3r,5r,7r)-S-(6-phenylhex-1-en-3-yl) adamantane-1-

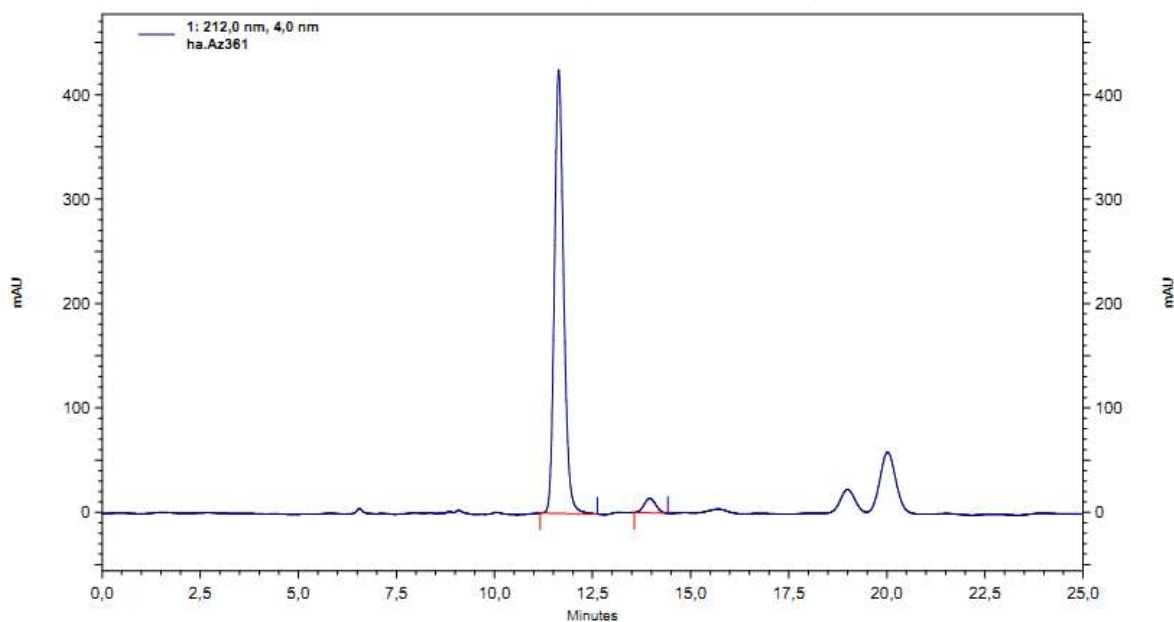
carbothioate (**4b**):



1: 212,0 nm, 4,0 nm

Results

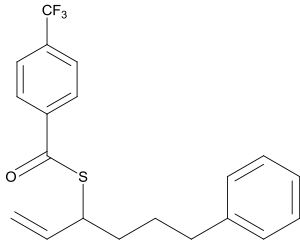
Peak Number	Retention Time	Area Percent	Area
1	11,637	50,771	119373221
2	13,943	49,229	115746189



