

# Enantioselective Additions of Boronates to Chromene Acetals Catalyzed by a Chiral Brønsted acid-Lewis acid System

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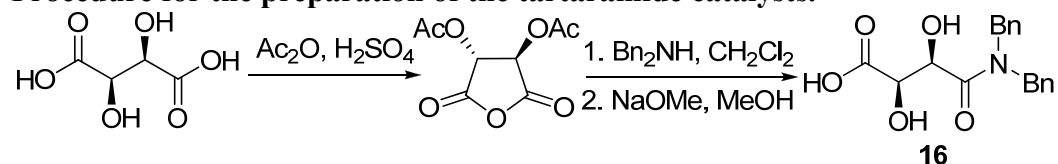
## Supporting Information

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**General Information.** All  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG,  $^1\text{H}$  400 MHz,  $^{13}\text{C}$  100 MHz) or Varian Gemini 300 (70.5 kG,  $^{13}\text{C}$  75 MHz) spectrometers. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and were reported as  $[\alpha]_D$  (concentration in grams/100 mL solvent). Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Chiral HPLC analysis was performed using an Agilent 1100 series HPLC or Waters Breeze HPLC System with a diode array detector. Chiral columns include Chiralcel<sup>®</sup>OD (Chiral Technologies Inc., 25cm × 4.6 mm I.D.) and Chiralpak<sup>®</sup>AD-H (Chiral Technologies Inc., 25cm × 4.6 mm I.D.). The ReactIR 4000 system (Mettler Toledo-AutoChem), running software version 3.1, was fitted with a FiberConduit and a 6 mm DiComp Probe. IR spectra, comprised of 64 scans per spectrum, were collected every one minute at a resolution of  $8\text{ cm}^{-1}$ .

**Procedure for the preparation of the tartaramide catalysts.<sup>1</sup>**



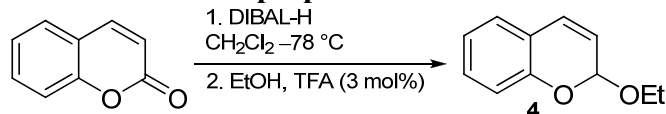
**(3R,4R)-2,5-dioxotetrahydrofuran-3,4-diyl diacetate:** To a 50 mL round-bottom flask equipped with stir bar was added L-(+)-tartaric acid (5.48 g, 36.6 mmol) and acetic anhydride (12 mL). The mixture was cooled to 0 °C and  $\text{H}_2\text{SO}_4$  (0.2 mL, 97% conc.) was added drop wise with vigorous stirring. After the exothermic reaction was complete, the mixture was refluxed for 10 min and cooled to 0 °C. The precipitate was vacuum-filtered and washed with toluene and  $\text{Et}_2\text{O}$  to give a crystalline solid (7.43 g, 94% yield). The solid can be stored dry at 0 °C under Ar for up to 1 month without decomposition of structure. **SMILES** = O=C(O)[C@H](OC(C)=O)[C@@H](OC(C)=O)C1=O **InChI** = 1/C8H8O7/c1-3(9)13-5-6(14-4(2)10)8(12)15-7(5)11/h5-6H,1-2H3/t5-,6-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-16,10-16,11-16,12-16,13-16,14-16,15-16

**(2R,3R)-4-(dibenzylamino)-2,3-dihydroxy-4-oxobutanoic acid (16):** A solution of anhydride (5.0 g, 23.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was cooled to 0 °C under Ar. Dibenzylamine (5.33 mL, 27.7 mmol) was added slowly and stirred for 20 min. The reaction was warmed to 35 °C and stirred for an additional 1 h. The solvent was removed under reduced pressure and the crude oil was dissolved in EtOAc (200 mL) and washed with 3 N HCl in saturated NaCl (50 mL). The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. Recrystallization of the crude material in EtOAc gave a white powder. The acetylated tartaramide (5.0 g, 12.1 mmol) was transferred to a 50 mL round-bottom flask and dissolved in MeOH (25 mL). NaOMe (2.29 g, 42.3 mmol) was added and the reaction was stirred at room temperature for 12 h. To quench the reaction, Amberlyst-15 was continuously added to the

1. Dobashi, Y. & Hara, S. A chiral stationary phase derived from (*R,R*)-tartaramide with broadened scope of application to the liquid chromatographic resolution of enantiomers. *J. Org. Chem.*, **52**, 2490-2496 (1987).

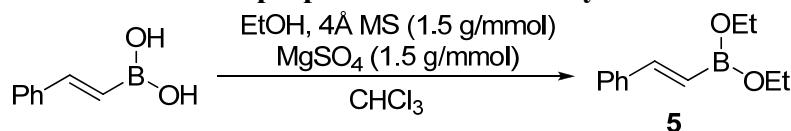
stirring mixture until a clear, homogenous solution was obtained and the pH was 3-4. (*Note:* The monosodium carboxylate salt of the tartaramide is soluble in organic solutions. This salt is an inactive catalyst in the boronate addition reaction, therefore, a low pH must be obtained in this step to ensure the fully protonated tartaric acid amide.) The solution was filtered through a pad of Celite to remove the Amberlyst-15 and the resin was washed with MeOH. Removal of the solvent in vacuo and recrystallization from boiling EtOAc afforded the product **16** as a fluffy white solid (4.4 g, 58% yield over two steps). The racemic tartaramide catalyst was synthesized by the same procedure using DL-tartaric acid.

#### Procedure for the preparation of the 2*H*-chromene acetals.<sup>2,3</sup>



To an oven-dried 250 mL round-bottom flask equipped with stir bar was added coumarin (7.39 g, 50 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (75 mL) under an atmosphere of Ar. The mixture was cooled to -78 °C and DIBAL-H (1.0 M in PhCH<sub>3</sub>, 52.5 mL, 52.5 mmol) was added drop wise via syringe pump over 1 h. The reaction was stirred for an additional 1 h at -78 °C and then allowed to warm to 0 °C and stirred for 15 min. The reaction was diluted with EtOAc (250 mL) and quenched with H<sub>2</sub>O (250 mL) and vigorously stirred and filtered through Celite. The aqueous layer was extracted with EtOAc (2 x 250 mL) and the organic layers were combined and washed with brine (250 mL) then dried with Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed under reduced pressure and the crude was redissolved in 50 mL EtOH. Trifluoroacetic acid (111 μL, 1.5 mmol) was added and the reaction was stirred for 3 h at room temperature. The reaction was quenched with K<sub>2</sub>CO<sub>3</sub> (276 mg, 2.0 mmol), filtered and concentrated under reduced pressure. The crude was subjected to flash chromatography over a silica gel column (gradient 2 - 5% EtOAc in hexanes) to afford the product **4** as pale yellow oil (3.87 g, 44% yield).

#### Procedure for the preparation of the diethyl boronates.<sup>4</sup>



To an oven-dried flask equipped with stir bar was added (*E*)-phenylvinylboronic acid (10 mmol), 4Å molecular sieves (15 g), and MgSO<sub>4</sub> (15 g). EtOH (10 mL) and CHCl<sub>3</sub> (20 mL) were added to the flask and the reaction mixture was refluxed for 24 h. The reaction was filtered through an oven-dried medium porosity grade fritted funnel and residue was washed with 10 mL dry CH<sub>2</sub>Cl<sub>2</sub>.

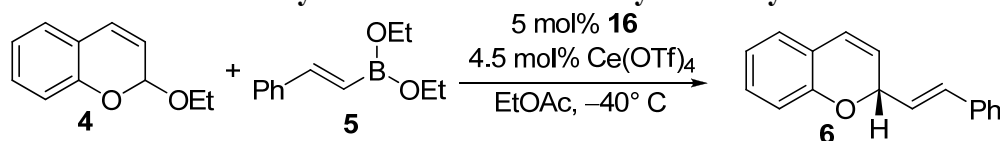
2. Loncar, L., Otocan, K., Mintas, M., Troetsch, T. & Mannschreck, A. Chiral chromenes: synthesis, separation of enantiomers and barriers to racemization. *Chiral 2H-pyrans. Part 3. Croat. Chem. Acta*, **66**, 209-216 (1993).

3. Coumarins were purchased from Sigma-Aldrich and used without additional purification. The 2-oxo-2*H*-chromen-7-yl dimethylcarbamate was synthesized according to literature: Janse van Rensburg, C. K. A. & Robinson, R. S. Synthesis of oxo- and thio-analogues of 2-oxo-2*H*-chromen-7-yl dimethylcarbamates. *S. Afr. J. Chem.* **62**, 143-148 (2009).

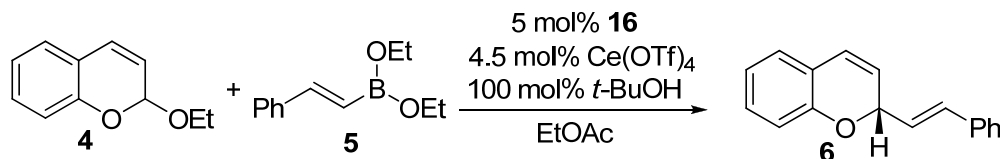
4. Bishop, J. A., Lou, S. & Schaus, S. E. Enantioselective addition of boronates to acyl imines catalyzed by chiral biphenols. *Angew. Chem. Int. Ed.*, **48**, 4337-4340 (2009).

The filtrate was concentrated under reduced pressure then dried under high vacuum for 1 h to afford the product as an oil in 70 - 95% yields. The diethyl styrylboronate **5** was dissolved in dry EtOAc to furnish a 2.0 M solution to be used in the reaction. The solution is stable at 0 °C for up to 2 months. **SMILES** = CCOB(OCC)/C=C/C1=CC=CC=C1 **InChI** = 1/C12H17BO2/c1-3-14-13(15-4-2)11-10-12-8-6-5-7-9-12/h5-11H,3-4H2,1-2H3/b11-10+/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-11,14-16,15-16

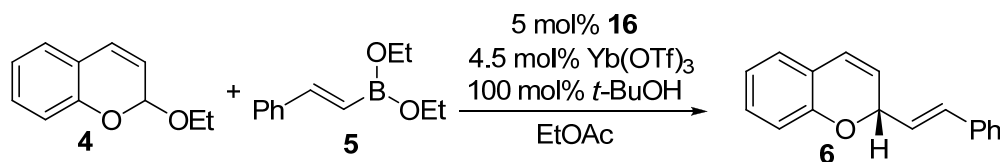
### Procedures for the asymmetric reaction of vinyl- and arylboronates to oxocarbeniums.



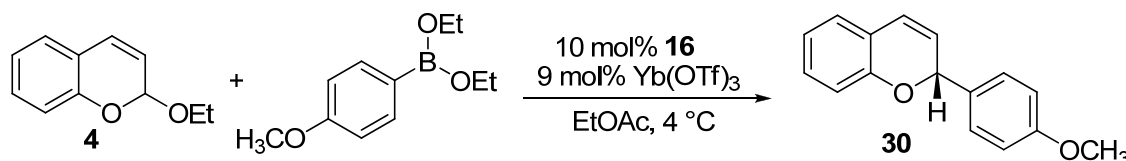
**Method A: Procedure for the acid-catalyzed addition of styrylboronate 5 to 2-ethoxy-2H-chromene 4.** To an oven-dried 5 mL round-bottom flask equipped with stir bar and rubber septum under Ar was added Ce(OTf)<sub>4</sub> (16.5 mg, 0.0225 mmol, 0.045 equiv.), tartaramide catalyst **16** (8.2 mg, 0.025 mmol, 0.05 equiv.) and EtOAc (0.625 mL). Boronate **5** (2.0 M in EtOAc, 375 μL, 0.75 mmol, 1.5 equiv.) was added in one portion via syringe and the reaction was cooled to -40 °C and stirred for 5 min. The chromene acetal **4** (88 mg, 0.5 mmol, 1.0 equiv.) was added drop wise over 1 min via syringe and the reaction was stirred vigorously for 16 h at -40 °C. The reaction was purified without work-up by flash chromatography over silica gel column (isocratic 2% EtOAc in hexanes) to afford the product **6** as a pale yellow oil (97 mg, 0.42 mmol, 83% yield). The product can be stored at -20 °C under Ar in the dark for up to two weeks without decomposition of the structure or deterioration of enantioselectivity. The racemic version of the reaction was run under the same conditions with the exception of the chiral tartaramide, which was replaced by the racemic tartaramide catalyst derived from DL-tartaric acid.



**Method B:** To an oven-dried 5 mL round-bottom flask equipped with stir bar and rubber septum under Ar was added Ce(OTf)<sub>4</sub> (16.5 mg, 0.0225 mmol, 0.045 equiv.), tartaramide catalyst **16** (8.2 mg, 0.025 mmol, 0.05 equiv.), *t*-BuOH (47.5 μL, 0.5 mmol, 1.0 equiv.) and EtOAc (0.625 mL). Boronate **5** (2.0 M in EtOAc, 375 μL, 0.75 mmol, 1.5 equiv.) was added in one portion via syringe and the reaction was cooled to the appropriate temperature and stirred for 5 min. The chromene acetal **4** (88 mg, 0.5 mmol, 1.0 equiv.) was added drop wise over 1 min via syringe and the reaction was stirred vigorously for 16 h. The reaction was purified without work-up by flash chromatography over silica gel column (isocratic 2% EtOAc in hexanes) to afford the product **6** as a pale yellow oil.



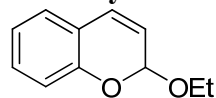
**Method C:** To an oven-dried 5 mL round-bottom flask equipped with stir bar and rubber septum under Ar was added Yb(OTf)<sub>3</sub> (14 mg, 0.0225 mmol, 0.045 equiv.), tartaramide catalyst **16** (8.2 mg, 0.025 mmol, 0.05 equiv.), *t*-BuOH (47.5  $\mu$ L, 0.5 mmol, 1.0 equiv.) and EtOAc (0.625 mL). Boronate **5** (2.0 M in EtOAc, 375  $\mu$ L, 0.75 mmol, 1.5 equiv.) was added in one portion via syringe and the reaction was cooled to the appropriate temperature and stirred for 5 min. The chromene acetal **4** (88 mg, 0.5 mmol, 1.0 equiv.) was added drop wise over 1 min via syringe and the reaction was stirred vigorously for 16 h. The reaction was purified without work-up by flash chromatography over silica gel column (isocratic 2% EtOAc in hexanes) to afford the product **6** as a pale yellow oil.



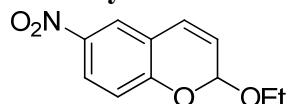
**Method D:** To an oven-dried 5 mL round-bottom flask equipped with stir bar and rubber septum under Ar was added Yb(OTf)<sub>3</sub> (14 mg, 0.0225 mmol, 0.045 equiv.), tartaramide catalyst **16** (8.2 mg, 0.025 mmol, 0.05 equiv.) and EtOAc (0.625 mL). Diethyl 4-methoxyphenylboronate (2.0 M in EtOAc, 750  $\mu$ L, 1.5 mmol, 3 equiv.) was added in one portion via syringe and the reaction was cooled to 4 °C and stirred for 5 min. The chromene acetal **4** (88 mg, 0.5 mmol, 1.0 equiv.) was added drop wise over 1 min via syringe and the reaction was stirred vigorously for 8 h at 4 °C. Afterwards, a second addition of Yb(OTf)<sub>3</sub> (14 mg, 0.0225 mmol) and tartaramide catalyst **16** (8.2 mg, 0.025 mmol) was added and the reaction continued to be stirred another 8 h at 4 °C. The reaction was purified without work-up by flash chromatography over silica gel column (gradient 2 - 5% EtOAc in hexanes) to afford the product **30** as a pale yellow oil.

### Analytical data for starting materials and products.

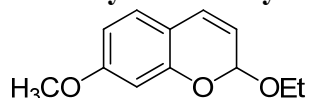
#### 2-ethoxy-2H-chromene (**4**)



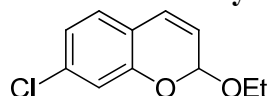
The reaction was run on a 50 mmol scale. The crude reaction was purified by flash column chromatography over silica gel (isocratic 2% ethyl acetate in hexanes) to afford the product as an oil. **Yield:** 3.87 g, 44%; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.41 – 7.09 (m, 2H), 7.06 – 6.88 (m, 2H), 6.74 (d, *J* = 9.7, 1H), 5.88 (dd, *J* = 3.8, 9.7, 1H), 5.71 (d, *J* = 3.8, 1H), 4.07 – 3.85 (m, 1H), 3.84 – 3.56 (m, 1H), 1.23 (t, *J* = 7.1, 3H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>):  $\delta$  151.76, 129.55, 127.32, 126.77, 121.67, 121.01, 120.23, 116.78, 95.14, 63.74, 15.55 **IR** (thin film, cm<sup>-1</sup>): 3044, 2912, 1643, 1607, 1572, 1488, 1457, 1406, 1332, 1228, 1205, 1117, 1080. **SMILES** = CCOC1OC2=CC=CC=C2C=C1. **InChI** = 1/C11H12O2/c1-2-12-11-8-7-9-5-3-4-6-10(9)13-11/h3-8,11H,2H2,1H3/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-16,13-16.

**2-ethoxy-6-nitro-2H-chromene**

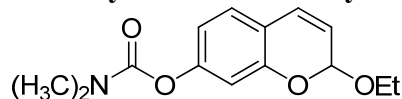
The reaction was performed on a 19.6 mmol scale. The crude reaction was purified by flash column chromatography over silica gel (isocratic 8% ethyl acetate in hexanes) to afford the product as a solid. **Yield:** 1.0 g, 23%; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.20 – 7.89 (m, 2H), 7.01 (d, *J* = 8.9, 1H), 6.74 (d, *J* = 9.8, 1H), 5.98 (dd, *J* = 3.6, 9.8, 1H), 5.79 (d, *J* = 3.6, 1H), 3.95 (dq, *J* = 7.1, 9.6, 1H), 3.69 (dq, *J* = 7.1, 9.6, 1H), 1.19 (t, *J* = 7.1, 3H) **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 156.9, 142.1, 125.3, 125.2, 125.1, 122.9, 122.3, 120.8, 117.3, 117.3, 95.9, 64.5, 15.4 **IR** (thin film, cm<sup>-1</sup>): 3073, 2979, 2930, 1647, 1615, 1577, 1516, 1484, 1345, 1258, 1237, 1080, 1000. **SMILES** = CCOC1OC2=CC=C([N+]([O-])=O)C=C2C=C1. **InChI** = 1/C11H11NO4/c1-2-15-11-6-3-8-7-9(12(13)14)4-5-10(8)16-11/h3-7,11H,2H2,1H3/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-14,13-16,14-16,15-16,16-16.

**2-ethoxy-7-methoxy-2H-chromene**

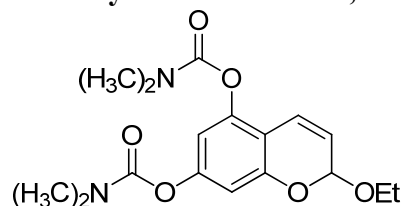
The reaction was performed on a 19.6 mmol scale. The crude reaction was purified by flash column chromatography over silica gel (isocratic 7% ethyl acetate in hexanes) to afford the product as an oil. **Yield:** 1.2 g, 29%; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.04 (d, *J* = 8.5, 1H), 6.67 (d, *J* = 9.5, 1H), 6.53 (d, *J* = 7.8, 2H), 5.79 – 5.63 (m, 2H), 4.03 – 3.87 (m, 1H), 3.80 (s, 3H), 3.66 (m, 1H), 1.21 (t, *J* = 7.1, 3H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 161.0, 152.7, 128.5, 126.4, 117.4, 114.4, 107.8, 102.3, 95.4, 63.5, 55.5, 15.5 **IR** (thin film, cm<sup>-1</sup>): 3045, 2975, 2932, 2912, 2837, 1642, 1616, 1570, 1506, 1465. **SMILES** = CCOC1OC2=CC(OC)=CC=C2C=C1. **InChI** = 1/C12H14O3/c1-3-14-12-7-5-9-4-6-10(13-2)8-11(9)15-12/h4-8,12H,3H2,1-2H3/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-16,14-16,15-16.

**7-chloro-2-ethoxy-2H-chromene**

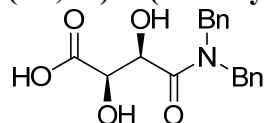
The reaction was run on a 50 mmol scale. The crude reaction was purified by flash column chromatography over silica gel (isocratic 2% ethyl acetate in hexanes) to afford the product as an oil. **Yield:** 4.2 g, 40%; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.15 – 6.81 (m, 3H), 6.68 (d, *J* = 9.7, 1H), 5.86 (dd, *J* = 3.7, 9.7, 1H), 5.68 (d, *J* = 3.7, 1H), 3.94 (dq, *J* = 7.1, 9.6, 1H), 3.66 (dq, *J* = 7.1, 9.6, 1H), 1.21 (t, *J* = 7.1, 3H) **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 152.3, 134.4, 128.0, 125.9, 120.3, 119.6, 117.2, 95.2, 64.0, 15.4 **IR** (thin film, cm<sup>-1</sup>): 3058, 2977, 2927, 1643, 1603, 1563, 1486, 1391, 1333, 1222, 1161, 1128, 1071, 1038. **SMILES** = ClC1=CC=C2C(OC(OCC)C=C2)=C1. **InChI** = 1/C11H11ClO2/c1-2-13-11-6-4-8-3-5-9(12)7-10(8)14-11/h3-7,11H,2H2,1H3/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-35,13-16,14-16.

**2-ethoxy-2H-chromen-7-yl dimethylcarbamate**

The reaction was performed on a 19.6 mmol scale. The crude reaction was purified by flash column chromatography over silica gel (isocratic 20% ethyl acetate in hexanes) to afford the product as a sticky oil. **Yield:** 1.06 g, 31%; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.08 (d, *J* = 8.2, 1H), 6.72 (ddd, *J* = 5.9, 13.1, 15.4, 3H), 5.80 (dd, *J* = 3.7, 9.7, 1H), 5.67 (d, *J* = 3.7, 1H), 3.92 (dq, *J* = 7.1, 9.6, 1H), 3.63 (dq, *J* = 7.1, 9.6, 1H), 3.06 (s, 3H), 2.99 (s, 3H), 1.18 (t, *J* = 7.1, 3H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 154.5, 152.1, 127.2, 125.9, 119.1, 118.0, 114.8, 110.3, 94.9, 63.5, 36.6, 36.4, 15.2 **IR** (thin film, cm<sup>-1</sup>): 3051, 2976, 2930, 1727, 1724, 1644, 1618, 1489, 1386, 1168. **SMILES** = O=C(N(C)C)OC1=CC=C2C(OC(OCC)C=C2)=C1. **InChI** = 1/C14H17NO4/c1-4-17-13-8-6-10-5-7-11(9-12(10)19-13)18-14(16)15(2)3/h5-9,13H,4H2,1-3H3/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-14,16-16,17-16,18-16,19-16.

**2-ethoxy-2H-chromene-5,7-diyl bis(dimethylcarbamate)**

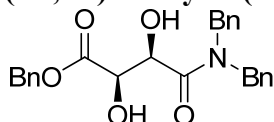
The reaction was performed on a 2.3 mmol scale. The crude reaction was purified by flash column chromatography over silica gel (isocratic 50% ethyl acetate in hexanes) to afford the product as a sticky oil. **Yield:** 282 mg, 35%; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 6.76 (d, *J* = 9.9, 1H), 6.65 (dd, *J* = 2.1, 5.6, 2H), 5.79 (dd, *J* = 3.7, 9.9, 1H), 5.65 (d, *J* = 3.7, 1H), 3.88 (dq, *J* = 7.1, 9.4, 1H), 3.60 (dq, *J* = 7.1, 9.4, 1H), 3.05 (s, 3H), 3.01 (s, 3H), 2.96 (s, 3H), 2.95 (s, 3H), 1.16 (t, *J* = 7.1, 3H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 154.1, 153.9, 152.3, 151.5, 147.3, 120.2, 119.1, 111.3, 109.1, 107.3, 94.9, 63.5, 36.7, 36.6, 36.3, 15.1 **IR** (thin film, cm<sup>-1</sup>): 3051, 2976, 2930, 1727, 1724, 1644, 1618, 1489, 1386, 1168. **SMILES** = O=C(N(C)C)OC1=CC(OC(N(C)C)=O)=C2C(OC(OCC)C=C2)=C1. **InChI** = 1/C17H22N2O6/c1-6-22-15-8-7-12-13(24-15)9-11(23-16(20)18(2)3)10-14(12)25-17(21)19(4)5/h7-10,15H,6H2,1-5H3/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-14,19-14,20-16,21-16,22-16,23-16,24-16,25-16.

**(2*R*,3*R*)-4-(dibenzylamino)-2,3-dihydroxy-4-oxobutanoic acid (16)**

**Yield:** 4.4 g, 55%; **[α]<sub>D</sub><sup>23</sup>** = +14.2° (c 1.0, CH<sub>3</sub>OH); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.39 – 7.21 (m, 6H), 7.12 (t, *J* = 5.9, 4H), 4.80 (d, *J* = 3.0, 1H), 4.59 (dd, *J* = 15.7, 24.3, 2H), 4.45 (dd, *J* = 6.9, 15.6, 2H), 4.38 (d, *J* = 3.0, 1H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 173.5, 172.2, 136.6, 136.2, 128.8, 128.5, 127.9, 127.6, 127.3, 127.0, 71.9, 70.8 **IR** (thin film, cm<sup>-1</sup>): 3420, 3056, 2929, 1733, 1684, 1652, 1558, 1506, 1472, 1455, 1265 **HRMS**: calc'd for (M+Na)<sup>+</sup> C<sub>18</sub>H<sub>19</sub>NO<sub>5</sub>: 252.1161; found: 252.1163. **SMILES** = O=C(N(CC1=CC=CC=C1)CC2=CC=CC=C2)[C@H](O)[C@@H]

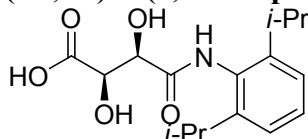
(O)C(O)=O. **InChI** = 1/C18H19NO5/c20-15(16(21)18(23)24)17(22)19(11-13-7-3-1-4-8-13)12-14-9-5-2-6-10-14/h1-10,15-16,20-21H,11-12H2,(H,23,24)/t15-,16-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-14,20-16,21-16,22-16,23-16,24-16.

**(2*R*,3*R*)-benzyl 4-(dibenzylamino)-2,3-dihydroxy-4-oxobutanoate (17)**



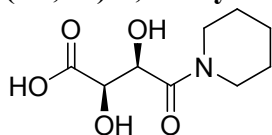
The esterification of tartaramide **16** was performed using the boric acid catalyzed ester condensation reported in literature.<sup>5</sup>  $[\alpha]_D^{23} = +5.3^\circ$  (c 1.0, CH<sub>3</sub>OH); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.52 – 7.11 (m, 15H), 4.91 (d, *J* = 5.7, 1H), 4.72 (d, *J* = 14.7, 1H), 4.54 (d, *J* = 15.5, 2H), 4.42 (dd, *J* = 4.5, 11.9, 3H), 3.41 (d, *J* = 7.5, 1H). <sup>13</sup>C NMR (75.0 MHz, CDCl<sub>3</sub>): δ 171.7, 171.1, 136.2, 135.2, 135.1, 129.4, 129.0, 128.8, 128.8, 128.6, 128.5, 128.3, 128.0, 127.0, 71.9, 70.1, 68.1, 49.2, 48.6. IR (thin film, cm<sup>-1</sup>): 3425, 3064, 2934, 1750, 1647, 1496, 1453, 1397, 1266, 1238, 1121, 1078. HRMS: calc'd for (M+Na)<sup>+</sup> C<sub>25</sub>H<sub>25</sub>ON<sub>5</sub>: 442.1630; found: 442.1610. **SMILES** = O=C(N(CC1=CC=CC=C1)CC2=CC=CC=C2)[C@H](O)[C@@H](O)C(OCC3=CC=CC=C3)=O. **InChI** = 1/C25H25NO5/c27-22(23(28)25(30)31-18-21-14-8-3-9-15-21)24(29)26(16-19-10-4-1-5-11-19)17-20-12-6-2-7-13-20/h1-15,22-23,27-28H,16-18H2/t22-,23-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-12,20-12,21-12,22-12,23-12,24-12,25-12,26-14,27-16,28-16,29-16,30-16,31-16.

**(2*R*,3*R*)-4-(2,6-diisopropylphenylamino)-2,3-dihydroxy-4-oxobutanoic acid (18)**

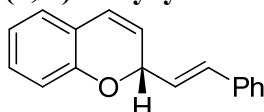


**Yield:** 240 mg, 44%;  $[\alpha]_D^{23} = +81.9^\circ$  (c 1.0, CH<sub>3</sub>OH); <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO): δ 9.06 (s, 1H), 7.32 – 7.16 (m, 1H), 7.11 (d, *J* = 7.7, 2H), 5.79 (s, 1H), 5.07 (s, 1H), 4.41 (d, *J* = 10.3, 2H), 3.12 (dt, *J* = 6.8, 13.6, 2H), 1.07 (d, *J* = 6.8, 12H). <sup>13</sup>C NMR (75.0 MHz, CD<sub>3</sub>OD): δ 174.3, 171.5, 146.6, 132.8, 127.2, 123.9, 122.6, 74.2, 72.8, 71.1, 28.6, 27.6, 25.5, 24.5, 23.5. IR (thin film, cm<sup>-1</sup>): 3333, 3071, 2965, 2870, 1739, 1661, 1518, 1382, 1255, 1123. HRMS: calc'd for (M)<sup>+</sup> C<sub>16</sub>H<sub>23</sub>NO<sub>5</sub>: 310.1654; found: 310.1660. **SMILES** = O=C(NC1=C(C(C)C)C=CC=C1C(C)C)[C@H](O)[C@@H](O)C(O)=O. **InChI** = 1/C16H23NO5/c1-8(2)10-6-5-7-11(9(3)4)12(10)17-15(20)13(18)14(19)16(21)22/h5-9,13-14,18-19H,1-4H3,(H,17,20)(H,21,22)/t13-,14-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-14,18-16,19-16,20-16,21-16,22-16.

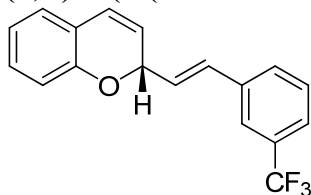


**(2*R*,3*R*)-2,3-dihydroxy-4-oxo-4-(piperidin-1-yl)butanoic acid (19)**

**Yield:** 3.65 g, 46%;  $[\alpha]_{\text{D}}^{23} = -8.1^{\circ}$  (c 1.0, CH<sub>3</sub>OH); **<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-DMSO): δ 4.58 (d, *J* = 3.1, 1H), 4.13 (d, *J* = 3.1, 1H), 3.42 (m 4H), 1.76 – 1.21 (m, 6H) **<sup>13</sup>C NMR** (75.0 MHz, CD<sub>3</sub>OD): δ 173.5, 168.9, 71.9, 70.4, 45.9, 44.2, 43.3, 26.2, 25.6, 24.4, 22.6, 22.1 **IR** (thin film, cm<sup>-1</sup>): 3348, 3019, 2982, 2939, 2861, 1734, 1636, 1605, 1484, 1216 **HRMS:** calc'd for (M)<sup>+</sup> C<sub>9</sub>H<sub>15</sub>NO<sub>5</sub>: 218.1028; found: 218.1034. **SMILES** = O=C(N1CCCCC1)[C@H](O)[C@@H](O)C(O)=O. **InChI** = 1/C9H15NO5/c11-6(7(12)9(14) 15)8(13)10-4-2-1-3-5-10/h6-7,11-12H,1-5H2,(H,14,15)/t6-,7-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-14,11-16,12-16,13-16,14-16,15-16.

**(*S,E*)-2-styryl-2*H*-chromene (6)**

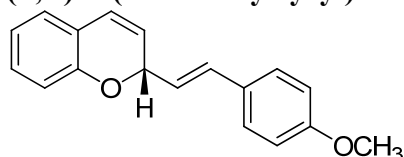
The reaction was performed using method A at the temperature of -40 °C. The crude reaction was purified by flash column chromatography (isocratic 2% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 97 mg, 83%; **er:** 99:1;  $[\alpha]_{\text{D}}^{23} = +244.9^{\circ}$  (c 1.0, CHCl<sub>3</sub>); **HPLC Analysis**, *t<sub>r</sub>* minor: 9.54 min., *t<sub>r</sub>* major: 10.34 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 99.7:0.3, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz 2H), 7.25 (m, 1H), 7.13 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.00 (dd, *J* = 3.6, 1.6 Hz, 1H), 6.87 (dt, *J* = 7.2, 0.8 Hz, 1H), 6.84 (d, *J* = 8 Hz, H) 6.68 (d, *J* = 15.6 Hz, 1H) 6.49 (dd, *J* = 10, 0.8 Hz, 1H) 6.37 (dd, *J* = 15.6, 6.8 Hz, 1H) 5.75 (dd, *J* = 9.6, 4 Hz, 1H) 5.48 (m, 1H) **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 153.0, 136.3, 132.1, 129.4, 128.6, 128.0, 127.1, 126.8, 126.6, 124.2, 123.8, 121.6, 121.2, 116.1, 75.6 **IR** (thin film, cm<sup>-1</sup>): 3058, 3026, 2961, 2924, 2852, 1485, 1456, 1225, 1200, 1113 **HRMS:** calc'd for (M+H)<sup>+</sup> C<sub>17</sub>H<sub>15</sub>O: 235.1123; found: 235.1185. **SMILES** = [H][C@@]1(/C=C/C2=CC=CC=C2)OC3=CC=CC=C3C=C1. **InChI** = 1/C17H14O/c1-2-6-14(7-3-1)10-12-16-13-11-15-8-4-5-9-17(15)18-16/h1-13,16H/b12-10+/t16-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-16.

**(*S,E*)-2-(3-(trifluoromethyl)styryl)-2*H*-chromene (20)**

The reaction was performed using method A at the temperature of 4 °C. The crude reaction was purified by flash column chromatography (isocratic 2% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 107 mg, 71%; **er:** 96.5:3.5;  $[\alpha]_{\text{D}}^{23} = +350.9^{\circ}$  (c 1.0, CHCl<sub>3</sub>); **HPLC Analysis**, *t<sub>r</sub>* minor: 6.40 min., *t<sub>r</sub>* major: 5.88 min., [Chiralpak<sup>®</sup> AD-H column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 99.7:0.3, 1.0 mL/min]; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.54 (s, 1H), 7.52 – 7.28 (m, 3H), 7.10 – 7.00 (m, 1H), 6.93 (dd, *J* = 1.6, 7.4, 1H), 6.80 (ddd, *J* = 4.6, 9.7,

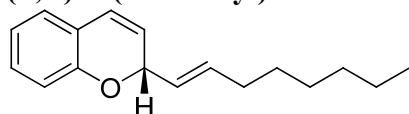
13.1, 2H), 6.62 (d,  $J = 15.9$ , 1H), 6.43 (d,  $J = 9.7$ , 1H), 6.35 (dd,  $J = 6.7$ , 15.9, 1H), 5.67 (dd,  $J = 3.9$ , 9.8, 1H), 5.46 – 5.37 (m, 1H)  $^{13}\text{C}$  NMR (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.1, 137.3, 129.8, 129.5, 129.3, 129.2, 126.7, 124.8, 123.5, 121.6, 120.2, 116.8, 116.3, 75.4 IR (thin film,  $\text{cm}^{-1}$ ): 3043, 2976, 2927, 1605, 1486, 1456, 1437, 1331, 1227, 1201, 1165, 1124, 1072 LRMS: calc'd for  $(\text{M}+\text{H})^+$   $\text{C}_{18}\text{H}_{13}\text{F}_3\text{O}$ : 303.09; found: 303.20. SMILES = [H][C@@]1(/C=C/C2=CC(C(F)(F)F)=CC=C2)OC3=CC=CC=C3C=C1. InChI = 1/C18H13F3O/c19-18(20,21)15-6-3-4-13(12-15)8-10-16-11-9-14-5-1-2-7-17(14)22-16/h1-12,16H/b10-8+/t16-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-19,20-19,21-19,22-16.

**(*S,E*)-2-(4-methoxystyryl)-2*H*-chromene (21)**



The reaction was performed using method B at the temperature of  $-40$  °C. The crude reaction was purified by flash column chromatography (gradient 2 - 4% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 94 mg, 71%; **er:** 98.5:1.5;  $[\alpha]_{\text{D}}^{23} = +351.5^\circ$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 15.15 min.,  $t_{\text{r}}$  major: 16.40 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 99.5:0.5, 0.8 mL/min];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.34 (d,  $J = 8.8$ , 2H), 7.13 (td,  $J = 1.7$ , 7.8, 1H), 7.01 (dd,  $J = 1.5$ , 7.4, 1H), 6.94 – 6.79 (m, 4H), 6.63 (d,  $J = 15.8$ , 1H), 6.49 (d,  $J = 9.8$ , 1H), 6.26 (dd,  $J = 7.3$ , 15.8, 1H), 5.75 (dd,  $J = 3.8$ , 9.8, 1H), 5.52 – 5.41 (m, 1H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.5, 153.0, 131.8, 129.3, 128.9, 128.0, 126.6, 124.9, 124.8, 124.1, 124.0, 124.0, 121.6, 121.1, 116.1, 113.9, 55.3, 55.2. IR (thin film,  $\text{cm}^{-1}$ ): 3039, 3004, 2956, 2932, 2835, 1642, 1606, 1511, 1485, 1455 HRMS: calc'd for  $(\text{M}+\text{H})^+$   $\text{C}_{18}\text{H}_{16}\text{O}_2$ : 265.1229; found: 265.1228. SMILES = [H][C@@]1(/C=C/C2=CC(OC)=C2)OC3=CC=CC=C3C=C1. InChI = 1/C18H16O2/c1-19-16-10-6-14(7-11-16)8-12-17-13-9-15-4-2-3-5-18(15)20-17/h2-13,17H,1H3/b12-8+/t17-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-16,20-16.

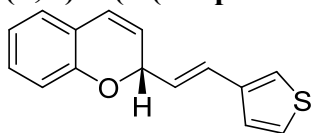
**(*S,E*)-2-(oct-1-enyl)-2*H*-chromene (22)**



The reaction was performed using method A at the temperature of  $-20$  °C. The crude reaction was purified by flash column chromatography (isocratic 1% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 91 mg, 75%; **er:** 99:1;  $[\alpha]_{\text{D}}^{23} = +124.0^\circ$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 19.66 min.,  $t_{\text{r}}$  major: 20.50 min., Chiralcel<sup>®</sup> OD column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 100:0, 0.8 mL/min];  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.21 – 6.66 (m, 7H), 6.41 (d,  $J = 9.3$ , 1H), 5.91 – 5.53 (m, 3H), 5.27 (s, 1H), 2.14 – 1.92 (m, 2H), 1.39 – 1.15 (m, 8H), 0.87 (d,  $J = 6.5$ , 3H).  $^{13}\text{C}$  NMR (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.4, 134.7, 129.3, 128.0, 126.6, 124.9, 123.9, 121.9, 121.2, 116.2, 32.4, 31.8, 29.9, 29.0, 22.8, 14.3. IR (thin film,  $\text{cm}^{-1}$ ): 3042, 2956, 2926, 2854, 1733, 1635, 1486, 1456, 1226, 1202, 1112 LRMS: calc'd for  $(\text{M}+\text{H})^+$   $\text{C}_{17}\text{H}_{23}\text{O}$ : 243.17; found: 243.31. SMILES = CCCCC/C=C/[C@]1([H])OC2=CC=CC=C2C=C1. InChI = 1/C17H22O/c1-2-3-4-5-6-7-11-

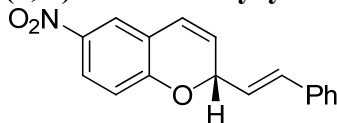
16-14-13-15-10-8-9-12-17(15)18-16/h7-14,16H,2-6H2,1H3/ b11-7+/t16-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-16.

**(*R,E*)-2-(2-(thiophen-3-yl)vinyl)-2*H*-chromene (23)**

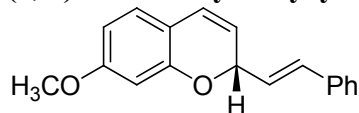


The reaction was performed using method B at the temperature of  $-40\text{ }^{\circ}\text{C}$ . The crude reaction was purified by flash column chromatography (isocratic 2% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 92 mg, 77%; **er:** 99.5:0.5;  $[\alpha]_{\text{D}}^{23} = +451.2^{\circ}$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 9.91 min.,  $t_{\text{r}}$  major: 10.65 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 99.7:0.3, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23 (d,  $J = 22.5$ , 3H), 7.13 (d,  $J = 6.0$ , 1H), 7.00 (d,  $J = 7.0$ , 1H), 6.86 (dt,  $J = 7.2$ , 13.6, 2H), 6.68 (dd,  $J = 5.7$ , 15.8, 1H), 6.49 (d,  $J = 9.7$ , 1H), 6.30 – 6.14 (m, 1H), 5.77 – 5.66 (m, 1H), 5.45 (s, 1H). **<sup>13</sup>C NMR** (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.0, 138.9, 129.9, 128.8, 127.3, 126.7, 125.9, 125.2, 124.5, 123.5, 122.6, 121.5, 120.5, 116.7, 115.5 **IR** (thin film,  $\text{cm}^{-1}$ ): 3100, 3041, 3024, 2958, 2925, 1640, 1604, 1572, 1485, 1271 **HRMS:** calc'd for ( $\text{M}+\text{H}$ )<sup>+</sup>  $\text{C}_{15}\text{H}_{12}\text{OS}$ : 241.0687; found: 241.0690. **SMILES** = [H][C@@]1(/C=C/C2=CSC=C2)OC3=CC=CC=C3C=C1. **InChI** = 1/C15H12OS/c1-2-4-15-13(3-1)6-8-14(16-15)7-5-12-9-10-17-11-12/h1-11,14H/b7-5+/t14-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-16,17-32.

