Electronic Supplementary Material (ESI) for ChemComm.

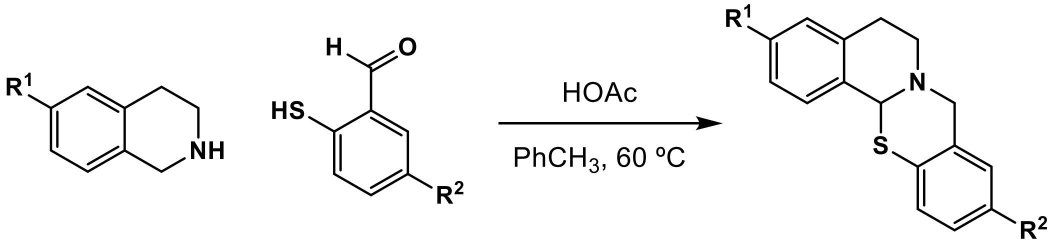
Supporting Information

General experimental considerations

Solvents and reagents were purchased from commercial distributors and used as received. All reactions requiring anhydrous conditions were performed under a positive pressure of nitrogen using flame-dried glassware. Reactions were monitored to completion by TLC and visualized by a dual short/long wave UV lamp and stained with an aqueous solution of potassium permanganate and/or iodine. Flash chromatography was performed on silica gel Siliaflash P60 (40-63 μm). DIMS mass spectra were determined by ESI. ^{1}H NMR and spectra were recorded at 500 MHz and 400 MHz spectrometers as indicated. The chemical shifts (δ) of proton resonances were reported relative to the deuterated solvent peak (7.26 ppm for $CDCl_3$, 3.31 for CD_3OD, 2.50 ppm for DMSO-d_6 and 7.16 ppm for Benzene-d_6) using the following format: chemical shift [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, bm = broad multiplet), coupling constant(s) (*J* in Hz), integral. ^{13}C NMR spectra were recorded at 126 MHz. The chemical shifts (δ) of carbon resonances were reported relative to the deuterated solvent peak (77.2 ppm for $CDCl_3$).

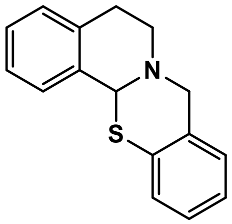
Experimental procedures

General procedure for the preparation of N,S-acetals[1]



To a 100 mL round bottom flask charged with a magnetic stir bar and 3Å molecular sieves (200 mg) was added aldehyde (1.0 mmol), toluene (10 mL), tetrahydroisoquinoline (1.3 mmol) and glacial acetic acid (0.1 mmol). The reaction was heated to 60 °C and monitored by TLC until complete consumption of aldehyde. The reaction mixture was cooled to room temperature and filtered through a plug of celite, washed with CH_2Cl_2 (50 mL), dried with Na_2SO_4, and concentrated under pressure. The crude material was washed with EtOAc (20 mL) and used without further purification.

5,13a-dihydro-6H,8H-benzo[5,6][1,3]thiazino[2,3-a]isoquinoline (**8a**).

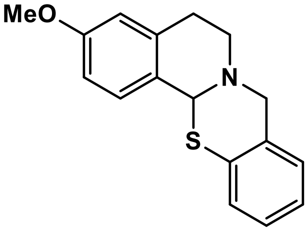


8a

Reaction preformed with 0.92 mmol of 2-mercaptobenzaldehyde (**10a**) and 1.20 mmol of tetrahydroisoquinoline (**9a**), isolated as a white solid (148 mg, 63% over two steps). Spectroscopic data for **8a** match those previously reported in literature.[1]

TLC: R_f = 0.54 (7:3 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.23 (qd, *J* = 6.7, 6.2, 1.8 Hz, 1H), 7.20 – 7.15 (m, 3H), 7.13 – 7.08 (m, 1H), 7.07 – 6.98 (m, 3H), 6.18 (s, 1H), 4.56 (d, *J* = 16.6 Hz, 1H), 3.96 (d, *J* = 16.6 Hz, 1H), 3.33 – 3.12 (m, 2H), 2.90 – 2.78 (m, 2H).
^{1}H NMR (400 MHz, Benzene-*d*$_6$) δ 7.03 – 6.89 (m, 4H), 6.80 (ddd, *J* = 14.4, 9.0, 7.3 Hz, 3H), 6.67 (d, *J* = 7.2 Hz, 1H), 5.86 (s, 1H), 4.10 (d, *J* = 16.6 Hz, 1H), 3.46 (d, *J* = 16.6 Hz, 1H), 3.13 (td, *J* = 11.9, 4.2 Hz, 1H), 2.88 (ddd, *J* = 18.3, 12.1, 6.7 Hz, 1H), 2.35 – 2.26 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.84, 134.79, 133.1, 129.3, 128.0, 127.9, 127.0, 126.6, 126.4, 126.3, 126.1, 124.2, 67.1, 57.8, 43.7, 28.8.
DIMS (ESI+): calculated for $C_{16}H_{16}NS$ *m/z* $[M+H]^+$ 254.1, Obsd. 254.0.

3-methoxy-5,13a-dihydro-6H,8H-benzo[5,6][1,3]thiazino[2,3-a]isoquinoline (**8b**).

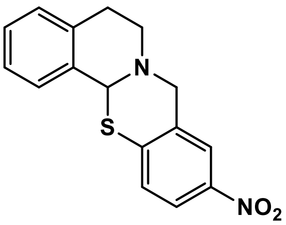


8b

Reaction preformed with 3.50 mmol of 2-mercaptobenzaldehyde (**10a**) and 4.55 mmol 6-methoxytetrahydroisoquinoline (**9b**), isolated as a white solid (435 mg, 44% over two steps). Spectroscopic data for **8b** match those previously reported in literature.[1]

TLC: R_f = 0.39 (7:3 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (dd, *J* = 8.8, 3.7 Hz, 2H), 7.05 – 6.96 (m, 3H), 6.74 (dd, *J* = 8.3, 2.6 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 6.13 (s, 1H), 4.60 – 3.88 (bm, 2H), 3.79 (s, 3H), 3.31 – 2.67 (bm, 4H).
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.04 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.89 (td, *J* = 7.5, 1.7 Hz, 1H), 6.85 (td, *J* = 7.4, 1.5 Hz, 1H), 6.76 – 6.73 (m, 1H), 6.63 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 5.95 (s, 1H), 4.21 (d, *J* = 16.6 Hz, 1H), 3.56 (d, *J* = 16.6 Hz, 1H), 3.29 (s, 3H), 3.22 (td, *J* = 11.8, 4.3 Hz, 1H), 2.94 (ddd, *J* = 18.2, 12.0, 6.6 Hz, 1H), 2.42 – 2.31 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.3, 135.2, 134.7, 128.1, 127.6, 127.8, 127.2, 126.9, 126.7, 124.3, 114.1, 112.5, 67.1, 58.1, 55.4, 43.8, 29.3.
DIMS (ESI+): calculated for $C_{17}H_{18}NOS$ *m/z* $[M+H]^+$ 284.1, Obsd. 284.1.

10-nitro-5,13a-dihydro-6H,8H-benzo[5,6][1,3]thiazino[2,3-a]isoquinoline (**8c**).

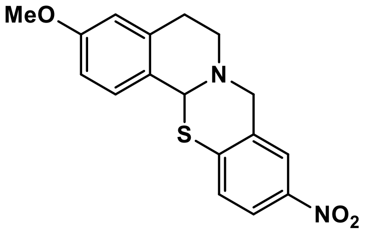


8c

Reaction preformed with 0.71 mmol of 2-mercapto-5-nitrobenzaldehyde (**10c**) and 0.92 mmol tetrahydroisoquinoline (**9a**), isolated as a yellow solid (123 mg, 77% over two steps). Spectroscopic data for **8c** match those previously reported in literature.[1]

TLC: R_f = 0.61 (7:3 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 10.4, 2.1 Hz, 2H), 7.29 – 7.08 (m, 5H), 6.27 (s, 1H), 4.32 (bs, 2H), 2.98 (bs, 4H).
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.61 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.03 – 6.92 (m, 3H), 6.86 (dd, *J* = 7.3, 1.5 Hz, 1H), 6.55 (d, *J* = 8.6 Hz, 1H), 5.72 (s, 1H), 3.80 – 3.69 (m, 1H), 3.21 (d, *J* = 16.8 Hz, 1H), 2.81 (s, 2H), 2.36 – 2.25 (m, 1H), 2.18 (s, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.0, 144.2, 133.9, 133.1, 129.6, 128.6, 127.2, 126.8, 126.6, 126.4, 123.1, 122.2, 77.5, 77.2, 77.0, 68.8, 57.8, 43.9, 28.8.
DIMS (ESI+): calculated for $C_{16}H_{15}N_2O_2S$ *m/z* $[M+H]^+$ 299.1, Obsd. 299.1.

3-methoxy-10-nitro-5,13a-dihydro-6H,8H-benzo[5,6][1,3]thiazino[2,3-a]isoquinoline (**8d**).

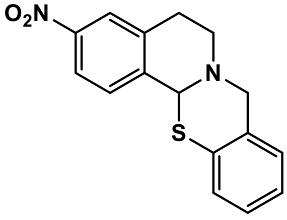


8d

Reaction preformed with 1.48 mmol of 2-mercapto-5-nitrobenzaldehyde (**10c**) and 1.92 mmol 6-methoxytetrahydroisoquinoline (**9b**), isolated as a yellow solid (304 mg, 92% over two steps).

TLC: R_f = 0.46 (6:4 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.09 (t, *J* = 9.3 Hz, 2H), 6.77 (d, *J* = 8.5, 1H), 6.70 (s, 1H), 6.25 (s, 1H), 4.30 (s, 2H), 3.81 (s, 3H), 2.97 (dd, *J* = 11.8, 5.0 Hz, 4H).
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.62 – 7.54 (m, 2H), 6.86 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.62 – 6.53 (m, 2H), 6.50 (s, 1H), 5.73 (s, 1H), 3.44 (bs, 2H), 3.25 (s, 3H), 2.51 (bs, 4H).
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.63 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.59 (d, *J* = 3.3 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.65 – 6.55 (m, 2H), 6.53 (d, *J* = 3.1 Hz, 1H), 5.77 (s, 1H), 3.47 (s, 2H), 3.28 (t, *J* = 2.1 Hz, 3H), 2.55 (s, 4H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 159.4, 146.1, 143.9, 134.4, 127.3, 127.0, 126.6, 126.1, 122.9, 122.0, 113.9, 112.6, 68.6, 57.7, 55.3, 43.6, 28.9.
DIMS (ESI+): calculated for $C_{17}H_{17}N_2O_3S$ *m/z* $[M+H]^+$ 329.1, Obsd. 329.1.

3-nitro-5,13a-dihydro-6H,8H-benzo[5,6][1,3]thiazino[2,3-a]isoquinoline (**8e**).

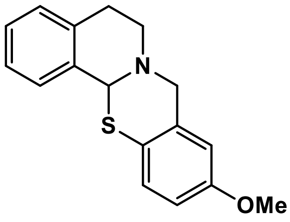


8e

Reaction preformed with 3.50 mmol of 2-mercaptobenzaldehyde (**10a**) and 4.55 mmol 6-nitrotetrahydroisoquinoline (**9c**), isolated as a yellow solid (343 mg, 33% over two steps).

TLC: R_f = 0.45 (6:4 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 – 8.02 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.07 – 7.03 (m, 2H), 7.01 – 6.97 (m, 1H), 6.20 (s, 1H), 4.55 (d, *J* = 16.7 Hz, 1H), 3.97 (d, *J* = 16.7 Hz, 1H), 3.31 – 3.20 (m, 2H), 3.00 – 2.82 (m, 2H).
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.65 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.58 (d, *J* = 2.4 Hz, 1H), 6.96 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.85 (pd, *J* = 7.4, 1.6 Hz, 2H), 6.72 – 6.68 (m, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 5.62 (s, 1H), 4.04 (d, *J* = 16.6 Hz, 1H), 3.42 (d, *J* = 16.7 Hz, 1H), 2.93 (td, *J* = 11.9, 4.1 Hz, 1H), 2.58 (ddd, *J* = 17.9, 12.0, 6.8 Hz, 1H), 2.17 (dd, *J* = 11.7, 6.7 Hz, 1H), 2.05 (dd, *J* = 16.6, 4.1 Hz, 1H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 141.8, 135.4, 133.9, 128.3, 127.5, 127.4, 126.8, 126.1, 124.9, 124.7, 121.5, 66.3, 57.6, 43.2, 29.0.
DIMS (ESI+): calculated for $C_{16}H_{15}N_2O_2S$ *m/z* $[M+H]^+$ 299.1, Obsd. 299.1.

10-methoxy-5,13a-dihydro-6H,8H-benzo[5,6][1,3]thiazino[2,3-a]isoquinoline (**8f**).

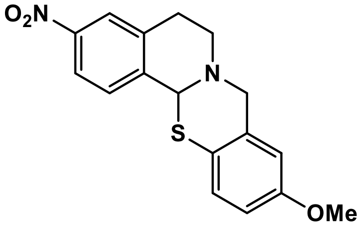


8f

Reaction preformed with 0.97 mmol of 2-mercapto-5-methoxybenzaldehyde (**10b**) and 1.26 mmol of tetrahydroisoquinoline (**9a**), isolated as a white solid (152 mg, 55%).

TLC: R_f = 0.78 (6:4 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 (qd, *J* = 6.9, 1.9 Hz, 1H), 7.18 – 7.14 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.71 (ddt, *J* = 8.6, 2.8, 0.6 Hz, 1H), 6.65 – 6.62 (m, 1H), 6.10 (s, 1H), 4.53 (d, *J* = 16.6 Hz, 1H), 3.91 (d, *J* = 16.7 Hz, 1H), 3.78 (s, 3H), 3.27 (td, *J* = 11.6, 4.0 Hz, 1H), 3.17 (ddd, *J* = 18.3, 12.2, 6.4 Hz, 1H), 2.86 – 2.78 (m, 2H).
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.13 – 7.09 (m, 1H), 7.04 – 6.97 (m, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.92 – 6.89 (m, 1H), 6.57 – 6.52 (m, 2H), 5.90 (s, 1H), 4.19 (d, *J* = 16.6 Hz, 1H), 3.51 (d, *J* = 16.7 Hz, 1H), 3.31 (s, 3H), 3.27 (dd, *J* = 11.7, 4.2 Hz, 1H), 2.96 (ddd, *J* = 16.4, 12.1, 6.8 Hz, 1H), 2.45 – 2.36 (m, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.9, 135.1, 133.3, 129.4, 128.0, 127.7, 127.6, 126.5, 126.2, 125.5, 113.7, 113.6, 67.0, 58.2, 55.6, 43.9, 29.0.
DIMS (ESI+): calculated for $C_{17}H_{18}NOS$ *m/z* $[M+H]^+$ 284.1, Obsd. 284.1.

10-methoxy-3-nitro-5,13a-dihydro-6H,8H-benzo[5,6][1,3]thiazino[2,3-a]isoquinoline (**8g**).

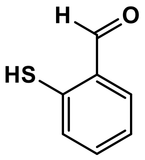


8g

Reaction preformed with 4.01 mmol of 2-mercapto-5-methoxybenzaldehyde (**10b**) and 5.21 mmol 6-nitrotetrahydroisoquinoline (**9c**), isolated as a yellow solid (345 mg, 26% over two steps).

TLC: R_f = 0.35 (6:4 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 – 8.01 (m, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 6.13 (s, 1H), 4.53 (d, *J* = 16.8 Hz, 1H), 3.93 (d, *J* = 16.8 Hz, 1H), 3.78 (d, *J* = 0.9 Hz, 3H), 3.32 – 3.19 (m, 2H), 3.00 – 2.80 (m, 2H).
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.65 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.57 – 6.50 (m, 2H), 5.60 (s, 1H), 4.07 (d, *J* = 16.7 Hz, 1H), 3.41 (d, *J* = 16.7 Hz, 1H), 3.30 (s, 3H), 3.02 (td, *J* = 11.8, 4.1 Hz, 1H), 2.60 (ddd, *J* = 18.0, 11.9, 6.8 Hz, 1H), 2.21 (dd, *J* = 11.6, 6.8 Hz, 1H), 2.07 (dd, *J* = 16.6, 3.9 Hz, 1H).
^{13}C NMR (125 MHz, Chloroform-*d*) δ 157.2, 147.4, 141.9, 135.4, 127.7, 127.4, 127.2, 124.6, 124.3, 121.5, 113.8, 66.1, 57.8, 55.6, 43.2, 29.0.
DIMS (ESI+): calculated for $C_{17}H_{17}N_2O_3S$ *m/z* $[M+H]^+$ 329.1, Obsd. 329.1.

2-mercaptobenzaldehyde (**10a**).

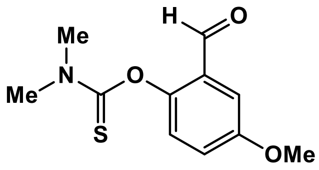


10a

To a flamed dried 100 mL round bottom flask was added TMEDA (0.74 mL, 4.95 mmol), thiophenol (0.23 mL, 2.25 mmol) and 7 mL hexanes. The solution was cooled to 0 °C and 1.8 M ^{n}BuLi solution in cyclohexane (3.1 mL, 4.95 mmol) was added dropwise. The resulting solution was allowed to warm to room temperature and stirred for 16 h. DMF (0.44 mL, 5.6 mmol) was then added dropwise and again allowed to stir for 20 h. Et_2O (10 mL) was added and stirred for 20 minutes. The reaction mixture was washed with 1 M HCL (25 mL) and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The crude material was used without further purification. Spectroscopic data for **10a** match those previously reported in literature.[2]

TLC: R_f = 0.25 (7:3 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.19 (d, *J* = 0.6 Hz, 1H), 7.85 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.77 – 7.73 (m, 1H), 7.47 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 7.37 (td, *J* = 7.4, 1.1 Hz, 1H).

O-(2-formyl-4-methoxyphenyl) dimethylcarbamothioate (**S-1**).

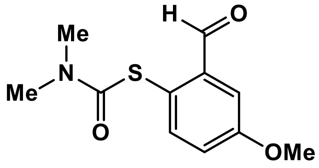


S-1

To a 100 mL round bottom flask was added 2-hydroxy-5-methoxybenzaldehyde (2 g, 13.1 mmol), and 1,4-diazabicyclo[2.2.2]octane (4.42 g, 39.4 mmol) dissolved in DMF (20 mL). To the solution, *N,N*-dimethylthiocarbamoyl chloride (4.87 g, 39.4 mmol) was added in one portion. The reaction was heated to 50 °C for 5 h, and then poured into water (40 mL). The product was extracted with CH_2Cl_2 (3 x 75 mL). The organic layers were combined and washed with 5% HCl (75 mL), 0.1M NaOH (75 mL), and brine (75 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude material was used without further purification. Spectroscopic data for **S-1** match those previously reported in literature.[3]

TLC: R_f = 0.25 (7:3 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.02 (d, *J* = 2.0 Hz, 1H), 7.37 (t, *J* = 2.7 Hz, 1H), 7.15 (ddd, *J* = 8.9, 3.2, 2.1 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.0 Hz, 1H), 3.85 (d, *J* = 3.1 Hz, 3H), 3.46 (d, *J* = 3.3 Hz, 3H), 3.40 (d, *J* = 2.5 Hz, 3H).

S-(2-formyl-4-methoxyphenyl) dimethylcarbamothioate (**S-2**).

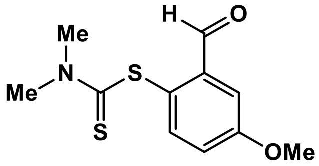


S-2

To a 50 mL round bottom flask was added O-(2-formyl-4-methoxyphenyl) dimethylcarbamothioate (100 mg, 0.42 mmol) and CAN (229 mg, 0.42 mmol) dissolved in DMSO (8.5 mL). The reaction mixture was stirred for 24 h. To the completed reaction mixture was added H_2O (60 mL) and the solution was extracted with Et_2O (4 x 60 mL). The combined organic layers were washed with 60 mL of H_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The crude reaction material was used without further purification. Spectroscopic data for **S-2** match those previously reported in literature.[4]

TLC: R_f = 0.31 (6:4 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.33 (s, 1H), 7.53 (d, *J* = 3.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.13 (dd, *J* = 8.6, 3.0 Hz, 1H), 3.87 (s, 3H), 3.26 – 2.96 (m, 6H).

2-formyl-4-methoxyphenyl dimethylcarbamodithioate (**S-3**).

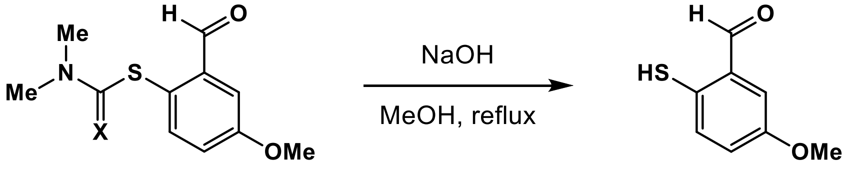


S-3

$CuCl_2$ (0.5 mg, 0.004 mmol), zinc powder (10 mg, 0.15 mmol), DMSO (2 mL), K_2CO_3 (16 mg, 0.11 mmol), tetramethylthiuram disulfide (55 mg, 0.23 mmol), and 2-iodo-5-methoxybenzaldehyde (100 mg, 0.38 mmol) were added to a 25 mL round bottom flask. The reaction mixture was stirred at 110 °C for 18 h. The mixture was cooled to room temperature and quenched with NH_4Cl (10 mL) and then extracted with EtOAc (3 x 10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was used without further purification. Spectroscopic data for **S-3** match those previously reported in literature.[5]

TLC: R_f = 0.39 (6:4 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.15 (s, 1H), 7.55 (d, *J* = 3.0 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.12 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.87 (s, 3H), 3.52 (d, *J* = 8.3 Hz, 6H).

General procedure for the preparation of 2-mercapto-5-methoxybenzaldehyde (10b)[5]

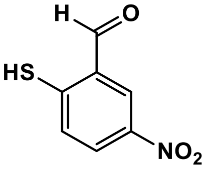


10b

To a 100 mL round bottom flask was added *S*-aryl compound **S-2** or **S-3** (3.0 mmol) and dissolved in MeOH (10 mL). 3N NaOH was added dropwise (12 mL) and refluxed for 2h. The reaction mixture was cooled to room temperature and acidified to pH 5 with 10% HCl. The mixture was extracted with ethyl acetate (3 x 15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was used without further purification. Spectroscopic data for **10b** match those previously reported in literature.[3]

TLC: R_f =0.4 (6:4 hexanes:EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.16 (d, *J* = 0.6 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.37 (d, *J* = 2.9 Hz, 1H), 7.08 (ddd, *J* = 8.7, 3.0, 0.6 Hz, 1H), 3.86 (d, *J* = 0.5 Hz, 3H).

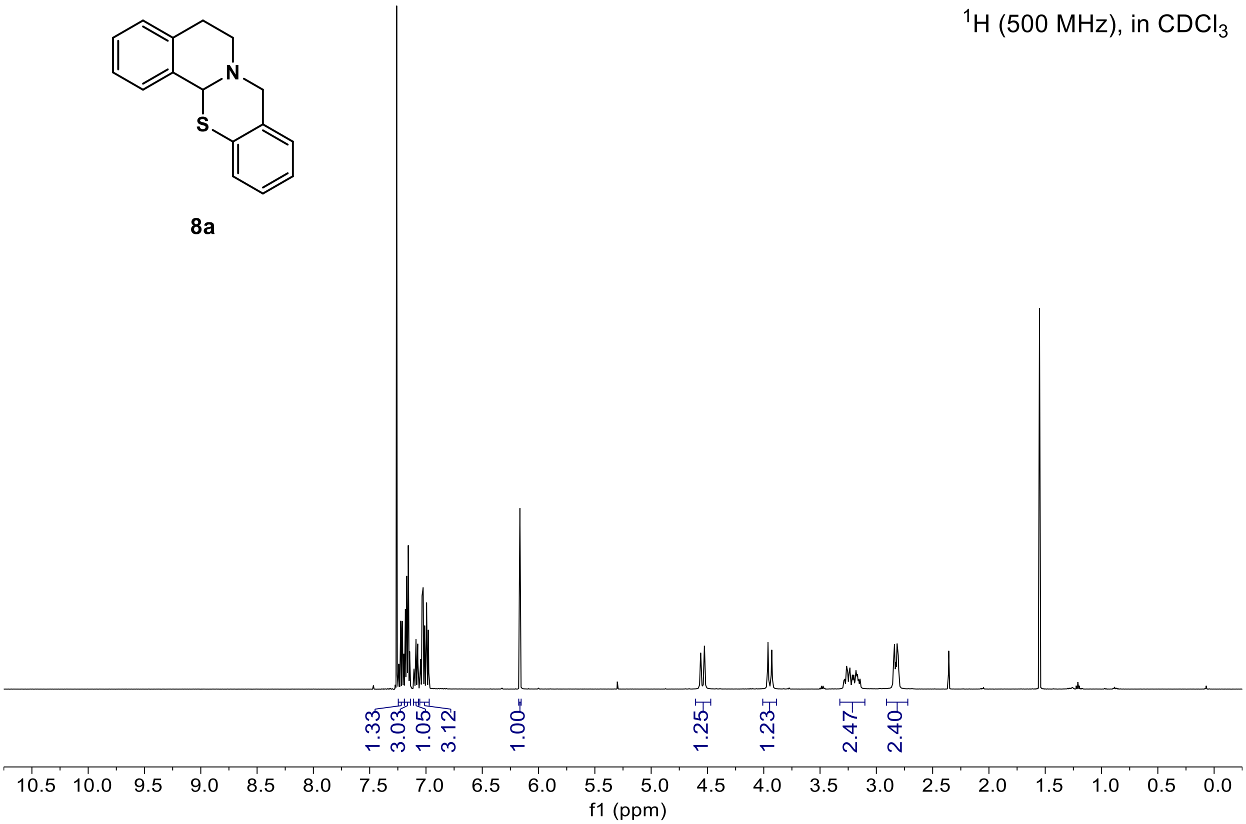
2-mercapto-5-nitrobenzaldehyde (**10c**).



