## **Electronic Supplementary Information**

Traceless solid phase synthesis of natural product inspired cis-1,2-dehydrodecalins

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### **General methods**

All solvents were purchased in the highest quality available. If required, they were distilled prior to use employing standard methods.

Thin Layer Chromatography (TLC) was carried out on Merck precoated silica gel plates (60F-254) using ultraviolet light irradiation at 254 nm or KMnO<sub>4</sub> solution as staining reagent (1 g KMnO<sub>4</sub>, 6.6 g K<sub>2</sub>CO<sub>3</sub>, 1.7 mL 5% NaOH solution, 100 mL H<sub>2</sub>O). Silica gel chromatography was performed using silica gel from J. T. Baker or Merck (particle size 40-60  $\mu$  m). <sup>1</sup> H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker DRX 500 (500 MHz (<sup>1</sup>H) and 125.7 MHz (<sup>13</sup>C)), a Bruker DRX 400 (400 MHz (<sup>1</sup>H) and 100.5 MHz (<sup>13</sup>C)) or a Varian Mercury 400 (400 MHz (<sup>1</sup>H) and 100.6 MHz (<sup>13</sup>C)) spectrometer. Chemical shifts are expressed in parts per million (ppm) and the spectra are calibrated to residual solvent signals of CDCl<sub>3</sub> (7.26 ppm (<sup>1</sup>H) and 77.0 ppm (<sup>13</sup>C)). Coupling constants are given in Hertz (Hz) and the following notations indicate the multiplicity of the signals: s (singlet), d (doublet), t (triplet), q (quartet), m (multiple), br (broad signal). Optical rotations were measured in a Schmidt + Haensch Polartronic HH8 polarimeter at 589 nm, with concentrations given in g/100mL. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained with a Bruker Tensor 27 spectrometer (ATR, neat). Wavenumbers v are given in cm<sup>-1</sup>. Preparative HPLC was performed on a Waters HPLC system using a Macherey Nagel C18 gravity 5 µm reversed phase column. The following gradients were used: from 10 % acetonitrile (with 0.1% TFA) in H<sub>2</sub>O (with 0.1% TFA) to 100 % acetonitrile (with 0.1% TFA) in 20 min at a flow of 20 mL/min. High Resolution Mass Spectra were recorded on a JEOL SX 102 A (FAB; matrix *m*-nitrobenzylalcohol) or Thermo Electron LTQ Orbitrap (ESI; source voltage 3.8 kV) spectrometer.

## **Experimental procedure**

## Preparation of the traceless linker moiety

### 4-(5-Diethylphosphonylthiomethyl)tetrazoyl-phenol 9

То 1-(4-hydroxyphenyl)-1H-tetrazole-5-thiol 10.3 diethyl а mixture of (2.0)g, mmol) and 4-methylbenzenesulfonyloxymethyl phosphonate (1.1 eq, 3.65 g, 11.3 mmol) in DMF (41 mL, 4 mL/mmol) was added K<sub>2</sub>CO<sub>3</sub> (1.0 eq., 1.4 g, 10.3 mmol) at room temperature. After stirring for 30 h at the same temperature, the mixture was filtered through a pad of Celite and diluted with H<sub>2</sub>O. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layers were washed with 1N HCl, aq. NaHCO3, brine and dried over MgSO4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluted with CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 15/1) to afford thioether 9 (6.0 g, 16.6 mmol, 91%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 (d, *J* = 9.0 Hz, 2H, a), 6.96 (d, *J* = 9.0 Hz, 1H, a), 4.20 (q, *J*<sub>c, d</sub> = 7.0 Hz, 1H, c), 4.18 (q, *J*<sub>c', d'</sub> = 7.0 Hz, 1H, c'), 3.77 (d, *J*<sub>gem</sub> = 13.4 Hz, 1H, b), 1.33 (t, *J*<sub>d, c</sub> = 7.0 Hz, 1H, d), 1.32 (t, *J*<sub>d', c'</sub> = 7.0 Hz, 1H, d). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  159.1, 153.1, 125.4, 124.6, 116.5, 63.8, 63.7,



26.7, 25.2, 16.3, 16.2.

IR (neat): 1518, 1018 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd. for  $C_{12}H_{18}N_4O_4SP [M+H]^+$  345.0786 found 345.0782. TLC  $R_f = 0.43$  (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 2/1)

