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Supporting Information

Light-Driven Rotary Molecular Motors on Gold Nanoparticles

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Experimental Section

General Remarks

Chemicals were purchased from Acros, Aldrich, Fluka or Merck. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All other reagents were recrystallized or distilled as necessary. Analytical TLC was performed with Merck silica gel 60 F254 plates and visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM). NMR spectra were obtained using a Varian Mercury Plus and a Varian Unity Plus Varian-500, operating at and 199.97, 299.97, 399.93 and 499.86 MHz, respectively, for the ^{1}H nucleus or at 50.29, 75.5, 100.57 and 125.70 MHz, respectively, for the ^{13}C nucleus. Chemical shifts are reported in δ=units (ppm) relative to the residual protonated solvent signals of $CDCl_3$ (^{1}H NMR: δ=7.26 ppm), DMSO-d_6 (^{1}H NMR: δ=2.49 ppm), toluene-d_8 (^{1}H NMR: δ=2.09 ppm) or Benzene-d_6 (^{1}H NMR: δ=7.15 ppm) or at the carbon absorption in $CDCl_3$ (^{13}C NMR: δ=77.0 ppm) DMSO-d_6 (^{13}C NMR: δ=39.5 ppm) toluene-d_8 (128.0 or 20.4 ppm) or Benzene-d_6 (^{13}C NMR: δ=128.2 ppm). MS (EI) spectra were obtained with a Jeol JMS-600 spectrometer. Irradiation of samples was performed with Spectroline model ENB-280C/FE lamp or with a 180 W Oriel Hg-lamp using a pyrex filter or 365 bandwidth filters. Photostationary states (PSS) were ensured by monitoring composition changes in time by taking UV or CD spectra at distinct intervals until no changes were observed. Irradiation experiments were performed. UV-Vis measurements were performed on a Hewlett-Packard HP 8453 FT spectrophotometer and CD spectra were recorded on a JASCO J-715 spectropolarimeter using Uvasol grade solvents (Merck). Thermal helix inversions were monitored by CD spectroscopy using the apparatus just described and a JASCO PFD-350S/350L Peltier type FDCD attachment with a temperature control. Hydrazone **6** was prepared according a literature procedure.[1]

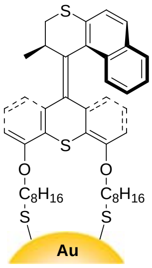
NMR spectroscopic analysis of 5

The remaining two protons in the ring at the 3'-position have absorptions at δ=3.06 and 3.70 ppm. This takes into account the structure in the solid state, in which the distance between the $Me_{2'ax}$ and both protons at the 3'-position is smaller for the proton in the pseudo-equatorial orientation ($H_{3'eq}$) than for the proton in the pseudo-axial orientation ($H_{3'ax}$), a larger NOE interaction between $Me_{2'ax}$ and $H_{3'eq}$ is expected. The signal at δ=3.06 is therefore assigned to $H_{3'eq}$ and the signal at δ=3.70 to $H_{3'ax}$. The NOE-signal between the $Me_{2'ax}$ and $H_{3'ax}$ is significantly weaker and was only observed during the ROESY-experiment. This assignment is in agreement with the coupling constants between $H_{2'eq}$ and both $H_{3'}$-protons according to the Karplus equation. As is already evident from the X-ray structure, the distances between $H_{2'eq}$ and $H_{3'ax}$ in the upper half of the molecule and the proton at the 1-position (H_1) in the lower of the molecule are relatively small, 2.46 and 2.48 Å, respectively, due to the twisted nature of the molecule. Therefore, a clear NOE-signal is observed and the protons H_2 and H_3 can be assigned.

Since the methoxy-signal at δ=4.00 shows a NOE-interaction with H_3, it can be concluded that it is located at the 4-position of the lower half. Similarly, the other methoxy signal at δ=3.81 exhibits an NOE-signal with an aromatic proton at δ=6.30 ppm, which is therefore H_6. This is in agreement with the large upfield shift of protons H_6, H_7 and H_8 due to the ring current anisotropy enforced by the naphthalene moiety in the upper half. The ^{1}H NMR spectrum of the motor functionalized gold colloids **4** shows severe line broadening of all proton absorptions and no additional information could be obtained from the spectrum.

Synthetic procedures

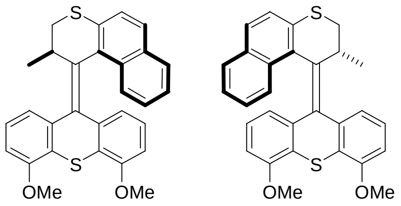
Motor-functionalized gold colloids ((2’R)-(M)-4)[2]



(2'*R*)-(*M*)-**4**

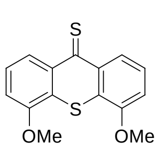
To a mixture of Oct_4NBr (13 mg, 24 μmol) in toluene (1.6 ml) was added a solution of $HAuCl_4 \cdot 3\ H_2O$ (5.5 mg, 13.3 μmol) in water (0.6 ml) to give an orange solution which was stirred for 5 min. The dithiol (2’*R*)-(*M*)-**43** (4.5 mg, 6.2 μmol) in a small amount of toluene (0.5 ml) was then added. The mixture was stirred again for 5 min and then a solution of $NaBH_4$ (5 mg, 0.13 mmol) was added immediately giving a black suspension. The reaction mixture was stirred for 16 h and the organic layer was washed with water (3x 2 ml). The toluene was then removed *in vacuo* and the colloids were dried *in vacuo*. For purification purposes, the colloids were redissolved in toluene (2 ml) and then precipitated with methanol repeatedly giving the pure gold colloids; UV-Vis: (toluene) λ (ε) 296 (28600), 321 (20400), 351 (15200), 526 (3900); CD in toluene, λ in nm (Δε in mdeg) 283 (+91.0), 324 (-15.8), 359 (-19.6). From this ratio together with the known CD and UV/Vis spectra of both pure (2'*R*)-(*M*)-**4** and the ≥ 280 nm photostationary state the CD and UV/Vis spectra for pure (2'*R*)-(*P*)-**4** was calculated (UV/Vis (toluene): ε / $dm^3\ mol^{-1}\ cm^{-1}$ (λ / nm): 3910 (347, shoulder), 10866 (315), 16886 (295); CD (toluene) Δε (λ/ nm): +13.5 (345); +26.2 (318); -66.0 (283)). TEM data for this material is provided in a separate section.

4,5-Dimethoxy-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene (stable 5 and unstable 5)[2]



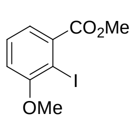
Under a nitrogen atmosphere copper powder (approx. 300 mg) was added to a stirred solution of episulfide **22** (232 mg, 0.46 mmol) in *p*-xylene (10 mL). After heating at reflux for 16 h, the reaction mixture was allowed to cool to rt and the brown copper residue was removed by filtration and washed with dichloromethane. The solvents were evaporated under reduced pressure to give the crude product, which was purified by column chromatography (SiO_2, hexane:CH_2Cl_2, 2:1) to yield olefin (206 mg, 0.44 mmol, 95%) as a colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.75 (d, *J* = 6.6 Hz, $Me_{2'ax.}$, 3H), 3.07 (dd, *J* = 11.4, 2.9 Hz, $H_{3'eq}$, 1H), 3.70 (dd, *J* = 11.4, 7.3 Hz, $H_{3'ax}$, 1H), 3.81 (s, OMe_5, 3H), 4.00 (s, OMe_4, 3H), 4.12 (dqd, *J* = 7.3, 6.6, 2.9 Hz, $H_{2'eq}$, 1H), 6.06 (dd, *J* = 7.7, 1.1 Hz, H_8, 1H), 6.29 (dd, *J* = 8.1, 1.1 Hz, H_6, 1H), 6.36-6.40 (m, H_7, 1H), 6.87 (dd, *J* = 8.1, 1.1 Hz, H_3, 1H), 7.00-7.04 (m, $H_{8'}$, 1H), 7.09-7.13 (m, $H_{9'}$, 1H), 7.23 (dd, *J* = 7.7, 1.1 Hz, H_1, 1H), 7.36-7.38 (m, H_2, 1H), 7.41 (d, *J* = 8.4 Hz, $H_{6'}$, 1H), 7.57 (d, *J* = 8.4 Hz, $H_{7'}$, 1H), 7.60 (d, *J* = 8.4 Hz, $H_{10'}$, 1H), 7.63 (d, *J* = 8.4 Hz, $H_{5'}$, 1H); ^{1}H NMR (toluene-d_8, 400 MHz, stable isomer, axial methyl substituent) δ=0.54 (d, *J* = 6.6 Hz, 3H), 2.69 (dd, *J* = 11.5, 2.7 Hz, 1H), 3.22 (s, 3H), 3.36 (s, 3H), 3.36-3.41 (m, 1H), 4.06-4.10 (m, 1H), 5.87 (d, *J* = 8.1 Hz, 1H), 6.16-6.20 (m, 1H), 6.32 (d, *J* = 7.0 Hz, 1H), 6.40 (d, *J* = 8.1 Hz, 1H), 6.87-6.91 (m, 1H), 6.97-7.09 (m, 2H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.31-7.37 (m, 3H), 7.88 (d, *J* = 8.4 Hz, 1H); ^{1}H NMR (toluene-d_8, 400 MHz, unstable isomer, equatorial methyl substituent) δ=0.90 (d, *J* = 7.0 Hz, 3H), 2.25-2.31 (m, 1H), 2.98-3.05 (m, 2H), 3.22 (s, 3H), 3.34 (s, 3H), 5.86 (d, *J* = 8.1 Hz, 1H), 6.14-6.18 (m, 1H), 6.29 (d, *J* = 7.7 Hz, 1H), 6.35-6.37 (m, 1H), 6.90-7.16 (m, 4H), 7.36-7.44 (m, 3H), 7.74 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=19.1 (q), 32.0 (d), 37.2 (t), 56.0 (2xq), 107.6 (d), 108.2 (d), 119.9 (d), 121.6 (d), 122.7 (s), 124.3 (d), 124.5 (d), 125.4 (d), 125.5 (d), 125.7 (d), 126.5 (d), 127.3 (d), 127.4 (d), 130.8 (s), 131.3 (s), 131.6 (s), 132.2 (s), 134.7 (s), 136.3 (s), 136.5 (s), 138.8 (s), 155.2 (s), 156.1 (s), one (s) signal was not observed; *m/z* (EI, %) = 468 (M^+, 100); HRMS (EI): calcd. for $C_{29}H_{24}O_2S_2$: 468.1218, found 468.1208; Synthesis yielded two enantiomers of **5** ((2'*R*)-(*M*)-**5** and (2'*S*)-(*P*)-**5**) which were resolved by preparative HPLC on a chiral stationary phase employing a Chiralcel AD column as the stationary phase and *n*-heptane : *i*-propanol 9:1 as the eluent (1 ml·min^{-1}). The first eluted fraction (5.1 min) was assigned by X-ray crystallography and CD spectroscopy to be (2'*R*)-(*M*)-**5** and second eluted fraction (6.4 min) was assigned to be (2'*S*)-(*P*)-**5**. The (2'*R*)-(*M*) isomer of **5** was used for all chiroptical studies. The absolute configuration of the molecule was determined by Flack's refinement (**x**= 0.01(5); UV-Vis and CD spectroscopic data for pure stable (2'*R*)-(*M*)-**5**: UV-Vis: (toluene) $\lambda_{max}(\varepsilon)$ 295 (16300), 323 (10500), 350 (shoulder, 6400); CD: (toluene) $\lambda_{max}(\Delta\varepsilon)$ 283 (+92.6), 322 (-15.2), 351 (-18.6); CD: (n-dodecane) λ ($\Delta\varepsilon$) 202 (+31.4), 214 (-67.5), 241 (-5.4), 251 (-46.0), 281 (+92.0), 321 (-14.8), 349 (-18.8); The spectroscopic data for pure unstable (2'*R*)-(*P*)-**5** was calculated using the UV and CD spectra of both pure (2'*R*)-(*M*)-**5** and the PSS_{365nm} comprised predominantly of 2'*R*)-(*P*)-**5**, assuming a PSS 94:6 unstable-**5**/stable-**5** (determined by ^{1}H NMR spectroscopy and HPLC). UV-Vis and CD spectroscopic data for (2'*R*)-(*P*)-**5**: UV-Vis (calc., toluene) $\lambda_{max}(\varepsilon)$ 295 (16900), 315 (10900), 347 (shoulder, 3900); CD: (calc., toluene) λ_{max} ($\Delta\varepsilon$) 283 (-66.0), 318 (+26.2), 345 (+13.5).

4,5-Dimethoxy-9*H*-thioxanthene-9-thione (7)



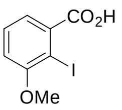
A mixture of 4,5-dimethoxy-9*H*-thioxanthene-9-one **15** (417 mg, 1.52 mmol) and P_4S_{10} (2.04 g, 4.59 mmol) in 25 mL of toluene was refluxed for 2 h. The deep green reaction mixture was filtered, and the residues were washed with CH_2Cl_2. The crude product, obtained after evaporation of all volatiles, was purified by column chromatography (SiO_2. toluene:CH_2Cl_2 = 1:1) and finally recrystallized from toluene to yield dark green needles of the thioketone **7** (354 mg, 1.23 mmol, 81%); m.p. 259.0-259.5 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ=4.06 (s, 6H), 7.13 (d, *J* = 7.7 Hz, 2H), 7.40 (m, 2H), 8.67 (dd, *J* = 8.6, 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=56.6 (q), 111.2 (d), 123.1 (s), 125.3 (d), 126.4 (d), 138.3 (s), 155.0 (s), due to the low solubility of this compound, no signal for the thiocarbonyl carbon atom was observed; *m/z* (EI, %) = 288 (M^+, 100), 273 (48); HRMS (EI): calcd. for $C_{15}H_{12}O_2S_2$: 288.0279, found 288.0268; elemental analysis calcd (%) for $C_{15}H_{12}O_2S_2$: C, 62.47; H, 4.19; S, 22.24; found: C, 61.98; H, 4.02; S, 22.43.

2-Iodo-3-methoxy-benzoic acid methyl ester (10)



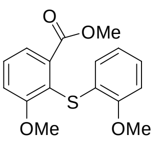
To an ice cooled suspension of 2-amino-3-methoxy-benzoic acid **9** (2.00 g, 12.0 mmol) in 40 ml of an aq. sol. of 20% HCl was added dropwise an ice-cooled solution of $NaNO_2$ (1.0 g, 14.5 mmol) in water (20 ml). After being stirred for 15 min at 0°C, the clear orange solution was poured slowly into a two-phase mixture of CH_2Cl_2 (50 ml) and KI (6.0 g, 36mmol) dissolved in water (50 ml) cooled at 0°C. Stirring was continued for 4 h at rt. Then, ether was added (100 ml) and the combined organic layers were washed with a dilute sol. aq. sol. of $NaHSO_3$ (2x 100 ml), water (2x 100 ml) and brine (100 ml) and dried over $MgSO_4$. Evaporation of all volatiles gave a beige solid (2.52 g) to which were added a mixture of DMF (25 ml), methyl iodide (2.0 ml, 32 mmol) and K_2CO_3 (2.0 g, 20 mmol) and stirred for 16 h. Ether (100 ml) was added to the mixture and the organic layer was washed with brine (5 x 100 ml) and dried ($MgSO_4$). The mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2, heptane:ethyl acetate= 16 :1, R_f= 0.20) to give the desired **10** as a slightly colored solid (2.25 g, 7.71 mmol, 64% over 2 steps); m.p. 53.0-55.0 °C (lit. 56-57°C)[3]; ^{1}H (300 MHz, $CDCl_3$) δ=3.91 (s, 3H), 3.94 (s, 3H), 6.92 (dd, *J*= 8.2 Hz, 1H), 7.23 (dd, *J*= 7.7, 1.5 Hz, 1H), 7.32-7.37 (m, 1H); ^{13}C (75 MHz, $CDCl_3$) δ=52.2 (q), 56.4 (q), 86.0 (s), 112.7 (d), 121.8 (d), 129.0 (d), 138.4 (s), 158.1 (s), 167.5 (s); *m/z* (EI, %) = 292 (M^+, 100), 261 (71); HRMS (EI): calcd. for $C_9H_9IO_3$: 291.9597, found 291.9607.

2-Iodo-3-methoxy-benzoic acid (11)



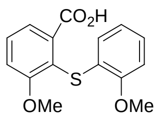
A mixture of ester **10** (0.81 g, 2.8 mmol) suspended in methanol (30 ml), water (10 ml) and LiOH (1.0 g, 42 mmol) was stirred for 16 h at rt. The mixture was then acidified with an aq. sol. of 30% HCl (50 ml) and extracted with ether (3x 75 ml). The combined organic layers were washed with water (2x 100 ml) and brine (2x 100 ml), dried ($MgSO_4$) and after removal of all volatiles gave acid **11** as a white solid (0.72 g, 2.59 mmol, 92%); m.p. 146.5-149.5 °C (lit.[1] 148-149 °C); ^{1}H (300 MHz, $CDCl_3$) δ=3.93 (s, 3H), 6.98-7.00 (dd, *J*= 8.0, 1.5 Hz, 1H), 7.36-7.41 (m, 1H), 7.46-7.49 (dd, *J*= 7.7, 1.5 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ=56.9 (q), 87.5 (s), 114.1 (d), 123.6 (d), 129.3 (d), 136.7 (s), 158.9 (s), 172.3 (s); *m/z* (EI, %) = 278 (M^+, 100), 261 (21); HRMS (EI): calcd. for $C_8H_7IO_3$: 277.9440, found 277.9437.

3-Methoxy-2-(2-methoxy-phenylsulfanyl)-benzoic acid methyl ester (13)



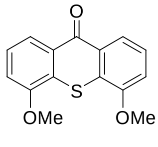
A mixture of acid **11** (2.90 g, 10.4 mmol), thiol **12** (1.90 g, 12.2 mmol), copper powder (200 mg, 3.1 mmol) and K_2CO_3 (5.0 g, 50 mmol) in DMF (125 ml) was refluxed for 7h. After cooling to rt, methyl iodide (5.0 ml, 80 mmol) was added and stirring was continued for 16 h. Water (300 ml) was added followed by extraction with ether (3x 100 ml). The combined organic layers were washed with water (7x 200 ml) and dried ($MgSO_4$). The oil obtained after removal of all volatiles was purified by column chromatography (SiO_2, heptane:ethyl acetate=4:1, R_f= 0.29) to yield **13** (2.27 g, 7.48 mmol, 72%) as a white solid; m.p. 118.0-118.5 °C; ^{1}H (300 MHz, $CDCl_3$) δ=3.74 (s, 3H), 3.79 (s, 3H), 3.86 (s, 3H), 6.70-6.78 (m, 2H), 6.80-6.83 (d, *J*= 8.1 Hz, 1H), 7.01-7.04 (d, *J*= 8.1 Hz, 1H), 7.06-7.11 (m, 1H), 7.22-7.24 (dd, *J*= 7.7, 1.1 Hz, 1H), 7.38-7.44 (m, 1H); ^{13}C (75 MHz, $CDCl_3$) δ=51.9 (q), 55.4 (q), 55.9 (q), 110.0 (d), 113.2 (2xd), 118.7 (s), 120.5 (d), 125.3 (s), 126.0 (d), 127.4 (d), 129.9 (d), 139.6 (s), 155.7 (s), 159.9 (s), 167.9 (s); *m/z* (EI, %) = 304 (M^+, 100); HRMS (EI): calcd. for $C_{16}H_{16}O_4S$: 304.0769, found 304.0778; elemental analysis calcd (%) for $C_{16}H_{16}O_4S$: C, 63.10; H, 5.30; S, 10.54; found (%): C, 62.90; H, 5.46; S, 10.54.

3-Methoxy-2-(2-methoxy-phenylsulfanyl)-benzoic acid (14)



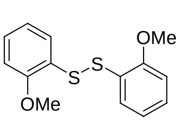
Ester **13** (2.27 g, 7.47 mmol) was suspended in a mixture of methanol (90 ml), water (30 ml) and LiOH (5.0 g, 0.2 mol) and stirred for 16 h at rt. The acid was obtained after workup as a colorless solid (1.92 mmol, 6.62 mmol, 89%); m.p. 160.0-162.5°C; ^{1}H (300 MHz, $CDCl_3$) δ=3.75 (s, 3H), 3.82 (s, 3H), 6.83-6.89 (m, 2H), 7.03-7.06 (d, *J*= 8.1 Hz, 1H), 7.20-7.24 (m, 2H), 7.41-7.46 (m, 1H), 7.67-7.69 (d, *J*= 8.1 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ=55.7 (q), 56.2 (q), 110.7 (d), 114.5 (d), 119.8 (s), 121.0 (d), 123.0 (d), 123.3 (s), 128.0 (d), 130.1 (d), 130.9 (d), 136.8 (s), 156.9 (s), 170.2 (s); *m/z* (EI, %) = 290 (M^+, 100); HRMS (EI): calcd. for $C_{15}H_{14}O_4S$: 290.0613, found 290.0617; elemental analysis calcd (%) for $C_{15}H_{14}O_4S$: C, 62.10; H, 5.05; S, 11.04; found (%): C, 61.70; H, 5.05; S, 11.57.

4,5-Dimethoxy-9H-thioxanthen-9-one (15)



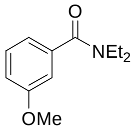
Method A: To PPA (10 mL) mechanically stirred at 60 °C was added acid **14** (0.22 g, 0.76 mmol). The mixture was heated to 110 °C, which resulted in a color change from colorless to dark red/brown. This mixture was stirred for 3 h, then poured (while hot) into ice-water (100 mL), and stirred for 12 h. The mixture was extracted with Et_2O (3 x 50 mL), and the combined organic layers were washed with sat'd aqueous $NaHCO_3$ (100 mL), brine (2 x 100 mL) dried ($MgSO_4$), and concentrated *in vacuo.* This mixture was purified by flash chromatography (heptane:EtOAc) to give the desired compound as a slightly yellow solid (0.92 g, 0.63 mmol, 82%); Method B: To a freshly prepared solution of LDA (17.6 mmol) in THF (50 ml) at 0 °C was added dropwise amide **9** (1.20 g, 3.48 mmol) dissolved in THF (25 ml). Upon completion of the addition, the ice bath was removed and the yellow solution was stirred at rt for 1h. A sat. aqueous sol. of NH_4Cl (100 ml) was added followed by extraction with ether (3x 100 ml). The crude product was obtained after drying over Na_2SO_4 and evaporation of all volatiles. Purification was performed by flash column chromatography (SiO_2, heptane:EtOAc) to give the desired compound as a slightly yellow solid (0.92 g, 3.38 mmol, 97%); m.p.>250°C; ^1H NMR (300 MHz, $CDCl_3$) δ=4.05 (s, 6H), 7.14 (d, *J* = 7.7 Hz, 2H), 7.42-7.47 (m, 2H), 8.25 (dd, *J* = 8.2, 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=56.4 (q), 112.1 (d), 121.4 (d), 125.9 (d), 127.6 (s), 129.9 (s), 154.8 (s), 180.2 (s); *m/z* (EI, %) = 272 (M^+, 100), 257 (46); HRMS (EI): calcd. for $C_{15}H_{12}O_3S$: 272.0507, found 272.0506; elemental analysis calcd (%) for $C_{15}H_{12}O_3S$: C, 66.20; H, 4.44; S, 12.44; found (%): C, 66.30; H, 4.41; S, 11.77.

Di(2-methoxyphenyl)disulfide (16)



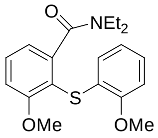
Following a literature procedure,[4] a mixture of $CuSO_4 \cdot 5\ H_2O$ (2.5 g, 10 mmol), $KMnO_4$ (2.5 g, 16 mmol), tetraoctylammonium bromide (0.5 g, 0.9 mmol) and 2-methoxybenzenethiol (1.0 g, 7.1 mmol) in CH_2Cl_2 (100 ml) was stirred for 3 h at rt. The solids were removed by filtration over celite and the desired compound was subsequently obtained pure by flash column chromatography (SiO_2, heptane:ethyl acetate) as a white solid (0.86 g, 3.1 mmol, 87%); m.p. 119.0-120.5°C; ^1H (300 MHz, $CDCl_3$) δ=3.90 (s, 3H), 6.85 (d, *J*= 8.1 Hz, 1H), 6.88-6.94 (m, 1H), 7.16-7.22 (m, 1H), 7.54(dd, *J* = 7.7, 1.5 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ=55.6 (q), 110.3 (d), 121.1 (d), 124.2 (s), 127.3 (d), 137.6 (d), 156.4 (s); *m/z* (EI, %) = 278 (M^+, 100); HRMS (EI): calcd. for $C_{14}H_{14}O_2S_2$: 278.0435, found 278.0440.

N,N-Diethyl-3-methoxy-benzamide (18)



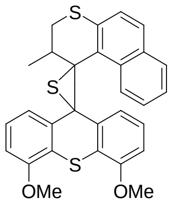
To 3-methoxybenzoic acid (19.0 g, 125 mmol) dissolved in CH_2Cl_2 (100 ml) was added $SOCl_2$ (22 ml, 36 g, 0.3 mol) and a drop of DMF. After refluxing this mixture for 1h, the solution was cooled down to 0°C and diethylamine (13.6 ml, 9.5 g, 130 mmol) and triethylamine (18.0 ml, 13.0 g, 130 mmol) were added carefully. While stirring, the temperature of the mixture was allowed to reach rt. After quenching the reaction with water (300 ml) after 2 h and addition of extra CH_2Cl_2 (100 ml), the organic layer was extracted with an aq. sol. of 10% HCl (2 x 200 ml) and a aqueous sol. of 1*N* NaOH (2 x 200 ml). The organic layer was then dried ($MgSO_4$) and concentrated *in vacuo* to give the desired amide **5** as a slightly yellow oil (23.8 g, 115 mmol, 92%); ^1H NMR (300 MHz, $CDCl_3$) δ=1.17 (br s, 3H), 1.29 (br s, 3H), 3.59 (br s, 2H), 3.85 (br s, 2H), 3.87 (s, 3H), 6.96-7.00 (m, 3H), 7.34 (d, *J* = 8.8 Hz, 1H); ^{13}C (75 MHz, $CDCl_3$) δ=12.5 (q), 13.9 (q), 38.8 (t), 42.9 (t), 54.8 (q), 111.3 (d), 114.5 (d), 117.9 (d), 129.1 (d), 138.1 (s), 159.1 (s), 170.5 (s); *m/z* (EI, %) = 207 (M^+, 38), 135 (100); HRMS (EI): calcd. for $C_{12}H_{17}NO_2$: 207.1259, found 207.1257.

N,N-Diethyl-3-methoxy-2-(2-methoxy-phenylsulfanyl)-benzamide (20)



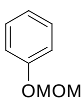
To THF (50 ml) cooled to –80°C were added *s*-BuLi (2.5 ml, 3.3 mmol) and TMEDA (0.48 ml, 3.3 mmol). After stirring for 30 min, amide **5** (0.62 g, 3.0 mmol) dissolved in THF (10 ml) was added and stirring was continued for 1h. To the then yellow suspension was added at –80°C disulfide **7** (1.52 g, 5.47 mmol) and stirring was continued for 16 h. The mixture was diluted with ether (100 ml) and washed with an aq. solution of 1*N* NaOH sol. (2x 100 ml), dried (Na_2SO_4), concentrated *in vacuo* to give a colorless oil. This oil was purified by column chromatography (SiO_2, heptane:EtOAc=2:1, R_f=0.14) to give **8** as a white solid (0.84 g, 2.52 mmol, 84%); m.p. 140.9-142.6°C; ^1H NMR (300 MHz, $CDCl_3$) δ=0.98 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 2.96-3.15 (m, 2H), 3.31-3.38 (m, 1H), 3.63-3.78 (m, 1H), 3.75 (s, 3H), 3.87 (s, 3H), 6.67-6.76 (m, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.93-6.95 (m, 2H), 7.02-7.07 (m, 1H), 7.41-7.46 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=12.1 (q), 13.6 (q), 38.2 (t), 42.4 (t), 55.4 (q), 55.8 (q), 109.9 (d), 111.0 (d), 115.6 (s), 118.3 (d), 120.6 (d), 125.1 (s), 125.5 (d), 126.5 (d), 130.9 (d), 144.8 (s), 155.3 (s), 160.3 (s), 168.4 (s); *m/z* (EI, %) = 345 (*M*$^+$, 100), 273 (74); HRMS (EI): calcd. for $C_{19}H_{23}NO_3S$: 345.1399, found 345.1390; elemental analysis calcd (%) for $C_{19}H_{23}NO_3S$: C, 66.10; H, 6.71; N, 4.05; S, 9.28; found (%): C, 66.00; H, 6.78; N, 4.04; S, 9.42.

Dispiro[2,3-dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1,2’-thiirane-3’,9’’-(4’’,5’’-dimethoxy-9’’*H*-thioxanthene)] (22)



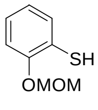
Under a nitrogen atmosphere, a solution of hydrazone **6**^{5} (273 mg, 0.98 mmol) in dry dichloromethane (10 mL) was cooled to 0 °C. $MgSO_4$ (approximately 400 mg), Ag_2O (454 mg, 1.96 mmol) and a sat. sol. of KOH in methanol (0.5 ml) were added subsequently. The mixture was stirred for 5 min at 0 °C when the color of the mixture turned red. After stirring for 30 min at 0 °C, the deep red suspension was filtered into another ice-cooled flask and the remaining residue was washed with cold dichloromethane. To the deep red solution was added a solution of thioketone **7** (283 mg, 0.98 mmol) in dichloromethane. Nitrogen evolution was observed and the red color of the solution slowly disappeared. The reaction mixture was stirred for 16 h while its temperature was allowed to reach rt. All volatiles were removed under reduced pressure to obtain the crude product. An excess of thioketone was removed by column chromatography (SiO_2, hexane:EtOAc, 16:1, R_f = 0.20), and the residue was purified by column chromatography (SiO_2, hexane:CH_2Cl_2 = 2:1, R_f = 0.18). After recrystallization from a hexane/CH_2Cl_2 mixture, the episulfide **11** was obtained as colorless needles (232 mg, 0.46 mmol, 47%), which consisted of only one of the two possible stereoisomers; m.p. 226.0-227.0 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz) δ=1.15 (d, *J* = 6.6 Hz, 3H), 2.14-2.19 (m, 1H), 2.54-2.69 (m, 2H), 3.79 (s, 3H), 3.98 (s, 3H), 6.15-6.20 (m, 1H), 6.33 (d, *J* = 6.9 Hz, 1H), 6.40 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.22-7.37 (m, 3H), 7.45-7.51 (m, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.70 (dd, *J* = 7.8, 0.6 Hz, 1H), 8.79 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=20.9 (q), 35.5 (t), 40.7 (d), 56.1 (q), 56.2 (q), 61.7 (s), 65.3 (s), 107.9 (d), 108.5 (d), 122.0 (d), 122.8 (s), 123.3 (d), 124.0 (d), 124.1 (d), 124.4 (d), 125.05 (d), 125.13 (d), 125.8 (d), 126.8 (d), 128.06 (s), 128.13 (d), 131.5 (s), 131.6 (s), 132.2 (s), 134.7 (s), 140.1 (s), 153.9 (s), 154.8 (s), one (s) signal could not be observed; *m/z* (EI, %) = 500 (*M*$^+$, 88), 468 (100).

Methoxymethoxybenzene (23)^6



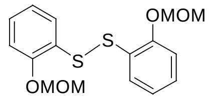
To a suspension of NaH (6.0 g, 0.25 mol) in THF (100 ml) was added at 0°C phenol (9.4 g, 0.10 mol). When the evolution of hydrogen had ceased, MOM-Cl (5.0 ml, 65 mmol) was added and the reaction mixture was stirred for 16 h. The excess NaH was quenched with an aq. sat. sol. of NH_4Cl (200 ml) followed by extraction with ether (3 x 50 ml). The organic layers were then washed with an aq. sol. of 1*N* NaOH (3 x 100 ml) and dried (Na_2SO_4). After removal of the organic solvents, the desired product was obtained as a colorless liquid (7.5 g, 54 mmol, 84%); ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.49 (s, 3H), 5.19 (s, 2H), 6.99-7.06 (m, 3H), 7.28-7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=55.6 (q), 94.1 (t), 116.0 (d), 121.6 (d), 129.3 (d), 157.1 (s); *m/z* (EI, %) = 138 (*M*$^+$, 100); HRMS (EI): calcd. for $C_8H_{10}O_2$: 138.0681, found 138.0696.

2-Methoxymethoxybenzenethiol (24)



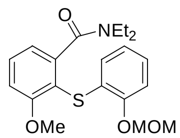
To a solution of **23** (6.9 g, 50 mmol) in THF (150 ml) at 0°C was added dropwise *n*-BuLi (1.6 M in hexane, 33 ml, 53 mmol). After stirring for 1h, the solution was cooled to -80°C and elemental sulfur (S_8, 1.76 g, 6.90 mmol) was added. The mixture was then allowed to reach rt, stirred for 16 h and quenched by the addition of sat. sol. of NH_4Cl (200 ml). Extraction with ether (2x 100 ml), drying (Na_2SO_4) and evaporation of the volatiles gave thiophenol **24** (6.7 g, 39 mmol, 79%) as a yellow liquid containing some impurities. The product was used directly in the next step; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.51 (s, 3H), 5.25 (s, 2H), 6.88-7.27 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ=56.0 (q), 94.6 (t), 114.4 (d), 121.5 (s), 122.1 (d), 126.1 (d), 129.2 (d), 152.4 (s); *m/z* (EI, %) = 170 (M^+, 100); HRMS (EI): calcd. for $C_8H_{10}O_2S$: 170.0401, found 170.0397.

Di(2-methoxymethoxyphenyl)disulfide (25)



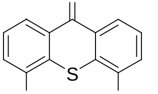
Following a literature procedure,[7] a mixture of $CuSO_4 \cdot 5\ H_2O$ (7.5 g, 30 mmol), $KMnO_4$ (7.5 g, 48 mmol), tetraoctylammonium bromide (0.5 g, 0.9 mmol) and thiol **24** (6.7 g, 39 mmol) in CH_2Cl_2 (200 ml) was stirred for 3 h at rt. The solids were removed by filtration over celite and the desired compound was subsequently obtained pure by flash column chromatography as a yellow liquid (4.2 g, 12.4 mmol, 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.52 (s, 6H), 5.25 (s, 4H), 6.95-6.99 (m, 2H), 7.09 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.14-7.19 (m, 2H), 7.55 (dd, *J* = 7.9, 1.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=56.3 (q), 94.8 (t), 114.4 (d), 122.5 (d), 125.6 (s), 127.5 (d), 127.7 (d), 154.2 (s); *m/z* (EI, %) = 338 (M^+, 66), 138 (100); HRMS (EI): calcd. for $C_{16}H_{18}O_4S_2$: 338.0646, found 338.0646.

N,N-Diethyl-3-methoxy-2-(2-methoxymethoxy-phenylsulfanyl)-benzamide (26)



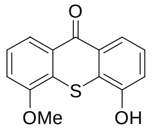
Prepared by following the procedure previously used for the synthesis of **20** (method B). Lithiated species **19** was generated by adding to **18** (3.02 g, 14.6 mmol) a solution of a complex of *s*-BuLi (11.3 ml, 14.6 mmol) and TMEDA (2.2 ml, 14.6 mmol) in THF (100 ml), at -80°C. The mixture was stirred for 30 min, after which disulfide **25** (3.95 g, 11.7 mmol) in THF (20 ml) was added. The mixture was stirred for 16 h while allowing the temperature to reach rt. The reaction was quenched with an aq. sat. sol. of NH_4Cl (200 ml), extracted with ether (3 x 100 ml), the organic layers combined and washed with brine (200 ml) dried ($MgSO_4$) and concentrated *in vacuo* to give a brown oil. The crude residue was purified by column chromatography (SiO_2, heptane:EtOAc = 1:1, $R_f = 0.3$) to give amide **23** as a light-yellow oil (2.30 g, 6.10 mmol, 52%); ^{1}H NMR (300 MHz, $CDCl_3$) δ=0.98 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H), 2.96-3.15 (m, 2H), 3.25-3.37 (m, 1H), 3.51 (s, 3H), 3.67-3.82 (m, 1H), 3.76 (s, 3H), 5.23 (s, 2H), 6.70 (d, *J* = 7.7 Hz, 1H), 6.76-6.81 (m, 1H), 6.93-6.96 (m, 2H), 6.99-7.06 (m, 2H), 7.41-7.47 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=12.2 (q), 13.6 (q), 38.2 (t), 42.4 (t), 55.8 (2xq), 94.7 (t), 111.0 (d), 114.3 (d), 115.6 (s), 118.4 (d), 122.0 (d), 125.5 (d), 126.4 (s), 126.7 (d), 131.0 (d), 144.9 (s), 153.0 (s), 160.3 (s), 168.4 (s); *m/z* (EI, %) = 375 (M^+, 100), 259 (48); HRMS (EI): calcd. for $C_{20}H_{25}NO_4S$: 375.1504, found 375.1491.

4-Methoxy-5-methoxymethoxy-9*H*-thioxanthen-9-one (27)



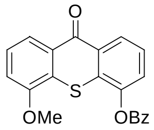
Following the procedure for the synthesis of ketone **15**, amide **26** (1.15 g, 3.07 mmol) was treated with freshly prepared LDA (12 mmol) in THF (70 ml) at 0 °C. After workup and purification by column chromatography (SiO_2, heptane:EtOAc=2:1, $R_f = 0.50$) the ketone **27** (0.69 g, 2.28 mmol, 75%) was obtained as a yellowish solid; m.p. 137.0-138.5°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ=3.57 (s, 3H), 4.06 (s, 3H), 5.40 (s, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 7.42-7.48 (m, 3H), 8.24-8.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=56.1 (q), 56.3 (q), 94.9 (t), 111.8 (d), 115.9 (d), 121.1 (d), 122.3 (d), 125.7 (2xd), 127.2 (s), 128.1 (s), 129.6 (s), 129.7 (s), 152.2 (s), 154.5 (s), 179.7 (s); *m/z* (EI, %) = 302 (M^+, 100); HRMS (EI): calcd. for $C_{16}H_{14}O_4S$: 302.0613, found 302.0613.

4-Hydroxy-5-methoxy-thioxanthen-9*H*-one (28)



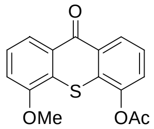
A mixture of thioxanthone **27** (0.39 g, 1.29 mmol), THF (40 ml) and an aq. sol. of 12*N* HCl (20 ml) was stirred for 16 h at rt. To the yellow solution was then added water (150 ml) followed by extraction with chloroform (3x 100 ml). After drying (Na_2SO_4) and evaporation of the organic volatiles, **28** was obtained as a relatively insoluble yellow solid which was sufficiently pure for further manipulations (0.30 g, 1.16 mmol, 90%); ^{1}H NMR (400 MHz, DMSO-d_6) δ=4.03 (s, 3H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.39-7.44 (m, 2H), 7.53 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (50 MHz, DMSO-d_6) δ=56.7 (q), 113.0 (d), 116.6 (d), 119.2 (d), 120.5 (d), 124.9 (s), 126.4 (d), 126.5 (d), 129.0 (s), 129.2 (s), 153.1 (2xs), 154.5 (s), 179.1 (s); *m/z* (EI, %) = 258 (M^+, 100), 243 (38); HRMS (EI): calcd. for $C_{14}H_{10}O_3S$: 258.0351, found 258.0354.

Benzoic acid 5-methoxy-9-oxo-9*H*-thioxanthen-4-yl ester (29)



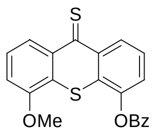
The phenol **28** (0.17 g, 0.66 mmol) was dissolved in $CHCl_3$ (50 ml) and benzoyl chloride (1.0 ml, 8.5 mmol) and triethylamine (1.0 ml, 7.2 mmol) were added. The mixture was then stirred for 16 h and ether (100 ml) was added. The organic layers were washed with an aq. sol. of 1*N* HCl (2x 100 ml), an aq. sol. of 2*N* NaOH (2x 100 ml), dried (Na_2SO_4) and then all organic volatiles including the excess benzoyl chloride were removed under reduced pressure. The yellow solid obtained was purified by column chromatography (SiO_2, heptane:EtOAc = 4:1, R_f= 0.29) and then by recrystallization from ethanol to give fine, slightly yellow needles (0.12 g, 0.33 mmol, 50%); m.p. 224.5-225.5°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.99 (s, 3H), 7.13-7.15 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.45-7.49 (t, *J* = 8.1 Hz, 1H), 7.55-7.63 (m, 4H), 7.72-7.74 (m, 1H), 8.25-8.27 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.34-8.37 (m, 2H), 8.57-8.59 (dd, *J* = 7.7, 1.8 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ=56.3 (q), 112.4 (d), 121.5 (d), 125.7 (d), 125.9 (d), 126.3 (d) 126.4 (s), 127.1 (d), 128.6 (s), 128.8 (d), 129.7 (s), 130.3 (s), 130.5 (d), 131.2 (s), 134.1 (d), 146.3 (s), 154.5 (s), 164.2 (s), 179.6 (s); *m/z* (EI, %) = 362 (M^+, 42), 105 (100); HRMS (EI): calcd. for $C_{21}H_{14}O_4S$: 362.0613, found 362.0603; elemental analysis calcd (%) for $C_{21}H_{14}O_4S$: C, 69.60; H, 3.89; S, 8.85; found (%): C, 69.10; H, 3.82; S, 9.02.

Acetic acid 5-methoxy-9-oxo-9*H*-thioxanthen-4-yl ester (30)



The phenol **28** (0.30 g, 1.16 mmol) was dissolved in $CHCl_3$ (50 ml) and acetyl chloride (2.0 ml, 28 mmol) and triethylamine (2.0 ml, 14 mmol) were added. The mixture was then stirred for 16 h and ether (100 ml) was added. The organic layers were washed with an aq. sol. of 1*N* HCl (2x 100 ml), an aq. sol. of 2*N* NaOH (2x 100 ml), dried (Na_2SO_4) and then all organic volatiles were removed under reduced pressure. The yellow solid obtained was purified by recrystallization from ethanol to give fine slightly beige needles (0.27 g, 0.90 mmol, 78%); m.p. 191.5-192.0°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.49 (s, 3H), 4.05 (s, 3H), 7.16 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.45-7.54 (m, 3H), 8.24 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.53 (dd, *J* = 7.9, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=20.9 (q), 56.4 (q), 112.4 (d), 121.5 (d), 125.6 (d), 125.8 (d), 126.2 (s), 126.3 (d), 127.0 (d), 129.7 (s), 130.3 (s), 130.8 (s), 146.1 (s), 154.5 (s), 168.5 (s), 179.5 (s); *m/z* (EI, %) = 300 (M^+, 32), 258 (100); HRMS (EI): calcd. for $C_{16}H_{12}O_4S$: 300.0456, found 300.0458; elemental analysis calcd (%) for $C_{16}H_{12}O_4S$: C, 63.99; H, 4.03; S, 10.68; found (%): C, 63.90; H, 4.10; S, 11.06.

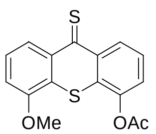
Benzoic acid 5-methoxy-9-thioxo-9*H*-thioxanthen-4-yl ester (31)



Compound **31** was synthesized following the procedure for **30**. Starting from ketone **29** (110 mg, 0.30 mmol), the desired thioketone **31** was obtained after flash column chromatography (SiO_2, heptane: EtOAc=8:1, R_f=0.32) as a brown/green solid (100 mg, 0.26 mmol, 87%); ^{1}H NMR (400 MHz, $CDCl_3$)

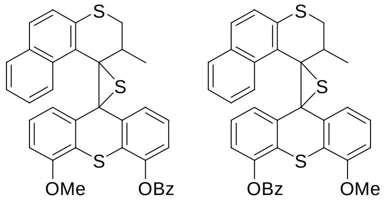
δ=3.98 (s, 3H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.37-7.75 (m, 6H), 8.33-8.36 (m, 2H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.94 (dd, *J* = 8.2, 1.2 Hz, 1H); due to the low solubility and limited stability of the compound, no ^{13}C analysis could be performed; *m/z* (EI, %) = 378 (M^+, 35), 362 (8), 105 (100); HRMS (EI): calcd. for $C_{21}H_{14}O_3S_2$: 378.0384, found 378.0392.

Acetic acid 5-methoxy-9-thioxo-9*H*-thioxanthen-4-yl ester (32)



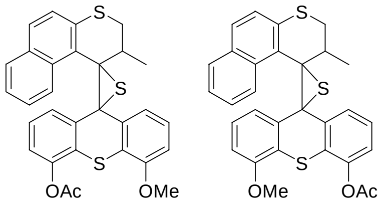
A suspension of ketone **27** (140 mg, 0.46 mmol) in toluene (10 ml) was heated to reflux in presence of P_4S_{10} (250 mg, 0.56 mmol). After 30 min the mixture turned dark green and was filtered to remove the solid residues. These were washed with CH_2Cl_2 and all organic volatiles were removed under reduced pressure. The resulting brown residue was purified by column chromatography (SiO_2, heptane:EtOAc=4:1, R_f=0.30) and was obtained as a light green solid (90 mg, 0.28 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ=2.50 (s, 3H), 4.05 (s, 3H), 7.13-7.15 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.38-7.46 (m, 3H), 8.59-8.61 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.88-8.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=20.9 (q), 56.5 (q), 111.5 (d), 121.5 (s), 124.7 (d), 125.2 (d), 125.9 (s), 126.2 (d), 126.7 (d), 130.6 (d), 138.2 (s), 138.6 (s), 146.2 (s), 154.6 (s), 168.5 (s), 210.6 (s); *m/z* (EI, %) = 316 (M^+, 45), 274 (100); HRMS (EI): calcd. for $C_{16}H_{12}O_3S_2$: 316.0228, found 316.0243.

E- and *Z*- Dispiro[2,3-dihydro-2-methyl-1*H*-naphtho[2,1-*b*]thiopyran-1,2'-thiirane-3',9''-(4''-benzoyl-5''-methoxy-9''*H*-thioxanthene)] (*E*-33 and *Z*-33)



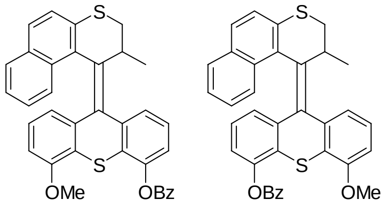
This mixture of stereoisomers was prepared according to the procedure used for **22**. Starting with hydrazone **6** (120 mg, 0.50 mmol) and thioketone **31** (100 mg, 0.26 mmol), the episulfide **33** was obtained as a mixture of *E* and *Z* diastereoisomers as a white solid (110 mg, 0.19 mmol, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.17 (d, *J* = 6.0 Hz, 3H), 1.18 (d, *J* = 6.0 Hz, 3H), 2.17 (dd, *J* = 11.9, 6.4 Hz, 1H), 2.24 (dd, *J* = 11.9, 5.3 Hz, 1H), 2.54-2.71 (m, 4H), 3.70 (s, 3H), 3.90 (s, 3H), 6.17-6.32 (m, 3H), 6.43 (d, *J* = 8.1 Hz, 1H), 6.64 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.70 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.23-7.72 (m, 18H), 8.00 (dd, *J* = 7.9 Hz, 1H), 8.30-8.37 (m, 4H), 8.73 (d, *J* = 8.4 Hz, 1H), 8.80 (d, *J* = 8.8 Hz, 1H); *m/z* (EI, %) = 590 (M^+, 19), 558 (94), 105 (100); HRMS (EI): calcd. for $C_{35}H_{26}O_3S_3$: 590.1044, found: 590.1048.

Dispiro[2,3-dihydro-2-methyl-1H-naphtho[2,1-b]thiopyran-1,2'-thiirane-3',9''-(4''-acetyl-5''-methoxy-9''H-thioxanthene)] (34)



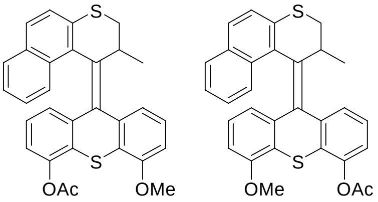
To a solution of hydrazone **6** (180 mg, 0.74 mmol) in CH_2Cl_2 (20 ml) were added Ag_2O (200 mg, 0.86 mmol), $MgSO_4$ (400 mg) and a sat. sol. of KOH in methanol (0.3 ml). After stirring for 60 min and the addition of additional portions of $MgSO_4$ (400 mg) and Ag_2O (200 mg), the suspension turned deep red and was filtered. To the solution was added a solution of the thioketone **32** (80 mg, 0.25 mmol) in cold CH_2Cl_2 (10 ml) and the reaction was stirred for 16 h. After evaporation of all volatiles, the crude episulfide was purified by column chromatography (SiO_2, heptane:EtOAc=8:1, R_f= 0.21) and obtained as a white solid as a 1:1 mixture of two isomers (100 mg, 0.19 mmol, 76%); ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.16 (d, *J* = 6.6 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 2.18 (dd, *J* = 11.5, 6.0 Hz, 1H), 2.23 (dd, *J* = 11.7, 5.1 Hz, 1H), 2.40 (s, 3H), 2.47 (s, 3H), 2.51-2.67 (m, 4H), 3.77 (s, 3H), 3.97 (s, 3H), 6.19-6.24 (m, 2H), 6.35 (dd, *J* = 8.1, 0.7 Hz, 1H), 6.47 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.57 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.64 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.26-7.38 (m, 6H), 7.47-7.53 (m, 2H), 7.59-7.63 (m, 2H), 7.71 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.97 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 8.82 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ=20.8 (q), 20.9 (q), 21.0 (q), 21.1 (q), 34.7 (t), 35.8 (t), 40.5 (d), 40.9 (d), 56.1 (q), 56.2 (q), 61.3 (s), 61.4 (s), 65.2 (s), 65.6 (s), 108.3 (d), 108.9 (d), 120.0 (d), 121.1 (d), 121.7 (s), 122.1 (d), 123.1 (d), 123.2 (d), 123.9 (s), 124.0 (d), 124.09 (d), 124.11 (d), 124.2 (d), 124.7 (d), 125.07 (d), 125.09 (d), 125.2 (d), 125.5 (d), 125.6 (d), 126.0 (d), 126.66 (d), 126.74 (d), 126.86 (d), 126.96 (s), 127.1 (s), 127.9 (s), 128.1 (d), 128.2 (d), 128.8 (d), 130.0 (s), 131.59 (s), 131.61 (s), 132.00 (s), 132.03 (s), 132.2 (s), 132.4 (s), 134.5 (s), 134.6 (s), 139.6 (s), 140.8 (s), 145.4 (s), 146.2 (s), 153.8 (s), 154.7 (s), 168.7 (s), 168.9 (s); *m/z* (EI, %) = 528(M^+, 100), 496 (97), 486 (76); HRMS(EI): calcd. for $C_{30}H_{24}O_3S_3$: 528.0887, found: 528.0873.

