

Enantioselective Total Synthesis of (+)-Lysergol: A Formal *anti*-Carbopalladation/Heck Cascade as Key Step

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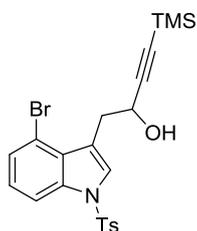
General Experimental

All solvents were distilled before use unless otherwise stated. Air and moisture sensitive reactions were carried out in oven-dried or flame-dried glassware, septum-capped under atmospheric pressure of argon. Commercially available compounds were used without further purification unless otherwise stated.

Proton (^1H), carbon (^{13}C) and fluorine (^{19}F) NMR spectra were recorded on a 300 or 600 MHz instrument using the residual signals from CHCl_3 , $\delta = 7.26$ ppm and $\delta = 77.16$ ppm, as internal references for ^1H and ^{13}C chemical shifts, respectively. ESI-HRMS mass spectrometry was carried out on a FTICR instrument. IR spectra were measured on an ATR spectrometer and UV spectra with a common photometer. Optical rotations were measured using a common optical rotation instrument. A HPLC system equipped with an analytical Chiralpak IG column (particle size: 5 μm , dimensions: 4.6 mm \varnothing x 150 mmL) was used to determine *ee* values.

Experimental Section

1-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-4-(trimethylsilyl)but-3-yn-2-ol (**13**)



Trimethylsilylacetylene (481 mg, 677 μ L, 4.90 mmol, 2.00 eq.) was dissolved in THF (25.0 mL) and the solution was cooled to -78 $^{\circ}$ C. *n*BuLi (2.5 M, 1.42 mL, 3.55 mmol, 1.45 eq.) was added dropwise and the reaction mixture was allowed to stir for 30 min. A solution of 2-(4-bromo-1-tosyl-1*H*-indol-3-yl)acetaldehyde¹ (960 mg, 2.45 mmol, 1.00 eq.) in THF (6.0 mL) was added dropwise at -78 $^{\circ}$ C and the mixture was stirred for 2.5 h while warming up to -15 $^{\circ}$ C and for 1.5 h at ambient temperature. Sat. aq. NH_4Cl -solution was added and the aqueous layer was extracted three times with EtOAc. The combined organic phases were washed once with sat. aq. NaCl-solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 10:1) afforded the desired product **13** (847 mg, 1.73 mmol, 71%) as light yellow solid.

R_f: 0.10 (*n*-hexane:EtOAc = 10:1).

m.p.: 60-61 $^{\circ}$ C.

¹H-NMR (300 MHz, CDCl_3): δ = 0.16 (s, 9 H), 1.95 (d, J = 5.2 Hz, 1 H), 2.35 (s, 3 H), 3.32 (ddd, J = 14.5, 6.7, 0.9 Hz, 1 H), 3.42 (ddd, J = 14.5, 6.6, 0.9 Hz, 1 H), 4.72 (td, J = 6.7, 5.1 Hz, 1 H), 7.08 – 7.15 (m, 1 H), 7.18 – 7.27 (m, 2 H), 7.37 (dd, J = 7.8, 0.9 Hz, 1 H), 7.60 (s, 1 H), 7.71 – 7.76 (m, 2 H), 7.94 (dd, J = 8.3, 0.9 Hz, 1 H).

¹³C-NMR (75 MHz, CDCl_3): δ = -0.2, 21.6, 34.4, 62.9, 90.5, 105.7, 112.9, 114.4, 117.6, 125.3, 126.8, 126.9, 127.9, 128.7, 130.0, 134.9, 136.3, 145.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3529, 2959, 1597, 1554, 1412, 1371, 1248, 1171.

UV (CH_3CN): λ_{max} (lg ϵ) = 296 (3.63), 261 (4.07), 220 (4.44), 196 (4.73).

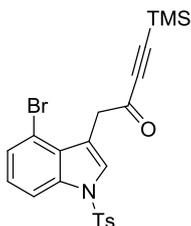
MS (ESI): m/z = 514.0 [$\text{M}+\text{Na}$]⁺.

C₂₂H₂₄BrNO₃Si (490.49)

calcd.: 514.0303

found: 514.0300, [$\text{M}+\text{Na}$]⁺ (ESI-HRMS).

1-(4-Bromo-1-tosyl-1H-indol-3-yl)-4-(trimethylsilyl)but-3-yn-2-one (14)



Secondary alcohol **13** (287 mg, 585 μmol , 1.00 eq.) was dissolved in CH_2Cl_2 (6.5 mL) and Dess-Martin periodinane (645 mg, 1.52 mmol, 2.6 eq.) was added. The reaction mixture was stirred for 26 h at ambient temperature. Sat. aq. NaHCO_3 -solution and sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ -solution were added to the mixture, which was allowed to stir for further 10 min.. The aqueous layer was extracted three times with Et_2O , the combined organic phases were washed once with sat. aq. NaHCO_3 -solution and once with sat. aq. NaCl -solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 8:1) afforded the desired product **14** (252 mg, 516 μmol , 88%) as light yellow, highly viscous oil.

R_f: 0.23 (*n*-hexane:EtOAc = 7:1).

¹H-NMR (600 MHz, CDCl_3): δ = 0.09 (s, 9 H), 2.35 (s, 3 H), 4.17 (s, 2 H), 7.10 – 7.16 (m, 1 H), 7.23 – 7.26 (m, 2 H), 7.37 (dd, J = 7.8, 0.9 Hz, 1H), 7.56 (s, 1 H), 7.72 – 7.78 (m, 2 H), 7.95 (dd, J = 8.4, 0.9 Hz, 1 H).

¹³C-NMR (150 MHz, CDCl_3): δ = -1.0, 21.7, 42.2, 100.3, 101.6, 112.9, 114.6, 114.7, 125.7, 127.0, 127.3, 127.8, 128.6, 130.1, 134.9, 136.2, 145.5, 184.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 2961, 1676, 1597, 1555, 1412, 1373, 1249, 1171, 1088.

UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 296 (3.69), 258 (4.11), 218 (4.52), 196 (4.73).

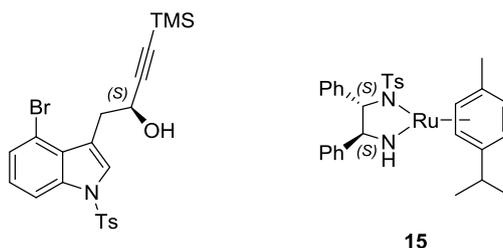
MS (ESI): m/z = 512.0 $[\text{M}+\text{Na}]^+$.

C₂₂H₂₂BrNO₃Si (488.47)

calcd.: 512.0145

found: 512.0144, $[\text{M}+\text{Na}]^+$ (ESI-HRMS).

(S)-1-(4-Bromo-1-tosyl-1H-indol-3-yl)-4-(trimethylsilyl)but-3-yn-2-ol (16)



Ketone **14** (252 mg, 516 μmol , 1.00 eq.) was dissolved in *i*PrOH (5.2 mL) and Ru complex **15**² (30.9 mg, 51.6 μmol , 10 mol%) was added. The reaction mixture was stirred for 17 h at ambient temperature.

Afterwards, the solvent was removed *in vacuo* and silica gel column chromatography (*n*-pentane:EtOAc = 10:1 \rightarrow 8:1) afforded the desired product **16** (223 mg, 455 μmol , 88%, 99% *ee*) as light brownish solid.

R_f: 0.10 (*n*-hexane:EtOAc = 10:1).

m.p.: 55-56 °C.

Specific Rotation: $[\alpha]_D^{23} = +21.9^\circ$ ($c = 5.7$ mM, CH_2Cl_2).

¹H-NMR (300 MHz, CDCl_3): $\delta = 0.16$ (s, 9 H), 1.95 (d, $J = 5.2$ Hz, 1 H), 2.35 (s, 3 H), 3.32 (ddd, $J = 14.5, 6.7, 0.9$ Hz, 1 H), 3.42 (ddd, $J = 14.5, 6.6, 0.9$ Hz, 1 H), 4.72 (td, $J = 6.7, 5.1$ Hz, 1 H), 7.08 – 7.15 (m, 1 H), 7.18 – 7.27 (m, 2 H), 7.37 (dd, $J = 7.8, 0.9$ Hz, 1 H), 7.60 (s, 1 H), 7.71 – 7.76 (m, 2 H), 7.94 (dd, $J = 8.3, 0.9$ Hz, 1 H).

¹³C-NMR (75 MHz, CDCl_3): $\delta = -0.2, 21.6, 34.4, 62.9, 90.5, 105.7, 112.9, 114.4, 117.6, 125.3, 126.8, 126.9, 127.9, 128.7, 130.0, 134.9, 136.3, 145.2$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}) = 3529, 2959, 1597, 1554, 1412, 1371, 1248, 1171.

UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 296 (3.63), 261 (4.07), 220 (4.44), 196 (4.73).

MS (ESI): $m/z = 514.0$ $[\text{M}+\text{Na}]^+$.

C₂₂H₂₂BrNO₃Si (490.49)

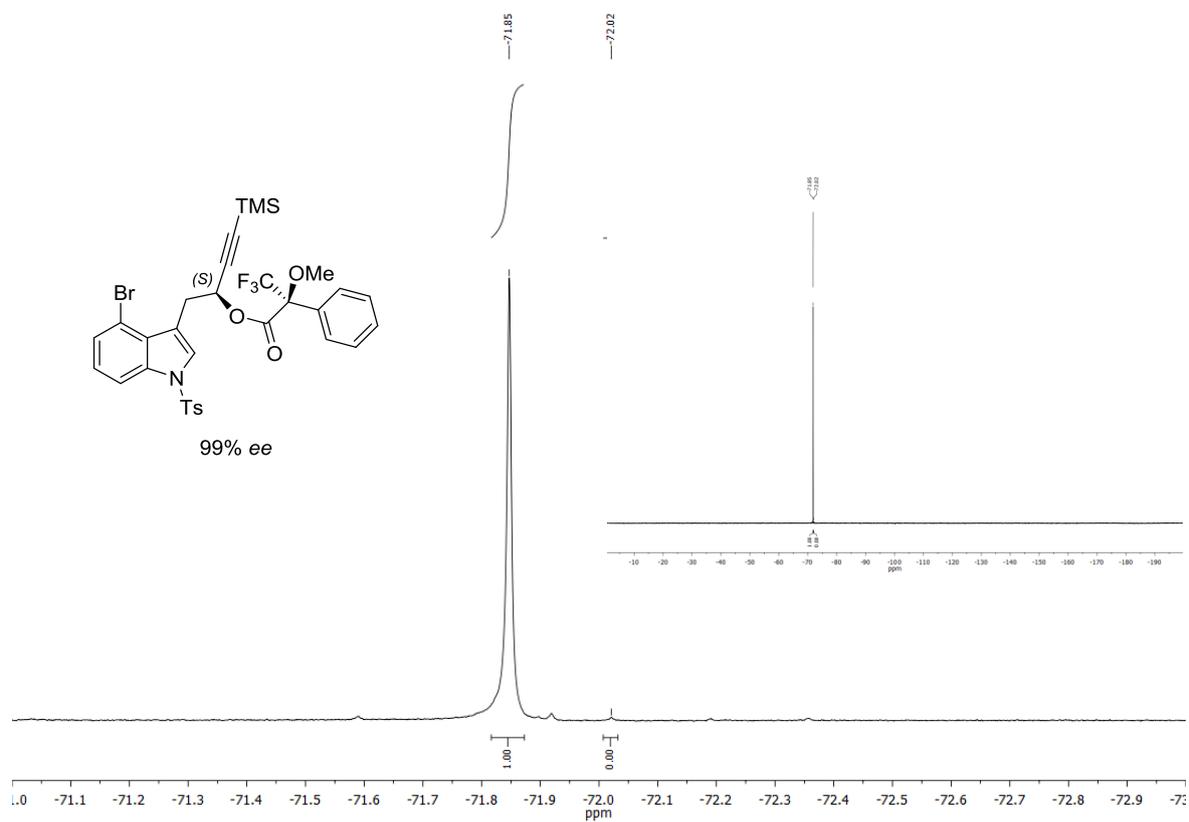
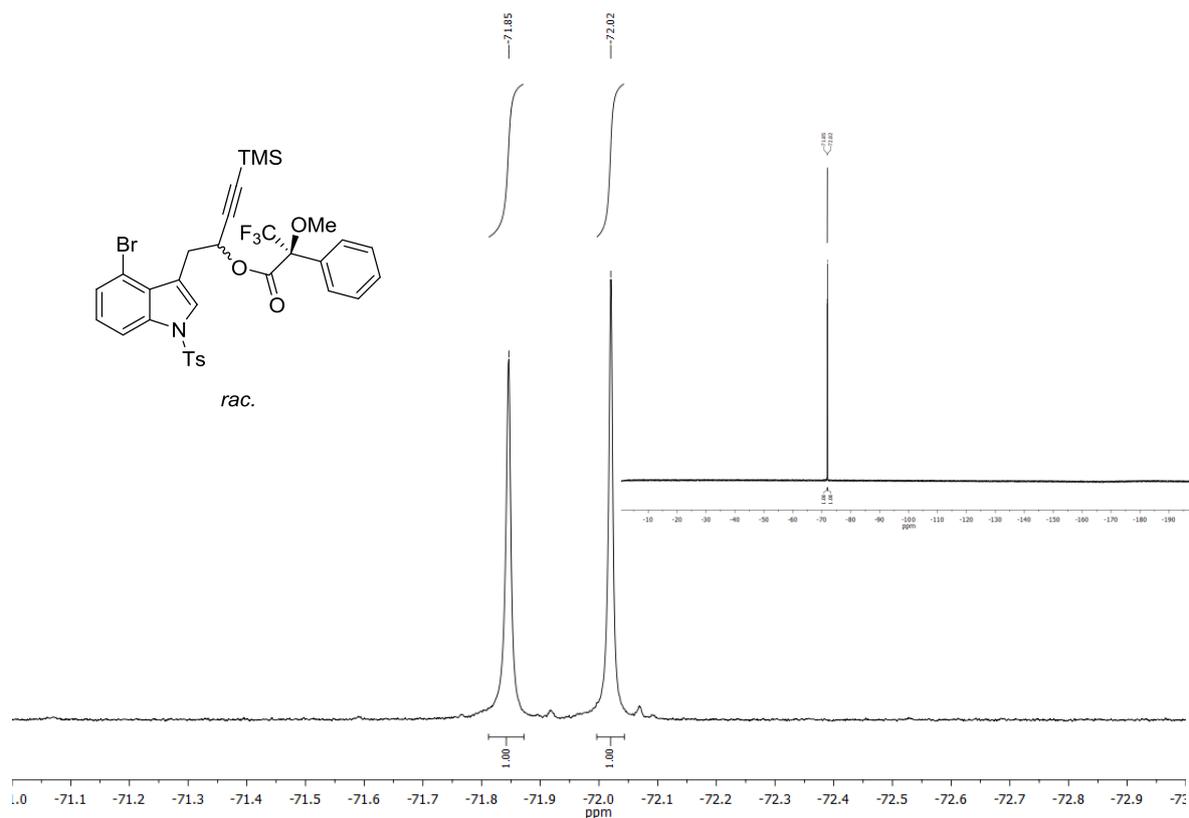
calcd.: 514.0303

found: 514.0300, $[\text{M}+\text{Na}]^+$ (ESI-HRMS).