## Allyl 4-(6-tetrahydropyranyloxyhexyl)oxy benzoate 4

To a mixture of 2-(6-bromohexyl)oxy-tetrahydro-2H-pyran **3** (1.1 eq, 5.0 g, 18.9 mmol) and allyl 4-hydroxybenzoate **2** (3.0 g, 17.1 mmol) in DMF (52 mL, 3 mL/mmol) was added  $K_2CO_3$  (1.0 eq., 2.4 g, 17.1 mmol) at room temperature. After stirring for 20 h at 80 °C, the mixture was filtered through a pad of Celite and diluted with H<sub>2</sub>O. The aqueous layer was extracted twice with ethyl acetate, and the combined organic layers were washed with 1N HCl, aq. NaHCO<sub>3</sub>, brine and dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluted with cyclohexane/ethyl acetate = 15/1) to afford hexyl ether **4** (6.0 g, 16.6 mmol, 97%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, J = 9.0 Hz, 2H, a), 6.86 (d, J = 9.0 Hz, 1H, a), 6.00 (ddt,  $J_{d, e} = 5.6$  Hz,  $J_{d, b} = 10.4$  Hz,  $J_{d, c} = 17.2$  Hz 1H, d), 5.35 (ddt,  $J_{c, b} = J_{c, e} = 1.5$  Hz,  $J_{c, d} = 17.2$ , 1H, c), 5.23 (ddt,  $J_{b, c} = J_{b, e} = 1.5$  Hz,  $J_{b, d} = 10.4$  Hz, 1H, b), 4.76 (dt,  $J_{e, b} = J_{e, c} = 1.5$  Hz,  $J_{e, d} = 5.6$  Hz, 1H, e), 4.54 (m, 1H, f), 3.97 (t, J = 6.5 Hz, 2H, g), 3.83 (m, 1H, i), 3.71 (dt, J = 6.8 Hz,  $J_{h, h'} = 9.6$  Hz, 1H, h), 3.47 (m, 1H, i'), 3.37 (dt, J = 6.6 Hz,  $J_{h', h} = 9.6$  Hz, 1H, h'), 1.41-1.81 (m, 14H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.8, 162.8, 132.4, 131,5, 122.2,

117.8, 113.9, 98.7, 67.9, 67.3, 65.0, 62.2, 30.6, 29.5, 28.4, 25.9, 25.7, 25.3, 19.6.

IR (neat): 1713 cm<sup>-1</sup>. HRMS (EI) calcd. for  $C_{21}H_{30}O_5$  [M]<sup>+</sup> 362.2093 found 362.2079. TLC  $R_f = 0.67$  (silica gel, cyclohexane/ethylacetate = 4/1).



To a solution of allyl 4-(6-tetrahydropyranyloxyhexyl)oxy benzoate **4** (6.0 g, 16.6 mmol) in  $CH_2Cl_2$  (33 mL, 2 mL/mmol) was added TFA (8.3 ml, 0.5 mmol/mL) at room temperature. After stirring for 16 h at room temperature, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (eluted with cyclohexane/ethyl acetate = 5/1) to afford free alcohol **5** (4.3 g, 15.4 mmol, 93%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d, J = 9.1 Hz, 2H, a), 6.87 (d, J = 9.1 Hz, 1H, a), 6.00 (ddt,  $J_{d, e} = 5.6$  Hz,  $J_{d, b} = 10.4$  Hz,  $J_{d, c} = 17.2$  Hz 1H, d), 5.37 (ddt,  $J_{c, b} = J_{c, e} = 1.5$  Hz,  $J_{c, d} = 17.2$ , 1H, c), 5.25 (ddt,  $J_{b, c} = J_{b, e} = 1.5$  Hz,  $J_{b, d} = 10.4$  Hz, 1H, b), 4.77 (dt,  $J_{e, b} = J_{e, c} = 1.5$  Hz,  $J_{e, d} = 5.6$  Hz, 1H, e), 3.98 (t, J = 6.5 Hz, 2H, f), 3.63 (t, J = 6.5 Hz 1H, g), 1.37-1.81 (m, 8H, i).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  166.0, 162.9, 132.4, 131,5, 122.2, 117.8, 113.9, 67.9, 65.2, 62.7, 32.5, 29.0, 25.8, 25.4. IR (neat): 1710 cm<sup>-1</sup>. HRMS (EI) calcd. for C<sub>16</sub>H<sub>22</sub>O<sub>4</sub> [M]<sup>+</sup> 278.1518 found 278.1509. TLC  $R_f = 0.43$ (silica gel, cyclohexane/ethyl acetate = 2/1).



