Rhodium-Catalyzed Asymmetric Allylic Substitution with Boronic Acid Nucleophiles

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Supporting Information

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General Experimental Procedures. All reactions were carried out under argon atmosphere, in flame-dried, single-neck, roundbottom flasks fitted with rubber septa, with magnetic stirring unless otherwise noted. Air- or water-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. 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 at 40 Torr (house 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 accomplished with 254 nm UV light and/or by immersion in potassium permanganate (KMnO₄), or acidic aqueous-ethanolic vanillin solution, followed by brief heating using a heat gun. Purification of reaction products was generally done by flash chromatography with Silicycle™ Ultra-Pure 230-400 mesh silica gel, as described by Still et al.¹

Materials. [Rh(cod)Cl]₂ was purchased from Strem Chemicals, Inc. and used as received. [Rh(cod)OH]₂ was prepared from [Rh(cod)Cl]₂ by a literature procedure.² All chiral phosphine ligands were purchased from Strem Chemicals Inc. All boronic acids were obtained from Aldrich and used without further purification, unless otherwise noted. Tetrahydrofuran, 1,4-dioxane and toluene were purified by distillation under N₂ from Na/benzophenone immediately prior to use. Ether and dichloromethane were purified by the

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

² Uson, R.; Oro, L.A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126.

method of Pangborn et al.³ *Cis*-2-cyclopentene-1,4-diol was prepared by a literature procedure and characterization data was fully consistent with that reported in the literature.⁴ *Meso-cis*-cyclopent-2-ene-1,4-diethyl carbonate (**1**) was prepared following a literature procedure.⁵

Instrumentation. Proton nuclear magnetic resonance spectra (¹H NMR) spectra and carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 23 °C with a Varian 400 (400 MHz/100 MHz) NMR spectrometer equipped with ATB8123-400 probe, or a Varian Mercury 400 (400 MHz/100 MHz) NMR spectrometer equipped with a Nalorac4N-400 probe. Recorded shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents (CHCl₃: δ 7.26, CHDCl₂: δ 5.29, C₆H₅: δ 7.15, CD₂HOD: 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 (CDCl₃: δ 77.0, CH₂Cl₂: δ 53.8, C₆D₆: δ 128.0, CD₃OD: δ 49.2). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintuplet, sx = sextet, sp = septuplet, m = multiplet, br = broad), integration and coupling constant (*J*, Hz). Infrared (IR) spectra were obtained using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer as a neat film on a NaCl plate. Data is presented as follows: frequency of absorption (cm⁻¹), intensity of absorption (s = strong, m = medium, w = weak, br = broad), and assignment. 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 5.0 or 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]_D^{T °C} (c = g/100 mL, solvent). Reported readings are an average of at least two measurements for each sample.

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 Daicel Chemical Industries Ltd, Chiralcel OD-H column (fitted with a 5.0 cm Chiralcel OD-H guard column), flow rate 1.0 mL/min, 30°C, typically using a 1:99 *i*-PrOH:hexane solvent mixture., injection 4.0 uL.

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

⁴ Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876.

⁵ Arnau, N.; Cortés, J.; Moreno-Mañas, M.; Pleixats, R.; Villaroya, M. *J. Heterocyclic Chem.* **1997**, *34*, 233.

Ligand Screening

The biaryl bisphosphine ligands were the only class of ligands which showed any appreciable activity. The use of Tol-BINAP (entry 2) led to an increase in the enantioselectivity of the 1,2-adduct, but a decrease in the enantioselectivity of the 1,4-adduct. Cl-OMe-BIPHEP (entry 6) gave excellent enantioselectivities for both adducts, however no regioselectivity was observed. The most useful result was obtained with Xyl-P-Phos (entry 10), which gave excellent enantioselectivity and good regioselectivity for the synthesis of the 1,2-adduct **2**.

Entry	Ligand ^b	Conv.% ^c	2:3 ^c	2 ee% ^d	3 ee% ^d
1	BINAP	45	2:1	76	72
2	Tol-BINAP	32	1:1	95	32
3	Xyl-BINAP	59	2:1	82	60
4	ChiraPhos	2	--	--	--
5	MonoPhos	3	--	--	--
6	Cl-MeO-BIPHEP	60	1:1	90	>98
7	Me-DuPhos	0	--	--	--
8	<i>i</i> -Pr-POX	0	--	--	--
9	SolPhos	11	--	--	--
10	Xyl-P-Phos	65	13:1	88	>98
11	C ₂ -Ferriphos	3	--	--	--
12	KenPhos	1	--	--	--
13	PPF-P(<i>t</i> -Bu) ₂	0	--	--	--
14	QUINAP	3	--	--	--
15	Trost	0	--	--	--
16	BDPP	0	--	--	--

^a Unless otherwise noted, substrate, PhB(OH)₂, catalyst, ligand, and base were added to a flask with stir bar and sealed and flushed with nitrogen before THF was added. ^b Determined by ¹H NMR.

^d Determined by chiral HPLC on the deprotected products.

Absolute stereochemistries of the products were assigned by MTPA ester derivatives⁶ of **4a**, and by correlation of optical rotations with reported data of known compounds **2** and **3**.⁷

⁶ See reference 12.

⁷ a) Piarulli, U.; Daubos, P.; Claverie, C.; Roux, M.; Gennari, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 234. b) Kobayashi, Y.; Murugesu, M. G.; Nakano, M.; Takahisa, E.; Usmani, S. B.; Ainai, T. *J. Org. Chem.* **2002**, *67*, 7110. c) Tueting, D. R.; Echavarren, A. M.; Stille, J. K. *Tetrahedron* **1989**, *45*, 979. d) Marino, J. P.; Fernández de la Pradilla, R.; Laborde, E. *J. Org. Chem.* **1987**, *52*, 4898.

Experimental Procedures

Typical procedure: Desymmetrization by Rhodium-catalyzed Asymmetric Allylic Substitution with Phenylboronic acid on *cis*-cyclopent-2-ene-1,4-diethyl carbonate (**1**).

To a 1 dram vial equipped with a magnetic stir bar was added rhodium cyclooctadiene hydroxide, [Rh(cod)OH]₂ (3.7 mg, 0.0082 mmol), (*S*)-Xyl-P-PHOS (14.9 mg, 0.020 mmol) and Cs₂CO₃ (53 mg, 0.164 mmol). The vial was sealed and flushed with argon, then distilled THF (0.8 mL) was added and the mixture was stirred for 30 min on a 60 °C oil bath. *Cis*-2-cyclopentene-1,4-diethyl carbonate **1** (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) and the reaction mixture was heated on a 60°C oil bath. After 1 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 mono-carbonates **2** and **3** was recovered as a colourless oil, 33 mg (87%). ¹H NMR analysis revealed an isomer ratio of 92:8 for the 1,2-product **2** over the 1,4-product **3**. The enantiomeric excess was determined on the deprotected alcohols (*vide infra*).

Typical deprotection of carbonates

The combined 1,2- and 1,4-mono-carbonates **2** and **3** isomers were dissolved in MeOH (0.02 M) and K₂CO₃ (10-14 equiv) was added. The white suspension was stirred at rt until complete conversion (usually < 3 h).⁸ One volume of NH₄Cl saturated aqueous solution was added and extracted three times with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure to yield a mixture of the alcohols **4** and **5**. The crude products were analyzed by HPLC (Daicel Chiralcel OD-H, 1:99 to 3:97 *i*-PrOH/hexane), and peaks due to the four enantiomers could be resolved. The 1,2- and 1,4-regioisomers **4** and **5** were separated and purified by column chromatography on silica gel (25% EtOAc/hexane) when significant amounts of **5** were present.⁹

Note: The use (*S*)-biarylphosphines ligands (BINAP and P-PHOS 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 readers.