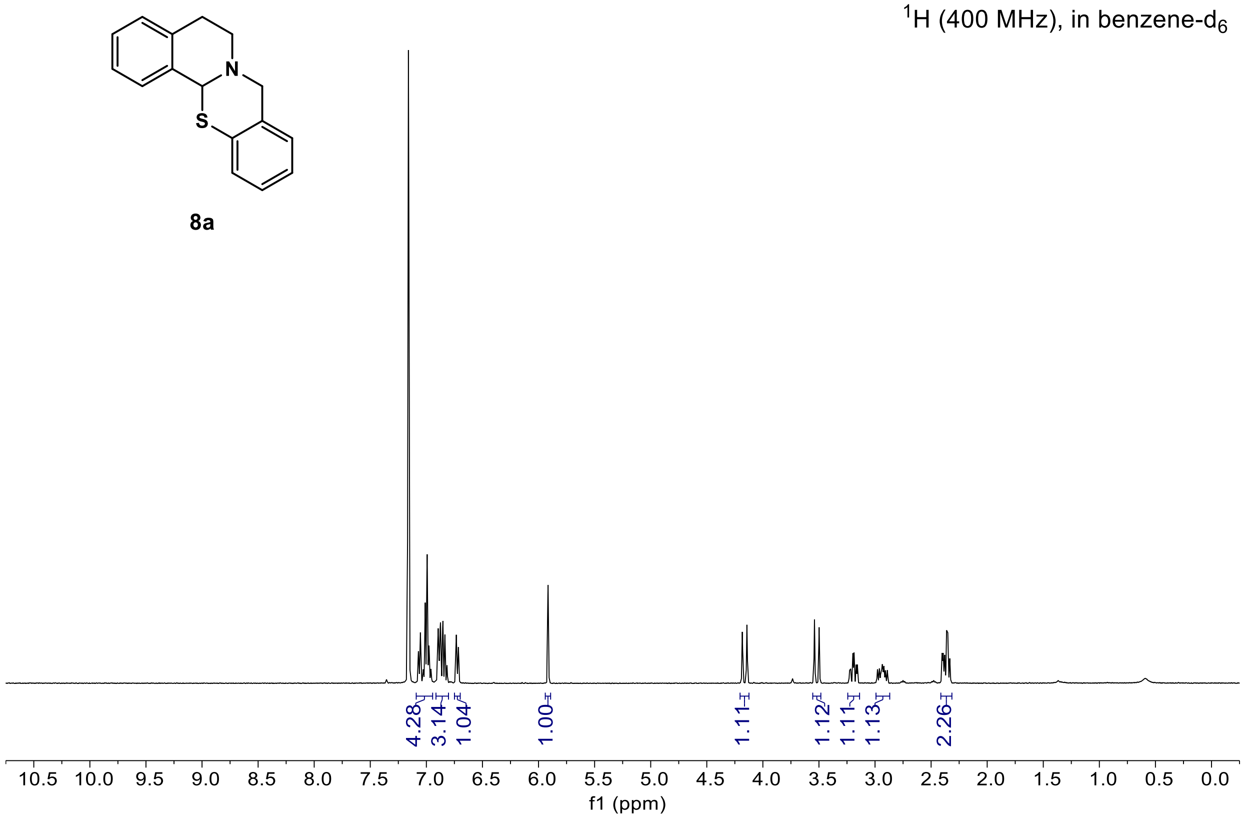
10c

In a 10 mL round bottom flask 2-fluoro-5-nitrobenzaldehyde (100 mg, 0.59 mmol), sodium sulfide (60 mg, 0.77 mmol) and DMF (1 mL) were added. The reaction was stirred for 1 h and quenched with 1 M NaOH (5 mL). The mixture was washed with CH_2Cl_2 (3 x 10 mL). The aqueous layer was acidified with 6 N HCl until formation of a white suspension (pH ~3) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude material was used without further purification. Spectroscopic data for **10c** match those previously reported in literature.[6]

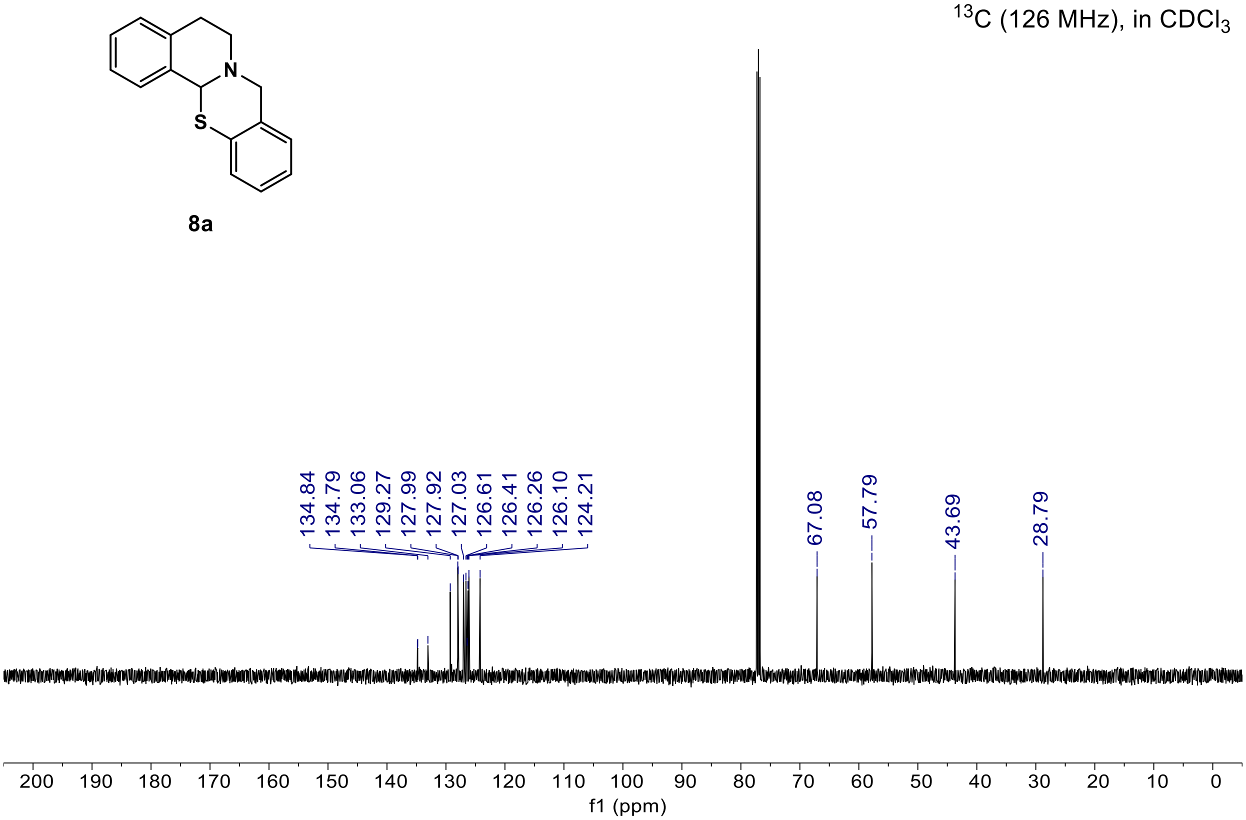
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.02 (d, *J* = 2.0 Hz, 1H), 7.37 (t, *J* = 2.7 Hz, 1H), 7.15 (ddd, *J* = 8.8, 3.2, 2.1 Hz, 1H), 7.04 (dd, *J* = 8.8, 1.9 Hz, 1H), 3.85 (d, *J* = 2.4 Hz, 3H).



8a
^{1}H (500 MHz), in CDCl$_3$
1.33
3.03
1.05
3.12
1.00
1.25
1.23
2.47
2.40
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

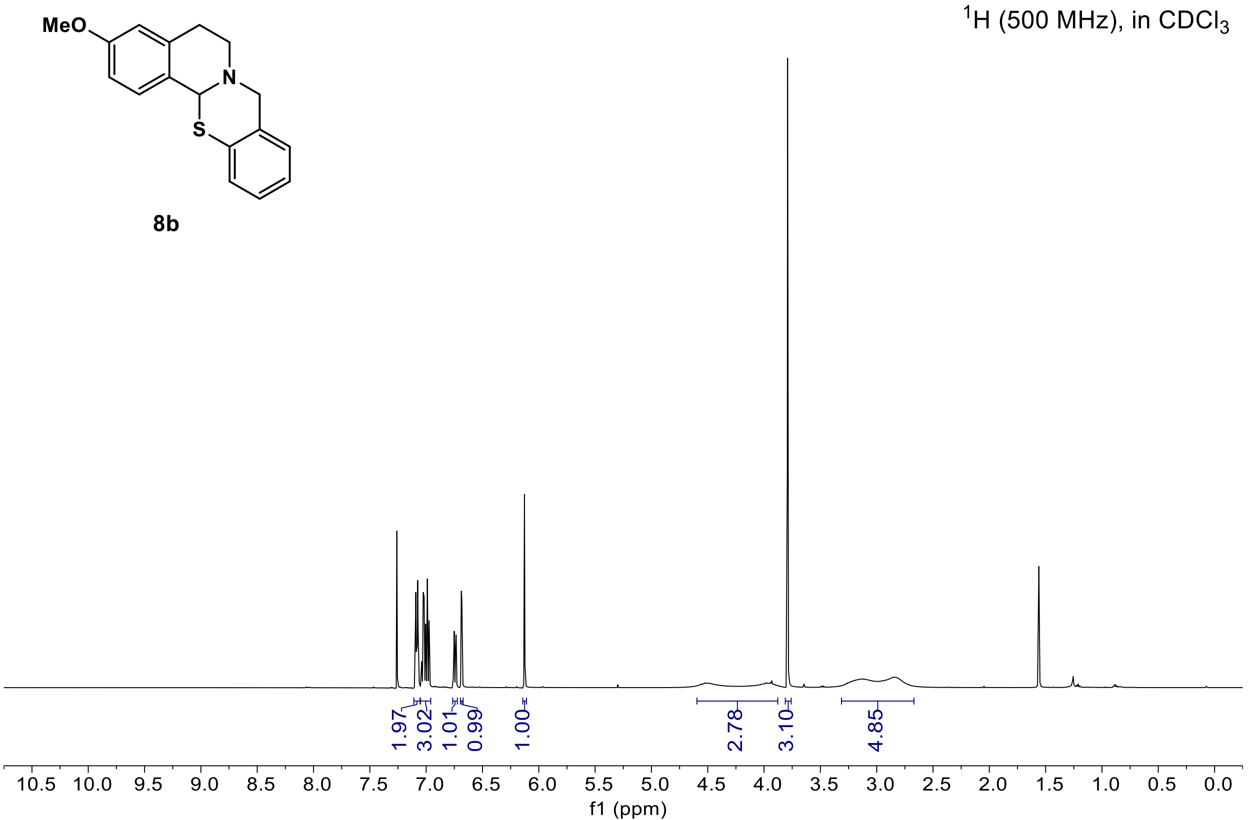


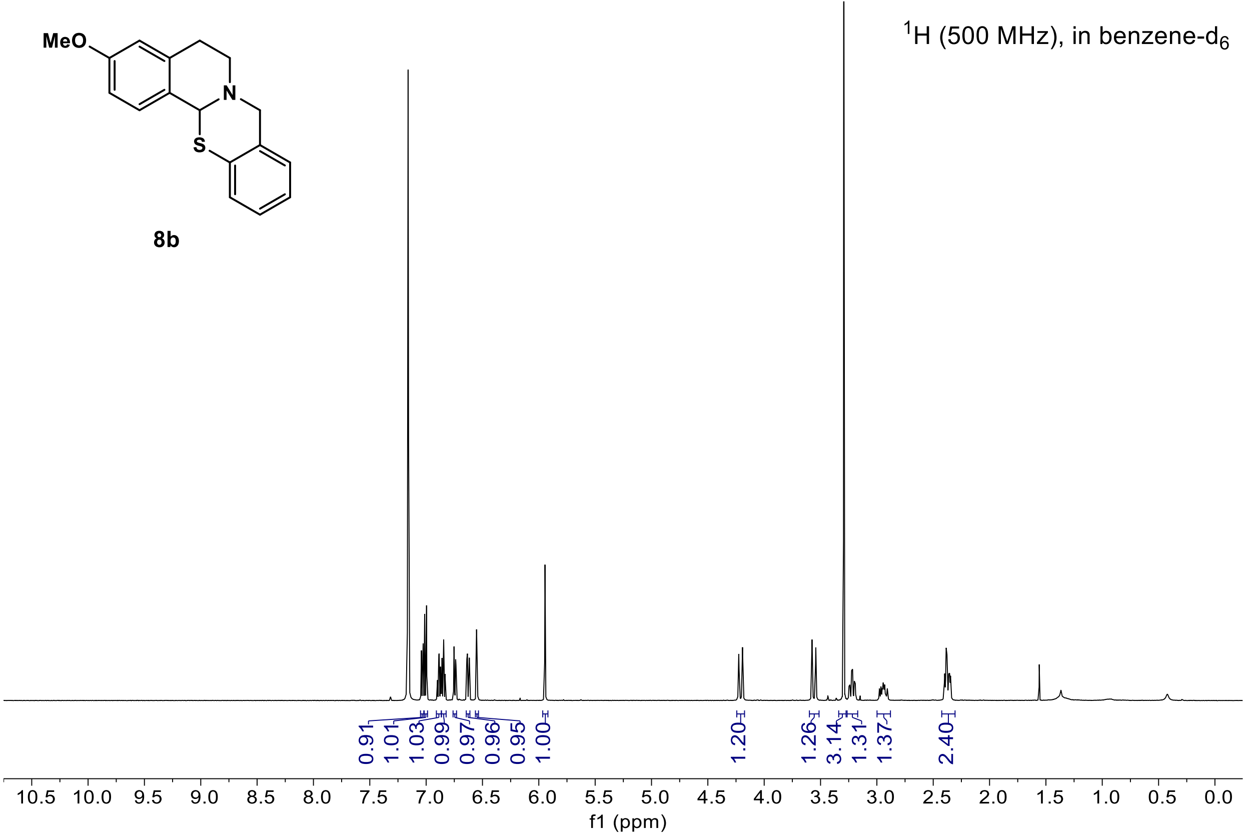
8a
^{1}H (400 MHz), in benzene-d$_6$
4.28
3.14
1.04
1.00
1.11
1.12
1.11
1.13
2.26
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

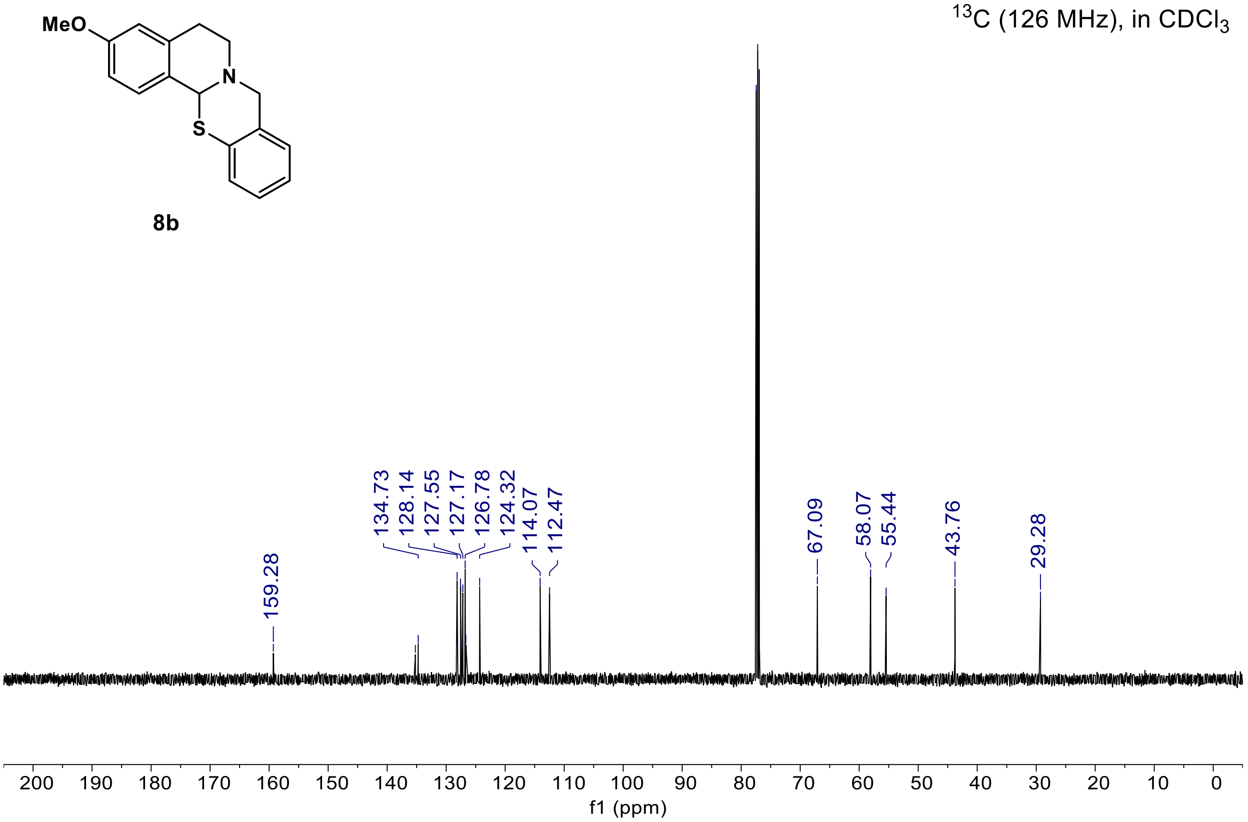


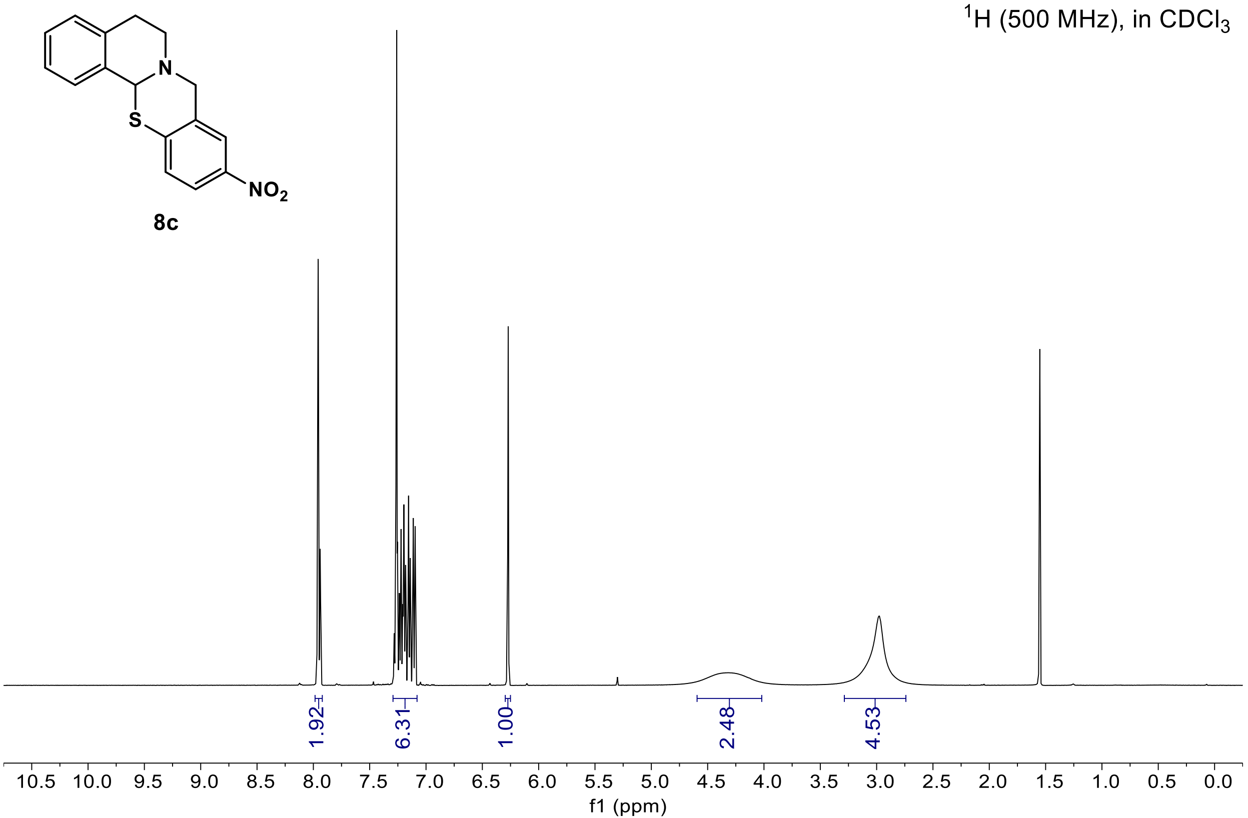
8a

^{13}C (126 MHz), in $CDCl_3$


MeO
N
S
8b
^{1}H (500 MHz), in CDCl$_3$
1.97
3.02
1.01
0.99
1.00
2.78
3.10
4.85
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

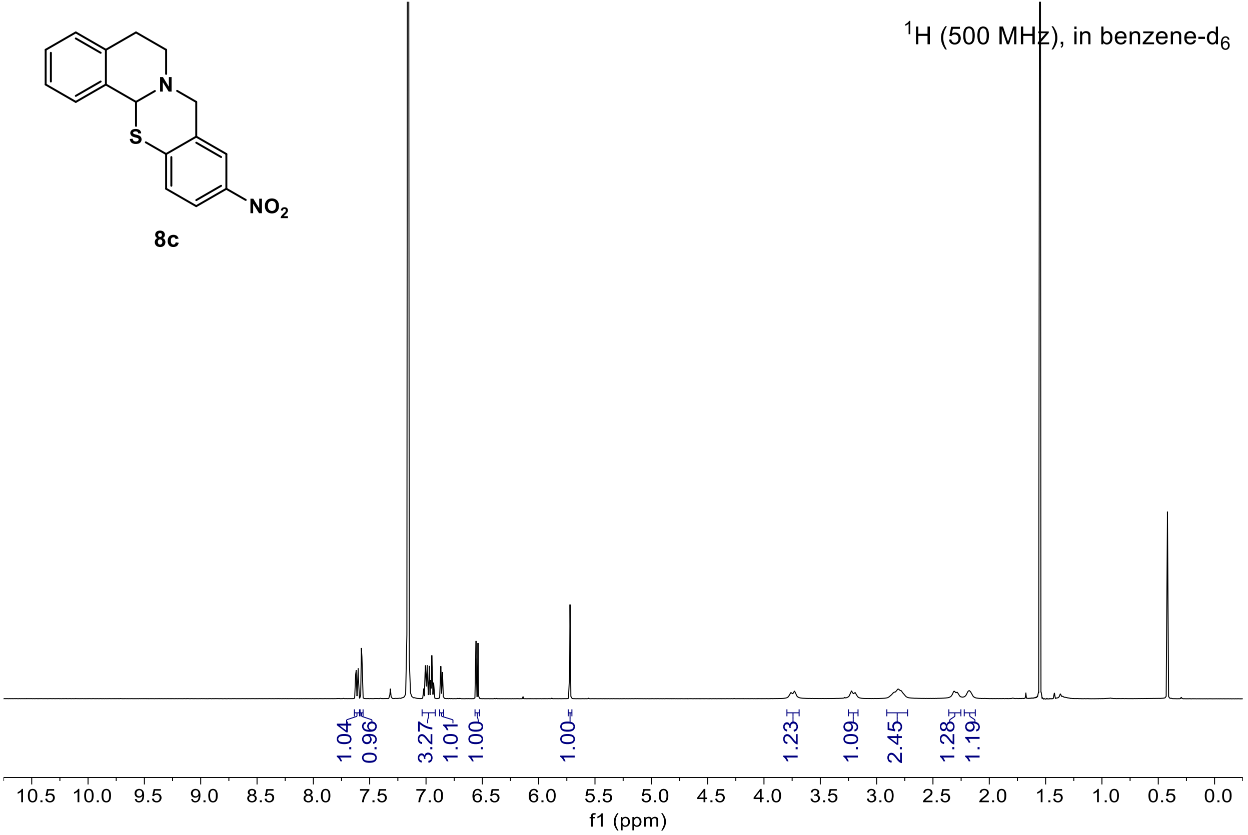

MeO
N
S
8b
^{1}H (500 MHz), in benzene-d$_6$
0.91
1.01
1.03
0.99
0.97
0.96
0.95
1.00
1.20
1.26
3.14
1.31
1.37
2.40
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


MeO
N
S
8b
^{13}C (126 MHz), in CDCl$_3$
159.28
134.73
128.14
127.55
127.17
126.78
124.32
114.07
112.47
67.09
58.07
55.44
43.76
29.28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



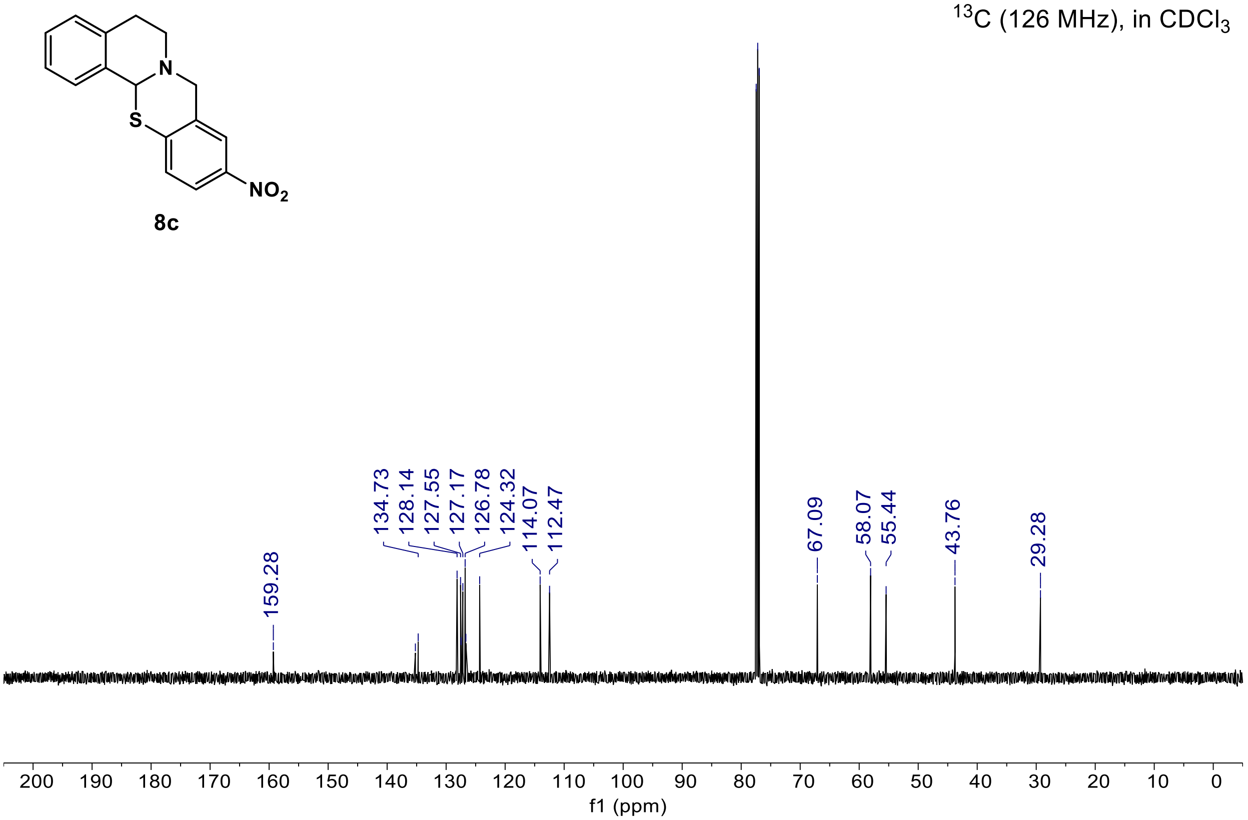
8c

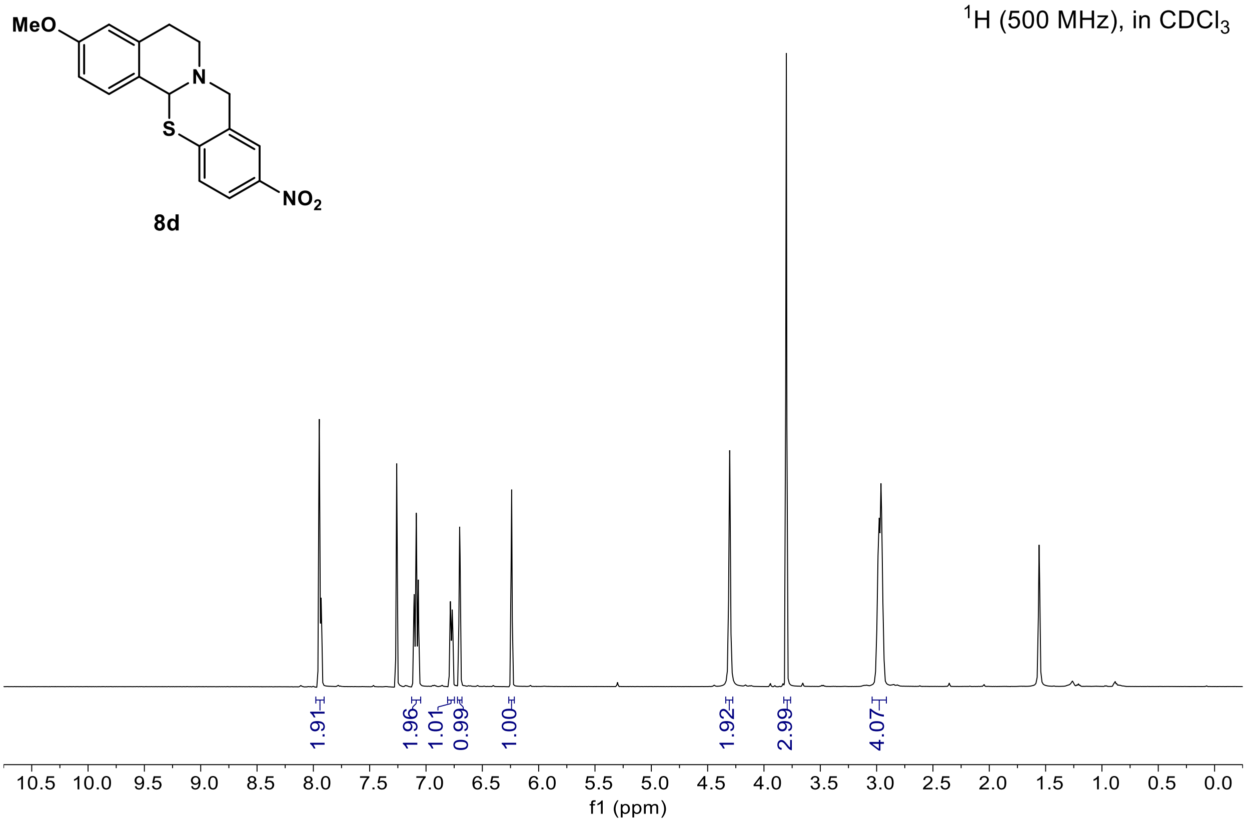
N
S
NO2
^{1}H (500 MHz), in CDCl$_3$
1.92
6.31
1.00
2.48
4.53
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