**(*S,E*)-6-nitro-2-styryl-2*H*-chromene (24)**

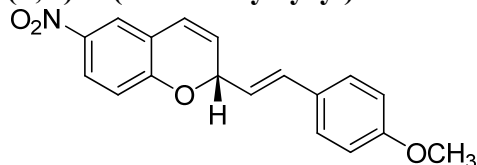


The reaction was performed using method C at the temperature of  $20\text{ }^{\circ}\text{C}$ . The crude reaction was purified by flash column chromatography (isocratic 8% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 110 mg, 79%; **er:** 96:4;  $[\alpha]_{\text{D}}^{23} = +244.9^{\circ}$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 23.94 min.,  $t_{\text{r}}$  major: 25.04 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 99.5:0.5, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (ddd,  $J = 0.7$ , 2.7, 8.9, 1H), 7.91 (d,  $J = 2.7$ , 1H), 7.48 – 7.18 (m, 6H), 6.86 (d,  $J = 8.9$ , 1H), 6.68 (d,  $J = 15.8$ , 1H), 6.53 (d,  $J = 10.0$ , 1H), 6.31 (ddd,  $J = 0.7$ , 7.1, 15.8, 1H), 5.89 (dd,  $J = 3.8$ , 10.0, 1H), 5.73 – 5.54 (m, 1H). **<sup>13</sup>C NMR** (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 141.7, 135.6, 133.9, 132.7, 129.3, 129.1, 128.0, 127.8, 126.2, 124.9, 123.3, 122.9, 121.6, 121.6, 117.1, 115.8 **IR** (thin film,  $\text{cm}^{-1}$ ): 3082, 3060, 3028, 2917, 2848, 2667, 1643, 1577, 1512, 1340 **HRMS:** calc'd for ( $\text{M}$ )<sup>+</sup>  $\text{C}_{17}\text{H}_{14}\text{NO}_3$ : 280.0974; found: 280.0977. **SMILES** = [H][C@@]1(/C=C/C2=CC=CC=C2)OC3=CC=C([N+](=O)[O-])C=C3C=C1. **InChI** = 1/C17H14NO3/c19-18(20)15-8-11-17-14(12-15)7-10-16(21-17)9-6-13-4-2-1-3-5-13/h1-12,16H/b9-6+/t16-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-14,19-16,20-16,21-16.

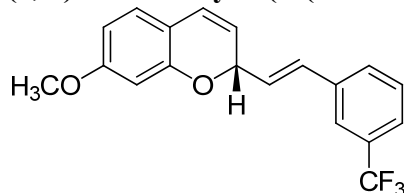
**(*S,E*)-7-methoxy-2-styryl-2*H*-chromene (25)**

The reaction was performed using method A at the temperature of  $-20\text{ }^{\circ}\text{C}$ . The crude reaction was purified by flash column chromatography (isocratic 7% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 97 mg, 74%; **er:** 96:4;  $[\alpha]_{\text{D}}^{23} = +424.9^{\circ}$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 14.27 min.,  $t_{\text{r}}$  major: 15.95 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 99.5:0.5, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47 – 7.36 (m, 2H), 7.30 (dt,  $J = 7.1, 17.5$ , 3H), 6.92 (d,  $J = 8.9$ , 1H), 6.67 (d,  $J = 15.9$ , 1H), 6.49 – 6.41 (m, 3H), 6.37 (dd,  $J = 7.1, 15.8$ , 1H), 5.61 (dd,  $J = 3.8, 9.8$ , 1H), 5.51 – 5.39 (m, 1H), 3.78 (s, 3H).

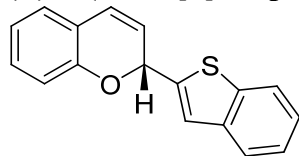
**<sup>13</sup>C NMR** (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.77, 154.2, 136.3, 132.0, 128.6, 128.4, 128.1, 127.3, 127.2, 126.8, 126.7, 123.8, 120.8, 120.7, 114.9, 106.9, 101.9, 55.2. **IR** (thin film,  $\text{cm}^{-1}$ ): 3060, 3019, 2978, 2931, 1641, 1613, 1566, 1504, 1464, 1313 **HRMS:** calc'd for ( $\text{M}+\text{H}$ )<sup>+</sup>  $\text{C}_{18}\text{H}_{17}\text{O}_2$ : 265.1229; found: 265.1239. **SMILES** = [H][C@@]1(/C=C/C2=CC=CC=C2)OC3=CC(OC)=CC=C3C=C1. **InChI** = 1/C18H16O2/c1-19-17-12-9-15-8-11-16(20-18(15)13-17)10-7-14-5-3-2-4-6-14/h2-13,16H,1H3/b10-7+/t16-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-16,20-16.

**(*S,E*)-2-(4-methoxystyryl)-6-nitro-2*H*-chromene (26)**

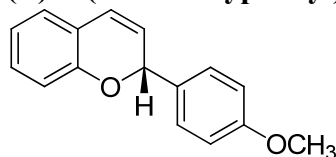
The reaction was performed using method C at the temperature of  $4\text{ }^{\circ}\text{C}$ . The crude reaction was purified by flash column chromatography (isocratic 10% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 108 mg, 70%; **er:** 91:9;  $[\alpha]_{\text{D}}^{23} = +121.5^{\circ}$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 32.78 min.,  $t_{\text{r}}$  major: 34.63 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 99.5:0.5, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01 (ddd,  $J = 1.2, 2.6, 8.9$ , 1H), 7.93 – 7.86 (m, 1H), 7.38 – 7.29 (m, 2H), 6.85 (d,  $J = 8.8$ , 3H), 6.56 (dd,  $J = 12.9, 42.3$ , 2H), 6.17 (ddd,  $J = 1.2, 7.4, 15.8$ , 1H), 5.92 – 5.81 (m, 1H), 5.64 – 5.54 (m, 1H), 3.80 (s, 3H). **<sup>13</sup>C NMR** (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.9, 158.6, 141.6, 133.7, 132.5, 128.8, 128.3, 127.58, 126.52, 126.4, 125.1, 124.7, 123.2, 121.6, 117.13, 115.8, 114.7, 113.4, 55.8. **IR** (thin film,  $\text{cm}^{-1}$ ): 3071, 3034, 3005, 2959, 2933, 2837, 1644, 1607, 1577, 1512 **HRMS:** calc'd for ( $\text{M}+\text{H}$ )<sup>+</sup>  $\text{C}_{18}\text{H}_{15}\text{NO}_4$ : 310.1079; found: 310.1067. **SMILES** = [H][C@@]1(/C=C/C2=CC=C(OC)C=C2)OC3=CC=C([N+])([O-])=O)C=C3C=C1. **InChI** = 1/C18H15NO4/c1-22-16-7-2-13(3-8-16)4-9-17-10-5-14-12-15(19(20)21)6-11-18(14)23-17/h2-12,17H,1H3/b9-4+/t17-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-14,20-16,21-16,22-16,23-16.

**(*S,E*)-7-methoxy-2-(3-(trifluoromethyl)styryl)-2*H*-chromene (27)**

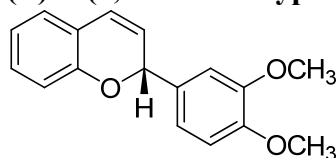
The reaction was performed using method B at the temperature of 4 °C. The crude reaction was purified by flash column chromatography (isocratic 2% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 119 mg, 72%; **er:** 94:6;  $[\alpha]_D^{23} = +310.0^\circ$  (c 1.0, CHCl<sub>3</sub>); **HPLC Analysis**,  $t_r$  minor: 10.73 min.,  $t_r$  major: 12.20 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 99.7:0.3, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.55 (s, 1H), 7.51 – 7.26 (m, 3H), 6.85 (d, *J* = 8.6, 1H), 6.61 (d, *J* = 15.9, 1H), 6.41 – 6.28 (m, 3H), 5.55 – 5.48 (m, 1H), 5.46 – 5.36 (m, 1H), 3.70 (s, 3H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 161.0, 137.3, 129.2, 124.7, 124.3, 123.5, 120.4, 114.9, 107.3, 102.2, 75.5, 55.5 **IR** (thin film, cm<sup>-1</sup>): 3068, 2932, 2854, 1652, 1616, 1558, 1506, 1456, 1331, 1274, 1159, 1120, 1073 **LRMS**: calc'd for (M+H)<sup>+</sup> C<sub>19</sub>H<sub>5</sub>F<sub>3</sub>O<sub>2</sub>: 333.10; found: 333.22. **SMILES** = [H][C@@]1(/C=C/C2=CC(C(F)(F)F)=CC=C2) OC3=CC(OC)=CC=C3C=C1. **InChI** = 1/C19H15F3O2/c1-23-17-10-7-14-6-9-16(24-18(14)12-17)8-5-13-3-2-4-15(11-13)19(20,21)22/h2-12,16H,1H3/b8-5+/t16-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-12,20-19,21-19,22-19,23-16,24-16.

**(*R*)-2-(benzo[*b*]thiophen-2-yl)-2*H*-chromene (28)**

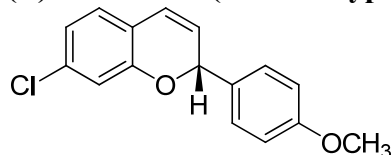
The reaction was performed using method D at the temperature of 4 °C. The crude reaction was purified by flash column chromatography (isocratic 2% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 95 mg, 72%; **er:** 95.5:4.5;  $[\alpha]_D^{23} = +156.3^\circ$  (c 1.0, CHCl<sub>3</sub>); **HPLC Analysis**,  $t_r$  minor: 8.95 min.,  $t_r$  major: 10.09 min., [(*R,R*) Whelk-O<sup>®</sup> column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 99.7:0.3, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.70 (d, *J* = 8.4, 1H), 7.64 (dd, *J* = 2.3, 6.3, 1H), 7.28 – 7.18 (m, 3H), 7.04 (dd, *J* = 4.6, 10.9, 1H), 6.97 (d, *J* = 7.4, 1H), 6.82 (dt, *J* = 4.3, 8.6, 1H), 6.75 (d, *J* = 8.1, 1H), 6.56 (d, *J* = 9.7, 1H), 6.10 (d, *J* = 4.0, 1H), 5.91 (dd, *J* = 4.0, 9.7, 1H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>): δ 152.4, 144.3, 140.1, 139.1, 129.6, 126.7, 124.9, 124.5, 124.2, 123.8, 123.3, 122.4, 121.6, 121.3, 116.4, 72.3 **IR** (thin film, cm<sup>-1</sup>): 3059, 2953, 2924, 2853, 1736, 1606, 1486, 1456, 1226, 1211, 1035 **HRMS**: calc'd for (M+H)<sup>+</sup> C<sub>17</sub>H<sub>12</sub>OS: 265.0687; found: 265.2017. **SMILES** = [H][C@@]1(C2=CC(C=CC=C3)=C3S2) OC4=CC=CC=C4C=C1. **InChI** = 1/C17H12OS/c1-3-7-14-12(5-1)9-10-15(18-14)17-11-13-6-2-4-8-16(13)19-17/h1-11,15H/t15-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-16,19-32.

**(R)-2-(4-methoxyphenyl)-2H-chromene (29)**

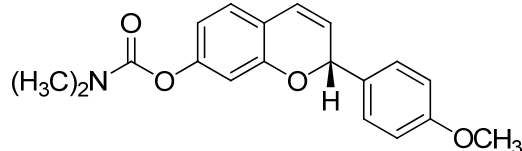
The reaction was performed using method D at the temperature of  $-10\text{ }^{\circ}\text{C}$ . The crude reaction was purified by flash column chromatography (gradient 2 - 5% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 84 mg, 71%; **er:** 98.5:1.5;  $[\alpha]_{\text{D}}^{23} = +267.7^{\circ}$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 27.60 min.,  $t_{\text{r}}$  major: 23.40 min., [Chiralcel<sup>®</sup> AD-H column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 99.7:0.3, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39 (d,  $J = 8.6$ , 2H), 7.10 (td,  $J = 1.6$ , 7.8, 1H), 7.02 (dd,  $J = 1.6$ , 7.4, 1H), 6.94 – 6.83 (m, 3H), 6.76 (d,  $J = 8.1$ , 1H), 6.55 (dd,  $J = 1.5$ , 9.8, 1H), 5.87 (dd,  $J = 1.8$ , 3.3, 1H), 5.79 (dd,  $J = 3.4$ , 9.8, 1H), 3.80 (s, 3H). **<sup>13</sup>C NMR** (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.7, 153.1, 132.8, 128.0, 126.8, 124.8, 124.0, 123.6, 121.7, 120.4, 116.6, 115.4, 114.6, 113.3, 104.9, 55.6, 55.0 **IR** (thin film,  $\text{cm}^{-1}$ ): 3041, 3002, 2956, 2934, 2835, 1610, 1585, 1512, 1485, 1456 **HRMS:** calc'd for  $(\text{M}+\text{H})^+$   $\text{C}_{16}\text{H}_{14}\text{O}_2$ : 239.1072; found: 239.1076. **SMILES** = [H][C@@]1(C2=CC=C(OC)C=C2)OC3=CC=CC=C3C=C1. **InChI** = 1/C16H14O2/c1-17-14-9-6-13(7-10-14)16-11-8-12-4-2-3-5-15(12)18-16/h2-11,16H, 1H3/t16-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-16,18-16.

**(R)-2-(3,4-dimethoxyphenyl)-2H-chromene (30)**

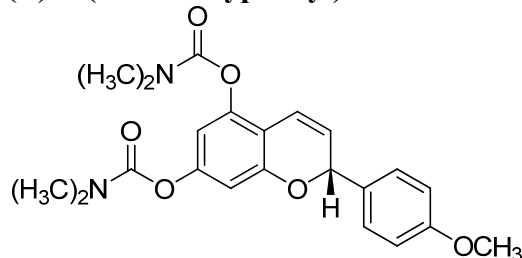
The reaction was performed using method D at the temperature of  $4\text{ }^{\circ}\text{C}$ . The crude reaction was purified by flash column chromatography (isocratic 8% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 91 mg, 68%; **er:** 97.5:2.5;  $[\alpha]_{\text{D}}^{23} = +165.0^{\circ}$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 25.99 min.,  $t_{\text{r}}$  major: 23.06 min., [Chiralcel<sup>®</sup> AD-H column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 99:1, 1.0 mL/min]; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.01 (td,  $J = 1.6$ , 7.8, 1H), 6.96 – 6.88 (m, 3H), 6.77 (ddd,  $J = 2.9$ , 6.6, 8.1, 2H), 6.69 (d,  $J = 8.0$ , 1H), 6.46 (dd,  $J = 1.7$ , 9.8, 1H), 5.77 (dd,  $J = 2.0$ , 3.1, 1H), 5.70 (dd,  $J = 3.3$ , 9.8, 1H), 3.77 (d,  $J = 2.6$ , 6H). **<sup>13</sup>C NMR** (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.3, 149.4, 133.4, 129.7, 126.7, 124.4, 121.4, 119.9, 116.2, 111.1, 110.6, 56.1, 56.0 **IR** (thin film,  $\text{cm}^{-1}$ ): 2933, 2834, 1604, 1516, 1485, 1456, 1419, 1262, 1227, 1203, 1139, 1027 **LRMS:** calc'd for  $(\text{M})^+$   $\text{C}_{17}\text{H}_{16}\text{O}_3$ : 269.11; found: 269.15. **SMILES** = [H][C@@]1(C2=CC=C(OC)C(OC)=C2)OC3=CC=CC=C3C=C1. **InChI** = 1/C17H16O3/c1-18-16-10-8-13(11-17(16)19-2)15-9-7-12-5-3-4-6-14(12)20-15/h3-11,15H,1-2H3/t15-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-16,19-16,20-16.

**(R)-7-chloro-2-(4-methoxyphenyl)-2H-chromene (31)**

The reaction was performed using method D at the temperature of 4 °C. The crude reaction was purified by flash column chromatography (isocratic 5% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 115 mg, 85%; **er:** 97:3;  $[\alpha]_D^{23} = +263.5^\circ$  (c 1.0, CHCl<sub>3</sub>); **HPLC Analysis**,  $t_r$  minor: 16.84 min.,  $t_r$  major: 14.34 min., Chiralcel<sup>®</sup> OD column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 99.7:0.3, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): 7.35 (d,  $J = 8.8$ , 2H), 6.89 (m, 4H), 6.83 – 6.72 (m, 1H), 6.56 – 6.47 (m, 1H), 5.86 (dd,  $J = 1.7, 3.5$ , 1H), 5.79 (dd,  $J = 3.5, 9.8$ , 1H), 3.81 (s, 3H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>):  $\delta$  160.1, 153.8, 134.4, 132.4, 128.9, 127.3, 125.0, 123.3, 121.4, 120.1, 116.7, 114.2, 55.5. **IR** (thin film, cm<sup>-1</sup>): 3064, 2957, 2929, 2836, 1733, 1636, 1601, 1563, 1512, 1483, 1441, 1249, 1222, 1174, 1074, 1034 **LRMS:** calc'd for (M+H)<sup>+</sup> C<sub>16</sub>H<sub>13</sub>ClO<sub>2</sub>: 273.06; found: 273.11. **SMILES** = ClC1=CC=C2C(O[C@](C3=CC=C(OC)C=C3)([H])C=C2)=C1. **InChI** = 1/C16H13ClO2/c1-18-14-7-3-11(4-8-14)15-9-5-12-2-6-13(17)10-16(12)19-15/h2-10,15H,1H3/t15-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-35,18-16,19-16.

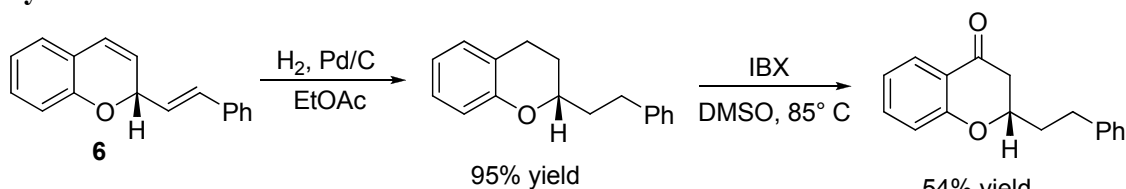
**(R)-2-(4-methoxyphenyl)-2H-chromen-7-yl dimethylcarbamate (32)**

The reaction was performed using method D with the minor change of 7.5 mol% **16** and 6.75 mol% Yb(OTf)<sub>3</sub> added twice at the temperature of 4 °C. The crude reaction was purified by flash column chromatography (isocratic 20% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 115 mg, 71%; **er:** 97:3;  $[\alpha]_D^{23} = +179.2^\circ$  (c 1.0, CHCl<sub>3</sub>); **HPLC Analysis**,  $t_r$  minor: 44.75 min.,  $t_r$  major: 41.10 min., [Chiralcel<sup>®</sup> AD-H column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 95:5, 0.8 mL/min]; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36 (d,  $J = 8.7$ , 2H), 6.97 (d,  $J = 8.2$ , 1H), 6.88 (d,  $J = 8.7$ , 2H), 6.63 (dd,  $J = 2.3, 8.2$ , 1H), 6.52 (dd,  $J = 1.8, 11.0$ , 2H), 5.85 (dd,  $J = 1.8, 3.2$ , 1H), 5.73 (dd,  $J = 3.4, 9.8$ , 1H), 3.79 (s, 3H), 3.04 (s, 3H), 2.98 (s, 3H). **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>):  $\delta$  154.6, 153.7, 152.2, 132.7, 129.2, 128.2, 128.0, 127.3, 126.0, 123.8, 123.0, 118.6, 114.8, 114.6, 113.9, 113.3, 110.3, 109.5, 55.0, 35.8 **IR** (thin film, cm<sup>-1</sup>): 3014, 2933, 2836, 1724, 1641, 1611, 1585, 1512, 1389, 1304 **HRMS:** calc'd for (M+Na)<sup>+</sup> C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>Na: 348.1212; found: 348.1209. **SMILES** = O=C(N(C)C)OC1=CC=C2C(O[C@](C3=CC=C(OC)C=C3)([H])C=C2)=C1. **InChI** = 1/C19H19NO4/c1-20(2)19(21)23-16-10-6-14-7-11-17(24-18(14)12-16)13-4-8-15(22-3)9-5-13/h4-12,17H,1-3H3/t17-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-12,20-14,21-16,22-16,23-16,24-16.

**(R)-2-(4-methoxyphenyl)-2H-chromene-5,7-diyl bis(dimethylcarbamate) (33)**

The reaction was performed using method D at the temperature of  $-10\text{ }^{\circ}\text{C}$ . The crude reaction was purified by flash column chromatography (gradient 50% - 80% ethyl acetate in hexanes) to afford the product as a pale yellow oil. **Yield:** 154 mg, 75%; **er:** 95:5;  $[\alpha]_{\text{D}}^{23} = +148.3^{\circ}$  (c 1.0,  $\text{CHCl}_3$ ); **HPLC Analysis**,  $t_{\text{r}}$  minor: 9.50 min.,  $t_{\text{r}}$  major: 16.79 min., [Chiralcel<sup>®</sup> AD-H column, 25 cm  $\times$  4.6 mm I.D., Hexanes:IPA = 75:25, 1.0 mL/min]; **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63 (d,  $J = 7.9$ , 1H), 7.28 (d,  $J = 8.3$ , 2H), 6.81 (d,  $J = 8.1$ , 2H), 6.50 (ddd,  $J = 0.8$ , 3.0, 6.1, 2H), 6.42 – 6.30 (m, 1H), 5.76 (s, 1H), 5.73 – 5.61 (m, 1H), 3.72 (s, 3H), 3.04 (s, 3H), 2.94 (s, 6H), 2.89 (s, 3H) **<sup>13</sup>C NMR** (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.7, 154.1, 154.0, 151.6, 147.1, 143.8, 135.2, 132.2, 128.7, 124.1, 117.9, 114.0, 113.1, 111.9, 108.7, 107.0, 61.8, 55.2, 36.7, 36.6, 36.4, 27.4 **IR** (thin film,  $\text{cm}^{-1}$ ): 2934, 2836, 1728, 1706, 1603, 1511, 1440, 1376, 1310, 1246, 1173, 1129 **HRMS**: calc'd for  $(\text{M}+\text{H})^+$   $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_6$ : 413.1713; found: 412.66. **SMILES** = O=C(N(C)C)OC1=CC(OC(N(C)C)C)=O=C2C(O[C@](C3=CC=C(OC)C=C3)([H])C=C2)=C1. **InChI** = 1/C22H24N2O6/c1-23(2)21(25)28-16-12-19-17(20(13-16)30-22(26)24(3)4)10-11-18(29-19)14-6-8-15(27-5)9-7-14/h6-13,18H,1-5H3/t18-/m1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-12,19-12,20-12,21-12,22-12,23-14,24-14,25-16,26-16,27-16,28-16,29-16,30-16.

**Absolute stereochemistry determination for vinyl- and arylboronate addition products.**  
**Synthesis of flindersiachromanone.**



$[\alpha]_{\text{D}}^{23} = -52.5^{\circ}$  (c 1.0,  $\text{CH}_3\text{OH}$ )  
 Lit.<sup>5</sup>  $[\alpha]_{\text{D}}^{23} = -77.8^{\circ}$  (c 1.2,  $\text{CH}_3\text{OH}$ , (S)-enantiomer)

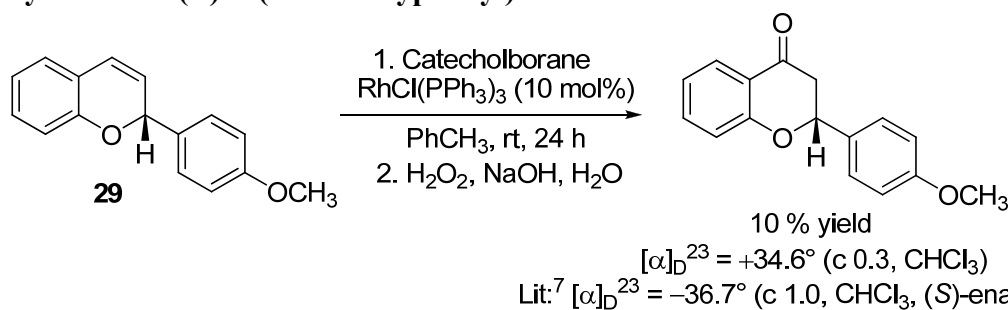
**(S)-2-phenethylchromane.** To an oven-dried 10 mL round-bottom flask was added (*R,E*)-2-styryl-2H-chromene **6** (98 mg, 0.42 mmol) and EtOAc (2.0 mL). The solution was purged with Ar and palladium on carbon (22 mg, 10% w/w, 0.021 mmol) was added. The flask was evacuated and placed under an atmosphere of  $\text{H}_2$  using a balloon. The reaction was stirred for 8 h and filtered through a pad of Celite and rinsed with EtOAc to afford pure product as a colorless oil (94 mg, 95 % yield). **Yield:** 94 mg, 95%;  $[\alpha]_{\text{D}}^{23} = -116.3^{\circ}$  (c = 1.0,  $\text{CHCl}_3$ ); **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.52 – 6.72 (m, 9H), 4.15 – 3.87 (m, 1H), 3.14 – 2.61 (m, 4H), 2.27 – 1.72 (m,



4H).  $^{13}\text{C}$  NMR (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.2, 142.2, 128.8, 128.6, 127.4, 126.1, 120.3, 117.0, 75.0, 37.4, 31.8, 27.8, 25.0 IR (thin film,  $\text{cm}^{-1}$ ): 3414, 3025, 2976, 2927, 1643, 1604, 1487, 1455, 1232, 1085, 1030 SMILES = [H][C@@]1(CCC2=CC=CC=C2)OC3=CC=CC=C3CC1. InChI = 1/C17H18O/c1-2-6-14(7-3-1)10-12-16-13-11-15-8-4-5-9-17(15)18-16/h1-9,16H,10-13H2/t16-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-16.

**(S)-flindersiachromanone.** A solution of the (*S*)-2-phenethylchromane (50 mg, 0.21 mmol) in DMSO (1.0 mL) was treated with IBX (176 mg, 0.63 mmol) and heated to 85 °C for 24 h. Reaction was cooled to ambient temperature, diluted with EtOAc (10 mL) and washed with saturated  $\text{NaHCO}_3$  (10 mL),  $\text{H}_2\text{O}$  (10 mL), and brine (10 mL). The organic layer was concentrated under reduced pressure and flash chromatography on silica gel (gradient 4 - 12% EtOAc in hexanes) afforded pure product as an oil (28 mg, 54% yield). All spectral and optical rotation data matched reported data for the (*S*)-enantiomer of flindersiachromanone.<sup>6,7</sup> **Yield:** 28 mg, 54%;  $[\alpha]_{\text{D}}^{23} = -52.5^\circ$  ( $c = 1.0$ ,  $\text{CH}_3\text{OH}$ ) Lit:<sup>5</sup>  $[\alpha]_{\text{D}}^{23} = -77.8^\circ$  ( $c = 1.2$ ,  $\text{CH}_3\text{OH}$ , 99.5:0.5 e.r., (*S*)-enantiomer);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (dd,  $J = 1.8, 8.0$ , 1H), 7.48 – 7.35 (m, 1H), 7.29 – 7.08 (m, 5H), 6.94 (m, 2H), 4.44 – 4.29 (m, 1H), 2.93 – 2.54 (m, 4H), 2.25 – 2.06 (m, 1H), 1.93 (m, 1H).  $^{13}\text{C}$  NMR (75.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.3, 161.5, 140.8, 136.0, 128.4, 126.1, 121.0, 117.8, 43.0, 36.5, 31.1 IR (thin film,  $\text{cm}^{-1}$ ): 3425, 3064, 2934, 1750, 1647, 1496, 1453, 1397, 1266, 1238, 1121, 1078. SMILES = O=C1C[C@@](C2=CC=CC=C2)([H])OC3=CC=CC=C31. InChI = 1/C17H16O2/c18-16-12-14(11-10-13-6-2-1-3-7-13)19-17-9-5-4-8-15(16)17/h1-9,14H,10-12H2/t14-/m0/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-12,18-16,19-16.

### Synthesis of (*R*)-2-(4-methoxyphenyl)chroman-4-one



**(*R*)-2-(4-methoxyphenyl)chroman-4-one.** To a dry 25 mL round bottom flask was added chromene **29** (183 mg, 0.75 mmol) and 10 mL dry toluene and purged with Ar.  $\text{RhCl}(\text{PPh}_3)_3$  (69 mg, 0.075 mmol) and catecholborane (160  $\mu\text{L}$ , 1.5 mmol) were added and the reaction was stirred for 24 h at room temperature.  $\text{NaOH}$  (5 mL, 3.0 M solution in  $\text{H}_2\text{O}$ ) was slowly added followed by slow addition of  $\text{H}_2\text{O}_2$  (5 mL, 30 % in  $\text{H}_2\text{O}$ ) and the biphasic mixture was stirred at room temperature for 3 h. The organic layer was separated and concentrated under reduced pressure. Flash chromatography on silica gel (gradient 10 – 20% EtOAc in hexanes) afforded

6. Kawasaki, M., Yoshikai, H., Kakuda, H., Toyooka, N., Tanaka, A., Goto, M. & Kometani, T. Asymmetric synthesis of flindersiachromanone using lipase-catalyzed reaction. *Heterocycles* **68**, 483-493 (2006).

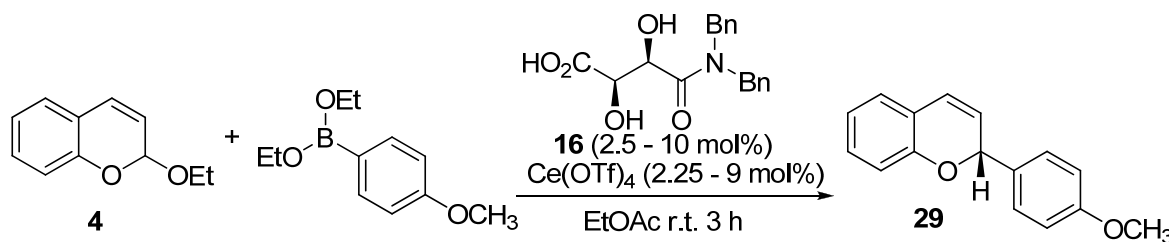
7. Biddle, M. M., Lin, M. & Scheidt, K. A. Catalytic enantioselective synthesis of flavanones and chromanones. *J. Am. Chem. Soc.* **129**, 3830-3831 (2007).

the desired flavanone as a sticky solid (19 mg, 10% yield). All spectral data matched reported data.<sup>8</sup> Optical rotation data was consistent with the opposite enantiomer reported the literature.<sup>7</sup>

**Yield:** 19 mg, 10%;  $[\alpha]_{\text{D}}^{23} = +34.6^{\circ}$  (c 0.3, CHCl<sub>3</sub>) Lit:<sup>7</sup>  $[\alpha]_{\text{D}}^{23} = -36.7^{\circ}$  (c 1.0, CHCl<sub>3</sub>, (S)-enantiomer); **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.78 (dd,  $J = 16.8, 2.8$ , 1H), 3.04 (dd,  $J = 16.8, 14.4$ , 1H), 3.76 (s, 3H), 5.42 (dd,  $J = 13.6, 2.8$ , 1H), 6.89 (d,  $J = 8.8$ , 2H), 6.98 (m, 2H), 7.34 (d,  $J = 8.8, 2\text{H}$ ), 7.43 (m, 1H), 7.86 (d,  $J = 8.4$ , 1H) **<sup>13</sup>C NMR** (75.0 MHz, CDCl<sub>3</sub>):  $\delta$  190.1, 161.7, 150.2, 137.2, 127.7, 127.0, 121.5, 118.1, 114.2, 55.3, 44.4 **CD** (CH<sub>3</sub>CN): 304 nm, ( $\theta = +5.79 \times 10^{-4}$  deg cm<sup>2</sup>dmol<sup>-1</sup>) 253 nm, ( $\theta = +1.52 \times 10^{-4}$  deg cm<sup>2</sup>dmol<sup>-1</sup>) 226 nm, ( $\theta = +5.87 \times 10^{-5}$  deg cm<sup>2</sup>dmol<sup>-1</sup>) **IR** (thin film, cm<sup>-1</sup>): 2924, 2851, 1691, 1604, 1515, 1463, 1303, 1251, 1226, 1177, 1115, 1027. **SMILES** = O=C1C[C@@](C2=CC=C(OC)C=C2)([H])OC3=CC=CC=C31. **InChI** = 1/C16H14O3/c1-18-12-8-6-11(7-9-12)16-10-14(17)13-4-2-3-5-15(13)19-16/h2-9,16H,10H2,1H3/t16-m/1/s1/i1-12,2-12,3-12,4-12,5-12,6-12,7-12,8-12,9-12,10-12,11-12,12-12,13-12,14-12,15-12,16-12,17-16,18-16,19-16

### Kinetic study.

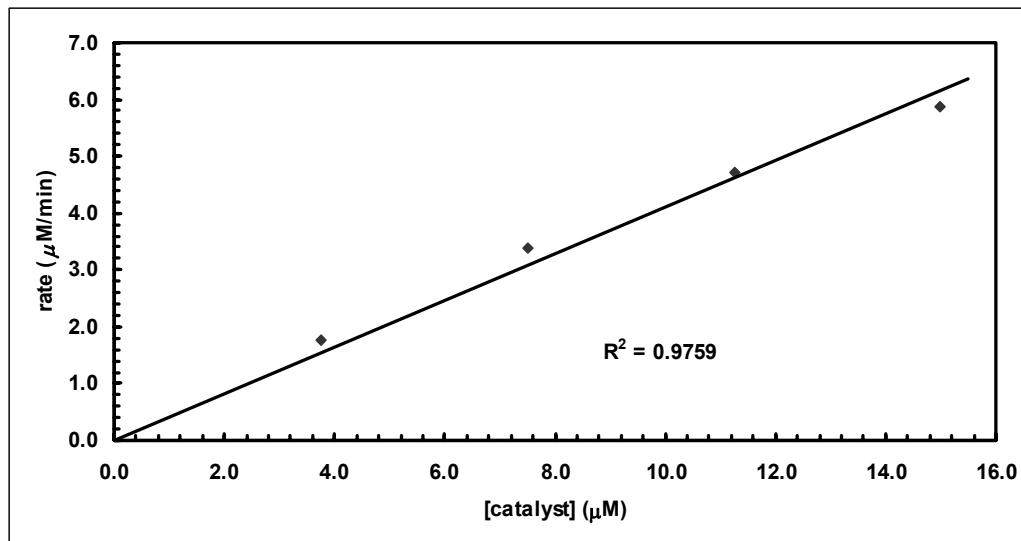
**Determination of the order in catalysts using the ReactIR.** Reactions run with varying amounts of catalysts were monitored by *in situ* FT-IR to determine the order in both the Lewis acid catalyst and the tartaramide catalyst. To a 20 mL vial equipped with stir bar was added tartaramide **16** (variable), Yb(OTf)<sub>3</sub> (variable) and EtOAc (2.625 mL). Boronate **35** (2.0 M solution in EtOAc, 375 mL, 0.75 mmol) was added and stirred for 5 min. Acetal **4** (88 mg, 0.5 mmol) was added dropwise and the vial was sealed with a septum and equipped with DiComp ReactIR 4000 Probe. The solution was stirred for 180 min and the olefin stretch of the product **29** at 1542.9 cm<sup>-1</sup> was monitored. The catalysts appear to be first-order in the reaction.



**Table S1.** Effect of catalyst complex concentration on the initial rate of the oxocarbenium addition reaction.

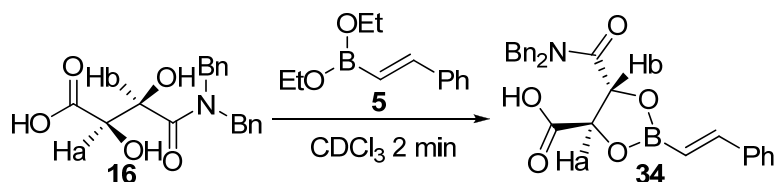
[Catalyst] <sub>initial</sub> (μM)	k <sub>obs</sub> (μM/min)
15	5.882353
11.25	4.705882
7.5	3.382353
3.75	1.764706

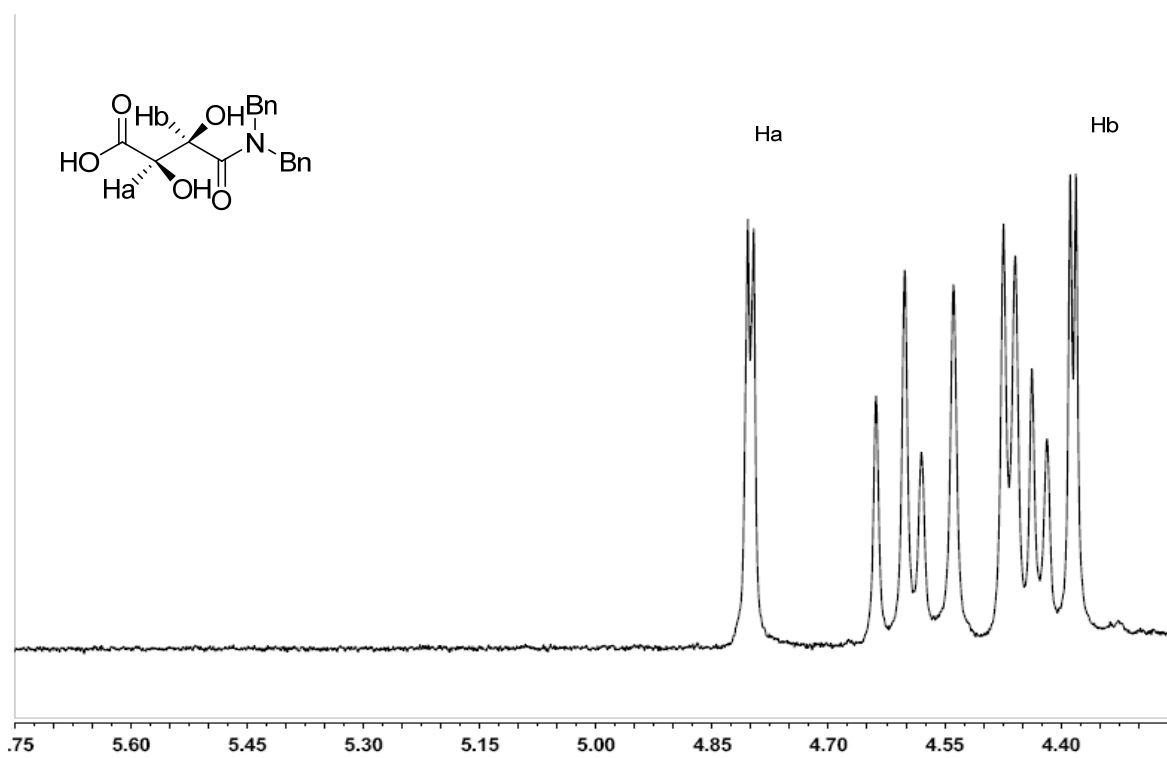
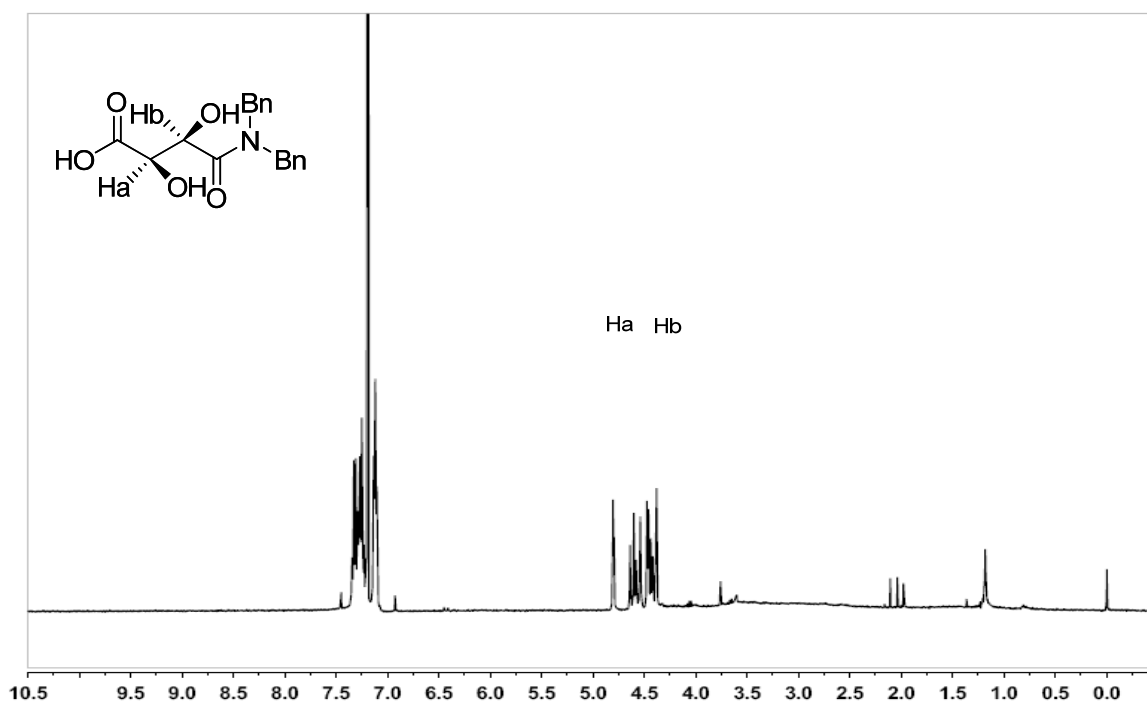
8. Ramadas, S. & Krupadanam, G. L. D. Enantioselective acylation of (±)-*cis*-flavan-4-ols catalyzed by lipase from *Candida cylindracea* (CCL) and the synthesis of enantiopure flavan-4-ones. *Tet. Asym.* **15**, 3381-3391 (2004).

