

# Ligand-Controlled Selectivity in the Desymmetrization of *meso* Cyclopenten-1,4-diols via Rhodium(I)-Catalyzed Addition of Arylboronic Acids

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## Supporting Information

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**General Experimental Procedures.** Unless otherwise noted, reactions were carried out under argon atmosphere, in flame-dried, single-neck, round bottom flasks fitted with a rubber septum, with magnetic stirring. No experiment was carried out in a glovebox, unless otherwise noted. Air- or water-sensitive liquids and solutions were transferred via syringe or stainless steel canula. Where necessary (so noted), solutions were deoxygenated by successive freeze-pump-thaw cycles ( $\geq$  three iterations). Organic solutions were concentrated by rotary evaporation at 23–40 °C under 20–40 Torr (water vacuum). Analytical thin layer chromatography (TLC) was performed with Silicycle™ normal phase glass plates (0.25 mm, 60-A pore size, 230-400 mesh). Visualization was done under a 254 nm UV light source and generally by immersion in acidic aqueous-ethanolic vanillin solution, or in potassium permanganate (KMnO<sub>4</sub>), followed by heating using a heat gun. Purification of reaction products was generally done by flash chromatography with 230-400 mesh silica gel, as described by Still *et al.*<sup>1</sup>

**Materials.** [Rh(cod)OH]<sub>2</sub> was conveniently prepared from [Rh(cod)Cl]<sub>2</sub> by a literature procedure.<sup>2</sup> Supplies of chiral Josiphos, the BIPHEP and P-Phos family of ligands were generously provided by the manufacturers. Other chiral phosphine ligands were purchased from commercial sources. Unless otherwise indicated, boronic acids were purchased from commercial sources and used without further purification. Tetrahydrofuran, 1,4-dioxane were purified by distillation under N<sub>2</sub> from Na/benzophenone immediately prior to use. Toluene and benzene were purified by distillation under N<sub>2</sub> from CaH<sub>2</sub> prior to use. Ether and

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<sup>1</sup> Still, W. C.; Kahn, M.; Mitra, A. J. *Org. Chem.* **1978**, *43*, 2923.

<sup>2</sup> Uson, R.; Oro, L.A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 129.

dichloromethane were purified by the method of Pangborn *et al.*<sup>3</sup> Hexanes and ethyl acetate for chromatographic purifications were used without further purification from the commercial sources. *Cis*-2-cyclopentene-1,4-diol **1** was prepared by a literature procedure and characterization data was fully consistent with that reported.<sup>4,5</sup> *Meso* dicarbonates **1a**, **1y**, and **1z** were prepared following literature procedures.<sup>6,7</sup> Characterization data for **2a–2p**, **3a**, **3b**, **3l**, **3m**, **4a–4k**, **4n–4p**, and **5a** was reported previously.<sup>8,12</sup>

**Instrumentation.** Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) spectra and carbon nuclear magnetic resonance spectra (<sup>13</sup>C NMR) were recorded at 23 °C using a 400 MHz NMR spectrometer equipped with a Nalorac4N-400 probe, a 400 MHz NMR spectrometer equipped with ATB8123-400 probe, or a 400 MHz NMR spectrometer equipped with BBFO-ATM probe. Recorded shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual deuterium in the NMR solvents (CHCl<sub>3</sub>: δ 7.26, CHDCl<sub>2</sub>: δ 5.29, C<sub>6</sub>HD<sub>5</sub>: δ 7.15, CD<sub>2</sub>HOD: δ 3.30). Chemical shifts for carbon resonances are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl<sub>3</sub>: δ 77.0, CH<sub>2</sub>Cl<sub>2</sub>: δ 53.8, C<sub>6</sub>D<sub>6</sub>: δ 128.0, CD<sub>3</sub>OD: δ 49.2). Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintuplet, sx = sextet, sp = septuplet, m = multiplet, br = broad), and coupling constant (*J*, Hz). Infrared (IR) spectra were obtained using a FT-IR spectrometer as a neat film on a NaCl plate. Data is presented as follows: frequency of absorption (cm<sup>-1</sup>), intensity of absorption (s = strong, m = medium, w = weak, br = broad). High resolution mass spectra were obtained from a SI2 Micromass 70S-250 mass spectrometer (EI) or an ABI/Sciex Qstar mass spectrometer (ESI). Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Optical rotations were measured in a 10.0 cm cell with a Rudolph Autopol IV polarimeter digital polarimeter equipped with a sodium lamp source (589 nm), and are reported as follows: [α]<sub>D</sub><sup>T</sup> °C (c = g/100 mL, solvent). The 500 W flood lamps used in the substrate preparation were bought from a local hardware store, and UV filters were removed.

**Determination of the Enantiomeric Excesses by HPLC Analysis.** The enantiomeric excess (ee) of substituted products was determined after hydrolysis of the carbonate to the parent alcohols, followed by HPLC analysis of the crude reaction mixture (see following section for details). Unless otherwise noted, enantiomeric excesses of the deprotected products were determined using a OD-H column (fitted with a 1.0 cm Chiralcel OD-H guard column), flow rate 1.0 mL/min, 26°C, injection 5.0 uL of a ~1.5 mg/mL solution, typically using a gradient of *i*-PrOH:hexane solvent mixture: 2%, 0 to 10 min; 2–5% gradient, 10 to 20 min; 5–10% gradient, 20 to 25 min; 10%, 25–30 min.

<sup>3</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

<sup>4</sup> Alternatively, diol **1** is also commercial from a common suppliers.

<sup>5</sup> Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

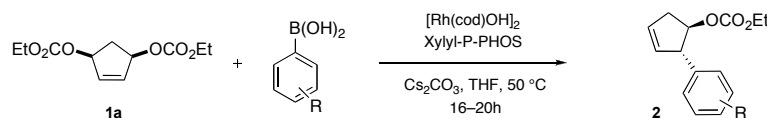
<sup>6</sup> Arnau, N.; Cortés, J.; Moreno-Mañas, M.; Pleixats, R.; Villaroya, M. J. *Heterocyclic Chem.* **1997**, *34*, 233.

<sup>7</sup> Yu, B.; Menard, F.; Isono, N.; Lautens, M. *Synthesis* **2009**, 853.

<sup>8</sup> Menard, F.; Chapman, T. M.; Dockendorff, C. J.; Lautens, M. *Org. Lett.* **2006**, *8*, 4569.

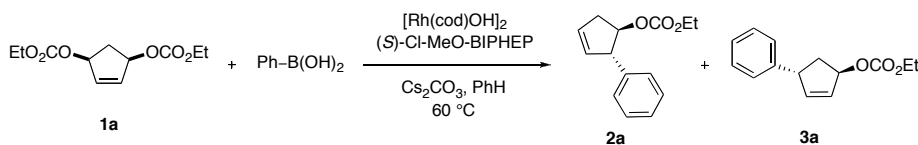
## EXPERIMENTAL PROCEDURES

### PROCEDURE A: Desymmetrization of *cis*-cyclopent-2-ene-1,4-diethyl dicarbonate by a Rh-catalyzed asymmetric allylic substitution with Xylyl-P-PHOS.



**Typical preparation of the 1,2-regioisomeric products 2:** To a 1 dram vial equipped with a magnetic stir bar was added  $[\text{Rh}(\text{cod})\text{OH}]_2$  (3.7 mg, 0.0082 mmol), (*S*)-Xyl-P-PHOS (14.9 mg, 0.020 mmol), and  $\text{Cs}_2\text{CO}_3$  (53 mg, 0.164 mmol). The vial was sealed and flushed with argon. Distilled THF (0.8 mL) was added and the mixture was stirred for 30 min on a 60 °C oil bath. Dicarbonate **1a** (40 mg, 0.164 mmol) and phenylboronic acid (40 mg, 0.32 mmol) were added together as a solution in distilled THF (0.8 mL). The reaction mixture was heated on a 60 °C oil bath. After 16 h, THF (5 mL) and hexanes (5 mL) were added to the reaction mixture and it was concentrated with silica gel, then applied to the top of a column of silica gel and purified by column chromatography (5 to 20% EtOAc/hexane as elution gradient). An inseparable mixture of the monocarbonates **2a** and **3a** was recovered as a colourless oil, 33 mg (87%).  $^1\text{H}$  NMR analysis revealed an isomer ratio of 92:8 favoring the 1,2-product **2a**. The enantiomeric excess was determined on the deprotected alcohols (see *Procedure C*).

### PROCEDURE B: Desymmetrization of *cis*-cyclopent-2-ene-1,4-diethyl dicarbonate by a Rh-catalyzed asymmetric allylic substitution with Cl-MeO-BIPHEP.

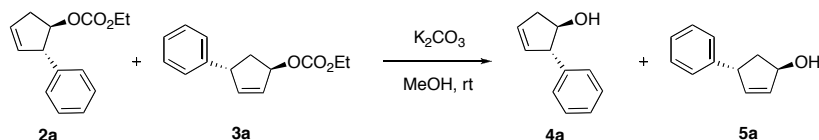


**Typical preparation favoring the 1,4-regioisomeric products 3:** In a 13x135 mm screw-cap tube equipped with a magnetic stir bar were weighed  $[\text{Rh}(\text{cod})\text{OH}]_2$  (7.4 mg, 0.0164 mmol) and (*S*)-Cl-MeO-BIPHEP (25.6 mg, 0.039 mmol). The tube was equipped with a screw-cap septum and flushed with argon, then benzene<sup>9</sup> (0.30 mL) was added and the mixture was stirred on a 60 °C oil bath for 15 min; the yellow solution turned to dark orange. Meanwhile, a solution of *cis*-2-cyclopentene-1,4-diethyl dicarbonate **1a** (80 mg, 0.32 mmol) in 0.40 mL benzene was prepared. The substrate solution was cannulated to the premixed complex solution at 60 °C; a slight darkening of the reddish solution occurred. Followed by phenylboronic acid (80 mg, 0.64 mmol) and  $\text{Cs}_2\text{CO}_3$  (80 mg, 0.26 mmol) added together as solids, by rapidly opening the screw cap (by taking the tube out of the oil bath, unscrewing the septum and quick addition of solids while minimizing the vessel exposition to air; the long tube provides a thick inert atmosphere blanket over the reaction mixture upon solids addition). The reaction vessel was flushed with Ar at r.t. for 2-5 min, then put back to heat at 60 °C for 16 h. Reaction showed near full conversion by TLC (15% EtOAc/Hex; UV and vanillin stain;  $R_f$  **1a** 0.35,  $R_f$  **2a+3a** 0.62). To the dark brown reaction mixture was added 5 mL  $\text{Et}_2\text{O}$  (heavy ppt) and 10 mL saturated  $\text{NH}_4\text{Cl}$  aqueous solution. The decanted aqueous layer was extracted with 3x20 mL  $\text{Et}_2\text{O}$ ; the combined organic phases were dried with brine and  $\text{MgSO}_4$ , then filtered, and concentrated under reduced pressure. The crude residue was applied to the top of a column of silica gel and purified by column chromatography (5 to 25% EtOAc/hexane as elution gradient). An inseparable mixture of the monocarbonates **2a** and **3a** was recovered as a colourless oil, 62 mg (82%).  $^1\text{H}$  NMR analysis

<sup>9</sup> Alternatively, toluene or dioxane can be used to obtain similar yields, however, the regioselectivity will not be optimal for the formation of **5**.

revealed a **2** : **3** ratio of 1 : 2.8. The enantiomeric excess was determined on the deprotected alcohols (see *Procedure C*). Racemic products were obtained following the same procedure with the achiral BIPHEP ligand.

#### PROCEDURE C: General deprotection of carbonates.



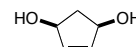
The combined monocarbonates isomers **2** and **3** were dissolved in MeOH (0.02 M) and  $K_2CO_3$  (10–14 equiv) was added. The white suspension was stirred at rt until complete conversion (usually < 3 h).<sup>10</sup> One volume of  $NH_4Cl$  saturated aqueous solution was added and extracted three times with  $Et_2O$ . The combined organic layers were dried over  $MgSO_4$ , filtered and concentrated under reduced pressure to yield a mixture of the alcohols **4** and **5**. The 1,2- and 1,4-regioisomers **4** and **5** were separated and purified by column chromatography on silica gel (10–25–40% gradient of  $EtOAc$ /hexane). The enantioenrichment of each regioisomers was measured on the isolated products, and compared to racemic samples.

*Note 1.* (*S*)-biarylphosphines ligands (BINAP, P-PHOS, and Cl-MeO-BIPHEP analogs) all lead to the (–) enantiomers, which have the absolute stereochemistry represented in this paper. The use of the (*R*)-biarylphosphines yield the (+) enantiomers, having the opposite stereochemistry of that represented. We arbitrarily opted to represent the (*1R*, *2S*)-stereochemistry for consistency and to avoid unnecessary complications for the reader.

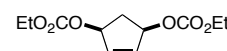
*Note 2.* Racemic products were obtained following the same procedure with the achiral BIPHEP.

## CHARACTERIZATION DATA

**Cyclopent-4-ene-1,3-diol (**1**).** Modified from a literature procedure,<sup>5</sup> dry MeOH (1.84 L) was placed in a 3L 3-necked roundbottom flask fitted with a cold finger condenser. Thiourea (14 g, 184 mmol) and rose bengal (367.5 mg) were added to the reaction and the suspension was cooled down to 5 °C.  $O_2$  was bubbled through the solution, then the cold finger was filled with acetone and dry ice. Freshly distilled cyclopentadiene (20 mL, 244 mmol) was kept on ice, until the addition. Half of the cyclopentadiene was added to the flask under vigorous stirring, and irradiation was started immediately using two 500 W flood lamps. After 30 min, the remainder of the cyclopentadiene was added. After 4 h,  $O_2$  bubbling and irradiation were stopped. On this scale, we found the distillation procedure reported to be highly inconvenient as the product crystallized on all surfaces; instead, the solvent was evaporated under reduced pressure and the remaining solid was dissolved and recrystallized sequentially in MeOH, THF and  $Et_2O$ , until the  $^1H$  NMR analysis of the filtrate looked clean. At that point, the product was a dark red paste (20.8 g, 85%), which was used as is for the next step, where the less polar dicarbonate is much easier to purify.  $^1H$  NMR (300 MHz,  $DMSO-d_6$ )  $\delta$ : 5.74 (s, 2H), 4.84 (dd, 2H,  $J = 7.8, 2.0$  Hz), 2.97–2.86 (m, 1H), 1.28–1.20 (m, 1H) ppm.



**Cyclopent-4-ene-1,3-diyl diethyl dicarbonate (**1a**).** In a 1L 3-necked round-bottom flask, half of the crude diol **1** (5 g, 50 mmol) was poured in and suspended in dry DCM (50 mL). Half of the pyridine (210 mmol, 17 mL) was added to the flask. The remaining of the diol (50 mmol, 5 g) was added, along with more DCM (450 mL) and pyridine (17 mL, 210 mmol). The reaction was allowed to cool down to 5 °C, under a  $N_2$  atmosphere. Ethylchloroformate (30 mL, 315 mmol) was added slowly, keeping the temperature constant between 5–10

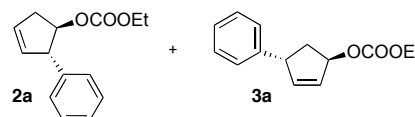


<sup>10</sup> It was verified that longer reaction times did not affect the ee (up to 48 h at rt).

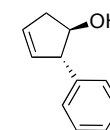
°C. The reaction was allowed to warm up to room temperature and stirred until complete by TLC analysis. The reaction was washed with 1N aqueous HCl (4x150 mL), and the aqueous layers were extracted with Et<sub>2</sub>O (2x150 mL). The combined organic layers were washed with brine, dried with MgSO<sub>4</sub>, filtered, and the solvent was evaporated under reduced pressure to give a yellow oil. The crude oil was loaded on a silica column and eluted with 10% EtOAc/Hex to give a clear, colourless oil (14 g, 55%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.16 (d, 2H, *J* = 0.5 Hz), 5.46 (ddd, 2H, *J* = 7.5, 4.0, 0.7 Hz), 4.21 (q, 4H, *J* = 7.0 Hz), 2.96 (quintet, 1H, *J* = 7.5 Hz), 1.93 (dt, 1H, *J* = 15.0, 4.0 Hz), 1.31 (t, 6H, *J* = 7.0 Hz) ppm.

**Cyclopent-4-ene-1,3-diyl diisopropyl dicarbonate (3b).**<sup>11</sup> White solid (2.4 g, 80%); mp 59-60 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), d: 6.14 (s, 2H), 5.43 (dd, 2H, *J* = 7.5, 4.0 Hz), 4.86 (sp, 2H, *J* = 6.2 Hz), 2.93 (dt, 1H, *J* = 15.0, 7.5 Hz), 1.90 (dt, 1H, *J* = 14.9, 4.0 Hz), 1.29 (dt, 12H, *J* = 6.2 Hz).

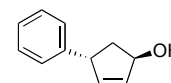
**(1*R*,2*S*)-trans-2-phenylcyclopent-3-enyl-ethylcarbonate (2a) and (1*R*,4*R*)-trans-4-phenylcyclopent-2-enyl-ethylcarbonate (3a).** Prepared according to the general procedure described above (using (*S*)-Xylyl-P-PHOS). The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2a** and **3a** were obtained as a colourless oil in 87% yield (33.0 mg), showing a 18:1 ratio of **2**:**3** by <sup>1</sup>H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2a:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.34-7.21 (5H, m), 5.94 (1H, ddd, *J* = 5.9, 4.1, 2.0 Hz), 5.82 (1H, ddd, *J* = 5.8, 4.2, 2.0 Hz), 5.04 (1H, dt, *J* = 6.6, 2.6 Hz), 4.20 (2H, q, *J* = 7.1 Hz), 4.00 (1H, br. s), 2.92 (1H, dddd, *J* = 17.8, 6.3, 4.0, 2.3 Hz), 2.48 (1H, dddd, *J* = 17.8, 7.9, 5.1, 2.4 Hz), 1.31 (3H, t, *J* = 7.1 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.1, 141.3, 132.0, 129.6, 128.8, 127.7, 127.1, 85.2, 64.1, 57.8, 39.0, 14.5. IR (NaCl, neat film): 3061, 3030, 2983, 2850, 1743, 1451, 1374, 1261, 1170, 1105, 1012 cm<sup>-1</sup>. **Minor regioisomer 3a:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.37-7.23 (5H, m), 6.12 (1H, dd, *J* = 5.6, 2.0 Hz), 6.01 (1H, dt, *J* = 5.5, 2.3 Hz), 5.70 (1H, ddd, *J* = 7.1, 4.1, 2.0 Hz), 4.13 (2H, q, *J* = 7.1 Hz), 4.09-4.05 (1H, m), 2.46-2.36 (1H, m), 2.06 (1H, ddd, *J* = 13.0, 7.1, 5.9 Hz), 1.25 (3H, t, *J* = 7.1 Hz).



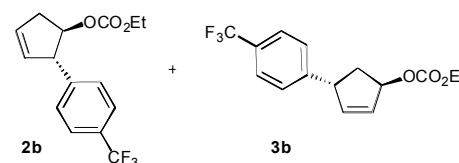
**(1*R*,2*S*)-trans-2-phenylcyclopent-3-enol (4a).** Deprotected and isolated according to *Procedure C*. Colourless oil. The characterization data was fully concordant with that already reported in the literature.<sup>12</sup> [ $\alpha$ ]<sub>D</sub><sup>26.7</sup><sub>589</sub> = -228 (*c* 1.60, CHCl<sub>3</sub>, for 92% ee). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.31-7.14 (5H, m), 5.87 (1H, ddt, *J* = 6.2, 4.4, 2.2 Hz), 5.75 (1H, ddd, *J* = 6.1, 4.2, 2.1 Hz), 4.29-4.25 (1H, m), 3.74 (1H, ddd, *J* = 5.7, 3.7, 1.8 Hz), 2.78 (1H, dddd, *J* = 16.9, 6.3, 3.9, 1.9 Hz), 2.35 (1H, dddd, *J* = 16.9, 6.1, 3.9, 1.8 Hz), 1.84 (1H, br. s, alcohol).



**(1*R*,4*R*)-trans-4-phenylcyclopent-2-enol (5a).** Colourless oil. The characterization data was fully concordant with that already reported in the literature.<sup>12b</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.25-7.05 (5H, m), 6.00-5.94 (2H, m), 5.00-4.96 (1H, m), 4.08 (1H, ddt, *J* = 5.9, 3.5, 1.9 Hz), 2.22 (1H, ddd, *J* = 14.0, 8.0, 2.7 Hz), 2.03 (1H, ddd, *J* = 14.0, 6.9, 5.5 Hz), 1.47 (1H, br. s).



**(1*R*,2*S*)-trans-2-(4'-Trifluoromethylphenyl)-cyclopent-3-enyl ethyl carbonate (2b) and (1*R*,4*R*)-trans-4-(4'-Trifluoromethylphenyl)-cyclopent-2-enyl ethyl carbonate (3b).** Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 81% yield



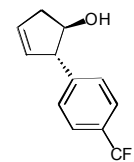
<sup>11</sup> Mori, M.; Nukui, S.; Shibasaki, M. *Chem. Letters* **1991**, 10, 1797.

<sup>12</sup> (a) Tueting, D. R.; Echavarren, A. M.; Stille, J. K. *Tetrahedron* **1989**, 45, 979. (b) Kobayashi, Y.; Muruges, M. G.; Nakano, M.; Takahisa, E.; Usmani, S. B.; Aina, T. *J. Org. Chem.* **2002**, 67, 7110.

