Stereodivergent Synthesis of Pseudotabersonine Alkaloids

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General Information

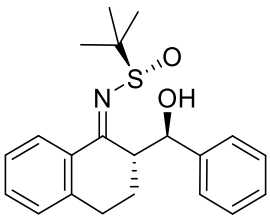
All reactions were carried out under argon atmosphere. Standard inert atmosphere techniques were used in handling all air and moisture sensitive reagents. Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel F-254 plates. Flash column chromatography was performed using silica gel (0.040-0.063 mm) or C18-silica gel (0.050 mm).

Nuclear magnetic resonance spectra were recorded on NMR spectrometers at the following frequencies: ^{1}H, 400 MHz; $^{13}C\{^{1}H\}$, 100.6 MHz. Chemical shifts are reported in parts per million (ppm) relative to TMS or with the residual solvent peak as an internal reference. High-resolution mass spectra (HRMS) were recorded on a mass spectrometer with a time-of-flight (TOF) mass analyzer using the ESI technique. Melting points are uncorrected.

Unless otherwise noted, all chemicals were used as received from commercial sources. Anhydrous THF, diethyl ether and CH_2Cl_2 were obtained by passing commercially available solvents through activated alumina columns. A 1M solution of $TiCl_2(O\text{-}i\text{Pr})_2$ in anhydrous CH_2Cl_2 was made from freshly distilled $TiCl_4$ and $Ti(O\text{-}i\text{Pr})_4$ directly prior to use.

General procedure for synthesis of imino alcohols (*S*$_S$,*R*,*R*)-7b–k

Imino alcohols (*S*$_S$,*R*,*R*)-**7b–k** were prepared according to the literature procedure.[1] Accordingly, triethylamine (4.0 equiv) was added dropwise to a stirred solution of ketimine (*E*,*S*)-**8** (1.0 equiv) in anhydrous CH_2Cl_2 (13 mL/mmol of ketimine (*E*,*S*)-**8**) at room temperature under argon atmosphere. In a separate flask to a solution of aldehyde (1.5 equiv) in anhydrous CH_2Cl_2 (30 mL/mmol of ketimine (*E*,*S*)-**8**) was added $TiCl_2(OiPr)_2$ (3.0 equiv, 1.0 M solution in anhydrous CH_2Cl_2), and the resulting yellow solution was added dropwise *via* cannula to the solution of ketimine (*E*,*S*)-**8** within approximately 10 minutes. The solution was stirred at room temperature and progress of the reaction was followed by LC or LC/MS methods. Typically, complete conversion of ketimine (*E*,*S*)-**8** required 90 minutes, whereupon the reaction mixture was poured into a mixture of crushed ice and brine and layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 85 mL/mmol of ketimine (*E*,*S*)-**8**) and the combined organic extracts were dried over anhydrous Na_2SO_4. Filtration and concentration under reduced pressure afforded crude product that was purified by column chromatography on silica gel.



(S)-N-((R,E)-2-((R)-Hydroxy(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((S*$_S$*,R,R)-7b)

Following the General Procedure, imine (*E*,*S*)-**8b** (100 mg, 0.40 mmol) was converted into (*S*$_S$,*R*,*R*)-**7b**. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 100% EtOAc afforded product as a white foam (140 mg, 98% yield).

TLC: R_f 0.50 (5:2 Hex/EtOAc).

IR (film, cm^{-1}) 3305, 2924, 1583, 1453, 1301, 1201, 1033.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (1H, dd, *J* = 8.0, 1.2 Hz), 7.52-7.46 (2H, m), 7.43 (1H, ddd, *J* = 7.4, 7.4, 1.3 Hz), 7.41-7.33 (2H, m), 7.33-7.27 (2H, m), 7.22 (1H, d, *J* = 7.7 Hz), 5.77 (1H, d, *J* = 10.5 Hz), 4.60 (1H, d, *J* = 10.6 Hz), 3.99 (1H, ddd, *J* = 10.8, 4.2, 2.7 Hz), 3.17

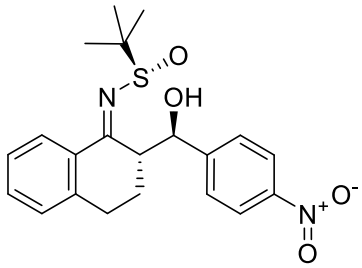
(1) Bartrum, H. E., Viceriat, A., Carret, S., Poisson, J.-F. *Org. Lett.* **2014**, *16*, 1972.

(1H, ddd, *J* = 18.4, 13.2, 5.5 Hz), 2.77 (1H, dd, *J* = 18.0, 5.8 Hz), 2.10-1.98 (1H, m), 1.61-1.53 (1H, m), 1.44 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 177.6, 143.5, 140.1, 132.3, 132.2, 129.2, 128.6, 128.3, 127.8, 126.7, 126.5, 71.4, 59.1, 48.0, 24.4, 24.1, 22.9.

HRMS-ESI (*m/z*) calcd for $C_{21}H_{26}NO_2S$ $[M+H]^+$: 356.1684; found 356.1681.

Optical rotation: $[\alpha]^{20}_D$ +36.7 (*c* 1.00, CH_2Cl_2).



(S)-N-((R,E)-2-((R)-Hydroxy(4-nitrophenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7c)

Following the General Procedure, imine (*E*,*S*)-**8b** (100 mg, 0.40 mmol) was converted into (*S*$_S$,*R*,*R*)-**7c**. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 100% EtOAc afforded product as a brown foam (80 mg, 50% yield).

TLC: R_f 0.69 (1:1 EtOAc/Hex).

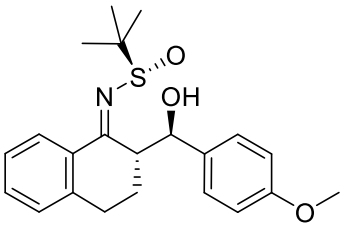
IR (film, cm^{-1}) 3270, 2925, 2866, 1583, 1521, 1347, 1031.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.26-8.21 (2H, m), 8.09 (1H, dd, *J* = 8.0, 1.4 Hz), 7.68-7.63 (2H, m), 7.46 (1H, td, *J* = 7.4, 1.4 Hz), 7.34-7.29 (1H, m), 7.25-7.22 (1H, m), 6.11 (1H, d, *J* = 10.4 Hz), 4.70 (1H, t, *J* = 10.6 Hz), 3.95 (1H, ddd, *J* = 10.8, 4.2, 2.8 Hz), 3.16 (1H, ddd, *J* = 18.4, 13.4, 5.4 Hz), 2.83 (1H, dd, *J* = 17.8, 5.6 Hz), 2.15-2.04 (1H, m), 1.55-1.48 (1H, m), 1.45 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 176.8, 151.1, 147.8, 139.9, 132.7, 132.2, 129.5, 128.5, 127.7, 127.1, 124.1, 70.7, 59.5, 48.0, 24.3, 24.2, 23.0.

HRMS-ESI (*m/z*) calcd for $C_{21}H_{25}N_2O_4S$ $[M + H]^+$ 401.1535, found 401.1536.

Optical rotation: $[\alpha]^{20}_D$ +39.8 (*c* 1.00, $CHCl_3$).



(S)-N-((R,E)-2-((R)-Hydroxy(4-methoxyphenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7d)

Following the General Procedure, imine (*E,S*)-**8b** (100 mg, 0.40 mmol) was converted into (*S$_S$,R,R*)-**7d**. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 100% EtOAc afforded product as a yellow foam (134 mg, 86% yield).

TLC: R_f 0.62 (1:1 EtOAc/Hex).

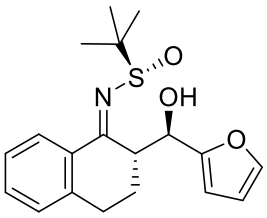
IR (film, cm^{-1}) 3316, 2957, 2927, 1611, 1583, 1514, 1248, 1050.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (1H, dd, *J* = 8.0, 1.4 Hz), 7.45-7.37 (3H, m), 7.31-7.27 (1H, m), 7.23-7.19 (1H, m), 6.93-6.88 (2H, m), 5.65 (1H, d, *J* = 10.4 Hz), 4.56 (1H, t, *J* = 10.6 Hz), 3.97 (1H, ddd, *J* = 10.6, 4.2, 2.6 Hz), 3.81 (3H, s), 3.14 (1H, ddd, *J* = 18.4, 13.2, 5.6 Hz), 2.75 (1H, dd, *J* = 18.0, 5.6 Hz), 2.09-1.97 (1H, m), 1.63-1.55 (1H, m, overlap with HDO), 1.43 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 177.9, 159.3, 140.3, 135.9, 132.5, 132.3, 129.4, 128.4, 127.8, 126.8, 114.2, 71.0, 59.2, 55.4, 48.3, 24.6, 24.3, 23.1.

HRMS-ESI (*m/z*) calcd for $C_{22}H_{27}NO_3NaS$ $[M + Na]^+$ 408.1609, found 408.1609.

Optical rotation: $[\alpha]^{20}_D$ +57.1 (*c* 1.00, $CHCl_3$).



(S)-N-((R,E)-2-((R)-Furan-2-yl(hydroxy)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7e)

Following the General Procedure, imine (*E,S*)-**8b** (100 mg, 0.40 mmol) was converted into (*S$_S$,R,R*)-**7e**. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 100% EtOAc afforded product as a brown foam (116 mg, 84% yield).

TLC: R_f 0.71 (1:1 EtOAc/Hex).

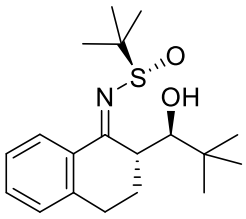
IR (film, cm^{-1}) 3291, 2960, 2925, 1583, 1051.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.07 (1H, dd, J = 8.0, 1.2 Hz), 7.44-7.39 (2H, m), 7.30-7.27 (1H, m), 7.21-7.17 (1H, m), 6.34 (2H, d, J = 1.4 Hz), 5.66 (1H, d, J = 10.4 Hz), 4.69 (1H, t, J = 10.6 Hz), 4.21 (1H, ddd, J = 11.0, 4.0, 2.8 Hz), 3.10 (1H, ddd, J = 18.4, 13.2, 5.4 Hz), 2.76 (1H, ddd, J = 18.0, 5.8, 1.2 Hz), 2.17-2.04 (1H, m), 1.72 (1H, dddd, J = 14.4, 5.4, 2.8, 1.8 Hz), 1.41 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 176.8, 155.8, 142.4, 140.3, 132.3, 132.3, 129.4, 128.4, 126.8, 110.2, 107.1, 64.8, 59.2, 45.7, 24.7, 24.2, 23.1.

HRMS-ESI (*m/z*) calcd for $C_{19}H_{23}NO_3NaS$ $[M + Na]^+$ 368.1296, found 368.1297.

Optical rotation: $[\alpha]^{20}_D$ +5.8 (*c* 1.00, $CHCl_3$).



(S)-N-((R,E)-2-((R)-1-Hydroxy-2,2-dimethylpropyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7f)

Following the General Procedure, imine (*E*,*S*)-**8b** (100 mg, 0.40 mmol) was converted into (*S*$_S$,*R*,*R*)-**7f**. The reaction required 2 hours to go to completion. Purification of the crude product by column chromatography on silica gel using gradient elution from 5% EtOAc in hexane to 100% EtOAc afforded product as a yellow solid (110 mg, 82% yield).

TLC: R_f 0.81 (1:1 EtOAc/Hex).

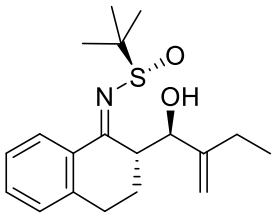
IR (film, cm^{-1}) 3347, 2956, 2924, 1584, 1040.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.97 (1H, dd, J = 8.0, 1.2 Hz), 7.39 (1H, td, J = 7.6, 1.4 Hz), 7.24 (1H, t, J = 7.4 Hz), 7.18 (1H, d, J = 7.6 Hz), 4.23 (1H, d, J = 11.4 Hz), 3.92 (1H, dt, J = 10.4, 3.3 Hz), 3.35 (1H, t, J = 10.8 Hz), 3.15 (1H, ddd, J = 18.2, 13.2, 5.0 Hz), 2.83 (1H, ddd, J = 18.0, 5.6, 1.4 Hz), 2.34 (1H, dddd, J = 15.0, 5.2, 3.2, 1.9 Hz), 2.13 (1H, dddd, J = 15.0, 13.2, 5.4, 3.4 Hz), 1.38 (9H, s), 1.07 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 180.8, 140.3, 133.5, 132.0, 128.9, 128.7, 126.7, 73.9, 58.3, 45.1, 36.8, 27.2, 26.0, 24.7, 22.8.

HRMS-ESI (*m/z*) calcd for $C_{19}H_{30}NO_2S$ $[M + H]^+$ 336.1997, found 336.1998.

Optical rotation: $[\alpha]^{20}_D$ –122.9 (*c* 1.00, $CHCl_3$).



(S)-N-((R,E)-2-((R)-1-Hydroxy-2-methylenebutyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7g)

Following the General Procedure, imine (*E*,*S*)-**8b** (100 mg, 0.40 mmol) was converted into (*S*$_S$,*R*,*R*)-**7g**. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 100% EtOAc afforded product as a white solid (120 mg, 90% yield).

TLC: R_f 0.19 (1:10 EtOAc/Hex).

mp: 102.5–103.2 ºC (EtOAc/heptanes, colorless needles).

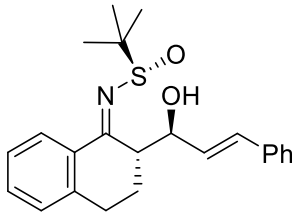
IR (film, cm^{-1}) 3350, 2966, 2920, 1583, 1456, 1361, 1040.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.03 (1H, dd, *J* = 8.0, 1.6 Hz), 7.39 (1H, ddd, *J* = 7.4, 7.4, 1.5 Hz), 7.25 (1H, dd, *J* = 7.8, 7.8 Hz), 7.17 (1H, dd, *J* = 7.7, 1.1 Hz), 5.31 (1H, d, *J* = 9.9 Hz), 5.05 (1H, d, *J* = 1.1 Hz), 4.96 (1H, dd, *J* = 3.1, 1.7 Hz), 4.15 (1H, dd, *J* = 10.8, 10.0 Hz), 3.83 (1H, ddd, *J* = 10.9, 4.0, 2.8 Hz), 3.06 (1H, ddd, *J* = 17.9, 13.2, 5.6 Hz), 2.74 (1H, ddd, *J* = 17.9, 5.9, 2.1 Hz), 2.38-2.26 (1H, m), 2.15-2.00 (2H, m), 1.90 (1H, dddd, *J* = 14.1, 5.6, 2.8, 1.8 Hz), 1.39 (9H, s), 1.13 (3H, t, *J* = 7.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 177.8, 151.4, 140.4, 132.5, 132.2, 129.3, 128.3, 126.7, 111.3, 73.8, 59.2, 43.6, 24.7, 23.9, 23.1, 21.0, 11.9.

