

Supporting Information

Highly Enantioselective Synthesis of Cyclopropylamine Derivatives via Ru(II)-Pheox Catalyzed Direct Asymmetric Cyclopropanation of Vinylcarbamates

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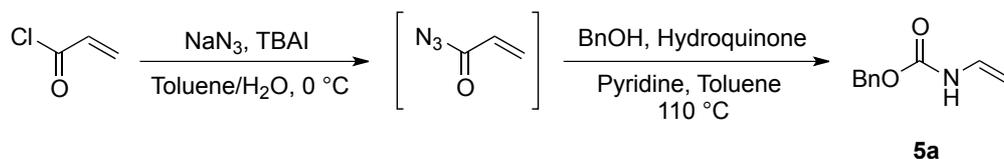
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General: All reactions were performed under an atmosphere of argon unless otherwise noted. Dichloromethane (CH₂Cl₂) was purchased from Kanto Chemical Co., Inc.. Acetonitrile was purchased from Wako Pure Chemical Industries, Ltd.. All reactions were monitored by thin layer chromatography (TLC), glass plates pre-coated with silica gel Merck KGaA 60 F₂₅₄, layer thickness 0.2 mm. All the starting materials are commercially available and were used after purification. The products were visualized by irradiation with UV light or by treatment with a solution of phosphomolybdic acid or by treatment with a solution of *p*-anisaldehyde. Flash column chromatography was performed using silica gel (Merck, Art. No. 7734). ¹H NMR (500 MHz, 400 MHz) and ¹³C NMR (125 MHz, 100 MHz) spectra were recorded on JEOL JNM-ECX500, JEOL JNM-ECS400 spectrometer. Chemical shifts are reported as δ values (ppm) relative to internal tetramethylsilane (0.00 ppm) in CDCl₃. Elemental analyses were measured on a Yanaco CHN CORDER MT-6. Optical rotations were performed with a JASCO P-1030 polarimeter at the sodium D line (1.0 ml sample cell).

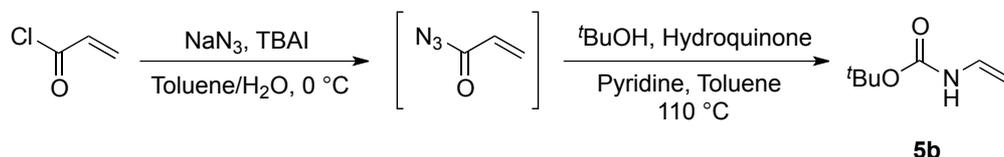
1. Synthesis of various vinylcarbamates

Benzyl *N*-vinylcarbamate (**5a**)



Using the procedure of Michalson,^{1,2} The mixture of acryloyl chloride (1.81 g, 20.0 mmol) and *tert*-butyl ammonium iodide (TBAI) (370 mg, 1.00 mmol) in toluene (10 mL), was added dropwise to cooled ($0\text{ }^\circ\text{C}$) solution of sodium azide (1.56 g, 24.0 mmol) in 20 mL of water. After finishing dropwise, the mixture was stirred at $0\text{ }^\circ\text{C}$ for 5 h. The organic layer was separated and washed with 10.0 mL of toluene. The organic solution was dried (Na_2SO_4) before use in the subsequent step. The toluene solution of acryloyl azide was added dropwise to a stirred and heated ($100\text{ }^\circ\text{C}$) mixture of hydroquinone (110 mg, 1.00 mmol), pyridine (98.0 μL , 1.20 mmol), and benzyl alcohol (2.5 mL, 24.0 mmol). The mixture was stirred for 30 min at $110\text{ }^\circ\text{C}$ after completion of addition, and then the toluene was removed by rotary evaporation. The residue was isolated by silica gel column chromatography to give a colorless solid product **5a** in 63% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.30–7.42 (m, 5H), 6.65–6.80 (m, 1H), 6.60 (br s, 1H), 5.12 (s, 2H), 4.45 (d, 1H, $J = 15.6$ Hz), 4.30 (d, 1H, $J = 8.8$ Hz).

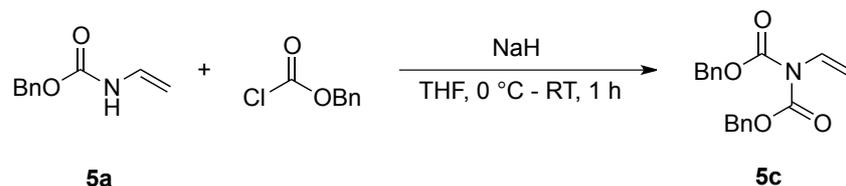
tert-Butyl *N*-vinylcarbamate (**5b**)



Using the procedure of Michalson,^{1,2} The mixture of acryloyl chloride (1.80 g, 20.0 mmol) and *tert*-butyl ammonium iodide (TBAI) (370 mg, 1.00 mmol) in toluene (10 mL) was added dropwise to cooled ($0\text{ }^\circ\text{C}$) solution of sodium azide (1.56 g, 24.0 mmol) in 20 mL of water. After finishing dropwise, the mixture was stirred at $0\text{ }^\circ\text{C}$ for 5 h. The organic layer was separated and washed with 10 mL of toluene. The organic solution was dried over Na_2SO_4 before use in the subsequent step. The toluene solution of acryloyl azide was stirred and heated ($110\text{ }^\circ\text{C}$) in the presence of hydroquinone (110 mg, 1.00 mmol) for 30 min. After that, the mixture was cooled down to room temperature and dropwise to a stirred and cooled ($0\text{ }^\circ\text{C}$) mixture of triethyl amine (1.20 mmol) and *t*-butyl alcohol (4.50 g, 60.0 mmol), and then the toluene was removed by rotary evaporation. The residue was isolated by silica gel column chromatography to give a crystalline solid product **5b** in 13% yield. ^1H NMR (400 MHz, CDCl_3) δ 6.68 (br s, 1H), 6.25 (br s, 1H), 4.40 (d, 1H, $J = 15.6$ Hz), 4.21 (d, 1H, $J = 8.4$ Hz),

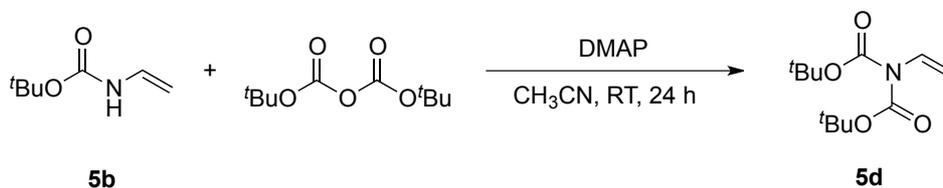
1.48 (s, 9H).

Benzyl carbobenzyloxy(vinyl)carbamate (**5c**)



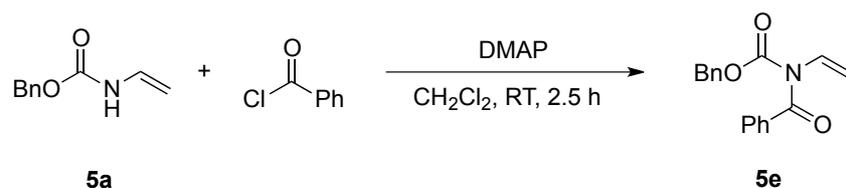
To a solution of benzyl vinylcarbamate (354 mg, 2.00 mmol) in 10 mL of anhydrous THF was added sodium hydride (144 mg, 60% in mineral oil, 3.60 mmol) at 0 °C. After 5 min, the reaction mixture was warmed to room temperature and stirred for 1 h. The solution was then cooled to 0 °C and benzyl chloroformate (0.6 mL, 4.00 mmol) was added. The reaction was warmed slowly to room temperature and stirred overnight. The reaction was monitored by TLC. After the reaction was completed, the reaction mixture was evaporated and extracted with water and ethyl acetate. The organic layer was dried over Na₂SO₄, and concentrated. The residue was purified by flash column chromatography with Hexane/EtOAc to give corresponding product **5c** as pale yellow liquid in 95% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.40 (m, 10H), 6.58 (dd, 1H, *J* = 9.2, 6.8 Hz), 5.25 (s, 4H), 5.06 (d, *J* = 16.0 Hz, 1H), 4.90 (d, 1H, *J* = 8.8 Hz).

tert-Butyl *tert*-butoxycarbonyl(vinyl)carbamate (**5d**)



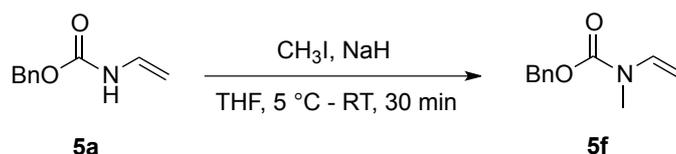
To a solution of *tert*-butyl *N*-vinylcarbamate (286 mg, 2.00 mmol) in acetonitrile (5 mL) was added a solution of boc-anhydride (1.30 g, 6.00 mmol) in acetonitrile (3 mL), then 4-*N*, *N*-dimethylaminopyridine (67.0 mg, 0.60 mmol) in one portion. The mixture was then stirred at room temperature overnight, followed by removal of solvent under reduced pressure. The residue was purified by flash column chromatography with Hexane/EtOAc to give the product **5d** as clear liquid in 89% yield. ¹H NMR (400 MHz, CDCl₃) δ 6.30 (dd, 1H, *J* = 9.2, 7.2 Hz), 4.82 (d, 1H, *J* = 16 Hz), 4.61 (d, 1H, *J* = 9.2 Hz), 1.52 (s, 18H).

Benzyl benzoyl(vinyl)carbamate (5e)



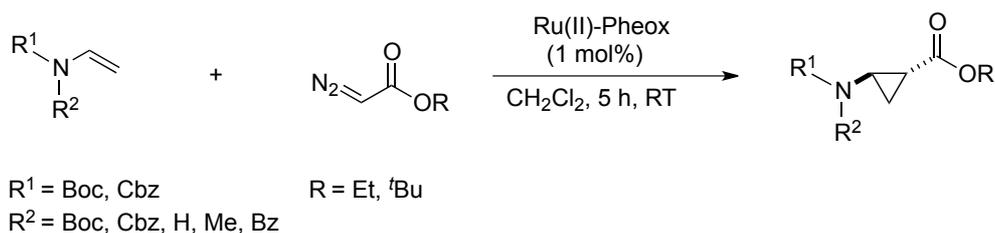
Benzoyl chloride (1.20 equiv) was added to a stirred solution of benzyl vinylcarbamate (1.00 equiv), triethylamine (4.00 equiv) and DMAP (0.12 equiv) in dichloromethane at room temperature under atmosphere of argon. The reaction was stirred for 2.5 h. The resulting mixture was concentrated under reduced pressure and isolated by silica gel column chromatography giving corresponding product **5e** in 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, 2H, *J* = 7.2 Hz), 7.53 (t, 1H, *J* = 7.2 Hz), 7.38 (t, 2H, *J* = 8.0 Hz), 7.20–7.30 (m, 2H), 6.97 (d, 2H, *J* = 8.4 Hz), 6.88 (dd, 1H, *J* = 6.8, 9.2 Hz), 5.04 (s, 2H), 4.98 (d, 1H, *J* = 15.6), 4.78 (d, 1H, *J* = 9.2 Hz).

Benzyl methyl(vinyl)carbamate (5f)



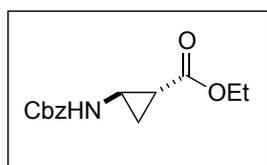
Sodium hydride (1.20 equiv) was added to the magnetically stirred benzyl vinylcarbamate (1.00 equiv) in anhydrous THF and then iodomethane (1.20 equiv) was added dropwise to the mixture at below 5 °C. After completing dropwise, the mixture was kept below 5 °C for 30 min and stirred at room temperature. The reaction was monitored by TLC. After the reaction was completed, the reaction mixture was partitioned between saturated aqueous NH₄Cl and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water, dried over Na₂SO₄, and concentrated. The residue was purified by flash column chromatography with Hexane/EtOAc to give corresponding product **5f** in 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.42 (m, 5H), 7.14–7.24 (m, 1H), 5.20 (s, 2H), 4.20–4.38 (m, 2H), 3.09 (s, 3H).

2. General procedure for catalytic asymmetric cyclopropanation of vinylcarbamates with diazoesters



The solution of diazoester (0.2 mmol) in CH_2Cl_2 (1.5 mL) was slowly added to a mixture of Ru(II)-Pheox catalyst (1.3 mg, 0.002 mmol) and vinylcarbamate (1.0 mmol) in CH_2Cl_2 (0.5 mL) for 4 h under argon atmosphere at RT. After the addition completed, the reaction mixture was then stirred for 1 h at RT. The progress of the reaction was monitored by TLC. Upon completion, solvent was removed and the residue was purified by flash column chromatography on silica gel eluted with EtOAc/Hexane (1/4) to give desired product. The *trans/cis* ratio was determined from the crude ^1H NMR spectra, and the ee value was determined by chiral HPLC analysis.

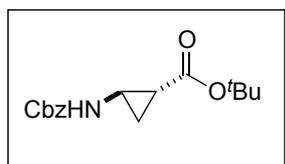
3. Analytical data for asymmetric cyclopropanation reaction products



(Ethyl 2-((benzyloxycarbonyl)amino)cyclopropanecarboxylate) (7a).

This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between benzyl vinylcarbamate **5a** (177 mg, 1.00 mmol) and ethyl diazoacetate (26.8 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4(v/v)) as an eluent to give the desired product in 99% yield (51.9 mg, 0.20 mmol) as white solid. $[\alpha]_D^{20} = -72.0$ (c 0.98, CHCl_3). *trans/cis* = 70/30, 90% *trans* ee, 94% *cis* ee. ^1H NMR (400 MHz, CDCl_3) (*trans* isomer) δ 7.30–7.40 (m, 5H), 5.11 (s, 2H), 4.96 (br s, 1H), 4.09–4.20 (m, 2H), 3.09 (br s, 1H), 1.75–1.79 (m, 1H), 1.40–1.46 (m, 1H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.11–1.15 (m, 1H) ppm. ^1H NMR (400 MHz, CDCl_3) (*cis* isomer) δ 7.30–7.40 (m, 5H), 5.57 (br s, 1H), 5.11 (s, 2H), 4.09–4.20 (m, 2H), 3.45 (br s, 1H), 1.88–1.94 (m, 1H), 1.29–1.35 (m, 1H), 1.26 (t, $J = 7$ Hz, 3H), 1.18–1.20 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) (*trans* and *cis* isomer) δ 172.3, 172.2, 156.6, 156.5, 136.5, 136.2, 128.6, 128.5, 128.3, 128.3, 128.1, 67.1, 66.9, 61.1, 60.9, 32.0, 31.7, 18.9, 15.8, 14.3, 14.2, 14.1 ppm. IR (neat) ν 3332, 3077, 3040, 3032, 2980, 2905, 1727 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALCEL OD), UV detector 230 nm, eluent: Hex/IPA = 6/1, Flow Rate = 0.50 mL/min, tR = 20.0 min (major product for *trans* isomer), tR = 21.5 min (minor product for *trans* isomer). Column (Chiral OJ-H), Hex/IPA = 5/1, tR = 21.0 min (minor product for *cis* isomer), tR = 23.5 min

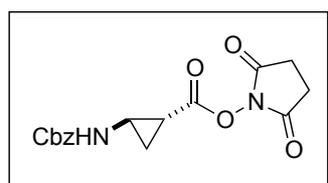
(major product for *cis* isomer). Anal. C₁₄H₁₇NO₄, Found: C 64.07, H 6.48, N 5.68%; Calcd: C 63.87, H 6.51, N 5.32%.



(*tert*-butyl 2-((benzyloxycarbonyl)amino)cyclopropanecarboxylate)

(7b). This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between benzyl vinylcarbamate **5a** (177 mg, 1.00 mmol) and *tert*-butyl diazoacetate (31.6 mg, 0.20 mmol).

The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4(v/v)) as an eluent to give the desired product in 91% yield (53.0 mg, 0.18 mmol) as colorless oil. $[\alpha]_D^{23} = -28.0$ (c 1.25, CHCl₃), (*trans/cis* = 52/48, 97% *trans* ee, 96% *cis* ee). ¹H NMR (400 MHz, CDCl₃) (*trans* isomer) δ 7.28–7.41 (m, 5H), 5.10 (s, 2H), 4.94 (br s, 1H), 3.04 (br s, 1H), 1.64–1.70 (m, 1H), 1.43 (s, 9H), 1.32–1.40 (m, 1H), 1.19–1.29 (m, 1H) ppm. ¹H NMR (400 MHz, CDCl₃) (*cis* isomer) δ 7.28–7.41(m, 5H), 5.56 (br s, 1H), 5.10 (s, 2H), 3.31–3.40 (m, 1H), 1.81–1.86 (m, 1H), 1.43 (s, 9H), 1.39–1.52 (m, 1H), 1.11–1.15 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) (*trans* and *cis* isomer) δ 171.5, 171.3, 156.9, 136.5, 136.4, 128.6, 128.5, 128.3, 128.2, 128.1, 81.3, 80.9, 67.0, 66.8, 64.4, 31.7, 31.3, 31.0, 28.2, 25.4, 23.3, 20.0, 15.6, 13.6 ppm. IR (neat) ν 3354, 3077, 3040, 3032, 2980, 2935, 1727 cm⁻¹. The ee values were determined by HPLC analysis. Column (CHIRALPAK IC), UV detector 230 nm, eluent: Hex/IPA = 9/1, Flow Rate = 1.00 mL/min. t_R = 16.0 min (minor product for *trans* isomer), t_R = 20.0 min (major product for *trans* isomer), t_R = 34.0 min (minor product for *cis* isomer), t_R = 36.0 min (major product for *cis* isomer). Anal. C₁₆H₂₁NO₄, Found: C 65.57, H 7.22, N 4.81%; Calcd: C 65.96, H 7.27, N 4.81%.

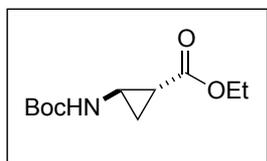


(Succinimidyl 2-((benzyloxycarbonyl)amino)cyclopropanecarboxylate)

(7c). This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between benzyl vinylcarbamate **5a** (177 mg, 1.00 mmol) and succinimidyl diazoacetate

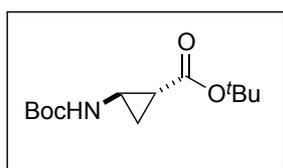
(36.6 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4 – 2/1(v/v)) as an eluent to give the desired product in 90% yield (60.0 mg, 0.18 mmol) as a white solid. $[\alpha]_D^{25} = -21.0$ (c 0.91, CHCl₃). (*trans/cis* = 43/57, 31% *trans* ee, 49% *cis* ee. ¹H NMR (400 MHz, CDCl₃) (*cis* isomer) δ 7.3–7.47 (m, 5H), 5.00–5.20 (m, 2H), 3.25–3.30 (m, 1H), 2.83 (s, 4H), 2.02–2.09 (m, 1H), 1.61–1.68 (m, 1H), 1.42–1.47 (q, *J* = 6.4 Hz, 1H). ¹H NMR (400 MHz, CDCl₃) (*trans* isomer) δ 7.3–7.47 (m, 5H), 5.00–5.20 (m, 2H), 3.57–3.65 (m, 1H), 2.83 (s, 4H), 2.18–2.25 (m, 1H), 1.53–1.62 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 167.8, 166.8, 156.6, 136.3, 136.1, 128.6, 128.5, 128.2, 128.1, 83.6, 67.1, 33.4, 25.6, 17.3, 15.2. IR (neat) ν 3332, 3070,

3024, 2949, 1787, 1734 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALCEL OD-H), UV detector 220 nm, eluent: Hex/IPA = 3/1, Flow Rate = 0.3 mL/min. t_R = 92.9 min (major product for *trans*), t_R = 114.5 min (minor product for *trans*), t_R = 100.7 min (major product for *cis*), t_R = 134.3 min (minor product for *cis*).



(Ethyl 2-((*tert*-butoxycarbonyl)amino)cyclopropanecarboxylate) (7d).

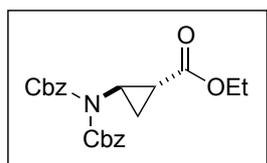
This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between *t*-butyl vinylcarbamate **5b** (145 mg, 1.00 mmol) and ethyl diazoacetate (26.8 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4 (v/v)) as an eluent to give the desired product in 89% yield (42.0 mg, 0.16 mmol) as white solid. $[\alpha]_D^{20} = -43.0$ (c 1.16, CHCl_3). *trans/cis* = 60/40, 89% *trans* ee, >99% *cis* ee. ^1H NMR (400 MHz, CDCl_3) (*trans* isomer) δ 4.74 (br s, 1H), 4.09–4.20 (m, 2H), 3.03 (br s, 1H), 1.72–1.75 (m, 1H), 1.44 (s, 9H) 1.38–1.42 (m, 1H), 1.27 (q, $J = 7.2$ Hz, 3H), 1.06–1.72 (m, 1H) ppm. ^1H NMR (400 MHz, CDCl_3) (*cis* isomer) δ 5.28 (br s, 1H), 4.09–4.19 (m, 2H), 3.35 (br, 1H), 1.82–1.91 (m, 1H), 1.43 (s, 9H), 1.38–1.43 (1H), 1.27 (q, $J = 7.2$ Hz, 3H), 1.12–1.19 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) (*trans* and *cis* isomer) δ 172.5, 172.2, 156.2, 155.9, 80.0, 79.7, 60.9, 60.8, 31.9, 31.5, 28.4, 19.1, 15.7, 14.3, 14.0 ppm. IR (neat) ν 3354, 2980, 2927, 1720 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALCEL OD), eluent: Hex/IPA = 9/1, Flow Rate = 1.0 mL/min, t_R = 6.5 min (major product for *trans*), t_R = 7.0 min (minor product for *trans*), t_R = 11 min (major product for *cis*), t_R = 12 min (minor product for *cis*).



(*tert*-butyl 2-((*tert*-butoxycarbonyl)amino)cyclopropanecarboxylate) (7e).

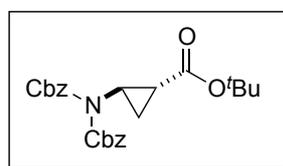
This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between *tert*-butyl vinyl carbamate **5b** (145 mg, 1.00 mmol) and *tert*-butyl diazoacetate (31.6 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4(v/v)) as an eluent to give the desired product in 82% yield (42.0 mg, 0.16 mmol) as colorless oil. $[\alpha]_D^{23} = -96.0$ (c 0.73, CHCl_3). *trans/cis* = 72/28, 93% *trans* ee, 91% *cis* ee. ^1H NMR (400 MHz, CDCl_3) (*trans* isomer) δ 5.22 (br s, 1H), 3.25 (br, 1H), 1.76–1.83 (m, 1H), 1.45 (s, 9H), 1.43 (s, 9H), 1.28–1.45 (m, 1H), 1.17–1.23 (m, 1H) ppm. ^1H NMR (400 MHz, CDCl_3) (*cis* isomer) δ 4.65 (br s, 1H, NH), 2.97 (br s, 1 H), 1.60–1.65 (m, 1H), 1.46 (s, 9H), 1.44 (s, 9H), 1.48–1.54 (m, 1H), 1.09–1.12 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) (*trans* isomer) δ 171.3, 156.4, 81.1, 79.8, 31.3, 28.5, 28.3, 20.2, 15.8, 13.5 ppm. IR (neat) ν 3370, 2980, 2919, 1712 cm^{-1} . The ee values were determined by

HPLC analysis. Column (CHIRALCEL OD), UV detector 230 nm, eluent: Hex/ IPA = 200/1, Flow Rate = 1.00 mL/min, tR = 10.7 min (major product for *trans* isomer), tR = 14.7 min (minor product for *trans* isomer). Column (CHIRALCEL OD-H), Hex/IPA = 100/1, tR = 19.5 min (major product for *cis* isomer), tR = 22.6 min (minor product for *cis* isomer). Anal. C₁₃H₂₃NO₄, Found: C 60.66, H 8.61, N 5.52%; Calcd: C 60.68, H 9.01, N 5.44%.



(Ethyl 2-((dibenzoyloxycarbonyl)amino)cyclopropanecarboxylate) (7f).