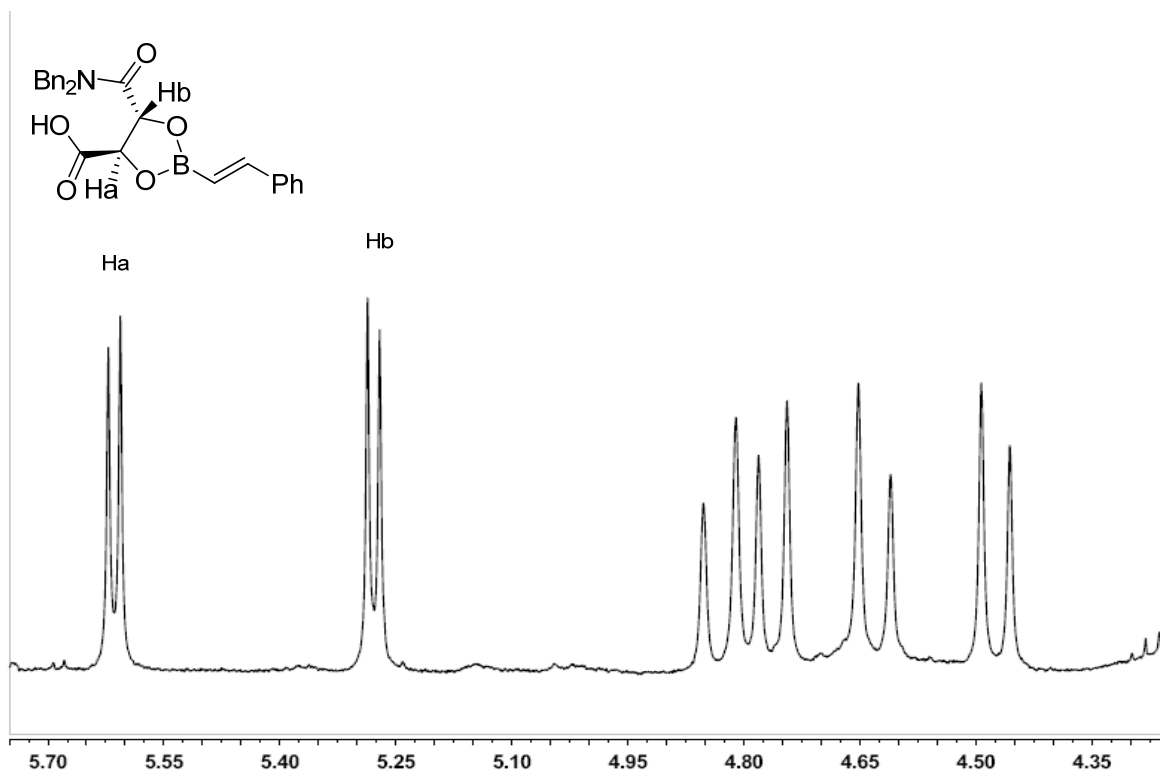
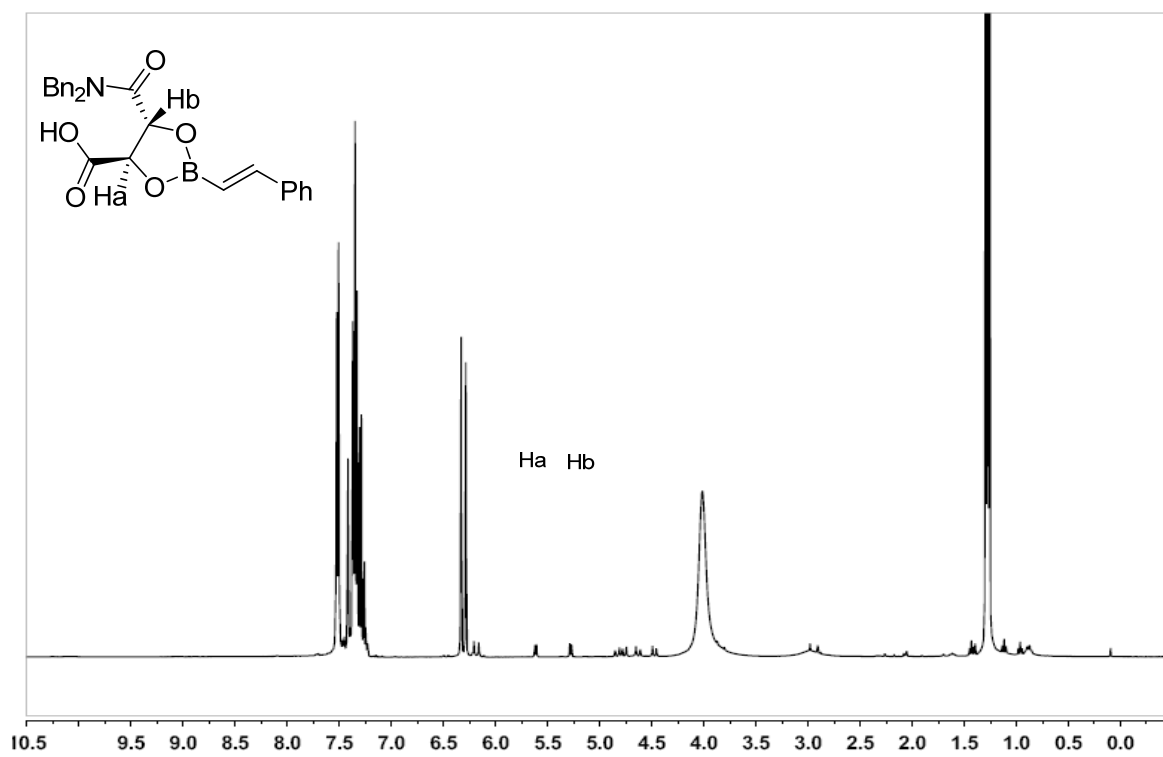


### <sup>1</sup>H NMR study of styrylboronate **5** and catalytic tartaramide **16**.

The tartaramide **16** (6.6 mg, 0.02 mmol) was dissolved in 0.75 mL CDCl<sub>3</sub> and placed in an NMR tube and a spectra was taken. Boronate **5** (40 μL, 0.2 mmol) was added to the NMR tube and shaken for 30 sec, afterwards another spectra was taken. A noticeable shift of both of the methine protons was observed indicating the double-exchange product. There was no observation of a single-exchange product.

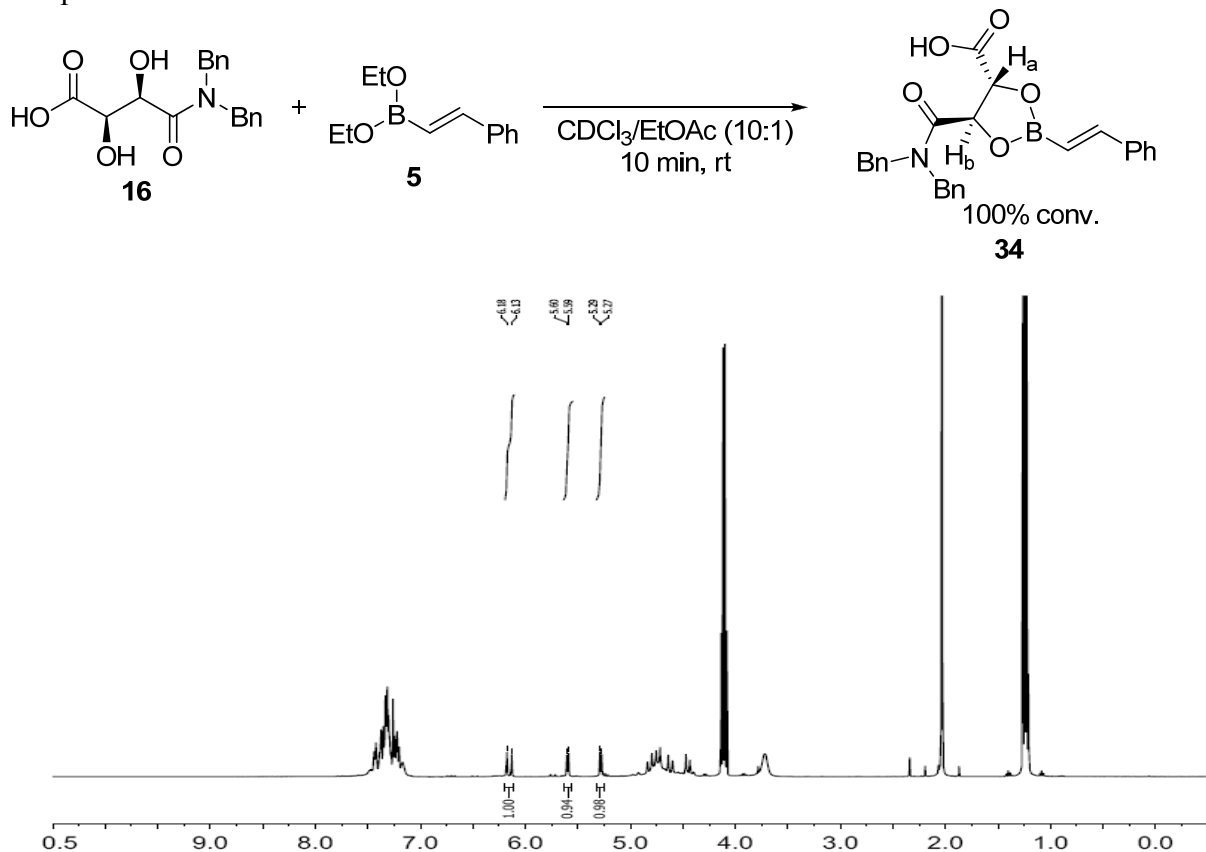
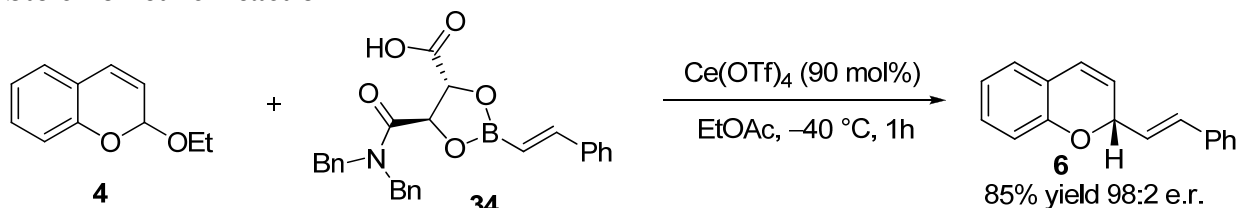






**<sup>1</sup>H NMR of complex 34**

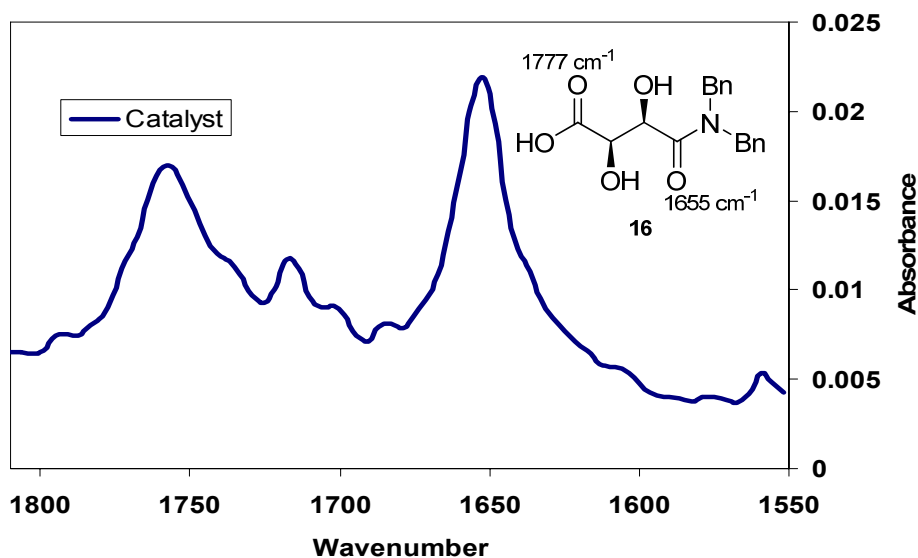
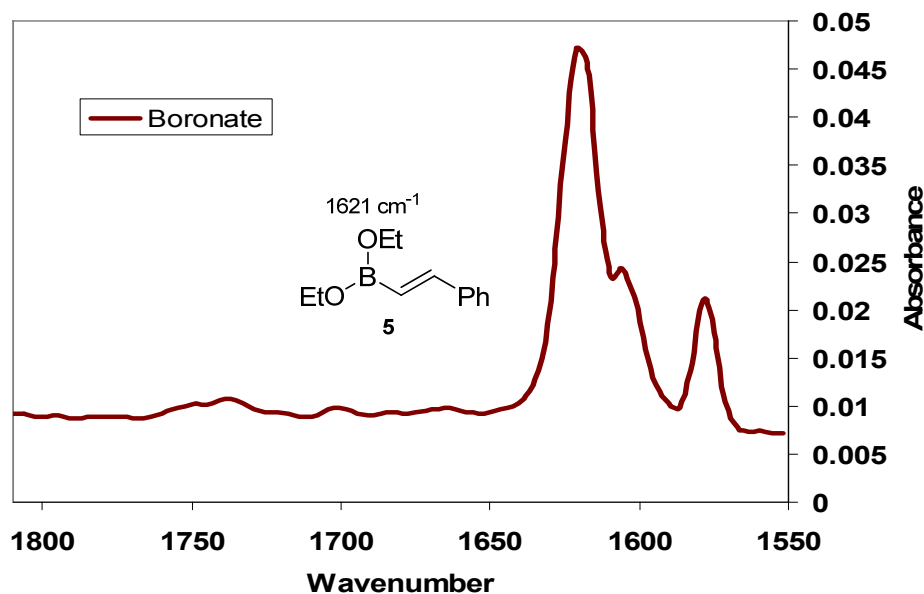
Catalyst **16** (32.9 mg, 0.1 mol) and diethyl styrylboronate **5** (50  $\mu$ L, 0.1 mol, 2.0 M solution in EtOAc) were added to 0.5 mL CDCl<sub>3</sub> and stirred for 5 min at room temperature. The clear solution was added to an NMR tube and the <sup>1</sup>H NMR was recorded. The <sup>1</sup>H NMR indicates the complete conversion to **34** in 10 min.

**Stoichiometric Reaction**

To an oven-dried reaction vessel equipped with stir bar under Ar was added tartaramide catalyst **16** (32.9 mg, 0.1 mmol) and EtOAc (0.95 mL). Boronate **5** (2.0 M in EtOAc, 50  $\mu$ L, 0.1 mmol) was added and the reaction stirred for 20 min. Ce(OTf)<sub>4</sub> (66.5 mg, 0.09 mmol) was added and the reaction was cooled to -40 °C and stirred for 5 min. The acetal **4** (17.6 mg, 0.1 mmol) was added drop wise and the reaction was stirred at -40 °C. Reaction monitoring by TLC showed disappearance of acetal **4** in 1 h. The reaction was purified by flash chromatography over a silica gel column (2% EtOAc in hexanes) to afford the product **6** as a pale yellow oil (97 mg, 85% yield and 98:2 e.r. by HPLC).

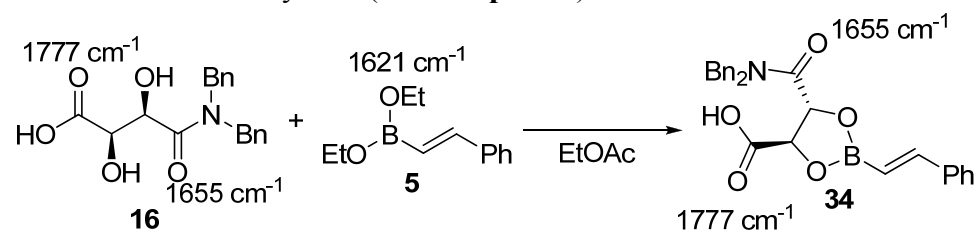
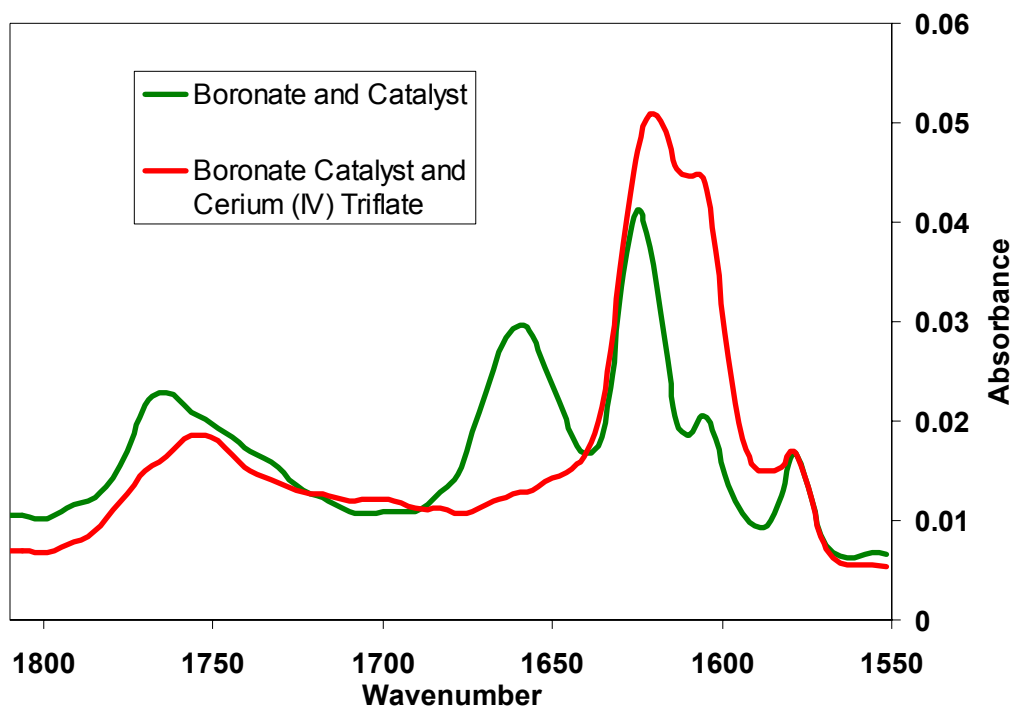
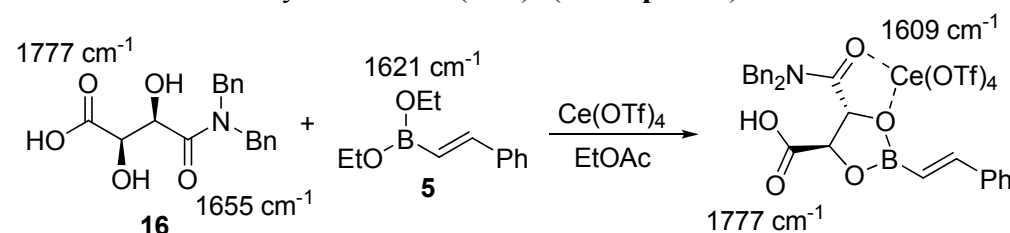
***In-situ* ReactIR™ study of Lewis Acid complex and dioxaborolane 34.**

**FT-IR of the reagents in solution.** Using the ReactIR 4000 the boronate **5** (102 mg, 0.5 mmol), catalyst **16** (164.5 mg, 0.2 mmol), and Ce(OTf)<sub>4</sub> (366 mg, 0.2 mmol) were individually dissolved in EtOAc (3 mL) and the infrared absorbance between 1800 cm<sup>-1</sup> and 1550 cm<sup>-1</sup> was measured. Diethyl styrylboronate **5** was observed to have a large peak at 1621 cm<sup>-1</sup> and two smaller peaks at 1605 cm<sup>-1</sup> and 1578 cm<sup>-1</sup>. Dibenzyl tartaramide **16** contains two prominent peaks at 1777 cm<sup>-1</sup> and 1655 cm<sup>-1</sup>, which correspond to the carboxylic acid carbonyl stretch and the amide carbonyl stretch, respectively. The identification of these peaks was further corroborated by the amide ester **17** which shows an ester carbonyl at 1752 cm<sup>-1</sup> and an amide carbonyl at 1655 cm<sup>-1</sup>. The Ce(OTf)<sub>4</sub> showed no significant peaks in this range.



**FT-IR of the dioxaborolane **34** and the dioxaborolane-Ce(OTf)<sub>4</sub> complex.**

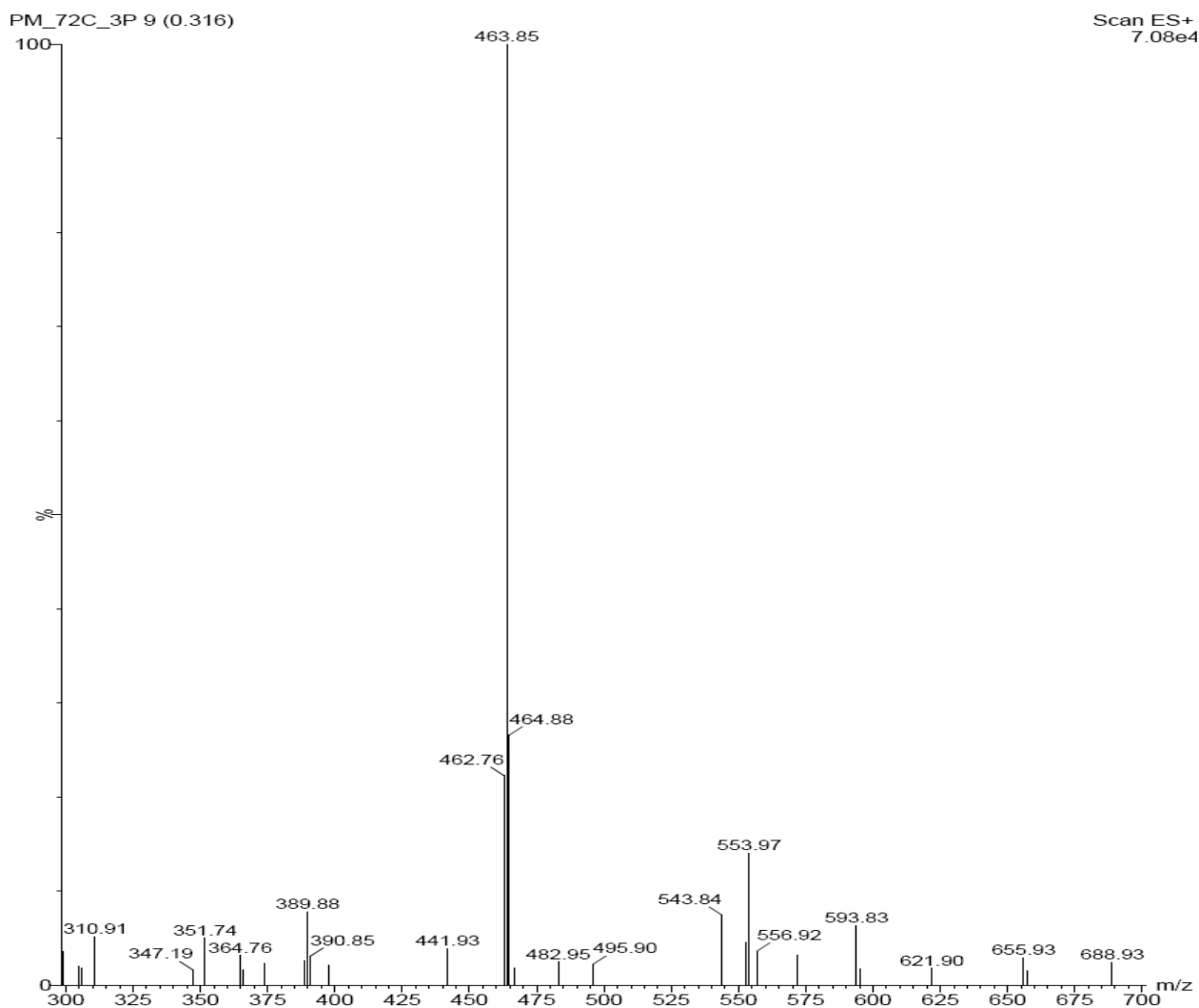
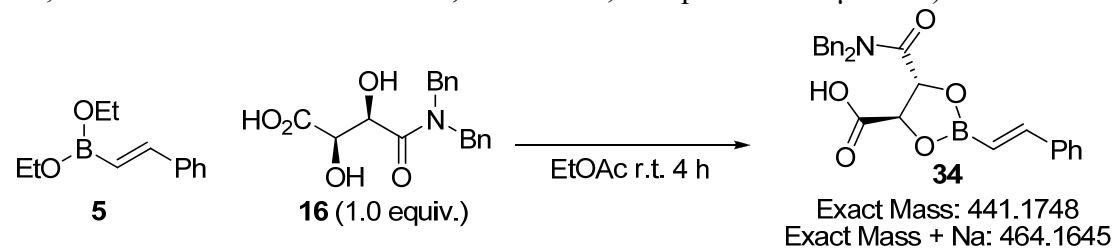
To a dry reaction vial styryl boronate **5** (102 mg, 0.5 mmol) and catalyst **16** (82.2 mg, 0.1 mmol) were dissolved in EtOAc (3 mL) and observed using the ReactIR 4000™. The carbonyl stretches of the catalyst **16** were unaffected by excess boronate **5** indicating that only the diol alcohols are involved in the exchange with the boronate to form dioxaborolane **34**. Ce(OTf)<sub>4</sub> (183 mg, 0.1 mmol) was then added to the reaction and the FT-IR spectra was recorded. The spectra showed the loss of the amide peak at 1655 cm<sup>-1</sup> and the new formation of the amide peak at 1609 cm<sup>-1</sup>. In the course of the reaction the carboxylic acid was unchanged indicating that the Ce(OTf)<sub>4</sub> binds exclusively to the amide at 1:1 stoichiometric ratio with the catalyst.

**Boronate **5** and Catalyst **16** (Green Spectra)****Boronate **5** and Catalyst **16** and Ce(OTf)<sub>4</sub> (Red Spectra)**



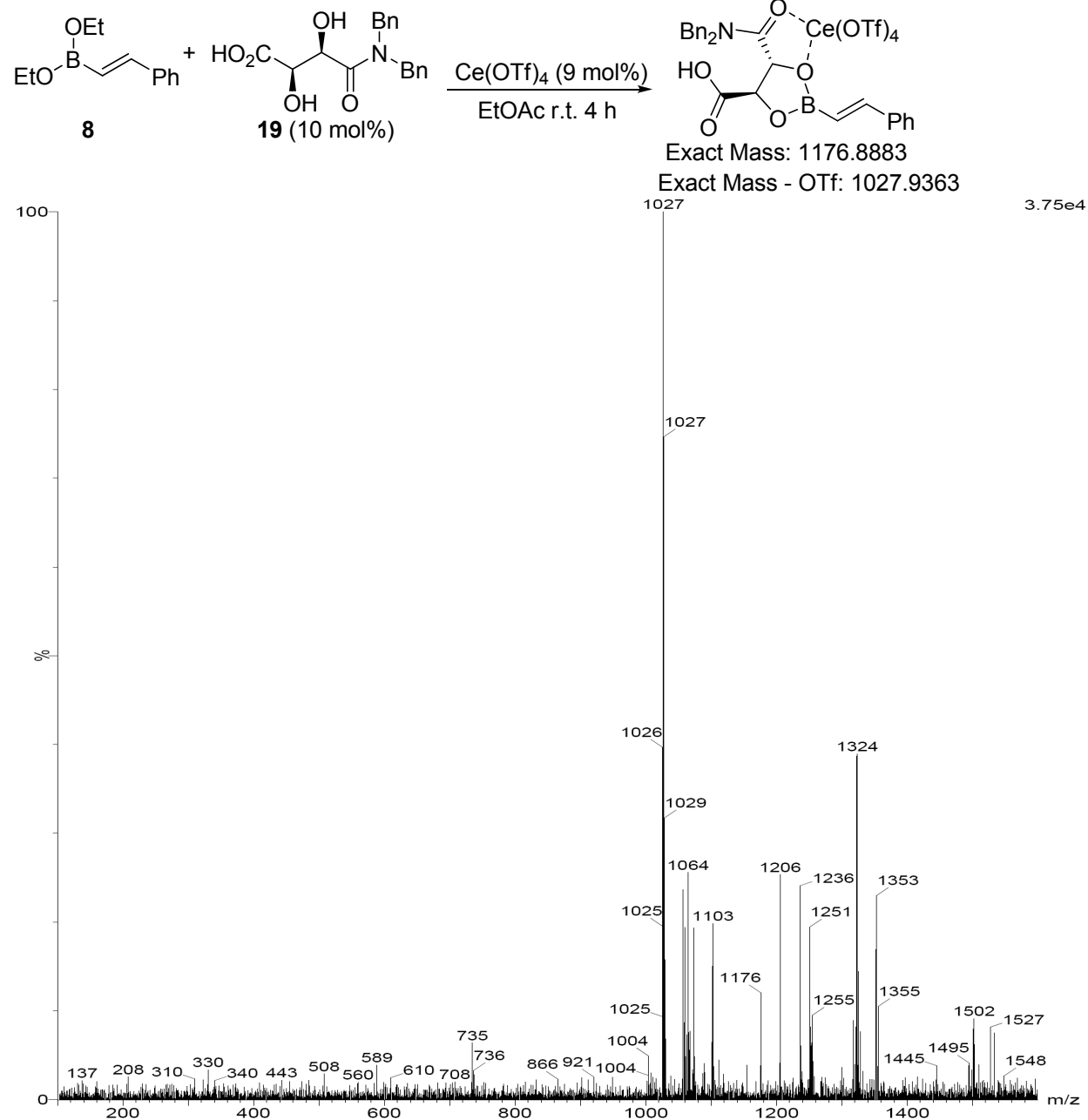
**ESI-MS studies.****ESI-MS of the boronate **5** with stoichiometric tartaramide **16**.**

To an oven-dried reaction vessel equipped with stir bar under Ar was added tartaramide catalyst **16** (32.9 mg, 0.1 mmol) and EtOAc (0.95 mL). Boronate **5** (2.0 M in EtOAc, 50  $\mu$ L, 0.1 mmol) was added and the reaction stirred for 5 min. An aliquot (100  $\mu$ L) was taken into a 0.5 mL syringe and diluted with CH<sub>3</sub>CN (0.4 mL). The solution was injected into MicroMass ZQ 2000 mass spectrometer via syringe pump (150  $\mu$ L/min). Positive electron spray ionization mode (ESI+, ES/voltages: capillary 3.01 KV, cone 30 V; Temperature: source 130 °C, desolvation 260 °C; Gas flow: desolvation 250 L/h, one 50 L/h; Pump flow: 250  $\mu$ L/min).



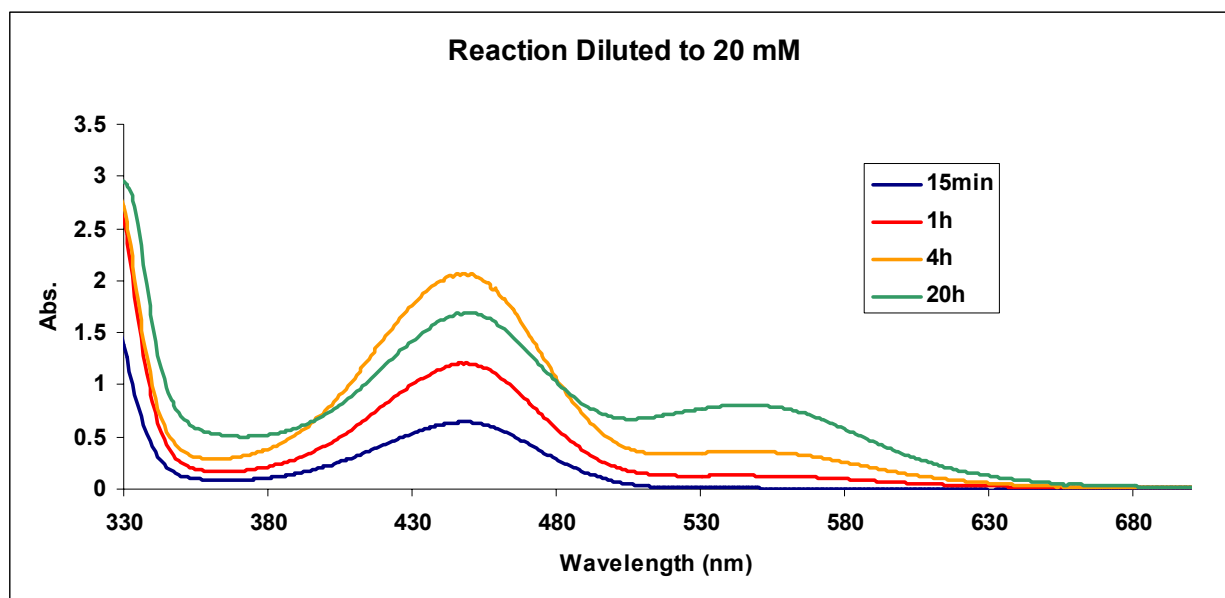
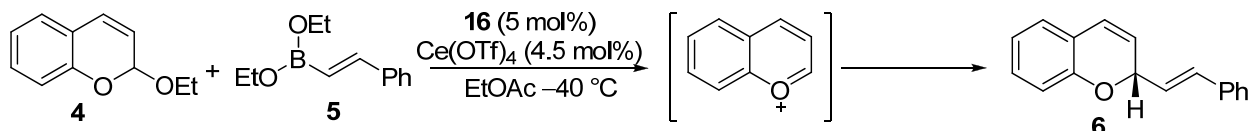
**ESI-MS of the boronate **5** with catalyst **16** and  $\text{Ce}(\text{OTf})_4$ .**

To an oven-dried reaction vessel equipped with stir bar under Ar was added  $\text{Ce}(\text{OTf})_4$  (16.5 mg, 0.0225 mmol), tartaramide catalyst **16** (8.2 mg, 0.025 mmol), boronate **5** (2.0 M in EtOAc, 375  $\mu\text{L}$ , 0.75 mmol) and EtOAc (0.625 mL). An aliquot (100  $\mu\text{L}$ ) was taken into a 0.5 mL syringe and diluted with  $\text{CH}_3\text{CN}$  (0.4 mL). The solution was injected into MicroMass ZQ 2000 mass spectrometer via syringe pump (150  $\mu\text{L}/\text{min}$ ). Negative electron spray ionization mode (ESI<sup>-</sup>, ES/voltages: capillary 3.01 KV, cone 30 V; Temperature: source 130 °C, desolvation 260 °C; Gas flow: desolvation 250 L/h, one 50 L/h; Pump flow: 250  $\mu\text{L}/\text{min}$ ).



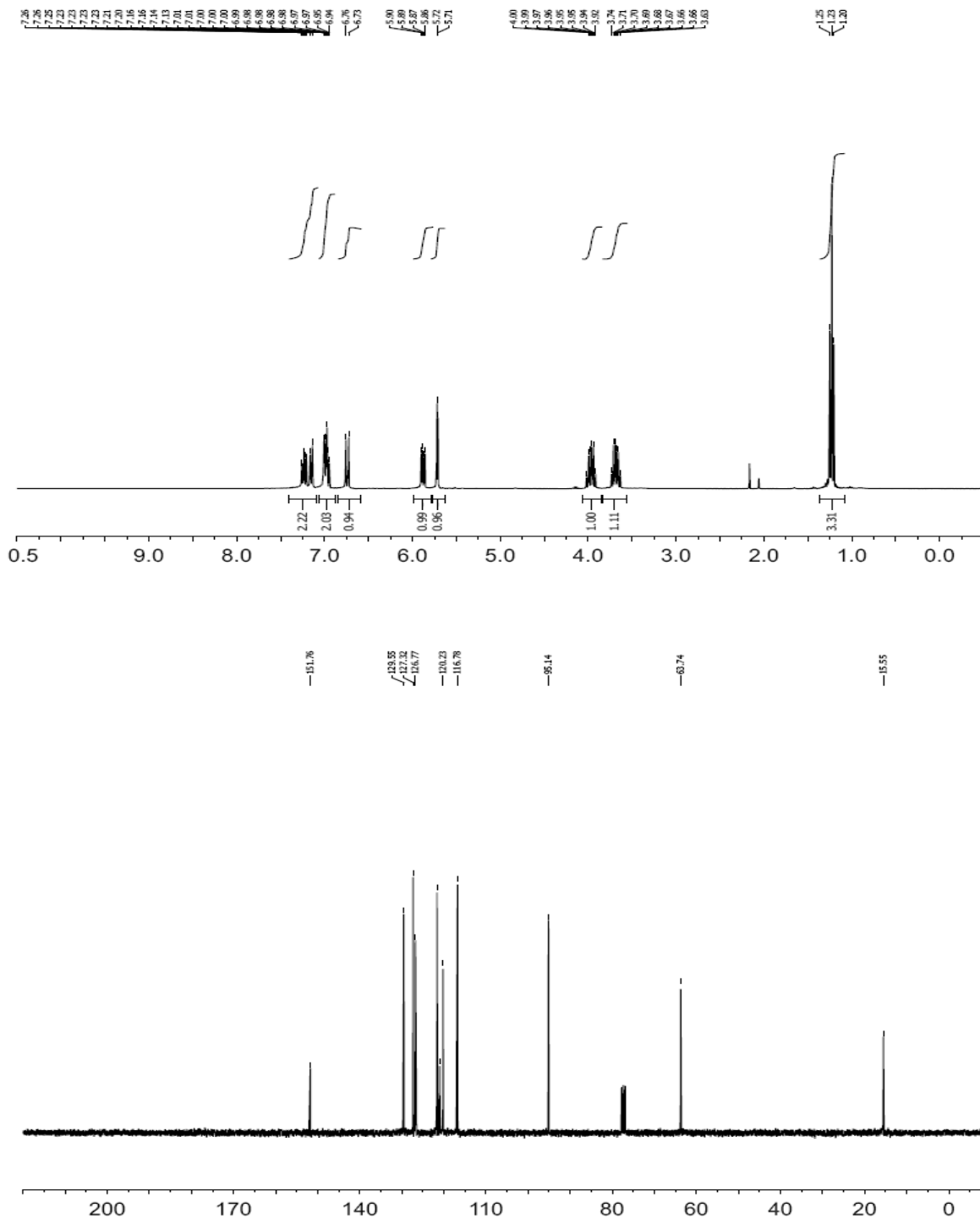
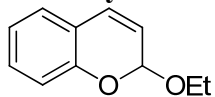
**UV-Vis study of the reaction.**

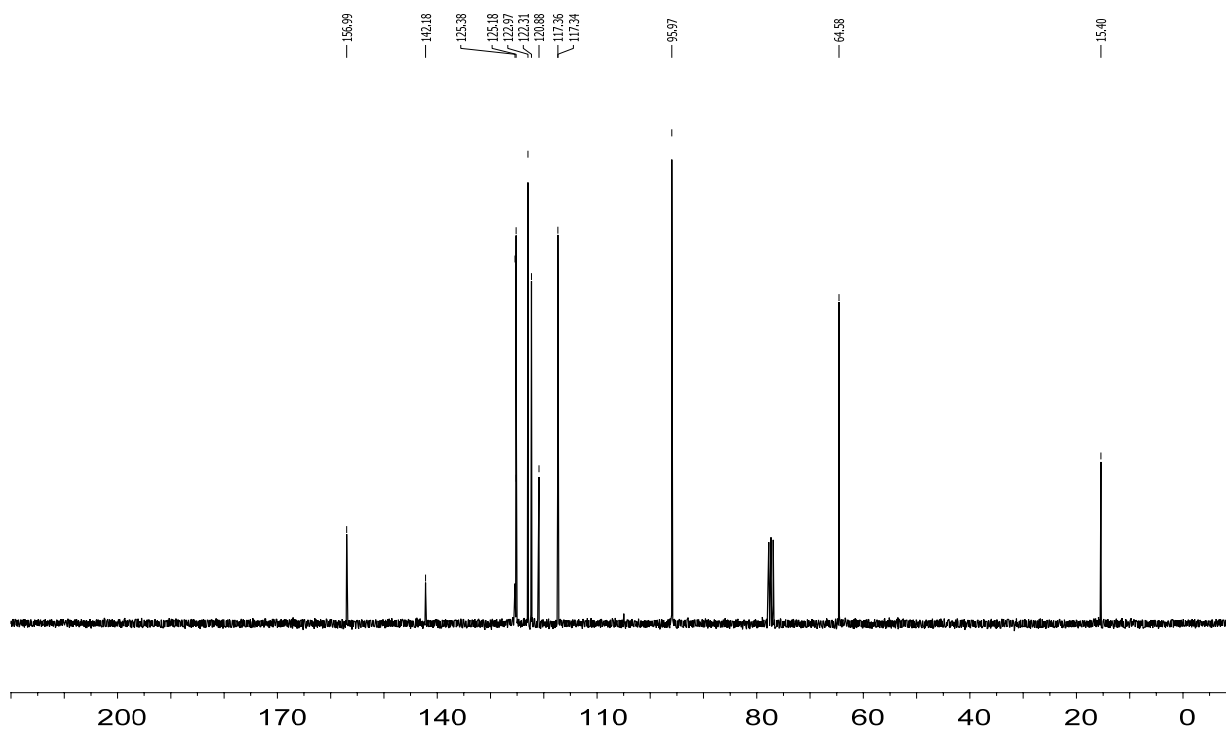
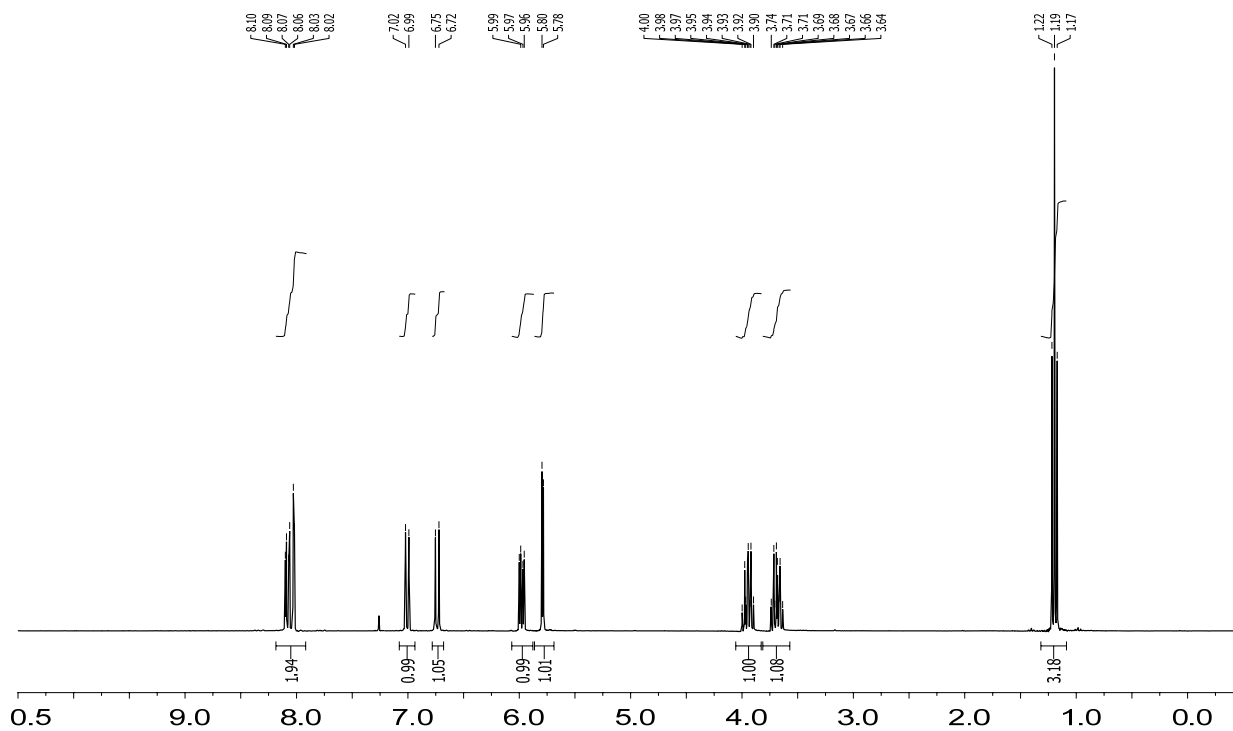
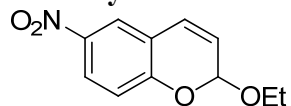
The reaction of acetal **4** with boronate **5** was set-up according to method A. After 15 min a 50  $\mu\text{L}$  aliquot was taken from the reaction, diluted to 20 mM in dry EtOAc and a UV-Vis spectra was recorded. At 1h, 4h and 20h aliquots of the reaction were taken, diluted to 20 mM, and measured by UV-Vis. A peak at 449 nm grows in during the course of the reaction. The peak at 449 nm correlates with data of reported oxonium species.<sup>9</sup> After 20 hrs the reaction is complete and a new peak at 546 nm appeared. The other components of the reaction show no features in the 350 - 700 nm range, therefore we believe these peaks are due to the oxonium intermediate at 449 nm and a by-product of the reaction at 546 nm.