Anal. Calcd for $C_{19}H_{27}NO_2S$: C, 68.43; H, 8.16; N, 4.20; Found: C, 68.64; H, 8.42; N, 4.23.

Optical rotation: $[\alpha]^{20}_D$ –47.1 (*c* 1.13, CH_2Cl_2).



(S)-N-((R,E)-2-((S,E)-1-Hydroxy-3-phenylallyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7h)

Following the General Procedure, imine (*E*,*S*)-**8b** (100 mg, 0.40 mmol) was converted into (*S*$_S$,*R*,*R*)-**7h**. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 100% EtOAc afforded product as a brown foam (135 mg, 88% yield).

TLC: R_f 0.70 (1:1 EtOAc/Hex).

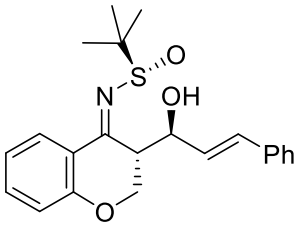
IR (film, cm^{-1}) 3306, 2981, 2925, 1610, 1582, 1452, 1301, 1036.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.07 (1H, dd, J = 8.0, 1.4 Hz), 7.44-7.39 (3H, m), 7.35-7.27 (3H, m), 7.25-7.18 (2H, m), 6.65 (1H, d, J = 15.8 Hz), 6.27 (1H, dd, J = 15.8, 7.8 Hz), 5.23 (1H, d, J = 10.0 Hz), 4.25 (1H, td, J = 10.2, 8.0 Hz), 3.76 (1H, dt, J = 10.4, 3.4 Hz), 3.11 (1H, ddd, J = 18.2, 12.5, 6.0 Hz), 2.81 (1H, ddd, J = 17.8, 5.4, 1.6 Hz), 2.22-2.06 (2H, m), 1.41 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 177.5, 140.4, 136.8, 132.5, 132.3, 131.9, 131.2, 129.4, 128.7, 128.3, 127.8, 126.8, 126.7, 70.0, 59.1, 46.9, 24.7, 24.2, 23.0.

HRMS-ESI (*m/z*) calcd for $C_{23}H_{27}NO_2NaS$ $[M + Na]^+$ 404.1660, found 404.1668.

Optical rotation: $[\alpha]^{20}_D$ –51.5 (*c* 1.00, $CHCl_3$).



(S)-N-((S,E)-3-((S,E)-1-Hydroxy-3-phenylallyl)chroman-4-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7i)

Following the General Procedure, imine (*E*,*S*)-**8i** (101 mg, 0.40 mmol) was converted into (*S$_S$*,*R*,*R*)-**7i**. Reaction mixture was quenched after 1 hour. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 100% EtOAc afforded product as a yellow oil (139 mg, 91% yield).

TLC: R_f 0.68 (1:1 EtOAc/Hex).

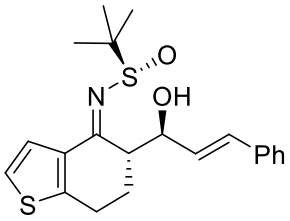
IR (film, cm^{-1}) 3305, 2982, 2924, 1590, 1479, 1310, 1264, 1215, 1039.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.94 (1H, dd, J = 8.0, 1.6 Hz), 7.46-7.38 (3H, m), 7.35-7.29 (2H, m), 7.28-7.22 (1H, m, overlap with $CDCl_3$), 7.01 (1H, ddd, J = 8.0, 7.2, 1.0 Hz), 6.97-6.92 (1H, m), 6.71 (1H, d, J = 15.8 Hz), 6.26 (1H, dd, J = 15.8, 7.9 Hz), 5.20 (1H, d, J = 10.6 Hz), 4.46-4.36 (2H, m), 4.31 (1H, dd, J = 12.0, 2.4 Hz), 3.55 (1H, dt, J = 10.2, 1.8 Hz), 1.40 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 170.7, 158.3, 136.6, 134.6, 132.9, 130.3, 128.7, 128.0, 127.9, 126.8, 121.8, 120.0, 117.9, 77.4, 69.1, 67.0, 59.5, 47.0, 23.0.

HRMS-ESI (*m/z*) calcd for $C_{22}H_{25}NO_3SNa$ $[M + Na]^+$ 406.1453, found 406.1447.

Optical rotation: $[\alpha]^{20}_D$ –67.0 (*c* 1.00, $CHCl_3$).



(S)-N-((R,E)-5-((S,E)-1-Hydroxy-3-phenylallyl)-6,7-dihydrobenzo[b]thiophen-4(5H)-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7j)

Following the General Procedure, imine (*E*,*S*)-**8j** (100 mg, 0.39 mmol) was converted into (*S*$_S$,*R*,*R*)-**7j**. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 30% EtOAc in hexane afforded product as a yellow oil (132 mg, 85% yield).

TLC: R_f 0.75 (1:1 EtOAc/Hex).

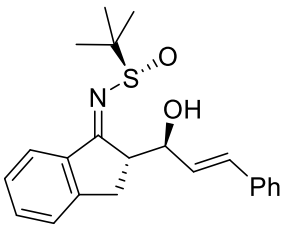
IR (film, cm^{-1}) 3305, 2960, 2926, 1576, 1038.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43-7.39 (2H, m), 7.37 (1H, d, J = 5.3 Hz), 7.35-7.29 (2H, m), 7.26-7.21 (1H, m, overlap with $CDCl_3$), 7.11 (1H, d, J = 5.3 Hz), 6.63 (1H, d, J = 15.8 Hz), 6.26 (1H, dd, J = 15.8, 8.0 Hz), 5.37 (1H, d, J = 10.2 Hz), 4.22 (1H, q, J = 10.2 Hz), 3.63 (1H, dt, J = 10.4, 3.3 Hz), 3.09 (1H, ddd, J = 17.7, 12.0, 5.7 Hz), 2.96-2.87 (1H, m), 2.29-2.12 (2H, m), 1.36 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 172.8, 148.3, 136.7, 135.5, 131.9, 131.5, 128.7, 127.9, 126.7, 125.8, 123.6, 70.2, 58.8, 46.2, 26.6, 22.9, 21.1.

HRMS-ESI (*m/z*) calcd for $C_{21}H_{25}NO_2NaS_2$ $[M + Na]^+$ 410.1224, found 410.1221.

Optical rotation: $[\alpha]^{20}_D$ –25.8 (*c* 1.00, $CHCl_3$).



(S)-N-((R,E)-2-((S,E)-1-Hydroxy-3-phenylallyl)-2,3-dihydro-1H-inden-1-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7k)

Imine (*E*,*S*)-**8b** (94 mg, 0.40 mmol) was converted into (*S*$_S$,*R*,*R*)-**7k** following a modified General Procedure. Thus, the reaction was perfomed at 0 ºC and and required 15 minutes to go to completion. Purification of the crude product by column chromatography on silica gel using gradient elution from 1% MeOH in CH_2Cl_2 to 10% MeOH in CH_2Cl_2 afforded product as a yellow oil (118 mg, 80% yield).

TLC: R_f 0.64 (9:1 CH_2Cl_2/MeOH).

IR (film, cm^{-1}) 3391, 3279, 2960, 2923, 1617, 1598, 1055.

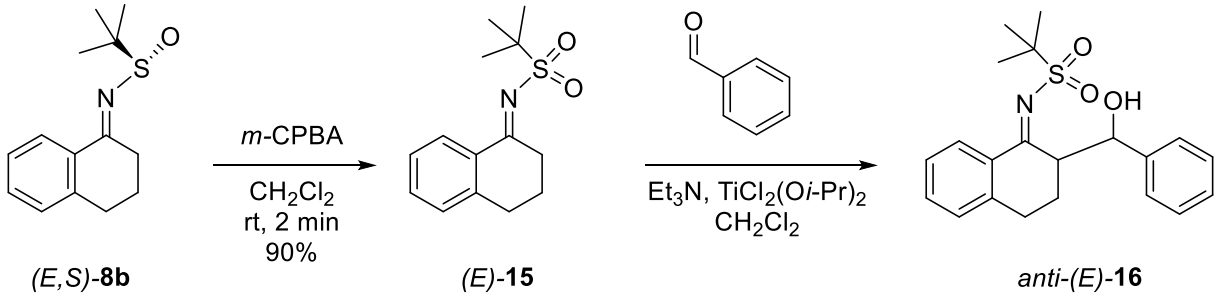
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.76 (1H, d, J = 7.8 Hz), 7.50 (1H, d, J = 7.4 Hz), 7.41-7.33 (4H, m), 7.32-7.28 (2H, m), 7.25-7.20 (1H, m), 6.59 (1H, d, J = 15.8 Hz), 6.24 (1H, dd, J = 15.8, 6.8 Hz), 5.56 (1H, d, J = 9.0 Hz), 3.80-3.67 (2H, m), 3.18 (1H, dd, J = 16.6, 5.6 Hz), 2.93 (1H, d, J = 16.6 Hz), 1.41 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 181.4, 147.4, 139.0, 136.8, 133.2, 131.8, 131.7, 128.6, 127.7, 126.7, 126.1, 124.1, 74.3, 59.1, 52.2, 34.7, 23.3.

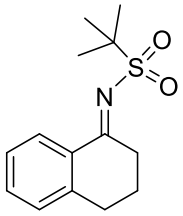
HRMS-ESI (*m/z*) calcd for $C_{22}H_{25}NO_2NaS$ $[M + Na]^+$ 390.1504, found 390.1502.

Optical rotation: $[\alpha]^{20}_D$ +13.2 (*c* 1.00, $CHCl_3$).

The aldol reaction with *tert*-butanesulfonyl ketimine (*E*)-15



(E,S)-**8b** *(E)*-**15** *anti-(E)*-**16**



(E)-N-(3,4-Dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfonamide ((E)-15)

To a solution of imine (*E,S*)-**8b** (112 mg, 0.45 mmol) in CH_2Cl_2 (15 mL) was added *m*-CPBA (116 mg, 0.47 mmol) at room temperature in one portion. After 2 minutes the reaction was completed. The white suspension was diluted with CH_2Cl_2 (100 mL) and washed with saturated aqueous solution of $NaHCO_3$ (2x50 mL). The organic phase was dried over Na_2SO_4 and concentrated. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 50% EtOAc in hexane afforded product *(E)*-**15** as a yellow solid (107 mg, 90% yield).

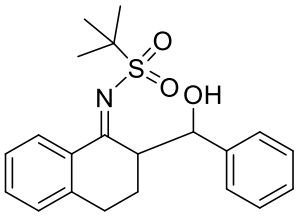
TLC: R_f 0.16 (1:10 EtOAc/Hex).

IR (film, cm^{-1}) 3068, 2962, 1610, 1580, 1296, 1119.

^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.13 (1H, d, J = 8.0 Hz), 7.48-7.42 (1H, m), 7.31-7.25 (1H, m, overlap with $CDCl_3$), 7.24-7.20 (1H, m), 3.32 (2H, t, J = 6.4 Hz), 2.89 (2H, t, J = 6.2 Hz), 2.07-1.99 (2H, m), 1.55 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 180.6, 144.3, 133.6, 132.4, 129.2, 127.3, 126.8, 59.2, 33.2, 29.5, 24.2, 22.4.

HRMS-ESI (*m/z*) calcd for $C_{14}H_{19}NO_2NaS$ $[M + Na]^+$ 288.1040, found 288.1034.



(E)-N-(2-(Hydroxy(phenyl)methyl)-3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfonamide (anti-(E)-16)

Imine (*E*)-**15** (50 mg, 0.19 mmol) was converted into *anti*-(*E*)-**16** following a modified General Procedure. Thus, a mixture of benzaldehyde and $TiCl_2(OiPr)_2$ was added to imine (*E*)-**15** and NEt_3 at -78 ºC (dry ice bath) whereupon the reaction temperature was gradually raised to 0 ºC (within approximately 4 h). Purification of the crude product by column chromatography on silica gel using gradient elution from 5% EtOAc in hexane to 20% EtOAc in hexane afforded product as a white solid (70 mg, 99% yield).

TLC: R_f 0.73 (1:1 EtOAc/Hex).

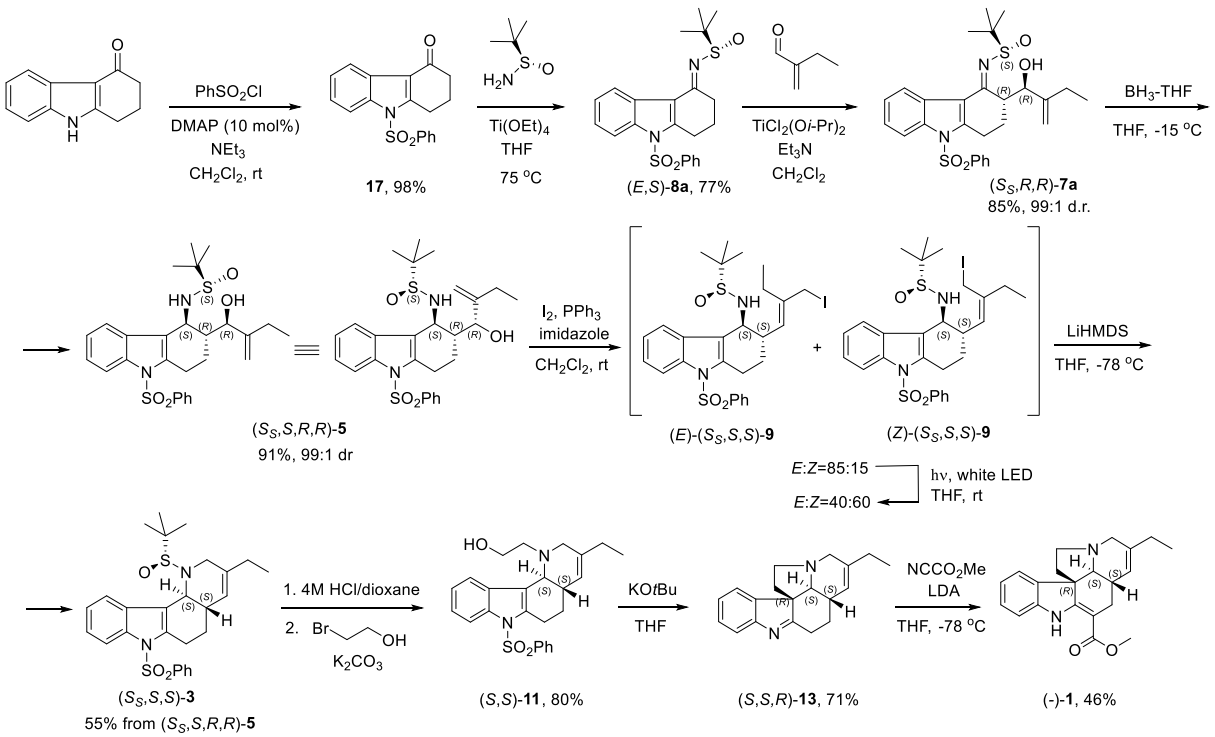
IR (film, cm^{-1}) 3448, 2985, 2930, 1609, 1546, 1258, 1111.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.12 (1H, dd, J = 8.0, 1.4 Hz), 7.52 (1H, td, J = 7.6, 1.4 Hz), 7.48-7.44 (2H, m), 7.42-7.37 (2H, m), 7.35-7.30 (2H, m), 7.28-7.24 (1H, m, overlap with $CDCl_3$), 4.67 (1H, t, J = 10.6 Hz), 4.60 (1H, d, J = 11.0 Hz), 4.27 (1H, dt, J = 8.0, 1.4 Hz), 3.22 (1H, ddd, J = 18.4, 13.0, 5.8 Hz), 2.86 (1H, dd, J = 18.2, 6.2 Hz), 2.14 (1H, dddd, J = 14.6, 13.0, 6.2, 4.0 Hz), 1.69 (1H, ddd, J = 5.8, 2.8, 1.4 Hz), 1.62 (9H, s).