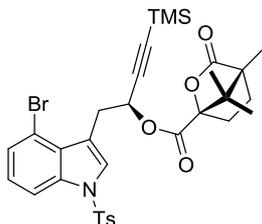
Determination of enantiomeric excess via Mosher ester formation:

(*R*)-(-)-Mosher ester acid chloride (1.3 mg, 1.0 μL , 5.14 μmol , 1.2 eq.) and 4-DMAP (1.1 mg, 8.56 μmol , 2.0 eq.) were added to a solution of the alcohol **13** or **16** (4.28 μmol , 1.0 eq.) in CH_2Cl_2 (1.0 mL) at ambient temperature. The reaction mixture was stirred for 15 min before aq. HCl (1.0 M) was added. The phases were separated and the organic layer was washed once with sat. aq. NaHCO_3 -

solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Via ^{19}F -NMR of the crude Mosher esters the enantiomeric excess was determined.



(S)-1-(4-Bromo-1-tosyl-1H-indol-3-yl)-4-(trimethylsilyl)but-3-yn-2-yl (1S,4R)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (18)



Chiral alcohol **16** (36.0 mg, 73.4 μmol , 1.00 eq.) was dissolved in CH_2Cl_2 (1.0 mL) and 4-DMAP (1.8 mg, 14.7 μL , 0.2 eq.), pyridine (11.6 mg, 11.8 μL , 147 μmol , 2.0 eq.) and (-)-camphanoyl chloride (31.8 mg, 147 μmol , 2.0 eq.) were added at 0 °C. The reaction mixture was allowed to stir for 25 h while warming up to ambient temperature. Sat. aq. NH_4Cl -solution was added and the aqueous layer was extracted three times with EtOAc. The combined organic phases were washed once with sat. aq. NaCl-solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 10:1 \rightarrow 8:1) afforded the desired product **18** (41.4 mg, 61.7 μmol , 84%) as white solid.

R_f: 0.07 (*n*-hexane:EtOAc = 10:1).

m.p.: 149-151 °C.

Specific Rotation: $[\alpha]_D^{23} = -31.8^\circ$ ($c = 4.2$ mM, CH_2Cl_2).

¹H-NMR (600 MHz, CDCl_3): $\delta = 0.15$ (s, 9 H), 0.90 (s, 3 H), 1.01 (s, 3 H), 1.10 (s, 3 H), 1.63 – 1.69 (m, 1 H), 1.87 – 1.93 (m, 2 H), 2.31 – 2.38 (m, 1 H), 2.35 (s, 3 H), 3.51 (ddd, $J = 14.8, 7.1, 0.9$ Hz, 1 H), 3.55 (ddd, $J = 14.8, 6.4, 0.9$ Hz, 1 H), 5.81 (t, $J = 6.7$ Hz, 1 H), 7.13 (t, $J = 8.1$ Hz, 1 H), 7.23 – 7.26 (m, 2 H), 7.38 (dd, $J = 7.8, 0.8$ Hz, 1 H), 7.57 (s, 1 H), 7.71 – 7.73 (m, 2 H), 7.92 (dd, $J = 8.4, 0.8$ Hz, 1 H).

¹³C-NMR (150 MHz, CDCl_3): $\delta = -0.4, 9.6, 16.5, 16.8, 21.6, 29.1, 30.2, 31.2, 54.6, 54.8, 65.1, 90.7, 92.2, 101.2, 112.8, 114.3, 116.3, 125.5, 126.8, 126.9, 127.9, 128.3, 130.1, 134.8, 136.1, 145.4, 166.1, 177.9$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3112, 2962, 1791, 1750, 1376, 1250, 1171, 1062.

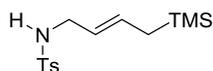
MS (ESI): $m/z = 694.1$ $[\text{M}+\text{Na}]^+$.

C₃₂H₃₆BrNO₆SSi (670.69)

calcd.: 694.1087

found: 694.1091, $[\text{M}+\text{Na}]^+$ (ESI-HRMS).

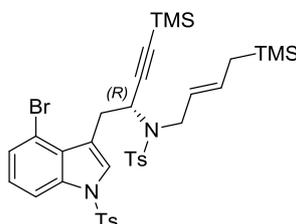
(E)-4-Methyl-N-(4-(trimethylsilyl)but-2-en-1-yl)benzenesulfonamide (17)



N-Allyl-4-methylbenzenesulfonamide (300 mg, 1.42 mmol, 1.00 eq.) and allyltrimethylsilane (811 mg, 1.13 mL, 7.10 mmol, 5.00 eq.) were dissolved in CH₂Cl₂ (4.8 mL) and heated to 50 °C. 1,4-Benzoquinone (76.7 mg, 710 μmol, 0.50 eq.) and Hoveyda-Grubbs catalyst 2nd generation (44.5 mg, 71.0 μmol, 5 mol%) were added and the vial was sealed under an argon atmosphere. The reaction mixture was allowed to stir for three days at 50 °C. After cooling to ambient temperature, the solvent was removed *in vacuo* and silica gel column chromatography (*n*-pentane:EtOAc = 12:1) afforded the desired product **17** (287 mg, 965 μmol, 68%, *E*:*Z* = ~3:1) as colorless oil.

All analytical data were in agreement with those previously reported.³

(R)-N-(1-(4-Bromo-1-tosyl-1*H*-indol-3-yl)-4-(trimethylsilyl)but-3-yn-2-yl)-4-methyl-N-(4-(trimethylsilyl)but-2-en-1-yl)benzenesulfonamide (10)



Chiral alcohol **16** (476 mg, 970 μmol, 1.00 eq.), sulfonamide **17** (577 mg, 1.94 mmol, 2.00 eq.) and PPh₃ (865 mg, 3.30 mmol, 3.40 eq.) were dissolved in THF (7.0 mL) and the solution was cooled to 0 °C. DIAD (569 mg, 553 μL, 2.81 mmol, 2.90 eq.) was added slowly over a period of one hour. The reaction mixture was allowed to warm to ambient temperature and stirring continued for 2 h. The solvent was removed *in vacuo* and silica gel column chromatography (*n*-pentane:EtOAc = 15:1) afforded the desired product **10** (554 mg, 720 μmol, 74%, *E*:*Z* = ~3:1) as white solid.

R_f: 0.22 (*n*-hexane:EtOAc = 10:1).

m.p.: 91-93 °C.

Specific Rotation: $[\alpha]_D^{23} = +30.9^\circ$ ($c = 4.6$ mM, CH₂Cl₂).

¹H-NMR (600 MHz, CDCl₃) of the major product: $\delta = -0.03$ (s, 9 H), -0.02 (s, 9 H), 1.34 – 1.40 (m, 2 H), 2.33 (s, 3 H), 2.40 (s, 3 H), 3.36 (dd, $J = 14.8, 7.4$ Hz, 1 H), 3.45 (dd, $J = 14.8, 8.1$ Hz, 1 H), 3.68 (dd, $J =$

15.5, 8.3 Hz, 1 H), 3.95 (dd, $J = 15.5, 4.9$ Hz, 1 H), 5.08 (t, $J = 7.7$ Hz, 1 H), 5.31 – 5.37 (m, 1 H), 5.60 – 5.69 (m, 1 H), 7.05 – 7.11 (m, 1 H), 7.23 – 7.26 (m, 4 H), 7.36 (dd, $J = 7.8, 0.9$ Hz, 1 H), 7.65 (s, 1 H), 7.69 – 7.72 (m, 2 H), 7.74 – 7.77 (m, 2 H), 7.89 (dd, $J = 8.3, 0.9$ Hz, 1 H).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3) of the major product: $\delta = -1.9, -0.4, 21.5, 21.6, 22.7, 32.2, 47.9, 52.0, 91.4, 101.3, 125.2, 125.4, 127.0, 127.2, 127.7, 127.7, 128.7, 129.3, 130.0, 131.0, 134.8, 136.1, 136.1, 143.1, 145.1$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2956, 1598, 1413, 1372, 1247, 1158, 1091.

UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 286 (3.73), 255 (4.11), 221 (4.59), 196 (4.96).

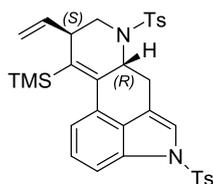
MS (ESI): $m/z = 793.1$ $[\text{M}+\text{Na}]^+$.

$\text{C}_{36}\text{H}_{45}\text{BrN}_2\text{O}_4\text{S}_2\text{Si}_2$ (769.96)

calcd.: 793.1414

found: 793.1421, $[\text{M}+\text{Na}]^+$ (ESI-HRMS).

(6a*R*,9*S*)-4,7-ditosyl-10-(trimethylsilyl)-9-vinyl-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline (9)



Domino precursor **10** (38.3 mg, 49.8 μmol , 1.00 eq.) was dissolved in DMA (2.0 mL) and the solution was degassed with argon for 20 min. Afterwards, Et_3N (25.2 mg, 34.5 μL , 249 μmol , 5.00 eq.), XPhos (4.84 mg, 9.95 μmol , 20 mol%) and $[\text{PdCl}_2(\text{PhCN})_2]$ (1.91 mg, 4.98 μmol , 10 mol%) were added and the vial was sealed under an argon atmosphere. The reaction mixture was stirred for 30 min at ambient temperature and for 2 h at 120 $^\circ\text{C}$. Sat. aq. NH_4Cl -solution was added to the mixture and the aqueous layer was extracted three times with EtOAc. The combined organic phases were washed three times with sat. aq. NaCl-solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 14:1 \rightarrow 8:1) afforded the desired product **9** (24.6 mg, 39.9 μmol , 80%, 99% *ee*) as light yellow solid.

R_f: 0.21 (*n*-hexane:EtOAc = 5:1).

m.p.: 110-112 $^\circ\text{C}$.

Specific Rotation: $[\alpha]_D^{22} = -69.2^\circ$ ($c = 10.4$ mM, CHCl_3).

$^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 0.02$ (s, 9 H), 2.37 (s, 3 H), 2.41 (s, 3 H), 2.97 (ddd, $J = 14.8, 11.8, 2.1$ Hz, 1 H), 3.11 – 3.16 (m, 2 H), 3.31 (dd, $J = 13.1, 3.5$ Hz, 1 H), 3.72 (dd, $J = 13.1, 1.5$ Hz, 1 H), 4.53 (dd, $J = 11.7, 4.6$ Hz, 1 H), 4.83 (ddd, $J = 10.0, 1.6, 0.7$ Hz, 1 H), 4.94 (ddd, $J = 17.1, 1.6, 1.0$ Hz, 1 H),

5.47 (ddd, $J = 17.1, 10.1, 7.7$ Hz, 1 H), 7.15 (d, $J = 1.6$ Hz, 1 H), 7.22 (dd, $J = 4.4, 0.9$ Hz, 2 H), 7.23 – 7.26 (m, 4 H), 7.64 – 7.67 (m, 2 H), 7.76 – 7.82 (m, 3 H).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3): $\delta = 1.7, 21.5, 21.6, 29.4, 42.6, 43.7, 55.1, 113.3, 116.9, 118.0, 120.2, 120.7, 124.5, 126.8, 127.3, 129.3, 129.4, 129.9, 132.6, 133.1, 135.4, 135.9, 138.0, 138.8, 142.5, 143.2, 144.9$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2955, 1597, 1435, 1339, 1249, 1173, 1112, 1089.

UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 293 (4.20), 229 (4.51), 193 (4.94).

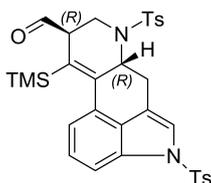
MS (ESI): $m/z = 639.2$ [$\text{M}+\text{Na}$] $^+$.

