

Supporting Information

Remote Chirality Control Based on the Organocatalytic Asymmetric Mannich Reaction of α -Thio Acetaldehydes

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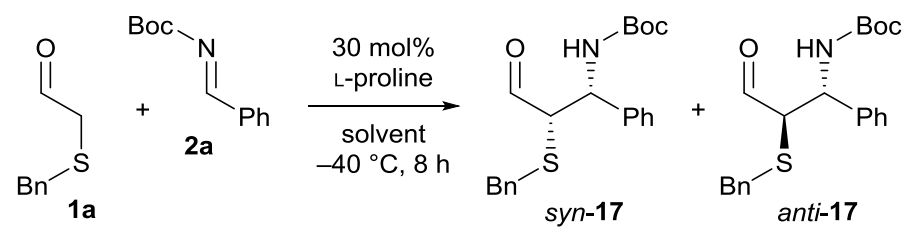
General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^1H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer and a JEOL JNM-ECA500 (500 MHz) spectrometer. Chemical shifts were reported in ppm from tetramethylsilane and dimethyl sulfoxide- D_6 as an internal standard. Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quintet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a JEOL JNM-FX400 (100 MHz) spectrometer and a JEOL JNM-ECA500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using a Daicel CHIRALPAK AD-H, IA, IC, ID, IE, IA3 and IC3, 4.6 mm \times 25 cm column. The high-resolution mass spectra (HRMS) were performed on Applied Biosystems Mariner 8295 API-TOF workstation. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230-400 mesh). For purification with preparative thin layer chromatography (PLC), Merck precoated PLC plates (silica gel 60 GF₂₅₄, 0.5 mm) were used.

In experiments requiring dry solvents, tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Kanto Chemical Co. Inc. as “Dehydrated”. The following products are all known: (benzylthio)acetaldehyde (**1a**),¹ (4-methoxyphenylthio)acetaldehyde (**1b**),² *tert*-Butyl glyoxylate (**15**),³ axially chiral amino sulfonamide (*S*)-**11**.⁴ *N*-Boc-protected imines (**2**) were prepared according to the literature procedure.⁵⁻⁶ (Dibromomethyl)benzene and (2,2-diiodoethyl)benzene were prepared according to the literature procedure.⁷ Other simple chemicals were purchased and used as such.

Optimization of the Reaction Conditions.

We first examined the Mannich reaction of (benzylthio)acetaldehyde (**1a**) (2 equiv) with an *N*-Boc-protected imine **2a** derived from benzaldehyde in the presence of 30 mol% of L-proline in acetonitrile at $-40\text{ }^{\circ}\text{C}$. Fortunately, the reaction proceeded to give the desired *syn*-Mannich product *syn*-**17** as a major diastereomer in excellent enantioselectivity (Table S1, entry 1). Use of increased amounts of **1a** (3 equiv) improved the yield (entry 2). Among the solvents tested, THF was found to be optimal in terms of both diastereo- and enantioselectivity, although the yield was not satisfactory due to low conversion (entry 6). The yield could be improved, when the reaction was performed at higher temperature with a longer reaction time (entry 7).

Table S1 Mannich reaction of α -thio acetaldehyde **1a** with imine **2a**^a



Entry	Solvent	Yield (%) ^b	<i>syn/anti</i> ^c	ee (%) ^d
1 ^e	MeCN	46	5.4/1	96
2	MeCN	69	5.3/1	98
3	CH ₂ Cl ₂	<5	-	-
4	toluene	<5	-	-
5	DMF	65	6.0/1	99
6	THF	22	10/1	99
7 ^f	THF	77	7.7/1	99
8 ^g	THF	59	4.6/1	99

^a The reaction of **1a** (0.375 mmol) with **2a** (0.125 mmol) was carried out in the presence of L-proline (0.0375 mmol) in a solvent (0.25 mL). ^b Isolated yield. ^c Determined by ¹H NMR analysis. ^d Determined by HPLC using a chiral column. ^e Using 2 equiv of **1a**. ^f Reaction performed at $-30\text{ }^{\circ}\text{C}$ for 24 h. ^g Reaction performed at $-20\text{ }^{\circ}\text{C}$ for 8 h.

General Procedure for the Proline-Catalyzed Asymmetric Mannich Reaction between (Benzylthio)acetaldehyde (**1a**) and *N*-Boc-Protected Imines (**2**) (Table 1, entries 1, 4 and 5):

To a solution of L-proline (4.3 mg, 0.0375 mmol) and (benzylthio)acetaldehyde (**1a**) (62.3 mg, 0.375 mmol) in THF (0.25 mL) was added *N*-Boc-protected imine (**2**) (0.125 mmol) at $-30\text{ }^{\circ}\text{C}$. After stirring for 24 h, the reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined

organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on cooled silica gel to afford the corresponding product. The enantiomeric excess of the product was determined after reduction by the method described below.

General Procedure for the Proline-Catalyzed Asymmetric Mannich Reaction between (Benzylthio)acetaldehyde (1a) and *N*-Boc-Protected Imines (2) (Table 1, entries 2 and 3):

To a solution of L-proline (4.3 mg, 0.0375 mmol) and (benzylthio)acetaldehyde (**1a**) (62.3 mg, 0.375 mmol) in THF (0.25 mL) was added *N*-Boc-protected imine (**2**) (0.125 mmol) at –30 °C. After stirring for 24 h, the reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was roughly purified by flash column chromatography on cooled silica gel to afford a Mannich product. To a solution of the Mannich product in CH₂Cl₂ (0.5 mL) and MeOH (0.5 mL) was added NaBH₄ (14 mg, 0.375 mmol) at –30 °C. After 1 h of stirring at –30 °C, the reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel to afford the corresponding product.

The reaction between (benzylthio)acetaldehyde (**1a**) and the *N*-Boc-protected aliphatic imine (R = cyclohexyl) under identical conditions resulted in no observable product formation.

***tert*-Butyl ((1*R*,2*S*)-2-(Benzylthio)-3-oxo-1-phenylpropyl)carbamate (Table 1, entry 1):** (99% ee (*syn*)); ¹H NMR (400 MHz, CDCl₃) δ 9.28 (1H, d, *J* = 3.9 Hz, CH₂O), 7.34-7.22 (10H, m, ArH), 5.09 (2H, br, CHNH₂Boc), 3.59 (1H, d, *J* = 13.1 Hz, SCH₂HPh), 3.49 (1H, d, *J* = 13.1 Hz, SCH₂HPh), 3.41 (1H, br, CHCHO), 1.41 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 191.3, 154.9, 139.4, 136.4, 129.2, 128.8, 128.6, 128.1, 127.5, 126.8, 80.1, 58.5, 52.4, 34.9, 28.3; IR (neat) 3374, 1705, 1682, 1520, 1250, 1167, 700 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₁H₂₅NNaO₃S: 394.1447 ([M + Na]⁺), Found: 394.1461 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min, retention time; 41.6 min and 50.0 min (major).

***tert*-Butyl ((1*R*,2*S*)-2-(Benzylthio)-3-hydroxy-1-(4-methoxyphenyl)propyl)carbamate (Table 1, entry 2):** (99% ee (*syn*)); ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.18 (5H, m, ArH), 7.03 (2H, d, *J* = 6.8 Hz, ArH), 6.90 (2H, d, *J* = 8.8 Hz, ArH), 5.35 (1H, d, *J* = 8.8 Hz, NH), 5.23 (1H, d, *J* = 8.8 Hz, CHNH₂Boc), 3.83 (3H, s, OMe), 3.66 (1H, br, CHHOH), 3.86-3.53 (1H, m, CH₂SBn), 3.44 (1H, br, CHHOH), 3.25

(1H, d, $J = 13.0$ Hz, SCHHPh), 3.10 (1H, d, $J = 13.0$ Hz, SCHHPh), 2.93-2.89 (1H, m, OH), 1.44 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 158.9, 156.6, 137.5, 131.8, 128.8, 128.5, 127.6, 127.2, 113.8, 80.5, 62.9, 55.3, 54.0, 52.2, 36.4, 28.3; IR (neat) 3400, 1674, 1497, 1165, 1057, 748 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₉NNaO₄S: 426.1710 ([M + Na]⁺), Found: 426.1706 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 39.7 min and 44.7 min (major).

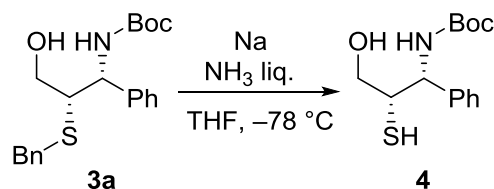
***tert*-Butyl ((1*R*,2*S*)-2-(Benzylthio)-1-(4-chlorophenyl)-3-oxopropyl)carbamate (Table 1, entry 3):** (99% ee (*syn*)); ¹H NMR (400 MHz, CDCl₃) δ 9.28 (1H, d, $J = 3.4$ Hz, CHO), 7.33-7.22 (7H, m, ArH), 7.15 (2H, d, $J = 8.5$ Hz, ArH), 5.08 (2H, br, CHNH₂Boc), 3.61 (1H, d, $J = 13.1$ Hz, SCHHPh), 3.51 (1H, d, $J = 13.1$ Hz, SCHHPh), 3.37 (1H, br, CHCHO), 1.40 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 191.2, 154.8, 138.1, 136.2, 133.8, 129.2, 128.9, 128.7, 128.2, 127.6, 80.3, 58.1, 51.9, 34.8, 28.2; IR(neat) 3368, 1705, 1680, 1520, 1166, 1091, 707 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₁H₂₄ClNNaO₃S: 428.1058 ([M + Na]⁺), Found: 428.1050 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 25.2 min (major) and 33.9 min.

***tert*-Butyl ((1*R*,2*S*)-2-(Benzylthio)-3-oxo-1-(*o*-tolyl)propyl)carbamate (Table 1, entry 4):** (98% ee (*syn*)); ¹H NMR (400 MHz, CDCl₃) δ 9.28 (1H, d, $J = 3.1$ Hz, CHO), 7.31-7.13 (9H, m, ArH), 5.38 (1H, br, NH), 4.98 (1H, d, $J = 8.5$ Hz, CHNH₂Boc), 3.59 (1H, d, $J = 12.8$ Hz, SCHHPh), 3.49 (1H, d, $J = 12.8$ Hz, SCHHPh), 3.44 (1H, br, CHCHO), 2.36 (3H, s, CH₃), 1.41 (9H, s, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 191.4, 154.9, 137.9, 136.4, 135.8, 131.0, 129.3, 128.6, 127.9, 127.5, 126.4, 125.9, 80.0, 58.4, 48.3, 35.0, 28.3, 19.4; IR (neat) 2976, 1701, 1495, 1366, 1165, 733 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₇NNaO₃S: 408.1604 ([M + Na]⁺), Found: 408.1612 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak IA, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 13.7 min and 15.2 min (major).

***tert*-Butyl ((1*R*,2*S*)-2-(Benzylthio)-3-hydroxy-1-(naphthalen-2-yl)propyl)carbamate (Table 1, entry 5):** (99% ee (*syn*)); ¹H NMR (500 MHz, CDCl₃) δ 7.85-7.83 (3H, m, ArH), 7.76 (1H, s, ArH), 7.53-7.48 (2H, m, ArH), 7.41 (1H, d, $J = 8.5$ Hz, ArH), 7.13 (3H, m, ArH), 6.89 (2H, m, ArH), 5.53 (1H, br, NH), 5.46 (1H, br, CHNH₂Boc), 3.73-3.42 (3H, m, CH₂OH, CH₂SBn), 3.15 (1H, d, $J = 12.8$ Hz, SCHHPh), 3.07 (1H, m, OH), 3.02 (1H, d, $J = 13.0$ Hz, SCHHPh), 1.47 (9H, s, C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 156.7, 137.3, 137.2, 133.2, 132.7, 128.7, 128.4, 128.2, 127.9, 127.7, 127.2, 126.4, 126.1, 125.3, 124.8, 80.6, 63.0, 53.8, 52.9, 36.4, 28.3; IR (neat) 3400, 1674, 1497, 1250, 1165, 1057, 748 cm⁻¹; HRMS

(ESI-TOF) Calcd. for $C_{25}H_{29}NNaO_3S$: 446.1760 ($[M + Na]^+$), Found: 446.1769 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min, retention time; 56.1 min (major) and 72.4 min.

***tert*-Butyl ((1*R*,2*S*)-3-Hydroxy-2-mercapto-1-phenylpropyl)carbamate (**4**) (Scheme 2):**



To a solution of **3a** (33.3 mg, 0.089 mmol) in NH₃ liq. and THF (0.5 mL) at -78 °C was added Na (12 mg, 0.534 mmol). After stirring for 2 h, the mixture was quenched with NH₄Cl aq. at -78 °C and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel to afford the corresponding product **4** (16.1 mg, 0.057 mmol, 98% ee). $[\alpha]_D^{21} = -3.21$ (*c* 1.10, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.28 (5H, m, ArH), 5.41-5.29 (2H, m, NH, CHNH₂Boc), 3.99 (1H, br, CHSH), 3.80-3.73 (1H, m, CHHOH), 3.47 (1H, br, OH), 3.40-3.35 (1H, m, CHHOH), 1.47 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 156.9, 139.2, 128.6, 127.6, 126.5, 80.8, 64.8, 52.9, 48.1, 28.3; IR (neat) 3297, 2979, 1669, 1537, 1166, 1057, 700 cm⁻¹; HRMS (ESI-TOF) Calcd. for $C_{14}H_{21}NNaO_3S$: 306.1134 ($[M + Na]^+$), Found: 306.1123 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 4/1, flow rate = 0.5 mL/min, retention time; 12.8 min (major) and 16.8 min.

General Procedure for the Proline-Catalyzed Asymmetric Mannich Reaction between (4-Methoxyphenylthio)acetaldehyde (1b**) and *N*-Protected Imines (**2**) (Table 2):**

To a solution of L-proline (4.3 mg, 0.0375 mmol) and (4-methoxyphenylthio)acetaldehyde (**1b**) (68.3 mg, 0.375 mmol) in THF (0.25 mL) was added *N*-protected imine (**2**) (0.125 mmol) at -30 °C. The mixture was stirred for 20-22 h. The reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. To a solution of the reaction mixture in CH₂Cl₂ (0.5 mL) and MeOH (0.5 mL) was added NaBH₄ (14 mg, 0.375 mmol) at -30 °C. After 1 h of stirring at -30 °C, the reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel to afford the corresponding product.

tert-Butyl ((1R,2S)-3-Hydroxy-2-((4-methoxyphenyl)thio)-1-phenylpropyl)carbamate (Table 2, entry 1): (99% ee (*syn*)), $[\alpha]_D^{21} = 82.3$ (*c* 1.30, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.16 (5H, m, ArH), 6.94 (2H, d, *J* = 6.8 Hz, ArH), 6.60 (2H, d, *J* = 8.0 Hz, ArH), 5.36 (1H, d, *J* = 8.2 Hz, NH), 5.18 (1H, br, CHNHBOc), 3.72-3.55 (2H, m, CHHOH, CHSAr), 3.66 (3H, s, OMe), 3.55-3.49 (1H, m, CHHOH), 3.22 (1H, m, OH), 1.38 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.5, 156.4, 139.6, 135.1, 128.4, 127.4, 126.7, 123.8, 114.4, 80.4, 62.7, 59.8, 55.3, 53.1, 28.3; IR (neat) 3399, 2976, 1688, 1493, 1245, 1170, 1030 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₁H₂₇NNaO₄S: 412.1553 ([M + Na]⁺), Found: 412.1554 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 33.7 min and 39.6 min (major).

tert-Butyl ((1R,2S)-3-Hydroxy-1-(4-methoxyphenyl)-2-((4-methoxyphenyl)thio) propyl)carbamate (Table 2, entry 2): (99% ee (*syn*)), $[\alpha]_D^{21} = 88.7$ (*c* 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.23 (2H, d, *J* = 8.7 Hz, ArH), 7.08 (2H, d, *J* = 8.7 Hz, ArH), 6.85 (2H, d, *J* = 8.7 Hz, ArH), 6.70 (2H, d, *J* = 8.7 Hz, ArH), 5.37 (1H, d, *J* = 9.2 Hz, NH), 5.18 (1H, br, CHNHBOc), 3.79 (3H, s, OMe), 3.75 (3H, s, OMe), 3.73-3.54 (3H, m, CH₂OH, CHSAr), 3.28 (1H, m, OH), 1.45 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.5, 158.8, 156.4, 135.1, 131.7, 127.8, 123.7, 114.5, 113.8, 80.4, 62.7, 59.6, 55.3 (two peaks overlap), 52.7, 28.3; IR (neat) 3378, 2932, 1688, 1511, 1493, 1243, 1164, 1031, 732 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₉NNaO₅S: 442.1659 ([M + Na]⁺), Found: 442.1654 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 54.5 min and 62.2 min (major).

tert-Butyl ((1R,2S)-1-(4-Bromophenyl)-3-hydroxy-2-((4-methoxyphenyl)thio)propyl)carbamate (Table 2, entry 3): (99% ee (*syn*)); ¹H NMR (400 MHz, CDCl₃) δ 7.41 (2H, d, *J* = 8.5 Hz, ArH), 7.16 (2H, d, *J* = 8.5 Hz, ArH), 7.04 (2H, d, *J* = 7.5 Hz, ArH), 6.70 (2H, d, *J* = 8.7 Hz, ArH), 5.44 (1H, d, *J* = 9.4 Hz, NH), 5.20 (1H, br, CHNHBOc), 3.82-3.65 (1H, br, CHSAr), 3.76 (3H, s, OMe), 3.60-3.48 (2H, m, CH₂OH), 3.28 (1H, m, OH), 1.45 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.7, 156.3, 138.8, 135.1, 131.4, 128.4, 123.3, 121.2, 114.6, 80.6, 62.6, 59.4, 55.3, 52.8, 28.2; IR (neat) 2975, 1714, 1491, 1245, 736 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₁H₂₆BrNNaO₄S: 490.0658 ([M + Na]⁺), Found: 490.0657 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 44.5 min and 67.1 min (major).

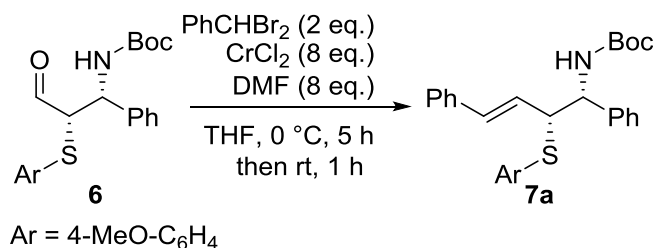
Benzyl ((1R,2S)-3-Hydroxy-2-((4-methoxyphenyl)thio)-1-phenylpropyl)carbamate (Table 2, entry 4): (99% ee (*syn*)); ¹H NMR (500 MHz, CDCl₃) δ 7.47-7.25 (10H, m, ArH), 7.04 (2H, br, ArH), 6.67

(2H, d, $J = 7.9$ Hz, ArH), 5.74 (1H, d, $J = 8.8$ Hz, NH), 5.22 (1H, m, CHNHCBz), 5.16-5.08 (2H, m, CH₂Ph), 3.73 (3H, s, OMe), 3.64 (1H, br, CHHOH), 3.56 (1H, br, CHSAr), 3.29 (2H, m, CHHOH, OH); ¹³C NMR (125 MHz, CDCl₃) δ 159.7, 156.6, 139.4, 136.1, 135.3, 128.54, 128.49, 128.3, 128.2, 127.6, 126.7, 123.2, 114.5, 67.3, 62.5, 59.4, 55.3, 54.3; IR (neat) 3331, 2938, 1694, 1492, 1243, 1028, 698 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₄H₂₅NNaO₄S: 446.1397 ([M + Na]⁺), Found: 446.1399 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak IC3, hexane/*i*-PrOH = 4/1, flow rate = 0.5 mL/min, retention time; 36.0 min (major) and 47.5 min.