⁸ It was verified that longer reaction times did not affect the ee (up to 48h at rt).

⁹ When relevant, the regioisomers **5** were analyzed independently by HPLC, thus confirming retention times assignments.

Characterization Data

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(2a) and (3a) : (1R, 2S)-trans-2-phenylcyclopent-3-enyl-ethylcarbonate and (1R, 4R)-trans-4-phenylcyclopent-2-enyl-ethylcarbonate. 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 ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols.

Major regioisomer 2a: ^1H NMR (400 MHz, CDCl_3): 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). ^{13}C NMR (100 MHz, CDCl_3): 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^{-1} . **Minor regioisomer 3a:** ^1H NMR (400 MHz, CDCl_3): 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).

(4a) : (1R, 2S)-trans-2-phenylcyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (25% EtOAc/hexanes). The alcohol **4a** was quantitatively isolated as a colourless oil. The characterization data was fully concordant with that already reported in the literature.¹⁰ ^1H

NMR (400 MHz, CDCl_3): 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). ^{13}C NMR (100 MHz, CDCl_3): δ 142.6, 132.3, 129.5, 128.6, 127.3, 126.6, 80.9, 60.7, 41.3. IR (NaCl, neat film): 3328 (br.), 3056, 3026, 2924, 2845, 1650, 1557, 1537, 1492, 1453, 1052 cm^{-1} . MS m/z (rel. intensity): 160 (M^+ , 84), 117 (50), 104 (100), 91 (70). HRMS (ESI) $^+$: Calc'd for $\text{C}_{11}\text{H}_{12}\text{O}$ [M^+]: 160.088815; found = 160.089202. The ee was determined by HPLC analysis : 92% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min); t_R = 31.1 min (1*S*,2*R*) minor; t_R = 38.2 min (1*R*,2*S*) major. $[\alpha]_{\text{D}}^{26.7} = -228$ (c 1.60, CHCl_3 , for 92% ee).^{11,12}

(5a) : (1R, 4R)-trans-4-phenylcyclopent-2-enol. Colourless oil. The characterization data was fully concordant with that already reported in the literature.^{10b} ^1H NMR (400

MHz, CDCl_3): 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).

¹⁰ 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.

¹¹ The enantiomeric ligands (R)-Xylyl-P-PHOS or (R)-BINAP gave the corresponding (+)-trans-cyclopentenol.

¹² The absolute stereochemistry of **4a** was assigned by the Mosher method on the MTPA ester derivative of **4a** (2 equiv (S)-MTPA acid, 2 equiv DCC and 0.2 equiv DMAP were stirred in DCM at rt for 10h; quantitative yield). For details, see : Dale, J. A., Mosher, H. S. *J. Am. Chem. Soc.* **1973**, 95, 512.

(2b) : (1R, 2S)-trans-2-(4-Methoxycarbonyl-phenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained as a colorless oil in 95% yield (45 mg), showing a >20:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 2b:* ^1H NMR (400 MHz, CDCl_3): δ 7.97 (2H, d, J = 8.3 Hz), 7.28 (2H, d, J = 8.2 Hz), 5.98 (1H, ddd, J = 5.9, 4.2, 2.2 Hz), 5.80 (1H, ddd, J = 5.9, 4.0, 2.0 Hz), 5.04 (1H, ddd, J = 6.3, 2.5, 2.5 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), 2.41 (1H, dddd, J = 17.8, 7.9, 5.1, 2.3 Hz), 1.31 (3H, t, J = 7.1 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 166.9, 154.9, 146.4, 131.1, 130.1, 129.9, 128.9, 127.6, 84.6, 64.0, 57.6, 52.0, 38.7, 14.2. IR (NaCl, neat film): 3061, 2982, 2952, 2925, 2853, 1741, 1722, 1651, 1611, 1436, 1374, 1262 cm^{-1} .

(4b) : (1R, 2S)-trans-2-(4-Methoxycarbonylphenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (25% EtOAc/hexanes). The alcohol **4b** was quantitatively isolated as a colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.97 (2H, d, J = 8.2 Hz), 7.25 (2H, d, J = 8.3 Hz), 5.94 (1H, ddd, J = 6.2, 4.4, 2.2 Hz), 5.76 (1H, ddd, J = 6.3, 4.4, 2.2 Hz), 4.28 (1H, dt, J = 7.1, 4.1 Hz), 3.90 (3H, s), 3.85-3.82 (1H, m), 2.81 (1H, dddd, J = 17.1, 6.8, 3.7, 2.2 Hz), 2.39 (1H, dddd, J = 17.1, 5.9, 3.9, 2.2 Hz), 1.95 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 148.0, 131.5, 130.2, 129.9, 128.6, 127.3, 80.8, 60.7, 52.0, 41.5. IR (NaCl, neat film): 3418 (br.), 3054, 2998, 2949, 2845, 1717, 1651, 1609, 1436, 1282, 1179 cm^{-1} . MS m/z (rel. intensity): 218 (M^+ , 100), 200 (14), 187 (40), 162 (67), 131 (95), 115 (47). HRMS (ESI) $^+$: Calc'd for $\text{C}_{13}\text{H}_{14}\text{O}_3$ [M^+]: 218.0943; found = 218.0947. The ee was determined by HPLC analysis: 90% ee (Chiralcel OD-H, hexane/iPrOH = 96/4, 1.0 mL/min); t_R = 19.5 min (*1S,2R*) minor; t_R = 20.4 min (*1R,2S*) major. $[\alpha]_D^{24.8} = -354$ (c 0.90, CHCl_3 , for 90% ee).

(5b) : (1R, 4R)-trans-4-(4-Methoxycarbonylphenyl)-cyclopent-2-enol. Colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.97 (2H, d, J = 8.2 Hz), 7.25 (2H, d, J = 8.3 Hz), 5.94 (1H, ddd, J = 6.2, 4.4, 2.2 Hz), 5.76 (1H, ddd, J = 6.3, 4.4, 2.2 Hz), 4.28 (1H, dt, J = 7.1, 4.1 Hz), 3.90 (3H, s), 3.85-3.82 (1H, m), 2.81 (1H, dddd, J = 17.1, 6.8, 3.7, 2.2 Hz), 2.39 (1H, dddd, J = 17.1, 5.9, 3.9, 2.2 Hz), 1.95 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 167.0, 148.0, 131.5, 130.2, 129.9, 128.6, 127.3, 80.8, 60.7, 52.0, 41.5.

(2c) : (1R, 2S)-trans-2-(4-Acetylphenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained as a colourless oil in 94% yield (42 mg), showing a > 20:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 2c:* ^1H NMR (400 MHz, CDCl_3): δ 7.91 (2H, d, J = 8.3 Hz), 7.32 (2H, d, J = 8.3 Hz), 5.98 (1H, ddd, J = 5.9, 4.2, 2.1 Hz), 5.80 (1H, ddd, J = 5.9, 4.0, 2.1 Hz), 5.03 (1H, dt, J = 6.7, 2.8 Hz), 4.20 (2H, q, J = 7.1 Hz), 4.05 (1H, m), 2.92 (1H, ddd, J = 17.9, 6.7, 2.0 Hz), 2.58 (3H, s), 2.52 (1H, ddd, J = 17.9, 5.1, 0 Hz), 1.31 (3H, t, J = 7.1 Hz).

