N-Alkoxyacrylamides as Substrates for Enantioselective Diels-Alder Reactions

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Supporting Information

General. Ether was freshly distilled under N₂ from sodium-benzophenone, THF from K, benzene and toluene from Na, CH₂Cl₂, and amines from CaH₂. Flash column chromatography (FC) and filtrations were performed using silica gel 60 Merck (0.063-0.200 mm) or Macherey-Nagel silica gel (0.063-0.200 mm). Lobar® chromatography were performed using silica gel 60 Merck (0.040-0.063 mm). All the reagents were obtained from Fluka, Aldrich or Acros and used as received unless otherwise specified. Solutions of Me₃Al were freshly prepared under strictly anhydrous conditions using neat Me₃Al (pract.) from Fluka or Aldrich. Thin layer chromatography (TLC) were performed using analytical plates: Macherey-Nagel SIL G-25 UV 254. Detection was done with UV, with a saturated aqueous solution of FeCl₃ or with a solution of KMnO₄ (3 g), K₂CO₃ (20 g), NaOH 5% (3 mL) and H₂O (300 mL) with subsequent heating. M.p.: not corrected; Reichert Thermovar Kofler hot stage apparatus. IR spectroscopy: Perkin-Elmer 16PC. FT-IR: Mattson Unicam 5000. GC: Carlo Erba HRGC 5300 serie. MS: Vacuum Generators Micromass VG 70/70E and DS 11-250; CI (CH₄), EI (70eV); m/z (%), FAB in 2-nitrobenzyl alcohol with Ar at 8 KV. High resolution mass spectra (HRMS) were recorded on a FTICR mass spectrometer Bruker 4.7T BioApex II. NMR Varian Gemini 200 (1H 200 MHz, 13C 50.3 MHz); Bruker-AM-360 (1H 360.13 MHz, 13C 90.6 MHz). Bruker-Avance-500 (1H 500.13 MHz, 13C 125.8 MHz). Spectra were recorded at room temperature in CDCl₃ unless otherwise specified. ¹H chemical shifts δ in ppm relative to SiMe₄ (= 0 ppm). ¹³C chemical shifts δ in ppm relative to CHCl₃ (= 77.0 ppm). Elemental analysis: EIF, CH-1700 Fribourg, Switzerland or Ilse Beetz, Microanalytisches Laboratorium, D-8640 Kronach, Germany.

General Procedure 1 (GP1): Non-Catalyzed Diels-Alder Reactions
Freshly distilled cyclopentadiene (660 mg, 10 mmol) was added dropwise under N₂ to a solution of the acrylamide derivative (1.0 mmol) in dry CH₂Cl₂ (5.0 mL). The mixture was stirred until completion of the reaction. Volatile were removed in vacuo and the residue was purified by FC.

General Procedure 2 (GP2): Aluminum-TADDOL Promoted Diels-Alder Reactions
A solution of i-Bu₃Al (1.10M in toluene, 0.13 mL, 0.14 mmol) was added dropwise at room temperature to a solution of (R,R)-1-NaphTADDOL (190 mg, 0.28 mmol) in CH₂Cl₂ (5.0 mL). The reaction mixture was stirred for 30 min at room temperature. A solution of 1g (220 mg, 1.0 mmol) in CH₂Cl₂ (1.0 mL) was then added dropwise. The reaction mixture was stirred for 1 h at room temperature and 30 min at –78 °C. Freshly distilled cyclopentadiene (660 mg, 10 mmol) was then added dropwise under N₂ to the solution at –78 °C and the mixture was allowed to warm up to room temperature overnight (12 h). Volatiles were removed in vacuo and the resulting product was dissolved in Et₂O and stirred for 1 h at room temperature with a 1N solution of citric acid. After extraction with Et₂O, the organic phase was dried (Na₂SO₄), filtered and concentrated. The crude product was purified by flash chromatography (hexane/EtOAc 10:1).
All the Diels-Alder reactions catalyzed by aluminum Lewis acids were run according to this procedure by varying the amount and the nature of the reagents as well as the reaction temperature (the catalysts were always prepared at room temperature).

General Procedure 3 (GP3): Zinc-Binaphthol Promoted Diels-Alder Reactions
A solution of Et₂Zn (15% wt in hexane, 1.1 mmol) was added dropwise at room temperature to a solution of (R)-BINOL (320 mg, 1.1 mmol) in CH₂Cl₂ (5.0 ml). The reaction mixture was heated at reflux for 1 h, cooled down to 0 °C and stirred for 30 min before to add a solution of 1c (180 mg, 1.0 mmol) in CH₂Cl₂ (1.0 mL). The resulting suspension was stirred for 1 h at 0 °C before to add freshly distilled cyclopentadiene (660 mg, 10 mmol). After completion of the reaction, volatiles were removed in vacuo and the resulting residue was dissolved in Et₂O and stirred for 1 h at room temperature with a 1N solution of citric acid. After extraction with Et₂O, the organic phase was dried (Na₂SO₄), filtered and concentrated. The crude product was purified by flash chromatography (hexane/EtOAc 8:1).

All the Diels-Alder reactions catalyzed by zinc Lewis acids were run according to this procedure by varying the amount and the nature of the reagents as well as the reaction temperature.


MeLi (3.8 mL of a 1.6 M solution in THF) was added dropwise at –78 °C under N₂ to a solution of 2c (240 mg, 1.0 mmol) resulting from the Diels-Alder reaction in THF (5.0 mL). The reaction mixture was allowed to warm up to rt overnight. The reaction mixture was cannulated on a 1:1 mixture of Et₂O and saturated NH₄Cl at 0 °C. The two phases were separated and the aqueous one was extracted three times with Et₂O. The collected organic phases were dried over Na₂SO₄ and filtered. Evaporation of the solvent and purification by FC (EtOAc/hexane 1:8) afforded the desired alcohol (150 mg, 99%).

Physical and spectral data are in accordance with the literature.¹ The enantiomeric excesses were measured by gas chromatography: 25 m fused silica; 0.32 mm id; stationary phase: heptakis-2,3-O-diethyl-6-O-tert-butyldimethylsilyl)-β-cyclodextrine in polymer diphenylether; df: 0.25 µm; temperature: 78 °C. Retention times: endo-(S) = 25.6 min, endo-(R) = 26.8 min; exo-(R) = 32.2 min, exo-(S) = 33.9 min. A copy of a chromatogram (racemic mixture) is annexed at the end of this document. For the determination of the absolute configuration, see ref 2.

