Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis of the indeno[1,2-*b*]indole core of janthitrem B

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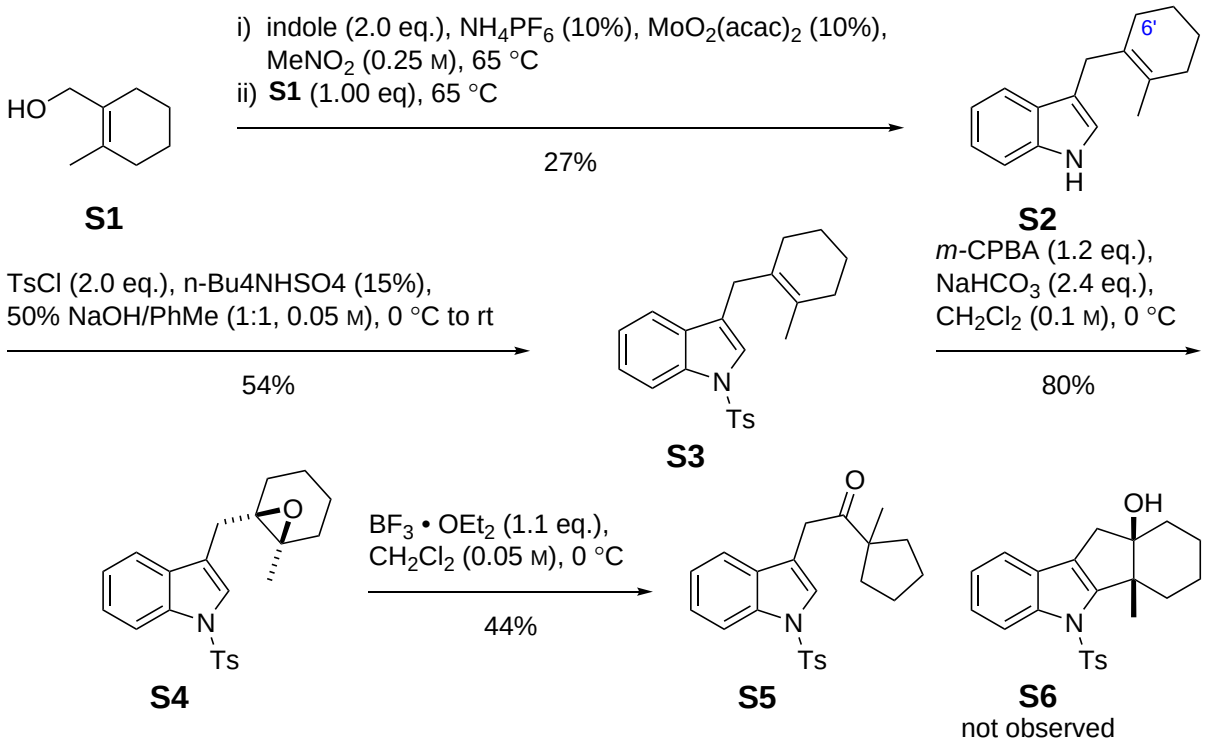
Contents

1.1 Synthesis of cyclopentadiene 9

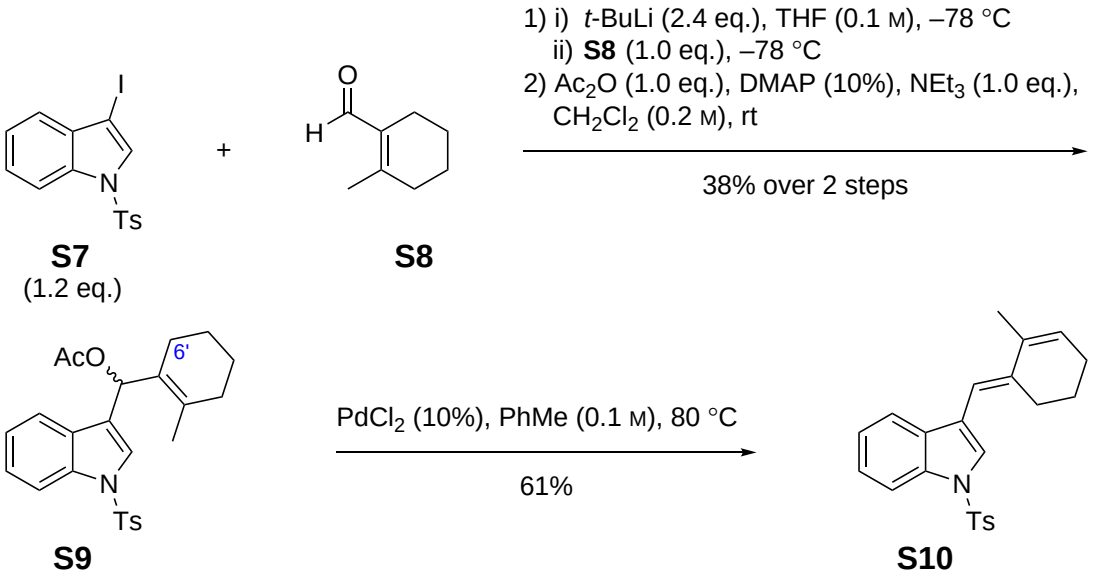
After considerable experimentation, we managed to allylate indole with 2-methylcyclohexenylmethanol (**S1**) in the presence of $MoO_2(acac)_2/NH_4PF_6$ (10%) in nitromethaneL[1] in modest yield (27%), whereby many side products formed (Scheme S1). We exposed purified allylindole **S2** to various Lewis acids and observed only decomposition (TMSOTf, TBSOTf, TIPSOTf, $AlCl_3$, $SnCl_4$) or no conversion ($Au(PPh_3)NTf_2$, $AgPF_6$). Our case differs from Dethe's examples, as the carbon next to the double bond (C-6') is secondary, while the published examples only contained quaternary carbons. We decided to N-tosylate the rather sensitive 3-allylated product **S2** to the more stable compound **S3** and attempted an epoxidation/ring opening/cyclization sequence. After tosyl protection, epoxidation with *m*-CPBA afforded cyclohexene oxide **S4** without affecting the indole nucleus. Upon exposure to $BF_3 \bullet OEt_2$, epoxide **S4** did not form the desired tetracycle **S6**, but underwent ring contraction to acyl cyclopentane **S5** by Meinwald rearrangement. The desired cyclization is probably not prevented by the N-tosyl group, since the free indole reacted in the same manner. In orienting experiments, we obtained the analogous epoxide and acylcyclopentane, which could not be fully characterized because of inseparable, colored by-products.



Scheme S1. Attempted epoxidation/ring opening/cyclization sequence to synthesize indeno[1,2-*b*]indole **S5**.

[1] H. Yang, L. Fang, M. Zhang, C. Zhu, *Eur. J. Org. Chem.* **2009**, *2009*, 666–672.

Ramasastry and coworkers reported the Pd-catalyzed 5-endo-trig cyclization of bisallylacetates affording N-tosylated indeno[*b*]indoles.[2] Thus, we synthesized the new bisallylacetate **S9** by hydroxyalkylation of 3-iodo-*N*-tosylindole with aldehyde **S8**, after iodine/Li exchange, followed by acetylation (Scheme S2). When the acid-sensitive allylic acetate **S9** was treated with $PdCl_2$ (10%) in toluene (80 °C), we did not observe any cyclization. Instead, elimination of HOAc had occurred, yielding dienylindole **S10** with a C-2'/C-3' cyclohexene double bond. The difference from the published case is again the absence of the geminal methyl groups at C-6', which may induce a conformation of the intermediate η^3-Pd complex, which favors cyclization.

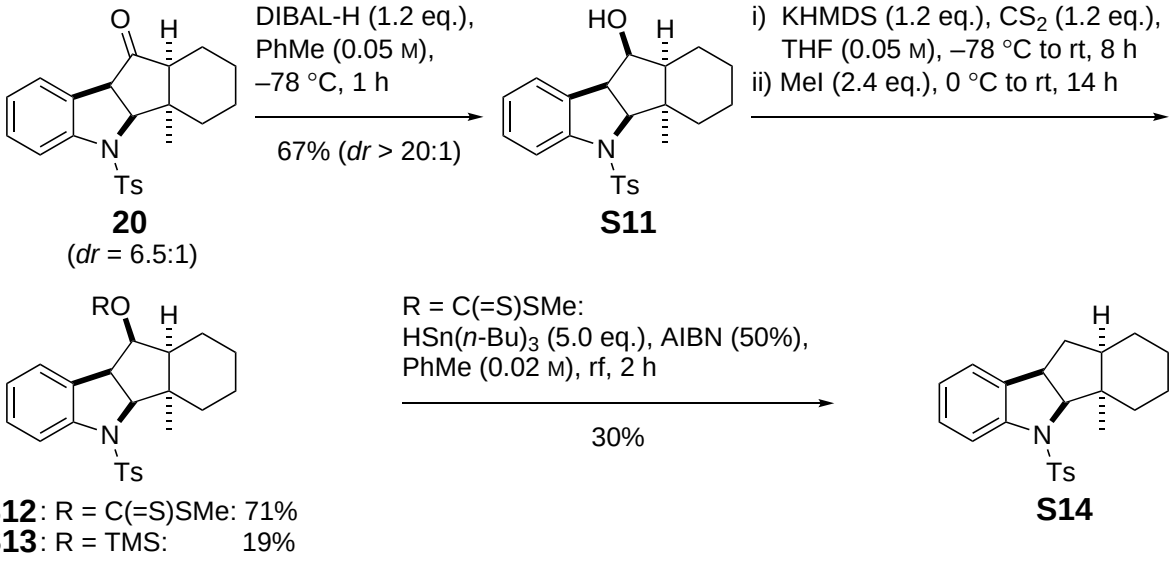


Scheme S2. Synthesis and attempted cyclizations of bisallylacetate **S9**.

[2] B. Singh, S. K. Bankar, K. Kumar, S. S. V. Ramasastry, *Chem. Sci.* **2020**, *11*, 4948–4953.

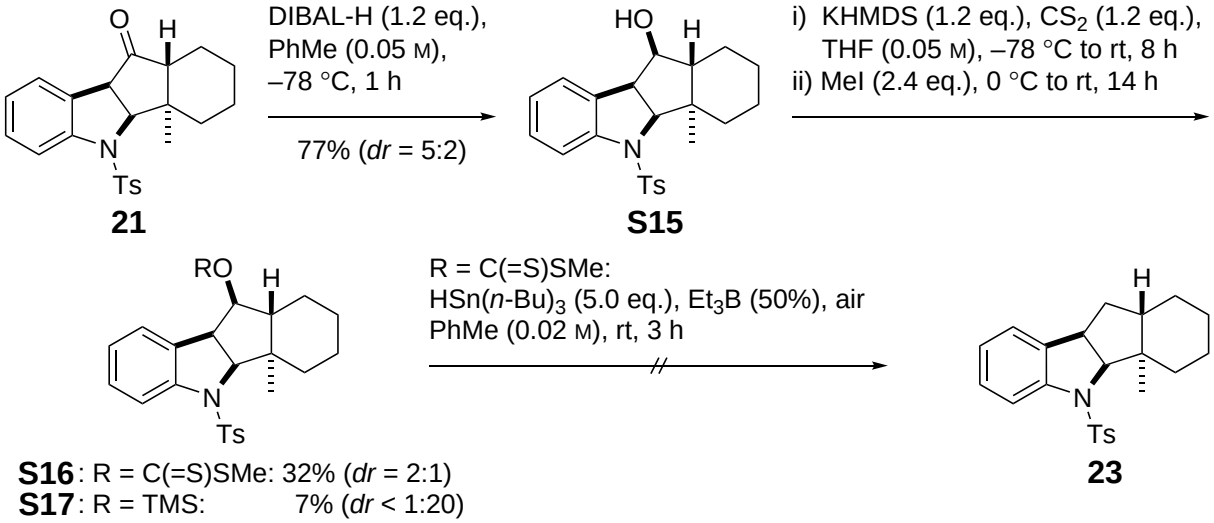
1.2 Attempted Barton-McCombie deoxygenation

Orienting experiments on a Barton-McCombie deoxygenation of *trans*-hydrindane **21** were conducted with the *cis*-isomer **20** in order to save precious material. DIBAL-H reduction of **20** occurred from the convex side and afforded alcohol **S11** diastereoselectively (Scheme S3). Conversion to xanthate **S12** was accompanied by the stable trimethylsilyl ether **S13**. Radical reduction ($HSn(n\text{-}Bu)_3$/AIBN) gave *cis*-hydrindane **S14**, albeit in modest yield (30%).



Scheme S3. Barton-McCombie deoxygenation of *cis*-hydrindanone **20**.

Next, we applied the same sequence with *trans*-hydrindanone **21**. DIBAL-H reduction afforded the secondary alcohol **S15**, this time as a mixture (5:2) of diastereomers (Scheme S4). These were converted into xanthates **S16** in low yield. Disastrously, the radical reduction employing Et_3B as radical starter to lower the reaction temperature, resulted only in decomposition. Since the conversion of alcohol **S15** into xanthate **S16** was already sluggish, we did not pursue this strategy any further.



Scheme S4. Attempted Barton-McCombie deoxygenation of *trans*-hydrindanone **21**.

2.1 General Methods

Air- and moisture-sensitive liquids were transferred by syringe. Analytical thin-layer chromatography (TLC) was performed using aluminum plates pre-coated with silica gel (silica gel 60 F_{254}, Merck or silica gel 60 RP-18 F_{254S}, Merck). TLC plates were visualized by exposure to ultraviolet light (λ = 254 nm) and then were stained by submersion in a vanillin solution (6.8 g vanillin dissolved in 200 mL EtOH and 2.5 mL H_2SO_4) followed by a brief heating. Concentration under reduced pressure was performed by rotary evaporation at 50 °C, unless otherwise noted. Flash column chromatography was performed on Merck silica gel 60 (40 – 63 µm). Column height was 15 cm, unless otherwise noted.

2.2 Materials

Chemicals were purchased from commercial suppliers and used without further purification. Solvents were dried prior to use by using standard methods[3], unless otherwise noted.

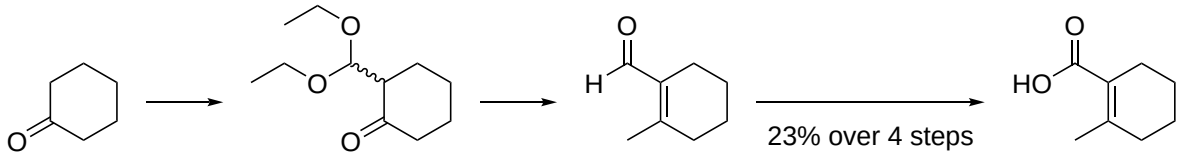
2.3 Instrumentation

NMR spectra were recorded with a Bruker AV III 400 (400 MHz for ^{1}H) or a Bruker AVIIIHD500 (500 MHz for ^{1}H) spectrometer at 299 K. ^{11}B, ^{13}C and ^{19}F NMR spectra were recorded with broadband ^{1}H-decoupling. ^{1}H chemical shifts are given in ppm (δ scale) relative to tetramethylsilane with tetramethylsilane as the internal standard (^{1}H = 0.00 ppm). ^{13}C chemical shifts are given in ppm (δ scale) relative to tetramethylsilane with the residual solvent peak as the internal standard (^{13}C = 77.16 ppm ($CDCl_3$), 128.06 ppm (C_6D_6)). The signals were assigned by ^{1}H,^{13}C-HSQC-, ^{1}H,^{13}C-HMBC-, ^{1}H,^{1}H-COSY-, and ^{1}H,^{1}H-NOESY-experiments. The multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sext (sextet), sept (septet), m (multiplet) or a combination thereof.
Mass spectra were obtained with a ThermoFinnigan MAT95XL or a ThermoFisher Scientific (LTQ-Orbitrap Velos) spectrometer.
IR spectra were recorded with a Bruker Tensor 27 spectrometer using diamond ATR technique.
UV/Vis spectra were measured with a Varian Cary 100 Bio UV/Vis spectrometer.
Irradiations were carried out in a Rayonet (RPR-200) reactor equipped with 16 x RPR-3000Å (λ_{max} = 300 nm) or 16 x RPR-3500Å (λ_{max} = 350 nm) using a self-made flow reactor. The flow reactor (Figure S1) consists of FEP tubing (inner diameter: 0.8 mm, outer diameter:1.6 mm, length: 10 m) wrapped around a 2.5 L amber glass bottle (outer diameter: 13 cm). The solutions were pumped through the reactor with a syringe or HPLC pump and collected in a flask wrapped in aluminum foil.

[3] W. L. F. Armarego, *Purification of laboratory chemicals*, Eighth edition / W.L.F. Armarego, Butterworth-Heinemann, Amsterdam, **2017**.

Figure S1. Flow reactor (left) and flow reactor inside the Rayonet reactor (right).

3.1 2-Methylcyclohex-1-ene-1-carboxylic acid (4)



S18 **S19** **S8** **4**

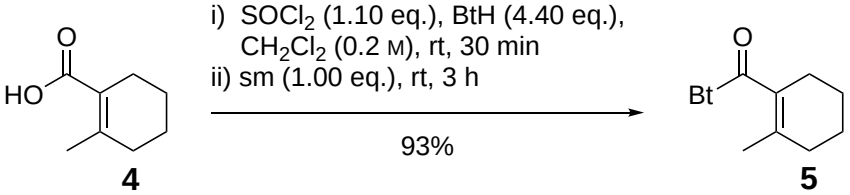
To triethyl orthoformate (67 mL, 400 mmol, 2.00 eq.) under argon was added dropwise a solution of $BF_3 \bullet OEt_2$ (61 mL, 480 mmol, 2.40 eq.) in CH_2Cl_2 (200 mL) at –30 °C. The mixture was stirred at 0 °C for 20 min. Cyclohexanone (**S18**, 21 mL, 200 mmol, 1.00 eq.) was added dropwise at –78 °C. DIPEA (100 mL, 600 mmol, 3.00 eq.) was added dropwise at –78 °C. The solution was stirred at –78 °C for 1 h and poured into sat. $NaHCO_3$ (400 mL), diluted with CH_2Cl_2 (100 mL) and stirred rapidly for 10 min. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x100 mL). The combined organic phases were washed with ice-cold 10% H_2SO_4, H_2O, dried over $MgSO_4$, filtered and concentrated. Distillation (0.8 mbar, oil bath temperature: 120 °C) of the residue afforded the crude ketone **S19** as a yellow oil (25.3 g).

Magnesium turnings (4.60 g, 189 mmol) were suspended in Et_2O (19 mL) under argon. At room temperature MeI (1.0 mL, 16 mmol) was added and the reaction mixture stirred until the exothermic reaction obviously started. A solution of MeI (11 mL, 173 mmol) in Et_2O (48 mL) was added dropwise at 0 °C. The mixture was stirred for 40 min under reflux. A solution of the crude ketone **S19** (25.3 g) in Et_2O (42 mL) was added dropwise at 0 °C and stirred at that temperature for 40 min. The mixture was diluted with Et_2O (42 mL) and stirred for 20 min under reflux. The reaction was quenched by the addition of 1 M HCl (210 mL) at 0 °C. The phases were separated and the aqueous phase was extracted with Et_2O (3x100 mL). The combined organic phases were washed with H_2O, dried over $MgSO_4$, filtered and concentrated. The obtained residue (19.3 g) was dissolved in acetone (76 mL) and 2 M HCl (24 mL). The solution was stirred for 2.5 h under reflux. H_2O (200 mL) was added at room temperature and the mixture was extracted with Et_2O (3x100 mL). The combined organic phases were washed with H_2O and sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Distillation (0.6 mbar, oil bath temperature: 80 °C) of the residue afforded the crude aldehyde **S8** as a colorless oil (10.8 g).

To a solution of the crude aldehyde **S8** (10.8 g) and 2-methyl-2-butene (28 mL, 262 mmol) in *t*-BuOH (260 mL) was added a solution of NaH_2PO_4 (20.9 g, 174 mmol) and $NaClO_2$ (18.9 g, 209 mmol) in H_2O (87 mL) dropwise at room temperature. The mixture was rapidly stirred for 20 h at room temperature. *t*-BuOH was removed under reduced pressure and the pH was adjusted to 3 by the addition of 2 M HCl. The mixture was extracted with TBME (3x200 mL). The combined organic phases were concentrated to about one-tenth of the original volume and extracted with sat. $NaHCO_3$ (5x50 mL). The pH of the combined aqueous phases was adjusted to 3 by the addition of 2 M HCl. The mixture was extracted with TBME (3x100 mL). The combined organic phases were washed with H_2O and sat. NaCl, dried over $MgSO_4$, filtered and concentrated. 2-Methylcyclohex-1-ene-1-carboxylic acid (**4**) was obtained as a colorless solid (6.35 g, 45.3 mmol, 23% over 4 steps). Analytical data are in agreement with the previously reported.[4]

[4] R. K. Dieter, Y. Jenkitkasemwong, J. W. Dieter, *J. Org. Chem.* **1984**, *49*, 3183–3195.

3.2 (1*H*-Benzo[*d*][1,2,3]triazol-1-yl)(2-methylcyclohex-1-en-1-yl)methanone (5)



4 **5**

To a solution of benzotriazole (13.2 g, 111 mmol, 4.40 eq.) in CH_2Cl_2 (130 mL) was added $SOCl_2$ (2.0 mL, 27.6 mmol, 1.10 eq.) dropwise at room temperature. The solution was stirred for 30 min at room temperature. Carboxylic acid **4** (3.52 g, 25.1 mmol, 1.00 eq.) was added and the mixture stirred for 3 h at room temperature. The suspension was filtered through a pad of silica gel (rinsed with CH_2Cl_2) and the filtrate concentrated. The residue was dissolved in TBME (100 mL) and washed with sat. $NaHCO_3$ (3x30 mL), dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (20:1)] afforded *N*-acylbenzotriazole **5** as a colorless solid (5.66 g, 23.5 mmol, 93%).

TLC [petroleum ether/EtOAc (8:1)]: R_f = 0.56 [vanillin: yellow].

^{1}H NMR (500 MHz, $CDCl_3$, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 8.35 – 8.30 (m, 1 H, 7-*H*), 8.16 – 8.10 (m, 1 H, 4-*H*), 7.69 – 7.64 (m, 1 H, 6-*H*), 7.54 – 7.48 (m, 1 H, 5-*H*), 2.51 – 2.44 (m, 2 H, 6*-*H*), 2.25 – 2.16 (m, 2 H, 3*-*H*), 1.82 – 1.75 (m, 4 H, 4*-*H*, 5*-*H*), 1.73 – 1.69 (m, 3 H, 2*-CH_3).

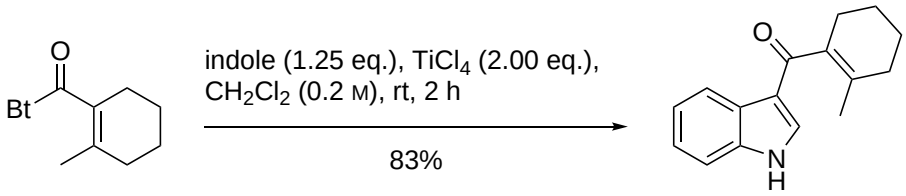
^{13}C NMR (126 MHz, $CDCl_3$, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 170.6 (1 C, 1-(*C*=O)-1*), 146.3 (1 C, *C*-3a*), 141.0 (1 C, *C*-2*), 131.5 (1 C, *C*-7a*), 130.3 (1 C, *C*-6), 127.2 (1 C, *C*-1*), 126.2 (1 C, *C*-5), 120.2 (1 C, *C*-4), 114.7 (1 C, *C*-7), 31.6 (1 C, *C*-3*), 27.6 (1 C, *C*-6*), 22.3 (1 C, *C*-4*), 22.2 (1 C, *C*-5*), 21.6 (1 C, 2*-*C*H_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2935 (m), 2853 (m), 2165 (m), 2024 (m), 1974 (m), 1707 (s), 1670 (m), 1600 (m), 1482 (m), 1442 (m), 1363 (s), 1319 (m), 1282 (s), 1227 (m), 1191 (m), 1135 (m), 1097 (m), 1040 (s), 1005 (m), 929 (s), 876 (s), 786 (s), 742 (s), 624 (s), 546 (m).

UV/Vis (THF): λ_{max} (lg ε) = 299 (3.40), 266 (3.31).

ESI-HRMS: calculated $[C_{14}H_{15}N_3O+Na]^+$: 264.11073
found: 264.11076 (0.11 ppm).

3.3 (1*H*-Indol-3-yl)(2-methylcyclohex-1-en-1-yl)methanone (6)

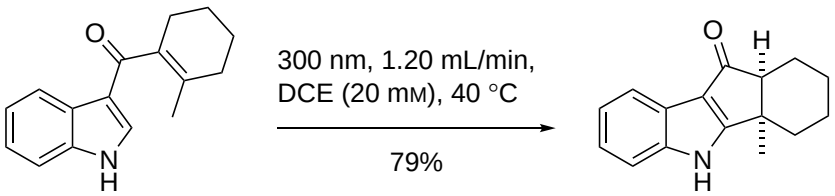


5 **6**

To a solution of *N*-acyl benzotriazole **5** (2.4 g, 10 mmol, 1.00 eq.) and indole (1.46 g, 12.5 mmol, 1.25 eq.) in CH_2Cl_2 (50 mL) was added $TiCl_4$ (2.2 mL, 20 mmol, 2.00 eq.) dropwise at room temperature. The solution was stirred for 2 h at room temperature. The reaction was quenched by the addition of 25% NaOH (13 mL, 100 mmol, 10.0 eq.) at 0 °C. The mixture was stirred rapidly while warming up to room temperature. The biphasic mixture was filtered through a pad of Celite 545 (rinsed with CH_2Cl_2). The filtrate was dried over $MgSO_4$, filtered and concentrated. The residue was filtered through a pad of silica gel (rinsed with $CHCl_3$/EtOAc 4:1) and the filtrate

concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (6:1) to (4:1) to (2:1) to (1:1)] afforded ketone **6** as an off-white solid (1.99 g, 8.32 mmol, 83%).
TLC [petroleum ether/EtOAc (2:1)]: R_f = 0.43 [vanillin: red].
^{1}H NMR (400 MHz, $CDCl_3$, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 9.16 (s, 1 H, 1-*H*), 8.41 – 8.33 (m, 1 H, 4-*H*), 7.75 (d, *J* = 3.0 Hz, 1 H, 2-*H*), 7.46 – 7.40 (m, 1 H, 7-*H*), 7.33 – 7.26 (m, 2 H, 5-*H*, 6-*H*), 2.36 – 2.26 (m, 2 H, 6*-*H*), 2.13 – 2.04 (m, 2 H, 3*-*H*), 1.80 – 1.66 (m, 4 H, 4*-*H*, 5*-*H*), 1.63 – 1.61 (m, 3 H, 2*-CH_3).
^{13}C NMR (101 MHz, $CDCl_3$, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 197.4 (1 C, 3-(*C*=O)-1*), 136.9 (1 C, *C*-7a), 134.5 (1 C, *C*-1*), 133.8 (1 C, *C*-2), 132.0 (1 C, *C*-2*), 125.6 (1 C, *C*-3a), 123.8 (1 C, *C*-6), 122.8 (1 C, *C*-5), 122.3 (1 C, *C*-4), 117.9 (1 C, *C*-3), 111.6 (1 C, *C*-7), 31.1 (1 C, *C*-3*), 27.9 (1 C, *C*-6*), 22.9 (1 C, *C*-4*), 22.6 (1 C, *C*-5*), 21.2 (1 C, 2*-*C*H_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3146 (w), 3063 (w), 2924 (m), 2861 (m), 2669 (w), 2294 (w), 2070 (w), 1925 (w), 1742 (w), 1663 (m), 1575 (m), 1516 (m), 1423 (s), 1380 (m), 1307 (m), 1272 (m), 1239 (m), 1169 (m), 1133 (m), 1002 (m), 933 (m), 878 (m), 779 (s), 737 (s), 653 (s), 606 (m), 548 (m).
UV/Vis (THF): λ_{max} (lg ε) = 292 (4.04), 259 (4.00), 240 (4.15).
ESI-HRMS: calculated $[C_{16}H_{17}NO+Na]^+$: 262.12023
found: 262.12015 (0.31 ppm).

3.4 *cis*-4a-Methyl-1,3,4,4a,5,10a-hexahydroindeno[1,2-*b*]indol-10(2*H*)-one (7)



6 **7**

A solution of ketone **6** (1.20 g, 5.00 mmol) in DCE (250 mL) was degassed by bubbling argon through it for 10 min. The solution was pumped through the flow reactor (1.2 mL min^{-1}, λ = 300 nm). The solution was concentrated (the DCE was collected and reused without affecting the yield). The residue was filtered through a pad of silica gel (rinsing with $CHCl_3$/EtOAc 2:1) and the filtrate concentrated. Flash column chromatography (dissolved in CH_2Cl_2 and dry-loaded on silica gel) on silica gel [petroleum ether/EtOAc (4:1) to (2:1) to (1:1)] afforded *cis*-hydrindanone **7** as an off-white solid (947 mg, 3.96 mmol, 79%).
TLC [petroleum ether/EtOAc (2:1)]: R_f = 0.29 [vanillin: red].
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 9.75 (s, 1 H, 5-*H*), 7.92 – 7.88 (m, 1 H, 9-*H*), 7.44 – 7.40 (m, 1 H, 6-*H*), 7.27 – 7.19 (m, 2 H, 7-*H*, 8-*H*), 2.77 (dd, *J* = 6.3 Hz, 4.2 Hz, 1 H, 10a-*H*), 2.17 (dddd, *J* = 14.0 Hz, 4.6 Hz, 4.6 Hz, 4.6 Hz, 1 H, 1-*H* (*syn* to 4a-CH_3)), 1.87 (ddd, *J* = 13.6 Hz, 8.2 Hz, 4.4 Hz, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.83 – 1.74 (m, 1 H, 1-*H* (*anti* to 4a-CH_3)), 1.70 (ddd, *J* = 13.6 Hz, 8.2 Hz, 4.4 Hz, 1 H, 4-*H* (*anti* to 4a-CH_3)), 1.57 – 1.27 (m, 2 H, 2-*H*, 3-*H*), 1.53 (s, 3 H, 4a-CH_3), 1.43 – 1.41 (m, 2 H, 2-*H*, 3-*H*).
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 197.9 (1 C, *C*-10), 174.0 (1 C, *C*-4b), 142.0 (1 C, *C*-5a), 123.8 (1 C, *C*-7), 122.6 (1 C, *C*-8), 121.6 (1 C, *C*-9a), 121.3 (1 C, *C*-9), 118.5 (1 C, *C*-9b), 112.4

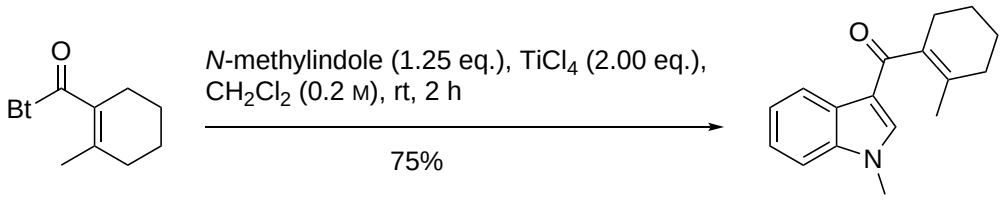
(1 C, *C*-6), 60.1 (1 C, *C*-10a), 39.1 (1 C, *C*-4a), 34.7 (1 C, *C*-4), 25.3 (1 C, 4a-*C*H_3), 22.0 (1 C, *C*-1), 19.8 (1 C, *C*-2), 19.2 (1 C, *C*-3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3182 (m), 3067 (m), 2931 (m), 2861 (m), 1645 (s), 1539 (w), 1502 (w), 1449 (s), 1309 (m), 1230 (m), 1156 (m), 1092 (m), 1010 (w), 939 (w), 869 (m), 846 (w), 812 (w), 738 (s), 675 (m), 635 (m), 559 (m).

UV/Vis (THF): λ_{max} (lg ε) = 288 (3.75), 256 (4.28), 234 (4.26).

ESI-HRMS: calculated $[C_{16}H_{17}NO+H]^+$: 240.13829
found: 240.13815 (0.58 ppm).

3.5 (1-Methyl-1*H*-indol-3-yl)(2-methylcyclohex-1-en-1-yl)methanone (S20)



5 **S20**

To a solution of *N*-acyl benzotriazole **5** (412 mg, 1.70 mmol, 1.00 eq.) and *N*-methylindole[5] (279 mg, 2.13 mmol, 1.25 eq.) in CH_2Cl_2 (13 mL) was added $TiCl_4$ (1 M in CH_2Cl_2, 3.4 mL, 3.41 mmol, 2.00 eq.) dropwise at room temperature. The solution was stirred for 2 h at room temperature. The reaction was quenched by the addition of sat. $NaHCO_3$. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (4:1) to (2:1)] afforded ketone **S20** as a yellow oil which solidified in the freezer (322 mg, 1.27 mmol, 75%).

TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.33 [vanillin: red].

^{1}H NMR (500 MHz, $CDCl_3$, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 8.37 – 8.31 (m, 1 H, 4-*H*), 7.59 (s, 1 H, 2-*H*), 7.37 – 7.28 (m, 3 H, 5-*H*, 6-*H*, 7-*H*), 3.84 (s, 3 H, 1-CH_3), 2.33 – 2.27 (m, 2 H, 6*-*H*), 2.12 – 2.07 (m, 2 H, 3*-*H*), 1.78 – 1.69 (m, 4 H, 4*-*H*, 5*-*H*), 1.64 – 1.60 (m, 3 H, 2*-CH_3).

^{13}C NMR (126 MHz, $CDCl_3$, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 196.5 (1 C, 3-(*C*=O)-1*), 137.9 (1 C, *C*-7a), 137.5 (1 C, *C*-2), 134.6 (1 C, *C*-1*), 131.5 (1 C, *C*-2*), 126.4 (1 C, *C*-3a), 123.4 (1 C, *C*-6), 122.7 (1 C, *C*-5), 122.5 (1 C, *C*-4), 116.4 (1 C, *C*-3), 109.8 (1 C, *C*-7), 33.7 (1 C, 1-*C*H_3), 31.1 (1 C, *C*-3*), 27.9 (1 C, *C*-6*), 22.9 (1 C, *C*-4*), 22.7 (1 C, *C*-5*), 21.2 (1 C, 2*-*C*H_3).

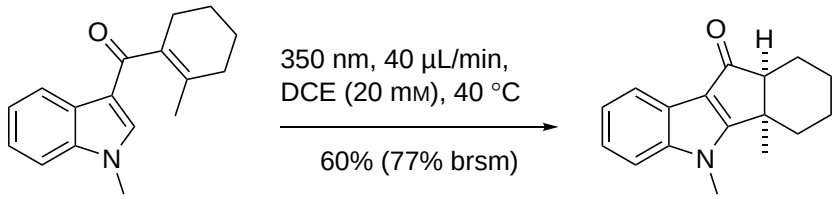
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2926 (m), 2858 (m), 1599 (m), 1519 (m), 1457 (m), 1365 (m), 1274 (w), 1220 (m), 1156 (w), 1115 (m), 1068 (m), 1011 (m), 933 (w), 867 (m), 782 (m), 739 (s), 634 (w), 580 (w).

UV/Vis (THF): λ_{max} (lg ε) = 299 (4.15), 246 (4.17).

ESI-HRMS: calculated $[C_{17}H_{19}NO+Na]^+$: 276.13589
found: 276.13595 (0.22 ppm).

[5] M. P. Tantak, V. Gupta, K. Nikhil, V. Arun, R. P. Singh, P. N. Jha, K. Shah, D. Kumar, *Bioorg. Med. Chem. Lett.* **2016**, *26*, 3167–3171.

3.6 *cis*-4a,5-Dimethyl-1,3,4,4a,5,10a-hexahydroindeno[1,2-*b*]indol-10(2*H*)-one (S21)



S20 **S21**

A solution of ketone **S20** (101 mg, 400 µmol) in DCE (20 mL) was degassed by bubbling argon through it for 10 min. The solution was pumped through the flow reactor (40 µL min^{-1}, λ = 350 nm). The solution was concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (6:1) to (4:1) to (2:1)] afforded *cis*-hydrindanone **S21** (61 mg, 241 µmol, 60%) as an off-white solid and unreacted ketone **S20** as a yellowish oil which solidified in the freezer (17 mg, 67 µmol, 17%).

TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.17 [vanillin: red].

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.97 – 7.93 (m, 1 H, 9-*H*), 7.33 – 7.24 (m, 3 H, 6-*H*, 7-*H*, 8-*H*), 3.82 (s, 3 H, 5-CH_3), 2.72 (dd, J = 6.3 Hz, 4.4 Hz, 1 H, 10a-*H*), 2.20 – 2.11 (m, 1 H, 1-*H* (*anti* to 4a-CH_3)), 1.98 – 1.90 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.84 – 1.67 (m, 2 H, 1-*H* (*syn* to 4a-CH_3), 4-*H* (*anti* to 4a-CH_3)), 1.62 – 1.31 (m, 2 H, 2-*H*, 3-*H*), 1.56 (s, 3 H, 4a-CH_3), 1.44 – 1.44 (m, 2 H, 2-*H*, 3-*H*).

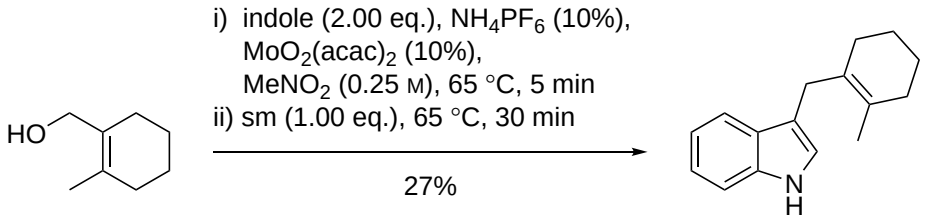
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 196.7 (1 C, *C*-10), 172.3 (1 C, *C*-4b), 143.3 (1 C, *C*-5a), 123.4 (1 C, *C*-7), 122.5 (1 C, *C*-8), 121.4 (1 C, *C*-9), 121.4 (1 C, *C*-9a), 117.8 (1 C, *C*-9b), 109.9 (1 C, *C*-6), 60.6 (1 C, *C*-10a), 39.6 (1 C, *C*-4a), 33.7 (1 C, *C*-4), 31.3 (1 C, 5-*C*H_3), 24.7 (1 C, 4a-*C*H_3), 21.8 (1 C, *C*-1), 19.7 (1 C, *C*-2), 19.2 (1 C, *C*-3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3054 (w), 2930 (m), 2859 (m), 1670 (s), 1523 (m), 1465 (s), 1449 (s), 1408 (s), 1326 (m), 1272 (w), 1213 (w), 1097 (m), 1052 (m), 1015 (w), 978 (w), 935 (w), 862 (m), 806 (m), 745 (s), 665 (w), 603 (w).

UV/Vis (THF): λ_{max} (lg ε) = 291 (3.84), 279 (3.99), 256 (4.23), 237 (4.25).

ESI-HRMS: calculated $[C_{17}H_{19}NO+H]^+$: 254.15394
found: 254.15404 (0.39 ppm).

3.7 3-((2-Methylcyclohex-1-en-1-yl)methyl)-1*H*-indole (S2)



S1 **S2**

To a solution of $MoO_2(acac)_2$ (163 mg, 500 µmol, 0.10 eq.) and NH_4PF_6 (82 mg, 500 µmol, 0.10 eq.) in nitromethane (20 mL) was added indole (1.17 g, 10.0 mmol, 2.00 eq.) at 65 °C. After stirring for 5 min at 65 °C, allylic alcohol[6] **S1** (631 mg, 5.00 mmol, 1.00 eq.) was added. The solution was stirred for 30 min at 65 °C and concentrated. Flash column chromatography on

[6] C. Ye, X. Kou, G. Yang, J. Shen, W. Zhang, *Tetrahedron Lett.* **2019**, *60*, 1148–1152.

silica gel [petroleum ether/EtOAc (40:1) to (30:1)] afforded indole **S2** as a brownish oil which solidified in the freezer (304 mg, 1.35 mmol, 27%).

TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.45 [vanillin: red].

^{1}H NMR (400 MHz, C_6D_6, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 7.75 – 7.72 (m, 1 H, 4-*H*), 7.26 – 7.18 (m, 2 H, 5-*H*, 6-*H*), 7.07 – 7.04 (m, 1 H, 7-*H*), 6.63 (s, 1 H, 1-*H*), 6.49 – 6.47 (m, 1 H, 2-*H*), 3.49 (s, 2 H, 3-CH_2-1*), 2.06 – 1.92 (m, 4 H, 3*-*H*, 6*-*H*), 1.76 (s, 3 H, 2*-CH_3), 1.60 – 1.45 (m, 4 H, 4*-*H*, 5*-*H*).

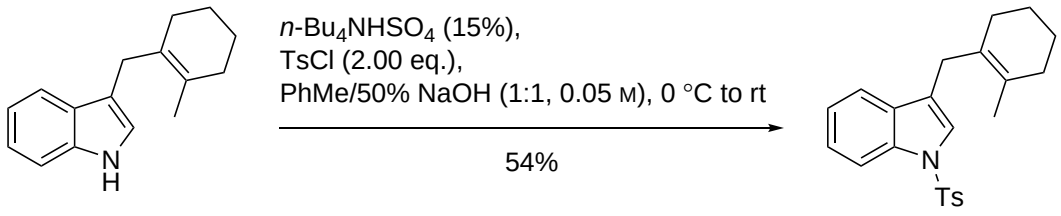
^{13}C NMR (101 MHz, C_6D_6, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 137.0 (1 C, *C*-7a), 129.5 (1 C, *C*-2*), 128.5 (1 C, *C*-3a), 126.6 (1 C, *C*-1*), 122.1 (1 C, *C*-6), 121.7 (1 C, *C*-2), 119.5 (1 C, *C*-5), 119.5 (1 C, *C*-4), 115.2 (1 C, *C*-3), 111.3 (1 C, *C*-7), 32.3 (1 C, *C*-3*), 29.9 (1 C, *C*-6*), 29.5 (1 C, 3-*C*H_2-1*), 24.0 (1 C, *C*-4*), 23.9 (1 C, *C*-5*), 19.6 (1 C, 2*-*C*H_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3411 (m), 3050 (w), 2919 (m), 2860 (m), 1616 (w), 1486 (w), 1448 (m), 1343 (m), 1225 (w), 1182 (w), 1136 (w), 1087 (m), 1045 (w), 1006 (w), 925 (w), 806 (w), 735 (s), 589 (m), 546 (w).

UV/Vis (THF): λ_{max} (lg ε) = 291 (3.70), 283 (3.76), 230 (4.18).

ESI-HRMS: calculated $[C_{16}H_{19}N+H]^+$: 226.15903
found: 226.15916 (0.57 ppm).

3.8 3-((2-Methylcyclohex-1-en-1-yl)methyl)-1-tosyl-1*H*-indole (S3)



S2 **S3**

To a solution of indole **S2** (196 mg, 870 µmol, 1.00 eq.) in PhMe (8.7 mL) was added 50% NaOH (8.7 mL), *n*-Bu_4NHSO_4 (44 mg, 131 µmol, 0.15 eq.) and TsCl (332 mg, 1.74 mmol, 2.00 eq.) at 0 °C. The solution was stirred for 1 h at room temperature. H_2O was added and the mixture extracted with TBME (3x50 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (50:1) to (20:1)] afforded tosylindole **S3** as a colorless solid (179 mg, 472 µmol, 54%).

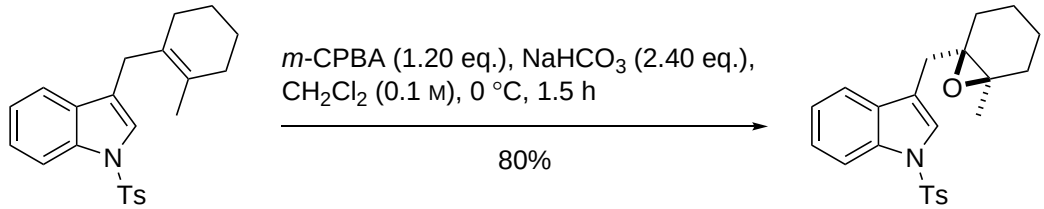
TLC [Petroleum ether/EtOAc (10:1)]: R_f = 0.50 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$, 2-methylcyclohexen-1-ene moiety marked with *): δ [ppm] = 7.98 – 7.95 (m, 1 H, 7-*H*), 7.71 – 7.68 (m, 2 H, *o*-H_{Ts}), 7.45 – 7.43 (m, 1 H, 4-*H*), 7.31 – 7.27 (m, 1 H, 6-*H*), 7.23 – 7.16 (m, 4 H, 2-*H*, 5-*H*, *m*-H_{Ts}), 3.32 (s, 2 H, 3-CH_2-1*), 2.31 (s, 3 H, *p*-C_{Ts}-CH_3), 2.05 – 1.99 (m, 2 H, 3*-*H*), 1.88 – 1.82 (m, 2 H, 6*-*H*), 1.71 – 1.70 (m, 3 H, 2*-CH_3), 1.63 – 1.52 (m, 4 H, 4*-*H*, 5*-*H*).

^{13}C NMR (126 MHz, $CDCl_3$, 2-methylcyclohexen-1-ene moiety marked with *): δ [ppm] = 144.7 (1 C, *p*-C_{Ts}), 135.8 (1 C, *C*-7a), 135.4 (1 C, *ipso*-C_{Ts}), 131.6 (1 C, *C*-3a), 129.8 (2 C, *m*-C_{Ts}), 128.5 (1 C, *C*-2*), 127.1 (1 C, *C*-1*), 126.8 (2 C, *o*-C_{Ts}), 124.7 (1 C, *C*-6), 123.5 (1 C, *C*-2), 123.2 (1 C, *C*-5), 122.4 (1 C, *C*-3), 119.7 (1 C, *C*-4), 114.0 (1 C, *C*-7), 32.0 (1 C, *C*-3*), 29.7 (1 C, *C*-6*), 29.0 (1 C, 3-*C*H_2-1*), 23.6 (1 C, *C*-5*), 23.4 (1 C, *C*-4*), 21.7 (1 C, *p*-C_{Ts}-*C*H_3), 19.5 (1 C, 2*-*C*H_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3112 (w), 3056 (w), 2926 (m), 2861 (w), 1596 (w), 1491 (w), 1443 (m), 1360 (m), 1277 (m), 1168 (s), 1105 (s), 1018 (w), 968 (m), 805 (m), 749 (s), 708 (w), 665 (s), 620 (w), 575 (s).
UV/Vis (THF): λ_{max} (lg ε) = 294 (3.60), 254 (4.11), 224 (4.33).
ESI-HRMS: calculated $[C_{23}H_{25}NO_2S+H]^+$: 402.14982
found: 402.14998 (0.40 ppm).

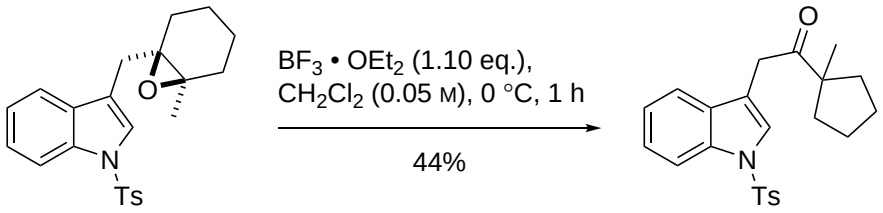
3.9 Epoxide S4



S3 **S4**

To a solution of alkene **S3** (169 mg, 445 µmol, 1.00 eq.) in CH_2Cl_2 (4.5 mL) was added $NaHCO_3$ (90 mg, 1.07 mmol, 2.40 eq.) and 70% *m*-CPBA (132 mg, 534 µmol, 1.20 eq.) at 0 °C. The suspension was stirred for 1.5 h at 0 °C. The reaction was quenched by the addition of sat. Na_2SO_3. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (30:1) to (20:1) to (10:1)] afforded epoxide **S4** as a colorless solid (140 mg, 354 µmol, 80%).
TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.28 [vanillin: brown].
^{1}H NMR (400 MHz, $CDCl_3$, 2-methylcyclohexane moiety marked with *): δ [ppm] = 8.01 – 7.96 (m, 1 H, 7-*H*), 7.75 – 7.70 (m, 2 H, *o*-H_{Ts}), 7.58 – 7.54 (m, 1 H, 4-*H*), 7.35 – 7.29 (m, 1 H, 6-*H*), 7.34 (s, 1 H, 2-*H*), 7.28 – 7.22 (m, 1 H, 5-*H*), 7.21 – 7.17 (m, 2 H, *m*-H_{Ts}), 2.97 (dd, *J* = 15.5 Hz, 1.1 Hz, 1 H, 3-CH_2-1*), 2.84 (dd, *J* = 15.5 Hz, 1.0 Hz, 1 H, 3-CH_2-1*), 2.33 (s, 3 H, *p*-C_{Ts}-CH_3), 2.03 – 1.70 (m, 1 H, 5*-*H*), 1.93 – 1.82 (m, 1 H, 5*-*H*), 1.69 – 1.62 (m, 2 H, 2*-*H*), 1.47 – 1.36 (m, 5 H, 3*-*H*, 4*-*H*, 6*CH_3), 1.36 – 1.12 (m, 2 H, 3*-*H*, 4*-*H*).
^{13}C NMR (101 MHz, $CDCl_3$, 2-methylcyclohexane moiety marked with *): δ [ppm] = 144.9 (1 C, *p*-C_{Ts}), 135.5 (1 C, *C*-7a), 135.4 (1 C, *ipso*-C_{Ts}), 131.5 (1 C, *C*-3a), 129.9 (2 C, *m*-C_{Ts}), 126.9 (2 C, *o*-C_{Ts}), 124.9 (1 C, *C*-6), 123.9 (1 C, *C*-2), 123.4 (1 C, *C*-5), 120.3 (1 C, *C*-4), 119.7 (1 C, *C*-3), 113.9 (1 C, *C*-7), 64.2 (1 C, *C*-1*), 62.6 (1 C, *C*-6*), 31.9 (1 C, *C*-5*), 30.8 (1 C, 3-*C*H_2-1*), 28.6 (1 C, *C*-2*), 21.7 (1 C, *p*-C_{Ts}-*C*H_3), 21.2 (1 C, *C*-3), 20.8 (1 C, 6*-*C*H_3), 20.5 (1 C, *C*-4*).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3053 (w), 2931 (m), 2857 (w), 1597 (w), 1444 (m), 1356 (s), 1279 (m), 1167 (s), 1119 (s), 1022 (m), 967 (m), 907 (w), 870 (w), 808 (m), 741 (s), 663 (s), 568 (s), 542 (m).
UV/Vis (THF): λ_{max} (lg ε) = 292 (3.60), 252 (4.11), 223 (4.26).
ESI-HRMS: calculated $[C_{23}H_{25}NO_3S+Na]^+$: 418.14474
found: 418.14494 (0.48 ppm).

3.10 1-(1-Methylcyclopentyl)-2-(1-tosyl-1*H*-indol-3-yl)ethan-1-one (S5)



S4 **S5**

To a solution of epoxide **S4** (128 mg, 324 µmol, 1.00 eq.) in CH_2Cl_2 (6.0 mL) was added $BF_3 \bullet OEt_2$ (50 µL, 356 µmol, 1.10 eq.) dropwise at 0 °C. The solution was stirred for 1 h at 0 °C. The reaction was quenched by the addition of sat. $NaHCO_3$. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (20:1) to (15:1) to (10:1)] afforded ketone **S5** as a colorless solid (57 mg, 144 µmol, 44%).

TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.25 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$, 1-methylcyclopentane moiety marked with *): δ [ppm] = 7.98 – 7.95 (m, 1 H, 7-*H*), 7.77 – 7.73 (m, 2 H, *o*-H_{Ts}), 7.52 – 7.51 (m, 1 H, 2-*H*), 7.43 – 7.40 (m, 1 H, 4-*H*), 7.32 – 7.28 (m, 1 H, 6-*H*), 7.24 – 7.18 (m, 3 H, 5-*H*, *m*-H_{Ts}), 3.85 (d, J = 1.0 Hz, 2 H, 3-CH_2-C(=O)-1*), 2.33 (s, 3 H, *p*-C_{Ts}-CH_3), 2.14 – 2.05 (m, 2 H, 2*-*H* (*syn* to 1*-CH_3), 5*-*H* (*syn* to 1*-CH_3)), 1.76 – 1.60 (m, 4 H, 3*-*H*, 4*-*H*), 1.51 – 1.43 (m, 2 H, 2*-*H* (*anti* to 1*-CH_3), 2*-*5* (*anti* to 1*-CH_3)), 1.29 (s, 3 H, 1*-CH_3).