General Procedure for the Takai Olefination Reactions (Scheme 3):

To a solution of L-proline (30 mol%) and (4-methoxyphenylthio)acetaldehyde (**1b**) (3.0 eq.) in THF (0.5 M) was added *N*-Boc-protected imine (**2**) (1.0 eq.) at -30 °C. The mixture was stirred for 20 h. The reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was roughly purified by flash column chromatography on cooled silica gel to afford the corresponding Mannich product **7**. The Mannich adduct **7** was used for the Takai olefination reaction by the methods described as below.⁸

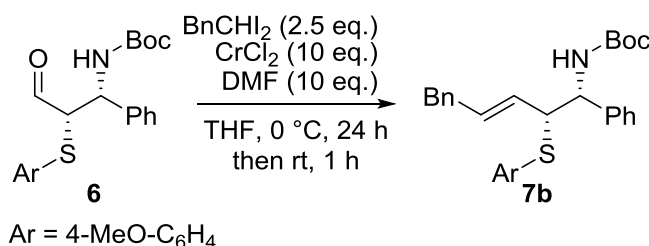
tert-Butyl ((1*R*,2*R*,*E*)-2-((4-Methoxyphenyl)thio)-1,4-diphenylbut-3-en-1-yl)carbamate (**7a**):



To a suspension of CrCl₂ (73.7 mg, 0.60 mmol) in THF (2.5 mL) was added DMF (0.047 mL, 0.60 mmol) at room temperature. After stirring for 30 min, a solution of the Mannich product **6** (29.1 mg, 0.075 mmol) and (dibromomethyl)benzene (35.5 mg, 0.15 mmol) in THF (1.5 mL) was added slowly at 0 °C. The mixture was stirred for 5 h at 0 °C and then stirred for 1 h at room temperature. The reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄, passed through silica gel and concentrated. The residue was purified by flash column chromatography on silica gel to afford **7a** (26.3 mg, 0.057 mmol, 99% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.15 (12H, m, ArH), 6.75 (2H, d, $J = 8.9$ Hz, ArH), 6.03-6.00 (2H, m, CH=CH), 5.34 (1H, br, NH), 4.99 (1H, br, CHNHBOC), 3.89 (1H, br, CHSAr), 3.75 (3H, s, OMe), 1.42

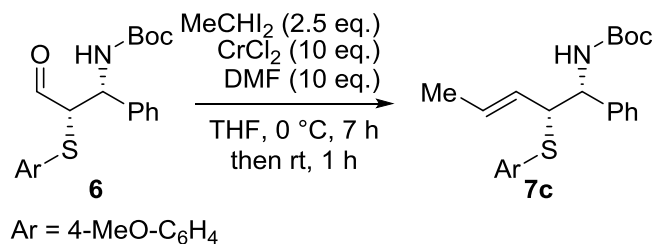
(9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.8, 155.0, 139.7, 136.6, 132.6, 128.5, 128.3, 128.2, 127.9, 127.6, 127.2, 126.7, 126.3, 123.5, 114.4, 79.8, 58.9, 57.6, 55.2, 28.3; IR (neat) 2975, 1699, 1492, 1245, 1170, 698 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₈H₃₁NNaO₃S: 484.1917 ([M + Na]⁺), Found: 484.1908 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 33.6 min (major) and 41.4 min.

***tert*-Butyl ((1*R*,2*R*,*E*)-2-((4-Methoxyphenyl)thio)-1,5-diphenylpent-3-en-1-yl)carbamate (**7b**):**



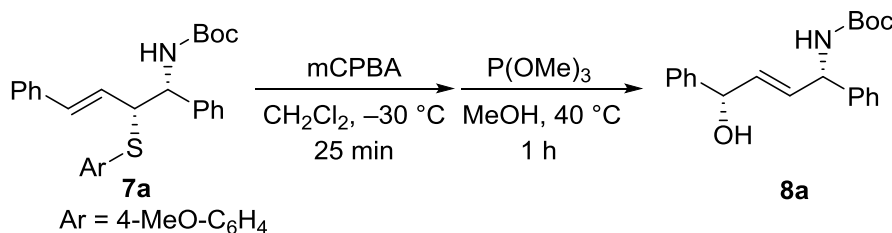
To a suspension of CrCl₂ (95.3 mg, 0.82 mmol) in THF (3.0 mL) was added DMF (0.061 mL, 0.82 mmol) at room temperature. After stirring for 30 min, a solution of the Mannich product **6** (31.9 mg, 0.082 mmol) and (2,2-diiodoethyl)benzene (72.8 mg, 0.205 mmol) in THF (2.0 mL) was added slowly at 0 °C. The mixture was stirred for 24 h at 0 °C and then stirred for 1 h at room temperature. The reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄, passed through short silica gel and concentrated. The residue was purified by flash column chromatography on silica gel to afford **7b** (23.4 mg, 0.049 mmol, 99% ee). ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.24 (8H, m, ArH), 7.20-7.12 (2H, m, ArH), 6.79 (2H, d, *J* = 7.4 Hz, ArH), 6.74 (2H, d, *J* = 8.8 Hz, ArH), 5.35-5.20 (3H, m, CH=CH, NH), 4.83 (1H, br, CHNH₂Boc), 3.77 (3H, s, OMe), 3.74 (1H, br, CHSAr), 3.18 (2H, m, BnCH₂), 1.41 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.7, 155.0, 140.2, 139.7, 136.5, 132.6, 128.8, 128.4, 128.24, 128.19, 127.4, 127.2, 125.9, 123.5, 114.3, 79.7, 58.3, 57.7, 55.2, 38.5, 28.3; IR (neat) 2976, 1900, 1493, 1245, 1170, 698 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₉H₃₃NNaO₃S: 498.2073 ([M + Na]⁺), Found: 498.2074 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak IC3, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 11.3 min (major) and 18.5 min.

***tert*-Butyl ((1*R*,2*R*,*E*)-2-((4-Methoxyphenyl)thio)-1-phenylpent-3-en-1-yl)carbamate (**7c**):**



To a suspension of CrCl₂ (91.2 mg, 0.93 mmol) in THF (2.3 mL) was added DMF (0.058 ml, 0.93 mmol) at room temperature. After stirring for 30 min, a solution of the Mannich product **6** (36 mg, 0.093 mmol) and 1,1-diiodoethane (52.3 mg, 0.233 mmol) in THF (1.5 mL) was added slowly at 0 °C. The mixture was stirred for 7 h at 0 °C and then stirred for 1 h at room temperature. The reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄, passed through short silica gel and concentrated. The residue was purified by flash column chromatography on silica gel to afford **7c** (19.5 mg, 0.048 mmol, 99% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.21 (7H, m, ArH), 6.76 (2H, d, *J* = 8.7 Hz, ArH), 5.32-5.14 (3H, m, CH=CH, NH), 4.84 (1H, br, CHNH₂Boc), 3.77 (3H, s, OMe), 3.69 (1H, br, CH₂SAr), 1.53 (3H, d, *J* = 6.3 Hz, CHCH₃), 1.40 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 155.0, 140.1, 136.3, 129.2, 128.1, 128.0, 127.4, 127.2, 124.0, 114.2, 79.7, 58.5, 57.5, 55.3, 28.4, 17.7; IR (neat) 2974, 1699, 1492, 1244, 1170 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₃H₂₉NNaO₃S: 422.1760 ([M + Na]⁺), Found: 422.1764 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 20/1, flow rate = 0.5 mL/min, retention time; 37.8 min (major) and 49.0 min.

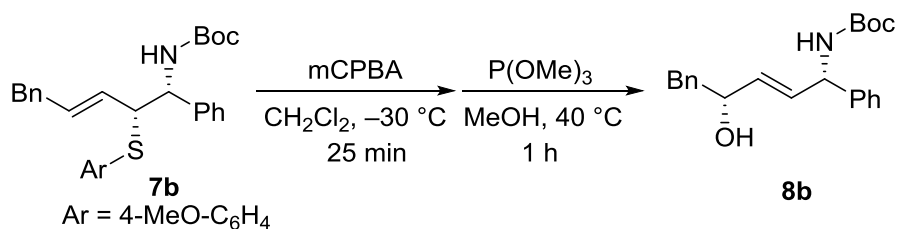
***tert*-Butyl ((1*S*,4*S*,*E*)-4-Hydroxy-1,4-diphenylbut-2-en-1-yl)carbamate (**8a**):**



To a solution of **7a** (19.5 mg, 0.042 mmol) in CH₂Cl₂ (1.0 mL) was added mCPBA (10.4 mg, 0.06 mmol) at -30 °C. The reaction mixture was stirred for 25 min at -30 °C and then quenched by addition of Na₂S₂O₄ aq. The reaction mixture was extracted with ethyl acetate. The combined organic layer was

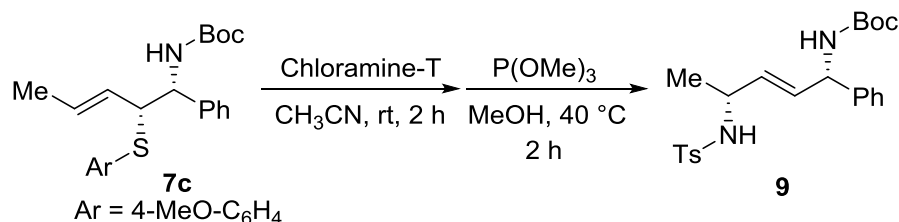
washed with water, dried over Na_2SO_4 and concentrated. The residue was roughly purified by flash column chromatography on silica gel to afford the corresponding sulfoxide. To a solution of the sulfoxide in MeOH (5.0 mL) was added $\text{P}(\text{OMe})_3$ (0.05 mL, 0.42 mmol). After 2 h of stirring at 40 °C, the reaction mixture was quenched with H_2O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel to afford **8a** (9.98 mg, 0.029 mmol, 99% ee). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.25 (10H, m, ArH), 5.96 (1H, dd, $J = 15.4, 5.0$ Hz, CH=CH), 5.86 (1H, dd, $J = 15.4, 5.5$ Hz, CH=CH), 5.32 (1H, br, CHNHBoc), 5.25 (1H, d, $J = 5.4$ Hz, CHOH), 4.87 (1H, br, NH), 2.02 (1H, br, OH), 1.41 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 154.9, 142.6, 141.1, 133.3, 131.0, 128.7, 128.6, 127.8, 127.5, 126.9, 126.4, 79.7, 74.3, 55.6, 28.3; IR (neat) 3337, 2977, 1690, 1493, 1167, 1016, 699 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{21}\text{H}_{25}\text{NNaO}_3$: 362.1727 ($[\text{M} + \text{Na}]^+$), Found: 362.1743 ($[\text{M} + \text{Na}]^+$); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 64.7 min (major) and 127.9 min.

***tert*-Butyl ((1*S*,4*R*,*E*)-4-Hydroxy-1,5-diphenylpent-2-en-1-yl)carbamate (**8b**):**



^1H NMR (400 MHz, CDCl_3) δ 7.33-7.14 (10H, m, ArH), 5.77 (1H, dd, $J = 15.5, 5.6$ Hz, CH=CH), 5.68 (1H, dd, $J = 16.1, 5.4$ Hz, CH=CH), 5.26 (1H, br, CHNHBoc), 4.84 (1H, br, NH), 4.38 (1H, app q, CHOH), 2.88-2.77 (2H, m, PhCH_2), 1.85 (1H, br, OH), 1.43 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 141.1, 137.5, 133.5, 131.0, 129.6, 128.6, 128.5, 127.4, 126.9, 126.5, 79.7, 72.8, 55.6, 43.9, 28.4; IR (neat) 3334, 2976, 1690, 1494, 1166, 1029, 699 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{22}\text{H}_{27}\text{NNaO}_3$: 376.1883 ($[\text{M} + \text{Na}]^+$), Found: 376.1878 ($[\text{M} + \text{Na}]^+$); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 9/1, flow rate = 0.5 mL/min, retention time; 40.0 min (major) and 90.0 min.

***tert*-Butyl ((1*S*,4*R*,*E*)-4-((4-Methylphenyl)sulfonamido)-1-phenylpent-2-en-1-yl)carbamate (**9**):**



To a solution of **7c** (18.4 mg, 0.046 mmol) in CH₃CN (1.0 mL) was added Chloramine-T trihydrate (16 mg, 0.055 mmol). The reaction mixture was stirred for 2 h at room temperature and then diluted by addition of ethyl acetate. After the filtration, the solvent was concentrated under reduced pressure. To a solution of the residue in MeOH (5.2 mL) was added P(OMe)₃ (0.055 mL, 0.46 mmol). After 2 h of stirring at 40 °C, the reaction mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel to **9** (19.0 mg, 0.044 mmol, 99% ee). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (2H, d, *J* = 8.2 Hz, ArH), 7.33-7.25 (5H, m, ArH), 7.14 (2H, d, *J* = 8.2 Hz, ArH), 5.60 (1H, dd, *J* = 15.3, 5.4 Hz, CH=CH), 5.39 (1H, ddd, *J* = 15.5, 6.3, 1.5 Hz, CH=CH), 5.13 (1H, br, CHNHBoc), 4.66 (1H, br, NH), 4.54 (1H, br, NH), 3.94 (1H, m, CHNHTs), 2.42 (3H, s, C₆H₄CH₃), 1.42 (9H, s, C(CH₃)₃), 1.17 (3H, d, *J* = 6.8 Hz, CHCH₃); ¹³C NMR (125 MHz, CDCl₃) δ 154.9, 143.3, 140.9, 138.0, 132.2, 131.1, 129.6, 128.6, 127.5, 127.2, 126.8, 79.8, 55.3, 50.9, 28.4, 21.9, 21.5; IR (neat) 3271, 2977, 1689, 1495, 1161 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₃H₃₀N₂NaO₄S: 453.1818 ([M + Na]⁺), Found: 453.1800 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak ID, hexane/*i*-PrOH = 9/1, flow rate = 0.5 mL/min, retention time; 117.0 min (major) and 131.5 min.

Explanation for the Stereoselectivity in the 2,3-Sigmatropic Rearrangement.

Since *Z*-isomers were not observed in the 2,3-sigmatropic rearrangement leading to **8** and **9**, the present rearrangement of the allylic sulfoxides or the allylic sulfimide via a five-membered envelope-like transition state would proceed through the sterically less congested **TS1** compared to **TS2** as shown in Fig. 1. The complete chirality transfer can also be rationalized by **TS1**.

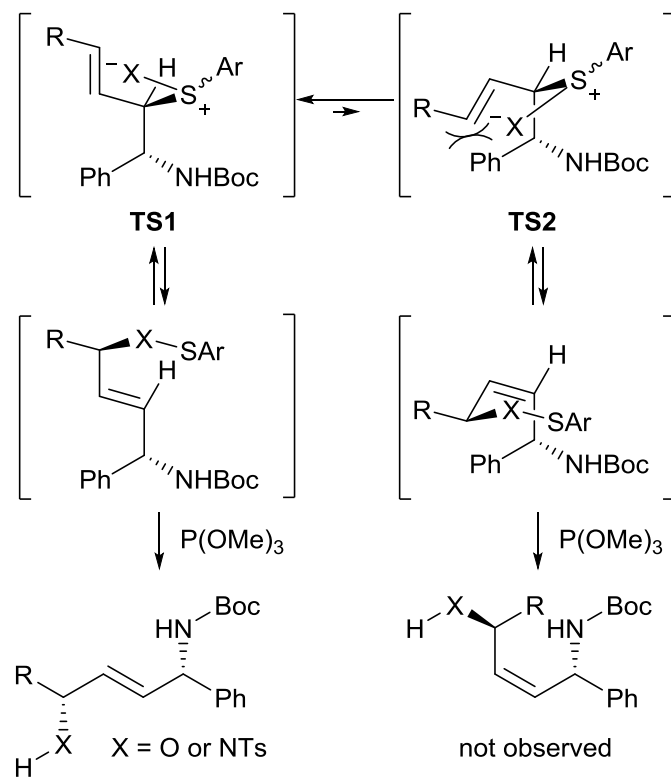


Fig. 1 Transition state models for the 2,3-sigmatropic rearrangement.

***anti*-Selective Asymmetric Mannich Reaction between (4-Methoxyphenylthio)acetaldehyde (**1b**) and *N*-Protected Imine (**2a**) Catalyzed by (*S*)-**10** (Scheme 4):**

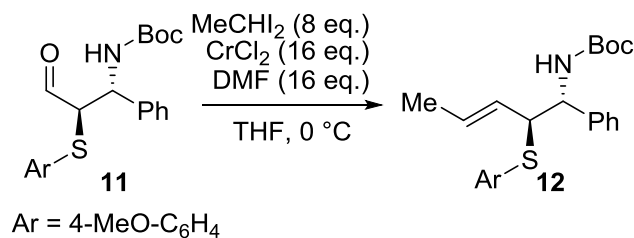
To a solution of (*S*)-**10** (5.4 mg, 0.0125 mmol) and (4-methoxyphenylthio)acetaldehyde (**1b**) (68.3 mg, 0.375 mmol) in THF (0.25 mL) was added *N*-Boc-protected imine **2a** (25.7 mg, 0.125 mmol) at $-30\text{ }^{\circ}\text{C}$. The mixture was stirred for 36 h. The reaction mixture was quenched with H_2O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na_2SO_4 and concentrated. The residue was roughly purified by flash column chromatography on cooled silica gel to afford the corresponding product **11**. The enantiomeric excess of the product was determined after reduction by the method described above.

***tert*-Butyl ((1*S*,2*S*)-3-Hydroxy-2-((4-methoxyphenyl)thio)-1-phenylpropyl)carbamate:**

^1H NMR (500 MHz, CDCl_3) δ 7.34-7.21 (7H, m, ArH), 6.80 (2H, d, $J = 7.7$ Hz, ArH), 5.72 (1H, br, NH), 5.05 (1H, br, CHNHBoc), 3.79 (3H, s, OMe), 3.76-3.55 (2H, m, HOCH₂), 3.32-3.23 (1H, m, CHSAr), 2.73 (1H, br, OH), 1.43 (9H, s, C(CH₃)₃); ^{13}C NMR (125 MHz, CDCl_3) δ 159.7, 155.6, 139.9, 135.6,

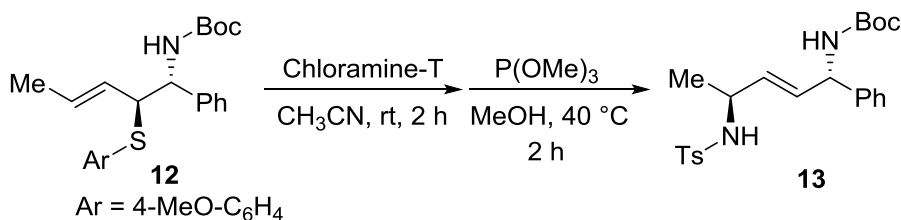
128.6, 127.7, 126.9, 124.3, 114.7, 79.9, 61.5, 58.6, 56.2, 55.3, 28.3; IR (neat) 3398, 2928, 1688, 1493, 1245, 1170 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{21}\text{H}_{27}\text{NNaO}_4\text{S}$: 412.1553 ($[\text{M} + \text{Na}]^+$), Found: 412.1558 ($[\text{M} + \text{Na}]^+$); HPLC analysis: Daicel Chiralpak AD-H, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 49.4 min (major) and 64.8 min.

***tert*-Butyl ((1*R*,2*S*,*E*)-2-((4-Methoxyphenyl)thio)-1-phenylpent-3-en-1-yl)carbamate (12):**



The title compound was prepared by the similar method described above. ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.16 (7H, m, ArH), 6.82 (2H, d, $J = 8.8$ Hz, ArH), 5.35-5.21 (3H, m, CH=CH, CHNH₂Boc), 4.81 (1H, br, NH), 3.79 (3H, s, OMe), 3.73 (1H, br, CHSAr), 1.59 (3H, d, $J = 5.1$ Hz, CHCH₃), 1.42 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 155.0, 140.0, 136.2, 129.5, 128.2, 127.3, 127.0, 124.4, 114.4, 79.6, 59.1, 57.3, 55.3, 28.3, 17.8; IR (neat) 2975, 1700, 1493, 1245, 1170 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{23}\text{H}_{29}\text{NNaO}_3\text{S}$: 422.1760 ($[\text{M} + \text{Na}]^+$), Found: 422.1745 ($[\text{M} + \text{Na}]^+$); HPLC analysis: Daicel Chiralpak IE, hexane/*i*-PrOH = 10/1, flow rate = 0.5 mL/min, retention time; 21.3 min and 23.0 min (major).

