Supplementary Material (ESI) for Chemical Communications

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ELECTRONIC SUPPLEMENTARY INFORMATION

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B E L O N G I N G TO T H E P A P E R

Hydrogen bond induced enantioselectivity in Mn(salen)-catalysed sulfoxidation reactions

Felix Voss, Eberhardt Herdtweck and Thorsten Bach

1. General Procedures

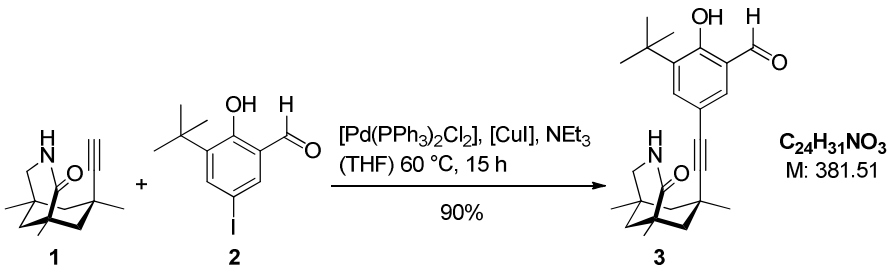
All reactions involving moisture-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under argon. TLC was performed on silica coated glass plates (silica gel 60 F_{254}) with detection by UV (254 nm) or $KMnO_4$ (0.5% in water) with subsequent heating. Flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh) with the indicated eluent. All solvents for chromatography were distilled prior to use. HPLC analyses were performed using a chiral stationary phase [ChiralPak AD-H (250 × 4.6 mm), ChiralCell OD (250 × 4.6 mm), Chiralpak AS-H (250 x 4.6 mm, 5 μm), ChiralCell OJ-H (250 × 4.6 mm), Daicel Chemical Industries] employing *n*-hexane/*i*-propanol as eluents and UV-detection at 20 °C. Semi-preparative HPLC separation was performed using a chiral stationary phase [Chiralpak AS-H (250 x 20 mm, 5 μm), Daicel Chemical Industries] employing *n*-hexane/*i*-propanol (70/30) as eluent (flow rate: 19 mL/min) and UV-detection.

IR-spectra were recorded on a JASCO IR-4100 (ATR), MS/HRMS-measurements were performed on a Finnigan MAT 8200 (EI), a Finnigan MAT 95S (HR-EI), a Finnigan LCQ classic (ESI) and a Thermo Finnigan LTQ FT (HRMS-ESI). ^{1}H and ^{13}C NMR-spectra were recorded at 303 K either on a Bruker AV-250, a Bruker AV-360 or a Bruker AV-500 spectrometer. The chemical shifts are reported relative to the solvent used ($CHCl_3$, DMSO, MeOH).[1] The multiplicities of the ^{13}C NMR signals were determined by DEPT experiments. Optical rotations were measured using a Perkin-Elmer 241 MC Polarimeter. Elemental analyses were carried out on a Elementar Vario EL in the chemistry department at the Technische Universität München. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis-spektrometer. Melting points were measured on a Koffler Thermopan and are uncorrected.

[1] V. Kotlyar and A. Nudelmann, *J. Org. Chem.*, 1997, **62**, 7512-7515.

2. Synthesis of catalyst 5

2.1. Synthesis of 3-(*tert*-butyl)-2-hydroxy-5-{[(1*R*,5*S*,7*R*)-1,5,7-trimethyl-2-oxo-3-azabicyclo[3.3.1]nonan-7-yl]ethynyl}benzaldehyde (3):

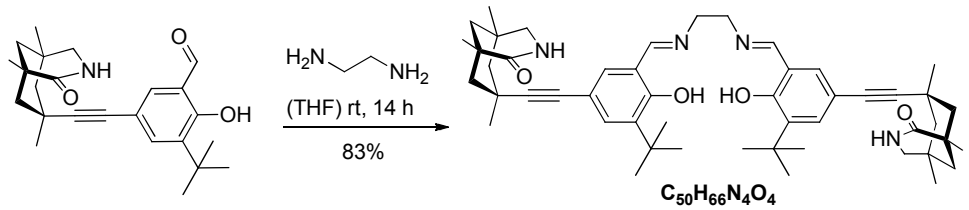


In a Schlenk flask a solution of alkyne **1**[2] (40.0 mg, 195 µmol, 1.00 eq.), aldehyde **2**[3] (77.2 mg, 254 µmol, 1.30 eq.) and triethylamine (514 µL, 375 mg, 3.71 mmol, 19.0 eq.) in dry tetrahydrofuran (2.7 mL) was degassed through three freeze-pump-thaw cycles. After addition of copper(I)iodide (3.7 mg, 19.5 µmol, 0.10 eq.) and bis(triphenylphosphine)-palladium(II)chloride (6.8 mg, 9.75 µmol, 0.05 eq.) the solution was degassed by another three freeze-pump-thaw cycles and heated to 60 °C for 15 hours. After cooling to ambient temperature, water (20 mL) was added and the mixture was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were washed with brine (15 mL), dried over sodium sulfate, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (eluent: pentane/ethyl acetate = 2/1 → 1/1) to afford 66.6 mg (90%) of aldehyde **3** as light-yellow solid; $R_f = 0.46$ (pentane/ethyl acetate = 1/1); m.p.: 165 °C; $[\alpha]_D^{20} = -1.4$ ($c = 0.7$, $CHCl_3$); IR (ATR): $\tilde{\nu} = 2963\ cm^{-1}$ (w), 2357 (w), 1654 (vs), 1498 (w), 1455 (m), 1140 (m), 912 (w), 767 (m), 723 (w); ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 11.83 (d, $^4J = 0.5$ Hz, 1 H), 9.83 (s, 1 H), 7.53 (d, $^4J = 2.1$ Hz, 1 H), 7.52 (dd, $^4J = 2.1$ Hz, $^4J = 0.5$ Hz, 1 H), 5.46 (br s, 1 H), 3.43 (ddd, $^2J = 11.8$ Hz, $^3J = 3.1$ Hz, $^4J = 1.5$ Hz, 1 H), 3.17 (d, $^2J = 11.8$ Hz, 1 H), 2.22 (dt, $^2J = 13.7$ Hz, $^4J = 2.1$ Hz, 1 H), 1.97 (d, $^2J = 13.7$ Hz, 1 H), 1.82 (dt, $^2J = 12.6$ Hz, $^4J = 2.0$ Hz, 1 H), 1.41-1.39 (m, 10 H), 1.34-1.33 (m, 4 H), 1.21 (s, 3 H), 1.17 (dd, $^2J = 13.7$ Hz, $^4J = 1.4$ Hz, 1 H), 1.04 (s, 3 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 197.0 (d), 176.6 (s), 160.6 (s), 138.6 (s), 136.8 (d), 135.2 (d), 120.4 (s), 114.9 (s), 94.4 (s), 78.6 (s), 52.6 (t), 51.4 (t), 48.6 (t), 44.3 (t), 38.5 (s), 34.9 (s), 33.6 (q), 30.9 (s), 30.7 (s), 29.9 (q), 29.1 (q), 25.6 (q); MS (EI, 70 eV): *m/z* (%) = 381 (68)

[2] F. Voss and T. Bach, *Synlett*, 2010, 1493-1496.
[3] M. Nielsen and K. V. Gothelf, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2440-2444.

[M^+], 366 (39) [$(M-CH_3)^+$], 313 (15), 298 (10), 257 (23), 133 (16), 124 (49), 71 (60), 57 (100) [$C_4H_9^+$], 43 (57); HRMS (EI) *m/z*: calcd. for $C_{24}H_{31}NO_3$: 381.2304 [M^+], found: 381.2304.

2.2. **Synthesis of salen ligand 4:**[4] **(1*R*,1'*R*,5*S*,5'*S*,7*R*,7'*R*)-7,7'-{[((1*E*,1'*E*)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(3-(*tert*-butyl)-4-hydroxy-5,1-phenylene)]bis(ethyne-2,1-diyl)}bis(1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-2-one)**



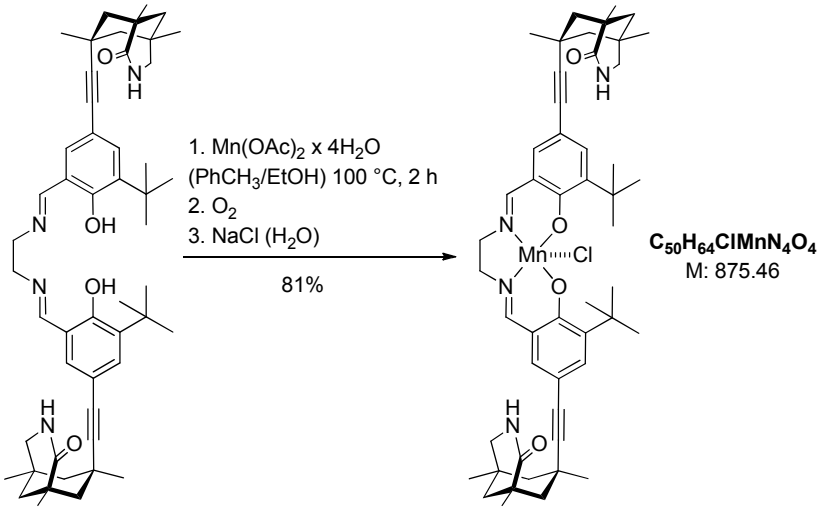
$C_{50}H_{66}N_4O_4$
M: 787.08

3 **4**

A solution of aldehyde **3** (65.0 mg, 170 µmol, 2.04 eq.) in dry tetrahydrofuran (1.4 mL) was added to a solution of freshly distilled ethylene diamine (5.0 mg, 83.5 µmol, 1.00 eq.) in dry tetrahydrofuran (0.7 mL) and the mixture was stirred at room temperature for 14 hours. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (eluent: ethyl acetate/methanol = 95/5) to afford 54.4 mg (83%) of salen **4** as pale yellow solid; $R_f = 0.44$ (ethyl acetate/methanol = 95/5); m.p.: 201 °C; $[\alpha]_D^{20} = -5.0$ (*c* = 1.0, $CHCl_3$); IR (ATR): $\tilde{\nu} = 2962\ cm^{-1}$ (w), 2924 (w), 2347 (w), 1659 (vs), 1625 (s), 1441 (s), 1271 (m), 1212 (m), 1164 (w), 1120 (w), 1033 (w), 849 (m); ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 13.95 (s, 2 H), 8.33 (s, 2 H), 7.31 (d, ^4J = 2.0 Hz, 2 H), 7.24 (d, ^4J = 2.0 Hz, 2 H), 5.49 (m, 2 H), 3.93-3.86 (m, 4 H), 3.43 (ddd, ^2J = 11.7 Hz, ^3J = 3.0 Hz, ^4J = 1.3 Hz, 2 H), 3.13 (d, ^2J = 11.7 Hz, 2 H), 2.20 (d, ^2J = 13.3 Hz, 2 H), 1.95 (dt, ^2J = 13.5 Hz, ^4J = 1.7 Hz, 2 H), 1.81 (dt, ^2J = 12.9 Hz, ^4J = 2.0 Hz, 2 H), 1.40 (s, 18 H), 1.32 (s, 6 H), 1.28-1.23 (m, 4 H), 1.20 (s, 6 H), 1.16 (d, ^2J = 13.5 Hz, 2 H), 1.02 (s, 6 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 176.5 (s), 166.9 (d), 160.2 (s), 137.6 (s), 133.3 (d), 132.5 (d), 118.4 (s), 113.1 (s), 93.2 (s), 79.5 (s), 59.4 (t), 52.4 (t), 51.5 (t), 48.6 (t), 44.4 (t), 38.5 (s), 34.8 (s), 33.7 (q), 30.8 (s), 30.7 (s), 30.0 (q), 29.2 (q), 25.7 (q); MS (EI, 70 eV): *m/z* (%) = 786 (83) [M^+], 758 (13) [$(M-CO)^+$], 423 (14) [$(M-C_{24}H_{29}NO_2)^+$], 393 (16) [$(M-C_{25}H_{33}N_2O_2)^+$], 379 (18) [$C_{24}H_{31}N_2O_2^+$], 109 (10), 71 (54), 44 (100); HRMS (+ESI) *m/z*: calcd. for $C_{50}H_{67}N_4O_4$: 787.5162 [$(M+H)^+$], found: 787.5161.

[4] Prepared according to the procedure of: J. Park, K. Lang, K. Abboud and S. Hong, *J. Am. Chem. Soc.*, 2008, **130**, 16484-16485.

2.3. **Synthesis of catalyst 5:**[5] **(1*R*,1'*R*,5*S*,5'*S*,7*R*,7'*R*)-7,7'-{[((1*E*,1'*E*)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(3-(*tert*-butyl)-4-hydroxy-5,1-phenylene)]bis(ethyne-2,1-diyl)}bis(1,5,7-trimethyl-3-azabicyclo[3.3.1]nonan-2-one) manganese(III)chloride**



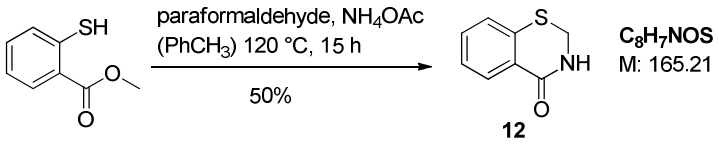
4 **5**

A suspension of salen ligand **4** (52.1 mg, 66.2 µmol, 1.00 eq.) in toluene (2.5 mL) was added to a boiling suspension of manganese(II)acetate tetrahydrate (48.7 mg, 199 µmol, 3.00 eq.) in ethanol (3.5 mL) over 20 minutes and the mixture was stirred under reflux for two hours. Mechanical stirring was stopped and the mixture was purged with oxygen until, according to TLC analysis, all of salen **4** had been consumed. Brine (3 mL) was added, the reaction mixture was allowed to cool to ambient temperature and toluene (10 mL) and water (10 mL) were added. The layers were separated and the organic layer was washed with water (10 mL) and brine (10 mL), dried over sodium sulfate, filtered and concentrated *in vacuo* to yield a brown solid. The solid was triturated under sonication in hexane (5 mL) and after decantation of the solvent and drying *in vacuo* 47.6 mg (81%) of the manganese(salen) catalyst **5** were obtained; UV-VIS (CH_2Cl_2): $\lambda_{max.}$ [nm] (ε) = 276 (35 714), 256 (34 921); $[\alpha]_D^{20} = -10.9$ ($c = 0.1$, $CHCl_3$); IR (ATR): $\tilde{\nu} = 2957\ cm^{-1}$ (w), 2919 (w), 2360 (m), 2077 (w), 1650 (s), 1615 (vs), 1537 (m), 1493 (m), 1437 (m), 1405 (m), 1387 (m), 1304 (m), 1202 (w), 1166 (m), 1109 (w), 825 (s); MS (+ESI): *m/z* (%) = 880 (42) [$(M-Cl+NaOH)^+$], 840 (100) [$(M-Cl)^+$]; HRMS (+ESI) *m/z*: cacld. for $C_{50}H_{64}MnN_4O_4$: 839.4308 [$(M-Cl)^+$], found: 839.4310.

[5] Prepared according to the procedure of: J. F. Larrow and E. N. Jacobsen, *Org. Synth.*, 1997, **75**, 1-6.

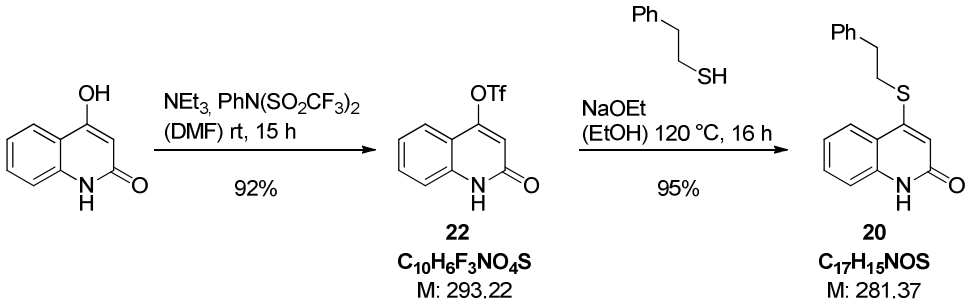
3. Synthesis of new substrates

3.1. Synthesis of 2*H*-benzo[e][1,3]thiazin-4(3*H*)-one[6]



A solution of methyl 2-mercaptobenzoate (300 mg, 1.78 mmol, 1.00 eq.), paraformaldehyde (80.0 mg, 2.68 mmol, 1.50 eq.) and ammonium acetate (274 mg, 3.56 mmol, 2.00 eq.) in toluene (15 mL) was heated to reflux for 15 hours. After cooling to ambient temperature the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (eluent: pentane/ethyl acetate = 1/1) to afford 148 mg (50%) of lactam **12** as a colourless solid; R_f = 0.43 (pentane/ethyl acetate = 1/1); m.p.: 94 °C; IR (ATR): $\tilde{\nu}$ = 3186 cm^{-1} (w), 3050 (w), 2909 (w), 1654 (s), 1591 (m), 1470 (m), 1450 (m), 1382 (m), 1145 (m), 1052 (m), 927 (w), 776 (m), 738 (vs); ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 8.03 (dd, ^3J = 7.8 Hz, ^4J = 1.6 Hz, 1 H), 7.84 (br s, 1 H), 7.35-7.30 (m, 1 H), 7.27-7.19 (m, 2 H), 4.51 (d, ^3J = 4.4 Hz, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 166.0 (s), 137.7 (s), 132.1 (d), 130.2 (d), 128.6 (s), 127.4 (d), 126.1 (d), 42.6 (t); MS (EI, 70 eV): *m/z* (%) = 165 (57) [M^+], 136 (100) [$(M–CHO)^+$], 108 (39) [$(M–C_2H_3NO)^+$], 82 (9), 69 (17); HRMS (EI) *m/z*: calcd. for C_8H_7NOS: 165.0243 [M^+], found: 165.0240.