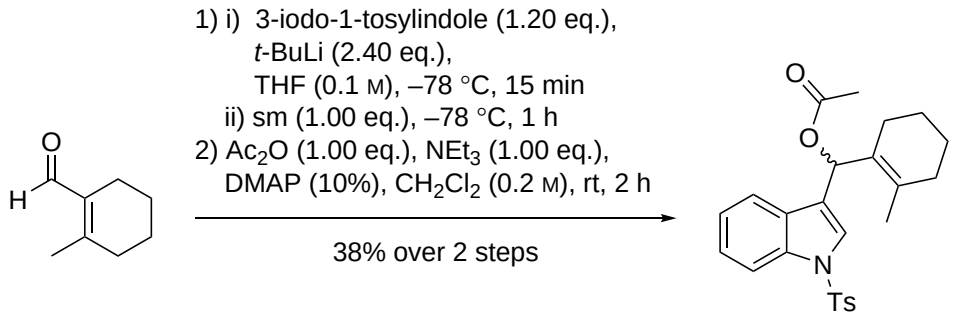
^{13}C NMR (126 MHz, $CDCl_3$, 1-methylcyclopentane moiety marked with *): δ [ppm] = 210.9 (1 C, 3-CH_2-*C*(=O)-1*), 144.9 (1 C, *p*-C_{Ts}), 135.5 (1 C, *ipso*-C_{Ts}), 135.2 (1 C, *C*-7a), 130.9 (1 C, *C*-3a), 130.0 (2 C, *m*-C_{Ts}), 127.0 (2 C, *o*-C_{Ts}), 124.9 (1 C, *C*-2), 124.8 (1 C, *C*-6), 123.3 (1 C, *C*-5), 119.6 (1 C, *C*-4), 116.2 (1 C, *C*-3), 113.9 (1 C, *C*-7), 56.3 (1 C, *C*-1*), 36.7 (2 C, *C*-2*, *C*-5*), 33.8 (1 C, 3-CH_2-C(=O)-1*), 25.3 (2 C, *C*-3*, *C*-4*), 24.8 (1 C, 1*-*C*H_3), 21.7 (1 C, *p*-C_{Ts}-*C*H_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3099 (w), 3057 (w), 2952 (m), 2869 (w), 1699 (m), 1597 (w), 1444 (m), 1363 (s), 1305 (m), 1280 (m), 1168 (s), 1124 (s), 1088 (s), 1016 (m), 969 (s), 814 (m), 749 (s), 697 (m), 664 (s), 604 (m), 569 (s), 542 (m).

UV/Vis (THF): λ_{max} (lg ε) = 293 (3.61), 255 (4.11).

ESI-HRMS: calculated $[C_{23}H_{25}NO_3S+Na]^+$: 418.14474
found: 418.14493 (0.45 ppm).

3.11 (2-Methylcyclohex-1-en-1-yl)(1-tosyl-1*H*-indol-3-yl)methyl acetate (S9)



S8 **S9**

To a solution of 3-iodo-1-tosylindole[7] (2.38 g, 6.00 mmol, 1.20 eq.) in dry THF (60 mL) under argon was added *t*-BuLi (1.6 M in pentane, 7.5 mL, 12.0 mmol, 2.40 eq.) dropwise at –78 °C. The solution was stirred for 15 min at –78 °C. 2-Methylcyclohex-1-ene-1-carbaldehyde[8] (**S8**, 621 mg, 5.00 mmol, 1.00 eq.) was added dropwise at –78 °C. The solution was stirred for 1 h at –78 °C. The reaction was quenched by the addition of sat. $NaHCO_3$. The phases were separated and the aqueous phase extracted with TBME (3x100 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (20:1) to (10:1) to (8:1) to (6:1) to (4:1), each +1% NEt_3] afforded the crude product as a purplish foam (1.00 g).

To a solution of the crude product, NEt_3 (700 µL, 5.00 mmol, 1.00 eq.) and Ac_2O (470 µL, 5.00 mmol, 1.00 eq.) in CH_2Cl_2 (30 mL) was added DMAP (61 mg, 500 µmol, 0.10 eq.) at room temperature. The solution was stirred for 2 h at room temperature. The reaction was quenched by the addition of sat. $NaHCO_3$. The phases were separated and the aqueous phase extracted with CH_2Cl_2 (3x50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (20:1) to (10:1) to (6:1), each +1% NEt_3] afforded allylic acetate **S9** as a colorless, sticky solid (824 mg, 1.88 mmol, 38% over 2 steps).

TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.31 [vanillin: brown].

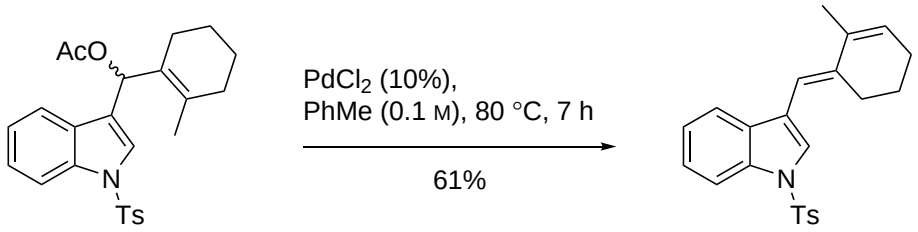
^{1}H NMR (400 MHz, C_6D_6, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 8.26 (ddd, J = 8.3 Hz, 0.8 Hz, 0.8 Hz, 1 H, 7-*H*), 7.81 (d, J = 1.4 Hz, 1 H, 2-*H*), 7.69 – 7.64 (m, 2 H, *o*-H_{Ts}), 7.46 (ddd, J = 7.9 Hz, 1.0 Hz, 0.9 Hz, 1 H, 4-*H*), 7.22 (d, J = 1.3 Hz, 1 H, 3-C*H*(O-C(=O)-CH_3)-1*), 7.18 – 7.12 (m, 1 H, 6-*H*), 7.03 (ddd, J = 8.1 Hz, 7.2 Hz, 0.9 Hz, 1 H, 5-*H*), 6.49 – 1.82 (m, 2 H, *m*-H_{Ts}), 2.14 – 2.03 (m, 1 H, 6*-*H*), 1.84 (s, 3 H, 2*-CH_3), 1.82 – 1.69 (m, 3 H, 3*-*H*, 6*-*H*), 1.68 (s, 3 H, 3-CH(O-C(=O)-CH_3)-1*), 1.61 (s, 3 H, *p*-C_{Ts}-CH_3), 1.46 – 1.32 (m, 3 H, 4*-*H*, 5*-*H*), 1.30 – 1.20 (m, 1 H, 5*-*H*).

^{13}C NMR (101 MHz, C_6D_6, 2-methylcyclohex-1-ene moiety marked with *): δ [ppm] = 169.2 (1 C, 3-CH(O-*C*(=O)-CH_3)-1*), 144.6 (1 C, *p*-C_{Ts}), 136.4 (1 C, *C*-7a), 135.9 (1 C, *ipso*-C_{Ts}), 133.2 (1 C, *C*-1*), 129.8 (2 C, *m*-C_{Ts}), 129.7 (1 C, *C*-3a), 127.8 (1 C, *C*-2* (HMBC)), 126.9 (2 C, *o*-C_{Ts}), 125.2 (1 C, *C*-6), 124.2 (1 C, *C*-2), 123.7 (1 C, *C*-5), 122.5 (1 C, *C*-3), 120.4 (1 C, *C*-4), 114.5 (1 C, *C*-7), 69.5 (1 C, 3-*C*H(O-C(=O)-CH_3)-1*), 32.4 (1 C, *C*-3*), 24.6 (1 C, *C*-6*), 23.1 (1 C, *C*-4*), 23.0 (1 C, *C*-5*), 21.0 (1 C, *p*-C_{Ts}-*C*H_3), 20.5 (1 C, 3-CH(O-C(=O)-*C*H_3)-1*), 19.6 (1 C, 2*-*C*H_3).

[7] B. Witulski, N. Buschmann, U. Bergsträßer, *Tetrahedron* **2000**, *56*, 8473–8480.
[8] S. M. Makin, R. I. Kruglikova, T. K. Tagirov, B. M. Arshava, *Zh. Org. Khim.* **1983**, *19*, 101–105.

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2927 (m), 2865 (w), 1735 (m), 1598 (w), 1487 (w), 1443 (m), 1367 (s), 1275 (m), 1230 (s), 1171 (s), 1124 (s), 1015 (m), 971 (s), 810 (m), 749 (s), 672 (s), 572 (s).
UV/Vis (THF): λ_{max} (lg ε) = 290 (3.63), 283 (3.67), 251 (4.15).
ESI-HRMS: calculated $[C_{25}H_{27}NO_4S+Na]^+$: 460.15530
found: 460.15544 (0.30 ppm).

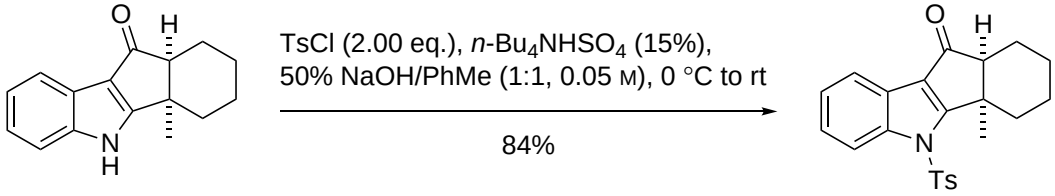
3.12 (*E*)-3-((2-Methylcyclohex-2-en-1-ylidene)methyl)-1-tosyl-1*H*-indole (S10)



S9 **S10**

A solution of allylic acetate **S9** (219 mg, 500 µmol, 1.00 eq.) and $PdCl_2$ (9 mg, 50 µmol, 0.1 eq.) in dry PhMe (5 mL) under argon was stirred for 7 h at 80 °C. Water was added and the mixture extracted with TBME (3x20 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (40:1)] afforded indole **S10** as a yellowish oil (116 mg, 307 µmol, 61%).
TLC [petroleum ether/EtoAc (4:1)]: R_f = 0.78 [vanillin: brown].
^{1}H NMR (400 MHz, $CDCl_3$, 2-methylcyclohex-2-en-1-ylidene moiety marked with *): δ [ppm] = 8.01 – 7.97 (m, 1 H, 7-*H*), 7.78 – 7.74 (m, 2 H, *o*-H_{Ts}), 7.58 – 7.54 (m, 1 H, 4-*H*), 7.51 (s, 1 H, 2-*H*), 7.32 (ddd, *J* = 7.7 Hz, 7.7 Hz, 1.2 Hz, 1 H, 6-*H*), 7.27 – 7.22 (m, 1 H, 5-*H*), 7.22 – 7.18 (m, 2 H, *m*-H_{Ts}), 6.40 (s, 1 H, 3-C*H*=1*), 5.86 – 5.82 (m, 2 H, 3*-*H*), 2.66 – 2.61 (m, 2 H, 6*-*H*), 2.32 (s, 3 H, *p*-C_{Ts}-CH_3), 2.23 – 2.16 (m, 2 H, 4*-*H*), 1.98 – 1.95 (m, 3 H, 2*-CH_3), 1.78 – 1.68 (m, 2 H, 5*-*H*).
^{13}C NMR (101 MHz, $CDCl_3$, 2-methylcyclohex-2-en-1-ylidene moiety marked with *): δ [ppm] = 145.0 (1 C, *p*-C_{Ts}), 140.2 (1 C, *C*-1*), 135.4 (1 C, *ipso*-C_{Ts}), 134.8 (1 C, *C*-7a), 133.4 (1 C, *C*-2*), 131.5 (1 C, *C*-3a), 130.0 (2 C, *m*-C_{Ts}), 129.8 (1 C, *C*-3*), 126.9 (2 C, *o*-C_{Ts}), 125.0 (1 C, *C*-6), 123.5 (1 C, *C*-2), 123.4 (1 C, *C*-5), 120.0 (1 C, *C*-3), 119.7 (1 C, *C*-4), 113.8 (1 C, *C*-7), 111.1 (1 C, 1-*C*H=1*), 28.5 (1 C, *C*-6*), 26.0 (1 C, *C*-4*), 22.9 (1 C, *C*-5*), 21.7 (1 C, *p*-C_{Ts}-*C*H_3), 20.3 (1 C, 2*-*C*H_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2928 (m), 2867 (w), 2867 (w), 1716 (w), 1667 (w), 1597 (w), 1545 (w), 1444 (m), 1365 (m), 1289 (m), 1216 (w), 1168 (s), 1127 (s), 1088 (m), 1025 (w), 970 (m), 870 (m), 805 (m), 748 (s), 707 (w), 664 (s), 568 (s).
UV/Vis (THF): λ_{max} (lg ε) = 303 (4.03), 255 (4.24).
ESI-HRMS: calculated $[C_{23}H_{23}NO_2S+Na]^+$: 400.13417
found: 400.13431 (0.35 ppm).

3.13 *cis*-Hydrindanone 8



7 **8**

To a solution of indole **7** (947 mg, 3.96 mmol, 1.00 eq.) and *n*-Bu_4NHSO_4 (202 mg, 594 µmol, 0.15 eq.) in PhMe (40 mL) was added 50% NaOH (40 mL) and TsCl (1.51 mg, 7.91 mmol, 2.00 eq.) at 0 °C. The biphasic mixture was stirred rapidly for 2 h at room temperature. The mixture was diluted with water (100 mL) and extracted with TBME (3x100 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (10:1) to (5:1)] afforded tosylindole **8** as a colorless foam (1.31 g, 3.34 mmol, 84%).

TLC [petroleum ether/EtOAc (2:1)]: R_f = 0.69 [vanillin: brown].

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.04 – 7.97 (m, 1 H, 6-*H*), 7.94 – 7.87 (m, 1 H, 9-*H*), 7.79 – 7.75 (m, 2 H, *o*-H_{Ts}), 7.37 – 7.29 (m, 2 H, 7-*H*, 8-*H*), 7.29 – 7.25 (m, 2 H, *m*-H_{Ts}), 2.72 (dd, *J* = 6.3 Hz, 3.8 Hz, 1 H, 10a-*H*), 2.38 (s, 3 H, *p*-C_{Ts}-CH_3), 2.32 (ddd, *J* = 13.8 Hz, 6.8 Hz, 3.8 Hz, 1 H, 4-*H* (*syn* to 4a-CH_3)), 2.21 (dddd, *J* = 13.9 Hz, 4.4 Hz, 4.4 Hz, 4.4 Hz, 1 H, 1-*H* (*syn* to 4a-CH_3)), 1.85 (ddd, *J* = 13.8 Hz, 9.8 Hz, 4.1 Hz, 1 H, 4-*H* (*anti* to 4a-CH_3)), 1.81 – 1.70 (m, 4 H, 1-*H* (*anti* to 4a-CH_3), 4a-CH_3), 1.62 – 1.42 (m, 2 H, 2-*H* (*anti* to 4a-CH_3), 3-*H* (*syn* to 4a-CH_3)), 1.41 – 1.23 (m, 2 H, 3-*H* (*anti* to 4a-CH_3), 2-*H* (*syn* to 4a-CH_3)).

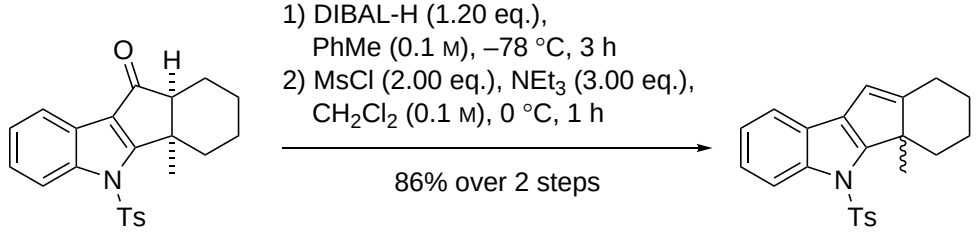
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 198.3 (1 C, *C*-10), 172.0 (1 C, *C*-4b), 145.8 (1 C, *p*-C_{Ts}), 141.1 (1 C, *C*-5a), 135.9 (1 C, *ipso*-C_{Ts}), 130.2 (2 C, *m*-C_{Ts}), 127.0 (2 C, *o*-C_{Ts}), 125.7 (1 C, *C*-7), 124.9 (1 C, *C*-8), 124.7 (1 C, *C*-9b), 122.2 (1 C, *C*-9a), 121.3 (1 C, *C*-9), 114.9 (1 C, *C*-6), 61.2 (1 C, *C*-10a), 43.5 (1 C, *C*-4a), 34.6 (1 C, *C*-4), 24.5 (1 C, 4a-CH_3), 21.8 (1 C, *p*-C_{Ts}-CH_3), 21.6 (1 C, *C*-1), 20.6 (1 C, *C*-2), 19.6 (1 C, *C*-3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2933 (w), 2858 (w), 1698 (m), 1593 (w), 1533 (w), 1476 (m), 1444 (m), 1410 (m), 1372 (m), 1318 (m), 1255 (m), 1176 (m), 1121 (m), 1081 (m), 1021 (m), 973 (m), 880 (w), 804 (m), 763 (m), 695 (w), 654 (m), 611 (w), 571 (m).

UV/Vis (THF): λ_{max} (lg ε) = 271 (4.03), 224 (4.47).

ESI-HRMS: calculated $[C_{23}H_{23}NO_3S+H]^+$: 416.12909
found: 416.12918 (0.22 ppm).

3.14 4a-Methyl-5-tosyl-1,2,3,4,4a,5-hexahydroindeno[1,2-*b*]indole (9)

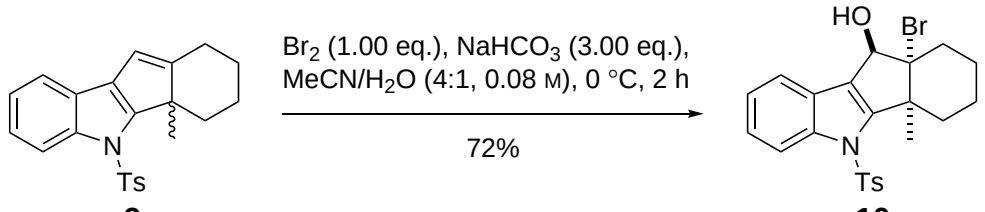


8 **9**

To a solution of *cis*-hydrindanone **8** (1.46 g, 3.71 mmol, 1.00 eq.) in dry PhMe (37 mL) under argon was added DIBAL-H (1.2 M in PhMe, 3.7 mL, 4.45 mmol, 1.20 eq.) dropwise at –78 °C.

The solution was stirred for 3 h at –78 °C. The reaction was quenched by the addition of MeOH at –78 °C. Sat. potassium sodium tartrate solution was added at room temperature and the mixture rapidly stirred for 30 min. The phases were separated and the aqueous phase was extracted with TBME (3x50 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated.
To a solution of the crude product in CH_2Cl_2 (37 mL) was added NEt_3 (1.6 mL, 11.1 mmol, 3.00 eq.) and MsCl (570 µL, 7.42 mmol, 2.00 eq.) at 0 °C. The solution was stirred for 1 h at 0 °C. The reaction was quenched by the addition of sat. $NaHCO_3$. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3x50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (20:1)] afforded alkene **9** as a colorless foam (1.21 g, 3.21 mmol, 86% over 2 steps).
TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.18 [vanillin: brown].
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.09 – 8.03 (m, 1 H, 6-*H*), 7.67 – 7.63 (m, 2 H, *o*-H_{Ts}), 7.52 – 7.47 (m, 1 H, 9-*H*), 7.26 – 7.19 (m, 2 H, 7-*H*, 8-*H*), 7.17 – 7.12 (m, 2 H, *m*-H_{Ts}), 6.31 (d, *J* = 1.9 Hz, 1 H, 10-*H*), 2.91 – 2.84 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 2.69 – 2.62 (m, 1 H, 1-*H* (*anti* to 4a-CH_3)), 2.37 – 2.27 (m, 1 H, 1-*H* (*syn* to 4a-CH_3)), 2.30 (s, 3 H, *p*-C_{Ts}-CH_3), 2.02 – 1.93 (m, 1 H, 2-*H* (*syn* to 4a-CH_3)), 1.72 – 1.62 (m, 2 H, 3-*H*), 1.46 (s, 3 H, 4a-CH_3), 1.32 – 1.11 (m, 2 H, 2-*H* (*anti* to 4a-CH_3), 4-*H* (*anti* to 4a-CH_3)).
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 156.5 (1 C, *C*-10a), 153.0 (1 C, *C*-4b), 144.5 (1 C, *p*-C_{Ts}), 140.4 (1 C, *C*-5a), 136.0 (1 C, *ipso*-C_{Ts}), 129.7 (2 C, *m*-C_{Ts}), 129.4 (1 C, *C*-9b), 126.8 (2 C, *o*-C_{Ts}), 125.0 (1 C, *C*-9a), 123.7 (1 C, *C*-7), 123.6 (1 C, *C*-8), 119.6 (1 C, *C*-9), 115.3 (1 C, *C*-6), 112.6 (1 C, *C*-10), 50.5 (1 C, *C*-4a), 36.0 (1 C, *C*-4), 29.1 (1 C, *C*-2), 27.8 (1 C, *C*-1), 21.6 (1 C, *p*-C_{Ts}-CH_3), 19.5 (1 C, 4a-CH_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3058 (w), 2929 (m), 2854 (m), 1596 (w), 1488 (w), 1444 (m), 1363 (s), 1307 (m), 1268 (w), 1218 (m), 1167 (s), 1121 (m), 1121 (m), 1086 (m), 1017 (w), 980 (m), 864 (m), 842 (m), 811 (m), 747 (s), 705 (w), 662 (s), 601 (w), 566 (m), 541 (m).
UV/Vis (THF): λ_{max} (lg ε) = 311 (3.62), 268 (3.91), 228 (4.61).
ESI-HRMS: calculated $[C_{23}H_{23}NO_2S+Na]^+$: 400.13417
found: 400.13418 (0.02 ppm).

3.15 Bromohydrin 10

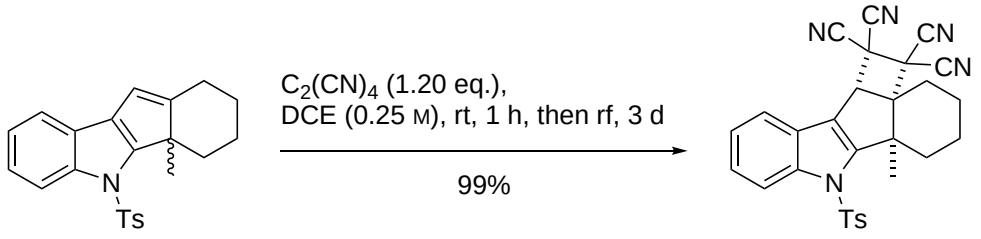


9 **10**

To a solution of alkene **9** (38 mg, 100 µmol, 1.00 eq.) and $NaHCO_3$ (25 mg, 300 µmol, 3.00 eq.) in MeCN (1.0 mL) and H_2O (250 µL) was added Br_2 (1 M in *n*-heptane, 100 µL, 100 µmol, 1.00 eq.) dropwise at 0 °C. The solution was stirred for 2 h at 0 °C. The reaction was quenched by the addition of sat. Na_2SO_3. The phases were separated and the aqueous phase was extracted with TBME (3x50 mL). The combined organic phases were washed with sat. NaCl, dried

over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (10:1) to (8:1)] afforded bromohydrin **10** as a colorless foam (34 mg, 72 µmol, 72%).
TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.53 [vanillin: brown].
^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.47 – 8.43 (m, 1 H, 6-*H*), 7.66 – 7.61 (m, 1 H, 9-*H*), 7.58 – 7.53 (m, 2 H, *o*-H_{Ts}), 7.15 – 7.07 (m, 2 H, 7-*H*, 8-*H*), 6.48 – 6.43 (m, 2 H, *m*-H_{Ts}), 5.30 (d, J = 6.1 Hz, 1 H, 10-*H*), 2.94 – 2.84 (m, 1 H, 4-*H* (*anti* to 4a-CH_3)), 2.20 – 2.11 (m, 1 H, 1-*H* (*anti* to 4a-CH_3)), 1.79 – 1.67 (m, 2 H, 1-*H* (*syn* to 4a-CH_3), 4-*H* (*syn* to 4a-CH_3)), 1.66 (s, 3 H, *p*-C_{Ts}-CH_3), 1.62 (s, 3 H, 4a-CH_3), 1.61 – 1.49 (m, 2 H, 10-O*H*, 3-*H*), 1.36 – 1.22 (m, 2 H, 2-*H*, 3-*H*), 0.76 – 0.62 (m, 1 H, 2-*H*).
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 146.7 (1 C, *C*-4b), 144.5 (1 C, *p*-C_{Ts}), 141.2 (1 C, *C*-5a), 137.4 (1 C, *ipso*-C_{Ts}), 129.8 (2 C, *m*-C_{Ts}), 126.6 (2 C, *o*-C_{Ts}), 126.5 (1 C, *C*-9a), 125.9 (1 C, *C*-9b), 124.8 (1 C, *C*-7), 124.0 (1 C, *C*-8), 120.1 (1 C, *C*-9), 115.7 (1 C, *C*-6), 84.1 (1 C, *C*-10a), 79.8 (1 C, *C*-10), 51.6 (1 C, *C*-4a), 34.8 (1 C, *C*-1), 33.0 (1 C, *C*-4), 27.7 (1 C, 4a-CH_3), 23.0 (1 C, *C*-2), 22.7 (1 C, *C*-3), 21.0 (1 C, *p*-C_{Ts}-CH_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3533 (br. s), 3410 (w), 2929 (m), 2861 (w), 1594 (w), 1482 (w), 1444 (m), 1362 (m), 1304 (m), 1218 (w), 1174 (s), 1081 (m), 1023 (m), 985 (m), 931 (w), 856 (w), 810 (m), 749 (s), 711 (m), 662 (s), 613 (w), 570 (s).
UV/Vis (THF): λ_{max} (lg ε) = 259 (4.18), 226 (4.42).
ESI-HRMS: calculated [$C_{23}H_{24}BrNO_3S$+Na]$^+$: 496.05525
found: 496.05528 (0.06 ppm).

3.16 Cyclobutane 11



9 **11**

A solution of alkene **9** (38 mg, 100 µmol, 1.00 eq.) and tetracyanoethene (16 mg, 120 µmol, 1.20 eq.) in DCE (400 µL) was stirred at room temperature for 1 h and under reflux for 3 d. The mixture was concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (20:1) to (15:1) to (10:1) to (8:1) to (6:1) to (4:1)] afforded cyclobutane **11** as a solid (50 mg, 99 µmol, 99%).
TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.54 [vanillin: brown].
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.04 – 8.00 (m, 1 H, 8-*H*), 7.88 – 7.83 (m, 2 H, *o*-H_{Ts}), 7.62 – 7.58 (m, 1 H, 11-*H*), 7.39 – 7.30 (m, 2 H, 9-*H*, 10-*H*), 7.29 – 7.25 (m, 2 H, *m*-H_{Ts}), 4.36 (s, 1 H, 11c-*H*), 2.74 – 2.60 (m, 2 H, 3-*H* (*anti* to 6a-CH_3), 6-*H* (*syn* to 6a-CH_3)), 2.38 (s, 3 H, *p*-C_{Ts}-CH_3), 2.24 – 2.13 (m, 1 H, 3-*H* (*syn* to 6a-CH_3)), 2.06 – 1.96 (m, 1 H, 4-*H* (*syn* to 6a-CH_3)), 1.87 (s, 3 H, 6a-CH_3), 1.68 – 1.51 (m, 1 H, 5-*H* (*anti* to 6a-CH_3)), 1.48 – 1.37 (m, 2 H, 4-*H* (*anti* to 6a-CH_3), 5-*H* (*syn* to 6a-CH_3)), 1.32 – 1.20 (m, 1 H, 6-*H* (*anti* to 6a-CH_3)).
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 153.8 (1 C, *C*-6b), 146.0 (1 C, *p*-C_{Ts}), 140.6 (1 C, *C*-7a), 135.5 (1 C, *ipso*-C_{Ts}), 130.3 (2 C, *m*-C_{Ts}), 127.2 (2 C, *o*-C_{Ts}), 125.8 (1 C, *C*-9), 124.4 (1 C, *C*-10), 124.0 (1 C, *C*-11a), 120.0 (1 C, *C*-11), 116.3 (1 C, *C*-11b), 115.0 (1 C, *C*-8), 111.9 (1 C,

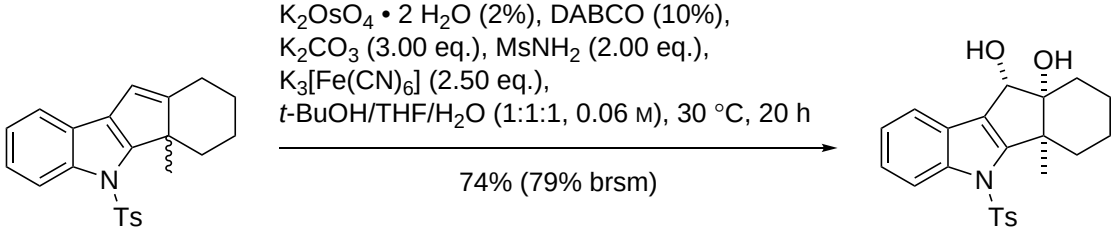
1-*C*N), 110.5 (1 C, 2-*C*N), 110.0 (1 C, 2-*C*N), 109.4 (1 C, 1-*C*N), 67.6 (1 C, *C*-2a), 49.0 (1 C, *C*-11c), 48.6 (1 C, *C*-6a), 44.4 (1 C, *C*-2), 41.0 (1 C, *C*-6), 36.8 (1 C, *C*-1), 29.3 (1 C, *C*-3), 22.6 (1 C, *C*-4), 21.8 (1 C, *p*-C_{Ts}-CH_3), 20.0 (1 C, *C*-5), 16.2 (1 C, 6a-CH_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2940 (m), 2863 (w), 1596 (w), 1548 (w), 1446 (m), 1367 (m), 1322 (m), 1254 (m), 1226 (w), 1175 (s), 1115 (m), 1086 (m), 1026 (m), 982 (m), 906 (m), 864 (w), 842 (w), 806 (m), 737 (s), 666 (s), 571 (s).

UV/Vis (THF): λ_{max} (lg ε) = 258 (4.10).

ESI-HRMS: calculated $[C_{29}H_{23}N_5O_2S+Na]^+$: 528.14647
found: 528.14659 (0.23 ppm).

3.17 Diol 14



9 **14**

To a solution of alkene **9** (1.28 g, 3.40 mmol, 1.00 eq.), DABCO (38 mg, 340 µmol, 0.10 eq.) and $MsNH_2$ (647 mg, 6.80 mmol, 2.00 eq.) in *t*-BuOH (20 mL), THF (20 mL) and H_2O (20 mL) was added K_2CO_3 (1.41 g, 10.2 mmol, 3.00 eq.), $K_3[Fe(CN)_6]$ (2.80 g, 8.50 mmol, 2.50 eq.) and $K_2OsO_4 \cdot 2\,H_2O$ (25 mg, 68 µmol, 0.02 eq.). The mixture was stirred rapidly for 20 h at 30 °C. The reaction was quenched by the addition of sat. Na_2SO_3. The phases were separated and the aqueous phase was extracted with TBME (3x100 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (10:1) to (4:1) to (3:1) to (2:1)] afforded diol **14** (1.04 g, 2.51 mmol, 74%) as a colorless foam and unreacted alkene **9** (70 mg, 189 µmol, 5%) as a colorless foam.

TLC [petroleum ether/EtOAc (2:1)]: R_f = 0.29 [vanillin: brown].

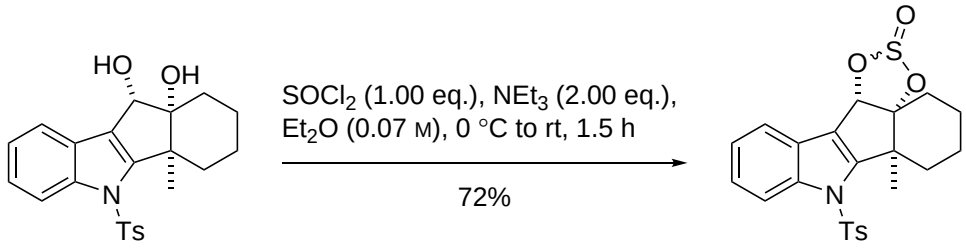
^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 8.44 – 8.42 (m, 1 H, 6-*H*), 7.69 – 7.67 (m, 1 H, 9-*H*), 7.66 – 7.63 (m, 2 H, *o*-H_{Ts}), 7.18 – 7.14 (m, 1 H, 7-*H*), 7.14 – 7.11 (m, 1 H, 8-*H*), 6.48 – 6.45 (m, 2 H, *m*-H_{Ts}), 4.66 (d, *J* = 8.0 Hz, 1 H, 10-*H*), 2.35 – 2.29 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 2.12 (d, *J* = 8.4 Hz, 1 H, 10-O*H*), 1.96 (s, 1 H, 10a-O*H*), 1.65 (s, 3 H, *p*-C_{Ts}-CH_3), 1.64 – 1.59 (m, 1 H, 1-*H* (*anti* to 4a-CH_3)), 1.63 (s, 3 H, 4a-CH_3), 1.49 – 1.42 (m, 2 H, 2-*H*, 4-*H* (*anti* to 4a-CH_3)), 1.36 (ddd, *J* = 13.9 Hz, 10.6 Hz, 4.4 Hz, 1 H, 1-*H* (*syn* to 4a-CH_3)), 1.27 – 1.19 (m, 1 H, 3-*H* (*syn* to 4a-CH_3)), 1.12 – 1.03 (m, 2 H, 2-*H*, 3-*H* (*anti* to 4a-CH_3)).

^{13}C NMR (151 MHz, C_6D_6): δ [ppm] = 151.1 (1 C, *C*-4b), 144.3 (1 C, *p*-C_{Ts}), 141.0 (1 C, *C*-5a), 137.5 (1 C, *ipso*-C_{Ts}), 129.7 (2 C, *m*-C_{Ts}), 127.2 (1 C, *C*-9a), 126.6 (2 C, *o*-C_{Ts}), 124.8 (1 C, *C*-9b), 124.5 (1 C, *C*-7), 124.0 (1 C, *C*-8), 120.0 (1 C, *C*-9), 115.6 (1 C, *C*-6), 85.9 (1 C, *C*-10a), 72.1 (1 C, *C*-10), 49.4 (1 C, *C*-4a), 37.1 (1 C, *C*-4), 31.5 (1 C, *C*-1), 22.8 (1 C, *C*-2), 21.2 (1 C, *C*-3), 21.0 (1 C, *p*-C_{Ts}-CH_3), 20.5 (1 C, 4a-CH_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3382 (br. s), 2931 (m), 2862 (w), 1595 (w), 1480 (w), 1447 (m), 1362 (m), 1308 (w), 1219 (w), 1174 (m), 1122 (w), 1055 (m), 984 (m), 936 (w), 892 (w), 812 (m), 750 (m), 711 (m), 661 (s), 624 (m), 572 (m).

UV/Vis (THF): λ_{max} (lg ε) = 258 (4.16), 222 (4.46).
ESI-HRMS: calculated $[C_{23}H_{25}NO_4S+Na]^+$: 434.13965
found: 434.13980 (0.35 ppm).

3.18 Sulfite 16

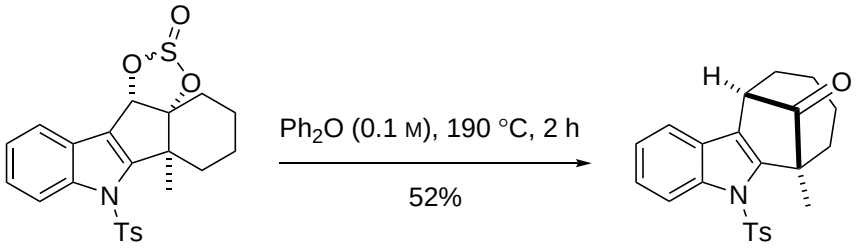


14 **16**

To a solution of diol **14** (142 mg, 357 µmol, 1.00 eq.) and NEt_3 (100 µL, 714 µmol, 2.00 eq.) in Et_2O (1.8 mL) was added a solution of $SOCl_2$ (26 µL, 357 mmol, 1.00 eq.) in Et_2O (3.6 mL) dropwise at 0 °C. The mixture was stirred for 1.5 h at room temperature. The reaction was quenched by the addition of H_2O and the mixture extracted with TBME (3x10 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (15:1) to (10:1)] afforded a mixture (4:3) of diastereomeric sulfites **16** as a colorless solid (34 mg, 72 µmol, 72%)
TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.49 [vanillin: brown].
^{1}H NMR (400 MHz, $CDCl_3$, major diastereomer): δ [ppm] = 8.08 – 8.02 (m, 1 H, 9-*H*), 7.72 – 7.67 (m, 2 H, *o*-H_{Ts}), 7.62 – 7.55 (m, 1 H, 12-*H*), 7.35 – 7.22 (m, 4 H, 10-*H*, 11-*H*, *m*-H_{Ts}), 6.08 (s, 1 H, 12c-*H*), 2.61 – 2.45 (m, 2 H, 4-*H*, 7-*H*), 2.37 (s, 3 H, *p*-C_{Ts}-CH_3), 2.24 – 2.15 (m, 1 H, 4-*H*), 1.95 – 1.82 (m, 1 H, 5-*H*), 1.67 (s, 3 H, 7a-CH_3), 1.63 – 1.32 (m, 4 H, 5-*H*, 6-*H*, 7-*H*).
^{13}C NMR (101 MHz, $CDCl_3$, major diastereomer): δ [ppm] = 151.4 (1 C, *C*-7b), 145.4 (1 C, *p*-C_{Ts}), 140.5 (1 C, *C*-8a), 136.2 (1 C, *ipso*-C_{Ts}), 130.1 (2 C, *m*-C_{Ts}), 126.7 (2 C, *o*-C_{Ts}), 125.0 (1 C, *C*-10), 124.7 (1 C, *C*-12a), 124.2 (1 C, C_{11}), 120.0 (1 C, *C*-12b), 119.5 (1 C, *C*-12), 115.2 (1 C, *C*-9), 105.4 (1 C, *C*-3a), 84.1 (1 C, *C*-12c), 49.7 (1 C, *C*-7a), 38.5 (1 C, *C*-7), 32.6 (1 C, *C*-4), 22.8 (1 C, *C*-5), 21.7 (1 C, *p*-C_{Ts}-CH_3), 19.30 (1 C, *C*-6), 19.29 (1 C, 7a-CH_3).
^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer): δ [ppm] = 8.02 – 7.96 (m, 1 H, 9-*H*), 7.62 – 7.55 (m, 1 H, 12-*H*), 7.54 – 7.49 (m, 2 H, *o*-H_{Ts}), 7.35 – 7.22 (m, 2 H, 10-*H*, 11-*H*), 7.21 – 7.17 (m, 2 H, *m*-H_{Ts}), 5.81 (s, 1 H, 12c-*H*), 2.61 – 2.45 (m, 1 H, 7-*H*), 2.33 (s, 3 H, *p*-C_{Ts}-CH_3), 2.03 – 1.96 (m, 2 H, 4-*H*), 1.95 – 1.82 (m, 1 H, 5-*H*), 1.64 (s, 3 H, 7a-CH_3), 1.63 – 1.32 (m, 4 H, 5-*H*, 6-*H*, 7-*H*).
^{13}C NMR (101 MHz, $CDCl_3$, minor diastereomer): δ [ppm] = 150.6 (1 C, *C*-7b), 144.9 (1 C, *p*-C_{Ts}), 141.1 (1 C, *C*-8a), 136.7 (1 C, *ipso*-C_{Ts}), 130.1 (2 C, *m*-C_{Ts}), 126.2 (2 C, *o*-C_{Ts}), 125.0 (1 C, *C*-10), 124.6 (1 C, *C*-12a), 124.3 (1 C, *C*-11), 122.4 (1 C, *C*-12b), 119.6 (1 C, *C*-12), 115.2 (1 C, *C*-9), 108.6 (1 C, *C*-3a), 82.9 (1 C, *C*-12c), 49.8 (1 C, *C*-7a), 39.2 (1 C, *C*-7), 31.0 (1 C, *C*-4), 22.7 (1 C, *C*-5), 21.7 (1 C, *p*-C_{Ts}-CH_3), 19.5 (1 C, *C*-6), 19.4 (1 C, 7a-CH_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2932 (w), 2861 (w), 1596 (w), 1479 (w), 1447 (m), 1369 (m), 1315 (w), 1260 (w), 1217 (m), 1177 (s), 1122 (m), 1084 (m), 1031 (w), 984 (m), 941 (m), 840 (m), 802 (m), 745 (m), 711 (m), 652 (s), 568 (s).
UV/Vis (THF): λ_{max} (lg ε) = 289 (3.40), 255 (4.16), 221 (4.50).

ESI-HRMS: calculated $[C_{23}H_{23}NO_5S_2+Na]^+$: 480.09099
found: 480.09149 (1.04 ppm).

3.19 Ketone 17



16 **17**

A solution of sulfite **16** (76 mg, 166 µmol) in Ph_2O (1.7 mL) was stirred for 2 h at 190 °C. Flash column chromatography on silica gel [petroleum ether to petroleum ether/EtOAc (20:1) to (15:1)] afforded ketone **17** as an off-white solid (34 mg, 86 µmol, 52%).

TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.50 [vanillin: brown].

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.21 – 8.16 (m, 1 H, 4-*H*), 7.72 – 7.66 (m, 2 H, *o*-H_{Ts}), 7.47 – 7.43 (m, 1 H, 1-*H*), 7.35 (ddd, *J* = 8.4 Hz, 7.2 Hz, 1.3 Hz, 1 H, 3-*H*), 7.29 (ddd, *J* = 7.5 Hz, 7.5 Hz, 0.8 Hz, 1 H, 2-*H*), 7.23 – 7.18 (m, 2 H, *m*-H_{Ts}), 3.70 (dd, *J* = 7.0 Hz, 1.5 Hz, 1 H, 11-*H*), 2.40 – 2.31 (m, 4 H, 7-*H*, *p*-C_{Ts}-CH_3), 2.05 – 1.95 (m, 1 H, 10-*H*), 1.71 – 1.63 (m, 1 H, 10-*H*), 1.62 (s, 3 H, 6-CH_3), 1.55 – 1.38 (m, 4 H, 7-*H*, 8-*H*, 9-*H*), 1.37 – 1.27 (m, 1 H, 9-*H*), 1.03 – 0.90 (m, 1 H, 8-*H*).

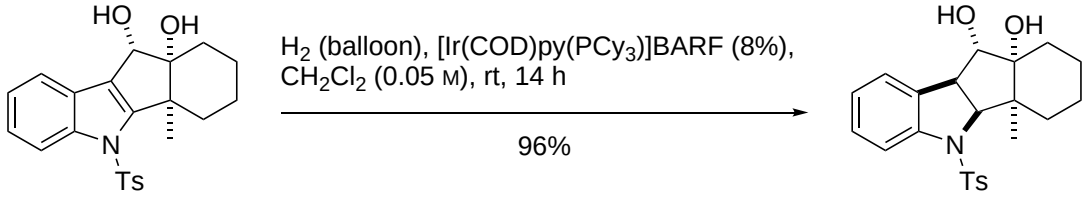
^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 215.4 (1 C, *C*-12), 145.1 (1 C, *p*-C_{Ts}), 143.0 (1 C, *C*-5a), 139.3 (1 C, *C*-4a), 136.5 (1 C, *ipso*-C_{Ts}), 130.0 (2 C, *m*-C_{Ts}), 126.7 (2 C, *o*-C_{Ts}), 125.6 (1 C, *C*-11a), 125.5 (1 C, *C*-11b), 125.0 (1 C, *C*-3), 123.9 (1 C, *C*-2), 119.5 (1 C, *C*-1), 115.2 (1 C, *C*-4), 55.4 (1 C, *C*-6), 46.7 (1 C, *C*-11), 38.9 (1 C, *C*-7), 27.6 (1 C, *C*-10), 25.7 (1 C, *C*-9), 24.7 (1 C, *C*-8), 21.7 (1 C, *p*-C_{Ts}-CH_3), 19.7 (1 C, 6-CH_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2928 (w), 2854 (w), 1752 (m), 1594 (w), 1483 (w), 1445 (m), 1363 (m), 1316 (w), 1257 (w), 1217 (m), 1166 (s), 1084 (m), 1026 (m), 981 (m), 935 (w), 871 (m), 840 (w), 805 (w), 750 (m), 710 (m), 660 (s), 630 (m), 570 (m), 548 (w).

UV/Vis (THF): λ_{max} (lg ε) = 264 (4.15), 221 (4.44).

ESI-HRMS: calculated $[C_{23}H_{23}NO_3S+Na]^+$: 416.12909
found: 416.12924 (0.36 ppm).

3.20 Diol 18

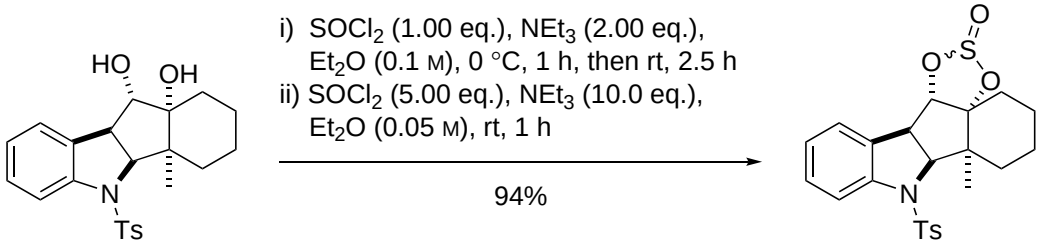


14 **18**

A solution of diol **14** (264 mg, 642 µmol, 1.00 eq.) and [Ir(COD)py(PCy_3)]BARF (78 mg, 51 µmol, 0.08 eq.) in dry CH_2Cl_2 (13 mL) under argon was degassed (three freeze-pump-thaw cycles) and back filled with H_2. The solution was stirred for 14 h at room temperature under H_2 and

concentrated afterwards. Flash column chromatography on silica gel [petroleum ether/EtOAc (2:1) to (1:2)] afforded indoline **18** as a colorless foam (254 mg, 614 µmol, 96%).
TLC [petroleum ether/EtOAc (1:1)]: R_f = 0.46 [vanillin: brown].
^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 8.09 (d, J = 8.1 Hz, 1 H, 6-*H*), 7.61 – 7.56 (m, 2 H, *o*-H_{Ts}), 7.18 – 7.14 (m, 1 H, 9-*H*), 7.08 – 7.01 (m, 1 H, 7-*H*), 6.83 (ddd, J = 7.5 Hz, 7.5 Hz, 1.1 Hz, 1 H, 8-*H*), 6.52 – 6.47 (m, 2 H, *m*-H_{Ts}), 4.79 (d, J = 11.0 Hz, 1 H, 4b-*H*), 3.99 (dd, J = 5.7 Hz, 5.7 Hz, 1 H, 10-*H*), 3.34 (dd, J = 11.0 Hz, 6.2 Hz, 1 H, 9b-*H*), 1.93 (d, J = 6.8 Hz, 1 H, 10-O*H*), 1.85 – 1.76 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.68 (s, 3 H, *p*-C_{Ts}-CH_3), 1.62 (s, 1 H, 10a-*H*), 1.57 (s, 3 H, 4a-CH_3), 1.46 – 1.39 (m, 1 H, 1-*H* (*syn* to 4a-CH_3)), 1.24 – 1.15 (m, 1 H, 3-*H*), 1.12 – 0.99 (m, 3 H, 1-*H* (*anti* to 4a-CH_3), 2-*H*), 0.86 – 0.67 (m, 2 H, 3-*H*, 4-*H* (*anti* to 4a-CH_3)).
^{13}C NMR (101 MHz, C_6D_6): δ [ppm] = 143.9 (1 C, *C*-5a), 143.4 (1 C, *p*-C_{Ts}), 137.3 (1 C, *C*-9a), 135.5 (1 C, *ipso*-C_{Ts}), 129.6 (2 C, *m*-C_{Ts}), 128.4 (1 C, *C*-7), 127.6 (2 C, *o*-C_{Ts}), 125.1 (1 C, *C*-8), 124.1 (1 C, *C*-9), 117.7 (1 C, *C*-6), 81.8 (1 C, *C*-10a), 79.5 (1 C, *C*-10), 75.4 (1 C, *C*-4b), 51.4 (1 C, *C*-9b), 48.1 (1 C, *C*-4a), 31.2 (1 C, *C*-3), 29.8 (1 C, *C*-1), 22.9 (1 C, *C*-3), 21.1 (1 C, *C*-2), 21.0 (1 C, *p*-C_{Ts}-*C*H_3), 18.4 (1 C, 4a-*C*H_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3489 (br. s), 2932 (w), 2863 (w), 1725 (w), 1597 (w), 1464 (w), 1401 (w), 1344 (m), 1241 (w), 1161 (m), 1079 (m), 1033 (m), 968 (m), 858 (w), 812 (m), 758 (m), 701 (m), 658 (m), 618 (w), 574 (m), 545 (w).
UV/Vis (THF): λ_{max} (lg ε) = 285 (3.59), 257 (3.85), 221 (4.28).
ESI-HRMS: calculated $[C_{23}H_{27}NO_4S+Na]^+$: 436.15530
found: 436.15549 (0.44 ppm).

3.21 Sulfite 19



18 **19**

To a solution of diol **18** (62 mg, 150 µmol, 1.00 eq.) and NEt_3 (21 µL, 300 µmol, 2.00 eq.) in Et_2O (750 µL) was added a solution of $SOCl_2$ (11 µL, 150 µmol, 1.00 eq.) in Et_2O (750 µL) dropwise at 0 °C. The solution was stirred for 1 h at 0 °C and for 2.5 h at room temperature. NEt_3 (110 µL, 1.50 mmol, 10.0 eq.) was added. Following, a solution of $SOCl_2$ (55 µL, 750 µmol, 5.00 eq.) in Et_2O (1.5 mL) was added dropwise at room temperature. The solution was stirred for 1 h at room temperature. The reaction was quenched by the addition of sat. $NaHCO_3$ and extracted with TBME (3x10 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether to petroleum ether/EtOAc (15:1) to (10:1) to (8:1)] afforded sulfite **19** as an off-white foam (65 mg, 141 µmol, 94%).
TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.53 [vanillin: brown].
^{1}H NMR (400 MHz, $CDCl_3$, major diastereomer): δ [ppm] = 7.71 – 7.65 (m, 1 H, 9-*H*), 7.52 – 7.46 (m, 2 H, *o*-H_{Ts}), 7.31 – 7.24 (m, 1 H, 10-*H*), 7.22 – 7.07 (m, 4 H, 11-*H*, 12-*H*, *m*-H_{Ts}), 5.21 (d, J = 2.9 Hz, 1 H, 12c-*H*), 4.55 (d, J = 10.3 Hz, 1 H, 7b-*H*), 3.37 – 3.31 (m, 1 H, 12b-*H*), 2.41

(ddd, J = 14.0 Hz, 3.3 Hz, 3.3 Hz, 1 H, 4-*H* (*anti* to 7a-CH_3)), 2.35 (s, 3 H, *p*-C_{Ts}-CH_3), 1.95 (ddd, J = 14.0 Hz, 14.0 Hz, 4.8 Hz, 1 H, 4-*H* (*syn* to 7a-CH_3)), 1.87 – 1.67 (m, 2 H, 5-*H*, 7-*H* (*syn* to 7a-CH_3)), 1.49 (s, 3 H, 4a-CH_3), 1.43 – 1.27 (m, 2 H, 6-*H*), 1.17 – 0.91 (m, 1 H, 5-*H*), 0.65 – 0.48 (m, 1 H, 7-*H* (*anti* to 7a-CH_3)).

^{13}C NMR (101 MHz, $CDCl_3$, major diastereomer): δ [ppm] = 144.4 (1 C, *p*-C_{Ts}), 143.1 (1 C, *C*-8a), 134.7 (1 C, *ipso*-C_{Ts}), 134.2 (1 C, *C*-12a), 129.8 (2 C, *m*-C_{Ts}), 129.2 (1 C, *C*-10), 127.2 (2 C, *o*-C_{Ts}), 125.7 (1 C, *C*-11), 124.0 (1 C, *C*-12), 118.0 (1 C, *C*-9), 103.5 (1 C, *C*-3a), 91.5 (1 C, *C*-12c), 74.8 (1 C, *C*-7b), 52.3 (1 C, *C*-12b), 49.0 (1 C, *C*-7a), 32.6 (1 C, *C*-7), 30.9 (1 C, *C*-4), 24.8 (1 C, *C*-5), 21.7 (1 C, *p*-C_{Ts}-CH_3), 20.2 (1 C, *C*-6), 18.4 (1 C, 7a-CH_3).

^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer): δ [ppm] = 7.71 – 7.65 (m, 1 H, 9-*H*), 7.52 – 7.46 (m, 2 H, *o*-H_{Ts}), 7.31 – 7.24 (m, 1 H, 10-*H*), 7.22 – 7.07 (m, 4 H, 11-*H*, 12-*H*, *m*-H_{Ts}), 4.94 (d, J = 2.9 Hz, 1 H, 12c-*H*), 4.89 (d, J = 10.1 Hz, 1 H, 7b-*H*), 3.95 – 3.89 (m, 1 H, 12b-*H*), 2.32 (s, 3 H, *p*-C_{Ts}-CH_3), 1.87 – 1.67 (m, 4 H, 4-*H*, 5-*H*, 7-*H* (*syn* to 7a-CH_3)), 1.50 (s, 3 H, 4a-CH_3), 1.43 – 1.27 (m, 2 H, 6-*H*), 1.17 – 0.91 (m, 1 H, 5-*H*), 0.65 – 0.48 (m, 1 H, 7-*H* (*anti* to 7a-CH_3)).