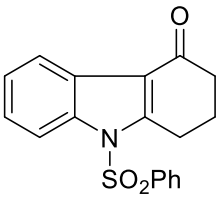
^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 184.1, 142.7, 142.0, 133.9, 131.8, 129.5, 128.9, 128.4, 128.2, 127.0, 126.6, 74.0, 59.8, 49.1, 24.2.

HRMS-ESI (*m/z*) calcd for $C_{21}H_{25}NO_3NaS$ $[M + Na]^+$ 394.1453, found 394.1450.

Synthesis of (–)-14-*epi*-pseudotabersonine 1 from carbazolone



Scheme S1. Synthesis of (–)-14-*epi*-pseudotabersonine (–)-**1** from 1,2,3,9-tetrahydro-4*H*-carbazol-4-one.



9-(Phenylsulfonyl)-1,2,3,9-tetrahydro-4H-carbazol-4-one (17)

To a stirred suspension of 1,2,3,9-tetrahydro-4*H*-carbazol-4-one (4.63 g, 25 mmol) in CH_2Cl_2 (200 mL) was successively added triethylamine (3.03 g, 30 mmol, 1.2 equiv), DMAP (305 mg, 2.5 mmol, 0.1 equiv) and benzenesulfonyl chloride (4.64 g, 26.25 mmol, 1.05 equiv). The resulting colorless suspension was stirred at room temperature. Solid material gradually dissolved and after 16 h the clear yellow solution was quenched with 1M aqueous HCl (20 mL) and water (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure. Yellow oily residue was dissolved in 1:1 MeOH/CH_2Cl_2 mixture (100 mL), transferred into petri dish and left for 2 h to crystallize. After washing with small amount of methanol and diethyl ether, **17** was afforded as colorless needles (7.96 g, 98% yield).

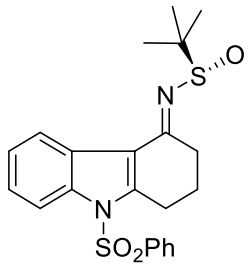
mp 170.6-171.1 ºC (lit.[2] mp 170 ºC).

(2) Göetz, P. H.; Bats, J. W.; Fritz, H. *Liebigs Ann. Chem.* **1986**, 2065.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.27-8.22 (1H, m), 8.19-8.13 (1H, m), 7.89-7.85 (2H, m), 7.60 (1H, ddd, J = 8.5, 2.2, 1.1 Hz), 7.52-7.46 (2H, m), 7.39-7.31 (2H, m), 3.33 (2H, t, J = 6.2 Hz), 2.59-2.53 (2H, m), 2.22 (2H, p, J = 6.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 195.1, 151.0, 138.6, 136.1, 134.6, 129.8, 126.7, 125.9, 125.6, 125.2, 122.0, 118.2, 113.9, 38.0, 24.7, 23.3.

Anal. Calcd for $C_{18}H_{15}NO_3S$: C, 66.44; H, 4.65; N, 4.30. Found: C, 66.24; H, 4.34; N, 4.30.



(S)-2-Methyl-N-(9-(phenylsulfonyl)-1,2,3,9-tetrahydro-4H-carbazol-4-ylidene)propane-2-sulfinamide ((E,S)-8a)

Pressure tube was charged with ketone **17** (4.88 g, 15 mmol), (*S*)-*tert*-butanesulfinamide (5.45 g, 45 mmol, 3 equiv) and $Ti(OEt)_4$ (17.1 g, 75 mmol, 6 equiv). THF (20 mL) was added, the pressure tube was closed and the resulting suspension was heated for 120 h at 75 °C. After being cooled to ambient temperature, the mixture was transferred into beaker with stirring bar, diluted with ethyl acetate (100 mL) and quenched with water (10 mL). The resulting slurry was stirred for 30 min and filtered through a short pad of Celite®. The filter cake was washed with ethyl acetate. The filtrate was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 1% MeOH in CH_2Cl_2 to 10% MeOH in CH_2Cl_2 to afford (*E,S*)-**8a** as brown-yellow solid (4.98 g, 77% yield) and starting ketone **17** (0.74 g, 15% recovery).

TLC: R_f 0.44 (95:5 CH_2Cl_2/MeOH).

mp 135.5-136.3 ºC (EtOAc/heptanes, brown-yellow prisms).

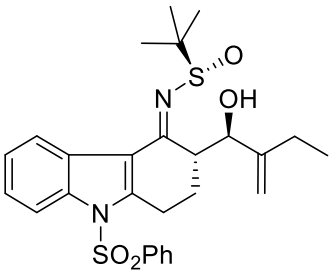
IR (film, cm^{-1}) 2980, 1571, 1448, 1378, 1174, 1075.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.34-8.30 (1H, m), 8.21-8.17 (1H, m), 7.86-7.81 (2H, m), 7.62-7.57 (1H, m), 7.50-7.45 (2H, m), 7.38-7.29 (2H, m), 3.34 (1H, ddd, J = 18.4, 6.5, 5.5 Hz), 3.26-3.14 (2H, m), 3.02 (1H, ddd, J = 17.0, 7.4, 4.5 Hz), 2.20-2.02 (2H, m), 1.34 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 175.3, 147.4, 138.7, 136.4, 134.5, 129.8, 126.6, 126.3, 125.5, 124.9, 122.8, 117.9, 114.1, 56.6, 31.1, 24.5, 23.0, 22.6.

Anal. Calcd for $C_{22}H_{24}N_2O_3S_2$: C, 61.66; H, 5.64; N, 6.54. Found: C, 61.73; H, 5.68; N, 6.57.

Optical rotation: $[\alpha]^{20}_D$ +57.6 (c 1.15, CH_2Cl_2).



(S)-N-((R)-3-((R)-1-Hydroxy-2-methylenebutyl)-9-(phenylsulfonyl)-1,2,3,9-tetrahydro-4H-carbazol-4-ylidene)-2-methylpropane-2-sulfinamide ((S$_S$,R,R)-7a)

Imine (*E*,*S*)-**8a** (100 mg, 0.40 mmol) was converted into (*S*$_S$,*R*,*R*)-**7a** following General Procedure for synthesis of imino alcohols (see page S3). The reaction required 6 hours to go to completion. Purification of the crude product by column chromatography on silica gel using gradient elution from 10% EtOAc in hexane to 50% EtOAc in hexane afforded product as a white foam (102 mg, 85 % yield).

TLC: R_f 0.28 (5:2 Hex/EA).

IR (film, cm^{-1}) 3303, 2964, 1569, 1447, 1379, 1173, 1033.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.24-8.20 (2H, m), 7.85-7.81 (2H, m), 7.63-7.58 (1H, m), 7.52-7.46 (2H, m), 7.40-7.30 (2H, m), 5.46 (1H, d, *J* = 9.8 Hz), 4.97-4.95 (1H, m), 4.94-4.92 (1H, m), 3.90 (1H, dd, *J* = 10.6, 10.0 Hz), 3.77 (1H, ddd, *J* = 10.7, 3.9, 2.7 Hz), 3.29 (1H, ddd, *J* = 19.3, 6.0, 1.6 Hz), 3.10 (1H, ddd, *J* = 19.3, 11.9, 5.6 Hz), 2.37-2.25 (1H, m), 2.16-1.95 (3H, m), 1.43 (9H, s), 1.13 (3H, t, *J* = 7.3 Hz,).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 175.5, 151.7, 145.2, 138.7, 136.7, 134.6, 129.8, 126.6, 126.5, 125.6, 124.8, 122.1, 116.9, 114.2, 111.3, 75.0, 58.5, 43.4, 25.2, 23.0, 21.0, 20.7, 11.9.

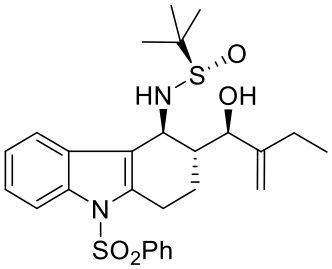
HRMS-ESI (*m/z*) calcd for $C_{27}H_{33}N_2O_4S_2$ $[M+H]^+$: 513.1882; found, 513.1873.

Optical rotation: $[\alpha]^{20}_D$ +5.1 (*c* 0.9, CH_2Cl_2).

Gram-scale synthesis of (*S*$_S$,*R*,*R*)-**7a.**

Triethylamine (1.30 mL, 9.33 mmol, 4 equiv) was added dropwise to a stirred solution of imine (*E*,*S*)-**8a** (1.0 g, 2.33 mmol) in CH_2Cl_2 (50 mL) at room temperature under argon atmosphere. In a separate flask, fresh $TiCl_4$ (1M solution in CH_2Cl_2, 3.5 mL, 3.5 mmol, 1.5 equiv) was diluted with CH_2Cl_2 (7 mL) and cooled to 0^o C (crushed ice). Neat $Ti(OiPr)_4$ (1.04 mL, 3.5 mmol, 1.5 equiv) and 2-methylenebutanal (392 mg, 4.66 mmol, 2 equiv) were added successively and the resulting red-brown solution was added dropwise via cannula over approximately 10 minutes to the solution of imine. After stirring at room temperature for 14 h, aqueous saturated Na_2CO_3 solution (1 mL) was added and after 10 min of stirring the resulting

suspension was filtered through a short pad of Celite®. The filter cake was washed with ethyl acetate. The filtrate was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The yellow-brown residue was purified by flash column chromatography using gradient elution from 10% EtOAc in hexane to 50% EtOAc in hexane to afford (S_S,*R*,*R*)-**7a** as white foam (955 mg, 80% yield).



(S)-N-((3R,4S)-3-((R)-1-Hydroxy-2-methylenebutyl)-9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1H-carbazol-4-yl)-2-methylpropane-2-sulfinamide ((S_S,S,R,R)-5)

A solution of (S_S,*R*,*R*)-**7a** (1.00 g, 1.95 mmol) in THF (50 mL) was cooled to -15 °C and borane-THF complex (1 M solution in THF, 2.5 mL, 2.5 mmol, 1.2 equiv) was added within 3 h by syringe pump, maintaining temperature between -10 – -15 °C. After addition was completed, colorless mixture was stirred for 1 h at -15 °C whereupon it was quenched by slow addition of MeOH (3 mL) (***Warning!*** vigorous gas evolution). The mixture was warmed to ambient temperature, stirred for 15 min and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 50% EtOAc in hexane to 100% EtOAc to afford (S_S,*S*,*R*,*R*)-**5** as white solid (913 mg, 91% yield).

TLC: R_f 0.17 (1:1 Hex/EA).

mp 181-–182 ºC dec (EtOAc/heptanes, colorless needles).

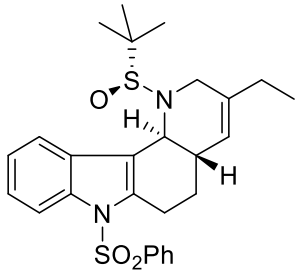
IR (film, cm^{-1}) 3322, 3075, 2961, 1368, 1170, 1045.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.14 (1H, d, J = 8.2 Hz), 7.78-7.71 (2H, m), 7.63 (1H, d, J = 7.6 Hz), 7.52 (1H, dd, J = 7.5, 7.5 Hz), 7.41 (2H, dd, J = 7.8, 7.8 Hz), 7.30-7.25 (1H, m, overlapped with $CDCl_3$), 7.22 (1H, dd, J = 7.4, 7.4 Hz), 4.95-4.85 (3H, m), 3.98 (1H, d, J = 2.9 Hz), 3.83 (1H, dd, J = 9.8, 5.3 Hz), 3.08-2.98 (1H, m), 2.96-2.86 (1H, m), 2.44-2.32 (2H, m), 2.32-2.21 (1H, m), 2.12-2.02 (1H, m), 2.02-1.94 (1H, m), 1.56-1.44 (1H, m), 1.11 (3H, t, J = 7.3 Hz), 1.09 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 152.1, 138.91, 138.3, 136.9, 133.8, 129.4, 128.9, 126.5, 124.6, 123.8, 112.0, 117.4, 114.5, 111.6, 78.9, 55.6, 51.4, 43.2, 22.8, 22.7, 22.5, 22.1, 12.1.

Anal. Calcd for $C_{27}H_{34}N_2O_4S_2$: C, 63.01; H, 6.66; N, 5.44. Found: C, 62.75; H, 6.75; N, 5.41.

Optical rotation: $[\alpha]^{20}_D$ +128.0 (c 0.95, CH_2Cl_2).