3.2. Synthesis of 4-(phenethylthio)quinolin-2(1*H*)-one (20)



2.2.1. Triflate **22**[7]

Triethylamine (258 µL, 188 mg, 1.86 mmol, 3.00 eq.) was added to a suspension of quinoline-2,4-diol (100 mg, 621 µmol, 1.00 eq.) in *N*,*N*-dimethylformamide (6.2 mL) and after stirring at room temperature for five minutes *N*-phenyl-bis(trifluoromethanesulfonimide) (266 mg, 745 µmol, 1.20 eq.) was added and the reaction mixture was stirred at room temperature for 15 hours. After addition of water (10 mL) and ethyl acetate (20 mL) the layers were separated and the organic layer was washed with brine (10 mL), dried over sodium sulfate, filtered and the solvent was removed *in vacuo*. The residue was purified by flash chromatography on silica gel (eluent: ethyl acetate/methanol = 100/0 → 95/5) to afford 167 mg (92%) of triflate **22** as colourless solid; $R_f = 0.62$ (ethyl acetate/methanol = 95/5); m.p.: 182 °C; IR (ATR): $\tilde{\nu}$ = 3002 cm^{-1} (w), 2851 (w), 1654 (s), 1606 (m), 1436 (s), 1381 (m), 1212 (s), 1140 (s), 1042 (s), 898 (m), 853 (m), 757 (vs); ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 12.50 (br s, 1 H), 7.79 (dd, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 1 H), 7.68 (ddd, ^3J = 8.4 Hz, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1 H), 7.50 (ddd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, ^5J = 0.5 Hz, 1 H), 7.37 (ddd, ^3J = 8.3 Hz, ^4J = 7.1 Hz, ^4J = 1.1 Hz, 1 H), 6.77 (s, 1 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 163.8 (s), 155.6 (s), 138.5 (s), 132.9 (d), 123.9 (d), 122.2 (d), 116.6 (d), 114.3 (d), 111.5 (s); MS (EI, 70 eV): *m/z* (%) = 293 (94) [M^+], 160 (14) [$(M–CF_3O_2S)^+$], 132 (100) [$(M–C_2F_3O_3S)^+$], 104 (17), 77 (26); HRMS (EI) *m/z*: calcd. for $C_{10}H_6F_3NO_4S$: 292.9964 [M^+], found: 292.9960.

2.2.1 Sulfide **20**

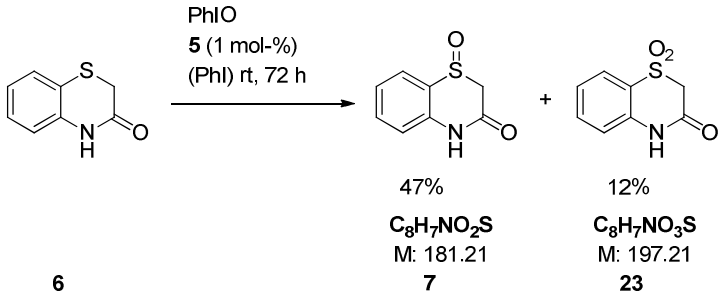
Sodium (14.0 mg, 598 µmol, 2.50 eq.) was dissolved in ethanol (1.2 mL), then 2-phenylethanethiol (48 µL, 49.0 mg, 359 µmol, 1.50 eq.) and triflate **22** (70.0 mg, 239 µmol, 1.00 eq.) were added and the reaction mixture was heated to reflux for 16 hours. After cooling to ambient temperature the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (eluent: pentane/ethyl acetate/ methanol = 100/100/0 → 0/100/0 → 0/95/5) to afford 64.0 mg (95%) of sulfide **20** as colourless solid; $R_f = 0.74$ (ethyl acetate/methanol = 95/5); m.p.: 163 °C; IR (ATR): $\tilde{\nu}$ = 3089 cm^{-1} (w), 2860 (w), 1649 (s), 1592 (m), 1498 (w), 1441 (w), 1372 (w), 1252 (vs), 1231 (m), 1169 (s), 1038 (s), 965 (w), 917 (m), 747 (m), 698 (m); ^{1}H-NMR (360 MHz,

[6] In analogy to: V. R. Solomon, W. Haq, K. Srivastava, S. K. Puri and S. B. Katti, *J. Med. Chem.*, 2006, **50**, 394-398.
[7] In analogy to: M. S. Tremblay, M. Halim and D. Sames, *J. Am. Chem. Soc.*, 2007, **129**, 7570-7577.

DMSO-d_6): δ [ppm] = 11.59 (br s, 1 H), 7.69 (dd, ^3J = 8.2 Hz, ^4J = 1.3 Hz, 1 H), 7.52 (ddd, ^3J = 8.2 Hz, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1 H), 7.34-7.30 (m, 5 H), 7.26-7.20 (m, 1 H), 7.20-7.15 (m, 1 H), 6.39 (s, 1 H), 3.39 (t, ^3J = 7.5 Hz, 2 H), 3.02 (t, ^3J = 7.5 Hz, 2 H); ^{13}C-NMR (90.6 MHz, DMSO-d_6): δ [ppm] = 160.2 (s), 149.5 (s), 139.5 (s), 137.8 (s), 130.8 (d), 128.5 (d), 128.3 (d), 126.4 (d), 123.3 (d), 121.7 (d), 117.4 (s), 115.7 (d), 114.2 (d), 33.2 (t), 31.0 (t); MS (EI, 70 eV): *m/z* (%) = 281 (35) [M^+], 177 (100) [$(M-C_8H_8)^+$], 149 (18), 116 (7), 104 (23), 91 (20) [$C_7H_7^+$], 44 (27); HRMS (EI) *m/z*: calcd. for $C_{17}H_{15}NOS$: 281.0874 [M^+], found: 281.0870.

4. Catalytic sulfoxidations

4.1. General Procedure for the synthesis of 2*H*-benzo[b][1,4]thiazin-3(4*H*)-one-1-oxide (7)



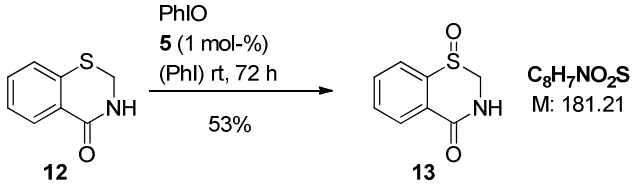
Manganese(salen) catalyst **5** (1.1 mg, 1.20 µmol, 0.01 eq.) and iodosobenzene[8] (34.3 mg, 156 µmol, 1.30 eq.) were consecutively added to a solution of sulfide **6** (19.8 mg, 120 µmol, 1.00 eq.) in iodobenzene (6.0 mL) and the resulting brown suspension was stirred at room temperature for 72 hours. The reaction mixture was purified directly by flash chromatography on silica gel (eluent: pentane/ethyl acetate/methanol = 100/100/0 → 0/100/0 → 0/95/5) to afford 10.2 mg (47%, 67% *ee*) of chiral sulfoxide **7**, 2.9 mg (12%) of sulfone **23** and 7.6 mg (38%) of recovered starting material **6** as colourless solids. Analytical data for sulfoxide **7**: R_f = 0.29 (ethyl acetate/methanol = 95/5); HPLC (AD-H, 250 × 4.6 mm, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.): t_R = 7.2 min (*S*), 13.3 min (*R*); $[\alpha]_D^{20}$ = +77.5 (*c* = 1.0, MeOH, 90% *ee*); m.p.: 182 °C; IR (ATR): $\tilde{\nu}$ = 3040 cm^{-1} (w), 2982 (w), 1668 (s), 1591 (m), 1479 (s), 1426 (w), 1372 (m), 1252 (w), 1013 (s), 927 (w), 853 (m), 762 (s); ^{1}H-NMR (360 MHz, DMSO-d_6): δ [ppm] = 11.02 (br s, 1 H), 7.79 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1 H), 7.58 (*virt*. td, $^3J \tilde{=}$ 7.8 Hz,

[8] H. Saltzman and J. G. Sharefkin, *Org. Synth.,* 1973, **5**, 658.

^4J = 1.5 Hz, 1 H), 7.23-7.15 (m, 2 H), 4.20 (d, ^2J = 15.7 Hz, 1 H), 4.02 (dd, ^2J = 15.7 Hz, ^4J = 0.8 Hz, 1 H); ^{13}C-NMR (90.6 MHz, DMSO-d_6): δ [ppm] = 162.1 (s), 137.1 (s), 133.6 (d), 130.0 (d), 123.8 (s), 123.0 (d), 117.8 (d), 51.1 (t); MS (EI, 70 eV): *m/z* (%) = 181 (100) [M^+], 165 (20) [$(M-O)^+$], 152 (27), 136 (26), 122 (24), 106 (32), 91 (16), 78 (14), 63 (17), 52 (10), 45 (12); CHN: calcd. for $C_8H_7NO_2S$: C: 53.02; H: 3.89; N: 7.73; found: C: 52.96; H: 4.01; N: 7.66.

Analytical data for sulfone **23**: R_f = 0.60 (pentane/ethyl acetate = 1/1); IR (ATR): $\tilde{\nu}$ = 3220 cm^{-1} (w), 3088 (w), 2987 (w), 1697 (vs), 1676 (s), 1492 (m), 1474 (m), 1377 (m), 1334 (vs), 1212 (vs), 1154 (s), 1106 (s), 1057 (m), 1028 (w), 917 (w), 868 (m), 762 (vs), 728 (vs), 689 (m); ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 8.38 (br s, 1 H), 7.95 (dd, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 1 H), 7.65-7.60 (m, 1 H), 7.33 (*virt*. td, $^3J \tilde{=}$ 7.7 Hz, ^4J = 1.0 Hz, 1 H), 7.06 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1 H), 4.24 (s, 2 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 161.7 (s), 146.1 (s), 135.1 (d), 134.7 (s), 124.8 (d), 124.3 (d), 118.4 (d), 56.7 (t); MS (EI, 70 eV): *m/z* (%) = 197 (27) [M^+], 185 (3), 123 (9), 113 (49), 104 (15), 71 (76), 57 (100), 43 (59); HRMS (EI) *m/z*: calcd. for $C_8H_7NO_3S$: 197.0147 [M^+], found: 197.0144.

4.2. **Synthesis of 2*H*-benzo[e][1,3]thiazin-4(3*H*)-one-1-oxide (13)**

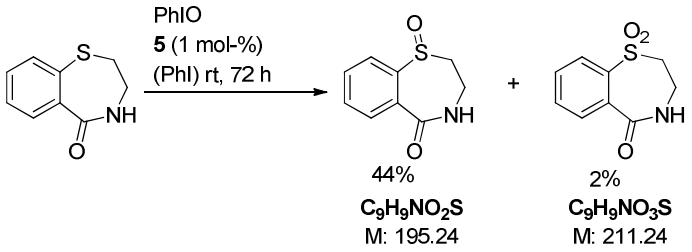


Following the general procedure, sulfide **12** (19.8 mg, 120 µmol, 1.00 eq.) was reacted with iodosobenzene (34.3 mg, 156 µmol, 1.30 eq.) in iodobenzene (6.0 mL) in the presence of catalyst **5** (1.1 mg, 1.20 µmol, 0.01 Äq.) and after purification by flash chromatography on silica gel (eluent: pentane/ethyl acetate/methanol = 500/100/0 → 0/100/0 → 0/95/5) 11.5 mg (53%, 13% *ee*) of chiral sulfoxide **13** and 8.1 mg (41%) of recovered starting material **12** were obtained as colourless solids; R_f = 0.28 (ethyl acetate/methanol = 95/5); HPLC (OJ-H, 250 × 4.6 mm, ^{n}Hex/^{i}PrOH = 80/20, 1 mL/min.): t_R = 18.9 min, 21.5 min; IR (ATR): $\tilde{\nu}$ = 3224 cm^{-1} (br), 3103 (w), 2992 (w), 1659 (s), 1571 (m), 1465 (w), 1164 (s), 1038 (m), 1013 (m), 936 (w), 800 (m), 747 (s); ^{1}H-NMR (360 MHz, CD_3OD): δ [ppm] = 8.18 (*virt*. dt, ^3J = 5.6 Hz, $J \tilde{=}$ 3.3 Hz, 1 H), 7.91-7.88 (m, 1 H), 7.85-7.79 (m, 2 H), 4.77 (d, ^2J = 13.9 Hz, 1 H), 4.62 (d, ^2J = 13.9 Hz, 1 H)*; ^{13}C-NMR (90.6 MHz, CD_3OD): δ [ppm] = 165.2 (s), 141.7

(s), 134.8 (d), 134.6 (d), 131.0 (d), 129.7 (d), 128.7 (s), 60.9 (t); MS (EI, 70 eV): *m*/*z* (%) = 181 (4) [M^+], 152 (100) [$(M–CH_2NH)^+$], 104 (8), 96 (19), 45 (19); HRMS (EI) *m*/*z*: calcd. for $C_7H_4O_2S$: 151.9932 [$(M–CH_2NH)^+$], found: 151.9931.

* the signal for the NH-proton is missing, probably due to fast exchange with the solvent CD_3OD.

4.3. **Synthesis of 3,4-dihydrobenzo[f][1,4]thiazepin-5(2*H*)-one-1-oxide (15)**

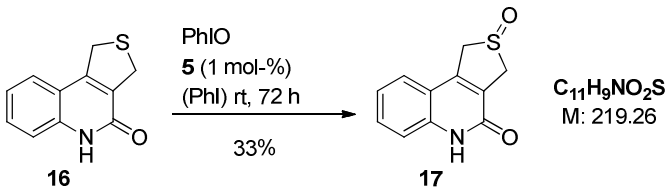


Following the general procedure, sulfide **14**[9] (21.5 mg, 120 µmol, 1.00 eq.) was reacted with iodosobenzene (34.3 mg, 156 µmol, 1.30 eq.) in iodobenzene (6.0 mL) in the presence of catalyst **5** (1.1 mg, 1.20 µmol, 0.01 eq.) and after purification by flash chromatography on silica gel (eluent: pentane/ethyl acetate/methanol = 100/100/0 → 0/95/5 → 0/70/30) 10.3 mg (44%, 20% *ee*) of chiral sulfoxide **15**, 0.6 mg (2%) of sulfone **24** and 11.1 mg (52%) of recovered starting material **14** were obtained as colourless solids. Analytical data for sulfoxide **15**: R_f = 0.44 (ethyl acetate/methanol = 70/20); HPLC (OJ-H, 250 × 4.6 mm, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.): t_R = 9.2 min (–), 13.6 min (+); $[\alpha]_D^{20} = -0.7$ (*c* = 0.7, MeOH, 20% *ee*); m.p.: 221 °C; IR (ATR): $\tilde{\nu}$ = 3200 cm^{-1} (br), 3069 (w), 1659 (vs), 1591 (m), 1436 (w), 1396 (m), 1353 (m), 1281 (w), 1227 (m), 1062 (s), 1042 (s), 994 (s), 858 (w), 747 (s); ^{1}H-NMR (360 MHz, DMSO-d_6): δ [ppm] = 8.50 (br t, ^3J = 6.2 Hz, 1 H), 7.86-7.77 (m, 2 H), 7.73-7.67 (m, 2 H), 4.16 (ddd, ^2J = 12.3 Hz, ^3J = 10.7 Hz, ^3J = 6.9 Hz, 1 H), 3.39-3.38 (m, 1 H), 3.19 (ddd, ^2J = 16.5 Hz, ^3J = 11.2 Hz, ^3J = 5.8 Hz, 1 H), 2.72 (ddd, ^2J = 12.3 Hz, ^3J = 5.8 Hz, ^3J = 2.2 Hz, 1 H); ^{13}C-NMR (90.6 MHz, DMSO-d_6): δ [ppm] = 168.3 (s), 139.3 (s), 131.9 (s), 131.8 (d), 131.1 (d), 128.2 (d), 123.2 (d), 56.8 (t), 36.6 (t); MS (EI, 70 eV): *m*/*z* (%) = 195 (12) [M^+], 152 (55) [$(M–CHNO)^+$], 121 (11), 104 (9), 96 (14), 76 (13), 43 (100) [$CHNO^+$]; HRMS (EI) *m*/*z*: calcd. for $C_9H_9NO_2S$: 195.0354 [M^+], found: 195.0345.

[9] H. Ishibashi, M. Uegaki, M. Sakai and Y. Takeda, *Tetrahedron*, 2001, **57**, 2115-2120.

Analytical data for sulfone **24**: $R_f = 0.23$ (ethyl acetate/methanol = 95/5); m.p.: 237 °C; IR (ATR): $\tilde{\nu} = 3263\ cm^{-1}$ (br), 3069 (w), 2084 (w), 1673 (m), 1634 (s), 1571 (m), 1450 (m), 1391 (m), 1353 (m), 1319 (vs), 1300 (vs), 1145 (vs), 1116 (vs), 1013 (m), 776 (m), 728 (s); ^{1}H-NMR (360 MHz, DMSO-d_6): δ [ppm] = 8.46 (br t, ^3J = 6.5 Hz, 1 H), 7.93 (dt, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1 H), 7.87 (dt, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1 H), 7.81 (dt, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 1 H), 7.76 (dt, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1 H), 3.65 (t, ^3J = 6.2 Hz, 2 H), 3.37 (t, ^3J = 6.2 Hz, 2 H); ^{13}C-NMR (90.6 MHz, DMSO-d_6): δ [ppm] = 168.6 (s), 134.9 (s), 134.5 (d), 134.0 (s), 131.3 (d), 130.0 (d), 125.9 (d), 59.1 (t), 36.9 (t); MS (EI, 70 eV): *m*/*z* (%) = 211 (6) [M^+], 193 (28) [$(M–H_2O)^+$], 169 (30) [$(M–CNO)^+$], 147 (22), 118 (13), 105 (47) [$C_7H_5O^+$], 90 (18), 76 (32), 43 (100); HRMS (EI) *m*/*z*: calcd. for $C_9H_9NO_3S$: 211.0303 [M^+], found: 211.0319.

