An Efficient Route to Tetrahydronaphthols via Addition of *ortho*-Lithiated Stilbene Oxides to α,β -Unsaturated Fischer Carbene Complexes

Vito Capriati,^a Saverio Florio,^{a,} Renzo Luisi,^a Filippo Maria Perna,^a*

Antonio Salomone,^a Francesco Gasparrini^b

^a Dipartimento Farmaco-Chimico, University of Bari, Via E. Orabona 4, I-70126 - Bari, C.N.R., Istituto di Chimica dei Composti OrganoMetallici "ICCOM", Sezione di Bari, Italy

^b Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive, Università "La Sapienza", P.le A. Moro 5, I-00185 Roma, Italy

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General Experimental Methods. Tetrahydrofuran (THF) was freshly distilled under a nitrogen atmosphere over sodium/benzophenone ketyl. Petroleum ether refers to the 40-60 °C boiling fraction. For the ^1H and ^{13}C NMR spectra (^1H NMR 300, 400, 500 MHz; ^{13}C NMR 75.4, 100 Mhz, 125 MHz), CDCl_3 was used as the solvent. GC-MS spectrometry analyses were performed on a gas-chromatograph HP 5890 (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector operating at 70 eV (EI). MS-ESI analyses were performed on Agilent 1100 LC/MSD trap system VL. Microanalyses were carried out on an EuroEA 3000 C, H, N, S analyzer. Optical rotations were performed on purified compounds and measured with a Perkin-Elmer 341 polarimeter, using a cell of 1 dm path length at 20 °C; the concentration (c) is expressed in g/100 mL. Melting points (uncorrected) were carried out on an Stuart SMP3 apparatus. Analytical thin layer chromatography (TLC) was carried out on Merck precoated 0.25 mm thick plates of Kieselgel 60 F254; visualization was accomplished by UV light (254 nm) or by spraying with a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 ml 17.6 % (w/v) aqueous sulphuric acid and heating to 200 °C for some time until blue spots appear. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique. Enantiomeric purity assay for compound (+)-**4g** and (+)-**5g** was carried out with both racemic and optically active substrates using ^1H NMR (500 MHz, CCl_4 with CDCl_3 as external standard) in the presence of the Chiral Solvating Agent (CSA) (*R*)-(-)-2,2,2-trifluoro-1-(9-anthryl)ethanol,¹ (CSA/epoxide molar ratio = 2/1). Tungsten complexes **3a-g**,² **3h**³ and *trans*-stilbene oxide derivatives **1a-d**⁴ were prepared according to the reported procedure. (*S,S*)-*o*-bromo *trans*-stilbene oxide (*S,S*)-**1a** (ee = 99%) was obtained by preparative HPLC separation of the racemic mixture (Chiralcel OD-H column 256 × 4.6 mm × ID; flow: 1 ml/min, eluent: *n*-hexane/IPA 90-95/5).

¹ Parker, D. *Chem. Rev.* **1991**, 91, 1441–1457.

² Seco, J. M.; Heinen, H. *Chem. Ber.* **1987**, 120, 537–540.

³ Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, 112, 3642-3659.

⁴ Akgun, E.; Glinski, M. B.; Dawan, K. L.; Durst, T. *J. Org. Chem.* **1981**, 46, 2730.

Preparation of Carbene Complexes 4. General Procedure. To a stirred solution of *o*-bromo stilbene oxide **1a** (1.0 mmol) in THF (6 mL), cooled at -78°C (dry ice/acetone bath), PhLi (0.9 mmol, 0.5 mL of a 1.8 M solution in dibutylether), was added and the resulting mixture stirred for 45 min. Then a solution of the tungsten complex **3** (0.75 mmol) in THF (2 mL) was added dropwise and the mixture stirred for 1 h at -78°C , allowed to warm to rt and stirred for further 2-4 hours. After this time it was poured into a rounded bottom flask containing 1 g of silica gel and the solvent evaporated *in vacuo*. The crude, adsorbed on silica gel, was column chromatographed (silica gel; petroleum ether/Et₂O 9/1÷95/5) to give compounds **4**, which showed the data below.