## Allyl 4-(6-p-toluenesulfonyloxyhexyl)oxy benzoate 6

To a mixture of allyl 4-(6-hydroxyhexyl)oxy benzoate **5** (4.3 g, 15.4 mmol), NEt<sub>3</sub> (2.0 eq., 4.3 ml, 30.8 mmol) and 4-dimethylaminopyridine (0.3 eq., 564 mg, 4.62 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (61 mL, 4 mL/mmol) was added tosyl chloride (1.3 eq., 3.8 g, 20.1 mmol) at 0 °C under argon. After stirring for 4 h, the mixture was poured into ice water and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with 1N HCl, aq. NaHCO<sub>3</sub>, brine and dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluted with cyclohexane/ethyl acetate = 10/1) to afford tosylate **6** (6.5 g, 15.0 mmol, 98%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d, J = 8.9 Hz, 2H, a), 7.94 (d, J = 8.3 Hz, 2H, h), 7.34 (d, J = 8.3 Hz, 2H, h), 6.88 (d, J = 8.9 Hz, 1H, a), 6.03 (ddt,  $J_{d,e} = 5.6$  Hz,  $J_{d,b} = 10.4$  Hz,  $J_{d,c} = 17.2$  Hz 1H, d), 5.39 (ddt,  $J_{c,b} = J_{c,e} = 1.5$  Hz,  $J_{c,d} = 17.2$ , 1H, c), 5.27 (ddt,  $J_{b,c} = J_{b,e} = 1.5$  Hz,  $J_{b,d} = 10.4$  Hz, 1H, b), 4.79 (dt,  $J_{e,b} = J_{e,c} = 1.5$  Hz,  $J_{e,d} = 5.6$  Hz, 1H, e), 4.04 (t,  $J_{f,l} = 6.4$  Hz, 2H, f), 3.97 (t,  $J_{g,m} = 6.4$  Hz 1H, g), 2.44 (s, 3H, i), 1.75 (tt, J = 4.5 Hz,  $J_{m,g} = 6.4$  Hz, 2H, m), 1.68 (tt, J = 4.2 Hz,  $J_{L,f} = 6.4$  Hz, 2H, 1), 1.35-1.47 (m, 4H, j).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.9, 162.8, 144.6, 133.2, 132.5,  $b \approx 131.6$ , 129.7, 127.8, 122.4, 117.9, 114.0, 70.3, 67.8, 65.2, 28.8, 28.7, 25.4, 25.1, 21.6. IR (neat): 1711, 1167 cm<sup>-1</sup>.



TLC 
$$R_f = 0.43$$
 (silica gel, cyclohexane/ethyl acetate = 2/1).

## Allyl 4-{6-[4-(5-diethylphosphonylmethylthio)tetrazoyl]phenoxy}hexyloxy benzoate 7

To a mixture of allyl 4-(6-*p*-toluenesulfonyloxyhexyl)oxy benzoate (1.1 eq, 3.0 g, 6.94 mmol) and 4-(5-diethylphosphonylthiomethyl)tetrazoyl phenol (2.2 g, 6.31 mmol) in DMF (25 mL, 6 mL/mmol) was added  $K_2CO_3$  (1.0 eq, 873 mg, 6.31 mmol) and KI (0.3 eq., 314 mg, 1.89 mmol) at room temperature. After stirring for 6 h, the mixture was filtered through a pad of Celite and diluted with H<sub>2</sub>O. The aqueous layer was extracted twice with ethyl acetate, and the combined organic layers were washed with 1N HCl, aq. NaHCO<sub>3</sub>, brine and dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluted with CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 5/1) to afford phosphonate (3.69g, 6.45 mmol, 93%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d, J = 8.9 Hz, 2H, a), 7.43 (d, J = 9.1 Hz, 2H, h), 7.01 (d, J = 9.1 Hz, 2H, h), 6.89 (d, J = 8.9 Hz, 1H, a), 6.02 (ddt,  $J_{d,e} = 5.6$  Hz,  $J_{d,b} = 10.4$  Hz,  $J_{d,c} = 17.2$  Hz 1H, d), 5.37 (ddt,  $J_{c,b} = J_{c,e} = 1.5$  Hz,  $J_{c,d} = 17.2$  Hz, 1H, c), 5.25 (ddt,  $J_{b,c} = J_{b,e} = 1.5$  Hz,  $J_{b,d} = 10.4$  Hz, 1H, b), 4.78 (dt,  $J_{e,b} = J_{e,c} = 1.5$  Hz,  $J_{e,d} = 5.6$  Hz, 1H, e), 4.15 (q,  $J_{f,k} = 7.0$  Hz, 2H, j), 4.13 (q,  $J_{j',k'} = 7.0$  Hz, 2H, j'), 4.02 (t,  $J_{f,m} = J_{g,n} = 6.4$  Hz 4H, f and g), 3.71 (d,  $J_{gem} = 13.7$  Hz 1H, i), 1.83-1.91 (m, 4H, m and n),

1.54-1.58 (m, 4H, l), 1.29 (t,  $J_{j,k} = 7.0$  Hz, 3H, k), 1.28 (t,  $J_{j',k'} = 7.0$  Hz, 3H, k'). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.9, 162.8, 160.4, 153.3, 132.4,



131.6, 125.7, 125.4, 122.3, 117.8, 115.4, 114.0, 68.2, 67.9, 65.1, 63.1, 63.0, 29.0, 28.9, 26.9, 25.7, 25.5, 16.3, 16.2. IR (neat): 1711, 1513, 1019 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd. for  $C_{28}H_{38}N_4O_7PS$  [M+H]<sup>+</sup> 605.2199 found 605.2187. TLC  $R_f = 0.55$  (silicagel, CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate = 1/1).