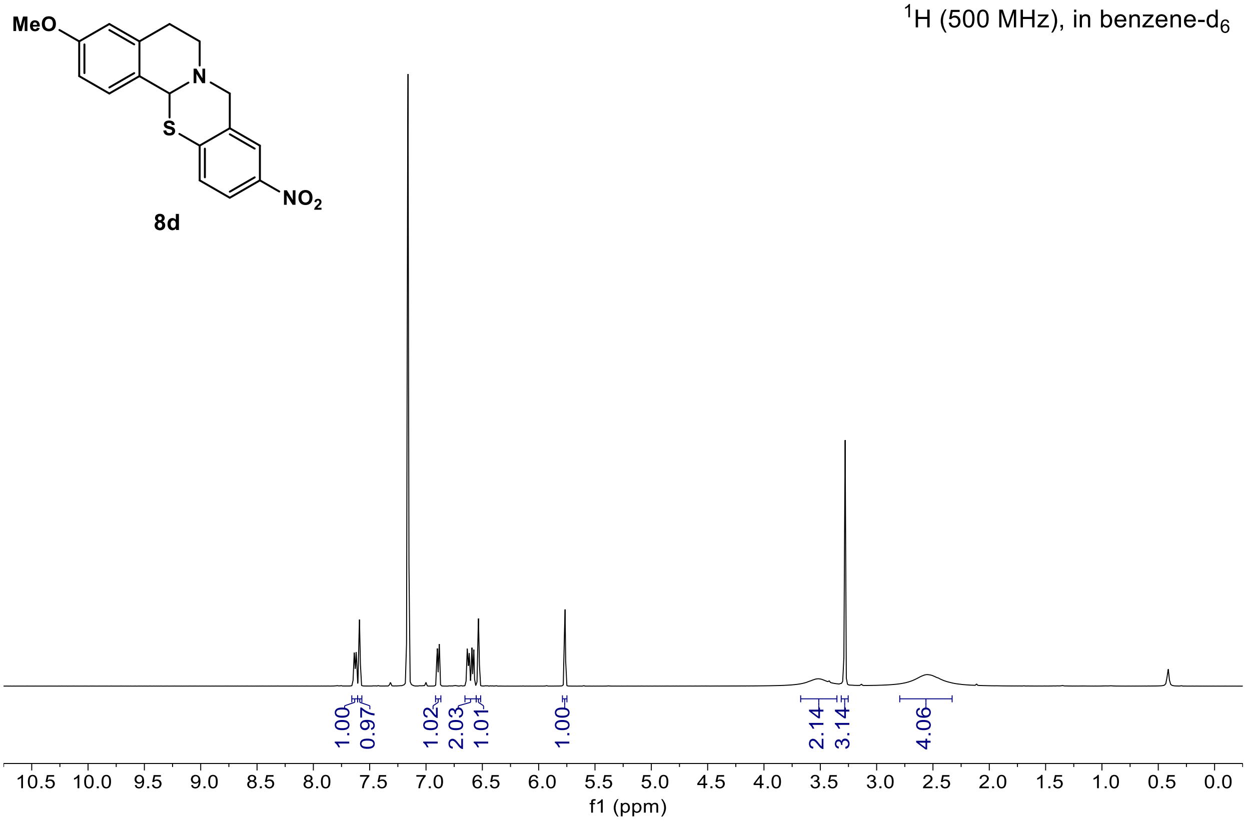


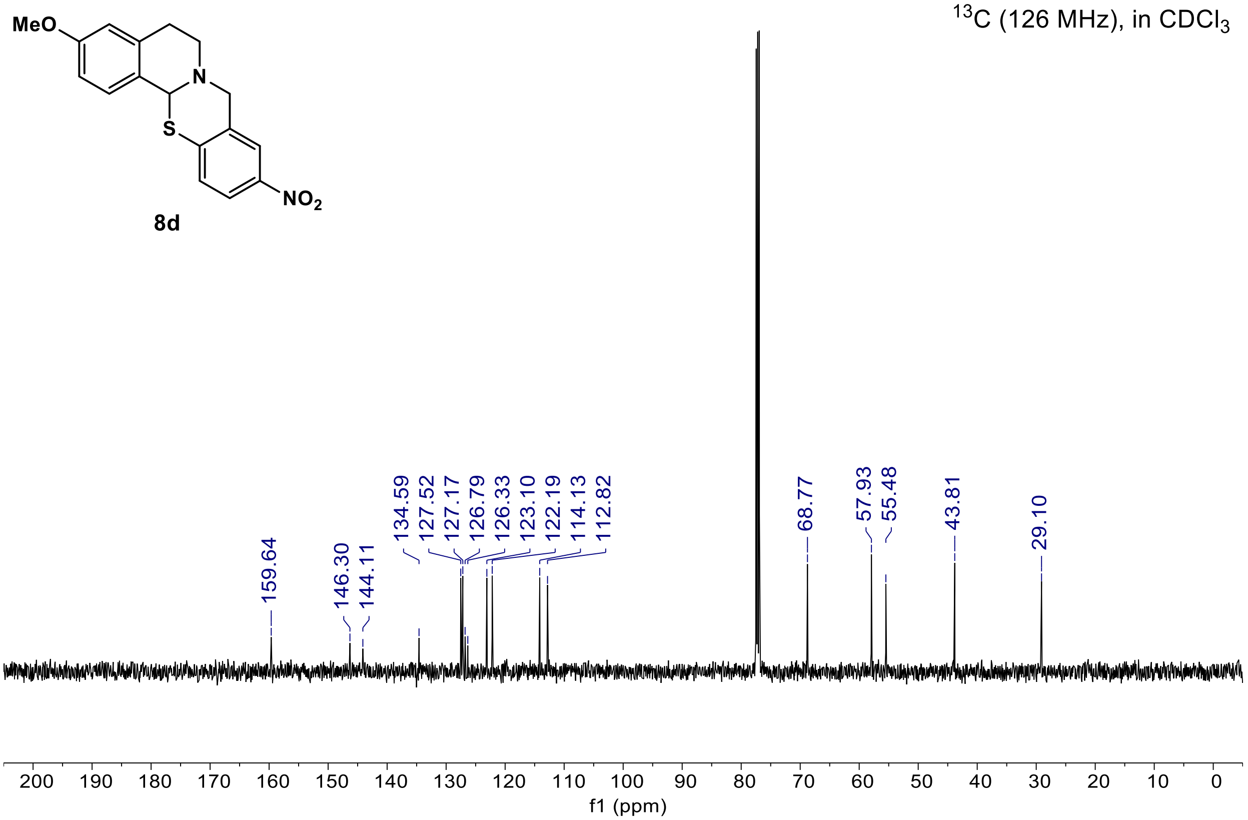
8c

N
S
NO2
^{1}H (500 MHz), in benzene-d$_6$
1.04
0.96
3.27
1.01
1.00
1.00
1.23
1.09
2.45
1.28
1.19
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


8c
N
S
NO2
13C (126 MHz), in CDCl3
159.28
134.73
128.14
127.55
127.17
126.78
124.32
114.07
112.47
67.09
58.07
55.44
43.76
29.28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

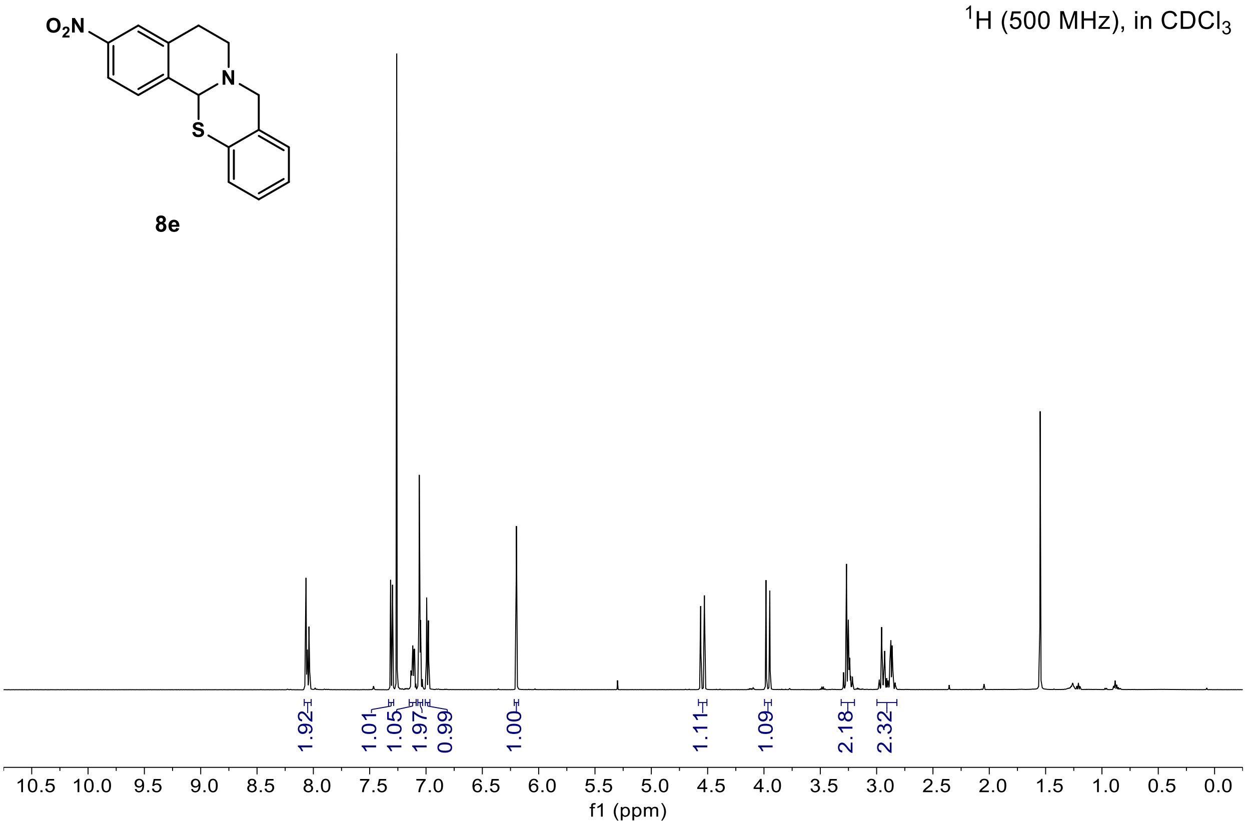

^{1}H (500 MHz), in CDCl$_3$
MeO
N
S
NO$_2$
8d
1.91
1.96
1.01
0.99
1.00
1.92
2.99
4.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


^{1}H (500 MHz), in benzene-d$_6$
MeO
N
S
NO$_2$
8d
1.00
0.97
1.02
2.03
1.01
1.00
2.14
3.14
4.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



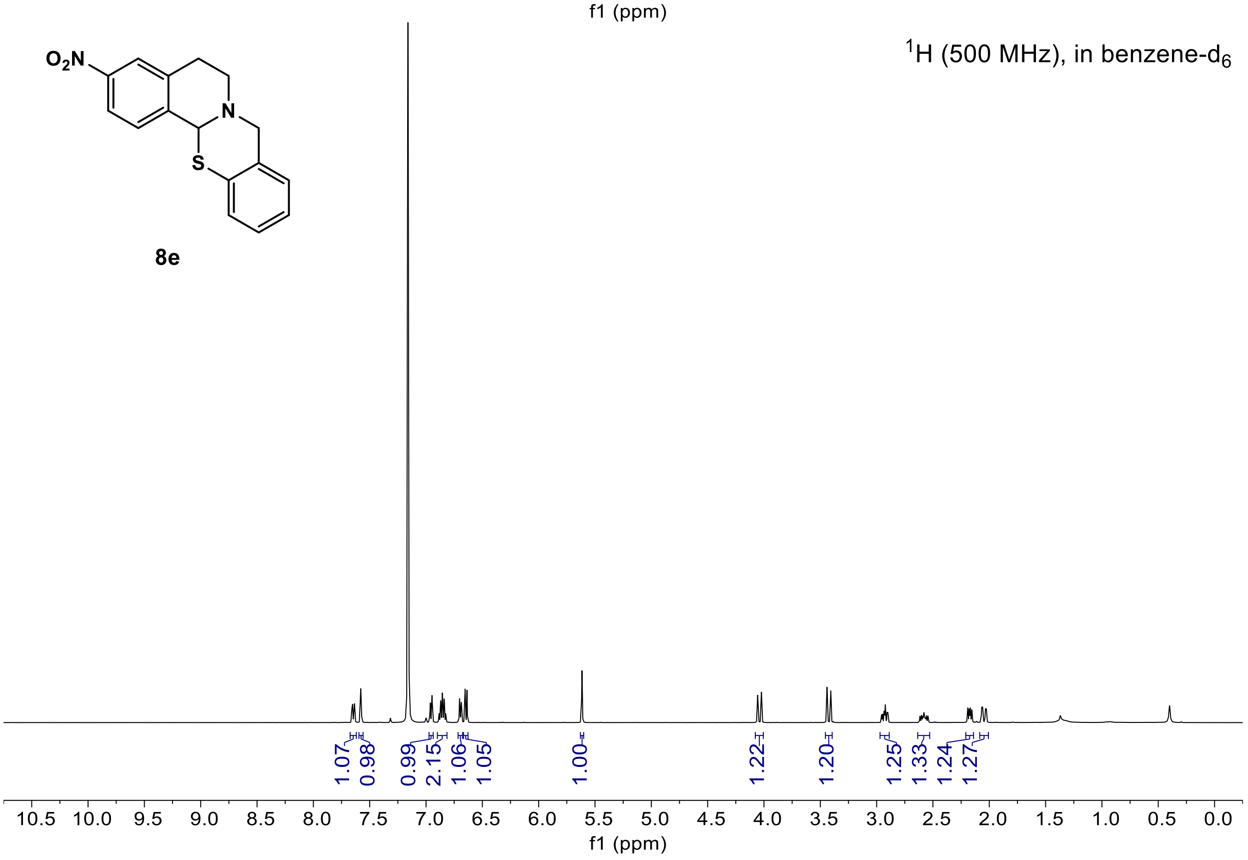
8d

^{13}C (126 MHz), in CDCl$_3$



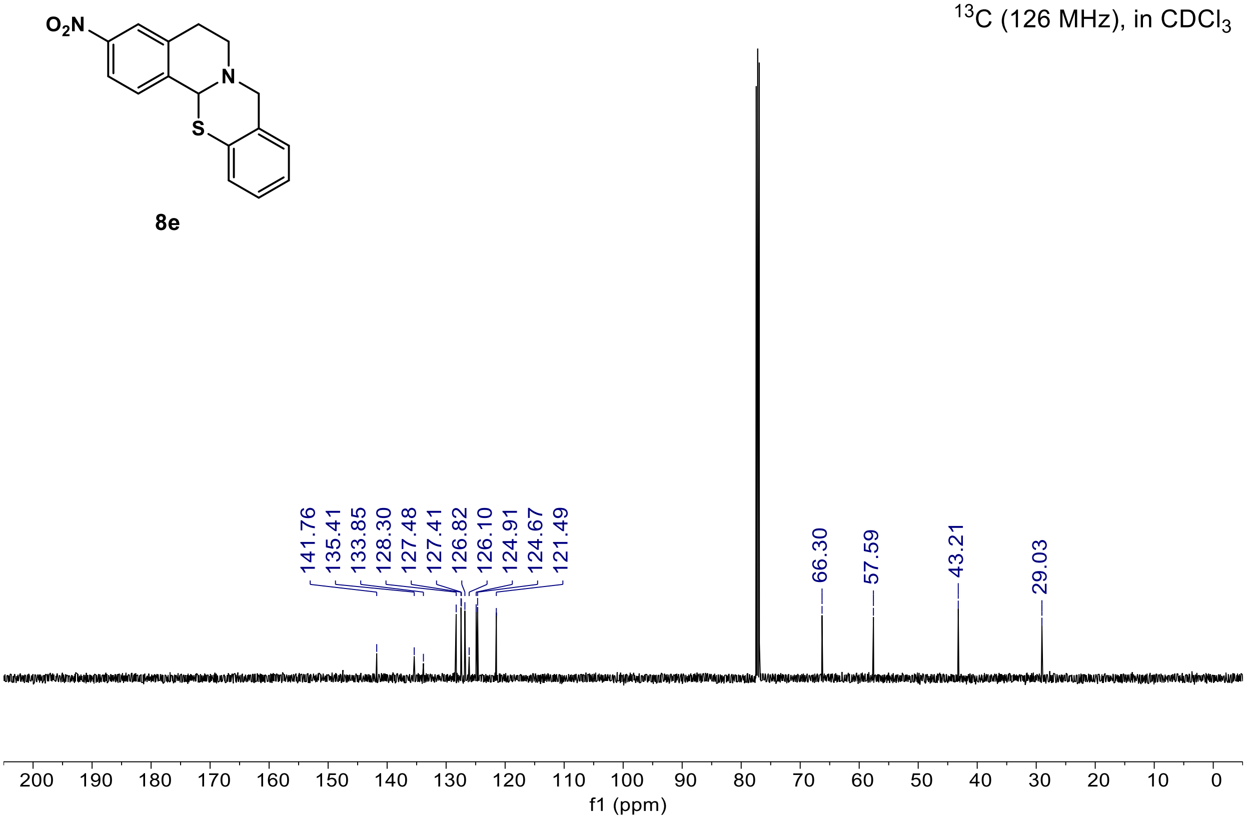
O$_2$N
N
S
^{1}H (500 MHz), in CDCl$_3$
1.92
1.01
1.05
1.97
0.99
1.00
1.11
1.09
2.18
2.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

8e



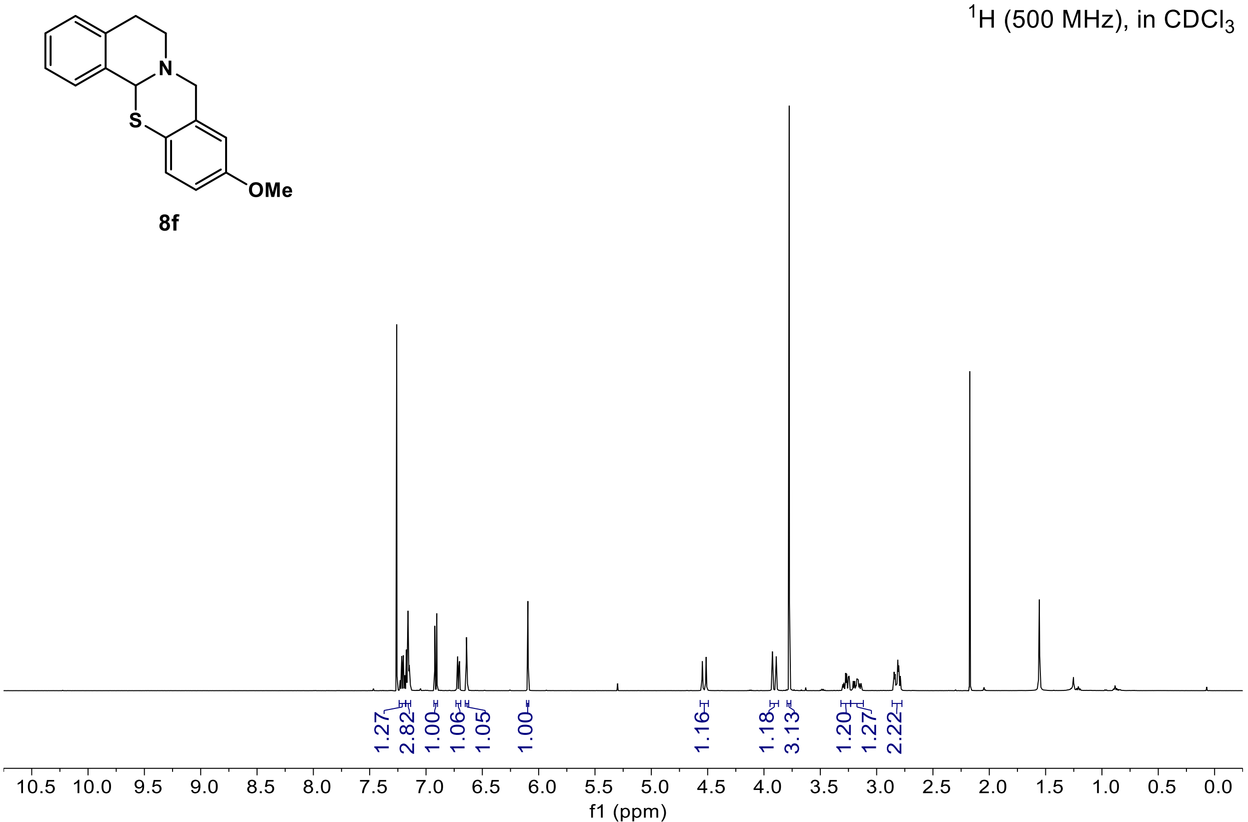
O$_2$N
N
S
^{1}H (500 MHz), in benzene-d$_6$
1.07
0.98
0.99
2.15
1.06
1.05
1.00
1.22
1.20
1.25
1.33
1.24
1.27
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

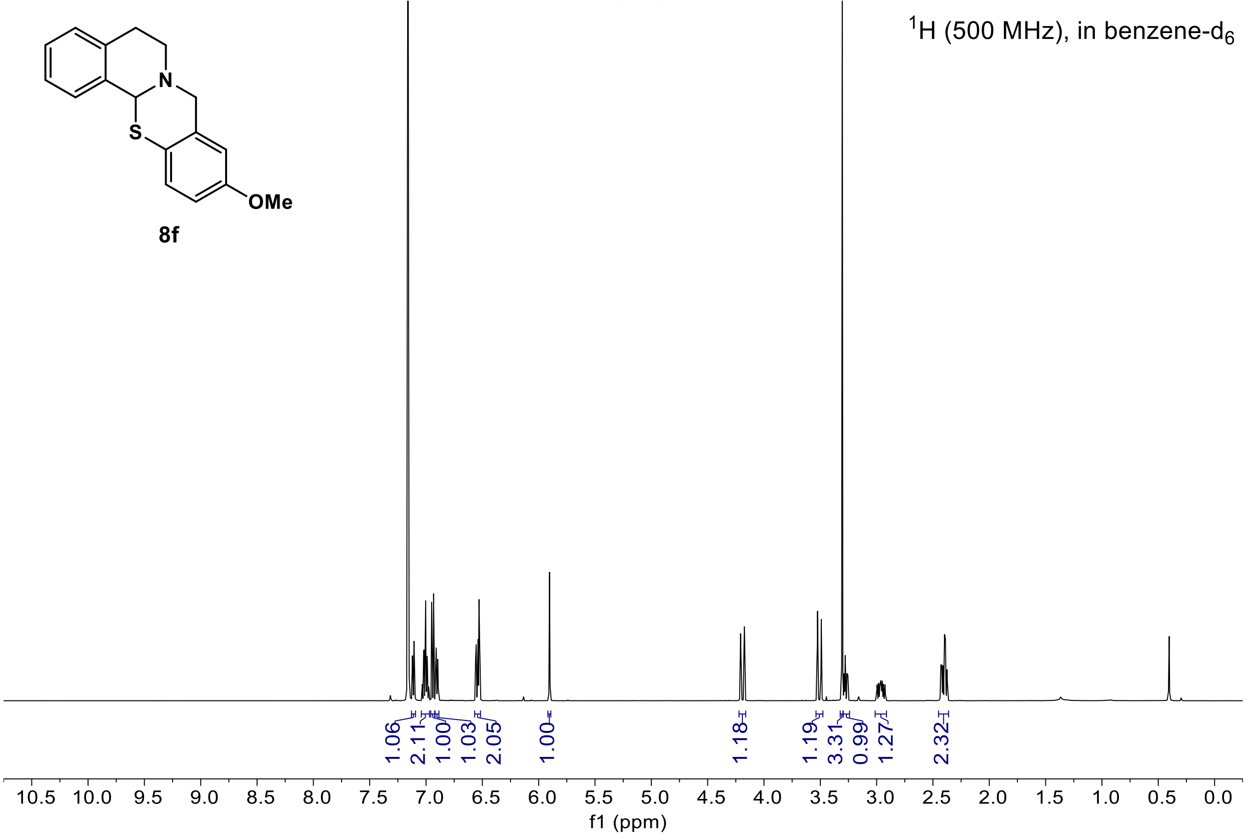
8e

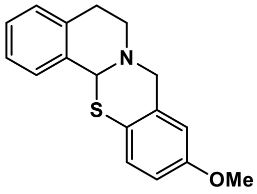


8e

^{13}C (126 MHz), in $CDCl_3$

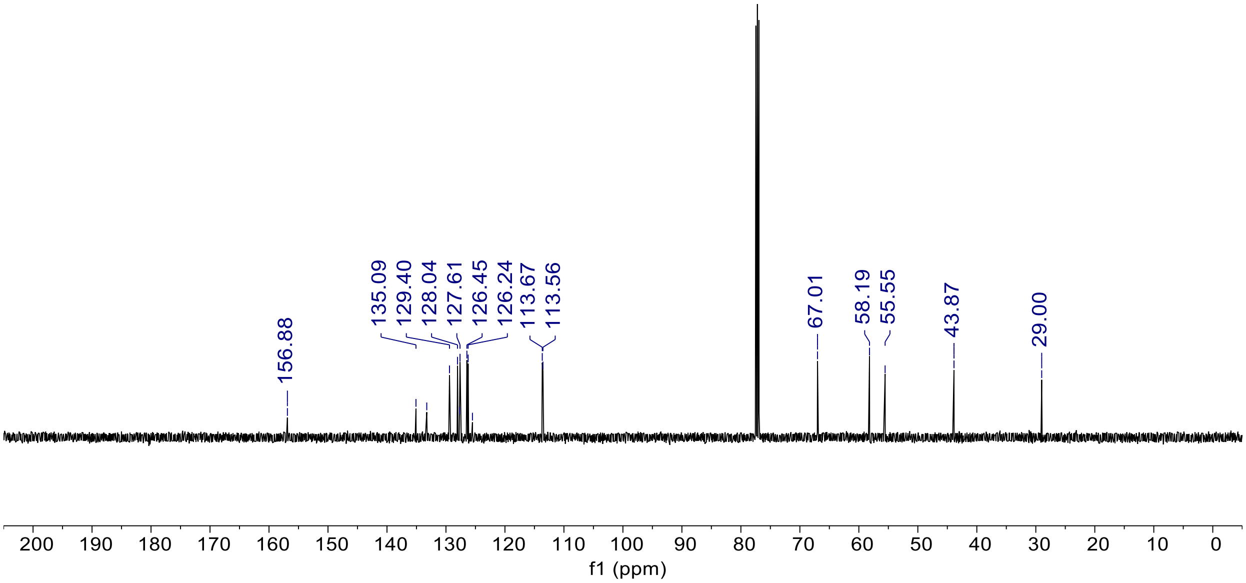

N
S
OMe
8f
^{1}H (500 MHz), in CDCl$_3$
1.27
2.82
1.00
1.06
1.05
1.00
1.16
1.18
3.13
1.20
1.27
2.22
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