The intermediate **2a** could be isolated (column chromatography, *R_f*, 0.6, ethyl acetate/petroleum ether, 8/2) by quenching the reaction at short reaction time with sat. NH₄Cl.

(2'*R,3'*R**,3*R**)-Pentacarbonyl-{3-(*N*-methylpyrrol-2-yl)-3-[2-(3-phenyloxiran-2-yl)phenyl]**

methoxypropylidene}tungsten (2a**):** yellow solid, mp 135-137 $^{\circ}\text{C}$ (dec.) (hexane), 53%; ¹H NMR (500 MHz) δ 3.08 (dd, $J^2 = 18.3$, $J^3 = 3.9$ Hz, 1 H), 3.15 (s, 3 H), 3.70 (d, $J = 1.8$ Hz, 1 H), 4.08 (d, $J = 1.8$ Hz, 1 H), 4.11 (s, 3 H), 4.30 (dd, $J^2 = 18.3$, $J^3 = 10.3$ Hz, 1 H), 4.83 (dd, $J^2 = 10.1$ Hz, $J^3 = 3.9$ Hz, 1 H), 5.98-5.99 (m, 1 H), 6.02-6.04 (m, 1 H), 6.49-6.50 (m, 1 H), 6.81-6.83 (m, 1 H), 7.20-7.41 (m, 8 H); ¹³C NMR (125 MHz) δ 33.64, 35.2, 61.0, 61.9, 70.3, 70.5, 106.6, 107.6, 122.3, 124.4, 125.2, 127.1, 127.4, 128.5, 128.6, 128.7, 132.2, 133.6, 136.7, 140.5, 197.0 (4 $\times$ C=O), 202.5 (C=O), 330.3 (C=W); MS (ESI); m/z 668 [M – H][–]; FT-IR (KBr, cm^{–1}) 2071, 1935, 1447, 1261, 1007, 951, 708.