(80 mg), showing a 1:2.8 ratio of **2:3** by  $^1\text{H}$  NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 3b*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55 (2H, d,  $J$  = 8.2 Hz), 7.24 (2H, d,  $J$  = 8.7 Hz), 6.19–6.11 (2H, m), 5.76 (1H, ddd,  $J$  = 9.1, 4.0, 2.0 Hz), 4.25–4.16 (1H, m), 4.21 (2H, q,  $J$  = 7.1 Hz), 2.54–2.46 (1H, m), 2.11 (2H, ddd,  $J$  = 14.6, 7.1, 5.6 Hz), 1.31 (3H, t,  $J$  = 7.1 Hz). *Minor regioisomer 2b*: spectroscopic data was concordant with that we reported previously.<sup>8</sup>

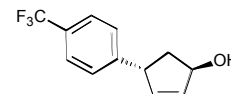
**(1*R*,2*S*)-trans-2-(4'-Trifluoromethylphenyl)-cyclopent-3-enol (4b).**

Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_{\text{D}}^{28.7}$  = +165 ( $c$  0.80,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 96.4:3.6, as determined by HPLC analysis (Chiralcel OD-H;  $t_{\text{R}}$  = 14.9 min (+),  $t_{\text{R}}$  = 16.6 min (-)).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.56 (2H, d,  $J$  = 8.2 Hz), 7.30 (2H, d,  $J$  = 8.1 Hz), 5.95 (1H, ddd,  $J$  = 5.9, 4.3, 2.2 Hz), 5.77 (1H, ddd,  $J$  = 6.0, 4.2, 2.1 Hz), 4.28 (1H, dt,  $J$  = 6.9, 4.3 Hz), 3.85–3.82 (1H, m), 2.82 (1H, dddd,  $J$  = 17.0, 6.8, 3.9, 2.0 Hz), 2.40 (1H, dddd,  $J$  = 17.0, 6.1, 4.3, 1.9 Hz), 1.83 (1H, br. s, alcohol).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.7, 131.4, 130.4, 127.7, 125.5 (q,  $J$  = 3.8 Hz,  $\text{CF}_3$ ), 122.9, 80.8, 60.4, 41.5.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ ):  $\delta$  -63.1 (s, 3F). IR (NaCl, neat film): 3324 (br.), 3061, 2922, 2850, 1618, 1418, 1328, 1163, 1126, 1070, 1018  $\text{cm}^{-1}$ . MS  $m/z$  (rel. intensity): 228 ( $\text{M}^+$ , 98), 210 (30), 172 (100), 159 (52), 131 (20), 115 (19). HRMS (ESI) $^+$ : Calc'd for  $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}$  [ $\text{M}^+$ ]: 228.0762; found = 228.0761.



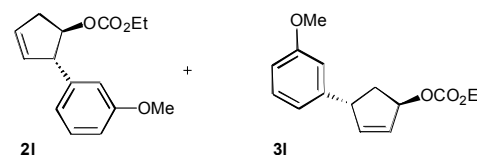
**(1*R*,4*R*)-trans-4-(4'-Trifluoromethylphenyl)-cyclopent-2-enol (5b).**

Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_{\text{D}}^{28.9}$  = +210 ( $c$  1.35,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 99.5:0.5, as determined by HPLC analysis (Chiralcel OD-H;  $t_{\text{R}}$  = 19.1 min (+),  $t_{\text{R}}$  = 20.6 min (-)).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (2H, d,  $J$  = 8.0 Hz), 7.24 (2H, d,  $J$  = 8.0 Hz), 6.09 (1H, dd,  $J$  = 5.7, 2.1 Hz), 6.03 (1H, ddd,  $J$  = 7.6, 2.2, 0.6 Hz), 5.09–5.03 (1H, m), 4.29–4.18 (1H, m), 2.32 (1H, ddd,  $J$  = 14.3, 8.0, 2.7 Hz), 2.08 (1H, ddd,  $J$  = 14.1, 6.9, 5.5 Hz), 1.57 (1H, br.s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.1 (d,  $J$  = 1.5 Hz), 138.3 (2), 135.1 (2), 128.7, 127.6 (2), 125.7 (q,  $J$  = 3.7 Hz,  $\text{CF}_3$ ), 77.5, 49.9, 44.1.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.8 (s, 3F). IR (NaCl, neat film): 3332 (br), 3057, 2967, 2936, 1619, 1416, 1254, 1163, 1122, 1068, 1017, 832, 790  $\text{cm}^{-1}$ . MS ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 228.1 ( $\text{M}^+$ , 8), 210 (100), 183 (12), 141 (89), 139 (16), 115 (45), 63 (17). HRMS ( $\text{EI}^+$ ): Calc'd for  $\text{C}_{12}\text{H}_{11}\text{OF}_3$  [ $\text{M}^+$ ]: 228.0762; found = 228.0765.

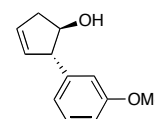


**(1*R*,2*S*)-trans-2-(3'-Methoxyphenyl)-cyclopent-3-enyl ethyl carbonate (2i) and (1*R*,4*R*)-trans-4-(3'-Methoxyphenyl)-cyclopent-2-enyl ethyl carbonate (3i).**

Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 80% yield (69 mg), showing a 1:1.8 ratio of **2:3** by  $^1\text{H}$  NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 3i*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.80–6.65 (3H, m), 7.31–7.20 (1H, m), 6.18 (1H, dd,  $J$  = 5.6, 1.9 Hz), 6.10–6.05 (1H, m), 5.74 (1H, dd,  $J$  = 7.2, 5.2, 2.6 Hz), 4.20 (2H, q,  $J$  = 7.2 Hz), 4.16–3.98 (1H, m), 3.79 (3H, s), 2.47–2.42 (1H, m), 2.13 (1H, ddd,  $J$  = 13.0, 7.0, 5.9 Hz), 1.31 (3H, t,  $J$  = 7.1 Hz). *Minor regioisomer 2i*: concordant to our previous report.<sup>8</sup>

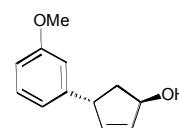


**(1*R*,2*S*)-trans-2-(3'-Methoxyphenyl)-cyclopent-3-enol (4i).** Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_{\text{D}}^{28.2}$  = +160 ( $c$  1.00,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 94.6:5.4, as determined by HPLC analysis (Chiralcel OD-H; 225 nm;  $t_{\text{R}}$  = 23.4 min (+),  $t_{\text{R}}$  = 28.6 min (-)). The characterization data was fully concordant with the literature.<sup>8</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.13 (1H, t,  $J$  = 7.4), 6.70–6.62 (3H, m), 5.80 (1H, ddd,  $J$  = 6.0, 4.4, 2.2 Hz), 5.67 (1H, ddd,  $J$  = 6.1, 4.1, 2.1 Hz), 4.18 (1H, dt,  $J$  = 6.7, 4.2 Hz), 3.70 (3H, s), 3.64 (1H, sp,  $J$  = 1.9 Hz), 2.70 (1H, dddd,  $J$  = 16.9, 6.7, 3.9, 2.1 Hz), 2.27 (1H, dsx,  $J$  = 16.9, 2.1 Hz), 1.80 (1H, br. s, alcohol).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.1, 144.3, 132.2, 129.8, 128.7, 120.1, 113.2, 112.1, 81.2, 60.8, 55.3, 41.6. IR (NaCl, neat film): 3323 (br.), 3055, 3023, 2909, 2842, 1588, 1484, 1406, 1073, 1010

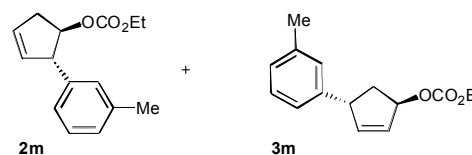


cm<sup>-1</sup>. **MS** *m/z* (rel. intensity): 190 (M<sup>+</sup>, 100), 172 (20), 162 (50), 147 (41), 134 (63), 129 (27), 121 (38), 115 (32), 91 (32).

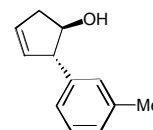
**(1*R*,4*R*)-trans-4-(3'-Methoxyphenyl)-cyclopent-2-enol (5l)**. Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{28.8} = +220$  (*c* 1.00, CHCl<sub>3</sub>) for an enantiomeric ratio was 99.4:0.6, as determined by HPLC analysis (Chiralcel OD-H; *t<sub>R</sub>* = 19.1 min (+), *t<sub>R</sub>* = 20.6 min (-)). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.21 (2H, t, *J* = 7.9 Hz), 6.77-6.67 (3H, m), 6.06-6.01 (2H, m), 5.08-5.02 (1H, m), 4.15-4.10 (1H, m), 3.79 (3H, s), 2.28 (1H, ddd, *J* = 14.1, 8.0, 2.8 Hz), 2.11 (1H, ddd, *J* = 14.1, 6.9, 6.0 Hz), 1.48 (1H, br. s). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 159.8, 146.5, 138.9, 134.1, 129.6, 119.5, 112.9, 111.5, 77.5, 55.2, 49.9, 44.0. **IR** (NaCl, neat film): 3333 (br), 3055, 3001, 2963, 2939, 2839, 1604, 1489, 1458, 1435, 1319, 1265, 1157, 1041, 1026, 771 cm<sup>-1</sup>. **MS** (EI<sup>+</sup>) *m/z* (rel. intensity): 190.1 (M<sup>+</sup>, 30), 172 (100), 157 (47), 129 (33), 128 (38), 127 (29), 115 (18), 85 (21), 84 (30). **HRMS** (EI<sup>+</sup>): Calc'd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub> [M<sup>+</sup>]: 190.0994; found = 190.0991.



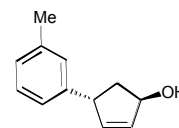
**(1*R*,2*S*)-trans-2-(3'-Methylphenyl)-cyclopent-3-enyl ethyl carbonate (2m) and (1*R*,4*R*)-trans-4-(3'-Methylphenyl)-cyclopent-2-enyl ethyl carbonate (3m)**. Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 99% yield (81 mg), showing a 1:2.2 ratio of 2:3 by <sup>1</sup>H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 3m**: **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.22–7.16 (1H, m), 7.07–7.00 (2H, m), 6.92 (1H, d, *J* = 6.9 Hz), 6.18 (1H, dd, *J* = 5.6, 1.9 Hz), 6.07 (1H, ddd, *J* = 5.0, 4.8, 2.3 Hz), 5.79–5.75 (1H, m), 4.20 (2H, q, *J* = 7.1 Hz), 4.15–4.08 (1H, m), 2.46 (1H, ddd, *J* = 14.7, 7.7, 2.3 Hz), 2.33 (3H, s), 2.12 (1H, ddd, *J* = 14.6, 7.1, 5.9 Hz), 1.31 (3H, t, *J* = 7.1 Hz). **Minor regioisomer 2m**: concordant to our previous report.<sup>8</sup>



**(1*R*,2*S*)-trans-2-(3'-Methylphenyl)-cyclopent-3-enol (4m)**. Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{27.5} = +197$  (*c* 1.00, CHCl<sub>3</sub>) for an enantiomeric ratio was 96.4:3.6, as determined by HPLC analysis (Chiralcel OD-H; 225 nm; *t<sub>R</sub>* = 13.6 min (+), *t<sub>R</sub>* = 16.3 min (-)). The characterization data was fully concordant with previous reports from the literature.<sup>8</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.21 (1H, t, *J* = 7.5 Hz), 7.06-6.97 (3H, m), 5.89 (1H, ddd, *J* = 5.0, 4.4, 2.2 Hz), 5.77 (1H, ddd, *J* = 6.0, 4.2, 2.1 Hz), 4.31-4.26 (1H, m), 3.73 (1H, sp, *J* = 1.9 Hz), 2.81 (1H, dddd, *J* = 16.9, 6.5, 4.1, 2.0 Hz), 2.37 (1H, dddd, *J* = 16.9, 6.3, 4.1, 2.0 Hz), 2.34 (3H, s), 1.88 (1H, br. s, alcohol). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 142.5, 138.2, 132.4, 129.4, 128.5, 128.1, 127.4, 124.4, 81.0, 60.7, 41.3. **IR** (NaCl, neat film): 3323 (br.), 3336 (br.), 3056, 3022, 2921, 2863, 1650, 1607, 1490, 1456, 1272, 1161, 1054 cm<sup>-1</sup>. **MS** *m/z* (rel. intensity): 174 (M<sup>+</sup>, 93), 156 (25), 146 (55), 131 (69), 128 (47), 118 (100), 115 (41), 105 (50), 91 (42). **HRMS** (ESI<sup>+</sup>): Calc'd for C<sub>12</sub>H<sub>14</sub>O [M<sup>+</sup>]: 174.104465; found = 174.104256.



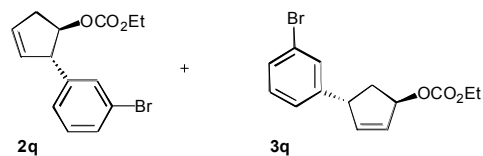
**(1*R*,4*R*)-trans-4-(3'-Methylphenyl)-cyclopent-2-enol (5m)**. Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{28.1} = +172$  (*c* 1.00, CHCl<sub>3</sub>) for an enantiomeric ratio was 99.5:0.5, as determined by HPLC analysis (Chiralcel OD-H; 225 nm; *t<sub>R</sub>* = 16.4 min (+), *t<sub>R</sub>* = 18.9 min (-)). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.18 (1H, t, *J* = 8.2 Hz), 7.01 (1H, d, *J* = 7.7 Hz), 6.95-6.92 (2H, m), 6.06-6.01 (2H, m), 5.07-5.03 (1H, m), 4.13-4.08 (1H, m), 2.33 (3H, s), 2.27 (1H, ddd, *J* = 14.1, 8.0, 2.6 Hz), 2.10 (1H, ddd, *J* = 14.1, 7.0, 5.5 Hz), 1.56 (1H, br. s, alcohol). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 144.7, 139.3, 138.2, 133.9, 128.5, 127.8, 127.1, 124.1, 77.5, 49.8, 44.1, 21.4. **IR** (NaCl, neat film): 3348 (br), 3055, 3024, 2962, 2924, 1705, 1604, 1589, 1489, 1435, 1257, 1172, 1111, 1026, 779, 702 cm<sup>-1</sup>. **MS** (EI<sup>+</sup>) *m/z* (rel. intensity): 174.1 (M<sup>+</sup>, 22), 156 (100), 141 (52), 128 (33), 115 (49), 91 (11), 84 (16). **HRMS** (EI<sup>+</sup>): Calc'd for C<sub>12</sub>H<sub>14</sub>O [M<sup>+</sup>]: 174.1045; found = 174.1046.



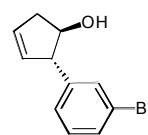
**(1*R*,2*S*)-trans-2-(3'-Bromophenyl)-cyclopent-3-enyl ethyl carbonate (2q)** and **(1*R*,4*R*)-trans-4-(3'-Bromophenyl)-cyclopent-2-enyl ethyl carbonate (3q)**. Prepared according to *Procedure B*. The crude product

was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 89% yield (89 mg), showing a 1:2.3

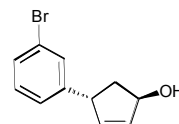
ratio of **2:3** by  $^1\text{H}$  NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 3q*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39–7.03 (4H, m), 6.15 (1H, dd,  $J$  = 5.6, 1.7 Hz), 6.10 (1H, ddd,  $J$  = 7.7, 5.6, 2.2 Hz), 5.77–5.72 (1H, m), 4.20 (2H, q,  $J$  = 7.1 Hz), 4.15–4.08 (1H, m), 2.46 (1H, dt,  $J$  = 6.8, 2.2 Hz), 2.10 (1H, ddd,  $J$  = 14.7, 7.1, 5.9 Hz), 1.31 (3H, t,  $J$  = 7.1 Hz). *Minor regioisomer 2q*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.39–7.03 (4H, m), 5.96 (1H, ddd,  $J$  = 5.8, 4.0, 2.0 Hz), 5.80–5.75 (1H, m), 5.00 (1H, ddd,  $J$  = 6.6, 2.6, 3.1 Hz), 4.20 (2H, q,  $J$  = 7.1 Hz), 3.96 (1H, br.s), 2.54–2.45 (1H, m), 2.91 (1H, dddd,  $J$  = 17.8, 6.3, 3.9, 2.1 Hz), 1.31 (3H, t,  $J$  = 7.1 Hz).



**(1*R*,2*S*)-trans-2-(3'-Bromophenyl)-cyclopent-3-enol (4q)**. Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_{\text{D}}^{26.3} = +146$  ( $c$  1.00,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 96.8 : 3.2, as determined by HPLC analysis (Chiralcel OD-H; 225 nm;  $t_{\text{R}}$  = 17.6 min (+),  $t_{\text{R}}$  = 20.8 min (-)).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.35–7.28 (2H, m), 7.15 (1H, t,  $J$  = 7.6 Hz), 7.09 (1H, dd,  $J$  = 7.6, 1.4 Hz), 5.90 (1H, ddd,  $J$  = 6.1, 4.3, 2.2 Hz), 5.71 (1H, ddd,  $J$  = 6.1, 4.1, 2.0 Hz), 4.28–4.19 (1H, m), 3.74–3.66 (1H, m), 2.77 (1H, ddd,  $J$  = 17.0, 3.0, 1.8 Hz), 2.34 (1H, ddd,  $J$  = 17.0, 3.9, 1.8 Hz), 2.08 (1H, br.s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.4, 131.2, 130.0, 129.9, 129.8, 129.4, 125.8, 122.5, 81.4, 61.3, 42.8. IR (NaCl, neat film): 3331 (br), 3057, 2906, 2843, 1592, 1564, 1475, 1426, 1287, 1265, 1163, 1072, 1052, 996, 950, 780, 720  $\text{cm}^{-1}$ . MS ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 240 ( $\text{M}^+$ , 14), 238 (17), 222 (33), 184 (40), 182 (44), 141 (65), 131 (75), 128 (44), 115 (100), 91 (14). HRMS ( $\text{EI}^+$ ): Calc'd for  $\text{C}_{11}\text{H}_{11}\text{BrO}$  [ $\text{M}^+$ ]: 237.9993; found = 237.9996.

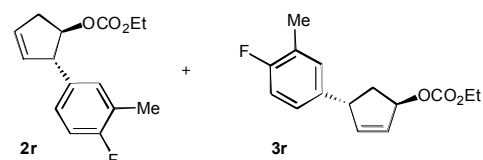


**(1*R*,4*R*)-trans-4-(3'-Bromophenyl)-cyclopent-2-enol (5q)**. Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_{\text{D}}^{27.0} = +181$  ( $c$  1.00,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 99.5:0.5, as determined by HPLC analysis (Chiralcel OD-H; 225 nm;  $t_{\text{R}}$  = 20.4 min (+),  $t_{\text{R}}$  = 21.6 min (-)).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.33 (1H, dd,  $J$  = 6.1, 1.2 Hz), 7.26 (1H, t,  $J$  = 2.2 Hz), 7.15 (1H, t,  $J$  = 7.8 Hz), 7.05 (1H, dd,  $J$  = 7.6, 1.2 Hz), 6.08–6.05 (1H, m), 6.01 (1H, dd,  $J$  = 4.7, 2.0 Hz), 5.12–5.01 (1H, m), 4.16–4.08 (1H, m), 2.28 (1H, ddd,  $J$  = 14.1, 8.0, 2.6 Hz), 2.07 (1H, ddd,  $J$  = 14.0, 7.0, 5.4 Hz), 1.57 (1H, br. s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.6, 137.8, 134.3, 129.8, 129.7, 129.1, 125.6, 122.5, 77.9, 50.8, 45.2. IR (NaCl, neat film): 3328 (br), 3057, 2963, 2930, 2876, 1592, 1476, 1424, 1350, 1110, 1072, 1052, 937, 791, 778, 743, 692  $\text{cm}^{-1}$ . MS ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 240 ( $\text{M}^+$ , 6), 238 (16), 222 (72), 141 (100), 139 (23), 115 (67), 86 (22), 84 (27). HRMS ( $\text{EI}^+$ ): Calc'd for  $\text{C}_{11}\text{H}_{11}\text{BrO}$  [ $\text{M}^+$ ]: 237.9993; found = 237.9990.



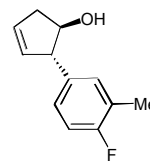
**(1*R*,2*S*)-trans-2-(4'-Fluoro-3-methylphenyl)-cyclopent-3-enyl ethyl carbonate (2r)** and **(1*R*,4*R*)-trans-4-(4'-Fluoro-3-methylphenyl)-cyclopent-2-enyl ethyl carbonate (3r)**. Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 69% yield

(60 mg), showing a 1:2.3 ratio of **2:3** by  $^1\text{H}$  NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 3r*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.03–6.96 (1H, m), 6.95–6.88 (2H, m), 6.14 (1H, dd,  $J$  = 5.6, 2.0 Hz), 6.07 (1H, dt,  $J$  = 5.6, 2.3 Hz), 5.74 (1H, dd,  $J$  = 6.9, 4.0, 2.1 Hz), 4.20 (2H, q,  $J$  = 7.1 Hz), 4.09 (1H, dddd,  $J$  = 7.8, 5.7, 4.2, 2.1 Hz), 2.45 (1H, ddd,  $J$  = 14.6, 7.9, 2.1 Hz), 2.24 (3H, s), 2.08 (1H, ddd,  $J$  = 14.6, 7.1, 1.3 Hz), 1.31 (3H, t,  $J$  = 7.1 Hz). *Minor regioisomer 2r*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.03–6.96 (1H, m), 6.95–6.88 (2H, m), 5.93 (1H, ddd,  $J$  = 5.9, 4.2, 2.1 Hz), 5.78 (1H, dd,  $J$  = 4.3, 2.2 Hz), 4.99 (1H, dt,  $J$  = 6.6, 2.7 Hz), 4.20 (2H, q,  $J$  = 7.1 Hz), 3.40 (1H, br.s), 2.90 (1H, dddd,  $J$  = 17.8, 6.6, 4.0, 1.8 Hz), 2.51–2.44 (1H, m), 2.24 (3H, s), 1.31 (3H, t,  $J$  = 7.1 Hz).