## 4-{6-[4-(5-Diethylphosphonylmethylthio)tetrazoyl]phenoxy}hexyloxy benzoic acid 8

To a mixture of allyl 4-{6-[4-(5-diethylphosphonylmethylthio)tetrazoyl]phenoxy}hexyloxy benzoate **7** (2.0 g, 3.3 mmol) and morpholine (3.0 eq., 871  $\mu$ L, 9.9 mmol) in THF (17 mL, 5 mL/mmol) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.2 eq., 762 mg, 0.66 mmol) at room temperature. After stirring for 1.5 h, the mixture was filtered through a pad of Celite and diluted with H<sub>2</sub>O. The aqueous layer was extracted twice with ethyl acetate, and the organic layer was washed with 1N HCl, brine and dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by silicagel column chromatography (eluted with CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 40/1) to afford acid **8** (1.8 g, 3.18 mmol, 96%) as a yellowish solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d, J = 8.9 Hz, 2H, a), 7.43 (d, J = 9.0 Hz, 2H, b), 7.00 (d, J = 9.0 Hz, 2H, b), 6.92 (d, J = 8.9 Hz, 1H, a), 4.17 (q,  $J_{d,g}$  = 7.1 Hz, 1H, d), 4.15 (q,  $J_{d',g'}$  = 7.1 Hz, 1H, d'), 4.05 (t,  $J_{e,i}$  = 6.5 Hz, 2H, e), 4.02 (t,  $J_{f,j}$  = 6.5 Hz, 2H, f), 3.74 (d,  $J_{gem}$  = 13.7 Hz 1H, i), 1.83-1.87 (m, 4H, I and j), 1.55-1.59 (m, 4H, h), 1.30 (t,  $J_{g,d}$  = 7.1 Hz, 3H, g), 1.29 (t,  $J_{g',d'}$  = 7.1 Hz, 3H, g').

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.7, 163.3, 160.4, 153.3, 132.2, 125.4, 121.7, 115.4, 114.1, 109.7, 68.2, 67.9, 63.3, 63.2, 28.9, 26.9, 25.7, 25.4, 16.3, 16.2.

IR (ATR): 1705, 1511, 1018 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd. for  $C_{25}H_{34}N_4O_7PS [M+H]^+$  565.1880 found 565.1874. TLC  $R_f = 0.63$  (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 6/1).



### Solid-phase synthesis

Conversion and purity of solid phase reactions were determined by reverse-phase HPLC-MS after cleavage from the polymeric support with 20% TFA in  $CH_2Cl_2$ .

### General procedure for the attachment of the traceless linker moiety onto the polymeric support

To a suspension of the polymer-supported amine (1.0 eq.) (dried under reduced pressure over night before use), 4-{6-[4-(5-diethylphosphonylmethylthio)tetrazoyl]phenoxy}hexyloxy benzoic acid (0.1 M) and DIEA (0.15 M) in DMF (0.7 mL/100 mg) was added a solution of HATU (0.1 M) in DMF (0.3 mL/100 mg) at room temperature under argon. After shaking for 12 h, the mixture was filtered off and the resin was washed three times each with dimethyl formamide, THF/H<sub>2</sub>O (3/1), MeOH and CH<sub>2</sub>Cl<sub>2</sub>. The resin was dried under high vacuum for 12 h to afford the polymer-supported phosphonate **1**. Total loading of the resin was initially estimated gravimetrically after coupling, washing and drying. This was found to be approx. 0.5 mmol/g

To a suspension of 1 (100 mg, ca. 0.08 mmol) in  $CH_2Cl_2$  (0.8 mL) was added TFA (0.2 mL) and shaken vigorously at room temperature. After being stirred for 30 min, the mixture was filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on flash short-pad silica gel to afford amide as a white solid (30 mg, 0.054 mmol). The loading amount of **7** was determined to be ca. 0.5 mmol/g by gravimetric analysis. Analytics of 1 after TFA release from resin:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, *J* = 8.8 Hz, 2H, a), 7.43 (d, *J* = 9.0 Hz, 2H, b), 7.01 (d, *J* = 9.0 Hz, 2H, b), 6.91 (d, *J* = 8.8 Hz, 1H, a), 4.16 (q, *J<sub>d,e</sub>* = 7.1 Hz, 2H, d), 4.14 (q, *J<sub>d',e'</sub>* = 7.1 Hz, 2H, d'), 4.04 (t, *J<sub>f,g</sub>* = 6.4 Hz, 2H, f), 4.03 (t, *J<sub>h,i</sub>* = 6.4 Hz, 2H, h), 3.73 (d, *J<sub>gem</sub>* = 13.7 Hz 1H, c), 1.83-1.88 (m, 4H, g and i), 1.55-1.59 (m, 4H, j), 1.30 (t, *J<sub>e,d</sub>* =

## $J_{e', d'} = 7.1$ Hz, 6H, k). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) $\delta$ 168.8,

162.1, 160.4, 153.3, 129.3, 125.8, 125.5, 115.4, 114.2,

68.2, 67.9, 63.2, 63.1, 29.0, 28.9, 27.0, 25.7, 25.6, 25.5,

16.3, 16.2. HRMS (ESI-TOF) calcd. for  $C_{25}H_{35}N_5O_6PS$ 

 $[M+H]^+$  564.1697 found 564.2033.