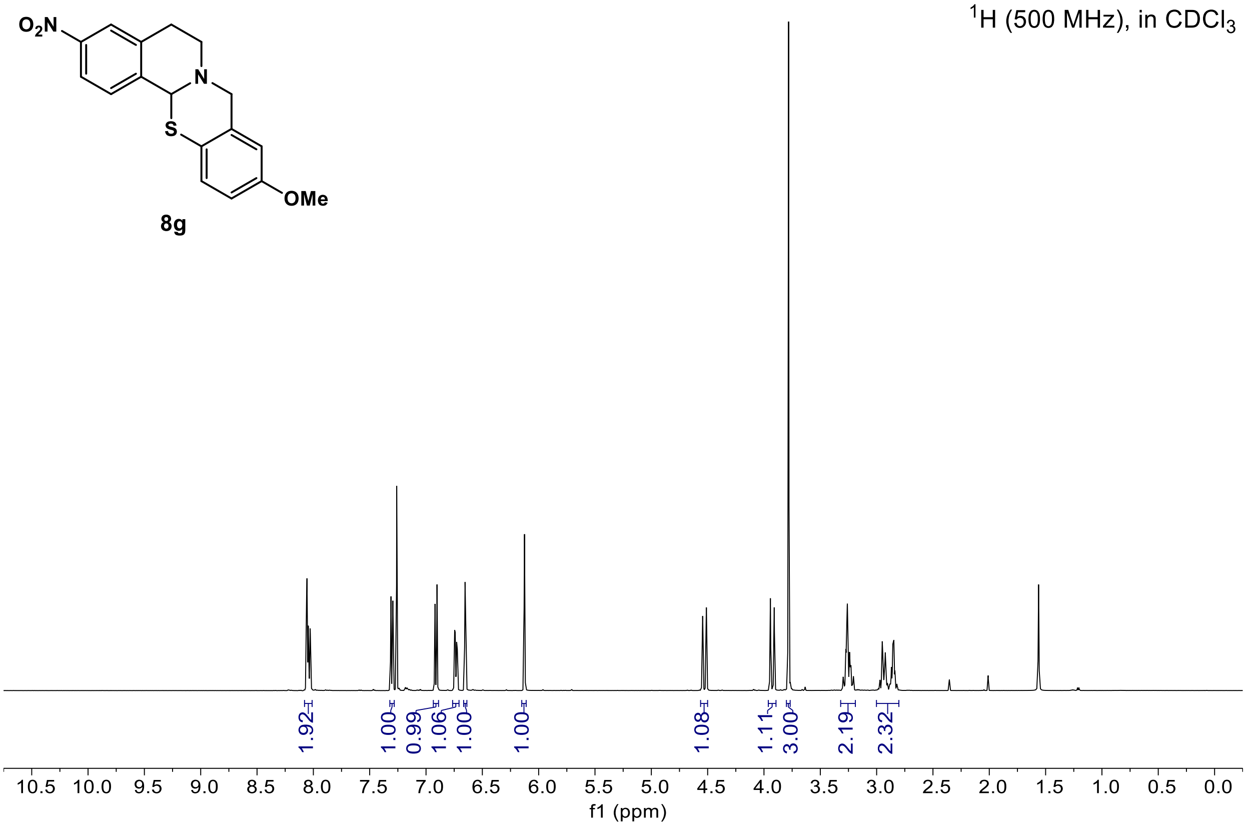

N
S
OMe
8f
^{1}H (500 MHz), in benzene-d$_6$
1.06
2.11
1.00
1.03
2.05
1.00
1.18
1.19
3.31
0.99
1.27
2.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

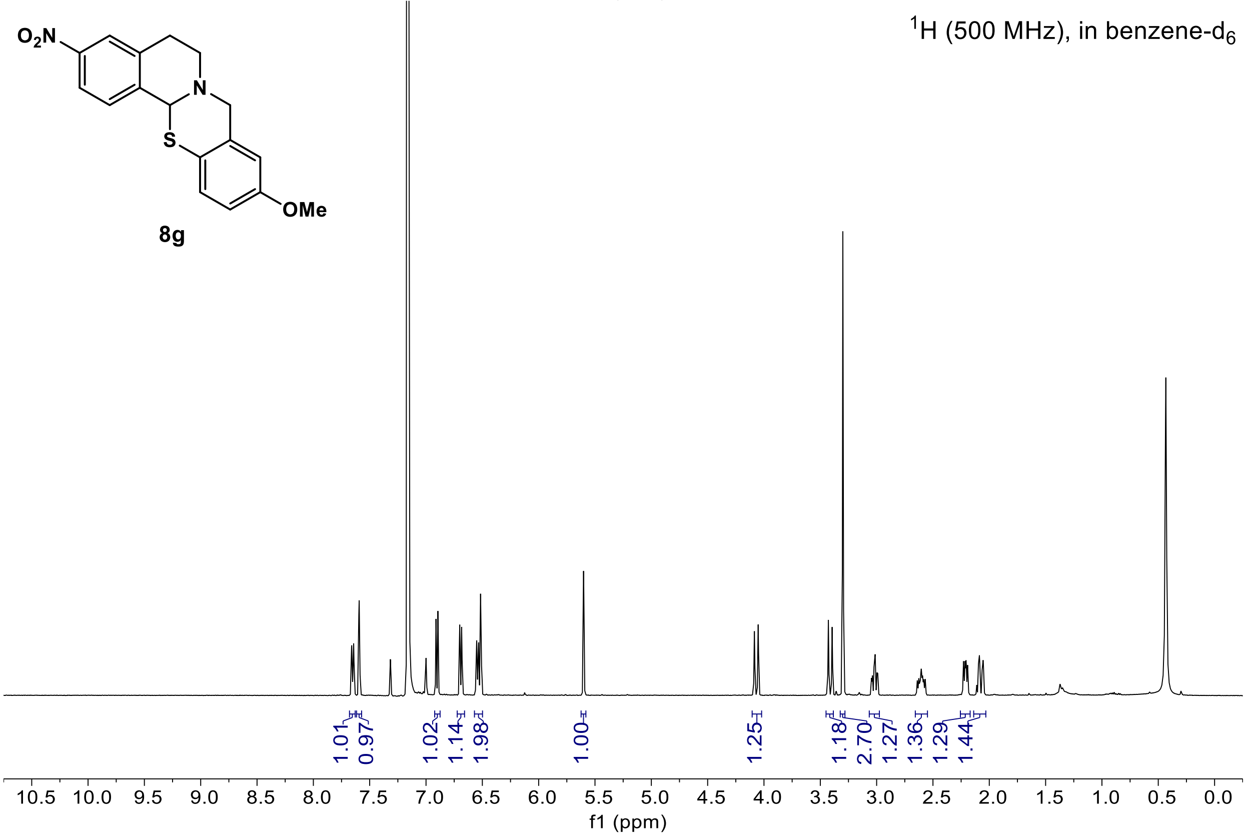


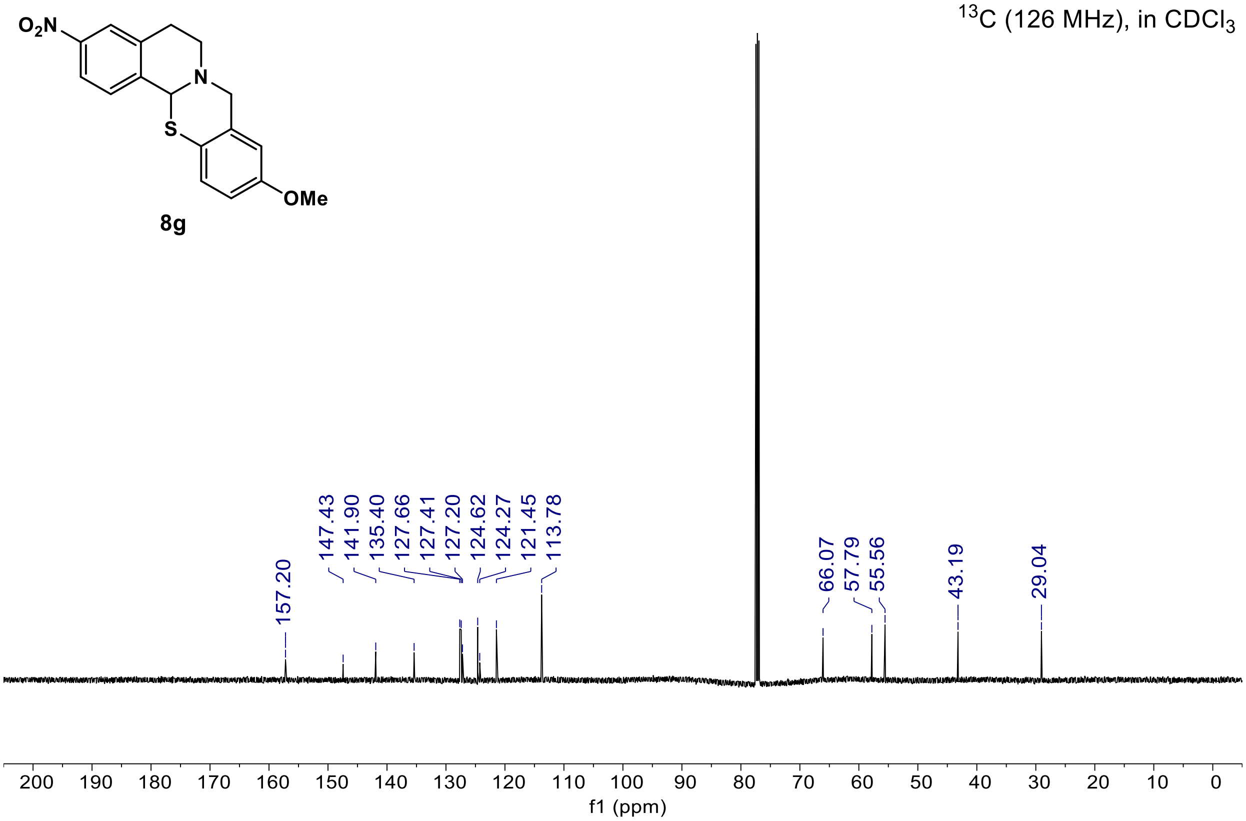
8f

^{13}C (126 MHz), in $CDCl_3$




8g
O_2N
N
S
OMe
^1H (500 MHz), in $CDCl_3$
1.92
1.00
0.99
1.06
1.00
1.00
1.08
1.11
3.00
2.19
2.32
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

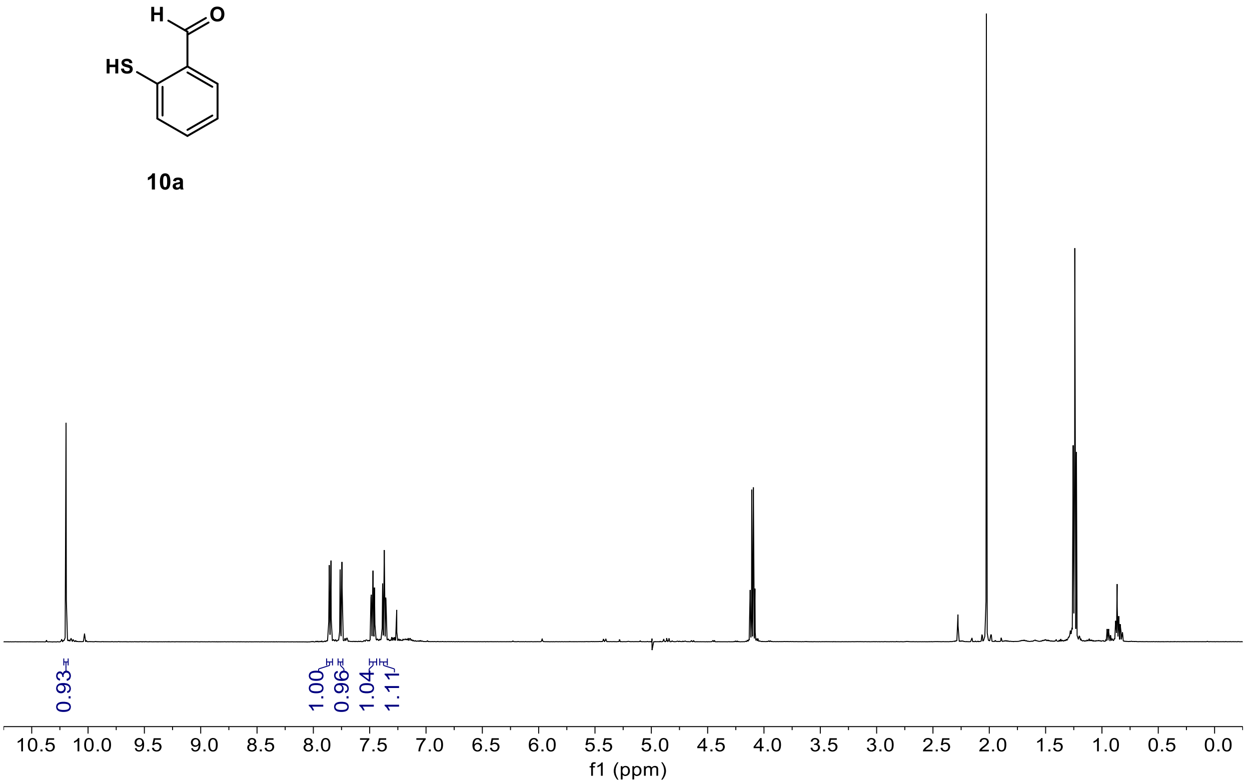

8g
O_2N
N
S
OMe
^1H (500 MHz), in benzene-d_6
1.01
0.97
1.02
1.14
1.98
1.00
1.25
1.18
2.70
1.27
1.36
1.29
1.44
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



