The 2-(N,N-Dimethylamino)phenylsulfinyl Group as an Efficient Chiral Auxiliary in Intramolecular Heck Reactions

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SUPPORTING INFORMATION: Representative experimental procedures and characterization data of compounds 1-15

Melting points are uncorrected. ^{1}H-NMR (in $CDCl_3$) were acquired at 200 or 300 MHz, ^{13}C-NMR (in $CDCl_3$) were acquired at 50 or 75 MHz (indicated in each case). Chemical shifts (δ) are reported in ppm relative to $CDCl_3$ (7.26 and 77.0 ppm). Mass espectra (MS) and high resolution mass espectra (HRMS) were determined at an ionizing voltage of 70 eV.

Sulfinylphosphonates 1

(±)-**1a**[1]: 1:1 mixture of epimers at carbon. Mp: 77-79ºC. ^{1}H-NMR (300 MHz):δ 7.34 and 7.16 (m, 8H, Tol), 4.13-3.99 (m, 8H), 2.80 (q, 1H, *J*= 7.4 Hz), 2.74 (q, 1H, *J*= 7.4 Hz), 2.27 (s, 6H), 1.29 and 1.19 (dt, 12H, *J*= 6.9 Hz), 1.19 (t, 3H, *J*= 7.4 Hz), 1.14 (d, 3H, *J*= 7.3 Hz).^{13}C-NMR (75 MHz):δ 141.3, 139.4, 139.3, 129.5, 124.1, 62.7, 62.6, 62.5, 62.4, 58.0, 56.2, 21.0, 16.1, 16.0, 4.7 (2C).

(±)-(**1b**): 1:1 mixture of epimers at carbon. ^{1}H-NMR (300 MHz):δ 4.20 (m, 8H), 3.09 (q, 1H, *J*= 7.6 Hz), 3.02 (q, 1H, *J*= 7.6 Hz), 1.33 (m, 18H), 1.23 (s, 18H).

(R_S)-**1c**: 1:1 mixture of epimers at carbon. ^{1}H-NMR (200 MHz):δ 7.80 (dd, 2H, *J*= 1.7 and 7.6 Hz), 7.44 (dt, 2H, *J*= 1.7 and 7.5 Hz), 7.26 (dt, 2H, *J*= 1.3 and 8.0 Hz), 7.11 (dd, 2H, *J*= 1.0 and 8.0 Hz), 4.38-4.17 (m, 8H), 3.69 (q, 1H, *J*= 7.4 Hz), 3.60 (q, 1H, *J*= 7.4 Hz), 2.75 (s, 12H), 1.45-1.35 (m, 12H), 1.11 (d, 3H, *J*= 7.4 Hz), 1.02 (d, 3H, *J*= 7.4 Hz). ^{13}C-NMR (75 MHz):δ 149.9, 135.1, 134.9, 131.5, 126.0, 123.5, 119.4, 62.7, 62.6, 62.5, 62.4, 52.2, 50.3, 44.2, 16.2, 16.1, 3.6. MS (EI)(m/e): 333(M^+, 6), 317 (M^+-OH, 12), 168 (46), 166 (26), 152 (29), 150 (100), 137 (46), 120 (20), 91 (47), 77 (21). $[\alpha]^{25}_D$= -258 (c=1.0, $CHCl_3$).

[1] Mikola*J*czyk, M.; Midura, W. *Tetrahedron* **1987**, *43*, 2967.

Aldehyde 2: ^{1}H-NMR (200 MHz): δ 9.73 (s, 1H), 6.06 (bs, 1H), 5.90 (bs, 1H, 4.22 (q, 4H, *J*= 7.0 Hz), 3.33 (s, 2H), 3.25 (s, 2H), 1.27 (t, 6H, *J*= 7.0 Hz).

General procedure for the synthesis of dienes 3, 7-9

To a solution of the corresponding phosphonate (1.9 mmol) in 15 mL of THF was added LDA 0.5M in THF (4.2 mL, 2.2 mmol) at –78ºC under argon. The solution was stirred for 30 min and then a solution of the corresponding aldehyde (2.3 mmol) in 4 mL of THF was added. The reaction mixture was slowly warmed to 0ºC and then kept at this temperature for 15 min. A saturated solution of NH_4Cl (15 mL) was added, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The resulting mixture of E:Z dienes was purified by flash chromatography (the eluent is indicated in each case).

Diene 3a

E:Z= 50:50. Eluent: ethyl acetate-hexane (1:2). Overall yield: 77%

Diene(*E*)-**3a**: ^{1}H-NMR (200 MHz):δ 7.45-7.24 (m, 4H), 6.32 (tq, 1H, *J*= 7.5 y 1.6 Hz), 6.06 (d, 1H, *J*=1.1 Hz), 5.89 (d, 1H, *J*= 1.6 Hz), 4.27-4.11 (m, 4H), 3.20 (bs, 2H), 2.90 (d, 2H, *J*= 7.0 Hz), 2.38 (s, 3H), 1.60 (bs, 3H), 1.24 (t, 3H, *J*= 7.0 Hz), 1.23 (t, 3H, *J*= 7.0 Hz).^{13}C-NMR (75 MHz):δ 169.6, 145.1, 141.2, 139.3, 131.4, 129.7, 128.1, 124.9, 100.7, 61.9, 57.0, 46.3, 30.4, 21.3, 13.9, 8.8. HRMS (IE) calcd for $C_{21}H_{27}IO_5S$: 518.0624, found: 518.0649