Benzoic acid 5-methoxy-9-(2',3'-dihydro-2'-methyl-1'H-naphtho[2,1-b]thiopyran-1-ylidene)-9H-thioxanthen-4-yl ester (35)



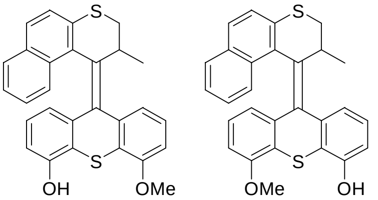
A solution of episulfide **33** (110 mg, 0.186 mmol) was heated at reflux in *p*-xylene (10 ml) in presence of triphenylphosphine (300 mg, 1.4 mmol) for 3 d. After cooling to rt, the reaction mixture was filtered and all volatiles were removed under reduced pressure. The alkene **35** was obtained as a white solid (80 mg, 0.143 mmol after column chromatography (SiO$_2$, heptane:EtOAc= 16:1, R_f=0.20) as a mixture the *cis*- and *trans*-isomers (64 mg, 0.116 mmol, 62%)(NB: when excess Ph$_3$P is used it can hamper chromatographic separation. In this case, we added 5 eq of MeI to the crude reaction mixture, allowed the mixture to stir, and filtered off the Ph$_3$PMeI before concentration *in vacuo*); *trans*-**32**: ^{1}H NMR (400 MHz, CDCl$_3$, δ=0.79-0.80 (d, *J* = 7.0 Hz, 3H), 3.08-3.10 (dd, *J* = 11.0, 2.9, 1H), 3.69-3.75 (m, 1H), 3.73 (s, 3H), 4.12-4.15 (m, 1H), 6.03-6.06 (dd, *J* = 7.9, 0.9 Hz, 1H), 6.27-6.30 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.37-6.40 (m, 1H), 6.95-6.99 (m, 1H), 7.07-7.11 (m, 1H), 7.25-7.73 (m, 11H), 8.36-8.38 (dd, *J* = 8.1, 1.1 Hz, 1H); *cis*-**32**: ^{1}H (400 MHz, CDCl$_3$, ca. 80% isomerically pure) δ=0.76-0.78 (d, *J* = 7.0 Hz, 3H), 3.05-3.09 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.68-3.73 (dd, *J* = 11.4, 7.3 Hz, 1H), 3.91 (s, 3H), 4.10-4.14 (m, 1H), 6.32 (dd, *J* = 8.8, 1.1 Hz, 1H), 6.43-6.47 (m, 1H), 6.67 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 7.16-7.71 (m, 12H), 8.32 (dd, *J* = 8.8, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, mixture of *cis* and *trans* isomers) δ=19.2 (q), 19.3 (q), 32.0 (d), 32.2 (d), 37.0 (t), 37.1 (t), 56.02 (q), 56.06 (q), 108.1 (d), 108.7 (d), 119.5 (d), 120.1 (d), 120.4 (d), 121.8 (d), 122.0 (s), 123.6 (s), 124.26 (d), 124.34 (d), 124.41 (d), 124.52 (d), 124.84 (d), 124.90 (d), 125.34 (d), 125.49 (d), 125.61 (d), 125.97 (d), 126.24 (d), 126.51 (d), 126.80 (d), 127.39 (d), 127.43 (d), 127.47 (d), 127.56 (d), 127.87 (s), 128.40 (d), 128.48 (d), 128.53 (d), 128.64 (d), 129.19 (s), 129.38 (s), 129.48 (s), 130.47 (d), 130.54 (d), 130.63 (s), 130.70 (s), 131.15 (s), 131.24 (s), 131.29 (s), 131.70 (s), 131.76 (s), 133.53 (d), 133.59 (d), 133.76 (d), 134.77 (s), 134.79 (s), 136.83 (s), 136.92 (s), 136.99 (s), 137.56 (s), 139.0 (s), 147.0 (s), 147.8 (s), 155.2 (s), 156.1 (s), 164.2 (s), 164.5 (s); *m/z* (EI, %) = 558 (M^+, 100), 105 (63); HRMS(EI): calcd. for $C_{35}H_{26}O_3S_2$: 558.1323, found: 558.1318; The *cis* and *trans*-isomers of **32** could only be separated using HPLC on a chiral stationary phase using a chiralcel OD column as the stationary phase eluting with heptane:*i*-propanol, 98:2. The retention times of the four fractions were: t_1= 8.26 min, t_2= 9.28 min, t_3= 10.87 min and t_4= 19.00 min.

(*E*)-5-methoxy-9-(2-methyl-2,3-dihydro-1*H*-benzo[*f*]thiochromen-1-ylidene)-9*H*-thioxanthen-4-yl acetate (*E*-36) and (*Z*)-5-methoxy-9-(2-methyl-2,3-dihydro-1*H*-benzo[*f*]thiochromen-1-ylidene)-9*H*-thioxanthen-4-yl acetate (*Z*-36)



A solution of episulfide **34** (100 mg, 0.19 mmol) and triphenylphosphine (200 mg, 0.76 mmol) in *p*-xylene (10 ml) was heated at reflux for 16 h. The solvent was removed followed by purified using column chromatography (SiO_2, heptane:EtOAc= 8:1, R_f= 0.22) to give the desired alkene (80 mg, 0.16 mmol, 85%) as a mixture of two isomers as a white solid. The least soluble isomer was obtained by precipitation from a mixture of heptane and EtOAc followed by recrystallization from chloroform as a white powder. The most soluble isomer was obtained 95% pure by evaporation of the mother liquor after recrystallization; Less soluble isomer; *trans*-**36**: ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.78 (d, *J* = 6.6 Hz, 3H), 2.49 (s, 3H), 3.08 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.70 (dd, *J* = 11.4, 7.3 Hz, 1H), 3.78 (s, 3H), 4.09 (dqd, *J* = 7.3, 7.0, 2.9 Hz, 1H), 6.04 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.33 (d, *J* = 8.1 Hz, 1H), 6.37-6.41 (m, 1H), 6.97-7.00 (m, 1H), 7.08-7.12 (m, 2H), 7.35-7.40 (m, 2H), 7.47-7.51 (m, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=19.2 (q), 21.0 (q), 32.0 (d), 37.1 (t), 56.2 (q), 108.1 (d), 120.4 (d), 121.8 (d), 121.9 (s), 124.35 (d), 124.42 (d), 124.8 (d), 125.4 (d), 125.5 (d), 126.0 (d), 126.5 (d), 127.4 (d), 127.5 (d), 129.2 (s), 130.7 (s), 131.3 (2xs), 131.7 (s), 134.8 (s), 137.0 (s), 137.6 (s), 139.0 (s), 147.6 (s), 155.2 (s), 169.0 (s); More soluble isomer; *cis*-**36**: ^{1}H (400 MHz, $CDCl_3$) δ=0.76 (d, *J* = 7.0 Hz, 3H), 2.42 (s, 3H), 3.07 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.70 (dd, *J* = 11.4, 7.3 Hz, 1H), 3.98 (s, 3H), 4.08-4.13 (m, 1H), 6.28 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.39-6.43 (m, 1H), 6.53 (dd, *J* = 7.9, 1.3 Hz, 1H), 6.87 (dd, *J* = 8.1, 0.7 Hz, 1H), 7.10-7.16 (m, 2H), 7.22-7.40 (m, 3H), 7.47-7.56 (m, 2H), 7.59 (d, *J* = 8.4 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ=19.2 (q), 20.9 (q), 32.1 (d), 37.0 (t), 56.1 (q), 108.7 (d), 119.4 (d), 120.0 (d), 123.5 (s), 124.2 (d), 124.4 (d), 125.3 (d), 125.6 (d), 126.2 (d), 126.4 (d), 126.8 (d), 127.4 (d), 127.5 (d), 130.6 (s), 131.1 (s), 131.3 (s), 131.7 (s), 134.8 (s), 136.8 (s), 137.0 (s), 139.7 (s), 146.8 (s), 156.1 (s), 168.6 (s); *m/z* (EI, %) = 496 (M^+, 100); HRMS(EI): calcd. for $C_{30}H_{24}O_3S_2$: 496.1167, found: 496.1175.

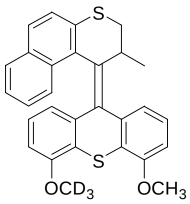
E-5-Methoxy-9-(2’,3’-dihydro-2’-methyl-1’*H*-naphtho[2,1-*b*]thiopyran-1-ylidene)-9*H*-thioxanthen-4-ol and *Z*-5-Methoxy-9-(2’,3’-dihydro-2’-methyl-1’*H*-naphtho[2,1-*b*]thiopyran-1-ylidene)-9*H*-thioxanthen-4-ol (*E*-37 and *Z*-37)

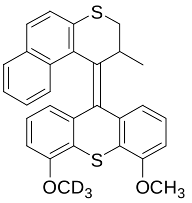


To a solution of *cis*-**35** (20 mg, 44 μmol) in ether (2 ml) and methanol (2 ml) was added $NaBH_4$ (100 mg, 2.6 mmol) at rt. The mixture was stirred for 2 h and another batch of $NaBH_4$ (100 mg, 2.6 mmol) was added. Stirring was continued for 2 h and then the reaction was quenched with a sat. sol. of aq. NH_4Cl (50 ml). The water layer was then extracted with CH_2Cl_2 (3 x 50 ml), the combined organic layers were dried (Na_2SO_4) and the solvent removed under reduced pressure to give a mixture of **35** and **37**. The mixture was separated by column chromatography (SiO_2, heptane:EtOAc=4:1, R_f= 0.18) to give the phenol *trans*-**37** as a white solid (14 mg, 70%). *Trans*-**37** obtained from most-soluble *cis*-**35**: ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.78 (d, *J* = 7.0 Hz, 3H), 3.05 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.69 (dd, *J* = 11.4, 7.3 Hz, 1H), 4.00 (s, 3H), 4.09-4.13 (m, 1H), 6.00 (dd, *J* = 5.9, 3.3 Hz, 1H), 6.35-6.37 (m, 2H), 6.88 (d, *J* = 8.1 Hz, 1H), 7.05-7.15 (m, 2H), 7.20-7.26 (m, 1H), 7.34-7.38 (m, 2H), 7.55-7.61 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=19.2 (q), 32.3 (d), 37.1 (t), 56.1 (q), 108.6 (d), 112.5 (d), 120.1 (s), 120.3 (d), 121.4 (d), 123.2 (s), 124.42 (d), 124.46 (d), 125.4 (d), 125.7 (d), 126.6 (d), 127.2 (d), 127.48 (d), 127.51 (d), 130.9 (s), 131.35 (s), 131.37 (s), 132.5 (s), 134.8 (s), 136.7 (s), 138.0 (s), 140.4 (s), 151.7 (s), 156.2 (s); *Cis*-**37** was prepared analogously by deprotecting *trans*-**35** (15 mg, 33 μmol) according to the procedure given above, to give material 80% enriched with *cis*-

37 (10 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.80 (d, *J* = 7.0 Hz, 3H), 3.07 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.68 (dd, *J* = 11.4, 7.3 Hz, 1H), 3.81 (s, 3H), 4.18-4.22 (m, 1H), 6.05 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.32 (dd, *J* = 8.2, 1.4 Hz, 1H), 6.40-6.44 (m, 1H), 6.93 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.01-7.05 (m, 1H), 7.10-7.13 (m, 1H), 7.21 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.27-7.31 (m, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.55-7.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=19.2 (q), 32.2 (d), 37.1 (t), 56.1 (q), 108.0 (d), 113.5 (d), 119.9 (d), 121.7 (d), 121.9 (d), 124.3 (d), 124.4 (d), 125.4 (d), 125.5 (d), 126.4 (d), 127.5 (d), 127.6 (d), 130.8 (s), 131.3 (s), 132.6 (s), 134.9 (s), 136.8 (s), 138.4 (s), 140.3 (s), 152.9 (s), 155.3 (s), one (d) and two (s) signals were not observed; *m/z* (EI, %) = 454 (*M*$^+$, 100); HRMS (EI): calcd. for $C_{28}H_{22}O_2S_2$: 454.1061, 454.1063.

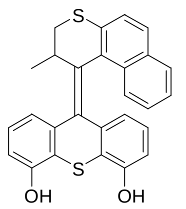
4-Methoxy(D$_3$)-5-methoxy-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene and 5-methoxy(D$_3$)-4-methoxy-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene (*cis*-38 and *trans*-38)[2]





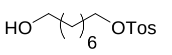
A mixture of *trans*-**37** (14 mg, 31 μmol), methyl-d$_3$ iodide (3 drops), K_2CO_3 (25 mg, 0.18 mmol) and DMF (1 ml) was stirred for 2 h at rt. When TLC indicated completion of the reaction, the mixture was poured into water (100 ml) and extracted with EtOAc (100 ml). The organic layer was washed with water (4 x 100 ml), dried (Na_2SO_4) and then all volatiles were removed under reduced pressure to give a yellow oil. This oil was purified by column chromatography (SiO_2, heptane:EtOAc, R_f= 0.42) to give *cis*-**38** as a white solid (13 mg, 28 μmol, 89%). According to ^{1}H NMR spectroscopy, the *cis-trans* ratio of the product was 80:20. In an analogous fashion, *trans*-**38** was prepared by alkylation of *cis*-**37** (8 mg, 18 μmol) by CD_3I (3 drops) in DMF using K_2CO_3 (25 mg, 0.18 mmol) as the base. The mixture was stirred for 2 h, diluted with water (100 mL), extracted with EtOAc (100 mL), washed with water (4 x 100 mL), dried (Na_2SO_4) and the solvent removed *in vacuo* to give a yellow oil. This oil was purified by column chromatography (SiO_2, heptane:EtOAc, R_f= 0.42) to give a white solid (6 mg, 13 μmol, 72%). According to ^{1}H NMR spectroscopy, the *cis-trans* ratio of the product was 17:83.; ^{1}H and ^{13}C NMR spectra were identical to those of **5** (the non-deuterated analogue), except for the lack of absorption from the protons that were exchanged for deuterons; *m/z* (EI, %) = 471 (*M*$^+$, 100); HRMS(EI): calcd. for $C_{29}D_3H_{21}O_2S_2$: 471.1403, found: 471.1410.

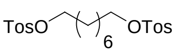
4,5-Dihydroxy-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-b]thiopyran-1'-ylidene)-9*H*-thioxanthene (39)



Under a nitrogen atmosphere BBr_3 (0.06 mL, 0.63 mmol) was added to a solution of dimethoxy ether **5** (100 mg, 0.21 mmol) in dichloromethane (12 mL) at 0 ºC. After stirring for 16 h at rt, the reaction was quenched by adding water. The water layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic layer was washed with water and brine, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to obtain the crude product. The product was purified by column chromatography (SiO_2, heptane:EtOAc=2:1, R_f=0.28) to give the bisphenol as a yellow powder (55 mg, 60%); ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.82 (d, *J* = 6.6 Hz, 3H), 3.06 (dd, *J* = 11.7, 3.3 Hz, 1H), 3.68 (dd, *J* = 11.4, 7.3 Hz, 1H), 4.19 (m, 1H), 5.29 (s, 1H), 5.30 (s, 1H), 6.02 (dd, *J* = 6.0, 2.7 Hz, 1H), 6.35-6.40 (m, 2H), 6.93 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.04-7.08 (m, 1H), 7.12-7.15 (m, 1H), 7.22-7.32 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.55-7.63 (m, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ=19.2 (q), 32.5 (d), 37.0 (t), 112.7 (d), 113.7 (d), 119.3 (s), 120.2 (d), 121.0 (s), 121.7 (d), 124.3 (d), 124.5 (d), 125.4 (d), 125.7 (d), 126.9 (d), 127.5 (d), 127.6 (d), 127.9 (d), 130.9 (s), 131.2 (s), 131.4 (s), 132.7 (s), 134.9 (s), 137.1 (s), 139.1 (s), 141.2 (s), 151.6 (s), 152.9 (s); *m/z* (EI, %) = 440 (*M*$^+$, 100), 242 (45); HRMS (EI): calcd. for $C_{27}H_{20}O_2S_2$: 440.0905, found 440.0889.

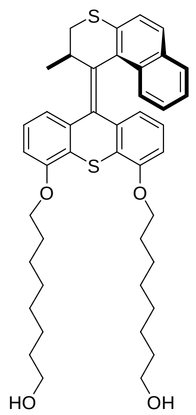
8-Hydroxy-1-tosyl-octane (40) *and* octane-1,8-diyl bis(4-methylbenzenesulfonate)





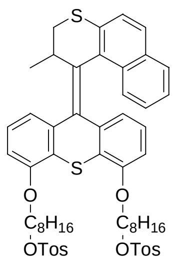
Under a nitrogen atmosphere, 1,8-octanediol (1.54 g, 10.5 mmol) and pyridine (1.70 mL, 21.1 mmol) were dissolved chloroform (15 ml). After being cooled to 0 ºC, tosyl chloride (2.41 g, 12.6 mmol) was added to this solution. The mixture was stirred for 16 h at rt. The reaction was quenched with water (100 ml), and the water layer was extracted with EtOAc (3 x 50 ml). The combined organic layer was washed with an aq. sol. of 10% HCl (100 ml) and a sat. aq. sol. of $NaHCO_3$ (100 ml), and dried ($MgSO_4$). The solvent was evaporated under reduced pressure to obtain the crude product. The crude product was purified by column chromatography (SiO_2, hexane:EtOAc = 3:1, R_f ditosyl= 0.55, R_f monotosyl= 0.19) to give ditosylate (first fraction, 1.11 g, 2.44 mmol, 23%) as a white solid and monotosylate (second fraction, 1.52 g, 5.05 mmol, 48%) as a colorless oil; Monotosylate **40**: ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.24-1.32 (m, 8H), 1.50-1.53 (m, 2H), 1.61-1.65 (m, 2H), 2.45 (s, 3H), 3.61 (t, *J* = 6.6 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.4 (q), 25.0 (t), 25.4 (t), 28.5 (t), 28.6 (t), 28.9 (t), 32.4 (t), 62.4 (t), 70.5 (t), 127.6 (d), 129.6 (d), 132.8 (s), 144.5 (s); HRMS (EI): calcd. for $C_{15}H_{24}O_4S$: 300.1395, found 300.1405; octane-1,8-diyl bis(4-methylbenzenesulfonate): white solid; m.p. 83.4-84.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.17-1.28 (m, 8H), 1.57-1.64 (m, 4H), 2.45 (s, 6H), 4.00 (t, *J* = 6.4 Hz, 4H), 7.35 (d, *J* = 8.6 Hz, 4H), 7.79 (d, *J* = 8.6 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=21.5 (q), 25.0 (t), 28.5 (t), 28.6 (t), 70.5 (t), 127.7 (d), 129.7 (d), 132.9 (s), 144.6 (s); HRMS (EI): calcd. for $C_{22}H_{30}O_6S_2$: 454.1484, found 454.1488; ele. ana., calc. (%): C, 58.10; H, 6.65; S, 14.11; found (%): C, 58.70; H, 6.82; S, 13.91.

4,5-Bis[(8-hydroxyoctyl)oxy]-9-(2',3'-dihydro-2'-methyl-1'H-naphtho[2,1-b]thiopyran-1'-ylidene)-9H-thioxanthene (41)



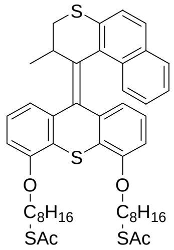
A mixture of **39** (92 mg, 0.21 mmol), monotosylate **40** (0.63 mmol, 189 mg) and Cs_2CO_3 (0.63 mmol, 205 mg) in DMF (10 ml) was heated up to 65ºC for 2 d. After cooling to rt, water (50 ml) was added and the reaction mixture was extracted with EtOAc (3x 25 ml). The combined organic layers were washed with an aq. sol. of 10% HCl (50 ml), water (2x 50 ml), a sat. aq. sol. of $NaHCO_3$ (50 ml) and brine (50 ml), and dried over $MgSO_4$. All volatiles were removed under reduced pressure to obtain a crude product, which was purified by column chromatography (SiO_2, CH_2Cl_2:acetone = 5:1, R_f= 0.42) to give pure product as a colorless oil (125 mg, 0.18 mmol, 86%); ^{1}H NMR (300 MHz, $CDCl_3$) δ=0.74 (d, *J* = 6.6 Hz, 3H), 1.41-1.69 (m, 20H), 1.77-1.87 (m, 2H), 1.90-1.97 (m, 2H), 3.08 (d, *J* = 11.4, 1H), 3.64-3.73 (m, 5H), 3.84-4.20 (m, 5H), 6.02 (d, *J* = 7.7 Hz, 1H), 6.26-6.36 (m, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.96-7.01 (m, 1H), 7.07-7.12 (m, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.29-7.35 (m, 2H), 7.49-7.58 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ=19.1 (q), 25.7 (t), 25.8 (t), 25.9 (t), 26.0 (t), 29.1 (t), 29.2 (t), 29.4 (t), 31.7 (d), 32.7 (t), 37.2 (t), 62.9 (t), 68.9 (t), 69.0 (t), 109.2 (d), 109.3 (d), 119.7 (d), 121.6 (d), 123.6 (s), 124.2 (d), 124.5 (d), 124.9 (s), 125.33 (d), 125.36 (d), 125.39 (d), 126.2 (d), 127.3 (d), 127.4 (d), 130.8 (s), 131.2 (s), 131.6 (s), 132.3 (s), 134.6 (s), 135.9 (s), 136.2 (s), 138.6 (s), 154.6 (s), 155.5 (s), due to overlap of the carbon absorptions, the signals in the alkyl-tails of the molecule, 5 (t) were not observed; *m/z* (EI, %) = 696 (M^+, 100); HRMS (EI): calcd. for $C_{43}H_{52}O_4S_2$: 696.3307, found 696.3276.

4,5-Bis({8-[(p-tosyl)oxy]octyl}oxy)-9-(2',3'-dihydro-2'-methyl-1'H-naphtho[2,1-b]thiopyran-1'-ylidene)-9H-thioxanthene (42)



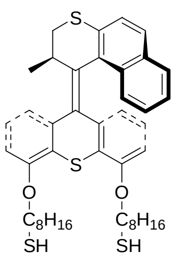
To a mixture of **41** (43 mg, 0.062 mmol) and pyridine (0.022 mL, 0.27 mmol) in $CHCl_3$ (5 mL) was added tosyl chloride (26 mg, 0.14 mmol) at 0ºC. The mixture was stirred and the reaction was followed by TLC. If starting material or monotosylated product was detected, more tosyl chloride was added to the reaction mixture. After stirring for 72 h, the mixture was quenched with water (20 ml) and subsequently extracted with EtOAc (3 x 10 ml). The combined organic layers were washed with an aq. sol. of 10% HCl (10 ml), water (10 ml), sat. aq. sol. $NaHCO_3$ (10 ml), water (10 ml) and brine (10 ml), and dried over $MgSO_4$. The solvents were evaporated under reduced pressure to obtain the crude product. This crude product was purified by column chromatography (SiO_2, hexane:EtOAc = 3:1, R_f= 0.33) to give pure ditosylate as a colorless oil (52 mg, 0.052 mmol, 83%); ^{1}H NMR (300 MHz, $CDCl_3$) δ=0.73 (d, *J* = 6.6 Hz, 3H), 1.23-1.95 (m, 24H), 2.41 (s, 3H), 2.42 (s, 3H), 3.05-3.09 (m, 1H), 3.67-3.73 (m, 1H), 3.82-4.18 (m, 9H); 6.02 (d, *J* = 7.2 Hz, 1H), 6.25-6.36 (m, 2H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.94-6.99 (m, 1H), 7.06-7.10 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.26-7.36 (m, 6H), 7.48-7.59 (m, 3H), 7.78-7.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=19.0 (q), 21.6 (q), 25.3 (t), 25.8 (t), 25.9 (t), 28.79 (t), 28.54 (t), 28.87 (t), 28.95 (t), 29.06 (t), 29.11 (t), 31.7 (d), 37.2 (t), 68.8 (t), 68.9 (t), 70.6 (t), 109.1 (d), 109.3 (d), 119.7 (d), 121.6 (d), 123.6 (s), 124.2 (d), 124.5 (d), 124.8 (s), 125.3 (2xd), 125.4 (d), 126.3 (d), 127.3 (d), 127.4 (d), 130.7(s), 131.2 (s), 131.5 (s), 132.2 (s), 133.1 (s), 134.6 (s), 135.9 (s), 136.2 (s), 138.6 (s), 144.6 (s), 154.5 (s), 155.5 (s); due to overlap the following were not observed: 1xq, 4xd, 4xt, 2xs; ESI-MS, 1027.5 (M+23(Na)).

4,5-Bis{[8-(acetylsulfanyl)octyl]oxy}-9-(2',3'-dihydro-2'-methyl-1'H-naphtho[2,1-b]thiopyran-1'-ylidene)-9H-thioxanthene (43)



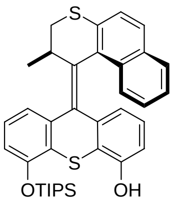
A mixture of ditosylate **42** (44 mg, 0.044 mmol) and potassium thioacetate (0.29 mmol, 33 mg) in DMF (or acetone, 5 mL) was stirred for 16 h at rt. The reaction was quenched by adding water (30 ml). The water layer was extracted with CH_2Cl_2 (3x 15 ml) and the combined organic layers were washed with water (25 ml) and brine (25 ml), and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give the crude product, which was purified by column chromatography (SiO_2, hexane:EtOAc = 4:1, R_f=0.40) to obtain the pure dithioacetate as a yellow oil (34 mg, 0.042 mmol, 95%); ^{1}H NMR (300 MHz, $CDCl_3$) δ=0.73-0.75 (d, *J* = 7.0 Hz, 3H), 1.20-1.65 (m, 20H), 1.76-1.83 (m, 2H), 1.88-1.95 (m, 2H), 2.32 (s, 3H), 2.33 (s, 3H), 2.86-2.90 (m, 4H), 3.05-3.09 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.67-3.73 (dd, *J* = 11.4, 7.3 Hz, 1H), 3.85-4.20 (m, 5H), 6.01 (d, *J* = 7.3 Hz, 1H), 6.25-6.36 (m, 2H), 6.84 (d, *J* = 8.1 Hz, 1H), 6.95-7.00 (m, 1H), 7.07-7.12 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.26-7.31 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.49-7.58 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ=19.1 (q), 25.9 (t), 26.1 (t), 26.1 (t), 26.2 (t), 28.8 (t), 29.1 (t), 29.16 (t), 29.22 (t), 29.5 (t), 29.7 (t), 29.8 (t), 30.6 (q), 31.8 (d), 37.2 (t), 68.9 (t), 69.0 (t), 109.2 (d), 109.4 (d), 119.7 (d), 121.7 (d), 123.7 (s), 124.2 (d), 124.6 (d), 125.0 (s), 125.4 (d), 126.2 (d), 127.3 (d), 127.4 (d), 130.8 (s), 131.3 (s), 131.7 (s), 132.4 (s), 134.7 (s), 135.9 (s), 136.3 (s), 138.6 (s), 154.6 (s), 155.6 (s), 196.0 (s), 7 signals could not be observed individually; a mass spectrum of this product could not be obtained; The enantiomers of dithioacetate **43** were resolved by preparative HPLC on a chiral stationary phase employing a Chiralcel AD column as the stationary phase and a mixture of *n*-heptane : *i*-propanol 49 : 1 as the eluent (1 ml·min^{-1}). The elution time of the first fraction was *t*= 12.7 min and the elution time of the second fraction was *t*= 14.9 min. The synthesis of the functionalized gold nanoparticles **1** was further performed with the second eluted fraction, which by CD spectroscopy was assigned to be (2'*S*)-(*P*)-**43**.

4,5-Bis[(8-sulfanyloctyl)oxy]-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-*b*]thiopyran-1'-ylidene)-9*H*-thioxanthene (44)

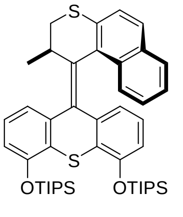


To the solution of dithioacetate (2'*S*)-(*P*)-**43** (32 mg, 0.039 mmol) in THF (2 mL) and methanol (2 mL) was added sodium methoxide (0.094 mmol, 5 mg). The mixture was stirred for 2 h at rt. The reaction was quenched with a sat. aq. sol of NH_4Cl. The water layer was extracted with EtOAc (twice) and the combined organic layers were washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated under the reduced pressure to obtain dithiol (23 mg, 0.032 mmol, 81%). This material was used directly in the subsequent reaction to avoid oxidation of the thiol moieties. (This procedure was performed analogously on the racemate as well) ^{1}H NMR (300 MHz, $CDCl_3$) δ=0.74 (d, *J* = 7.0 Hz, 3H), 1.20-1.65 (m, 20H), 1.87-2.00 (m, 4H), 2.50-2.58 (m, 4H), 3.08 (dd, *J* = 11.4, 2.6 Hz, 1H), 3.72 (dd, *J* = 11.4, 7.3 Hz, 1H), 3.90-4.20 (m, 5H), 6.02 (dd, *J* = 7.7, 1.1 Hz, 1H), 6.26-6.36 (m, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.96-7.01 (m, 1H), 7.07-7.12 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.26-7.32 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.49-7.59 (m, 3H), the absorptions from the two SH protons were not observed.

(E)-9-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-5-(triisopropylsilyloxy)-9H-thioxanthen-4-ol (45) and (9-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-9H-thioxanthene-4,5-diyl)bis(oxy)bis(triisopropylsilane)

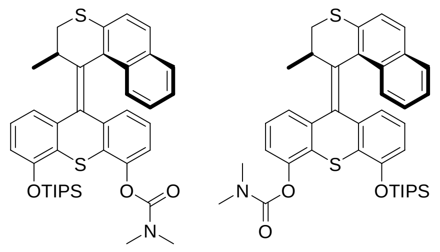


TIPSOTf (520 mg, 1.70 mmol) and imidazole (136 mg, 2.0 mmol) was added to a solution of the diphenol **39** (660 mg, 1.50 mmol) in DMF (5 mL) at rt. This mixture was stirred for 8 h, diluted with EtOAc (15 mL), washed with water (4 x 5 mL) dried (Na_2SO_4) and concentrated *in vacuo.* The resulting residue was purified by flash chromatography (heptane:EtOAc, 10:1) to give a mixture of *E* and *Z* isomers total (402 mg, 40%) as well as some remaining diphenol **39** (130 mg). Separation of the cis and trans diastereomers was difficult, and gave predominantly fractions that were enriched (~90%) with one diastereomer. Complete separation of some of this material was achieved for characterization after 3 consecutive flash-chromatographic separations on silica gel (14:1, hexanes:EtOAc) or on a preparative scale employing HPLC (column, heptane:^{i}PrOH, 99:1). The first eluting isomer was found to be the *trans* isomer: ^{1}H NMR (500 MHz, C_6D_6) δ=0.49 (d, *J* = 6.5 Hz, 3H), 1.14 (d, *J* = 8.8 Hz, 9H), 1.16 (d, *J* = 8.8 Hz, 9H), 1.13-1.21 (m, 3H), 2.62 (dd, *J* = 3.2, 11.2 Hz, 1H), 3.28 (dd, *J* = 7.5, 11.5 Hz, 1H), 4.05 (quin, *J* = 3.6 Hz, 1H), 6.01 (ABX dd, *J* = 8.0, 1.2 Hz, 1H), 6.11 (ABM t, *J* = 8.2 Hz, 1H), 6.31 (dd, *J* = 1.2, 7.6 Hz, 1H), 6.82 (dd, *J* = 0.8, 7.8 Hz, 1H), 6.93 (dt, *J* = 1.0, 7.4 Hz, 1H), 7.03 (ddd, *J* = 1.2, 6.8, 8.4 Hz, 1H), 7.18 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), ^{13}C NMR (100 MHz, C_6D_6) δ=153.6, 152.3, 141.0, 138.5, 137.2, 135.6, 133.5, 132.3, 132.0, 131.6, 128.2, 128.0, 127.5, 126.6, 126.5, 125.9, 125.0, 124.8, 124.7, 122.8, 122.3, 120.3, 115.4, 113.7, 37.1, 32.7, 19.0, 18.3, 18.2, 13.3, *m/z* MS (EI, %) 596.3 (M^+, 89.3%), 553.3 (M^+-43, $CH(CH_3)_2$), 100%, HRMS (EI) calcd for $C_{36}H_{40}O_2S_2Si$ 596.2239, found 596.2235.



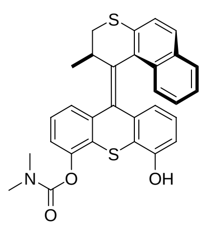
Bis silyl ether: m.p.= 143-145°C, ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.79 (d, 3H, *J* = 7.0 Hz), 1.17 (d, *J* = 8.8 Hz, 9H), 1.22 (d, *J* = 8.8 Hz, 9H), 1.27 (d, *J* = 7.6 Hz, 18H), 1.32-1.42 (m, 3H), 1.42-1.52 (m, 3H), 3.10 (dd, *J* = 3.2, 11.2 Hz, 1H), 3.10 (d, 1H, *J* = 3.2, 11.2 Hz), 3.74 (dd, 1H, *J* = 11.2, 7.8 Hz), 4.10-4.25 (m, 1H), 6.07 (dd, 1H, *J* = 7.2, 2.4 Hz), 6.26-6.34 (ABM m, 2H), 6.89-6.91 (m, 1H), 7.08 (dt, 1H, *J* = 7.2, 1.2 Hz), 7.14 (dt, 1H, *J* = 7.2, 1.2 Hz), 7.25 (d, 1H, *J* = 8.0 Hz), 7.42 (d, 1H, *J* = 8.8 Hz), 7.55-7.65 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=152.5, 151.5, 138.7, 136.2, 135.6, 134.6, 132.7, 132.0, 131.2, 130.9, 127.5, 127.3, 127.1, 125.8, 125.7, 125.4, 125.0, 124.4, 124.1, 121.3, 119.9, 115.6, 114.1, 37.3, 31.9, 19.1, 18.17, 18.13, 13.1, 13.0, (1 C not resolved).

(E)-9-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-5-(triisopropylsilyloxy)-9H-thioxanthen-4-yl dimethylcarbamate (Z)-9-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-5-(triisopropylsilyloxy)-9H-thioxanthen-4-yl dimethylcarbamate (trans-46 and cis-46)



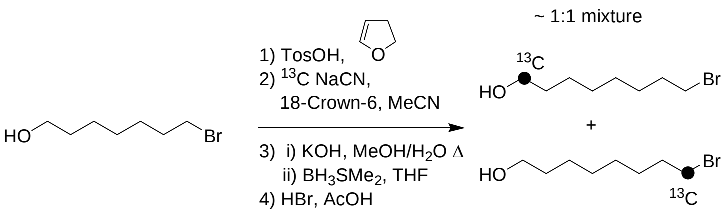
Dimethylcarbamoyl chloride (214 mg, 2.00 mmol) was added to solution of a mixture 3/2 mixture of cis and trans isomers of **45** (305 mg, 0.520 mmol) in pyridine (5 mL). This mixture was stirred 3 h at 50 °C, cooled to rt, concentrated in vacuo, and purified by careful flash chromatography (heptane:EtOAc, 10:1) to give the cis (107 mg) and trans (166 mg) isomers in a 39:61 ratio, respectively (273 mg, 81% overall). First eluting isomer: ***trans*-46** : ^{1}H NMR (400 MHz, C_6D_6) δ=0.56 (d, *J* = 6.5 Hz, 3H), 1.16 (d, *J* = 7.2 Hz, 9H), 1.16 (d, *J* = 7.2 Hz, 9H), 1.25-1.35 (m, 3H), 2.64 (dd, *J* = 4.3, 11.4 Hz, 1H), 2.75 (s, 3H), 2.80 (s, 3H), 3.34 (dd, *J* = 11.2, 7.2 Hz, 1H), 4.08 (ddq, *J* = 6.5, 6.5, 3.2 Hz, 1H), 6.14 (t, *J* = 7.8 Hz, 1H), 6.49 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.01 (dt, *J* = 6.8, 1.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.33-7.38 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.52 (dt, *J* = 1.2, 8.0 Hz, 1H), 8.00 (dd, *J* = 8.4, 0.8 Hz, 1H); ^{13}C (400 MHz, C_6D_6) δ=13.4, 18.3, 19.1, 33.0, 36.2, 36.6, 37.1, 116.5, 120.3, 120.9, 125.0, 125.1, 125.8, 125.8, 126.0, 126.7, 127.4, 127.7, 128.9, 131.4, 131.98, 132.03, 132.9, 135.6, 137.3, 138.3, 140.3, 148.5, 153.2, 153.5. HRMS (EI): calcd. for $C_{39}H_{45}O_3S_2Si$: 667.2610, found: 667.2578. second eluting ***cis*-46**: ^{1}H NMR (500 MHz, C_6D_6) δ=0.49 (d, *J* = 6.5 Hz, 3H), 1.10 (s, 6H), 1.15 (s, 12H), 1.13-1.21 (m, 3H), 2.62 (dd, *J* = 2.3, 11.3 Hz, 1H), 2.74 (s, 3H), 2.92 (s, 3H), 3.28 (dd, *J* = 7.5, 11.5 Hz, 1H), 3.90- 4.00 (m, 1H), 6.16 (ABX dt, *J* =1.2, 8.0 Hz, 1H), 6.17 (ABMX dt, *J* = 8.0, 1.3 Hz, 1H), 6.37 (d, *J* = 7.0 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 7.03 (dt, *J* = 1.3, 7.8 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 1.3, 6.5 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 6.0 Hz, 1H), 7.41 (dd, *J* = 1.3, 8.5 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), ^{13}C NMR (125 MHz, C_6D_6) δ=153.6, 152.1, 149.3, 140.2, 137.6, 137.2, 135.6, 132.9, 132.4, 132.0, 131.6, 130.3, 126.4 (2C), 126.2, 125.9, 125.5, 124.9, 124.7, 124.5, 122.3, 121.2, 115.4, 37.1, 36.6, 36.2, 32.6, 18.9, 18.3, 13.3 (1 C not obs likely due to overlap with solvent); *m/z* MS (EI, %) 667.1 (M^+, 100%), 624.1 (M^+-43 (-CH(CH_3)$_2$), 64.1%), 595.1 (M^+-72 (-C(O)N(CH_3)$_2$), 64.1%).

(E)-5-hydroxy-9-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-9H-thioxanthen-4-yl dimethylcarbamate (47)



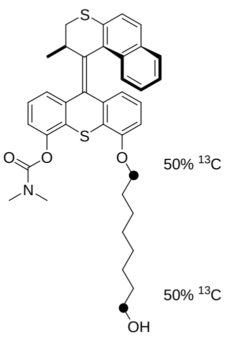
TBAF (0.2 mL of a 1.0 M solution in THF) was added to a solution of TIPS ether *cis*-**46** (110 mg, 0.167 mmol) in THF (15 mL). The mixture was stirred at rt for 20 min, diluted with aq. sat'd NH_4Cl (10 mL) and extracted with EtOAc (2 x 10 mL). The combined organic fractions were washed with water, brine, dried (Na_2SO_4), the solvent removed *in vacuo* was and the residue purified by flash chromatography (heptane:EtOAc; 2:1, R_f = 0.45 in 1:1, heptane:EtOAc) to give the title compound as a colorless glass. Recrystalization from benzene gave fine white needles (75 mg, 86%). Dec 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.79 (d, *J* = 7.0 Hz, 3H), 3.06 (d, *J* = 3.0, 11.5 Hz, 1H), 3.12 (s, 3H), 3.27 (s, 3H), 3.68 (dd, *J* = 11.3, 7.3 Hz, 1H), 4.02-4.12 (m, 1H), 5.96 (dd, *J* = 2.0, 6.5 Hz, 1H), 6.26-6.34 (ABM m, 2H), 7.01 (t, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=154.0, 151.7, 148.4, 140.2, 138.4, 136.9, 134.6, 132.1, 131.2, 131.1, 130.7, 128.7, 127.5, 127.4, 126.8, 126.6, 125.6, 125.3, 124.5, 124.4, 124.4, 121.2, 120.6, 119.4, 112.6, 37.1, 37.0, 36.8, 32.4, 19.3, 17.3. *m/z* MS (EI, %) 510.9 (M^+, 100%), 438.9 (M^+-72 (-C(O)N(CH_3)$_2$), 30.3%, HRMS (EI) calcd for $C_{30}H_{25}NO_3S_2$ 511.1276, found 511.1287.

^{13}C-Labelled 8-bromo-octan-1-ol (48)



p-Toluene sulfonic acid (0.34 g, 1.8 mmol) was added to a solution of 7-bromo-1-heptanol (3.63 g, 18.0 mmol) and 3,4-dihydro-2*H*-pyran at 0 ºC. The mixture was stirred for 16 h at rt, filtered over celite, and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO$_2$, pentane:AcOEt, 3:1) to give the protected bromoalcohol *2-(7-bromo-heptyloxy)-tetrahydro-pyran* as a colorless oil (4.24 g, 88 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.34 – 1.89 (m, 16H), 3.34 – 3.52, 3.71 (m, 1H), 3.84 (m, 1H), 4.56 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 19.2 (CH$_2$), 25.1 (CH$_2$), 25.7 (CH$_2$), 27.7 (CH$_2$), 28.2 (CH$_2$), 29.2 (CH$_2$), 30.4 (CH$_2$), 32.3 (CH$_2$), 33.4 (CH$_2$Br), 61.7 (CH$_2$O), 67.0 (CH$_2$O), 98.3 (OCHO). A mixture of *2-(7-Bromo-heptyloxy)-tetrahydro-pyran* (2.09 g, 7.5 mmol), K^{13}CN (0.496 g, 7.5 mmol), 18-crown-6 (0.198 g, 0.75 mmol) and acetonitrile (30 mL) was stirred for 16 h at r.t. The mixture was then diluted with H$_2$O (50 mL) and extracted with CH$_2$Cl$_2$ (2 x 50 mL), dried (MgSO$_4$) and concentrated *in vacuo*. The crude residue was purified by column chromatography (SiO$_2$, pentane:AcOEt, 3:1) to give the protected cyanoalcohol *8-(Tetrahydro-pyran-2-yloxy)-octane-^{13}C-nitrile* as a colorless oil (1.36 g, 80 %). ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.33-1.85 (m, 16H), 2.30-2.36 (m, 2H), 3.30-3.40 (m, 1H), 3.46-3.54 (m, 1H), 3.65-3.75 (m, 1H), 3.81-3.91 (m, 1H), 4.56 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 28.2 (d, $^1J_{CC}$ = 55.9 Hz, CH$_2$), 19.5 (CH$_2$), 25.1 (d, $^3J_{CC}$ = 2.2 Hz, CH$_2$), 25.3, 25.8, 28.3, 28.4, 29.4, 30.5, 62.1, 67.2, 98.6, 119.6 (100% ^{13}CN). A solution of *8-^{13}C-8-(tetrahydro-pyran-2-yloxy)-octanenitrile* (1.36 g, 6.00 mmol) and KOH (1.12 g, 20.0 mmol) in H$_2$O/MeOH 1:1 (25 mL) was refluxed for 1.5 h. The resulting solution was neutralized with Na$_2$HPO$_4$ to pH = 5 and extracted with Et$_2$O (2 × 25 mL), dried (MgSO$_4$) and concentrated *in vacuo*. The resulting crude acid was dissolved in CH$_2$Cl$_2$ (25 mL), to which a solution of BH$_3$•Me$_2$S in THF (2M, 2.5 mL, 7.5 mmol) was then added. The mixture was allowed to stir at rt for 16 h, and the resulting solution was washed with H$_2$O (25 mL), dried (MgSO$_4$), and concentrated under *in vacuo*. The crude residue was purified by column chromatography (SiO$_2$, pentane:AcOEt = 3:1), affording the *1-^{13}C-1,8-octanediol* as a colorless oil (0.74 g, 84 %). Following a procedure that was known for the isotopically unenriched compound[8], a mixture of *1-^{13}C-1,8-octanediol* (0.735 g, 5.00 mmol), 48% aq HBr (0.66 mL, 11 mmol), and tetrabutylammonium bromide (0.322 g, 1.00 mmol) was exposed to microwave irradiation (50 watt pulses with a maximum temperature of 100 ºC). After 1 h of irradiation, the reaction mixture was cooled, extracted with dichloromethane (2 × 20 mL), washed with saturated sodium bicarbonate solution (20 mL), water (20 mL), brine (20 mL), dried (MgSO$_4$), and concentrated *in vacuo*. The crude residue was purified by flash chromatography (heptane:EtOAc, 5:1) to give the bromoalcohol as an amber oil (468 mg) which appeared pure by ^{1}H NMR, however an impurity was observed in the ^{13}C NMR spectrum which was impossible to separate chromatographically in our hands. Kugelrohr (130 °C, 2x10^{-1} torr) distillation gave the bromoalcohol as a 50 % mixture of 1-^{13}C and 8-^{13}C labeled molecules as an amber oil (364 mg, 35%). ^{1}H NMR (500 MHz, CDCl$_3$) δ=1.20-1.30 (m, 6H), 1.32-1.40 (m, 2H), 1.45-1.52 (m, 2H), 1.75-1.82 (m, 2H), 2.3-2.6 (br s, 1H), 3.35 (50%t, 50%dt, $^1J_{\mathrm{CH}}$ = 147.5 Hz, $^3J_{\mathrm{HH}}$ = 6.8 Hz, 2H), 3.54 (50% t, 50% dt, $^3J_{\mathrm{HH}}$ = 6.8 Hz, $^1J_{\mathrm{CH}}$ = 138 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ=25.6, 28.0, 28.6 (50% d, 50% s, J = 4.75 Hz), 29.1 (50% d, 50% s, J = 4.25 Hz), 32.5 (50% d, 50% s, J = 34.5 Hz), 32.7 (50% d, 50% s, J = 32.9 Hz), 33.9 (^{13}C enriched), 62.5 (^{13}C enriched). *m/z* MS (CI, %) 227.1 (M + NH$_4^+$, 100%).

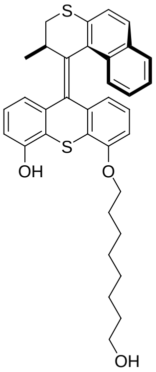
^{13}C-(E)-5-(8-hydroxyoctyloxy)-9-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-9H-thioxanthen-4-yl dimethylcarbamate (49)



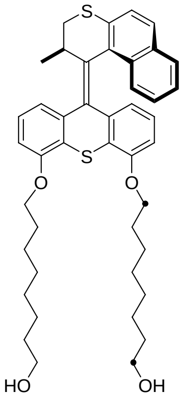
8-Bromooctan-1-ol (50% ^{13}C enrichment at each terminal carbon) (600 uL of a DMF solution of 100 mg/mL, 0.288 mmol) was added to a stirred suspension of motor phenol (60 mg, 0.12 mmol) and Cs_2CO_3 (40 mg) in DMF (1 mL). This mixture was stirred for 4 h at 65 °C, diluted with EtOAc (5 mL), washed with water (4x4 mL), dried (Na_2SO_4) and concentrated in vacuo to give an amber residue. Purification of the product was performed by flash chromatography (SiO_2, R_f = 0.3, hexane:EtOAc, 1:1) to give a colorless glass (62 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.77 (d, *J* = 6.5 Hz, 3H), 1.35-1.65 (m, 8H), 1.70-1.85 (m, 2H), 3.05-3.13 (m, 1H), 3.12 (s, 3H), 3.29 (s, 3H), 3.64 (50% t, 50% dt, $^3J_{HH}$ = 6.5 Hz, $^1J_{CH}$ = 112.8 Hz, 4H total), 3.71 (dd, *J* = 7.5, 8.8 Hz, 1H), 3.70-4.15 (m, 5H), 6.01 (d, *J* = 8.0 Hz, 1H), 6.28 ($\underline{A}$B d, $J_{apparent}$ = 8.0 Hz, 1H), 6.35 (A$\underline{B}$XY dt, $J_{apparent}$ = 8.0, 1.2 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.34-7.39 (m, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.49-7.55 (m, 2H), 7.58 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ=19.2, 25.8, 26.0, 29.2 (50% s, 50% d, $^1J_{CC}$ = 30.6 Hz), 29.4 (50% s, 50% d, $^2J_{CC}$ = 4.3 Hz), 29.5 (50% s, 50% d, *J* = 3.9 Hz), 31.9, 32.8 (50% s, 50% d, $^1J_{CC}$ = 29.6 Hz), 36.7, 37.0, 37.2, 63.0 (from ^{13}C label), 68.9 (from ^{13}C label), 109.4, 120.5, 121.7, 122.7, 124.1, 124.2, 124.4, 125.3, 125.4, 125.7, 126.2, 127.29, 127.30, 129.4, 130.6, 131.2, 131.1, 131.9, 134.6, 136.5, 137.2, 138.8, 148.2, 154.0, 154.5; *m/z* MS (EI, %) 640.2 (M^+, 100%), 568.1 (M^+-72 (-C(O)N(CH_3)$_2$), 18.9%, HRMS (EI) calcd for $C_{37}[^{13}C]H_{41}NO_4S_2$ 640.2510, found 640.2484.

^{13}C-(Z)-5-(8-hydroxyoctyloxy)-9-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-9H-thioxanthen-4-ol (50)

$LiAlH_4$ (7.6 mg, 0.20 mmol) was added to a solution of carbamate **49** (61 mg, 0.097 mmol) in THF (4 mL) at 0 °C. The mixture was allowed to warm to rt and stir for 2 h (TLC: neutral Al_2O_3, CH_2Cl_2:EtOAc, 9:1, $R_{f\,product}$ = 0.15, $R_{f\,starting\ material}$ = 0.35). The reaction was quenched by the portionwise addition of Na_2SO_4•10H_2O (ca. 100 mg, *H_2(g) evolution*!), followed by 30 min of vigorous stirring. Filtration of the reaction mixture, concentration *in vacuo* followed by flash chromatography (SiO_2, 2:1, pentane:EtOAc) gave the title compound as a colorless film (43 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.80 (d, *J* = 6.8 Hz, 3H), 1.35-1.70 (m, 10H), 1.70 -1.85 (m, 2H), 3.07 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.45-4.22 (m, 6H), 6.02 (d, *J* = 7.6 Hz, 1H), 6.05 (br s, 1H), 6.30 ($\underline{A}$B d, $J_{apparent}$ = 7.2 Hz, 1H), 6.38 (A$\underline{B}$X t, $J_{apparent}$ = 8.0 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.23-7.30 (m, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.51-7.60 (m, 3H); ^{13}C NMR (C_6D_6, 100 MHz) δ=19.1, 25.9, 26.5 (50% s, 50% d, $^1J_{CC}$ = 33.4 Hz), 29.6 (50% s, 50% d, $^2J_{CC}$ = 4.6 Hz), 29.9 (50% s, 50% d, $^2J_{CC}$ = 4.6 Hz), 32.6, 33.1 (50% s, 50% d, J_{CC} = 32.0 Hz), 37.3, 63.1, 69.1, 109.6, 113.7, 119.9, 120.0, 122.1, 123.6, 124.8, 125.1, 125.9, 126.1, 127.2, 127.9, 128.3, 131.6, 132.0, 132.2, 133.5, 135.5, 136.7, 138.2, 140.4, 154.1, 155.4, 1C not obs. likely due to overlap with solvent. HRMS (EI) ($^{13}C_1$)$^{12}C_{34}H_{36}O_3S_2$ 569.2139 found 569.2113.

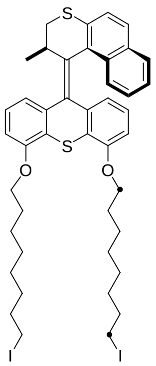


^{13}*C-8,8'-(9-(2-methyl-2,3-dihydro-1*H*-benzo[f]thiochromen-1-ylidene)-9*H*-thioxanthene-4,5-diyl)bis(oxy)dioctan-1-ol (52)*



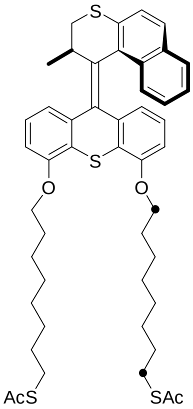
A solution of 8-bromooctan-1-ol (not ^{13}C enriched) in DMF (300 uL solution of 100 mg/mL, 0.144 mmol) was added to a stirred suspension of phenol **51** (42 mg, 74 µmol) and Cs_2CO_3 (40 mg) in DMF (1 mL). This mixture was stirred for 6 h at 65 °C, diluted with EtOAc (5 mL), washed with water (3 x 3 mL), dried (Na_2SO_4) and concentrated *in vacuo* to give an amber residue. Purification of the product was performed by flash chromatography (SiO_2, R_f = 0.3, heptane:EtOAc, 1:1) to give a colorless film (43 mg, 83%). ^{1}H (400 MHz, $CDCl_3$) δ=0.73 (d, J = 6.8 Hz, 3H), 1.41-1.69 (m, 20H), 1.77-1.87 (m, 2H), 1.90-1.97 (m, 2H), 3.08 (dd, J = 11.4, 2.8 Hz, 1H), 3.64 (50% of peak as t, 50% dt, with additional splitting from ^{13}C: $^3J_{HH}$ = 6.4 Hz, $^2J_{CH}$ = 140.8 Hz, 2H), 3.66 (t, J = 6.4 Hz, 2H) 3.65-3.72 (m, 1H), 3.84-4.20 (m, 6H), 6.01 (d, J = 7.6 Hz, 1H), 6.27 (AB d, J_{app} = 8.0 Hz, 1H), 6.34 (ABX t, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 7.10 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ=19.2, 25.5, 25.91, 25.94, 26.0, 29.1, 29.2, 29.3 (50% s, 50% d, $^1J_{CC}$ = 40.0 Hz), 31.7, 32.7 (50% s, 50% d, $^1J_{CC}$ = 36.9 Hz), 37.2, 62.9, 68.9, 69.0, 109.2, 109.3, 119.7, 121.6, 123.6, 124.2, 124.5, 124.9, 125.33, 125.36, 125.39, 126.2, 127.3, 127.4, 130.8, 131.2, 131.6, 132.3, 134.6, 136.0, 136.3, 138.6, 154.6, 155.5, due to overlap of absorptions by carbons in the aliphatic chains, 5 aliphatic carbons were not observed; HRMS calcd for $C_{42}(^{13}C)H_{52}O_4S_2$ 697.3340, found 697.3345.