(1*S,2*S**,3*R**,4*R**)-Pentacarbonyl{[4-hydroxy-1-(*N*-methyl-2-pyrrolyl)-3-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl]methoxymethylene}tungsten (**4a**):** yellow solid, mp 146-147 °C (dec.) (hexane), 53 %; ¹H NMR (500 MHz) δ 2.43 (br s, 1 H), 3.22 (s, 3 H), 3.97 (dd, J = 3.7, 2.1 Hz, 1 H), 4.19 (s, 3 H), 4.42 (d, J = 11.9 Hz, 1 H), 4.98 (d, J = 2.1 Hz, 1 H), 5.51 (dd, J = 11.9, 3.7 Hz, 1 H), 5.76 (m, 1 H), 5.96 (m, 1 H), 6.44 (m, 1 H), 6.70 (m, 2 H), 6.88 (m, 1 H), 7.16-7.31 (m, 5 H), 7.41 (m, 1 H). ¹³C NMR (125 MHz) δ 34.7, 36.4, 49.4, 69.5, 71.6, 71.7, 106.6, 109.1, 122.7, 127.1, 127.2, 128.1, 128.9, 129.9, 131.5, 135.8, 137.8, 139.2, 196.9 (4 $\times$ C=O), 202.6 (C=O), 338.7 (C=W); MS (ESI); m/z 668 [M – H][–]. FT-IR (KBr, cm^{–1}) 3471, 2069, 1933, 1451, 1267, 1046, 967, 706.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[4-hydroxy-1-(4-methoxyphenyl)-3-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl]methoxymethylene}tungsten (**4b**):** yellow oil, 80 %; ¹H NMR (500 MHz) δ 3.42 (br s, exchanges with D₂O, 1 H), 3.74 (s, 3 H), 3.89 (dd like t, J = 3.1, 2.8 Hz, 1 H), 4.12 (d, J = 11.5 Hz, 1 H), 4.19 (s, 3 H), 5.02 (d, J = 2.8 Hz, 1 H), 5.32 (dd, J = 10.5, 3.1 Hz, 1 H), 6.70-6.72 (m, 2 H), 6.76-6.81 (m, 4 H), 6.96-6.98 (m, 2 H), 7.16-7.30 (m, 5 H). ¹³C NMR (125 MHz) δ 43.4, 49.2, 55.2, 69.5, 71.8, 74.8, 113.9, 127.05, 127.1, 128.2, 128.6, 128.7, 129.0, 129.6, 130.4, 135.3, 136.7, 138.3, 140.4, 158.3, 196.9 (4 $\times$ C=O), 202.6 (C=O), 338.4 (C=W). MS (ESI); m/z 695 [M – H][–]. FT-IR (film, cm^{–1}) 3417, 2068, 1933, 1608, 1511, 1247, 1034, 757, 701.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[1-(4-chlorophenyl)-4-hydroxy-3-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl]methoxymethylene}tungsten (4c):** yellow solid, mp 142-150 °C (Et₂O), 74 %; ¹H NMR (500 MHz) δ 2.37 (br. s, 1 H), 3.91 (dd like t, J = 3.1 Hz, 1 H), 4.16 (d partially overlapping s at δ 4.18, J = 11.0, 1 H), 4.18 (s, 3 H), 5.01 (d, J = 3.1 Hz, 1 H), 5.31 (dd, J = 11.0, 3.1 Hz, 1 H), 6.69–6.70 (m, 3 H), 7.03–7.05 (m, 2 H), 7.17–7.33 (m, 8 H); ¹³C NMR (125 MHz) δ 43.7, 49.2, 69.5, 71.7, 74.5, 127.2, 127.3, 128.2, 128.7, 128.9, 129.5, 129.8, 130.8, 132.6, 136.8, 138.0, 139.6, 141.9, 196.8 (4 $\times$ C=O), 202.4 (C=O), 338.9 (C=W); MS (ESI); m/z 699 [M – H][–]; FT-IR (KBr, cm^{–1}) 3405, 3028, 2923, 2069, 1935, 1489, 1014, 759, 701.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[(4-hydroxy-3-phenyl-1-*p*-tolyl-1,2,3,4-tetrahydronaphthalen-2-yl]methoxymethylene}tungsten (4d):** yellow solid, mp 143-144 °C (hexane), 72 %; ¹H NMR (500 MHz) δ 2.28 (s, 3 H), 2.30 (br s, exchanges with D₂O, 1 H), 3.91-3.92 (br s, 1 H), 4.15 (d, J = 11.0 Hz, 1 H), 4.20 (s, 3 H), 5.02 (d, J = 2.5 Hz, 1 H), 5.34 (dd, J = 11.0, 3.0 Hz, 1 H), 6.73 (d, J = 6.5 Hz, 2 H), 6.82 (d, J = 7.5 Hz, 1 H), 6.95 and 7.04 (2 $\times$ d, AB system, J = 8.0 Hz, 4 H), 7.18-7.30 (m, 5 H), 7.46 (d, J = 8.0 Hz, 1 H); ¹³C NMR (125 MHz) δ 21.2, 44.2, 49.5, 69.7, 72.1, 75.0, 127.3, 127.34, 128.4, 128.8, 129.3, 129.4, 129.6, 129.8, 129.9, 136.5, 137.1, 138.6, 140.4, 140.6, 197.1 (4 $\times$ C=O), 202.9 (C=O), 340.1 (C=W); MS (ESI); m/z 679 [M – H][–]. FT-IR (KBr, cm^{–1}) 3026, 2915, 2069, 1926, 1451, 1263. Anal. Calcd for C₃₀H₂₄O₇W: C, 52.96; H, 3.56. Found: C, 53.31; H, 3.27.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[(4-hydroxy-3-phenyl-1-*o*-tolyl 1,2,3,4-tetrahydronaphthalen-2-yl)methoxymethylene}tungsten (4e):** yellow solid, mp 115-120 °C (dec.) (hexane), 52 %; ¹H NMR (500 MHz) δ 2.12 (br s, 3 H), 4.04-4.09 (2 br s, 4 H), 4.41 (br d, J = 11.0, 1 H), 5.02 (br s, 1 H), 5.53 (br s, 1 H), 7.08-7.45 (m, 13 H); ¹³C NMR (125 MHz) δ 19.2, 38.8, 49.7, 69.4, 72.0, 73.6, 125.7, 126.5, 126.6, 127.0, 127.1, 128.1, 128.5, 128.8, 129.0, 129.6, 129.9, 138.1, 140.1, 140.8, 155.0, 155.8, 196.9 (4 $\times$ C=O), 202.4 (C=O), 338.6 (C=W); MS (ESI); m/z 679 [M – H][–]; FT-IR (KBr, cm^{–1}) 3432, 2069, 1916, 1451, 1269, 1206, 1045, 968, 759.