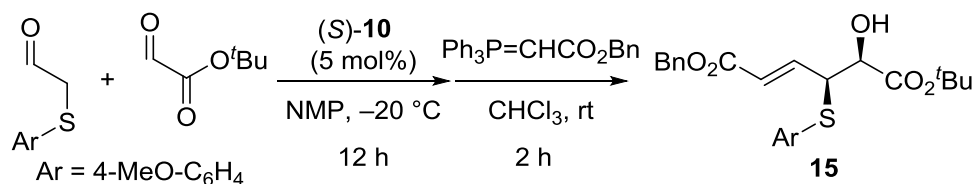
***tert*-Butyl ((1*S*,4*S*,*E*)-4-((4-Methylphenyl)sulfonamido)-1-phenylpent-2-en-1-yl)carbamate (13):**



The title compound was prepared by the similar method described above. ¹H NMR (500 MHz, CDCl₃) δ 7.71 (2H, d, $J = 8.2$ Hz, ArH), 7.34-7.25 (5H, m, ArH), 7.12 (2H, d, $J = 8.2$ Hz, ArH), 5.60 (1H, dd, $J = 15.4, 5.2$ Hz, CH=CH), 5.36 (1H, ddd, $J = 15.5, 6.1, 1.6$ Hz, CH=CH), 5.12 (1H, br, CHNH₂Boc), 4.67 (1H, br, NH), 4.43 (1H, br, NH), 3.97 (1H, m, CHNHTs), 2.42 (3H, s, C₆H₄CH₃), 1.42 (9H, s, C(CH₃)₃),

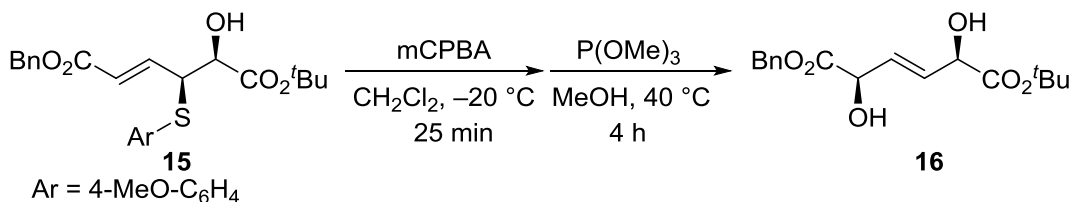
1.17 (3H, d, $J = 6.8$ Hz, CHCH_3); ^{13}C NMR (125 MHz, CDCl_3) δ 154.8, 143.4, 140.8, 138.1, 132.5, 131.1, 129.6, 128.7, 127.6, 127.2, 126.8, 79.8, 55.4, 50.8, 28.4, 22.0, 21.6; IR (neat) 2976, 1689, 1495, 1161 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{NaO}_4\text{S}$: 453.1818 ($[\text{M} + \text{Na}]^+$), Found: 453.1806 ($[\text{M} + \text{Na}]^+$); HPLC analysis: Daicel Chiralpak IE, hexane/*i*-PrOH = 7/1, flow rate = 0.5 mL/min, retention time; 101.6 min and 109.4 min (major).

1-Benzyl 6-(*tert*-Butyl) (4*S*,5*S*,*E*)-5-Hydroxy-4-((4-methoxyphenyl)thio)hex-2-enedioate (**15**)



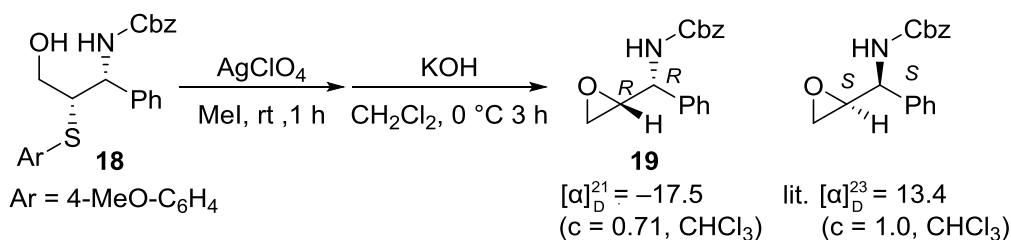
To a stirred solution of (*S*)-**10** (2.7 mg, 0.00625 mmol) in NMP (250 μL) were added *tert*-butyl glyoxylate (**14**) (16.3 mg, 0.125 mmol) and (4-methoxyphenylthio)acetaldehyde (**1b**) (68.3 mg, 0.375 mmol) in this sequence at -20 $^{\circ}\text{C}$. The mixture was stirred for 12 h, and then quenched with water. After extraction with ethyl acetate, the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was dissolved in CHCl_3 (1.25 mL). To a stirred solution of the reaction mixture was added benzyl(triphenylphosphoranylidene)acetate (180 mg, 0.438 mmol). The reaction mixture was stirred for 2 h, and then concentrated. The residue was purified by flash column chromatography on silica gel to afford the corresponding product **15** (50.8 mg, 0.109 mmol, 91% ee). ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.30 (7H, m, ArH), 7.05 (1H, dd, $J = 15.5, 9.4$ Hz, $\text{BnO}_2\text{CCH}=\text{CH}$), 6.81 (2H, d, $J = 8.7$ Hz, ArH), 5.63 (1H, d, $J = 15.5$ Hz, $\text{CH}=\text{CHCH}$), 5.16 (2H, s, PhCH_2), 4.29 (1H, dd, $J = 5.3, 3.6$ Hz, CHOH), 3.81-3.76 (4H, m, OMe, CHSAr), 3.22 (1H, d, $J = 5.3$ Hz, OH), 1.52 (9H, s, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3) δ 171.0, 165.7, 160.1, 144.2, 136.3, 135.9, 128.5, 128.2, 128.1, 123.0, 121.8, 114.7, 83.9, 72.2, 66.2, 56.3, 55.3, 28.1; IR (neat) 3486, 2977, 1719, 1494, 1247, 1155, 830 cm^{-1} ; HRMS (ESI-TOF) Calcd. for $\text{C}_{24}\text{H}_{28}\text{NaO}_6\text{S}$: 467.1499 ($[\text{M} + \text{Na}]^+$), Found: 467.1478 ($[\text{M} + \text{Na}]^+$); HPLC analysis: Daicel Chiralpak IC3, hexane/*i*-PrOH = 4/1, flow rate = 0.5 mL/min, retention time; 30.6 min and 53.9 min (major).

1-Benzyl 6-(*tert*-Butyl) (2*R*,5*R*,*E*)-2,5-Dihydroxyhex-3-enedioate (**16**)



The title compound was synthesized by the method described as above. ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.33 (5H, m, ArH), 6.04-6.03 (2H, m, CH=CH), 5.27 (1H, d, *J* = 12.2 Hz, PhCHH), 5.17 (1H, d, *J* = 12.2 Hz, PhCHH), 4.76 (1H, m, CHOH), 4.57 (1H, m, CHOH), 3.07 (2H, br, OH), 1.46 (9H, s, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃) δ 172.9, 172.1, 134.9, 129.5, 128.7, 128.6, 128.3, 128.0, 83.3, 70.7, 70.6, 67.8, 28.0; IR (neat) 3465, 2979, 2928, 1728, 1255, 1157, 1125, 968, 698 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₁₇H₂₂NaO₆: 345.1309 ([M + Na]⁺), Found: 345.1302 ([M + Na]⁺); HPLC analysis: Daicel Chiralpak IC3, hexane/*i*-PrOH = 3/1, flow rate = 0.5 mL/min, retention time; 26.5 min and 67.5 min (major).

Determination of Relative and Absolute Configuration of the Mannich Product

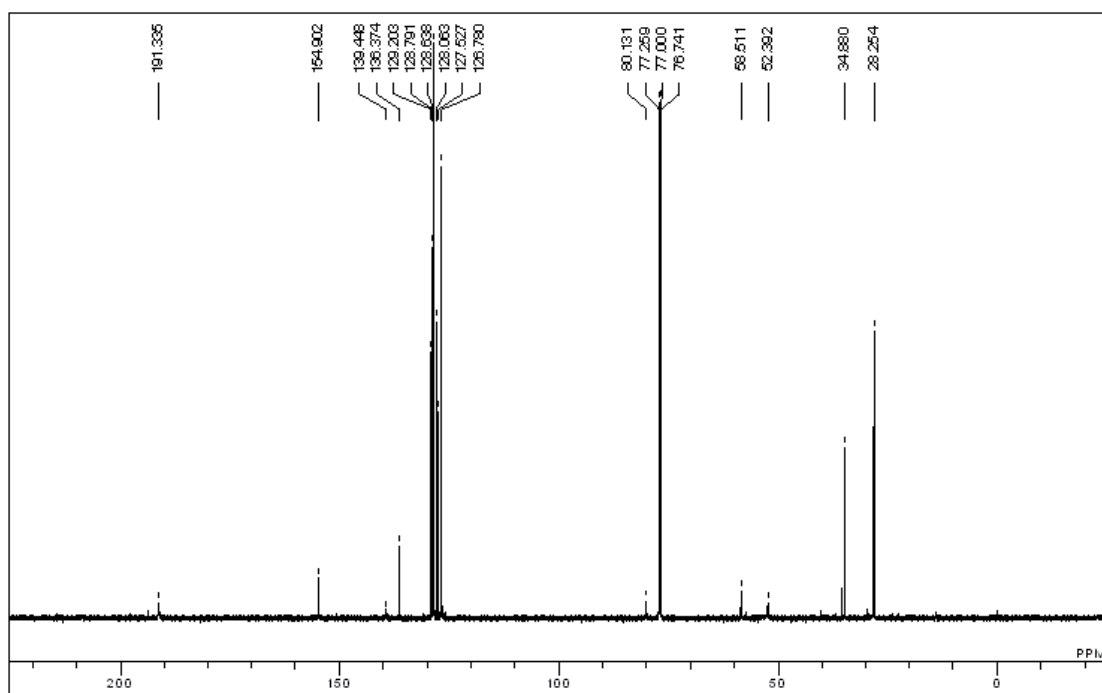
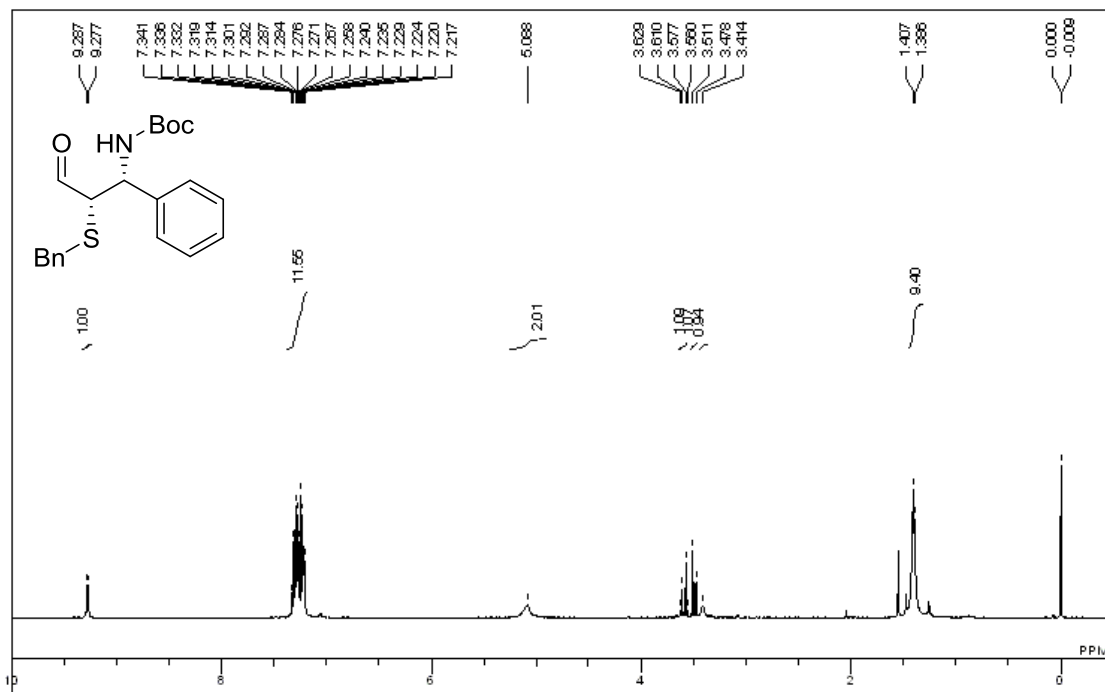


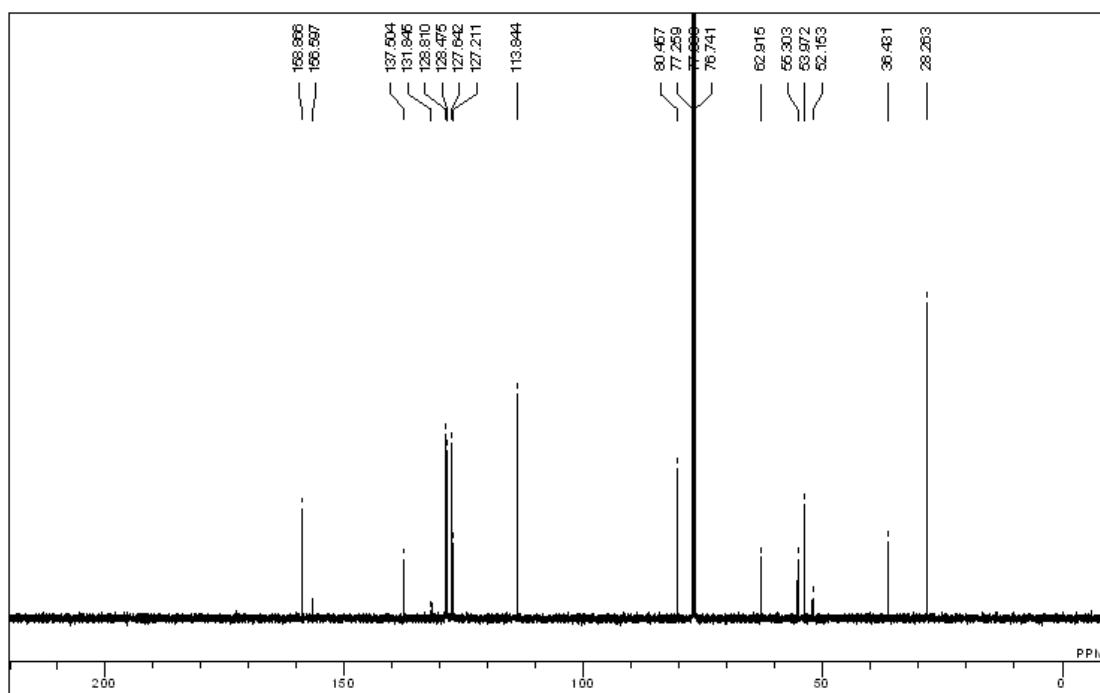
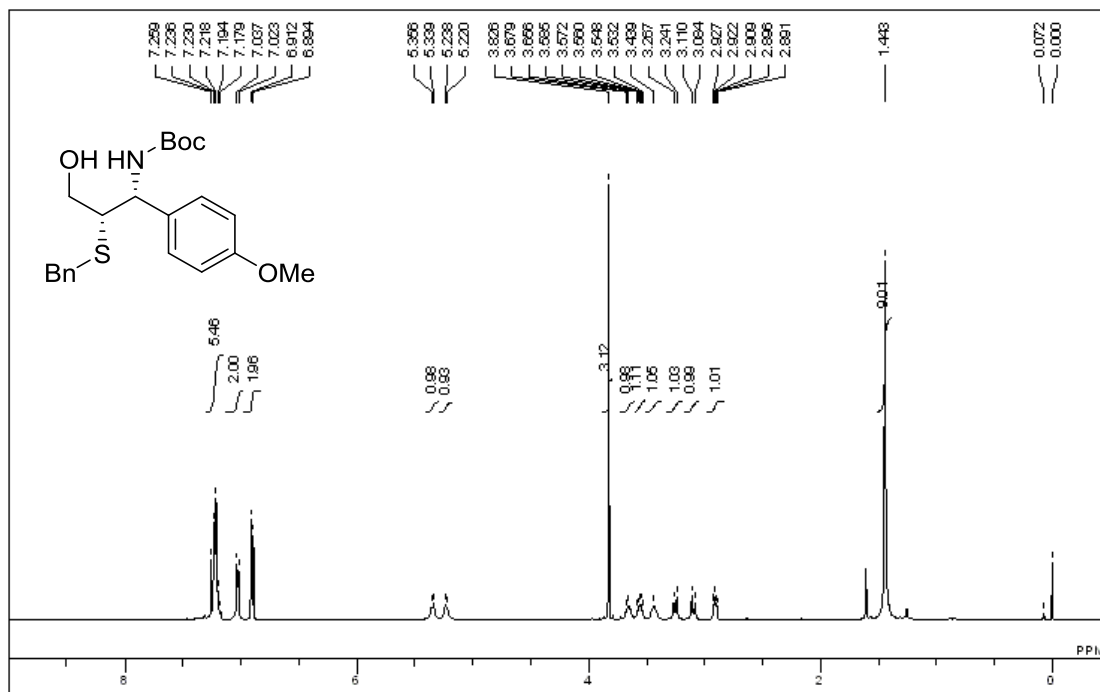
To a solution of **18** (40.2 mg, 0.0944 mmol) in MeI (1.0 mL) was added AgClO₄ (19.6 mg, 0.0944 mmol). The reaction mixture was stirred for 2 h and filtered through celite. After removal of the solvent under reduced pressure, the residue was dissolved in CH₂Cl₂ (5.0 mL). To the reaction mixture was added KOH (5.3 mg, 0.0944 mmol) at 0 °C and the reaction mixture was stirred for 3 h. The mixture was quenched with H₂O and extracted with ethyl acetate. The combined organic layer was washed with water, dried over Na₂SO₄ and concentrated. The residue was purified by flash column chromatography on silica gel to give benzyl ((*R*)-(*R*)-oxiran-2-yl)(phenyl)methylcarbamate (**19**) (7.1 mg, 0.025 mmol, 99% ee). $[\alpha]_D^{21} = -17.5$ (c 0.71, CHCl₃). The relative and absolute configuration was determined by comparison with ¹H NMR spectra and optical rotation of the literature data (lit $[\alpha]_D^{23} = 13.4$ (c 1.0, CHCl₃)).⁹ HPLC

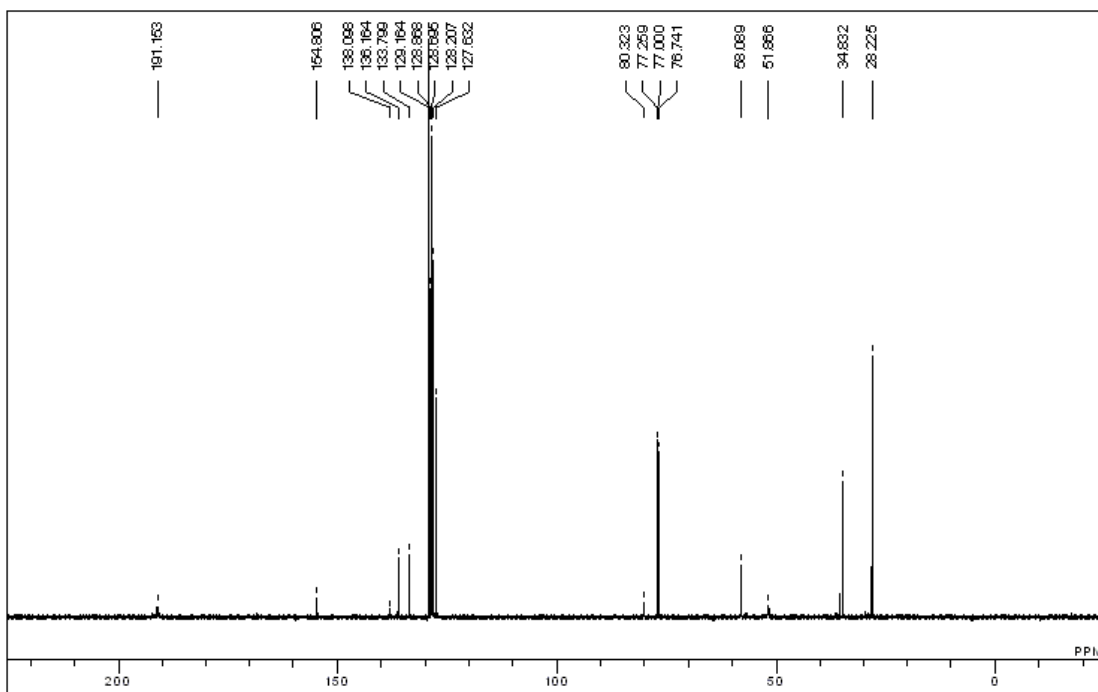
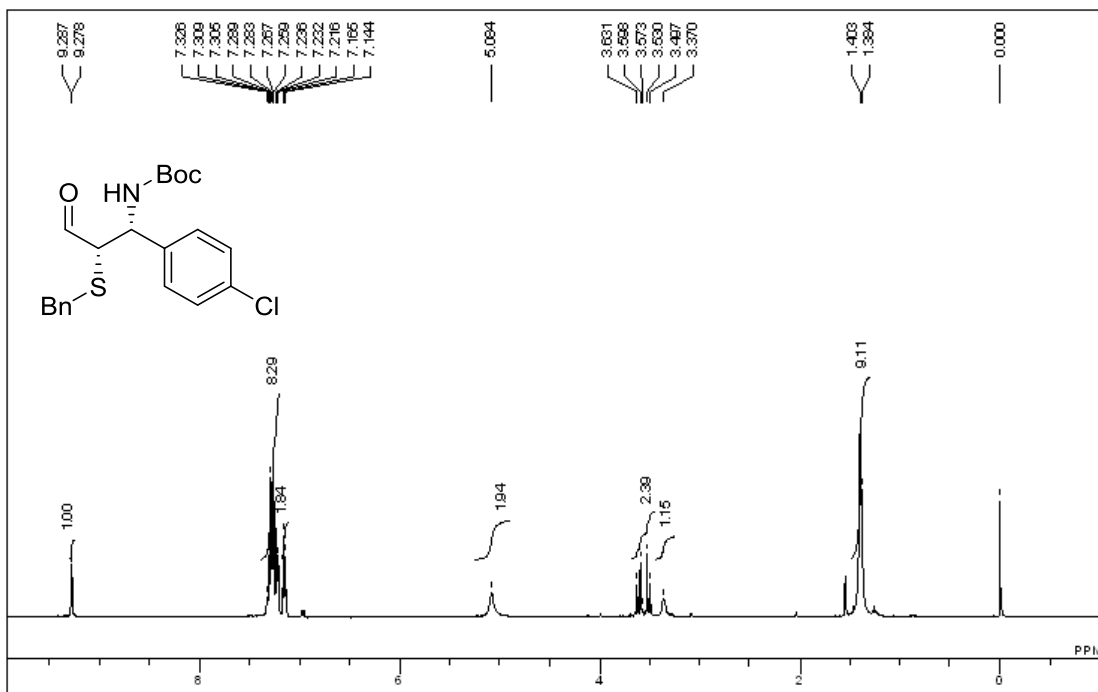
analysis: Daicel Chiralpak IA3, hexane/ethanol = 92/8, flow rate = 0.5 mL/min, retention time; 31.2 min and 41.7 min (major).