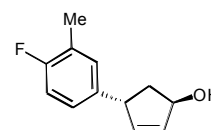




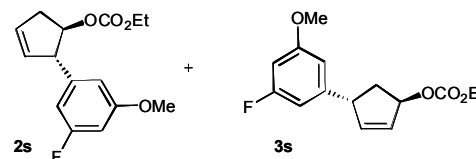
**(1*R*,2*S*)-trans-2-(4'-Fluoro-3'-methylphenyl)-cyclopent-3-enol (4r).** Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{28.2} = +187$  (*c* 0.50, CHCl<sub>3</sub>) for an enantiomeric ratio was 97.1:2.9, as determined by HPLC analysis (Chiralcel OD-H; 215 nm; *t<sub>R</sub>* = 13.9 min (+), *t<sub>R</sub>* = 15.4 min (-)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.96 (1H, d, *J* = 8.0 Hz), 6.94–6.86 (2H, m), 5.87 (1H, dd, *J* = 5.9, 2.3 Hz), 5.71 (1H, dd, *J* = 6.0, 2.0 Hz), 4.20 (1H, dt, *J* = 6.6, 4.1 Hz), 3.70–3.64 (1H, m), 3.76 (1H, ddd, *J* = 16.9, 6.7, 2.0 Hz), 3.34 (1H, ddd, *J* = 16.8, 4.1, 2.1 Hz), 2.23 (3H, d, *J* = 2.0 Hz), 2.04 (1H, br.s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.0 (d, *J* = 243.1 Hz), 138.1 (d, *J* = 3.8 Hz), 132.4, 130.5 (d, *J* = 5.2 Hz), 129.7, 126.1 (d, *J* = 7.9 Hz), 125.0 (d, *J* = 17.2 Hz), 115.1 (d, *J* = 22.1 Hz), 81.2, 60.1, 41.5, 14.7. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>): δ -121.4 (dd, *J* = 7.6, 1.9 Hz, 1F). IR (NaCl, neat film): 3337 (br), 3056, 3017, 2962, 2844, 1501, 1252, 1236, 1207 1118, 1051, 949, 819, 756 cm<sup>-1</sup>. MS (EI<sup>+</sup>) *m/z* (rel. intensity): 192.1 (M<sup>+</sup>, 47), 174 (51), 159 (43), 146 (48), 136 (100), 133 (44), 123 (30), 109 (30). HRMS (EI<sup>+</sup>): Calc'd for C<sub>12</sub>H<sub>13</sub>OF [M<sup>+</sup>]: 192.0950; found = 192.0950.



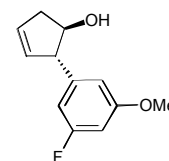
**(1*R*,4*R*)-trans-4-(4'-Fluoro-3'-methylphenyl)-cyclopent-2-enol (5r).** Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{28.1} = +204$  (*c* 1.00, CHCl<sub>3</sub>) for an enantiomeric ratio was 99.3 : 0.7, as determined by HPLC analysis (Chiralcel OD-H; 215 nm; *t<sub>R</sub>* = 16.5 min (+), *t<sub>R</sub>* = 18.0 min (-)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.95–6.86 (3H, m), 6.06–5.98 (2H, m), 5.09–5.00 (1H, m), 4.14–4.06 (1H, m), 2.27 (1H, ddd, *J* = 14.1, 8.0, 2.6 Hz), 2.24 (3H, d, *J* = 2.0 Hz), 2.05 (1H, ddd, *J* = 14.2, 6.8, 5.5 Hz), 1.58 (1H, br. s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 160.7 (d, *J* = 243.1 Hz), 140.3 (d, *J* = 3.7 Hz), 139.3, 134.2, 130.1 (d, *J* = 5.9 Hz), 125.9, 125.8, 115.1 (d, *J* = 22.4 Hz), 77.6, 49.3, 44.4, 14.7 (d, *J* = 3.8). <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>): δ -121.7 (dd, *J* = 13.3, 5.7 Hz, 1F). IR (NaCl, neat film): 3326 (br), 3055, 3018, 2962, 2927, 2891, 1501, 1325, 1245, 1205, 1118, 1028, 882, 790, 756 cm<sup>-1</sup>. MS (EI<sup>+</sup>) *m/z* (rel. intensity): 192.1 (M<sup>+</sup>, 5), 175 (15), 174 (100), 159 (82), 146 (29), 133 (54), 109 (11). HRMS (EI<sup>+</sup>): Calc'd for C<sub>12</sub>H<sub>13</sub>OF [M<sup>+</sup>]: 192.0950; found = 192.0949.



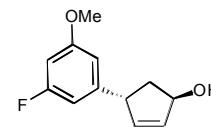
**(1*R*,2*S*)-trans-2-(3'-Fluoro-5'-methoxyphenyl)-cyclopent-3-enyl ethyl carbonate (2s) and (1*R*,4*R*)-trans-4-(3'-Fluoro-5'-methoxyphenyl)-cyclopent-2-enyl ethyl carbonate (3s).** Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 78% yield (72 mg), showing a 1:2.4 ratio of **2**:**3** by <sup>1</sup>H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 3s**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.59–6.40 (3H, m), 6.15 (1H, dd, *J* = 5.6, 1.8 Hz), 6.09 (1H, ddd, *J* = 5.6, 3.2, 2.2 Hz), 5.76–5.71 (1H, m), 4.20 (2H, q, *J* = 7.1 Hz), 4.13–4.05 (1H, m), 3.77 (3H, s), 2.45 (1H, ddd, *J* = 14.6, 7.8, 2.2 Hz), 2.11 (1H, ddd, *J* = 14.6, 7.1, 5.8 Hz), 1.31 (3H, t, *J* = 7.1 Hz). **Minor regioisomer 2s**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.59–6.40 (3H, m), 5.95 (1H, ddd, *J* = 5.9, 4.1, 2.1 Hz), 5.79–5.73 (1H, m), 5.02 (1H, dt, *J* = 6.6, 2.7 Hz), 4.20 (2H, q, *J* = 7.1 Hz), 3.94 (1H, br.s), 3.77 (3H, s), 2.90 (1H, dddd, *J* = 17.8, 6.6, 3.9, 1.8 Hz), 2.52–2.43 (1H, m), 1.31 (3H, t, *J* = 7.1 Hz).



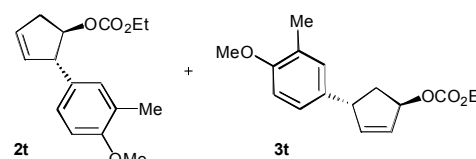
**(1*R*,2*S*)-trans-2-(3'-Fluoro-5'-methoxyphenyl)-cyclopent-3-enol (4s).** Deprotected and isolated according to *Procedure C*. Colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.55–6.43 (3H, m), 5.91 (1H, ddd, *J* = 12.2, 5.8, 2.4 Hz), 5.73 (1H, ddd, *J* = 8.0, 6.1, 1.9 Hz), 4.25 (1H, ddd, *J* = 8.2, 6.6, 3.1 Hz), 3.77 (3H, s), 3.74–3.68 (1H, m), 2.79 (1H, ddd, *J* = 17.0, 6.9, 2.1 Hz), 2.36 (1H, ddd, *J* = 17.0, 4.1, 2.2 Hz), 1.98 (1H, br. s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.8 (d, *J* = 245.0 Hz), 161.0 (d, *J* = 11.4 Hz), 145.8 (d, *J* = 8.9 Hz), 131.5, 130.2, 109.0 (d, *J* = 2.6 Hz), 106.4 (d, *J* = 21.7 Hz), 99.6 (d, *J* = 25.7 Hz), 80.7, 60.6 (d, *J* = 2.0 Hz), 55.5, 41.4. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>): δ -112.2 (t, *J* = 9.8 Hz, 1F). IR (NaCl, neat film): 3332 (br), 3055, 3010, 2963, 2938, 28340, 1604, 1502, 1457, 1318, 1255, 1229, 1045, 1024, 821, 765 cm<sup>-1</sup>. MS (EI<sup>+</sup>) *m/z* (rel. intensity): 208.1 (M<sup>+</sup>, 97), 190 (99), 180 (100), 175 (33), 152 (35), 146 (50), 139 (32), 86 (27), 84 (45). HRMS (EI<sup>+</sup>): Calc'd for C<sub>12</sub>H<sub>13</sub>O<sub>2</sub>F [M<sup>+</sup>]: 208.0900; found = 208.0905.



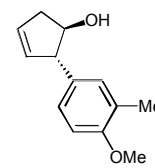
**(1*R*,4*R*)-trans-4-(3'-Fluoro-5'-methoxyphenyl)-cyclopent-2-enol (5s).** Deprotected and isolated according to *Procedure C*. Colourless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.42–6.34 (3H, m), 5.97 (1H, ddd, *J* = 5.5, 3.3, 2.1 Hz), 5.93 (1H, dd, *J* = 5.5, 2.0 Hz), 4.97 (1H, ddd, *J* = 7.0, 4.6, 2.1 Hz), 4.06–3.97 (1H, m), 3.70 (3H, s), 2.19 (1H, ddd, *J* = 14.1, 8.1, 2.7 Hz), 2.00 (1H, ddd, *J* = 14.1, 8.7, 5.4 Hz), 1.62 (1H, br. s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 163.8 (d, *J* = 244.8 Hz), 161.0 (d, *J* = 11.4 Hz), 148.1 (d, *J* = 8.8 Hz), 138.2, 134.7, 108.9 (d, *J* = 2.6 Hz), 106.1 (d, *J* = 21.7 Hz), 99.3 (d, *J* = 25.3 Hz), 77.3, 55.5, 49.9 (d, *J* = 2.1 Hz), 43.8. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>): δ -112.2 (t, *J* = 9.7 Hz, 1F). IR (NaCl, neat film): 3334 (br), 3053, 3010, 2959, 2843, 1601, 1499, 1254, 1237, 1116, 1052, 949, 789 cm<sup>-1</sup>. MS (EI<sup>+</sup>) *m/z* (rel. intensity): 208.1 (M<sup>+</sup>, 7), 190 (100), 175 (23), 147 (20), 146 (51), 133 (17), 127 (13), 86 (14), 84 (28). HRMS (EI<sup>+</sup>): Calc'd for C<sub>12</sub>H<sub>13</sub>O<sub>2</sub>F [M<sup>+</sup>]: 208.0900; found = 208.0903.



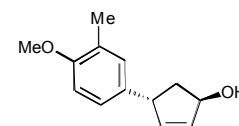
**(1*R*,2*S*)-trans-2-(4'-Methoxy-3'-methylphenyl)-cyclopent-3-enyl ethyl carbonate (2t) and (1*R*,4*R*)-trans-4-(4'-Methoxy-3'-methylphenyl)-cyclopent-2-enyl ethyl carbonate (3t).** Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 66% yield (60 mg), showing a 1:1.3 ratio of **2t**:**3t** by <sup>1</sup>H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 3t**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.03–6.97 (1H, m), 6.94–6.88 (1H, m), 6.74 (1H, d, *J* = 6.7 Hz), 6.16 (1H, dd, *J* = 5.6, 2.0 Hz), 6.05 (1H, dt, *J* = 5.6, 2.3 Hz), 5.72 (1H, ddd, *J* = 6.9, 3.8, 2.1 Hz), 4.20 (2H, q, *J* = 7.1 Hz), 4.10–4.04 (1H, m), 3.81 (3H, s), 2.45 (1H, ddd, *J* = 14.5, 7.8, 2.0 Hz), 2.20 (3H, m), 2.10 (1H, ddd, *J* = 14.6, 7.1, 5.8 Hz), 1.31 (3H, t, *J* = 7.1 Hz). **Minor regioisomer 2t**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.03–6.97 (1H, m), 6.94–6.88 (1H, m), 6.76 (1H, d, *J* = 3.8 Hz), 5.90 (1H, ddd, *J* = 5.9, 4.1, 2.1 Hz), 5.81–5.76 (1H, m), 5.00 (1H, ddd, *J* = 6.6, 3.7, 2.7 Hz), 4.16 (2H, q, *J* = 7.1 Hz), 3.92 (1H, br.s), 3.81 (3H, s), 2.91 (1H, dddd, *J* = 17.7, 6.6, 4.0, 1.8 Hz), 2.49–2.43 (1H, m), 2.20 (3H, s), 1.31 (3H, t, *J* = 7.1 Hz).



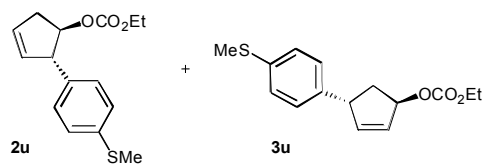
**(1*R*,2*S*)-trans-2-(4'-Methoxy-3'-methylphenyl)-cyclopent-3-enol (4t).** Deprotected and isolated according to *Procedure C*. Colourless oil. [α]<sub>D</sub><sup>28.5</sup> = +172 (c 1.00, CHCl<sub>3</sub>) for an enantiomeric ratio was 89.7 : 10.3, as determined by HPLC analysis (Chiralcel OD-H; 235 nm; t<sub>R</sub> = 17.5 min (+), t<sub>R</sub> = 19.5 min (-)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.93–6.85 (2H, m), 6.69 (1H, d, *J* = 7.9 Hz), 5.78 (1H, ddd, *J* = 5.9, 4.4, 2.2 Hz), 5.68 (1H, ddd, *J* = 5.9, 4.1, 2.1 Hz), 4.22–4.14 (1H, m), 3.74 (3H, s), 3.63–3.59 (1H, m), 2.71 (1H, dddd, *J* = 23.6, 6.7, 3.9, 1.8 Hz), 2.27 (1H, ddt, *J* = 16.8, 4.1, 2.0 Hz), 2.13 (3H, s), 1.75 (1H, br.s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.6, 134.1, 132.7, 129.7, 129.1, 126.8, 125.4, 110.0, 81.1, 59.9, 55.4, 41.2, 16.2. IR (NaCl, neat film): 3348 (br), 3055, 2993, 2916, 2839, 1612, 1504, 1465, 1257, 1219, 1134, 1033, 949, 810 cm<sup>-1</sup>. MS (EI<sup>+</sup>) *m/z* (rel. intensity): 204.1 (M<sup>+</sup>, 14), 172 (8), 161 (35), 148 (100), 128 (49), 115 (43), 91 (23), 71 (22). HRMS (EI<sup>+</sup>): Calc'd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> [M<sup>+</sup>]: 204.1150; found = 204.1147.



**(1*R*,4*R*)-trans-4-(4'-Methoxy-3'-methylphenyl)-cyclopent-2-enol (5t).** Deprotected and isolated according to *Procedure C*. Colourless oil. [α]<sub>D</sub><sup>28.6</sup> = +228 (c 1.00, CHCl<sub>3</sub>) for an enantiomeric ratio was 99.6 : 0.4, as determined by HPLC analysis (Chiralcel OD-H; 225 nm; t<sub>R</sub> = 18.1 min (+), t<sub>R</sub> = 19.3 min (-)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.95–6.86 (2H, m), 6.74 (1H, d, *J* = 8.2 Hz), 6.05–5.96 (2H, m), 5.04 (1H, ddd, *J* = 7.0, 3.7, 2.2 Hz), 4.09–4.03 (1H, m), 3.80 (3H, s), 2.25 (1H, ddd, *J* = 14.1, 8.1, 2.6 Hz), 2.19 (3H, s), 2.07 (1H, ddd, *J* = 14.2, 7.0, 5.6 Hz), 1.69 (1H, br.s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.5, 139.9, 136.6, 133.7, 129.6, 126.9, 125.3, 110.2, 77.7, 55.6, 49.3, 44.5, 16.4. IR (NaCl, neat film): 3348 (br), 3055, 2993, 2947, 2831, 1705 (w), 1612, 1504, 1465, 1249, 1219, 1134, 1111, 1033, 910, 810 cm<sup>-1</sup>. MS (EI<sup>+</sup>) *m/z* (rel. intensity): 204.1 (M<sup>+</sup>, 22), 186 (88), 171 (100), 127 (11), 115 (45), 84 (5). HRMS (EI<sup>+</sup>): Calc'd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> [M<sup>+</sup>]: 204.1150; found = 204.1154.

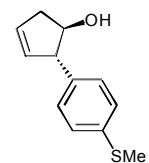


**(1*R*,2*S*)-trans-2-(4'-Methylsulfanylphenyl)-cyclopent-3-enyl ethyl carbonate (2u)** and **(1*R*,4*R*)-trans-4-(4'-Methylsulfanylphenyl)-cyclopent-2-enyl ethyl carbonate (3u)**. Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 80% yield (72 mg),



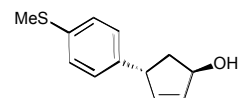
showing a 1:2.6 ratio of **2**:**3** by  $^1\text{H}$  NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 3u*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24 (2H, dd,  $J = 11.4, 1.6$  Hz), 7.14 (2H, dd,  $J = 8.4, 1.8$  Hz), 6.16 (1H, dd,  $J = 5.6, 1.9$  Hz), 6.08 (1H, ddd,  $J = 5.5, 3.1, 2.3$  Hz), 5.75 (1H, ddd,  $J = 7.0, 3.9, 2.1$  Hz), 4.20 (2H, q,  $J = 7.1$  Hz), 4.15–4.08 (1H, m), 2.46 (3H, s), 2.48–2.42 (1H, m), 2.09 (1H, ddd,  $J = 14.6, 7.1, 5.9$  Hz), 1.31 (3H, t,  $J = 7.1$  Hz). *Minor regioisomer 2u*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.20 (2H, dd,  $J = 5.6, 3.3$  Hz), 7.05 (2H, dd,  $J = 8.3, 1.8$  Hz), 5.93 (1H, ddd,  $J = 5.8, 4.1, 2.1$  Hz), 5.80 (1H, dd,  $J = 4.3, 2.1$  Hz), 5.00 (1H, dt,  $J = 6.6, 2.7$  Hz), 4.20 (2H, q,  $J = 7.1$  Hz), 3.96 (1H, br.s), 2.89 (1H, dddd,  $J = 17.7, 6.6, 3.9, 1.8$  Hz), 2.46 (3H, s), 2.52–2.48 (1H, m), 1.31 (3H, t,  $J = 7.1$  Hz).

**(1*R*,2*S*)-trans-2-(4'-Methylsulfanylphenyl)-cyclopent-3-enol (4u)**. Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_{\text{D}}^{28.9} = +205$  ( $c$  1.00,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 95.6 : 4.4,



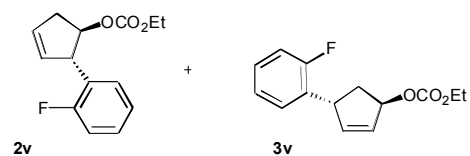
as determined by HPLC analysis (Chiralcel OD-H; 262 nm;  $t_{\text{R}} = 21.6$  min (+),  $t_{\text{R}} = 23.7$  min (-)).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22 (2H, ddd,  $J = 8.4, 4.3, 2.2$  Hz), 7.11 (1H, ddd,  $J = 8.2, 4.1, 2.2$  Hz), 5.90 (1H, ddd,  $J = 5.8, 2.4, 2.2$  Hz), 5.75 (1H, ddd,  $J = 5.9, 2.2, 2.0$  Hz), 4.24 (1H, ddd,  $J = 6.6, 5.8, 4.3$  Hz), 3.74–3.72 (1H, m), 2.80 (1H, dddd,  $J = 15.3, 6.8, 3.9, 2.2$  Hz), 2.47 (3H, s), 2.37 (1H, dddd,  $J = 17.0, 6.1, 4.1, 2.0$  Hz), 1.81 (1H, br.s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  139.8, 136.6, 132.3, 129.9, 128.1 (2C), 127.4 (2C), 81.2, 60.4, 41.6, 16.4. IR (NaCl, neat film): 3348 (br), 3055, 3016, 2962, 2916, 2839, 1489, 1435, 1404, 1319, 1049, 949, 817, 732  $\text{cm}^{-1}$ . MS ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 206.1 ( $\text{M}^+$ , 25), 188 (8), 150 (100), 129 (34), 128 (53), 116 (39), 115 (51), 91 (17), 89 (9). HRMS ( $\text{EI}^+$ ): Calc'd for  $\text{C}_{12}\text{H}_{14}\text{OS}$  [ $\text{M}^+$ ]: 206.0765; found = 206.0760.

**(1*R*,4*R*)-trans-4-(4'-Methylsulfanylphenyl)-cyclopent-2-enol (5u)**. Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_{\text{D}}^{28.1} = +298$  ( $c$  1.00,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 99.5:0.5, as determined by HPLC analysis (Chiralcel OD-H; 262 nm);  $t_{\text{R}} = 21.7$  min



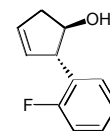
(+),  $t_{\text{R}} = 22.5$  min (-)).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.20 (2H, dd,  $J = 9.4, 1.8$  Hz), 7.05 (2H, dd,  $J = 8.2, 1.8$  Hz), 6.06–5.97 (2H, m), 5.08–5.01 (1H, m), 4.15–4.05 (1H, m), 2.46 (3H, s), 2.27 (1H, ddd,  $J = 14.0, 8.0, 2.8$  Hz), 2.06 (1H, ddd,  $J = 14.2, 7.2, 4.6$  Hz), 1.66 (1H, br.s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  142.1, 139.2, 136.2, 134.4, 127.8 (2C), 127.4 (2C), 77.6, 49.6, 44.3, 16.5. IR (NaCl, neat film): 3333 (br), 3055, 3016, 2962, 2931, 2885, 1489, 1435, 1411, 1319, 1026, 817, 732  $\text{cm}^{-1}$ . MS ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 206.1 ( $\text{M}^+$ , 5), 150 (15), 142 (41), 128 (40), 115 (100), 102 (31), 89 (42), 63 (41). HRMS ( $\text{EI}^+$ ): Calc'd for  $\text{C}_{12}\text{H}_{14}\text{OS}$  [ $\text{M}^+$ ]: 206.0765; found = 206.0766.

**(1*R*,2*S*)-trans-2-(2'-Fluorophenyl)-cyclopent-3-enyl ethyl carbonate (2v)** and **(1*R*,4*R*)-trans-4-(2'-Fluorophenyl)-cyclopent-2-enyl ethyl carbonate (3v)**. Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 16% yield (13 mg), showing a 1:1.3

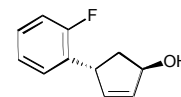


ratio of **2**:**3** by  $^1\text{H}$  NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 3v*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24–7.16 (1H, m), 7.10–6.98 (3H, m), 6.18 (1H, dd,  $J = 5.6, 2.0$  Hz), 6.10 (1H, ddd,  $J = 5.6, 3.2, 2.4$  Hz), 5.74 (1H, ddd,  $J = 7.9, 4.4, 2.3$  Hz), 4.44 (1H, dddd,  $J = 13.7, 7.9, 4.3, 2.2$  Hz), 4.20 (2H, q,  $J = 7.1$  Hz), 2.53–2.47 (1H, m), 2.14 (1H, ddd,  $J = 14.6, 7.2, 5.8$  Hz), 1.31 (3H, t,  $J = 7.1$  Hz). *Minor regioisomer 2v*:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.24–7.16 (1H, m), 7.10–6.98 (3H, m), 5.93 (1H, ddd,  $J = 5.9, 4.3, 2.2$  Hz), 5.77 (1H, dd,  $J = 4.1, 2.2$  Hz), 5.16 (1H, dt,  $J = 6.8, 2.9$  Hz), 4.28 (1H, br.s.), 4.20 (2H, q,  $J = 7.1$  Hz), 2.96 (1H, dddd,  $J = 17.9, 6.8, 4.0, 2.1$  Hz), 2.55–2.49 (1H, m), 1.31 (3H, t,  $J = 7.1$  Hz).