4.4. **Synthesis of 3,5-dihydrothieno-[3,4-c]quinoline-4(1*H*)-one-2-oxide (17)**

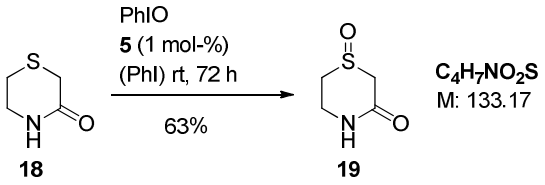


Following the general procedure, sulfide **16**[10] (24.4 mg, 120 µmol, 1.00 Äq.) was reacted with iodosobenzene (34.3 mg, 156 µmol, 1.30 eq.) in iodobenzene (6.0 mL) in the presence of catalyst **5** (1.1 mg, 1.20 µmol, 0.01 eq.) and after purification by flash chromatography on silica gel (eluent: pentane/ethyl acetate/methanol = 100/100/0 → 0/95/5 → 0/70/30) 8.6 mg (33%, 66% *ee*) of chiral sulfoxide **17** and 15.0 mg (61%) of recovered starting material **16** were obtained as cream solids; $R_f = 0.29$ (ethyl acetate/methanol = 95/5); HPLC (AD-H, 250 × 4.6 mm, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.): t_R = 9.9 min (–), 17.3 min (+); $[\alpha]_D^{20}$ = +6.3 (*c* = 0.6, MeOH, 66% *ee*); m.p.: 154 °C; IR (ATR): $\tilde{\nu} = 3010\ cm^{-1}$ (w), 2913 (w), 1640 (vs), 1573 (m), 1500 (m), 1429 (m), 1390 (w), 1342 (w), 1231 (w), 1126 (m), 1015 (s), 865 (w), 751 (m), 717 (w), 674 (m); ^{1}H-NMR (360 MHz, DMSO-d_6): δ [ppm] = 12.01 (br s, 1 H), 7.68 (d, ^3J = 7.9 Hz, 1 H), 7.56 (*virt.* t, $^3J \tilde{=}$ 7.7 Hz, 1 H), 7.41 (d, ^3J = 8.1 Hz, 1 H), 7.25 (*virt.* t, $^3J \tilde{=}$ 7.6 Hz, 1 H), 4.67 (d, ^2J = 17.4 Hz, 1 H), 4.44 (d, ^2J = 17.4 Hz, 1 H), 4.35 (d, ^2J = 17.4 Hz, 1 H), 3.86 (d, ^2J = 17.4 Hz, 1 H); ^{13}C-NMR (90.6 MHz, DMSO-d_6): δ [ppm] = 160.0 (s), 145.0 (s), 139.0 (s), 130.5 (d), 127.0 (s), 125.3 (d), 122.1 (d), 117.4 (s),

[10] L. A. White and R. C. Storr, *Tetrahedron*, 1996, **52**, 3117-3134.

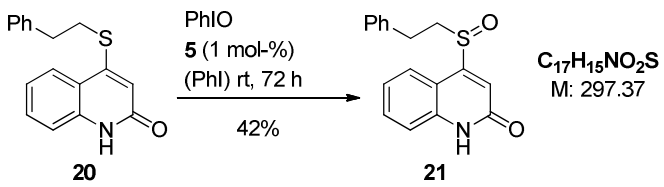
115.4 (d), 59.2 (t), 59.0 (t); MS (EI, 70 eV): *m/z* (%) = 219 (32) [M^+], 201 [$(M–H_2O)^+$], 184 (22), 171 (92) [$(M–SO)^+$], 143 (19) [$(M–C_2H_4OS)^+$], 128 (26), 115 (22), 105 (12), 87 (25), 73 (18), 57 (100), 43 (80); HRMS (EI) *m/z*: calcd. for $C_{11}H_7NOS$: 201.0248 [$(M–H_2O)^+$], found: 201.0243.

4.5. **Synthesis of thiomorpholine-3-one-1-oxide (19)**[11]



Following the general procedure, sulfide **18**[9] (14.1 mg, 120 µmol, 1.00 eq.) was reacted with iodosobenzene (34.3 mg, 156 µmol, 1.30 eq.) in iodobenzene (6.0 mL) in the presence of catalyst **5** (1.1 mg, 1.20 µmol, 0.01 eq.) and after purification by flash chromatography on silica gel (eluent: pentane/ethyl acetate/methanol = 100/100/0 → 0/100/0 → 0/70/30) 10.0 mg (63%, 59% *ee*) of chiral sulfoxide **19** and 1.9 mg (13%) of recovered starting material **18** were obtained as colourless solids; $R_f = 0.25$ (ethyl acetate/methanol = 70/30); HPLC (OJ-H, 250 × 4.6 mm, ^{n}Hex/^{i}PrOH = 80/20, 0.8 mL/min.): t_R = 17.9 min (–), 23.3 min (+); $[\alpha]_D^{20}$ = –1.6 (*c* = 0.7, $CHCl_3$, 59% *ee*); IR (ATR): $\tilde{\nu}$ = 3273 cm^{-1} (w), 33089 (br), 2933 (w), 1633 (m), 1624 (s), 1406 (m), 1334 (m), 1236 (w), 1120 (m), 1023 (vs), 1009 (vs), 936 (m), 728 (vs); ^{1}H-NMR (360 MHz, DMSO-d_6): δ [ppm] = 8.02 (br s, 1 H), 3.79-3.66 (m, 1 H), 3.67 (d, ^2J = 16.6 Hz, 1 H), 3.46-3.30 (m, 1 H), 3.33 (d, ^2J = 16.6 Hz, 1 H), 3.08-2.92 (m, 2 H); ^{13}C-NMR (90.6 MHz, DMSO-d_6): δ [ppm] = 162.9 (s), 50.1 (t), 42.6 (t), 33.6 (t); MS (EI, 70 eV): *m/z* (%) = 133 (52) [M^+], 117 (8), 84 (47) [$(M–SO)^+$], 70 (11), 63 (22), 44 (100).

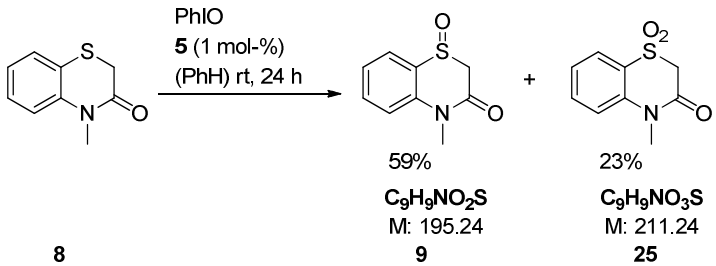
4.6. **Synthesis of 4-(phenethylsulfinyl)quinoline-2(1*H*)-one (21)**



[11] H. Lehr, S. Karlan and M. W. Goldberg, *J. Med. Chem.*, 1963, **6**, 136-141.

Following the general procedure, sulfide **20** (33.8 mg, 120 µmol, 1.00 eq.) was reacted with iodosobenzene (34.3 mg, 156 µmol, 1.30 eq.) in iodobenzene (6.0 mL) in the presence of catalyst **5** (1.1 mg, 1.20 µmol, 0.01 eq.) and after purification by flash chromatography on silica gel (eluent: pentane/ethyl acetate/methanol = 100/100/0 → 0/100/0 → 0/95/5) 14.9 mg (42%, 64% *ee*) of chiral sulfoxide **21** and 11.5 mg (34%) of recovered starting material **20** were obtained as cream solids; $R_f = 0.50$ (ethyl acetate/methanol = 95/5); HPLC (AD-H, 250 × 4.6 mm, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.): $t_R = 7.9$ min (+), 12.9 min (–); $[\alpha]_D^{20} = -17.7$ ($c = 0.4$, MeOH, 64% *ee*); m.p.: 150 °C; IR (ATR): $\tilde{\nu} = 3069$ cm^{-1} (w), 3040 (w), 2856 (w), 1644 (vs), 1566 (m), 1498 (m), 1367 (m), 1276 (w), 1057 (s), 965 (w), 873 (m), 829 (w), 757 (s), 698 (s); ^{1}H-NMR (360 MHz, DMSO-d$_6$): δ [ppm] = 12.07 (br s, 1 H), 7.59 (*virt*. t, $^3J \cong 7.7$ Hz, 1 H), 7.49 (d, $^3J = 8.0$ Hz, 1 H), 7.41 (d, $^3J = 8.2$ Hz, 1 H), 7.33-7.16 (m, 6 H), 6.88 (s, 1 H), 3.52-3.33 (m, 1 H), 3.17-3.04 (m, 2 H), 2.92-2.83 (m, 1 H); ^{13}C-NMR (90.6 MHz, DMSO-d$_6$): δ [ppm] = 160.1 (s), 154.5 (s), 138.7 (s), 138.6 (s), 131.3 (d), 128.4 (d), 128.4 (d), 126.4 (d), 122.5 (d), 122.2 (d), 118.3 (d), 116.9 (d), 114.3 (s), 54.3 (t), 27.1 (t); MS (EI, 70 eV): *m/z* (%) = 297 (8) [M$^+$], 281 (17) [(M–O)$^+$], 193 (34) [(M–C$_8$H$_8$)$^+$], 177 (48) [(M–C$_8$H$_8$O)$^+$], 149 (10), 105 (100) [C$_8$H$_9^+$], 77 (30) [C$_6$H$_5^+$], 51 (20), 44 (21); HRMS (EI) *m/z*: calcd. for $C_{17}H_{15}NO_2S$: 297.0823 [M$^+$], found: 297.0823.

4.7. **Synthesis of 4-methyl-2*H*-benzo[b][1,4]thiazin-3(4*H*)-one-1-oxide (9)**[12]



Manganese(salen) catalyst **5** (1.1 mg, 1.20 µmol, 0.01 eq.) and iodosobenzene (34.3 mg, 156 µmol, 1.30 eq.) were consecutively added to a solution of sulfide **8**[13] (21.5 mg, 120 µmol, 1.00 eq.) in benzene (6.0 mL) and the resulting brown suspension was stirred at room temperature for 24 hours. The reaction mixture was purified directly by flash chromatography on silica gel (eluent: pentane/ethyl acetate = 1/1 → 1/0) to afford 13.8 mg (59%, <1% *ee*) of chiral sulfoxide **9** and 5.8 mg (23%) of sulfone **25** as colourless solids. Analytical data for

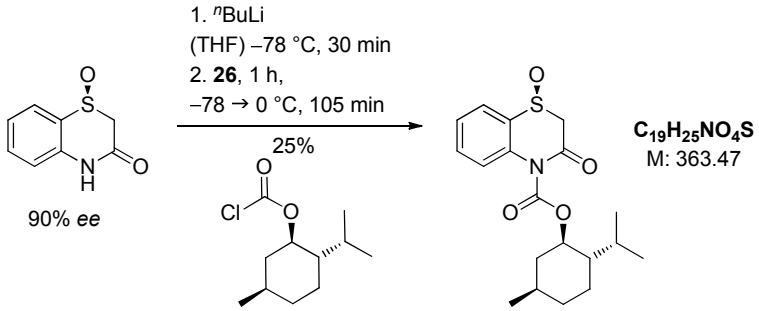
[12] F. Eiden and F. Meinel, *Arch. Pharm.,* 1979, **312**, 302-312.

sulfoxide **9**[11]: $R_f = 0.24$ (ethyl acetate); HPLC (AS-H, 250 × 4.6 mm, ^{n}Hex/^{i}PrOH = 50/50, 1 mL/min.): t_R = 29.4 min, 39.7 min; ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 7.76 (d, ^3J = 7.5 Hz, 1 H), 7.63 (*virt*. td, $^3J \tilde{=}$ 7.9 Hz, ^4J = 1.5 Hz, 1 H), 7.30-7.26 (m, 2 H), 4.21 (d, ^2J = 15.0 Hz, 1 H), 3.74 (d, ^2J = 15.0 Hz, 1 H), 3.54 (s, 3 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 160.6 (s), 139.1 (s), 133.9 (d), 129.8 (d), 127.0 (s), 124.0 (d), 117.7 (d), 52.4 (t), 31.5 (q).

Analytical data for sulfone **25**: $R_f = 0.69$ (EtOAc); ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 7.98 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H), 7.69 (ddd, ^3J = 8.4 Hz, ^3J = 5.5 Hz, ^4J = 1.6 Hz, 1 H), 7.37-7.30 (m, 2 H), 4.24 (s, 2 H), 3.53 (s, 3 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 160.8 (s), 139.0 (s), 135.0 (d), 128.0 (s), 124.5 (d), 124.3 (d), 118.0 (d), 56.7 (t), 32.1 (q).

5. Proof of the absolute configuration of sulfoxide 7

5.1. Synthesis of 4-[(1*R*,2*S*,5*R*)-2-*iso*-propyl-5-methylcyclohexyl]-2*H*-benzo[e][1,4]thiazin-3-one-1-oxide (10)

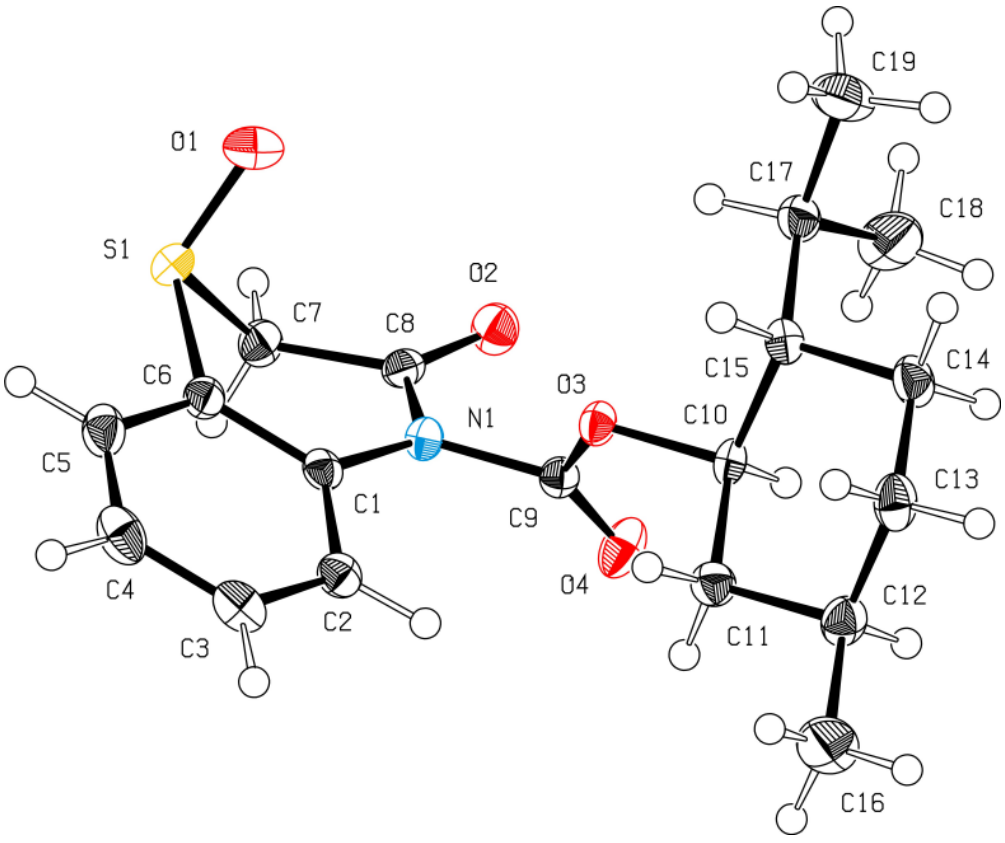


^{n}BuLi (2.5 M in Hexan, 59.0 µL, 146 µmol, 1.10 eq.) was added over a period of 10 minutes to a solution of the sulfoxide **7** (enriched to 90% *ee* by semi-preparative HPLC, 24.1 mg, 133 µmol, 1.00 eq.) in tetrahydrofuran (3.5 mL) at −78 °C and the reaction mixture was stirred for 30 minutes. (−)-Menthyl chloroformate (**26**) (34.0 µL, 35.0 mg, 160 µmol, 1.20 eq.) was added and the solution was stirred 45 minutes at −78 °C and one hour at 0 °C. The reaction mixture was quenched with saturated ammonium chloride solution (0.3 mL) and was concentrated *in vacuo*. After addition of water (10 mL) and dichloromethane (20 mL) the layers were separated and the aqueous layer was extracted with dichloromethane (2 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered and concentrated *in*

[13] J. W. Worley, K. W. Ratts and K. L. Cammack, *J. Org. Chem.*, 1975, **40**, 1731-1734.

vacuo. The residue was purified by flash chromatography on silica gel (eluent: pentane/ethyl acetate = 5/1 → 1/1) to afford 12.1 mg (25%) of sulfoxide **10** as a single diastereoisomer; R_f = 0.43 (EtOAc/MeOH = 95/5); m.p.: 160 °C; $[\alpha]_D^{20}$ = +18.6 (c = 0.7, $CHCl_3$); IR (ATR): $\tilde{\nu}$ = 3089 cm^{-1} (w), 2957 (w), 1761 (m), 1683 (m), 1644 (w), 1580 (w), 1484 (m), 1309 (m), 1227 (vs), 1111 (w), 1062 (s), 1018 (m), 951 (m), 771 (m); ^{1}H-NMR (360 MHz, $CDCl_3$): δ [ppm] = 7.78 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H), 7.61-7.55 (m, 1 H), 7.35 (*virt.* td, $^3J \cong$ 7.6 Hz, ^4J = 1.1 Hz, 1 H), 7.15 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1 H), 4.92 (*virt.* dt, ^3J = 10.9 Hz, $^3J \cong$ 4.3 Hz, 1 H), 4.17 (d, ^2J = 14.2 Hz, 1 H), 3.77 (d, ^2J = 14.2 Hz, 1 H), 2.27-2.21 (m, 1 H), 2.09-1.99 (m, 1 H), 1.76-1.67 (m, 2 H), 1.57-1.43 (m, 2 H), 1.25-1.05 (m, 3 H), 0.96 (d, ^3J = 6.5 Hz, 3 H), 0.90 (d, ^3J = 7.0 Hz, 3 H), 0.86 (d, ^3J = 7.0 Hz, 3 H); ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ [ppm] = 159.8 (s), 151.8 (s), 135.5 (s), 133.5 (d), 129.4 (d), 127.9 (s), 125.7 (d), 120.2 (d), 80.8 (d), 53.5 (t), 46.6 (d), 39.9 (t), 33.9 (t), 31.5 (d), 25.9 (d), 23.1 (t), 21.9 (q), 20.7 (q), 16.0 (q); MS (EI, 70 eV): m/z (%) = 363 (6) [M^+], 182 (88) [$C_{11}H_{18}O_2^+$], 166 (16), 153 (19), 132 (17), 97 (18) [$C_7H_{13}^+$], 83 (100) [$C_6H_{11}^+$], 55 (53) [$C_4H_7^+$], 41 (24) [$C_3H_5^+$]; HRMS (EI) m/z: calcd. for $C_{19}H_{25}NO_4S$: 363.1504 [M^+], found: 363.1501.