**N-Methoxy-N-methylacrylamide (1a):** Dry pyridine (8.7 g, 8.9 ml, 110 mmol) was added dropwise at 0 °C to a solution of acryloyl chloride (4.5 g, 4.1 ml, 50 mmol) and O-methylhydroxylamine hydrochloride (4.6 g, 55 mmol) in dry chloroform exempt of ethanol (170 ml). At the end of the addition, the reaction mixture was stirred for 30 min at rt. The solvent was then evaporated and a saturated aqueous NaCl solution (170 ml) was added. Evaporation of the solvent afforded an oil which was purified by FC (EtOAc/hexane 1:2) to give 1a (9.1 g, 72%) as a colorless oil. IR (NaCl): 3564, 3500, 3101, 2970, 2939, 2821, 1930, 1659, 1620, 1460, 1423, 1401, 1180, 1103, 997, 789, 600.¹ H-NMR (500 MHz, CDCl₃): 6.73 (dd, Jₑ = 17.08, J₂ = 10.43, 1H); 6.42 (dd, Jₑ = 17.08, Jₖ = 1.99, 1H); 5.74 (dd, Jₑ = 10.43, Jₖ = 1.99, 1H); 3.71 (s, 3H); 3.26 (s, 3H). 13C-NMR (125.8 MHz, CDCl₃, -50 °C): 175.32; 137.13; 131.72; 61.09; 49.76; 45.39; 42.27; 40.35; 31.90. EI-MS (70 eV): 115 (14, M⁺); 85 (17); 61 (7); 55 (100); 46 (7). Anal. calc. for C₅H₉NO₂ (115.13): C 52.16, H 7.88; found C 52.21, H 7.93.

**N-methoxy-N-methylbicyclo[2.2.1]hept-5-ene-2-carboxamide (2a):** According to GP 3 from 1a (120 mg, 1.0 mmol) and (R)-BINOL. After purification by FC (EtOAc/hexane 1:4) the product 2a (170 mg, 93%) was isolated as an oil (endo:exo 7:1). The endo and exo isomers were separated by Lobar® chromatography (EtOAc/hexane 1:6). Endo-2a: 89% ee, [α]D²⁰ = 146.6° (c = 1.2, CHCl₃), (R)-configuration. IR (NaCl): 3560, 3500, 3061, 2960, 2872, 2798, 1643, 1416, 1383, 1175, 1101, 1007, 968, 717.¹ H-NMR (500 MHz, CDCl₃): 6.17 (dd, J = 5.6, 3.0, 1H); 5.95 (dd, J = 5.7, 2.7, 1H); 3.72 (s, 3H); 3.20 (br. s, 2H); 3.14 (s, 3H); 2.88 (br. s, 1H); 1.93-1.88 (m, 1H), 1.44-1.40 (m, 2H); 1.32-1.30 (m, 1H).¹³C-NMR (125.8 MHz, CDCl₃, -50 °C): 175.32; 137.13; 131.72; 61.09; 49.76; 45.39; 42.27; 40.35; 31.76; 29.24.
exo-2a: 91% ee, (R)-configuration. IR (NaCl): 3059, 2968, 2952, 2872, 1664, 1445, 1381, 1338, 1175, 1101, 1007, 717. 1H-NMR (500 MHz, CDCl3): 6.17-6.12 (m, 2H); 3.68 (s, 3H); 3.20 (s, 3H); 2.94-2.91 (m, 2H); 2.52 (br. s, 1H), 1.89-1.83 (m, 1H); 1.68-1.62 (m, 1H); 1.41-1.35 (m, 2H). El-MS (70 eV): 181 (5, M); 150 (9); 121 (20); 93 (26); 66 (15); 55 (100); 39 (11). Anal. calc. for C10H15NO2 (181.23): C 66.27, H 8.34; found C 66.31, H 8.40.

N-tert-Butyl-N-hydroxyacrylamide. Acryloyl chloride (2.3 g, 2.0 mL, 25 mmol) was added dropwise at 0 °C to a vigorously stirred solution of N-tert-butylhydroxylamine hydrochloride (3.1 g, 25 mmol), Et2O (50 mL), H2O (25 mL) and NaHCO3 (8.4 g, 100 mmol). At the end of the addition, the reaction mixture was stirred for 10 min at 0 °C. The two phases were separated and the aqueous one was acidified with a 1N solution of citric acid and extracted three times with Et2O. The collected organic phases were dried over Na2SO4 and filtered. Evaporation of the solvent afforded a yellow oil that was purified by FC (CH2Cl2 then hexane/EtOAc 2:1) to give 5 (1.4 g, 40%) as a white crystalline solid. M.p. 79–82 °C. IR (NaCl): 3196, 2972, 2874, 1638, 1601, 1429, 1365, 1206, 1115, 986, 959, 903. 1H-NMR (500 MHz, CDCl3): 8.67 (br. s, 1H); 6.80 (dd, JF = 17.1, JG = 10.4, 1H); 6.19 (d, JF = 17.1, JG = 10.4, 1H); 5.60 (d, JF = 10.4, 1H); 1.47 (s, 9H). 1H-NMR (500 MHz, DMSO-d6): 9.57 (s, 1H); 6.79 (dd, JF = 17.3, JG = 10.45, 1H); 6.05 (dd, JF = 17.3, JG = 2.3, 1H); 5.58 (dd, JF = 10.45, JG = 2.3, 1H); 1.35 (s, 9H). 13C-NMR (90.6 MHz, CDCl3): 174.71; 128.97; 126.90; 61.36; 27.92. EI-MS (70 eV): 157 (18); 1207, 1090, 1032, 972, 791, 719. 1H-NMR (500 MHz, CDCl3): 6.17-6.12 (m, 2H); 3.68 (s, 3H); 3.20 (s, 3H); 2.94-2.91 (m, 2H); 2.52 (br. s, 1H), 1.89-1.83 (m, 1H); 1.68-1.62 (m, 1H); 1.41-1.35 (m, 2H). El-MS (70 eV): 181 (5, M); 150 (9); 121 (20); 93 (26); 66 (15); 55 (100); 39 (11). Anal. calc. for C10H15NO2 (181.23): C 66.27, H 8.34; found C 66.31, H 8.40.

N-tert-Butyl-N-methoxyacrylamide (1b). A solution of N-tert-butyl-N-hydroxyacrylamide (1.4 g, 10 mmol), anhydrous K2CO3 (4.8 g, 35 mmol) and MeI (4.9 g, 2.2 ml, 35 mmol) in dry acetone (37 ml) was stirred at reflux under N2 overnight. The solvent was evaporated and the crude solid was dissolved in CH2Cl2 and washed with a 1 M solution of NaOH. The two phases were separated and the aqueous one was extracted three times with CH2Cl2. The combined organic phases were dried over Na2SO4, filtered and evaporated. The resulting oil was purified by FC (EtOAc/hexane 1:6) to give 1b (1.5 g, 95%) as a colorless oil. IR (NaCl): 2970, 2935, 2818, 1739, 1666, 1628, 1404, 1365, 1325, 1273, 1207, 1090, 1032, 791, 719, 1175, 1090, 1032, 906, 839, 710. 1H-NMR (500 MHz, CDCl3): 6.69 (dd, JF = 17.1, JG = 10.4, 1H); 6.36 (dd, JF = 17.1, JG = 2.3, 1H); 5.68 (dd, JF = 10.4, JG = 2.3, 1H); 3.73 (s, 3H); 1.49 (s, 9H). 13C-NMR (125.8 MHz, CDCl3, -50 °C): 167.23; 128.89; 127.75; 66.00; 61.79; 27.51. El-MS (70 eV): 157 (18, M); 150 (31); 137 (37); 121 (70); 101 (32); 55 (100). Anal. calc. for C8H15NO2 (157.21): C 58.72, H 9.15; found C 58.5, H 9.38.

