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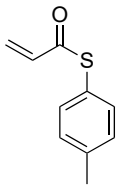
1) General Information

Except where stated, all reagents were purchased from commercial sources and used without further purification. Anhydrous CH_2Cl_2 and THF were obtained from an Innovative Technology Inc. PureSolv® solvent purification system. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL ECX400 or JEOL ECS400 spectrometer (operating at 400 MHz and 100 MHz). All Spectroscopic data was acquired at 295 K unless stated otherwise. Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peaks, δ_H 7.26 and δ_c 77.16 for $CDCl_3$ were used as a reference. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are: br s broad singlet, s singlet, d doublet, br d broad doublet, t triplet, br t broad triplet, q quartet, p pentet, dd doublet of doublets, ddd doublet of doublet of doublets, dddd doublet of doublet of doublet of doublets, dt doublet of triplets, ddt doublet of doublet of triplets, td triplet of doublets, m multiplet. Signal assignment was achieved by analysis of DEPT, COSY, HMBC and HSQC experiments where required. In cases where products were formed as a mixture of rotamers, their ratio was determined by integration of signals in the ^1H NMR spectrum. NMR data were processed using MestReNova. Infrared (IR) spectra were recorded on a PerkinElmer UATR 2 spectrometer as a thin film dispersed from either CH_2Cl_2 or $CDCl_3$. Mass spectra (high-resolution) were obtained by the University of York Mass Spectrometry Service, using Electrospray Ionisation (ESI) on a Bruker Daltonics, Micro-tof spectrometer. Melting points were determined using Gallenkamp apparatus. Thin layer chromatography was carried out on Merck silica gel $60F_{254}$ pre-coated aluminium foil sheets and were visualised using UV light (254 nm) and stained with basic aqueous potassium permanganate or ceric ammonium nitrate. Flash column chromatography was carried out using slurry packed Fluka silica gel (SiO_2), 35–70 μm, 60 Å, under a light positive pressure, eluting with the specified solvent system. There are five compounds that feature in this document but not the main manuscript, and labelled as compound numbers **S1**–**S5**.

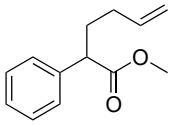
2) Synthetic procedures, characterisation and HPLC data

Thioacrylic acid S-p-tolyl ester (2a)



To a solution of NaOH (15% w/w aq., 20 mL) was added $NaBH_4$ (0.04 g, 0.97 mmol) and *p*-thiocresol (4.00 g, 32.0 mmol) which was then stirred at rt for 3 hours. In another flask, a solution of butylated hydroxytoluene (BHT, 0.11 g, 0.48 mmol) and acryloyl chloride (3.90 mL, 48.3 mmol) in cyclohexane (30 mL) was cooled to 0 °C. The aqueous solution of *p*-thiocresol was added dropwise to the acyrolyol chloride solution and the reaction warmed to room temperature. The reaction was then heated to 55 °C for 35 mins. After this time the reaction mixture was cooled to room temperature and extracted with Et_2O (80 mL). The combined organics were washed with saturated brine solution (100 mL), and then dried over $MgSO_4$. Compound **2a** was yielded as a pale-yellow oil (2.90 g, 51% yield) after column chromatography (1:49 Et_2O:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3023, 2921, 1682, 1612, 1493, 1394, 1160, 1018, 986, 940, 806, 721, 528, 470; δ_H (400 MHz, $CDCl_3$) 7.33 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.26 (2H, d, *J* = 3.76 Hz, Ar**H**), 6.46 (1H, dd, *J* = 17.1, 9.6 Hz, C**H**), 6.38 (1H, dd, *J* = 17.2, 1.7 Hz, =C**H**H'), 5.76 (1H, dd, *J* = 9.6, 1.6 Hz, =CH**H'**), 2.39 (3H, s, C**H**$_3$); δ_C (100 MHz, $CDCl_3$) 189.1 (**C**O), 139.4 (**C**CH_3), 134.7 (Ar**C**), 134.5 (**C**H), 130.2 (Ar**C**), 127.4 (**C**HH), 123.7 (**C**Ar), 21.5 (**C**H_3). **HRMS (ESI)**: calcd. for $C_{10}H_{11}OS$, 179.0526. Found: $[M+H]^+$, 179.0525 (−0.7 ppm error).

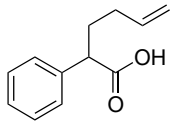
Methyl 2-phenylhex-5-enoate (S1)



To a solution of LiHMDS (1M in THF, 11 mL, 11 mmol) in dry THF (5 mL) at −78 °C under N_2 was added methyl 2-phenylacetate (1.42 mL, 10 mmol) in dry THF (5 mL) over 3 mins and stirred at −78 °C for 45 mins. 4-bromo-1-butene (2.00 mL, 20.0 mmol) was added dropwise over 2 mins at −78 °C and the reaction warmed to rt and stirred for 20 hours. The reaction was quenched with 1 M aq. HCl (10 mL) and extracted with Et_2O (3 x 30 mL). The combined

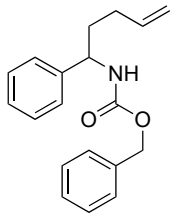
organics were washed with saturated brine solution (30 mL) and dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (1:49 ethyl acetate:hexane → 1:19 ethyl acetate:hexane) to provide the title compound as colourless oil (1.10 g, 55% yield); R_f 0.54 (1:19 ethyl acetate:hexane). **IR** (ATR): υ_{max}/cm^{-1} 2951, 1734, 1161, 913, 734, 698, 512; δ_H (400 MHz, $CDCl_3$) 7.29 - 7.18 (5H, m, Ar**H**), 5.73 (1H, ddt, *J* = 16.9, 10.3, 6.5 Hz, C**H**), 4.99 – 4.93 (2H, m, =C**HH'**), 3.61 (3H, s, C**H**$_3$), 3.54 (1H, t, C**H**CAr), 2.19 – 2.10 (1H, m, C**H**$_2$), 2.00 – 1.93 (2H, m, C**H**$_2$), 1.87 – 1.79 (1H, m, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 174.5 (**C**O), 139.0 (**C**Ar), 137.7 (**C**H), 128.8 (Ar**C**H), 128.1 (Ar**C**H), 127.4 (Ar**C**H), 115.5 (=**C**HH'), 52.1 (**C**H$_3$), 50.8 (CH**C**Ar), 32.6 (**C**H$_2$), 31.6 (**C**H$_2$). **HRMS (ESI)**: calcd. for $C_{13}H_{16}NaO_2$, 227.1049. Found: $[M+Na]^+$, 227.1043 (−2.7 ppm error).

2-Phenyhex-5-enoic acid (12)



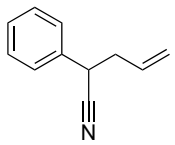
To a solution of ester **S1** (1.06 g, 5.20 mmol) in MeOH (70 mL) was added NaOH (20% w/w, 18 mL) and the reaction heated to reflux while stirring overnight. Reaction was cooled to rt and diluted with H_2O (70 mL) and partitioned with Et_2O (140 mL). The aqueous layer was acidified to pH 1 with 2M aq. HCl and then extracted with Et_2O (3 x 100 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the title compound as a colourless oil (0.957 g, 97% yield); R_f 0.73 (1:9 ethyl acetate:hexane). **IR** (ATR): υ_{max}/cm^{-1} 2951, 1698, 910, 726, 696; δ_H (400 MHz, $CDCl_3$) 7.33 - 7.27 (5H, m, Ar**H**), 5.83 – 5.72 (1H, m, C**H**), 5.03 – 4.98 (2H, m, =C**HH'**), 3.59 (1H, ddd, *J* = 15.1, 7.5, 1.8 Hz, C**H**CAr), 2.23 – 2.14 (1H, m, C**H**$_2$), 2.05 – 2.00 (2H, m, C**H**$_2$), 1.93 – 1.84 (1H, m, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 180.3 (**C**O), 138.3 (**C**Ar), 137.5 (**C**H), 128.8 (Ar**C**H), 128.3 (Ar**C**H), 127.6 (Ar**C**H), 115.7 (=**C**HH'), 50.8 (CH**C**Ar), 32.1 (**C**H$_2$), 31.5 (**C**H$_2$). **HRMS (ESI)**: calcd. for $C_{13}H_{14}NaO_2$, 213.0884. Found: $[M+Na]^+$, 213.0886 (0.7 ppm error).

Benzyl (1-phenylpent-4-en-1-yl)carbamate (5a)



To a solution of carboxylic acid **12** (598.00 mg, 3.14 mmol) in dry toluene (10.5 mL) under N_2 was added DPPA (0.74 mL, 3.45 mmol) and Et_3N (0.53 mL, 3.77 mmol) and the reaction was stirred at 90 °C. After 2 hours, benzyl alcohol (0.49 mL, 4.71 mmol) was added and the reaction was stirred at 90 °C for 48 hours. The reaction was then quenched with H_2O (20 mL) and extracted with EtOAc (3 x 30 mL). The combined organics were washed with saturated brine solution (30 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo.* The crude material was purified by column chromatography (1:9 ethyl acetate:hexane) to the title compound as a colourless oil (0.630 g, 68% yield); R_f 0.21 (1:9 ethyl acetate:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3321, 3064, 3031, 2938, 1692, 1530, 1454, 1243, 1044, 911, 748, 697; δ_H (400 MHz, $CDCl_3$) 7.36 - 7.27 (10H, m, Ar**H**), 5.85 – 5.75 (1H, m, C**H**), 5.10 (1H, d, *J* = 12.2 Hz, N**H**), 5.06 – 4.97 (4H, m, =C**HH'** and C$\mathbf{H}_2$), 4.73 – 4.69 (C**H**CAr), 2.11 – 1.98 (2H, m, C$\mathbf{H}_2$), 1.95 – 1.80 (2H, m, C$\mathbf{H}_2$); δ_C (100 MHz, $CDCl_3$) 155.8 (**C**O), 142.4 (**C**Ar), 137.6 (**C**H), 136.6 (**C**Ar), 128.8 – 126.5 (Ar**C**H), 115.5 (=**C**HH'), 66.9 (O**C**H_2), 55.2 (**C**H), 35.9 (**C**H_2), 30.4 (**C**H_2). **HRMS (ESI)**: calcd. for $C_{19}H_{21}NNaO_2$, 318.1468. Found: $[M+Na]^+$, 318.1464 (−1.2 ppm error).

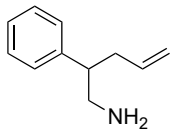
2-Phenylpent-4-enenitrile (14)



To a solution of diisopropylamine (1.3 mL, 8.54 mmol) in dry THF (5 mL) at −78 °C under N_2 was added n-BuLi (2.08 M in hexane, 9.39 mmol) and the solution stirred for 45 mins. A solution of phenylacetonitrile (1 mL, 8.54 mmol) in dry THF (3.5 mL) was added over 3 minutes at −78 °C and the reaction stirred for 45 mins. Allyl bromide (0.7 mL, 8.54 mmol) was added over 2 minutes at −78 °C and the reaction warmed to rt. and stirred overnight. The reaction was stirred overnight and quenched with 1M aq. HCl (10 mL) and then extracted with Et_2O (3

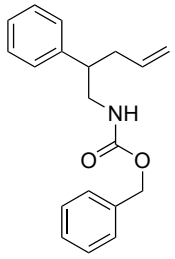
x 15 mL). The combined organics were washed with saturated brine solution (15 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (1:49 ethyl acetate:hexane) to form the title compound as a colorless oil (574 mg, 43% yield); R_f 0.33 (1:49 ethyl acetate:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3072, 2913, 2241, 1643, 1495, 994, 925, 754, 698, 622, 511; δ_H (400 MHz, $CDCl_3$) 7.41 - 7.31 (5H, m, Ar**H**), 5.86 – 5.75 (1H, m, C**H**), 5.22 – 5.17 (2H, m, =C**HH'**), 3.86 (1H, dd, *J* = 7.9, 6.6 Hz, CC**H**), 2.67 – 2.62 (2H, m, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 135.3 (**C**Ar), 132.7 (**C**H), 129.2 (Ar**C**H), 128.3 (Ar**C**H), 127.5 (Ar**C**H), 120.4 (**C**N), 119.5 (=**C**HH'), 40.0 (**C**H_2), 37.6 (C**C**H). **HRMS (ESI)**: calcd. for $C_{11}H_{12}N$, 158.0964. Found: $[M+H]^+$, 158.0964 (−0.3 ppm error).

2-Phenylpent-4-enenitrile (S2)



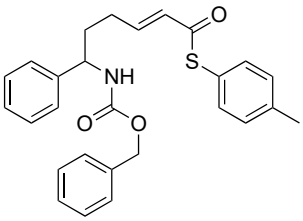
A solution of nitrile **14** (0.57 g, 3.63 mmol) in dry diethyl ether (10 mL) at 0 °C under N_2 was added to $LiAlH_4$ (0.21 g, 5.53 mmol) in dry diethyl ether (10 mL) over 5 minutes and stirred for 30 minutes. The reaction was then warmed to rt and stirred overnight. The reaction was cooled to 0 °C before H_2O (0.2 mL) was added, followed by NaOH solution (15% w/w aq, 0.2 mL), followed by H_2O (0.6 mL) and warmed to rt. The solution was filtered through a Celite and concentrated *in vacuo* to give the title compound as a colourless oil (553.97 mg, 94% yield); R_f 0.18 (1:19 ethyl acetate:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3063, 3027, 2920, 2241, 1639, 1493, 1452, 994, 991, 759, 699, 648, 543; δ_H (400 MHz, $CDCl_3$) 7.34 - 7.17 (5H, m, Ar**H**), 5.74 – 5.64 (1H, m, C**H**), 5.02 – 4.92 (2H, m, =C**HH'**), 2.96 (1H, dd, *J* = 12.7, 5.2 Hz, C**H**$_2$), 2.85 (1H, dd, *J* = 12.7, 8.7 Hz, C**H**$_2$), 2.72 – 2.64 (1H, m, C**H**), 2.45 – 2.32 (2H, m, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 143.1 (**C**Ar), 136.7 (**C**H), 128.6 (Ar**C**H), 128.1 (Ar**C**H), 126.6 (Ar**C**H), 116.2 (=**C**HH'), 49.5 (C**C**H), 47.5 (**C**H_2), 38.4 (**C**H_2). **HRMS (ESI)**: calcd. for $C_{11}H_{16}N$, 162.129. Found: $[M+H]^+$, 162.1277 (−0.8 ppm error).

Benzyl (2-phenylpent-4-en-1-yl) carbamate (5b)



A solution of amine **S2** (0.51 g, 3.16 mmol) in 1,4-dioxane (15 mL) was treated with K_2CO_3 solution (0.52 g, 3.79 mmol) followed by benzyl chloroformate (0.65 g, 3.79 mmol) and the reaction was stirred for almost 3 hours at rt until TLC monitoring showed complete conversion. The reaction was quenched with H_2O (20 mL) and extracted with DCM (3 x 20 mL). The combined organics were washed with saturated brine solution (20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude material was purified by column chromatography (1:19 ethyl acetate:hexane) to form the title compound as a yellow oil (0.56 g, 60% yield); R_f 0.30 (1:4 ethyl acetate:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3336, 3030, 2927, 1702, 1516, 1453, 1294, 1140, 997, 914, 755, 699; δ_H (400 MHz, $CDCl_3$) 7.38 - 7.15 (10H, m, Ar**H**), 5.73 – 5.63 (1H, m, C**H**), 5.01 – 4.95 (4H, m, 2 x C**H**$_2$), 4.60 (1H, s, N**H**), 3.67 – 3.53 (1H, m, C**H**$_2$), 3.25 (1H, ddd, *J* = 13.7, 9.1, 4.6 Hz, C**H**), 2.91 – 2.77 (1H, m, C**H**$_2$), 2.45 – 2.33 (2H, m, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 156.4 (**C**O), 142.1 (**C**Ar), 136.6 (**C**H), 135.9 (**C**Ar), 128.8 – 127.0 (Ar**C**H), 116.8 (=**C**HH'), 66.7 (O**C**H$_2$), 46.1 (**C**H$_2$), 45.8 (**C**H), 38.2 (**C**H$_2$). **HRMS (ESI)**: calcd. for $C_{19}H_{21}NNaO_2$, 318.1469. Found: $[M+Na]^+$, 318.1464 (−1.3 ppm error).

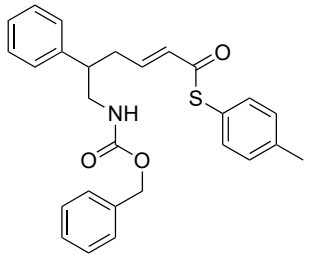
***S*-(*p*-Tolyl) (*E*)-6-(((benzyloxy)carbonyl) amino)-6-phenylhex-2-enethioate (6a)**



A solution of thioester **2a** (3.7 mg, 2.07 mmol) in 1,2-DCE (10 mL) was added under N_2 to a dry flask containing Hoveyda-Grubbs Catalyst™ 2nd generation (43.9 mg, 0.07 mmol) and copper iodide (131.84 mg, 0.69 mmol) while stirring. A solution of Cbz-amine **5a** (203 mg, 0.69 mmol) in 1,2-DCE (10 mL) was added and the reaction mixture was stirred at 50 °C for 24 hours. The reaction was cooled to rt and then concentrated in *vacuo*. The crude was purified

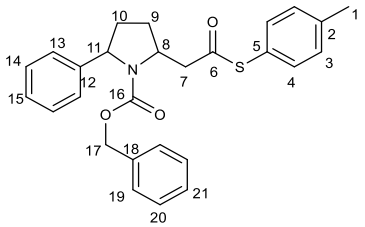
by column chromatography (1:9 ethyl acetate:hexane) to form the title compound as pale-yellow oil (249.5 mg, 81% yield); R_f 0.07 (1:9 ethyl acetate:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3331, 3030, 2946, 1690, 1631, 1526, 1454, 1242, 1044, 808, 699; δ_H (400 MHz, $CDCl_3$) 7.34 - 7.21 (14H, m, Ar**H**), 6.95 – 6.88 (1H, m, C**H**), 6.15 (1H, d, *J* = 15.5 Hz, C**H**), 5.12 (1H, d, *J* = 12.2 Hz, N**H**), 5.07 – 5.04 (2H, m, OC**H**$_2$), 4.74 – 4.65 (1H, m, C**H**), 2.30 – 2.13 (2H, m, C**H**$_2$), 2.05 (3H, s, C**H**$_3$), 2.03 – 1.79 (2H, m, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 188.5 (**C**O), 155.8 (**C**O), 144.9 (**C**H), 141.6 (**C**Ar), 139.8 (**C**Ar), 136.4 (**C**Ar), 134.7 (**C**H), 130.1 – 126.5 (Ar**C**H), 124.1 (**C**Ar), 67.0 (**C**H$_2$), 55.3 (**C**H), 34.9 (**C**H$_2$), 29.2 (**C**H$_2$), 21.4 (**C**H$_3$). **HRMS (ESI)**: calcd. for $C_{27}H_{27}NNaO_3S$, 468.1617. Found: $[M+Na]^+$, 468.1604 (−2.9 ppm error).

***S*-(*p*-tolyl) (*E*)-6-(((benzyloxy)carbonyl) amino)-5-phenylhex-2-enethioate (6b)**



Compound **6b** was synthesis using the same procedure used to make isomer **6a** above, with thioester **2a** (991 mg, 5.6 mmol), copper iodide (353 mg, 1.85 mmol), Hoveyda-Grubbs Catalyst ™ 2nd generation (157 mg, 0.19 mmol) and Cbz amine **5b** (547 mg, 1.85 mmol). The title compound was obtained as a pale yellow oil (524 mg, 63%); R_f 0.07 (1:9 ethyl acetate:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3030, 22252, 1712, 1514, 1494, 1243, 1017, 904, 808, 726, 648; δ_H (400 MHz, $CDCl_3$) 7.35 - 7.14 (14H, m, Ar**H**), 6.82 – 6.75 (1H, m, C**H**), 6.12 (1H, d, *J* = 15.5, Hz, C**H**), 5.14 – 5.04 (2H, m, C**H**$_2$), 4.63 – 4.58 (1H, m, N**H**), 3.65 – 3.53 (1H, m, C**H**$_2$), 3.30 (1H, ddd, *J* = 13.6, 7.9, 5.0 Hz, C**H$_2$**), 3.02 – 2.91 (1H, m, C**H**), 2.63 – 2.49 (2H, m, C**H**$_2$), 2.37 (3H, s, C**H**$_3$); δ_C (100 MHz, $CDCl_3$) 188.4 (**C**O), 156.4 (**C**O), 143.2 (**C**H), 140.9 (**C**Ar), 139.7 (**C**Ar), 136.9 (**C**Ar), 135.4 (**C**H), 130.1 – 127.4 (Ar**C**H), 124.0 (**C**Ar), 66.9 (**C**H$_2$), 46.2 (**C**H$_2$), 45.3 (**C**H), 36.5 (**C**H$_2$), 21.4 (**C**H$_3$). **HRMS (ESI)**: calcd. for $C_{27}H_{27}NNaO_3S$, 468.1610. Found: $[M+Na]^+$, 468.1604 (−1.3 ppm error).

Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-phenylpyrrolidine-1-carboxylate (rac-7a)

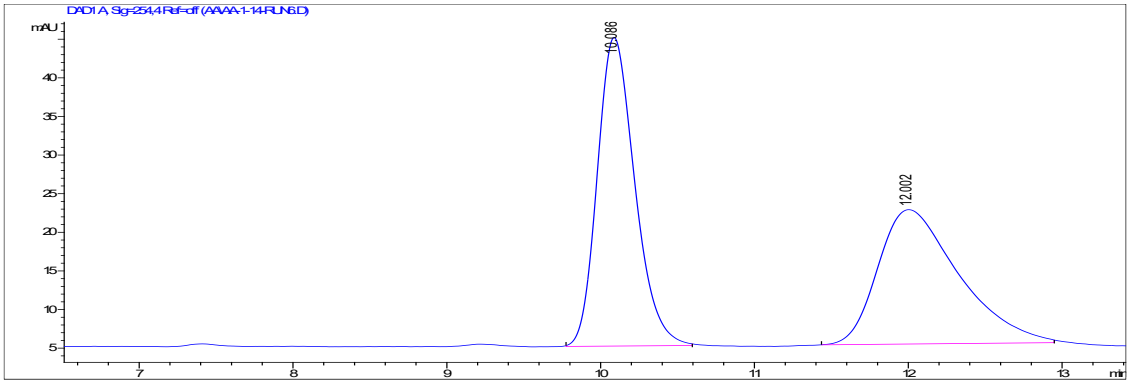


A solution of **6a** (163.14 mg, 0.37 mmol) in 1,2-DCE (38 mL) was added to rac-CSA (255.16 mg, 1.10 mmol) under N_2 and the reaction heated to 60 °C for 24 hours. The reaction was quenched with saturated $NaHCO_3$ (35 mL) and extracted with DCM (3 x 35 mL). The combined organics were washed with saturated brine (35 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (1:9 ethyl acetate:hexane) to afford the title compound as a colourless oil (122.91 mg, 75% yield); R_f 0.31 (1:9 ethyl acetate:hexane). **IR** (ATR): ν_{max}/cm^{-1} 3338, 3031, 2923, 2856, 1689, 1630, 1494, 1453, 1240, 1043, 996, 807, 754, 698. In solution in $CDCl_3$, the product exists as a 1:3 mixture of diastereoisomers; δ_H (400 MHz, $CDCl_3$) 7.43 – 6.78 (28H, both diastereoisomers, m, Ar**H**), 5.05 – 4.99 (2H, m, C**H**$_2$), 4.90 (1H, d, *J* = 12.6 Hz, C**H**), 4.65 − 4.56 (1H, m, C**H**), 3.47 (1H, dd, *J* = 14.8, 3.1 Hz, C**H**$_2$), 2.82 (1H, dd, *J* = 14.9, 9.7 Hz, C**H**$_2$), 2.46 – 2.32 (6H, both diastereoisomers, m, H-1), 2.22 – 2.12 (1H, m, C**H**$_2$), 1.89 – 1.75 (3H, m, C**H**$_2$). ^{13}C NMR data for the major diastereoisomer only; δ_C (100 MHz, $CDCl_3$) 196.1 (**C**O), 154.5 (**C**O), 144.2 – 124.2 (Ar**C**H and **C**Ar), 66.7 (**C**H$_2$), 61.7 (**C**H), 56.1 (**C**H), 46.2 (**C**H$_2$), 32.7 (**C**H$_2$), 26.8 (**C**H$_2$), 21.5 (**C**H$_3$). **HRMS (ESI)**: calcd. for $C_{27}H_{27}NNaO_3S$, 468.1610. Found: $[M+Na]^+$, 468.1604 (−1.3 ppm error).

NMR data for the minor diastereoisomer only; δ_H (400 MHz, $CDCl_3$) 5.22 (1H, d, *J* = 12.6 Hz, C**H**$_2$), 5.13 (1H, d, *J* = 12.4 Hz, C**H**$_2$), 3.22 (1H, dd, *J* = 14.8, 2.7 Hz, C**H**$_2$), 2.73 (1H, dd, *J* = 14.8, 10.0 Hz, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 195.9 (**C**O), 154.0 (**C**O), 67.2 (**C**H$_2$), 61.7 (**C**H), 55.4 (**C**H), 47.5 (**C**H$_2$), 31.7 (**C**H$_2$), 27.7 (**C**H$_2$) 21.4 (**C**H$_3$).

Chiral HPLC analysis of rac-7a

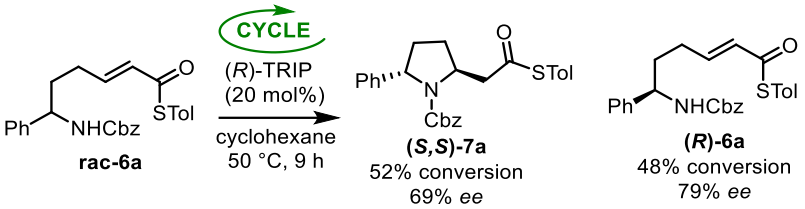
The two enantiomers of each of **rac-7a**, were resolved using chiral HPLC. Good separation of four stereoisomers was observed using an IA column, eluting with 80:20 of hexane:IPA at a flow rate of 1.0 mL/min at 40 °C. The *cis*- and *trans*- diastereoisomers of **rac-7a** were not observed by this method, but the enantiomers were, enabling the overall *ee* of **rac-7a** to be measured .



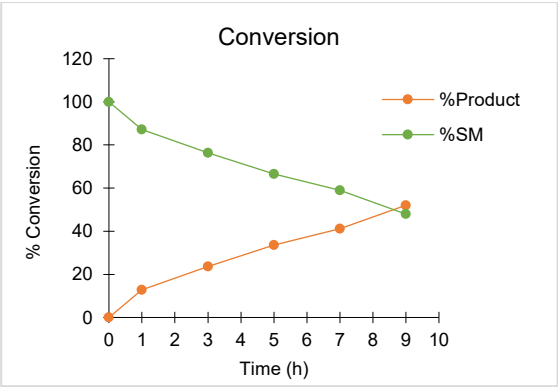
Hexane:IPA	Peak 1 (Time / min)	Area (%)	Peak 2 (Time / min)	Area (%)	Flow rate (mL / min)
80:20	10.086	51.6	12.002	48.4	1

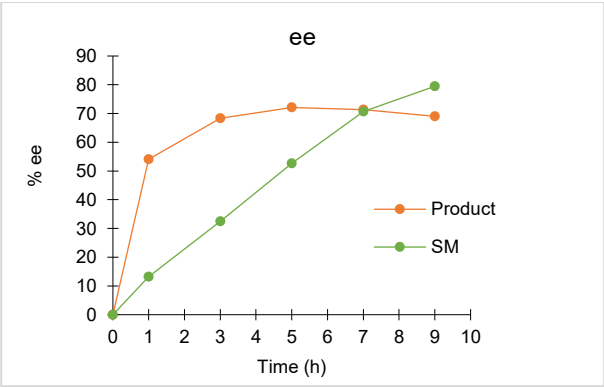
Kinetic resolution of rac-6a to form (S,S)-7a

The reaction set up for the *kinetic resolution of* ***rac-6a*** was the same as that used to prepare **rac-7a** above, using the following reagent quantities: **rac-6a** (25.7 mg, 0.06 mmol) and (*R*)-TRIP (8.04 mg, 0.01 mmol) in cyclohexane (0.02M) and the reaction was heated to 50 °C for 9 hours. Small reaction aliquots were taken a t = 0 h, 1 h, 3 h, 7 h and 9 h and analysed by chiral HPLC using the conditions described above, with the HPLC-measured conversions and *ee* summarised below in tabular and graphical forms.

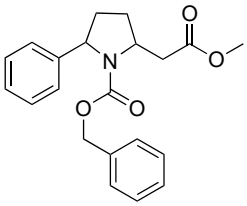


	%Conversion		%ee	
Time(h)	% Product (7a)	%SM (6a)	Product (7a)	SM (6a)
0	0	100	0	0
1	12.817	87.183	54.077	13.229
3	23.602	76.398	68.340	32.471
5	33.528	66.472	72.077	52.617
7	41.083	58.917	71.319	70.717
9	52.048	47.953	69.027	79.479





Benzyl 2-(2-methoxy-2-oxoethyl)-5-phenylpyrrolidine-1-carboxylate (S3)

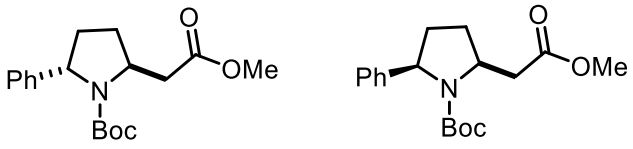


To solution of pyrrolidine **rac-7a** (22.44 mg, 0.05 mmol) in dry MeOH/DCM (1:1, 0.8 mL) was added AgOTf (38.82 mg, 0.15 mmol) and the reaction was stirred for 3 hours at rt. The reaction was quenched with Et_2O (3 mL) and filtered through a silica plug followed by Et_2O. The combined filtrate was concentrated in *vacuo* and the crude material was purified by column chromatography (1:4 ethylacetate:hexane) to afford the title compound as a pale yellow oil (14.82 mg, 83% yield); R_f 0.18 (1:4 ethyl acetate:hexane).). **IR** (ATR): ν_{max}/cm^{-1} 3030, 2951, 2925, 2853, 1735, 1698, 1405, 1348, 1307, 1164, 1114, 750, 699. δ_H (400 MHz, $CDCl_3$) 7.39 – 7.08 (13H, both diastereoisomers, m, Ar**H**), 6.79 (2H, d, *J* = 6.9 Hz, Ar**H**), 5.06 – 5.00 (2H, m, C$\mathbf{H}_2$ and C**H**), 4.88 (1H, d, *J* = 12.6 Hz, C$\mathbf{H}_2$), 4.62 – 4.52 (1H, m, C**H**), 3.70 (3H, s, C$\mathbf{H}_3$), 3.17 (1H, dd, *J* = 15.3, 3.4 Hz, C$\mathbf{H}_2$), 2.45 – 2.36 (2H, m, C$\mathbf{H}_2$), 2.25 – 2.15 (1H, m, C$\mathbf{H}_2$), 1.81 – 1.72 (2H, m, C$\mathbf{H}_2$); ^{13}C NMR data for the major diastereoisomer only; δ_C (100 MHz, $CDCl_3$) 172.0 (**C**O), 154.5 (**C**O), 144.3 (**C**Ar), 136.6 (**C**Ar), 128.6 (Ar**C**H), 128.2 (Ar**C**H), 128.1 (Ar**C**H), 127.6 (Ar**C**H), 127.4 (Ar**C**H), 126.9 (Ar**C**H), 66.6 (**C**H_2), 61.6 (**C**H), 55.6 (**C**H), 51.8 (**C**H_3), 37.7 (**C**H_2), 32.6 (**C**H_2), 27.2 (**C**H_2); **HRMS (ESI)**: calcd. for $C_{21}H_{23}NNaO_4$, 376.1521. Found: $[M+Na]^+$, 376.1519 (−0.3 ppm error).

Characteristic NMR data for the minor diastereoisomer can be found at: δ_H (400 MHz, $CDCl_3$) 5.19 – 5.12 (2H, m, C$\mathbf{H}_2$), 3.67 (3H, s, C$\mathbf{H}_3$), 2.95 (1H, dd, *J* = 15.3, 2.9 Hz, C$\mathbf{H}_2$); δ_C (100 MHz,

$CDCl_3$) 171.8 (**C**O), 154.1 (**C**O), 143.2 (**C**Ar), 136.8 (**C**Ar), 128.6 (Ar**C**H), 127.0 (Ar**C**H), 125.3 (Ar**C**H), 67.1 (**C**H_2), 61.8 (**C**H), 55.0 (**C**H), 51.8 (**C**H_3), 38.9 (**C**H_2), 31.7 (**C**H_2), 28.1 (**C**H_2).

***tert*-Butyl 2-(2-methoxy-2-oxoethyl)-5-phenylpyrrolidine-1-carboxylate (15)**



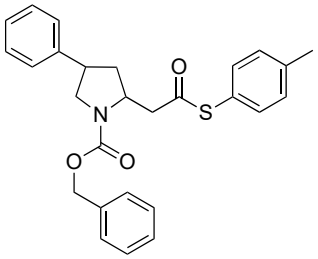
major minor

To a solution of **S3** (103.0 mg, 0.29 mmol) and 10 % Pd/C (106.40 mg) in MeOH (8 mL) was added $NaBH_4$ (11.0 mg, 0.29 mmol). The reaction was completed (monitored by TLC, 5-10 min) and filtered through a glass pipet. Then the reaction was neutralized with 2 M aq. HCl, followed by saturated aq. $NaHCO_3$ solution and extracted with EtOAc. The combined organics were washed with saturated brine solution, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material (the free amine) was used in the next step without purification. A solution of free amine (27.9 mg, 0.079 mmol) and Boc_2O (20.7 mg, 0.095 mmol) were dissolved in THF (0.5 mL). Et_3N (0.03 mL) in THF (0.2 mL) was then added at 0 °C over 1 minute. The reaction allowed to warm to room temperature before being heated at 40 °C for 3 hours. The reaction was cooled to room temperature, quenched with H_2O (1mL) and extracted with Et_2O (3x5 mL). The combined organics were washed with brine solution, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (1:9 ethylacetate:hexane) to afford the title compound as a colourless oil (10.14 mg, 40% yield). **IR** (ATR): ν_{max}/cm^{-1} 2974, 1736, 1689, 1452, 1385, 1366, 1308, 1254, 1164, 1119, 1060, 910, 701. In solution in $CDCl_3$, the product exists as a 1:3 mixture of diastereoisomers δ_H (400 MHz, $CDCl_3$) 7.30 – 7.25 (4H, both diastereoisomers, m, Ar**H**), 7.22 – 7.17 (1H, both diastereoisomers, m, Ar**H**), 7.10 – 7.08 (3H, both diastereoisomers, m, Ar**H**), 4.85 (1H, d, *J* = 8.2 Hz, C**H**), 4.57 – 4 .51 (1H, m, C**H**), 3.69 (3H, s, CH_3), 3.11 (1H, dd, *J* = 15.0, 3.5 Hz, CH_2), 2.41 – 2.31 (2H, m, CH_2), 1.78 – 1.69 (3H, m, CH_2), 1.13 (9H, s, CH_3); ^{13}C NMR data for the major diastereoisomer only; δ_C (100 MHz, $CDCl_3$) 172.2 (**C**O), 154.0 (**C**O), 145.1 (**C**Ar), 128.3 (Ar**C**H), 126.7 (Ar**C**H), 125.3 (Ar**C**H), 79.6 (**C**CH_3), 61.9 (**C**H), 55.1 (**C**H), 51.8

(**C**H_3), 38.1 (**C**H_2), 32.5 (**C**H_2), 28.6 (**C**H_2), 28.2 (**C**H_2); **HRMS (ESI)**: calcd. for $C_{18}H_{25}NNaO_4$, 342.1676. Found: $[M+Na]^+$, 342.1676 (−0.0 ppm error).