$\text{C}_{33}\text{H}_{36}\text{N}_2\text{O}_4\text{S}_2\text{Si}$ (616.87)

calcd.: 639.1778

found: 639.1780, [$\text{M}+\text{Na}$] $^+$ (ESI-HRMS).

(6a*R*,9*R*)-4,7-Ditosyl-10-(trimethylsilyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline-9-carbaldehyde (20)



Domino product **9** (31.9 mg, 51.7 μmol , 1.00 eq.) was dissolved in a mixture of THF (0.50 mL), H_2O (58 μL) and acetone (0.6 mL). 2,6-Lutidine (11.1 mg, 12.0 μL , 103 μmol , 2.00 eq.) and NMO (12.1 mg, 103 μmol , 2.00 eq.) were added and the solution was cooled to 0 $^\circ\text{C}$. OsO_4 (2.5 wt% in *t*BuOH, 158 μL , 15.5 μmol , 0.30 eq.) was added in one portion and the reaction mixture was allowed to stir for 2 d and 15 h at 0 $^\circ\text{C}$. Afterwards, aq. sat. Na_2SO_3 -solution was added and stirring continued for 10 min while warming up to ambient temperature. The aqueous layer was extracted three times with EtOAc. The combined organic phases were washed once with sat. aq. NaCl-solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*.

The crude diol was dissolved in a mixture of THF (1.2 mL) and H_2O (0.4 mL) and NaIO_4 (44.2 mg, 207 μmol , 4.00 eq.) was added. After being stirred for 4 h at ambient temperature, the suspension was diluted with EtOAc. The aqueous layer was extracted three times with EtOAc. The combined organic phases were washed once with sat. aq. NaCl-solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 5:1) afforded the desired product **20** (18.8 mg, 30.4 μmol , 59%) as yellow solid.

R_f: 0.40 (*n*-hexane:EtOAc = 5:3).

m.p.: 109-111 $^\circ\text{C}$.

Specific Rotation: $[\alpha]_D^{22} = -168.7^\circ$ ($c = 12.1$ mM, CHCl_3).

$^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 0.06$ (s, 9 H), 2.37 (s, 3 H), 2.43 (s, 3 H), 2.99 (ddd, $J = 14.5, 11.9, 2.1$ Hz, 1 H), 3.17 (dd, $J = 14.9, 4.6$ Hz, 1 H), 3.26 (dt, $J = 3.7, 1.8$ Hz, 1 H), 3.34 (dd, $J = 13.7, 3.7$ Hz, 1 H), 4.15 (dd, $J = 13.7, 1.2$ Hz, 1 H), 4.66 (dd, $J = 11.8, 4.7$ Hz, 1 H), 7.18 (d, $J = 1.8$ Hz, 1 H), 7.23 – 7.28 (m, 4 H), 7.28 – 7.31 (m, 2 H), 7.67 – 7.70 (m, 2 H), 7.77 – 7.80 (m, 2 H), 7.83 (dd, $J = 7.6, 1.3$ Hz, 1 H), 9.26 (d, $J = 2.1$ Hz, 1 H).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3): $\delta = 1.4, 21.6, 21.6, 29.2, 38.5, 51.1, 55.1, 113.8, 117.3, 120.5, 120.8, 124.7, 126.8, 127.2, 129.3, 129.9, 130.0, 130.1, 132.0, 133.0, 135.3, 137.0, 144.0, 145.0, 145.8, 199.6$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2954, 1718, 1597, 1436, 1356, 1340, 1172, 1158, 1112, 1088.

UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 293 (4.10), 231 (4.49), 193 (4.87).

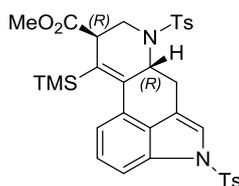
MS (ESI): $m/z = 641.2$ $[\text{M}+\text{Na}]^+$.

$\text{C}_{32}\text{H}_{34}\text{N}_2\text{O}_5\text{S}_2\text{Si}$ (618.84)

calcd.: 641.1571

found: 641.1571, $[\text{M}+\text{Na}]^+$ (ESI-HRMS).

Methyl (6a*R*,9*R*)-4,7-ditosyl-10-(trimethylsilyl)-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline-9-carboxylate (8)



Aldehyde **20** (43.3 mg, 70.0 μmol , 1.00 eq.) and 2-methylbut-2-ene (295 mg, 444 μL , 4.20 mmol, 60.0 eq.) were dissolved in THF (1.5 mL) and *t*BuOH (1.5 mL). A solution of NaClO_2 (80%, 75.9 mg, 672 μmol , 9.6 eq.) and NaH_2PO_4 (80.6 mg, 672 μmol , 9.6 eq.) in H_2O (0.7 mL) was added dropwise and the reaction mixture was stirred for 1.5 h at ambient temperature. Sat. aq. NaCl-solution was added and the aqueous layer was extracted three times with EtOAc. The combined organic phases were washed once with sat. aq. NaCl-solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*.

The crude carboxylic acid was dissolved in PhMe (1.5 mL) and MeOH (0.8 mL) and cooled to 0 $^\circ\text{C}$ before TMSCHN_2 (2.0 M in hexane, 350 μL , 700 μmol , 10.0 eq.) was added dropwise. After being stirred for 30 min at 0 $^\circ\text{C}$, the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 5:1) afforded the desired product **8** (40.7 mg, 62.7 μmol , 90%, 99% *ee*) as light yellow solid.

R_f: 0.34 (*n*-hexane:EtOAc = 3:1).

m.p.: 84-86 °C.

Specific Rotation: $[\alpha]_D^{21} = -33.3^\circ$ ($c = 16.6$ mM, CHCl_3).

$^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 0.05$ (s, 9 H), 2.37 (s, 3 H), 2.41 (s, 3 H), 3.03 (ddd, $J = 14.8, 11.8, 2.1$ Hz, 1 H), 3.22 (dd, $J = 14.8, 4.6$ Hz, 1 H), 3.34 (dd, $J = 13.4, 4.3$ Hz, 1 H), 3.39 (dd, $J = 4.4, 1.6$ Hz, 1 H), 3.41 (s, 3 H), 4.16 (dd, $J = 13.3, 1.3$ Hz, 1 H), 4.60 (dd, $J = 11.8, 4.6$ Hz, 1 H), 7.17 (d, $J = 1.8$ Hz, 1 H), 7.23 – 7.28 (m, 5 H), 7.32 – 7.34 (m, 1 H), 7.65 – 7.70 (m, 2 H), 7.76 – 7.80 (m, 2 H), 7.82 (d, $J = 8.3$ Hz, 1 H).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3): $\delta = 1.4, 21.5, 21.6, 29.0, 40.7, 44.6, 52.0, 55.3, 113.5, 117.7, 120.4, 120.7, 124.6, 126.8, 127.4, 129.3, 129.5, 129.9, 131.6, 132.3, 133.1, 135.4, 137.5, 143.3, 144.6, 144.9, 172.0$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2952, 1732, 1597, 1376, 1248, 1172, 1153, 1108, 1088, 1018.

UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 291 (4.17), 230 (4.51), 194 (4.92).

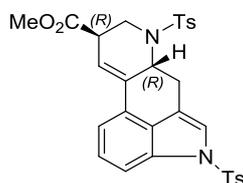
MS (ESI): $m/z = 671.2$ $[\text{M}+\text{Na}]^+$.

$\text{C}_{33}\text{H}_{36}\text{N}_2\text{O}_6\text{S}_2\text{Si}$ (648.87)

calcd.: 671.1676

found: 671.1678, $[\text{M}+\text{Na}]^+$ (ESI-HRMS).

Methyl (6a*R*,9*R*)-4,7-ditosyl-4,6,6a,7,8,9-hexahydroindolo[4,3-*fg*]quinoline-9-carboxylate (21**)**



Ester **8** (53.5 mg, 82.5 μmol , 1.00 eq.) was dissolved in CHCl_3 (1.4 mL) and at 0 °C TFA (1.4 mL) was added dropwise. The ice bath was removed and the reaction mixture was stirred for 4.5 h in an open flask at ambient temperature. The solution was treated with sat. aq. NaHCO_3 -solution and the aqueous layer was extracted three times with EtOAc. The combined organic phases were washed once with sat. aq. NaCl -solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 2:1) afforded the desired product **21** (45.4 mg, 78.7 μmol , 95%) as light yellow solid.

R_f: 0.22 (*n*-hexane:EtOAc = 2:1).

m.p.: 119-121 °C.

Specific Rotation: $[\alpha]_D^{22} = -129.4^\circ$ ($c = 21.9$ mM, CHCl_3).

$^1\text{H-NMR}$ (600 MHz, CDCl_3): $\delta = 2.35$ (s, 3 H), 2.40 (s, 3 H), 2.89 (ddd, $J = 14.8, 12.0, 2.1$ Hz, 1 H), 3.26 – 3.29 (m, 1 H), 3.35 – 3.41 (m, 2 H), 3.48 (s, 3 H), 4.30 (d, $J = 13.7$ Hz, 1 H), 4.64 – 4.69 (m, 1 H), 6.35

(dd, $J = 6.1, 1.8$ Hz, 1 H), 7.19 (d, $J = 1.7$ Hz, 1 H), 7.22 – 7.31 (m, 6 H), 7.67 – 7.70 (m, 2 H), 7.75 – 7.78 (m, 2 H), 7.80 (dd, $J = 7.5, 1.3$ Hz, 1 H).

$^{13}\text{C-NMR}$ (150 MHz, CDCl_3): $\delta = 21.3, 21.4, 27.8, 40.5, 41.2, 52.0, 53.4, 112.8, 115.9, 117.0, 118.8, 120.4, 125.6, 126.5, 127.1, 128.0, 129.3, 129.7, 129.7, 133.1, 134.9, 135.1, 137.5, 143.1, 144.7, 170.8$.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2953, 1733, 1597, 1434, 1357, 1341, 1153, 1110, 1088.

UV (CH_3CN): λ_{max} ($\lg \epsilon$) = 285 (4.16), 230 (4.52), 193 (4.84).

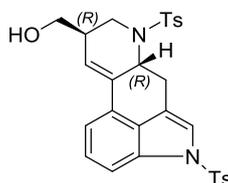
MS (ESI): $m/z = 599.1$ [$\text{M}+\text{Na}$] $^+$.

$\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_6\text{S}_2$ (576.68)

calcd.: 599.1281

found: 599.1280, [$\text{M}+\text{Na}$] $^+$ (ESI-HRMS).

((6*aR*,9*R*)-4,7-Ditosyl-4,6,6*a*,7,8,9-hexahydroindolo[4,3-*fg*]quinolin-9-yl)methanol (22)