Diene(*Z*)-**3a**: ^{1}H-NMR (200 MHz):δ 7.43-7.25 (m, 4H), 6.19 (bs, 1H), 5.98 (d, 1H, *J*= 1.6 Hz), 5.79 (ddq, 1H, *J*= 1.6, 4.8 and 10.2 Hz), 4.30-4.15 (m, 4H), 3.55 (dd, 1H, *J*= 10.2 and 15.6 Hz), 3.22 (bs, 2H, *J*= 16.1 Hz), 2.99 (ddq, 1H, *J*= 2.1, 4.8 and 15.6 Hz), 2.37 (s, 3H), 1.69 (bs, 3H), 1.27 (t, 3H, *J*= 7.0 Hz), 1.26 (t, 3H, *J*= 7.0 Hz). ^{13}C-NMR (75 MHz):δ 169.6, 145.3, 140.7, 139.3, 131.8, 130.3, 129.7, 124.0, 100.4, 62.1, 62.0, 57.1, 46.4, 30.8, 21.3, 13.9, 12.5. MS (EI)(m/e): 518 (M^+, 3), 501 (M^+-OH, 62), 391 (M^+-I, 33), 281 (14), 150 (60), 139 (66), 91 (100), 77 (59). HRMS (IE) calcd for $C_{21}H_{27}IO_5S$: 518.0624, found: 518.0629.

Diene 3b

E:Z= 2:98. Eluent: ethyl acetate-hexane (1:2). Yield: 83%

Diene(*Z*)-**3b**: ^{1}H-NMR (300 MHz):δ 6.13 (bs, 1H), 5.95 (d, 1H, *J*= 1.6 Hz), 5.92 (m, 1H), 4.30-4.10 (m, 4H), 3.22 (dd, 1H, *J*= 11.2 and 15.9 Hz), 3.20 and 3.10 (AB system, 2H, *J*= 15.2 Hz), 2.61 (dq, 1H, *J*= 2.7 and 15.9 Hz), 1.94 (bs, 3H), 1.30-1.20 (m, 6H), 1.24 (s, 9H). ^{13}C-NMR (75 MHz):δ 169.6, 169.5, 141.5, 132.2, 131.8, 100.3, 62.0, 58.0, 57.2, 46.3, 31.1, 24.0, 15.1, 14.0, 13.9.

Diene 3c

E:Z= 15:85. Eluent: ethyl acetate-hexane (1:4). Overall yield: 88%

Diene(*E*)-**3c**: ^{1}H-NMR (200 MHz):δ 7.77 (dd, 1H, *J*= 1.5 and 7.7 Hz), 7.38 (td, 1H, *J*= 1.6 and 7.7 Hz), 7.19 (bt, 1H, *J*= 7.5 Hz), 7.06 (bd, 1H, *J*= 7.9 Hz), 6.22 (bt, 1H, *J*= 7.5 Hz), 5.96 (bs, 1H), 5.86 (d, 1H, *J*= 0.9 Hz), 4.19 (q, 4H, *J*= 7.1 Hz), 3.16 (bs, 2H, *J*= 15.1 Hz), 2.86 (d, 2H, *J*= 7.4 Hz), 2.75 (s, 6H), 1.57 (bs, 3H), 1.25 (t, 6H, *J*= 7.1 Hz).^{13}C-NMR (75 MHz):δ 169.6, 151.9, 143.6, 135.9, 131.7, 131.3, 128.1, 125.8, 123.7, 119.5, 100.9, 61.9, 56.9, 46.1, 44.9, 30.5, 13.9, 8.5.

Diene (*Z*)-**3c**: ^{1}H-NMR (200 MHz):δ 7.82 (dd, 1H, *J*= 1.7 and 7.6 Hz), 7.39 (td, 1H, *J*= 1.6 and 7.5 Hz), 7.28 (td, 1H, *J*= 0.8 and 7.5 Hz), 7.16 (bd, 1H, *J*= 7.8 Hz), 6.21 (bs, 1H), 5.99 (d, 1H, *J*= 1.4 Hz), 5.75 (ddq, 1H, *J*= 1.2, 3.1 and 11.2 Hz), 4.32-4.17 (m, 4H), 3.64 (dd, 1H, *J*= 11.2 and 16.0 Hz), 3.20 and 3.28 (AB system, 2H, *J*= 15.3 Hz), 2.82 (dq, 1H, *J*= 2.4 and 16.0 Hz), 2.68 (s, 6H), 1.57 (bs, 3H), 1.29 (t, 3H, *J*= 7.1 Hz), 1.26 (t, 3H, *J*= 7.1 Hz). ^{13}C-NMR (50 MHz):δ 169.9, 169.8, 151.4, 143.6, 137.9, 131.8, 131.3, 130.1, 126.0, 124.8, 120.7, 100.8, 62.0, 61.9, 57.0, 46.4, 45.0, 31.1, 14.0, 12.2. MS (EI)(m/e): 547 (M^+, 6), 530 (M^+-OH, 86), 420 (M^+-I, 2), 403 (3), 152 (34), 150 (100), 120 (24), 91 (27), 77 (18). Anal calcd for $C_{22}H_{30}INO_5S$: C, 48.27%; H, 5.52%; N, 2.56%; S, 5.86%. Found: C, 48.22%; H, 5.30%; N, 2.47%; S, 5.80%. Enantiomer (*Ss*)-(*Z*)-**3c** $[\alpha]^{25}_{D}$= +135.0 (c=1.0, $CHCl_3$) [ee>95%, determined by ^{1}H-NMR analysis using 3 equiv of (*R*)-2,2,2-trifluoro-1-(9-anthryl)ethanol].