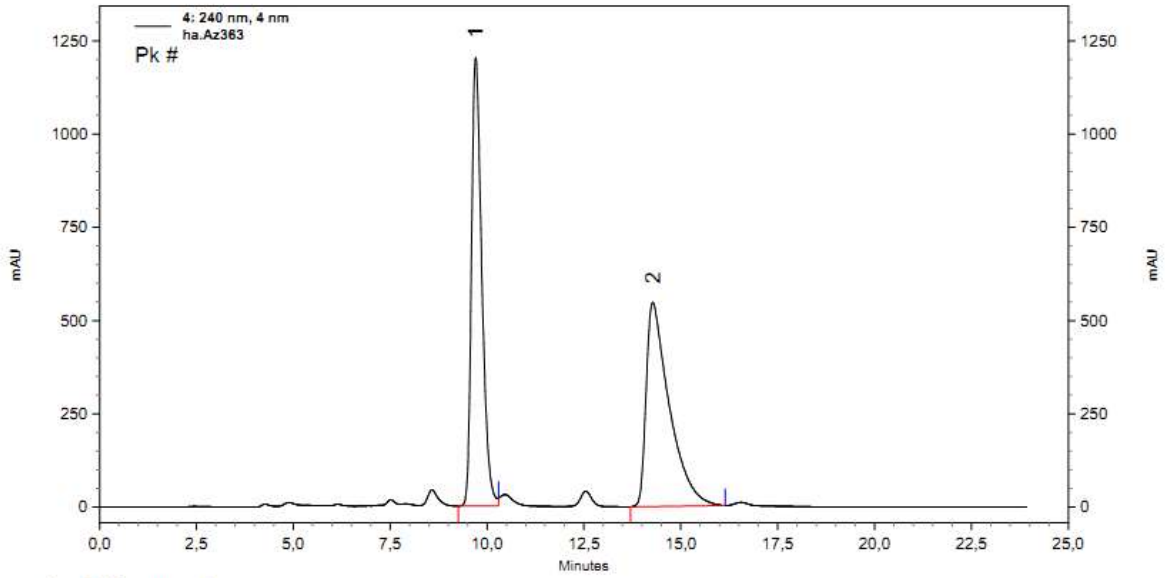
1: 212,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	11,637	96,078	933643028
2	13,960	3,922	38108179

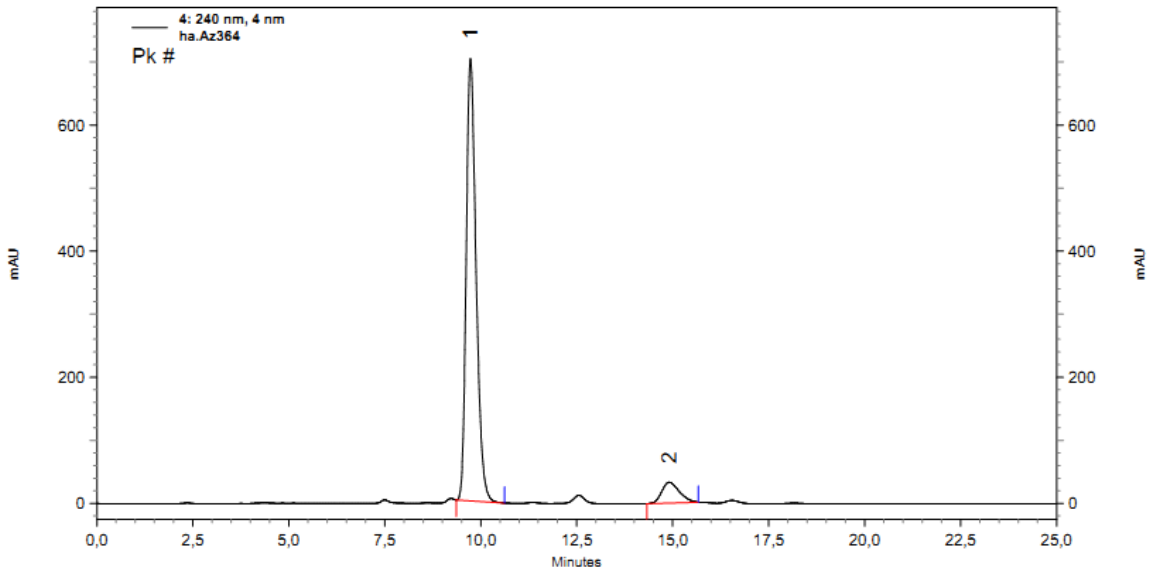


*S*-(6-phenylhex-1-en-3-yl) 4-(trifluoromethyl)benzothioate (**4c**):



4: 240 nm, 4 nm Results

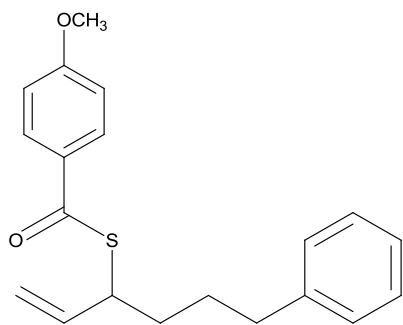
Pk #	Retention Time	Area Percent	Lambda Max
1	9,707	49,533	200
2	14,280	50,467	198