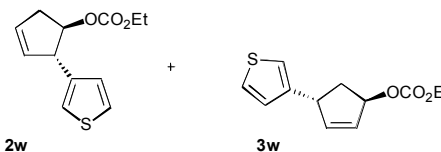
**(1R,2S)-trans-2-(2'-Fluorophenyl)-cyclopent-3-enol (4v).** Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{28.8} = +150$  ( $c$  0.30,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 94.1 : 5.9, as determined by HPLC analysis (Chiralcel OD-H; 215 nm;  $t_R = 14.1$  min (+),  $t_R = 16.3$  min (-)).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23–7.17 (1H, m), 7.10–7.02 (3H, m), 5.95 (1H, ddd,  $J = 5.9, 4.4, 2.2$  Hz), 5.75 (1H, ddd,  $J = 5.9, 4.3, 2.2$  Hz), 4.35 (1H, dt,  $J = 6.6, 3.3$  Hz), 4.10 (1H, br.s), 2.80 (1H, dddd,  $J = 17.2, 6.7, 4.1, 2.1$  Hz), 2.39 (1H, ddt,  $J = 17.2, 3.6, 2.0$  Hz), 1.97 (1H, br.s).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.2 (d,  $J = 245.0$  Hz), 130.7 (d,  $J = 9.7$  Hz), 129.4 (d,  $J = 15.0$  Hz), 128.4 (d,  $J = 4.5$  Hz), 128.3 (d,  $J = 8.2$  Hz), 124.3 (d,  $J = 3.4$  Hz), 115.6, 115.4, 79.8, 54.1 (d,  $J = 1.5$  Hz), 41.5.  **$^{19}\text{F}$  NMR** (375 MHz,  $\text{CDCl}_3$ ):  $\delta$  -118.3 (d,  $J = 8.6$  Hz, F). **IR** (NaCl, neat film): 3348 (br), 3055, 2993, 2924, 2847, 1720 (w), 1581, 1489, 1450, 1226, 1041, 949, 864, 756  $\text{cm}^{-1}$ . **MS** ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 178.1 ( $\text{M}^+$ , 3), 146 (21), 135 (44), 133 (51), 122 (100), 115 (14), 109 (45), 75 (30), 63 (24). **HRMS** ( $\text{EI}^+$ ): Calc'd for  $\text{C}_{11}\text{H}_{11}\text{FO}$  [ $\text{M}^+$ ]: 178.0794; found = 178.0800.



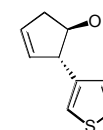
**(1R,4R)-trans-4-(2'-Fluorophenyl)-cyclopent-2-enol (5v).** Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{28.5} = +98$  ( $c$  0.82,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 98.2 : 1.8, as determined by HPLC analysis (Chiralcel OD-H; 215 nm;  $t_R = 17.6$  min (+),  $t_R = 18.7$  min (-)).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22–7.14 (1H, m), 7.10–6.97 (3H, m), 6.09–6.00 (2H, m), 5.08–5.01 (1H, m), 4.48–4.40 (1H, m), 2.31 (1H, ddd,  $J = 14.1, 8.1, 2.8$  Hz), 2.11 (1H, ddd,  $J = 13.8, 6.8, 5.5$  Hz), 1.58 (1H, br.s).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.0 (d,  $J = 245.3$  Hz), 137.7, 134.8, 131.7 (d,  $J = 14.7$  Hz), 128.1 (d,  $J = 2.6$  Hz), 128.0, 124.4 (d,  $J = 3.3$  Hz), 115.6, 115.4, 77.3, 42.8 (d,  $J = 2.6$  Hz), 42.7.  **$^{19}\text{F}$  NMR** (375 MHz,  $\text{CDCl}_3$ ):  $\delta$  -119.0 to -119.1 (m, rotamers). **IR** (NaCl, neat film): 3317 (br), 3063, 2963, 2931, 1581, 1489, 1450, 1350, 1226, 1111, 1026, 756  $\text{cm}^{-1}$ . **MS** ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 178.1 ( $\text{M}^+$ , 20), 160 (100), 159 (72), 133 (75), 122 (19), 109 (34), 86 (24), 84 (44). **HRMS** ( $\text{EI}^+$ ): Calc'd for  $\text{C}_{11}\text{H}_{11}\text{FO}$  [ $\text{M}^+$ ]: 178.0794; found = 178.0791.



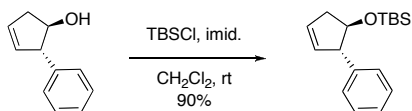
**(1R,2S)-trans-2-(Thiophen-3'-yl)-cyclopent-3-enyl ethyl carbonate (2w)** and **(1R,4R)-trans-4-(Thiophen-3'-yl)-cyclopent-2-enyl ethyl carbonate (3w).** Prepared according to *Procedure B*. The crude product was purified by column chromatography. The inseparable regioisomers were obtained as a colourless oil in 31% yield (24 mg), showing a 1:3.5 ratio of **2:3** by  $^1\text{H}$  NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 3w:**  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.22–6.98 (1H, m), 6.89–6.86 (1H, m), 6.81 (1H, dd,  $J = 4.9, 1.1$  Hz), 6.14 (1H, dd,  $J = 5.6, 2.0$  Hz), 5.96 (1H, dt,  $J = 5.6, 2.3$  Hz), 5.67 (1H, ddd,  $J = 7.1, 4.1, 2.1$  Hz), 4.21–4.14 (1H, m), 4.13 (2H, q,  $J = 7.1$  Hz), 2.37 (1H, dd,  $J = 14.5, 7.8, 2.4$  Hz), 2.10 (1H, ddd,  $J = 14.1, 7.1, 5.7$  Hz), 1.24 (3H, t,  $J = 7.1$  Hz). **Minor regioisomer 2w:**  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.23–7.18 (1H, m), 6.97–6.91 (2H, m), 5.85–5.76 (2H, m), 4.99 (1H, dt,  $J = 6.5, 2.3$  Hz), 4.13 (2H, q,  $J = 7.1$  Hz), 4.00 (1H, br.s), 2.82 (1H, dddd,  $J = 17.8, 6.5, 3.8, 1.8$  Hz), 2.45–2.36 (1H, m), 1.24 (3H, t,  $J = 7.1$  Hz).



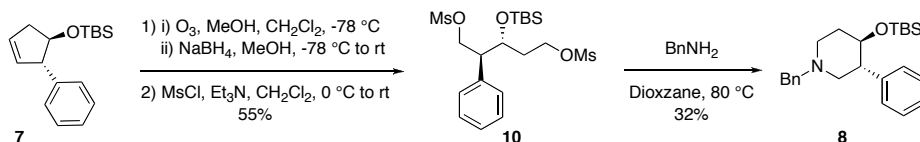
**(1R,2S)-trans-2-(Thiophen-3'-yl)-cyclopent-3-enol (4w).** Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{27.6} = +108$  ( $c$  0.40,  $\text{CHCl}_3$ ) for an enantiomeric ratio was 94.4 : 5.6, as determined by HPLC analysis (Chiralcel OD-H; 235 nm;  $t_R = 19.4$  min (+),  $t_R = 20.8$  min (-)).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.28 (1H, dd,  $J = 4.9, 3.0$  Hz), 6.99–6.96 (1H, m), 6.95 (1H, dd,  $J = 4.1, 1.2$  Hz), 5.87 (1H, ddd,  $J = 5.9, 4.1, 2.0$  Hz), 5.82 (1H, ddd,  $J = 5.9, 4.0, 2.0$  Hz), 4.31 (1H, dt,  $J = 6.9, 3.7$  Hz), 3.89–3.84 (1H, m), 2.80 (1H, ddd,  $J = 6.5, 3.6, 1.8$  Hz), 2.35 (1H, ddt,  $J = 17.0, 3.7, 1.8$  Hz), 1.84 (1H, br.s).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.3, 133.2, 129.8, 127.3, 126.1, 120.3, 80.0, 56.1, 41.5. **IR** (NaCl, neat film): 3333 (br), 3101, 3055, 2916, 2847, 1527, 1411, 1319, 1257, 1157, 1049, 940, 841, 779, 748, 640  $\text{cm}^{-1}$ . **MS** ( $\text{EI}^+$ )  $m/z$  (rel. intensity): 166.0 ( $\text{M}^+$ , 37), 148 (27), 147 (53), 138 (38), 135 (42), 123 (54), 110 (100), 97 (58), 91 (19), 84 (30), 77 (17). **HRMS** ( $\text{EI}^+$ ): Calc'd for  $\text{C}_9\text{H}_{10}\text{OS}$  [ $\text{M}^+$ ]: 166.0452; found = 166.0452.



**(1*R*,4*R*)-trans-4-(Thiophen-3'-yl)-cyclopent-2-enol (5w).** Deprotected and isolated according to *Procedure C*. Colourless oil.  $[\alpha]_D^{27.8} = +269$  (*c* 0.50, CHCl<sub>3</sub>) for an enantiomeric ratio was 99.6 : 0.4, as determined by HPLC analysis (Chiralcel OD-H; 235 nm; *t<sub>R</sub>* = 22.7 min (+), *t<sub>R</sub>* = 23.5 min (-)). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30–7.20 (1H, m), 6.97–6.82 (2H, m), 6.07 (1H, br.s), 5.99 (1H, br.s), 5.02 (1H, br.s), 4.22 (1H, br.s), 2.30–2.08 (2H, m), 1.58 (1H, br.s). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 145.5, 138.9, 133.9, 127.1, 126.1, 119.6, 77.5, 45.2, 43.2. IR (NaCl, neat film): 3317 (br), 3101, 3055, 2962, 2931, 2893, 1527, 1411, 1319, 1157, 1111, 1026, 779 cm<sup>-1</sup>. MS (EI<sup>+</sup>) *m/z* (rel. intensity): 166.0 (M<sup>+</sup>, 32), 148 (99), 147 (91), 135 (21), 123 (23), 121 (52), 115 (100), 97 (29), 63 (30). HRMS (EI<sup>+</sup>): Calc'd for C<sub>9</sub>H<sub>10</sub>OS [M<sup>+</sup>]: 166.0452; found = 166.0451.



***Tert*-butyldimethyl((1*R*,2*S*)-2-phenylcyclopent-3-enyloxy)silane (7).** Based on a literature protocol,<sup>13</sup> a solution of **4a** (100 mg, 0.62 mmol) in dry DCM (10 mL) was stirred at 0 °C under N<sub>2</sub>. *tert*-Butyldimethylsilyl chloride (207 mg, 1.37 mmol) and imidazole (127 mg, 1.87 mmol) were added. The reaction was allowed to stir overnight at room temperature. Water (5 mL) was added and the layers were decanted. The aqueous layer was extracted with DCM (3x15 mL), the combined organic layers were washed with brine, dried with MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to give an oil. The product was purified by column chromatography (10% EtOAc/Hex) to afford a colourless oil (152 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.43–7.28 (m, 5H), 5.90 (ddd, 1H, *J* = 6.1, 4.0, 2.1 Hz), 5.84 (ddd, 1H, *J* = 6.0, 4.0, 2.0 Hz), 4.35–4.31 (m, 1H), 3.86–3.83 (m, 1H), 2.82 (dddd, 1H, *J* = 16.2, 9.4, 7.0, 2.4 Hz), 2.47 (dddd, 1H, *J* = 16.4, 7.6, 5.5, 2.4 Hz), 0.96 (s, 9H), 0.14 (s, 6H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ: 143.7, 132.7, 129.6, 127.8, 127.7, 126.6, 82.6, 60.6, 26.1, 26.0, 18.3, -4.7 ppm. IR (CHCl<sub>3</sub>) *v*: 3060, 3029, 2956, 2929, 2857, 1471, 1361, 1252, 1113, 897 cm<sup>-1</sup>. HRMS (EI<sup>+</sup>): Calc'd for C<sub>13</sub>H<sub>17</sub>OSi [M<sup>+</sup>]: 217.1049; found: 217.1051.



**(2*S*,3*R*)-3-(*tert*-butyldimethylsilyloxy)-2-phenylpentane-1,5-diol.** Modified from a literature protocol,<sup>14</sup> cyclopentene **7** (162 mg, 1.12 mmol) was dissolved in dry DCM (36 mL) and MeOH (40 mL) and cooled down to -78 °C. A stream of ozone was bubbled through until solution turned blue, then N<sub>2</sub> was bubbled through until all the blue colour disappeared. Sodium borohydride (212 mg, 5.6 mmol) was added in four equal portions every 15 mins for the duration of one hour, while maintaining the temperature at -78 °C. The reaction was left to stir at room temperature until complete by TLC analysis. The solvent was removed under reduced pressure; the residue was retaken in EtOAc (25 mL) and was washed with brine. The aqueous wash was extracted with EtOAc (5x25 mL), and the combined organic layers were dried with MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to give an oil, which was purified using column chromatography (50 to 100% EtOAc/Hex, then 5% MeOH/DCM) to give the diol as a white solid (100 mg, 55%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ: 7.27–7.17 (m, 5H), 4.14 (ddd, 1H, *J* = 9.8, 5.1, 1.6 Hz), 4.03 (dd, 1H, *J* = 10.9, 7.4 Hz), 3.86 (dd, 1H, *J* = 10.9, 7.4 Hz), 3.60 (td, 2H, *J* = 7.4, 1.4 Hz), 3.01 (ddd, 1H, *J* = 11.6, 7.3, 4.4 Hz), 0.084 (s, 9H), 0.03 (s, 6H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ: 143.9, 133.8, 133.2, 131.7, 77.3, 68.2, 64.5, 57.4, 40.4, 30.6, 22.7, -0.5 ppm. IR (CHCl<sub>3</sub>) *v*: 3338, 2956, 2925, 2883, 2852, 1473, 1251, 1098, 1031, 915 cm<sup>-1</sup>. HRMS (EI<sup>+</sup>): Calc'd for C<sub>13</sub>H<sub>19</sub>O<sub>2</sub>Si [M-75]<sup>+</sup>: 235.1154; found 235.1165.

**(2*S*,3*R*)-3-(*tert*-butyldimethylsilyloxy)-2-phenylpentane-1,5-diyl dimethanesulfonate (10).** Following a literature protocol,<sup>15</sup> the above diol (55 mg, 0.31 mmol) was dissolved in dry DCM (8 mL) under N<sub>2</sub> at 0 °C. Triethylamine (0.18

<sup>13</sup> Knapp, S.; Yu, Y. *Org. Lett.* **2007**, *9*, 1359–1362.

<sup>14</sup> Majetich, G.; Grieco, A. P.; Nishizawa, M. *J. Org. Chem.* **1977**, *42*, 2327–2329.

<sup>15</sup> Marvin, C. C.; Voight, A. E.; Burke, D. S. *Org. Lett.* **2007**, *9*, 5357–5359.

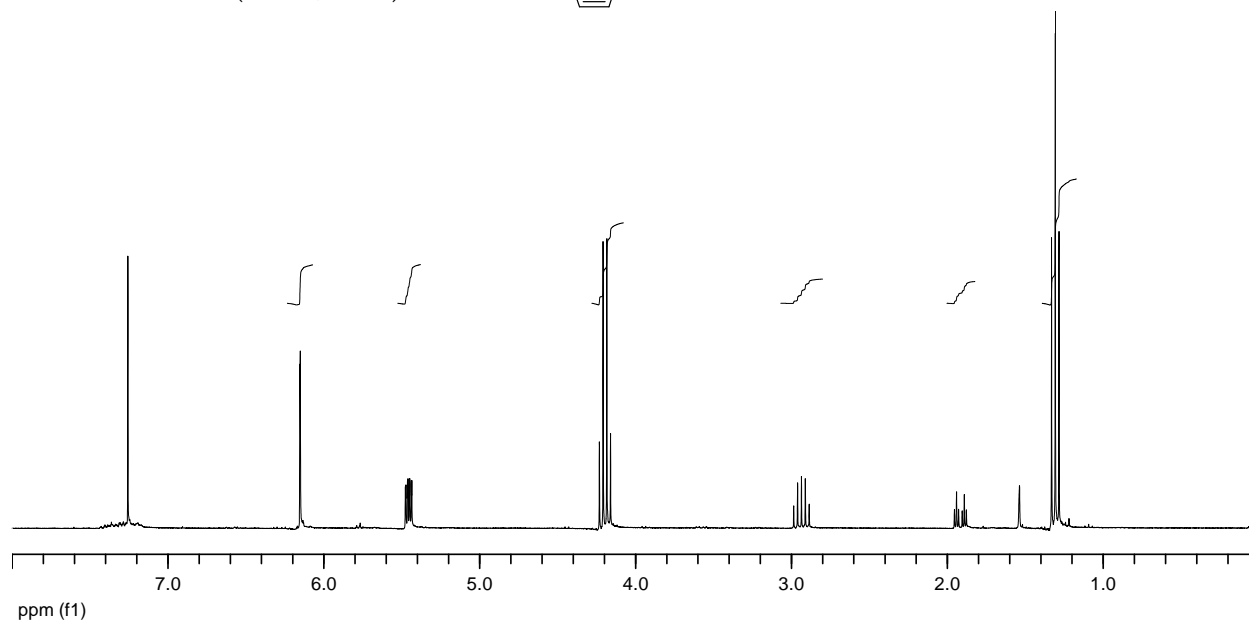
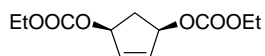
mL 1.3 mmol) and methanesulfonyl chloride (0.05 mL, 0.67 mmol) were added to the flask and the reaction was allowed to warm up to room temperature and stirred for 16 h. Water (30 mL) was added to quench the reaction, and the aqueous layer was extracted with DCM (5x20 mL). The combined organic layers were dried with MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to give **10** as a brown oil (135 mg, 100%) which was used without further purification in the next step.

**(3*S*,4*R*)-1-benzyl-4-(tert-butyldimethylsilyloxy)-3-phenylpiperidine (8).** Bissulfonate **10** (135 mg, 0.29 mmol) was dissolved in dry dioxane (15 mL). Benzylamine (0.473 mL, 4.34 mmol) and triethylamine (0.081 mL, 0.58 mmol) were added and the reaction was allowed to stir at 80 °C overnight. The reaction was washed with H<sub>2</sub>O (20 mL) and 3M NaOH (2 mL). The aqueous layer was extracted with Et<sub>2</sub>O (3x25 mL). The combined organic layers were washed with brine, dried with MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to give a red oil, which was purified using column chromatography (40% EtOAc/Hex) to give piperidine **8** as a red oil (35 mg, 32%). **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ: 7.84-7.64 (m, 10H), 4.12 (td, 1H, J = 9.8, 4.8 Hz), 4.04 (d, 2H, J = 2.8 Hz), 3.44 (dt, 2H, J = 11.4, 1.7 Hz), 3.32-3.24 (m, 2H), 2.78-2.60 (m, 2H), 2.43-2.19 (m, 2H), 1.18 (s, 9H), 0.33 (s, 6H) ppm. **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ: 147.8, 134.6, 134.2, 133.8, 133.6, 132.6, 132.0, 80.0, 68.3, 64.0, 57.8, 56.7, 40.8, 31.2, 23.4, 0.9 ppm. **IR** (CHCl<sub>3</sub>) ν: 3029, 2627, 2855, 2801, 1495, 1472, 1361, 1252, 1108, 835 cm<sup>-1</sup>. **HRMS** (EI<sup>+</sup>): Calc'd for C<sub>24</sub>H<sub>35</sub>NOSi [M]<sup>+</sup>: 381.2488; found: 381.2469.