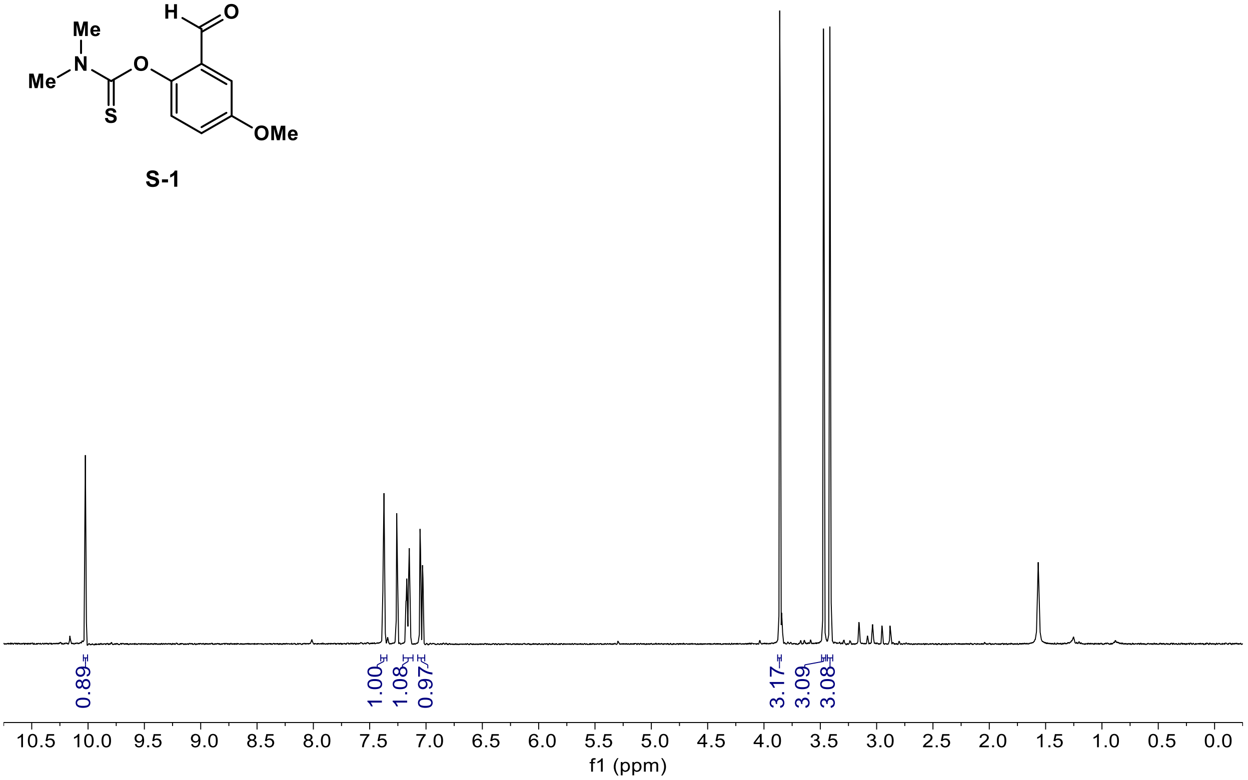
8g

^{13}C (126 MHz), in CDCl$_3$

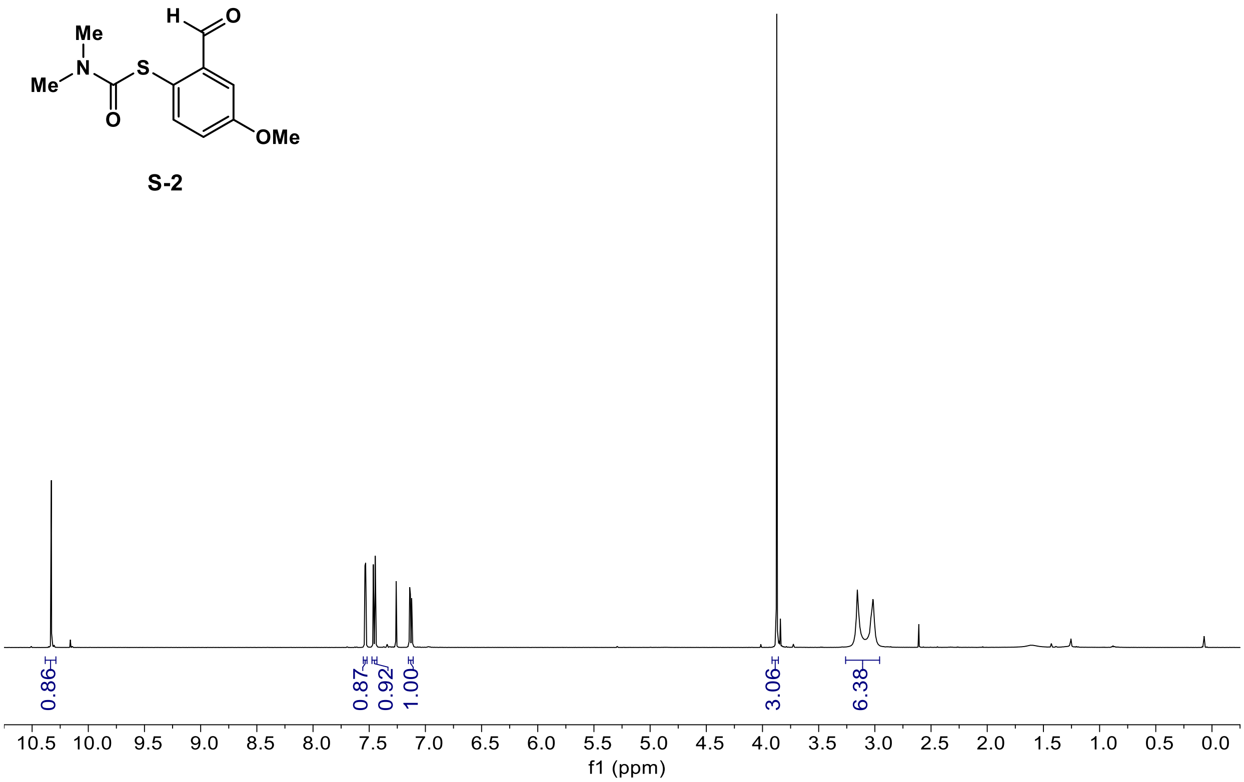
^{1}H (500 MHz), in CDCl$_3$



^{1}H (500 MHz), in CDCl$_3$

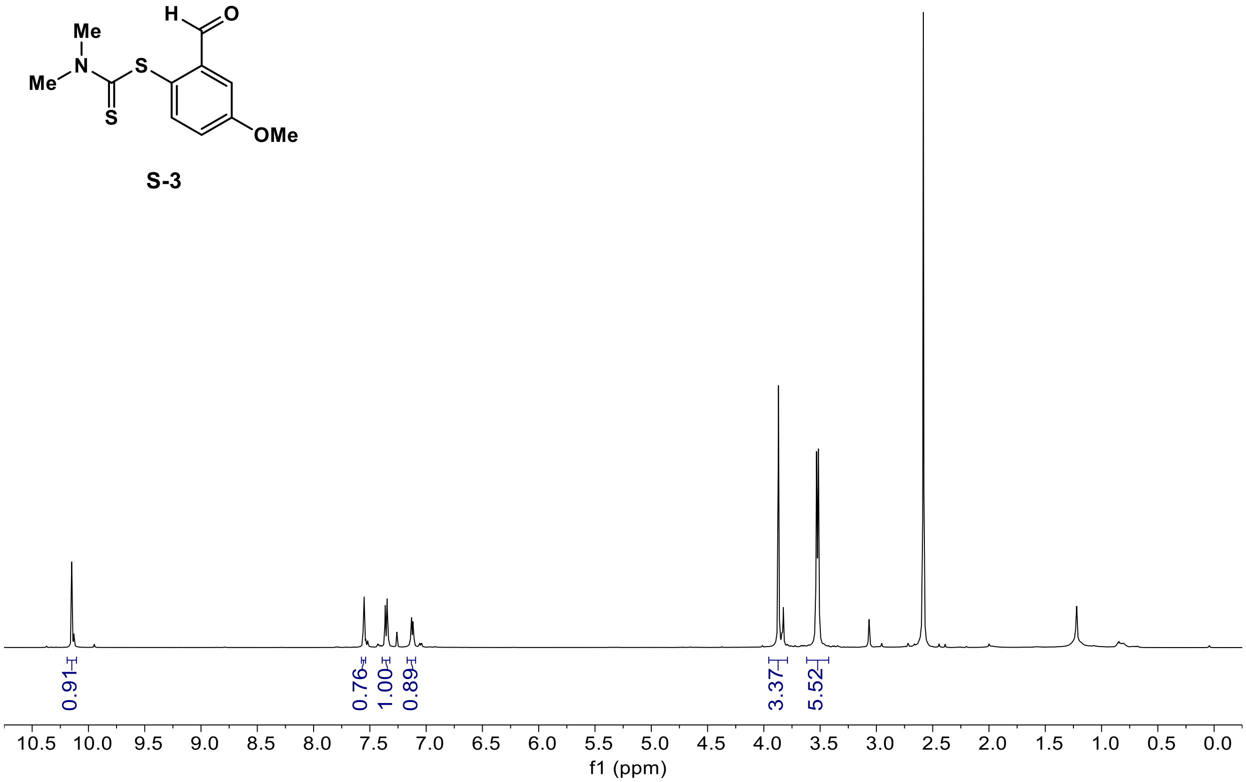


^1H (500 MHz), in $CDCl_3$



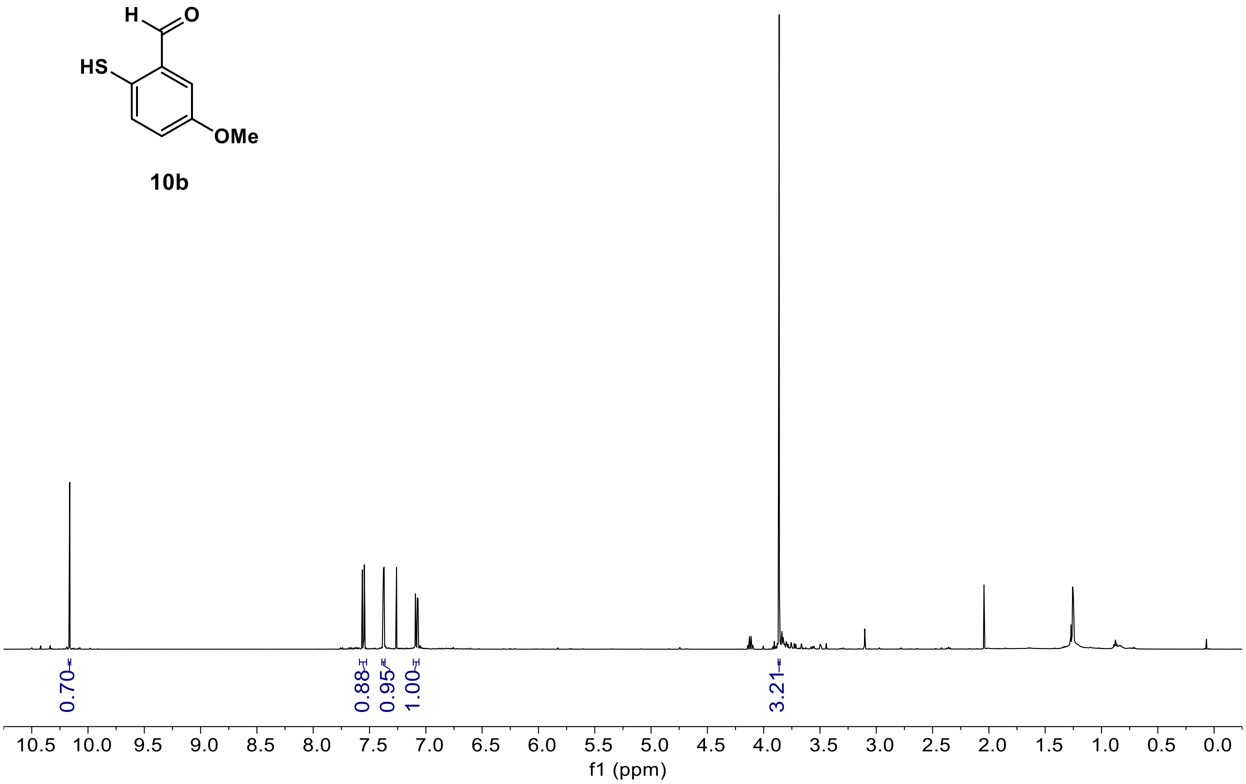
S-2

^1H (500 MHz), in $CDCl_3$



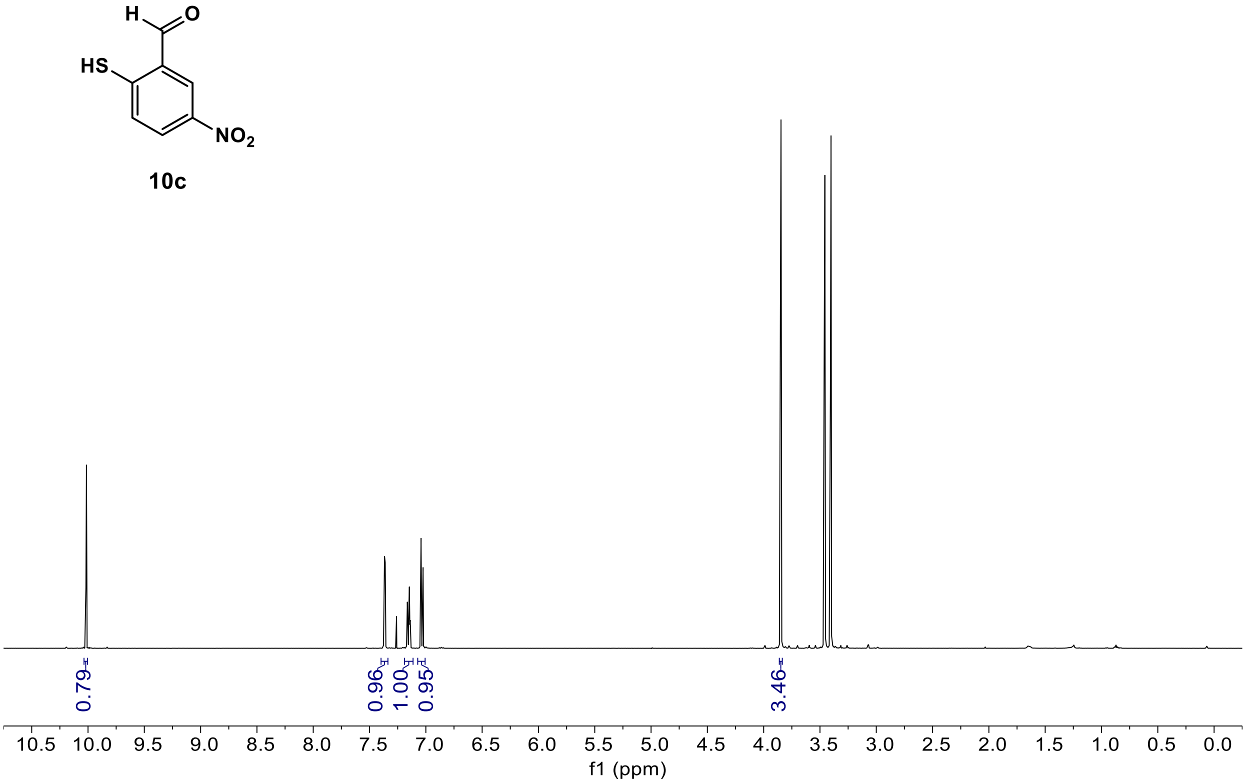
S-3

^1H (500 MHz), in $CDCl_3$



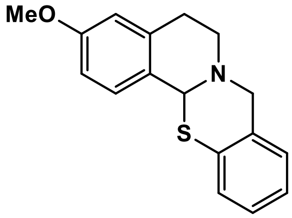
10b

^1H (500 MHz), in $CDCl_3$



10c

Variable temperature ^{1}H NMR of 8b



8b

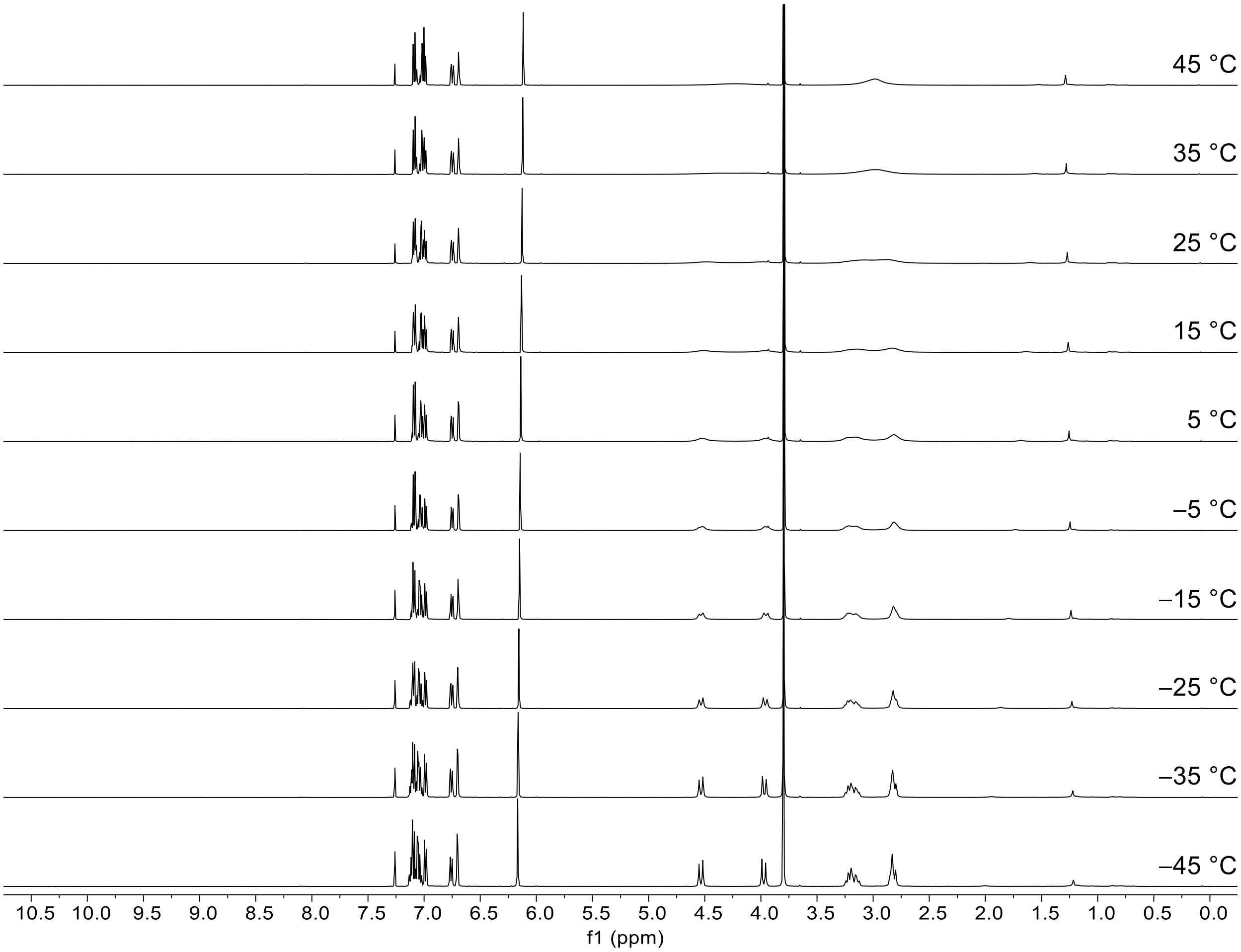
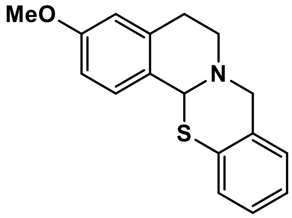


Figure S-1. Variable temperature ^{1}H NMR spectroscopy of **8b** in $CDCl_3$ from –45 °C to 45 °C.

^{1}H NMR solvent screen of compound 8b



8b

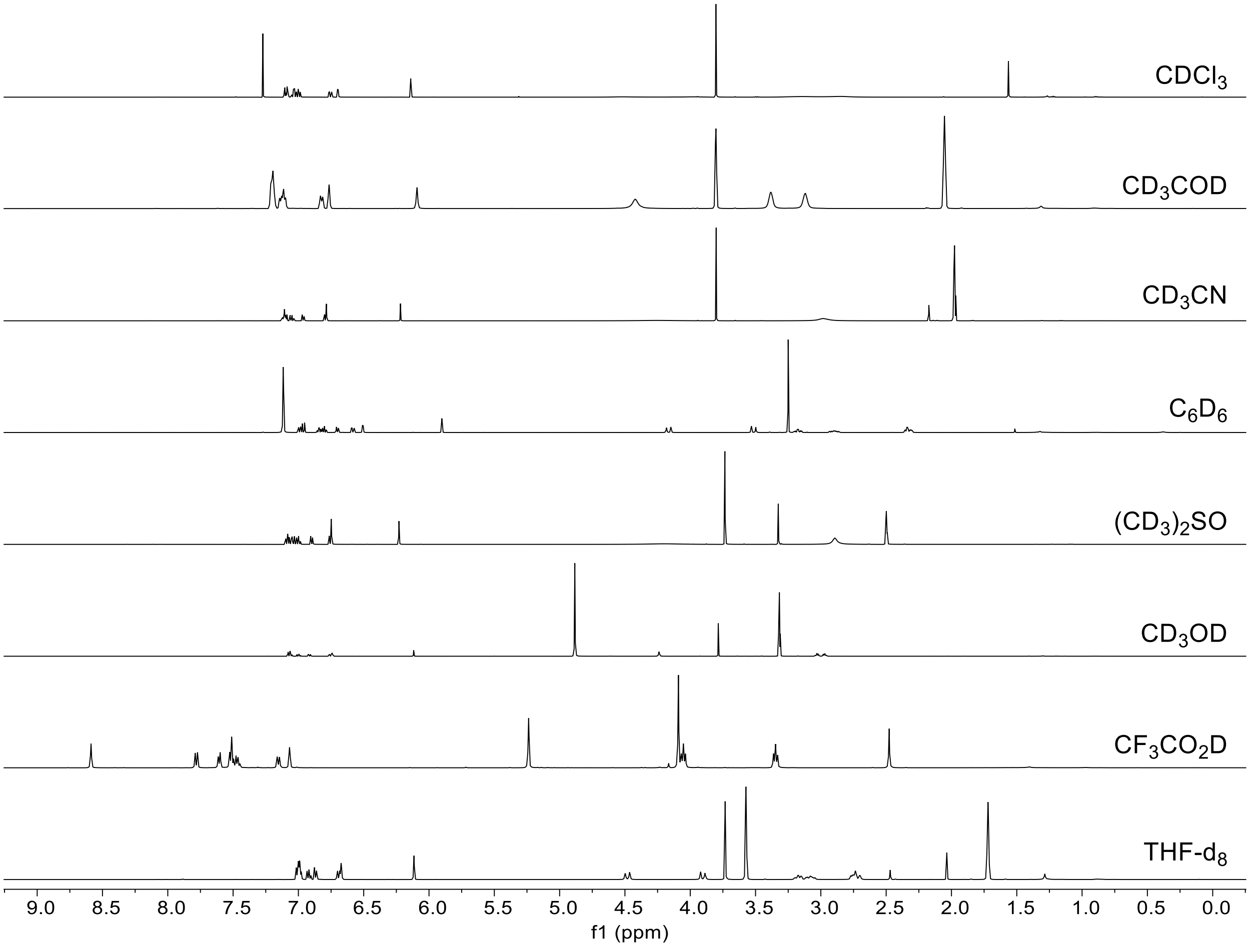


Figure S-2. ^{1}H NMR solvent screen of compound **8b**.

^{1}H NMR (500 MHz, D_2O) δ 7.42 – 7.29 (m, 4H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.04 (m, 2H), 6.39 (s, 1H), 4.47 (s, 1H), 4.04 (s, 3H), 3.30 – 3.18 (m, 4H).

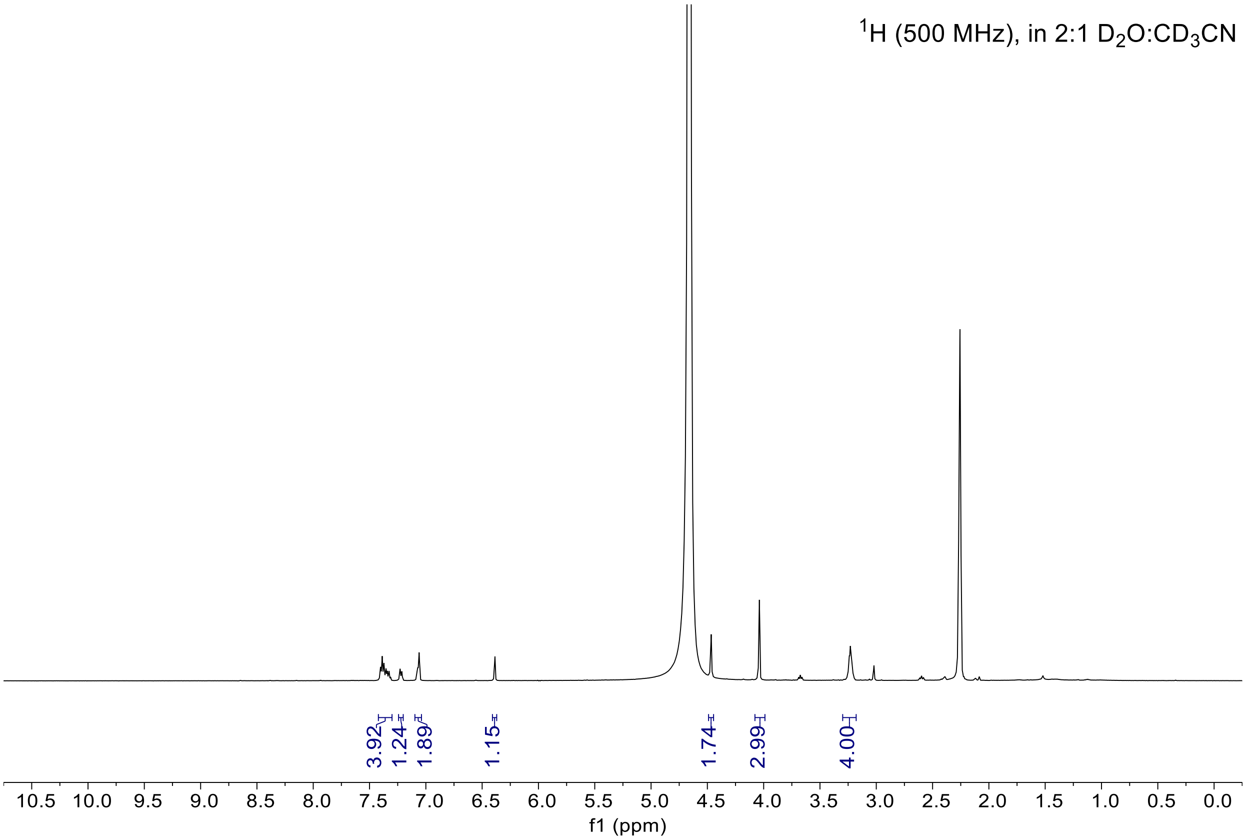
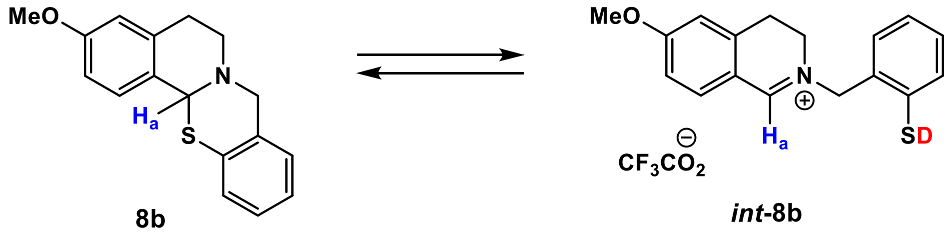


Figure S-3. ^{1}H NMR of compound **8b** in 2:1 D_2O:CD_3CN.

Chemically induced dynamic ^{1}H NMR spectroscopy of 8b



8b

H$_a$ 6.14 ppm

***int*-8b**

H$_a$ 8.57 ppm

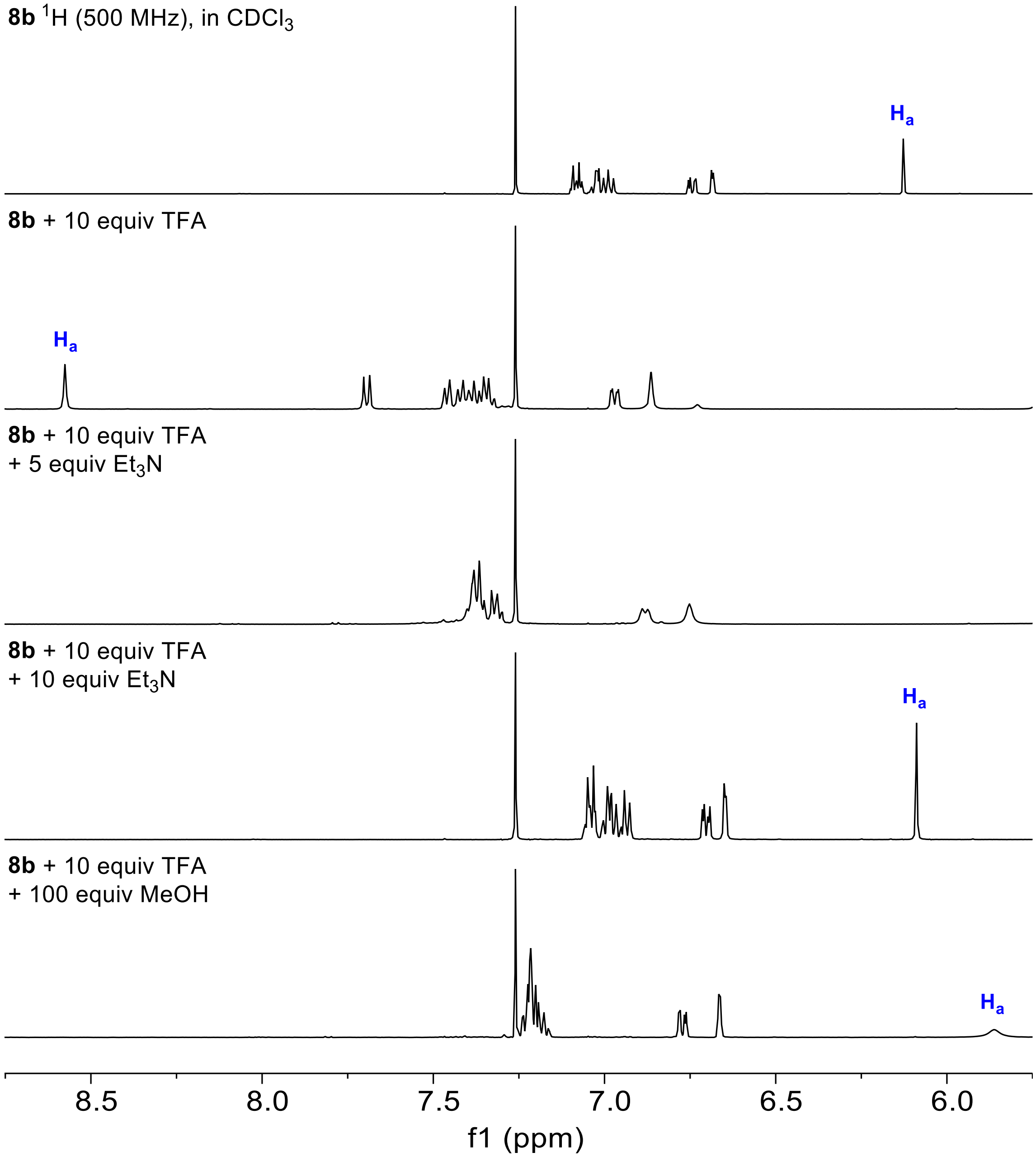
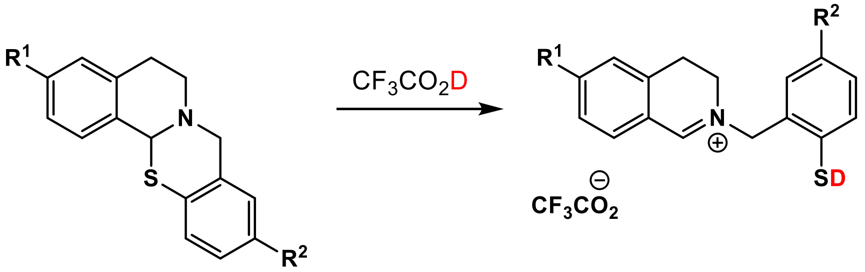
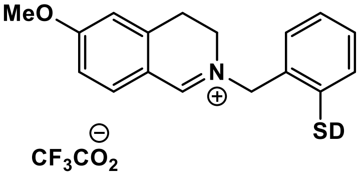


Figure S-4. Chemically induced dynamic iminium formation (*int*-**8b**) and N,S-acetal closure (**8b**).

Structural characterization of iminium intermediates

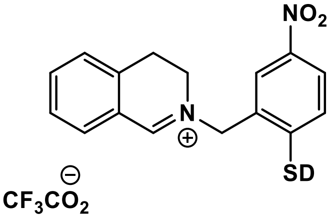




***int*-8b**

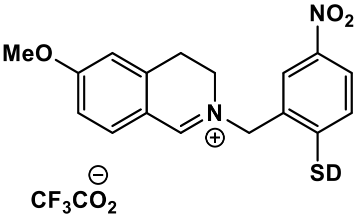
^{1}H NMR (500 MHz, TFA) δ 8.57 (s, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.53 – 7.41 (m, 3H), 7.13 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 5.22 (s, 2H), 4.07 (s, 3H), 4.03 (t, *J* = 8.1 Hz, 2H), 3.33 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR (126 MHz, TFA) δ 169.4, 163.9, 139.6, 137.2, 132.8, 131.8, 131.8, 131.2, 127.8, 127.4, 116.8, 115.4, 114.4, 114.1, 62.1, 55.2, 47.4, 25.2.



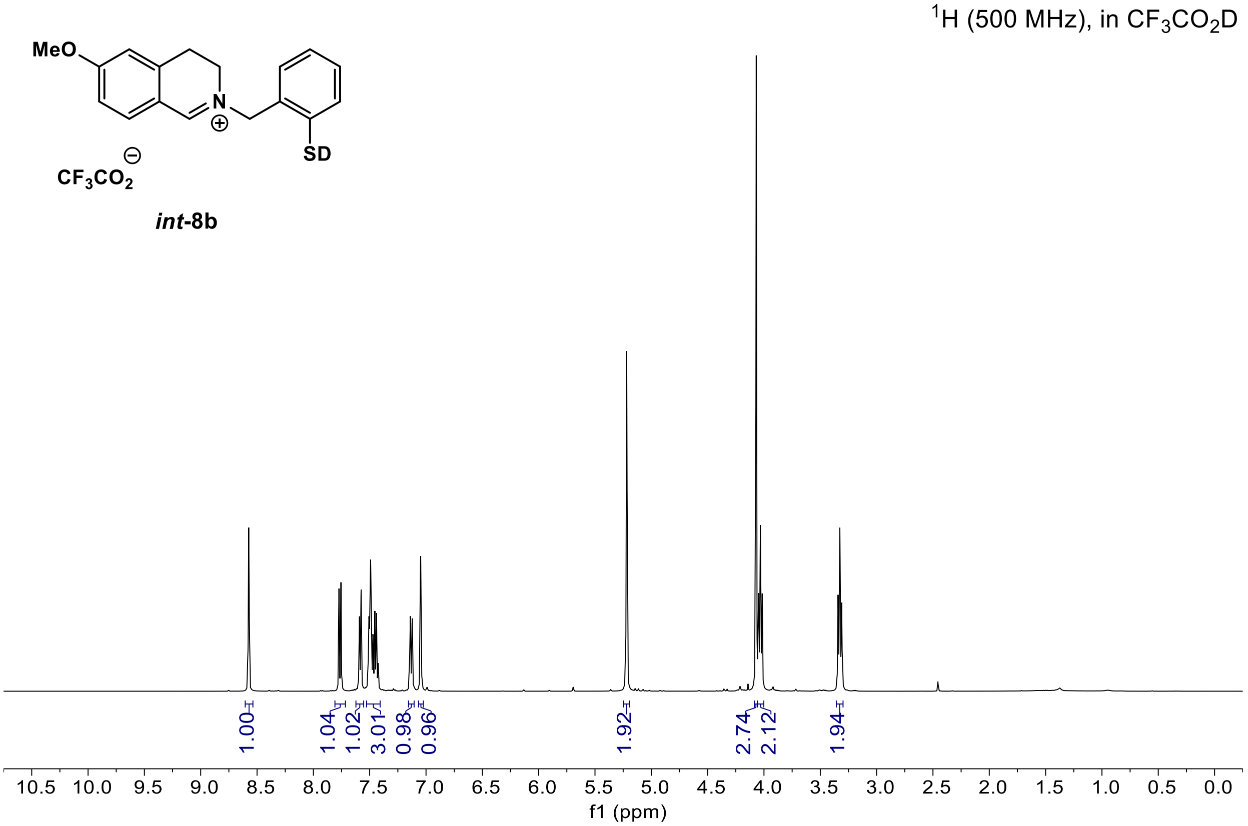
***int*-8c**

Observed as a mixture of isomers with the major isomer being *int-**8c*** along with two other unidentified isomers in a 4:2:1 ratio.



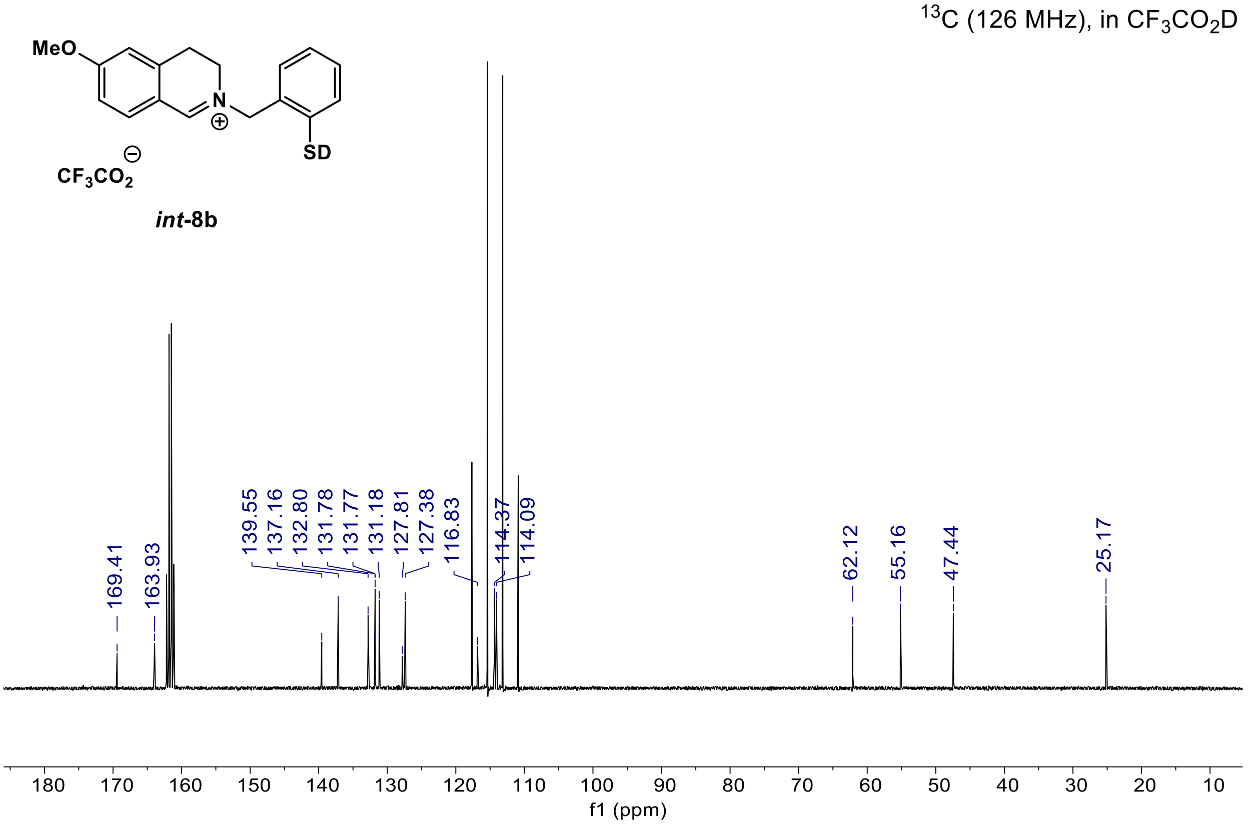
***int*-8d**

^{1}H NMR (500 MHz, TFA) δ 8.83 (s, 1H), 8.57 (d, *J* = 2.5 Hz, 1H), 8.43 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.25 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 5.41 (s, 2H), 4.17 (s, 3H), 4.14 (t, *J* = 8.0 Hz, 2H), 3.45 (t, *J* = 8.0 Hz, 2H).