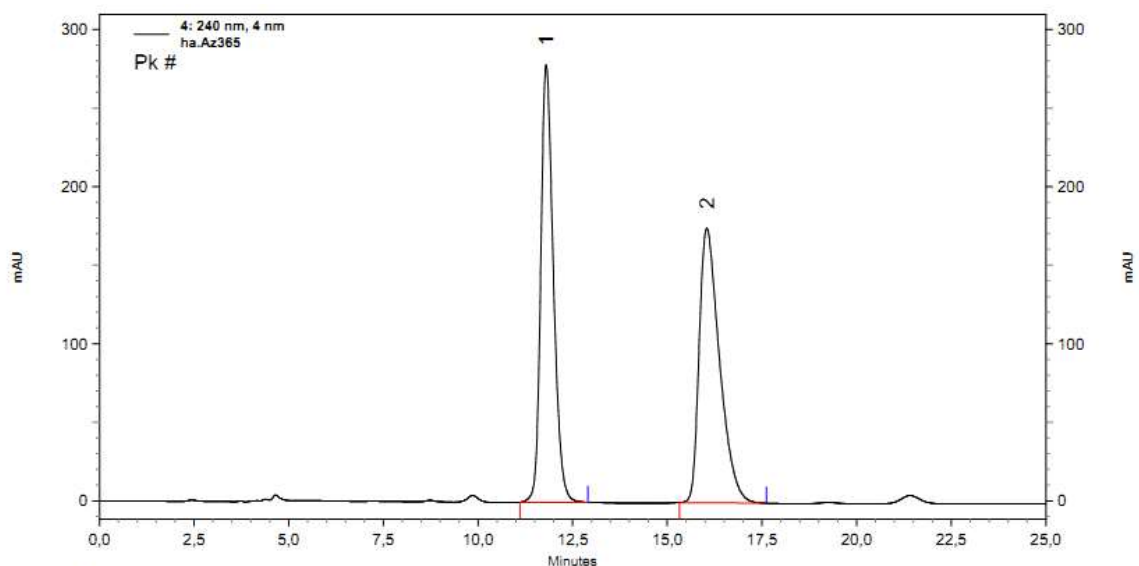
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	9,733	92,325	199
2	14,907	7,675	193