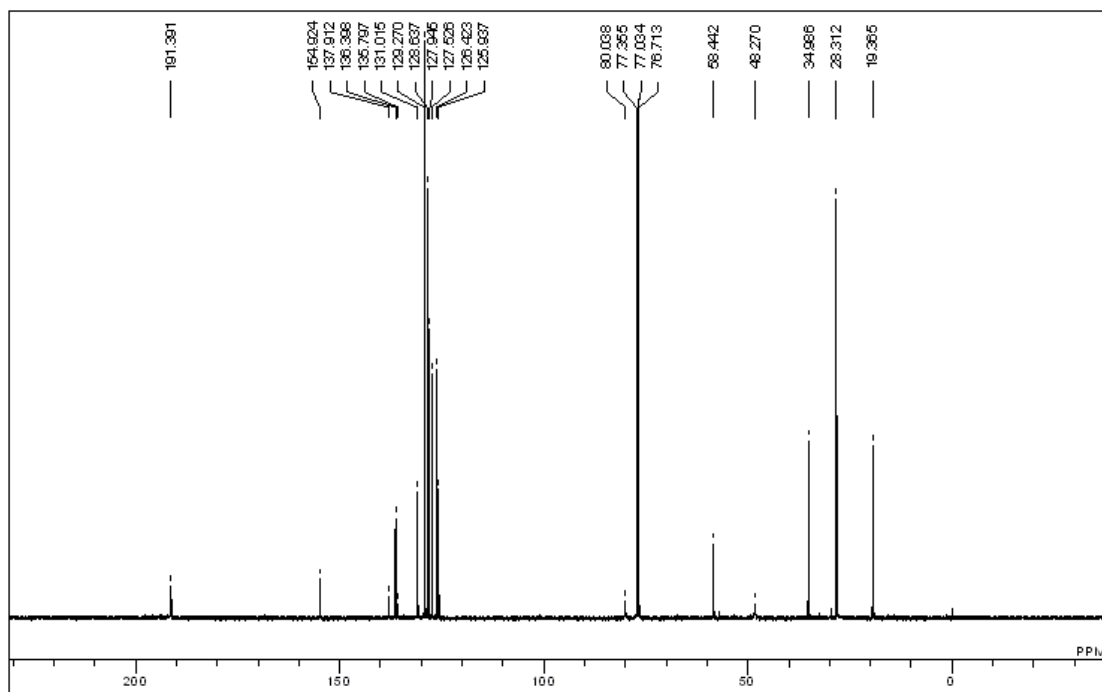
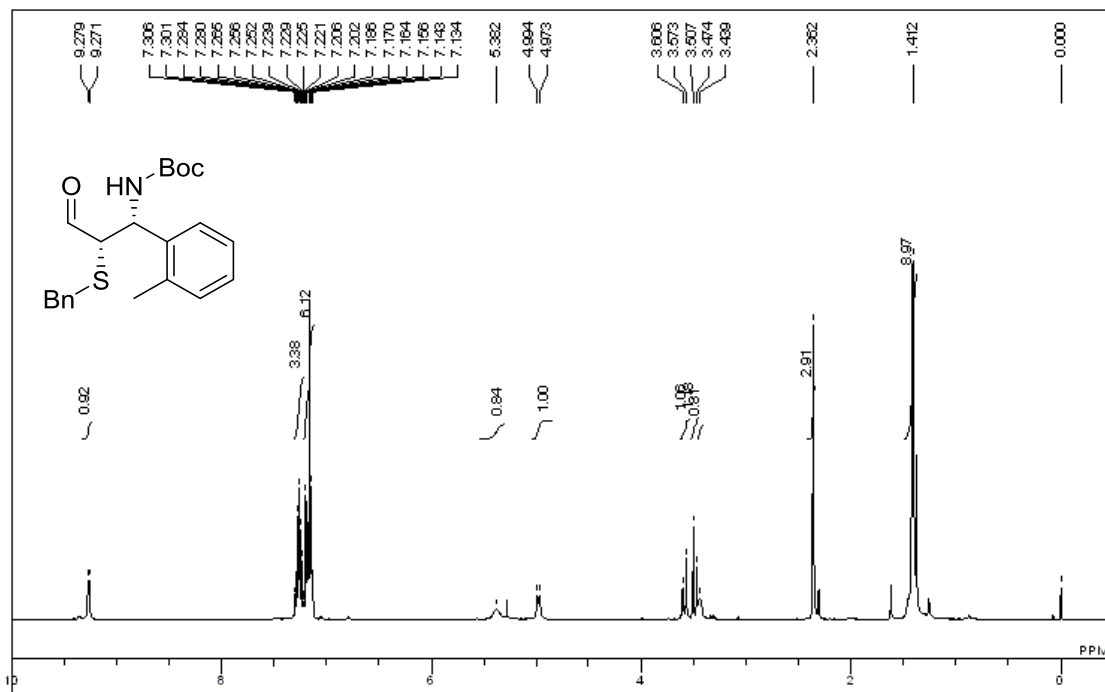
References

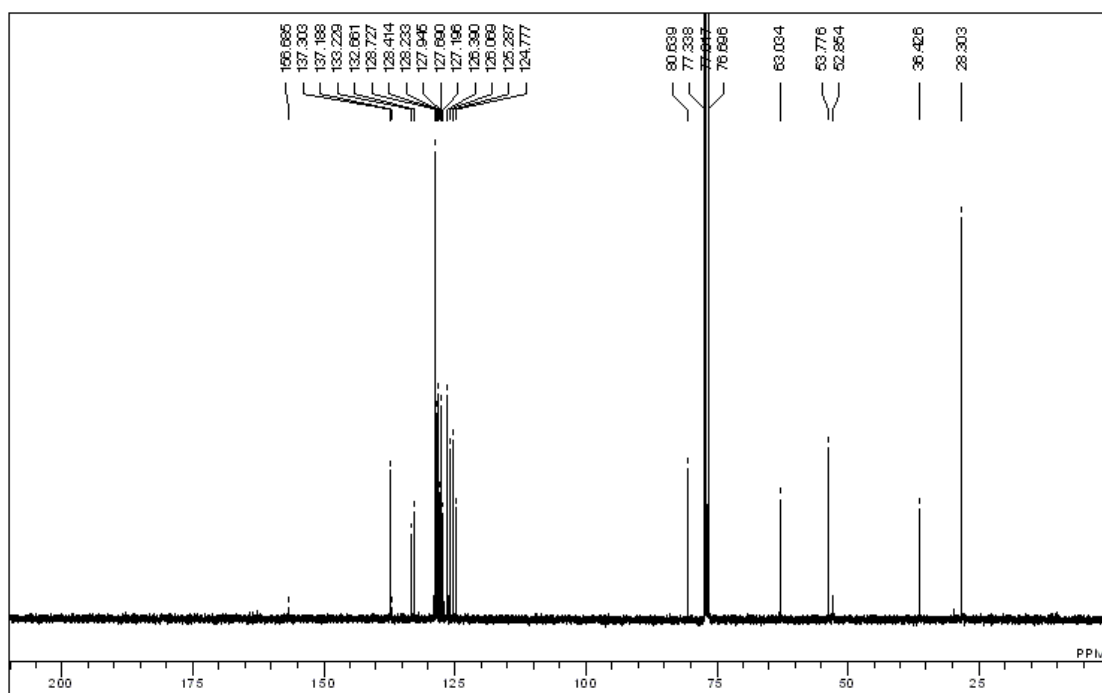
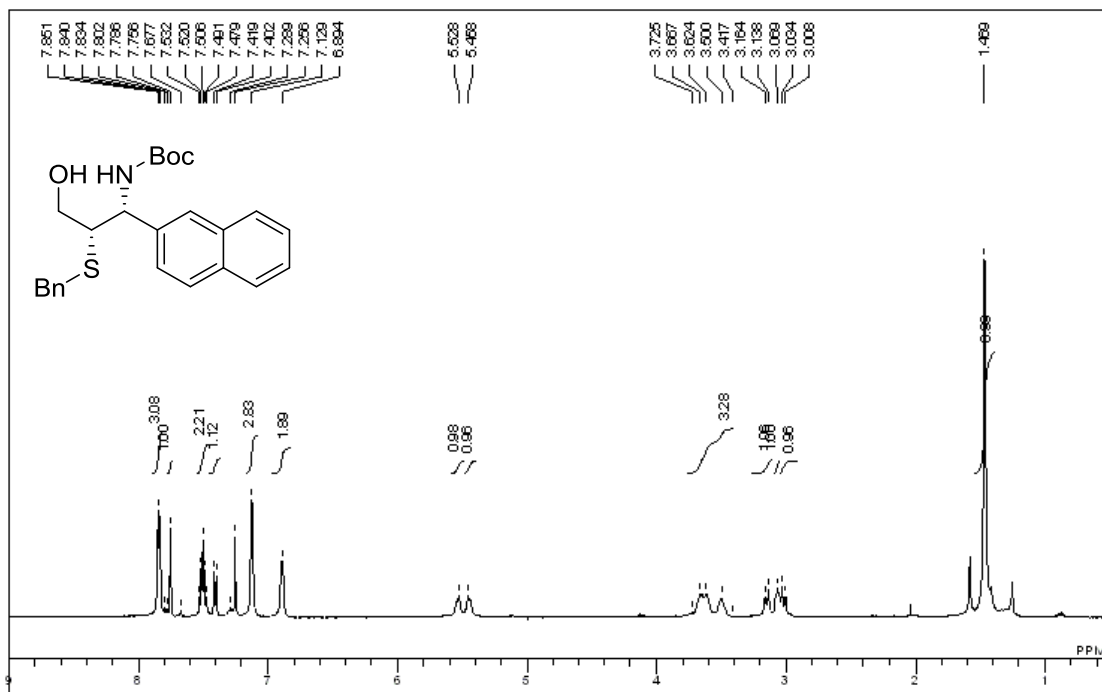
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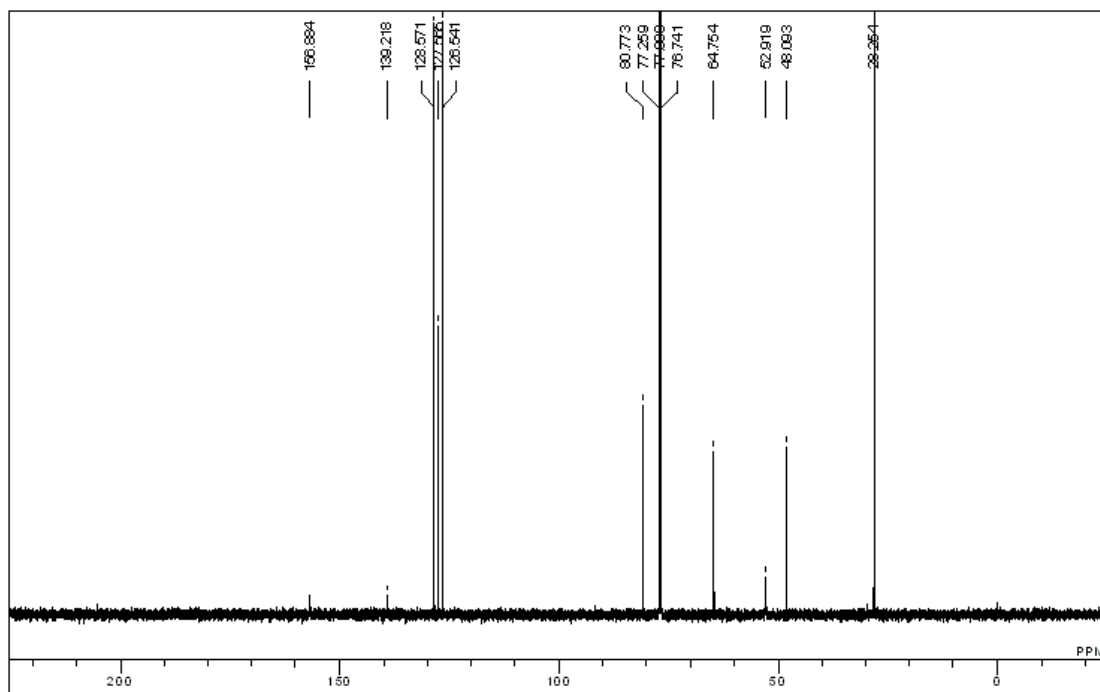
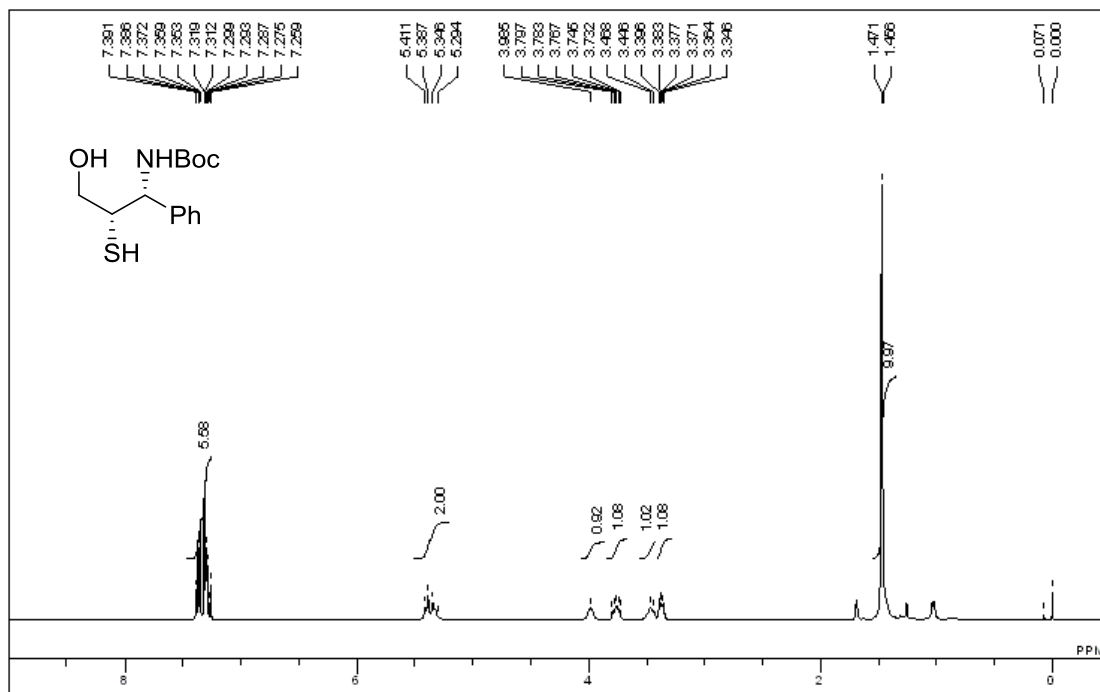


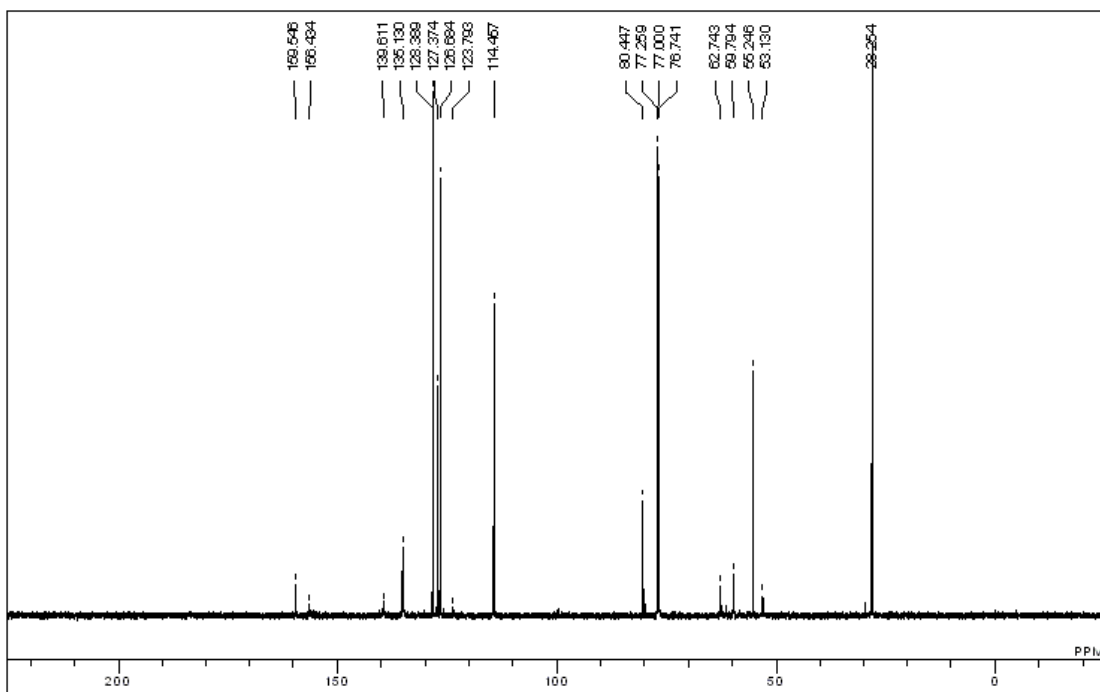
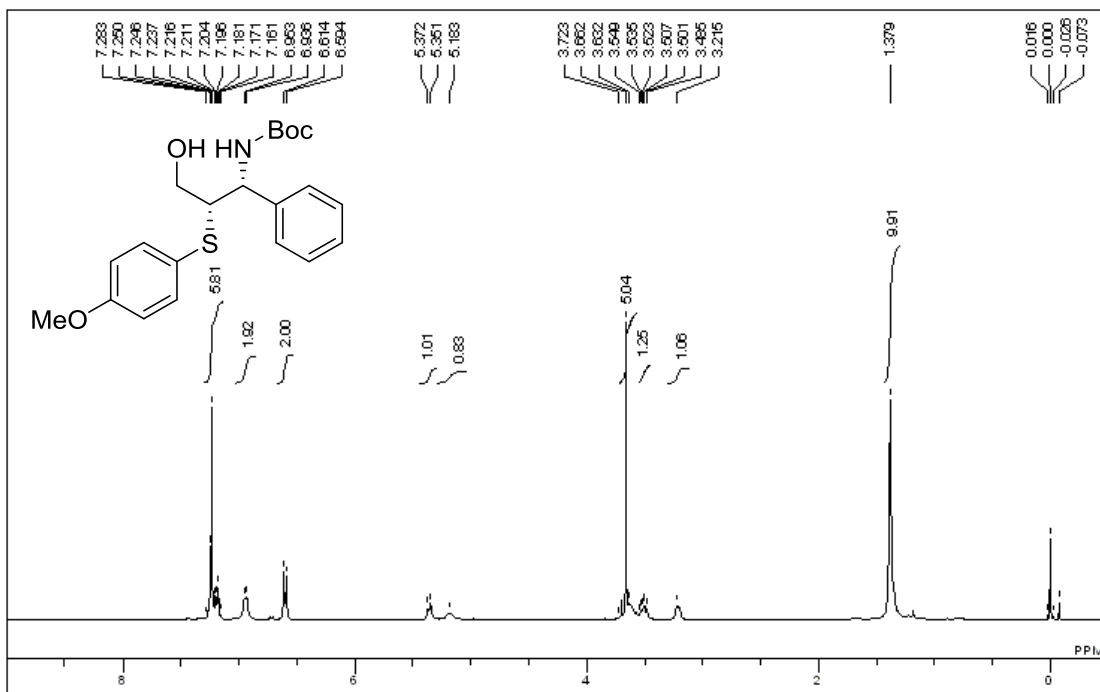