^{13}*C-1-(4,5-bis(8-iodooctyloxy)-9*H*-thioxanthen-9-ylidene)-2-methyl-2,3-dihydro-1*H*-benzo[f]thiochromene (53)*



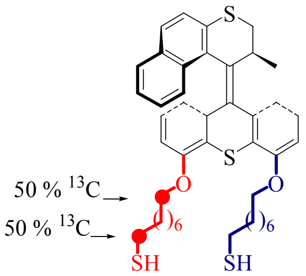
Methyl triphenoxyphosphonium iodide (freshly recrystallized from Et_2O, acetone)[9] (29 mg, 0.063 mmol) was added to a solution of diol **52** (22 mg, 0.032 mmol) in DMF (1 mL). As judged by ^{1}H and ^{13}C NMR of the crude as well as TLC, the reaction was complete in 30 min. The mixture was diluted with water (3 mL) and brine (2 mL) and extracted with EtOAc (3 x 5 mL). The combined organic fractions were washed with water (5 x 4 mL), dried (Na_2SO_4) and concentrated *in vacuo*, and purified by flash chromatography (R_f = 0.4, 9:1; heptane:EtOAc) in EtOAc:pentane, 10:1, to give the diiodide **53** as a colorless film (26 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.74 (d, J = 7.0 Hz, 3H), 1.35-1.50 (m, 14H), 1.50-1.65 (m, 4H), 1.78-1.88 (m, 6H), 1.95 (pent, J = 7.0 Hz, 2H), 3.07 (dd, J = 2.5, 11.3 Hz, 1H), 3.20 (50% t, 50% dt $^3J_{HH}$ = 7.0 Hz, $^1J_{CH}$ = 150 Hz, 2H), 3.21 (t, J = 7.0 Hz, 2H), 3.70 (dd, J = 7.3 Hz, 1H), 3.85-4.00 (m, 1H), 4.00-4.20 (m, 4H), 6.02 (d, J = 7.5 Hz, 1H), 6.27 ($\underline{A}$B d, $J_{apparent}$ = 8.5 Hz, 1H), 6.34 (A$\underline{B}$X t, $J_{apparent}$ = 7.8 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.5 Hz, 1H), 7.51 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ=7.4 (^{13}C enriched), 19.2, 26.0, 26.1, 28.59, 28.62 (overlapping d and s, $^1J_{CC}$ = 2.4 Hz), 29.123, 29.2 (overlapping d and s, $^1J_{CC}$ = 2.1 Hz), 29.27, 29.29, 30.57, 30.58, 31.8, 33.6 (overlapping d and s, $^1J_{CC}$ = 35 Hz), 34.1, 37.3, 68.9 (^{13}C enriched), 109.1, 109.2, 119.6, 121.6, 123.5, 124.1, 124.5, 124.8, 125.29, 125.30, 125.34, 126.2, 127.3, 130.7, 131.1, 131.5, 132.2, 134.5, 135.8, 136.2, 138.5, 154.4, 155.4; *m/z* MS (EI, %) 917.5 (M^+, 100%), 791.7 (M^+-126 (-I), 33.5%).

^{13}C-labelled S,S'-8,8'-(9-(2-methyl-2,3-dihydro-1*H*-benzo[f]thiochromen-1-ylidene)-9*H*-thioxanthene-4,5-diyl)bis(oxy)bis(octane-8,1-diyl) diethanethioate (54)



KSAc (5 mg) was added to a solution of **53** (15 mg, 16.5 µmol) in dry DMF (2 mL). This mixture was stirred 7 h at rt, diluted with water, extracted with EtOAc (2 x 4 mL). The combined organic fractions were washed with water (4 x 3 mL), brine and dried (Na_2SO_4) and reduced *in vauo* to give a film (slightly yellow) which was purified by column chromatography (SiO_2, hexane:EtOAc = 4:1, R_f=0.40) to give the pure dithioacetate as a yellow oil (11 mg, 82%); ^{1}H NMR (300 MHz, $CDCl_3$) δ= 0.74 (d, J = 7.2 Hz, 3H), 1.20-1.65 (m, 20H), 1.72-1.79 (m, 2H), 1.92 (quin, J = 6.9 Hz, 2H), 2.88 (m, 3H), 2.88 (dt, $^3J_{HH}$ = 7.4 Hz, $^1J_{CH}$ = 141 Hz, 1H, ^{13}CH_2SH,), 3.08 (dd, J = 11.4, 2.6 Hz, 1H), 3.72 (dd, J = 11.2, 7.6 Hz, 1H), 3.63-4.00 (m, 2H), 4.00-4.19 (m, 3H), 6.01 (d, J = 7.6 Hz, 1H), 6.26 (AB doublet, 1H), 6.33 (ABX triplet, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.49-7.59 (m, 3H).

^{13}C-Labelled 4,5-bis[(8-sulfanyloctyl)oxy]-9-(2',3'-dihydro-2'-methyl-1'*H*-naphtho[2,1-b]thiopyran-1'-ylidene)-9*H*-thioxanthene (55)



Prepared according to the procedure used for (2*R'*)-(*M*)-**44**, employing **54** (11 mg, 14 µmol) as the substrate. ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.74 (d, J = 7.2 Hz, 3H), 1.20-1.65 (m, 20H), 1.72-1.79 (m, 2H), 1.92 (quin, J = 6.9 Hz, 2H), 2.88 (m, 3H), 2.88 (dt, $^3J_{HH}$ = 7.4 Hz, $^1J_{CH}$ = 141 Hz, 1H, ^{13}CH_2SH,), 3.08 (dd, J = 11.4, 2.6 Hz, 1H), 3.72 (dd, J = 11.2, 7.6 Hz, 1H), 3.63-4.00 (m, 2H), 4.00-4.19 (m, 3H), 6.01 (d, J = 7.6 Hz, 1H), 6.26 (AB doublet, 1H), 6.33 (ABX triplet, 1H), 6.83 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 7.8 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.49-7.59 (m, 3H), SH not observed.

Transmission electron microscopy (TEM)

TEM investigations were carried out with a Philips CEM 120 transmission electron microscope, equipped with a LaB6 filament. The microscope was operated at 120 kV. Images were acquired with a built-in Gatan 794 CCD-camera (1024×1024 pixels), controlled by Gatan Digital Micrograph v3.5 software. A TEM sample of motor-coated NPs 4 was investigated using an amorphous carbon support-film of several nanometers thickness on a 3 mm 400 µm mesh copper grid, on which. the cluster material was deposited from a dilute solution in toluene. The size distribution was determined by digital image analysis of 1246 nanoparticles using Matrox Inspector 2.1. Similarly, the minimum separation of the motor-coated NPs **4** was determined, based on the distances between the metal cores of 100 nanoparticles in the pseudo-close-packed areas (as marked in the micrograph in figure 2). This analysis showed a separation of 2.4 ± 0.4 nm.

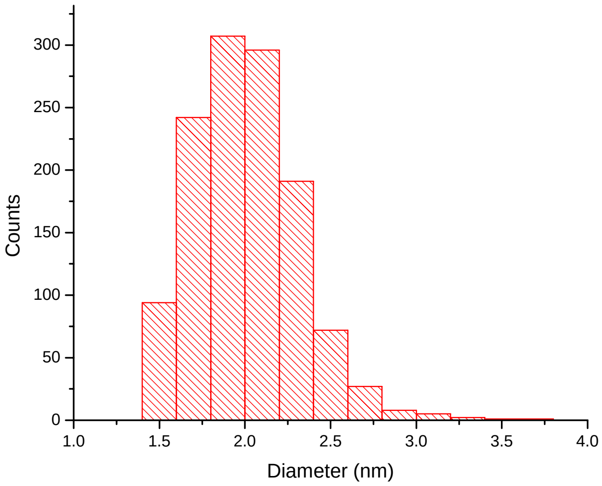


Figure S1. Distribution of nanoparticle (core) sizes measured by TEM.

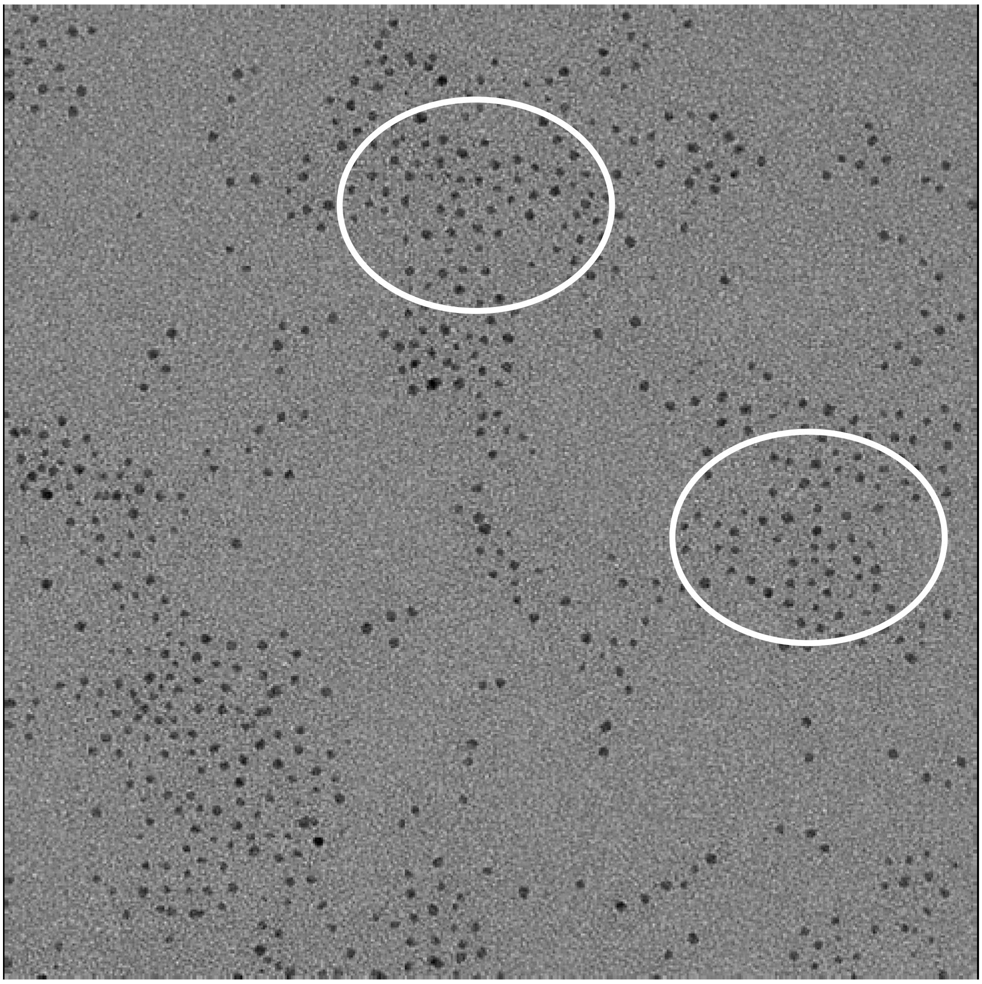
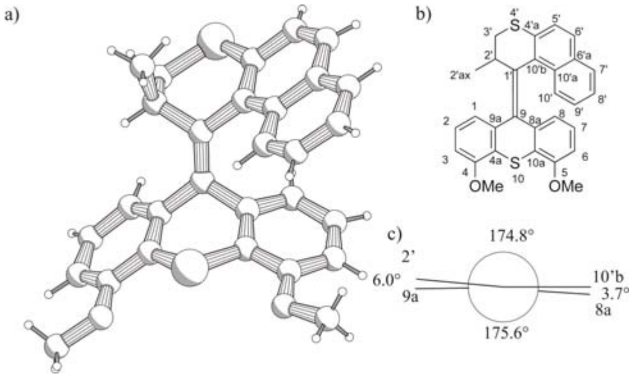


Figure S2. TEM used for the determination of the mean separation of the nanoparticles **4.**

Dynamic Light Scattering (DLS)

Zetasizer 5000 instrument (Malvern Instruments, Ltd., U.K.) at a wavelength (λ_0) 633.3 nm using a solution of 1 mg of nanoparticles in 1 mL of toluene. Prior to measurement, the samples were centrifuged for 5 min at 3000 rpm to remove any interfering dust particles from the scattering volume. The intensity-mean hydrodynamic diameter was 6.3 nm (the intensity autocorrelation functions were analyzed using CONTIN[10]).

X-ray analysis of dimethoxy motor 5^2 (note that the references for the x-ray section are located immediately after the x-ray data)



Compound **5** in the solid state is characterized as follows: central double bond, $C_{1'}$-C_9 = 1.360 Å; bond angles around the central double bond, C_{8a}-C_9-C_{9a} = 112.4°, C_{9a}-C_9-$C_{1'}$ = 122.3°, C_{8a}-C_9-$C_{1'}$ = 125.2° (total angle around C_9 is 359.9°), $C_{10'b}$-$C_{1'}$-$C_{2'}$ = 113.0°, $C_{10'b}$-$C_{1'}$-C_9 = 124.7°, $C_{2'}$-$C_{1'}$-C_9 = 122.1° (total angle around $C_{1'}$ is 359.8°); the torsion angle between the naphthalene plane of the upper part and the central double bond, $C_{10'a}$-$C_{10'b}$-$C_{1'}$-C_9 = -54.6°; torsion angles at the central double bond, $C_{10'b}$-$C_{1'}$-C_9-C_{8a} = 3.7°, $C_{2'}$-$C_{1'}$-C_9-C_{9a} = -6.0°, C_{8a}-C_9-$C_{1'}$-$C_{2'}$ = 178.5°, C_{9a}-C_9-$C_{1'}$-$C_{10'b}$ = 179.2°. The helical structure of the molecule is especially evident from the torsion angles between the thioxanthene arene moieties of the lower part and the central double bond, $C_{1'}$-C_9-C_{9a}-C_1 = 57.9°, $C_{1'}$-C_9-C_{8a}-C_8 = -52.3° and the angle between the least square planes of both arenes: 44.7°. The geometry of residue 2 is characterized as follows: central double bond, $C_{1'}$-C_9 = 1.357 Å; bond angles around central double bond, C_{8a}-C_9-C_{9a} = 112.4°, C_{8a}-C_9-$C_{1'}$ = 123.3°, C_{9a}-C_9-$C_{1'}$ = 124.1° (total angle around C_9 is 359.8°), $C_{10'b}$-$C_{1'}$-$C_{2'}$ = 113.6°, $C_{10'b}$-$C_{1'}$-C_9 = 123.7°, $C_{2'}$-$C_{1'}$-C_9 = 122.6° (total angle around $C_{1'}$ is 359.9°); the dihedral angle between the naphthalene plane of the upper part and the central double bond, $C_{10'a}$-$C_{10'b}$-$C_{1'}$-C_9 = -48.5°; torsion angles at the central double bond, $C_{10'b}$-$C_{1'}$-C_9-C_{8a} = 4.6°, $C_{2'}$-$C_{1'}$-C_9-C_{9a} = -5.5°, C_{8a}-C_9-$C_{1'}$-$C_{2'}$ = -179.9°, C_{9a}-C_9-$C_{1'}$-$C_{10'b}$ = 179.0°; torsion angles between the thioxanthene arene moieties of the lower part and the central double bond, $C_{1'}$-C_9-C_{9a}-C_1 = 58.9°, $C_{1'}$-C_9-C_{8a}-C_8 = -51.8° and the angle between the least-square planes of both arenes: 44.0°.

X-RAY DATA

Summary of key info: "IUPAC-name", $C_{29}H_{24}O_2S_2$, M_r = 468.64, monoclinic, $P2_1$, a = 8.9625(6), b = 22.785(2), c = 11.6435(8) Å, β = 90.127(1)°, V = 2377.7(3) Å^3, Z = 4, D_x = 1.309 gcm^{-3}, $F(000)$ = 984, μ = 2.49 cm^{-1}, λ(MoK$\overline{\alpha}$) = 0.71073 Å, T = 110 K, $GooF$ = 1.036, $wR(F^2)$ = 0.0863 for 11841 reflections and 786 parameters and $R(F)$ = 0.0420 for 10878 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability.
The asymmetric unit consists of two molecule of the title compound.

Experimental

X-ray diffraction: Crystal and Molecular Structure.

Crystals were obtained by recrystallisation from methanol.
A colorless parallelepiped-shaped crystal with the dimensions of 0.13 x 0.11 x 0.09 mm mounted on a glass fiber was aligned on a *Bruker*[1] *SMART APEX CCD* diffractometer (Platform with full three-circle goniometer). The diffractometer was equipped with a 4K *CCD* detector set 60.0 mm from the crystal. The crystal was cooled to 110 K using the *Bruker KRYOFLEX* low-temperature device. Intensity measurements were performed using graphite monochromated Mo-K$\overline{\alpha}$ radiation from a sealed ceramic diffraction tube (*SIEMENS*). Generator settings were 50 KV/ 40 mA. *SMART* was used for preliminary determination of the unit cell constants and

data collection control. The intensities of reflections of a hemisphere were collected by a combination of 3 sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time of 20 s per frame. The overall data collection time was 14.5 h. Data integration and global cell refinement were performed with the program *SAINT*. The final unit cell was obtained from the *xyz* centroids of 6907 reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*)[2], and reduced to F_o^2. The program suite *SHELXTL* was used for space group determination (*XPREP*).

The unit cell was identified as monoclinic; space group $P2_1$ was derived from the systematic extinctions. Reduced cell calculations did indicate higher (pseudo-orthorhombic) metric lattice symmetry[3], but with space group $P22_12$ no chemical reasonable solution could be found. Examination of the final atomic coordinates of the structure did not yield extra crystallographic symmetry elements.[4,5]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[7] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined.

The hydrogen atoms were generated by geometrical considerations, which coordinates and isotropic displacement parameters were refined.

Refinement was complicated (frustrated) by a twin problem: during the refinement the *wR* value did not drop while going anisotropic. The β-angle was suspicious for a possible twin. After introducing a twin matrix ([-1 0 0 0 -1 0 0 0 1], 180° rotation about the *c*-axis) with scale factors for the fractional contributions of the various twin components the remainder of the structure refined smoothly The s.o.f. of the major component of the twin model refined to a value of 0.6868(7).

Final refinement on F^2 carried out by full-matrix least-squares techniques. Convergence was reached at $wR(F^2) = 0.0863$ for 11841 reflections and 786 parameters and $R(F) = 0.0420$ for 10878 reflections with $F_o \geq 4.0\ \sigma(F_o)$. The final difference Fourier map was essentially featureless: no significant peaks (0.4(5) e/Å^3) having chemical meaning above the general background were observed.

The absolute structure of the molecule actually chosen was determined by Flack's[8,9]-refinement ($\mathbf{x} = 0.01(5)$).

The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum_h[w(|(F_o^2) - k(F_c^2)|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_0 and F_c are the observed and calculated structure factor amplitudes, respectively; *a* (=0.0377) and *b* (= 0.0) were refined.

Crystal data and numerical details on data collection and refinement are given in Table 1. Final fractional atomic coordinates, equivalent displacement parameters and anisotropic displacement parameters for the non-hydrogen atoms are given in Table 2. Molecular geometry data are collected in Table 3. Tables of atom positions, displacement parameters, comprehensive distances and angles and tables of (F_o^2), (F_c^2) and $\sigma(F_o^2)$ are given as supplementary material[*11] for this paper. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables for Crystallography*[10] All refinement calculations and graphics were performed on a Pentium-III / Debian-Linux computer at the University of Groningen with the program packages *SHELXL*[11] (least-square refinements), *PLATON*[12] (calculation of geometric data and the *ORTEP*[12] illustrations) and a locally modified version of the program *PLUTO*[13] (preparation of illustrations).

Results and discussion.

The adopted atom numbering scheme of the atoms and the configuration are shown in the *PLUTO* drawings of Fig. 1.; the packing of the molecules is shown in the unit cell in Fig. 2.

Each asymmetric unit contains two formula units (molecules) with no atom setting at special position. The monoclinic unit cell contains four discrete units of the title compound separated by normal van der Waals distances[15] (Fig. 2).

No classic hydrogen bonds, no missed symmetry (*MISSYM*) were detected by procedures implemented in *PLATON.* [16] The unit cell contains a potential solvent area (voids) of 77.7 Å^3.[17]

Legends to the Figures.

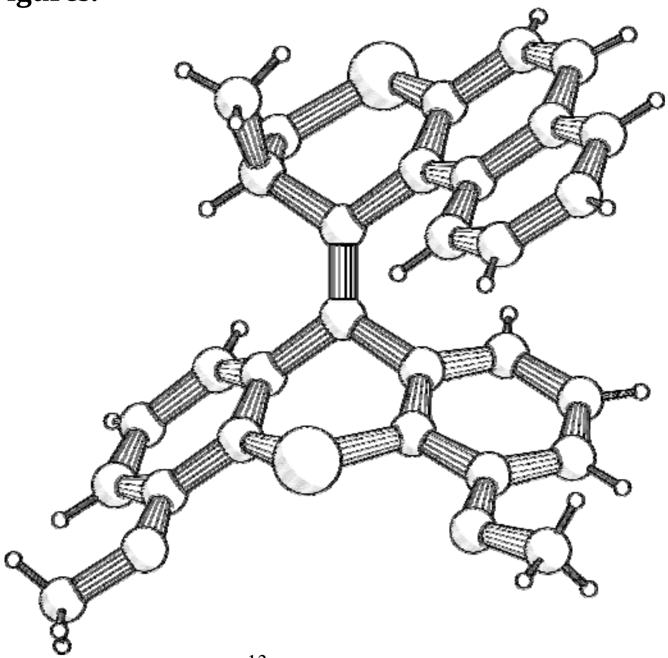


Fig. 1. Perspective *PLUTO*[13] drawings showing the configuration of the title compound and the adopted labeling scheme for non-hydrogen atoms.

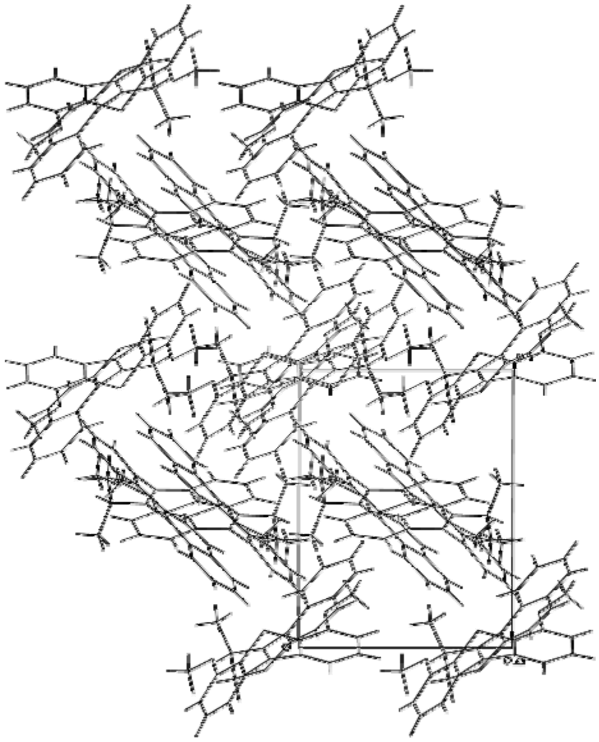


Fig. 2. Projections of the crystal structure down the unit cell axes and a view of an unit cell with minimal overlap.

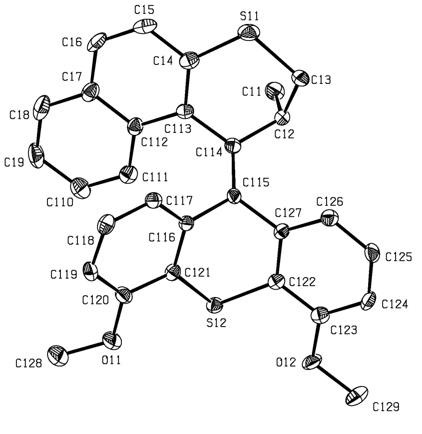


Fig. 3. Perspective *ORTEP*[12] drawings of the title compound with the atom-labeling scheme for the non-hydrogen atoms. All non-hydrogen atoms are represented by their displacement ellipsoids drawn at the 50% probability level; the hydrogen atoms are drawn with an arbitrary radius.

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Table 1.
a. Crystal data and details of the structure determination.

Moiety_Formula	$C_{29}H_{24}O_2S_2$
Formula_Weight, g.mol^{-1}	468.64
Crystal system	monoclinic
Space group, no.^{18}	$P2_1$, 4
a, Å	8.9625(6)
b, Å	22.785(2)
c, Å	11.6435(8)
β, deg	90.127(1)
V, Å^3	2377.7(3)
θ range unit cell: min.-max., deg; reflections	2.27 - 27.06 ; 6907
Formula_Z	4
SpaceGroup_Z	2
Z' (= Formula_Z / SpaceGroup_Z)	2
ρ_{calc}, g.cm^{-3}	1.309
F(000), electrons	984
μ(Mo K$\bar{\alpha}$), cm^{-1}	2.49
Color, habit	Colorless, parallelepiped
Approx. crystal dimension, mm	0.13 x 0.11 x 0.09

b. Data collection.

λ(Mo K$\bar{\alpha}$), Å	0.71073
Monochromator	Graphite
Measurement device type	*CCD* area-detector diffractometer
Detector Area resolution (pixels / mm)	4096 x 4096 / 62 x 62 (binned 512)
Temperature, K	110(2)
Measurement method	φ- and ω-scans
θ range; min. max., deg	2.27, 29.04
Index ranges	h: -12→11; k: -30→31; l: -15→15
X-ray exposure time, h	14.5
Total data	22162
Unique data	11841
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	10878
$R_{int} = \sum [\lvert F_o^2 - F_o^2 (\text{mean})\rvert] / \sum [F_o^2]$	0.0366
$R_{sig} = \sum \sigma(F_o^2) / \sum [F_o^2]$	0.0644

c. Refinement.

Number of reflections	11841
Number of refined parameters	786
Final agreement factors:	
$wR(F^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$	0.0863
Weighting scheme: *a, b*	0.0377, 0.0
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
and $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \sum (\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert) / \sum \lvert F_o \rvert$	0.0420
For $F_o > 4.0\ \sigma\ (F_o)$	
Absolute-Structure parameter Flack's **x**	0.01(5)
GooF = S $=[\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	1.036
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
Difference Fourier map, e/Å^3	-0.28, 0.4(5)
Max. (shift/σ) final cycle	<0.600
Average (shift/σ) final cycle	0.001

Table 2. Final fractional atomic coordinates and equivalent isotropic displacement parameters with s.u.'s in parentheses.
Atoms of the Asymmetric Unit.

Non-Hydrogen parameters

Residue: 1.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
S11	0.76595(10)	0.30364(3)	0.59261(7)	0.0268(2)
S12	0.62199(7)	-0.00256(3)	0.48874(6)	0.01764(17)
O11	0.3096(2)	-0.02118(9)	0.45638(19)	0.0276(7)
O12	0.8441(2)	-0.07797(8)	0.58437(18)	0.0235(6)
C11	0.9403(4)	0.21191(15)	0.4056(3)	0.0244(9)
C12	0.8807(3)	0.19377(13)	0.5237(2)	0.0185(7)
C13	0.8973(4)	0.24276(13)	0.6125(3)	0.0224(9)
C14	0.6308(3)	0.27590(13)	0.4952(2)	0.0214(8)
C15	0.5330(4)	0.31957(13)	0.4509(3)	0.0258(9)
C16	0.4259(3)	0.30473(14)	0.3722(3)	0.0264(9)
C17	0.4129(3)	0.24647(14)	0.3305(3)	0.0225(9)
C18	0.3079(4)	0.23126(17)	0.2454(3)	0.0313(10)
C19	0.2998(4)	0.17486(16)	0.2025(3)	0.0318(10)
C110	0.4004(4)	0.13234(16)	0.2424(3)	0.0262(9)
C111	0.5038(3)	0.14533(13)	0.3248(2)	0.0207(8)
C112	0.5124(3)	0.20226(13)	0.3743(2)	0.0188(8)
C113	0.6175(3)	0.21728(12)	0.4642(2)	0.0164(7)
C114	0.7188(3)	0.17365(12)	0.5198(2)	0.0162(7)
C115	0.6729(3)	0.12295(11)	0.5703(2)	0.0154(7)
C116	0.5150(3)	0.10395(12)	0.5692(2)	0.0157(7)
C117	0.3990(3)	0.14105(13)	0.6056(2)	0.0180(8)
C118	0.2515(3)	0.12392(13)	0.5917(3)	0.0226(9)
C119	0.2164(3)	0.07005(14)	0.5403(3)	0.0221(8)
C120	0.3309(3)	0.03231(12)	0.5082(2)	0.0205(8)
C121	0.4803(3)	0.04816(12)	0.5271(2)	0.0167(8)
C122	0.7617(3)	0.01995(12)	0.5879(2)	0.0160(7)
C123	0.8580(3)	-0.02304(12)	0.6324(2)	0.0200(8)
C124	0.9590(3)	-0.00895(13)	0.7194(2)	0.0208(8)
C125	0.9626(3)	0.04814(13)	0.7626(3)	0.0215(9)
C126	0.8717(3)	0.09199(13)	0.7163(2)	0.0197(8)
C127	0.7736(3)	0.07845(12)	0.6252(2)	0.0155(8)
C128	0.1682(4)	-0.03097(16)	0.4033(3)	0.0305(10)
C129	0.9481(4)	-0.12254(15)	0.6214(3)	0.0294(10)

Residue: 2.

S21	0.84332(10)	0.19143(3)	1.07707(7)	0.0299(2)
S22	0.83718(8)	0.50083(3)	0.93567(6)	0.02166(19)
O21	1.1207(3)	0.54031(9)	0.8695(2)	0.0330(7)
O22	0.5958(3)	0.56310(9)	1.03745(18)	0.0260(6)
C21	0.6157(4)	0.26901(15)	0.9057(3)	0.0275(10)
C22	0.6829(3)	0.29356(13)	1.0184(3)	0.0211(8)
C23	0.7007(4)	0.24606(14)	1.1106(3)	0.0267(10)
C24	0.9608(3)	0.22719(13)	0.9785(3)	0.0218(8)
C25	1.0773(3)	0.19082(14)	0.9350(3)	0.0240(8)
C26	1.1789(4)	0.21243(13)	0.8596(3)	0.0258(9)
C27	1.1634(4)	0.26993(12)	0.8131(2)	0.0223(8)
C28	1.2626(4)	0.29230(13)	0.7293(3)	0.0252(9)
C29	1.2389(4)	0.34588(15)	0.6781(3)	0.0269(10)
C210	1.1125(4)	0.37891(13)	0.7090(3)	0.0223(8)
C211	1.0158(3)	0.35954(12)	0.7918(2)	0.0174(8)
C212	1.0414(3)	0.30538(13)	0.8510(2)	0.0187(8)
C213	0.9471(3)	0.28517(12)	0.9424(2)	0.0181(8)
C214	0.8326(3)	0.32368(12)	1.0003(2)	0.0170(7)
C215	0.8620(3)	0.37855(12)	1.0397(2)	0.0169(8)
C216	1.0078(3)	0.40869(12)	1.0226(2)	0.0184(8)
C217	1.1461(3)	0.38327(12)	1.0511(2)	0.0204(8)
C218	1.2779(4)	0.41078(15)	1.0202(3)	0.0287(9)
C219	1.2754(4)	0.46385(14)	0.9590(3)	0.0279(9)
C220	1.1389(3)	0.48978(12)	0.9327(3)	0.0240(8)
C221	1.0059(3)	0.46390(13)	0.9697(2)	0.0201(8)
C222	0.7264(3)	0.47391(12)	1.0496(2)	0.0179(8)
C223	0.6170(3)	0.51117(11)	1.0951(2)	0.0212(8)
C224	0.5372(3)	0.49426(14)	1.1918(2)	0.0212(8)
C225	0.5672(4)	0.44010(14)	1.2433(3)	0.0234(9)
C226	0.6708(4)	0.40191(13)	1.1953(2)	0.0200(8)
C227	0.7485(3)	0.41746(12)	1.0957(2)	0.0180(8)
C228	1.2462(5)	0.56011(17)	0.8050(4)	0.0371(11)
C229	0.4841(4)	0.60196(14)	1.0806(3)	0.0276(10)

Hydrogen parameters

Residue: 1.

Atom	*x*	*y*	*z*	*Ueq (Å2)**
H11	0.918(4)	0.1833(18)	0.353(3)	0.038(11)
H11'	1.045(4)	0.2215(14)	0.412(3)	0.024(9)
H11"	0.893(5)	0.2454(18)	0.372(4)	0.043(11)
H12	0.950(3)	0.1625(12)	0.547(2)	0.006(6)
H13	1.004(3)	0.2602(12)	0.608(2)	0.007(7)
H13'	0.888(4)	0.2298(14)	0.693(3)	0.017(8)
H15	0.534(4)	0.3537(16)	0.482(3)	0.026(9)
H16	0.352(4)	0.3289(16)	0.343(3)	0.035(10)
H18	0.240(4)	0.2611(16)	0.219(3)	0.035(10)
H19	0.237(4)	0.1610(15)	0.154(3)	0.023(9)
H110	0.393(4)	0.0952(19)	0.214(3)	0.040(11)
H111	0.567(4)	0.1148(14)	0.350(3)	0.017(8)
H117	0.427(4)	0.1770(16)	0.636(3)	0.028(9)
H118	0.165(3)	0.1480(12)	0.614(2)	0.013(7)
H119	0.115(3)	0.0568(12)	0.524(2)	0.007(7)
H124	1.031(3)	-0.0380(13)	0.751(2)	0.00868(-)
H125	1.026(3)	0.0588(12)	0.825(2)	0.030(6)
H126	0.867(3)	0.1328(12)	0.746(2)	0.006(6)
H128	0.091(5)	-0.0356(19)	0.458(4)	0.050(12)
H128'	0.178(4)	-0.0673(17)	0.359(3)	0.032(10)
H128"	0.144(4)	-0.0019(17)	0.352(3)	0.030(9)
H129	1.049(4)	-0.1089(16)	0.608(3)	0.032(10)
H129'	0.925(4)	-0.1553(14)	0.574(3)	0.022(9)
H129"	0.938(4)	-0.1365(15)	0.698(3)	0.021(8)

Residue: 2.

H21	0.681(4)	0.2409(14)	0.875(3)	0.019(8)
H21'	0.609(3)	0.2970(14)	0.844(3)	0.014(7)
H21"	0.520(5)	0.2554(17)	0.916(3)	0.042(11)
H22	0.614(3)	0.3215(12)	1.049(2)	0.007(7)
H23	0.616(5)	0.2268(17)	1.121(4)	0.044(12)
H23'	0.721(4)	0.2628(13)	1.189(3)	0.017(8)
H25	1.086(3)	0.1533(14)	0.963(3)	0.015(8)
H26	1.261(4)	0.1891(16)	0.832(3)	0.035(10)
H28	1.345(4)	0.2743(13)	0.713(3)	0.013(7)
H29	1.299(4)	0.3593(16)	0.615(3)	0.040(11)
H210	1.091(3)	0.4128(12)	0.666(2)	0.006(6)
H211	0.925(3)	0.3841(11)	0.814(2)	0.030(6)
H217	1.145(4)	0.3445(14)	1.088(3)	0.026(8)
H218	1.380(4)	0.3920(13)	1.035(3)	0.014(8)
H219	1.369(4)	0.4788(15)	0.936(3)	0.031(9)
H224	0.469(4)	0.5161(18)	1.221(3)	0.03717(-)
H225	0.520(3)	0.4301(14)	1.314(3)	0.014(8)
H226	0.690(3)	0.3692(14)	1.229(2)	0.007(7)
H228	1.322(5)	0.5783(19)	0.853(4)	0.054(13)
H228'	1.213(4)	0.5891(16)	0.756(3)	0.024(9)
H228"	1.285(4)	0.5319(16)	0.756(3)	0.029(9)
H229	0.382(4)	0.5852(14)	1.079(3)	0.022(8)
H229'	0.483(3)	0.6325(14)	1.021(3)	0.014(7)
H229"	0.508(4)	0.6179(14)	1.164(3)	0.022(8)

*) $U_{eq} = 1/3 \sum_{i} \sum_{j} U_{ij} a_i^{*} a_j^{*} \mathbf{a_i . a_j}$ [19]

Anisotropic (displacement) parameters (Å^2)

Residue: 1.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S11	0.0367(4)	0.0160(3)	0.0277(4)	-0.0050(3)	-0.0034(3)	-0.0010(3)
S12	0.0194(3)	0.0152(3)	0.0183(3)	-0.0018(3)	-0.0011(3)	0.0015(3)
O11	0.0254(12)	0.0203(10)	0.0372(12)	-0.0056(9)	-0.0057(10)	-0.0019(9)
O12	0.0291(11)	0.0130(9)	0.0284(11)	0.0010(8)	-0.0025(10)	0.0060(9)
C11	0.0231(16)	0.0229(15)	0.0271(16)	0.0002(14)	0.0004(13)	-0.0022(13)
C12	0.0169(13)	0.0159(12)	0.0226(13)	0.0025(12)	-0.0031(11)	-0.0001(12)
C13	0.0248(16)	0.0179(14)	0.0246(15)	0.0000(12)	-0.0065(12)	-0.0043(12)
C14	0.0252(16)	0.0209(14)	0.0181(13)	0.0040(11)	0.0040(12)	0.0001(12)
C15	0.0329(18)	0.0138(14)	0.0306(16)	0.0036(12)	0.0076(14)	0.0014(12)
C16	0.0245(16)	0.0229(15)	0.0318(16)	0.0127(14)	0.0026(13)	0.0101(14)
C17	0.0192(15)	0.0256(15)	0.0227(15)	0.0083(12)	0.0028(12)	0.0033(12)
C18	0.0233(17)	0.042(2)	0.0286(16)	0.0125(15)	-0.0036(14)	0.0073(15)
C19	0.0247(18)	0.046(2)	0.0247(15)	0.0024(15)	-0.0116(13)	-0.0057(15)
C110	0.0248(16)	0.0311(17)	0.0228(14)	-0.0014(14)	0.0016(12)	-0.0050(14)
C111	0.0210(15)	0.0229(15)	0.0181(13)	0.0036(11)	0.0027(12)	0.0003(12)
C112	0.0171(14)	0.0222(16)	0.0170(13)	0.0039(11)	-0.0003(11)	0.0005(12)
C113	0.0184(14)	0.0154(12)	0.0153(12)	0.0008(10)	0.0031(11)	-0.0006(11)
C114	0.0183(13)	0.0148(12)	0.0154(12)	-0.004(1)	-0.0008(10)	0.0001(10)
C115	0.0147(13)	0.0149(12)	0.0165(12)	-0.0025(10)	-0.0029(11)	0.0004(10)
C116	0.0173(13)	0.0153(13)	0.0144(12)	0.0009(10)	-0.0027(11)	-0.0003(11)
C117	0.0224(15)	0.0165(13)	0.0152(12)	0.0003(11)	-0.0022(11)	-0.0010(12)
C118	0.0195(15)	0.0240(15)	0.0242(15)	-0.0016(12)	0.0022(12)	0.0081(12)
C119	0.0138(14)	0.0249(15)	0.0275(15)	-0.0007(12)	-0.0032(12)	-

						0.0014(12)
C120	0.0215(14)	0.0200(14)	0.0199(13)	-0.0006(11)	-0.0033(12)	-0.0050(12)
C121	0.0149(13)	0.0184(13)	0.0169(14)	0.0009(11)	0.0021(11)	0.0029(11)
C122	0.0167(13)	0.0170(12)	0.0142(12)	0.0019(10)	0.0037(10)	0.0006(10)
C123	0.0213(15)	0.0194(13)	0.0193(12)	0.0013(10)	0.0033(11)	0.0000(12)
C124	0.0183(14)	0.0219(15)	0.0222(13)	0.0063(12)	-0.0030(11)	0.0058(12)
C125	0.0202(15)	0.0258(16)	0.0186(14)	0.0020(12)	-0.0072(12)	-0.0033(12)
C126	0.0206(15)	0.0188(14)	0.0196(14)	0.0006(11)	0.0003(12)	-0.0009(12)
C127	0.0138(13)	0.0161(13)	0.0167(13)	0.0026(10)	0.0029(10)	0.0021(11)
C128	0.0305(18)	0.0282(18)	0.0329(18)	-0.0047(16)	-0.0041(15)	-0.0037(15)
C129	0.037(2)	0.0205(16)	0.0307(18)	0.0026(14)	-0.0002(15)	0.0116(15)

Residue: 2.

S21	0.0457(5)	0.0163(3)	0.0278(4)	0.0063(3)	0.0012(4)	0.0009(4)
S22	0.0266(4)	0.0174(3)	0.0210(3)	0.0045(3)	0.0053(3)	0.0030(3)
O21	0.0379(14)	0.0196(10)	0.0417(14)	0.0027(10)	0.0132(11)	-0.0043(10)
O22	0.0330(12)	0.0188(10)	0.0262(11)	0.0031(9)	0.0077(9)	0.0071(9)
C21	0.0277(18)	0.0268(16)	0.0279(16)	-0.0006(14)	-0.0036(14)	-0.0081(15)
C22	0.0228(15)	0.0178(14)	0.0226(14)	0.0006(12)	0.0010(12)	-0.0002(11)
C23	0.035(2)	0.0225(15)	0.0227(16)	0.0002(12)	0.0064(13)	-0.0058(14)
C24	0.0294(16)	0.0170(14)	0.0189(14)	-0.0019(11)	-0.0066(12)	-0.0005(12)
C25	0.0360(17)	0.0130(12)	0.0229(14)	-0.0021(12)	-0.0114(13)	0.0067(13)
C26	0.0310(18)	0.0220(14)	0.0243(15)	-0.0098(12)	-0.0088(14)	0.0079(14)
C27	0.0253(15)	0.0211(14)	0.0206(14)	-0.0087(11)	-0.0088(12)	0.0028(12)
C28	0.0226(16)	0.0256(17)	0.0275(16)	-0.0108(12)	0.0010(13)	0.0060(13)
C29	0.0275(17)	0.0329(18)	0.0204(15)	0.0001(13)	0.0034(13)	-0.0037(14)
C210	0.0271(16)	0.0193(14)	0.0206(14)	0.0002(12)	-0.0019(13)	-0.0018(13)
C211	0.0205(15)	0.0170(13)	0.0148(12)	-0.0036(10)	-0.0036(11)	0.0041(11)
C212	0.0209(14)	0.0161(13)	0.0192(13)	-0.0053(11)	-0.0060(11)	-0.0009(12)
C213	0.0255(15)	0.0140(12)	0.0148(13)	-0.0019(10)	-0.0075(11)	-0.0012(12)
C214	0.0215(14)	0.0153(12)	0.0143(12)	0.0009(10)	0.0012(11)	0.0028(11)
C215	0.0204(15)	0.0155(12)	0.0149(12)	0.000(1)	-0.0001(11)	0.0012(11)
C216	0.0238(15)	0.0167(13)	0.0146(13)	-0.0055(11)	0.0014(12)	-0.0011(12)
C217	0.0257(16)	0.0186(14)	0.0169(13)	-0.0063(11)	-0.0031(12)	0.0008(12)
C218	0.0198(15)	0.0318(17)	0.0344(17)	-0.0145(14)	-0.0033(14)	-0.0002(14)
C219	0.0192(15)	0.0284(16)	0.0362(17)	-0.0132(14)	0.0057(13)	-0.0097(13)
C220	0.0281(16)	0.0175(14)	0.0264(14)	-0.0060(12)	0.0046(12)	-0.0057(12)

C221	0.0203(14)	0.0194(14)	0.0205(14)	-0.0051(12)	-0.0003(11)	0.0038(11)
C222	0.0199(14)	0.0172(13)	0.0167(13)	-0.0014(10)	0.0004(11)	-0.0032(11)
C223	0.0269(15)	0.0168(14)	0.0200(13)	0.0005(10)	0.0000(11)	-0.0003(12)
C224	0.0220(14)	0.0216(14)	0.0200(13)	-0.0061(12)	0.002(1)	0.0025(13)
C225	0.0299(17)	0.0233(15)	0.0170(14)	0.0004(12)	0.0060(12)	-0.0045(13)
C226	0.0264(16)	0.0159(14)	0.0176(12)	0.0016(11)	-0.0004(12)	0.0002(12)
C227	0.0199(14)	0.0154(13)	0.0188(13)	-0.002(1)	-0.0021(12)	-0.0022(11)
C228	0.043(2)	0.0273(18)	0.041(2)	-0.0052(17)	0.0213(18)	-0.0090(17)
C229	0.0334(19)	0.0190(15)	0.0305(16)	0.0001(14)	0.0024(15)	0.0085(13)

Thermal vibration amplitudes (Å^2)

$$F(\mathbf{h}) = F_o(\mathbf{h}) \exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} \mathrm{h}_i \mathrm{h}_l \mathrm{a}_\mathrm{i}^* \mathrm{a}_j^* Uij\right)$$

or

$$F(\mathbf{h}) = F_o(\mathbf{h}) \exp\left(-8\pi^2 U_{iso} (\sin(\theta)/\lambda)^2\right)$$

Table 3. Selected data on the geometry.
Standard deviations in the last decimal place are given in parentheses.

Residue: 1.

Interatomic Distances (Å)

S(11)	-C(13)	1.834(3)	C(112)	-C(113)	1.448(4)
S(11)	-C(14)	1.774(3)	C(113)	-C(14)	1.389(4)
S(12)	-C(121)	1.775(3)	C(113)	-C(114)	1.493(4)
S(12)	-C(122)	1.777(3)	C(114)	-C(12)	1.522(4)
O(11)	-C(120)	1.373(3)	C(114)	-C(115)	1.360(4)
O(11)	-C(128)	1.426(4)	C(115)	-C(116)	1.480(4)
O(12)	-C(123)	1.376(3)	C(115)	-C(127)	1.500(4)
O(12)	-C(129)	1.444(4)	C(116)	-C(117)	1.406(4)
C(11)	-C(12)	1.533(4)	C(116)	-C(121)	1.397(4)
C(12)	-C(13)	1.529(4)	C(117)	-C(118)	1.388(4)
C(14)	-C(15)	1.422(4)	C(118)	-C(119)	1.401(4)
C(15)	-C(16)	1.368(5)	C(119)	-C(120)	1.391(4)
C(16)	-C(17)	1.418(5)	C(120)	-C(121)	1.404(4)
C(17)	-C(18)	1.408(5)	C(122)	-C(123)	1.404(4)
C(18)	-C(19)	1.381(5)	C(122)	-C(127)	1.406(4)
C(110)	-C(19)	1.402(5)	C(123)	-C(124)	1.394(4)
C(110)	-C(111)	1.365(4)	C(124)	-C(125)	1.395(4)
C(111)	-C(112)	1.421(4)	C(125)	-C(126)	1.397(4)
C(112)	-C(17)	1.438(4)	C(126)	-C(127)	1.410(4)

Bond Angles (deg.)

C(13)	-S(11)	-C(14)	104.39(15)
C(121)	-S(12)	-C(122)	98.75(12)
C(120)	-O(11)	-C(128)	116.9(2)
C(123)	-O(12)	-C(129)	117.4(2)
C(11)	-C(12)	-C(13)	112.1(3)
C(11)	-C(12)	-C(114)	112.9(2)
C(13)	-C(12)	-C(114)	109.4(2)
S(11)	-C(13)	-C(12)	113.9(2)
S(11)	-C(14)	-C(15)	113.7(2)
S(11)	-C(14)	-C(113)	124.5(2)
C(15)	-C(14)	-C(113)	121.8(2)
C(14)	-C(15)	-C(16)	120.1(3)
C(15)	-C(16)	-C(17)	121.2(3)
C(16)	-C(17)	-C(18)	121.7(3)
C(16)	-C(17)	-C(112)	118.9(3)
C(18)	-C(17)	-C(112)	119.3(3)
C(17)	-C(18)	-C(19)	121.2(3)
C(18)	-C(19)	-C(110)	119.3(3)
C(19)	-C(110)	-C(111)	121.2(3)
C(110)	-C(111)	-C(112)	121.3(3)
C(17)	-C(112)	-C(111)	117.5(2)
C(17)	-C(112)	-C(113)	119.5(3)
C(111)	-C(112)	-C(113)	122.9(2)
C(14)	-C(113)	-C(112)	118.1(2)
C(14)	-C(113)	-C(114)	118.4(2)
C(112)	-C(113)	-C(114)	123.4(2)
C(12)	-C(114)	-C(113)	113.0(2)
C(12)	-C(114)	-C(115)	122.1(2)
C(113)	-C(114)	-C(115)	124.7(2)
C(114)	-C(115)	-C(116)	122.3(2)
C(114)	-C(115)	-C(127)	125.2(2)
C(116)	-C(115)	-C(127)	112.4(2)
C(115)	-C(116)	-C(117)	122.0(2)
C(115)	-C(116)	-C(121)	118.8(2)
C(117)	-C(116)	-C(121)	119.2(2)
C(116)	-C(117)	-C(118)	120.0(3)
C(117)	-C(118)	-C(119)	120.6(3)
C(118)	-C(119)	-C(120)	119.4(2)
O(11)	-C(120)	-C(119)	124.4(2)
O(11)	-C(120)	-C(121)	115.4(2)
C(119)	-C(120)	-C(121)	120.2(3)
S(12)	-C(121)	-C(116)	121.5(2)
S(12)	-C(121)	-C(120)	118.4(2)
C(116)	-C(121)	-C(120)	120.0(2)
S(12)	-C(122)	-C(123)	118.0(2)
S(12)	-C(122)	-C(127)	121.8(2)
C(123)	-C(122)	-C(127)	120.1(2)
O(12)	-C(123)	-C(122)	115.4(2)
O(12)	-C(123)	-C(124)	124.2(2)
C(122)	-C(123)	-C(124)	120.3(2)
C(123)	-C(124)	-C(125)	119.4(3)
C(124)	-C(125)	-C(126)	121.0(3)
C(125)	-C(126)	-C(127)	119.7(3)
C(115)	-C(127)	-C(122)	117.7(2)
C(115)	-C(127)	-C(126)	123.1(2)
C(122)	-C(127)	-C(126)	119.1(2)

Torsion Angles (deg.)