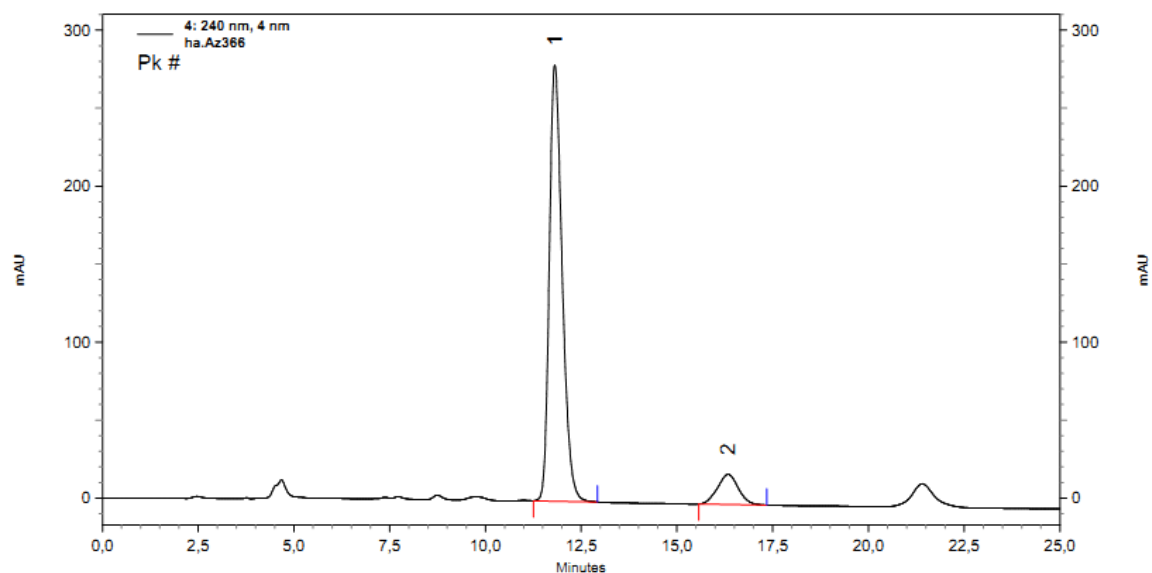


*S*-(6-phenylhex-1-en-3-yl) 4-methoxybenzothioate (**4d**):



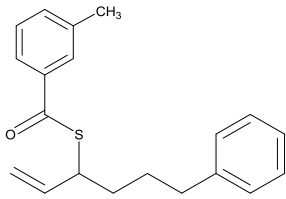
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	11,800	49,670	199
2	16,047	50,330	198

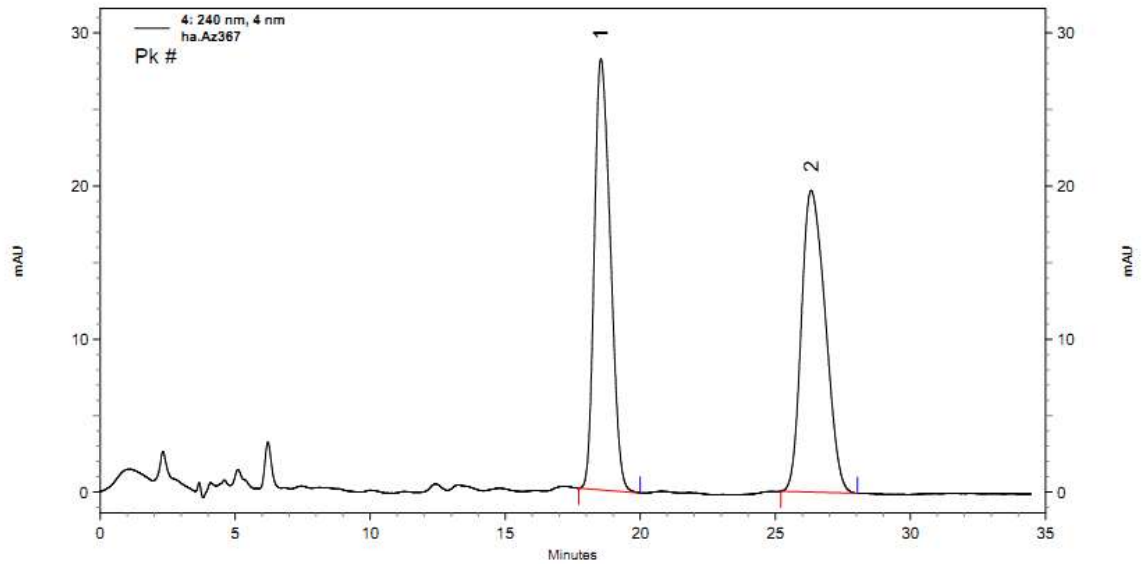


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	11,813	89,895	199
2	16,333	10,105	193