(1*S,2*R**,3*R**,4*R**)-Pentacarbonyl{[(1-(2-furyl)-4-hydroxy-3-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)methoxymethylene}tungsten (4f):** yellow solid, mp 84-85 °C (hexane), 63 %; ¹H NMR (300 MHz) δ 2.35 (br. s, exchanges with D₂O, 1 H), 3.91 (dd, J = 3.7, 3.0 Hz, 1 H), 4.25 (s, 3 H), 4.30 (d, J = 10.4 Hz, 1 H), 5.02 (d, J = 3.0 Hz, 1 H), 5.42 (dd, J = 10.4, 3.74 Hz, 1 H), 6.01–6.03 (m, 1 H), 6.26–6.28 (m, 1 H), 6.73–6.76 (m, 2 H) 6.92–6.95 (m, 1 H), 7.20–7.34 (m, 6 H), 7.49–7.51 (m, 1 H); ¹³C NMR (125 MHz) δ 19.3, 37.7, 49.1, 69.6, 71.5, 108.1, 109.8, 127.1, 127.5, 128.2, 128.5, 128.6, 128.9, 129.8, 136.6, 136.7, 138.1, 142.1, 196.7 (4 $\times$ C=O), 202.7 (C=O), 335.2 (C=W); MS (ESI); m/z 655 [M – H][–]; FT-IR (film, cm^{–1}): 3424, 3031, 2965, 2065, 1920, 1250, 1165, 702.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[(4-hydroxy-1,3-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)methoxymethylene]tungsten (4g):** yellow solid, mp 132–133 °C, 71 %; ¹H NMR (500 MHz) δ 2.23 (br. s, exchanges with D₂O, 1 H), 3.94 (dd, *J* = 3.5, 3.0 Hz, 1 H), 4.18 (d, *J* = 10.6 Hz, 1 H), 4.20 (s, 3 H), 5.02 (d, *J* = 3.0 Hz, 1 H), 5.37 (dd, *J* = 10.6, 3.0 Hz, 1 H), 6.72–6.82 (m, 3 H), 7.06–7.29 (m, 10 H), 7.44–7.50 (m, 1 H); ¹³C NMR (125 MHz) δ 44.6, 49.5, 69.7, 72.1, 74.8, 127.0, 127.4, 128.4, 128.8₀, 128.8₄, 128.8₆, 129.3, 129.8, 129.9₁, 129.9₃, 137.1, 138.6, 140.5, 143.6, 197.1 (4 × C=O), 202.9 (C=O), 339.4 (C=W); MS (ESI); *m/z* 581 [M – (CO)₃ – H][–]; FT-IR (film, cm^{–1}): 3415, 3030, 2974, 2067, 1917, 1480, 1256, 751. Anal. Calcd for C₂₉H₂₂O₇W: C, 52.27; H, 3.33. Found: C, 52.59; H, 3.18. **(+)-(1*S*,2*R*,3*S*,4*S*)-4g:** 72 %; [α]_D²⁰ = +243 (*c* 1, CHCl₃).