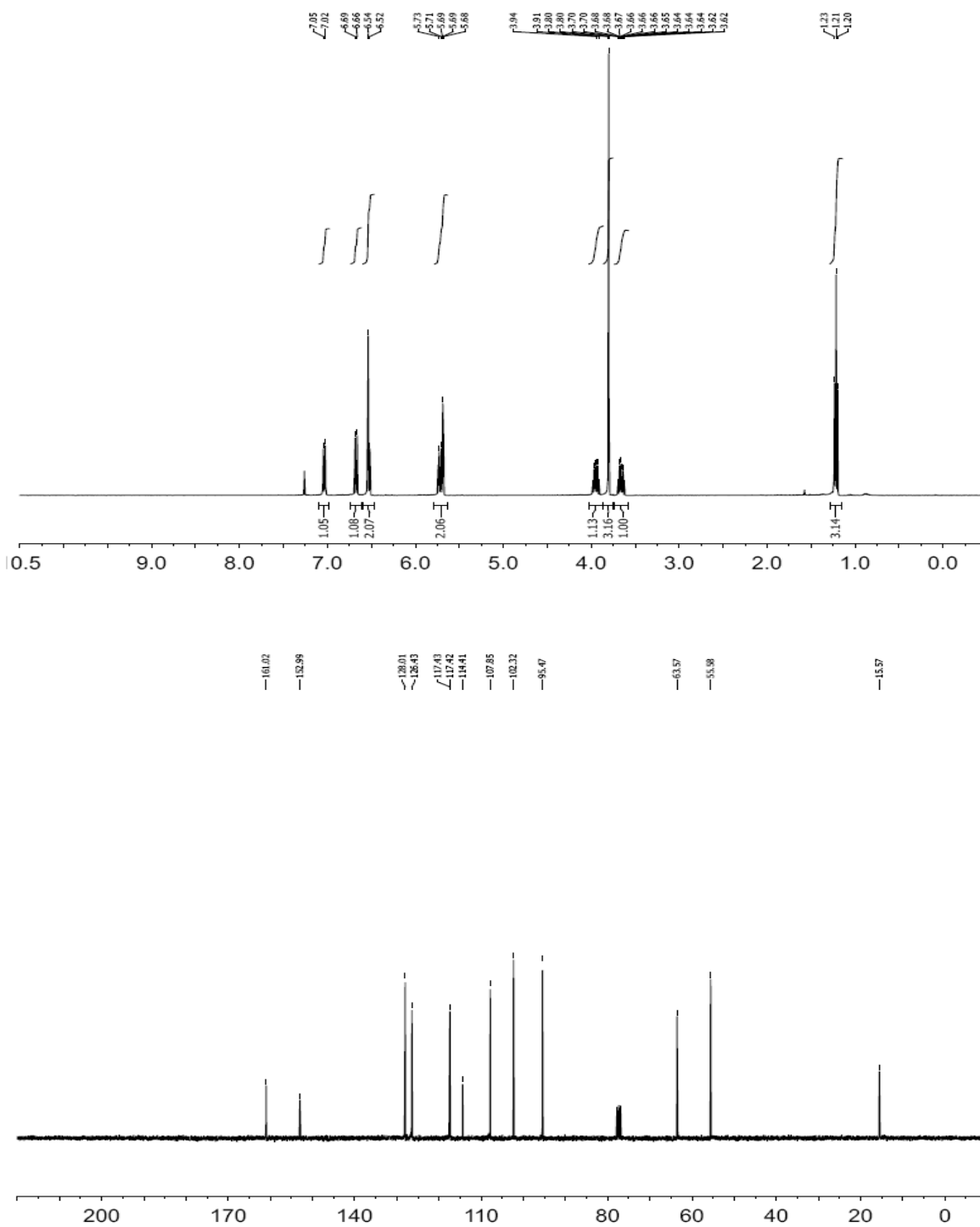
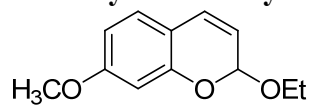


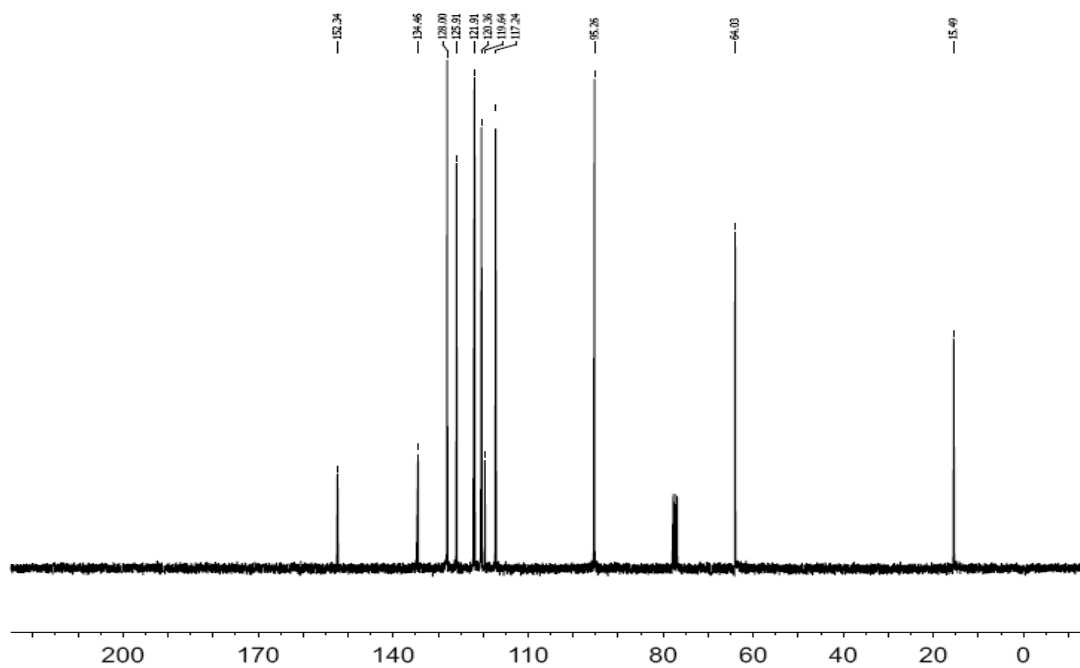
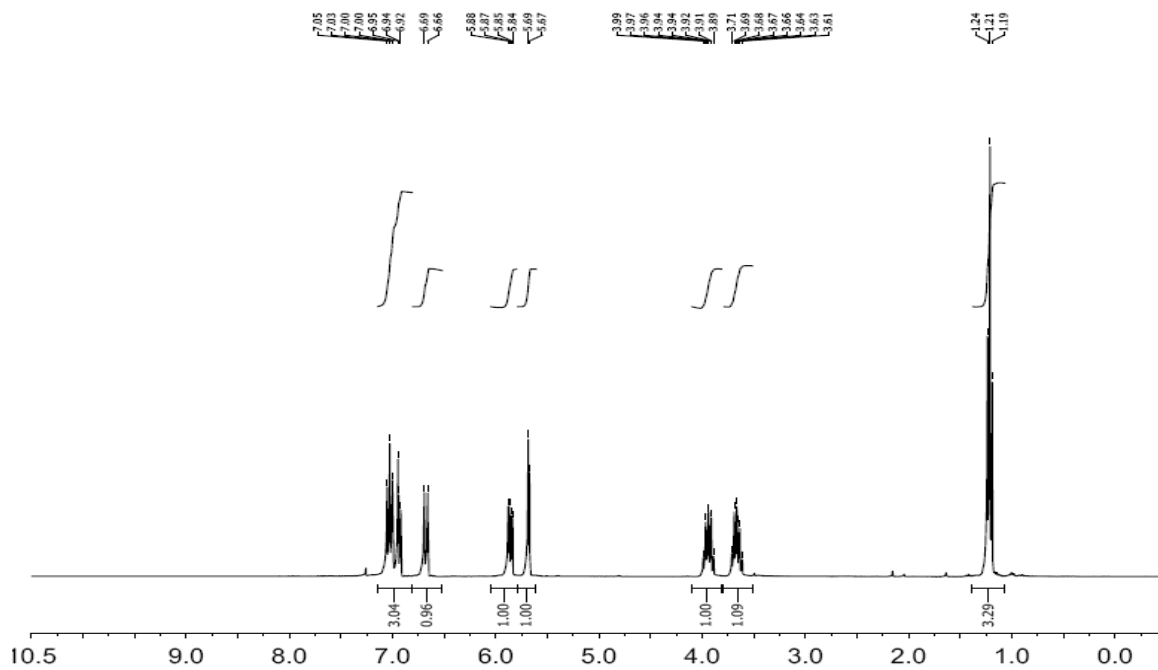
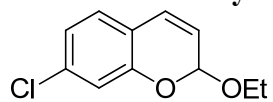
9. Katritzky, A. R., Czerney, P., Levell, J. R. & Du, W. Molecular engineering of benzo[b]pyrylium salts by indirect electrophilic substitution. *Eur. J. Org. Chem.* 2623-2629 (1998).

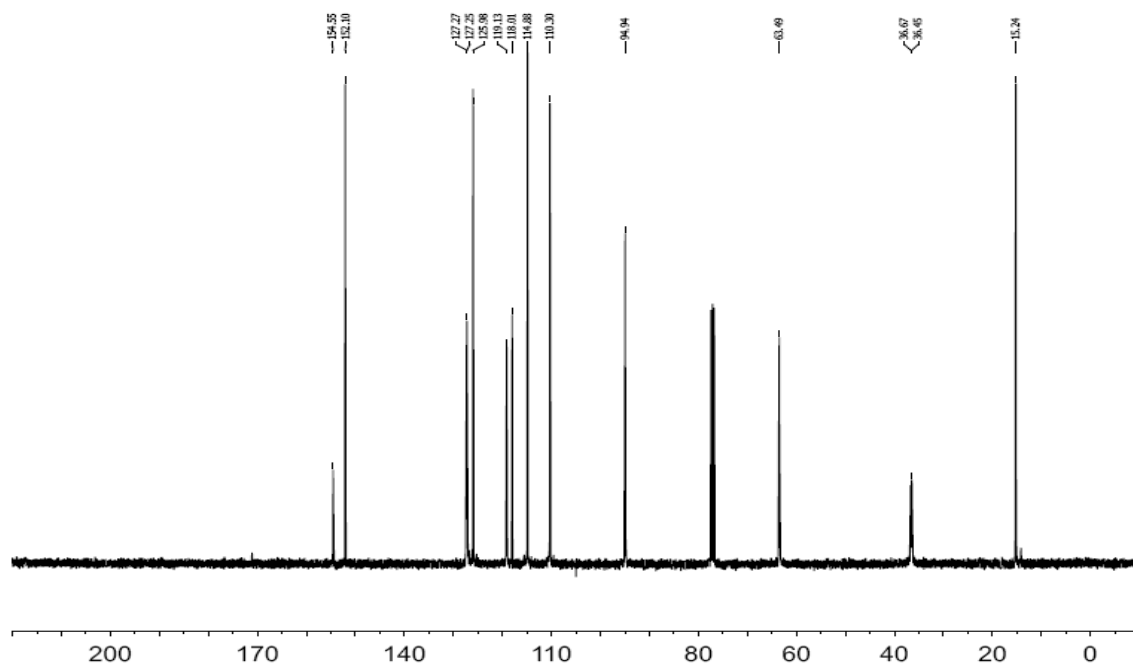
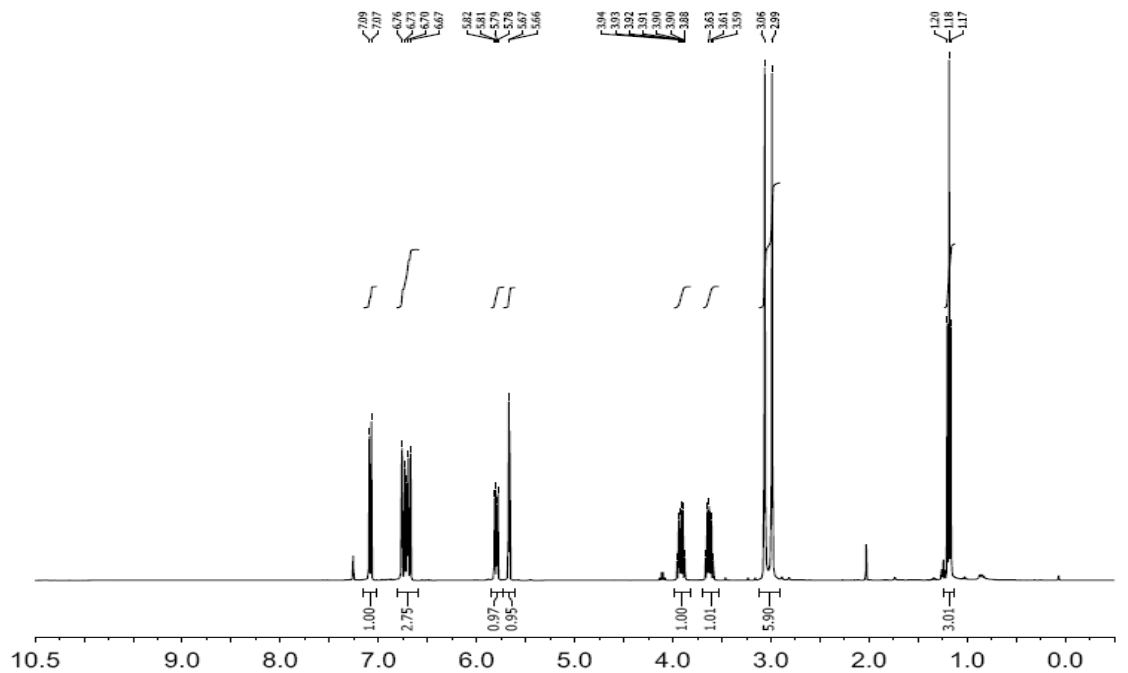
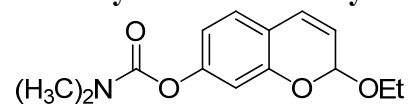
## NMR spectra

2-ethoxy-2*H*-chromene (4) in CDCl<sub>3</sub>

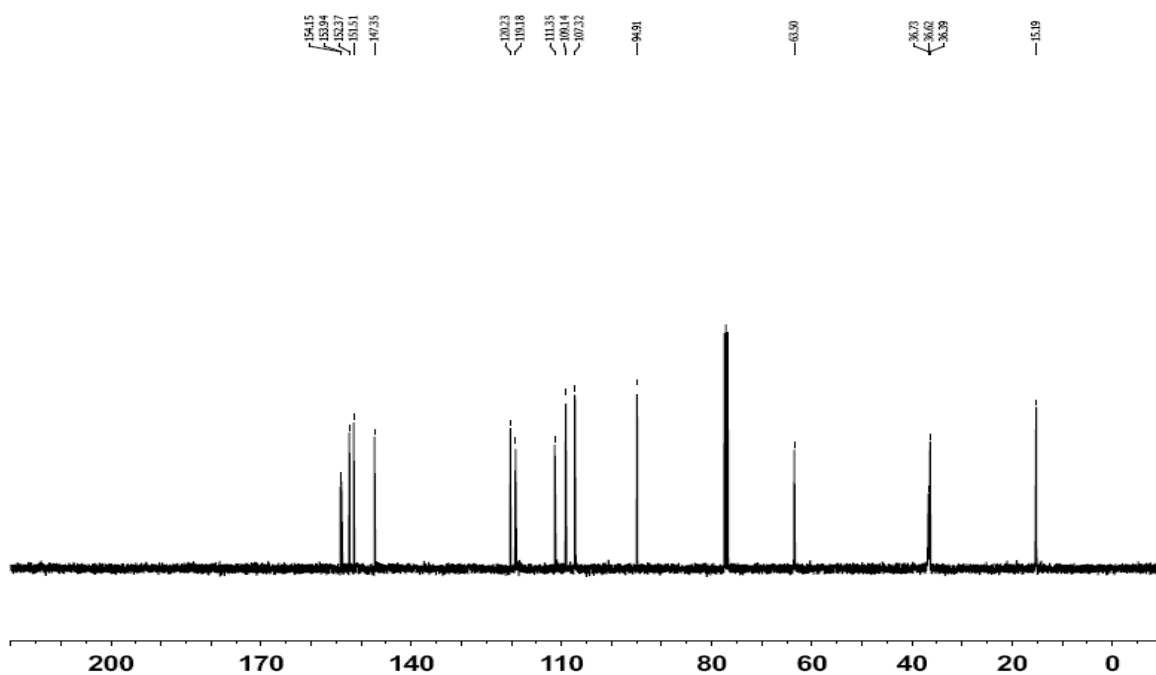
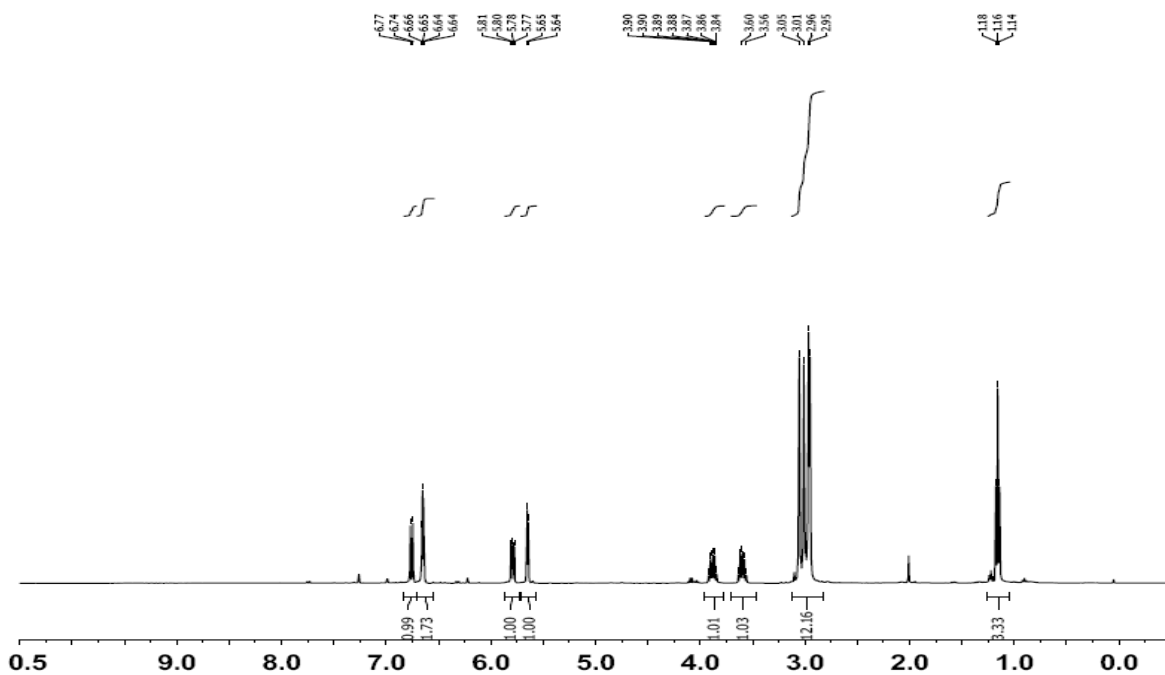
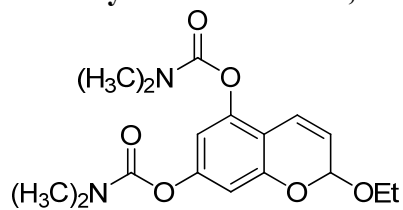
2-ethoxy-6-nitro-2H-chromene in CDCl<sub>3</sub>

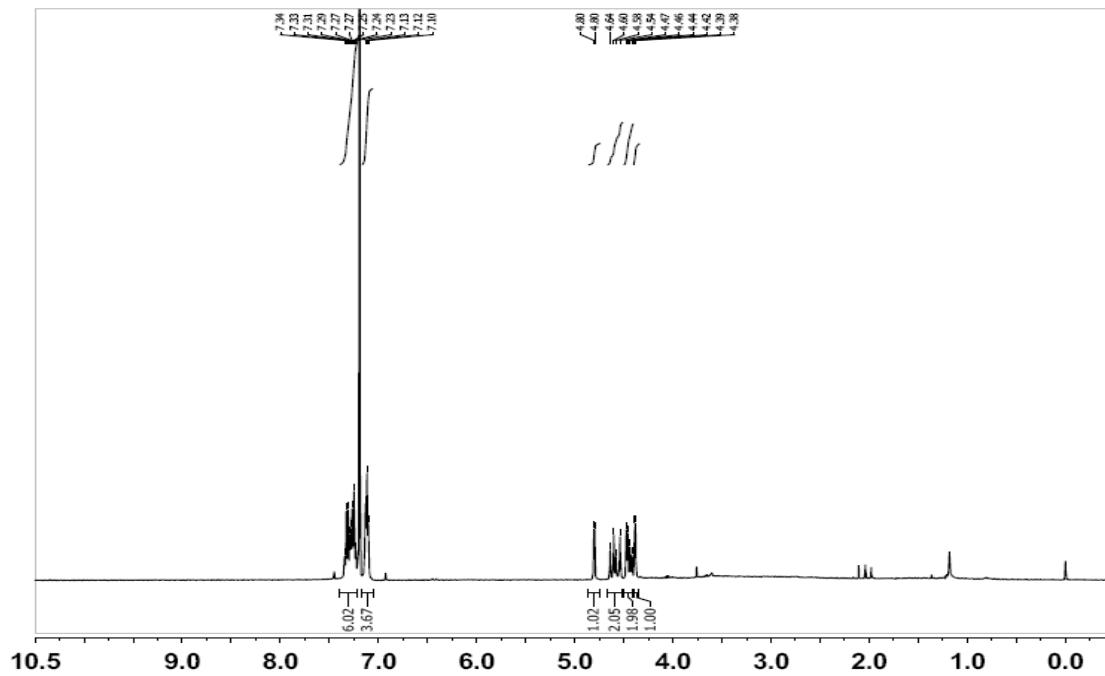
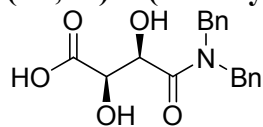
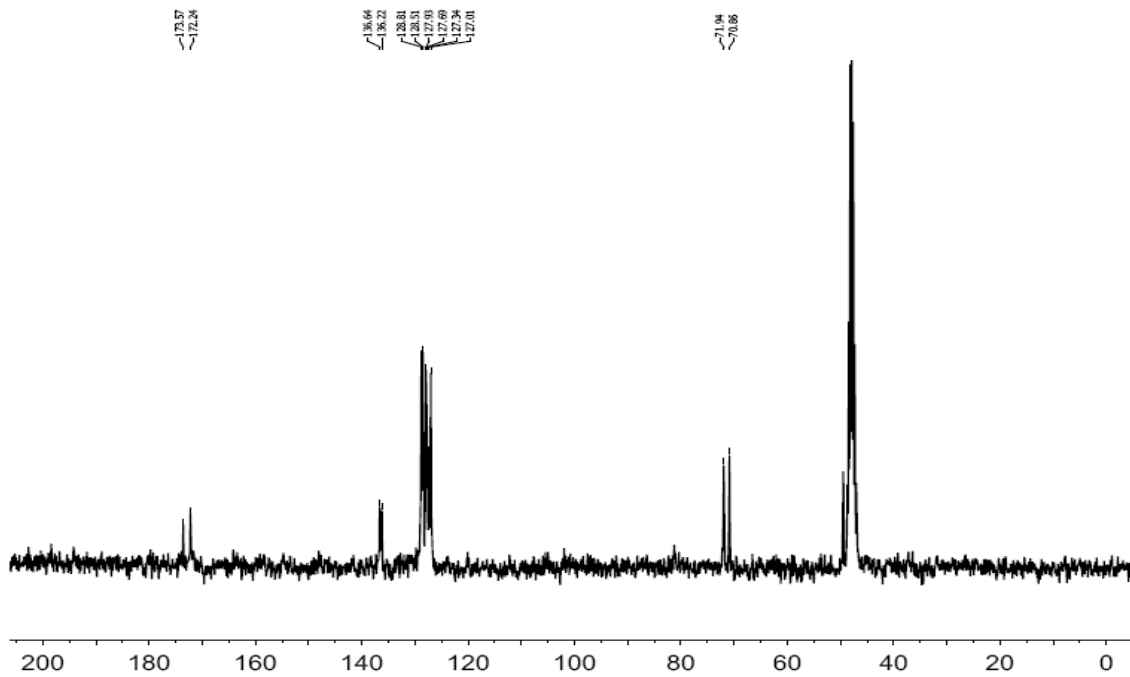
2-ethoxy-7-methoxy-2H-chromene in CDCl<sub>3</sub>

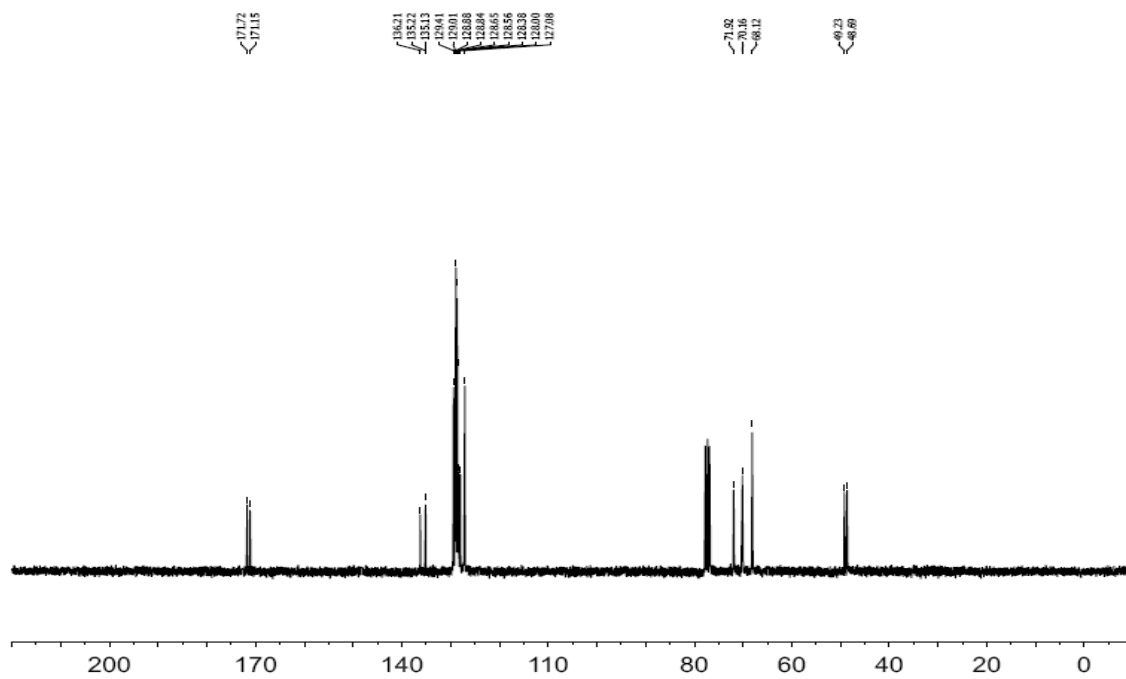
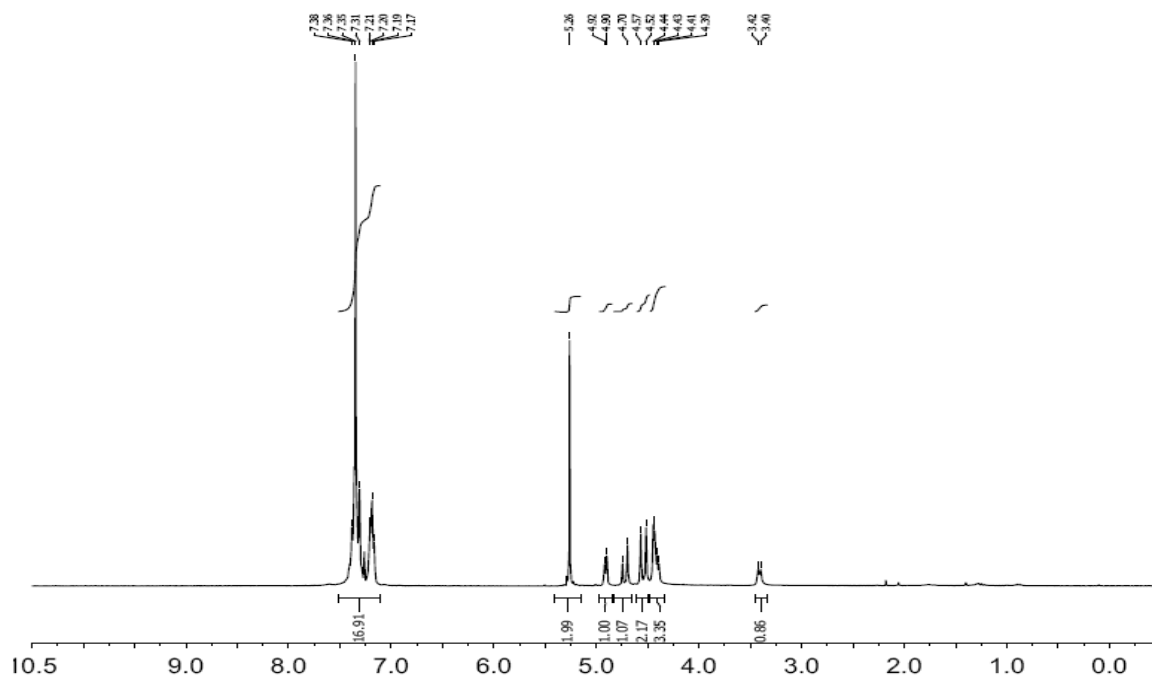
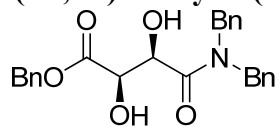
7-chloro-2-ethoxy-2H-chromene in CDCl<sub>3</sub>

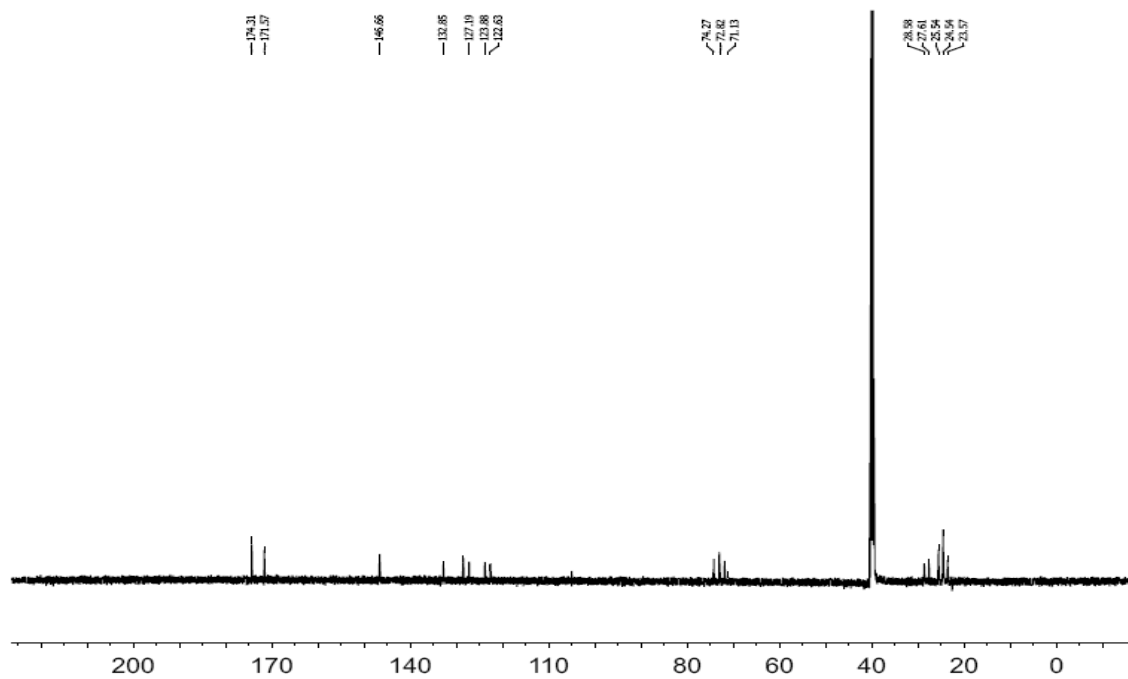
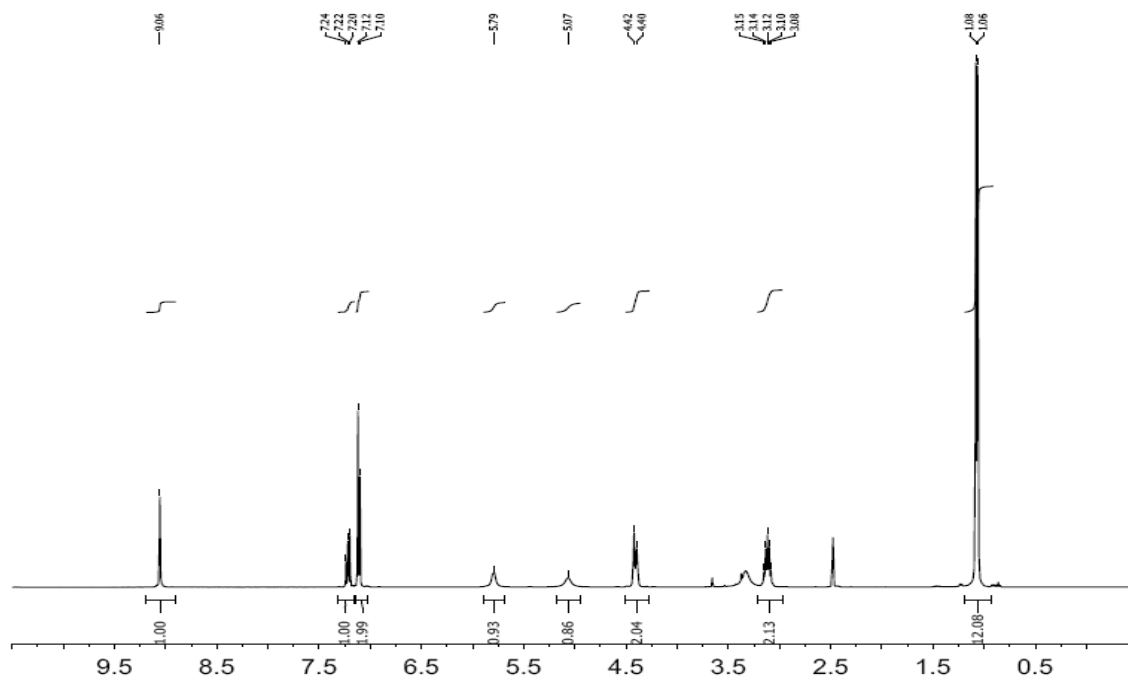
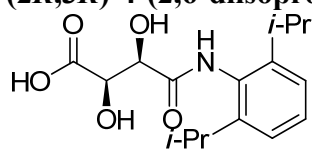
2-ethoxy-2*H*-chromen-7-yl dimethylcarbamate in CDCl<sub>3</sub>