(4aS,11cS)-1-((S)-tert-Butylsulfinyl)-3-ethyl-7-(phenylsulfonyl)-2,4a,5,6,7,11c-hexahydro-1H-pyrido[3,2-c]carbazole ((S$_S$,S,S)-3)

Aminoalcohol (*S*$_S$,*S*,*R*,*R*)-**5** (200 mg, 0.39 mmol) and imidazole (106 mg, 1.56 mmol, 4 equiv) were dissolved in CH_2Cl_2 (7 mL) and stirred for 5 min. In separate vial to a solution of iodine (198 mg, 0.78 mmol, 2 equiv) in CH_2Cl_2 (3 mL) was added triphenylphosphine (204 mg, 0.78 mmol, 2 equiv). The resulting A yellow solution of the formed iodotriphenylphosphonium iodide was added dropwise to the stirred solution of aminoalcohol (*S*$_S$,*S*,*R*,*R*)-**5** and imidazole. After 10 min of stirring at room temperature hexane (2 mL) was added and resulting suspension was filtered through a short pad of silica (2 g). The silica pad was washed with 2:1 CH_2Cl_2/hexane mixture (3 mL), filtrates were combined and evaporated under reduced pressure. Yellow foamy residue (~300 mg) was dissolved in THF (10 mL) and irradiated with white LED lamp (30W, 2000 lm) for 1 h (NOTE: mixture can heat up to 50 °C). Yellow mixture was cooled to -78 °C and LiHMDS (1.0 M solution in THF, 0.39 mL, 0.39 mmol, 1 equiv) was added dropwise. Stirring for 10 min was followed by addition of TFA (30 μL, 0.39 mmol, 1 equiv) whereupon the yellow mixture was allowed to warm to room temperature. A sequence comprising irradiation with white LED, treatment with LiHMDS and addition of TFA was repeated two times to achieve complete conversion of starting aminoalcohol (*S*$_S$,*S*,*R*,*R*)-**5** (NOTE: mixture should not be basic upon irradiation, otherwise significant amount of isothiazolo[4,3-*c*]carbazole byproduct (*S*$_R$,*R*,*R*,*S*)-**14** is formed). After addition of the third LiHMDS portion and stirring for 10 min, the yellow-brown reaction mixture was quenched with aqueous saturated NH_4Cl solution (10 mL). Layers were separated and aqueous layer was extracted with EtOAc (2×10 mL). Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by reverse phase flash column chromatography using gradient elution from 30% MeCN in water to 80% MeCN in water to afford (*S*$_S$,*S*,*S*)-**3** as yellowish foam (106 mg, 55% yield).

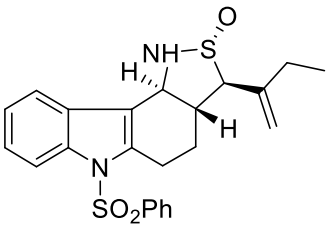
IR (film, cm^{-1}) 2962, 1449, 1374, 1173, 1025.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (1H, d, J = 8.3 Hz), 7.73-7.69 (2H, m), 7.53-7.49 (1H, m), 7.49-7.45 (1H, m), 7.41-7.35 (2H, m), 7.26-7.21 (1H, m, overlapped with $CDCl_3$), 7.17-7.11 (1H, m), 5.53-5.50 (1H, m), 4.19 (1H, ddd, J = 9.6, 2.8, 1.1 Hz), 4.05-3.98 (1H, m), 3.68 (1H, dd, J = 18.0, 3.4 Hz), 3.25-3.16 (1H, m), 3.11-3.02 (1H, m), 3.02-2.93 (1H, m), 2.11-2.05 (1H, m), 2.05-1.92 (2H, m), 1.53-1.43 (1H, m), 1.07 (3H, t, J = 7.5 Hz), 1.03 (9H, s).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 139.8, 138.9, 138.4, 137.5, 133.7, 129.2, 128.9, 126.4, 124.4, 123.5, 123.0, 121.3, 119.3, 115.0, 61.9, 58.7, 47.5, 38.2, 29.4, 26.9, 26.1, 25.0, 12.2.

HRMS-ESI (*m/z*) calcd for $C_{27}H_{33}N_2O_3S_2$ $[M+H]^+$: 497.1933; found, 497.1929.

Optical rotation: $[\alpha]^{20}_D$ +116.7 (*c* 1.16, CH_2Cl_2).



(2R,3R,3aR,10cS)-3-(But-1-en-2-yl)-6-(phenylsulfonyl)-1,2,3,3a,4,5,6,10c-octahydro-2l4-isothiazolo[4,3-c]carbazol-2-ol ((R$_S$,R,R,S)-14)

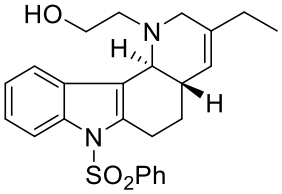
IR (film, cm^{-1}) 3171, 2966, 1448, 1373, 1174, 1042.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.17 (1H, d, *J* = 8.3 Hz), 7.85-7.78 (2H, m), 7.68 (1H, d, *J* = 7.6 Hz), 7.57 (1H, ddd, *J* = 6.9, 3.9, 1.2 Hz), 7.49-7.43 (2H, m), 7.33-7.28 (1H, m), 7.27-7.22 (1H, m, overlapped with $CDCl_3$), 5.16-5.13 (1H, m), 5.08 (1H, s), 4.98-4.91 (1H, m), 4.39 (1H, d, *J* = 8.8 Hz), 3.39 (1H, d, *J* = 12.2 Hz), 3.36-3.28 (1H, m), 3.12-3.01 (1H, m), 2.33-2.18 (2H, m), 2.19-2.11 (1H, m), 2.08-1.97 (1H, m), 1.83-1.71 (1H, m), 1.15 (3H, t, *J* = 7.3 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 143.3, 139.1, 136.4, 135.8, 134.1, 129.6, 127.4, 126.5, 124.8, 124.0, 119.9, 117.8, 114.5, 113.3, 87.1, 61.6, 51.6, 28.8, 25.7, 23.5 12.3.

HRMS-ESI (*m/z*) calcd for $C_{23}H_{25}N_2O_3S_2$ $[M+H]^+$: 441.1307; found, 441.1294.

Optical rotation: $[\alpha]^{20}_D$ +121.1 (*c* 0.85, CH_2Cl_2).



2-((4aS,11cS)-3-Ethyl-7-(phenylsulfonyl)-2,4a,5,6,7,11c-hexahydro-1H-pyrido[3,2-c]carbazol-1-yl)ethan-1-ol ((S,S)-11)

To a stirred solution of tetracycle (*S$_S$*,*S*,*S*)-**3** (100 mg, 0.2 mmol) in THF (2 mL) was added MeOH (0.2 mL) and HCl (4M solution in dioxane, 0.2 mL, 0.8 mmol, 4 equiv). Yellow mixture was stirred for 10 min at room temperature and evaporated under reduced pressure. The yellow oily residue was dissolved in EtOH (2 mL) and transferred into a 5 mL pressure tube. 2-Bromoethanol (71 µL, 1 mmol, 5 equiv) and K_2CO_3 (165 mg, 1.2 mmol, 6 equiv) were added and the resulting suspension was stirred at 80 °C for 24 h. After cooling to room temperature, the suspension was filtered through a pad of Celite® and evaporated under reduced pressure. The residue was purified by flash column

chromatography using gradient elution from 20% EtOAc in hexane to 50% EtOAc in hexane to afford (*S,S*)-**11** as colorless oil (70 mg, 80% yield). Spectral data match with those reported by Martin.[3]

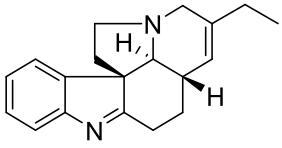
TLC: R_f 0.37 (2:5 EtOAc/Hex).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.13 (1H, d, *J* = 8.2 Hz), 7.90 (1H, d, *J* = 7.4 Hz), 7.79-7.71 (2H, m), 7.55-7.49 (1H, m), 7.41 (2H, dd, *J* = 7.8, 7.8 Hz), 7.29-7.24 (1H, m, overlapped with $CDCl_3$), 7.24-7.18 (1H, m), 5.48 (1H, s), 3.92 (1H, d, *J* = 9.6 Hz), 3.73-3.64 (1H, m), 3.60 (1H, d, *J* = 17.4 Hz), 3.48 (1H, ddd, *J* = 10.9, 5.9, 3.4 Hz), 3.22 (1H, d, *J* = 18.3 Hz), 3.19-3.10 (1H, m), 3.05-2.93 (1H, m), 2.50-2.41 (1H, m), 2.41-2.34 (1H, m), 2.33-2.24 (1H, m), 2.12 (1H, brs), 2.10-2.05 (1H, m), 2.02-1.89 (2H, m), 1.53 (1H, ddd, *J* = 19.1, 12.7, 6.3 Hz), 1.04 (3H, t, *J* = 7.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 139.1, 138.2, 137.6, 136.9, 133.7, 129.4, 129.0, 126.4, 124.3, 123.6, 122.3, 120.7, 119.6, 114.5, 61.8, 60.0, 53.2, 48.3, 31.5, 28.6, 27.6, 25.7, 12.4.

HRMS-ESI (*m/z*) calcd for $C_{25}H_{29}N_2O_3S$ $[M+H]^+$: 437.1899; found, 437.1897.

Optical rotation: $[\alpha]^{20}_D$ 85.4 (*c* 1.1, CH_2Cl_2).



(3aS,3a1S,10bR)-2-Ethyl-3a,3a1,4,5,11,12-hexahydro-1H-indolizino[8,1-cd]carbazole ((S,S,R)-13)

A solution of aminoalcohol (*S,S*)-**11** (44 mg, 0.1 mmol) in THF (1 mL) was cooled to 0 °C (crushed ice), KOtBu (1.6M in THF, 0.15 mL, 0.25 mol, 2.5 equiv) was added and orange mixture was stirred at 0 °C for 30 min. Aqueous saturated NaCl solution (1 mL) and Et_2O (2 mL) were then added and layers were separated. Aqueous layer was extracted with CH_2Cl_2 (3x2 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on basic Al_2O_3 using 10% EtOAc in hexane as a mobile phase to afford (*S,S,R*)-**13** as yellowish oil (20 mg, 71%). Spectral data match with those reported by Martin.[3]

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.59 (1H, d, *J* = 7.4 Hz), 7.54 (1H, d, *J* = 7.7 Hz), 7.30 (1H, ddd, *J* = 7.6, 7.6, 1.3 Hz), 7.19 (1H, ddd, *J* = 7.4, 7.4, 0.8 Hz), 5.50-5.46 (1H, m), 3.64-3.56 (2H, m), 3.24 (1H, d, *J* = 18.6 Hz), 3.08 (1H, ddd, *J* = 10.8, 9.0, 5.0 Hz), 2.97 (1H, ddd, *J*

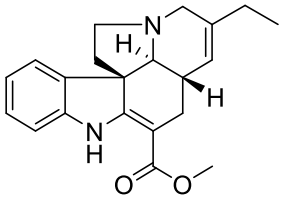
(3) Cheng, B.; Sunderhaus, J. D.; Martin, S. F. *Org. Lett.* **2010**, *12*, 3622.

= 13.3, 3.7, 2.4 Hz), 2.68 (1H, ddd, *J* = 13.2, 13.2, 5.3 Hz), 2.46 (1H, ddd, *J* = 13.3, 10.9, 5.1 Hz), 2.41-2.34 (1H, m), 2.32 (1H, d, *J* = 9.4 Hz), 2.15-2.07 (1H, m), 1.97-1.88 (3H, m), 1.24-1.19 (1H, m), 1.01 (3H, t, *J* = 7.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 186.6, 153.9, 146.3, 140.3, 127.5, 125.4, 123.3, 121.1, 119.8, 72.2, 63.2, 51.5, 51.5, 31.6, 31.2, 31.1, 30.8, 27.4, 12.5.

HRMS-ESI (*m/z*) calcd for $C_{19}H_{23}N_2$ $[M+H]^+$: 279.1861; found 279.1862.

Optical rotation: $[\alpha]^{20}_D$ –17.4 (*c* 0.98, CH_2Cl_2).



(–)-14-epi-Pseudotabersonine 1

Pentacycle (*S*,*S*,*R*)-**13** (20 mg, 0.07 mmol) was dried by triple vacuum evaporations of a solution in anhydrous benzene (3x3 mL), dissolved in THF (1 mL) and cooled to -78 °C (acetone/dry ice). LDA (0.7 M solution in THF/hexane, 0.3 mL 0.21 mmol, 3 equiv) was added dropwise. Orange mixture was gradually warmed to -20 °C and stirred for 30 min. whereupon it was cooled back to -78 °C, and methylcyanoformate (24 mg, 22 µL, 0.28 mmol, 4 equiv) was added. Orange mixture was stirred for 30 min at -78 °C and quenched with aqueous saturated NaCl solution (1 mL). Layers were separated, aqueous layer was extracted with EtOAc (3×2 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 1% EtOAc in hexane to 5% EtOAc in hexane to afford **1** as a white foam (11 mg, 46% yield).

TLC: R_f 0.17 (95:5 Hex/EA).

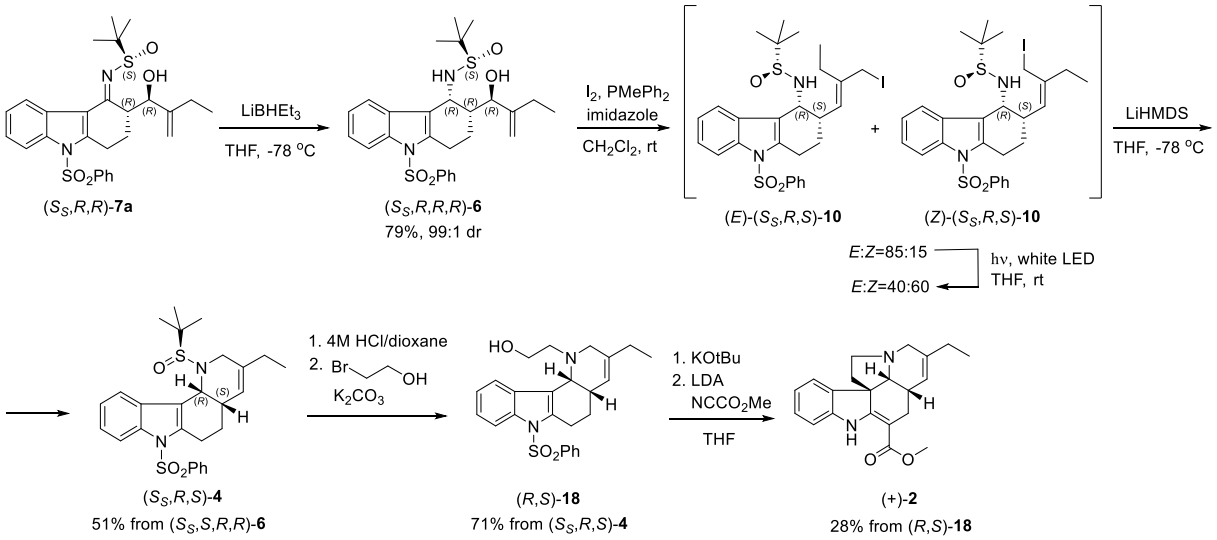
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.07 (1H, s), 7.52 (1H, d, *J* = 7.4 Hz), 7.12-7.03 (1H, m), 6.83 (1H, dd, *J* = 7.5, 7.5 Hz), 6.75 (1H, d, *J* = 7.7 Hz), 5.51 (1H, s), 3.75 (3H, s), 3.77-7.66 (1H, m), 3.39 (1H, ddd, *J* = 9.0, 9.0, 5.5 Hz), 3.20 (1H, ddd, *J* = 18.6, 2.3, 2.3 Hz), 2.92 (1H, ddd, *J* = 10.9, 8.9, 4.6 Hz), 2.81 (1H, d, *J* = 9.8 Hz), 2.72 (1H, dd, *J* = 15.5, 5.4 Hz), 2.59-2.48 (2H, m), 2.06 (1H, dd, *J* = 15.6, 12.7 Hz), 2.02-1.94 (2H, m), 1.90 (1H, ddd, *J* = 13.2, 8.9, 4.5 Hz), 1.05 (3H, t, *J* = 7.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 169.3, 165.4, 144.3, 139.1, 138.3, 127.5, 123.2, 121.3, 120.9, 109.3, 95.1, 63.5, 55.2, 51.6, 51.2, 49.9, 40.8, 29.5, 28.2, 27.4, 12.4.