Diene 7

E:Z= 5:95. Eluent: ethyl acetate-hexane (1:3). Overall yield: 85%

Diene(*Z*)-**7**: ^{1}H-NMR (300 MHz):δ 7.88 (dd, 1H, *J*= 1.1 and 7.3 Hz), 7.42 (dt, 1H, *J*= 1.1 and 7.3 Hz), 7.31 (dt, 1H, *J*= 1.0 and 7.3 Hz), 7.18 (dd, 1H, *J*= 1.0 and 7.7 Hz), 6.11 (s, 1H), 5.86 (bt, 1H, *J*= 6.9 Hz), 5.75 (s, 1H), 2.64 (s, 6H), 2.85-2.04 (m, 4H), 1.73 (m, 2H, *J*= 7.3 Hz), 1.57 (bs, 3H). ^{13}C-NMR (75 MHz):δ 151.4, 140.1, 137.1, 133.9, 131.3, 126.2, 126.0, 124.9, 120.8, 111.5, 45.0, 44.7, 28.6, 27.3, 12.6. MS (EI)(m/e): 403 (M^+-7), 386 (M^+-OH, 99), 276 (M^+-I, 2), 152 (36), 150 (100), 120 (19), 91 (32), 77 (24). HRMS (IE) calcd for $C_{16}H_{22}NIOS$: 403.0467, found: 403.0473.

Diene 8

E:Z= 18:82. Eluent: ethyl acetate-hexane (1:6). Overall yield: 65%

Diene (*E*)-**8**: ^{1}H-NMR (200 MHz):δ 7.76 (dd, 1H, *J*= 1.7 and 7.7 Hz), 7.38 (dt, 1H, *J*= 1.7 and 7.7 Hz), 7.20 (dt, 1H, *J*= 1.0 and 7.7 Hz), 7.06 (dd, 1H, *J*= 1.0 and 7.7 Hz), 6.20 (bt, 1H, *J*= 7.2 Hz), 6.10 (d, 1H, *J*= 1.5 Hz), 5.87 (d, 1H, *J*= 1.5 Hz), 4.20 (m, 4H), 3.20 (bs, 2H), 2.90 (dd, 2H, *J*= 2.7 and 7.2 Hz), 2.75 (s, 6H), 2.10 (m, 2H), 1.25 (m, 6H), 0.73 (t, 3H, *J*= 7.5 Hz). ^{13}C-NMR (75 MHz):δ 169.7, 152.2, 149.2, 136.9, 131.8, 131.4, 127.0, 125.8, 124.0, 119.5, 100.9, 62.1, 61.9, 58.9, 46.2, 45.0, 44.8, 30.2, 17.8, 13.9, 13.8.

Diene (*Z*)-**8**: ^{1}H-NMR (200 MHz):δ 7.85 (dd, 1H, *J*= 2.1 and 7.5 Hz), 7.40 (dt, 1H, *J*= 2.1 and 7.5 Hz), 7.26 (dt, 1H, *J*= 1.1 and 7.5 Hz), 7.15 (dd, 1H, *J*= 1.1 and 7.5 Hz), 6.19 (d, 1H, *J*= 1.6 Hz), 5.97 (d, 1H, *J*= 1.6 Hz), 5.75 (ddd, 1H, *J*= 1.6, 3.5 and 11.3 Hz), 4.20 (m, 4H), 3.65 (dd, 1H, *J*= 11.3 and 16.0 Hz), 3.20 and 3.30 (AB system, 2H, *J*= 15.1 Hz), 2.85 (dq, 1H, *J*= 15.6 and 3.2 Hz), 2.65 (s, 6H), 2.25 (dq, 1H, *J*= 1.6 and

7.5 Hz)1.65 (dq, 1H, *J*= 1.6 and 7.5 Hz), 1.28 and 1.25 (dt, 6H, *J*= 7.0 Hz), 0.75 (t, 3H, *J*= 7.5 Hz). ^{13}C-NMR (75 MHz):δ 169.9, 169.7, 151.4, 148.8, 138.3, 131.6, 131.2, 128.7, 125.9, 125.0, 120.8, 100.8, 62.0, 61.9, 57.1, 46.5, 44.9, 44.8, 31.0, 14.0, 13.9, 13.2. MS (EI)(m/e): 561 (M^+, 5), 544 (M^+-OH, 97), 486 (7), 434 (M^+-I, 2), 416 (4), 178 (50), 150 (100), 136 (29), 120 (32), 91 (36).
HRMS (IE) calcd for $C_{23}H_{32}NIO_5S$: 561.1046, found: 561.1044.