**2-ethoxy-2H-chromene-5,7-diyl bis(dimethylcarbamate)**

**(2*R*,3*R*)-4-(dibenzylamino)-2,3-dihydroxy-4-oxobutanoic acid (16) in CDCl<sub>3</sub>****CD<sub>3</sub>OD**

**(2*R*,3*R*)-benzyl 4-(dibenzylamino)-2,3-dihydroxy-4-oxobutanoate (17) in CDCl<sub>3</sub>**

**(2*R*,3*R*)-4-(2,6-diisopropylphenylamino)-2,3-dihydroxy-4-oxobutanoic acid (18) in CD<sub>3</sub>OD**

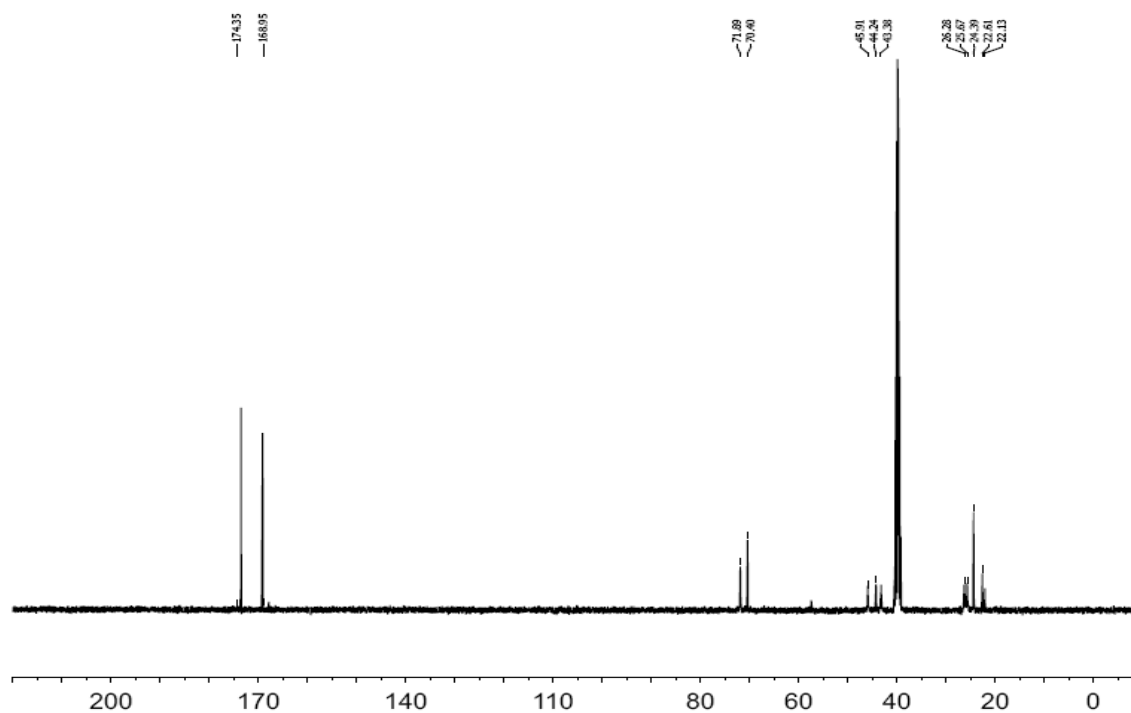
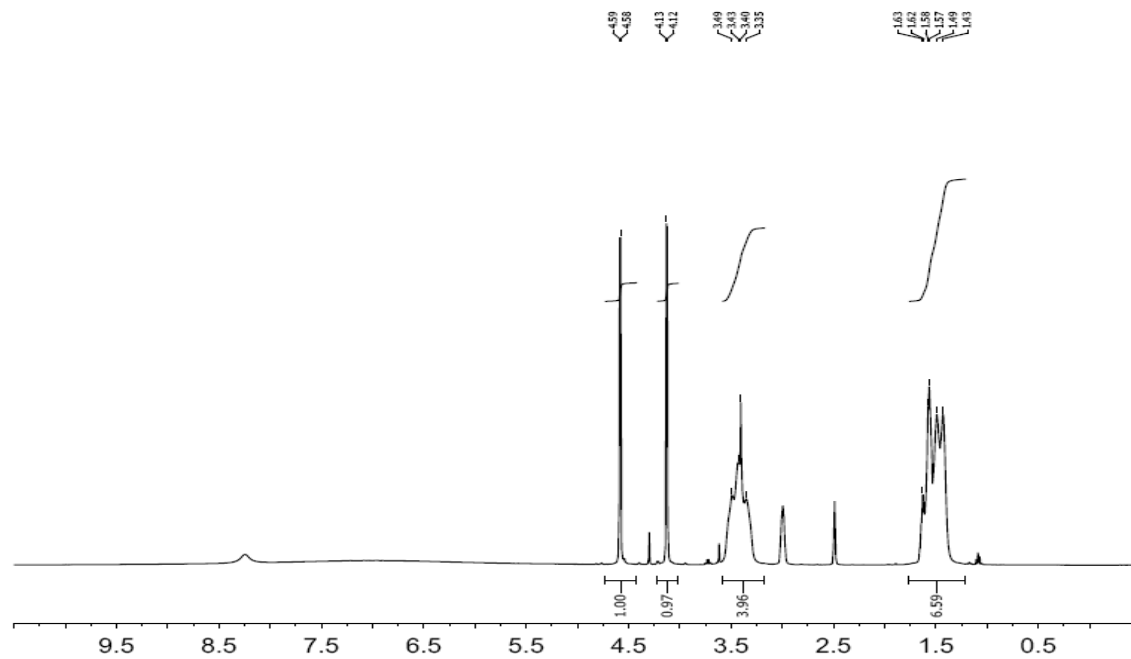
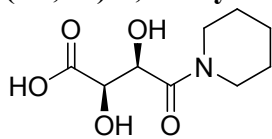
**(2*R*,3*R*)-2,3-dihydroxy-4-oxo-4-(piperidin-1-yl)butanoic acid (19) in CD<sub>3</sub>OD**

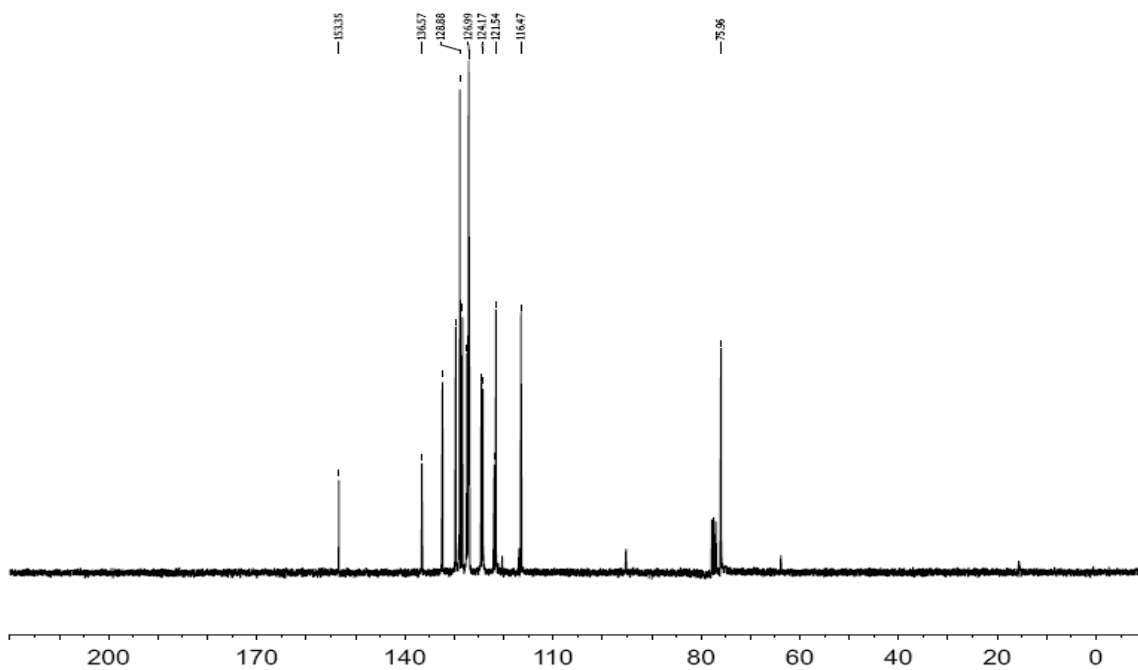
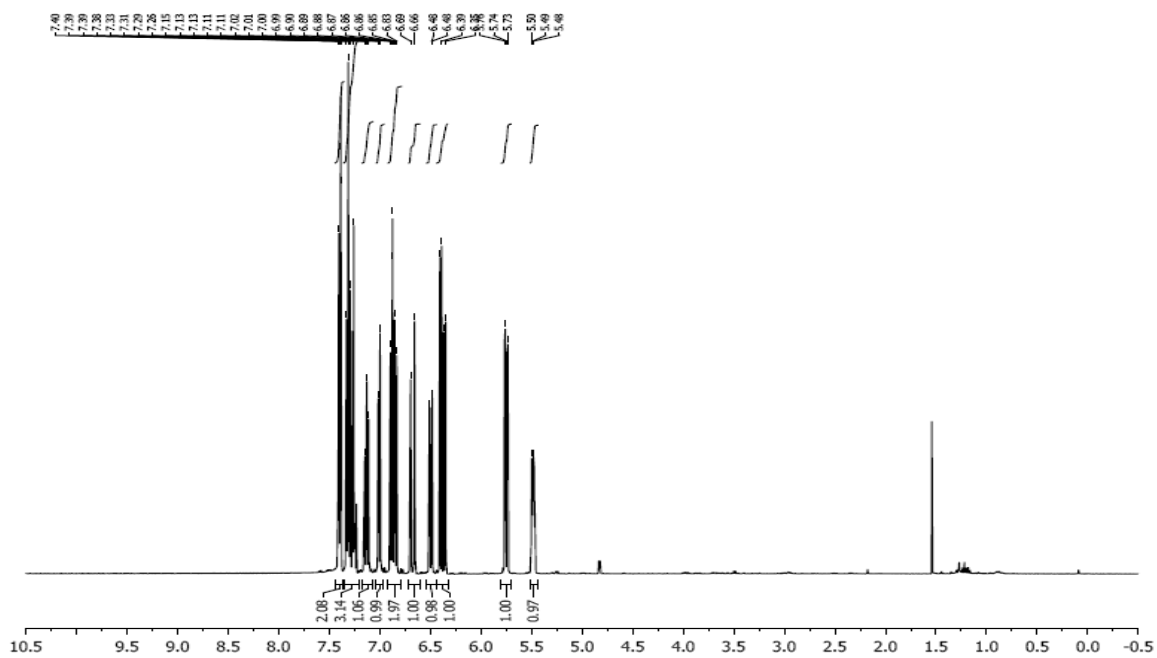
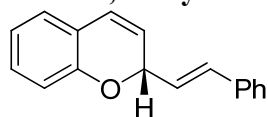
Table 3, entry 1: 6 in CDCl<sub>3</sub>

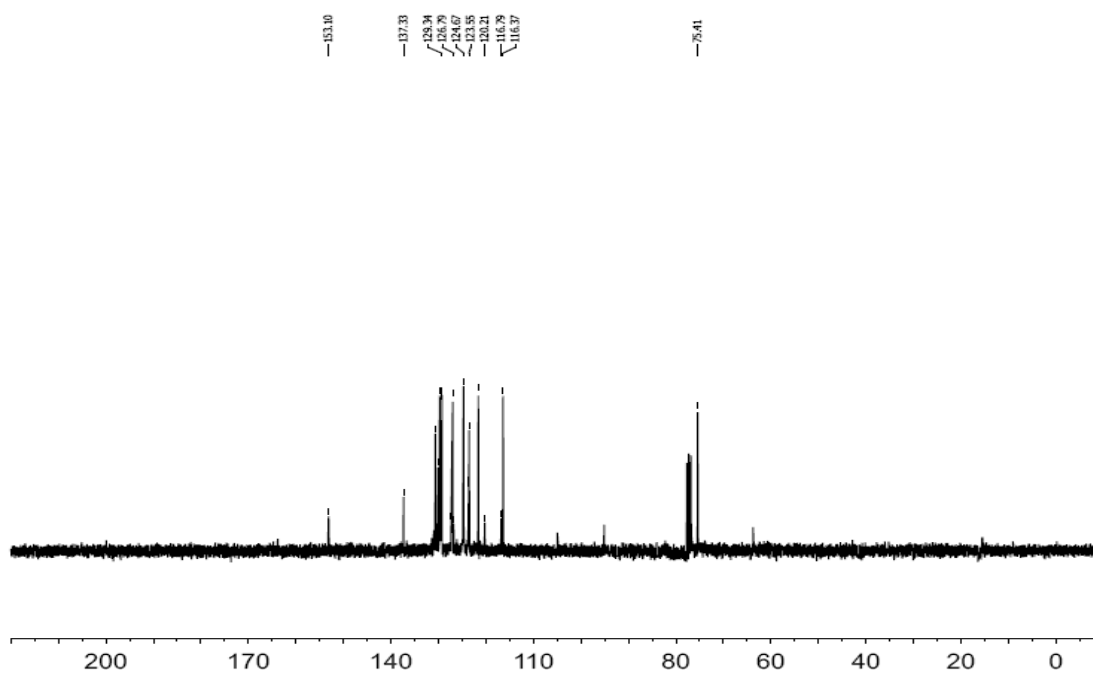
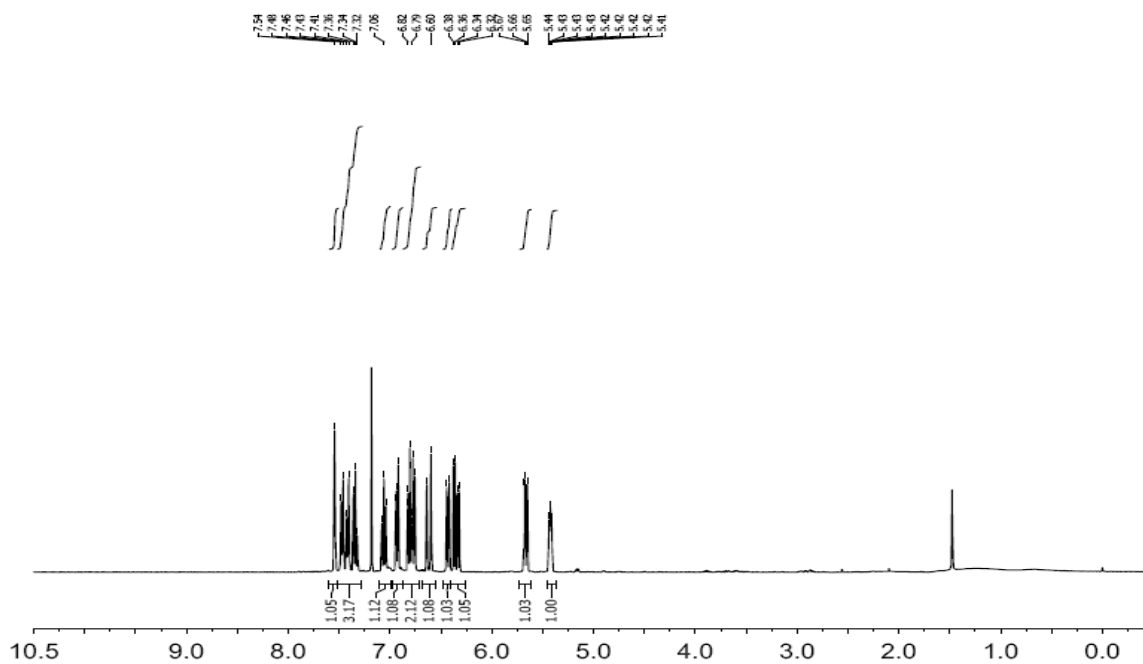
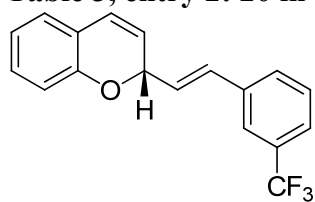
Table 3, entry 2: 20 in CDCl<sub>3</sub>

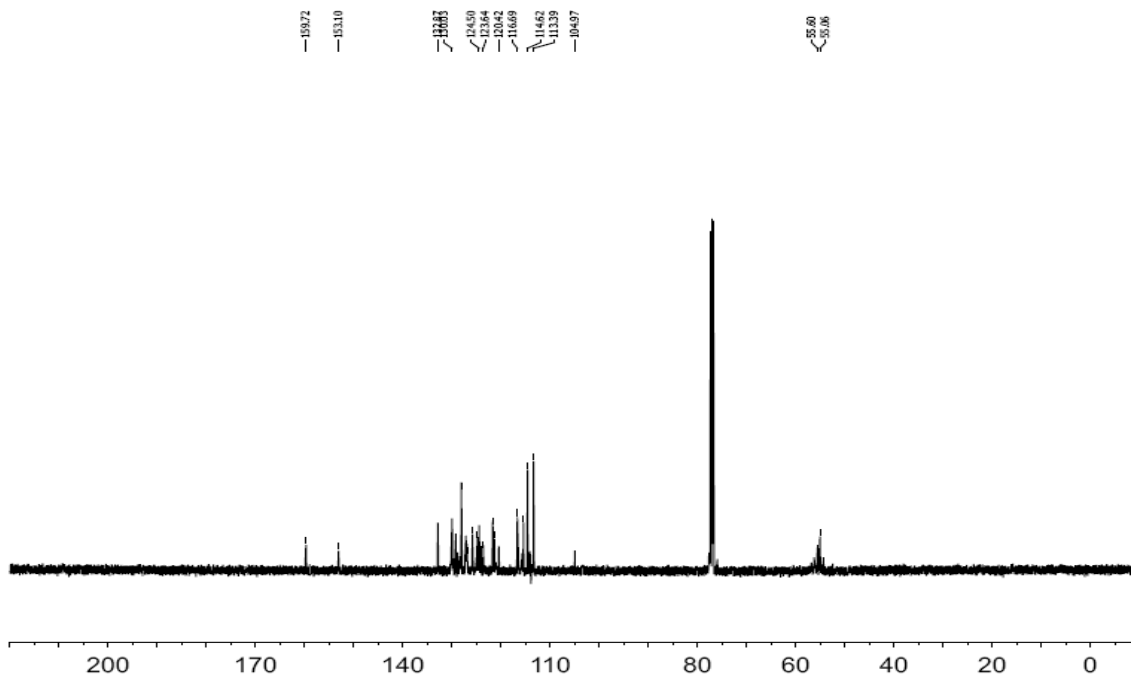
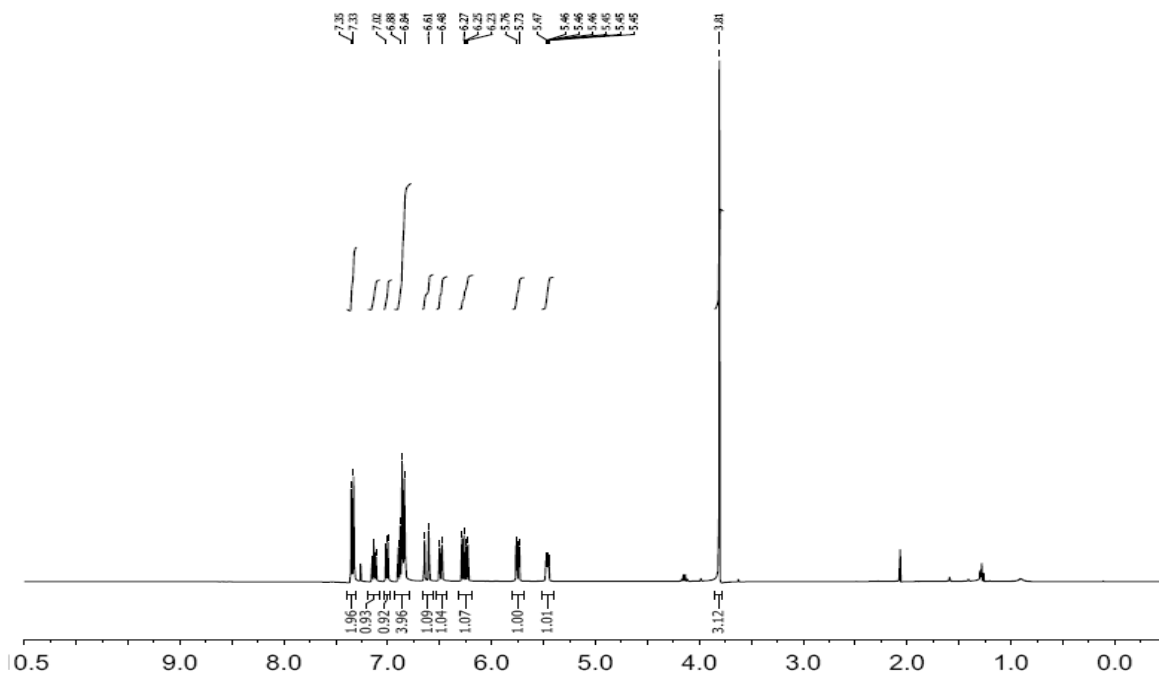
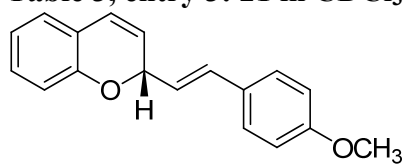
Table 3, entry 3: 21 in CDCl<sub>3</sub>



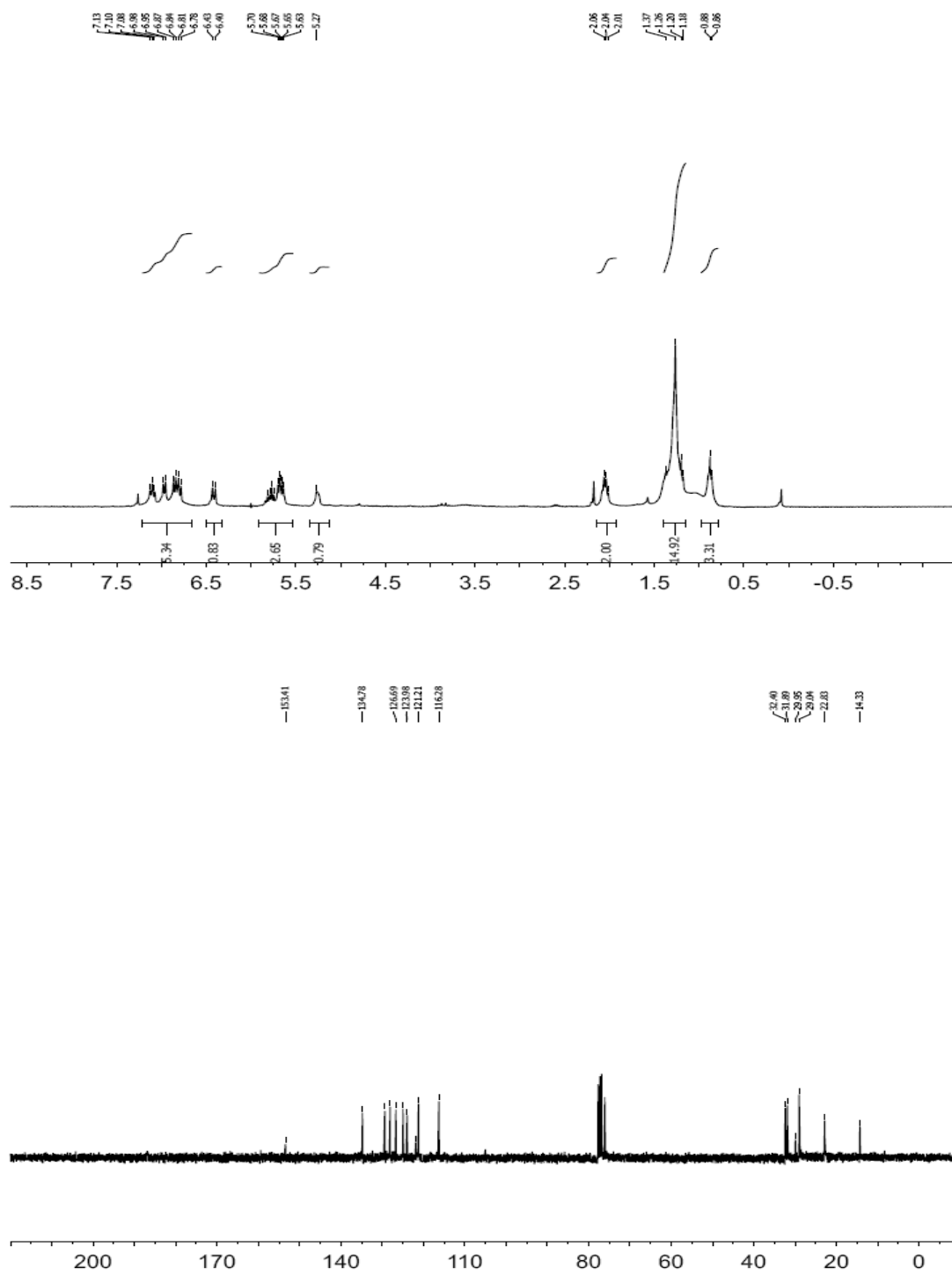
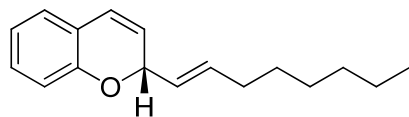
Table 3, entry 4: 22 in CDCl<sub>3</sub>

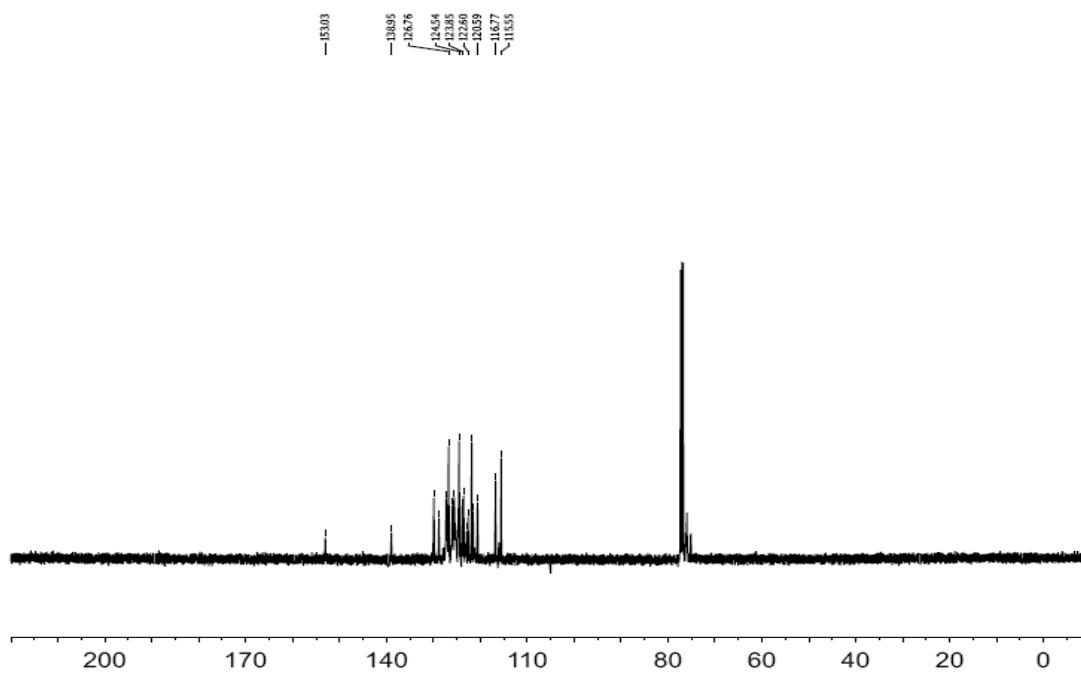
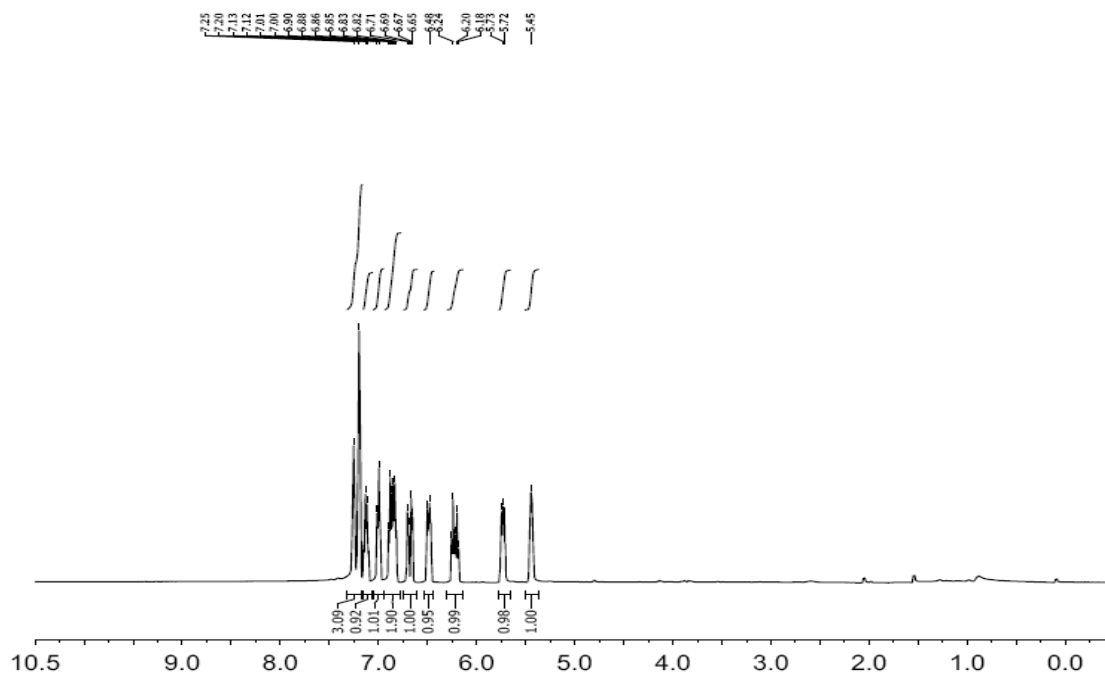
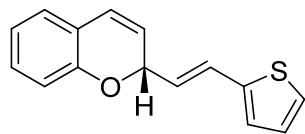
Table 3, entry 5: 23 in CDCl<sub>3</sub>

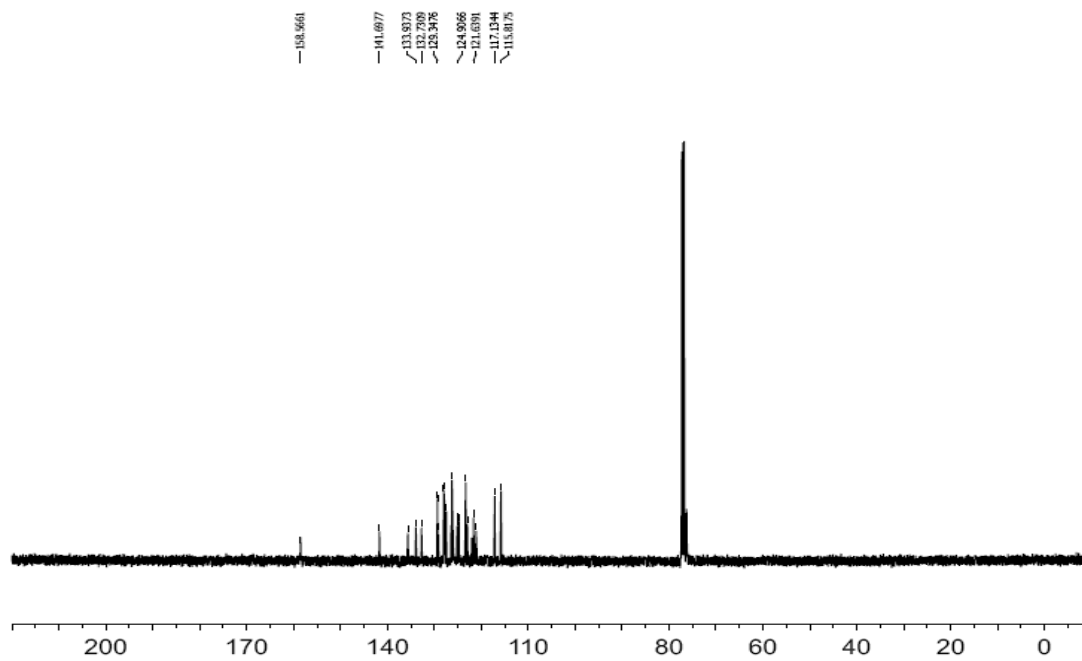
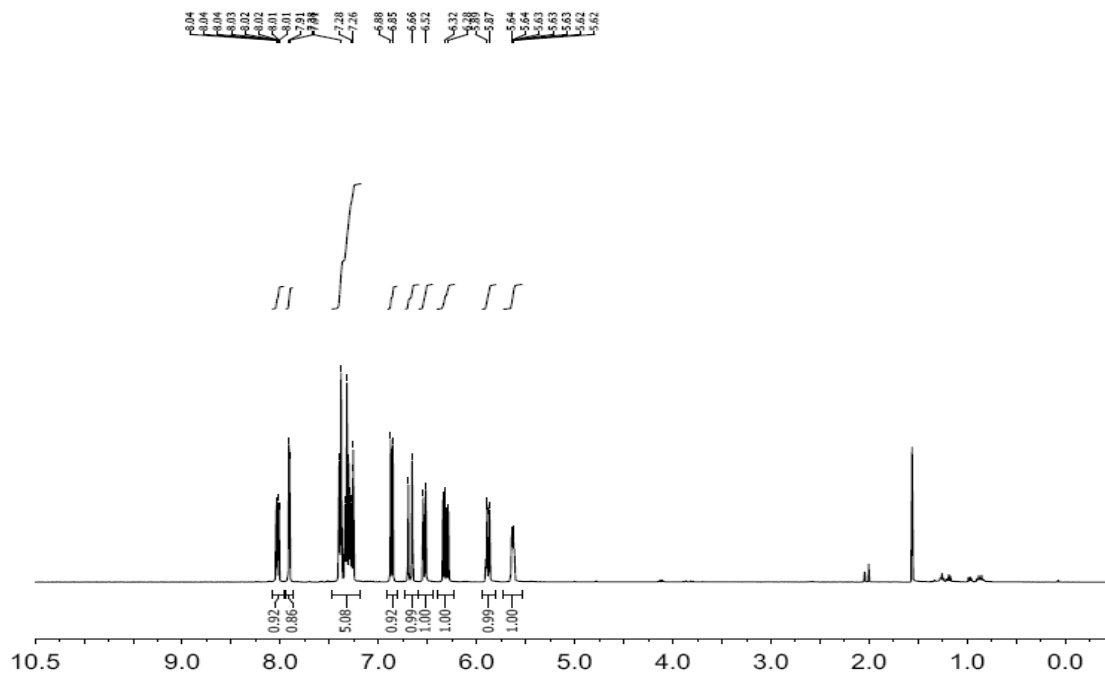
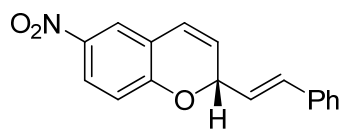
Table 3, entry 6: 24 in CDCl<sub>3</sub>

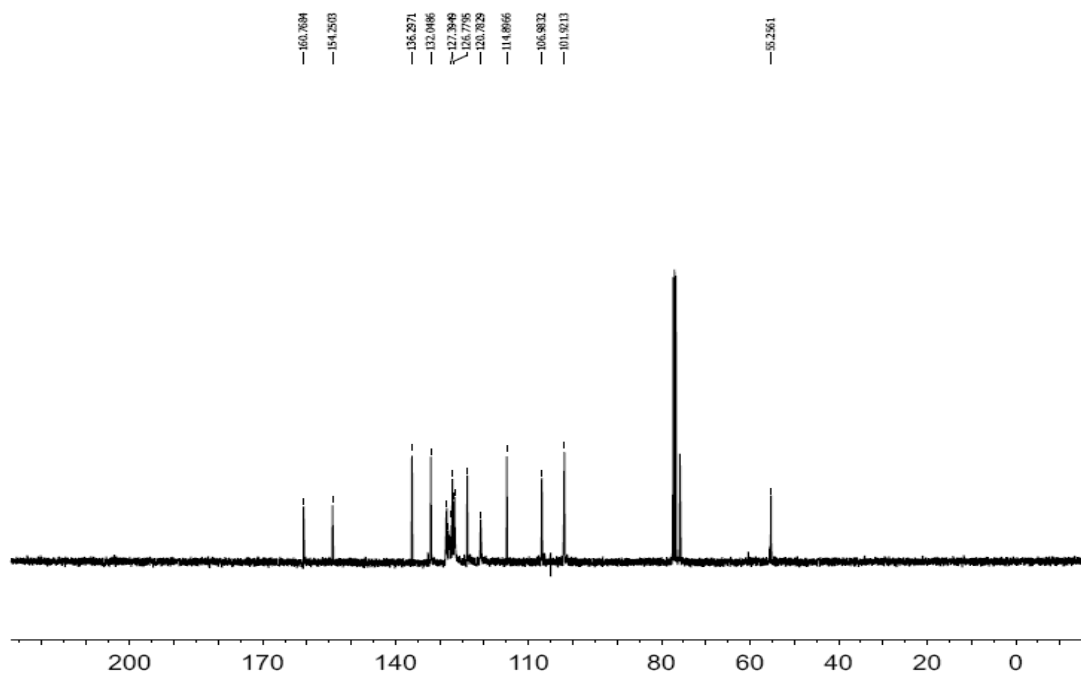
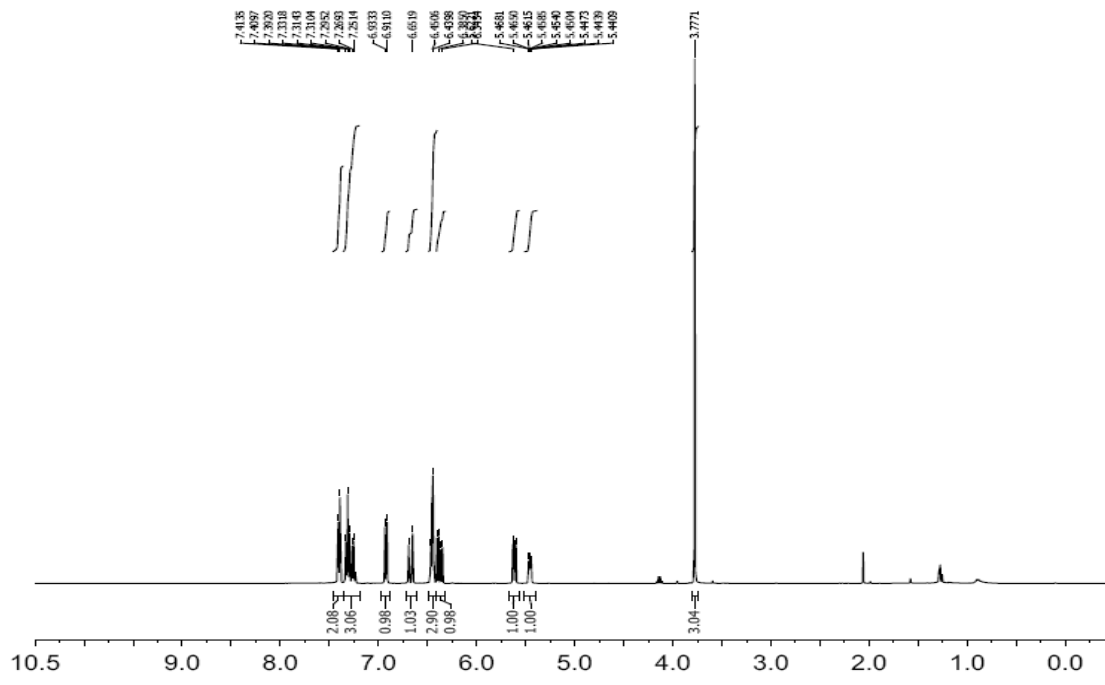
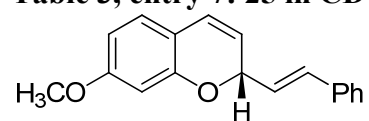
Table 3, entry 7: 25 in CDCl<sub>3</sub>

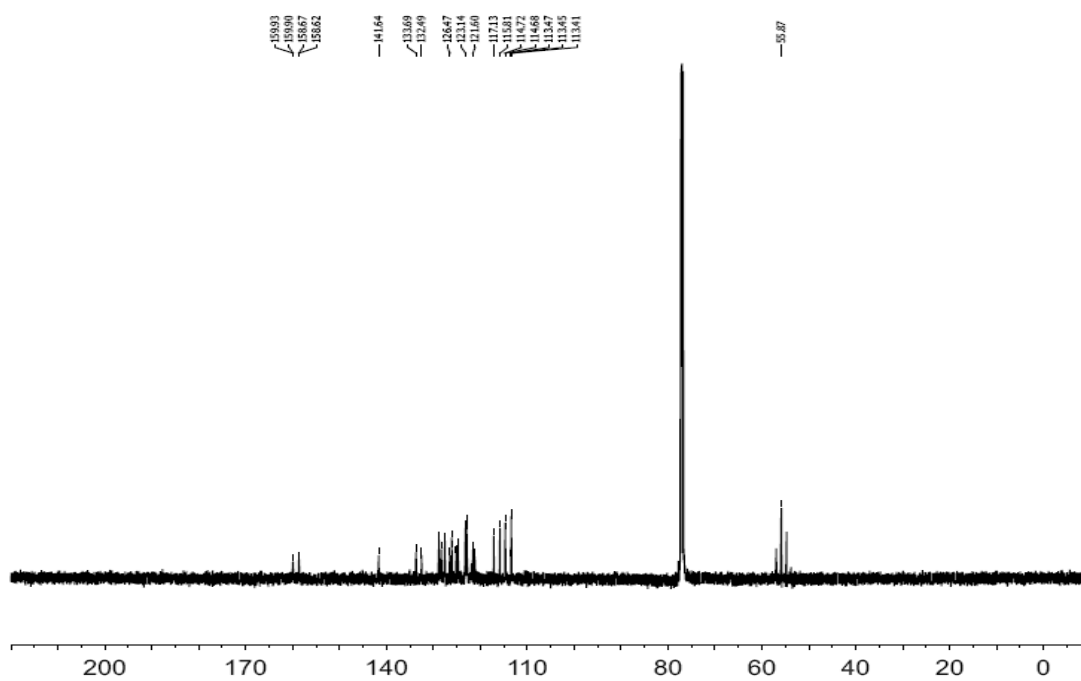
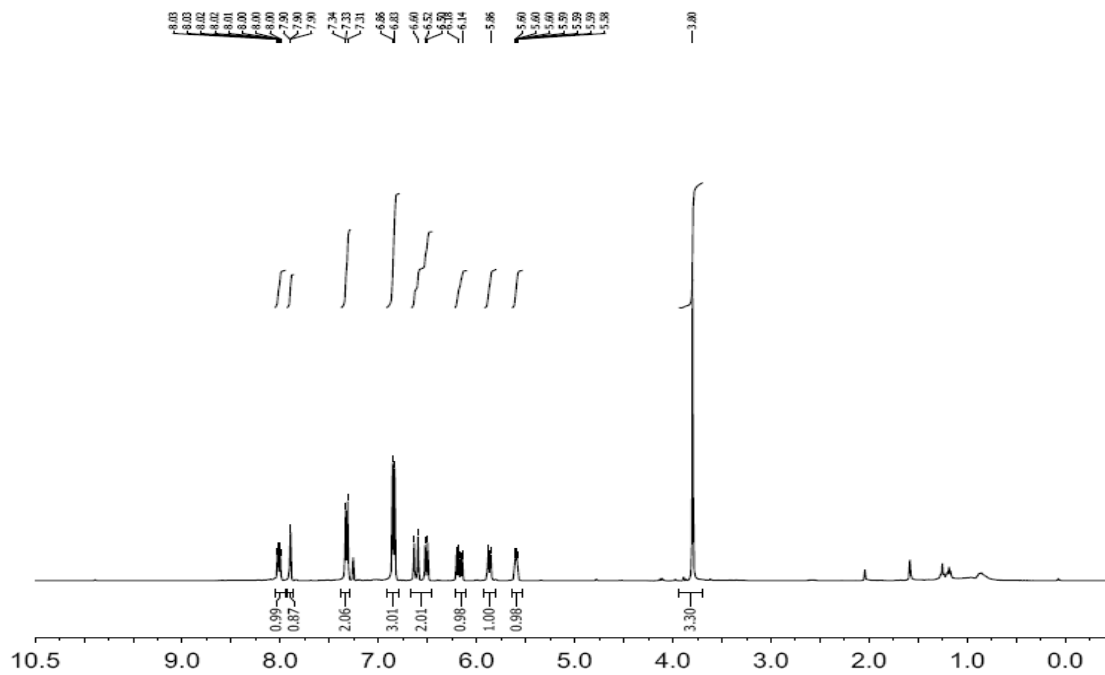
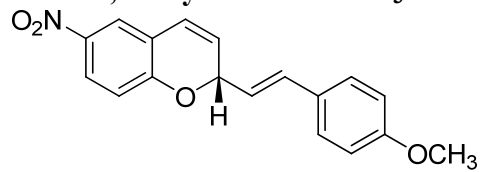
Table 3, entry 8: 26 in CDCl<sub>3</sub>