(4c) : (1R, 2S)-trans-2-(4-Acetylphenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol **4c** was quantitatively isolated as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.91 (2H, d, $J = 8.3$ Hz), 7.28 (2H, d, $J = 8.4$ Hz), 5.95 (1H, ddd, $J = 5.9, 4.2, 2.0$ Hz), 5.77 (1H, ddd, $J = 6.0, 4.0, 2.0$ Hz), 4.27-4.22 (1H, m), 3.84 (1H, br. s), 2.83 (1H, ddd, $J = 17.0, 6.8, 2.2$ Hz), 2.59 (3H, s), 2.41 (1H, dddd, $J = 17.0, 6.2, 4.1, 2.2$ Hz), 1.85 (1H, br. s, alcohol). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 197.9, 148.5, 135.6, 131.4, 130.3, 128.7, 127.6, 80.7, 60.6, 41.5, 26.6. **IR** (NaCl, neat film): 3390 (br), 3056, 3003, 2920, 2844, 1682, 1606, 1560, 1417, 1361, 1273 cm^{-1} . **MS** m/z (rel. intensity): 202 (M^+ , 57), 187 (100), 173 (37), 159 (17), 131 (62), 115 (35), 91 (28). **HRMS** (ESI) $^+$: Calc'd for $\text{C}_{13}\text{H}_{14}\text{O}_2$ [M^+]: 202.099380; found = 202.099888. The ee was determined by HPLC analysis : 88% ee (Chiralcel OD-H, hexane/iPrOH = 96/3, 1.0 mL/min); $t_R = 39.4$ min (*1S,2R*) minor; $t_R = 49.2$ min (*1R,2S*) major.

(5c) : (1R, 4R)-trans-4-(4-Acetylphenyl)-cyclopent-2-enol. Colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.88 (2H, d, $J = 8.4$ Hz), 7.22 (2H, d, $J = 8.2$ Hz), 6.09 (1H, ddd, $J = 7.5, 5.3, 2.2$ Hz), 6.04 (1H, ddd, $J = 7.4, 5.7, 2.0$ Hz), 5.09-5.04 (1H, m), 4.23-4.19 (1H, m), 2.58 (3H, s), 2.32 (1H, ddd, $J = 14.3, 8.1, 2.6$ Hz), 2.09 (1H, ddd, $J = 13.8, 6.8, 4.5$ Hz), 1.59 (1H, br. s, alcohol). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 197.7, 150.5, 138.2, 135.5, 134.8, 128.8, 127.3, 110.0, 49.9, 43.8, 26.6.

(2d) : (1R, 2S)-trans-2-(4-Trifluoromethylphenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained as a colourless oil in 86% yield (42 mg), showing a 13:1 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 2d*: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.56 (2H, d, $J = 8.1$ Hz), 7.34 (2H, d, $J = 8.0$ Hz), 5.99 (1H, ddd, $J = 5.9, 4.2, 2.1$ Hz), 5.80 (1H, ddd, $J = 6.0, 4.3, 2.2$ Hz), 5.01 (1H, dt, $J = 6.7, 2.8$ Hz), 4.21 (2H, q, $J = 7.1$ Hz), 4.07-4.03 (1H, br. s), 2.92 (1H, dddd, $J = 17.9, 6.6, 4.1, 2.2$ Hz), 2.56-2.48 (1H, m), 1.32 (3H, t, $J = 7.1$ Hz).

(4d) : (1R, 2S)-trans-2-(4'-Trifluoromethylphenyl)-cyclopent-2-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 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, CDCl_3): δ 146.7, 131.4, 130.4, 127.7, 125.5 (q, $J = 3.8$ Hz, CF_3), 122.9, 80.8, 60.4, 41.5. **IR** (NaCl, neat film): 3324 (br.), 3061, 2922, 2850, 1618, 1418, 1328, 1163, 1126, 1070, 1018 cm^{-1} . **MS** m/z (rel. intensity): 228 (M^+ , 98), 210 (30), 172 (100), 159 (52), 131 (20), 115 (19). **HRMS** (ESI) $^+$: Calc'd for $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}$ [M^+]: 228.07200; found = 228.076170. The ee was determined by HPLC analysis : 88% ee (Chiralcel OD-H, hexane/iPrOH = 98/2, 1.0 mL/min); $t_R = 14.9$ min (*1S,2R*) minor; $t_R = 17.0$ min (*1R,2S*) major.

(2e) : (1R, 2S)-trans-2-(4-Fluorophenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained as a colourless oil in 46% yield (19 mg), showing a 7:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2e:** ^1H NMR (400 MHz, CDCl_3): δ 7.16-7.08 (2H, m), 6.96-6.89 (2H, m), 5.87 (1H, ddd, $J = 6.1, 4.2, 2.1$ Hz), 5.72 (1H, ddd, $J = 5.8, 4.5, 2.3$ Hz), 4.91 (1H, dt, $J = 6.6, 2.7$ Hz), 4.13 (2H, q, $J = 7.1$ Hz), 3.93-3.89 (1H, br. s), 2.82 (1H, dddd, $J = 17.8, 6.3, 4.0, 2.1$ Hz), 2.41 (1H, dddd, $J = 17.7, 5.2, 3.7, 2.7$ Hz), 1.31 (3H, t, $J = 7.1$ Hz).

(4e) : (1R, 2S)-trans-2-(4-Fluorophenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.16-7.11 (2H, m), 7.02-6.96 (2H, m), 5.90 (1H, ddd, $J = 6.0, 4.4, 2.3$ Hz), 5.75 (1H, ddd, $J = 6.2, 4.3, 2.1$ Hz), 4.26-4.21 (1H, m), 3.75 (1H, sp, $J = 1.9$ Hz), 2.80 (1H, dddd, $J = 16.9, 6.6, 4.4, 2.2$ Hz), 2.37 (1H, dsx, $J = 16.9, 2.1$ Hz), 1.82 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 162.0 ($J = 241$ Hz), 138.4 ($J = 3.3$ Hz), 132.3, 129.9, 128.9 ($J = 7.8$ Hz), 115.5 ($J = 20.9$ Hz), 81.2, 60.1, 41.6. IR (NaCl, neat film): 3338 (br.), 3059, 2965, 2852, 1603, 1511, 1417, 1223, 1158, 1054, 950 cm^{-1} . MS m/z (rel. intensity): 178 (M^+ , 67), 135 (41), 122 (100), 109 (60), 57 (32). HRMS (ESI) $^+$: Calc'd for $\text{C}_{11}\text{H}_{11}\text{FO}$ [M^+]: 178.079393; found = 178.079724. The ee was determined by HPLC analysis: 86% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min); $t_R = 28.9$ min (*1S,2R*) minor; $t_R = 30.9$ min (*1R,2S*) major.

(5e) : (1R, 4R)-trans-2-(4-Fluorophenyl)-cyclopent-2-enol. Colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.10-7.06 (2H, m), 7.00-6.94 (2H, m), 6.05-6.00 (2H, m), 5.08-5.02 (1H, m), 4.15-4.11 (1H, m), 2.28 (1H, ddd, $J = 14.3, 8.0, 2.8$ Hz), 2.05 (1H, ddd, $J = 14.0, 6.9, 5.3$ Hz), 1.30 (1H, br. s, alcohol).