## General procedure for the Horner-Wadsworth-Emmons reaction with methacrolein on polymeric support

To a suspension of the polymer-supported phosphonate (1 eq.) (dried under reduced pressure over night before use) in THF was added a solution of LiHMDS (0.5 M) in THF at 0  $^{\circ}$ C under argon. After stirring for 1 h at the same temperature, a solution of methacrolein (0.3 M) in THF was added. The resulting mixture was allowed to warm up to room temperature. After shaking for 16 h, the mixture was filtered off and the resin was washed three times each with THF, MeOH and CH<sub>2</sub>Cl<sub>2</sub>. The resin was dried under high vacuum for 12 h to afford the polymer-supported diene **10**. Analytics of **10** after TFA release from resin:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, J = 8.8 Hz, 2H, a), 7.34 (d, J = 8.9 Hz, 2H, b), 6.97 (d, J = 8.9 Hz, 2H, b), 6.86 (d, J = 8.8 Hz, 1H, a), 6.69 (d,  $J_{c,d} = 15.5$  Hz, 1H, c), 6.57 (d,  $J_{d,c} =$ 

15.5 Hz, 1H, d), 5.07 (brd, J = 15.0 Hz, 1H, f), 4.96 (d,  $J_{d,e} = 10.4$  Hz, 1H, f), 3.98 (t,  $J_{g,k} = 6.3$  Hz, 2H, g), 3.96 (t,  $J_{k,g} = 6.3$  Hz, 2H, k), 1.87 (s, 3H, e), 1.76-1.83 (m, 4H, h and j), 1.48-1.53 (m, 4H, i). HRMS (ESI-TOF) calcd. for C<sub>25</sub>H<sub>30</sub>N<sub>5</sub>O<sub>3</sub>S [M+H]<sup>+</sup> 480.2064 found 480.2056.



# General procedure for the Lewis acid-catalyzed Diels-Alder reaction on polymeric support with cyclohexenone derivatives

To a suspension of the polymer-supported diene (1.0 eq.) (dried under reduced pressure over night before use) and 2-methoxycarbonyl cyclohexenone **11** (0.1 M) in  $CH_2Cl_2$  (1.0 mL/100 mg) was added  $Sc(OTf)_3$  (0.02 M) at 0 °C under argon. After stirring for 5 h, the mixture was quenched with DIEA and filtered off. The resin was washed three times each with THF/H<sub>2</sub>O (3/1), MeOH and  $CH_2Cl_2$  and then dried under high vacuum for 12 h to afford polymer-supported *cis*-decalin derivative **12**.

Analytics of 12 after TFA release from resin:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.78 (d, *J* = 8.7 Hz, 2H, a), 7.41 (d, *J* = 8.9 Hz, 2H, b), 6.98 (d, *J* = 8.9 Hz, 2H, b), 6.92 (d, *J* = 8.7 Hz, 1H, a), 6.29 (brs, 2H, 1), 5.58 (brs, 1H, d), 5.54 (brs, 1H, e), 4.03 (t, *J<sub>i,m</sub>* = 5.7 Hz, 1H, i), 4.02 (t, *J<sub>k,m</sub>* = 5.7 Hz, 2H, k), 3.65 (s, 3H, o), 2.87-2.95 (m, 1H, h), 2.69-2.78 (m, 1H, c), 2.31-2.41 (m, 1H, c'), 2.09-2.15 (m, 2H, g and q), 1.80-1.91 (m, 8H, g, m, n, p and q), 1.65 (s, 3H, f), 1.53-1.59 (m, 4H, j).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.6, 162.4, 160.2 155.0, 135.1, 129.4, 126.0, 125.7, 120.2, 115.3, 114.4, 114.3, 109.7, 68.9, 67.9, 64.7, 53.6, 46.7, 38.2, 32.4, 29.0, 28.9, 26.6, 25.7, 25.6, 24.2, 23.1. HRMS (ESI-TOF) calcd. for  $C_{33}H_{40}N_5O_6S$ [M+H]<sup>+</sup> 634.2621 found 634.2690.



# General procedure for the Lewis acid-catalyzed Diels-Alder reaction on polymeric support with quinone derivatives

To a suspension of polymer-supported diene (1.0 eq.) (dried under reduced pressure over night before use) and 2-methoxycarbonyl quinone (0.1 M) in  $CH_2Cl_2$  (1.0 mL/100 mg) was added  $Gd(OTf)_3$  (0.02 M) at 0 °C under argon. After stirring for 5 h, the mixture was quenched with aq. NaHCO<sub>3</sub> and filtered off. The resin was washed three times each with THF/H<sub>2</sub>O (3/1), MeOH and CH<sub>2</sub>Cl<sub>2</sub>. The resin was dried under high vacuum for 12 h to afford polymer-support *cis*-decalin derivative **16**.