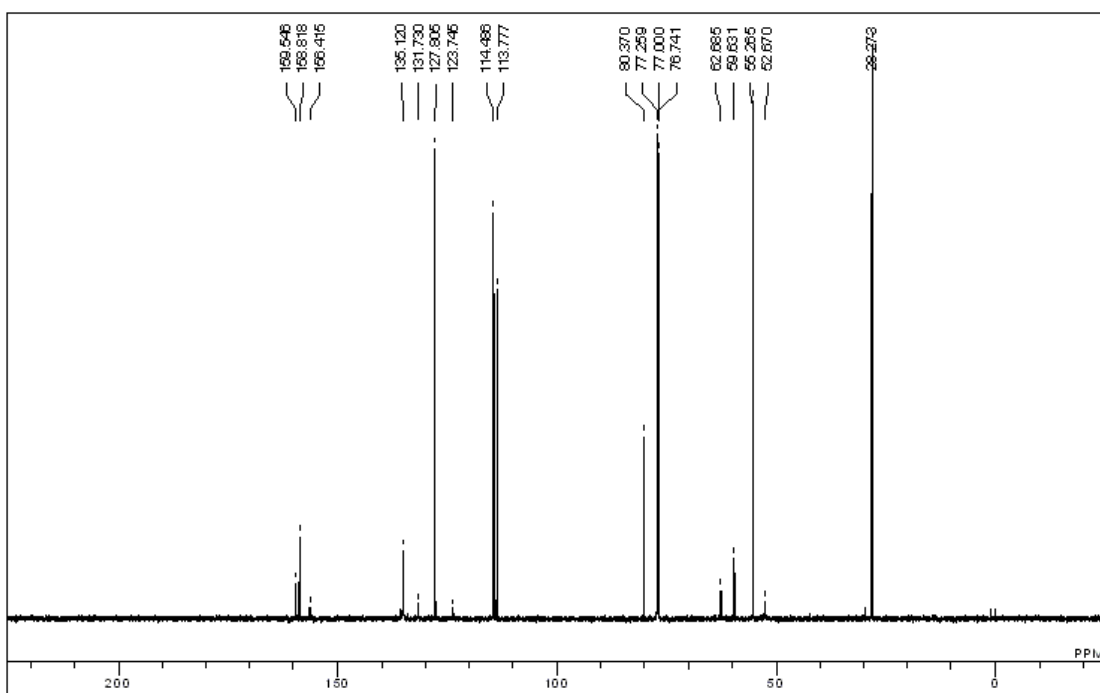
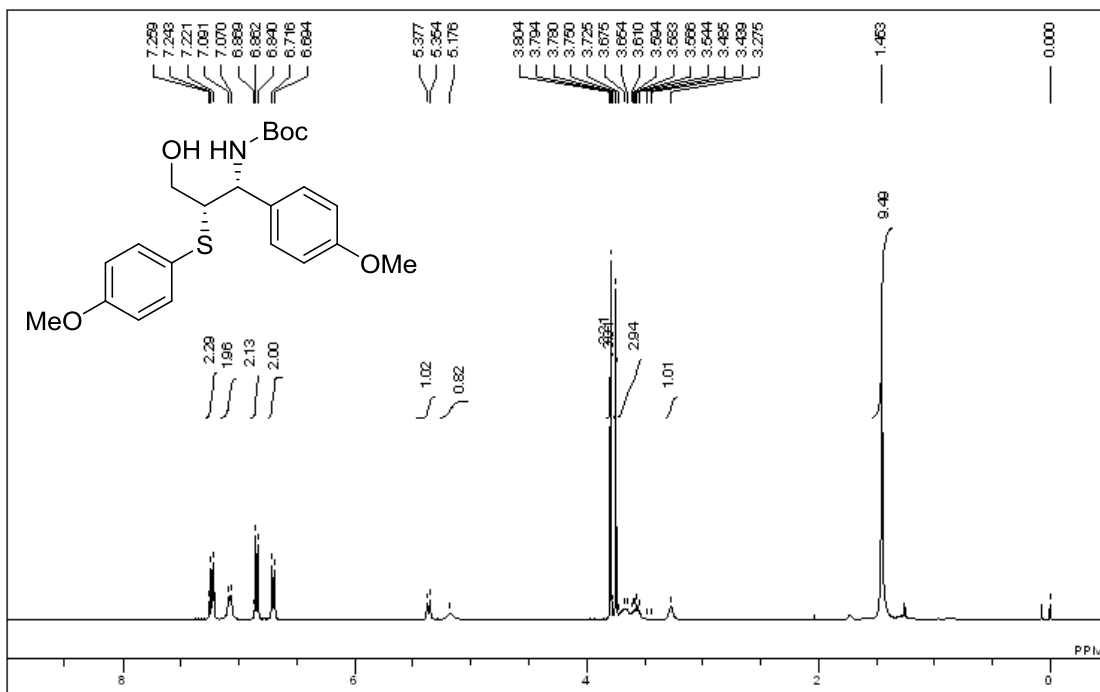


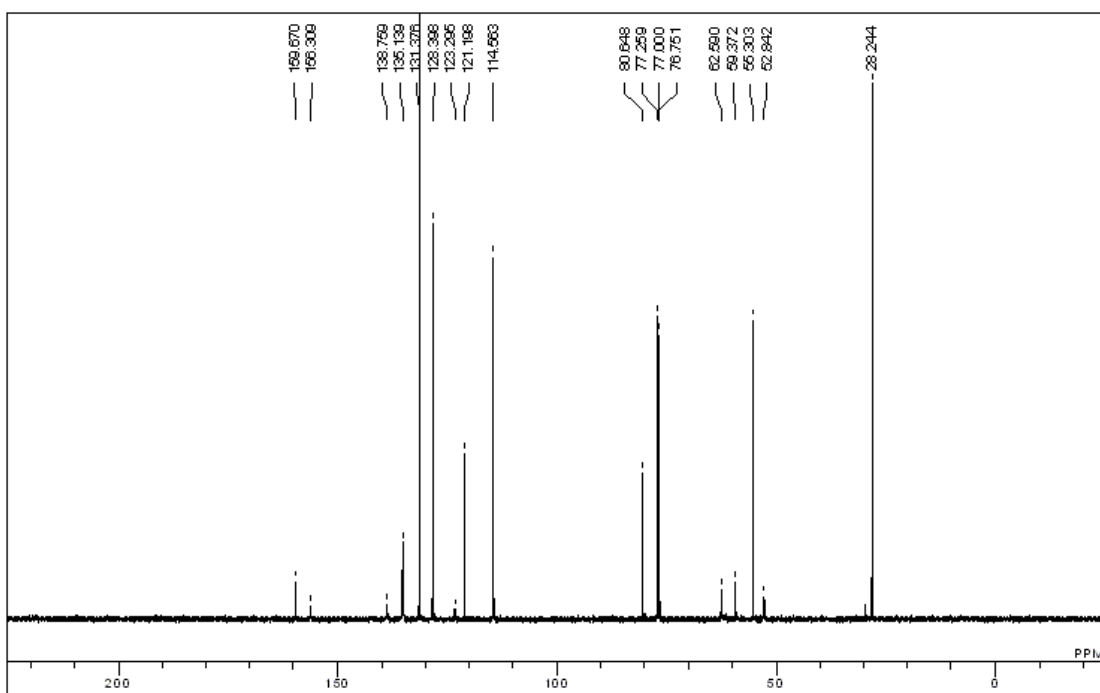
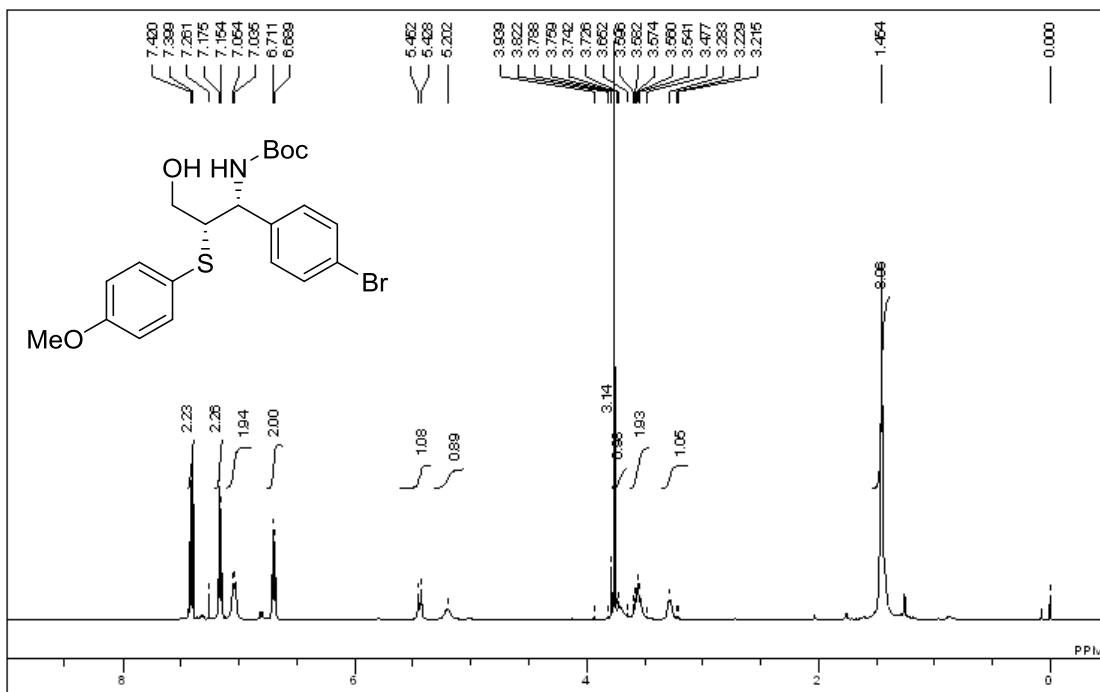


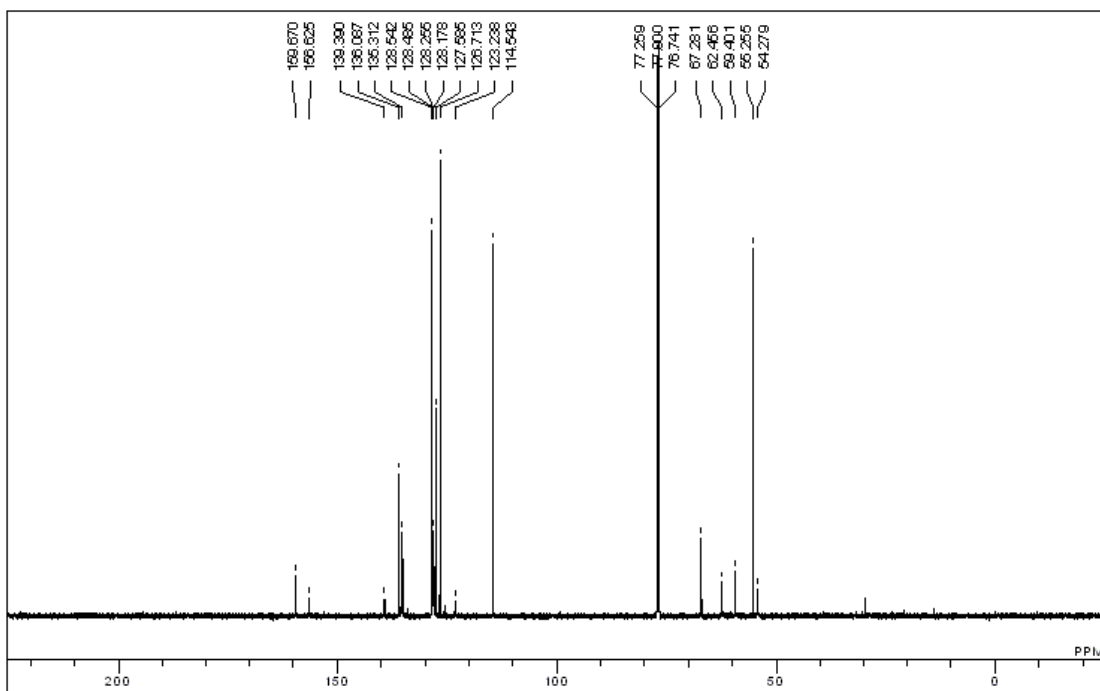
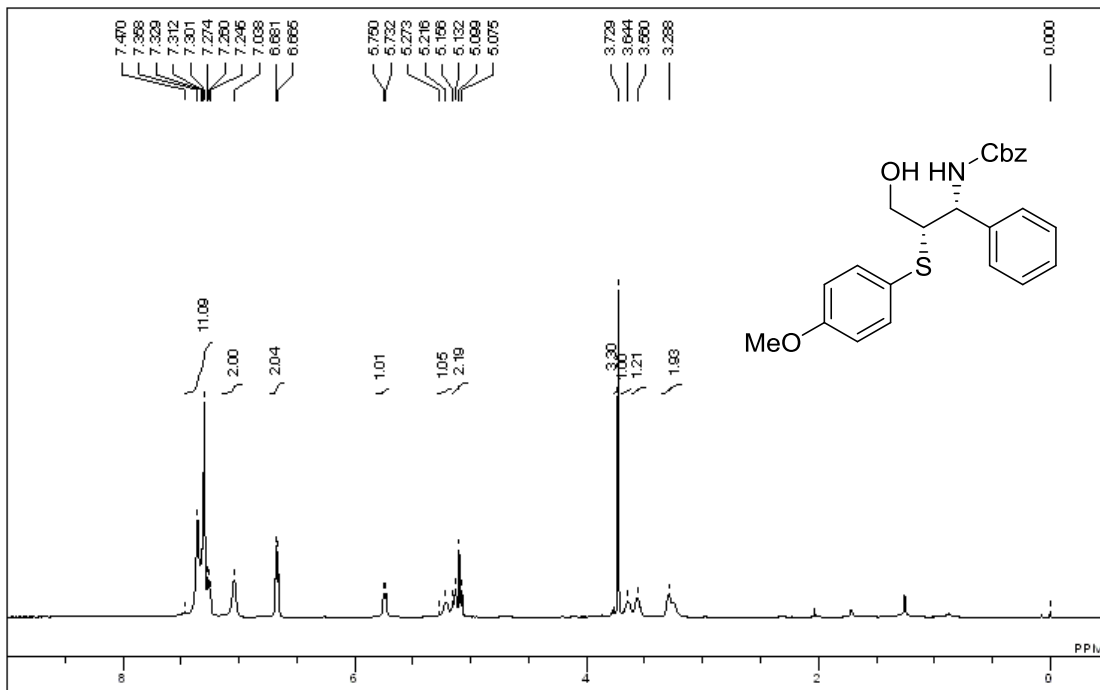


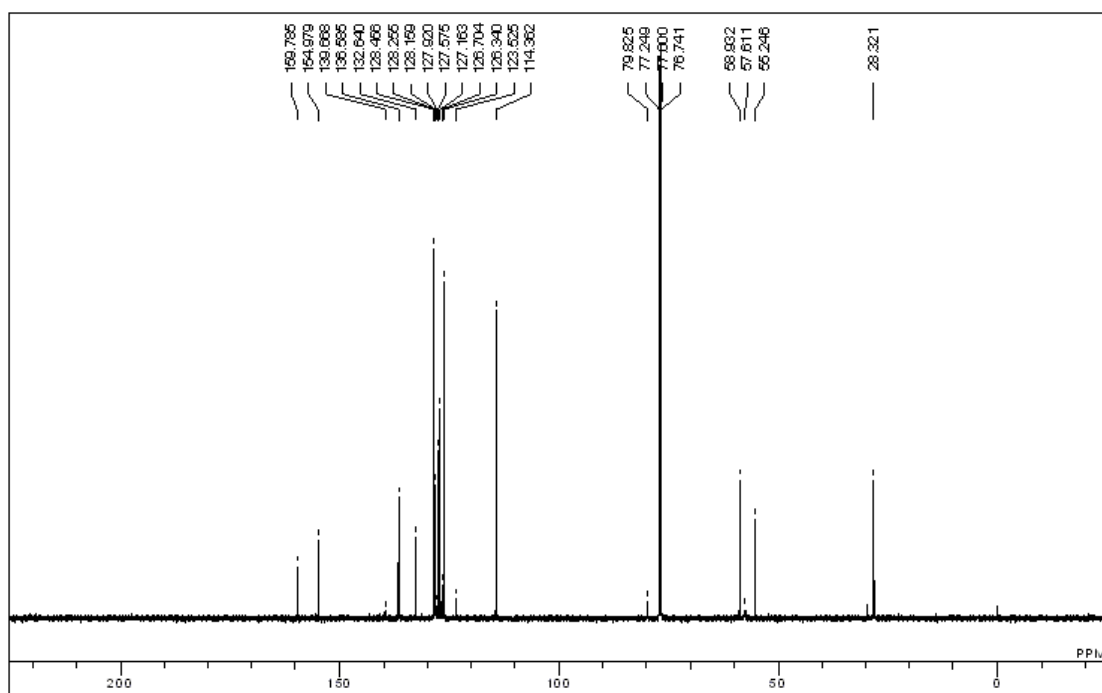
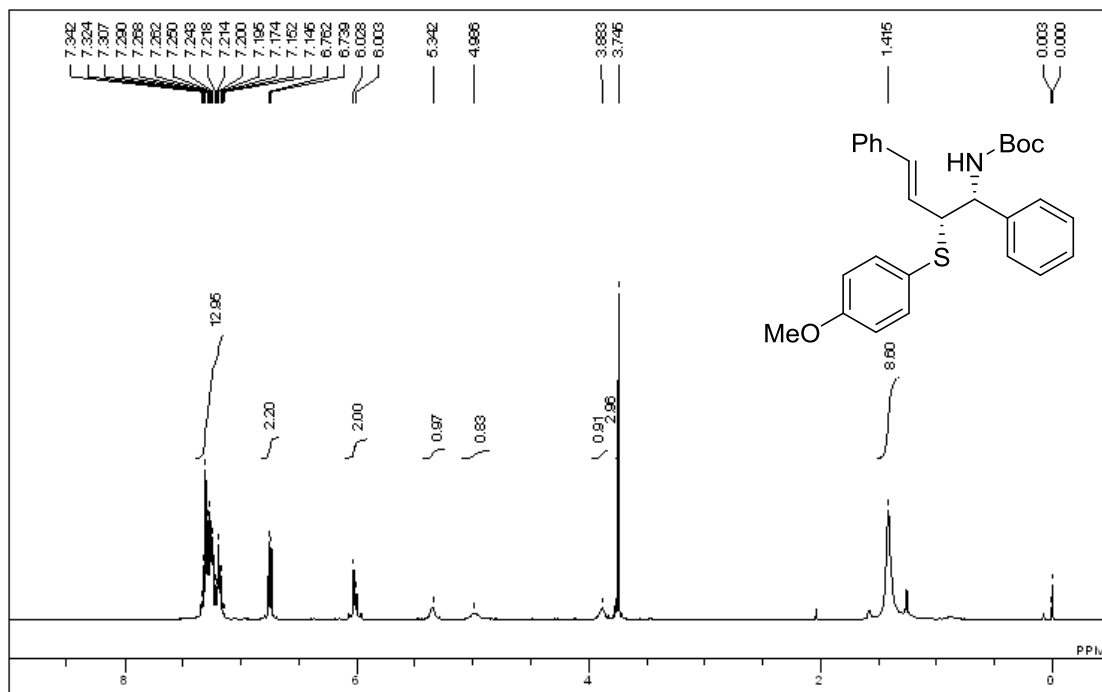