Diene 9

E:Z= 14:86. Eluent: ethyl acetate-hexane (1:4). Overall yield: 77%

Diene (*E*)-**9**: ^{1}H-NMR (significant signals, 200 MHz):δ 7.79 (dd, 1H, *J*= 1.6 and 7.5 Hz), 6.40 (m, 1H), 6.09 (d, 1H, *J*= 1.1 Hz), 5.90 (d, 1H, *J*= 1.6 Hz), 3.17 (bs, 2H), 2.70 (s, 6H), 2.40 (t, 2H, *J*= 7.5 Hz), 1.81 (ddd, 2H, *J*= 2.1, 7.5 and 15.1 Hz), 1.51 (d, 3H, *J*= 1.1 Hz).

Diene (*Z*)-**9**: ^{1}H-NMR (300 MHz):δ 7.81 (dd, 1H, *J*= 1.6 and 7.7 Hz), 7.37 (dt, 1H, *J*= 1.6 and 7.7 Hz), 7.26 (dt, 1H, *J*= 1.2 and 7.7 Hz), 7.15 (bd, 1H, *J*= 7.7 Hz), 6.13 (bs, 1H), 5.90 (bd, 1H, *J*= 1.6 Hz), 5.79 (m, 1H), 4.20 (m, 4H), 3.24 and 3.18 (AB system, 2H, *J*= 15.8 Hz), 2.70 (m, 1H), 2.58 (s, 6H), 2.16 (m, 3H), 1.52 (s, 3H), 1.25 (m, 6H). ^{13}C-NMR (75 MHz):δ 170.1, 151.4, 140.4, 137.7, 136.0, 131.3, 131.0, 126.1, 124.9, 120.8, 100.9, 61.7, 61.6, 57.3, 46.0, 45.0, 30.6, 23.9, 13.9, 12.4. MS (EI)(m/e): 561 (M^+, 8), 544 (M^+-OH, 84), 434 (M^+-I, 5), 218 (10), 178 (17), 169 (12), 150 (100), 136 (30), 120 (35), 91 (39). Anal calcd for $C_{23}H_{32}INO_5S$: C, 49.20%; H, 5.74%; N, 2.49%; S, 5.71%. Found: C, 49.28%; H, 5.81%; N, 2.22%; S, 5.72%.

General procedure for the Heck reaction

In a round bottom flask were sequentally added at room temperature the diene (1.17 mmol), silver carbonate (2.34 mmol), palladium acetate (0.11 mmol), dppf (0.12 mmol) and 18 ml of CH_3CN. The reaction was stirred vigorously at 60ºC under argon for 5h. The mixture was cooled to room temperature, dilueted with diethyl ether and filtered through a pad of celite. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography providing the adduct (the yields are indicated in each case).

Heck products 4a, 4b, 4c, 5, 10, 11 and 12

Aduct 4a: Starting diene: (*Z*)-**3a**. Mixture **4aA**:**4aB**= 54:46. Overall yield: 77%

Aduct (3*S**,*S*s*)-**4aA**: ^{1}H-NMR (200 MHz):δ 7.54-7.26 (m, 4H), 6.18 (s, 1H), 5.75 (s, 1H), 5.00 (q, 1H, *J*= 2.2 Hz), 4.64 (q, 1H, *J*= 2.3 Hz), 4.20-4.02 (m, 4H), 3.20 (bt, 1H, *J*= 9.2 Hz), 2.96 (m, 2H), 2.39 (s, 3H), 2.31 (dd, 1H, *J*= 8.3 and 13.2 Hz), 1.90 (dd, 1H, *J*= 10.1 and 13.0 Hz), 1.24-1.14 (m, 6H). ^{13}C-NMR (75 MHz, significant signals):δ 170.9, 157.4, 148.3, 141.9, 129.9, 125.4, 117.3, 110.0, 58.5, 21.4, 13.9

Aduct (3*R**,*S*s*)-**4aB**: ^{1}H-NMR (200 MHz):δ 7.54-7.26 (m, 4H), 6.18 (s, 1H), 5.74 (s, 1H), 4.93 (q, 1H, *J*= 2.2 Hz), 4.59 (q, 1H, *J*= 2.3 Hz), 4.20-4.02 (m, 4H), 3.09 (bt,

1H, *J*= 9.2 Hz), 2.96 (m, 2H), 2.39 (s, 3H), 2.27 (dd, 1H, *J*= 7.8 and 13.6 Hz), 2.00 (dd, 1H, *J*= 10.7 and 13.3 Hz), 1.24-1.14 (m, 6H). ^{13}C-NMR (75 MHz, significant signals):δ 156.9, 149.2, 129.7, 125.6, 117.6, 109.14, 58.1, 21.4 y 13.9. MS (EI)(m/e): 390 (M^+, 4), 373 (M^+-OH, 10), 299 (12), 251 (19), 177 (100), 91 (33), 77 (24). Anal calcd for $C_{21}H_{26}O_5S$: C, 64.61%; H, 6.66%; S, 8.22%. Found: C, 64.84%; H, 6.54%; S, 8.06%.