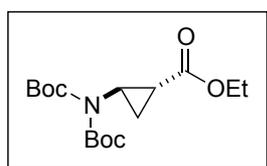
This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between benzyl carbobenzyloxy(vinyl)carbamate **5c** (311 mg, 1.00 mmol) and ethyl diazoacetate (26.8 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/7 – 1/3(v/v)) as an eluent to give the desired product in 91% yield (72.3 mg, 0.18 mmol) as pale yellow oil. $[\alpha]_D^{25} = -41.0$ (c 1.34, CHCl₃). *trans/cis* = 88/12, 96% *trans* ee, 88% *cis* ee. ¹H NMR (400 MHz, CDCl₃) (*trans* isomer) δ 7.30–7.45 (m, 10H), 5.15–5.28 (m, 4H), 4.07–4.15 (m, 1H), 3.95–4.04 (m, 1H), 3.15–3.21 (m, 1H), 1.84–1.90 (m, 1H), 1.55–1.61 (m, 1H), 1.13–1.24 (m, 1H), 1.19 (t, 3H, *J* = 7.2 Hz) ppm. ¹³C NMR (100 MHz, CDCl₃) (*trans* isomer) δ 171.9, 153.3, 135.1, 128.7, 128.6, 128.4, 128.3, 69.0, 60.9, 36.0, 24.7, 18.3, 14.2 ppm. ¹H NMR (400 MHz, CDCl₃) (*cis* isomer) δ 7.3–7.45 (m, 10H), 5.15–5.28 (m, 4H), 3.88–3.95 (m, 2H), 3.02–3.09 (m, 1H), 2.03–2.11 (m, 1H), 1.48–1.54 (m, 2H), 1.19 (t, 3H, *J* = 7.2 Hz) ppm. IR (neat) ν 3070, 3032, 2980, 2905 1809, 1757, 1734 cm⁻¹. The ee values were determined by HPLC analysis. Column (CHIRALPAK IC), UV detector 230 nm, eluent: Hex/IPA = 5/1, Flow Rate = 1.0 mL/min. tR = 45.1 min (minor product for *trans* isomer), tR = 47 min (major product for *trans* isomer), tR = 57.6 min (major product for *cis* isomer), tR = 130 min (minor product for *cis* isomer). Anal. C₂₂H₂₃NO₆, Found: C 66.62, H 5.91, N 3.58%; Calcd: C 66.49, H 5.83, N 3.52%.



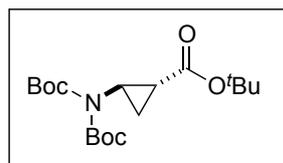
(tert-butyl 2-((dibenzoyloxycarbonyl)amino)cyclopropanecarboxylate) (7g).

This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between benzyl carbobenzyloxy(vinyl)carbamate **5c** (311 mg, 1.00 mmol) and *tert*-butyl diazoacetate (31.6 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/7 – 1/3(v/v)) as an eluent to give the desired product in 77% yield (65.5 mg, 0.15 mmol) as pale yellow liquid. $[\alpha]_D^{25} = -30.0$ (c 0.95, CHCl₃). *trans/cis* = 86/14, 97% *trans* ee, >99% *cis* ee. ¹H NMR (400 MHz, CDCl₃) (*trans* isomer) δ 7.28–7.43 (m, 10H), 5.23 (d, 4H, *J* = 7.6 Hz), 3.10–3.18 (m, 1H), 1.76–1.83 (m, 1H), 1.50–1.55 (m, 1H), 1.38 (s, 9H), 1.12–1.17

(m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 153.4, 135.1, 128.7, 128.6, 128.5, 128.3, 81.1, 68.9, 35.7, 28.0, 25.7, 18.1 ppm. ^1H NMR (400 MHz, CDCl_3) (*cis* isomer) δ 7.28–7.43 (m, 10H), 5.13–5.32 (m, 4H), 2.98–3.30 (m, 1H), 1.96–2.30 (m, 1H), 1.42–1.53 (m, 1H), 1.37 (s, 9H), 0.86–0.93 (m, 1H) ppm. IR (neat) ν 3070, 3024, 2980, 2905 1802, 1750, 1734 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALPAK IA), UV detector 230 nm, eluent: Hex/IPA = 10/1, Flow Rate = 0.50 mL/min. t_R = 16.5 min (major product for *trans* isomer), t_R = 19.5 min (minor product for *trans* isomer), t_R = 24 min (major product for *cis* isomer), t_R = 31.5 min (minor product for *cis* isomer). Anal. $\text{C}_{24}\text{H}_{27}\text{NO}_6$, Found: C 67.44, H 6.52, N 3.69%; Calcd: C 67.44, H 6.52, N 3.69%.

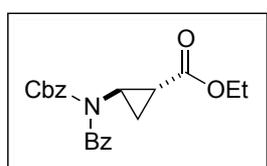


(1R,2R)-(Ethyl 2-((di-*tert*-butoxycarbonyl)amino)cyclopropanecarboxylate) (7h). This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between *tert*-butyl *tert*-butoxycarbonyl(vinyl)carbamate **5d** (243 mg, 1.00 mmol) and ethyl diazoacetate (26.8 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4 (v/v)) as an eluent to give the desired product in 88% yield (57.9 mg, 0.17 mmol) as clear liquid. $[\alpha]_D^{20} = -34.0$ (c 1.16, CHCl_3) *trans/cis* = 91/9, 96% *trans* ee, 84% *cis* ee. ^1H NMR (400 MHz, CDCl_3) (*trans* isomer) δ 4.05–4.18 (m, 2H), 3.01–3.08 (m, 1H), 1.77–1.84 (m, 1H), 1.51–1.59 (m, 1H), 1.48 (s, 18H), 1.26 (t, $J = 7.2$ Hz, 3H), 1.15–1.22 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) (*trans* isomer) δ 172.2, 152.1, 82.9, 60.9, 36.2, 28.1, 25.0, 18.7, 14.3 ppm. ^1H NMR (400 MHz, CDCl_3) (*cis* isomer) δ 4.05–4.18 (m, 2H), 2.89–2.97 (m, 1H), 1.97–2.05 (m, 1H), 1.47 (s, 18H), 1.41–1.47 (m, 1H), 1.28–1.33 (m, 1H), 1.26 (t, $J = 7.2$ Hz, 3H) ppm. IR (neat) ν 2987, 2942, 1802, 1742 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALPAK IC), UV detector 230 nm, eluent: Hex/IPA = 50/1, Flow Rate = 1.00 mL/min. t_R = 19.1 min (minor product for *cis* isomer), t_R = 27.5 min (major product for *trans* isomer), t_R = 39.3 min (major product for *cis* isomer), t_R = 41.7 min (minor product for *trans* isomer). Anal. $\text{C}_{16}\text{H}_{27}\text{NO}_6$, Found: C 58.18, H 8.08, N 4.48%; Calcd: C 58.34, H 8.26, N 4.25%.



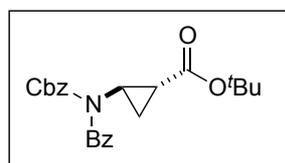
(*tert*-butyl 2-((di-*tert*-butoxycarbonyl)amino)cyclopropanecarboxylate) (7i). This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between *tert*-butyl *tert*-butoxycarbonyl(vinyl)carbamate **5d** (243 mg, 1.00 mmol) and *tert*-butyl diazoacetate (31.6 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4 (v/v)) as an eluent to give the desired product in 72% yield

(51.4 mg, 0.14 mmol) as clear liquid. $[\alpha]_{\text{D}}^{20} = -38.0$ (c 1.16, CHCl_3) (*trans/cis* = 90/10, 95% *trans* ee. ^1H NMR (400 MHz, CDCl_3) (*trans* isomer) δ 2.98–2.03 (m, 1H), 1.68–1.73 (m, 1H), 1.49 (s, 18H), 1.45–1.48 (m, 1H), 1.43 (s, 9H), 1.07–1.13 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) (*trans* isomer) δ 171.3, 152.2, 82.8, 81.0, 35.7, 28.2, 28.1, 26.0, 18.6 ppm. ^1H NMR (400 MHz, CDCl_3) (*cis* isomer) δ 2.82–2.90 (m, 1H), 1.85–1.94 (m, 1H), 1.55–1.60 (m, 1H), 1.48 (s, 18H), 1.41 (s, 9H), 1.35–1.39 (m, 1H) ppm. IR (neat) ν 2987, 2942, 1802, 1742 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALPAK AD-3), UV detector 230 nm, eluent: Hex/ IPA= 50/1, Flow Rate = 1.00 mL/min. tR = 19.5 min (major product for *trans* isomer), tR = 26.5 min (minor product for *trans* isomer). Anal. $\text{C}_{18}\text{H}_{31}\text{NO}_6$, Found: C 60.59, H 8.42, N 3.97%; Calcd: C 60.48, H 8.74, N 3.92%.



(Ethyl 2-(N-(benzyloxycarbonyl)benzamido)cyclopropanecarboxylate) (7j).

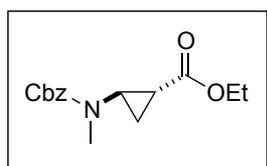
This compound was prepared according to the typical procedure for asymmetric cyclopropanation reaction between benzyl benzoyl(vinyl)carbamate **5e** (281 mg, 1.00 mmol) and ethyl diazoacetate (26.8 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/2(v/v)) as an eluent to give the desired product in 90% yield (66.0 mg, 0.18 mmol) as a white solid. $[\alpha]_{\text{D}}^{25} = -29.0$ (c 1.00, CHCl_3). *trans/cis* = 92/8, 97% *trans* ee. ^1H NMR (400 MHz, CDCl_3) δ 7.48–7.57 (m, 3H), 7.34–7.50 (m, 2H), 7.25–7.30 (m, 3H), 7.02–7.08 (m, 2H), 5.06 (s, 2H), 4.05–4.20 (m, 2H), 3.33–3.39 (m, 1H), 1.94–2.00 (m, 1H), 1.62–1.70 (m, 1H), 1.25–1.31 (m, 1H), 1.24 (t, $J = 7.2$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 171.4, 154.6, 136.0, 134.6, 132.4, 128.5, 128.4, 68.8, 61.0, 36.2, 24.2, 17.4, 14.3 ppm. IR (neat) ν 3070, 3032, 2980, 2905, 1742, 1679 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALCEL OJ-H), UV detector 230 nm, eluent: Hex/IPA = 8/1, Flow Rate = 1.00 mL/min. tR = 105.3 min (major product for *trans* isomer), tR = 117.7 min (minor product for *trans* isomer). Anal. $\text{C}_{21}\text{H}_{21}\text{NO}_5$, Found: C 68.67, H 5.89, N 4.07%; Calcd: C 68.65, H 5.76, N 3.81%.



(tert-butyl 2-(N-(benzyloxycarbonyl)benzamido)cyclopropanecarboxylate) (7k).

This compound was prepared according to the typical procedure for asymmetric cyclopropanation reactions between benzyl benzoyl(vinyl)carbamate **5e** (281 mg, 1.00 mmol) and *tert*-butyl diazoacetate (31.6 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/4(v/v)) as an eluent to give the desired product in 77% yield (61.0 mg, 0.15 mmol) as a white solid. $[\alpha]_{\text{D}}^{20} = -67.0$ (c 1.04, CHCl_3). *trans/cis* = 94/6, 97% *trans* ee, 97% *cis* ee. ^1H NMR (400 MHz, CDCl_3) δ 7.55–7.60 (m, 2H), 7.48–7.52 (m, 1H), 7.34–7.40 (m, 2H),

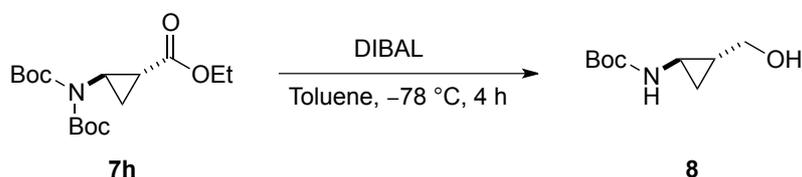
7.23–7.30 (m, 3H), 7.06–7.10 (m, 2H), 5.08 (s, 2H), 3.28–3.33 (m, 1H), 1.85–1.92 (m, 1H), 1.51–1.57 (m, 1H), 1.42 (s, 9H), 1.18–1.25 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 173.3, 171.0, 154.6, 136.0, 134.7, 132.4, 128.5, 128.4, 81.1, 68.7, 36.0, 28.1, 25.4, 17.2 ppm. IR (neat) ν 3070, 3032, 2980, 2905, 1750, 1734, 1704 cm^{-1} . The ee values were determined by HPLC analysis: Column (CHIRALPAK IC), UV detector 230 nm, eluent: Hex/IPA = 9/1, Flow Rate = 1.00 mL/min. t_R = 34.3 min (major product for *trans* isomer), t_R = 56.5 min (minor product for *trans* isomer), t_R = 11.6 min (major product for *cis* isomer), t_R = 14.8 min (minor product for *cis* isomer). Anal. $\text{C}_{23}\text{H}_{25}\text{NO}_5$, Found: C 69.88, H 6.44, N 3.76%; Calcd: C 69.86, H 6.37, N 3.54%.



(Ethyl 2-((benzyloxycarbonyl)(methyl)amino)cyclopropanecarboxylate) (7i). This compound was prepared according to the typical procedure for asymmetric cyclopropanation reactions between benzyl methyl(vinyl)carbamate **5f** (191 mg, 1.00 mmol) and ethyl diazoacetate

(26.8 mg, 0.20 mmol). The resulting mixture was purified by silica gel column chromatography with EtOAc/Hexane (1/2(v/v)) as eluent to give the desired product in 97% yield (54.0 mg, 0.19 mmol) as a white solid. $[\alpha]_{\text{D}}^{25} = -60.0$ (c 1.16, CHCl_3). *trans/cis* = 93/7, 99% *trans* ee. ^1H NMR (400 MHz, CDCl_3) (*trans* isomer) δ 7.28–7.36 (m, 5H), 5.14 (d, $J = 2.8$ Hz, 2H), 4.00–4.18 (m, 2H), 3.07–3.11 (m, 1H), 2.91 (s, 3H), 1.82–1.88 (m, 1H), 1.40–1.47 (m, 1H), 1.20–1.24 (m, 4H) ppm. ^{13}C NMR (100 MHz, CDCl_3) (*trans* isomer) δ 172.3, 157.1, 136.6, 128.5, 128.0, 127.9, 67.4, 60.8, 38.7, 34.7, 23.3, 16.6, 14.3 ppm. IR (neat) ν 3077, 3069, 3034, 2990, 2903, 1729 cm^{-1} . The ee values were determined by HPLC analysis. Column (CHIRALPAK ID), UV detector 230 nm, eluent: Hex/IPA = 30/1, Flow Rate = 0.50 mL/min. t_R = 54.0 min (major product for *trans* isomer), t_R = 57.0 min (minor product for *trans* isomer). Anal. $\text{C}_{15}\text{H}_{19}\text{NO}_4$, Found: C 64.96, H 6.91, N 5.05%; Calcd: C 64.97, H 6.91, N 5.05%.

4. Preparation of (1*R*,2*R*)-2-((*tert*-butoxycarbonyl)amino)cyclopropylmethanol (**8**)



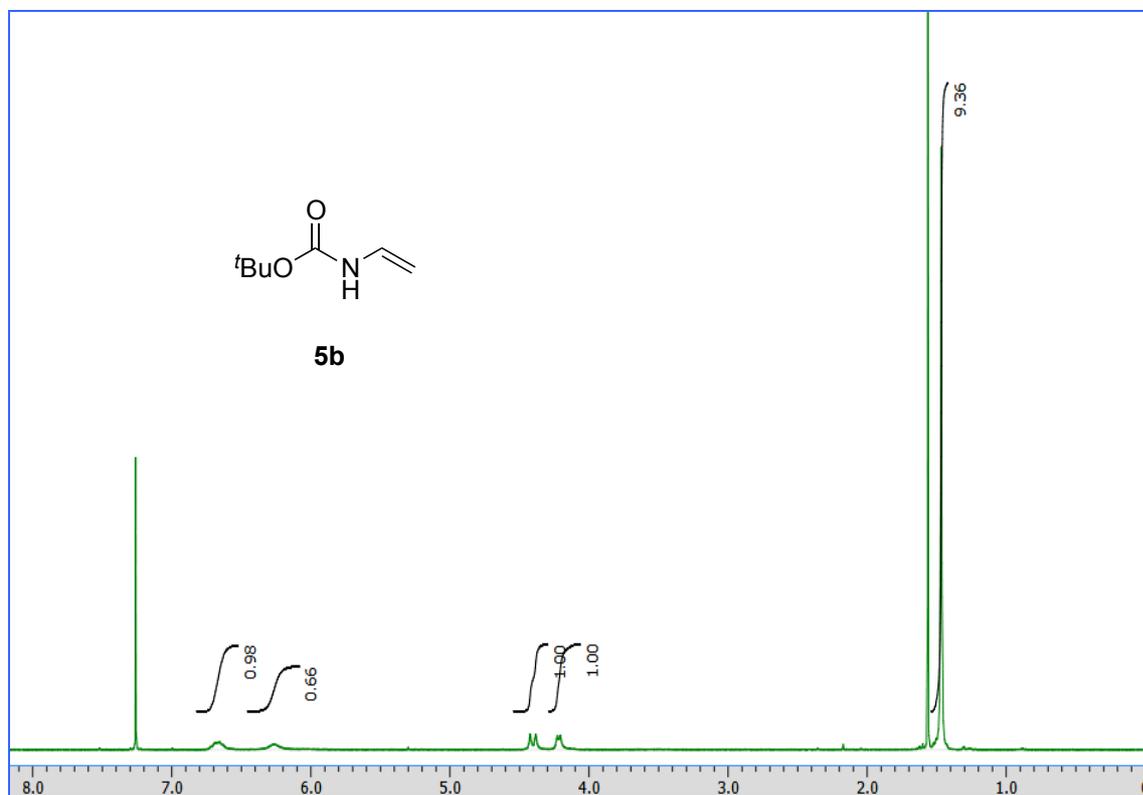
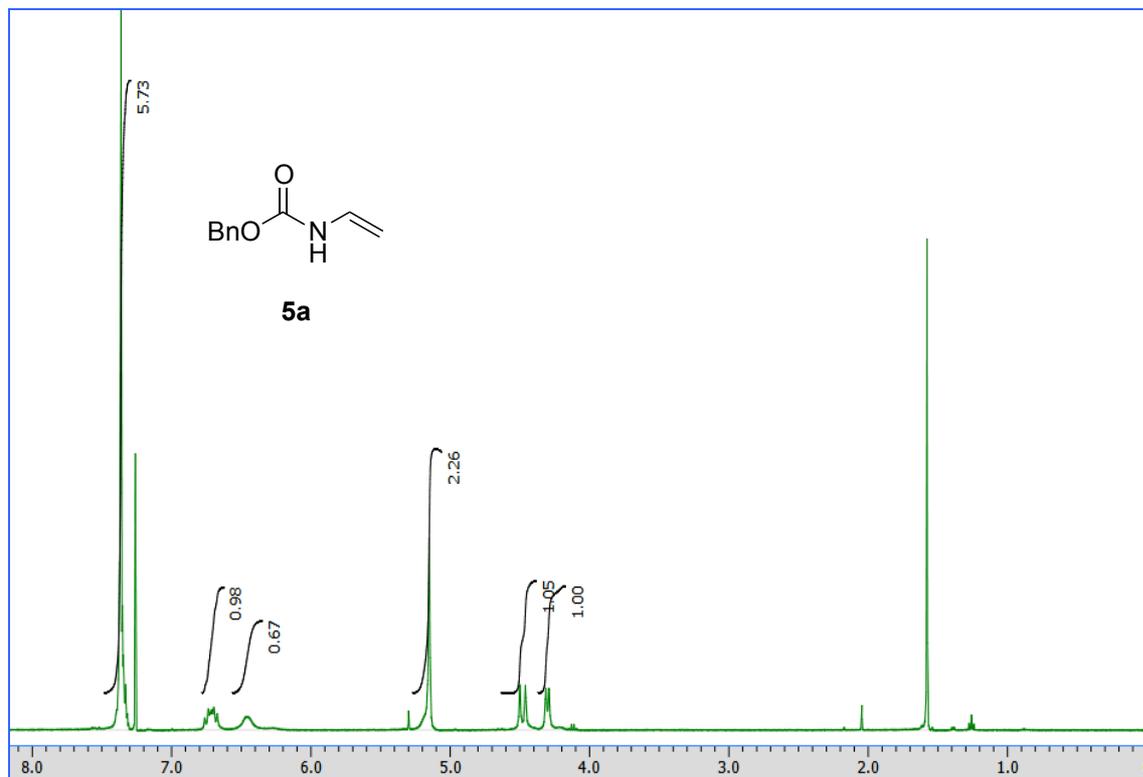
The toluene solution of DIBAL (1 mL, 1.00 mmol, 5.0 equiv) was cooled to -78 $^{\circ}\text{C}$ under argon. A solution of ethyl 2-((di-*tert*-butoxycarbonyl)amino)cyclopropanecarboxylate **7h** (62.8 mg, 0.20 mmol, 1.0 equiv.) in toluene (2 mL) was slowly added at that temperature over a period of 1 h. Stirring at -78 $^{\circ}\text{C}$ was continued for 3h and the reaction was quenched by successive addition of methanol (1 mL of a 10% solution in toluene), methanol (0.1 mL) and water (2 mL). The mixture was allowed to warm

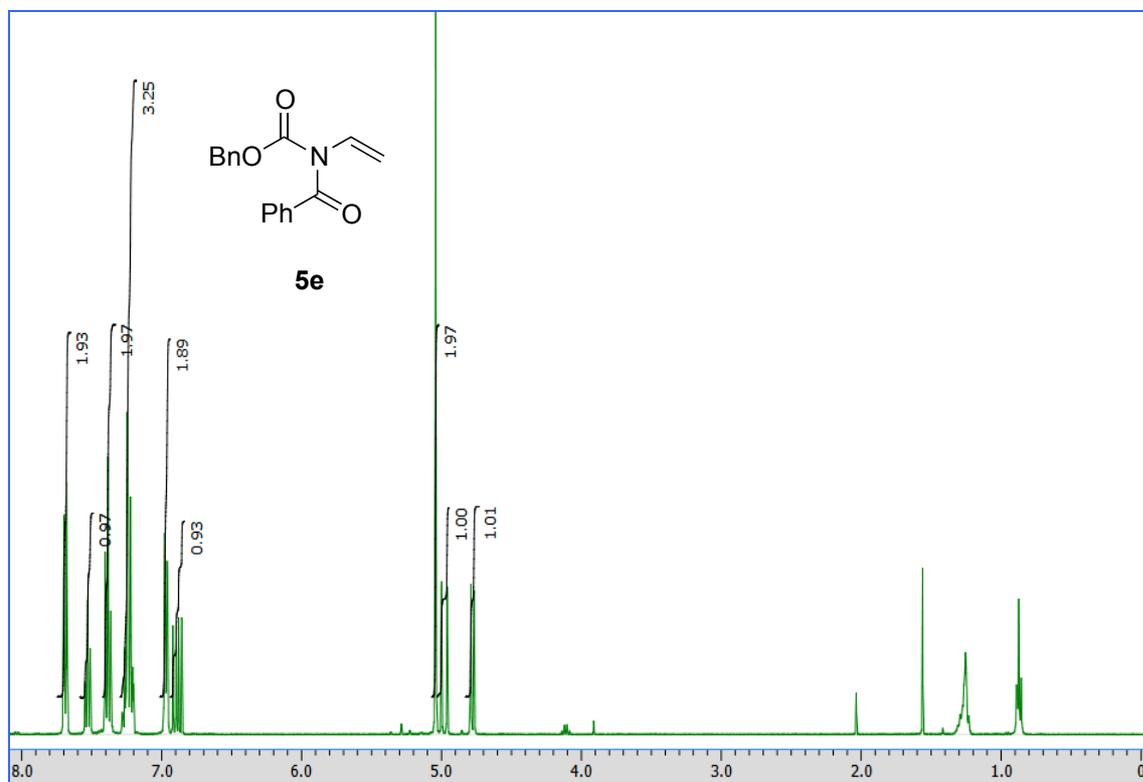
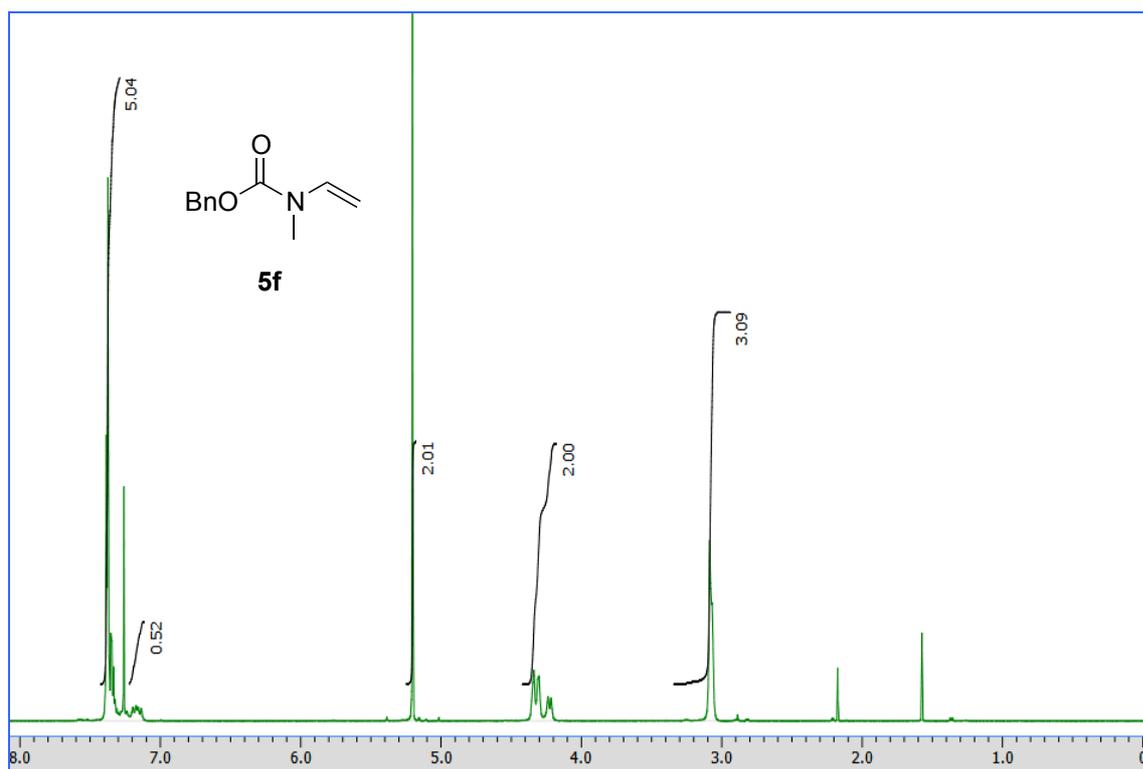
to room temperature. The white precipitate was filtered off and washed with EtOAc. The washing and filtrate were combined, dried (Na₂SO₄) and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography with Hexane/EtOAc (3/1 – 1/1(v/v)) to afford (1*R*,2*R*)-2-((*tert*-butoxycarbonyl)amino)cyclopropylmethanol **8** in 60% yield (22.4 mg, 0.13 mmol). $[\alpha]_D^{21} = +19.0$ (c 1.15, CDCl₃). 96% *trans* ee. ¹H NMR (400 MHz, CDCl₃) δ 4.85 (br s, 1H), 3.84 (br s, 1H), 3.05–3.12 (m, 1H), 2.78 (br s, 1H), 2.28–2.33 (m, 1H), 1.44 (s, 9H), 1.18–1.27 (m, 1H), 0.78–0.83 (m, 1H), 0.69–0.74 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 80.5, 65.0, 28.6, 24.0, 11.4 ppm. The ee values were determined by HPLC analysis. Column (CHIRALPAK AD-3), UV detector 230 nm, eluent: Hex/IPA = 20/1, Flow Rate = 1.00 mL/min. tR = 11.0 min (major product for *trans* isomer), tR = 13.2 min (minor product for *trans* isomer).