Selected NMR data for the minor diastereoisomer; δ_H (400 MHz, $CDCl_3$) 4.99 (1H, d, *J* = 8.2 Hz, C**H**), 4.45 – 4.40 (1H, m, C**H**), 3.71 (3H, s, C**H**$_3$), 2.98 (1H, dd, *J* = 15.1, 2.5 Hz, C**H**$_2$), 1.46 (9H, s, C**H**$_3$); δ_C (100 MHz, $CDCl_3$) 172.1 (**C**O), 153.6 (**C**O), 143.7 (**C**Ar), 128.5 (Ar**C**H), 126.8 (Ar**C**H), 125.3 (Ar**C**H), 80.1 (**C**CH_3), 61.2 (**C**H), 55.1 (**C**H), 51.8 (**C**H_3), 38.9 (**C**H_2), 31.8 (**C**H_2), 28.5 (**C**H_2), 27.9 (**C**H_2).

Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-4-phenylpyrrolidine-1-carboxylate (rac-7b)

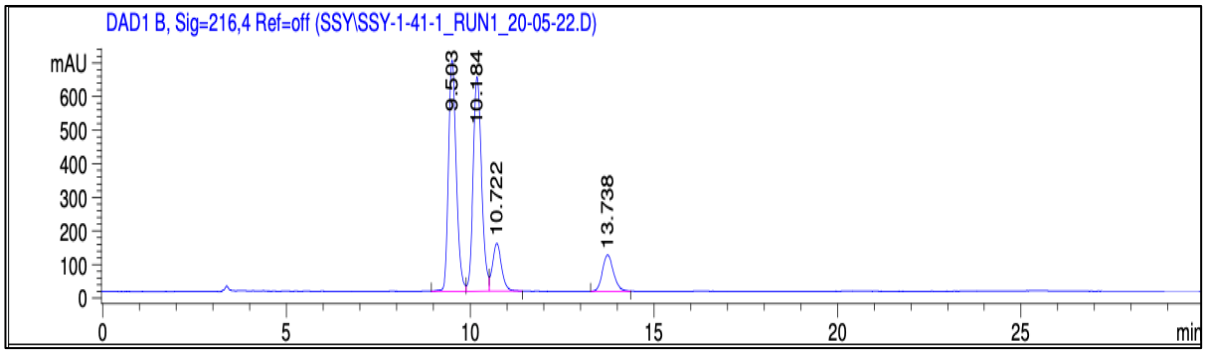


A solution of **6b** (87.69 mg, 0.20 mmol) in 1,2-DCE (21 mL) was added to rac-CSA (137.15 mg, 0.59 mmol) under N_2 and the reaction heated to 60 °C for 24 hours. The reaction was quenched with saturated $NaHCO_3$ (25 mL) and extracted with DCM (3 x 25 mL). The combined organics were washed with saturated brine solution (25 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (1:9 ethyl acetate:hexane) to afford the title compound as a colourless oil (122.91 mg, 75% yield) as a 4:1 mixture of diastereoisomers based on HPLC analysis. **IR** (ATR): ν_{max}/cm^{-1} 3030, 2922, 2854, 1702, 1454, 1413, 1355, 1108, 989, 807, 756, 698. NMR data for the major diastereoisomer; δ_H (400 MHz, $CDCl_3$) 7.41 – 7.20 (14H, m, Ar**H**), 5.18 (2H, d, *J* = 20.9 Hz, C**H**$_2$), 4.20 – 4.04 (1H, m, C**H**$_2$), 3.60 – 3.41 (1H, m, C**H**$_2$), 3.36 – 3.24 (2H, m, C**H**$_2$ and C**H**), 3.02 – 2.84 (1H, m, C**H**$_2$), 2.37 (3H, s, C**H**$_3$), 2.07 – 1.94 (1H, m, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 196.1 (**C**O), 154.9 (**C**O), 140.1 – 127.1 (Ar**C**H and **C**Ar), 67.0 (**C**H_2), 55.7 (**C**H), 53.2 (**C**H_2), 47.2 (**C**H_2), 43.1 (**C**H), 39.1 (**C**H_2), 21.5 (**C**H_3). **HRMS (ESI)**: calcd. for $C_{27}H_{27}NNaO_3S$, 468.1613. Found: $[M+Na]^+$, 468.1604 (−1.9 ppm error).

Chiral HPLC analysis of rac-7b

The enantiomers of each of the *cis*- and *trans*-diastereoisomers of for **rac-7b**, were resolved using chiral HPLC, with good separation of four stereoisomers observed using an IA column,

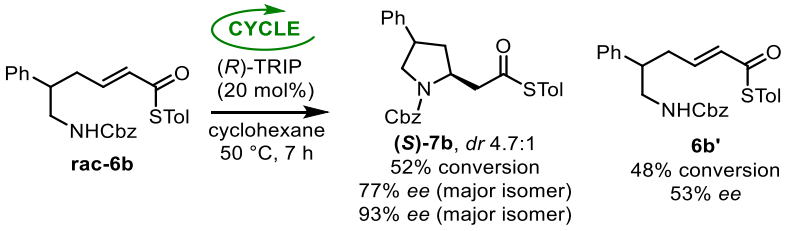
eluting with 80:20 of hexane:IPA at a flow rate of 1.0 mL/min at 40 °C. The diastereomeric ratio of **rac-7b** was determined as being 4:1.



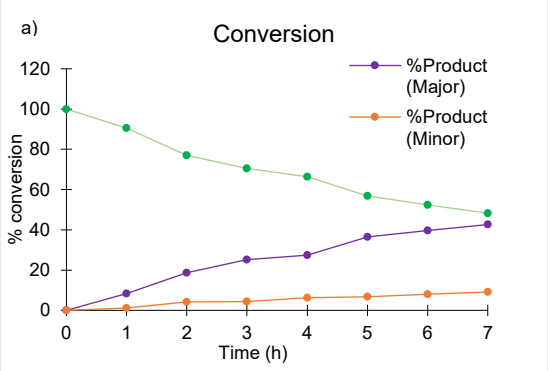
Racemic Substrate	Hexane:IPA	Major isomer (Time / min)	Area (%)	Minor isomer (Time / min	Area (%)	dr
rac-7b	80:20	9.503	40.6	10.722	9.7	4.3 : 1
		10.184	40.7	13.738	9.0	

Kinetic resolution of rac-6b

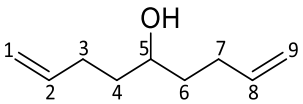
The reaction set up for the *kinetic resolution of* ***rac-6b*** was the same as that used to prepare **rac-7b** above with the following reagent quantities used: **rac-6b** (25.65 mg, 0.06 mmol) and (R)-TRIP (8.04 mg, 0.01 mmol) in cyclohexane (0.02M) and the reaction was heated to 50 °C for 7 hours. Small reaction aliquots were taken a t = 0 h, 1 h, 2 h, 3 h, 4 h, 5 h, 6 h and 7 h and analysed by chiral HPLC using the conditions described above, with the HPLC-measured conversions and *ee* summarised below in tabular and graphical forms.



	% Conversion			% ee		
Time (h)	%Product (Major)	%Product (Minor)	%SM	Product (Major)	Product (Minor)	SM
0	0	0	100	0	0	0
1	8.270	1.095	90.528	70.316	83.289	4.087
2	18.729	4.177	77.093	69.643	79.353	14.905
3	25.149	4.362	70.488	77.841	92.438	23.203
4	27.383	6.271	66.346	85.154	62.270	31.739
5	36.439	6.679	56.881	78.772	91.849	38.521
6	39.677	7.969	52.354	78.565	85.569	47.105
7	42.611	9.116	48.273	76.539	92.058	53.523

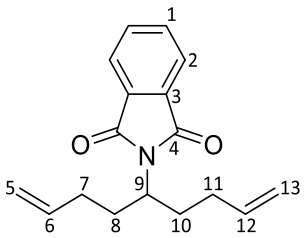


Nona-1,8-dien-5-ol (**S4**)



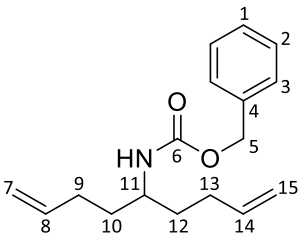
Magnesium turnings (1.22 g, 50.0 mmol) and iodine (1 crystal) were added to a flame dried flask under N_2, which was warmed until the iodine sublimed. The flask was allowed to cool to room temperature before the addition of dry THF (40 mL). To this mixture, 4-bromo-1-butene (5.08 mL, 50.0 mmol) was added slowly at room temperature (the flask was placed in a water bath to control the temperature). The resulting reaction mixture was then stirred at room temperature for 1 h to form the Grignard reagent. The reaction was then cooled to 0 °C before the addition of ethyl formate **21** (1.62 mL, 20.0 mmol) in dry THF (10 mL) over 10 mins. The reaction mixture was then stirred at room temperature overnight. The reaction mixture was cooled to 0 °C and quenched with saturated NH_4Cl solution (50 mL). The aqueous phase was then extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 5% EtOAc/hexane) to afford the title compound as a yellow oil (2.42 g, 17.3 mmol, 86% yield). *Data were consistent with those reported in the literature*.[1] **TLC (SiO_2)** R_f = 0.19 (10% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 5.84 (2H, ddt, *J* = 16.9, 10.1, 6.8 Hz, H-2,8), 5.05 (2H, ddd, *J* = 17.3, 3.6, 1.4 Hz, H-1,9), 4.97 (2H, dd, *J* = 10.1, 1.4 Hz, H-1,9), 3.69 – 3.61 (1H, m, H-5), 2.27 – 2.07 (4H, m, CH_2), 1.63 – 1.47 (5H, m, CH_2 and OH) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 138.7 (C-2,8), 114.9 (C-1,9), 71.1 (C-5), 36.6 (C-4,6), 30.2 (C-3,7) ppm; **IR (ATR)**: ν_{max} 3342, 3078, 2978, 2933, 1641, 1449, 1416, 1314, 1079, 992, 908, 639, 556 cm^{-1}; **HRMS (APCI)** 141.1271 ($M + H^+$. $C_9H_{17}O$ requires 141.1274).

2-(Nona-1,8-dien-5-yl)isoindoline-1,3-dione (**S5**)



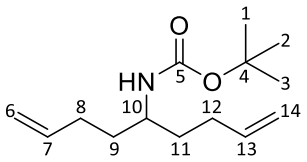
Phthalimide (1.44 g, 9.80 mmol) and triphenylphosphine (2.57 g, 9.80 mmol) were dissolved in THF (50 mL). Secondary alcohol **S4** (1.10 g, 7.84 mmol) was then added followed by DEAD (5.00 mL, 11.0 mmol) at room temperature over 20 min. The reaction mixture was stirred at room temperature for 24 h. The solvent was then removed under reduced pressure and the resulting crude oil triturated with hexane/Et_2O (2:1 mixture) until complete removal of the solids. The combined organic layers were concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 2% EtOAc/pentane) to afford *N*-alkyl phthalimide **113** as a colourless oil (1.23 g, 4.56 mmol, 58% yield). **TLC (SiO_2)** R_f = 0.29 (5% EtOAc/pentane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.82 (2H, dd, *J* = 5.5, 3.2 Hz, H-2), 7.71 (2H, dd, *J* = 5.5, 3.1 Hz, H-1), 5.75 (2H, ddt, *J* = 17.0, 10.1, 6.7 Hz, H-6,12), 4.96 (2H, ddd, *J* = 17.0, 3.3, 1.4 Hz, H-5,13), 4.90 (2H, dd, *J* = 10.1, 1.4, Hz, H-5,13), 4.23 (1H, m, H-9), 2.28 – 2.17 (2H, m, CH_2), 2.10 – 1.95 (4H, m, CH_2), 1.85 – 1.75 (2H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 168.9 (C-4), 137.6 (C-6,12), 134.0 (C-1), 131.9 (C-3), 123.3 (C-2), 115.3 (C-5,13), 51.4 (C-9), 31.7 (C-8,10), 31.0 (C-7,11) ppm; **IR (ATR)**: ν_{max} 3078, 2929, 1772, 1704, 1641, 1613, 1468, 1453, 1393, 1368, 1334, 1172, 1068, 992, 911, 880, 794, 719, 699, 641, 609, 550, 531, 510, cm^{-1}; **HRMS (APCI)** 270.1479 ($M + H^+$. $C_{17}H_{20}NO_2$ requires 270.1489).

Benzyl nona-1,8-dien-5-ylcarbamate (**16a**)



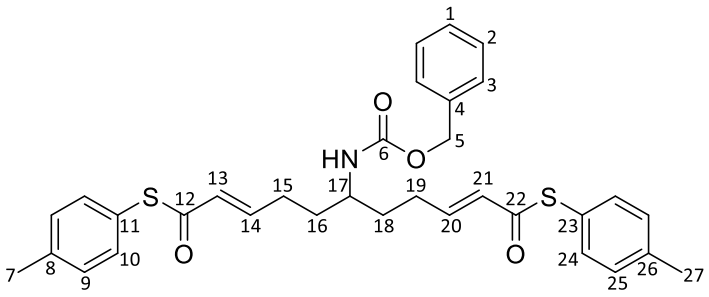
Phthalimide **S5** (2.00 g, 7.46 mmol) was dissolved in EtOH (70 mL). Hydrazine hydrate (1.08 mL, 22.28 mmol) was then added and the reaction mixture was refluxed overnight, during this time a white solid precipitated. The reaction was cooled to room temperature and quenched with concentrated HCl (37% w/w, 28 mL). The solvent was removed under reduced pressure and the residual aqueous solution was diluted with H_2O (80 mL) and then washed with Et_2O (3 x 80 mL). The aqueous layer was treated with NaOH until pH 12 and then extracted with Et_2O (3 x 80 mL). The combined organic layers were washed with 2M HCl (aq, 5 x 80 mL). The aqueous layer was concentrated *in vacuo* to give the amine HCl salt (1.18 g, 6.72 mmol, 90% yield). To a portion of this amine HCl salt (188 mg, 1.07 mmol) was added K_2CO_3 (50% w/w, aq, 0.37 mL, 2.67 mmol) and 1,4-dioxane (5 mL) and the resulting mixture was stirred for 15 min to generate the free amine. Benzyl chloroformate (0.18 mL, 1.28 mmol) was then added. The reaction mixture was stirred at room temperature for 5 h. The reaction was quenched with H_2O (5 mL) and extracted with DCM (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% EtOAc/hexane) to the title compound as a white solid (237 mg, 0.87 mmol, 81% yield). **TLC (SiO_2)** R_f = 0.21 (10% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.41 – 7.28 (5H, m), 5.81 (2H, ddt, *J* = 17.2, 10.1, 6.6 Hz, H-8,14), 5.09 (2H, s, H-5), 5.01 (2H, bd, *J* = 17.2 Hz, H-7,15), 4.96 (2H, bd, *J* = 10.1 Hz, H-7,15), 4.52 (1H, d, *J* = 9.2 Hz, H-NH), 3.75 – 3.58 (1H, m, H-11), 2.18 – 2.02 (4H, m, CH_2), 1.64 – 1.55 (2H, m, CH_2), 1.53 – 1.42 (2H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 156.2 (C-6), 138.1 (C-8,14), 136.8 (C-4), 128.7 (C-1/2/3), 128.2 (C-1/2/3), 115.1 (C-7,15), 66.7 (C-5), 50.8 (C-11), 34.8 (C-10,12), 30.2 (C-9,13) ppm; **IR (ATR)**: ν_{max} 3321, 3075, 2935, 2852, 1692, 1640, 1532, 1452, 1415, 1330, 1230, 1243, 1215, 1046, 1028, 994, 910, 774, 736, 696, 642, 458, cm^{-1}; **HRMS (ESI)** 296.1616 ($M + Na^+$. $C_{17}H_{23}NNaO_2$ requires 296.1621).

***tert*-Butyl nona-1,8-dien-5-ylcarbamate** (**16b**)



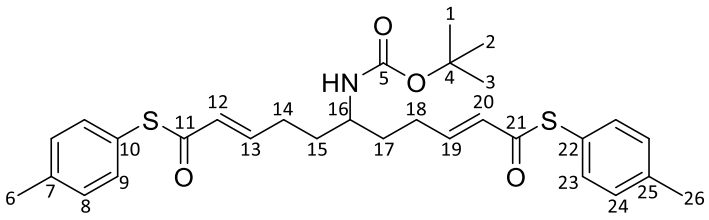
Phthalimide **S5** (2.00 g, 7.46 mmol) was dissolved in EtOH (70 mL). Hydrazine hydrate (1.08 mL, 22.28 mmol) was then added and the reaction mixture was refluxed overnight, during this time a white solid precipitated. The reaction was cooled to room temperature and quenched with concentrated HCl (37% w/w, 28 mL). The solvent was removed under reduced pressure and the residual aqueous solution was diluted with H_2O (80 mL) and then washed with Et_2O (3 x 80 mL). The aqueous layer was treated with NaOH until pH 12 and then extracted with Et_2O (3 x 80 mL). The combined organic layers were washed with 2M HCl (aq, 5 x 80 mL). The aqueous layer was concentrated *in vacuo* to give the amine HCl salt (1.18 g, 6.72 mmol, 90% yield). To a portion of this HCl salt (500 mg, 2.85 mmol) and di-*tert*-butyl dicarbonate (747 mg, 3.42 mmol) in THF (12 mL) at 0 °C was added Et_3N (1.00 mL, 7.13 mmol) in THF (7 mL) over 10 min. The reaction mixture was allowed to warm to room temperature before being heated at 40 °C for 2 h. The reaction was cooled to room temperature and the salts removed by filtration before being concentrated *in vacuo*. The residue was dissolved in DCM (40 mL) and washed with a saturated solution NH_4Cl (aq), a saturated solution $NaHCO_3$ (aq) and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% Et_2O/hexane) to afford the title compound as a white solid (492 mg, 1.93 mmol, 68% yield). *Data were consistent with those reported in the literature*.[1] **TLC (SiO_2)** R_f = 0.33 (20% Et_2O/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 5.81 (2H, ddt, *J* = 17.0, 10.1, 6.5 Hz, H-7,13), 5.01 (2H, ddd, *J* = 17.0, 3.3, 1.6 Hz, H-6,14), 4.95 (2H, dd, *J* = 10.1, 1.6 Hz, H-6,14), 4.27 (1H, bd, *J* = 9.5 Hz, H-NH), 3.66 – 3.53 (1H, m, H-10), 2.18 – 2.01 (4H, m, CH_2), 1.62 – 1.52 (2H, m, CH_2), 1.48 – 1.39 (2H, m, CH_2), 1.43 (9H, s, H-1,2,3) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 155.7 (C-5), 138.3 (C-7,13), 114.9 (C-6,14), 79.0 (C-4), 50.0 (C-10), 34.9 (C-9,11), 30.3 (C-8,12), 28.5 (C-1,2,3) ppm; **IR (ATR)**: ν_{max} 3336, 3078, 2978, 2931, 2859, 1684, 1641, 1524, 1451, 1391, 1366, 1301, 1247, 1172, 1046, 1024, 993, 909, 874, 777, 640, cm^{-1}; **HRMS (ESI)** 262.1778 ($M + Na^+$. $C_{14}H_{25}NNaO_2$ requires 262.1777).

(2*E*,9*E*)-*S*,*S*-Di-*p*-tolyl 6-(((benzyloxy)carbonyl)amino)undeca-2,9-dienebis(thiolate) (17a)



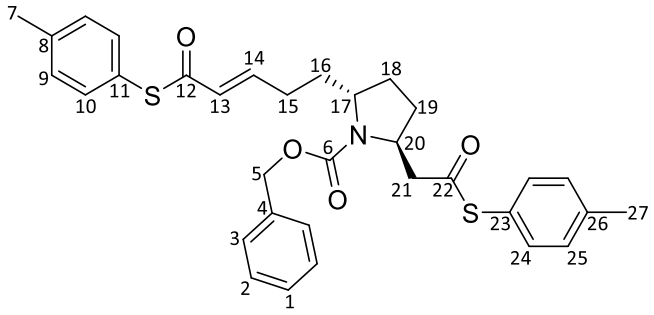
Thioacrylate **2a** (587 mg, 3.29 mmol) was dissolved in 1,2-DCE (10 mL) and placed under N_2. diene **16a** (150 mg, 0.549 mmol) was dissolved in 1,2-DCE (10 mL) and placed under N_2. To a flame dried flask under N_2 were added Hoveyda-Grubbs Catalyst™ 2nd generation (34.0 mg, 0.0549 mmol) and copper iodide (105 mg, 0.549 mmol), followed by the solutions of thioacrylate and diene. The flask was then degassed and backfilled with N_2 (x3). The reaction mixture was heated to 50 °C for 24 h. The reaction was then cooled to room temperature and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10%-50% EtOAc/hexane) to afford the title compound as a brown oil (235 mg, 0.409 mmol, 74% yield). **TLC (SiO_2)** R_f = 0.13 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.38 – 7.28 (9H, m, H-1,2,3,10,24), 7.21 (4H, d, *J* = 8.1 Hz, H-9,25), 6.93 (2H, dt, *J* = 15.5, 6.9 Hz, H-14,20), 6.18 (2H, bd, *J* = 15.5 Hz, H-13,21), 5.20 – 5.00 (2H, m, H-5), 4.53 (1H, d, *J* = 9.5 Hz, H-NH), 3.75 – 3.62 (1H, m, H-17), 2.37 (6H, s, H-7,27), 2.35 – 2.20 (4H, m, CH_2), 1.74 – 1.63 (2H, m, CH_2), 1.59 – 1.48 (2H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.6 (C-12/22), 156.2 (C-6), 145.1 (C-14,20), 139.8 (C-8,26), 134.7 (C-10,24), 130.1 (C-9,25), 128.7/128.4 (C-1,2,3), 128.3 (C-13,21), 124.1 (C-11,23), 67.1 (C-5), 51.0 (C-17), 34.1 (C-16,18), 29.0 (C-15,19), 21.5 (C-7,27) ppm; **IR (ATR)**: ν_{max} 3347, 3031, 2922, 2859, 1682, 1630, 1525, 1494, 1449, 1400, 1337, 1287, 1236, 1181, 1141, 1090, 1053, 1017, 974, 807, 736, 698, 649, 536, 475 cm^{-1}; **HRMS (ESI)** 596.1890 ($M + Na^+$. $C_{33}H_{35}NNaO_4S_2$ requires 596.1900).

(2*E*,9*E*)-*S*,*S*-Di-*p*-tolyl 6-((*tert*-butoxycarbonyl)amino)undeca-2,9-dienebis(thiolate) (**17b**)



Thioacrylate **2a** (684 mg, 3.89 mmol) was dissolved in 1,2-DCE (10 mL) and placed under N_2. Diene **16b** (150 mg, 0.549 mmol) was dissolved in 1,2-DCE (10 mL) and placed under N_2. To a flame dried flask under N_2 were added Hoveyda-Grubbs Catalyst™ 2nd generation (40.1 mg, 0.0639 mmol) and copper iodide (122 mg, 0.639 mmol), followed by the solutions of thioacrylate and diene. The flask was then degassed and backfilled with N_2 (x3). The reaction mixture was heated to 50 °C for 24 h. The reaction was then cooled to room temperature and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10%-50% EtOAc/hexane) to afford the title compound as a brown oil (198 mg, 0.367 mmol, 67% yield). **TLC (SiO_2)** R_f = 0.18 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.31 (4H, d, *J* = 8.0 Hz, H-9,23), 7.21 (4H, d, *J* = 7.9 Hz, H-8,24), 6.95 (2H, dt, *J* = 15.5, 6.9 Hz, H-13,19), 6.19 (2H, dd, *J* = 15.5, 1.6 Hz, H-12,20), 4.28 (1H, d, *J* = 9.6 Hz, H-NH), 3.69 – 3.56 (1H, m, H-16), 2.38 (6H, s, H-6,26), 2.35 – 2.25 (4H, m, CH_2), 1.73 – 1.62 (2H, m, CH_2), 1.59 – 1.51 (2H, m, CH_2), 1.46 (9H, s, H-1,2,3) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.6 (C-11,21), 155.7 (C-5), 145.4 (C-13,19), 139.8 (C-7,25), 134.7 (C-9,23), 130.2 (C-8,24), 128.3 (C-12,20), 124.1 (C-10,22), 79.7 (C-4), 50.4 (C-16), 34.3 (C-15,17), 29.1 (C-14,18), 28.5 (C-1,2,3), 21.5 (C-6,26) ppm; **IR (ATR)**: ν_{max} 3374, 2976, 2924, 1710, 1683, 1631, 1598, 1514, 1494, 1449, 1391, 1365, 1288, 1245, 1169, 1091, 1052, 1017, 975, 935, 863, 807, 705, 648, 618, 536, 475 cm^{-1}; **HRMS (ESI)** 562.2065 ($M + Na^+$. $C_{30}H_{37}NNaO_4S_2$ requires 562.2056).

(2*S*,5*R*)-Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-5-oxo-5-(p-tolylthio)pent-3-en-1-yl)pyrrolidine-1-carboxylate (rac-18a and (*S,R*)-18a)



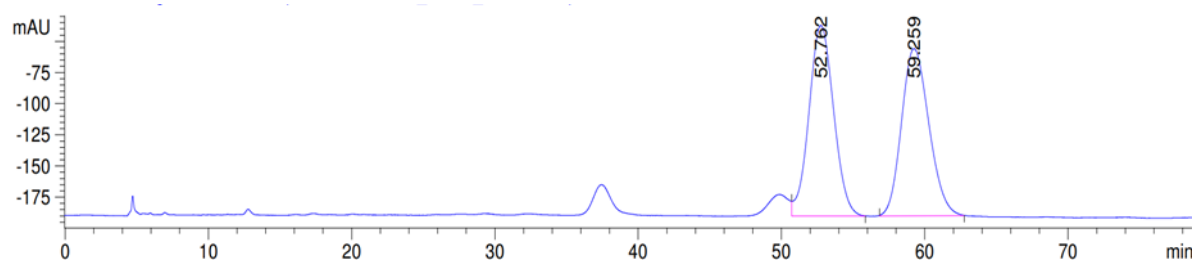
Racemic cyclisation: A solution of diene **17a** (16.0 mg, 0.028 mmol) dissolved in 1,2-DCE (1.4 mL) was added to racemic CSA (20.0 mg, 0.084 mmol) under N_2. The reaction mixture was the heated to 50 °C for 24 h. The reaction was cooled to room temperature, quenched with Et_3N (0.15 mL), diluted with DCM (10 mL) and then washed with saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% EtOAc/hexane) to afford Cbz-pyrrolidine **rac-18a** as a colourless oil (12.3 mg, 0.021 mmol, 75% yield). Spectroscopic data as for **(*S,R*)-18a** below (excluding $[\alpha]_D^{20}$)

Asymmetric cyclisation: A solution of diene **17a** (89.0 mg, 0.155 mmol) dissolved in cyclohexane (10 mL) was added to (*R*)-TRIP (23.3 mg, 0.031 mmol) under N_2. The reaction mixture was the heated to 80 °C for 24 h. The reaction was cooled to room temperature, quenched with Et_3N (0.6 mL) and then concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 5%-10% EtOAc/hexane) to afford Cbz-pyrrolidine **(*S,R*)-18a** as a colourless oil (73.2 mg, 0.128 mmol, 83% yield, 86% ee, major diastereomer)) as a 1:1 mixture of rotamers. **TLC (SiO_2)** R_f = 0.22 (20% EtOAc/hexane).**^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.43 – 7.18 (13H, m, H-1,2,3,9,10,24,25), 6.96 (1H, dt, *J* = 15.6, 6.6 Hz, H-14, *rotamer 1*), 6.86 (1H, dt, *J* = 15.6, 6.6 Hz, H-14, *rotamer 2*), 6.22 (1H, d, *J* = 15.6 Hz, H-13, *rotamer 1*), 6.12 (1H, d, *J* = 15.6 Hz, H-13, *rotamer 2*), 5.30 – 5.07 (2H, m, H-5), 4.37 – 4.25 (1H, m, H-20), 3.91 – 3.78 (1H, m, H-17), 3.36 (1H, dd, *J* = 14.8, 3.2 Hz, H-21, *rotamer 1*), 3.07 (1H, dd, *J* = 14.8, 3.2 Hz, H-21, *rotamer 2*), 2.67 (1H, dd, *J* = 15.0, 9.8 Hz, H-21, *rotamer 1*), 2.59 (1H, dd, *J* = 15.0, 9.8 Hz, H-21, *rotamer 2*), 2.37 (6H, s, H-7,27), 2.29 – 1.75 (6H, m, CH_2), 1.73 – 1.64 (1H, m, CH_2), 1.51 – 1.37 (1H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1 and 195.9 (C-22), 188.6 and 188.4 (C-12), 154.1 and 153.9 (C-6), 145.4 and 145.1 (C-14), 140.0, 139.9, 139.8 and 139.7 (C-8,26), 136.7 and 136.6 (C-4), 134.7 (ArCH), 134.5 (ArCH), 134.4 (ArCH), 130.2 (ArCH),

130.1 (ArCH), 130.1 (ArCH), 128.7 (ArCH), 128.7 (ArCH), 128.3 (ArCH), 128.3 (ArCH), 128.2 (C-13, both rotamers), 124.2, 124.1, 124.0 and 123.9 (C-11,23), 67.0 (C-5, both rotamers), 57.9 and 57.3 (C-17), 55.2 and 54.7 (C-20), 47.2 and 45.7 (C-21), 32.2, 31.0, 29.5, 29.4, 28.4, 27.5, 27.4 and 26.6 (C-15, C-16, C-18, C-19), 21.5 (CH_3, C-7,27, both rotamers overlapping) ppm; **IR (ATR)**: ν_{max} 2923, 1692, 1631, 1598, 1494, 1453, 1404, 1354, 1330, 1305, 1211, 1182, 1103, 1061, 1017, 989, 807, 771, 734, 698, 604, 534, 474 cm^{-1}; **HRMS (ESI)** 596.1915 ($M + Na^+$. $C_{33}H_{35}NNaO_4S_2$ requires 596.1900); **$[\alpha]_D^{20}$** –17.3 (c 0.99, $CHCl_3$).

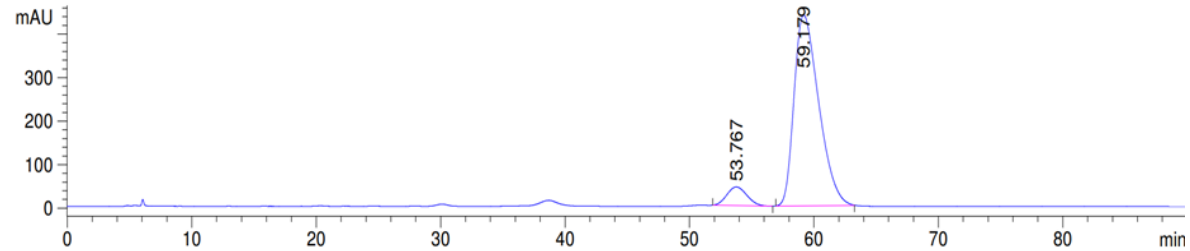
The enantiomers of **18a** were separated *via* chiral HPLC analysis using a CHIRALPAK IG column with a hexane/IPA (50:50) solvent system, at 25 °C and a flow rate of 0.7 mL/min. This gave good separation of the enantiomers with retention times of ≈52 min and ≈59 min.

HPLC trace for rac-18a



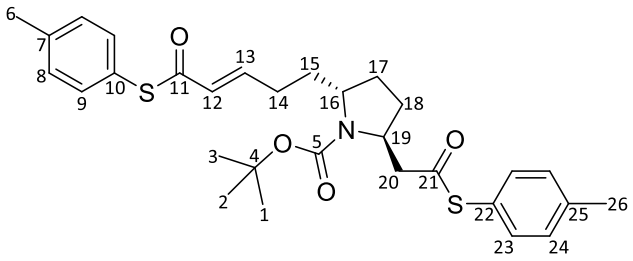
Peak	**Retention Time** (min)	**Area** (%)
1	52.762	50.7031
2	59.259	49.2969

HPLC trace for (*S,R*)-18a



Peak	**Retention Time** (min)	**Area** (%)
1	53.767	7.3342
2	59.179	92.6658

(2*S*,5*R*)-*tert*-Butyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-5-oxo-5-(*p*-tolylthio)pent-3-en-1-yl)pyrrolidine-1-carboxylate (**rac-18b and (*S,R*)-18b**)



Racemic cyclisation

A solution of diene **17b** (50.0 mg, 0.093 mmol) dissolved in 1,2-DCE (10 mL) was added to racemic CSA (65.0 mg, 0.28 mmol) under N_2. The reaction mixture was the heated to 50 °C for 24 h. The reaction was cooled to room temperature, quenched with Et_3N (0.5 mL), diluted with DCM (10 mL) and then washed with saturated $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% EtOAc/hexane) to afford Boc-pyrrolidine **rac-18b** as a yellow oil (24.2 mg, 0.045 mmol, 48% yield).

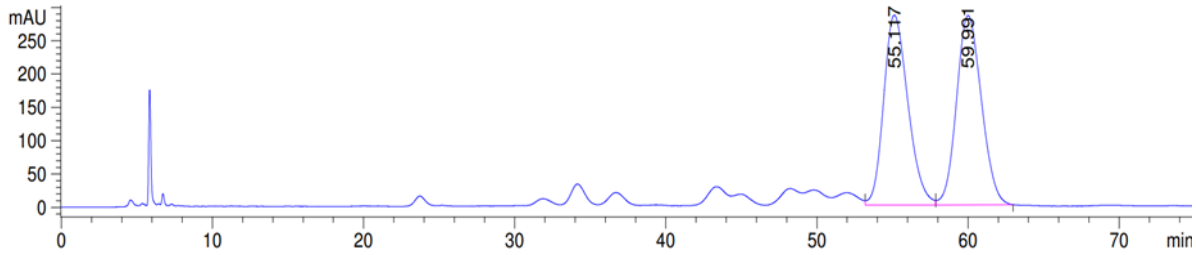
Asymmetric cyclisation

A solution of diene **17b** (56.0 mg, 0.104 mmol) dissolved in cyclohexane (5 mL) was added to (R)-TRIP (15.8 mg, 0.021 mmol) under N_2. The reaction mixture was the heated to 80 °C for 24 h. The reaction was cooled to room temperature, quenched with Et_3N (0.5 mL) and then concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 5%-10% EtOAc/hexane) to afford Boc-pyrrolidine **(*S,R*)-18b** as a yellow oil (44.5 mg, 0.082 mmol, 79% yield, 84% ee, major diastereomer)) as a 1:1 mixture of rotamers. **TLC (SiO_2)** R_f = 0.30 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.33 – 7.26 (4H, m, H-9,23), 7.25 – 7.19 (4H, m, H-8,24), 7.01 – 6.89 (1H, m, H-13), 6.21 (1H, d, *J* = 15.8 Hz, H-12, *rotamer 1*), 6.17 (1H, d, *J* = 15.8 Hz, H-12, *rotamer 2*), 4.31 – 4.23 (1H, m, H-19, *rotamer 1*), 4.21 – 4.14 (1H, m, H-19, *rotamer 2*), 3.84 – 3.77 (1H, m, H-16, *rotamer 1*), 3.75 – 3.68 (1H, m, H-16, *rotamer 2*), 3.33 (1H, dd, , *J* = 14.7, 3.2 Hz, H-20, *rotamer 1*), 3.11 (1H, dd, , *J* = 14.7, 3.2 Hz, H-20, *rotamer 2*), 2.66 (1H, dd, , *J* = 14.6, 9.6 Hz, H-20, *rotamer 1*), 2.62 (1H, dd, , *J* = 14.6, 9.6 Hz, H-20, *rotamer 2*), 2.37 (6H, s, H-6,26), 2.30 – 1.80 (6H, m, CH_2), 1.70 – 1.63 (1H, m, CH_2), 1.51 (9H, s, H-1,2,3, *rotamer 1*), 1.48 (9H, s, H-1,2,3, *rotamer 2*), 1.46 – 1.35 (1H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1 and 196.0 (C-21), 188.6 and 188.5 (C-11), 153.6 and 153.5

(C-5), 145.6 and 145.4 (C-13), 140.0, 139.9, 139.8 and 139.7 (C-7,25), 134.8 (ArCH), 134.7 (ArCH), 134.5 (ArCH), 134.4 (ArCH), 130.2 (ArCH), 130.2 (ArCH), 130.2 (ArCH), 130.1 (ArCH), 128.4 and 128.2 (C-12), 124.3, 124.2, 124.0 and 123.9 (C-10,22), 80.2 and 79.9 (C-4), 57.5 and 57.1 (C-16), 54.9 and 54.8 (C-19), 47.4 (CH_2), 45.9 (CH_2), 32.3 (CH_2), 31.2 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 28.7 (C-1,2,3, both rotamers), 28.2 (CH_2), 27.4 (CH_2), 27.4 (CH_2), 26.6 (CH_2), 21.5 (C-6,26, both rotamers, overlapping) ppm; **IR (ATR)**: ν_{max} 2971, 2926, 1685, 1632, 1598, 1494, 1477, 1454, 1386, 1365, 1305, 1277, 1256, 1167, 1119, 1104, 1016, 991, 887, 807, 774, 732, 647, 608, 575, 534, 474 cm^{-1}; **HRMS (ESI)** 562.2061 (M + Na^+. $C_{30}H_{37}NNaO_4S_2$ requires 562.2056); **$[\alpha]_D^{20}$** -16.2 (c 0.95, $CHCl_3$)

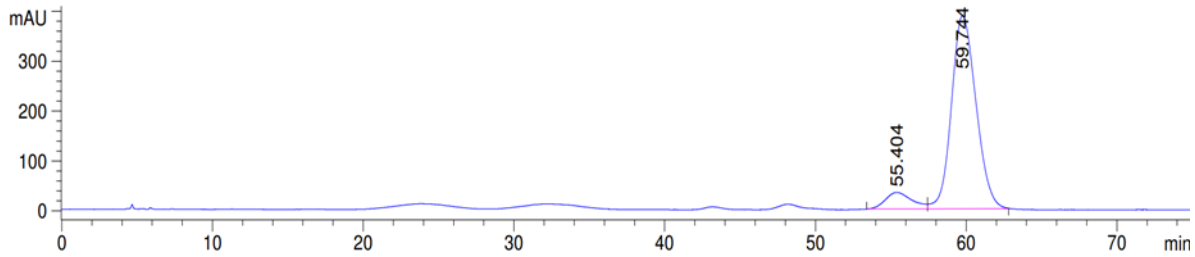
The enantiomers of **18b** were separated *via* chiral HPLC analysis using a CHIRALPAK IG column with a hexane/IPA (90:10) solvent system, at 25 °C and a flow rate of 0.7 mL/min. This gave good separation of the enantiomers with retention times of ≈55 min and 59 min.