Aduct 4b: Starting diene: (*Z*)-**3b**. Mixture **4bA**:**4bB**= 83:17. Overall yield: 35%

Aduct (3*S**,*Ss**)-**4bA**:^{1}H-NMR (200 MHz):δ 5.90 (s, 1H), 5.88 (s, 1H), 5.09 (q, 1H, *J*= 2.2 Hz), 4.91 (q, 1H, *J*= 2.3 Hz), 4.30-4.10 (m, 4H), 3.48 (bt, 1H, *J*= 10.0 Hz), 3.08 (m, 2H), 2.85 (dd, 1H, *J*= 7.9 and 13.0 Hz), 2.11 (dd, 1H, *J*= 10.8 and 12.9 Hz) 1.25 (t, 6H, *J*= 7.3 Hz), 1.25 (s, 9H). ^{13}C-NMR (75 MHz, significant signals):δ 153.6, 149.0, 120.4, 109.7 y 23.4.

Aduct (3*R**,*Ss**)-**4bB**: ^{1}H-NMR (200 MHz, significant signals):δ 5.87 (s, 1H), 5.84 (s, 1H), 5.04 (q, 1H, *J*= 2.4 Hz), 4.91 (m, 1H). ^{13}C-NMR (75 MHz, significant signals):δ 153.2, 149.9, 120.6, 108.9, 23.3.

Aduct 4c: Starting diene: (*Ss*)-(*Z*)-**3c**. **4cA**:**4cB=** >98:<2. Yield: 75%

Aduct (3*S*,*Ss*)-**4cA**: ^{1}H-NMR (200 MHz):δ 7.79 (dd, 1H, *J*= 1.8 and 7.8 Hz), 7.40 (dt, 1H, *J*= 1.7 and 7.5 Hz), 7.22 (dt, 1H, *J*= 1.4 and 7.5 Hz), 7.10 (dd, 1H, *J*= 1.0 and 8.0 Hz), 6.08 (s, 1H), 5.68 (s, 1H), 4.95 (q, 1H, *J*= 2.3 Hz), 4.59 (q, 1H, *J*= 2.3 Hz), 4.12 (q, 4H, *J*= 7.1 Hz), 3.37 (bt, 1H, *J*= 9.3 Hz), 2.95 (m, 2H), 2.75 (s, 6H), 2.10 (dd, 1H, *J*= 8.3 and 13.2 Hz), 1.87 (dd, 1H, *J*= 10.4 and 13.0 Hz), 1.20 (t, 6H, *J*= 7.1 Hz). ^{13}C-NMR (75 MHz):δ 171.0, 157.3, 152.2, 149.3, 137.0, 132.0, 125.7, 124.4, 119.9, 118.1, 109.5, 61.6, 61.5, 58.5, 44.8, 42.2, 40.7, 14.0. Anal calcd for $C_{22}H_{29}NO_5S$: C, 62.98%; H, 6.97%;N, 3.34; S, 7.64%. Found: C, 62.33%; H, 6.56%; N, 3.20; S, 7.52%. $[\alpha]^{25}_D$= -29 (c= 1.0, $CHCl_3$) [e.e= 95.4%, determined by HPLC, column Daicel Chiralcel OD; eluent: hexane/2-propanol 98:2; flow: 1.0ml/min, 254 nm; retention time (3*S*, S*s*)-**4cA**=17.4 min; (3*R*, S*s*)-**4cB**= 19.9 min.]

Aduct 5: Starting diene: (*E*)-**3c**, mixture: **4cA**:**4cB**:**5**= 8:32:80. **4c** and **5** were separated by flash chromatography, eluent: ethyl acetate-hexane (1:4). Yield: 34% (mixture **4cA**:**4cB**= 20:80) + 48% **5**.

Aduct (3*R**,*Ss**)-**4cB**: ^{1}H-NMR (200 MHz):δ 7.75 (dd, 1H, *J*= 1.1 and 7.5 Hz), 7.40 (dt, 1H, *J*= 1.6 and 7.1 Hz), 7.20 (bt, 1H, *J*= 7.5 Hz), 7.10 (bd, 1H, *J*= 8.1 Hz), 6.10 (s, 1H), 5.69 (s, 1H), 4.86 (q, 1H, *J*= 2.2 Hz), 4.42 (q, 1H, *J*= 2.2 Hz), 4.21-4.07 (m, 4H), 3.24 (bt, 1H, *J*= 8.6 Hz), 2.95 (m, 2H), 2.80 (s, 6H), 2.40 (dd, 1H, *J*= 8.1 and 12.9 Hz), 2.02 (dd, 1H, *J*= 10.7 and 13.4 Hz), 1.28-1.15 (t, 6H, *J*= 7.1 Hz). ^{13}C-NMR (75 MHz):δ 171.1, 156.7, 152.4, 149.8, 136.5, 132.0, 126.2, 124.1, 119.7, 117.9, 108.6, 61.5, 61.4, 58.3, 44.8, 42.0, 40.6, 14.0.