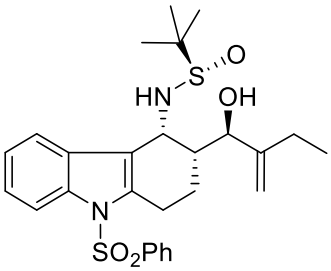
HRMS-ESI (*m/z*) calcd for $C_{21}H_{24}N_2O_2$ $[M+H]^+$: 337.1916; found, 337.1929.

Optical rotation: $[\alpha]^{20}_{D}$ -581.1 (*c* 0.70, CH_2Cl_2).

Synthesis of (+)-pseudotabersonine 2 from imine (*S*$_S$,*R*,*R*)-7a



Scheme S2. Synthesis of (+)-pseudotabersonine **2** from imine (*S*$_S$,*R*,*R*)-**7a.**



(S)-N-((3R,4R)-3-((R)-1-Hydroxy-2-methylenebutyl)-9-(phenylsulfonyl)-2,3,4,9-tetrahydro-1H-carbazol-4-yl)-2-methylpropane-2-sulfinamide ((S$_S$,R,R,R)-6)

Imine (*S*$_S$,*R*,*R*)-**7a** (1.0 .g, 1.95 mmol) was dissolved in THF (50 mL), cooled to -78 °C and $LiBHEt_3$ (1.7M in THF, 5.62 mL, 9.56 mmol, 7 equiv) was added dropwise. After stirring at -78 °C for 3 h colorless mixture was gradually warmed to 0 °C and MeOH (5 mL) was added (***Warning!*** vigorous gas evolution). Mixture was stirred for 10 min and quenched with aqueous saturated NH_4Cl solution (30 mL). Layers were separated, aqueous layer was extracted with EtOAc (2×30 mL). Combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 40% EtOAc in hexane to 70% EtOAc in hexane to afford (*S*$_S$,*R*,*R*,*R*)-**6** as a white foam (794 mg, 79% yield).

TLC: R_f 0.19 (1:1 Hex/EA).

IR (film, cm^{-1}) 3357, 2962, 1448, 1371, 1173, 1042.

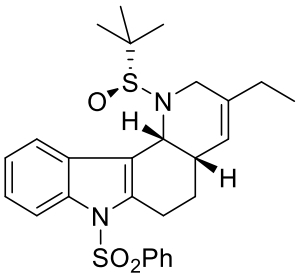
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.14 (1H, d, *J* = 8.2 Hz), 7.79- 7.73 (2H, m), 7.59-7.52 (1H, m), 7.51(1H, d, *J* = 7.5 Hz), 7.47-7.39 (2H, m), 7.29 (1H, ddd, *J* = 8.4, 7.2, 1.5 Hz), 7.23

(1H, ddd, *J* = 7.5, 7.5, 1.1 Hz), 5.01 (1H, s), 4.99-4.93 (2H, m), 4.15-4.08 (1H, m), 4.05 (1H, d, *J* = 5.9 Hz), 3.74 (1H, d, *J* = 9.2 Hz), 3.27 (1H, ddd, *J* = 18.2, 5.7, 2.2 Hz), 2.76 (1H, ddd, *J* = 17.9, 11.0, 6.4 Hz), 2.31-2.18 (1H, m), 2.10-1.94 (2H, m), 1.84-1.76 (1H, m), 1.53-1.40 (1H, m), 1.16 (9H, s), 1.10 (3H, t, *J* = 7.4 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 151.2, 139.2, 136.8, 136.7, 133.9, 129.5, 128.7, 126.5, 124.6, 123.5, 120.1, 119.2, 114.5, 111.5, 75.6, 56.8, 50.3, 42.1, 24.5, 23.2, 23.1, 21.3, 12.3.

HRMS-ESI (*m/z*) calcd for $C_{27}H_{34}N_2O_4S_2Na$ $[M + Na]^+$: 537.1858; found, 537.1860.

Optical rotation: $[\alpha]^{20}_D$ –20.8 (*c* 0.97, CH_2Cl_2).



(4aS,11cR)-1-((S)-tert-Butylsulfinyl)-3-ethyl-7-(phenylsulfonyl)-2,4a,5,6,7,11c-hexahydro-1H-pyrido[3,2-c]carbazole ((S$_S$,R,S)-4)

Aminoalcohol (*S*$_S$,*R*,*R*,*R*)-**6** (150 mg, 0.29 mmol) and imidazole (119 mg, 1.75 mmol, 6 equiv) were dissolved in CH_2Cl_2 (7 mL) and stirred for 5 min. In separate vial to a solution of iodine (222 mg, 0.87 mmol, 3 equiv) in CH_2Cl_2 (3 mL) was added methyldiphenylphosphine (175 mg, 0.87 mmol, 3 equiv). A yellow solution of the formed phosphonium iodide was added dropwise to the stirred solution of aminoalcohol (*S*$_S$,*R*,*R*,*R*)-**6** and imidazole. After 10 min of stirring at room temperature hexane (2 mL) was added and resulting suspension was filtered through a short pad of silica (2 g). The silica pad was washed with 4:1 CH_2Cl_2/hexane mixture (5 mL), filtrates were combined and evaporated under reduced pressure. Yellow foamy residue (~220 mg) was dissolved in THF (10 mL) and irradiated with white LED lamp (30W, 2000 lm) for 1h (NOTE: mixture can heat up to 50 °C). Yellow mixture was cooled to -78 °C and 1M LiHMDS (1 M solution in THF, 0.29 mL, 0.29 mmol, 1 equiv) was added dropwise. Stirring for 10 min was followed by addition of TFA (23 μL, 0.29 mmol, 1 equiv) whereupon the yellow mixture was allowed to warm to room temperature. A sequence comprising irradiation with white LED, treatment with LiHMDS and addition of TFA was repeated two times to achieve complete conversion of starting aminoalcohol (*S*$_S$,*R*,*R*,*R*)-**6** (NOTE: mixture should not be basic upon irradiation to avoid the formation of byproducts). After addition of the third LiHMDS portion and stirring for 10 min, the yellow-brown reaction mixture was quenched with aqueous saturated NH_4Cl solution (10 mL). Layers were separated, aqueous layer was extracted with EtOAc (2×10 mL). Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by reverse phase flash column chromatography using

gradient elution from 50% MeCN in water to 75% MeCN in water to afford (*S*S,*R*,*S*)-**4** as yellowish foam (73 mg, 51% yield).

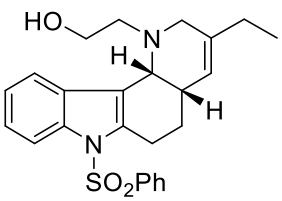
IR (film, cm^{-1}) 2964, 1453, 1372, 1173, 1024.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.20-8.13 (1H, m), 7.86 (1H, d, *J* = 7.0 Hz), 7.73-7.64 (2H, m), 7.53-7.46 (1H, m), 7.40-7.33 (2H, m), 7.30-7.22 (2H, m, overlapped with CHCl3), 5.33 (1H, s), 4.55 (1H, s), 3.51 (1H, d, *J* = 17.4 Hz), 3.11-3.00 (1H, m), 3.00-2.74 (3H, m), 2.12-1.99 (1H, m), 1.93-1.80 (2H, m), 1.80-1.65 (1H, m), 1.18 (9H, s), 0.89 (3H, t, *J* = 7.4 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 139.6, 139.1, 137.7, 136.4, 133.7, 130.0, 129.3, 129.28, 126.3, 126.25, 124.3, 123.9, 119.9, 119.7, 117.0, 114.5, 58.7, 55.1, 42.7, 33.5, 27.1, 26.4, 23.6 (($\underline{C}H_3)_3$–C), 22.1, 12.0.

HRMS-ESI (*m/z*) calcd for $C_{27}H_{33}N_2O_3S_2$ $[M+H]^+$: 497.1933; found, 497.1931.

Optical rotation: $[\alpha]^{20}_D$ –14.2 (*c* 0.71, CH_2Cl_2).



2-((4aS,11cR)-3-Ethyl-7-(phenylsulfonyl)-2,4a,5,6,7,11c-hexahydro-1H-pyrido[3,2-c]carbazol-1-yl)ethan-1-ol (R,S)-18))

To a stirred solution of tetracycle (*S*S,*R*,*S*)-**4** (150 mg, 0.3 mmol) in THF (3 mL) was added MeOH (0.3 mL) and HCl (4M in doxane, 0.3 mL, 1.2 mmol, 4 equiv). Yellow mxture was stirred for 10 min at room temperature and evaporated under reduced pressure. The yellow oily residue was transferred to a 5mL glass pressure tube, and K_2CO_3 (250 mg, 1.8 mmol, 6 equiv), 2-bromoethanol (107 µL, 1.5 mmol, 5 equiv) and EtOH (3 mL) were added. The pressure vial was sealed and the resulting yellow suspension was stirred at 80 °C for 24 h. After cooling to room temperature and filtration through a pad of Celite®, volatiles were removed under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 20% EtOAc in hexane to 50% EtOAc in hexane to afford (*R*,*S*)-**18** as colorless oil (94 mg, 71% yield).

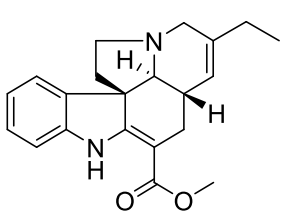
TLC: R_f 0.34 (1:1 Hex/EA).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.18-8.11 (1H, m), 7.72-7.66 (2H, m), 7.63 (1H, d, *J* = 7.6 Hz), 7.52-7.45 (1H, m), 7.40-7.34 (2H, m), 7.30-7.24 (1H, m, overlapped with CDCl3), 7.24-7.19 (1H, m), 5.36 (1H, s), 4.03 (1H, d, *J* = 4.8 Hz), 3.65-3.67 (1H, m), 3.56-3.48 (1H, m), 3.02-

2.94 (2H, m), 2.92-2.82 (2H, m), 2.82-2.65 (3H, m), 2.60 (1H, s), 2.07-1.95 (1H, m), 1.89-1.71 (3H, m), 0.92 (3H, t, J = 7.5 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 139.0, 138.2, 136.8, 133.7, 130.3, 129.3, 126.3, 124.2, 123.8, 120.4, 119.85, 118.5, 114.7, 110.25, 77.4, 59.0, 55.9, 53.9, 29.8, 27.7, 26.8, 22.5, 12.1; HRMS-ESI (*m/z*) calcd for $C_{25}H_{29}N_2O_3S$ $[M+H]^+$: 437.1899; found, 437.1902.

Optical rotation: $[\alpha]^{20}_D$ –51.1 (*c* 0.63, CH_2Cl_2).



*(+)-Pseudotabersonine (**2**)*

A solution of aminoalcohol (*R,S*)-**18** (87 mg, 0.20 mmol) in THF (2 mL) was cooled to 0 °C (crushed ice), KOtBu (1.6 M in THF, 0.37 mL, 0.60 mol, 3 equiv) was added and the orange mixture was stirred at 0 °C for 30 min. Aqueous saturated NaCl (1 mL) and Et_2O (2 mL) were added and layers were separated. Aqueous layer was extracted with CH_2Cl_2 (3x2 mL). Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was dissolved in a 1:1 EtOAc/hexane mixture (1 mL) and filtered through a short pad of silica. Filtrate was concentrated under reduced pressure. The yellow oily residue was dried by triple vacuum evaporations of a solution in anhydrous benzene (3x3 mL), then it was dissolved in THF (2 mL) and cooled to -78 °C. LDA (0.7 M in THF/hexane, 0.86 mL 0.6 mmol, 3 equiv) was added dropwise. Orange mixture gradually warmed to -20 °C and stirred for 30 min, whereupon the reaction was cooled back to -78 °C followed by addition of methylcyanoformate (68 mg, 63 µL, 0.8 mmol, 4 equiv). After stirring for 30 min at -78 °C, aqueous saturated NaCl (1 mL) was added and layers were separated. Aqueous layer was extracted with EtOAc (3×3 mL), combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 1% EtOAc in hexanes to 15% EtOAc in hexane to afford **2** as yellowish foam (19 mg, 28% yield).

TLC: R_f 0.27 (10:1 Hex/EA).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.98 (1H, s), 7.30 (1H, d, *J* = 7.4 Hz), 7.15 (1H, ddd, *J* = 7.7, 7.7, 1.2 Hz), 6.88 (1H, ddd, *J* = 7.5, 7.5, 1.0 Hz), 6.81 (1H, d, *J* = 7.7 Hz), 5.53-5.49 (1H, m), 3.77 (3H, s), 3.36 (1H, d, *J* = 15.6 Hz), 3.27 (1H, d, *J* = 15.7 Hz), 3.07-2.99 (2H, m), 2.84-

2.76 (1H, m), 2.68 (1H, ddd, *J* = 15.1, 3.8, 1.3 Hz), 2.15 (1H, dd, *J* = 14.8, 11.4 Hz), 2.10-2.01 (3H, m), 1.90 (1H, ddd, *J* = 11.8, 5.2, 2.1 Hz), 1.77 (1H, brs), 1.06 (3H, t, *J* = 7.5 Hz).