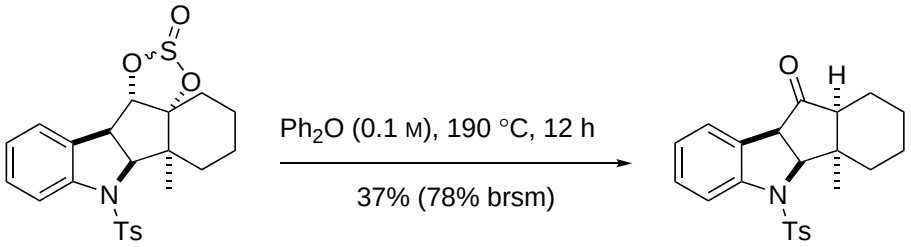
^{13}C NMR (101 MHz, $CDCl_3$, minor diastereomer): δ [ppm] = 144.3 (1 C, *p*-C_{Ts}), 143.3 (1 C, *C*-8a), 135.1 (1 C, *C*-12a), 134.5 (1 C, *ipso*-C_{Ts}), 129.8 (2 C, *m*-C_{Ts}), 128.9 (1 C, *C*-10), 127.3 (2 C, *o*-C_{Ts}), 125.7 (1 C, *C*-11), 123.7 (1 C, *C*-12), 118.2 (1 C, *C*-9), 106.3 (1 C, *C*-3a), 90.1 (1 C, *C*-12c), 75.1 (1 C, *C*-7b), 51.7 (1 C, *C*-12b), 48.0 (1 C, *C*-7a), 32.5 (1 C, *C*-7), 29.8 (1 C, *C*-4), 24.1 (1 C, *C*-5), 21.7 (1 C, *p*-C_{Ts}-CH_3), 20.3 (1 C, *C*-6), 18.3 (1 C, 7a-CH_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2941 (w), 2870 (w), 1597 (w), 1463 (w), 1353 (m), 1304 (w), 1275 (w), 1216 (m), 1162 (m), 1093 (w), 1036 (w), 987 (m), 919 (w), 855 (w), 811 (m), 764 (m), 704 (m), 658 (m), 620 (w), 573 (m), 544 (w).

UV/Vis (THF): λ_{max} (lg ε) = 255 (3.90), 222 (4.21).

ESI-HRMS: calculated $[C_{23}H_{25}NO_5S_2+Na]^+$: 482.10664
found: 482.10696 (0.66 ppm).

3.22 *cis*-Hydrindanone 20



19 **20**

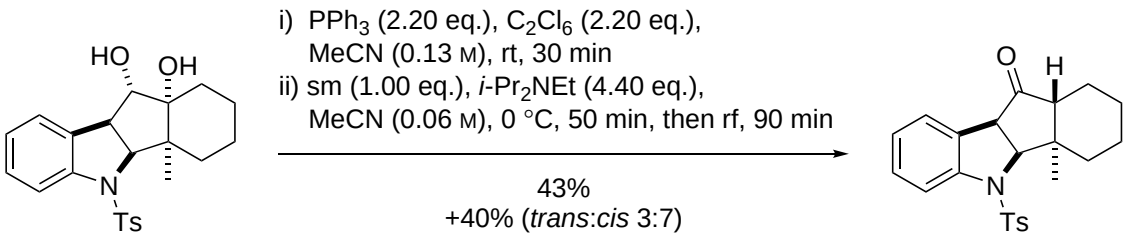
A solution of sulfite **19** (22 µg, 48 µmol) in Ph_2O (480 µL) was stirred for 12 h at 190 °C. Flash column chromatography on silica gel [petroleum ether to petroleum ether/EtOAc (20:1) to (10:1) to (8:1)] afforded ketone **20** (7 mg, 18 µmol, 37%) as a colorless foam and unreacted sulfite **19** (9 mg, 20 µmol, 41%) as an off-white foam.

TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.18 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.71 – 7.68 (m, 1 H, 6-*H*), 7.51 – 7.48 (m, 2 H, *o*-H_{Ts}), 7.42 – 7.39 (m, 1 H, 9-*H*), 7.29 – 7.25 (m, 1 H, 7-*H*), 7.16 – 7.13 (m, 2 H, *m*-H_{Ts}), 7.08 (ddd, J = 7.6 Hz, 7.6 Hz, 1.0 Hz, 1 H, 8-*H*), 4.48 (d, J = 10.3 Hz, 1 H, 4b-*H*), 3.53 – 3.49 (m, 1 H, 9b-*H*), 2.34 (s, 3 H, *p*-C_{Ts}-CH_3), 2.18 – 2.13 (m, 1 H, 10a-*H*), 2.07 – 2.00 (m, 1 H, 1-*H* (*anti* to 4a-CH_3)), 1.66 – 1.60 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.53 (s, 3 H, 4a-CH_3), 1.48 – 1.37 (m, 2 H,

1-*H* (*syn* to 4a-CH_3), 2-*H* (*syn* to 4a-CH_3)), 1.37 – 1.22 (m, 2 H, 3-*H*), 0.92 – 0.80 (m, 1 H, 2-*H* (*anti* to 4a-CH_3)), 0.46 (ddd, J = 13.3 Hz, 13.3 Hz, 4.3 Hz, 1 H, 4-*H* (*anti* to 4a-CH_3)).
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 211.6 (1 C, *C*-10), 144.2 (1 C, *p*-C_{Ts}), 142.6 (1 C, *C*-5a), 134.7 (1 C, *ipso*-C_{Ts}), 130.7 (1 C, *C*-9a), 129.7 (2 C, *m*-C_{Ts}), 128.8 (1 C, *C*-7), 127.3 (2 C, *o*-C_{Ts}), 125.3 (1 C, *C*-8), 124.6 (1 C, *C*-9), 117.8 (1 C, *C*-6), 71.5 (1 C, *C*-4b), 55.0 (1 C, *C*-10a), 51.1 (1 C, *C*-9b), 43.1 (1 C, *C*-4a), 29.8 (1 C, *C*-4), 23.6 (1 C, 4a-CH_3), 22.1 (1 C, *C*-2), 21.7 (1 C, *p*-C_{Ts}-CH_3), 20.9 (1 C, *C*-3), 19.6 (1 C, *C*-1).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3035 (w), 2935 (m), 2863 (w), 1741 (m), 1597 (w), 1461 (m), 1346 (s), 1302 (m), 1255 (m), 1199 (w), 1158 (s), 1092 (m), 1034 (m), 965 (m), 873 (w), 807 (m), 755 (s), 709 (m), 660 (s), 609 (m), 569 (s).
UV/Vis (THF): λ_{max} (lg ε) = 256 (3.84), 228 (4.05).
ESI-HRMS: calculated $[C_{23}H_{25}NO_3S+Na]^+$: 418.14474
found: 418.14490 (0.38 ppm).

3.23 *trans*-Hydrindanone 21

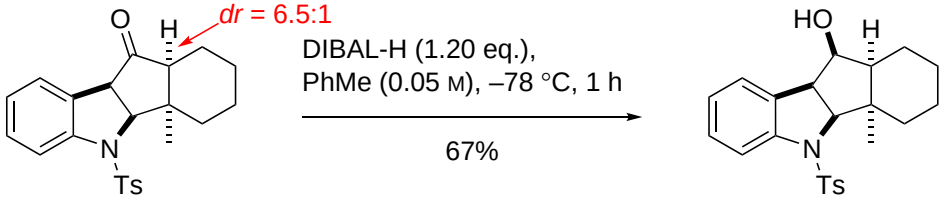


18 **21**

A solution of PPh_3 (354 mg, 1.35 mmol, 2.20 eq.) and C_2Cl_6 (320 mg, 1.35 mmol, 2.20 eq.) in dry MeCN (4.9 mL) under argon was stirred for 30 min at room temperature. To the solution *i*-Pr_2NEt (460 µL, 2.70 mmol, 4.40 eq.) was added at 0 °C . A solution of diol **18** (254 mg, 614 µmol, 1.00 eq.) in dry MeCN (4.9 mL) was added dropwise at 0 °C. The solution was stirred for 50 min at 0 °C and for 90 min under reflux. The reaction was quenched by the addition of H_2O at 0 °C and extracted with TBME (3x50 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (11:1) to (8:1), each +1% NEt_3] afforded *trans*-hydrindanone **21** (104 mg, 263 µmol, 43%) as a colorless foam and a mixture of *trans*-hydrindanone **21** and *cis*-hydrindanone **20** (98 mg, 248 µmol, 40%**21**:**20** = 3:7) as a colorless foam.
TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.57 [vanillin: brown].
^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 8.00 – 7.98 (m, 1 H, 6-*H*), 7.59 – 7.56 (m, 2 H, *o*-H_{Ts}), 7.11 – 7.08 (m, 1 H, 9-*H*), 6.96 – 6.92 (m, 1 H, 7-*H*), 6.66 (ddd, J = 7.5 Hz, 7.5 Hz, 1.0 Hz, 1 H, 8-*H*), 6.59 – 6.56 (m, 2 H, *m*-H_{Ts}), 4.47 (d, J = 8.2 Hz, 1 H, 4b-*H*), 3.35 (d, J = 8.5 Hz, 1 H, 9b-*H*), 2.22 – 2.11 (m, 2 H, 4-*H*), 1.97 (dd, J = 11.9 Hz, 3.4 Hz, 1 H, 10a-*H*), 1.70 (s, 3 H, *p*-C_{Ts}-CH_3), 1.52 – 1.47 (m, 1 H, 1-*H* (*anti* to 4a-CH_3)), 1.46 – 1.40 (m, 1 H, 3-*H* (*anti* to 4a-CH_3)), 1.37 – 1.32 (m, 1 H, 2-*H* (*syn* to 4a-CH_3)), 1.25 – 1.09 (m, 2 H, 1-*H* (*syn* to 4a-CH_3), 3-*H* (*syn* to 4a-CH_3)), 0.72 (s, 3 H, 4a-CH_3), 0.56 (ddddd, J = 13.4 Hz, 13.4 Hz, 13.4 Hz, 4.5 Hz, 4.5 Hz, 1 H, 2-*H* (*anti* to 4a-CH_3)).
^{13}C NMR (151 MHz, C_6D_6): δ [ppm] = 209.6 (1 C, *C*-10), 144.3 (1 C, *C*-5a), 144.0 (1 C, *p*-C_{Ts}), 134.7 (1 C, *ipso*-C_{Ts}), 129.6 (1 C, *C*-9a), 129.6 (2 C, *m*-C_{Ts}), 128.9 (1 C, *C*-7), 128.1 (2 C, *o*-C_{Ts}), 125.1 (1 C, *C*-8), 125.1 (1 C, *C*-9), 117.3 (1 C, *C*-6), 73.2 (1 C, *C*-4b), 53.5 (1 C, *C*-9b),

50.5 (1 C, *C*-10a), 43.7 (1 C, *C*-4a), 34.4 (1 C, *C*-4), 24.7 (1 C, *C*-2), 21.5 (1 C, *C*-3), 21.0 (1 C, *p*-C_{Ts}-CH_3), 19.7 (1 C, *C*-1), 19.6 (1 C, 4a-CH_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2932 (m), 2860 (w), 1744 (m), 1594 (w), 1463 (m), 1352 (m), 1352 (m), 1301 (w), 1242 (w), 1161 (s), 1094 (m), 1034 (m), 973 (m), 939 (m), 858 (w), 811 (m), 752 (m), 710 (m), 667 (s), 620 (m), 572 (s).
UV/Vis (THF): λ_{max} (lg ε) = 290 (3.46), 257 (3.85), 221 (4.34).
ESI-HRMS: calculated $[C_{23}H_{25}NO_3S+K]^+$: 434.11867
found: 434.11891 (0.55 ppm).

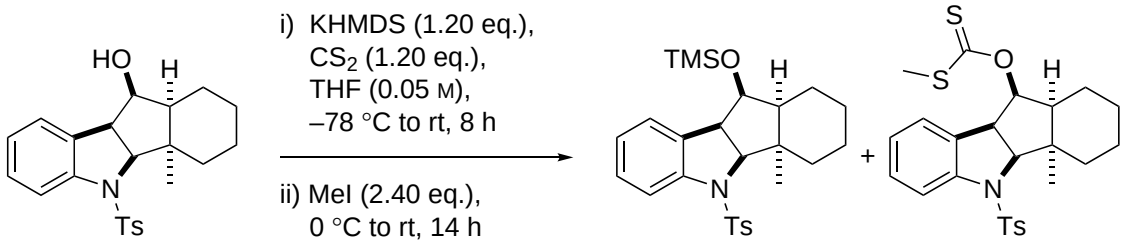
3.24 Alcohol S11



20 **S11**

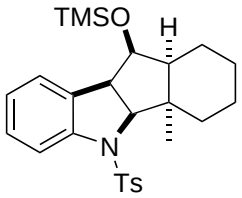
To a solution of ketone **20** and **21** (102 mg, 258 µmol, 1.00 eq., **20**:**21** = 6.5:1) in dry PhMe (5.2 mL) under argon was added DIBAL-H (1.2 M in PhMe, 260 µL, 309 µmol, 1.20 eq.) dropwise at –78 °C. The solution was stirred at –78 °C for 1 h. The reaction was quenched by the addition of MeOH at –78 °C. Sat. sodium potassium tartrate was added and the mixture stirred vigorously for 30 min at room temperature. The mixture was extracted with TBME (3x20 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (4:1)] afforded a alcohol **S11** as a colorless foam (69 mg, 174 µmol, 67%.)
TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.30 [vanillin: brown].
^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.76 – 7.73 (m, 1 H, 6-*H*), 7.50 – 7.47 (m, 2 H, *o*-H_{Ts}), 7.28 – 7.23 (m, 1 H, 7-*H*), 7.15 – 7.08 (m, 3 H, *m*-H_{Ts}, 9-*H*), 7.04 (ddd, *J* = 7.4 Hz, 7.4 Hz, 1.0 Hz, 1 H, 8-*H*), 4.49 (dd, *J* = 6.7 Hz, 6.7 Hz, 1 H, 10-*H*), 4.16 (d, *J* = 10.2 Hz, 1 H, 4b-*H*), 3.67 (dd, *J* = 10.2 Hz, 7.8 Hz, 1 H, 9b-*H*), 2.33 (s, 3 H, *p*-C_{Ts}-CH_3), 1.94 – 1.84 (m, 1 H, 4-*H*), 1.63 (ddd, *J* = 6.0 Hz, 6.0 Hz, 6.0 Hz, 1 H, 10a-*H*), 1.60 – 1.45 (m, 5 H, 1-*H*, 2-*H*, 3-*H*, 4-*H*), 1.30 – 1.17 (m, 5 H, 2-*H*, 4a-CH_3, 10-O*H*), 1.12 – 1.02 (m, 1 H, 1-*H*).
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 144.0 (1 C, *C*-5a), 143.9 (1 C, *p*-C_{Ts}), 134.3 (1 C, *ipso*-C_{Ts}), 132.1 (1 C, *C*-9a), 129.5 (2 C, *m*-C_{Ts}), 128.6 (1 C, *C*-7), 127.6 (2 C, *o*-C_{Ts}), 125.7 (1 C, *C*-9), 124.5 (1 C, *C*-8), 117.6 (1 C, *C*-6), 76.6 (1 C, *C*-10), 76.4 (1 C, *C*-4b), 50.2 (1 C, *C*-9b), 48.8 (1 C, *C*-10a), 43.8 (1 C, *C*-4a), 31.8 (1 C, *C*-4), 28.6 (1 C, 4a-CH_3), 23.4 (1 C, *C*-2), 22.5 (1 C, *C*-1), 21.8 (1 C, *C*-3), 21.6 (1 C, *p*-C_{Ts}-CH_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3553 (br. s), 2925 (m), 2862 (w), 1597 (w), 1465 (m), 1400 (w), 1345 (s), 1293 (w), 1241 (w), 1161 (s), 1089 (m), 1034 (m), 974 (m), 951 (m), 908 (m), 811 (m), 723 (s), 664 (s), 573 (s).
UV/Vis (THF): λ_{max} (lg ε) = 258 (3.78), 223 (4.14).
ESI-HRMS: calculated $[C_{23}H_{27}NO_3S+Na]^+$: 420.16039
found: 420.16061 (0.52 ppm).

3.25 Silyl ether S13 and xanthate S12



S11 | **S13** 19% | **S12** 71%

To a solution of alcohol **S11** (62 mg, 156 µmol, 1.00 eq.) and CS_2 (10 µL, 187 µmol, 1.20 eq.) in dry THF (3.1 mL) under argon was added KHMDS (0.5 M in PhMe, 370 µL, 187 µmol, 1.20 eq.) dropwise at –78 °C. The solution was stirred for 10 min at –78 °C and for 8 h at room temperature. MeI (20 µL, 374 µmol, 2.40 eq.) was added at 0 °C. The solution was stirred for 14 h at room temperature. The reaction was quenched by the addition of sat. NH_4Cl and extracted with TBME (3x10 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (30:1) to (20:1) to (15:1)] afforded silyl ether **S13** (14 mg, 30 µmol, 19%) as a colorless solid and xanthate **S12** (54 mg, 111 µmol, 71%) as a yellow oil.



TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.69 [vanillin: brown].

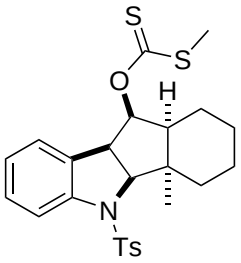
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.68 – 7.64 (m, 1 H, 6-*H*), 7.48 – 7.43 (m, 2 H, *o*-H_{Ts}), 7.22 – 7.17 (m, 1 H, 7-*H*), 7.16 – 7.12 (m, 1 H, 9-*H*), 7.12 – 7.08 (m, 2 H, *m*-H_{Ts}), 6.97 (ddd, *J* = 7.4 Hz, 7.4 Hz, 1.1 Hz, 1 H, 8-*H*), 4.59 (dd, *J* = 8.3 Hz, 6.5 Hz, 1 H, 10-*H*), 4.10 (d, *J* = 9.3 Hz, 1 H, 4b-*H*), 3.47 (dd, *J* = 8.8 Hz, 8.8 Hz, 1 H, 9b-*H*), 2.39 – 2.30 (m, 4 H, 4-*H*, *p*-C_{Ts}-CH_3), 1.55 – 1.23 (m, 6 H, 1-*H*, 2-*H*, 3-*H*, 4-*H*, 10a-*H*), 1.16 (s, 3 H, 4a-CH_3), 1.00 – 0.80 (m, 1 H, 3-*H*), 0.45 – 0.29 (m, 1 H, 1-*H*), 0.09 (s, 9 H, 10-O-Si(CH_3)$_3$).

^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 143.7 (1 C, *p*-C_{Ts}), 142.9 (1 C, *C*-5a), 134.6 (1 C, *ipso*-C_{Ts}), 134.4 (1 C, *C*-9a), 129.4 (2 C, *m*-C_{Ts}), 127.7 (1 C, *C*-7), 127.5 (2 C, *o*-C_{Ts}), 127.1 (1 C, *C*-9), 124.0 (1 C, *C*-8), 117.1 (1 C, *C*-6), 75.7 (1 C, *C*-10), 74.6 (1 C, *C*-4b), 49.5 (1 C, *C*-10a), 49.4 (1 C, *C*-9b), 43.2 (1 C, *C*-4a), 33.3 (1 C, *C*-4), 31.7 (1 C, 4a-CH_3), 23.8 (1 C, *C*-3), 23.4 (1 C, *C*-1), 23.0 (1 C, *C*-2), 21.6 (1 C, *p*-C_{Ts}-CH_3), 0.1 (3 C, 10-O-Si(CH_3)$_3$).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2929 (m), 2860 (w), 1596 (w), 1463 (m), 1394 (w), 1347 (m), 1298 (w), 1249 (m), 1159 (s), 1101 (s), 1052 (m), 961 (m), 893 (m), 835 (s), 739 (s), 665 (s), 638 (m), 569 (s), 541 (w).

UV/Vis (THF): λ_{max} (lg ε) = 259 (3.82), 222 (4.25).

ESI-HRMS: calculated $[C_{26}H_{35}NO_3SSi+Na]^+$: 492.19991
found: 492.19972 (0.39 ppm).



TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.54 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.73 (d, J = 8.2 Hz, 1 H, 6-*H*), 7.49 – 7.46 (m, 2 H, *o*-H_{Ts}), 7.25 – 7.21 (m, 1 H, 7-*H*), 7.15 – 7.11 (m, 2 H, *m*-H_{Ts}), 6.99 (ddd, J = 7.5 Hz, 7.5 Hz, 1.1 Hz, 1 H, 8-*H*), 6.93 – 6.90 (m, 1 H, 9-*H*), 6.54 (dd, J = 7.8 Hz, 5.9 Hz, 1 H, 10-*H*), 4.22 (d, J = 10.4 Hz, 1 H, 4b-*H*), 3.92 (dd, J = 10.1 Hz, 7.9 Hz, 1 H, 9b-*H*), 2.33 (s, 3 H, *p*-C_{Ts}-CH_3), 2.16 (s, 3 H, 10-O-C(=S)-SCH_3), 1.95 (ddd, J = 5.9 Hz, 5.9 Hz, 5.9 Hz, 1 H, 10a-*H*), 1.76 (ddd, J = 13.8 Hz, 10.0 Hz, 3.7 Hz, 1 H, 4-*H* (*anti* to 4a-CH_3)), 1.66 – 1.46 (m, 5 H, 1-*H*, 2-*H*, 3-*H*, 4-*H* (*syn* to CH_3)), 1.38 – 1.20 (m, 5 H, 4a-CH_3, 1-*H*, 3-*H*).

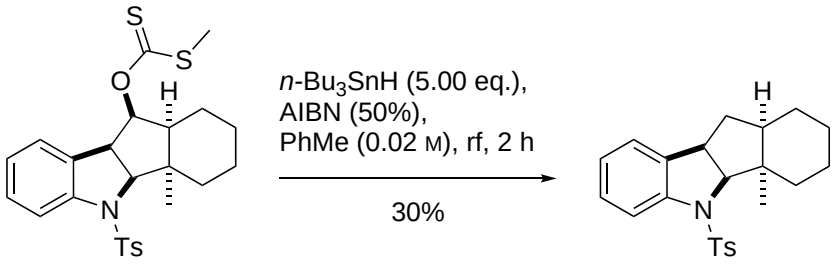
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 215.3 (1 C, 10-O-*C*(=S)-SCH_3), 144.1 (1 C, *p*-C_{Ts}), 143.4 (1 C, *C*-5a), 134.2 (1 C, *ipso*-C_{Ts}), 131.7 (1 C, *C*-9a), 129.6 (2 C, *m*-C_{Ts}), 128.4 (1 C, *C*-7), 127.5 (2 C, *o*-C_{Ts}), 126.0 (1 C, *C*-9), 124.6 (1 C, *C*-8), 117.2 (1 C, *C*-6), 86.4 (1 C, *C*-10), 76.3 (1 C, *C*-4b), 48.8 (1 C, *C*-9b), 48.1 (1 C, *C*-10a), 44.0 (1 C, *C*-4a), 30.3 (1 C, *C*-4), 27.3 (1 C, 4a-*C*H_3), 22.6 (1 C, *C*-3), 22.3 (1 C, *C*-1), 21.7 (1 C, *p*-C_{Ts}-*C*H_3), 21.3 (1 C, *C*-2), 18.4 (1 C, 10-O-C(=S)-S*C*H_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2919 (m), 2860 (m), 1596 (w), 1467 (m), 1348 (m), 1254 (w), 1216 (s), 1159 (s), 1093 (m), 1040 (s), 955 (s), 903 (m), 809 (m), 761 (m), 732 (m), 667 (s), 576 (s).

UV/Vis (THF): λ_{max} (lg ε) = 280 (4.12), 223 (4.31).

ESI-HRMS: calculated $[C_{25}H_{29}NO_3S_3+Na]^+$: 510.12018
found: 510.12015 (0.06 ppm).

3.26 *cis*-Hydrindane S14



S12 **S14**

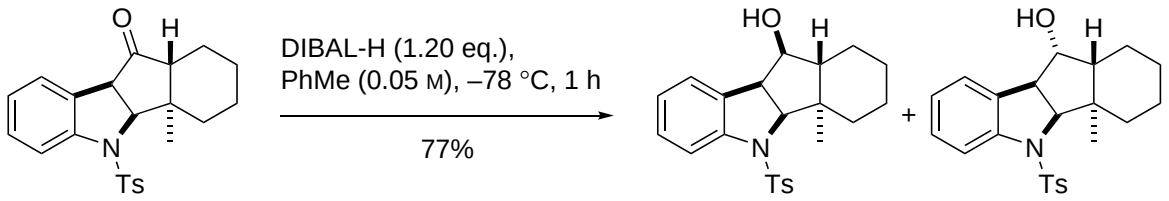
A solution of xanthate **S12** (42 mg, 86 µmol, 1.00 eq.), n-Bu_3SnH (120 µL, 431 µmol, 5.00 eq.) and AIBN (7 mg, 43 µmol, 0.50 eq.) in dry PhMe (4.3 mL) was degassed (three freeze-pump-thaw cycles) and back filled with Ar. The solution was stirred under reflux for 2 h and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (100:1) to (60:1) to (30:1) to (20:1)] afforded *cis*-hydrindane **S14** as a colorless solid (10 mg, 26 µmol, 30%).

TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.50 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.68 – 7.65 (m, 1 H, 6-*H*), 7.50 – 7.47 (m, 2 H, *o*-H_{Ts}), 7.21 – 7.16 (m, 1 H, 7-*H*), 7.14 – 7.10 (m, 2 H, *m*-H_{Ts}), 7.03 (ddd, J = 7.4 Hz, 7.4 Hz, 1.0 Hz, 1 H,

8-*H*), 7.00 – 6.97 (m, 1 H, 9-*H*), 4.11 (d, *J* = 10.6 Hz, 1 H, 4b-*H*), 3.32 (ddd, *J* = 10.1 Hz, 10.1 Hz, 6.6 Hz, 1 H, 9b-*H*), 2.33 (s, 3 H, *p*-C_{Ts}-CH_3), 2.06 – 1.96 (m, 1 H, 10-*H* (*syn* to 4a-CH_3)), 1.78 – 1.68 (m, 2 H, 10-*H* (*anti* to 4a-CH_3), 10a-*H*), 1.59 (dddd, *J* = 13.6 Hz, 13.6 Hz, 4.0 Hz, 4.0 Hz, 1 H, 1-*H*), 1.48 – 1.11 (m, 9 H, 1-*H*, 2-*H*, 3-*H*, 4-*H*, 4a-CH_3), 0.90 – 0.82 (m, 1 H, 4-*H*).
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 143.6 (1 C, *p*-C_{Ts}), 142.9 (1 C, *C*-5a), 139.4 (1 C, *C*-9a), 135.1 (1 C, *ipso*-C_{Ts}), 129.5 (2 C, *m*-C_{Ts}), 127.6 (1 C, *C*-7), 127.3 (2 C, *o*-C_{Ts}), 125.0 (1 C, *C*-8), 124.0 (1 C, *C*-9), 117.3 (1 C, *C*-6), 78.3 (1 C, *C*-4b), 44.1 (1 C, *C*-10a), 44.0 (1 C, *C*-4a), 42.9 (1 C, *C*-9b), 34.1 (1 C, *C*-10), 27.5 (1 C, *C*-4), 23.8 (1 C, *C*-1), 23.5 (1 C, 4a-*C*H_3), 21.8 (1 C, *C*-3), 21.6 (1 C, *p*-C_{Ts}-*C*H_3), 20.5 (1 C, *C*-2).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2926 (m), 2863 (w), 1597 (w), 1461 (m), 1344 (m), 1258 (w), 1227 (w), 1158 (s), 1092 (m), 1023 (m), 955 (m), 894 (w), 805 (m), 755 (m), 714 (w), 665 (m), 622 (w), 570 (m).
UV/Vis (THF): λ_{max} (lg ε) = 258 (3.81).
ESI-HRMS: calculated $[C_{23}H_{27}NO_2S+Na]^+$: 404.16547
found: 404.16558 (0.27 ppm).

3.27 Alcohols S15 and S22



21 **S15** **S22**

To a solution of ketone **21** (40 mg, 101 µmol, 1.00 eq.) in dry PhMe (2.0 mL) under argon was added DIBAL-H (1.2 M in PhMe, 100 µL, 120 µmol, 1.20 eq.) dropwise at –78 °C. The solution was stirred at –78 °C for 1 h. The reaction was quenched by the addition of MeOH at –78 °C. Sat. sodium potassium tartrate was added and the mixture stirred vigorously for 30 min at room temperature. The mixture was extracted with TBME (3x10 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (4:1)] afforded a inseparable mixture of alcohols **S15** and **S22** as a colorless foam (31 mg, 78 µmol, 77%, **S15**:**S22** = 5:2).
TLC [petroleum ether/EtOAc (4:1)]: R_f = 0.23 [vanillin: brown].
^{1}H NMR (600 MHz, C_6D_6, major diastereomer): δ [ppm] = 8.05 – 8.02 (m, 1 H, 6-*H*), 7.60 – 7.57 (m, 2 H, *o*-H_{Ts}), 7.08 – 7.05 (m, 1 H, 9-*H*), 7.03 – 7.00 (m, 1 H, 7-*H*), 6.79 – 6.74 (m, 1 H, 8-*H*), 6.59 – 6.54 (m, 2 H, *m*-H_{Ts}), 4.28 (d, *J* = 8.5 Hz, 1 H, 4b-*H*), 3.68 (ddd, *J* = 9.8 Hz, 9.8 Hz, 9.8 Hz, 1 H, 10-*H*), 3.35 (dd, *J* = 8.3 Hz, 8.3 Hz, 1 H, 9b-*H*), 2.24 (ddd, *J* = 13.3 Hz, 3.2 Hz, 3.2 Hz, 1 H, 4-*H* (*syn* to 4a-CH_3)), 2.01 (ddd, *J* = 13.4 Hz, 13.4 Hz, 4.2 Hz, 1 H, 4-*H* (*anti* to 4a-CH_3)), 1.69 (s, 3 H, *p*-C_{Ts}-CH_3), 1.59 – 1.30 (m, 4 H, 1-*H*, 2-*H* (*anti* to 4a-CH_3), 3-*H*), 1.05 (dddd, *J* = 12.7 Hz, 12.7 Hz, 12.7 Hz, 3.8 Hz, 1 H, 2-*H* (*syn* to 4a-CH_3)), 0.92 – 0.76 (m, 5 H, 1-*H*, 4a-CH_3, 10a-*H*), 0.42 (d, *J* = 10.3 Hz, 1 H, 10-O*H*).
^{13}C NMR (151 MHz, C_6D_6, major diastereomer): δ [ppm] = 145.3 (1 C, *C*-5a), 143.6 (1 C, *p*-C_{Ts}), 135.2 (1 C, *ipso*-C_{Ts}), 130.7 (1 C, *C*-9a), 129.5 (2 C, *m*-C_{Ts}), 128.3 (1 C, *C*-7), 128.0 (2 C, *o*-C_{Ts}), 127.8 (1 C, *C*-9), 123.9 (1 C, *C*-8), 116.6 (1 C, *C*-6), 75.9 (1 C, *C*-10), 75.1 (1 C, *C*-4b),

49.5 (1 C, *C*-10a), 47.4 (1 C, *C*-9b), 43.2 (1 C, *C*-4a), 35.7 (1 C, *C*-4), 25.7 (1 C, *C*-1), 23.2 (1 C, *C*-2), 21.8 (1 C, *C*-3), 21.0 (1 C, *p*-C_{Ts}-CH_3), 19.5 (1 C, 4a-CH_3).

^{1}H NMR (600 MHz, C_6D_6, minor diastereomer): δ [ppm] = 8.02 – 8.00 (m, 1 H, 6-*H*), 7.64 – 7.61 (m, 2 H, *o*-H_{Ts}), 6.99 – 6.96 (m, 1 H, 7-*H*), 6.79 – 6.74 (m, 2 H, 8-*H*, 9-*H*), 6.59 – 6.54 (m, 2 H, *m*-H_{Ts}), 4.60 (d, *J* = 8.7 Hz, 1 H, 4b-*H*), 3.60 (d, *J* = 4.0 Hz, 1 H, 10-*H*), 3.49 (d, *J* = 8.6 Hz, 1 H, 9b-*H*), 2.37 (ddd, *J* = 13.2 Hz, 3.1 Hz, 3.1 Hz, 1 H, 4-*H* (*syn* to 4a-CH_3)), 2.01 (ddd, *J* = 13.4 Hz, 13.4 Hz, 4.2 Hz, 1 H, 4-*H* (*anti* to 4a-CH_3)), 1.67 (s, 3 H, *p*-C_{Ts}-CH_3), 1.59 – 1.30 (m, 7 H, 1-*H*, 2-*H*, 3-*H*, 4a-CH_3), 1.18 – 1.12 (m, 2 H, 2-*H*, 10a-*H*), 0.92 – 0.76 (m, 2 H, 1-*H*, 10-O*H*).

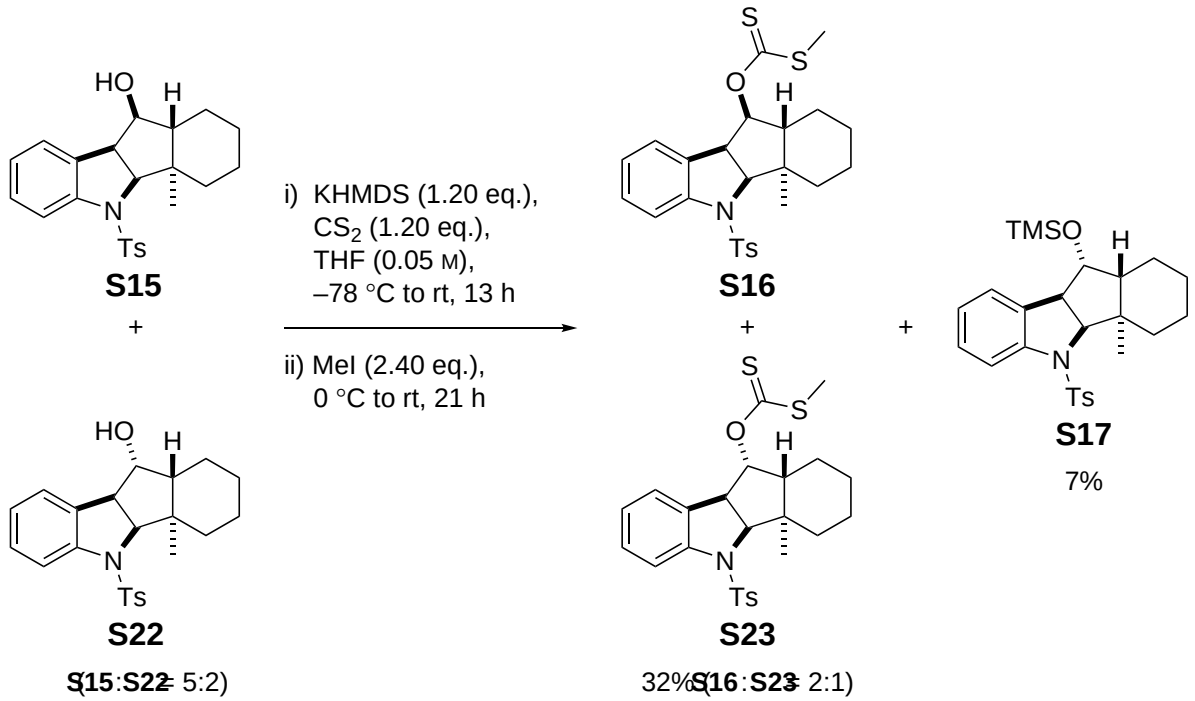
^{13}C NMR (151 MHz, C_6D_6, minor diastereomer): δ [ppm] = 144.1 (1 C, *C*-5a), 143.5 (1 C, *p*-C_{Ts}), 135.3 (1 C, *ipso*-C_{Ts}), 134.5 (1 C, *C*-9a), 129.5 (2 C, *m*-C_{Ts}), 128.2 (1 C, *C*-7 (HSQC)), 128.0 (2 C, *o*-C_{Ts}), 125.3 (1 C, *C*-9), 124.5 (1 C, *C*-8), 117.0 (1 C, *C*-6), 83.0 (1 C, *C*-10), 76.8 (1 C, *C*-4b), 55.4 (1 C, *C*-9b), 48.5 (1 C, *C*-10), 46.3 (1 C, *C*-4a), 37.0 (1 C, *C*-4), 26.1 (1 C, *C*-1), 22.0 (1 C, 4a-CH_3), 21.7 (1 C, *C*-3), 21.6 (1 C, *C*-2), 21.0 (1 C, *p*-C_{Ts}-CH_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3528 (w), 3454 (w), 2927 (m), 2861 (w), 1596 (w), 1467 (m), 1346 (m), 1238 (w), 1159 (s), 1090 (m), 1032 (m), 978 (w), 935 (m), 807 (m), 755 (m), 675 (m), 616 (w), 568 (s), 543 (w).

UV/Vis (THF): λ_{max} (lg ε) = 262 (3.77), 222 (4.21).

ESI-HRMS: calculated $[C_{23}H_{27}NO_3S+Na]^+$: 420.16039
found: 420.16059 (0.48 ppm).

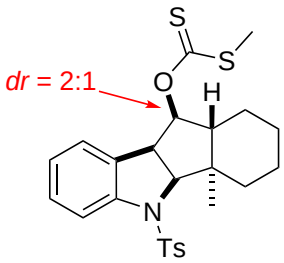
3.28 Xanthates S16 and S23 and silyl ether S17



S15:**S22** = 5:2) 32% (**S16**:**S23** = 2:1)

To a solution of alcohols **S15** and **S22** (72 mg, 181 µmol, 1.00 eq., **S15**:**S22** = 5:2) and CS_2 (13 µL, 217 µmol, 1.20 eq.) in dry THF (3.6 mL) under argon was added KHMDS (0.5 M in PhMe, 430 µL, 217 µmol, 1.20 eq.) dropwise at –78 °C. The solution was stirred for 10 min at –78 °C and for 13 h at room temperature. MeI (27 µL, 435 µmol, 2.40 eq.) was added at 0 °C. The solution was stirred for 21 h at room temperature. The reaction was quenched by the addition of sat. NH_4Cl and extracted with TBME (3x10 mL). The combined organic phases were washed

with sat. NaCl, dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (30:1) to (20:1) to (15:1)] afforded silyl ether **S17** (6 mg, 13 µmol, 7%) as a colorless solid and xanthates **S16** and **S23** (28 mg, 57 µmol, 32%, **S16**:**S23** = 2:1) as a yellow oil.



TLC [petroleum ether/EtOAc (20:1)]: R_f = 0.31 [vanillin: brown].

^{1}H NMR (600 MHz, C_6D_6, major diastereomer): δ [ppm] = 8.05 – 8.02 (m, 1 H, 6-*H*), 7.58 – 7.55 (m, 2 H, *o*-H_{Ts}), 7.09 – 7.06 (m, 1 H, 9-*H*), 7.02 – 6.97 (m, 1 H, 7-*H*), 6.83 – 6.77 (m, 1 H, 8-*H*), 6.58 – 6.55 (m, 2 H, *m*-H_{Ts}), 5.72 (dd, *J* = 11.9 Hz, 7.9 Hz, 1 H, 10-*H*), 4.36 (d, *J* = 8.5 Hz, 1 H, 4b-*H*), 4.16 (dd, *J* = 8.2 Hz, 8.2 Hz, 1 H, 9b-*H*), 2.26 – 2.20 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 2.08 – 1.98 (m, 4 H, 4-*H* (*anti* to 4a-CH_3), 10-O-C(=S)-SCH_3), 1.71 – 1.64 (m, 4 H, 10a-*H*, *p*-C_{Ts}-CH_3), 1.53 – 1.22 (m, 4 H, 1-*H*, 2-*H*, 3-*H*), 1.04 (dddd, *J* = 12.8 Hz, 12.8 Hz, 12.8 Hz, 3.9 Hz, 1 H, 1-*H*), 0.81 (s, 3 H, 4a-CH_3), 0.79 – 0.66 (m, 1 H, 2-*H*).

^{13}C NMR (151 MHz, C_6D_6, major diastereomer): δ [ppm] = 216.8 (1 C, 10-O-*C*(=S)-SCH_3), 145.1 (1 C, *C*-5a), 143.8 (1 C, *p*-C_{Ts}), 135.0 (1 C, *ipso*-C_{Ts}), 130.1 (1 C, *C*-9a), 129.5 (2 C, *m*-C_{Ts}), 128.6 (1 C, *C*-7), 128.0 (2 C, *o*-C_{Ts} (HSQC)), 127.4 (1 C, *C*-9), 124.2 (1 C, *C*-8), 116.7 (1 C, *C*-6), 87.2 (1 C, *C*-10), 75.2 (1 C, *C*-4b), 46.0 (1 C, *C*-10a), 45.3 (1 C, *C*-9b), 42.6 (1 C, *C*-4a), 35.5 (1 C, *C*-4), 25.2 (1 C, *C*-2), 23.1 (1 C, *C*-1), 21.6 (1 C, *C*-3), 21.0 (1 C, *p*-C_{Ts}-CH_3), 19.4 (1 C, 4a-CH_3), 18.6 (1 C, 10-O-C(=S)-SCH_3).

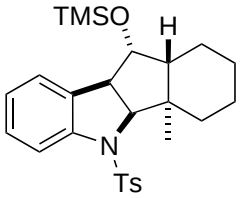
^{1}H NMR (600 MHz, C_6D_6, minor diastereomer): δ [ppm] = 8.02 – 7.99 (m, 1 H, 6-*H*), 7.68 – 7.66 (m, 1 H, 9-*H*), 7.61 – 7.58 (m, 2 H, *o*-H_{Ts}), 7.02 – 6.97 (m, 1 H, 7-*H*), 6.83 – 6.77 (m, 1 H, 8-*H*), 6.58 – 6.55 (m, 2 H, *m*-H_{Ts}), 5.59 (d, *J* = 4.0 Hz, 1 H, 10-*H*), 4.46 (d, *J* = 8.6 Hz, 1 H, 4b-*H*), 3.85 (d, *J* = 8.7 Hz, 1 H, 9b-*H*), 2.40 – 2.35 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 2.08 – 1.98 (m, 4 H, 4-*H* (*anti* to 4a-CH_3), 10-O-C(=S)-SCH_3), 1.71 – 1.64 (m, 3 H, *p*-C_{Ts}-CH_3), 1.53 – 1.22 (m, 5 H, 1-*H*, 2-*H*, 3-*H*, 10a-*H*), 1.20 (s, 3 H, 4a-CH_3), 1.14 – 1.09 (m, 1 H, 1-*H*), 0.79 – 0.66 (m, 1 H, 2-*H*).

^{13}C NMR (151 MHz, C_6D_6, minor diastereomer): δ [ppm] = 215.6 (1 C, 10-O-*C*(=S)-SCH_3), 144.1 (1 C, *C*-5a), 143.7 (1 C, *p*-C_{Ts}), 135.1 (1 C, *ipso*-C_{Ts}), 132.9 (1 C, *C*-9a), 129.5 (2 C, *m*-C_{Ts}), 128.9 (1 C, *C*-7), 128.0 (2 C, *o*-C_{Ts} (HSQC)), 126.3 (1 C, *C*-9), 125.0 (1 C, *C*-8), 116.8 (1 C, *C*-6), 93.2 (1 C, *C*-10), 76.1 (1 C, *C*-4b), 52.6 (1 C, *C*-9b), 47.4 (1 C, *C*-10a), 46.9 (1 C, *C*-4a), 36.9 (1 C, *C*-4), 25.9 (1 C, *C*-2), 21.7 (1 C, *C*-1), 21.5 (1 C, *C*-3), 21.4 (1 C, 4a-CH_3), 21.0 (1 C, *p*-C_{Ts}-CH_3), 18.6 (1 C, 10-O-C(=S)-SCH_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2930 (m), 2860 (w), 1596 (w), 1467 (m), 1353 (m), 1301 (w), 1213 (m), 1161 (s), 1055 (s), 975 (m), 935 (m), 806 (m), 754 (m), 674 (m), 571 (s).

UV/Vis (THF): λ_{max} (lg ε) = 278 (4.16), 222 (4.36).

ESI-HRMS: calculated $[C_{25}H_{29}NO_3S_3+Na]^+$: 510.12018
found: 510.12017 (0.02 ppm).



TLC [petroleum ether/EtOAc (20:1)]: R_f = 0.46 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.65 – 7.62 (m, 1 H, 6-*H*), 7.54 – 7.50 (m, 2 H, *o*-H_{Ts}), 7.18 – 7.11 (m, 3 H, 7-*H*, *m*-H_{Ts}), 7.05 – 7.02 (m, 1 H, 9-*H*), 6.98 (ddd, *J* = 7.4 Hz, 7.4 Hz, 1.0 Hz, 1 H, 8-*H*), 4.35 (d, *J* = 8.6 Hz, 1 H, 4b-*H*), 3.88 (d, *J* = 4.3 Hz, 1 H, 10-*H*), 3.54 (d, *J* = 8.5 Hz, 1 H, 9b-*H*), 2.32 (s, 3 H, *p*-C_{Ts}-CH_3), 1.98 – 1.93 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.76 – 1.69 (m, 2 H, 1-*H*, 4-*H* (*anti* to 4a-CH_3)), 1.67 – 1.60 (m, 1 H, 3-*H*), 1.58 – 1.45 (m, 2 H, 2-*H*, 3-*H*), 1.39 – 1.32 (m, 1 H, 2-*H*), 1.19 (s, 3 H, 4a-CH_3), 1.18 – 1.06 (m, 2 H, 1-*H*, 10a-*H*), 0.10 (s, 9 H, 10-O-Si(CH_3)$_3$).

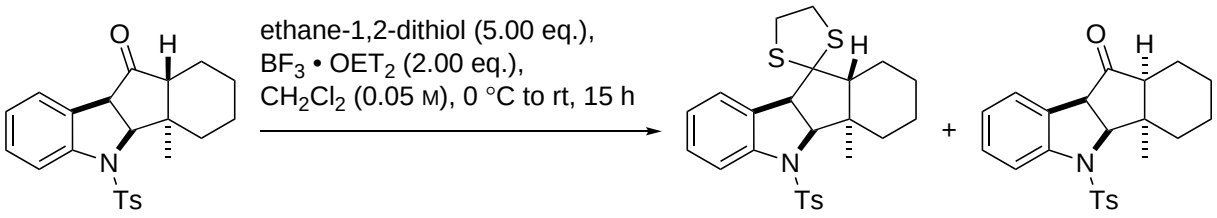
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 143.8 (1 C, *p*-C_{Ts}), 143.2 (1 C, *C*-5a), 134.44 (1 C, *C*-9a), 134.42 (1 C, *ipso*-C_{Ts}), 129.5 (2 C, *m*-C_{Ts}), 128.0 (1 C, *C*-7), 127.8 (2 C, *o*-C_{Ts}), 124.9 (1 C, *C*-9), 124.5 (1 C, *C*-8), 116.7 (1 C, *C*-6), 83.0 (1 C, *C*-10), 76.5 (1 C, *C*-4b), 56.1 (1 C, *C*-9b), 48.1 (1 C, *C*-10a), 46.2 (1 C, *C*-4a), 36.6 (1 C, *C*-4), 26.0 (1 C, *C*-1), 22.1 (1 C, *C*-2), 21.6 (1 C, *p*-C_{Ts}-CH_3), 21.55 (1 C, 4a-CH_3), 21.51 (1 C, *C*-3), 0.2 (3 C, 10-O-Si(CH_3)$_3$).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3052 (w), 2927 (m), 2859 (m), 1597 (w), 1468 (m), 1451 (m), 1351 (m), 1293 (w), 1247 (m), 1159 (s), 1095 (s), 1023 (s), 972 (m), 930 (m), 840 (s), 759 (s), 699 (m), 662 (s), 573 (s).

UV/Vis (THF): λ_{max} (lg ε) = 260 (3.85), 222 (4.32).

ESI-HRMS: calculated $[C_{26}H_{35}NO_3SSi+Na]^+$: 492.19991
found: 492.19993 (0.04 ppm).

3.29 Dithiolane 22



To a solution of ketone **21** (33 mg, 83 µmol, 1.00 eq.) and ethane-1,2-dithiol (34 µL, 417 µmol, 5.00 eq.) in dry CH_2Cl_2 (1.6 mL) under argon was added $BF_3 \bullet OEt_2$ (20 µL, 166 µmol, 2.00 eq.) dropwise at 0 °C. The solution was stirred at room temperature for 15 h. The reaction was quenched by the addition of sat. $NaHCO_3$ and extracted with CH_2Cl_2 (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (20:1) to (10:1)] afforded dithiolane **22** as a colorless solid (11 mg, 23 µmol, 28%), and a mixture of ketones **21** and **20** as a colorless foam (21 mg, 53 µmol, 64%, **21**:**20** = 5.6:1).

TLC [petroleum ether/EtOAc (20:1)]: R_f = 0.21 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.64 – 7.61 (m, 1 H, 6-*H*), 7.46 – 7.43 (m, 2 H, *o*-H_{Ts}), 7.34 – 7.31 (m, 1 H, 9-*H*), 7.22 – 7.18 (m, 1 H, 7-*H*), 7.12 – 7.08 (m, 2 H, *m*-H_{Ts}), 6.97 (td,

J = 7.6 Hz, 1.1 Hz, 1 H, 8-*H*), 4.34 (d, J = 8.7 Hz, 1 H, 4b-*H*), 4.03 (d, J = 8.9 Hz, 1 H, 9b-*H*), 3.32 – 3.17 (m, 1 H, 10-S-CH_2-CH_2-S-10 (*syn* to 4a-CH_3)), 3.26 – 3.24 (m, 1 H, 10-S-CH_2-CH_2-S-10 (*syn* to 4a-CH_3)), 3.15 – 3.06 (m, 2 H, 10-S-CH_2-CH_2-S-10 (*anti* to 4a-CH_3)), 2.31 (s, 3 H, *p*-C_{Ts}-CH_3), 2.11 – 2.04 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.83 – 1.64 (m, 4 H, 1-*H*, 2-*H* (*syn* to 4a-CH_3), 3-*H*, 4-*H* (*anti* to 4a-CH_3)), 1.61 (dd, J = 11.9 Hz, 2.5 Hz, 1 H, 10a-*H*), 1.59 – 1.48 (m, 2 H, 1-*H*, 3-*H*), 1.26 (s, 3 H, 4a-CH_3), 1.23 – 1.11 (m, 1 H, 2-*H* (*anti* to 2-H)).

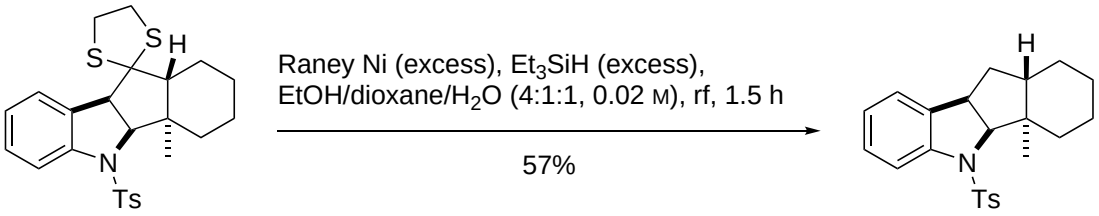
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 144.0 (1 C, *p*-C_{Ts}), 143.3 (1 C, *C*-5a), 133.8 (1 C, *ipso*-C_{Ts}), 132.4 (1 C, *C*-9a), 129.7 (1 C, *C*-9), 129.4 (2 C, *m*-C_{Ts}), 128.5 (1 C, *C*-7), 127.9 (2 C, *o*-C_{Ts}), 123.1 (1 C, *C*-8), 116.0 (1 C, *C*-6), 78.3 (1 C, *C*-10), 76.1 (1 C, *C*-4b), 61.8 (1 C, *C*-9b), 55.1 (1 C, *C*-10a), 45.2 (1 C, *C*-4a), 41.2 (1 C, 10-S-CH_2 (*syn* to 4a-CH_3)), 38.4 (1 C, 10-S-CH_2 (*anti* to 4a-CH_3)), 37.6 (1 C, *C*-4), 25.9 (1 C, *C*-2), 22.4 (1 C, *C*-1), 21.7 (1 C, *C*-3), 21.6 (1 C, *p*-C_{Ts}-CH_3), 21.3 (1 C, 4a-CH_3).

IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2921 (m), 2857 (w), 1594 (w), 1466 (m), 1343 (m), 1242 (w), 1158 (s), 1093 (m), 1030 (m), 974 (m), 931 (m), 871 (w), 854 (w), 805 (m), 756 (m), 690 (m), 673 (m), 656 (m), 619 (w), 568 (s).

UV/Vis (THF): λ_{max} (lg ε) = 260 (3.73), 222 (4.23).

ESI-HRMS: calculated $[C_{25}H_{29}NO_2S_3+Na]^+$: 494.12526
found: 494.12507 (0.38 ppm).

3.30 *trans*-Hydrindane 23



22 **23**

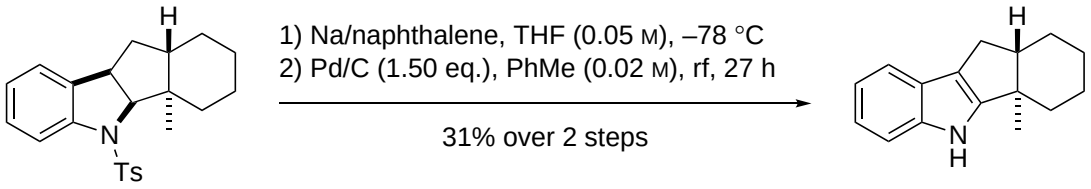
To a solution of dithiolane **22** (11 mg, 23 µmol, 1.00 eq.) and Et_3SiH (50 µL, 313 µmol, 13.6 eq.) in EtOH (800 µL) and dioxane (230 µL) under argon was added a slurry of Raney Ni in H_2O (230 µL, 672 mg, this equals approx. $1.167 \cdot (672\,\text{mg} - (230\,\mu\text{L} \cdot 0.997\,\text{mg}\,\mu\text{L}^{-1}))$ = 470 mg Ni, 8.01 mmol, 348 eq.). The reaction was stirred rapidly under reflux for 1.5 h. The mixture was filtered through Celite 545 (rinsed with CH_2Cl_2) and the filtrate dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (30:1)] afforded an inseparable mixture (6 mg) of *trans*-hydrindane **23** and two other products (1.0:0.1:0.1, ^{1}H NMR). [Based on analysis of the mixture (NMR and MS), we preliminary assigned these side-products as the C-10/C-10a dehydrogenated product and the mono-desulfurized starting material.]