## SPECTRA

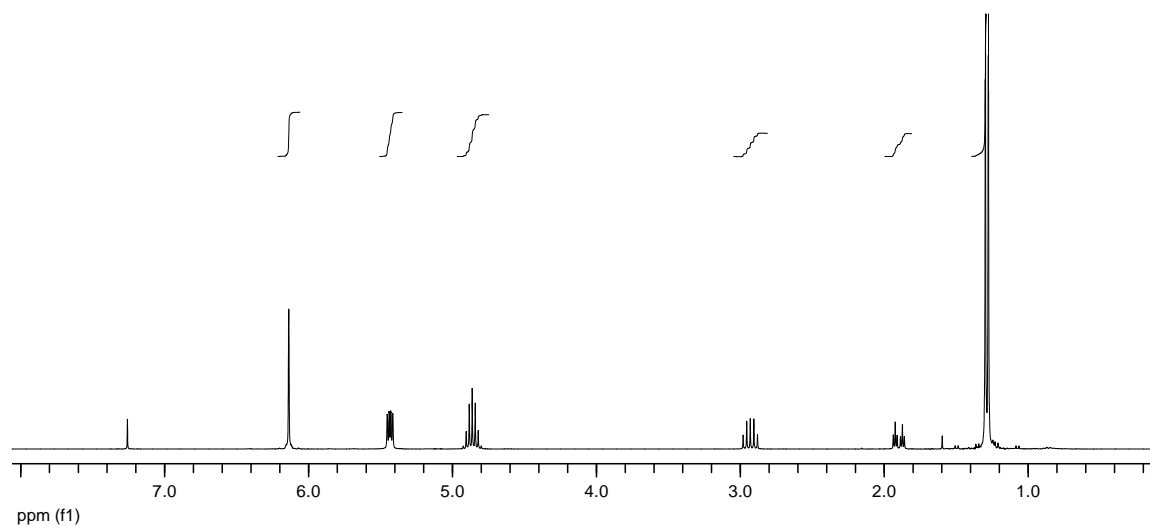
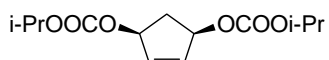
### (1a): *cis*-1,4-Diethylcyclopent-2-enedicarboxylate

$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ , 25 °C):



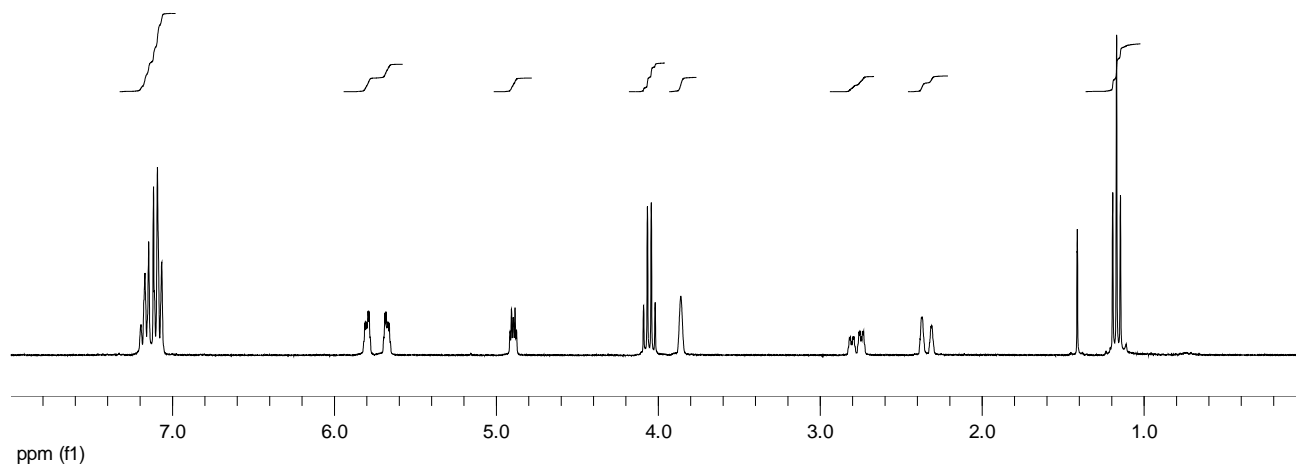
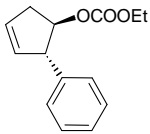
### (1aa): *cis*-1,4-Diisopropylcyclopent-2-enedicarboxylate

$^1\text{H}$  NMR 400 MHz ( $\text{CDCl}_3$ , 25 °C):



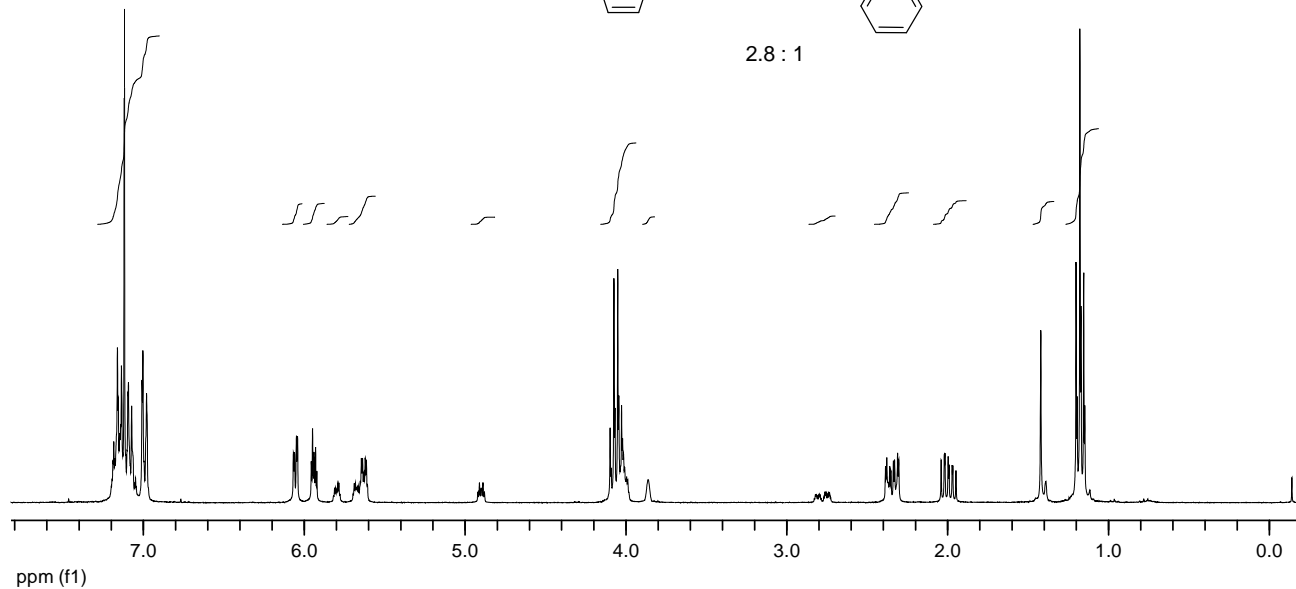
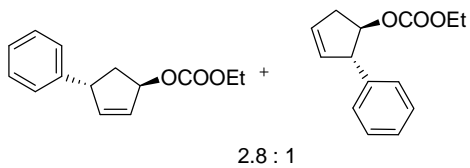
**(2a): (1R, 2S)-trans-2-phenylcyclopent-3-enyl-ethylcarbonate**

$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ , 25 °C):



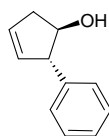
**(3a + 2a): (1R, 2S)-trans-2-phenylcyclopent-3-enyl-ethylcarbonate**

$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ , 25 °C):

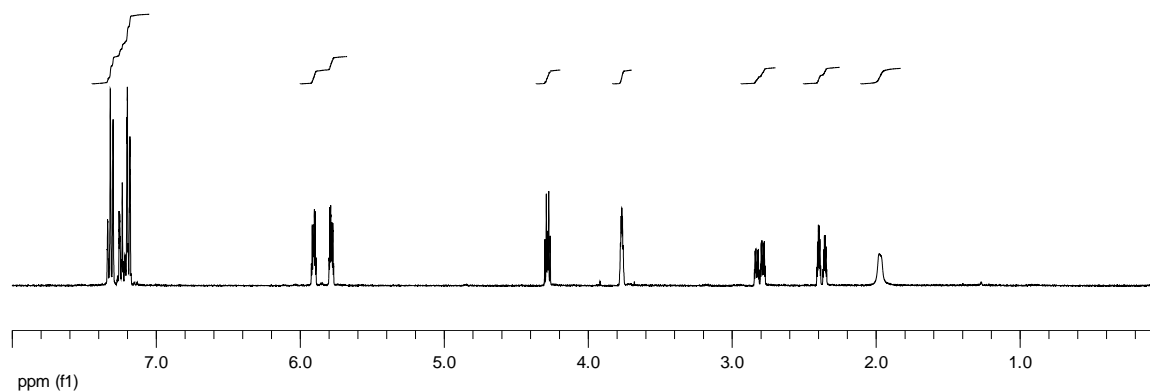




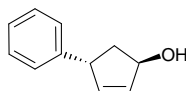
**(4a) : (1R, 2S)-trans-2-phenylcyclopent-3-enol**



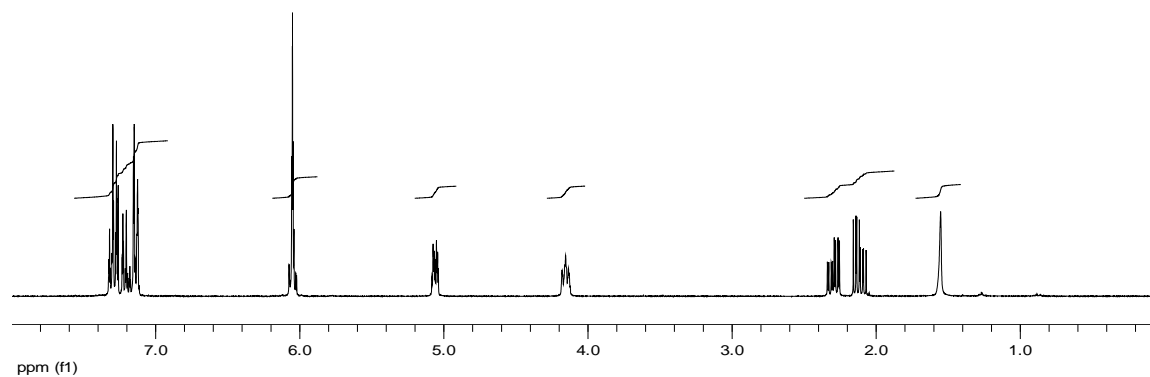
$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):



**(5a) : (1R, 4R)-trans-4-phenylcyclopent-2-enol**

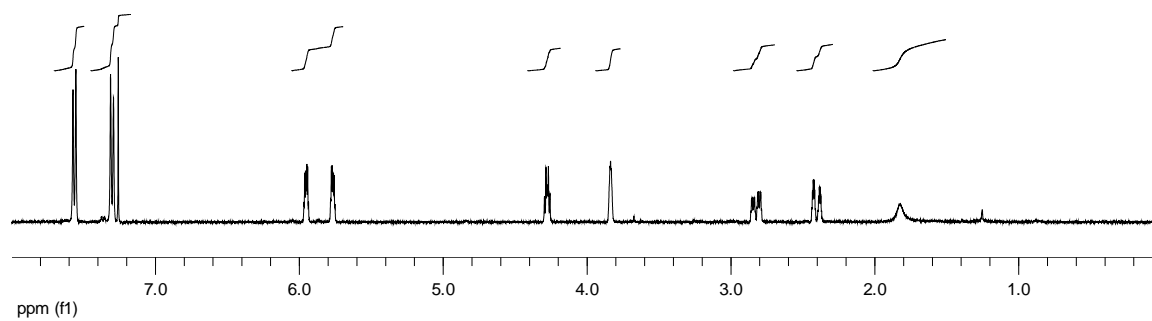
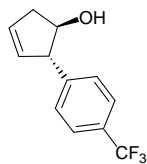


$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ , 25  $^\circ\text{C}$ ):

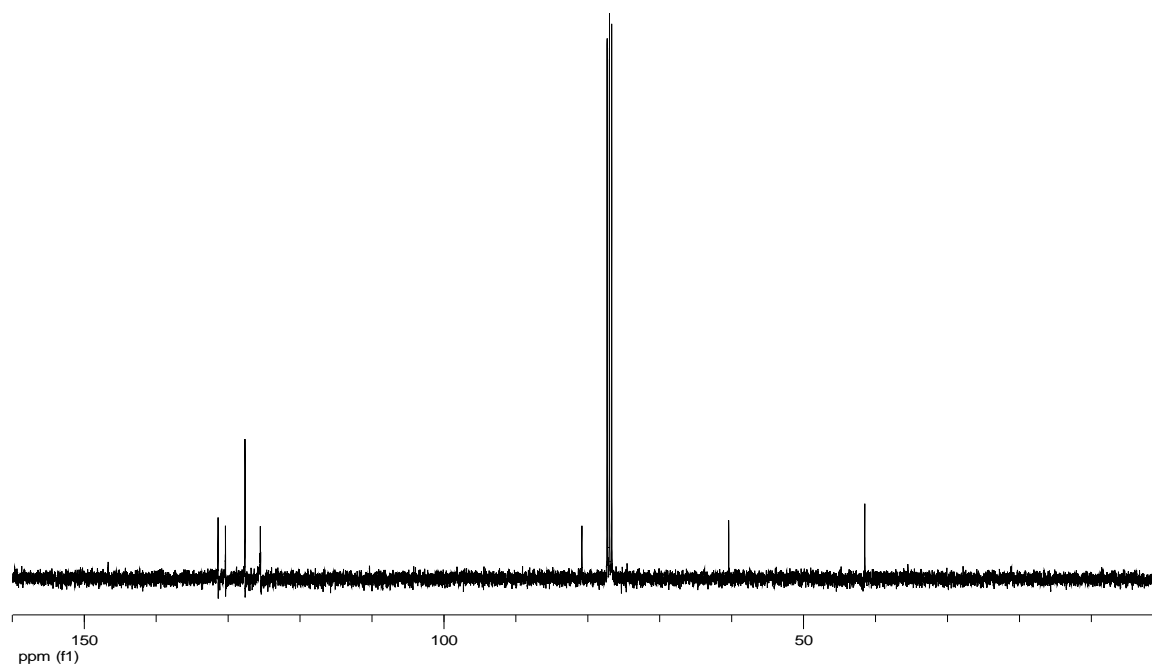


**(4b) : (1R,2S)-trans-2-(4'-Trifluoromethylphenyl)-cyclopent-2-enol.**

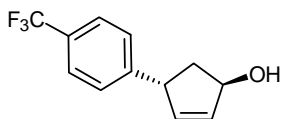
**<sup>1</sup>H NMR 300 MHz (CDCl<sub>3</sub>, 25 °C):**



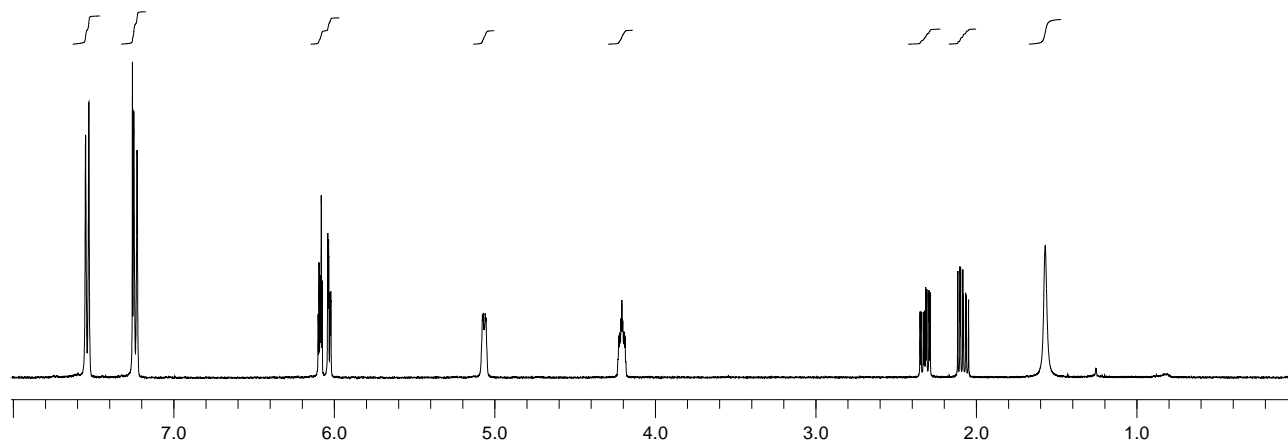
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



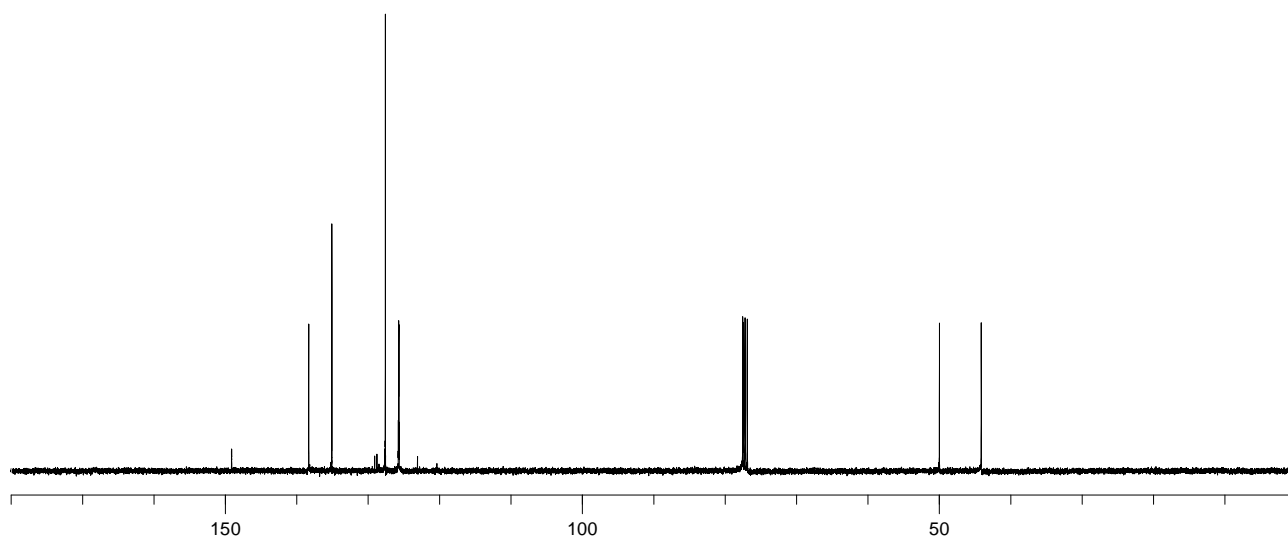
**(5b): *trans*-(1*R*,4*R*)-4-(4-Trifluoromethylphenyl)-cyclopent-2-enol.**



**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**

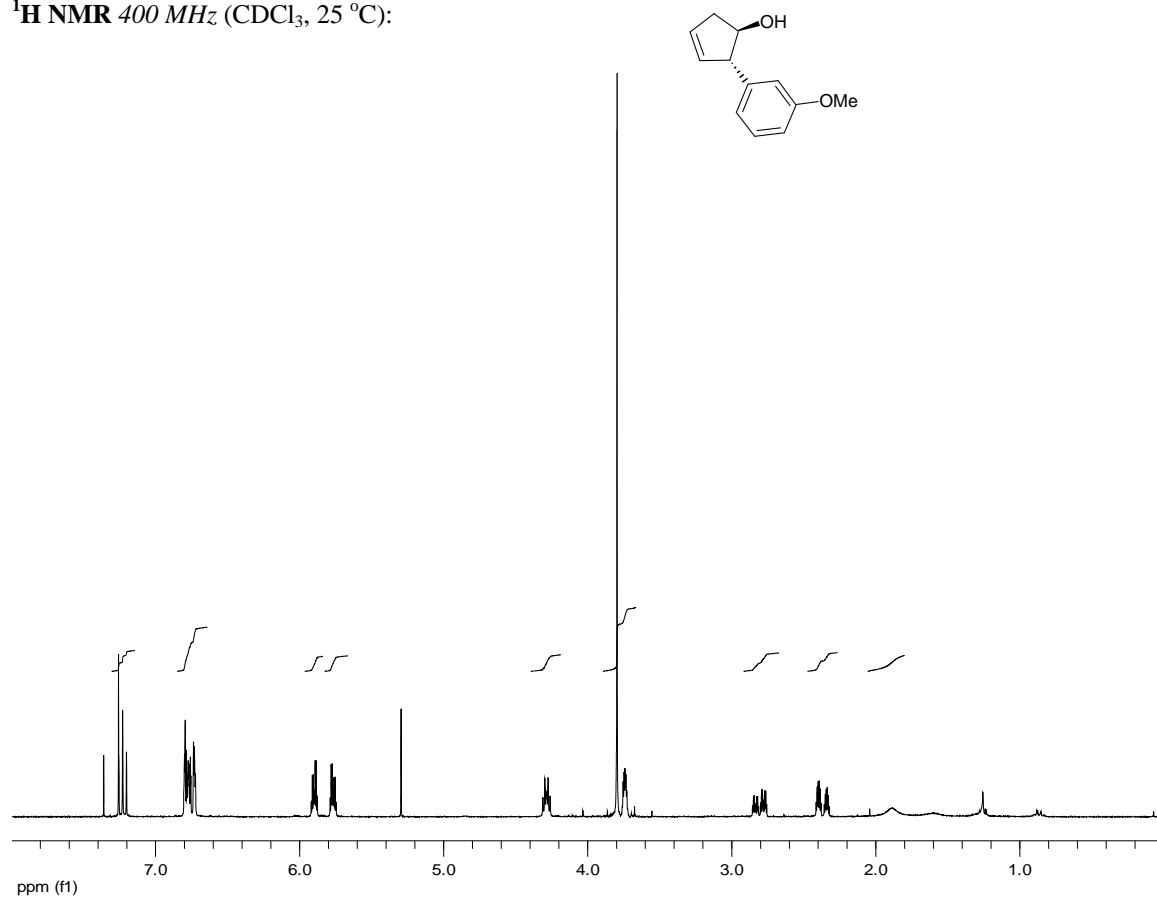


**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**

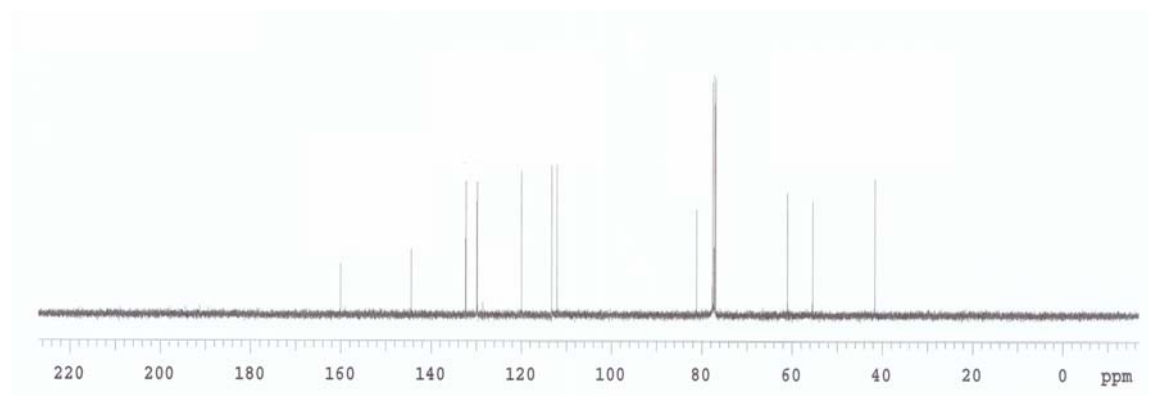


**(4l): (1R,2S)-trans-2-(3-Methoxyphenyl)-cyclopent-3-enol.**

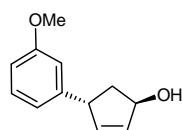
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