(2f) : (1R, 2S)-trans-2-(4-Chlorophenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 53% yield (23 mg), showing a 13:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2f:** ^1H NMR (400 MHz, CDCl_3): δ 7.27 (2H, d, $J = 8.8$ Hz), 7.16 (2H, d, $J = 8.3$ Hz), 5.95 (1H, ddd, $J = 5.9, 4.3, 2.0$ Hz), 5.78 (1H, ddd, $J = 5.9, 4.3, 2.0$ Hz), 4.98 (1H, dt, $J = 6.6, 2.8$ Hz), 4.20 (2H, q, $J = 7.1$ Hz), 3.99-3.94 (1H, br. s), 2.89 (1H, dddd, $J = 17.8, 6.6, 4.0, 2.2$ Hz), 2.49 (1H, dddd, $J = 17.8, 4.4, 2.8, 1.2$ Hz), 1.32 (3H, t, $J = 7.1$ Hz).

(4f) : (1R, 2S)-trans-2-(4-Chlorophenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.27 (2H, d, $J = 8.4$ Hz), 7.11 (2H, d, $J = 8.2$ Hz), 5.91 (1H, ddd, $J = 5.9, 4.5, 2.2$ Hz), 5.74 (1H, ddd, $J = 6.0, 4.2, 2.1$ Hz), 4.23 (1H, dt, $J = 6.7, 4.2$ Hz), 3.74 (1H, qn, $J = 1.9$ Hz), 2.80 (1H, dddd, $J = 17.0, 6.8, 2.2, 1.9$ Hz), 2.37 (1H, dddd, $J = 17.3, 6.0, 4.2, 2.1$ Hz), 1.84 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 141.0, 132.4, 131.8, 130.0, 128.7, 80.9,

60.0, 41.4. **IR** (NaCl, neat film): 3317 (br.), 3057, 2924, 2847, 1651, 1491, 1406, 1318, 1091 cm^{-1} . **MS** m/z (rel. intensity): 194 (M^+ , 75), 176 (13), 151 (26), 138 (100), 125 (40), 115 (39), 91 (18). **HRMS** (ESI) $^+$: Calc'd for $\text{C}_{11}\text{H}_{11}\text{ClO}$ [M^+]: 194.049843; found = 194.049690. The ee was determined by HPLC analysis : 90% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min), t_R = 32.7 min (*1S,2R*), t_R = 36.1 min (*1R,2S*). $[\alpha]_{589}^{26.0} = -187$ (c 0.66, CHCl_3 , for 87% ee).

(5f) : (1R, 4R)-trans-2-(4-Chlorophenyl)-cyclopent-2-enol. Colourless oil. **^1H NMR** (400 MHz, CDCl_3): δ 7.25 (2H, d, J = 8.0 Hz), 7.06 (2H, d, J = 8.6 Hz), 6.05 (1H, dt, J = 5.5, 2.1 Hz), 6.01 (1H, ddd, J = 5.6, 2.0, 0.6 Hz), 5.04 (1H, ddd, J = 7.0, 2.0, 0.7 Hz), 4.12 (1H, ddd, J = 7.4, 4.1, 2.0 Hz), 2.28 (1H, ddd, J = 14.2, 8.0, 2.6 Hz), 2.05 (1H, ddd, J = 14.2, 7.0, 5.5 Hz), 1.60 (1H, br. s, alcohol).

(2g) : (1R, 2S)-trans-2-(4-Bromophenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 35% yield (18 mg), showing a 10:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2g**: **^1H NMR** (400 MHz, CDCl_3): δ 7.35 (2H, d, J = 8.4 Hz), 7.03 (2H, d, J = 8.3 Hz), 5.88 (1H, ddd, J = 6.2, 4.4, 2.3 Hz), 5.71 (1H, ddd, J = 5.9, 4.3, 2.0 Hz), 4.91 (1H, dt, J = 6.6, 2.8 Hz), 4.13 (2H, q, J = 7.1 Hz), 3.90-3.85 (1H, br. s), 2.82 (1H, dddd, J = 17.8, 6.6, 4.0, 2.2, Hz), 2.42 (1H, dddd, J = 17.8, 2.9, 2.0, 1.1, Hz), 1.24 (3H, t, J = 7.1 Hz).

(4g) : (1R, 2S)-trans-2-(4-Bromophenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. **^1H NMR** (400 MHz, CDCl_3): δ 7.45-7.40 (2H, m), 7.08-7.04 (2H, m), 5.91 (1H, ddd, J = 6.1, 4.4, 2.2 Hz), 5.74 (1H, ddd, J = 6.1, 3.2, 2.1 Hz), 4.23 (1H, dt, J = 6.6, 2.2 Hz), 3.73 (1H, qn, J = 1.9 Hz), 2.79 (1H, dddd, J = 16.9, 6.6, 3.9, 2.1 Hz), 2.37 (1H, dsx, J = 17.0, 2.0 Hz), 1.86 (1H, br. s, alcohol). **^{13}C NMR** (100 MHz, CDCl_3): δ 141.8, 132.0, 131.9, 130.3, 129.3, 120.6, 81.1, 60.3, 41.6. **IR** (NaCl, neat film): 3338 (br.), 3056, 2924, 2848, 1485, 1404, 1315, 1200, 1158, 1072, 1010 cm^{-1} . **MS** m/z (rel. intensity): 240 (M^+ , 71), 238 (M^+ , 73), 222 (6), 220 (6), 184 (98), 182 (100), 171 (26), 169 (27), 141 (24), 128 (51), 116 (68), 91 (28). **HRMS** (ESI) $^+$: Calc'd for $\text{C}_{11}\text{H}_{11}\text{BrO}$ [M^+]: 237.999326; found = 237.999879. The ee was determined by HPLC analysis : 86% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min); t_R = 35.7 min (*1S,2R*) minor; t_R = 40.2 min (*1R,2S*) major.

(5g) : (1R, 4R)-trans-2-(4-Bromophenyl)-cyclopent-2-enol. Colourless oil. **^1H NMR** (400 MHz, CDCl_3): δ 7.42-7.38 (2H, m), 7.03-6.98 (2H, m), 6.05 (1H, dt, J = 5.5, 2.1 Hz), 6.00 (1H, dd, J = 5.6, 1.5 Hz), 5.07-5.01 (1H, m), 4.14-4.07 (1H, m), 2.28 (1H, ddd, J = 14.1, 8.0, 2.7 Hz), 2.04 (1H, ddd, J = 14.1, 7.0, 5.5 Hz), 1.51 (1H, br. s, alcohol).

(2h) : (1R, 2S)-trans-2-(4-Methylphenyl)-cyclopent-3-enyl ethylcarbonate.

Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 70% yield (28 mg), showing a 20:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2h:** ^1H NMR (400 MHz, CDCl_3): δ 7.20-7.02 (4H, m), 5.91 (1H, ddd, $J = 6.0, 4.1, 2.0$ Hz), 5.79 (1H, ddd, $J = 5.9, 4.2, 2.1$ Hz), 5.00 (1H, dt, $J = 6.1, 2.6$ Hz), 4.19 (2H, q, $J = 7.1$ Hz), 3.96 (1H, br. s), 2.80 (1H, dddd, $J = 17.7, 6.4, 4.0, 2.3$ Hz), 2.47 (1H, br. d, $J = 17.7$ Hz), 2.32 (3H, s), 1.31 (3H, t, $J = 7.1$ Hz).