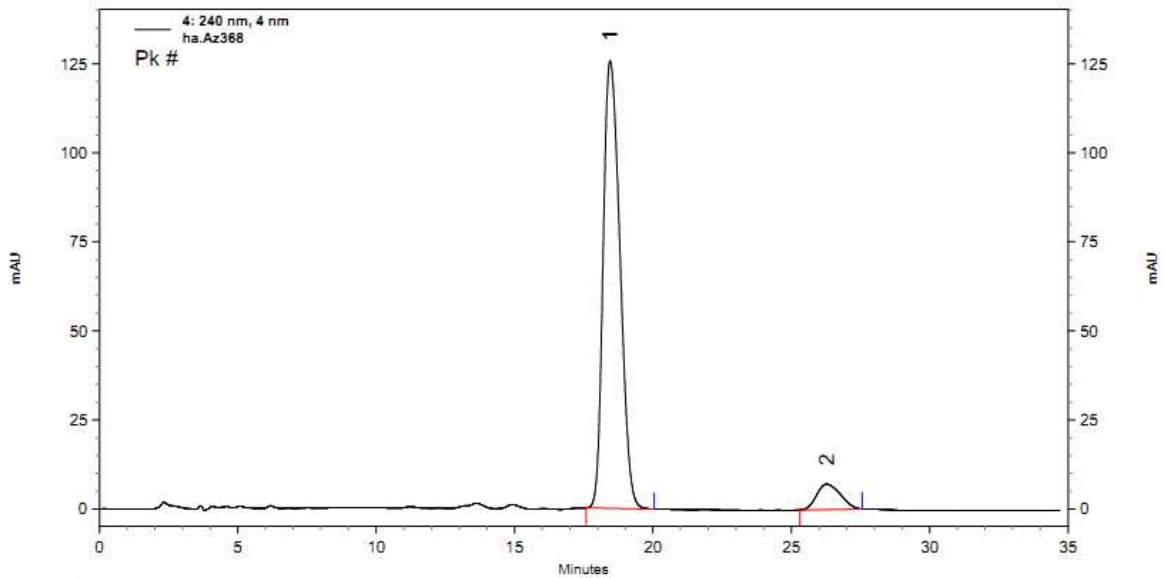


*S*-(6-phenylhex-1-en-3-yl) 3-methylbenzothioate (**4e**):



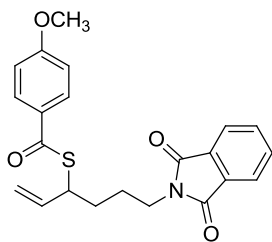
4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18,540	48,987	192
2	26,327	51,013	192

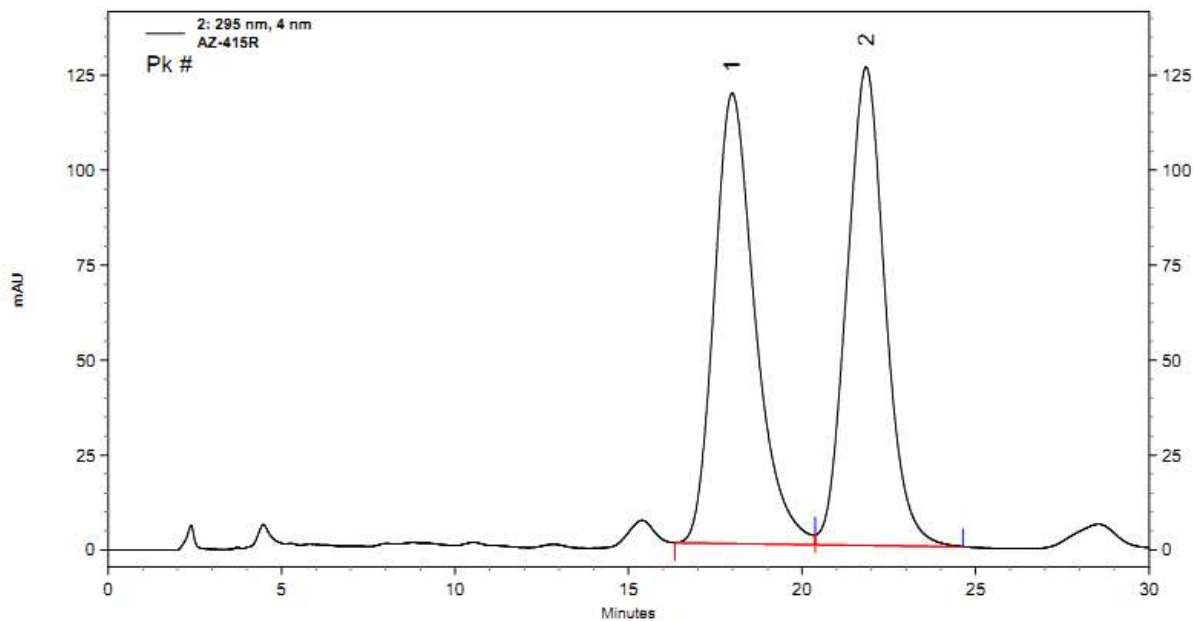


4: 240 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18,453	92,583	193
2	26,280	7,417	191