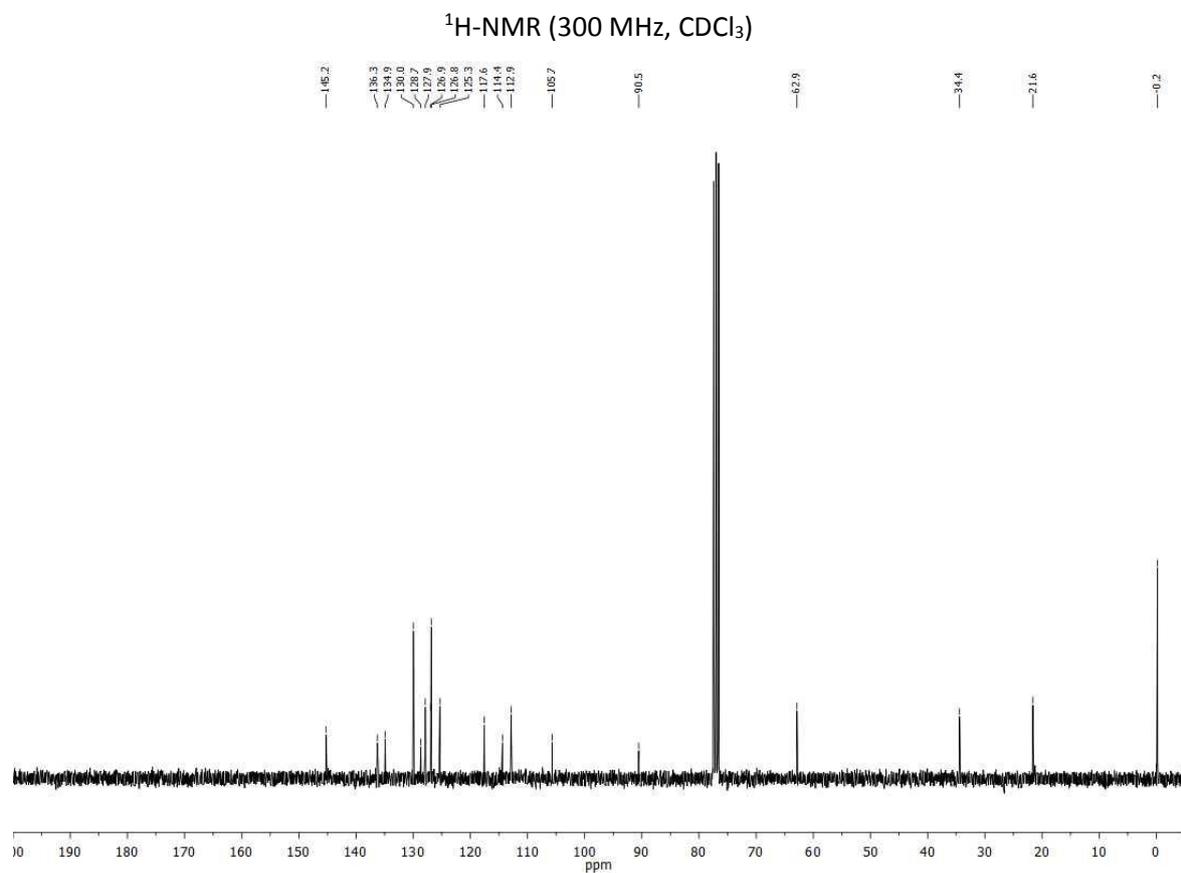
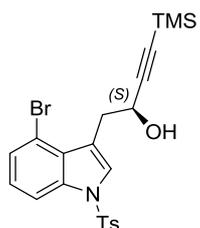
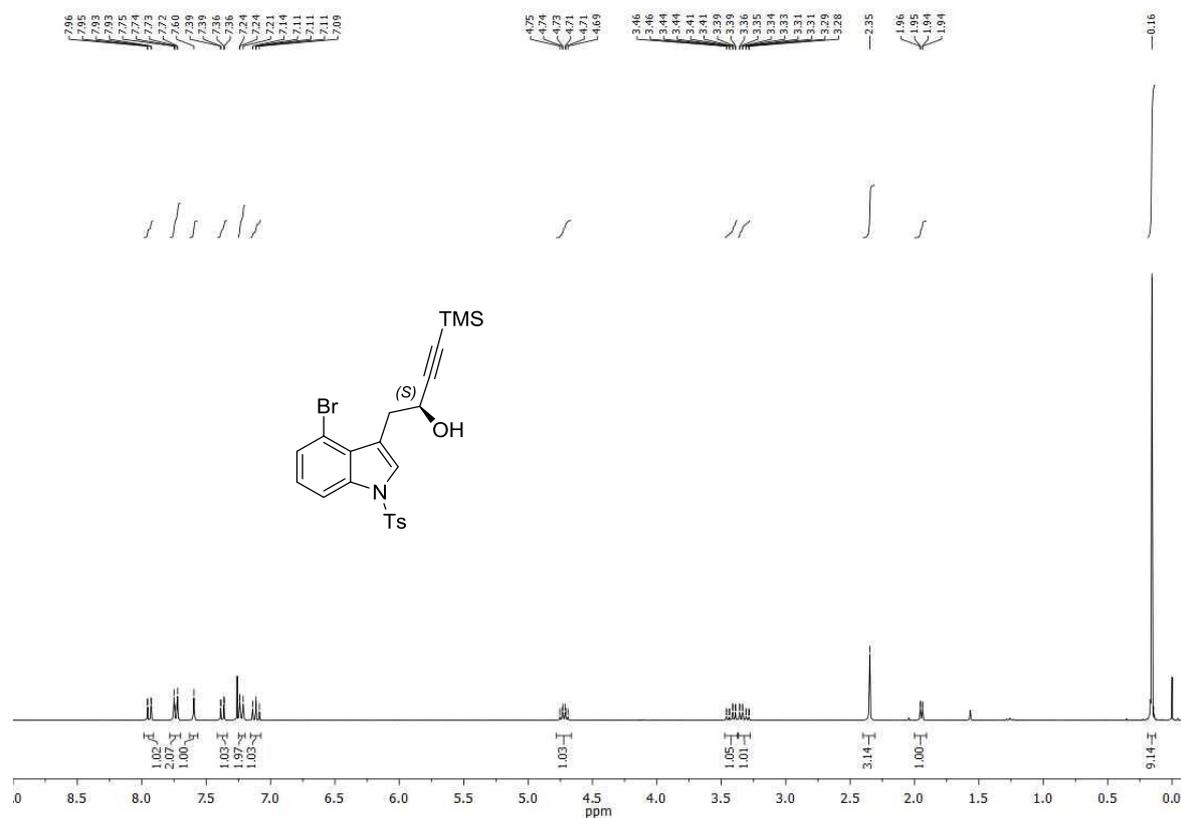


Ester **21** (10.5 mg, 18.2 μmol , 1.00 eq.) was dissolved in THF (0.5 mL) and at -78 $^\circ\text{C}$ DIBAL-H (1.0 M, 54.6 μL , 54.6 μmol , 3.00 eq.) was added dropwise. The reaction mixture was stirred for 1 h and 20 min before being warmed up to 0 $^\circ\text{C}$. Stirring continued for 30 min at 0 $^\circ\text{C}$ and for 45 min at ambient temperature. Further DIBAL-H (1.0 M, 54.6 μL , 54.6 μmol , 3.00 eq.) was added and after 1.5 h sat. aq. Rochelle salt solution was used to terminate the reaction. The solution was stirred for 15 min and afterwards the aqueous layer was extracted three times with EtOAc. The combined organic phases were washed once with sat. aq. NaCl-solution, dried over Na_2SO_4 and the solvent was removed *in vacuo*. Silica gel column chromatography (*n*-pentane:EtOAc = 1:1) afforded the desired product **22** (9.0 mg, 16.4 μmol , 90%) as light yellow solid.

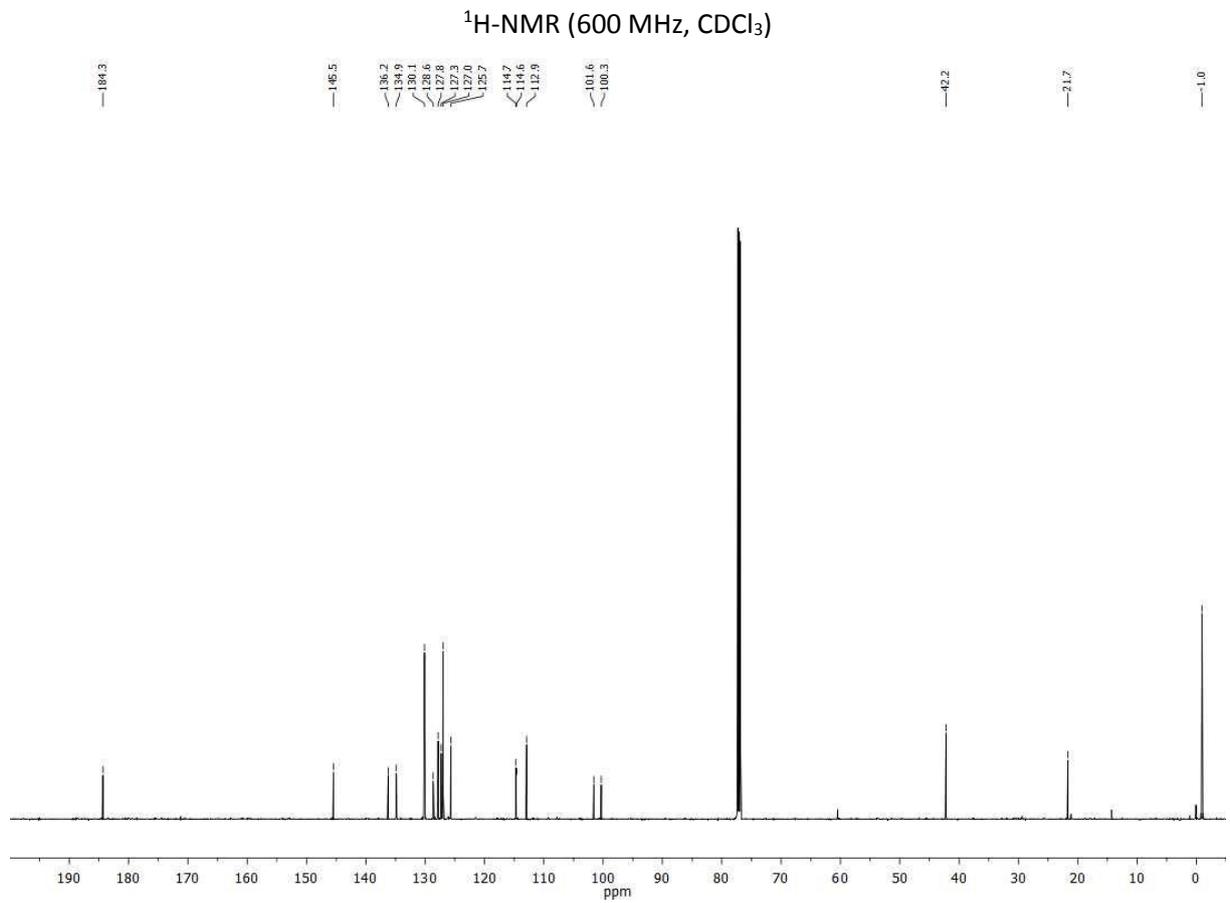
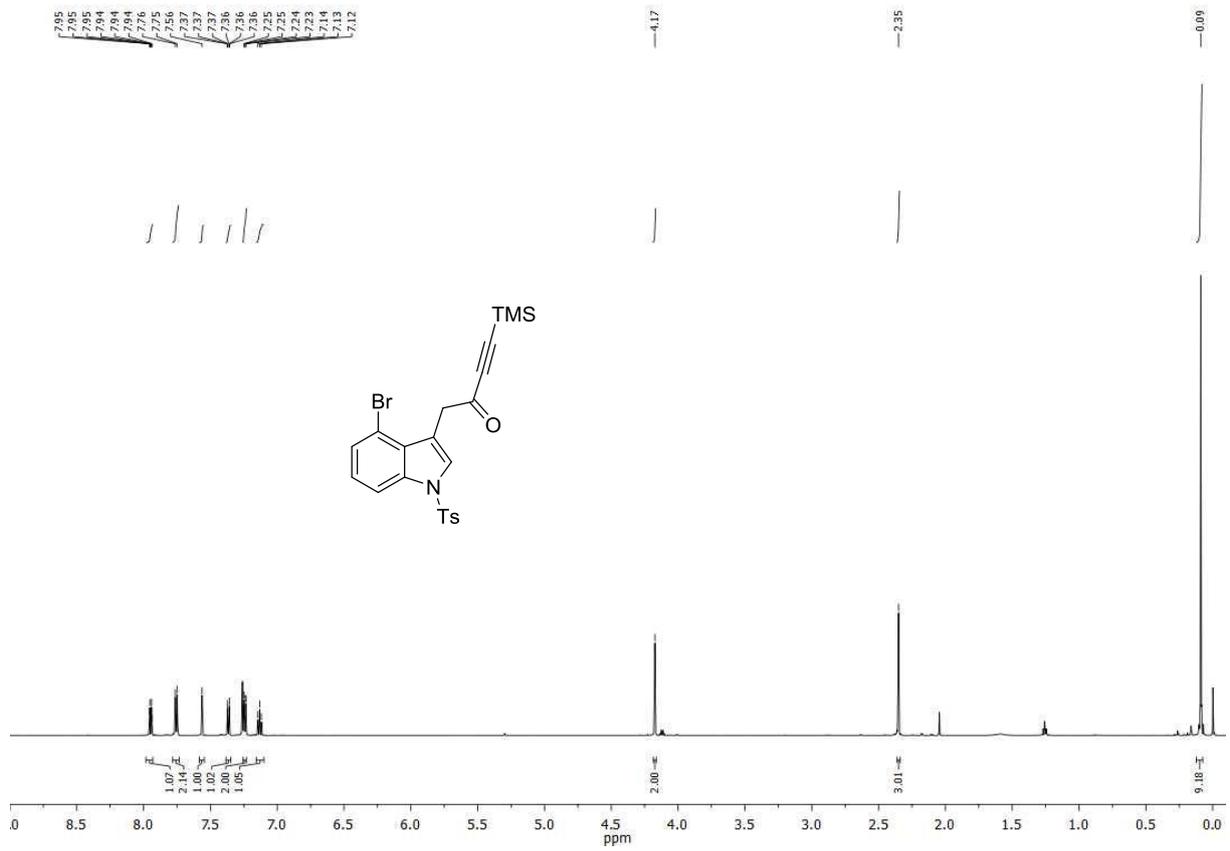
All analytical data were in agreement with those previously reported.⁴