Chiral HPLC Analysis of racemate: Chiracel OD (4.6x250 mm) at 1.00 mlmin<sup>-1</sup> of isocratic i-PrOH:Hexane (20:80) over 80 min.  $Tr_1$  39 min (50% area),  $Tr_2$  49.5 min (50% area)

Analytics of 16 after TFA release from resin:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.77 (d, J = 8.8 Hz, 2H, a), 7.39 (d, J = 9.0 Hz, 2H, b), 7.00 (d, J = 9.0 Hz, 2H, b), 6.92 (d, J = 8.8 Hz, 1H, a), 6.70 (d, J = 10.4 Hz, 1H, c), 6.60 (d,  $J_{d,e} = 1.0$  Hz,  $J_{d,e} = 10.4$  Hz, 1H, c), 6.05 (brs, 2H, l), 5.67 (brs, 1H, d), 5.38 (dd, J = 2.3 Hz, J = 4.7 Hz, 1H, e), 4.04 (t,  $J_{i,m} = 6.3$  Hz, 2H, i), 4.03 (t,  $J_{k,n} = 6.3$  Hz, 2H, k), 3.76 (brt, J = 7.9 Hz 1H, h), 3.72 (s, 3H, o), 2.28 (m, 2H, g), 1.83-1.86 (m, 2H, m and n), 1.69 (s, 3H, f), 1.52-1.59 (m, 4H, j).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.0, 193.5, 169.4, 169.2,
162.3, 160.3, 154.2, 139.6, 138.5, 134.5, 129.3, 126.2,
125.9, 125.5, 121.0, 115.3, 115.1, 114.3, 68.2, 67.9, 62.4,
53.7, 50.2, 47.1, 29.0, 28.9, 25.75, 25.74, 22.8.



HRMS (ESI-TOF) calcd. for  $C_{33}H_{36}N_5O_7S [M+H]^+ 699.1592$  found 699.1532.

## General procedure for the Michael addition of cuprates

To a suspension of the corresponding polymeric support (1.0 eq.) (dried under reduced pressure over night before use) in THF (0.7 mL/100 mg) was added a solution of PhMgBr (0.15 M) and CuBr (0.09 M) in THF (0.3 mL/100 mg) at 0  $^{\circ}$ C under argon. After shaking for 5 h at room temperature, the mixture was quenched with aq. NH<sub>4</sub>Cl and filtered off. The resin was washed three times each with THF/H<sub>2</sub>O (1/1), MeOH and CH<sub>2</sub>Cl<sub>2</sub> and then dried under high vacuum for 12 h to afford polymer-supported Michael adduct **18**.



## General procedure for the enantioselective Diels-Alder reaction on polymeric support

To a mixture of Gd(OTf)<sub>3</sub> and (*R*,*R*)-*i*-Pr Pybox was added dry CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL/100 mg based on the polymer-support, dried over MS 4A before use) under argon and stirred for 2 h at room temperature. After 2 h, the mixture was transferred dropwise to a suspension of the corresponding polymer-supported diene (1.0 eq.) and 2-methoxycarbonyl quinone (0.1 M) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL/100 mg) at -78 °C under argon. After stirring for 5 h, the reaction mixture was quenched with aq. NaHCO<sub>3</sub> and filtered off. The resin was washed three times each with THF/H<sub>2</sub>O (1/1), MeOH and CH<sub>2</sub>Cl<sub>2</sub> and dried under high vacuum for 12 h to afford the polymer-supported *cis*-decalin derivative **16**. TFA cleavage of a sample for HPLC analysis was carried out as in the racemic case. Chiral HPLC Analysis: Chiracel OD (4.6x250 mm) at 1.00 mlmin<sup>-1</sup> of isocratic iPrOH:Hexane (20:80) over 80 min. Tr<sub>1</sub> 39 min (85.99% area), Tr<sub>2</sub> 49.5 min (14.01% area)

To a suspension of polymer-supported Diels-Alder product (1 eq) in  $CH_2Cl_2$  (1 mL/100 mg) was added AgOTf (0.1 M) at room temperature. After shaking for 5 h, the mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo. The residue was purified with silicagel column chromatography (eluted with cyclohexane/ethyl acetate = 5/1) to afford the cleaved product **17** (yield 15% based on loading onto the polymeric-support).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.68 (brs, 2H total, b and b'), 6.37 (d, J = 9.9 Hz, 1H, c), 5.85 (d, J = 9.9 Hz, 1H, d), 5.09 (m, 1H, h), 5.06 (brs, 1H, h), 3.78 (s, 3H, e), 3.60 (dd,  $J_{f,g} = 4.3$  Hz,  $J_{f,g'} = 7.9$  Hz, 1H, f), 2.81 (ddt, J = 1.5 Hz,  $J_{g,f} = 7.9$  Hz,  $J_{gem} = 15.4$  Hz, 1H, g), 2.43 (ddt, J = 1.6 Hz,  $J_{g',f} = 4.3$  Hz,  $J_{gem} = 15.4$  Hz, 1H, g'). HRMS (ESI-TOF) calcd. for C<sub>39</sub>H<sub>42</sub>N<sub>5</sub>O<sub>7</sub>S [M+H]<sup>+</sup> 232.0736 found 232.0730. [ $\alpha$ ]<sup>D</sup> = +5.0. (c = 0.12, CHCl<sub>3</sub>)



