Stereoselective Synthesis of Thiazino[4,3-*a*]indoles using ThiaPictet-Spengler Reaction of Indoles Bearing *N*-Tethered Thiols and Vinylogous Thiocarbonates

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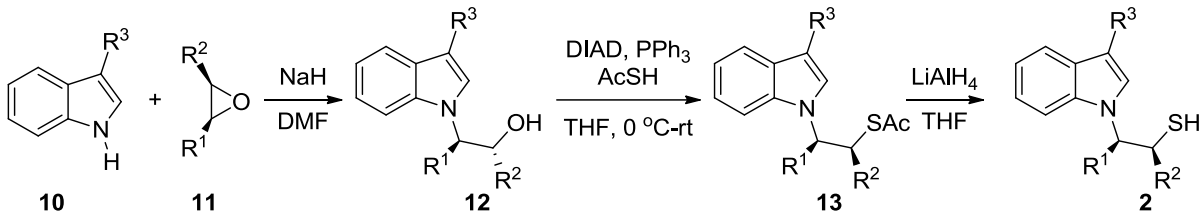
General experimental:

Melting points are recorded using sigma melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ (7.26 ppm for ^{1}H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.

High resolution mass measurements were carried out using Maxis impact (brucker) instrument using direct inlet mode. X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. Analytical thin-layer chromatographies (TLC) were performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and hexanes were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ stain. All small-scale dry reactions were carried out using standard syringe septum technique. Dry dichloromethane was prepared by refluxing over anhydrous P_2O_5 and distillation on to calcium chloride. Dry DMF was prepared by stirring over calcium hydride followed by downward distillation under reduced pressure onto molecular sieves. $BF_3{\cdot}OEt_2$, $InCl_3$, TFA, TMSOTf, $BiBr_3$, TfOH, $SnCl_4$, PPh_3, DIAD, $LiAlH_4$ and cyclohexanecarboxaldehyde were obtained from Aldrich. All other Lewis/Bronsted acids, aldehydes, NMM, ethylpropiolate, and thioacetic acid are commercial reagents and were used as such without further purification.

Experimental Procedure

Preparation of thiols (2) from indole:



General procedure for preparation of alcohol (12):

To magnetically stirred solution of NaH (1 equiv.) in DMF wad added indole **10** (1 equiv.) at 0 ^{o}C. After 30 min, epoxide **11** (1.1 equiv.) was added dropwise over 10 min and reaction was monitored by TLC. After complete consumption of starting material, it was quenched with saturated aqueous solution of NH_4Cl and diluted with H_2O, extracted with ethyl acetate, dried over anhydrous Na_2SO_4. Evaporation of solvent and purification of the residue by silica gel column chromatography afforded alcohol **12**.

General procedure for preparation of thioester (13):

In a 250 ml round bottom flask, PPh_3 (2 equiv.) was dissolve in minimal amount of dry THF, followed by dropwise addition of DIAD (2 equiv.) at 0 ^{o}C, reaction mixture was, stirred at same temperature to get white precipitate, after 1 hour a mixture of alcohol **12** (1 equiv.) and AcSH (thioacetic acid) (2 equiv.) in dry THF was added dropwise for 15 mins. Reaction was monitored by TLC. After completion of starting material, crude mixture was evaporated and purified by silica gel column chromatography to afford thioester **13**.

General procedure for preparation of thiol (2):

To a stirred solution of **13** (1 equiv.) in dry THF was added $LiAlH_4$ (2 equiv.) at 0 ^{o}C and allowed to stirred for 4 hours at room temperature, excess $LiAlH_4$ was quenched with saturated aq. solution of Na_2SO_4, filtered, evaporated, purified by column chromatography to afford **2.**

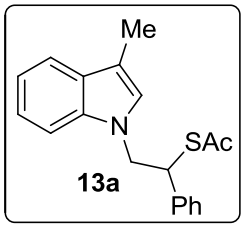
***S**-(2-(3-methyl-1*H*-indol-1-yl)-1-phenylethyl) ethanethioate (13a):**

Reaction of PPh_3 (16.7 g, 63.71 mmol) with DIAD (12.5 mL, 63.71 mmol), **12a** (R^3-Me, R^2-Ph, R^1-H) (8 g, 31.58 mmol) and AcSH (4.5 mL, 63.71 mmol) in dry THF (90 mL) following general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thioester **13a** (6 g, 66%) as colourless liquid.

Physical appearance: Colourless liquid.

R_f: 0.1 (1:9, ethyl acetate-petroleum ether).

IR (neat): 2924, 1652, 1465, 1259, 1214, 1165, 1112, 1016, 740, 698 cm^{-1}.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.51 (m, 2H), 7.28-7.22 (m , 4H), 7.16-7.10 (m, 3H), 6.5 (d, *J* = 0.8 Hz, 1H), 5.03 (t, *J* = 5.6 Hz, 1H), 4.59 (dd, *J* = 14.0, 5.6 Hz, 1H), 4.35 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.3 (s, 3H), 2.23 (d, *J* = 0.8 Hz, 3H).

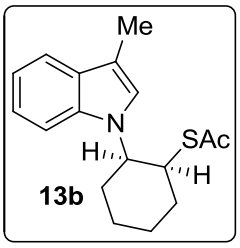
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 194.6 (C), 138.2 (C), 136.4 (C), 128.8 (2 × CH), 128.7 (2 × CH), 128.8 (C), 128.1 (CH), 128.0 (CH), 125.9 (CH), 121.7 (CH), 118.9 (CH), 110.4 (C), 109.6 (CH), 51.8 (CH_2), 48.2 (CH), 30.6 (CH_3), 9.6 (CH_3).

LRMS (ESI, M+Na^+): m/z: 332.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{19}H_{19}NNaOS$ 332.1071, found 332.1080.

***S**-((1*S**,2*R**)-2-(3-methyl-1H-indol-1-yl)cyclohexyl) ethanethioate (13b):**

Reaction of PPh_3 (9 g, 34.9 mmol) with DIAD (6.8 mL, 34.9 mmol), **12b** (R^3-Me) (4 g, 17.45 mmol) and AcSH (2.5 mL, 34.9 mmol) in dry THF (80 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thioester **13b** (3 g, 60%) as colourless liquid.



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2929, 1657, 1469, 1250, 1217, 1169, 1019, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.6 Hz , 1H), 7.32 (d, *J* = 7.6 Hz , 1H), 7.21-7.19 (m, 1H), 7.14-7.09 (m, 1H), 6.96 (s, 1H), 4.98 (q, *J* = 9.2 Hz, 1H), 4.58-4.55 (m, 1H), 4.36 (d, *J* = 3.2 Hz, 1H), 2.32 (d, *J* = 3.2 Hz, 2H), 2.21-2.17 (m, 2H), 2.10 (s, 3H), 2.06-2.01 (m, 2H), 1.91-1.81 (m, 2H), 1.51-1.43 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 194.1 (C), 136.3 (C), 132.3 (C), 122.6 (CH), 121.6 (CH), 121.4 (CH), 109.1 (CH), 56.1 (CH), 46.9 (CH), 31.6 (CH_2), 30.8 (CH_3), 29.1 (CH_2), 28.1 (CH_2), 25.7 (CH_2), 9.8 (CH_3).

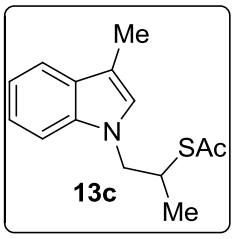
LRMS (ESI, M+Na^+): m/z: 310.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{21}NNaOS$ 310.1237, found 310.1238.

***S**-(1-(3-methyl-1*H*-indol-1-yl)propan-2-yl) ethanethioate (13c):**

Reaction of PPh_3 (5.5 g, 31.7 mmol) with DIAD (6.0 mL, 31.7 mmol), **12c** (R^3-Me, R^2-Me, R^1-H) (3 g, 15.8 mmol) and AcSH (4.0 mL, 31.7 mmol) in dry THF (60 mL), as described in the general procedure, followed by purification on silica gel column using

ethyl acetate-petroleum ether (1:99) as eluent furnished thioester **13c** (3 g, 75%) as yellow colour liquid.



Physical appearance: Yellow colour liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2925, 2829, 1685, 1652, 1465, 1259, 1214, 1165, 1112, 1016, 740, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.28 (td, *J* = 8.0, 0.8 Hz, 2H), 6.90 (d, *J* = 0.4 Hz, 1H), 4.42-4.39 (m, 2H), 3.61-3.59 (m, 1H), 2.30 (s, 3H), 2.35 (d, *J* = 0.4 Hz, 3H), 1.28 (d, *J* = 6.4 Hz, 3H).

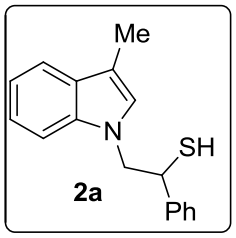
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 195.5 (C), 136.6 (C), 128.8 (C), 125.9 (CH), 121.8 (CH), 119.0 (CH), 118.9 (C), 110.7 (CH), 109.7 (CH), 51.4 (CH_2), 39.1 (CH), 22.8 (CH_3), 9.6 (CH_3), 5.6 (CH_3).

LRMS (ESI, M+Na^+): m/z: 270.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{14}H_{17}NNaOS$ 270.0921, found 270.0923.

***S**-2-(3-methyl-1*H*-indol-1-yl)-1-phenylethane-1-thiol (2a):**

Reaction of the thioester (1.5 g, 4.85 mmol) with $LiAlH_4$ (369 mg, 9.07 mmol) in dry THF (30 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiol **2a (**1 g, 77%) as colourless liquid.



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3029, 2919, 2861, 2556, 1652, 1614, 1465, 1387, 1354, 1331, 1216, 1177, 1014, 926, 741, 667 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.6, Hz, 1H), 7.29-7.01 (m, 8H), 6.69 (s, 1H), 4.49-5.11 (m, 1H), 4.44-4.29 (m, 2H), 2.21 (s, 3H), 1.84 (d, *J* = 4.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 140.6 (C), 136.2 (C), 129.1 (2 × CH), 129 (C), 128.8 (2 × CH), 128.3 (CH), 121.7 (CH), 119.3 (CH), 119.0 (CH), 110.7 (CH), 109.2 (CH), 107.6 (C), 54.9 (CH_2), 44.5 (CH), 9.7 (CH_3).

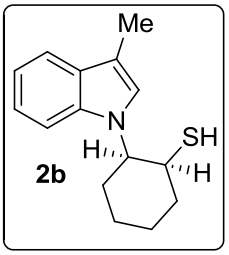
LRMS (ESI, M+Na^+): m/z: 290.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{17}NNaS$ 290.0981, found 290.0974.

(1*S,2*R**)-2-(3-methyl-1*H*-indol-1-yl)cyclohexanethiol (2b):**

Reaction of the thioester **13b** (1.5 g, 5.2 mmol) with $LiAlH_4$ (400 mg, 10.4 mmol) in dry THF (20 mL) as described in the general procedure, followed by purification on silica gel

column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiol **2b (**566 mg, 58%) as colourless liquid.



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9, EtOAc: Petroleum ether).

IR (neat): 2937, 2862, 2353, 1662, 1461, 1356, 1317, 1293, 1356, 1225, 1193, 1128, 791, 768, 687, 563 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.23 (td, *J* = 4.0, 3.2 Hz, 1H), 7.11-7.12 (m, 2H), 4.53 (dt, *J* = 12.0, 3.6 Hz, 1H), 3.9 (bs, 1H), 2.56 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.37 (s, 3H), 2.22-2.01 (m, 2H), 1.68-1.59 (m, 1H), 1.58-1.54 (m, 1H), 1.66-1.53 (m, 1H), 1.56-1.51 (m, 2H), 1.01 (d, *J* = 6.0 Hz, 1H).

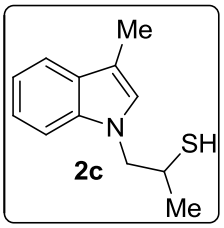
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 135.6 (C), 129.1 (C), 123.9 (CH), 121.3 (CH), 119.3 (CH), 119.0 (CH), 109.5 (C), 108.9 (CH), 57.4 (CH), 41.9 (CH), 32.3 (CH_2), 26.1 (CH_2), 25.6 (CH_2), 19.9 (CH_2), 9.8 (CH_3).

LRMS (ESI M+Na^+): m/z: 268.

HRMS (ESI M+Na^+): m/z calcd. for $C_{15}H_{19}NNaS$ 268.1141, found 268.1130.

1-(1*H*-indol-1-yl)propane-2-thiol (2c):

Reaction of the thioester **13c** (4 g, 8.0 mmol), and $LiAlH_4$ (500 mg, 16.0 mmol) in dry THF (20 mL) as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiol **2c** (2.8 g, 80%) as a colourless liquid.



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3054, 2962, 2920, 2553, 1614, 1465, 1354, 1332, 1207, 1188, 1127, 1081, 1014, 909, 791, 768, 629 cm^{-1}.

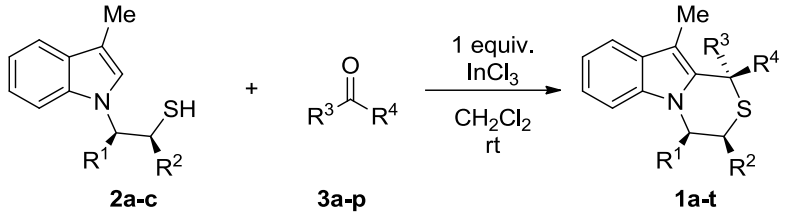
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0, Hz, 1H), 7.37 (d, *J* = 8.0, Hz, 1H), 7.35 (t, *J* = 8.0, Hz, 2H), 6.95 (s, 1H), 4.42-4.41 (m, 1H), 4.45-4.44 (m, 1H), 3.42-3.41 (m,1H), 2.40 (s, 3H), 1.60 (d, *J* = 6.4, Hz, 1H), 1.34 (d, *J* = 6.8, Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 136.4 (C), 128.9 (C), 126.1 (CH), 121.7 (CH), 119.2 (CH), 119.0 (C), 110.7 (C), 109.3 (CH), 55.3 (CH_2), 35.4 (CH), 22.6 (CH), 9.7 (CH_3).

LRMS (ESI, M+Na^+): m/z: 228.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{12}H_{15}NS$ 228.0817, found 228.0812.

General procedure for intermolecular thia-Pictet-Spengler cyclization for stereoselective synthesis of thiazinoindole 1:

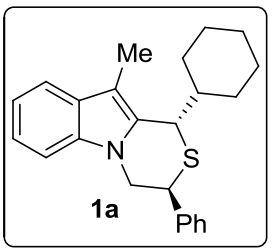


To a magnetically stirred solution of thiol **2** (1 equiv.) in dry CH_2Cl_2 was added aldehyde **3** (1 equiv.) at rt followed by $InCl_3$ (1 equiv.). Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion, extracted with CH_2Cl_2 (3 × 5 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc-petroleum ether as eluent to furnish thiazinoindole **1**.

(***Note***: In the cases where diastereomeric mixture of products was obtained, the isomers could not be separated and data for the major isomer is mentioned. In the cases where *ca*. 1:1 mixture of diastereomers was formed, all the peaks are mentioned.).

(1*S,3*S**)-1-cyclohexyl-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1a):**

Reaction of the thiol **2a** (40 mg, 0.149 mmol) with aldehyde **3a** (20 μL, 0.149 mmol) and $InCl_3$ (37 mg, 0.149 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1a** (50 mg, 93%) as a mixture of diastereomers (dr-9:1).



Physical appearance: Yellow colour liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2852, 2926, 1466, 1453, 1350, 1217, 1180, 1016, 698, 668 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.53-7.52 (m , 4H), 7.48-7.46 (m, 1H), 7.39-7.36 (m, 2H), 7.26-7.23 (m, 1H), 4.72 (dd, *J* = 10.4 , 4.1 Hz, 1H), 4.32 (m, 2H), 4.18 (dd, *J* = 10.4, 6.0 Hz, 2H), 2.39 (s, 3H), 2.31-2.32 (m, 1H), 1.75-1.85 (m, 5H), 1.26-1.35 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 138.9 (C), 136.8 (C), 131.9 (C), 129.01 (2 × CH), 128.5 (2 × CH), 128.3 (C), 121.3 (CH), 120.3 (CH), 119.4 (CH), 118.9 (CH), 108.5 (CH),

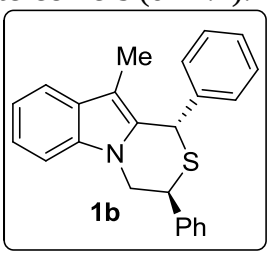
107.5 (C), 49.7 (CH_2), 48.2 (CH), 47.8 (CH), 44.9 (CH), 31.2 (2 × CH_2), 30.7 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 9.35 (CH_3).

LRMS (ESI, M+H$^+$): m/z: 362.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{24}H_{28}NS$ 362.1933, found 362.1937.

(1*S,3*S**)-10-methyl-1,3-diphenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1b):**

Reaction of the thiol **2a** (50 mg, 0.18 mmol) with aldehyde **3b** (21 μL, 0.18 mmol) and $InCl_3$ (42 mg, 0.18 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1b** (62 mg, 93%) as a mixture of diastereomers (dr-1:1).



Physical appearance: Colourless liquid.

R$_f$: 0.1 (1:9, ethyl acetate-petroleum ether).

IR (neat): 2188, 1603, 1453, 1354, 1176, 812, 743, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 2.4 Hz, 1H), 7.51-7.49 (m , 2H), 7.46-7.45 (m, 2H), 7.36-7.33 (m, 2H), 7.21-7.19 (m, 2H), 7.19-7.17 (m, 5H), 5.54 (s, 1H), 4.69 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.49 (dd, *J* = 12.0, 3.6 Hz, 1H), 4.31 (t, *J* = 12.0, 0.0 Hz, 1H), 1.96 (s, 3H).

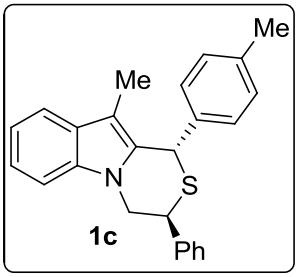
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 142.1 (C), 138.3 (C), 137.1 (C), 129.3 (C), 129.1 (2 × CH), 129.0 (2 × CH), 128.8 (CH), 128.8 (2 × CH), 128.5 (2 × CH), 127.1 (CH), 121.6 (CH), 120.1 (C), 119.9 (CH), 118.8 (CH), 110.7 (CH), 107.8 (C), 50.9 (CH_2), 44.4 (CH), 40.5 (CH), 8.5 (CH_3).

LRMS (ESI, M+K$^+$): m/z: 394.

HRMS (ESI, M+K$^+$): m/z calcd. for $C_{24}H_{21}NKS$ 394.1018, found 394.1026.

(1*S,3*S**)-10-methyl-3-phenyl-1-(*p*-tolyl)-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1c):**

Reaction of the thiol **2a** (64 mg, 0.239 mmol) with aldehyde **3c** (25 μL, 0.239 mmol) and $InCl_3$ (50 mg, 0.239 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1c** (68 mg, 93%) as a mixture of diastereomers (dr-2:1).



Physical appearance: Colourless liquid**.**

R$_f$: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2118, 1603, 1453, 1354, 1176, 812, 743, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 0.8 Hz, 1H), 7.48-7.40 (m, 6H), 7.39-7.28 (m, 3H), 7.26-7.15 (m, 3H), 5.53 (s, 1H), 4.73 (dd, *J* = 12.0, 3.6 Hz 1H), 4.39 (dd, *J* = 12.0, 3.6 Hz 1H), 4.23 (t, *J* = 12.0, 0.0 Hz 1H), 2.41 (s, 3H), 2.20 (s, 3H).

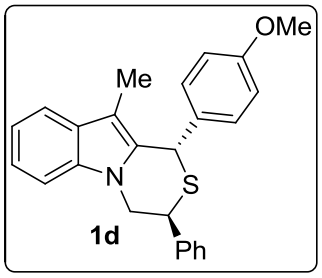
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 139.05 (C), 138.2 (C), 137.7 (C), 130.4 (C), 129.9 (2 × CH), 129.5 (2 × CH), 129.0 (C), 128.9 (CH), 128.6 (C), 128.5 (2 × CH), 121.4 (2 × CH), 120 (CH), 119.0 (CH), 118.8 (CH), 109.2 (CH), 107.6 (C), 50.5 (CH_2), 46.8 (CH), 41.1 (CH), 20.7 (CH_3), 9.2 (CH_3).

LRMS (ESI, M+K^+): m/z: 408.

HRMS (ESI, M+K^+): m/z calcd. for $C_{25}H_{23}NKS$ 408.1184, found 408.1183.

(1*S,3*S**)-1-(4-methoxyphenyl)-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1d):**

Reaction of the thiol **2a** (50 mg, 0.180 mmol) with aldehyde **3d** (18 μL, 0.180 mmol) and $InCl_3$ (42 mg, 0.180 mmol) in dry CH_2Cl_2 (5 mL), as described for in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1d** (68 mg, 85%) as a mixture of diastereomers (dr-3:1).



Physical appearance: White solid.

m.p.:158-160 ºC.

R_f: 0.3 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2921, 2854, 1608, 1582, 1508, 1454, 1354, 1250, 1033, 909, 834, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 6.0 Hz, 1H), 7.50-7.21 (m, 8H), 7.17 (d, *J* = 6.8 Hz, 2H), 6.87 (d, *J* = 6.8 Hz 2H), 5.53 (s, 1H), 4.7 (dd, *J* = 11.6 , 3.6 Hz, 1H), 4.36 (dd, *J* = 11.6, 5.6 Hz, 1H), 4.22 (dd, J = 11.6, 0.0 Hz, 1H), 3.85 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 158.6 (C), 138.41 (C), 137.0 (C), 134.0 (C), 129.6 (CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.3 (C), 128.2 (CH), 127.9 (2 × CH), 121.5 (C), 119.9 (CH), 118.7 (CH), 113.7 (2 × CH), 108.9 (CH), 107.6 (C), 55.3 (CH_3), 50.8 (CH_2), 40.9 (CH), 40.5 (CH), 8.4 (CH_3).

LRMS (ESI, M+Na^+): m/z: 408.

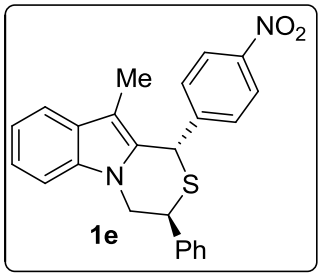
HRMS (ESI, M+Na^+): m/z calcd. for $C_{25}H_{23}NNaOS$ 408.1393, found 408.1394.

(1*S,3*S**)-10-methyl-1-(4-nitrophenyl)-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1e):**

Reaction of the thiol **2a** (50 mg, 0.186 mmol) with aldehyde **3e** (28 mg, 0.186 mmol) and $InCl_3$ (42 mg, 0.186 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure,

followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1e** (63 mg, 85%) as a mixture of diastereomers (dr-1.5:1)..

Physical appearance: Yellow colour liquid**.**



R_f: 0.4 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2924, 1602, 1520, 1466, 1346, 1178, 849, 741, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.39-7.20 (m, 11H), 5.54 (s, 1H), 4.69 (dd, *J* = 8.4, 0.0 Hz, 1H), 4.23-4.18 (m, 2H), 2.13 (s, 3H).

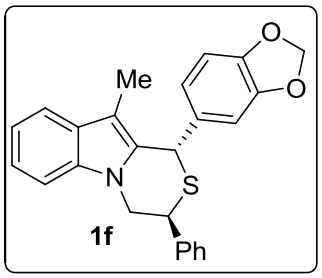
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 149.7 (C), 146.9 (C), 137.4 (C), 137.1 (C), 129.0 (2 × CH), 128.7 (2 × CH), 128.6 (CH), 128.2 (C), 127.8 (2 × CH), 127.4 (C), 123.7 (2 × CH), 122.1 (CH), 120.3 (CH), 118.9 (CH), 109.1 (CH), 107.6 (C), 50.6 (CH_2), 40.8 (CH), 40.7 (CH), 8.4 (CH_3).

LRMS (ESI M+H^+): m/z: 401.

HRMS (ESI M+H^+): m/z calcd. for $C_{24}H_{21}N_2O_2S$ 401.1318, found 401.1367.

(1*S,3*S**)-1-(benzo[*d*][1,3]dioxol-5-yl)-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1f):**

Reaction of the thiol **2a** (65 mg, 0.224 mmol) with aldehyde **3f** (36 mg, 0.224 mmol) and $InCl_3$ (54 mg, 0.224 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1f** (76 mg, 89%) as a mixture of diastereomers (dr-8:1).



Physical appearance: Brown colour liquid**.**

R_f: 0.3 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2978, 1520, 1425, 1216, 1044, 928, 909, 759, 671 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.48-7.18 (m , 8H), 6.81 (d, *J* = 1.6 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.60-6.57 (m, 1H), 5.97 (AB, *J* = 2.8, 1.2 Hz, 2H), 5.45 (s, 1H), 4.68 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.38 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.19 (dd, *J* = 4.0, 0.0 Hz, 1H), 2.17 (s, 3H).

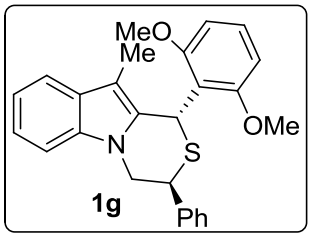
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 147.8 (C), 146.6 (C), 138.3 (C), 137.01 (C), 136.1 (C), 129.4 (C), 129 (2 × CH), 128.4 (C), 128.3 (CH), 127.9 (2 × CH), 121.7 (C), 121.6 (CH), 121.3 (CH), 119.9 (CH), 118.8 (CH), 108.9 (CH), 108.5 (CH), 107.8 (CH), 101.2 (CH_2), 50.8 (CH_2), 41.3 (CH), 40.5 (CH), 8.4 (CH_3).

LRMS (ESI, M+K$^+$): m/z: 438.

HRMS (ESI, M+K$^+$): m/z calcd. for $C_{25}H_{21}NO_2SK$ 438.0938, found 438.0925.

(1*S,3*S**)-1-(2,6-dimethoxyphenyl)-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-a]indole (1g):**

Reaction of the thiol **2b** (30 mg, 0.112 mmol) with aldehyde **3g** (19 mg, 0.112 mmol) and $InCl_3$ (25 mg, 0.112 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (2:98) as eluent furnished thiazinoindole **1g** (52 mg, 85%) as a mixture of diastereomers (dr-4:1).



Physical appearance: White solid.

R$_f$: 0.2 (1:9 ethyl acetate-petroleum ether).

m.p.:178-180 ^oC.

IR (neat): 2933, 2859, 1559, 1501, 1484, 1460, 1446, 1354, 1250, 1236, 1179, 1092, 1039, 938, 795, 739, 613 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 1H), 7.46-7.30 (m, 6H), 7.25-7.15 (m , 2H), 6.88 (d, *J* = 5.2 Hz, 1H), 6.76 (dd, *J* = 8.2, 3.2 Hz 1H), 6.28 (d, *J* = 2.8 Hz, 1H), 5.82 (s, 1H), 4.74 (dd, *J* = 9.3 , 4.0 Hz, 1H), 4.36 (dd, *J* = 9.3, 4.0 Hz, 1H), 4.22 (dd, J = 9.3 Hz, 1H), 3.93 (s, 3H), 3.67 (s, 3H), 2.08 (s, 3H).

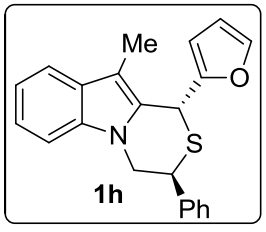
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.0 (C), 150.6 (C), 138.4 (C), 136.9 (C), 132,4 (C), 129.1 (C), 128.9 (2 × CH), 128.5 (C), 128.3 (CH), 128.1 (2 × CH), 121.3 (CH), 119.8 (CH), 118.7 (CH), 113.4 (CH), 11.4 (CH), 110.8 (CH), 108.9 (CH),107.5 (C), 56.2 (CH_3), 52.2 (CH_3), 51.1 (CH_2), 40.6 (CH), 45.5 (CH), 8.4 (CH_3).

LRMS (ESI, M+Na$^+$): m/z: 438.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{26}H_{25}NNaO_2S$ 438.1499, found 438.1498.

(1*R,3*S**)-1-(furan-2-yl)-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1h):**

Reaction of the thiol **2a** (50 mg, 0.186 mmol) with aldehyde **3h** (19 μL, 0.186 mmol) and $InCl_3$ (42 mg, 0.186 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (2:98) as eluent furnished thiazinoindole **1h** (52 mg, 87%) as a mixture of diastereomers (dr-8:1).



Physical appearance: Colourless liquid.

R$_f$: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3020, 2978, 1520, 1425, 1216, 1044, 928, 909, 759, 671 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.43-7.35 (m , 5H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 2H), 6.29 (t, *J* =2.8 Hz, 1H), 5.91 (d, *J* = 2.8 Hz, 1H), 5.53 (s, 1H), 4.68 (dd, J = 12.0, 3.8 Hz, 1H), 4.55 (dd, J = 12.0, 3.8 Hz, 1H), 4.16 (dd, J = 12.0, 0.0 Hz, 1H), 2.22 (s, 3H).

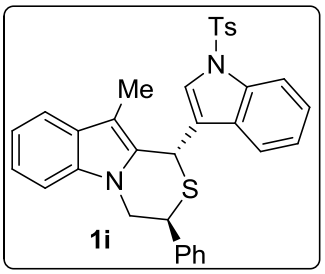
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.2 (C), 142.6 (CH),138.1 (C), 137.0 (C), 129.1 (2 × CH), 128.5 (CH), 128.2 (C), 128.2 (2 × CH), 127.3 (C), 121.8 (CH), 120.0 (CH), 119.0 (CH), 110.3 (CH), 109.0 (CH), 108.1 (CH), 108.0 (C), 50.9 (CH_2), 41.5 (CH), 36.0 (CH), 8.4 (CH_3).

LRMS (ESI, M+K^+): m/z: 384.

HRMS (ESI, M+K^+): m/z calcd. for $C_{22}H_{19}NKOS$ 384.0819, found 384.0816.

(1*S,3*S**)-10-methyl-3-phenyl-1-(1-tosyl-1*H*-indol-3-yl)-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1i):**

Reaction of the thiol **2a** (68 mg, 0.235 mmol) with aldehyde **3i** (70 mg, 0.235 mmol) and $InCl_3$ (52 mg, 0.235 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (8:92) as eluent furnished thiazinoindole **1i** (130 mg, 99%) as a mixture of diastereomers (dr-4:1).



Physical appearance: Brown solid.

m.p.:167-169 ºC.

R_f: 0.8 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3025, 2960, 2927, 1466, 1455, 1354, 1355, 1345, 1298, 1201, 1213, 1257, 1198, 1180, 1013, 898, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.69-7.64 (m, 3H), 7.21-7.41 (m, 12H), 6.89 (d, *J* = 1.2 Hz, 1H), 5.64 (d, *J* = 1.2. Hz, 1H), 4.71 (dd, *J* = 11.6, 3.2 Hz, 1H), 4.29 (dd, *J* = 11.6, 3.2 Hz, 1H), 4.21-4.16 (m, 1H), 2.36 (s, 3H), 2.11 (s, 3H).