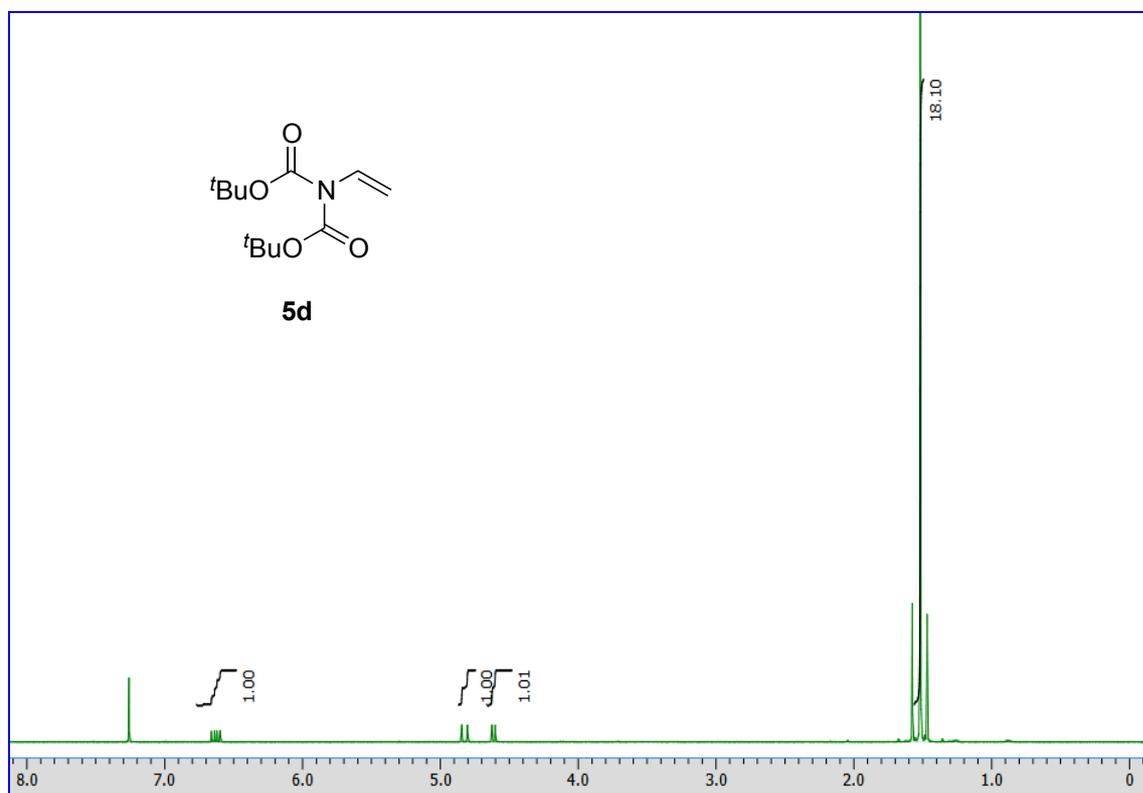
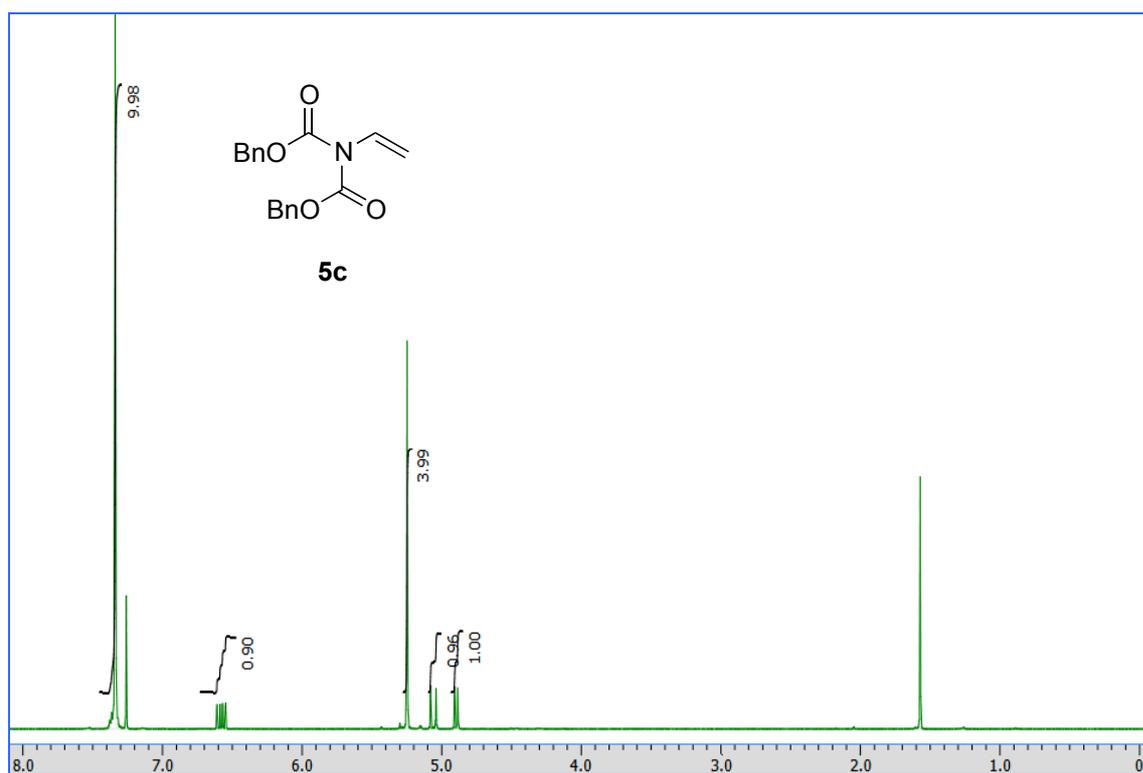
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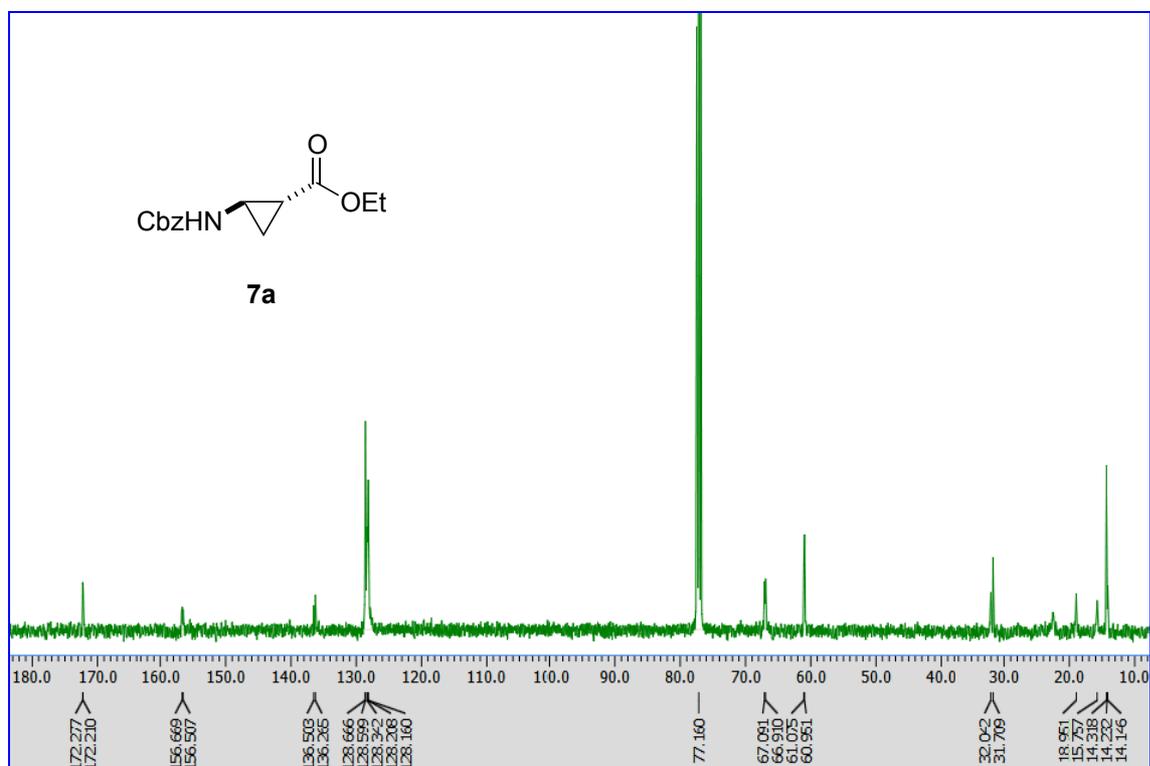
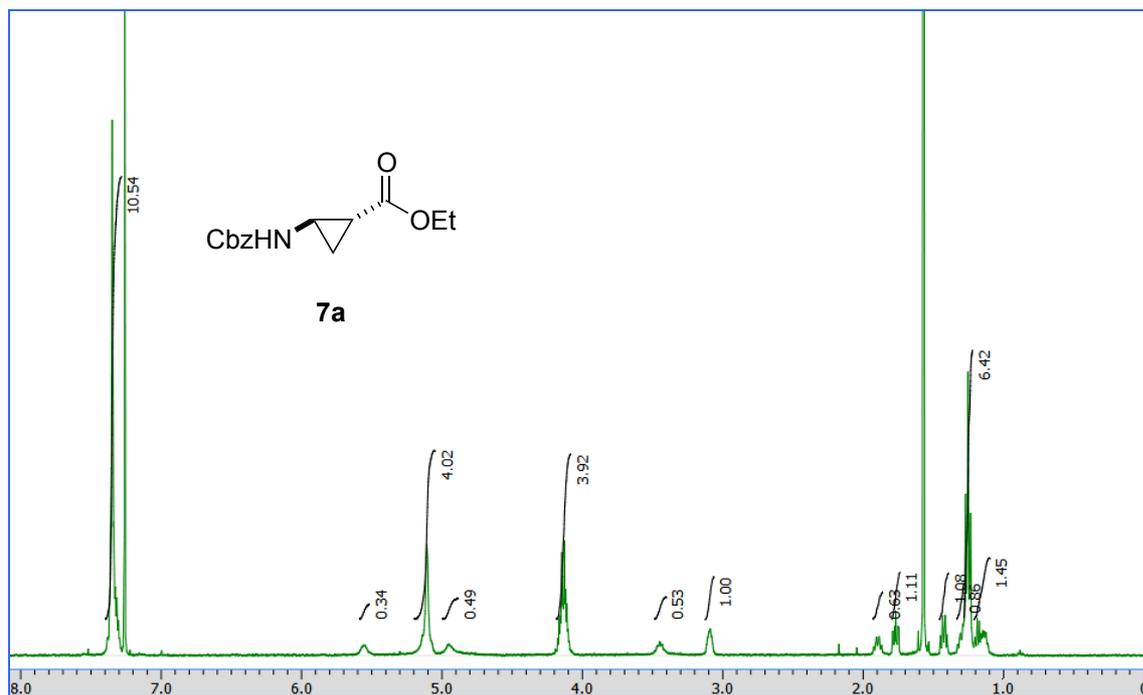
1. Wieber, G. M.; Hegedus, L. S.; Akermark, B.; Michalson, E. T. *J. Org. Chem.* **1989**, *54*, 4649–4653.
2. Terada, M.; Sorimachi, K. *J. Am. Chem. Soc.* **2007**, *129*, 292–293.

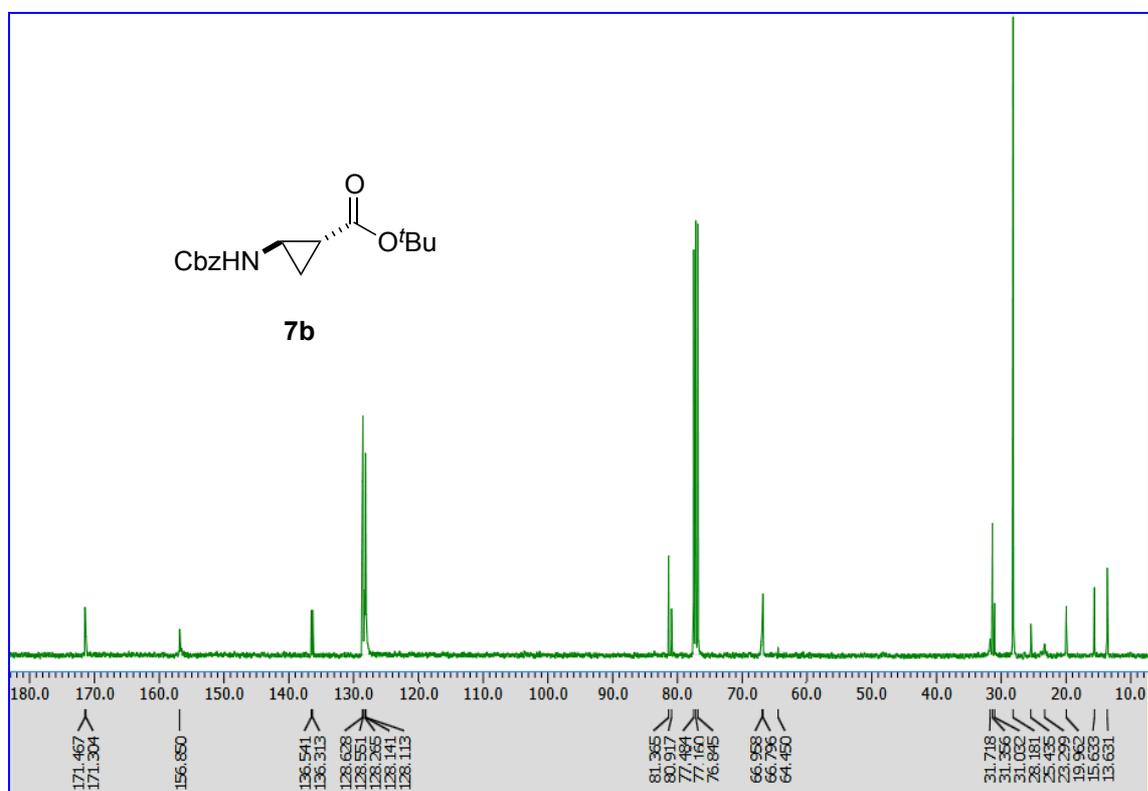
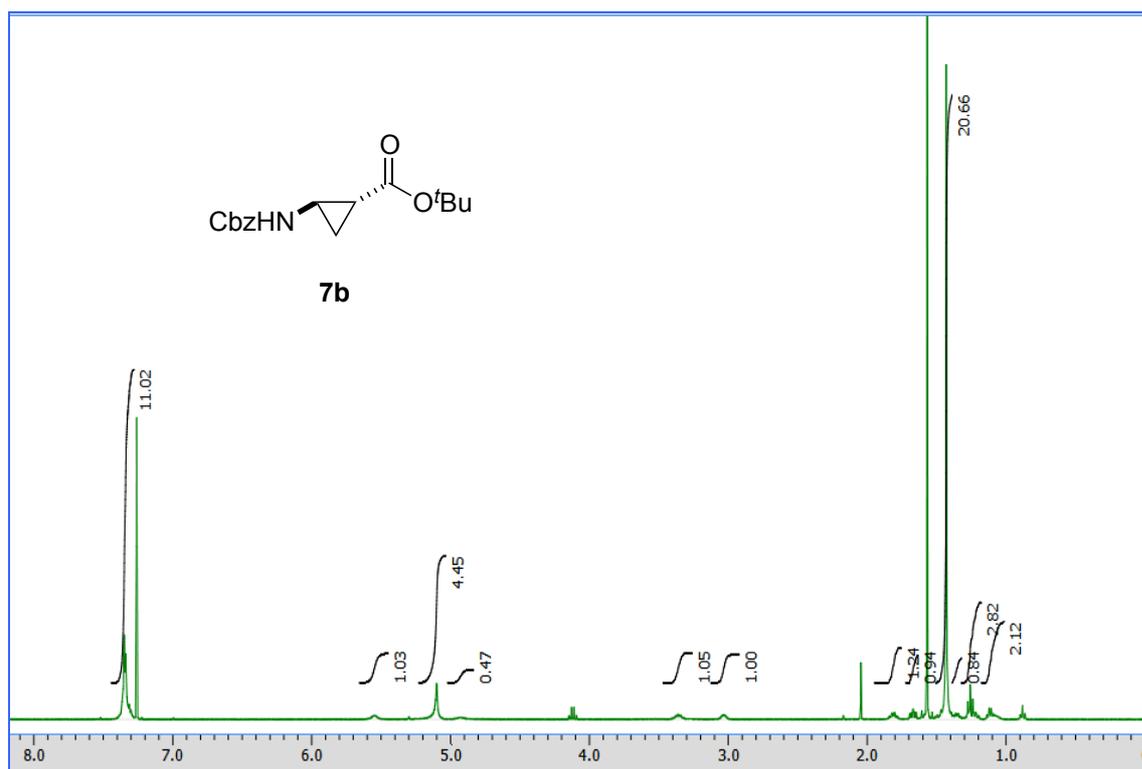
5. NMR Spectral data

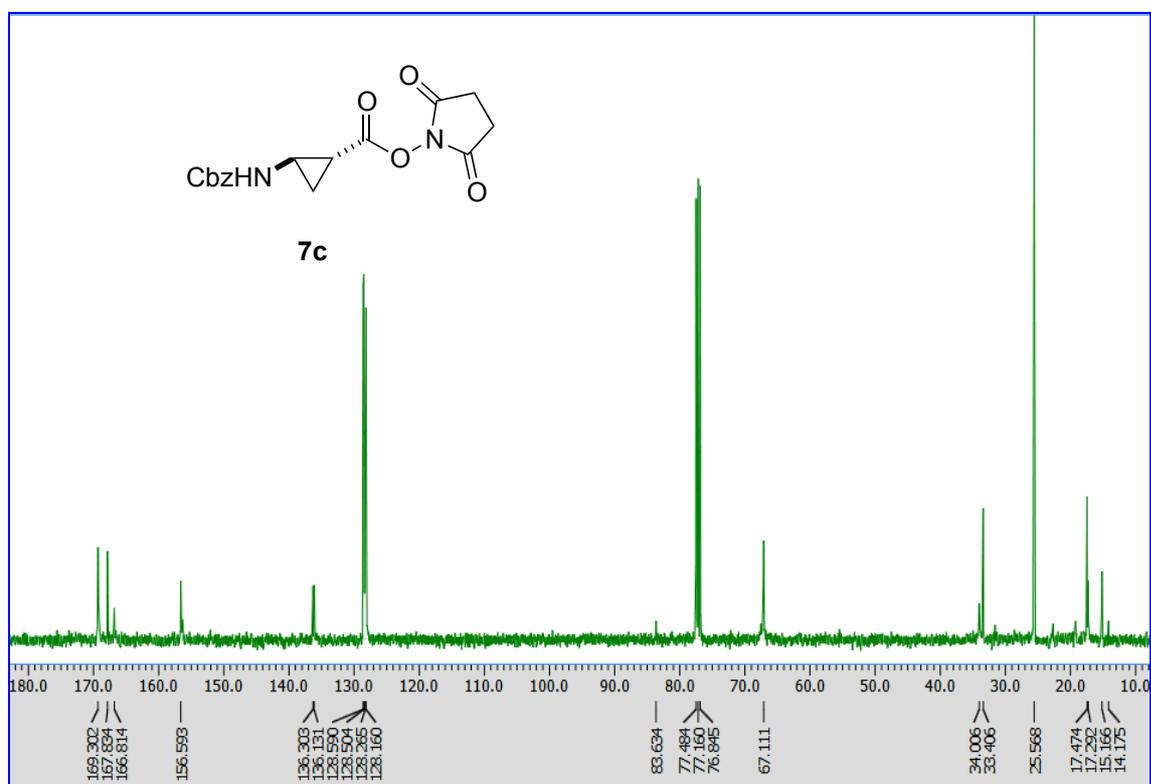
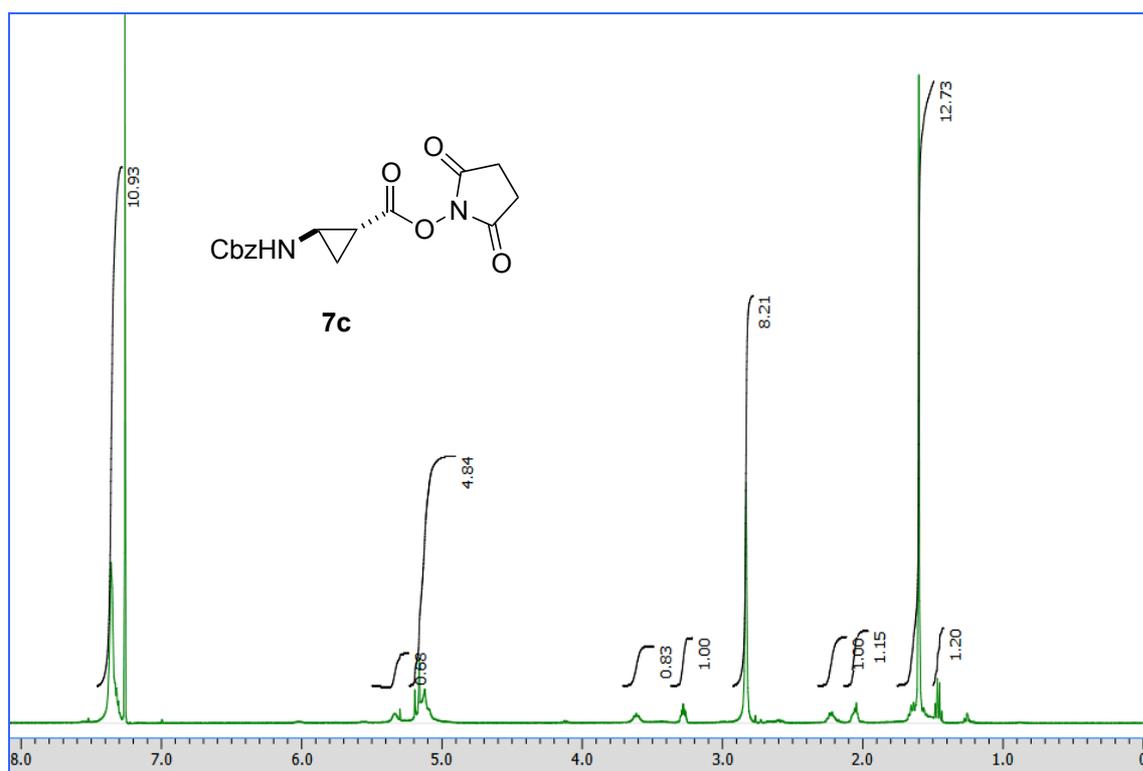