(4h) : (1R, 2S)-trans-2-(4-Methylphenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. The characterization data was fully concordant with that already reported in the literature.^{10b}

^1H NMR (400 MHz, CDCl_3): δ 7.12 (2H, d, $J = 7.9$ Hz), 7.07 (2H, d, $J = 7.9$ Hz), 5.89 (1H, ddd, $J = 6.1, 4.4, 2.1$ Hz), 5.76 (1H, ddd, $J = 6.2, 4.2, 2.1$ Hz), 4.29-4.24 (1H, m), 3.73 (1H, sp, $J = 1.9$ Hz), 2.80 (1H, dddd, $J = 16.9, 6.2, 4.2, 2.1$ Hz), 2.36 (1H, dsx, $J = 16.9, 1.9$ Hz), 1.79 (1H, d, $J = 5.5$ Hz, alcohol). ^{13}C NMR (100 MHz, CDCl_3): 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): 3342 (br.), 3052, 3022, 2920, 2865, 1650, 1492, 1456, 1272, 1159, 1054 cm^{-1} . The ee was determined by HPLC analysis : 84% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min); $t_R = 23.0$ min (*1S,2R*) minor; $t_R = 28.5$ min (*1R,2S*) major.

(2i) : (1R, 2S)-trans-2-(4-[t-Butoxycarbonylamino]-phenyl)-cyclopent-3-enyl ethylcarbonate.

Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 32% yield (18 mg), showing a > 20:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2i:** ^1H NMR (400 MHz, CDCl_3): δ 7.32-7.26 (2H, m), 7.15-7.11 (2H, m), 6.46 (1H, br. s, NHBoc), 5.91 (1H, ddd, $J = 6.1, 4.2, 2.1$ Hz), 5.78 (1H, ddd, $J = 6.1, 4.2, 2.2$ Hz), 4.99 (1H, dt, $J = 6.6, 3.9$ Hz), 4.19 (2H, q, $J = 7.1$ Hz), 3.95 (1H, br. s), 2.88 (1H, dddd, $J = 17.7, 6.3, 5.0, 2.2$ Hz), 2.46 (1H, br. d, $J = 17.8$ Hz), 1.51 (9H, s), 1.31 (3H, t, $J = 7.1$ Hz).

(4i) : (1R, 2S)-trans-2-(4-[t-Butoxycarbonylamino]-phenyl)-cyclopent-3-enol.

Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.28 (2H, d, $J = 8.4$ Hz), 7.10-7.07 (2H, m), 6.51 (1H, br. s, NHBoc), 5.88 (1H, ddd, $J = 5.9, 4.4, 2.2$ Hz), 5.74 (1H, ddd, $J = 6.1, 4.2, 2.1$ Hz), 4.25-4.20 (1H, m), 3.72-3.68 (1H, m), 2.77 (1H, dddd, $J = 16.9, 6.5, 3.9, 1.9$ Hz), 2.34 (1H, d sx, $J = 16.9, 2.0$ Hz), 2.02 (1H, br. s, alcohol), 1.51 (9H, s). ^{13}C NMR (100 MHz, CDCl_3): δ 153.1, 137.4, 137.1, 132.5, 129.7, 128.0, 119.2, 81.2, 80.7, 60.3, 41.5, 28.6. IR (NaCl, neat film): 3317 (br.), 3055, 2977, 2931, 2858, 1710, 1530, 1315, 1244, 1161, 1055 cm^{-1} . MS m/z (rel. intensity): 275 (M^+ , 20), 219 (73), 163 (51), 132 (26), 119 (35), 57 (100). HRMS (ESI) $^+$: Calc'd for $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{Na}$ [$\text{M}-\text{Na}^+$]: 298.1413; found = 298.1408. The ee was determined by HPLC analysis: 84% ee (Chiralcel OD-H, hexane/iPrOH = 97/3, 1.0 mL/min); $t_R = 45.3$ min (*1S,2R*) minor; $t_R = 49.0$ min (*1R,2S*) major.

(2j) : (1R, 2S)-trans-2-(4-Methoxyphenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 49% yield (21 mg), showing a > 20:1 ratio of **2**:**3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 2j*: ^1H NMR (400 MHz, CDCl_3): δ 7.14 (2H, d, J = 8.5 Hz), 6.84 (2H, d, J = 8.8 Hz), 5.92 (1H, ddd, J = 6.0, 4.1, 2.0 Hz), 5.80 (1H, ddd, J = 6.2, 4.3, 2.0 Hz), 4.99 (1H, dt, J = 6.6, 2.6 Hz), 4.20 (2H, q, J = 7.1 Hz), 3.95 (1H, br. s), 3.79 (3H, s), 2.89 (1H, dddd, J = 17.8, 6.3, 3.9, 2.2, Hz), 2.47 (1H, dddd, J = 17.8, 4.3, 2.7, 1.1 Hz), 1.31 (3H, t, J = 7.1 Hz).

(4j) : (1R, 2S)-trans-2-(4-Methoxyphenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. The characterization data was fully concordant with that already reported in the literature. 10b ^1H NMR (400 MHz, CDCl_3): δ 7.10 (2H, d, J = 8.8 Hz), 6.85 (2H, d, J = 8.7 Hz), 5.88 (1H, ddd, J = 6.3, 4.4, 2.3 Hz), 5.76 (1H, ddd, J = 6.0, 4.2, 2.1 Hz), 4.24 (1H, dt, J = 6.7, 4.1 Hz), 3.79 (3H, s), 3.72 (1H, qn, J = 1.9 Hz), 2.79 (1H, dddd, J = 16.9, 6.7, 3.9, 1.8 Hz), 2.35 (1H, dddd, J = 16.9, 6.3, 4.2, 1.9 Hz), 1.85 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 158.4, 134.5, 132.5, 129.2, 128.3, 114.0, 81.0, 59.9, 55.3, 41.2. IR (NaCl, neat film): 3348 (br.), 3055, 3001, 2931, 2907, 2838, 1651, 1614, 1539, 1511, 1459, 1250, 1179 cm^{-1} . MS m/z (rel. intensity): 190 (M^+ , 61), 172 (8), 147 (45), 134 (100), 121 (44), 115 (21), 91 (29). HRMS (ESI) $^+$: Calc'd for $\text{C}_{12}\text{H}_{14}\text{O}_2$ [M^+]: 190.099380; found = 190.099729. The ee was determined by HPLC analysis : 89% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min); t_R = 48.9 min (1S,2R) minor; t_R = 50.6 min (1R,2S) major.

(5j) : (1R, 4R)-trans-4-(4-Methoxyphenyl)-cyclopent-2-enol. Colourless oil. The characterization data was fully concordant with that already reported in the literature. 10b ^1H NMR (400 MHz, CDCl_3): δ 7.04 (2H, d, J = 8.8 Hz), 6.83 (2H, d, J = 8.7 Hz), 6.01 (1H, dt, J = 1.9, 1.6 Hz), 5.06-5.01 (1H, m), 4.12-4.08 (1H, m), 3.79 (3H, s), 2.26 (1H, ddd, J = 15.1, 8.0, 2.6 Hz), 2.06 (1H, ddd, J = 14.0, 6.9, 5.5 Hz).