N-tert-Butyl-N-methoxybicyclo[2.2.1]hept-5-ene-2-carboxamide acid -amide (2b). According to GP 3 from 1b (160 mg, 1.0 mmol) and (R)-BINOL. After purification by FC (EtOAc/hexane 1:15) the product 2b (210 mg, 96% yield) was isolated as an oil (endoexo 7:1). The endo and exo isomers were separated by Lobar® chromatography (EtOAc/hexane 1:20).

Endo-2b: 60% ee, (R)-configuration. IR (NaCl): 3063, 2970, 2870, 1676, 1458, 1395, 1364, 1340, 1281, 1207, 1030, 976, 906, 839, 710. 1H-NMR (360 MHz, CDCl3) broad signals at rt and at -50 °C. 1H-NMR (500 MHz, CDCl3, rt): 2 rotamers in a 2.5:1 ratio: 6.21 (dd, J = 5.5, 3.1, major rotamer, 1H); 6.19 (dd, J = 5.2, 2.8, minor rotamer, 1H); 6.11 (dd, J = 5.2, 3.1, minor rotamer, 1H); 5.78 (dd, J = 5.5, 2.9, major rotamer, 1H); 3.77 (s, minor rotamer, 3H); 3.76 (s, major rotamer, 3H); 3.28 (br. s, major rotamer, 1H); 3.14-3.11 (m, minor rotamer, 1H); 3.11-3.09 (m, major rotamer, 1H); 3.06 (br. s, minor rotamer, 1H); 2.91 (br. s, major rotamer, 1H); 2.81 (br. s, minor rotamer, 1H); 2.07-2.01 (m, minor rotamer, 1H), 1.77-1.73 (m, major rotamer, 1H), 1.65-1.62 (m, minor rotamer, 1H); 1.58-1.54 (m, major rotamer, 1H); 1.41 (s, major rotamer, 9H); 1.38 (s, minor rotamer, 9H); 1.31-1.28 (m, major rotamer, 2H); 1.15-1.11 (m, minor rotamer, 2H). 13C-NMR (125.8 MHz, CDCl3, -50 °C): 179.89 (minor rotamer); 178.25 (major rotamer); 137.68 (major rotamer); 135.49 (minor rotamer); 134.75 (minor rotamer); 130.59 (major rotamer); 65.64 (major rotamer); 65.39 (minor rotamer); 62.40 (major rotamer); 62.10 (minor rotamer); 50.24 (major rotamer); 49.15 (minor rotamer); 45.51 (major rotamer); 44.85 (minor rotamer); 43.86 (minor rotamer); 42.83 (major rotamer); 42.31 (major rotamer); 41.71 (minor rotamer); 31.75 (minor rotamer).
rotamers); 27.82 (major rotamer); 27.61 (major and minor rotamers). EI-MS (70 eV): 223 (9, M); 167 (9); 121 (54); 93 (61); 79 (20); 66 (22); 55 (100); 41 (19). Anal. calc. for C₁₃H₂₁NO₂ (223.31): C 69.92, H 9.48; found C 70.02, H 9.38.

**Exo-2b: 43% ee, (R)-configuration.** IR (NaCl): 3063, 2970, 2870, 1676, 1458, 1395, 1364, 1340, 1281, 1207, 1030, 976, 839, 710. ¹H-NMR (360 MHz, CDCl₃) broad signals at rt and at –50 °C. ¹H-NMR (500 MHz, CDCl₃, rt): 2 rotamers in a 1:1 ratio: 6.17-6.13 (m, two rotamers, 2H); 3.70 (s, one rotamer, 3H); 3.69 (s, one rotamer, 3H); 2.96 (br. s, one rotamer, 1H); 2.91 (br. s, one rotamer, 1H); 2.88 (br. s, one rotamer, 1H); 2.86 (br. s, one rotamer, 1H); 2.51-2.48 (m, one rotamer, 1H); 2.37-2.34 (m, one rotamer, 1H); 2.09-2.04 (m, one rotamer, 1H); 1.64 (br. s, one rotamer, 1H); 1.62 (br. s, one rotamer, 1H); 1.57-1.53 (m, one rotamer, 1H); 1.48-1.42 (m, two rotamers, 2H); 1.44 (s, one rotamer, 9H); 1.43 (s, one rotamer, 9H); 1.29-1.21 (m, two rotamers, 2H). ¹³C-NMR (125.8 MHz, CDCl₃, –50 °C): 181.35 (one rotamer); 179.55 (one rotamer); 138.18 (one rotamer); 136.38 (one rotamer); 135.97 (one rotamer); 66.16 (one rotamer); 65.72 (one rotamer); 65.09 (one rotamer); 53.79 (one rotamer); 47.48 (one rotamer); 46.43 (one rotamer); 45.07 (one rotamer); 44.03 (one rotamer); 41.59 (one rotamer); 41.10 (one rotamer); 31.01 (one rotamer); 29.11 (one rotamer); 27.82 (major rotamer); 27.61 (major and minor rotamers). EI-MS (70 eV): 223 (9, M); 167 (9); 121 (54); 93 (61); 79 (20); 66 (22); 55 (100); 41 (19). Anal. calc. for C₁₃H₂₁NO₂ (223.31): C 69.92, H 9.48; found C 70.02, H 9.38.

**N-phenylhydroxylamine.** Nitrobenzene (120 g, 100 mL, 1.0 mol) was added at rt to a solution of NH₄Cl (62 g, 1.2 mol) in H₂O (2.0 L). Zinc powder (140 g, 2.2 mol) was then added under vigorous stirring in small portions. The reaction temperature increased to about 65 °C and the rate of addition of zinc was adjusted in order to maintain this temperature. At the end of the addition, the mixture was vigorously stirred for 20 min and finally heated at 65 °C and filtrated. The filtrate was washed with 200 mL of hot water. The mother liquor was saturated with NaCl (about 750 g), stirred and crystallized at –15 °C for 4 h. The resulting solid was isolated by filtration, dissolved in Et₂O and dried (Na₂SO₄). After filtration, the solvent was evaporated to afford a yellow solid which was recrystallized from benzene and hexane to afford N-phenylhydroxylamine (71 g, 65%) as a white solid that was stored under N₂ at –20 °C to avoid decomposition. M.p. 84–86 °C. IR (KBr): 3244, 2833, 1957, 1934, 1853, 1726, 1601, 1492, 1419, 1057. ¹H-NMR (360 MHz, CDCl₃): 7.30-7.25 (m, 1H); 7.45-7.41 (m, 1H); 7.19-7.16 (m, 1H); 5.70 (dd, J₁₂ = 10.8, minor rotamer, 1H); 6.46 (dd, J₁₂ = 10.8, minor rotamer, 1H); 6.20 (br. s, 1H). ¹H-NMR (360 MHz, DMSO-d₆) broad signals at rt: 10.77 (br. m, 1H); 7.45-7.41 (m, 1H); 7.19-7.16 (m, 1H). ¹³C-NMR (50.3 MHz, CDCl₃): 149.20; 128.92; 122.61; 114.99. EI-MS (70 eV): 109 (91, M); 93 (21); 92 (100); 79 (13); 66 (70). Anal. calc. for C₆H₇NO (109.13): C 66.04, H 6.47, N 12.84; found C 65.95, H 6.57, N 12.83.