C(14)	-S(11)	-C(13)	-C(12)	14.1(3)
C(13)	-S(11)	-C(14)	-C(15)	-168.9(2)
C(13)	-S(11)	-C(14)	-C(113)	11.8(3)
C(122)	-S(12)	-C(121)	-C(116)	30.6(2)
C(122)	-S(12)	-C(121)	-C(120)	-153.0(2)
C(121)	-S(12)	-C(122)	-C(123)	146.8(2)
C(121)	-S(12)	-C(122)	-C(127)	-30.8(2)
C(128)	-O(11)	-C(120)	-C(119)	18.6(4)
C(128)	-O(11)	-C(120)	-C(121)	-160.7(2)
C(129)	-O(12)	-C(123)	-C(122)	175.6(2)
C(129)	-O(12)	-C(123)	-C(124)	-4.4(4)
C(11)	-C(12)	-C(13)	-S(11)	73.2(3)
C(114)	-C(12)	-C(13)	-S(11)	-52.8(3)
S(11)	-C(14)	-C(15)	-C(16)	178.1(3)
C(113)	-C(14)	-C(15)	-C(16)	-2.6(5)
C(14)	-C(15)	-C(16)	-C(17)	-2.0(5)
C(15)	-C(16)	-C(17)	-C(18)	-176.9(3)
C(15)	-C(16)	-C(17)	-C(112)	1.5(5)
C(16)	-C(17)	-C(18)	-C(19)	177.7(3)
C(112)	-C(17)	-C(18)	-C(19)	-0.7(5)
C(17)	-C(18)	-C(19)	-C(110)	-1.6(5)
C(111)	-C(110)	-C(19)	-C(18)	1.6(5)
C(19)	-C(110)	-C(111)	-C(112)	0.7(5)
C(110)	-C(111)	-C(112)	-C(17)	-2.9(4)
C(110)	-C(111)	-C(112)	-C(113)	178.1(3)
C(111)	-C(112)	-C(17)	-C(16)	-175.5(3)
C(111)	-C(112)	-C(17)	-C(18)	2.8(4)
C(113)	-C(112)	-C(17)	-C(16)	3.5(4)
C(113)	-C(112)	-C(17)	-C(18)	-178.2(3)
C(17)	-C(112)	-C(113)	-C(14)	-7.7(4)
C(17)	-C(112)	-C(113)	-C(114)	176.3(2)
C(111)	-C(112)	-C(113)	-C(14)	171.2(2)
C(111)	-C(112)	-C(113)	-C(114)	-4.8(4)
C(112)	-C(113)	-C(14)	-S(11)	-173.37(19)
C(112)	-C(113)	-C(14)	-C(15)	7.4(4)
C(114)	-C(113)	-C(14)	-S(11)	2.8(3)
C(114)	-C(113)	-C(14)	-C(15)	-176.4(3)
C(14)	-C(113)	-C(114)	-C(12)	-45.7(3)
C(14)	-C(113)	-C(114)	-C(115)	129.4(3)
C(112)	-C(113)	-C(114)	-C(12)	130.2(3)
C(112)	-C(113)	-C(114)	-C(115)	-54.6(4)
C(113)	-C(114)	-C(12)	-C(11)	-53.2(3)
C(113)	-C(114)	-C(12)	-C(13)	72.3(3)
C(115)	-C(114)	-C(12)	-C(11)	131.4(3)
C(115)	-C(114)	-C(12)	-C(13)	-103.1(3)
C(12)	-C(114)	-C(115)	-C(116)	178.5(2)
C(12)	-C(114)	-C(115)	-C(127)	-6.0(4)
C(113)	-C(114)	-C(115)	-C(116)	3.7(4)

C(113)	-C(114)	-C(115)	-C(127)	179.2(2)
C(114)	-C(115)	-C(116)	-C(117)	-52.3(3)
C(114)	-C(115)	-C(116)	-C(121)	125.6(3)
C(127)	-C(115)	-C(116)	-C(117)	131.6(2)
C(127)	-C(115)	-C(116)	-C(121)	-50.5(3)
C(114)	-C(115)	-C(127)	-C(122)	-126.1(3)
C(114)	-C(115)	-C(127)	-C(126)	57.9(4)
C(116)	-C(115)	-C(127)	-C(122)	49.8(3)
C(116)	-C(115)	-C(127)	-C(126)	-126.2(3)
C(115)	-C(116)	-C(117)	-C(118)	173.1(3)
C(121)	-C(116)	-C(117)	-C(118)	-4.8(4)
C(115)	-C(116)	-C(121)	-S(12)	6.3(3)
C(115)	-C(116)	-C(121)	-C(120)	-170.1(2)
C(117)	-C(116)	-C(121)	-S(12)	-175.77(18)
C(117)	-C(116)	-C(121)	-C(120)	7.8(4)
C(116)	-C(117)	-C(118)	-C(119)	-0.7(4)
C(117)	-C(118)	-C(119)	-C(120)	3.2(5)
C(118)	-C(119)	-C(120)	-O(11)	-179.4(3)
C(118)	-C(119)	-C(120)	-C(121)	-0.1(4)
O(11)	-C(120)	-C(121)	-S(12)	-2.6(3)
O(11)	-C(120)	-C(121)	-C(116)	173.9(2)
C(119)	-C(120)	-C(121)	-S(12)	178.0(2)
C(119)	-C(120)	-C(121)	-C(116)	-5.5(4)
S(12)	-C(122)	-C(123)	-O(12)	6.8(3)
S(12)	-C(122)	-C(123)	-C(124)	-173.2(2)
C(127)	-C(122)	-C(123)	-O(12)	-175.6(2)
C(127)	-C(122)	-C(123)	-C(124)	4.4(4)
S(12)	-C(122)	-C(127)	-C(115)	-5.5(3)
S(12)	-C(122)	-C(127)	-C(126)	170.64(19)
C(123)	-C(122)	-C(127)	-C(115)	177.0(2)
C(123)	-C(122)	-C(127)	-C(126)	-6.9(4)
O(12)	-C(123)	-C(124)	-C(125)	-179.4(2)
C(122)	-C(123)	-C(124)	-C(125)	0.6(4)
C(123)	-C(124)	-C(125)	-C(126)	-3.1(4)
C(124)	-C(125)	-C(126)	-C(127)	0.6(4)
C(125)	-C(126)	-C(127)	-C(115)	-179.7(3)
C(125)	-C(126)	-C(127)	-C(122)	4.4(4)

The sign of the torsion angle is positive if when looking from atom-2 to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.

Residue: 2.

Interatomic Distances (Å)

S(21)	-C(23)	1.827(3)
S(21)	-C(24)	1.759(3)
S(22)	-C(221)	1.775(3)
S(22)	-C(222)	1.768(3)
O(21)	-C(220)	1.376(4)
O(21)	-C(228)	1.427(5)
O(22)	-C(223)	1.373(3)
O(22)	-C(229)	1.429(4)
C(21)	-C(22)	1.547(5)
C(22)	-C(23)	1.532(5)
C(24)	-C(25)	1.427(4)
C(25)	-C(26)	1.359(5)
C(26)	-C(27)	1.424(4)
C(27)	-C(28)	1.416(5)
C(28)	-C(29)	1.375(5)
C(210)	-C(29)	1.407(5)
C(210)	-C(211)	1.371(4)
C(211)	-C(212)	1.432(4)
C(212)	-C(27)	1.430(4)
C(212)	-C(213)	1.436(4)
C(213)	-C(24)	1.392(4)
C(213)	-C(214)	1.510(4)
C(214)	-C(22)	1.522(4)
C(214)	-C(215)	1.357(4)
C(215)	-C(216)	1.490(4)
C(215)	-C(227)	1.500(4)
C(216)	-C(217)	1.407(4)
C(216)	-C(221)	1.401(4)
C(217)	-C(218)	1.385(4)
C(218)	-C(219)	1.404(5)
C(219)	-C(220)	1.392(4)
C(220)	-C(221)	1.399(4)
C(222)	-C(223)	1.402(4)
C(222)	-C(227)	1.408(4)
C(223)	-C(224)	1.390(4)
C(224)	-C(225)	1.398(4)
C(225)	-C(226)	1.391(5)
C(226)	-C(227)	1.400(4)

Bond Angles (deg.)

C(23)	-S(21)	-C(24)	104.12(15)
C(221)	-S(22)	-C(222)	98.49(12)
C(220)	-O(21)	-C(228)	117.0(3)
C(223)	-O(22)	-C(229)	117.3(2)
C(21)	-C(22)	-C(23)	112.2(3)
C(21)	-C(22)	-C(214)	112.8(3)
C(23)	-C(22)	-C(214)	109.0(2)
S(21)	-C(23)	-C(22)	113.8(2)
S(21)	-C(24)	-C(25)	113.7(2)
S(21)	-C(24)	-C(213)	125.7(2)
C(25)	-C(24)	-C(213)	120.5(3)
C(24)	-C(25)	-C(26)	120.7(3)
C(25)	-C(26)	-C(27)	120.9(3)
C(26)	-C(27)	-C(28)	122.1(3)
C(26)	-C(27)	-C(212)	118.4(3)
C(28)	-C(27)	-C(212)	119.4(3)
C(27)	-C(28)	-C(29)	121.4(3)
C(28)	-C(29)	-C(210)	119.2(3)
C(29)	-C(210)	-C(211)	121.2(3)
C(210)	-C(211)	-C(212)	121.0(3)
C(27)	-C(212)	-C(211)	117.4(2)
C(27)	-C(212)	-C(213)	119.9(2)
C(211)	-C(212)	-C(213)	122.6(2)
C(24)	-C(213)	-C(212)	118.5(3)
C(24)	-C(213)	-C(214)	118.4(2)
C(212)	-C(213)	-C(214)	123.1(2)
C(22)	-C(214)	-C(213)	113.6(2)
C(22)	-C(214)	-C(215)	122.6(2)
C(213)	-C(214)	-C(215)	123.7(2)
C(214)	-C(215)	-C(216)	123.3(2)
C(214)	-C(215)	-C(227)	124.1(2)
C(216)	-C(215)	-C(227)	112.4(2)
C(215)	-C(216)	-C(217)	123.4(2)
C(215)	-C(216)	-C(221)	117.6(2)
C(217)	-C(216)	-C(221)	118.9(2)
C(216)	-C(217)	-C(218)	120.2(3)
C(217)	-C(218)	-C(219)	120.6(3)
C(218)	-C(219)	-C(220)	119.4(3)
O(21)	-C(220)	-C(219)	125.2(3)
O(21)	-C(220)	-C(221)	114.7(2)
C(219)	-C(220)	-C(221)	120.2(3)
S(22)	-C(221)	-C(216)	122.2(2)
S(22)	-C(221)	-C(220)	117.2(2)
C(216)	-C(221)	-C(220)	120.3(3)
S(22)	-C(222)	-C(223)	117.9(2)
S(22)	-C(222)	-C(227)	121.6(2)
C(223)	-C(222)	-C(227)	120.5(2)
O(22)	-C(223)	-C(222)	115.7(2)
O(22)	-C(223)	-C(224)	124.3(2)
C(222)	-C(223)	-C(224)	120.0(2)
C(223)	-C(224)	-C(225)	119.6(3)
C(224)	-C(225)	-C(226)	120.5(3)
C(225)	-C(226)	-C(227)	120.6(3)
C(215)	-C(227)	-C(222)	118.0(2)
C(215)	-C(227)	-C(226)	123.4(2)
C(222)	-C(227)	-C(226)	118.5(2)

Torsion Angles (deg.)

C(24)	-S(21)	-C(23)	-C(22)	22.3(3)
C(23)	-S(21)	-C(24)	-C(25)	-176.6(2)
C(23)	-S(21)	-C(24)	-C(213)	3.1(3)
C(222)	-S(22)	-C(221)	-C(216)	31.4(2)
C(222)	-S(22)	-C(221)	-C(220)	-153.9(2)
C(221)	-S(22)	-C(222)	-C(223)	146.6(2)
C(221)	-S(22)	-C(222)	-C(227)	-31.9(2)
C(228)	-O(21)	-C(220)	-C(219)	14.8(5)
C(228)	-O(21)	-C(220)	-C(221)	-164.2(3)
C(229)	-O(22)	-C(223)	-C(222)	179.4(3)
C(229)	-O(22)	-C(223)	-C(224)	0.0(4)
C(21)	-C(22)	-C(23)	-S(21)	68.6(3)
C(214)	-C(22)	-C(23)	-S(21)	-57.0(3)
S(21)	-C(24)	-C(25)	-C(26)	-178.8(3)
C(213)	-C(24)	-C(25)	-C(26)	1.5(5)
C(24)	-C(25)	-C(26)	-C(27)	-6.4(5)
C(25)	-C(26)	-C(27)	-C(28)	-176.2(3)
C(25)	-C(26)	-C(27)	-C(212)	2.4(5)
C(26)	-C(27)	-C(28)	-C(29)	174.4(3)
C(212)	-C(27)	-C(28)	-C(29)	-4.2(5)
C(27)	-C(28)	-C(29)	-C(210)	-0.6(5)
C(211)	-C(210)	-C(29)	-C(28)	2.3(5)
C(29)	-C(210)	-C(211)	-C(212)	1.0(5)
C(210)	-C(211)	-C(212)	-C(27)	-5.6(4)
C(210)	-C(211)	-C(212)	-C(213)	176.6(3)
C(211)	-C(212)	-C(27)	-C(26)	-171.5(3)
C(211)	-C(212)	-C(27)	-C(28)	7.1(4)
C(213)	-C(212)	-C(27)	-C(26)	6.3(4)
C(213)	-C(212)	-C(27)	-C(28)	-175.0(3)
C(27)	-C(212)	-C(213)	-C(24)	-11.0(4)
C(27)	-C(212)	-C(213)	-C(214)	169.7(2)
C(211)	-C(212)	-C(213)	-C(24)	166.7(3)
C(211)	-C(212)	-C(213)	-C(214)	-12.6(4)
C(212)	-C(213)	-C(24)	-S(21)	-172.5(2)
C(212)	-C(213)	-C(24)	-C(25)	7.2(4)
C(214)	-C(213)	-C(24)	-S(21)	6.8(4)
C(214)	-C(213)	-C(24)	-C(25)	-173.5(3)
C(24)	-C(213)	-C(214)	-C(22)	-43.7(3)
C(24)	-C(213)	-C(214)	-C(215)	132.2(3)
C(212)	-C(213)	-C(214)	-C(22)	135.7(3)
C(212)	-C(213)	-C(214)	-C(215)	-48.5(4)
C(213)	-C(214)	-C(22)	-C(21)	-55.4(3)
C(213)	-C(214)	-C(22)	-C(23)	69.9(3)
C(215)	-C(214)	-C(22)	-C(21)	128.7(3)
C(215)	-C(214)	-C(22)	-C(23)	-105.9(3)
C(22)	-C(214)	-C(215)	-C(216)	-179.9(2)
C(22)	-C(214)	-C(215)	-C(227)	-5.5(4)
C(213)	-C(214)	-C(215)	-C(216)	4.6(4)

C(213)	-C(214)	-C(215)	-C(227)	179.0(2)
C(214)	-C(215)	-C(216)	-C(217)	-51.8(4)
C(214)	-C(215)	-C(216)	-C(221)	124.7(3)
C(227)	-C(215)	-C(216)	-C(217)	133.3(2)
C(227)	-C(215)	-C(216)	-C(221)	-50.2(3)
C(214)	-C(215)	-C(227)	-C(222)	-125.3(3)
C(214)	-C(215)	-C(227)	-C(226)	58.9(4)
C(216)	-C(215)	-C(227)	-C(222)	49.6(3)
C(216)	-C(215)	-C(227)	-C(226)	-126.2(3)
C(215)	-C(216)	-C(217)	-C(218)	172.2(3)
C(221)	-C(216)	-C(217)	-C(218)	-4.3(4)
C(215)	-C(216)	-C(221)	-S(22)	5.9(3)
C(215)	-C(216)	-C(221)	-C(220)	-168.6(2)
C(217)	-C(216)	-C(221)	-S(22)	-177.44(19)
C(217)	-C(216)	-C(221)	-C(220)	8.1(4)
C(216)	-C(217)	-C(218)	-C(219)	-0.8(5)
C(217)	-C(218)	-C(219)	-C(220)	2.1(5)
C(218)	-C(219)	-C(220)	-O(21)	-177.3(3)
C(218)	-C(219)	-C(220)	-C(221)	1.7(5)
O(21)	-C(220)	-C(221)	-S(22)	-2.5(4)
O(21)	-C(220)	-C(221)	-C(216)	172.2(2)
C(219)	-C(220)	-C(221)	-S(22)	178.4(2)
C(219)	-C(220)	-C(221)	-C(216)	-6.8(4)
S(22)	-C(222)	-C(223)	-O(22)	7.0(3)
S(22)	-C(222)	-C(223)	-C(224)	-173.7(2)
C(227)	-C(222)	-C(223)	-O(22)	-174.5(2)
C(227)	-C(222)	-C(223)	-C(224)	4.9(4)
S(22)	-C(222)	-C(227)	-C(215)	-4.4(3)
S(22)	-C(222)	-C(227)	-C(226)	171.6(2)
C(223)	-C(222)	-C(227)	-C(215)	177.1(2)
C(223)	-C(222)	-C(227)	-C(226)	-6.9(4)
O(22)	-C(223)	-C(224)	-C(225)	179.5(3)
C(222)	-C(223)	-C(224)	-C(225)	0.2(4)
C(223)	-C(224)	-C(225)	-C(226)	-3.2(5)
C(224)	-C(225)	-C(226)	-C(227)	1.0(5)
C(225)	-C(226)	-C(227)	-C(215)	179.8(3)
C(225)	-C(226)	-C(227)	-C(222)	4.0(4)

The sign of the torsion angle is positive if when looking from atom-2 to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.

^{1}H, ^{13}C and 2D NMR Spectra

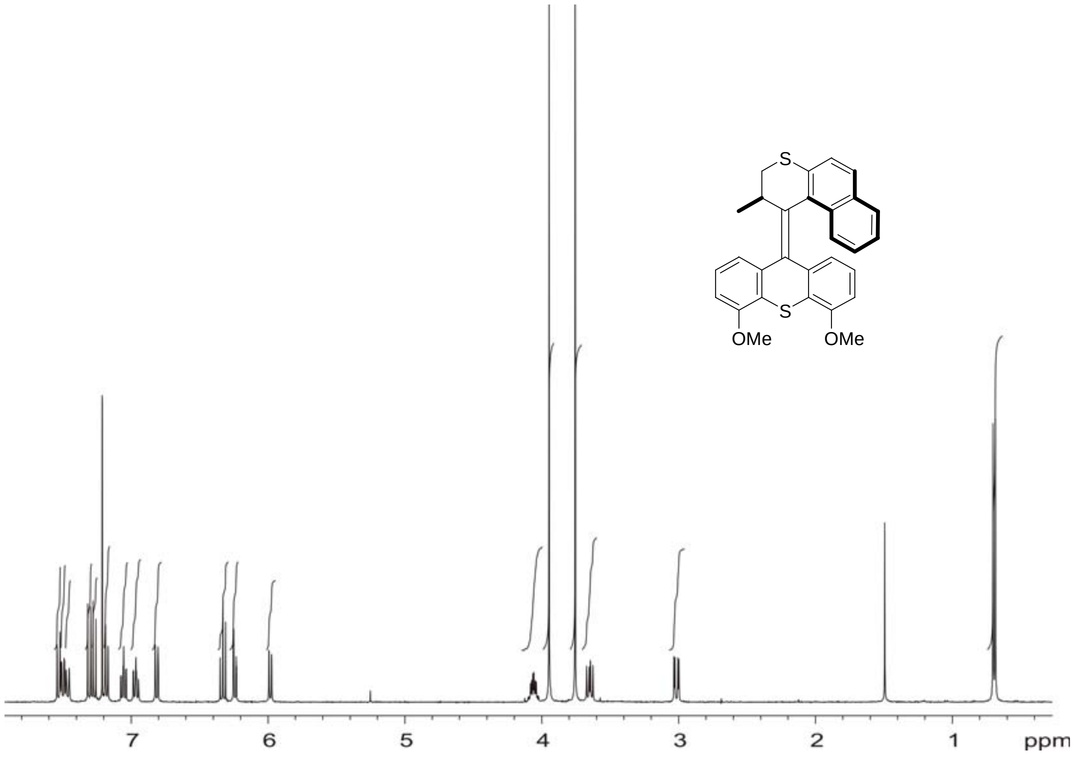


Figure 3. ^{1}H NMR spectrum of **5** taken at 400 MHz in $CDCl_3$.

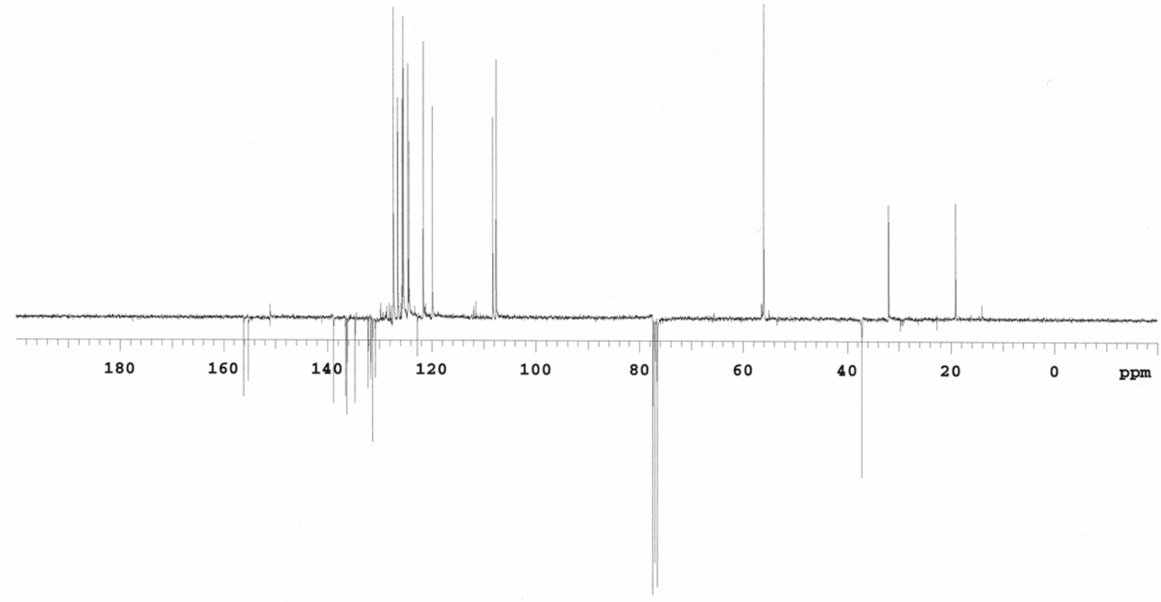


Figure 4. 100 MHz APT spectrum of **5** in $CDCl_3$.

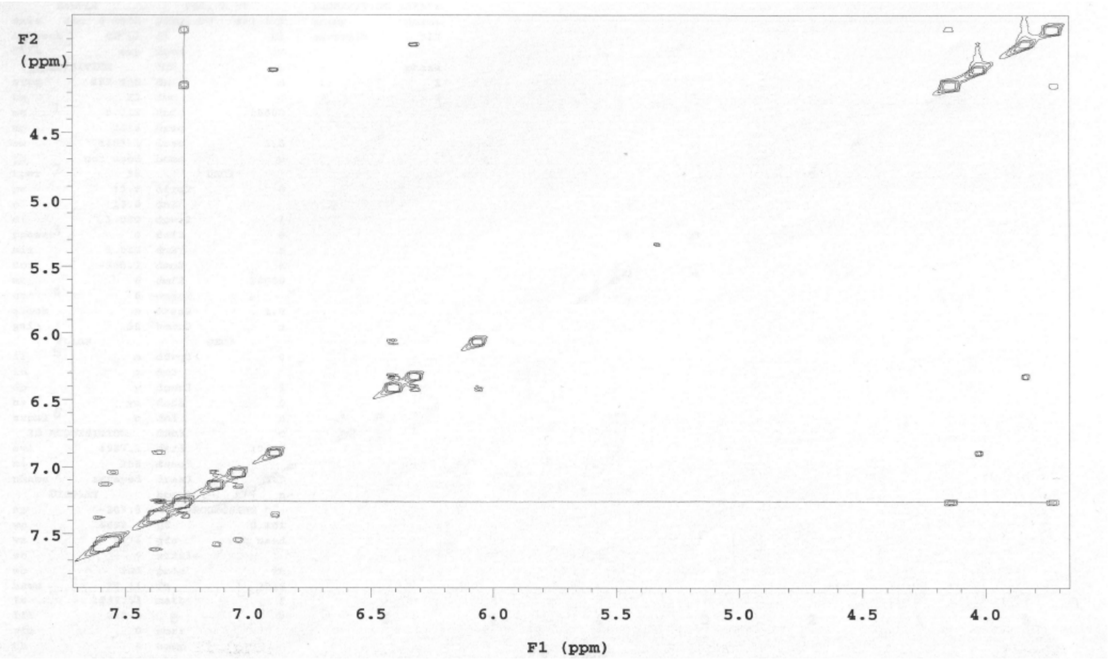


Figure 5. NOESY spectrum of **5** in $CDCl_3$ taken at 500 MHz.

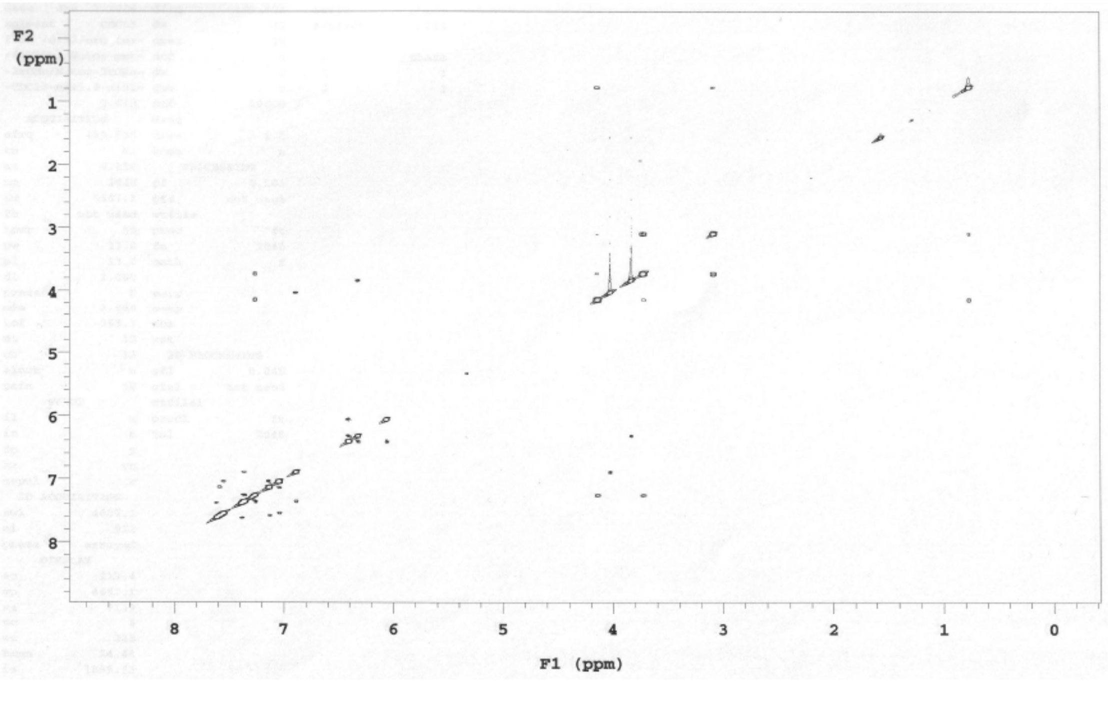
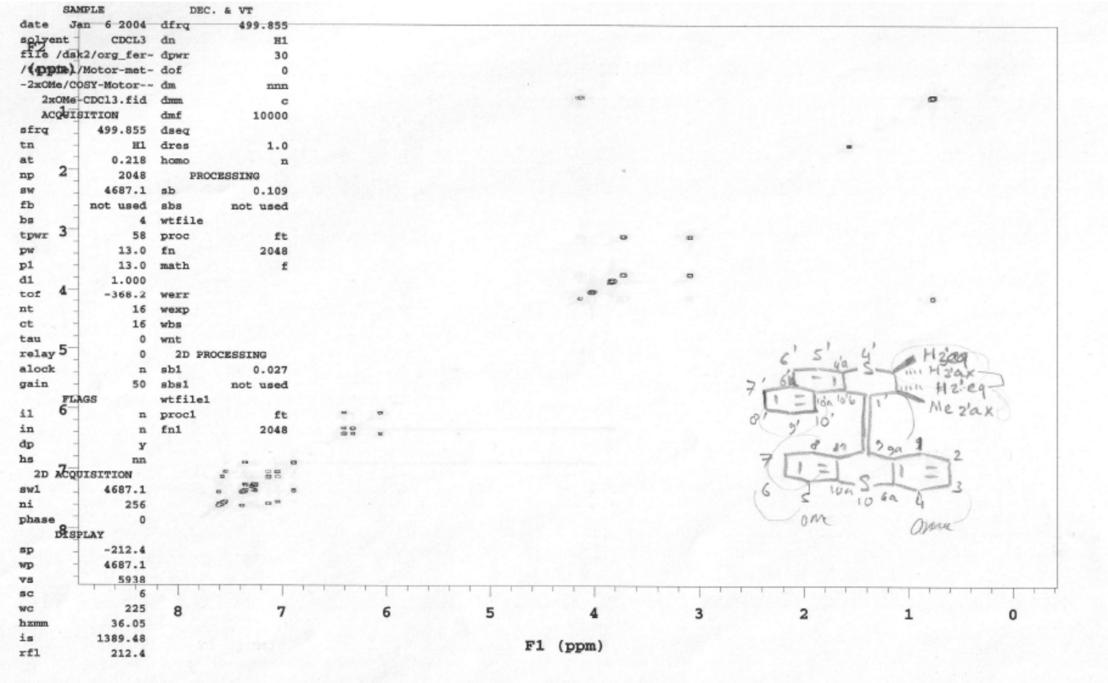


Figure 6. NOESY spectrum of **5** in $CDCl_3$ taken at 500 MHz.



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solvent       CDCL3  dn               H1
file /dsk2/org_fer-  dpwr             30
/(ppm)/Motor-met-    dof               0
-2xOMe/COSY-Motor--  dm              nnn
   2xOMe-CDCl3.fid   dmm               c
   ACQUISITION       dmf           10000
sfrq        499.855  dseq
tn               H1  dres            1.0
at            0.218  homo              n
np             2048      PROCESSING
sw           4687.1  sb            0.109
fb         not used  sbs        not used
bs                4  wtfile
tpwr             58  proc             ft
pw             13.0  fn             2048
p1             13.0  math              f
d1            1.000
tof          -368.2  werr
nt               16  wexp
ct               16  wbs
tau               0  wnt
relay             0    2D PROCESSING
alock             n  sb1           0.027
gain             50  sbs1       not used
     FLAGS           wtfile1
il                n  proc1            ft
in                n  fn1            2048
dp                y
hs               nn
  2D ACQUISITION
sw1          4687.1
ni              256
phase             0
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sp           -212.4
wp           4687.1
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sc                6
wc              225
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is          1389.48
rfl           212.4
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Figure 7. GCOSY spectrum of **5** in $CDCl_3$ taken at 500 MHz.

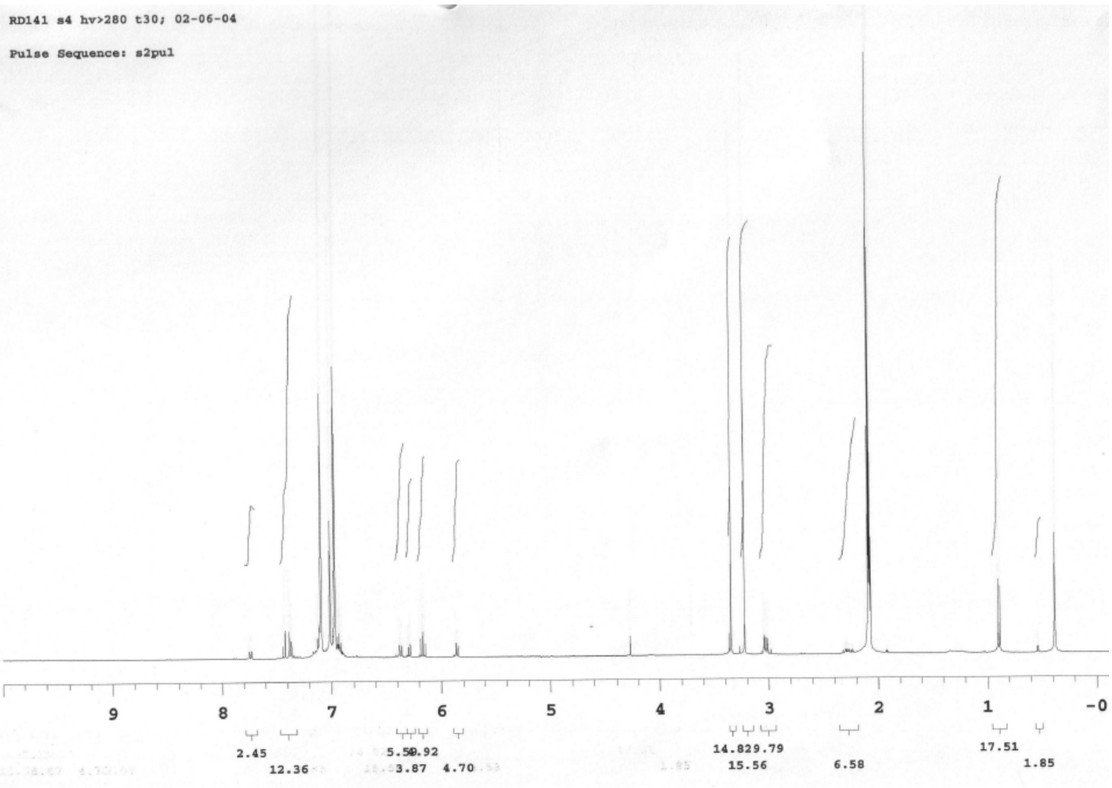


Figure 8. 400 MHz ^{1}H NMR spectrum of the $PSS_{>280nm}$ of **5**, containing predominantly unstable-**5** in Toluene-D_8.

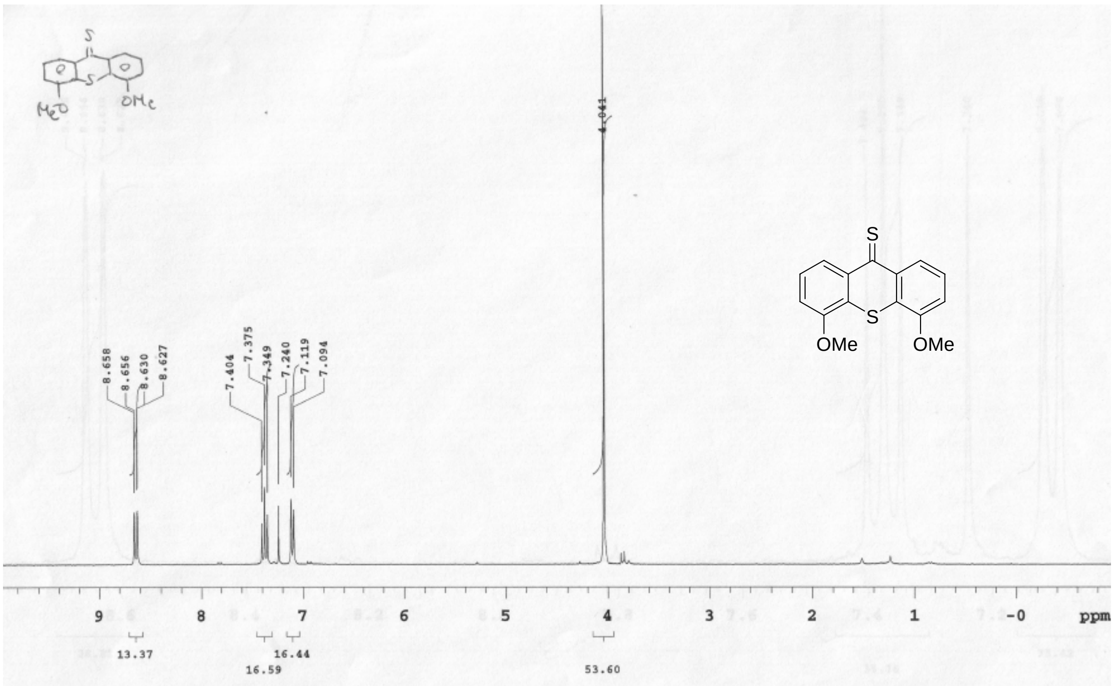


Figure 9. 300 MHz ^{1}H NMR spectrum of **7** in $CDCl_3$.

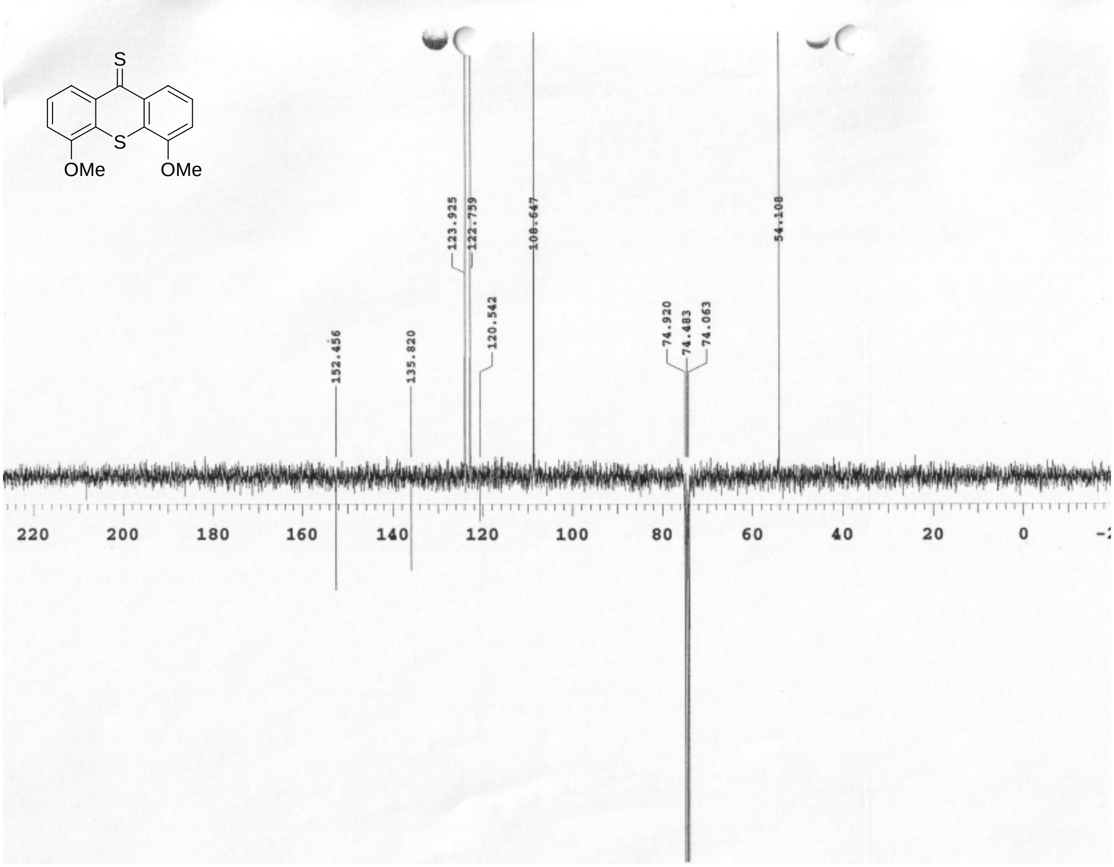


Figure 10. 50 MHz ^{13}C NMR spectrum of **7** in $CDCl_3$.

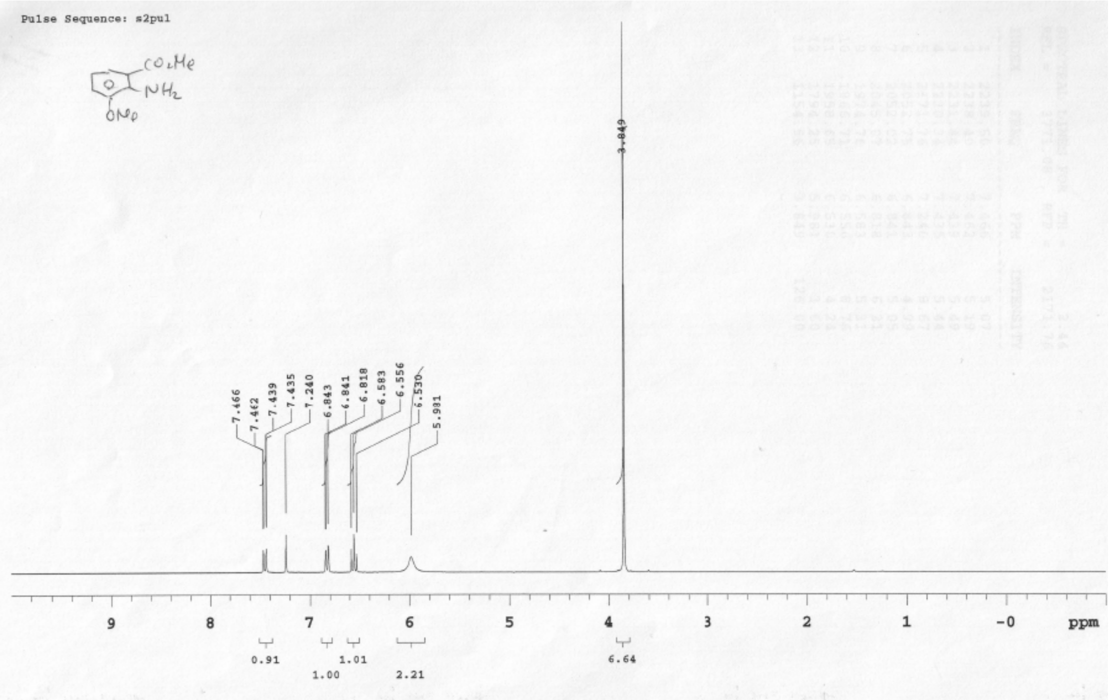


Figure 11. 300 MHz ^{1}H NMR spectrum of **9** in CDCl$_3$.

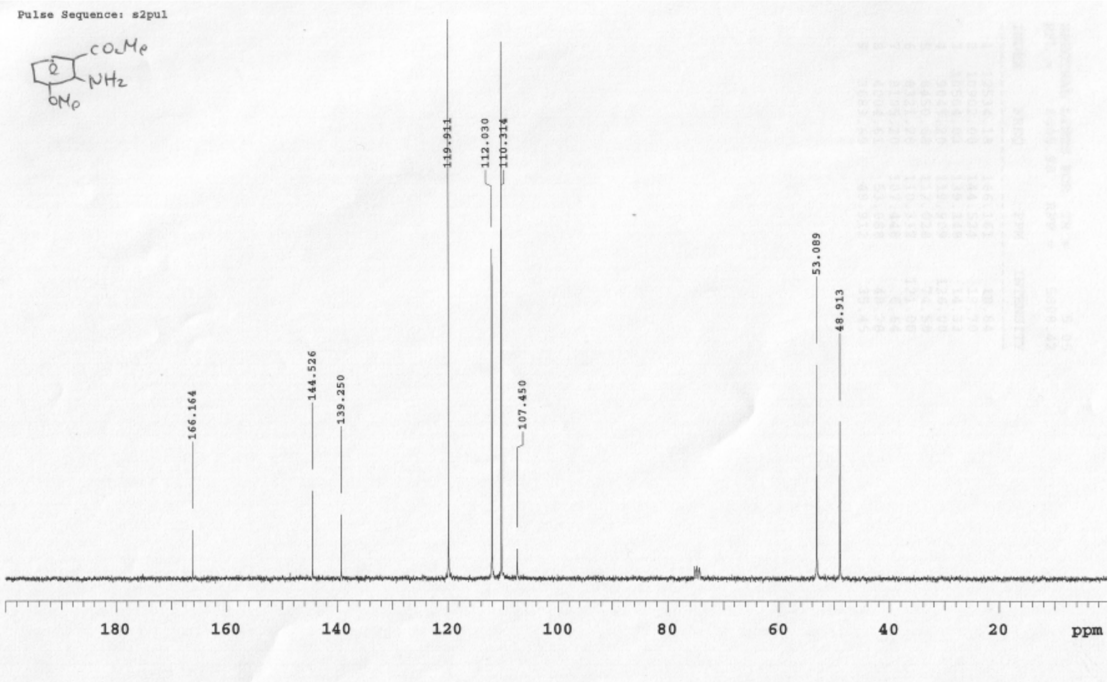


Figure 12. 50 MHz ^{13}C NMR spectrum of **9** in CDCl$_3$.

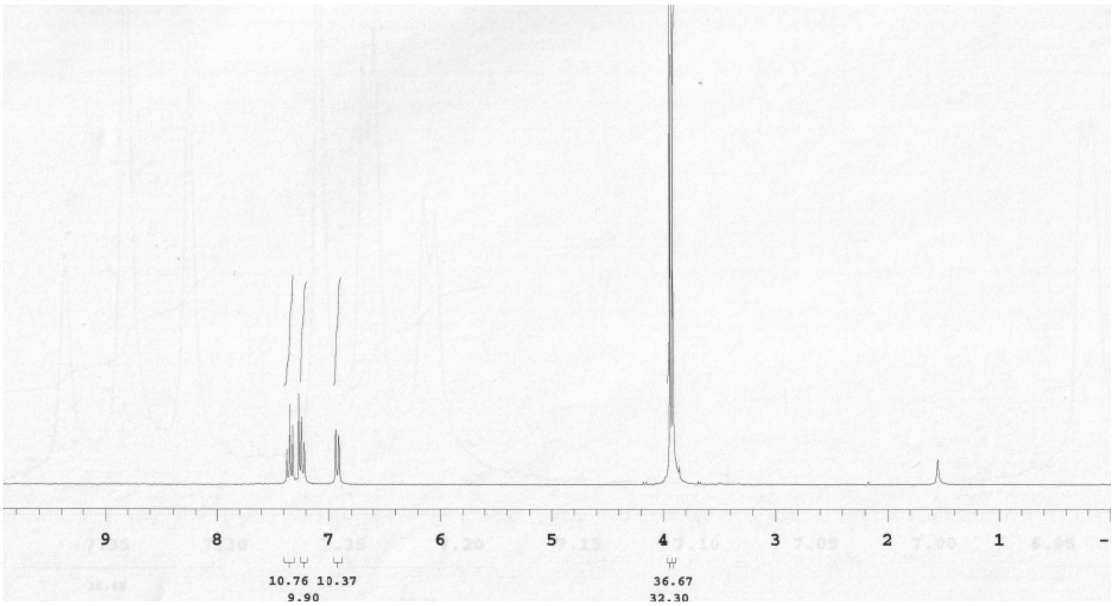


Figure 13. 300 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$.

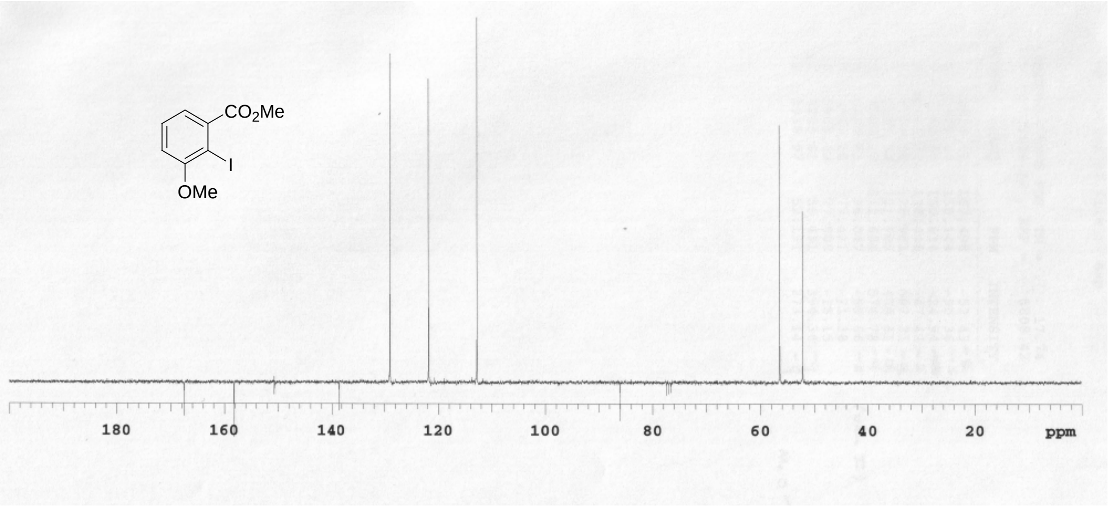


Figure 14. 75 MHz ^{1}H NMR spectrum of **10** in $CDCl_3$.

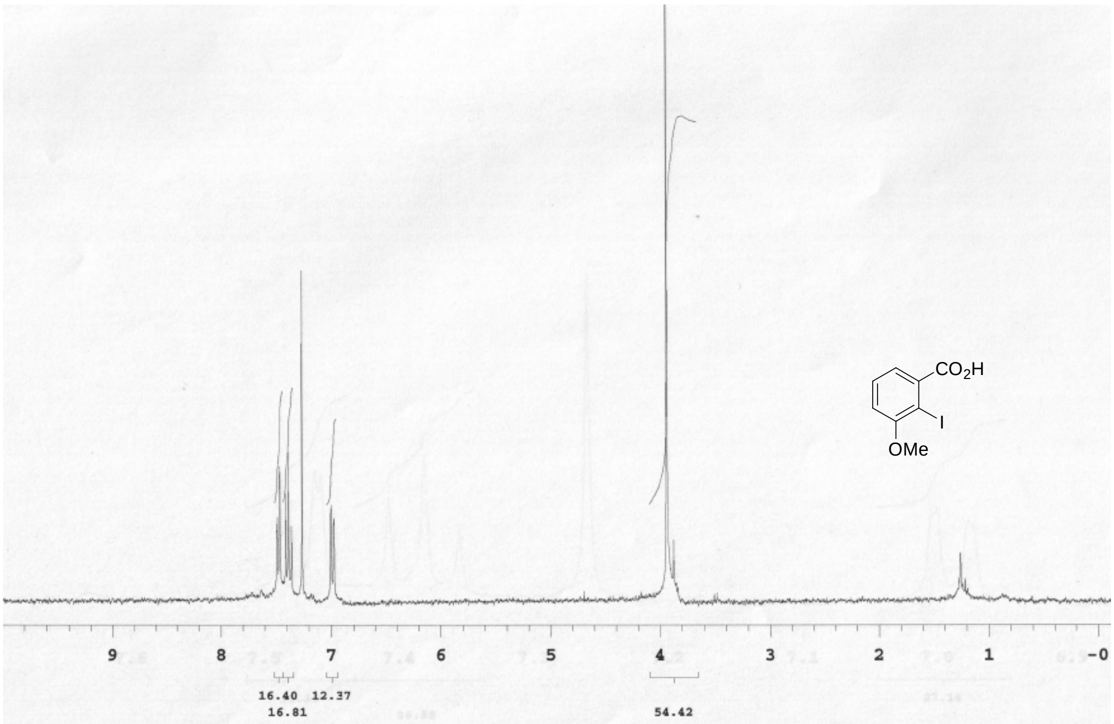


Figure 15. 300 MHz ^{1}H NMR spectrum of **11** in $CDCl_3$.

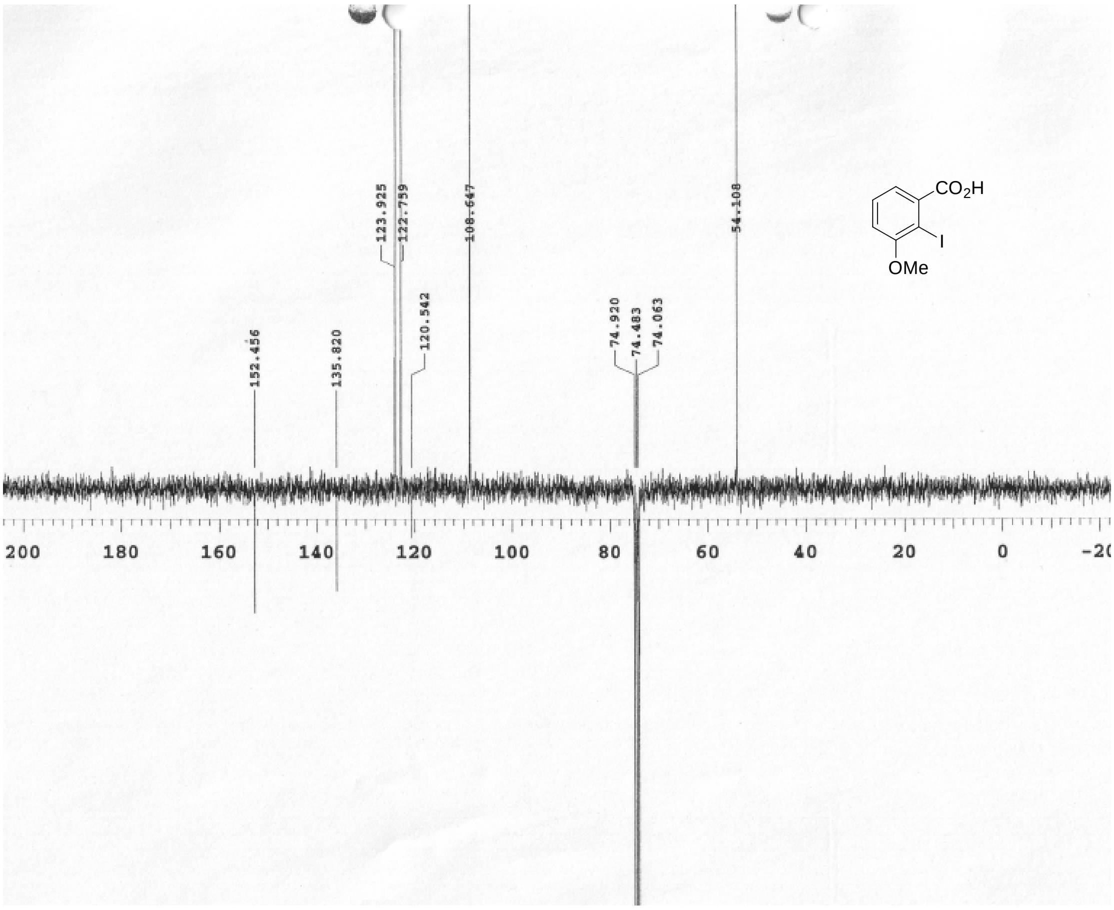


Figure 16. 75 MHz ^{13}C NMR spectrum of **11** in $CDCl_3$.