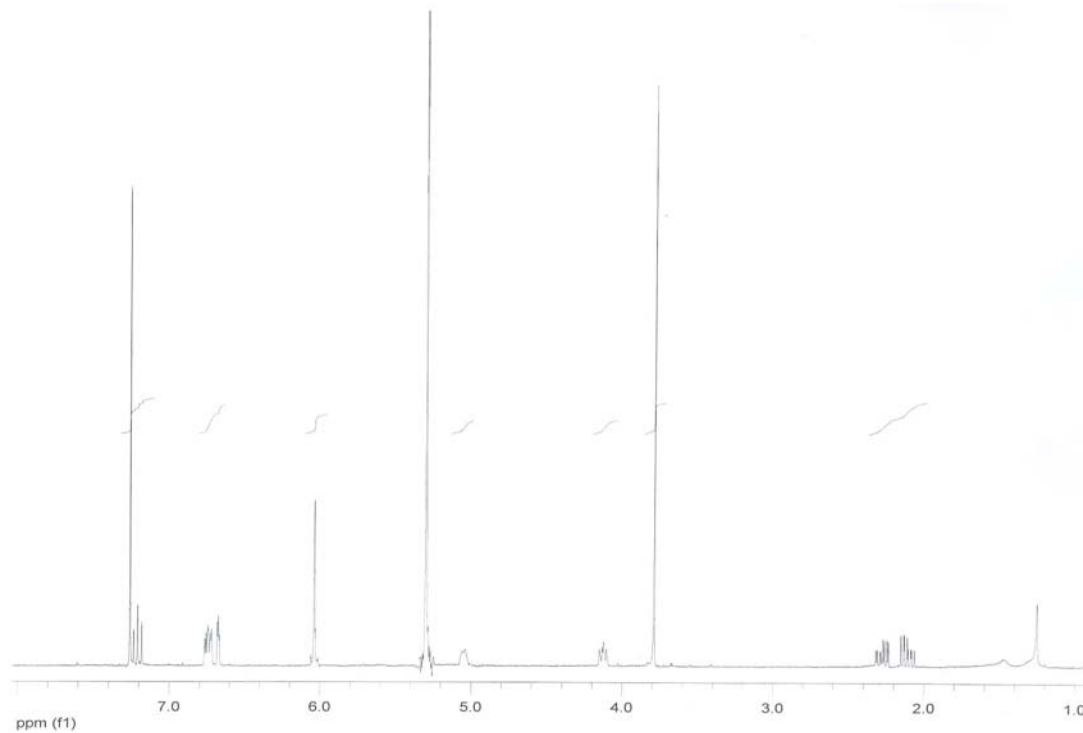
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



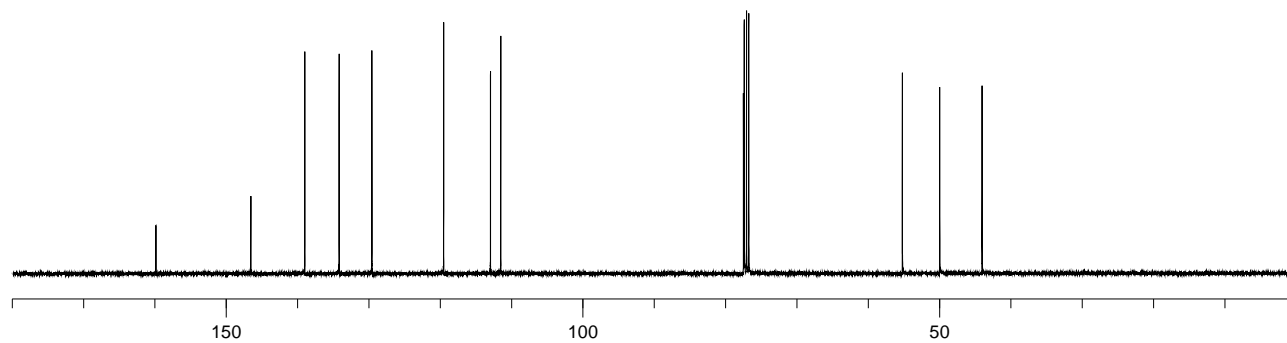
**(5l): *trans*-(1*R*,4*R*)-4-(3-Methoxyphenyl)-cyclopent-2-enol.**



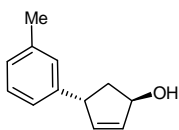
**$^1\text{H}$  NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



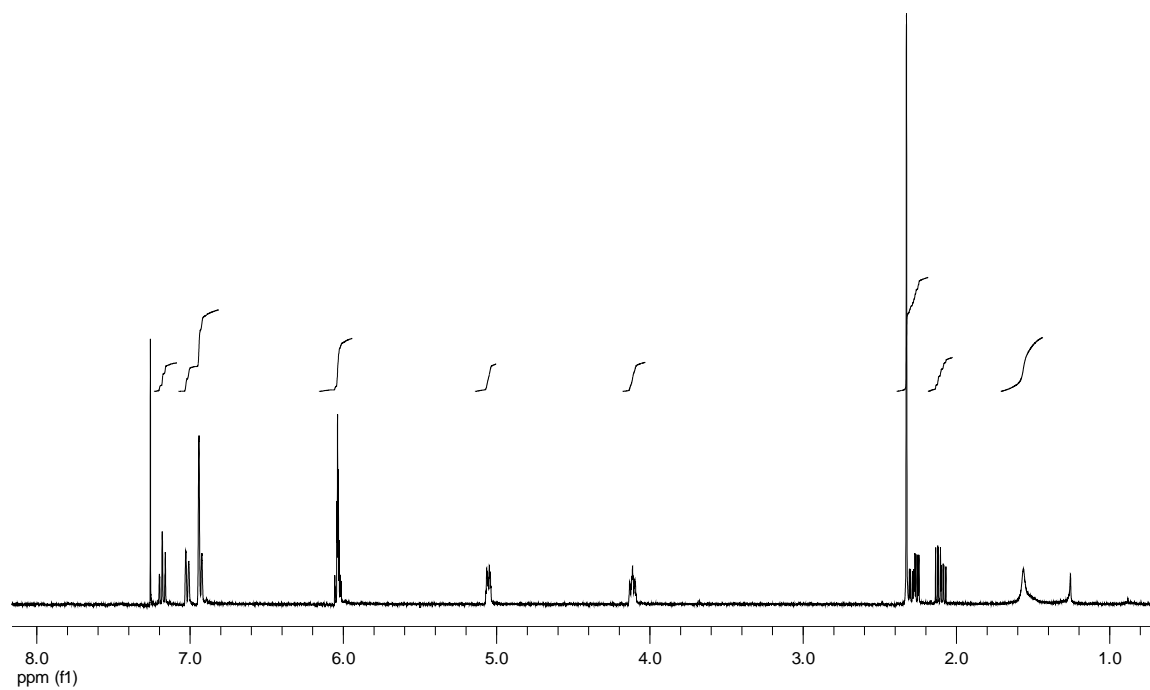
**$^{13}\text{C}$  NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



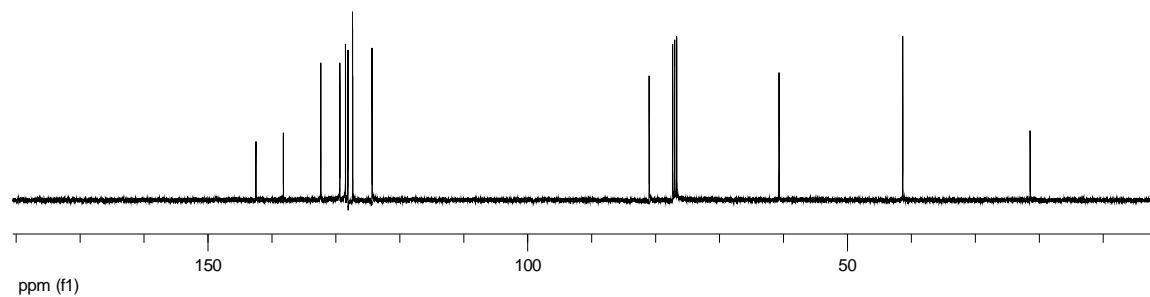
**(5m): *trans*-(1*R*,4*R*)-4-(3-Methylphenyl)-cyclopent-2-enol.**



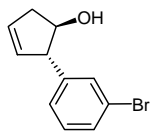
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



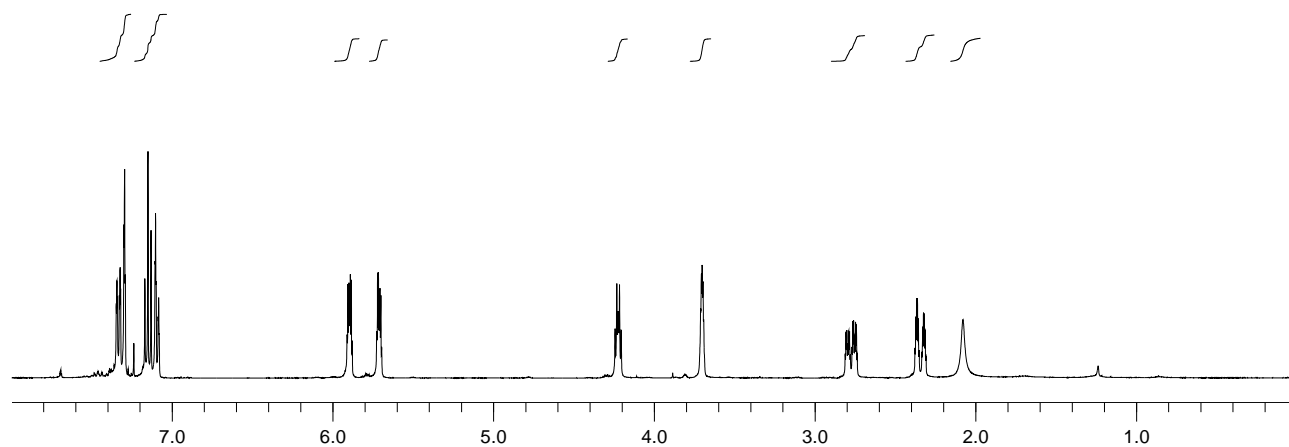
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



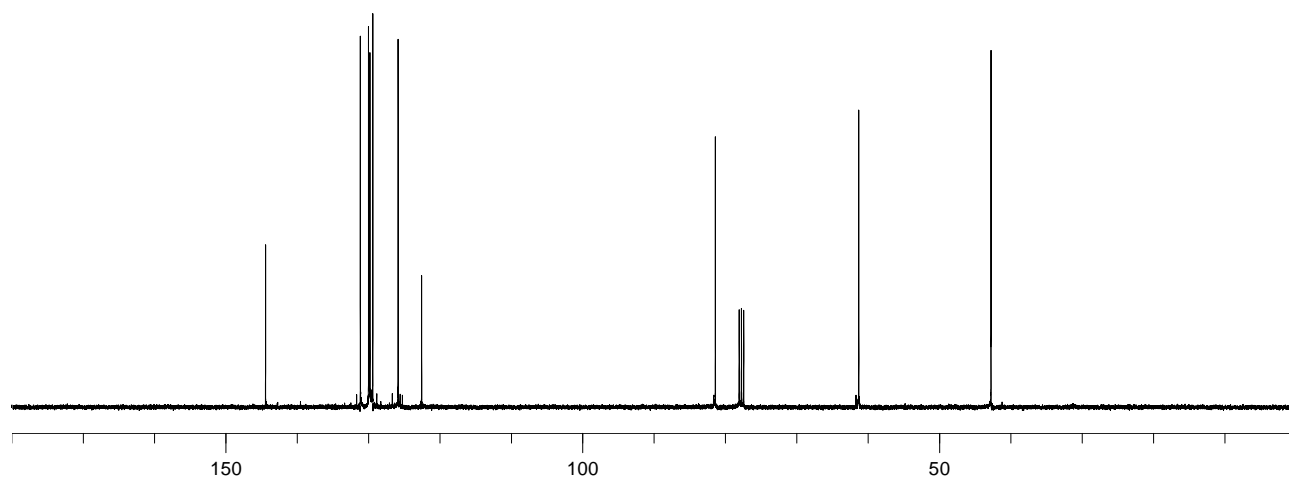
**(4q):** *trans*-(1*R*,2*S*)-2-(3-Bromophenyl)-cyclopent-3-enol.



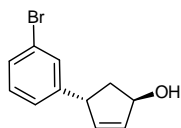
**<sup>1</sup>H NMR** 400 MHz (CDCl<sub>3</sub>, 25 °C):



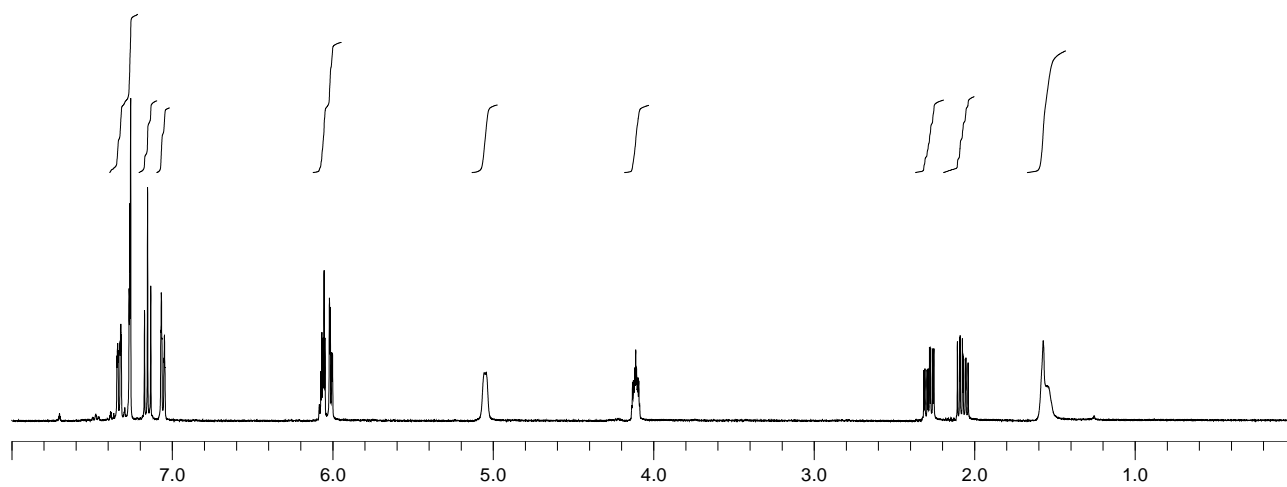
**<sup>13</sup>C NMR** 100 MHz (CDCl<sub>3</sub>, 25 °C):



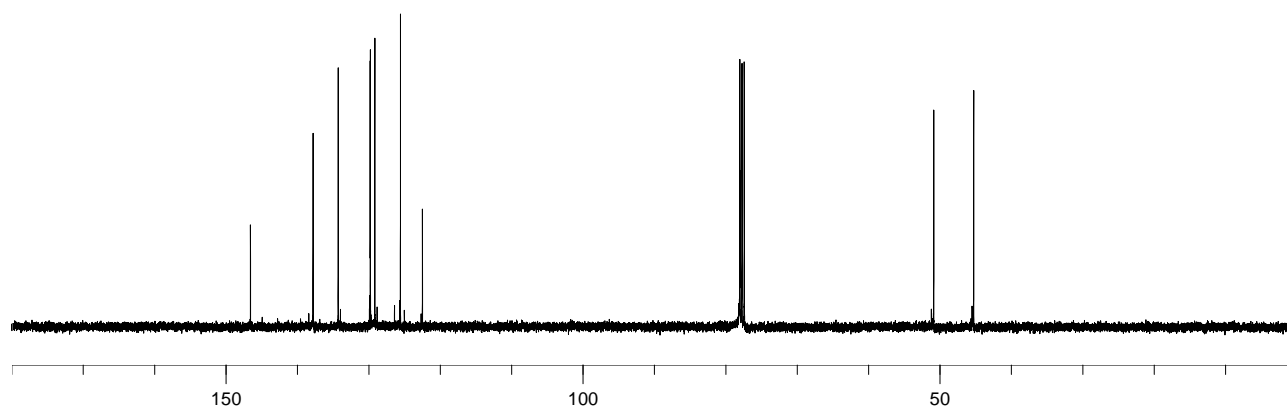
**(5q): *trans*-(1*R*,4*R*)-4-(3-Bromophenyl)-cyclopent-2-enol.**



**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**

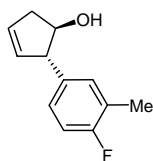


**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**

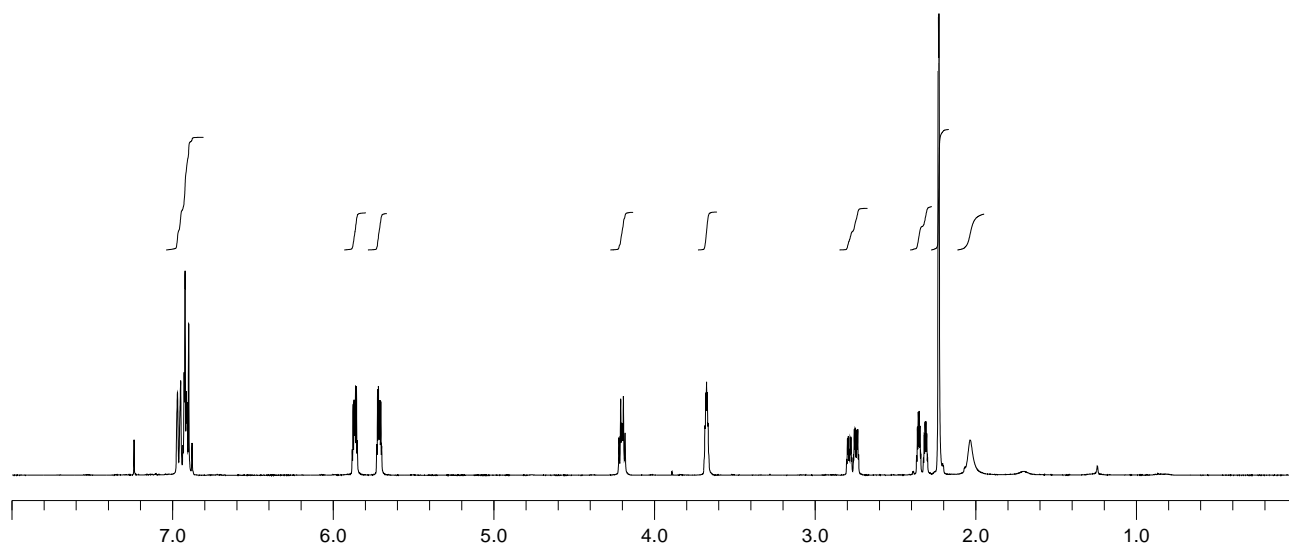




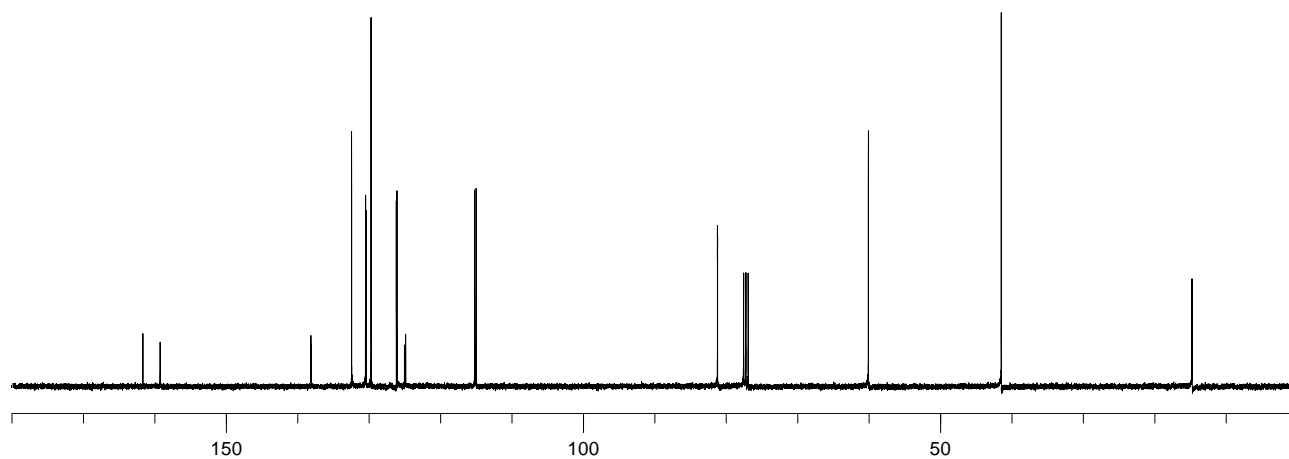
**(4r): *trans*-(1*R*,2*S*)-2-(4-Fluoro-3-methylphenyl)-cyclopent-3-enol.**



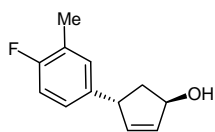
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



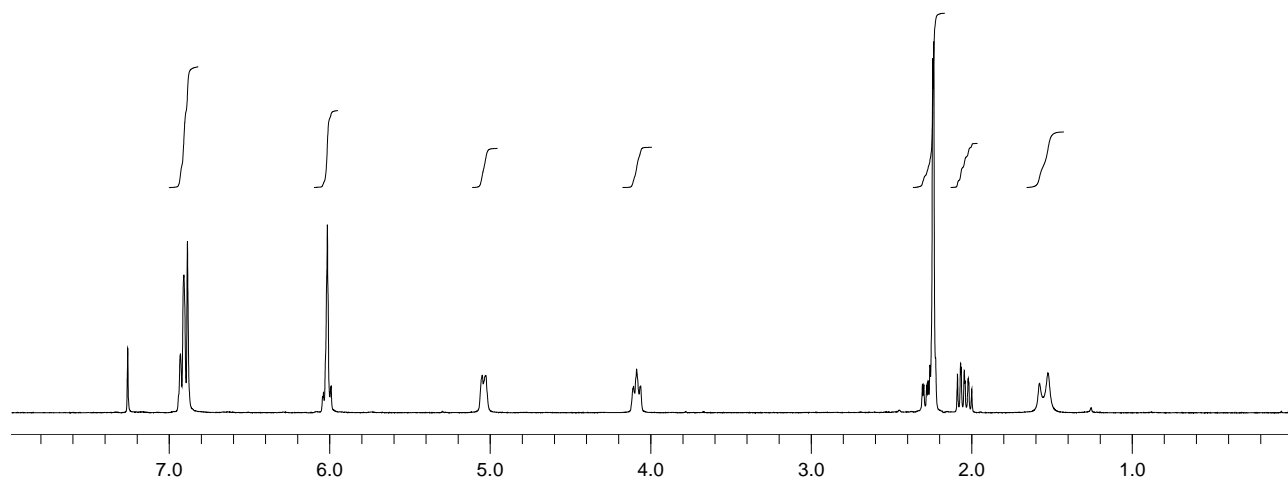
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