To a solution of the crude product in CH_2Cl_2 (600 µL) was added 70% *m*-CPBA (6 mg, 24 µmol, 1.05 eq.). The solution was stirred for 2 h at room temperature. The reaction was quenched by the addition $NaHCO_3$ and extracted with CH_2Cl_2 (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (30:1)] afforded *trans*-hydrindane **23** as a colorless solid (5 mg, 13 µmol, 57%).

TLC [petroleum ether/EtOAc (10:1)]: R_f = 0.53 [vanillin: brown].

^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.63 – 7.60 (m, 1 H, 6-*H*), 7.53 – 7.49 (m, 2 H, *o*-H_{Ts}), 7.17 – 7.10 (m, 3 H, 7-*H*, *m*-H_{Ts}), 7.01 – 6.97 (m, 2 H, 8-*H*, 9-*H*), 4.15 (d, *J* = 8.4 Hz, 1 H, 4b-*H*), 3.57 (dd, *J* = 8.2 Hz, 8.2 Hz, 1 H, 9b-*H*), 2.32 (s, 3 H, *p*-C_{Ts}-CH_3), 2.02 – 1.94 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.80 – 1.69 (m, 2 H, 10-*H* (*syn* to 4a-CH_3), 4-*H* (*anti* to 4a-CH_3)), 1.69 – 1.61 (m, 2 H, 2-*H*, 3-*H*), 1.59 – 1.42 (m, 3 H, 1-*H*, 3-*H*, 10-*H* (*anti* to 4a-CH_3)), 1.30 – 1.02 (m, 3 H, 1-*H*, 2-*H*, 10a-*H*), 0.90 (s, 3 H, 4a-CH_3).
^{13}C NMR (126 MHz, $CDCl_3$): δ [ppm] = 143.8 (1 C, *p*-C_{Ts}), 143.4 (1 C, *C*-5a), 137.3 (1 C, *C*-9a), 134.5 (1 C, *ipso*-C_{Ts}), 129.5 (2 C, *m*-C_{Ts}), 127.7 (2 C, *o*-C_{Ts}), 127.6 (1 C, *C*-7), 124.9 (1 C, *C*-9), 124.7 (1 C, *C*-8), 116.3 (1 C, *C*-6), 76.2 (1 C, *C*-4b), 45.7 (1 C, *C*-4a), 43.5 (1 C, *C*-9b), 42.8 (1 C, *C*-10a), 37.9 (1 C, *C*-10), 34.8 (1 C, *C*-4), 26.1 (1 C, *C*-2), 25.3 (1 C, *C*-1), 21.6 (1 C, *p*-C_{Ts}-CH_3), 21.5 (1 C, *C*-3), 18.4 (1 C, 4a-CH_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 2926 (m), 2860 (m), 1596 (w), 1465 (m), 1384 (w), 1344 (s), 1292 (w), 1259 (w), 1224 (w), 1156 (s), 1093 (m), 1029 (m), 982 (m), 907 (m), 809 (m), 743 (s), 667 (s), 616 (m), 569 (s).
UV/Vis (THF): λ_{max} (lg ε) = 260 (3.74).
ESI-HRMS: calculated $[C_{23}H_{27}NO_2S+Na]^+$: 404.16547
found: 404.16553 (0.15 ppm).

3.31 *trans*-Hydrindane 24

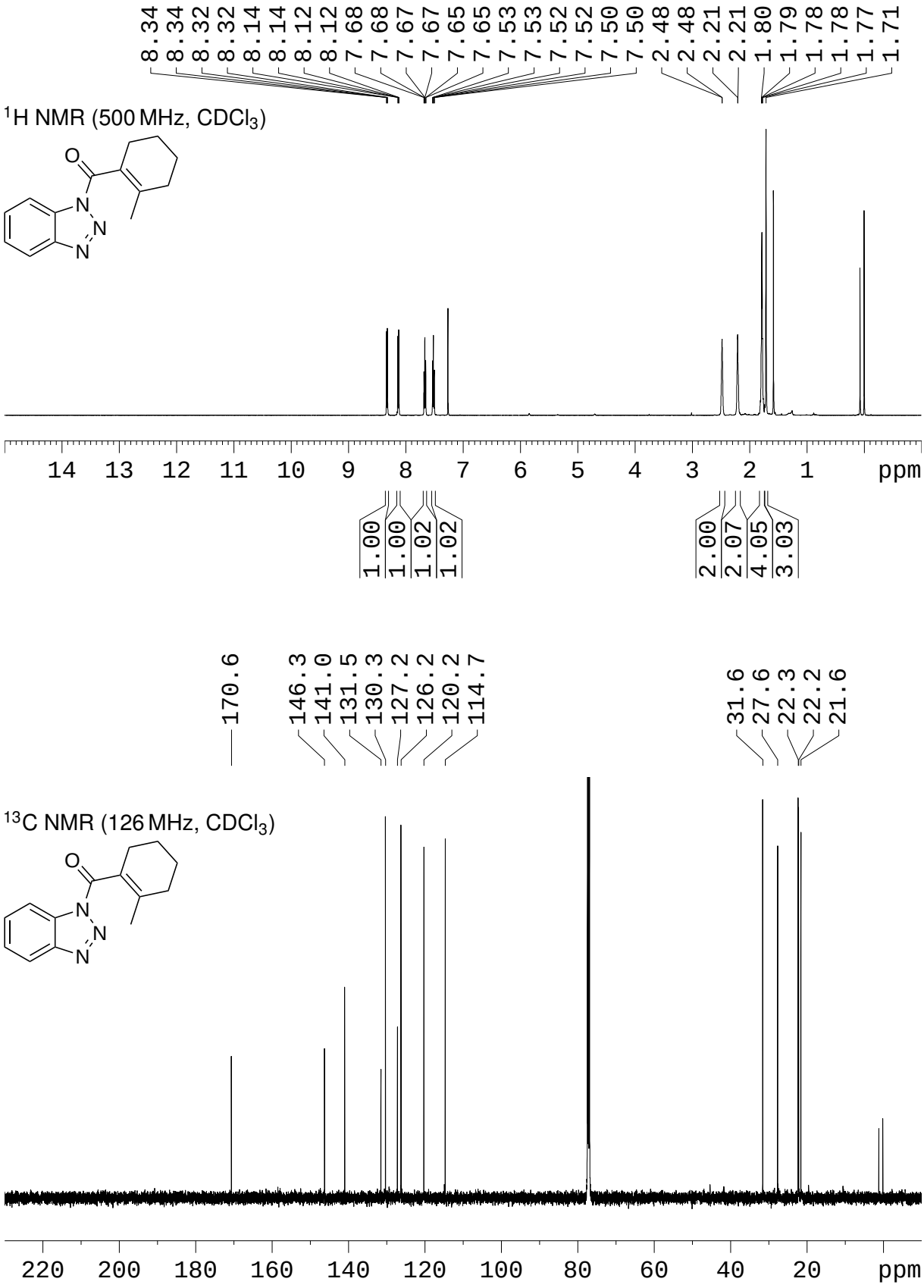


23 **24**

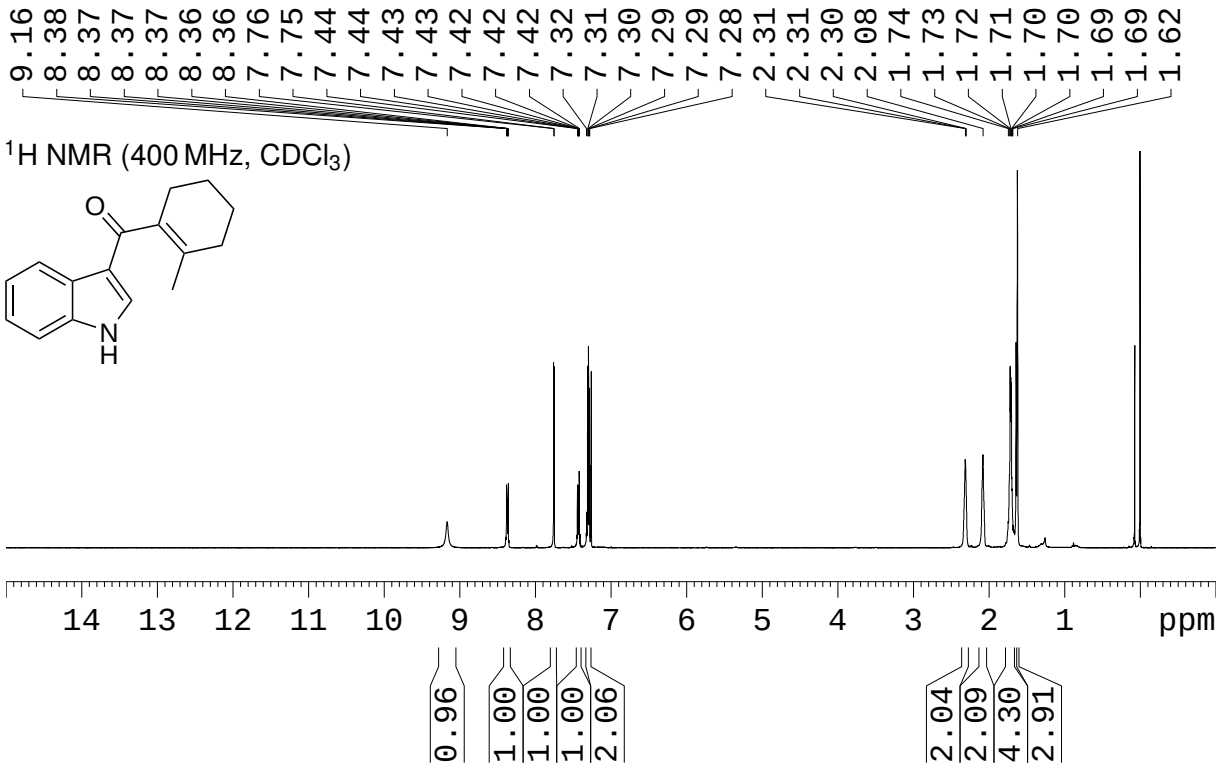
Sulfonamide **23** (44 mg, 115 µmol, 1.00 eq.) was dissolved in dry THF (2.3 mL) and cooled to –78 °C. Separately, freshly cut sodium (80 mg, 3.46 mmol, 30.0 eq.) was added to a solution of naphthalene (222 mg, 1.73 mmol, 15.0 eq.) in dry THF (9 mL). This suspension was treated by sonication for 30 min, which gave a deep green solution (~0.2 M). The Na/naphthalene solution was added dropwise to the starting material at –78 °C. After full consumption of the starting material (monitored by TLC), the reaction was quenched by the addition of sat. NH_4Cl and extracted with TBME (3x20 mL). The combined organic phases were washed with sat. NaCl, dried over $MgSO_4$, filtered, and concentrated. Flash chromatography on silica gel [petroleum ether/EtOAc (60:1) to (30:1)] afforded the crude product (22 mg).
To a solution of the crude product in dry PhMe (5.8 mL) under argon was added Pd/C (10 wt% Pd on C, 184 mg, 173 µmol, 1.50 eq.). The mixture was degassed (three freeze-pump-thaw cycles) and back filled with argon. The mixture was stirred for 27 h under reflux and then filtered through Celite 545 (rinsed with TBME) and the filtrate concentrated. Flash column chromatography on silica gel [petroleum ether/EtOAc (30:1)] afforded *trans*-hydrindane **24** as a colorless solid (8 mg, 36 µmol, 31% over 2 steps).
TLC [petroleum ether/EtOAc (20:1)]: R_f = 0.43 [vanillin: brown].
^{1}H NMR (500 MHz, C_6D_6): δ [ppm] = 7.65 – 7.60 (m, 1 H, 9-*H*), 7.26 – 7.20 (m, 2 H, 7-*H*, 8-*H*), 7.14 – 7.09 (m, 1 H, 6-*H*), 6.62 (s, 1 H, 5-*H*), 2.64 (dd, *J* = 13.3 Hz, 6.3 Hz, 1 H, 10-*H* (*anti* to 4a-CH_3)), 2.37 (dd, *J* = 13.1 Hz, 11.0 Hz, 1 H, 10-*H* (*syn* to 4a-CH_3)), 2.26 – 2.17 (m, 1 H,

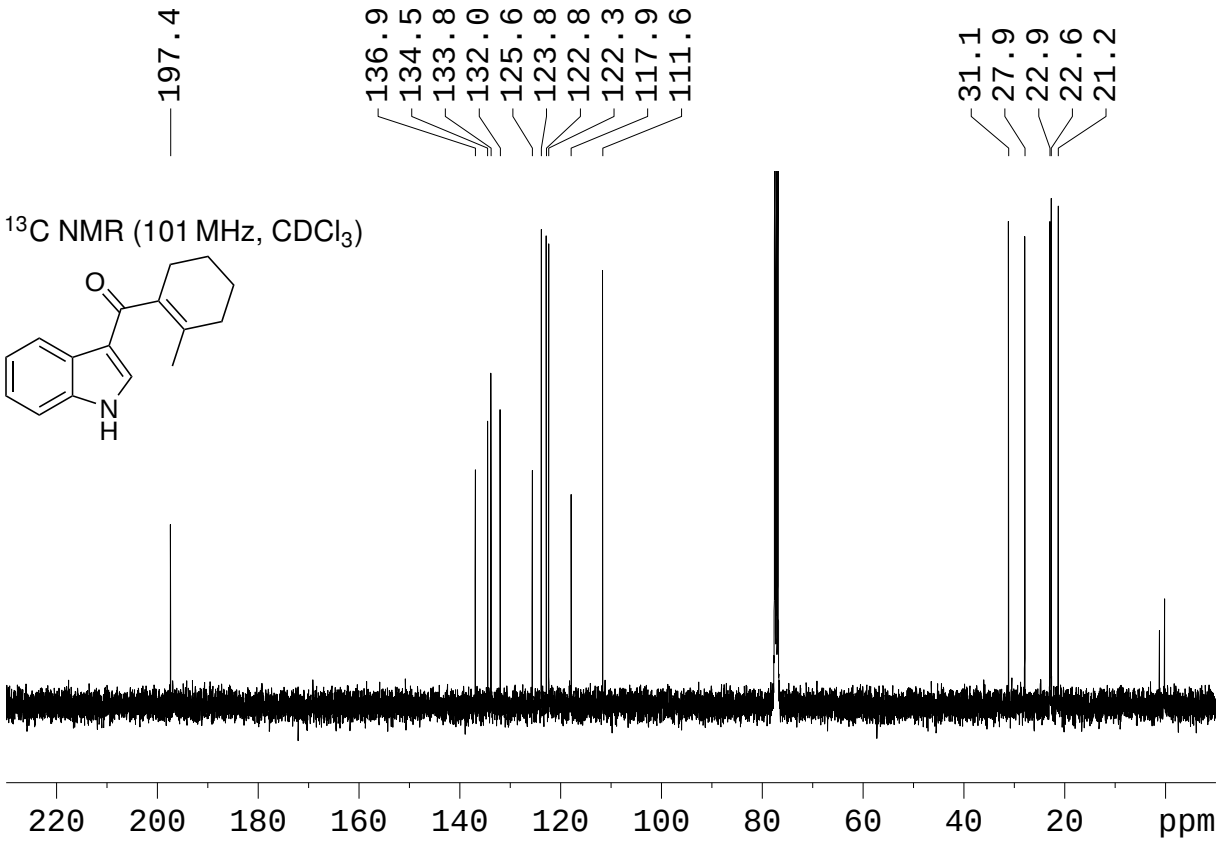
10a-*H*), 1.83 – 1.77 (m, 1 H, 4-*H* (*syn* to 4a-CH_3)), 1.74 – 1.67 (m, 1 H, 2-*H*), 1.60 – 1.45 (m, 5 H, 1-*H*, 3*H*, 4-*H* (*anti* to 4a-CH_3)), 1.30 – 1.21 (m, 1 H, 2-*H*), 0.87 (s, 3 H, 4a-CH_3).
^{13}C NMR (126 MHz, C_6D_6): δ [ppm] = 152.5 (1 C, *C*-4b), 140.0 (1 C, *C*-5a), 125.9 (1 C, *C*-9a), 120.6 (1 C, *C*-7), 120.0 (1 C, *C*-8), 119.1 (1 C, *C*-9), 116.9 (1 C, *C*-9b), 112.0 (1 C, *C*-6), 55.9 (1 C, *C*-10a), 42.3 (1 C, *C*-4a), 35.3 (1 C, *C*-4), 28.3 (1 C, *C*-10), 27.2 (1 C, *C*-2), 25.0 (1 C, *C*-1), 21.7 (1 C, *C*-3), 17.2 (1 C, 4a-*C*H_3).
IR (diamond ATR): $\tilde{\nu}$ [cm^{-1}] = 3400 (m), 3056 (w), 2923 (m), 2854 (m), 1656 (w), 1608 (w), 1452 (m), 1366 (w), 1301 (m), 1254 (m), 1150 (w), 1094 (m), 1019 (m), 973 (w), 923 (w), 868 (w), 805 (m), 741 (m), 704 (m), 657 (w), 614 (w), 579 (w).
UV/Vis (THF): λ_{max} (lg ε) = 281 (3.69), 230 (4.36).
ESI-HRMS: calculated $[C_{16}H_{19}N–H]^-$: 224.14447
found: 224.14465 (0.80 ppm).

(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)(2-methylcyclohex-1-en-1-yl)methanone (5)

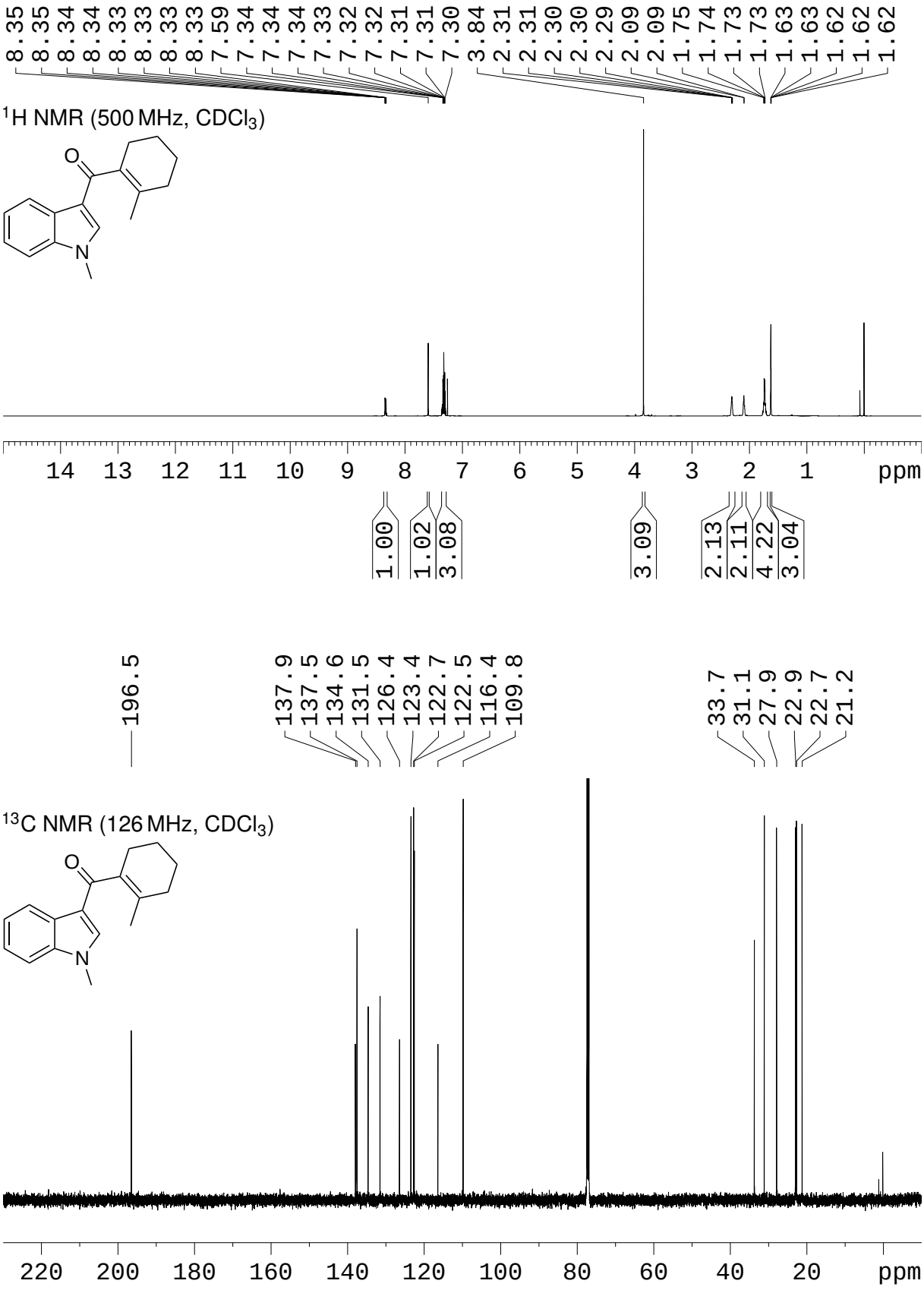


(1*H*-Indol-3-yl)(2-methylcyclohex-1-en-1-yl)methanone (6)

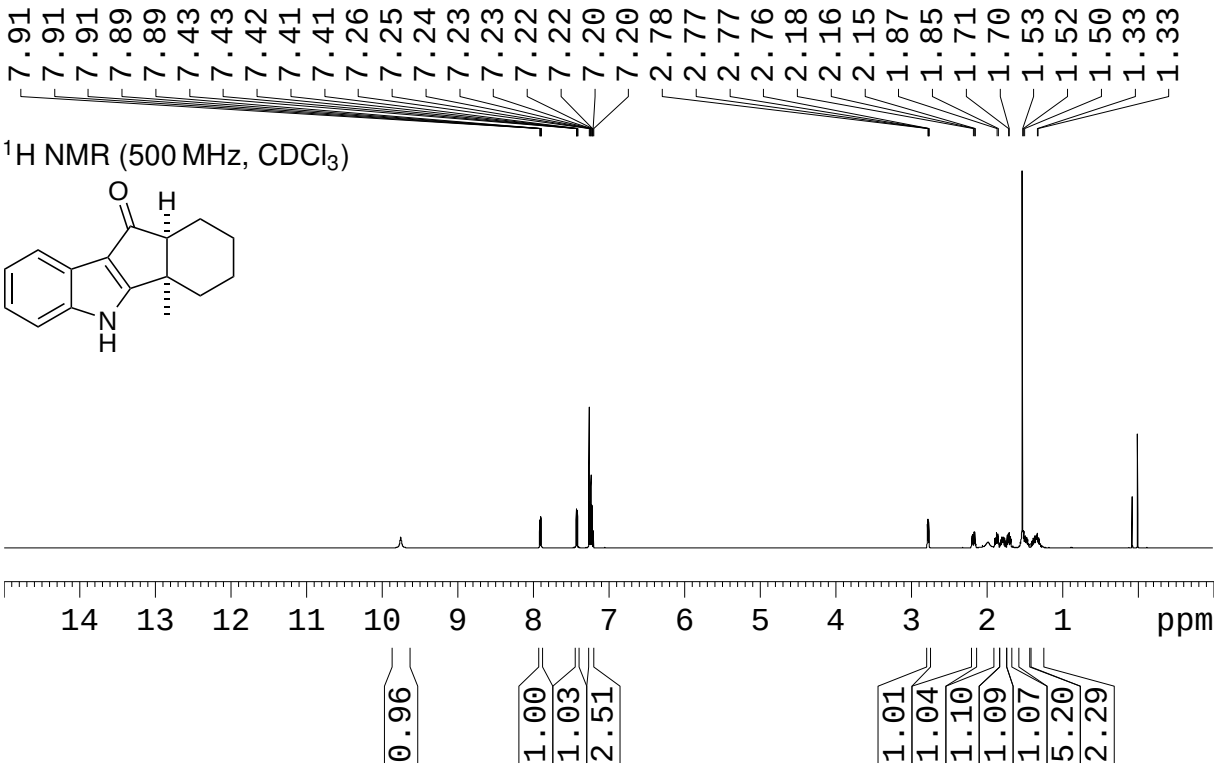


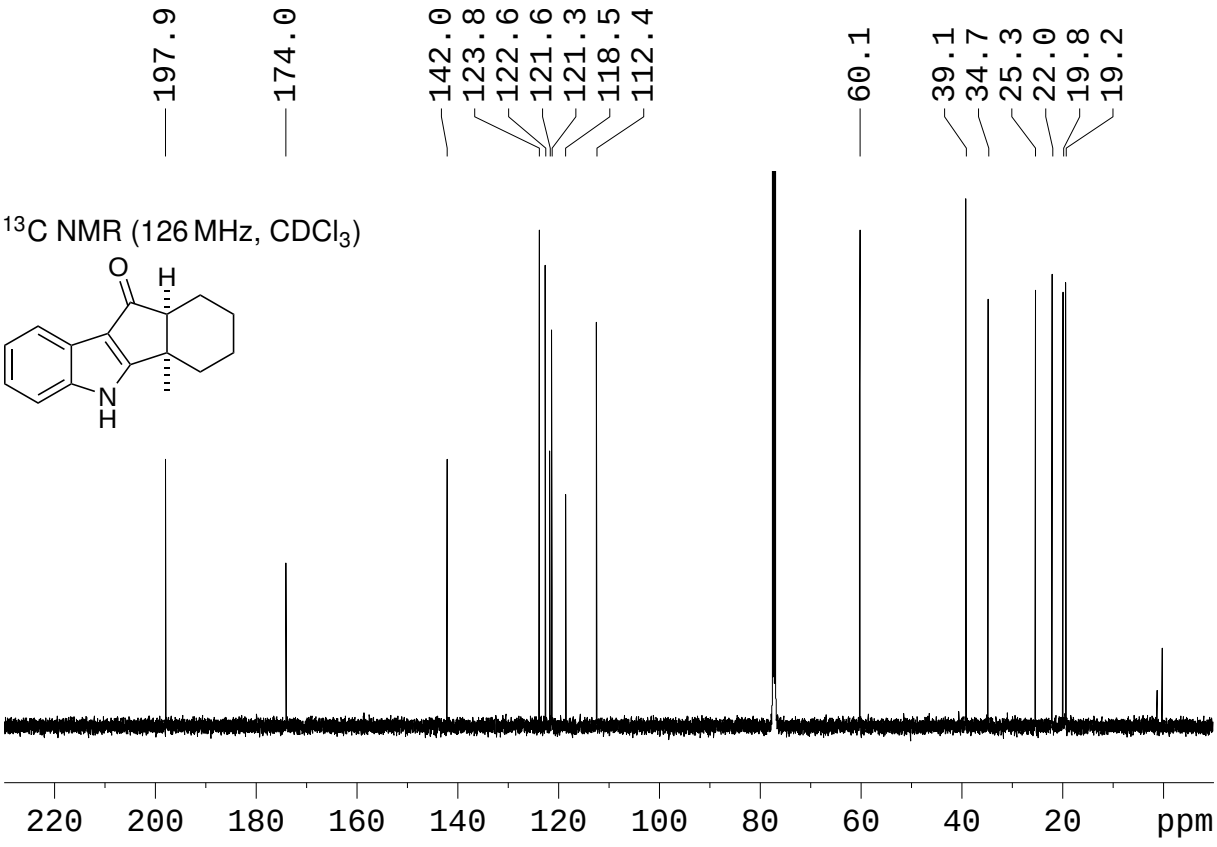


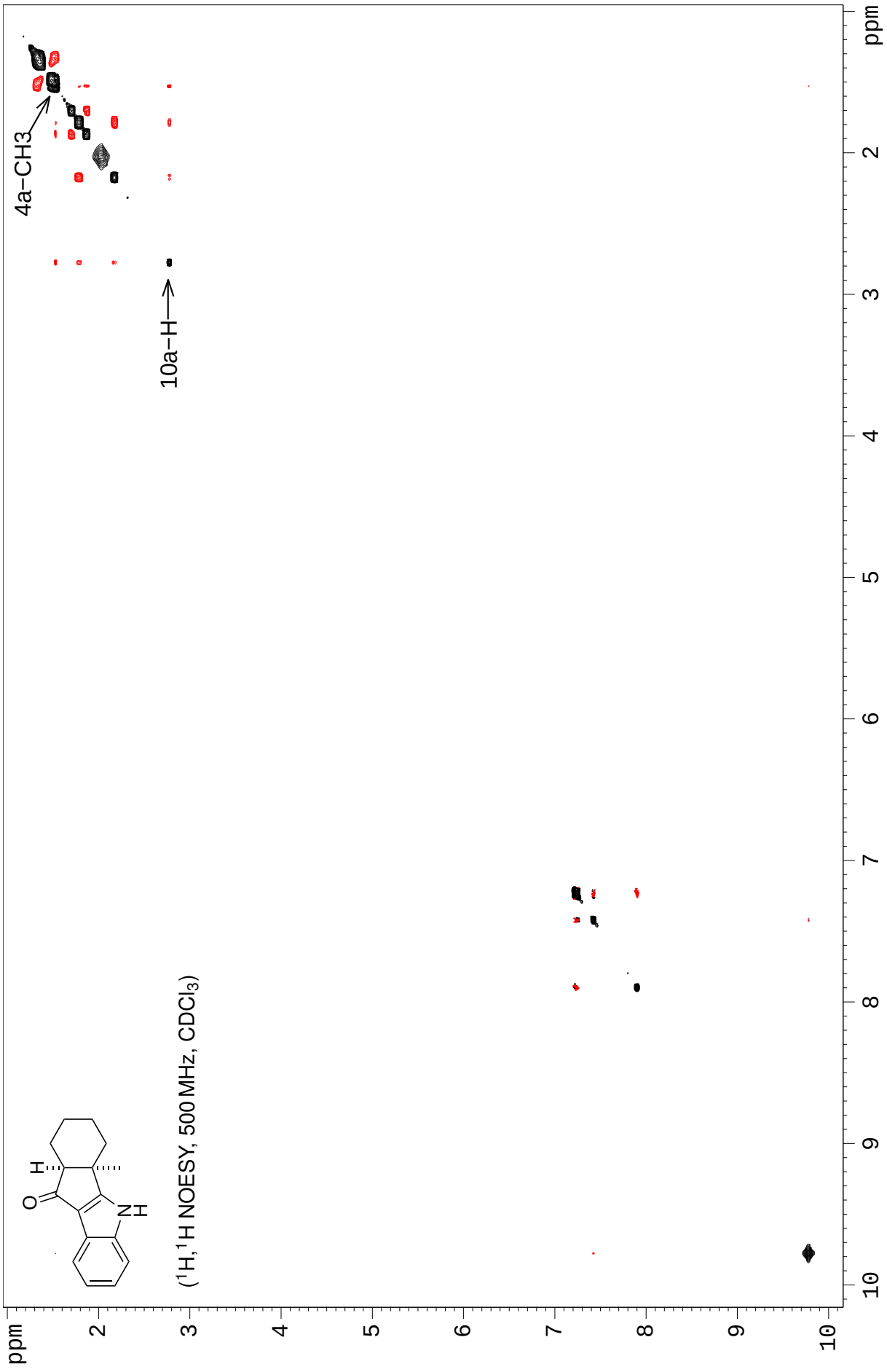
(1-Methyl-1*H*-indol-3-yl)(2-methylcyclohex-1-en-1-yl)methanone (S20)



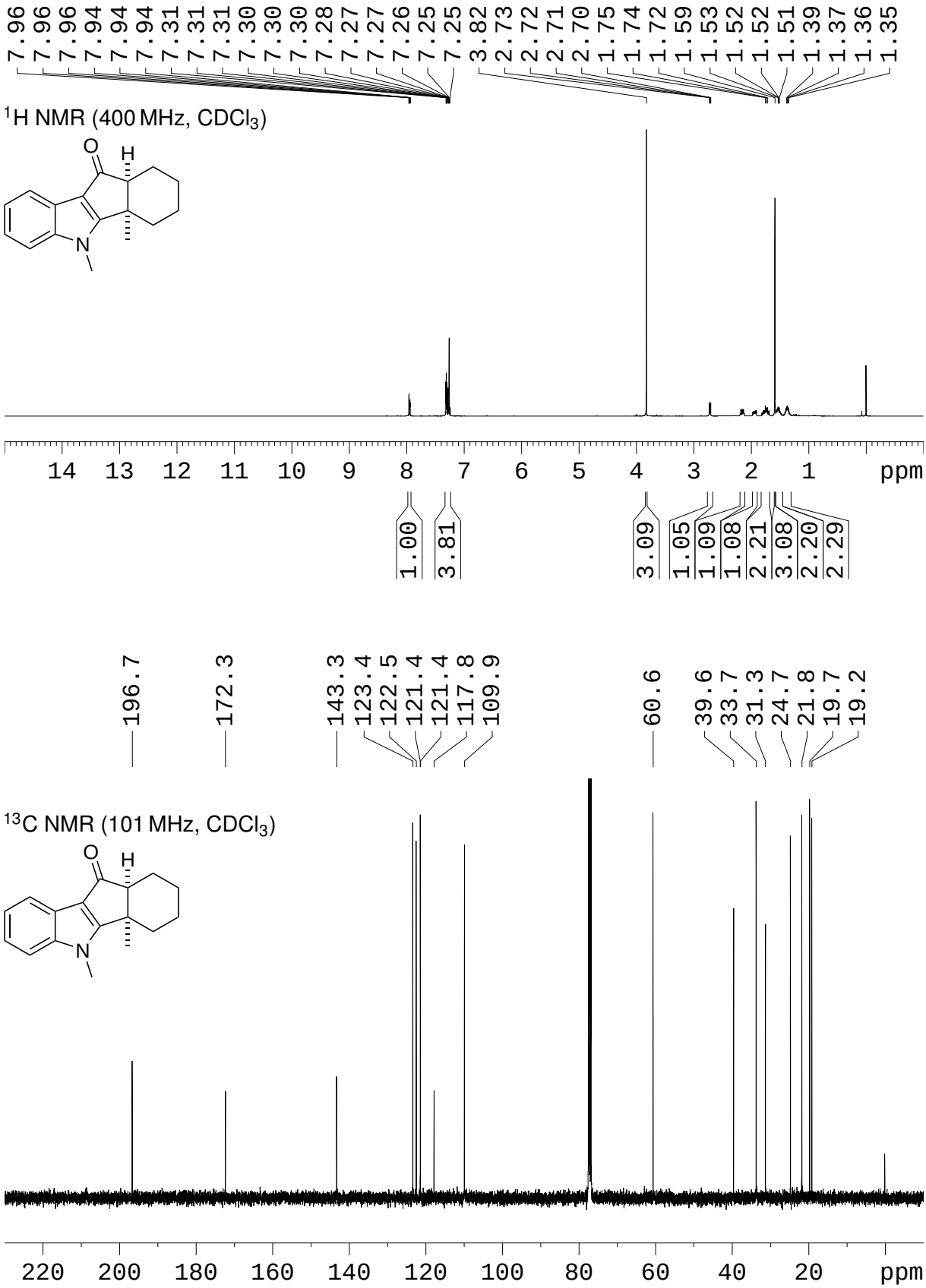
cis-4a-Methyl-1,3,4,4a,5,10a-hexahydroindeno[1,2-*b*]indol-10(2*H*)-one (7)

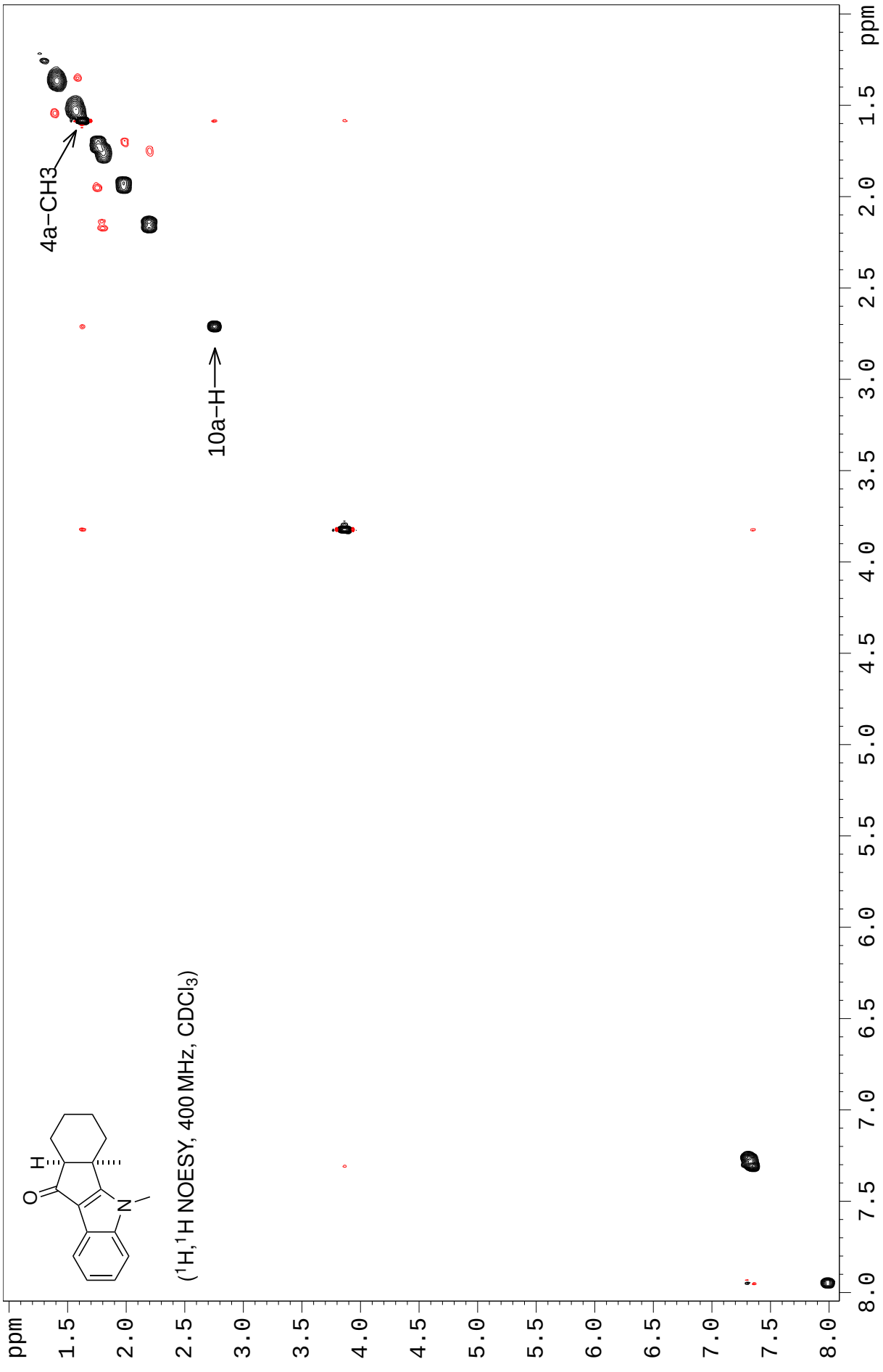




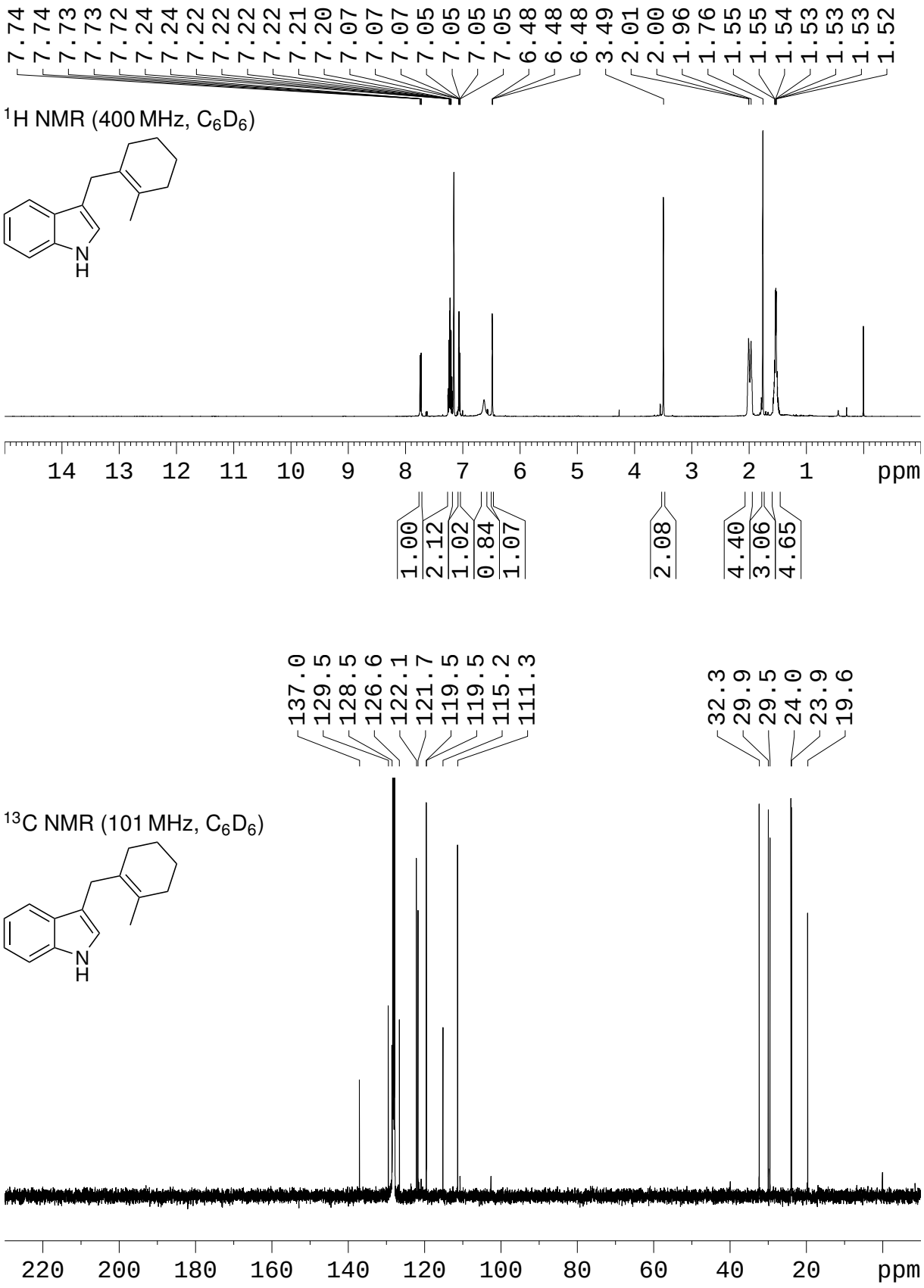

4a−CH3
10a−H
(1H,1H NOESY, 500 MHz, CDCl3)
ppm
ppm

cis-4a,5-Dimethyl-1,3,4,4a,5,10a-hexahydroindeno[1,2-_b_]indol-10(2_H_)-one (S21)

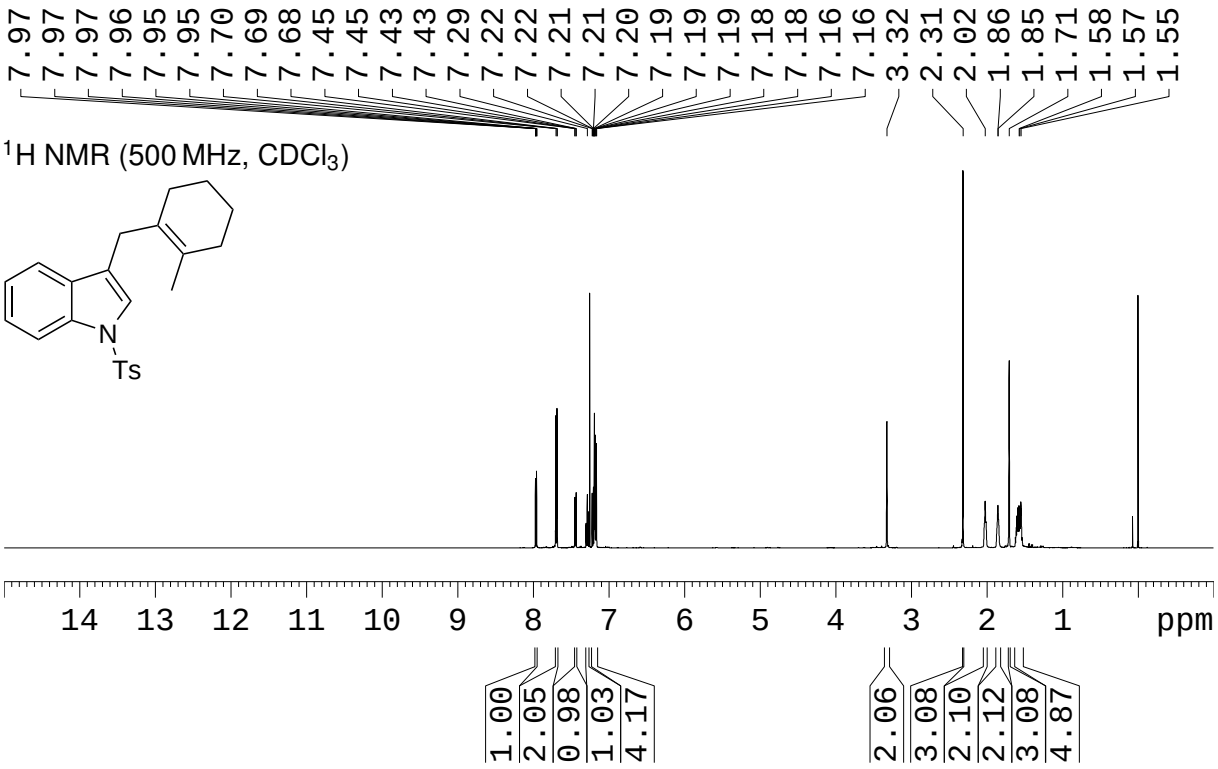


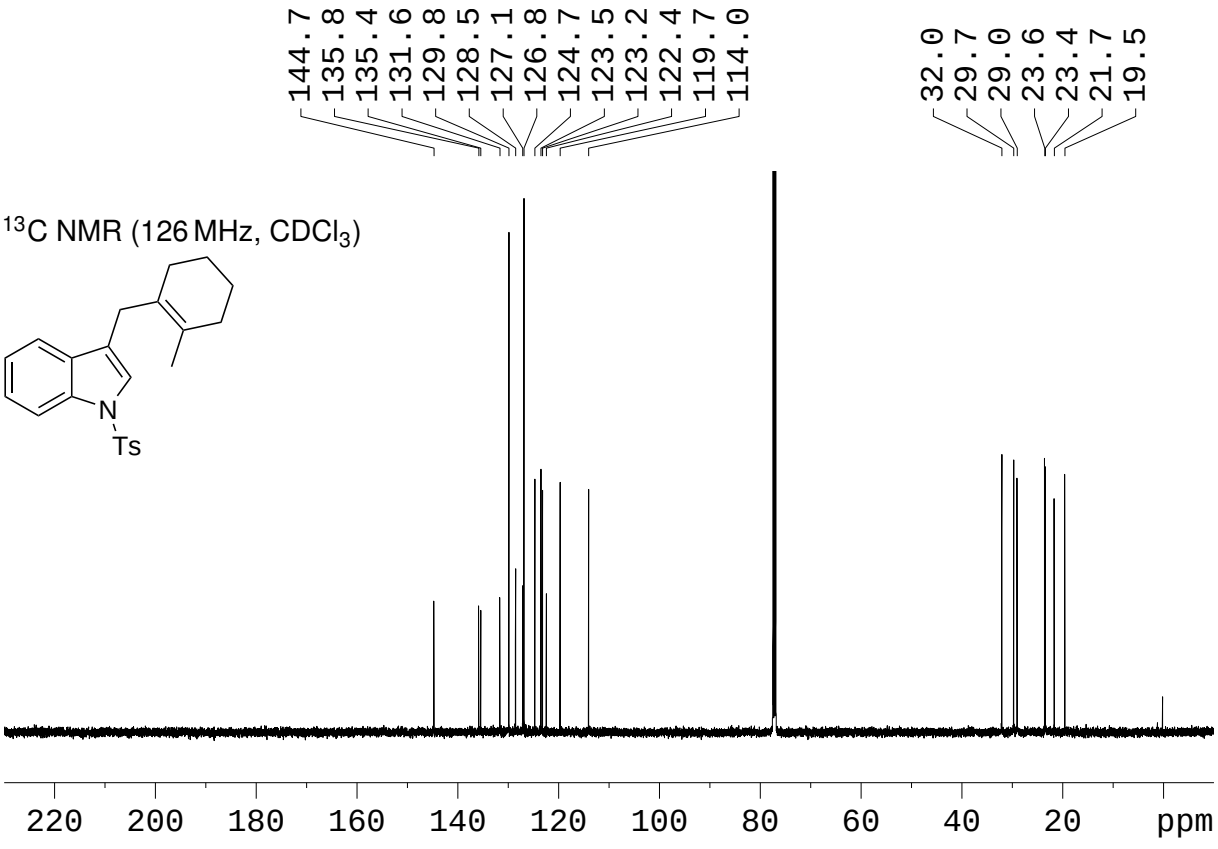

4a−CH3
10a−H
(1H,1H NOESY, 400 MHz, CDCl3)
O
H
N
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5

3-((2-Methylcyclohex-1-en-1-yl)methyl)-1*H*-indole (S2)

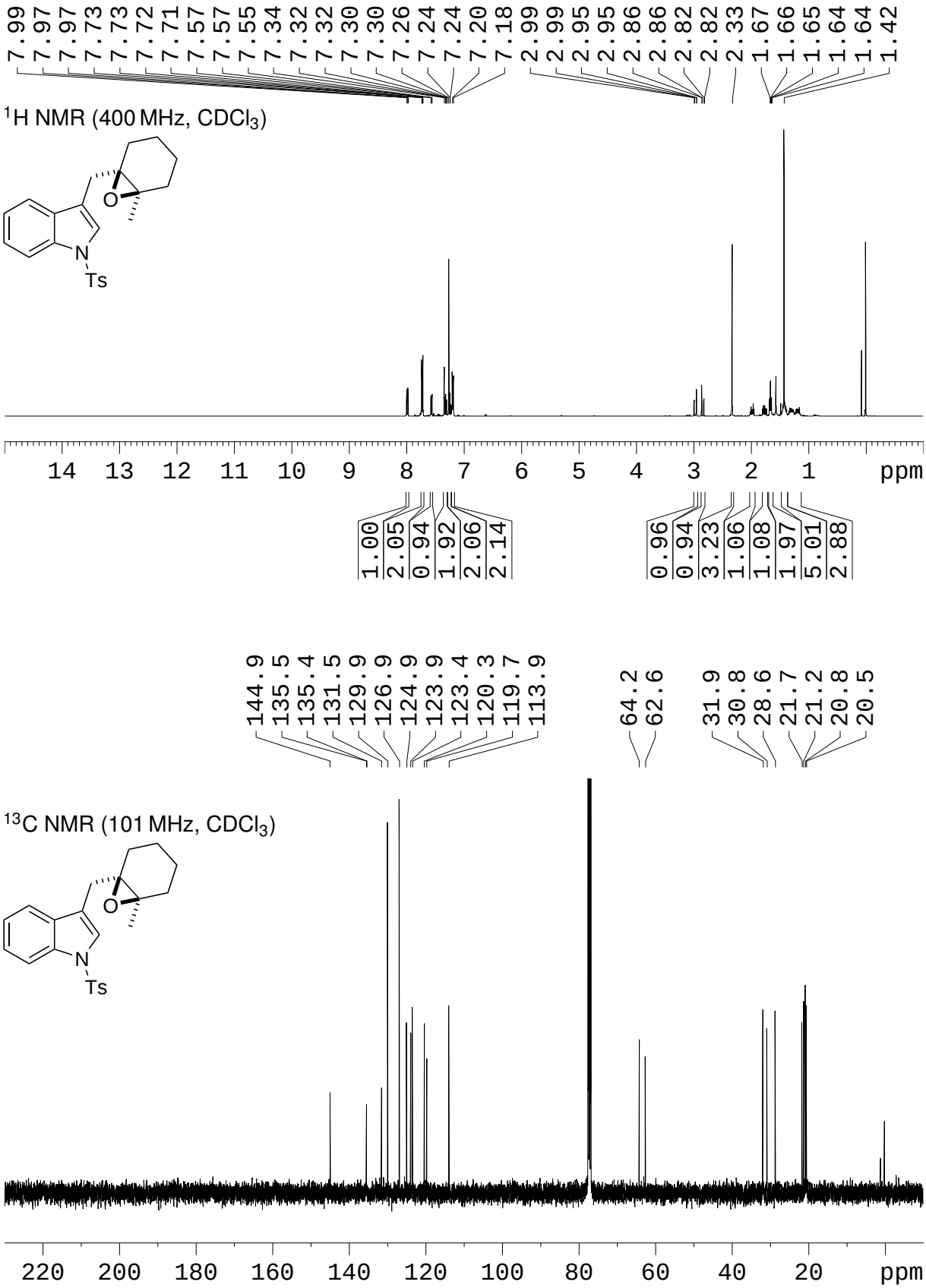


3-((2-Methylcyclohex-1-en-1-yl)methyl)-1-tosyl-1*H*-indole (S3)