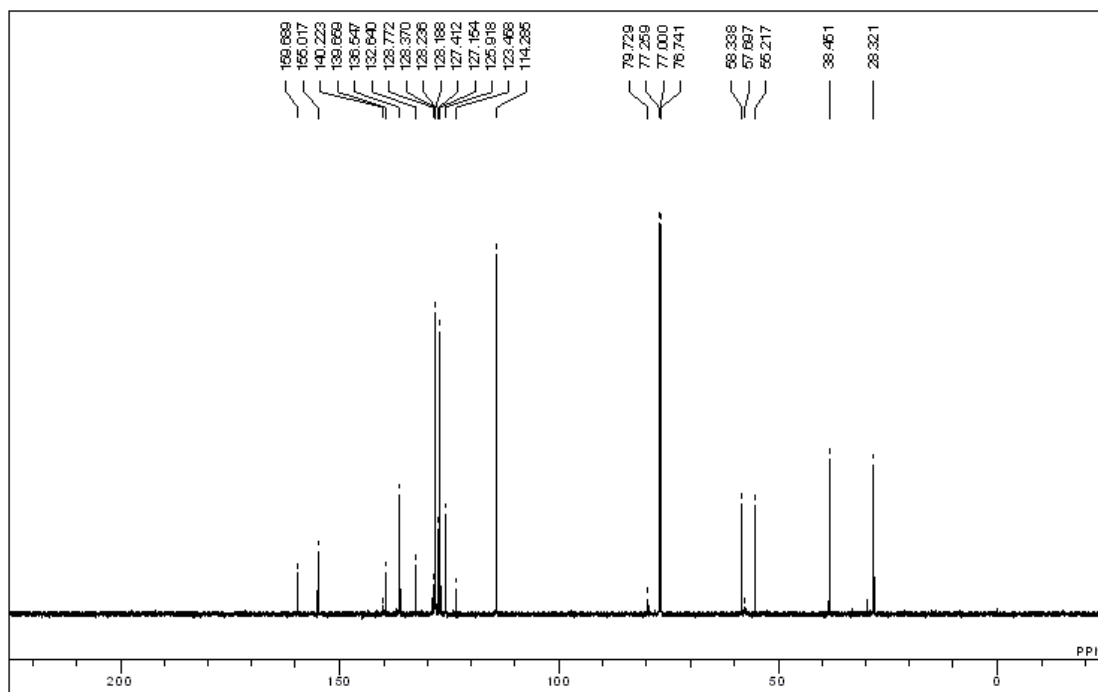
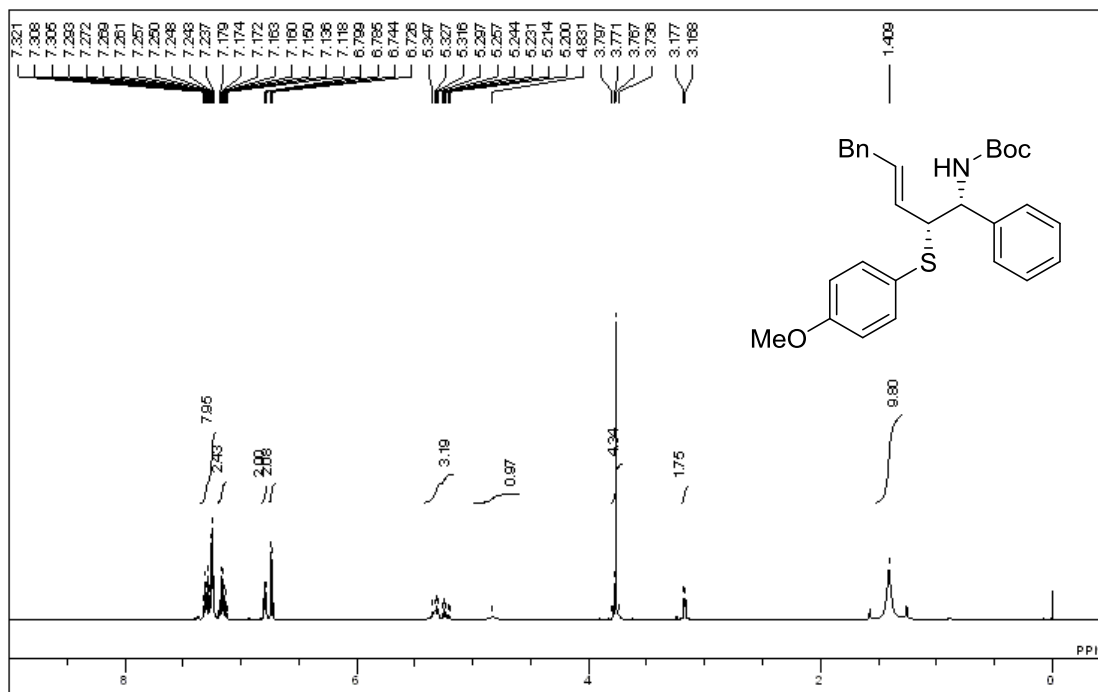


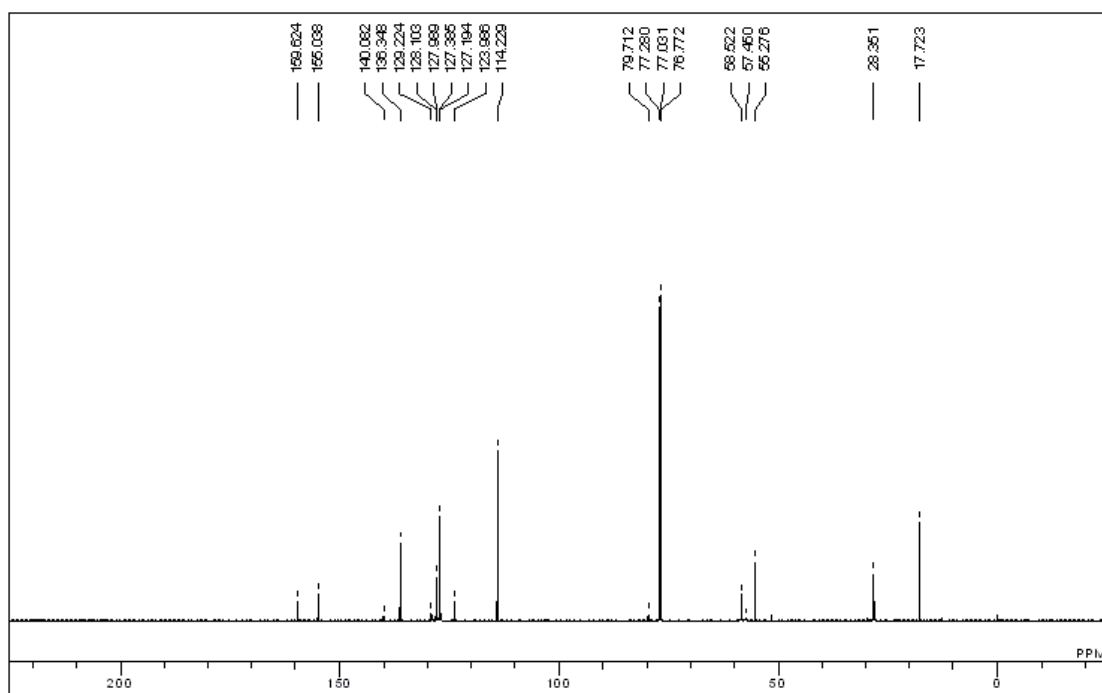
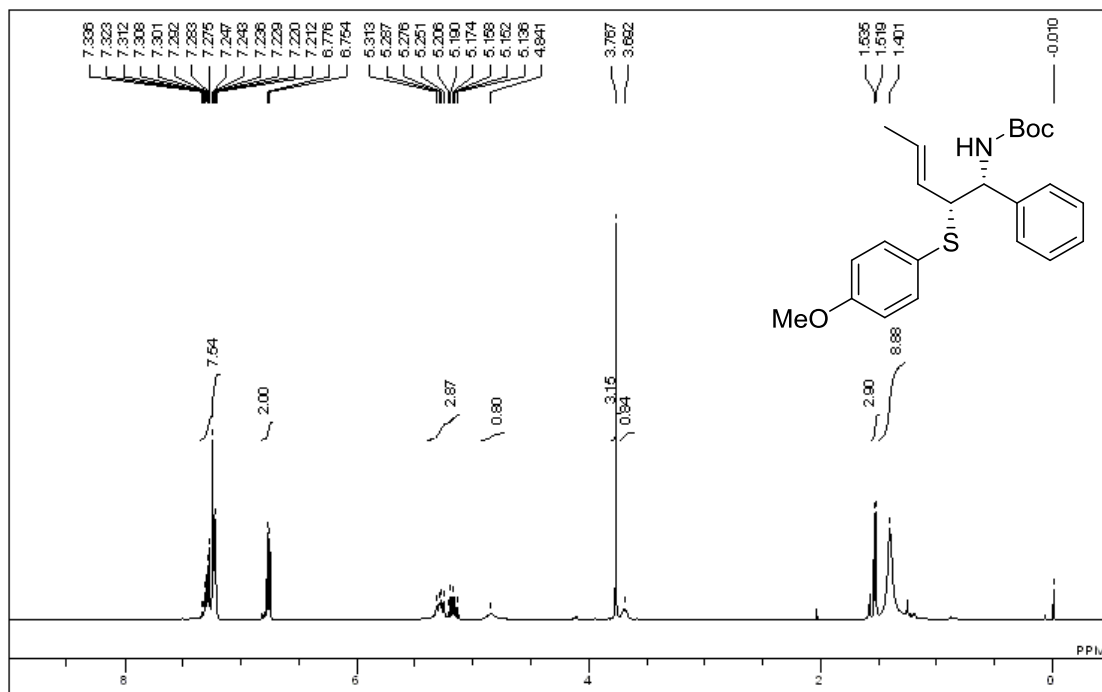


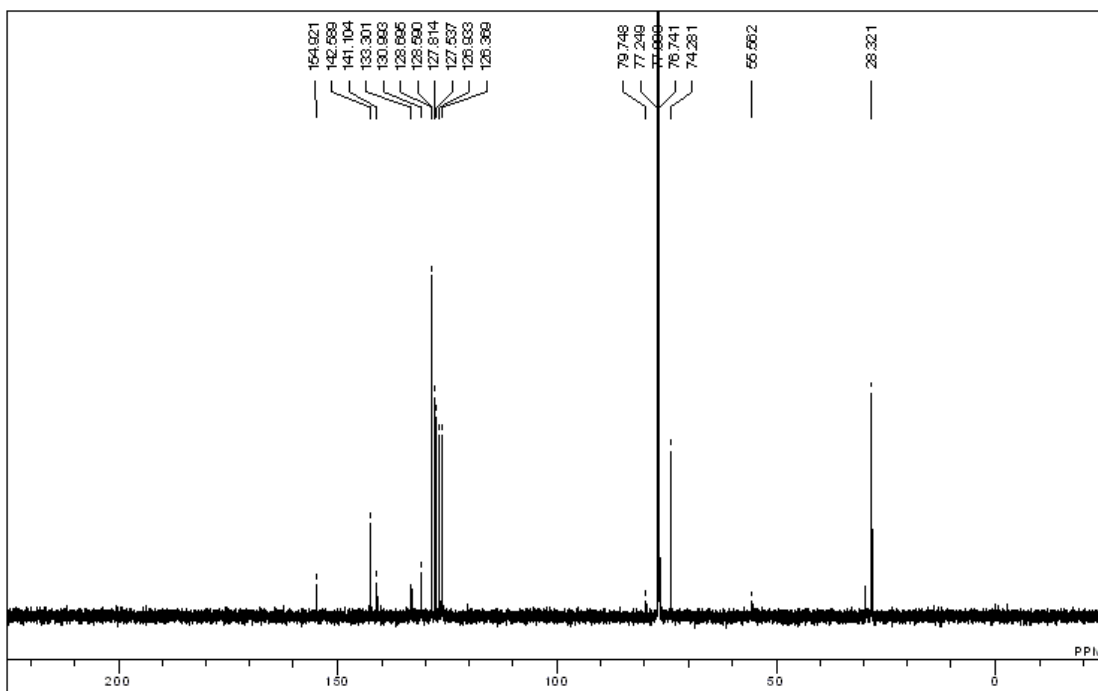
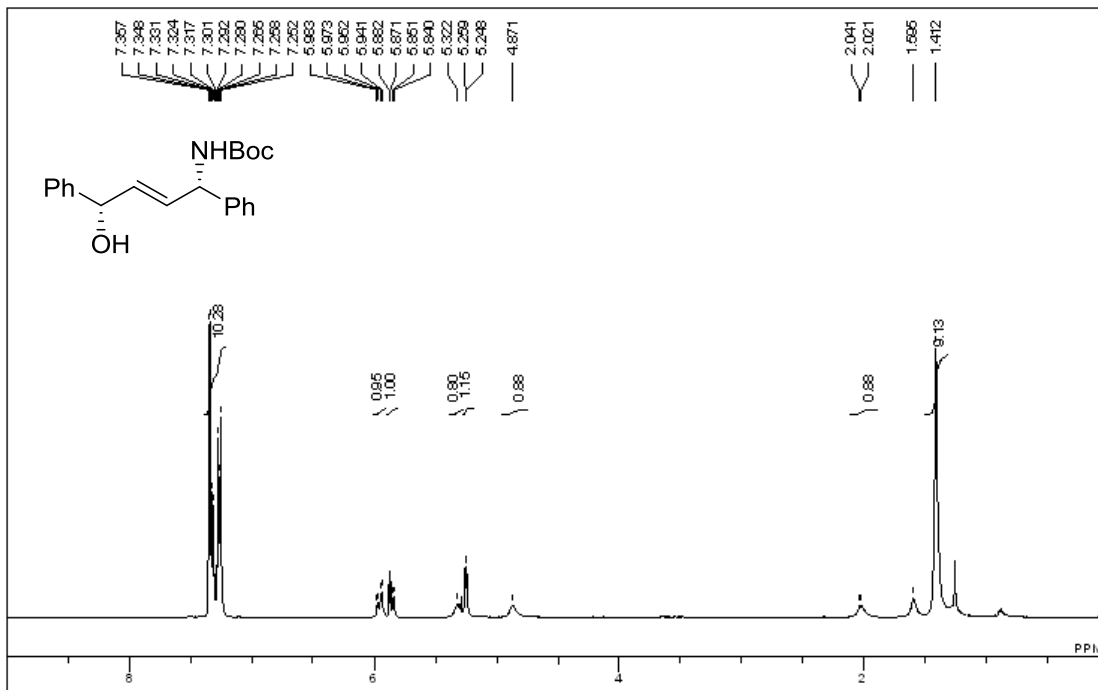


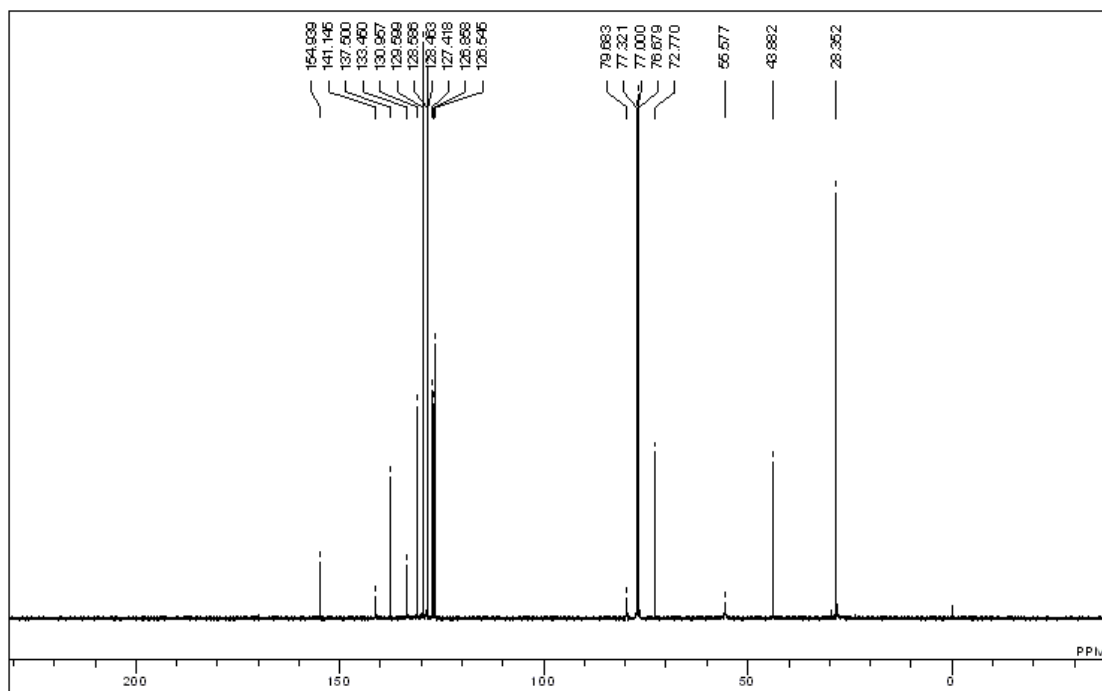
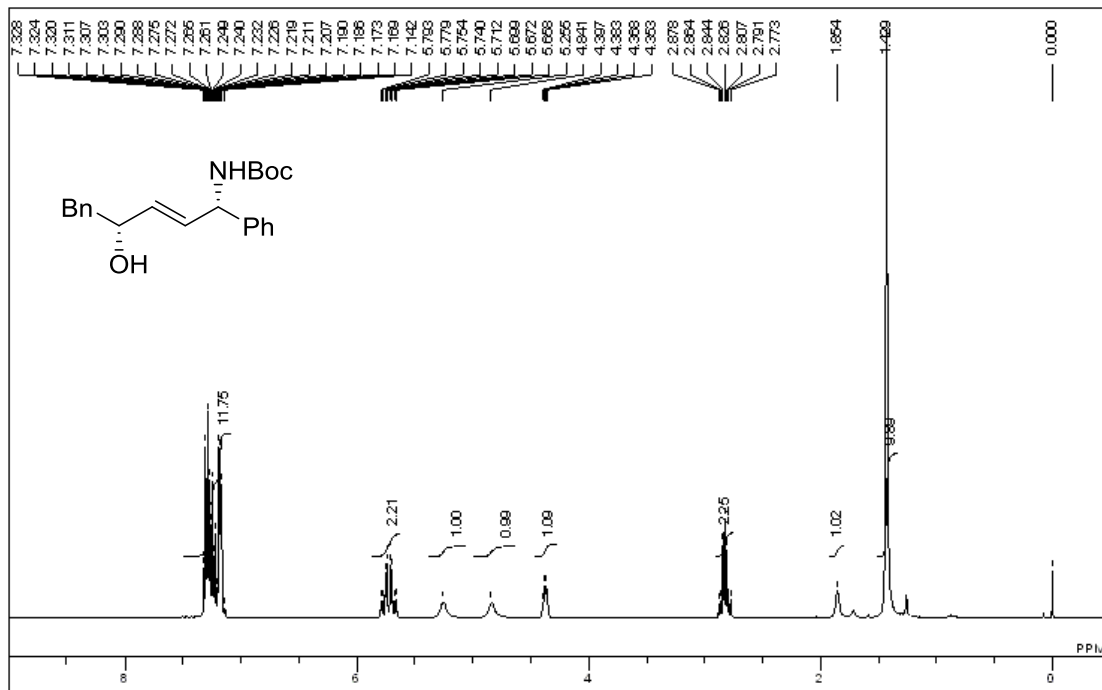


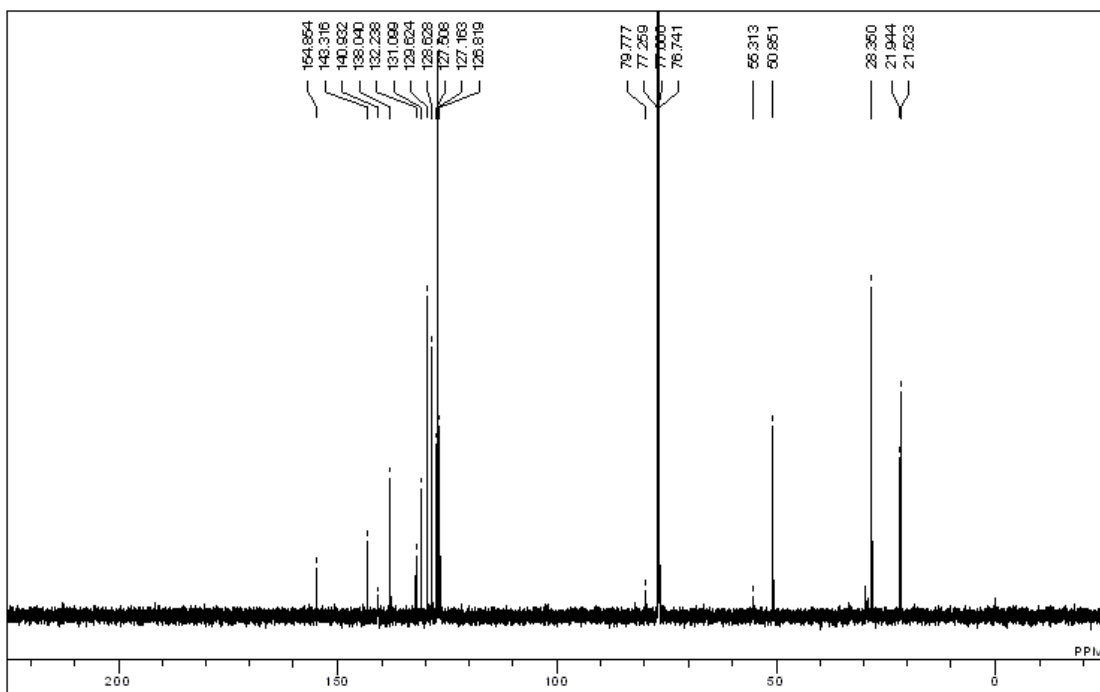
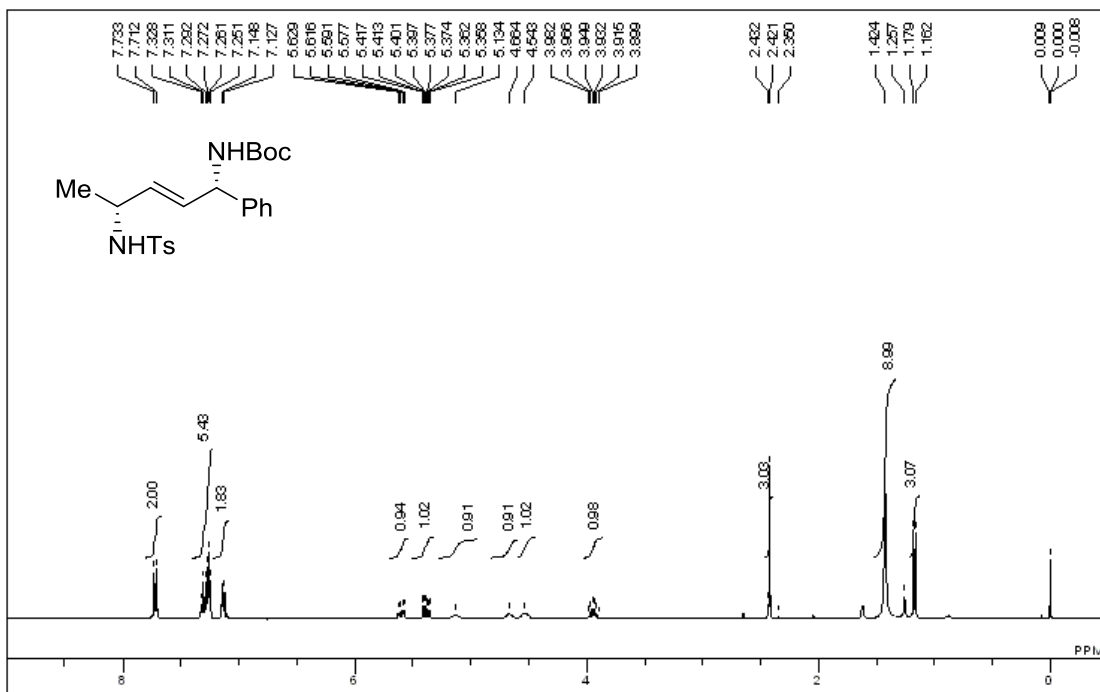