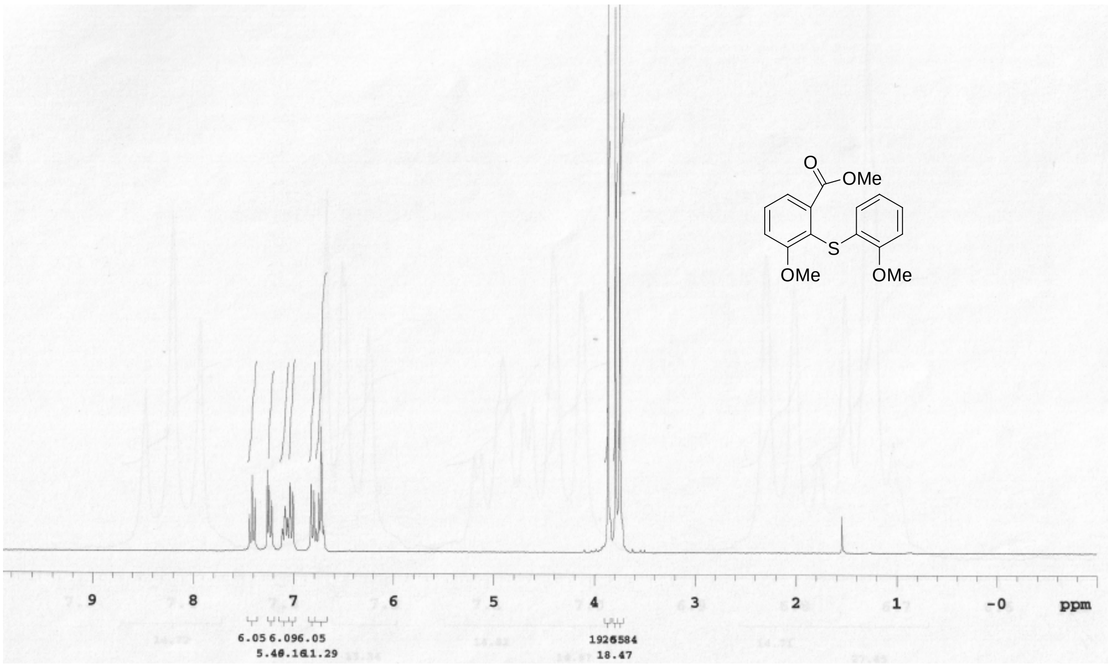


Figure 17. 300 MHz ^{1}H NMR spectrum of **13** in $CDCl_3$.

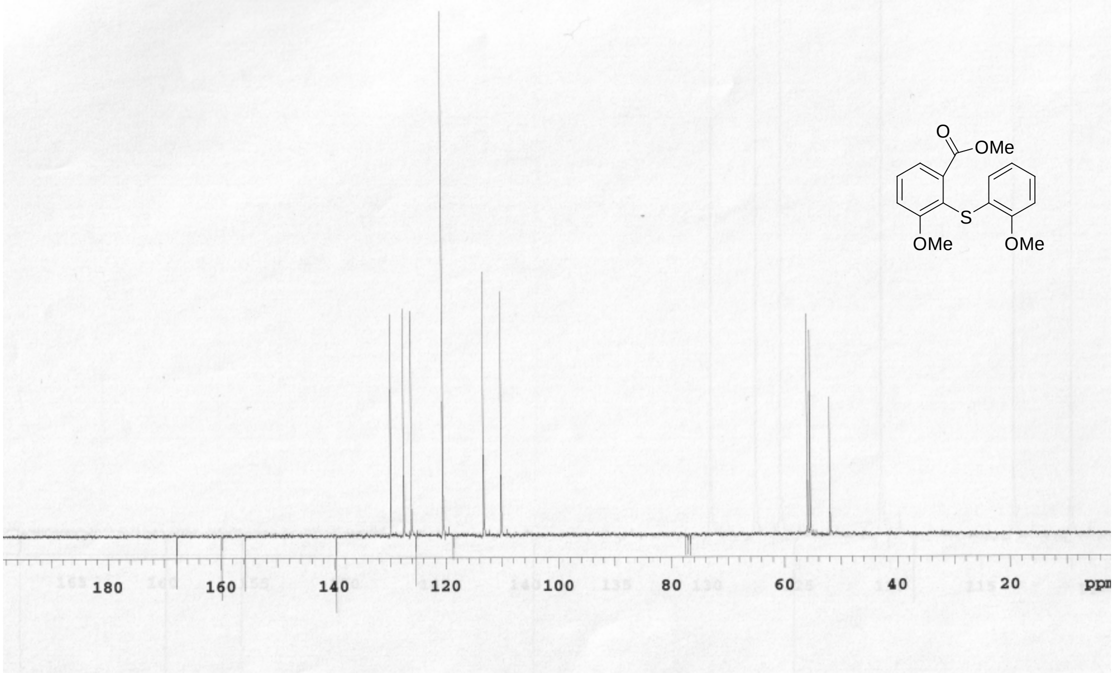


Figure 18. 75 MHz ^{13}C NMR spectrum of **13** in $CDCl_3$.

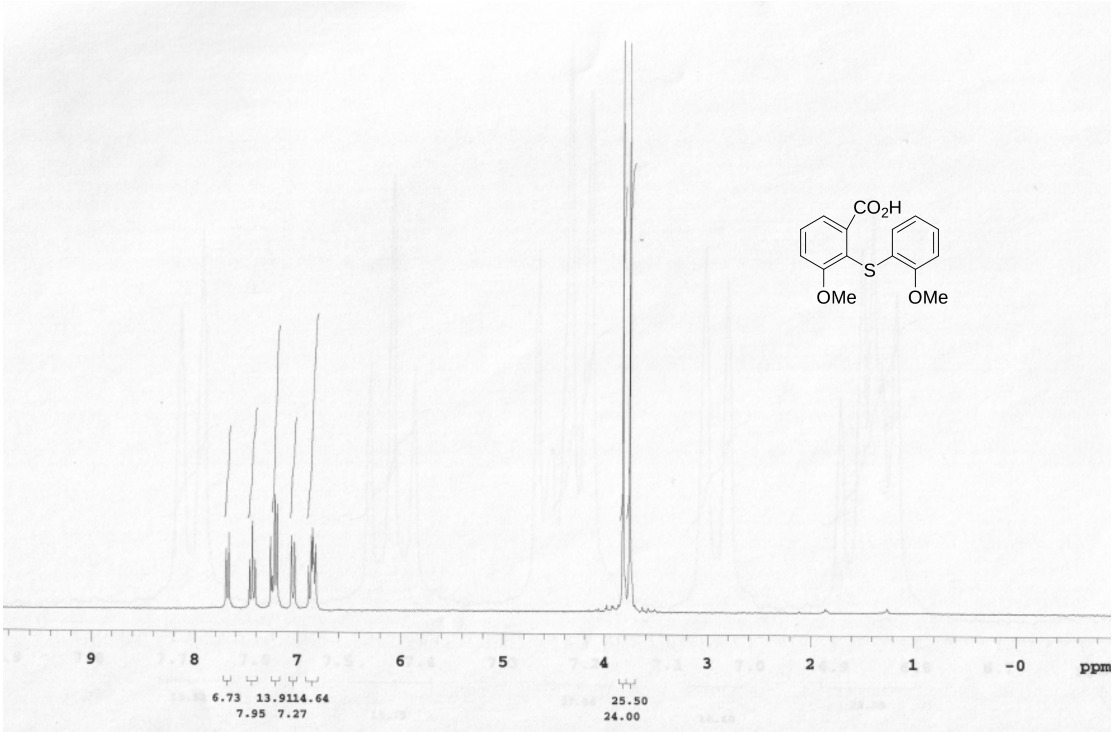


Figure 19. 300 MHz ^{1}H NMR spectrum of **14** in CDCl$_3$.

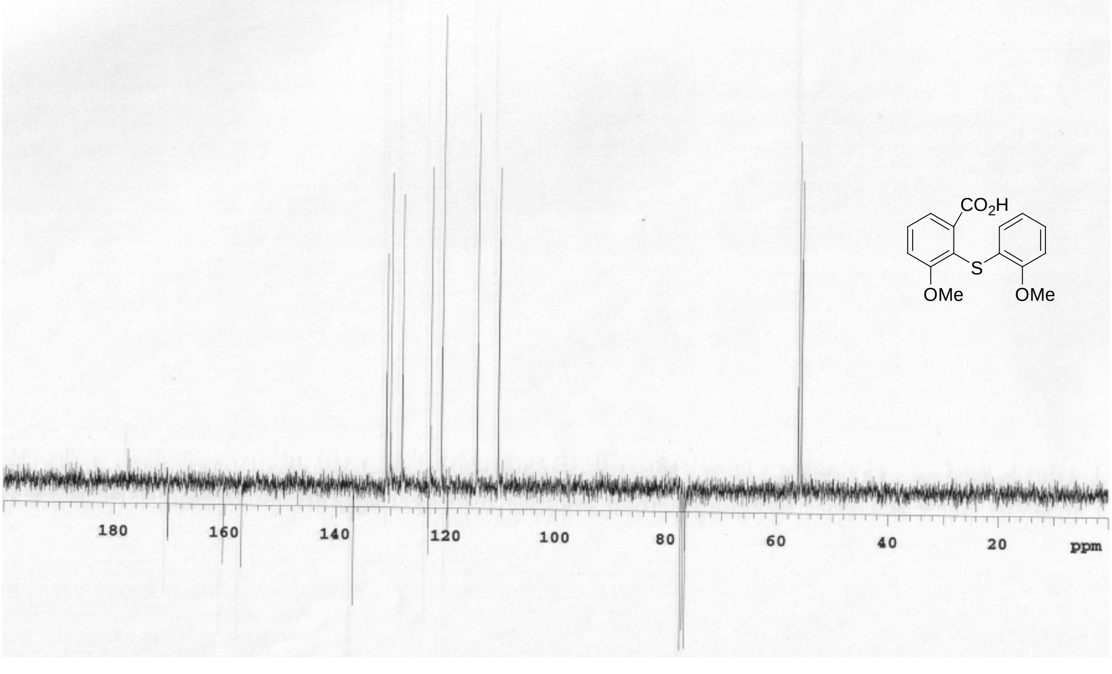


Figure 20. 75 MHz ^{13}C NMR spectrum of **14** in CDCl$_3$.

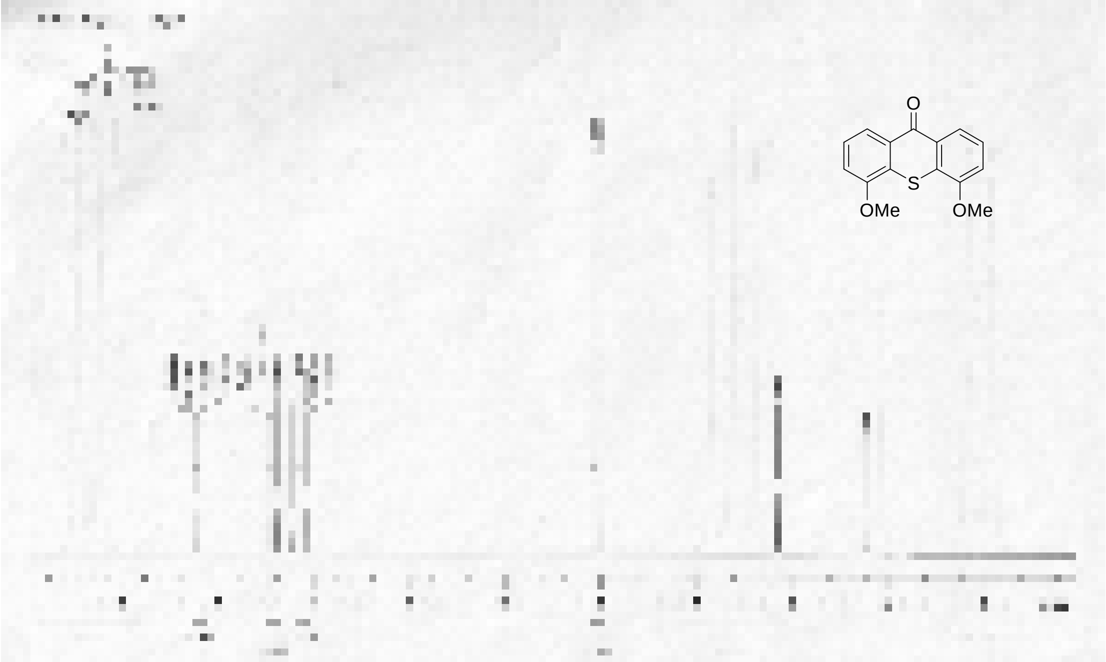


Figure 21. 300 MHz ^{1}H NMR spectrum of **15** in $CDCl_3$.

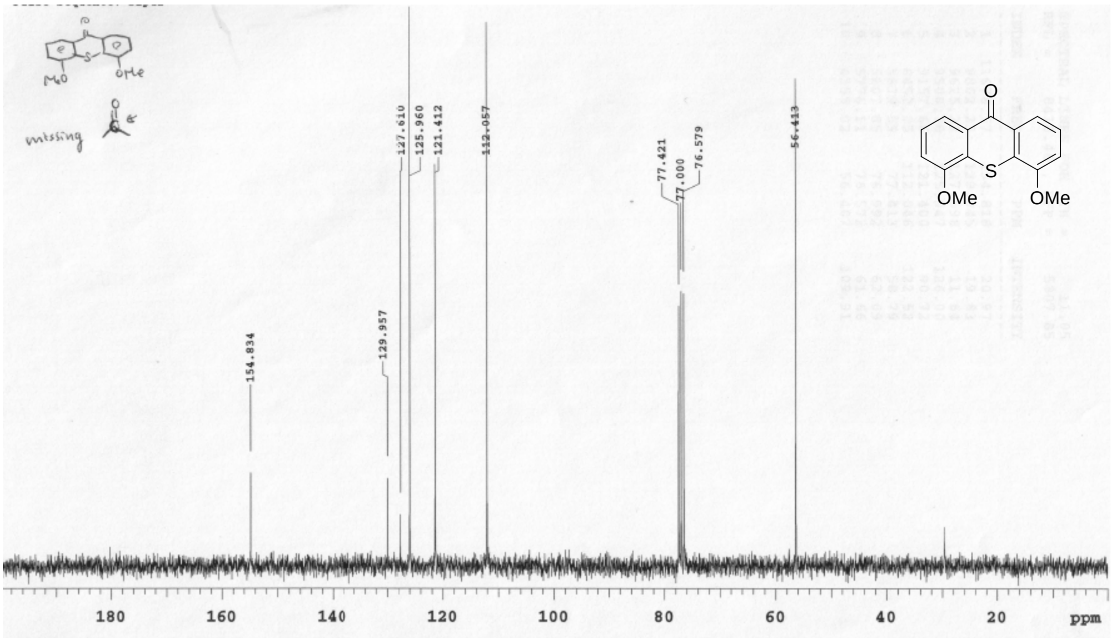


Figure 22. 75 MHz ^{13}C NMR spectrum of **15** in $CDCl_3$.

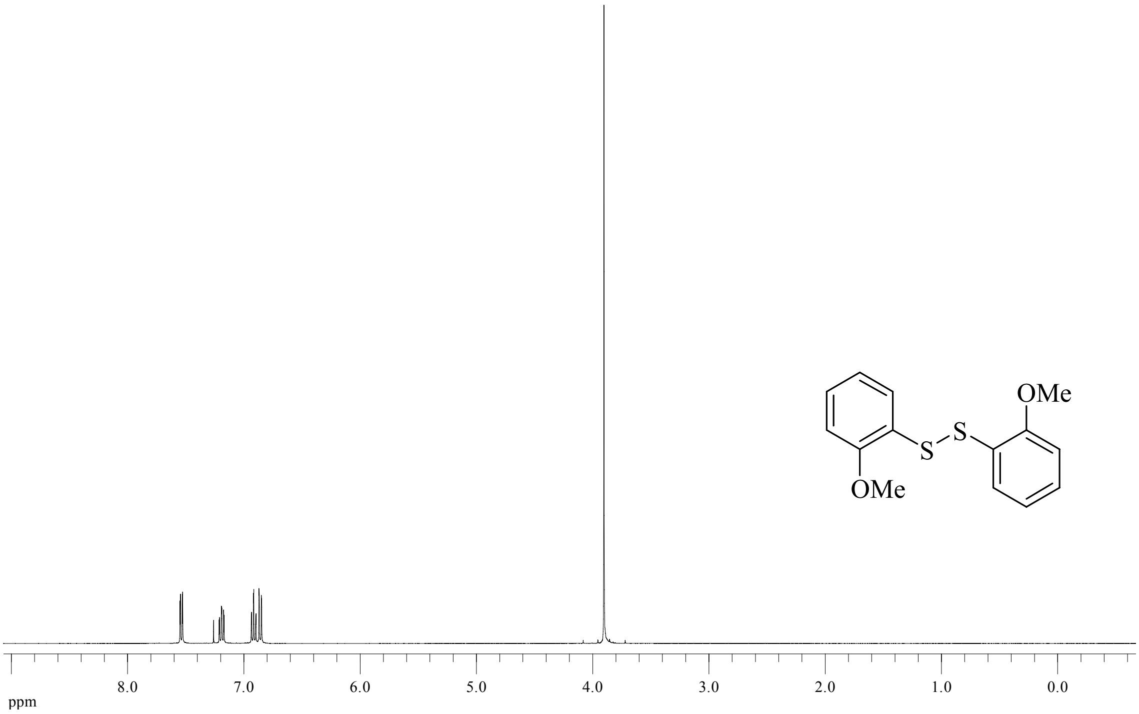


Figure 23. 400 MHz ^{1}H NMR spectrum of **16** in CDCl$_3$.

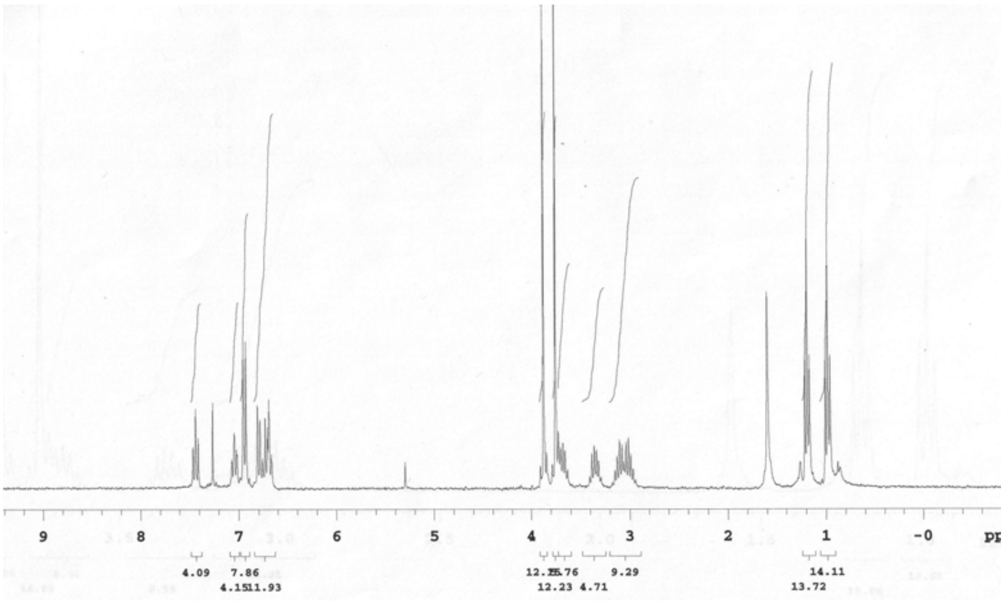


Figure 24. 300 MHz ^{1}H NMR spectrum of **20** in CDCl$_3$.

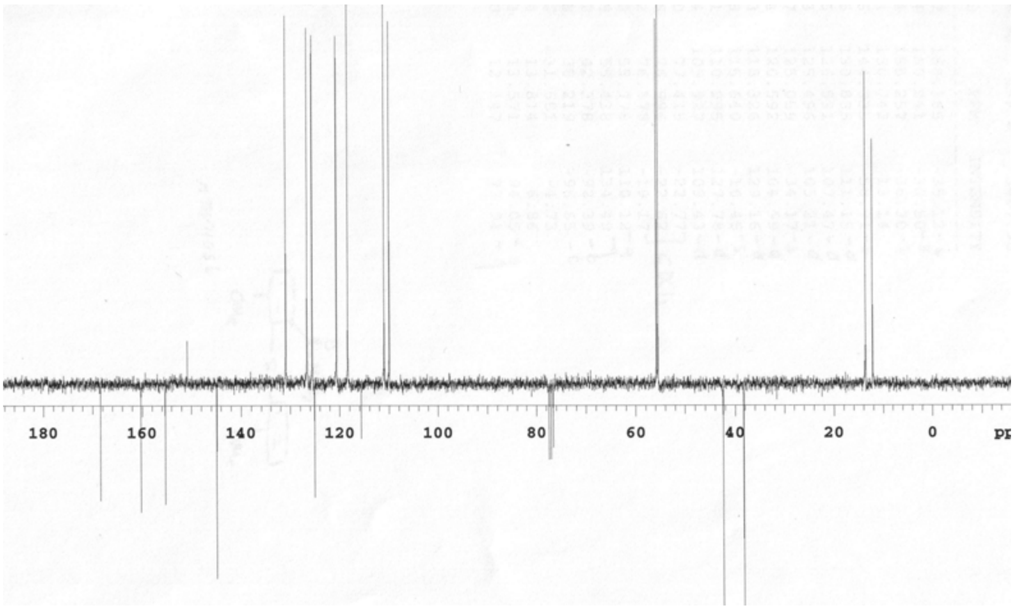


Figure 25. 100 MHz ^{13}C NMR spectrum of **20** in $CDCl_3$.

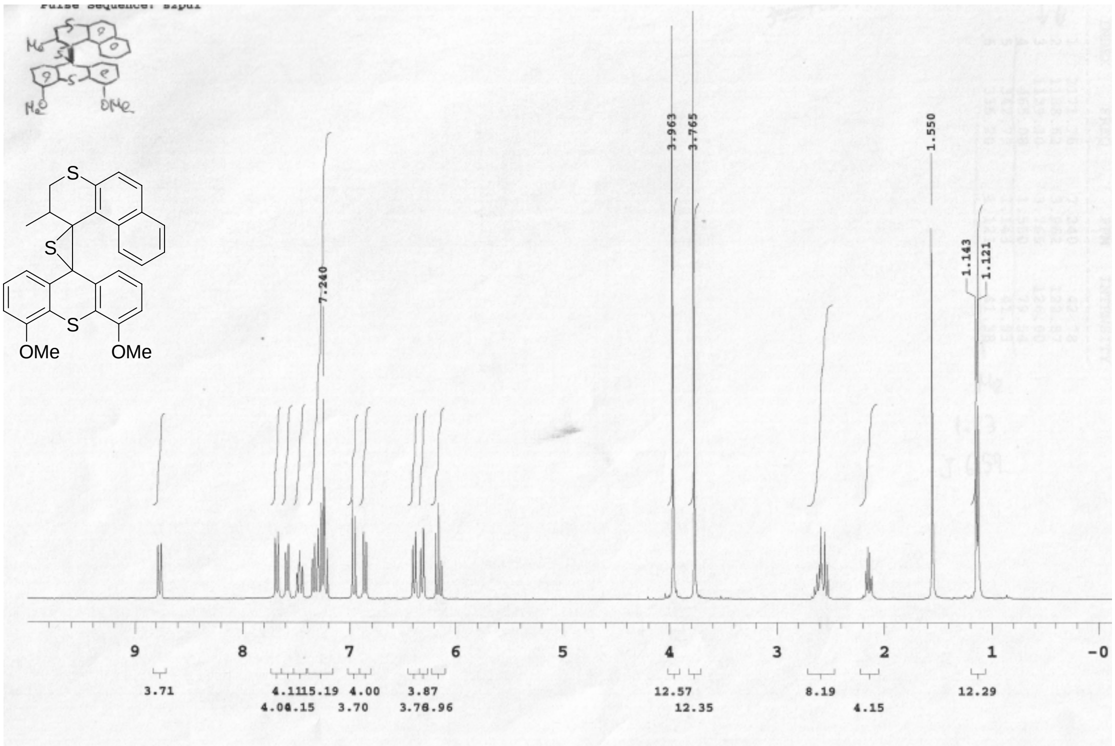


Figure 26. 300 MHz ^1H NMR spectrum of **22** in $CDCl_3$.

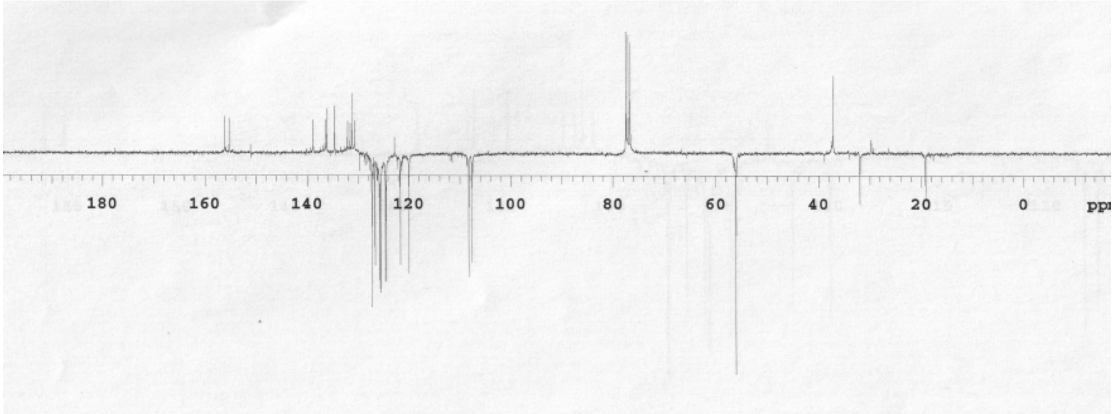


Figure 27. 50 MHz ^{13}C NMR spectrum of **22** in $CDCl_3$.

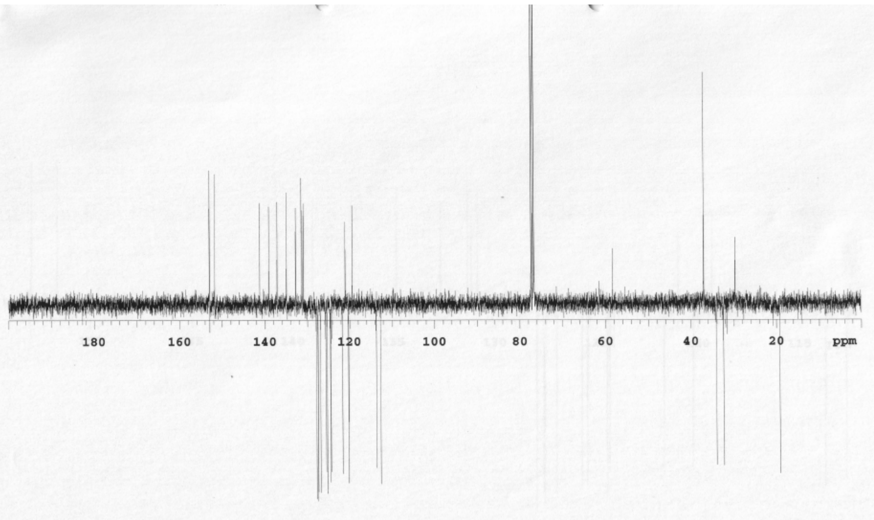


Figure 28. 100 MHz ^{13}C NMR spectrum of **22** in $CDCl_3$.

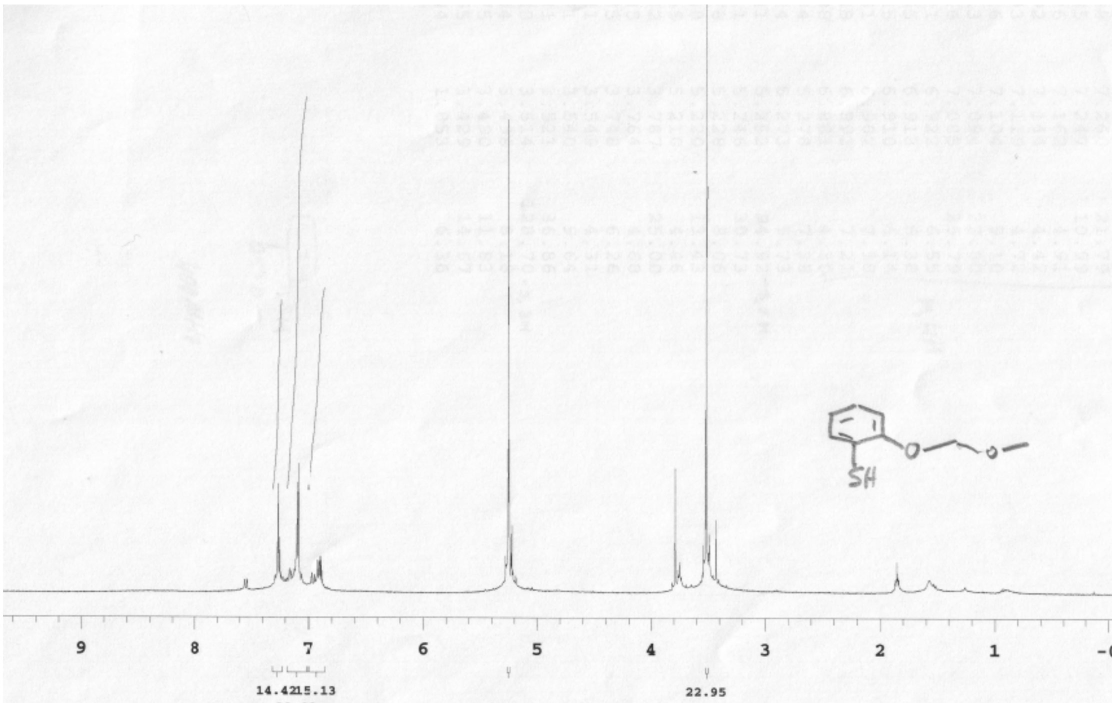


Figure 29. 400 MHz ^{1}H NMR spectrum of **24** in $CDCl_3$.

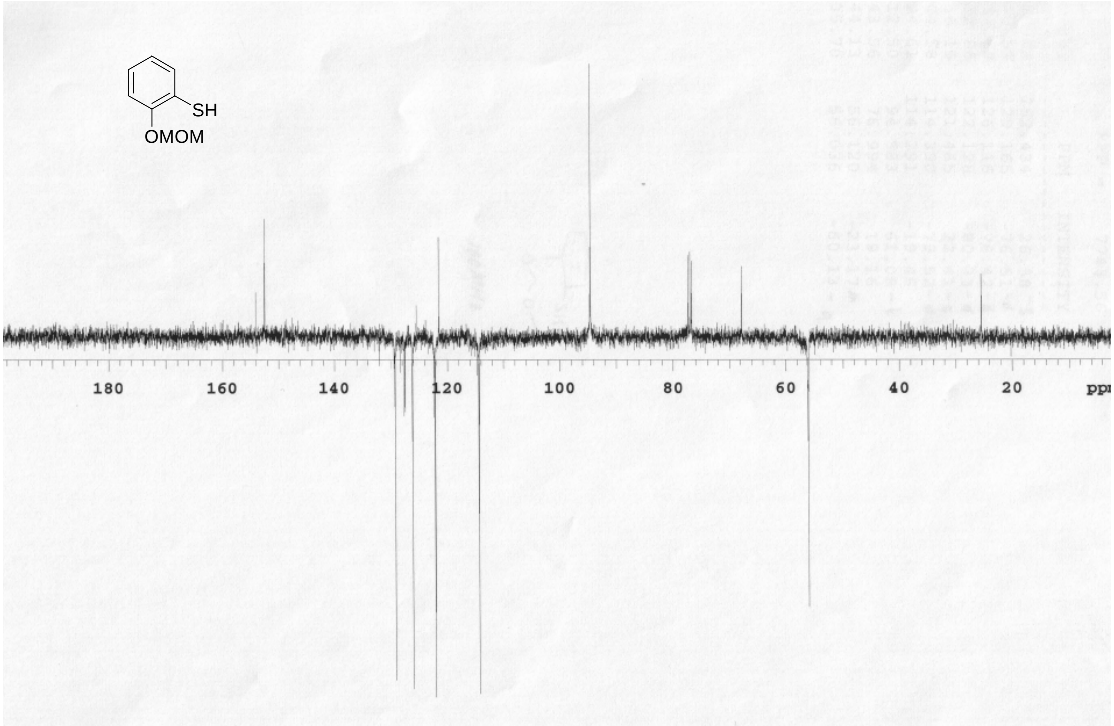


Figure 30. 50 MHz ^{13}C NMR spectrum of **24** in $CDCl_3$.

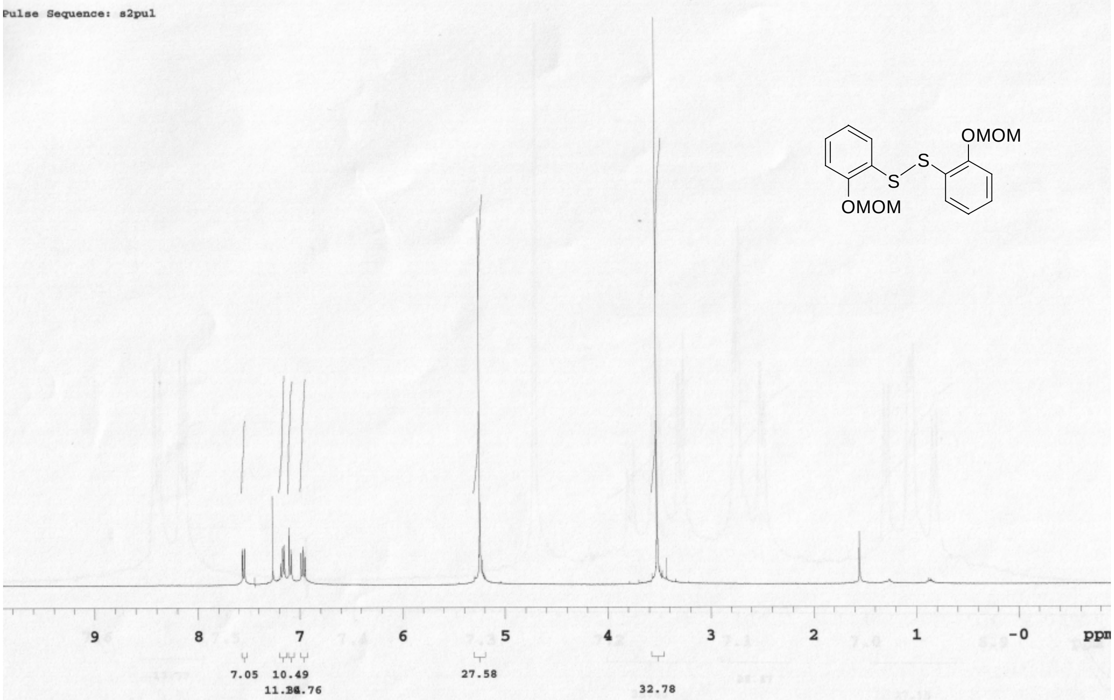


Figure 31. 400 MHz ^{1}H NMR spectrum of **25** in $CDCl_3$.

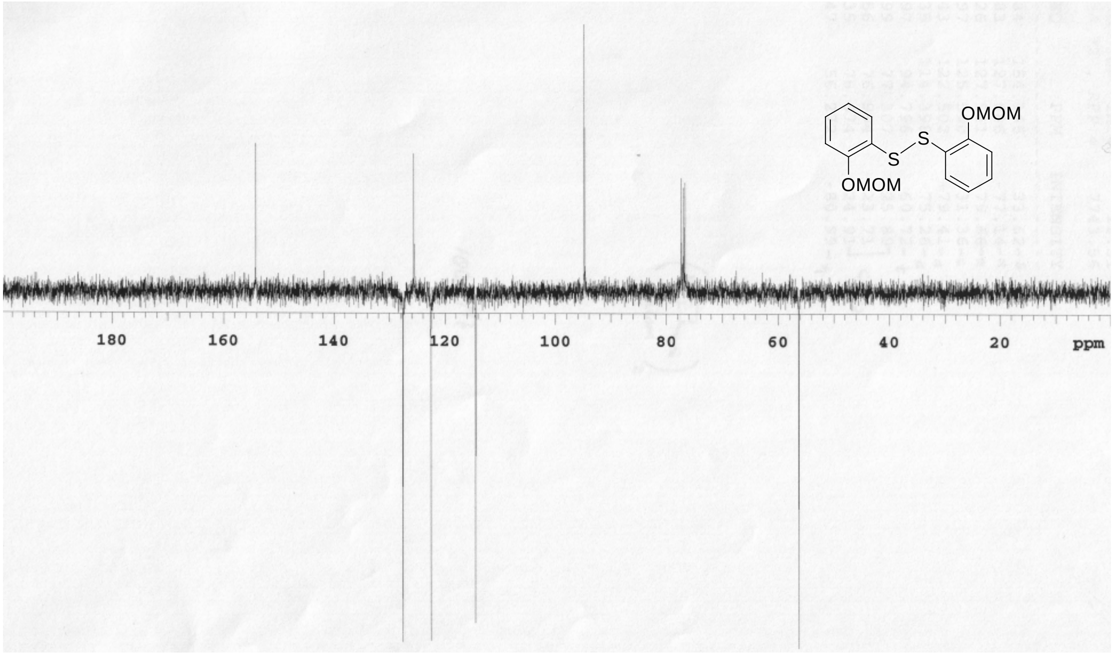


Figure 32. 50 MHz ^{13}C NMR spectrum of **25** in $CDCl_3$.

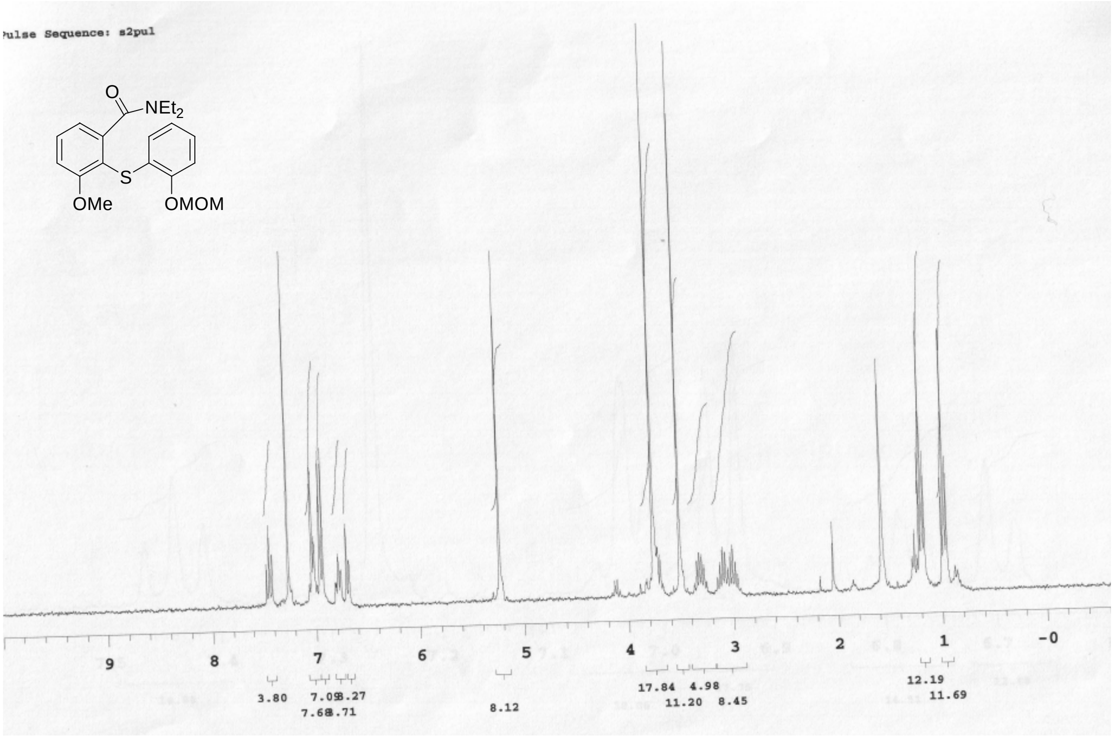


Figure 33. 300 MHz ^{1}H NMR spectrum of **26** in $CDCl_3$.

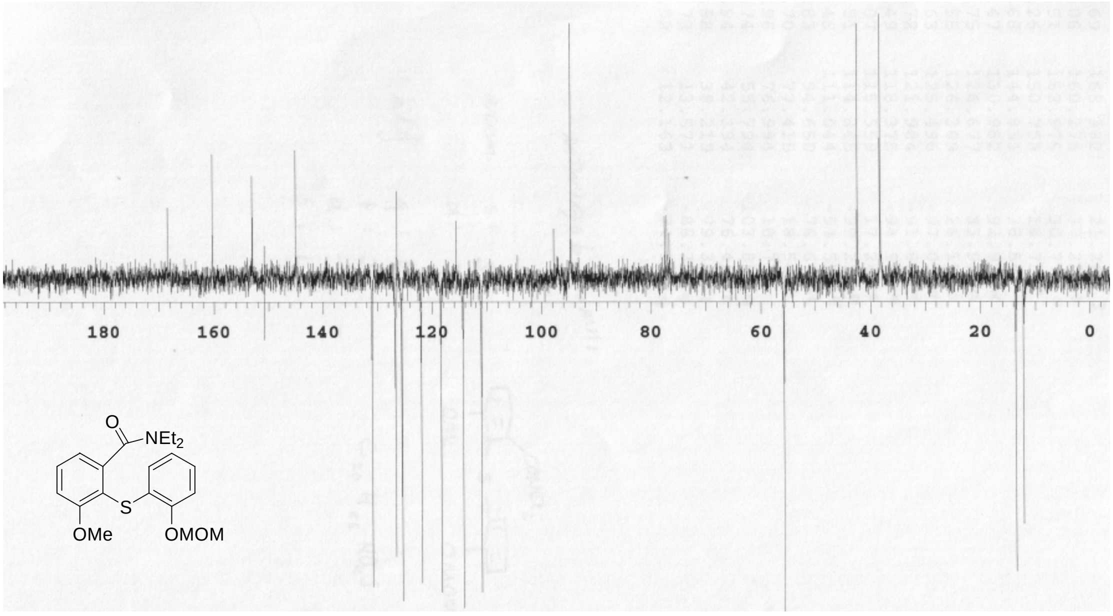


Figure 34. 50 MHz ^{13}C NMR spectrum of **26** in CDCl$_3$.

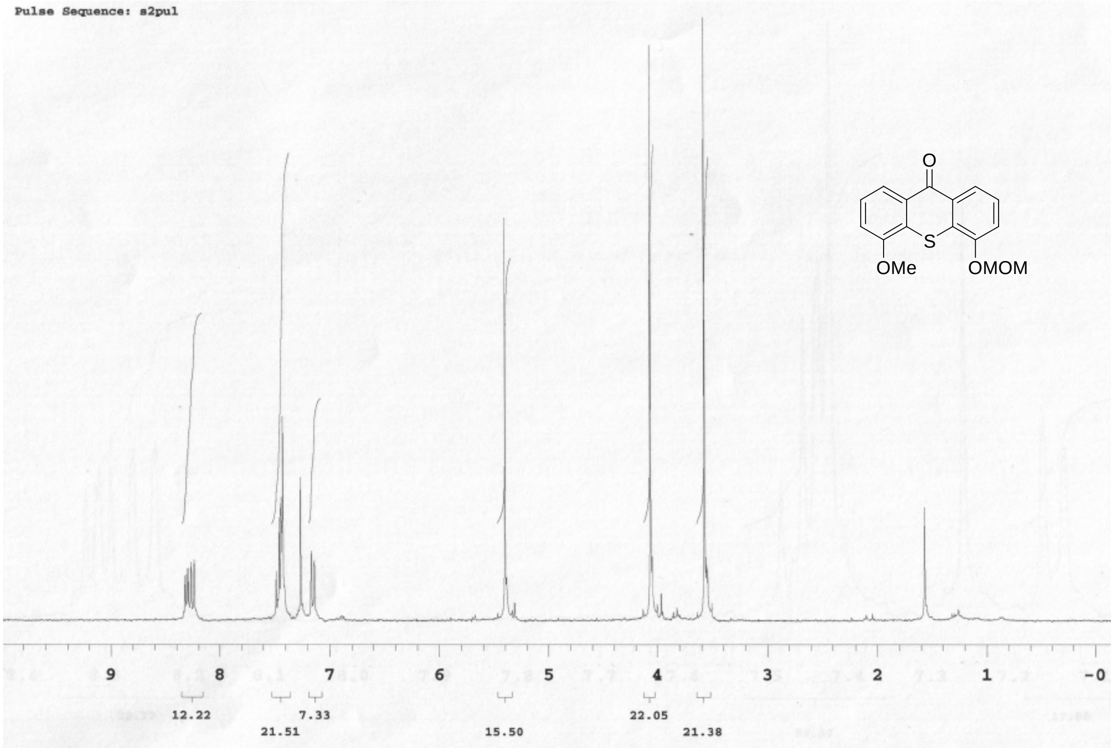


Figure 35. 300 MHz ^{1}H NMR spectrum of **27** in CDCl$_3$.

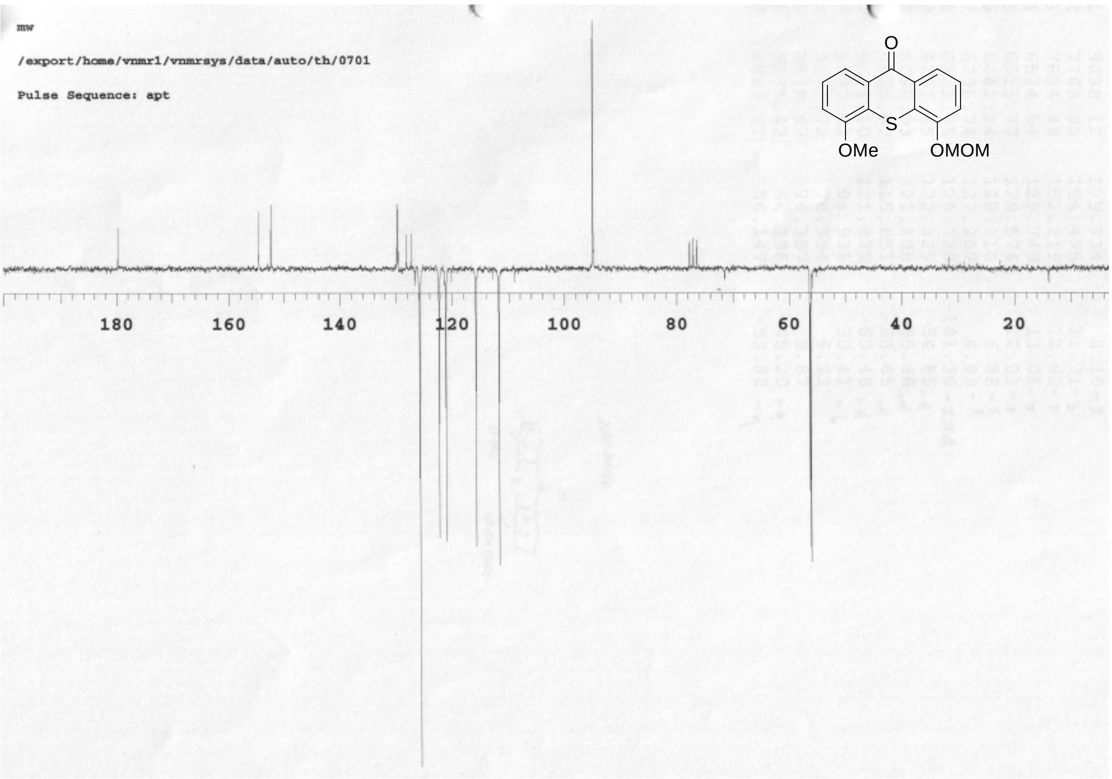


Figure 36. 50 MHz ^{13}C NMR spectrum of **27** in CDCl$_3$.

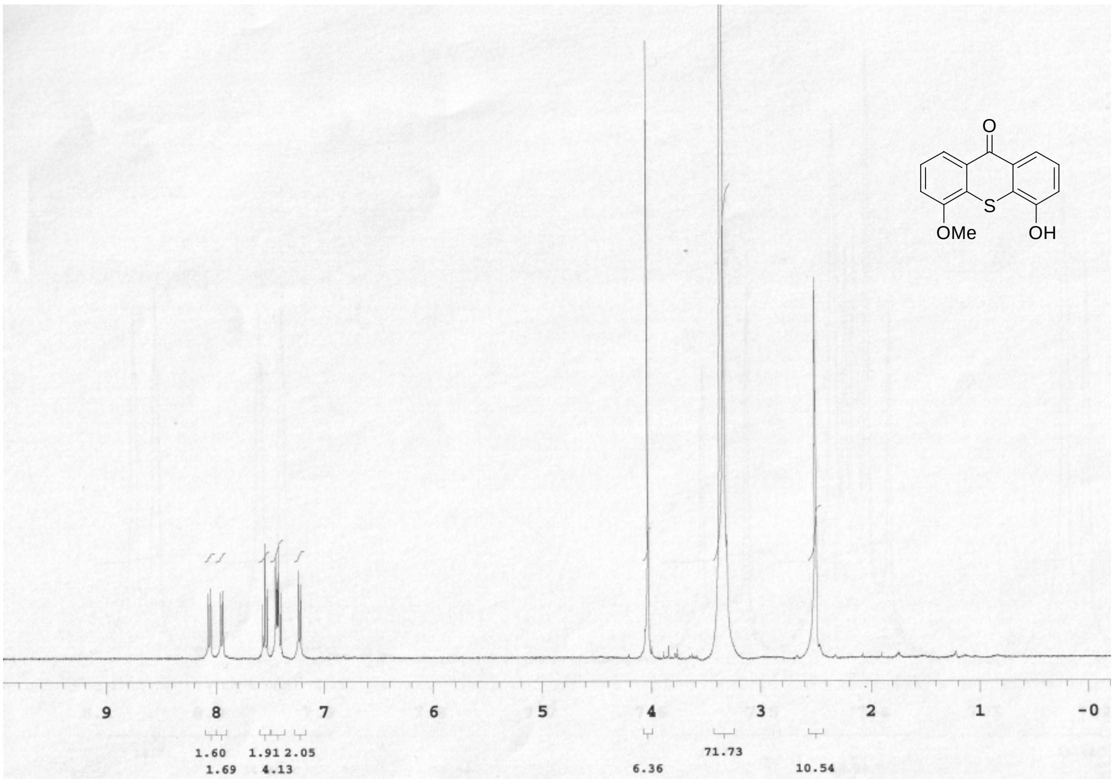


Figure 37. 200 MHz ^{1}H NMR spectrum of **28** in DMSO-d$_6$.

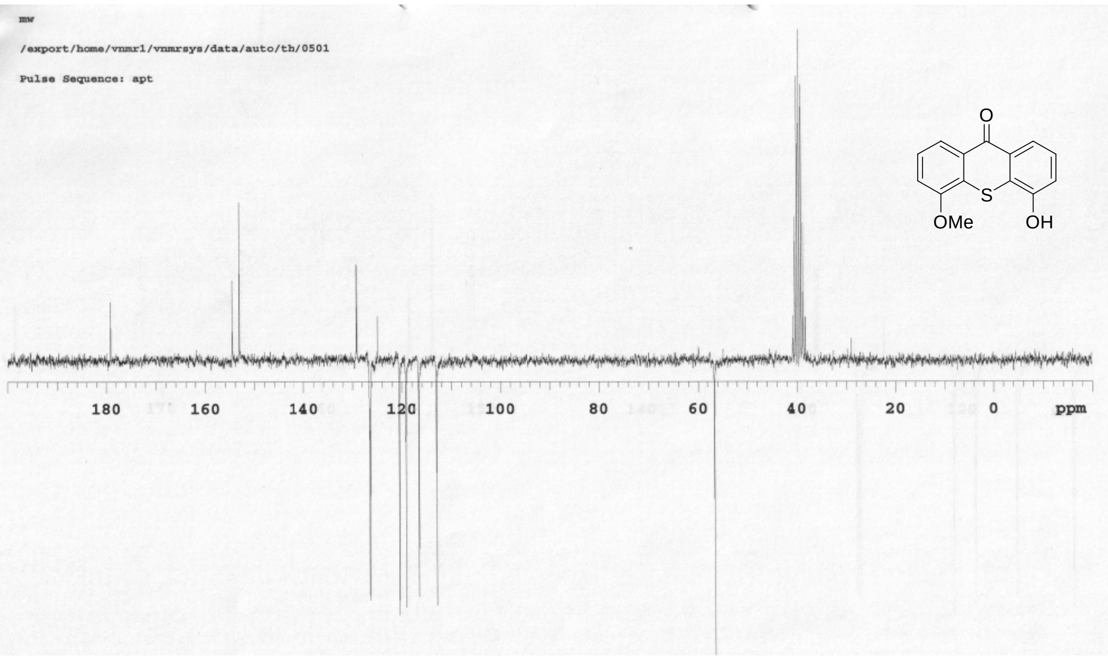


Figure 38. 50 MHz APT spectrum of **28** in DMSO-d_6 .