¹H- and ¹³C-NMR Spectra of all New Compounds

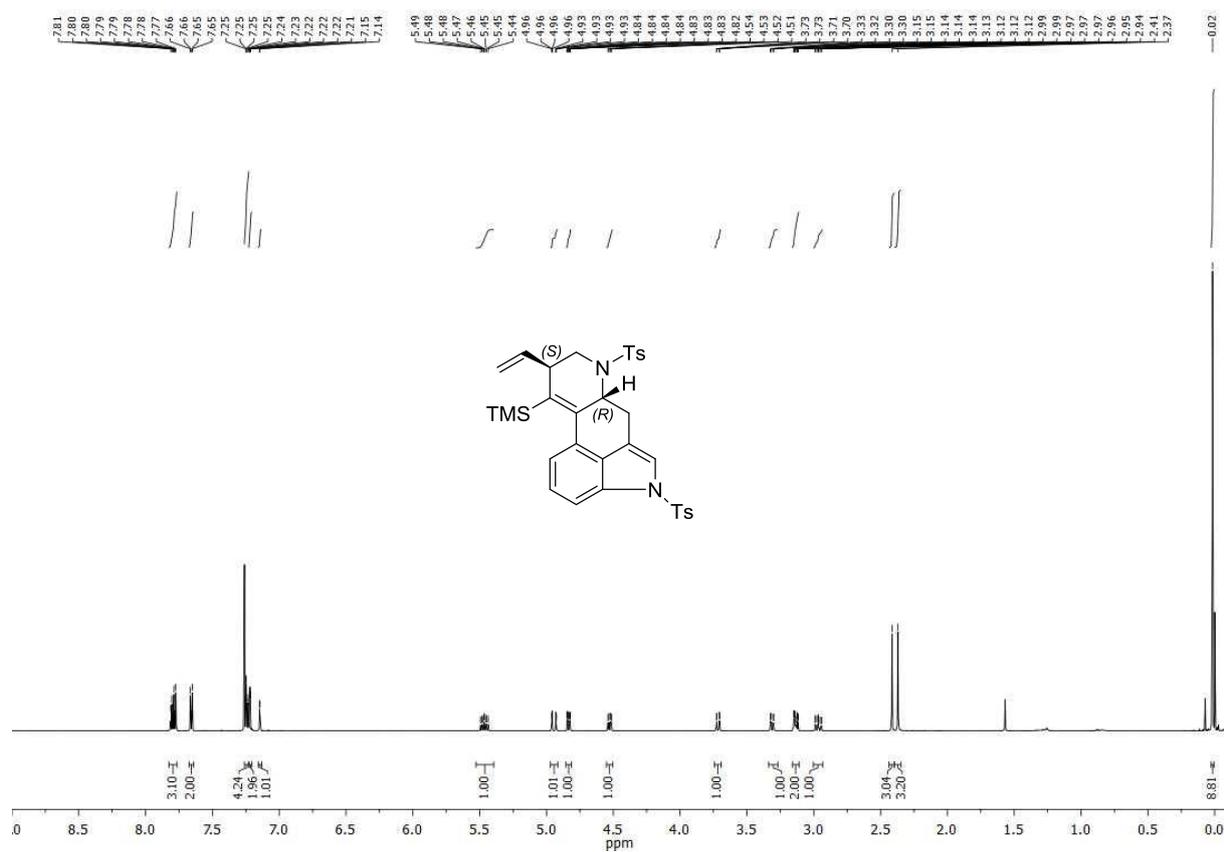
Compound 16



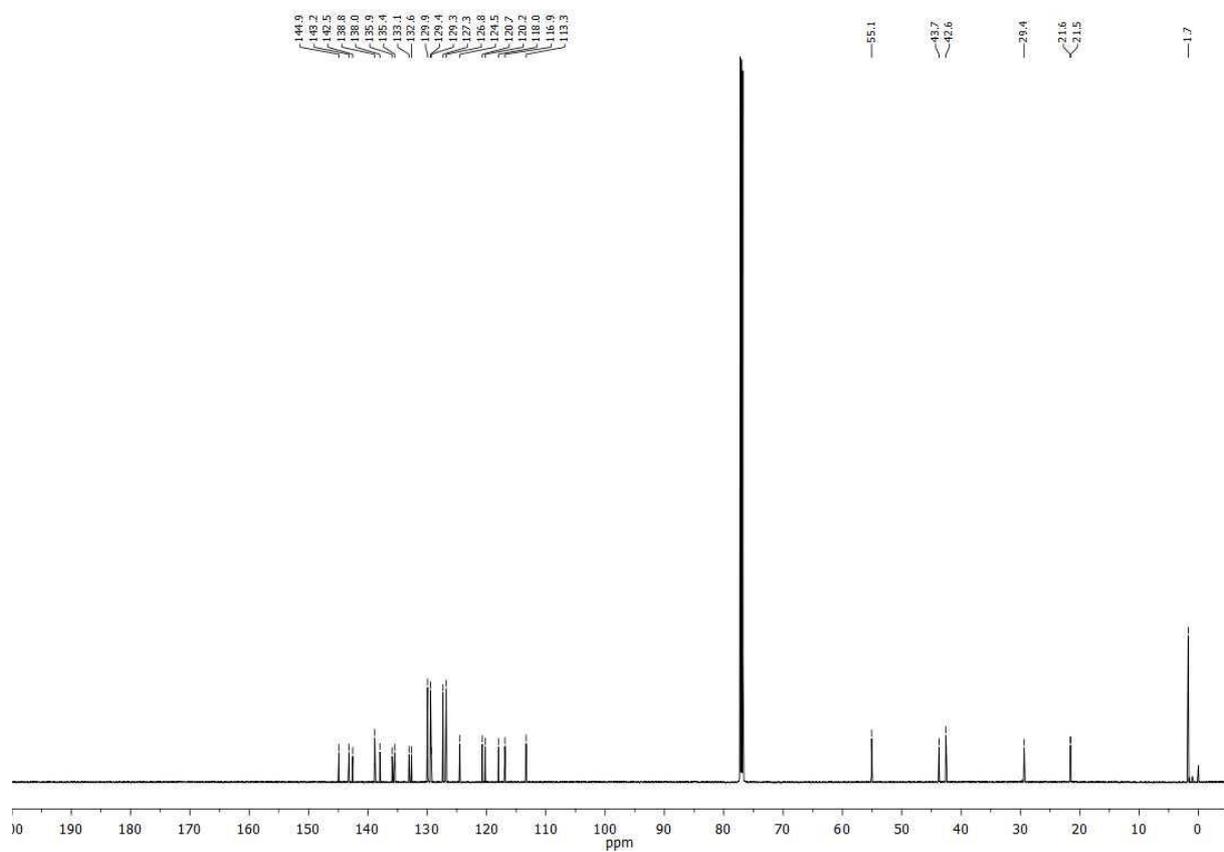
Compound 14



Compound 9

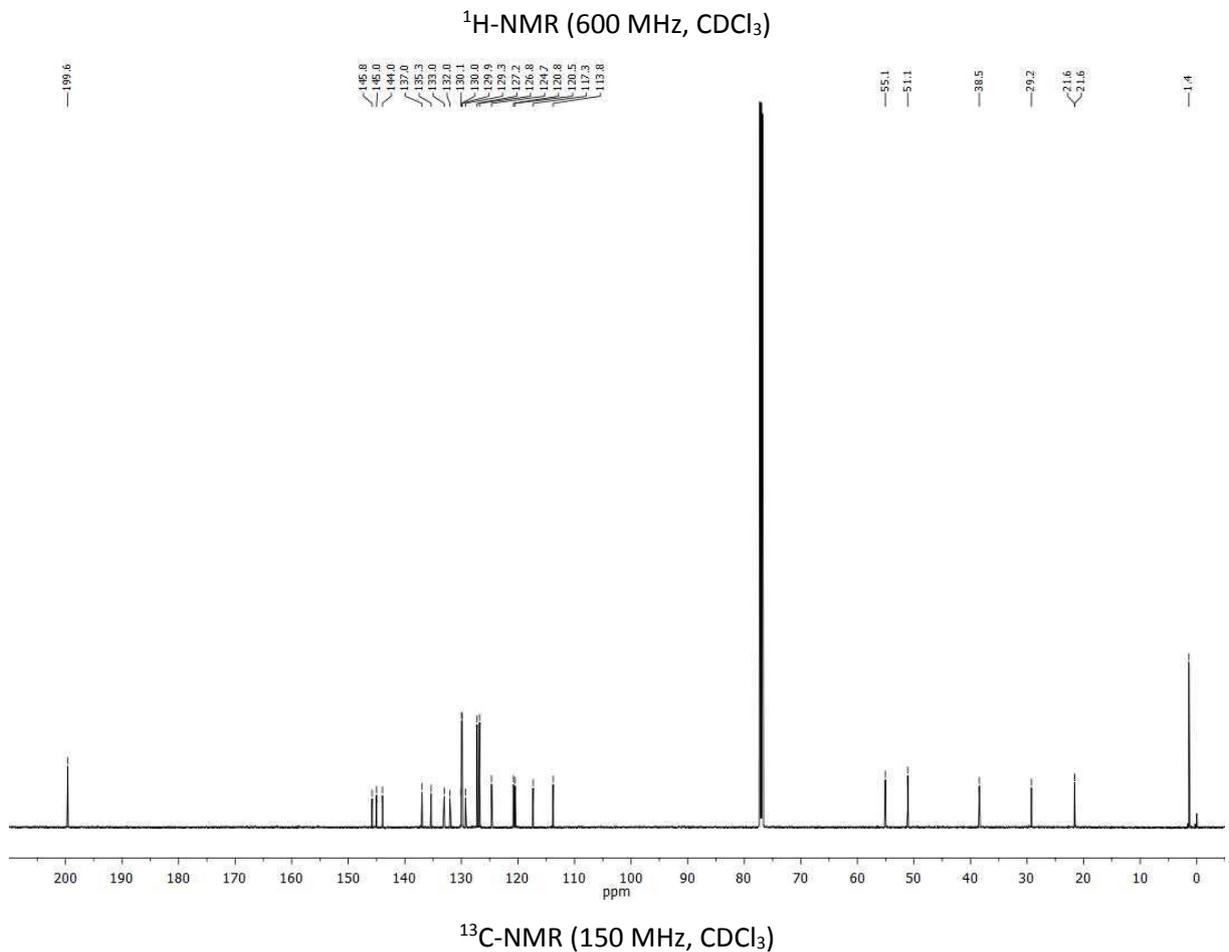
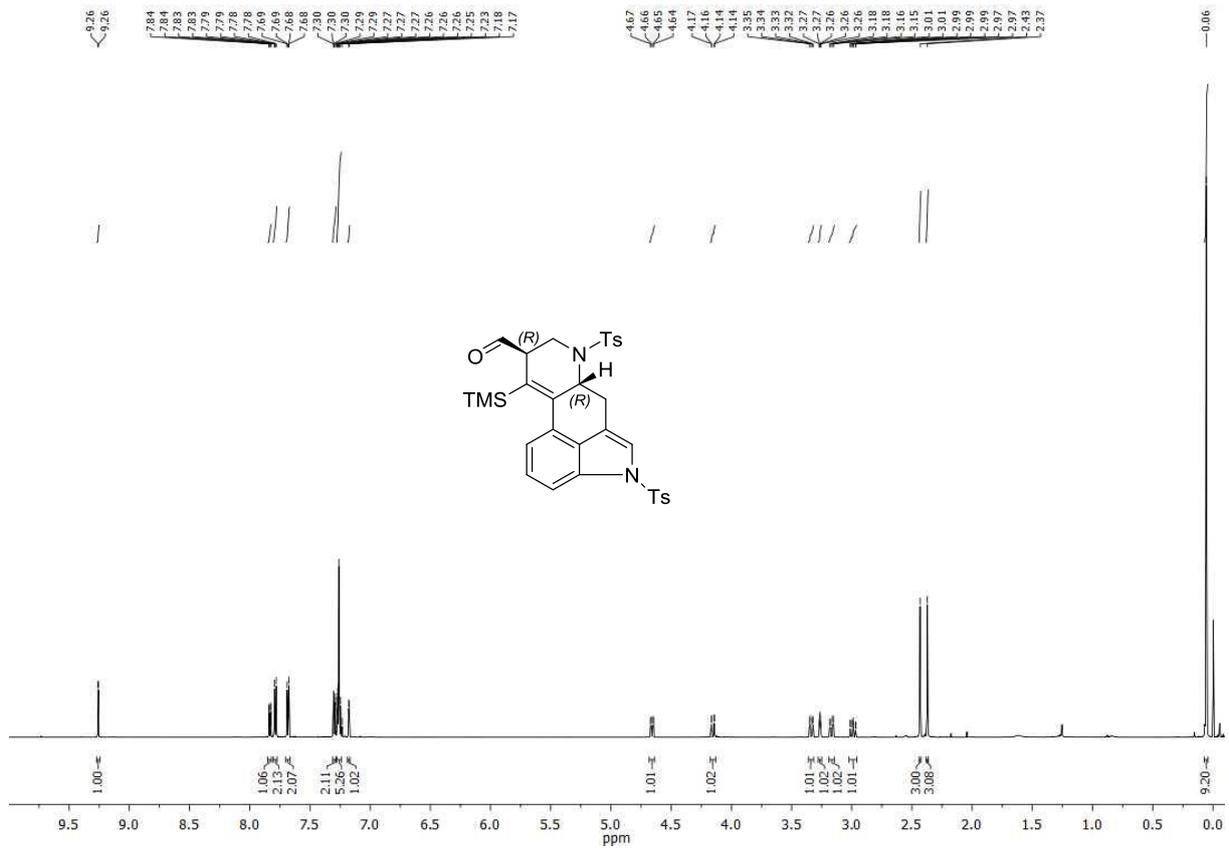


¹H-NMR (600 MHz, CDCl₃)