Aduct 5: ^{1}H-NMR (200 MHz):δ 7.88 (dd, 1H, *J*= 1.9 and 7.5 Hz), 7.44 (dt, 1H, *J*= 1.8 and 7.3 Hz), 7.35 (dt, 1H, *J*= 1.6 and 7.2 Hz), 7.23 (dd, 1H, *J*= 1.5 and 7.5 Hz), 5.31 (t, 1H, *J*= 1.9 Hz), 5.24 (t, 1H, *J*= 1.9 Hz), 4.23 (m, 4H), 3.81 (bd, 1H, *J*= 17.9 Hz), 3.55 (dq, 1H, *J*= 2.2 and 17.7 Hz), 3.18 (bd, 1H, *J*= 15.5 Hz), 2.95 (dt, 1H, *J*=

2.0 and 15.5 Hz), 2.61 (s, 6H), 1.75 (t, 3H, *J*= 2.0 Hz), 1.28 and 1.27 (dt, 6H, *J*= 7.2 Hz). ^{13}C-NMR (75 MHz):δ 171.3, 170.8, 151.8, 144.9, 141.7, 138.7, 135.3, 131.2, 126.2, 125.6, 121.4, 114.6, 61.8, 61.7, 57.1, 45.1, 42.3, 39.6, 14.0, 9.9. MS (EI)(m/e): 419 (M^+, 1), 402 (M^+-OH, 13), 191 (12), 150 (100), 120 (13), 91 (21), 77 (18).

Aduct 10: Starting diene: (*Z*)-**7**. Mixture **10A**:**10B**= 92:8. Overall yield: 54%

Aduct (1*S**, *Ss**)-**10A**: ^{1}H-NMR (200 MHz):δ 7.78 (dd, 1H, *J*= 1.6 and 7.5 Hz), 7.39 (dt, 1H, *J*= 1.6 and 7.5 Hz), 7.21 (dt, 1H, *J*= 1.1 and 7.5 Hz), 7.10 (dd, 1H, *J*= 1.1 and 8.1 Hz), 6.03 (s, 1H), 5.61 (s, 1H), 4.91 (q, 1H, *J*= 2.1 Hz), 4.60 (q, 1H, *J*= 2.1 Hz), 3.13 (bt, 1H, *J*= 6.5 Hz), 2.76 (s, 6H), 2.32 (m, 2H), 1.69-1.25 (m, 4H). ^{13}C-NMR (75 MHz):δ 158.5, 153.3, 152.5, 137.4, 131.8, 125.8, 124.3, 119.8, 116.8, 107.8, 44.8, 42.6, 35.7, 33.0, 24.5. MS (EI)(m/e): 275 (M^+, 1), 258 (M^+-OH, 84), 169 (64), 150 (100), 107 (20), 91 (42), 77 (28). HRMS (IE) calcd for $C_{16}H_{21}NOS$: 275.1344, found: 275.1344

Aduct 11: Starting diene: (*Z*)-**8**. **11A**:**11B=** >98:<2 (mixture E:Z= 15:85). Overall yield: 70%

Aduct (3*S**,*Ss**)-(*Z*)-**11A**: ^{1}H-NMR (200 MHz):δ 7.84 (dd, 1H, *J*= 1.7 and 7.5 Hz), 7.42 (dt, 1H, *J*= 1.7 and 7.5 Hz), 7.31 (dt, 1H, *J*= 1.2 and 7.5 Hz), 7.15 (dd, 1H, *J*= 1.2 and 7.5 Hz), 6.12 (q, 1H, *J*= 7.1 Hz), 4.97 (q, 1H, *J*= 2.4 Hz), 4.87 (q, 1H, *J*= 2.4 Hz), 4.06 (m, 4H), 3.35 (tt, 1H, *J*= 2.5 and 8.3 Hz), 3.07 (bd, 1H, *J*= 16.7 Hz), 2.78 (dq, 1H, *J*= 2.4 and 16.7 Hz), 2.64 (s, 6H), 2.11 (d, 3H, *J*= 7.1 Hz), 1.47 (dd, 1H, *J*= 11.5 and 13.0 Hz), 1.24 (m, 1H), 1.15 (m, 6H). ^{13}C-NMR (75 MHz):δ 171.3, 170.7, 151.4, 151.3, 147.7, 138.4, 134.6, 131.3, 125.6, 125.3, 120.6, 108.8, 61.3, 58.1, 44.8, 43.0, 40.7, 38.5, 14.9, 13.9, 13.8.