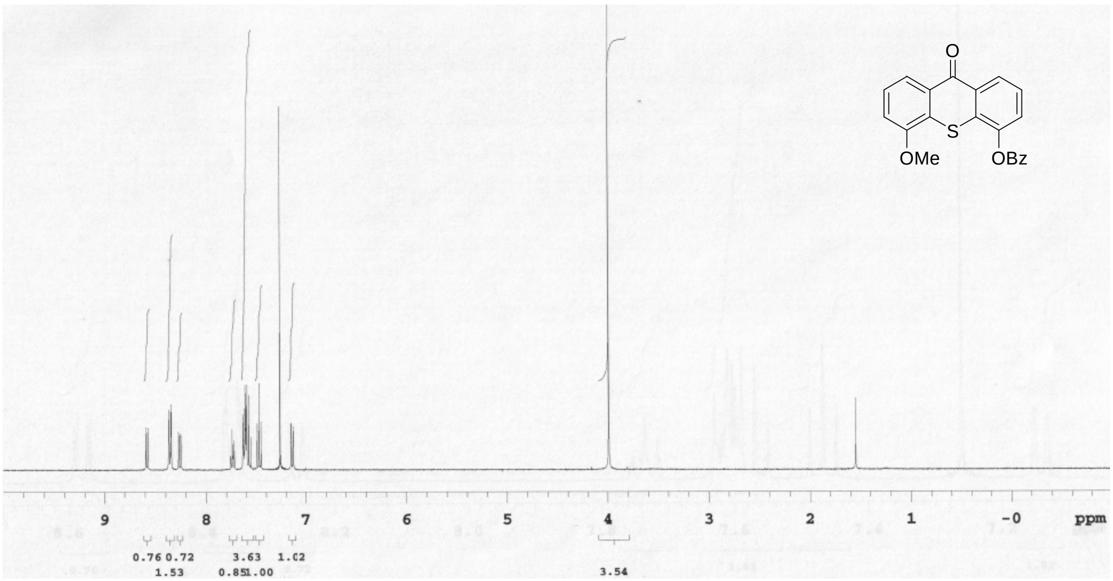


Figure 39. 400 MHz ^{1}H NMR spectrum of **29** in $CDCl_3$.

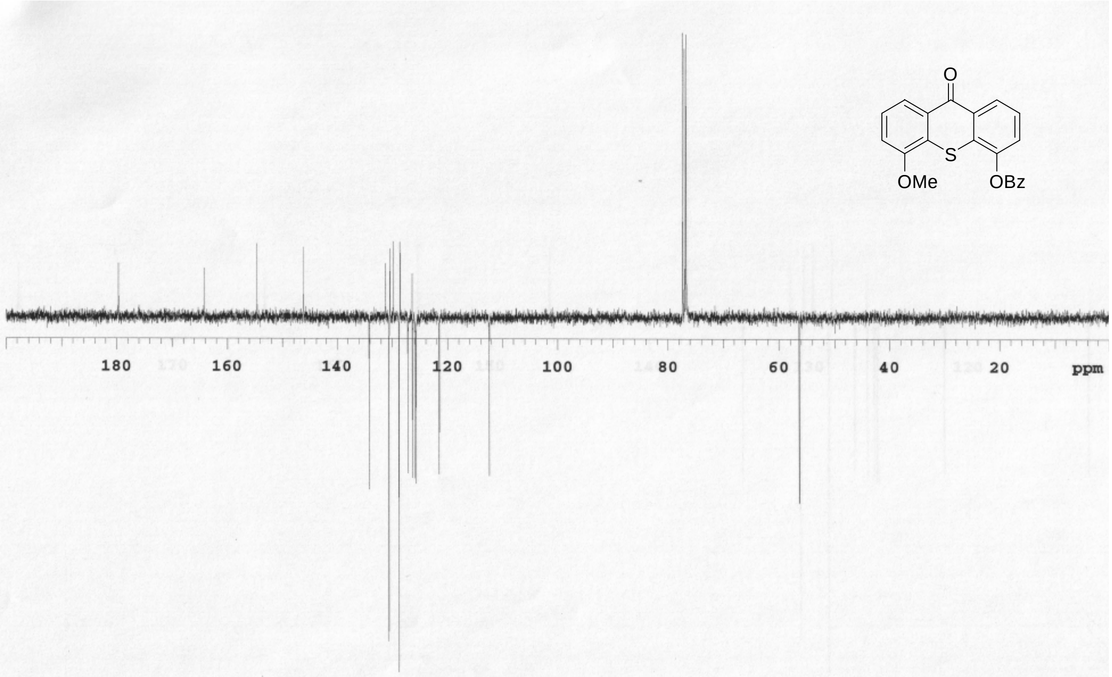


Figure 40. 100 MHz ^{13}C NMR spectrum of **29** in $CDCl_3$.

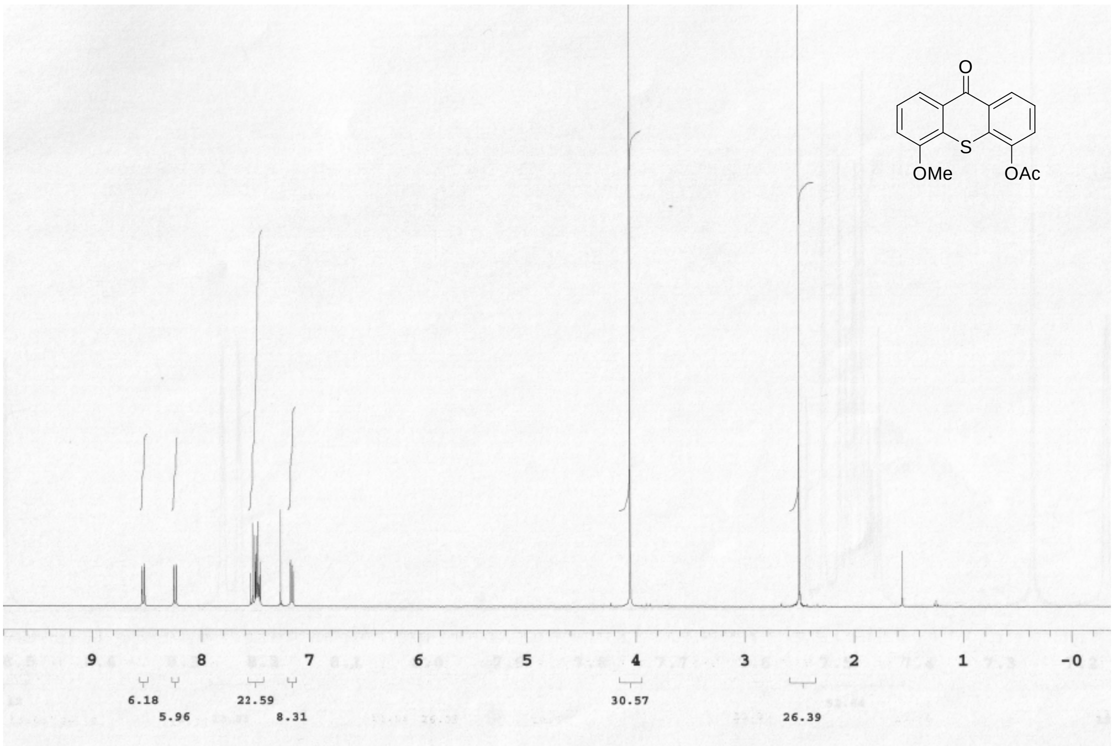


Figure 41. 400 MHz ^{1}H NMR spectrum of **30** in $CDCl_3$.

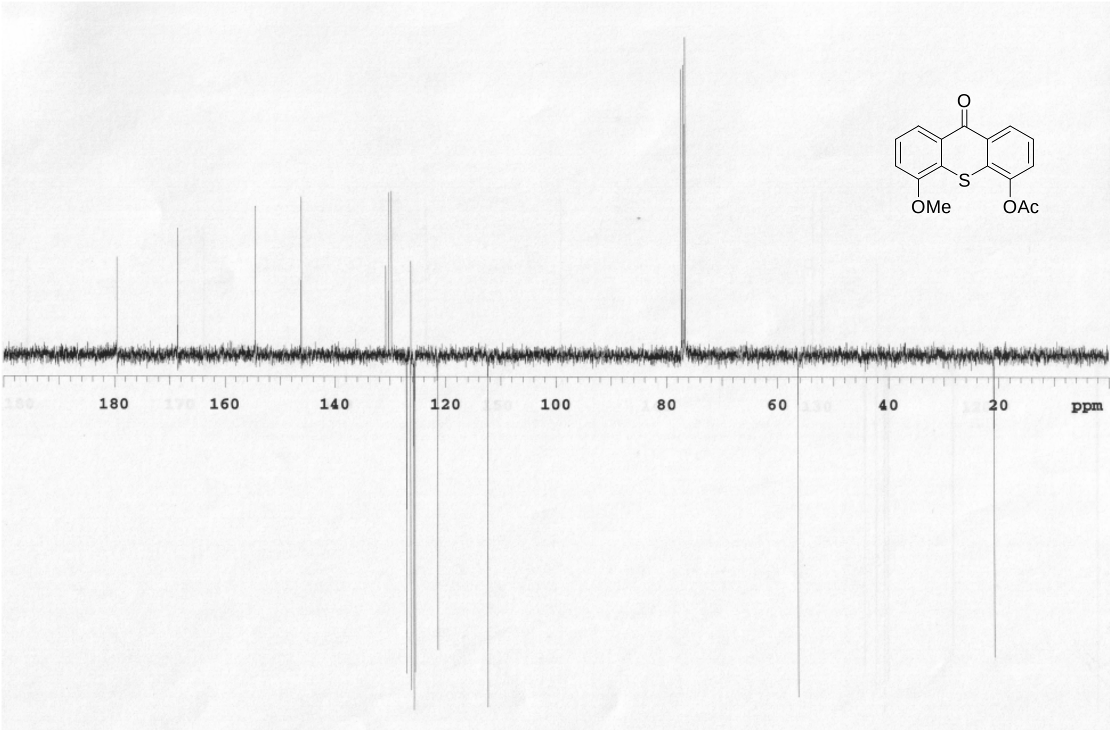


Figure 42. 100 MHz ^{13}C NMR spectrum of **30** in CDCl$_3$.

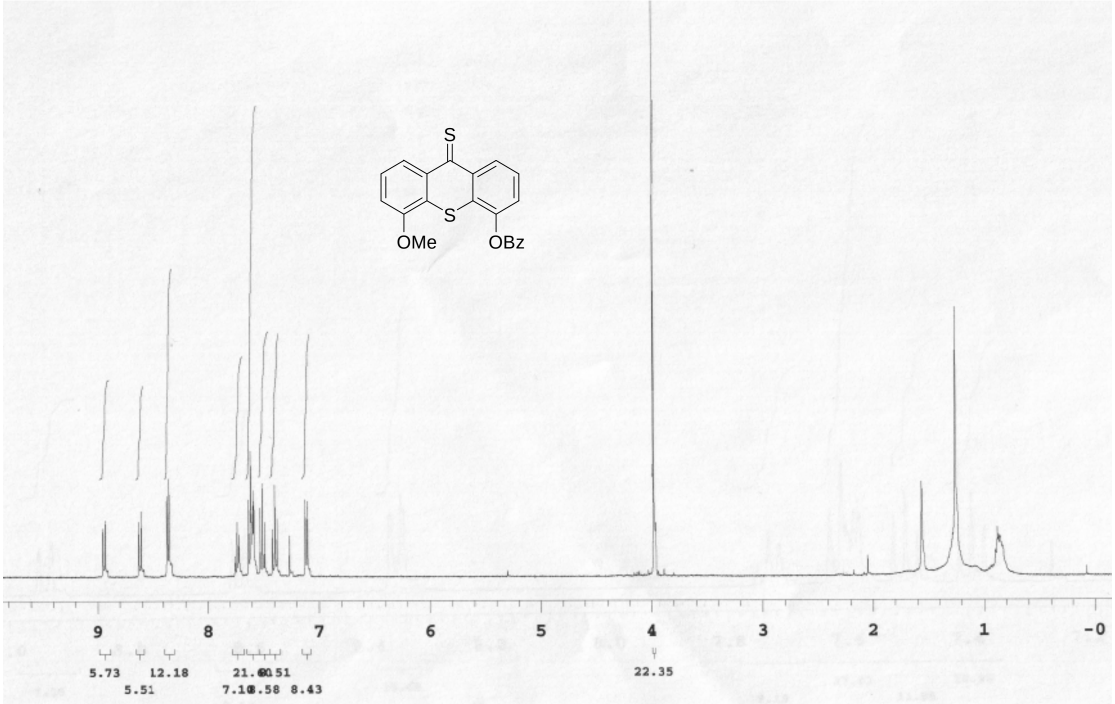


Figure 43. 400 MHz ^{1}H NMR spectrum of **31** in CDCl$_3$.

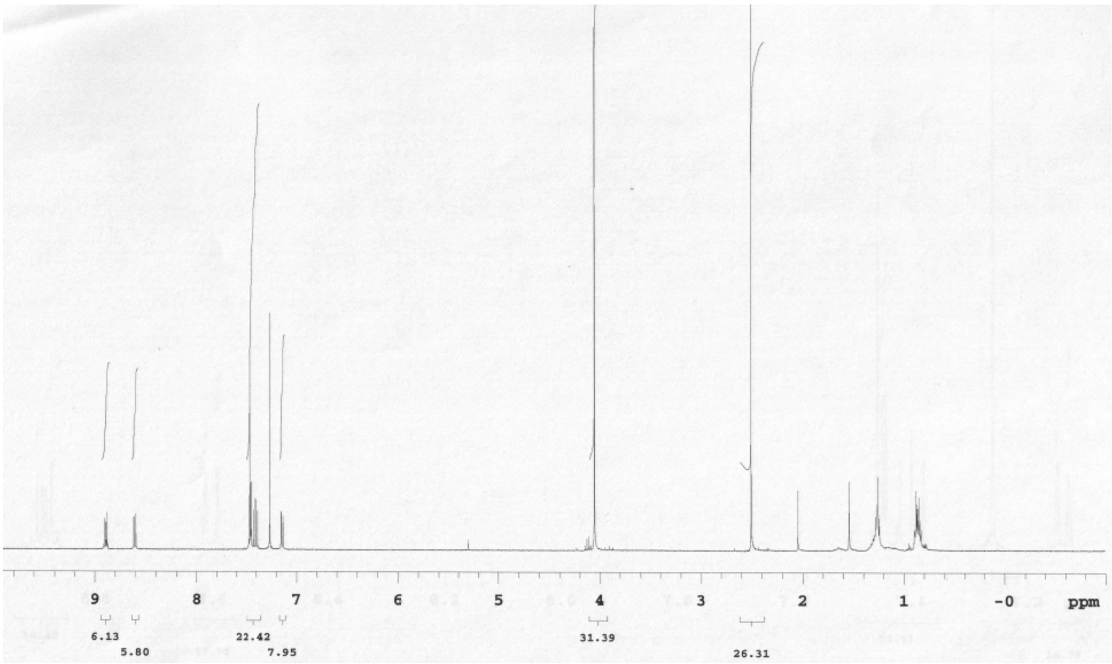


Figure 44. 400 MHz ^{1}H NMR spectrum of **32** in $CDCl_3$.

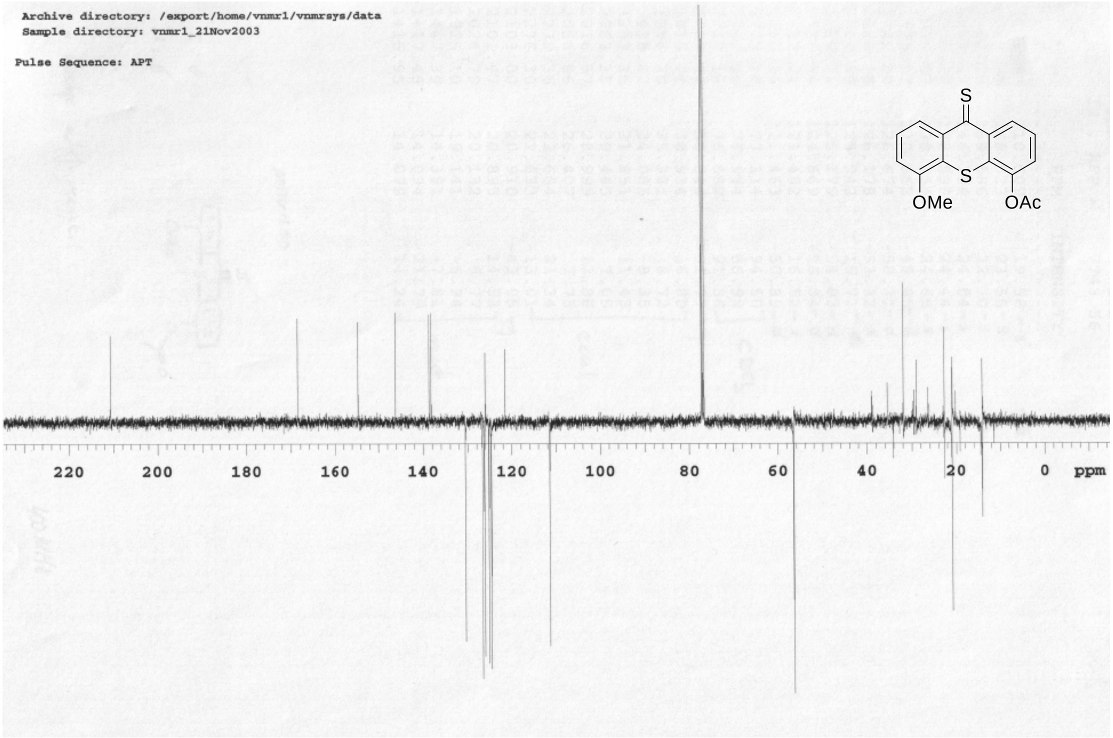


Figure 45. 100 MHz ^{13}C NMR spectrum of **32** in $CDCl_3$.

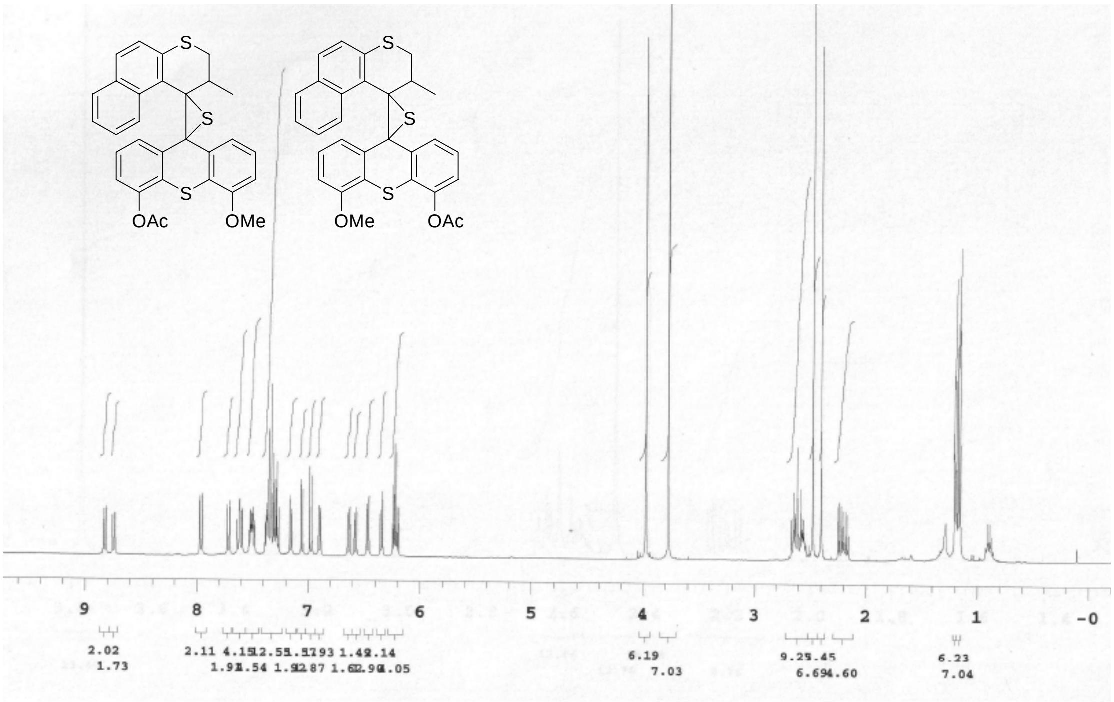


Figure 46. 400 MHz ^{1}H NMR spectrum of *E*-**34** and *Z*-**34** in CDCl$_3$.

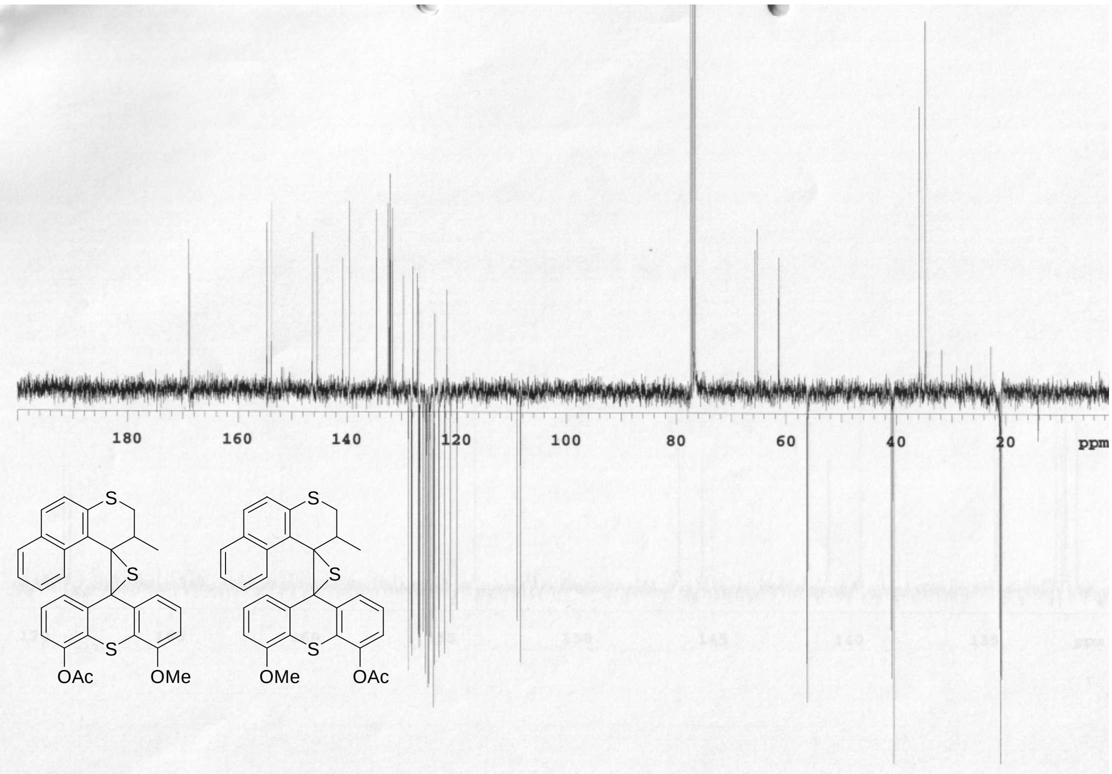


Figure 47. 100 MHz ^{13}C NMR spectrum of *E*-**34** and *Z*-**34** in CDCl$_3$.

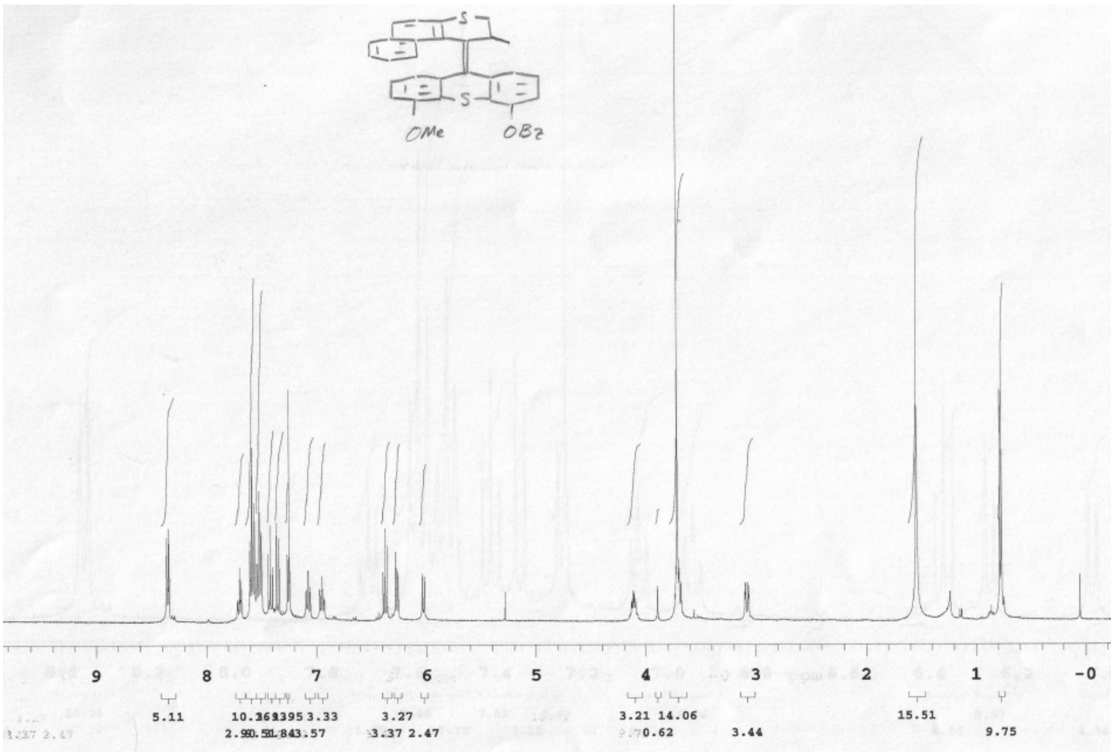


Figure 48. ^{1}H NMR spectrum of *E*-**35** in $CDCl_3$ taken at 400 MHz.

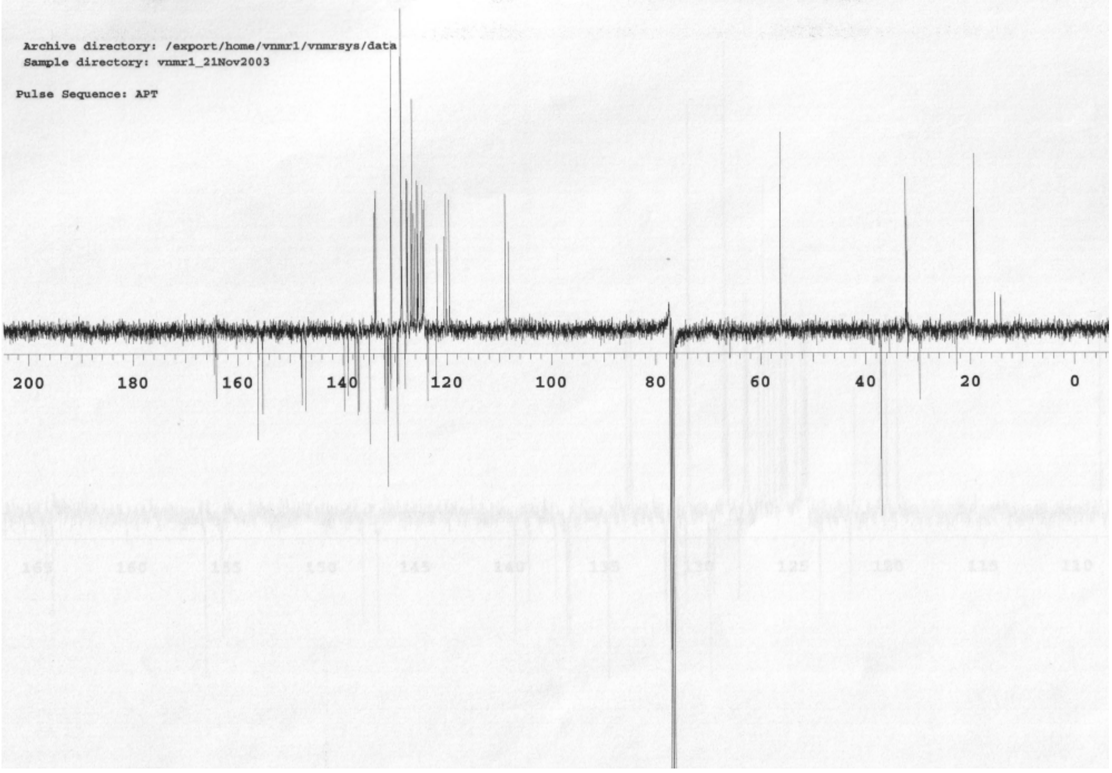


Figure 49. ^{13}C NMR spectrum of *E*-**35** in $CDCl_3$ taken at 100 MHz.

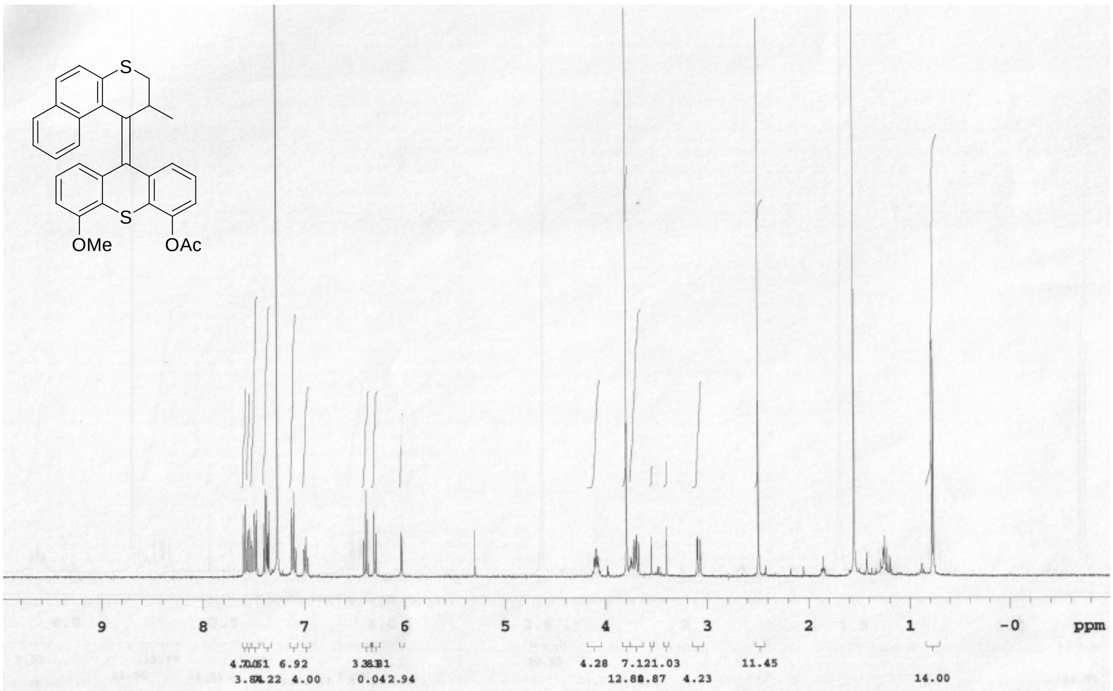


Figure 50. ^{1}H NMR spectrum of *E*-**36** in CDCl$_3$ taken at 400 MHz.

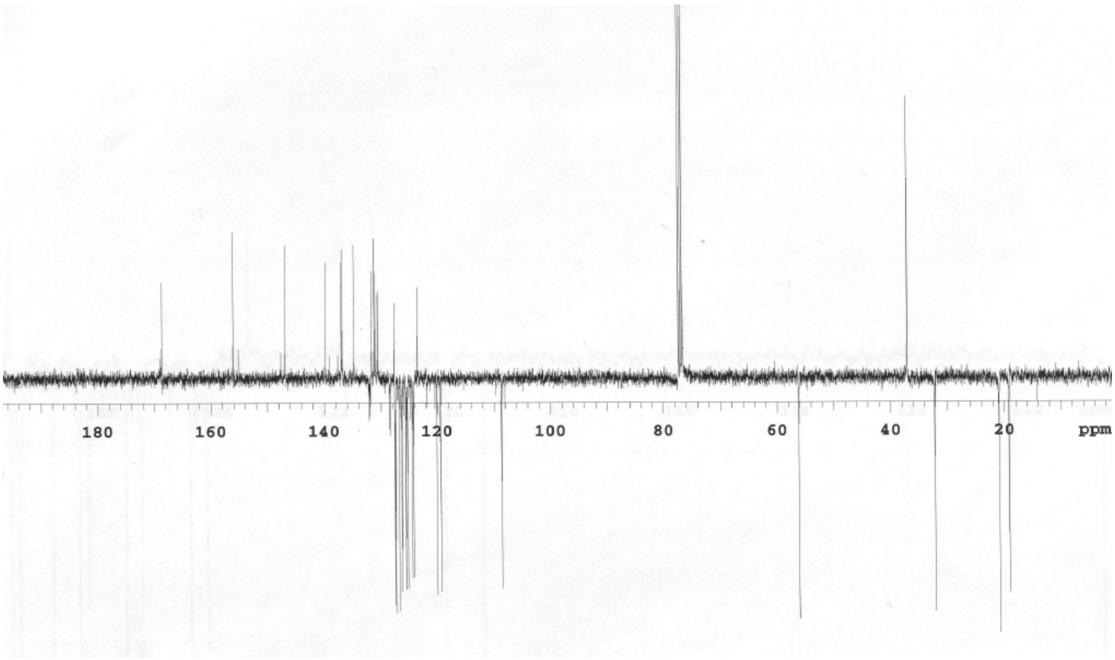


Figure 51. ^{13}C NMR spectrum of *E*-**36** in CDCl$_3$ taken at 100 MHz.

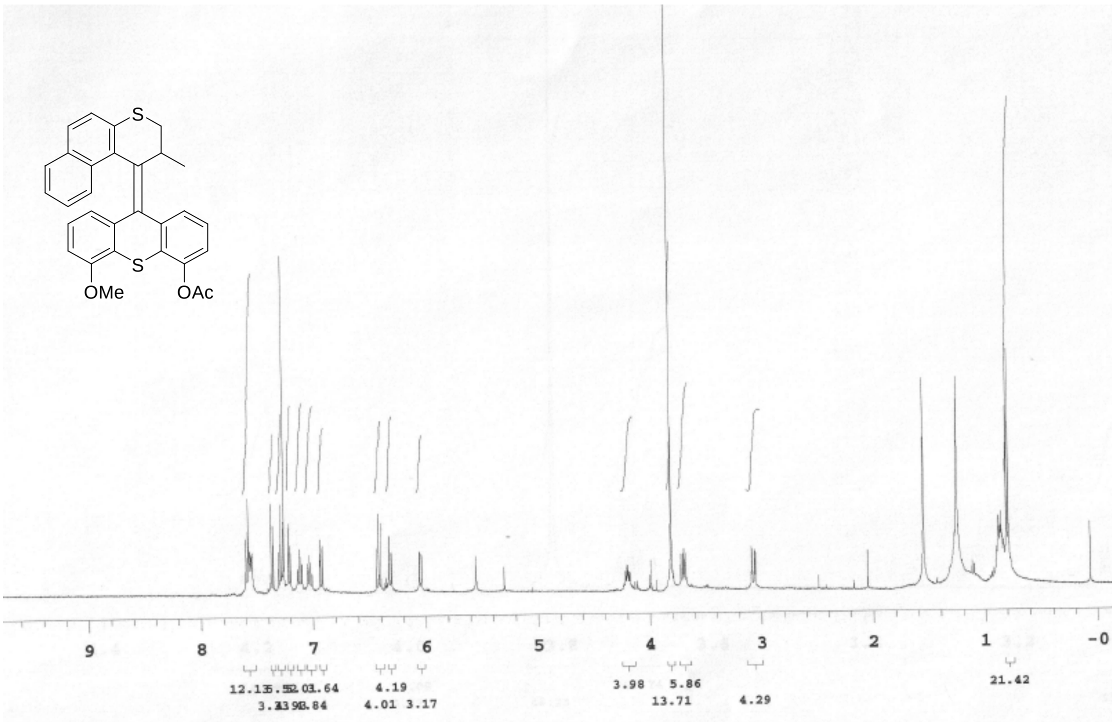


Figure 52. ^{1}H NMR spectrum of *Z*-**36** in $CDCl_3$ taken at 400 MHz.

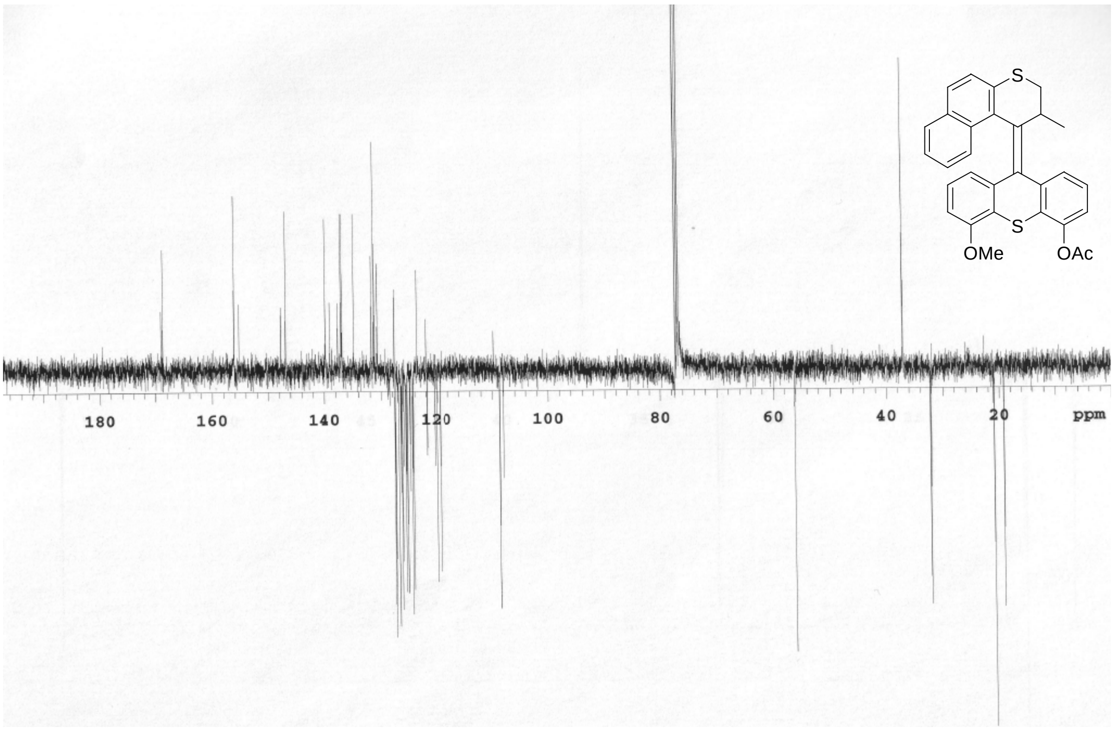


Figure 53. ^{13}C NMR spectrum of *Z*-**36** in $CDCl_3$ taken at 100 MHz.

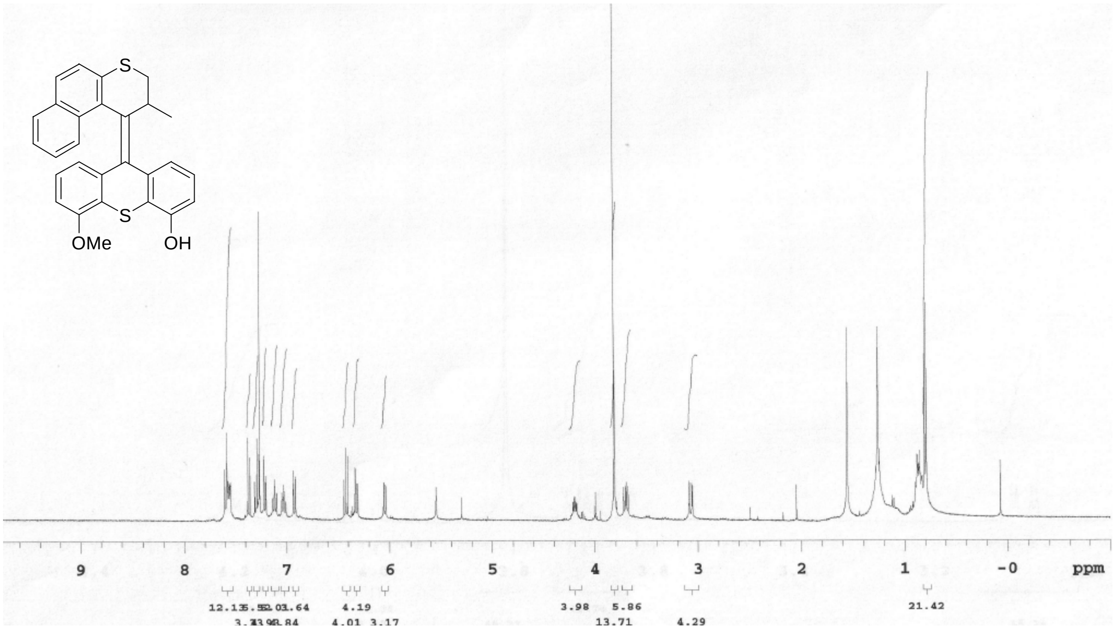


Figure 54. ^{1}H NMR spectrum of *Z*-**37** in $CDCl_3$ taken at 400 MHz.

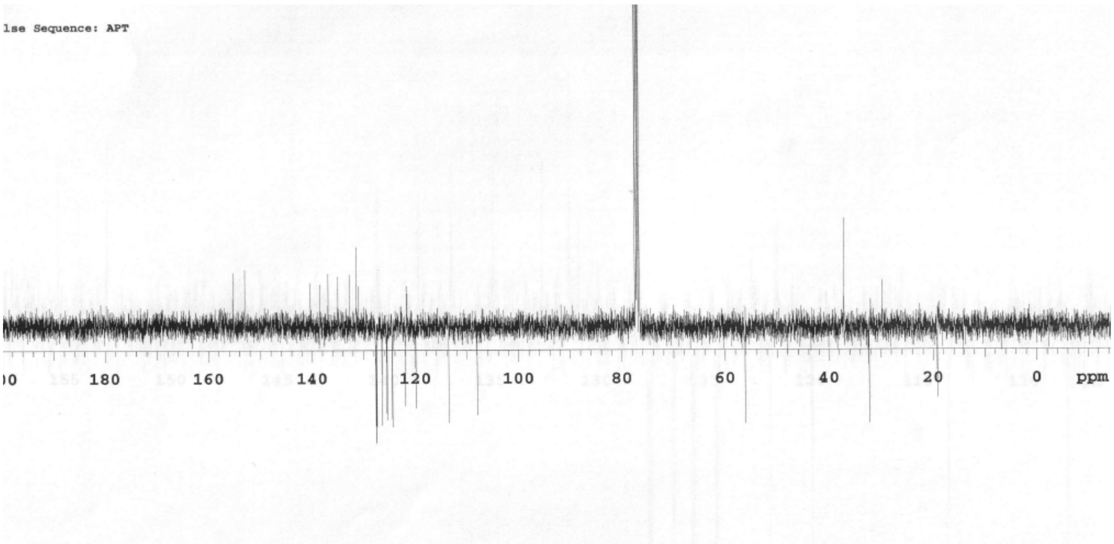


Figure 55. ^{13}C NMR spectrum of *Z*-**37** in $CDCl_3$ taken at 100 MHz.

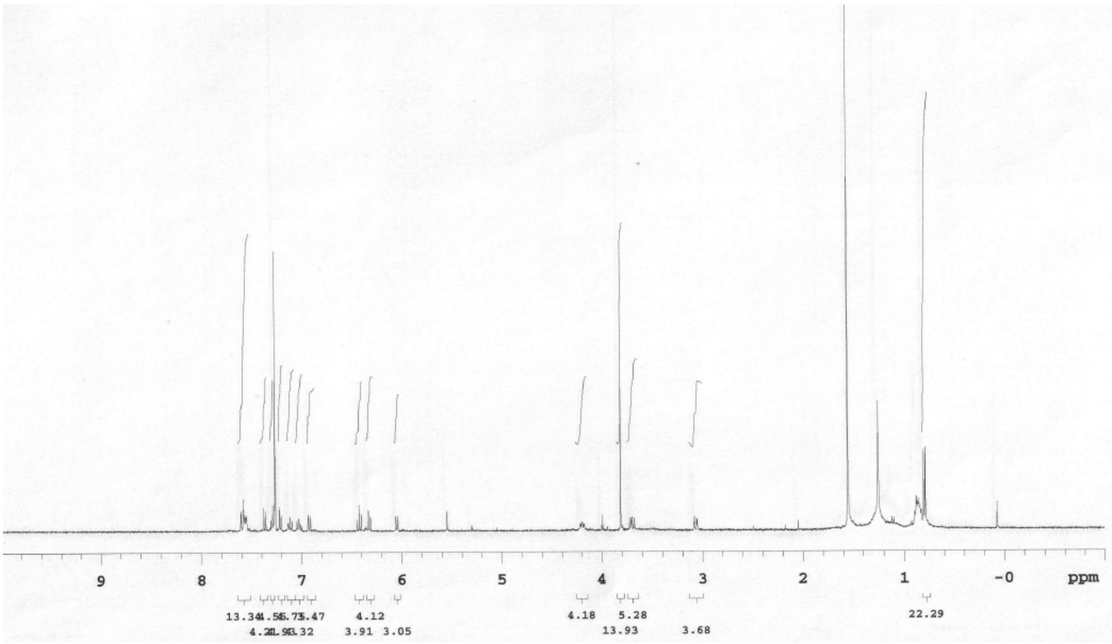


Figure 56. ^{1}H NMR spectrum of *E*-**37** in $CDCl_3$ taken at 400 MHz.

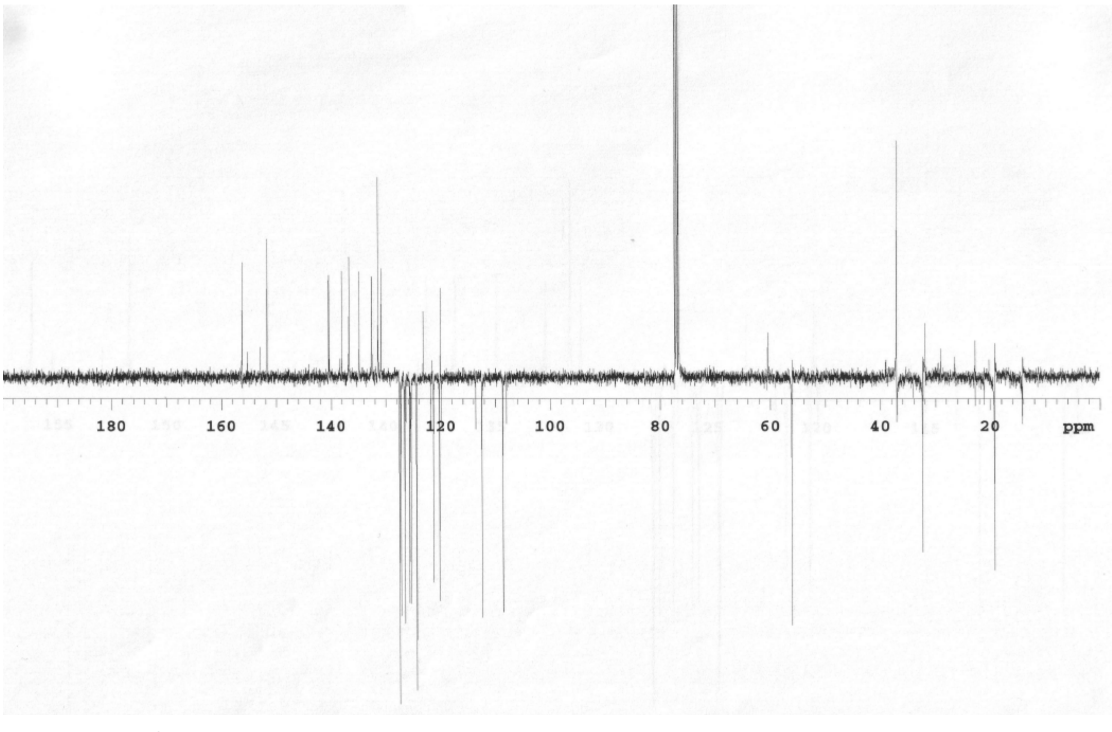


Figure 57. ^{13}C NMR spectrum of *E*-**37** in $CDCl_3$ taken at 100 MHz.

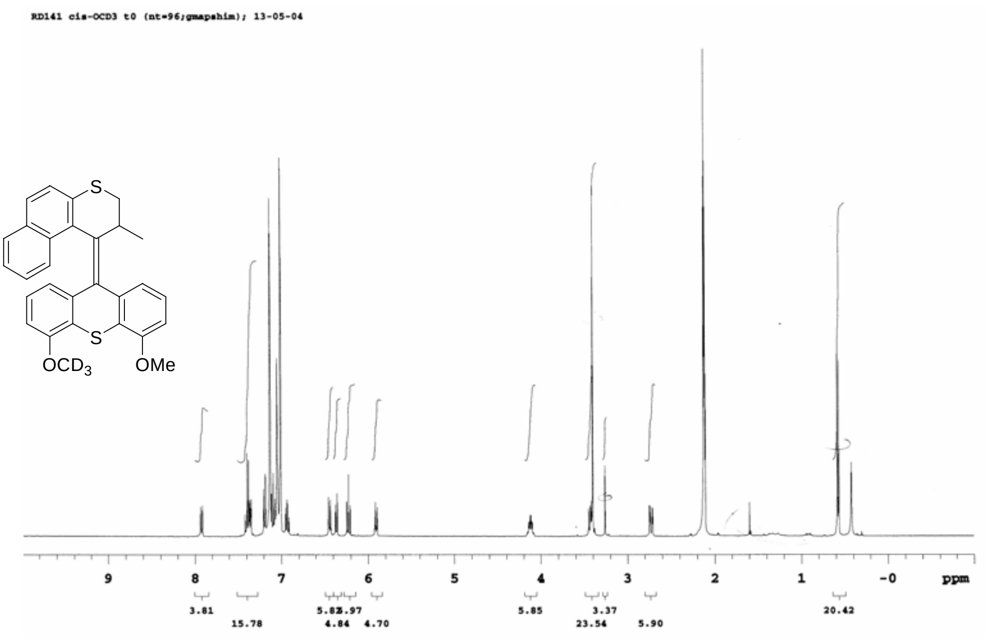


Figure 58: 400 MHz ^{1}H NMR spectrum of *E*-**38**.

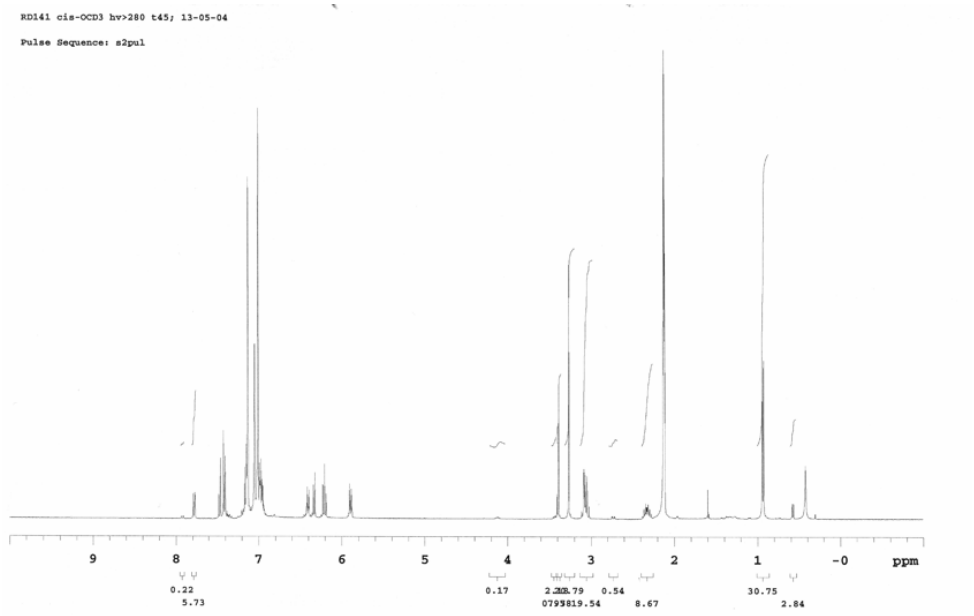


Figure 59: 400 MHz ^{1}H NMR spectrum of a sample of 80% diastereomerically pure *E*-**3**8 in toluene-D$_8$ after irradiation at λ>280nm, now containing predominantly unstable *Z*-**38**.