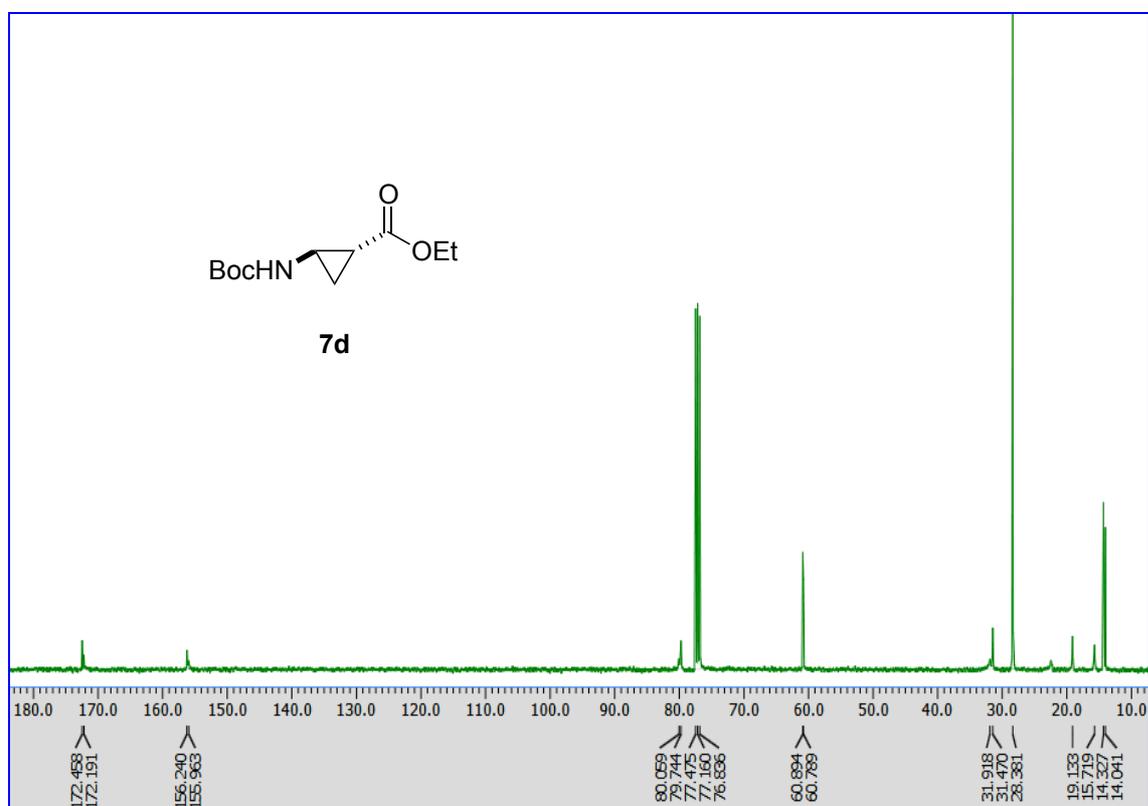
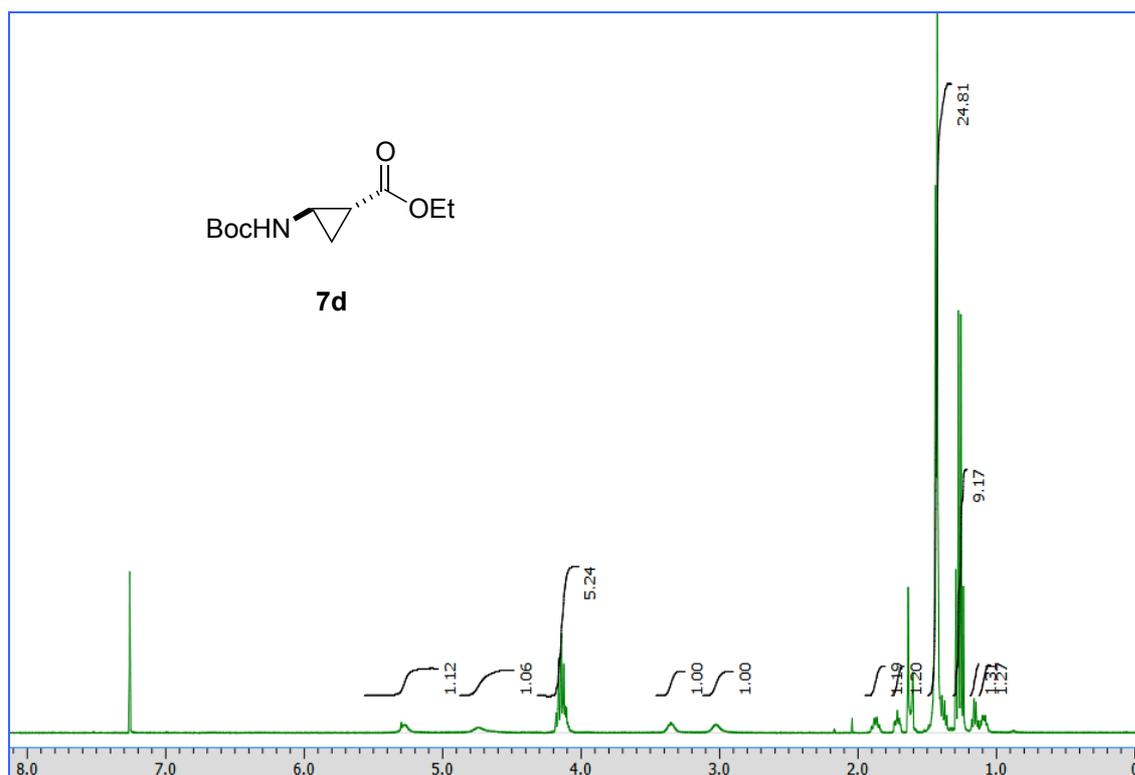


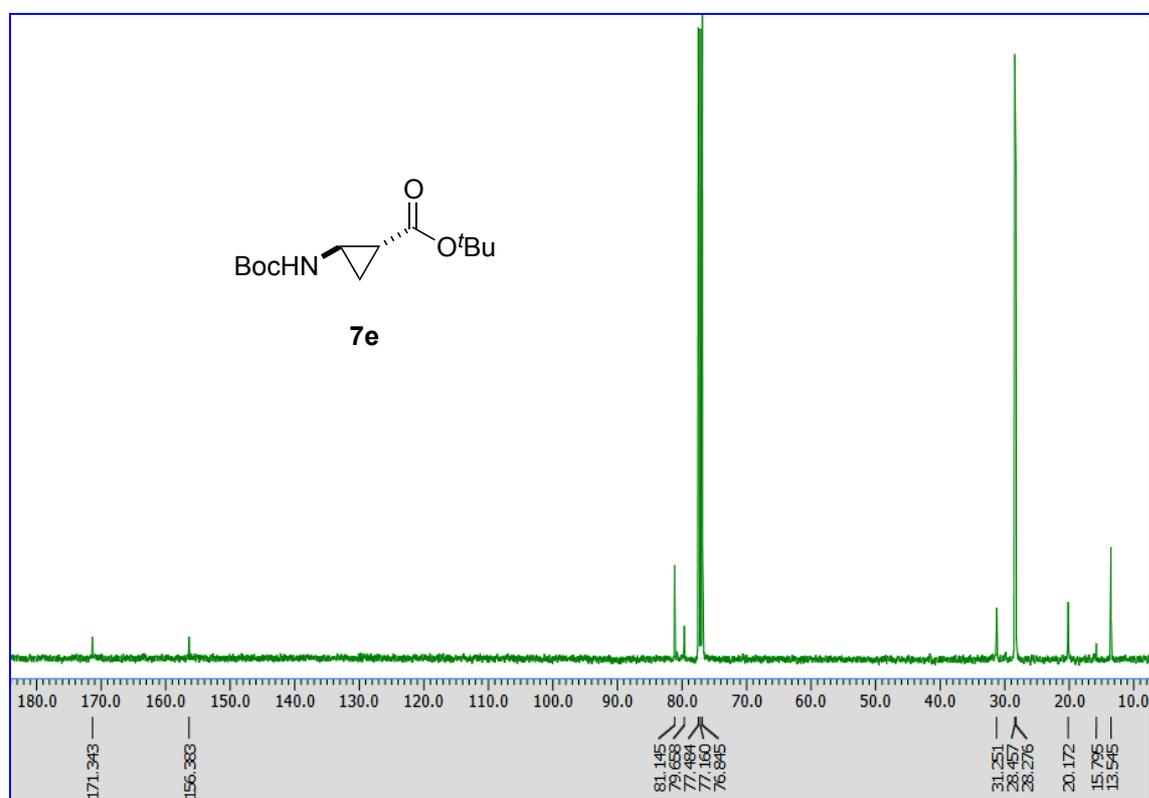
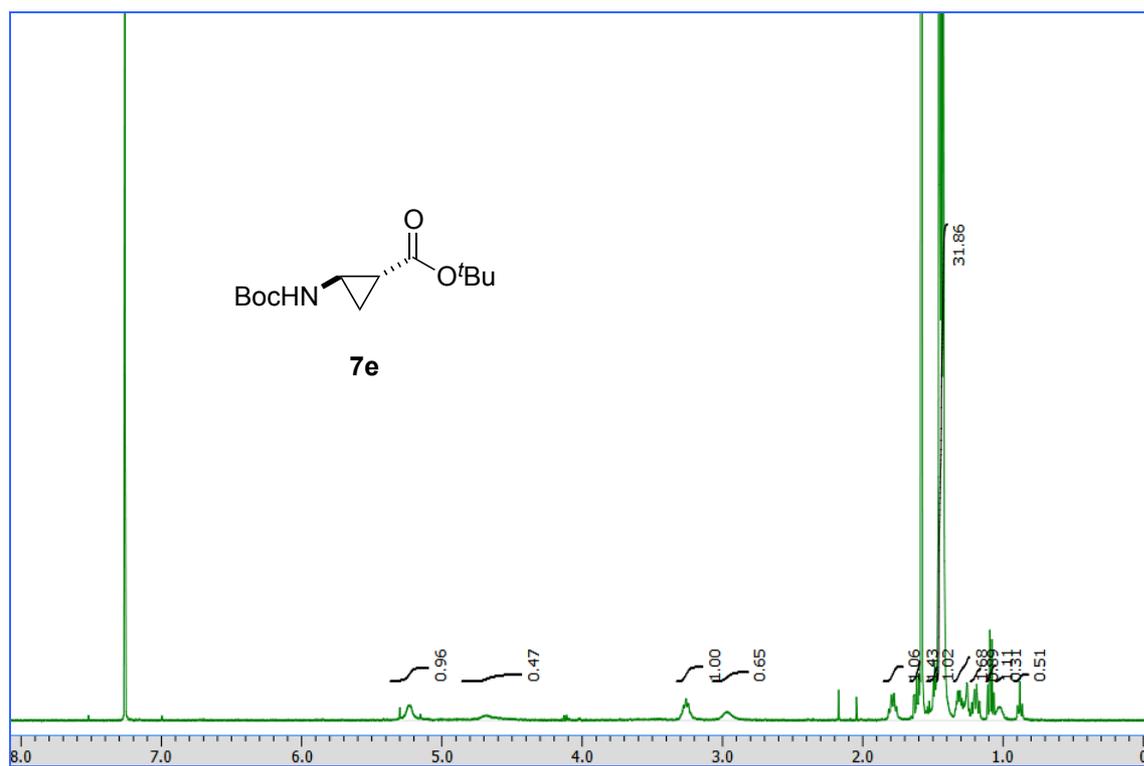


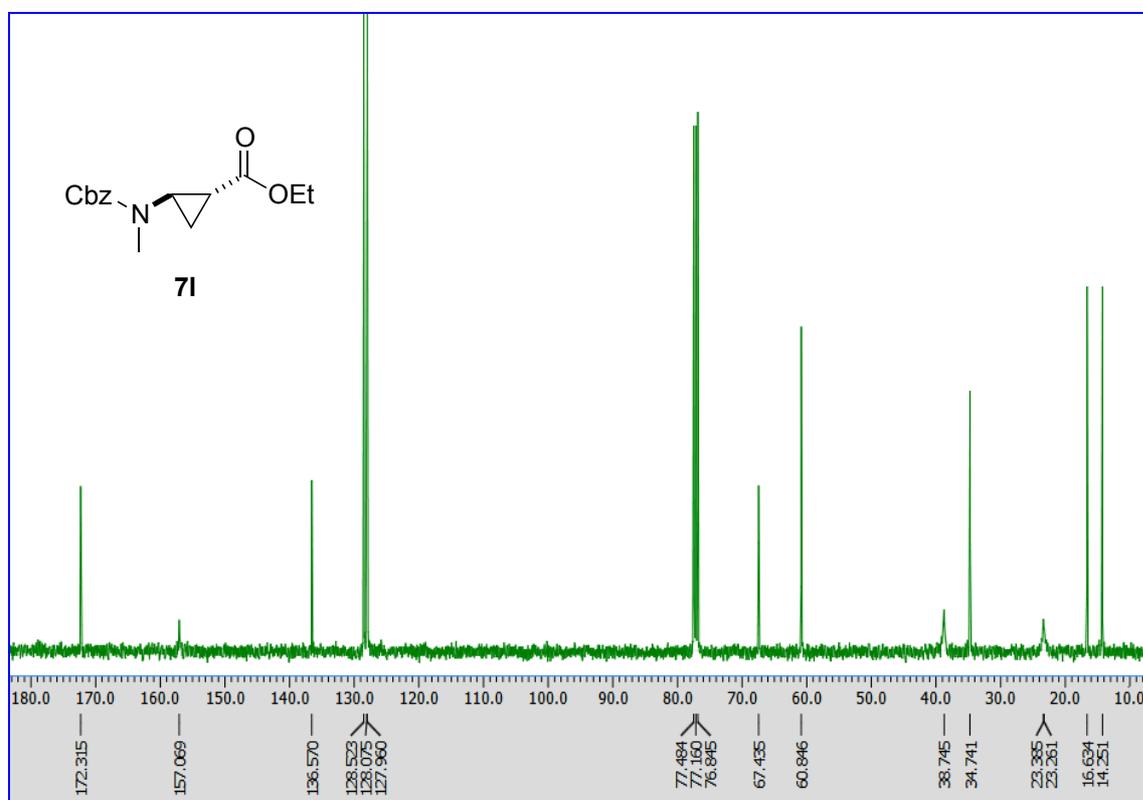
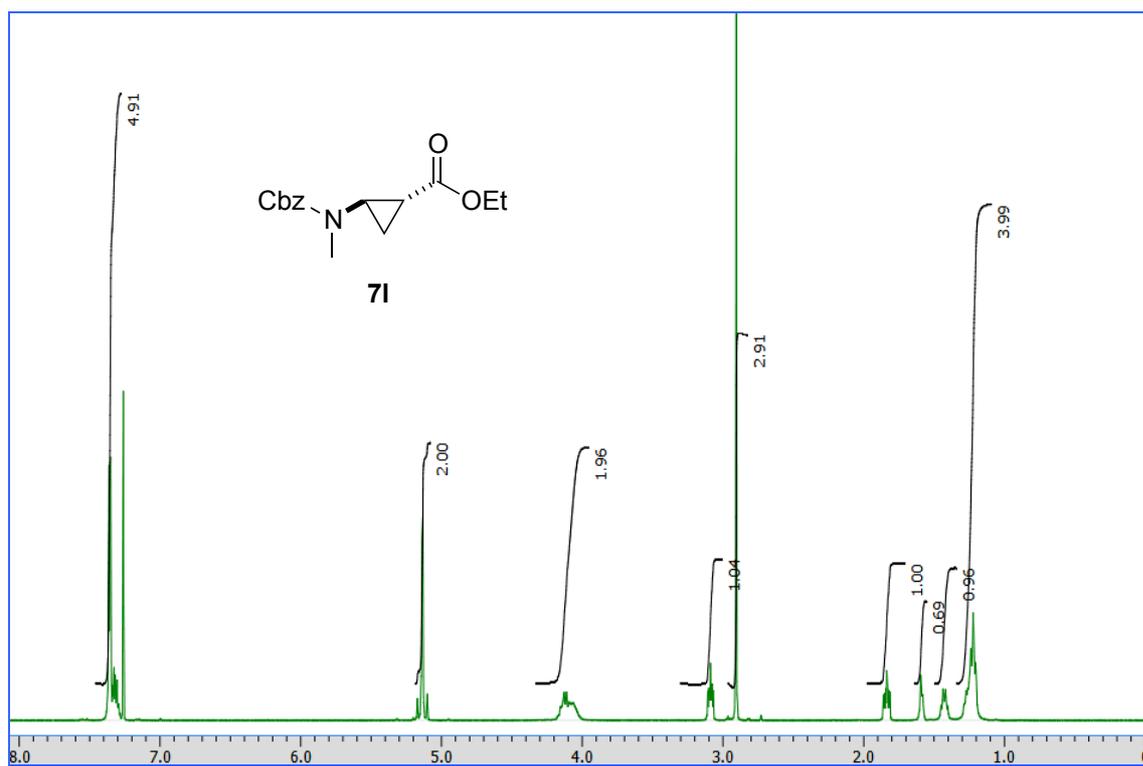


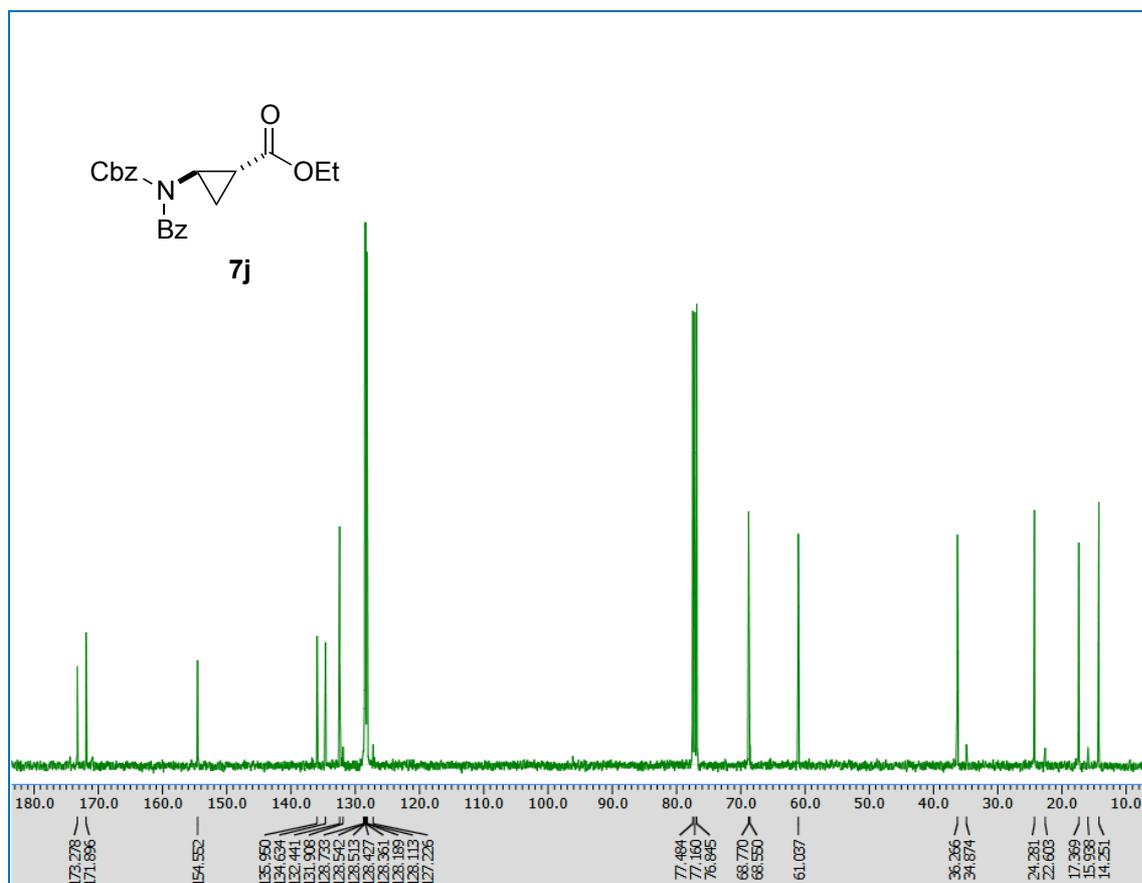
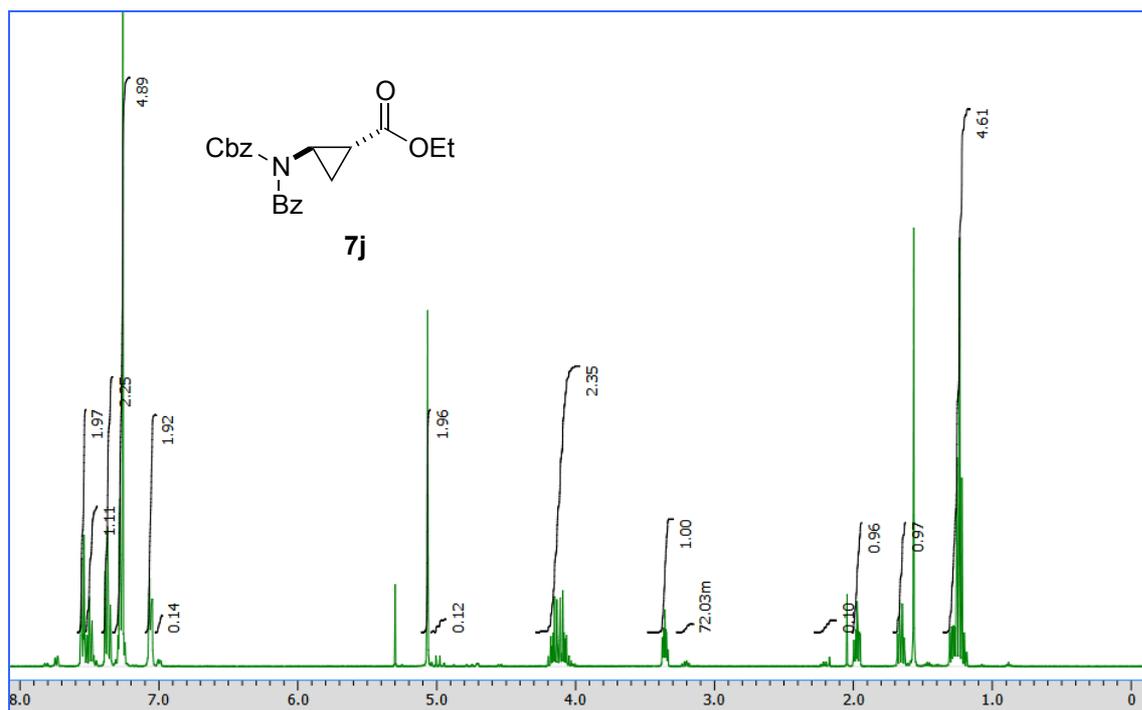


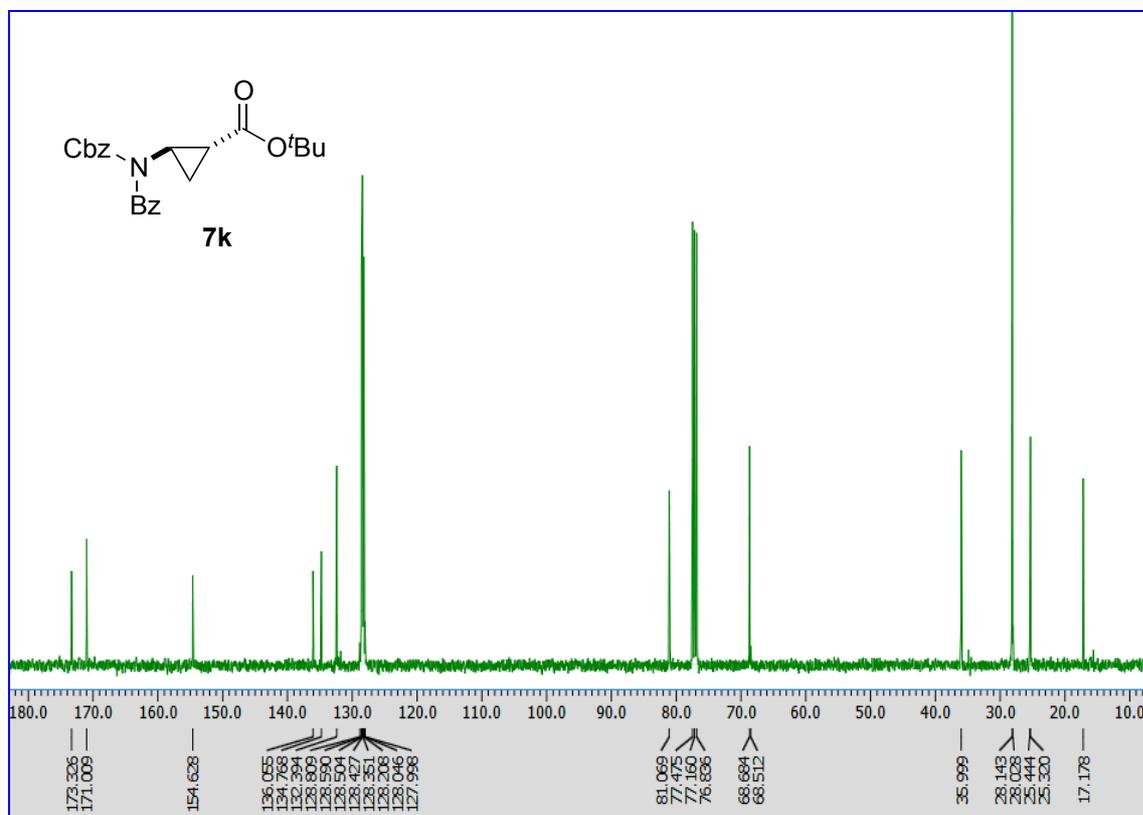
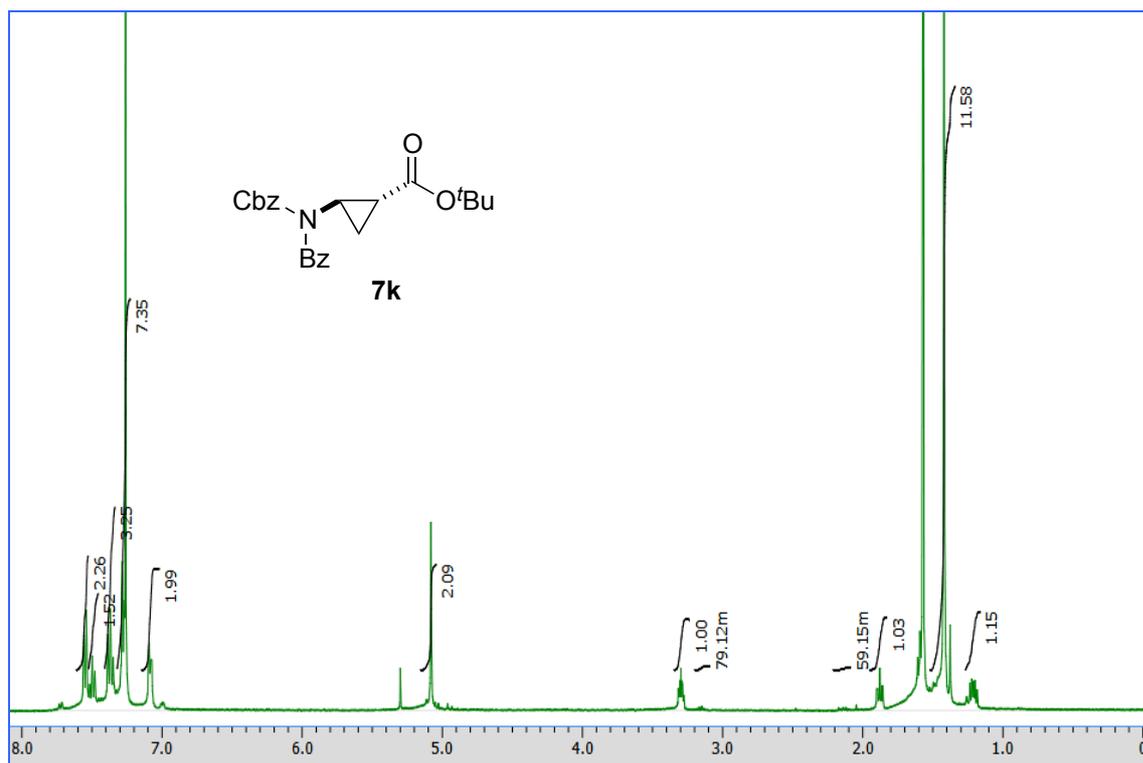