5.2. **Single crystal X-Ray structure determination of compound 10**



Operator:	*** Herdtweck ***
Molecular Formula:	$C_{19}H_{25}NO_4S$
Crystal Color / Shape	Colorless fragment
Crystal Size	Approximate size of crystal fragment used for data collection: 0.25 × 0.30 × 0.64 mm
Molecular Weight:	363.47 a.m.u.
F_{000}:	776
Systematic Absences:	h00: h≠2n; 0k0: k≠2n, 00l: l≠2n
Space Group:	Orthorhombic $P\,2_12_12_1$ (I.T.-No.: 19)
Cell Constants:	Least-squares refinement of 9229 reflections with the programs "APEX suite" and "SAINT"[14,15]; theta range 4.43° < θ < 66.53°; Cu($K\overline{\alpha}$); λ = 154.180 pm
	a = 928.13(2) pm
	b = 1394.05(3) pm
	c = 1430.69(3) pm
	V = 1851.11(7)· 10^6 pm^3; Z = 4; D_{calc} = 1.304 g cm^{-3}; Mos. = 0.76
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); sealed tube; graphite monochromator; 40 kV; 30 mA; λ = 154.180 pm; Cu($K\overline{\alpha}$)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	4.43° < θ < 66.53°; h: -10/10, k: -15/16, l: -16/16
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 30 runs; 5758 films / scaled: 30 runs; 5758 films
	φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 1.00°; dx = 35.0 mm
LP - Correction:	Yes[15]
Intensity Correction	No/Yes; during scaling[14]
Absorption Correction:	Multi-scan; during scaling; μ = 1.747 mm^{-1} [15]
	Correction Factors: T_{min} = 0.5140 T_{max} = 0.7528
Reflection Data:	46387 reflections were integrated and scaled
	192 reflections systematic absent and rejected
	46195 reflections to be merged
	3167 independent reflections
	0.033 R_{int}: (basis F_o^2)
	3167 independent reflections (all) were used in refinements
	3130 independent reflections with $I_o > 2\sigma(I_o)$
	97.4 % completeness of the data set
	327 parameter full-matrix refinement
	9.7 reflections per parameter
Solution:	Direct Methods[16]; Difference Fourier syntheses
Refinement Parameters:	In the asymmetric unit:

[14] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
[15] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
[16] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, "**SIR92**" *J. Appl. Cryst.*, 1994, **27**, 435-436.

	25	Non-hydrogen atoms with anisotropic displacement parameters
	25	Hydrogen atoms with isotropic displacement parameters
Hydrogen Atoms:	All hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion[17]	
Extinction Correction:	F_c (korr) = kF_c[1+ 0.001 · ε · F_c^2 · λ^3/sin(2Θ)]$^{-1/4}$ SHELXL-97 [5[18]]	
	ε refined to ε = 0.0021(1)	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)$+(a∗P)^2+b∗P	
	with a: 0.0198; b: 0.4064; P: [Maximum(0 or F_o^2)+2∗F_c^2]/3	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	+0.17 e_0^-/Å^3; -0.16 e_0^-/Å^3	
R1:	Σ(||F_o|-|F_c||)/Σ|F_o|	
[$F_o > 4\sigma(F_o)$; N=3130]:		= 0.0190
[all reflctns; N=3167]:		= 0.0193
wR2:	[$\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2$]$^{1/2}$	
[$F_o > 4\sigma(F_o)$; N=3130]:		= 0.0475
[all reflctns; N=3167]:		= 0.0476
Goodness of fit:	[$\Sigma w(F_o^2-F_c^2)^2$/(NO-NV)]$^{1/2}$	= 1.069
Flack's Parameter :	x = 0.03(1)	
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$ [18,19,20]	
	The correct enantiomer is proved by Flack's Parameter.	
	The correct enantiomer is proved by synthesis	

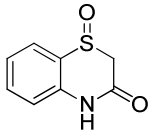
[17] A. J. C. Wilson, *Tables for Crystallography*, 1992, **Vol. C**, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Kluwer Academic Publishers, Dordrecht, The Netherlands.

[18] G. M. Sheldrick, "**SHELXL-97**", University of Göttingen, Göttingen, Germany, (1998).

[19] A. L. Spek, "**PLATON**", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).

[20] L. J. Farrugia, "**WinGX** (Version 1.70.01 January 2005) ", *J. Appl. Cryst.*, 1999, **32**, 837-838.

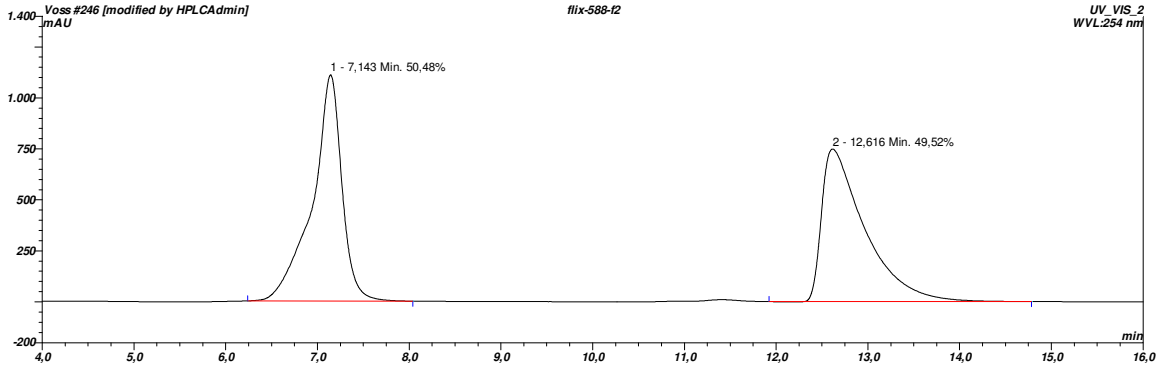
6. HPLC traces of chiral sulfoxides



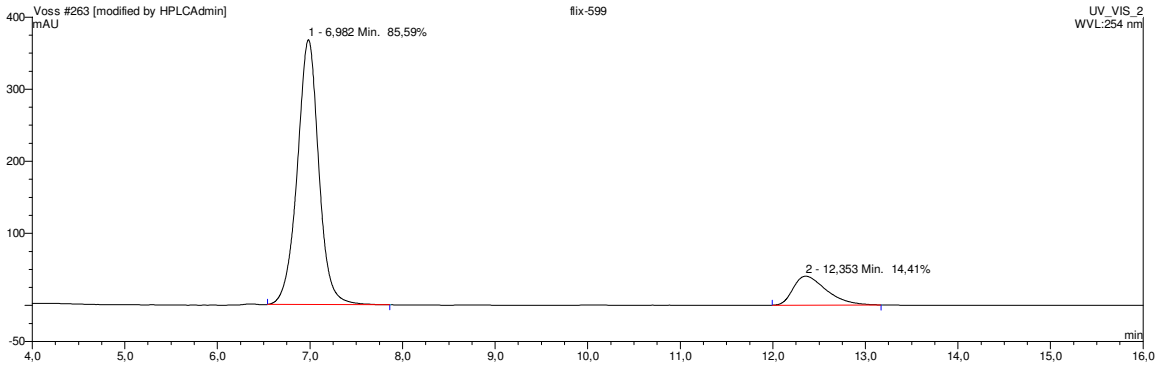
7

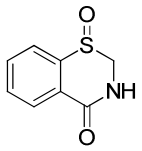
AD-H, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.

Racemate



enantioenriched

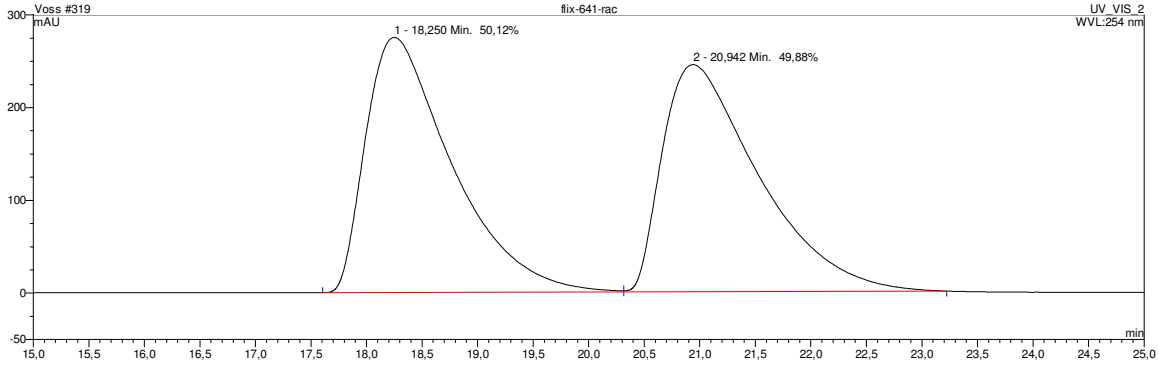




13

OJ-H, ^{n}Hex/^{i}PrOH = 80/20, 1 mL/min.

Racemate



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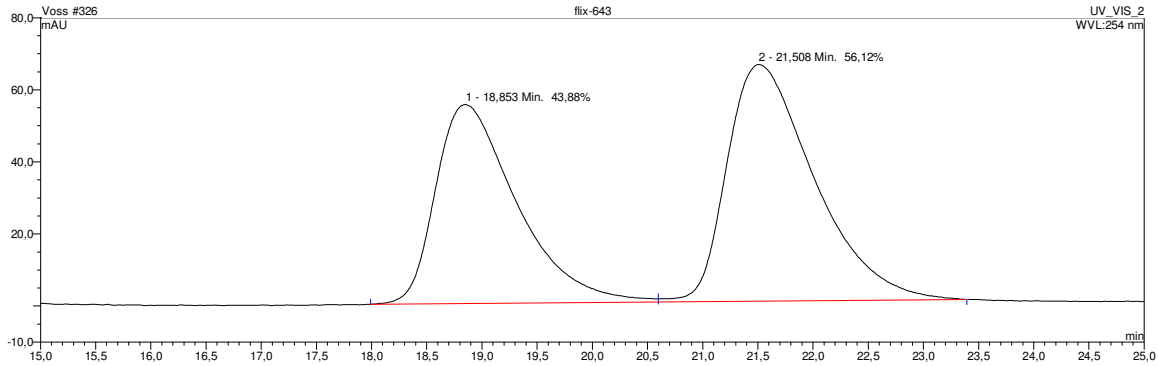
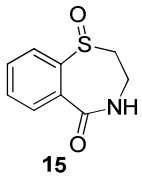
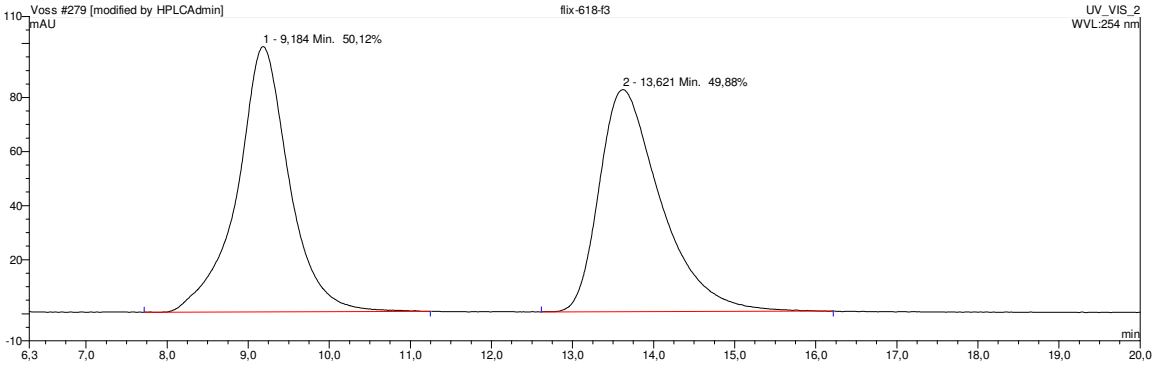




15

OJ-H, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.

Racemate



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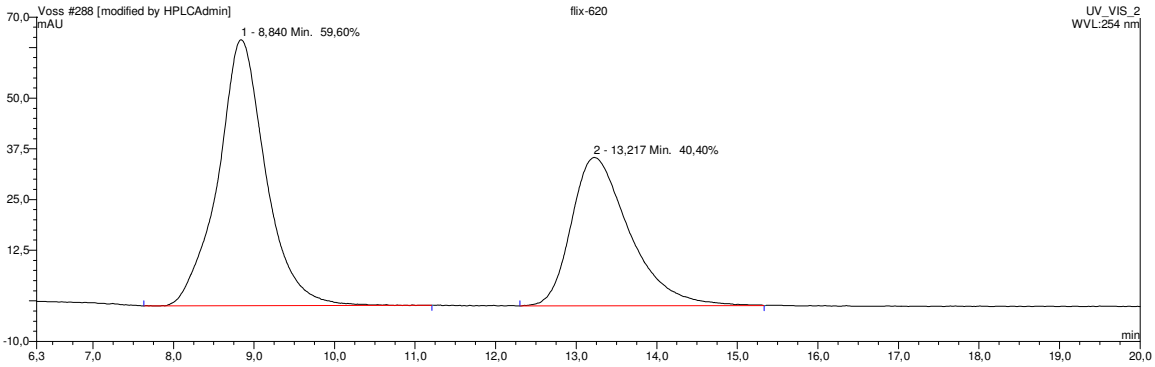
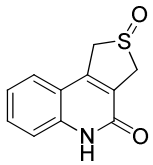
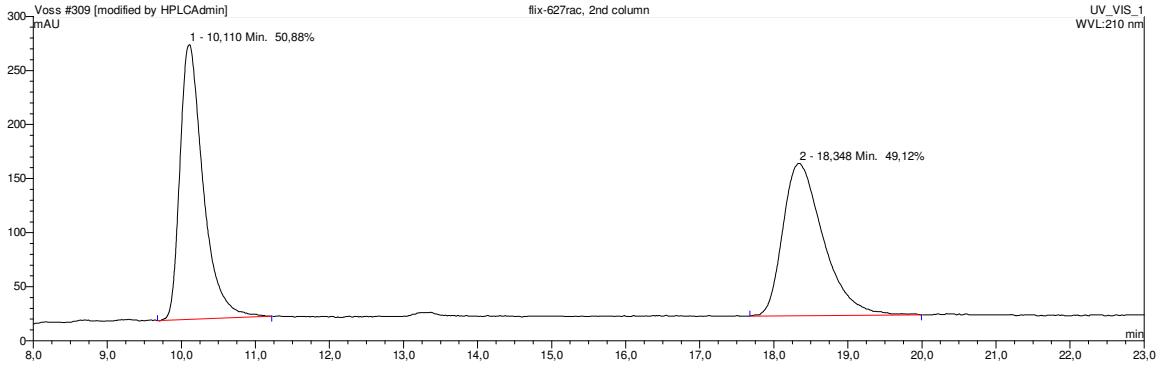




17

AD-H, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.

Racemate



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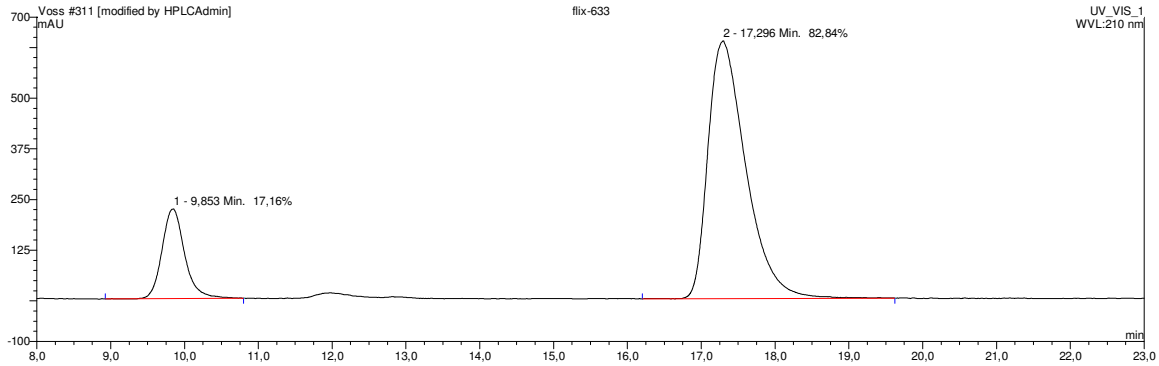
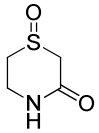
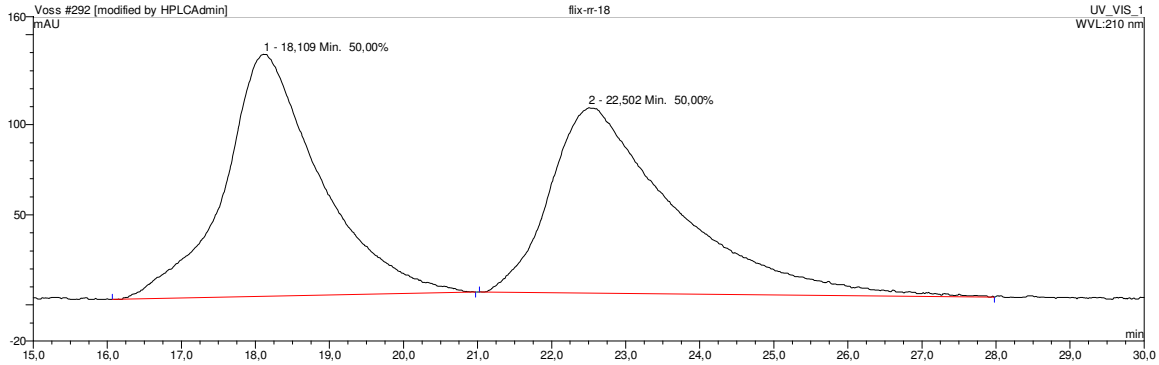




19

OJ-H, ^{n}Hex/^{i}PrOH = 80/20, 0.8 mL/min.