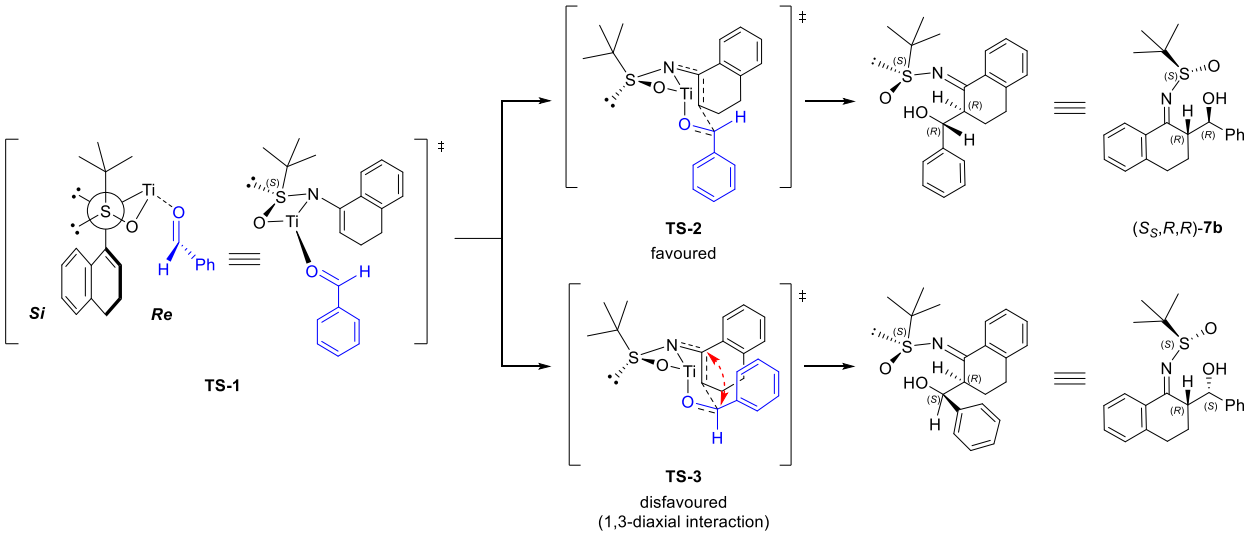
^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 168.8, 166.0, 143.7, 139.5, 138.2, 127.8, 122.0, 121.5, 120.7, 109.3, 95.6, 65.3, 55.6, 53.4, 51.1, 44.6, 37.0, 28.0, 26.5, 12.6.

HRMS-ESI (*m/z*) calcd for $C_{21}H_{24}N_2O_2$ $[M+H]^+$: 337.1916; found, 337.1919.

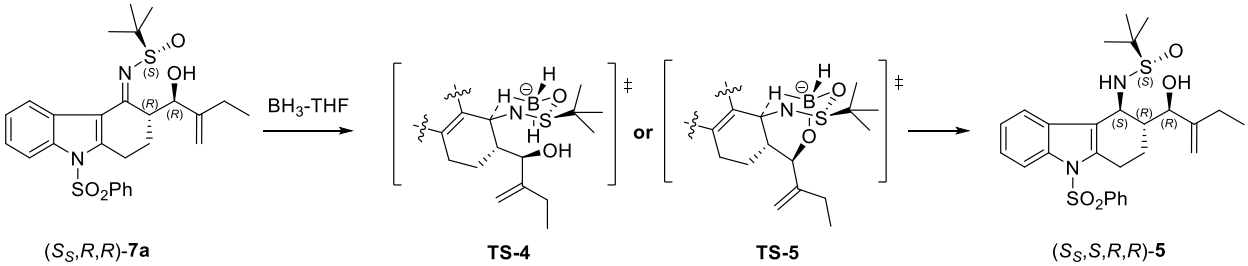
Optical rotation: $[\alpha]^{20}_D$ +297.1 (*c* 0.40, MeOH), lit.[4] $[\alpha]_D$ 320 (MeOH).

(4) Zeches, M.; Debray, M.-M.; Ledouble, G.; Le Men-Olivier, L.; Le Men, J. *Phytochemistry* **1975**, *14*, 1122.

Proposed stereoinduction models for the aldol-type reaction and for the reduction of ketimine (*S*$_S$,*R*,*R*)–7 with borane

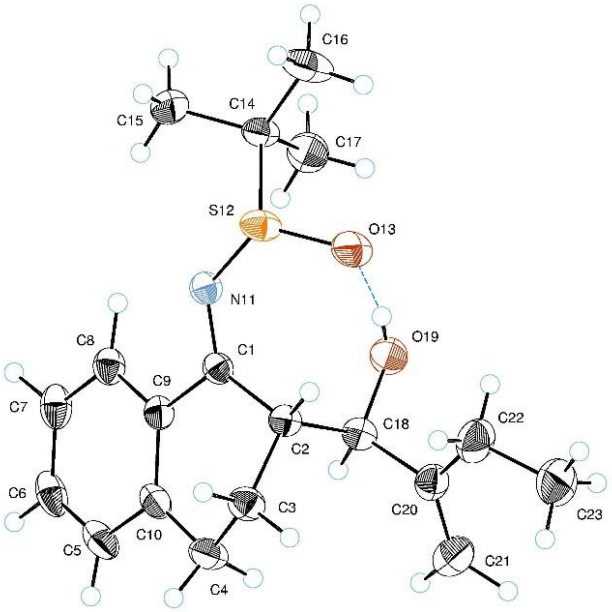


Scheme S3. Proposed mechanism of the aldol-type reaction.



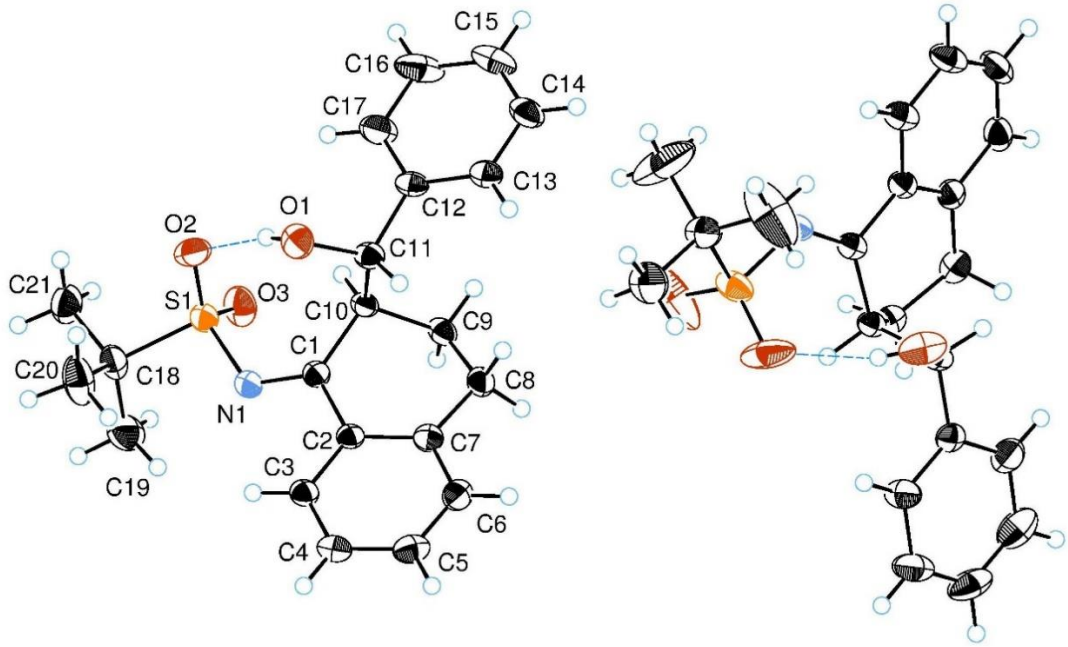
Scheme S4. Transition states for diastereoselective reduction of ketimine (*S*$_S$,*R*,*R*)–**7** with BH$_3$–THF.

X-ray structure, crystal data and structure refinement for (*S*S,*R*,*R*)-7g



Identification code	Kazak
Empirical formula	C19 H27 N O2 S
Formula weight	333.48
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 7.4989(2) A alpha = 90 deg. b = 11.9755(3) A beta = 90 deg. c = 20.6566(6) A gamma = 90 deg.
Volume	1855.03(9) A^3
Z	4
Density (calculated)	1.194 Mg/m^3
Absorption coefficient	0.184 mm^-1
F(000)	720
Crystal size	0.27 x 0.22 x 0.21 mm
Two-theta max. for data	60.0 deg.
Index ranges	-10<=h<=10, -16<=k<=16, -28<=l<=29
Reflections collected	5347
Independent reflections	5343 [R(int) = 0.0204]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5343 / 0 / 212
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0608, wR2 = 0.1081
R indices (all data)	R1 = 0.0979, wR2 = 0.1233
Absolute structure parameter	0.06(9)
Largest diff. peak and hole	0.239 and -0.245 e.A^-3

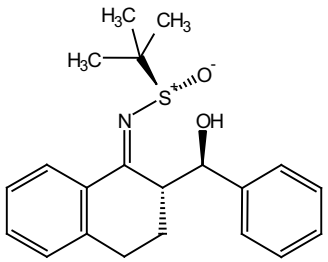
X-ray structure, crystal data and structure refinement for (*E*)-16



Identification code	MPS-858
Empirical formula	C21 H25 N1 O3 S1
Formula weight	371.48
Temperature	190(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 12.5138(3) A alpha = 90 deg. b = 17.6266(4) A beta = 117.4430(10) deg. c = 19.7375(4) A gamma = 90 deg.
Volume	3863.70(15) A^3
Z, Calculated density	8, 1.277 Mg/m^3
Absorption coefficient	0.188 mm^-1
F(000)	1584
Crystal size	0.45 x 0.42 x 0.25 mm
Two-theta max. for data	55.0 deg.
Limiting indices	-16<=h<=16, -22<=k<=20, -25<=l<=25
Reflections collected / unique	14864 / 8687 [R(int) = 0.0380]
Completeness to theta = 27.5	98.50%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8687 / 0 / 477
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1133
R indices (all data)	R1 = 0.0946, wR2 = 0.1297
Extinction coefficient	0
Largest diff. peak and hole	0.445 and -0.420 e.A^-3

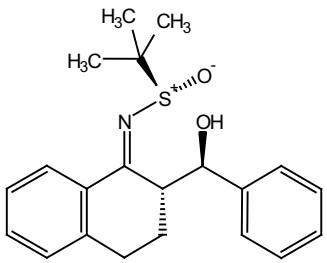
Spectroscopic Data

OSPT_MKW-III-51_20Feb14_PROTON_cdcl3_01



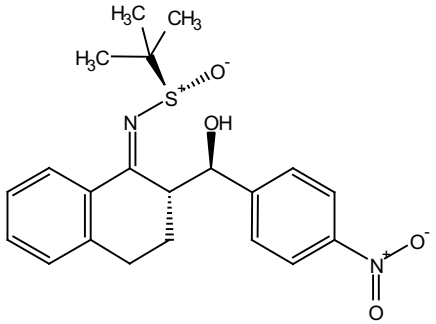
(S_S,*R*,*R*)-**7b**

OSPT_MKW-III-51_20Feb14_CARBON_cdcl3_01



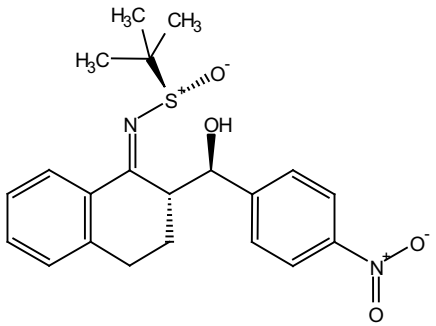
(S_S,*R*,*R*)-**7b**

OSPT_MPS-722_FN_31Oct16_PROTON_cdcl3_01



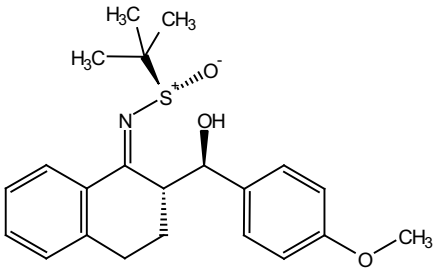
(S_S,*R*,*R*)-**7c**

OSPT_MPS-722_FN_31Oct16_CARBON_cdcl3_01



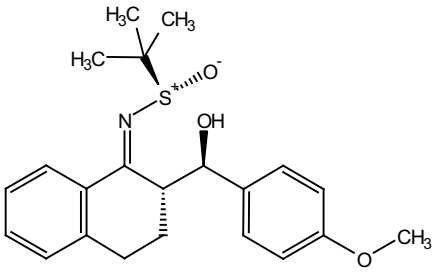
(S_S,*R*,*R*)-**7c**

OSPT_MPP-723_FF_16Nov16_PROTON_cdcl3_01



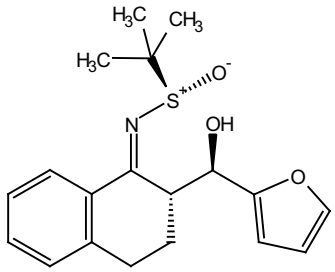
(*S*$_S$,*R*,*R*)-**7d**

OSPT_MPP-723_FF_16Nov16_CARBON_cdcl3_01



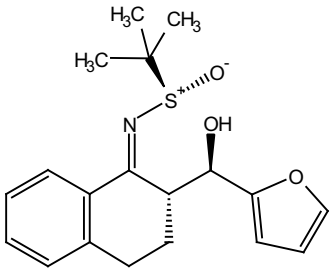
(*S*$_S$,*R*,*R*)-**7d**

OSPT-MPS-746-FF_16Nov16_PROTON_cdcl3_01



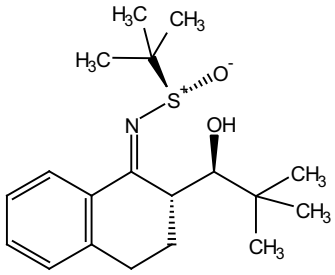
(*S*$_S$,*R*,*R*)-**7e**

OSPT-MPS-746-FF_16Nov16_CARBON_cdcl3_01



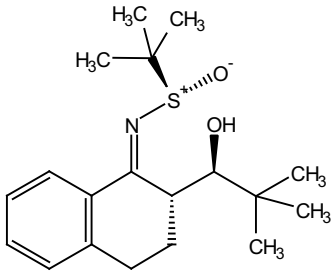
(*S*$_S$,*R*,*R*)-**7e**

OSPT-MPS-736-EV_23Jan2015_PROTON_cdcl3_01



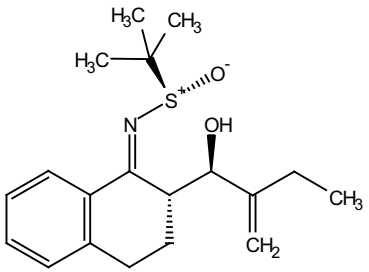
(S_S,*R*,*R*)-**7f**

OSPT-MPS-736-EV_23Jan2015_CARBON_cdcl3_01



(*S*$_S$,*R*,*R*)-**7f**

OSPT_MKW-III-152_26May15_PROTON_cdcl3_01

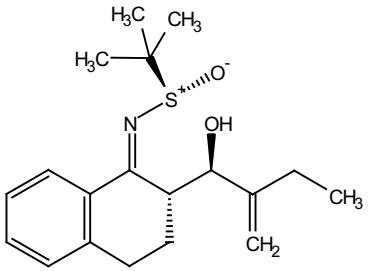


(*S*$_S$,*R*,*R*)-**7g**

f1 (ppm)