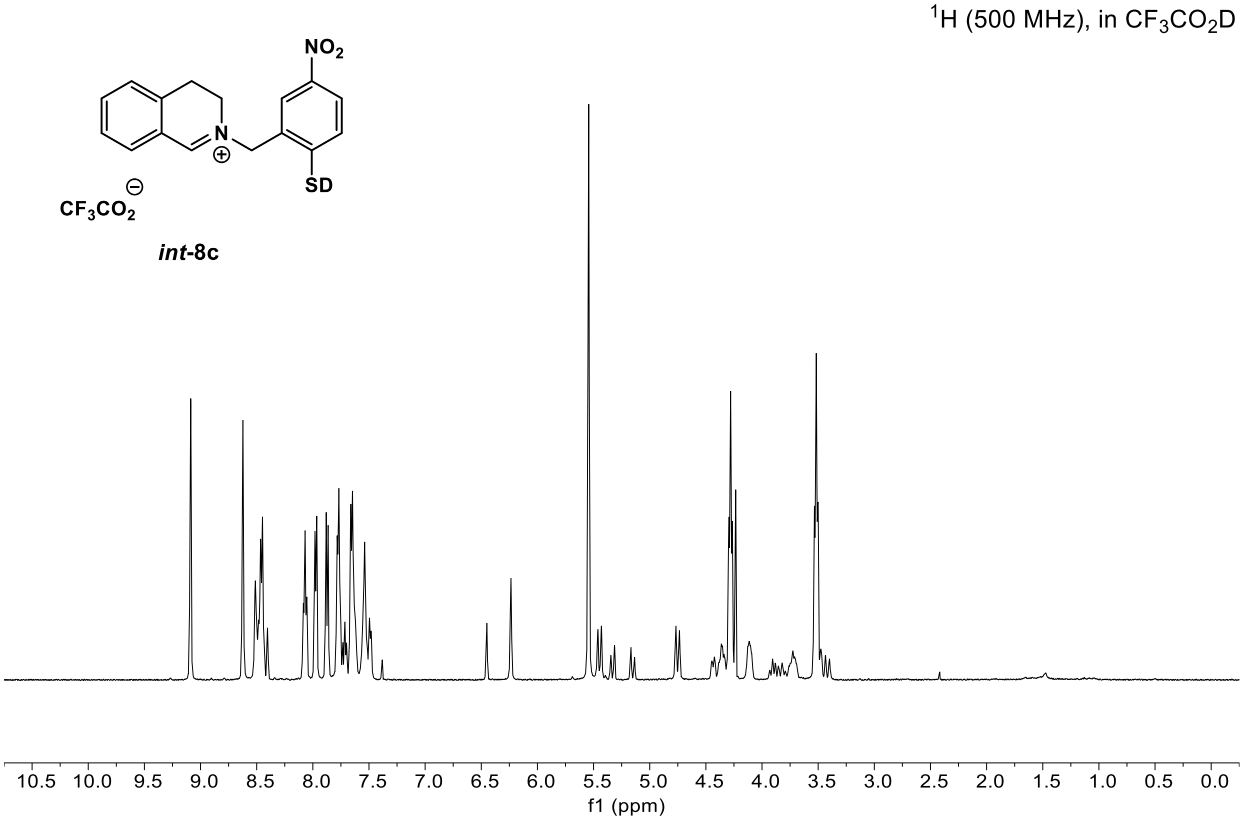
^1H (500 MHz), in CF_3CO_2D

***int*-8b**

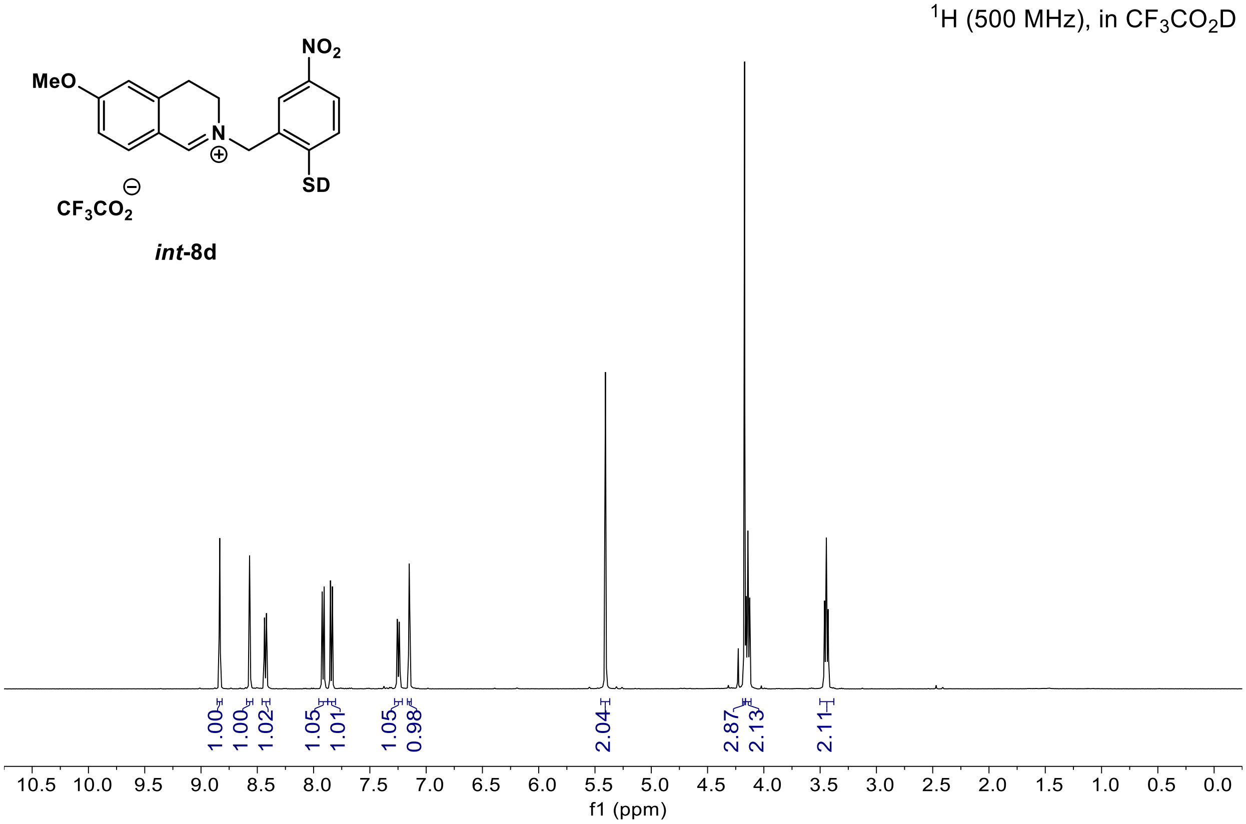


^{13}C (126 MHz), in CF_3CO_2D

***int*-8b**


^{1}H (500 MHz), in CF_3CO_2D
NO_2
N
⊕
SD
$CF_3CO_2^{\ominus}$
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

int-**8c**


^{1}H (500 MHz), in CF_3CO_2D
MeO
NO_2
N
⊕
SD
$CF_3CO_2^{\ominus}$
1.00
1.00
1.02
1.05
1.01
1.05
0.98
2.04
2.87
2.13
2.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

int-**8d**

2-D structural characterization of *int*-8b

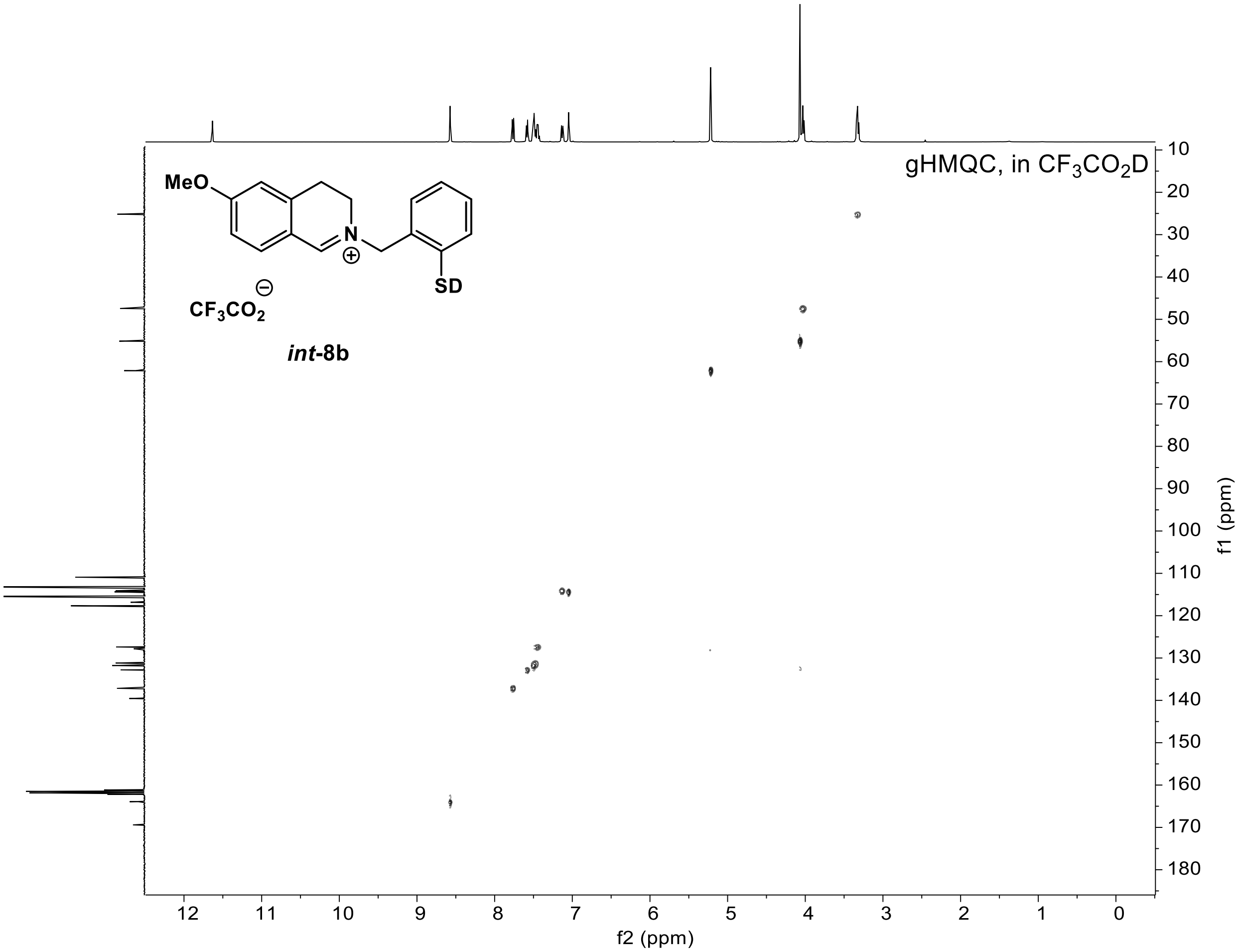


Figure S-5. 2-D HMQC NMR characterization of *int*-**8b** in CF$_3$CO$_2$D.

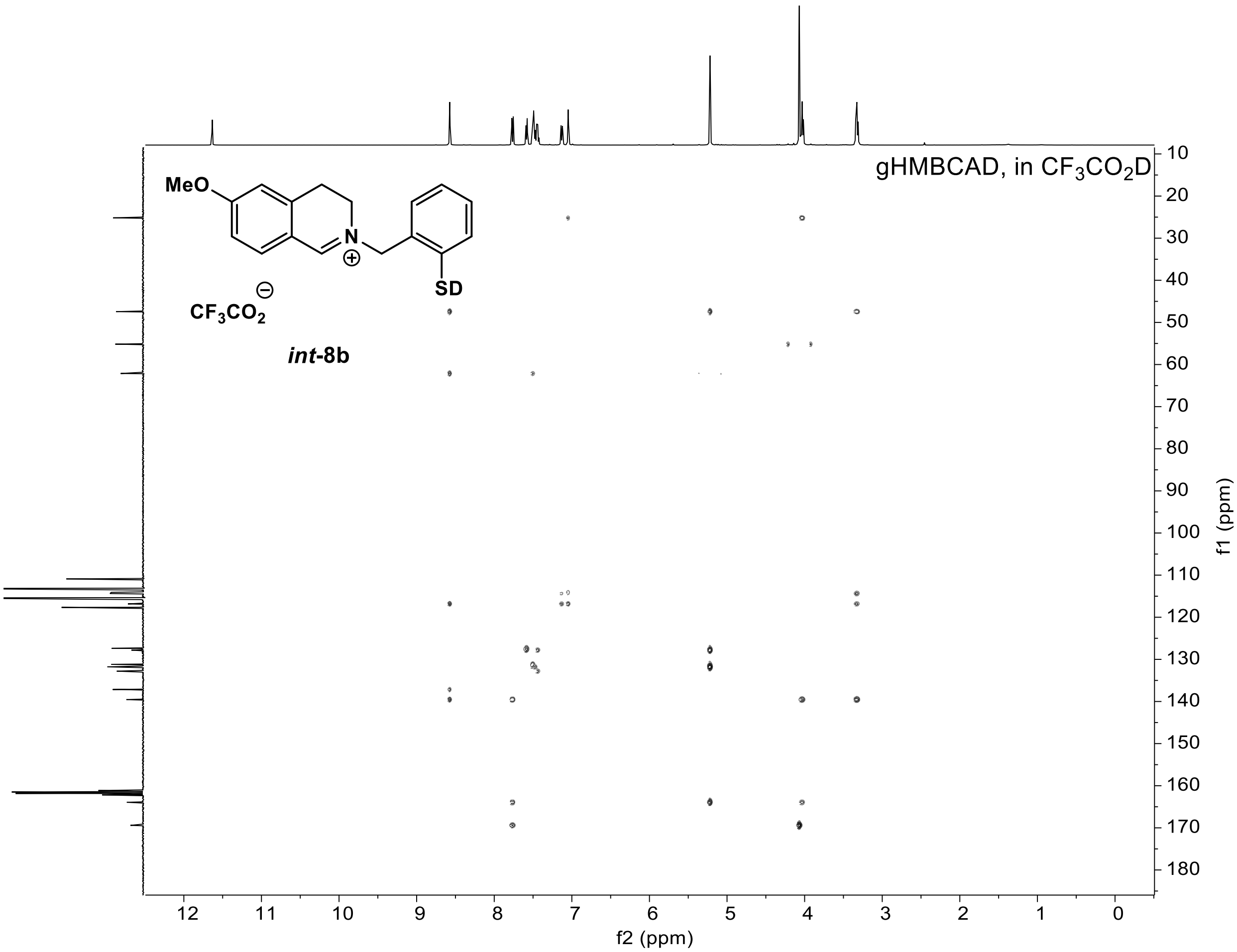
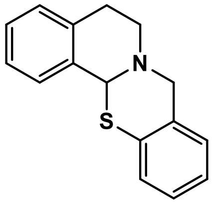
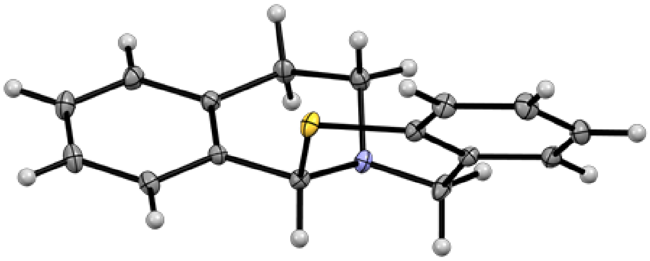


Figure S-6. 2-D HMBCAD NMR characterization of *int*-**8b** in CF$_3$CO$_2$D

Crystal structure report for compounds 8a, 8b, 8d



8a



A clear colourless hexagonal prism-like specimen of $C_{16}H_{15}NS$, approximate dimensions 0.065 mm x 0.390 mm x 0.600 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table 1: Data collection details for 20181003AR.

Axis	dx mm	2θ °	ω °	φ °	χ °	Width °	Frames	Time s	Wavelength Å	Voltage kV	Current mA	Temperature K
Omega	40.001	-28.00	-28.00	0.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	40.001	-28.00	-28.00	90.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	40.001	20.00	20.00	0.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Phi	40.001	-34.98	-35.08	-150.34	24.00	0.30	736	10.00	0.71073	50	35.0	103
Omega	40.001	-34.98	-34.22	40.00	-55.50	0.30	298	10.00	0.71073	50	35.0	103
Omega	40.001	-34.98	-34.22	0.00	-55.50	0.30	298	10.00	0.71073	50	35.0	103
Omega	40.001	-34.98	-138.44	-80.00	54.74	0.30	343	10.00	0.71073	50	35.0	103
Omega	40.001	-34.98	-138.44	-160.00	54.74	0.30	343	10.00	0.71073	50	35.0	103
Omega	40.001	-34.98	-34.22	120.00	-55.50	0.30	298	10.00	0.71073	50	35.0	103
Omega	40.001	-34.98	-138.44	0.00	54.74	0.30	343	10.00	0.71073	50	35.0	103

A total of 2695 frames were collected. The total exposure time was 7.49 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 31106 reflections to a maximum θ angle of 35.63° (0.61 Å resolution), of which 5713 were independent (average redundancy 5.445, completeness = 100.0%, R_{int} = 2.27%, R_{sig} = 1.65%) and 4999 (87.50%) were greater than 2σ(F^2). The final cell constants of a = 12.2588(10) Å, b = 7.5269(6) Å, c = 13.4609(11) Å, β = 93.275(2)°, volume = 1240.02(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9977 reflections above 20 σ(I) with 4.371° < 2θ < 73.61°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.938. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8690 and 0.9850.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/n 1, with Z = 4 for the formula unit, $C_{16}H_{15}NS$. The final anisotropic full-matrix least-squares refinement on F^2 with 163 variables converged at R1 = 2.99%, for the observed data and wR2 = 8.63% for all data. The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was 0.593 $e^-/Å^3$ and the largest hole was -0.214 $e^-/Å^3$ with an RMS deviation of 0.057 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.357 $g/cm^3$and F(000), 536 e^-.

Table 2. Sample and crystal data for 20181003AR.

Identification code	20181003AR	
Chemical formula	$C_{16}H_{15}NS$	
Formula weight	253.35 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.065 x 0.390 x 0.600 mm	
Crystal habit	clear colourless hexagonal prism	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 12.2588(10) Å	α = 90°
	b = 7.5269(6) Å	β = 93.275(2)°
	c = 13.4609(11) Å	γ = 90°
Volume	1240.02(17) $Å^3$	
Z	4	
Density (calculated)	1.357 g/cm^3	
Absorption coefficient	0.240 mm^{-1}	
F(000)	536	

Table 3. Data collection and structure refinement for 20181003AR.

Theta range for data collection	2.31 to 35.63°
Index ranges	-20<=h<=20, -12<=k<=12, -22<=l<=19
Reflections collected	31106
Independent reflections	5713 [R(int) = 0.0227]
Coverage of independent reflections	100.0%
Absorption correction	Multi-Scan

Max. and min. transmission	0.9850 and 0.8690	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	Σ w(F_o^2 - F_c^2)^2	
Data / restraints / parameters	5713 / 0 / 163	
Goodness-of-fit on F^2	1.047	
Δ/σ_{max}	0.001	
Final R indices	4999 data; I>2σ(I)	R1 = 0.0299, wR2 = 0.0824
	all data	R1 = 0.0359, wR2 = 0.0863
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0463P)^2+0.3211P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.593 and -0.214 eÅ^{-3}	
R.M.S. deviation from mean	0.057 eÅ^{-3}	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 20181003AR.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S1	0.33862(2)	0.51906(2)	0.56071(2)	0.01327(5)
N1	0.42405(5)	0.24145(8)	0.67786(4)	0.01154(10)
C1	0.44926(5)	0.41737(9)	0.64624(5)	0.01096(10)
C2	0.46296(5)	0.54747(9)	0.73110(5)	0.01041(10)
C3	0.50989(6)	0.71322(9)	0.71415(5)	0.01338(11)
C4	0.51841(6)	0.83965(10)	0.78936(6)	0.01629(12)
C5	0.48146(7)	0.79922(10)	0.88285(6)	0.01724(13)
C6	0.43622(6)	0.63367(10)	0.90035(5)	0.01450(12)
C7	0.42542(5)	0.50609(9)	0.82468(5)	0.01136(11)
C8	0.37541(6)	0.32682(10)	0.84335(5)	0.01503(12)
C9	0.33567(6)	0.23569(9)	0.74681(5)	0.01391(11)
C10	0.41418(6)	0.11560(9)	0.59548(5)	0.01461(12)
C11	0.33290(5)	0.15980(9)	0.50965(5)	0.01117(10)
C12	0.29397(6)	0.02137(9)	0.44763(5)	0.01320(11)
C13	0.22272(6)	0.05262(10)	0.36527(5)	0.01570(12)
C14	0.18907(6)	0.22622(11)	0.34373(5)	0.01710(13)
C15	0.22696(6)	0.36549(10)	0.40410(5)	0.01517(12)
C16	0.29890(5)	0.33338(9)	0.48701(5)	0.01145(11)

Table 5. Bond lengths (Å) for 20181003AR.

S1-C16	1.7661(7)	S1-C1	1.8901(7)
N1-C1	1.4300(9)	N1-C10	1.4582(9)
N1-C9	1.4669(9)	C1-C2	1.5066(9)
C1-H1	1.0	C2-C3	1.3980(9)
C2-C7	1.4006(9)	C3-C4	1.3890(10)
C3-H3	0.95	C4-C5	1.3952(11)
C4-H4	0.95	C5-C6	1.3895(11)
C5-H5	0.95	C6-C7	1.4006(10)
C6-H6	0.95	C7-C8	1.5091(10)
C8-C9	1.5245(10)	C8-H8A	0.99
C8-H8AB	0.99	C9-H9A	0.99
C9-H9AB	0.99	C10-C11	1.5188(10)
C10-H10A	0.99	C10-H10B	0.99
C11-C16	1.3997(9)	C11-C12	1.4017(10)
C12-C13	1.3916(10)	C12-H12	0.95
C13-C14	1.3957(11)	C13-H13	0.95
C14-C15	1.3899(11)	C14-H14	0.95
C15-C16	1.4034(10)	C15-H15	0.95

Table 6. Bond angles (°) for 20181003AR.

C16-S1-C1	100.77(3)	C1-N1-C10	112.65(5)
C1-N1-C9	113.30(5)	C10-N1-C9	115.45(6)
N1-C1-C2	113.13(5)	N1-C1-S1	113.36(5)
C2-C1-S1	104.10(4)	N1-C1-H1	108.7
C2-C1-H1	108.7	S1-C1-H1	108.7
C3-C2-C7	120.31(6)	C3-C2-C1	119.04(6)
C7-C2-C1	120.61(6)	C4-C3-C2	120.46(6)
C4-C3-H3	119.8	C2-C3-H3	119.8
C3-C4-C5	119.56(7)	C3-C4-H4	120.2
C5-C4-H4	120.2	C6-C5-C4	120.11(7)
C6-C5-H5	119.9	C4-C5-H5	119.9
C5-C6-C7	120.91(6)	C5-C6-H6	119.5
C7-C6-H6	119.5	C6-C7-C2	118.64(6)
C6-C7-C8	120.96(6)	C2-C7-C8	120.40(6)
C7-C8-C9	111.92(6)	C7-C8-H8A	109.2
C9-C8-H8A	109.2	C7-C8-H8AB	109.2
C9-C8-H8AB	109.2	H8A-C8-H8AB	107.9
N1-C9-C8	108.32(6)	N1-C9-H9A	110.0
C8-C9-H9A	110.0	N1-C9-H9AB	110.0

C8-C9-H9AB	110.0	H9A-C9-H9AB	108.4
N1-C10-C11	117.30(6)	N1-C10-H10A	108.0
C11-C10-H10A	108.0	N1-C10-H10B	108.0
C11-C10-H10B	108.0	H10A-C10-H10B	107.2
C16-C11-C12	118.51(6)	C16-C11-C10	122.98(6)
C12-C11-C10	118.45(6)	C13-C12-C11	121.71(7)
C13-C12-H12	119.1	C11-C12-H12	119.1
C12-C13-C14	119.24(7)	C12-C13-H13	120.4
C14-C13-H13	120.4	C15-C14-C13	119.98(7)
C15-C14-H14	120.0	C13-C14-H14	120.0
C14-C15-C16	120.59(7)	C14-C15-H15	119.7
C16-C15-H15	119.7	C11-C16-C15	119.98(6)
C11-C16-S1	123.18(5)	C15-C16-S1	116.81(5)

Table 7. Torsion angles (°) for 20181003AR.

C10-N1-C1-C2	-178.29(5)	C9-N1-C1-C2	48.34(7)
C10-N1-C1-S1	63.47(6)	C9-N1-C1-S1	-69.90(6)
C16-S1-C1-N1	-39.39(5)	C16-S1-C1-C2	-162.74(4)
N1-C1-C2-C3	166.60(6)	S1-C1-C2-C3	-69.90(7)
N1-C1-C2-C7	-15.89(9)	S1-C1-C2-C7	107.61(6)
C7-C2-C3-C4	-0.93(10)	C1-C2-C3-C4	176.59(6)
C2-C3-C4-C5	1.09(11)	C3-C4-C5-C6	-0.16(11)
C4-C5-C6-C7	-0.95(11)	C5-C6-C7-C2	1.10(10)
C5-C6-C7-C8	-179.47(7)	C3-C2-C7-C6	-0.17(10)
C1-C2-C7-C6	-177.65(6)	C3-C2-C7-C8	-179.59(6)
C1-C2-C7-C8	2.93(10)	C6-C7-C8-C9	160.22(6)
C2-C7-C8-C9	-20.36(9)	C1-N1-C9-C8	-66.25(7)
C10-N1-C9-C8	161.74(6)	C7-C8-C9-N1	49.59(8)
C1-N1-C10-C11	-55.69(8)	C9-N1-C10-C11	76.63(8)
N1-C10-C11-C16	24.26(10)	N1-C10-C11-C12	-158.70(6)
C16-C11-C12-C13	-0.27(10)	C10-C11-C12-C13	-177.44(6)
C11-C12-C13-C14	0.01(11)	C12-C13-C14-C15	0.18(11)
C13-C14-C15-C16	-0.11(11)	C12-C11-C16-C15	0.34(10)
C10-C11-C16-C15	177.38(6)	C12-C11-C16-S1	178.19(5)
C10-C11-C16-S1	-4.78(9)	C14-C15-C16-C11	-0.16(11)
C14-C15-C16-S1	-178.14(6)	C1-S1-C16-C11	10.93(6)
C1-S1-C16-C15	-171.16(5)		

Table 8. Anisotropic atomic displacement parameters (Å^2) for 20181003AR.