(2k) : (1R, 2S)-trans-2-(3-Methoxyphenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 63% yield (27 mg), showing a > 20:1 ratio of **2**:**3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 2k*: ^1H NMR (400 MHz, CDCl_3): δ 7.19-7.12 (1H, m), 6.77-6.69 (3H, m), 5.86 (1H, ddd, J = 5.9, 4.1, 2.0 Hz), 5.73 (1H, ddd, J = 5.9, 4.2, 2.0 Hz), 4.97 (1H, dt, J = 6.6, 2.8 Hz), 4.12 (2H, q, J = 7.1 Hz), 3.93-3.88 (1H, m), 3.72 (3H, s), 2.84 (1H, dddd, J = 17.8, 6.3, 4.0, 2.2 Hz), 2.45-2.36 (1H, m), 1.24 (3H, t, J = 7.1 Hz).

(4k) : (1R, 2S)-trans-2-(3-Methoxyphenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. The characterization data was fully concordant with that already reported in the literature. 10b ^1H NMR (400 MHz, CDCl_3): δ 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}C NMR (100 MHz, CDCl_3): δ 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^{-1} . MS m/z (rel. intensity): 190 (M^+ , 100), 172 (20), 162 (50), 147 (41), 134 (63), 129 (27), 121 (38), 115 (32), 91 (32). HRMS (ESI) $^+$: Calc'd for $\text{C}_{12}\text{H}_{14}\text{O}_2$ [M^+]: 190.099380; found = 190.099915. The ee was determined by HPLC analysis : 92% ee (Chiralcel OD-H, hexane/iPrOH = 98/2 to 96/4 gradient, 1.0 mL/min); $t_R = 35.5$ min (*1S,2R*) minor; $t_R = 50.1$ min (*1R,2S*) major.

(5k) : (1R, 4R)-trans-4-(3-Methoxyphenyl)-cyclopent-2-enol. Colourless oil. The characterization data was fully concordant with that already reported in the literature.^{10b} ^1H NMR (400 MHz, CDCl_3): 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).

(2l) : (1R, 2S)-trans-2-(3-Chlorophenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 87% yield (38 mg), showing a 10:1 ratio of **2:3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2l:** ^1H NMR (400 MHz, CDCl_3): δ 7.26-7.11 (4H, m), 5.96 (1H, ddd, $J = 6.1, 4.2, 2.1$ Hz), 5.77 (1H, ddd, $J = 6.2, 4.3, 2.0$ Hz), 5.00 (1H, dt, $J = 6.6, 2.8$ Hz), 4.20 (2H, q, $J = 7.1$ Hz), 3.99-3.96 (1H, m), 2.91 (1H, dddd, $J = 17.8, 6.4, 4.0, 2.3$ Hz), 2.53-2.45 (1H, m), 1.31 (3H, t, $J = 7.1$ Hz).

(4l) : (1R, 2S)-trans-2-(3-Chlorophenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.26-7.15 (3H, m), 7.08-7.05 (1H, m), 5.92 (1H, ddd, $J = 6.3, 4.4, 2.2$ Hz), 5.74 (1H, ddd, $J = 6.0, 4.4, 2.1$ Hz), 4.25 (1H, dt, $J = 6.8, 4.1$ Hz), 3.73 (1H, sp, $J = 1.9$ Hz), 2.80 (1H, dddd, $J = 17.0, 6.8, 3.9, 1.7$ Hz), 2.37 (1H, dddd, $J = 17.0, 6.5, 4.2, 2.1$ Hz), 2.07 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 144.7, 134.4, 131.5, 130.2, 129.8, 127.4, 126.8, 125.6, 80.8, 60.3, 41.4. IR (NaCl, neat film): 3323 (br.), 3059, 2931, 2906, 2841, 1596, 1572, 1478, 1426, 1195, 1078 cm^{-1} . MS m/z (rel. intensity): 194 (M^+ , 100), 176 (20), 166 (32), 151 (25), 141 (47), 138 (91), 128 (44), 125 (42), 115 (49), 91 (21). HRMS (ESI) $^+$: Calc'd for $\text{C}_{11}\text{H}_{11}\text{ClO}$ [M^+]: 194.049843; found = 194.049579. The ee was determined by HPLC analysis : 90% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min); $t_R = 31.8$ min (*1S,2R*) minor; $t_R = 40.4$ min (*1R,2S*) major.

(5l) : (1R, 4R)-trans-4-(3-Chlorophenyl)-cyclopent-2-enol. Colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.26-7.16 (2H, m), 7.11-7.10 (1H, m), 7.03-7.00 (1H, m), 6.06 (1H, dt, $J = 5.5, 2.2$ Hz), 6.00 (1H, dd, $J = 5.6, 2.0$ Hz), 5.07-5.03 (1H, m), 4.12 (1H, dddd, $J = 9.8, 7.6, 4.1, 2.0$ Hz), 2.29 (1H, ddd, $J = 14.1, 8.0, 2.7$ Hz), 2.07 (1H, ddd, $J = 14.2, 7.0, 5.5$ Hz), 1.58 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 146.9, 138.3, 134.7, 134.4, 129.8, 127.2, 126.5, 125.3, 77.3, 49.6, 43.9.

(2m) : (1R, 2S)-trans-2-(3-Methylphenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained

in 78% yield (32 mg), showing a 20:1 ratio of **2**:**3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 2m*: ^1H NMR (400 MHz, CDCl_3): δ 7.22-7.01 (4H, m), 5.92 (1H, ddd, $J = 5.9, 4.0, 2.0$ Hz), 5.80 (1H, ddd, $J = 5.9, 4.4, 2.1$ Hz), 5.04 (1H, dt, $J = 5.9, 2.7$ Hz), 4.19 (2H, q, $J = 7.1$ Hz), 3.98-3.94 (1H, m), 2.92 (1H, dddd, $J = 17.7, 6.4, 4.0, 2.3$ Hz), 2.51-2.43 (1H, m), 2.33 (3H, s), 1.31 (3H, t, $J = 7.1$ Hz).

(4m) : (1R, 2S)-trans-2-(3-Methylphenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. The characterization data was fully concordant with that reported.^{10b} ^1H NMR (400 MHz, CDCl_3): 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). ^{13}C NMR (100 MHz, CDCl_3): 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^{-1} . MS m/z (rel. intensity): 174 (M^+ , 93), 156 (25), 146 (55), 131 (69), 128 (47), 118 (100), 115 (41), 105 (50), 91 (42). HRMS (ESI) $^+$: Calc'd for $\text{C}_{12}\text{H}_{14}\text{O}$ [M^+]: 174.104465; found = 174.104256. The ee was determined by HPLC analysis: 92% ee (Chiralcel OD-H, hexane/iPrOH = 99/1, 1.0 mL/min); $t_R = 20.4$ min (*1S,2R*) minor; $t_R = 26.4$ min (*1R,2S*) major.

(5m) : (1R, 4R)-trans-4-(3-Methylphenyl)-cyclopent-2-enol. Colourless oil. The characterization data was fully concordant with that already reported in the literature.^{10b} ^1H NMR (400 MHz, CDCl_3): 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). ^{13}C NMR (100 MHz, CDCl_3): 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.