**N-Hydroxy-N-phenylacrylamide.** Acryloyl chloride (54 g, 49 mL, 0.6 mol) was added dropwise at 0 °C to a vigorously stirred solution of N-phenylhydroxylamine (66 g, 0.6 mmol), Et₂O (1.2 L), H₂O (600 mL) and NaHCO₃ (150 g, 1.8 mol). At the end of the addition, the reaction mixture was stirred for 10 min at 0 °C. The two phases were separated and the aqueous one was acidified with a 1N solution of citric acid and extracted three times with Et₂O. The collected organic phases were dried over Na₂SO₄ and filtered. Evaporation of the solvent afforded a yellow solid that was recrystallized from hot EtOAc (5.0 mL for 10 g). After filtration and washing with EtOAc followed by hot hexane, pure N-hydroxy-N-phenylacrylamide (94 g, 96%) was isolated as a white solid. M.p. 88–89 °C. IR (KBr): 3134, 2359, 2002, 1979, 1917, 1853, 1773, 1640, 1587, 1499, 1415, 1358. ¹H-NMR (360 MHz, DMSO-d₆) broad signals at rt: 10.77 (br. s, 1H); 7.64-7.62 (br. m, 3H); 7.39-7.34 (br. m, 2H); 7.18-7.14 (br. m, 1H); 6.95 (br. s, 1H); 6.27 (dd, J₁₂ = 17.25, J₁₁ = 1.82, 1H); 5.80 (d, J₁₂ = 9.99, 1H). ¹H-NMR (360 MHz, CDCl₃) broad signals at rt: 9.37 (br. s, 1H); 7.45-7.41 (br. m, 5H); 6.46 (d, J₁₂ = 15.4, 1H); 6.27 (br. s, 1H); 5.69 (d, J₁₂ = 11.8, 1H). ¹H-NMR (500 MHz, CDCl₃, –40 °C): two rotamers in a 6.5:1 ratio: 11.21 (br. s, major rotamer, 1H); 10.41 (br. s, minor rotamer, 1H); 7.62-7.60 (m, minor rotamer, 1H); 7.50-7.42 (m, major rotamer, 5H); 7.32-7.29 (m, minor rotamer, 3H); 7.19-7.16 (m, minor rotamer, 1H); 77.05 (dd, J₁₂ = 17.0, J₁₁ = 10.8, minor rotamer, 1H); 6.46 (dd, J₁₂ = 16.8, J₁₁ = 1.0, major rotamer, 1H); 6.36 (d, J₁₂ = 17.0, minor rotamer, 1H); 6.20 (dd, J₁₂ = 16.8, J₁₁ = 10.5, major rotamer, 1H); 5.74 (d, J₁₂ = 10.8, minor rotamer, 1H). ¹³C-NMR (125.8 MHz, CDCl₃, –40 °C): 165.64 (minor rotamer); 162.07 (major rotamer); 140.13 (minor rotamer);
138.41 (major rotamer); 129.49 (minor rotamer); 129.15 (major rotamer); 128.93 (minor rotamer); 128.90 (major rotamer); 128.27 (minor rotamer); 127.13 (major rotamer); 126.57 (major rotamer); 126.05 (major rotamer); 125.65 (minor rotamer); 121.41 (major rotamer). El-MS (70 eV): 163 (14, M); 147 (20); 94 (33); 78 (30); 55 (100). Anal. calc. for C16H18NO2 (163.18): C 66.25, H 5.56; found C 66.45, H 5.58.

**N-Methoxy-N-phenylacrylamide (1e):** A solution of N-hydroxy-N-phenylacrylamide (20 g, 120 mmol), anhydrous K2CO3 (59 g, 430 mmol) and MeI (61 g, 27 ml, 430 mmol) in dry acetone (450 ml) was stirred at reflux under N2 overnight. The solvent was evaporated and the crude solid was dissolved in CH2Cl2 and washed with a 1 M solution of NaOH. The two phases were separated and the aqueous one was extracted three times with CH2Cl2. The combined organic phases were dried over Na2SO4, filtered and evaporated. The crude oil was distilled (46-48 °C at 7 • 10^-6 mbar) or purified by FC (EtOAc/hexane 1:6) to give 1e (21 g, 95%) as a yellow oil. IR (NaCl): 3329, 3281, 3067, 2972, 2938, 2897, 2818, 1946, 1667, 1593, 1408, 1346, 1273, 997, 760. 1H-NMR (500 MHz, CDCl3) broad signals at rt: 7.55-7.53 (m, 2H); 7.42-7.39 (m, 2H); 7.27-7.24 (m, 1H); 6.73 (br. s, 1H); 6.53 (dd, J = 17.01, Jgem = 1.92, 1H); 5.79 (d, J = 11.81, 1H); 3.75 (s, 3H). 13C-NMR (125.8 MHz, CDCl3) is resolved at -40 °C showing two rotamers in a 3:3:1 ratio: 7.64-7.61 (m, major rotamer, 2H); 7.53-7.50 (m, minor rotamer, 2H); 7.50-7.44 (m, major rotamer, 2H); 7.38-7.36 (m, minor rotamer, 2H); 7.31-7.27 (m, major and minor rotamers, 1H); 6.97 (dd, J = 17.1, J = 10.3, major rotamer, 1H); 6.64 (dd, J = 17.1, Jgem = 1.7, major rotamer, 1H); 6.54 (dd, J = 16.8, Jgem = 1.5, minor rotamer, 1H); 6.09 (dd, J = 16.8, J = 10.4, minor rotamer, 1H); 5.97 (dd, J = 10.3, Jgem = 1.7, major rotamer, 1H); 5.70 (dd, J = 10.4, Jgem = 1.46, minor rotamer, 1H); 3.83 (s, minor rotamer, 3H); 3.77 (s, major rotamer, 3H). 13C-NMR (125.8 MHz, CDCl3, -50 °C): 164.33 (major rotamer); 161.95 (minor rotamer); 137.08 (minor rotamer); 136.87 (major rotamer); 130.86 (major rotamer); 129.30 (major rotamer); 129.17 (minor rotamer); 129.04 (minor rotamer); 128.90 (major rotamer); 127.18 (minor rotamer); 127.03 (minor rotamer); 126.11 (major rotamer); 121.76 (major and minor rotamers); 62.43 (major rotamer); 61.25 (minor rotamer). El-MS (70 eV): 177 (64, M); 162 (14); 146 (21); 123 (82); 107 (41); 92 (32); 78 (69); 65 (36); 56 (100). Anal. calc. for C16H18NO2 (177.20): C 67.78, H 6.26; found C 67.78, H 6.21.