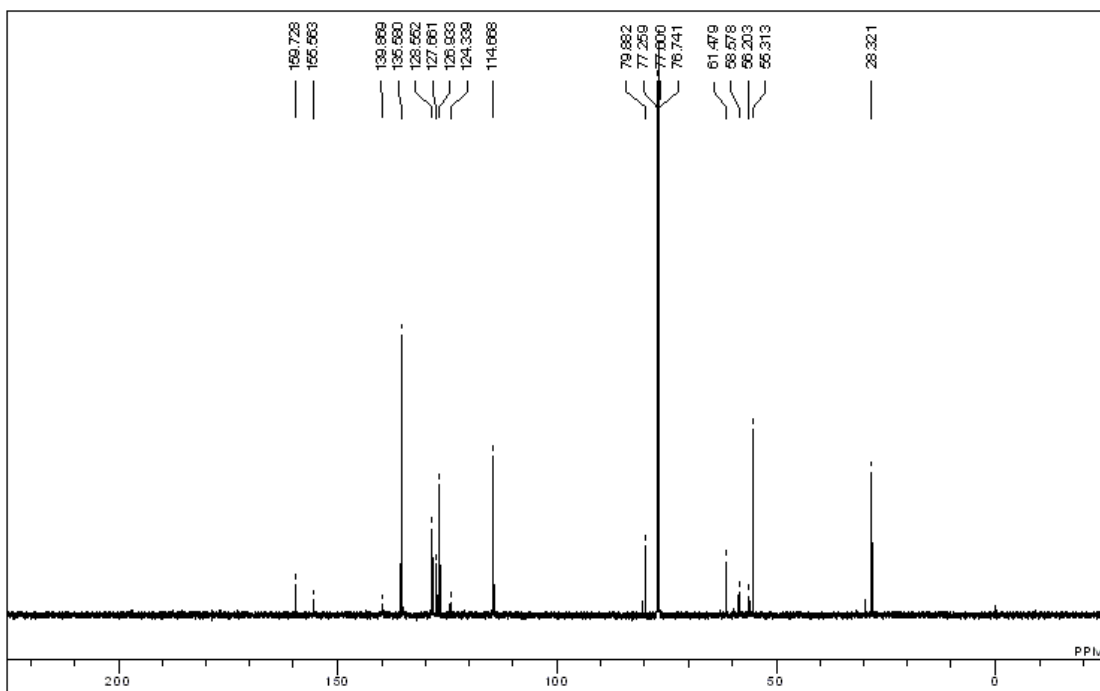
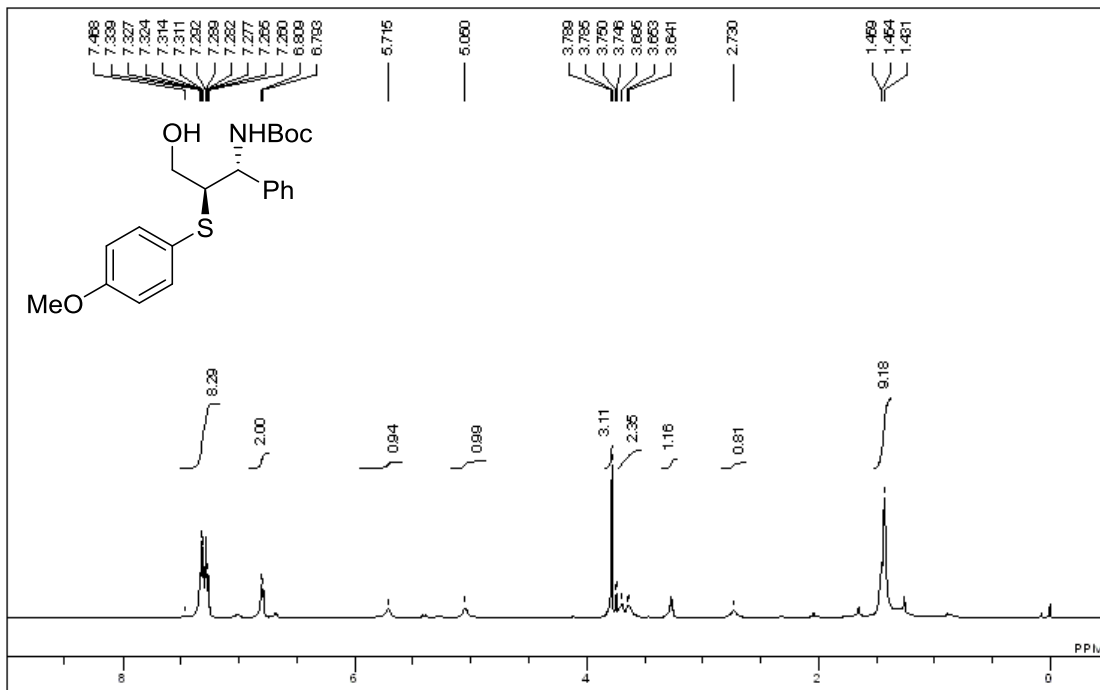


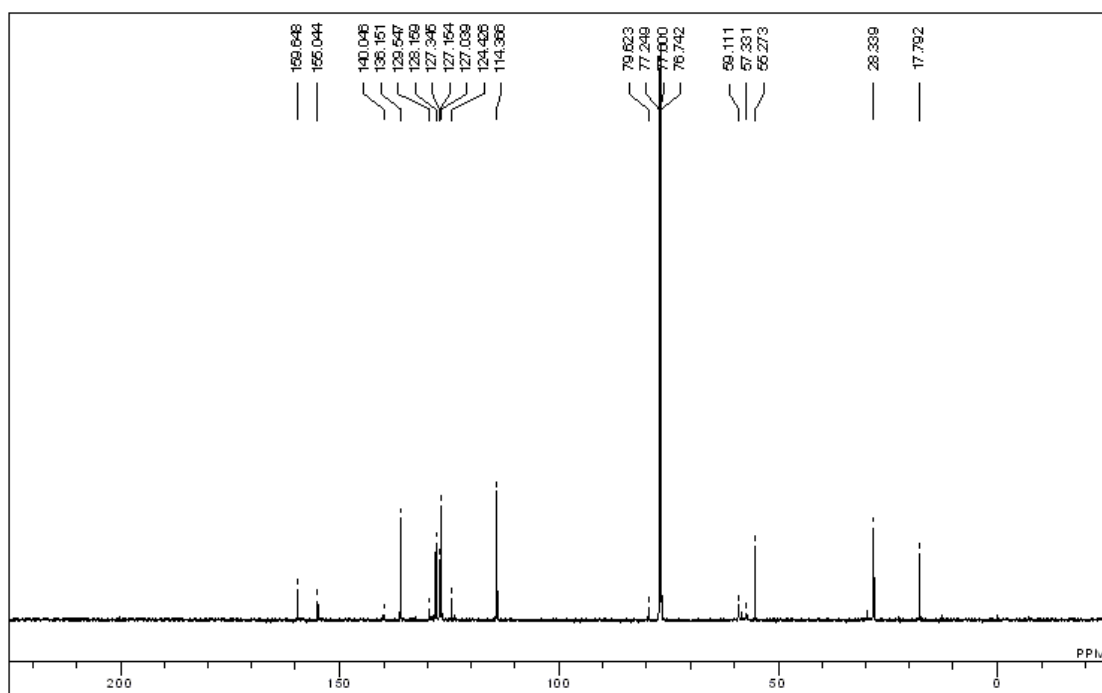
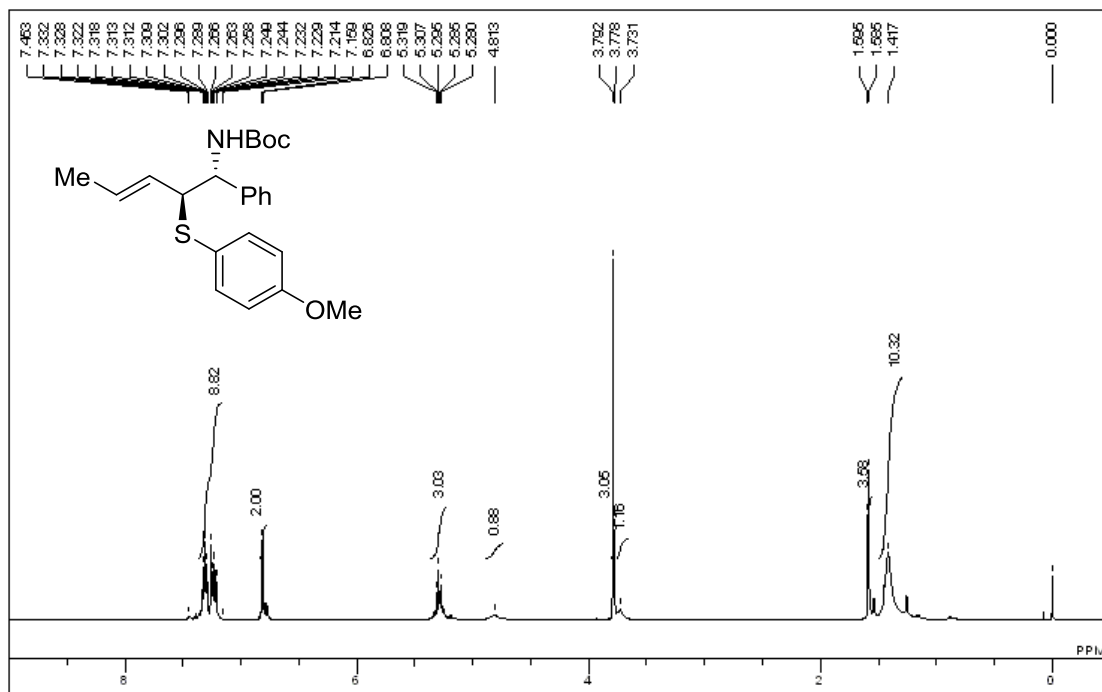


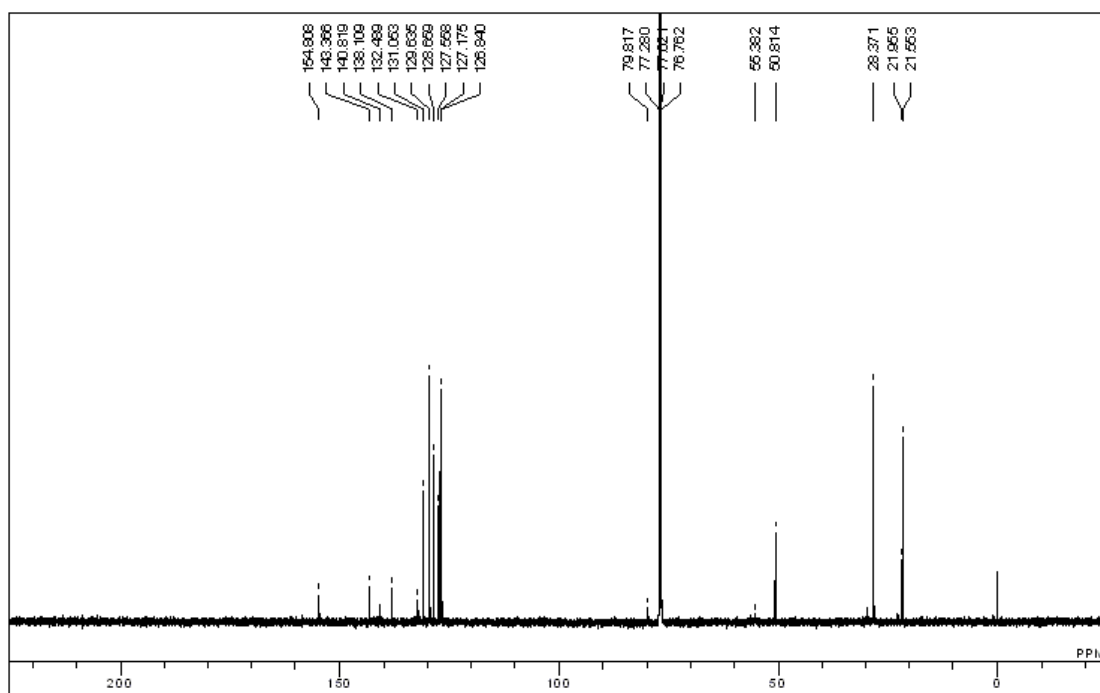
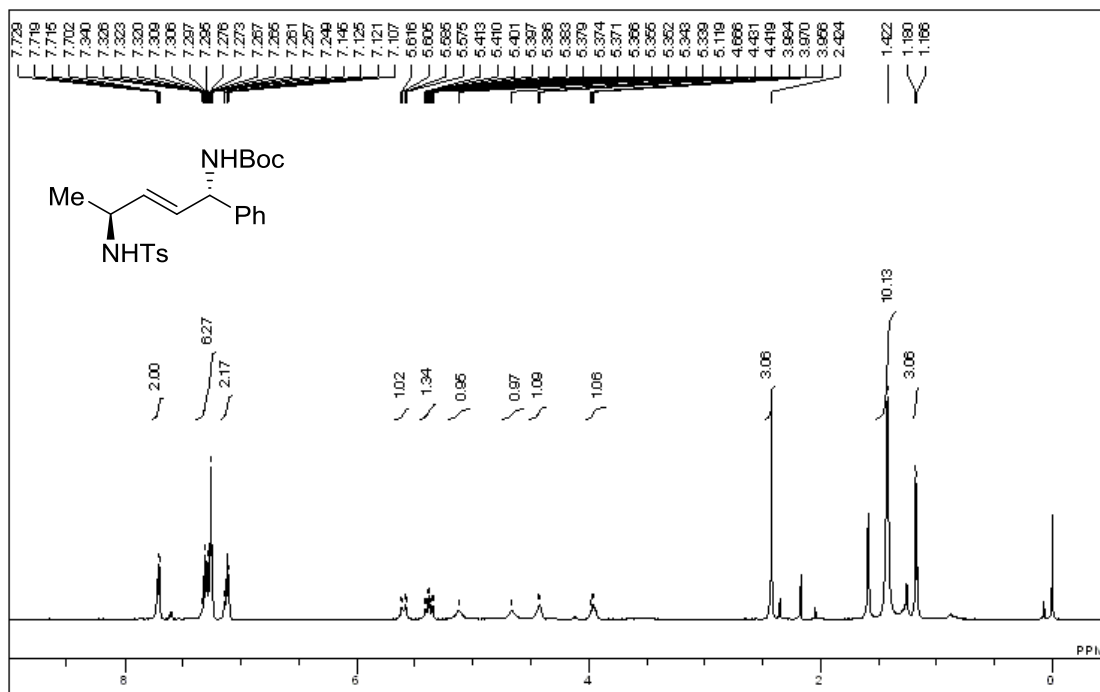


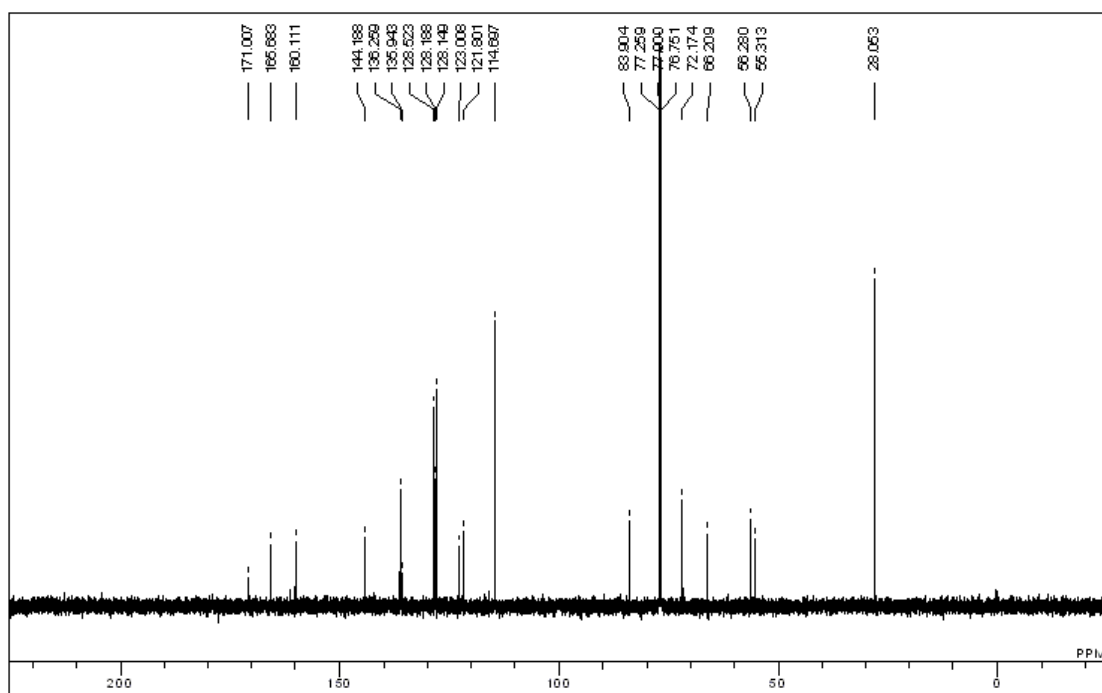
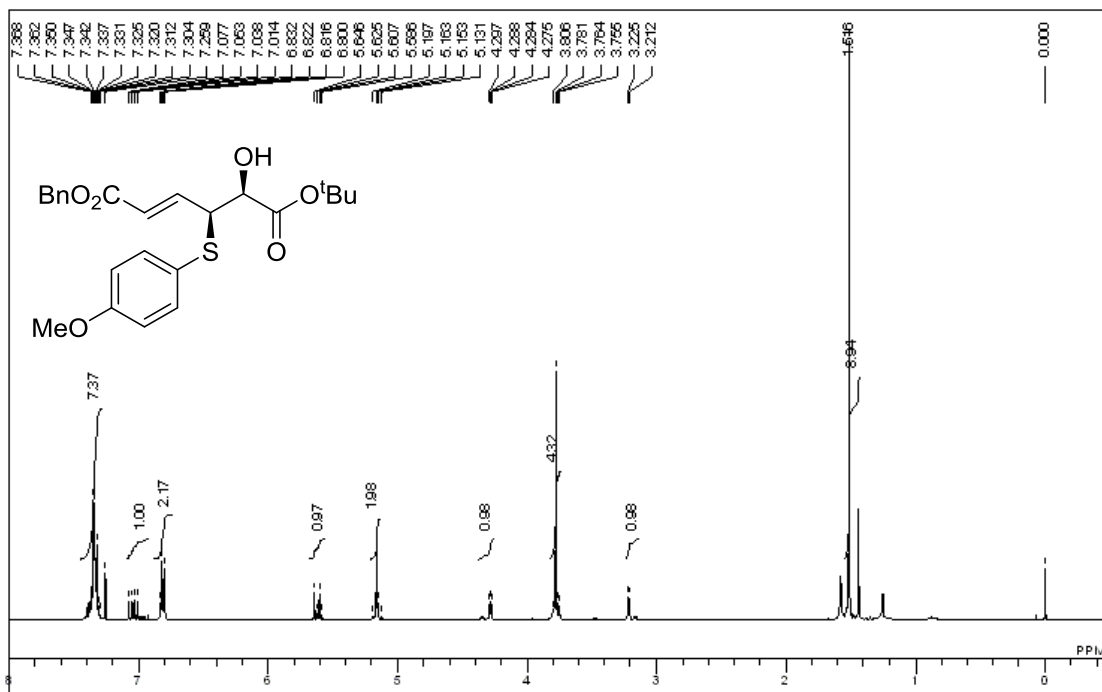