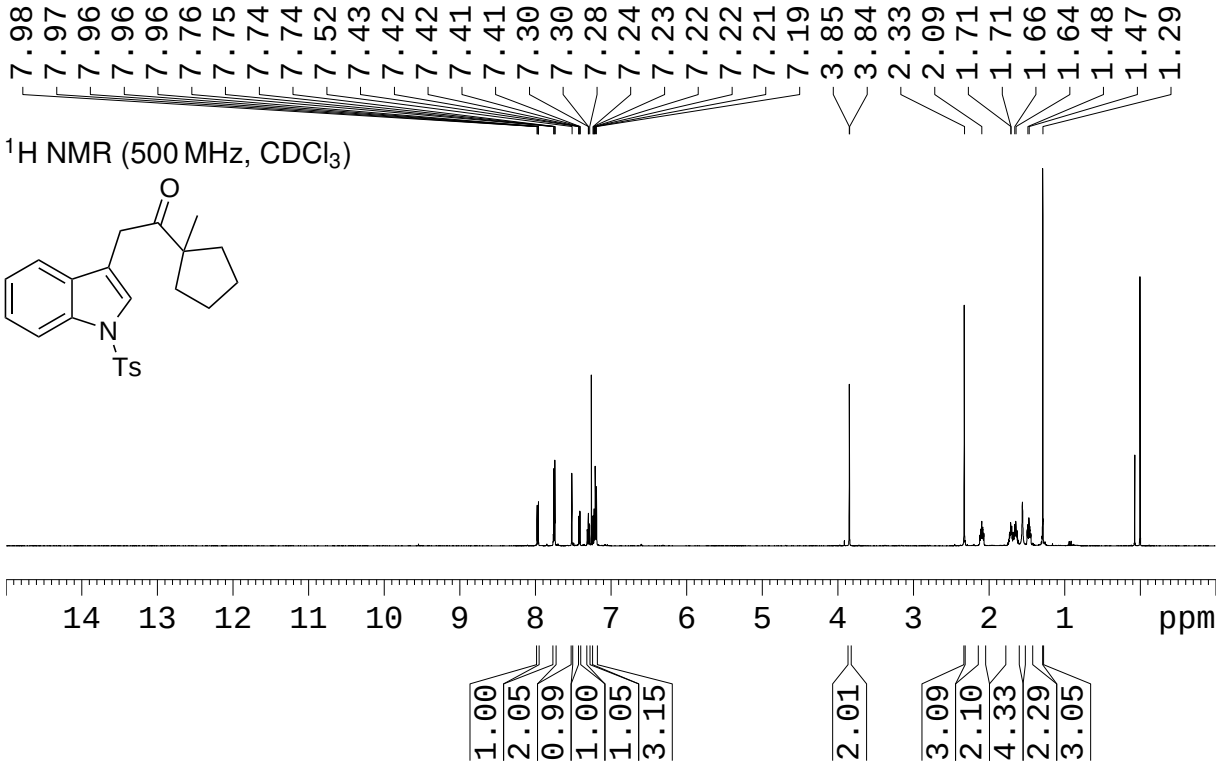


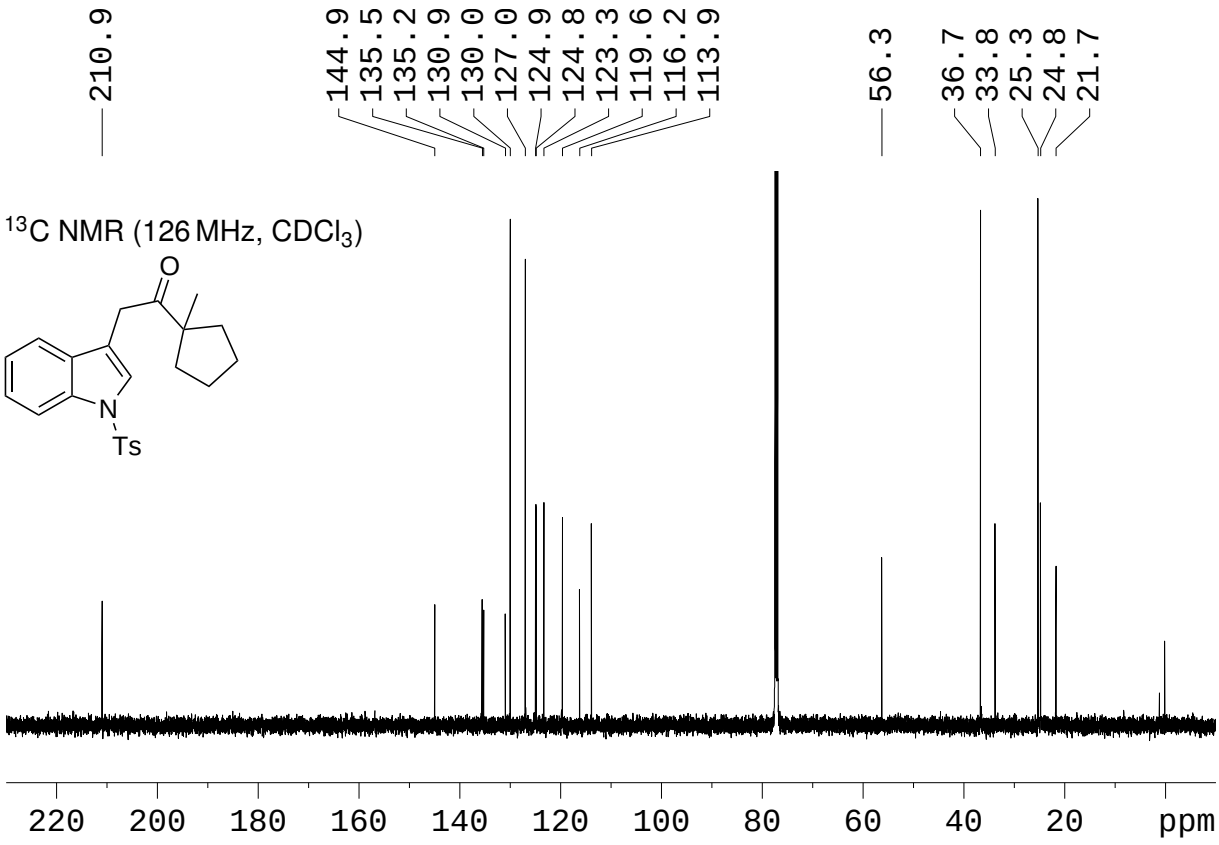


Epoxide S4

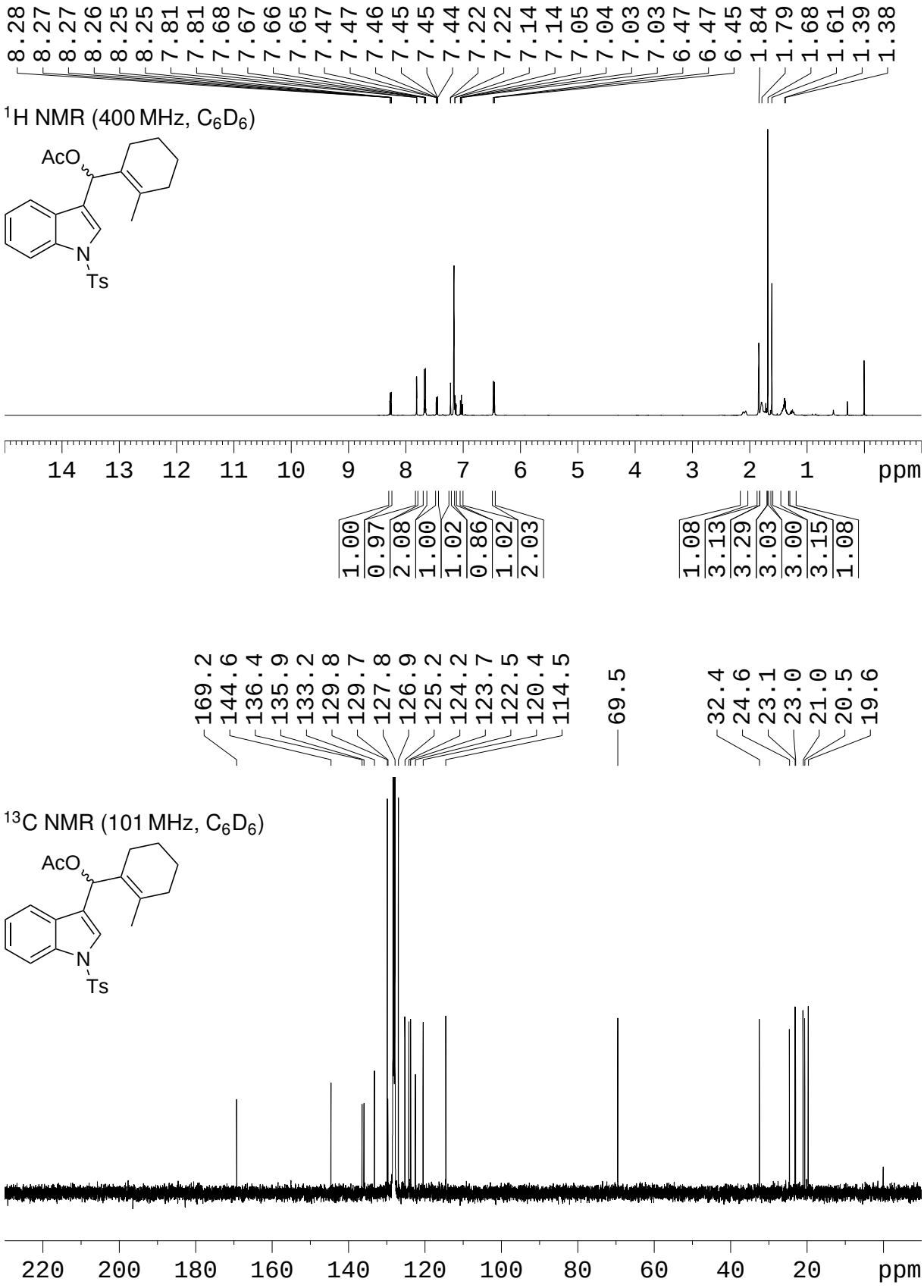

7.99
7.97
7.97
7.73
7.73
7.72
7.71
7.57
7.57
7.55
7.34
7.32
7.32
7.30
7.30
7.26
7.24
7.24
7.20
7.18
2.99
2.99
2.95
2.95
2.86
2.86
2.82
2.82
2.33
1.67
1.66
1.65
1.64
1.64
1.42
1H NMR (400 MHz, CDCl3)
O
N
Ts
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.05
0.94
1.92
2.06
2.14
0.96
0.94
3.23
1.06
1.08
1.97
5.01
2.88
144.9
135.5
135.4
131.5
129.9
126.9
124.9
123.9
123.4
120.3
119.7
113.9
64.2
62.6
31.9
30.8
28.6
21.7
21.2
20.8
20.5
13C NMR (101 MHz, CDCl3)
O
N
Ts
220 200 180 160 140 120 100 80 60 40 20 ppm

1-(1-Methylcyclopentyl)-2-(1-tosyl-1*H*-indol-3-yl)ethan-1-one (S5)

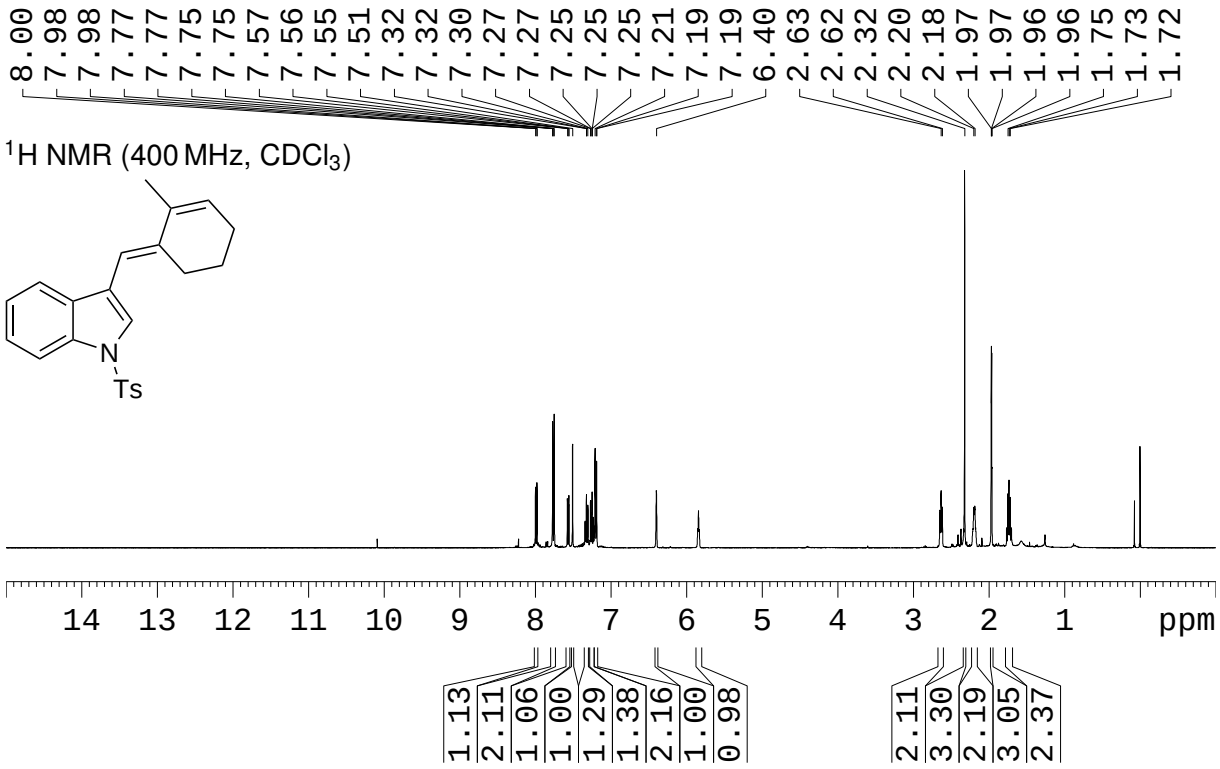


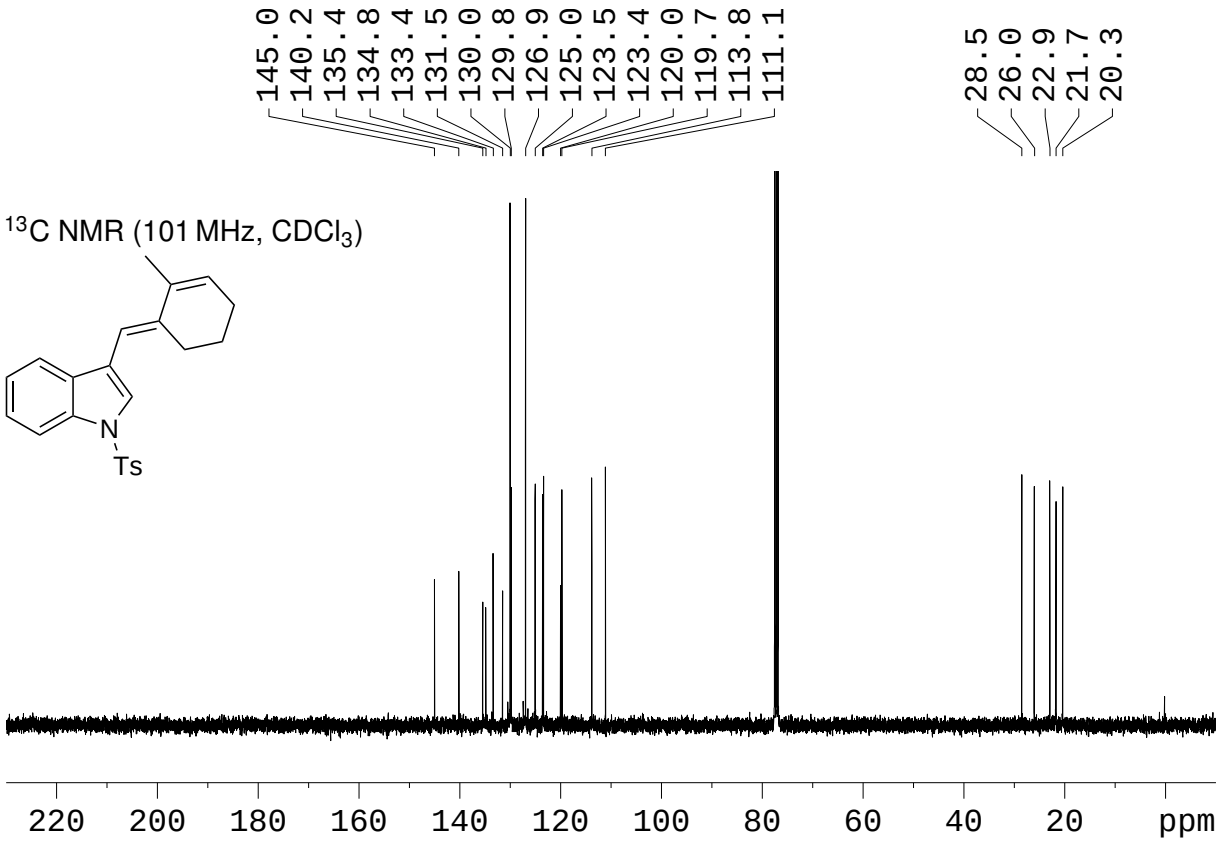


(2-Methylcyclohex-1-en-1-yl)(1-tosyl-1*H*-indol-3-yl)methyl acetate (S9)

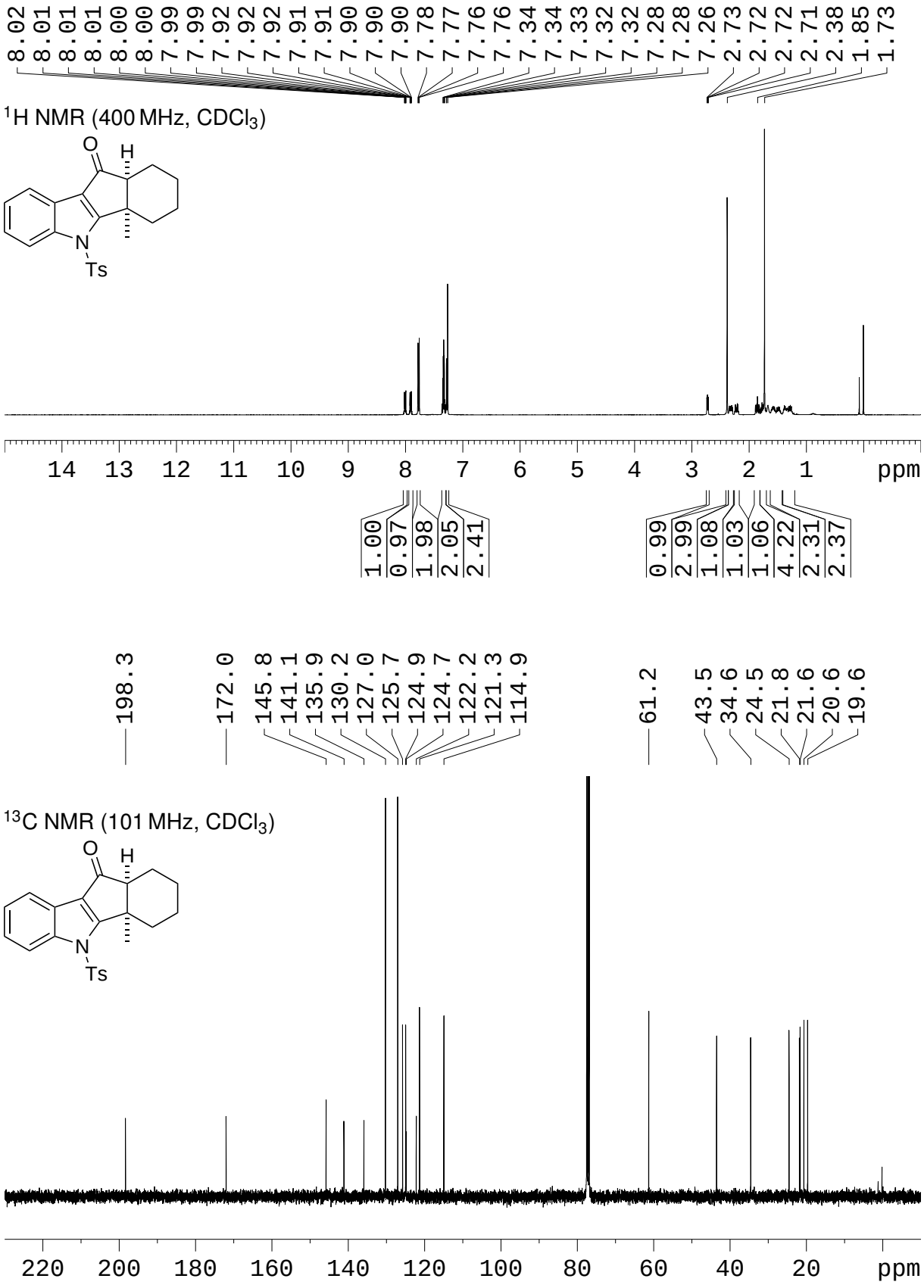


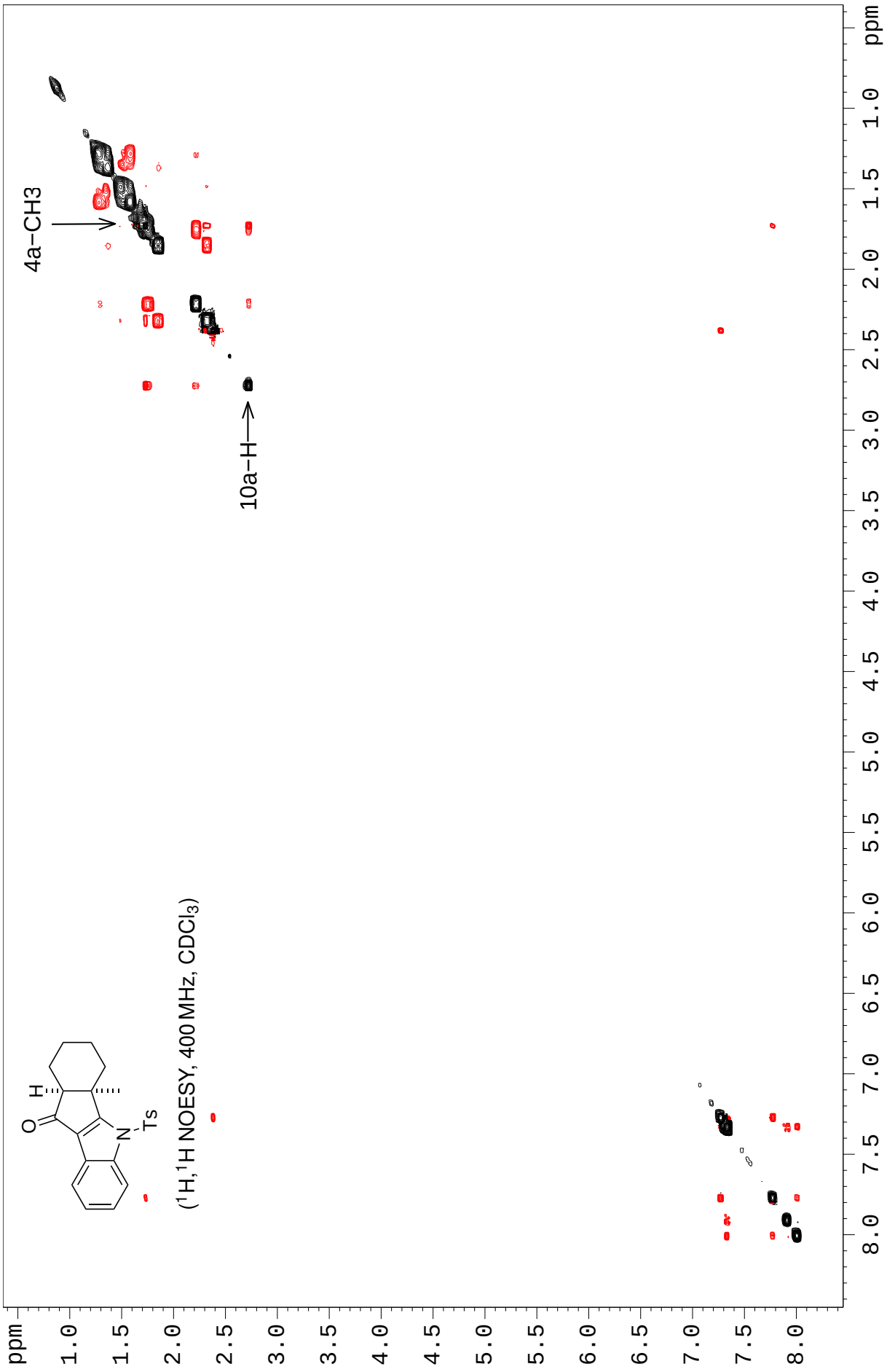
(*E*)-3-((2-Methylcyclohex-2-en-1-ylidene)methyl)-1-tosyl-1*H*-indole (S10)



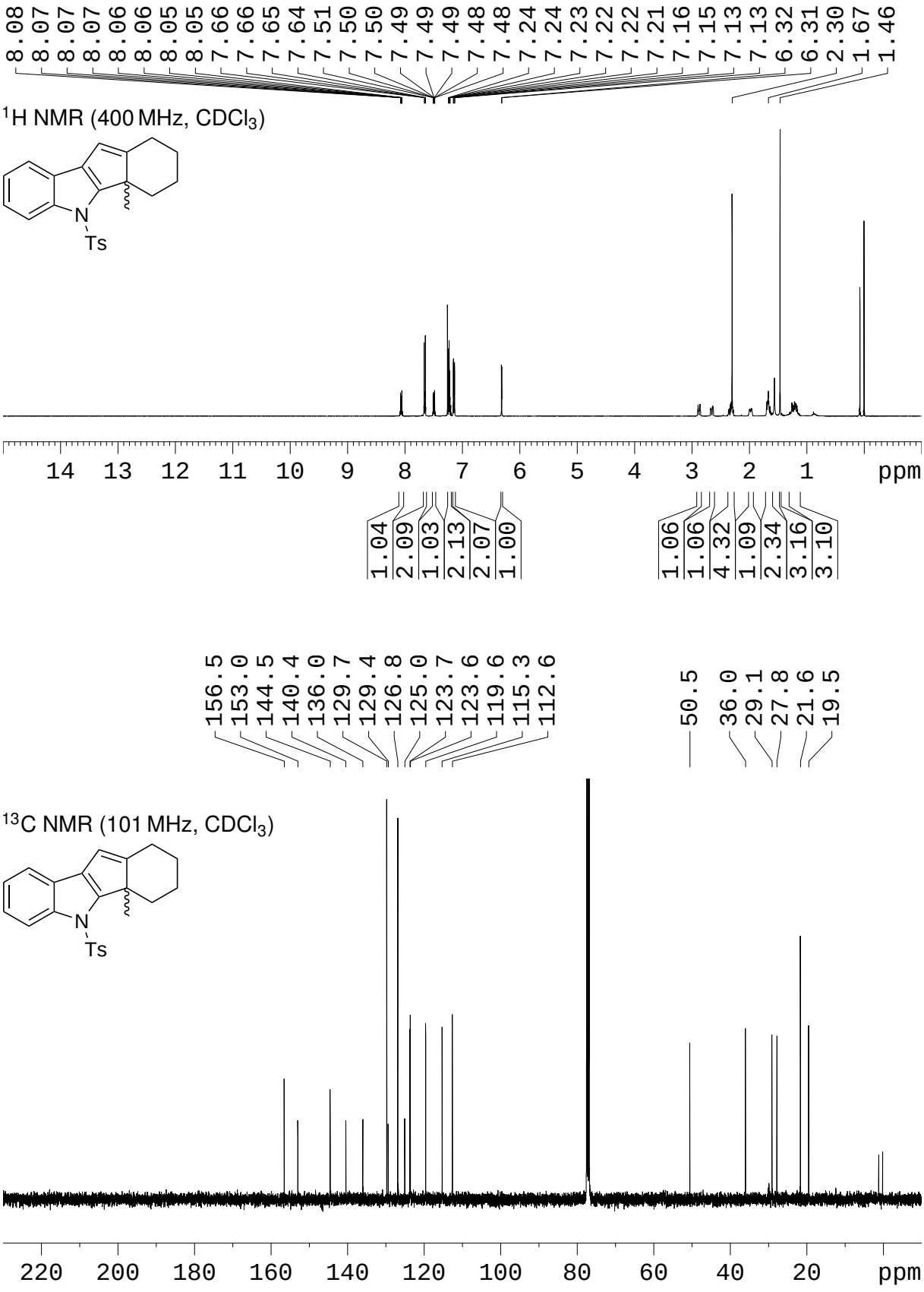


cis-Hydrindanone 8

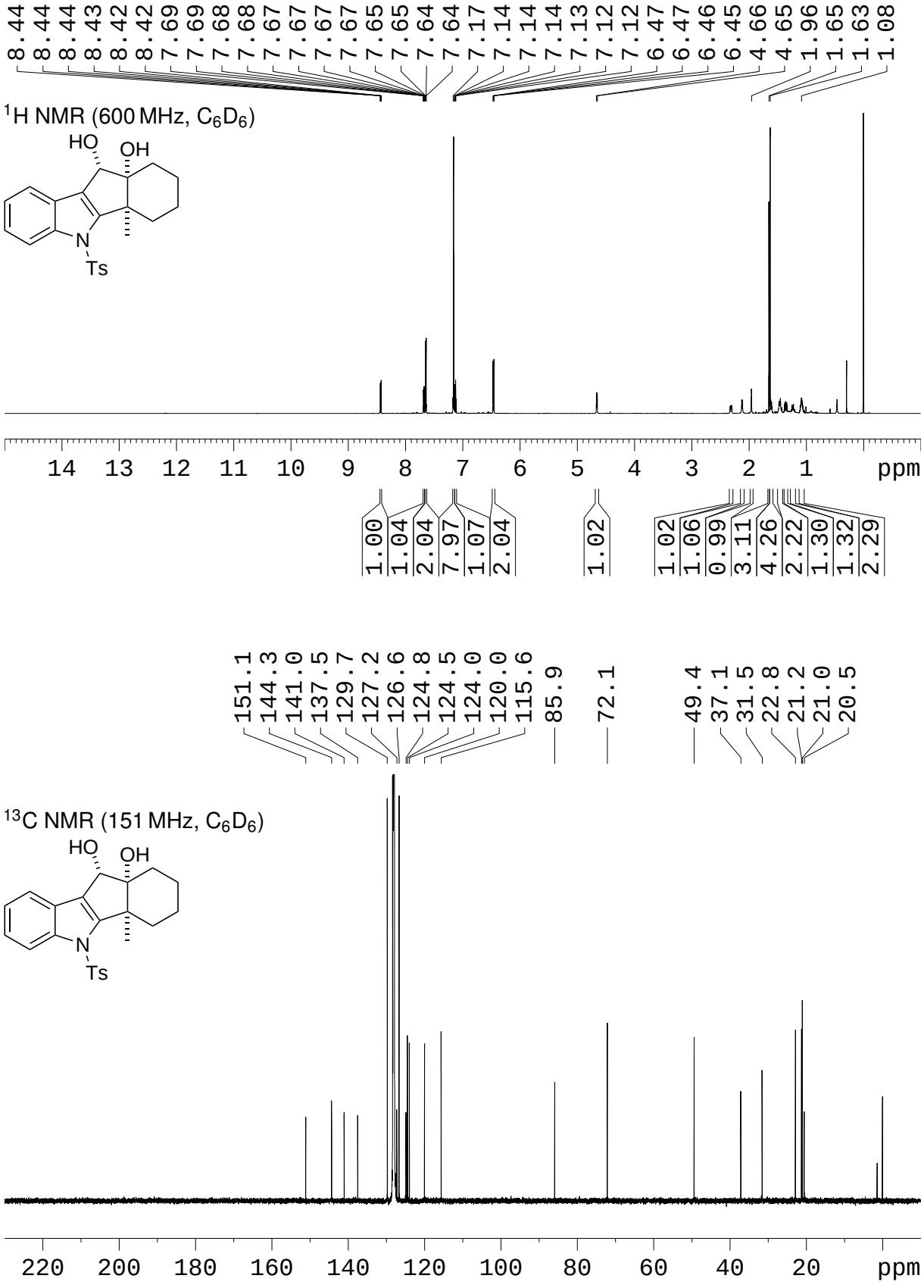


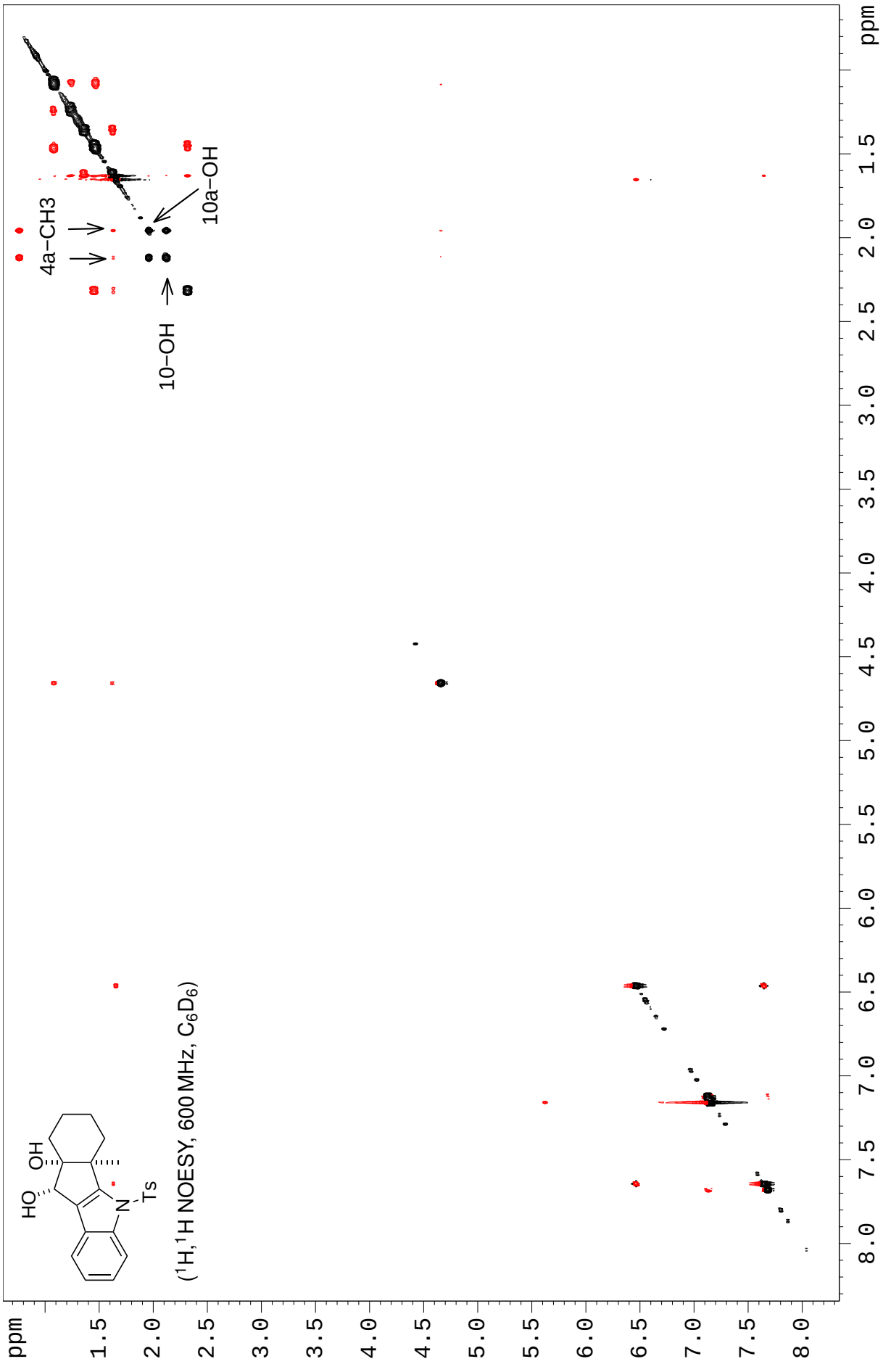

4a−CH3
10a−H
(^{1}H,^{1}H NOESY, 400 MHz, CDCl$_3$)
O
H
N
Ts
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

4a-Methyl-5-tosyl-1,2,3,4,4a,5-hexahydroindeno[1,2-*b*]indole (9)

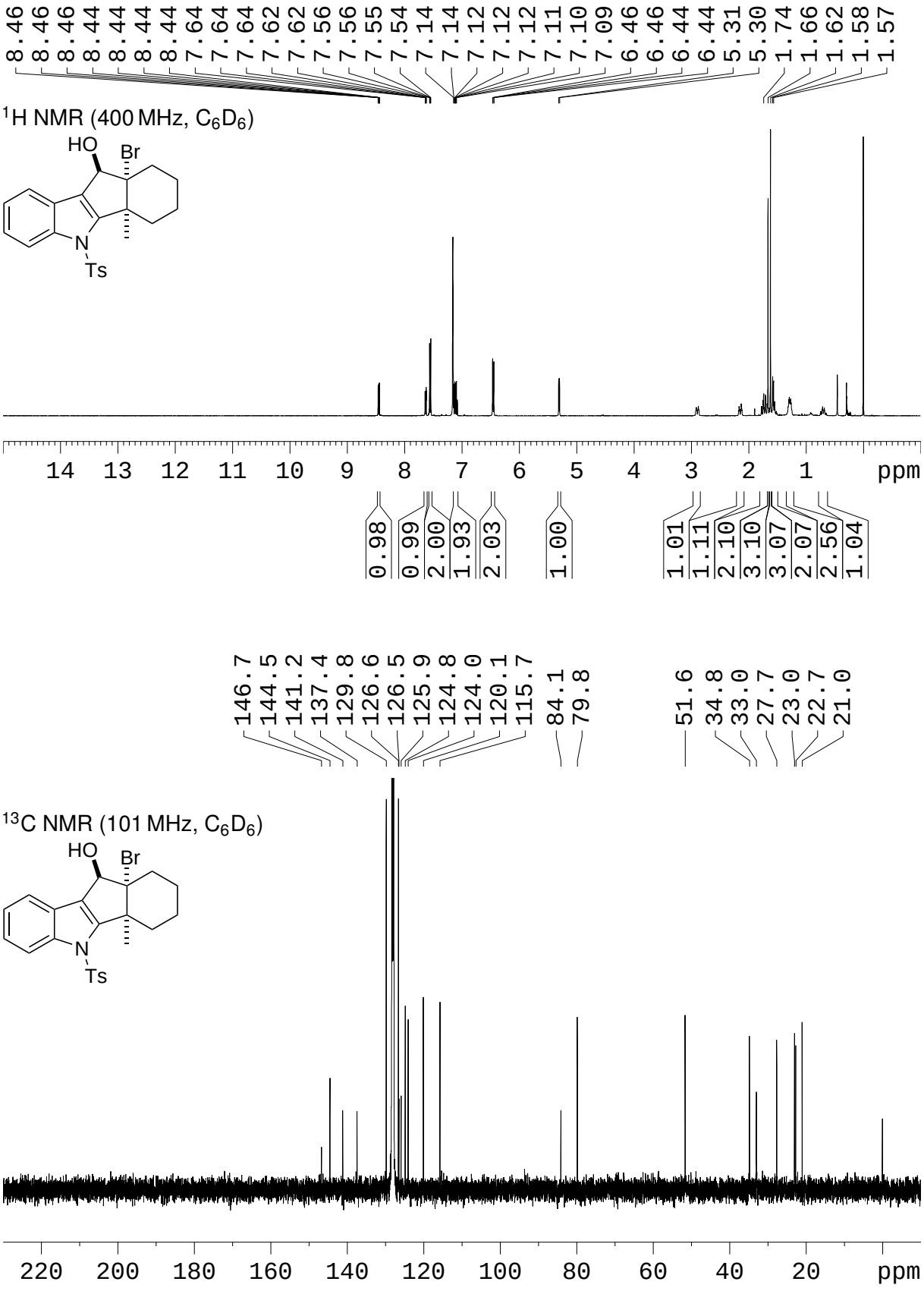


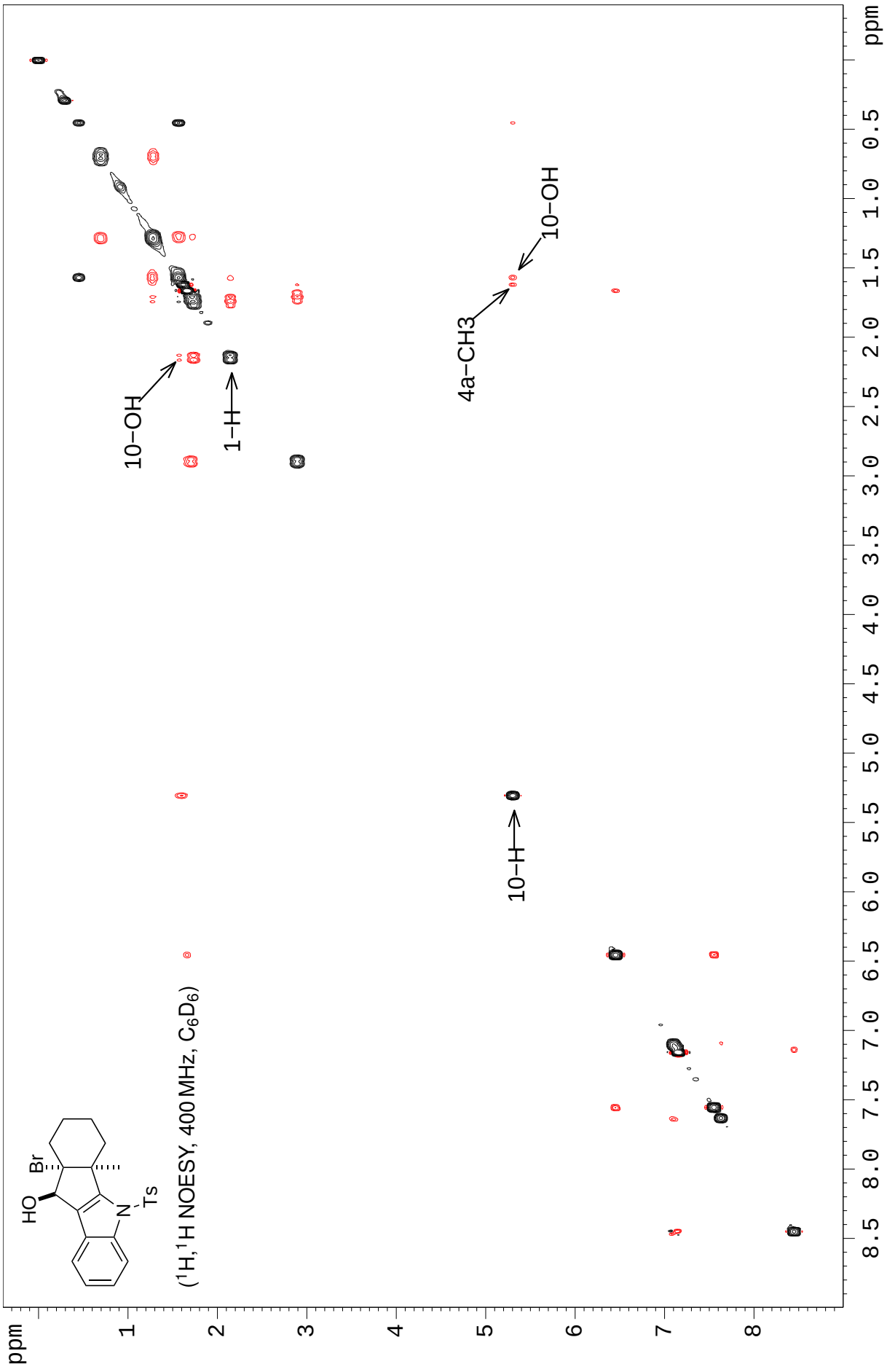
Diol 14


8.44 8.44 8.44 8.43 8.42 8.42 7.69 7.69 7.68 7.68 7.67 7.67 7.67 7.67 7.65 7.65 7.64 7.64 7.17 7.14 7.14 7.14 7.13 7.12 7.12 6.47 6.47 6.46 6.45 4.66 4.65 1.96 1.65 1.63 1.08
^{1}H NMR (600 MHz, C_6D_6)
HO
OH
N
Ts
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 1.04 2.04 7.97 1.07 2.04 1.02 1.02 1.06 0.99 3.11 4.26 2.22 1.30 1.32 2.29
151.1 144.3 141.0 137.5 129.7 127.2 126.6 124.8 124.5 124.0 120.0 115.6 85.9 72.1 49.4 37.1 31.5 22.8 21.2 21.0 20.5
^{13}C NMR (151 MHz, C_6D_6)
HO
OH
N
Ts
220 200 180 160 140 120 100 80 60 40 20 ppm

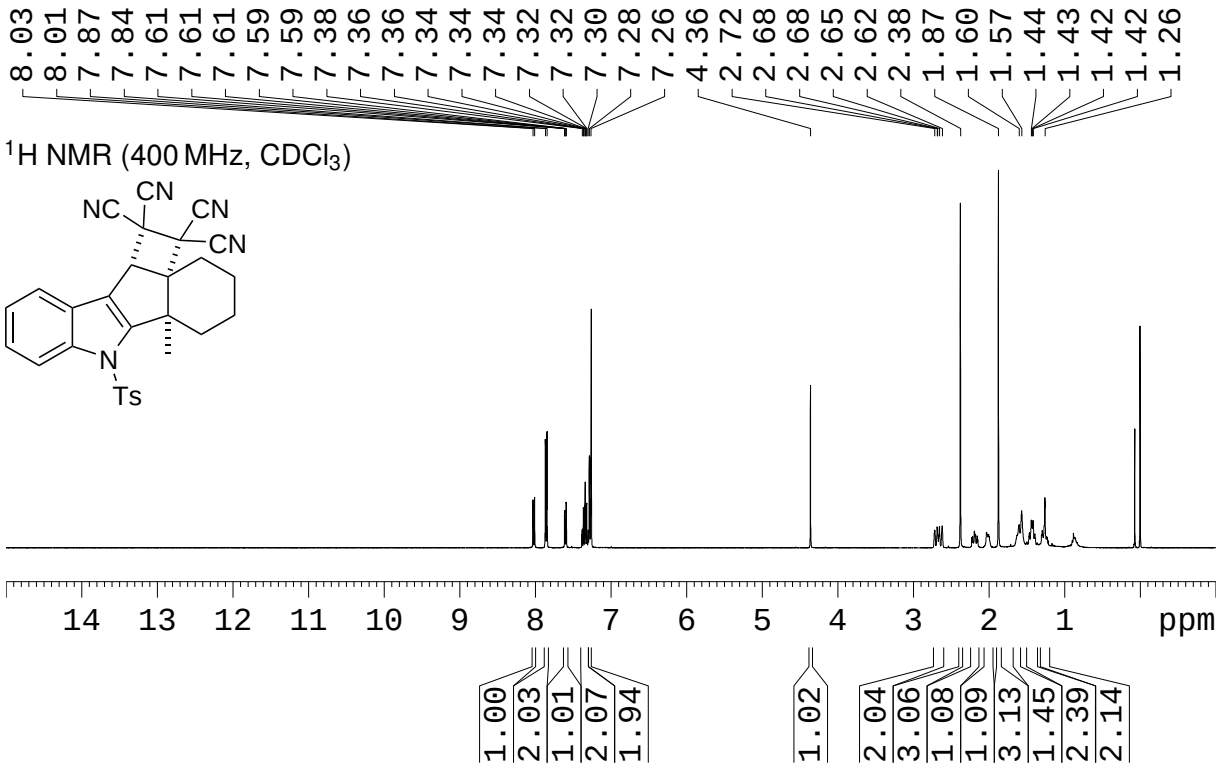

4a–CH3
10a–OH
10–OH
(^{1}H,^{1}H NOESY, 600 MHz, C_6D_6)
HO
OH
N
Ts
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