(1*S,2*S**,3*R**,4*R**)-Pentacarbonyl{[(4-hydroxy-1-methy-3-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)methoxymethylene]tungsten (4h):** yellow solid, mp 109–112 °C (hexane), 71 %; ¹H NMR (500 MHz) δ 1.38 (d, *J* = 6.7 Hz, 3 H), 2.13 (br. s, exchanges with D₂O, 1 H), 3.08 (dq, like pentet, *J* = 7.3, 6.7 Hz, 1 H), 3.6 (dd like t, *J* = 4.3 Hz, 1 H), 4.30 (s, 3 H), 4.84 (dd, *J* = 7.3, 4.2 Hz, 1 H), 5.00 (d, *J* = 4.8 Hz, 1 H), 6.79–6.81 (m, 2 H), 7.20–7.34 (m, 6 H), 7.44–7.48 (m, 1 H); ¹³C NMR (125 MHz) δ 20.9, 32.5, 49.2, 69.9, 71.5, 75.3, 126.7, 127.1, 127.3, 128.3, 128.4, 129.0, 129.2, 136.6, 138.8, 140.4, 197.1 (4 × C=O), 202.9 (C=O), 337.4 (C=W); MS (ESI); *m/z* 603 [M – H][–]; FT-IR (KBr, cm^{–1}): 3358, 2069, 1941, 1444, 1249, 1042, 972, 769, 704.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[1-(4-chlorophenyl)-4-hydroxy-3-(*p*-tolyl)1,2,3,4-tetrahydronaphthalen-2-yl]methoxymethylene}tungsten (4i)** yellow solid, mp 140-141 °C, 83 %; ¹H NMR (500 MHz) δ 2.36 (s, 3 H), 2.39 (br. s, exchanges with D₂O, 1 H) 3.90 (dd like t, *J* = 3.1 Hz, 1 H), 4.18 (d, *J* = 10.4 Hz, 1 H), 4.24 (s, 3 H), 5.01 (d, *J* = 3.0 Hz, 1 H), 5.32 (dd, *J* = 10.4, 3.0 Hz, 1 H), 6.59 (d, *J* = 7.9 Hz, 2 H); 6.75 (d, *J* = 7.9 Hz, 1 H), 6.99–7.04 (m, 4 H), 7.20–7.33 (m, 4 H), 7.47 (d, *J* = 7.9 Hz, 1 H); ¹³C NMR (125 MHz) δ 21.0, 43.7, 48.9, 69.6, 71.8, 74.5, 127.3, 128.6₁, 128.6₃, 128.8, 128.9, 129.8, 130.8, 132.5, 134.8, 136.8, 136.9, 139.6, 142.0, 196.8 (4 × C=O), 202.4 (C=O), 339.1 (C=W); MS (ESI); *m/z* 713 [M – H][–]; FT-IR (film, cm^{–1}): 3429, 3033, 2971, 2066, 1921, 1525, 1247, 798.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[4-hydroxy-3-(2,5-dimethoxyphenyl)-1-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl]methoxymethylene}tungsten (4j):** yellow oil, 81 %; ¹H NMR (500 MHz) δ 2.37 (br. s, exchanges with D₂O, 1 H), 3.44 (s, 3 H), 3.74 (s, 3 H), 4.12 (d, *J* = 11.2 Hz, 1 H), 4.21 (s, 3 H), 4.28 (dd, *J* = 3.1, 2.3 Hz, 1 H), 4.87 (d, *J* = 2.3 Hz, 1 H), 5.40 (dd, *J* = 11.2, 3.1 Hz, 1 H), 6.14 (d, *J* = 2.9 Hz, 1 H); 6.69–6.9 (m, 3 H), 7.04–7.06 (m, 2 H), 7.16–7.27 (m, 5 H), 7.46 (d, *J* = 7.6 Hz, 1 H); ¹³C NMR (125 MHz) δ 39.6, 44.7, 55.0, 56.2, 69.2, 71.9, 73.8, 110.8, 112.1, 114.3, 126.6, 127.1, 128.1, 128.3, 128.4, 129.5, 129.7, 137.0, 140.6, 142.8, 151.3, 153.1, 197.2 (4 × C=O), 203.2 (C=O), 337.6 (C=W); MS (ESI); *m/z* 725 [M – H][–]; FT-IR (film, cm^{–1}): 3441, 3031, 2966, 2061, 1927, 1531, 1260 1247, 1119, 798, 700.