Racemate



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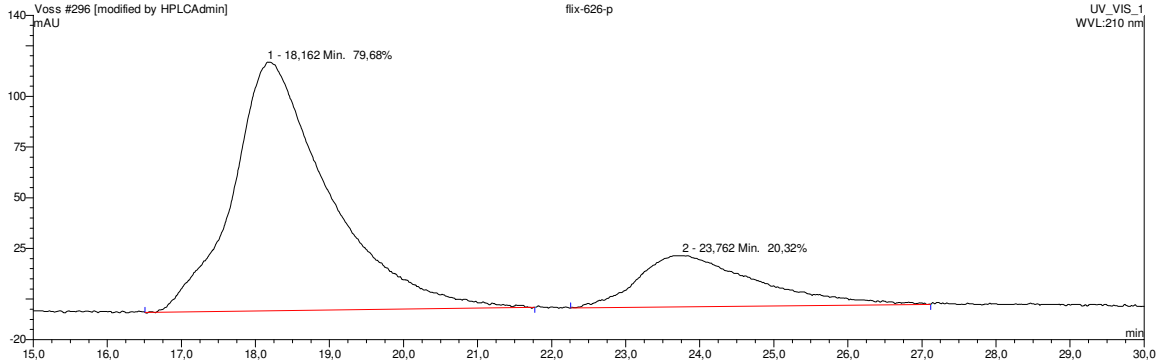
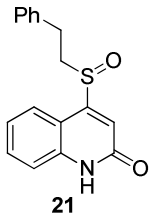
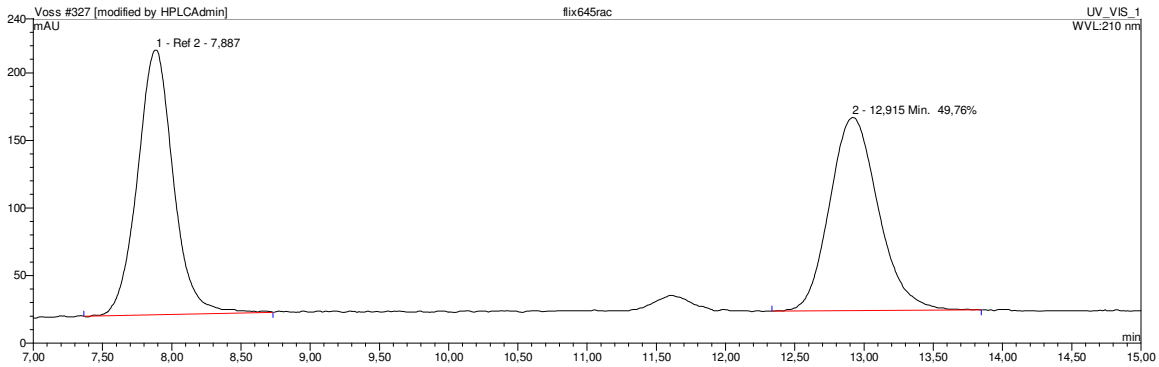




21

AD-H, ^{n}Hex/^{i}PrOH = 70/30, 1 mL/min.

Racemate



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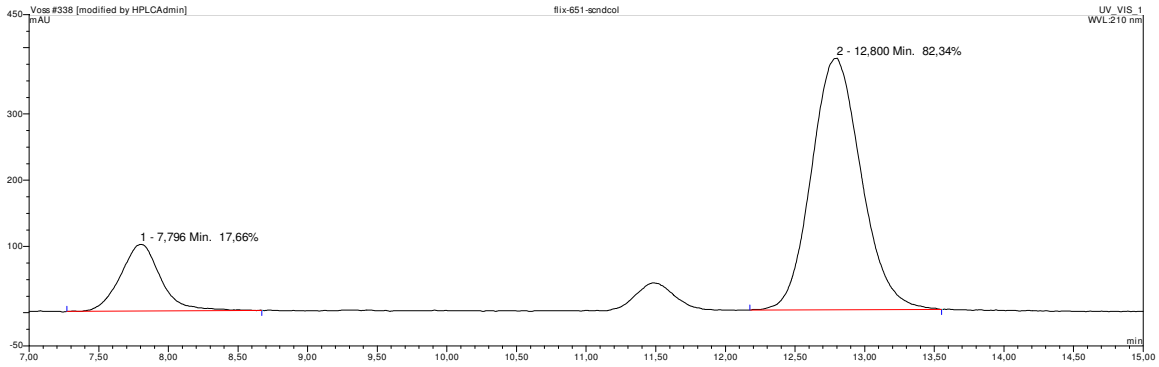
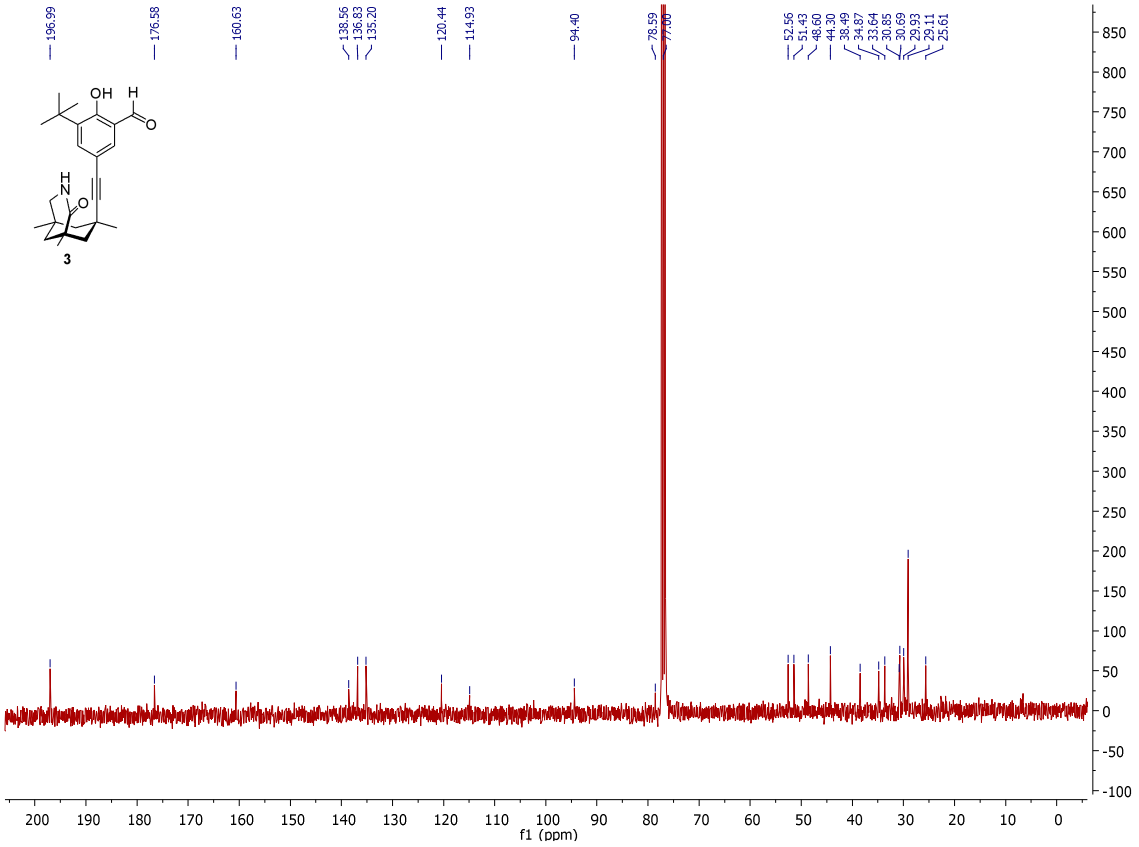
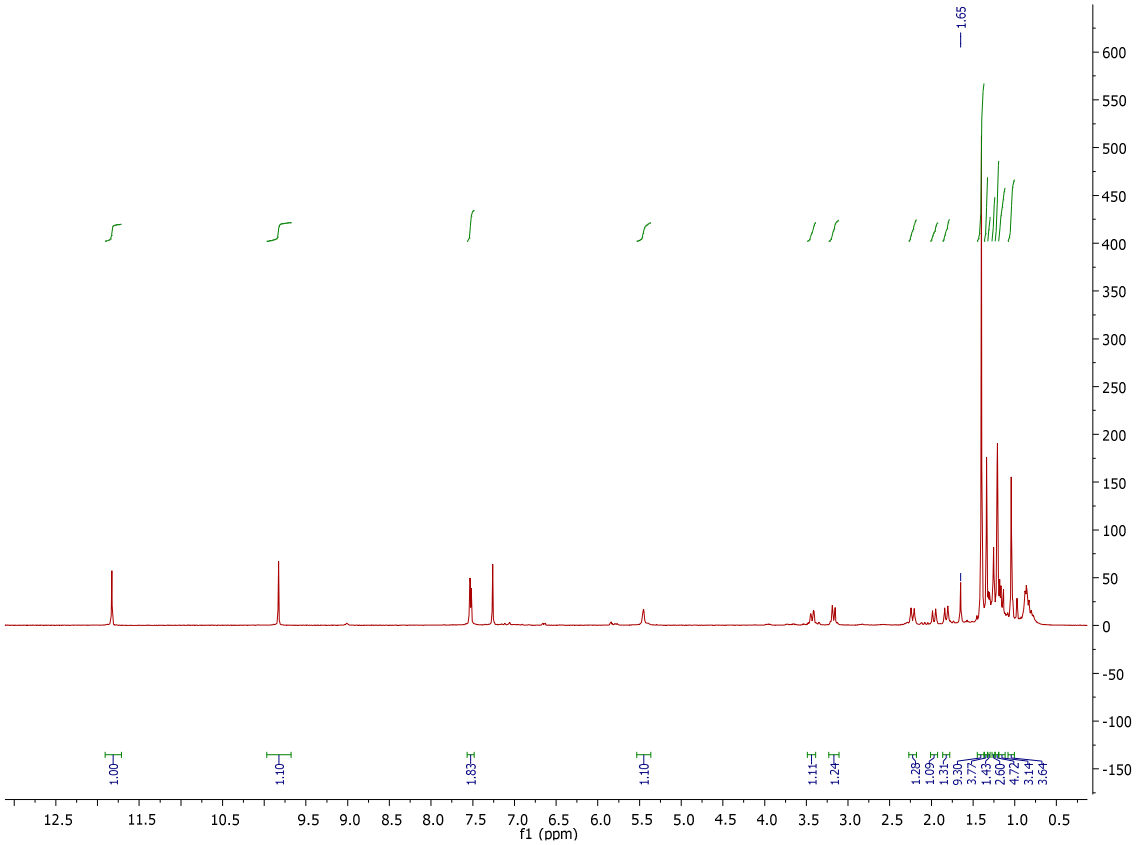
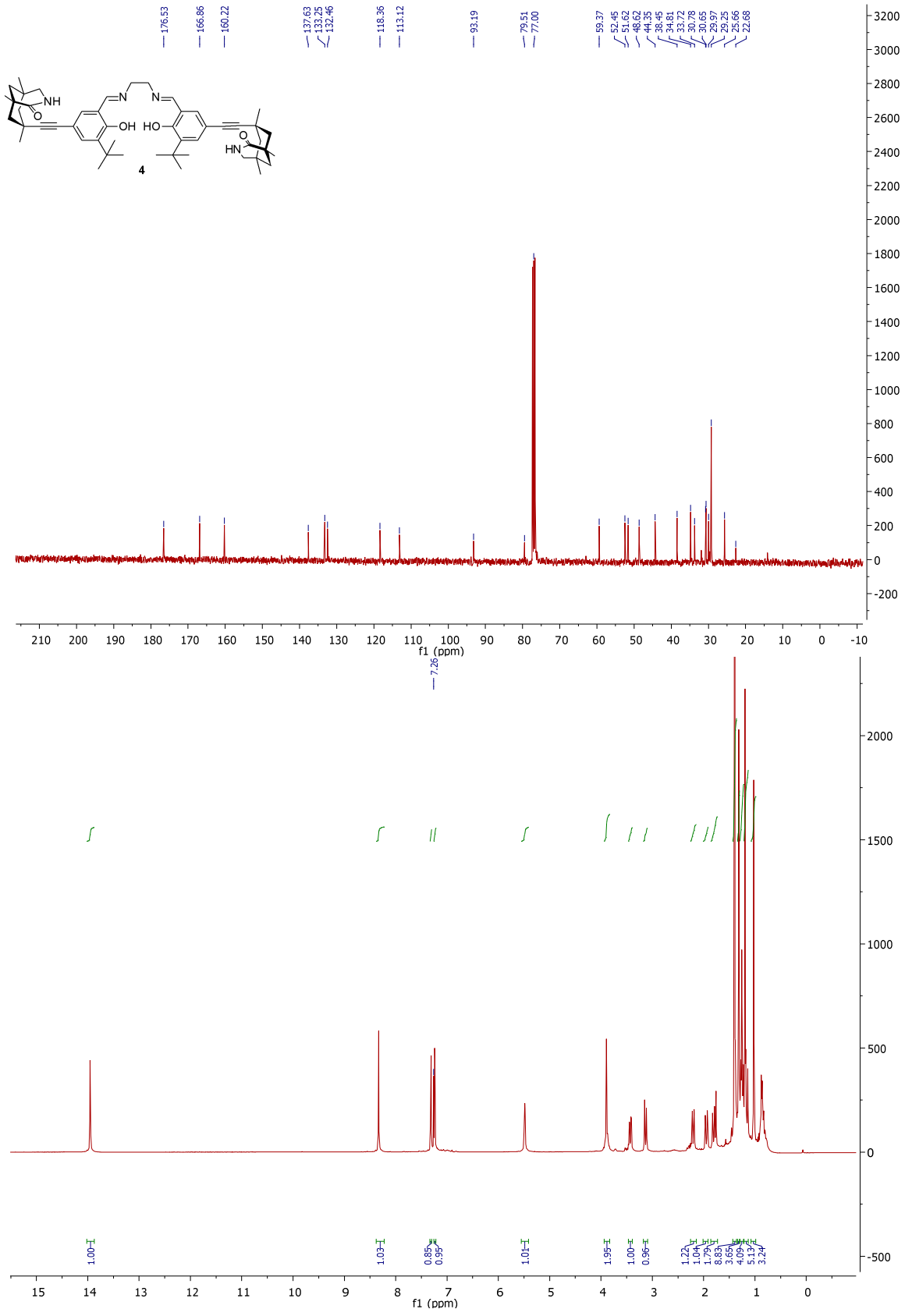