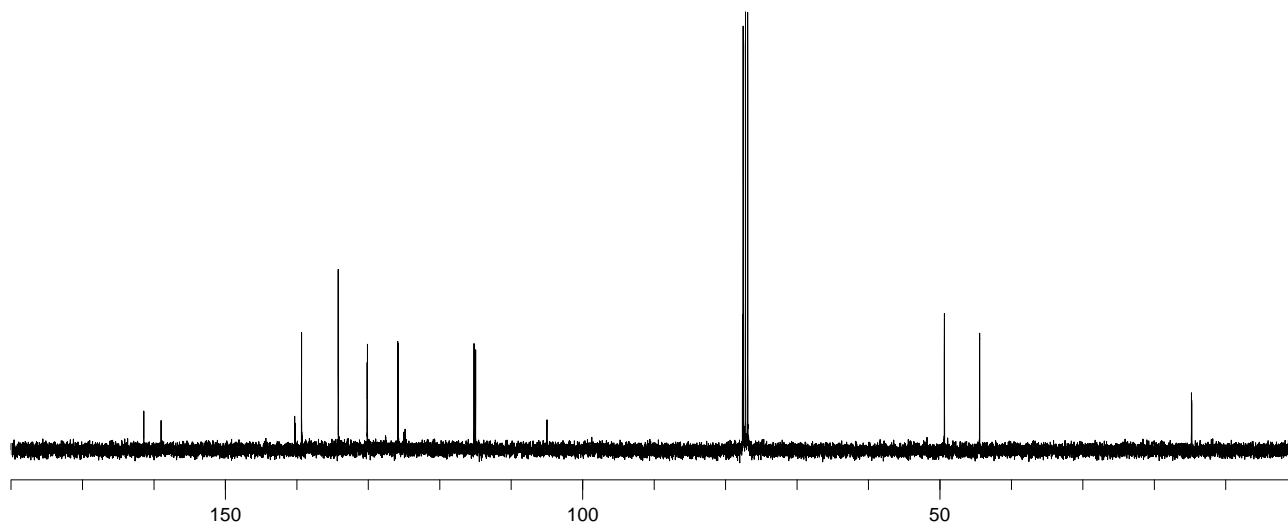
**(5r): *trans*-(1*R*,4*R*)-4-(4-Fluoro-3-methylphenyl)-cyclopent-2-enol.**



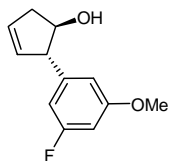
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



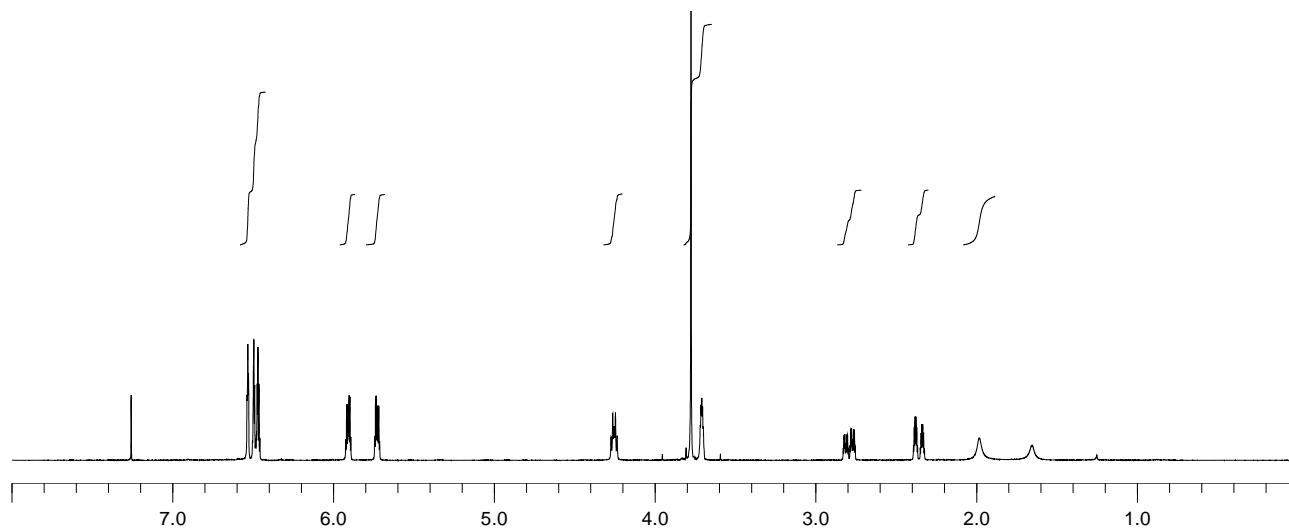
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



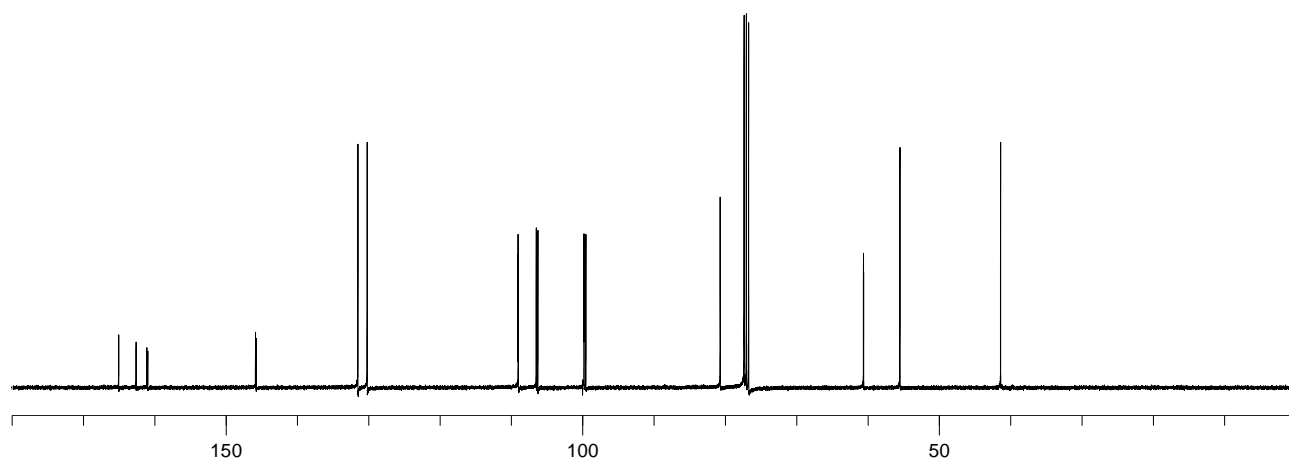
**(4s): *trans*-(1*R*,2*S*)-2-(3-Fluoro-5-methoxyphenyl)-cyclopent-3-enol.**



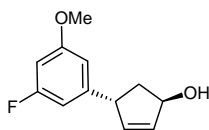
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



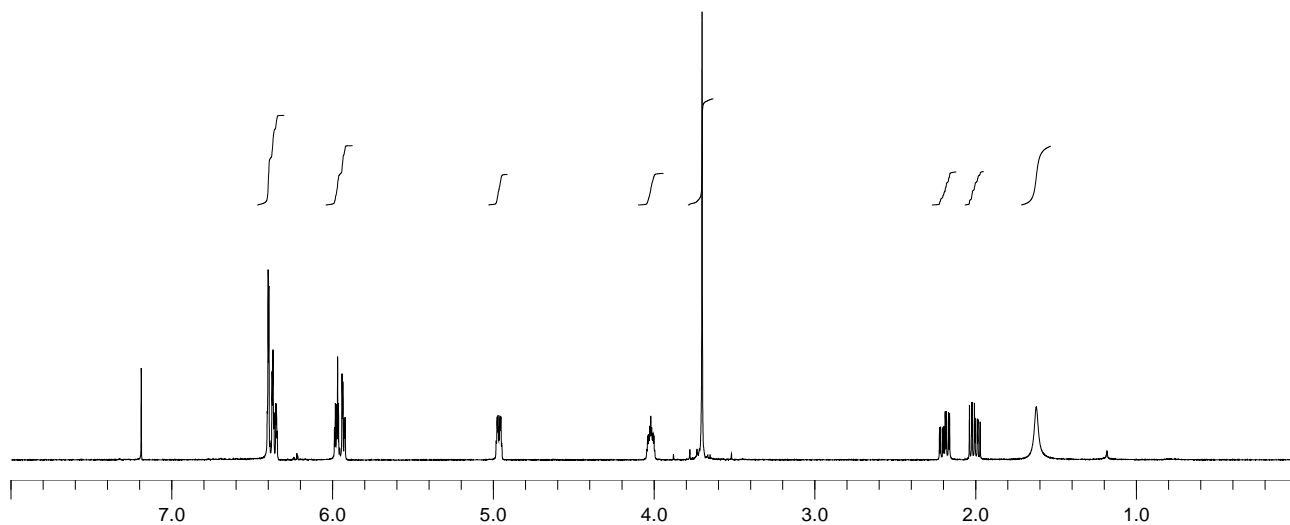
**$^{13}\text{C}$  NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



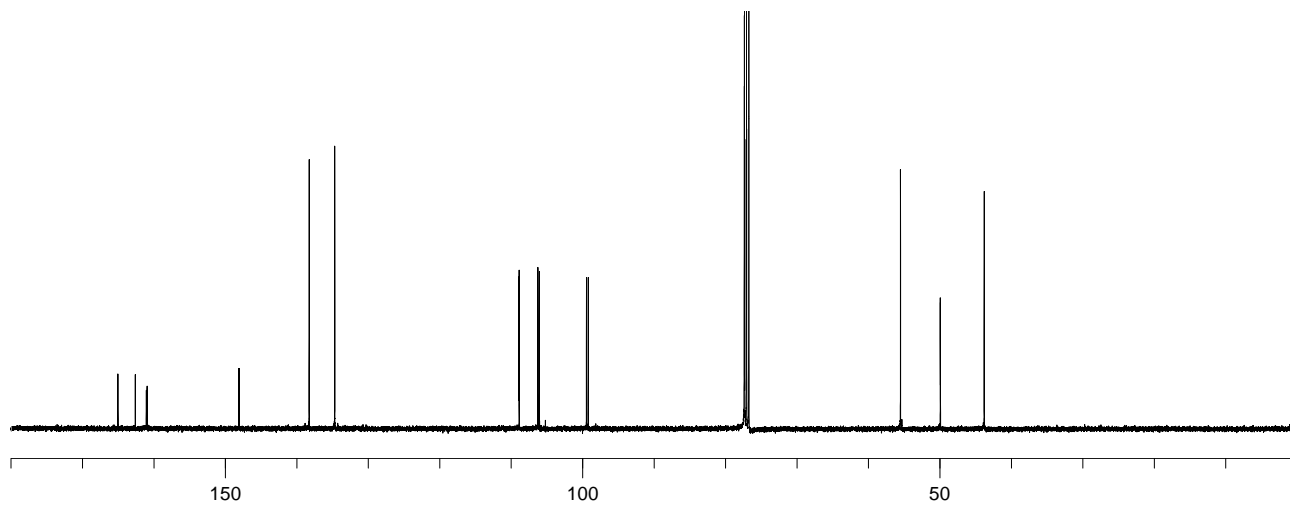
**(5s): *trans*-(1*R*,4*R*)-4-(3-Fluoro-5-methoxyphenyl)-cyclopent-2-enol.**



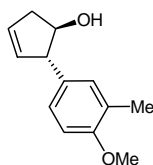
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



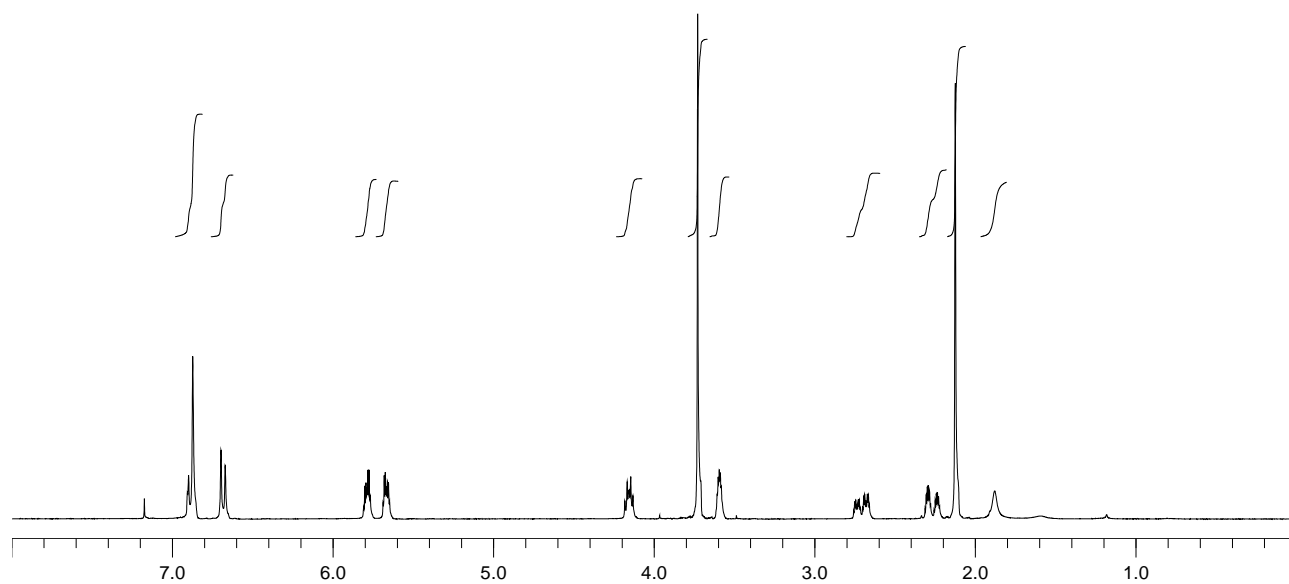
**<sup>13</sup>C NMR** 100 MHz (CDCl<sub>3</sub>, 25 °C):



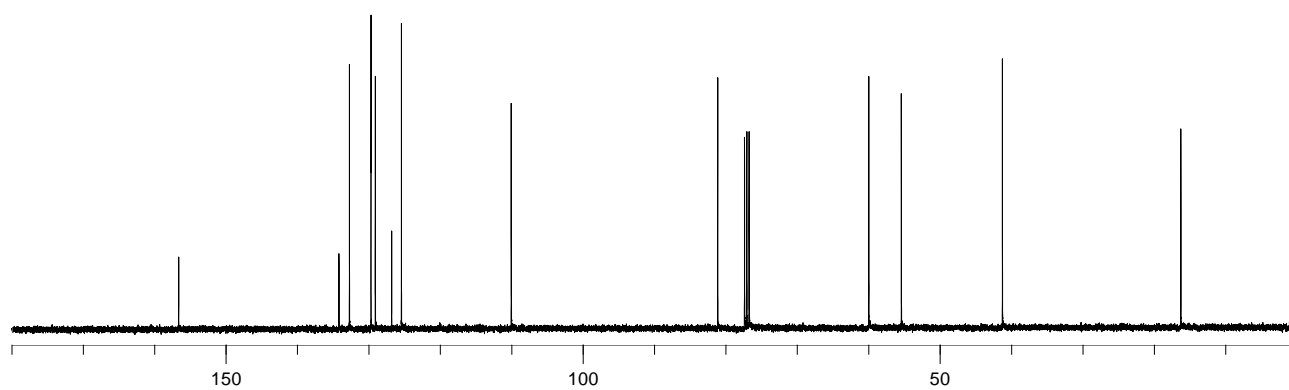
**(4t): *trans*-(1*R*,2*S*)-2-(4-Methoxy-3-methylphenyl)-cyclopent-3-enol.**



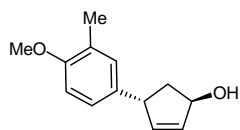
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



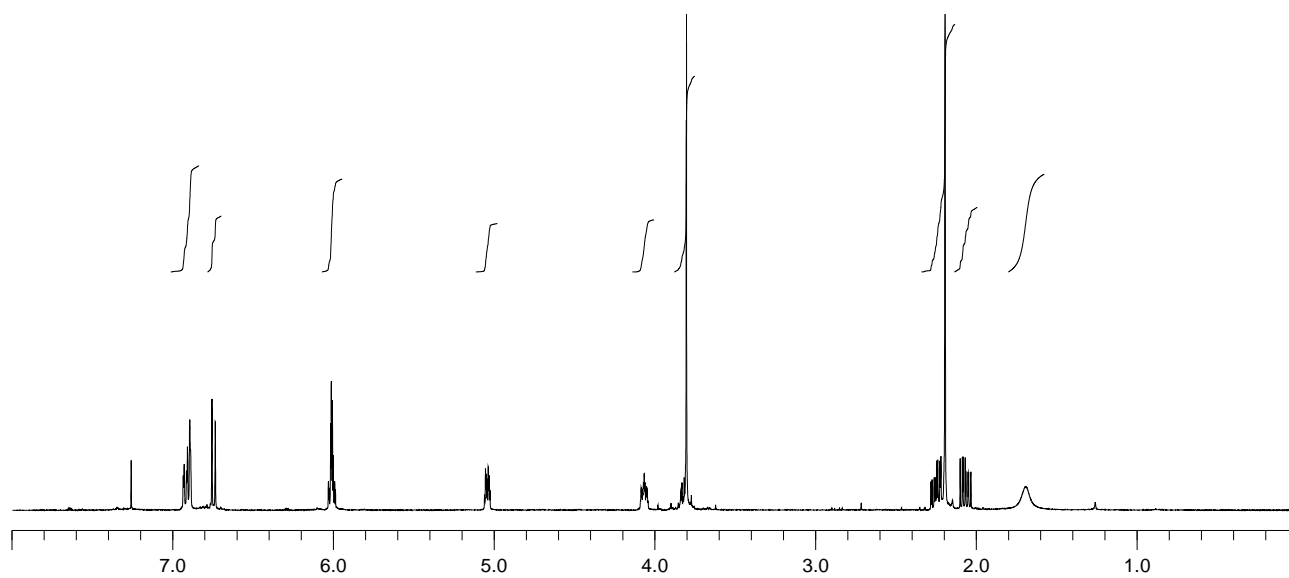
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



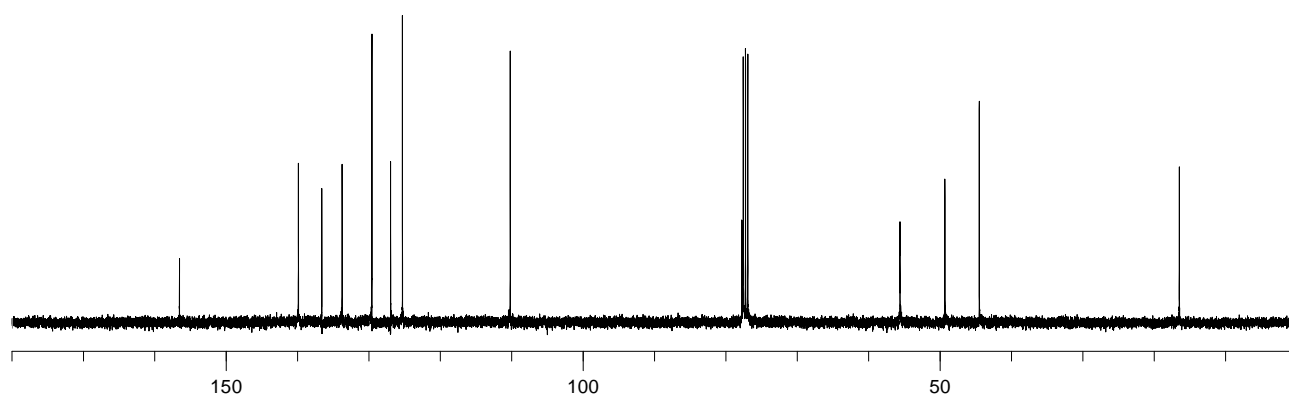
**(5t): *trans*-(1*R*,4*R*)-4-(4-Methoxy-3-methylphenyl)-cyclopent-2-enol.**



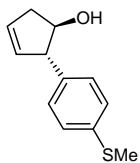
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



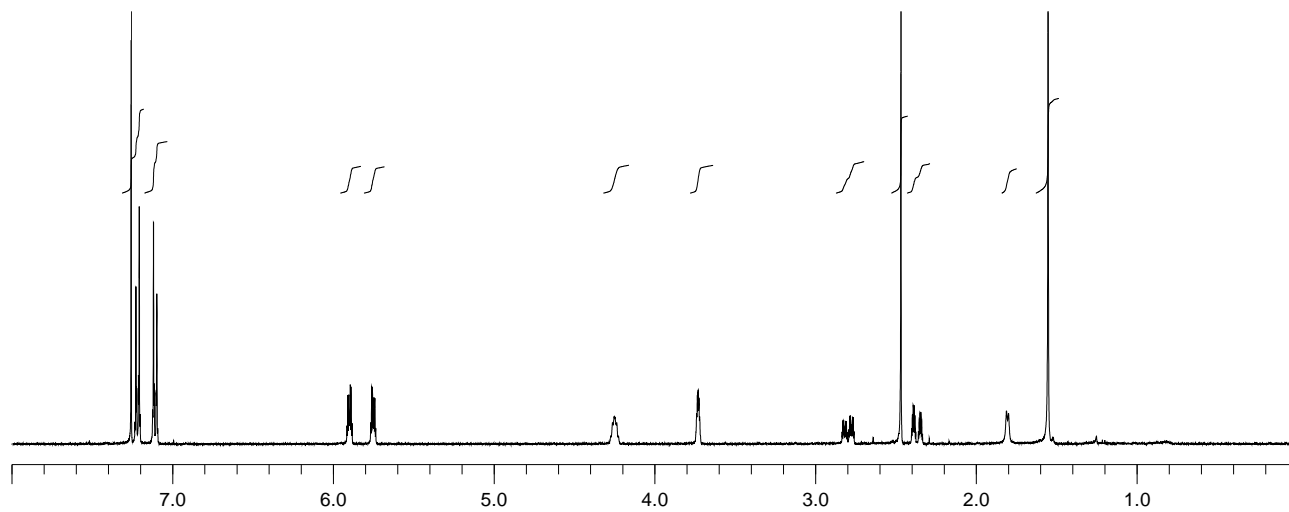
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



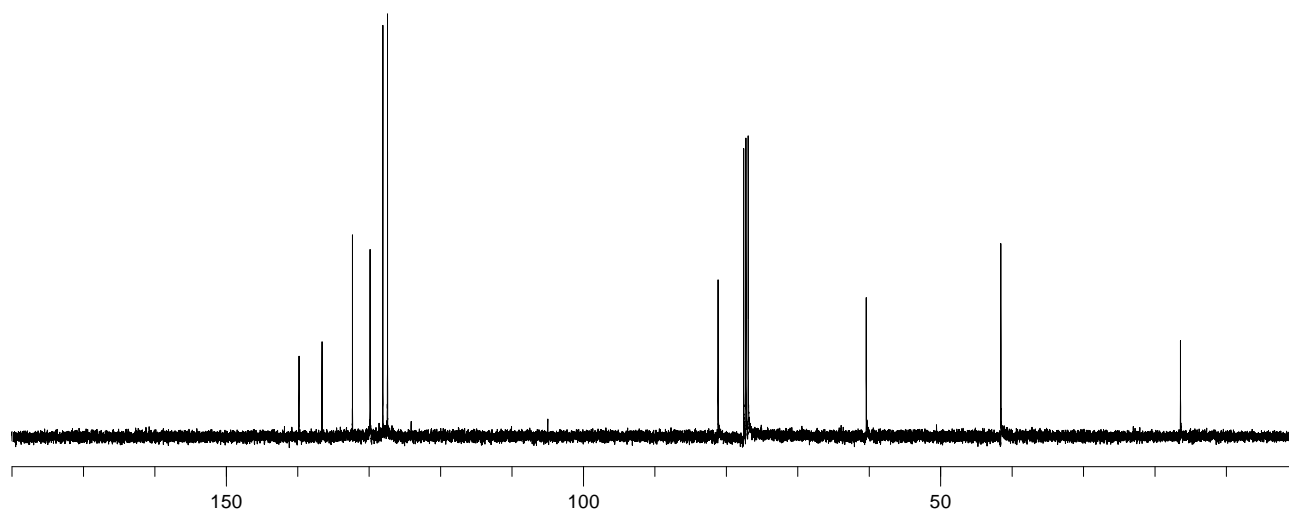
**(4u):** *trans*-(1*R*,2*S*)-2-(4-Methylsulfonylphenyl)-cyclopent-3-enol.