(1*R,2*S**,3*R**,4*R**)-Pentacarbonyl{[4-hydroxy-1-phenyl-3-(4-trifluoromethylphenyl)1,2,3,4-tetrahydronaphthalen-2-yl]methoxymethylene}tungsten (4k):** Yellow oil, 78 %. ¹H NMR (400 MHz) δ 3.98 (dd like t, *J* = 3.5, 2.6 Hz, 1 H), 4.13 (d, *J* = 11.3 Hz, 1 H), 4.19 (s, 3 H), 4.97 (d, *J* = 2.6 Hz, 1 H), 5.14 (br. s, exchanges with D₂O, 1 H), 5.39 (dd, *J* = 11.3, 3.5 Hz, 1 H), 6.80 (d, *J* = 7.8 Hz, 1 H), 6.84 (d, *J* = 7.8 Hz, 2 H), 7.05–7.07 (m, 2 H), 7.17–7.31 (m, 7 H), 7.45 (d, *J* = 7.8 Hz, 1 H); ¹³C NMR (125 MHz) δ 44.2, 48.9, 69.4, 71.5, 74.1, 125.0 (q, *J*³_{C-F} = 3.9 Hz), 125.5 (q, *J*³_{C-F} = 3.9 Hz), 126.1, 126.8, 127.3, 127.4 (q, *J*¹_{C-F} = 198.3 Hz), 128.1, 128.6, 129.3, 129.4, 129.5 (q, *J*²_{C-F} = 42.9 Hz), 139.1, 139.9, 144.4, 146.0 196.7 (4 × C=O), 202.4 (C=O), 339.0 (C=W); MS (ESI); *m/z* 733 [M – H][–]; FT-IR (film, cm^{–1}): 3417, 3029, 2966, 2934, 2071, 1930, 1492, 1326, 1265, 1126, 1070, 973, 705.

Preparation of Tetrahydronaphthalenecarboxylates 5. General Procedure. To a stirred solution of the tungsten complex **5** (0.5 mmol) in THF (5 ml) at rt pyridine *N*-oxide was added (1.5 mmol). The resulting mixture was stirred for 24-48 h until the carbene complex (yellow spot on TLC) disappeared. Then the reaction mixture was poured into 20 mL of sat. aq. NH₄Cl, extracted with Et₂O (3 × 10 mL), dried (Na₂SO₄), and evaporated under reduced pressure. The crude mixture was column chromatographed (silica gel; petroleum ether/Et₂O 9/1÷7/3) to give tetrahydronaphthalenecarboxylates **5**, which showed the following data:

(1*R,2*S**,3*R**,4*R**)-1-(4-Chlorophenyl)-4-hydroxy-3-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (5c):** colorless oil, 81 %; ¹H NMR (500 MHz) δ 2.28 (br. s, exchanges with D₂O, 1 H), 3.52 (s, 3 H), 3.69-3.74 (m, 2 H), 4.35 (d, *J* = 8.9 Hz, 1 H), 5.13 (d, *J* = 3.3 Hz, 1 H), 6.84 (d, *J* = 7.8 Hz, 1 H), 6.90 (dd, *J* = 1.6 Hz, *J* = 7.7 Hz, 2 H), 7.13–7.29 (m, 9 H), 7.45 (dd, *J* = 1.0 Hz, *J* = 7.8 Hz, 1 H); ¹³C NMR (125 MHz) δ 43.2, 48.6, 49.1, 51.4, 70.8, 127.2, 127.3, 128.2, 128.4, 128.5, 128.6, 129.1, 130.2, 131.0, 132.3, 136.8, 138.0, 138.4, 143.2, 173.0; GC-MS (70 eV) *m/z* (%) 392 (*M*⁺, 1), 374 (3), 360 (21), 358 (64), 215 (100), 145 (13), 78 (11); FT-IR (film, cm⁻¹) 3488, 3041, 2980, 1745, 1513, 1257, 1164, 1089, 811, 706.