7. NMR spectra of new compounds



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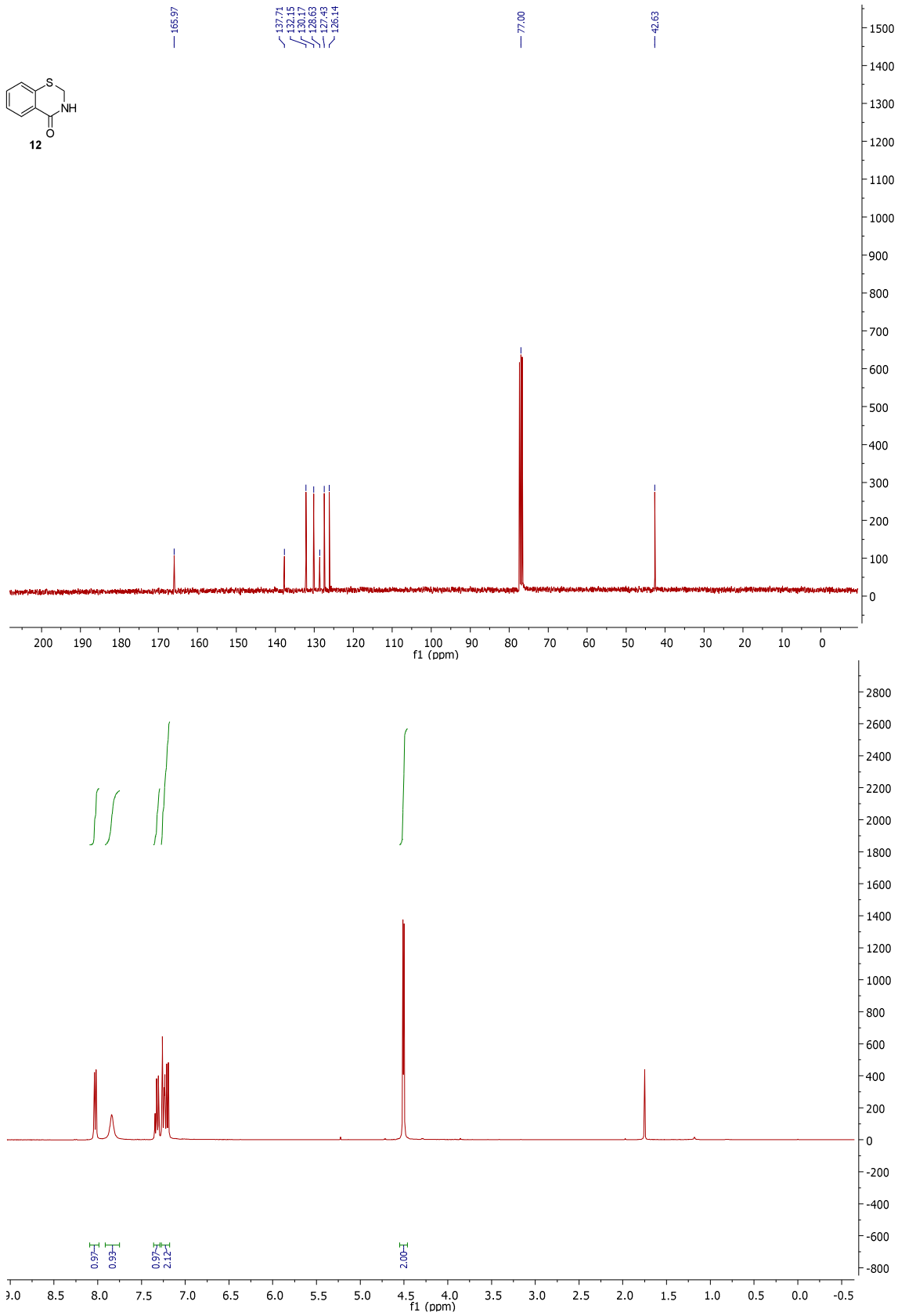
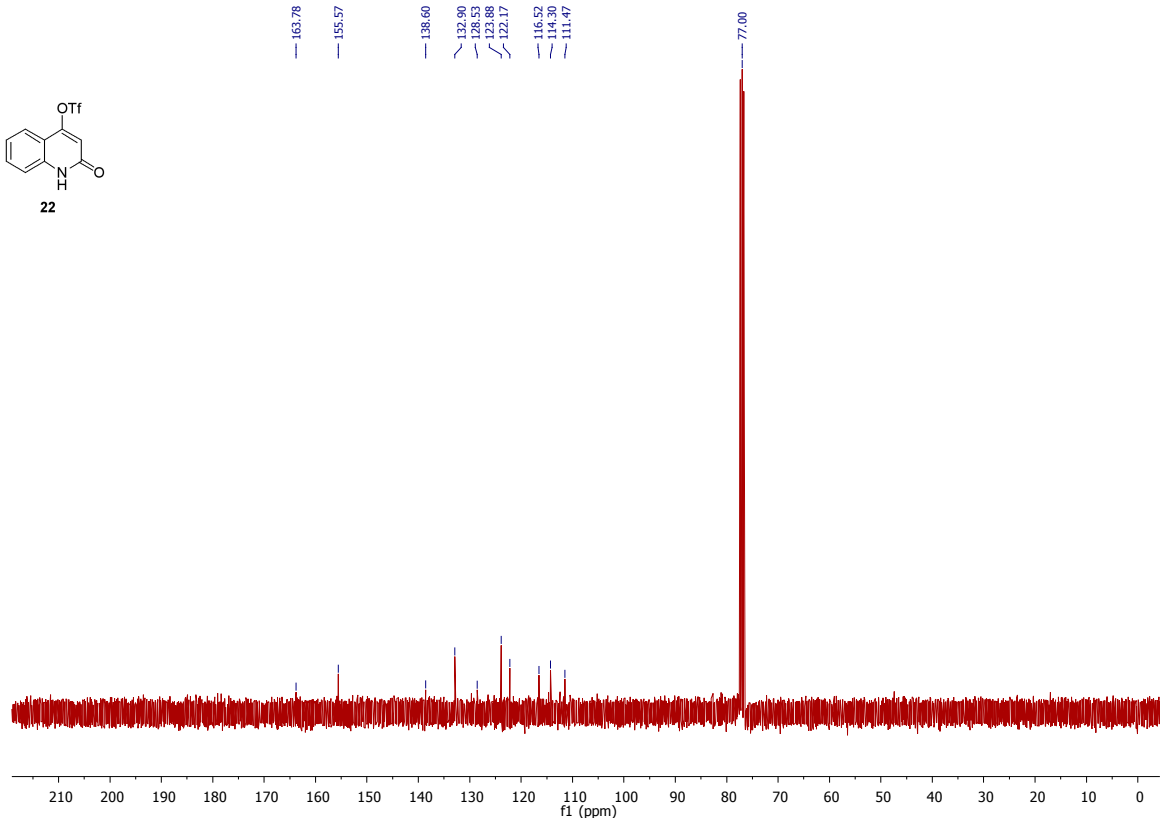
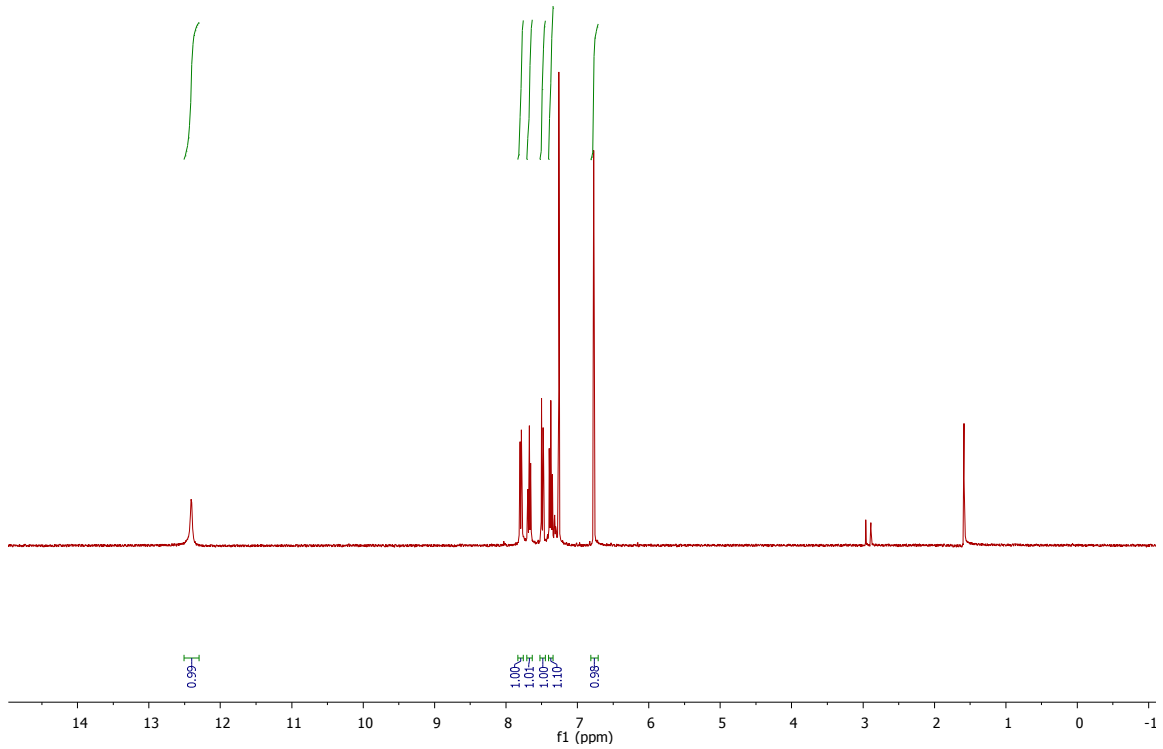
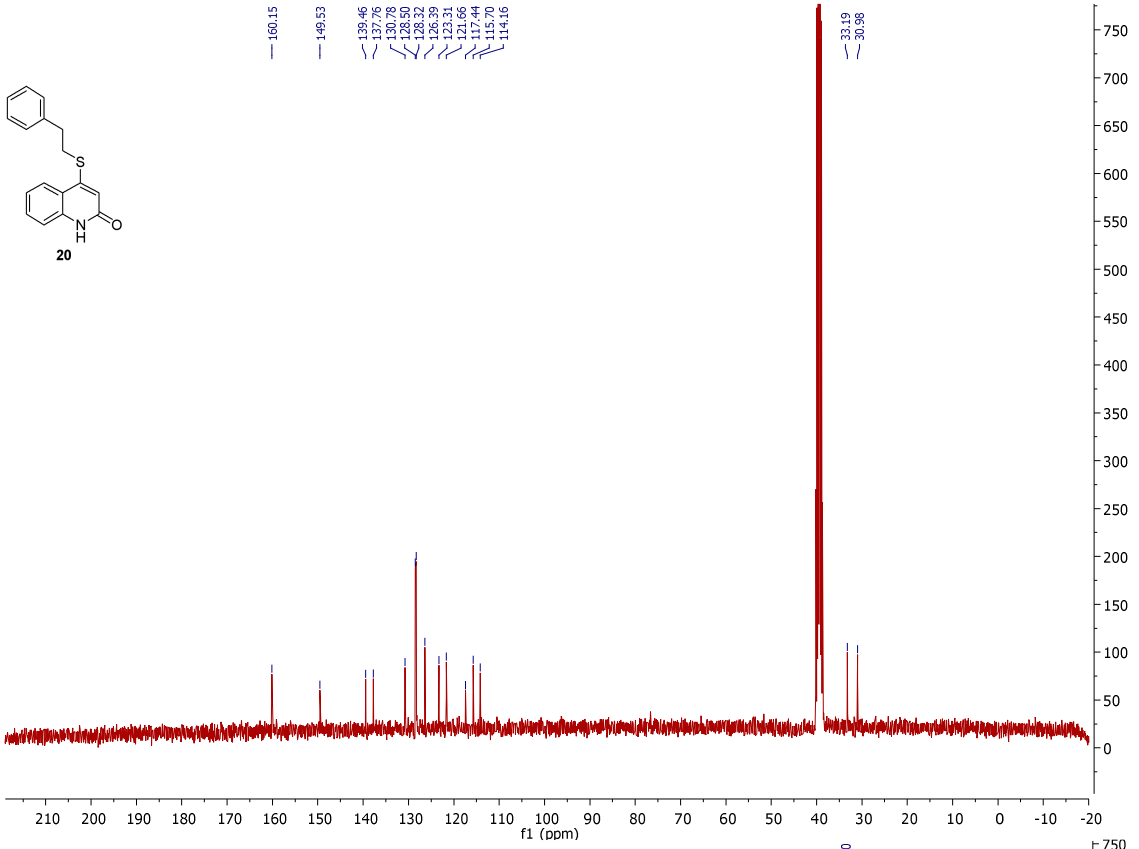
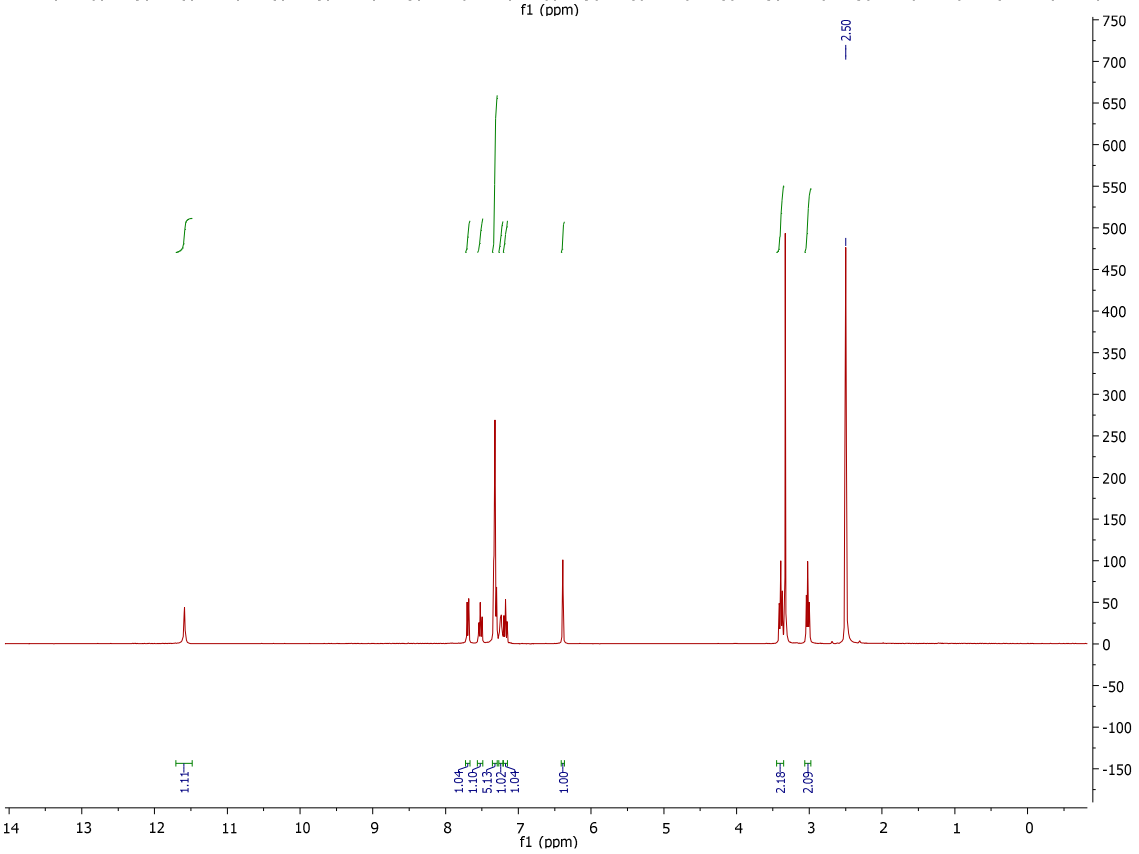
166.86
160.22
137.63
133.25
132.46
118.36
113.12
93.19
79.51
77.00
59.37
52.45
51.62
48.62
44.35
38.45
34.81
33.72
30.78
30.65
29.97
29.25
25.66
22.68
NH
O
N
N
OH
HO
O
HN
4
f1 (ppm)
7.26
1.00
1.03
0.85
0.95
1.01
1.95
1.00
0.96
1.22
1.04
1.79
8.83
3.65
4.09
5.13
3.24
f1 (ppm)


165.97
137.71
132.15
130.17
128.63
127.43
126.14
77.00
42.63
S
NH
O
12
f1 (ppm)
0.97
0.93
0.97
2.12
2.00
f1 (ppm)


163.78
155.57
138.60
132.90
128.53
123.88
122.17
116.52
114.30
111.47
77.00
OTf
N
H
O
22
f1 (ppm)


0.99
1.00
1.01
1.00
1.10
0.98
f1 (ppm)