OSPT_MKW-III-152_26May15_CARBON_cdcl3_01

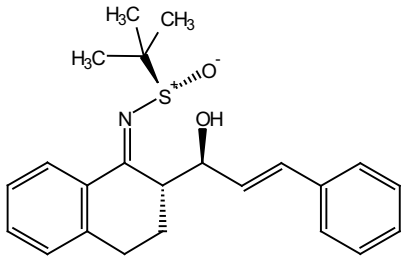
177.78
151.36
140.43
132.51
132.19
129.32
128.31
126.67
111.29
77.16 Chloroform-d
73.82
59.20
43.62
24.68
23.93
23.08
21.03
11.92



(*S*$_S$,*R*,*R*)-**7g**

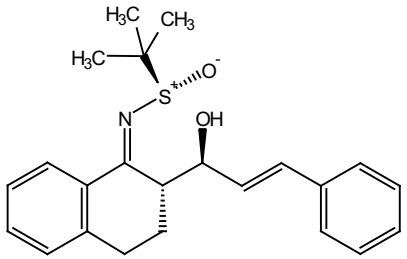
f1 (ppm)

OSPT_MPS-726_FF



(S_S,*R*,*R*)-**7h**

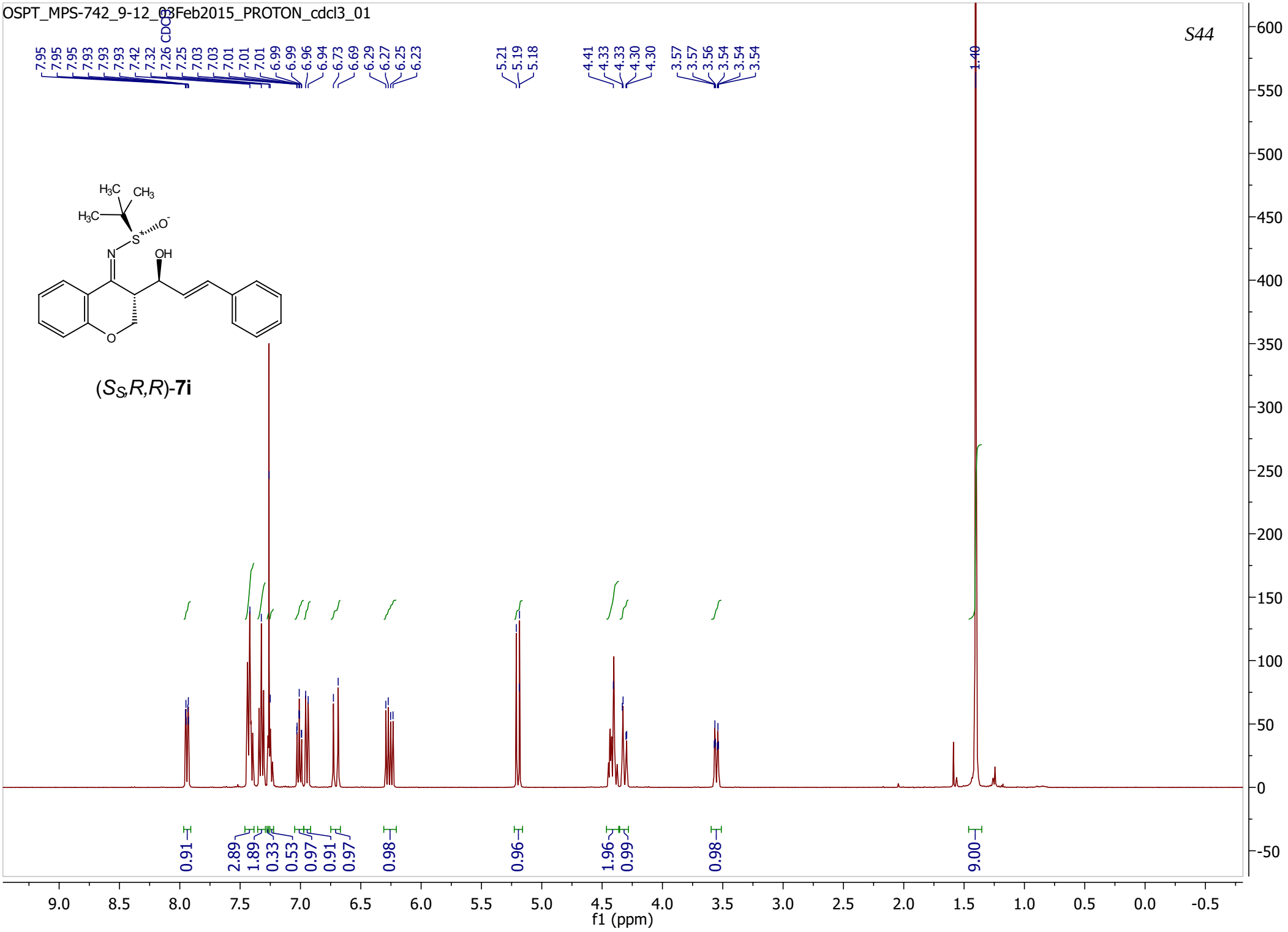
OSPT_MPS-726_FF



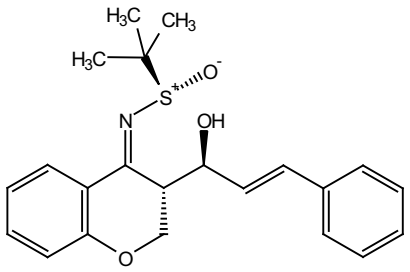
(*S*$_S$,*R*,*R*)-**7h**

177.5
140.4
136.8
132.5
132.3
131.9
131.2
129.4
128.7
128.3
127.8
126.8
126.7
77.2 CDCl3
70.0
59.1
46.9
24.7
24.2
23.0

f1 (ppm)

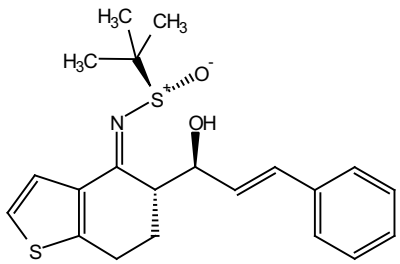

OSPT_MPS-742_9-12_03Feb2015_PROTON_cdcl3_01
7.95 7.95 7.95 7.93 7.93 7.93 7.42 7.32 7.26 CDCl3 7.25 7.03 7.03 7.01 7.01 7.01 6.99 6.99 6.96 6.94 6.73 6.69 6.29 6.27 6.25 6.23
5.21 5.19 5.18
4.41 4.33 4.33 4.30 4.30
3.57 3.57 3.56 3.54 3.54 3.54
1.40
H3C CH3
H3C
S
O
N
OH
O
(SS,R,R)-7i
0.91 2.89 1.89 0.33 0.53 0.97 0.91 0.97 0.98 0.96 1.96 0.99 0.98 9.00
f1 (ppm)

OSPT_MPS-742_9-12_03Feb2015_CARBON_cdcl3_01



(S_S,*R*,*R*)-**7i**

OSPT_MPP-859_prod.10.fid

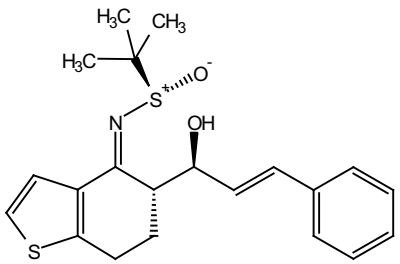


(S_S,*R*,*R*)-**7j**

water

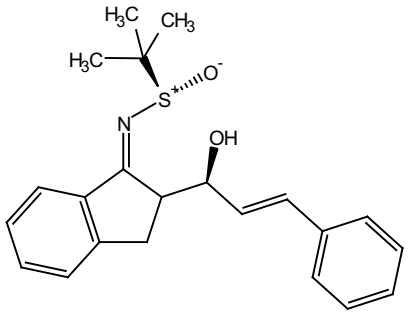
f1 (ppm)

OSPT_MPS-859_prod_10May17_CARBON_cdcl3_01



(*S*$_S$,*R*,*R*)-**7j**

OSPT_MPS-739_16Nov16_PROTON_cdcl3_01



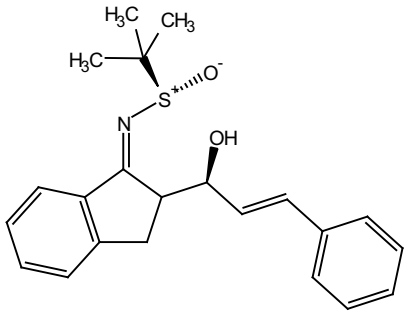
(*S*$_S$,*R*,*R*)-**7k**

water

f1 (ppm)

OSPT_MPS-739_16Nov16_CARBON_cdcl3_01

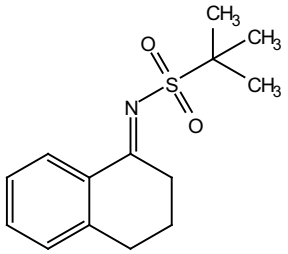
181.4
147.4
139.0
136.8
133.2
131.8
131.7
128.6
127.7
126.7
126.1
124.1
77.2 CDCl3
74.3
59.1
52.2
34.7
23.3



(S_S,*R*,*R*)-**7k**

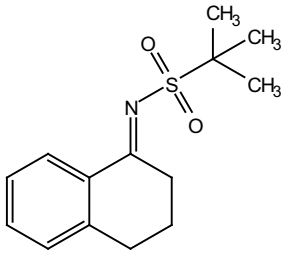
f1 (ppm)

OSPT-MPS-861_15Jun17_PROTON_cdcl3_01



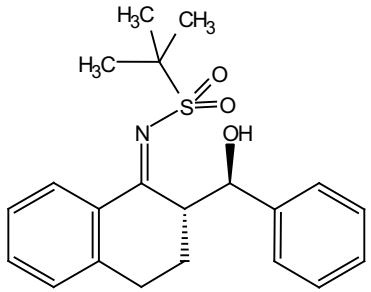
(*E*)-**15**

OSPT-MPS-861_15Jun17_CARBON_cdcl3_01



(*E*)-**15**

OSPT-MPS-858-22-24_06Jun17_PROTON_cdcl3_01



(*E*)-**16**

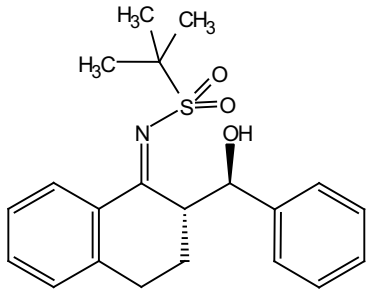
1.4-dioxane 0.6%

water

f1 (ppm)

OSPT-MPS-858-22-24_06Jun17_CARBON_cdcl3_01

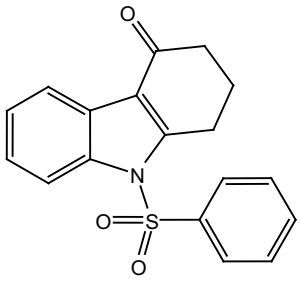
184.1
142.7
142.0
133.9
131.8
129.5
128.9
128.4
128.2
127.0
126.6
77.2 CDCl3
74.0
59.8
49.1
24.2



(*E*)-**16**

f1 (ppm)

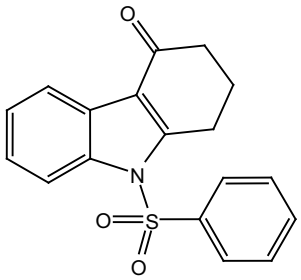
OSPT_MKW-III-65_27Feb14_PROTON_cdcl3_01



17

OSPT_MKW-III-65_27Feb14_CARBON_cdcl3_01

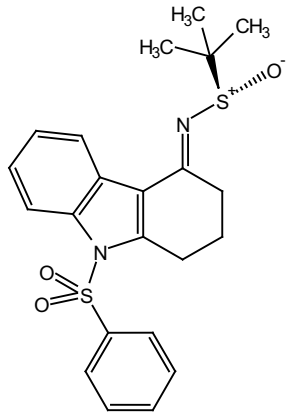
195.14
150.99
138.64
136.10
134.60
129.78
126.67
125.90
125.56
125.15
122.04
118.21
113.94
77.16 Chloroform-d
37.98
24.65
23.33



17

f1 (ppm)

OSPT_MKW-III-67_15Dec15_PROTON_cdcl3_01



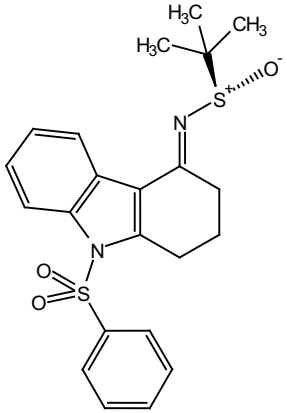
(*E*,*S*$_S$)-**8a**

EtOAc 0.7%

f1 (ppm)

OSPT_MKW-III-67_16Dec15_CARBON_cdcl3_01

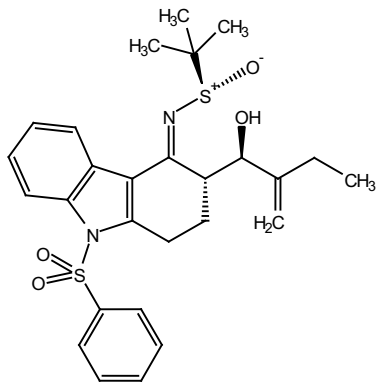
175.28
147.44
138.70
136.43
134.53
129.76
126.62
126.35
125.46
124.91
122.83
117.92
114.08
77.16 Chloroform-d
56.58
31.06
24.46
23.01
22.56



(*E*,*S*$_S$)-**8a**

f1 (ppm)

OSPT_MKW-IV-53_12Mar2015_PROTON_cdcl3_01



(*S*S,*R*,*R*)-**7a**

Chloroform

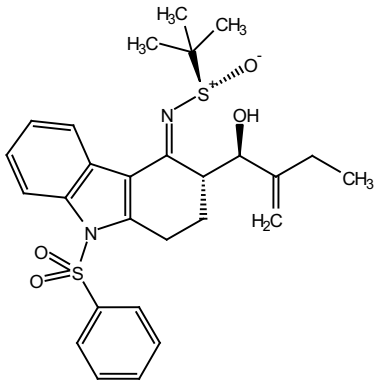
water

EtOAc 1%

f1 (ppm)