(1*R,2*S**,3*R**,4*R**)-4-Hydroxy-3-phenyl-1-*p*-tolyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (5d):** white solid, mp 65–66 °C (hexane), 55 %; ¹H NMR (500 MHz) δ 2.32 (s, 3 H), 2.39 (br s, exchanges with D₂O, 1 H), 3.50 (s, 3 H), 3.67–3.75 (m, 2 H), 4.35 (d, J = 10.5 Hz, 1 H), 5.16 (d, J = 4.5 Hz, 1 H), 6.86–6.95 (m, 3 H), 7.08 (s, 4 H), 7.18–7.29 (m, 5 H), 7.46 (d, J = 13.0 Hz, 1 H). ¹³C NMR (125 MHz) δ 20.9, 43.7, 48.5, 49.6, 51.3, 70.8, 126.9, 127.2, 128.3, 128.38, 128.4, 128.9, 129.0, 129.4, 130.2, 136.0, 137.1, 138.6, 138.9, 141.6, 173.3. GC-MS (70 eV) m/z (%) 372 (M^+ , 5), 354 (60), 295 (68), 263 (100), 221 (50), 196 (98), 165 (28), 91 (23). FT-IR (film, cm⁻¹) 3406, 3027, 2924, 1741, 1453, 1167, 1036, 806, 701. Anal. Calcd for C₂₅H₂₄O₃: C, 80.62; H, 6.49. Found: C, 80.88; H, 6.48.

(1*S,2*R**,3*R**,4*R**)-1-(2-Furyl)-4-hydroxy-3-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (5f):** colorless oil, 59 %; ¹H NMR (500 MHz) δ 2.13, (br. s, exchanges with D₂O, 1 H) 3.55 (s, 3 H), 3.64 (dd like t, J = 4.8 Hz, 1 H), 3.82 (dd, J = 7.9, 4.4 Hz, 1 H), 4.48 (d, J = 4.4 Hz, 1 H), 5.22 (d, J = 4.9 Hz, 1 H), 6.07 (d, J = 3.1 Hz, 1 H), 6.29 (dd, J = 3.1, 1.8 Hz, 1 H), 6.98–7.00 (m, 2 H), 7.07 (d, J = 7.3 Hz, 1 H), 7.22–7.33 (m, 6 H), 7.52 (d, J = 7.3 Hz, 1 H); ¹³C NMR (125 MHz) δ 38.6, 46.7, 48.3, 51.5, 70.2, 108.3, 110.2, 126.1, 126.2, 127.3, 127.5, 128.3, 128.5, 129.0, 129.2, 135.3, 137.2, 138.5, 141.8, 173.0; GC-MS (70 eV) m/z (%) 348 (M^+ , 6), 330 (100), 281 (59), 202 (17), 91 (20), 77 (12); FT-IR (film, cm⁻¹) 3492, 3044, 3031, 2981, 1737, 1262, 1109, 976, 751, 701.

(1*R,2*S**,3*R**,4*R**)-4-Hydroxy-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (5g):** white solid, mp 96-97 °C (Et₂O), 76 %. ¹H NMR (300 MHz) δ 2.16 (br. s, exchanges with D₂O, 1 H), 3.50 (s, 3 H), 3.69 (dd, *J* = 8.5, 4.4 Hz, 1 H), 3.74 (dd like t, *J* = 4.4 Hz, 1 H), 4.38 (d, *J* = 8.5 Hz, 1 H), 5.17 (d, *J* = 4.4 Hz, 1 H), 6.85–6.98 (m, 4 H), 7.06–7.49 (m, 10 H); ¹³C NMR (125 MHz) δ 44.0, 48.5, 49.6, 51.4, 70.8, 126.6, 127.2, 127.3, 128.4₀, 128.4₁, 128.5, 128.6, 129.0, 129.6, 130.2, 137.1, 138.4, 138.8, 144.7, 173.2; GC-MS (70 eV) *m/z* (%) 358 (M⁺, 5), 340 (80), 281 (73), 249 (91), 196 (100), 178 (46), 91 (31); FT-IR (film, cm⁻¹): 3415, 3023, 2923, 1736, 1492, 1167, 1033, 761, 700. Anal. Calcd for C₂₄H₂₂O₃: C, 80.42; H, 6.19. Found: C, 80.73; H, 6.22.

(+)-(1*S*,2*R*,3*S*,4*S*)-5g: 75 %; [α]_D²⁰ = +104 (*c* 1, CHCl₃).