160.15
149.53
139.46
137.76
130.78
128.50
128.32
126.39
123.31
121.66
117.44
115.70
114.16
33.19
30.98
S
N
H
O
20
f1 (ppm)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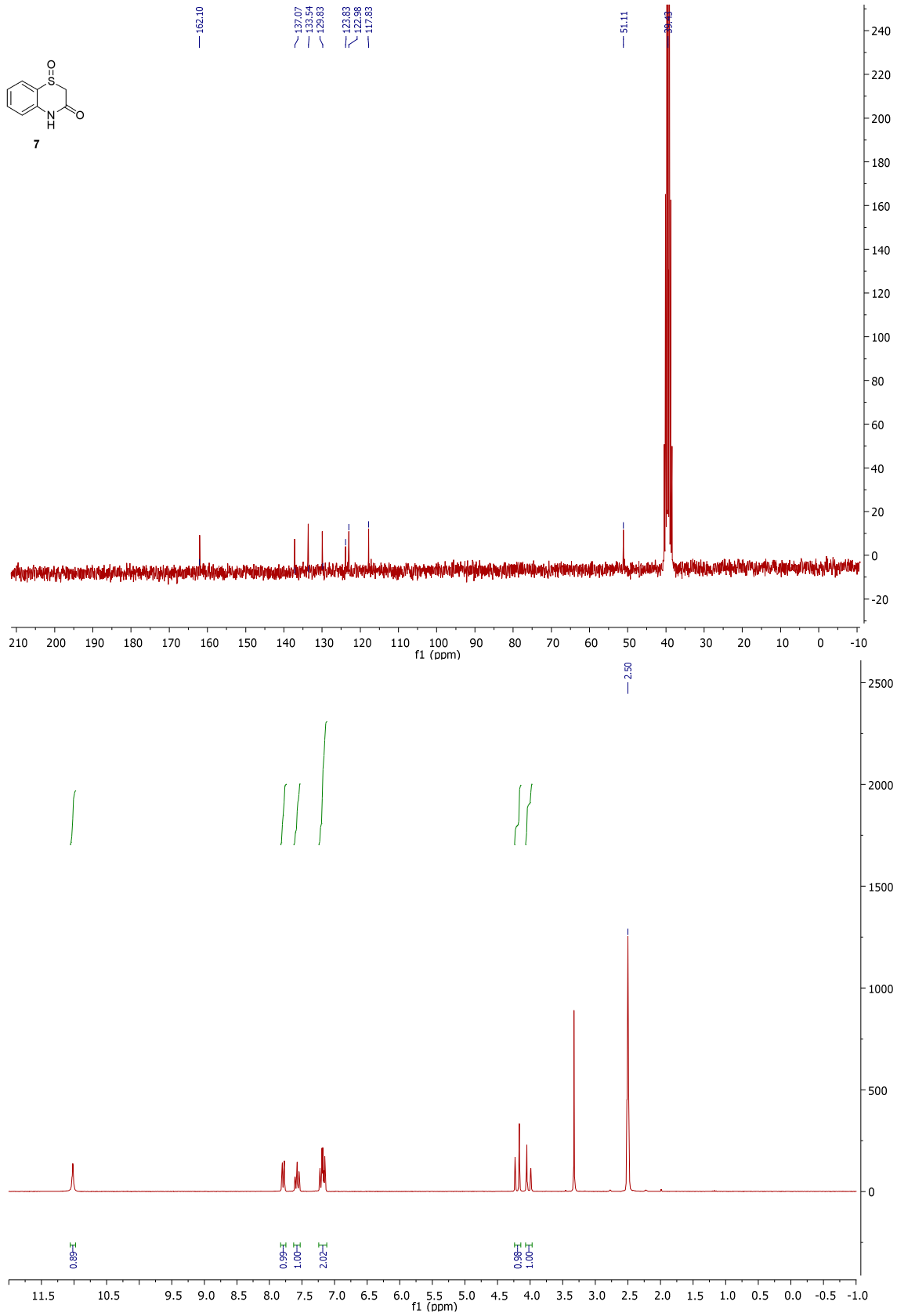
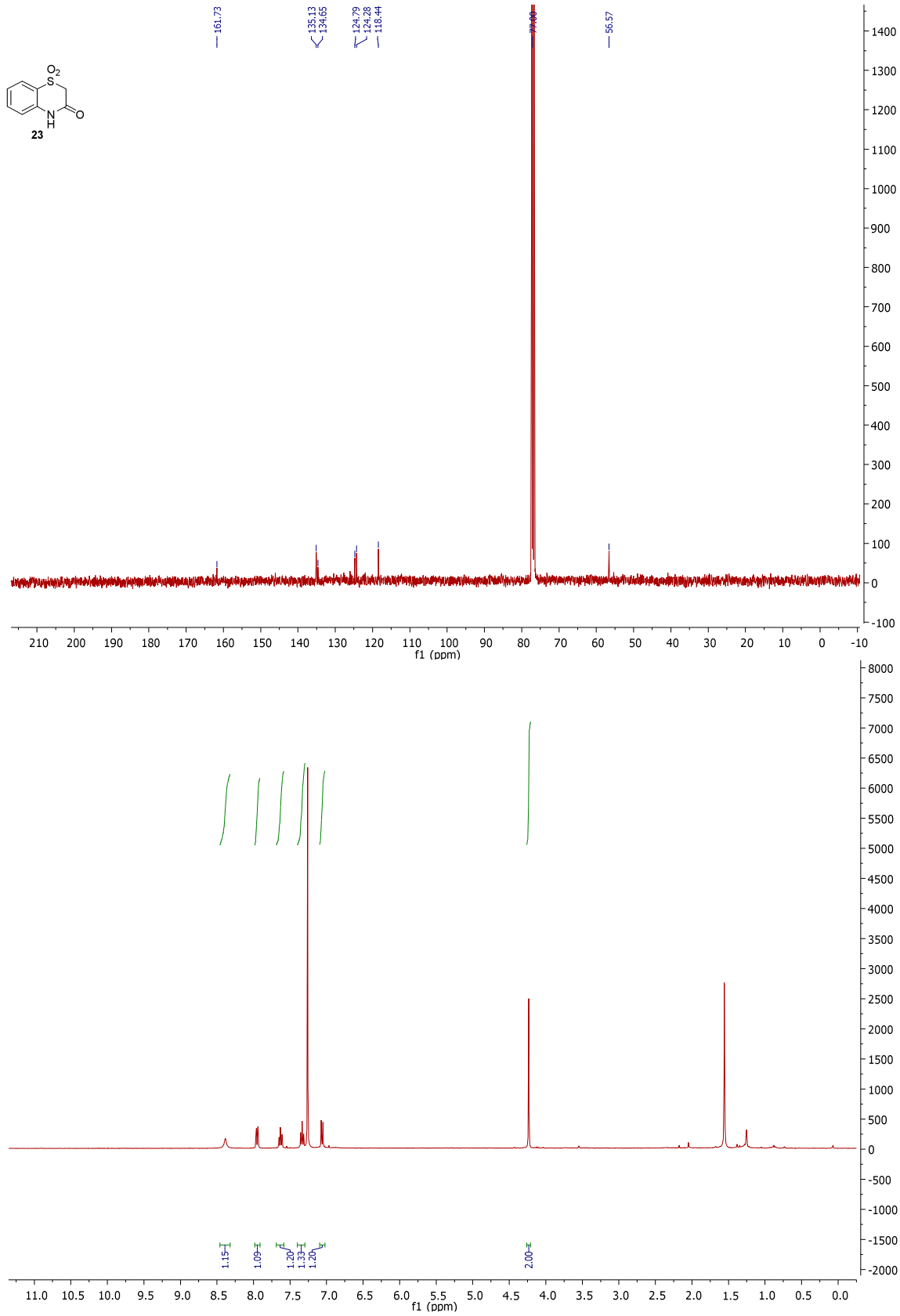
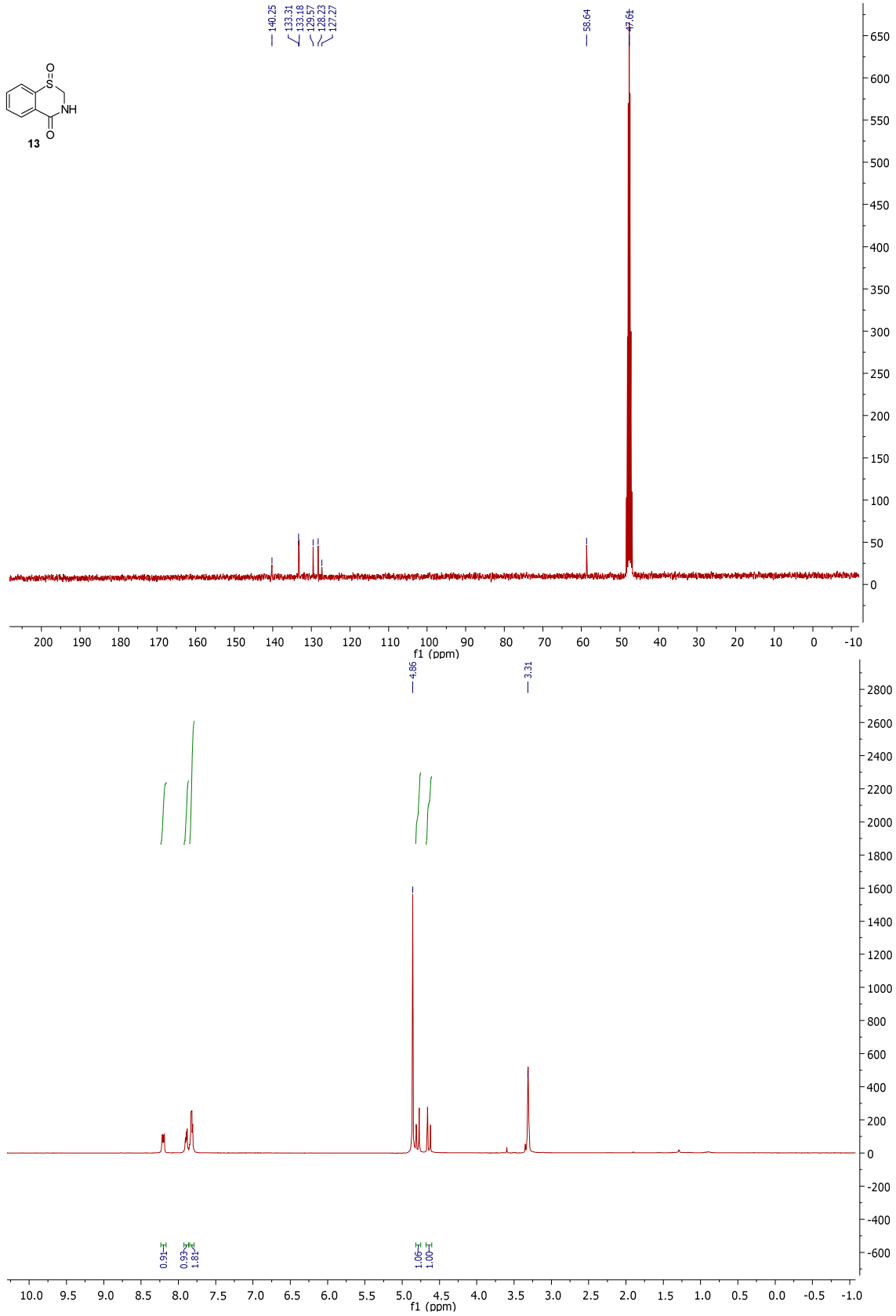
1.11
1.04
1.10
5.13
1.02
1.04
1.00
2.18
2.09
f1 (ppm)


7
162.10
137.07
133.54
129.83
123.83
122.98
117.83
51.11
39.43
f1 (ppm)
2.50
0.89
0.99
1.00
2.02
0.98
1.00
f1 (ppm)


161.73
135.13
134.65
124.79
124.28
118.44
77.00
56.57
23
f1 (ppm)
1.15
1.09
1.20
1.33
1.20
2.00
f1 (ppm)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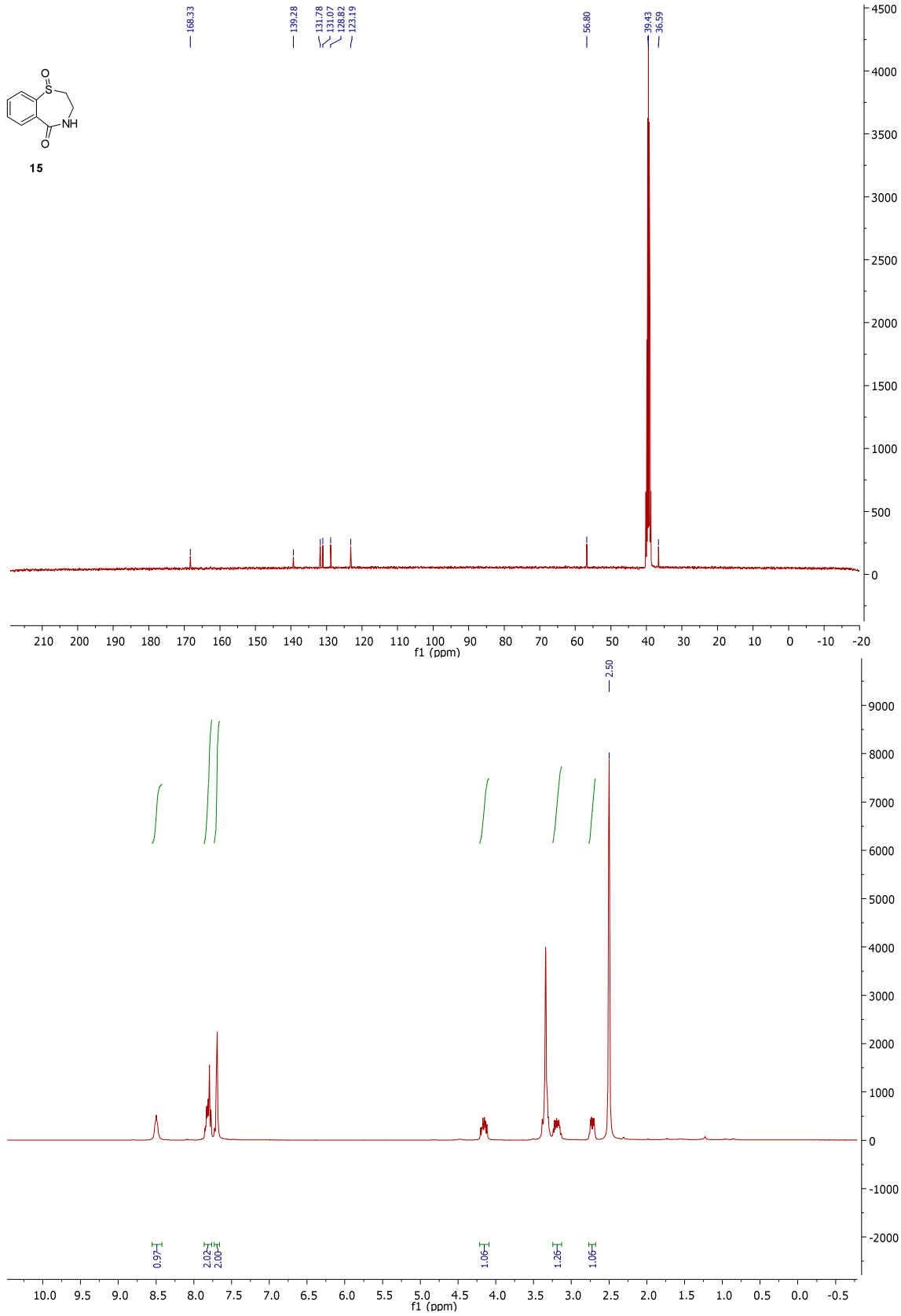
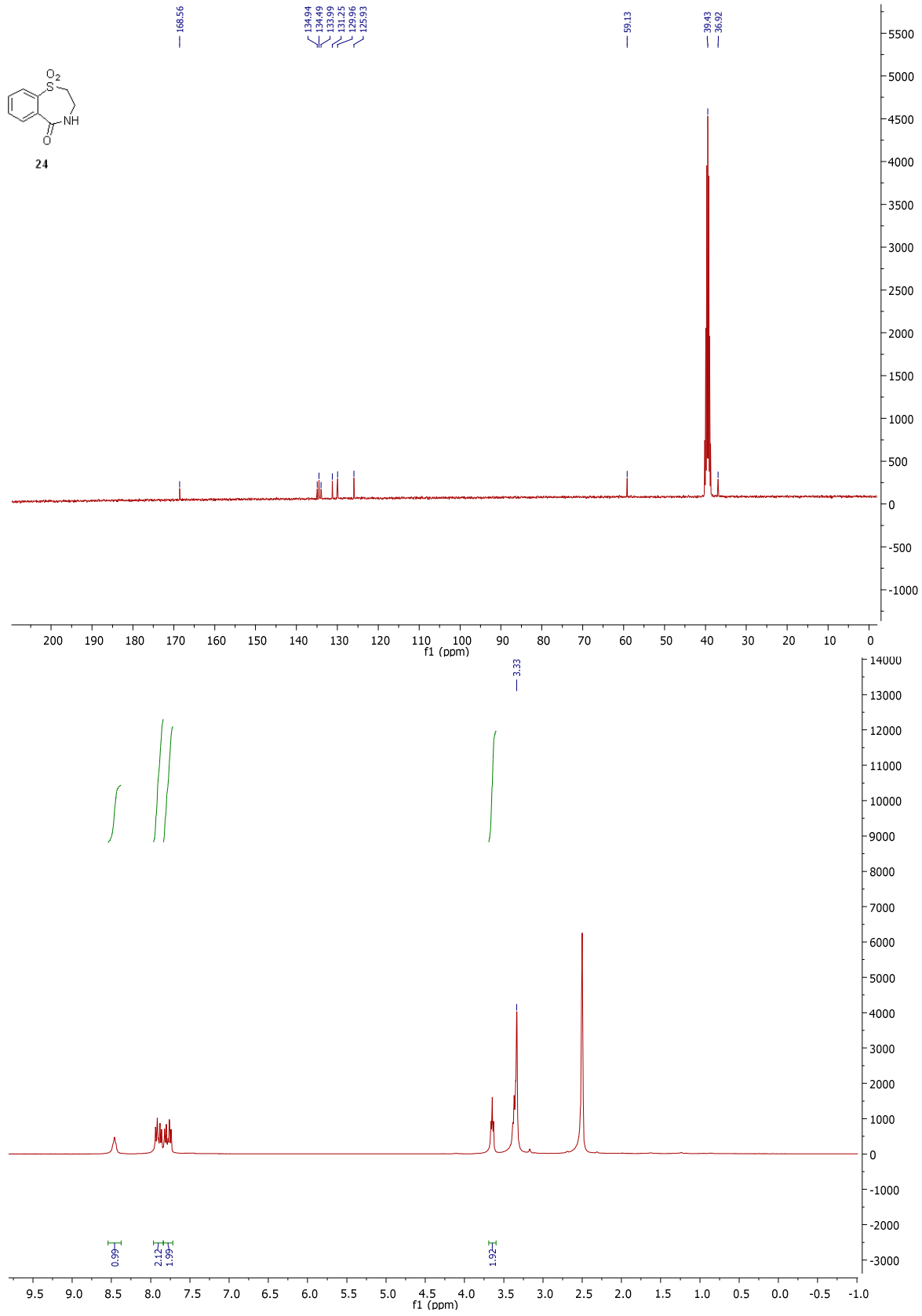
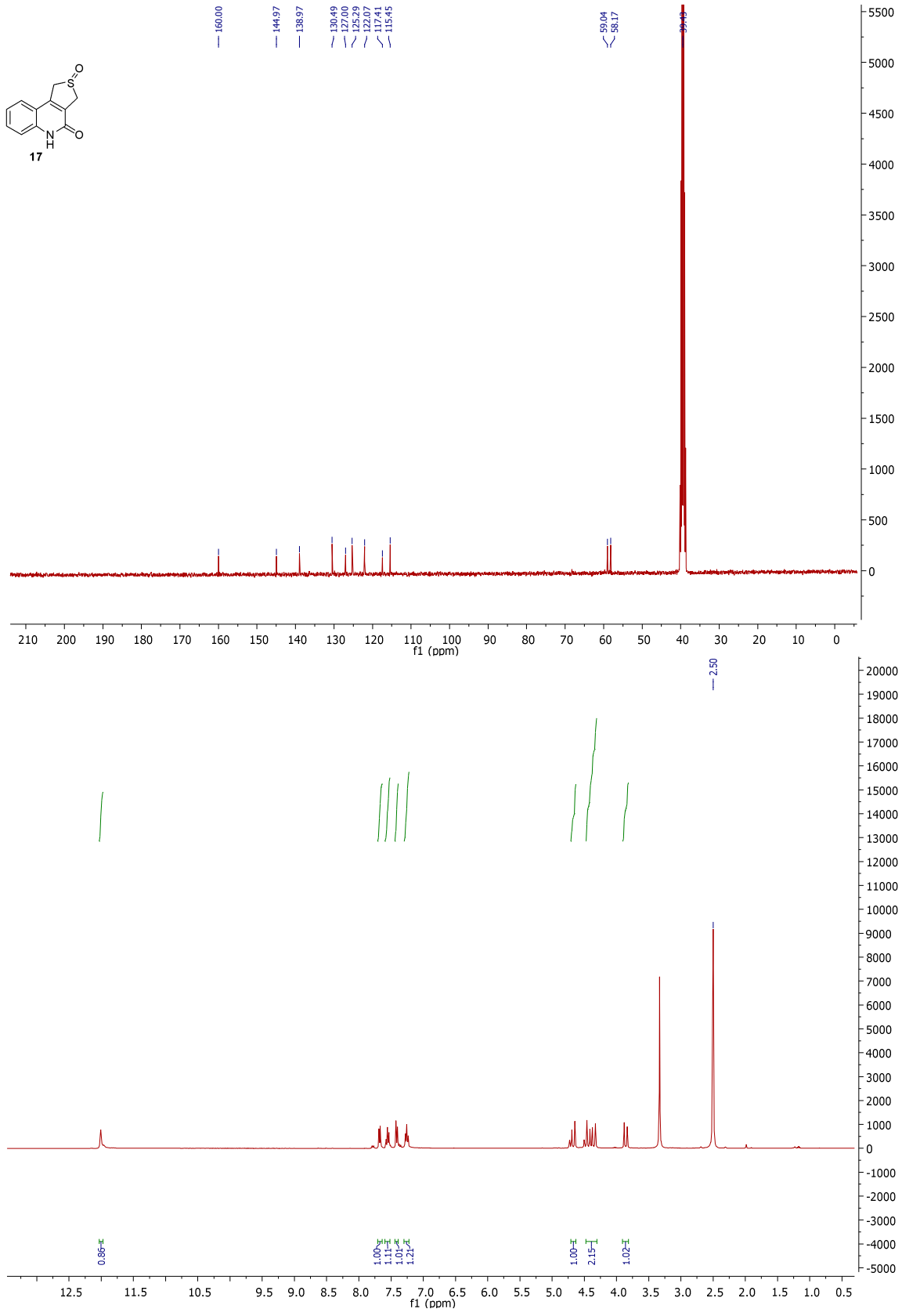
133.31
133.18
129.57
128.23
127.27
58.64
47.61
O
S
NH
O
13
f1 (ppm)
4.86
3.31
0.91
0.93
1.81
1.06
1.00
f1 (ppm)