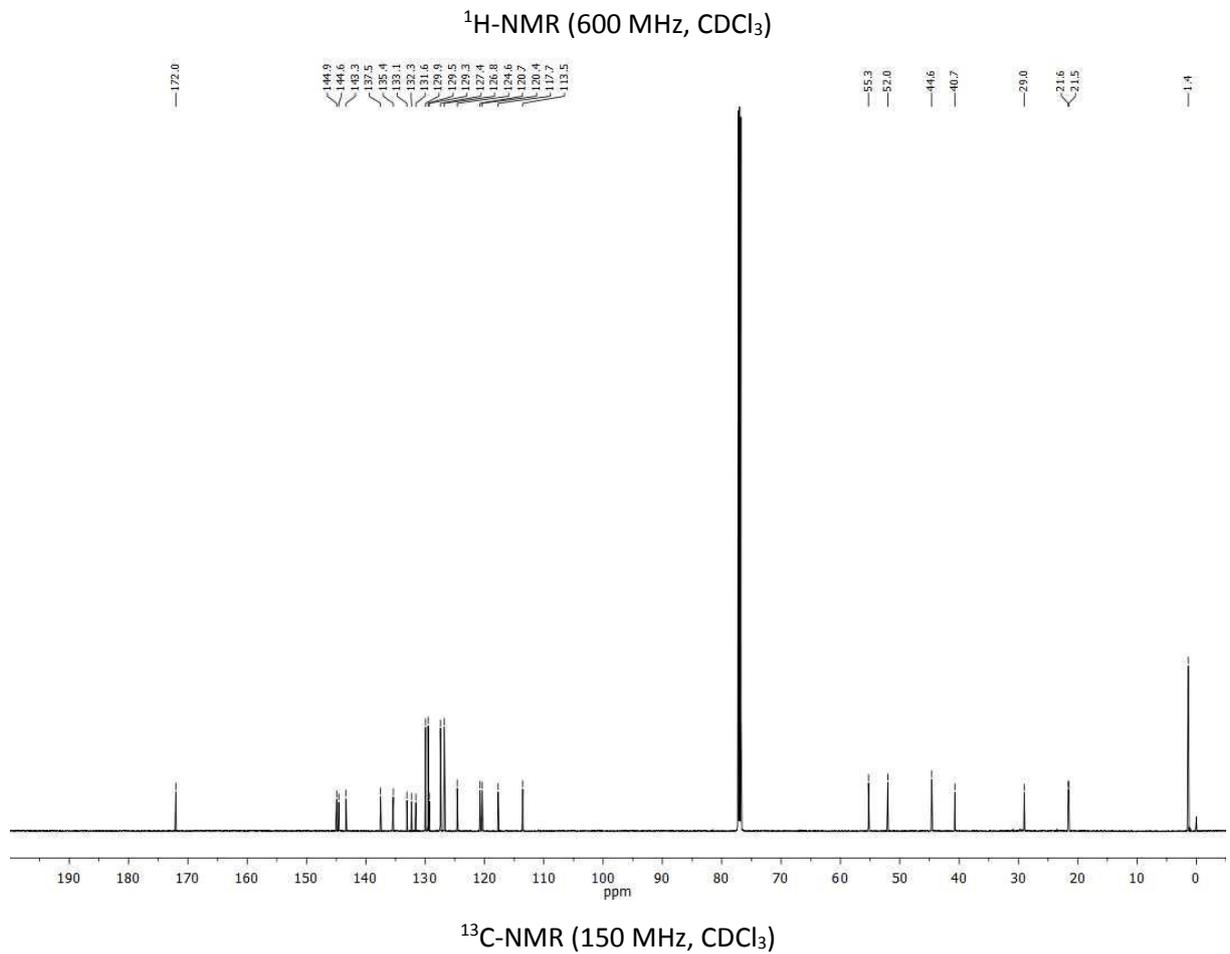
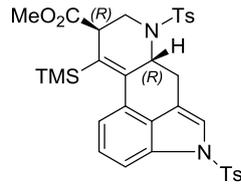
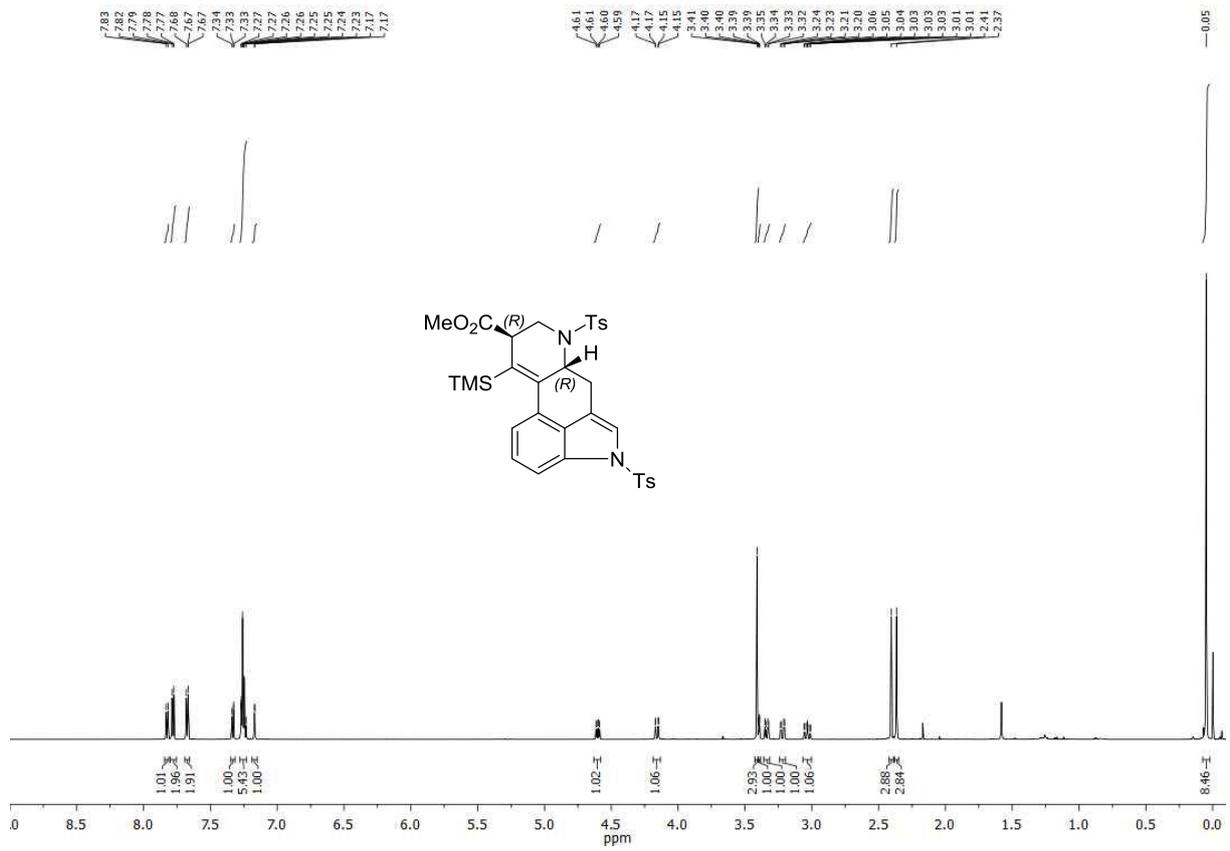


¹³C-NMR (150 MHz, CDCl₃)

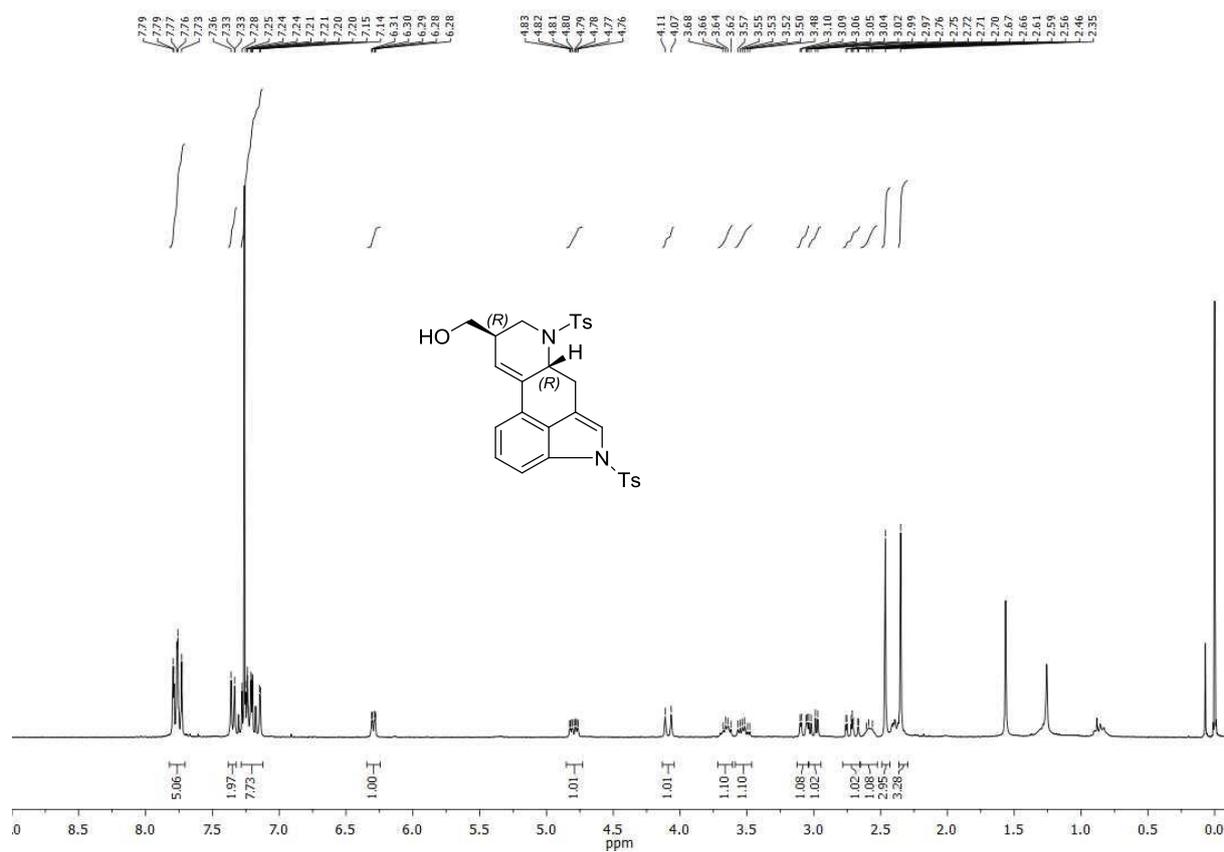
Compound 20



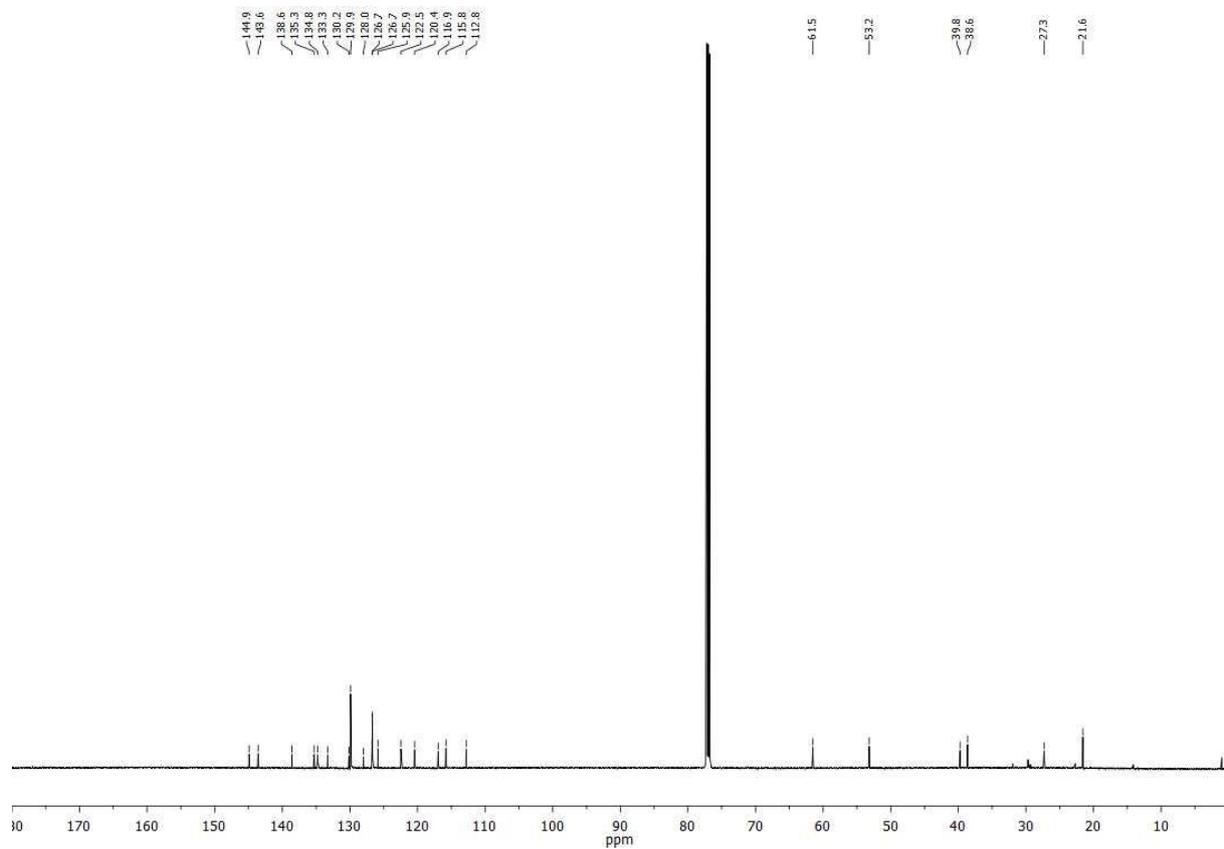
Compound 8



Compound 22



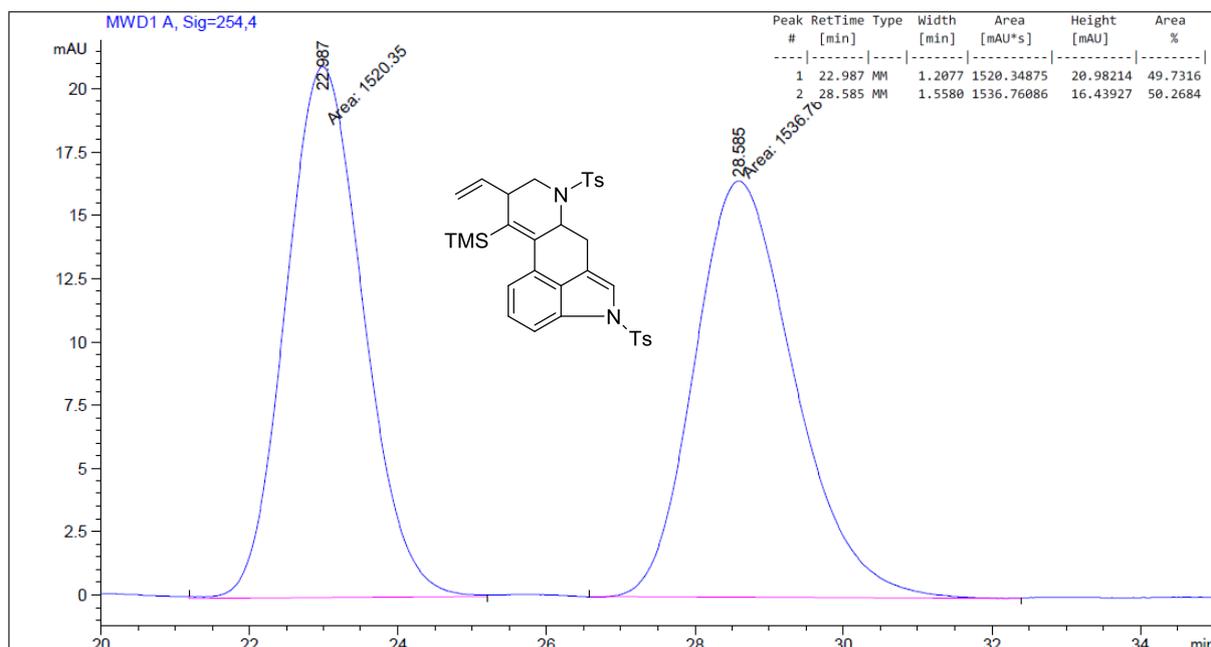
¹H-NMR (300 MHz, CDCl₃)