OSPT_MKW-IV-53_12Mar2015_CARBON_cdcl3_01

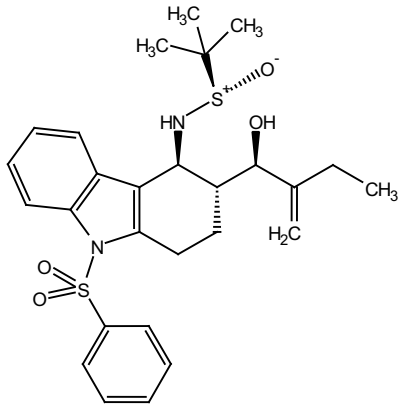
175.45
151.71
145.17
138.66
136.71
134.63
129.81
126.55
126.49
125.57
124.80
122.13
116.91
114.17
111.31
77.16 Chloroform-d
74.98
58.51
43.44
25.24
22.97
21.00
20.67
11.89



(S_S,*R*,*R*)-**7a**

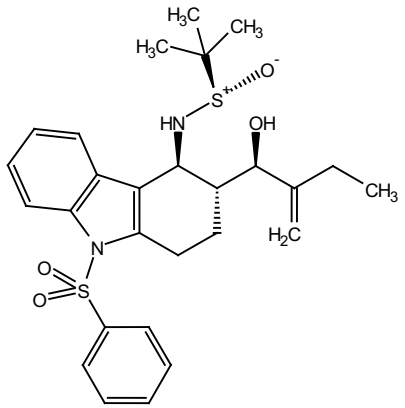
f1 (ppm)

OSPT_MKW_IV_42_17May15_PROTON_cdcl3_01



(*S*$_S$,*S*,*R*,*R*)-**5**

OSPT_MKW_IV_42_17May15_CARBON_cdcl3_01

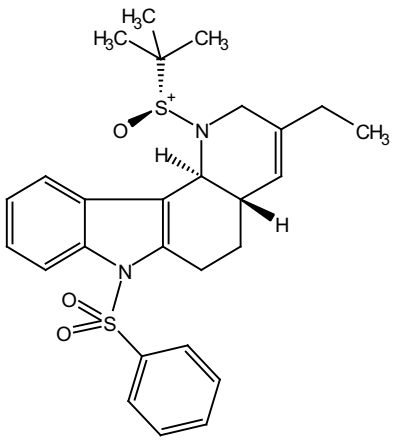


(*S*$_S$,*S*,*R*,*R*)-**5**

152.14
138.91
138.28
136.91
133.83
129.40
128.88
126.45
124.62
123.79
119.98
117.38
114.54
111.59
78.93
77.16 Chloroform-d
55.61
51.35
43.17
22.77
22.65
22.45
22.05
12.07

f1 (ppm)

OSPT_MKW_IV_75_17May15_PROTON_cdcl3_01

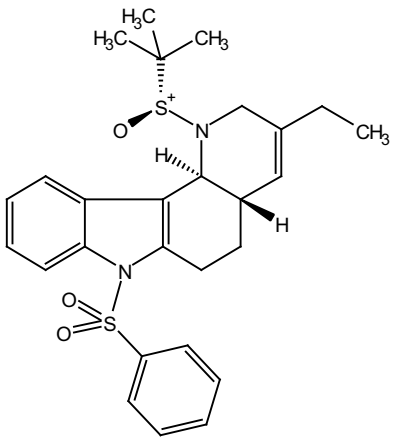


(*S*$_S$,*S*,*S*)-**3**

EtOAc 2%

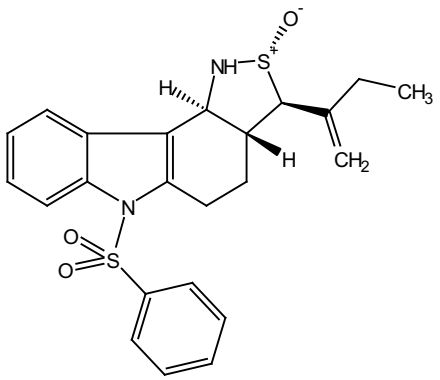
f1 (ppm)

OSPT_MKW_IV_75_17May15_CARBON_cdcl3_01



(*S*$_S$,*S*,*S*)-**3**

OSPT_MKW_IV_75_bp_18May15_PROTON_cdcl3_01

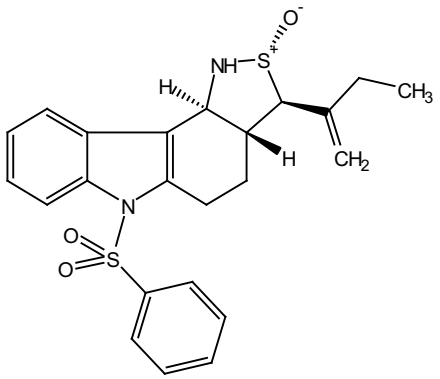


(S_R,*R*,*R*,*S*)-**14**

f1 (ppm)

OSPT_MKW_IV_75_bp_18May15_CARBON_cdcl3_01

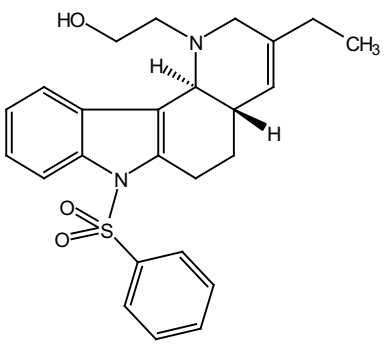
143.29
139.08
136.39
135.79
134.10
129.60
127.40
126.53
124.77
123.95
119.85
117.78
114.50
113.28
87.14
77.16 Chloroform-d
61.64
51.57
28.78
25.56
23.52
12.27



(S_R,*R*,*R*,*S*)-**14**

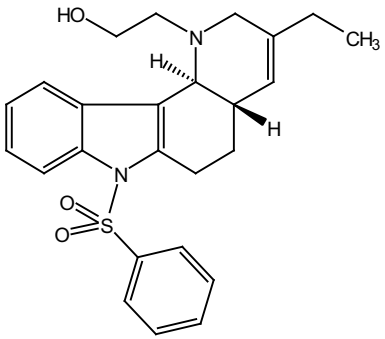
f1 (ppm)

OSPT_MKW-IV-80_22May15_PROTON_cdcl3_01



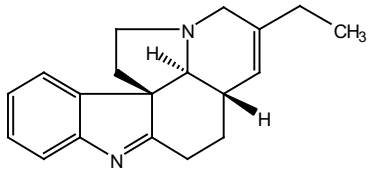
(*S*,*S*)-**11**

OSPT_MKW-IV-80_24May15_CARBON_cdcl3_01



(*S*,*S*)-**11**

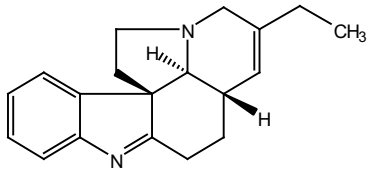
OSPT-MKW-IV-100_26Aug15_PROTON_cdcl3_01



(*S*,*S*,R)-**13**

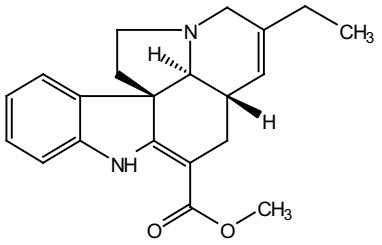
f1 (ppm)

OSPT-MKW-IV-100_26Aug15_CARBON_cdcl3_01



(*S*,*S*,R)-**13**

OSPT-MKW-IV-156_20Jan16_PROTON_cdcl3_01

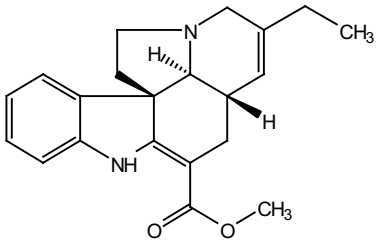


(-)-14-*epi*-Pseudotabersonine **1**

f1 (ppm)

OSPT_MKW-IV-156_21Jan16_CARBON_cdcl3_01

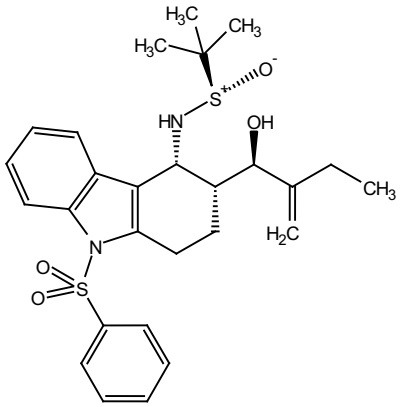
169.27
165.41
144.29
139.05
138.28
127.45
123.23
121.27
120.93
109.30
95.08
77.16 Chloroform-d
63.49
55.16
51.64
51.19
49.91
40.84
29.47
28.24
27.44
12.42



(-)-14-*epi*-Pseudotabersonine **1**

f1 (ppm)

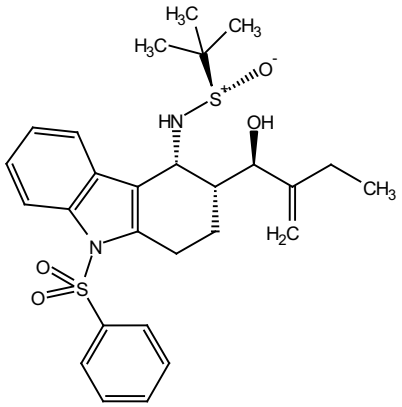
OSPT_MKW-IV-140_pr_12Dec15_PROTON_cdcl3_01



(*S*$_S$,*R*,*R*,*R*)-**6**

f1 (ppm)

OSPT_MKW-IV-140_pr_12Dec15_CARBON_cdcl3_01

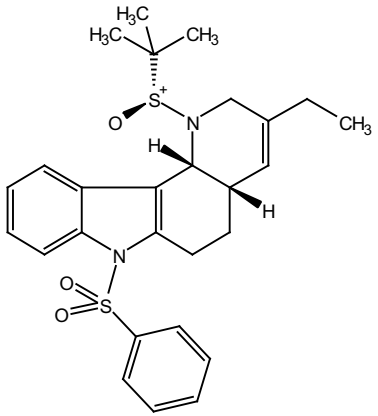


(S_S,*R*,*R*,*R*)-**6**

151.20
139.15
136.78
136.73
133.92
129.46
128.73
126.49
124.61
123.54
120.08
119.24
114.46
111.50
77.16 Chloroform-d
75.57
56.76
50.31
42.09
24.51
23.24
23.08
21.27
12.31

f1 (ppm)

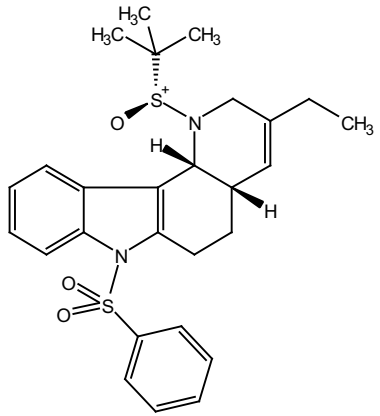
OSPT-MKW-9_22Sep16_PROTON_cdcl3_01-1



(*S*$_S$,*R*,*S*)-**4**

f1 (ppm)

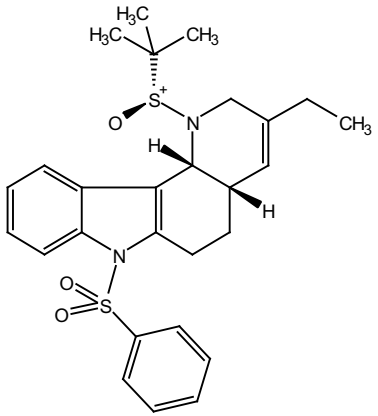
OSPT-MKW-9_22Sep16_CARBON_cdcl3_01



(S_S,*R*,*S*)-**4**

f1 (ppm)

OSPT-MKW-9_22Sep16_CARBON_cdcl3_01

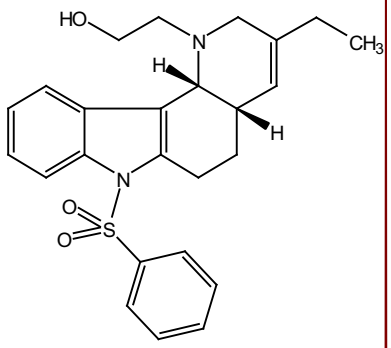


(S_S,*R*,*S*)-**4**

Exponential (3.50 Hz) and Gaussian (3.50 GB [Hz]) multiplication applied

f1 (ppm)

OSPT_MKW-14_30Sep16_PROTON_cdcl3_01

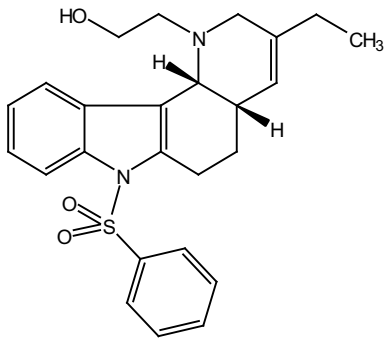


(*R*,*S*)-**18**

Grease

f1 (ppm)

OSPT_MKW-14_30Sep16_CARBON_cdcl3_01

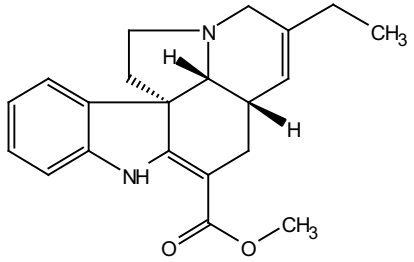


(*R*,*S*)-**18**

139.01
138.16
136.81
133.66
130.27
129.26
126.27
124.23
123.77
120.39
119.75
118.50
114.72
110.15
77.36
77.16 Chloroform-d
58.96
55.94
53.85
29.83
27.68
26.79
22.45
12.11

f1 (ppm)

OSPT-MKW-74-ext_07Jun17_PROTON_cdcl3_01

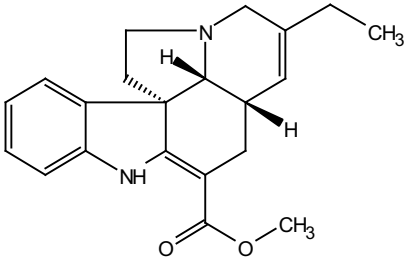


(+)-Pseudotabersonine **2**

f1 (ppm)

OSPT-MKW-74-ext_07Jun17_CARBON_cdcl3_01

168.83
166.04
143.70
139.45
138.15
127.82
122.00
121.53
120.73
109.29
95.60
77.16-CDCl3
65.33
55.61
53.38
51.13
44.55
36.97
27.97
26.50
12.61



(+)-Pseudotabersonine **2**

f1 (ppm)