## Procedure for the release by Pd(0)-catalyzed reaction

To a suspension of polymer-supported decalin derivatives **12** (1 eq.) and PhSO<sub>2</sub>Na (0.1 M) in THF-MeOH (3:1, 1 mL/100 mg) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 M) at room temperature. The resulting mixture was heated up to 80 °C and stirred for 8 h. The mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo. The residue was purified with silicagel column chromatography (eluted with cyclohexane/ethyl acetate = 7/1) to afford the desired PhSO<sub>2</sub>-substituted product **15**.

Yield: 38% for three steps (average 72%), TLC  $R_f = 0.68$  (silica gel, cyclohexane/ethyl acetate = 2/1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.34 (d, *J* = 8.1 Hz, 2H, a), 7.14-7.20 (m, 3H, a), 5.58-5.60 (m, 1H, b), 4.30-4.42 (m, 1H, c), 3.22 (s, 3H, d), 2.79-2.86 (m, 1H, e), 2.14-2.35 (m, 4H, f and h), 1.82-1.90 (m, 2H, J), 1.72-1.75 (m, 1H, i), 1.56 (s, 3H, g), 1.40-1.45 (m, 1H, i').

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.4, 169.1, 134.8, 133.2, 132.6, 128.5, 127.2, 120.3, 64.3, 51.7, 47.0, 40.1, 34.0, 30.9, 25.7, 23.1, 22.9. IR (neat): 1712 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd. for  $C_{19}H_{23}O_5S$  [M+H]<sup>+</sup> 363.1261 found 363.1266.

## Procedure for the release by Cu-mediated reaction with PhMgBr

To a suspension of polymer-supported decalin derivatives **12** (1.0 eq.) in dry THF (1.0 mL/100 mg) was added a mixture of PhMgBr (0.1 M) and CuBr (0.06 M) in THF at 0  $^{\circ}$ C under argon. The resulting mixture was heated up to 50

 $^{\circ}$ C and stirred for 5 h. The mixture was quenched with aq. NH<sub>4</sub>Cl and extracted with ethyl acetate. The organic layer was washed with aq. NaHCO<sub>3</sub>, brine and dried over MgSO<sub>4</sub>. The filtrate was concentrated in vacuo and the residue was purified with silica gel column chromatography (eluted with cyclohexane/ethyl acetate = from 9/1 to 7/1) to afford the desired Ph-substituted derivative **13**.

Yield: 29% for 3 steps (average 67%), TLC  $R_f = 0.65$  (silicagel, cyclohexane/ethyl acetate = 2/1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.51-7.56 (m, 5H, a), 6.70 (d, J = 10.4 Hz, 1H, b), 6.62 (dd,  $J_{b'f} = 0.8$  Hz, J = 10.4 Hz, 1H, b'), 3.75 (s, 1H, d), 2.60 (brd, J = 12.5 Hz, 1H, e), 2.50 (ddd, J = 6.6 Hz, J = 13.1 Hz,  $J_{gem} = 13.4$  Hz, 1H, f), 2.20 (brd,  $J_{gem} = 13.4$  Hz, 1H, f'), 1.76-2.20 (m, 3H, g and h), 1.55-1.68 (m, 2H, c), 1.38-1.42 (s and m, 4H, g' and i). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  207.6, 171.5, 147.1, 137.5, 129.5, 128.1, 127.9, 126.6, 126.0, 125.0, 62.9, 52.8, 40.8, 40.7, 40.5, 35.4, 29.9, 28.3, 22.7. IR (neat): 1714 cm<sup>-1</sup>. HRMS (EI) calcd. for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub> [M]<sup>+</sup> 298.1569 found 298.1563.

## Procedure for the release by Ag-mediated reaction

To a suspension of polymer-supported decalin derivatives (1.0 eq.) and 1-Me indole (0.1 M) in dry  $CH_2Cl_2$  (1.0 mL/100 mg) was added AgOTf (0.1 M) at 0 °C under argon. After stirring for 3 h, the mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuo. The residue was purified by silica gel column chromatography (eluted with cyclohexane/ethyl acetate = 2/1) to afford the desired 1-Me indole-substituted derivative **14**.