HPLC trace of **rac-18b**



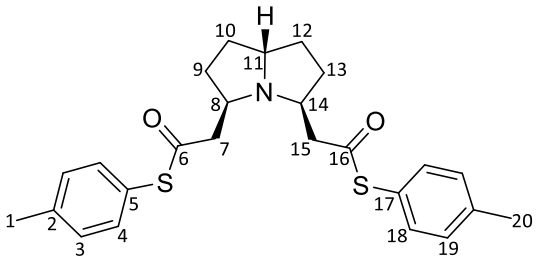
Peak	**Retention Time** (min)	**Area** (%)
1	55.117	49.4286
2	59.991	50.5714

HPLC trace of **(*S,R*)-18b**



Peak	**Retention Time** (min)	**Area** (%)
1	55.404	8.5719
2	59.744	91.4281

***S*,*S*'-Di-*p*-tolyl 2,2'-((3*R*,5*S*,7a*s*)-hexahydro-1*H*-pyrrolizine-3,5-diyl)diethanethioate** (**19a**)



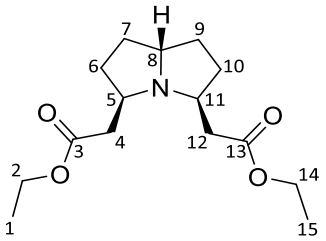
From (*S,R*)-18a

Cbz-pyrrolidine **(*S,R*)-18a** (37.0 mg, 0.064 mmol) was dissolved in DCM (4 mL), 1M solution of boron trichloride in DCM (0.322 mL, 0.322 mmol) was then added at 0 °C and the reaction stirred at room temperature for 24 h. The reaction mixture was diluted with DCM (5 mL) and quenched with a saturated aqueous solution of $NaHCO_3$. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 1:1 Et_2O/hexane, column deadened with 1% Et_3N) to afford pyrrolizidine **19a** as a colourless oil (10.5 mg, 0.024 mmol, 38% yield).

From (*S,R*)-18b

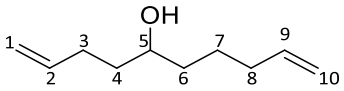
Boc-pyrrolidine **(*S,R*)-18b** (50.0 mg, 0.093 mmol) was dissolved in a 4M solution of HCl in 1,4-dioxane (1 mL) and then stirred at room temperature for 24 h. The reaction mixture was diluted with DCM (2 mL) and quenched with solid K_2CO_3. The reaction was then washed with brine and extracted with DCM (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 1:1 Et_2O/hexane, column deadened with 1% Et_3N) to afford pyrrolizidine **19a** as a colourless oil (14.5 mg, 0.033 mmol, 35% yield). **TLC (SiO_2)** R_f = 0.32 (1:1 Et_2O/hexane, plates deadened with 1% Et_3N). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.31 – 7.27 (4H, m, H-4,18), 7.21 (4H, d, *J* = 8.1 Hz, H-3,19), 3.62 (1H, quintet, *J* = 6.7 Hz, H-11), 3.31 – 3.23 (2H, m, H-8,14), 2.90 (2H, dd, *J* = 14.8, 6.0 Hz, H-7,15), 2.60 (2H, dd, *J* = 14.8, 7.9 Hz, H-7,15), 2.37 (6H, s, H-1,21), 2.06 – 1.91 (4H, m, CH_2), 1.60 – 1.49 (2H, m, CH_2), 1.49 – 1.38 (2H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8 (C-6,16), 139.7 (C-2,20), 134.6 (C-4,18), 130.2 (C-3,19), 124.5 (C-5,17), 64.5 (C-11), 63.5 (C-8,14), 50.5 (C-7,15), 31.4 (C-CH_2), 31.2 (C-CH_2), 30.5 (C-CH_2), 21.48 (C-1,21) ppm; **IR (ATR)**: ν_{max} 2954, 1700, 1598, 1494, 1400, 1354, 1182, 1088, 985, 807, 751, 534, 473 cm^{-1}; **HRMS (ESI)** 462.1535 (M + Na^+. $C_{25}H_{29}NNaO_2S_2$ requires 462.1532)

Diethyl 2,2'-((3*R*,5*S*,7as)-hexahydro-1H-pyrrolizine-3,5-diyl)diacetate (**22**)



Boc-pyrrolidine **(*SR*)-18b** (83.6 mg, 0.155 mmol) was dissolved in a 4M solution of HCl in 1,4-dioxane (1 mL) and then stirred at room temperature for 24 h. The reaction mixture was concentrated *in vacuo,* dissolved in EtOH (1 mL), and then treated with 1M solution of NaOEt (3 equiv) for 24 h. The reaction was filtered and concentrated *in* vacuo. The crude residue was then dissolved in EtOAc, washed with a saturated aqueous solution of K_2CO_3 and the aqueous layer extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (Al_2O_3, 20% EtOAc/hexane) to afford pyrrolizidine **22** as a yellow oil (23.6 mg, 0.083 mmol, 54% yield). *Data were consistent with those reported in the literature*.[2] **TLC (Al_2O_3)** R_f = 0.35 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 4.11 (4H, q, *J* = 7.3 Hz, H-2,14), 3.58 (1H, quintet, *J* = 6.5 Hz, H-8), 3.23 – 3.14 (2H, m, H-5,11), 2.54 (2H, dd, *J* = 15.0, 6.0 Hz, H-4,12), 2.24 (2H, dd, *J* = 15.0, 8.2 Hz, H-4,12), 2.05 – 1.89 (4H, m, CH_2), 1.53 – 1.37 (4H, m, CH_2), 1.25 (6H, t, *J* = 7.3 Hz, H-1,15) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.5 (C-3,13), 64.5 (C-8), 63.0 (C-5,11), 60.3 (C-2,14), 41.7 (C-4,12), 31.5 (C-6,10), 31.2 (C-7,9), 14.4 (C-1,15) ppm; **IR (ATR)**: ν_{max} 2919, 2850, 1731, 1464, 1448, 1417, 1370, 1296, 1268, 1250, 1170, 1141, 1105, 1086, 1032, 952, 920, 852, 805, 732, 642, 570, 503 cm^{-1}; **HRMS (ESI)** 284.1853 ($M + H^+$. $C_{15}H_{26}NO_4$ requires 284.1856).

Deca-1,9-dien-5-ol (**24**)

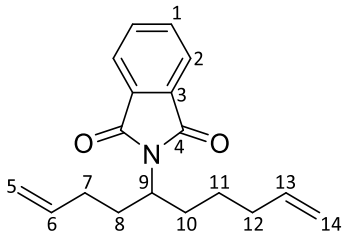


Oxalyl chloride (2.90 mL, 34.3 mmol) was dissolved in DCM (50 mL), DMSO (4.70 mL, 66.2 mmol) was then added dropwise within 5 min at –78 °C. The reaction mixture was stirred at -78 °C for 10 min before 5-hexen-1-ol (2.50 mL, 20.8 mmol) in DCM (7.5 mL) was added dropwise over 10 min. The resulting reaction mixture was stirred at –78 °C for 1 h. Triethylamine (9.20 mL, 66.0 mmol) was added over 10 min and the reaction mixture allowed to warm to 0 °C, after which H_2O (60 mL) and DCM (60 mL) were added and the phases separated. The aqueous phase was then extracted with DCM (3 x 60 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo* (up to 500 mbar). The crude product was purified by flash column chromatography (SiO_2, pentane/Et_2O 9/1) to afford aldehyde 5-hexen-1-al **23** as a pale-yellow solution (1.80 g, 18.0 mmol, 88% yield; the aldehyde was kept in a solution of pentane/Et_2O due to its volatility. Yield calculated from NMR).

Magnesium turnings (446 mg, 18.3 mmol) and iodine (1 crystal) were added to a flame dried flask under N_2, which was warmed until the iodine sublimed. The flask was allowed to cool to room temperature before the addition of dry THF (50 mL). To this mixture, 4-bromo-1-butene (1.86 mL, 18.3 mmol) was added slowly at room temperature (the flask was placed in a water bath to control the temperature). The resulting reaction mixture was then stirred at room temperature for 1 h to form the Grignard reagent. The reaction was then cooled to 0 °C before the dropwise addition of aldehyde **23** (900 mg, 9.17 mmol) over 10 min. The reaction was stirred at room temperature overnight. The reaction mixture was then cooled to 0 °C and quenched with saturated aqueous solution of NH_4Cl (50 mL). The aqueous phase was extracted with Et_2O (3 x 50 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% EtOAc/hexane) to afford the title compound as a yellow oil (746.1 mg, 4.84 mmol, 53% yield). *Data were consistent with those reported in the literature*.[3] **TLC (SiO_2)** R_f = 0.16 (10% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 5.83 (2H, ddt, *J* = 16.9, 10.4, 6.6 Hz, H-2,9), 5.80 (2H, ddt, *J* = 16.9, 10.1, 6.6 Hz, H-2,9), 5.08 – 4.92 (4H, m, H-1,10), 3.67 – 3.58 (1H, m, H-5), 2.26 – 2.00 (4H, m, CH_2), 1.62 – 1.38 (7H, m, CH_2 and OH) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 138.8/138.7 (C-2,9), 114.9/114.8 (C-1,10), 71.5 (C-5), 37.0/36.6 (C-4,6),

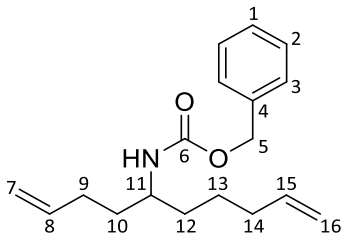
33.8/30.2 (C-3,8), 25.0 (C-7) ppm; **IR (ATR)**: ν_{max} 3343, 3078, 2978, 2931, 2860, 1641, 1441, 1416, 1262, 993, 908, 827, 636, 554 cm^{-1}; **HRMS (APCI)** 155.1436 ($M + H^+$. $C_{10}H_{19}O$ requires 155.1430).

2-(Deca-1,9-dien-5-yl)isoindoline-1,3-dione (**25**)



Phthalimide (596 mg, 4.05 mmol) and triphenylphosphine (1.06 g, 4.05 mmol) were dissolved in THF (25 mL). Secondary alcohol **24** (500 mg, 3.24 mmol) was then added followed by DEAD (2.06 mL, 4.54 mmol) at room temperature over 20 min. The reaction mixture was stirred at room temperature for 24 h. The solvent was then removed under reduced pressure and the resulting crude oil triturated with hexane/Et_2O (2:1 mixture) until complete removal of the solids. The combined organic layers were concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 5% EtOAc/hexane) to afford the title compound as a yellow oil (525 mg, 1.85 mmol, 57% yield). **TLC (SiO_2)** R_f = 0.33 (10% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.81 (2H, dd, *J* = 5.5, 3.2 Hz, H-2), 7.71 (2H, dd, *J* = 5.5, 3.2 Hz, H-1), 5.75 (1H, ddt, *J* = 17.0, 10.2, 6.5 Hz, H-6,13), 5.72 (1H, ddt, *J* = 17.0, 10.2, 6.5 Hz, H-6,13) 5.00 – 4.87 (4H, m, H-5,14), 4.22 (1H, m, H-9), 2.28 – 1.97 (6H, m, CH_2), 1.84 – 1.66 (2H, m, CH_2), 1.42 – 1.26 (2H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 168.9 (C-4), 138.4 and 137.6 (C-6,13), 134.0 (C-1), 131.9 (C-3), 123.3 (C-2), 115.3 and 114.9 (C-5,14), 51.8 (C-9), 33.4 and 31.9 (C-8,10), 31.7 and 31.0 (C-7,12), 26.0 (C-11) ppm; **IR (ATR)**: ν_{max} 3077, 2928, 2860, 1772, 1704, 1641, 1613, 1468, 1456, 1393, 1369, 1332, 1261, 1172, 1068, 995, 911, 871, 794, 719, 698, 642, 531, 510 cm^{-1}; **HRMS (ESI)** 284.1642 ($M + H^+$. $C_{18}H_{22}NO_2$ requires 284.1645).

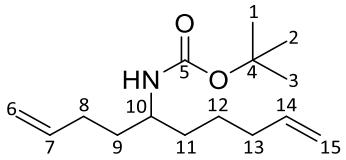
Benzyl deca-1,9-dien-5-ylcarbamate (**16c**)



Phthalimide **25** (362 mg, 1.28 mmol) was dissolved in EtOH (20 mL). Hydrazine hydrate (0.12 mL, 2.56 mmol) was then added and the reaction mixture was refluxed overnight, during this time a white solid precipitated. The reaction was cooled to room temperature and quenched with concentrated HCl (37% w/w, 5 mL). The solvent was removed under reduced pressure and the residual aqueous solution was diluted with H_2O (30 mL) and then washed with Et_2O (3 x 30 mL). The aqueous layer was treated with NaOH until pH 12 and then extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with 2M HCl (aq, 5 x 30 mL). The aqueous layer was concentrated *in vacuo* to give the amine HCl salt **26** (230 mg, 1.21 mmol, 94% yield).

To amine HCl salt **26** (50.8 mg, 0.268 mmol) was added K_2CO_3 (50% w/w, aq, 0.127 mL, 0.670 mmol) and 1,4-dioxane (2 mL) and the resulting mixture was stirred for 15 min to generate the free amine. Benzyl chloroformate (0.050 mL, 0.32 mmol) was then added. The reaction mixture was stirred at room temperature for 5 h. The reaction was quenched with H_2O (5 mL) and extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% EtOAc/hexane) to afford the title compound as a white solid (26.2 mg, 0.0911 mmol, 34% yield). **TLC (SiO_2)** R_f = 0.25 (10% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.38 – 7.28 (5H, m, H-1,2,3), 5.86 – 5.70 (2H, m, H-8,15), 5.09 (2H, s, H-5) 5.05 – 4.91 (4H, m, H-7,16), 4.49 (1H, bd, *J* = 9.6 Hz, H-NH), 3.72 – 3.59 (1H, m, H-11), 2.16 – 1.97 (4H, m, CH_2), 1.62 – 1.30 (6H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 156.2 (C-6), 138.6 and 138.2 (C-8,15), 136.8 (C-4), 128.7 and 128.2 (C-1,2,3), 115.0 and 114.9 (C-7,16), 66.7 (C-5), 51.0 (C-11), 34.9 and 34.8 (C-10,12), 33.6 and 30.3 (C-9,14), 25.2 (C-13) ppm; **IR (ATR)**: ν_{max} 3323, 3074, 2935, 2857, 1693, 1641, 1532, 1455, 1415, 1243, 1053, 1028, 995, 910, 774, 736, 697, 642 cm^{-1}; **HRMS (ESI)** 310.1778 ($M + Na^+$. $C_{18}H_{25}NNaO_2$ requires 310.1777)

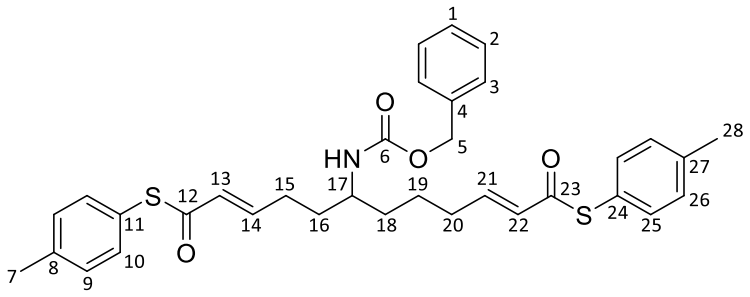
***tert*-Butyl deca-1,9-dien-5-ylcarbamate** (**16d**)



Phthalimide **25** (362 mg, 1.28 mmol) was dissolved in EtOH (20 mL). Hydrazine hydrate (0.12 mL, 2.56 mmol) was then added and the reaction mixture was refluxed overnight, during this time a white solid precipitated. The reaction was cooled to room temperature and quenched with concentrated HCl (37% w/w, 5 mL). The solvent was removed under reduced pressure and the residual aqueous solution was diluted with H_2O (30 mL) and then washed with Et_2O (3 x 30 mL). The aqueous layer was treated with NaOH until pH 12 and then extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with 2M HCl (aq, 5 x 30 mL). The aqueous layer was concentrated *in vacuo* to give the amine HCl salt **26** (230 g, 1.21 mmol, 94% yield).

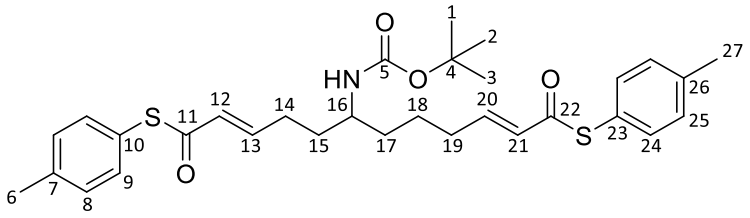
Amine HCl salt **26** (230 mg, 1.21 mmol) and Et_3N were added to DCM (10 mL) and stirred for 15 min to generate free amine. The reaction was then cooled to 0 °C before the addition of Di-*tert*-butyl dicarbonate (528 mg, 2.42 mmol). The reaction was stirred at room temperature for 24 h. The reaction was quenched with citric acid (0.1M aq. 15 mL) and extracted with DCM (3 x 30 mL). The combined organic layers were washed with a saturated solution $NaHCO_3$ (aq) and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 5% Et_2O/hexane) to the title compound as a yellow oil (152 mg, 0.60 mmol, 49% yield). *Data was consistent with those reported in the literature*.[3] **TLC (SiO_2)** R_f = 0.25 (10% Et_2O/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 5.87 – 5.73 (2H, m, H-7,14), 5.05 – 4.91 (4H, m, H-6,15), 4.27 (1H, bd, *J* = 9.6 Hz, H-NH), 3.66 – 3.49 (1H, m, H-10), 2.19 – 1.96 (4H, m, CH_2), 1.60 – 1.27 (6H, m, CH_2), 1.44 (9H, s, H-1,2,3) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$); δ 155.8 (C-5), 138.8 and 138.4 (C-7,14), 114.9 and 114.8 (C-6,15), 79.1 (C-4), 50.2 (C-10), 35.1and 35.0 (C-9,11), 33.7 and 30.4 (C-8,13), 28.6 (C-1,2,3), 25.2 (C-12) ppm; **IR (ATR)**: ν_{max} 3342, 3078, 2978, 2932, 2858, 1687, 1641, 1519, 1453, 1391, 1365, 1247, 1171, 1050, 995, 909, 864, 777, 641 cm^{-1}; **HRMS (ESI)** 276.1934 (M + Na^+. $C_{15}H_{27}NNaO_2$ requires 276.1934)

(2*E*,10*E*)-*S*,*S*-Di-*p*-tolyl 6-(((benzyloxy)carbonyl)amino)dodeca-2,10-dienebis(thioate) (17c)



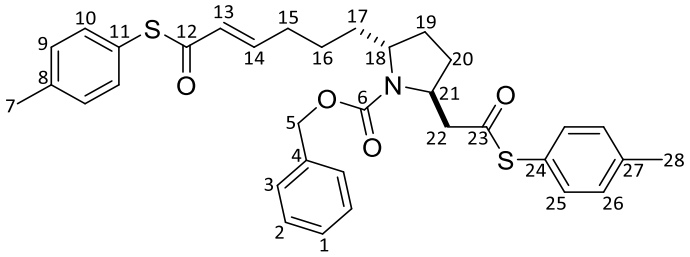
Thioacrylate **2a** (93.0 mg, 0.522 mmol) was dissolved in 1,2-DCE (2.5 mL) and placed under N_2. Diene **16c** (25.0 mg, 0.087 mmol) was dissolved in 1,2-DCE (2.5 mL) and placed under N_2. To a flame dried flask under N_2 were added Hoveyda-Grubbs Catalyst™ 2nd generation (5 mg, 0.009 mmol) and copper iodide (16 mg, 0.087 mmol), followed by the solutions of thioacrylate and diene. The flask was then degassed and backfilled with N_2 (x3). The reaction mixture was then heated to 50 °C for 24 h. The reaction was then cooled to room temperature and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10%-50% EtOAc/hexane) to afford amino-thioester **17c** as a brown oil (33 mg, 0.056 mmol, 64% yield). **TLC (SiO_2)** R_f = 0.15 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.39 – 7.28 (9H, m, H-1,2,3,10,25), 7.22 (4H, dd, *J* = 8.1, 2.4 Hz, H-9,26), 7.00 – 6.86 (2H, m, H-14,21), 6.18 (2H, bd, *J* = 14.4 Hz, H-13,22), 5.20 – 5.03 (2H, m, H-5), 4.47 (1H, d, *J* = 9.5 Hz, H-N-H), 3.75 – 3.62 (1H, m, H-17), 2.38 (6H, s, H-7,28), 2.35 – 2.14 (4H, m, CH_2), 1.75 – 1.35 (6H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.7 and 188.6 (C-12,23), 156.2 (C-6), 145.8 and 145.3 (C-14,21), 139.8 (C-8,27), 134.7 (C-10,25), 130.1 (C-9,26), 128.7 (C-1,2,3), 128.3 and 128.3 (C-13/22), 124.1 (C-11,24), 67.0 (C-5), 51.0 (C-17), 35.3 (C-16/18), 34.2 (C-16,18), 32.1 and 29.1 (C-15,20), 24.5 (C-19), 21.5 (C-7,28) ppm; **IR (ATR)**: ν_{max} 3346, 3030, 2925, 2859, 1683, 1630, 1524, 1494, 1452, 1399, 1237, 1055, 1017, 807, 738, 698, 649, 535, 475 cm^{-1}; **HRMS (ESI)** 610.2056 (M + Na^+. $C_{34}H_{37}NNaO_4S_2$ requires 610.2056).

(2*E*,10*E*)-*S*,*S*-Di-*p*-tolyl 6-((*tert*-butoxycarbonyl)amino)dodeca-2,10-dienebis(thioate) (17d)



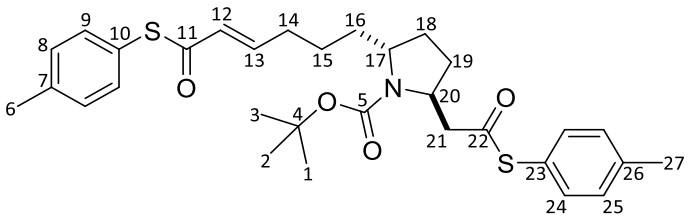
Thioacrylate **2a** (422 mg, 2.37 mmol) was dissolved in 1,2-DCE (9 mL) and placed under N_2. diene **16d** (100 mg, 0.395 mmol) was dissolved in 1,2-DCE (9 mL) and placed under N_2. To a flame dried flask under N_2 were added Hoveyda-Grubbs Catalyst™ 2nd generation (25.0 mg, 0.0395 mmol) and copper iodide (75.0 mg, 0.395 mmol), followed by the solutions of thioacrylate and diene. The flask was then degassed and backfilled with N_2 (x3). The reaction mixture was heated to 50 °C for 24 h. The reaction was then cooled to room temperature and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10%-30% EtOAc/hexane) to afford amino-thioester **17d** as a brown oil (131.8 mg, 0.238 mmol, 60% yield). **TLC (SiO_2)** R_f = 0.19 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.31 (4H, dd, *J* = 8.2, 1.6 Hz, H-9,24), 7.22 (4H, d, *J* = 8.2 Hz, H-8,25), 7.00 – 6.89 (2H, m, H-13,20), 6.19 (1H, d, *J* = 15.5 Hz, H-12 or H-21), 6.19 (1H, d, *J* = 15.5 Hz, H-12 or H-21, overlapping), 4.26 (1H, d, *J* = 9.6 Hz, H-NH), 3.68 – 3.54 (1H, m, H-16), 2.38 (6H, s, H-6,27), 2.35 – 2.18 (4H, m, H-14,19), 1.73 – 1.48 (6H, m, H-15,17,18), 1.46 (9H, s, H-1,2,3) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.7 and 188.6 (C-11,22), 155.8 (C-5), 145.9 and 145.6 (C-13,20), 139.8 (C-7,26), 134.7 (C-9,24), 130.1 (C-8,25), 128.3 and 128.2 (C-12,21), 124.1 (C-10,23), 79.5 (C-4), 50.2 (C-16), 35.4 and 34.3 (C-15,17), 32.1 and 29.1 (C-14,19), 28.5 (C-1,2,3), 24.5 (C-18), 21.5 (C-6,26) ppm; **IR (ATR)**: ν_{max} 3368, 2975, 2928, 2863, 1681, 1630, 1598, 1511, 1494, 1450, 1391, 1365, 1303, 1245, 1167, 1105, 1092, 1053, 1017, 982, 807, 733, 705, 684, 617, 535, 475 cm^{-1}; **HRMS (ESI)** 576.2225 ($M + Na^+$. $C_{31}H_{39}NNaO_4S_2$ requires 576.2213).

(±)-Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-6-oxo-6-(*p*-tolylthio)hex-4-en-1-yl)pyrrolidine-1-carboxylate (**18c**)



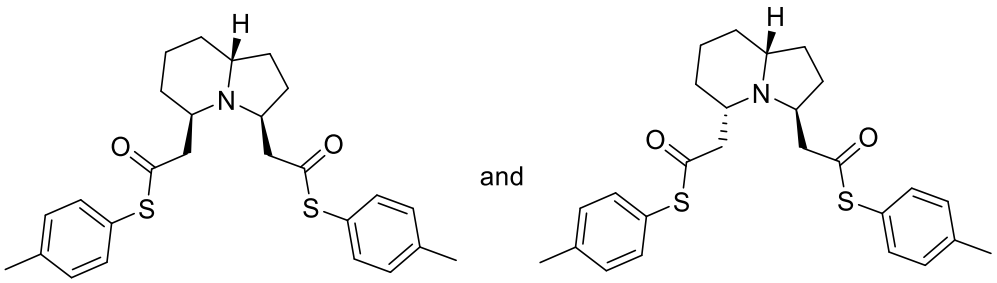
Diene **17c** (30.0 mg, 0.051 mmol) dissolved in 1,2-DCE (2.5 mL) was added to racemic CSA (36.0 mg, 0.153 mmol) under N_2. The reaction mixture was the heated to 50 °C for 24 h. The reaction was cooled to room temperature, quenched with Et_3N (0.3 mL), diluted with DCM (10 mL) and then washed with saturated aqueous solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10%-20% EtOAc/hexane) to afford Cbz-pyrrolidine **18c** as a colourless oil (17.3 mg, 0.029 mmol, 57% yield) as a 1:1 mixture of rotamers. **TLC (SiO_2)** R_f = 0.21 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.44 – 7.19 (13H, m, H-1,2,3,9,10,25,26), 6.94 (1H, dt, *J* = 15.6, 6.5 Hz, H-14, *rotamer 1*), 6.91 (1H, dt, *J* = 15.6, 6.5 Hz, H-14, *rotamer 2*), 6.17 (1H, d, *J* = 15.6 Hz, H-13, *rotamer 1*), 6.11 (1H, d, *J* = 15.6 Hz, H-13, *rotamer 2*), 5.24 – 5.08 (2H, m, H-5), 4.35 – 4.25 (1H, m, H-21), 3.88 – 3.76 (1H, m, H-18), 3.37 (1H, dd, *J* = 14.8, 3.2 Hz, H-22, *rotamer 1*), 3.07 (1H, dd, *J* = 14.8, 3.2 Hz, H-22, *rotamer 2*), 2.67 (1H, dd, *J* = 14.9, 9.8 Hz, H-22, *rotamer 1*), 2.59 (1H, dd, *J* = 14.9, 9.8 Hz, H-22, *rotamer 2*), 2.37 (6H, s, H-7,28), 2.35 – 1.81 (6H, m, CH_2), 1.73 – 1.62 (1H, m, CH_2), 1.53 – 1.27 (3H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1 and 195.9 (C-23), 188.7 and 188.5 (C-12), 154.2 and 153.9 (C-6), 146.1 and 145.8 (C-14), 140.0, 139.8, 139.8 and 139.7 (C-8,27), 136.8 and 136.7 (C-4), 134.7 (ArCH), 134.7 (ArCH), 134.5 (ArCH), 134.5 (ArCH), 130.2 (ArCH), 130.1 (ArCH), 128.7 (ArCH), 128.7 (ArCH), 128.2 (ArCH), 128.2 (ArCH), 128.1 (C-13, both rotamers), 124.1, 124.0 and 123.9 (C-11,24), 66.7 (C-5, both rotamers), 58.2 and 57.7 (C-18), 55.1 and 54.6 (C-21), 47.2 (CH_2), 45.8 (CH_2), 33.8 (CH_2), 32.5, (CH_2), 32.3 (CH_2), 28.4 (CH_2), 27.6 (CH_2), 27.5 (CH_2), 26.5 (CH_2), 25.2 (CH_2), 25.1 (CH_2), 21.5 (C-7,28, both rotamers, overlapping) ppm; **IR (ATR)**: ν_{max} 2923, 1689, 1631, 1494, 1454, 1404, 1353, 1330, 1305, 1281, 1211, 1181, 1103, 1017, 985, 806, 771, 733, 698, 648, 603, 534, 474 cm^{-1}; **HRMS (ESI)** 610.2064 ($M + Na^+$. $C_{34}H_{37}NNaO_4S_2$ requires 610.2056).

(±)-*tert*-butyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-6-oxo-6-(*p*-tolylthio)hex-4-en-1-yl)pyrrolidine-1-carboxylate (**18d**)



Diene **17d** (53.0 mg, 0.096 mmol) dissolved in 1,2-DCE (5 mL) was added to racemic CSA (67.0 mg, 0.288 mmol) under N_2. The reaction mixture was the heated to 50 °C for 24 h. The reaction was cooled to room temperature, quenched with Et_3N (0.5 mL), diluted with DCM (10 mL) and then washed with saturated aqueous solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% EtOAc/hexane) to afford Boc-pyrrolidine **18d** as a yellow oil (20.6 mg, 0.036 mmol, 38% yield) as a 1:1 mixture of rotamers. **TLC (SiO_2)** R_f = 0.29 (20% EtOAc/hexane). **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.33 – 7.26 (4H, m, H-9,24), 7.25 – 7.18 (4H, m, H-8,25), 6.94 (1H, dt, *J* = 14.6, 9.6 Hz, H-13), 6.19 (1H, d, *J* = 15.5 Hz, H-12, *rotamer 1*), 6.16 (1H, d, *J* = 15.5 Hz, H-12, *rotamer 2*), 4.30 – 4.21 (1H, m, H-20, *rotamer 1*), 4.20 – 4.12 (1H, m, H-20, *rotamer 2*), 3.81 – 3.73 (1H, m, H-17, *rotamer 1*), 3.72 – 3.64 (1H, m, H-17, *rotamer 2*), 3.33 (1H, dd, *J* = 14.7, 3.2 Hz, H-21, *rotamer 1*), 3.11 (1H, dd, *J* = 14.7, 3.2 Hz, H-21, *rotamer 2*), 2.65 (1H, dd, *J* = 14.8, 9.7 Hz, H-21, *rotamer 1*), 2.58 (1H, dd, *J* = 14.8, 9.7 Hz, H-21, *rotamer 2*), 2.37 (6H, s, H-6,27), 2.34 – 1.80 (6H, m, CH_2), 1.69 – 1.60 (2H, m, CH_2), 1.51 (9H, s, H-1,2,3, *rotamer 1*), 1.48 (9H, s, H-1,2,3, *rotamer 2*), 1.46 – 1.36 (2H, m, CH_2) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.2 and 196.1 (C-22), 188.7 and 188.5 (C-11), 153.7 and 153.5 (C-5), 146.3 and 145.9 (C-13), 140.0, 139.8, 139.8 and 139.7 (C-7,26), 134.7 (ArCH), 134.5 (ArCH), 134.5 (ArCH), 130.2 (ArCH), 130.1 (ArCH), 128.3, 128.2, 128.0 and 127.9 (C-12 and ArCH), 124.3, 124.2 and 124.0 (C-10,23), 80.0 and 79.7 (C-4), 57.7 and 57.6 (C-17), 54.8 and 54.7 (C-20), 47.4 (CH_2), 47.3 (CH_2), 46.0 (CH_2), 45.9 (CH_2), 33.8 (CH_2), 32.6 (CH_2), 32.3 (CH_2), 28.7 (C-1,2,3), 28.2 (CH_2), 27.5 (CH_2), 27.5 (CH_2), 26.5 (CH_2), 25.3 (CH_2), 25.2 (CH_2), 21.5 (C-6,27, both rotamers, overlapping) ppm; **IR (ATR)**: ν_{max} 2972, 2924, 1685, 1632, 1598, 1494, 1454, 1387, 1365, 1257, 1168, 1117, 1017, 987, 911, 889, 806, 773, 731, 647, 608, 573, 534, 474 cm^{-1}; **HRMS (ESI)** 576.2213 (M + Na^+. $C_{31}H_{39}NNaO_4S_2$ requires 576.2213).