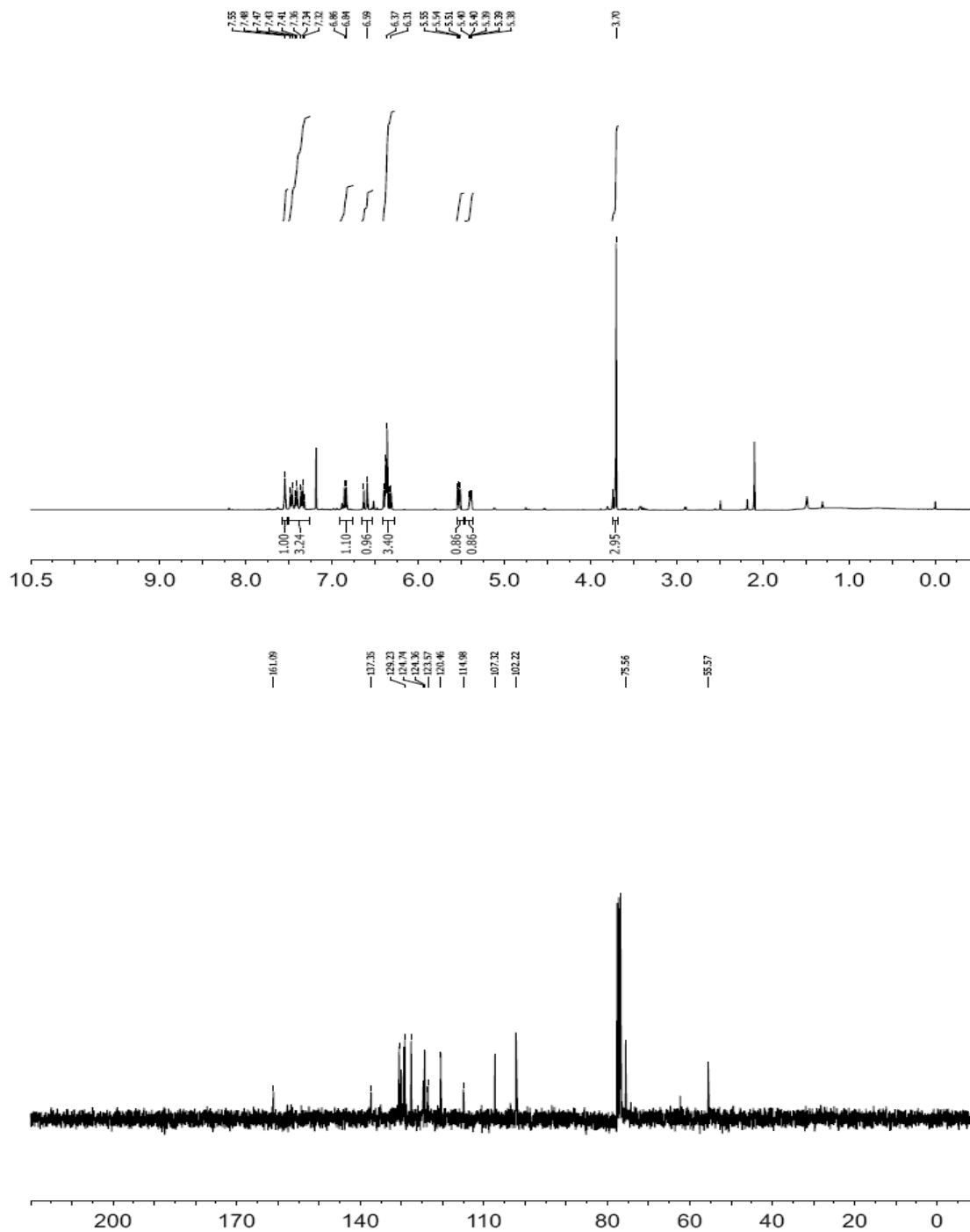
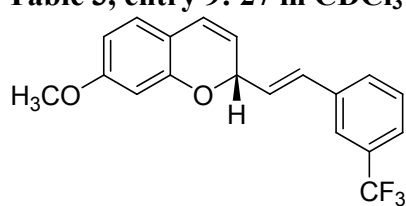
Table 3, entry 9: 27 in CDCl<sub>3</sub>

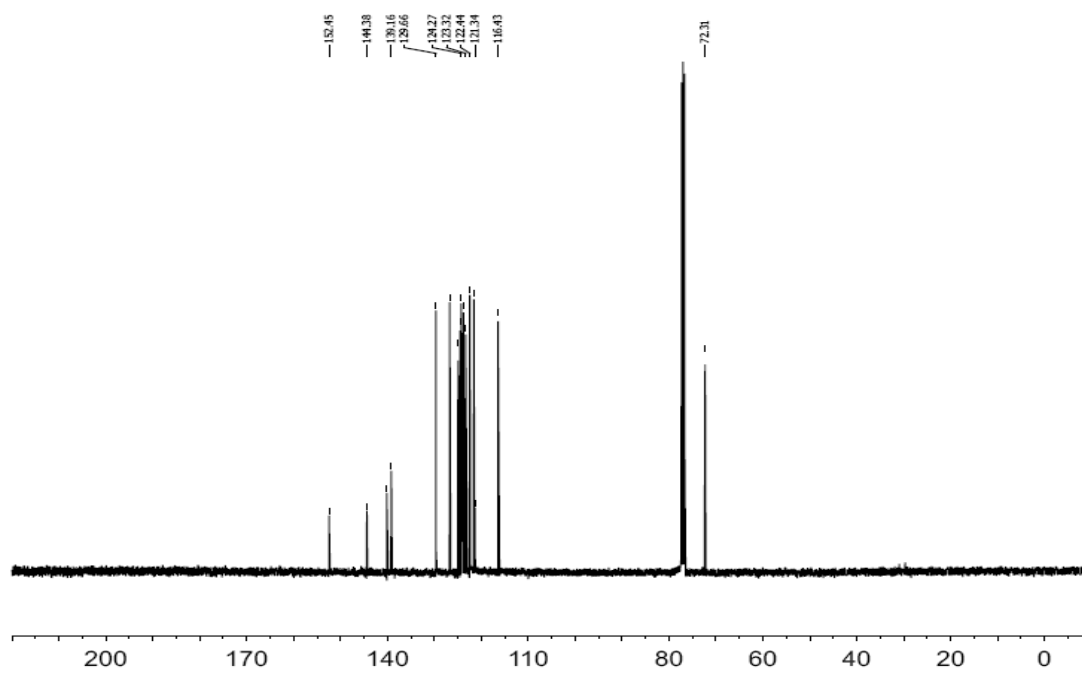
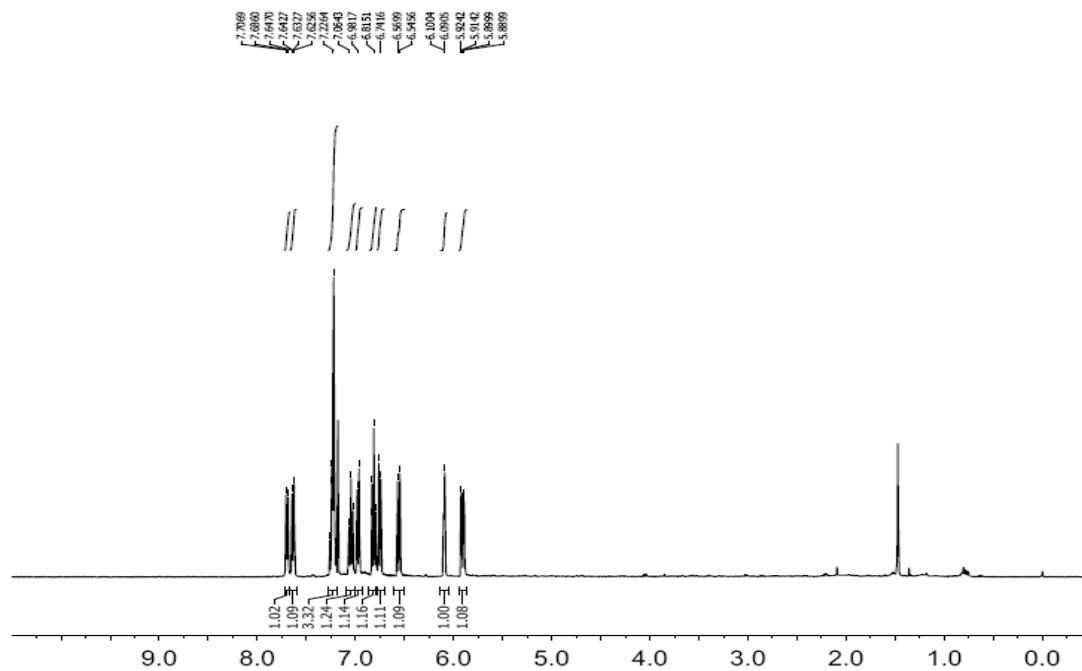
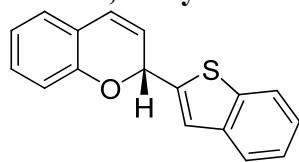
Table 3, entry 10: 28 in CDCl<sub>3</sub>

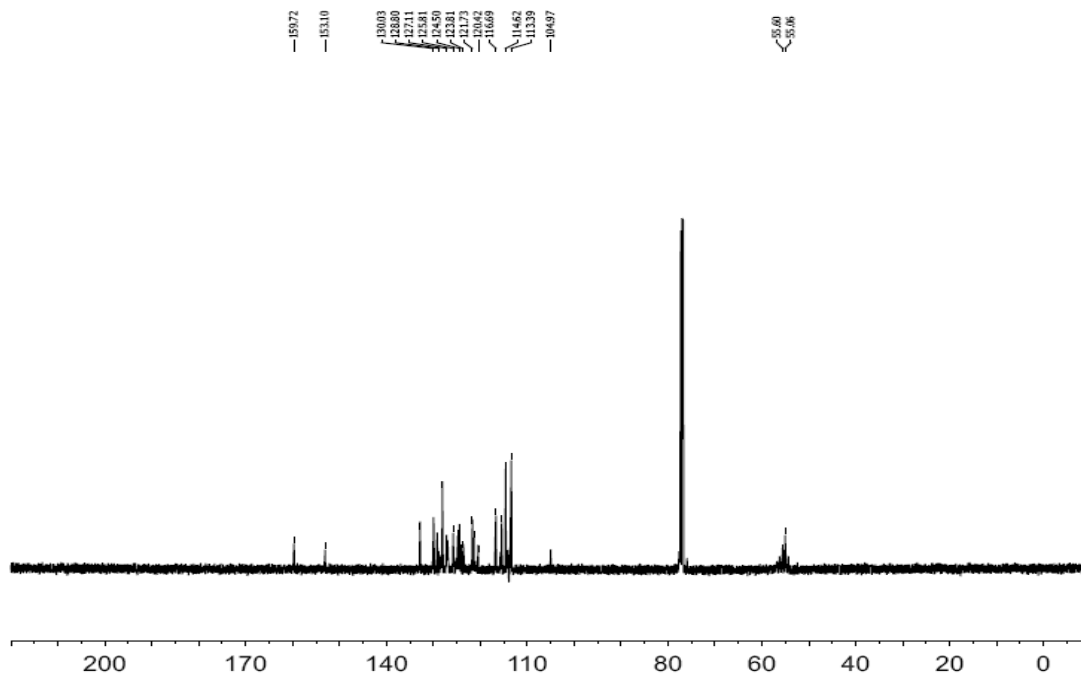
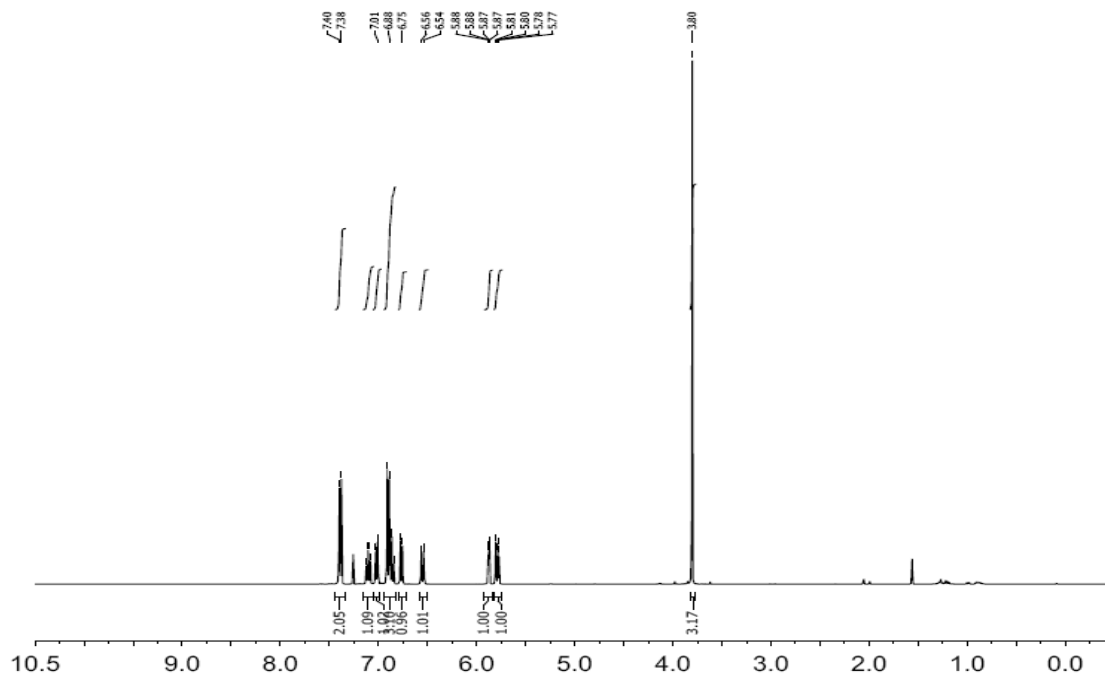
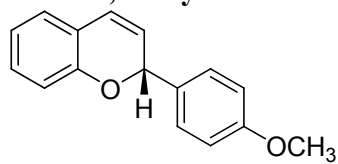
Table 3, entry 11: 29 in CDCl<sub>3</sub>



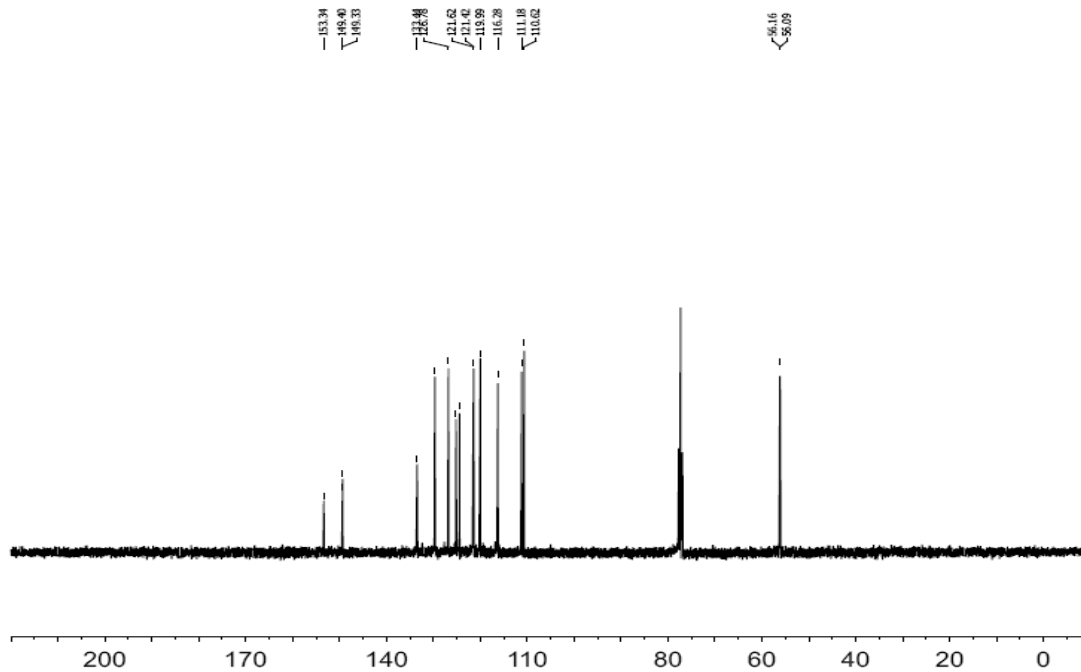
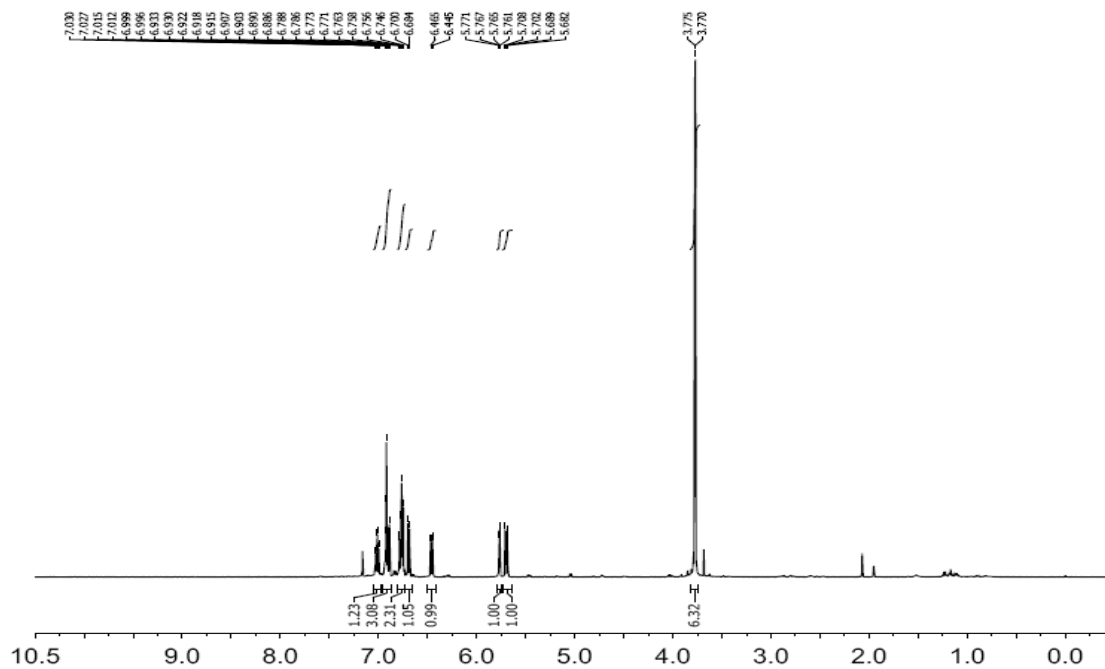
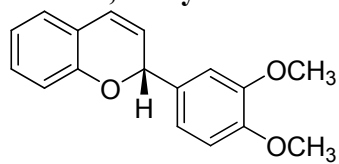
Table 3, entry 12: 30 in CDCl<sub>3</sub>

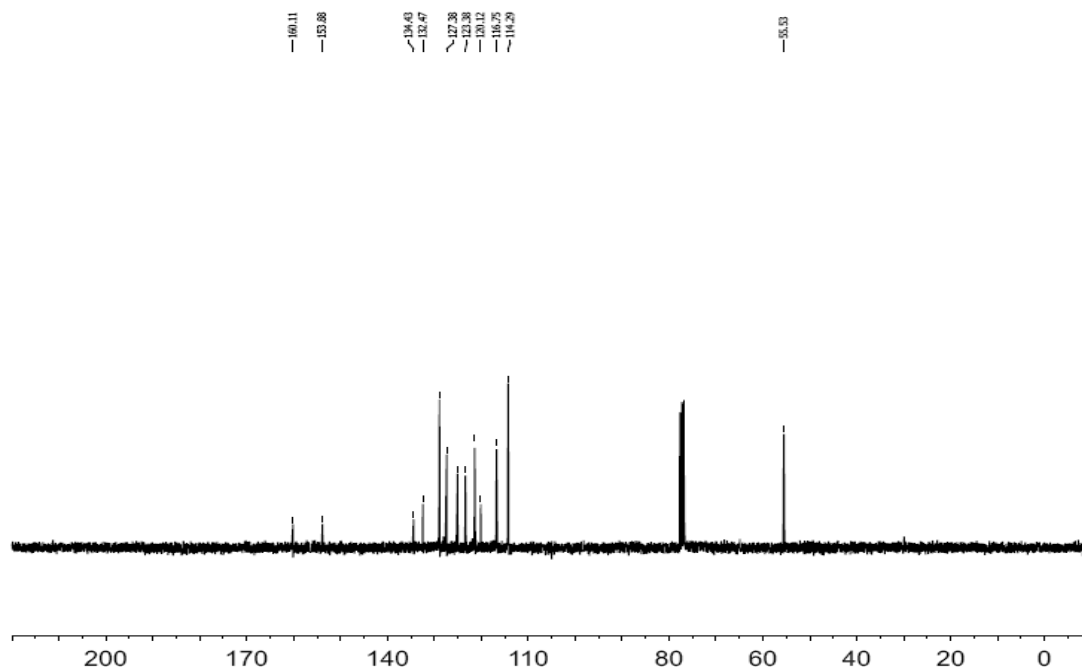
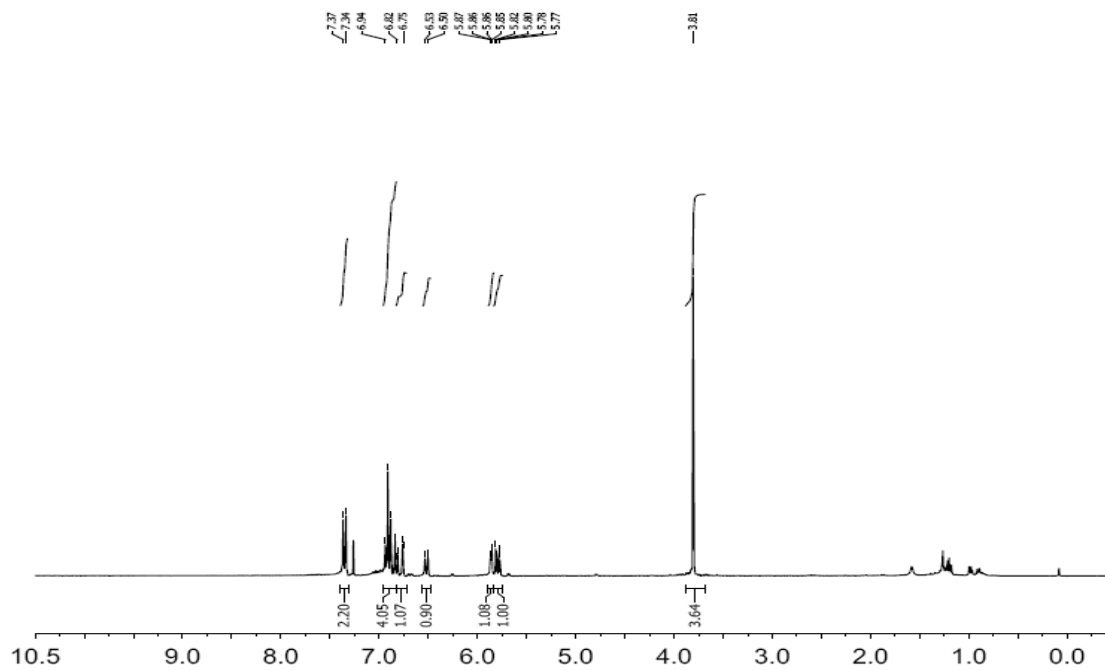
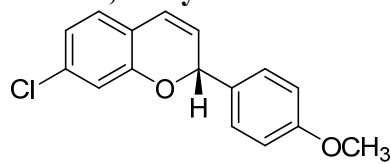
Table 3, entry 13: 31 in CDCl<sub>3</sub>

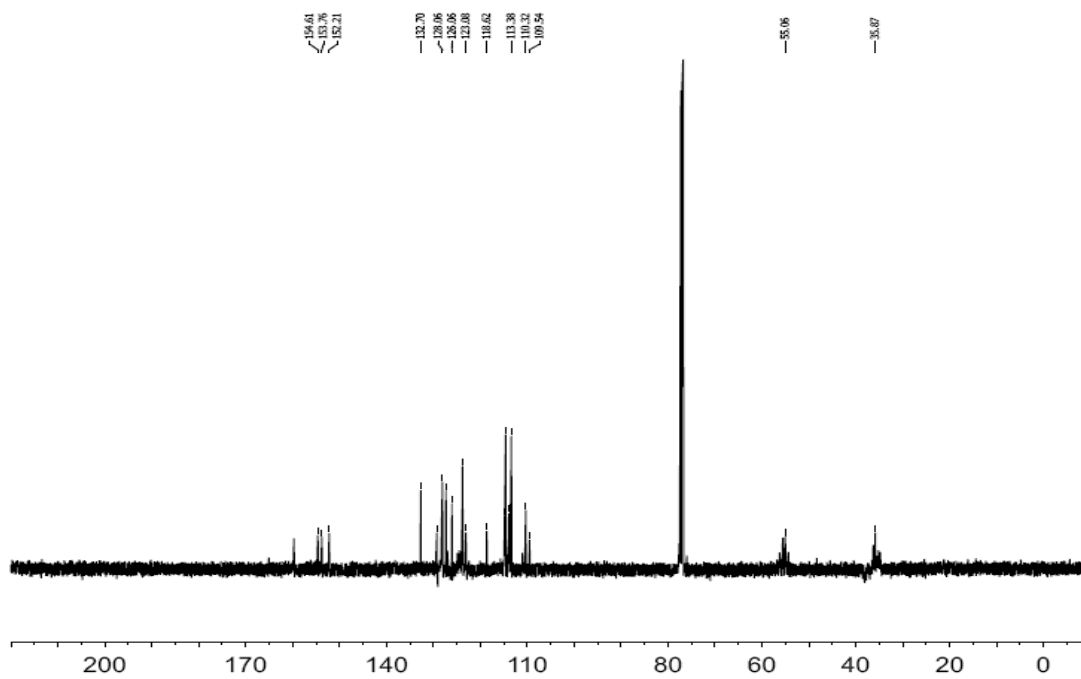
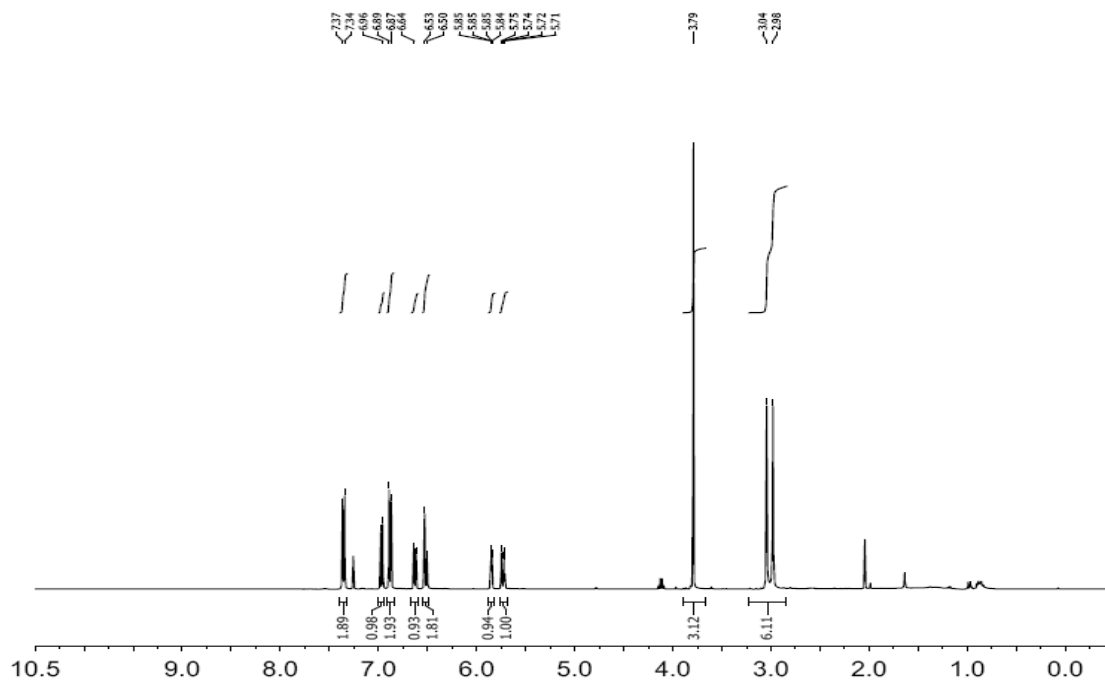
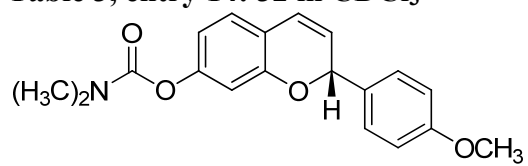
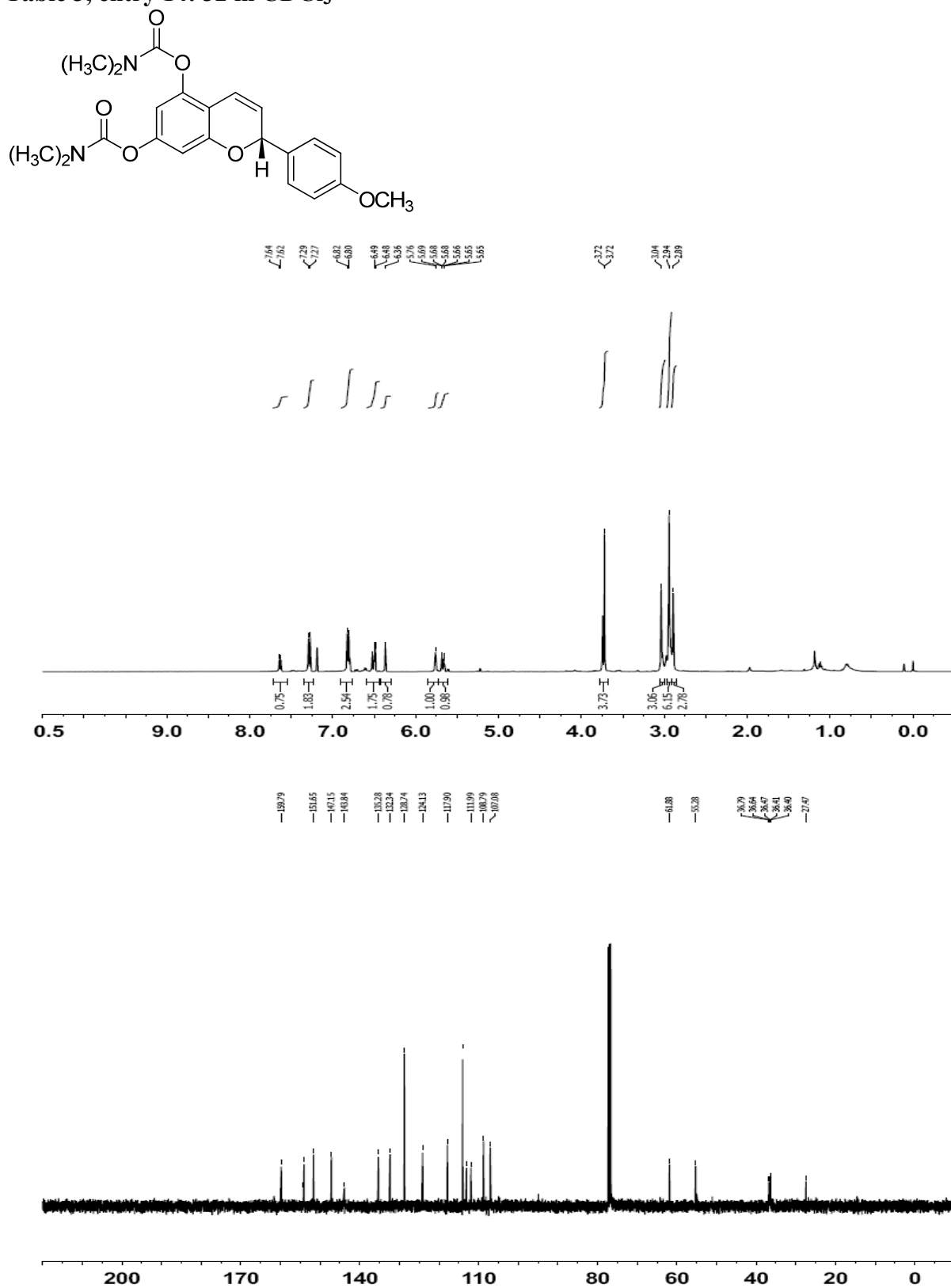
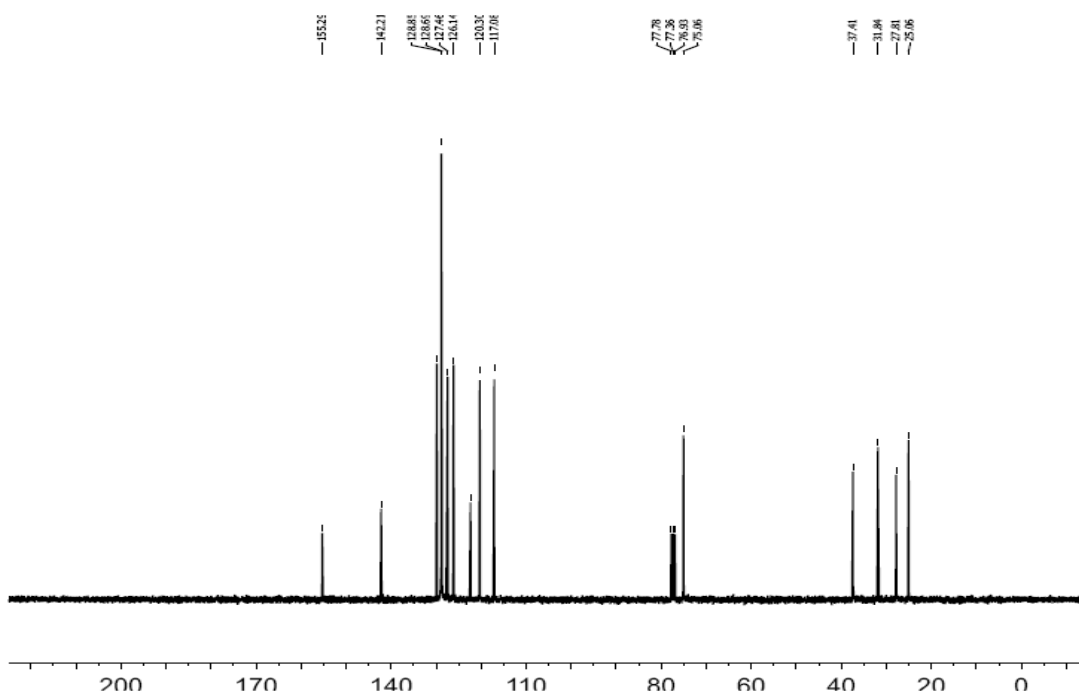
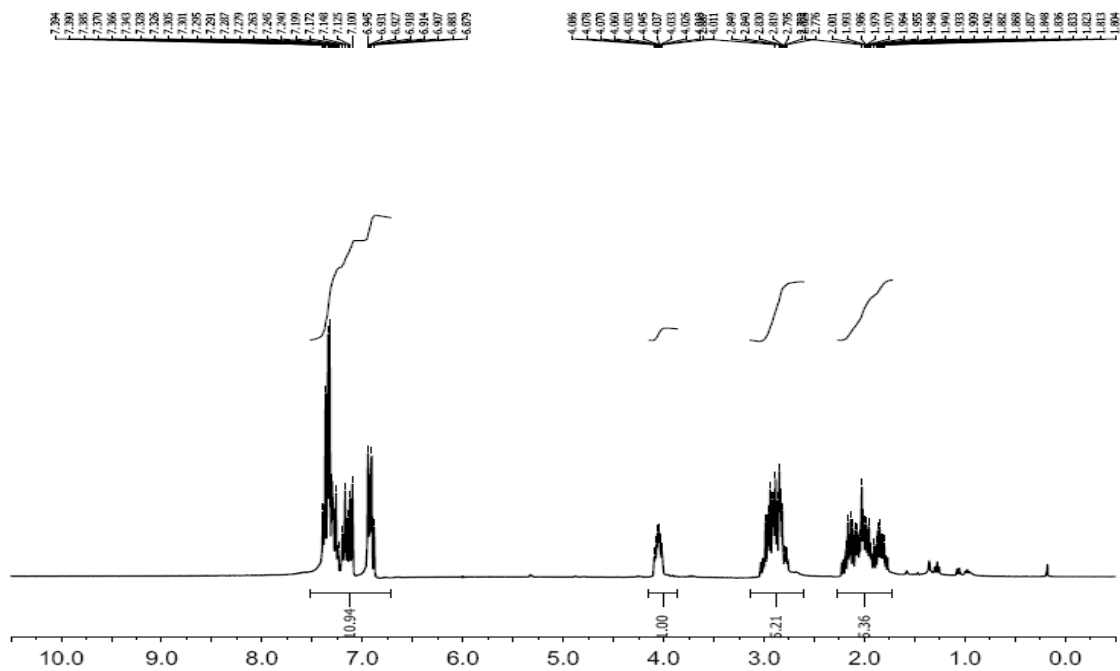
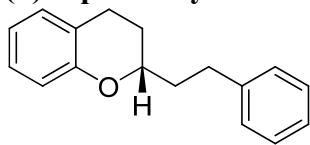
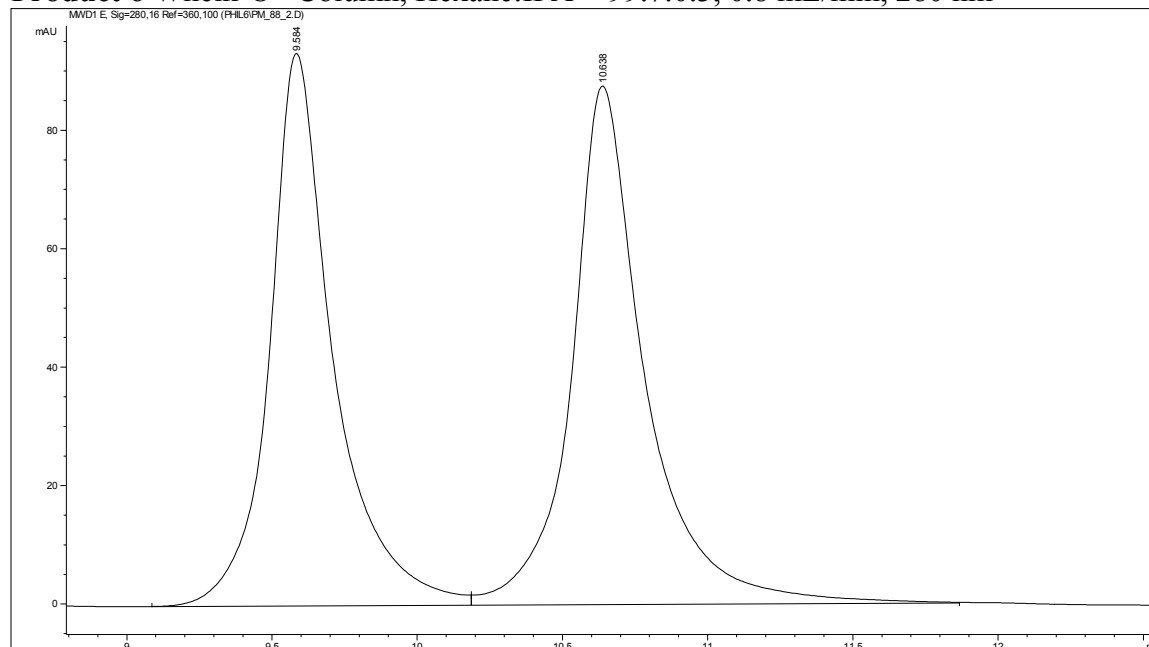
Table 3, entry 14: 32 in CDCl<sub>3</sub>