168.33
139.28
131.78
131.07
128.82
123.19
56.80
39.43
36.59
O
S
NH
O
15
f1 (ppm)
2.50
0.97
2.02
2.00
1.06
1.26
1.06
f1 (ppm)


168.56
134.94
134.49
133.99
131.25
129.96
125.93
59.13
39.43
36.92
O2
S
NH
O
24
f1 (ppm)
3.33
0.99
2.12
1.99
1.92
f1 (ppm)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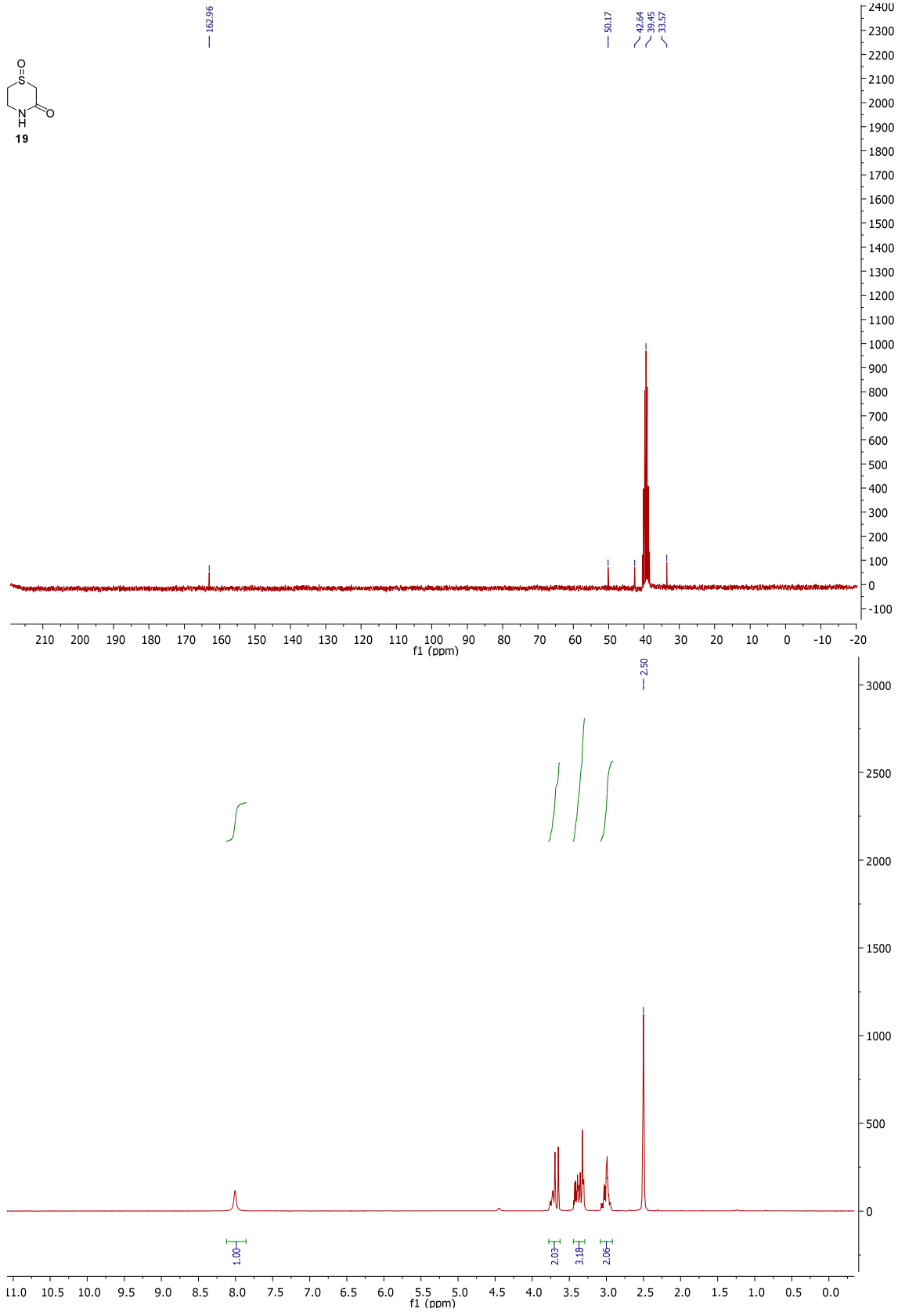
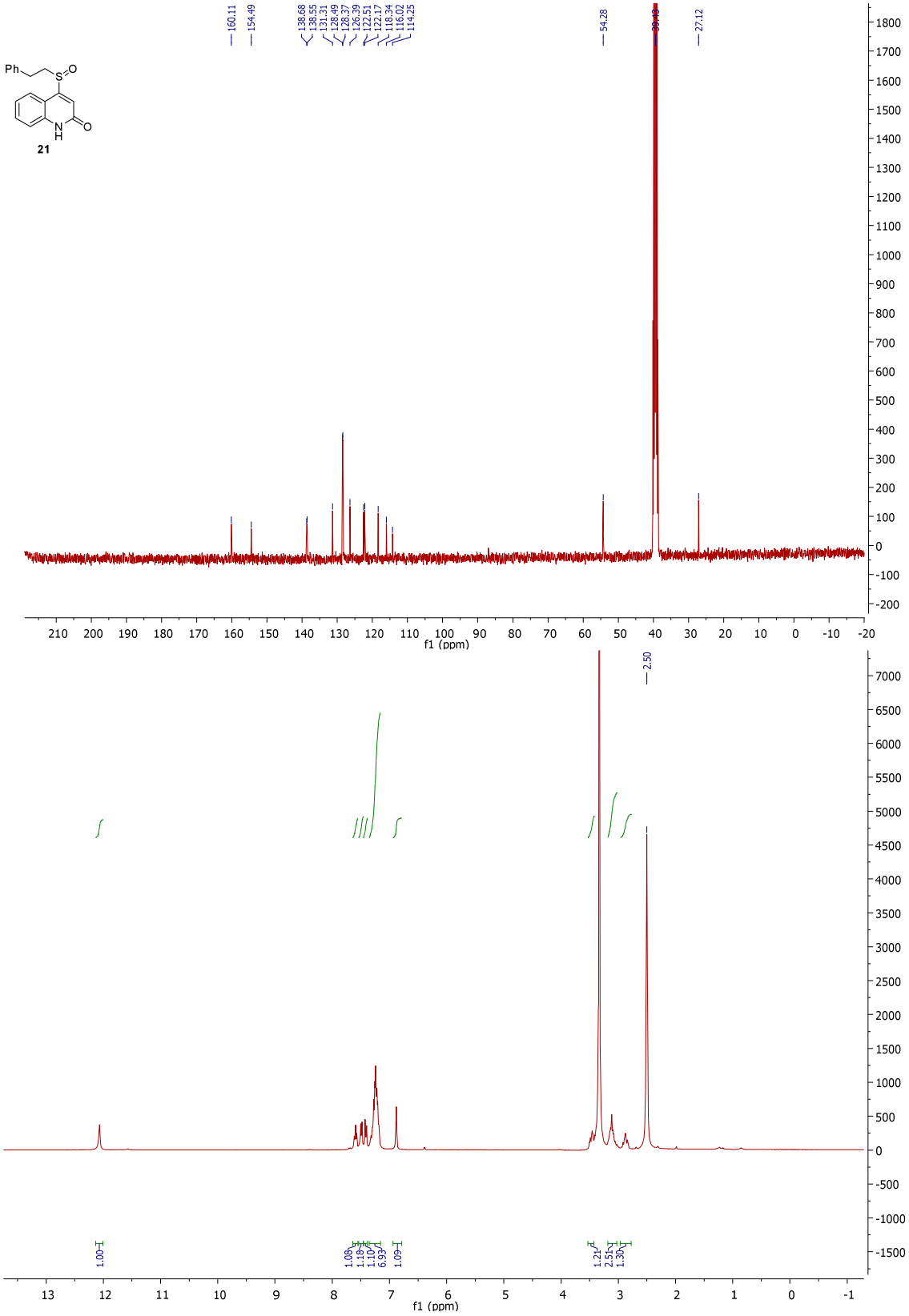
144.97
138.97
130.49
127.00
125.29
122.07
117.41
115.45
59.04
58.17
39.43
17
f1 (ppm)
2.50
0.86
1.00
1.11
1.01
1.21
1.00
2.15
1.02
f1 (ppm)


19
162.96
50.17
42.64
39.45
33.57
f1 (ppm)
2.50
1.00
2.03
3.18
2.05
f1 (ppm)


160.11
154.49
138.68
138.55
131.31
128.49
128.37
126.39
122.51
122.17
118.34
116.02
114.25
54.28
40.13
27.12
Ph
S
O
N
H
O
21
f1 (ppm)
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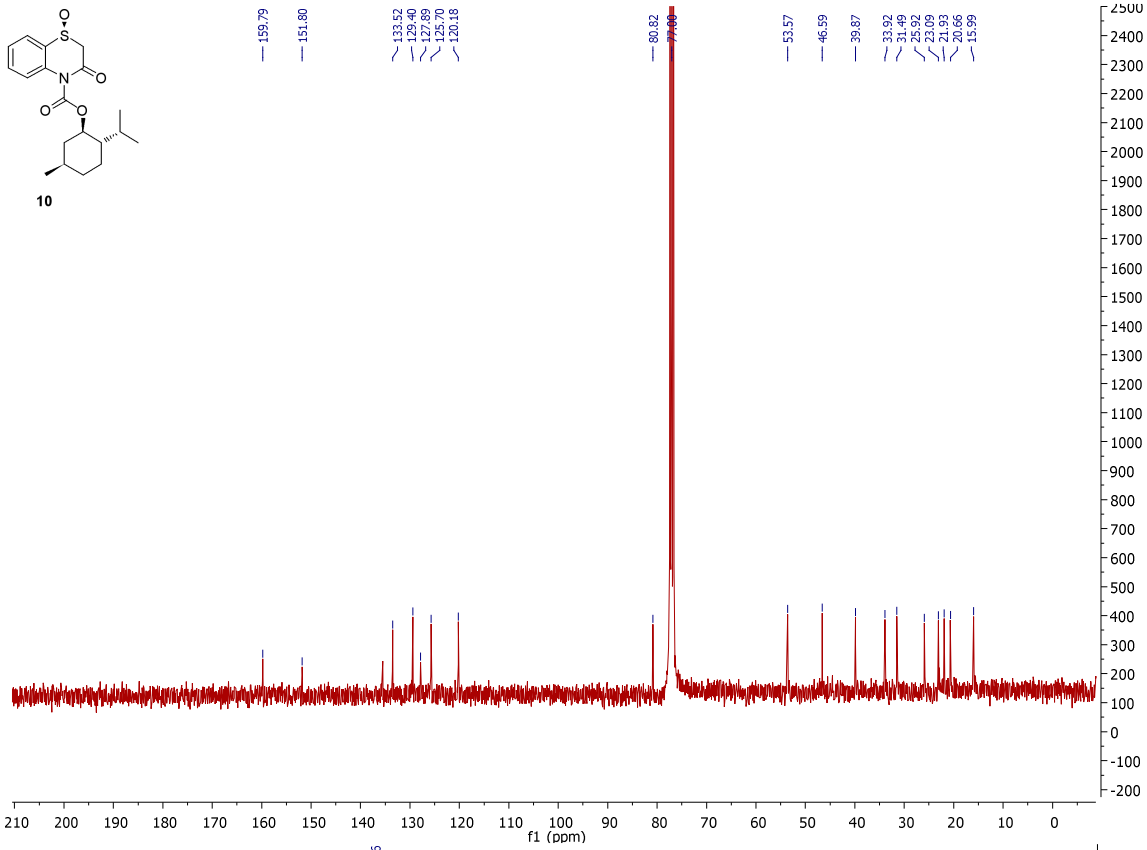
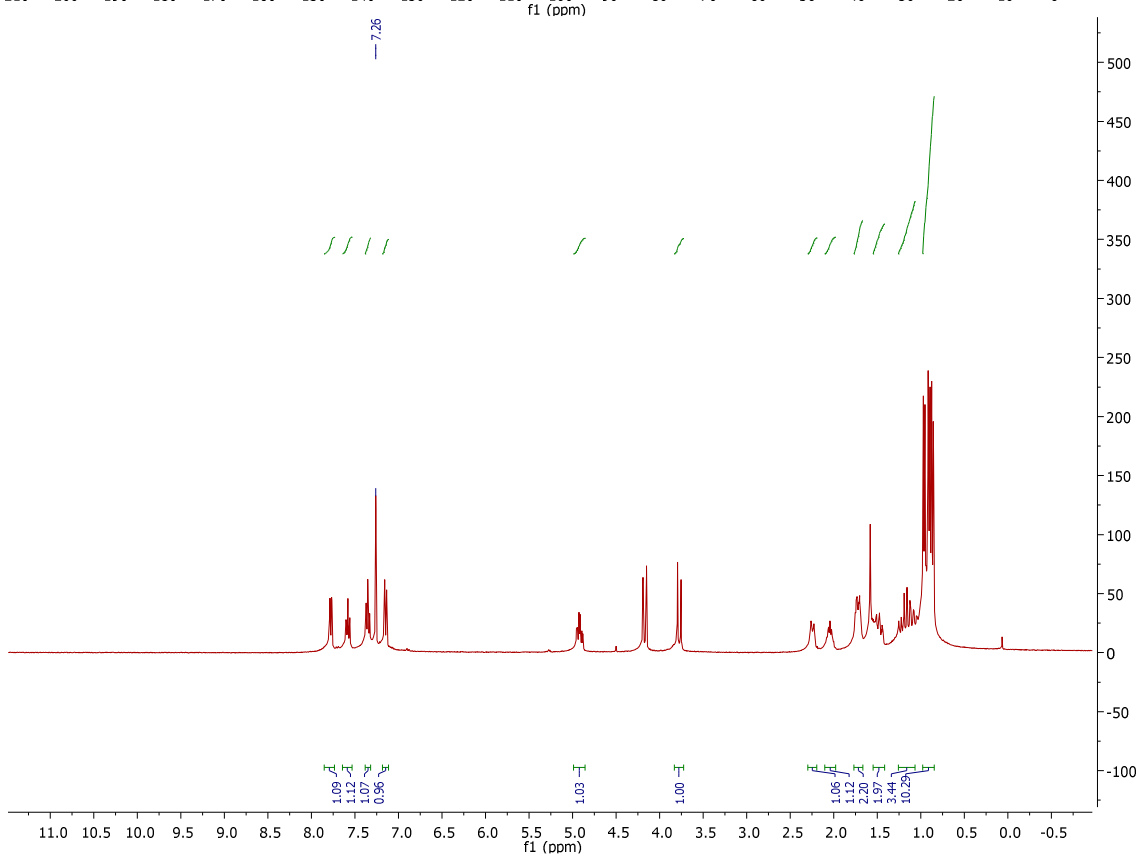
1.09
1.22
2.51
1.30
f1 (ppm)


10
159.79
151.80
133.52
129.40
127.89
125.70
120.18
80.82
77.00
53.57
46.59
39.87
33.92
31.49
25.92
23.09
21.93
20.66
15.99
f1 (ppm)


7.26
1.09
1.12
1.07
0.96
1.03
1.00
1.06
1.12
2.20
1.97
3.44
10.25
f1 (ppm)