**N-Methoxy-N-phenylbicyclo[2.2.1]hept-5-ene-2-carboxamide (2c):** According to GP 3 from 1c (177 mg, 1.0 mmol) and (R)-Binally. After purification by FC (EtOAc/hexane 1:8) the product 2c (220 mg, 95%) was isolated as a colorless oil (endo:exo 69:1). The endo and exo isomers were separated by Lobar® chromatography (EtOAc/hexane 1:10).

**Endo-2c:** 96% ee, [α]D20 = +117.0° (c = 1, CHCl3), (R)-configuration. IR (NaCl): 3506, 3061, 2970, 2930, 2870, 2814, 1678, 1489, 1379, 1300, 1067, 1016, 773, 750, 712. 1H-NMR (500 MHz, CDCl3) broad signals at rt: 7.46-7.44 (m, 2H); 7.39-7.35 (m, 2H); 7.23-7.20 (m, 1H); 6.19 (dd, J = 5.6, 3.1, 1H); 6.01 (dd, J = 5.6, 2.9, 1H); 3.71 (s, 3H); 3.30 (br. s, 1H); 3.24 (br. s, 1H); 2.91 (s, 1H); 1.98-1.90 (br. m, 1H); 1.53-1.45 (br. m, 1H); 1.45-1.43 (br. m, 1H). 1H-NMR (500 MHz, CDCl3) is resolved at -40 °C showing two rotamers in a 9:1 ratio. 1H-NMR (500 MHz, CDCl3, -50 °C): 7.46-7.44 (m, major and minor rotamers, 2H); 7.39-7.35 (m, major and minor rotamers, 2H); 7.23-7.20 (m, major and minor rotamers, 1H); 6.28 (dd, J = 5.6, 3.0, minor rotamer, 1H); 6.25 (dd, J = 5.6, 3.0, major rotamer, 1H); 6.05 (dd, J = 5.5, 2.4, minor rotamer, 1H); 6.00 (dd, J = 5.5, 2.8, major rotamer, 1H); 3.76 (s, major and minor rotamers, 3H); 3.42-3.39 (m, major and minor rotamers, 1H); 3.35 (s, major rotamer, 1H); 2.99 (s, major rotamer, 1H); 2.86 (s, minor rotamer, 1H); 2.80 (s, minor rotamer, 1H); 2.06-2.01 (m, major rotamer, 1H); 1.67-1.62 (m, minor rotamer, 1H); 1.55-1.52 (m, major rotamer, 1H); 1.49-1.47 (m, major rotamer, 1H); 1.43-1.42 (m, major rotamer, 1H); 1.30-1.22 (m, minor rotamer, 1H); 1.25-1.18 (m, minor rotamer, 1H); 1.91-1.83 (m, minor rotamer, 1H).
N-Ethoxy-N-phenylacrylamide (1d): A solution of N-hydroxy-N-phenylacrylamide (20 g, 120 mmol), anhydrous K$_2$CO$_3$ (59 g, 430 mmol) and EtI (67 g, 34 ml, 430 mmol) in dry acetone (450 ml) was stirred at reflux under N$_2$ overnight. The solvent was evaporated and the crude solid was dissolved in CH$_2$Cl$_2$ and washed with a 1 M solution of NaOH. The two phases were separated and the aqueous one was extracted three times with CH$_2$Cl$_2$. The combined organic phases were dried over Na$_2$SO$_4$, filtered and evaporated. The crude oil was purified by FC (EtOAc/hexane 1:1) to give 1d (22 g, 95%) as a yellow oil. IR (NaCl): 3502, 3066, 2982, 2937, 2891, 1948, 1882, 1674, 1618, 1593, 1487, 1408, 1346, 1271, 1090, 1024, 984, 760, 694. $^1$H-NMR (500 MHz, CDCl$_3$) broad signals at rt: 7.56-7.55 (m, 2H); 7.41-7.38 (m, 2H); 7.25-7.22 (m, 1H); 6.78 (br. s, 1H); 6.52 (dd, $J_E = 17.0$, $J_{gem} = 1.7$, 1H); 5.79 (dd, $J_z = 10.4$, $J_{gem} = 1.7$, 1H); 3.95 (q, $J = 7.0$, 2H); 1.29 (t, $J = 7.0$, 3H). $^{13}$C-NMR (125.8 MHz, CDCl$_3$, -50 °C): 175.14 (major rotamer); 172.57 (minor rotamer); 138.06 (major rotamer); 137.96 (minor rotamer); 137.20 (major rotamer); 135.81 (major rotamer); 135.63 (minor rotamer); 129.34 (rotamer, 1H); 129.14 (minor rotamer); 128.74 (major rotamer); 127.46 (minor rotamer); 127.24 (major rotamer, 1H); 126.70 (minor rotamer); 126.09 (rotamer, 1H); 125.65 (major rotamer); 125.65 (rotamer, 1H); 61.61 (major rotamer); 1.90-1.30 (m, minor rotamer, 1H); 1.90-1.30 (m, minor rotamer, 1H); 1.90-1.30 (m, minor rotamer, 1H).
**Endo-2d:** 86% ee, \([\alpha]_{D}^{20} = +100.2^\circ \) (c = 1, CHCl₃), (R)-configuration. IR (NaCl): 3061, 2976, 2941, 2870, 1680, 1595, 1491, 1369, 1281, 1261, 1026, 758, 696. \(^1\)H-NMR (500 MHz, CDCl₃) broad signals at rt: 7.50-7.48 (m, 2H); 7.39-7.36 (m, 2H); 7.23-7.20 (m, 1H); 6.17-6.14 (br. m, 2H); 3.90 (m, 2H); 3.05 (br. s, 1H); 2.93 (br. s, 1H); 2.59 (br. s, 1H); 1.99-1.95 (br. m, 1H); 1.70-1.68 (m, 1H); 1.41-1.36 (br. m, 2H); 1.26 (t, \(J = 7.0,3\)H). \(^1\)H-NMR (500 MHz, CDCl₃) is resolved at -50 °C showing two rotamers in a 8:1 ratio: 7.58-7.56 (m, major and minor rotamer, 2H); 7.51-7.46 (m, minor rotamer, 1H); 7.46-7.41 (m, major rotamer, 2H); 7.40-7.38 (m, minor rotamer, 2H); 7.26-7.23 (m, major rotamer, 1H); 6.24 (dd, \(J = 11.5, 5.5, \) major rotamer, 1H); 6.23 (dd, \(J = 11.5, 5.5, \) major rotamer, 1H); 6.04 (dd, \(J = 5.5, 2.9, \) minor rotamer, 1H); 5.91 (dd, \(J = 5.5, 2.9, \) minor rotamer, 1H); 4.03 (q, \(J = 7.0, \) minor rotamer, 2H); 3.92 (A part of ABX, \(J_{AB} = J_{AX} = 7.1, \) 1H); 3.88 (B part of ABX, \(J_{AB} = J_{AX} = 7.1, \) 1H); 3.12 (s, major rotamer, 1H); 2.98 (s, major rotamer, 1H); 2.95 (s, minor rotamer, 1H); 2.90 (s, minor rotamer, 1H); 2.65-2.62 (m, major rotamer, 1H); 2.01-1.98 (m, major rotamer, 1H); 1.86-1.83 (m, minor rotamer, 1H); 1.59-1.57 (m, major rotamer, 1H); 1.55-1.51 (m, major rotamer, 1H); 1.40-1.38 (m, major rotamer, 1H); 1.31 (t, \(J = 7.1, \) major rotamer, 3H); 1.29 (t, \(J = 7.0, \) minor rotamer, 3H); 1.23-1.22 (m, minor rotamer, 2H); 1.06-1.00 (m, minor rotamer, 1H); 0.90-0.83 (m, minor rotamer, 1H). \(^1\)C-NMR (125.8 MHz, CDCl₃, -50 °C): 175.35 (major rotamer); 172.92 (minor rotamer); 138.84 (minor rotamer); 138.35 (major rotamer); 138.09 (minor rotamer); 138.02 (major rotamer); 135.96 (major rotamer); 135.82 (minor rotamer); 129.42 (major rotamer); 128.61 (major rotamer); 127.87 (major rotamer); 126.51 (major rotamer); 124.98 (major and minor rotamers); 69.67 (major rotamer); 69.07 (minor rotamer); 46.55 (minor rotamer); 46.39 (major rotamer); 46.26 (major rotamer); 45.55 (minor rotamer); 41.43 (major rotamer); 40.73 (minor rotamer); 31.45 (minor rotamer); 30.63 (major rotamer); 13.42 (major rotamer); 8.46 (minor rotamer). EI-MS (70 eV): 205 (10, \(M \)), 128.61 (major rotamer); 127.87 (major rotamer); 126.51 (major and minor rotamers); 124.98 (major and minor rotamers); 113.82 (major and minor rotamers); 108.81 (major and minor rotamers); 94.61 (major and minor rotamers); 86.80 (major and minor rotamers); 75.63 (minor rotamer); 74.22, 73.91, 72.61, 71.31, 70.22, H 7.37; found C 70.30, H 7.41.