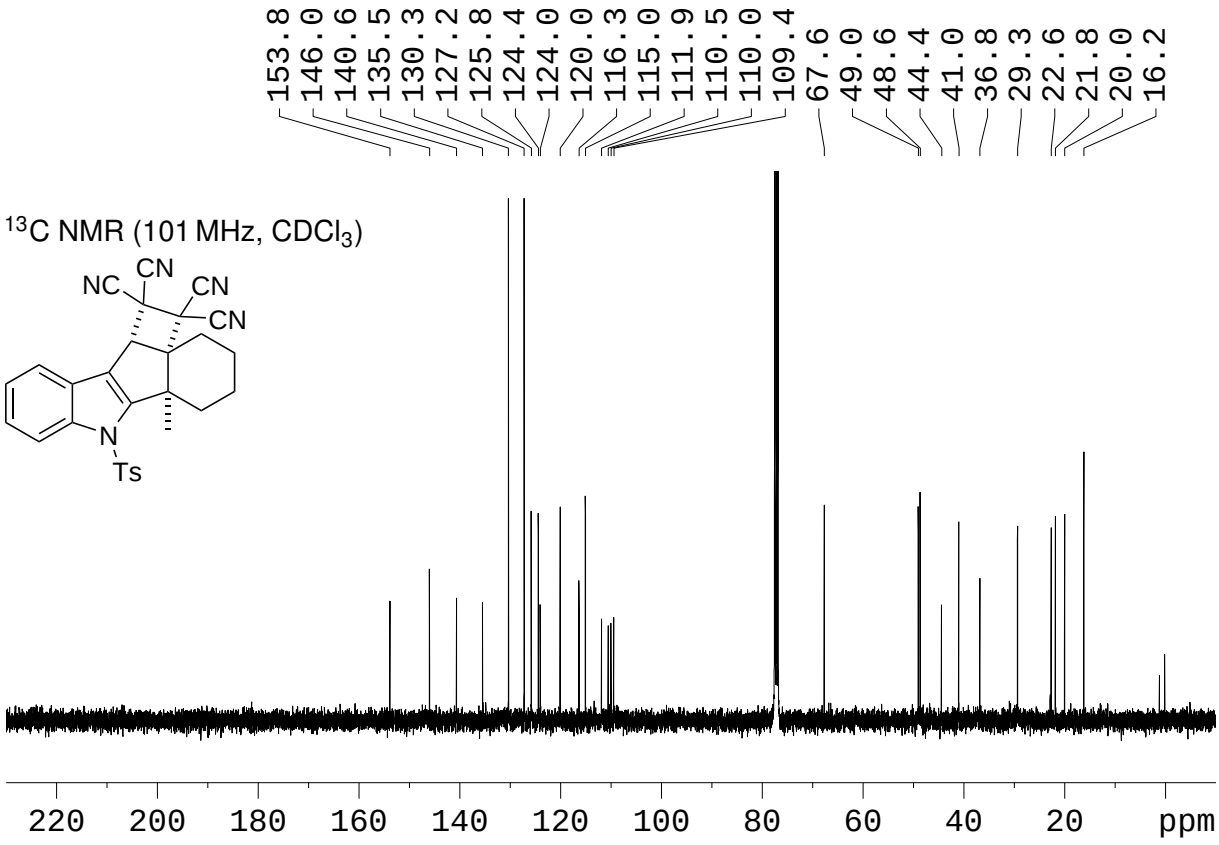
Bromohydrin 10

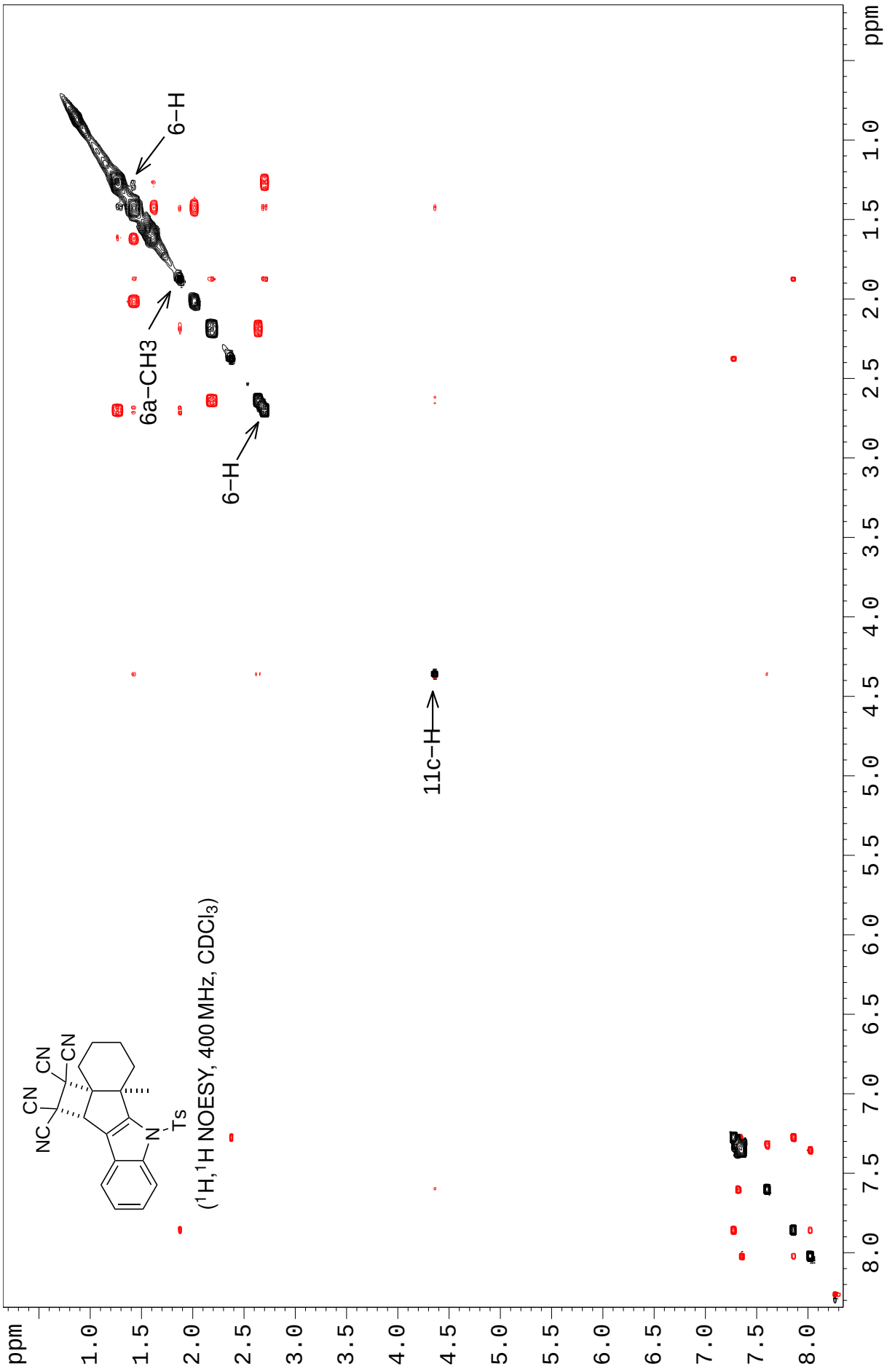



10–OH
1–H
4a–CH3
10–OH
10–H
(1H,1H NOESY, 400 MHz, C6D6)
HO
Br
N
Ts
ppm
ppm

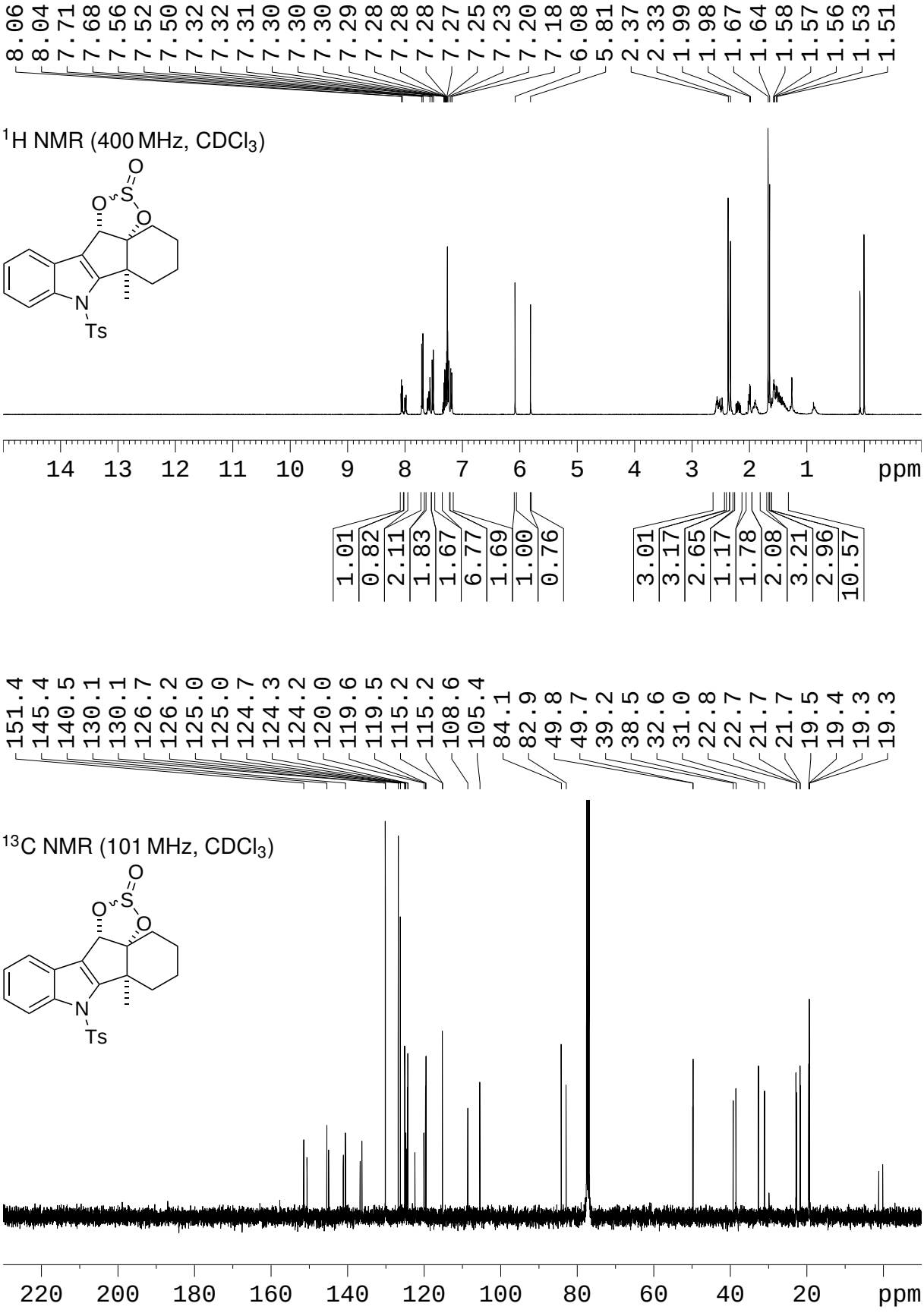
Cyclobutane 11



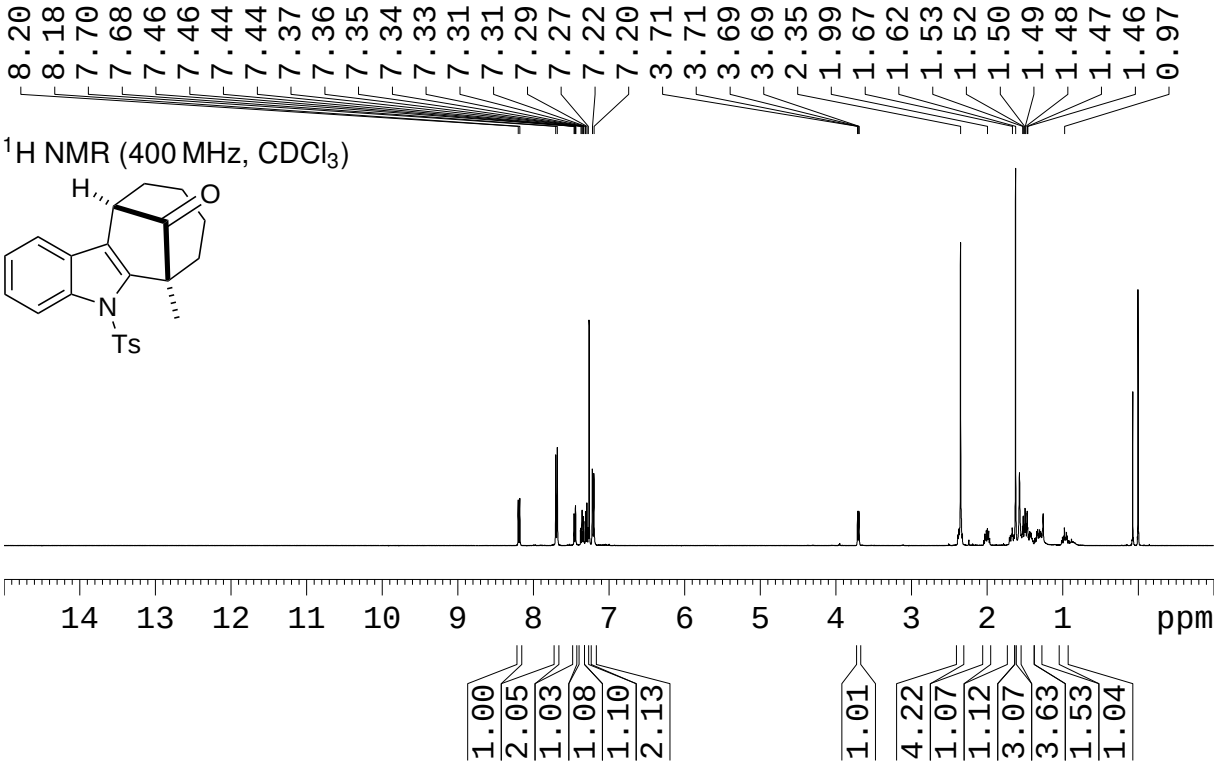


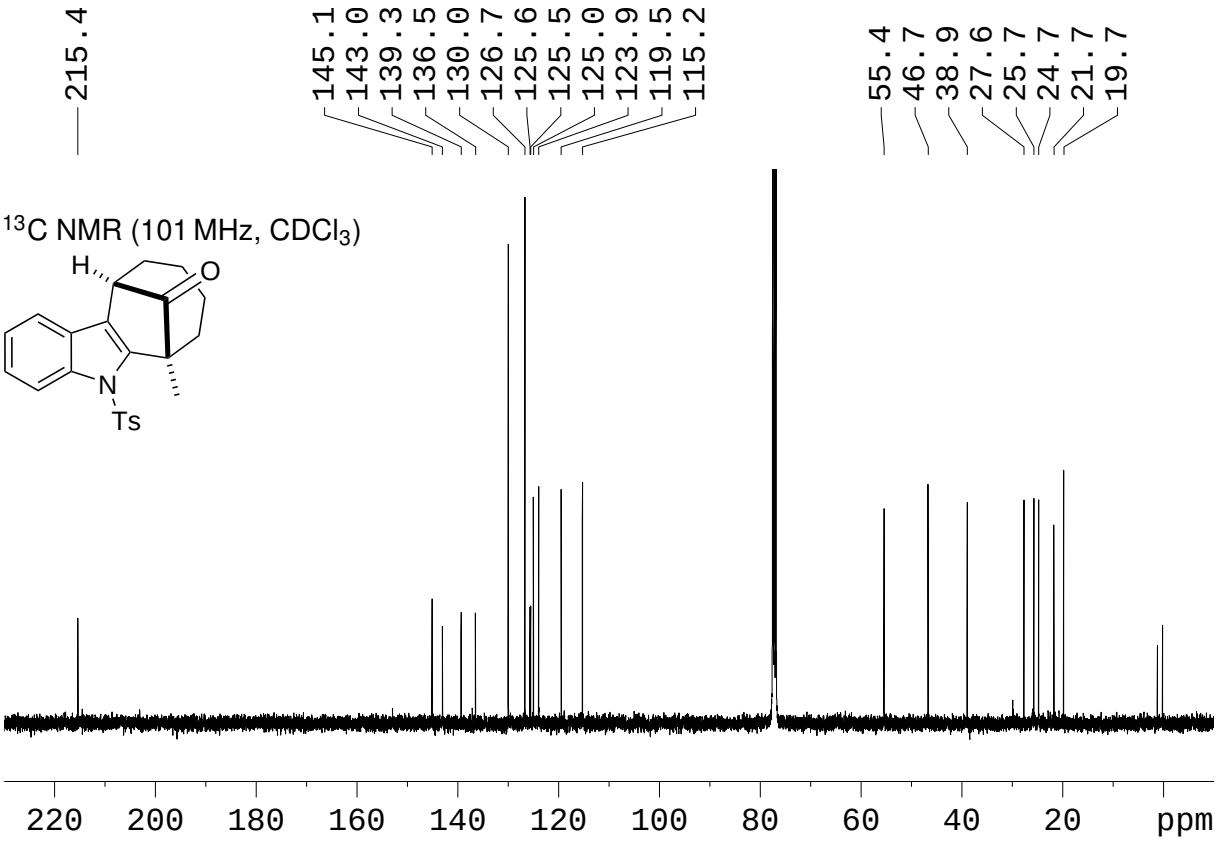

6–H
6a–CH3
6–H
11c–H
(^{1}H,^{1}H NOESY, 400 MHz, CDCl$_3$)
NC
CN
CN
N
Ts
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

Sulfite 16

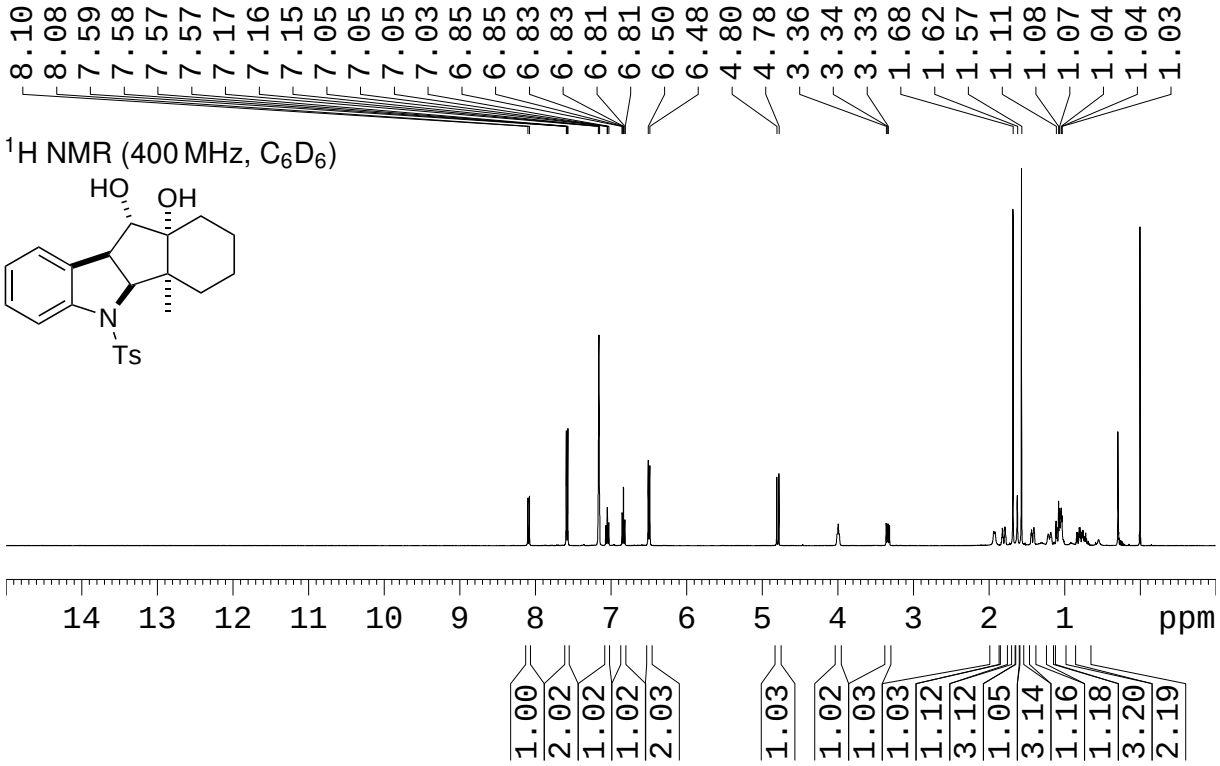

8.06 8.04 7.71 7.68 7.56 7.52 7.50 7.32 7.32 7.31 7.30 7.30 7.30 7.29 7.28 7.28 7.28 7.27 7.25 7.23 7.20 7.18 6.08 5.81 2.37 2.33 1.99 1.98 1.67 1.64 1.58 1.57 1.56 1.53 1.51
1H NMR (400 MHz, CDCl3)
O
S
O
O
N
Ts
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.01 0.82 2.11 1.83 1.67 6.77 1.69 1.00 0.76
3.01 3.17 2.65 1.17 1.78 2.08 3.21 2.96 10.57
151.4 145.4 140.5 130.1 130.1 126.7 126.2 125.0 125.0 124.7 124.3 124.2 120.0 119.6 119.5 115.2 115.2 108.6 105.4 84.1 82.9 49.8 49.7 39.2 38.5 32.6 31.0 22.8 22.7 21.7 21.7 19.5 19.4 19.3 19.3
13C NMR (101 MHz, CDCl3)
O
S
O
O
N
Ts
220 200 180 160 140 120 100 80 60 40 20 ppm

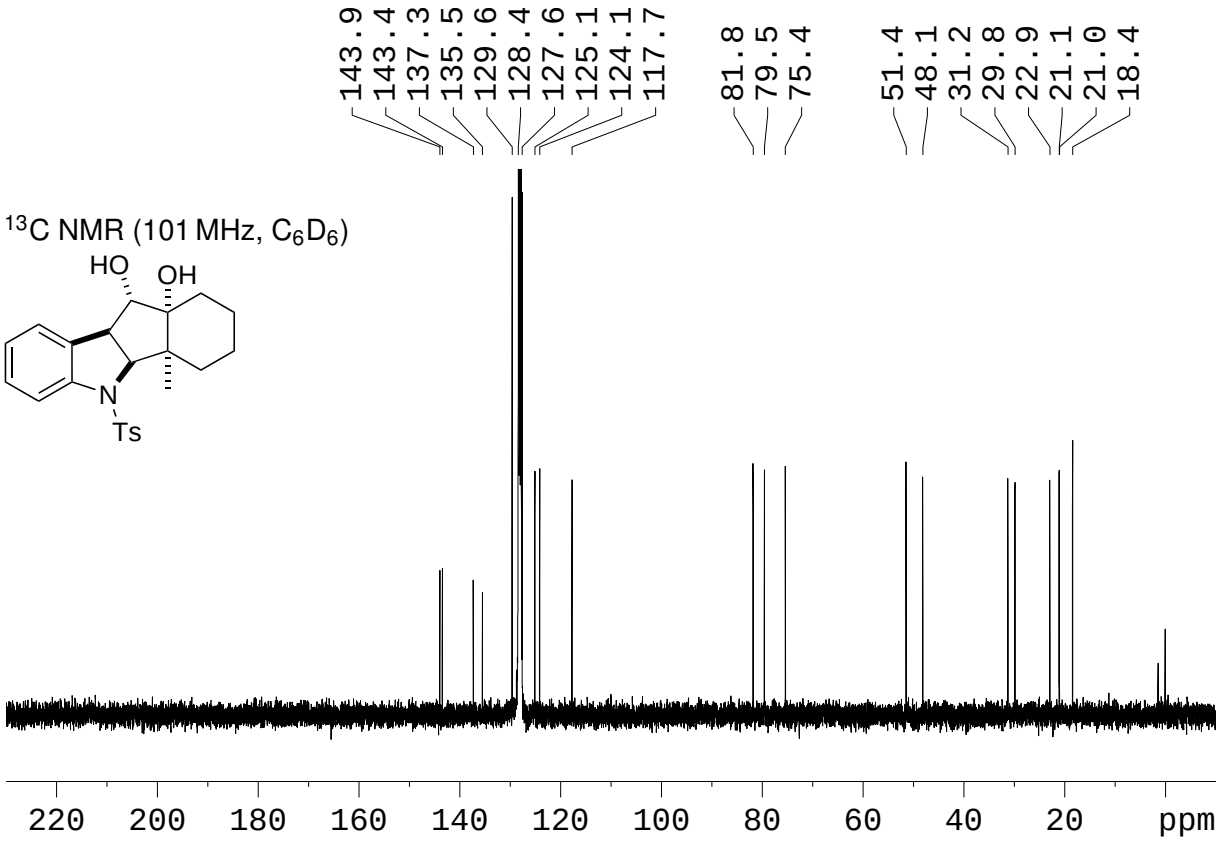
Ketone 17

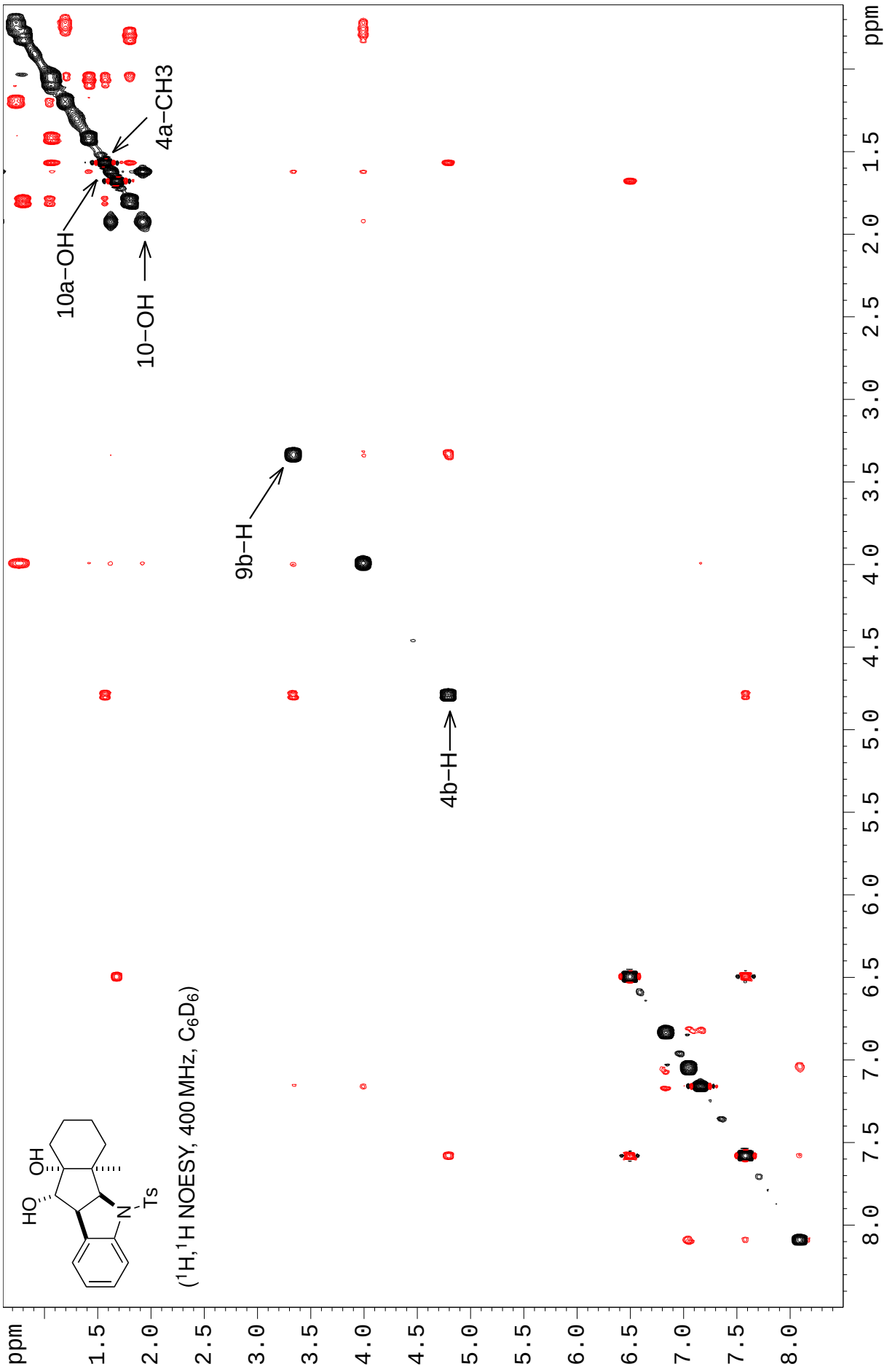

8.20
8.18
7.70
7.68
7.46
7.46
7.44
7.44
7.37
7.36
7.35
7.34
7.33
7.31
7.31
7.29
7.27
7.22
7.20
3.71
3.71
3.69
3.69
2.35
1.99
1.67
1.62
1.53
1.52
1.50
1.49
1.48
1.47
1.46
0.97
1H NMR (400 MHz, CDCl3)
H
O
N
Ts
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.05
1.03
1.08
1.10
2.13
1.01
4.22
1.07
1.12
3.07
3.63
1.53
1.04


215.4
145.1
143.0
139.3
136.5
130.0
126.7
125.6
125.5
125.0
123.9
119.5
115.2
55.4
46.7
38.9
27.6
25.7
24.7
21.7
19.7
13C NMR (101 MHz, CDCl3)
H
O
N
Ts
220 200 180 160 140 120 100 80 60 40 20 ppm

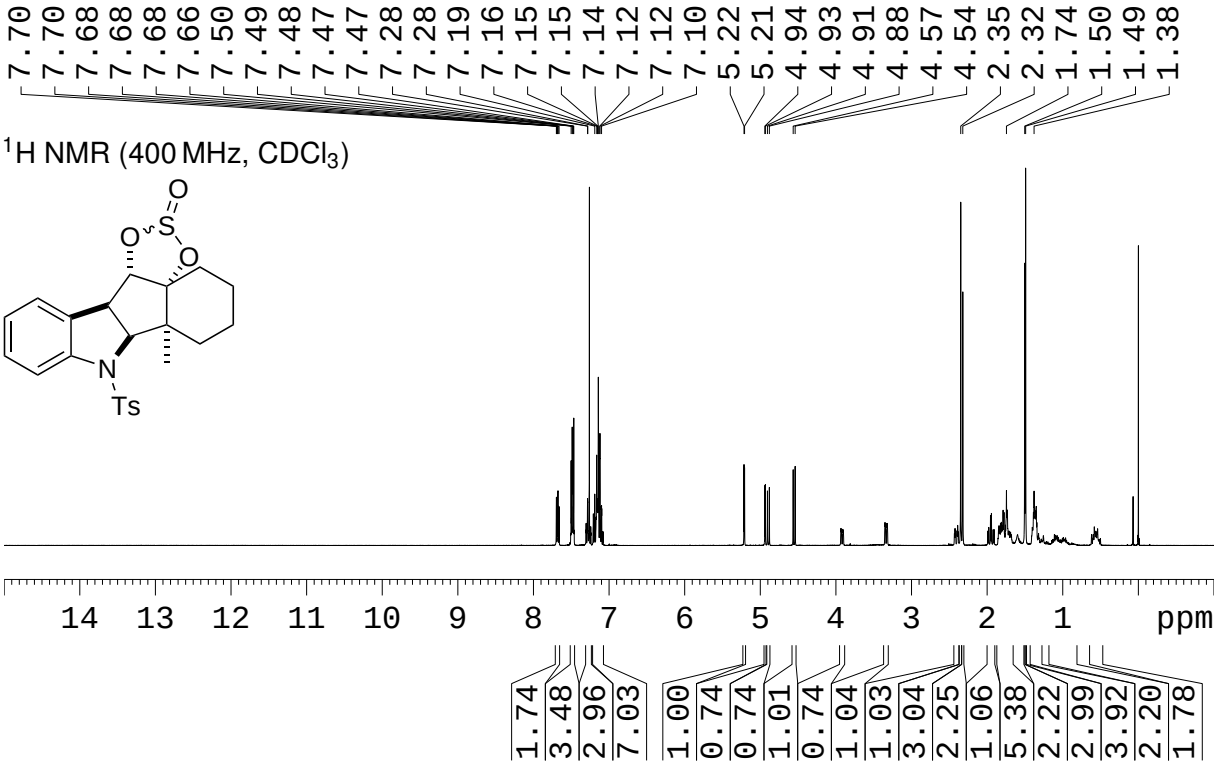
Diol 18

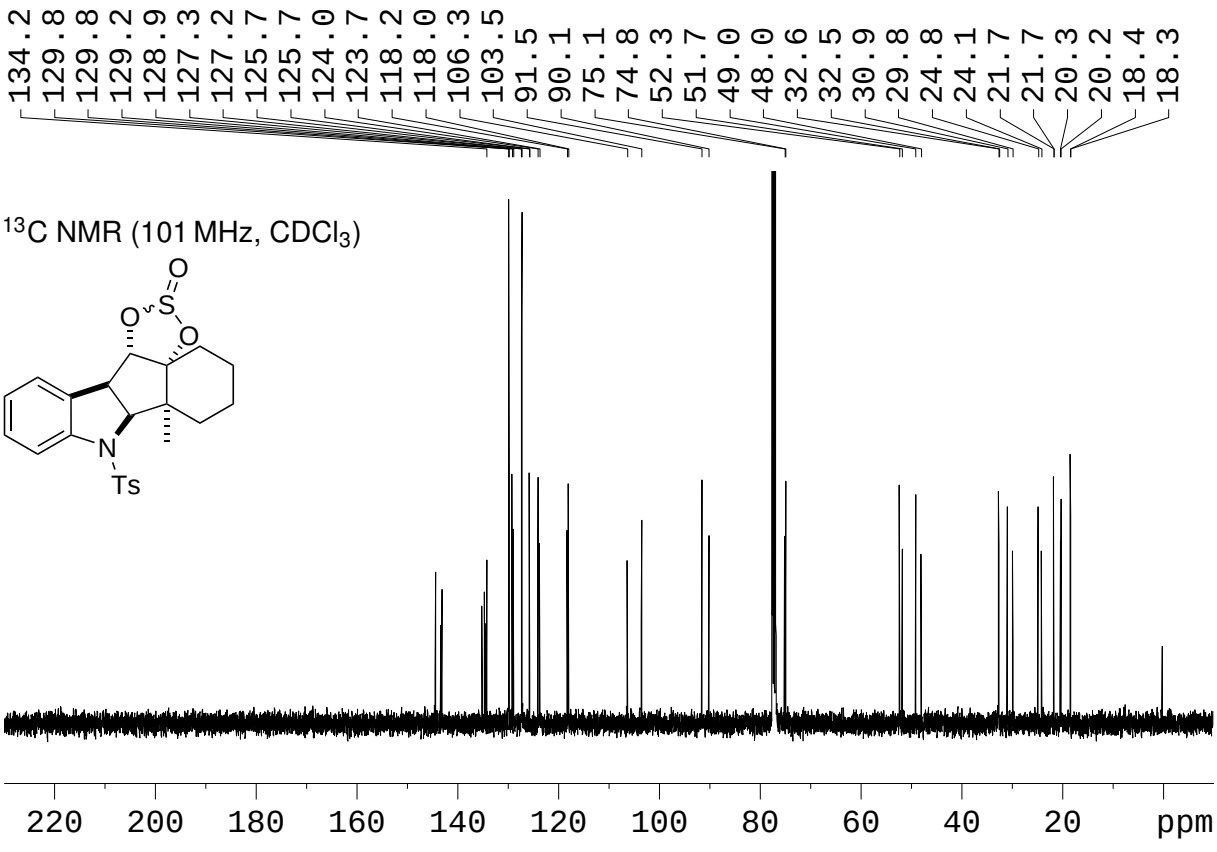

8.10
8.08
7.59
7.58
7.57
7.57
7.17
7.16
7.15
7.05
7.05
7.05
7.03
6.85
6.85
6.83
6.83
6.81
6.81
6.50
6.48
4.80
4.78
3.36
3.34
3.33
1.68
1.62
1.57
1.11
1.08
1.07
1.04
1.04
1.03
1H NMR (400 MHz, C6D6)
HO
OH
N
Ts
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.02
1.02
1.02
2.03
1.03
1.02
1.03
1.03
1.12
3.12
1.05
3.14
1.16
1.18
3.20
2.19


143.9
143.4
137.3
135.5
129.6
128.4
127.6
125.1
124.1
117.7
81.8
79.5
75.4
51.4
48.1
31.2
29.8
22.9
21.1
21.0
18.4
13C NMR (101 MHz, C6D6)
HO
OH
N
Ts
220 200 180 160 140 120 100 80 60 40 20 ppm

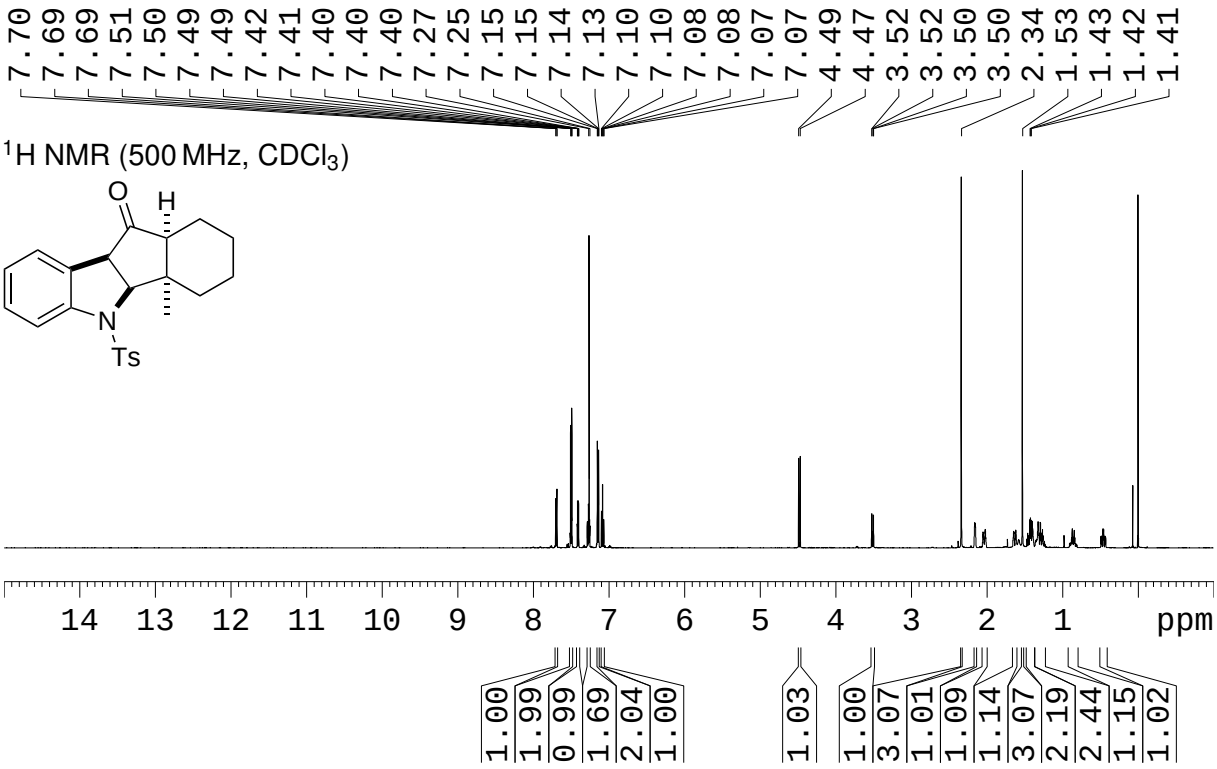

4a–CH3
10a–OH
10–OH
9b–H
4b–H
(1H,1H NOESY, 400 MHz, C6D6)
HO
OH
N
Ts
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

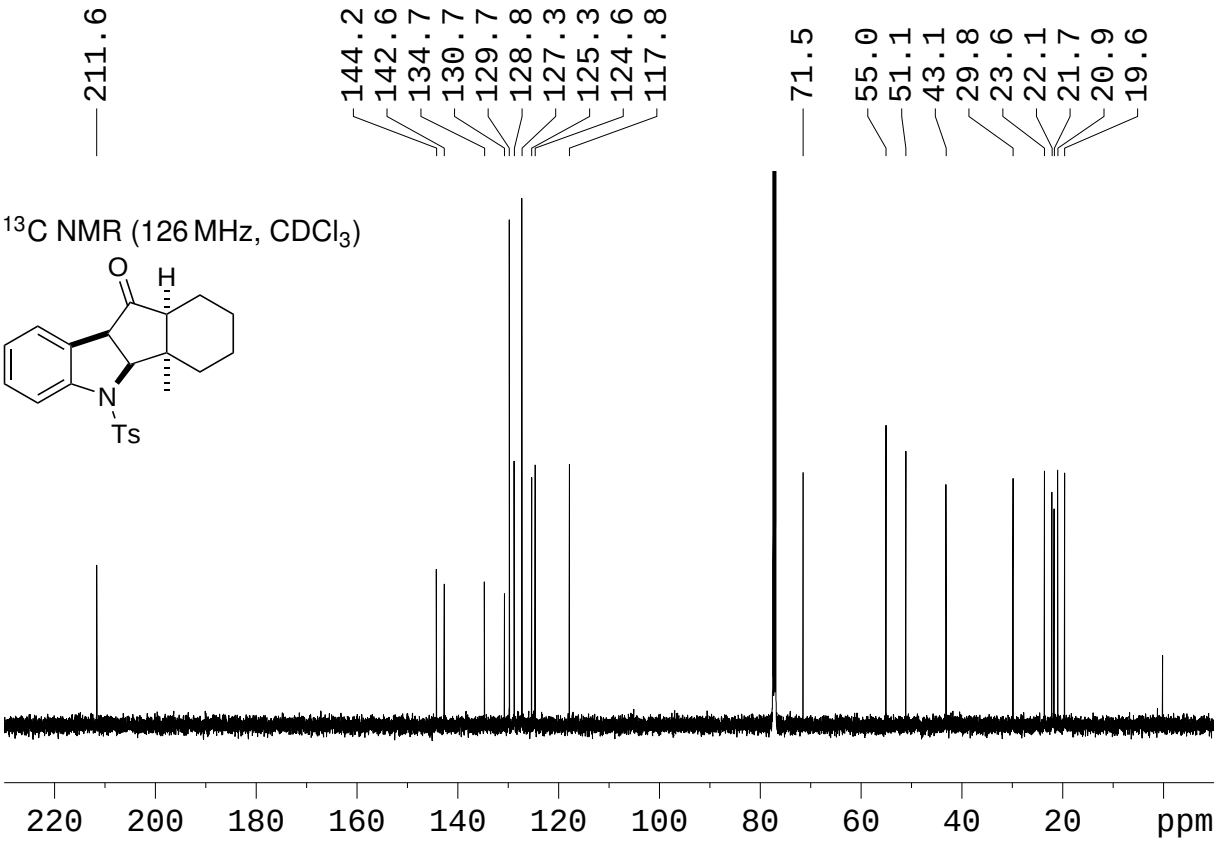
Sulfite 19

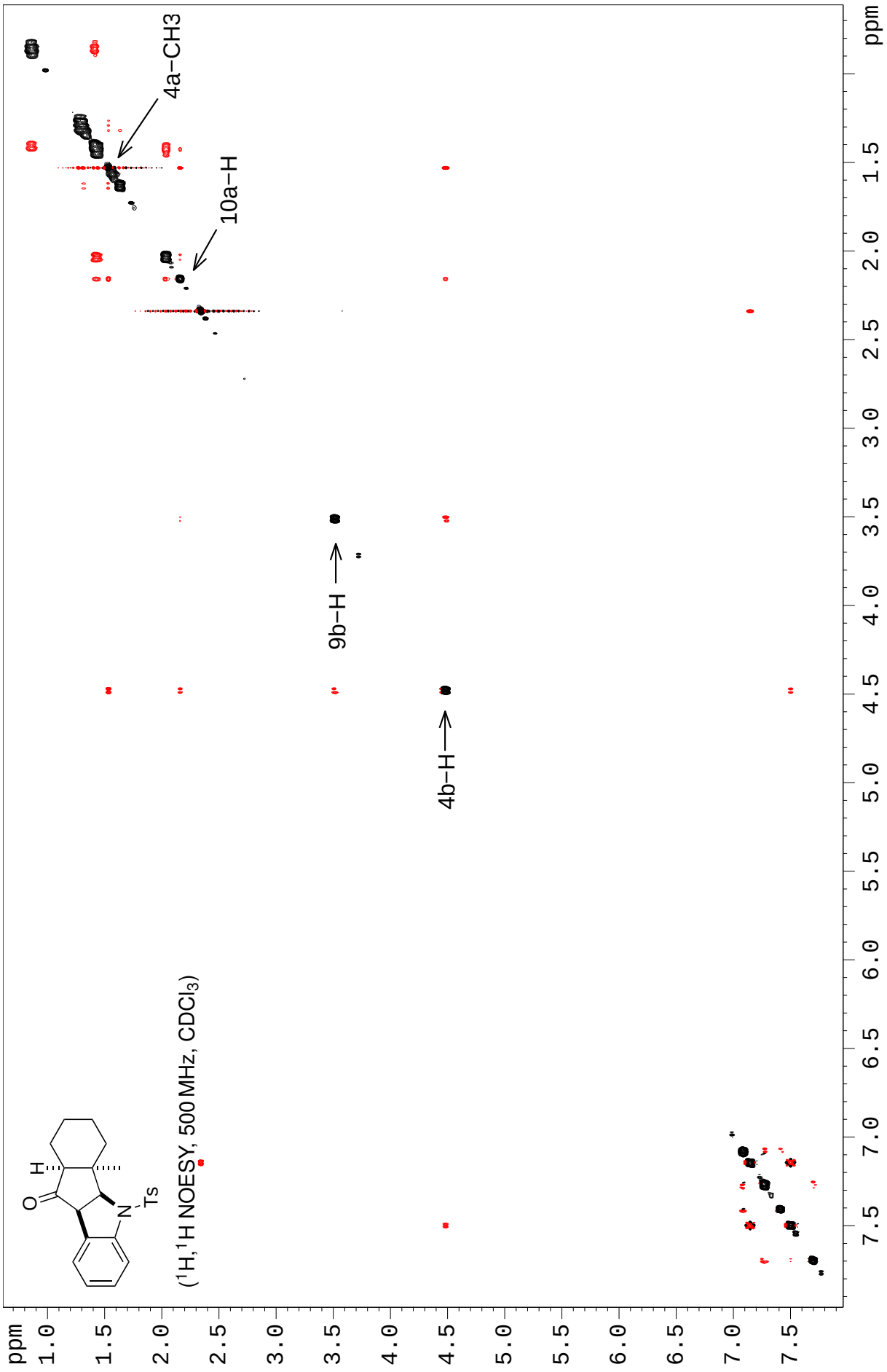

7.70 7.70 7.68 7.68 7.68 7.66 7.50 7.49 7.48 7.47 7.47 7.28 7.28 7.19 7.16 7.15 7.15 7.14 7.12 7.12 7.10 5.22 5.21 4.94 4.93 4.91 4.88 4.57 4.54 2.35 2.32 1.74 1.50 1.49 1.38
1H NMR (400 MHz, CDCl3)
O
S
O
O
N
Ts
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.74 3.48 2.96 7.03 1.00 0.74 0.74 1.01 0.74 1.04 1.03 3.04 2.25 1.06 5.38 2.22 2.99 3.92 2.20 1.78


134.2 129.8 129.8 129.2 128.9 127.3 127.2 125.7 125.7 124.0 123.7 118.2 118.0 106.3 103.5 91.5 90.1 75.1 74.8 52.3 51.7 49.0 48.0 32.6 32.5 30.9 29.8 24.8 24.1 21.7 21.7 20.3 20.2 18.4 18.3
13C NMR (101 MHz, CDCl3)
O
S
O
O
N
Ts
220 200 180 160 140 120 100 80 60 40 20 ppm

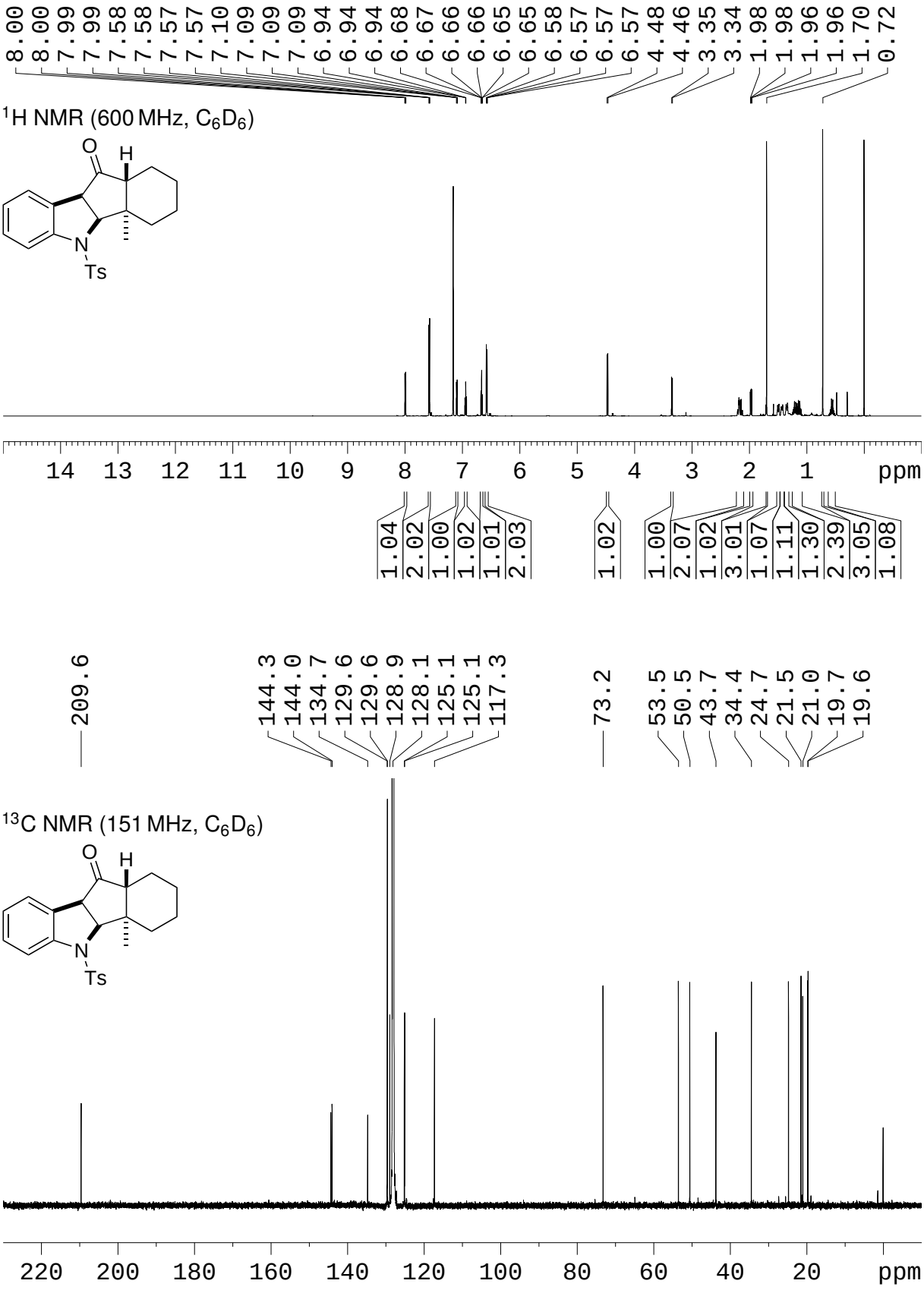
cis-Hydrindanone 20

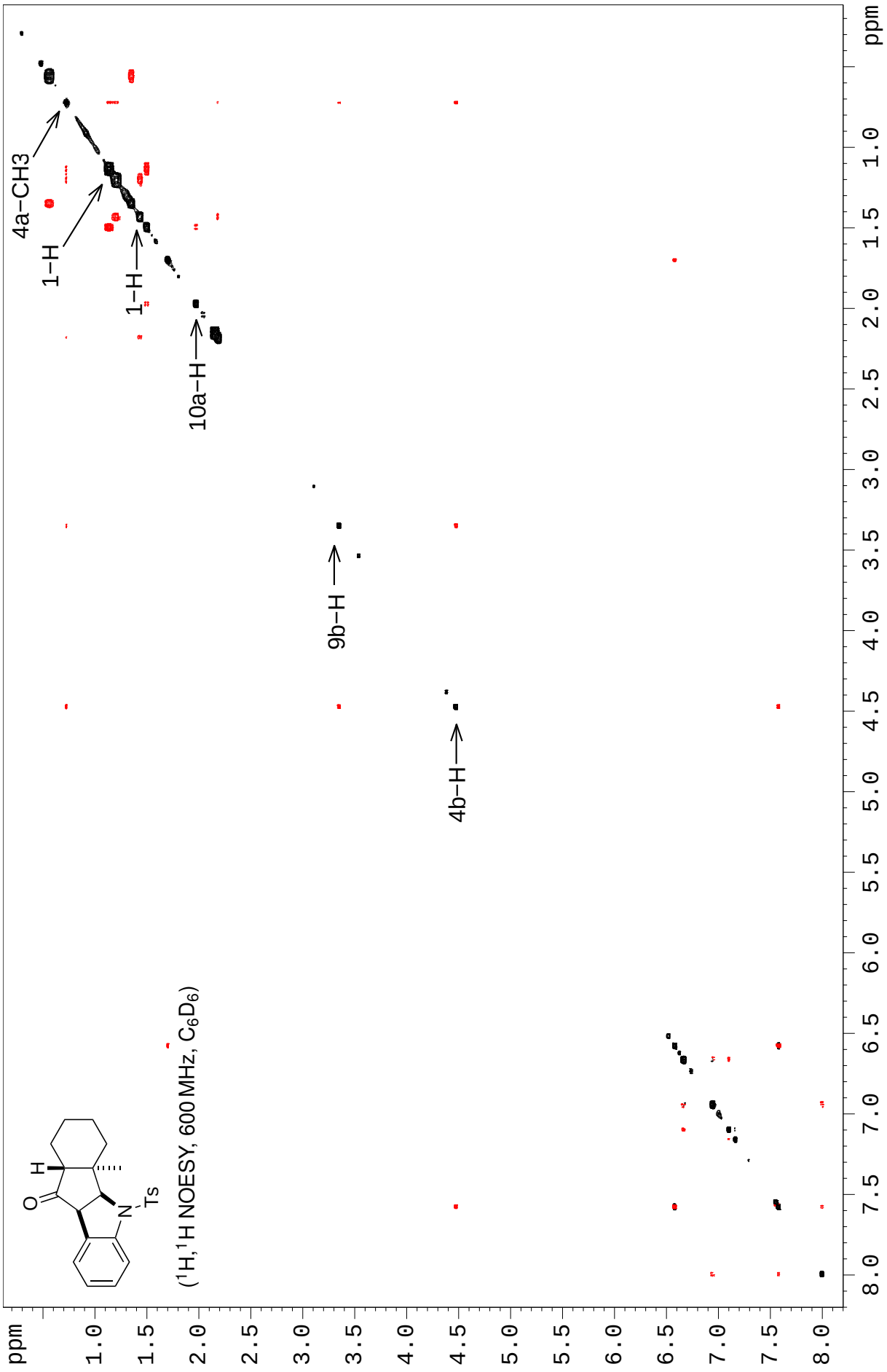




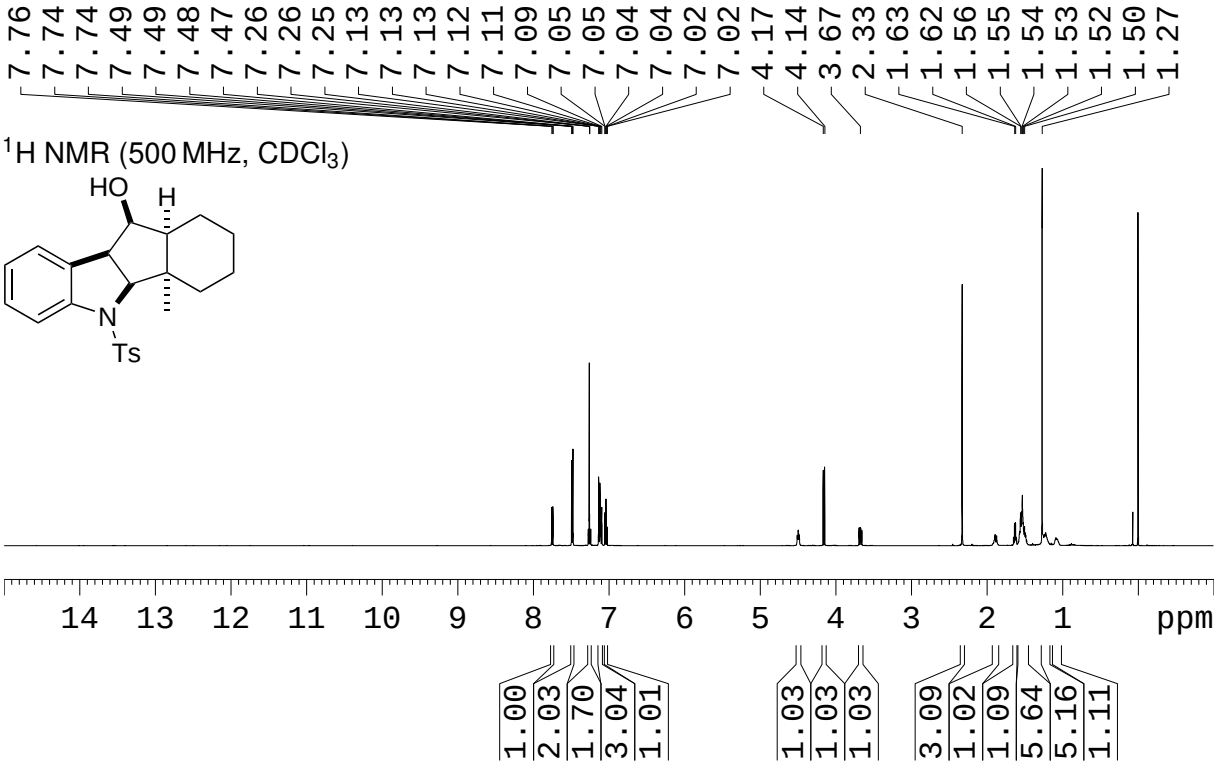

4a–CH3
10a–H
9b–H
4b–H
(^{1}H,^{1}H NOESY, 500 MHz, CDCl$_3$)
O
H
N
Ts
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