(1*R,2*S**,3*R**,4*R**)-1-(4-Chlorophenyl)-4-hydroxy-3-*p*-tolyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (5i):** colorless oil, 79 %; ¹H NMR (500 MHz) δ 1.83 (br. s, exchanges with D₂O, 1 H) 2.27 (s, 3 H), 3.53 (s, 3 H), 3.66-3.71 (m, 2 H), 4.34 (d, *J* = 9.5 Hz, 1 H), 5.10 (d, *J* = 3.5 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 2 H), 6.84 (d, *J* = 7.7 Hz, 1 H), 7.00 (d, *J* = 7.9 Hz, 2 H), 7.14 (d, *J* = 8.3 Hz, 2 H), 7.22–7.31 (m, 4 H), 7.44 (d, *J* = 7.5 Hz, 1 H); ¹³C NMR (125 MHz) δ 20.9, 29.6, 43.2, 48.3, 49.1, 71.0, 125.6, 127.2, 128.1, 128.5, 128.6, 129.1, 130.1, 131.0, 132.3, 134.9, 136.9, 137.3, 138.5, 143.3, 173.1; GC-MS (70 eV) *m/z* (%) 406 (M⁺, 2), 390 (20), 388 (61), 331 (34), 329 (100), 294 (44), 278 (29), 202 (31), 138 (12); FT-IR (film, cm⁻¹) 3446, 3033, 2977, 1744, 1521, 1266, 1118, 1011, 809, 701.

(1*R,2*S**,3*R**,4*R**)-3-(2,5-Dimethoxyphenyl)-4-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (5j):** colorless oil, 69 %; ^1H NMR (400 MHz) δ 3.43 (s, 3 H), 3.53 (s, 3 H), 3.55 (s, 3 H), 3.62 (dd, $J = 8.5, 4.2$ Hz, 1 H), 4.05 (dd like t, $J = 4.8, 4.2$ Hz, 1 H), 4.20 (br. s, exchanges with D_2O , 1 H); 4.33 (d, $J = 8.5$ Hz, 1 H), 5.13 (d, $J = 4.8$ Hz, 1 H), 6.48 (d, $J = 2.4$ Hz, 1 H), 6.67–6.70 (m, 2 H), 6.84 (d, $J = 7.9$ Hz, 1 H), 7.13–7.29 (m, 7 H), 7.51 (d, $J = 7.0$ Hz, 1 H) ; ^{13}C NMR (125 MHz) δ 39.6, 44.8, 48.8, 52.3, 55.0, 56.2, 71.9, 110.7, 112.0, 114.3, 126.6, 127.1, 128.1, 128.4, 128.5, 129.6, 129.8, 137.0, 140.6, 142.7, 151.3, 153.0, 173.0 ; GC-MS (70 eV) m/z (%) 418 (M^+ , 22), 400 (10), 368 (12), 221 (25), 178 (26), 138 (100); FT-IR (film, cm^{-1}) 3515, 3039, 2976, 1744, 1266, 1262, 1117, 812, 751, 701.

(1*R,2*S**,3*R**,4*R**)-4-Hydroxy-1-phenyl-3-(4-trifluoromethylphenyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid methyl ester (5k):** colorless oil, 72 %; ^1H NMR (400 MHz) δ 3.19 (br.s, exchanges with D_2O , 1 H) 3.48 (s, 3 H), 3.68 (d, $J = 10.1$ Hz, 1 H); 5.14–5.17 (m, 2 H), 5.42 (br. s, 1 H), 7.05–7.30 (m, 10 H), 7.57 (d, $J = 7.8$ Hz, 1 H), 7.68 (d, $J = 7.8$ Hz, 2 H); ^{13}C NMR (125 MHz) δ 43.9, 49.0, 51.3, 59.7, 72.8, 125.5 (m, $J^3_{\text{C-F}} = 3.1$ Hz, 2 C_{ortho}), 126.6, 126.8, 126.9 (q, $J^1_{\text{C-F}} = 198.9$ Hz), 128.1, 128.3, 129.6, 129.8 (q, $J^2_{\text{C-F}} = 34.9$ Hz), 130.1, 137.0, 139.1, 142.8, 146.1; FT-IR (film, cm^{-1}) 3501, 3035, 2977, 1737, 1496, 1264, 1161, 1050, 753, 706.

Ortep view of compound **4g**