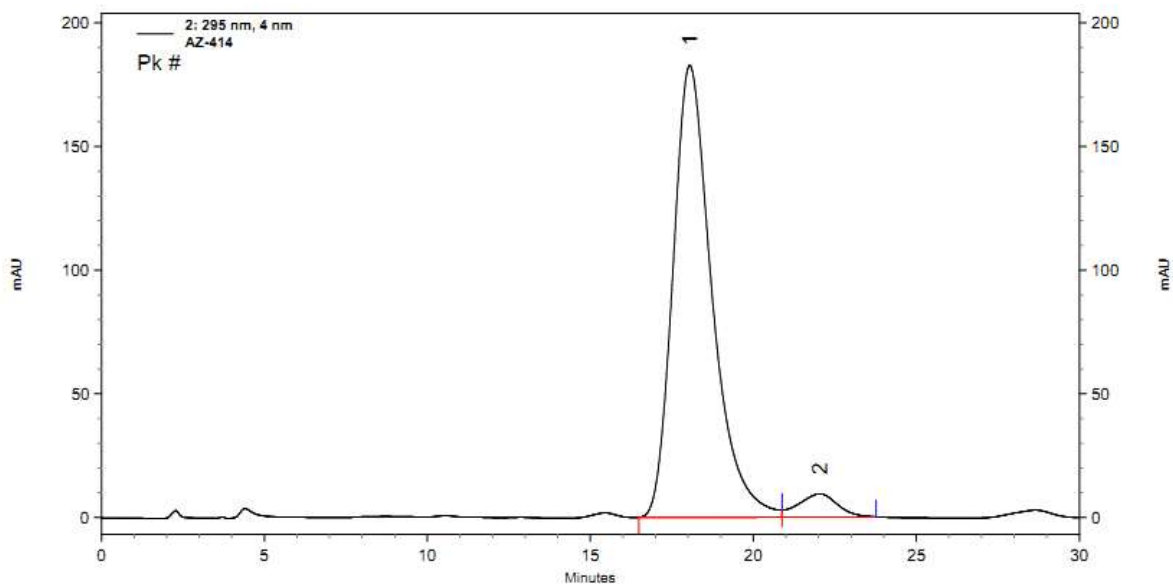


*S*-(6-(1,3-dioxisoindolin-2-yl)hex-1-en-3-yl) 4-methoxybenzothioate (**4f**)



2: 295 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	17,987	50,095	219
2	21,847	49,905	219

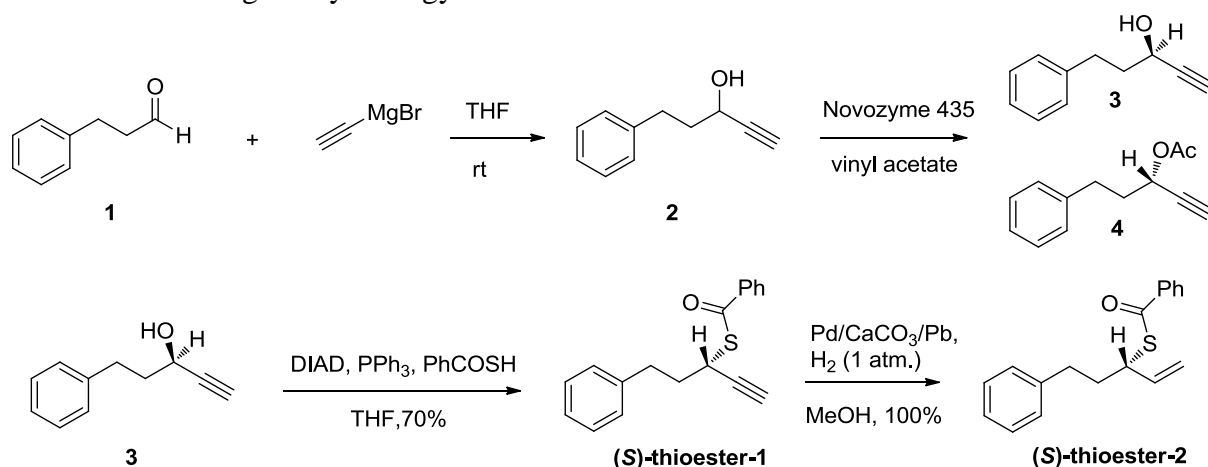


2: 295 nm, 4 nm Results

Pk #	Retention Time	Area Percent	Lambda Max
1	18,047	95,158	219
2	22,033	4,842	219