**N-Isopropoxy-N-phenylacrylamide (1e):** A solution of N-hydroxy-N-phenylacrylamide (20 g, 120 mmol), anhydrous K₂CO₃ (59 g, 430 mmol) and tBuI (73 g, 43 ml, 430 mmol) in dry acetone (450 ml) was stirred at reflux under N₂ overnight. The solvent was evaporated and the crude solid was dissolved in CH₂Cl₂ and washed with a 1 M solution of NaOH. The two phases were separated and the aqueous one was extracted three times with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄. Evaporation of the solvent afforded an oil which was purified by FC (EtOAc/hexane 1:6) to give 1e (84 g, 95%) as a yellow oil. IR (NaCl): 3055, 2983, 2409, 2305, 1666, 1618, 1491, 1406, 1346, 1265, 1088, 897, 739, 706. \(^1\)H-NMR (500 MHz, CDCl₃) broad signals at rt: 7.54-7.52 (m, 2H); 7.40-7.37 (m, 2H); 7.24-7.21 (m, 1H); 6.84 (br. s, 1H); 6.50 (dd, \(J_{E} = 17.1, J_{gem} = 2.0, \) 1H); 5.77 (dd, \(J_{E} = 10.4, J_{gem} = 2.0, \) 1H); 4.11 (sept, \(J = 6.2, \) 1H); 1.29 (d, \(J = 6.2, \) 1H). \(^1\)H-NMR (500 MHz, CDCl₃) is resolved at -50 °C showing two rotamers in a 9:1 ratio. 7.59-7.58 (m, major rotamer, 2H); 7.49-7.37 (m, major and minor rotamers, 3H); 7.30-7.25 (m, major and minor rotamers, 1H); 7.11-7.09 (m, minor rotamer, 1H); 7.01 (dd, \(J_{E} = 17.1, J_{Z} = 10.4, \) major rotamer, 1H); 6.57 (dd, \(J_{E} = 17.1, J_{Z} = 1.6, \) major rotamer, 1H); 6.54 (dd, \(J_{E} = 16.9, \) minor rotamer, 1H); 6.14 (dd, \(J_{E} = 16.9, J_{Z} = 10.3, \) minor rotamer, 1H); 5.91 (dd, \(J_{E} = 10.4, J_{Z} = 1.6, \) major rotamer, 1H); 5.67 (d, \(J_{Z} = 10.3, \) minor rotamer, 1H); 4.16 (sep, \(J = 6.0, \) minor rotamer, 1H); 4.09 (sept, \(J = 6.0, \) major rotamer, 1H); 1.28 (d, \(J = 6.0, \) major and minor rotamers, 6H). \(^1\)C-NMR (125.8 MHz, CDCl₃, -50 °C): 165.36 (major rotamer); 163.00 (minor rotamer); 138.93 (major rotamer); 138.11 (major rotamer); 130.32 (major rotamer); 129.06 (minor rotamer); 128.92 (minor rotamer); 127.24 (major rotamer); 126.82 (major and minor rotamers); 126.21 (major rotamer); 122.71 (major and minor rotamers); 75.84 (major rotamer); 75.63 (minor rotamer); 21.73 (minor rotamer); 20.61 (major rotamer). EI-MS (70 eV): 205 (10, \(M \)), 163 (34); 108 (22); 91 (22); 55 (100). Anal. calc. for C₁₆H₁₉NO₂ (257.33): C 74.68, H 7.44; found C 74.64, H 7.38.

**exo-2d:** 65% ee, (R)-configuration.
N-Isopropoxy-N-phenylbicyclo[2.2.1]hept-5-ene-2-carboxamide (2e): According to GP 2 starting form 1e (210 mg, 1.0 mmol) and (R,R)-1-NaphTADDOL. After purification by FC (EtOAc/hexane 1:1) the product 2e (260 mg, 95%) was isolated as colorless oil (endo:exo 33:1). The endo and exo isomers were separated by lobar chromatography (EtOAc/hexane 1:14). Endo-2e: 89% ee, [α]D = -97.8° (c = 1, CHCl3), (S)-configuration. IR (NaCl): 3061, 2974, 2939, 2870, 1680, 1593, 1491, 1373, 1279, 1198, 1113, 1084, 1065, 906, 829, 759, 698.