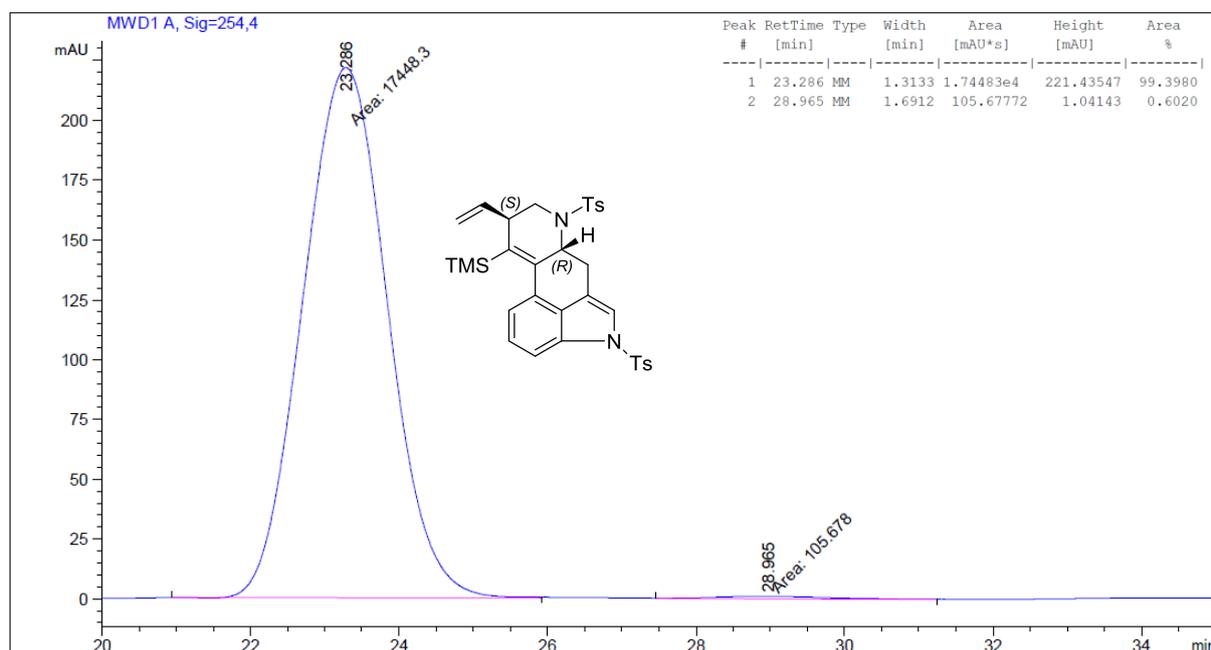
¹³C-NMR (150 MHz, CDCl₃)

HPLC Chromatograms

Chromatogram of compound 9 (rac)



Chromatogram of compound 9



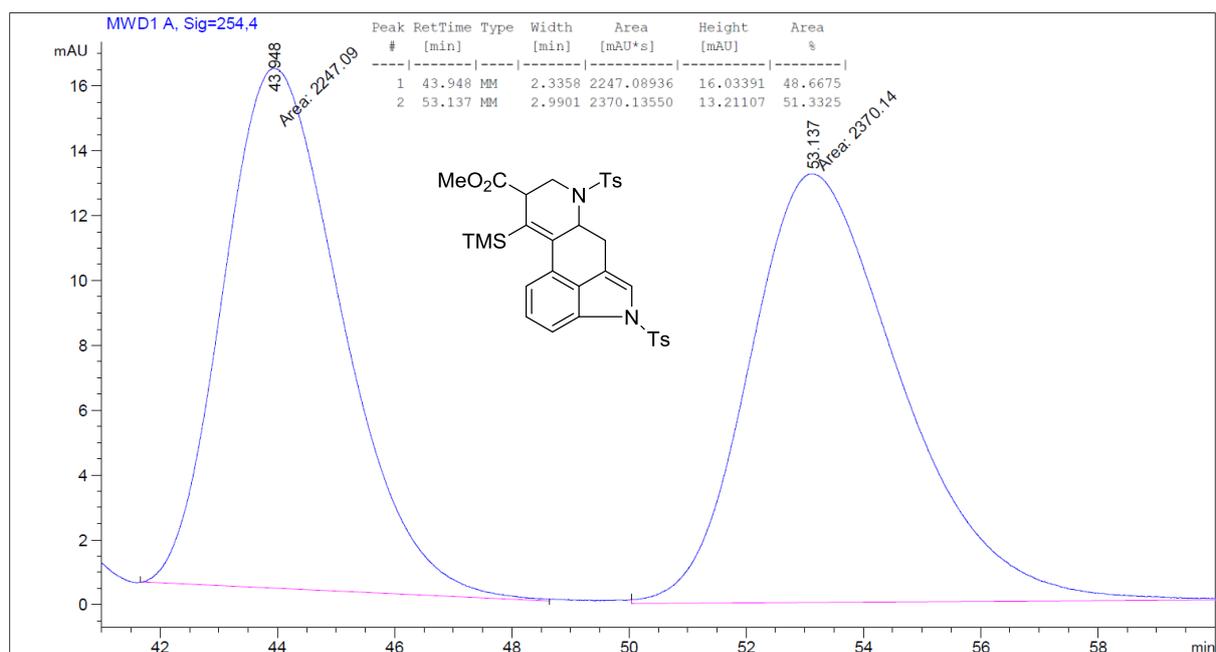
Column: Chiralpak IG

Detection: 254 nm

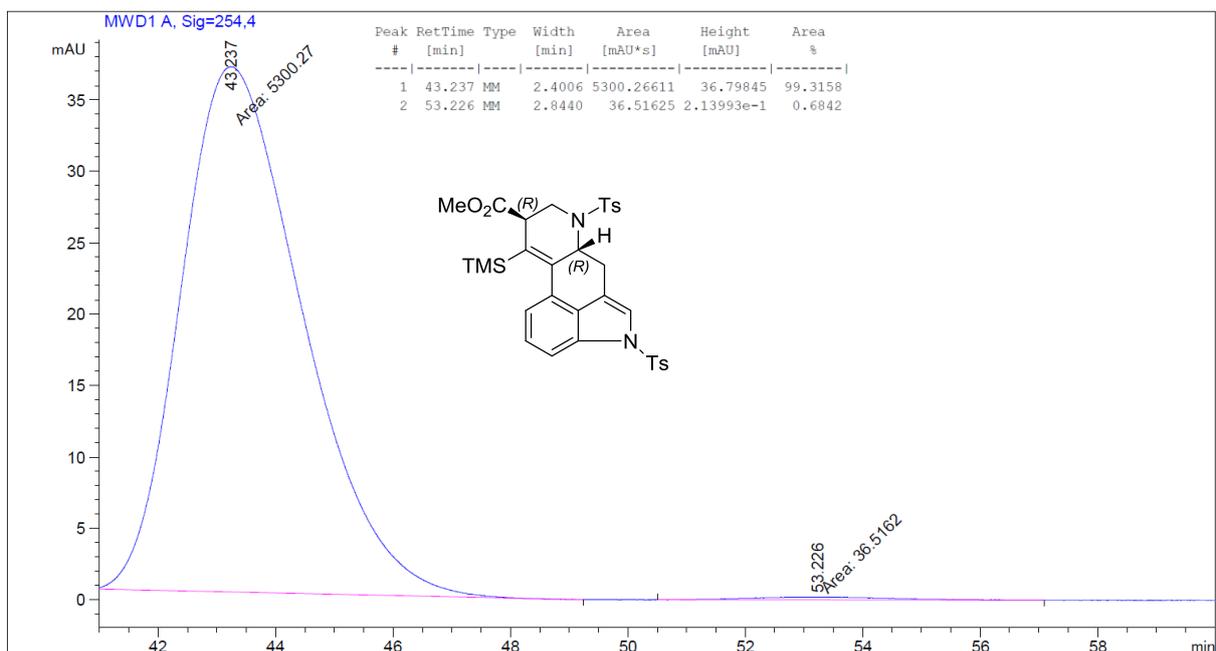
Mobile Phase: MeCN/H₂O = 70:30

Flow Rate: 1.0 ml/min

Chromatogram of compound **8** (rac)



Chromatogram of compound **8**



Column: Chiralpak IG

Detection: 254 nm

Mobile Phase: MeCN/H₂O = 60:40

Flow Rate: 1.0 ml/min

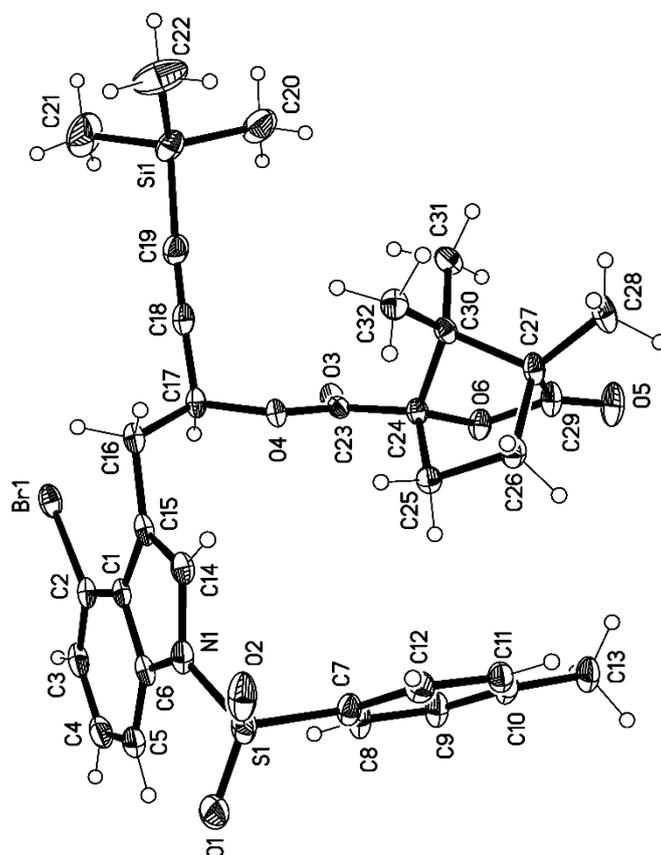
Crystallographic Data

The toluol solvate of **18** crystallizes in space group $P2_1$ with $a = 6.04388(8)$, $b = 22.18157(15)$, $c = 13.72525(15)$ Å, $\beta = 92.9646(12)^\circ$, $V = 1837.58$ Å³, $Z = 2$. Data were registered to $2\theta_{\max} 152^\circ$ at 100 K using Cu $K\alpha$ radiation on an Oxford Diffraction Nova A diffractometer. The structure was refined on F^2 using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany) to $wR2$ 0.0964 (all 7682 unique reflections), $R1$ 0.0365 ($F > 4\sigma(F)$). The toluol molecule was severely disordered and its effects were mathematically subtracted from the observed data using the routine SQUEEZE (part of the PLATON suite; A. L. Spek, University of Utrecht, Netherlands). The Flack parameter refined to $-0.011(12)$.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1535010 (**18**). Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Table 1: Crystallographic data.