Aduct (3*S**,*Ss**)-(*E*)-**11A**: ^{1}H-NMR (significant signals, 200 MHz):δ 6.50 (q, 1H, *J*= 7.2 Hz), 4.65 (q, 1H, *J*= 2.3 Hz), 2.69 (s, 6H), 1.71 (d, 3H, *J*= 7.2 Hz). ^{13}C-NMR (significant signals, 75 MHz):δ 147.9, 145.5, 132.9, 131.5, 125.4, 124.1, 119.9, 107.9, 58.5, 44.6, 40.0, 39.2, 38.4, 15.3. MS (EI)(m/e): 433 (M^+, 3), 416 (M^+-OH, 69), 388 (12), 342 (10), 271 (8), 225 (2), 208 (5), 191 (38), 169 (100), 150 (99), 136 (32), 117 (31), 91 (45). HRMS (IE) calcd for $C_{23}H_{31}NO_5S$: 433.1923, found: 433.1914

Aduct 12: Starting diene: (*Z*)-**9**. **12A**:**12B**= >98:<2. Yield: 61%

Aduct (3*S**,*Ss**)-**12A**: ^{1}H-NMR (200 MHz):δ 7.76 (dd, 1H, *J*= 1.6 and 8.0 Hz), 7.37 (dt, 1H, *J*= 1.6 and 7.5 Hz), 7.19 (dt, 1H, *J*= 1.6 and 7.53), 7.06 (dd, 1H, *J*= 1.6 and 7.5 Hz), 6.11 (s, 1H), 5.56 (s, 1H), 4.70 (bs, 1H), 4.55 (bs, 1H), 4.14 (m, 4H), 2.95 (m, 1H), 2.86 (dd, 1H, *J*= 1.6 and 13.9 Hz), 2.75 (s, 6H), 2.52 (bd, 1H, *J*= 13.5 Hz), 2.24 (ddd, 1H, *J*= 2.1, 4.8 and 15.1 Hz), 1.72 (m, 2H), 1.40 (m, 1H), 1.21 (t, 6H, *J*= 7.0 Hz). ^{13}C-NMR (75 MHz):δ 171.3, 170.5, 154.7, 152.4, 143.2, 137.1, 132.0, 125.9, 124.4, 119.8, 118.3, 112.1, 61.5, 61.3, 56.3, 44.9, 41.0, 39.5, 30.7, 30.5, 14.2, 14.1. MS (EI)(m/e): 433 (M^+, 3), 416 (M^+-OH, 91), 388 (29), 342 (7), 265 (12), 191 (85), 169 (92), 150 (100), 136 (28), 117 (34), 91 (48). HRMS (IE) calcd for $C_{23}H_{31}NO_5S$: 433.1923, found: 433.1934

Desulfinylation sequences

Diols 6+6'

Diol 6: Mp.= 124-126ºC. ^{1}H-NMR (300 MHz):δ 7.82 (dd, 1H, *J*= 1.6 and 7.8 Hz), 7.47 (dt, 1H, *J*= 1.6 and 7.6 Hz), 7.34 (dt, 1H, *J*= 1.1 and 7.7 Hz), 7.18 (dd, 1H, *J*= 1.0 and 7.7 Hz), 6.18 (s, 1H), 5.84 (s, 1H), 4.94 (s, 1H), 4.21-4.07 (m, 4H), 3.57 (dd, 1H, *J*= 3.5 and 11.4 Hz), 3.33 (t, 1H, *J*= 10.6 Hz), 3.13 (dd, 1H, *J*= 3.8 and 9.7 Hz), 2.68 (m, 1H), 2.62 (s, 6H), 2.36 (dd, 1H, *J*= 9.1 and 13.4 Hz), 2.65 and 2.34 (AB system, 2H, *J*= 14.8 Hz), 2.08 (dd, 1H, *J*= 10.3 and 13.7 Hz), 1.20 (t, 3H, *J*= 7.1 Hz), 1.15 (t, 3H, *J*= 7.1 Hz). ^{13}C-NMR (75 MHz):δ 172.0, 171.5, 151.7, 150.9, 134.8, 132.4, 126.2, 125.0, 123.2, 121.2, 80.6, 65.9, 61.8, 61.7, 57.5, 47.0, 44.6, 42.2, 38.3, 13.9. MS (EI)(m/e): 453 (M^+, 2), 436 (M^+-OH, 5), 422 (16), 404 (17), 169 (64), 152 (100), 91 (13), 77 (8). $[\alpha]^{25}_D$= -31.0 (c= 1.0, $CHCl_3$).

Diol 6': ^{1}H-NMR (300 MHz):δ 7.83 (dd, 1H, *J*= 1.6 and 7.8 Hz), 7.46 (dt, 1H, *J*= 1.6 and 7.5 Hz), 7.31 (dt, 1H, *J*= 1.1 and 7.6 Hz), 7.15 (dd, 1H, *J*= 1.0 and 7.9 Hz), 6.23 (s, 1H), 6.05 (s, 1H), 4.91 (dd, 1H, *J*= 6.6 and 8.8 Hz), 4.20-3.95 (m, 4H), 3.59 (dd, 1H, *J*= 6.5 and 12.0 Hz), 3.42 (dd, 1H, *J*= 8.8 and 12.0 Hz), 2.93 (bs, 1H), 2.65 (s, 6H), 2.47 (dd, 1H, *J*= 7.1 and 13.1 Hz), 2.38 and 2.24 (AB system, 2H, *J*= 14.5 Hz), 2.22 (t, 1H, *J*= 12.9 Hz), 1.52 (dd, 1H, *J*= 7.1 and 12.9 Hz), 1.19 and 1.14 (dt, 6H, *J*= 7.3 Hz). ^{13}C-NMR (75 MHz):δ 172.1, 171.5, 151.7, 148.7, 135.0, 132.1, 125.5, 125.4, 124.6, 120.8, 81.1, 66.9, 61.8, 61.6, 56.6, 44.6, 43.2, 41.3, 40.8. 13.9. $[\alpha]^{25}_D$= -39.5 (c= 1.0, $CHCl_3$).