1H-NMR (500 MHz, CDCl3) broad signals either at rt or at -50 °C. 1H-NMR (500 MHz, CDCl3) at rt: 7.44-7.43 (m, 1H); 7.42-7.41 (m, 1H); 7.37-7.33 (m, 2H); 7.22-7.18 (m, 1H); 6.15 (dd, J = 5.6, 3.0 1H); 5.95 (dd, J = 5.6, 2.9 2H); 4.10 (sep., J = 6.2, 1H); 3.30 (br. s, 1H); 3.24 (br. s, 1H); 2.88 (br. s, 1H); 1.92-1.88 (br. m, 1H); 1.50-1.47 (m, 1H); 1.42-1.40 (m, 1H); 1.24 (d, J = 6.2, 6H). 13C-NMR (125.8 MHz, CDCl3, -50 °C): 175.01 (minor rotamer); 172.68 (major rotamer); 140.36 (minor rotamer); 138.94 (major rotamer); 130.81 (major rotamer); 129.78 (major and minor rotamers); 129.40 (minor rotamer); 129.23 (minor rotamer); 129.00 (minor and major rotamers); 128.94 (minor rotamer); 128.84 (major rotamer); 128.47 (minor rotamer); 127.25 (minor rotamer); 126.45 (major rotamer); 126.26 (major rotamer); 122.38 (major and minor rotamers); 77.44 (major rotamer); 75.65 (minor rotamer); 75.31 (major rotamer); 49.66 (major rotamer); 46.36 (minor rotamer); 45.23 (minor rotamer); 42.51 (major rotamer); 41.27 (major rotamer); 38.89 (minor rotamer); 37.45 (minor rotamer); 36.17 (minor rotamer); 34.12 (minor rotamer); 30.46 (major rotamer) 20.81 (minor rotamer); 20.37 (minor rotamer); 129.33 (major rotamer); 127.63 (minor rotamer); 125.62 (major rotamer); 122.54 (major rotamer); 121.62 (major rotamer); 119.51 (minor rotamer); 118.50 (minor rotamer); 108.50 (minor rotamer); 106.50 (minor rotamer); 73.22 (minor rotamer); 72.02 (minor rotamer); 70.82 (minor rotamer); 69.62 (minor rotamer); 68.42 (minor rotamer); 67.22 (minor rotamer); 66.02 (minor rotamer); 64.82 (minor rotamer); 63.62 (minor rotamer); 62.42 (minor rotamer); 61.22 (minor rotamer); 59.02 (minor rotamer); 57.82 (minor rotamer); 56.62 (minor rotamer); 55.42 (minor rotamer); 54.22 (minor rotamer); 53.02 (minor rotamer); 51.82 (minor rotamer); 50.62 (minor rotamer); 49.42 (minor rotamer); 48.22 (minor rotamer); 47.02 (minor rotamer); 45.82 (minor rotamer); 44.62 (minor rotamer); 43.42 (minor rotamer); 42.22 (minor rotamer); 41.02 (minor rotamer); 39.82 (minor rotamer); 38.62 (minor rotamer); 37.42 (minor rotamer); 36.22 (minor rotamer); 35.02 (minor rotamer); 33.82 (minor rotamer); 32.62 (minor rotamer); 31.42 (minor rotamer); 30.22 (minor rotamer); 29.02 (minor rotamer); 27.82 (minor rotamer); 26.62 (minor rotamer); 25.42 (minor rotamer); 24.22 (minor rotamer); 23.02 (minor rotamer); 21.82 (minor rotamer); 20.62 (minor rotamer); 19.42 (minor rotamer); 18.22 (minor rotamer); 17.02 (minor rotamer); 15.82 (minor rotamer); 14.62 (minor rotamer); 13.42 (minor rotamer); 12.22 (minor rotamer); 11.02 (minor rotamer); 9.82 (minor rotamer); 8.62 (minor rotamer); 7.42 (minor rotamer); 6.22 (minor rotamer); 5.02 (minor rotamer); 3.82 (minor rotamer); 2.62 (minor rotamer); 1.42 (minor rotamer).

N-Benzoyloxy-N-phenylacrylamide (1f): A solution of N-hydroxy-N-phenylacrylamide (20.0 g, 120 mmol), anhydrous K2CO3 (59 g, 430 mmol) and BzBr (73 g, 51 ml, 430 mmol) in dry acetone (450 ml) was stirred at reflux under N2 overnight. The solvent was evaporated and the crude solid was dissolved in CH2Cl2 and washed with a 1 M solution of NaOH. The two phases were separated and the aqueous one was extracted three times with CH2Cl2. The combined organic phases were dried over Na2SO4. Evaporation of the solvent afforded an oil which was purified by FC (EtOAc/hexane 1:4) to give 1f (25 g, 95%) as a yellow oil. IR (NaCl): 3064, 3034, 2939, 2879, 1952, 1668, 1616, 1593, 1491, 1404, 1344, 1269, 1203, 1070, 982, 912, 760, 696. 1H-NMR (500 MHz, CDCl3) is resolved at -50 °C showing two rotamers in a 6:1 ratio. 7.70-7.68 (m, major rotamer, 2H); 7.51-7.41 (m, major rotamer, 7H and minor rotamers, 8H); 7.39-7.37 (m, minor rotamer, 2H); 7.33-7.29 (m, major rotamer, 1H); 7.27 (d, J = 16.8, minor rotamer, 1H); 6.91 (dd, Je = 17.0, Je = 10.4, major rotamer, 1H); 6.54 (dd, Je = 17.0, Je = 1.4, major rotamer, 1H); 6.10 (dd, Je = 16.8, Je = 10.3, minor rotamer, 1H); 5.87 (dd, Je = 10.4, Je = 1.4, major rotamer, 1H); 5.68 (dd, Je = 10.3, minor rotamer, 1H); 5.03 (s, minor rotamer, 2H); 4.84 (s, major rotamer, 2H). 13C-NMR (125.8 MHz, CDCl3, -50 °C): 168.17 (major rotamer); 164.71 (minor rotamer); 162.52 (major rotamer); 138.18 (minor rotamer); 138.33 (major rotamer); 134.10 (minor rotamer); 132.92 (major rotamer); 130.81 (major rotamer); 129.78 (major and minor rotamers); 129.40 (minor rotamer); 129.23 (minor rotamer); 129.00 (minor and major rotamers); 128.94 (major rotamer); 128.84 (major rotamer); 128.47 (minor rotamer); 127.25 (minor rotamer); 126.45 (major rotamer); 126.26 (major rotamer); 122.38 (major and minor rotamers); 77.44 (major rotamer); 75.45 (minor rotamer). EI-MS (70 eV): 253 (7, M); 147 (11); 108 (12); 93 (28); 91 (100); 77 (22); 55 (63). Anal. calc. for C18H15NO2 (253.30): C 75.78, H 5.97; found C 75.68, H 6.06.