S,S'-di-p-tolyl 2,2'-((3S,5R,8aR)-octahydroindolizine-3,5-diyl)diethanethioate and S,S'-di-p-tolyl 2,2'-((3S,5S,8aR)-octahydroindolizine-3,5-diyl)diethanethioate (20a)



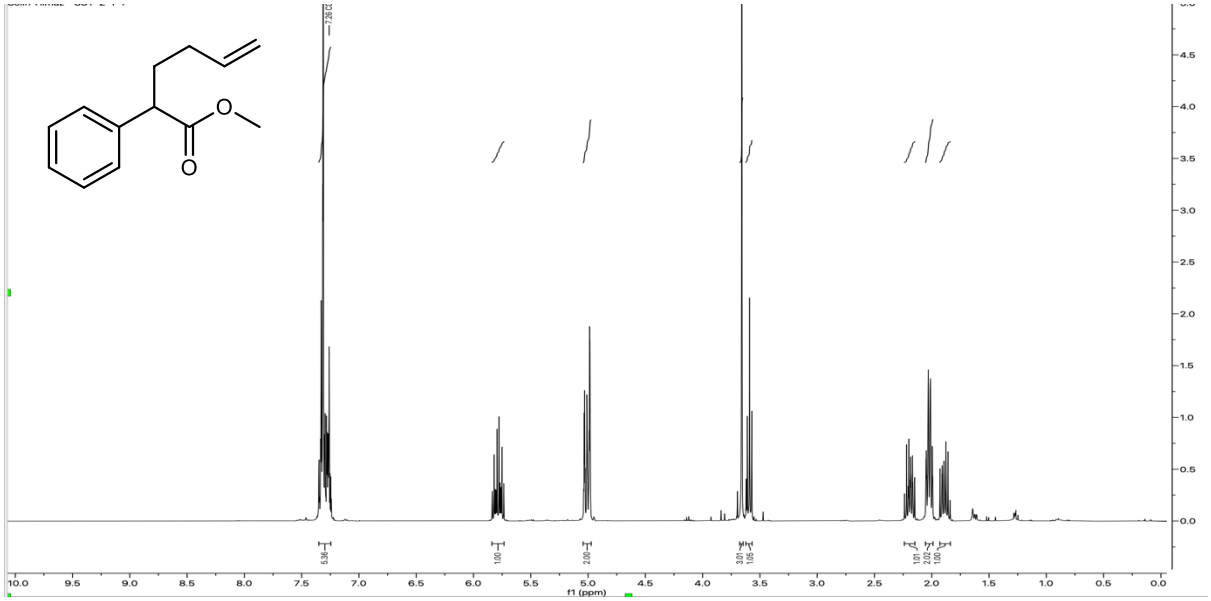
Boc-pyrrolidine **18d** (113 mg, 0.204 mmol) was dissolved in a 4M solution of HCl in 1,4-dioxane (2 mL) and then stirred at room temperature for 24 h. The reaction mixture was diluted with DCM (2 mL) and quenched with solid K_2CO_3. The reaction was then washed with brine and extracted with DCM (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, 10% EtOAc/hexane, column deadened with 1% Et_3N) to afford indolizidine **20a** as a colourless oil as a roughly 1:1 mixture of diastereoisomers (31.8 mg overall, 34%). The two diastereoisomers were isolated separately by flash column chromatography and hence were characterised separately: Diastereomer **A** (16.1 mg, 0.0355 mmol, 17% yield) and diastereomer **B** (15.7 mg, 0.0346 mmol, 17% yield) were both obtained as colourless oils.

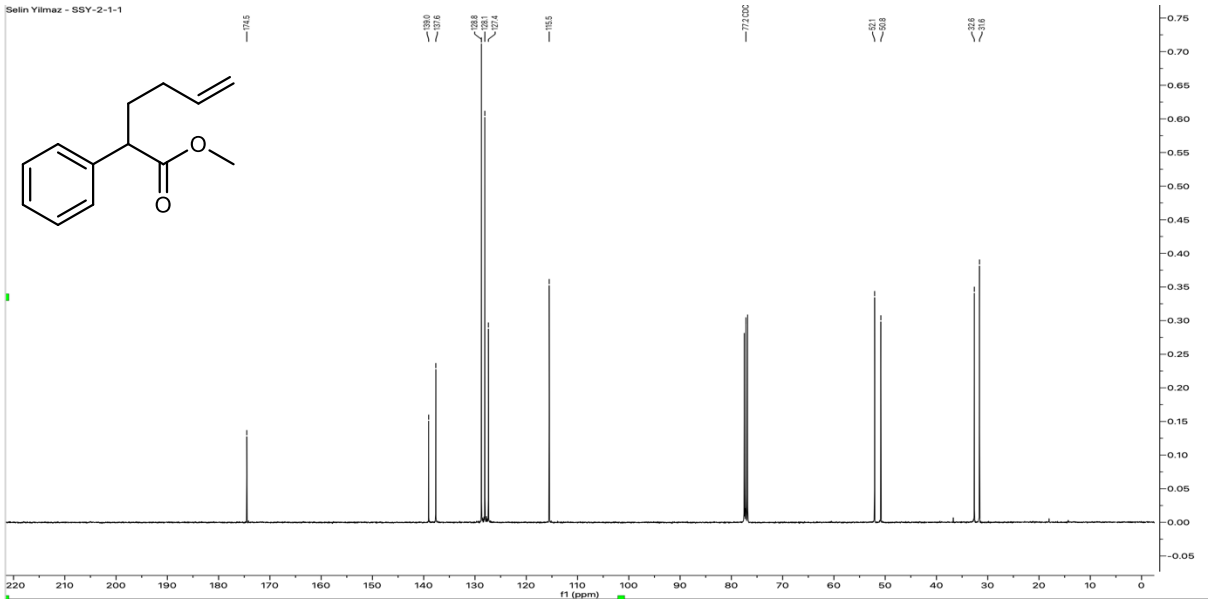
Data for diastereomer A: R_f = 0.35 (20% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.29 – 7.15 (8H, m, Ar-CH), 3.71–3.75 (1H, m, NCH), 3.01 – 2.96 (2H, m, COC**H**H' and NC**H**), 2.87 (1H, dd, *J* = 14.3, 4.1, COC**H**H'), 2.73 (1H, dd, *J* = 14.3, 8.9 Hz, 1H, COCH**H'**), 2.55 (dd, *J* = 14.6, 8.3 Hz, 1H, COCH**H'**), 2.47–2.38 (1H, m, NCH), 2.36 and 2.35 (6H, 2 x s, 2 x CH_3), 1.96–1.06 (10H, 5 x CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.3 and 196.5 (2 x C=O), 139.6 and 139.5 (2 x Ar-C), 134.4 (2 x Ar-CH), 130.0 (2 x Ar-CH), 124.4 and 124.3 (2 x Ar-C), 56.1 (NCH), 55.7 (NCH), 51.0 (NCH), 47.8 (**C**H_2CO), 37.4 (**C**H_2CO), 32.2 (CH_2), 26.9 (CH_2), 29.0 (CH_2), 28.2 (CH_2), 21.3 (2 x CH_3), 19.2 (CH_2) ppm; **IR (ATR)**: ν_{max} 2926, 1698, 1493, 1400, 1016, 985, 805, 473 cm^{-1}; **HRMS (ESI)** 454.1877 (M + H$^+$. $C_{26}H_{32}NNaO_2S_2$ requires 454.1869).

Data for diastereomer B: R_f = 0.26 (20% EtOAc/hexane); **^{1}H NMR** (400 MHz, $CDCl_3$); δ 7.30 – 7.16 (8H, m, Ar-CH), 4.88–4.80 (1H, m, NCH), 3.07 (dd, *J* = 14.6, 3.4 Hz, 1H, COC**H**H'), 2.90–2.81 (2H, m, NCH, COC**H**H'), 2.64–2.55 (1H, m, NCH), 2.52 (d, *J* = 14.6, 1H, COCH**H'**), 2.49 (d, *J* = 14.1, 1H, COCH**H'**), 2.36 (6H, s, 2 x CH_3), 2.03–1.02 (10H, 5 x CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.1 and 196.3 (2 x C=O), 139.7 (2 x Ar-C), 134.4 and 134.3 (2 x Ar-CH), 130.0 (2 x Ar-CH), 124.2 (2 x Ar-C), 59.2 (NCH), 56.4 (NCH), 54.2 (NCH), 48.2 (**C**H_2CO), 40.5 (**C**H_2CO), 31.8 (CH_2), 31.6 (CH_2), 29.4 (CH_2), 26.7 (CH_2), 24.0 (CH_2), 21.3 (2 x CH_3) ppm; **IR (ATR)**: ν_{max} 2928, 1698, 1493, 1400, 1016, 987, 806, 472 cm^{-1}; **HRMS (ESI)** 454.1883 ($M + H^+$. $C_{26}H_{32}NNaO_2S_2$ requires 454.1869).

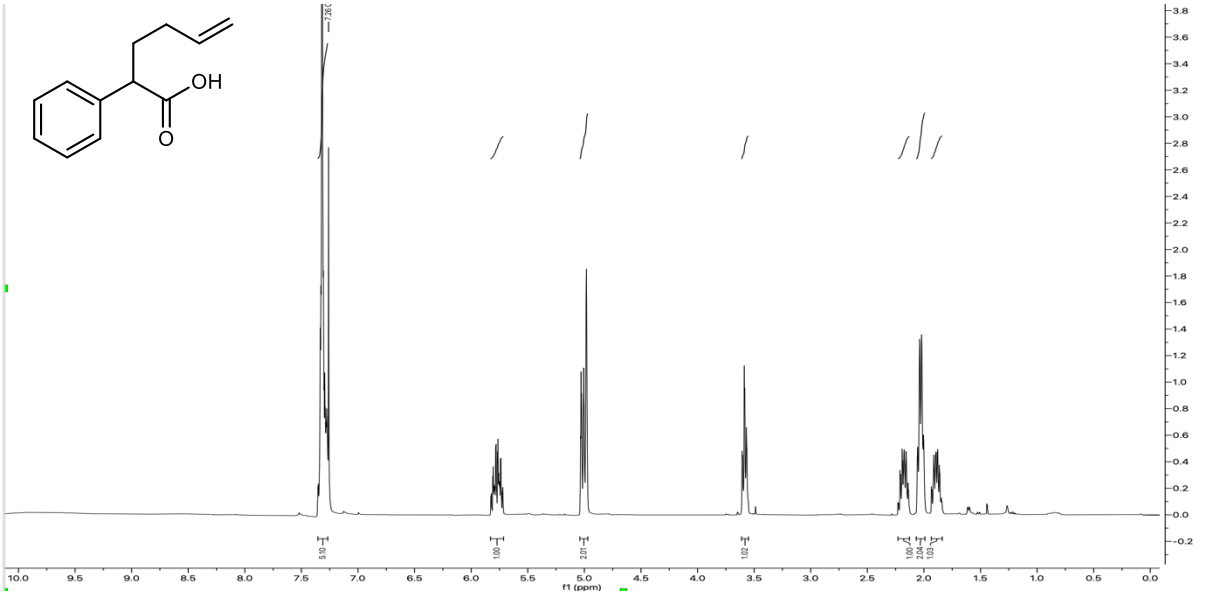
3) ^{1}H and ^{13}C NMR spectra

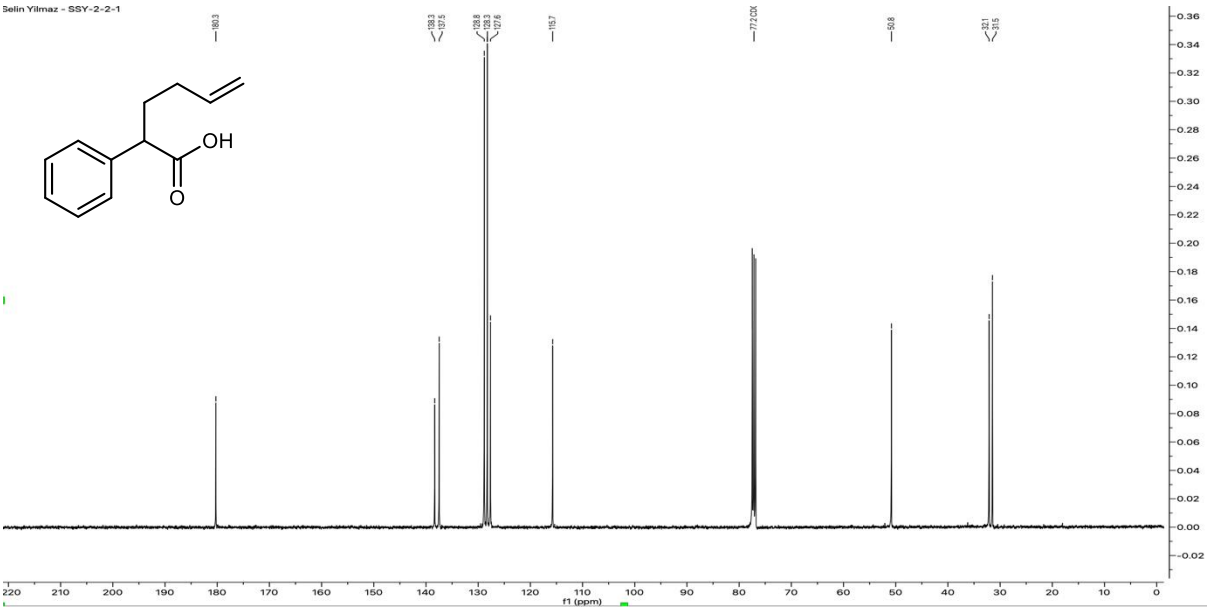
Methyl 2-phenylhex-5-enoate (S1)



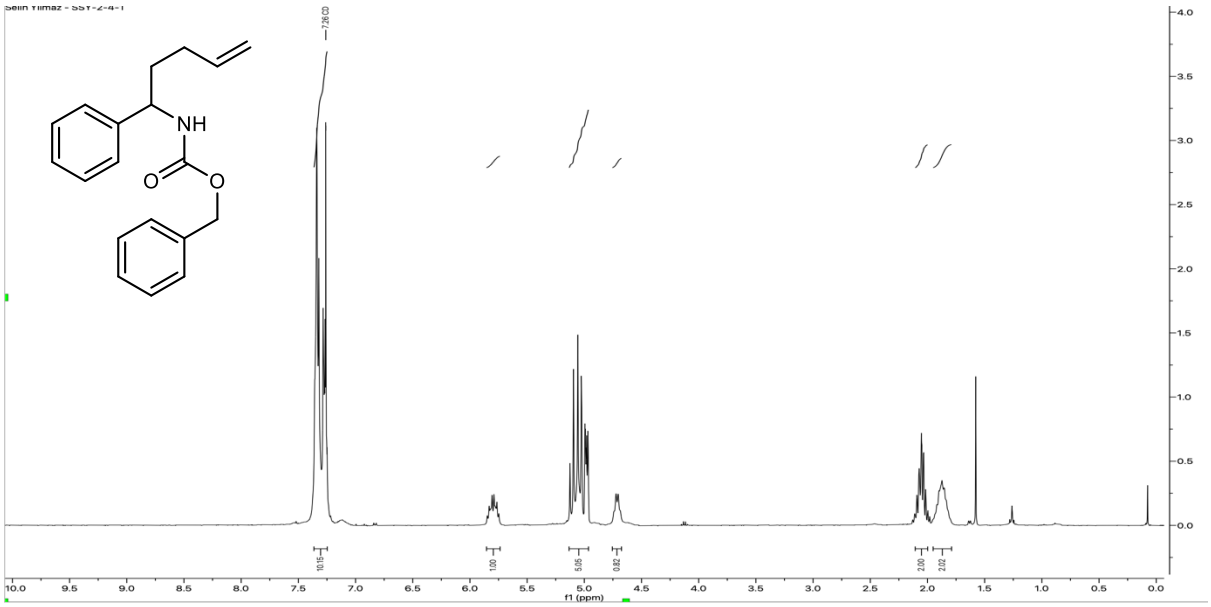


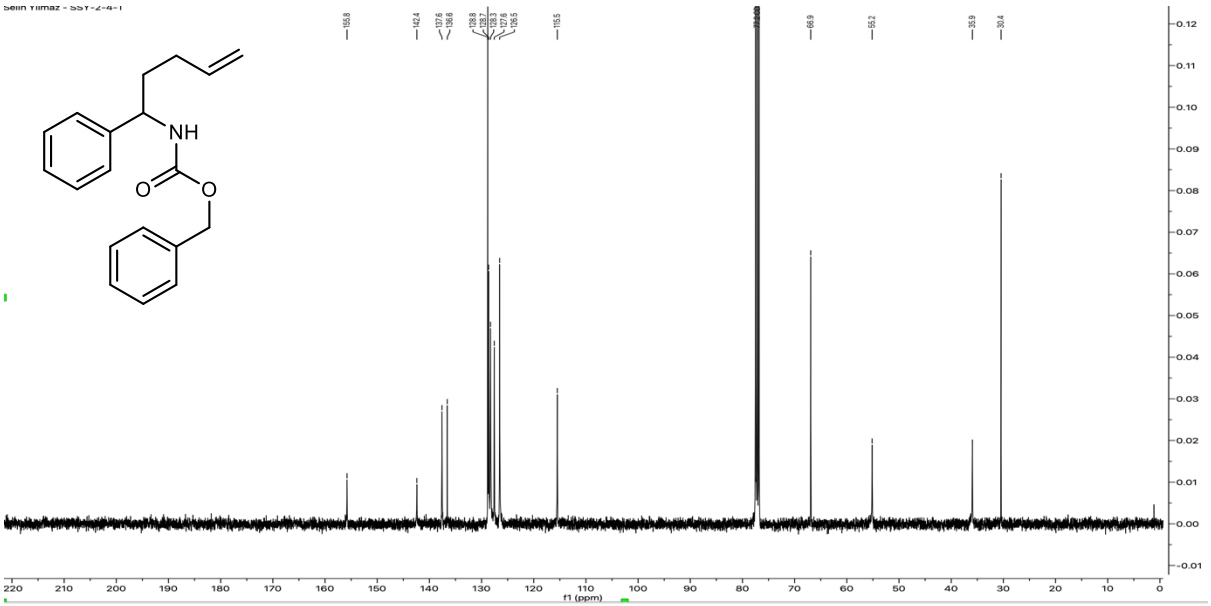
2-Phenyhex-5-enoic acid (12)



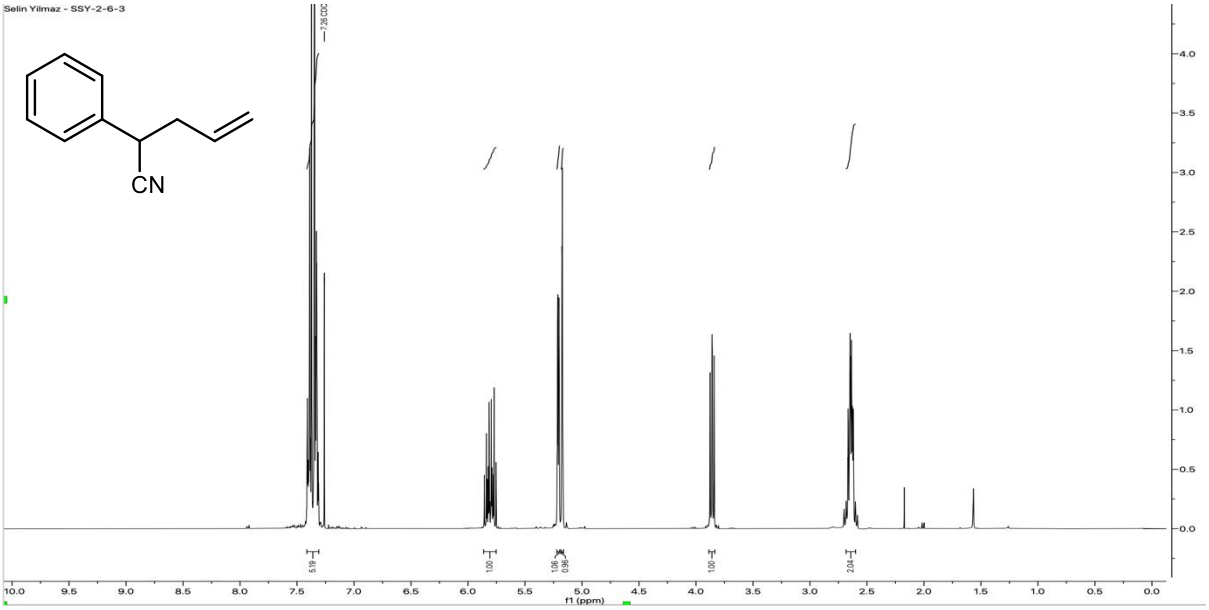


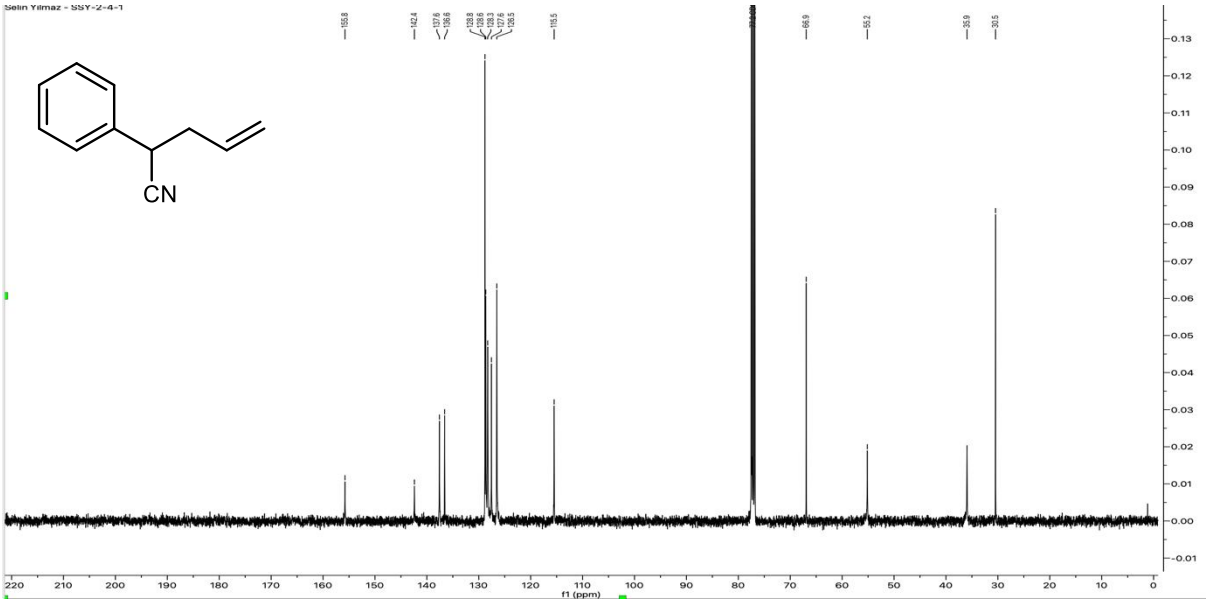
Benzyl (1-phenylpent-4-en-1-yl)carbamate (5a)



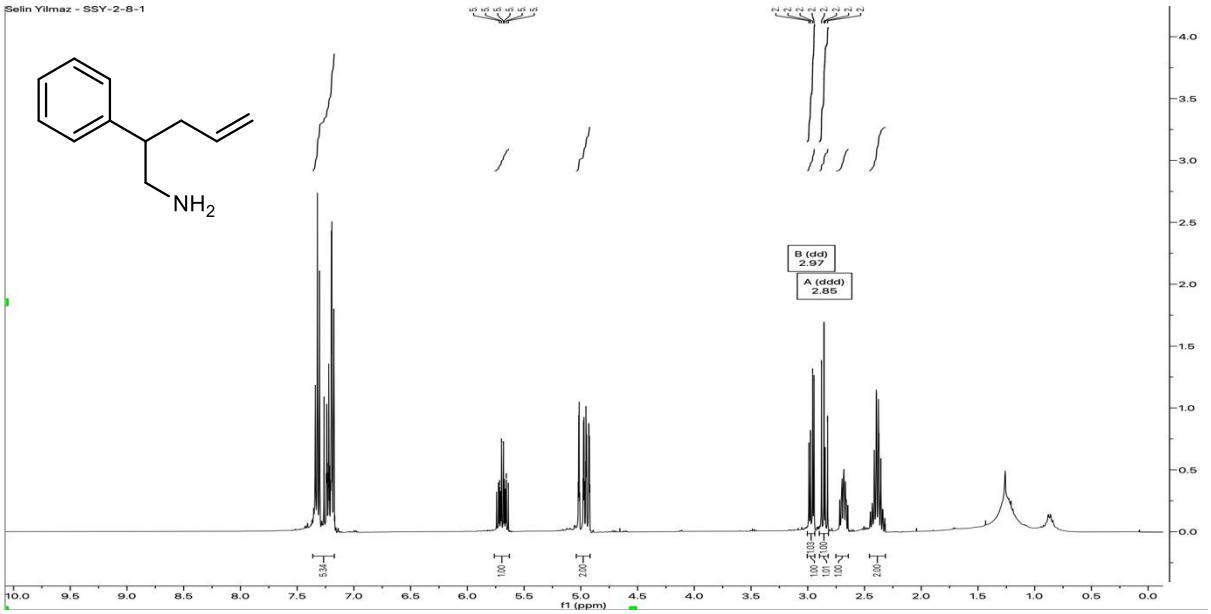


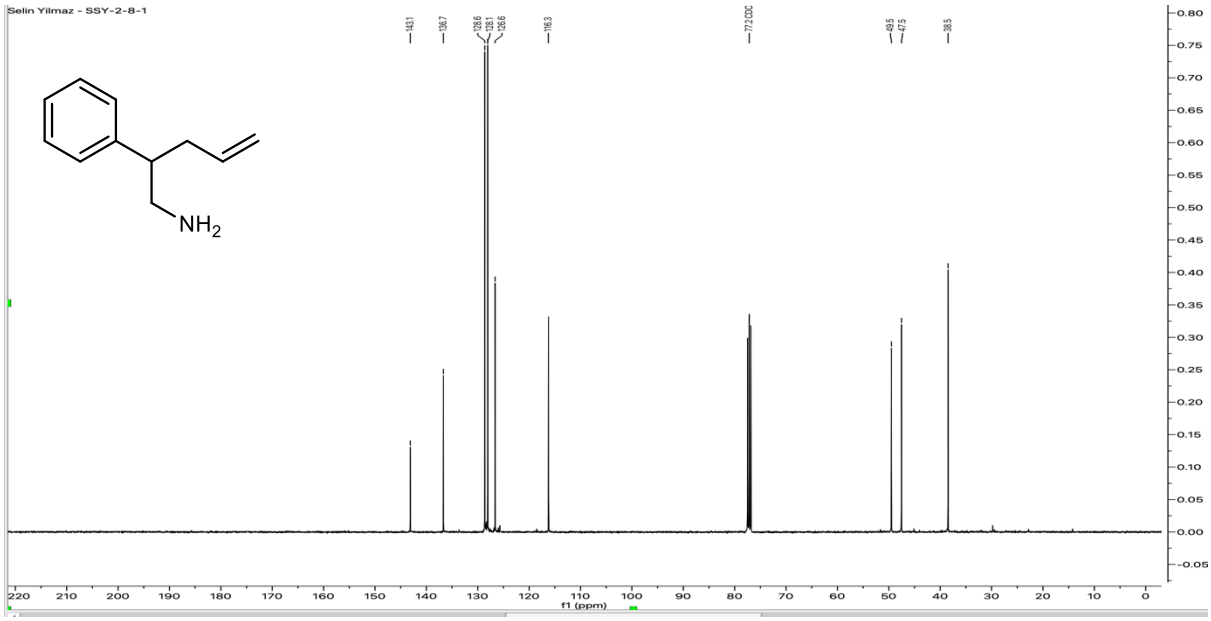
2-Phenylpent-4-enenitrile (14)



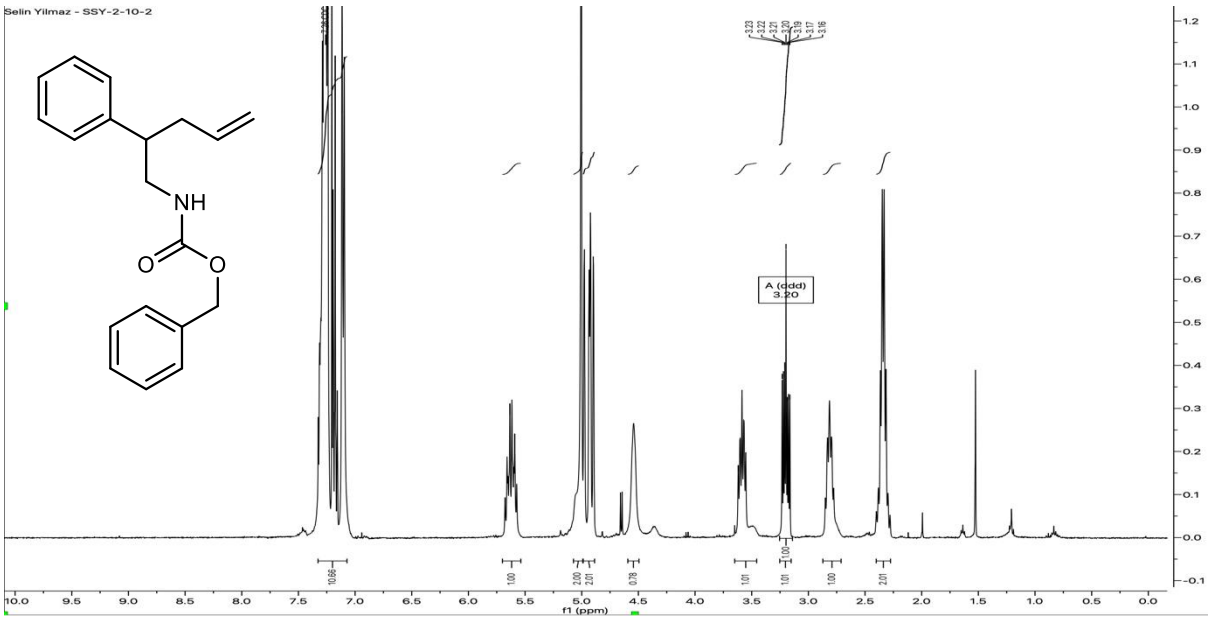


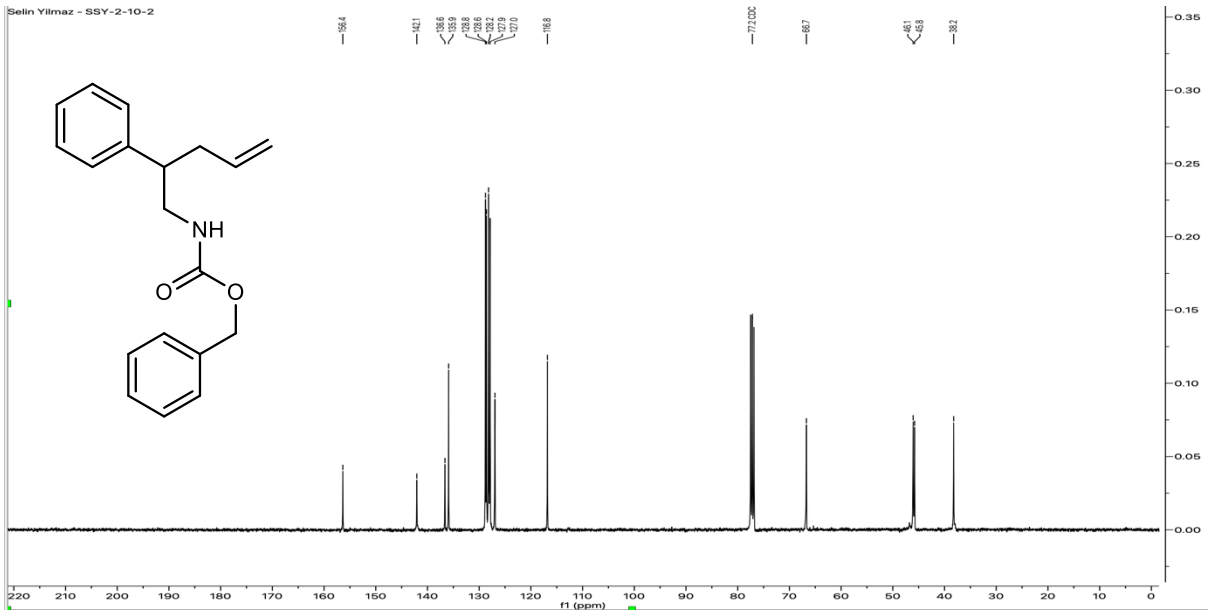
2-Phenylpent-4-enenitrile (S2)



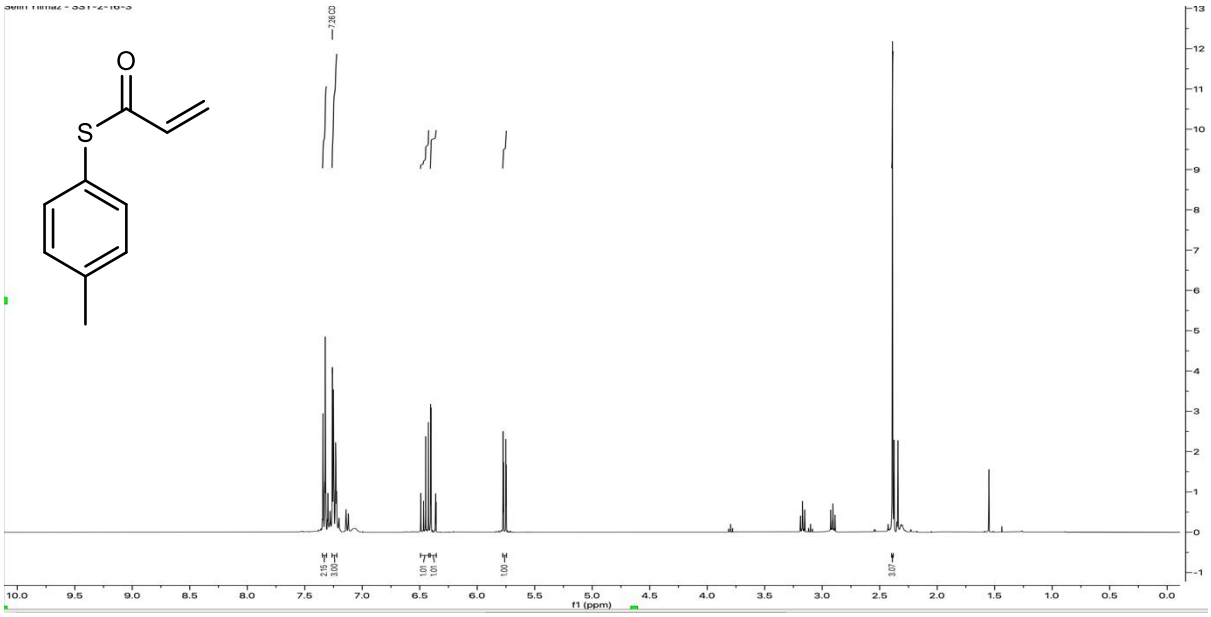


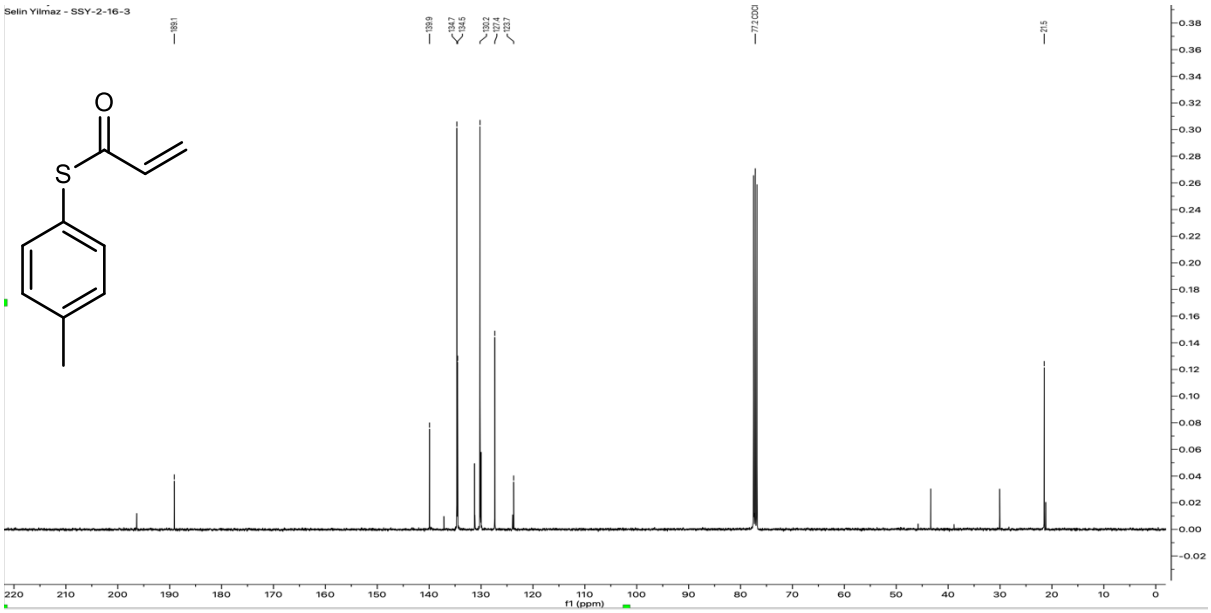
Benzyl (2-phenylpent-4-en-1-yl) carbamate (5b)



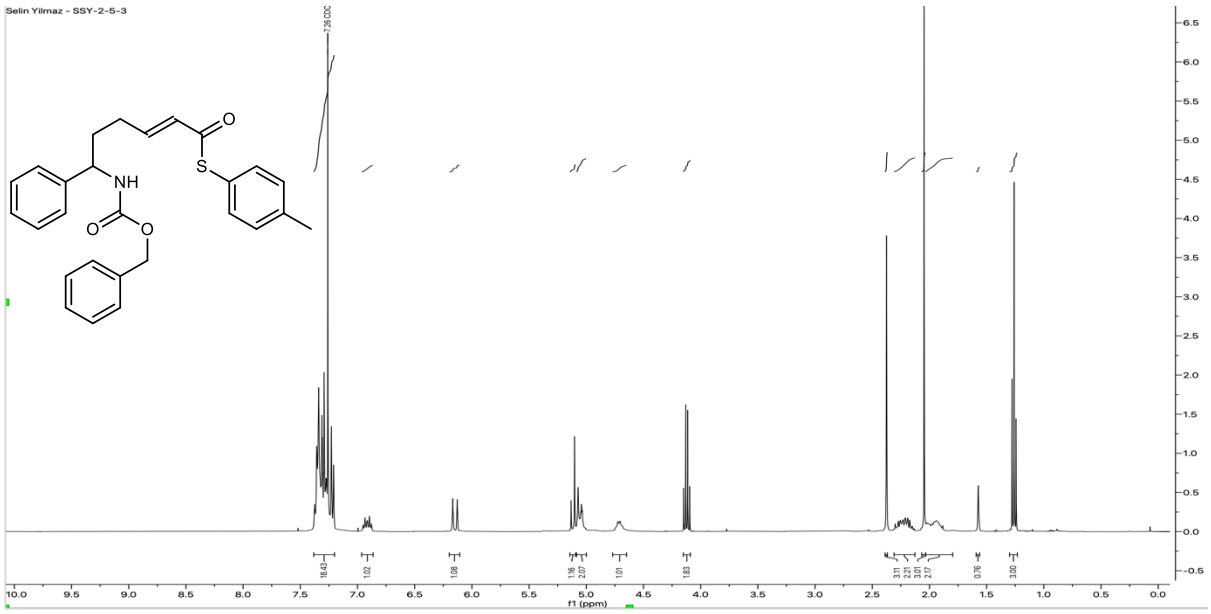


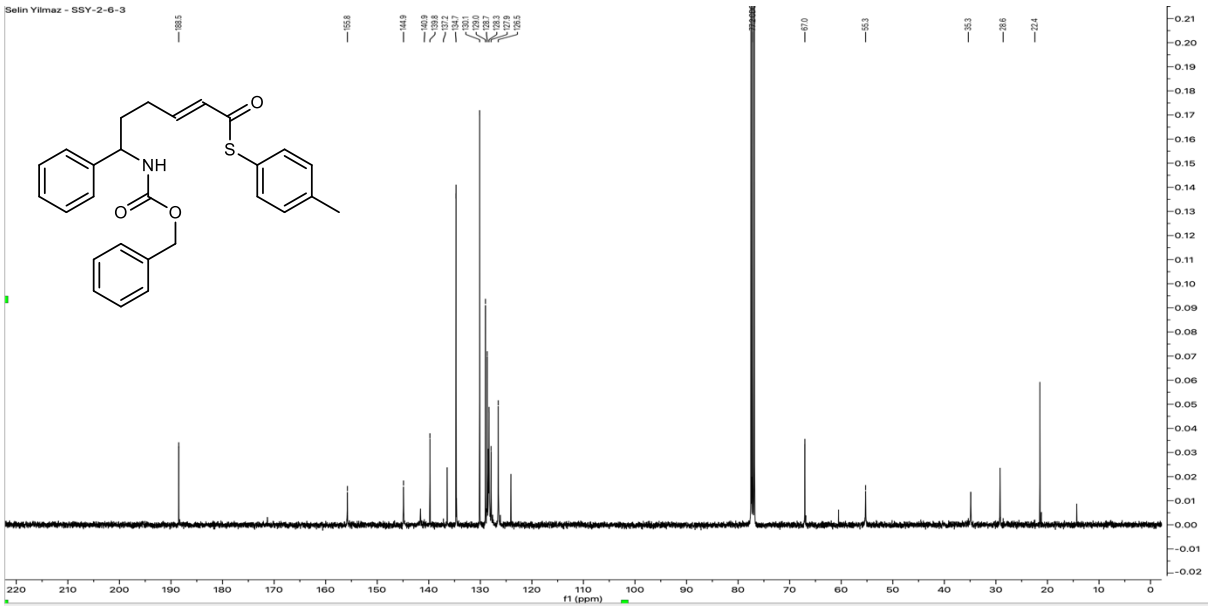
S-(*p*-tolyl) prop-2-enethioate (2a)



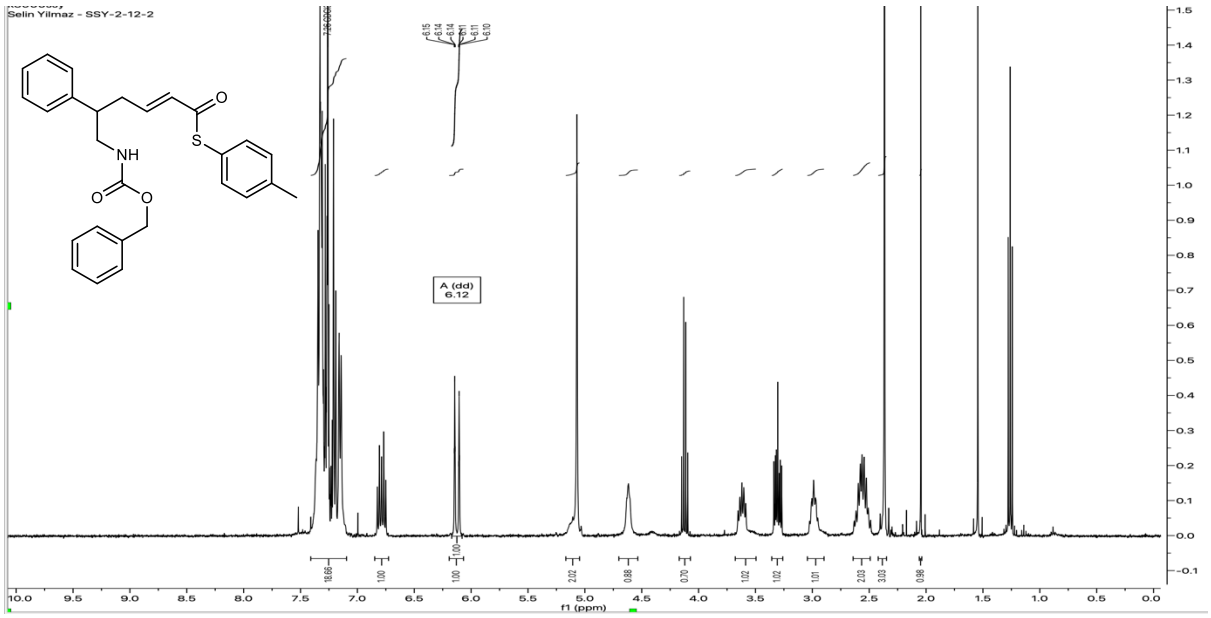


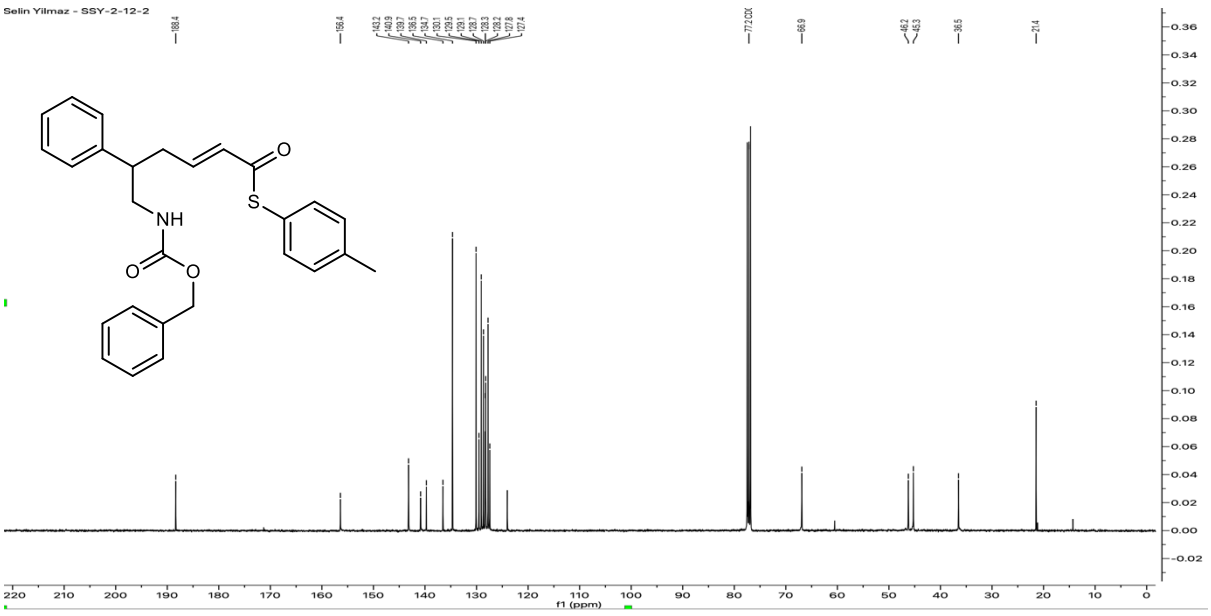
S-(*p*-Tolyl) (*E*)-6-(((benzyloxy)carbonyl) amino)-6-phenylhex-2-enethioate (6a)



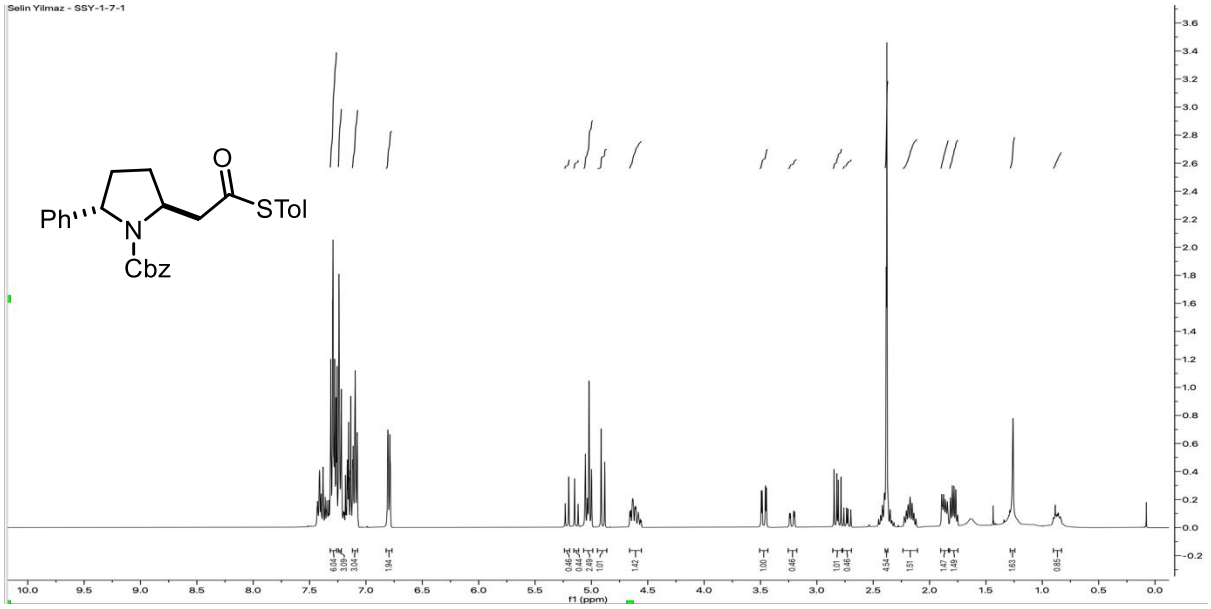


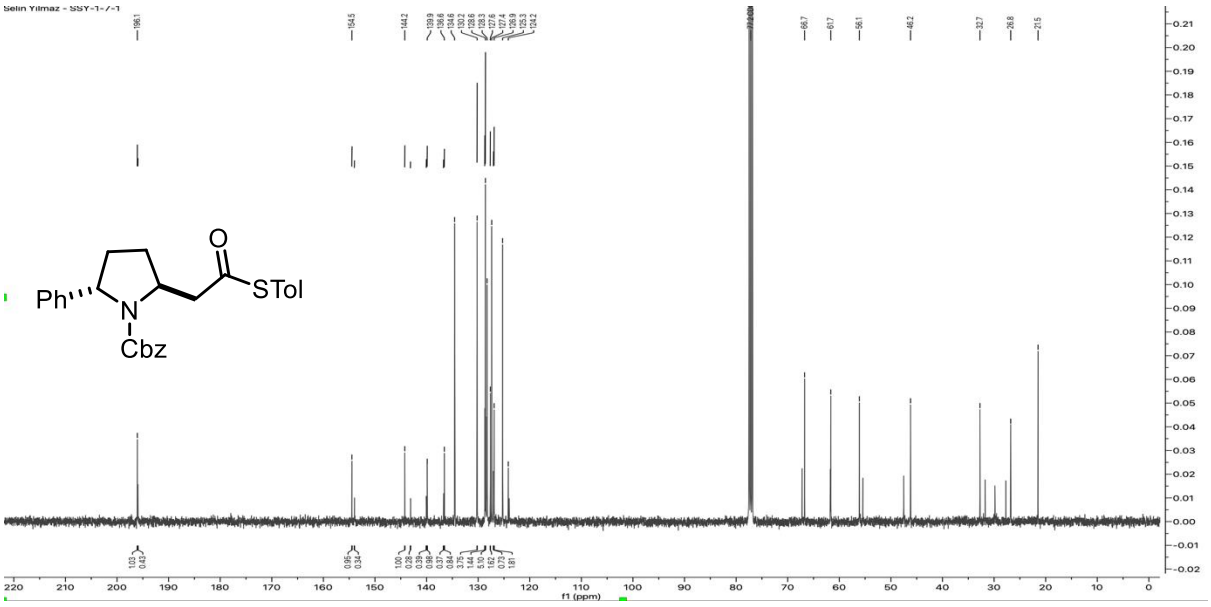
***S*-(*p*-tolyl) (*E*)-6-(((benzyloxy)carbonyl) amino)-5-phenylhex-2-enethioate (6b)**



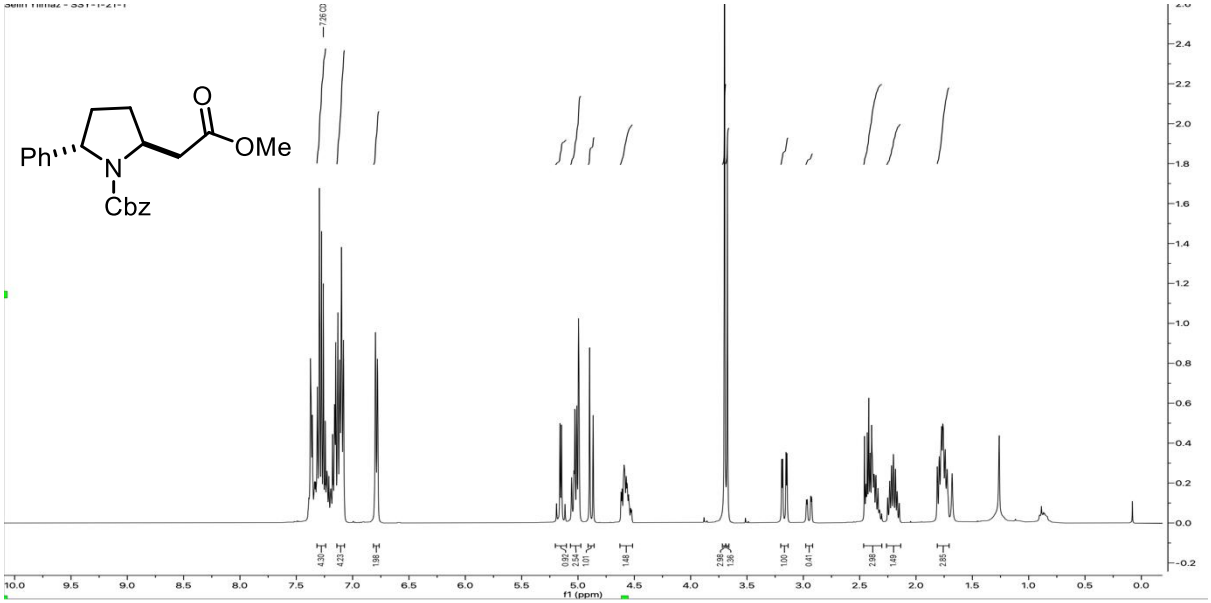


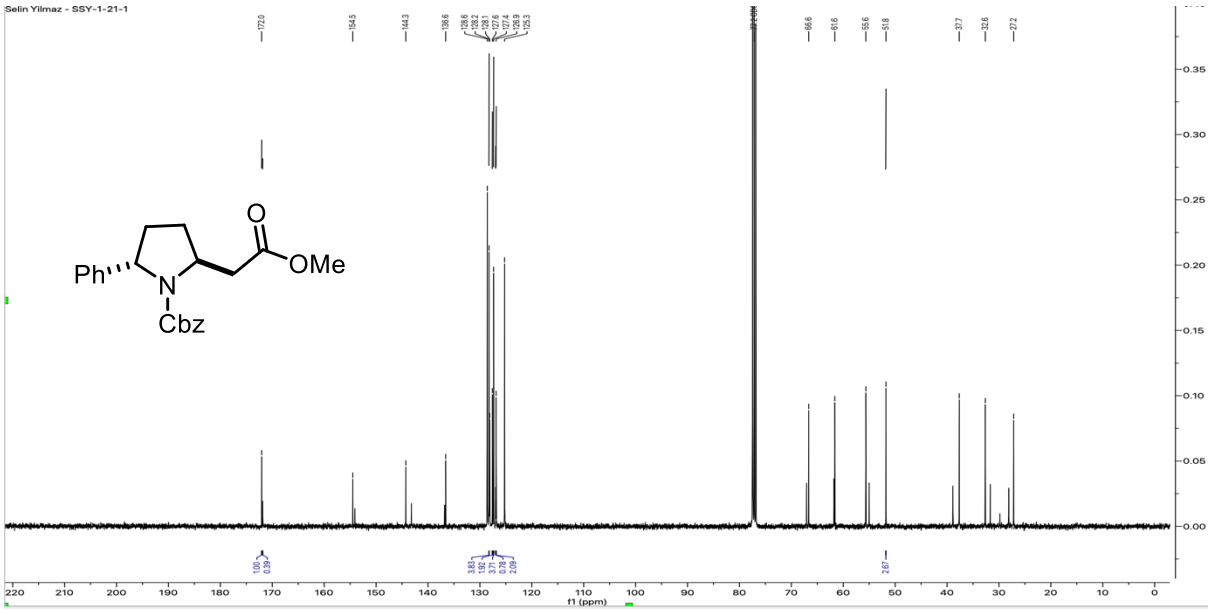
Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-phenylpyrrolidine-1-carboxylate (rac-7a)



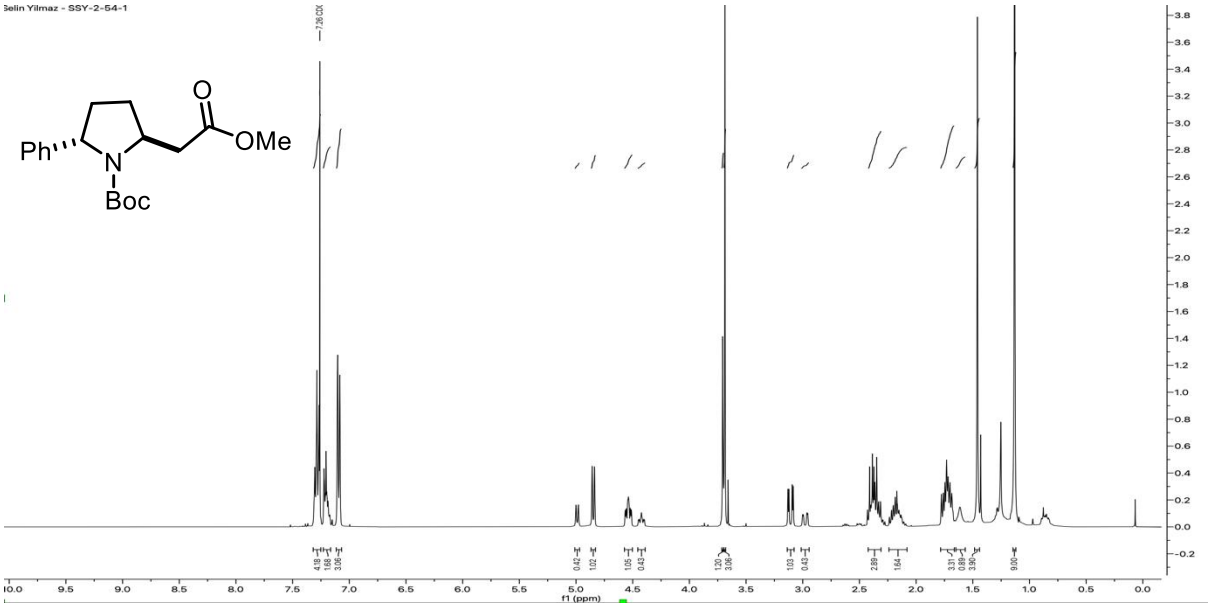


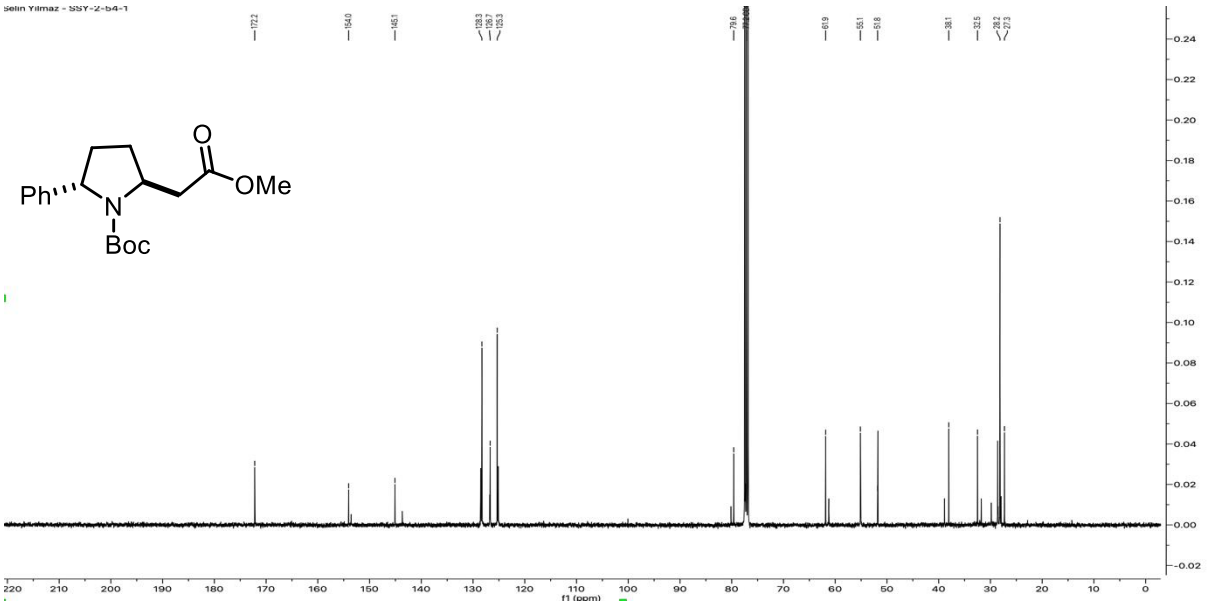
Benzyl 2-(2-methoxy-2-oxoethyl)-5-phenylpyrrolidine-1-carboxylate (S3)



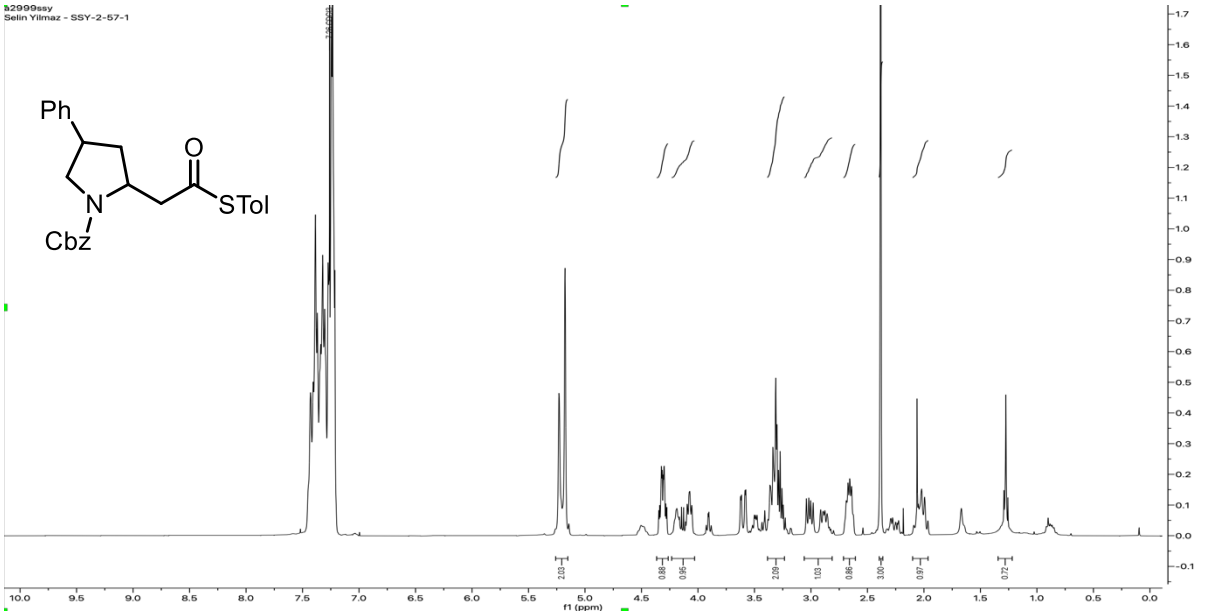


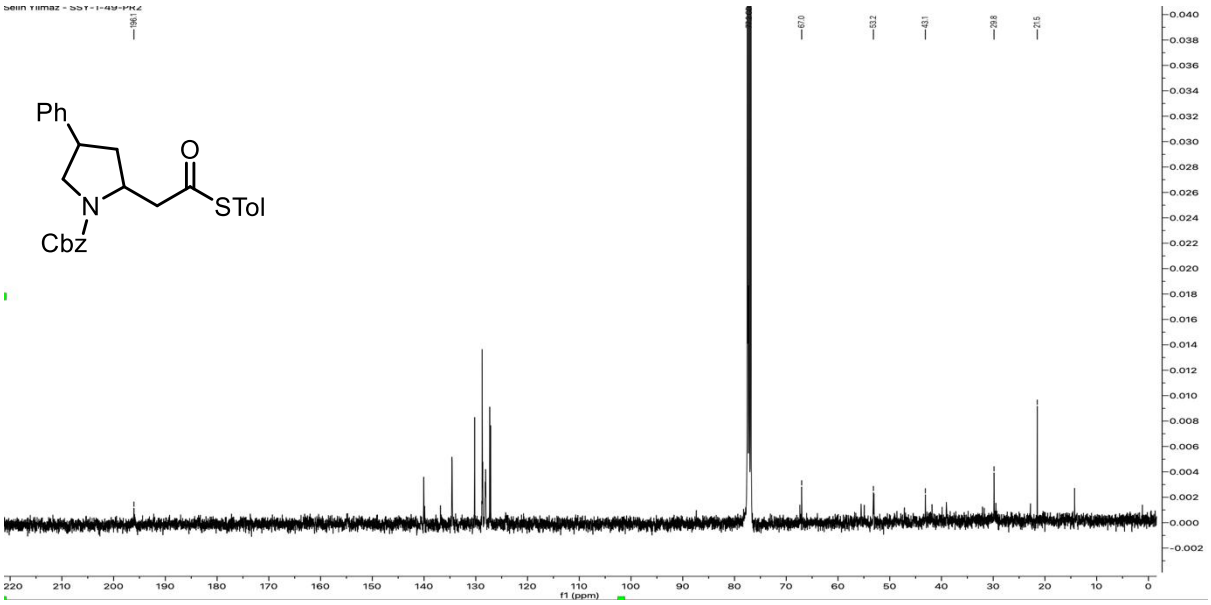
tert-Butyl 2-(2-methoxy-2-oxoethyl)-5-phenylpyrrolidine-1-carboxylate (15)



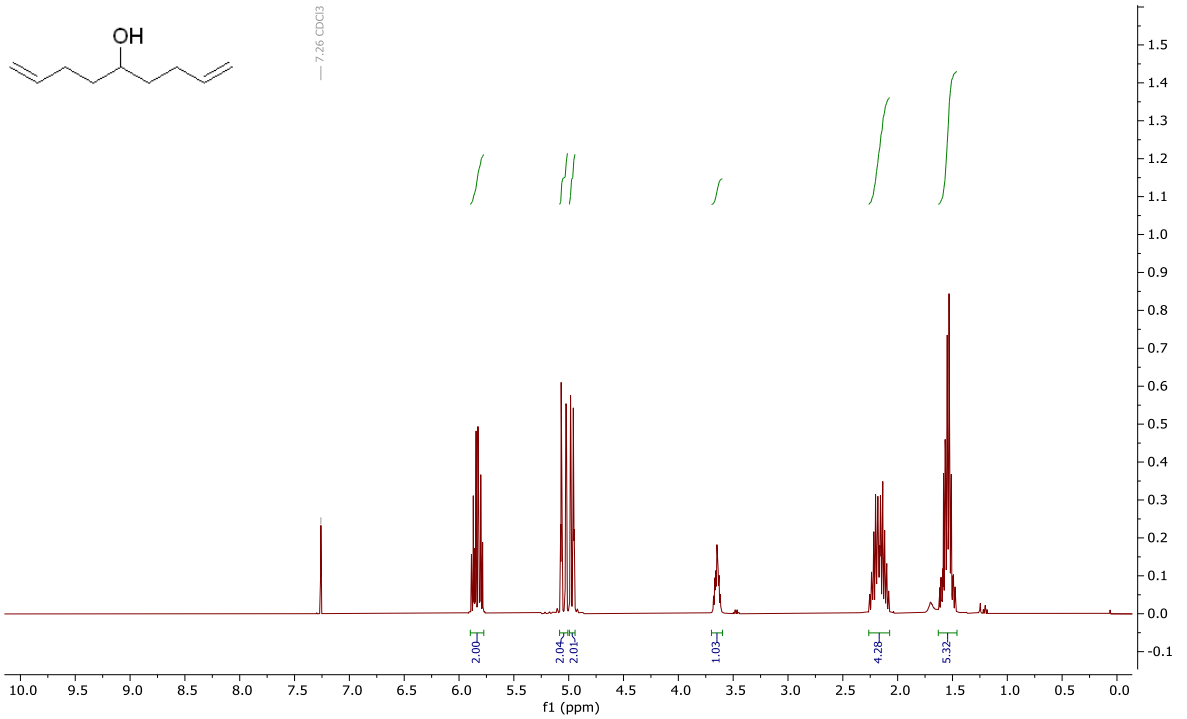


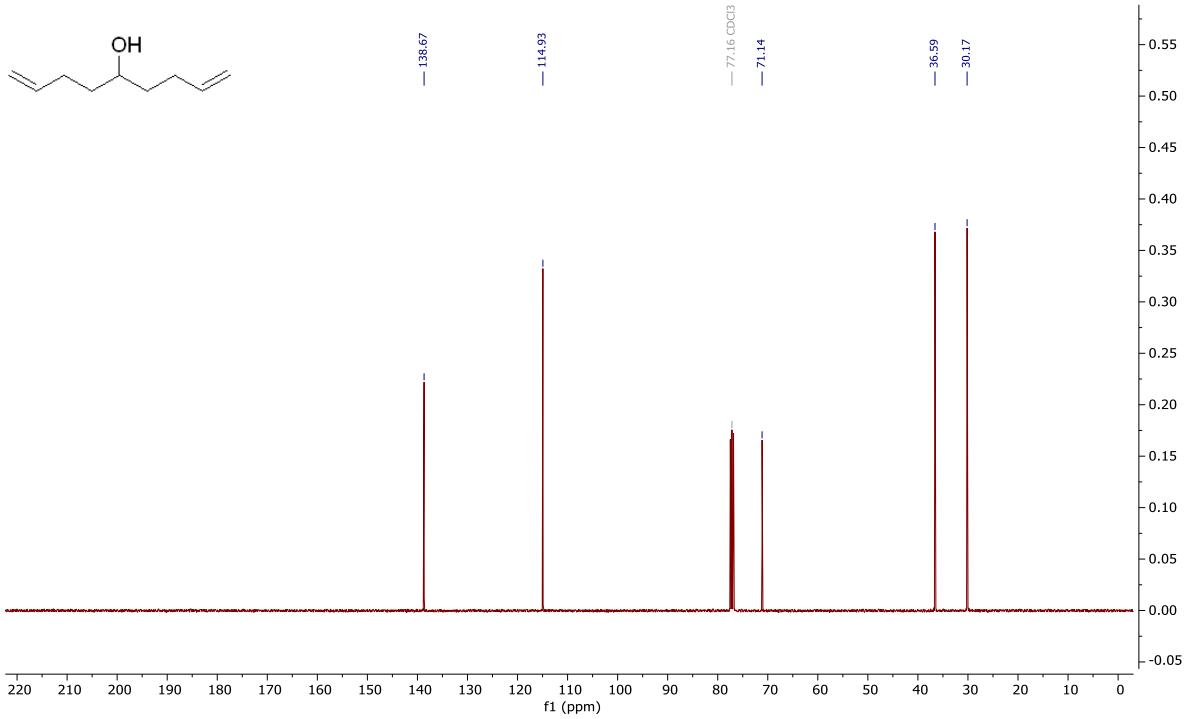
Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-4-phenylpyrrolidine-1-carboxylate (rac-7b)



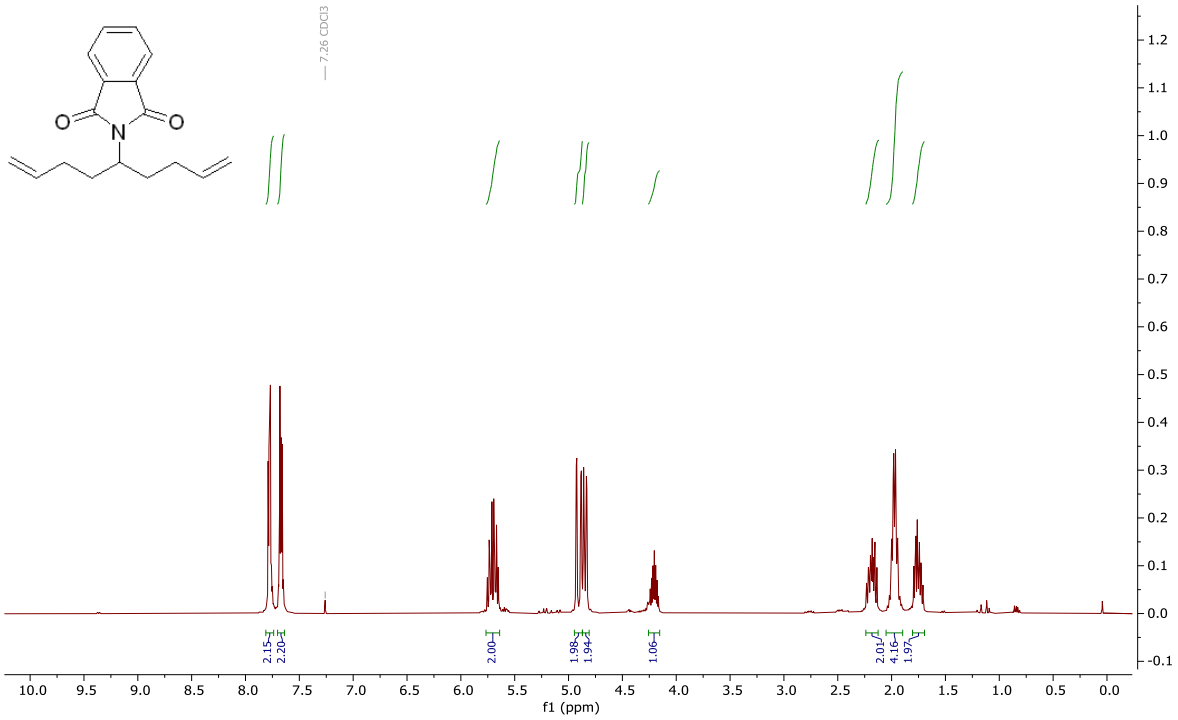


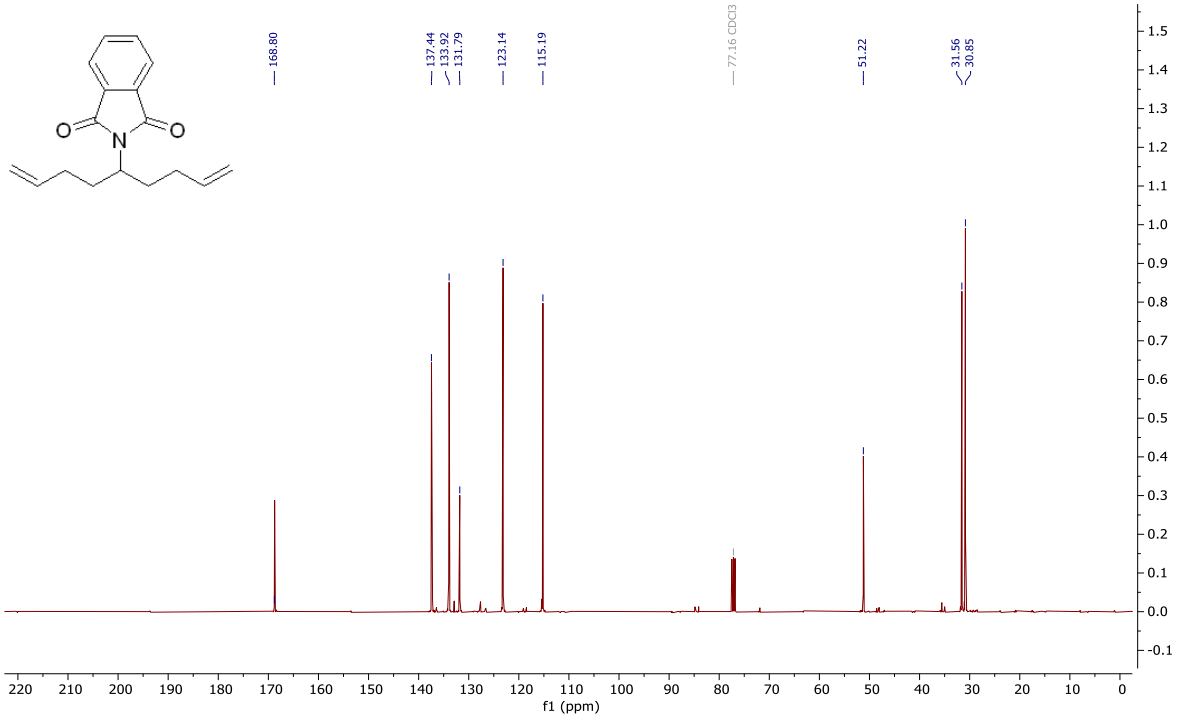
Nona-1,8-dien-5-ol (S4)



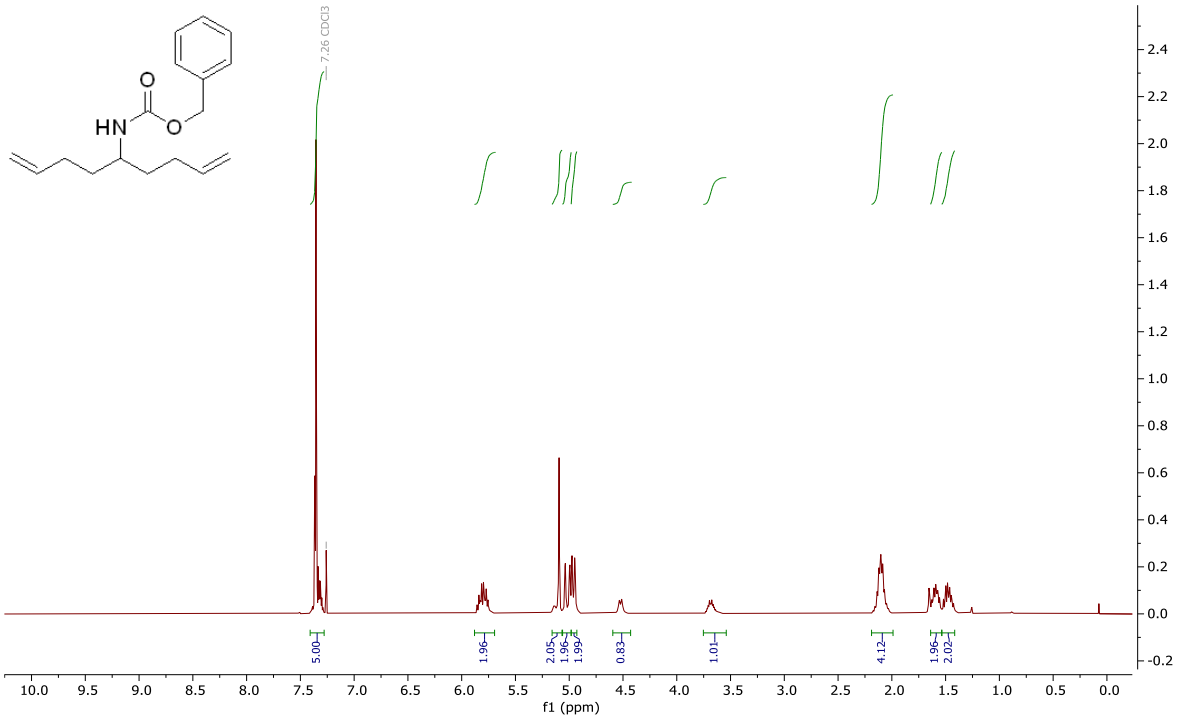


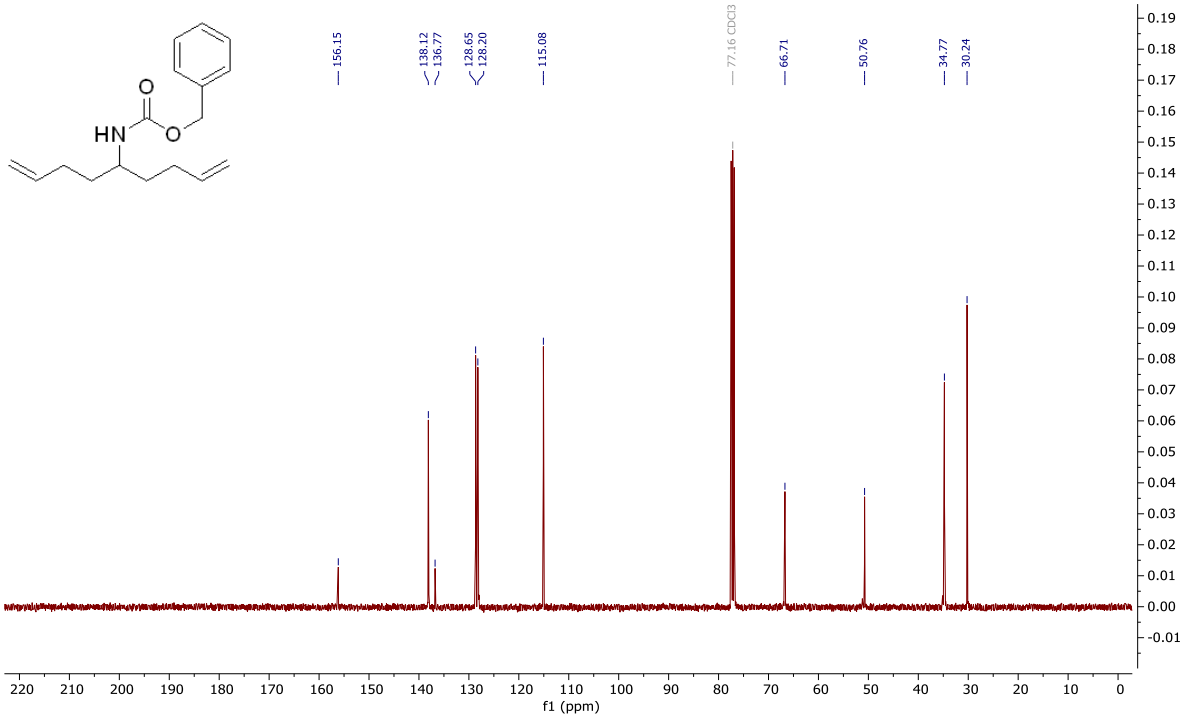
2-(Nona-1,8-dien-5-yl)isoindoline-1,3-dione (S5)



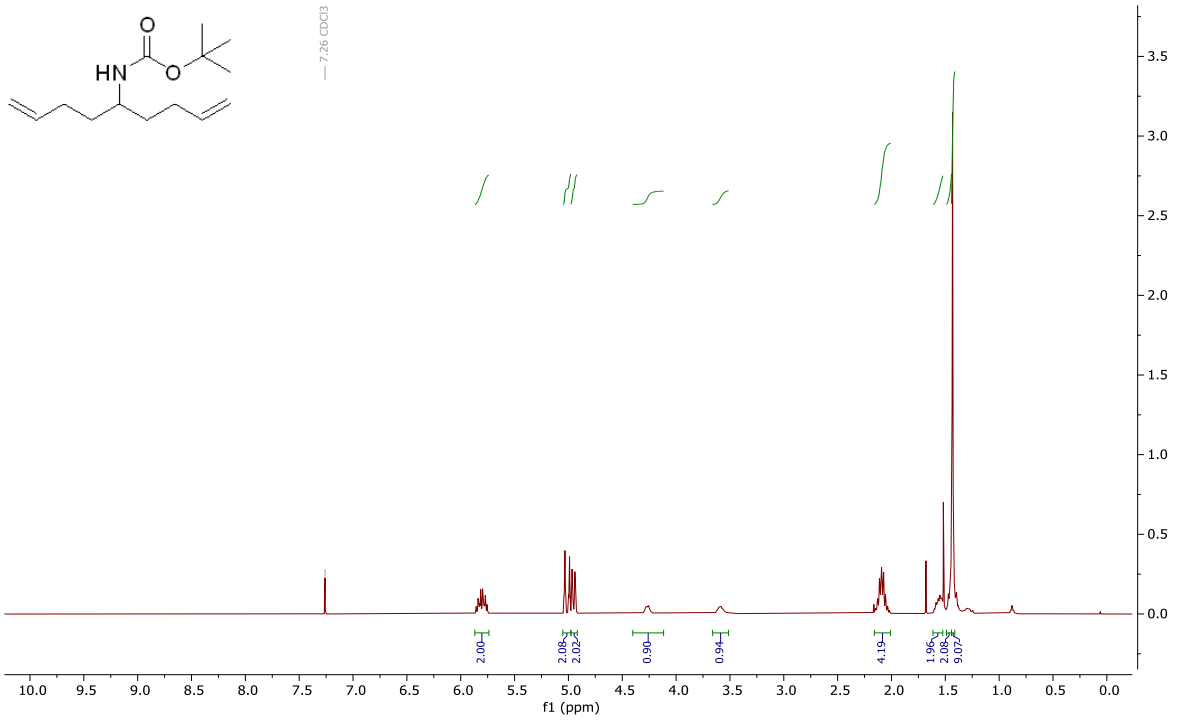


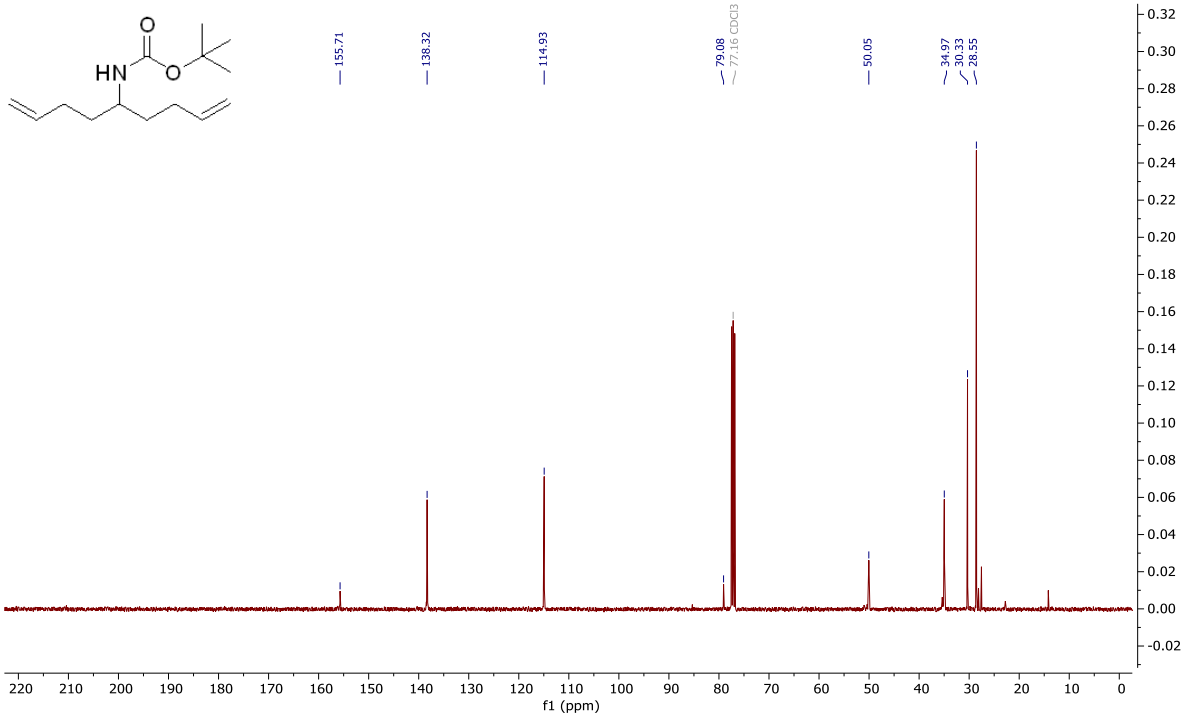
Benzyl nona-1,8-dien-5-ylcarbamate (16a)



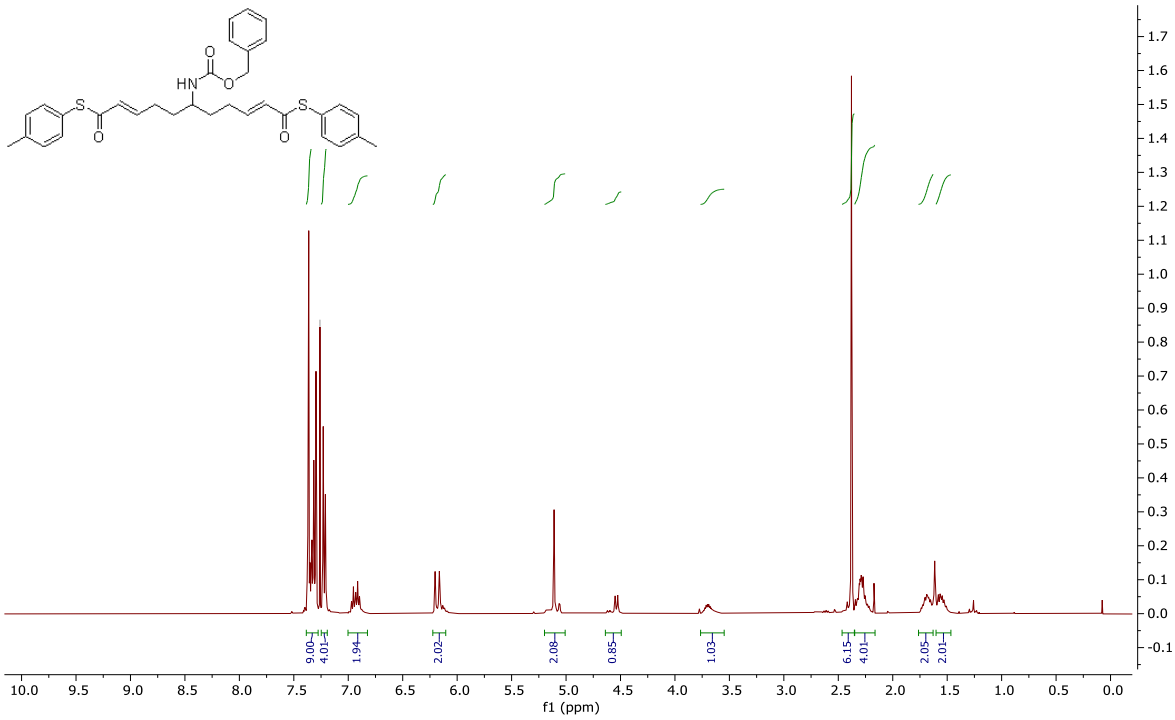


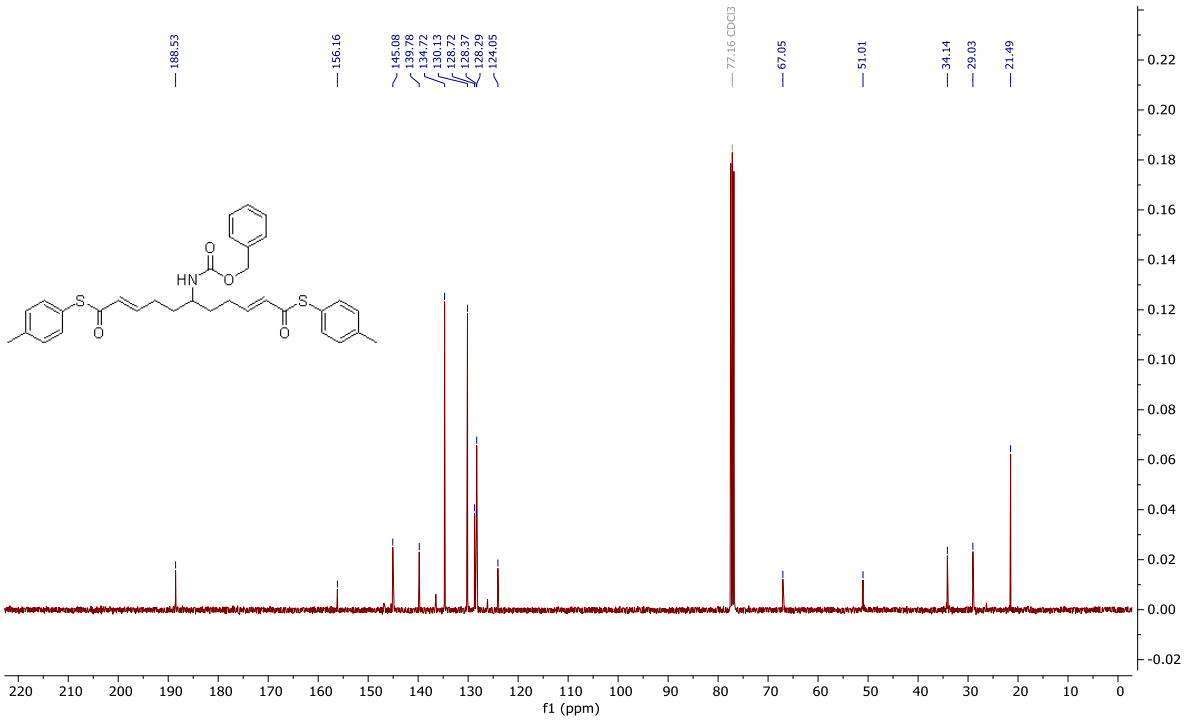
tert-Butyl nona-1,8-dien-5-ylcarbamate (16b)



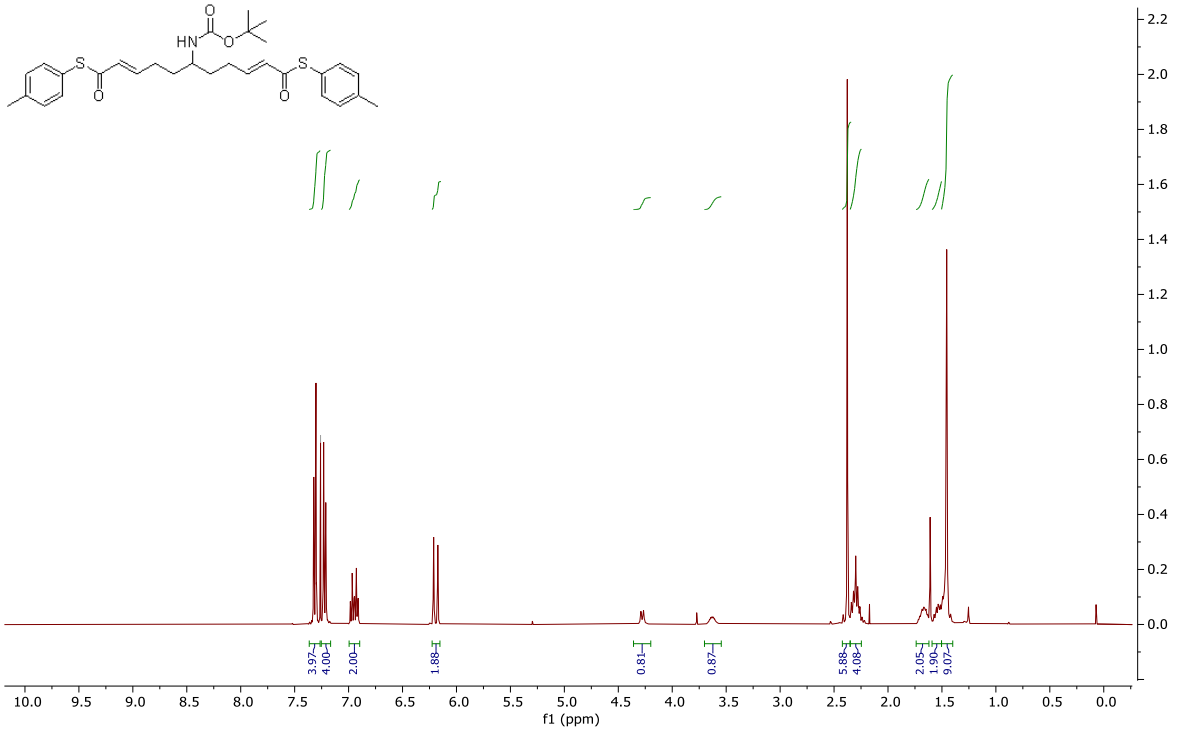


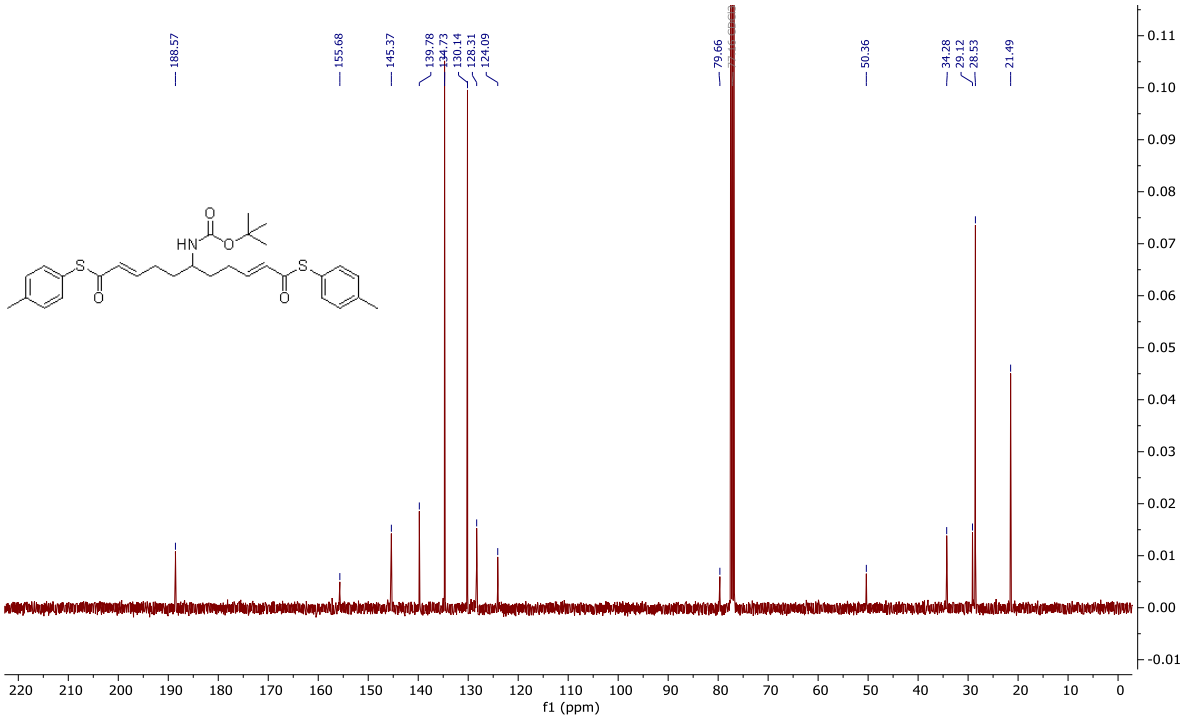
(2*E*,9*E*)-*S*,*S*-Di-*p*-tolyl 6-(((benzyloxy)carbonyl)amino)undeca-2,9-dienebis(thiolate) (17a)



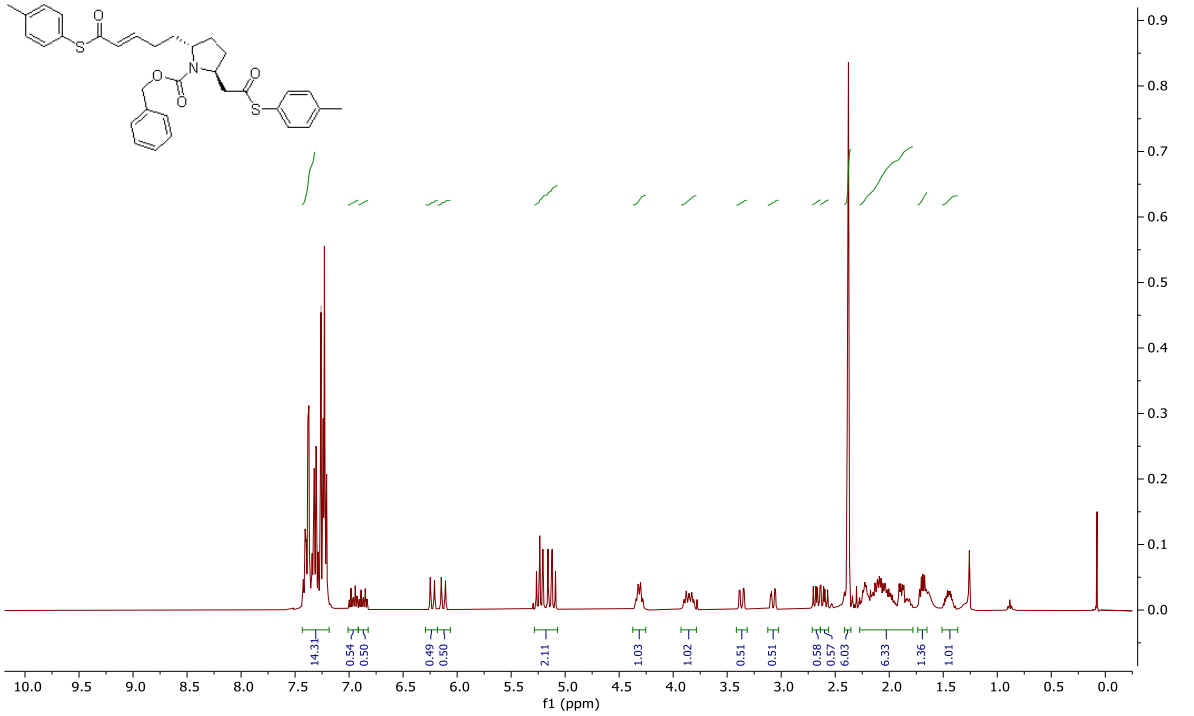


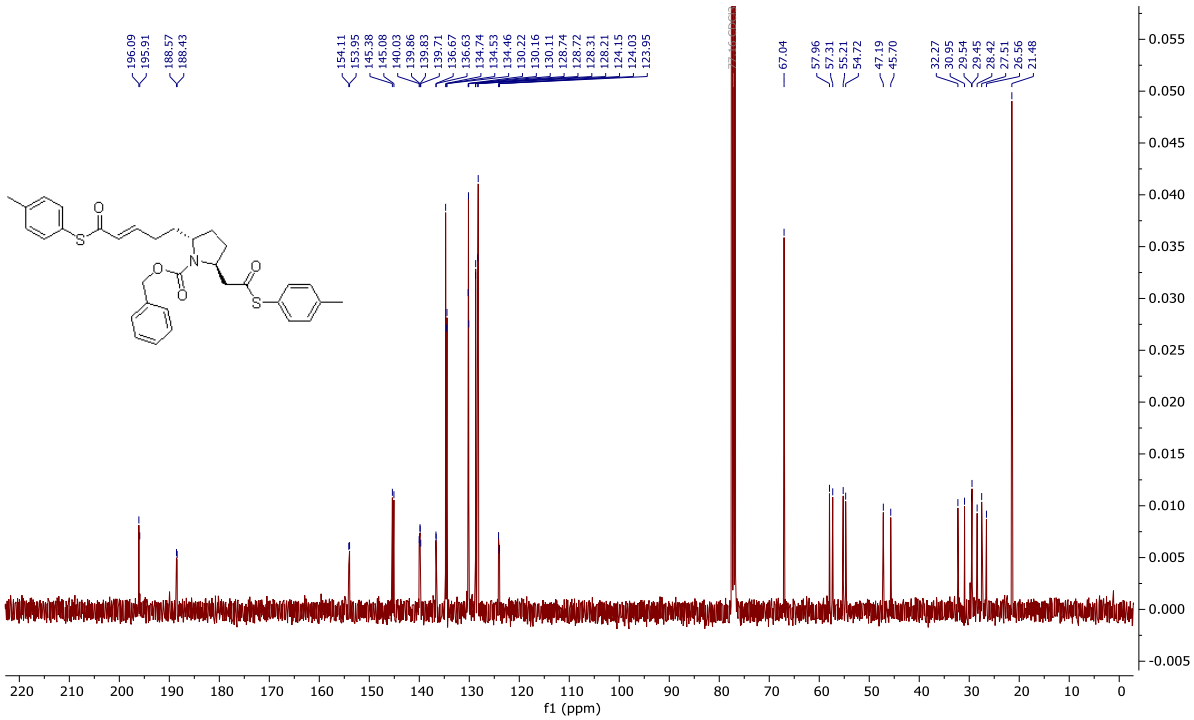
(2*E*,9*E*)-*S*,*S*-Di-*p*-tolyl 6-((*tert*-butoxycarbonyl)amino)undeca-2,9-dienebis(thiolate) (17b)



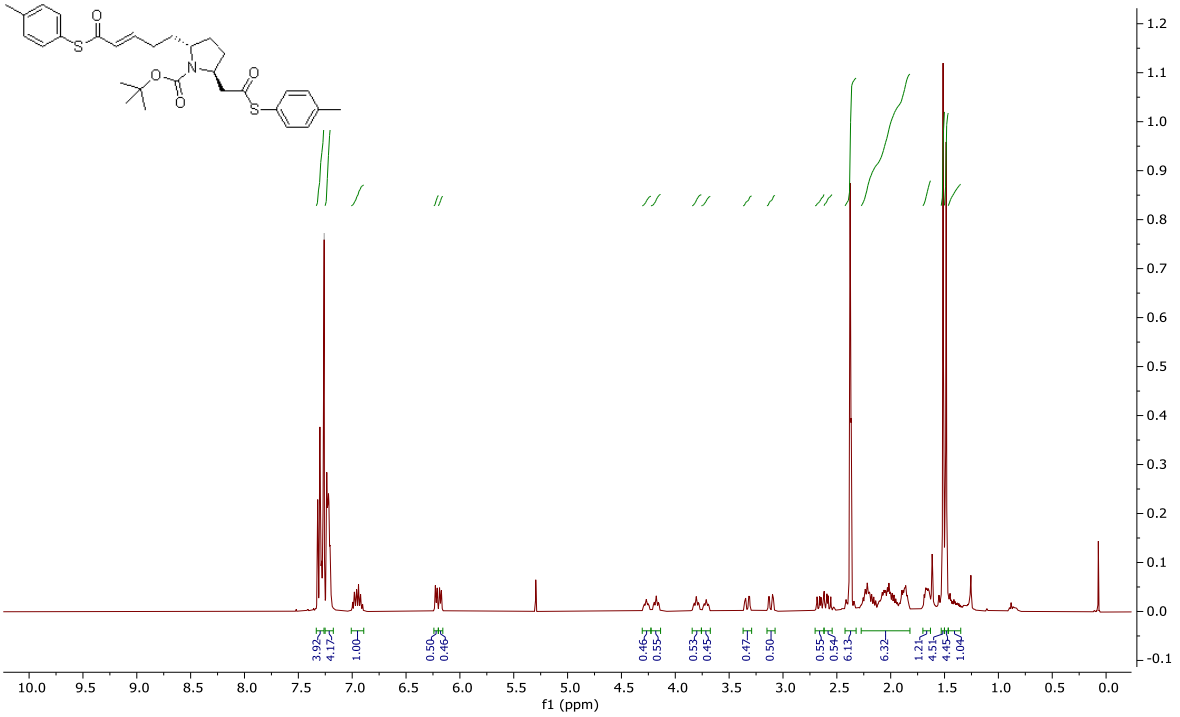


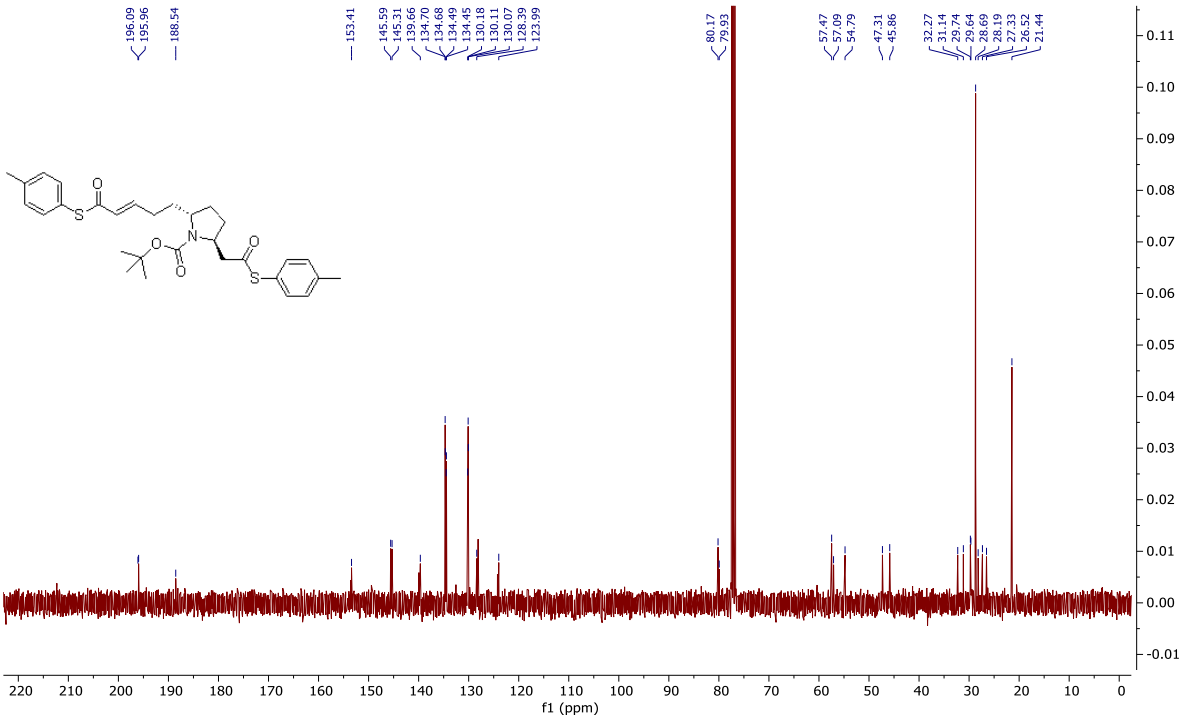
(2*S*,5*R*)-Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-5-oxo-5-(p-tolylthio)pent-3-en-1-yl)pyrrolidine-1-carboxylate (rac-18a and (*SR*)-18a)



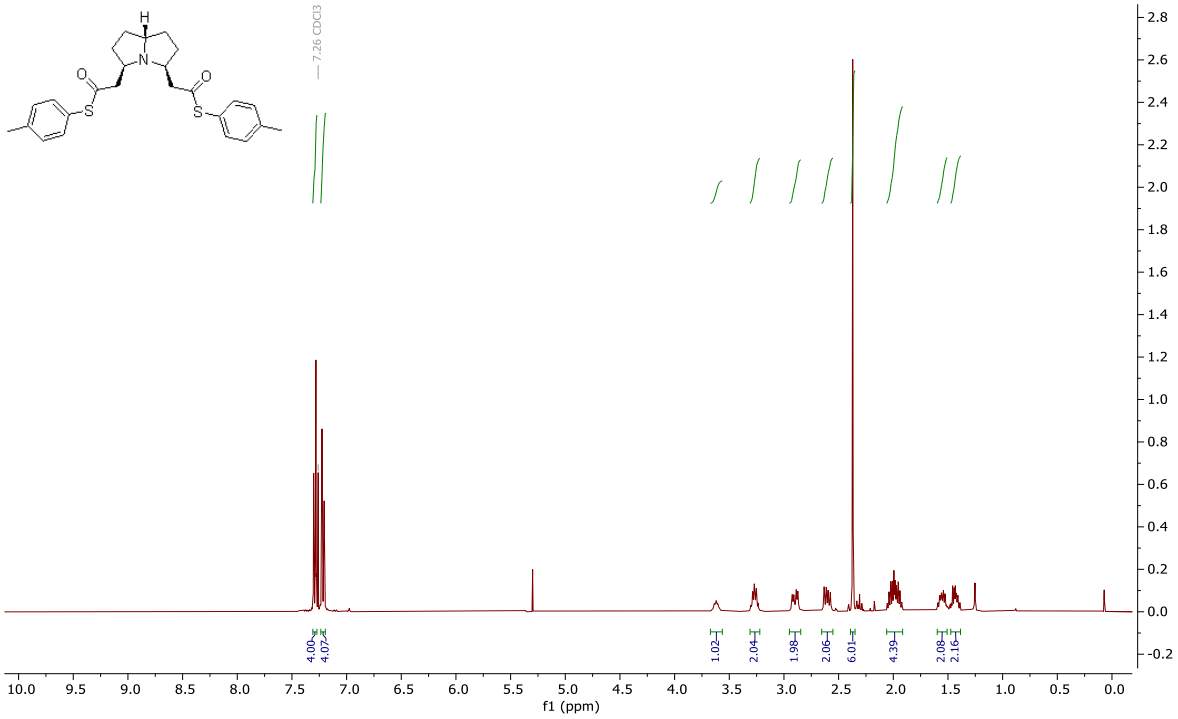


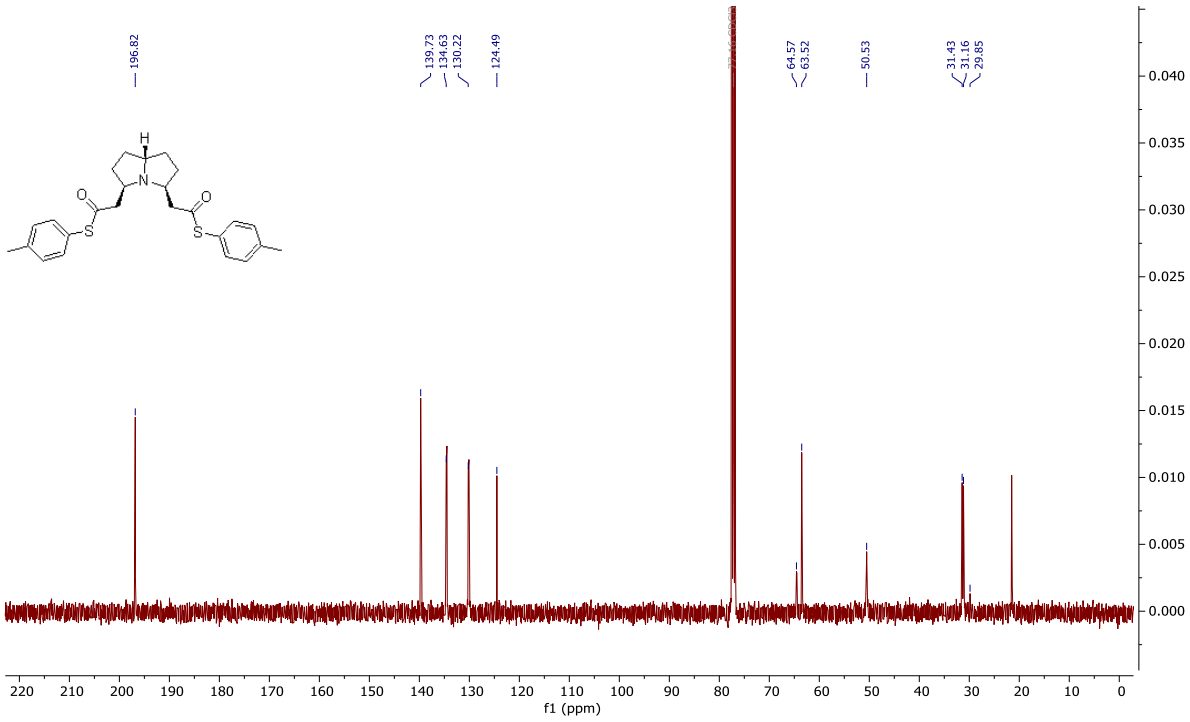
(2*S*,5*R*)-*tert*-Butyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-5-oxo-5-(*p*-tolylthio)pent-3-en-1-yl)pyrrolidine-1-carboxylate (**rac-18b and (*SR*)-18b**)



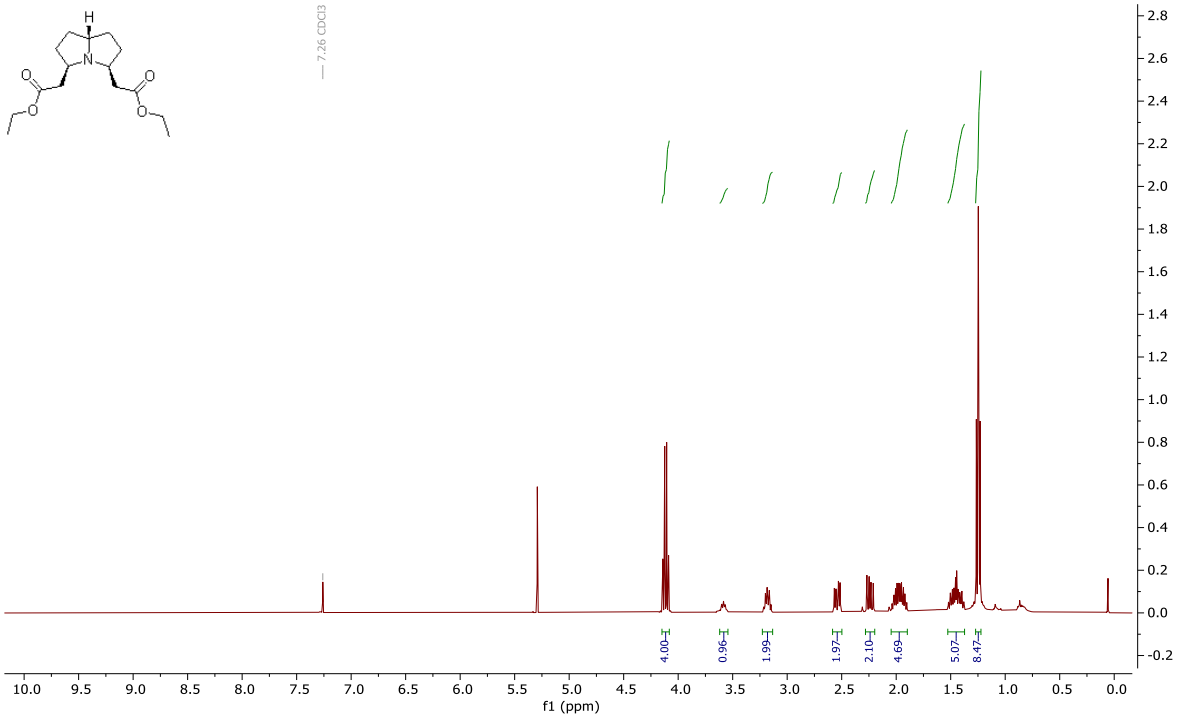


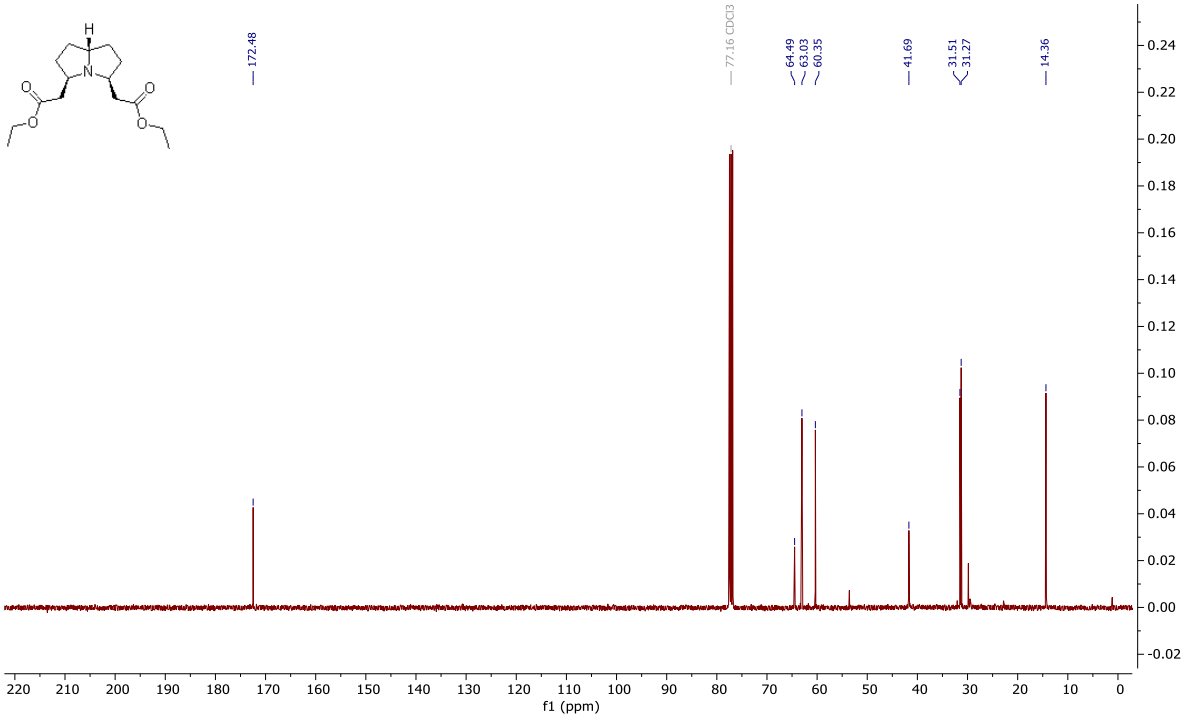
_S_,_S_'-Di-_p_-tolyl 2,2'-((3_R_,5_S_,7a_s_)-hexahydro-1_H_-pyrrolizine-3,5-diyl)diethanethioate (19a)



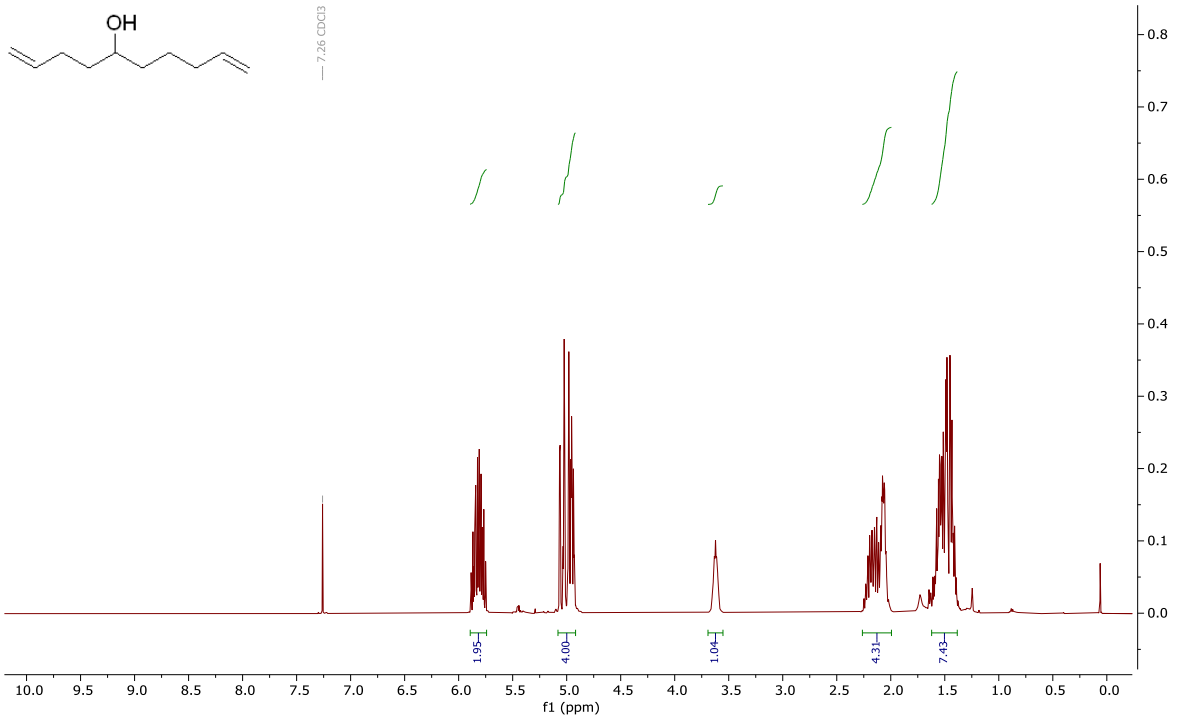


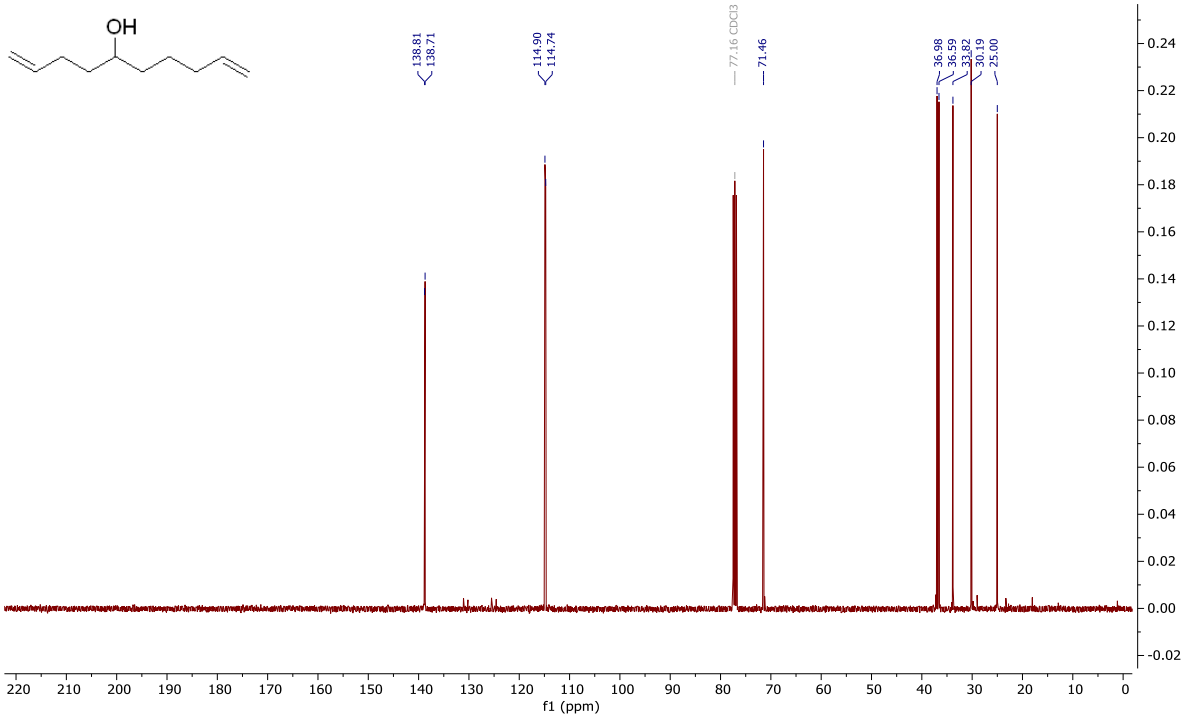
Diethyl 2,2'-((3*R*,5*S*,7as)-hexahydro-1H-pyrrolizine-3,5-diyl)diacetate (22)



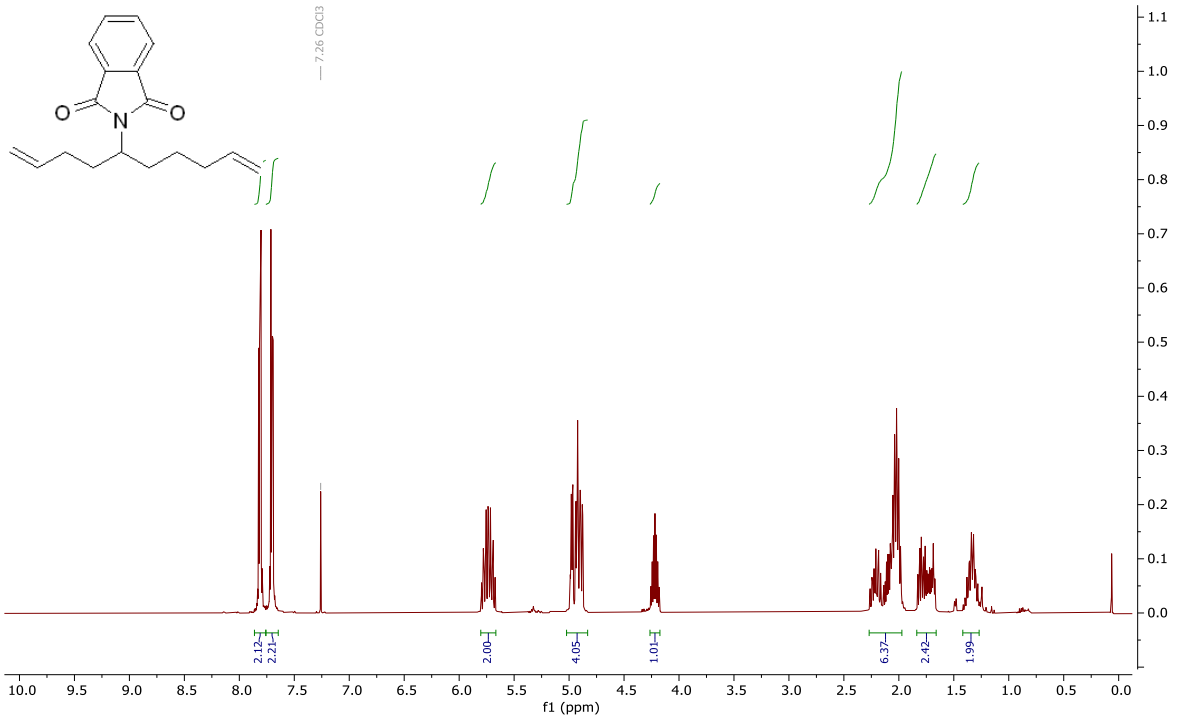


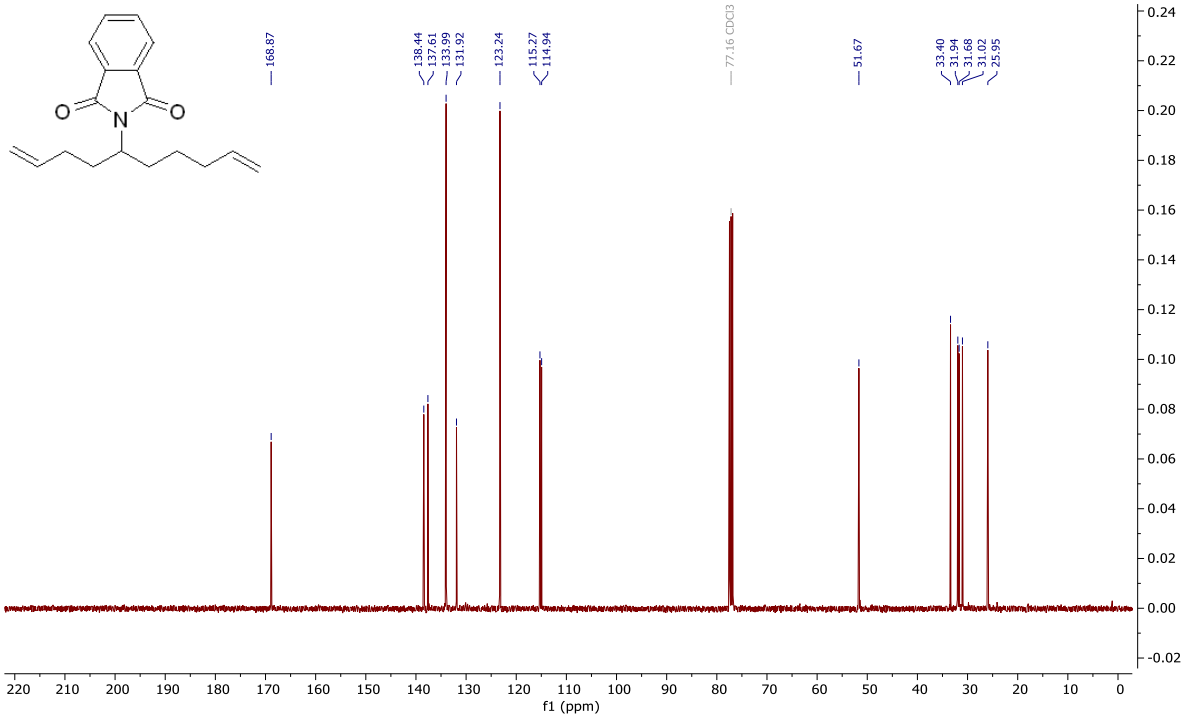
Deca-1,9-dien-5-ol (24)



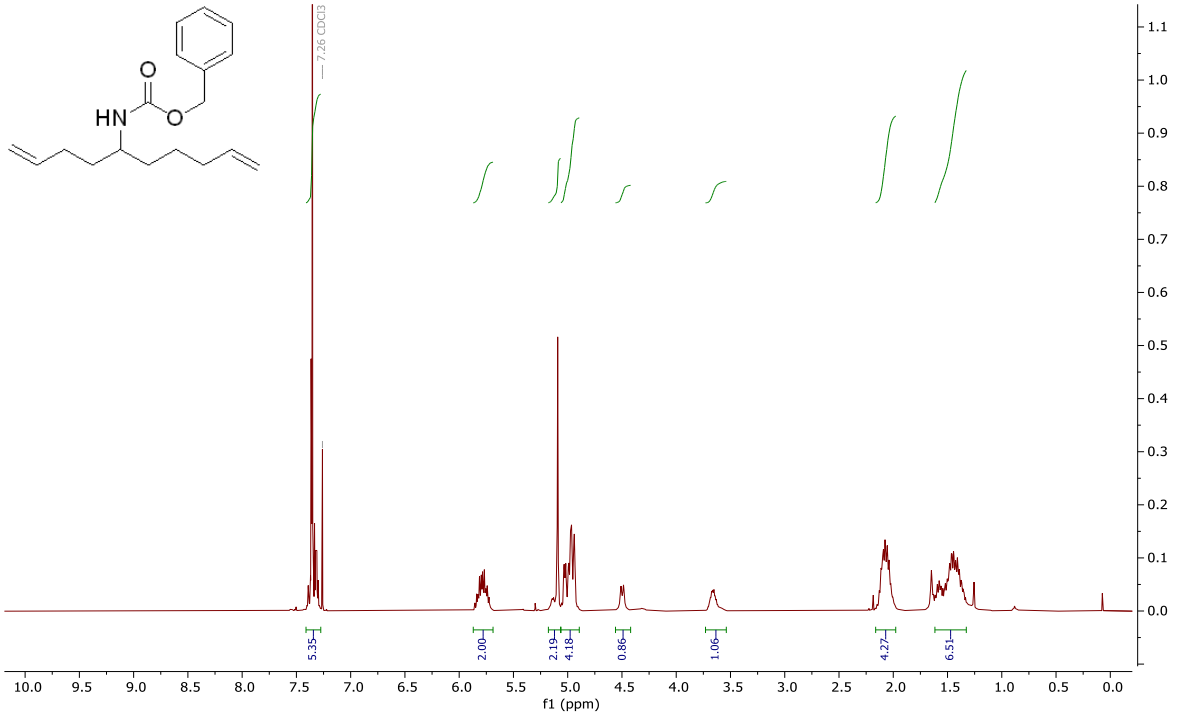


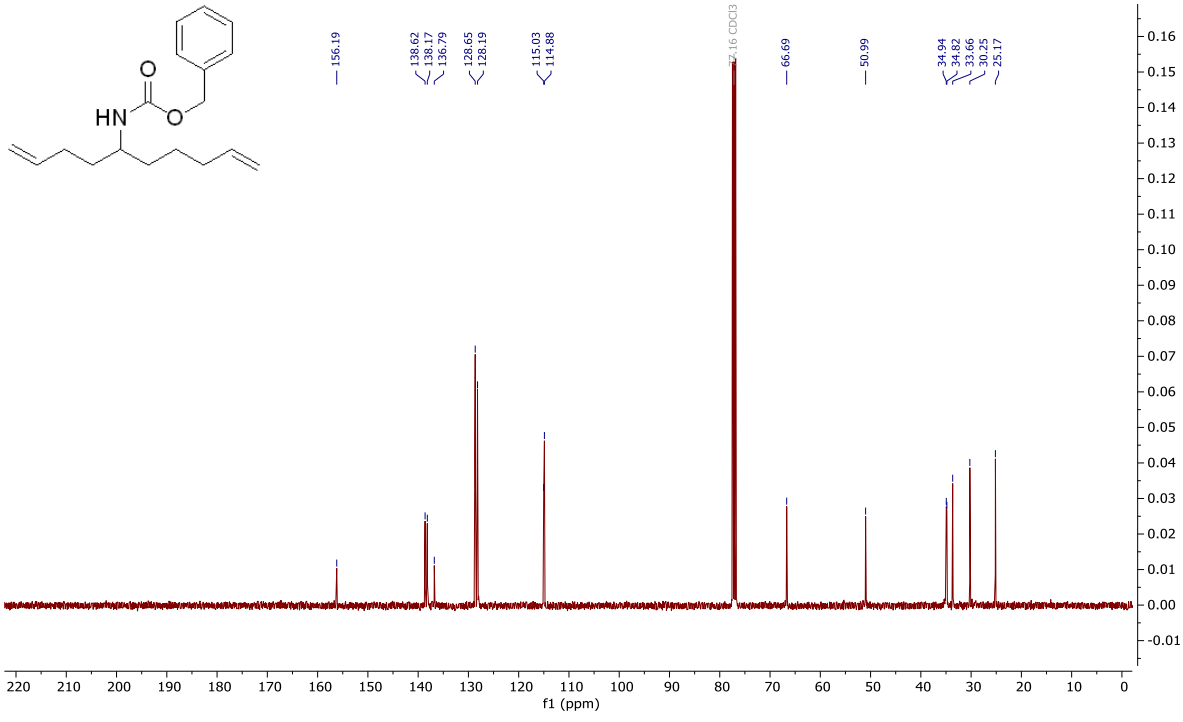
2-(Deca-1,9-dien-5-yl)isoindoline-1,3-dione (25)



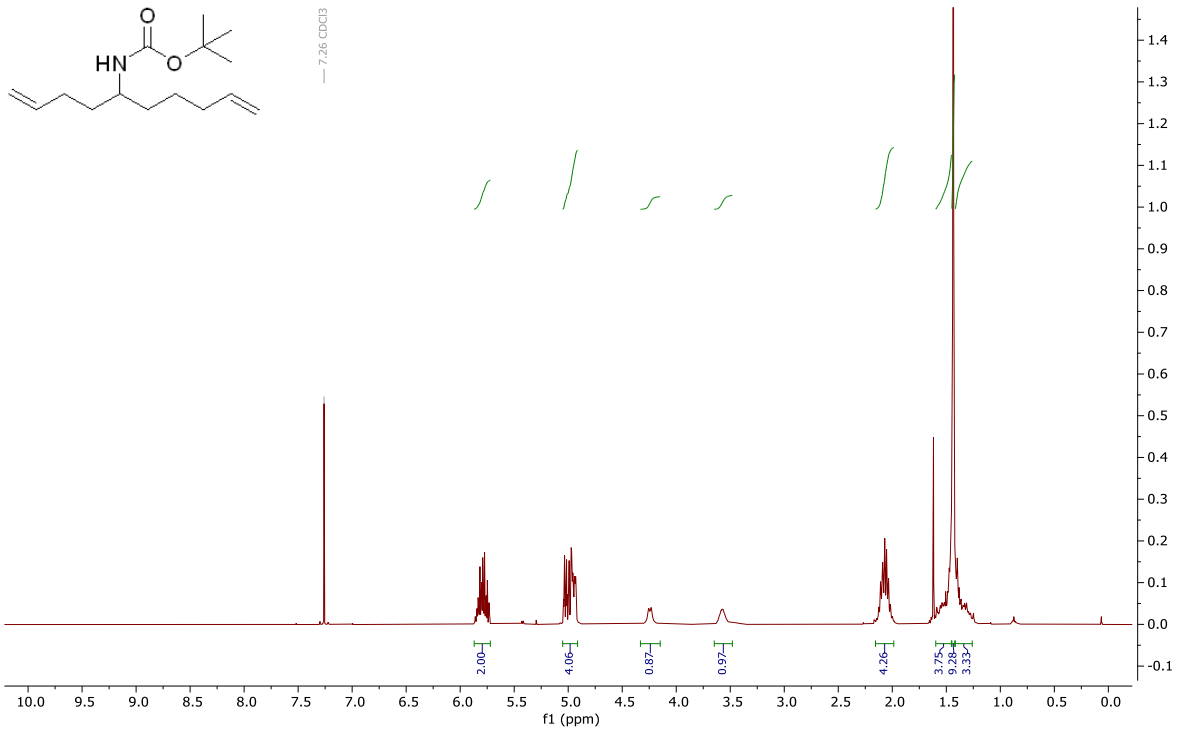


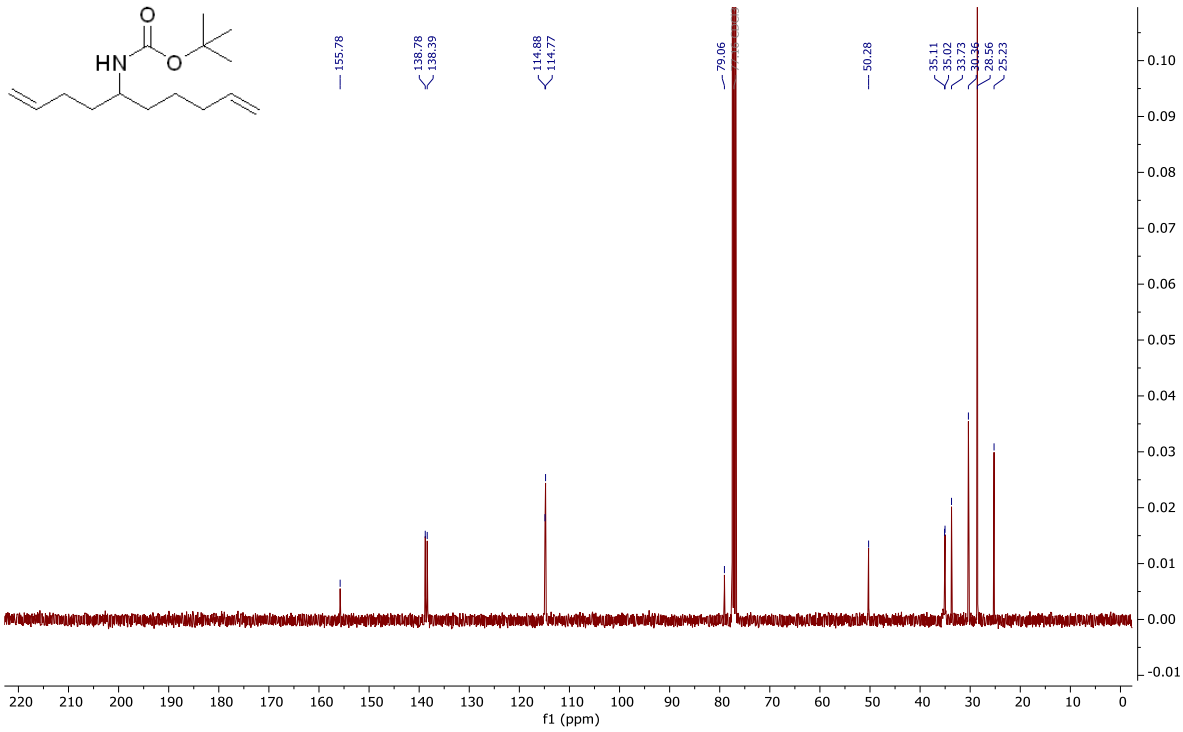
Benzyl deca-1,9-dien-5-ylcarbamate (16c)