Sulfone (*S*)-13: ^{1}H-NMR (200 MHz):δ 8.11 (dd, 1H, *J*= 1.6 and 7.9 Hz), 7.57 (dt, 1H, *J*= 1.6 and 8.1 Hz), 7.30 (bd, 1H, *J*= 8.1 Hz), 7.26 (dt, 1H, *J*= 1.1 and 7.6 Hz), 6.35 (s, 1H), 5.89 (s, 1H), 5.05 (q, 1H, *J*= 2.2 Hz), 4.79 (q, 1H, *J*= 2.3 Hz), 4.15 and 4.11 (dq, 4H, *J*= 7.0 Hz), 3.47 (bt, 1H, *J*= 8.9 Hz), 2.98 (m, 2H), 2.70 (s, 6H), 2.51 (dd, 1H, *J*= 8.1 and 13.2 Hz), 2.05 (dd, 1H, *J*= 10.6 and 13.3 Hz), 1.22 and 1.18 (dt, 6H, *J*= 7.1 Hz). ^{13}C-NMR (75 MHz):δ 171.0, 154.4, 153.4, 148.9, 134.7, 134.3, 131.3, 124.4, 123.8, 123.1, 110.0, 61.7, 61.6, 58.4, 46.4, 43.1, 42.0, 40.8, 14.0. MS (EI)(m/e): 435 (M^+, 13), 390 (20), 298 (5), 185 (16), 121 (100), 91 (39), 77 (22). Anal calcd for $C_{22}H_{29}NO_6S$: C, 60.67%; H, 6.71%; N, 3.22%; S, 7.36%. Found: C, 60.63%; H, 6.61%; N, 3.11%; S, 7.10%. $[\alpha]^{25}_D$= +74.3 (c= 0.7, $CHCl_3$) [e.e= 95.4%, determined by HPLC, column Daicel Chiralcel OD; eluent: hexane/2-propanol 98:2; flow: 0.4 ml/min, 254 nm; retention time (*R*)-**13**= 31.5 min; (*S*)-**13**= 34.3 min.]

Diene (*R*)-14: ^{1}H-NMR (200 MHz):δ 5.65 (dt, 1H, *J*= 8.6 and 17.5 Hz), 5.10 (q, 1H, *J*= 2.7 Hz), 5.00 (m, 2H), 4.81 (q, 1H, *J*= 2.2 Hz), 4.25-4.13 (m, 4H), 3.18 (m, 1H), 3.08 (bd, 1H, *J*= 17.2 Hz), 2.94 (dq, 1H, *J*= 1.6 and 16.7 Hz), 2.57 (dd, 1H, *J*= 7.5 and 12.9 Hz), 2.00 (dd, 1H, *J*= 10.7 and 12.5 Hz), 1.25 (t, 6H, *J*= 7.0 Hz). ^{13}C-NMR (75 MHz):δ 171.5, 150.7, 139.2, 115.9, 107.9, 61.5, 58.6, 47.7, 40.2, 14.0. $[\alpha]^{25}_D$ = +13.7 (c= 0.8, $CHCl_3$).

Cyclopentanone (*S*)-15: ^{1}H-NMR (300 MHz):δ 4.23 and 4.22 (dq, 4H, *J*= 7.2 Hz), 2.95 (dt, 1H, *J*= 1.7 and 18.9 Hz), 2.82 (ddd, 1H, *J*= 2.1, 8.4 and 13.1 Hz), 2.71 (d, 1H, *J*= 18.9 Hz), 2.31 (dddd, 1H, *J*= 1.4, 4.6, 8.5 and 11.9 Hz), 2.01 (dd, 1H, *J*= 13.0 and 11.9 Hz), 1.81 (ddq, 1H, *J*= 4.7, 7.6 and 14.0 Hz), 1.36 (ddq, 1H, *J*= 1.6, 7.4 and

14.0 Hz), 1.27 and 1.26 (dt, 6H, *J*= 7.1 Hz), 0.94 (t, 3H, *J*= 7.5 Hz). ^{13}C-NMR (75 MHz):δ 215.4, 171.1, 170.9, 62.1, 62.0, 55.0, 49.0, 45.2, 35.8, 22.7, 14.0 y 11.6. MS (EI)(m/e): 256 (M^+, 28), 200 (71), 183 (22), 154 (100), 109 (22), 81 (27). HRMS (IE) calcd for $C_{13}H_{20}O_5$: 256.1311, found: 256.1308. $[\alpha]^{25}_D$= +95.8 (c=1.2, $CHCl_3$) [e.e>95%, determined by ^{1}H-NMR using 3 equiv de (*R*)-2,2,2-trifluoro-1-(9-anthryl)ethanol].