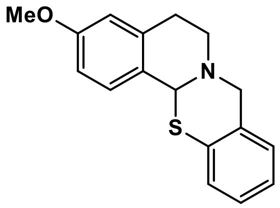
The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.01774(8)	0.01015(7)	0.01149(7)	-0.00044(5)	-0.00280(5)	0.00319(5)
N1	0.0149(2)	0.0092(2)	0.0104(2)	-0.00039(17)	-0.00049(17)	0.00107(17)
C1	0.0118(2)	0.0112(2)	0.0098(2)	0.00029(19)	0.00035(19)	0.00112(19)
C2	0.0105(2)	0.0106(2)	0.0100(2)	0.00018(19)	-0.00003(18)	0.00002(19)
C3	0.0143(3)	0.0125(3)	0.0131(3)	0.0022(2)	-0.0011(2)	-0.0016(2)
C4	0.0195(3)	0.0116(3)	0.0171(3)	0.0008(2)	-0.0045(2)	-0.0030(2)
C5	0.0214(3)	0.0143(3)	0.0155(3)	-0.0032(2)	-0.0038(2)	-0.0007(2)
C6	0.0163(3)	0.0160(3)	0.0111(2)	-0.0021(2)	-0.0002(2)	0.0001(2)
C7	0.0115(2)	0.0122(2)	0.0103(2)	-0.00023(19)	0.00027(19)	-0.00056(19)
C8	0.0193(3)	0.0146(3)	0.0114(3)	0.0003(2)	0.0030(2)	-0.0040(2)
C9	0.0154(3)	0.0127(3)	0.0137(3)	0.0002(2)	0.0008(2)	-0.0029(2)
C10	0.0180(3)	0.0120(3)	0.0132(3)	-0.0026(2)	-0.0041(2)	0.0051(2)
C11	0.0119(2)	0.0115(2)	0.0101(2)	-0.00070(19)	0.00034(19)	0.00153(19)
C12	0.0137(3)	0.0129(3)	0.0130(3)	-0.0019(2)	0.0005(2)	0.0005(2)
C13	0.0157(3)	0.0173(3)	0.0137(3)	-0.0028(2)	-0.0018(2)	-0.0015(2)
C14	0.0172(3)	0.0197(3)	0.0138(3)	-0.0006(2)	-0.0043(2)	0.0001(2)
C15	0.0159(3)	0.0159(3)	0.0132(3)	0.0010(2)	-0.0033(2)	0.0023(2)
C16	0.0120(2)	0.0123(3)	0.0099(2)	-0.00017(19)	-0.00026(19)	0.00143(19)

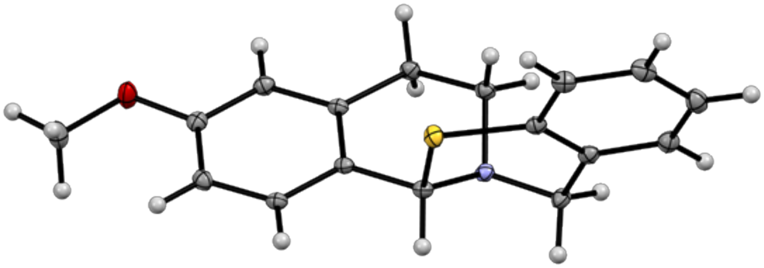
Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 20181003AR.

	x/a	y/b	z/c	U(eq)
H1	0.5186	0.4136	0.6107	0.013
H3	0.5361	0.7396	0.6507	0.016
H4	0.5492	0.9529	0.7772	0.02
H5	0.4872	0.8850	0.9346	0.021
H6	0.4123	0.6066	0.9645	0.017
H8A	0.3131	0.3418	0.8863	0.018
H8AB	0.4303	0.2504	0.8792	0.018
H9A	0.3157	0.1109	0.7602	0.017
H9AB	0.2703	0.2975	0.7173	0.017
H10A	0.3940	-0.0014	0.6226	0.018
H10B	0.4871	0.1023	0.5684	0.018
H12	0.3168	-0.0969	0.4622	0.016
H13	0.1973	-0.0431	0.3242	0.019

	x/a	y/b	z/c	U(eq)
H14	0.1403	0.2492	0.2878	0.021
H15	0.2039	0.4835	0.3891	0.018



8b



A clear colourless rhombic prism-like specimen of $C_{17}H_{17}NOS$, approximate dimensions 0.050 mm x 0.250 mm x 0.290 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table 1: Data collection details for 20181010AR.

Axis	dx mm	2θ °	ω °	φ °	χ °	Width °	Frames	Time s	Wavelength Å	Voltage kV	Current mA	Temperature K
Omega	39.895	-28.00	-28.00	0.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	39.895	-28.00	-28.00	90.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	39.895	20.00	20.00	0.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-136.98	80.00	54.74	1.30	79	20.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-136.98	160.00	54.74	1.30	79	20.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-31.92	-40.00	-55.50	1.30	67	20.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-136.98	120.00	54.74	1.30	79	20.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-31.92	-80.00	-55.50	1.30	67	20.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-136.98	-120.00	54.74	1.30	79	20.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-31.92	40.00	-55.50	1.30	67	20.00	0.71073	50	35.0	103
Omega	39.895	-33.72	-136.98	-40.00	54.74	1.30	79	20.00	0.71073	50	35.0	103

A total of 632 frames were collected. The total exposure time was 3.41 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 24293 reflections to a maximum θ angle of 34.88° (0.62 Å resolution), of which 5960 were independent (average redundancy 4.076, completeness = 99.9%, R_{int} = 4.97%, R_{sig} = 4.67%) and 4375 (73.41%) were greater than $2\sigma(F^2)$. The final cell constants of <u>a</u> = 18.2786(14) Å, <u>b</u> = 5.5078(4) Å, <u>c</u> = 13.6680(11) Å, β = 95.902(2)°, volume = 1368.73(18) $Å^3$, are based upon the refinement of the XYZ-centroids of 5782 reflections above 20 σ(I) with 5.991° < 2θ < 67.82°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.896. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9360 and 0.9890.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 4 for the formula unit, $C_{17}H_{17}NOS$. The final anisotropic full-matrix least-squares refinement on F^2 with 182 variables converged at R1 = 4.43%, for the observed data and wR2 = 10.88% for all data. The goodness-of-fit was 1.026. The largest peak in the final difference electron density synthesis was 0.598 $e^-/Å^3$ and the largest hole was -0.292 $e^-/Å^3$ with an RMS deviation of 0.071 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.375g/cm^3 and F(000), 600 e^-.

Table 2. Sample and crystal data for 20181010AR.

Identification code	20181010AR	
Chemical formula	$C_{17}H_{17}NOS$	
Formula weight	283.37 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.250 x 0.290 mm	
Crystal habit	clear colourless rhombic prism	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 18.2786(14) Å	α = 90°
	b = 5.5078(4) Å	β = 95.902(2)°
	c = 13.6680(11) Å	γ = 90°
Volume	1368.73(18) $Å^3$	
Z	4	
Density (calculated)	1.375 g/cm^3	
Absorption coefficient	0.231 mm^{-1}	
F(000)	600	

Table 3. Data collection and structure refinement for 20181010AR.

Theta range for data collection	3.00 to 34.88°
Index ranges	-20<=h<=29, -8<=k<=8, -21<=l<=21

Reflections collected	24293	
Independent reflections	5960 [R(int) = 0.0497]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9890 and 0.9360	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5960 / 0 / 182	
Goodness-of-fit on F^2	1.026	
Δ/σ_{max}	0.001	
Final R indices	4375 data; I>2σ(I)	R1 = 0.0443, wR2 = 0.0985
	all data	R1 = 0.0706, wR2 = 0.1088
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0475P)^2+0.5247P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.598 and -0.292 eÅ^{-3}	
R.M.S. deviation from mean	0.071 eÅ^{-3}	

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 20181010AR.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S1	0.34375(2)	0.75754(5)	0.48034(2)	0.01285(7)
O1	0.05954(5)	0.32765(17)	0.65734(7)	0.01816(18)
N1	0.24202(5)	0.69012(18)	0.31552(7)	0.01080(17)
C1	0.37789(6)	0.9468(2)	0.39136(8)	0.01154(19)
C2	0.42818(6)	0.1267(2)	0.42660(9)	0.0143(2)
C3	0.45823(7)	0.2832(2)	0.36213(9)	0.0165(2)
C4	0.43759(7)	0.2651(2)	0.26165(9)	0.0167(2)
C5	0.38571(6)	0.0919(2)	0.22708(9)	0.0143(2)
C6	0.35512(6)	0.9314(2)	0.29032(8)	0.01164(19)
C7	0.29793(6)	0.7486(2)	0.24936(8)	0.01252(19)
C8	0.19802(6)	0.9021(2)	0.33778(8)	0.0124(2)
C9	0.13245(6)	0.8261(2)	0.39100(8)	0.0123(2)
C10	0.15044(6)	0.6286(2)	0.46627(8)	0.01049(19)
C11	0.09949(6)	0.5631(2)	0.53046(8)	0.0128(2)
C12	0.11358(6)	0.3736(2)	0.59710(8)	0.0126(2)
C13	0.17944(6)	0.2443(2)	0.60052(8)	0.01295(19)

	x/a	y/b	z/c	U(eq)
C14	0.23033(6)	0.3105(2)	0.53641(8)	0.01143(19)
C15	0.21687(6)	0.5008(2)	0.46993(8)	0.01039(19)
C16	0.27349(6)	0.5683(2)	0.40248(8)	0.01100(19)
C17	0.06988(7)	0.1221(2)	0.72084(10)	0.0189(2)

Table 5. Bond lengths (Å) for 20181010AR.

S1-C1	1.7638(12)	S1-C16	1.8940(11)
O1-C12	1.3729(14)	O1-C17	1.4274(15)
N1-C16	1.4328(14)	N1-C8	1.4674(15)
N1-C7	1.4684(14)	C1-C2	1.4028(16)
C1-C6	1.4032(16)	C2-C3	1.3859(17)
C2-H2	0.95	C3-C4	1.3900(18)
C3-H3	0.95	C4-C5	1.3927(17)
C4-H4	0.95	C5-C6	1.3931(16)
C5-H5	0.95	C6-C7	1.5164(16)
C7-H7A	0.99	C7-H7AB	0.99
C8-C9	1.5232(16)	C8-H8A	0.99
C8-H8AB	0.99	C9-C10	1.5100(16)
C9-H9A	0.99	C9-H9AB	0.99
C10-C11	1.3912(16)	C10-C15	1.3997(15)
C11-C12	1.3918(16)	C11-H11	0.95
C12-C13	1.3953(16)	C13-C14	1.3907(16)
C13-H13	0.95	C14-C15	1.3923(15)
C14-H14	0.95	C15-C16	1.5018(15)
C16-H16	1.0	C17-H17A	0.98
C17-H17B	0.98	C17-H17C	0.98

Table 6. Bond angles (°) for 20181010AR.

C1-S1-C16	101.84(5)	C12-O1-C17	116.90(10)
C16-N1-C8	112.49(9)	C16-N1-C7	111.61(9)
C8-N1-C7	112.58(9)	C2-C1-C6	119.87(11)
C2-C1-S1	116.51(9)	C6-C1-S1	123.56(9)
C3-C2-C1	120.64(11)	C3-C2-H2	119.7
C1-C2-H2	119.7	C2-C3-C4	119.90(11)
C2-C3-H3	120.0	C4-C3-H3	120.0
C3-C4-C5	119.38(11)	C3-C4-H4	120.3
C5-C4-H4	120.3	C4-C5-C6	121.78(11)

C4-C5-H5	119.1	C6-C5-H5	119.1
C5-C6-C1	118.36(11)	C5-C6-C7	119.84(10)
C1-C6-C7	121.79(10)	N1-C7-C6	114.54(9)
N1-C7-H7A	108.6	C6-C7-H7A	108.6
N1-C7-H7AB	108.6	C6-C7-H7AB	108.6
H7A-C7-H7AB	107.6	N1-C8-C9	110.80(9)
N1-C8-H8A	109.5	C9-C8-H8A	109.5
N1-C8-H8AB	109.5	C9-C8-H8AB	109.5
H8A-C8-H8AB	108.1	C10-C9-C8	113.36(9)
C10-C9-H9A	108.9	C8-C9-H9A	108.9
C10-C9-H9AB	108.9	C8-C9-H9AB	108.9
H9A-C9-H9AB	107.7	C11-C10-C15	118.79(10)
C11-C10-C9	120.23(10)	C15-C10-C9	120.91(10)
C10-C11-C12	121.09(10)	C10-C11-H11	119.5
C12-C11-H11	119.5	O1-C12-C11	115.76(10)
O1-C12-C13	123.87(10)	C11-C12-C13	120.37(10)
C14-C13-C12	118.41(10)	C14-C13-H13	120.8
C12-C13-H13	120.8	C13-C14-C15	121.59(10)
C13-C14-H14	119.2	C15-C14-H14	119.2
C14-C15-C10	119.75(10)	C14-C15-C16	120.01(10)
C10-C15-C16	120.24(10)	N1-C16-C15	112.45(9)
N1-C16-S1	113.55(8)	C15-C16-S1	105.16(7)
N1-C16-H16	108.5	C15-C16-H16	108.5
S1-C16-H16	108.5	O1-C17-H17A	109.5
O1-C17-H17B	109.5	H17A-C17-H17B	109.5
O1-C17-H17C	109.5	H17A-C17-H17C	109.5
H17B-C17-H17C	109.5		

Table 7. Torsion angles (°) for 20181010AR.

C16-S1-C1-C2	175.10(9)	C16-S1-C1-C6	-2.24(11)
C6-C1-C2-C3	-2.87(17)	S1-C1-C2-C3	179.68(9)
C1-C2-C3-C4	1.08(18)	C2-C3-C4-C5	1.17(18)
C3-C4-C5-C6	-1.68(18)	C4-C5-C6-C1	-0.10(17)
C4-C5-C6-C7	179.05(11)	C2-C1-C6-C5	2.35(16)
S1-C1-C6-C5	179.60(9)	C2-C1-C6-C7	-176.78(10)
S1-C1-C6-C7	0.48(15)	C16-N1-C7-C6	-65.48(12)
C8-N1-C7-C6	62.13(12)	C5-C6-C7-N1	-147.29(10)
C1-C6-C7-N1	31.83(15)	C16-N1-C8-C9	-62.99(12)
C7-N1-C8-C9	169.87(9)	N1-C8-C9-C10	39.89(13)
C8-C9-C10-C11	171.02(10)	C8-C9-C10-C15	-11.91(15)

C15-C10-C11-C12	-0.30(17)	C9-C10-C11-C12	176.83(10)
C17-O1-C12-C11	175.09(11)	C17-O1-C12-C13	-5.38(17)
C10-C11-C12-O1	179.31(10)	C10-C11-C12-C13	-0.23(17)
O1-C12-C13-C14	-179.14(11)	C11-C12-C13-C14	0.37(17)
C12-C13-C14-C15	0.02(17)	C13-C14-C15-C10	-0.55(17)
C13-C14-C15-C16	179.47(10)	C11-C10-C15-C14	0.68(16)
C9-C10-C15-C14	-176.43(10)	C11-C10-C15-C16	-179.34(10)
C9-C10-C15-C16	3.55(16)	C8-N1-C16-C15	53.88(12)
C7-N1-C16-C15	-178.46(9)	C8-N1-C16-S1	-65.38(11)
C7-N1-C16-S1	62.27(10)	C14-C15-C16-N1	156.11(10)
C10-C15-C16-N1	-23.87(14)	C14-C15-C16-S1	-79.84(11)
C10-C15-C16-S1	100.18(10)	C1-S1-C16-N1	-28.24(9)
C1-S1-C16-C15	-151.58(7)		

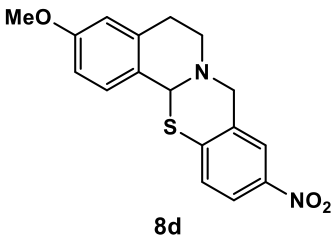
Table 8. Anisotropic atomic displacement parameters (Å^2) for 20181010AR.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.01358(12)	0.01405(13)	0.01041(11)	0.00090(9)	-0.00127(8)	-0.00091(10)
O1	0.0149(4)	0.0212(4)	0.0193(4)	0.0073(3)	0.0064(3)	0.0027(3)
N1	0.0115(4)	0.0115(4)	0.0092(4)	-0.0004(3)	0.0006(3)	0.0018(3)
C1	0.0100(4)	0.0118(5)	0.0128(4)	-0.0003(4)	0.0011(3)	0.0020(4)
C2	0.0112(5)	0.0150(5)	0.0163(5)	-0.0016(4)	-0.0008(4)	0.0006(4)
C3	0.0119(5)	0.0146(5)	0.0227(6)	-0.0015(4)	0.0009(4)	-0.0014(4)
C4	0.0142(5)	0.0159(5)	0.0204(5)	0.0033(4)	0.0031(4)	0.0003(4)
C5	0.0131(5)	0.0157(5)	0.0142(5)	0.0012(4)	0.0018(4)	0.0018(4)
C6	0.0100(4)	0.0125(5)	0.0124(4)	-0.0002(4)	0.0008(3)	0.0021(4)
C7	0.0137(5)	0.0140(5)	0.0101(4)	-0.0014(4)	0.0021(3)	-0.0007(4)
C8	0.0138(5)	0.0109(5)	0.0122(4)	0.0006(4)	0.0003(4)	0.0025(4)
C9	0.0116(5)	0.0127(5)	0.0124(4)	0.0016(4)	-0.0001(4)	0.0035(4)
C10	0.0107(4)	0.0094(4)	0.0110(4)	-0.0008(3)	-0.0005(3)	0.0010(4)
C11	0.0110(5)	0.0137(5)	0.0137(5)	-0.0005(4)	0.0012(4)	0.0016(4)
C12	0.0122(5)	0.0135(5)	0.0120(4)	-0.0009(4)	0.0013(4)	-0.0011(4)
C13	0.0146(5)	0.0119(5)	0.0120(4)	0.0013(4)	-0.0002(4)	0.0003(4)
C14	0.0116(5)	0.0101(4)	0.0123(4)	-0.0010(3)	-0.0002(4)	0.0018(4)
C15	0.0111(5)	0.0097(4)	0.0102(4)	-0.0016(3)	0.0003(3)	0.0009(4)
C16	0.0112(4)	0.0103(5)	0.0114(4)	-0.0011(4)	0.0003(3)	0.0008(4)
C17	0.0188(6)	0.0195(6)	0.0191(5)	0.0065(5)	0.0041(4)	-0.0016(5)

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 20181010AR.

	x/a	y/b	z/c	U(eq)
H2	0.4418	1.1414	0.4953	0.017
H3	0.4929	1.4027	0.3866	0.02
H4	0.4587	1.3698	0.2170	0.02
H5	0.3708	1.0830	0.1585	0.017
H7A	0.2729	0.8131	0.1871	0.015
H7AB	0.3233	0.5969	0.2337	0.015
H8A	0.1803	0.9864	0.2758	0.015
H8AB	0.2291	1.0169	0.3795	0.015
H9A	0.1138	0.9697	0.4243	0.015
H9AB	0.0927	0.7684	0.3419	0.015
H11	0.0543	0.6492	0.5288	0.015
H13	0.1893	0.1142	0.6456	0.016
H14	0.2754	0.2239	0.5380	0.014
H16	0.2980	0.4165	0.3824	0.013
H17A	0.0276	0.1059	0.7590	0.028
H17B	0.1148	0.1440	0.7657	0.028
H17C	0.0744	-0.0247	0.6814	0.028



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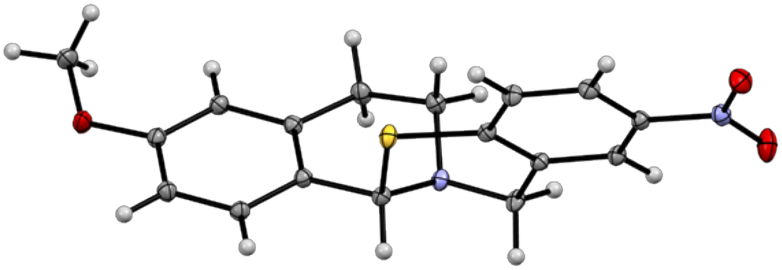


A clear colourless 'rhombic prism'-like specimen of $C_{17}H_{16}N_2O_3S$, approximate dimensions 0.160 mm x 0.210 mm x 0.290 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å).

Table 1: Data collection details for 20181011AR.

Axis	dx mm	2θ °	ω °	φ °	χ °	Width °	Frames	Time s	Wavelength Å	Voltage kV	Current mA	Temperature K
Omega	39.825	-28.00	-28.00	0.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	39.825	-28.00	-28.00	90.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	39.825	20.00	20.00	0.00	54.00	0.50	12	10.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	-120.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	0.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	160.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	80.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	-40.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	-160.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	-80.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	120.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-42.82	40.00	-55.50	2.00	49	20.00	0.71073	50	35.0	103

Axis	**dx** **mm**	**2θ** **°**	**ω** **°**	**φ** **°**	**χ** **°**	**Width** **°**	**Frames**	**Time** **s**	**Wavelength** **Å**	**Voltage** **kV**	**Current** **mA**	**Temperature** **K**
Omega	39.825	-34.24	-136.79	160.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-13.69	-116.24	90.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	-120.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	0.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	120.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	40.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	-80.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	-160.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	-40.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	80.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-43.69	-146.25	160.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-34.24	-136.79	-120.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-34.24	-136.79	-40.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-34.24	-136.79	80.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-13.69	-116.24	180.00	54.74	2.00	51	20.00	0.71073	50	35.0	103
Omega	39.825	-13.69	-116.24	270.00	54.74	2.00	51	20.00	0.71073	50	35.0	103

A total of 1293 frames were collected. The total exposure time was 7.08 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 52965 reflections to a maximum θ angle of 37.78° (0.58 Å resolution), of which 7991 were independent (average redundancy 6.628, completeness = 99.8%, R_{int} = 3.78%, R_{sig} = 2.67%) and 6454 (80.77%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.2999(3) Å, b = 8.7882(3) Å, c = 12.8272(5) Å, α = 70.7810(10)°, β = 74.6590(10)°, γ = 80.3970(10)°, volume = 746.48(5) Å^3, are based upon the refinement of the XYZ-centroids of 9847 reflections above 20 σ(I) with 4.927° < 2θ < 79.30°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.952. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9350 and 0.9630.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 2 for the formula unit, $C_{17}H_{16}N_2O_3S$. The final anisotropic full-matrix least-squares refinement on F^2 with 209 variables converged at R1 = 3.58%, for the observed data and wR2 = 10.04% for all data. The goodness-of-fit was 1.069. The largest peak in the final difference electron density synthesis was 0.670 $e^-/Å^3$ and the largest hole was -0.240 $e^-/Å^3$ with an RMS deviation of 0.068 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.461 g/cm^3 and F(000), 344 e^-.

Table 2. Sample and crystal data for 20181011AR.

Identification code	20181011AR	
Chemical formula	$C_{17}H_{16}N_2O_3S$	
Formula weight	328.38 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.160 x 0.210 x 0.290 mm	
Crystal habit	clear colourless 'rhombic prism'	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.2999(3) Å	α = 70.7810(10)°
	b = 8.7882(3) Å	β = 74.6590(10)°
	c = 12.8272(5) Å	γ = 80.3970(10)°
Volume	746.48(5) Å^3	
Z	2	
Density (calculated)	1.461 g/cm^3	
Absorption coefficient	0.234 mm^{-1}	
F(000)	344	

Table 3. Data collection and structure refinement for 20181011AR.

Theta range for data collection	2.46 to 37.78°
Index ranges	-12<=h<=12, -15<=k<=15, -22<=l<=22
Reflections collected	52965
Independent reflections	7991 [R(int) = 0.0378]

Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9630 and 0.9350
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7991 / 0 / 209
Goodness-of-fit on F^2	1.069
Δ/σ_{max}	0.001
Final R indices	6454 data; $I>2\sigma(I)$ R1 = 0.0358, wR2 = 0.0924
	all data R1 = 0.0514, wR2 = 0.1004
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0493P)^2+0.1762P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.670 and -0.240 eÅ^{-3}
R.M.S. deviation from mean	0.068 eÅ^{-3}

Table 4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for 20181011AR.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
S1	0.62664(3)	0.54997(2)	0.20377(2)	0.01347(5)
O1	0.82946(9)	0.92720(8)	0.48824(5)	0.01674(11)
O2	0.00488(10)	0.24633(9)	0.04584(7)	0.02276(14)
O3	0.24476(10)	0.06559(8)	0.03751(6)	0.01970(12)
N1	0.27126(9)	0.70936(8)	0.26364(6)	0.01214(11)
N2	0.16689(10)	0.19170(9)	0.05763(6)	0.01371(11)
C1	0.48031(10)	0.45210(9)	0.16282(6)	0.01116(12)
C2	0.56253(11)	0.30914(9)	0.13699(7)	0.01310(12)
C3	0.46004(11)	0.22261(9)	0.10324(7)	0.01322(12)
C4	0.27361(11)	0.28111(9)	0.09589(6)	0.01148(12)
C5	0.18701(11)	0.42001(9)	0.12353(6)	0.01176(12)
C6	0.28961(11)	0.50753(9)	0.15817(6)	0.01088(11)
C7	0.19278(11)	0.66027(10)	0.18697(7)	0.01360(13)
C8	0.23352(12)	0.60571(10)	0.38126(7)	0.01423(13)
C9	0.28397(12)	0.68640(10)	0.45758(7)	0.01525(13)
C10	0.47187(11)	0.76076(9)	0.40792(6)	0.01204(12)
C11	0.56202(11)	0.80385(10)	0.47659(7)	0.01296(12)
C12	0.72998(11)	0.88018(9)	0.42933(7)	0.01270(12)
C13	0.80889(11)	0.91604(10)	0.31310(7)	0.01408(13)

	x/a	y/b	z/c	U(eq)
C14	0.72038(11)	0.87272(10)	0.24542(7)	0.01282(12)
C15	0.55234(11)	0.79468(9)	0.29232(6)	0.01146(12)
C16	0.46714(11)	0.73851(9)	0.21852(6)	0.01163(12)
C17	0.77666(15)	0.87010(11)	0.60875(7)	0.01939(16)

Table 5. Bond lengths (Å) for 20181011AR.

S1-C1	1.7487(8)	S1-C16	1.8929(8)
O1-C12	1.3658(9)	O1-C17	1.4242(11)
O2-N2	1.2286(10)	O3-N2	1.2323(9)
N1-C16	1.4255(10)	N1-C8	1.4633(11)
N1-C7	1.4633(10)	N2-C4	1.4579(10)
C1-C2	1.4020(11)	C1-C6	1.4061(10)
C2-C3	1.3796(11)	C2-H2	0.95
C3-C4	1.3884(11)	C3-H3	0.95
C4-C5	1.3872(11)	C5-C6	1.3940(10)
C5-H5	0.95	C6-C7	1.5198(11)
C7-H7A	0.99	C7-H7AB	0.99
C8-C9	1.5270(11)	C8-H8A	0.99
C8-H8AB	0.99	C9-C10	1.5090(11)
C9-H9A	0.99	C9-H9AB	0.99
C10-C15	1.3925(11)	C10-C11	1.4007(11)
C11-C12	1.3907(11)	C11-H11	0.95
C12-C13	1.3966(11)	C13-C14	1.3829(11)
C13-H13	0.95	C14-C15	1.3984(11)
C14-H14	0.95	C15-C16	1.4994(10)
C16-H16	1.0	C17-H17A	0.98
C17-H17B	0.98	C17-H17C	0.98

Table 6. Bond angles (°) for 20181011AR.