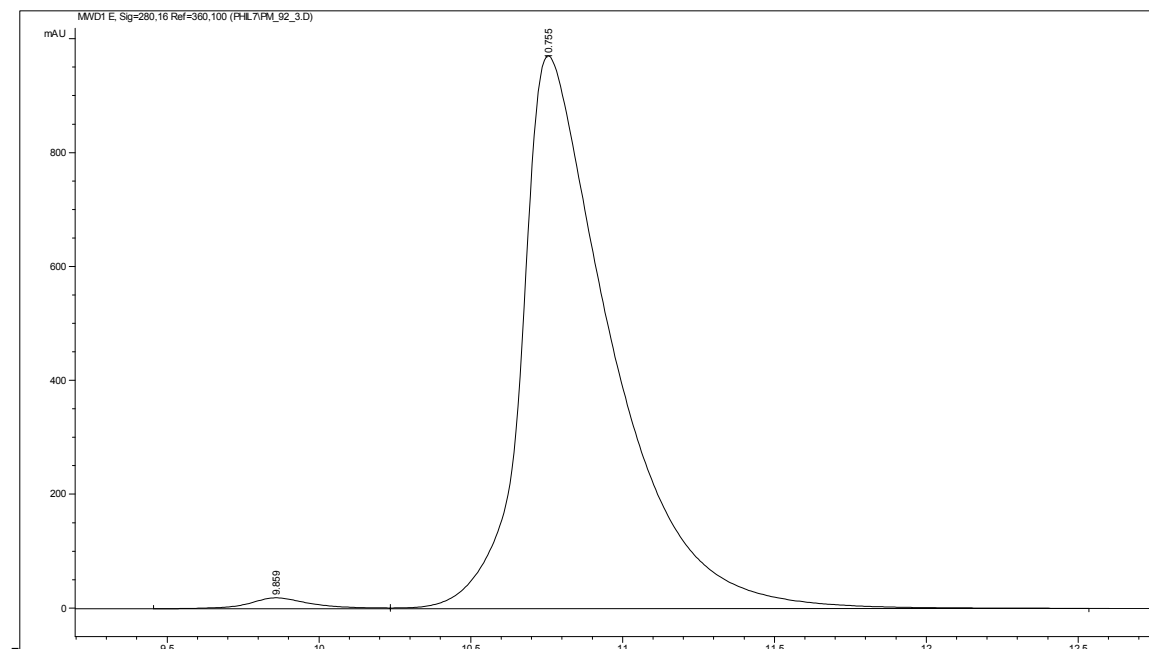
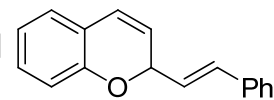
Table 3, entry 14: 32 in CDCl<sub>3</sub>

**(S)-2-phenethylchroman in CDCl<sub>3</sub>**

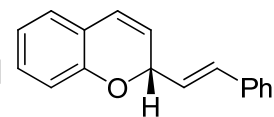
## HPLC Data

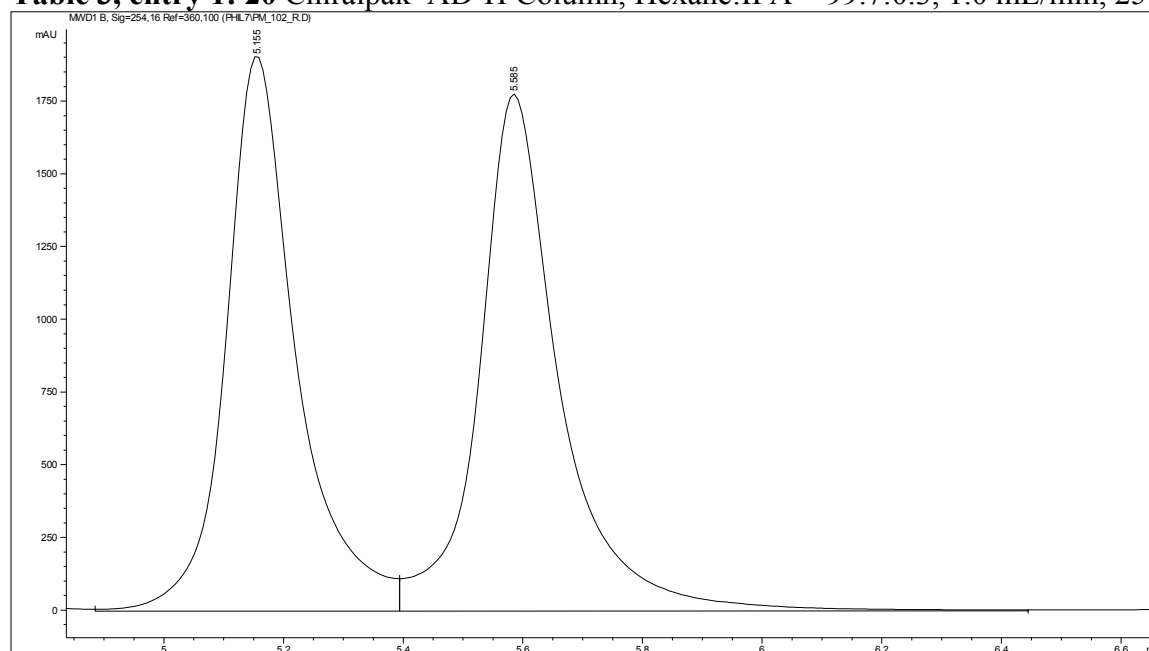
Product 6 Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.7:0.3, 0.8 mL/min, 280 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.584	PV	0.2183	1426.50977	93.33916	48.0020
2	10.638	VB	0.2518	1545.26282	87.59104	51.9980

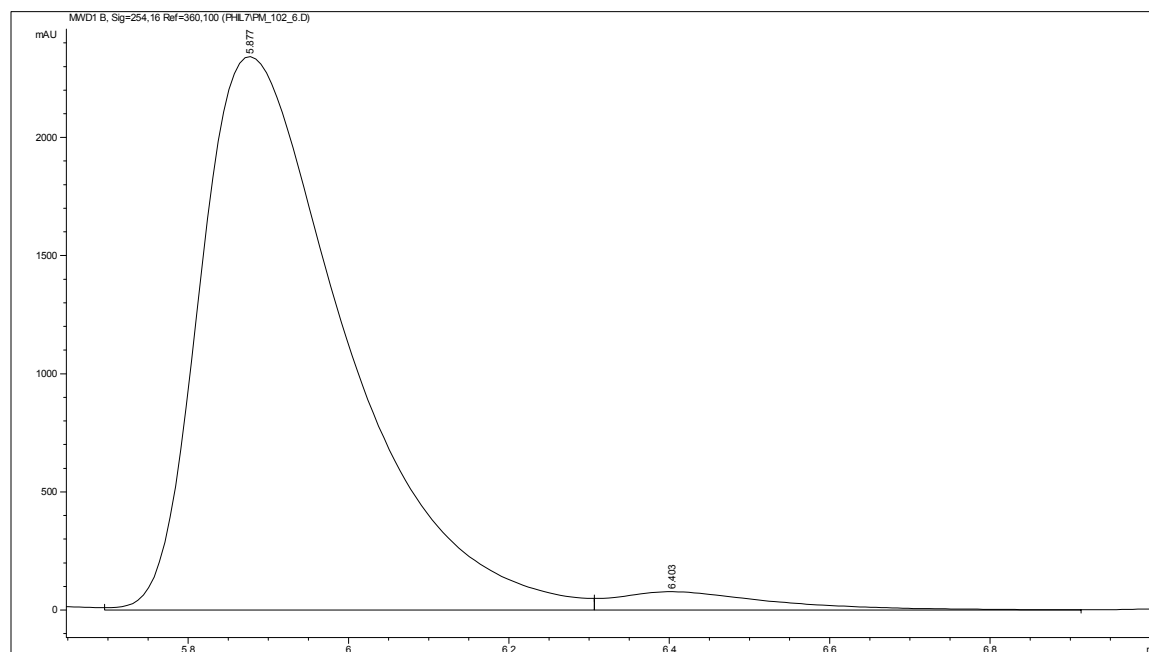
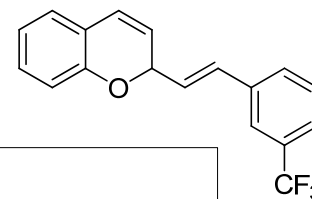


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.859	BV	0.2100	274.71393	19.07368	1.3432
2	10.755	VB	0.2964	2.01773e4	971.10236	98.6568

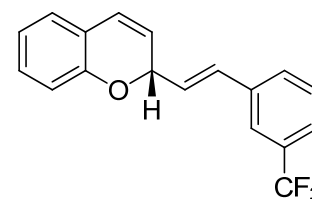


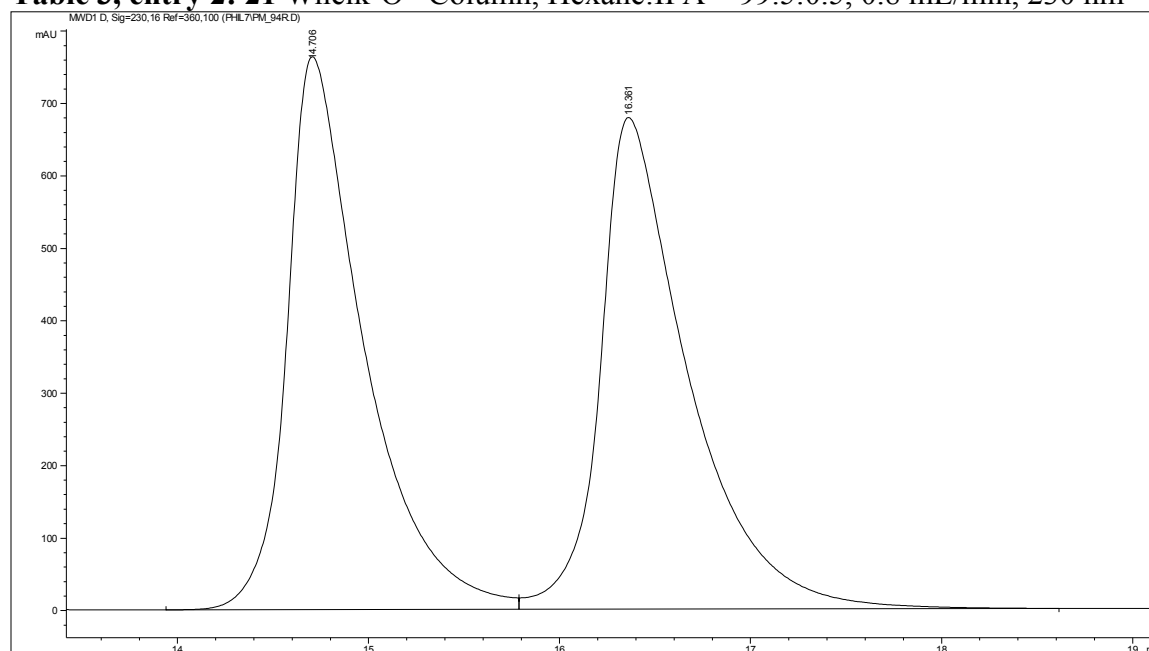
**Table 3, entry 1: 20** Chiralpak® AD-H Column, Hexane:IPA = 99.7:0.3, 1.0 mL/min, 254 nm

Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.155	VV	0.1194	1.56282e4	1910.57397	48.4948
2	5.585	VV	0.1349	1.65983e4	1778.17944	51.5052

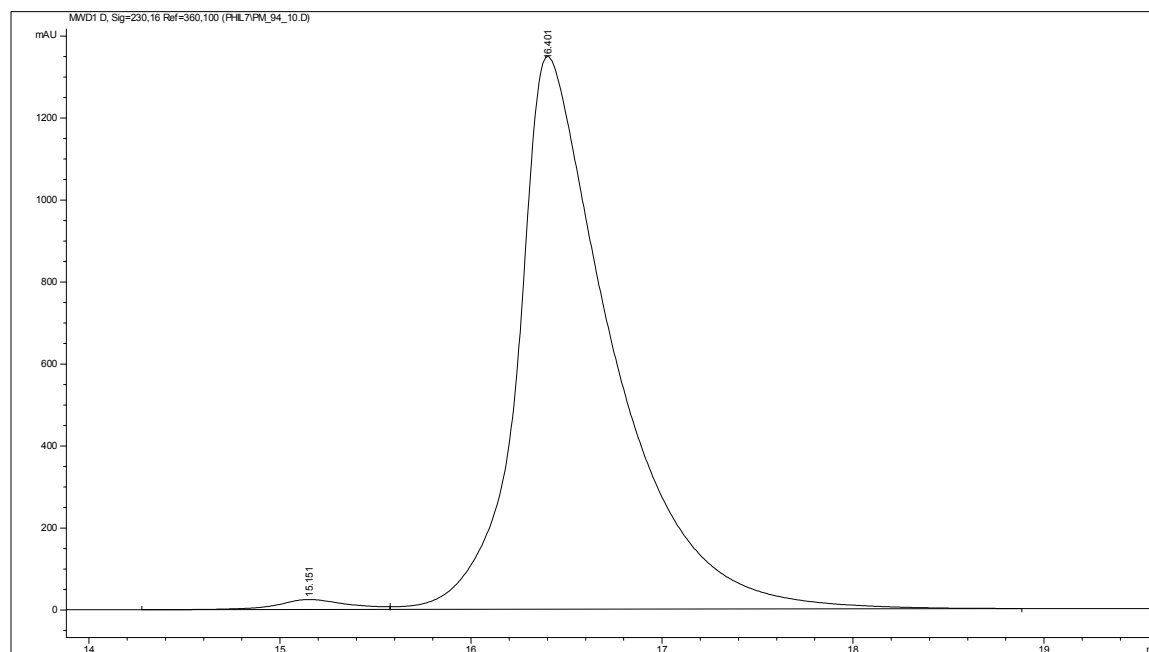
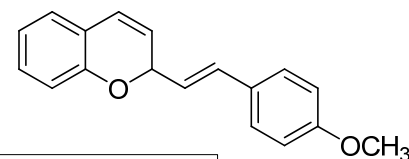


Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.877	VV	0.1873	2.95721e4	2342.59888	96.5590
2	6.403	VV	0.1925	1053.84326	77.57892	3.4410

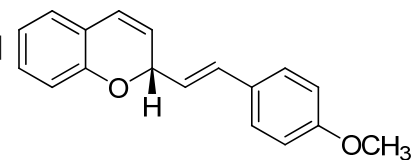


**Table 3, entry 2: 21** Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.5:0.5, 0.8 mL/min, 230 nm

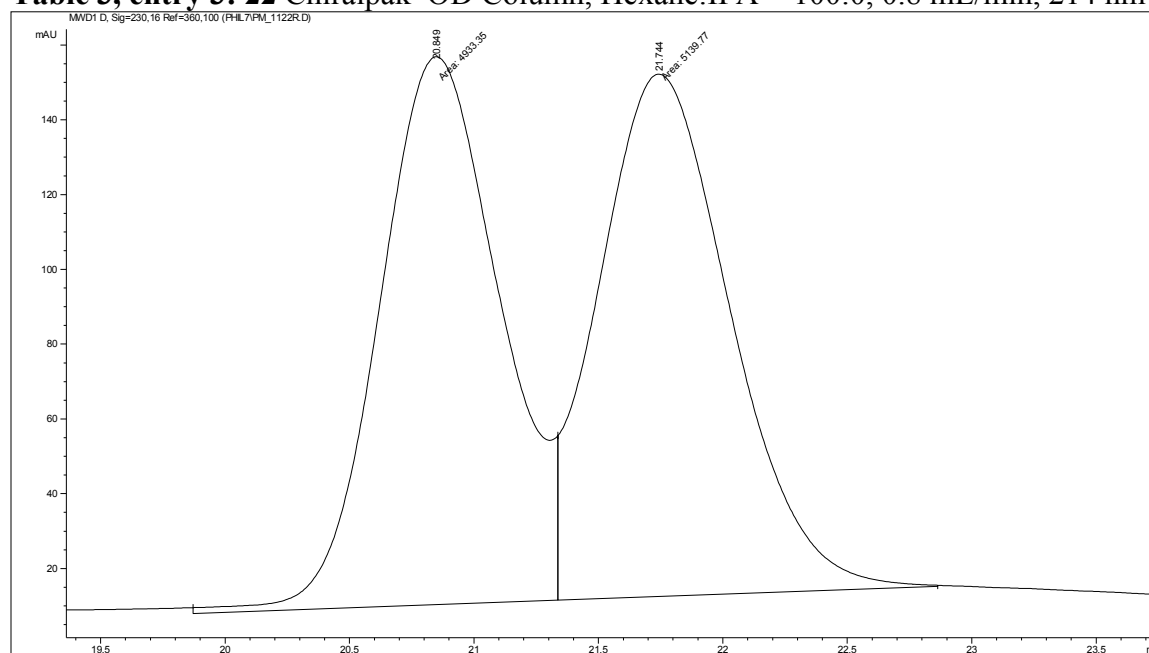
Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.706	PV	0.4040	2.14633e4	763.40472	49.6186
2	16.361	VB	0.4587	2.17932e4	678.63403	50.3814



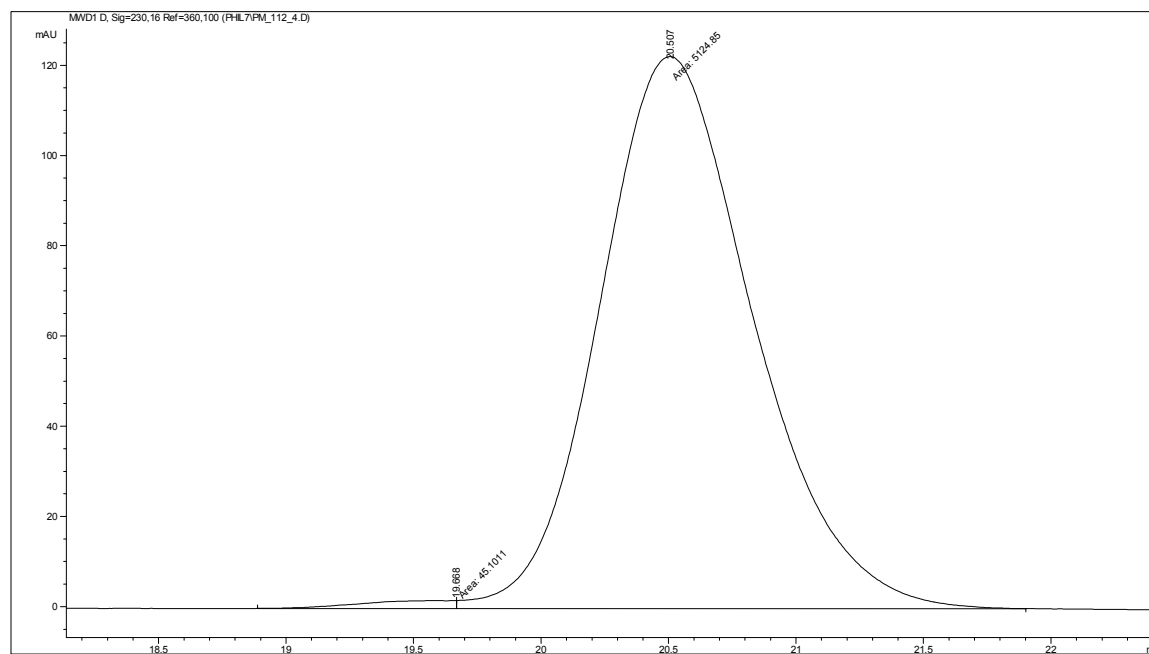
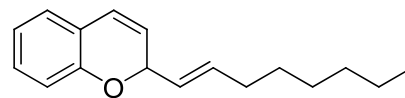
Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.151	PV	0.3700	629.70392	24.49078	1.3217
2	16.401	VB	0.4808	4.70120e4	1348.32922	98.6783



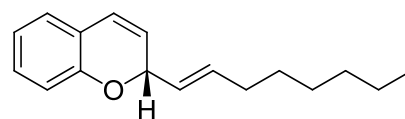


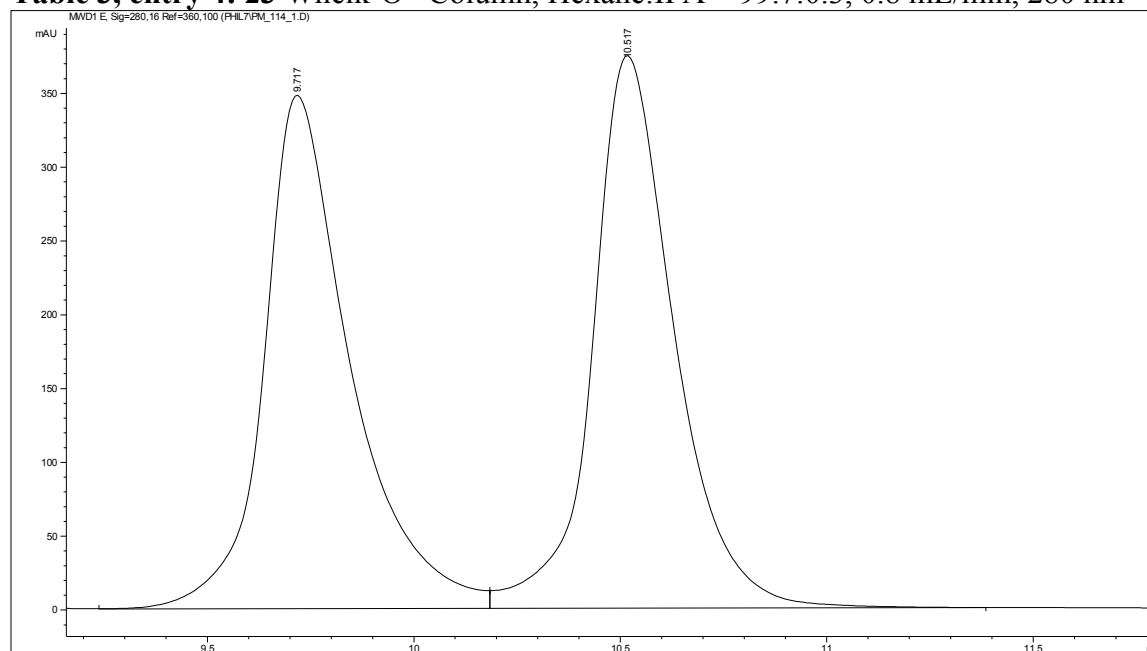
**Table 3, entry 3: 22 Chiralpak® OD Column, Hexane:IPA = 100:0, 0.8 mL/min, 214 nm**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.849	MF	0.5610	4933.34668	146.55122	48.9754
2	21.744	FM	0.6132	5139.77393	139.70380	51.0246

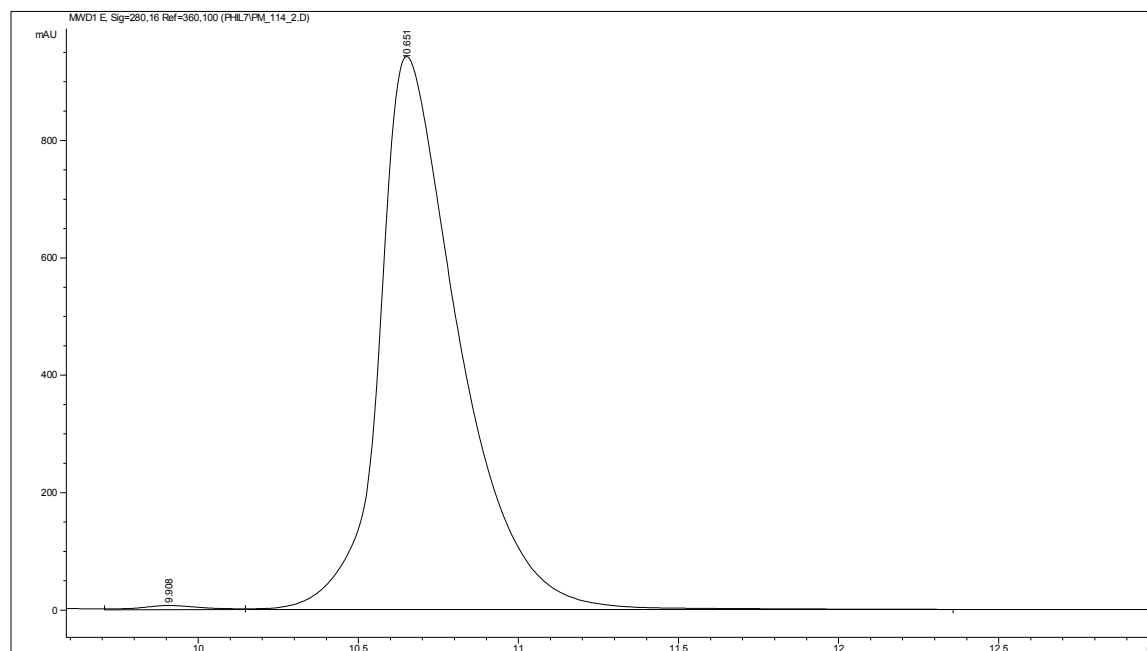
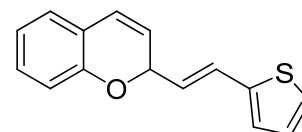


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.668	MF	0.4211	45.10107	1.78503	0.8724
2	20.507	FM	0.6978	5124.85498	122.40617	99.1276

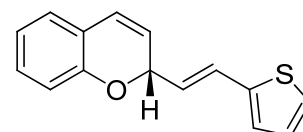


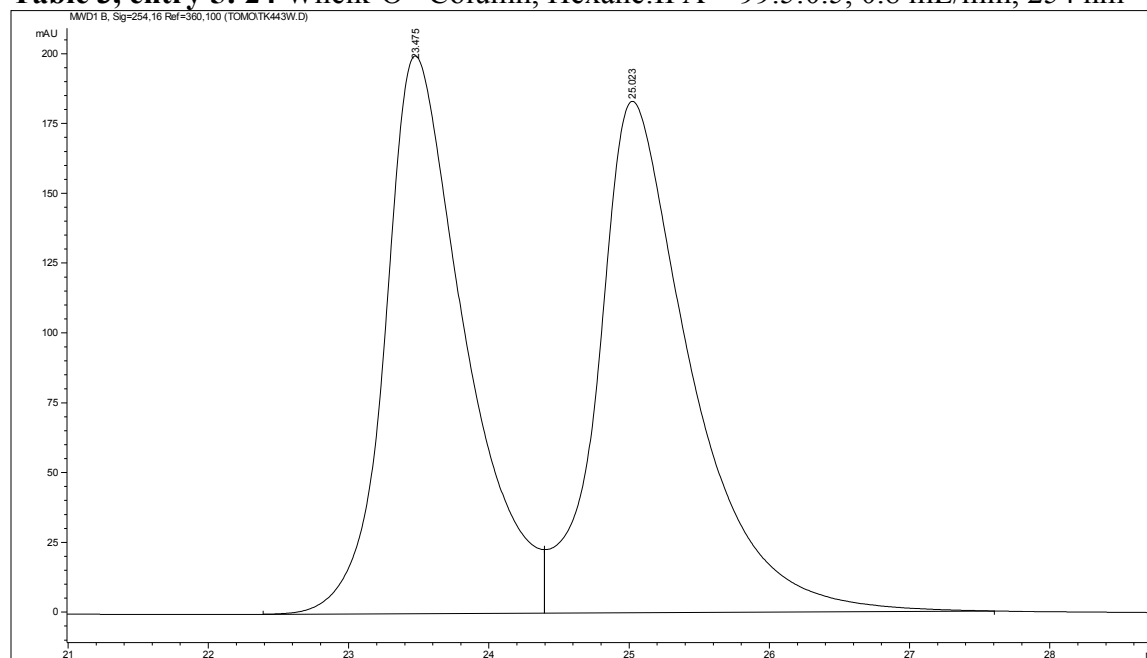
**Table 3, entry 4: 23** Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.7:0.3, 0.8 mL/min, 280 nm

Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.717	VV	0.2120	5068.87256	347.88516	49.5699
2	10.517	VB	0.2067	5156.84082	374.46661	50.4301

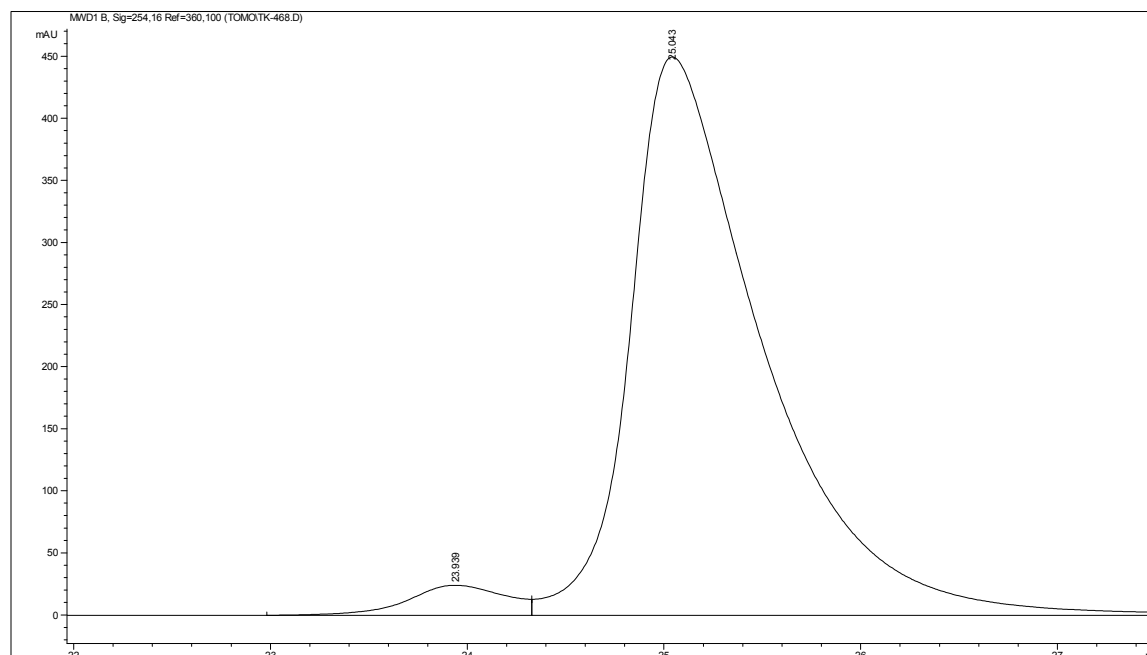
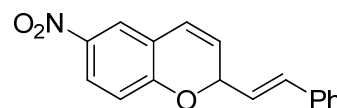


Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.908	VV	0.1992	96.32668	7.05740	0.5853
2	10.651	VB	0.2564	1.63604e4	942.85840	99.4147

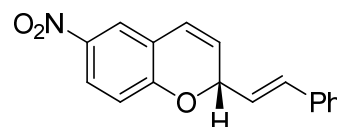


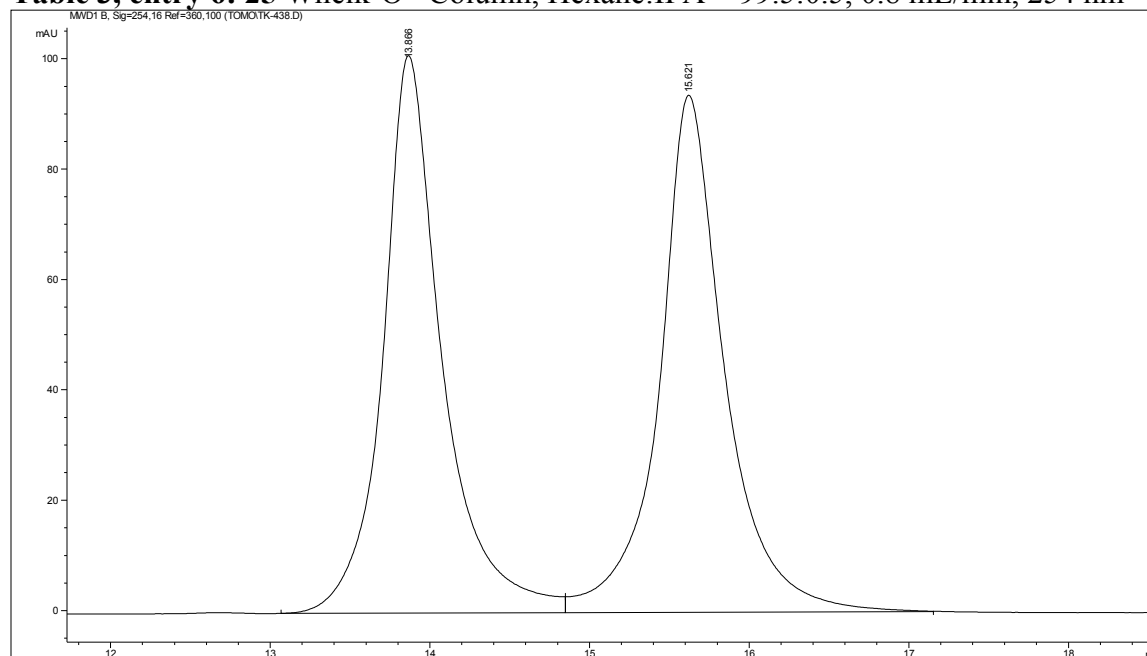
**Table 3, entry 5: 24** Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.5:0.5, 0.8 mL/min, 254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.475	BV	0.5762	7915.04297	199.80463	48.3945
2	25.023	VB	0.6676	8440.22559	183.17671	51.6055

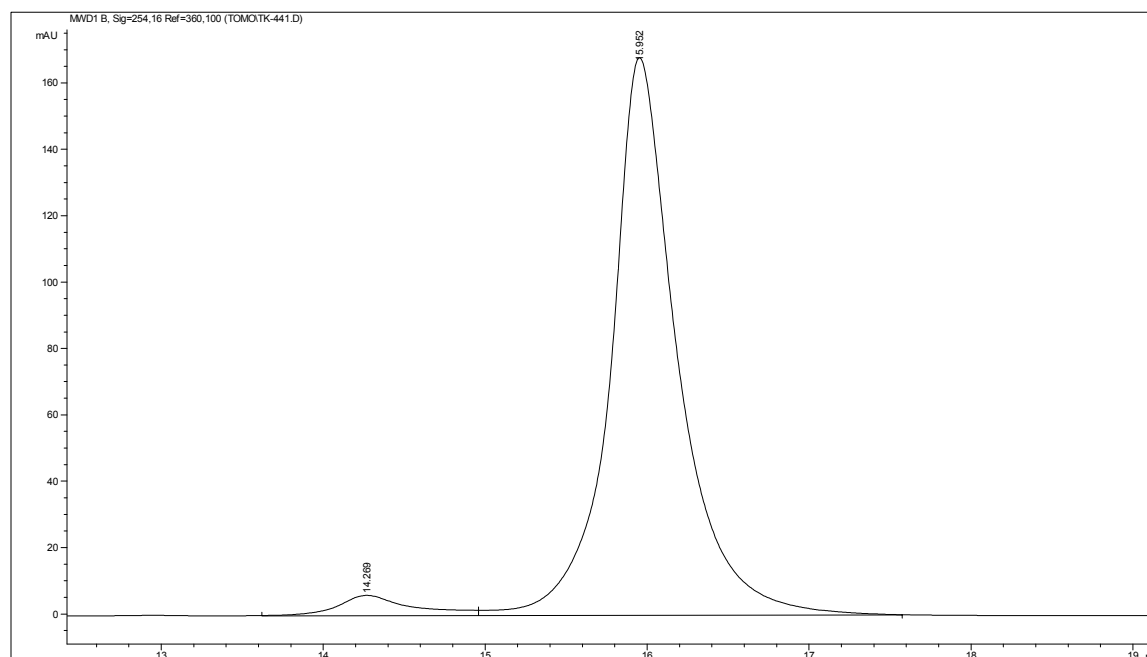
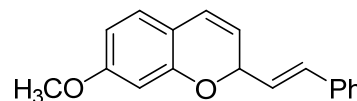


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.939	BV	0.5170	844.65424	24.33344	3.8217
2	25.043	VBA	0.6833	2.12571e4	449.87335	96.1783

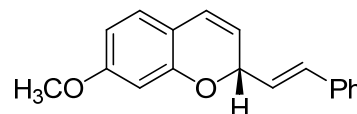


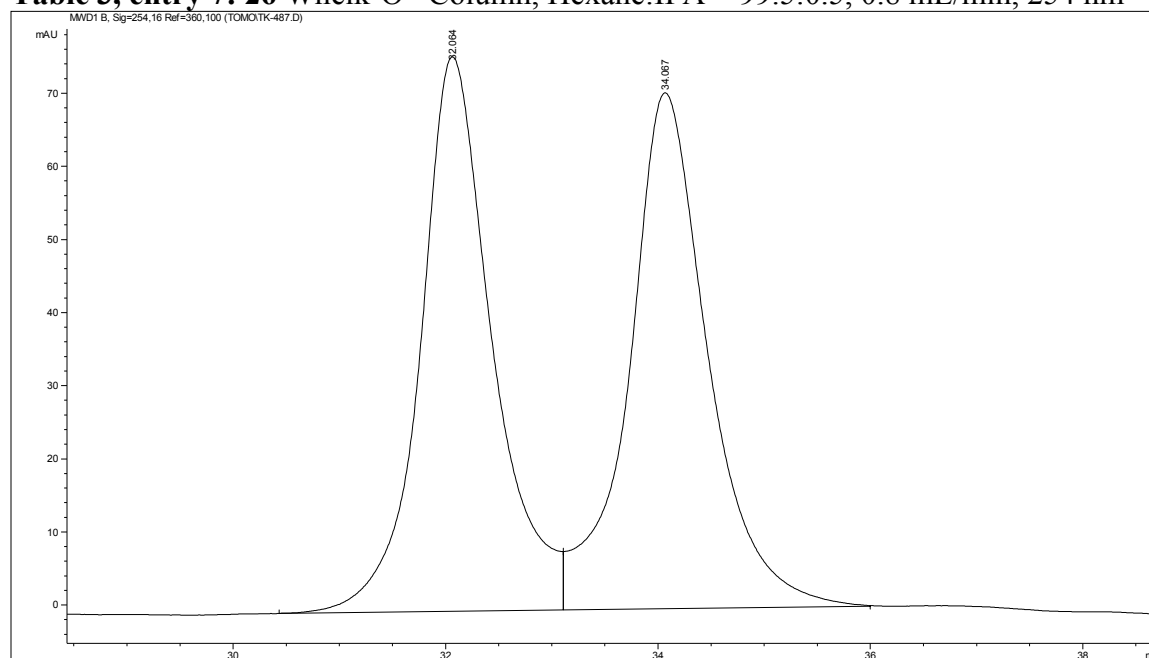
**Table 3, entry 6: 25 Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.5:0.5, 0.8 mL/min, 254 nm**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.866	BV	0.3698	2614.16724	101.06818	49.3758
2	15.621	VB	0.4097	2680.25757	93.71259	50.6242

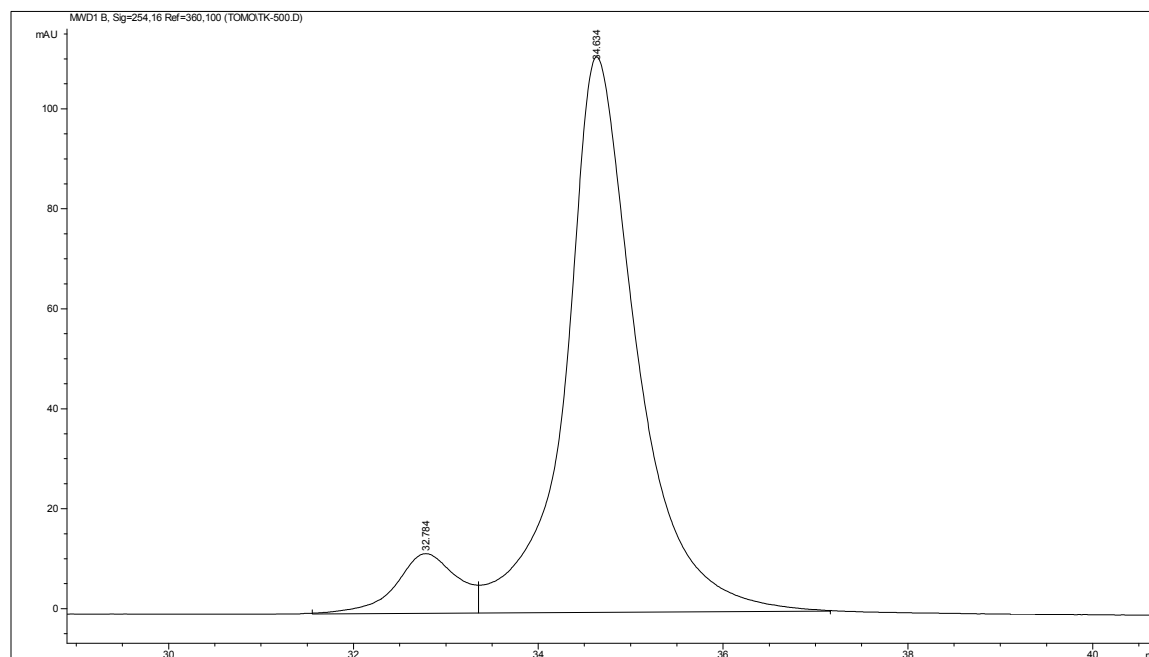
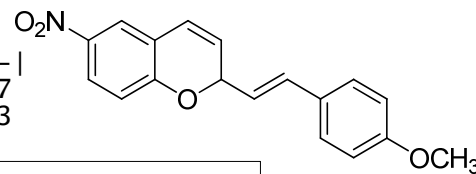