### Determination of absolute configuration for 3b

The absolute configuration of **3b** was determined as *S* by chemical correlation to (*S*)-thioester-2 according to the following reactions. The absolute configuration of other thioesters was assigned by analogy.



**Preparation of propargylic alcohol 2:** An oven dried 500 mL round-bottom flask containing a magnetic stir bar was charged with 3-phenylpropanal (60 mmol, 1 equiv) and dry THF (100 mL, 0.5 M) and the resulting solution was cooled to 0 °C in an ice bath. Ethynylmagnesium bromide (132 mL, 66 mmol, 1.1 equiv, 0.5 M in THF) was added over 10 minutes and the solution was stirred for 10 minutes before warming to room temperature. After 2 hours, the reaction was quenched with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (100 mL) and the reaction was diluted with  $\text{H}_2\text{O}$  (150 mL) and extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (150 mL), dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The crude residue was purified by flash column chromatography [ $\text{SiO}_2$ , EtOAc:PE (2:8)].<sup>6</sup>

**Synthesis of chiral alcohol (R)-3:** 5-Phenylpent-1-yn-3-ol (6.60 g, 50.0 mmol, 1.0 equiv.), *Candida Antarctica* Lipase (Novozyme 435) resin, vinyl acetate (4.60 mL, 4.30 g, 50.0 mmol, 110 equiv.) and toluene (300 mL) were added to the flask. The reaction mixture was stirred for 16 h at RT. Then the conversion was checked by  $^1\text{H-NMR}$  (50 % conversion). The mixture was filtered through a plug of celite. The solvent was removed under reduced pressure. The ester and the remaining alcohol were separated by column chromatography ( $\text{SiO}_2$ , hexanes:Et<sub>2</sub>O = 5:1) to afford the pure products (alcohol:  $R_f = 0.10$  (hexanes:Et<sub>2</sub>O = 5:1), ester:  $R_f = 0.20$  (hexanes:Et<sub>2</sub>O = 5:1)).<sup>6</sup>

**Procedure for the Synthesis of (S)-thioester-1 from chiral alcohol 3:** DIAD (1.20 eq, 727 mg, 3.6 mmol) was added dropwise over 5 min to a stirred solution of  $\text{PPh}_3$  (1.20 eq, 943 mg, 3.6 mmol) in THF (8 ml) at 0 °C (ice) under a nitrogen atmosphere. After stirring for 20 min at 0 °C a solution of **3** (1.20 eq, 3.6 mmol) and thiobenzoic acid (1.00 eq, 414 mg, 3 mmol) in THF (6 ml) was added and the mixture stirred at 0 °C for 5 h. The volatiles were removed in vacuo and the residue was triturated with pentane (20 ml). The white suspension was filtered and the filter cake washed with pentane (3 x 20 ml). The solvent was removed in vacuo and the residue purified by flash column chromatography eluting with ethyl acetate/*n*-pentane (1/20) to give pure (*S*)-thioester-1.<sup>7</sup>

**Procedure for the reduction of (S)-thioester-1 to (S)-thioester-2:** Lindlar catalyst (4 mg) was added at room temperature to a solution of (S)-thioester-1 (20 mg, 0.071 mmol) and MeOH (4 mL). This mixture was placed under H<sub>2</sub> (1 atm). After 2 h, the mixture was filtered through Celite, the Celite was washed with MeOH (20 mL), and the eluent was concentrated to provide (S)-thioester-2 (100%) as a colorless oil.<sup>8</sup>

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