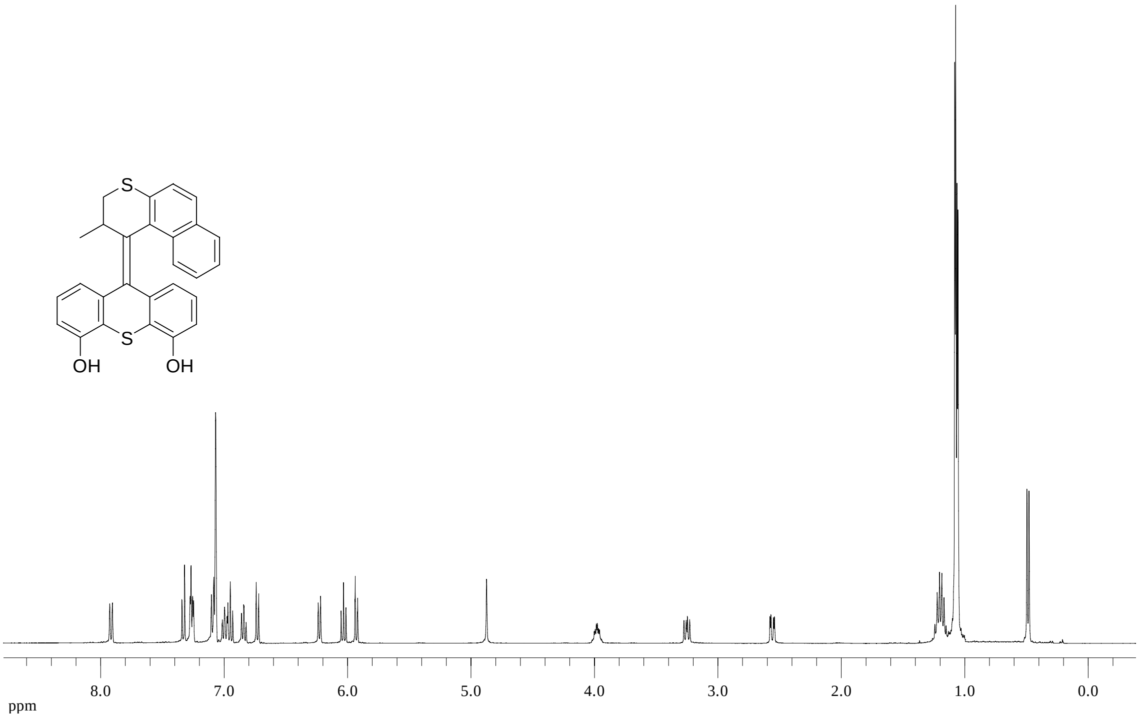


Figure 60. 400 MHz ^{1}H NMR spectrum of **39** in C_6D_6 .

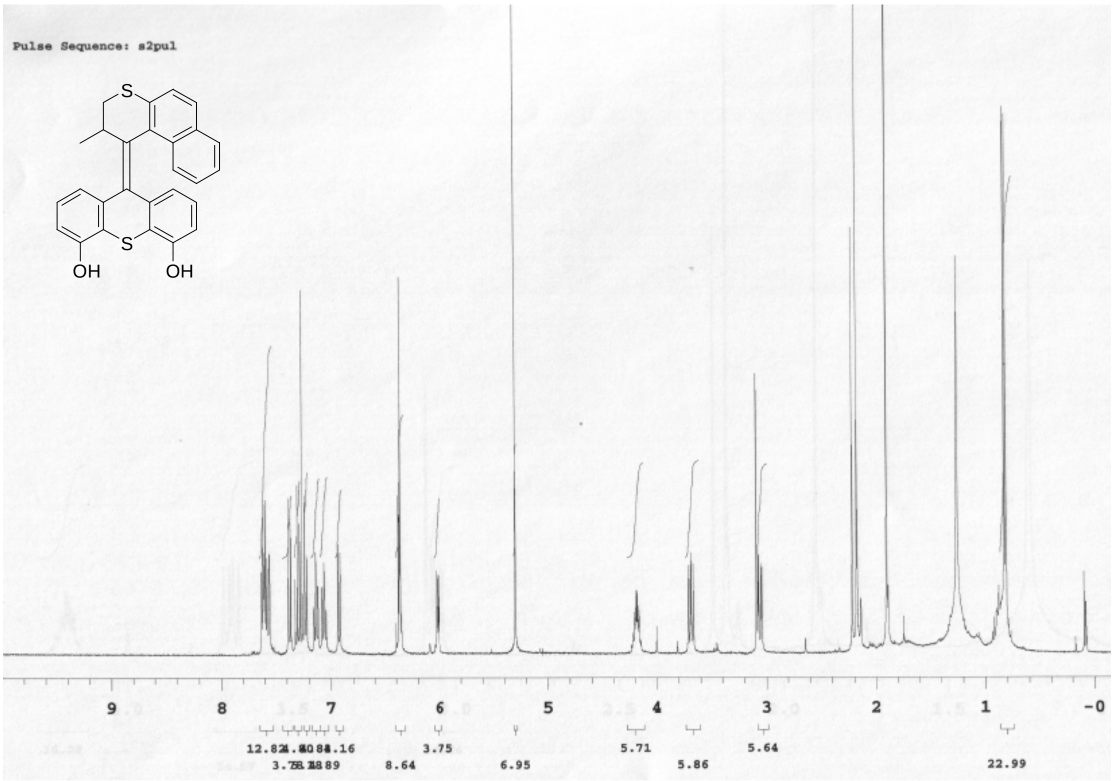


Figure 61. 400 MHz ^{1}H NMR spectrum of **39** in $CDCl_3$.

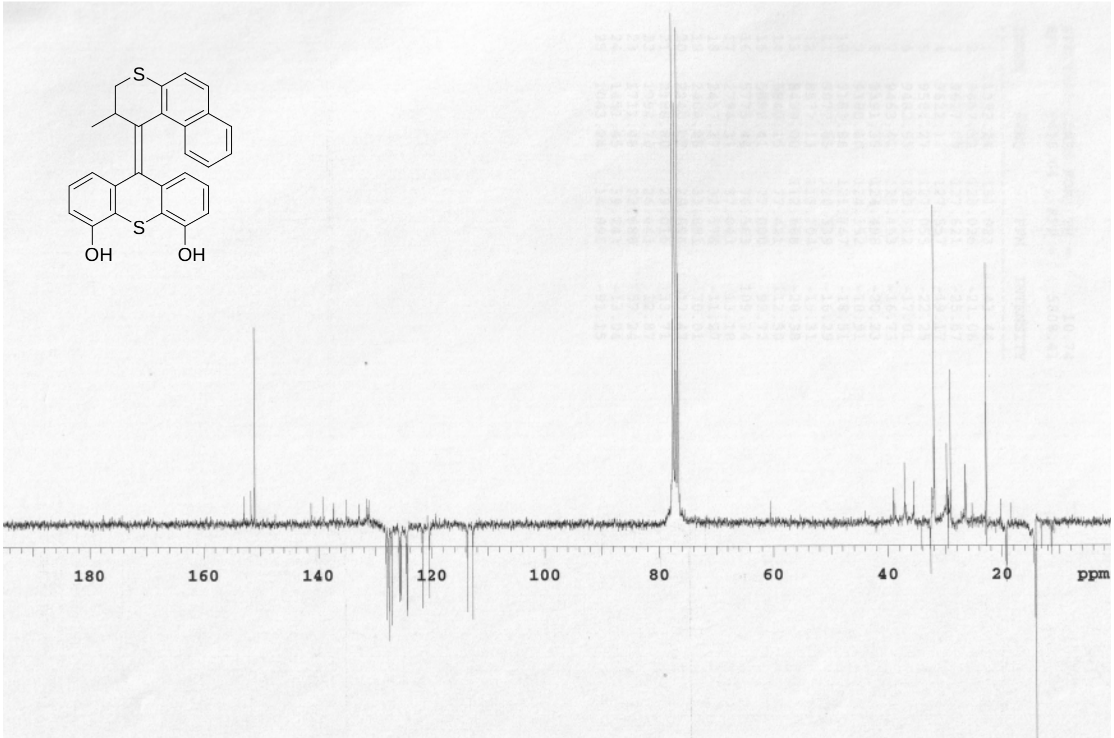


Figure 62. 100 MHz ^{13}C NMR spectrum of **39** in $CDCl_3$.

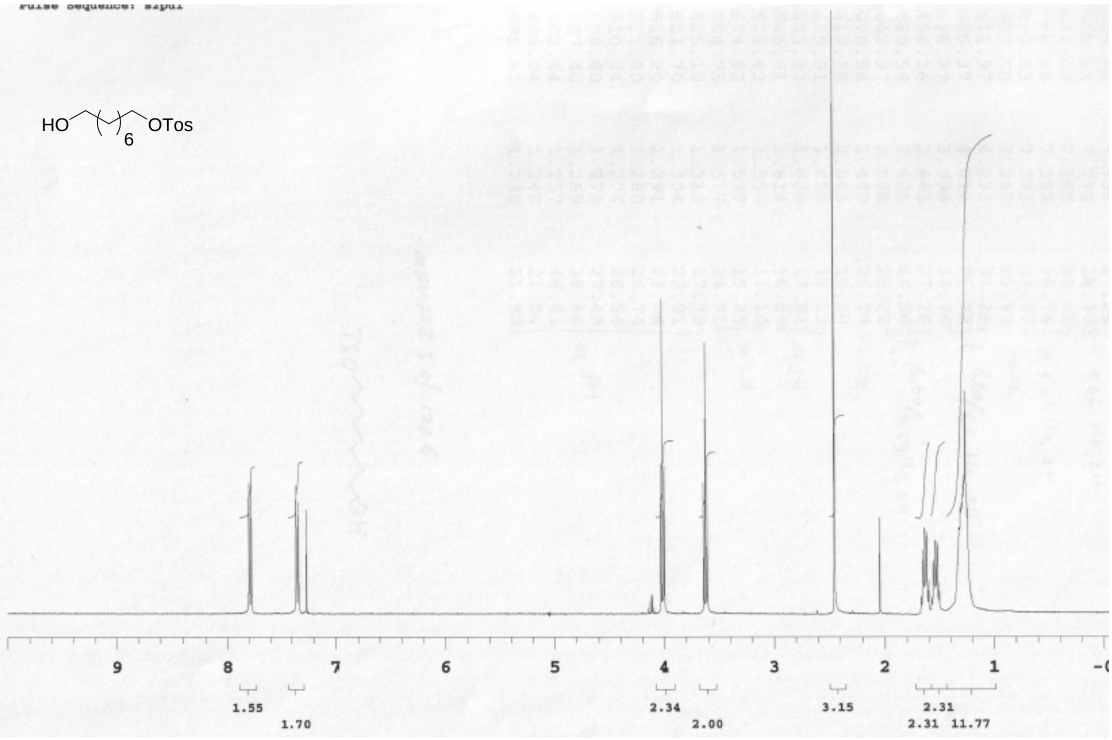


Figure 63. 300 MHz ^{1}H NMR spectrum of **40** in $CDCl_3$.

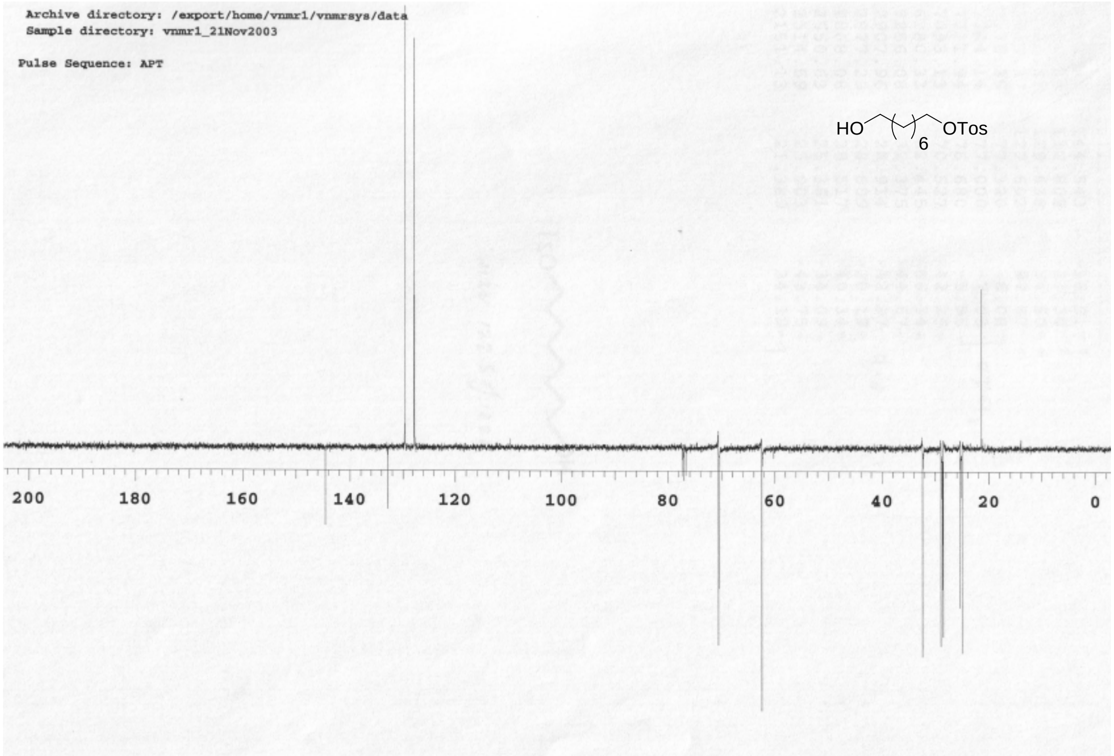


Figure 64. 50 MHz ^{13}C NMR spectrum of **40** in $CDCl_3$.

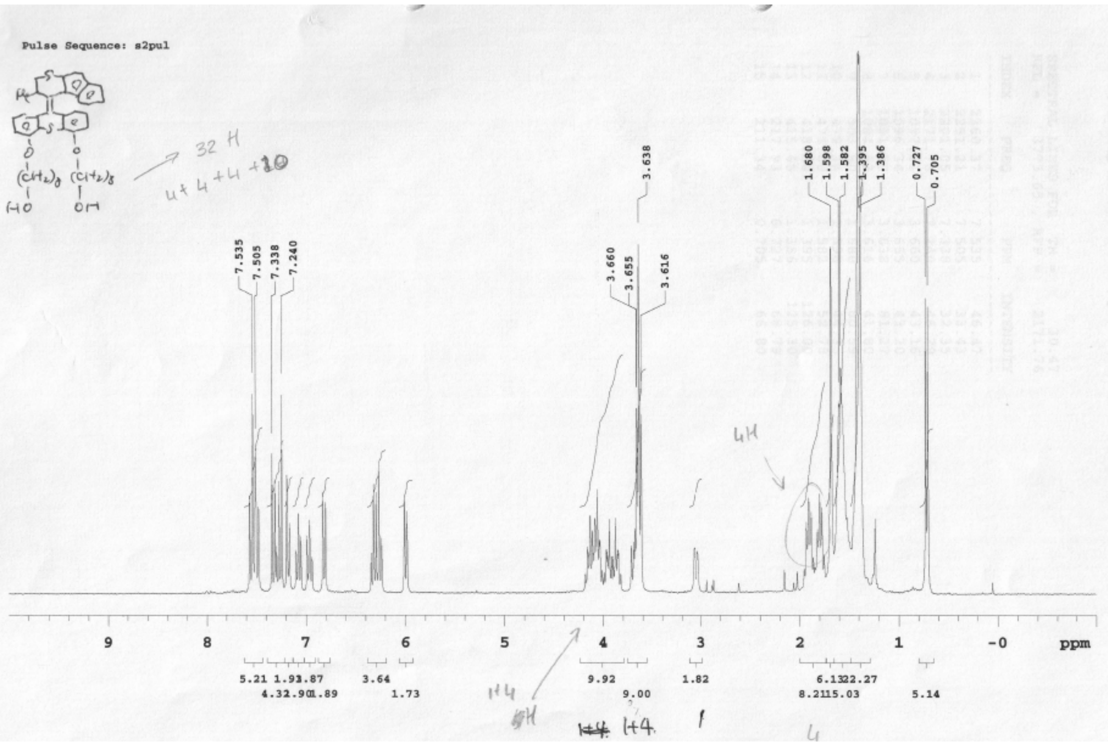


Figure 65. 300 MHz ^{1}H NMR spectrum of **41** in $CDCl_3$.

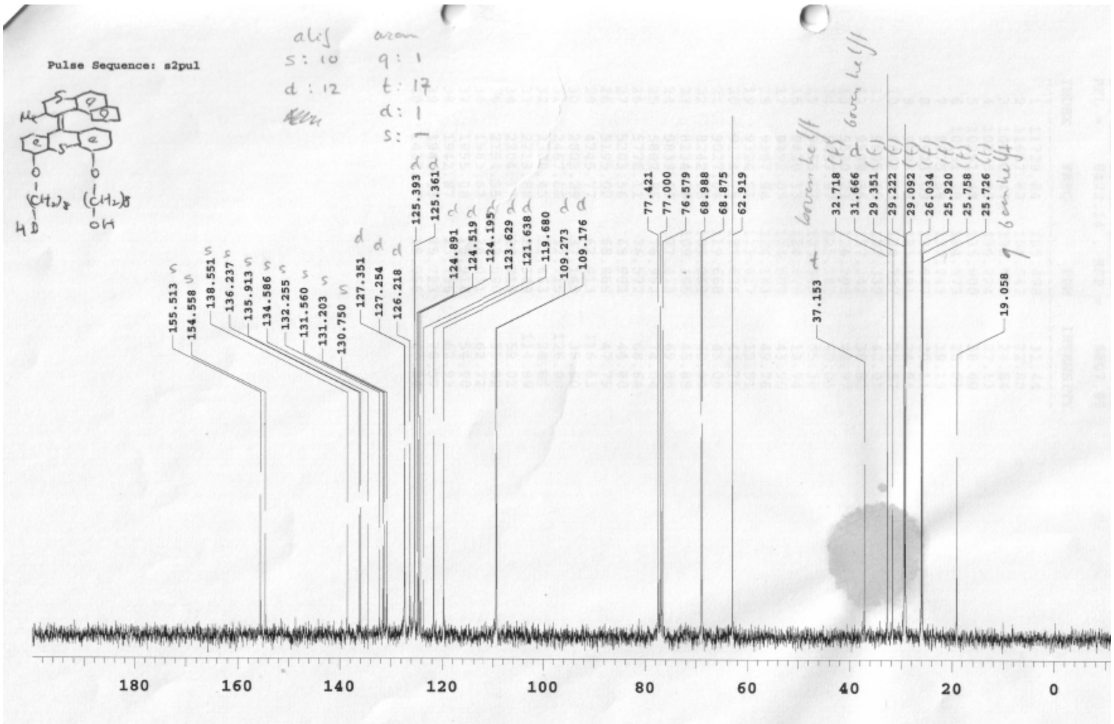


Figure 66. 100 MHz ^{13}C NMR spectrum of **41** in $CDCl_3$.

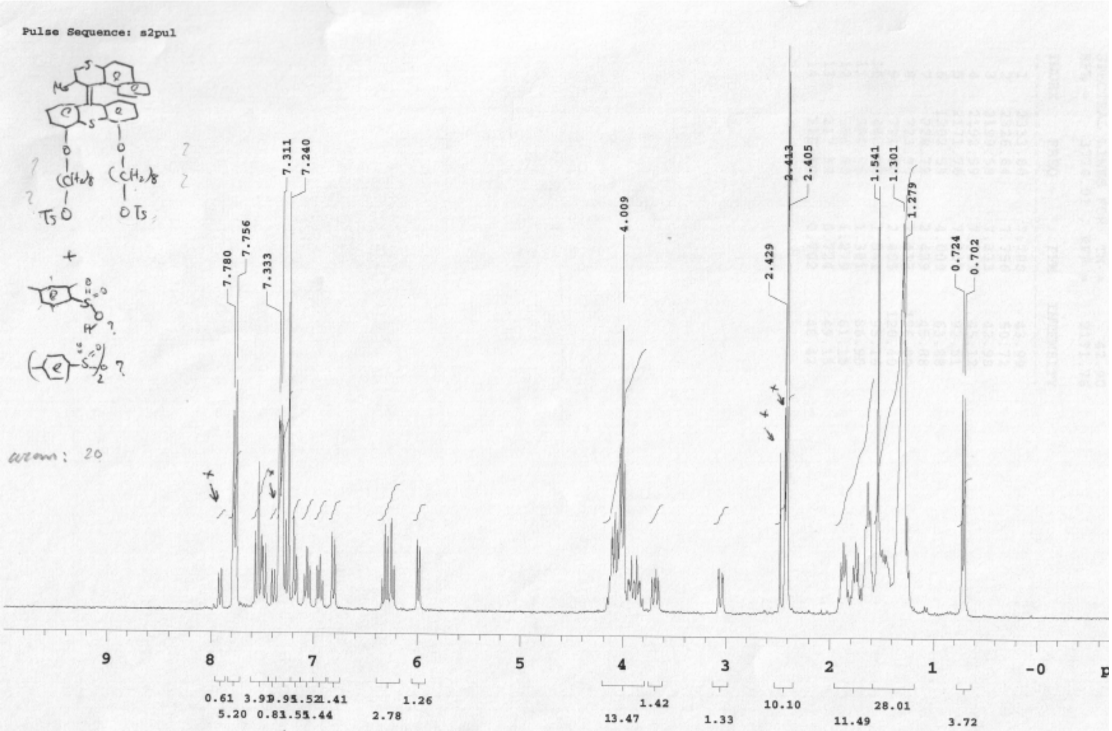


Figure 67. 300 MHz ^{1}H NMR spectrum of **42** in $CDCl_3$.

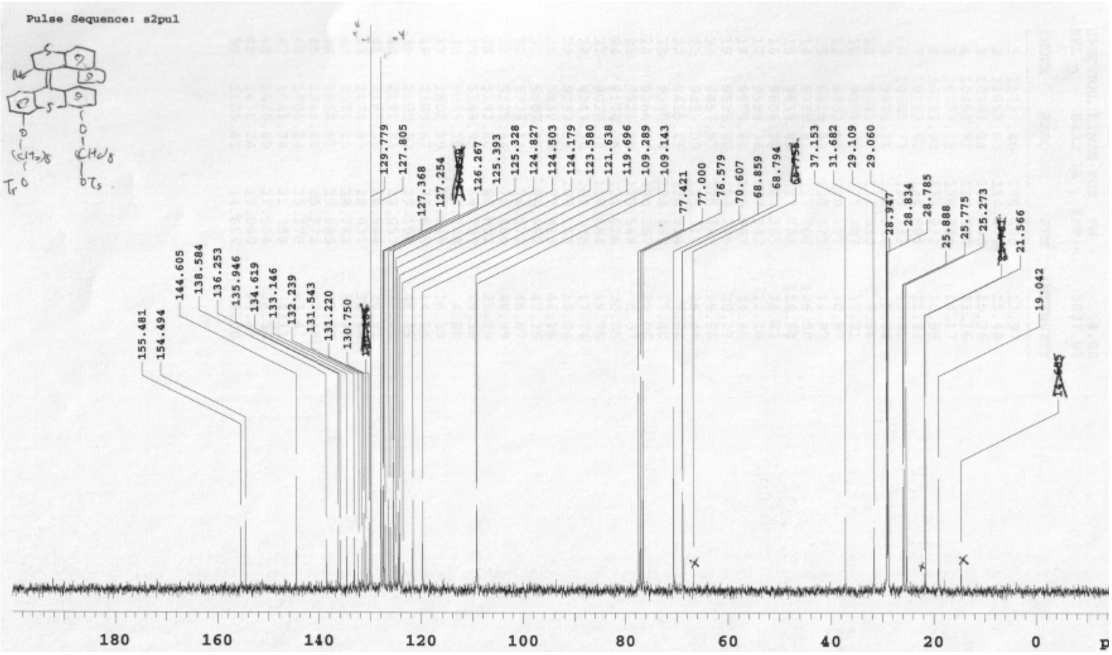


Figure 68. 50 MHz ^{13}C NMR spectrum of **42** in CDCl$_3$.

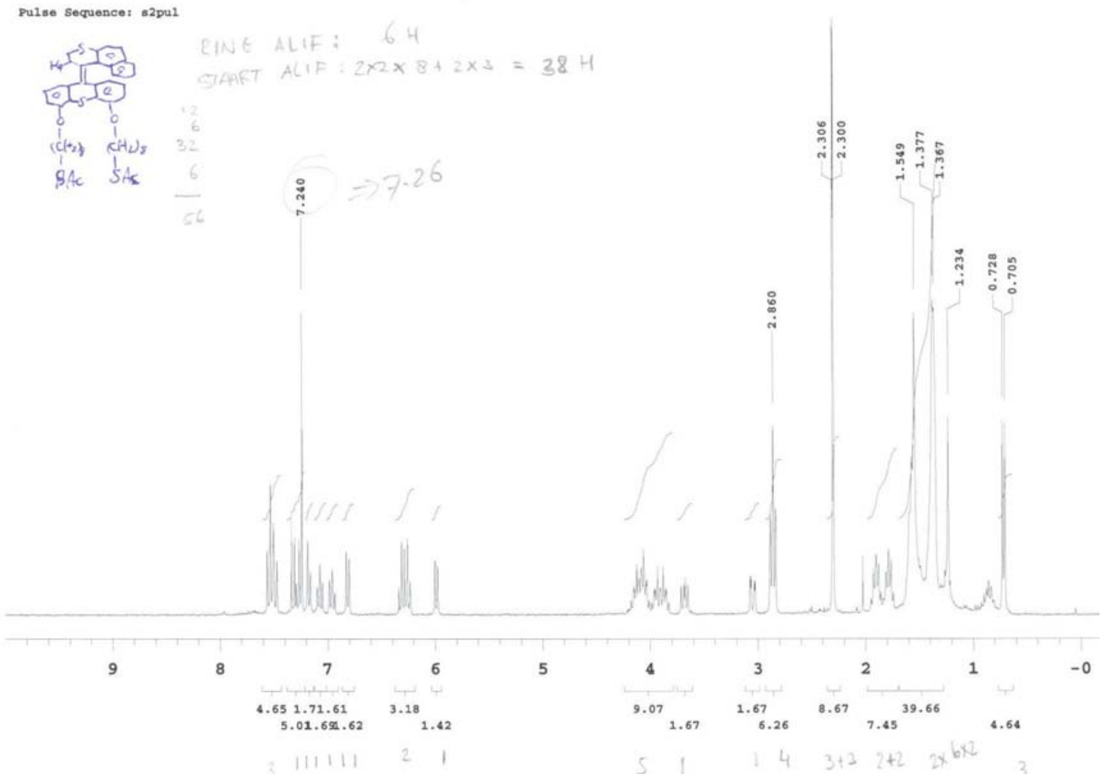


Figure 69. 300 MHz ^{1}H NMR spectrum of **43** in CDCl$_3$.

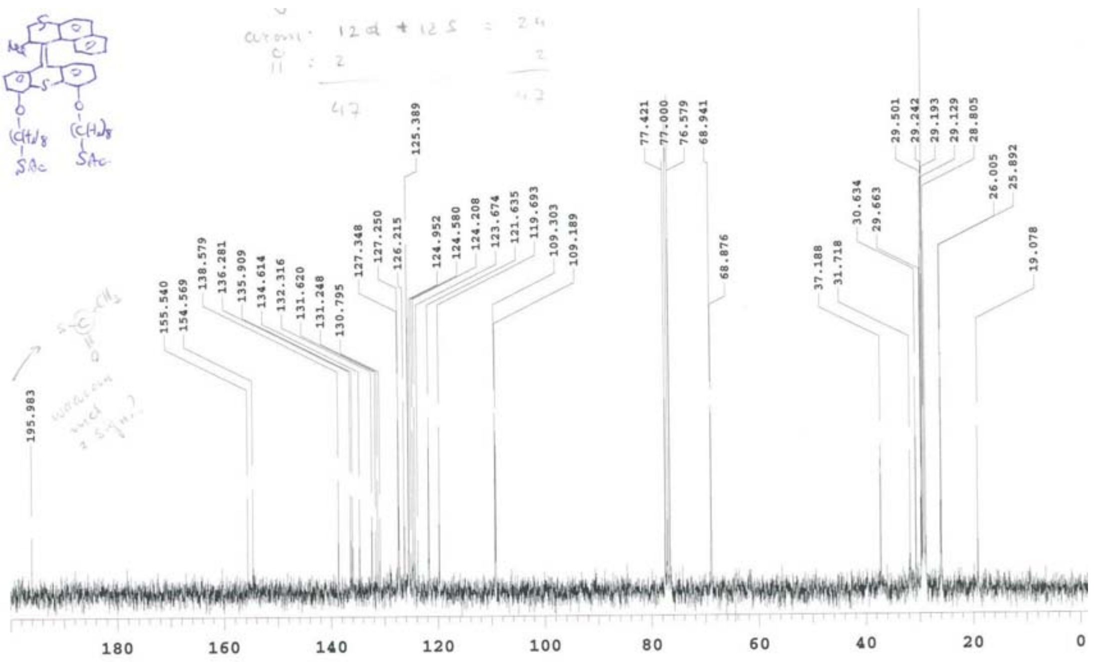


Figure 70. 75 MHz ^{13}C NMR spectrum of **43** in $CDCl_3$.

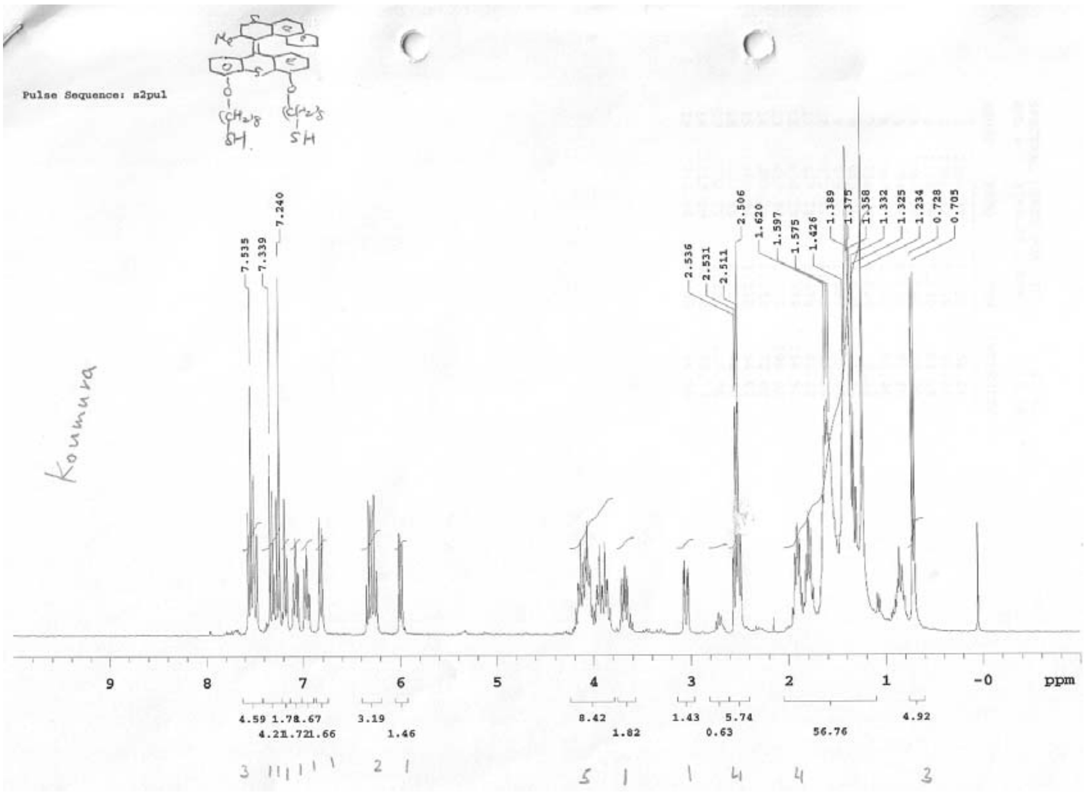


Figure 71. 400 MHz ^{1}H NMR spectrum of **44** in $CDCl_3$.

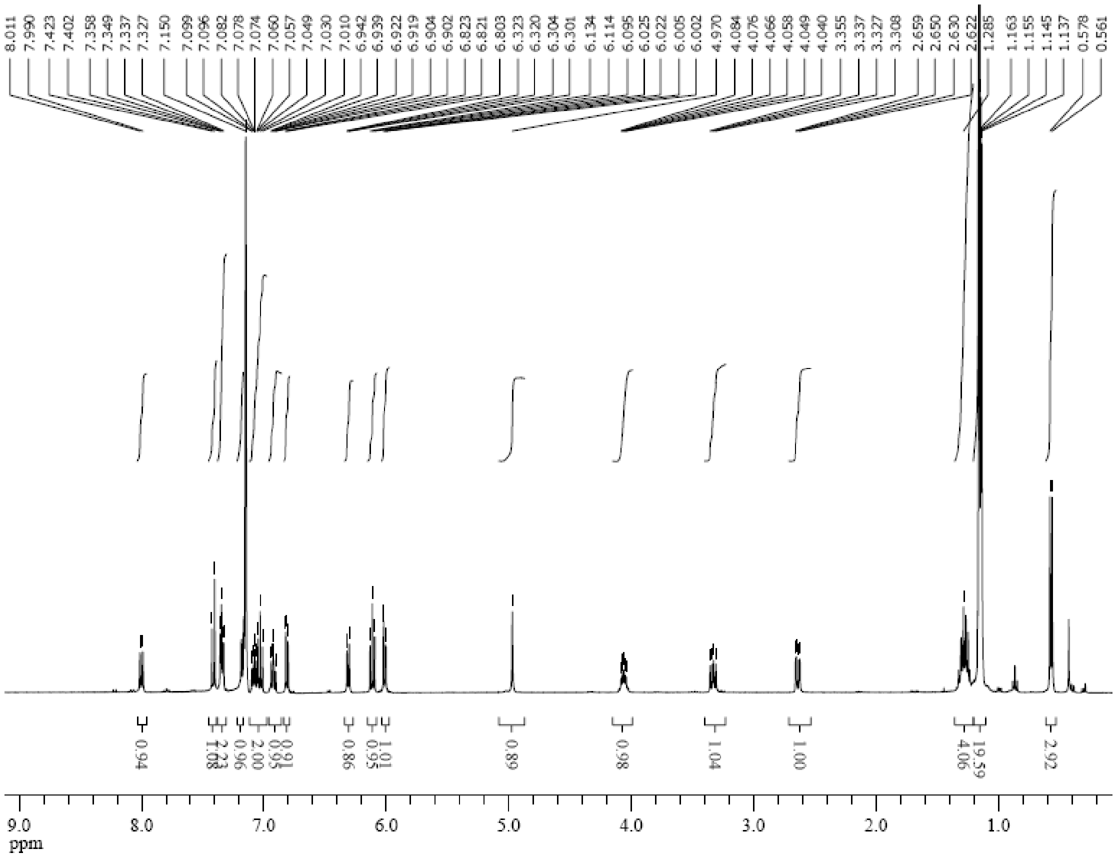


Figure 72. 400 MHz ^{1}H NMR spectrum of *trans*-**45** in C_6D_6.

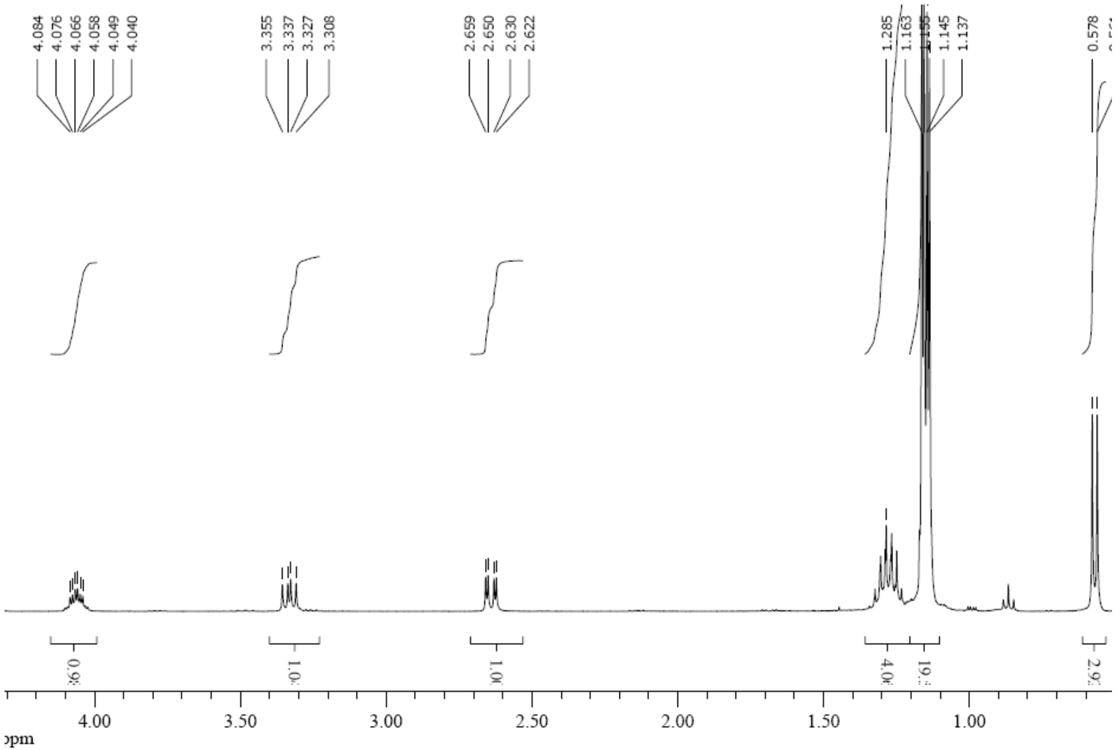


Figure 73. ^{1}H NMR spectrum of *trans*-**45** in C_6D_6 taken at 400 MHz (expansion).

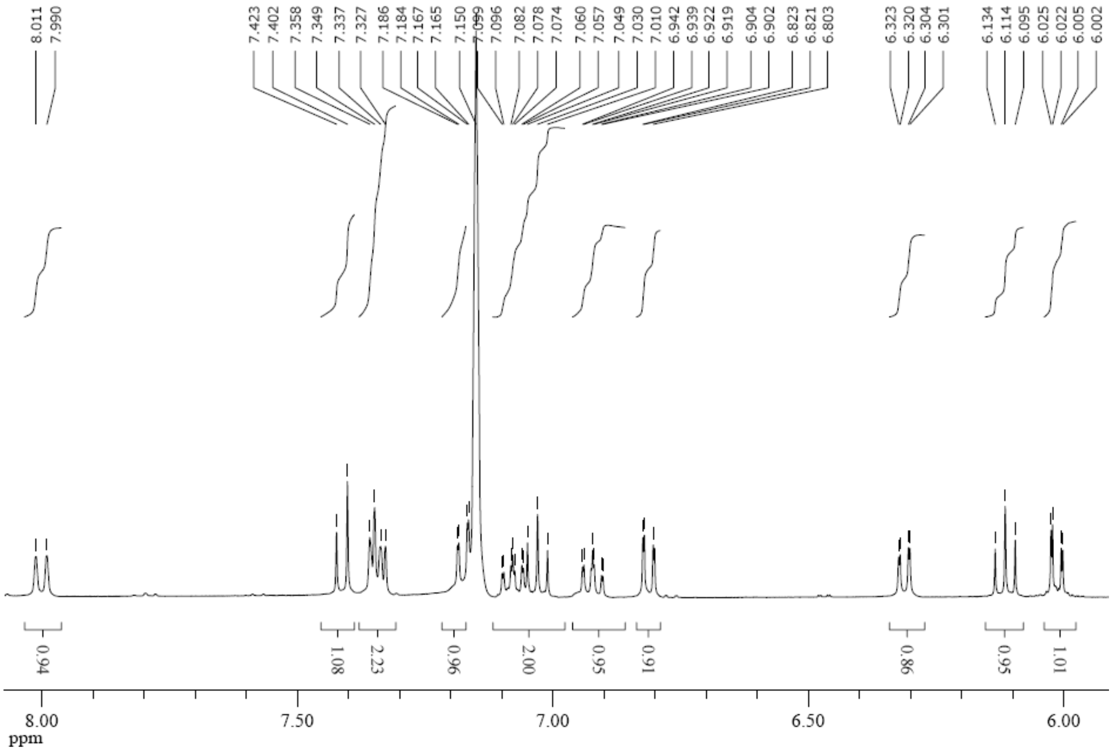


Figure 74. ^{1}H NMR spectrum of *trans*-**45** in C_6D_6 taken at 400 MHz (expansion).

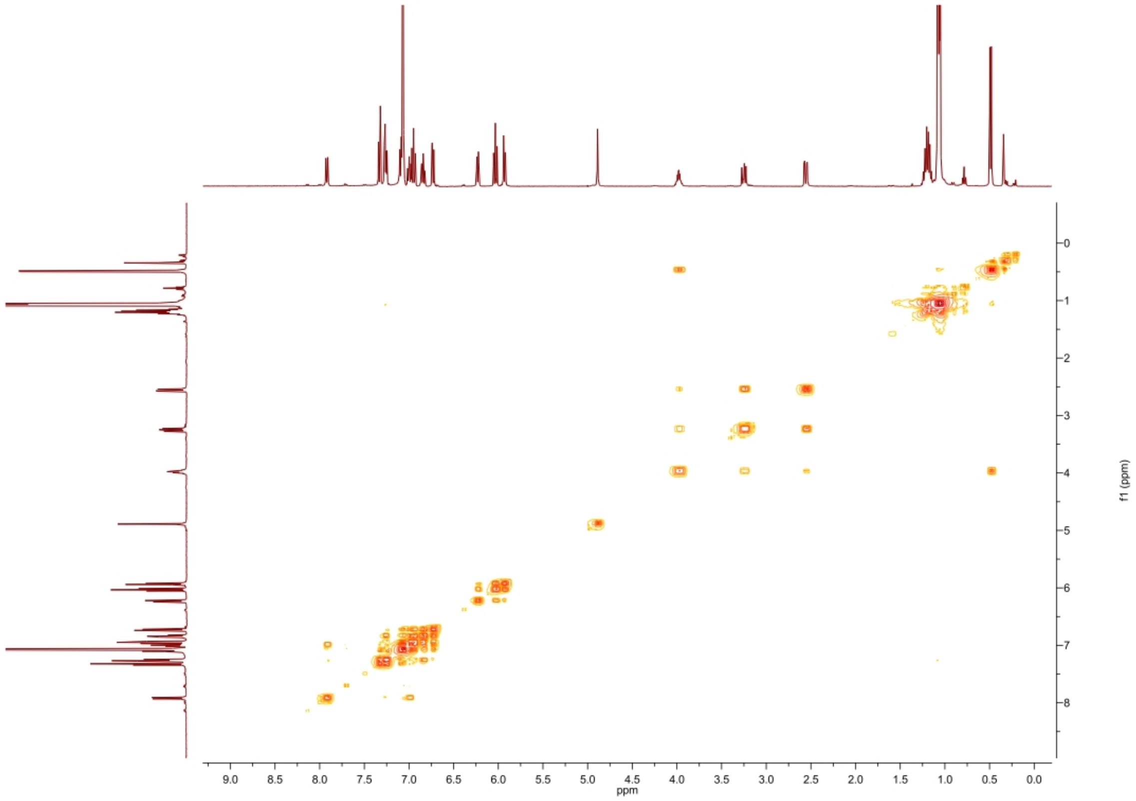


Figure 75. 400 MHz GCOSY spectrum of ***trans*-45** in C_6D_6.

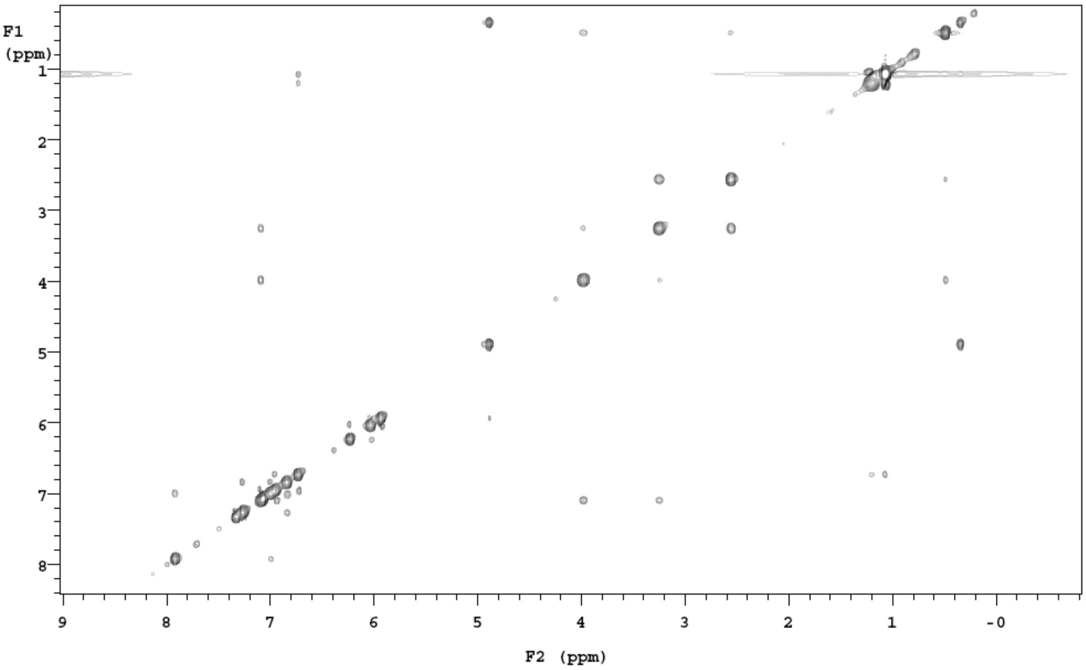


Figure 76. 125 MHz NOESY spectrum of *trans*-**45** in C_6D_6.

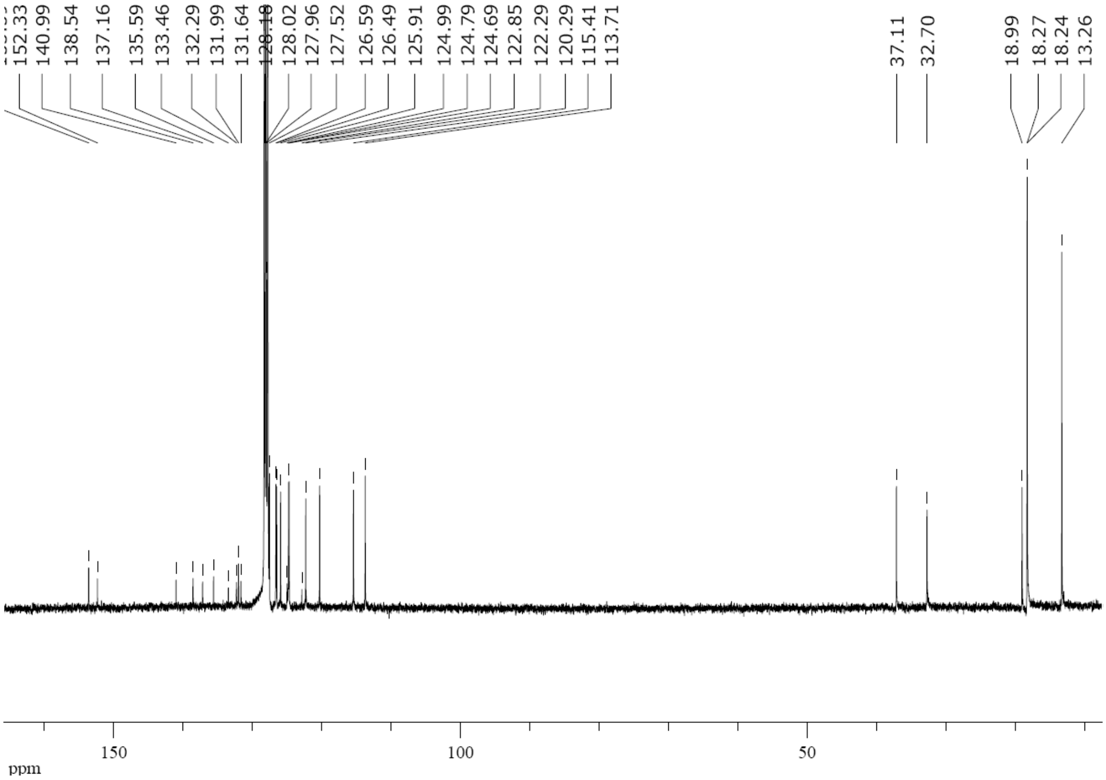


Figure 77. 100 MHz ^{13}C NMR spectrum of *trans*-**45** in C_6D_6.

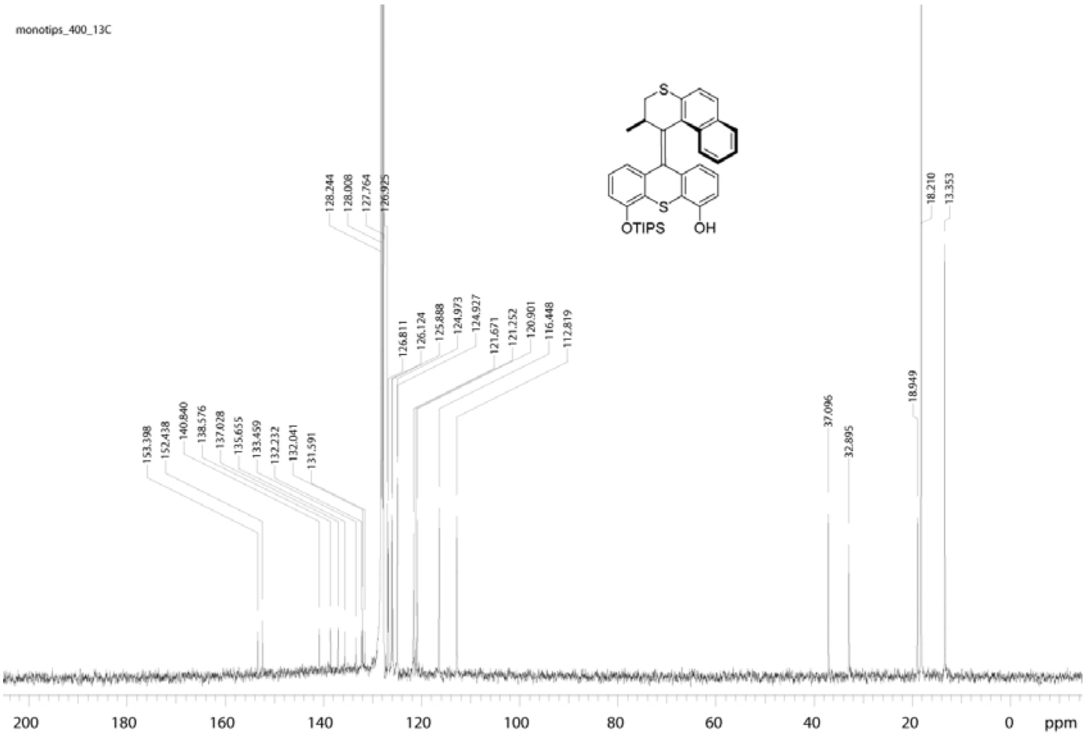


Figure 78. 100 MHz ^{13}C NMR spectrum of *trans*-**45** in C_6D_6.