Yield: 23% for 3 steps (average 61%), TLC  $R_f = 0.25$  (silicagel, cyclohexane/ethyl acetate = 2/1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (dd,  $J_{a,c} = 1.1$  Hz,  $J_{a,b} = 8.0$  Hz, 1H, a), 7.29 (dd,  $J_{d,b} = 1.1$  Hz,  $J_{d,c} = 8.2$  Hz, 1H, d), 7.21 (ddd,  $J_{c,a} = 1.1$  Hz,  $J_{c,b} = 7.0$  Hz,  $J_{c,d} = 8.2$  Hz, 1H, c), 7.08 (ddd,  $J_{b,d} = 1.1$  Hz,  $J_{b,c} = 7.0$  Hz,  $J_{b,a} = 8.0$  Hz, 1H, b), 6.71 (s, 1H, e), 6.05 (dd,  $J_{f,m} = 1.5$  Hz,  $J_{f,g} = 9.9$  Hz, 1H, f), 5.84 (d,  $J_{g,f} = 9.9$  Hz, 1H, g), 3.75 (s, 3H, h), 3.73 (s, 3H, i), 2.70 (m, 1H, j), 2.40-2.53 (m, 2H, k), 2.03 (ddd,  $J_{m,g} = 1.5$  Hz, J = 1.8 Hz,  $J_{m,m} = 13.2$  Hz, 1H, m), 1.85-1.97 (m,

3H, l and o), 1.58 (dd,  $J_{m',j} = J_{m',m} = 13.2$  Hz, 1H, m'), 1.55 (s, 3H, n), 1.38-1.41 (m, 1H, o'). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  207.8, 171.7, 138.6, 137.9, 127.7, 125.4, 123.9, 121.1, 120.7, 120.1, 118.4, 109.5, 63.1, 52.7, 40.9, 38.0, 37.3, 36.1, 32.6, 29.2, 28.3, 23.1. IR (neat): 1717 cm<sup>-1</sup>. HRMS (ESI-TOF) calcd. for C<sub>22</sub>H<sub>26</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 352.1907 found 352.1909.



## Procedure for the release by Cu-mediated reaction with C5H11MgBr

To a suspension of polymer-supported decalin derivatives (1.0 eq.) in dry THF (1.0 mL/100 mg) was added a mixture of  $C_5H_{11}MgBr$  (0.1 M) and CuBr (0.06 M) in THF at 0 °C under argon. The resulting mixture was heated up to 50 °C and stirred for 3 h. The mixture was quenched with aq. NH<sub>4</sub>Cl and extracted with ethyl acetate. The organic layer was washed with aq. NaHCO<sub>3</sub>, brine and dried over MgSO<sub>4</sub>. The filtrate was concentrated in vacuo and the residue was purified with silicagel column chromatography (eluted with cyclohexane/ethyl acetate = from 15/1 to 10/1) to afford the desired *n*-pentyl-substituted derivative **19**.

Yield: 9% for 5 steps (average 63%), TLC  $R_f = 0.55$  (silica gel, cyclohexane/ethyl acetate = 3/1), 75% ee,  $[\alpha]^D = +155$  (c = 0.165, CHCl<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31-7.36 (m, 2H, a), 7.26-7.29 (m, 1H, a), 7.18-7.20 (m, 2H, a), 6.11 (d,  $J_{d,c}$  = 10.0 Hz,



1H, d), 5.69 (dd,  $J_{c,g} = 1.4$  Hz,  $J_{c,d} = 10.0$  Hz, 1H, c), 4.05 (dd,  $J_{i,b'} = 7.4$  Hz,  $J = J_{i,b} = 9.7$  Hz, 1H, i), 3.57 (s, 3H, e), 3.17 (dd,  $J_{b,i} = 9.7$  Hz  $J_{b,b'} = 17.6$  Hz, 1H, b), 3.15 (dd,  $J_{b',i} = 7.4$  Hz,  $J_{b',b} = 17.6$  Hz, 1H, b), 2.88 (dd,  $J_{f,g} = 2.7$  Hz,  $J_{f,g'} = 12.1$  Hz, 1H, f), 2.14 (ddd,  $J_{g,c} = 1.4$  Hz,  $J_{g,f} = 2.7$  Hz,  $J_{g,g'} = 14.3$  Hz, 1H, g), 1.61 (dd,  $J_{g',f} = 12.1$  Hz,  $J_{g',g} = 14.5$  Hz, 1H, g'), 1.15-1.35 (m, 8H, 1), 1.00 (s, 3H, h), 0.85 (t, J = 7.1 Hz, 3H, j).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 205.8, 20.18, 168.9, 140.5, 137.9, 128.9, 127.9, 127.5, 120.9, 61.7, 53.3, 51.6, 46.6, 43.6, 41.1, 35.2, 32.5, 31.2, 29.6, 27.5, 24.0, 22.5, 14.0. IR (neat): 1719 cm<sup>-1</sup>. HRMS (EI) calcd. for  $C_{24}H_{30}O_4$  [M]<sup>+</sup> 382.2144 found 382.2136.



























