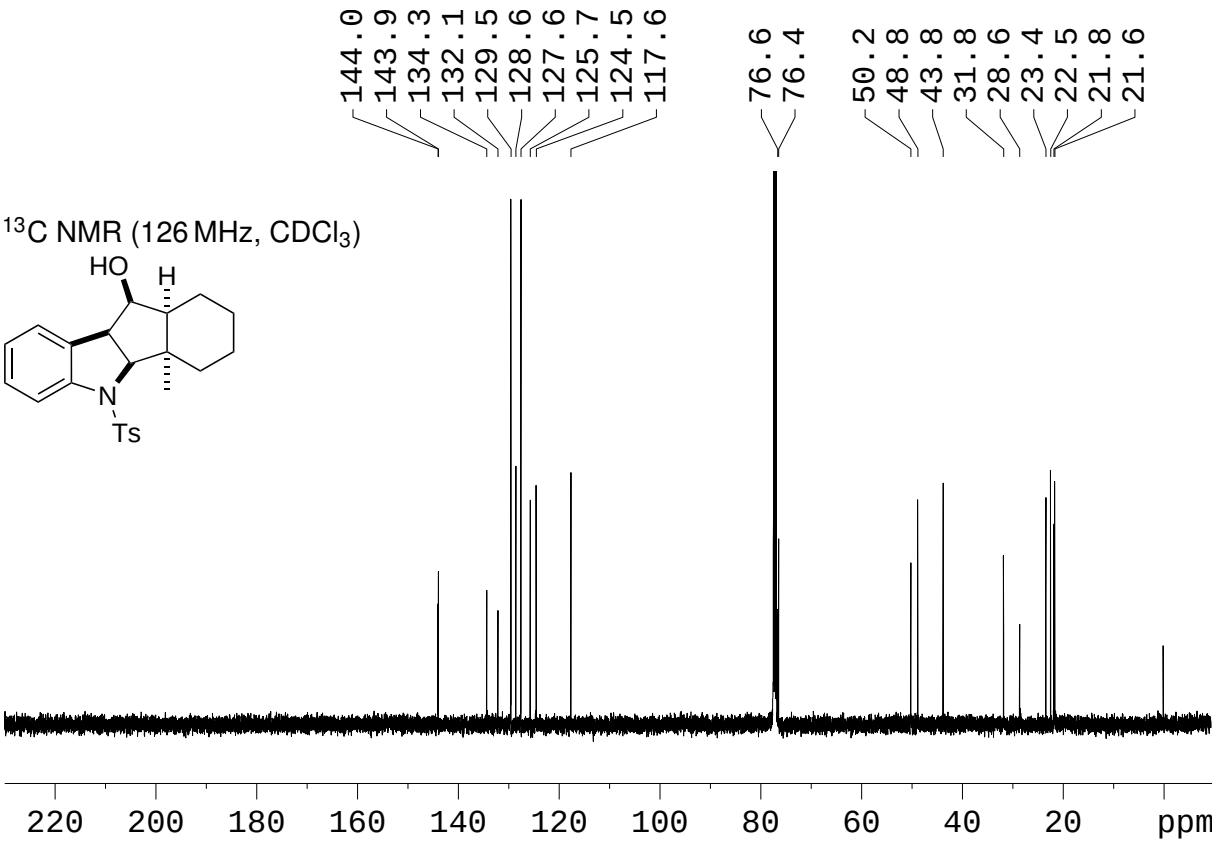
trans-Hydrindanone 21

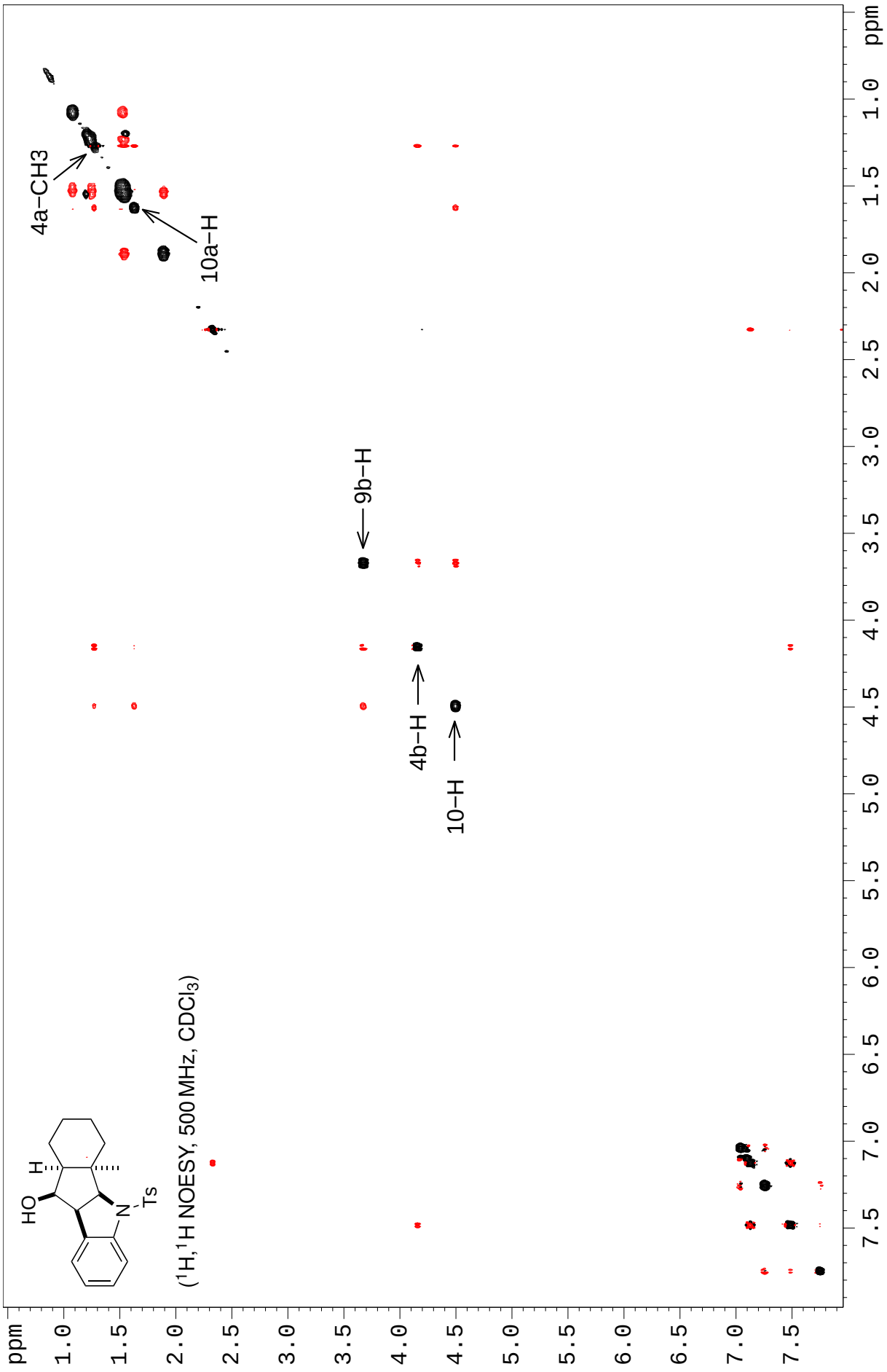



4a−CH3
1−H
1−H
10a−H
9b−H
4b−H
(1H,1H NOESY, 600 MHz, C6D6)
O
H
N
Ts
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

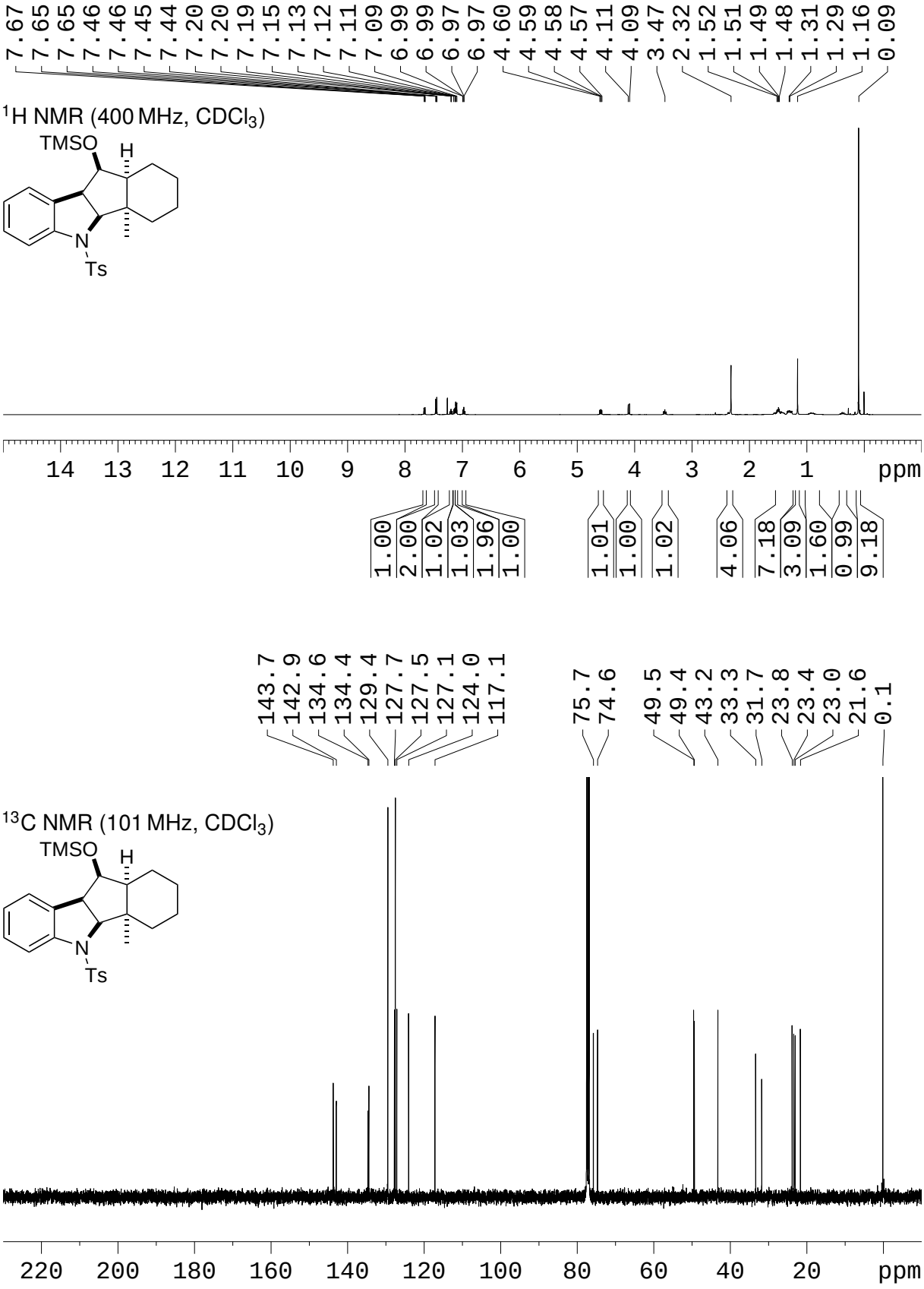
Alcohol S11

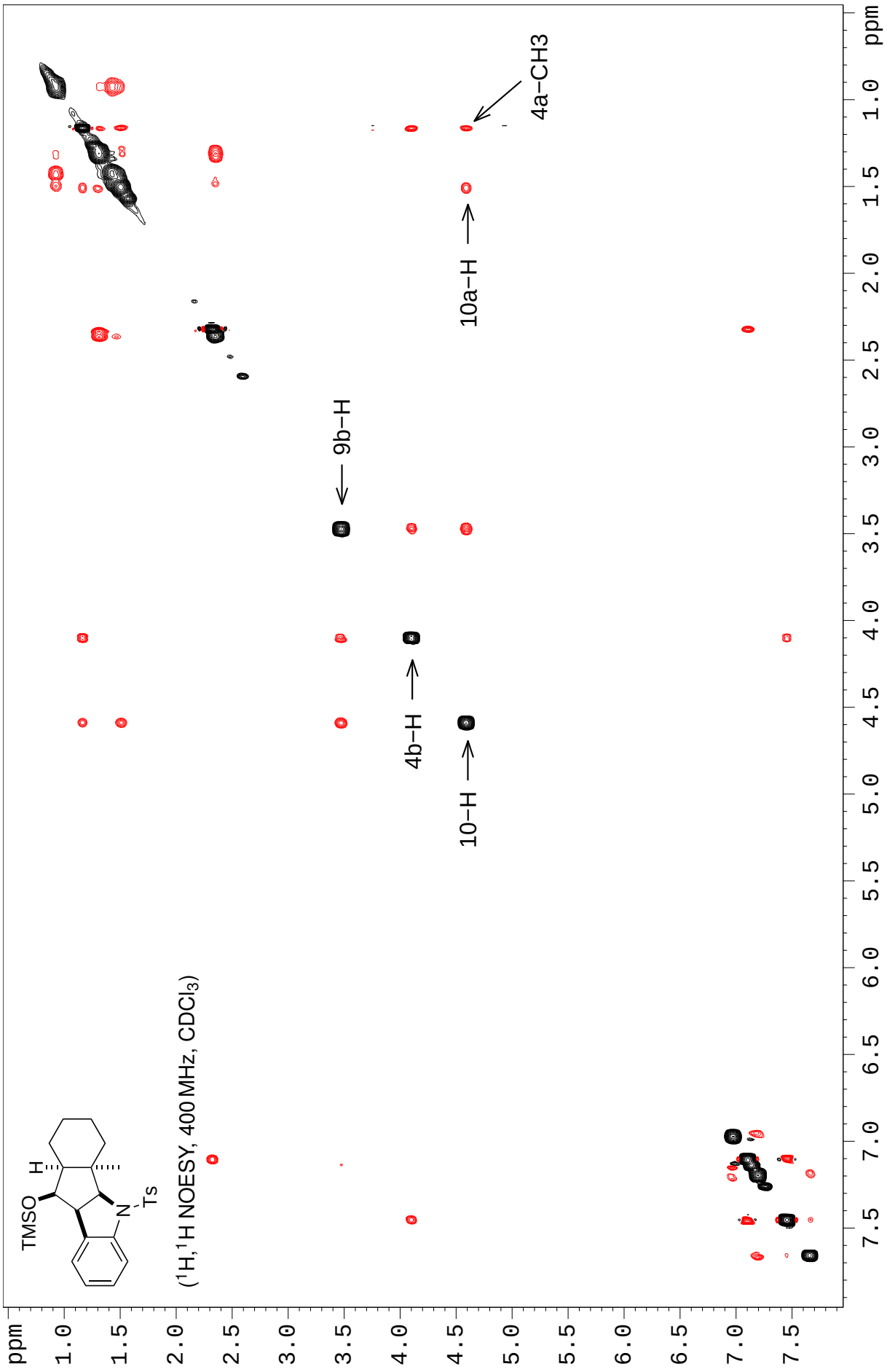

7.76 7.74 7.74 7.49 7.49 7.48 7.47 7.26 7.26 7.25 7.13 7.13 7.13 7.12 7.11 7.09 7.05 7.05 7.04 7.04 7.02 7.02 4.17 4.14 3.67 2.33 1.63 1.62 1.56 1.55 1.54 1.53 1.52 1.50 1.27
1H NMR (500 MHz, CDCl3)
HO
H
N
Ts
14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00 2.03 1.70 3.04 1.01 1.03 1.03 1.03 3.09 1.02 1.09 5.64 5.16 1.11


144.0 143.9 134.3 132.1 129.5 128.6 127.6 125.7 124.5 117.6 76.6 76.4 50.2 48.8 43.8 31.8 28.6 23.4 22.5 21.8 21.6
13C NMR (126 MHz, CDCl3)
HO
H
N
Ts
220 200 180 160 140 120 100 80 60 40 20 ppm

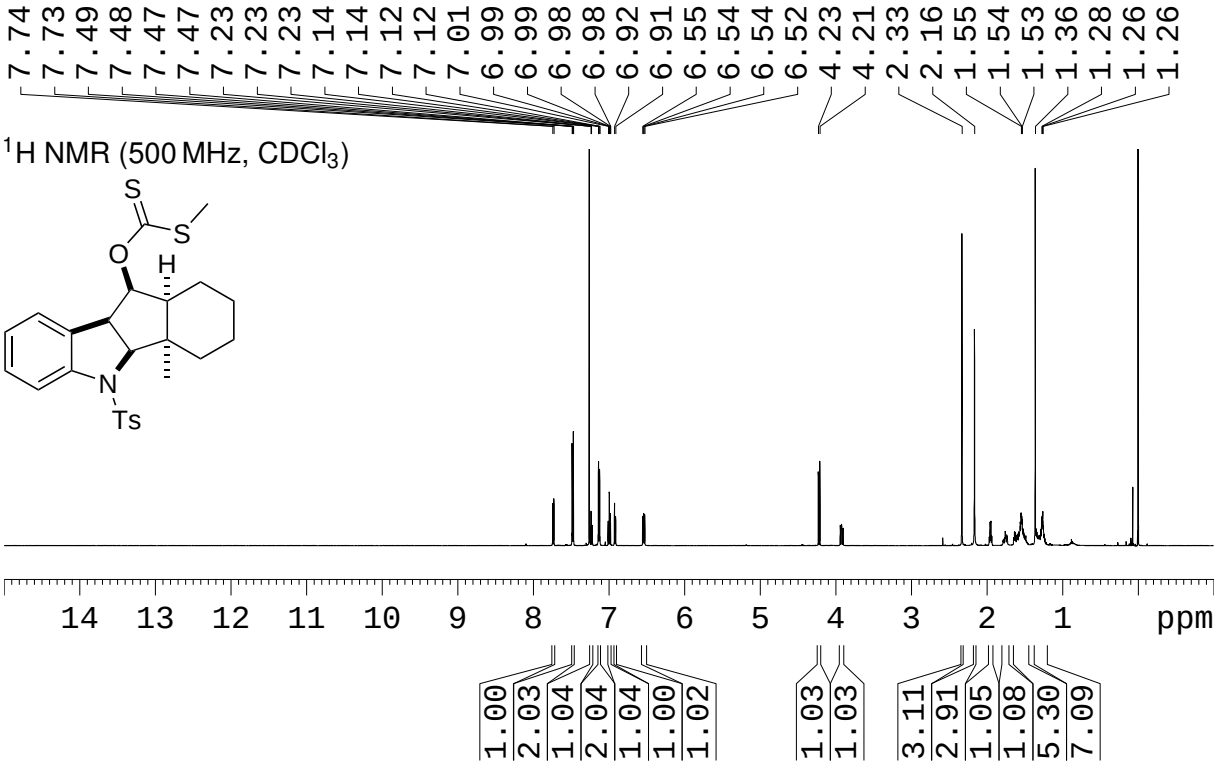

4a–CH3
10a–H
9b–H
4b–H
10–H
(1H,1H NOESY, 500 MHz, CDCl3)
HO
H
N
Ts
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

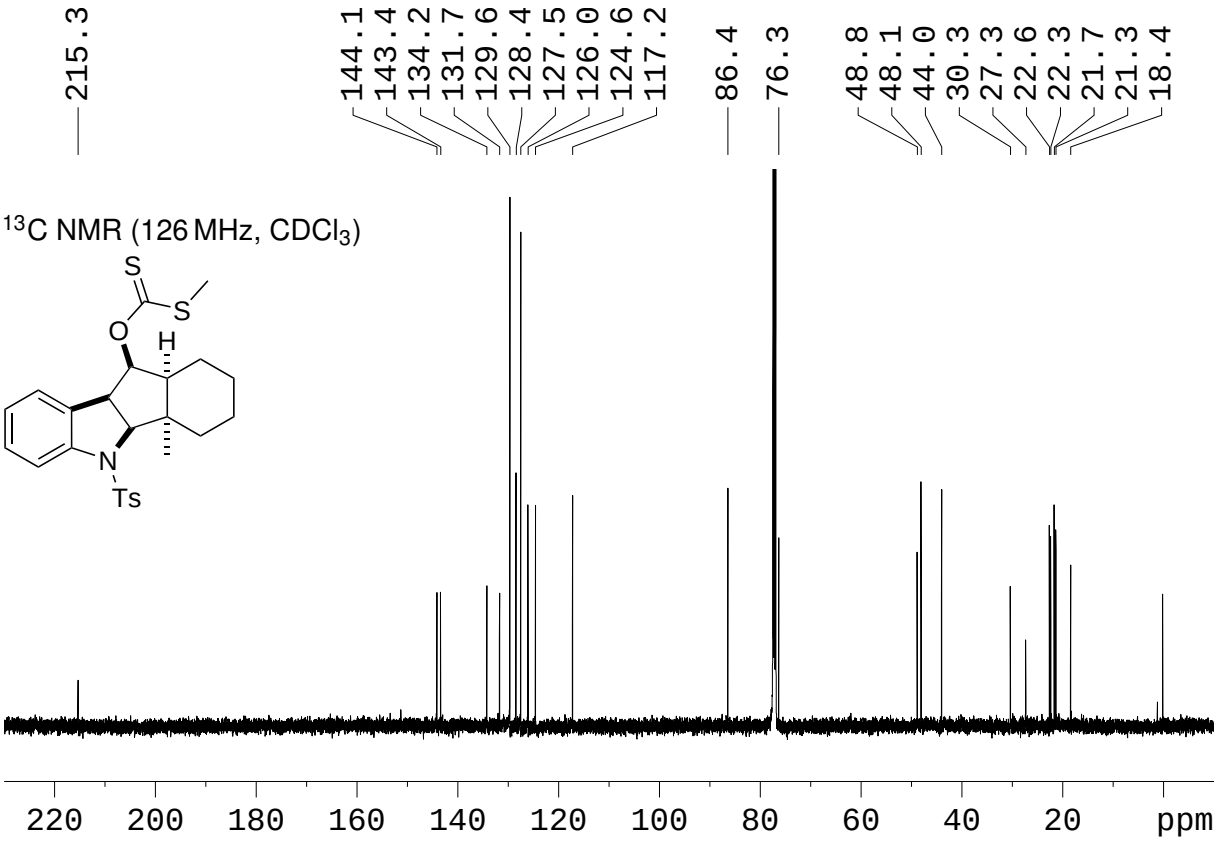
Silyl ether S13

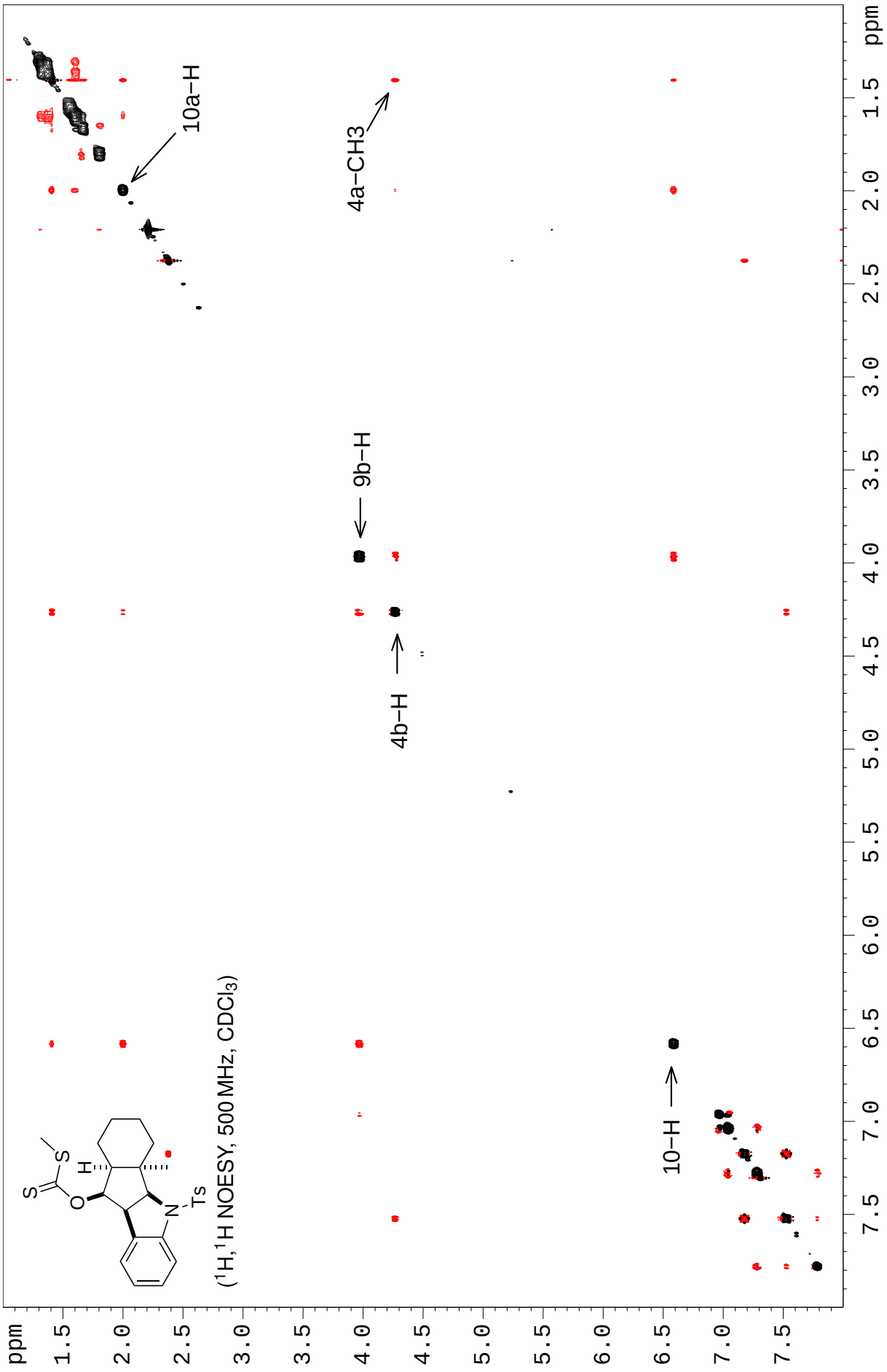



4a–CH3
10a–H
9b–H
4b–H
10–H
TMSO
H
N
Ts
(^{1}H,^{1}H NOESY, 400 MHz, CDCl$_3$)
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

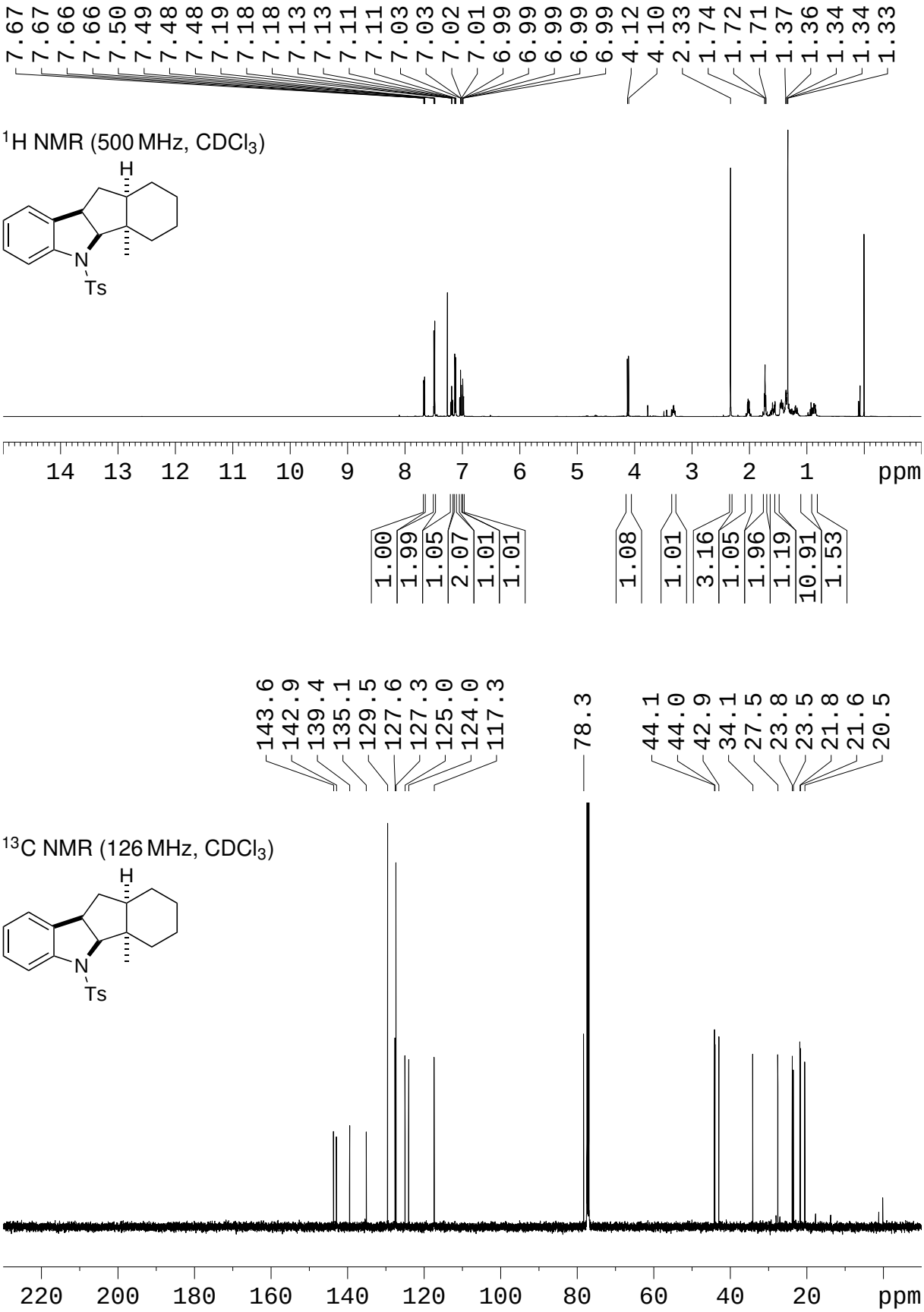
Xanthate S12

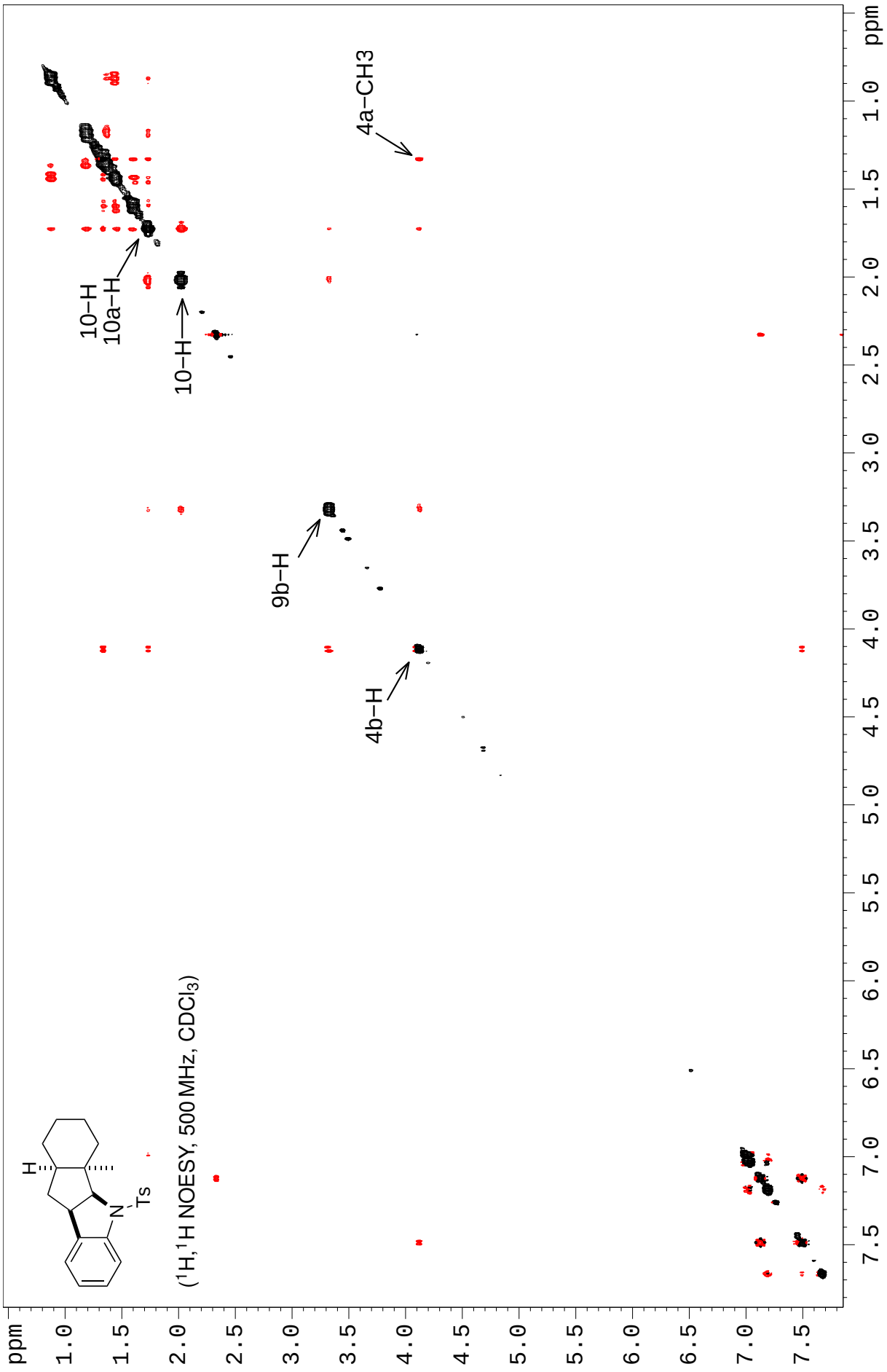




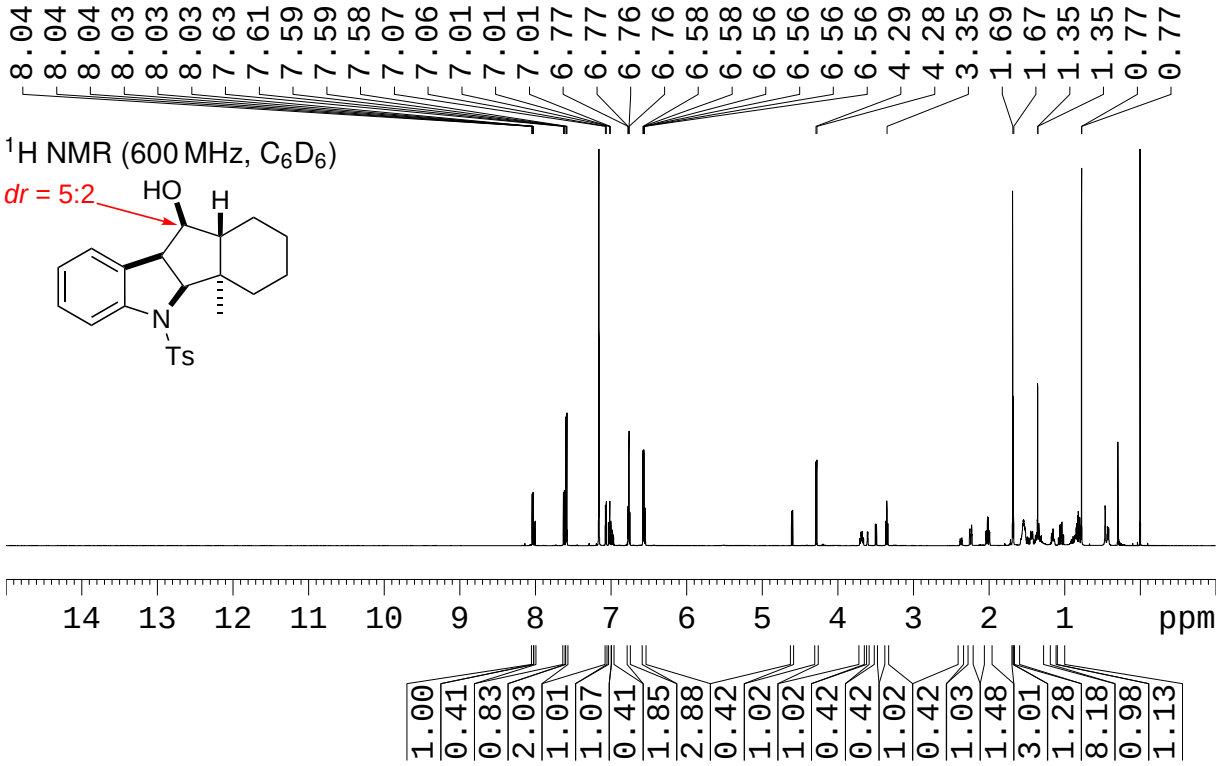

10a–H
4a–CH3
9b–H
4b–H
10–H
(^{1}H,^{1}H NOESY, 500 MHz, CDCl$_3$)
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

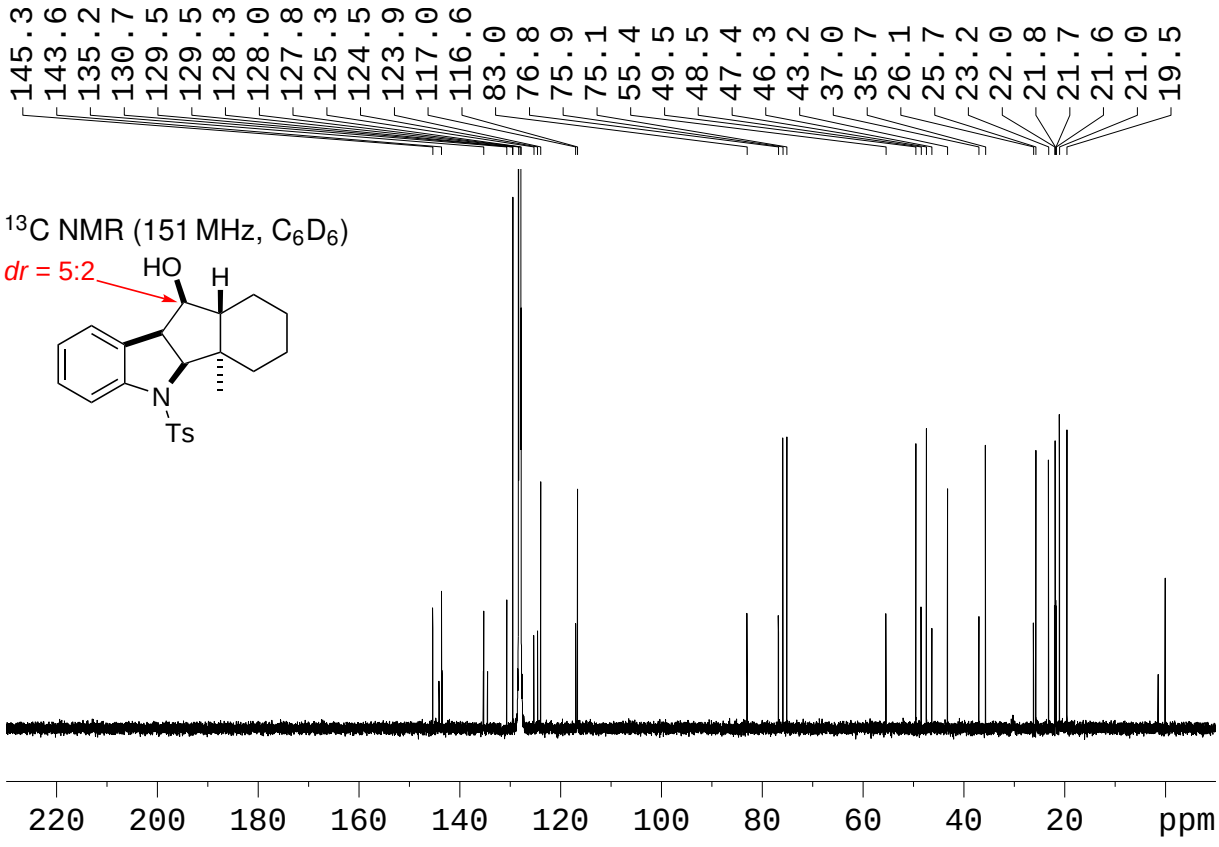
cis-Hydrindane S14

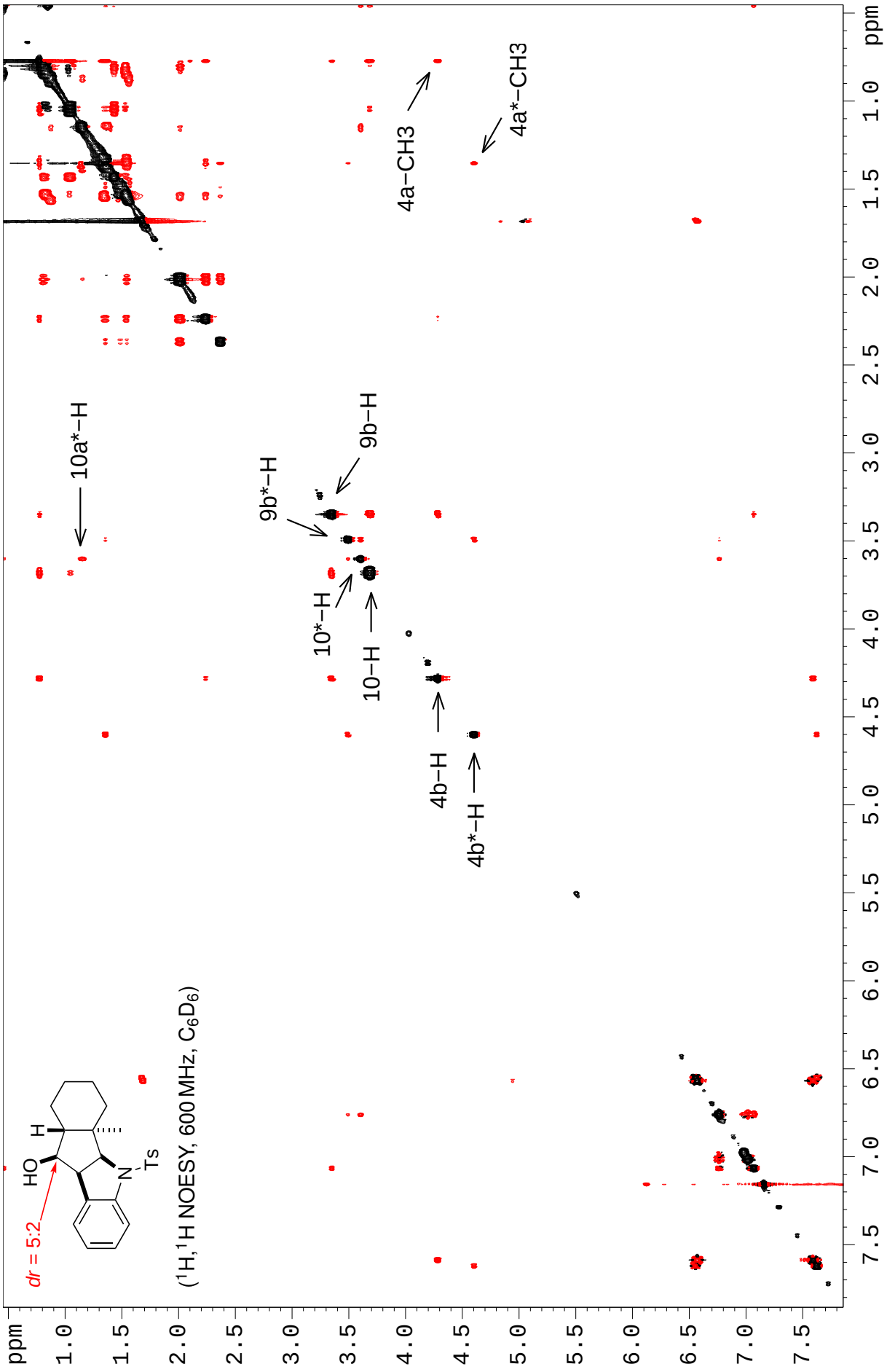



4a–CH3
10–H
10a–H
10–H
9b–H
4b–H
(1H,1H NOESY, 500 MHz, CDCl3)
H
N
Ts
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

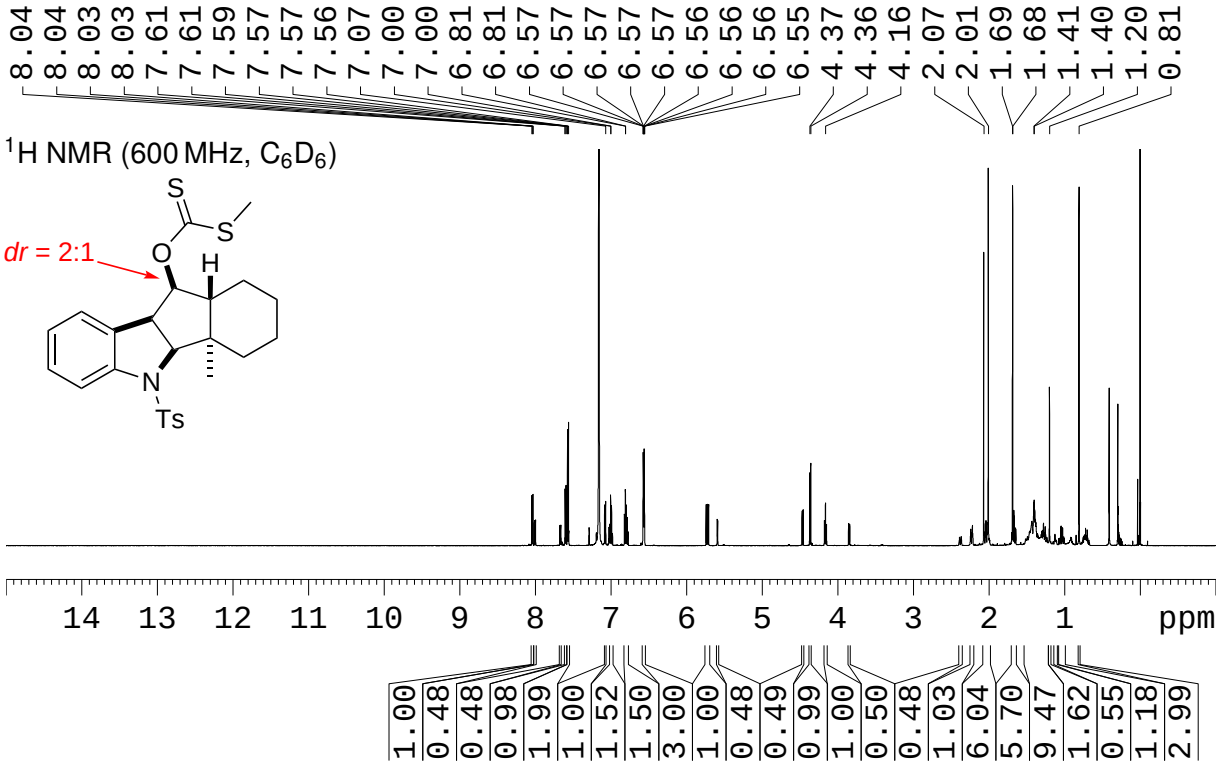
Alcohols S15 and S22

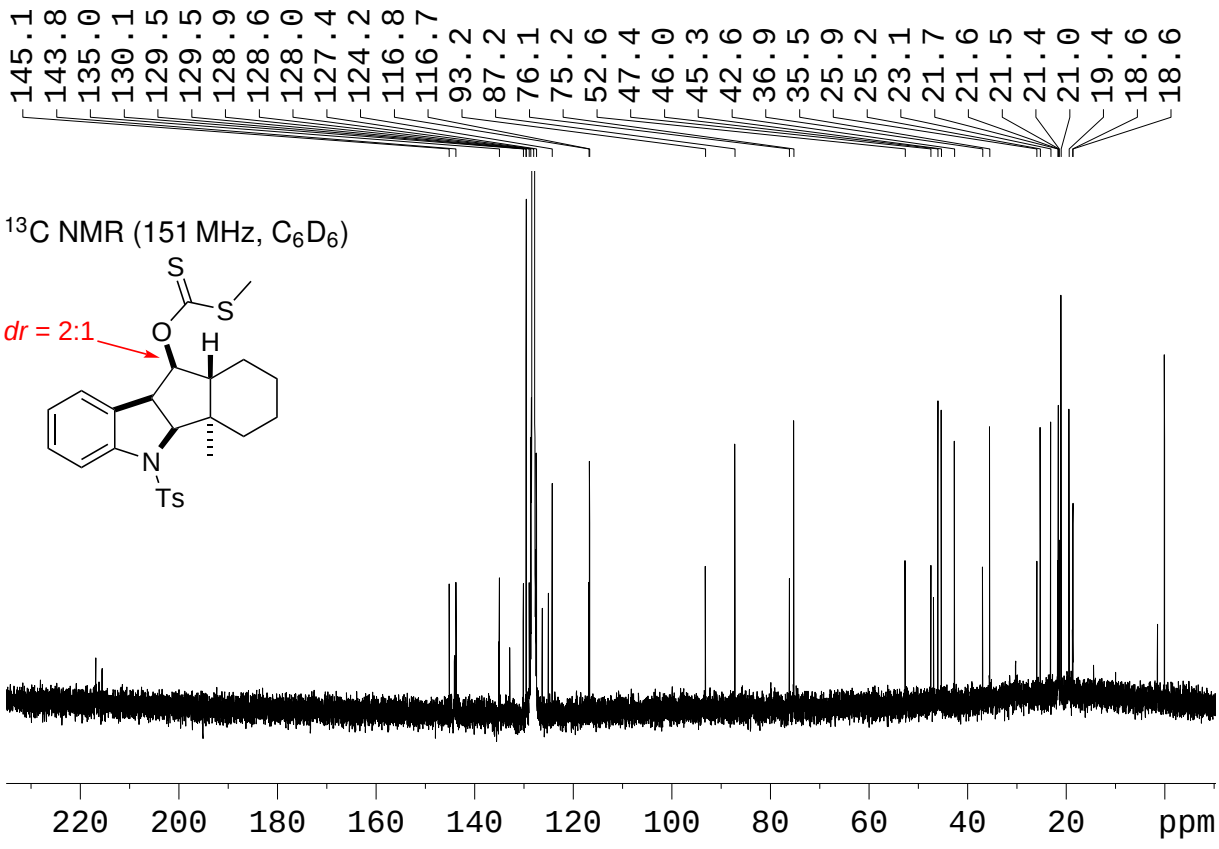


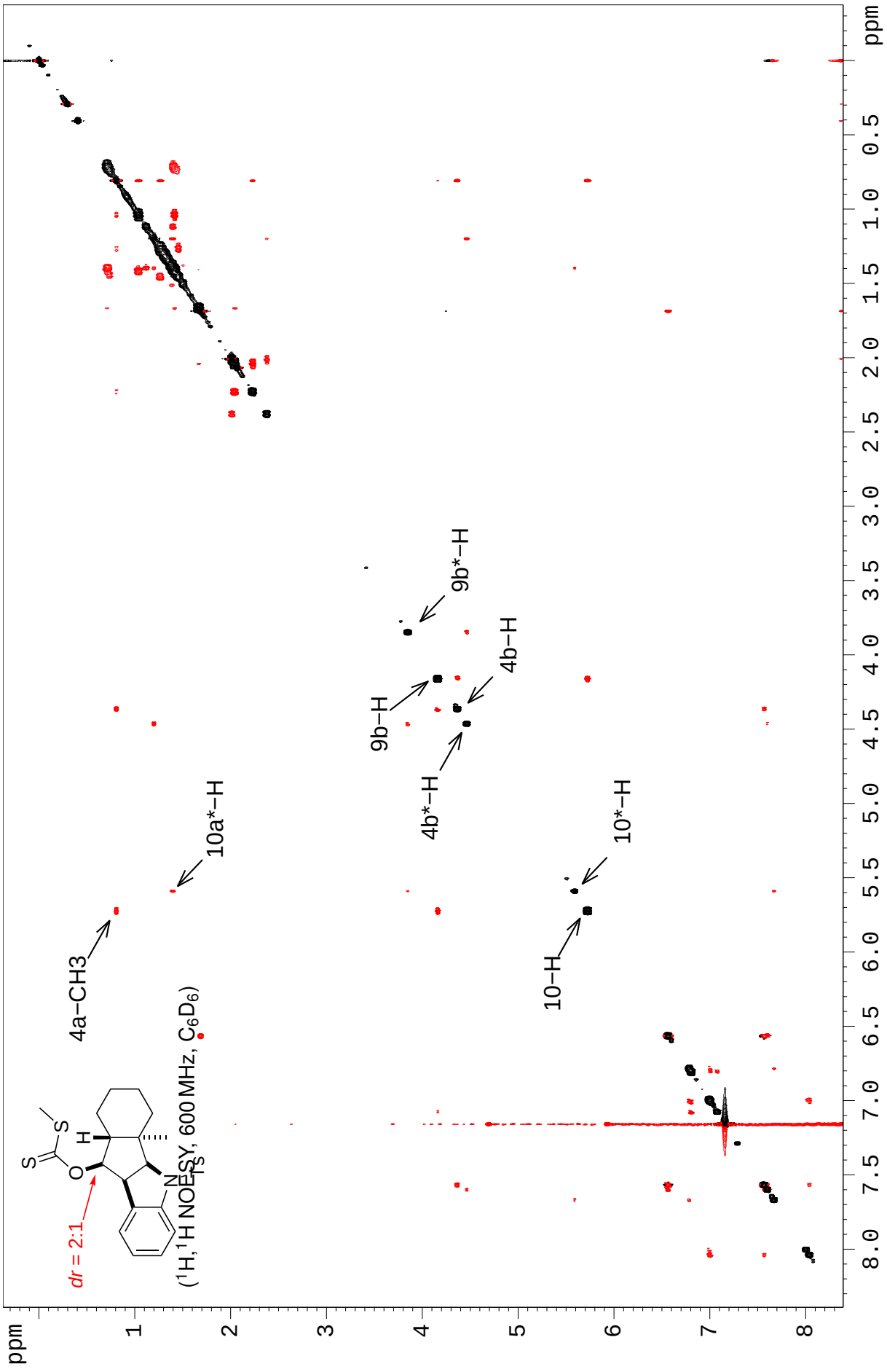



10a*–H
9b*–H
9b–H
10*–H
10–H
4b–H
4b*–H
4a–CH3
4a*–CH3
dr = 5:2
HO
H
N
Ts
(^{1}H,^{1}H NOESY, 600 MHz, C_6D_6)
ppm