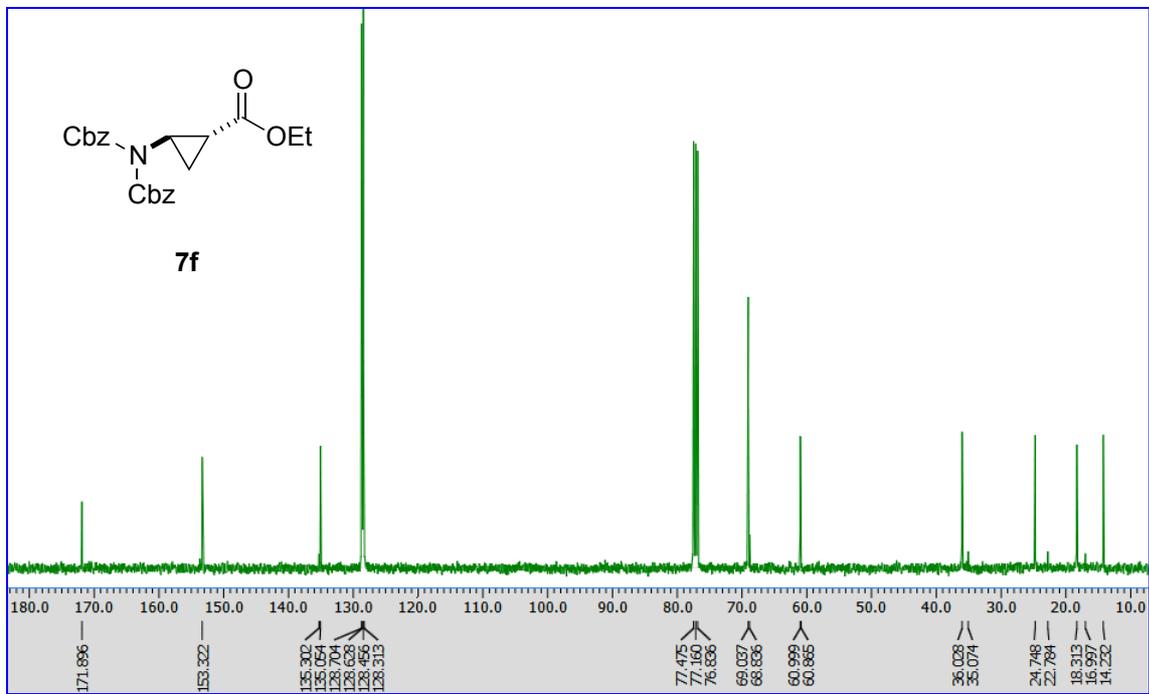
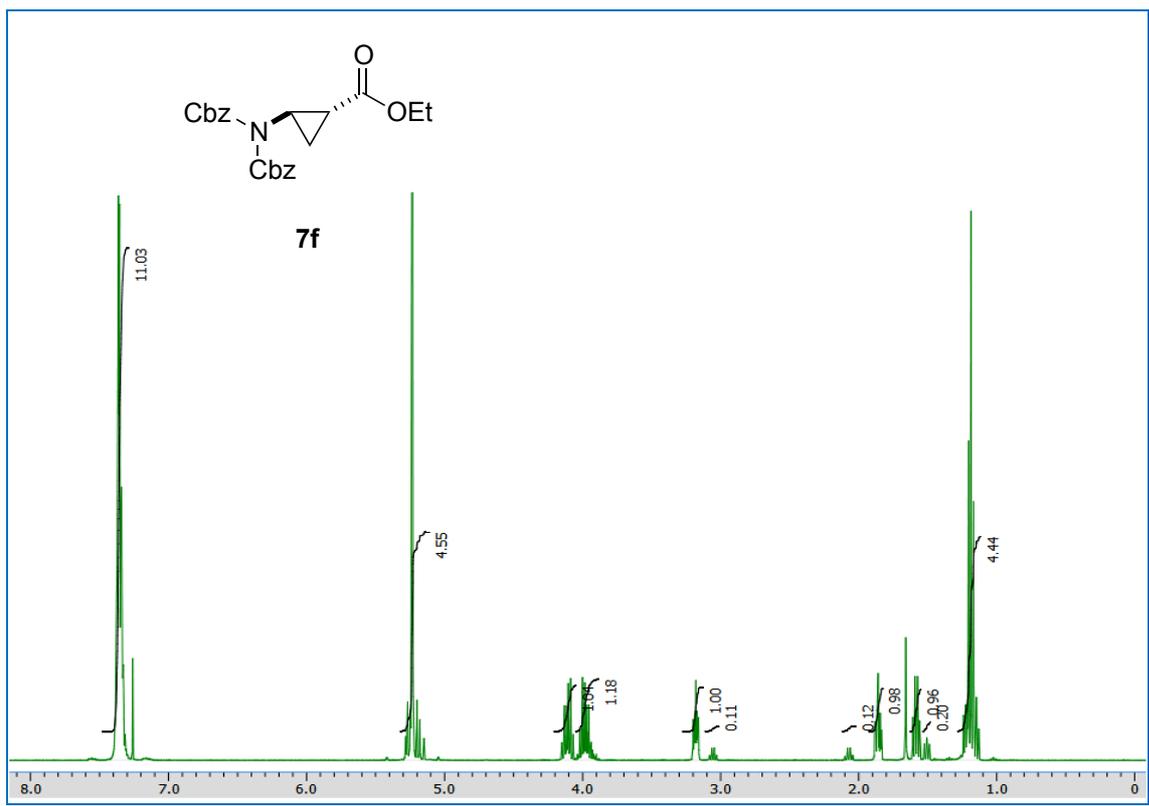


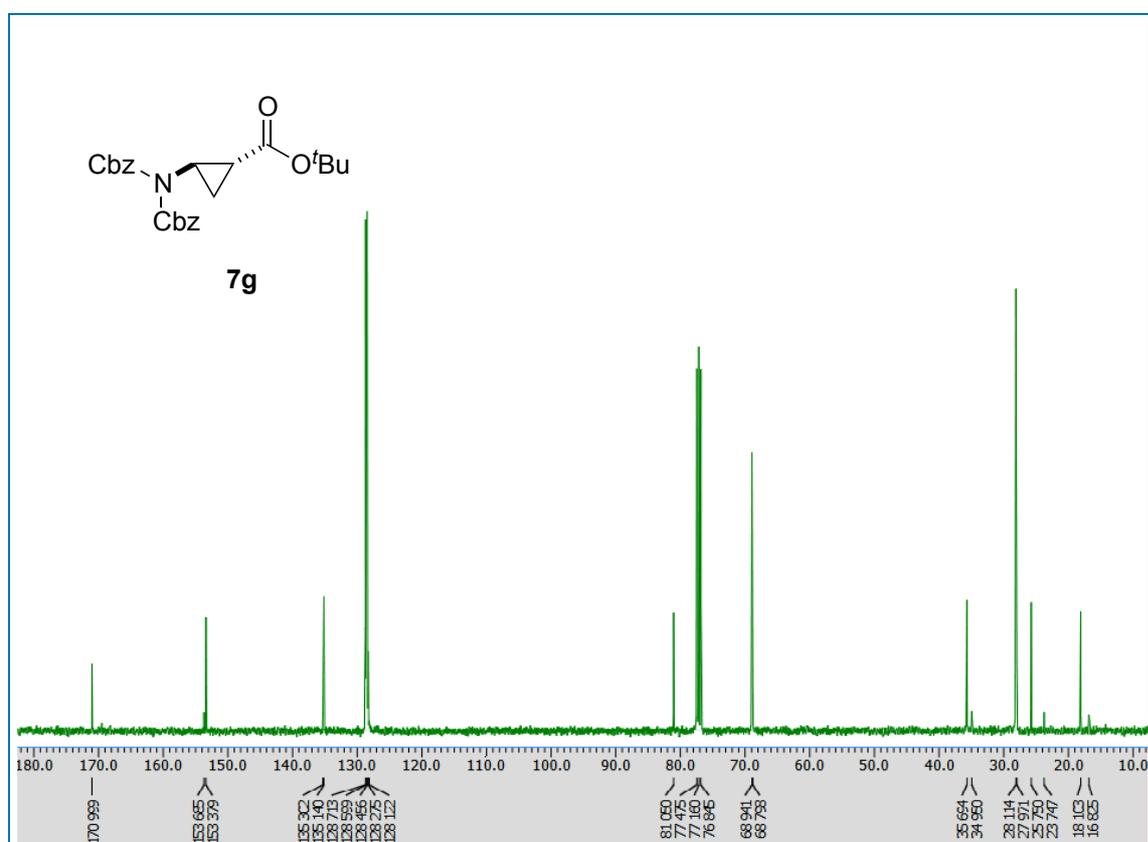
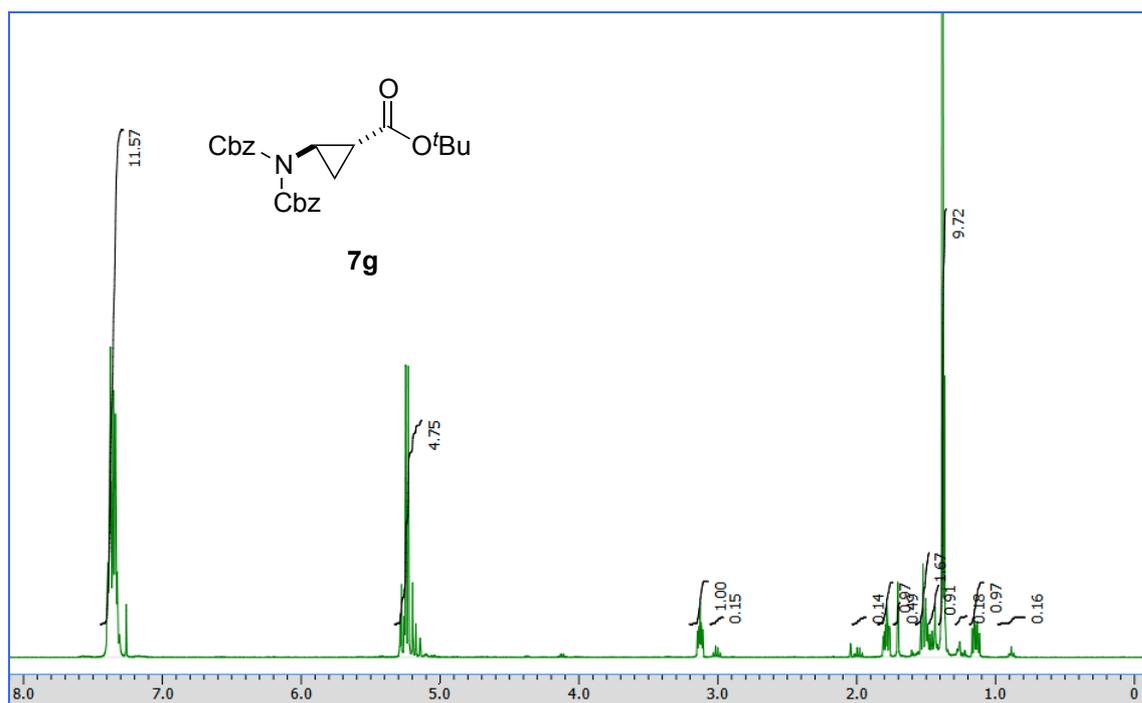


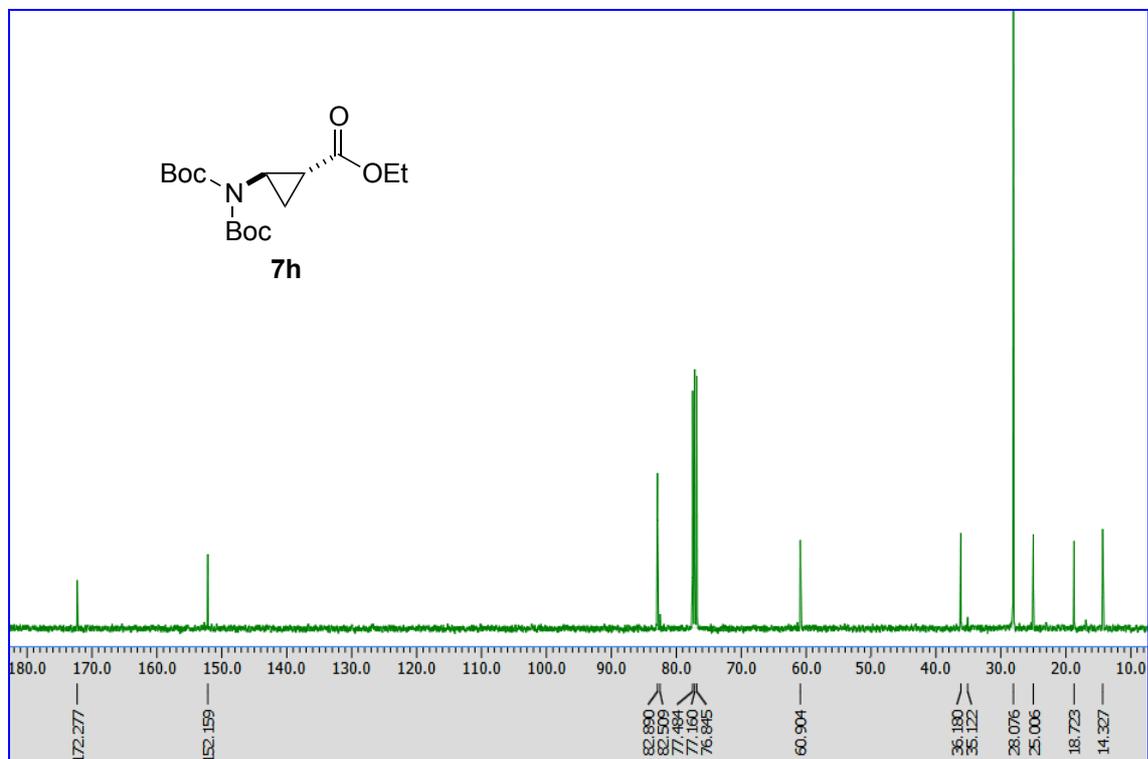
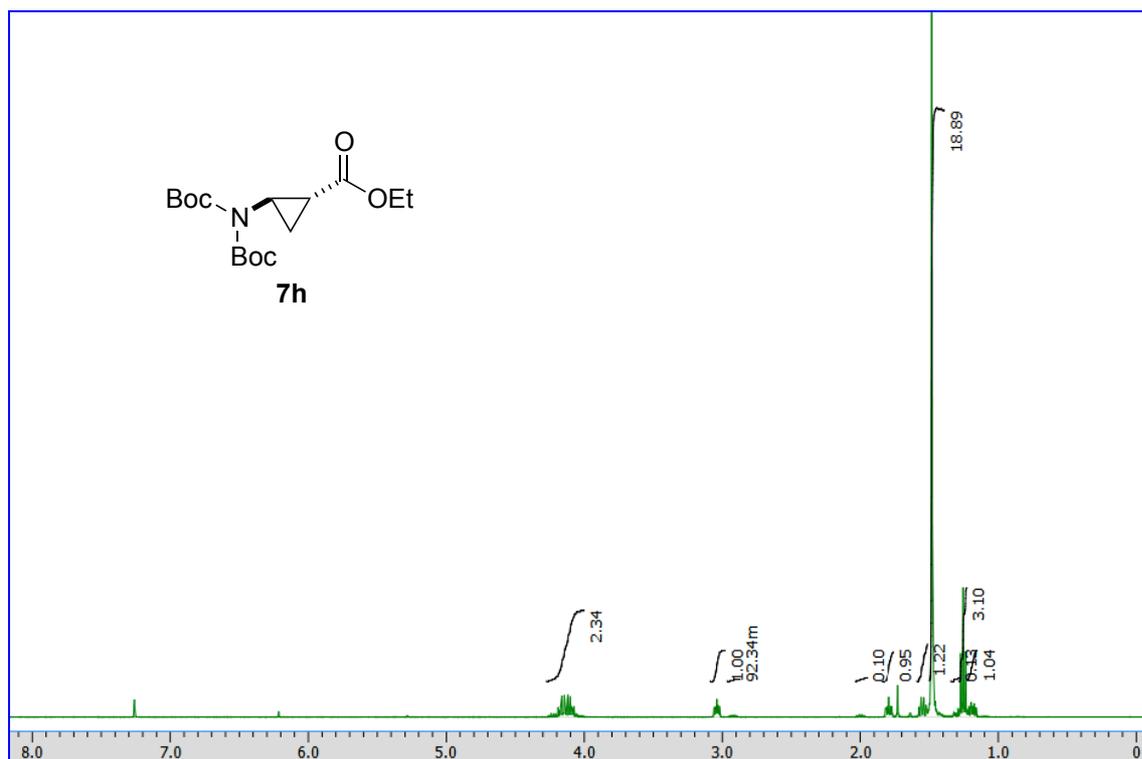


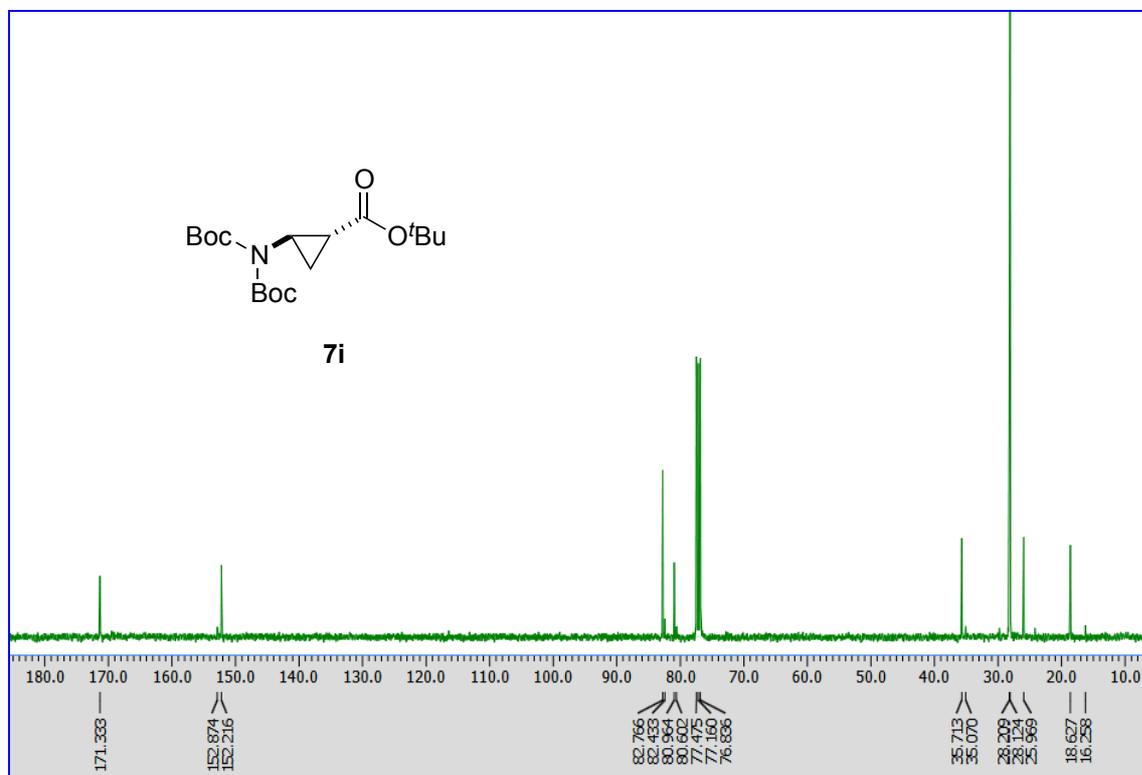
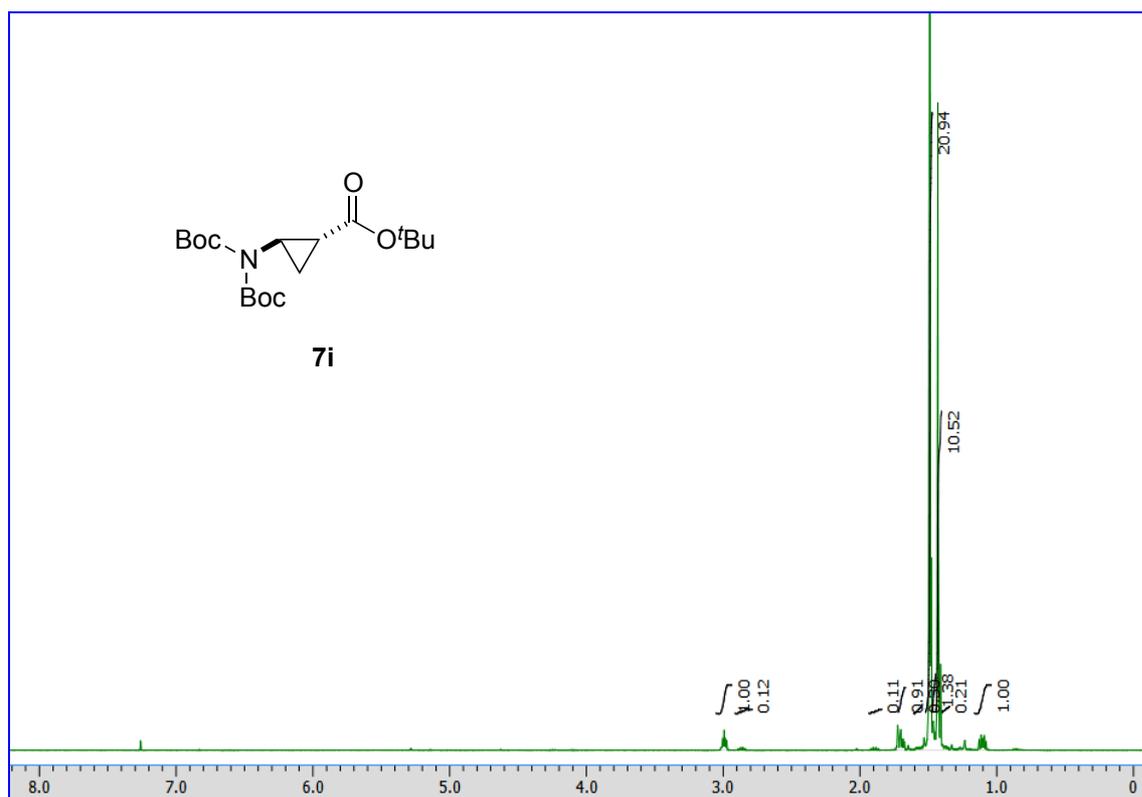


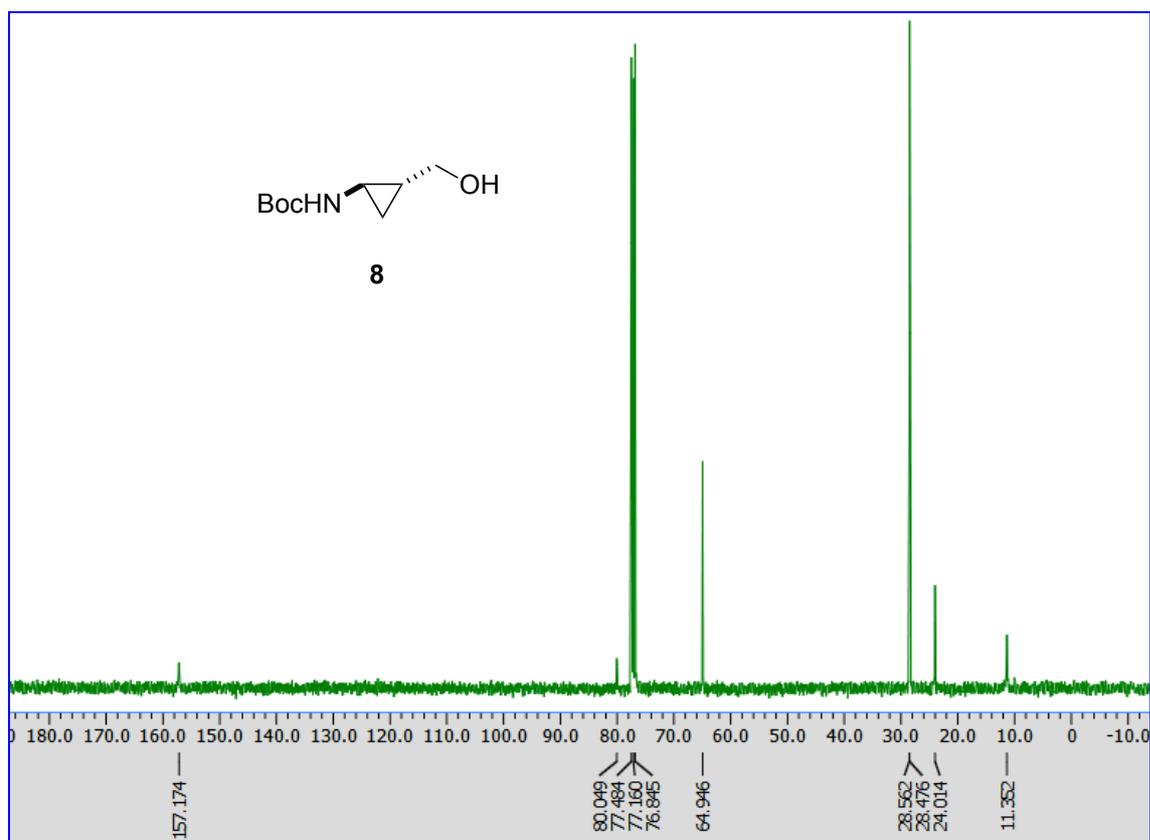
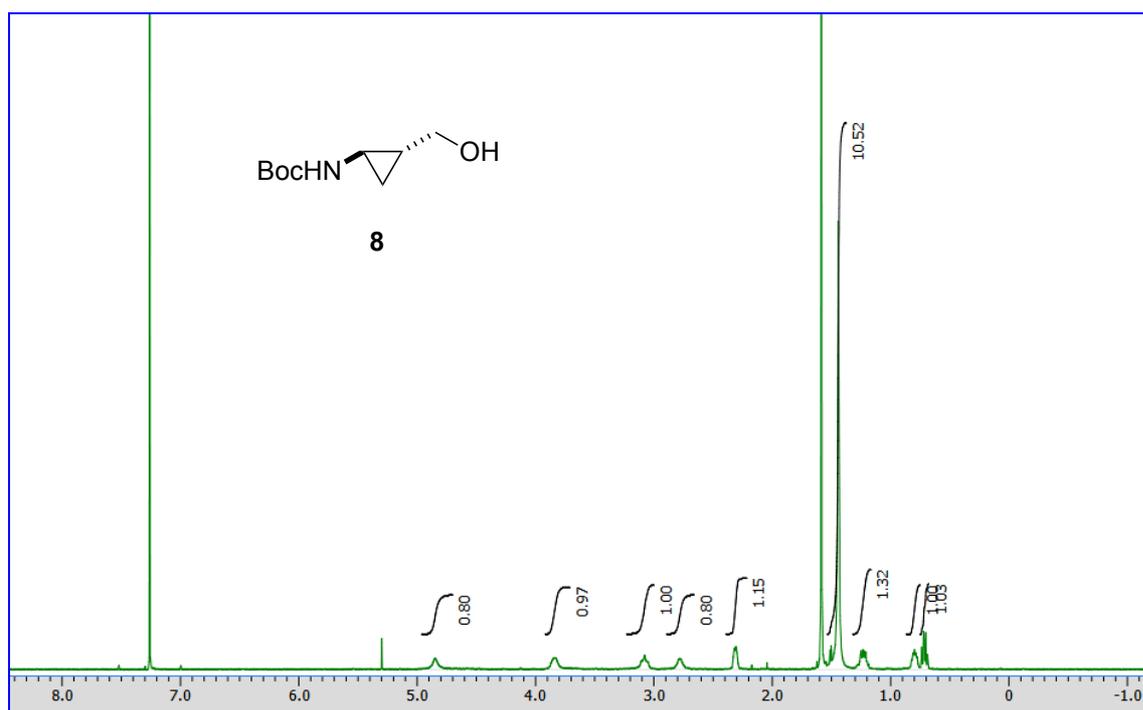




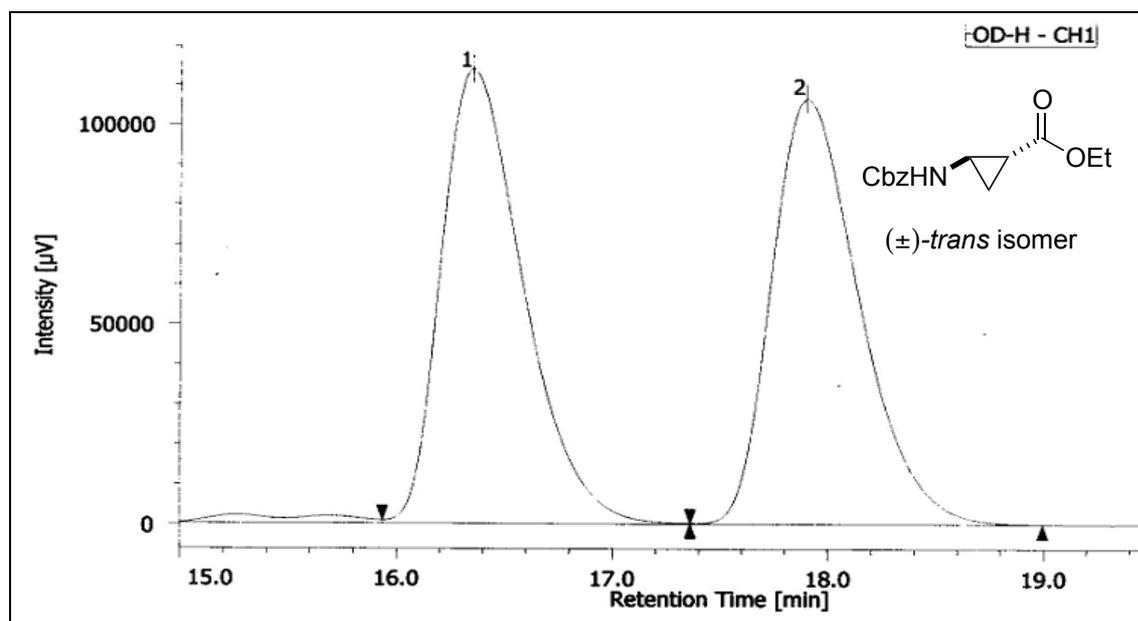




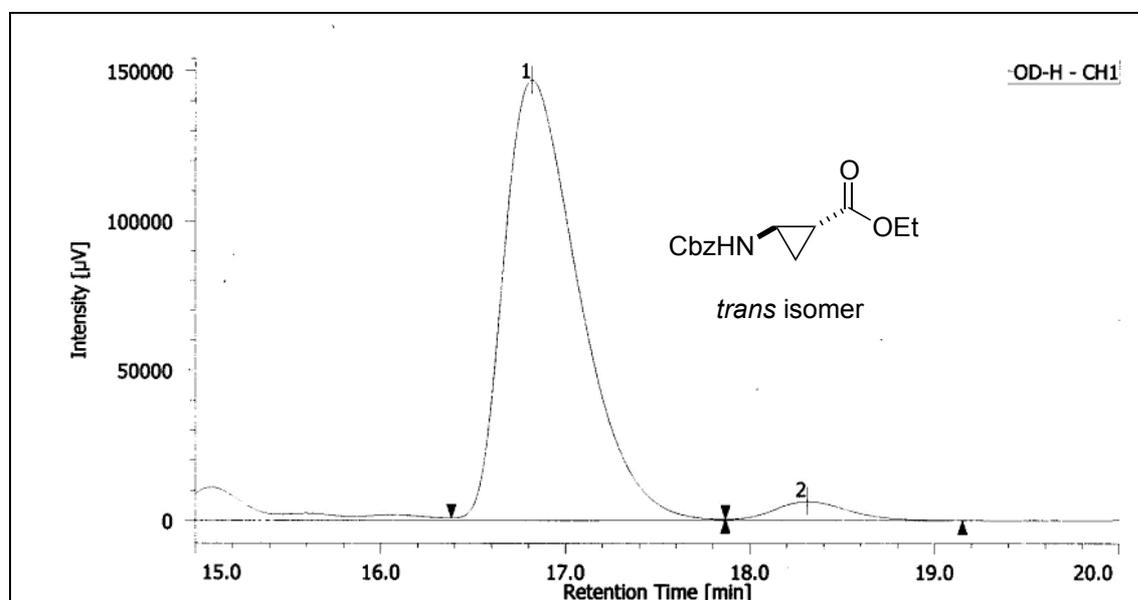




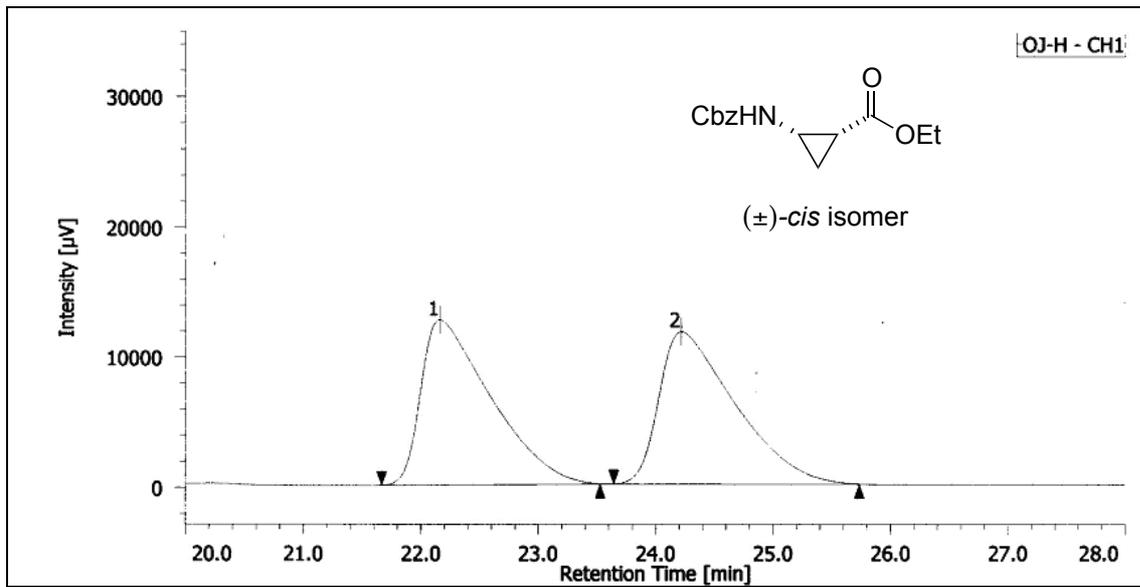
6. HPLC Spectral data



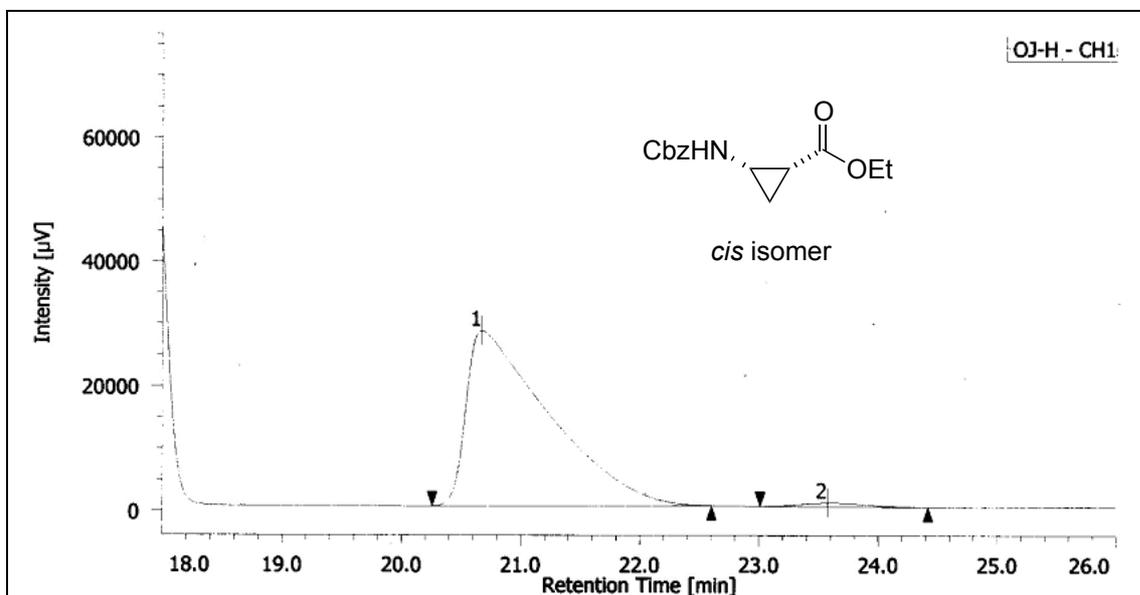
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	16.350	2999594	113766	50.005	51.675
2	17.892	2998942	106392	49.995	48.325



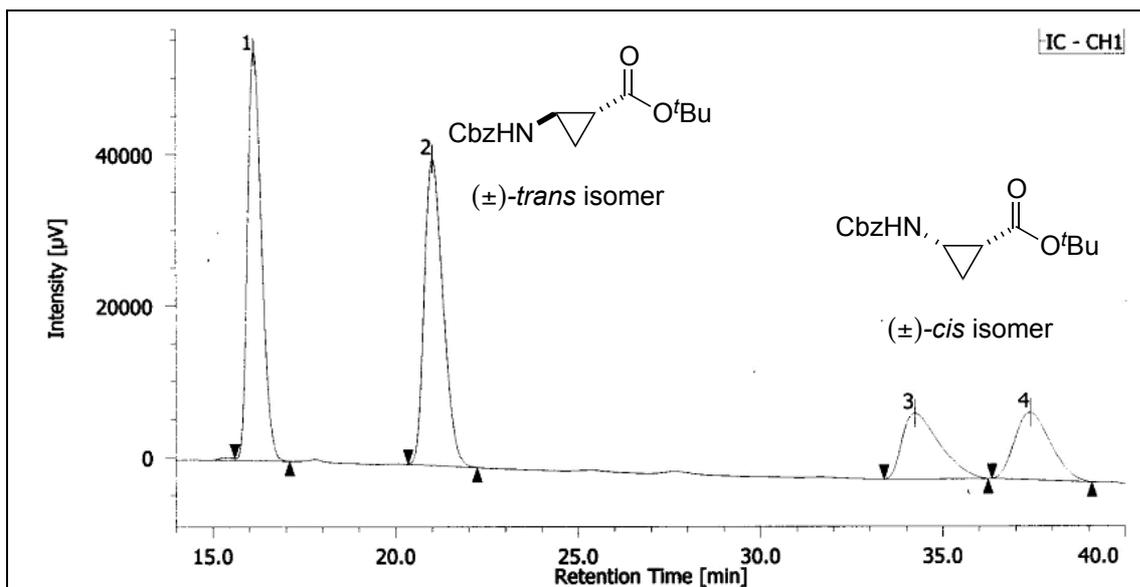
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	16.817	4151857	146855	95.864	95.838
2	18.308	179144	6377	4.136	4.162



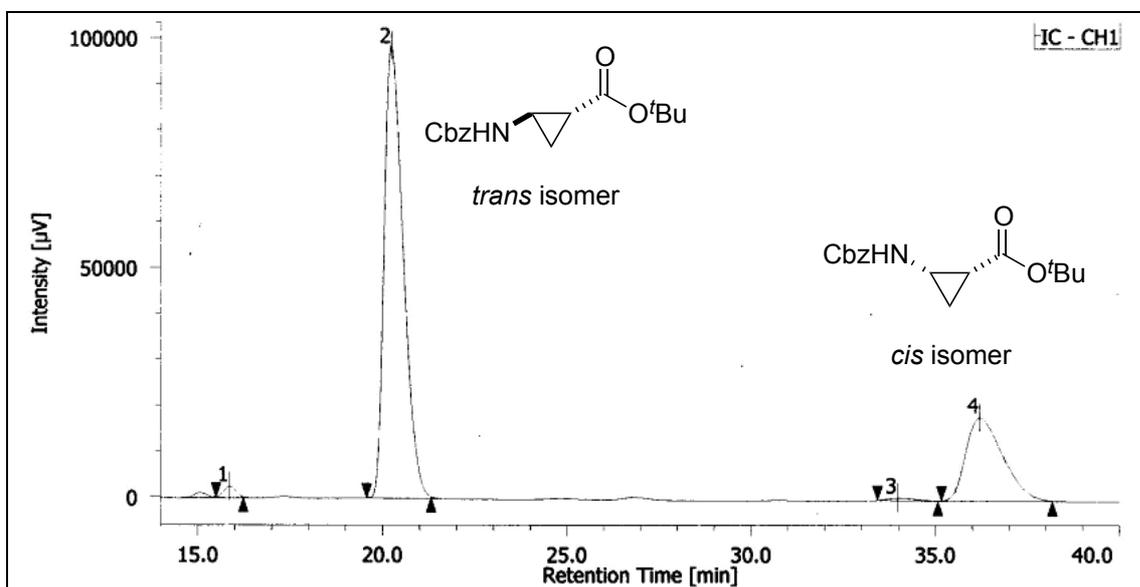
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	22.158	521347	12670	49.888	51.999
2	24.217	523689	11695	50.112	48.001



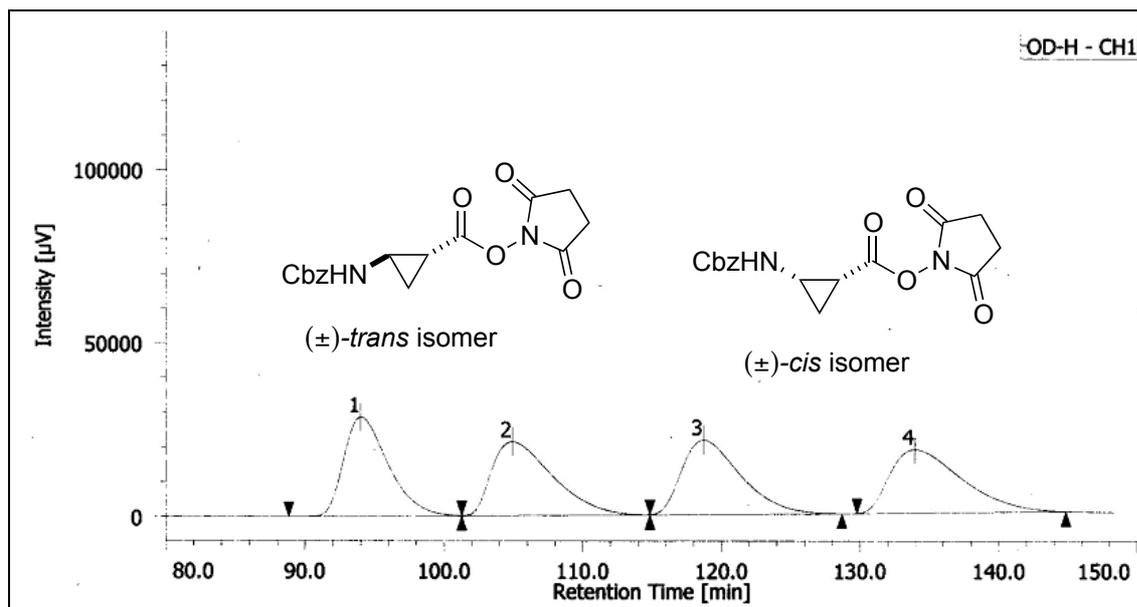
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	20.675	1351293	28047	98.333	97.800
2	23.575	22910	631	1.667	2.200



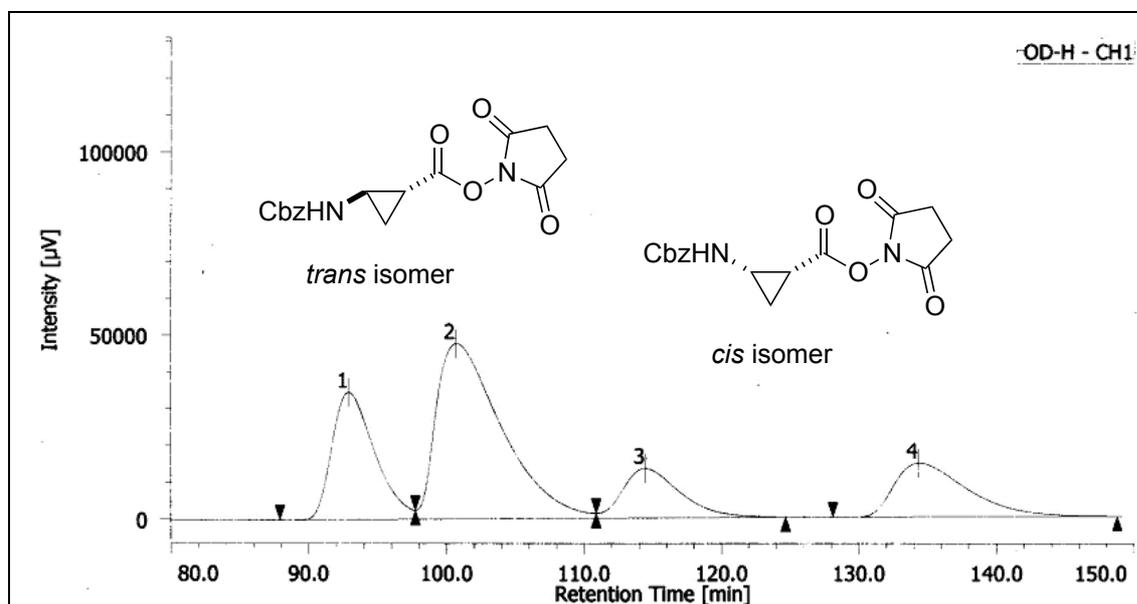
PEAK	RT [min]	AREA [μV-sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	16.117	1438261	53853	35.080	48.173
2	21.008	1440187	40435	35.107	36.170
3	34.225	616291	8645	15.023	7.733
4	37.392	607521	8857	14.809	7.923



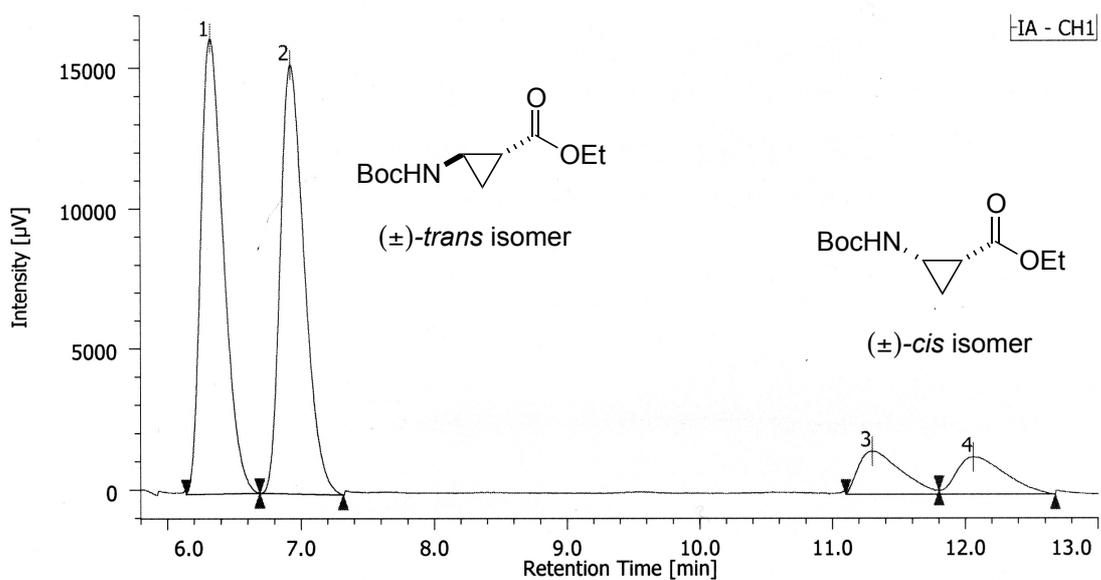
PEAK	RT [min]	AREA [μV-sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	15.850	58603	2530	1.197	2.112
2	20.233	3552332	98585	72.551	82.300
3	33.967	27732	549	0.566	0.458
4	36.192	1257648	18123	25.686	15.129



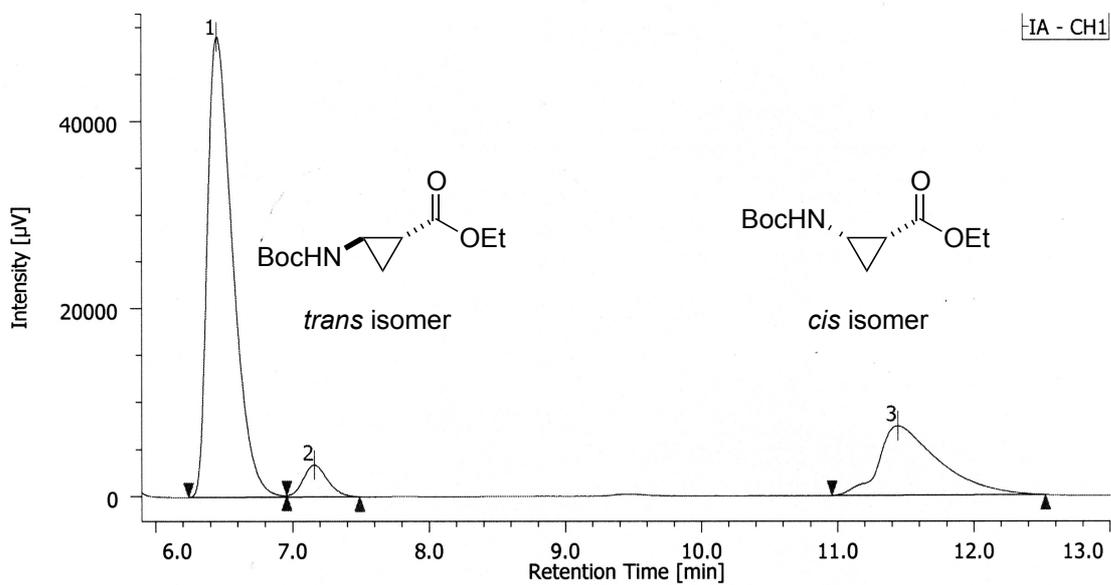
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	93.975	6339968	28539	24.567	31.852
2	104.917	6507972	21285	25.218	23.756
3	118.700	6367479	21500	24.674	23.996
4	133.925	6591011	18275	25.540	20.396



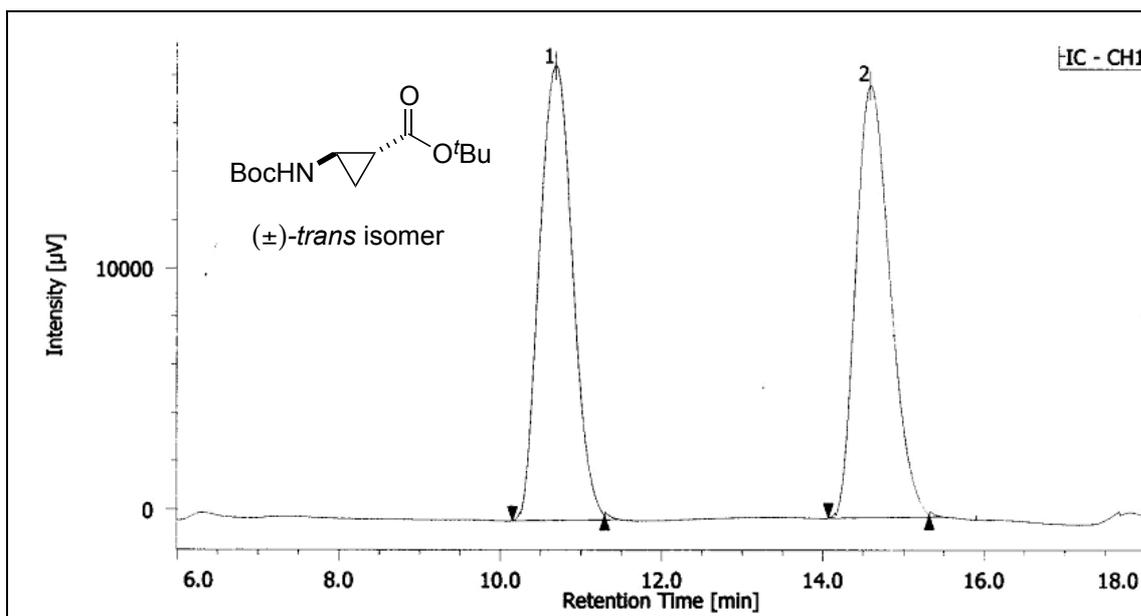
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	92.883	7385548	34527	22.833	31.382
2	100.667	15749613	47583	48.690	43.249
3	114.450	3872999	13427	11.974	12.204
4	134.292	5338258	14484	16.503	13.164



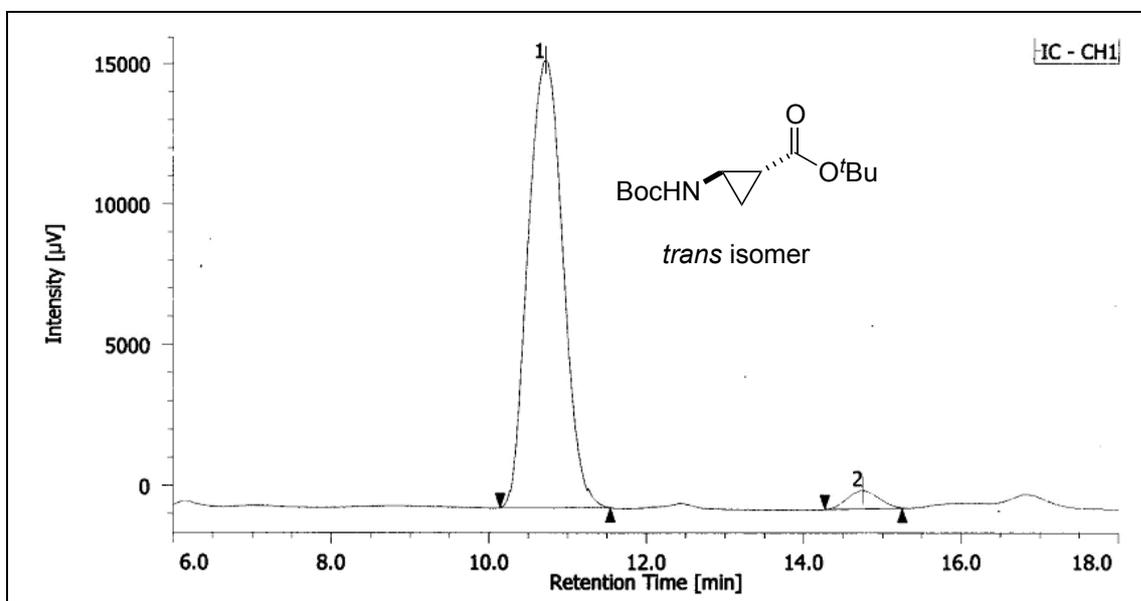
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	6.325	191067	16186	42.465	47.326
2	6.925	191296	15241	42.516	44.477
3	11.300	33958	1520	7.547	4.436
4	12.058	33614	1320	7.471	3.852



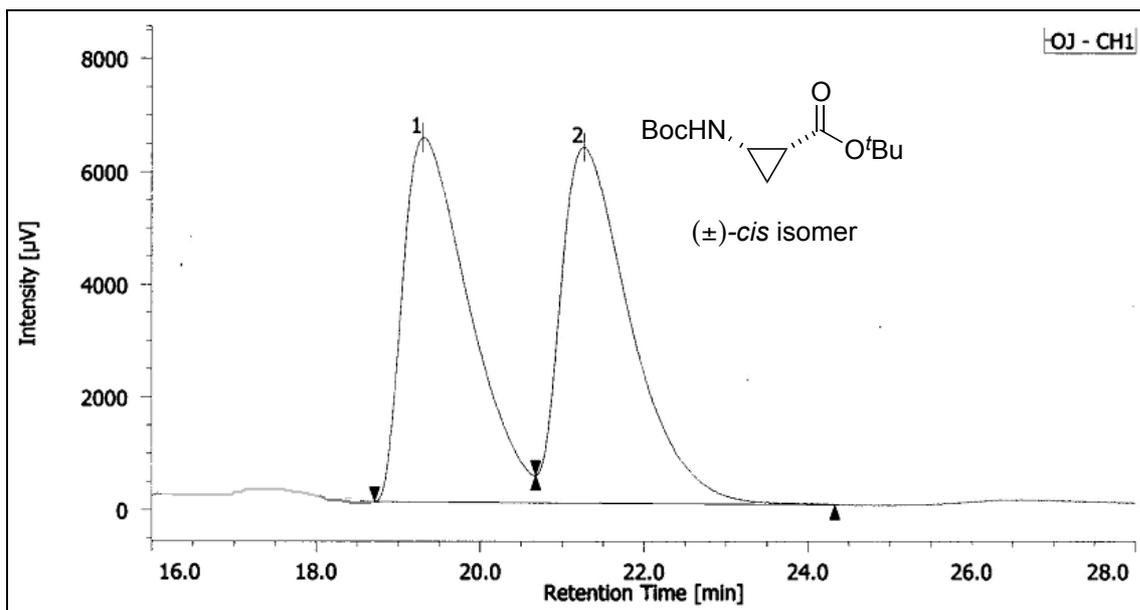
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	6.450	629800	49055	70.287	82.018
2	7.158	42056	3391	4.694	5.669
3	11.442	224188	7364	25.020	12.313



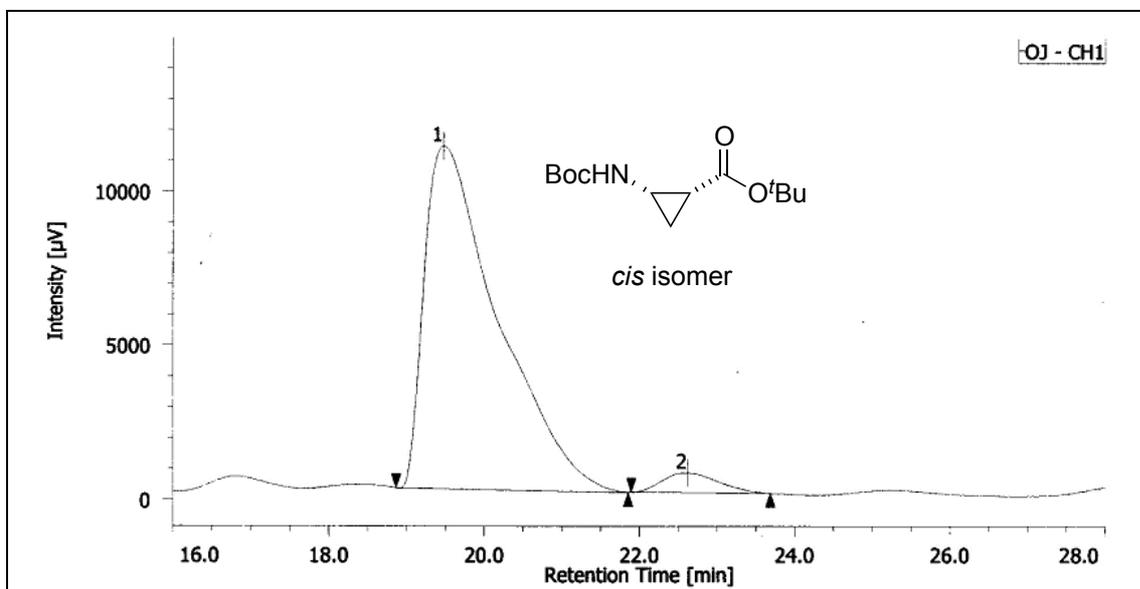
PEAK	RT [min]	AREA [μV-sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	10.683	537256	18863	50.440	51.287
2	14.583	527893	17916	49.560	48.713



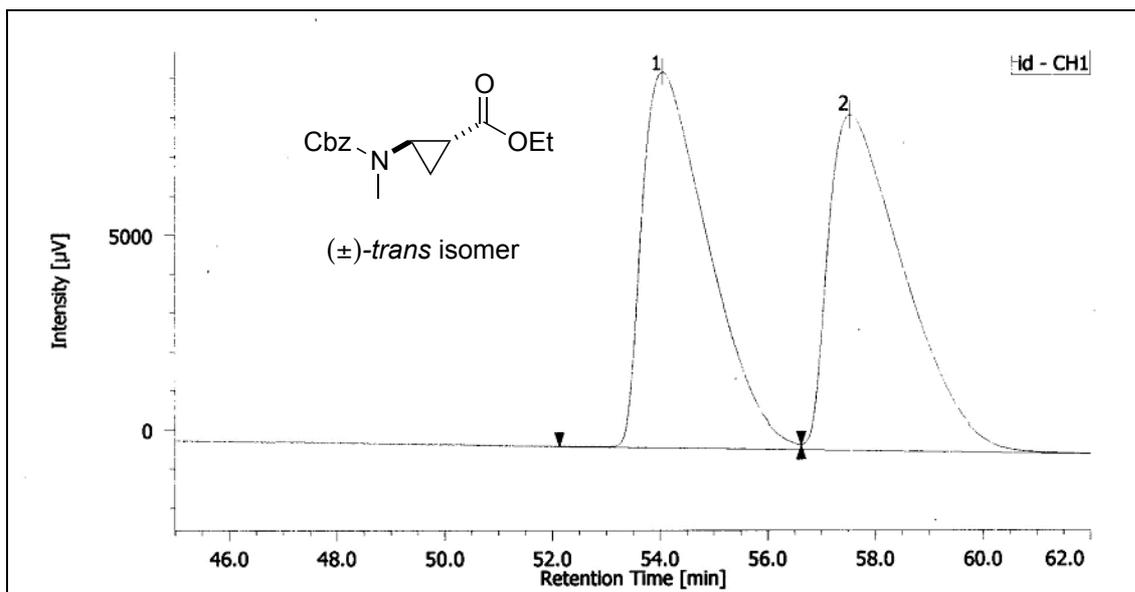
PEAK	RT [min]	AREA [μV-sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	10.717	488432	15913	96.482	96.168
2	14.758	17810	634	3.518	3.832



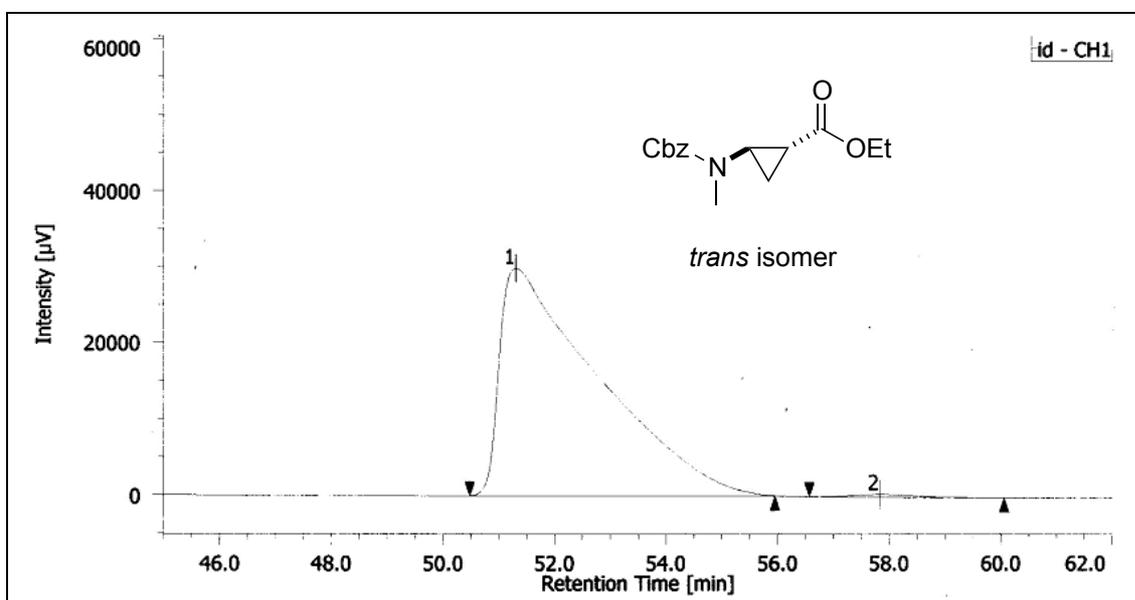
PEAK	RT [min]	AREA [μV-sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	19.300	364255	6473	49.265	50.598
2	21.267	375130	6320	50.735	49.402



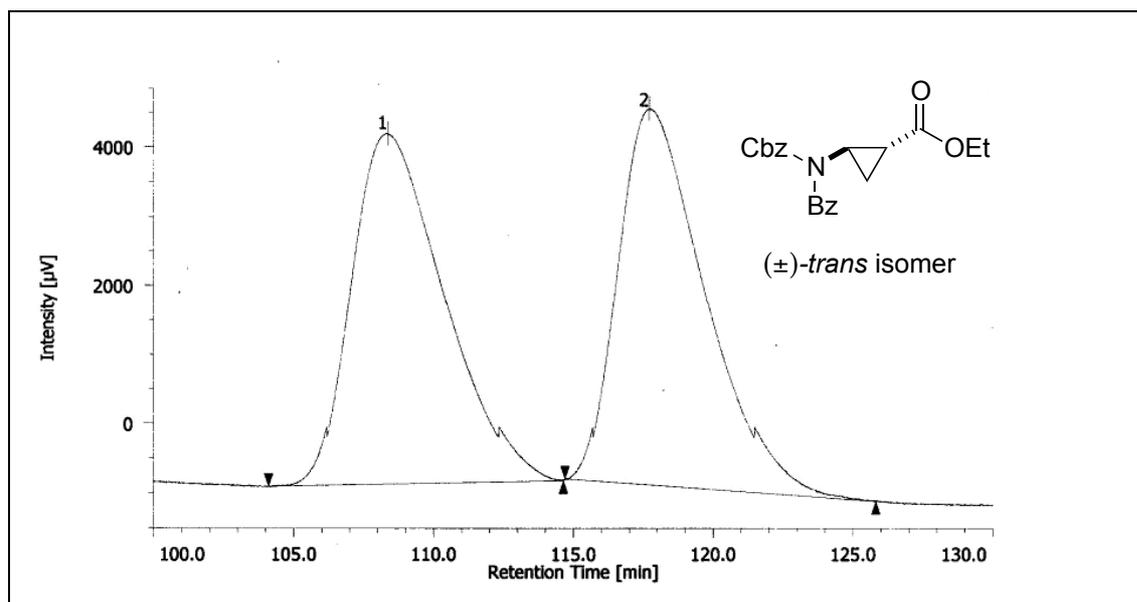
PEAK	RT [min]	AREA [μV-sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	19.475	731780	11131	95.858	94.579
2	22.617	31619	638	4.142	5.421



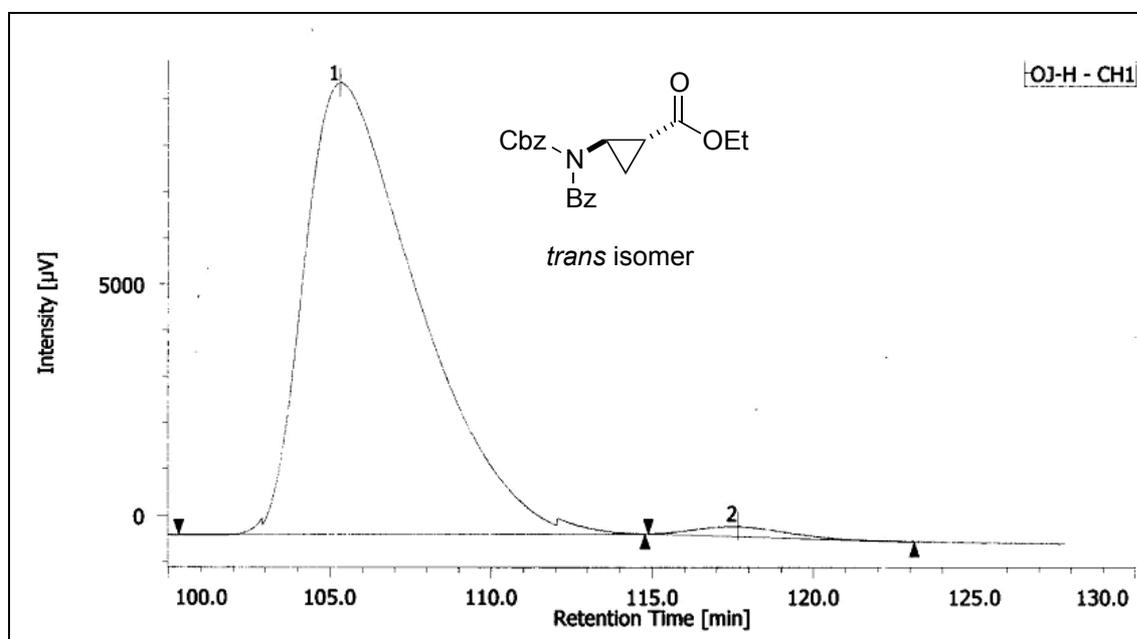
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	54.050	830046	9627	49.599	52.813
2	57.525	843483	8602	50.401	47.187



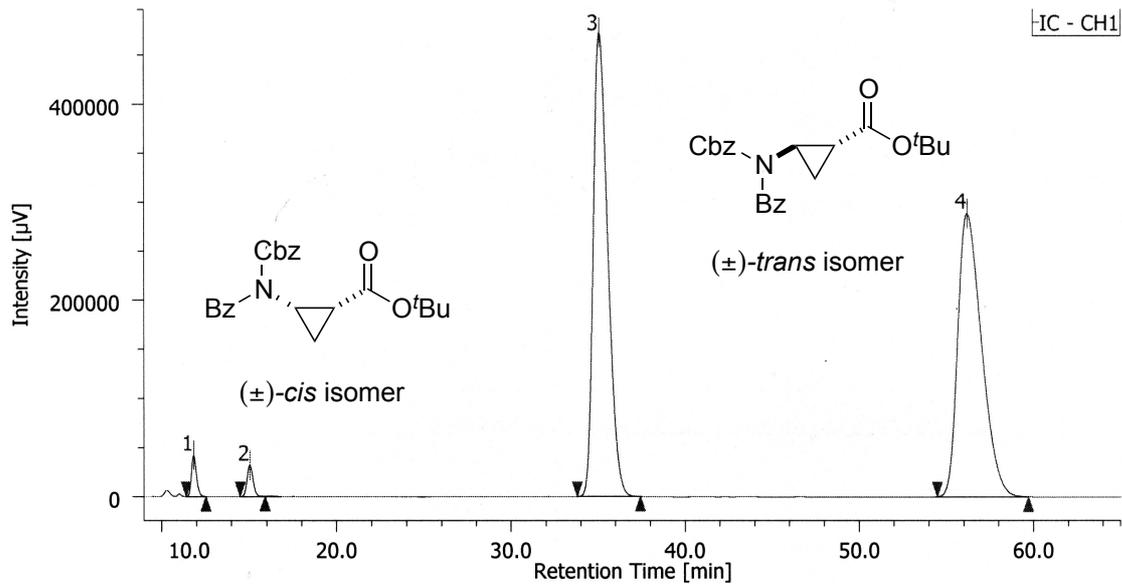
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	51.300	3654732	29873	99.308	98.842
2	57.825	25451	350	0.692	1.158



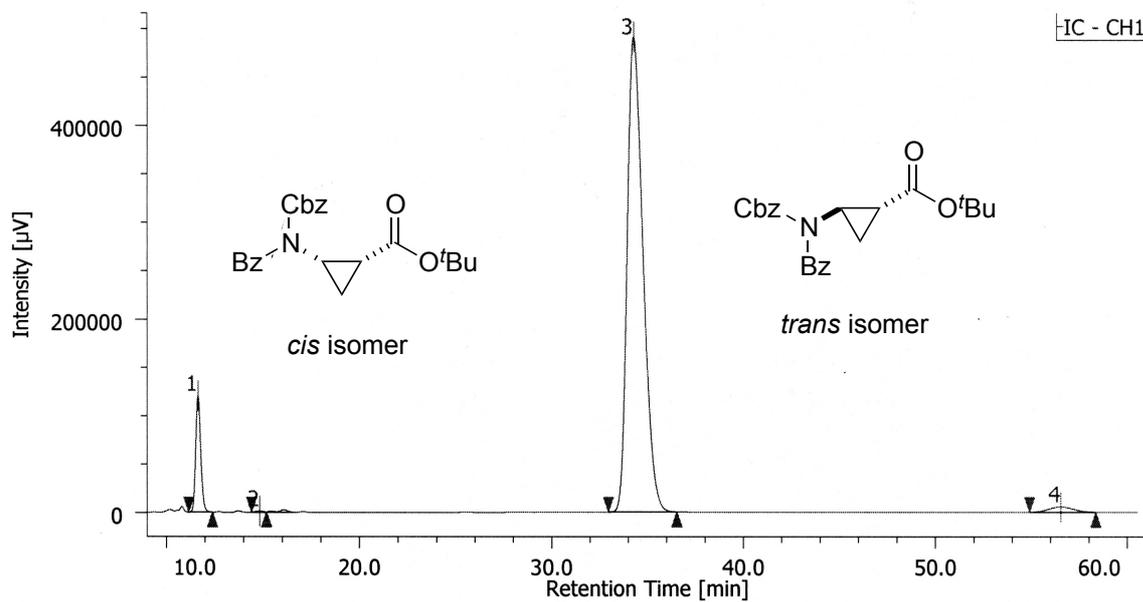
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	108.358	1163768	5073	49.723	48.226
2	117.700	1176750	5446	50.277	51.774



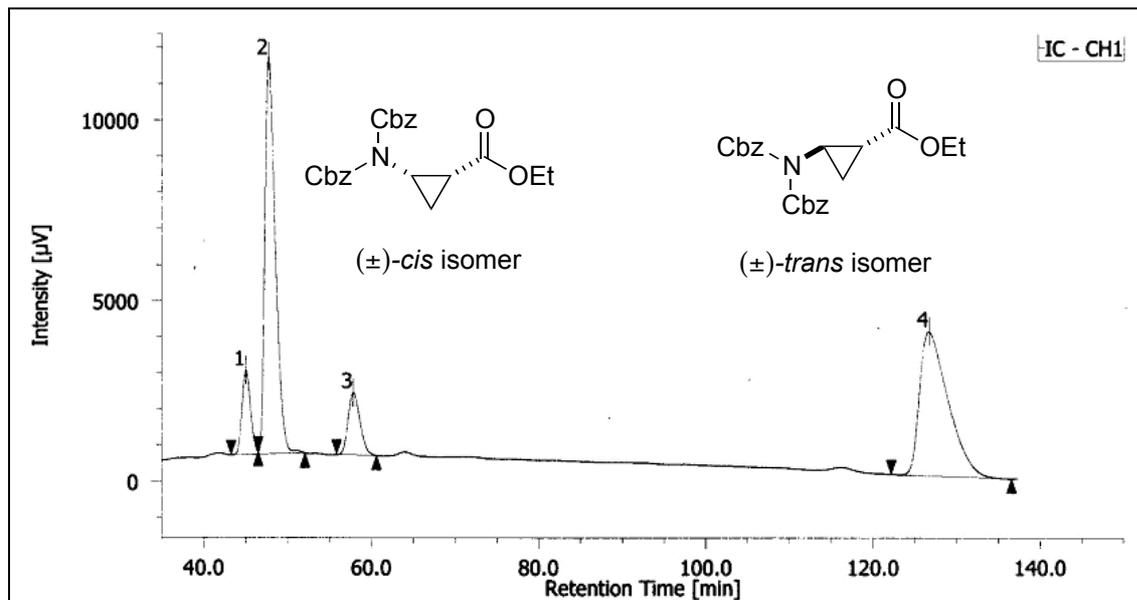
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	105.317	2398599	9764	98.285	97.711
2	117.658	41848	229	1.715	2.289



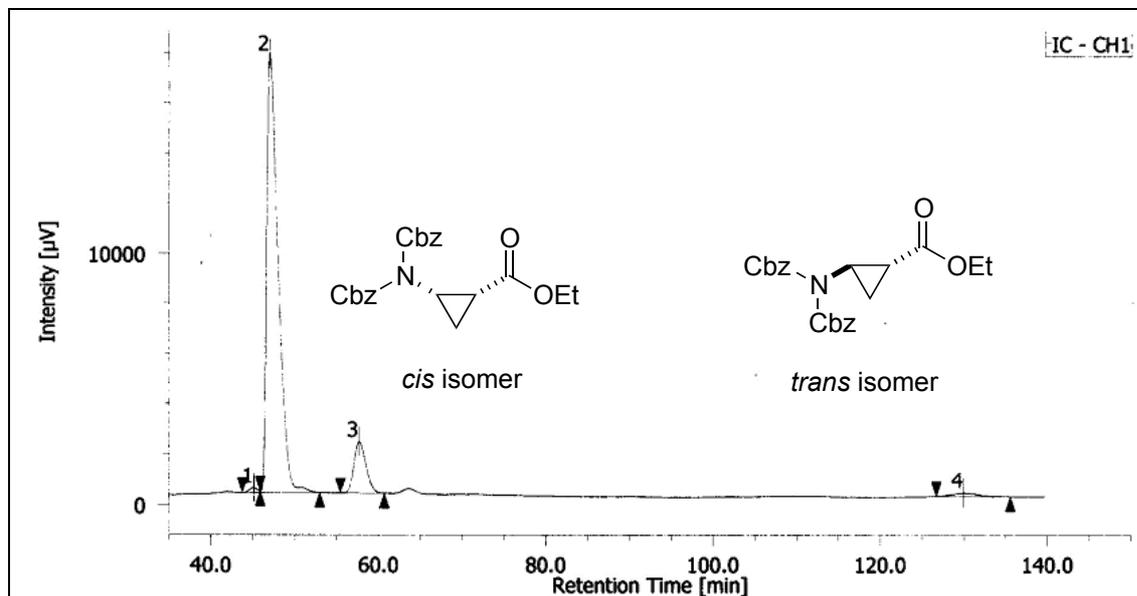
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	11.842	835206	42013	1.483	5.034
2	15.050	775314	31811	1.377	3.812
3	35.075	27340150	472403	48.553	56.605
4	56.175	27359370	288336	48.587	34.549



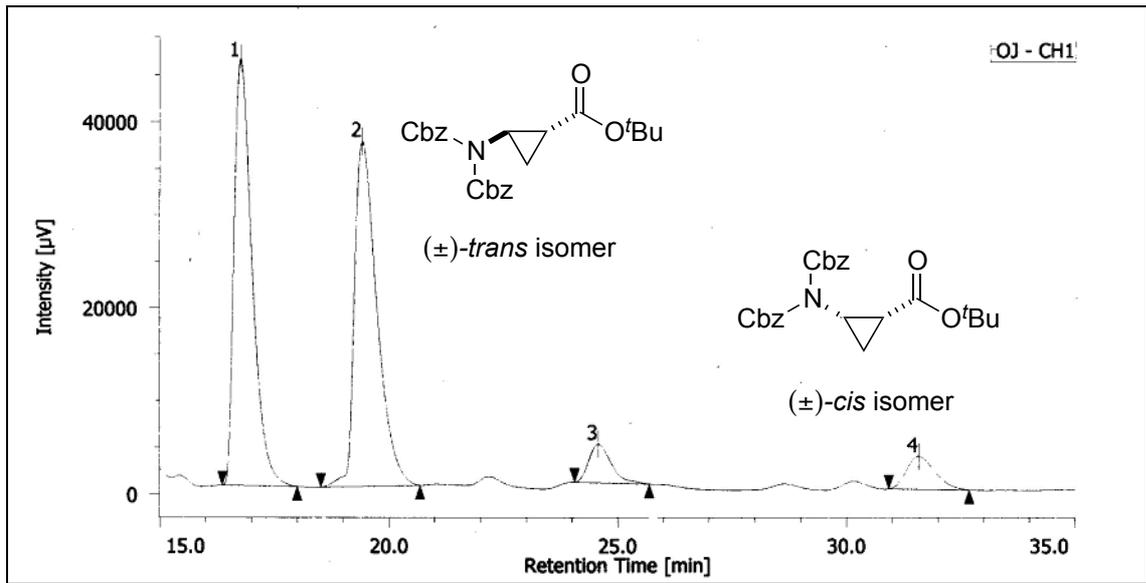
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	11.642	2203343	120163	7.125	19.449
2	14.825	30068	1254	0.097	0.203
3	34.283	28190697	490826	91.161	79.441
4	56.525	500114	5604	1.617	0.907



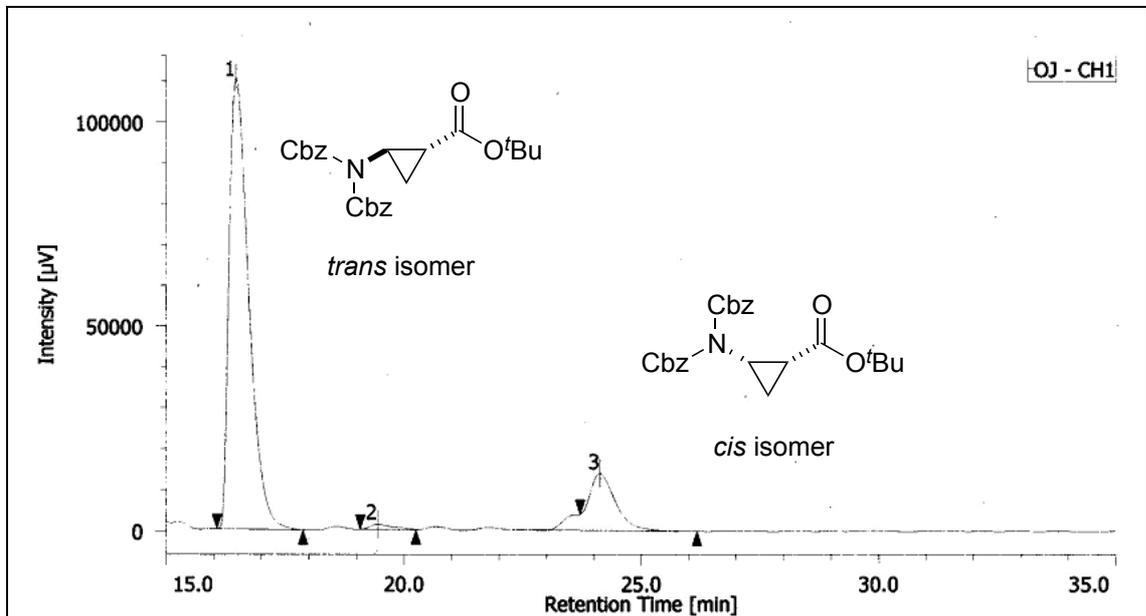
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	45.000	165310	2335	7.399	12.253
2	47.667	955171	10993	42.753	57.682
3	57.817	167333	1723	7.490	9.043
4	126.658	946358	4007	42.358	21.023



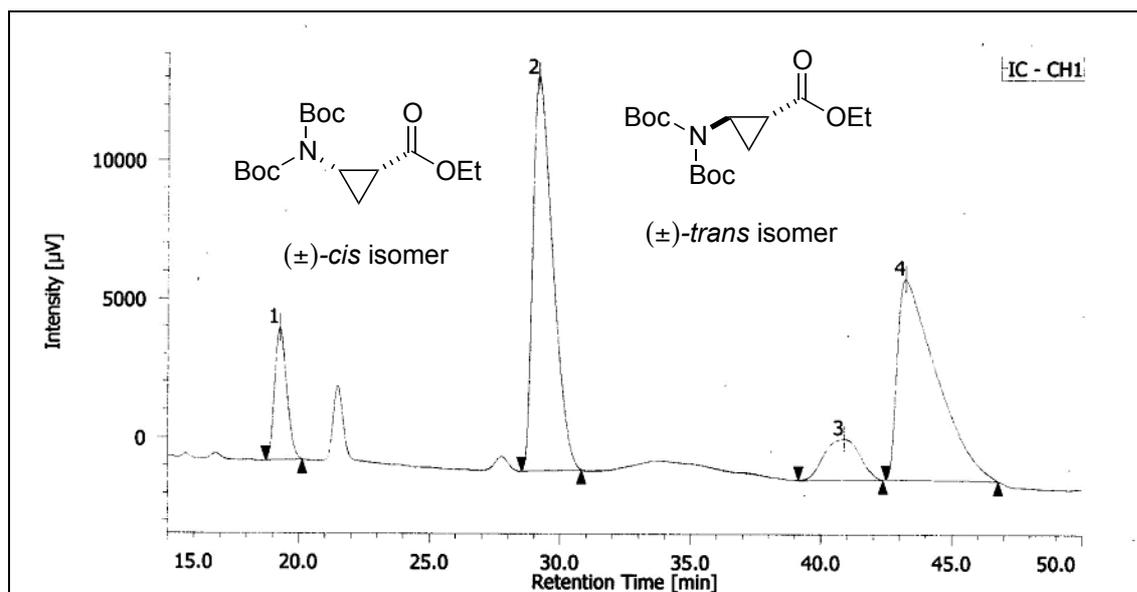
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	45.117	12928	199	0.680	1.003
2	47.000	1658649	17501	87.266	88.015
3	57.633	198984	2032	10.469	10.218
4	129.950	30125	152	1.585	0.764



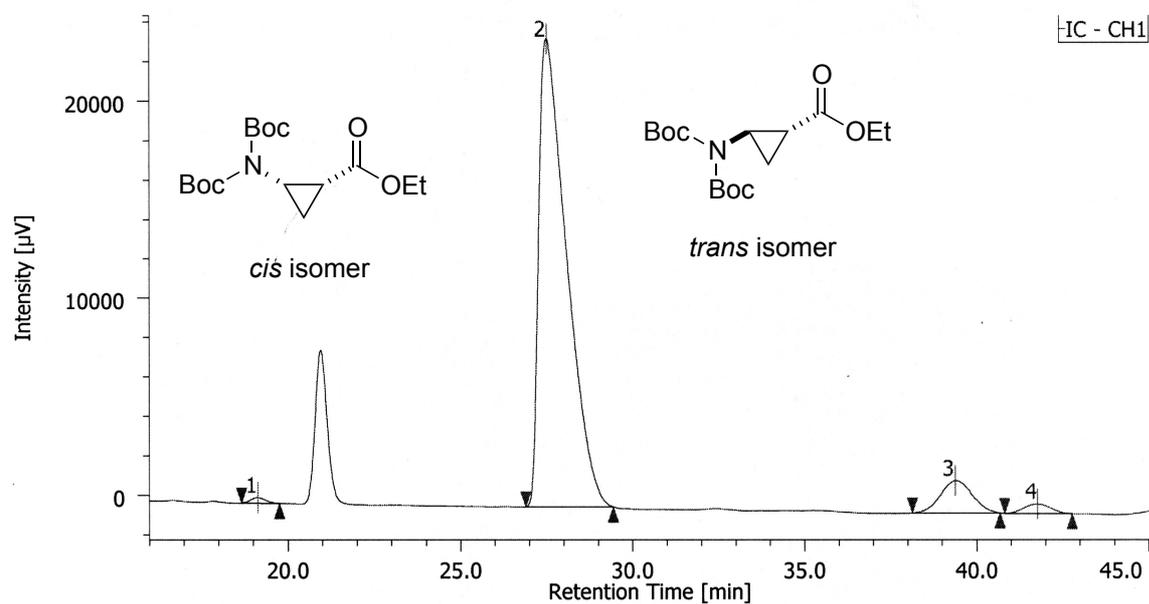
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	16.758	1252820	45789	44.590	50.602
2	19.417	1263841	37064	44.982	40.960
3	24.567	141079	4125	5.021	4.558
4	31.575	151899	3510	5.406	3.879



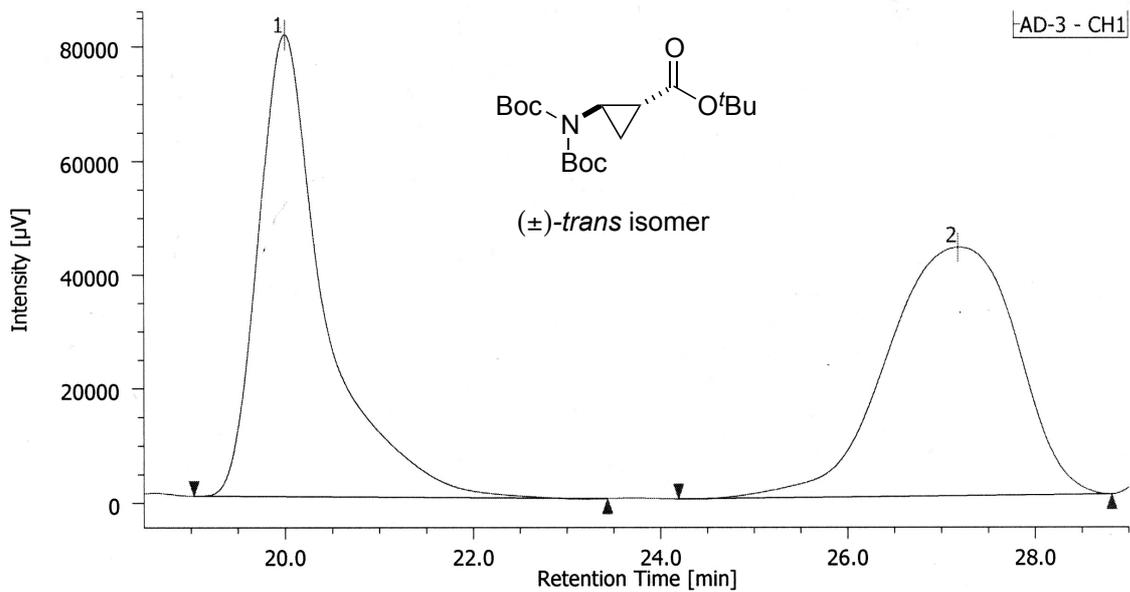
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	16.458	3156833	110200	84.482	87.997
2	19.442	42206	1247	1.130	0.995
3	24.125	537647	13785	14.388	11.007



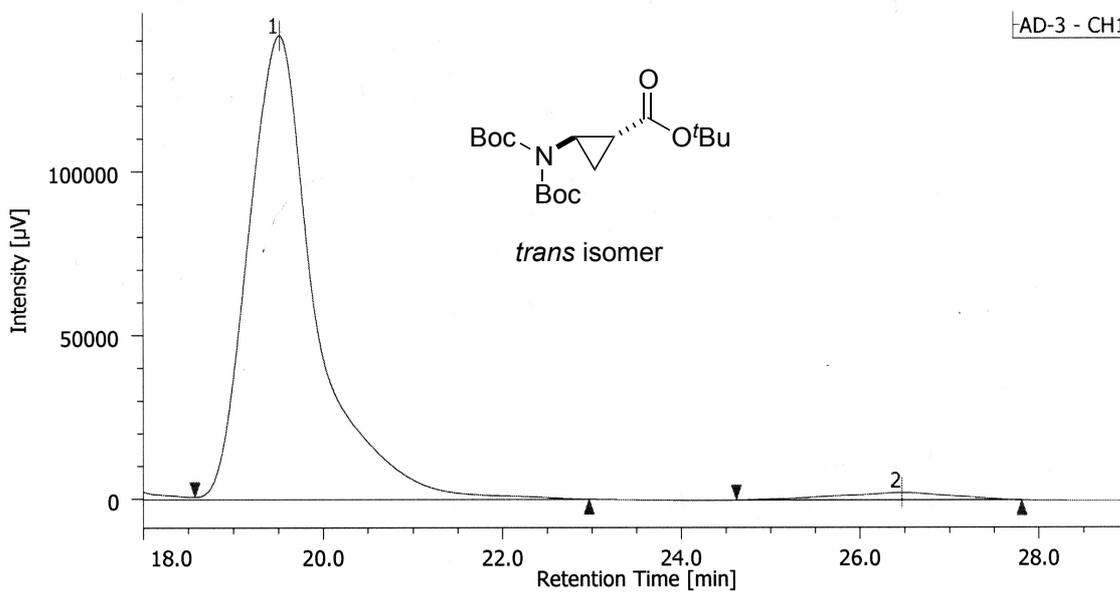
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	19.267	152256	4757	8.446	17.185
2	29.167	754814	14236	41.873	51.431
3	40.883	140567	1471	7.798	5.315
4	43.217	755008	7216	41.883	26.069



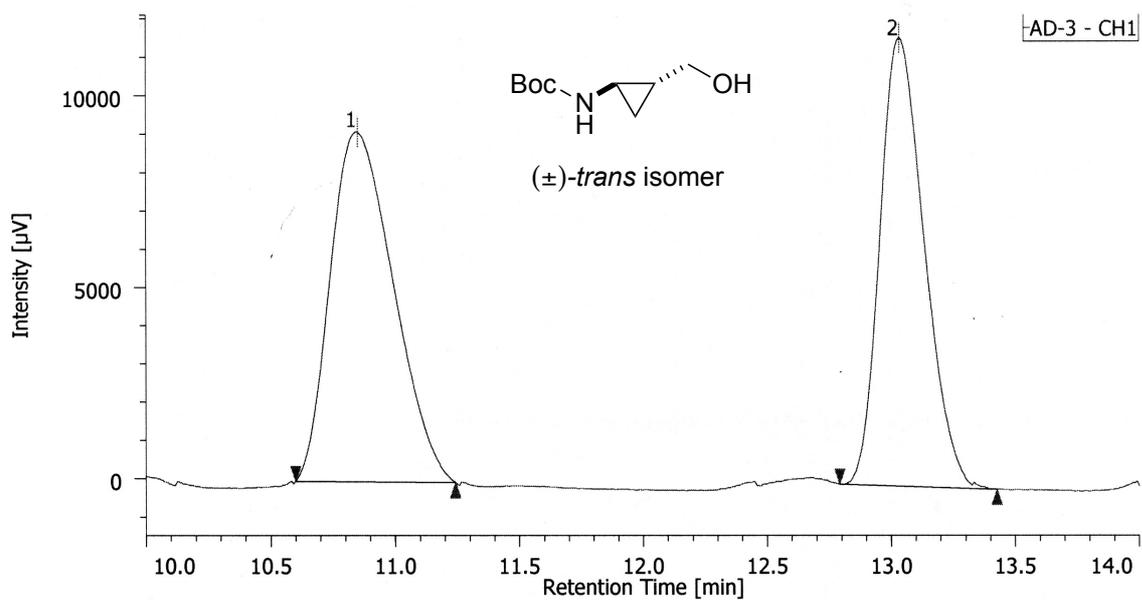
PEAK	RT [min]	AREA [$\mu\text{V}\cdot\text{sec}$]	HEIGHT [μV]	AREA%	HEIGHT%
1	19.133	8851	302	0.605	1.157
2	27.500	1322775	23703	90.432	90.665
3	39.367	104516	1646	7.145	6.294
4	41.758	26594	493	1.818	1.884



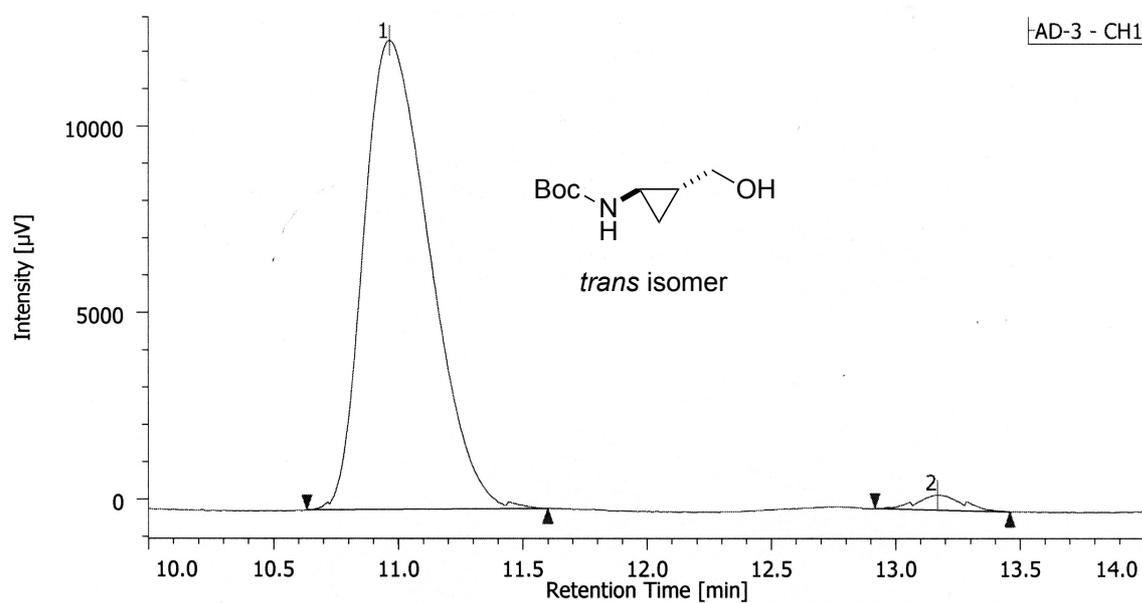
PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	20.000	3994639	80890	48.870	65.026
2	27.175	4179290	43507	51.130	34.974



PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	19.525	7370432	141686	97.324	98.424
2	26.467	202651	2268	2.676	1.576



PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	10.850	161454	9137	52.641	43.884
2	13.033	145252	11684	47.359	56.116



PEAK	RT [min]	AREA [µV-sec]	HEIGHT [µV]	AREA%	HEIGHT%
1	10.967	229804	12555	97.822	96.901
2	13.167	5117	402	2.178	3.099