C1-S1-C16	101.16(3)	C12-O1-C17	117.52(7)
C16-N1-C8	113.02(6)	C16-N1-C7	111.75(6)
C8-N1-C7	114.93(6)	O2-N2-O3	123.18(7)
O2-N2-C4	118.60(7)	O3-N2-C4	118.22(7)
C2-C1-C6	120.59(7)	C2-C1-S1	115.94(6)
C6-C1-S1	123.45(6)	C3-C2-C1	120.76(7)
C3-C2-H2	119.6	C1-C2-H2	119.6
C2-C3-C4	118.07(7)	C2-C3-H3	121.0
C4-C3-H3	121.0	C5-C4-C3	122.45(7)
C5-C4-N2	119.51(7)	C3-C4-N2	118.04(7)

C4-C5-C6	119.72(7)	C4-C5-H5	120.1
C6-C5-H5	120.1	C5-C6-C1	118.37(7)
C5-C6-C7	118.91(6)	C1-C6-C7	122.71(7)
N1-C7-C6	115.97(6)	N1-C7-H7A	108.3
C6-C7-H7A	108.3	N1-C7-H7AB	108.3
C6-C7-H7AB	108.3	H7A-C7-H7AB	107.4
N1-C8-C9	110.30(6)	N1-C8-H8A	109.6
C9-C8-H8A	109.6	N1-C8-H8AB	109.6
C9-C8-H8AB	109.6	H8A-C8-H8AB	108.1
C10-C9-C8	113.06(7)	C10-C9-H9A	109.0
C8-C9-H9A	109.0	C10-C9-H9AB	109.0
C8-C9-H9AB	109.0	H9A-C9-H9AB	107.8
C15-C10-C11	119.37(7)	C15-C10-C9	120.26(7)
C11-C10-C9	120.30(7)	C12-C11-C10	120.10(7)
C12-C11-H11	119.9	C10-C11-H11	119.9
O1-C12-C11	124.95(7)	O1-C12-C13	114.66(7)
C11-C12-C13	120.38(7)	C14-C13-C12	119.49(7)
C14-C13-H13	120.3	C12-C13-H13	120.3
C13-C14-C15	120.54(7)	C13-C14-H14	119.7
C15-C14-H14	119.7	C10-C15-C14	120.10(7)
C10-C15-C16	120.41(7)	C14-C15-C16	119.37(7)
N1-C16-C15	113.76(6)	N1-C16-S1	113.00(5)
C15-C16-S1	102.94(5)	N1-C16-H16	109.0
C15-C16-H16	109.0	S1-C16-H16	109.0
O1-C17-H17A	109.5	O1-C17-H17B	109.5
H17A-C17-H17B	109.5	O1-C17-H17C	109.5
H17A-C17-H17C	109.5	H17B-C17-H17C	109.5

Table 7. Torsion angles (°) for 20181011AR.

C16-S1-C1-C2	175.93(6)	C16-S1-C1-C6	-5.78(7)
C6-C1-C2-C3	1.96(12)	S1-C1-C2-C3	-179.70(6)
C1-C2-C3-C4	-0.12(12)	C2-C3-C4-C5	-1.48(12)
C2-C3-C4-N2	178.57(7)	O2-N2-C4-C5	3.33(11)
O3-N2-C4-C5	-177.44(7)	O2-N2-C4-C3	-176.72(8)
O3-N2-C4-C3	2.51(11)	C3-C4-C5-C6	1.22(12)
N2-C4-C5-C6	-178.83(7)	C4-C5-C6-C1	0.64(11)
C4-C5-C6-C7	179.41(7)	C2-C1-C6-C5	-2.19(11)
S1-C1-C6-C5	179.60(6)	C2-C1-C6-C7	179.09(7)
S1-C1-C6-C7	0.88(11)	C16-N1-C7-C6	59.47(9)
C8-N1-C7-C6	-71.06(9)	C5-C6-C7-N1	156.10(7)
C1-C6-C7-N1	-25.19(11)	C16-N1-C8-C9	61.95(8)

C7-N1-C8-C9	-168.14(6)	N1-C8-C9-C10	-44.31(9)
C8-C9-C10-C15	18.98(11)	C8-C9-C10-C11	-164.28(7)
C15-C10-C11-C12	0.18(12)	C9-C10-C11-C12	-176.58(7)
C17-O1-C12-C11	11.29(12)	C17-O1-C12-C13	-169.33(8)
C10-C11-C12-O1	-179.95(7)	C10-C11-C12-C13	0.70(12)
O1-C12-C13-C14	179.55(7)	C11-C12-C13-C14	-1.03(12)
C12-C13-C14-C15	0.48(12)	C11-C10-C15-C14	-0.73(11)
C9-C10-C15-C14	176.03(7)	C11-C10-C15-C16	175.27(7)
C9-C10-C15-C16	-7.96(11)	C13-C14-C15-C10	0.40(12)
C13-C14-C15-C16	-175.64(7)	C8-N1-C16-C15	-50.47(9)
C7-N1-C16-C15	178.03(6)	C8-N1-C16-S1	66.44(7)
C7-N1-C16-S1	-65.06(7)	C10-C15-C16-N1	22.98(10)
C14-C15-C16-N1	-160.99(7)	C10-C15-C16-S1	-99.65(7)
C14-C15-C16-S1	76.38(8)	C1-S1-C16-N1	36.96(6)
C1-S1-C16-C15	160.09(5)		

Table 8. Anisotropic atomic displacement parameters (Å^2) for 20181011AR.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

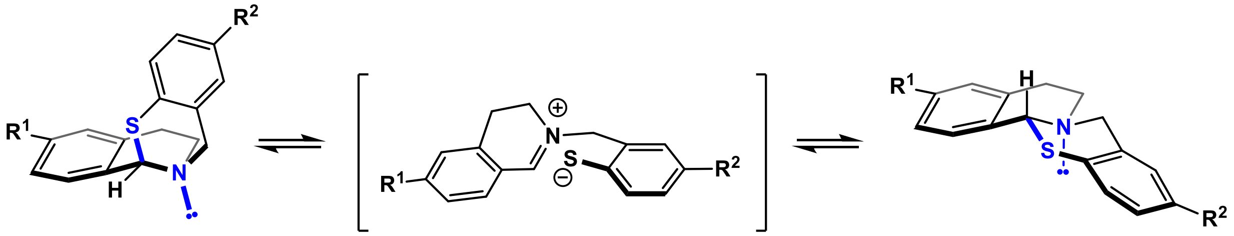
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.00996(8)	0.01538(9)	0.01765(9)	-0.00835(7)	-0.00440(6)	0.00094(6)
O1	0.0192(3)	0.0206(3)	0.0128(2)	-0.0042(2)	-0.0054(2)	-0.0071(2)
O2	0.0128(3)	0.0291(3)	0.0332(4)	-0.0177(3)	-0.0065(2)	-0.0007(2)
O3	0.0252(3)	0.0139(3)	0.0238(3)	-0.0095(2)	-0.0083(3)	0.0005(2)
N1	0.0103(2)	0.0136(3)	0.0137(3)	-0.0058(2)	-0.0031(2)	0.0000(2)
N2	0.0143(3)	0.0144(3)	0.0128(3)	-0.0048(2)	-0.0018(2)	-0.0031(2)
C1	0.0100(3)	0.0118(3)	0.0114(3)	-0.0037(2)	-0.0023(2)	-0.0001(2)
C2	0.0108(3)	0.0132(3)	0.0157(3)	-0.0059(2)	-0.0033(2)	0.0017(2)
C3	0.0130(3)	0.0121(3)	0.0146(3)	-0.0053(2)	-0.0028(2)	0.0010(2)
C4	0.0120(3)	0.0114(3)	0.0117(3)	-0.0041(2)	-0.0027(2)	-0.0013(2)
C5	0.0104(3)	0.0125(3)	0.0129(3)	-0.0047(2)	-0.0030(2)	0.0001(2)
C6	0.0103(3)	0.0109(3)	0.0113(3)	-0.0037(2)	-0.0027(2)	0.0002(2)
C7	0.0116(3)	0.0135(3)	0.0182(3)	-0.0075(3)	-0.0063(2)	0.0027(2)
C8	0.0137(3)	0.0142(3)	0.0150(3)	-0.0050(3)	-0.0016(2)	-0.0033(2)
C9	0.0152(3)	0.0183(3)	0.0127(3)	-0.0058(3)	-0.0002(2)	-0.0051(3)
C10	0.0125(3)	0.0117(3)	0.0121(3)	-0.0042(2)	-0.0023(2)	-0.0012(2)
C11	0.0144(3)	0.0135(3)	0.0114(3)	-0.0041(2)	-0.0030(2)	-0.0017(2)
C12	0.0141(3)	0.0123(3)	0.0131(3)	-0.0044(2)	-0.0050(2)	-0.0008(2)
C13	0.0133(3)	0.0158(3)	0.0134(3)	-0.0038(2)	-0.0030(2)	-0.0034(2)
C14	0.0129(3)	0.0143(3)	0.0111(3)	-0.0037(2)	-0.0022(2)	-0.0020(2)
C15	0.0123(3)	0.0112(3)	0.0114(3)	-0.0040(2)	-0.0032(2)	-0.0006(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C16	0.0113(3)	0.0123(3)	0.0119(3)	-0.0043(2)	-0.0029(2)	-0.0004(2)
C17	0.0284(4)	0.0190(4)	0.0129(3)	-0.0019(3)	-0.0080(3)	-0.0082(3)

Table 9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for 20181011AR.

	x/a	y/b	z/c	U(eq)
H2	0.6903	0.2714	0.1428	0.016
H3	0.5154	0.1258	0.0855	0.016
H5	0.0583	0.4553	0.1189	0.014
H7A	0.1995	0.7502	0.1155	0.016
H7AB	0.0563	0.6444	0.2215	0.016
H8A	0.3101	0.5004	0.3865	0.017
H8AB	0.0971	0.5853	0.4070	0.017
H9A	0.1817	0.7717	0.4712	0.018
H9AB	0.2894	0.6049	0.5317	0.018
H11	0.5083	0.7809	0.5556	0.016
H13	0.9225	0.9698	0.2808	0.017
H14	0.7742	0.8962	0.1664	0.015
H16	0.4804	0.8216	0.1424	0.014
H17A	0.6464	0.9140	0.6350	0.029
H17B	0.8645	0.9053	0.6405	0.029
H17C	0.7828	0.7517	0.6336	0.029

Computational studies of 8a, 8d, and 8g[1]



8 *antiperiplanar* *favored diastereomer*

int-**8**

8 *synperiplanar*

(M06-2X-D3 / def2-TZVPP / IEFPCM (toluene) / / TPSS-D2 / 6-31+G(d,p) / IEFPCM (toluene))

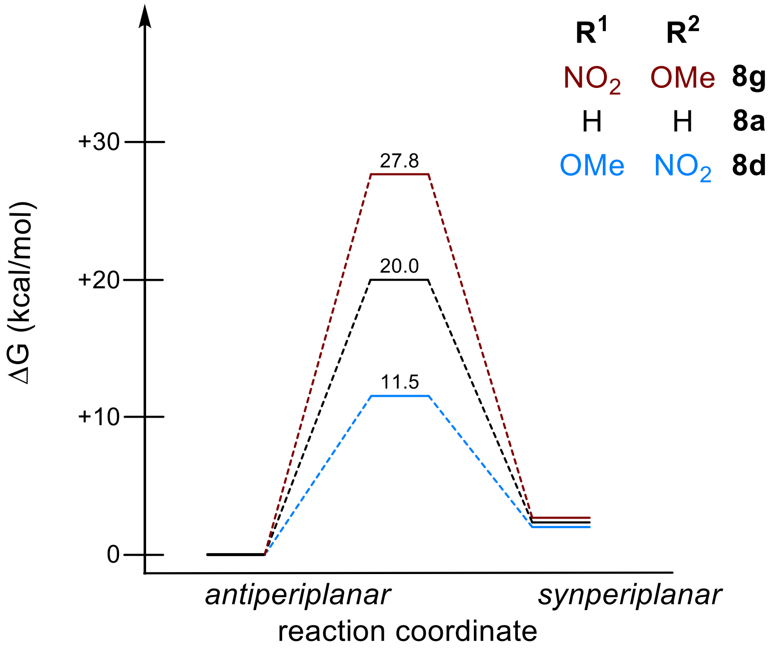


Figure S-7. Proposed equilibration of diastereoisomeric forms: Computational support of electronics on structural dynamics (**8a**, **8d**, **8g**).

Conformational searches were performed with MacroModel[7] using the OPLS3 force field.[8] All DFT calculations were performed with GAUSSIAN 09.[9] Ground state structures were obtained using the meta-GGA functional TPSS[10] with Grimme's dispersion-correction D2,[11] and the double-ζ basis set 6-31+G(d,p). All optimized geometries were verified as zero imaginary frequencies. Single-point energy calculations were completed on these structures using the M06-2X functional[12] and a triple-ζ def2-TZVPP basis set,[13] with Grimme's dispersion-correction D3.[14] The integral equation formalism polarizable continuum model (IEFPCM) was used to account for solvation by toluene in all calculations. [15] Entropic influences of the reported free energies were calculated using partition functions evaluated with Truhlar's quasiharmonic approximation.[16]

Cartesian Coordinates and Calculated Energies

Compound 8a anti

SCF energy: -1071.645263
Corrected free energy: -1071.418155
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	2.847237	-1.244524	0.793565
C	2.010963	-0.170555	0.437031
C	2.468714	0.818105	-0.458348
C	3.765879	0.701958	-0.989201
C	4.596561	-0.372174	-0.640780
C	4.136964	-1.349590	0.258465
C	0.619104	-0.099761	1.007241
N	0.001185	1.173692	0.862386
C	0.111862	1.721277	-0.505960
C	1.589041	2.006518	-0.801654
S	-0.391971	-1.551050	0.100274
C	-2.003163	-0.801940	-0.062557
C	-2.360876	0.420490	0.554592
C	-1.368840	1.192303	1.407996
C	-2.945269	-1.469745	-0.876751
C	-4.232054	-0.947939	-1.054158
C	-4.593241	0.265827	-0.445104
C	-3.648851	0.941176	0.339694
H	2.477476	-1.999175	1.488228
H	4.122652	1.463888	-1.682668
H	5.596358	-0.446313	-1.065861
H	4.777662	-2.183728	0.539240
H	0.591607	-0.403900	2.057626
H	-0.479427	2.643959	-0.542337
H	-0.302486	1.011389	-1.243371
H	1.910726	2.873174	-0.203544
H	1.713365	2.272148	-1.860680
H	-1.314546	0.771811	2.423731
H	-1.689948	2.239033	1.489813
H	-2.663325	-2.401529	-1.365910
H	-4.945913	-1.484924	-1.677105
H	-5.588457	0.682999	-0.588358
H	-3.906690	1.893582	0.805676

Compound 8a syn

SCF energy: -1071.664446
Corrected free energy: -1071.414545
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	2.429236	-1.543687	0.683688
C	1.912085	-0.305501	0.253451
C	2.776814	0.657312	-0.304875
C	4.143988	0.351948	-0.439840
C	4.652346	-0.887620	-0.031609
C	3.789800	-1.839361	0.538729
C	0.432119	-0.020340	0.438963
N	-0.010031	1.267761	-0.091039
C	0.982793	2.338457	0.113797
C	2.235156	2.014183	-0.703848
S	-0.532632	-1.367546	-0.429241
C	-2.174070	-0.711702	-0.187127
C	-2.412107	0.624571	0.205101
C	-1.308362	1.632490	0.487126
C	-3.262477	-1.578510	-0.429954
C	-4.578498	-1.129287	-0.278915
C	-4.825879	0.193400	0.126202
C	-3.744463	1.050782	0.362640
H	1.755339	-2.276632	1.126938
H	4.810539	1.103723	-0.863216
H	5.713075	-1.106214	-0.144843
H	4.174636	-2.801902	0.871294
H	0.172242	-0.118237	1.511414
H	1.242767	2.453227	1.186665
H	0.526514	3.275698	-0.229256
H	3.003460	2.783523	-0.544871
H	1.967215	2.018953	-1.771010
H	-1.218785	1.773092	1.587892
H	-1.598212	2.601847	0.060146
H	-3.069438	-2.607220	-0.732258
H	-5.405099	-1.811496	-0.470977
H	-5.845927	0.552739	0.249363
H	-3.926877	2.082503	0.666692

Compound *int*-8a

SCF energy: -1071.612246
Corrected free energy: -1071.386361
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	-2.54352	1.95732	-0.02143
C	-1.97510	0.68105	0.18698
C	-2.72388	-0.49678	-0.08003
C	-4.03792	-0.37150	-0.53609
C	-4.60966	0.90166	-0.72591
C	-3.86354	2.06526	-0.47236
C	-0.61501	0.55824	0.65642
N	-0.10356	-0.58663	1.04326
C	-0.97940	-1.77761	1.19751
C	-2.01374	-1.82788	0.06963
S	1.51607	-1.87298	-1.09898
C	2.42064	-0.46237	-0.59133
C	2.25067	0.07876	0.72218
C	1.28154	-0.61780	1.63282
C	3.34311	0.20983	-1.44004
C	4.04526	1.34084	-1.00789
C	3.85852	1.86028	0.28848
C	2.95169	1.21995	1.14568
H	-1.94934	2.84822	0.17749
H	-4.61837	-1.26760	-0.75172
H	-5.63635	0.98256	-1.07839
H	-4.30823	3.04566	-0.62910
H	0.05500	1.41734	0.66582
H	-1.46486	-1.69409	2.18302
H	-0.32339	-2.65047	1.16794
H	-1.48446	-2.05867	-0.86601
H	-2.72966	-2.63349	0.27340
H	1.52353	-1.68298	1.73049
H	1.23280	-0.13973	2.62148
H	3.49908	-0.17685	-2.44593
H	4.74367	1.82630	-1.68985
H	4.40337	2.74298	0.61867
H	2.78710	1.59946	2.15581

Compound 8d anti

SCF energy: -1390.687763
Corrected free energy: -1390.432592
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	1.724208	-2.026208	-0.209521
C	2.654350	-0.844441	-0.006450
C	2.227478	0.266295	0.744785
C	0.836555	0.328944	1.294854
N	0.131960	-0.893022	1.265803
C	3.961972	-0.874783	-0.523928
C	4.838801	0.199967	-0.295167
C	4.413453	1.312412	0.462031
C	3.118097	1.335881	0.973087
C	0.258687	-1.623216	-0.013543
S	-0.112519	1.760715	0.186361
C	-1.721007	1.060701	0.021462
C	-2.163100	-0.070661	0.764005
C	-1.250355	-0.766302	1.759585
C	-2.599202	1.659182	-0.919968
C	-3.889004	1.173615	-1.110021
C	-4.305673	0.054105	-0.368936
C	-3.448590	-0.571477	0.548175
O	6.126180	0.258716	-0.764693
C	6.592456	-0.861248	-1.541011
N	-5.648752	-0.477898	-0.566812
O	-6.396340	0.094353	-1.391838
O	-5.992969	-1.483091	0.096519
H	1.979202	-2.812136	0.518029
H	1.861352	-2.447837	-1.214553
H	0.787817	0.778025	2.289874
H	4.278131	-1.741379	-1.100156
H	5.106463	2.132778	0.633815
H	2.784841	2.195098	1.555228
H	-0.387351	-2.506834	0.044058
H	-0.084053	-0.991526	-0.851943
H	-1.206740	-0.205721	2.705043
H	-1.636025	-1.770924	1.973143
H	-2.255693	2.514911	-1.498202
H	-4.567523	1.634041	-1.821956
H	-3.796903	-1.444146	1.095996
H	7.622298	-0.616955	-1.813077
H	5.977994	-0.985556	-2.444700
H	6.564324	-1.783261	-0.941862

Compound 8d syn

SCF energy: -1390.683526
Corrected free energy: -1390.429123
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	-2.181416	2.331878	-0.795413
C	-2.903548	1.077965	-0.347197
C	-2.174828	0.037353	0.270032
C	-0.677137	0.136476	0.469261
N	-0.065442	1.336304	-0.085613
C	-4.290259	0.956715	-0.494733
C	-4.965892	-0.190521	-0.041832
C	-4.247909	-1.225686	0.589002
C	-2.861649	-1.093939	0.741819
C	-0.917670	2.534182	0.044776
S	0.121360	-1.354155	-0.361361
C	1.818912	-0.889853	-0.207439
C	2.232148	0.412500	0.178387
C	1.263369	1.542264	0.496230
C	2.789005	-1.877787	-0.512136
C	4.148915	-1.599641	-0.420818
C	4.542407	-0.313481	-0.015495
C	3.601242	0.682234	0.276339
O	-6.323459	-0.203916	-0.244834
C	-7.041948	-1.362579	0.219856
N	5.965908	-0.000852	0.093320
O	6.789716	-0.899918	-0.184816
O	6.293809	1.149622	0.460073
H	-2.845389	3.201383	-0.698581
H	-1.887808	2.244198	-1.852041
H	-0.431803	0.019004	1.542157
H	-4.864978	1.758402	-0.956146
H	-4.748672	-2.115126	0.960662
H	-2.305581	-1.892191	1.233616
H	-1.185166	2.731469	1.102519
H	-0.336591	3.386831	-0.327884
H	1.199077	1.667677	1.599485
H	1.668101	2.475253	0.084194
H	2.463452	-2.871738	-0.813566
H	4.898801	-2.351330	-0.647536
H	3.947191	1.670995	0.568703
H	-8.088056	-1.177234	-0.036569
H	-6.680158	-2.269287	-0.286737
H	-6.930421	-1.474758	1.308341

Compound *int*-8d

SCF energy: -1390.668697
Corrected free energy: -1390.414321
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	-3.11953	0.78400	1.74401
C	-2.22234	1.36105	0.78785
C	-2.21845	0.76313	-0.52546
C	-3.02250	-0.32965	-0.83538
C	-3.87958	-0.86583	0.14400
C	-3.92954	-0.30046	1.43870
C	-1.29659	1.33544	-1.56612
N	0.13792	1.13435	-1.16728
C	0.55871	-0.04911	-0.78696
C	1.92350	-0.31161	-0.43499
C	2.81793	0.78410	-0.24933
C	2.23017	2.17711	-0.33959
C	1.10891	2.23902	-1.38125
C	2.37667	-1.63550	-0.24543
C	3.70609	-1.89017	0.09058
C	4.59064	-0.79976	0.25653
C	4.13705	0.53432	0.09440
S	-1.19226	2.68904	1.18051
O	5.90128	-0.92732	0.58154
C	6.42311	-2.26369	0.77657
N	-4.69739	-2.00536	-0.17916
O	-5.46524	-2.46628	0.70501
O	-4.61085	-2.50373	-1.33448
H	-3.15354	1.21926	2.74040
H	-3.00417	-0.77537	-1.82755
H	-4.60051	-0.72919	2.17810
H	-1.42554	2.42026	-1.64901
H	-1.44482	0.85654	-2.54320
H	-0.19296	-0.83606	-0.72754
H	2.99907	2.91663	-0.59174
H	1.79844	2.44201	0.63728
H	0.54669	3.17104	-1.28718
H	1.50185	2.13015	-2.40408
H	1.68298	-2.46480	-0.37516
H	4.04663	-2.91223	0.22393
H	4.84005	1.34878	0.25714
H	6.31612	-2.84968	-0.14613
H	7.47790	-2.12364	1.02157
H	5.89726	-2.75709	1.60477

Compound 8g anti

SCF energy:	-1390.686403
Corrected free energy:	-1390.431201
Charge:	0
Solvation:	Toluene (PCM)
Spin multiplicity:	1
Imaginary frequencies:	0

Cartesian Coordinates

C	-1.262423	2.115234	-0.382793
C	-2.196160	0.960239	-0.074845
C	-1.776675	-0.094151	0.766615
C	-0.373335	-0.125366	1.311847
N	0.308284	1.123314	1.209533
C	-3.500363	0.940761	-0.587741
C	-4.357228	-0.114596	-0.253587
C	-3.961666	-1.163543	0.589561
C	-2.662164	-1.139202	1.096898
C	0.201807	1.736962	-0.132018
S	0.518269	-1.586453	0.334930
C	2.156366	-0.900781	0.120519
C	2.610932	0.260066	0.793007
C	1.691401	1.034117	1.722122
C	3.020554	-1.549965	-0.780374
C	4.328806	-1.091570	-0.994562
C	4.777145	0.059393	-0.320872
C	3.905464	0.734297	0.551699
O	6.032431	0.605874	-0.460464
C	6.938093	-0.072733	-1.350134
N	-5.724674	-0.120144	-0.804127
O	-6.061434	0.820836	-1.547546
O	-6.474950	-1.066578	-0.497322
H	-1.528987	2.966072	0.262034
H	-1.395279	2.434197	-1.425203
H	-0.355275	-0.466572	2.351221
H	-3.855080	1.735179	-1.239268
H	-4.658010	-1.960439	0.831230
H	-2.322574	-1.939680	1.752578
H	0.839095	2.628586	-0.138378
H	0.561952	1.043879	-0.911478
H	1.635544	0.551702	2.709365
H	2.072737	2.053812	1.859583
H	2.673284	-2.429646	-1.320710
H	4.971844	-1.625586	-1.688826
H	4.252660	1.639573	1.049069
H	7.866956	0.502287	-1.314200
H	7.114694	-1.103473	-1.008571
H	6.537173	-0.084863	-2.374563

Compound 8g syn

SCF energy: -1390.681551
Corrected free energy: -1390.427049
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	-1.883052	2.328510	-0.614963
C	-2.513547	1.007623	-0.229455
C	-1.710239	-0.031586	0.288615
C	-0.209941	0.136281	0.435824
N	0.312842	1.399555	-0.078502
C	-3.898447	0.813761	-0.336632
C	-4.457167	-0.402297	0.068935
C	-3.679862	-1.440972	0.601833
C	-2.303728	-1.239796	0.710633
C	-0.589024	2.537574	0.175659
S	0.615741	-1.259689	-0.489973
C	2.310250	-0.747713	-0.240038
C	2.664032	0.562791	0.156921
C	1.651043	1.654196	0.469707
C	3.323915	-1.692151	-0.485693
C	4.678570	-1.362194	-0.346346
C	5.028923	-0.061298	0.060606
C	4.019972	0.883730	0.308817
O	6.320455	0.378307	0.237515
C	7.368901	-0.570743	-0.029245
N	-5.914649	-0.590070	-0.049958
O	-6.591333	0.347064	-0.519030
O	-6.396801	-1.677702	0.324583
H	-2.588338	3.147533	-0.420938
H	-1.644594	2.331890	-1.688551
H	0.063474	-0.006465	1.500126
H	-4.541189	1.599989	-0.724041
H	-4.150300	-2.366717	0.918253
H	-1.674473	-2.028161	1.120266
H	-0.811928	2.649525	1.256831
H	-0.073909	3.445068	-0.162239
H	1.599310	1.789231	1.572927
H	2.005783	2.601409	0.043126
H	3.054899	-2.703106	-0.789087
H	5.435019	-2.115869	-0.546677
H	4.308759	1.888276	0.616666
H	8.302327	-0.033994	0.158842
H	7.286215	-1.437517	0.643318
H	7.327567	-0.908116	-1.075631

Compound *int*-8g

SCF energy: -1390.640685
Corrected free energy: -1390.386868
Charge: 0
Solvation: Toluene (PCM)
Spin multiplicity: 1
Imaginary frequencies: 0

Cartesian Coordinates

C	-3.50833	-0.37834	1.65661
C	-2.62319	-1.04774	0.77856
C	-2.63426	-0.62783	-0.58641
C	-3.47744	0.39067	-1.04026
C	-4.36622	1.01720	-0.14664
C	-4.37700	0.62780	1.20705
C	-1.66821	-1.31680	-1.50905
N	-0.26660	-1.15925	-0.98595
C	0.18696	0.06179	-0.75917
C	1.56596	0.32319	-0.44850
C	2.45159	-0.76940	-0.21661
C	1.86366	-2.16791	-0.22249
C	0.69549	-2.27055	-1.20732
C	2.03704	1.65634	-0.36612
C	3.37682	1.91226	-0.08221
C	4.23606	0.82048	0.12567
C	3.78878	-0.51390	0.06834
S	-1.53413	-2.32624	1.28113
O	-5.16387	2.00496	-0.68486
C	-6.07319	2.66159	0.21557
N	5.64917	1.07778	0.41572
O	6.40093	0.09346	0.59360
O	6.03215	2.26762	0.46853
H	-3.52562	-0.66418	2.70655
H	-3.46017	0.70650	-2.08274
H	-5.04696	1.10502	1.91804
H	-1.69946	-0.90158	-2.52597
H	-1.84610	-2.39914	-1.52722
H	-0.54784	0.86498	-0.77140
H	1.49130	-2.40280	0.78394
H	2.62555	-2.90953	-0.49032
H	1.04472	-2.19294	-2.24898
H	0.13782	-3.19909	-1.06377
H	1.34743	2.48120	-0.53514
H	3.76607	2.92369	-0.02067
H	4.49082	-1.32235	0.25327
H	-5.52190	3.16828	1.02197
H	-6.60973	3.39368	-0.39376
H	-6.77860	1.93713	0.64940

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