(2n) : (1R, 2S)-trans-2-(2-Naphthalenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained as a colourless oil in 78% yield (36 mg), showing a > 20:1 ratio of **2**:**3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. *Major regioisomer 2n*: ^1H NMR (400 MHz, CDCl_3): δ 7.86-7.77 (3H, m), 7.62 (1H, s), 7.49-7.39 (3H, m), 6.01 (1H, ddd, $J = 6.1, 4.0, 2.1$ Hz), 5.90 (1H, ddd, $J = 5.8, 4.0, 2.0$ Hz), 5.12 (1H, dt, $J = 6.0, 2.7$ Hz), 4.21 (2H, q, $J = 7.1$ Hz), 4.19-4.16 (1H, m), 2.97 (1H, dddd, $J = 17.8, 6.2, 4.4, 2.5$ Hz), 2.57-2.49 (1H, m), 1.32 (3H, t, $J = 7.1$ Hz).

(4n) : (1R, 2S)-trans-2-(2-Naphthalenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.83-7.78 (3H, m), 7.62 (1H, s), 7.49-7.42 (2H, m), 7.33 (1H, dd, $J = 8.5, 1.7$ Hz), 5.97 (1H, ddd, $J = 6.0, 4.4, 2.2$ Hz), 5.87 (1H, ddd, $J = 6.2, 4.2, 2.1$ Hz), 4.37 (1H, dt, $J = 6.7, 4.1$ Hz), 3.94 (3H, sp, $J = 1.9$ Hz), 2.86 (1H, dddd, $J = 16.9, 6.3, 3.9, 2.0$ Hz), 2.42 (1H, dddd, $J = 17.0, 6.0, 3.9, 2.0$ Hz), 1.99 (1H, br. s, alcohol). ^{13}C NMR (100 MHz, CDCl_3): δ 139.9, 133.5, 132.5, 132.2, 129.8, 128.3, 127.6, 126.1, 126.0, 125.5, 125.4, 80.8, 60.9, 41.4. IR (NaCl, neat film): 3028 (br.), 3054, 3017, 2925, 2854, 1650, 1633, 1506, 1456, 1271, 1216, 1050 cm^{-1} . MS m/z (rel. intensity): 210 (M^+ , 100), 192 (24), 179 (46), 165 (58), 154 (96), 141 (48), 128 (36), 115 (19). HRMS

(ESI)⁺: Calc'd for C₁₅H₁₄O [M⁺]: 210.104465; found = 210.105000. The ee was determined by HPLC analysis : 90% ee (Chiralcel OD-H, hexane/iPrOH = 98/2, 1.0 mL/min); t_R = 34.3 min (*1S,2R*) minor; t_R = 51.8 min (*1R,2S*) major.

(5n) : (*1R, 4R*)-trans-4-(2-Naphthalenyl)-cyclopent-2-enol. Colourless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.76 (3H, m), 7.58 (1H, s), 7.44 (2H, ddd, *J* = 13.1, 6.9, 1.6 Hz), 7.26-7.23 (1H, m), 6.13 (1H, dd, *J* = 5.5, 2.0 Hz), 6.10 (1H, dt, *J* = 5.5, 2.2 Hz), 5.13-5.08 (1H, m), 4.35-4.30 (1H, m), 2.35 (1H, ddd, *J* = 14.3, 8.2, 2.8 Hz), 2.20 (1H, ddd, *J* = 14.2, 6.8, 5.5 Hz), 1.71 (1H, br. s, alcohol). ¹³C NMR (100 MHz, CDCl₃): δ 142.1, 139.0, 134.3, 133.5, 132.3, 128.3, 127.6, 127.5, 126.1, 125.7, 125.4, 125.2, 77.6, 50.1, 44.0.

(2o) : (*1R, 2S*)-trans-2-(1-Naphthalenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 50% yield (23 mg), showing a 1:1 ratio of **2**:**3** by ¹H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2o:** ¹H NMR (400 MHz, CDCl₃): δ 8.18 (1H, d, *J* = 8.2 Hz), 7.87 (1H, dd, *J* = 8.0, 1.5 Hz), 7.76 (1H, d, *J* = 8.2 Hz), 7.56 (1H, dt, *J* = 6.9, 1.6 Hz), 7.50 (1H, dt, *J* = 6.9, 1.5 Hz), 7.40 (1H, t, *J* = 8.2 Hz), 7.26 (1H, s), 6.04 (1H, ddd, *J* = 5.9, 4.0, 2.0 Hz), 5.94 (1H, ddd, *J* = 5.9, 4.3, 2.0 Hz), 5.18 (1H, dt, *J* = 6.5, 2.4 Hz), 4.80 (1H, br. s), 4.18 (2H, q, *J* = 7.1 Hz), 2.97 (1H, dddd, *J* = 17.9, 6.4, 4.2, 2.1 Hz), 2.54 (1H, dddd, *J* = 17.9, 4.1, 2.5, 1.0 Hz), 1.31 (3H, t, *J* = 7.1 Hz).

(4o) : (*1R, 2S*)-trans-2-(1-Naphthalenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. ¹H NMR (400 MHz, CDCl₃): δ 8.33 (1H, d, *J* = 8.4 Hz), 7.88 (1H, d, *J* = 7.9 Hz), 7.75 (1H, d, *J* = 8.2 Hz), 7.58 (1H, dt, *J* = 6.9, 1.2 Hz), 7.52 (1H, dt, *J* = 6.8, 1.0 Hz), 7.39 (1H, t, *J* = 8.0 Hz), 7.22 (1H, d, *J* = 8.0 Hz), 6.06 (1H, ddd, *J* = 5.7, 4.1, 2.0 Hz), 5.95 (1H, ddd, *J* = 5.8, 4.2, 2.1 Hz), 4.60 (1H, br. s), 4.41-4.35 (1H, m), 2.81 (1H, dddd, *J* = 17.3, 6.3, 4.1, 2.0 Hz), 2.44 (1H, dm, *J* = 17.3 Hz), 2.02 (1H, br. s). ¹³C NMR (100 MHz, CDCl₃): δ 137.9, 134.0, 132.1, 131.8, 130.3, 128.8, 127.2, 126.1, 125.6, 125.4, 123.9, 123.4, 79.6, 56.6, 41.7. IR (NaCl, neat film): 3347 (br.), 3050, 3010, 2927, 2843, 1595, 1511, 1431, 1396, 1287, 1207, 1066, 1033 cm⁻¹. MS *m/z* (rel. intensity): 210 (M⁺, 100), 191 (15), 179 (43), 165 (75), 154 (76), 141 (46), 128 (29), 115 (17). HRMS (ESI)⁺: Calc'd for C₁₅H₁₄O [M⁺]: 210.104465; found = 210.105004. The ee was determined by HPLC analysis : 70% ee (Chiralcel OD-H, hexane/iPrOH = 98/2, 0.75 mL/min); t_R = 48 min (*1S,2R*) minor; t_R = 50.6 min (*1R,2S*) major.

(5o) : (*1R, 4R*)-trans-4-(1-Naphthalenyl)-cyclopent-2-enol. Colourless oil. ¹H NMR (400 MHz, CDCl₃): δ 8.07 (1H, d, *J* = 7.2 Hz), 7.88 (1H, d, *J* = 7.9 Hz), 7.74 (1H, d, *J* = 8.2 Hz), 7.57 (1H, dt, *J* = 7.5, 1.5 Hz), 7.51 (1H, dt, *J* = 8.0, 1.4 Hz), 7.41 (1H, t, *J* = 7.2 Hz), 7.34 (1H, d, *J* = 6.8 Hz), 6.16-6.13 (1H, m), 6.05-5.98 (1H, m), 5.15-5.10 (1H, m), 4.38 (1H, m), 3.13 (1H, ddd, *J* = 17.4, 8.9, 2.4 Hz), 2.65 (1H, dddd, *J* = 17.4, 4.0, 2.7, 1.5 Hz), 1.82 (1H, d, *J* = 6.2 Hz). MS *m/z* (rel. intensity): 210 (M⁺, 100), 191 (40), 178 (27), 165 (87), 152 (57), 141 (47), 128 (55), 115 (17), 82 (45). HRMS (ESI)⁺: Calc'd for C₁₅H₁₄O [M⁺]: 210.104465; found = 210.105018.