Compound	18
Formula	C ₃₉ H ₄₄ BrNO ₆ SSi
<i>M_r</i>	762.81
Cryst. size (mm)	0.25 × 0.10 × 0.03
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁
Temperature (K)	100(2)
Cell constants:	
<i>a</i> (Å)	6.04388(8)
<i>b</i> (Å)	22.18157(15)
<i>c</i> (Å)	13.72525(15)
α (°)	90
β (°)	92.9646(12)
γ (°)	90
<i>V</i> (Å ³)	1837.58(3)
<i>Z</i>	2
<i>D_x</i> (Mg m ⁻³)	1.379
λ (Å)	1.54184
μ (mm ⁻¹)	2.751
Transmissions	0.6768 – 1.0000
<i>F</i> (000)	796
2 θ _{max}	152
Refl. measured	105118
Refl. indep.	7682
<i>R</i> _{int}	0.0626
Parameters	386
Restraints	1
<i>wR</i> (<i>F</i> ² , all refl.)	0.096
<i>R</i> (<i>F</i> , >4 σ (<i>F</i>))	0.037
<i>S</i>	1.02
max. $\Delta\rho$ (e Å ⁻³)	0.86



The structure of compound **18** in the crystal. Ellipsoids correspond to 50% probability levels.

Table 2: Bond lengths [Å] and angles [°] for **18**.

C(1)-C(6)	1.406(4)	C(7)-C(8)	1.370(4)
C(1)-C(2)	1.409(4)	C(7)-C(12)	1.395(4)
C(1)-C(15)	1.451(4)	C(8)-C(9)	1.390(4)
C(2)-C(3)	1.377(4)	C(9)-C(10)	1.390(4)
C(2)-Br(1)	1.897(3)	C(10)-C(11)	1.396(4)
C(3)-C(4)	1.382(5)	C(10)-C(13)	1.513(4)
C(4)-C(5)	1.396(5)	C(11)-C(12)	1.392(4)
C(5)-C(6)	1.391(4)	C(14)-C(15)	1.352(4)
C(6)-N(1)	1.418(4)	C(15)-C(16)	1.491(4)
N(1)-C(14)	1.398(4)	C(16)-C(17)	1.533(4)
N(1)-S(1)	1.664(2)	C(17)-C(18)	1.454(4)
S(1)-O(1)	1.427(3)	C(17)-O(4)	1.461(3)
S(1)-O(2)	1.429(3)	C(18)-C(19)	1.218(4)
S(1)-C(7)	1.762(3)	C(19)-Si(1)	1.843(3)
Si(1)-C(20)	1.837(4)	N(1)-S(1)-C(7)	105.22(13)
Si(1)-C(22)	1.846(5)	C(8)-C(7)-C(12)	121.5(3)
Si(1)-C(21)	1.857(5)	C(8)-C(7)-S(1)	119.3(2)

C(23)-O(3)	1.197(3)	C(12)-C(7)-S(1)	119.2(2)
C(23)-O(4)	1.346(3)	C(7)-C(8)-C(9)	119.2(3)
C(23)-C(24)	1.502(3)	C(8)-C(9)-C(10)	121.2(3)
C(24)-O(6)	1.457(3)	C(9)-C(10)-C(11)	118.7(3)
C(24)-C(25)	1.529(3)	C(9)-C(10)-C(13)	120.8(3)
C(24)-C(30)	1.559(3)	C(11)-C(10)-C(13)	120.5(3)
C(25)-C(26)	1.543(4)	C(12)-C(11)-C(10)	120.8(3)
C(26)-C(27)	1.552(4)	C(11)-C(12)-C(7)	118.7(3)
C(27)-C(28)	1.510(4)	C(15)-C(14)-N(1)	110.6(2)
C(27)-C(29)	1.521(4)	C(14)-C(15)-C(1)	106.7(2)
C(27)-C(30)	1.558(3)	C(14)-C(15)-C(16)	123.7(2)
C(29)-O(5)	1.197(4)	C(1)-C(15)-C(16)	129.6(3)
C(29)-O(6)	1.370(3)	C(15)-C(16)-C(17)	112.4(2)
C(30)-C(32)	1.516(4)	C(18)-C(17)-O(4)	109.1(2)
C(30)-C(31)	1.535(4)	C(18)-C(17)-C(16)	113.5(2)
		O(4)-C(17)-C(16)	104.5(2)
C(6)-C(1)-C(2)	116.9(2)	C(19)-C(18)-C(17)	177.7(3)
C(6)-C(1)-C(15)	108.2(2)	C(18)-C(19)-Si(1)	176.9(3)
C(2)-C(1)-C(15)	134.8(3)	C(20)-Si(1)-C(19)	107.55(16)
C(3)-C(2)-C(1)	121.0(3)	C(20)-Si(1)-C(22)	110.3(3)
C(3)-C(2)-Br(1)	117.5(2)	C(19)-Si(1)-C(22)	108.63(17)
C(1)-C(2)-Br(1)	121.5(2)	C(20)-Si(1)-C(21)	111.5(3)
C(2)-C(3)-C(4)	119.9(3)	C(19)-Si(1)-C(21)	109.0(2)
C(3)-C(4)-C(5)	122.0(3)	C(22)-Si(1)-C(21)	109.7(3)
C(6)-C(5)-C(4)	116.8(3)	O(3)-C(23)-O(4)	125.4(2)
C(5)-C(6)-C(1)	123.2(3)	O(3)-C(23)-C(24)	126.3(2)
C(5)-C(6)-N(1)	130.4(3)	O(4)-C(23)-C(24)	108.3(2)
C(1)-C(6)-N(1)	106.4(2)	C(23)-O(4)-C(17)	116.35(19)
C(14)-N(1)-C(6)	108.1(2)	O(6)-C(24)-C(23)	108.24(19)
C(14)-N(1)-S(1)	121.57(19)	O(6)-C(24)-C(25)	105.70(19)
C(6)-N(1)-S(1)	128.4(2)	C(23)-C(24)-C(25)	118.1(2)
O(1)-S(1)-O(2)	121.03(17)	O(6)-C(24)-C(30)	103.06(18)
O(1)-S(1)-N(1)	106.09(15)	C(23)-C(24)-C(30)	115.9(2)
O(2)-S(1)-N(1)	106.06(14)	C(25)-C(24)-C(30)	104.4(2)
O(1)-S(1)-C(7)	108.84(15)	C(24)-C(25)-C(26)	101.3(2)
O(2)-S(1)-C(7)	108.48(15)	C(25)-C(26)-C(27)	103.9(2)
C(28)-C(27)-C(29)	114.4(2)	O(6)-C(29)-C(27)	107.0(2)
C(28)-C(27)-C(26)	116.2(2)	C(32)-C(30)-C(31)	110.0(2)
C(29)-C(27)-C(26)	102.6(2)	C(32)-C(30)-C(27)	115.3(2)

C(28)-C(27)-C(30)	118.6(2)	C(31)-C(30)-C(27)	113.1(2)
C(29)-C(27)-C(30)	99.7(2)	C(32)-C(30)-C(24)	114.6(2)
C(26)-C(27)-C(30)	102.82(19)	C(31)-C(30)-C(24)	112.3(2)
O(5)-C(29)-O(6)	121.9(3)	C(27)-C(30)-C(24)	90.58(18)
O(5)-C(29)-C(27)	131.1(3)	C(29)-O(6)-C(24)	105.9(2)

Table 2: Torsion angles [°] for compound **18**.

C(6)-C(1)-C(2)-C(3)	-2.3(4)
C(15)-C(1)-C(2)-C(3)	176.4(3)
C(6)-C(1)-C(2)-Br(1)	176.73(18)
C(15)-C(1)-C(2)-Br(1)	-4.6(4)
C(1)-C(2)-C(3)-C(4)	1.9(4)
Br(1)-C(2)-C(3)-C(4)	-177.1(2)
C(2)-C(3)-C(4)-C(5)	0.7(4)
C(3)-C(4)-C(5)-C(6)	-2.6(4)
C(4)-C(5)-C(6)-C(1)	2.2(4)
C(4)-C(5)-C(6)-N(1)	-177.4(3)
C(2)-C(1)-C(6)-C(5)	0.2(4)
C(15)-C(1)-C(6)-C(5)	-178.8(2)
C(2)-C(1)-C(6)-N(1)	179.9(2)
C(15)-C(1)-C(6)-N(1)	0.9(3)
C(5)-C(6)-N(1)-C(14)	177.6(3)
C(1)-C(6)-N(1)-C(14)	-2.1(3)
C(5)-C(6)-N(1)-S(1)	13.7(4)
C(1)-C(6)-N(1)-S(1)	-166.03(19)
C(14)-N(1)-S(1)-O(1)	168.8(2)
C(6)-N(1)-S(1)-O(1)	-29.1(3)
C(14)-N(1)-S(1)-O(2)	39.0(2)
C(6)-N(1)-S(1)-O(2)	-159.0(2)
C(14)-N(1)-S(1)-C(7)	-75.9(2)
C(6)-N(1)-S(1)-C(7)	86.1(2)
O(1)-S(1)-C(7)-C(8)	55.4(3)
O(2)-S(1)-C(7)-C(8)	-171.1(2)
N(1)-S(1)-C(7)-C(8)	-57.9(3)
O(1)-S(1)-C(7)-C(12)	-123.3(2)
O(2)-S(1)-C(7)-C(12)	10.2(3)
N(1)-S(1)-C(7)-C(12)	123.3(2)
C(12)-C(7)-C(8)-C(9)	0.1(5)
S(1)-C(7)-C(8)-C(9)	-178.7(3)
C(7)-C(8)-C(9)-C(10)	0.1(5)
C(8)-C(9)-C(10)-C(11)	-0.1(5)
C(8)-C(9)-C(10)-C(13)	-177.4(3)
C(9)-C(10)-C(11)-C(12)	-0.2(4)
C(13)-C(10)-C(11)-C(12)	177.2(3)

C(10)-C(11)-C(12)-C(7)	0.4(4)
C(8)-C(7)-C(12)-C(11)	-0.3(4)
S(1)-C(7)-C(12)-C(11)	178.4(2)
C(6)-N(1)-C(14)-C(15)	2.6(3)
S(1)-N(1)-C(14)-C(15)	167.86(19)
N(1)-C(14)-C(15)-C(1)	-2.0(3)
N(1)-C(14)-C(15)-C(16)	179.5(2)
C(6)-C(1)-C(15)-C(14)	0.7(3)
C(2)-C(1)-C(15)-C(14)	-178.1(3)
C(6)-C(1)-C(15)-C(16)	179.0(2)
C(2)-C(1)-C(15)-C(16)	0.2(5)
C(14)-C(15)-C(16)-C(17)	102.5(3)
C(1)-C(15)-C(16)-C(17)	-75.6(3)
C(15)-C(16)-C(17)-C(18)	175.4(2)
C(15)-C(16)-C(17)-O(4)	-65.8(3)
O(3)-C(23)-O(4)-C(17)	-2.7(3)
C(24)-C(23)-O(4)-C(17)	174.77(18)
C(18)-C(17)-O(4)-C(23)	-75.4(3)
C(16)-C(17)-O(4)-C(23)	162.90(19)
O(3)-C(23)-C(24)-O(6)	-15.9(3)
O(4)-C(23)-C(24)-O(6)	166.58(18)
O(3)-C(23)-C(24)-C(25)	-135.9(3)
O(4)-C(23)-C(24)-C(25)	46.6(3)
O(3)-C(23)-C(24)-C(30)	99.2(3)
O(4)-C(23)-C(24)-C(30)	-78.3(2)
O(6)-C(24)-C(25)-C(26)	69.9(2)
C(23)-C(24)-C(25)-C(26)	-168.9(2)
C(30)-C(24)-C(25)-C(26)	-38.5(2)
C(24)-C(25)-C(26)-C(27)	2.0(3)
C(25)-C(26)-C(27)-C(28)	165.9(2)
C(25)-C(26)-C(27)-C(29)	-68.5(2)
C(25)-C(26)-C(27)-C(30)	34.7(3)
C(28)-C(27)-C(29)-O(5)	19.5(5)
C(26)-C(27)-C(29)-O(5)	-107.2(4)
C(30)-C(27)-C(29)-O(5)	147.2(4)
C(28)-C(27)-C(29)-O(6)	-163.4(2)
C(26)-C(27)-C(29)-O(6)	69.9(3)
C(30)-C(27)-C(29)-O(6)	-35.7(3)
C(28)-C(27)-C(30)-C(32)	-66.3(3)

C(29)-C(27)-C(30)-C(32)	168.8(2)
C(26)-C(27)-C(30)-C(32)	63.4(3)
C(28)-C(27)-C(30)-C(31)	61.4(3)
C(29)-C(27)-C(30)-C(31)	-63.5(3)
C(26)-C(27)-C(30)-C(31)	-168.9(2)
C(28)-C(27)-C(30)-C(24)	176.0(2)
C(29)-C(27)-C(30)-C(24)	51.1(2)
C(26)-C(27)-C(30)-C(24)	-54.3(2)
O(6)-C(24)-C(30)-C(32)	-171.3(2)
C(23)-C(24)-C(30)-C(32)	70.7(3)
C(25)-C(24)-C(30)-C(32)	-61.1(3)
O(6)-C(24)-C(30)-C(31)	62.3(3)
C(23)-C(24)-C(30)-C(31)	-55.7(3)
C(25)-C(24)-C(30)-C(31)	172.6(2)
O(6)-C(24)-C(30)-C(27)	-53.0(2)
C(23)-C(24)-C(30)-C(27)	-171.1(2)
C(25)-C(24)-C(30)-C(27)	57.2(2)
O(5)-C(29)-O(6)-C(24)	178.1(3)
C(27)-C(29)-O(6)-C(24)	0.7(3)
C(23)-C(24)-O(6)-C(29)	158.3(2)
C(25)-C(24)-O(6)-C(29)	-74.2(2)
C(30)-C(24)-O(6)-C(29)	35.0(3)

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