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.269	BV	0.4488	197.39458	6.14436	3.9186
2	15.952	VB	0.4099	4839.92139	168.09242	96.0814

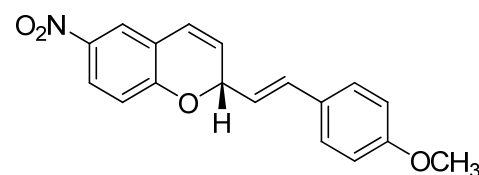


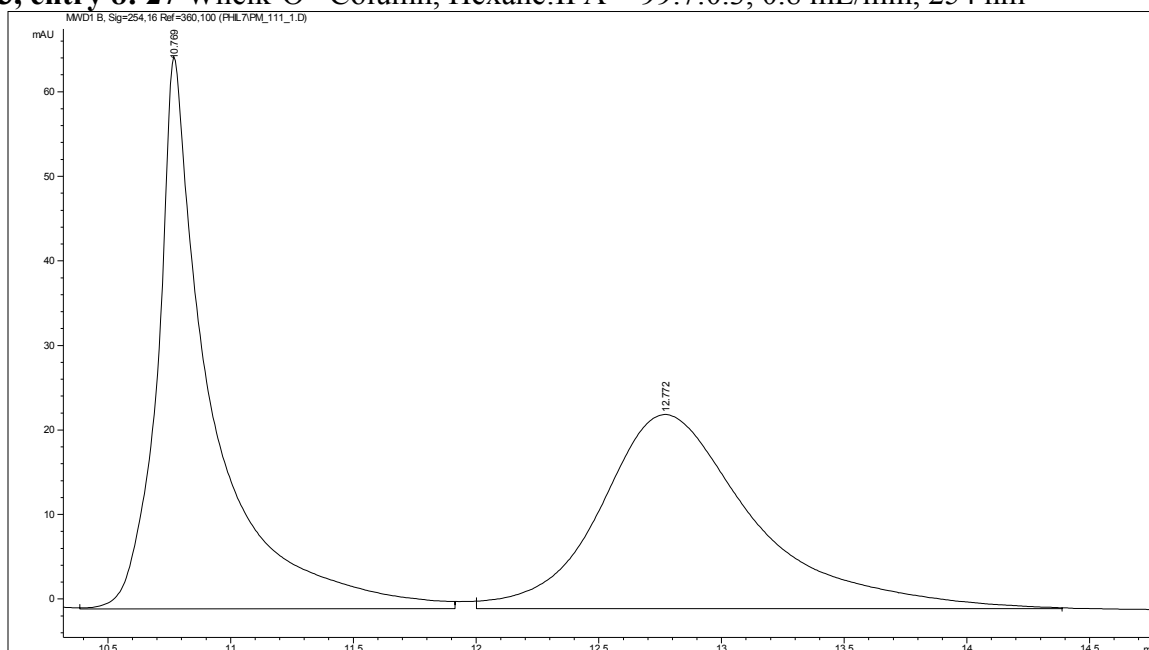
**Table 3, entry 7: 26** Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.5:0.5, 0.8 mL/min, 254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.064	BV	0.6900	3550.48657	75.85816	49.3307
2	34.067	VB	0.7530	3646.83130	70.55642	50.6693

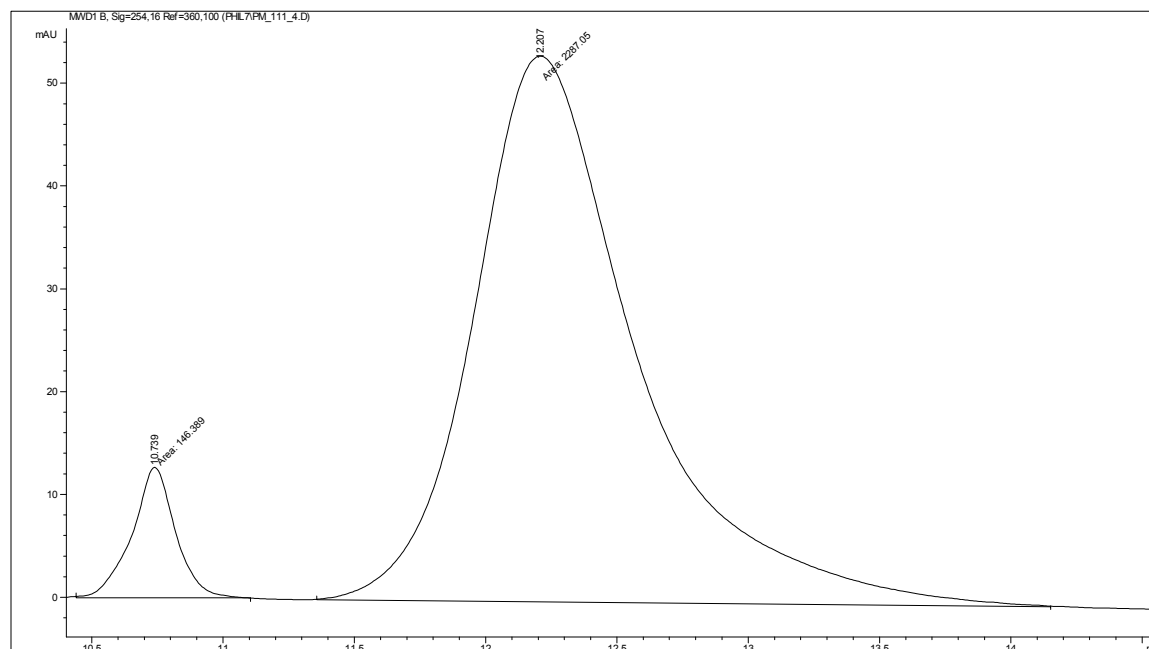
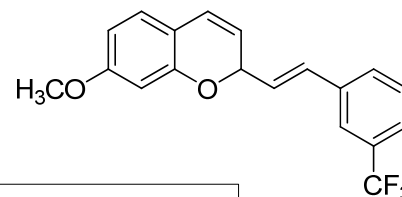


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.784	BV	0.6459	557.15753	11.90659	8.5030
2	34.634	VB	0.7754	5995.35791	111.13667	91.4970

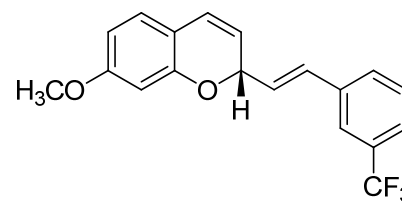


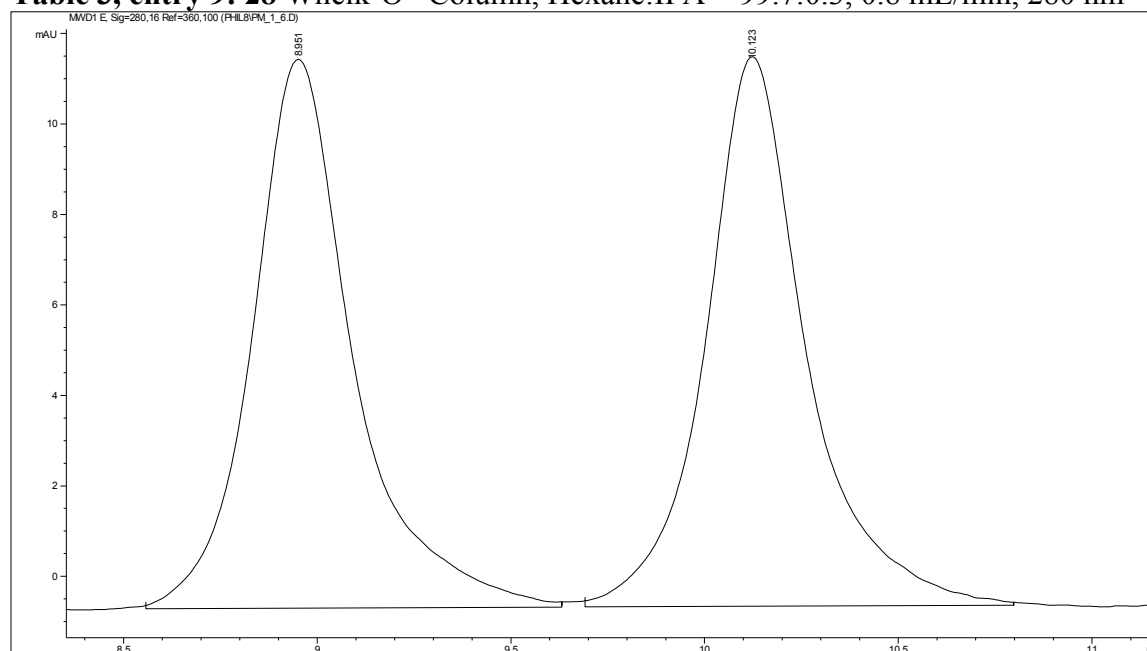
**Table 3, entry 8: 27 Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.7:0.3, 0.8 mL/min, 254 nm**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.769	VB	0.1980	1008.54413	65.36830	50.1769
2	12.772	BB	0.6226	1001.43109	22.97199	49.8231



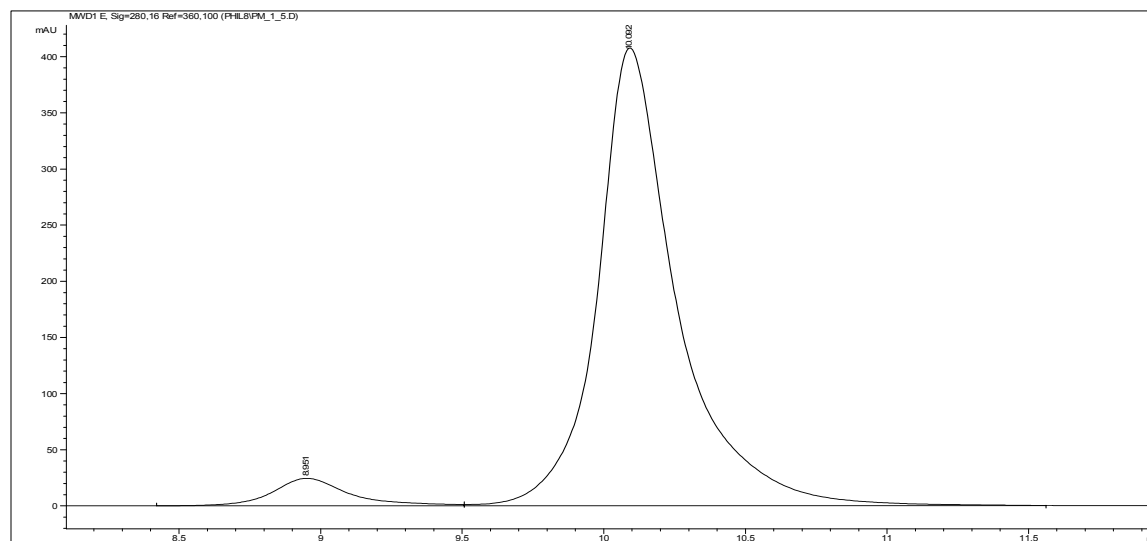
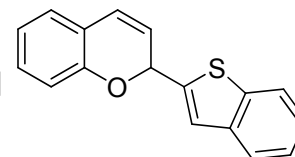
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.739	MM	0.1922	146.38931	12.69446	6.0157
2	12.207	MM	0.7180	2287.05005	53.08805	93.9843



**Table 3, entry 9: 28** Whelk-O<sup>®</sup> Column, Hexane:IPA = 99.7:0.3, 0.8 mL/min, 280 nm

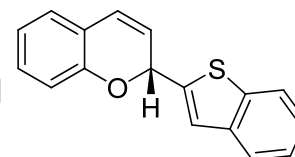
Signal 5: MWD1 E, Sig=280,16 Ref=360,100

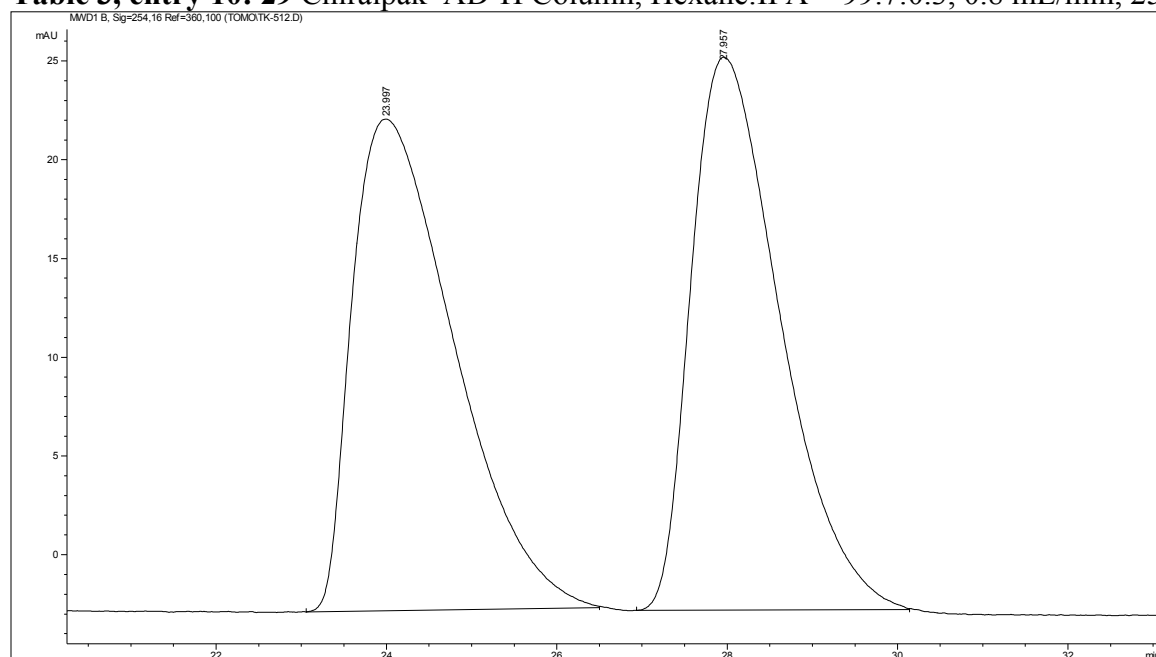
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.951	BB	0.2654	219.86804	12.13613	49.9627
2	10.123	BB	0.2634	220.19601	12.15336	50.0373



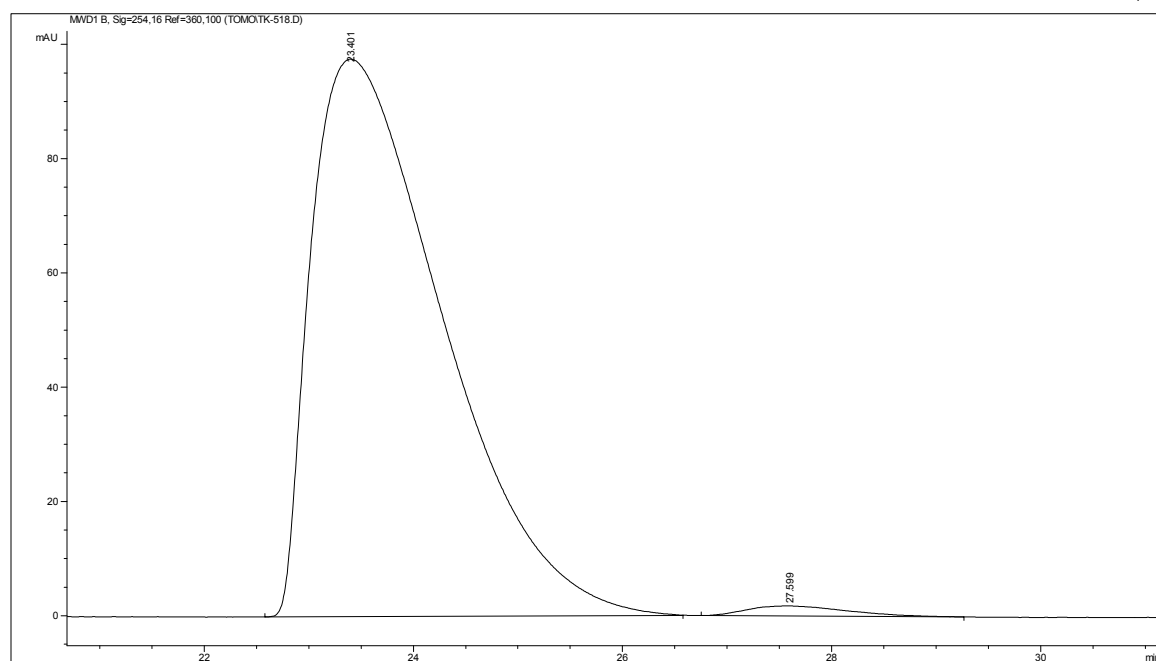
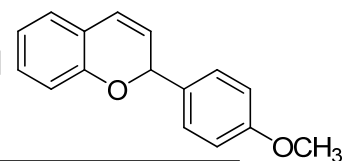
Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.951	PV	0.2751	458.03351	24.38594	5.4397
2	10.092	VB	0.2819	7962.14941	407.56906	94.5603

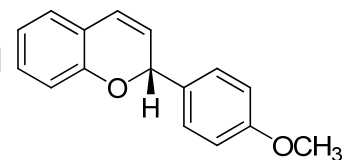


**Table 3, entry 10: 29** Chiralpak® AD-H Column, Hexane:IPA = 99.7:0.3, 0.8 mL/min, 254 nm

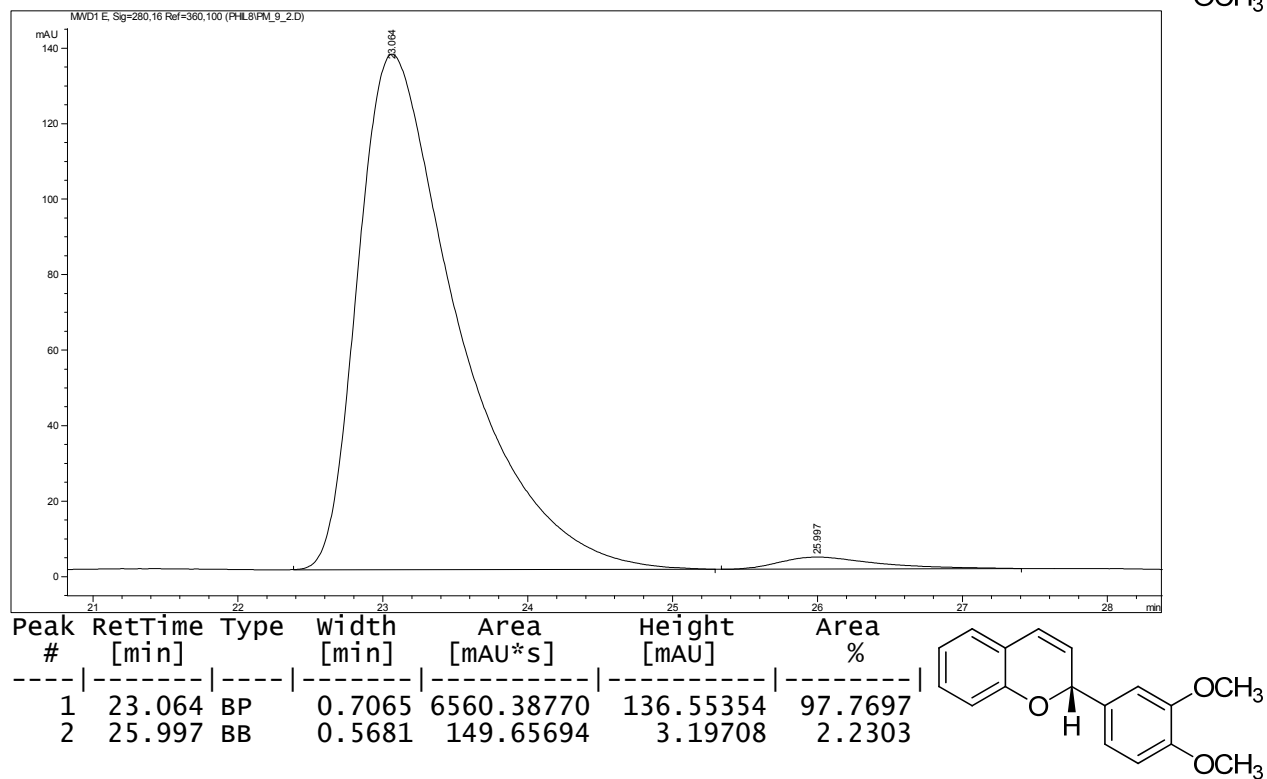
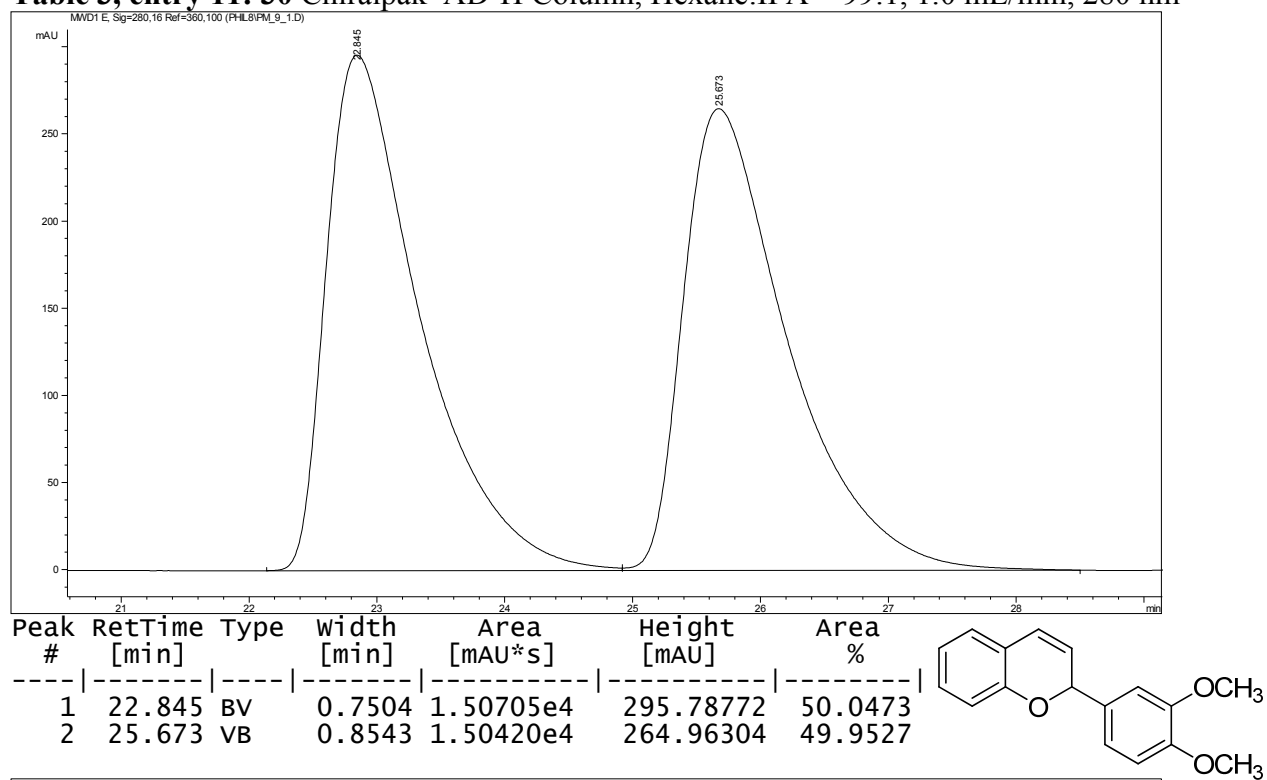
Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.997	PB	0.9844	2070.39111	24.89253	50.4479
2	27.957	BB	1.0352	2033.62891	28.00469	49.5521

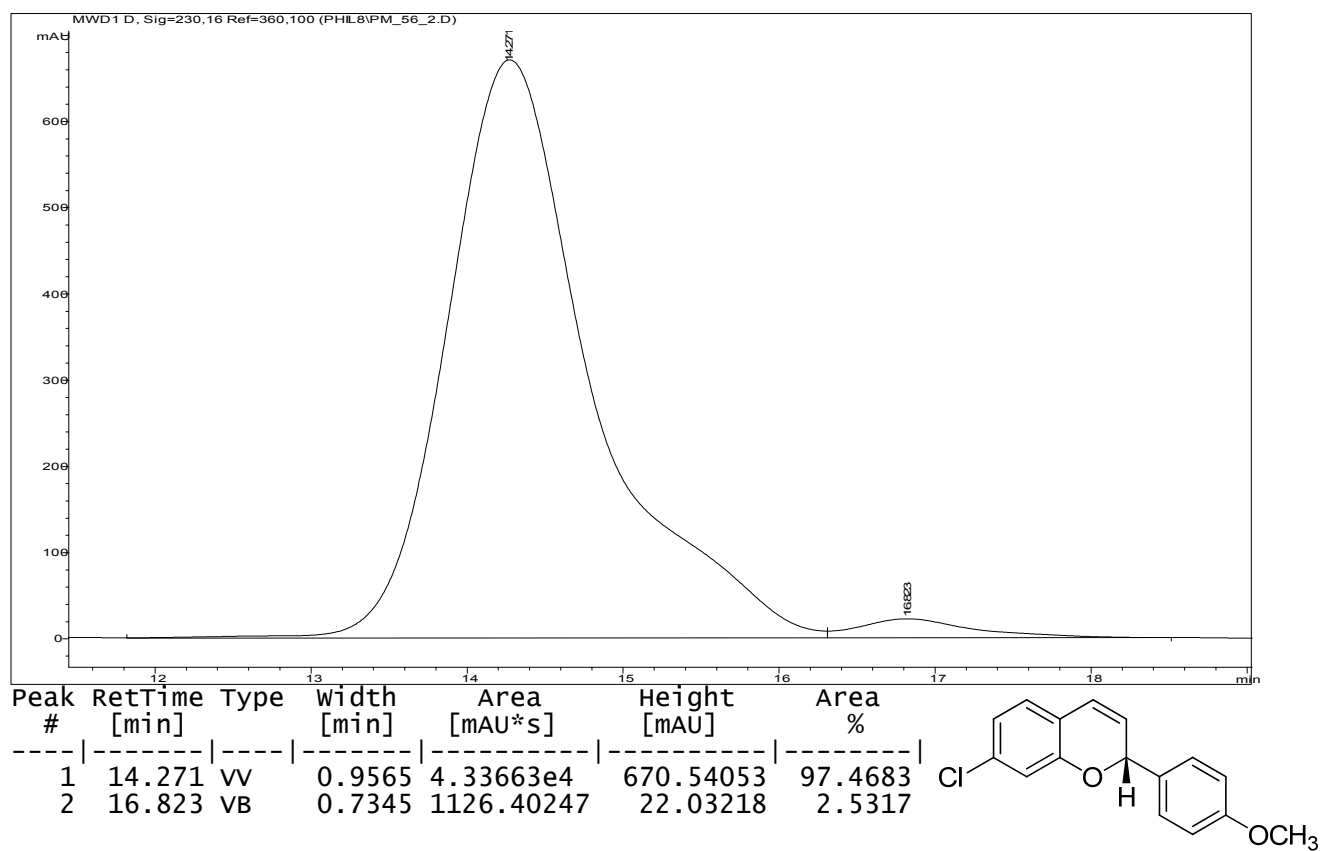
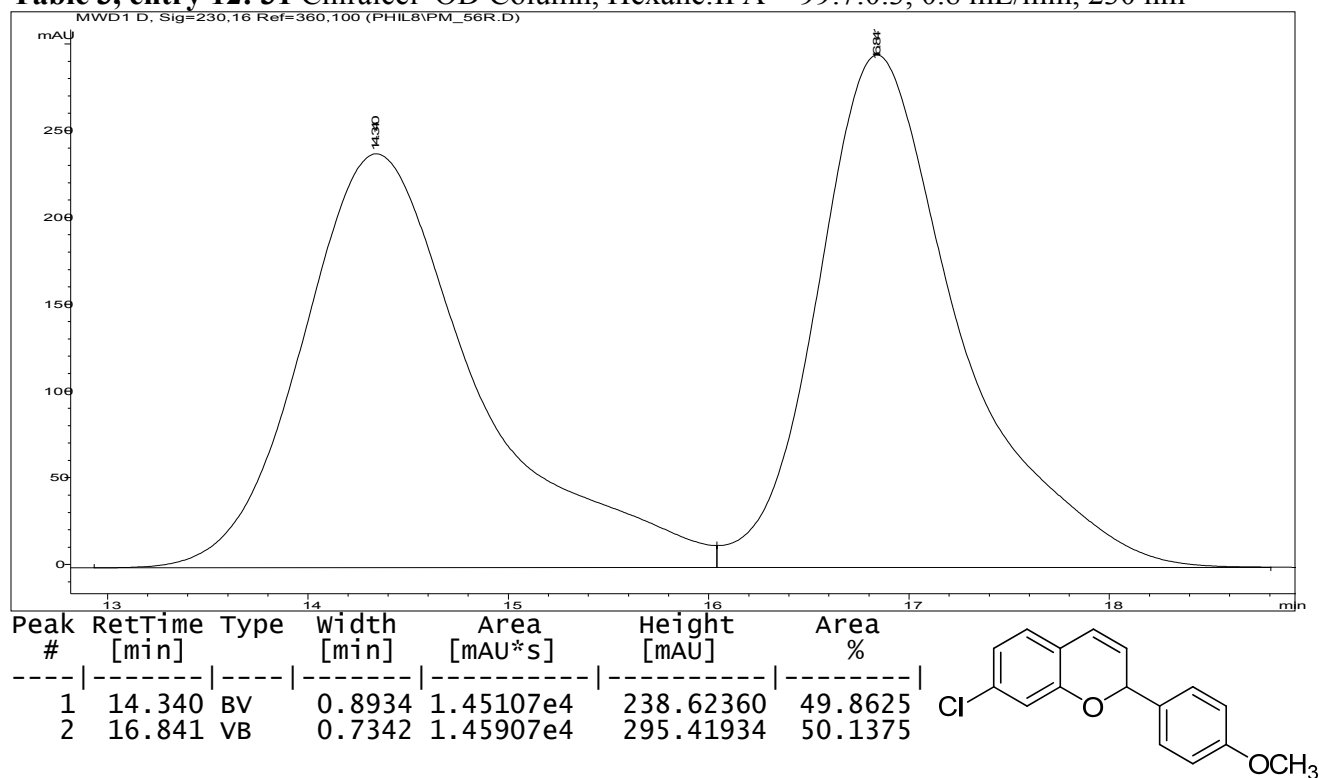


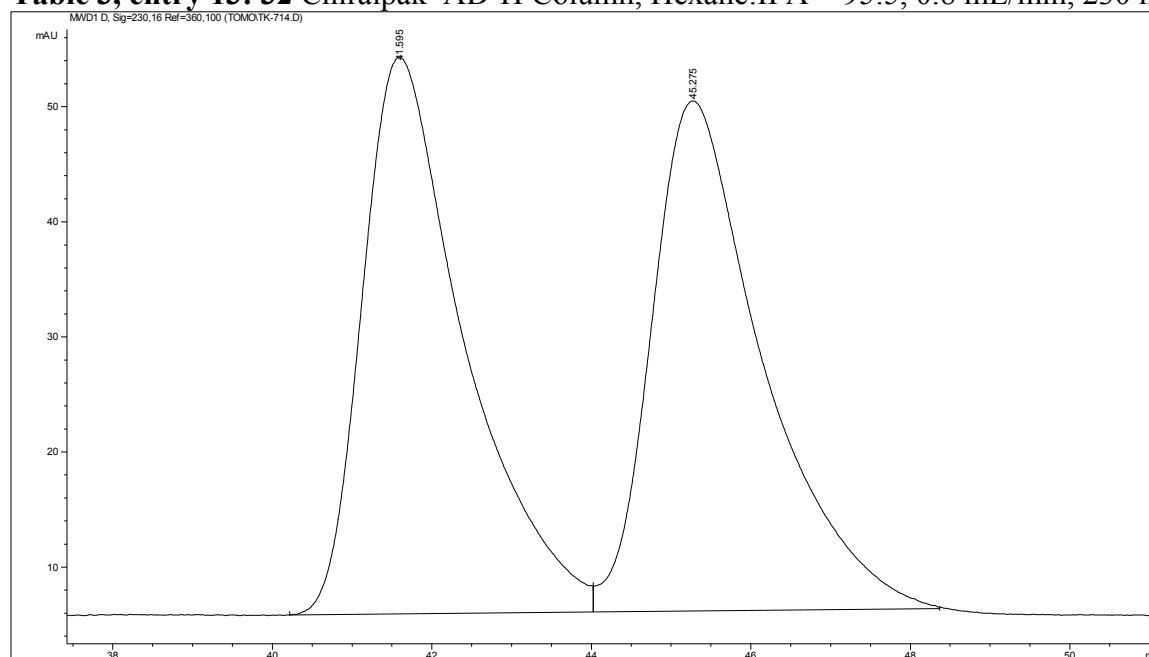
Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.401	PB	1.2793	8544.03125	97.60050	98.6502
2	27.599	PB	0.7848	116.90774	1.76490	1.3498



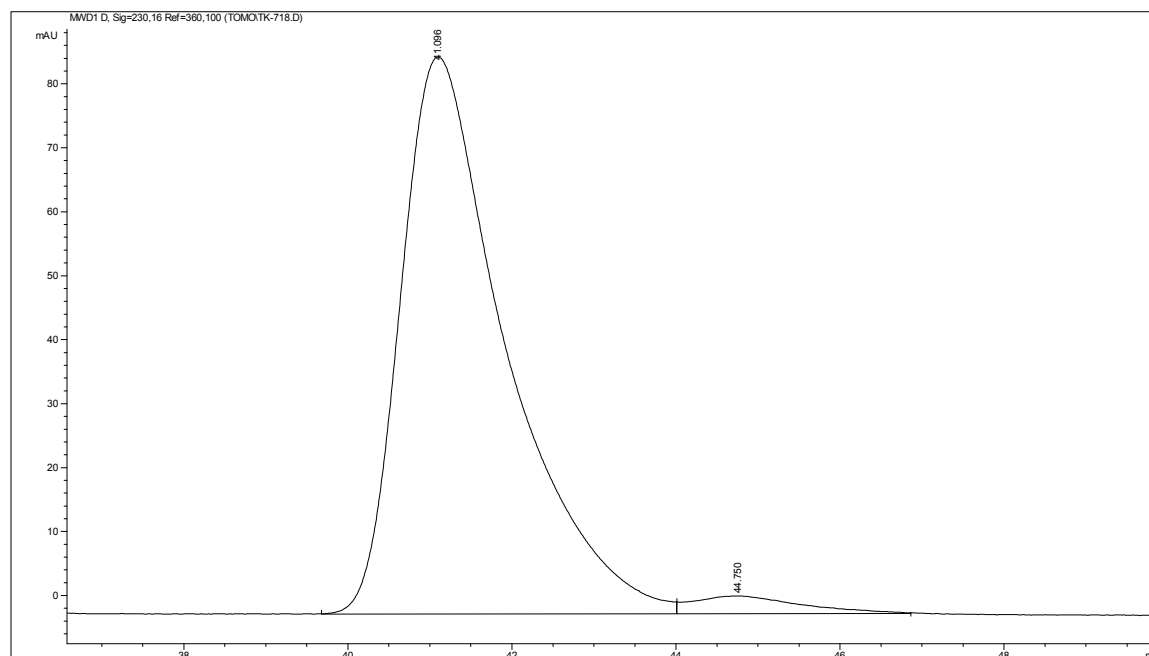
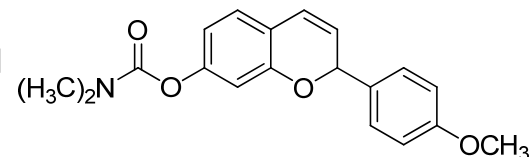


**Table 3, entry 11: 30** Chiralpak® AD-H Column, Hexane:IPA = 99:1, 1.0 mL/min, 280 nm

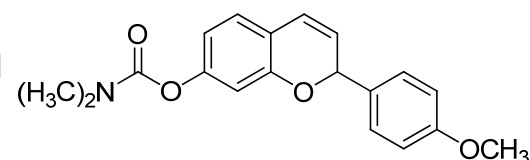
**Table 3, entry 12: 31 Chiralcel<sup>®</sup> OD Column, Hexane:IPA = 99.7:0.3, 0.8 mL/min, 230 nm**

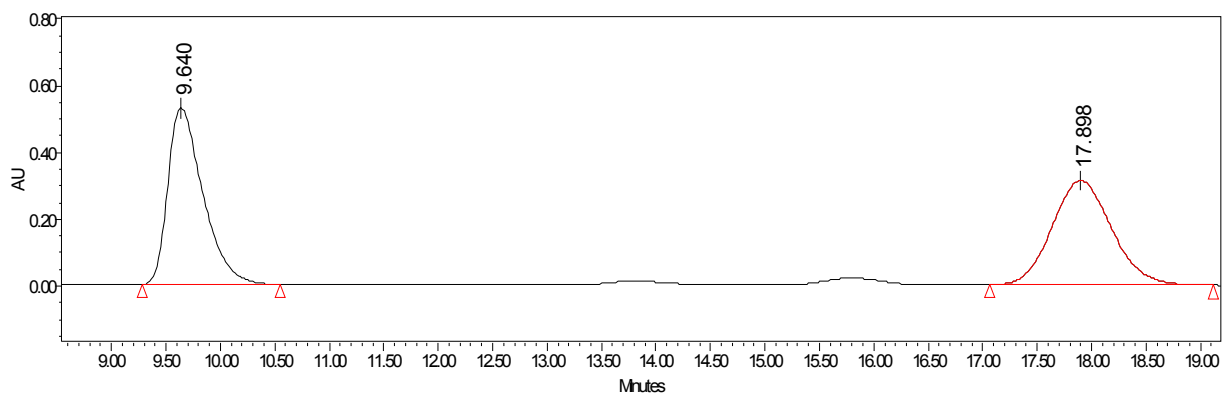
**Table 3, entry 13: 32** Chiralpak® AD-H Column, Hexane:IPA = 95:5, 0.8 mL/min, 230 nm

Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.595	BB	1.1675	4294.73047	48.38936	50.0818
2	45.275	BB	1.2613	4280.70947	44.30300	49.9182

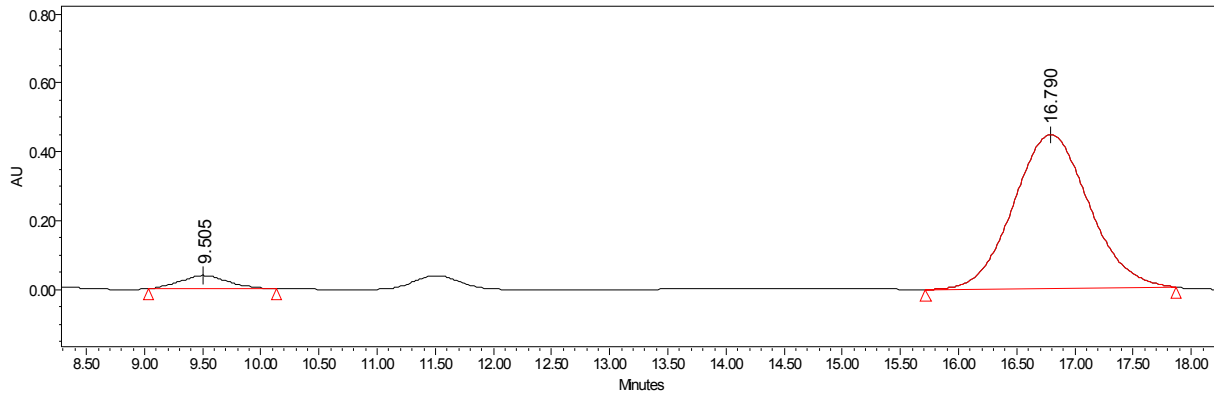
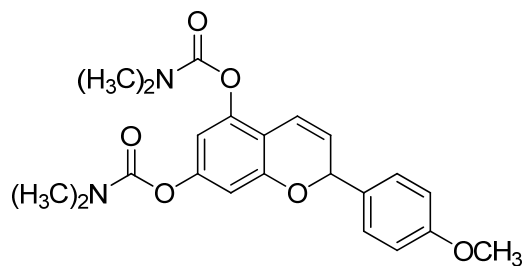


Peak #	RetTime [min]	Type	width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.096	VB	1.2291	7754.62158	87.06683	96.8452
2	44.750	BV	1.0724	252.61452	2.76875	3.1548



**Table 3, entry 14: 33** Chiralpak® AD-H Column, Hexane:IPA = 75:25, 1.0 mL/min, 214 nm

	Name	Retention Time	Area	% Area	Height	Int Type
1		9.640	11825069	49.81	528486	bb
2		17.898	11916289	50.19	312524	bb



	Name	Retention Time	Area	% Area	Height	Int Type
1		9.505	1090166	5.15	38533	bb
2		16.790	20083528	94.85	446610	bb