(2p) : (1R, 2S)-trans-2-(2-Methylphenyl)-cyclopent-3-enyl ethylcarbonate. Prepared according to the general procedure described above. The crude product was purified by column chromatography (dry loaded). The inseparable regioisomers **2** and **3** were obtained in 25% yield (10 mg), showing a 6:1 ratio of **2**:**3** by ^1H NMR spectroscopy. The regioisomers were submitted directly to the deprotection conditions and characterized as the free alcohols. **Major regioisomer 2p:** ^1H NMR (400 MHz, CDCl_3): δ 7.19-7.11 (3H, m), 7.03-6.98 (1H, m), 5.95 (1H, ddd, $J = 6.0, 4.1, 2.0$ Hz), 5.78 (1H, ddd, $J = 6.9, 4.3, 2.0$ Hz), 5.06 (1H, dt, $J = 6.5, 2.6$ Hz), 4.24-4.21 (1H, m), 4.18 (2H, q, $J = 7.1$ Hz), 2.94 (1H, dddd, $J = 17.8, 6.4, 4.1, 2.2$ Hz), 2.47 (1H, dddd, $J = 17.8, 4.3, 2.6, 1.0$ Hz), 2.40 (3H, s), 1.31 (3H, t, $J = 7.1$ Hz).

(4p) : (1R, 2S)-trans-2-(2-Methylphenyl)-cyclopent-3-enol. Obtained by methanolysis of the isolated carbonates mixture (*vide supra*) and purified by column chromatography (10-25% EtOAc/hexanes gradient). The alcohol was quantitatively isolated as a colourless oil. The characterization data was fully concordant with that already reported.^{10b} ^1H NMR (400 MHz, CDCl_3): δ 7.22-7.09 (3H, m), 7.03-6.98 (1H, m), 5.96 (1H, ddd, $J = 6.1, 4.2, 2.0$ Hz), 5.77 (1H, ddd, $J = 6.9, 4.1, 2.1$ Hz), 4.29-4.22 (1H, m), 4.04 (1H, br. s), 2.79 (1H, dddd, $J = 17.8, 6.1, 4.2, 2.0$ Hz), 2.47 (3H, s), 2.34 (1H, br. d, $J = 17.7$ Hz), 2.40 (3H, s), 1.79 (1H, br. s). **MS** m/z (rel. intensity): 174 (M^+ , 100), 156 (22), 131 (52), 128 (39), 118 (72), 115 (37), 105 (41), 91 (33). **HRMS** (ESI) $^+$: Calc'd for $\text{C}_{12}\text{H}_{14}\text{O}$ [M^+]: 174.104465; found = 174.104454. The ee was determined by HPLC analysis : 92% ee (Chiralcel OD-H, hexane/iPrOH = 98/2, 1.0 mL/min); $t_R = 15.4$ min (*IS,2R*) minor; $t_R = 20.4$ min (*IR,2S*) major.

(5p) : (1R, 4R)-trans-4-(2-Methylphenyl)-cyclopent-2-enol. Colourless oil. The characterization data was fully concordant with that already reported.^{10b} ^1H NMR (400 MHz, CDCl_3): δ 7.16-7.10 (3H, m), 7.00 (1H, dd, $J = 6.3, 1.7$ Hz), 6.09-6.05 (2H, m), 5.03 (1H, br. s), 4.36 (1H, dt, $J = 5.7, 1.7$ Hz), 2.36 (3H, s), 2.32 (1H, ddd, $J = 14.2, 8.2, 2.6$ Hz), 1.98 (1H, ddd, $J = 14.1, 6.8, 5.8$ Hz), 0.88 (1H, br. s).

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

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

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

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

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

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

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

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

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

(4h) : (1R, 2S)-trans-2-(4-Methylphenyl)-cyclopent-3-enol.

(4i) : (1*R*, 2*S*)-trans-2-(4-[*t*-Butoxycarbonylamino]-phenyl)-cyclopent-3-enol.

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

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

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

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

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

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

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

(2b) : (1*R*, 2*S*)-trans-2-(4-Methoxycarbonyl-phenyl)-cyclopent-3-enyl ethyl-carbonate.

(2c) : (1*R*, 2*S*)-trans-2-(4-Acetylphenyl)-cyclopent-3-enyl ethylcarbonate.

(2d) : (1*R*, 2*S*)-trans-2-(4-Trifluoromethyl-phenyl)-cyclopent-3-enyl ethylcarbonate.

(2e) : (1*R*, 2*S*)-trans-2-(4-Fluorophenyl)-cyclopent-3-enyl ethylcarbonate.

(2f) : (1*R*, 2*S*)-trans-2-(4-Chlorophenyl)-cyclopent-3-enyl ethylcarbonate.

(2g) : (1R, 2S)-trans-2-(4-Bromophenyl)-cyclopent-3-enyl ethylcarbonate.

(2h) : (1R, 2S)-trans-2-(4-Methylphenyl)-cyclopent-3-enyl ethylcarbonate.

(2i) : (1R, 2S)-trans-2-(4-[*t*-Butoxycarbonylamino]-phenyl)-cyclopent-3-enyl ethylcarbonate.

(2j) : (1*R*, 2*S*)-trans-2-(4-Methoxyphenyl)-cyclopent-3-enyl ethylcarbonate.

(2k) : (1*R*, 2*S*)-trans-2-(3-Methoxyphenyl)-cyclopent-3-enyl ethylcarbonate.

(2l) : (1R, 2S)-trans-2-(3-Chlorophenyl)-cyclopent-3-enyl ethylcarbonate.

(2m) : (1R, 2S)-trans-2-(3-Methylphenyl)-cyclopent-3-enyl ethylcarbonate.

(2n) : (1R, 2S)-trans-2-(2-Naphthalenyl)-cyclopent-3-enyl ethylcarbonate.

(2o) : (1R, 2S)-trans-2-(1-Naphthalenyl)-cyclopent-3-enyl ethylcarbonate.

(2p) : (1*R*, 2*S*)-*trans*-2-(2-Methylphenyl)-cyclopent-3-enyl ethylcarbonate.

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

(5c) : (1*R*, 4*R*)-trans-4-(4-Acetylphenyl)-cyclopent-2-enol

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

(5f) : (1R, 4R)-trans-2-(4-Chlorophenyl)-cyclopent-2-enol.

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

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

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

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

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

(5n) : (1*R*, 4*R*)-trans-4-(2-Naphthalenyl)-cyclopent-2-enol.

(5o) : (1*R*, 4*R*)-*trans*-4-(1-Naphthalenyl)-cyclopent-2-enol.

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

HPLC Representative Traces

HPLC Trace for racemic-**4a**:

HPLC Trace for enantiomerically enriched-**4a**:

HPLC System Agilent 1100 Series
Column: Daicel Chiralcel OD-H
Eluent: 1:99, 2-Propanol:Hexane
Flow: 1.0 mL/min
Injection: 4.0 μ L
Temp. col.: 30 $^{\circ}$ C
Detector freq.: 210 nm