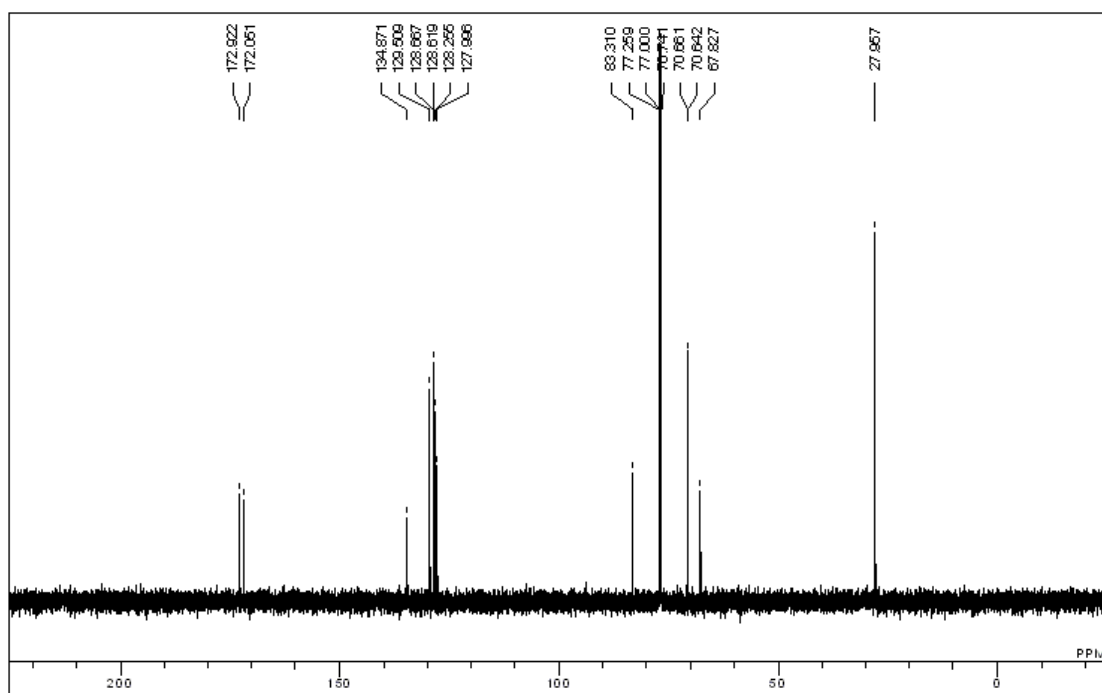
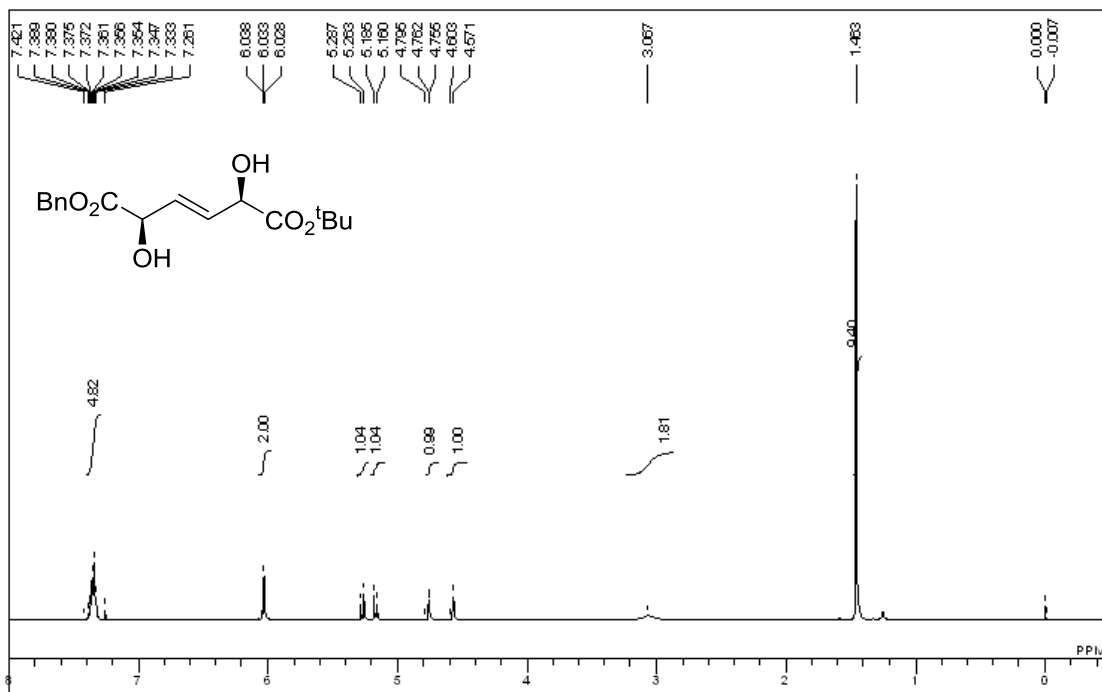




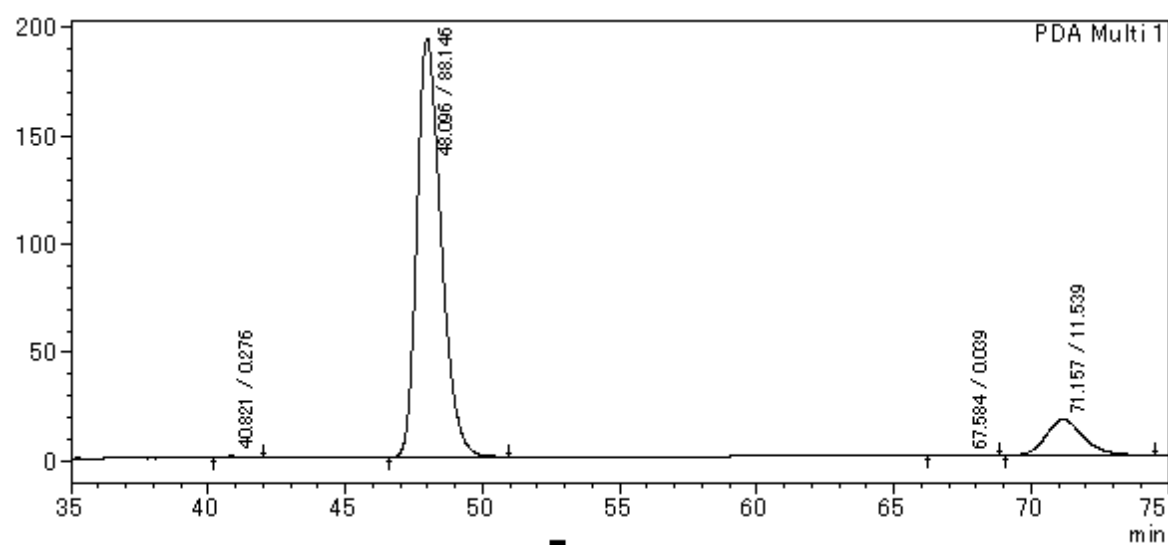
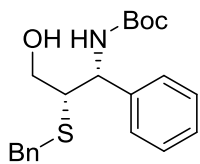
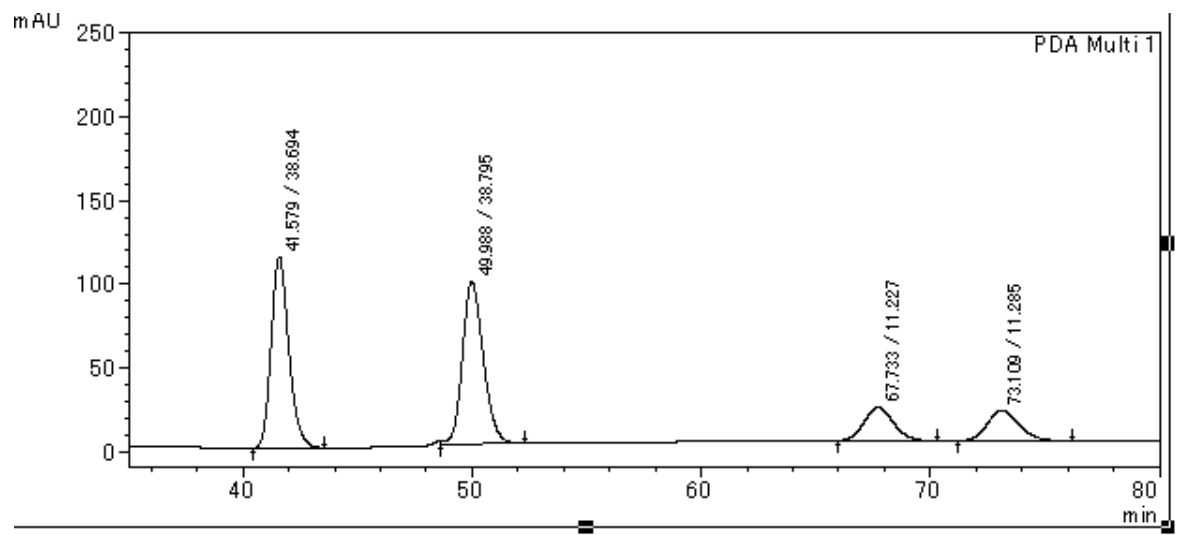
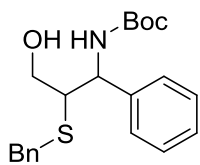


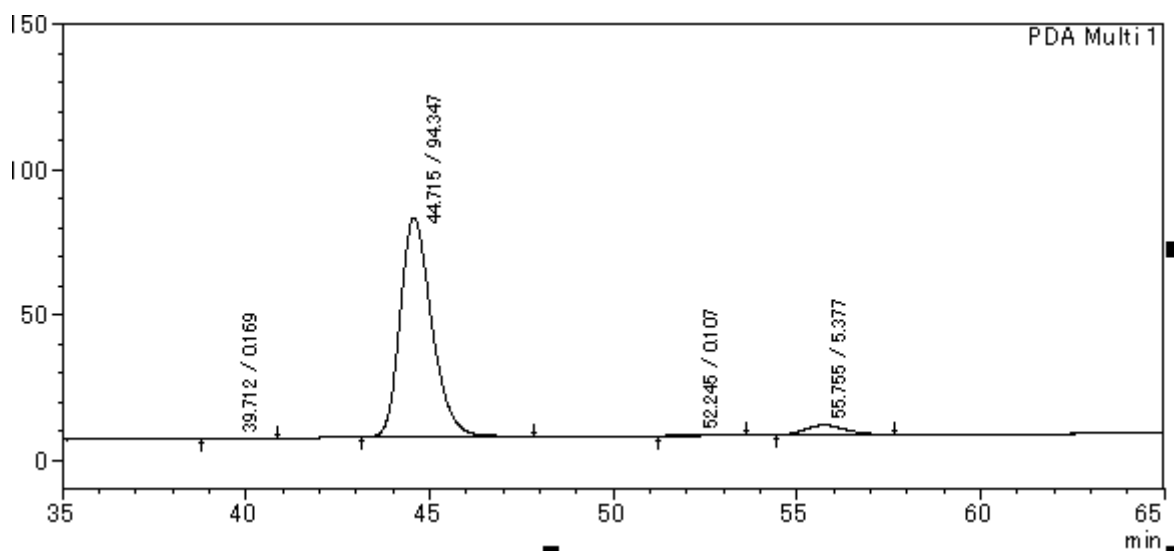
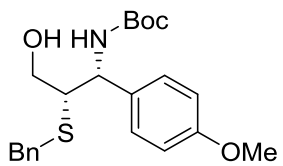
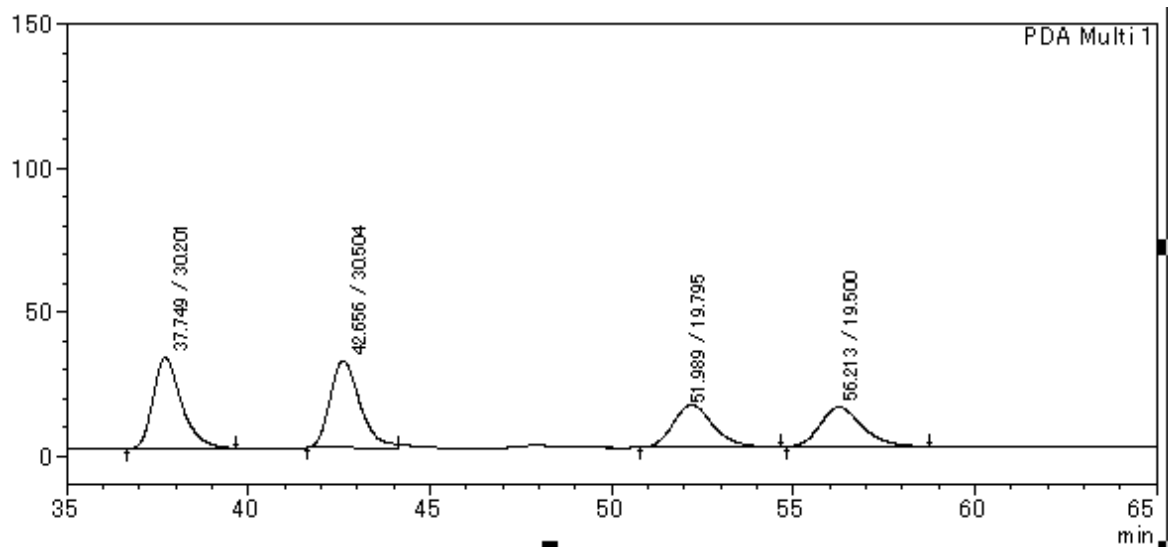
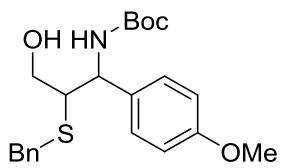


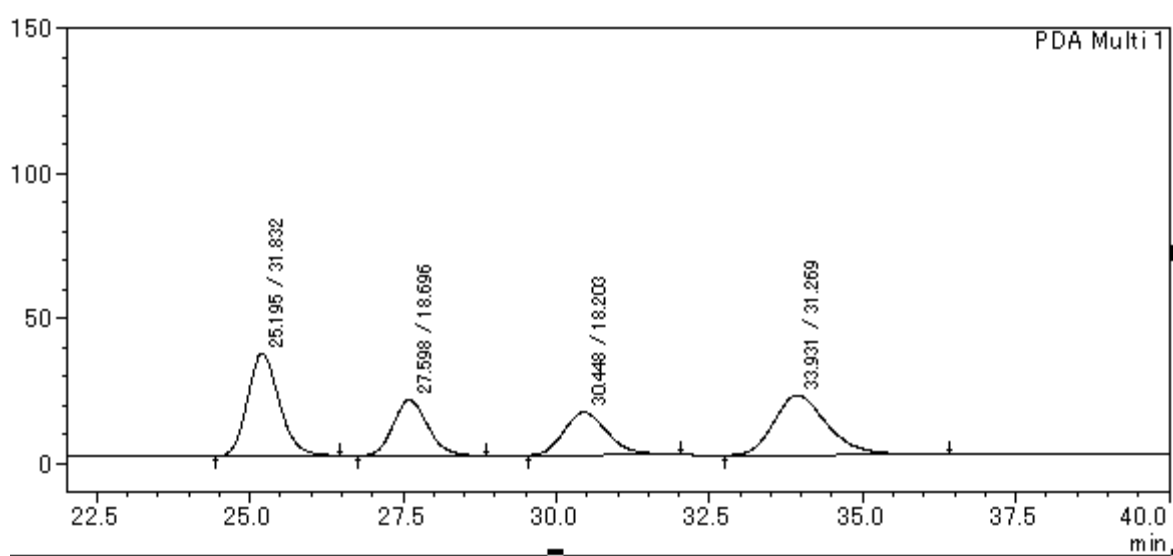
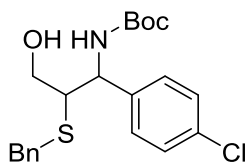




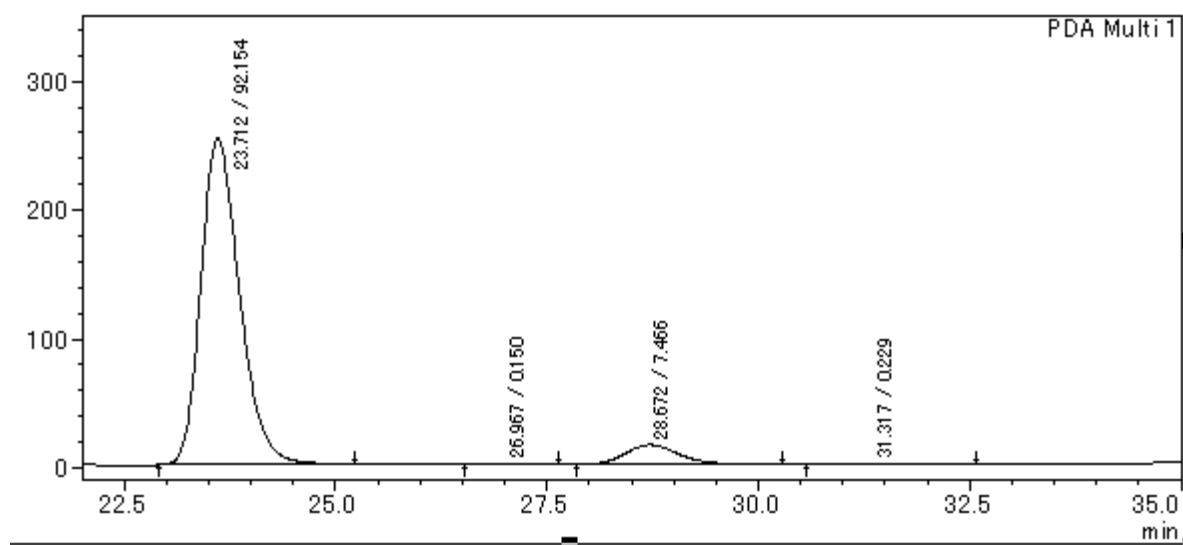
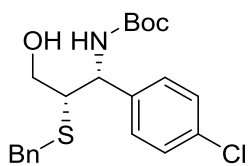
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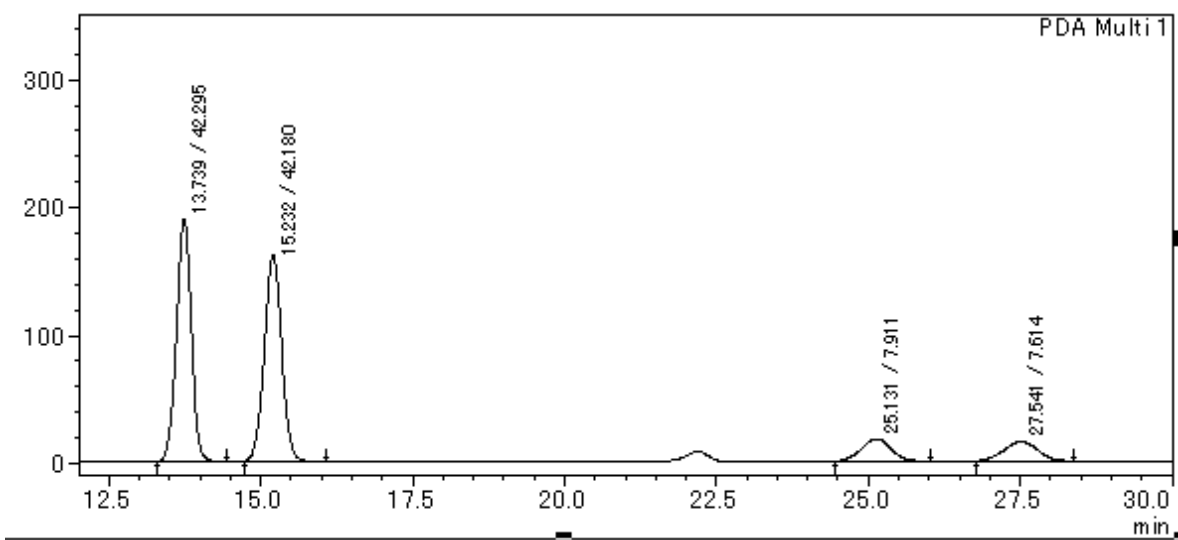
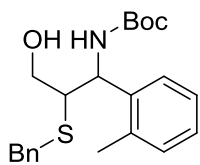






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