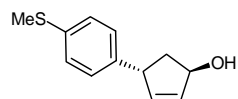
**<sup>1</sup>H NMR** 400 MHz (CDCl<sub>3</sub>, 25 °C):



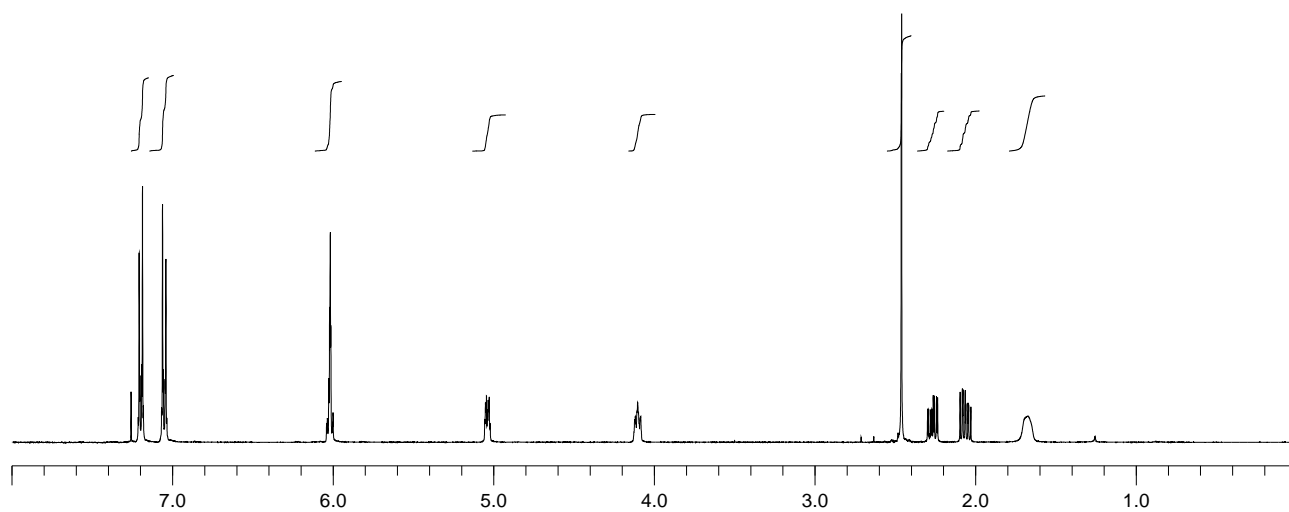
**<sup>13</sup>C NMR** 100 MHz (CDCl<sub>3</sub>, 25 °C):



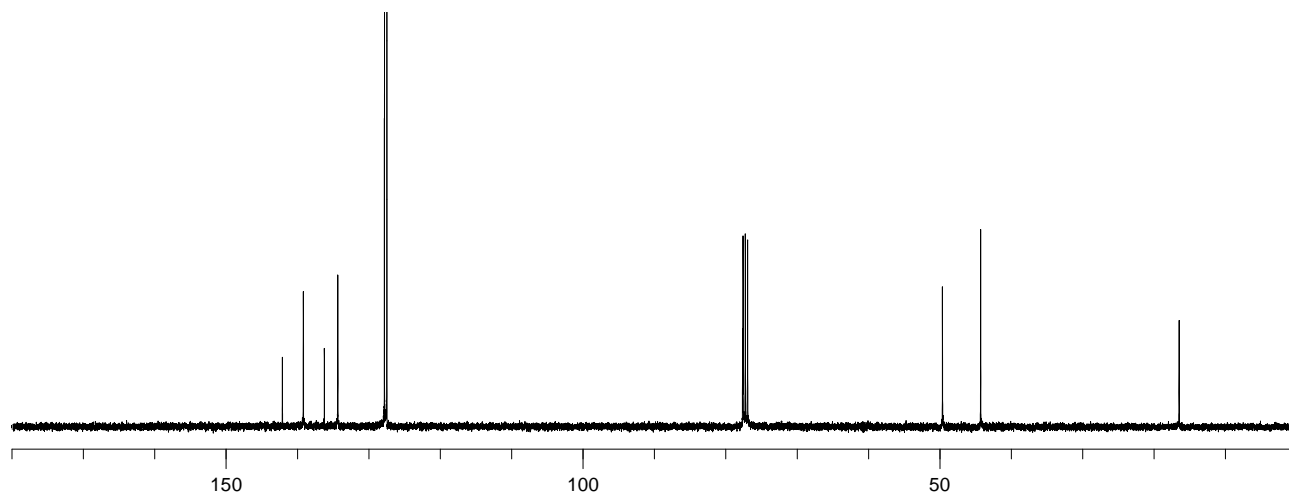
**(5u):** *trans*-(1*R*,4*R*)-4-(4-Methylsulfanylphenyl)-cyclopent-2-enol.



**<sup>1</sup>H NMR** 400 MHz (CDCl<sub>3</sub>, 25 °C):

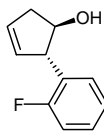


**<sup>13</sup>C NMR** 100 MHz (CDCl<sub>3</sub>, 25 °C):

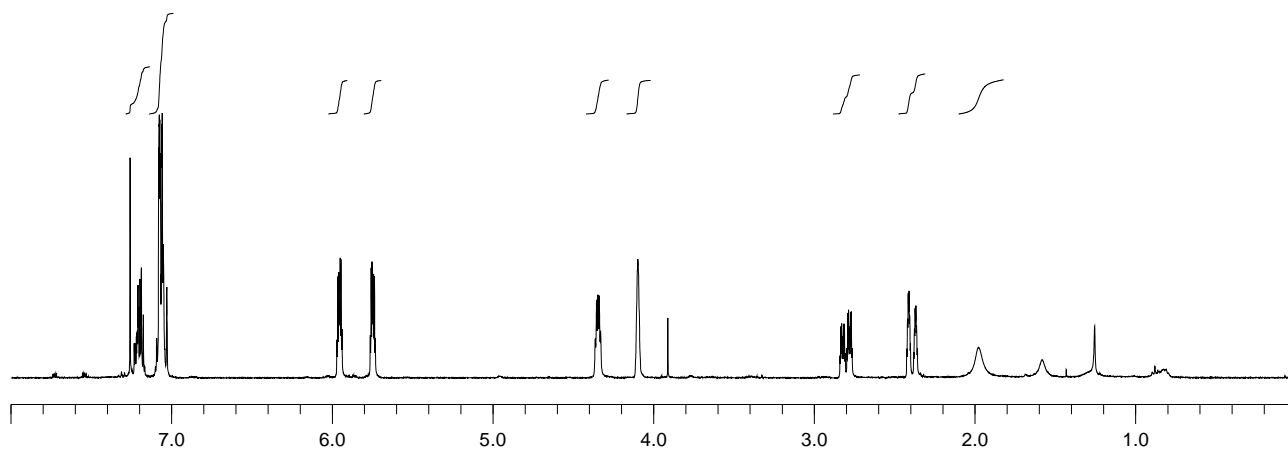




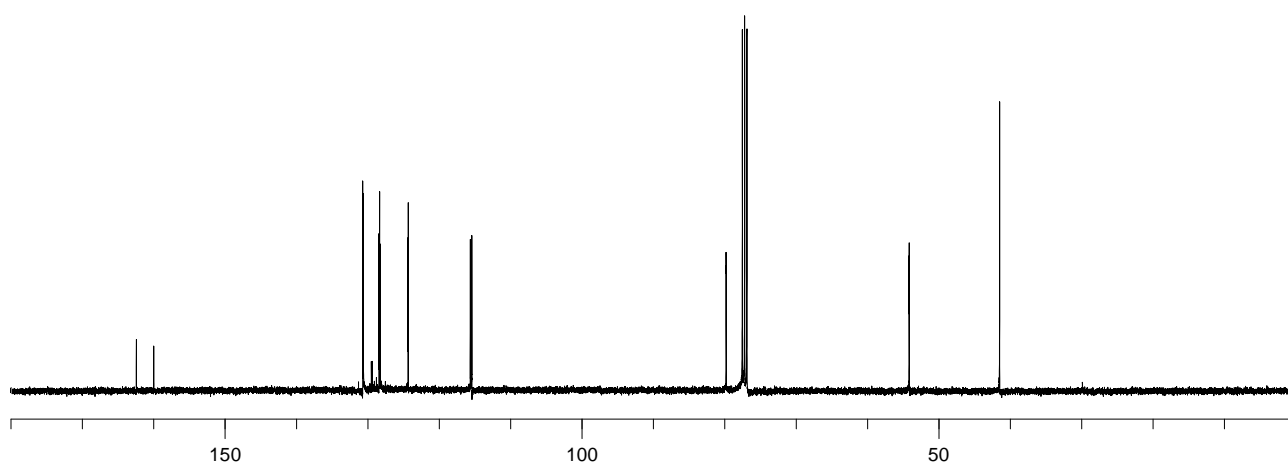
**(4v): *trans*-(1*R*,2*S*)-2-(2-Fluorophenyl)-cyclopent-3-enol.**



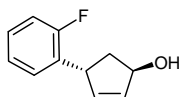
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



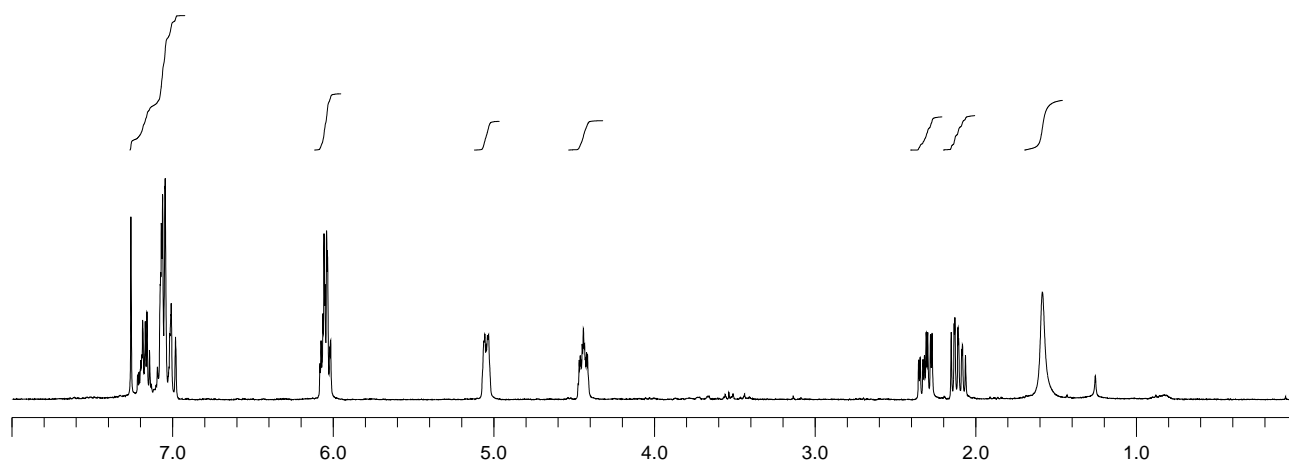
**$^{13}\text{C}$  NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



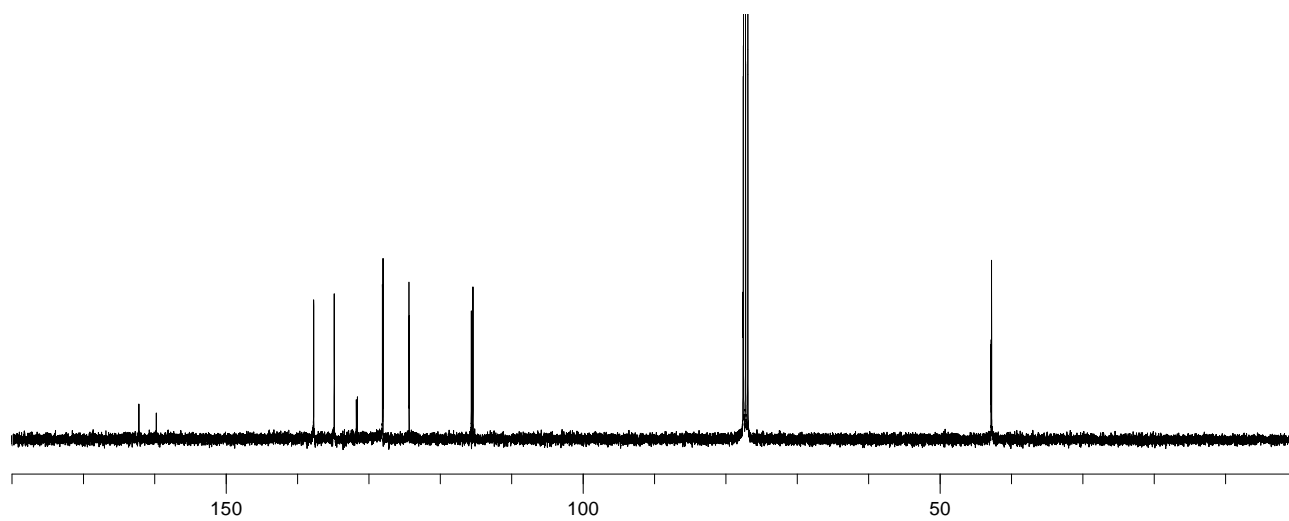
**(5v): *trans*-(1*R*,4*R*)-4-(2-Fluorophenyl)-cyclopent-2-enol.**



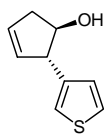
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



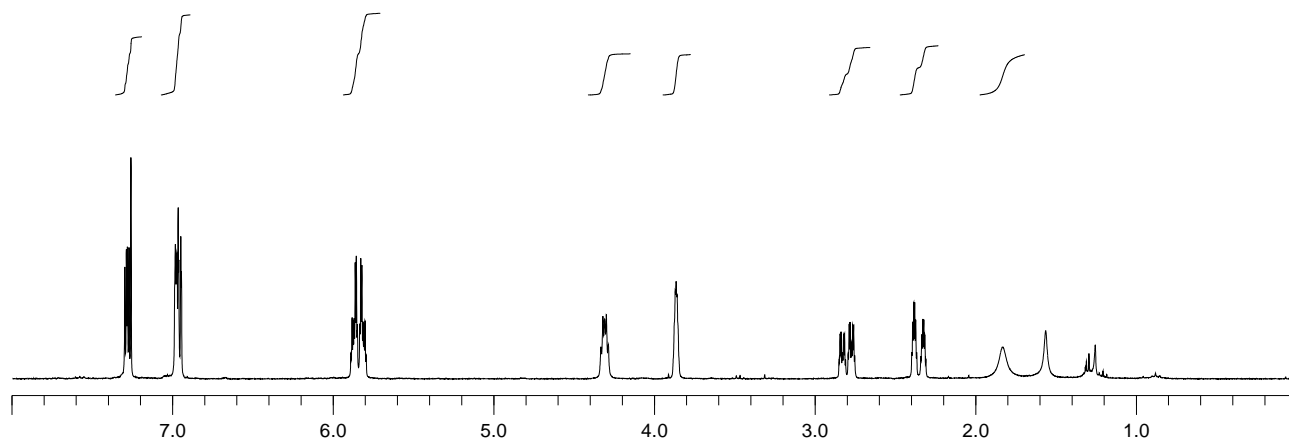
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



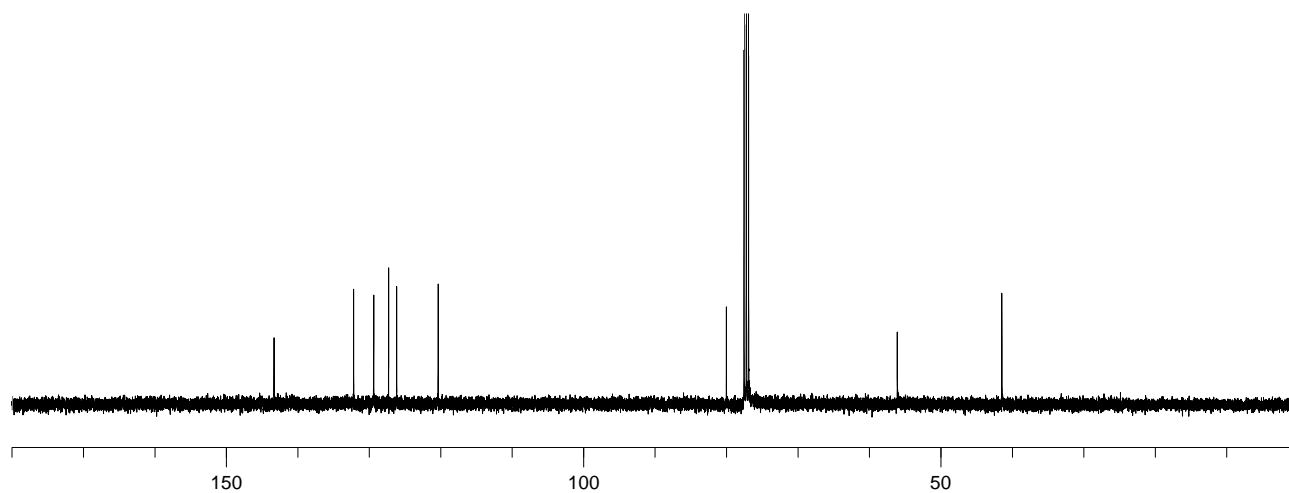
**(4w): *trans*-(1*R*,2*S*)-2-(Thiophen-3-yl)-cyclopent-3-enol.**



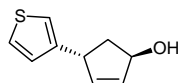
**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



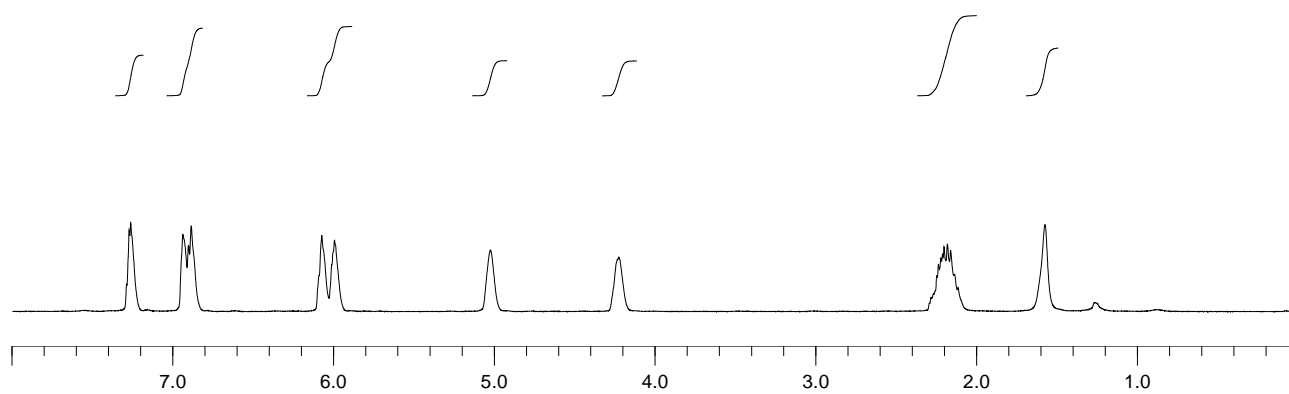
**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**



**(5w): *trans*-(1*R*,4*R*)-4-(Thiophen-3-yl)-cyclopent-2-enol.**



**<sup>1</sup>H NMR 400 MHz (CDCl<sub>3</sub>, 25 °C):**



**<sup>13</sup>C NMR 100 MHz (CDCl<sub>3</sub>, 25 °C):**