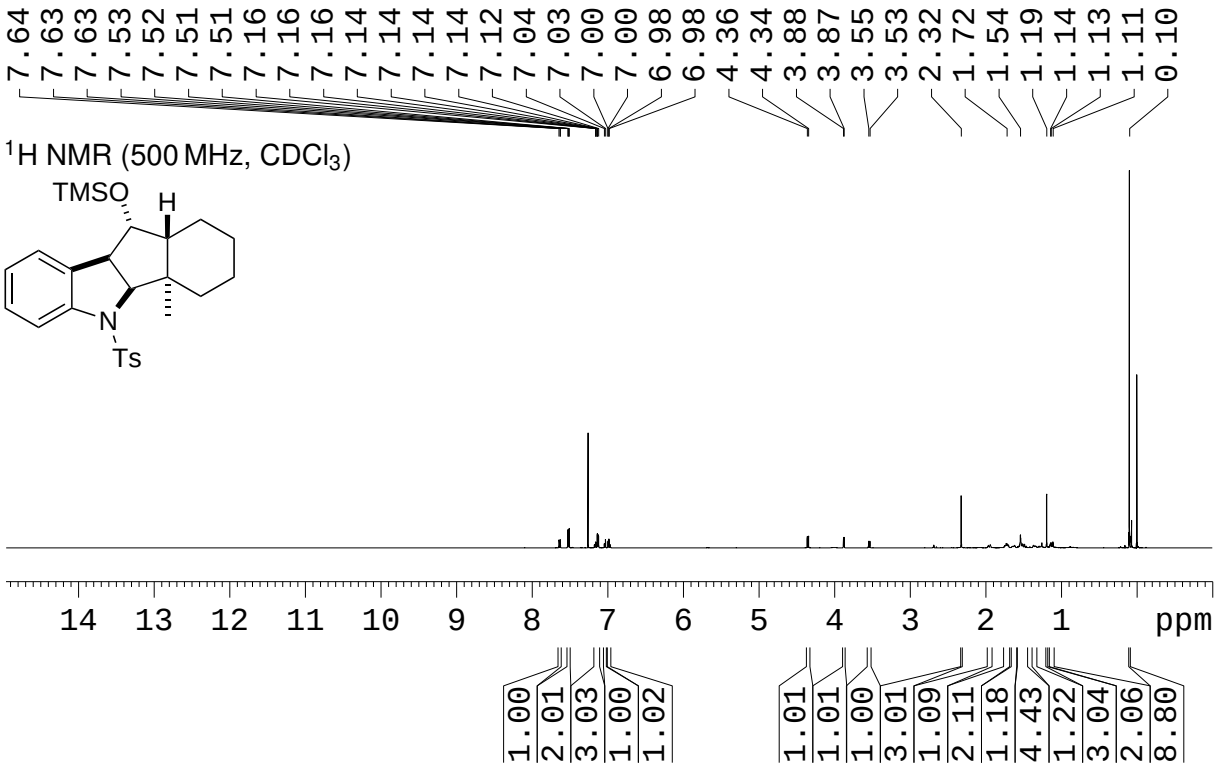
Xanthates S16 and S23

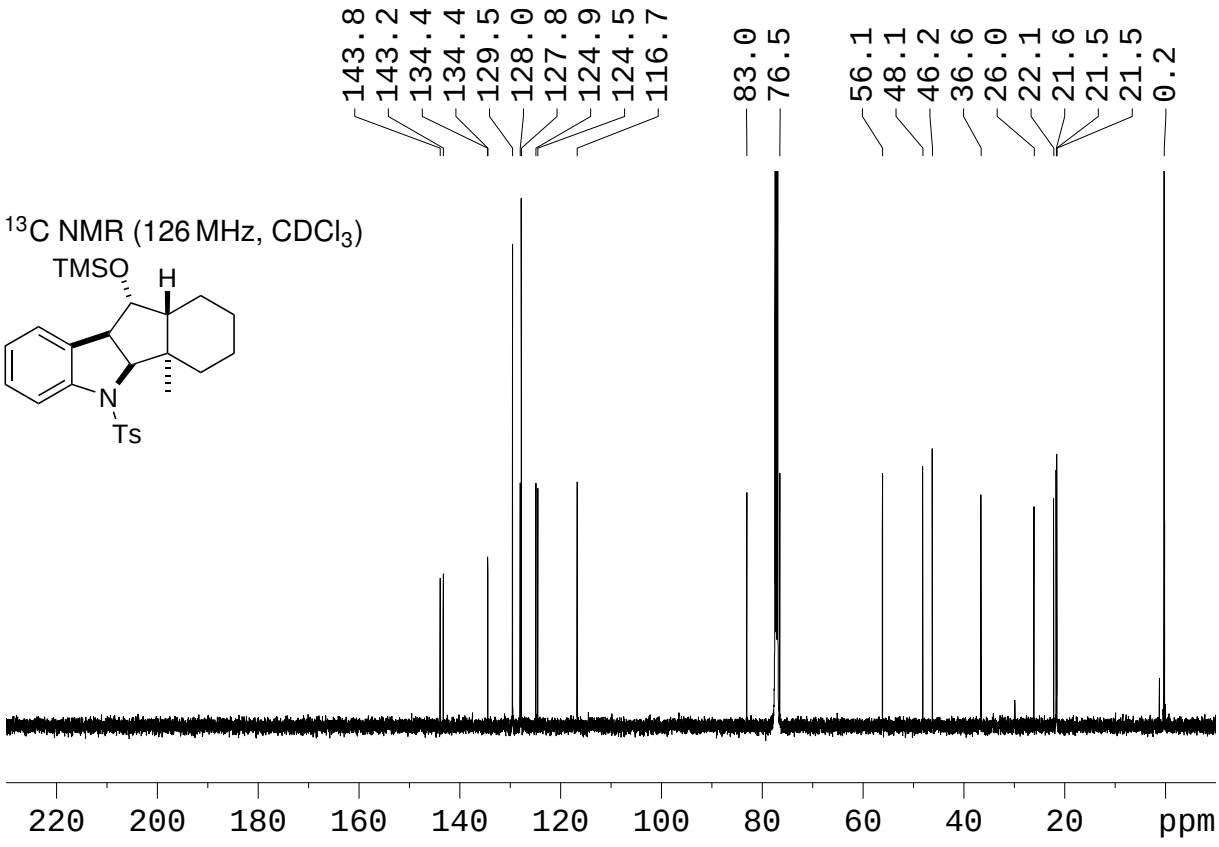


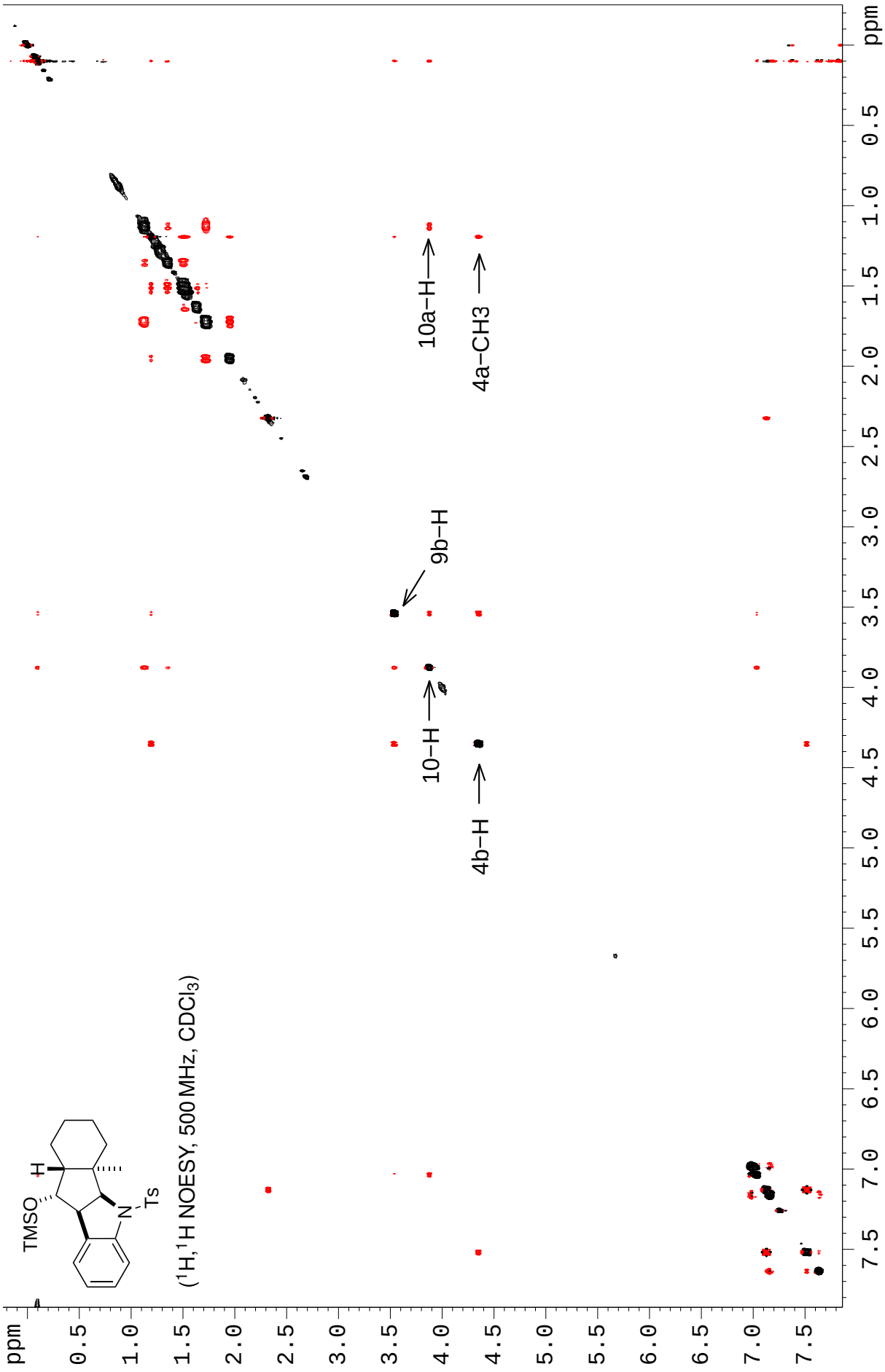



4a–CH3
10a*–H
9b–H
9b*–H
4b–H
4b*–H
10–H
10*–H
dr = 2:1
(1H,1H NOESY, 600 MHz, C6D6)
ppm
ppm

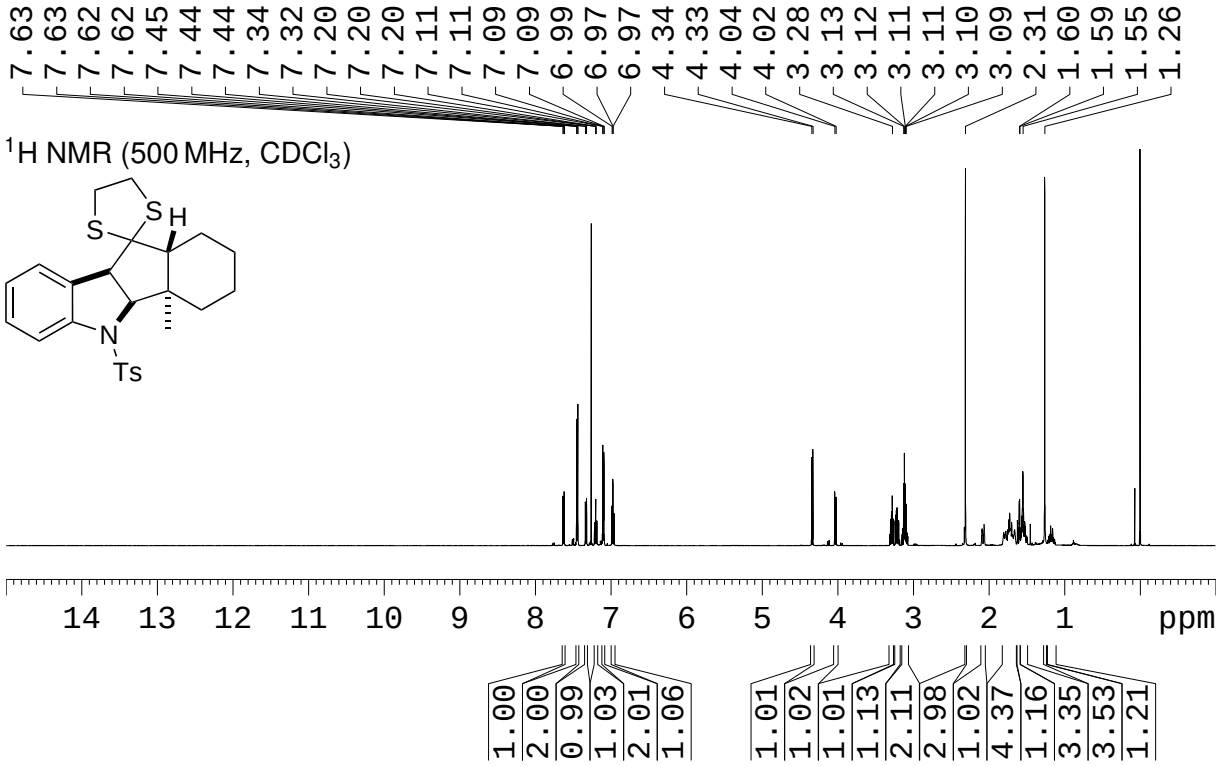
Silyl ether S17

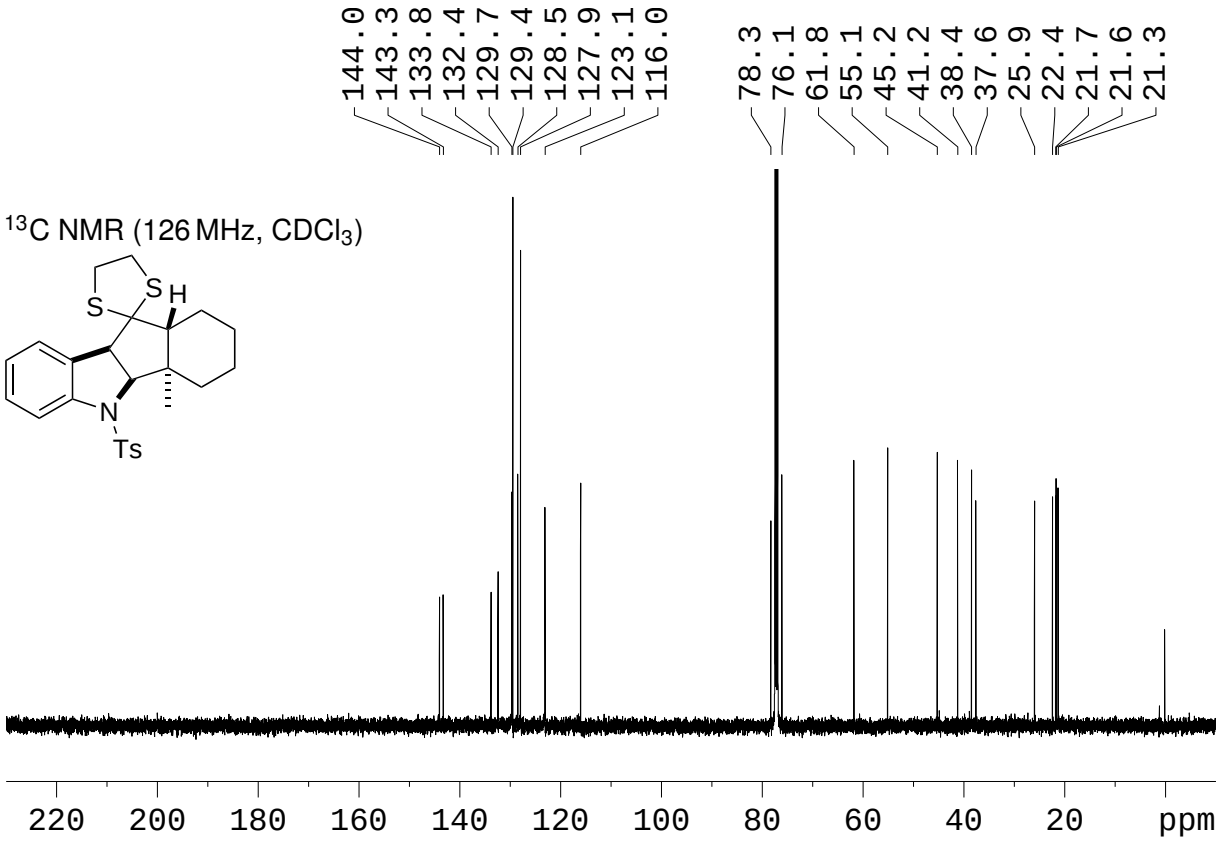


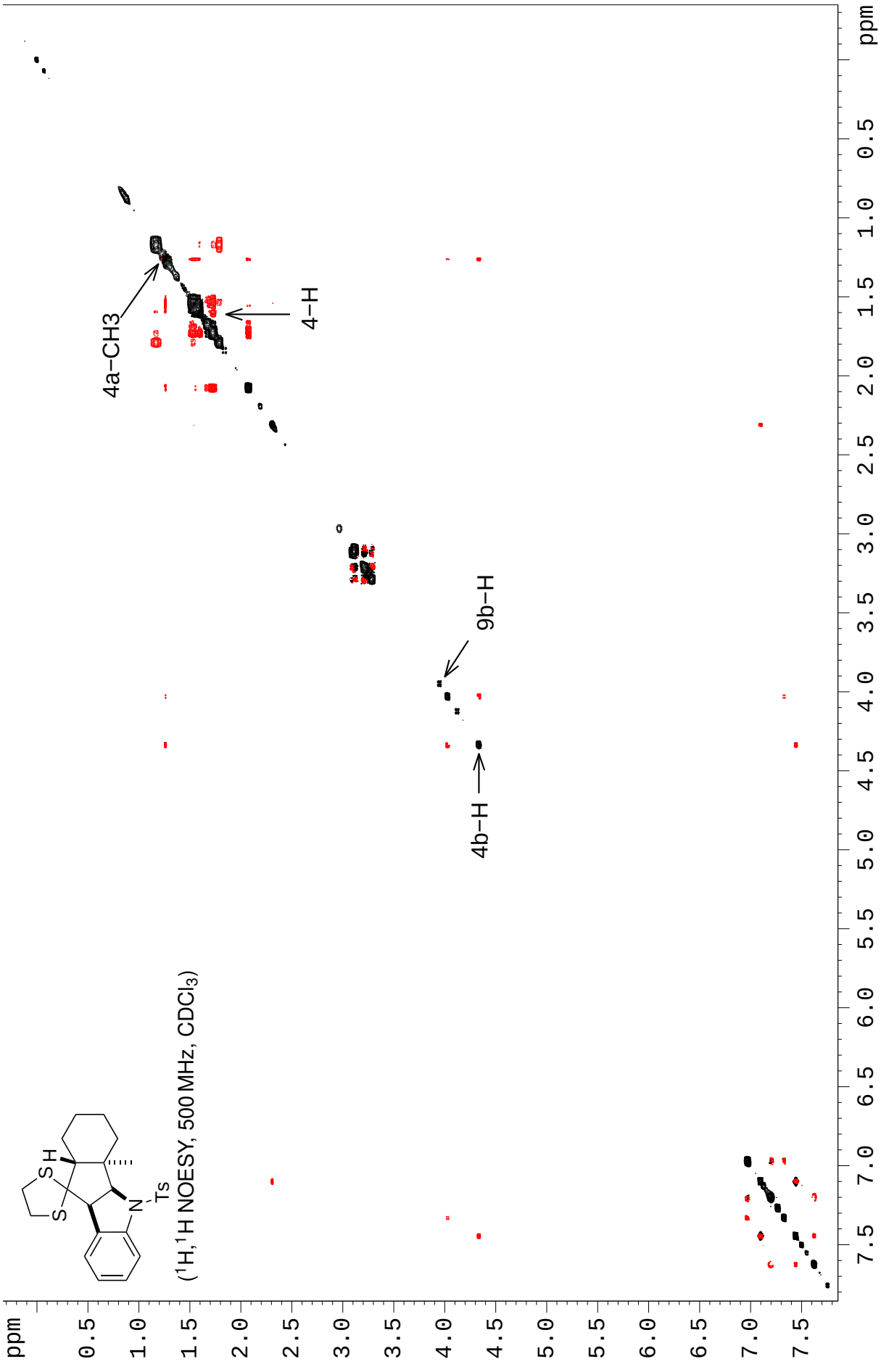



10a–H
4a–CH3
9b–H
10–H
4b–H
(^{1}H,^{1}H NOESY, 500 MHz, CDCl$_3$)
TMSO
H
N
Ts
ppm

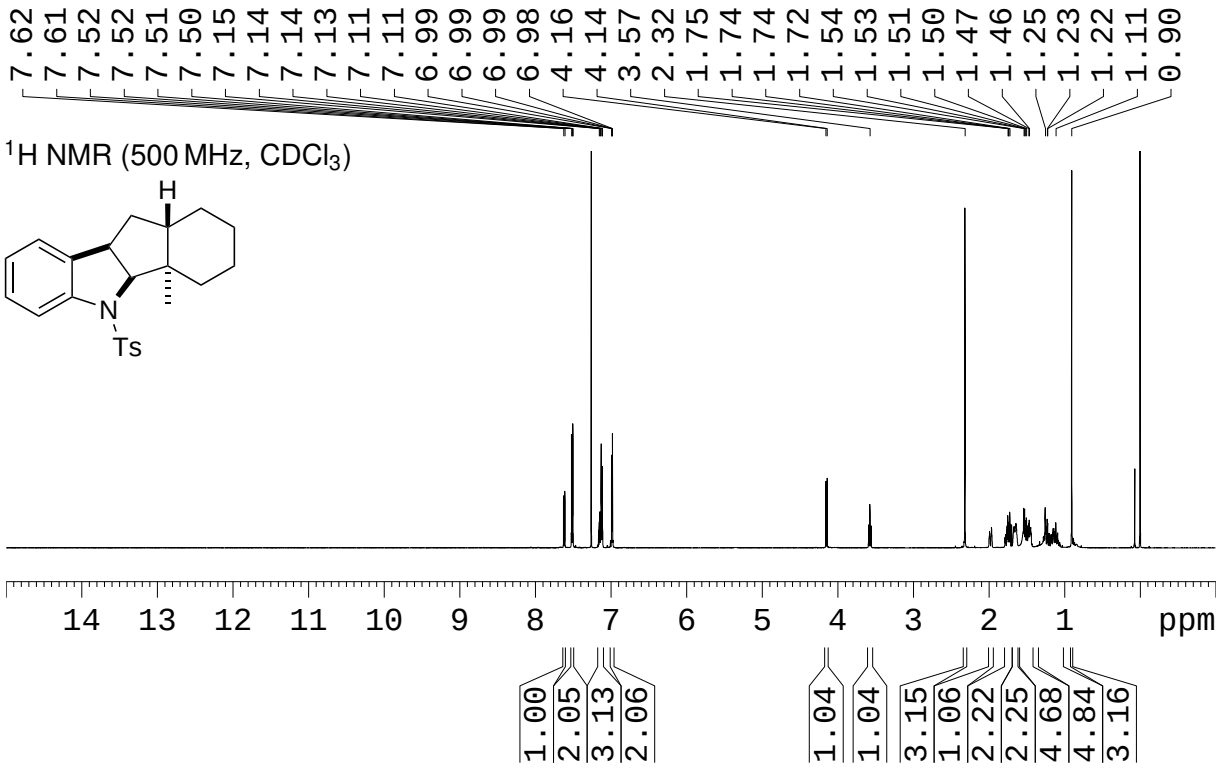
Dithiolane 22

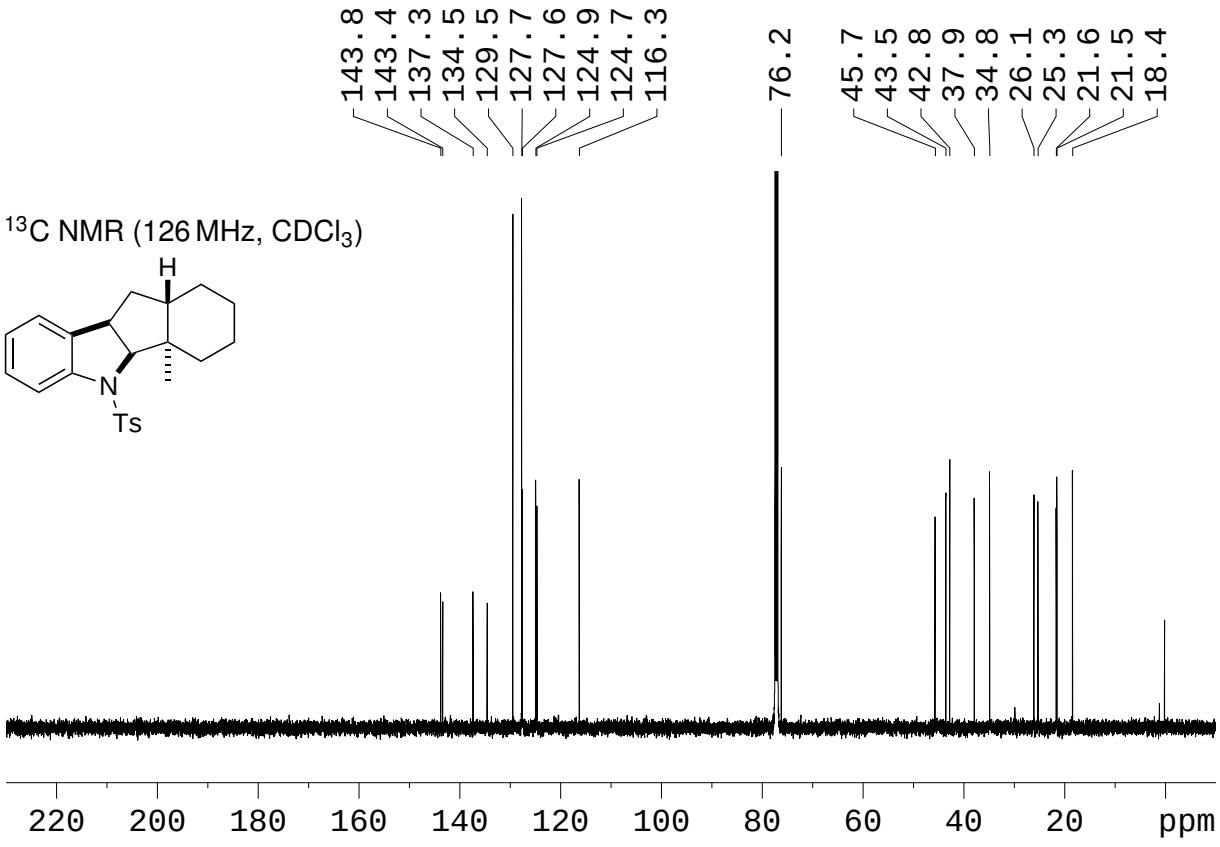


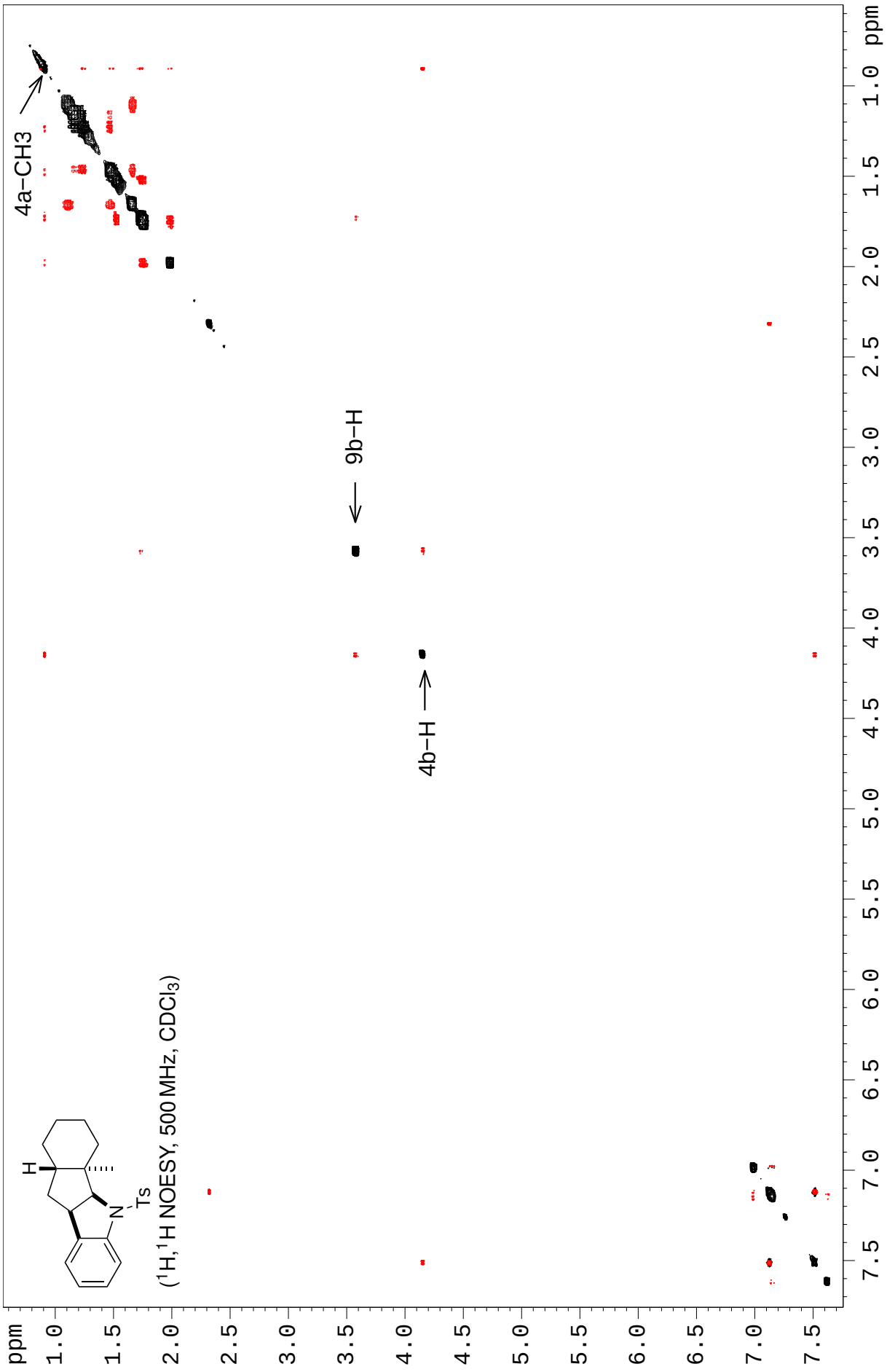



4a–CH3
4–H
9b–H
4b–H
(^{1}H,^{1}H NOESY, 500 MHz, CDCl$_3$)
Ts
ppm

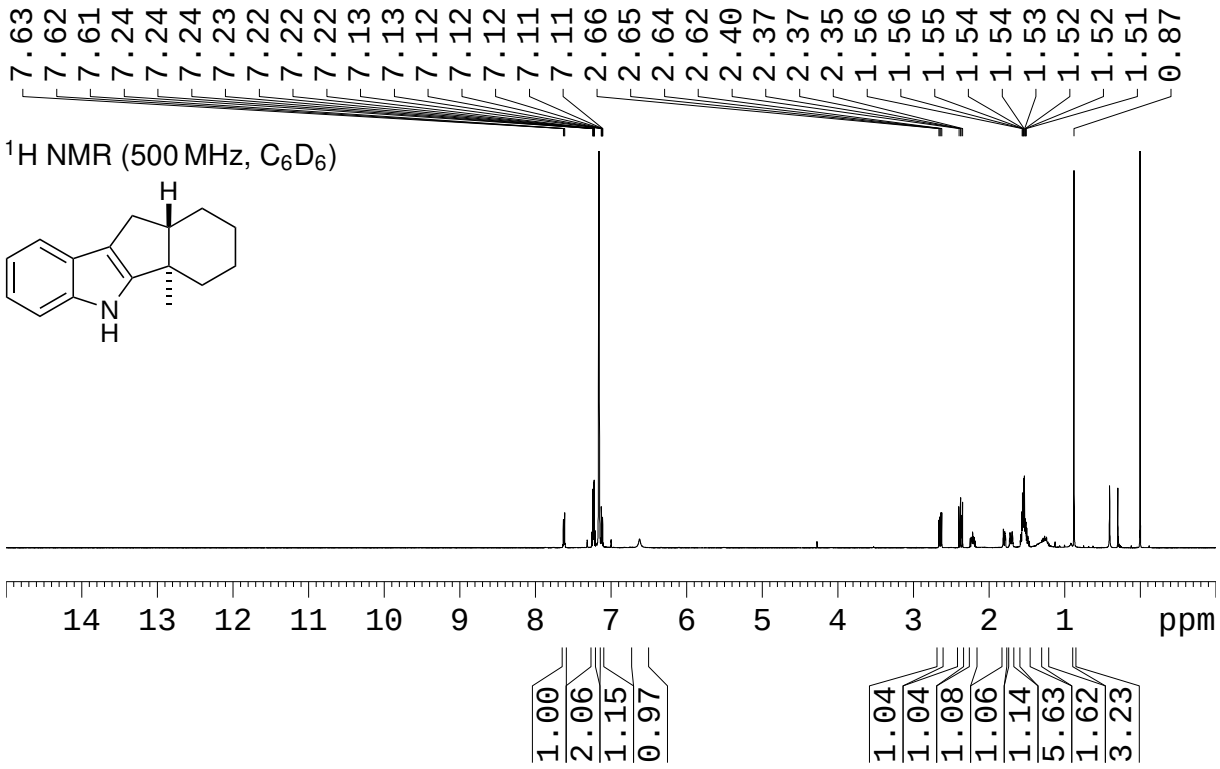
trans-Hydrindane 23

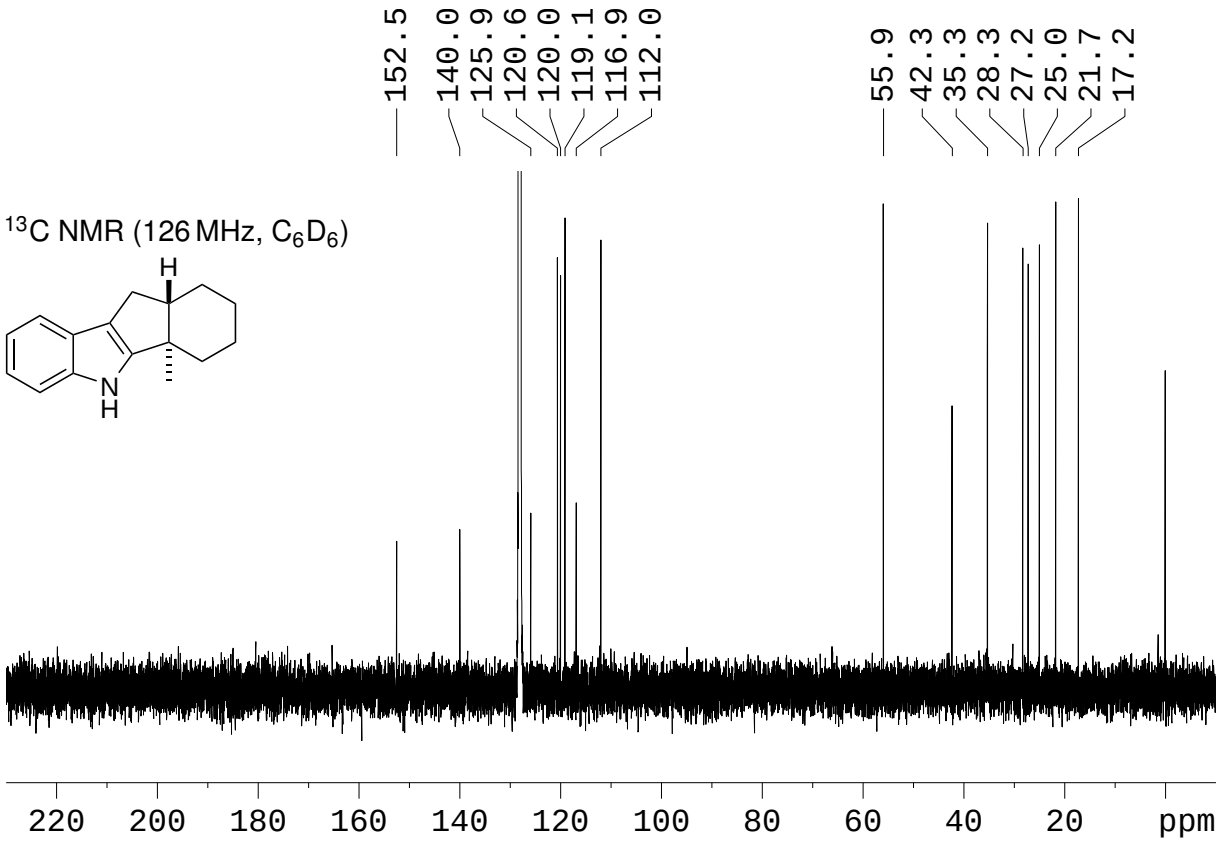


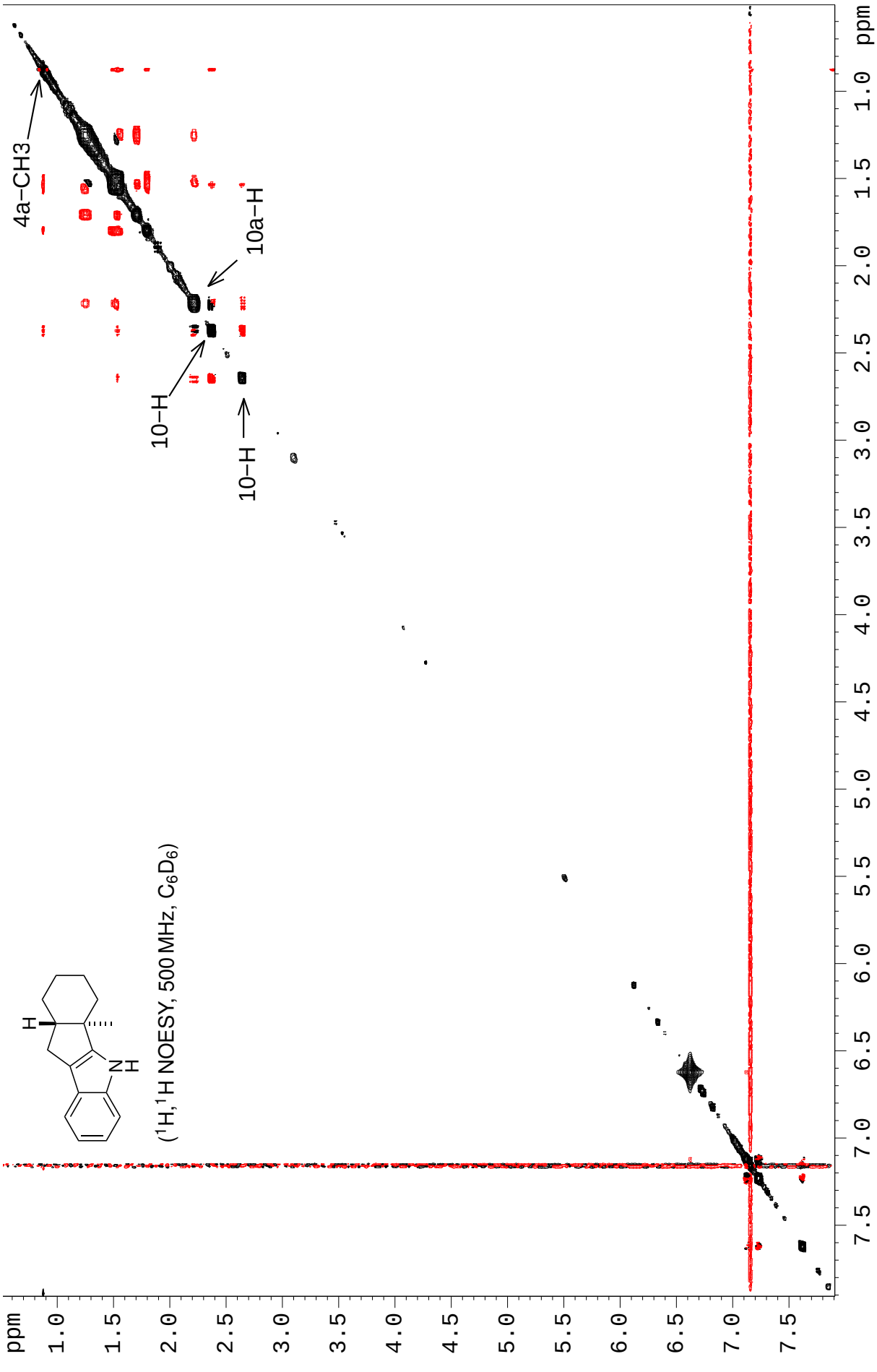



4a−CH3
9b−H
4b−H
(1H,1H NOESY, 500 MHz, CDCl3)
H
N
Ts
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

trans-Hydrindane 24






4a−CH3
10a−H
10−H
10−H
(1H,1H NOESY, 500 MHz, C6D6)
H
N
H
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

Crystal Structure Determinations of Compounds 7 and 23

Crystals for both compounds were obtained by evaporation from a mixture of *t*-butyl methyl ether and *n*-heptane. The selected crystals were mounted in inert oil on Hampton loops and transferred to the cold gas stream of a Rigaku/OD XtaLAB Synergy diffractometer. Mirror-focussed Mo-$K\alpha$ or Cu-$K\alpha$ radiation was employed for the intensity measurements of **7** and **23** respectively. Absorption corrections were implemented on the basis of multi-scans. The structure was refined anisotropically on F^2 using the program SHELXL-2019.[9] The hydrogen atoms of the NH groups of **7** were refined freely, but with N-H distances restrained to be approximately equal (command "SADI"); other hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions.

Special features and exceptions: The structure was refined as a two-component pseudomerohedral twin (by 180° rotation about the α axis). The relative volume of the minor twin component refined to 0.0977(9). The size of the integration box (used in the data reduction) was multiplied by 1.5 to enable better measurement of the split reflections, but this may have a systematic effect on the cell constants. The hydrogen atoms of the NH groups were refined freely. In the second independent molecule, the atoms C1' to C4' are disordered over two sets of positions. The occupation factors of the minor disorder component refined to 0.078(5). Appropriate restraints were employed to improve refinement stability, but the dimensions of disordered groups should always be intepreted with caution. CHECKCIF suggests the higher symmetry space group $Pca2_1$, but only with an 87% fit. However, the clear deviation of the β angle from 90° rules out this possibility. Compound **23** also crystallizes in a non-centrosymmetric space groups, with three independent molecules. The usual checks did not indicate any higher symmetry. The structure was refined as a two-component inversion twin; the relative volume of the smaller component refined to 0.471(10).

Crystallographic data are summarized in Table S1, and ellipsoid plots are presented as Figures S2 and S3. Figure S4 shows a packing diagram for **7**; the packing of **23** is extremely complex and we do not analyze it here. Complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 2289675-6. Copies of the data can be obtained free of charge from `www.ccdc.cam.ac.uk/data_request/cif`.

[9] G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Adv.* **2015**, *71*, 3–8.

Table S1. Crystallographic data and structure refinement details for compounds **7** and **23**.

Compound	**7**	**23**
Formula	$C_{16}H_{17}NO$	$C_{23}H_{27}NO_2S$
M_r	239.30	381.51
Crystal habit	colourless tablet	colourless needle
Cryst. size (mm)	0.25 x 0.2 x 0.15	0.15 x 0.03 x 0.02
Crystal system	monoclinic	monoclinic
Space group	*Pc*	*Ia*
Temperature (°C)	–173	–173
a (Å)	6.14568(10)	12.34580(14)
b (Å)	12.1476(2)	27.6089(3)
c (Å)	16.5252(3)	18.0509(2)
α (°)	90	90
β (°)	90.6799(16)	105.9373(12)
γ (°)	90	90
V (Å^3)	1233.61	5916.24
Z	4	12
*D*x (Mg m^{-3})	1.289	1.285
λ (Å)	0.71073	1.54184
μ(mm^{-1})	0.08	1.6
Transmissions	0.733 – 1.000	0.635 – 1.000
F(000)	512	2448
$2\theta_{max}$	41.1	80.5
Refl. measured	123169	116565
Refl. indep.	16066	12388
R_{int}	0.040	0.042
Parameters	353	737
Restraints	31	2
wR(F^2, all refl.)	0.106	0.079
R(*F*, >4σ(*F*))	0.038	0.030
S	1.08	1.04
Max. Δp (e Å^{-3})	0.66, –0.30	0.34, –0.33

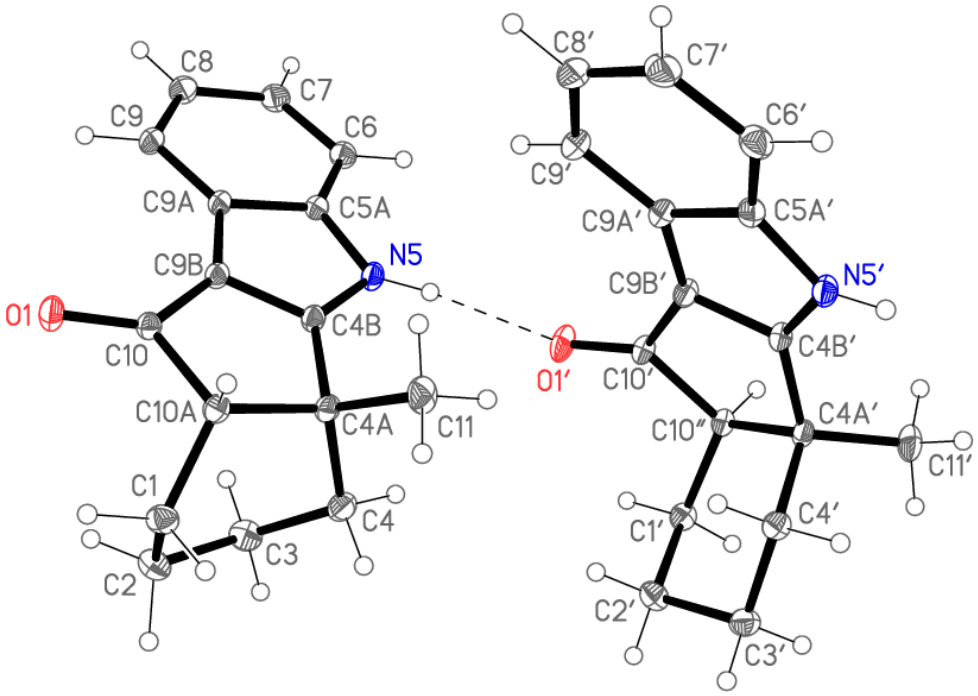


Figure S2. The two independent molecules of compound **7** in the crystal. Ellipsoids correspond to 50% probability levels. Only the major orientation of the slightly disordered atoms C1' – C4' is shown. The dashed line indicates a hydrogen bond.

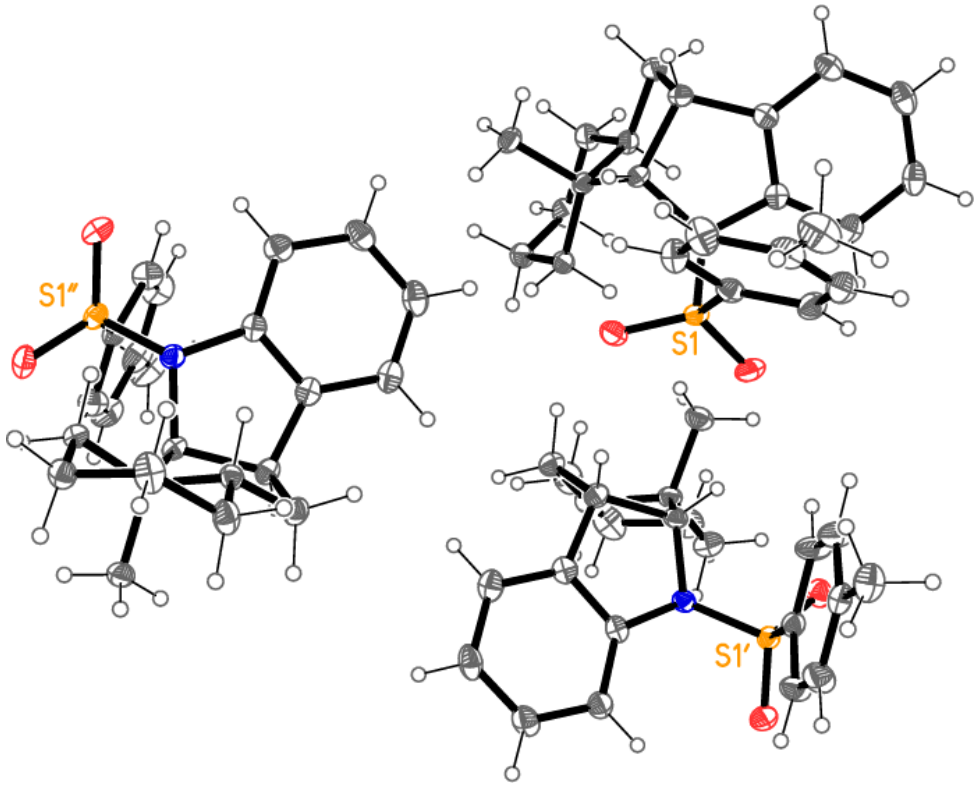


Figure S3. The three independent molecules of compound **23** in the crystal (one of these is shown in more detail in the main paper). Ellipsoids correspond to 50% probability levels. For clarity, only the sulfur atoms are labeled.

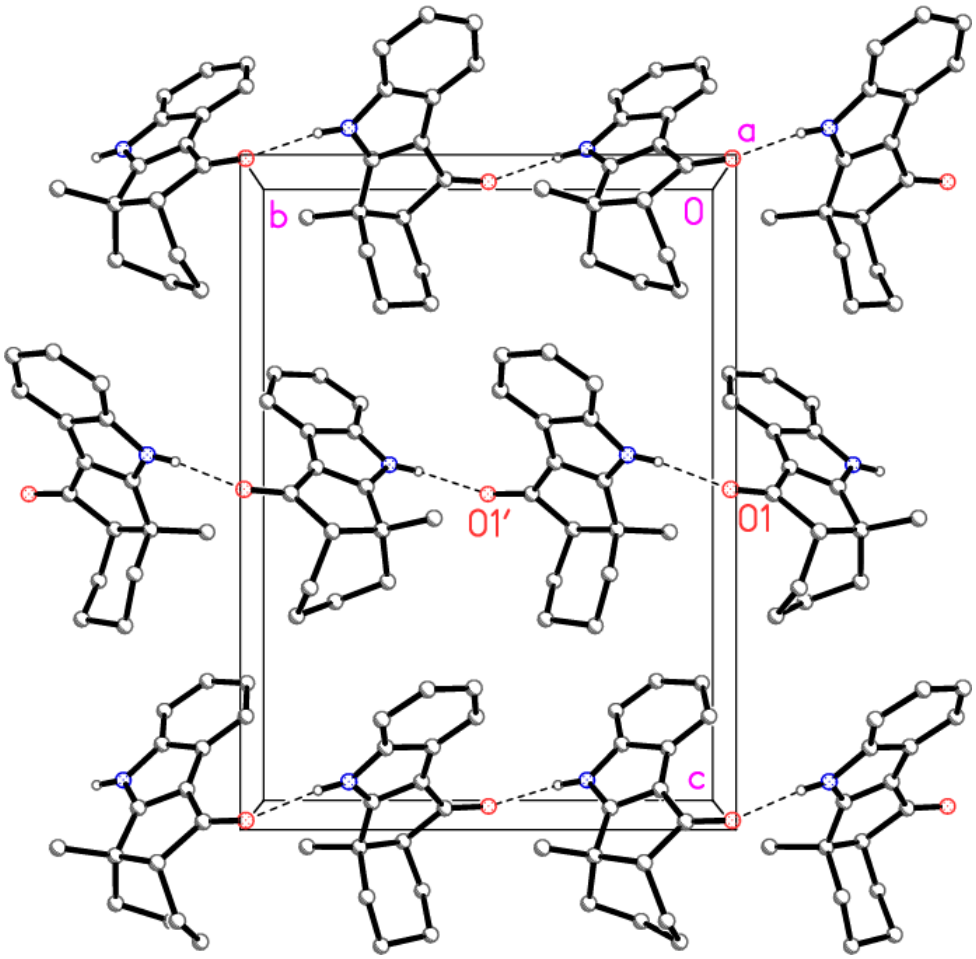


Figure S4. Packing diagram of compound **7**, viewed parallel to the *a* axis and showing the formation of simple chains of molecules, in which the two independent molecules alternate, parallel to the *b* axis The dashed lines indicate hydrogen bonds. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.