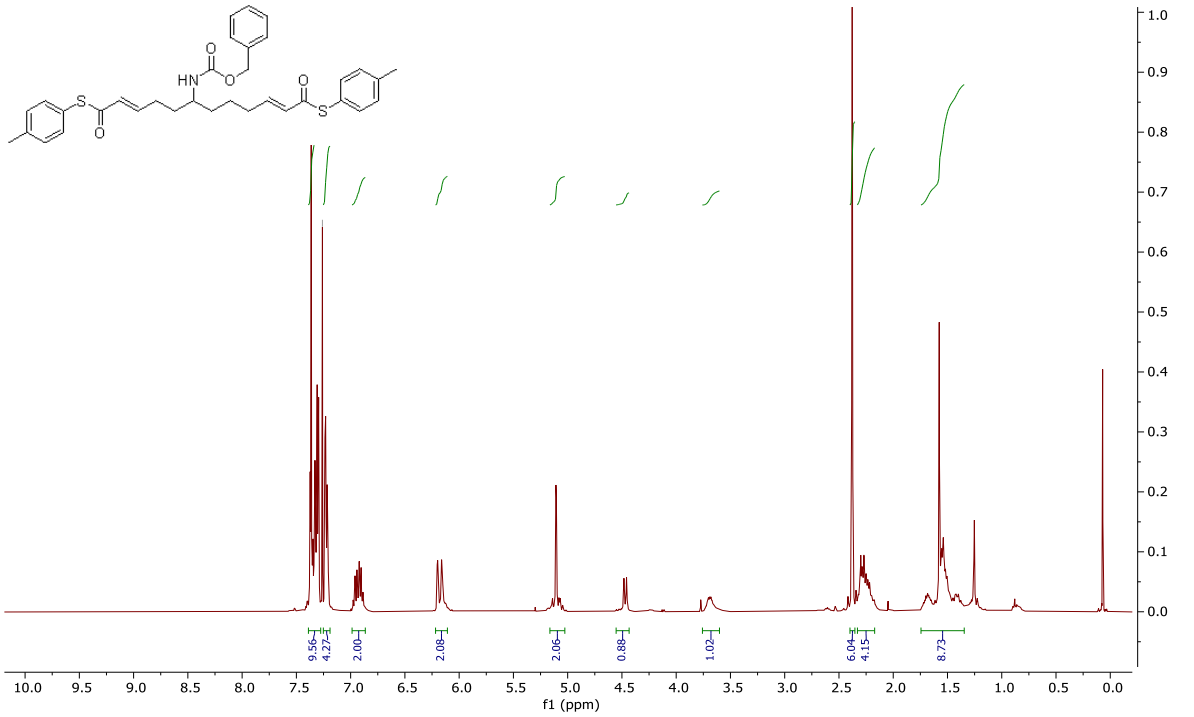


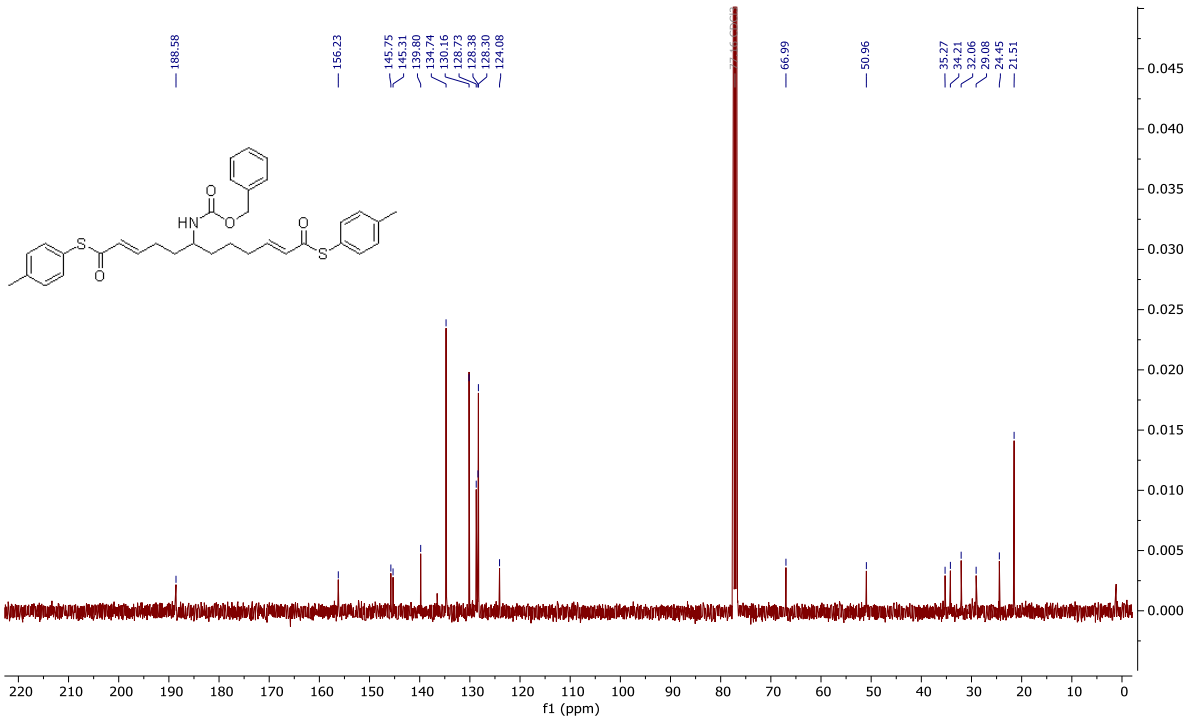
tert-Butyl deca-1,9-dien-5-ylcarbamate (16d)



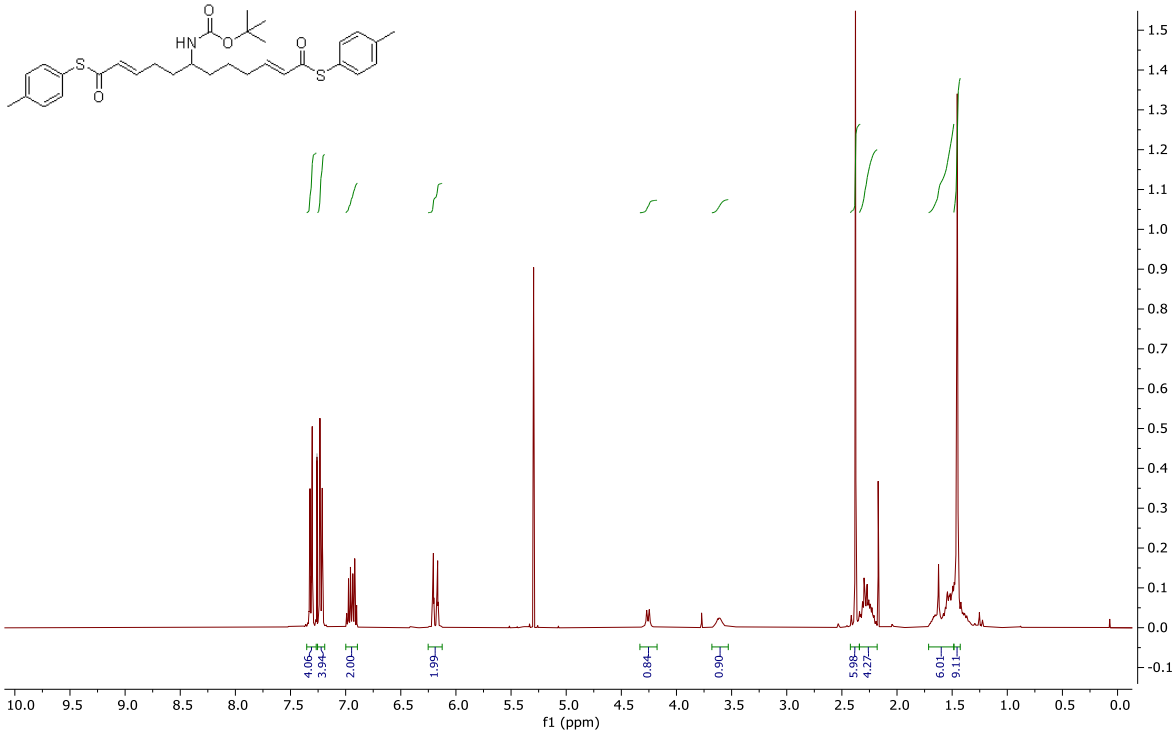


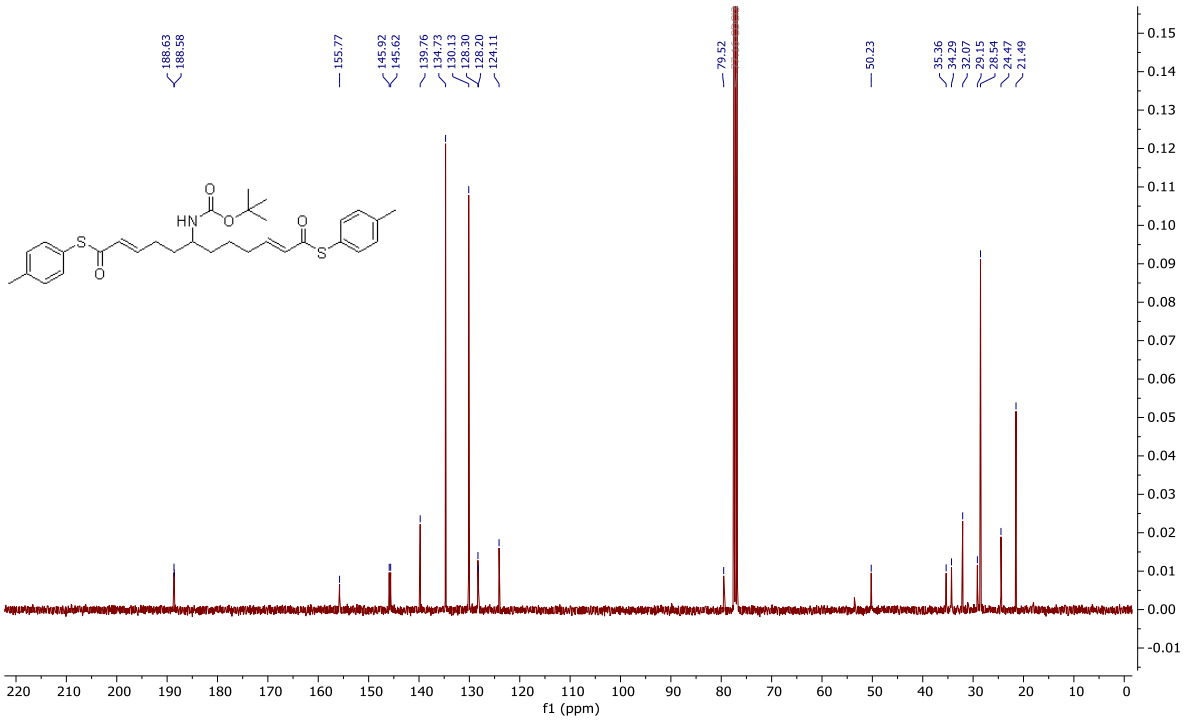
(2*E*,10*E*)-*S*,*S*-Di-*p*-tolyl 6-(((benzyloxy)carbonyl)amino)dodeca-2,10-dienebis(thioate) (17c)



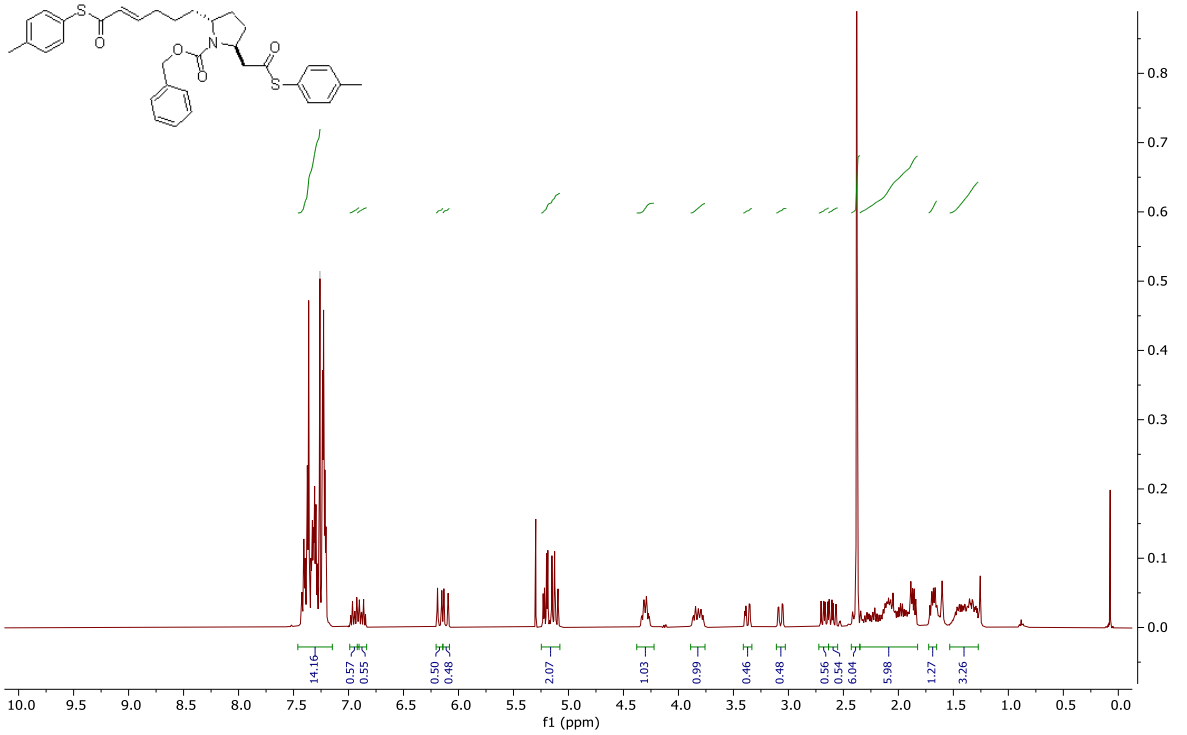


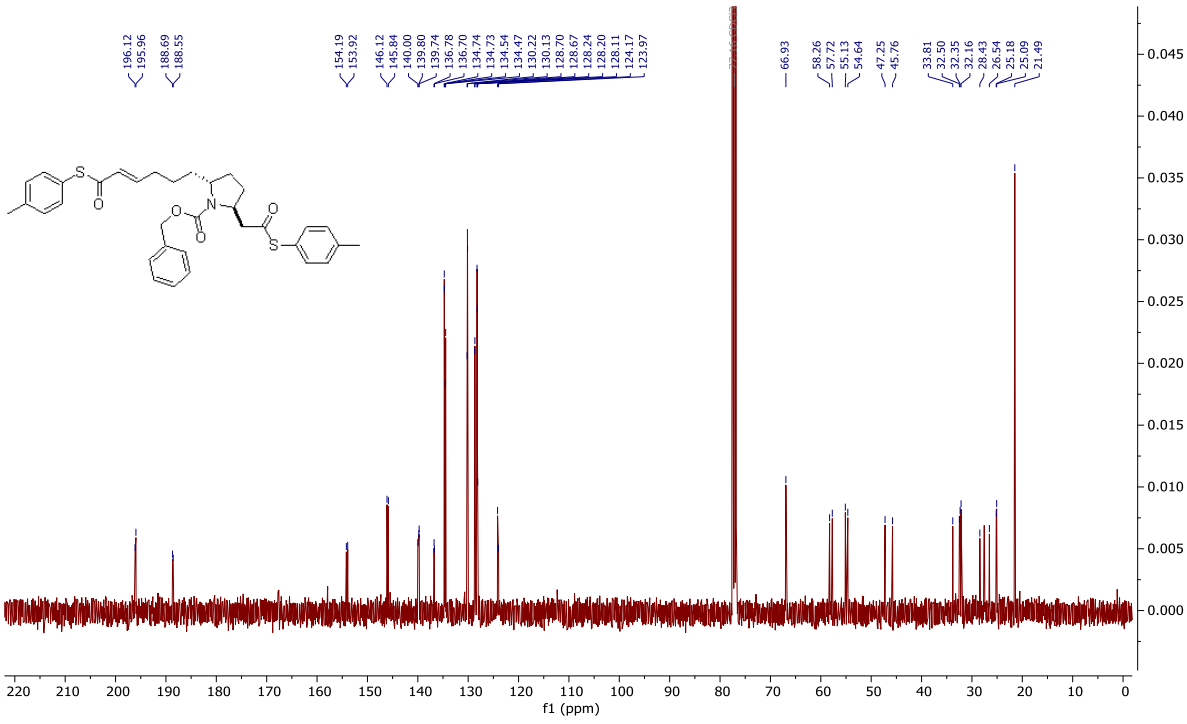
(2*E*,10*E*)-*S*,*S*-Di-*p*-tolyl 6-((*tert*-butoxycarbonyl)amino)dodeca-2,10-dienebis(thioate) (17d)



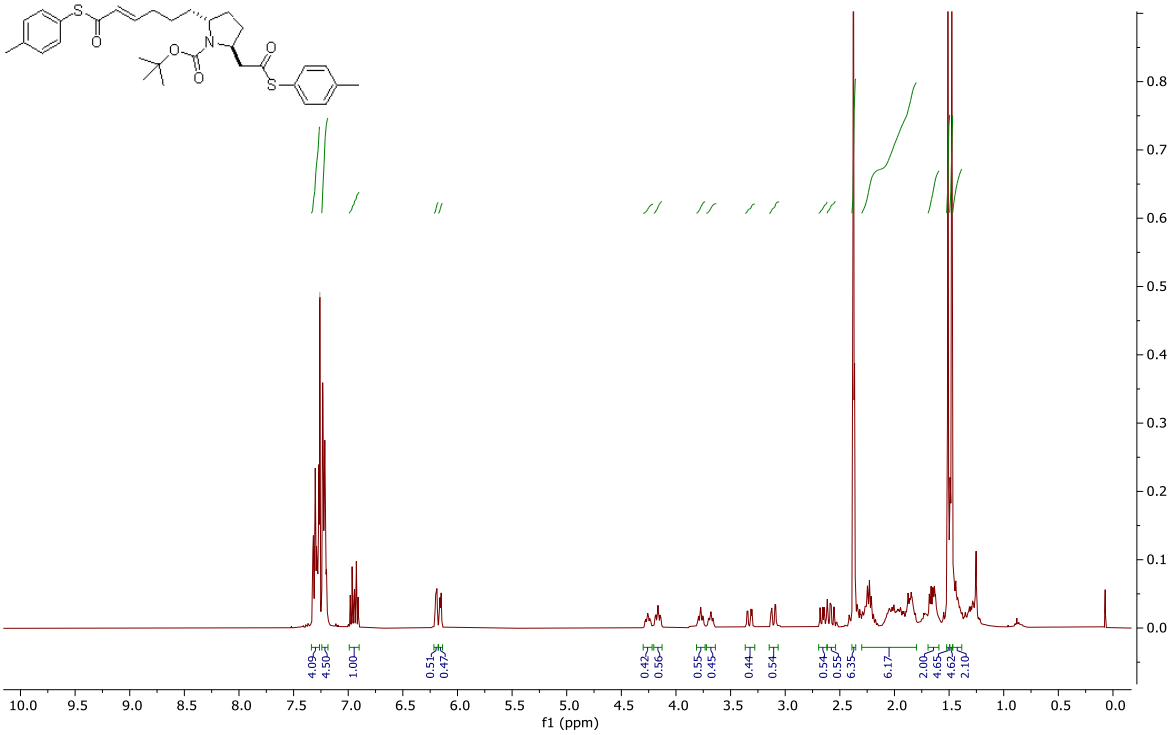


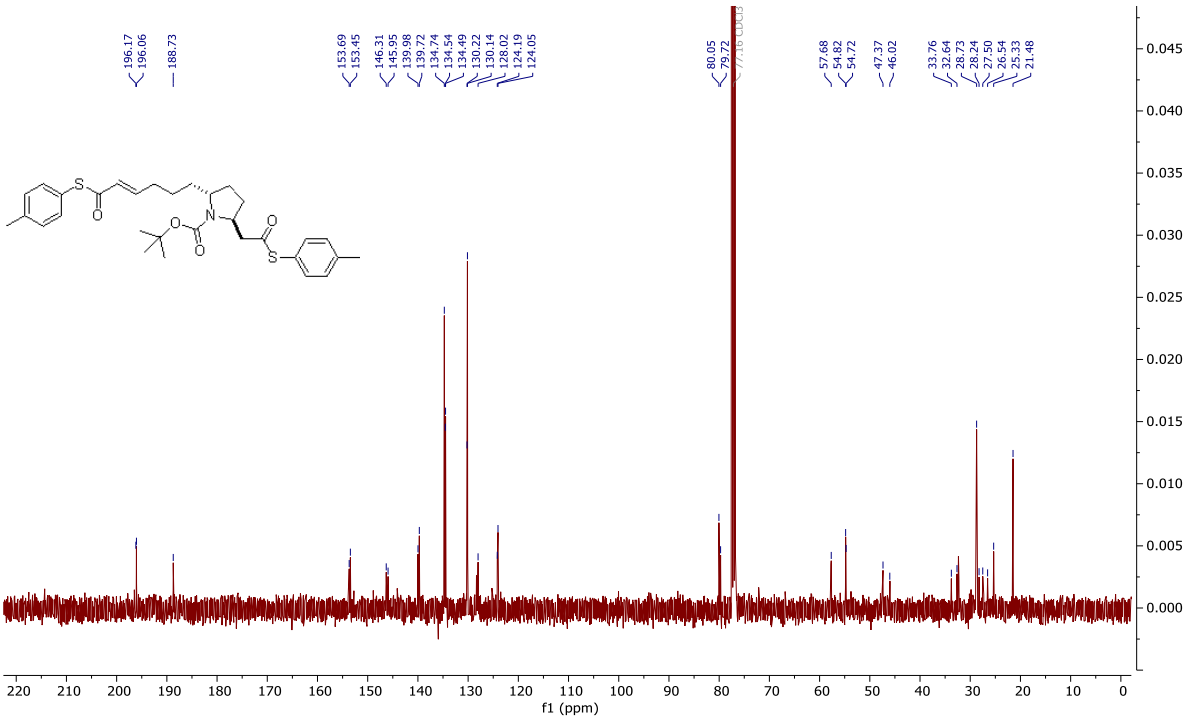
(±)-Benzyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-6-oxo-6-(*p*-tolylthio)hex-4-en-1-yl)pyrrolidine-1-carboxylate (18c)



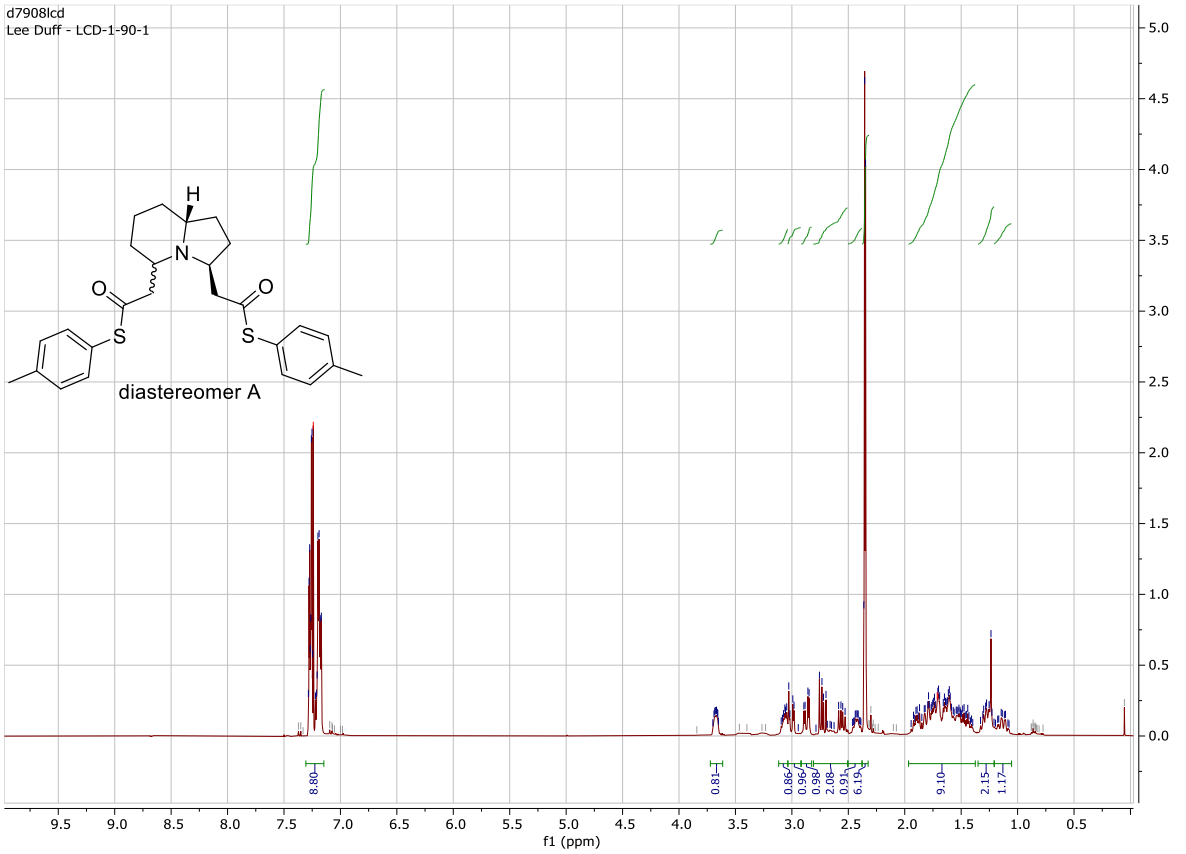


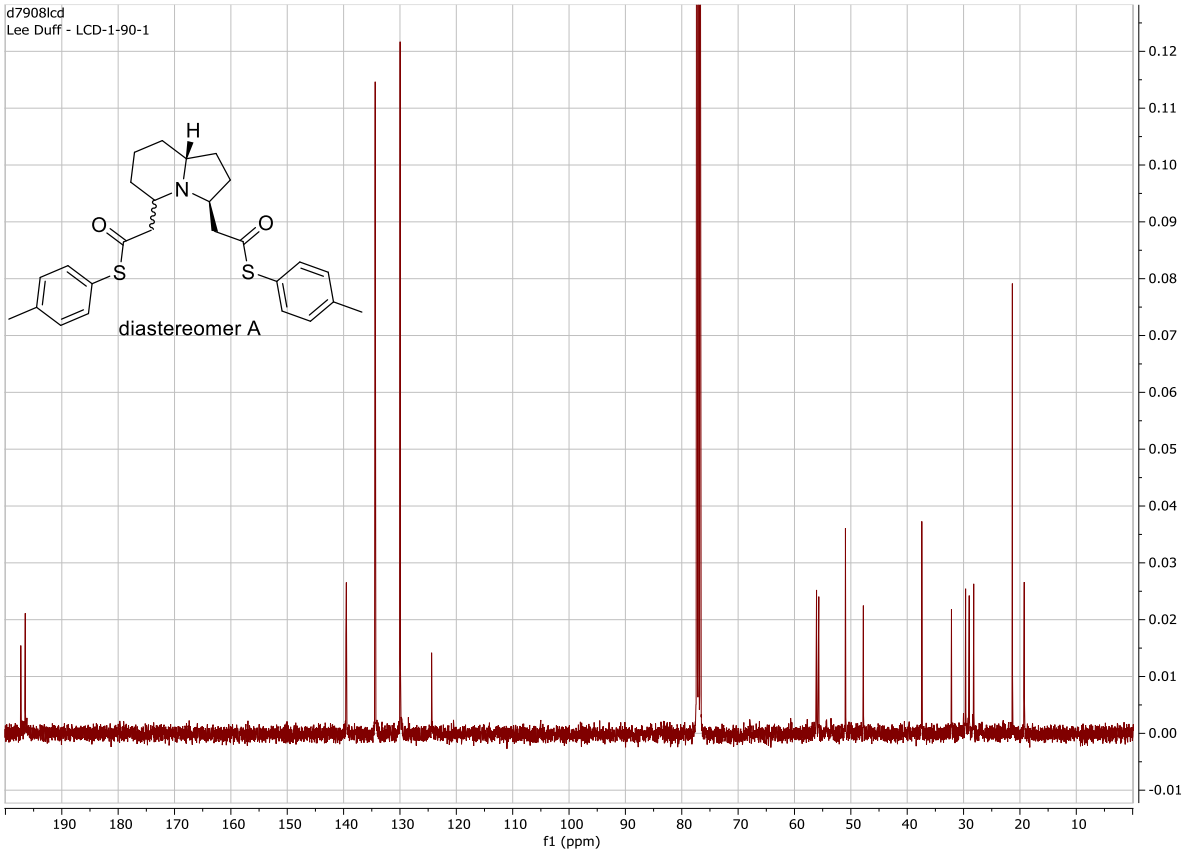
(±)-*tert*-butyl 2-(2-oxo-2-(*p*-tolylthio)ethyl)-5-((*E*)-6-oxo-6-(*p*-tolylthio)hex-4-en-1-yl)pyrrolidine-1-carboxylate (18d)



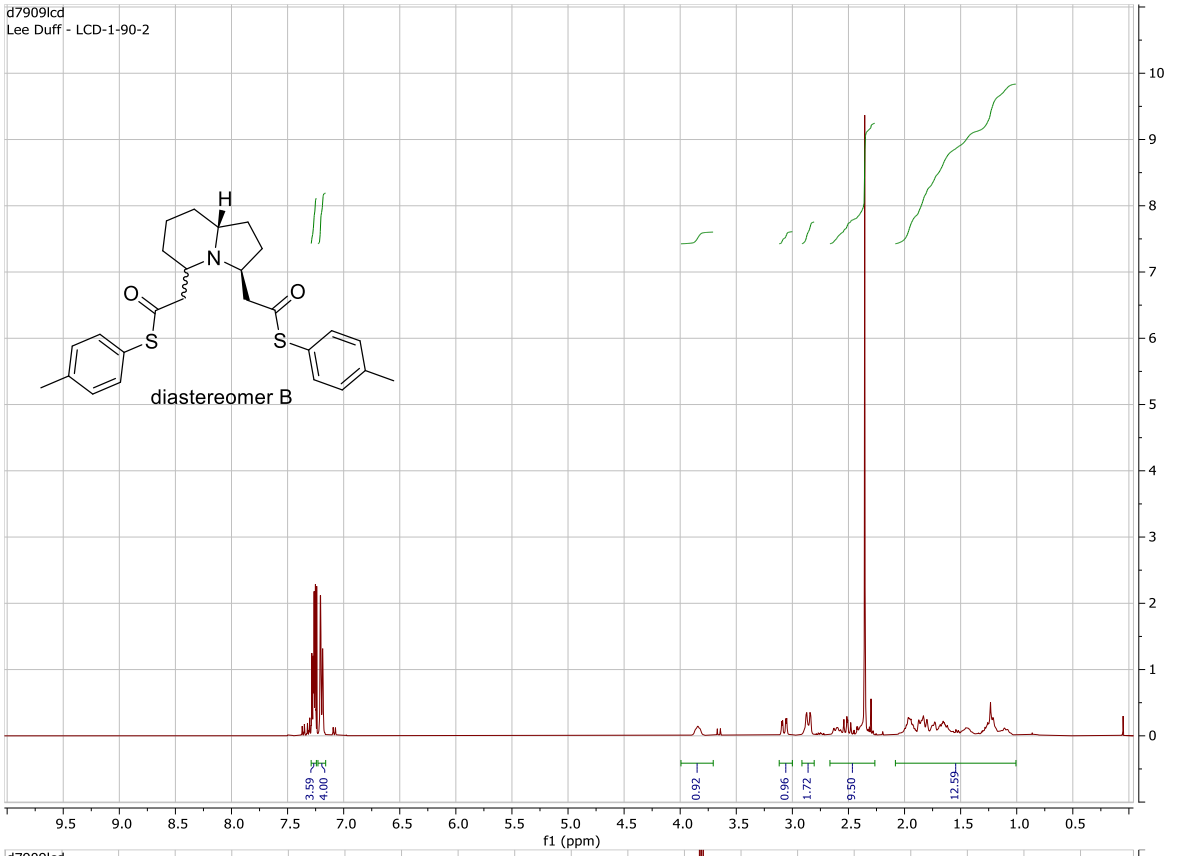


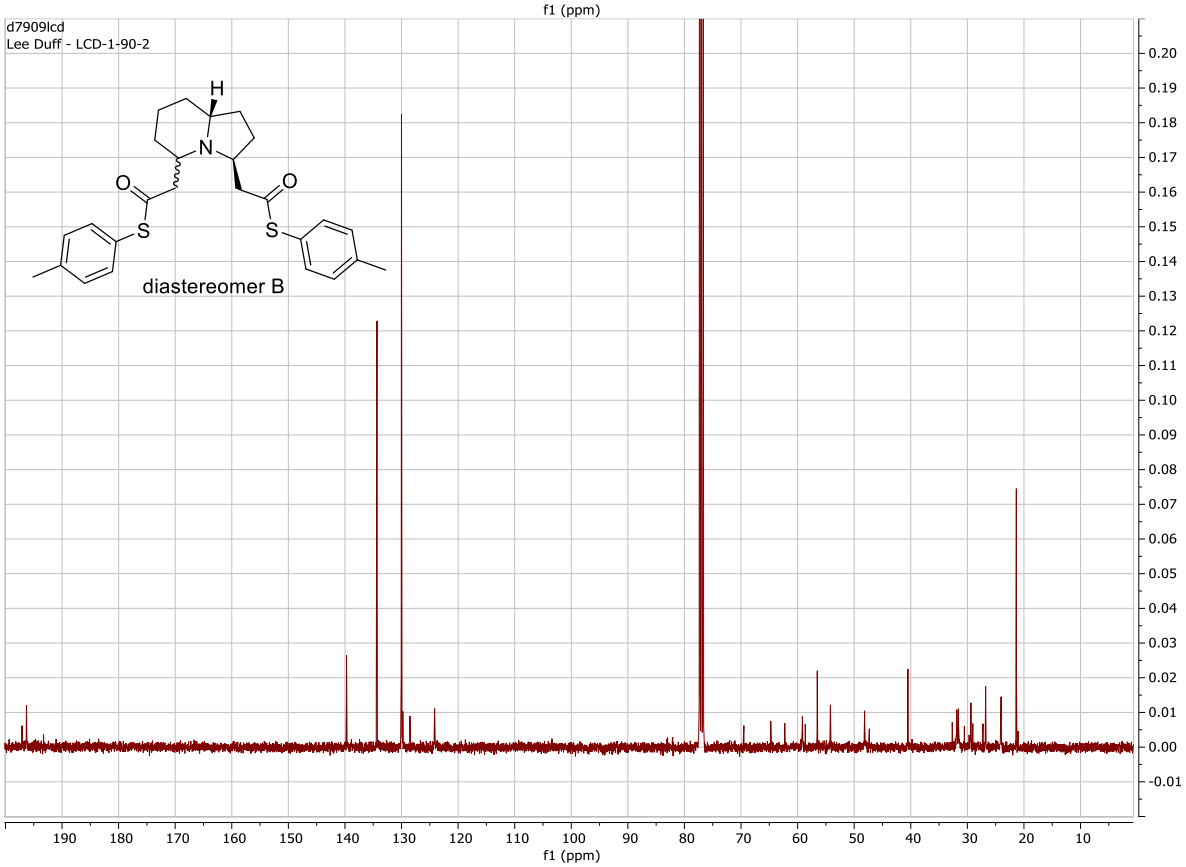
S,S'-di-p-tolyl 2,2'-((3S,5R,8aR)-octahydroindolizine-3,5-diyl)diethanethioate and S,S'-di-p-tolyl 2,2'-((3S,5S,8aR)-octahydroindolizine-3,5-diyl)diethanethioate (20a) – Diastereomer A





S,S'-di-p-tolyl 2,2'-((3S,5R,8aR)-octahydroindolizine-3,5-diyl)diethanethioate and S,S'-di-p-tolyl 2,2'-((3S,5S,8aR)-octahydroindolizine-3,5-diyl)diethanethioate (20a) – Diastereomer B





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2) J. C. Legeay, W. Lewis and R. A. Stockman, *Chem. Commun*., 2009, 2207–2209

3) M. D. Galvilan, W. R. J. D. Galloway, K. M. G. O'Connell, J. T. Hodkingson and D. R. Spring, *Chem. Commun*., 2010, **46**, 776–778