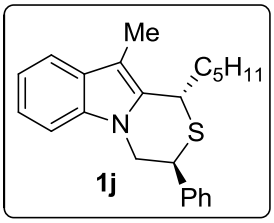
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 145.1 (C), 137.8 (C), 137.1 (C), 136.1 (C), 135.1 (C), 129.9 (2 × CH), 129.9 (C), 129.0 (C), 128.9 (2 × CH), 128.4 (C), 128.3 (CH), 128.1 (C), 127.9 (2 × CH), 126.8 (2 × CH), 125.2 (CH), 125.1 (CH), 123.5 (CH), 121.8 (CH), 120.5 (CH), 120.1 (CH), 118.9 (CH), 114.2 (CH), 109.1 (CH), 107.3 (C), 51.1 (CH_2), 41.4 (CH), 34.2 (CH), 21.6 (CH_3), 8.4 (CH_3).

LRMS (ESI, M+Na^+): m/z: 571.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{33}H_{28}N_2O_2SNa$ 571.1488, found 571.1484.

(1*S,3*S**)-10-methyl-1-pentyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1j):**

Reaction of the thiol **2a** (40 mg, 0.149 mmol) with aldehyde **3j** (18 μL, 0.149 mmol) and $InCl_3$ (32 mg, 0.149 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1j** (52 mg, 92%) as a mixture of diastereomers (dr-2:1).



Physical appearance: Colourless liquid**.**

R*f*: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3029, 2953, 2925, 2868, 1466, 1353, 1181, 910, 739, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 1H), 7.55-7.51 (m, 2H), 7.47 (t, *J* = 6.0 Hz, 2H), 7.42 (t, *J* = 6.0 Hz, 2H), 7.32-7.21 (m, 2H), , 4.67 (dd, *J* = 7.2, 3.2 Hz, 1H), 4.41 (dt, *J* = 12.0, 6.0 Hz, 1H), 4.21 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.10 (t, *J* = 10.0 Hz, 1H), , 2.37 (s, 3H), 1.93-1.92 (m, 1H), 1.46-1.45 (m, 5H), 1.12-1.11 (m, 2H), 1.01 (t, *J* = 5.6 Hz, 3H).

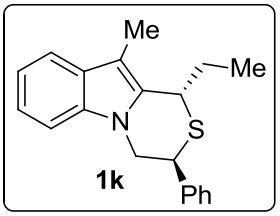
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 138.8 (C), 136.9 (C), 132.7 (C), 129.0 (2 × CH), 128.5 (C), 128.3 (CH), 127.9 (2 × CH), 121.3 (CH), 119.8 (CH), 118.4 (CH), 108.9 (CH), 106.5 (C), 51.0 (CH_2), 40.3 (CH), 38.4 (CH), 37.0 (CH_2), 31.4 (CH_2), 27.6 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 8.5 (CH_3).

LRMS (ESI, M+Na$^+$): m/z: 372.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{23}H_{27}NNaS$ 372.1758, found 372.1756.

(1*S,3*S**)-1-ethyl-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1k):**

Reaction of the thiol **2a** (50 mg, 0.186 mmol), aldehyde **3k** (15 mg, 0.186 mmol) and $InCl_3$ (0.186 mmol, 42 mg) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1k** (51 mg, 91%) as a mixture of diastereomers (dr-1:1).



Physical appearance: Colourless liquid.

R*f*: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3025, 2960, 2927, 1466, 1455, 1354, 1213, 1180, 1013, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 3.2 Hz, 1H), 7.52-7.47 (m, 2H), 7.46-7.41 (m, 2H), 7.39-7.7.33 (m, 1H), 7.28-7.25 (m, 2H), 7.24-7.21 (m, 1H), 4.31 (dd, *J* = 7.6, 4.2 Hz, 1H), 4.27 (dd, *J* = 9.6, 4.2 Hz, 1H), 4.2 (t, *J* = 7.6 Hz, 1H), 3.91 (dd, *J* = 9.6, 0 Hz, 1H), 2.23 (s, 3H), 1.92 (td, *J* = 7.64, 7.6 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H).

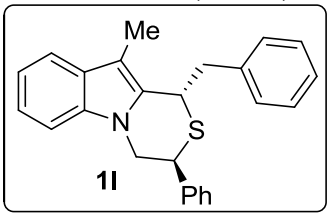
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 139.1 (C), 136.6 (C), 132.1 (C), 129.1 (C), 128.7 (2 × CH), 128.6 (2 × CH), 128.3 (CH), 127.9 (CH), 121.2 (CH), 119.9 (CH), 108.5 (CH), 106.7 (C), 49.1 (CH_2), 47.4 (CH), 40.1 (CH), 30.2 (CH), 34.7 (CH_2), 11.6 (CH_3), 8.6 (CH_3).

LRMS (ESI, M+K^+): m/z-346.

HRMS (ESI, M+K^+): m/z calcd. for $C_{20}H_{21}NKS$ 346.1016, found 346.1026.

(1*S,3*S**)-1-ethyl-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1l):**

Reaction of the thiol **2a** (50 mg, 0.186 mmol) with aldehyde **3l** (15 μL, 0.186 mmol) and $InCl_3$ (42 mg, 0.186 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1l** (51 mg, 91%) as a mixture of diastereomers (dr-3:1).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3027, 2961, 2927, 1464, 1455, 1354, 1213, 1180, 1013, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 4.0 Hz, 1H), 7.56-7.39 (m, 6H), 7.37-7.26 (m, 4H), 7.25-7.16 (m, 2H), 7.03 (dd, *J* = 7.2, 2.0 Hz, 1H), 4.75 (dd, *J* = 7.6, 4.2 Hz, 1H), 4.27 (dd, *J* = 9.6, 4.2 Hz, 1H), 4.23 (t, *J* = 9.6 Hz, 1H), 4.06 (dd, *J* = 9.6, 0.0 Hz, 1H), 3.33 (dd, *J* = 12.6, 6.0 Hz, 2H), 1.98 (s, 3H).

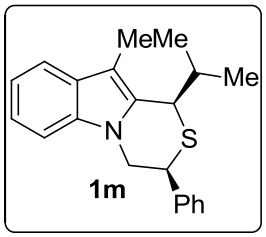
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 138.5 (C), 137.2 (C), 136.2 (C), 130.1 (C), 129.9 (2 × CH), 129.0 (C), 128.5 (2 × CH), 128.3 (2 × CH), 128.2 (2 × CH), 127.9 (CH), 127.3 (CH), 126.8 (CH), 121.3 (CH), 119.3 (CH), 108.4 (CH), 107.2 (C), 49.2 (CH_2), 47.6 (CH), 40.4 (CH), 39.8 (CH_2), 8.2 (CH_3).

LRMS (ESI, M+H^+): m/z: 370.

HRMS (ESI, M+H^+): m/z calcd. for $C_{25}H_{24}NS$ 370.1624, found 370.1628.

(1*S,3*S**)-1-isopropyl-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1m):**

Reaction of the thiol **2a** (50 mg, 0.186 mmol) with aldehyde **3m** (20 μL, 0.186 mmol) and $InCl_3$ (42 mg, 0.186 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1m** (53 mg, 89%) as a mixture of diastereomers (dr-9:1).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2960, 2927, 1466, 1455, 1354, 1213, 1257, 1198, 1180, 1013, 898, 741 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ 7.62 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.25-7.20 (m, 2H), 7.18-7.15 (m, 2H), 7.12-6.99 (m, 3H), 6.93 (dd, *J* = 6.0, 2.0 Hz, 1H), 4.22 (dd, *J* = 12.4, 2.8 Hz, 1H), 4.12 (d, *J* = 8.4 Hz, 1H), 3.81 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.87 (dd, *J* = 11.6, 0.0 Hz, 1H), 2.16 (s, 3H), 2.11(m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H).

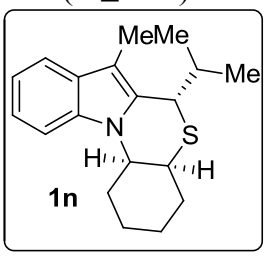
^{13}C NMR (100 MHz, C_6D_6, DEPT): δ 138.9 (C), 136.71 (C), 132 (C), 129.3 (C), 128.6 (2 × CH), 128.2 (2 × CH), 127.9 (CH), 121.4 (CH), 119.5 (CH), 118.9 (CH), 108.5 (CH), 106.7 (C), 49.4 (CH_2), 47.7 (CH), 45.6 (CH), 37.4 (CH), 20.4 (CH_3), 19.6 (CH_3), 8.9 (CH_3).

LRMS (ESI, M+Na^+): m/z: 344.

HRMS (ESI, M+Na^+): m/z calcd for $C_{21}H_{23}NNaS$ 344.1438, found 344.1443.

(4a*S,6*S**,12a*R**)-6-isopropyl-7-methyl-2,3,4,4a,6,12a-hexahydro-1*H*-benzo[5,6][1,4]thiazino[4,3-a]indole(1n):**

Reaction of the thiol **2b** (50 mg, 0.203 mmol) with aldehyde **3n** (19 μL, 0.203 mmol) and $InCl_3$ (51 mg, 0.203 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1n** (57 mg, 89%) as a single diastereomer (dr≥19:1).



Physical appearance: Colourless liquid.

R_f: 0.3 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2933, 2859, 1559, 1501, 1484, 1460, 1446, 1354, 1250, 1236, 1179, 1092, 1039, 938, 795, 739, 613, 500 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.35-7.33 (m, 1H), 7.28-7.17 (m, 2H), 4.69 (d, *J* = 5.0, Hz, 1H), 4.44 (dd, *J* = 12.5, 4.0 Hz, 1H), 3.52 (bs, 1H), 2.62-2.52 (m, 1H), 2.35 (s, 3H), 2.15-2.07 (m, 3H), 1.99-1.87 (m, 3H), 1.61-1.55 (m, 2H), 1.14 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H).

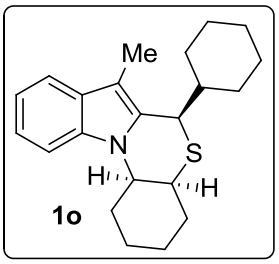
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 136.4 (C), 131.1 (C), 128.6 (C), 121.0 (CH), 119.3 (CH), 118.2 (CH), 108.7 (CH), 106.9 (C), 56.0 (CH), 45.0 (CH), 40.4 (CH), 34.2 (CH), 30.5 (CH_2), 28.0 (CH_2), 25.2 (CH_2), 20.7 (CH_3), 20.2 (CH_2), 17.6 (CH_3), 10.0 (CH_3).

LRMS (ESI, M+K^+): m/z: 338

HRMS (ESI, M+K^+): m/z calcd. for $C_{19}H_{25}NKS$ 338.1340, found 338.1344.

(4a*S,6*S**,12a*R**)-6-cyclohexyl-7-methyl-1,2,3,4,4a,12a-hexahydro-6*H*-benzo[5,6][1,4]thiazino[4,3-*a*]indole (1o):**

Reaction of the thiol **2b** (50 mg, 0.203 mmol), aldehyde **3a** (24 μL, 0.203 mmol) and $InCl_3$ (51 mg, 0.203 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1o** (65 mg, 93%) as a single diastereomer (dr≥19:1).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2923, 2860, 1521, 1511, 1485, 1460, 1420, 1354, 1250, 1236, 938, 795, 739, 613, 500 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.28-7.24 (m, 1H), 7.21 (t, *J* = 9.0 Hz, 1H), 4.66 (d, *J* = 4.5, Hz, 1H), 4.47 (dd, *J* = 10.0, 9.0 Hz, 1H), 3.53 (bs, 1H), 2.55 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.37 (s, 3H), 2.31-2.30 (m, 2H), 2.18-2.07 (m, 4H), 2.01-1.73 (m, 4H), 1.63-1.42 (m, 5H), 1.37-1.23 (m, 3H).

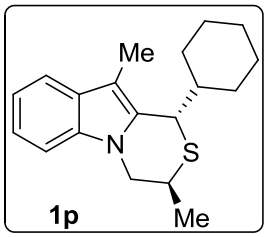
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 136.4 (C), 131.2 (C), 128.6 (C), 121.0 (CH), 119.3 (CH), 118.2 (CH), 108.7 (CH), 106.9 (C), 56.0 (CH), 45.0 (CH), 45.1 (CH), 40.4 (CH), 34.2 (2 × CH_2), 30.5 (CH_2), 28.0 (2 × CH_2), 25.2 (CH_2), 20.7 (CH_2), 20.0 (CH_2), 17.6 (CH_2), 10.1 (CH_3).

LRMS (ESI, M +K^+): m/z: 378.

HRMS (ESI, M +K^+): m/z calcd. for $C_{22}H_{29}NKS$ 378.1669, found 378.1652.

(1*S,3*S**)-1-cyclohexyl-3,10-dimethyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1p):**

Reaction of the thiol **2c** (100 mg, 0.487 mmol) with aldehyde **3a** (60 μL, 0.487 mmol) and $InCl_3$ (107 mg, 0.487 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished



thiazinoindole **1p** (140 mg, 92%) as a mixture of diastereomers (dr-1:1).

Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2901, 2849, 1509, 1501, 1454, 1420, 1419, 1354, 1255, 1236, 1175, 1094, 1039, 938, 795, 739, 500 cm^{-1}.

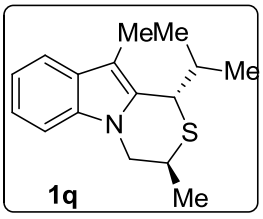
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.35-7.25 (m, 2H), 7.29-7.18 (m, 4H), 4.56 (dd, *J* = 9.6, 3.2 Hz, 1H), 4.57 (dd, *J* = 12.8, 3.2 Hz, 1H), 4.46 (dd, *J* = 12.0, 3.2 Hz, 1H), 4.59 (d, *J* = 8.1 Hz, 1H), 3.93 (d, *J* = 8.8 Hz, 1H), 3.86 (t, *J* = 9.6 Hz, 1H), 3.73 (t, *J* = 9.6 Hz, 1H), 3.69-3.63 (m, 1H), 3.16-3.11 (m, 1H), 2.35 (s, 3H), 2.34 (s, 3H), 2.31-2.28 (m, 1H), 2.19-2.16 (m, 1H), 1.87-1.85 (m, 3H), 1.77-1.68 (m, 5H), 1.65-1.61 (m, 5H), 1.27 (d, *J* = 6.7 Hz, 6H), 1.23-1.15 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 137.8 (C), 136.2 (C), 131.9 (C), 131.8 (C), 128.6 (C), 128.4 (C), 121.2 (CH), 121.1 (CH), 119.6 (CH), 119.1 (CH), 118.7 (CH), 118.5 (CH), 108.8 (CH), 108.3 (CH), 107.3 (C), 107.1 (C), 51.1 (CH_2), 50.1 (CH_2), 47.5 (CH), 45.1 (CH), 44.1 (CH), 43.2 (CH), 38.2 (CH), 32.9 (CH). 31.6 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 30.4 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 26.4 (2 × CH_2), 26.3 (2 × CH_2), 19.9 (CH_3), 19.2 (CH_3), 9.6 (CH_3), 9.3 (CH_3).

LRMS (ESI, M+Na^+): m/z: 322.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{19}H_{25}NNaS$ 322.1600, found 322.1609.

(1*S,3*S**)-1-isopropyl-3,10-dimethyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1q):** Reaction of the thiol **2c** (100 mg, 0.487 mmol) with aldehyde **3m** (44 μL, 0.487 mmol) and $InCl_3$ (107 mg, 0.487 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1q** (119 mg, 91%) as a mixture of diastereomers (dr-1:1).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2921, 2820, 1569, 1519, 1255, 1236, 1175, 1094, 1039, 938, 795, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.35-7.19 (m, 6H), 4.26 (d, *J* = 12.0, Hz, 1H), 4.29 (dd, *J* = 7.2, 3.6 Hz, 1H), 3.82 (dd, *J* = 7.4, 3.5 Hz, 1H), 3.72 (d, *J* = 12.0, Hz, 1H), 3.34 (t, *J* = 7.2 Hz, 1H), 3.24 (t, *J* = 6.0 Hz, 1H), 2.71-2.61 (m,1H), 3.16-3.12 (m, 1H), 2.36 (s, 6H), 2.21-2.11 (m, 2H), 1.43 (d, *J* = 6.8 Hz, 6H), 1.21 (d, *J* = 6.4 Hz, 6H), 1.02 (d, *J* = 6.4 Hz, 6H).

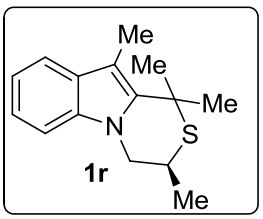
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 137.6 (C), 136.1 (C), 132.2 (C), 132.1 (C), 128.6 (C), 128.3 (C), 121.6 (CH), 121.2 (CH), 121.1 (CH), 119.5 (CH), 119.2 (CH), 118.6 (CH), 108.3 (CH), 108.2 (CH), 106.8 (C), 106.9 (C), 51.0 (CH_2), 51.1 (CH_2), 44.9 (CH), 44.1 (CH), 37.8 (CH), 37.6 (CH), 35.5 (CH), 32.8 (CH), 21.1 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 19.7 (CH_3), 19.6 (CH_3), 19.1 (CH_3), 9.6 (CH_3), 9.1 (CH_3).

LRMS (ESI, M+Na$^+$): m/z: 282.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{16}H_{21}NNaS$ 282.1287, found 282.1286.

(*S)-1,1,3,10-tetramethyl-3,4-dihydro-1H-[1,4]thiazino[4,3-a]indole (1r):**

Reaction of the thiol **2c** (50 mg, 0.243 mmol) with 2, 2-dimethoxy propane **3n (**33 μL, 0.243 mmol) and $InCl_3$ (58 mg, 0.243 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1r** (72 mg, 89%).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2973, 2859, 1559, 1551, 1484, 1460, 1449, 1354, 1255, 1236, 1175, 1094, 1039, 938, 795, 739, 500 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.40-7.18 (m, 3H), 4.52 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.69 (t, *J* = 11.6 Hz, 1H), 3.42-3.56 (m, 1H), 2.48 (s, 3H), 1.93 (s, 3H), 1.85 (s, 3H), 1.45 (d, *J* = 6.4 Hz, 3H).

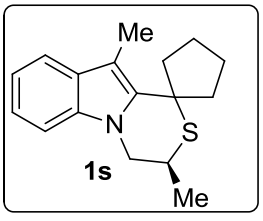
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 136.3 (C), 135.5 (C), 128.7 (C), 121.4 (CH), 119.5 (CH), 119.2 (CH), 108.8 (CH), 105.1 (C), 51.5 (CH_2), 42.1 (C), 32.6 (CH), 32.1 (CH_3), 29.9 (CH_3), 18.1 (CH_3), 10.8 (CH_3).

LRMS (ESI, M+Na$^+$): m/z: 268.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{15}H_{19}NNaS$ 268.1130, found 268.1129.

(*S)-3',10'-dimethyl-3',4'-dihydrospiro[cyclopentane-1,1'-[1,4]thiazino[4,3-*a*]indole](1s):**

Reaction of the thiol **2c** (60 mg, 0.292mmol) with cyclopentanone **3o (**51 μL, 0.292 mmol) and $InCl_3$ (65 mg, 0.292 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1s** (80 mg, 92%).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2982, 2832, 1520, 1501, 1482, 1460, 1449, 1354, 1255, 1094, 1039, 938, 795, 739, 500 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.32-7.18 (m, 3H), 4.53 (dd, *J* = 12, 3.6 Hz, 1H), 3.81 (t, *J* = 12.0 Hz, 1H), 3.43-3.41 (m, 1H), 2.44 (s, 3H), 2.41-2.33 (m, 1H), 2.22-2.21 (m, 1H), 2.11-2.01 (m, 6H), 1.45 (d, *J* = 6.8 Hz, 3H).

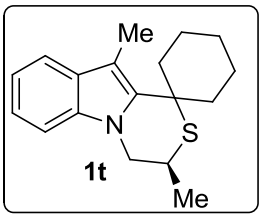
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 135.8 (C), 135.4 (C), 128.7 (C), 121.2 (CH), 119.5 (CH), 118.1 (CH), 108.6 (CH), 104.3 (C), 52.2 (C), 51.5 (CH_2), 43.7 (CH_2), 40.6 (CH_2), 33.8 (CH), 25.5 (CH_2), 25.4 (CH_2), 18.1 (CH_3), 10.4 (CH_3).

LRMS (ESI, M+Na^+): m/z: 294.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{17}H_{21}NNaS$ 294.1287, found 294.1279.

(*S)-3',10'-dimethyl-3',4'-dihydrospiro[cyclohexane-1,1'-[1,4]thiazino[4,3-*a*]indole](1t):**

Reaction of the thiol **2c** (50 mg, 0.243 mmol) with cyclohexanone **3p** (33 μL, 0.243 mmol) and $InCl_3$ (58 mg, 0.243 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **1t** (72 mg, 89%).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2963, 2852, 1532, 1540, 1496, 1433, 1449, 1354, 1255, 1236, 1175, 1094, 1039, 938, 795, 739, 500 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.38 (m, 2H), 7.32-7.23 (m, 2H), 4.61 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.84 (t, *J* =11.3 Hz, 1H), 3.88-3.36 (m, 1H), 2.74 (td, *J* = 7.2, 1.2 Hz, 1H), 2.62 (s, 3H), 2.45-2.11 (m, 3H), 1.94-1.71 (m, 6H), 1.54 (d, *J* = 6.5 Hz, 3H).

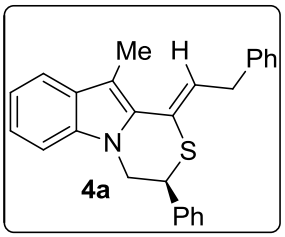
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 136.5 (C), 135.4 (C), 128.9 (C), 121.3 (CH), 119.5 (CH), 118.1 (CH), 108.8 (CH), 105.3 (C), 51.9 (CH_2), 48.9 (C), 37.7 (CH_2), 36.6 (CH), 32.1 (CH_2), 25.8 (CH_2), 22.3 (2 × CH_2), 18.3 (CH_3), 11.7 (CH_3).

LRMS (ESI, M+Na^+): m/z: 308.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{18}H_{23}NNaS$ 308.1433, found 308.1433.

(*S)-(*Z*)-10-methyl-3-phenyl-1-(2-phenylethylidene)-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (4a):**

Reaction of the thiol **2a** (100 mg, 0.373 mmol) with cinnamaldehyde **3q** (49 μL, 0.373 mmol) and $InCl_3$ (123 mg, 0.559 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **4a** (92 mg, 69%) as a mixture of diastereomers (dr-1.2:1).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2995, 2973, 2859, 1559, 1551, 1484, 1460, 1449, 1354, 938, 795, 739, 500 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65-7.63 (m, 1H), 7.51-7.15 (m, 13H), 6.31 (t, *J* = 7.2 Hz, 1H), 4.78 (dd, *J* = 12.5, 3.0 Hz, 1H), 4.53 (dd, *J* = 12.5, 3.0 Hz, 1H), 4.45-4.41 (m, 1H), 3.79 (dd, *J* = 7.2, 3.0 Hz, 2H), 2.52 (s, 3H).

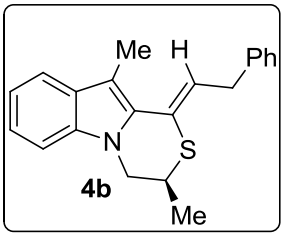
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 140.3 (C), 135.5 (C), 133.6 (C), 132.6 (C), 129.8 (C), 128.6 (2 × CH), 128.7 (2 × CH), 128.5(C), 128.4 (CH), 123.2 (2 × CH), 126.4 (CH), 126.2 (CH), 124.9 (CH), 122.0 (CH), 119.4 (CH), 119.1 (CH), 108.4 (CH), 107.8 (C), 50.1 (CH_2), 37.2 (CH), 35.7 (CH), 18.8 (CH_2), 11.1 (CH_3).

LRMS (ESI, M+K^+): m/z: 420.

HRMS (ESI, M+K^+): m/z calcd. for $C_{26}H_{23}NKS$ 420.1183, found 420.1179.

(*S)-(*Z*)-3,10-dimethyl-1-(2-phenylethylidene)-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (4b):**

Reaction of the thiol **2c** (100 mg, 0.487 mmol) with cinnamaldehyde **3q (**64 μL, 0.487 mmol) and $InCl_3$ (161 mg, 0.730 mmol) in dry CH_2Cl_2 (5 mL), as described in the general procedure, followed by purification on silica gel column using ethyl acetate-petroleum ether (1:99) as eluent furnished thiazinoindole **4b** (120 mg, 78%) as a single diastereomer (dr≥19:1).



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2980, 2863, 1554, 1551, 1484, 1460, 1449, 1354, 1255, 1236, 1175, 938, 795, 739, 500 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.27-7.24 (m, 2H), 7.19-7.11 (m, 5H), 7.14-6.98 (m, 1H), 6.13 (t, *J* = 7.2 Hz, 1H), 4.44 (dd, *J* =12.4, 2.8 Hz, 1H), 3.94 (dd, *J* = 12.8, 4 Hz, 1H), 3.66 (dd, *J* =7.2, 3.2 Hz, 2H), 3.44-3.37 (m, 1H), 2.37 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 3H).

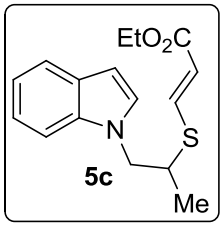
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 140.3 (C), 135.5 (C), 129.8 (C), 128.6 (2 × CH), 128.5 (C), 128.4 (2 × CH), 126.4 (CH), 126.2 (CH), 124.9 (C), 122.0 (CH), 119.4 (CH), 119.1 (CH), 108.4 (CH), 107.8 (C), 50.1 (CH_2), 37.2 (CH), 35.7 (CH_2), 18.8 (CH_3), 11.1 (CH_3).

LRMS (ESI, M+K^+): m/z: 358.

HRMS (ESI, M+K^+): m/z calcd. for $C_{21}H_{21}NKS$ 358.1026, found 358.1029.

Ethyl (*E*)-3-((1-(1*H*-indol-1-yl)propan-2-yl)thio)acrylate (5c):

To a stirred solution of **2d** (R^3-H, R^1-H, R^2-Me) (450 mg, 2.35 mmol) in dry CH_2Cl_2 (5 mL), was added NMM (N-methylmorpholine) (240 μL, 2.350 mmol), followed by ethylpropiolate (280 μL, 2.820 mmol) at 0 °C and allowed to stirred for overnight at room temperature, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (1:99) as eluent to afford **5c** (570 mg, 83.5%) as a colourless liquid.



Physical appearance: Colourless liquid.

R_f: 0.1 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2342, 2075, 1708, 1520, 1432, 1272, 1157, 1007, 951, 519 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.43 (d, *J* = 15.2 Hz, 1H), 7.32 (dd, *J* = 8, 0.3 Hz, 1H), 7.25-7.18 (m, 1H), 7.14 (m, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.52 (dd, *J* = 3.2, 0.8 Hz, 1H) 5.78 (d, *J* = 15.2 Hz, 1H), 4.32 (dd, *J* = 14.6, 6.4 Hz, 1H), 4.23 (dd, *J* = 14.6, 6.4 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.60-3.58 (m, 2H), 1.33 (d, *J* = 6.8 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

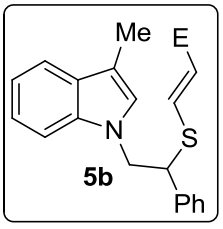
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 165.2 (C), 157.4 (C), 144.4 (C), 136.1 (C), 128.8 (C), 128.3 (CH), 121.1 (CH), 121.39 (CH), 119.9 (CH), 116.1 (CH), 109.3 (CH), 102.2 (CH), 60.5 (CH_2), 51.9 (CH_2), 42.17 (CH), 18.9 (CH_3).

LRMS (ESI, M+H^+): m/z: 290.

HRMS (ESI, M+H^+): m/z calcd. for $C_{16}H_{20}NO_2S$ 290.1202, found 290.1213

Ethyl (*E*)-3-((2-(3-methyl-1*H*-indol-1-yl)-1-phenylethyl)thio)acrylate (5b):

To a stirred solution of **2c** (R^3-Me, R^1-H, R^2-Ph) (317 mg, 1.252 mmol) in dry CH_2Cl_2 (5 mL), was added NMM (0.15 mL, 1.503 mmol), followed by ethylpropiolate (0.12 mL, 1.252 mmol) at 0 °C and allowed to stirred for overnight, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (3:97) as eluent to afford **5b** (387 mg, 96%) as a colourless liquid.



Physical appearance: Colourless liquid.

R_f: 0.3 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2342, 2075, 1708, 1520, 1432, 1272, 1157, 1007, 951, 519 cm^{-1}.

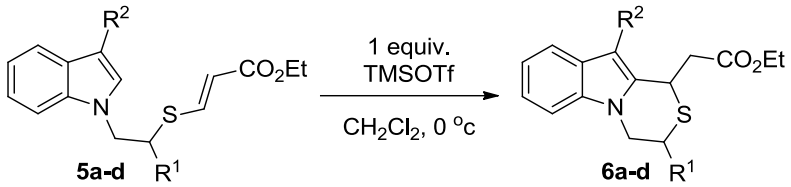
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.6 Hz, 3H), 7.37-7.32 (m, 3H), 7.29-7.28 (m, 4H), 7.22-7.21 (m, 1H), 6.22 (d, *J* = 0.8 Hz, 1H) 5.68 (d, *J* = 15.2 Hz, 1H), 4.58-4.59 (m, 1H), 4.56-4.57 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.24 (d, *J* = 0.8 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 164.8 (C), 146.7 (CH), 138.5 (C), 138.02 (C), 129.1(2 × CH), 129.1 (C), 128.51 (CH), 128.3 (2 × CH), 125.8 (CH), 121.8 (CH), 119.3 (CH), 116.1 (CH), 113.8 (CH), 109.01 (CH), 108.3 (C), 60.3 (CH_2), 53.68 (CH_2), 51.9 (CH), 14.3 (CH_3), 9.6 (CH_3).

LRMS (ESI, M+H^+): m/z: 388.

HRMS (ESI, M+H^+): m/z calcd. for $C_{22}H_{23}NO_2S$ 388.1345, found 388.1342.

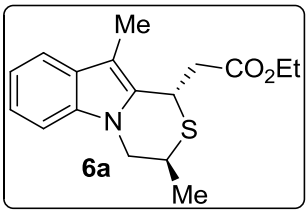
Procedure for intra-molecular thia-Pictet-Spengler cyclization:



Ethyl-2-((1*S,3*S**)-3,10-dimethyl-3,4-dihydro-1H-[1,4]thiazino[4,3-a]indol-1-yl)acetate (6a):**

To a stirred solution of **5a** (80 mg, 0.264 mmol) in dry CH_2Cl_2 (5 mL), was added TMSOTf (55 μL, 0.264 mmol) at 0 °C and monitored by TLC, quenched with saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2 (3 × 5 mL), dried over anhydrous Na_2SO_4, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (3:97) as eluent to afford **6a** (78 mg, 92%) as a mixture of diastereomers (dr-1:1).

Physical appearance: Colourless liquid.



R_f: 0.3 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2827, 1733, 1602, 1472, 1312, 1156, 1111, 996, 905, 892, 617 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.31-7.28 (m, 2H), 7.26-7.22 (m, 2H), 7.19-7.16 (m, 2H), 4.94 (dd, *J* = 13.5, 5.5 Hz, 1H), 4.72 (dd, *J* = 11.2, 4.5 Hz, 1H), 4.56 (dd, *J* = 13.0, 3.5 Hz, 1H), 4.49-4.44 (m, 1H), 4.27 (q, *J* = 7.5 Hz, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 3.87 (dd, *J* = 13.5, 6.0 Hz, 1H), 3.62- 3.55 (m, 2H), 3.23-3.19 (m, 1H), 3.02-2.88(m, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 1.43-1.41 (m, 6H), 1.34 (t, *J* = 7.5 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H).

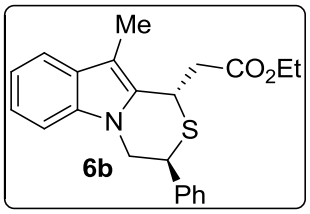
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.5 (2 × C), 136.8 (C), 136.4 (C), 131.0 (C), 130.4(C), 128.3 (C), 128.2 (C), 121.6 (CH), 121.5 (CH), 119.8 (CH), 118.5 (CH), 119.4 (C), 118.9 (C), 118.6 (CH), 108.9 (CH), 108.4 (CH), 106.5 (C), 106.2 (C), 61.0 (CH_2), 51.2 (CH_2), 49.8 (CH_2), 46.0 (CH), 42.3 (CH), 37.9 (CH), 33.2 (CH), 33.0 (CH), 19.3 (CH_3), 18.4 (CH_3), 14.4 (CH_3), 14.3 (CH_3), 8.7 (CH_3), 8.5 (CH_3).

LRMS (ESI, M+H$^+$): m/z: 304.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{17}H_{22}NO_2S$ 304.1366, found 304.1369.

Ethyl-2-((1*S,3*S**)-10-methyl-3-phenyl-3,4-dihydro-1H-[1,4]thiazino[4,3-a]indol-1-yl)acetate (6b):**

To a stirred solution of **5b** (50 mg, 0.136 mmol) in dry CH_2Cl_2 (5 mL) was added TMSOTf (30 μL, 0.136 mmol) at 0 °C and monitored by TLC, quenched with saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2 (3 × 5 mL), dried over anhydrous Na_2SO_4, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (3:97) as eluent to afford **6b** (46 mg, 91%) as a mixture of diastereomers (dr-1:1).



Physical appearance: Colourless liquid.

R_f: 0.3 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2973, 2859, 1559, 1551, 1484, 1460, 1449, 1354, 1255, 1236, 1175, 1094, 1039, 938, 795, 739, 500 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 6.8 Hz, 4H), 7.49- 7.48 (m, 3H), 7.39 -7.38 (m, 5H), 7.26 -7.25 (m, 2H), 7.21- 7.18 (m, 4H), 5.01 (4.82, dd, *J* = 7.2, 8.2 Hz, 1H) (dd, *J* = 11.2, 4.4 Hz, 1H), 4.71- 4.60 (m, 4H), 4.37 (q, *J* = 7.0 Hz, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 4.04 (dd, *J* = 13.2, 0.7 Hz, 2H), 3.15-2.97 (m, 4H), 2.36 (s, 3H), 2.34 (s, 3H), 1.33-1.29 (m, 6H).

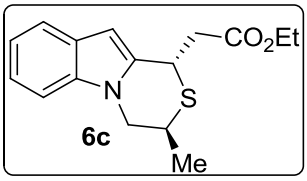
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.4 (C), 170.3 (C), 138.3 (C), 138.0 (C), 136.9 (C), 136.8 (C), 130.1 (C), 130.2 (C), 129.0 (2 × CH), 128.9 (2 × CH), 128.4 (CH), 128.3 (CH), 128.2 (C), 128.2 (C), 127.9 (2 × CH), 121.7 (2 × CH), 121.6 (CH), 120.0 (CH), 119.4 (CH), 119.5 (CH), 119.0 (CH), 118.6 (CH), 108.9 (CH), 108.4 (CH), 106.5 (C), 106.6 (C), 61.1 (CH_2), 61.0 (CH_2), 50.6 (CH_2), 49.1 (CH_2), 47.5 (CH), 46.0 (CH), 42.0 (CH), 40.5 (CH), 34.1 (CH_2), 33.8 (CH_2), 14.4 (CH_3), 14.2 (CH_3), 8.5 (CH_3), 8.6 (CH_3).

LRMS (ESI, M+Na$^+$): m/z: 388.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{22}H_{23}NNaO_2S$ 388.1340, found 388.1342.

Ethyl-2-((1*S,3*S**)-((3,10-dimethyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indol-1-yl)acetate (6c):**

To a stirred solution of **5c** (150 mg, 0.517mmol) in dry CH_2Cl_2 (5 mL) was added TMSOTf (93 μL, 0.517mmol) at 0 ^oC and monitored by TLC, quenched with saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2 (3x5 mL), dried over anhydrous Na_2SO_4, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (3:97) as eluent to afford **6c** (104 mg, 69%) as a mixture of diastereomers (dr-1:1).



Physical appearance: Colourless liquid.

R*f*: 0.3 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2878, 1733, 1662, 1590, 1294, 1123, 1011, 975, 767, 555 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 9.8 Hz, 2H), 7.31- 7.29 (m, 2H), 7.13 -7.12 (m, 2H), 7.13- 7.12 (m, 2H), 6.33 (s, 1H), 6.30 (s, 3H), 4.77-4.72 (m, 2H), 4.49-4.42 (m, 2H), 4.27-4.12 (m, 4H), 3.80-3.69 (m, 1H), 3.48-3.45 (m, 2H), 3.55-3.49 (m, 2H), 3.22 (dd, *J* = 16.0, 7Hz, 1H), 3.05 (dd, *J* = 16.0, 7.0 Hz, 2H), 2.83-2.77 (m,1H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.28 (m, 6H).

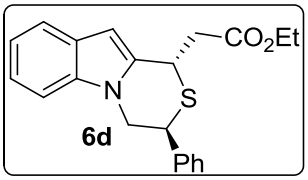
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.9 (C), 170.6 (C), 137.3 (C), 136.9 (C), 136.1 (C), 135.2 (C), 127.6 (C), 127.5 (C), 121.6 (CH), 121.4 (CH), 120.6 (CH), 120.5 (CH),120.4 (CH), 120.3 (CH), 108.9 (CH), 108.9 (CH), 98.8 (CH), 97.6 (CH), 61.1 (CH_2), 61.0 (CH_2), 50.7 (CH_2), 50.6 (CH_2), 43.2 (CH), 39.4 (CH), 37.0 (CH_2). 36.0 (CH), 33.8 (CH), 32.5 (CH_2), 19.0 (CH_3), 18.7 (CH_3), 14.3 (2 × CH_3).

LRMS (ESI, M+H$^+$): m/z: 290

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{16}H_{20}NO_2S$ 290.1202, found 290.1228.

Ethyl-2-((1*S,3*S**)-(3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indol-1-yl)acetate (6d):**

To a stirred solution of **5d** (54 mg, 0.153 mmol) in dry CH_2Cl_2 (5 mL) was added TMSOTf (30 μL, 0.153 mmol) at 0 ^oC and monitored by TLC, quenched with saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2 (3 x 5 mL), dried over anhydrous Na_2SO_4, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (3:97) as eluent to afford **6d** (34 mg, 64%) as a mixture of diastereomers (dr-1:1).



Physical appearance: Colourless liquid.

R*f*: 0.3 (1:9 ethyl acetate-petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.47-7.48 (m, 2H), 7.40-7.39 (m, 8H), 7.24-7.22 (m, 2H), 7.16 -7.15 (m, 4H), 6.38 (s, 1H), 6.37 (s, 1H), 4.95-4.91- (m, 1H),4.86-4.83 (m, 1H), 4.67-4.95 (m, 4H), 4.27-4.18 (m, 4H), 3.25 (dd, *J* = 18.6, 6.0 Hz, 1H),3.20-3.04 (m, 2H), 2.88 (dd, *J* = 18.6, 6.0 Hz, 1H), 1.33-1.26 (m, 6H).

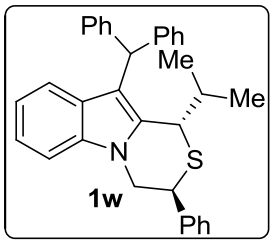
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 170.7 (C), 170.5 (C), 138.4 (C), 138.3 (C), 137.4 (C), 135.8 (C), 129.01 (2 × CH), 129.5 (2 × CH), 128.4 (CH), 128.0 (CH), 127.6 (2 × CH), 127.5 (2 × CH), 127.9 (C), 127.7 (CH), 127.5 (C),121.8 (CH), 121.7 (CH), 120.6 (CH), 120.6 (CH), 120.5 (CH), 108.8 (CH), 108.7 (CH), 98.9 (CH), 98.1 (CH), 61.3 (CH_2), 61.1 (CH_2), 50.3 (CH_2), 49.7 (CH_2), 46.7 (2 × CH), 42.6 (CH), 42.4 (CH), 39.9 (CH_2), 37.0 (CH_2), 14.3 (2 × CH_3).

LRMS (ESI, M+Na^+): m/z: 374.

HRMS (ESI, M+Na^+): m/z calcd. for $C_{21}H_{21}NNaO_2S$ 374.1185, found 374.1185.

(1*S,3*S**)-10-benzhydryl-1-isopropyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1w):**

Reaction of the thiol **2e** (R^3-H, R^1-H, R^2-Ph) (50 mg, 0.197 mmol) was reacted with diphenyl methanol (36 mg, 0.197 mmol) in CH_2Cl_2 (5 mL) followed by $InCl_3$ (54 mg, 0.197 mmol), once starting materials were over aldehyde **3m** (15 μL, 0.197 mmol) was added. Monitored by TLC, quenched with saturated aqueous solution of $NaHCO_3$ solution, extracted with CH_2Cl_2, purified by silica gel chromatography using ethyl acetate-petroleum ether (2:98) as eluent to furnish product **1w** (72 mg, 65%) as a mixture of diastereomers (dr-9:1).



Physical appearance: Colourless liquid.

R_f: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2976, 2856, 1556, 1551, 1484, 1460, 1449, 1354, 1255, 1236, 1175, 1094, 1039, 938, 795, 739, 500 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ 7.31-7.21 (m, 4H), 7.21-7.01 (m, 4H), 7.01-6.98 (m, 7H), 7.97-6.89 (m, 4H), 5.77 (s, 1H), 4.23 (dd, *J* = 8.0, 3.6 Hz, 2H), 3.92-3.84 (m, 2H), 2.01-2.05 (m, 1H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.68 (d, *J* = 6.4 Hz, 3H).

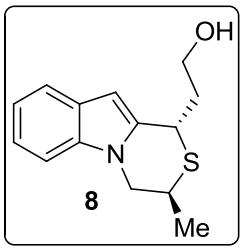
^{13}C NMR (100 MHz, C_6D_6, DEPT): δ 145.1 (C), 143.9 (C), 139.6 (C), 137.7 (C), 134.7 (CH), 130.1 (CH), 129.9 (CH), 129.3 (C), 129.1 (2 × CH), 128.9 (2 × CH), 128.9 (CH), 128.8 (2 × CH), 128.6 (C), 128.3 (2 × CH), 128.1 (CH), 126.9 (CH), 126.8 (2 × CH), 122.0 (CH), 120.7 (CH), 114.5 (C), 109.5 (CH), 49.8 (CH_2), 48.7 (CH), 48.2 (CH), 46.3 (CH), 38.1 (CH), 21.5 (CH_3), 19.7 (CH_3).

LRMS (ESI, M+Na$^+$): m/z: 496.

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{33}H_{31}NNaS$ 496.2069, found 496.2079.

2-((1*S,3*S**)-3-methyl-3,4-dihydro-1H-[1,4]thiazino[4,3-a]indol-1-yl)ethanol (8):**

To a stirred solution of **6c** (150 mg, 0.518 mmol) in dry THF (5 mL) was added $LiAlH_4$ (24 mg, 0.622 mmol) at 0 ºC and allowed to stirred for 2 hr, quenched with saturated aqueous solution of Na_2SO_4, filtered over anhydrous Na_2SO_4, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (3:97) as eluent to afford **8** (115 mg, 89%) as a mixture of diastereomers (dr-1:1).



Physical appearance: Colourless liquid.

R$_f$: 0.8 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3461, 1374, 1242, 1131, 1121, 1048, 1011, 948, 938, 847, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5 (d, *J* = 7.6 Hz, 1H), 7.23-7.24 (m, 1H), 7.16 (t, *J* = 6.8 Hz, 1H), 7.09-7.11 (m, 1H), 6.32 (s, 1H), 4.41 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.30 (dd, *J* = 12, 4.4 Hz, 1H), 3.60 (t, *J* = 11.2 Hz, 2H), 3.44-3.36 (m, 2H), 2.23-2.24 (m, 2H),1.36 (d, *J* = 6.8 Hz, 3H).

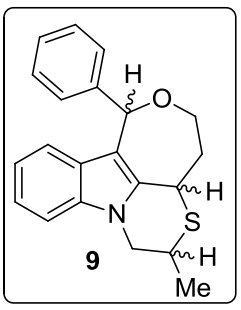
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 137.2 (C), 136.8 (C), 127.6 (C), 121.3 (CH), 120.4 (CH), 120.2 (CH), 108.8 (CH), 98.4 (CH), 60.5 (CH_2), 50.7 (CH_2), 36.5 (CH), 36.0 (CH_2), 34.7 (CH), 18.3 (CH_3).

LRMS (ESI, M+H$^+$): m/z: 248.

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{14}H_{18}NOS$ 248.1104, found 248.1108.

2-methyl-7-phenyl-1,2,3a,4,5,7-hexahydro-6-oxa-3-thia-11b azacyclohepta[*jk*]fluorene (9):

To a stirred solution of indolyl alcohol **8** (90 mg, 0.363 mmol) in CH_2Cl_2 (5 mL) was added benzaldehyde **2b** (38 μL, 0.363 mmol) at 0 ºC followed by $BF_3.OEt_2$ (45 μL, 0.363 mmol) and allowed to stirred for 30 mins, quenched with saturated aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2, evaporated, purified by column chromatography using ethyl acetate-petroleum ether (2:98) as eluent to afford **9** (92 mg, 78%) as a mixture of diastereomers.



Physical appearance: Colourless liquid.

R$_f$: 0.2 (1:9 ethyl acetate-petroleum ether).

IR (neat): 2926, 1701, 1699, 1605, 1495, 1455, 1368, 1187, 1026, 910, 742, 668 cm^{-1}.

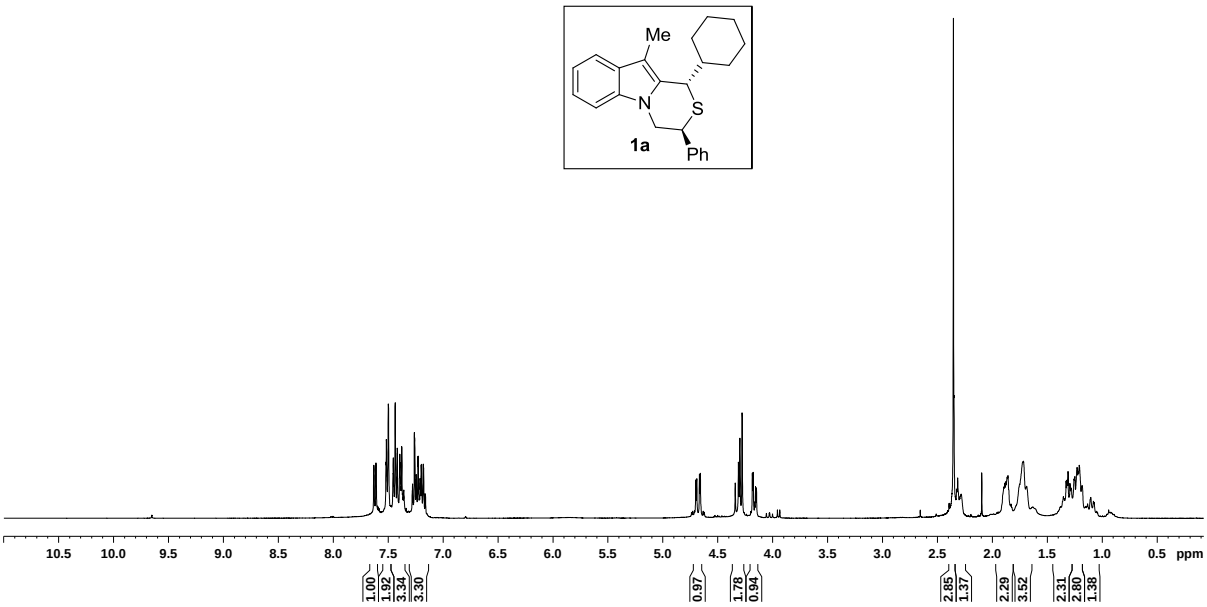
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.23-7.24 (m, 4H), 7.16-7.17 (m, 2H), 7.09-7.11 (m, 2H), 6.96 (s, 1H), 4.41-4.43 (m, 1H), 4.33-4.36 (m, 1H), 3.60 (t, *J* = 11.2 Hz, 2H), 3.44-3.47 (m, 2H), 2.22-2.24 (m, 2H), 1.36 (d, *J* = 6.8 Hz, 3H).

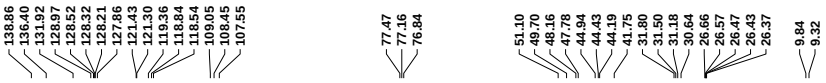
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 141.1 (C), 137.3 (C), 136.5 (C), 128.2 (2 × CH), 128.1 (CH), 127.9 (2 × CH), 127.6 (C), 121.3 (CH), 120.37 (CH), 120.18 (CH), 108.8 (CH), 98.4 (C), 79.5 (CH), 60.8 (CH_2), 50.7 (CH_2), 36.5 (CH), 36.01 (CH_2), 34.7 (CH), 18.3 (CH_3).

LRMS (ESI, M+K^+): m/z: 374.

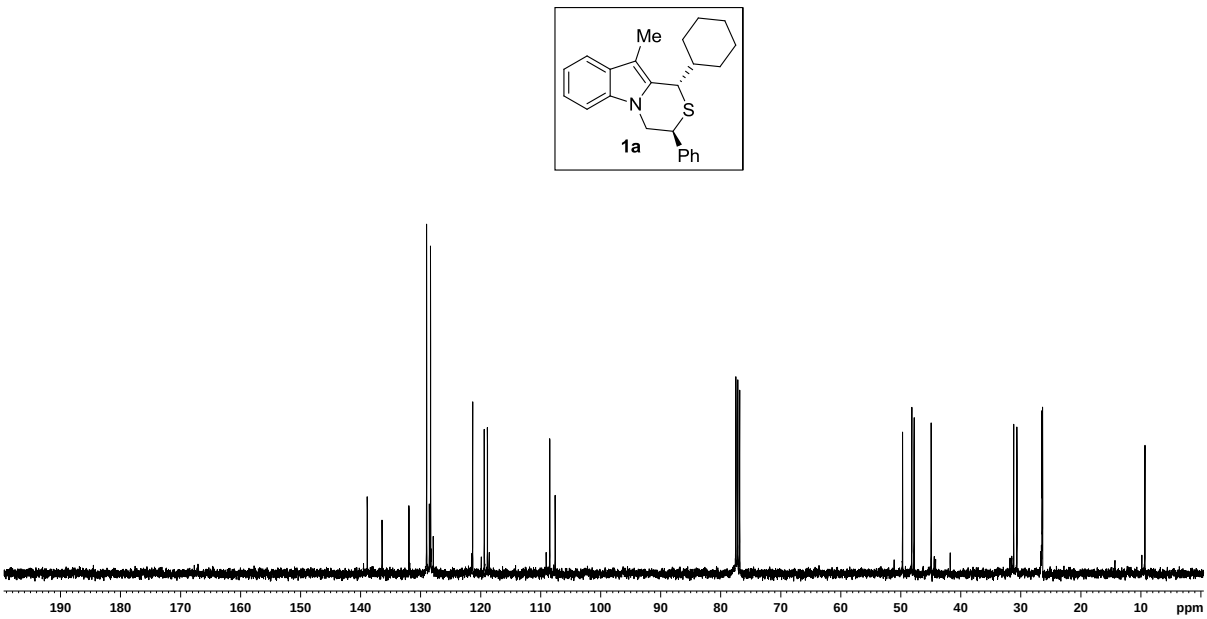
HRMS (ESI, M+K^+): m/z calcd. for $C_{21}H_{21}NOKS$ 374.0978, found 374.0969.

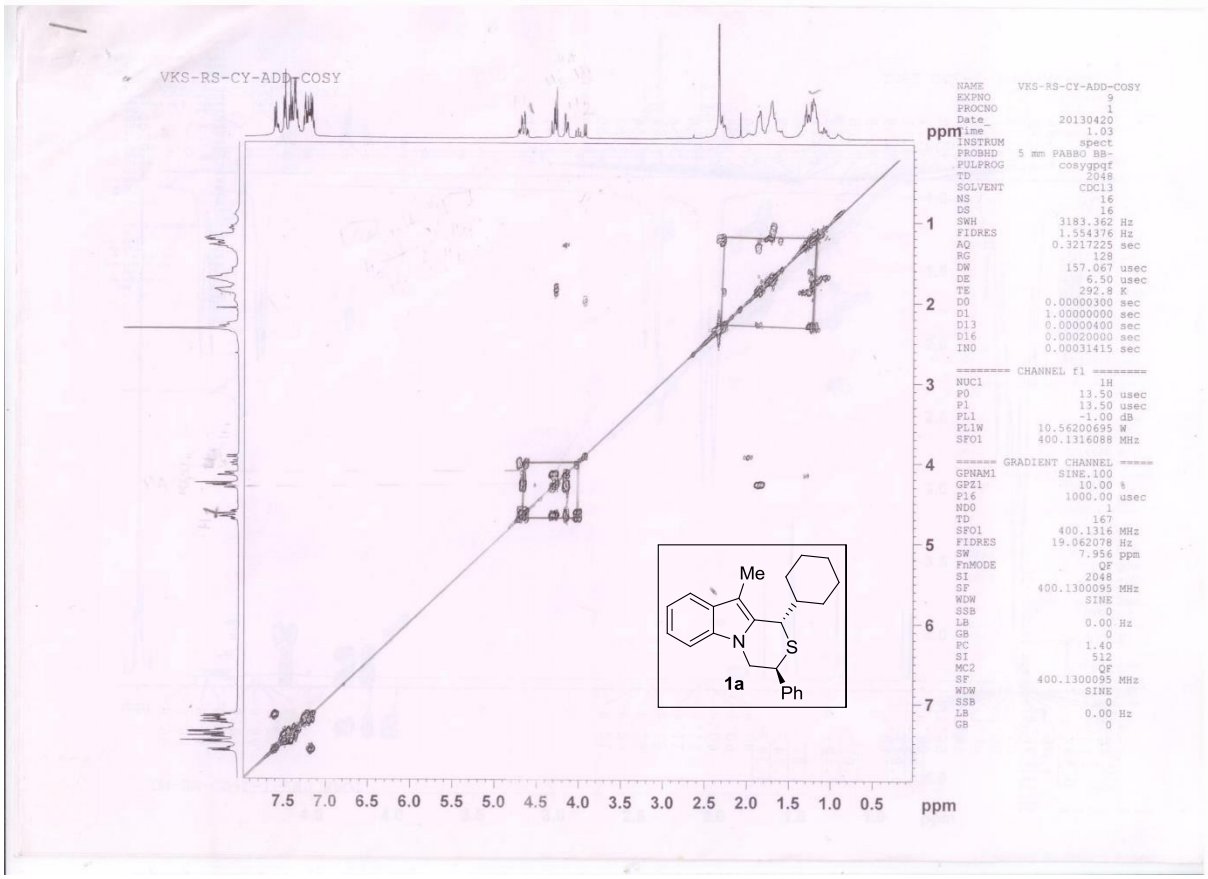
VKS-RS-Cy-Add-1H





VKS-RS-Cy-Add-13C





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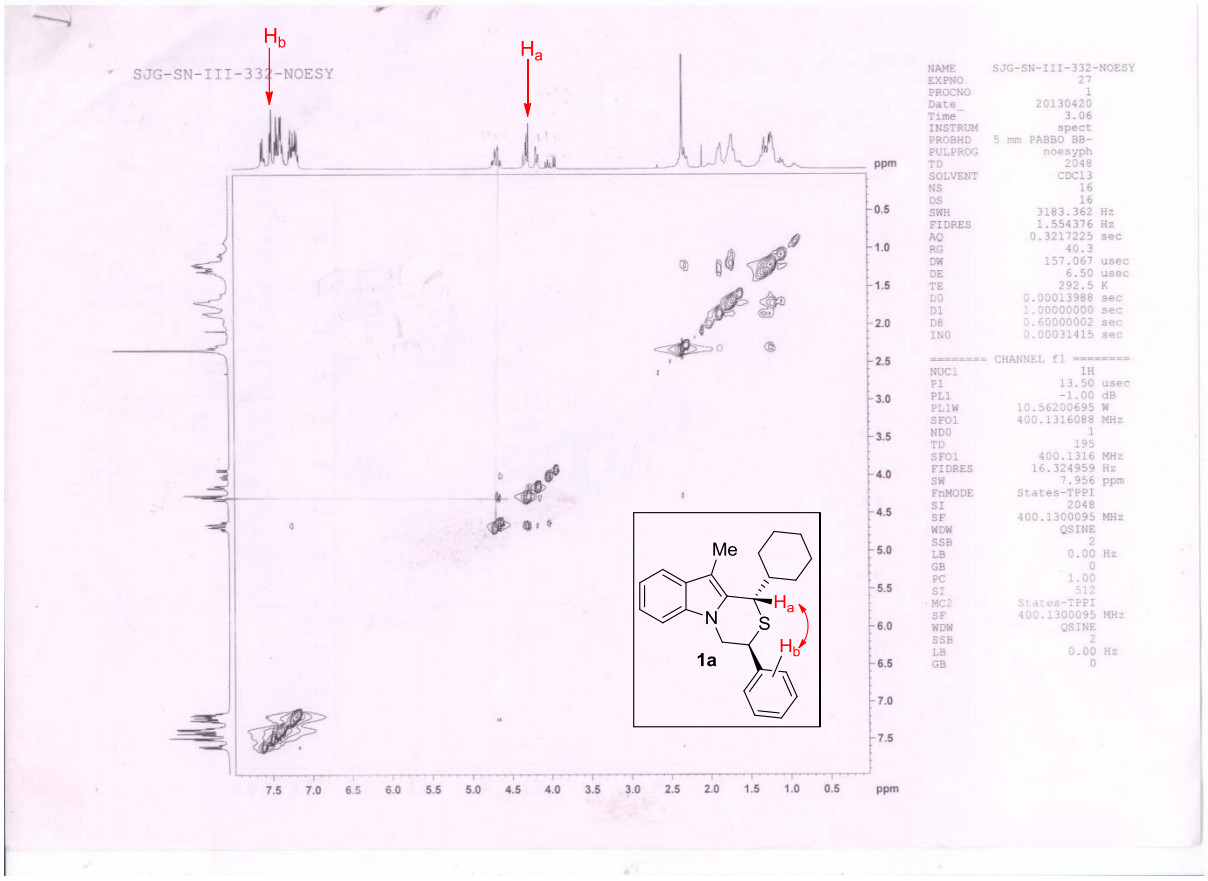
EXPNO 9
PROCNO 1
Date_ 20130420
Time 1.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG cosygpqf
TD 2048
SOLVENT CDCl3
NS 16
DS 16
SWH 3183.362 Hz
FIDRES 1.554376 Hz
AQ 0.3217225 sec
RG 128
DW 157.067 usec
DE 6.50 usec
TE 292.8 K
D0 0.00000300 sec
D1 1.00000000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00031415 sec

======== CHANNEL f1 ========
NUC1 1H
P0 13.50 usec
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1316088 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPZ1 10.00 %
P16 1000.00 usec
ND0 1
TD 167
SFO1 400.1316 MHz
FIDRES 19.062078 Hz
SW 7.956 ppm
FnMODE QF
SI 2048
SF 400.1300095 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
SI 512
MC2 QF
SF 400.1300095 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0



NAME SJG-SN-III-332-NOESY
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PROCNO 1
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INSTRUM spect
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PULPROG noesyph
TD 2048
SOLVENT CDCl3
NS 16
DS 16
SWH 3183.362 Hz
FIDRES 1.554376 Hz
AQ 0.3217225 sec
RG 40.3
DW 157.067 usec
DE 6.50 usec
TE 292.5 K
D0 0.00013988 sec
D1 1.00000000 sec
D8 0.60000002 sec
IN0 0.00031415 sec

======== CHANNEL f1 ========
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P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1316088 MHz
ND0 1
TD 195
SFO1 400.1316 MHz
FIDRES 16.324959 Hz
SW 7.956 ppm
FnMODE States-TPPI
SI 2048
SF 400.1300095 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
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PC 1.00
SI 512
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SF 400.1300095 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
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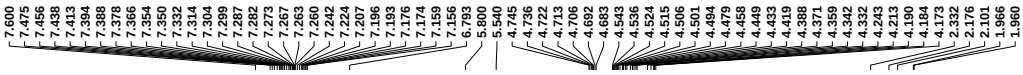
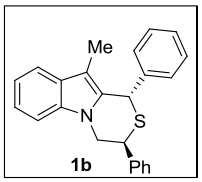
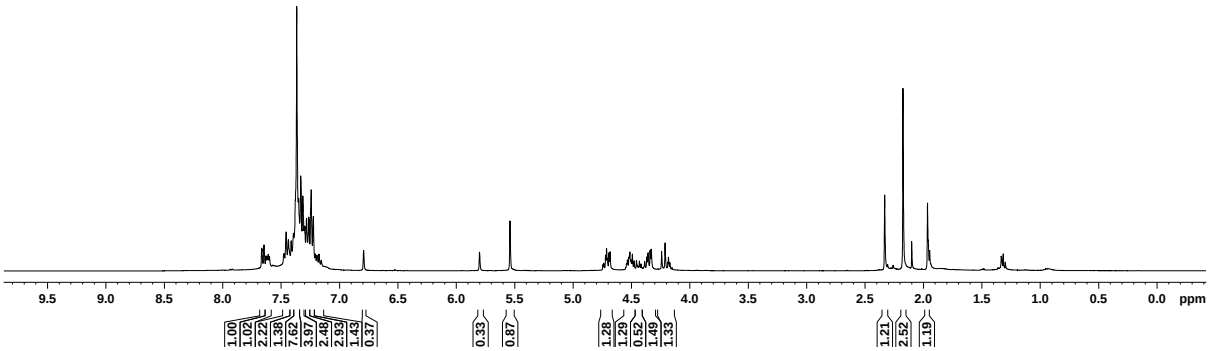
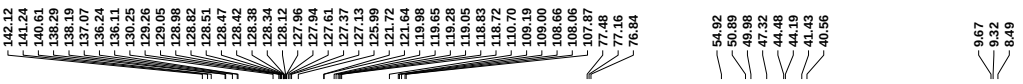


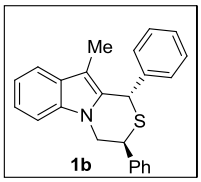
SJG-SN-III-325-1H

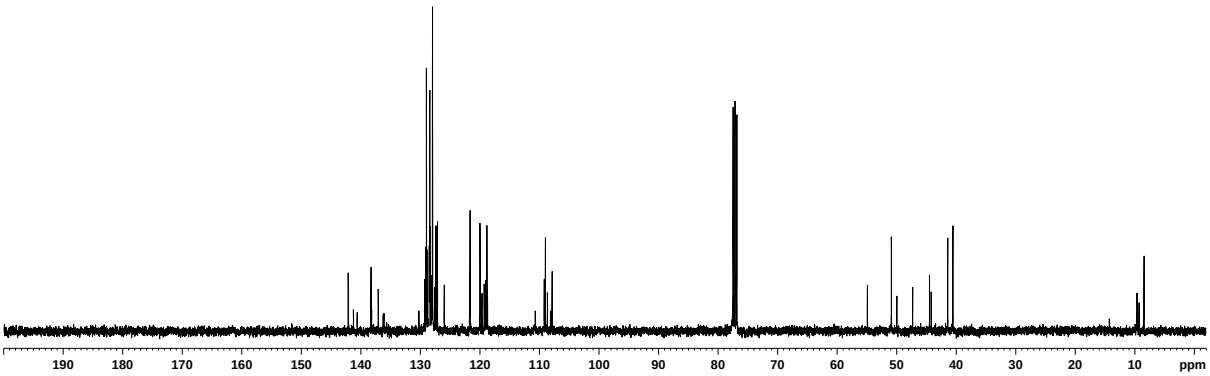


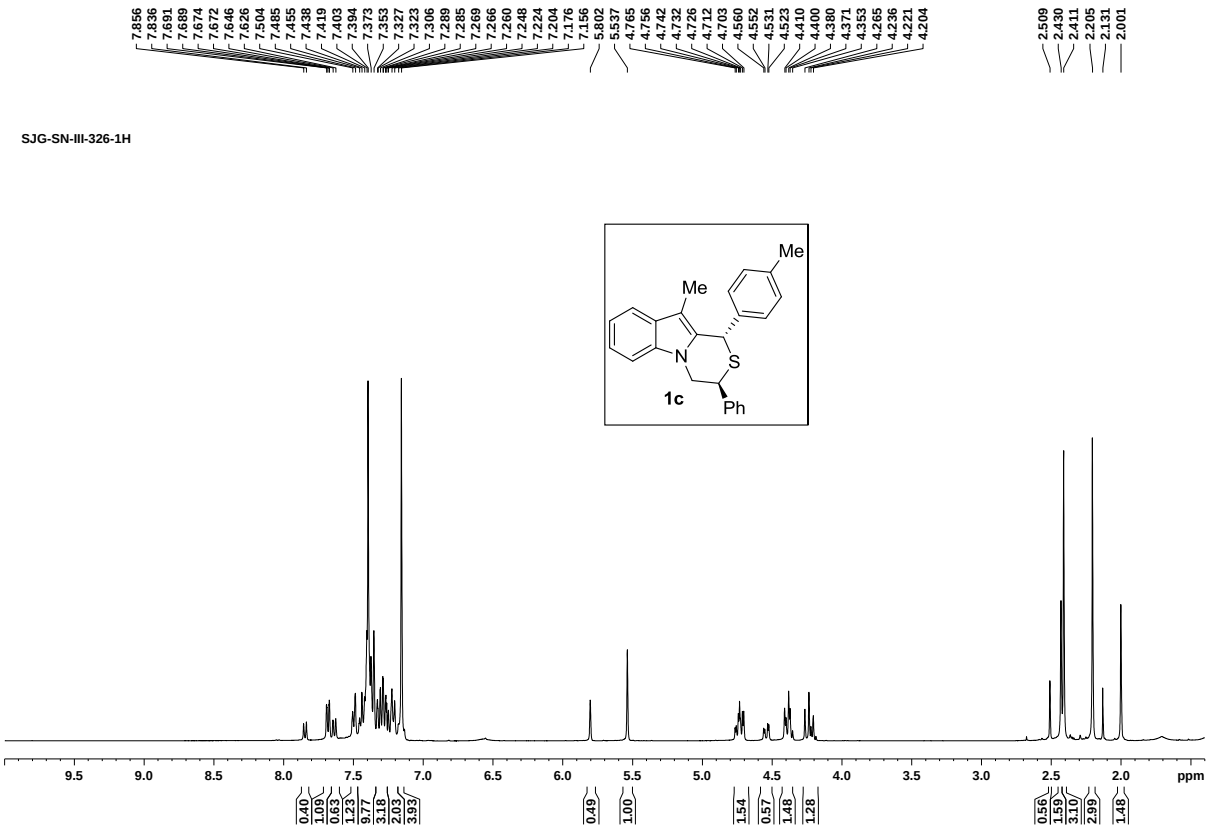




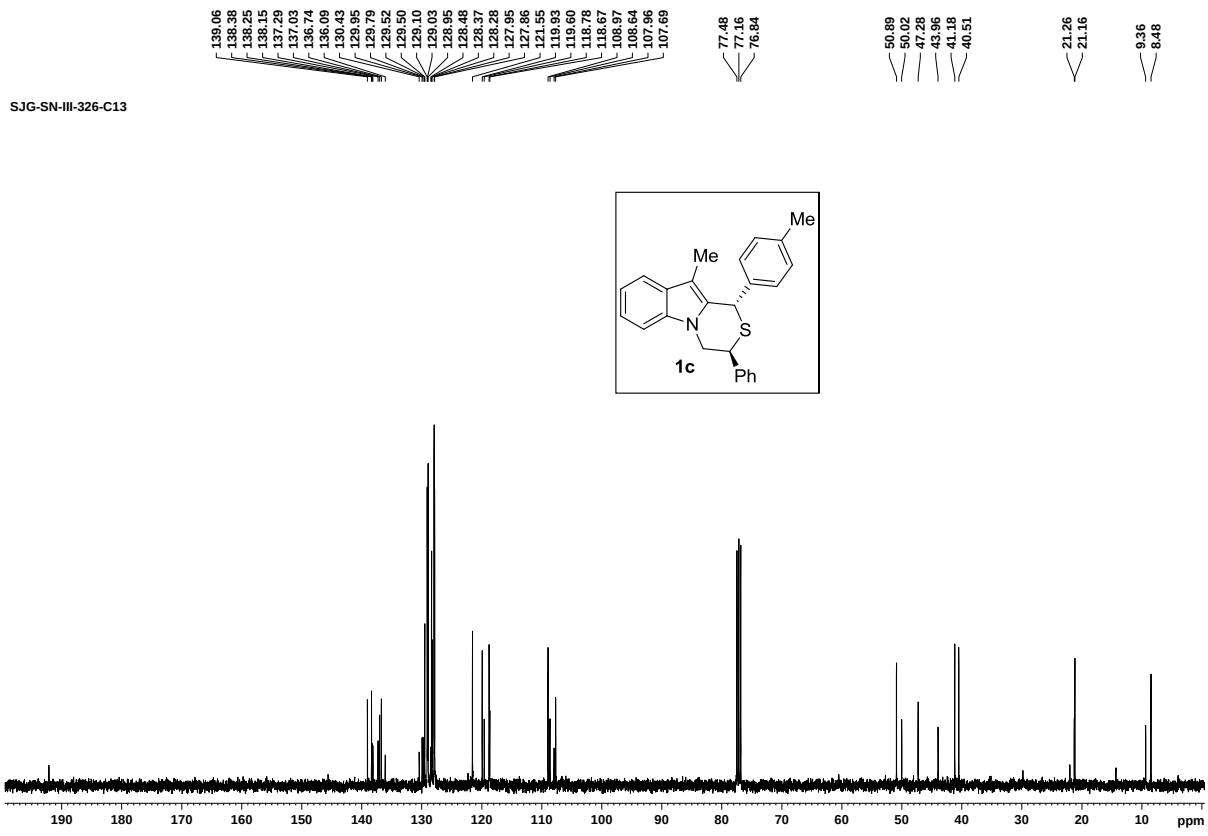
SJG-SN-III-325-C13



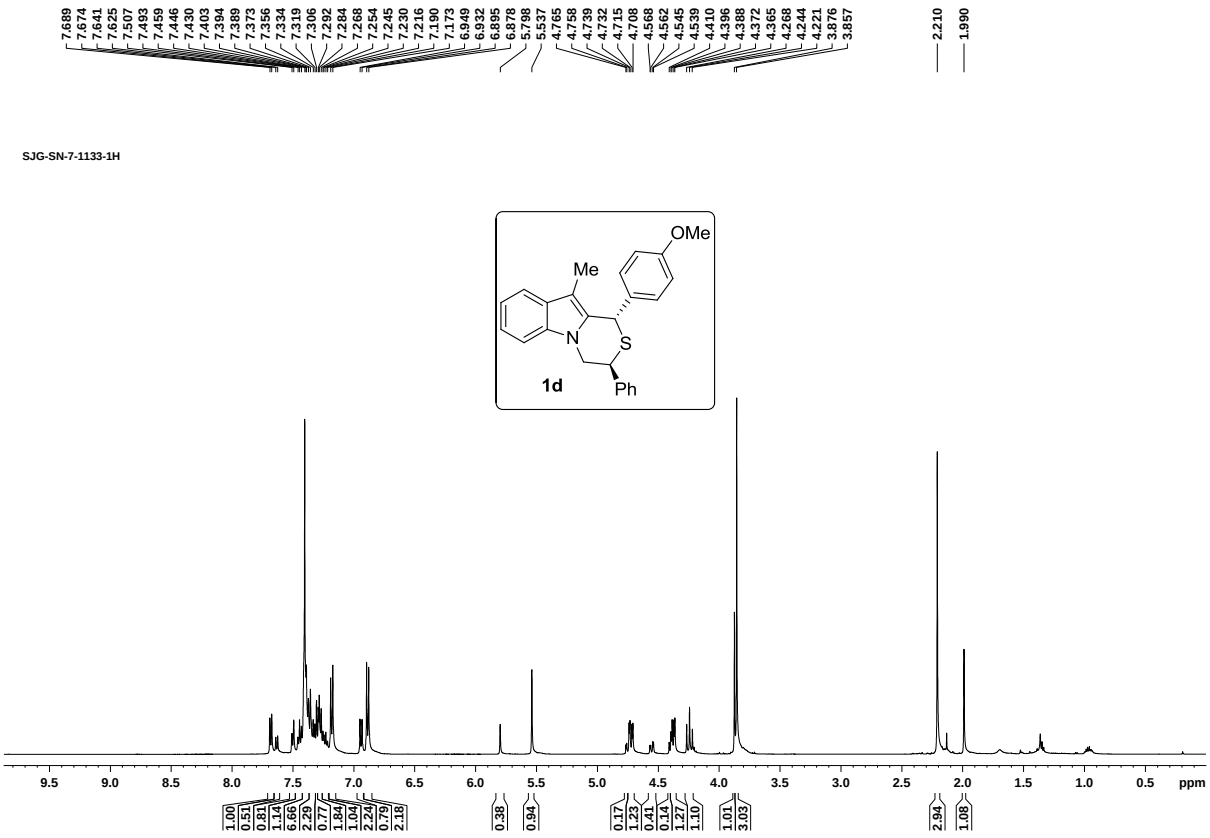




SJG-SN-III-326-1H



SJG-SN-III-326-C13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4.715
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4.562
4.545
4.539
4.410
4.396
4.388
4.372
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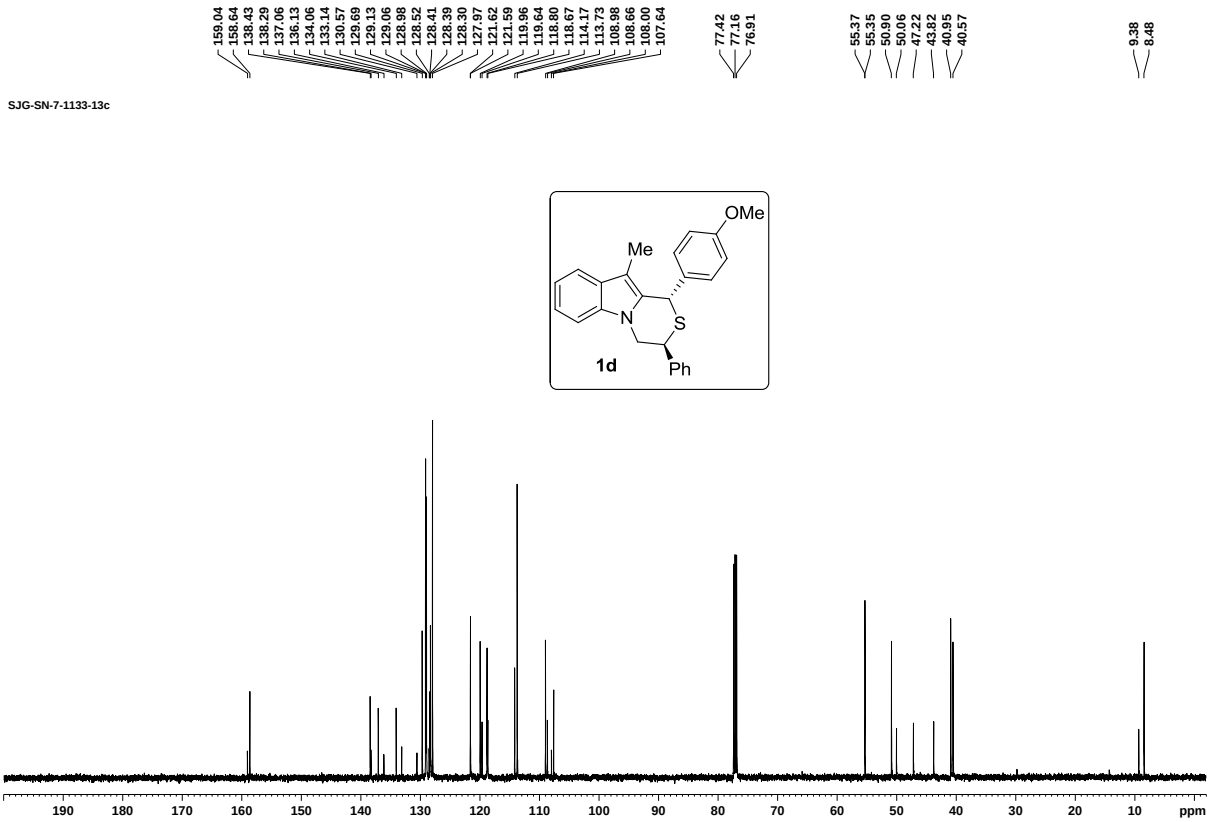
4.268
4.244
4.221
3.876
3.857
2.210
1.990
SJG-SN-7-1133-1H
OMe
Me
N
S
1d
Ph
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.51 0.81 1.14 6.66 2.29 0.77 1.84 1.04 2.24 0.79 2.18 0.38 0.94 0.17 1.23 0.41 0.14 1.27 1.10 1.01 3.03 2.94 1.08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128.52
128.41
128.39
128.30
127.97
121.62
121.59
119.96
119.64
118.80
118.67
114.17
113.73
108.98
108.66
108.00
107.64
77.42
77.16
76.91
55.37
55.35
50.90
50.06
47.22
43.82
40.95
40.57
9.38
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OMe
Me
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S
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Ph
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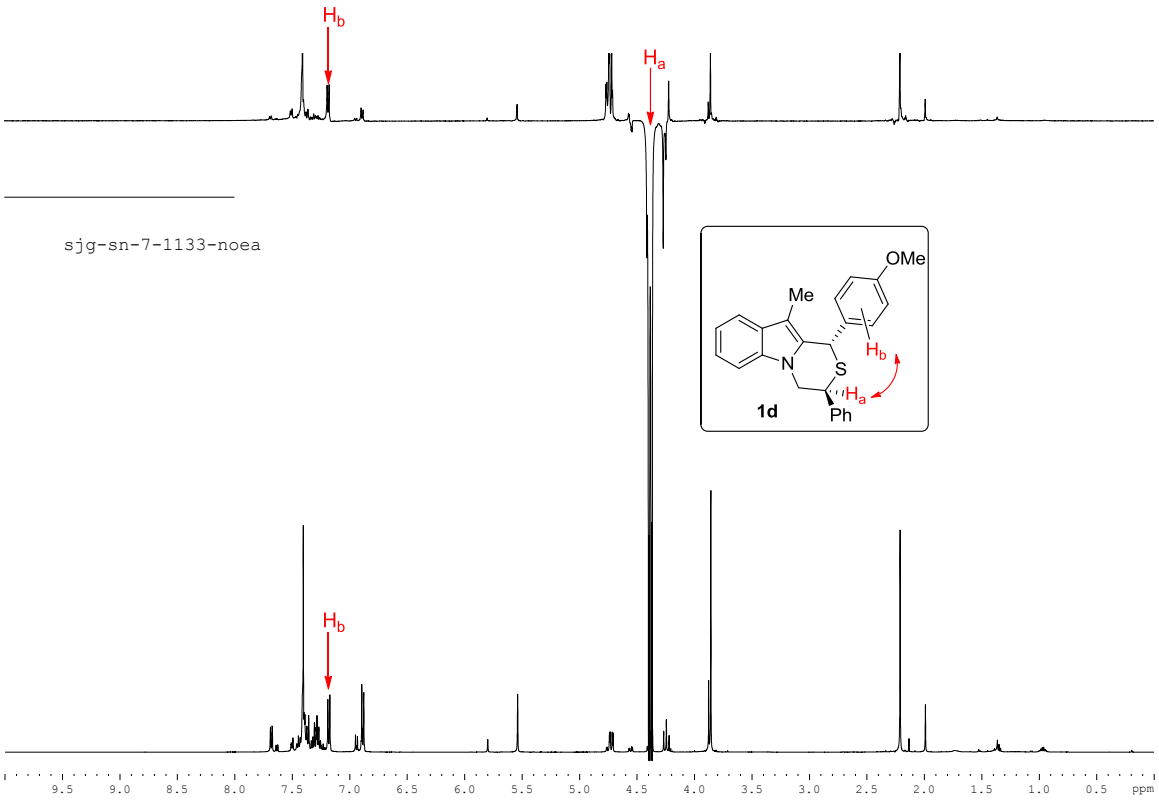

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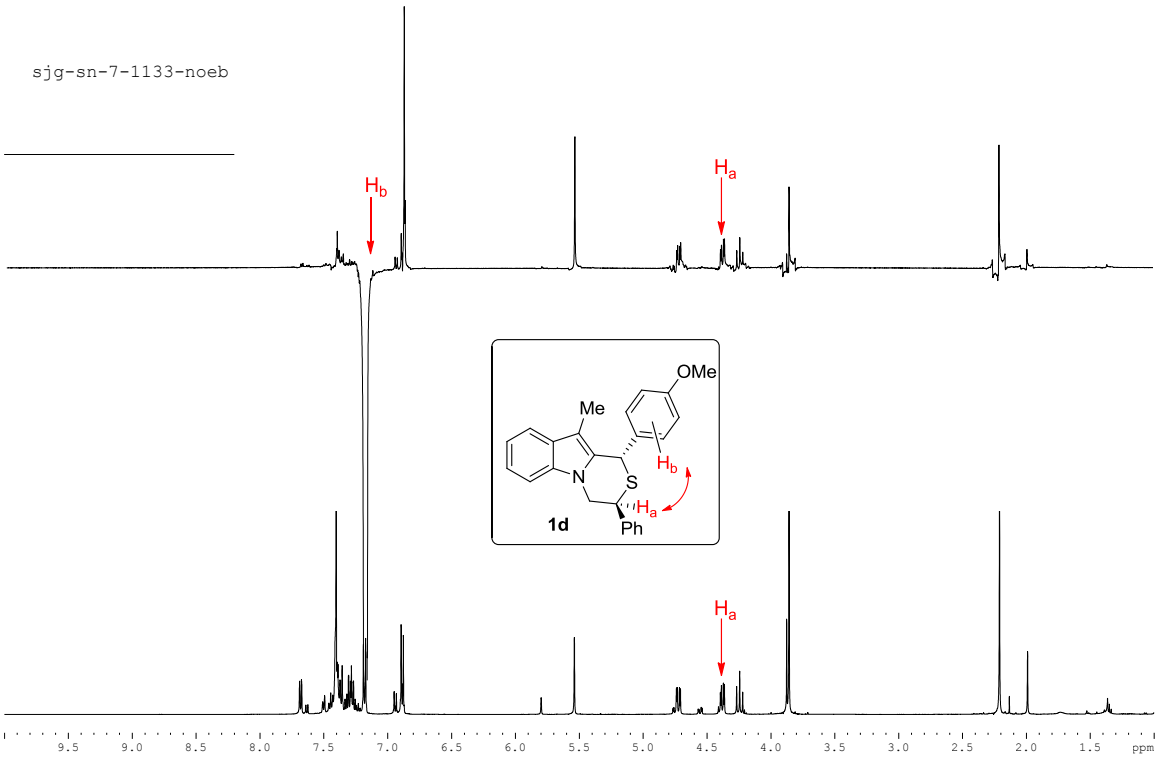
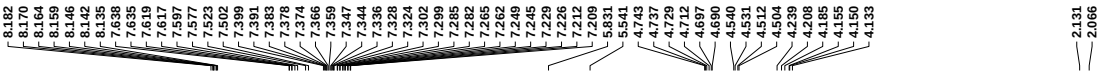
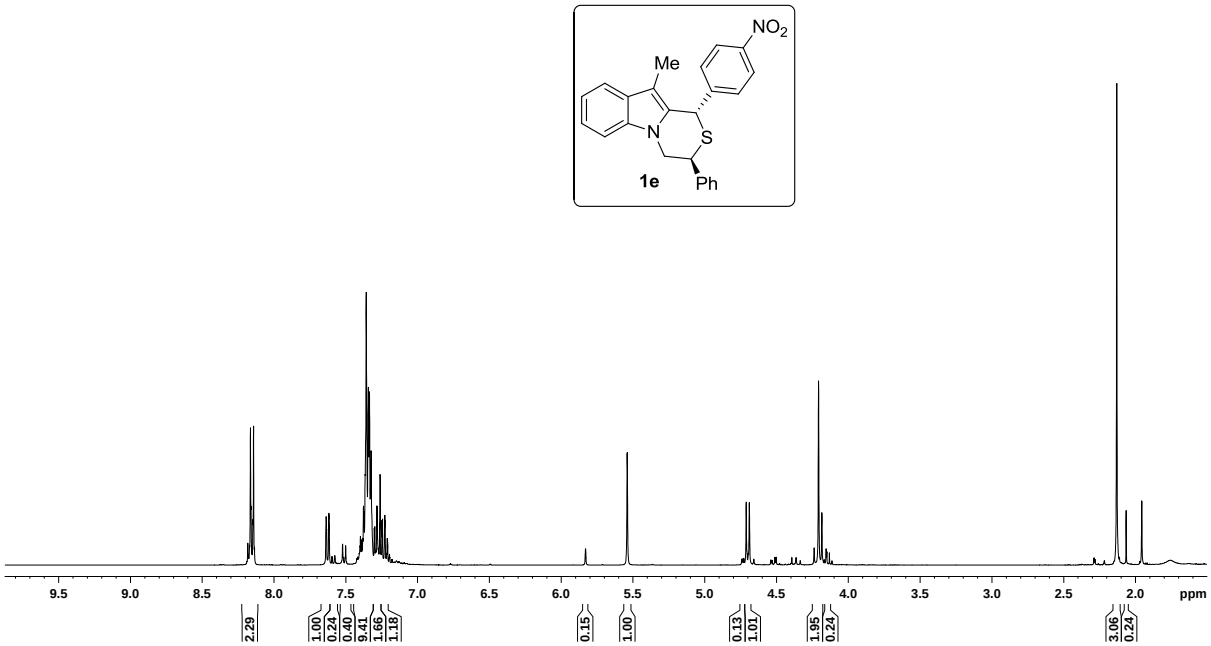


NOE enhancement-4%



sjg-sn-7-1131-s1-1h



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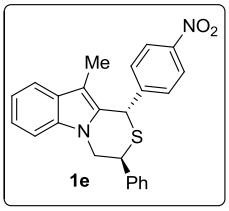
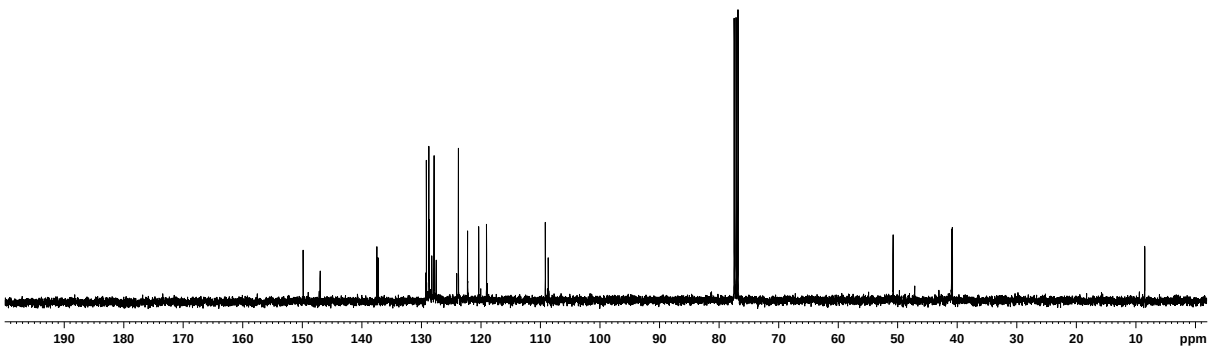
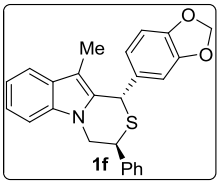
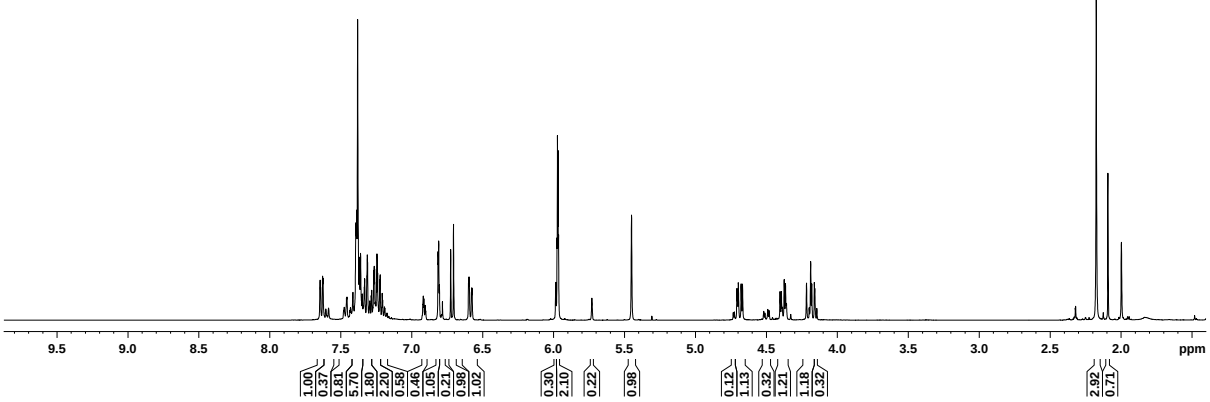




SJG-SN-7-1130-1H





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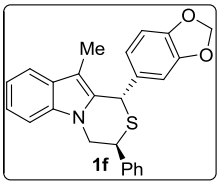
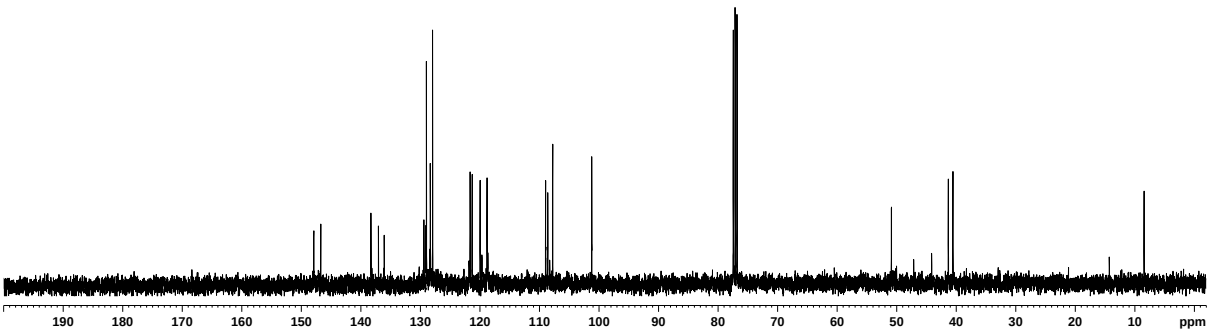
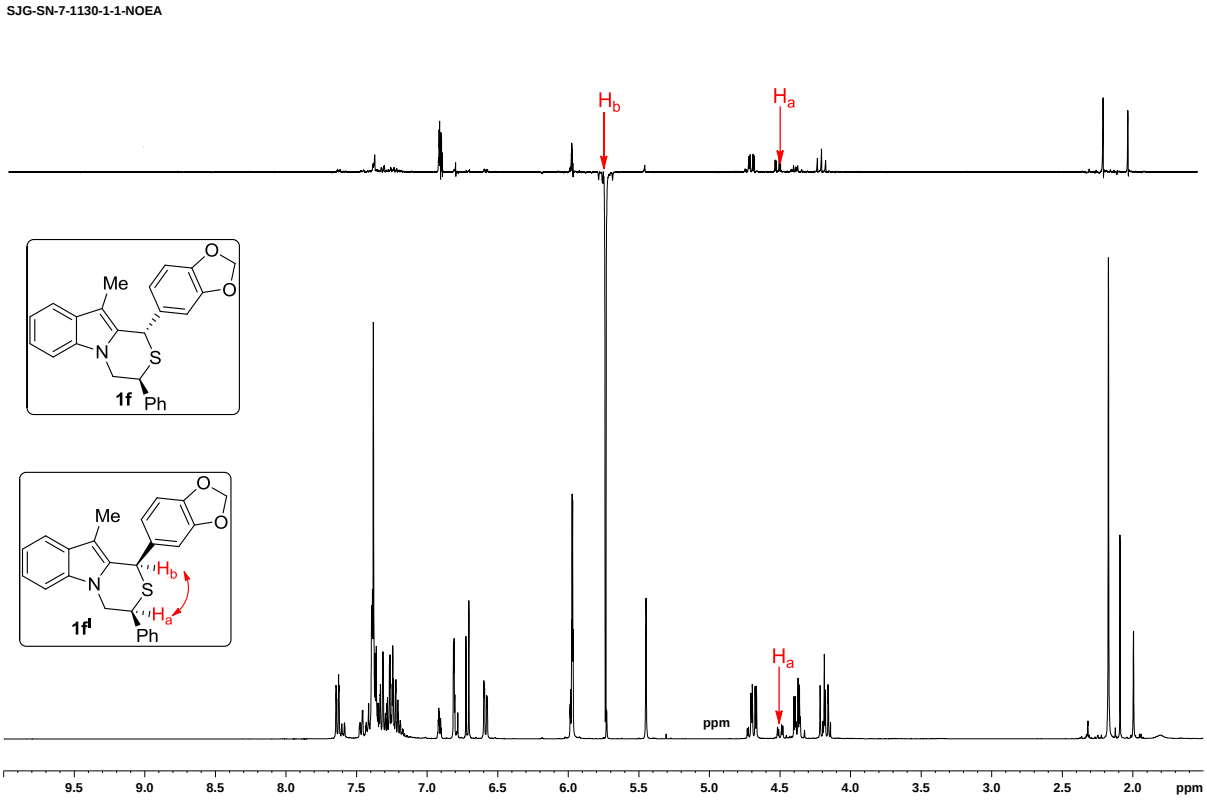
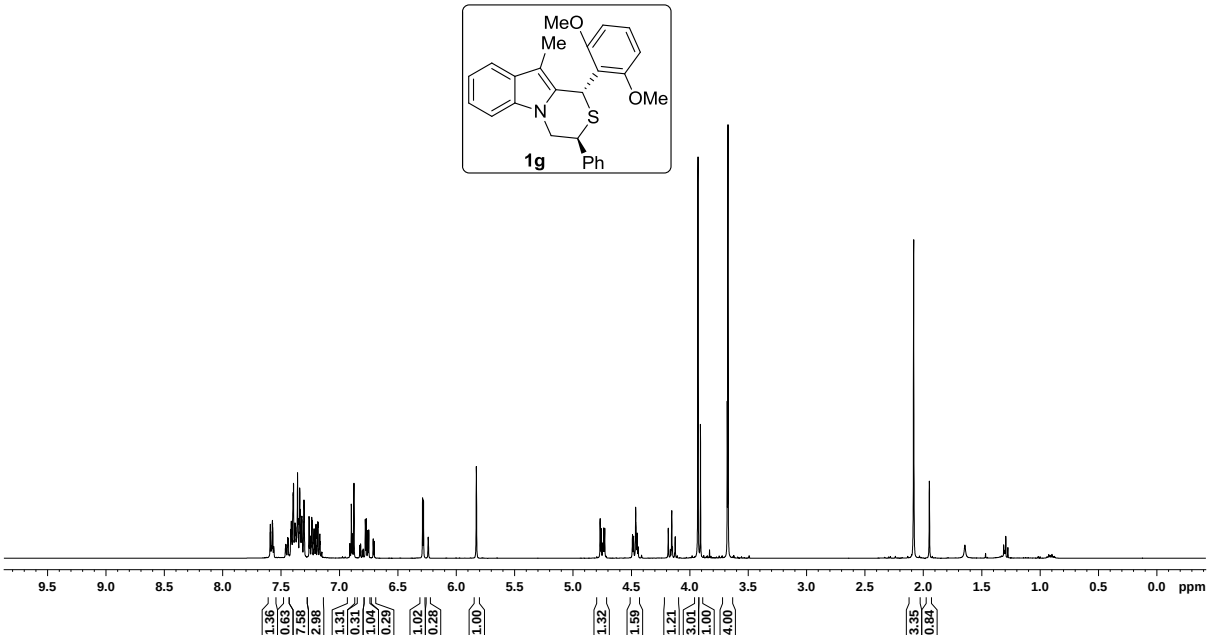


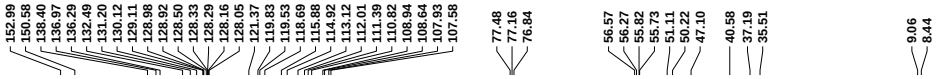




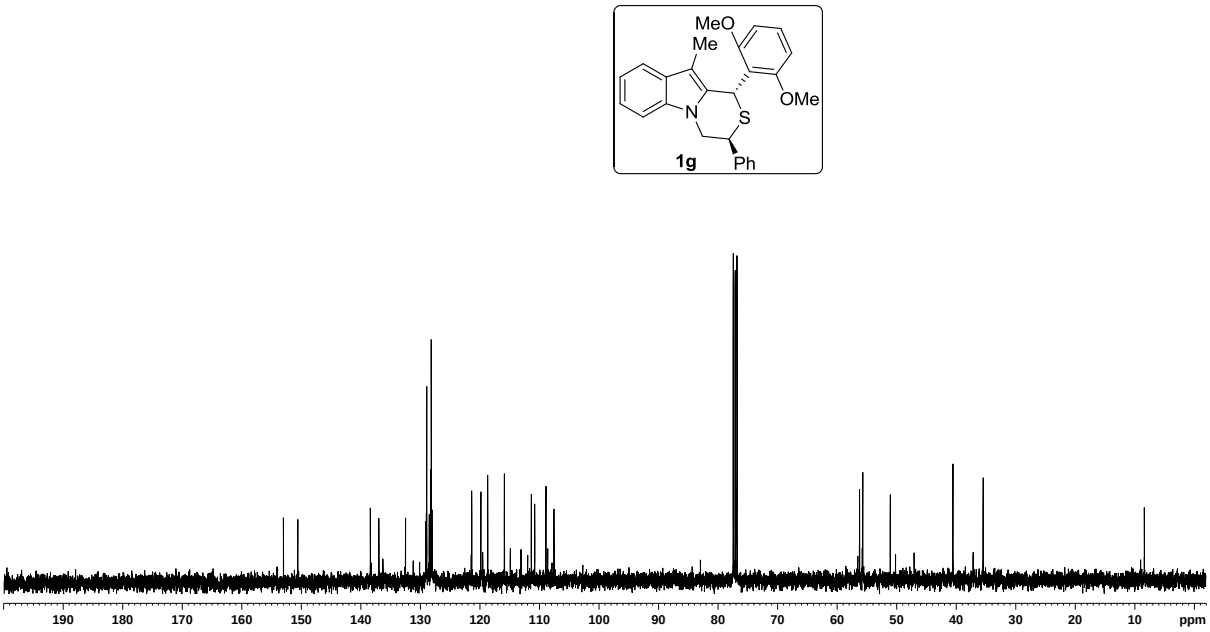
NOE enhancement-4%

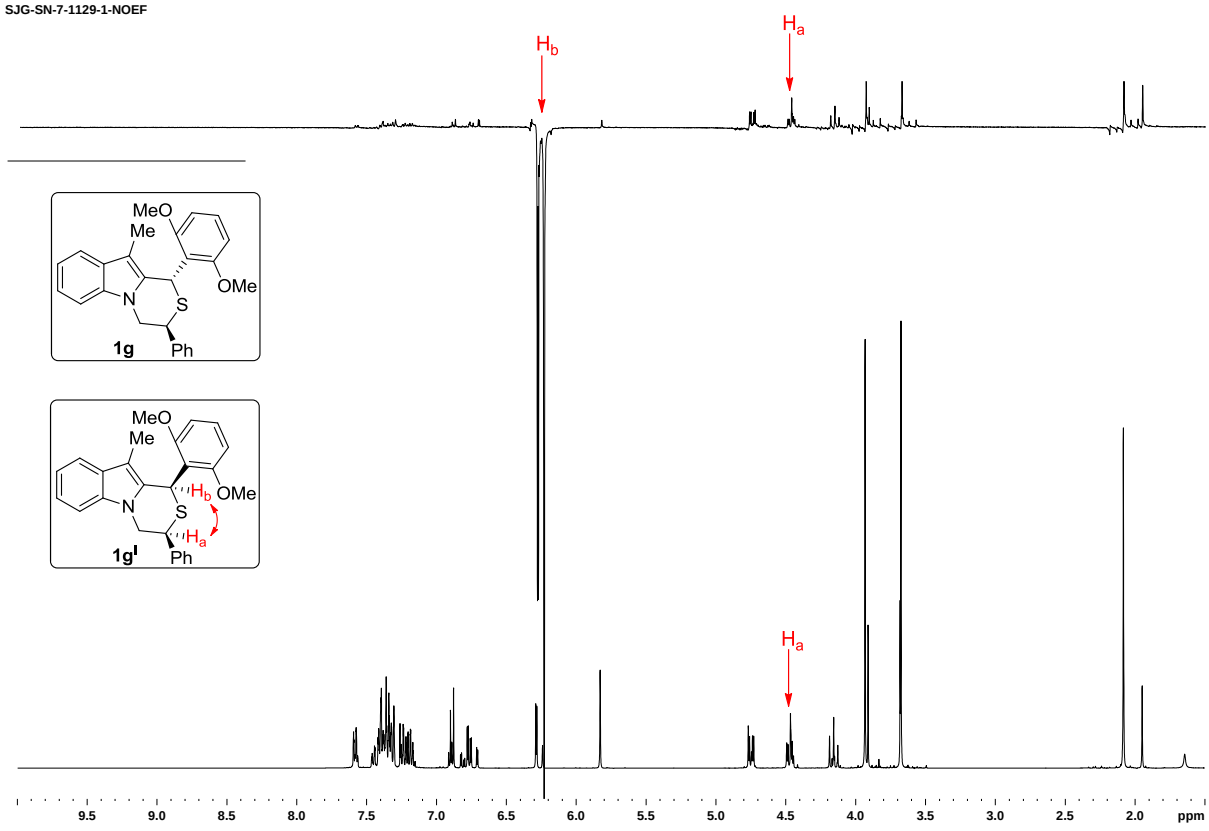
SJG-SN-7-1129-1H





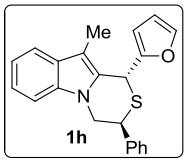
SJG-SN-7-1129-13C

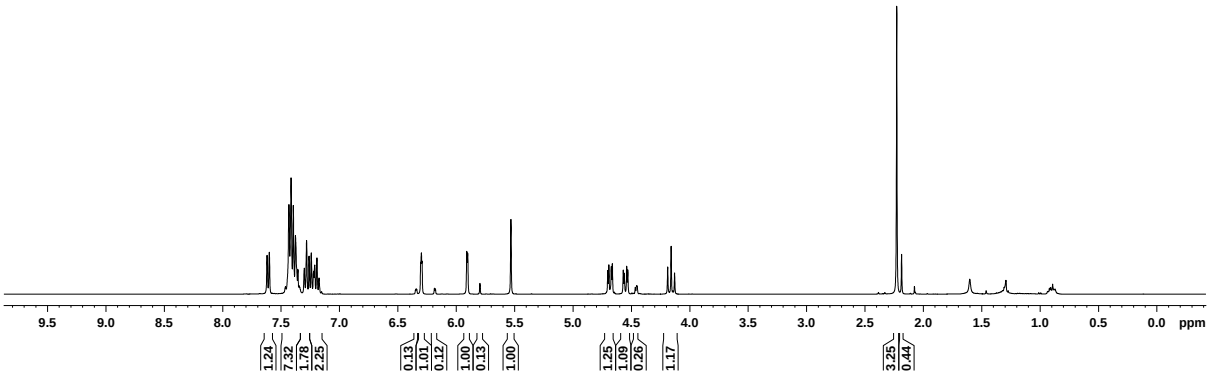




NOE enhancement-4%

SJG-SN-7-1134-1H





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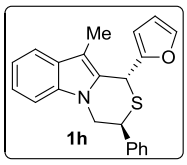

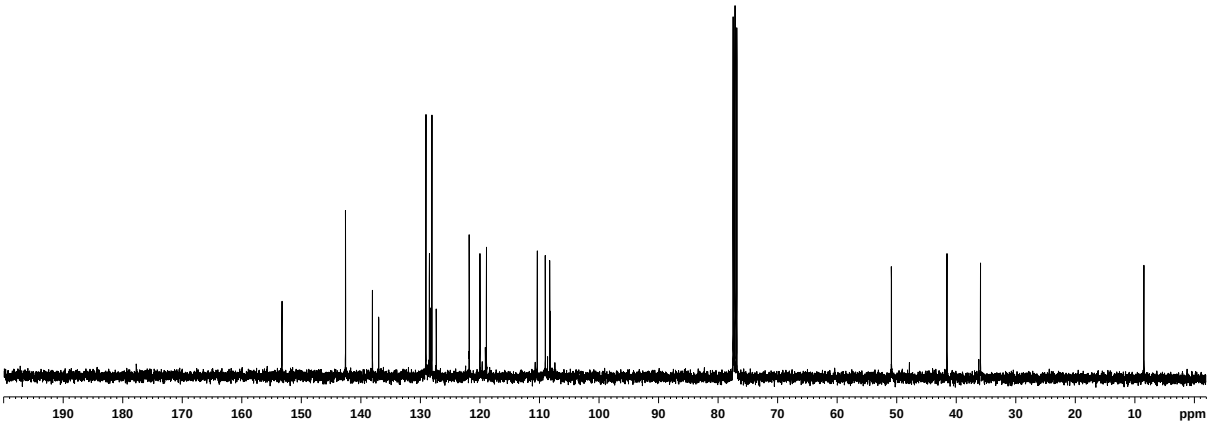

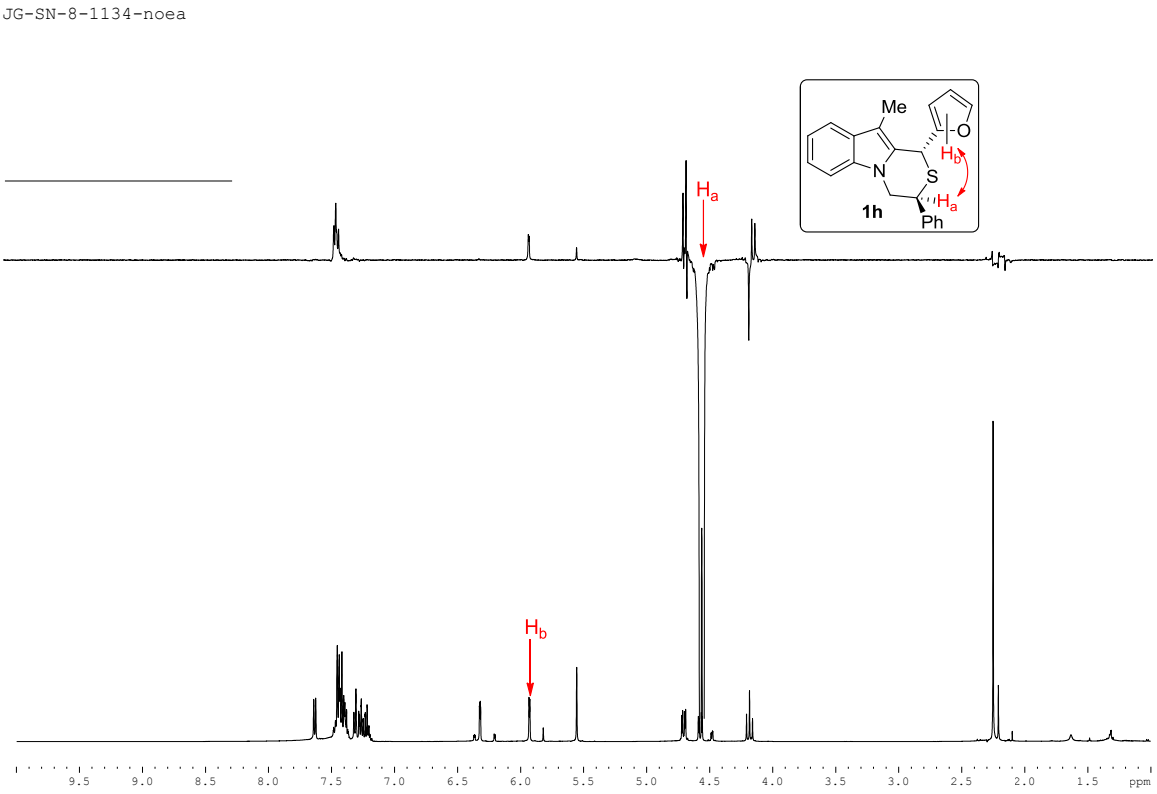

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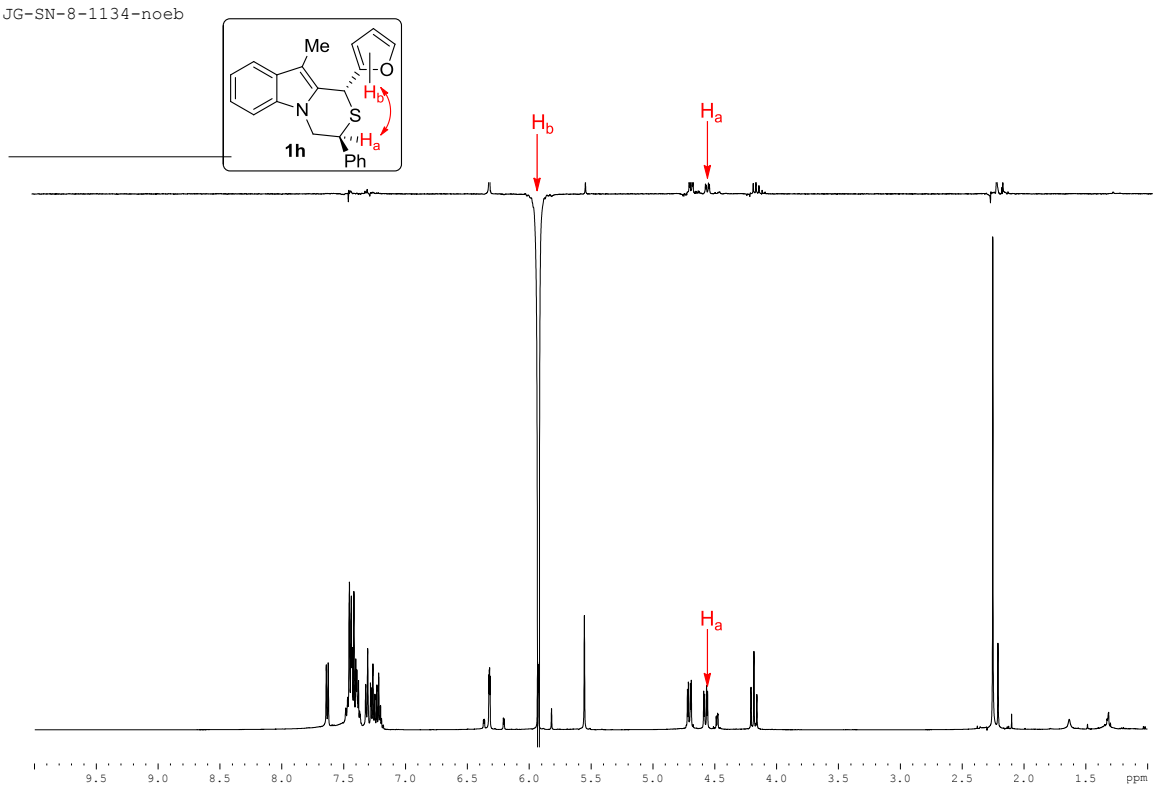

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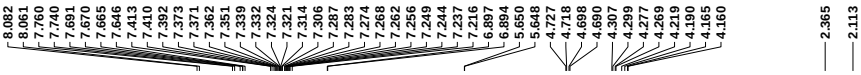
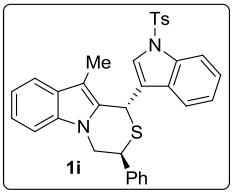
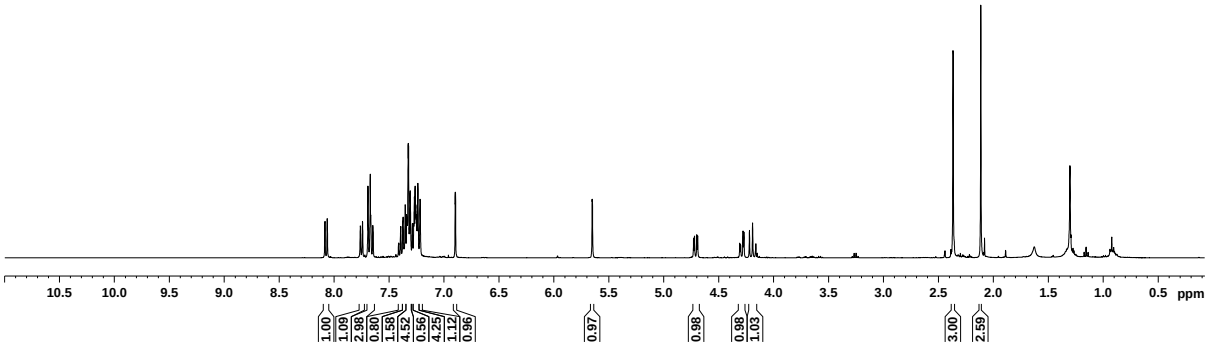
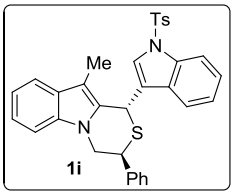


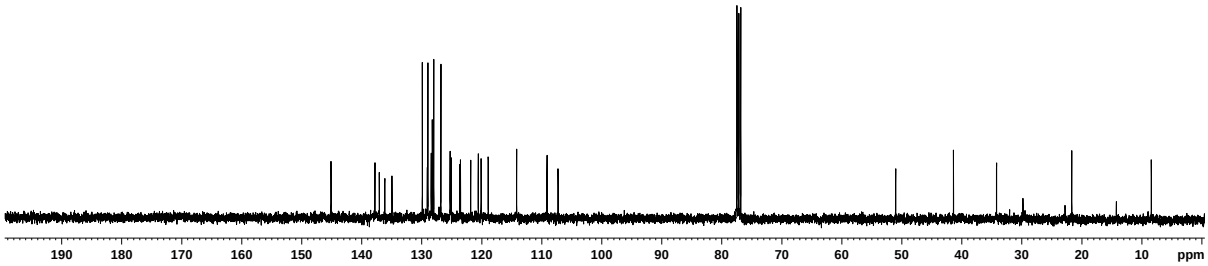
SJG-SN-4-542-PURE-H1

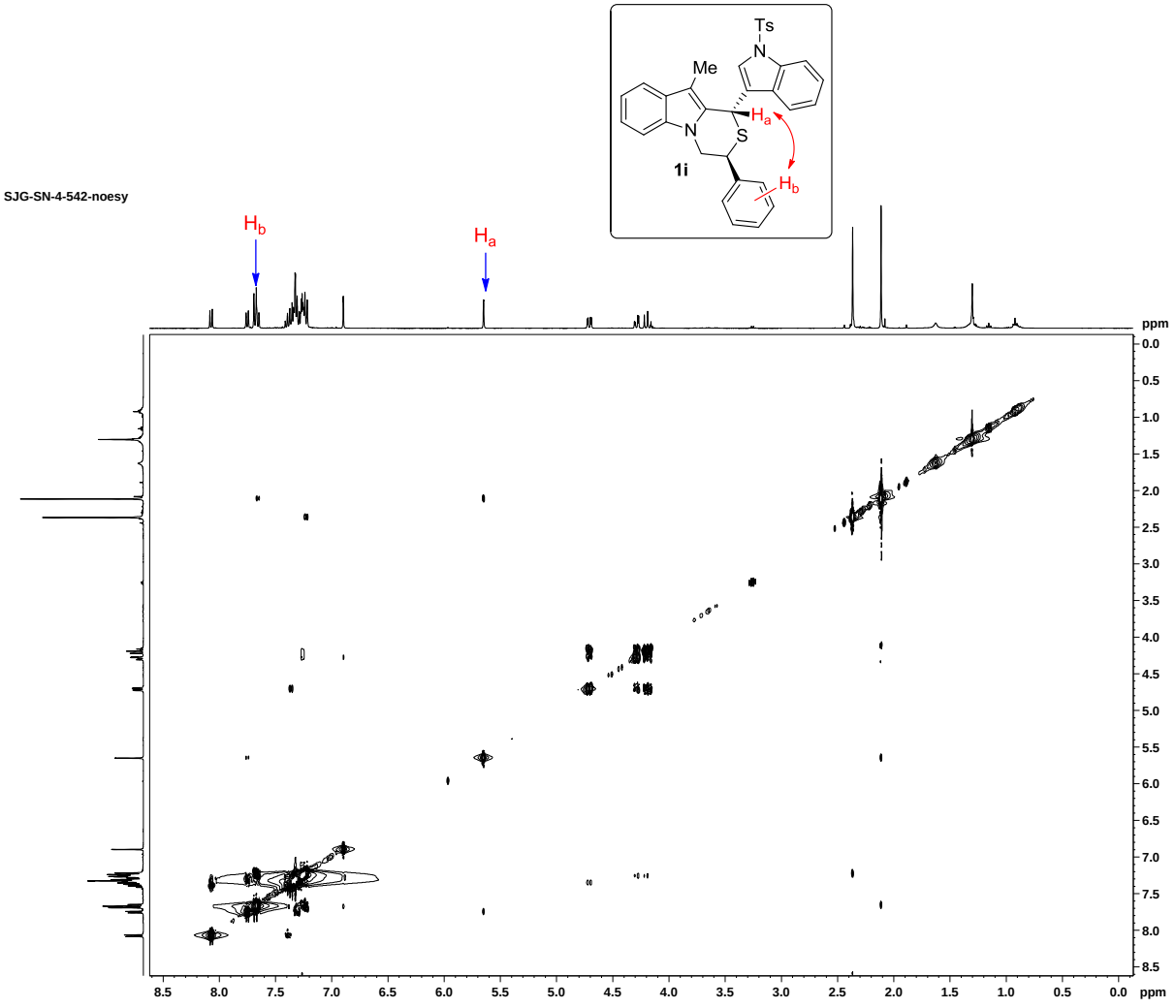




SJG-SN-4-542-PURE-C13






SJG-SN-4-542-noesy
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S
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1i
Hb
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3.5
4.0
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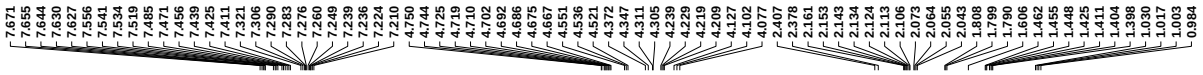
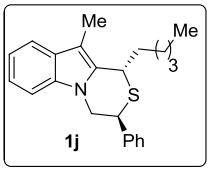
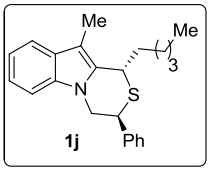
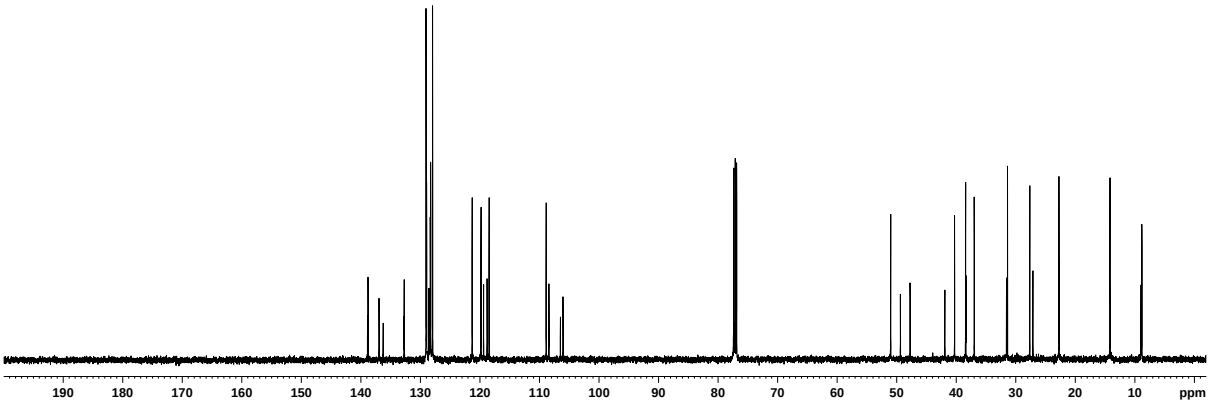


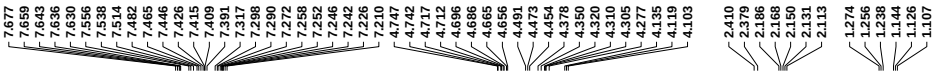
SJG-SN-7-1132-1H



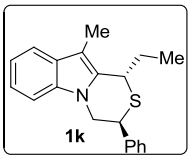
SJG-SN-7-1132-13c

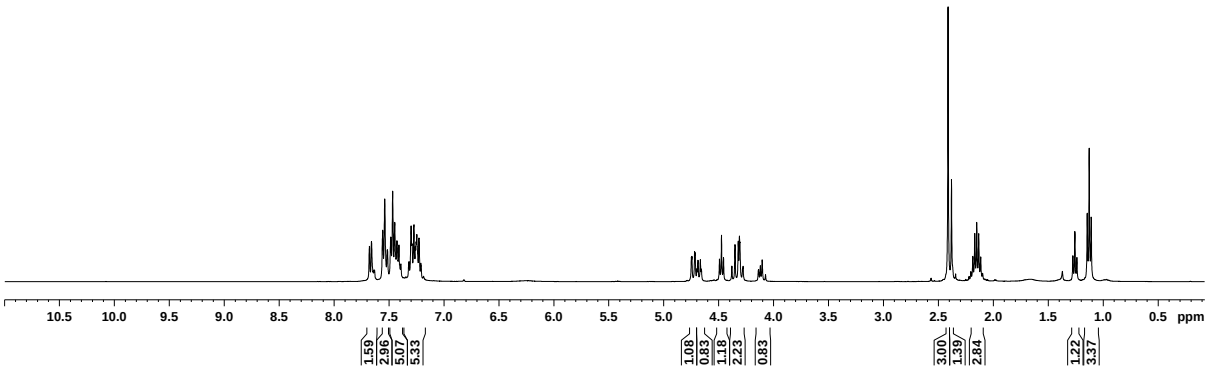


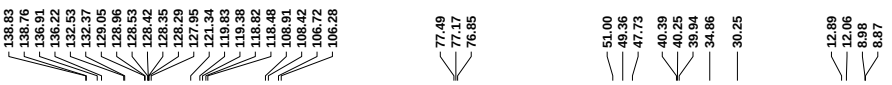




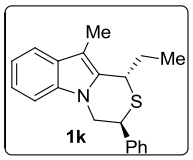
SJG-SNN-3-333-H1







SJG-SNN-3-333-C13



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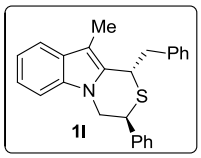

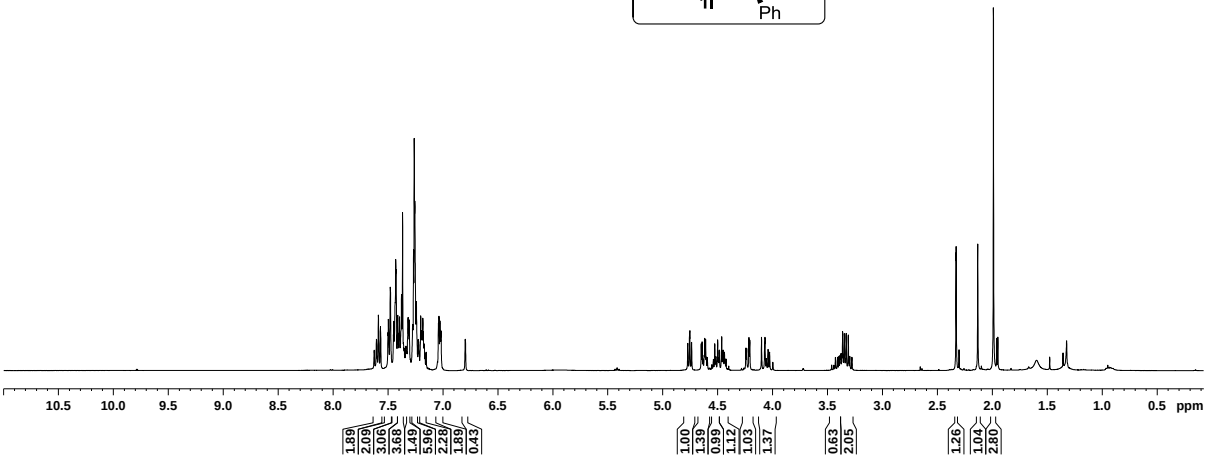

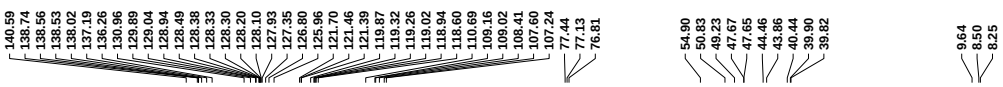

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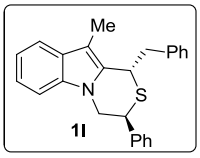

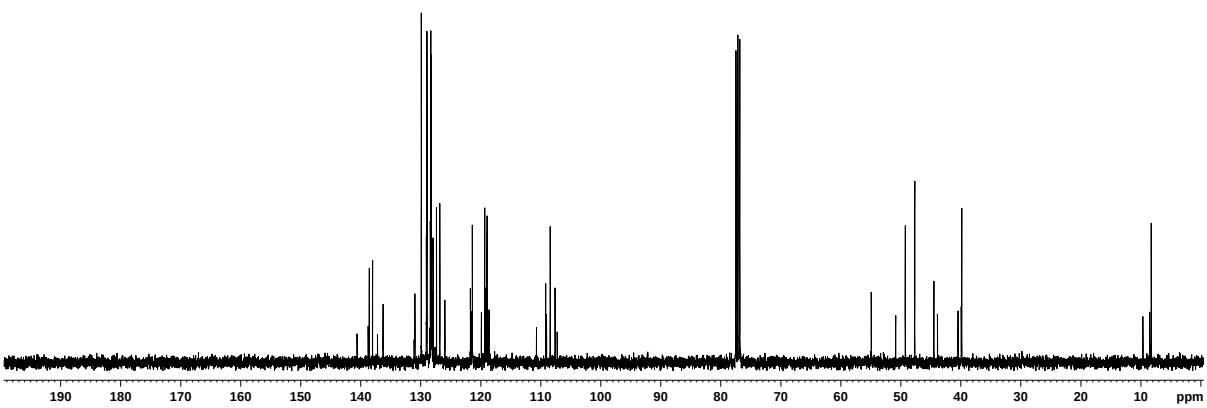

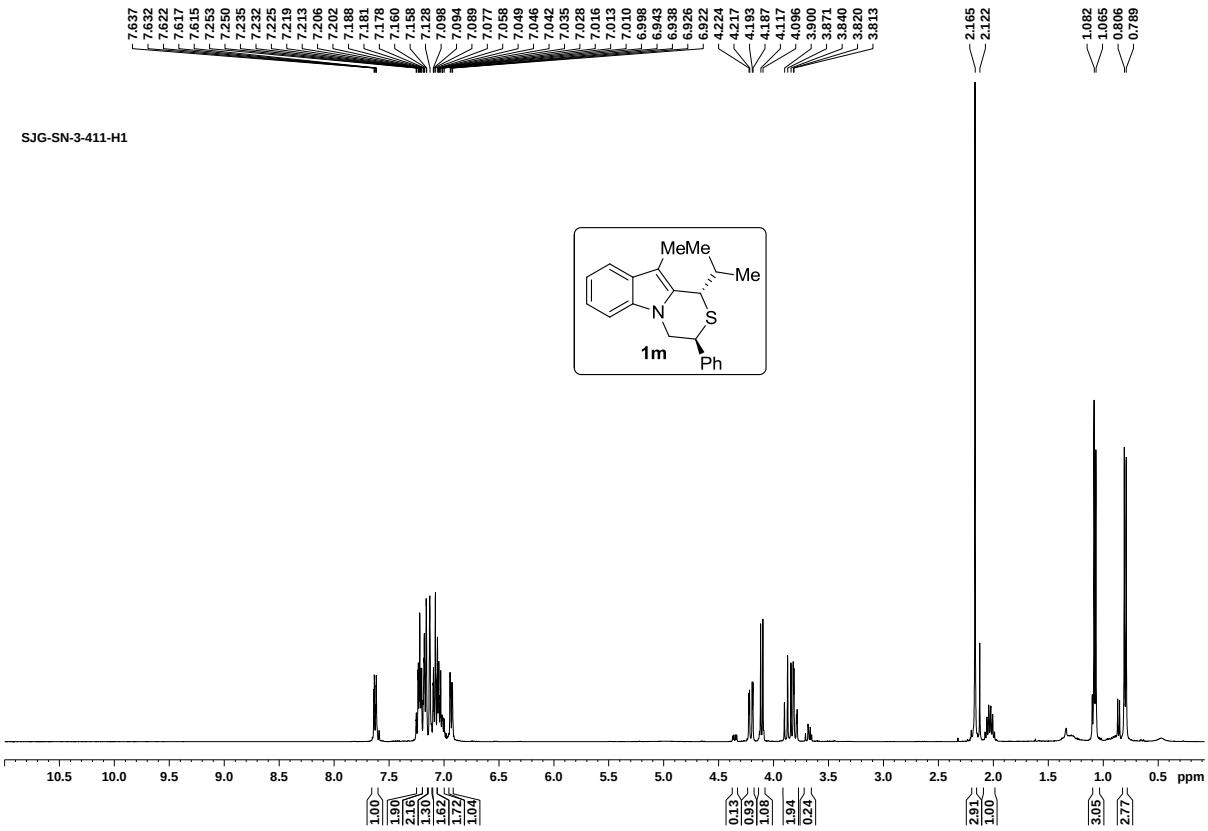
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7.632
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7.617
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7.235
7.232
7.225
7.219
7.213
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7.202
7.188
7.181
7.178
7.160
7.158
7.128
7.098
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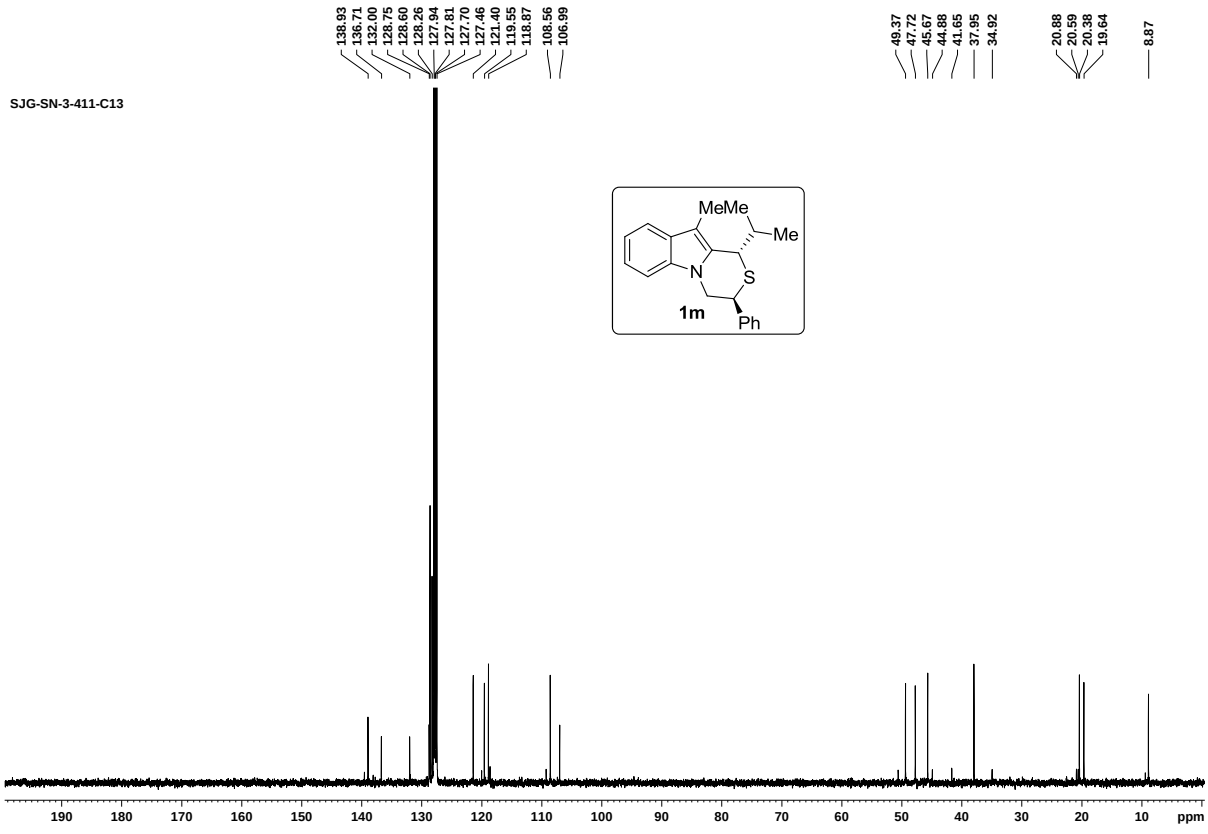
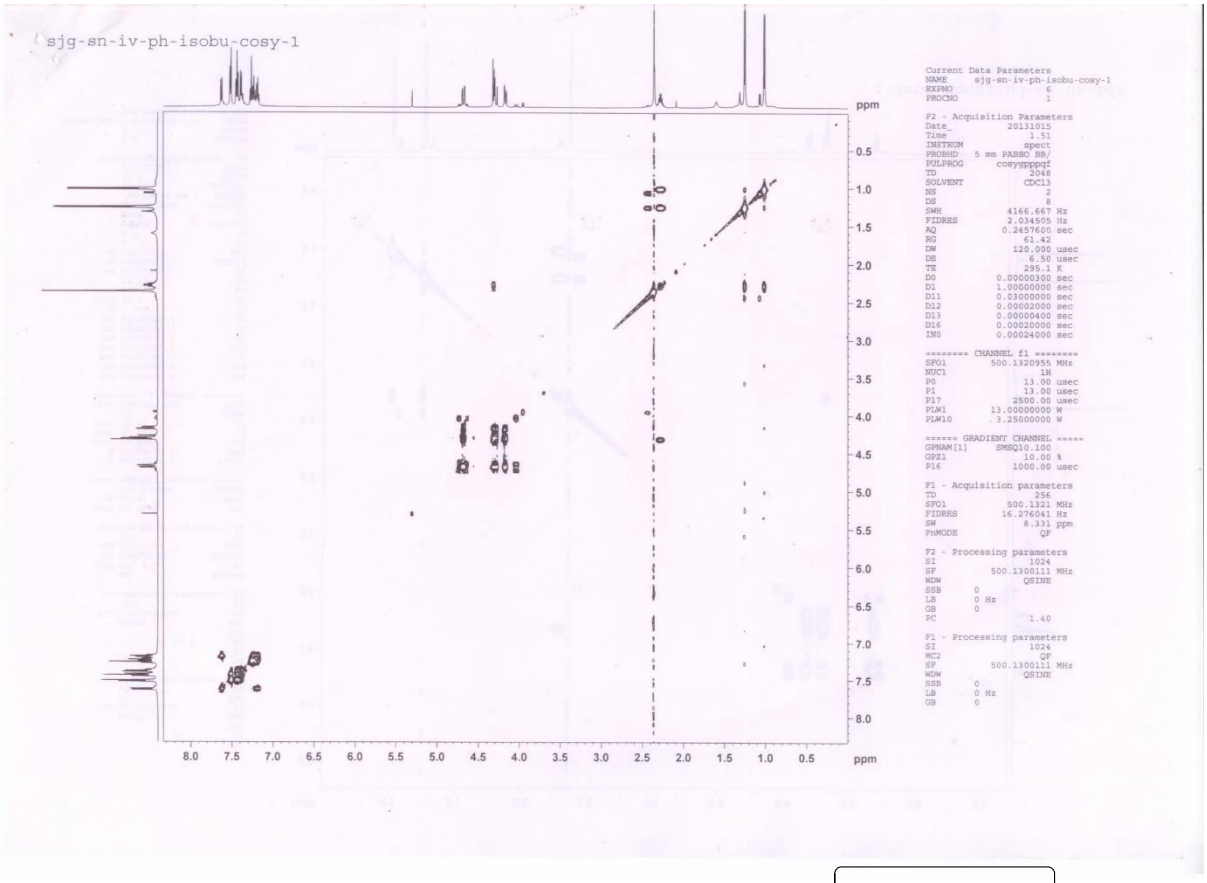
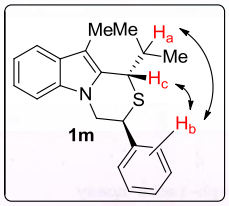
7.089
7.077
7.058
7.049
7.046
7.042
7.035
7.028
7.016
7.013
7.010
6.998
6.943
6.938
6.926
6.922
4.224
4.217
4.193
4.187
4.117
4.096
3.900
3.871
3.840
3.820
3.813
2.165
2.122
1.082
1.065
0.806
0.789
SJG-SN-3-411-H1
MeMe
Me
N
S
1m
Ph
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 1.90 2.16 1.30 1.62 1.72 1.04
0.13 0.93 1.08 1.94 0.24
2.91 1.00
3.05 2.77


138.93
136.71
132.00
128.75
128.60
128.26
127.94
127.81
127.70
127.46
121.40
119.55
118.87
108.56
106.99
49.37
47.72
45.67
44.88
41.65
37.95
34.92
20.88
20.59
20.38
19.64
8.87
SJG-SN-3-411-C13
MeMe
Me
N
S
1m
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


sjg-sn-iv-ph-isobu-cosy-1
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 0.5 ppm
Current Data Parameters
NAME sjg-sn-iv-ph-isobu-cosy-1
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20131015
Time 1.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG cosygppqf
TD 2048
SOLVENT CDCl3
NS 2
DS 8
SWH 4166.667 Hz
FIDRES 2.034505 Hz
AQ 0.2457600 sec
RG 61.42
DW 120.000 usec
DE 6.50 usec
TE 295.1 K
D0 0.00000300 sec
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
D13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00024000 sec
======== CHANNEL f1 ========
SFO1 500.1320955 MHz
NUC1 1H
P0 13.00 usec
P1 13.00 usec
P17 2500.00 usec
PLW1 13.00000000 W
PLW10 3.25000000 W
====== GRADIENT CHANNEL =====
GPNAM[1] SMSQ10.100
GPZ1 10.00 %
P16 1000.00 usec
F1 - Acquisition parameters
TD 256
SFO1 500.1321 MHz
FIDRES 16.276041 Hz
SW 8.331 ppm
FnMODE QF
F2 - Processing parameters
SI 1024
SF 500.1300111 MHz
WDW QSINE
SSB 0
LB 0 Hz
GB 0
PC 1.40
F1 - Processing parameters
SI 1024
MC2 QF
SF 500.1300111 MHz
WDW QSINE
SSB 0
LB 0 Hz
GB 0

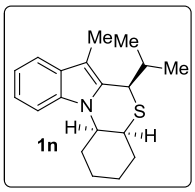

MeMe
Ha
Me
Hc
N
S
Hb
1m

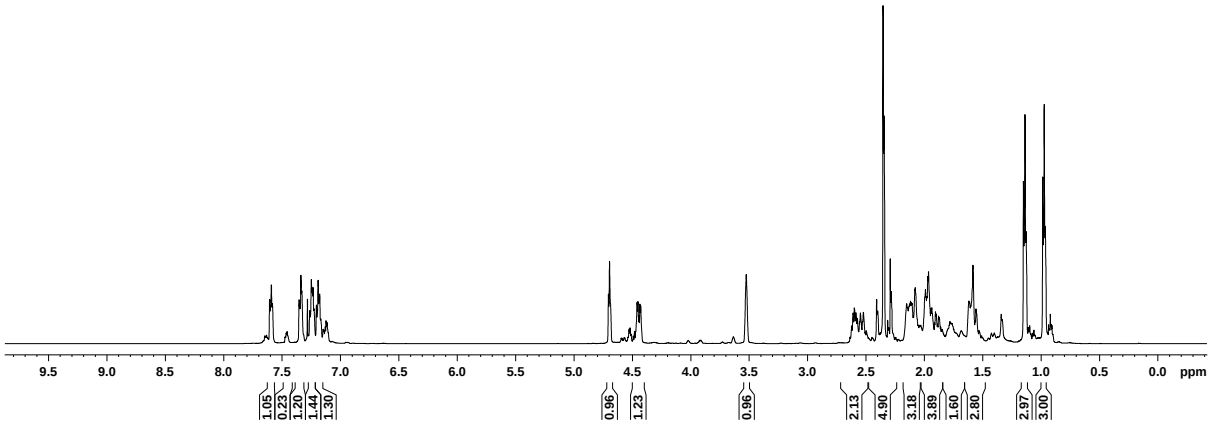
sjg-sn-iv-ph-isobu-noesy
Hb
Hc
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
Current Data Parameters
NAME sjg-sn-iv-ph-isobu-noesy
EXPNO 9
PROCNO 1
F2 - Acquisition Parameters
Date_ 20131015
Time 2.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG noesygppph
TD 2048
SOLVENT CDCl3
NS 8
DS 32
SWH 4166.667 Hz
FIDRES 2.034505 Hz
AQ 0.2457600 sec
RG 106.54
DW 120.000 usec
DE 6.50 usec
TE 295.0 K
D0 0.00010345 sec
D1 1.00000000 sec
D8 0.60000002 sec
D16 0.00020000 sec
IN0 0.00024000 sec
======== CHANNEL f1 ========
SFO1 500.1320955 MHz
NUC1 1H
P1 13.00 usec
P2 26.00 usec
PLW1 13.00000000 W
====== GRADIENT CHANNEL =====
GPNAM[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec
F1 - Acquisition parameters
TD 273
SFO1 500.1321 MHz
FIDRES 15.262515 Hz
SW 8.331 ppm
FnMODE TPPI
F2 - Processing parameters
SI 1024
SF 500.1300111 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00
F1 - Processing parameters
SI 1024
MC2 TPPI
SF 500.1300111 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

7.606 7.591 7.583 7.354 7.346 7.338 7.331 7.283 7.263 7.249 7.242 7.235 7.226 7.205 7.191 7.182 7.178

4.707 4.697 4.461 4.453 4.445 4.437 4.430 3.526 2.624 2.611 2.600 2.587 2.574 2.556 2.548 2.523 2.506 2.498 2.409 2.401 2.355 2.346 2.293 2.287 2.283 2.152 2.127 2.120 2.111 2.106 2.095 2.082 2.079 1.991 1.980 1.972 1.965 1.944 1.937 1.906 1.899 1.879 1.872 1.619 1.605 1.584 1.566

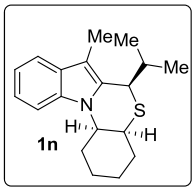
sjg-sn-7-cz-1so

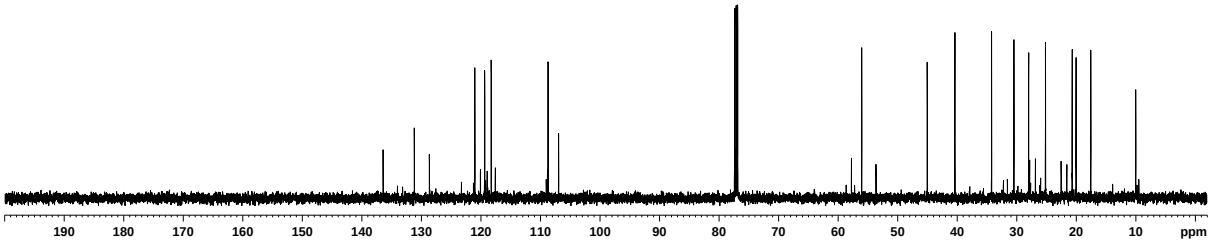


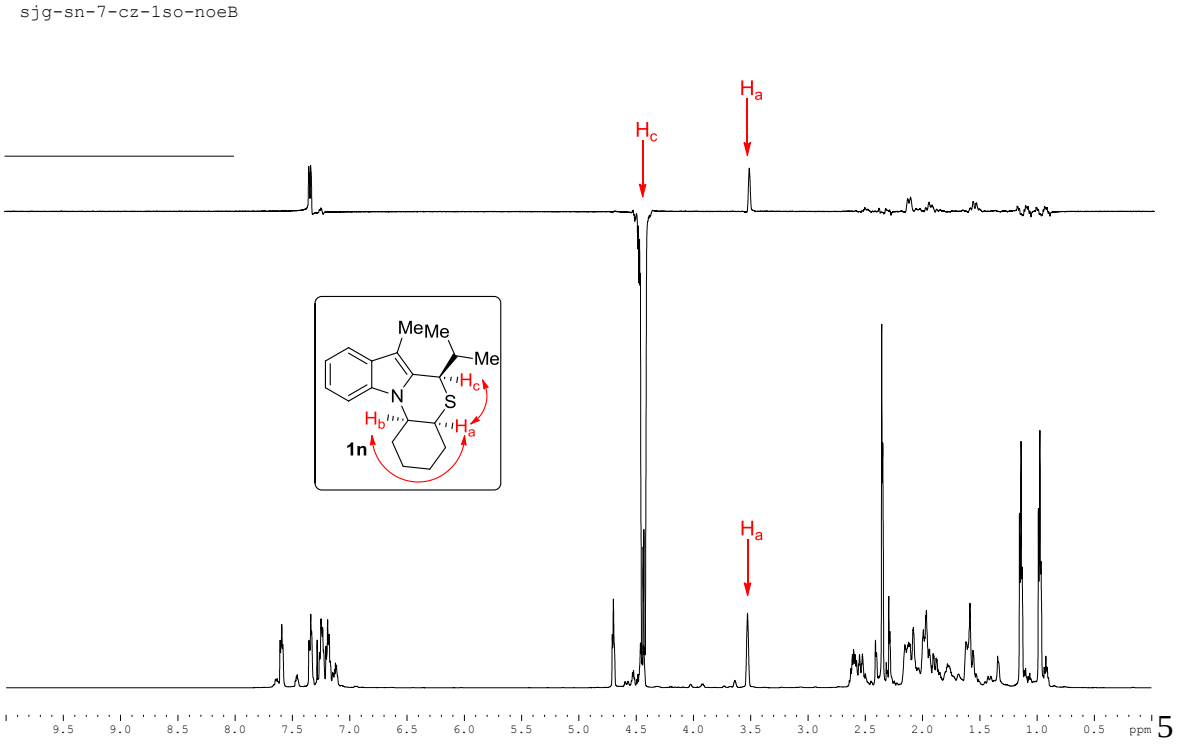


136.43 131.17 128.66 121.02 119.37 118.27 108.72 106.95 77.42 77.16 76.91 56.08 45.07 40.42 34.26 30.51 28.03 25.20 20.72 20.06 17.60 10.06

sjg-sn-7-cz-1so-13C

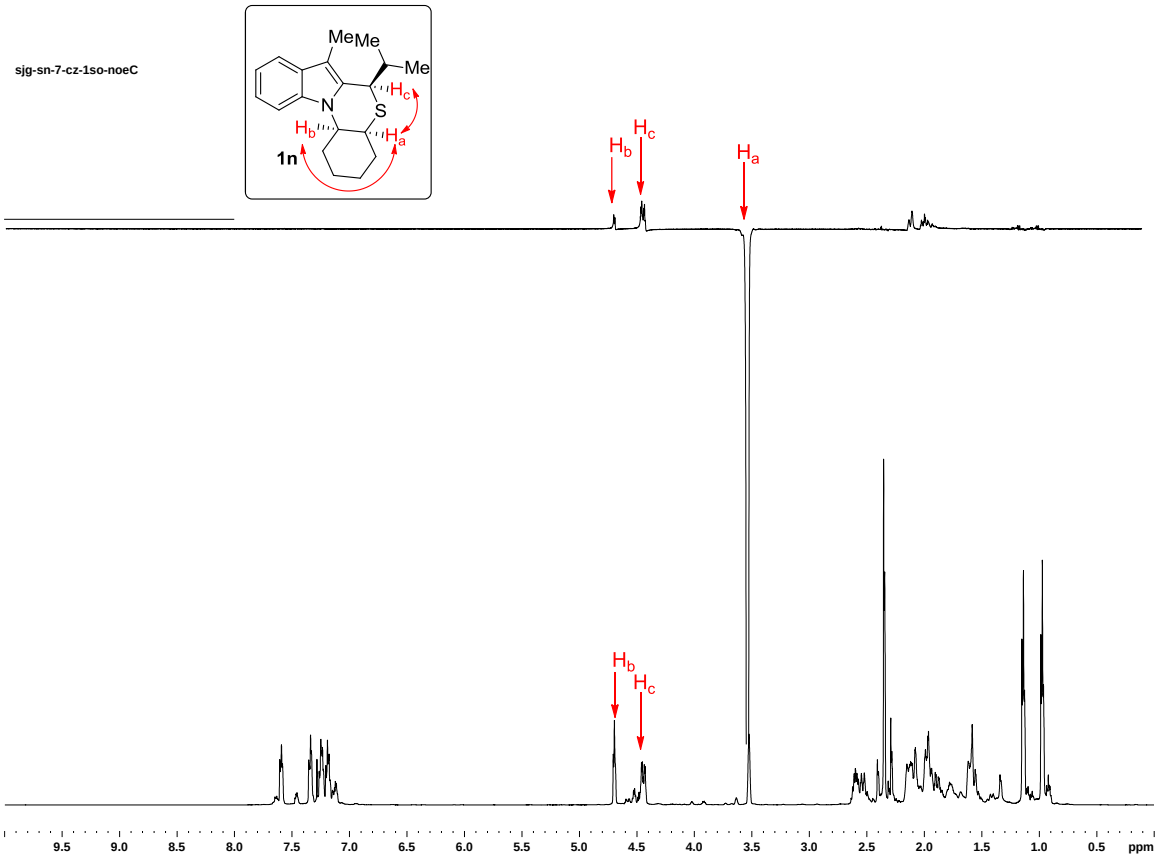






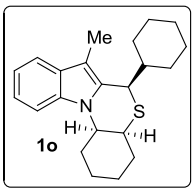
5

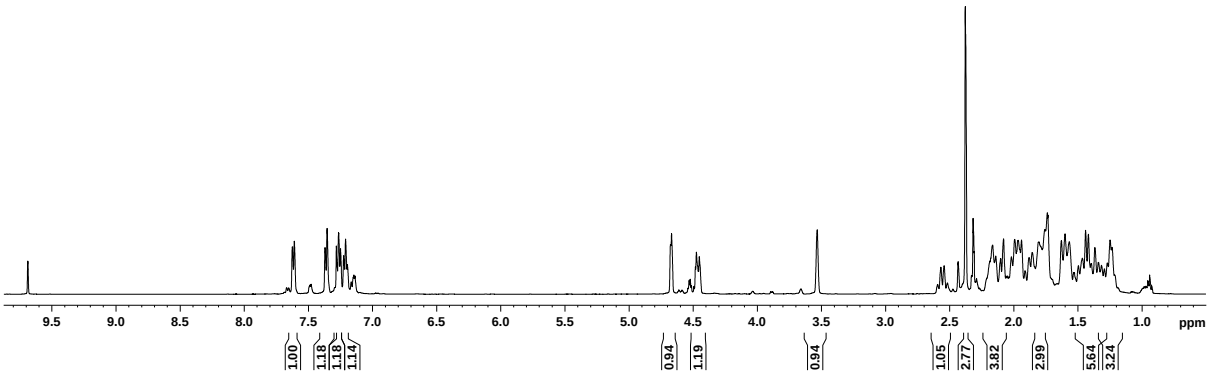
NOE enhancement-5%



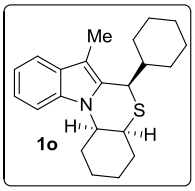
NOE enhancement-5%

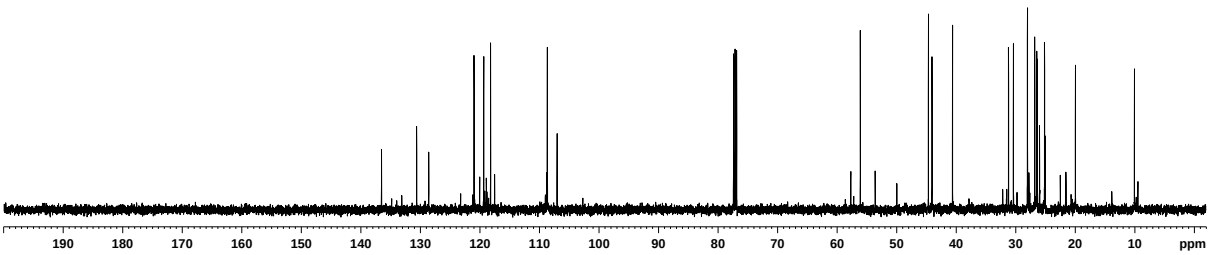
sjg-sn-7-cY-CY-1H

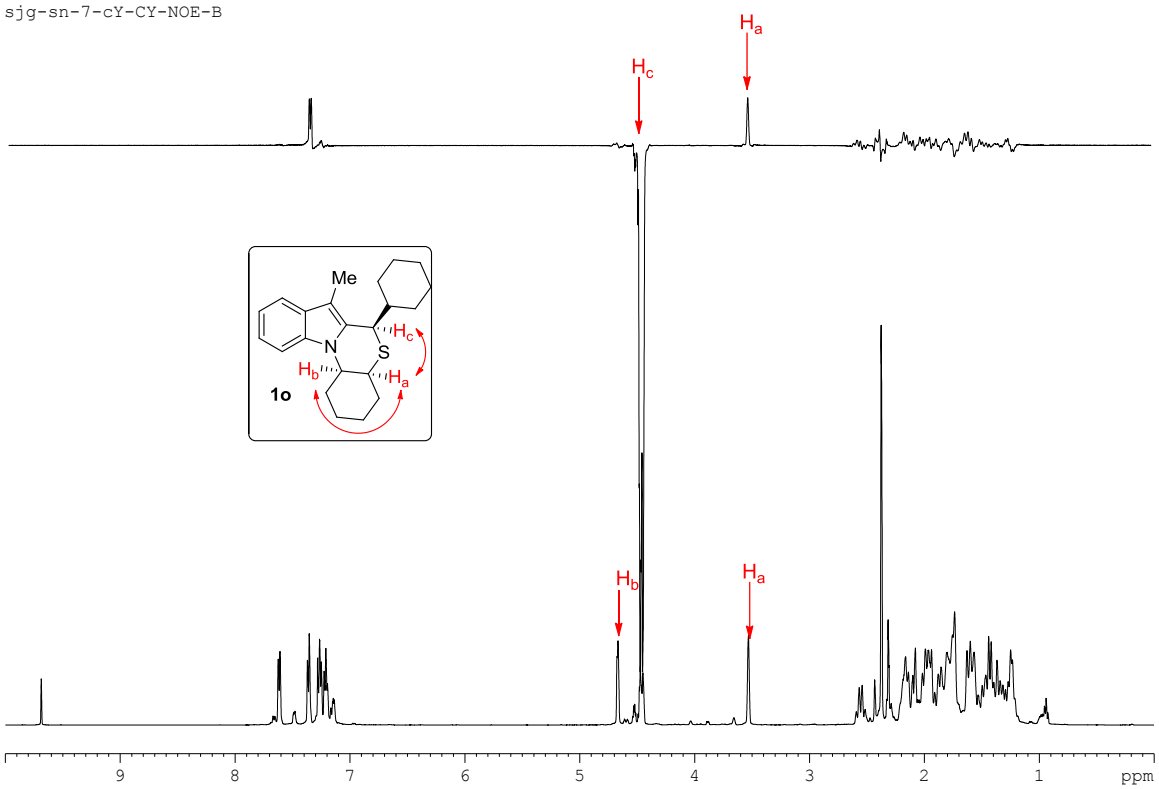




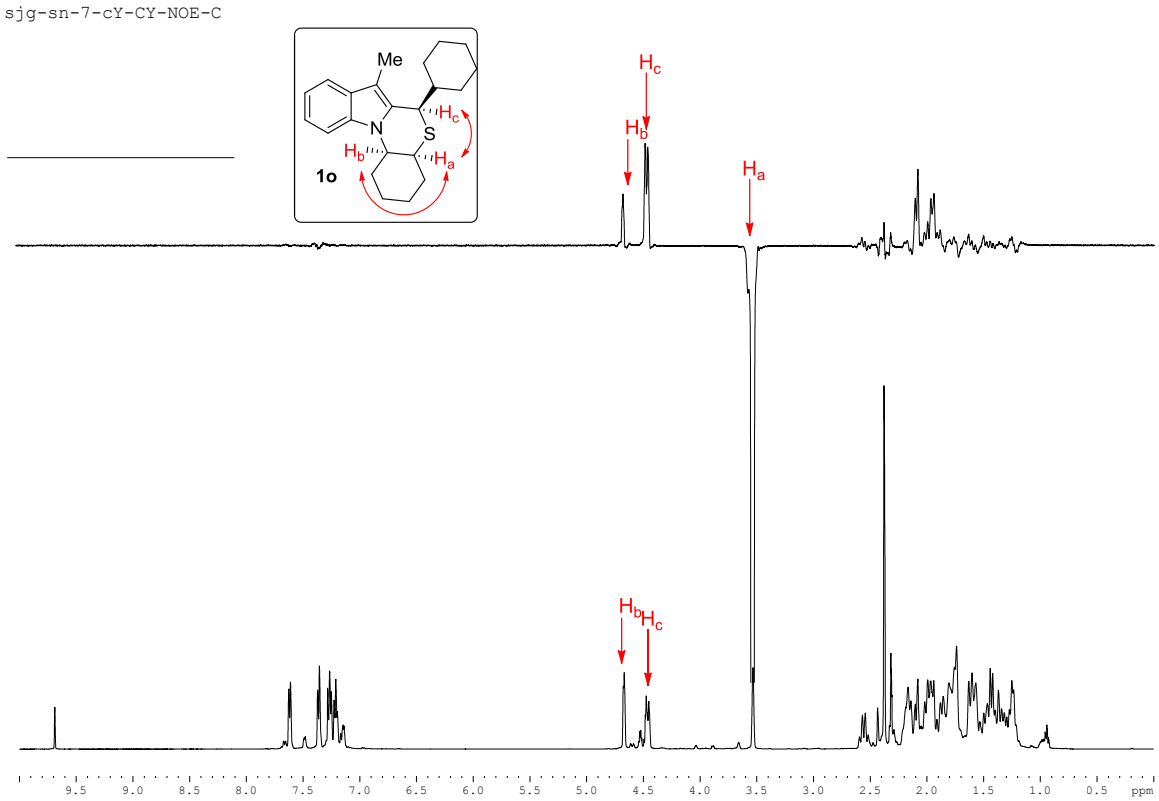
sjg-sn-7-cY-CY-13C





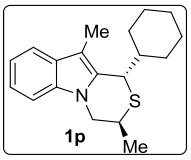


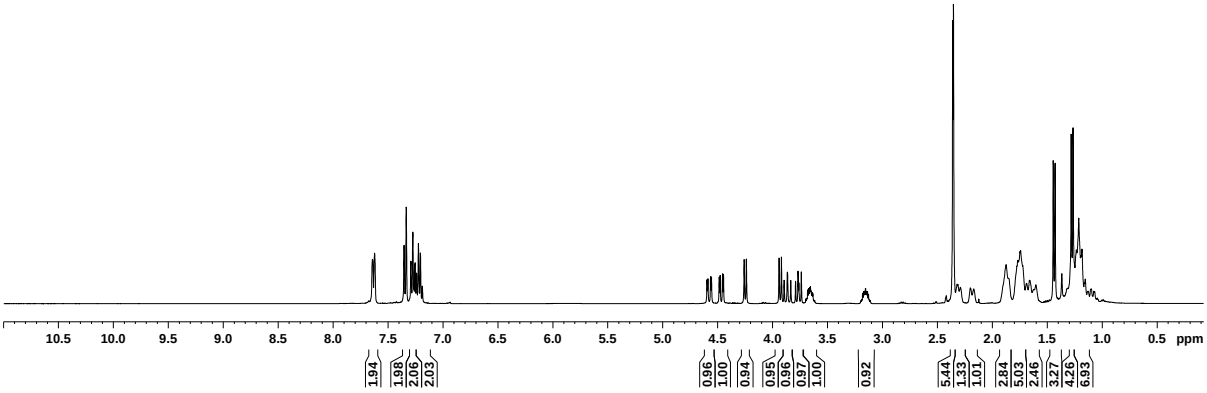
NOE enhancement-5%

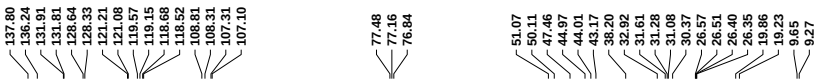


NOE enhancement-5%

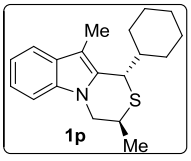
SJG-SN-3-424-H1

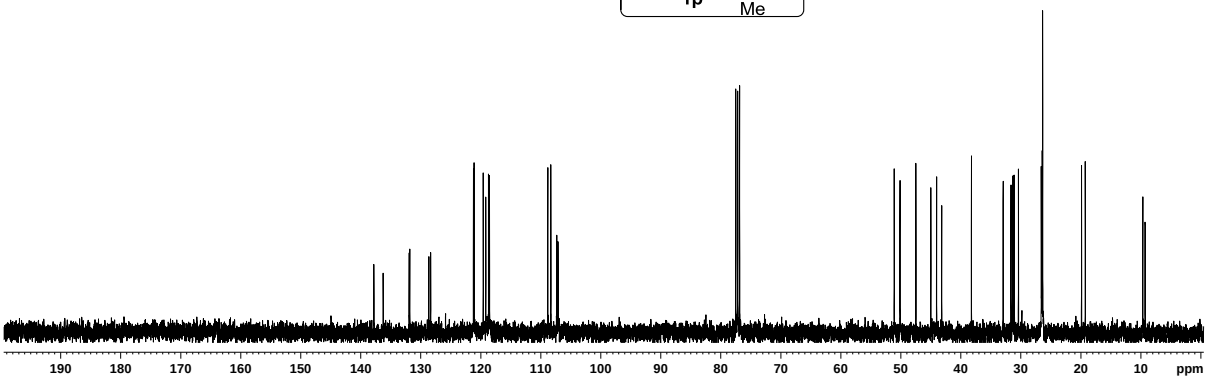




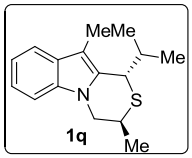


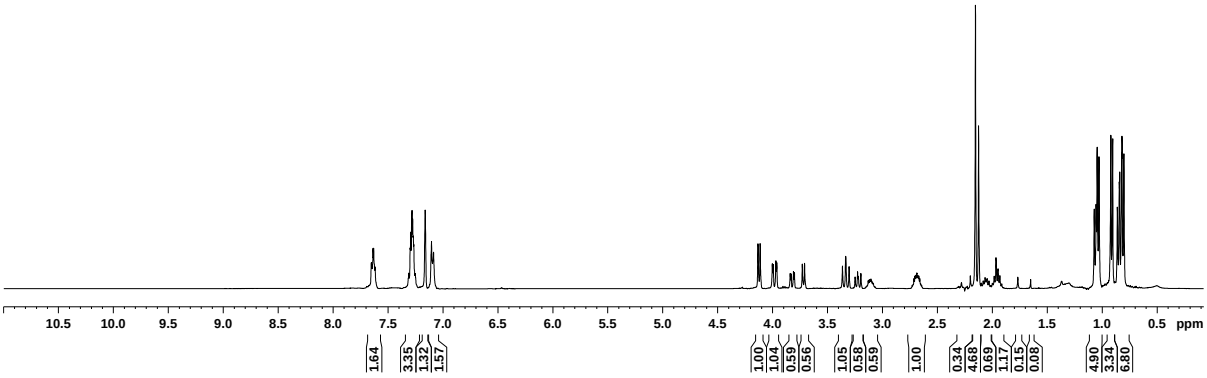
SJG-SN-3-424-C13





SJG-SN-III-425-1H





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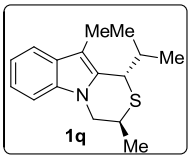
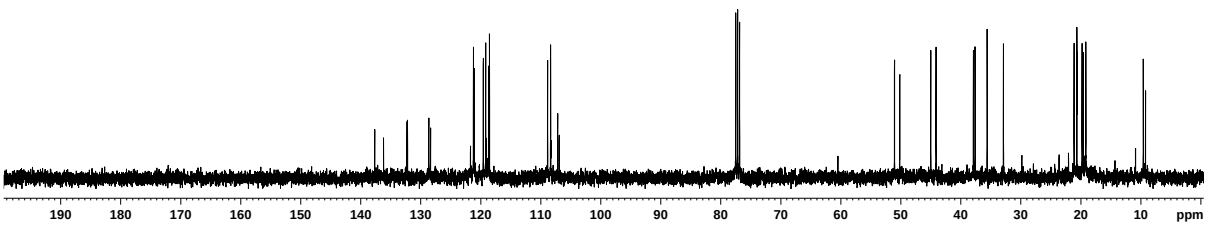
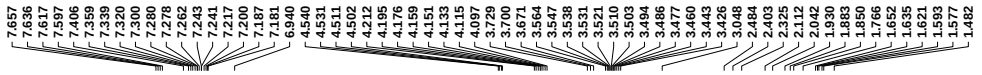
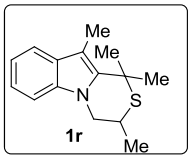
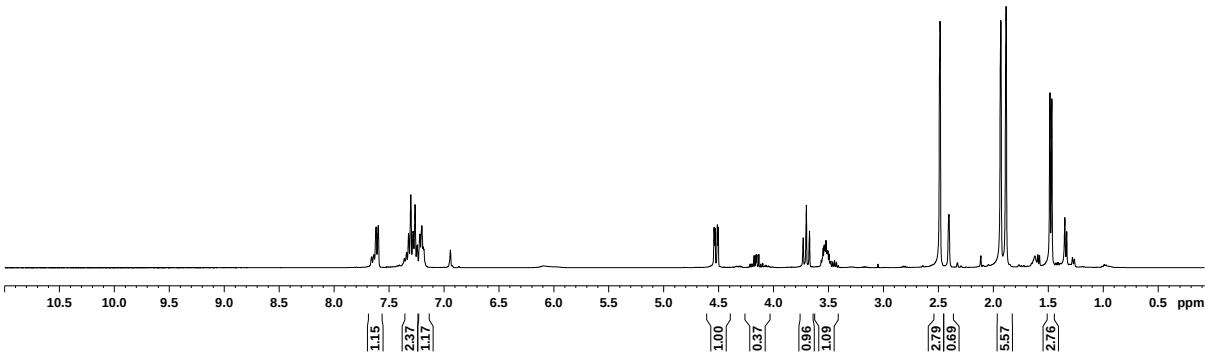




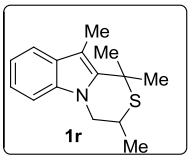


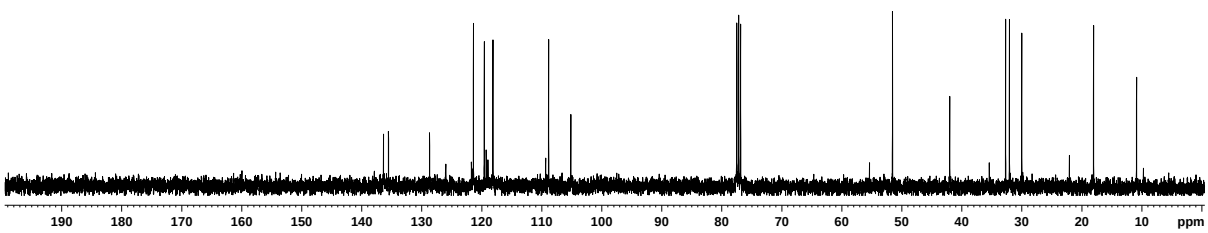
SJG-SN-3-485-H1

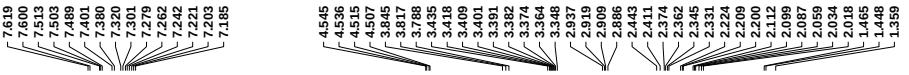




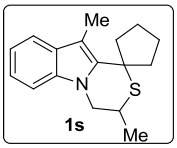
SJG-SN-3-485-C13

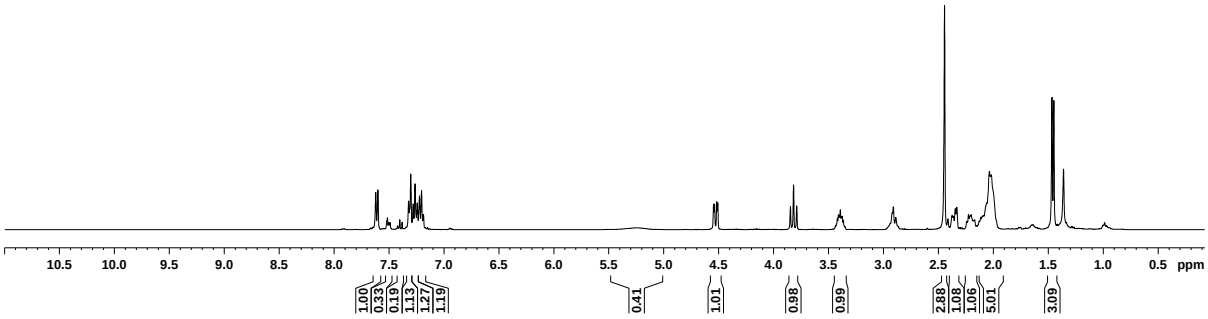


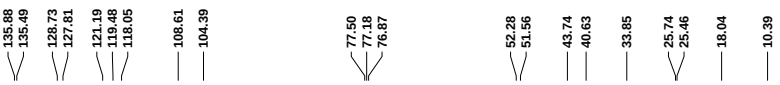




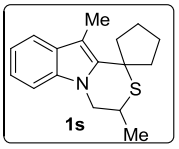
SJG-SN-3-468-H1

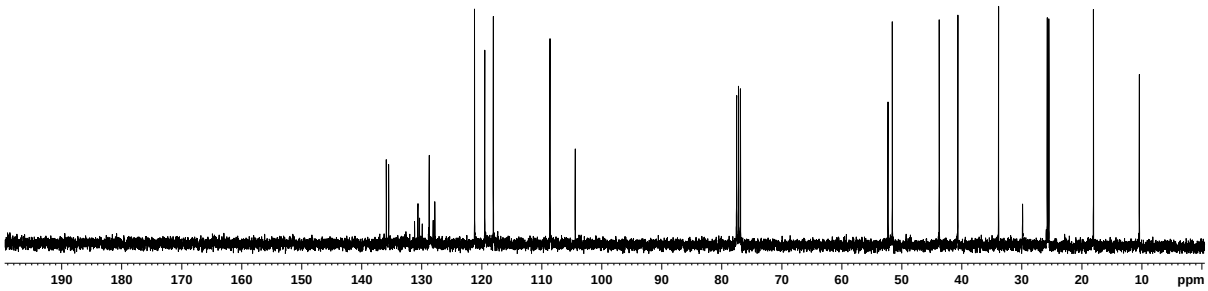


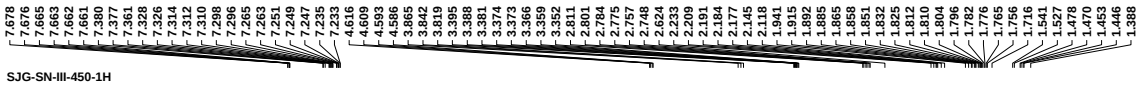




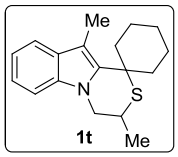
SJG-SN-3-468-C13

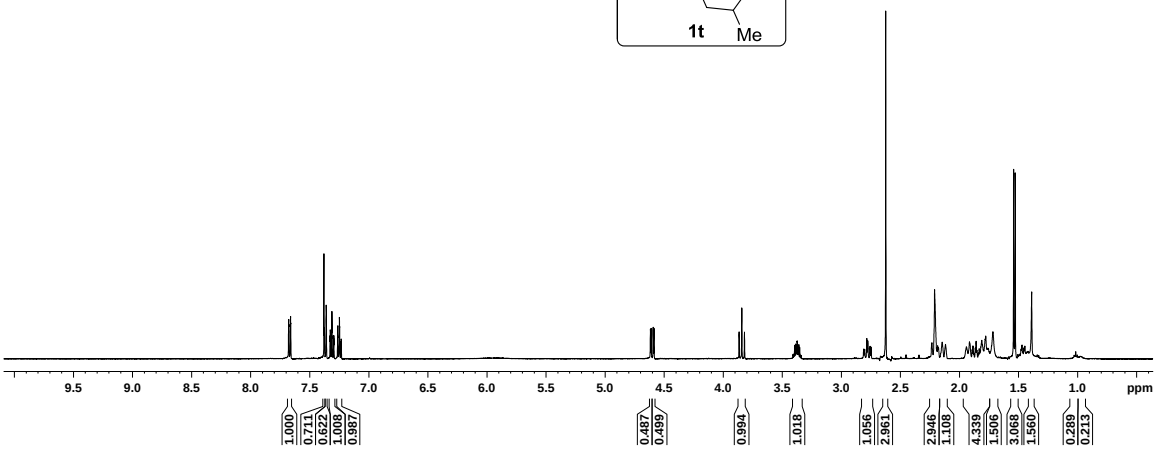


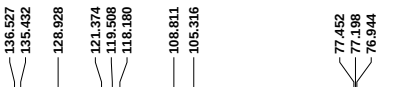




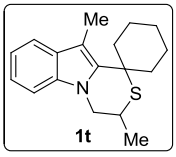
SJG-SN-III-450-1H

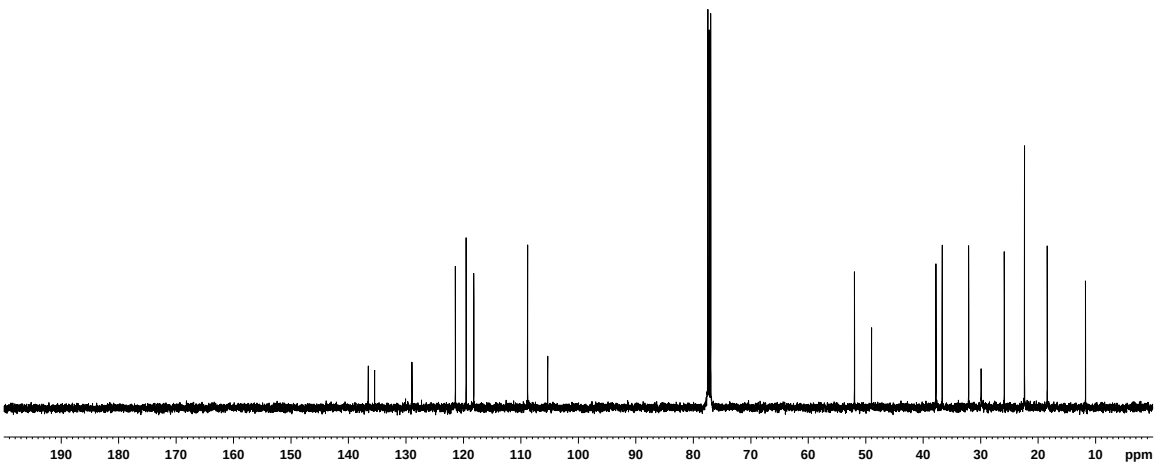


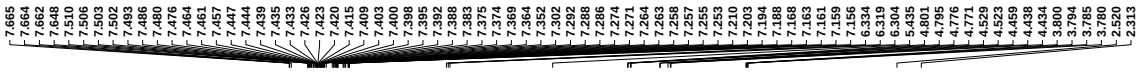




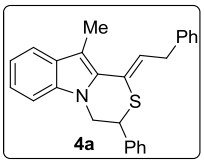
SJG-SN-III-450-13C

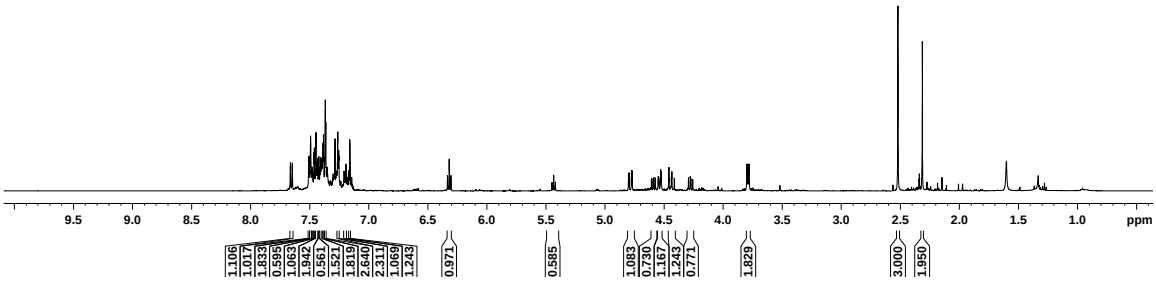


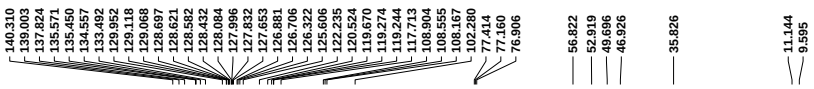




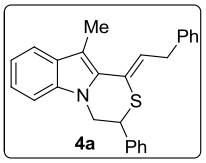
SJG-SN-4-528-H1

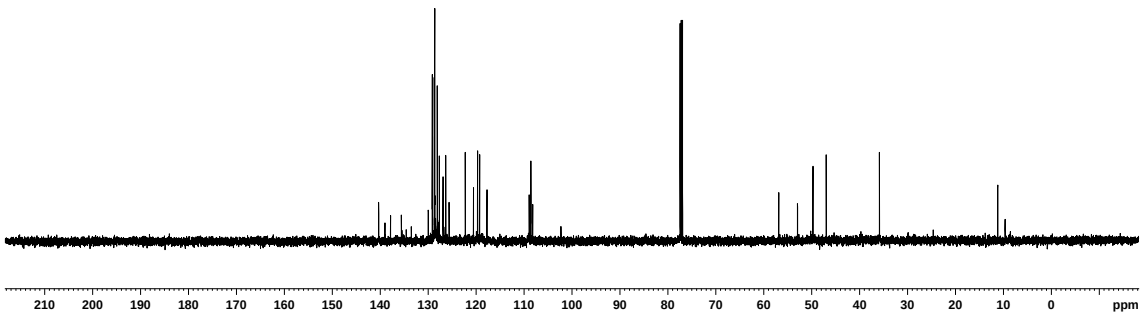


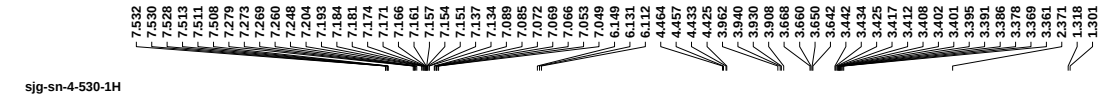




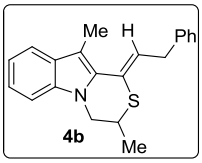
SJG-SN-4-528-C13

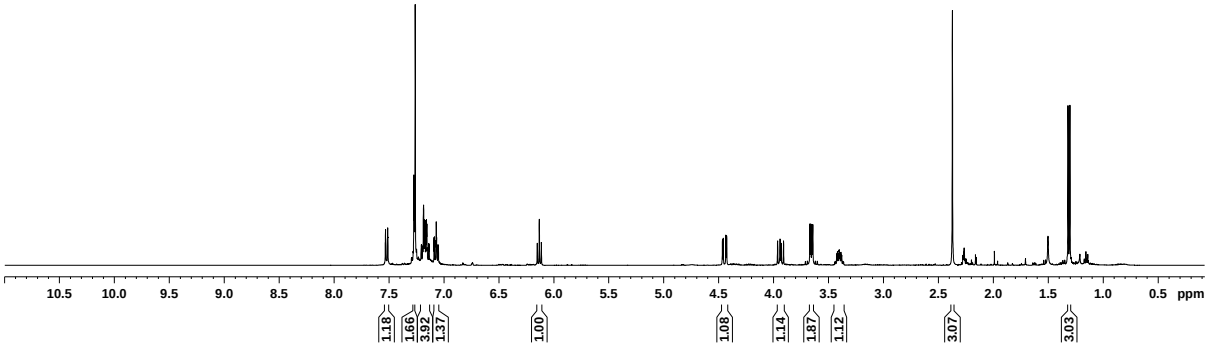


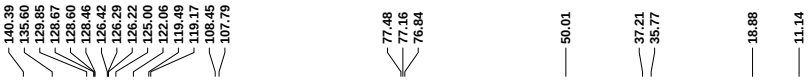




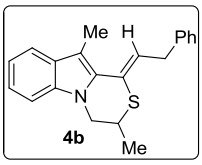
sjg-sn-4-530-1H

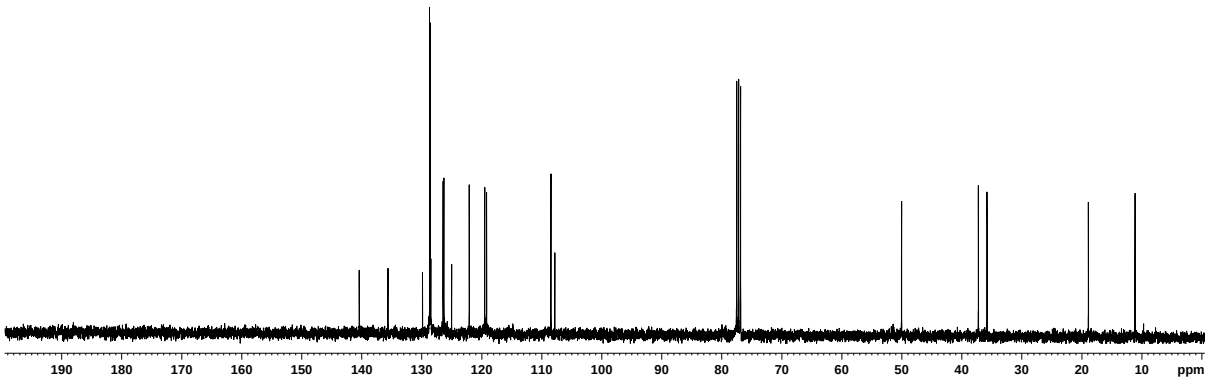


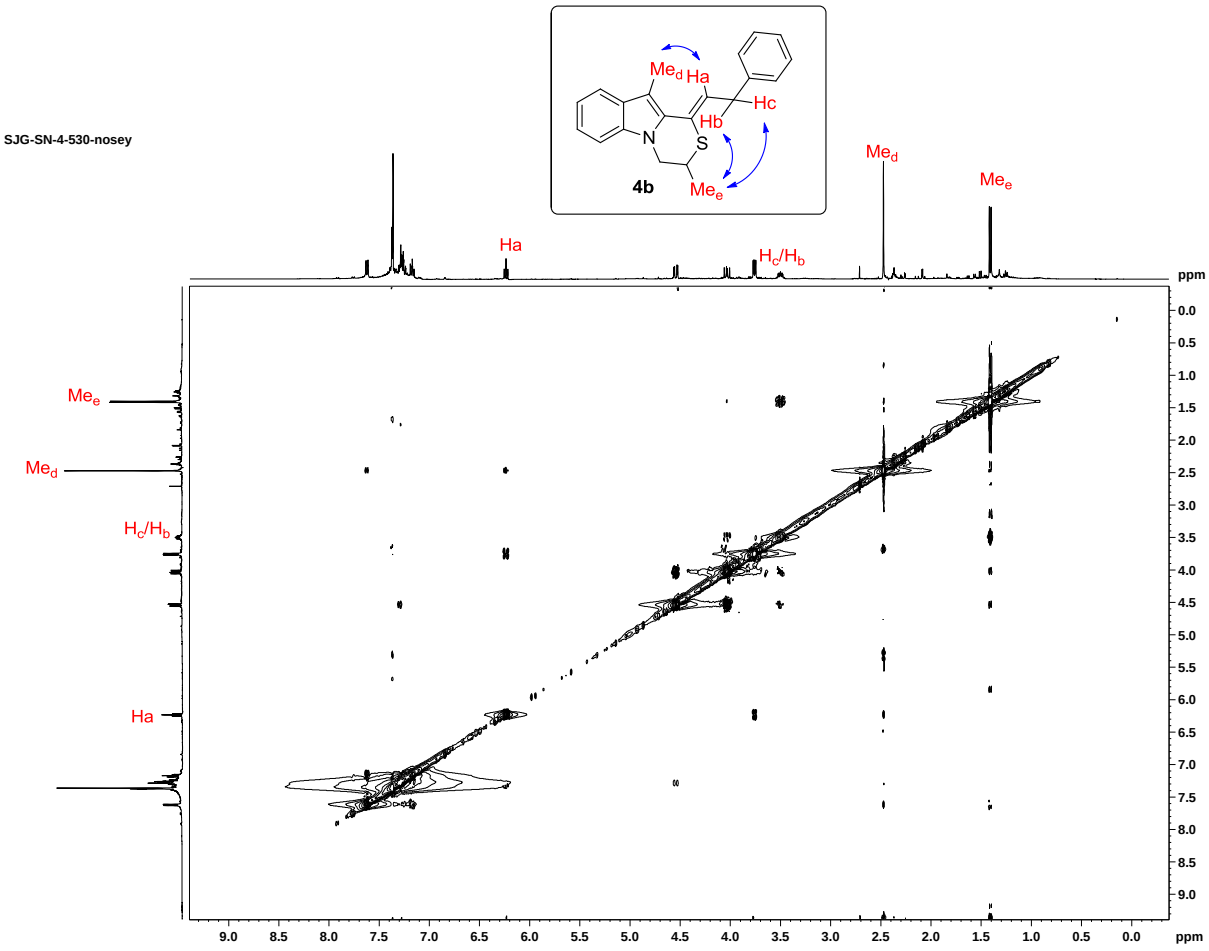




sjg-sn-4-530-13C






SJG-SN-4-530-nosey
Med Ha
Hc
Hb
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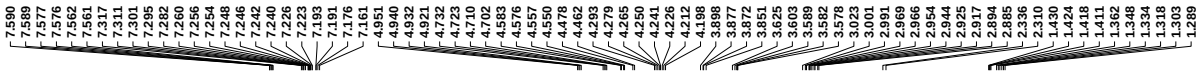
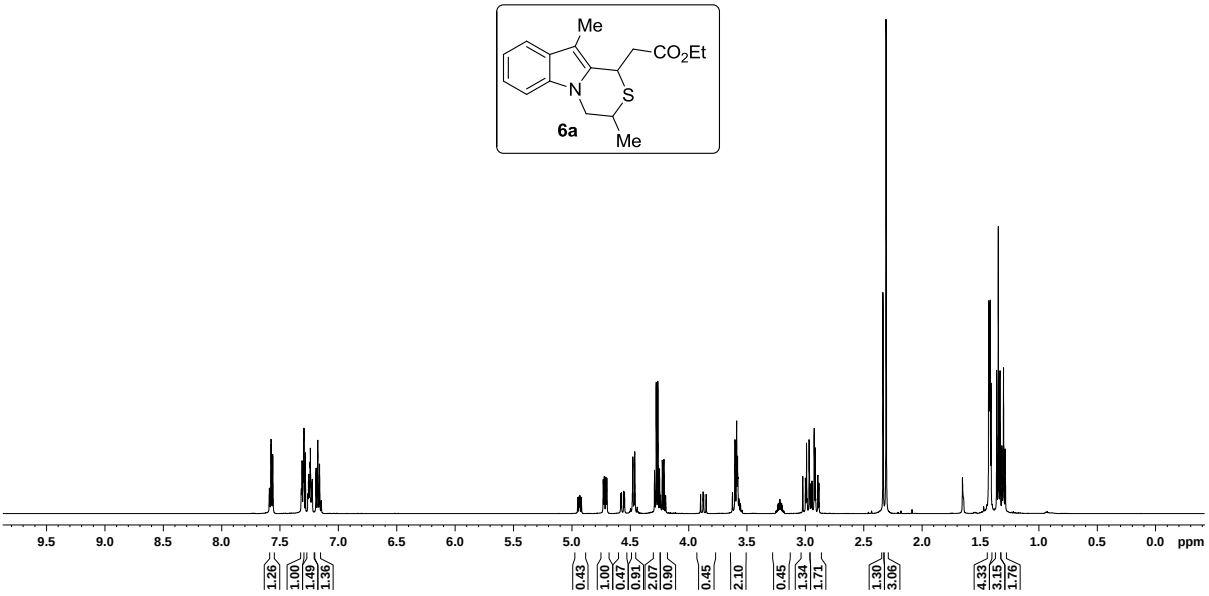
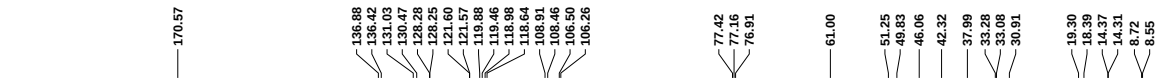
S
Me e
4b
Med
Mee
Ha
Hc/Hb
ppm
Mee
Med
Hc/Hb
Ha
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0

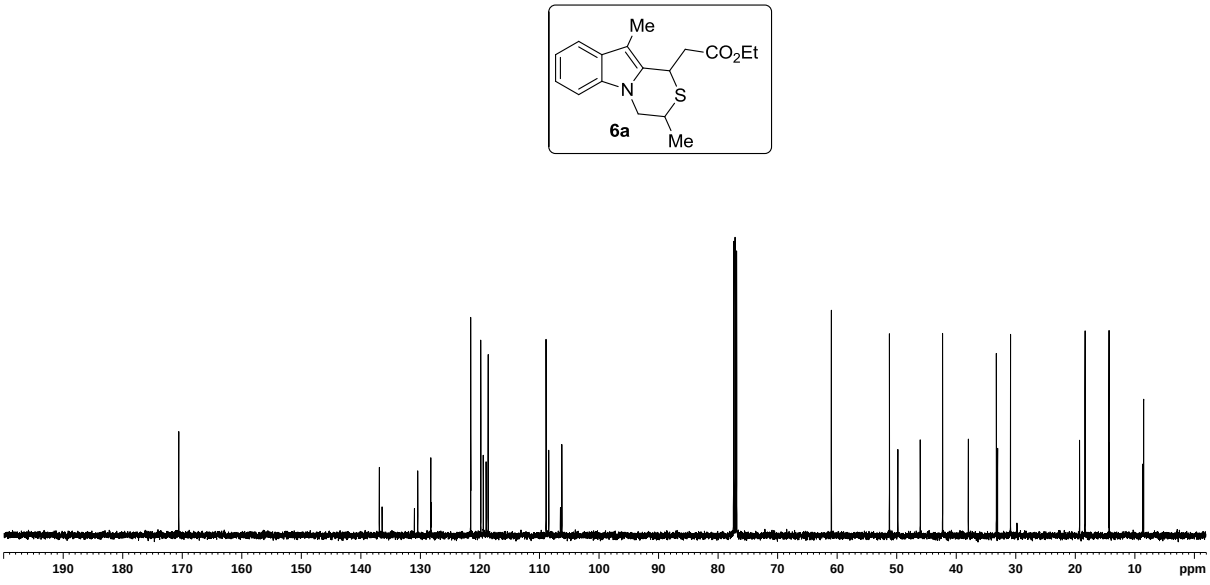


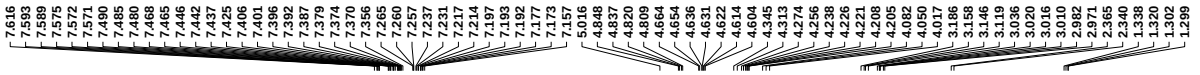
SJG-SN-7-1096-1H



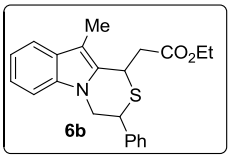


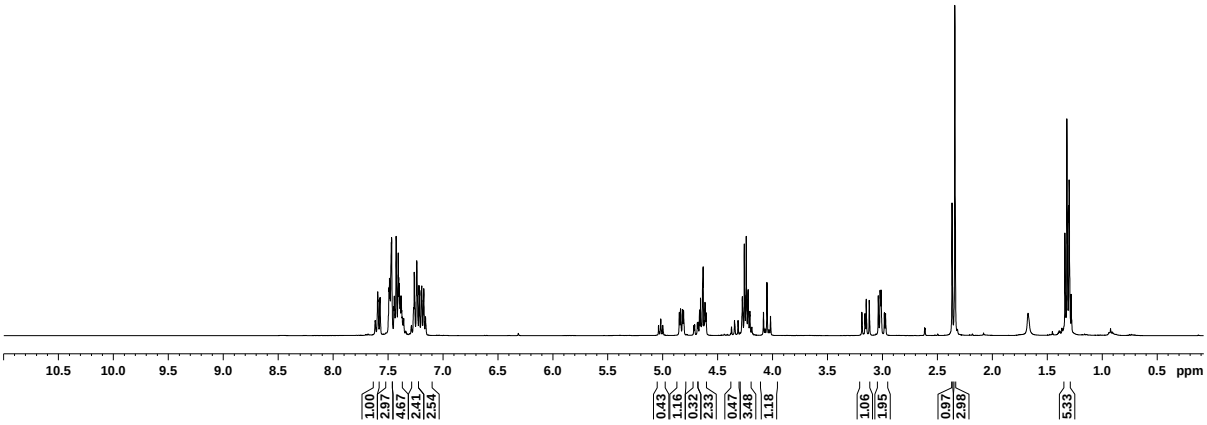
SJG-SN-7-1096-13C



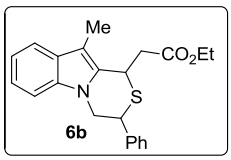


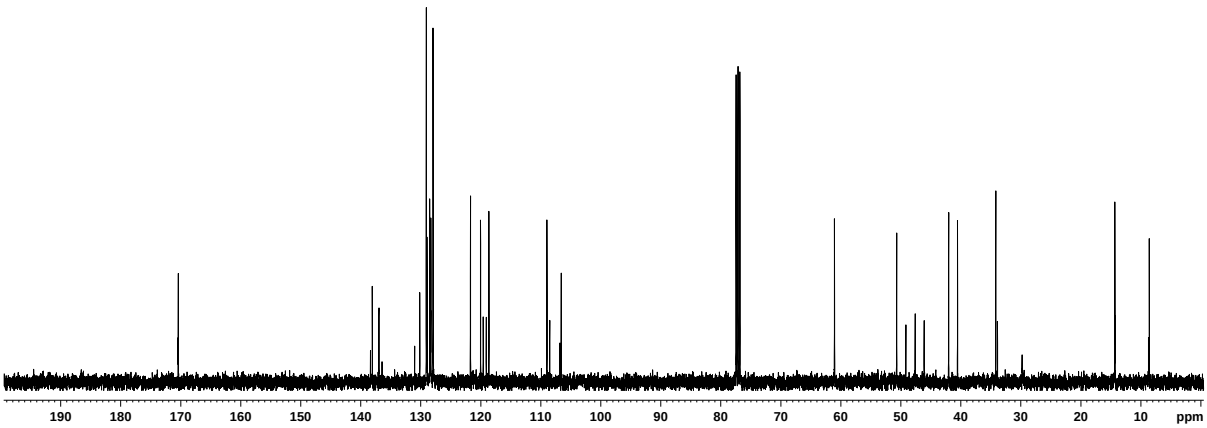
SJG-SN-3-398-H1



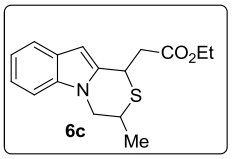


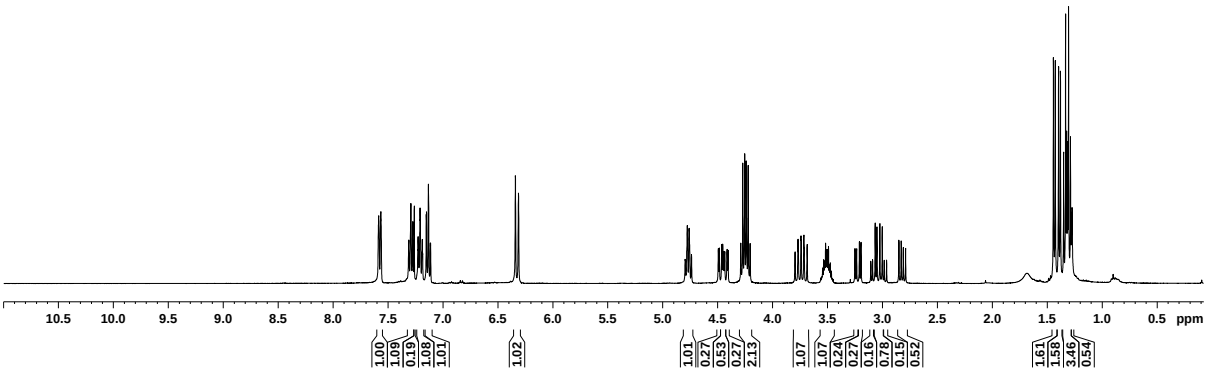
SJG-SN-3-398-C13

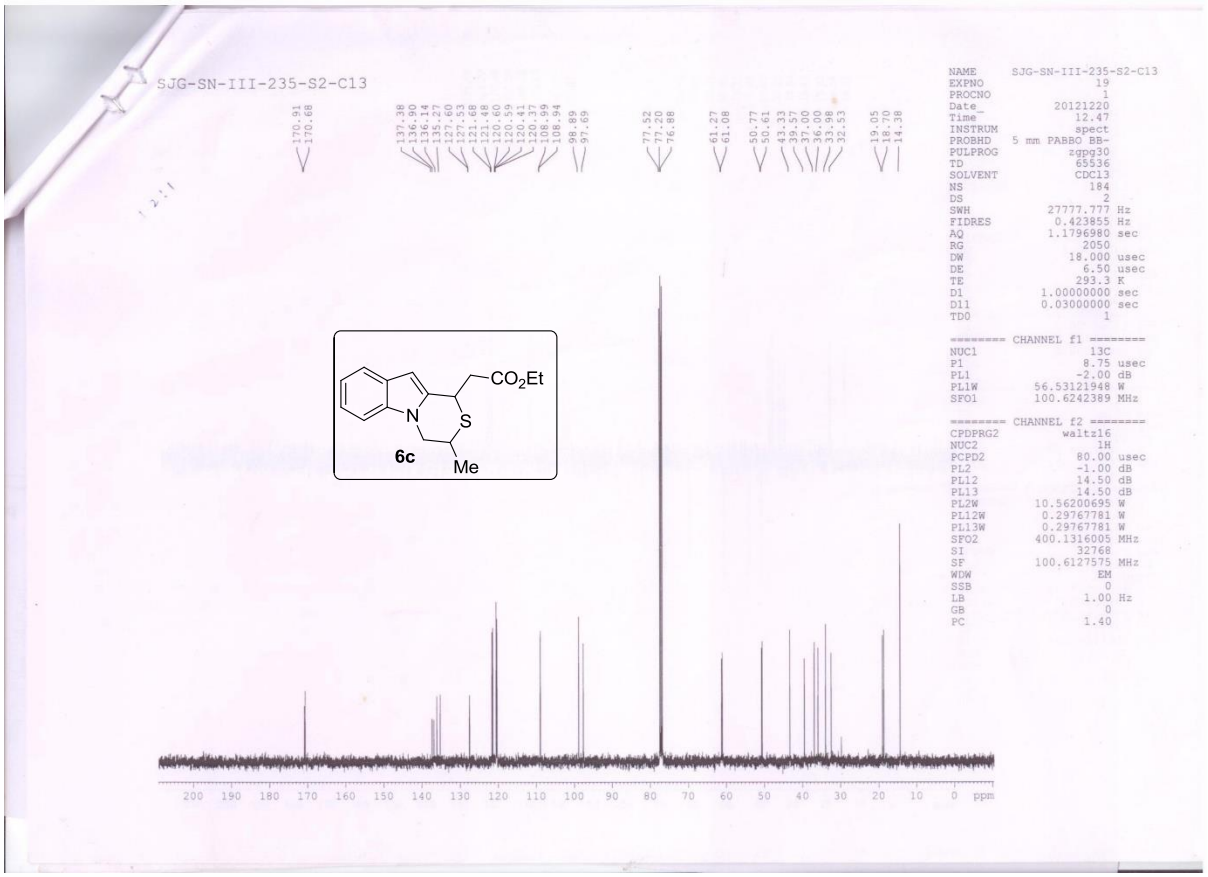


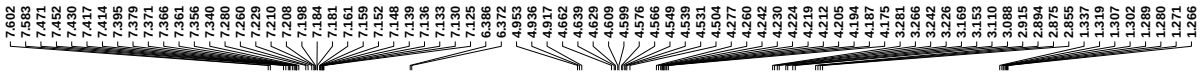


SJG-SN-III-235-S2-1H

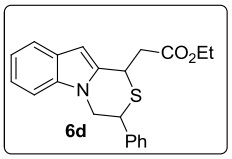


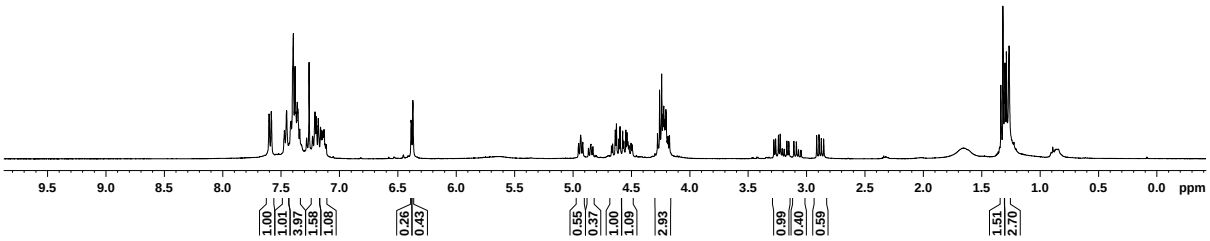


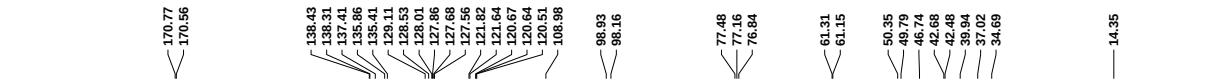




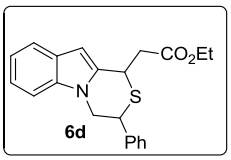
SJG-SN-III-275-1H

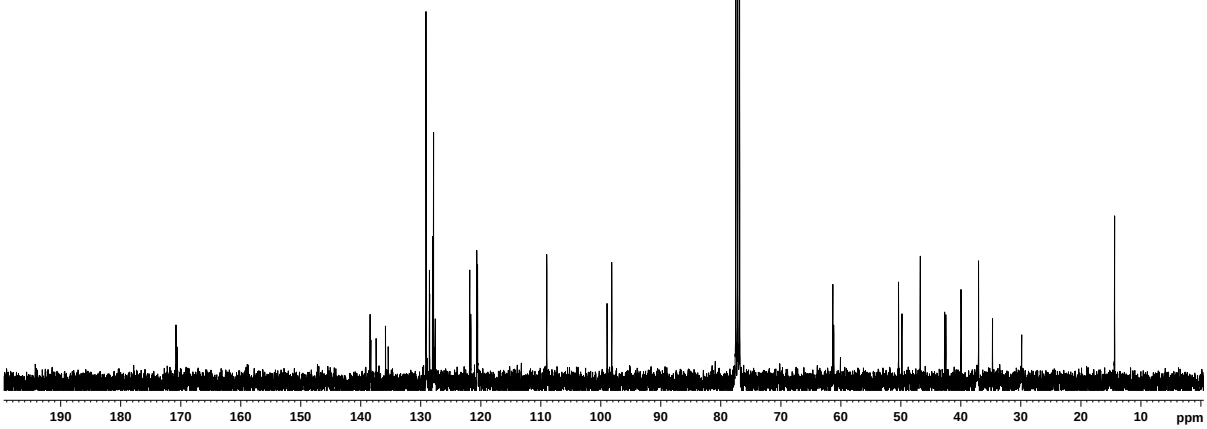


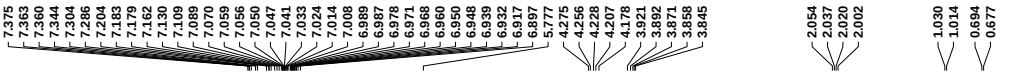




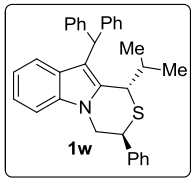
SJG-SN-III-275-C13

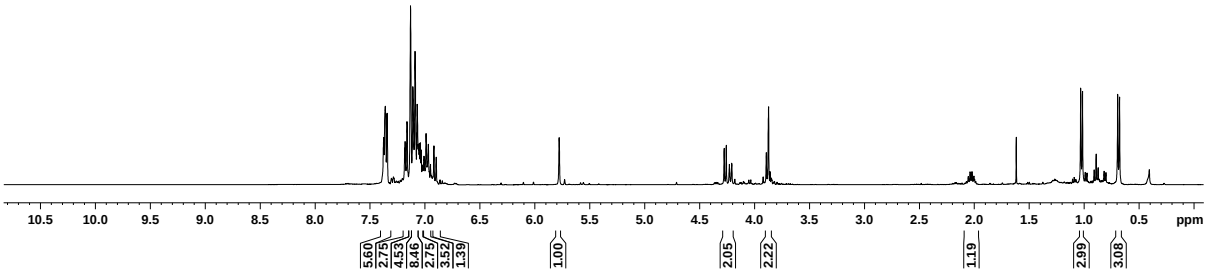


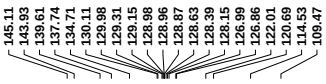




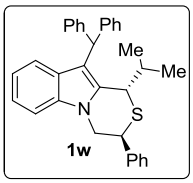
SJG-SN-4-634-1H

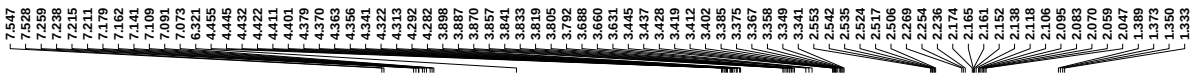




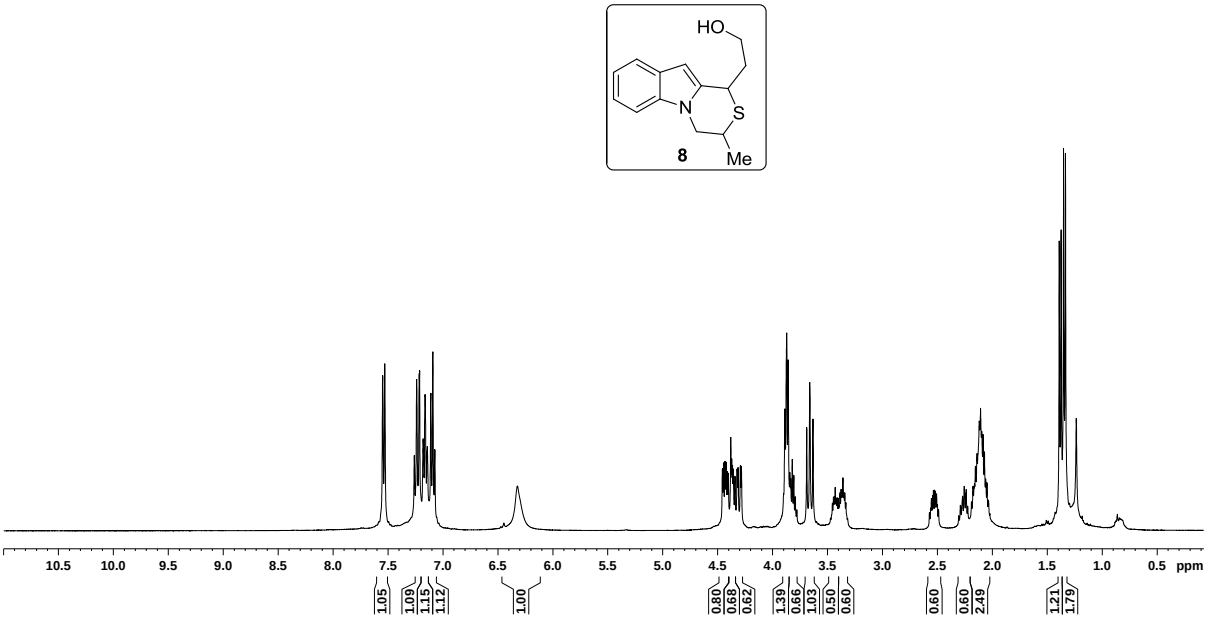


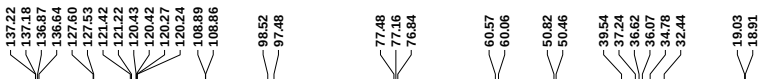
SJG-SN-4-634-13C



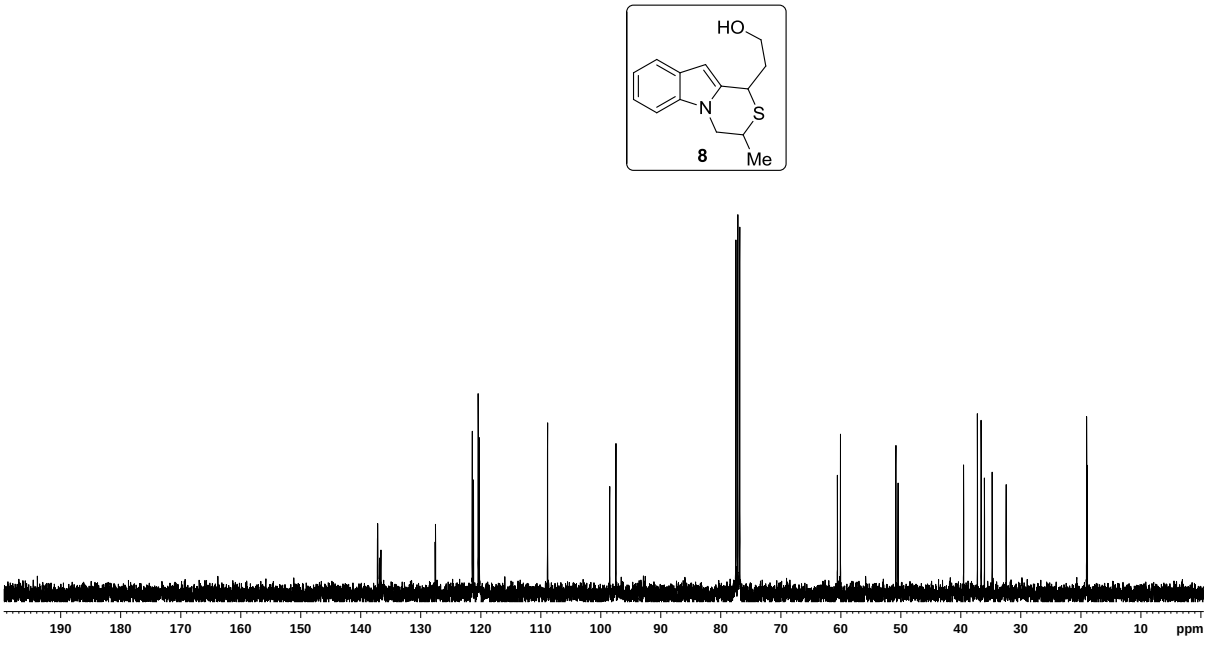


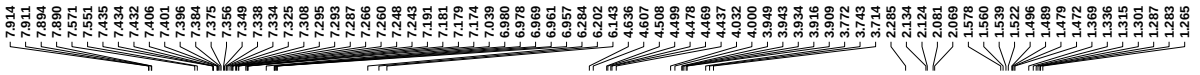
SJG-SN-III-265-1H



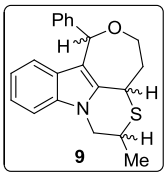


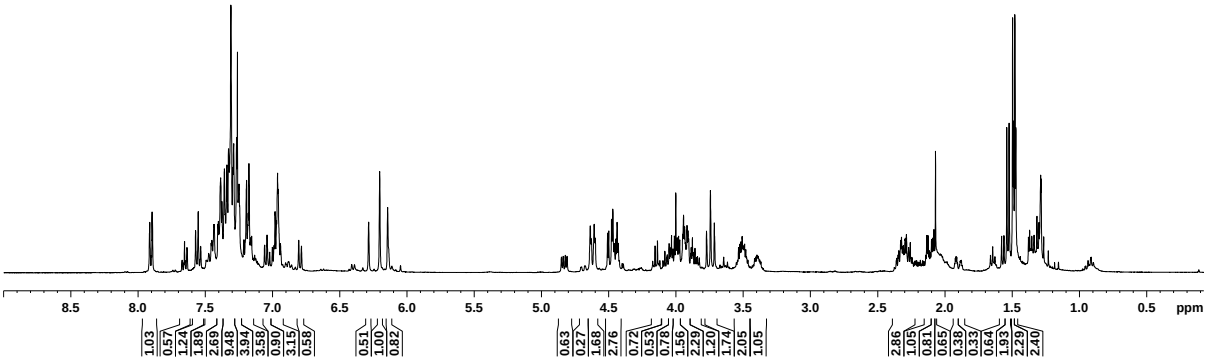
SJG-SN-III-265-C13

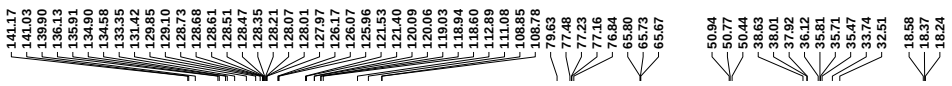




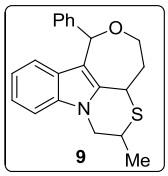
SJG-SN-III-266-1H

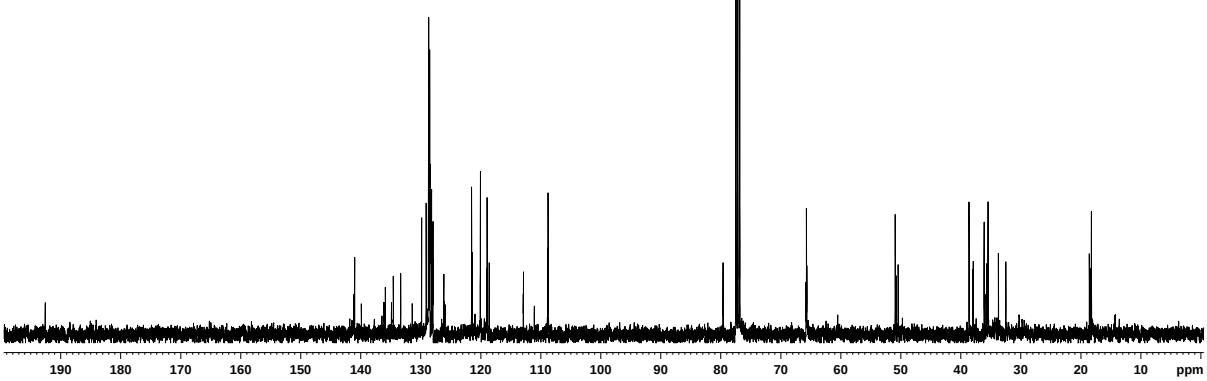




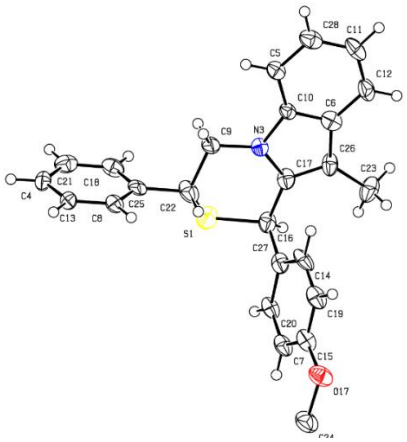


SJG-SN-III-266-C13





(1*S,3*S**)-1-(4-methoxyphenyl)-10-methyl-3-phenyl-3,4-dihydro-1*H*-[1,4]thiazino[4,3-*a*]indole (1d):**



Bond precision: C-C = 0.0093 A Wavelength=0.71075
Cell: a=8.0511(10) b=13.583(16) c=9.587(11)
alpha=90 beta=109.730(19) gamma=90
Temperature: 100 K
Calculated
Volume 986.9(16) 986.9(16)
Space group P 21 P 1 21 1
Hall group P 2yb P 2yb
Moiety formula C25 H20 N O S 0.67(C25 H20 N O S)
Sum formula C25 H20 N O S
C16.67 H13.33 N0.67 O0.67
S0.67
Mr 382.49 254.99
Dx,g cm-3 1.287 1.287
Z 2 3
Mu (mm-1) 0.179 0.179
F000 402.0 402.0
F000’ 402.39
h,k,lmax 9,16,11 9,16,11
Nref 3629[1897] 3171
Tmin,Tmax 0.946,0.984 0.889,0.984
Tmin’ 0.887
Correction method= numerical

Data completeness= 1.67/0.87 Theta(max)= 25.400

R(reflections)= 0.0867(2716)
wR2(reflections)= 0.2389(3171)
S = 1.035 Npar= 253