N-Benzoyloxy-N-phenylbicyclo[2.2.1]hept-5-ene-2-carboxamide (2f): According to GP 2 from 2f (250 mg, 1.0 mmol) and (R,R)-1-NaphTADDOL. After purification by FC (EtOAc/hexane 1:15) the product 2f (290 mg, 92%) was isolated as a colorless oil (endo:exo 21:1). The endo and exo isomers were separated by Lobar® chromatography (EtOAc/hexane 1:18).
**N-tert-Butyl-N-phenylacrylamide (1g):** Concentrated sulfuric acid (0.1 mL) was added at -15 °C to a well stirred solution of N-hydroxy-N-phenylacrylamide (820 mg, 5.0 mmol) and isobutylene (1.4 g, 24 mmol) in CH₂Cl₂ (7.0 ml). The reaction mixture was allowed to warm to room temperature and stirred for 2 days. It is then diluted with CH₂Cl₂, washed with Na₂CO₃, brine, dried over Na₂SO₄. Evaporation of the solvent afforded an oil which was purified by FC (EtOAc/hexane 1:18) to give 1g (710 mg, 65%) as a yellow oil. IR (NaCl): 3064, 3032, 2972, 2941, 2870, 1680, 1593, 1491, 1335, 1259, 1182, 1085, 989, 844, 773, 694. ¹H-NMR (500 MHz, CDCl₃): 7.50-7.48 (m, 2H); 7.37-7.33 (m, 2H); 7.23-7.19 (m, 1H); 6.85 (dd, Jₑ = 17.1, Jₑ = 10.4, 1H); 6.47 (dd, Jₑ = 17.1, Jₑ = 2.0, 1H); 5.74 (dd, Jₑ = 10.4, Jₑ = 2.0, 1H); 1.25 (s, 9H). ¹³C-NMR (125.8 MHz, CDCl₃, -50 °C): 164.48 (major rotamer); 165.23 (minor rotamer); 142.59 (minor rotamer); 141.96 (major rotamer); 130.29 (major rotamer); 129.36 (minor rotamer); 128.99 (major rotamer); 128.22 (major rotamer); 127.77 (minor rotamer); 126.97 (major rotamer); 126.29 (minor rotamer); 126.16 (major rotamer); 123.59 (minor rotamer); 123.44 (major rotamer); 85.00 (major rotamer); 84.97 (minor rotamer); 74.47 (major and minor rotamers). EI-MS (70 eV): 279 (11); 219 (15, M); 163 (72); 91 (28); 57 (47); 55 (100). Anal. calc. for C₁₃H₁₇NO₂: C 78.97, H 6.63; found C 78.89, H 6.64.

**N-tert-Butyl-N-phenylbicyclo[2.2.1]hept-5-ene-2-carboxamide (2g):** According to GP 2 from 1g (220 mg, 1.0 mmol) and (R,R)-1-NaphTADDOL. After purification by FC (EtOAc/hexane 1:10) the product 2g (270 mg, 93%) was isolated as a colorless oil (endo:exo >50:1).

**Endo-2g:** 92% ee, [α]₂₀ = -99.1° (c = 1, CHCl₃), (S)-configuration. IR (NaCl): 3061, 2976, 2937, 2870, 1689, 1593, 1489, 1367, 1254, 1184, 1080, 839, 764, 696. ¹H-NMR (500 MHz, CDCl₃) broad signals at rt or at -50 °C. ¹H-NMR (500 MHz, CDCl₃) at rt: 7.43-7.40 (m, 2H); 7.36-7.32 (m, 2H); 7.23-7.19 (m, 1H); 6.15-6.11 (br, m, 1H); 5.91 (br, s, 1H); 3.25 (br, s, 1H); 2.85 (br, s, 1H); 1.81 (br, s, 1H); 1.44-1.42 (br, m, 1H); 1.42-1.41 (m, 1H); 1.26-1.24 (m, 1H); 1.22 (s, 9H). ¹³C-NMR (125.8 MHz, CDCl₃, -50 °C): 175.44 (major rotamer); 174.90 (minor rotamer); 142.86 (major rotamer); 137.41 (major rotamer); 137.27 (minor rotamer); 131.97 (major rotamer); 129.36 (minor rotamer); 128.99 (major rotamer); 128.22 (major rotamer); 126.16 (major rotamer); 123.59 (minor rotamer); 123.44 (major rotamer); 85.00 (major rotamer); 84.97 (minor rotamer); 74.47 (major and minor rotamers).
130.87 (minor rotamer); 128.05 (major rotamer); 127.68 (minor rotamer); 125.62 (major rotamer); 123.80 (major and minor rotamers); 83.93 (major rotamer); 50.22 (major rotamer); 49.91 (minor rotamer); 45.30 (major rotamer); 41.42 (major rotamer); 41.48 (minor rotamer); 41.08 (major rotamer); 28.56 (major and minor rotamers); 27.74 (major rotamer) 27.64 (major rotamer). EI-MS (70 eV): 285 (27, M); 229 (50); 163 (17); 121 (90); 93 (76); 91 (37); 77 (32); 57 (53); 55 (100). Anal. calc. for C_{18}H_{23}NO_{2} (285.38): C 75.76, H 8.12; found C 75.78, H 8.16.

1-Bicyclo[2.2.1]hept-5-en-2-yl-1-ethanone. A 1.6M solution of MeLi (3.8 mL, 6.0 mmol) in THF was added dropwise at –78 °C under N₂ to a solution of 2a (170 mg, 1.0 mmol) in THF (5.0 mL). The reaction mixture was allowed to warm up to room temperature overnight. The mixture was then cannulated on a 1:1 mixture of Et₂O and saturated NH₄Cl at 0 °C. The two phases were separated, the aqueous one was extracted three times with Et₂O. The collected organic phases were dried over Na₂SO₄ and filtered. Evaporation of the solvent and purification by FC (EtOAc:hexane 1:10) afforded the desired methyl ketone (150 mg, 99%) as a colorless oil. Physical and spectral data are in accordance with the literature.⁴

The enantiomeric excesses were measured by gas chromatography: 25 m fused silica; 0.32 mm id; stationary phase: heptakis-2,3-O-diethyl-6-0-tert-butyldimethylsilyl)-β-cyclodextrine in polymer diphenylether; df: 0.25 µm; temperature: 78 °C. Retention time: endo-(R) = 23.9 min, endo-(S) = 28.6 min; exo-(R or S) = 25.5 min, exo-(S or R) = 26.9 min. A copy of a chromatogram (racemic mixture) is annexed at the end of this document.

Chromatogram of racemic 2-bicyclo[2.2.1]hept-5-en-2-ylpropan-2-ol:
Chromatogram of racemic 1-bicyclo[2.2.1]hept-5-en-2-yl-1-ethanone: