Supporting Information

Expeditious Diastereoselective Synthesis of Medium Ring Heterocycle-Fused Chromenes *via* Tandem 8/9-*endo-dig* and 8-*exo-dig* Hydroalkoxylation-Formal-[4+2]-Cycloaddition

Santosh. J. Gharpure,* Santosh K. Nanda,† Dipak J. Fartade†

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai - 400076

India. Fax: +91-22-2576 7152; Tel: +91-22-2576 7171; E-mail: sjgharpure@iitb.ac.in

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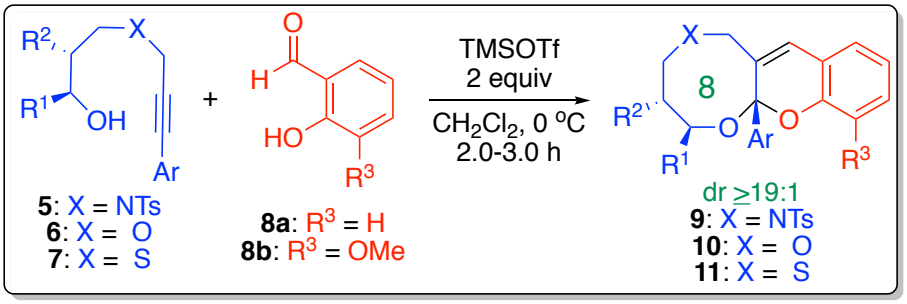
1. General experimental:

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 hydride. Dry DMF was prepared by stirring on CaH and distillation on to molecular sevies. CuI, $Rh_2(OAc)_4$ and TMSOTf were obtained from Aldrich. All other Lewis/Bronsted acids, phenyl acetylene, NaH (60% dispersion in mineral oil), benzyl bromide, propargyl bromide (80% in toluene), Mg turning, DMP, $[Pd(PPh_3)_2]Cl_2$, aryl iodides, TMSCN, are commercial reagents and were used as such without further purification. All other alkyne and alkynols were prepared using literature established protocol.

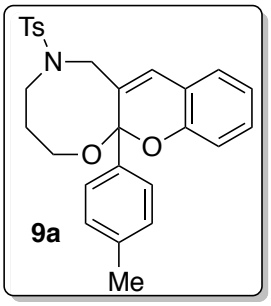
2. Experimental procedure for the diastereoslective synthesis of medium ring heterocycle-fused Chromenes:



(***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).

12a-(p-tolyl)-5-tosyl-3,4,5,6-tetrahydro-2H,12aH-chromeno[2,3-b][1,5]oxazocine (9a):

To a magnetically stirred solution of alkynol **5a** (50 mg, 0.139 mmol), salicylaldehyde (**8a**) (15 µL, 0.139 mmol) in dry CH_2Cl_2 (8.0 mL) was added dropwise TMSOTf (50 µL, 0.278 mmol) at 0 °C. Reaction was monitored by TLC, quenched with saturated aq. solution of NaOH 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 ethyl acetate-petroleum ether (10:90) as eluent furnished a separable mixture of oxazepino chromene **9a** (55 mg, 82%) as a single diastereomer (dr ≥19:1).



Physical appearance: Sticky solid.

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

IR (neat): 3019, 2925, 1657, 1335, 1216, 1158, 759 cm^{-1}.

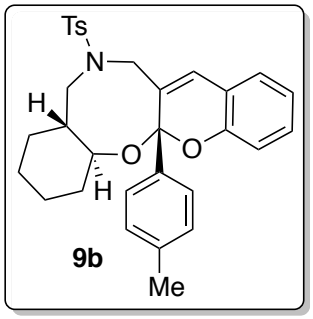
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.22 (td, *J* = 9.0, 1.5 Hz, 1H) 7.18 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 1H), 6.94 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.08 (d, *J* = 14.0 Hz, 1H), 4.02 (dd, *J* = 10.5, 3.0 Hz, 2H), 3.50 (dt, *J* = 14.0, 4.5 Hz, 1H), 3.23 (d, *J* = 10.0 Hz, 1H), 3.16-3.21 (m, 1H), 2.43 (s, 3H), 2.24 (s, 3H), 2.05-2.09 (m, 1H), 1.78-1.82 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 152.7 (C), 143.3 (C), 138.9 (C), 138.7 (C), 136.8 (C), 130.7 (CH), 130.4 (CH), 129.8 (2 × CH), 129.4 (C), 128.9 (2 × CH), 127.4 (CH), 127.0 (2 × CH), 125.7 (2 × CH), 121.0 (CH), 118.2 (C), 115.5 (CH), 105.2 (C), 62.0 (CH_2), 52.7 (CH_2), 47.3 (CH_2), 30.1 (CH_2), 21.6 (CH_3), 21.3 (CH_3);

HRMS (ESI-TOF) m/z: calcd. for $C_{27}H_{27}NNaO_4S$ $[M+Na]^+$: 484.1553, found 484.1553.

(4a*R,13a*S**,14a*S**)-13a-(*p*-tolyl)-6-tosyl-1,3,4,4a,5,6,7,14a-octahydro-2*H*,13a*H*-benzo[*b*]chromeno[3,2-*g*][1,5]oxazocine (9b):**

Reaction of alkynol **5b** (86 mg, 0.209 mmol), salicylaldehyde (**8a**) (23 μL, 0.210 mmol) with TMSOTf (76 μL, 0.418 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished the oxazocino chromene **9b** (75mg, 71%) as a as a single diastereomer (dr ≥19:1).



Physical appearance: Sticky solid.

R*f*: 0.5 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3019, 2919, 1698, 1595, 1354, 1245, 1019, 998, 765 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.21 (t, *J* = 14.0, 7.2 Hz, 1H), 7.13 (t, *J* = 14, 8.0 Hz, 3H), 6.92 (q, *J* = 11.6, 7.6 Hz, 2H), 6.80 (s, 1H), 3.53-3.60 (m, 3H), 3.24 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.90 (bs, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 2.00-2.02 (m, 1H), 1.90 (bs, 1H), 1.50-1.67 (m, 4H), 1.17-1.32 (m, 1H), 1.04-1.10 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.1 (C), 143.2 (2 × C), 139.2 (C), 138.5 (C), 136.0 (C), 130.4 (CH), 129.8 (2 × CH), 129.6 (CH), 128.7 (2 × CH), 127.2 (2 × CH), 127.1 (CH), 126.0 (2 × CH), 120.8 (CH), 117.9 (C), 115.1 (CH), 104.3 (C), 77.11 (CH), 53.7 (CH_2), 53.5 (CH_2) 44.7 (CH), 34.6 (CH_2), 29.9 (CH_2), 25.3 (CH_2), 25.1 (CH_2), 21.5 (CH_3), 21.3 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{31}H_{33}NNaO_4S$ $[M+Na]^+$: 538.2023, found 538.2022.

(7S*,8aS*)-7-methyl-8a-phenyl-5-tosyl-6,7-dihydro-5H,8aH-benzo[e]chromeno[3,2-g][1,4]oxazocine (9c):

Reaction of alkynol **5c** (80 mg, 0.197 mmol), salicylaldehyde (**8a**) (21 μL, 0.197 mmol) with TMSOTf (71 μL, 0.394 mmol) in dry CH_2Cl_2 (8.0 mL) at 0 °C as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished the oxazocine chromene **9c** (95 mg, 95%) a single diastereomer (dr ≥19:1).

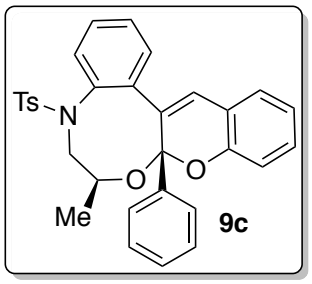
Physical appearance: White Solid.

R*f*: 0.4 (1:9 ethyl acetate-petroleum ether).

m.p.: 222-224 °C.

IR (neat): 2983, 1458, 1448, 1375, 1245, 1093, 918, 847, 758, 736, 608 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.19-7.27 (m, 10H), 7.16 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.96-7.04 (m, 4H), 6.56 (s, 1H), 4.63-4.70 (m, 1H), 4.12 (dd, *J* = 14.8, 0.0 Hz, 1H), 3.24 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.44 (s, 3H), 1.27 (d, *J* = 6.8 Hz, 3H).

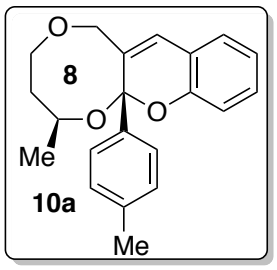


^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.0 (C), 143.3 (C), 142.4 (C), 140.2 (C), 139.7 (C), 132.7 (C), 132.1 (CH), 129.9 (CH), 129.7 (2 × CH), 128.8 (CH), 128.5 (CH), 128.3 (CH), 127.7 (2 × CH), 127.6 (CH), 127.6 (C), 127.5 (CH), 127.3 (2 × CH), 126.8 (CH), 125.8 (2 × CH), 121.2 (CH), 118.2 (C), 115.1 (CH), 104.5 (C), 72.8 (CH), 58.5 (CH_2), 21.6 (CH_3), 20.4 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{31}H_{27}NNaO_4S$ $[M+Na]^+$: 532.1553, found 532.1561.

(2S*,12aS*)-2-methyl-12a-(p-tolyl)-3,4-dihydro-2H,6H,12aH-[1,5]dioxocino[2,3-b]chromene (10a):

Reaction of alkynol **6a** (83 mg, 0.380 mmol), salicylaldehyde (**8a**) (40 μL, 0.380 mmol) with TMSOTf (137 μL, 0.76 mmol) in dry CH_2Cl_2 (8.0 mL) at 0 °C as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished the dioxocino chromene **10a** (83 mg, 68%) as a single diastereomer (dr ≥19:1).

Physical appearance: Sticky solid.



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

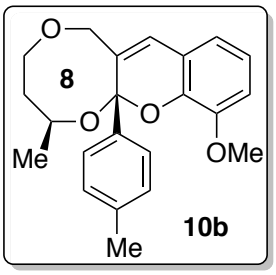
IR (neat): 3020, 1522, 928, 761, 670, 626 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.22 (td, *J* = 8.0, 1.6 Hz, 1H), 7.13-7.16 (m, 3H), 6.92-6.95 (m, 2H), 6.79 (s, 1H), 4.14-4.19 (m, 1H), 4.05 (d, *J* = 12.8 Hz, 1H), 3.83 (d, *J* = 12.8 Hz, 1H), 3.74-3.86 (m, 2H), 2.34 (s, 3H), 1.74-1.83 (m, 1H), 1.58-1.65 (m, 1H), 1.28 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 153.2 (C), 139.6 (C), 138.3 (C), 132.1 (C), 130.3 (CH), 129.2 (CH), 128.8 (2 × CH), 127.2 (CH), 126.0 (2 × CH), 120.8 (CH), 118.3 (C), 115.4 (CH), 104.7 (C), 73.9 (CH_2), 69.8 (CH), 69.0 (CH_2), 38.5 (CH_2), 23.4 (CH_3), 21.3 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{21}H_{22}NaO_3$ $[M+Na]^+$: 345.1461, found 345.1460.

(2S*,12aS*)-11-methoxy-2-methyl-12a-(p-tolyl)-3,4-dihydro-2H,6H,12aH-[1,5]dioxocino[2,3-b]chromene (10b):

Reaction of alkynol **6a** (77 mg, 0.352 mmol), *o*-vanillin (**8b**) (53 mg, 0.352 mmol) with TMSOTf (127 μL, 0.704 mmol) in dry CH_2Cl_2 (8.0 mL) at 0 °C as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished the dioxocino chromene **10b** (82 mg, 66%) as a single diastereomer (dr ≥19:1).



Physical appearance: Sticky solid.

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

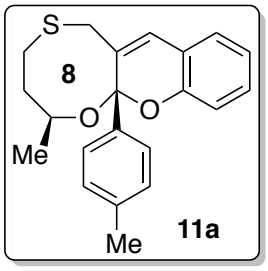
IR (neat): 3012, 2971, 2879, 1659, 1588, 1423, 1312, 1255, 1132, 1008, 756, 678 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 4.14-4.18 (m, 1H), 4.05 (d, *J* = 12.8 Hz, 1H), 3.83 (s, 3H), 3.77-3.85 (m, 3H), 2.32 (s, 3H), 1.73-1.82 (m, 1H), 1.57-1.65 (m, 1H), 1.29 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 147.4 (C), 142.7 (C), 139.6 (C), 138.1 (C), 132.2 (C), 129.0 (CH), 128.7 (2 × CH), 126.1 (2 × CH), 120.3 (CH), 119.4 (CH), 118.9 (C), 113.7 (CH), 104.8 (C), 73.9 (CH_2), 69.8 (CH), 69.0. (CH_2), 56.5 (CH_3), 38.6 (CH_2), 23.4 (CH_3), 21.2 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{22}H_{25}O_4$ $[M+H]^+$: 353.1474, found 353.1476.

(2S*,12aS*)-2-methyl-12a-(p-tolyl)-3,4-dihydro-2H,6H,12aH-[1,5]oxathiocino[2,3-b]chromene (11a):

Reaction of alkynol **7a** (73 mg, 0.308 mmol), salicylaldehyde (**8a**) (37 μL, 0.308 mmol) with TMSOTf (111 μL, 0.616 mmol) in dry CH_2Cl_2 (8.0 mL) at 0 °C as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished the oxathiocino chromene **11a** (89 mg, 85%) as a single diastereomer (dr ≥19:1).



Physical appearance: Sticky solid.

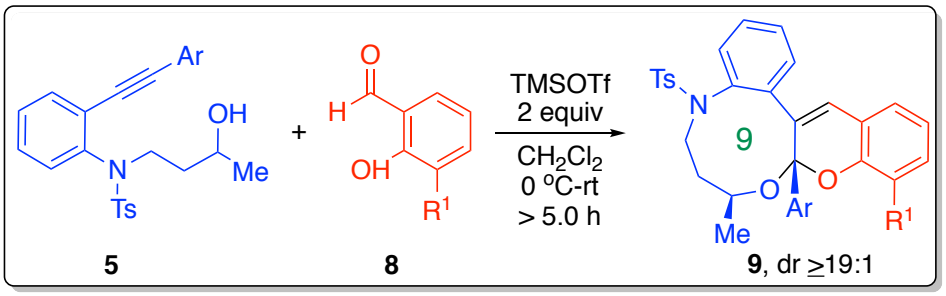
R_f: 0.4 (1:9 ethyl acetate-petroleum ether).

IR (neat): 3019, 1528, 1426, 1216, 847, 765, 670 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.43 (m, 2H), 7.19 (ddd, *J* = 9.2, 7.2, 1.2 Hz, 1H), 7.14-7.17 (m, 2H), 7.12 (d, *J* = 1.6 Hz, 1H), 6.93 (td, *J* = 7.2, 0.8 Hz, 1H),

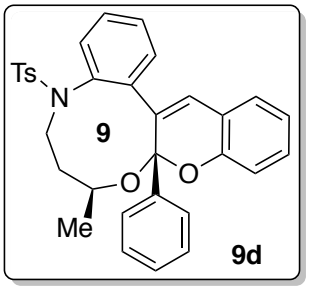
6.88 (d, J = 8.4 Hz, 1H), 6.80 (s, 1H), 4.26-4.31 (m, 1H), 3.25 (d, J = 13.6 Hz, 1H), 2.79-2.92 (m, 2H), 2.79 (d, J = 13.6 Hz, 1H), 2.34 (s, 3H), 1.93 (m, 1H), 1.58-1.66 (m, 1H), 1.31 (d, J = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 151.9 (C), 140.0 (C), 138.4 (C), 134.3 (C), 129.7 (CH), 128.8 (2 × CH), 127.0 (CH), 126.7 (CH), 125.9 (2 × CH), 120.9 (CH), 118.8 (C), 115.2 (CH), 105.0 (C), 69.4 (CH), 37.8 (CH_2), 36.4 (CH_2), 31.8 (CH_2), 22.8 (CH_3), 21.3 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{21}H_{23}O_2S$ $[M+H]^+$: 339.1413, found 339.1410.



(8S*,9aS*)-8-methyl-9a-phenyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9d):

Reaction of alkynol **5d** (100 mg, 0.238 mmol), salicylaldehyde (**8a**) (28 µL, 0.262 mmol) with TMSOTf (86 µL, 0.476 mmol) in dry CH_2Cl_2 (8.0 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished oxazepino chromene **9d** (72 mg, 58%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.: 193-195 °C

IR (neat): 3013, 2998, 1657, 1345, 1134, 1098, 768, 667 cm^{-1}.

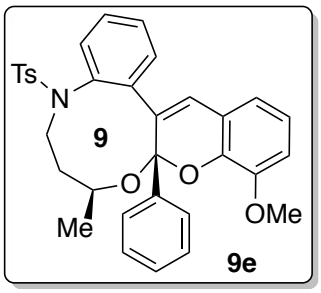
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 6.4 Hz, 2H), 7.30 (bd, J = 6.0 Hz, 3H), 7.13-7.22 (m, 6H), 7.01-7.06 (m, 3H), 6.81 (t. J = 6.0 Hz, 1H), 6.71 (s, 1H), 6.66 (d, J = 6.4 Hz. 1H), 6.18 (d, J = 6.0 Hz, 1H), 4.45-4.54 (m, 1H), 3.88 (dd, J = 14.5, 6.5 Hz, 1H), 3.27 (td, J = 14.0, 5.5 Hz, 1H), 2,47 (s, 3H), 2.27-2.32 (m, 1H), 1.63-1.71 (m, 1H), 1.27 (d, J = 5.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 152.4 (C), 143.7 (C), 143.3 (C), 142.7 (C), 139.2 (C), 136.1 (C), 132.9 (CH), 130.5 (C), 129.8 (CH), 129.6 (2 × CH), 128.4 (CH), 128.4 (2 × CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 127.5 (2 × CH), 127.3

(CH), 127.1 (CH), 126.5 (2 × CH), 121.3 (CH), 118.5 (C), 115.4 (CH), 103.1 (C), 66.7 (CH), 51.4 (CH_2), 37.4 (CH_2), 23.2 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{32}H_{29}NNaO_4S$ $[M+Na]^+$: 546.1710, found 546.1713.

(8*S,9a*S**)-11-methoxy-8-methyl-9a-phenyl-5-tosyl-5,6,7,8-tetrahydro-9a*H*-benzo[*f*]chromeno[3,2-*h*][1,5]oxazonine (9e):**

Reaction of alkynol **5d** (200 mg, 0.476 mmol), *o*-vanillin (**8b**) (73 mg, 0.476 mmol) with TMSOTf (172 μL, 0.952 mmol) in dry CH_2Cl_2 (8.0 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished oxazepino chromene **9e** (165 mg, 62%) as a single diastereomer (dr ≥19:1).



9e

Physical appearance: White Solid.

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

m.p.: 211-213 °C

IR (neat): 3016, 2973, 1672, 1355, 1235, 1078, 769, 665 cm^{-1}.

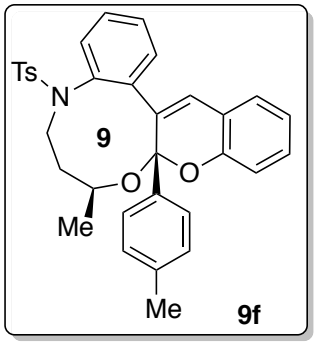
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.17-7.19 (m, 2H),7.10-7.15 (m, 3H), 7.03 (td, *J* = 8.0, 1.5 Hz, 1H), 6.94-6.97 (m, 2H), 6.84 (dd, *J* = 6.5, 2.0 Hz, 1H), 6.79 (td, 7.5, 1.0 Hz, 1H), 6.67 (s, 1H), 6.66 (d, *J* = 6.5 Hz, 1H), 6.16 (dd, *J* = 7.5, 1.0 Hz, 1H), 4.84-4.52 (m, 1H), 3.90 (s, 3H), 3.86 (dd, *J* = 17.5, 6.5 Hz, 1H), 3.27 (ddd, *J* = 18.0, 12.5, 5.5 Hz, 1H), 2.47 (s, 3H), 2.24-2.31 (m, 1H), 1.64-1.69 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 147.2 (C), 143.7 (C), 143.3 (C), 142.8 (C), 141.7 (C), 139.3 (C), 136.2 (C), 132.9 (CH), 130.8 (C), 129.6 (2 × CH), 128.4 (2 × CH),128.4 (CH), 128.0 (CH), 127.8 (CH), 127.4 (2 × CH), 127.3 (CH), 127.1 (CH), 126.7 (2 × CH), 120.9 (CH), 119.7 (CH), 119.2 (C), 112.6 (CH), 103.1 (C), 67.1 (CH), 56.2 (CH_3), 51.5 (CH_2), 37.5 (CH_2), 22.7 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{33}H_{31}NNaO_5S$ $[M+Na]^+$: 576.1815, found 576.1815.

(8*S,9a*S**)-8-methyl-9a-(*p*-tolyl)-5-tosyl-5,6,7,8-tetrahydro-9a*H*-benzo[*f*]chromeno[3,2-*h*][1,5]oxazonine (9f):**

Reaction of alkynol **5e** (85 mg, 0.196 mmol), salicylaldehyde (**8a**) (22 μL, 0.205 mmol) with TMSOTf (71 μL, 0.3920 mmol) in dry CH_2Cl_2 (8 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel

column using ethyl acetate-petroleum ether (20:80) as eluent furnished the oxazonine chromene **9f** (66 mg, 63%) as a single diastereomer (dr ≥19:1).



Physical appearance: White solid.

R_f: 0.6 (2:8 ethyl acetate-petroleum ether).

m.p.: 214-216 °C

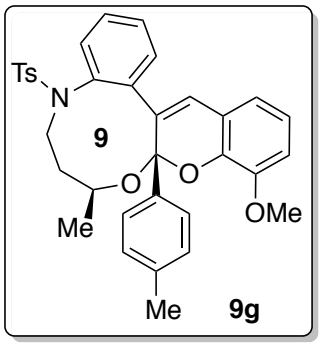
IR (neat): 2978**,** 2923, 1598, 1487, 1456, 1347, 1242, 1181, 1163, 1118, 1094, 1031, 1003, 909, 820, 753, 734, 570, 550 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65(d, *J* = 8.0 Hz, 2H), 7.26-7.30 (m, 3H), 7.20 (d, *J* = 6.0 Hz, 1H), 6.95-7.02 (m, 7H), 6.40 (t, *J* = 15.0, 7.5 Hz, 1H), 6.68-6.69 (m, 2H), 6.23 (d, *J* = 7.5 Hz, 1H), 4.50 (quint, *J* = 10.0, 5.5 Hz, 1H), 3.89 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.28 (td, *J* = 13.0, 5.5 Hz, 1H), 2.50 (s, 3H), 2.27-2.31 (m, 4H), 1.66 (td, *J* = 16.0, 5.5 Hz, 1H), 1.26 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 152.5 (C), 143.7(C), 142.7 (C), 140.5 (C), 139.3 (C), 137.8 (C), 136.2 (C), 133.1 (CH), 130.7 (C), 129.7 (CH), 129.6 (2 × CH), 128.4 (2 × CH), 128.4 (CH), 128.1 (2 × CH), 127.8 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 126.4 (2 × CH) 121.2 (CH), 118.5 (C), 115.4 (CH), 103.2 (C), 66.7 (CH), 51.5 (CH_2), 37.4 (CH_2) 23.3 (CH_3), 21.7 (CH_3), 21.2 (CH_3); HRMS (ESI-TOF) m/z: calcd. For $C_{33}H_{31}NNaO_4S$ $[M+Na]^+$: 560.1866 found 560.1866.

(8*S,9a*S**)-11-methoxy-8-methyl-9a-phenyl-5-tosyl-5,6,7,8-tetrahydro-9a*H*-benzo[*f*]chromeno[3,2-*h*][1,5]oxazonine (9g):**

Reaction of alkynol **5e** (85 mg, 0.196 mmol), *o*-vanillin (**8b**) (28 mg, 0.180 mmol) with TMSOTf (71 μL, 0.392 mmol) in dry CH_2Cl_2 (8 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethyl acetate-petroleum ether (20:80) as eluent furnished the oxazonine chromene **9g** (69 mg, 62 %) as a a single diastereomer (dr ≥19:1).



Physical appearance: White solid.

R_f: 0.5 (2:8 ethyl acetate-petroleum ether).

m.p.: 241-243 °C

IR (neat): 2931**,** 2841, 1580, 1478, 1446, 1346, 1268, 1242, 1163, 1085, 1076, 1005, 912, 814, 772, 731, 569, 548 cm^{-1}.

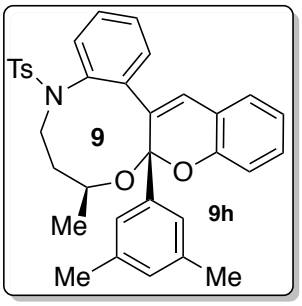
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 6.81-7.06 (m, 9H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 6.20 (d, *J* = 7.5 Hz, 1H),

4.47-4.50 (m, 1H), 3.85-3.89 (m, 4H), 3.27 (td, *J* = 14.0, 5.5 Hz, 1H), 2.46 (s, 3H), 2.21-2.31(m, 4H), 1.64 (td, *J* = 15.5, 5.5 Hz, 1H), 1.25 (d, *J* = 5.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 147.2 (C), 143.6 (C), 142.7 (C), 141.8 (C), 140.5 (C), 139.4 (C), 137.5 (C), 136.2 (C), 133.0 (CH), 131.0 (C), 129.6 (2 × CH), 128.4 (2 × CH), 128.3 (CH), 128.0 (2 × CH), 127.6 (CH), 127.3 (CH), 127.1 (CH), 126.6 (2 × CH), 120.7 (CH) 119.7 (CH), 119.2 (C), 112.6 (CH), 103.1 (C), 67.0 (CH), 56.2 (CH_3), 51.5 (CH_2), 37.5 (CH_2) 22.7 (CH_3), 21.7 (CH_3), 21.2 (CH_3); HRMS (ESI-TOF) m/z: calcd. For $C_{34}H_{33}NNaO_5S$ $[M+Na]^+$: 590.1972 found 590.1970.

(8S*,9aS*)-9a-(3,5-dimethylphenyl)-8-methyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9h):

Reaction of alkynol **5f** (50 mg, 0.111 mmol), salicylaldehyde (**8a**) (12 μL, 0.111 mmol) with TMSOTf (41 μL, 0.223 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9h** (32 mg, 52%)as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.:161-163 °C

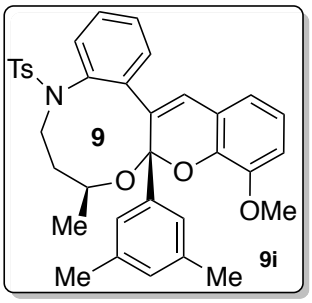
IR (neat): 3011, 2919, 1674, 1632, 1356, 1293, 987, 876, 768 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.26-7.30 (m, 3H), 7.20 (d, *J* = 6.8 Hz, 1H), 7.00-7.07 (m, 3H), 6.70-6.86 (m, 6H), 6.22 (d, *J* = 7.2 Hz, 1H), 4.46-4.48 (m, 1H), 3.87 (dd, *J* = 14.4, 6.4 Hz, 1H), 3.28 (td, *J* = 14.0, 5.2 Hz 1H), 2.47 (s, 3H), 2.24-2.29 (m, 1H), 2.13 (s, 6H), 1.63-1.71 (m, 1H), 1.25 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 152.5 (C), 143.7 (C), 142.9 (C), 142.7 (C), 139.3 (C), 136.9 (2 × C), 136.2 (C), 133.1 (CH), 130.7 (C), 129.7 (CH), 129.6 (2 × CH), 128.5 (2 × CH), 128.4 (CH), 127.7 (CH), 127.6 (2 × CH), 127.3 (CH), 127.0 (CH), 124.3 (2 × CH), 121.2 (CH), 118.5 (C), 115.4 (CH), 103.2 (C), 66.7 (CH), 51.5 (CH_2), 37.4 (CH_2), 23.3 (CH_3), 21.7 (CH_3) 21.4 (2 × CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{34}H_{33}NNaO_4S$ $[M+Na]^+$: 574.2023, found 574.2021.

(8S*,9aS*)-9a-(3,5-dimethylphenyl)-11-methoxy-8-methyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9i):

Reaction of alkynol **5f** (53 mg, 0.118 mmol), o-vanillin (**8b**) (17 mg, 0.112 mmol) with TMSOTf (43 μL, 0.236 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9i** (42 mg, 61%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.: 221-223 °C

IR (neat): 3091, 2917, 2896, 1654, 1454, 1352, 1123, 1089, 984, 865, 567 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.04 (td, *J* = 8.0, 1.5 Hz, 1H), 6.94-6.98 (m, 2H), 6.81-6.84 (m, 2H), 6.77 (s, 1H), 6.73 (s, 2H), 6.65-6.69 (m, 2H), 6.17 (dd, *J* = 8.0, 1.5 Hz, 1H), 4.43-4.49 (m, 1H), 3.90 (s, 3H), 3.87 (dd, *J* = 14.5, 6.0 Hz, 1H), 3.29 (ddd, *J* = 18.0, 12.5, 5.5 Hz 1H), 2.46 (s, 3H), 2.22-2.29 (m, 1H), 2.12 (s, 6H), 1.62-1.69 (m, 1H), 1.25 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 147.2 (C), 143.6 (C), 142.9 (C), 142.7 (C), 141.7 (C), 139.4 (C), 136.6 (2 × C), 136.2 (C), 133.1 (CH), 130.9 (C), 129.6 (2 × CH), 129.4 (CH), 128.4 (2 × CH), 128.3 (CH), 127.4 (CH), 127.2 (CH), 126.9 (CH), 124.6 (2 × CH), 120.7 (CH), 119.7 (CH), 119.2 (C), 112.5 (CH), 103.1 (C), 66.7 (CH), 56.2 (CH_3), 51.5 (CH_2), 37.5 (CH_2), 22.7 (CH_3), 21.7 (CH_3) 21.4 (2 × CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{35}H_{35}NNaO_5S$ $[M+Na]^+$: 604.2128, found 604.2129.

(8S*,9aS*)-8-methyl-9a-(m-tolyl)-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9j):

Reaction of alkynol **5g** (107 mg, 0.246 mmol), salicylaldehyde (**8a**)(29 μL, 0.271 mmol) with TMSOTf (90 μL, 0.493 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9j** (56 mg, 42%) as a single diastereomer (dr ≥19:1).

Physical appearance: White Solid.

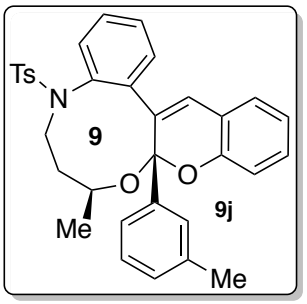
R_f:0.4 (1:9 ethyl acetate-petroleum ether).

m.p.: 193-195 °C

IR (neat): 3112, 2987, 1867, 1623, 1611, 1567, 1465, 1236, 1098, 971, 863, 765 cm^{-1}.

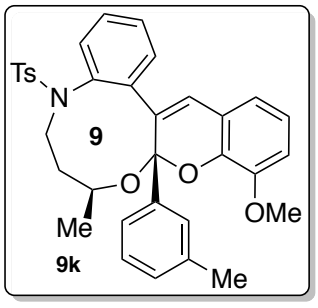
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.29-7.31 (m, 3H), 7.04 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.94-7.07 (m, 7H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.67-6.69 (m, 2H), 6.19 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.46-4.53 (m, 1H), 3.87 (dd, *J* = 14.5, 6.0 Hz, 1H), 3.29 (ddd, *J* = 18.0, 12.5, 5.5 Hz, 1H), 2.47 (s, 3H), 2.25-2.32 (m, 1H), 2.20 (s, 3H), 1.65-1.71 (m, 1H), 1.25 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 152.4 (C), 143.7 (C), 143.1 (C), 142.7 (C), 139.3 (C), 137.0 (C), 136.1 (C), 133.0 (CH), 130.6 (C), 129.7 (CH), 129.6 (2 × CH), 128.8 (CH), 128.4 (3 × CH), 127.8 (CH), 127.6 (CH), 127.3 (2 × CH), 127.2 (CH), 127.1 (CH), 123.6 (CH), 121.3 (CH), 118.5 (C), 115.4 (CH), 103.2 (C), 66.7 (CH), 51.5 (CH_2), 37.4 (CH_2), 23.4 (CH_3), 21.7 (CH_3) 21.5 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{33}H_{31}NNaO_4S$ $[M+Na]^+$: 560.1866, found 560.1864.



(8S*,9aS*)-11-methoxy-8-methyl-9a-(m-tolyl)-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9k):

Reaction of alkynol **5g** (105 mg, 0.242 mmol), o-vanillin (**8b**)(39 mg, 0.254 mmol) with TMSOTf (88 μL, 0.484 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9k** (67 mg, 49%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.: 192-194 °C

IR (neat): 3121, 3091, 2985, 1654, 1623, 1572, 1453, 1287, 1198, 1076, 973, 769 cm^{-1}.

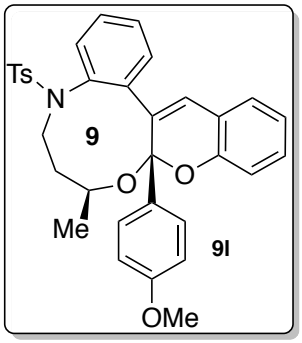
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.04 (td, *J* = 8.0, 1.5 Hz, 1H), 6.91-6.99 (m, 6H), 6.80-6.85 (m, 2H), 6.66-6.68 (m, 2H), 6.17 (dd, *J* = 8.0, 1.5 Hz, 1H), 4.45-4.51 (m, 1H), 3.90 (s, 3H), 3.86 (dd, *J* = 14.5, 6.0 Hz, 1H), 3.28 (ddd, *J* = 18.5, 12.0, 5.5 Hz, 1H), 2.46 (s, 3H), 2.23-2.30 (m, 1H), 2.18 (s, 3H), 1.62-1.69 (m, 1H), 1.25 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 147.2 (C), 143.6 (C), 143.1 (C), 142.7 (C), 141.7 (C), 139.3 (C), 136.9 (C), 136.2 (C), 133.0 (CH), 130.9 (C), 129.6 (2 × CH),

128.6 (CH), 128.4 (2 × CH), 128.4 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 127.2 (CH), 127.0 (CH), 123.8 (CH), 120.8 (CH), 119.7 (CH), 119.2 (C), 112.5 (CH), 103.1 (C), 67.1 (CH), 56.2 (CH_3), 51.5 (CH_2), 37.5 (CH_2), 22.7 (CH_3), 21.7 (CH_3) 21.4 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{34}H_{33}NNaO_5S$ $[M+Na]^+$: 590.1972, found 590.1967.

(8S*,9aS*)-9a-(4-methoxyphenyl)-8-methyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9l):

Reaction of alkynol **5h** (49 mg, 0.108 mmol), salicylaldehyde (**8a**) (12 μL, 0.108 mmol) with TMSOTf (40 μL, 0.217 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9l** (29 mg, 48%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.:173-175 °C

IR (neat): 3112, 3098, 2984, 1652, 1564, 1456, 1342, 1254, 1123, 987, 765, 567 cm^{-1}.

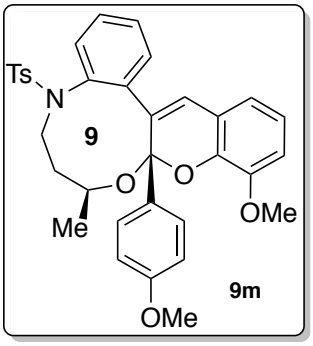
^{1}H NMR (500 MHz, $CDCl_3$):δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.26-7.30 (m, 3H), 7.19 (d, *J* = 6.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.99-7.07 (m, 3H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.66-6.68 (m, 4H), 6.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 4.44-4.50 (m, 1H), 3.86 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.74 (s, 3H), 3.25 (ddd, *J* = 18.5, 13.0, 6.0 Hz, 1H), 2.47 (s, 3H), 2.23-2.30 (m, 1H), 1.62-1.68 (m, 1H), 1.24 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 159.4 (C), 152.5 (C), 143.7 (C), 142.8 (C), 139.4 (C), 136.2 (C), 136.0 (C), 133.1 (CH), 130.8 (C), 129.7 (CH), 129.6 (2 × CH), 128.5 (2 × CH), 128.4 (CH), 127.8 (2 × CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 121.3 (CH), 118.5 (C), 115.4 (CH), 112.8 (2 × CH), 103.1 (C), 66.7 (CH), 55.4 (CH_3), 51.4 (CH_2), 37.4 (CH_2), 23.3 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{33}H_{31}NNaO_5S$ $[M+Na]^+$: 576.1815, found 576.1816.

(8S,9aS)-11-methoxy-9a-(4-methoxyphenyl)-8-methyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9m):

Reaction of alkynol **5h** (45 mg, 0.100 mmol), o-vanillin (**8b**) (15 mg, 0.100 mmol) with TMSOTf (37 μL, 0.200 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column

using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9m** (42 mg, 72%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.: 260-262 °C

IR (neat): 3018 2998, 1652, 1457, 1352, 1242, 987, 769 cm^{-1}.

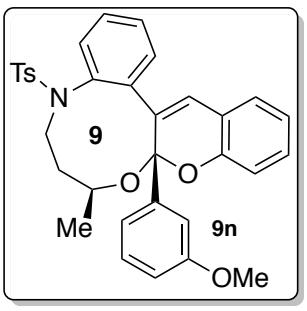
^{1}H NMR (400 M, Hz, $CDCl_3$):δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.03-7.09 (m, 3H), 6.92-6.98 (m, 2H), 6.82-6.86 (m, 2H), 6.63-6.68 (m, 4H), 6.21 (d, *J* = 6.8 Hz, 1H), 4.45-4.50 (m, 1H), 3.89 (s, 3H), 3.86 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.73 (s, 3H), 3.25 (ddd, *J* = 18.0, 12.8, 5.6 Hz, 1H), 2.46 (s, 3H), 2.21-2.30 (m, 1H), 1.60-1.67 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 159.4 (C), 147.2 (C), 143.6 (C), 142.7 (C), 141.8 (C), 139.4 (C), 136.2 (C), 136.0 (C), 133.0 (CH), 131.0 (C), 129.6 (2 × CH), 128.4 (2 × CH), 128.4 (CH), 127.9 (2 × CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 120.8 (CH), 119.7 (CH), 119.2 (C), 112.7 (2 × CH), 112.5 (CH), 103.0 (C), 67.1 (CH), 56.2 (CH_3), 55.4 (CH_3), 51.5 (CH_2), 37.5 (CH_2), 22.7 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{34}H_{33}NNaO_6S$ $[M+Na]^+$: 606.1921, found 606.1917.

(8S,9aS)-9a-(3-methoxyphenyl)-8-methyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9n):

Reaction of alkynol **5i** (110 mg, 0.244 mmol), salicylaldehyde (**8a**)(29 μL, 0.269 mmol) with TMSOTf (89 μL, 0.489 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9n** (40 mg, 30%) as a single diastereomer (dr ≥19:1).

Physical appearance: White Solid.



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

m.p.: 192-194 °C

IR (neat): 3112, 2918, 2876, 1652, 1543, 1234, 1091, 876, 768 cm^{-1}.

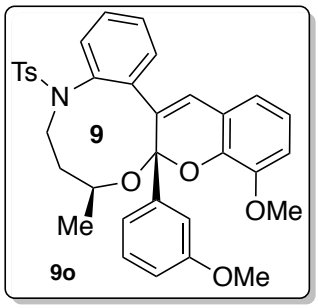
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.27-7.30 (m, 3H), 7.21 (d, *J* = 6.5, Hz, 1H), 7.00-7.09 (m, 4H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.70-6.74 (m, 3H), 6.66 (d, *J* = 8.0, Hz, 1H), 6.26

(d, *J* = 7.5 Hz, 1H), 4.46-4.51 (m, 1H), 3.87 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.61 (s, 3H), 3.26 (ddd, *J* = 18.0, 13.0, 5.5 Hz, 1H), 2.47 (s, 3H), 2.25-2.32 (m, 1H), 1.63-1.69 (m, 1H), 1.25 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 159.0 (C), 152.3 (C), 144.7 (C), 143.7 (C), 142.7 (C), 139.3 (C), 136.1 (C), 132.9 (CH), 130.4 (C), 129.8 (CH), 129.6 (2 × CH), 128.5 (CH), 128.5 (CH), 128.4 (2 × CH), 127.9 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 121.4 (CH), 119.3 (CH), 118.5 (C), 115.4 (CH), 113.7 (CH), 112.3 (CH), 103.0 (C), 66.8 (CH), 55.3 (CH_3), 51.5 (CH_2), 37.4 (CH_2), 23.2 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF), m/z: calcd. for $C_{33}H_{31}NNaO_5S$ $[M+Na]^+$: 576.1815, found 576.1814.

(8S,9aS)-11-methoxy-9a-(3-methoxyphenyl)-8-methyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9o):

Reaction of alkynol **5i** (100 mg, 0.222 mmol), o-vanillin (**8b**)(36 mg, 0.233 mmol) with TMSOTf (81 μL, 0.445 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9o** (57 mg, 44%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.: 218-220 °C

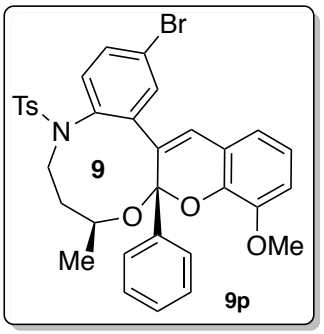
IR (neat): 3112, 3098, 2917, 1672, 1543, 1243, 1123, 1087, 987, 762 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.02-7.06 (m, 2H), 6.93-6.98 (m, 2H), 6.80-6.85 (m, 3H), 6.65-6.71 (m, 4H), 6.24 (d, *J* = 6.5 Hz, 1H), 4.47-4.51 (m, 1H), 3.90 (s, 3H), 3.86 (dd, *J* = 15.0, 6.5 Hz, 1H), 3.60 (s, 3H), 3.26 (ddd, *J* = 18.0, 12.5, 5.5 Hz, 1H), 2.46 (s, 3H), 2.23-2.31 (m, 1H), 1.62-1.68 (m, 1H), 1.25 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 158.9 (C), 147.2 (C), 144.7 (C), 143.6 (C), 142.7 (C), 141.6 (C), 139.3 (C), 136.1 (C), 132.8 (CH), 130.6 (C), 129.6 (2 × CH), 128.4 (CH), 128.4 (2 × CH), 128.4 (CH), 127.7 (CH), 127.3 (CH), 127.2 (CH), 120.8 (CH), 119.7 (CH), 119.5 (CH), 119.2 (C), 113.6 (CH), 112.5 (2 × CH), 102.8 (C), 67.1 (CH), 56.2 (CH_3), 55.3 (CH_3), 51.5 (CH_2), 37.5 (CH_2), 22.7 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{34}H_{33}NNaO_6S$ $[M+Na]^+$: 606.1921, found 606.1924.

(8S*,9aS*)-2-bromo-11-methoxy-8-methyl-9a-phenyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9p):

Reaction of alkynol **5j** (36 mg, 0.072 mmol), o-vanillin (**8b**) (11 mg, 0.070 mmol) with TMSOTf (27 μL, 0.144 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9p** (16 mg, 35%) as a single diastereomer (dr ≥19:1).



Physical appearance: Sticky Solid.

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

IR (neat): 3012, 2999, 2876, 1652, 1543, 1432, 1365, 1297, 1198, 986, 767 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14-7.22 (m, 5H), 6.94-6.99 (m, 2H), 6.83 (dd, *J* = 6.5, 2.0 Hz, 2H), 6.65 (s, 1H), 6.50 (d, *J* = 8.5 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 4.40-4.47 (m, 1H), 3.90 (s, 3H), 3.84 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.20 (ddd, *J* = 18.0, 12.5, 5.5 Hz, 1H), 2.47 (s, 3H), 2.22-2.29 (m, 1H), 1.63-1.70 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 147.2 (C), 143.9 (2 × C), 142.8 (C), 141.8 (C), 141.7 (C), 141.3 (C), 135.9 (CH), 135.8 (C), 131.6 (CH), 129.7 (2 × CH), 129.6 (C), 128.8 (CH), 128.4 (2 × CH), 128.0 (CH), 127.6 (2 × CH), 126.6 (2 × CH), 121.8 (CH), 119.7 (CH), 118.8 (C), 112.8 (2 × CH), 102.8 (C), 67.2 (CH), 56.2 (CH_3), 51.5 (CH_2), 37.4 (CH_2), 22.7 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{33}H_{30}BrNNaO_5S$ $[M+Na]^+$: 654.0913, found 654.0911.

(8S*,9aS*)-2,8-dimethyl-9a-phenyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9q):

Reaction of alkynol **5k** (58 mg, 0.133 mmol), salicylaldehyde (**8a**) (14 μL, 0.133 mmol) with TMSOTf (49 μL, 0.267 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9p** (25 mg, 35%) as a single diastereomer (dr ≥19:1).

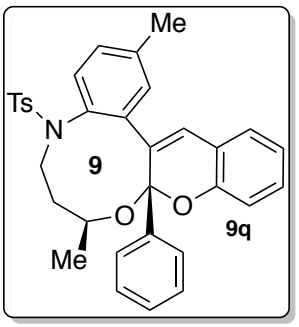
Physical appearance: White Solid.

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

m.p.: 207-209 °C

IR (neat): 3098, 2987, 2932, 1657, 1575, 1452, 1123, 987, 769 cm^{-1}.

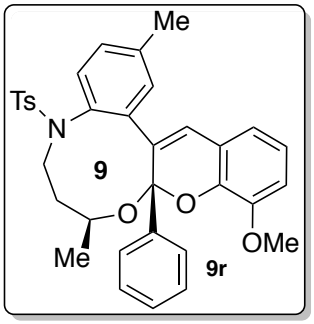
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.26-7.30 (m, 3H), 7.13-7.21 (m, 6H), 7.00-7.04 (m, 2H), 6.83 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.68 (s, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 1H), 4.45-4.52 (m, 1H), 3.85 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.23 (ddd, *J* = 18.5, 13.0, 6.0 Hz, 1H), 2.47 (s, 3H), 2.23-2.30 (m, 1H), 1.90 (s, 3H), 1.57-1.69 (m, 1H), 1.25 (d, *J* = 6.0 Hz, 3H).



^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 152.5 (C), 143.6 (C), 143.3 (C), 140.2 (C), 138.8 (C), 137.1 (C), 136.3 (C), 133.7 (CH), 130.7 (C), 129.7 (CH), 129.6 (2 × CH), 129.1 (CH), 128.4 (2 × CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 127.4 (2 × CH), 126.9 (CH), 126.6 (2 × CH), 121.3 (CH), 118.6 (C), 115.4 (CH), 103.0 (C), 66.8 (CH), 51.6 (CH_2), 37.5 (CH_2), 23.2 (CH_3), 21.7 (CH_3), 20.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{33}H_{31}NNaO_4S$ $[M+Na]^+$: 560.1866, found 560.1865.

(8S*,9aS*)-11-methoxy-2,8-dimethyl-9a-phenyl-5-tosyl-5,6,7,8-tetrahydro-9aH-benzo[f]chromeno[3,2-h][1,5]oxazonine (9r):

Reaction of alkynol **5k** (49 mg, 0.113 mmol), o-vanillin (**8b**) (17 mg, 0.113 mmol) with TMSOTf (41 μL, 0.226 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazonine chromene **9r** (32 mg, 50%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.: 215-217 °C

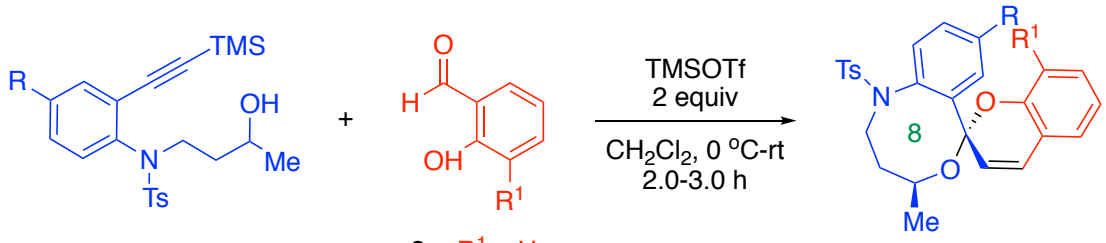
IR (neat): 3012, 2987, 2786, 1652, 1342, 1123, 976, 867, 765 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.09-7.18 (m, 5H), 6.93-6.98 (m, 2H), 6.81-6.84 (m, 2H), 6.65 (s, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.91 (d, *J* = 1.6 Hz, 1H), 4.44-4.52 (m, 1H), 3.90 (s, 3H), 3.85 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.24 (ddd, *J* = 18.6, 12.4, 5.6 Hz, 1H), 2.46 (s, 3H), 2.21-2.30 (m, 1H), 1.90 (s, 3H), 1.61-1.68 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 147.2 (C), 143.5 (C), 143.3 (C), 141.7 (C), 140.2 (C), 138.8 (C), 137.0 (C), 136.3 (C), 133.7 (CH), 131.0 (C), 129.6 (2 × CH), 129.0 (CH), 128.4 (2 × CH), 127.9 (CH), 127.5 (CH), 127.3 (2 × CH), 126.9 (CH), 126.8 (2 × CH), 120.8 (CH), 119.7 (CH), 119.3 (C), 112.5 (CH), 103.1 (C), 67.1

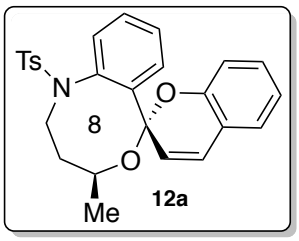
(CH), 56.2 (CH_3), 51.6 (CH_2), 37.5 (CH_2), 22.8 (CH_3), 21.7 (CH_3), 20.6 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{34}H_{33}NNaO_5S$ $[M+Na]^+$: 590.1972, found 590.1971.

Stereoselective Synthesis of *Spiro*-cyclic Chromene 12:



(4S*,6S*)-4-methyl-1-tosyl-1,2,3,4-tetrahydrospiro[benzo[c][1,5]oxazocine-6,2'-chromene] (12a):

Reaction of alkynol **5m** (81 mg, 0.194 mmol), salicylaldehyde (**8a**)(21 µL, 0.194 mmol) with TMSOTf (71 µL, 0.389 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazocine chromene **12a** (37 mg, 43%) as a single diastereomer (dr ≥19:1).



Physical appearance: White Solid.

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

m.p.: 201-203 °C

IR (neat): 3087, 3011, 2982, 1654, 1456, 1352, 986, 567 cm^{-1}.

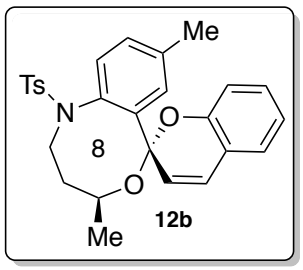
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.34-7.40 (m, 3H), 7.24-7.30 (m, 2H), 7.21 (d, *J* = 7.0 Hz, 1H), 6.99-7.02 (m, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 10.0 Hz, 1H), 6.45 (d, *J* = 9.5 Hz, 1H), 4.19-4.23 (m, 1H), 4.14 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.05 (td, *J* = 16.0, 4.0 Hz, 1H), 2.46 (s, 3H), 2.03-2.11 (m, 1H), 1.39 (d, *J* = 13.5 Hz, 1H), 1.09 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 151.6 (C), 143.5 (C), 142.3 (C), 138.7 (C), 138.0 (C), 132.0 (CH), 130.1 (CH), 129.9 (CH), 129.8 (2 × CH), 129.2 (CH), 128.9 (CH), 128.0 (2 × CH), 127.2 (CH), 126.2 (CH), 123.6 (CH), 121.6 (CH), 120.5 (C), 116.5 (CH), 100.5 (C), 69.7 (CH), 52.1 (CH_2), 35.7 (CH_2), 23.4 (CH_3), 21.7 (CH_3); HRMS (ESI-TOF), m/z: calcd. for $C_{26}H_{25}NNaO_4S$ $[M+Na]^+$: 470.1396, found 470.1390.

(4S*,6S*)-4,8-dimethyl-1-tosyl-1,2,3,4-tetrahydrospiro[benzo[c][1,5]oxazocine-6,2'-chromene] (12b):

Reaction of alkynol **5n** (51 mg, 0.118 mmol), salicylaldehyde (**8a**) (14 μL, 0.118 mmol) with TMSOTf (43 μL, 0.237 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazocine chromene **12b** (14 mg, 25%) as a single diastereomer (dr ≥19:1).

Physical appearance: White Solid.



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

m.p.: 162-164 °C

IR (neat): 3011, 2987, 1654, 1575, 1456, 1172, 987, 765, 564 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 1.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20-7.28 (m, 2H), 7.07 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.98-7.04 (m, 2H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 9.6 Hz, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 4.17-4.24 (m, 1H), 4.13 (dd, *J* = 14.8, 4.0 Hz, 1H), 3.03 (td, *J* = 12.8, 3.6 Hz, 1H), 2.46 (s, 3H), 2.34 (s, 3H), 2.00-2.12 (m, 1H), 1.37 (d, *J* = 10.0 Hz, 1H), 1.08 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 151.6 (C), 143.4 (C), 142.8 (C), 139.0 (C), 138.2 (C), 136.1 (C), 132.6 (CH), 130.7 (CH), 129.9 (CH), 129.7 (2 × CH), 129.2 (CH), 128.0 (2 × CH), 127.2 (CH), 126.4 (CH), 123.5 (CH), 121.6 (CH), 120.6 (C), 116.5 (CH), 100.5 (C), 69.8 (CH), 52.2 (CH_2), 35.8 (CH_2), 23.4 (CH_3), 21.7 (CH_3), 21.4 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{27}H_{27}NNaO_4S$ $[M+Na]^+$: 484.1553, found 484.1556.

(4S*, 6S*)-8'-methoxy-4,8-dimethyl-1-tosyl-1,2,3,4 tetrahydrospiro[benzo[c][1,5]oxazocine-6,2'-chromene] (12c):

Reaction of alkynol **5n** (76 mg, 0.176 mmol), o-vanillin (**8b**) (26 mg, 0.176 mmol) with TMSOTf (64 μL, 0.3528 mmol) in dry CH_2Cl_2 (6 mL) at 0 °C to rt as described for the oxazepino chromene **9a** followed by purification on a silica gel column using ethylacetate-petroleum ether (10:90) as eluent furnished oxazocine chromene **12c** (17 mg, 20%) as a single diastereomer (dr ≥19:1).

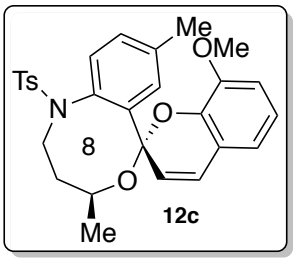
Physical appearance: White Solid.

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

m.p.: 194-196 °C

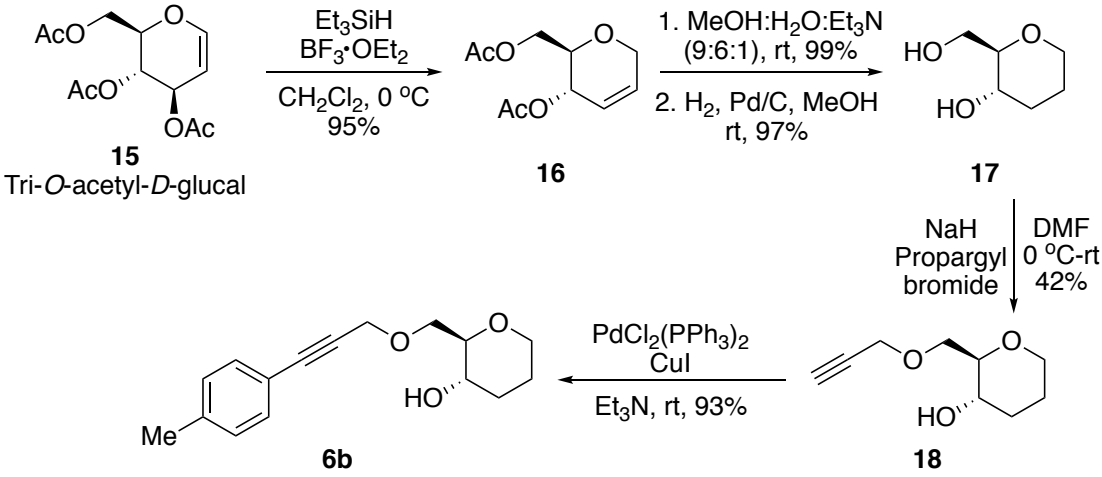
IR (neat): 3123, 3012, 2976, 1656, 1567, 1234, 1082, 972, 763,cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.52 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.04 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.90-6.97 (m, 2H), 6.85 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 9.5 Hz, 1H), 6.44 (d, *J* = 9.5 Hz, 1H), 4.26 (sext, *J* = 6.0 Hz, 1H), 4.13 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.90 (s, 3H), 3.02 (td, *J* = 16.5, 3.5 Hz, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.06-2.14 (m, 1H), 1.38 (d, *J* = 14.5 Hz, 1H), 1.06 (d, *J* = 6.5 Hz, 3H).



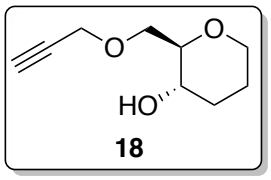
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 148.2 (C), 143.3 (C), 141.8 (C), 140.5 (C), 139.2 (C), 138.2 (C), 136.0 (C), 132.8 (CH), 130.6 (CH), 129.8 (CH), 129.7 (2 × CH), 127.9 (2 × CH), 126.6 (CH), 123.5 (CH), 121.4 (C), 121.2 (CH), 119.5 (CH), 111.9 (CH), 100.5 (C), 69.9 (CH), 56.0 (CH_3), 52.2 (CH_2), 35.9 (CH_2), 22.9 (CH_3), 21.7 (CH_3), 21.4 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{28}H_{29}KNO_5S$ $[M+K]^+$: 530.1398, found 530.1399.

Synthesis of D-Glucal-fused alkynol 6b from Tri-*O*-acetyl-*D*-Glucal:



(2*R*,3*S*)-2-((prop-2-yn-1-yloxy)methyl)tetrahydro-2*H*-pyran-3-ol (18):

The diol **17** was prepared from Tri-*O*-acetyl-*D*-glucal (**15**) in 3-steps by following literature established protocol.[1] 60% NaH (206 mg, 5.145 mmol) was added to a solution of diol **17** (680 mg, 5.145 mmol) in dry DMF (20 mL). After stirring for 0.5 h at 0 °C, propargyl bromide (438 µL, 5.145 mmol) was added drop wise at room temperature. The reaction mixture was quenched with saturated aq. solution of NH_4Cl upon completion, extracted with EtOAc (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 ethyl acetate-petroleum ether (30:70) as eluent furnished terminal alkyne **18** (365 mg, 42%) as a yellow liquid.

Physical appearance: Yellow liquid.

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

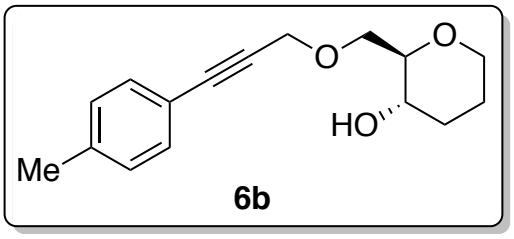
IR (neat): 3448, 3018, 2928, 2352, 1759, 1522, 1509, 1345, 1007, 916, 757, 638 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.16-4.23 (m, 2H), 3.90 (dt, *J* = 18.0, 2.0 Hz, 1H), 3.66-3.84 (m, 2H), 3.54 (ddd, *J* = 19.0, 9.0, 4.5 Hz, 1H), 3.23 (td, *J* = 15.0, 7.5, 3.5 Hz, 1H), 3.24 (quint, *J* = 4.5 Hz, 1H), 2.44 (t, *J* = 4.0 Hz, 1H), 2.35 (bs, 1H), 2.08-2.17 (m, 1H), 1.61-1.72 (m, 2H), 1.39 (dddd, *J* = 23.5, 12.5, 5.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 80.6 (C), 80.4 (CH), 79.5 (CH), 75.0 (CH_2), 70.7 (CH), 68.0 (CH_2), 67.8 (CH_2), 58.8 (CH_2), 32.3 (CH_2), 25.3 (CH_2); HRMS (ESI-TOF) m/z: calcd. for $C_9H_{14}NaO_3$ $[M+Na]^+$: 193.0835, found 193.0832.

(2*R*,3*S*)-2-(((3-(*p*-tolyl)prop-2-yn-1-yl)oxy)methyl)tetrahydro-2*H*-pyran-3-ol (6b):

To a mixture of terminal alkyne **18** (150 mg, 0.881 mmol), 4-iodotoluene (192 mg, 0.881 mmol), $PdCl_2(PPh_3)_2$ (12 mg, 0.017 mmol) and CuI (6 mg, 0.035 mmol) was added Et_3N (5 mL) at room temperature. The reaction was strirred for 12 h at the same temperature. Excess Et_3N was evaporated under reduced pressure and the residue was purified on a silica gel column using ethyl acetate-petroleum ether (30:70) as eluent furnished the alkynol **6b** (213 mg, 93%) as a yellow sticky solid.



6b

Physical appearance: Yellow sticky solid.

R_f: 0.4 (2:8 ethyl acetate-petroleum ether).

IR (neat): 3443, 2926, 2355, 1739, 1599, 1510, 1355, 1087, 816, 754, 532 cm^{-1}.

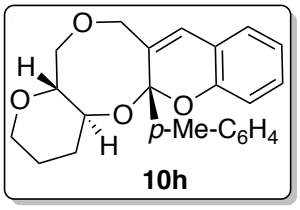
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.12 (AB, *J* = 17.6, 15.2 Hz, 2H), 3.91 (dt, *J* = 11.2, 2.0 Hz, 1H), 3.83 (dd, *J* = 10.0, 5.2 Hz, 1H), 3.79 (dd, *J* = 9.6, 4.4 Hz, 1H), 3.58 (ddd, *J* = 14.0, 12.0, 4.8 Hz, 1H), 3.34 (td, *J* = 11.6, 3.6 Hz, 1H), 3.26 (quint, *J* = 4.8 Hz, 1H), 2.57 (bs, 1H), 2.32 (s, 3H), 2.09-2.13 (m, 1H), 1.61-1.74 (m, 2H), 1.41 (ddd, *J* = 23.6, 8.4, 4.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 138.7 (C), 131.7 (2 × CH), 129.1 (2 × CH), 119.4 (C), 86.9 (C), 84.1 (C), 80.3 (CH), 70.9 (CH_2), 68.3 (CH), 67.8 (CH_2),

59.7 (CH_2), 32.2 (CH_2), 25.3 (CH_2), 21.5 (CH_3); HRMS (ESI-TOF) m/z: calcd. for $C_{16}H_{20}NaO_3$ $[M+Na]^+$: 283.1305, found 283.1312.

(4aR,13aR,14aS)-13a-(p-tolyl)-1,2,3,4a,5,14a-hexahydro-7H,13aH-pyrano[2',3':7,8][1,5]dioxocino[2,3-b]chromene (10c):

Reaction of alkynol **6b** (65 mg, 0.249 mmol), salicyaldehyde (**8a**) (32 µL, 0.262 mmol) with TMSOTf (90.4 µL, 0.499 mmol) in dry CH_2Cl_2 (8 mL) at 0 °C as described for the oxazepino chromene **9a** followed by purification on a silica gel column using methanol- dichloromethane (2:98) as eluent furnished the dioxocino chromene **10c** (38 mg, 42 %) as a colourless liquid.



10h

Physical appearance: colourless liquid.

R_f: 0.8 (2:98 methanol-dichloromethane).

$[\alpha]_D^{25}$: 65.147 (c 0.19, CH_2Cl_2).

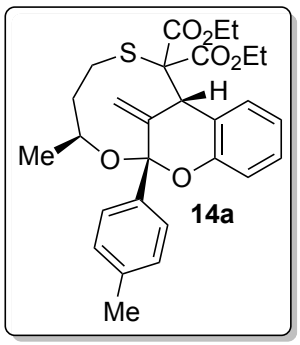
IR (neat): 2933**,** 2847, 1606, 1466, 1252, 1166, 1097, 954, 937, 828, 754 cm^{-1}.

^{1}H NMR (400 MHz, C_6D_6): δ 7.70 (d, *J* = 8.0 Hz, 2H), 6.96-7.00 (m, 4H), 6.87-6.89 (m, 1H), 6.77 (m, 1H), 6.28 (s, 1H), 3.93-4.03 (m, 3H), 3.69-3.77 (m, 2H), 3.54 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.39 (ddd, *J* = 9.2, 7.4, 4.0, Hz, 1H), 2.95 (td, *J* = 12.4, 2.4 Hz, 1H), 2.15-2.19 (m, 1H), 2.05 (s, 3H), 1.59-1.69 (m, 1H), 1.14(qd, *J* =.17.6, 4.0 Hz, 1H), 1.00-1.04 (m, 1H).

^{13}C NMR (100 MHz, C_6D_6, DEPT): δ 154.1 (C), 140.4 (C), 138.6 (C), 132.4 (C), 131.0 (CH), 129.7 (CH), 129.2 (2 × CH), 127.9 (CH), 127.0 (2 × CH), 121.5 (CH), 119.0 (C), 115.8 (CH), 105.5 (C), 80.2 (CH), 74.5 (CH_2), 73.4 (CH), 72.9 (CH_2) 68.1 (CH_2), 32.1 (CH_2), 25.6 (CH_2) 20.7 (CH_3); HRMS (ESI-TOF) m/z: calcd. For $C_{23}H_{24}NaO_4$ $[M+Na]^+$: 387.1567 found 387.1566.

diethyl (2R*,4S*,9S*)-4-methyl-14-methylene-2-(p-tolyl)-5,6-dihydro-4H-2,9-methanobenzo[j][1,3]dioxa[7]thiacycloundecine-8,8(9H)-dicarboxylate (14a):

To a magnetically stirred solution of ketal **11a** (30 mg, 0.088 mmol) in dry benzene (5 mL) was added diazo ester **13** (50 mg, 0.265 mmol) followed by $Rh_2(OAc)_4$ (2 mg, 0.004 mmol) and the reaction mixture was refluxed at 80 °C for 4 h. The solvent was evaporated and purification of the residue over a silica gel column using ethyl acetate-petroleum ether (10:90) as eluent furnished bridge bicyclic ketal **14a** (40 mg, 91%) as a single diastereomer (dr ≥19:1).



14a

Physical appearance: Sticky solid.

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

IR (neat): 2983, 2944, 1742, 1447, 1374, 1244, 1094, 1048, 937, 918, 758 cm^{-1}.

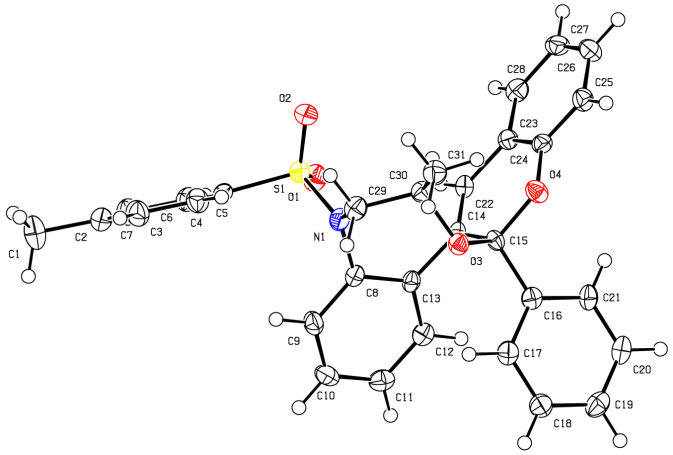
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.26-7.29 (m, 1H), 7.19 (d, 7.5 Hz, 2H), 6.98-7.02 (m, 2H), 5.33 (s, 1H), 4.91 (s, 1H), 4.58 (s, 1H), 4.23-4.39 (m, 5H), 3.65 (dd, *J* = 15.0, 10.5 Hz, 1H), 2.39 (s, 3H), 2.36-2.41 (m, 1H), 1.86-1.91 (m, 1H), 1.79-1.85 (m, 1H), 1.34 (dd, *J* = 13.0, 7.0 Hz, 6H), 0.99 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 170.8 (C), 167.8 (C), 152.9 (C), 145.0 (C), 138.2 (C), 136.8 (C), 131.2 (CH), 128.8 (CH), 128.3 (2 × CH), 128.2 (2 × CH), 124.9 (C), 120.9 (CH), 120.8 (CH_2), 116.6 (CH), 101.4 (C), 68.4 (C), 68.0 (CH), 62.9 (CH_2), 61.7 (CH_2), 48.2 (CH), 38.5 (CH_2), 28.9 (CH_2), 21.3 (CH_3), 20.7 (CH_3), 141.1 (CH_3), 14.0 (CH_3); HRMS (ESI-TOF) m/z: calcd. For $C_{28}H_{32}NaO_6S$ $[M+Na]^+$: 519.1812 found 519.1812.

Refernce:

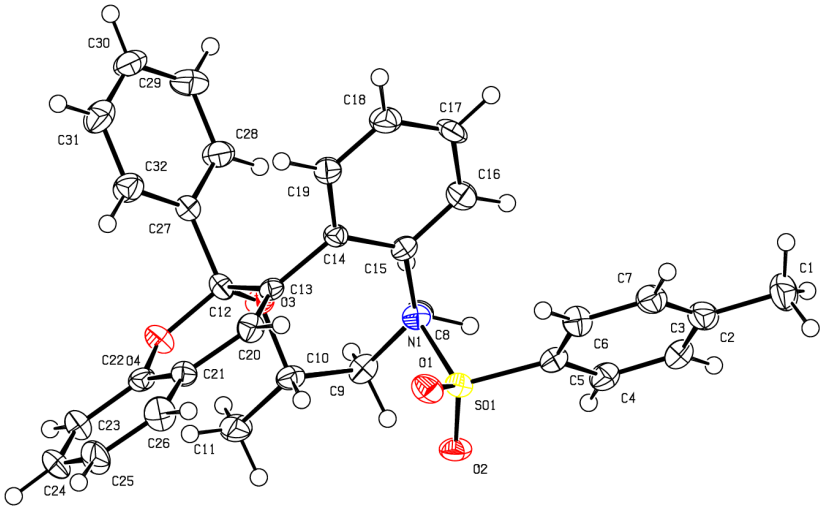
1. Gharpure, S. J.; Mane, S. P.; Nanda, L. N.; Shukla, M. K. *Isr. J. Chem.* **2016**, *56*, 553.

X-Ray crystallographic analysis:
Crystal data and structure refinement for 9c:



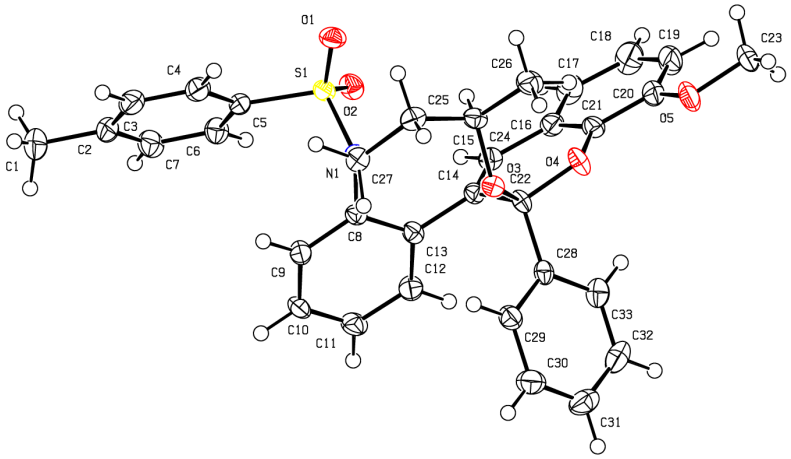
Identification code		**9c**	
Solvent		EtOAc	
CCDC		1885265	
Bond precision:	C-C = 0.0046 A	Wavelength= 0.71073	
Cell:	a= 15.6522(10)	b= 13.6042(7)	c= 12.4636(8)
	alpha= 90	beta= 107.449(7)	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	2531.8 (3)	2531.8 (3)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C31 H27 N O4 S	C31 H27 N O4 S	
Sum formula	C31 H27 N O4 S	C31 H27 N O4 S	
Mr	509.59	509.59	
Dx, g cm-3	1.337	1.337	
Z	4	4	
Mu (mm-1)	0.167	0.167	
F000	1072.0	1072.0	
F000’	1072.97		
h,k,l max	18,16,14	18,16,14	
Nref	4456	4454	
Tmin,Tmax	0.961,0.995	0.411,1.000	
Tmin’	0.940		
Correction method =	Numerical		
Data completeness =	1.000	Theta(max)= 25.000	
R(reflections) =	0.0560(3337)	wR2(reflections)= 0.1878(4454)	
S = 1.090			
	Npar= 336		

Crystal data and structure refinement for 9d:



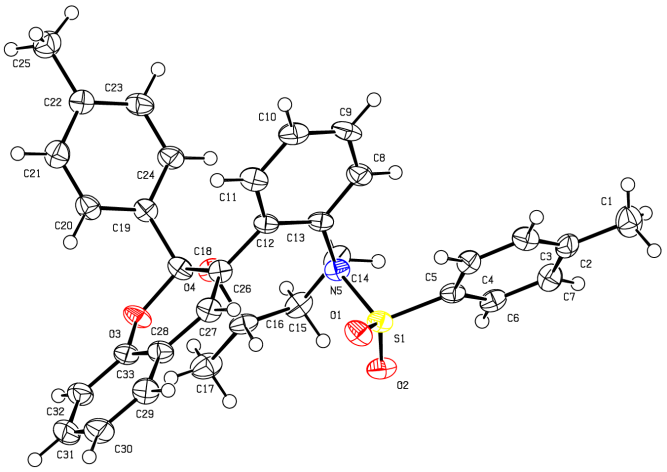
Identification code		**9d**	
Solvent		EtOAc	
CCDC		1885266	
Bond precision:	C-C = 0.0090	Wavelength= 0.71073	
Cell:	a= 9.2331(7)	b= 9.4073(7)	c= 15.2033(12)
	alpha= 90	beta= 91.611(7)	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	1320.02 (17)	1320.01 (18)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C32 H29 N O4 S	C32 H29 N O4 S	
Sum formula	C32 H29 N O4 S	C32 H29 N O4 S	
Mr	523.62	523.62	
Dx, g cm-3	1.317	1.317	
Z	2	2	
Mu (mm-1)	0.162	0.162	
F000	552.0	552.0	
F000’	552.49		
h,k,l max	10,11,18	10,11,18	
Nref	4636[2472]	4523	
Tmin,Tmax	0.977,0.982	0.602,1.000	
Tmin’	0.971		
Correction method =	Numerical		
Data completeness =	1.83/0.98	Theta(max)= 24.999	
R(reflections) =	0.0560(3777)	wR2(reflections)= 0.1724(4523)	
S = 1.097			
	Npar= 345		

Crystal data and structure refinement for 9e:



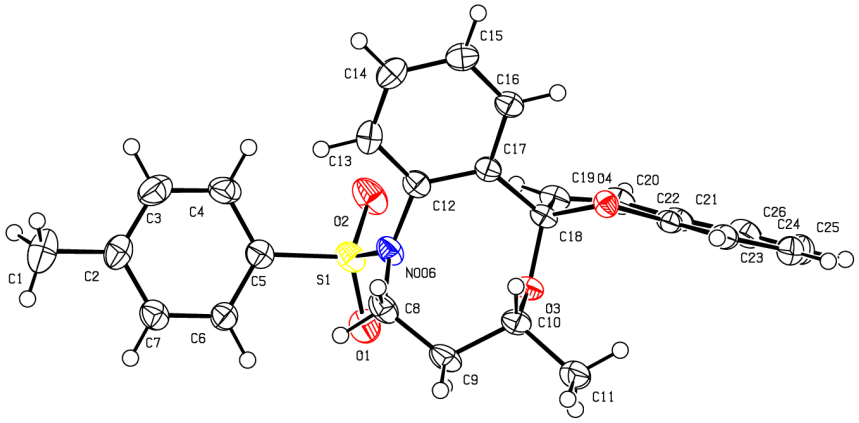
Identification code		**9e**	
Solvent		EtOAc	
CCDC		1894452	
Bond precision:	C-C = 0.0042 A	Wavelength= 0.71073	
Cell:	a= 9.1034(2)	b= 9.5264(3)	c= 15.9591(4)
	alpha= 90	beta= 91. 547(2)	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	1383.51(6)	1383.51(6)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C33 H31 N O5 S	C33 H31 N O5 S	
Sum formula	C33 H31 N O5 S	C33 H31 N O5 S	
Mr	523.65	523.65	
Dx, g cm-3	1.329	1.329	
Z	2	2	
Mu (mm-1)	0.161	0.161	
F000	584.0	584.0	
F000’	584.51		
h,k,l max	10,11,18	10,11,18	
Nref	4876[2598]	4843	
Tmin,Tmax	0.977,0.991	0.908,1.000	
Tmin’	0.963		
Correction method =	Numerical		
Data completeness =	1.86/0.99	Theta(max)= 24.986	
R(reflections) =	0.0324(4615)	wR2(reflections)= 0.0933(4843)	
S = 0.927			
	Npar= 364		

Crystal data and structure refinement for 9f:



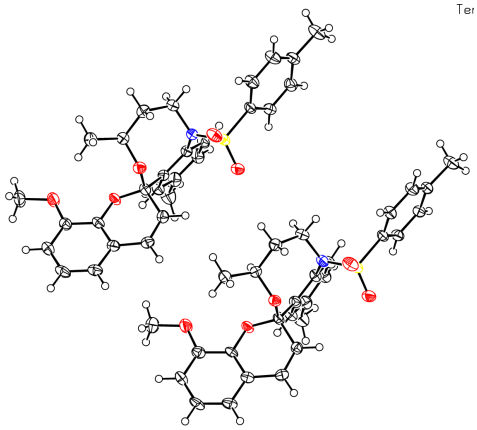
Identification code		**9f**	
Solvent		EtOAc	
CCDC		1894451	
Bond precision:	C-C = 0.0051A	Wavelength= 0.71073	
Cell:	a= 9.2545(7)	b=9.0908(5)	c= 32.563(3)
	alpha= 90	beta= 96.115(7)	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	2724.0(4)	2724.0(3)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C33 H31 N O4 S	C33 H31 N O4 S	
Sum formula	C33 H31 N O4 S	C33 H31 N O4 S	
Mr	537.65	537.65	
Dx, g cm-3	1.311	1.311	
Z	4	4	
Mu (mm-1)	0.159	0.159	
F000	1136.0	1136.0	
F000’	1136.98		
h,k,l max	11,10,38	10,10,38	
Nref	4802	4633	
Tmin,Tmax	0.972,0.981	0.645,1.000	
Tmin’	0.967		
Correction method =	Numerical		
Data completeness =	0.965	Theta(max)= 24.996	
R(reflections) =	0.0709(3241)	wR2(reflections)= 0.1715(4633)	
S = 1.068			
	Npar= 355		

Crystal data and structure refinement for 12a:

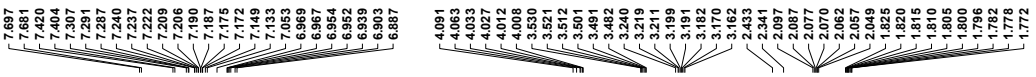


Identification code		**12a**	
Solvent		EtOAc	
CCDC		1944770	
Bond precision:	C-C = 0.0037 A	Wavelength= 0.71073	
Cell:	a= 8.3119(4)	b= 24.2166(14)	c= 11.0613(5)
	alpha= 90	beta= 93.864(5)	gamma= 90
Temperature:	150 K		
	Calculated	Reported	
Volume	2221.4(2)	2221.4(2)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C26 H25 N O4 S	2(C26 H25 N O4 S)	
Sum formula	C26 H25 N O4 S	C52 H50 N2 O8 S2	
Mr	447.53	895.06	
Dx, g cm-3	1.338	1.338	
Z	4	4	
Mu (mm-1)	0.179	0.179	
F000	944.0	944.0	
F000’	944.92		
h,k,l max	9,28,13	9,28,13	
Nref	3899	3798	
Tmin,Tmax	0.974,0.993	0.596,1.000	
Tmin’	0.967		
Correction method =	Numerical		
Data completeness =	0.974	Theta(max)= 24.999	
R(reflections) =	0.0503(3012)	wR2(reflections)= 0.1321(3798)	
S = 1.042			
	Npar= 291		

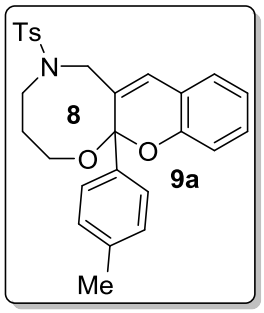
Crystal data and structure refinement for 12c:

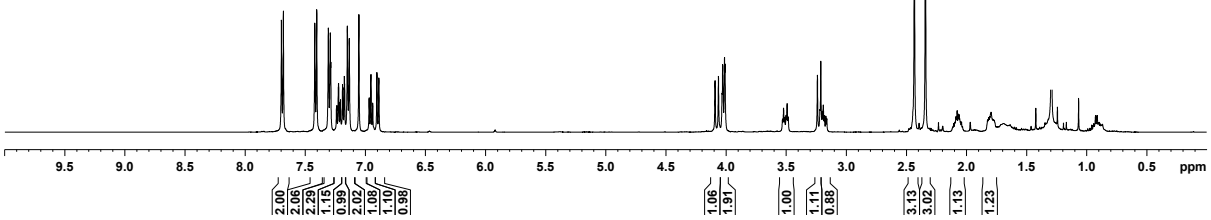


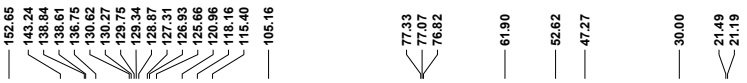
Identification code		**12c**	
Solvent		EtOAc	
CCDC		1944769	
Bond precision:	C-C = 0.0042 A	Wavelength= 0.71073	
Cell:	a= 10.6050(4)	b= 16.0358(5)	c= 16.1366(5)
	alpha= 69.467(3)	beta= 72.006(3)	gamma=89.666(3)
Temperature:	150 K		
	Calculated	Reported	
Volume	2427.91(16)	2427.91(15)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C28 H29 N O5 S	2(C28 H29 N O5 S)	
Sum formula	C28 H29 N O5 S	C56 H58 N2 O10 S2	
Mr	491.58	983.16	
Dx, g cm-3	1.345	1.345	
Z	4	2	
Mu (mm-1)	0.174	0.174	
F000	1040.0	1040.0	
F000’	1040.98		
h,k,l max	12,19,19	12,19,19	
Nref	8557	8552	
Tmin,Tmax	0.966,0.993	0.808,1.000	
Tmin’	0.966		
Correction method =	Numerical		
Data completeness =	0.999	Theta(max)= 25.000	
R(reflections) =	0.0571(6503)	wR2(reflections)= 0.1489(8552)	
S = 1.044			
	Npar= 639		



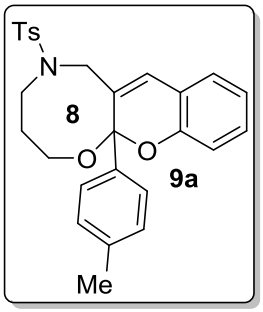
SJG-SN-9-1453-1H

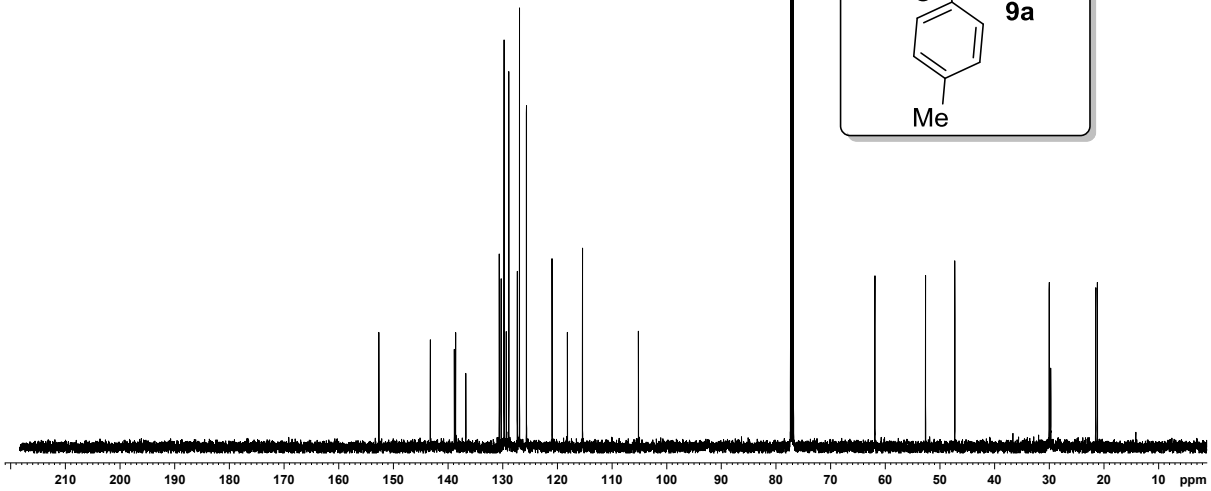


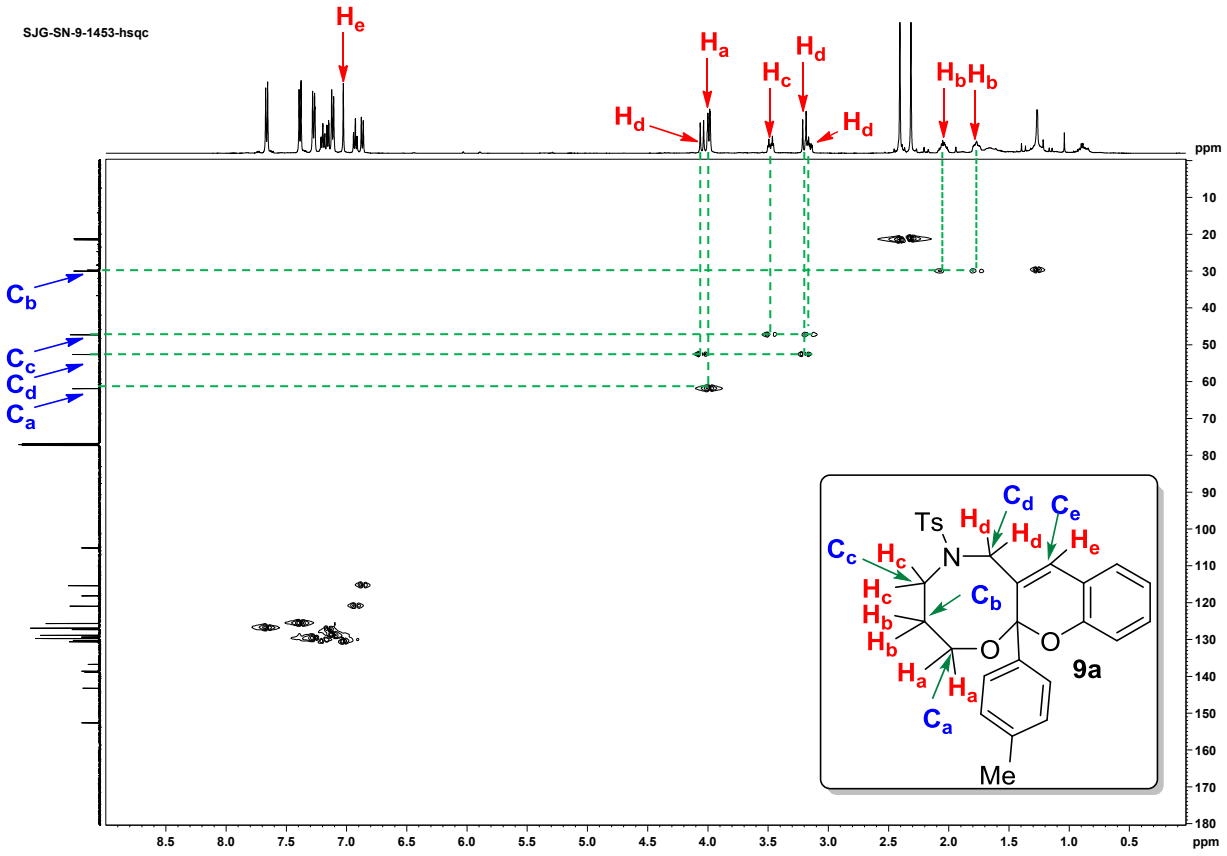


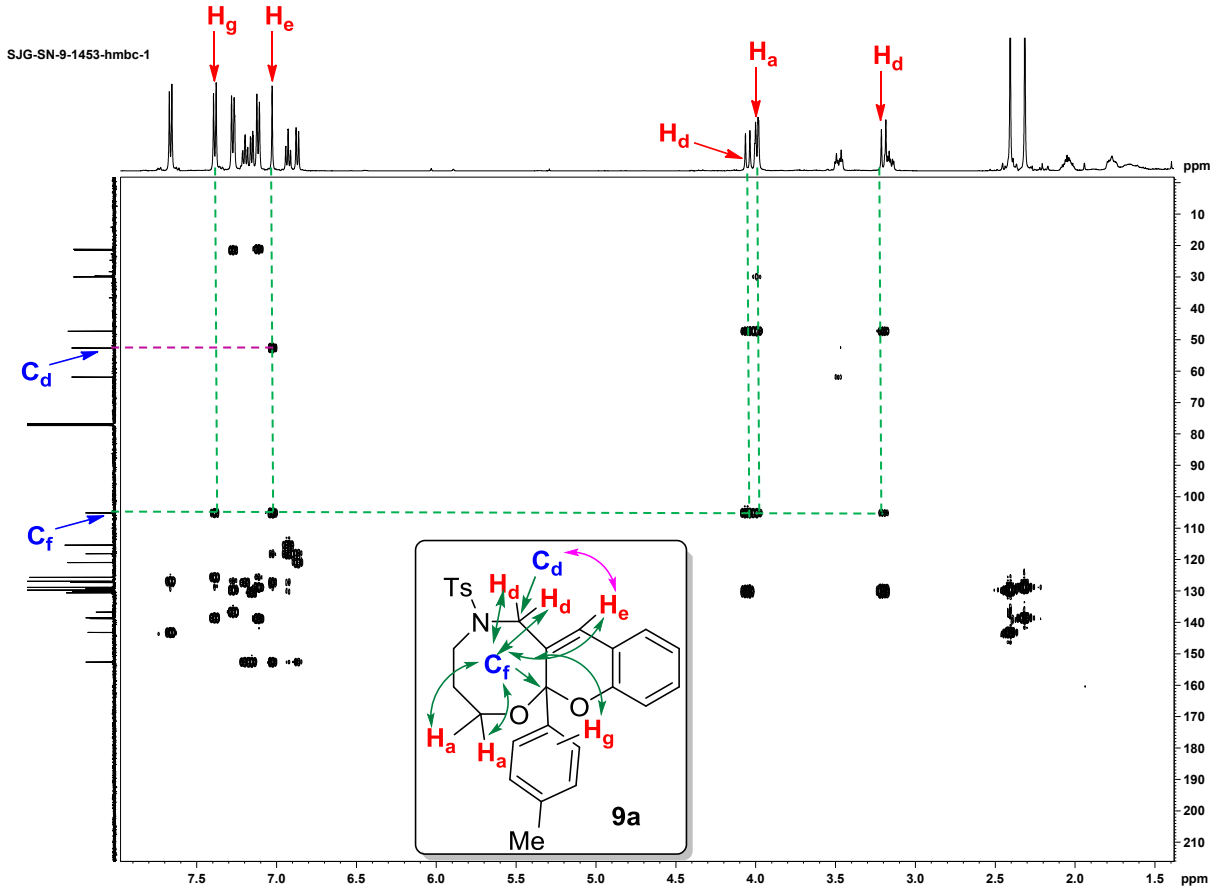


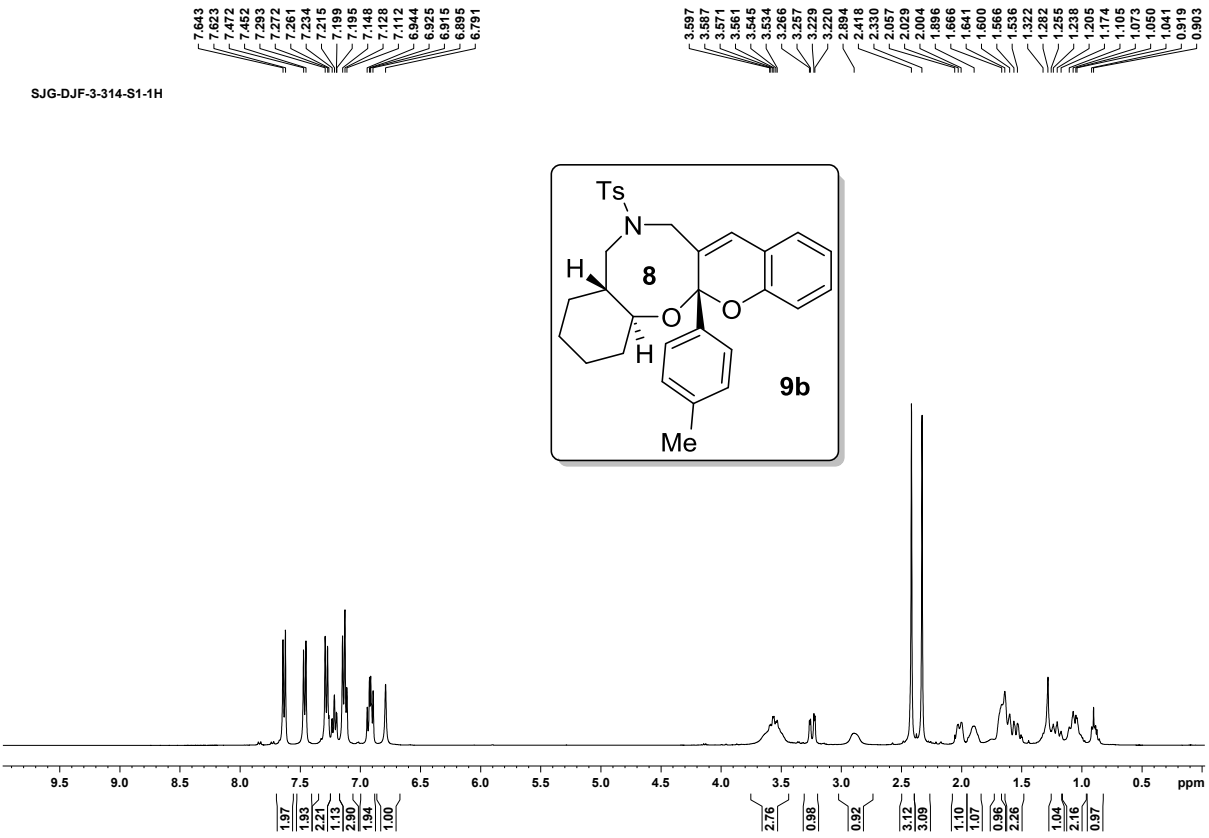
SJG-SN-9-1453-13C






SJG-SN-9-1453-hsqc
He
Ha
Hc
Hd
Hd
Hd
HbHb
Hd
Cb
Cc
Cd
Ca
ppm
Ts
N
O
O
Me
9a


SJG-SN-9-1453-hmbc-1
Hg
He
Ha
Hd
Hd
Cd
Cf
ppm
Ts
N
O
O
Me
9a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7.234
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7.199
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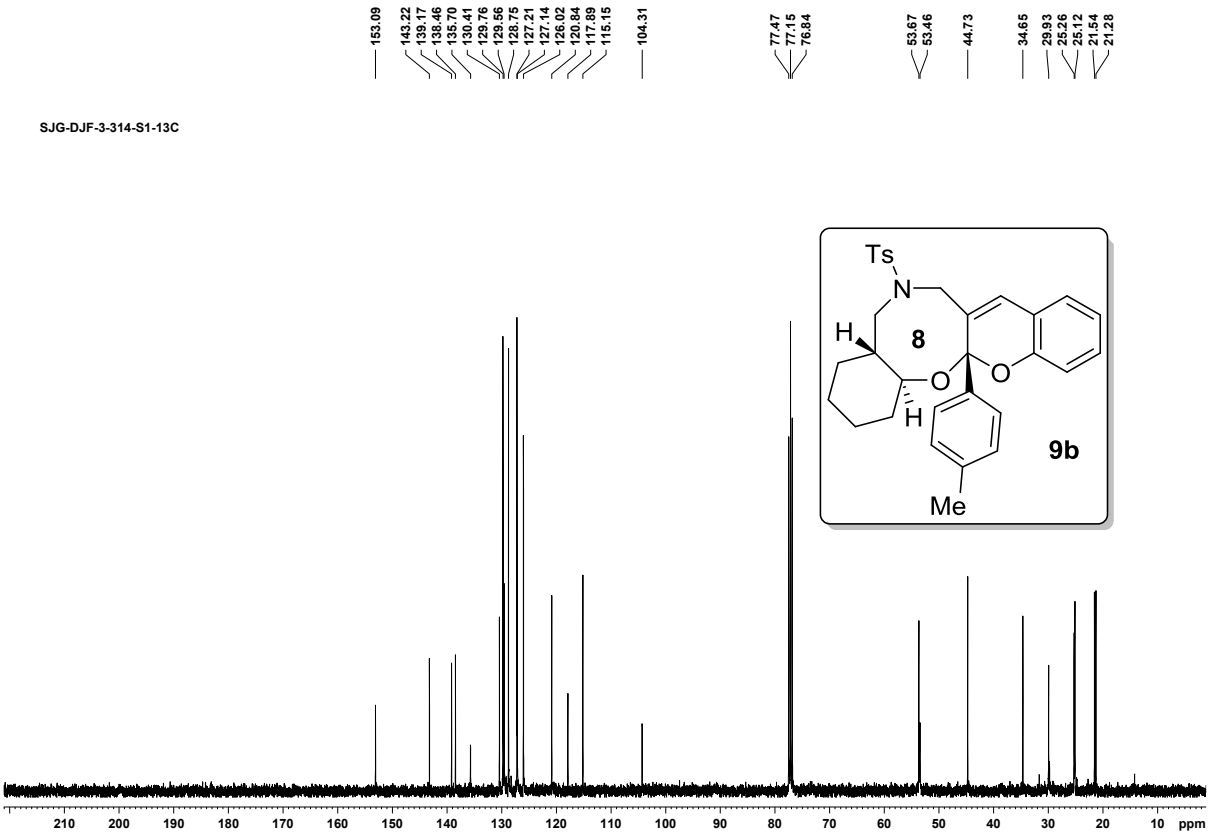
7.128
7.112
6.944
6.925
6.915
6.895
6.791
3.597
3.587
3.571
3.561
3.545
3.534
3.266
3.257
3.229
3.220
2.894
2.418
2.330
2.057
2.029
2.004
1.896
1.666
1.641
1.600
1.566
1.536
1.322
1.282
1.255
1.238
1.205
1.174
1.105
1.073
1.050
1.041
0.919
0.903
SJG-DJF-3-314-S1-1H
Ts
N
H
8
O
O
H
9b
Me
9.5
9.0
8.5
8.0
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
1.97
1.93
2.21
1.13
2.90
1.94
1.00
2.76
0.98
0.92
3.12
3.09
1.10
1.07
0.96
2.26
1.04
2.16
0.97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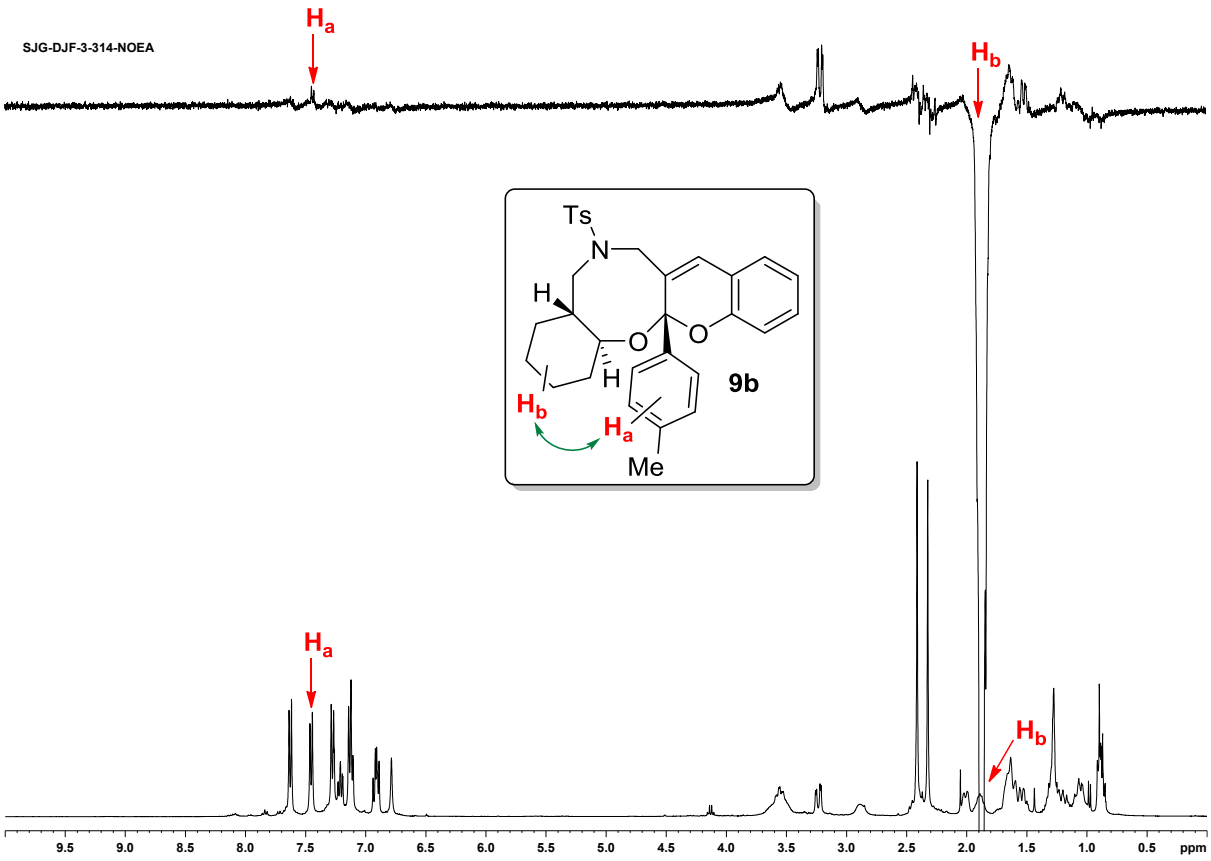
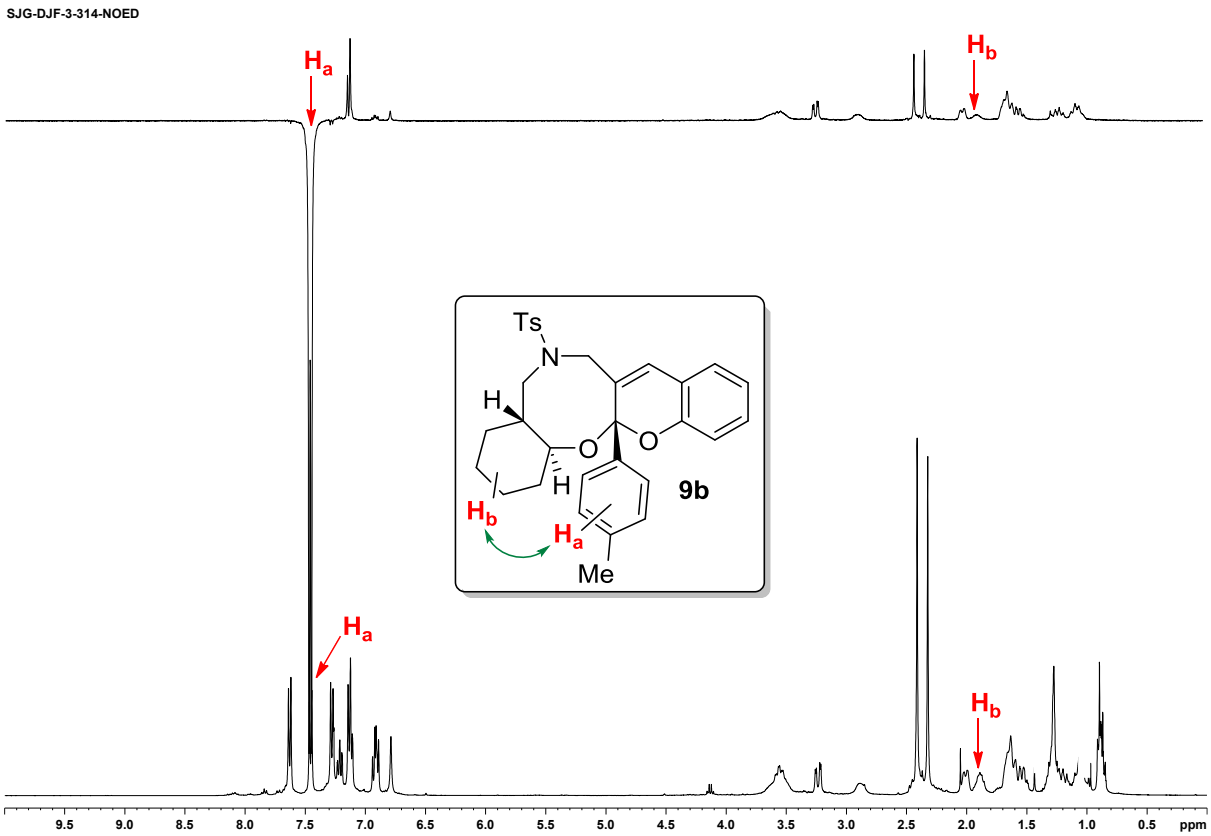
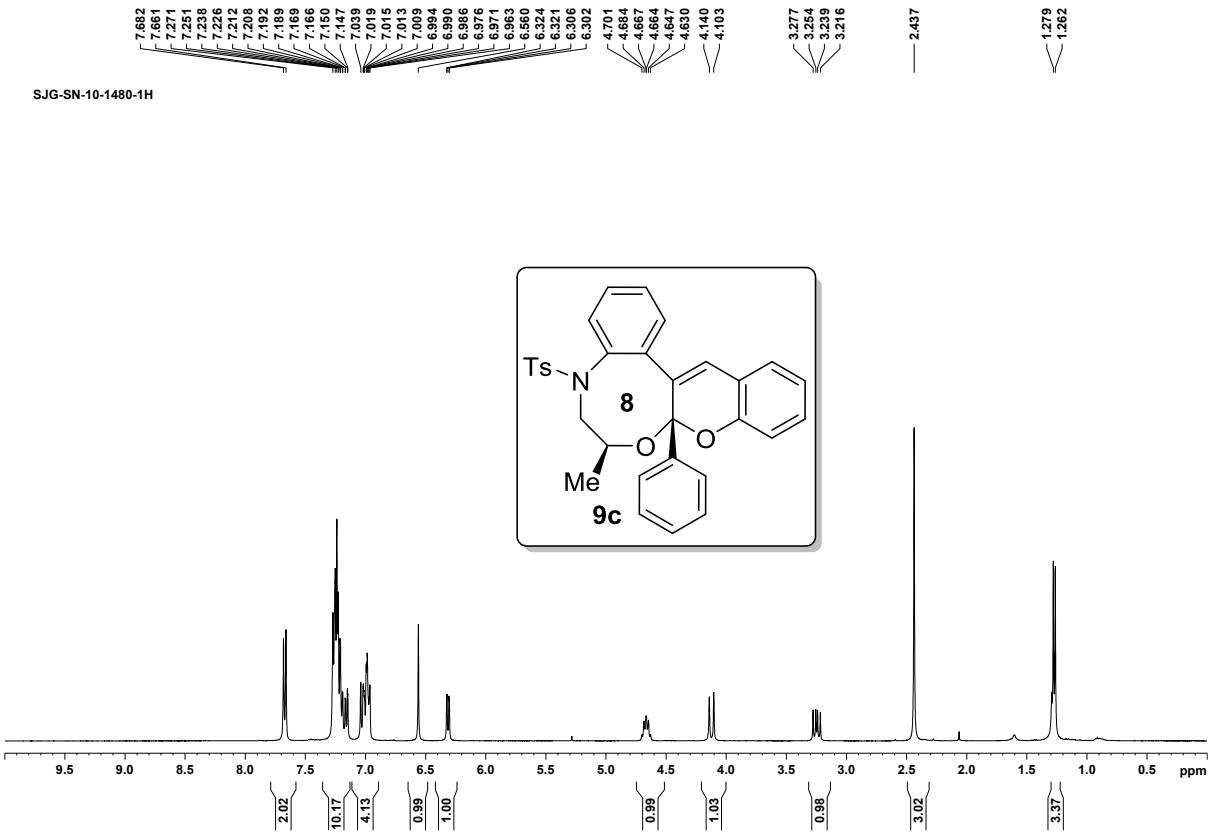
139.17
138.46
135.70
130.41
129.76
129.56
128.75
127.21
127.14
126.02
120.84
117.89
115.15
104.31
77.47
77.15
76.84
53.67
53.46
44.73
34.65
29.93
25.26
25.12
21.54
21.28
SJG-DJF-3-314-S1-13C
Ts
N
H
8
O
O
H
9b
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



NOE enhancement-2%



NOE enhancement-2%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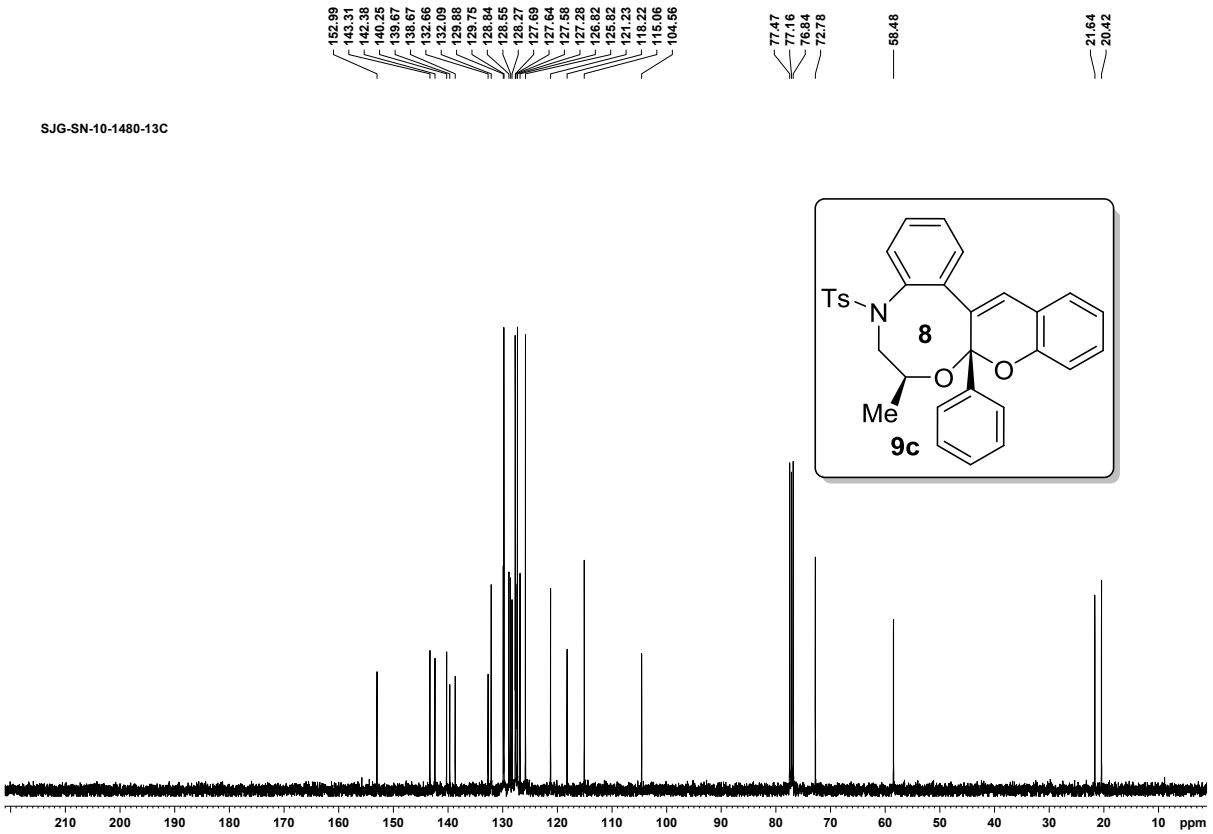
7.212
7.208
7.192
7.189
7.169
7.166
7.150
7.147
7.039
7.019
7.015
7.013
7.009
6.994
6.990
6.986
6.976
6.971
6.963
6.560
6.324
6.321
6.306
6.302
4.701
4.684
4.667
4.664
4.647
4.630
4.140
4.103
3.277
3.254
3.239
3.216
2.437
1.279
1.262
SJG-SN-10-1480-1H
Ts
N
8
O
O
Me
9c
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
10.17
4.13
0.99
1.00
0.99
1.03
0.98
3.02
3.37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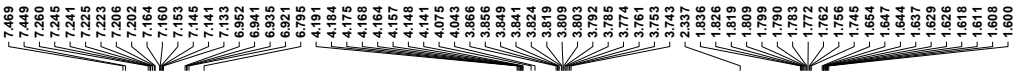
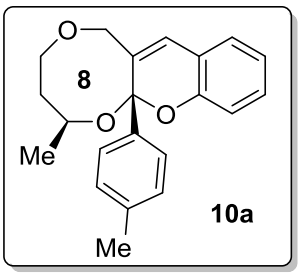
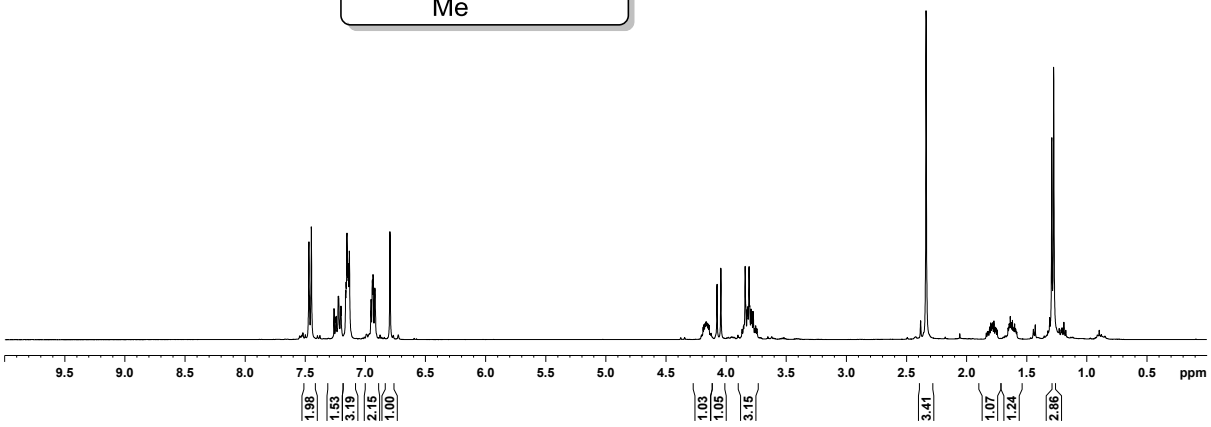
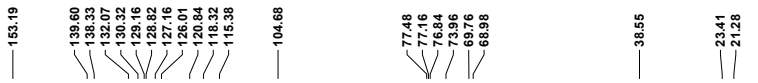
140.25
139.67
138.67
132.66
132.09
129.88
129.75
128.84
128.55
128.27
127.69
127.64
127.58
127.28
126.82
125.82
121.23
118.22
115.06
104.56
77.47
77.16
76.84
72.78
58.48
21.64
20.42
SJG-SN-10-1480-13C
Ts
N
8
O
O
Me
9c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



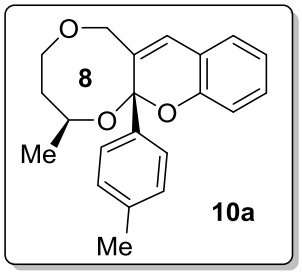
SJG-SN-10-1475-1H

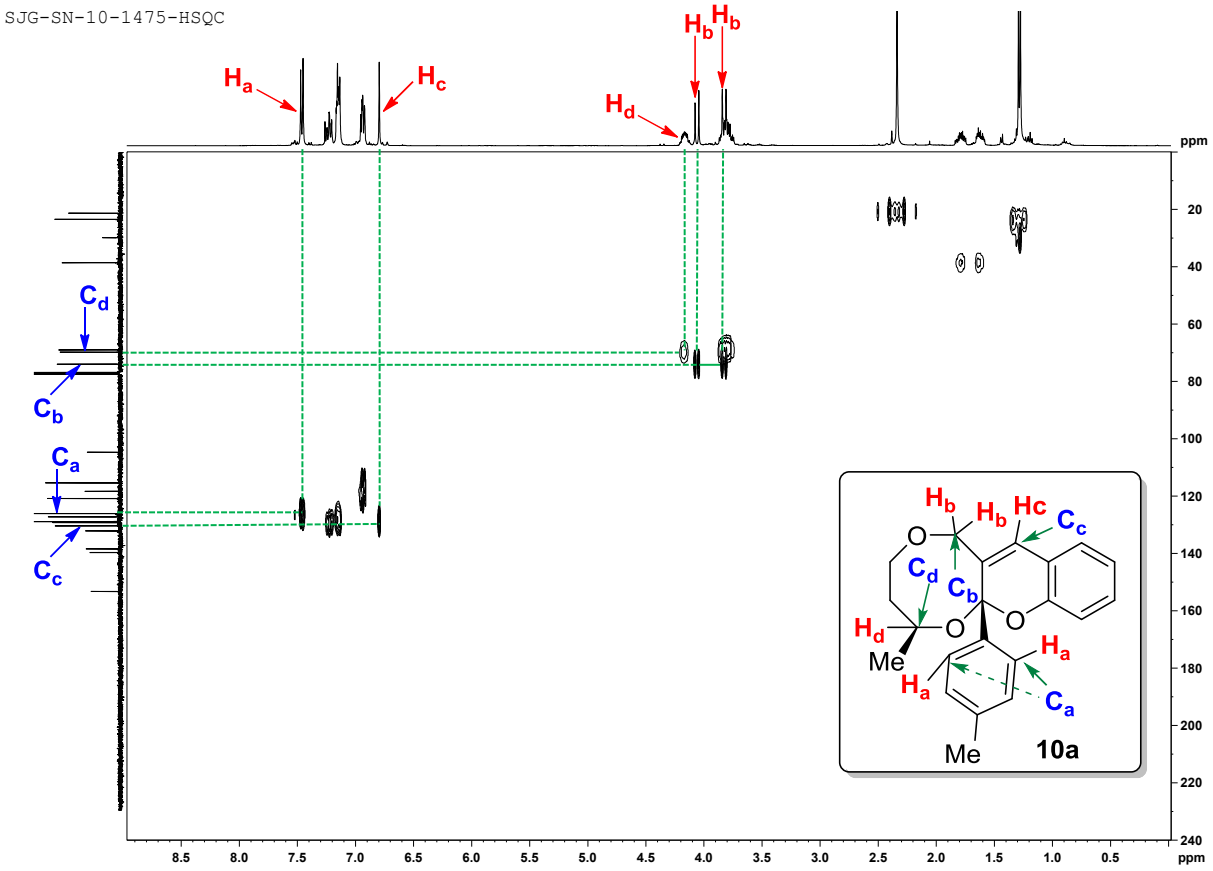






SJG-SN-10-1475-13C

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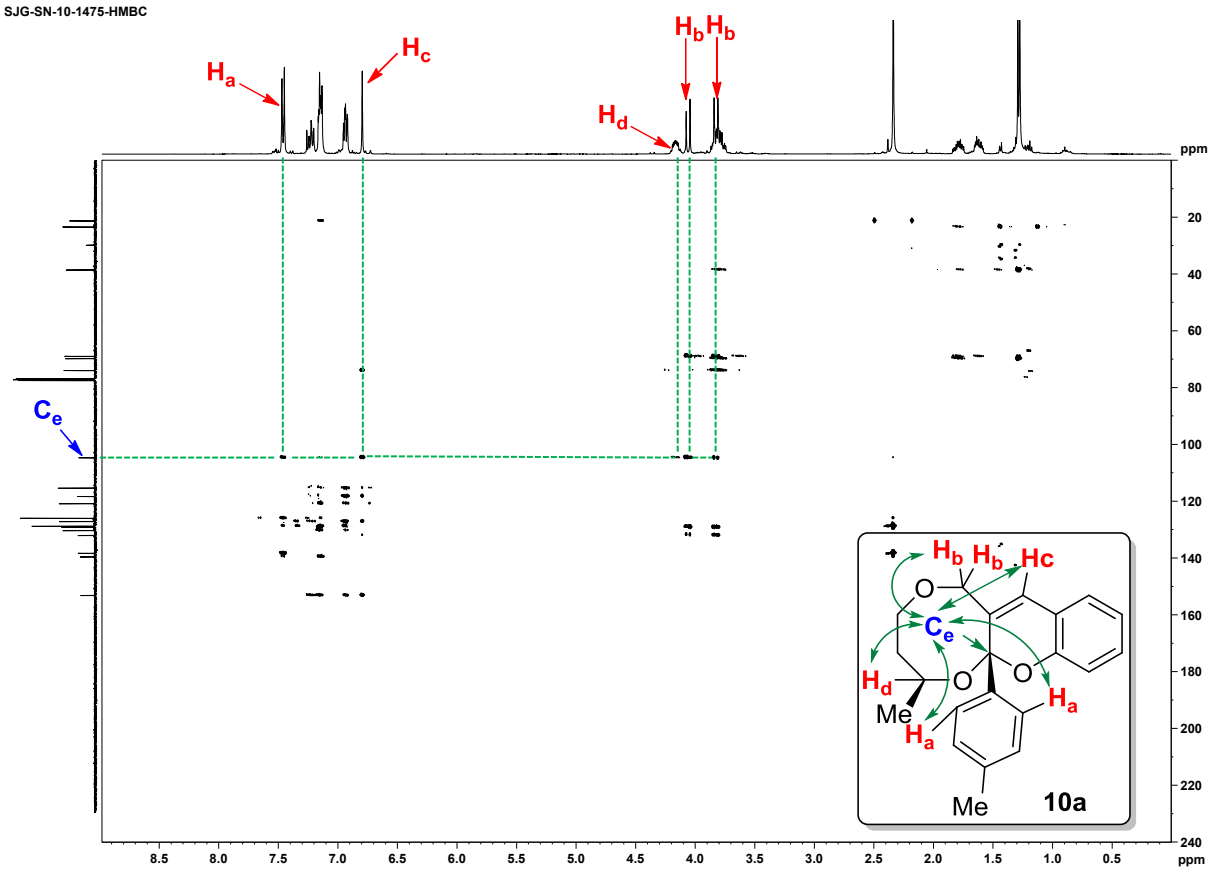
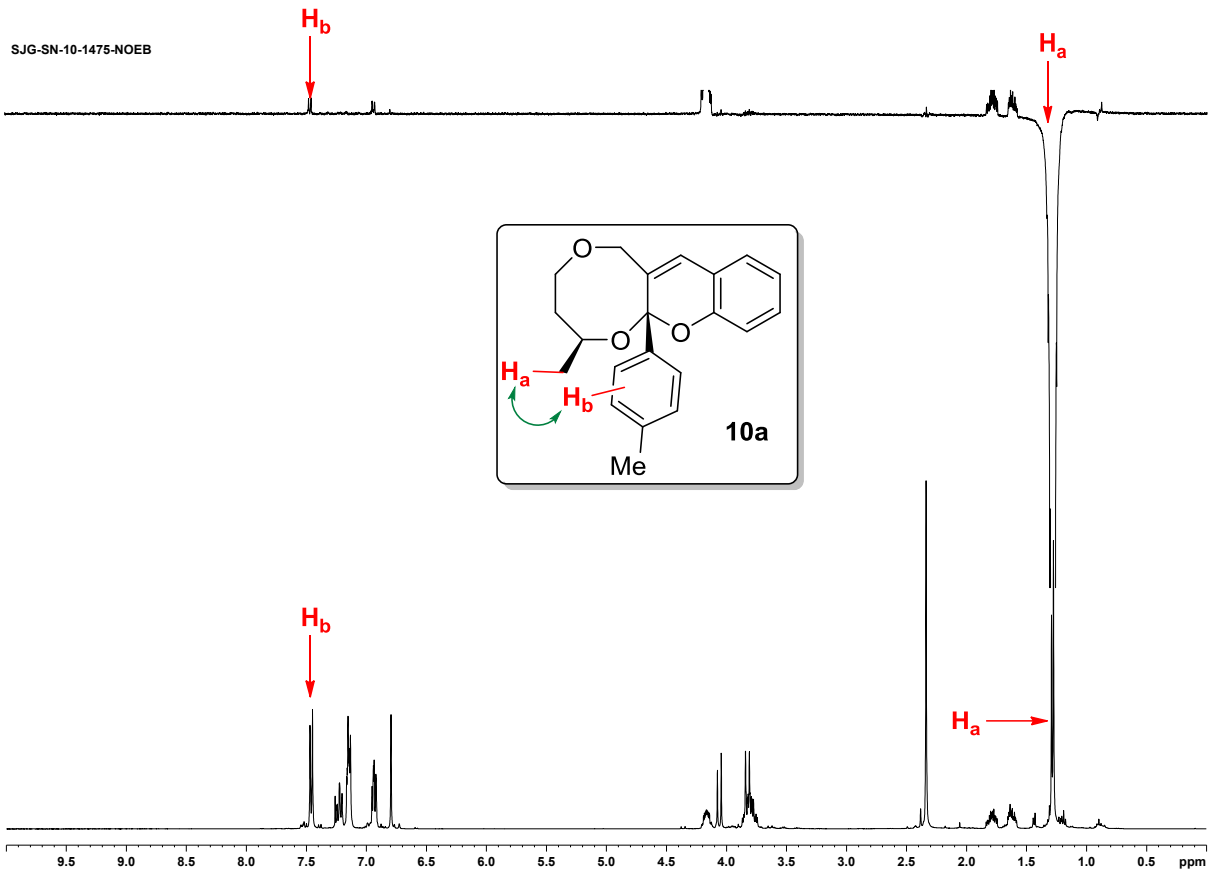
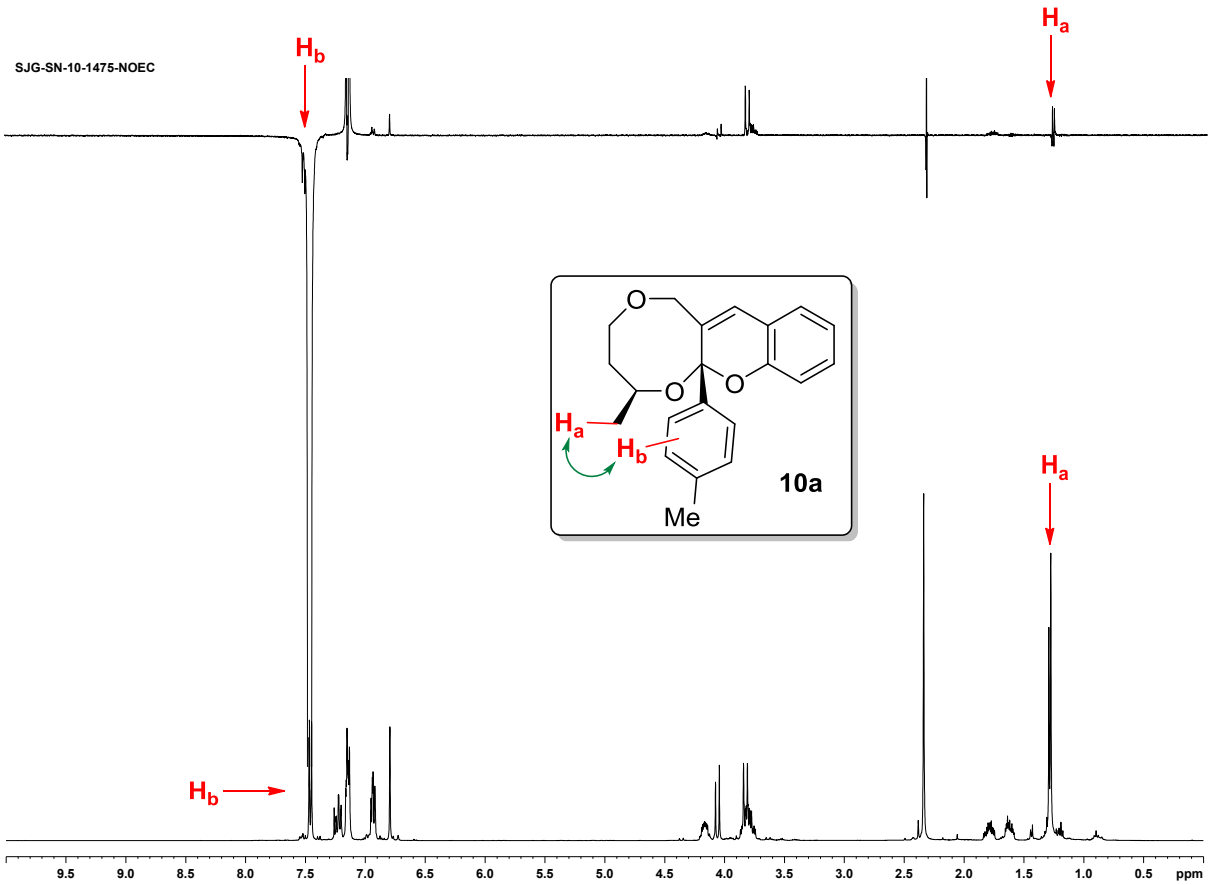
Ha
Hc
Hb Hb
Hd
Cd
Cb
Ca
Cc
Hb Hb Hc
Cc
Cd
Cb
Hd
Me
Ha
Ha
Ca
Me
10a
ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
20 40 60 80 100 120 140 160 180 200 220 240


SJG-SN-10-1475-HMBC
Ha
Hc
Hb Hb
Hd
Ce
Hb Hb Hc
Ce
Hd
Me
Ha
Ha
Me
10a
ppm
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
20 40 60 80 100 120 140 160 180 200 220 240

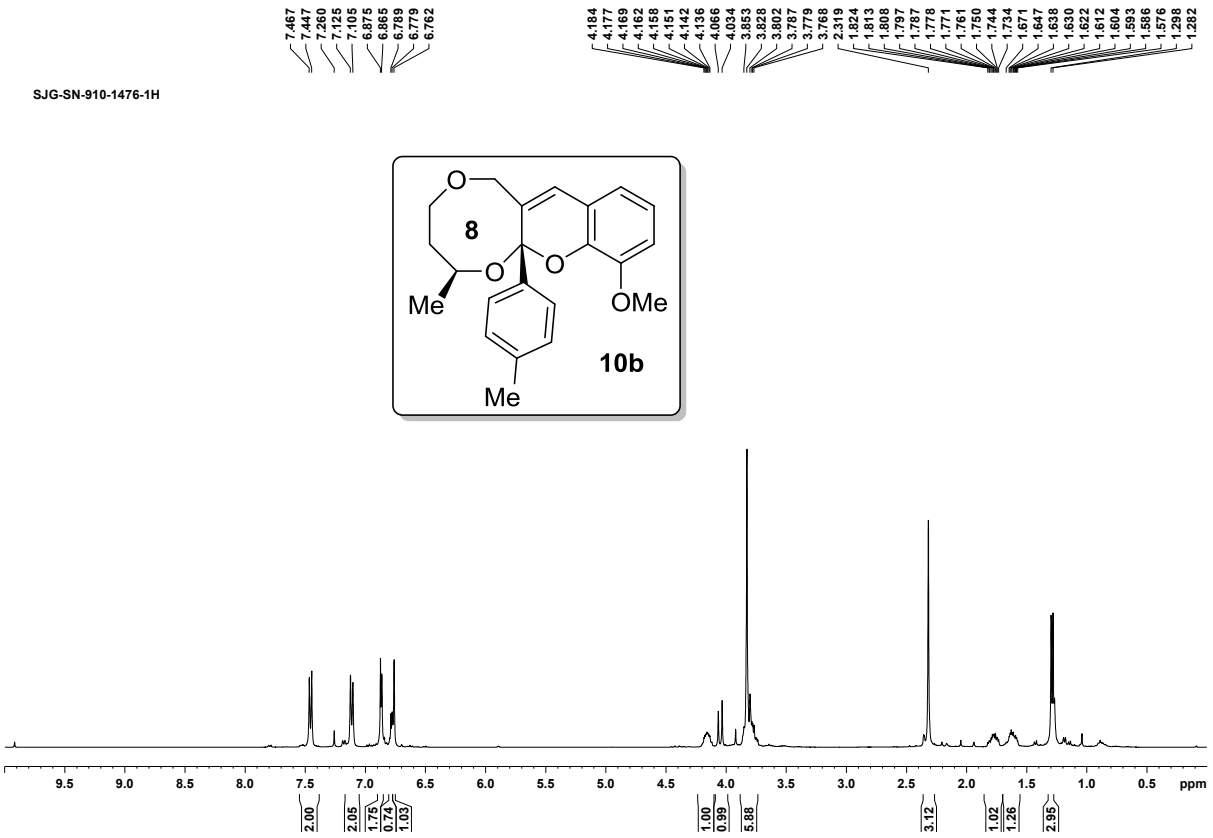


NOE enhancement-2%

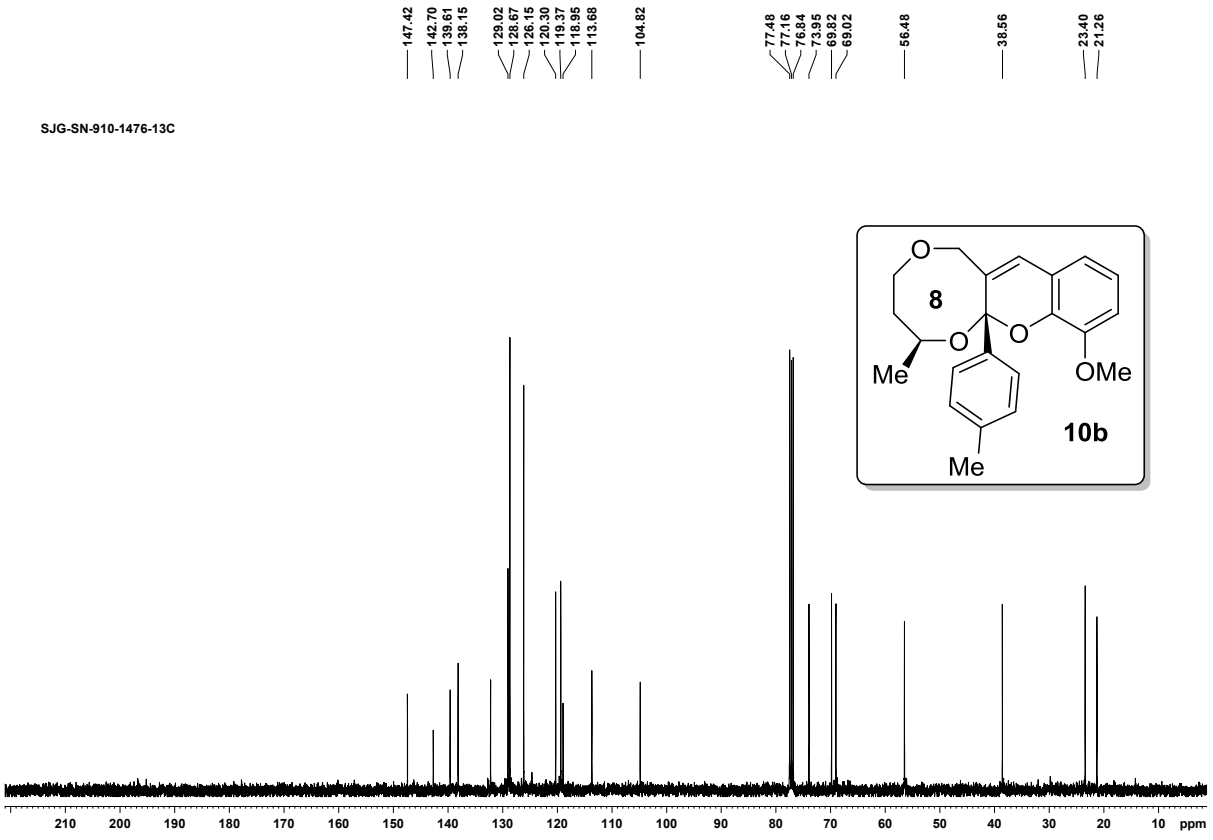


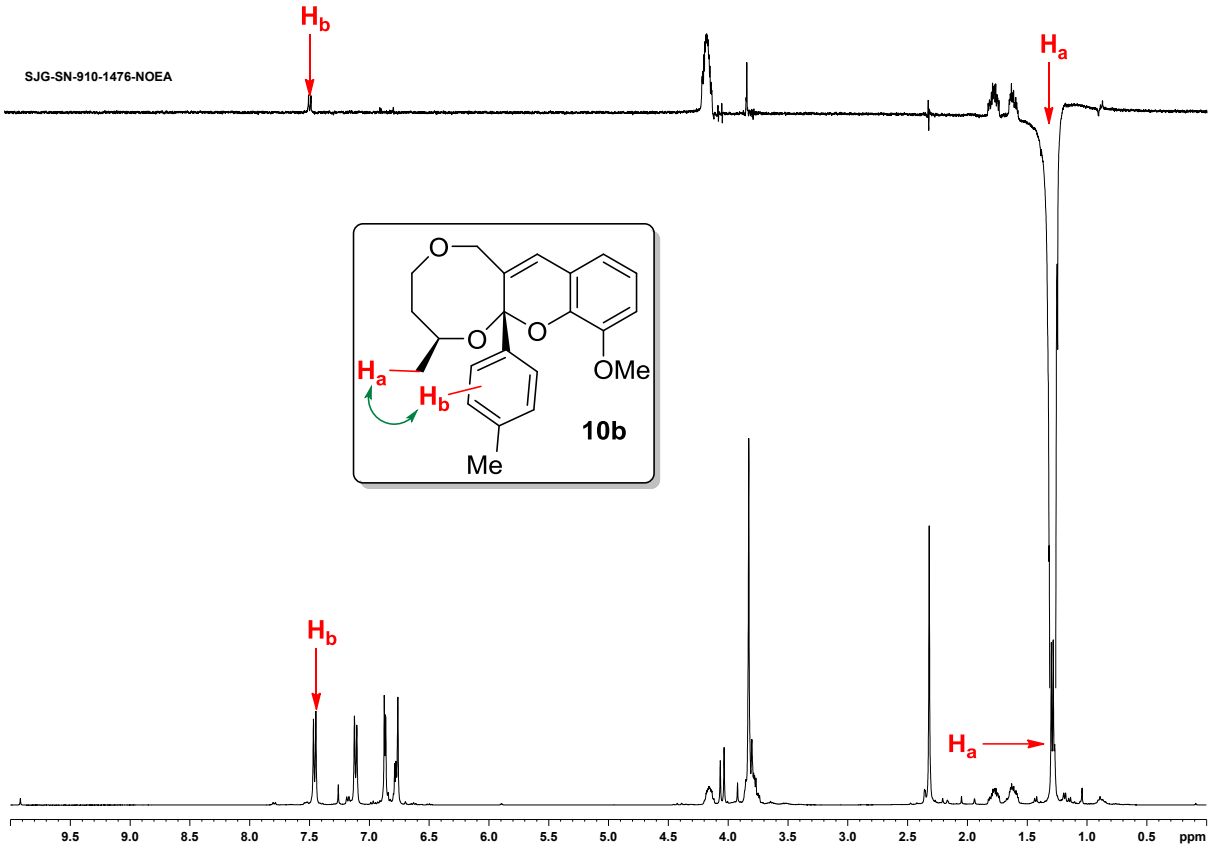
NOE enhancement-2%

SJG-SN-910-1476-1H



SJG-SN-910-1476-13C





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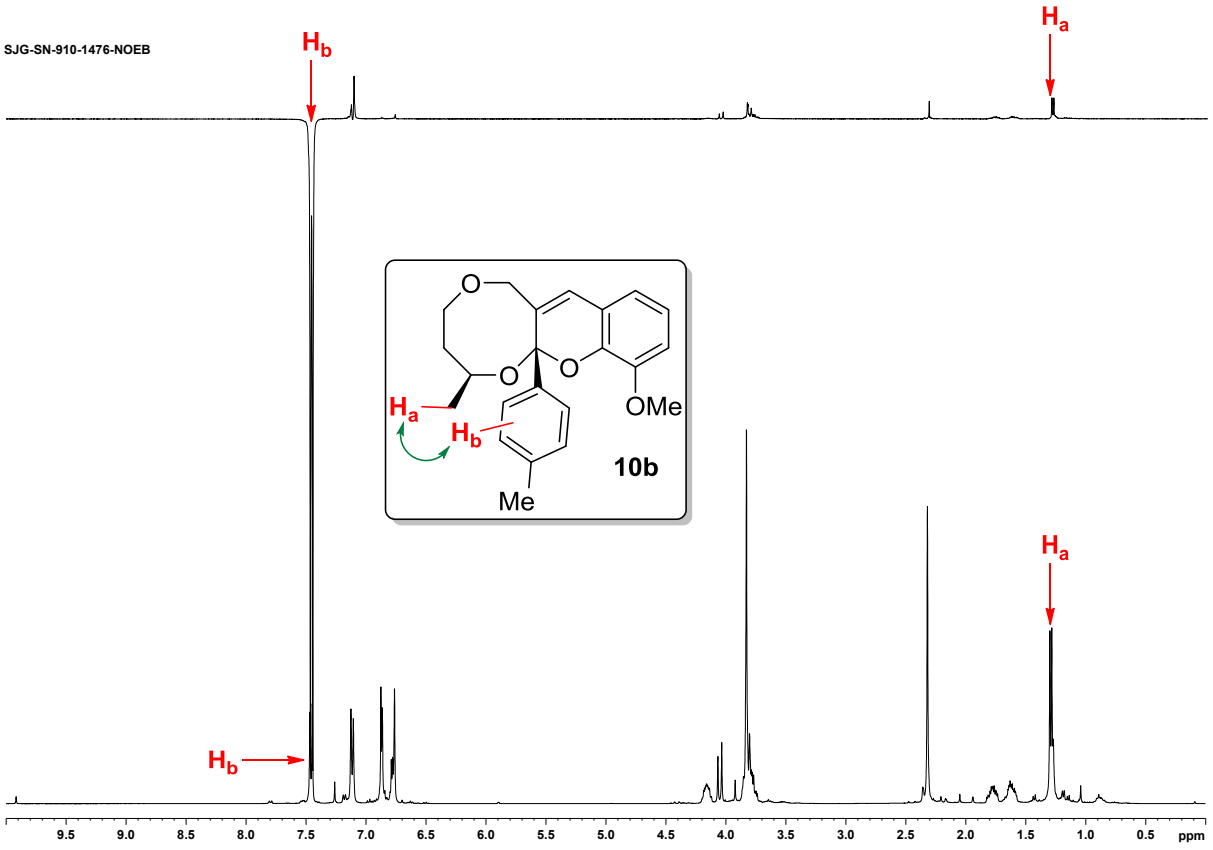

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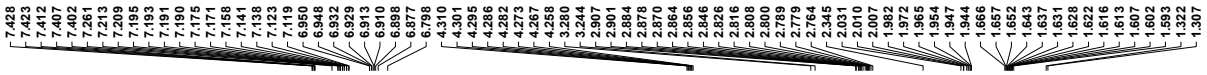
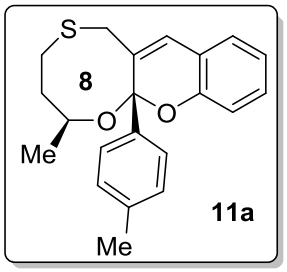
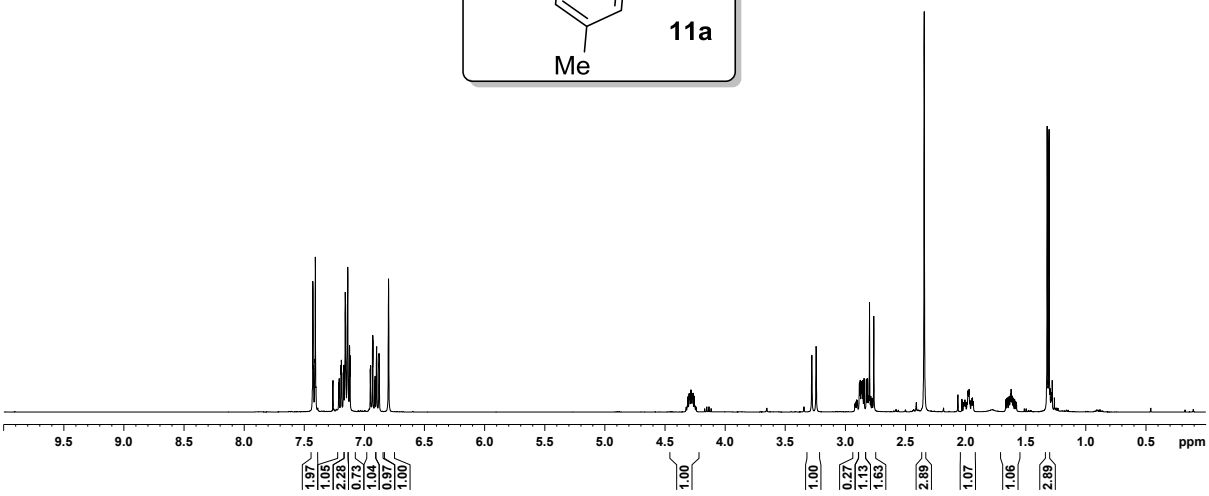
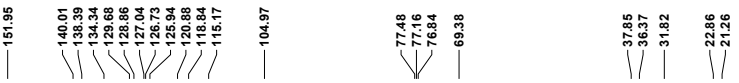


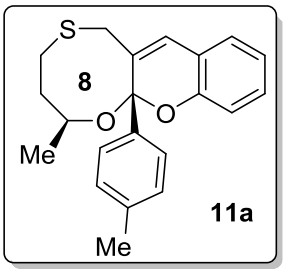
SJG-SN-10-1516-1H

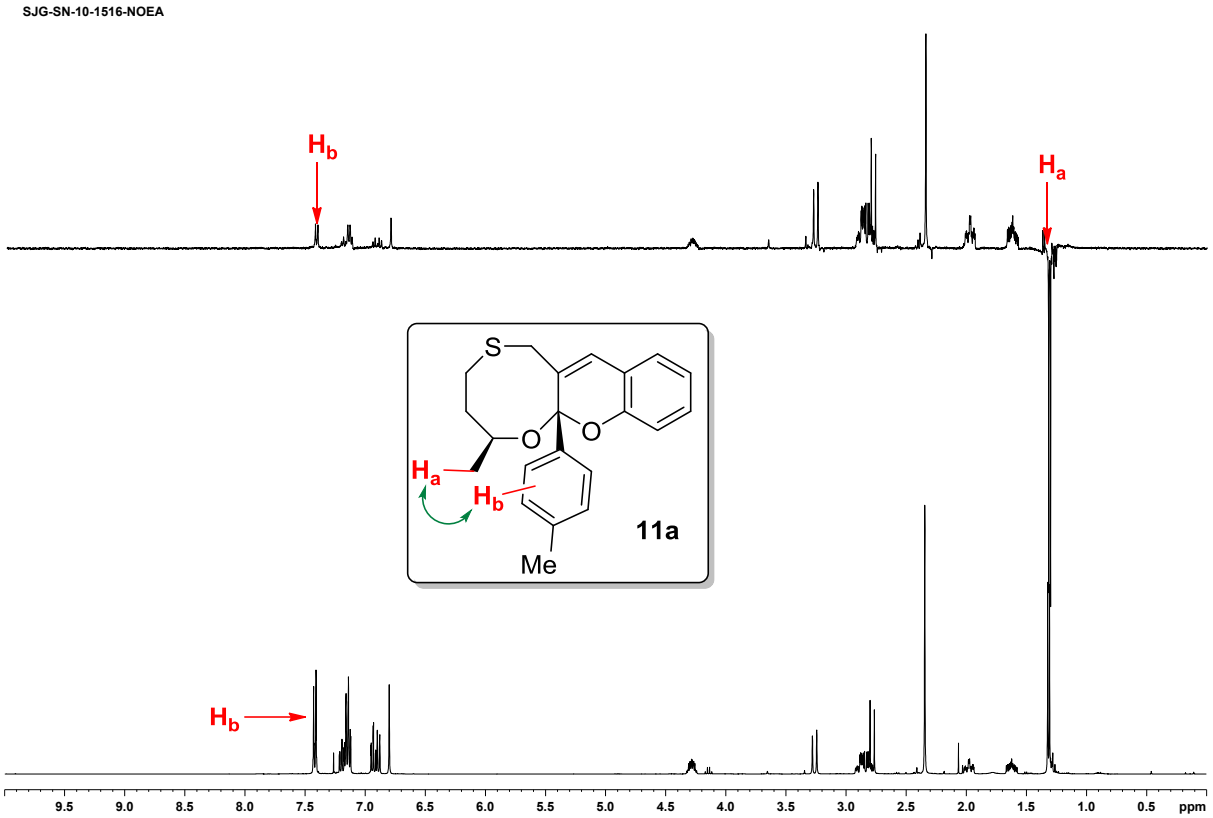






SJG-SN-10-1516-13C





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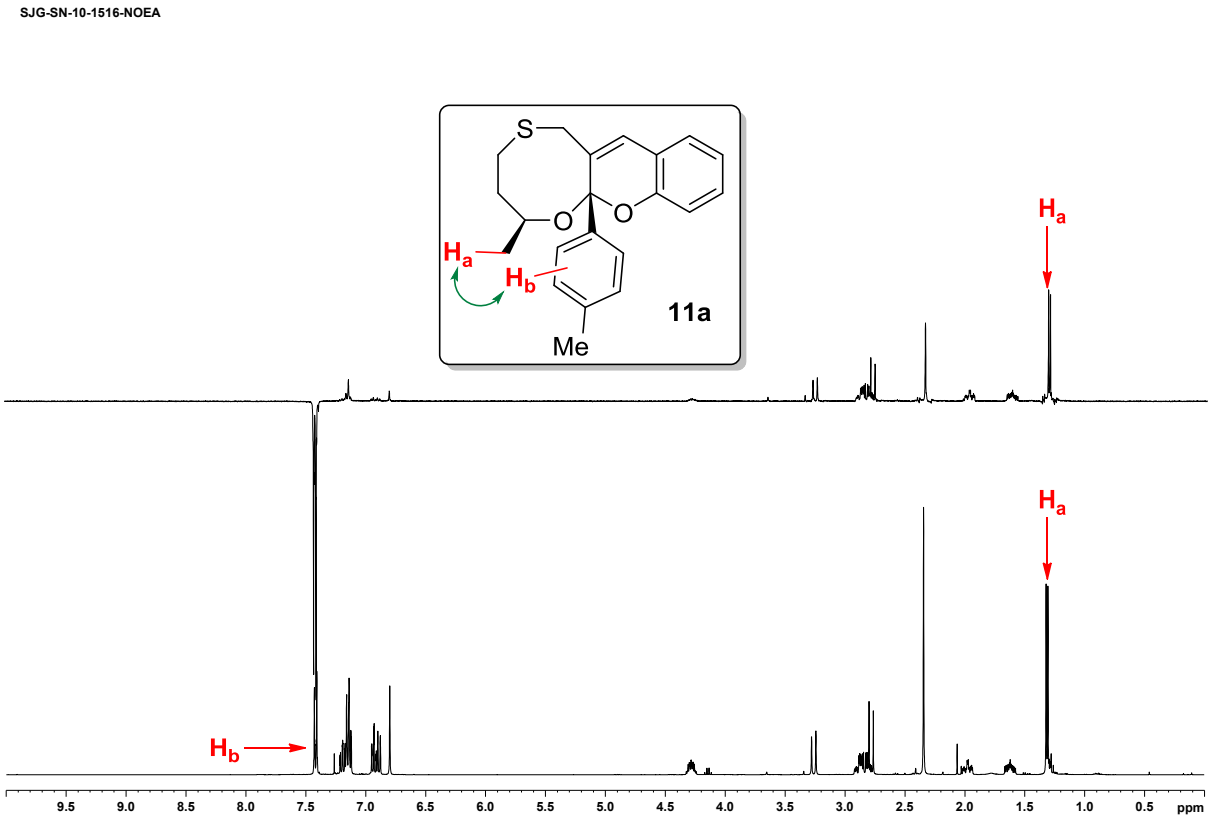
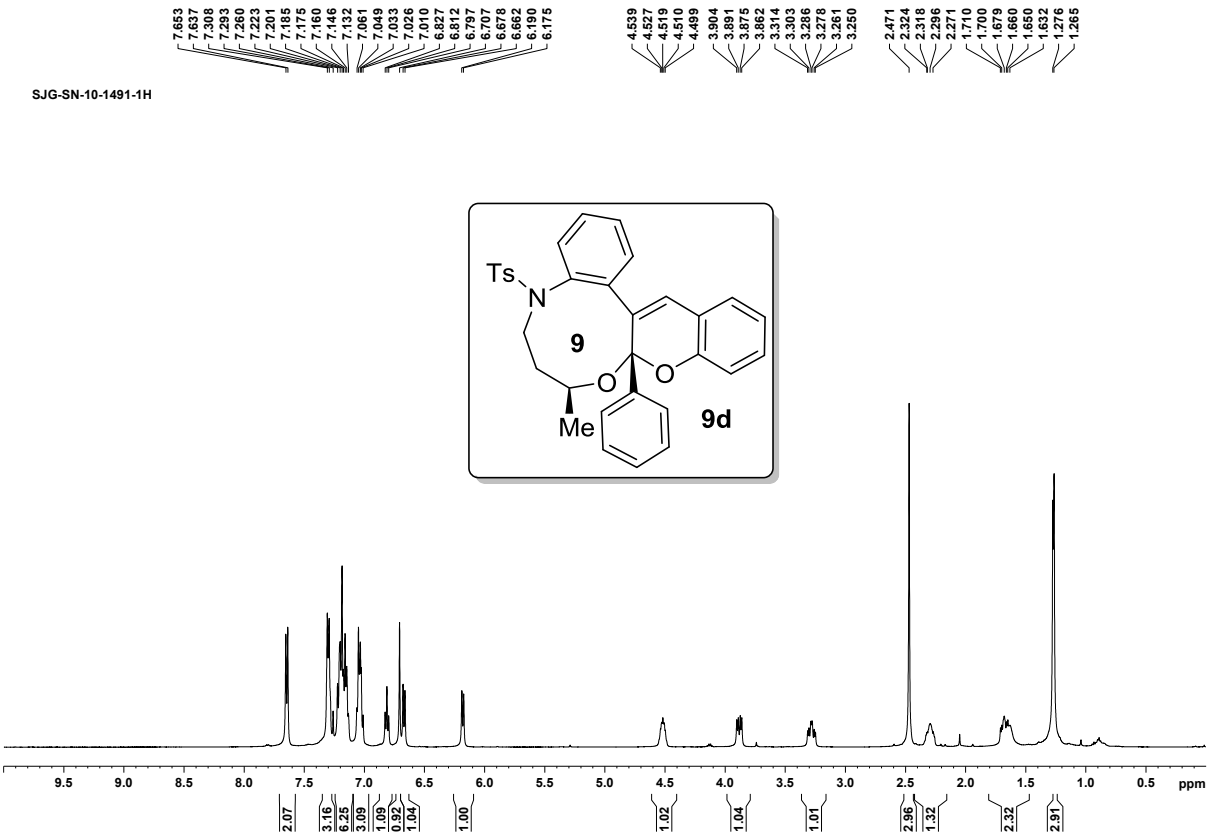


NOE enhancement-4%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7.049
7.033
7.026
7.010
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6.812
6.797
6.707
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6.662
6.190
6.175
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4.527
4.519
4.510
4.499
3.904
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3.261
3.250
2.471
2.324
2.318
2.296
2.271
1.710
1.700
1.679
1.660
1.650
1.632
1.276
1.265
SJG-SN-10-1491-1H
Ts
N
9
O
O
Me
9d
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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
2.07
3.16
6.25
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1.09
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1.04
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1.02
1.04
1.01
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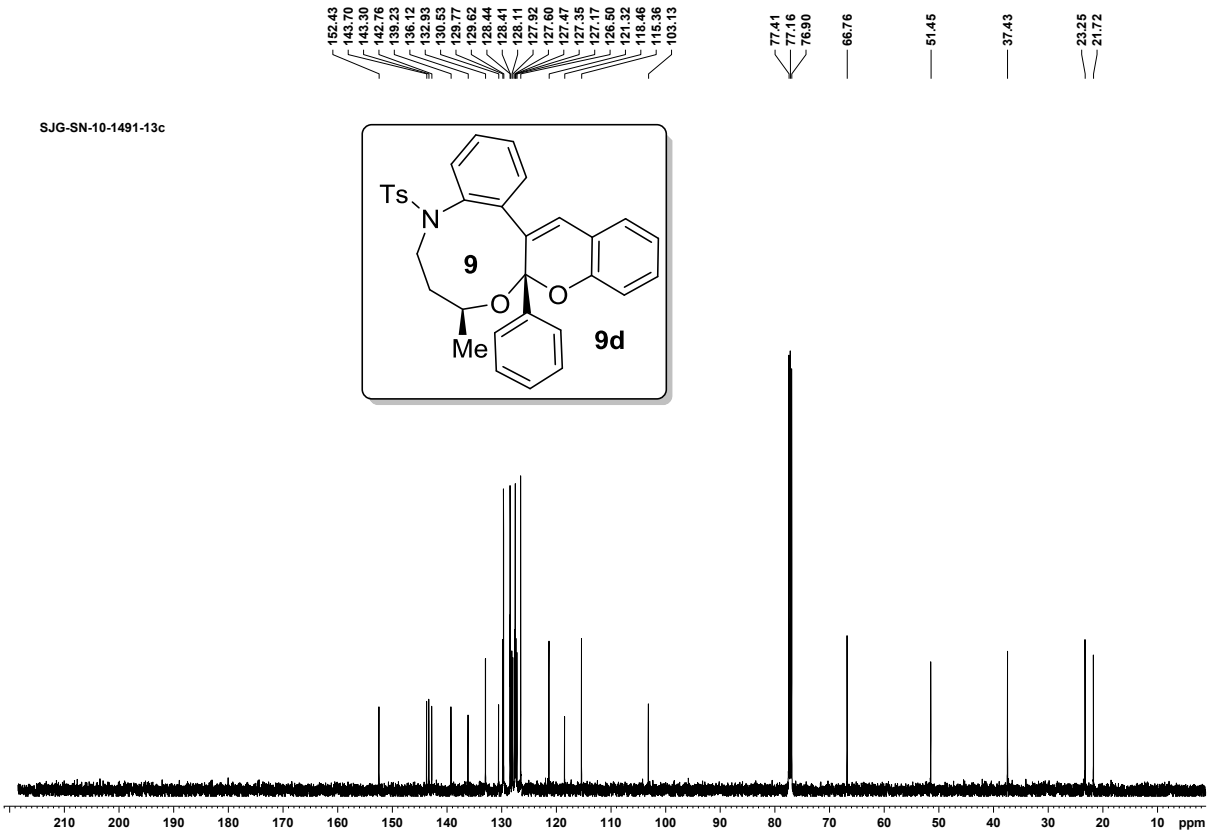
1.32
2.32
2.91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143.30
142.76
139.23
136.12
132.93
130.53
129.77
129.62
128.44
128.41
128.11
127.92
127.60
127.47
127.35
127.17
126.50
121.32
118.46
115.36
103.13
77.41
77.16
76.90
66.76
51.45
37.43
23.25
21.72
SJG-SN-10-1491-13c
Ts
N
9
O
O
Me
9d
210
200
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150
140
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120
110
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80
70
60
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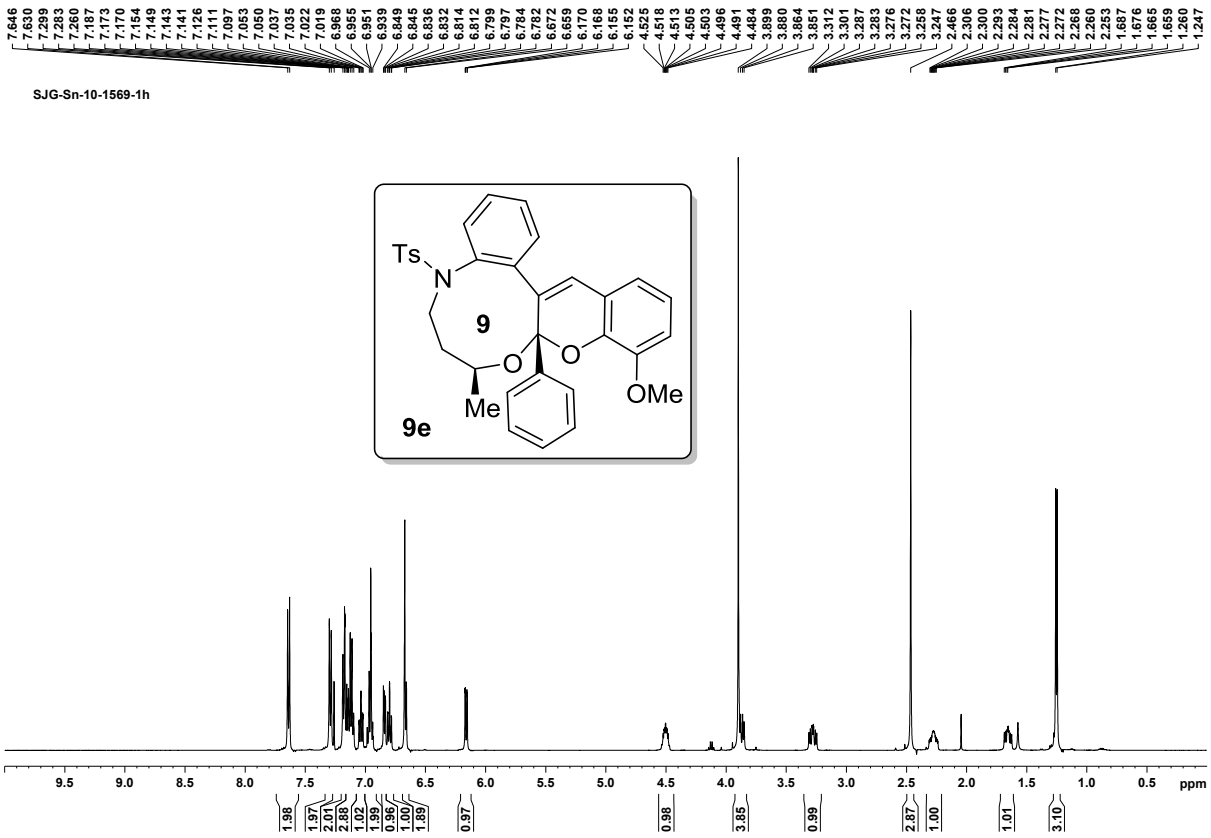
30
20
10
ppm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7.170
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7.149
7.143
7.141
7.126
7.111
7.097
7.053
7.050
7.037
7.035
7.022
7.019
6.968
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6.951
6.939
6.849
6.845
6.836
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6.152
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4.491
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3.899
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3.247
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2.300
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2.268
2.260
2.253
1.687
1.676
1.665
1.659
1.260
1.247
SJG-Sn-10-1569-1h
Ts
N
9
O
O
Me
OMe
9e
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9.0
8.5
8.0
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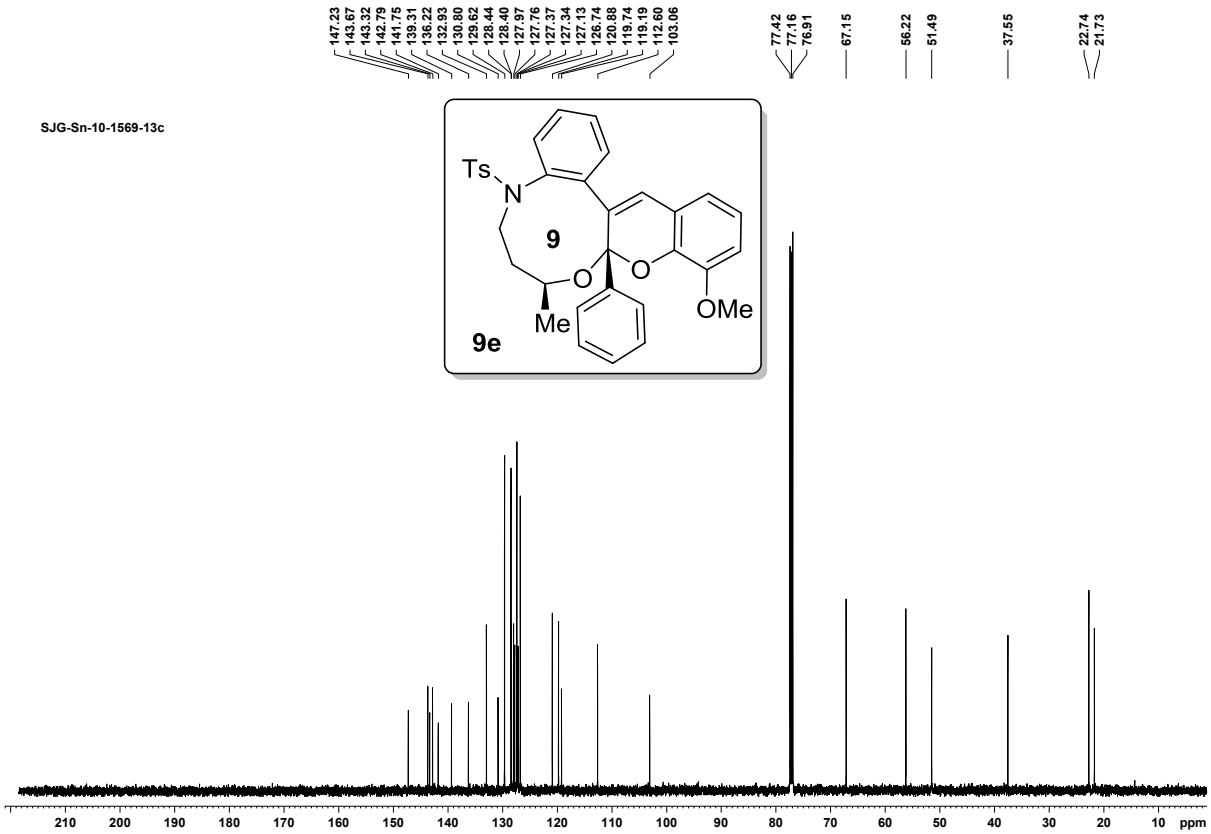
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.98
1.97
2.01
2.88
1.02
1.99
0.96
1.00
1.89
0.97
0.98
3.85
0.99
2.87
1.00
1.01
3.10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143.32
142.79
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139.31
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132.93
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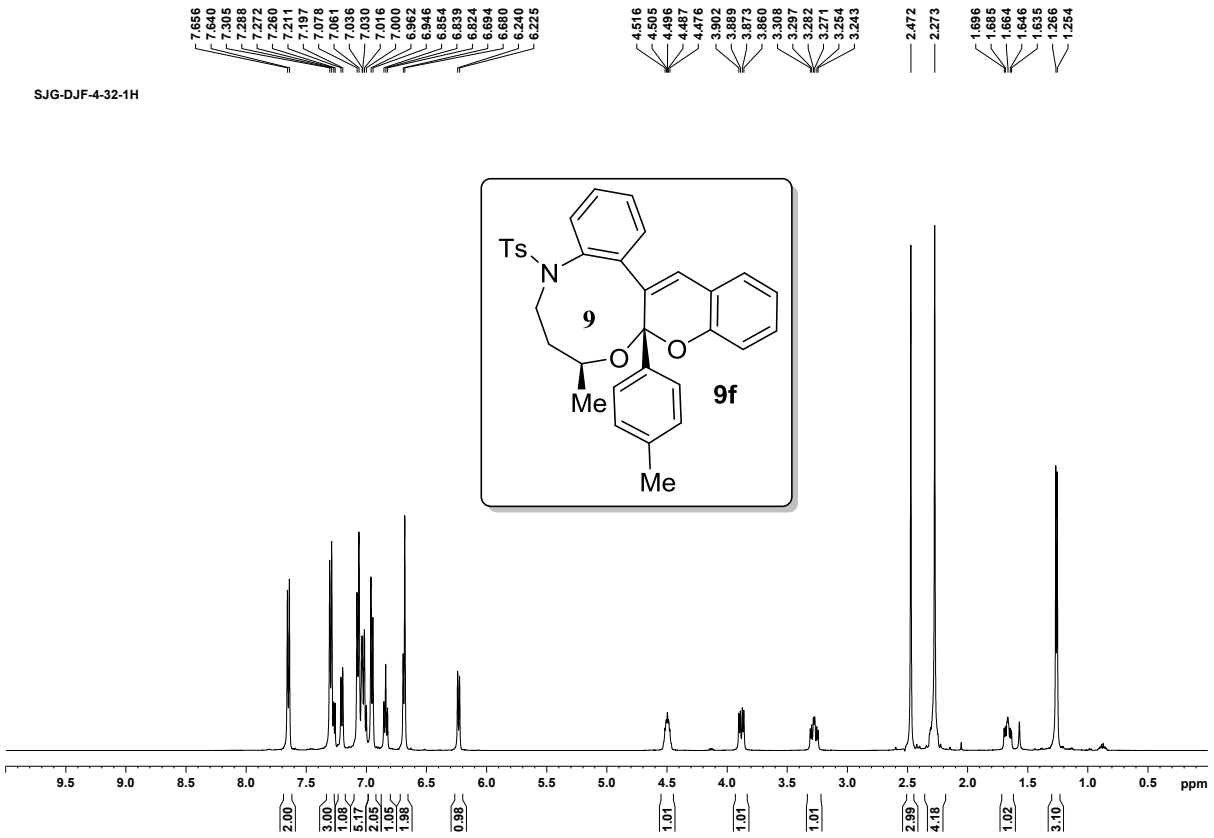
129.62
128.44
128.40
127.97
127.76
127.37
127.34
127.13
126.74
120.88
119.74
119.19
112.60
103.06
77.42
77.16
76.91
67.15
56.22
51.49
37.55
22.74
21.73
SJG-Sn-10-1569-13c
Ts
N
9
O
O
Me
OMe
9e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.640
7.305
7.288
7.272
7.260
7.211
7.197
7.078
7.061
7.036
7.030
7.016
7.000
6.962
6.946
6.854
6.839
6.824
6.694
6.680
6.240
6.225
4.516
4.505
4.496
4.487
4.476
3.902
3.889
3.873
3.860
3.308
3.297
3.282
3.271
3.254
3.243
2.472
2.273
1.696
1.685
1.664
1.646
1.635
1.266
1.254
SJG-DJF-4-32-1H
Ts
N
9
O
O
Me
9f
Me
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
2.00
3.00
1.08
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1.05
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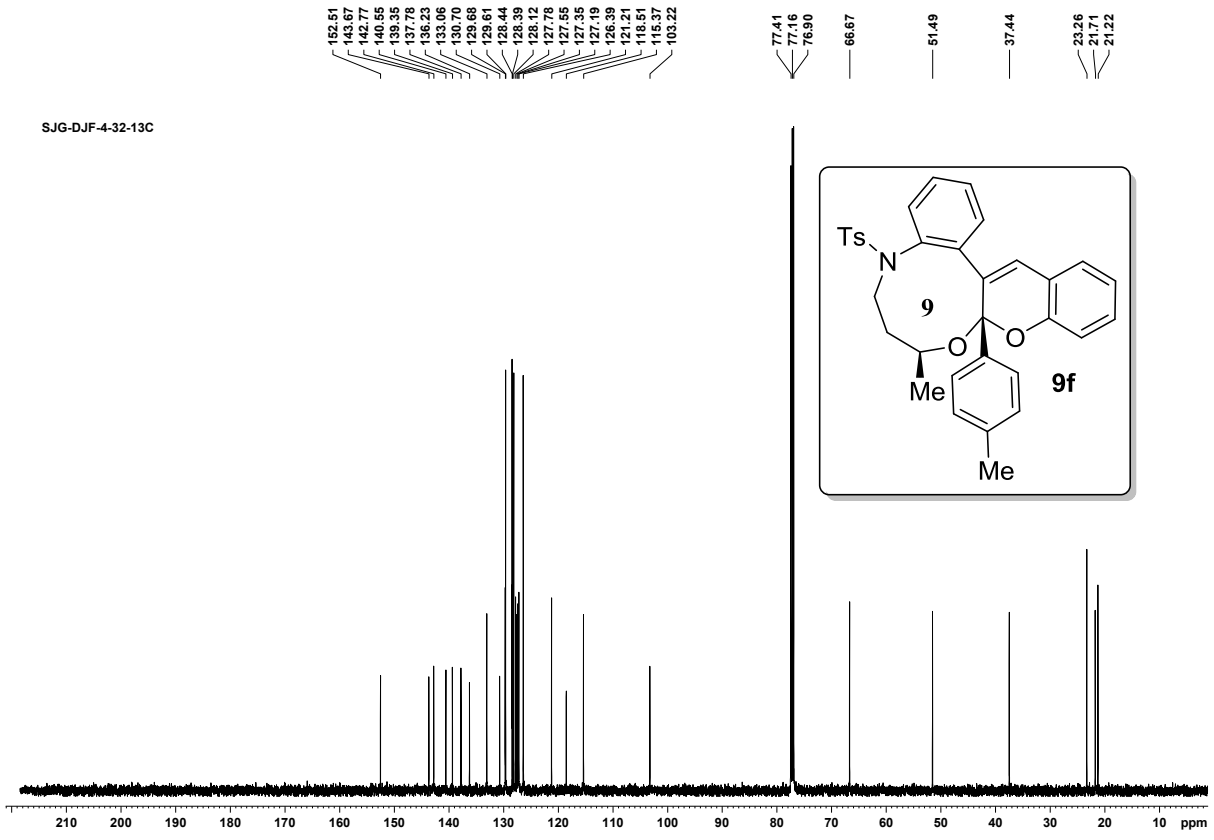
0.98
1.01
1.01
1.01
2.99
4.18
1.02
3.10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133.06
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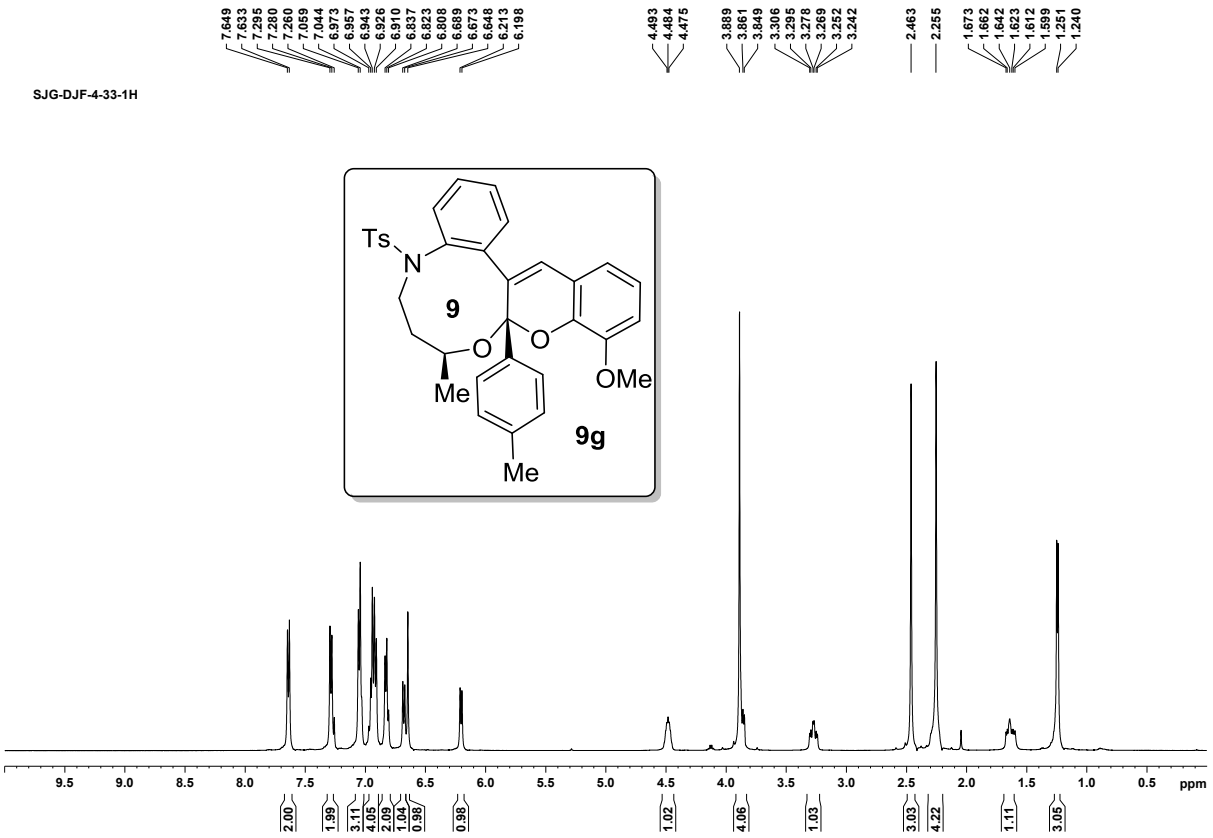
128.39
128.12
127.78
127.55
127.35
127.19
126.39
121.21
118.51
115.37
103.22
77.41
77.16
76.90
66.67
51.49
37.44
23.26
21.71
21.22
SJG-DJF-4-32-13C
Ts
N
9
O
O
Me
9f
Me
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.295
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6.973
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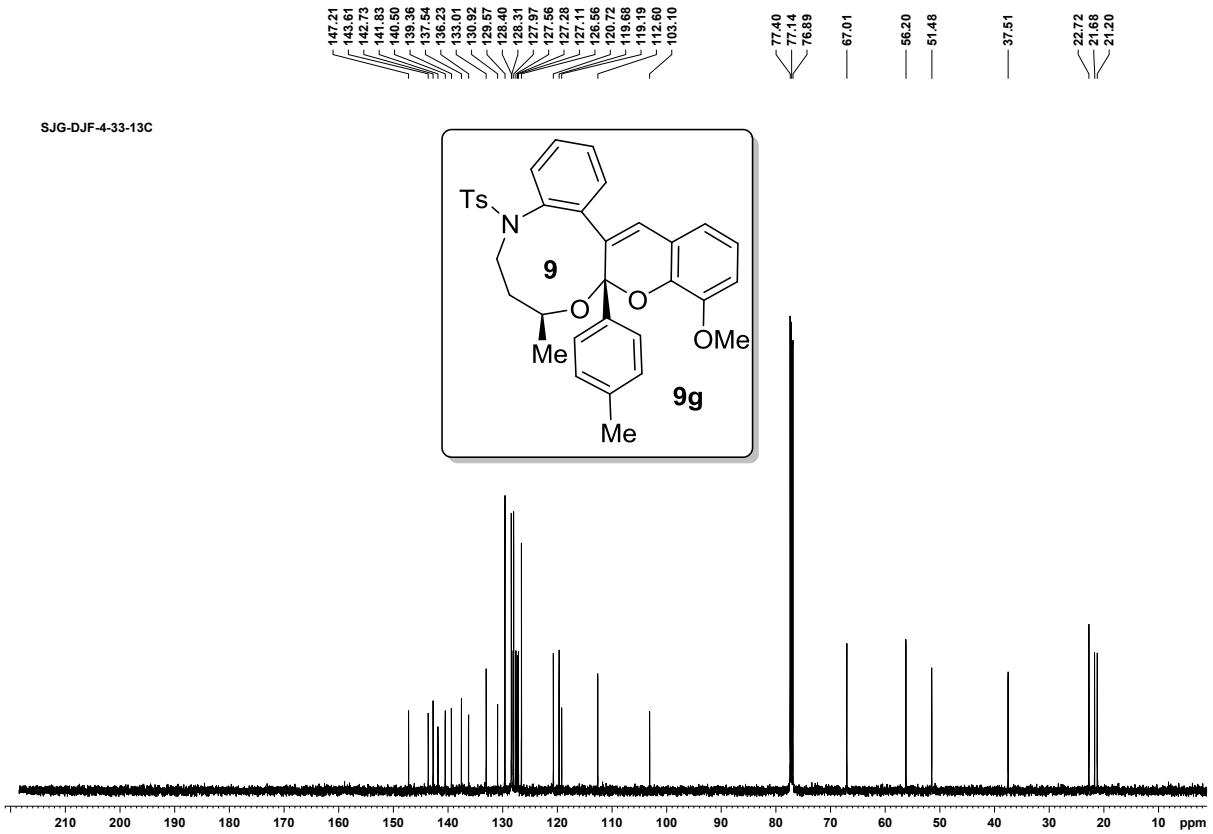
6.926
6.910
6.837
6.823
6.808
6.689
6.673
6.648
6.213
6.198
4.493
4.484
4.475
3.889
3.861
3.849
3.306
3.295
3.278
3.269
3.252
3.242
2.463
2.255
1.673
1.662
1.642
1.623
1.612
1.599
1.251
1.240
SJG-DJF-4-33-1H
Ts
N
9
O
O
Me
OMe
9g
Me
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.99
3.11
4.05
2.09
1.04
0.98
0.98
1.02
4.06
1.03
3.03
4.22
1.11
3.05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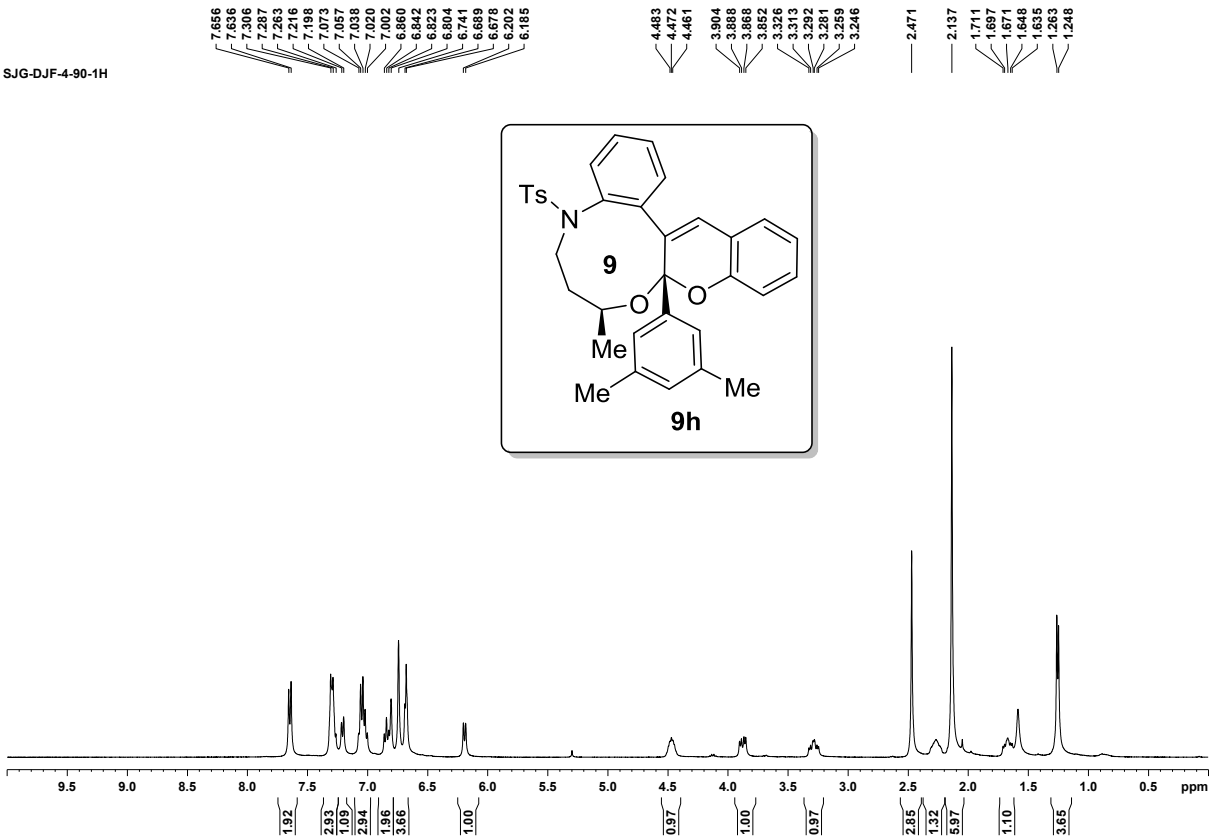
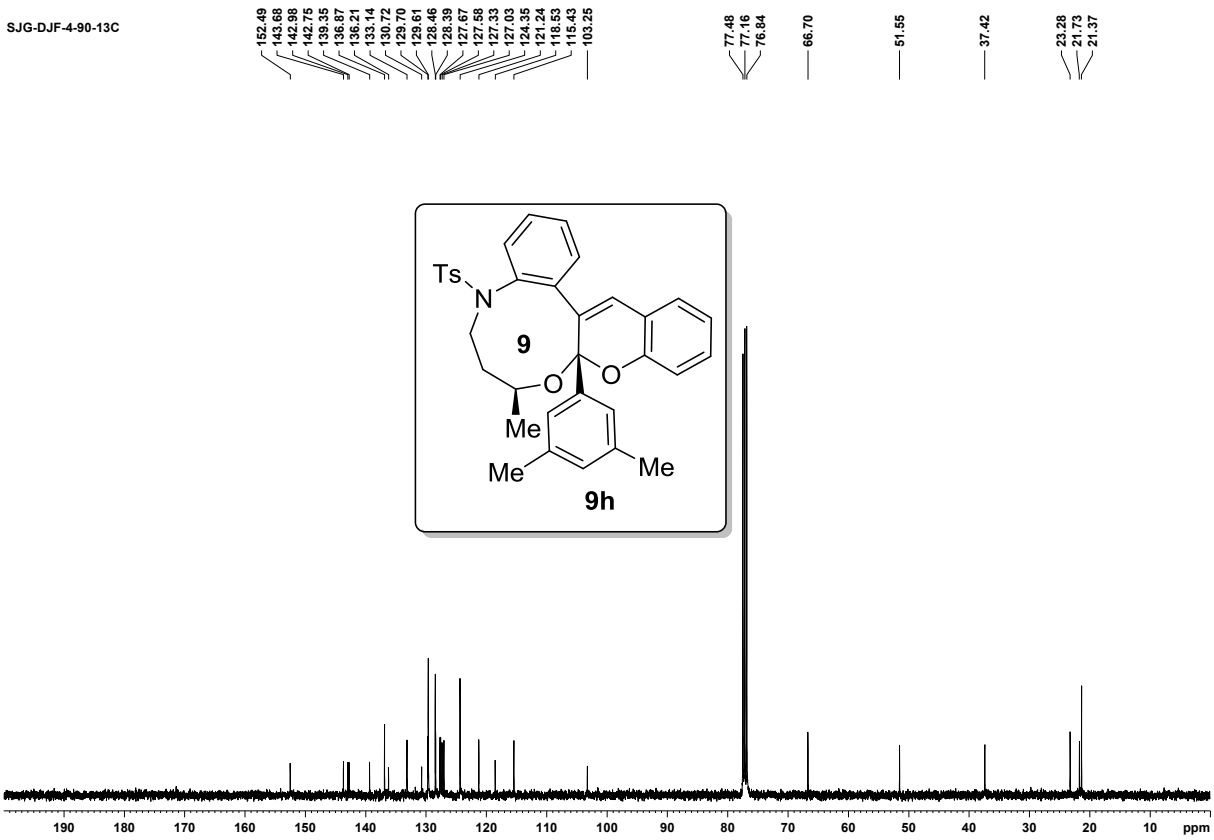
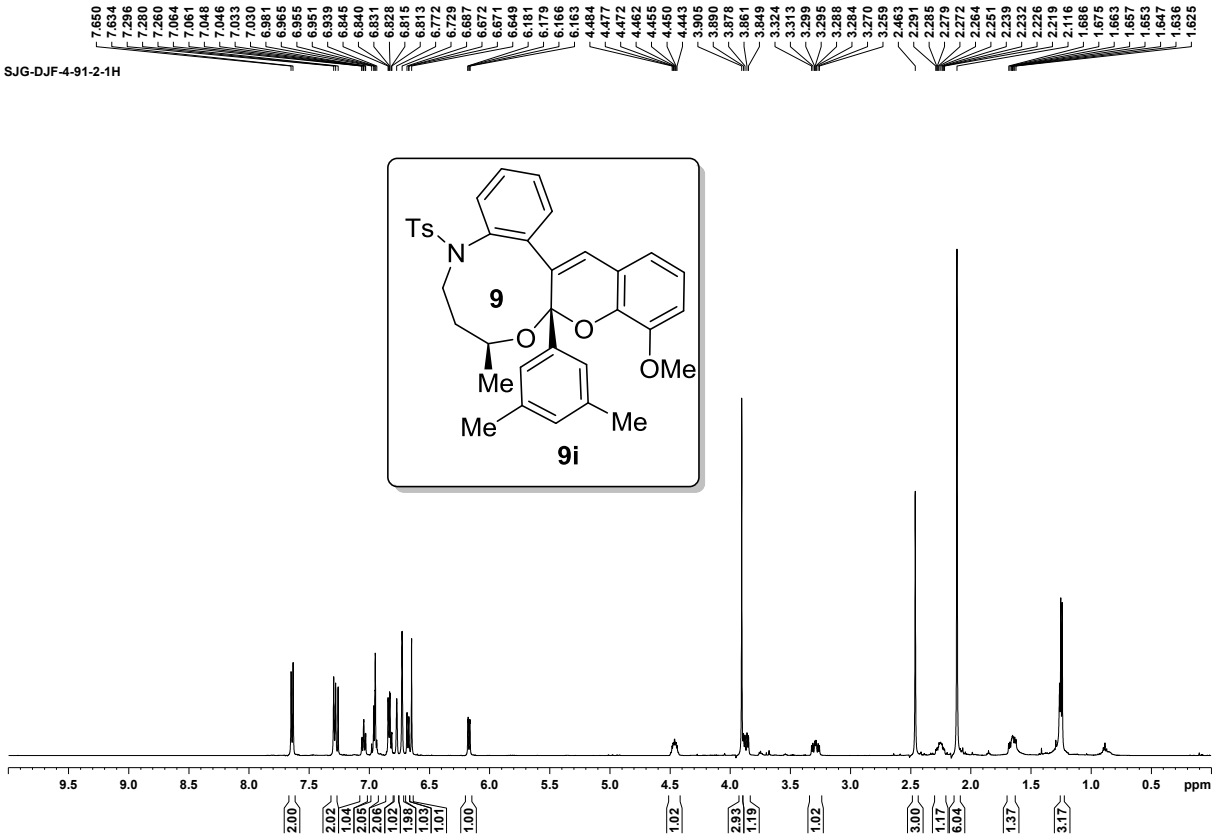
141.83
140.50
139.36
137.54
136.23
133.01
130.92
129.57
128.40
128.31
127.97
127.56
127.28
127.11
126.56
120.72
119.68
119.19
112.60
103.10
77.40
77.14
76.89
67.01
56.20
51.48
37.51
22.72
21.68
21.20
SJG-DJF-4-33-13C
Ts
N
9
O
O
Me
OMe
9g
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

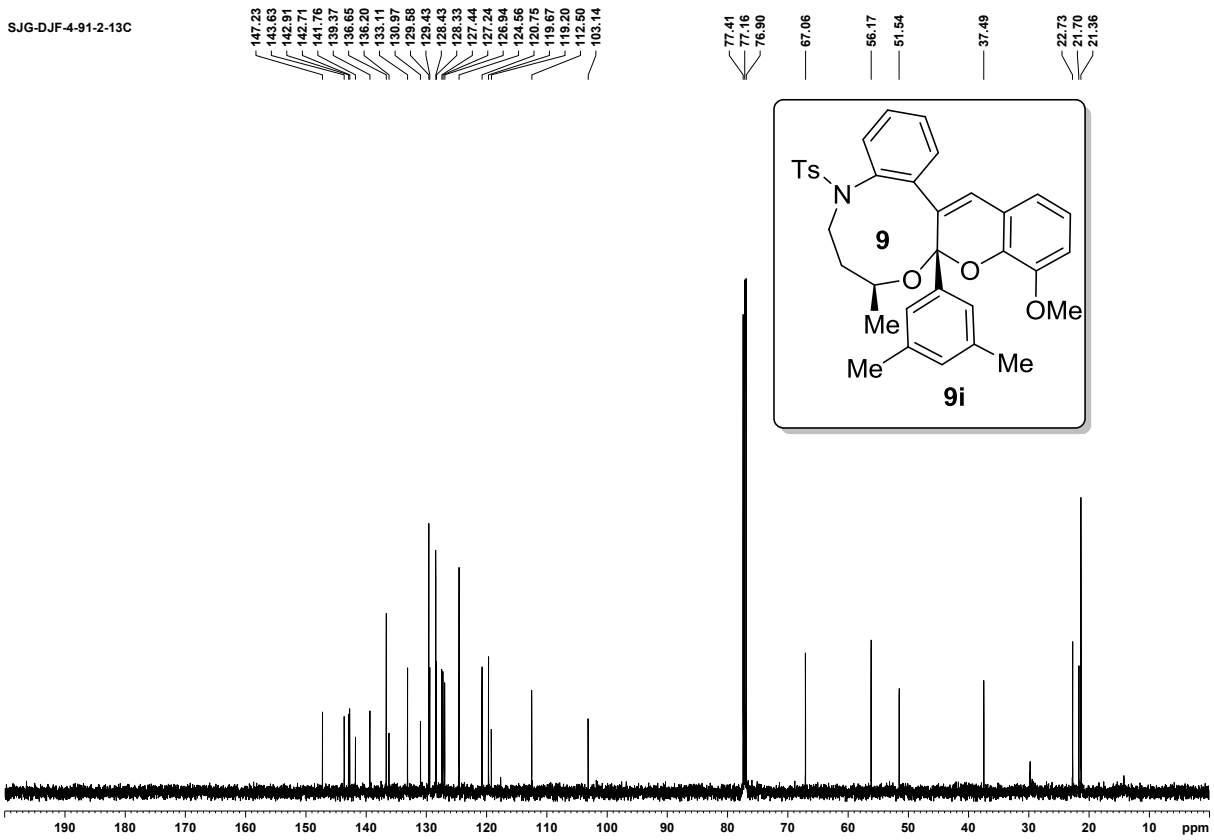
SJG-DJF-4-90-1H

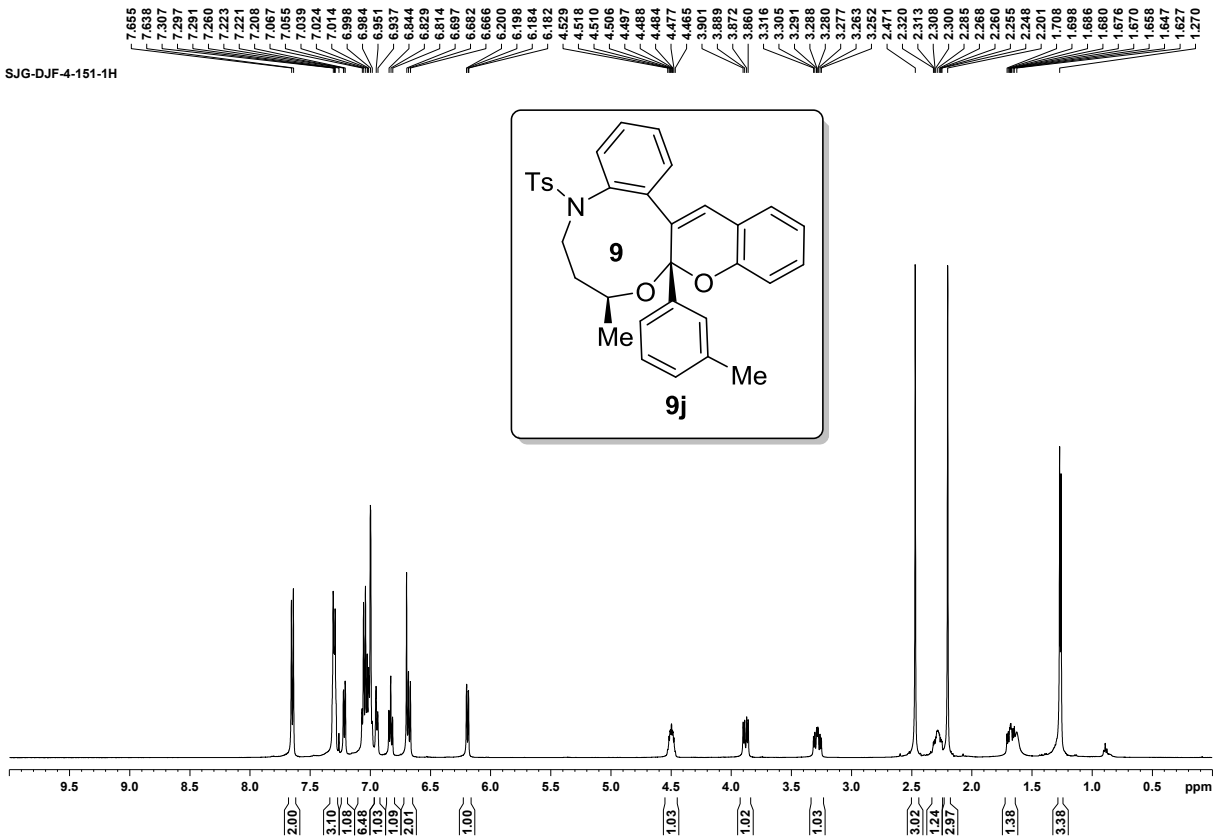


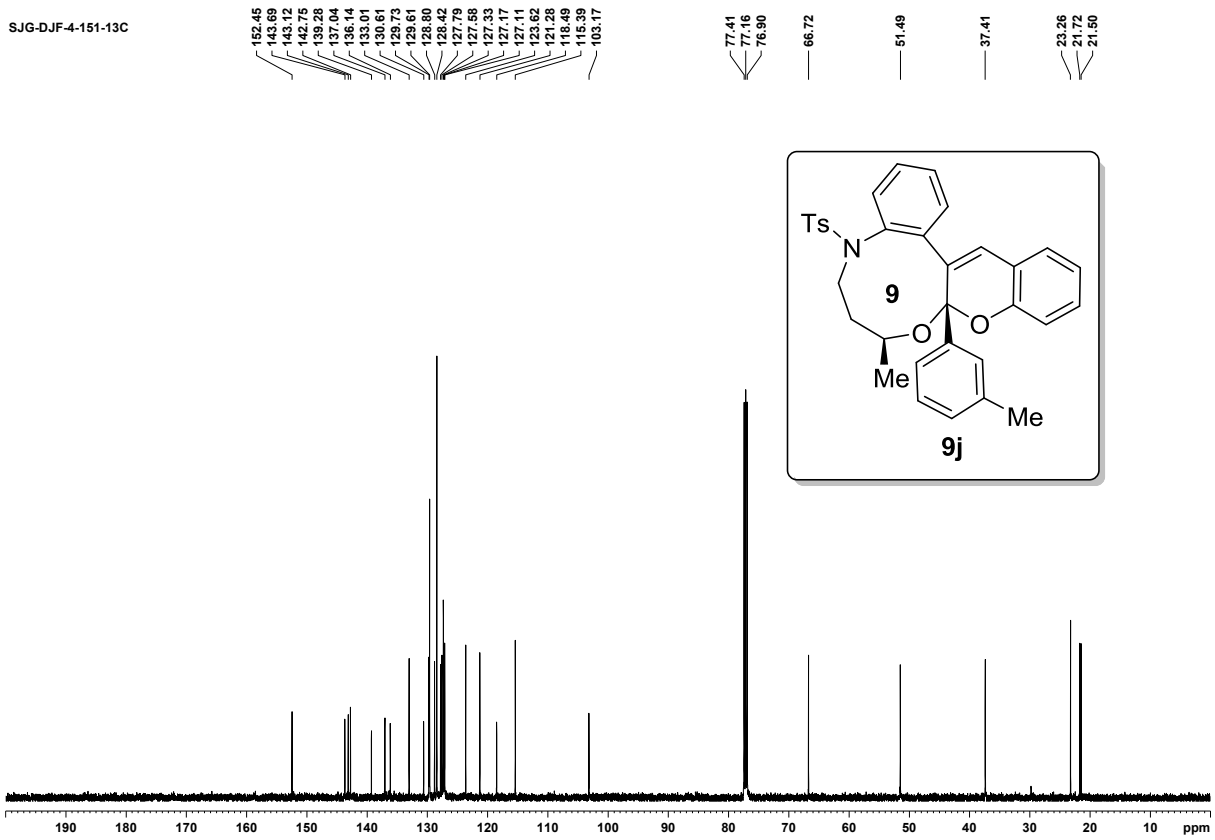
SJG-DJF-4-90-13C

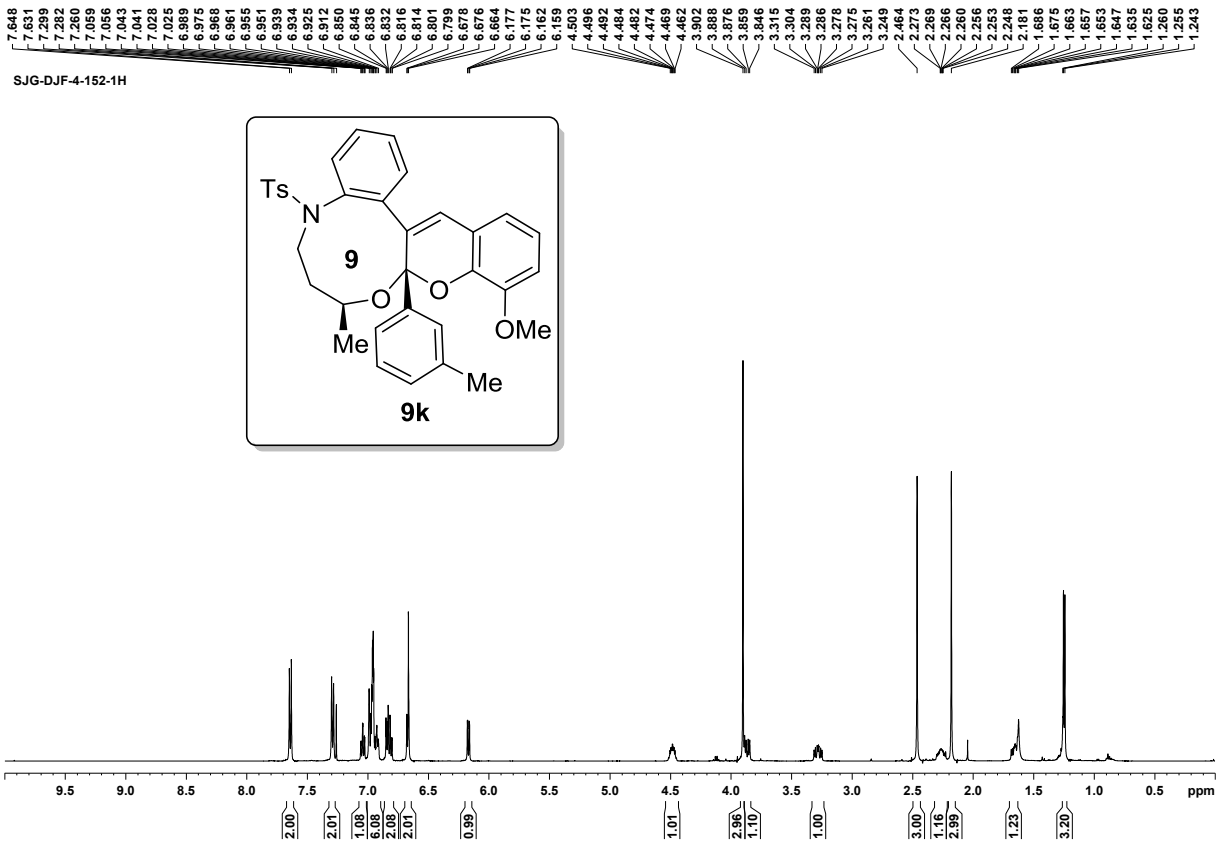


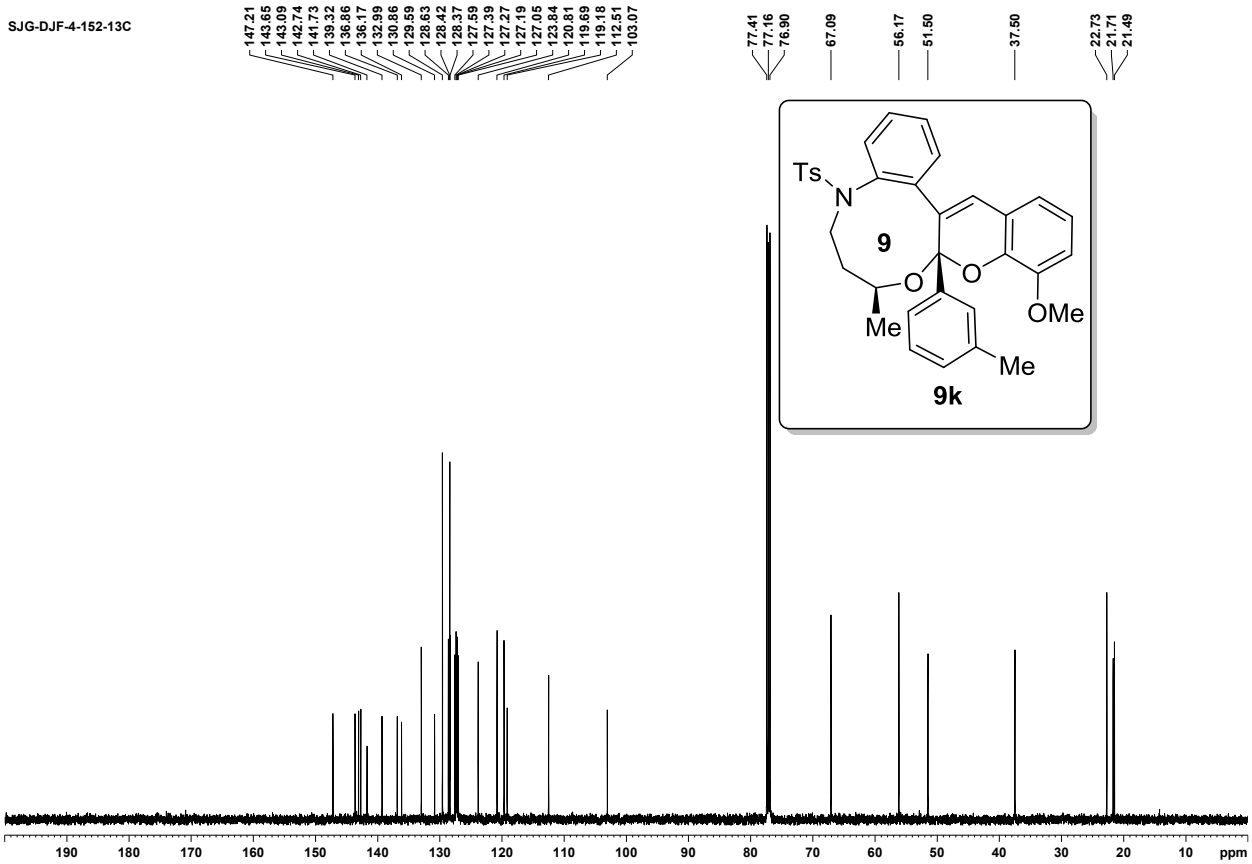

SJG-DJF-4-91-2-1H
7.650 7.634 7.296 7.280 7.260 7.064 7.061 7.048 7.046 7.033 7.030 6.981 6.965 6.955 6.951 6.939 6.845 6.840 6.831 6.828 6.815 6.813 6.772 6.729 6.687 6.672 6.671 6.649 6.181 6.179 6.166 6.163 4.484 4.477 4.472 4.462 4.455 4.450 4.443 3.905 3.890 3.878 3.861 3.849 3.324 3.313 3.299 3.295 3.288 3.284 3.270 3.259 2.463 2.291 2.285 2.279 2.272 2.264 2.251 2.239 2.232 2.226 2.219 2.116 1.686 1.675 1.663 1.657 1.653 1.647 1.636 1.625
Ts
N
9
O
O
OMe
Me
Me
Me
9i
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
2.00 2.02 1.04 2.05 2.06 1.02 1.98 1.03 1.01 1.00 1.02 2.93 1.19 1.02 3.00 1.17 6.04 1.37 3.17

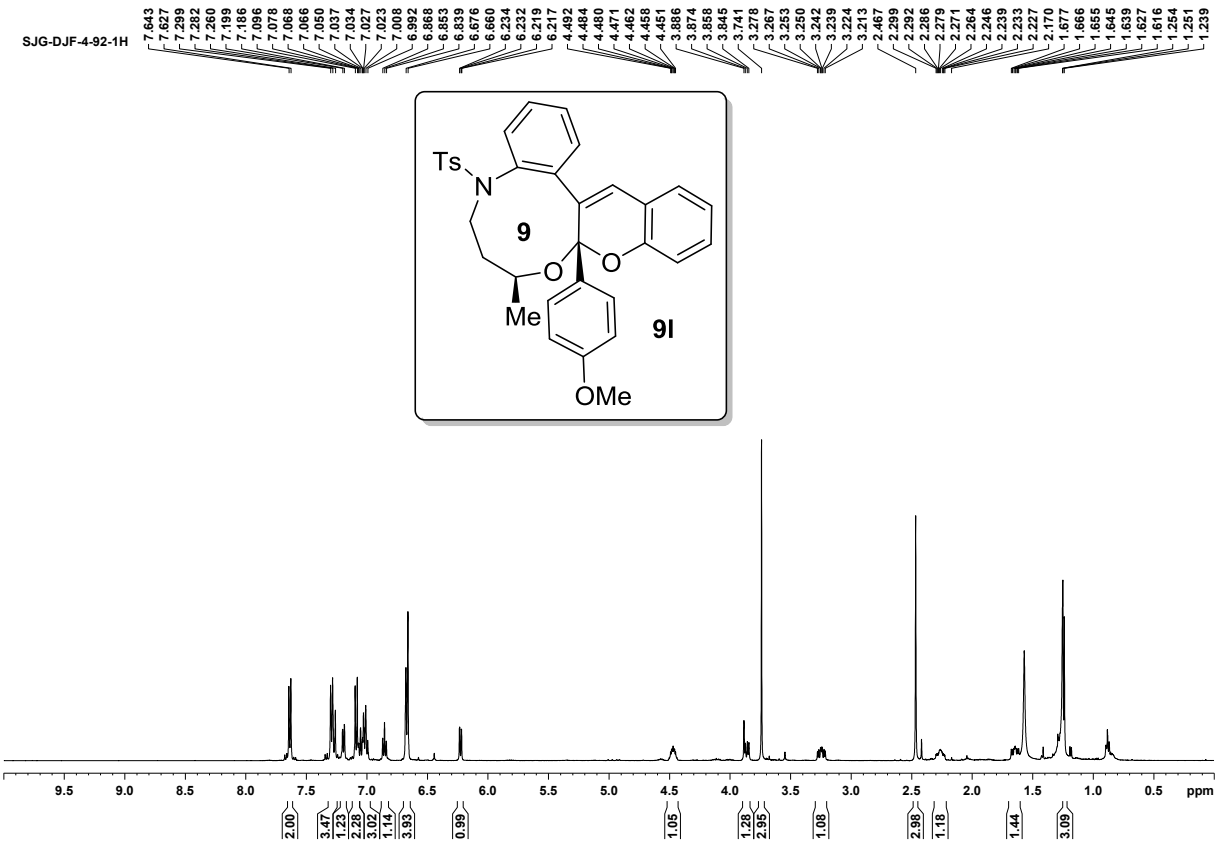

SJG-DJF-4-91-2-13C
147.23 143.63 142.91 142.71 141.76 139.37 136.65 136.20 133.11 130.97 129.58 129.43 128.43 128.33 127.44 127.24 126.94 124.56 120.75 119.67 119.20 112.50 103.14
77.41 77.16 76.90 67.06 56.17 51.54 37.49 22.73 21.70 21.36
Ts
N
9
O
O
OMe
Me
Me
Me
9i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

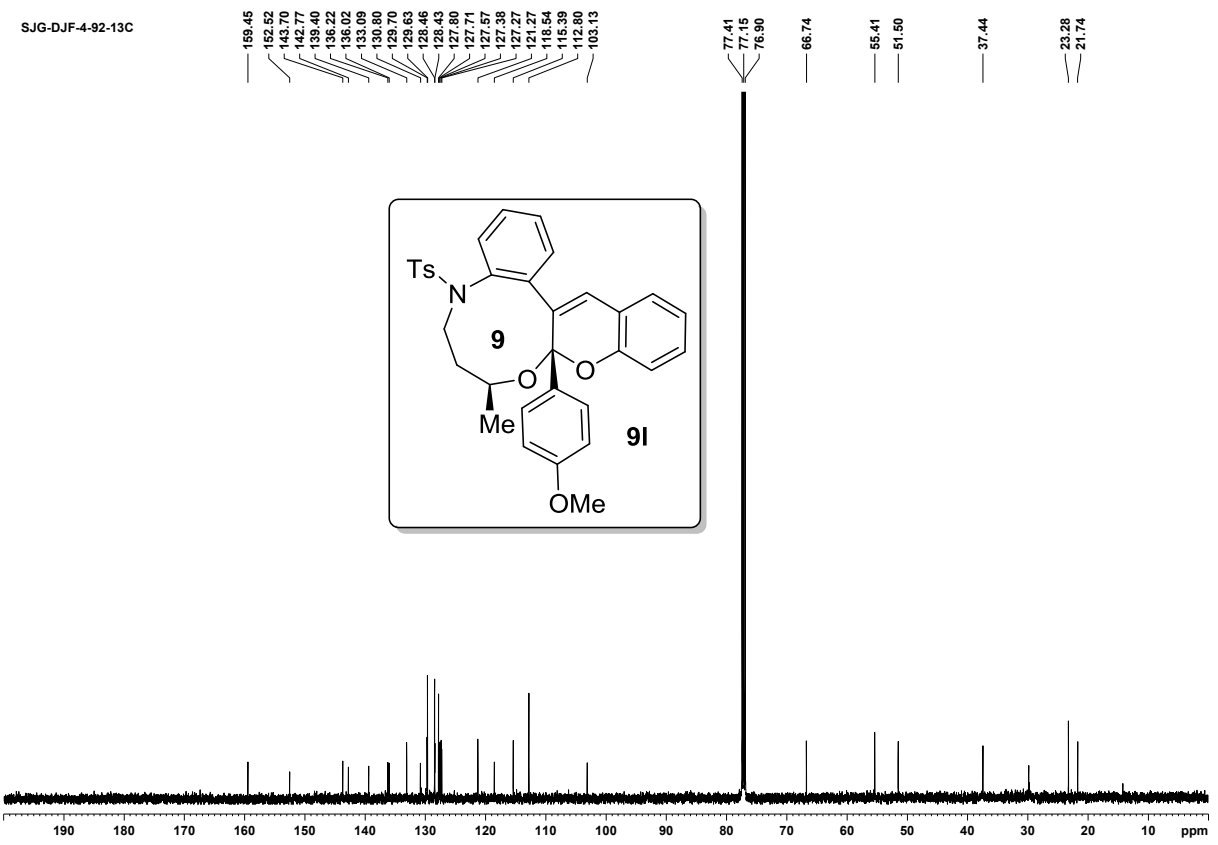

SJG-DJF-4-151-1H
7.655 7.638 7.307 7.297 7.291 7.260 7.223 7.221 7.208 7.067 7.055 7.039 7.024 7.014 6.998 6.984 6.951 6.937 6.844 6.829 6.814 6.697 6.682 6.666 6.200 6.198 6.184 6.182 4.529 4.518 4.510 4.506 4.497 4.488 4.484 4.477 4.465 3.901 3.889 3.872 3.860 3.316 3.305 3.291 3.288 3.280 3.277 3.263 3.252 2.471 2.320 2.313 2.308 2.300 2.285 2.268 2.260 2.255 2.248 2.201 1.708 1.698 1.686 1.680 1.676 1.670 1.658 1.647 1.627 1.270
Ts
N
9
O
O
Me
Me
9j
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
2.00 3.10 1.08 6.48 1.03 1.09 2.01 1.00 1.03 1.02 1.03 3.02 1.24 2.97 1.38 3.38


SJG-DJF-4-151-13C
152.45 143.69 143.12 142.75 139.28 137.04 136.14 133.01 130.61 129.73 129.61 128.80 128.42 127.79 127.58 127.33 127.17 127.11 123.62 121.28 118.49 115.39 103.17
77.41 77.16 76.90 66.72 51.49 37.41 23.26 21.72 21.50
Ts
N
9
O
O
Me
Me
9j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

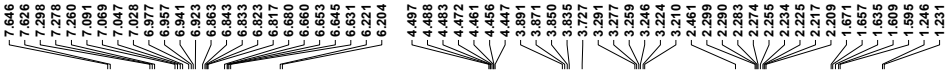

SJG-DJF-4-152-1H
Ts
N
9
O
O
Me
OMe
Me
9k
ppm

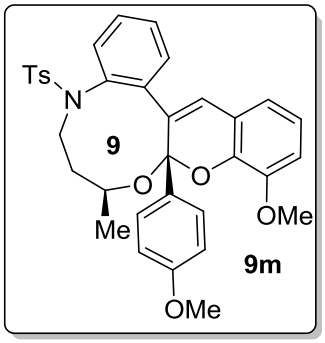

SJG-DJF-4-152-13C
Ts
N
9
O
O
Me
OMe
Me
9k
ppm

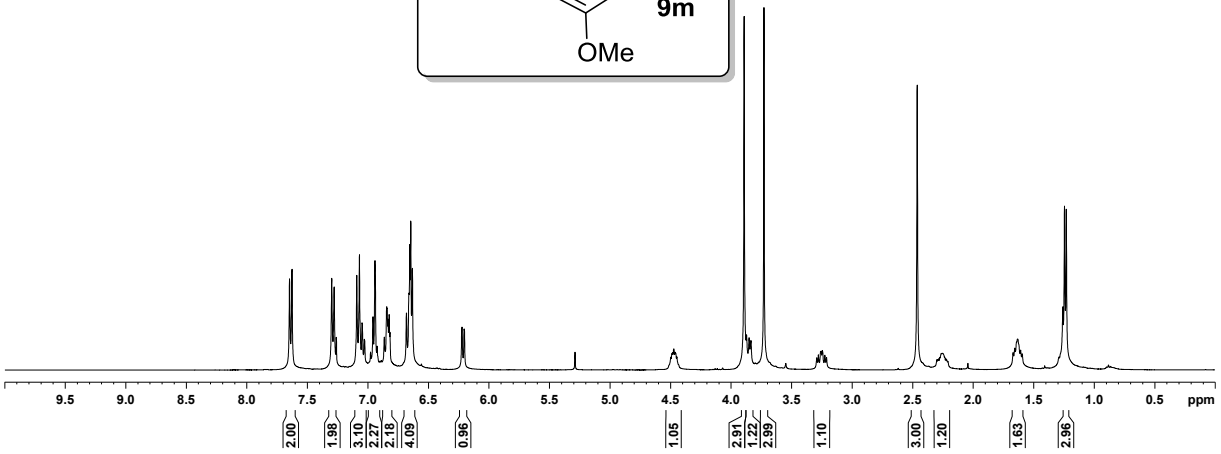

SJG-DJF-4-92-1H
Ts
N
9
O
O
Me
9l
OMe
ppm


SJG-DJF-4-92-13C
Ts
N
9
O
O
Me
9l
OMe
ppm

SJG-DJF-4-93-1H







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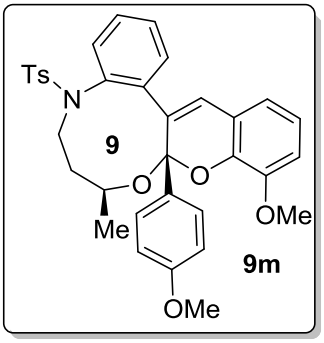

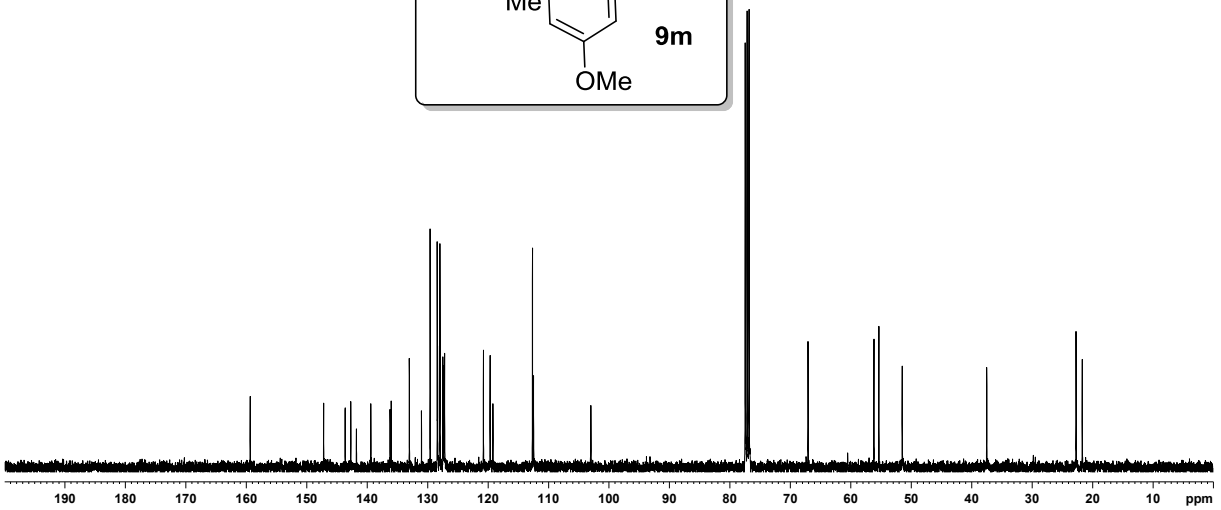

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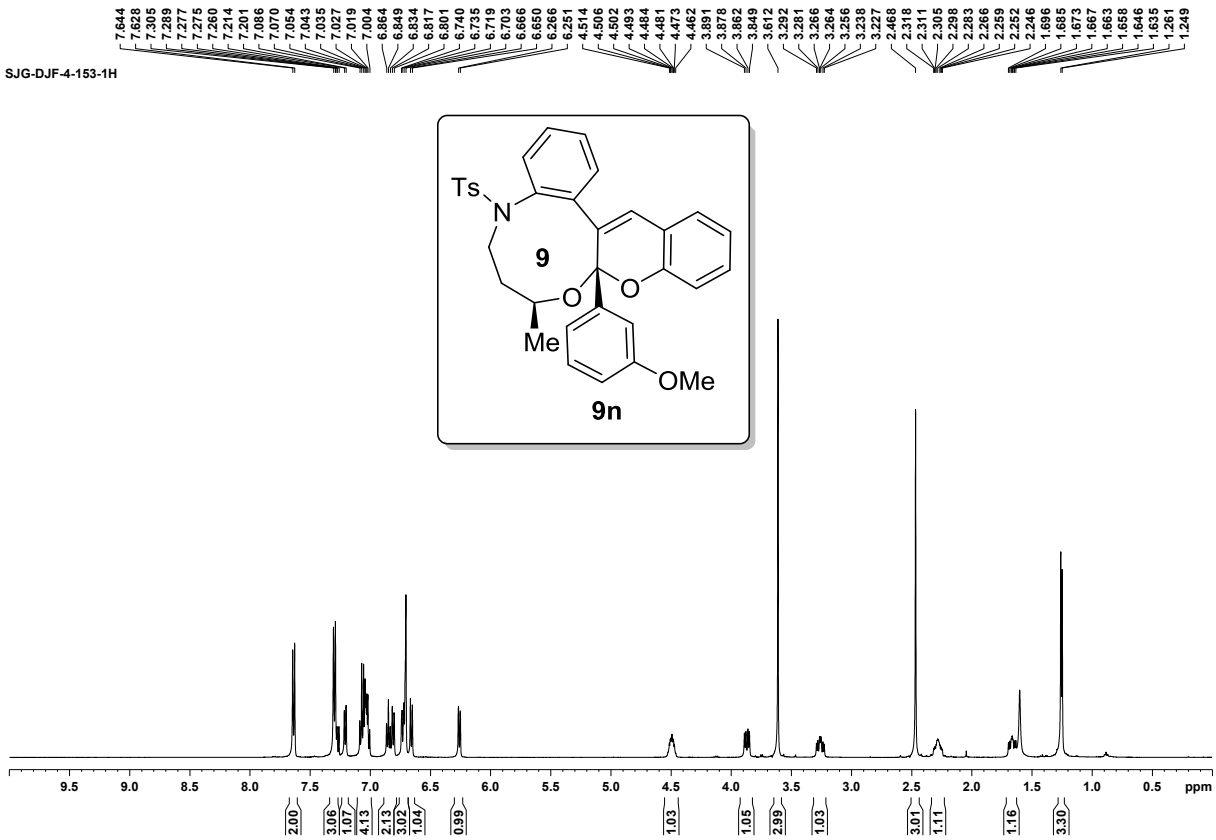

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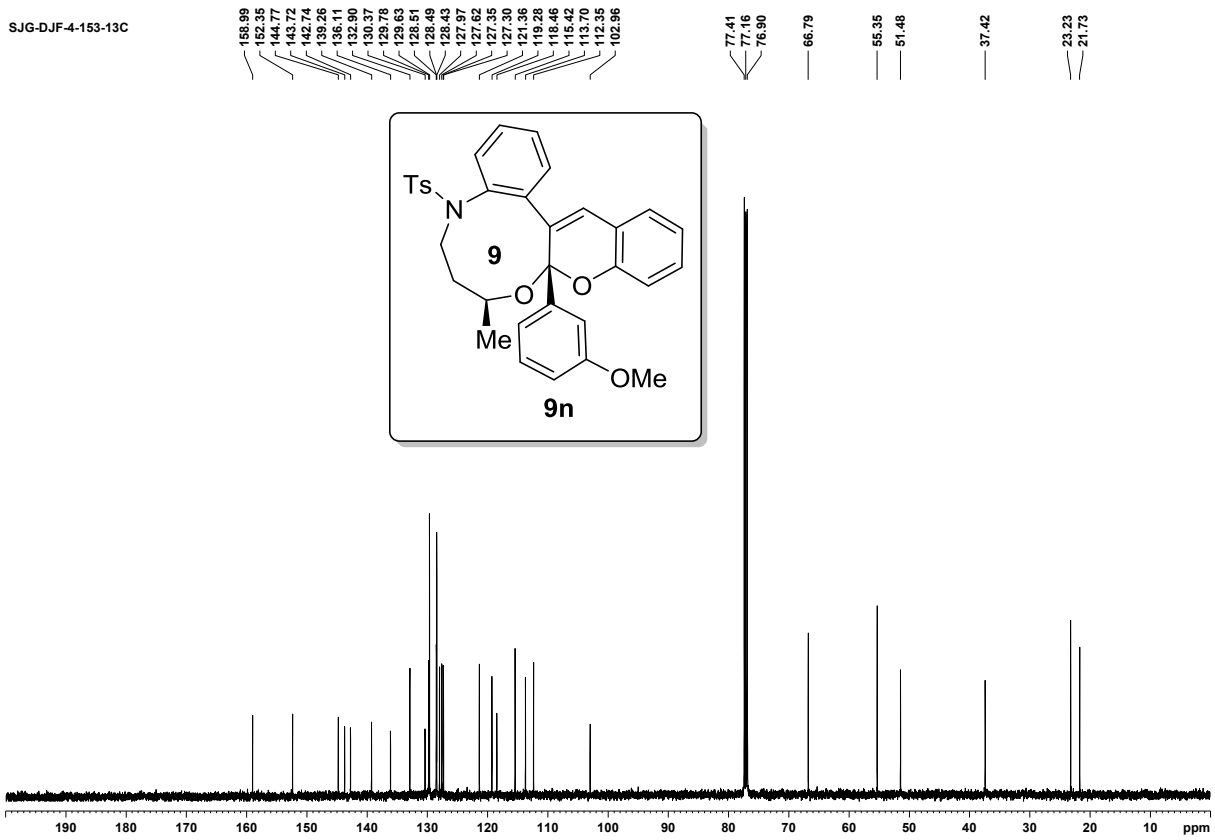

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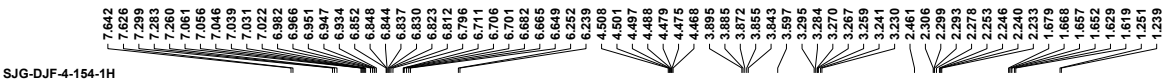

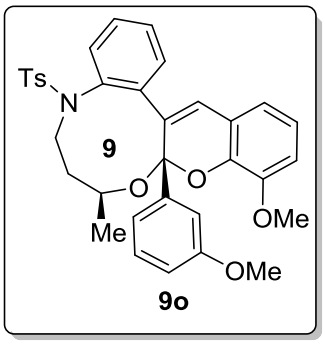

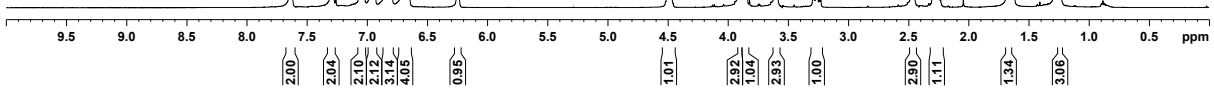

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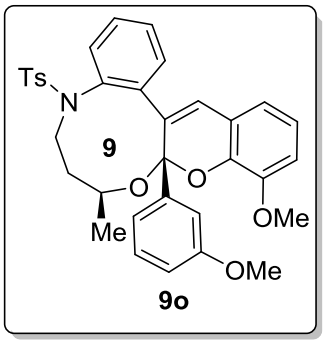

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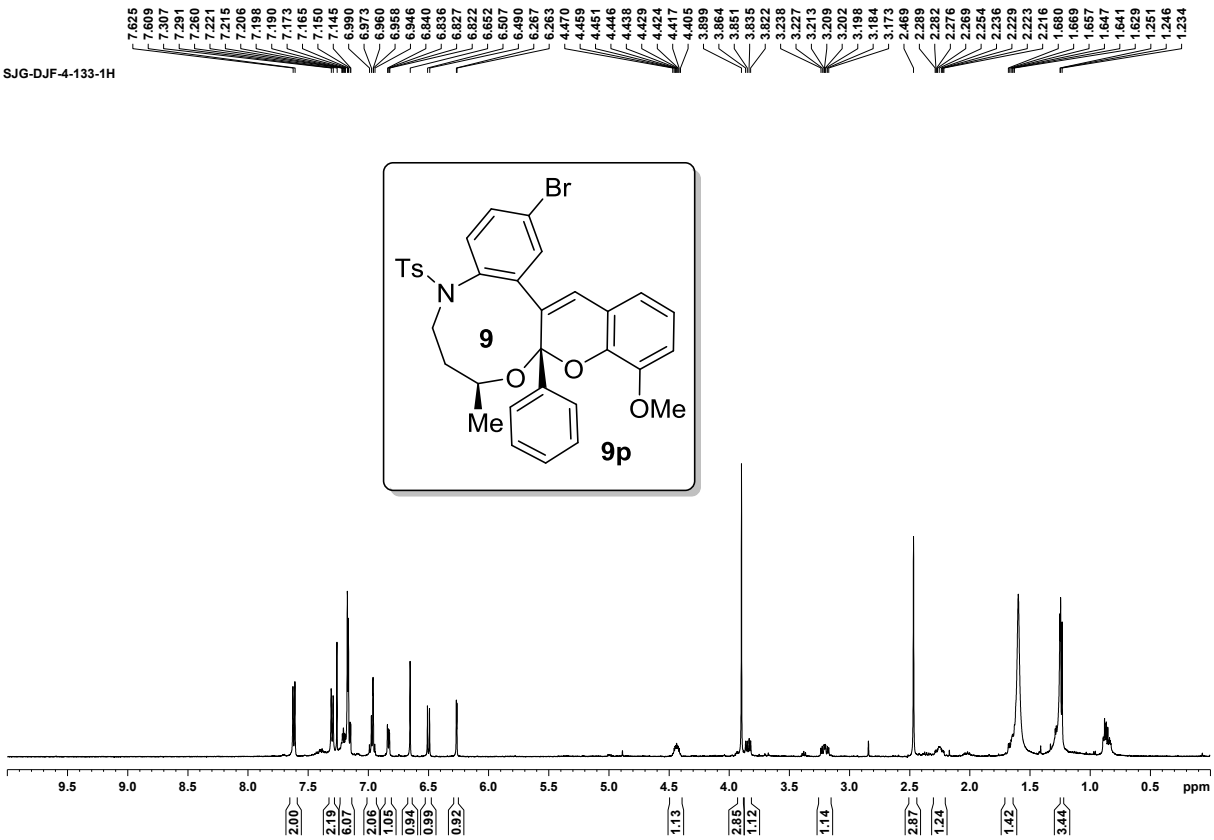

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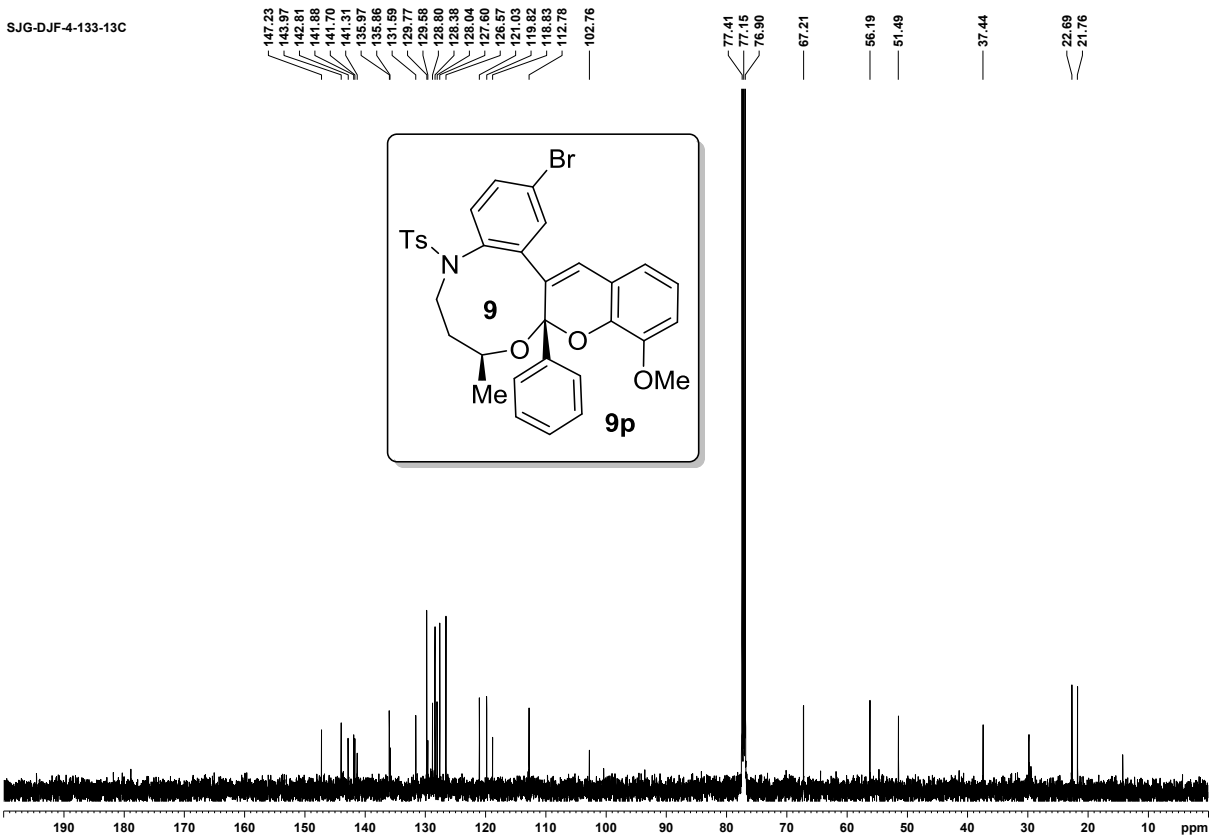
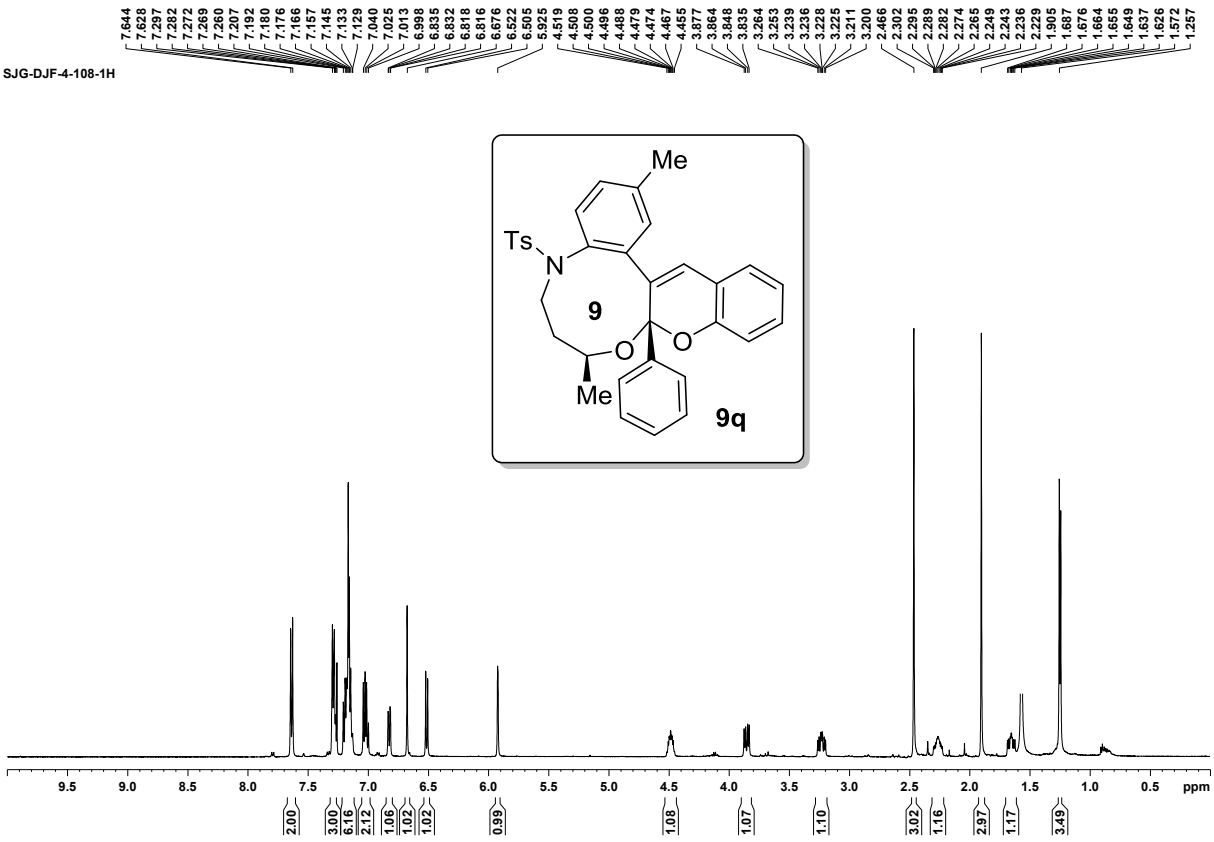
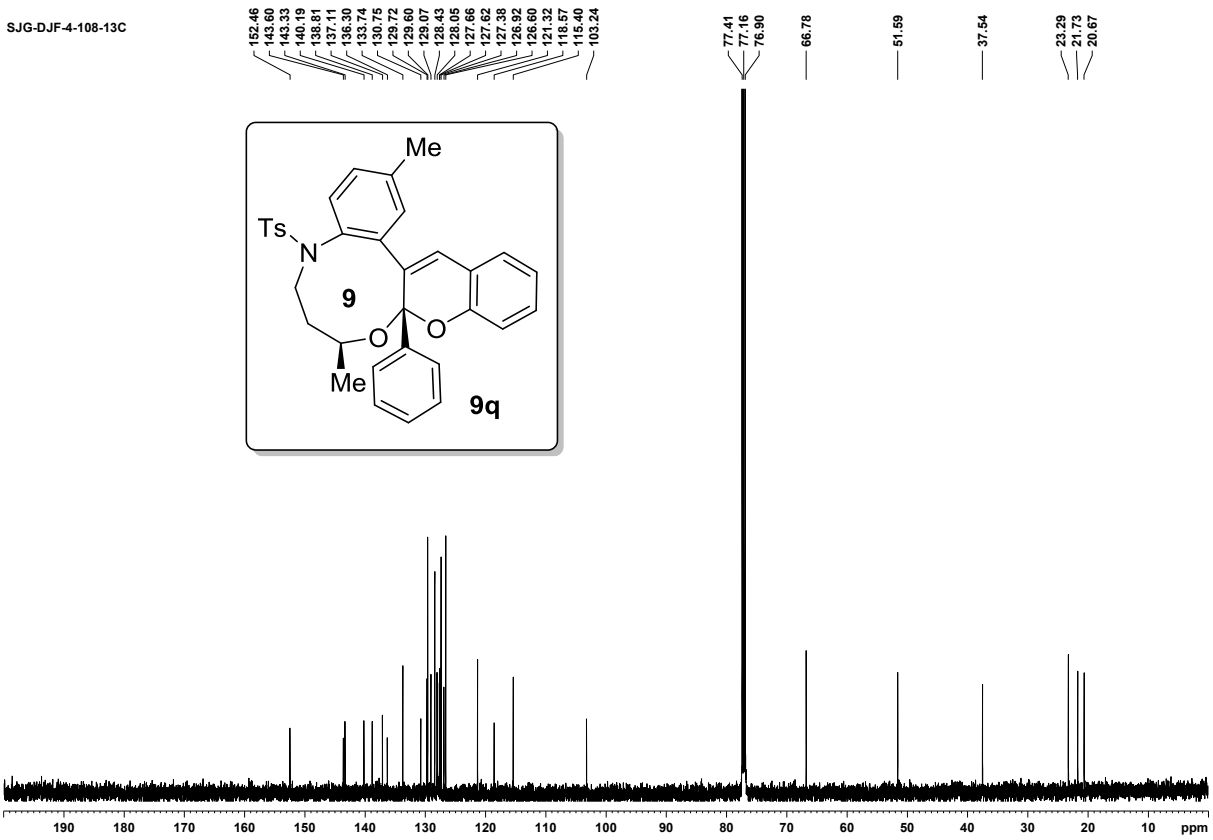


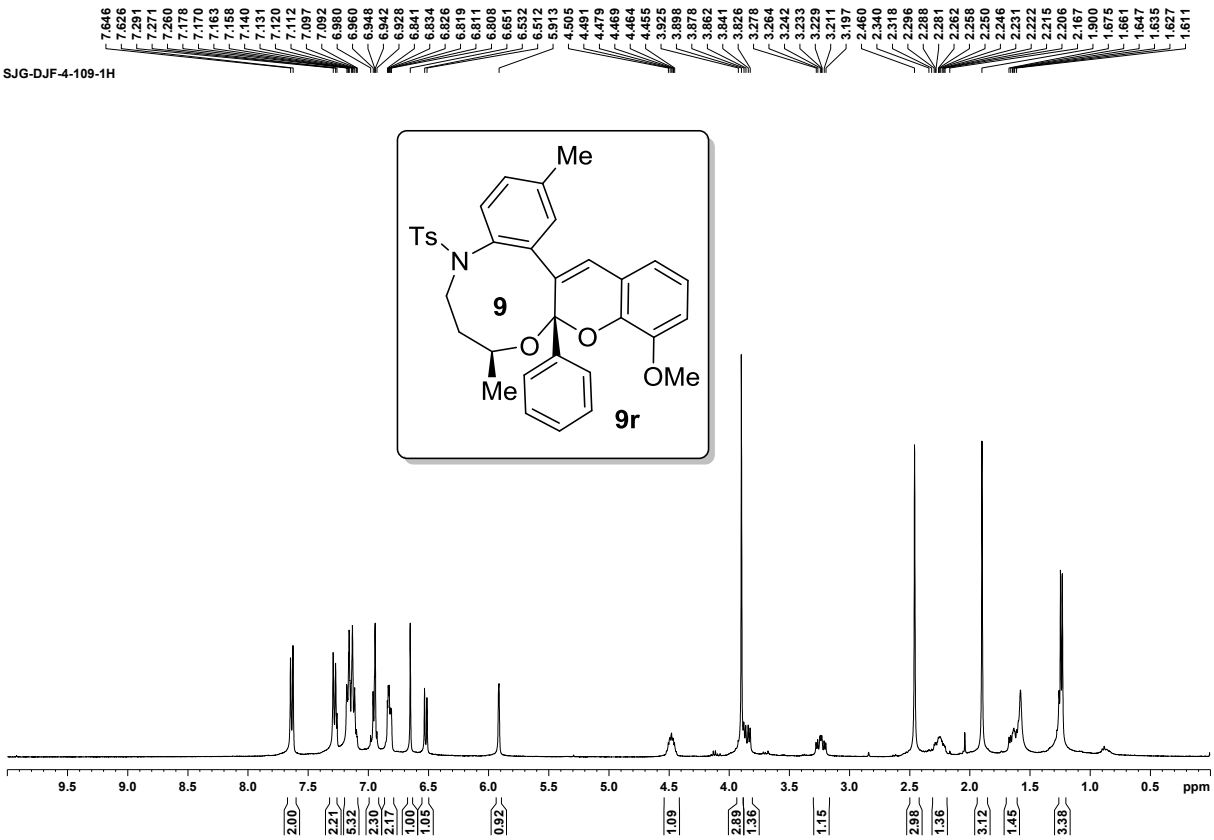
SJG-DJF-4-108-1H



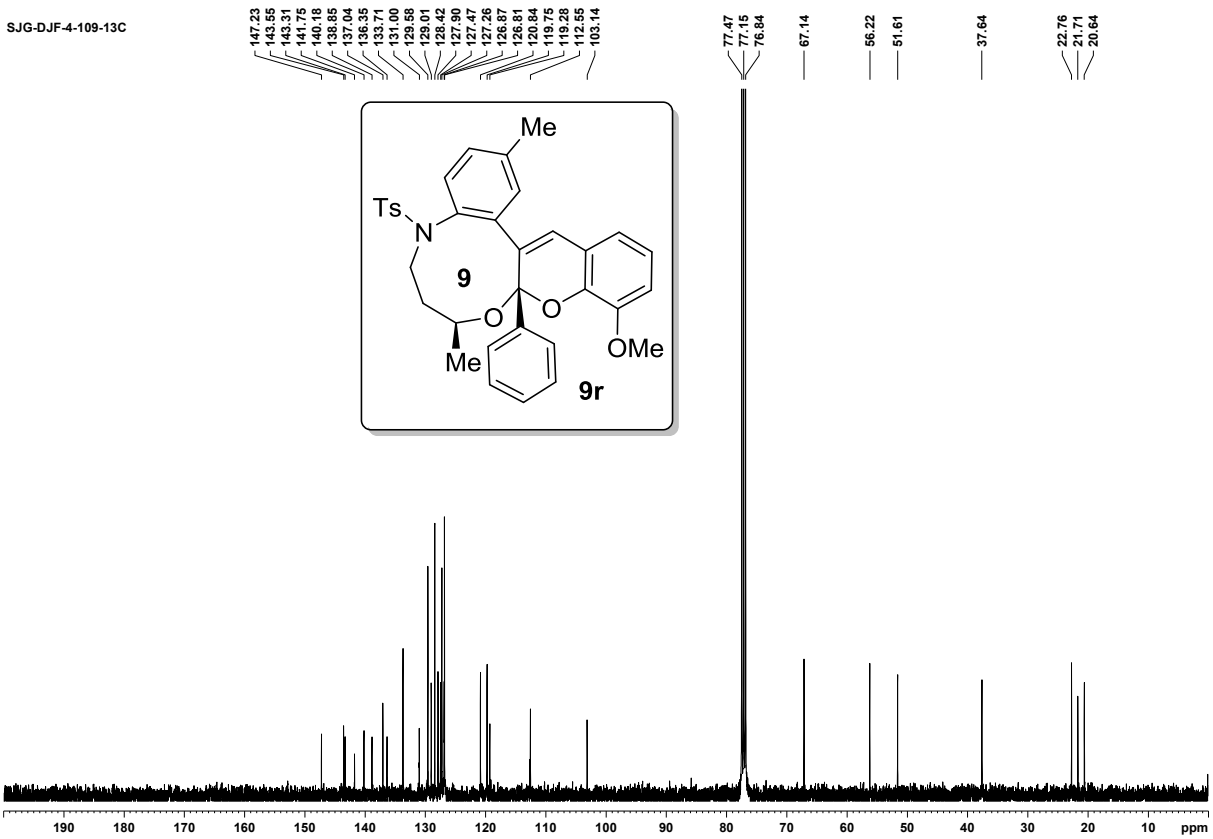
SJG-DJF-4-108-13C



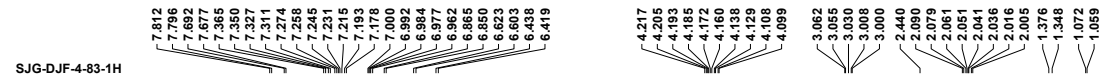
SJG-DJF-4-109-1H

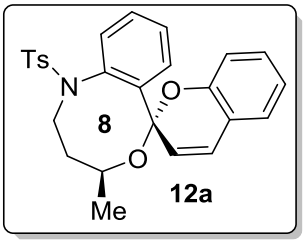


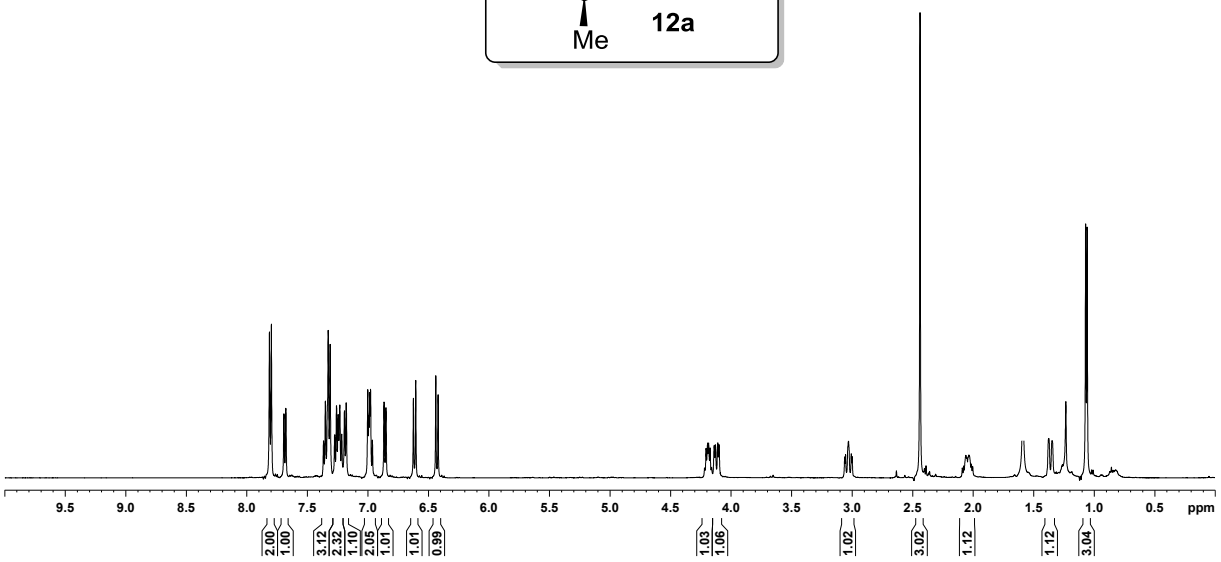
SJG-DJF-4-109-13C



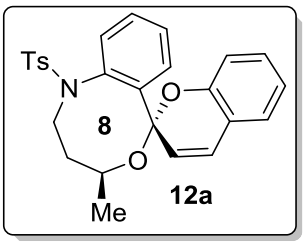
SJG-DJF-4-83-1H



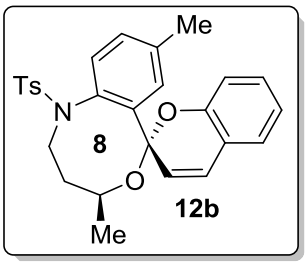


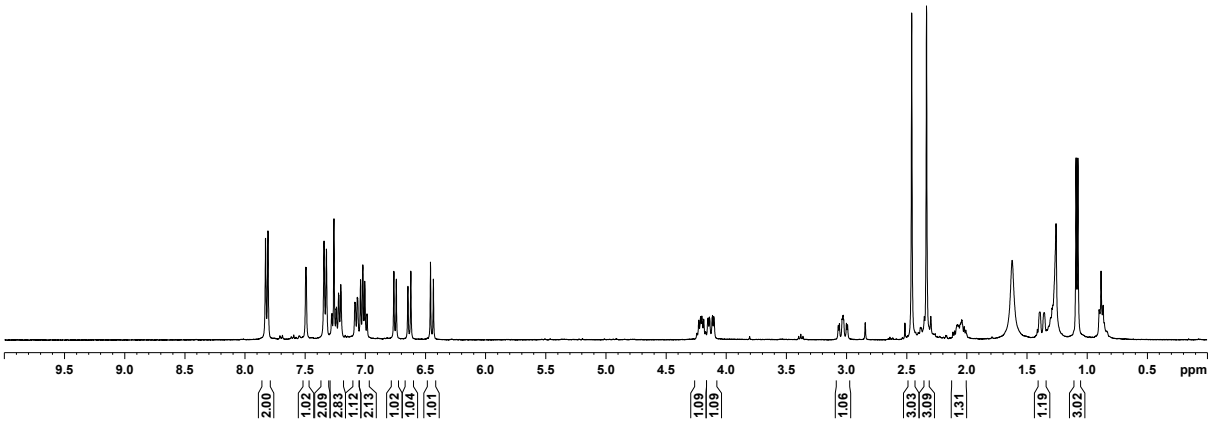


SJG-DJF-4-83-13C

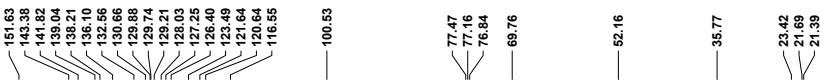


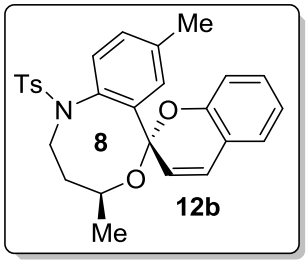
SJG-DJF-4-121-S1-1H



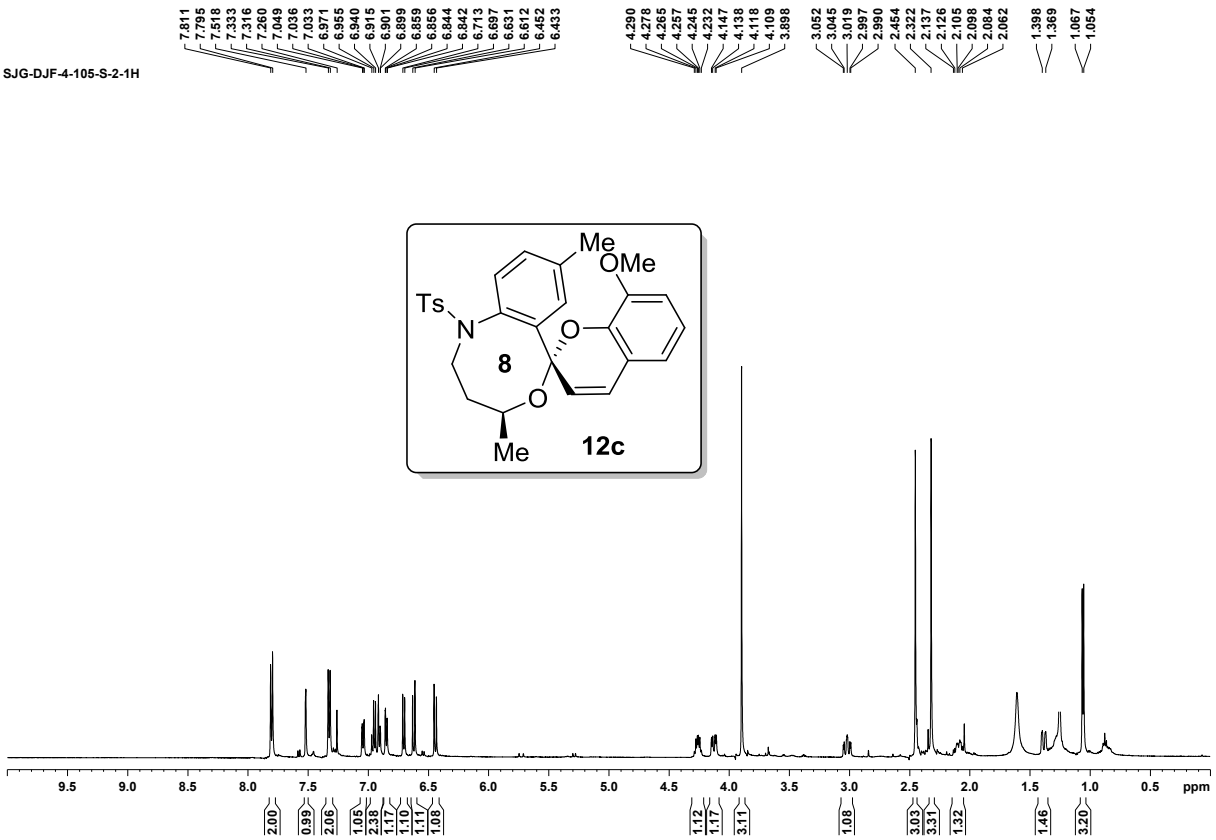


SJG-DJF-4-121-S1-13C





SJG-DJF-4-105-S-2-1H



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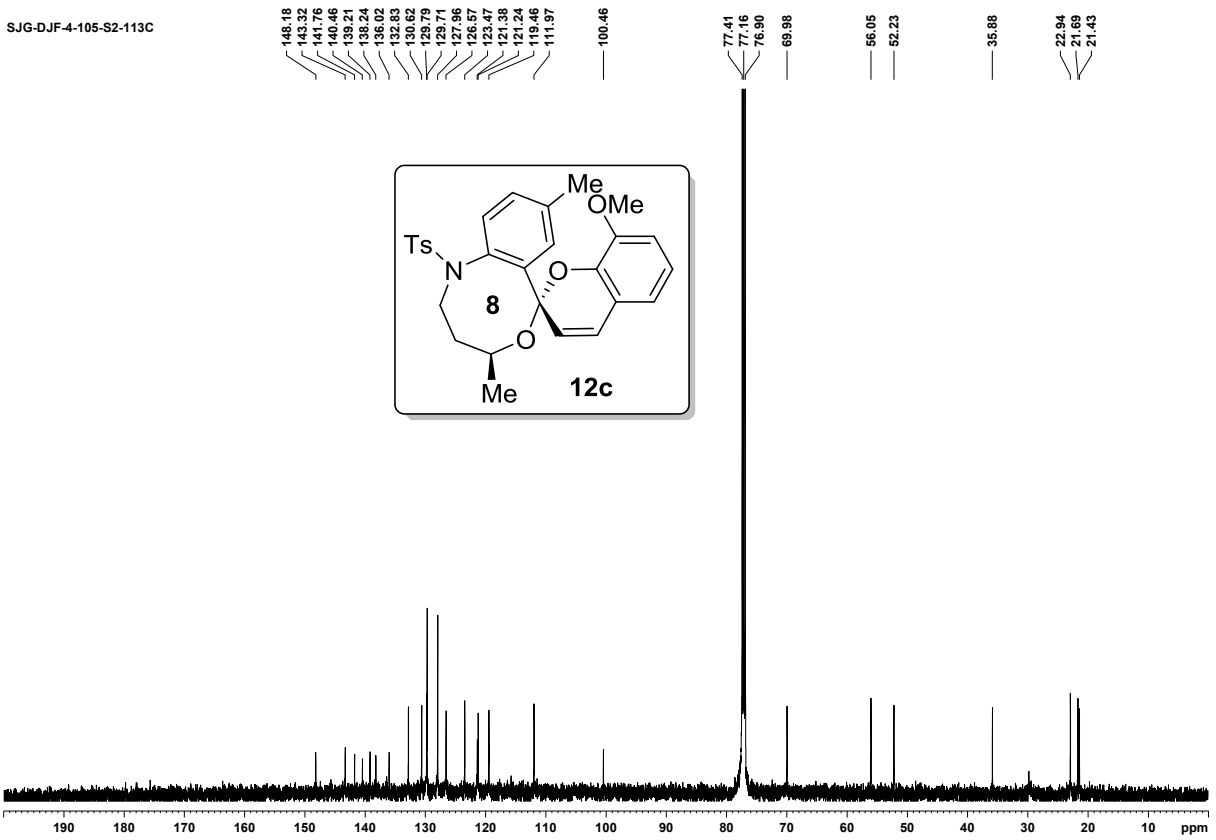
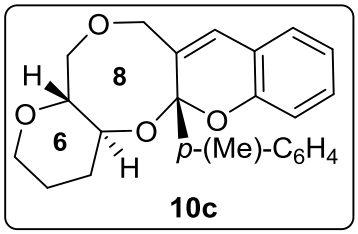
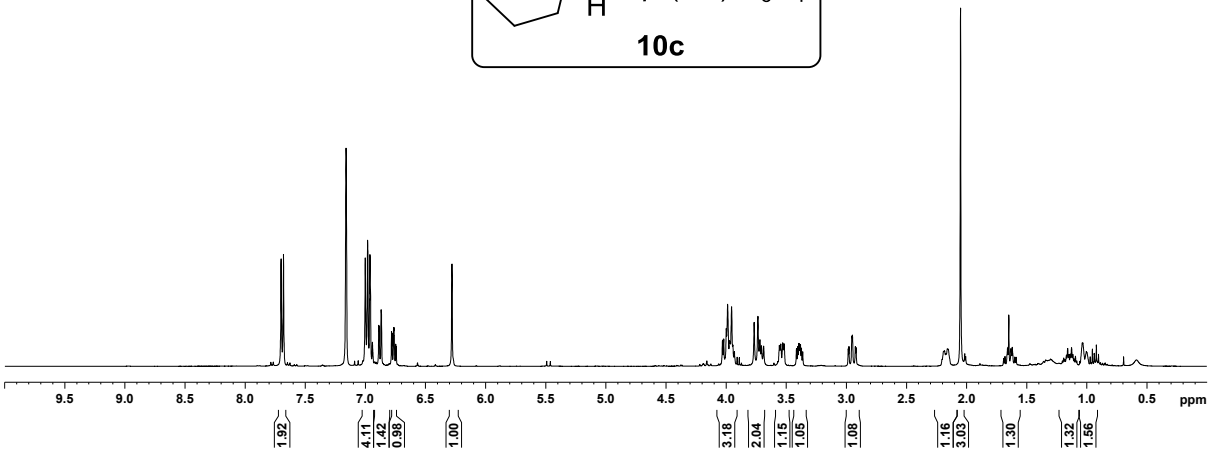
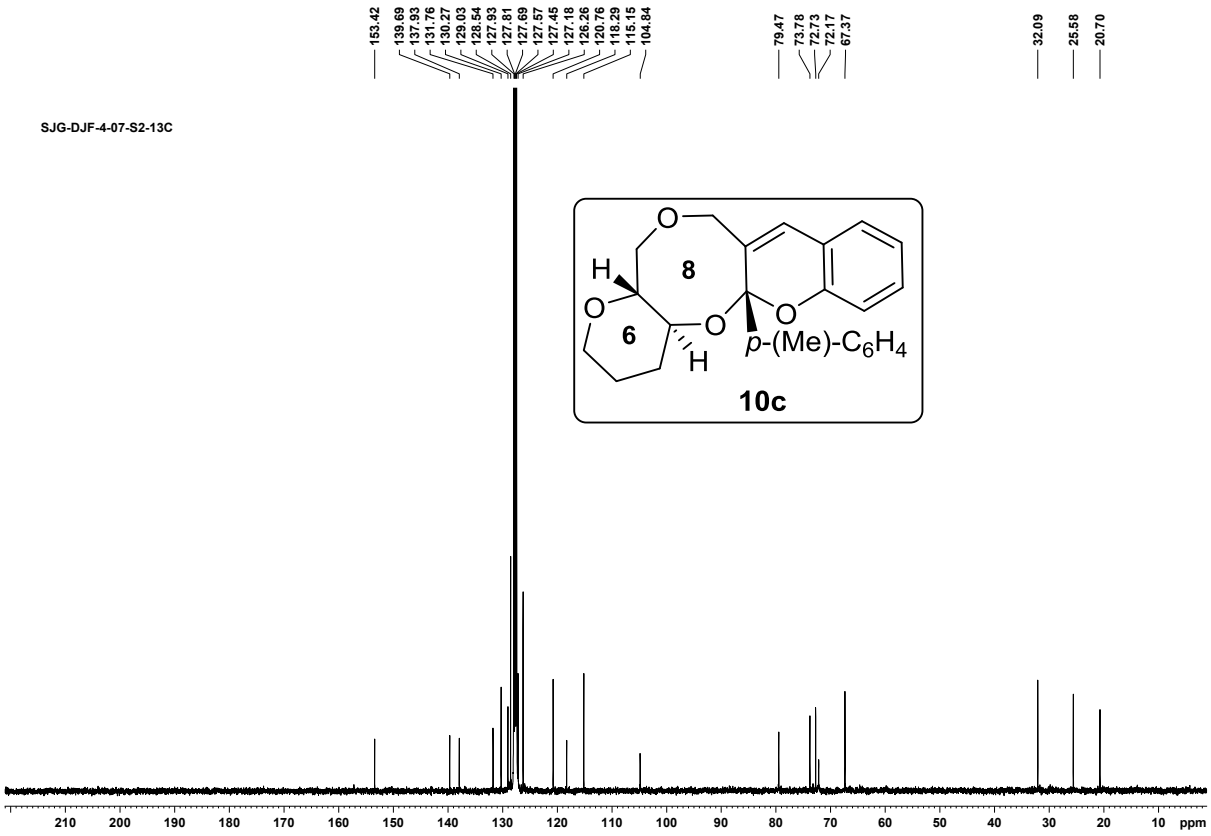


SJG-DJF-4-07-S2-1H



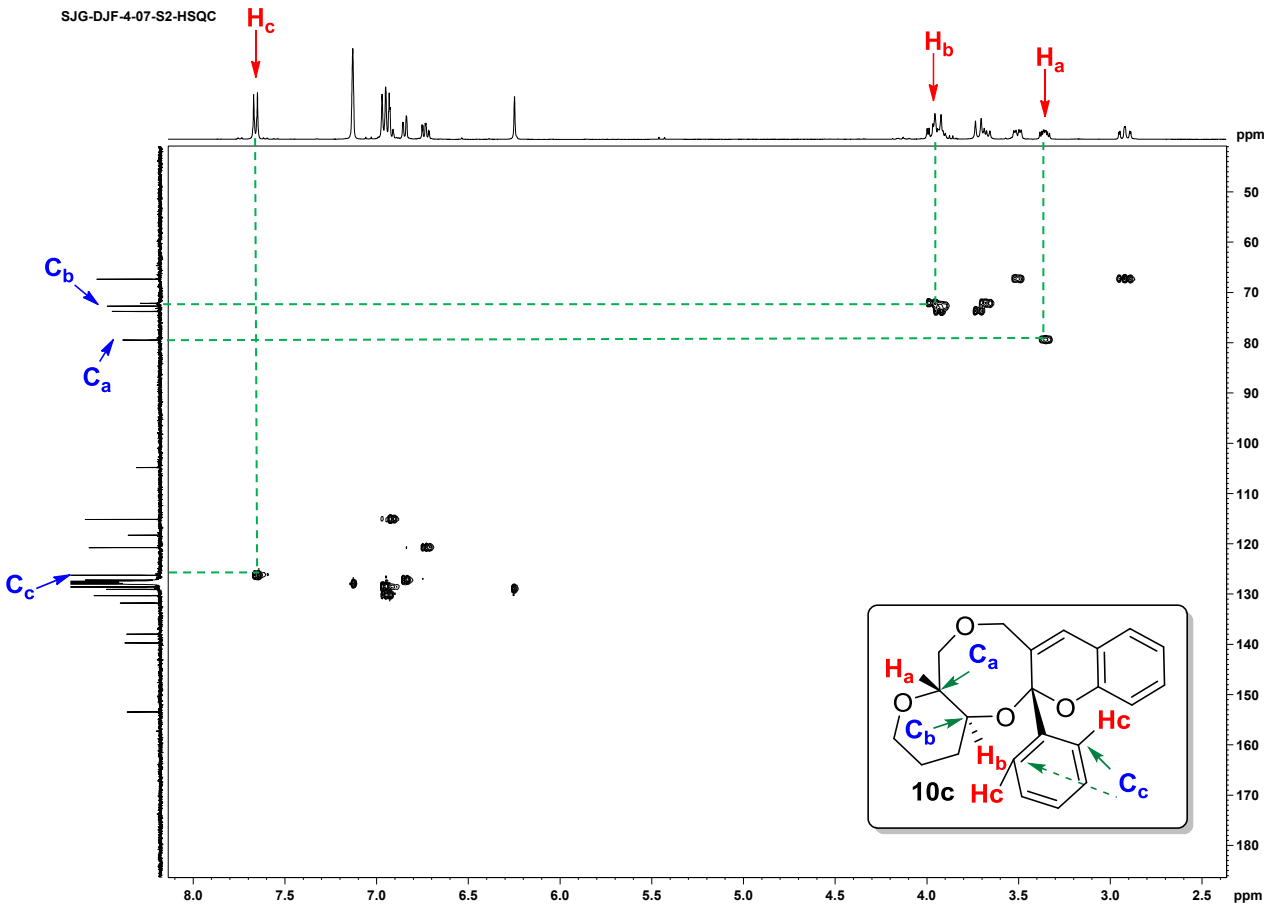
10c





SJG-DJF-4-07-S2-13C

10c


SJG-DJF-4-07-S2-HSQC
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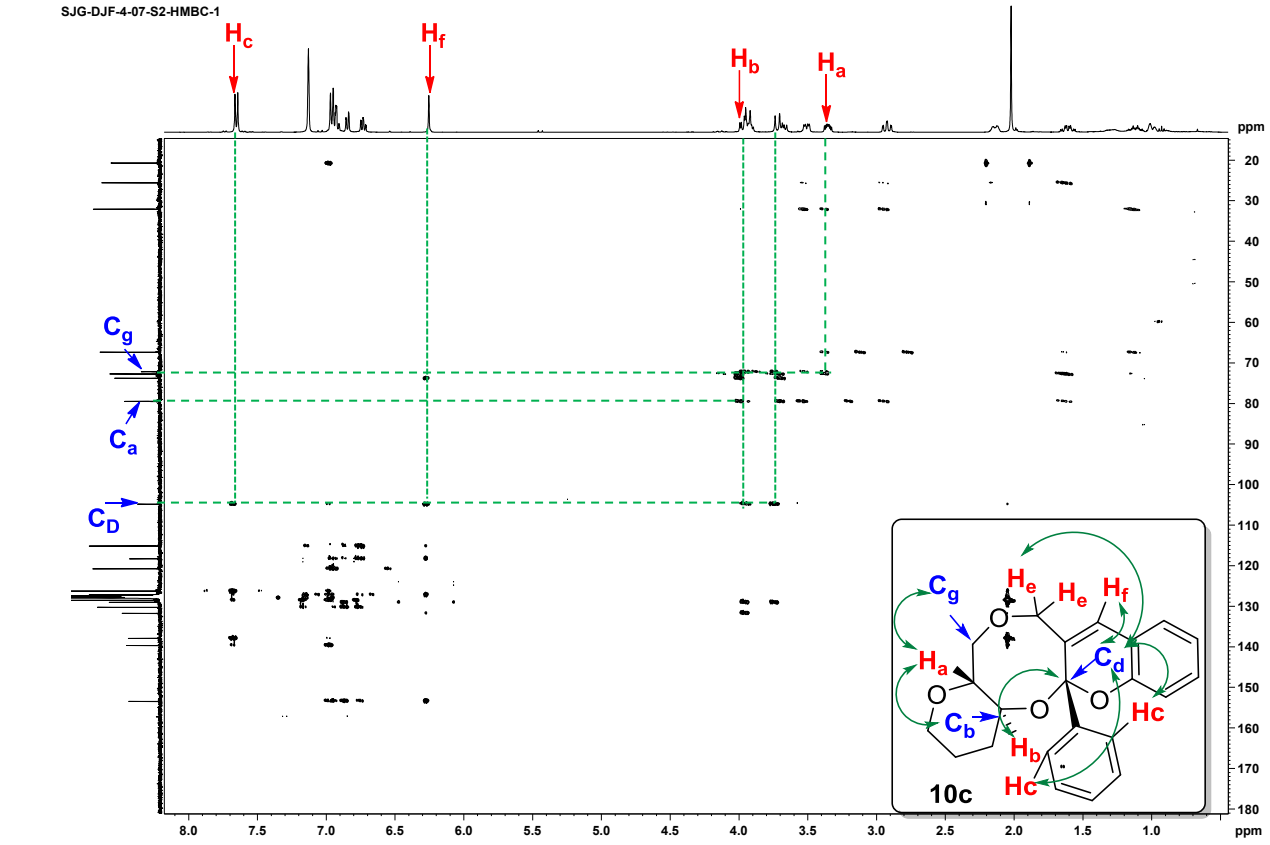
Hb
Ha
Cb
Ca
Cc
ppm
10c


SJG-DJF-4-07-S2-HMBC-1
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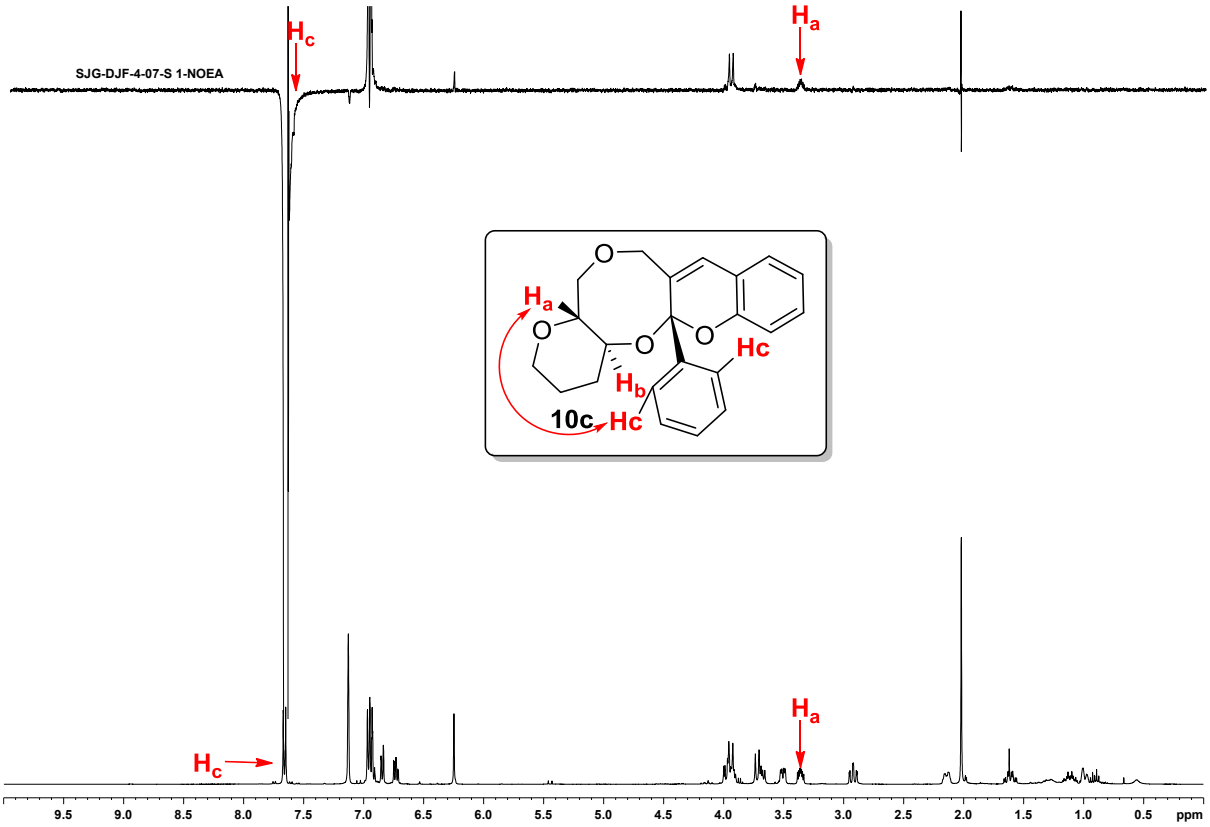
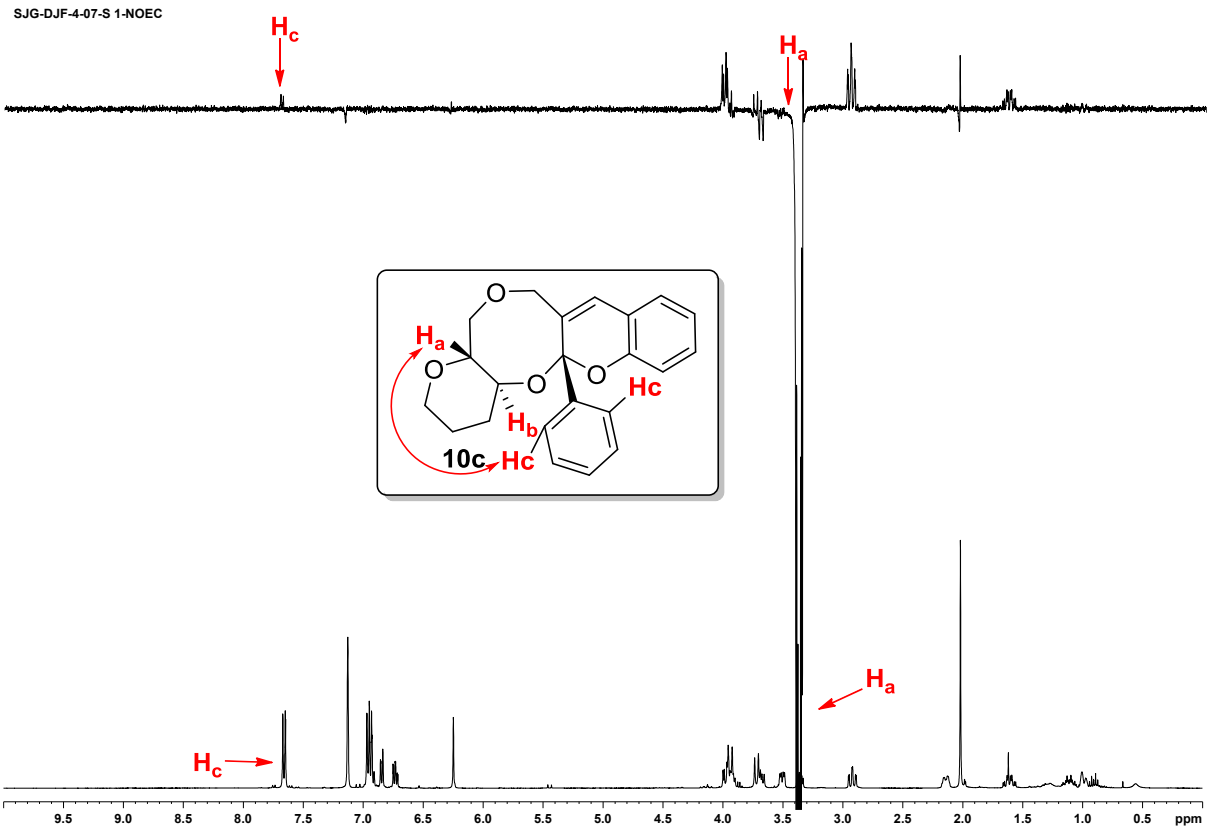
Hf
Hb
Ha
Cg
Ca
CD
ppm
10c

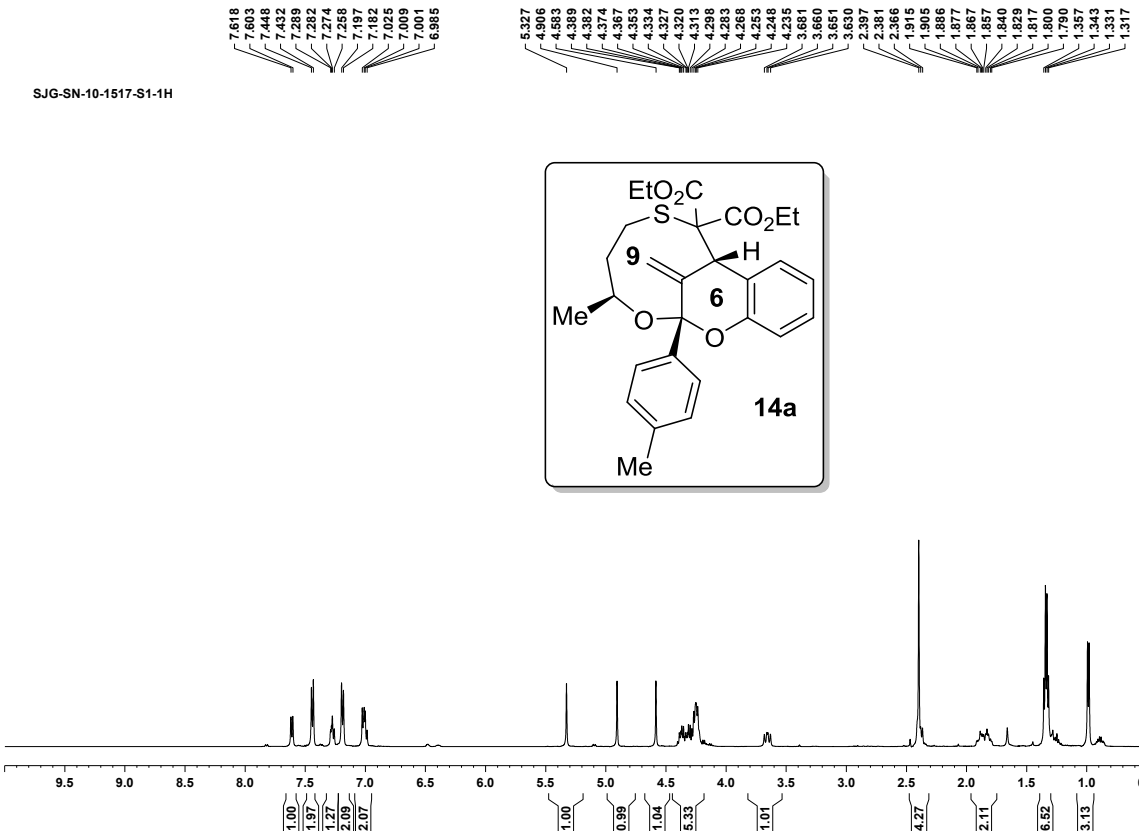


NOE enhancement-2%

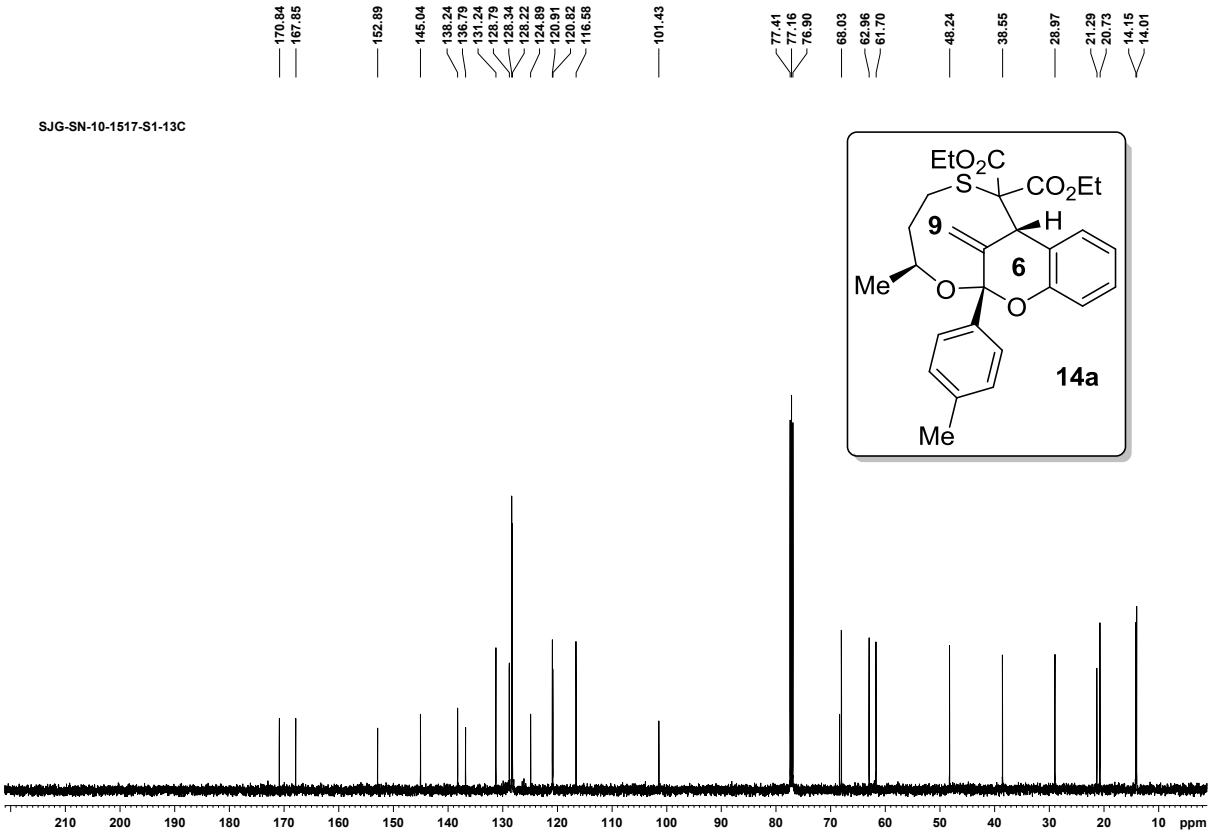


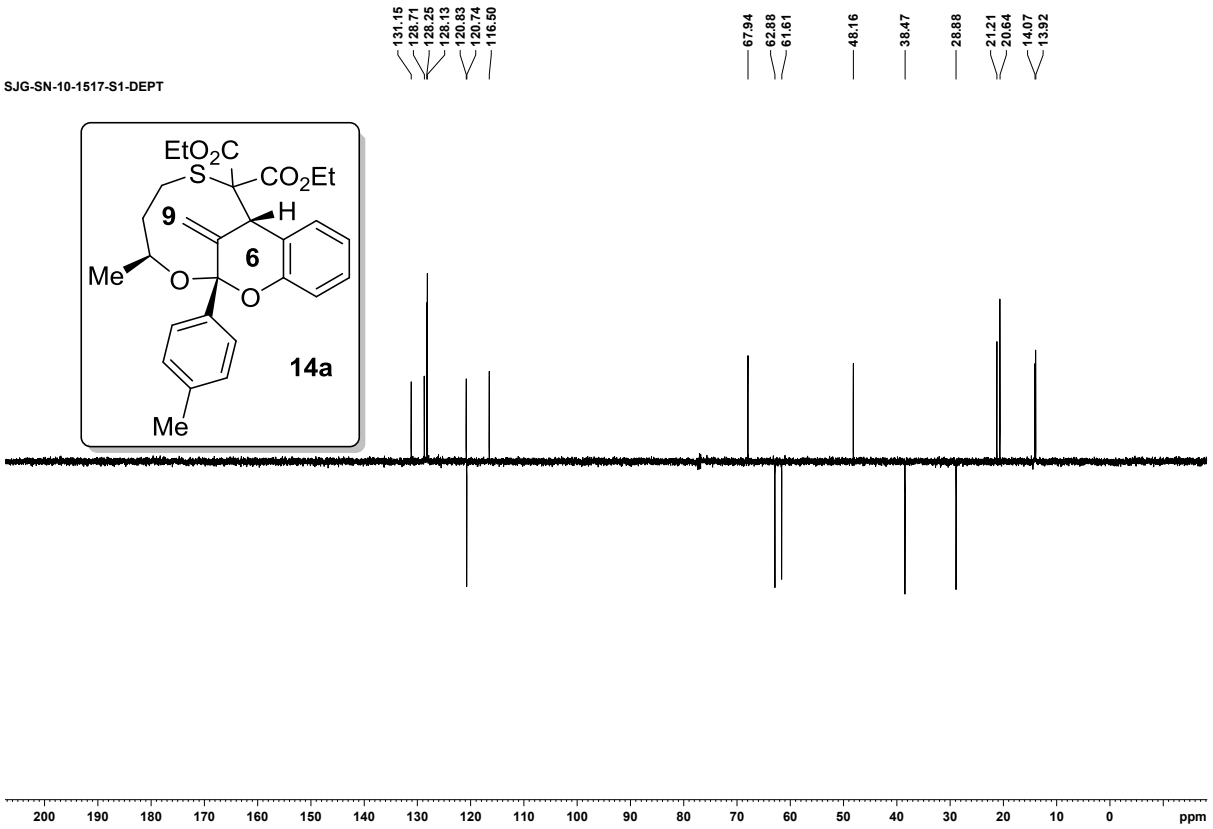
NOE enhancement-2%

SJG-SN-10-1517-S1-1H



SJG-SN-10-1517-S1-13C




131.15
128.71
128.25
128.13
120.83
120.74
116.50
67.94
62.88
61.61
48.16
38.47
28.88
21.21
20.64
14.07
13.92
SJG-SN-10-1517-S1-DEPT
EtO2C
S
CO2Et
9
H
6
Me
O
O
14a
Me
200
190
180
170
160
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120
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100
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60
50
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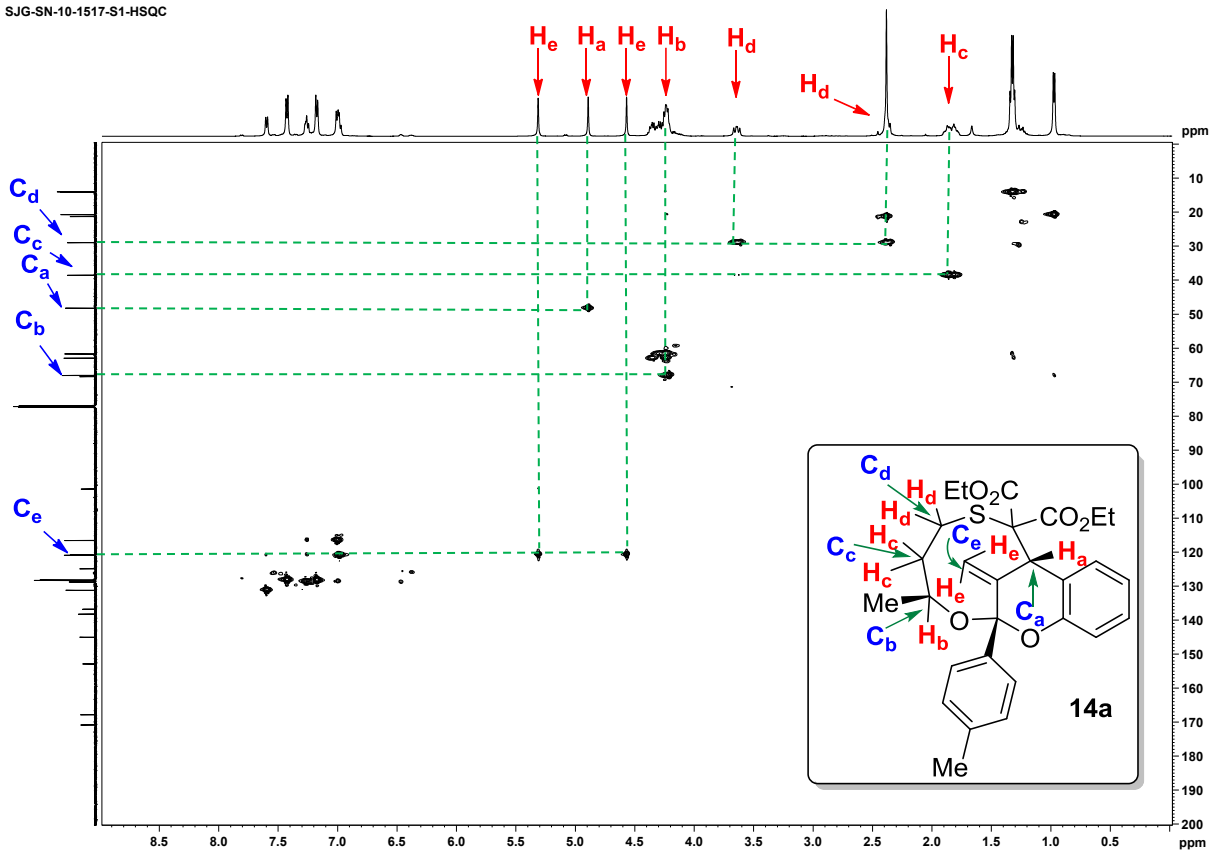
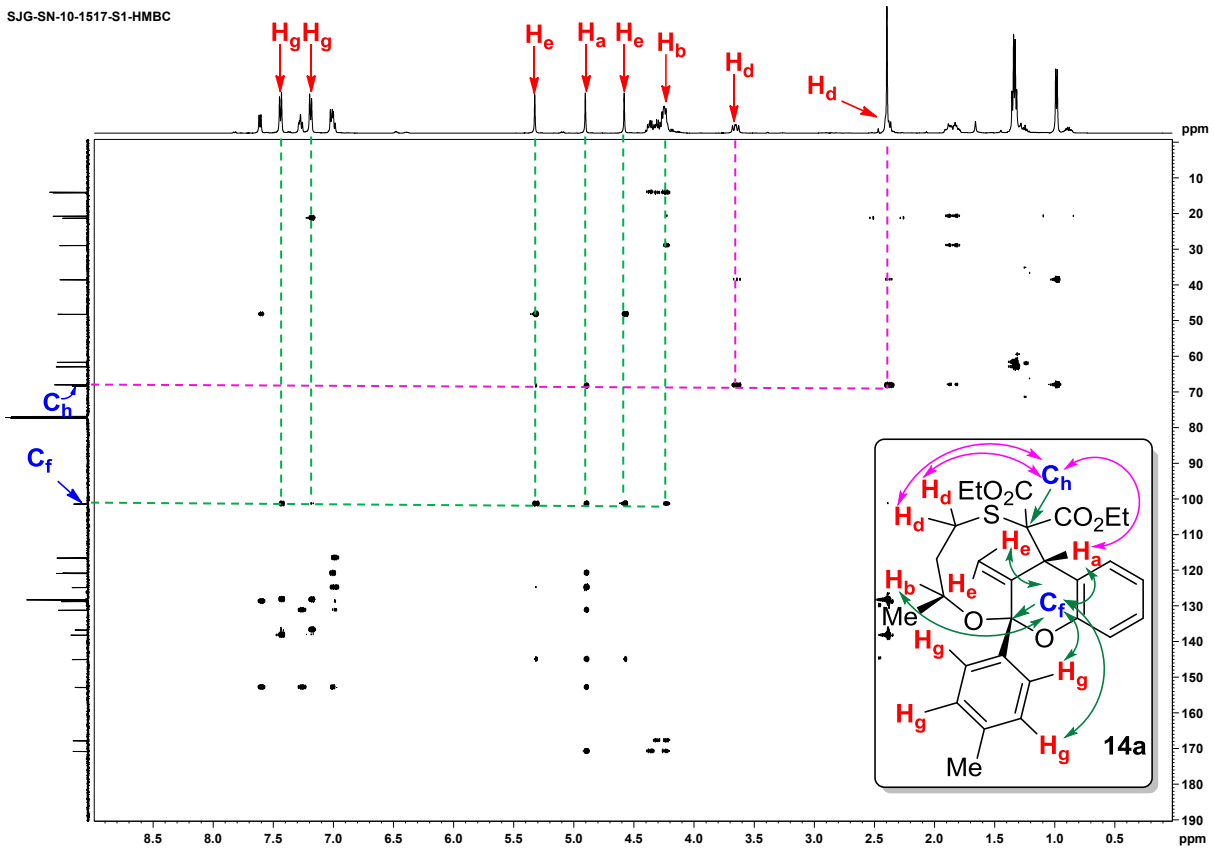
20
10
0
ppm


SJG-SN-10-1517-S1-HSQC
He Ha He Hb Hd
Hd
Hc
Cd
Cc
Ca
Cb
Ce
ppm
14a


SJG-SN-10-1517-S1-HMBC
Hg Hg
He Ha He Hb Hd
Hd
Ch
Cf
ppm
14a