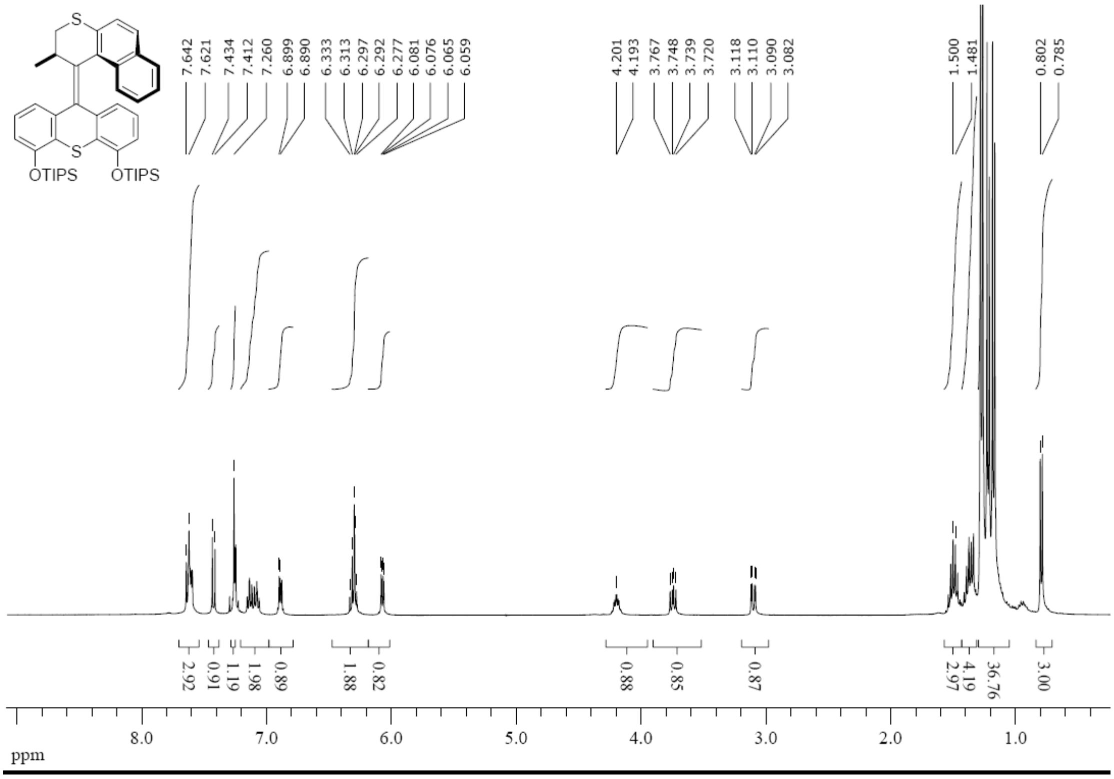


Figure 79. 400 MHz ^{1}H NMR spectrum of bis-TIPS ether in $CDCl_3$.

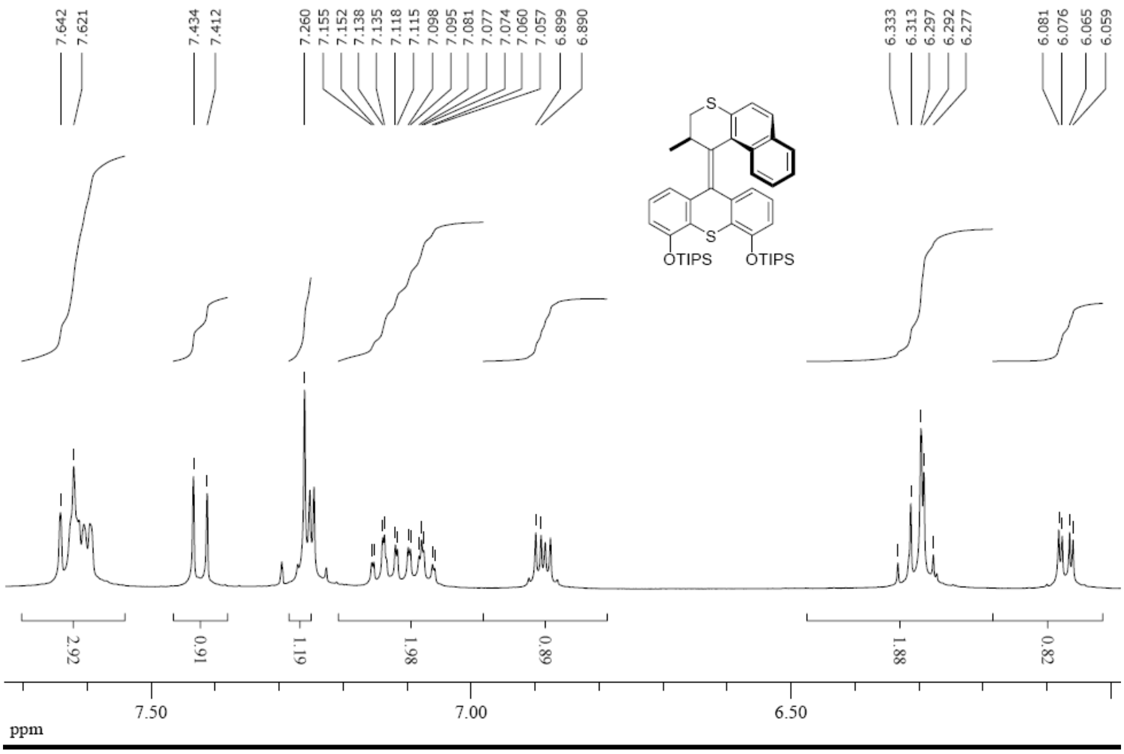


Figure 80. 400 MHz ^{1}H NMR spectrum of bis-TIPS ether in $CDCl_3$ (expansion).

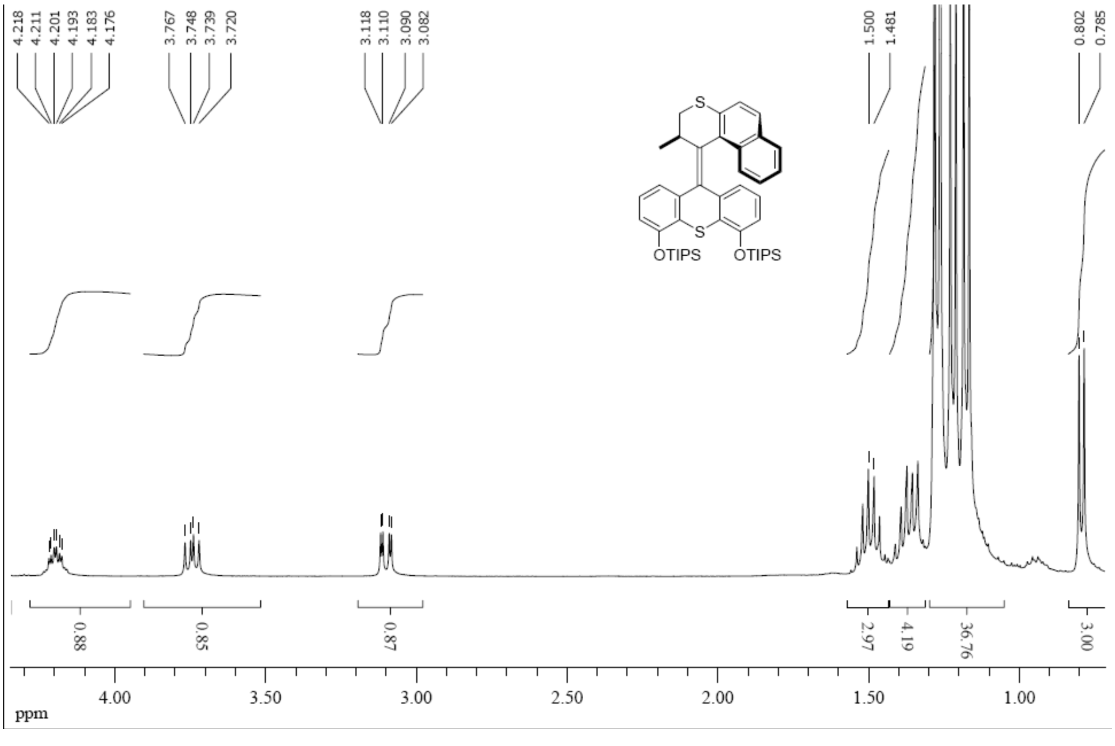


Figure 81. 400 MHz ^{1}H NMR spectrum of bis-TIPS ether in $CDCl_3$ (expansion).

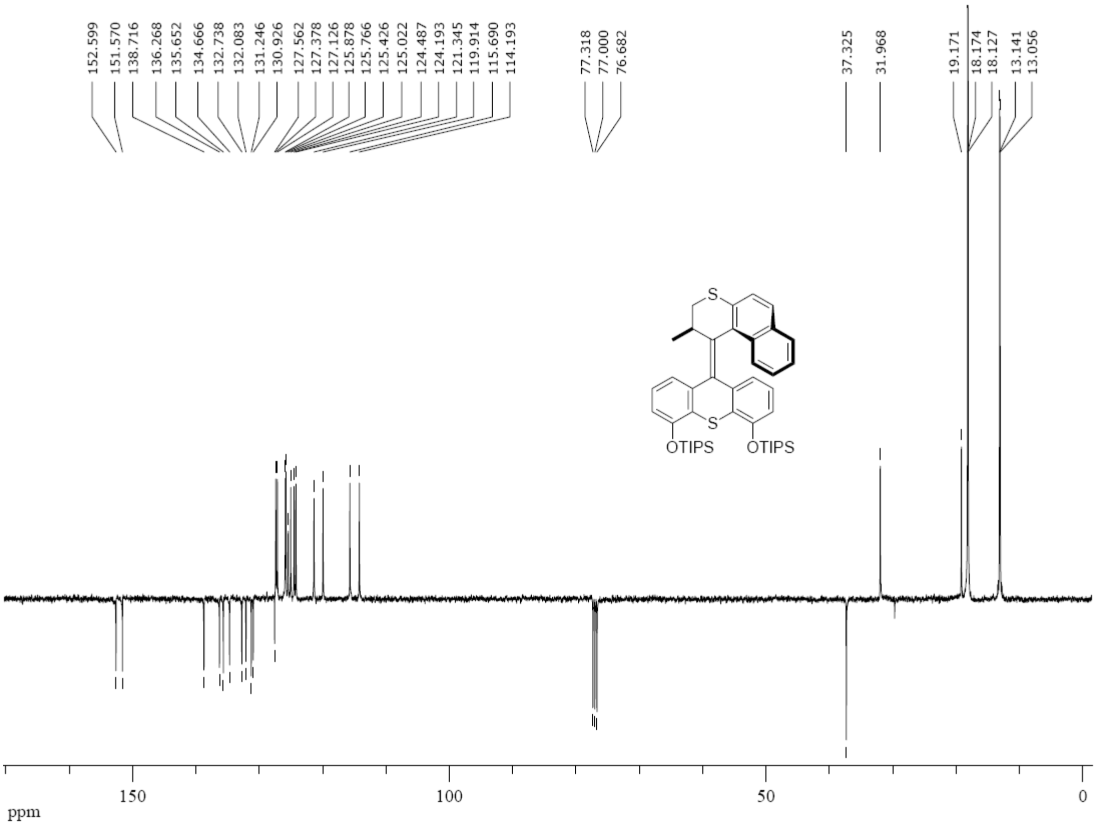


Figure 82. 100 MHz ^{13}C NMR spectrum of bis-TIPS ether in $CDCl_3$.

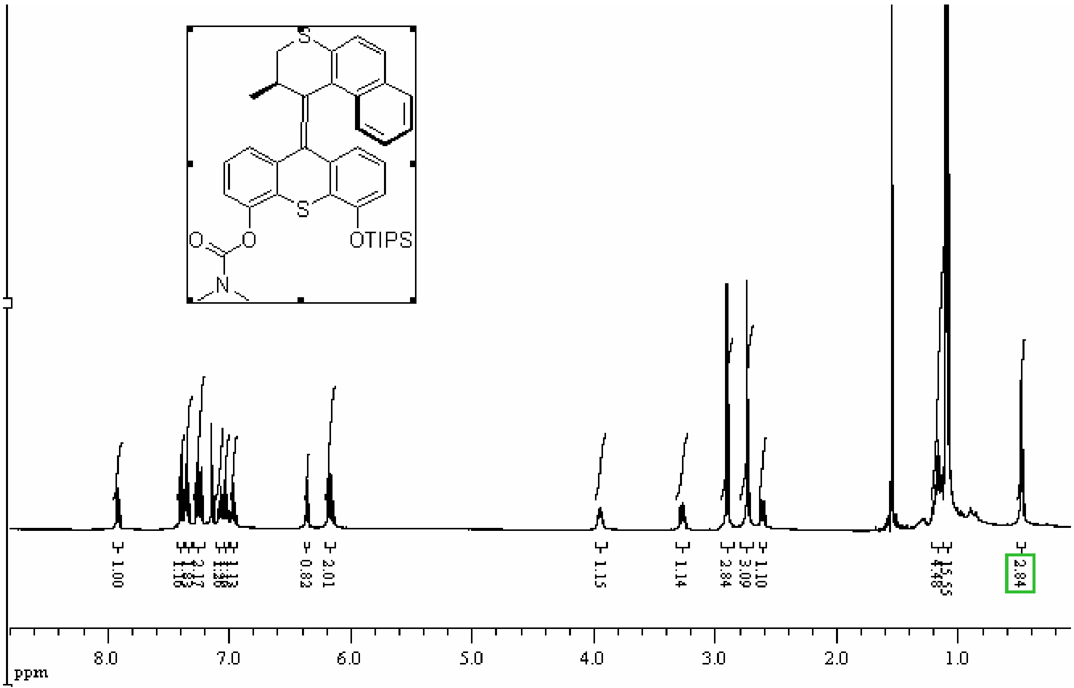


Figure 83. 500 MHz ^{1}H NMR spectrum of *cis*-**46** in C_6D_6.

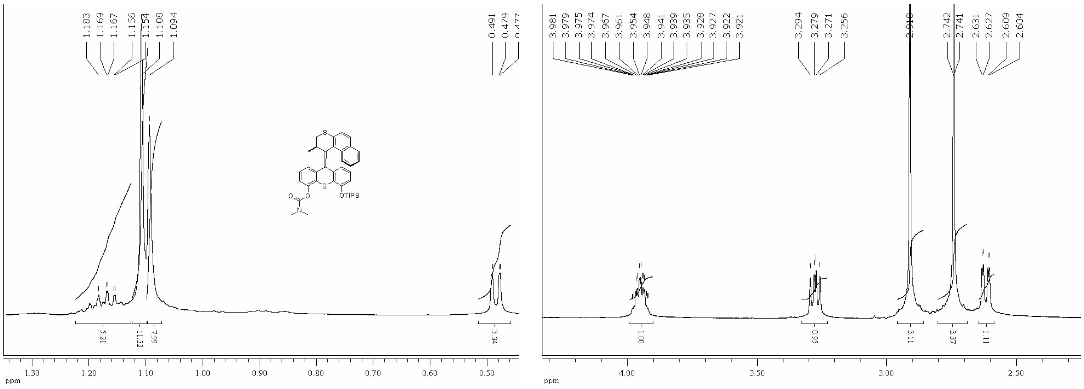


Figure 84. 500 MHz ^{1}H NMR spectrum of *cis*-**46** in C_6D_6 (expansion).

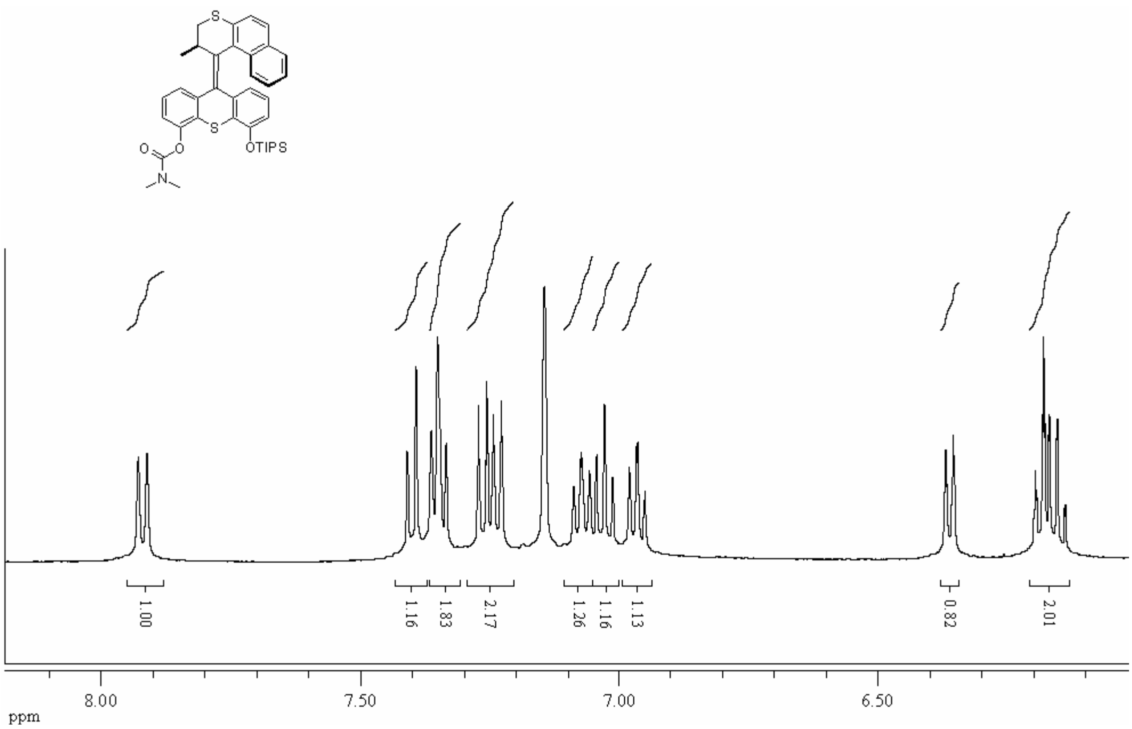


Figure 85. 500 MHz ^{1}H NMR spectrum of *cis*-**46** in C_6D_6 (expansion).

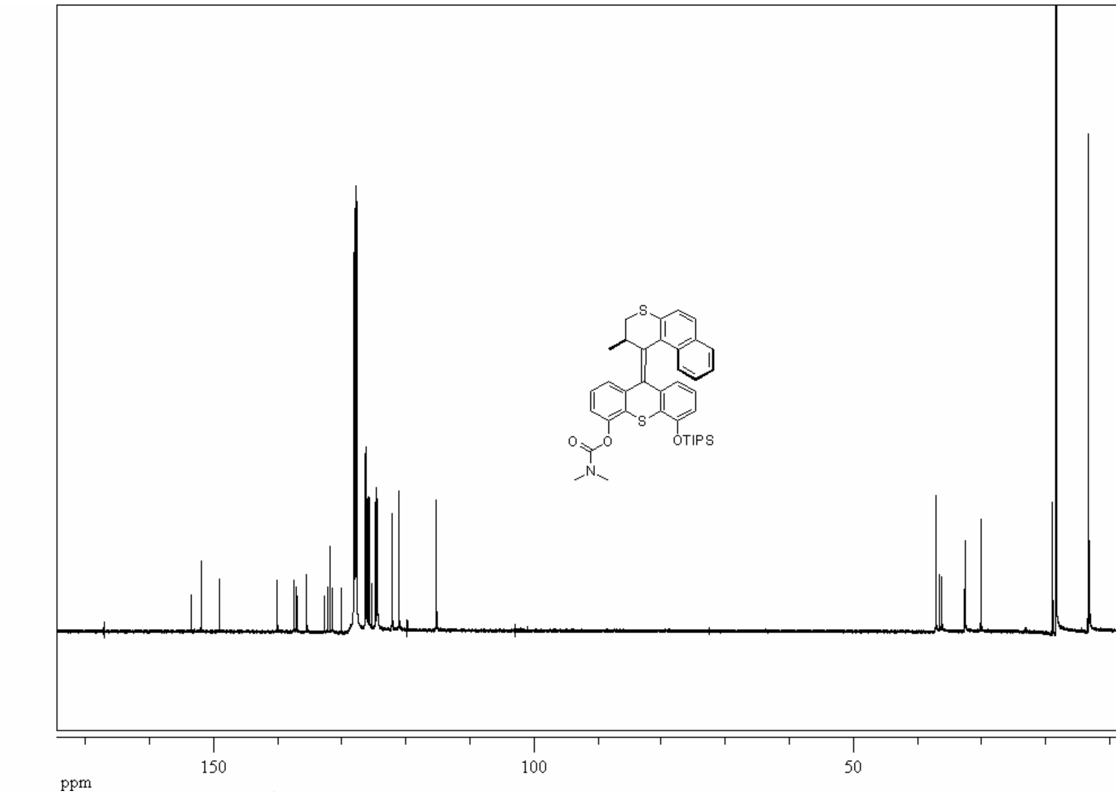


Figure 86. 100 MHz ^{13}C NMR spectrum of *cis*-**46** in C_6D_6.

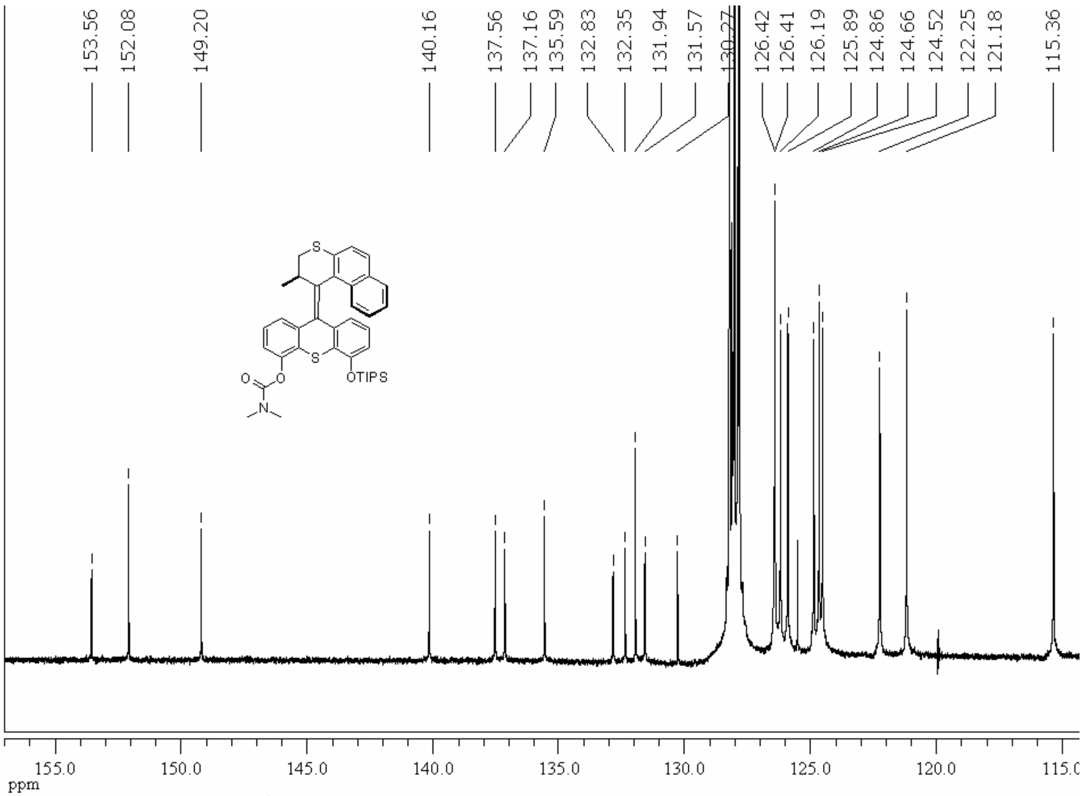


Figure 87. 100 MHz ^{13}C NMR spectrum of *cis*-**46** in C_6D_6.

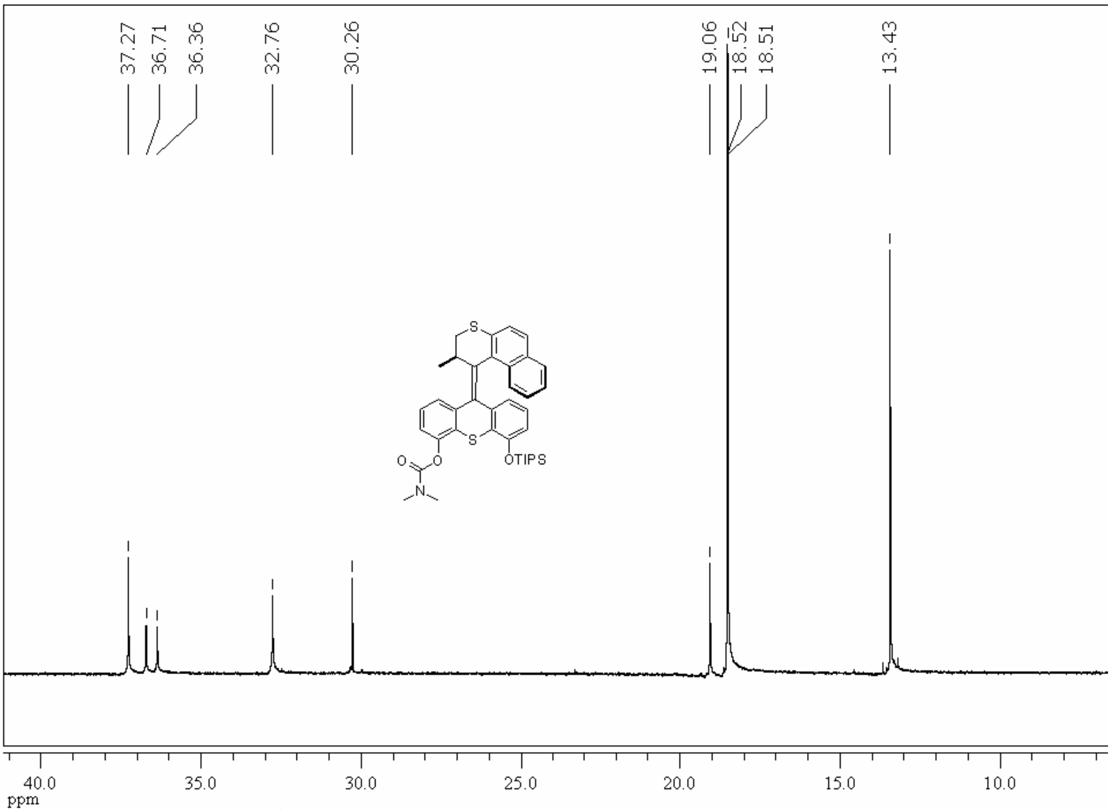


Figure 88. 100 MHz ^{13}C NMR spectrum of *cis*-**46** in C_6D_6.

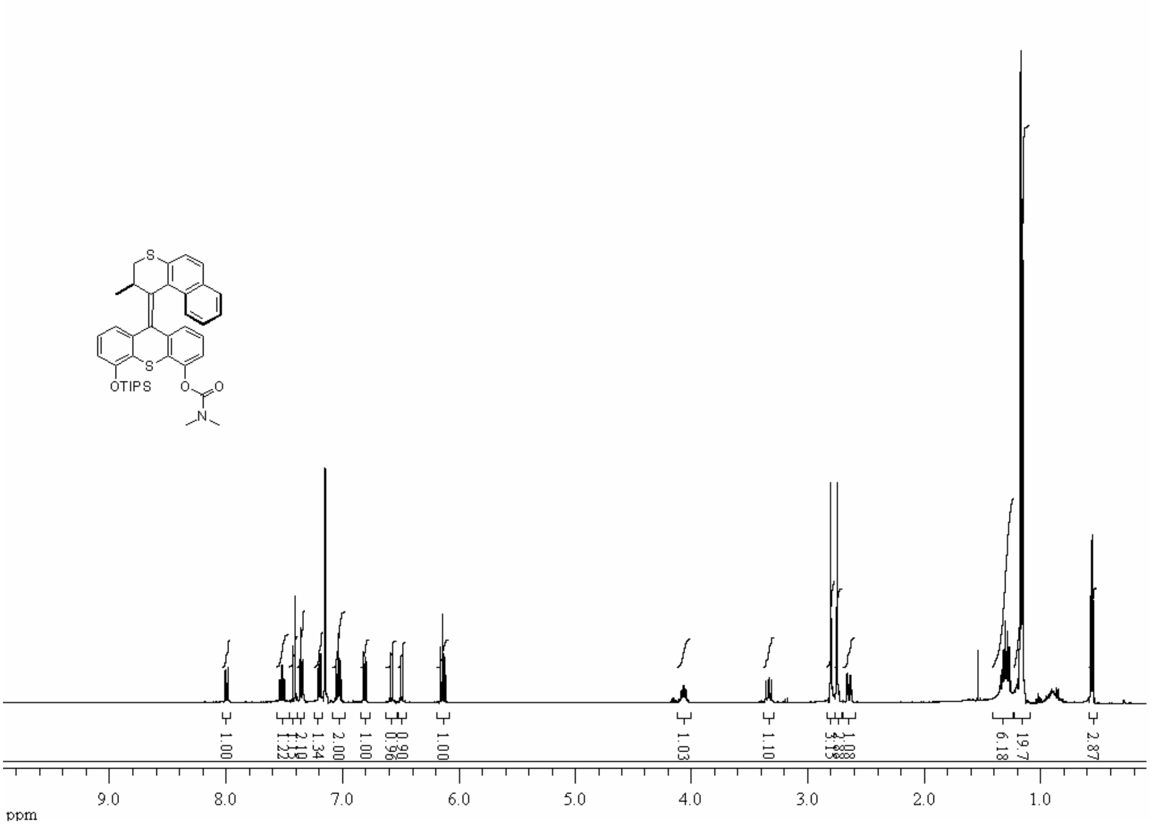


Figure 89. 400 MHz ^1H NMR spectrum of *cis*-**46** in C_6D_6.

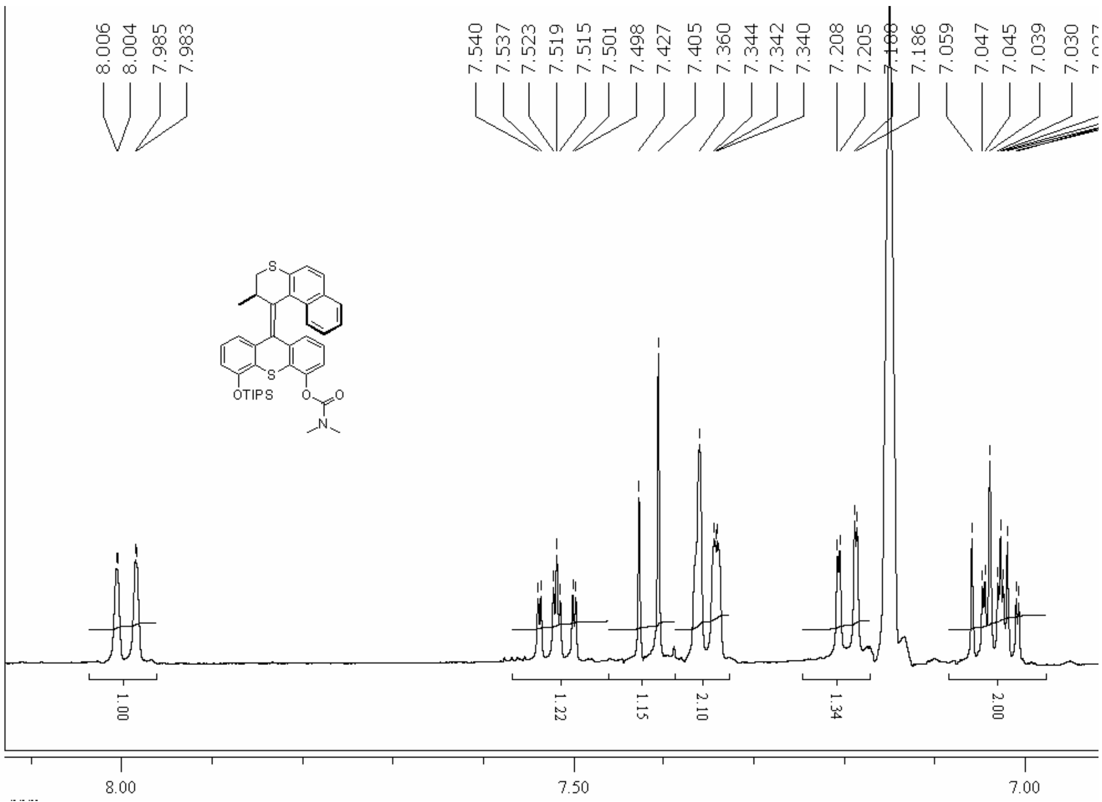


Figure 90. 400 MHz ^{1}H NMR spectrum of *cis*-**46** in CDCl$_3$ (expansion).

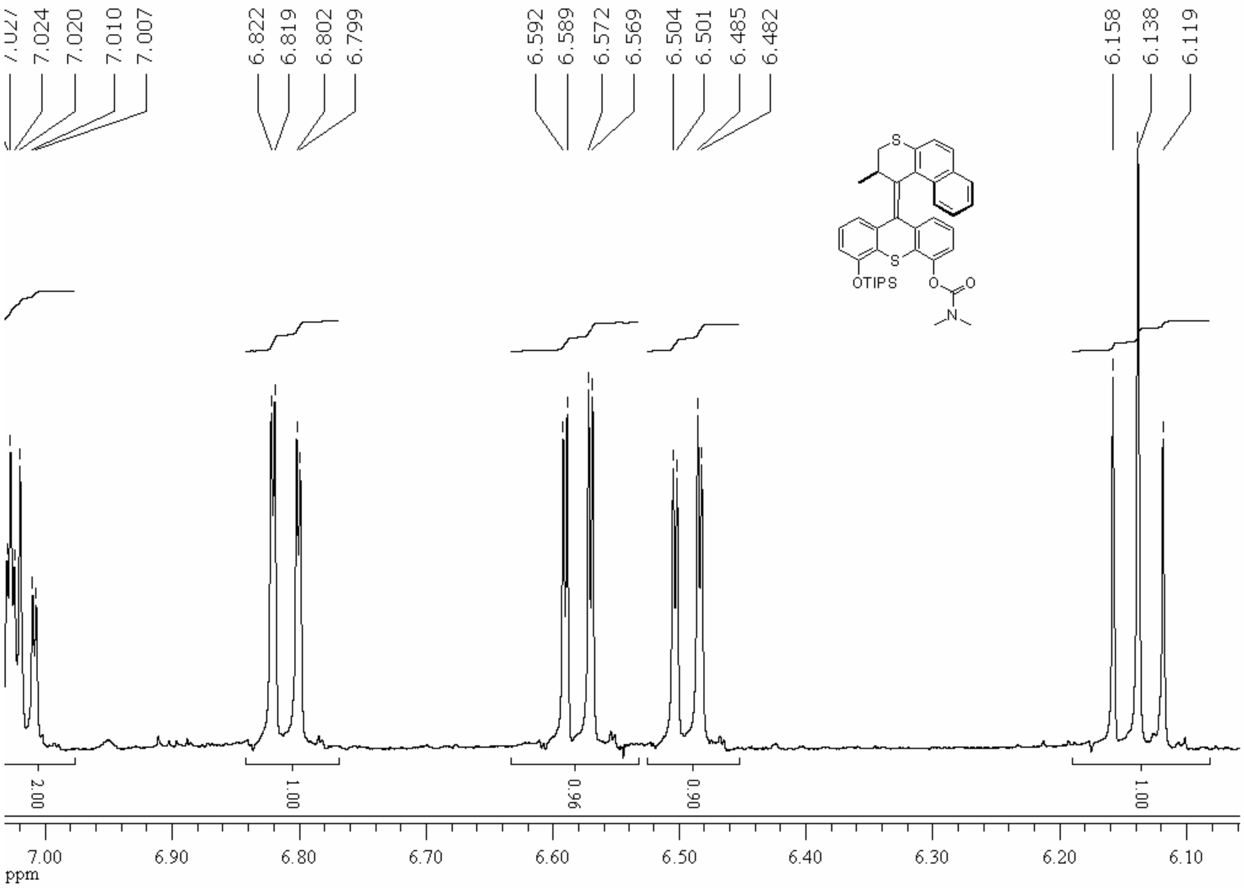


Figure 91. 400 MHz ^{1}H NMR spectrum of *cis*-**46** in CDCl$_3$ (expansion).

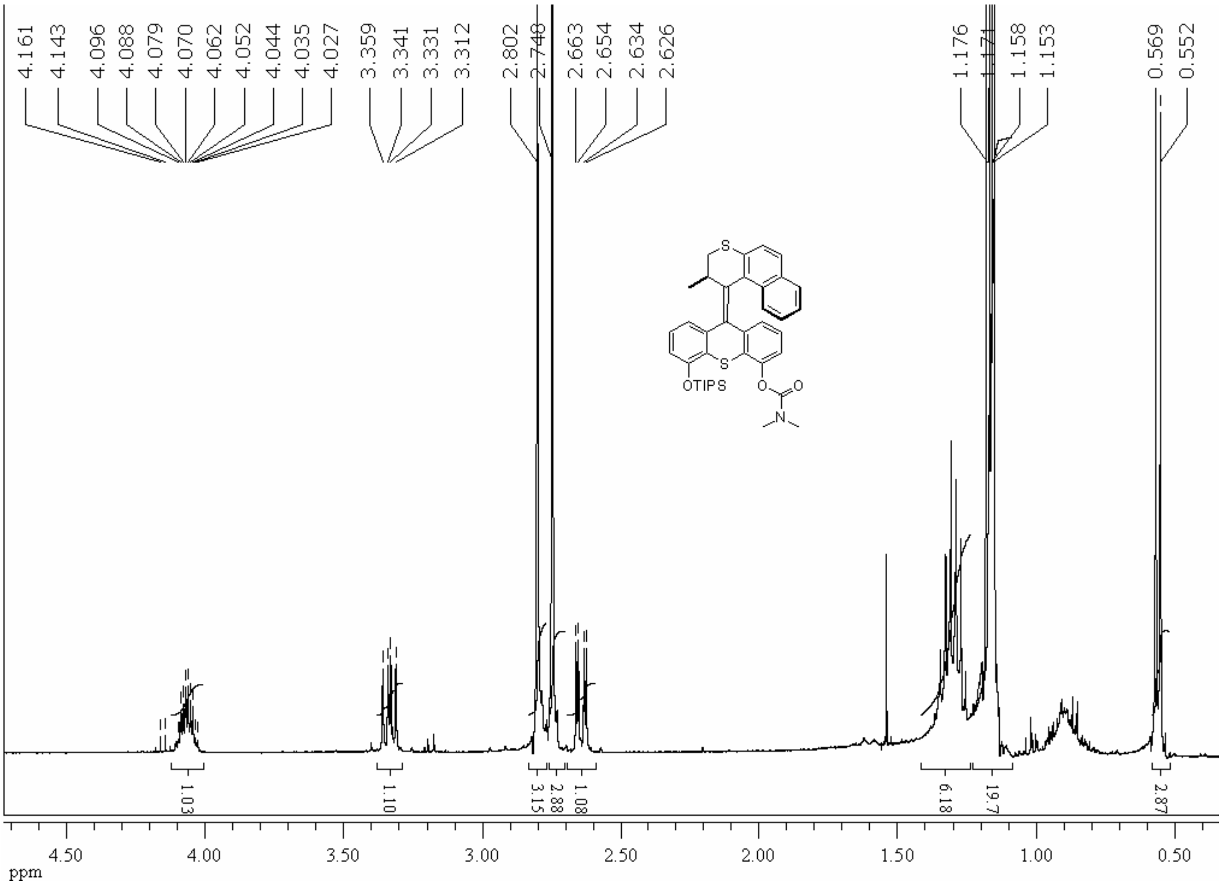


Figure 92. 400 MHz ^{1}H NMR spectrum of *cis*-**46** in C_6D_6 (expansion).

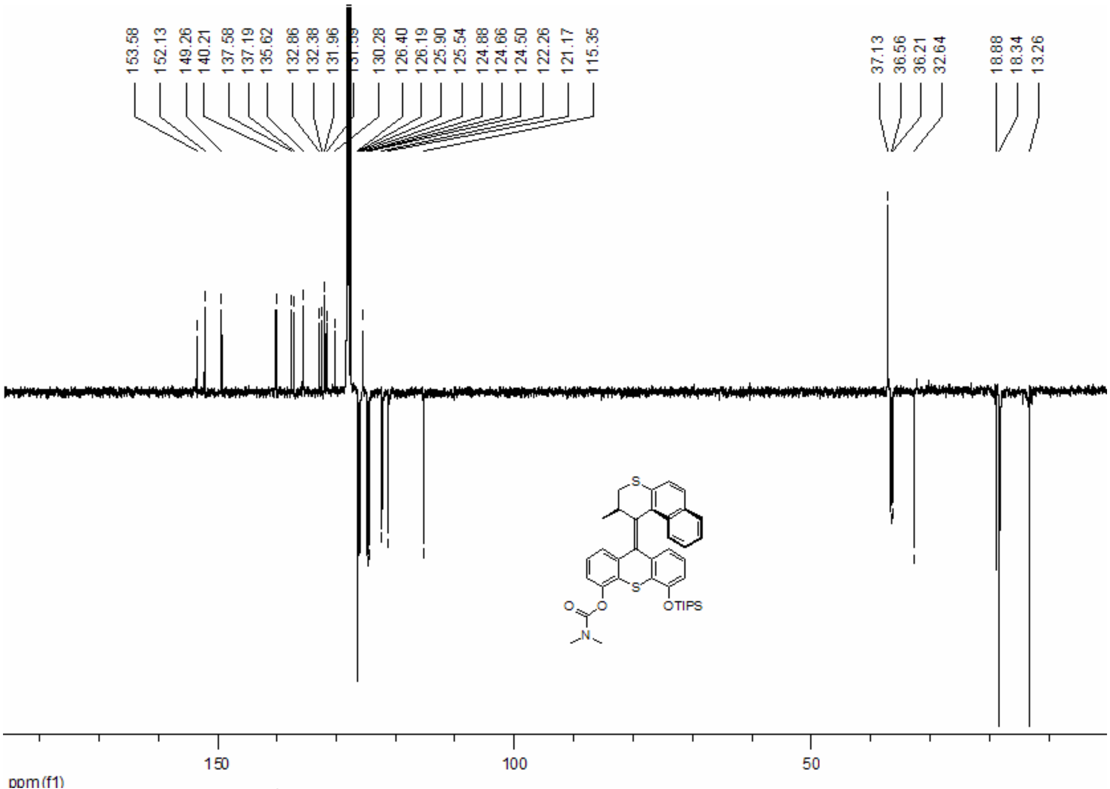


Figure 93. 100 MHz ^{13}C NMR spectrum of *trans*-**46** in C_6D_6.

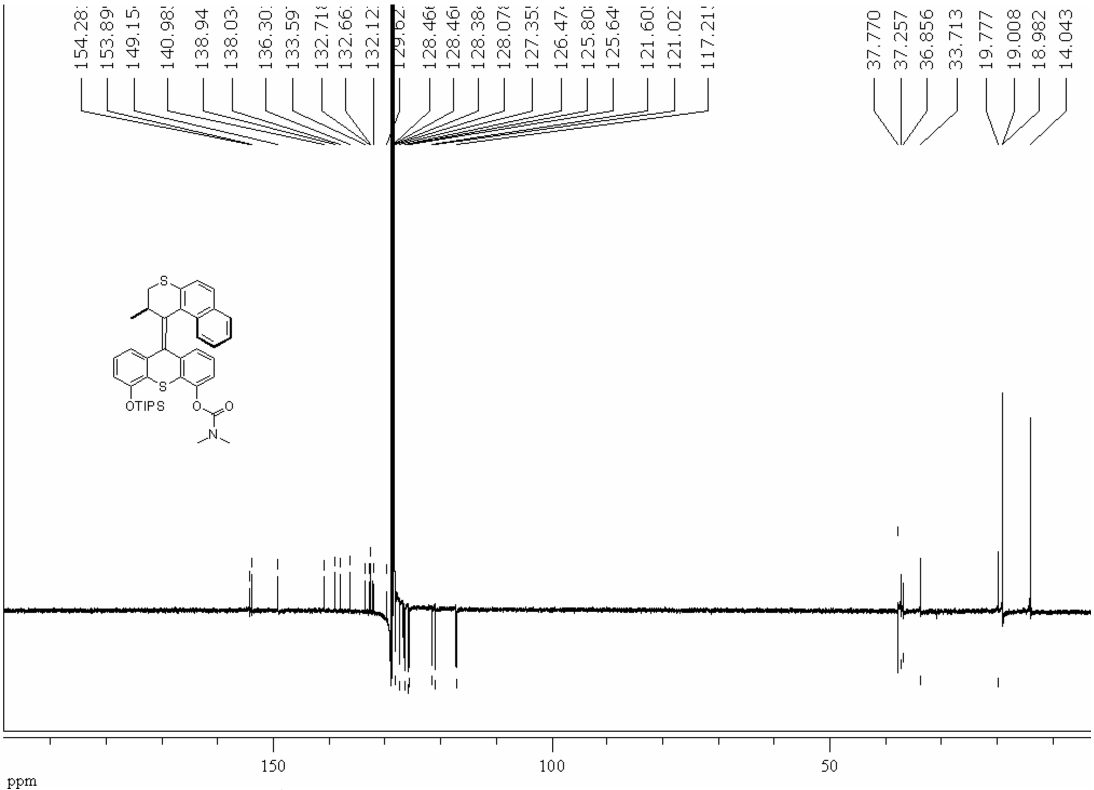


Figure 94. 100 MHz ^{13}C NMR spectrum of *trans*-**46** in C_6D_6.

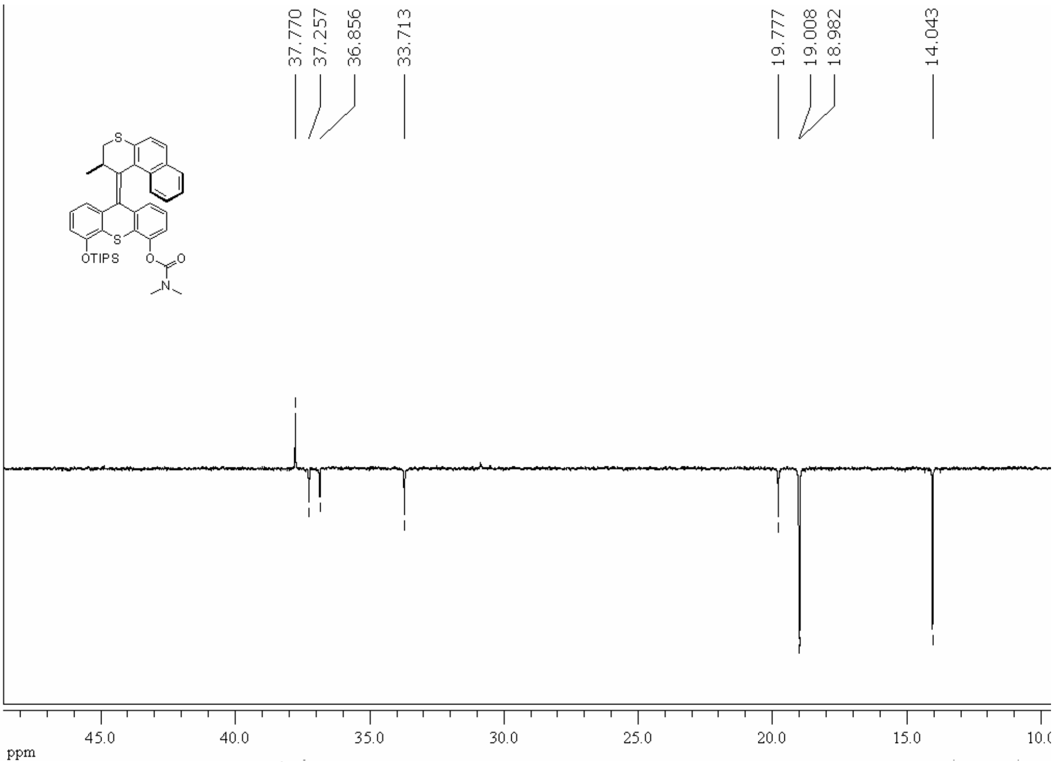


Figure 95. 100 MHz ^{13}C NMR spectrum of *trans*-**46** in C_6D_6.

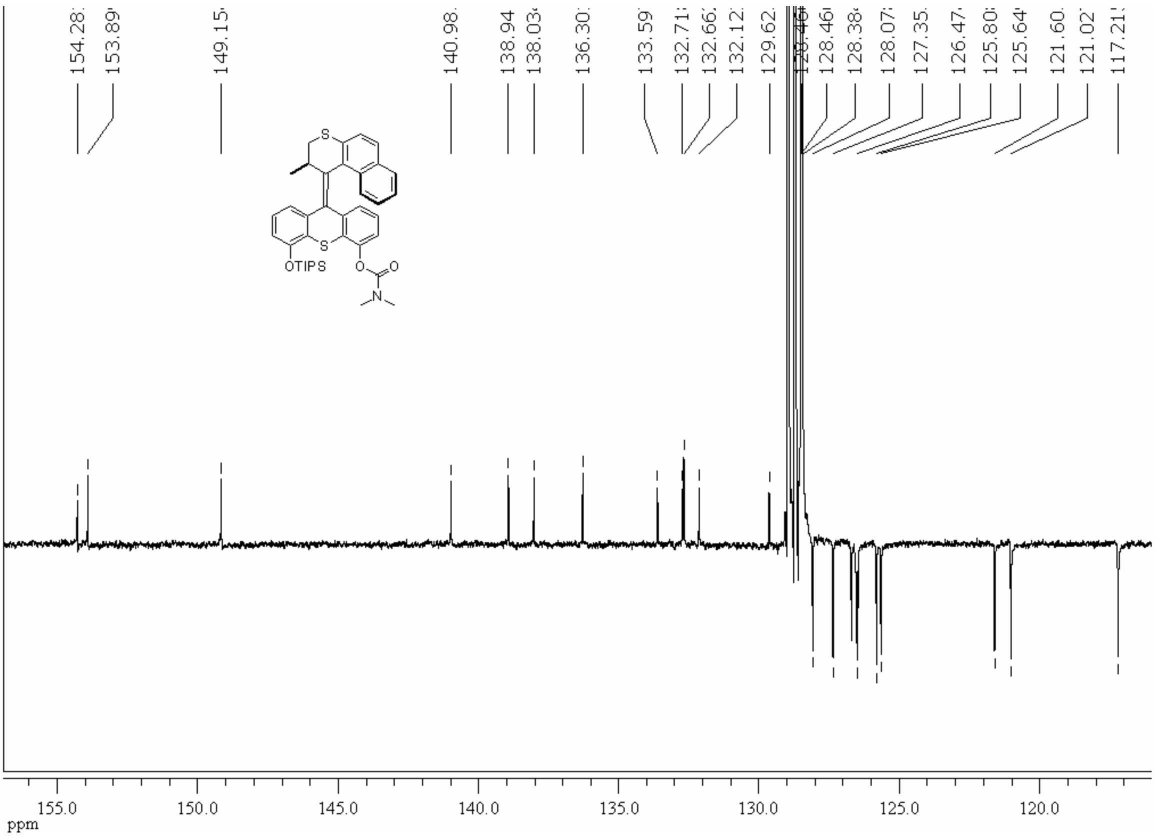


Figure 96. 100 MHz ^{13}C NMR spectrum of *trans*-**46** in C_6D_6.

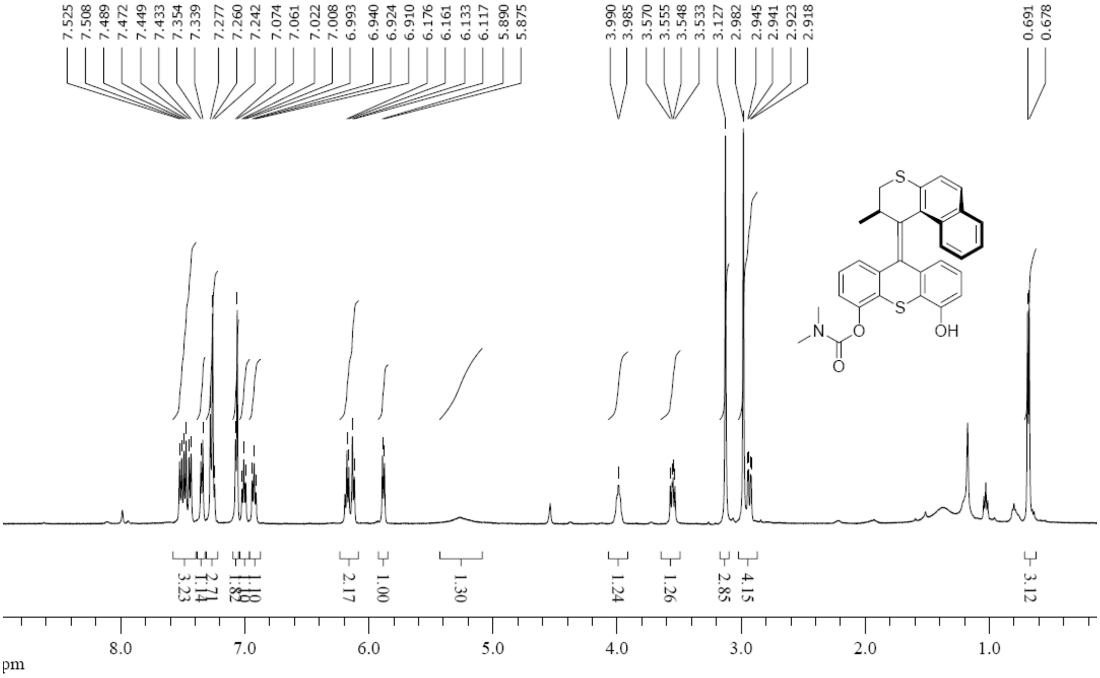


Figure 97. 400 MHz ^{1}H NMR spectrum of *trans*-**47** in $CDCl_3$.

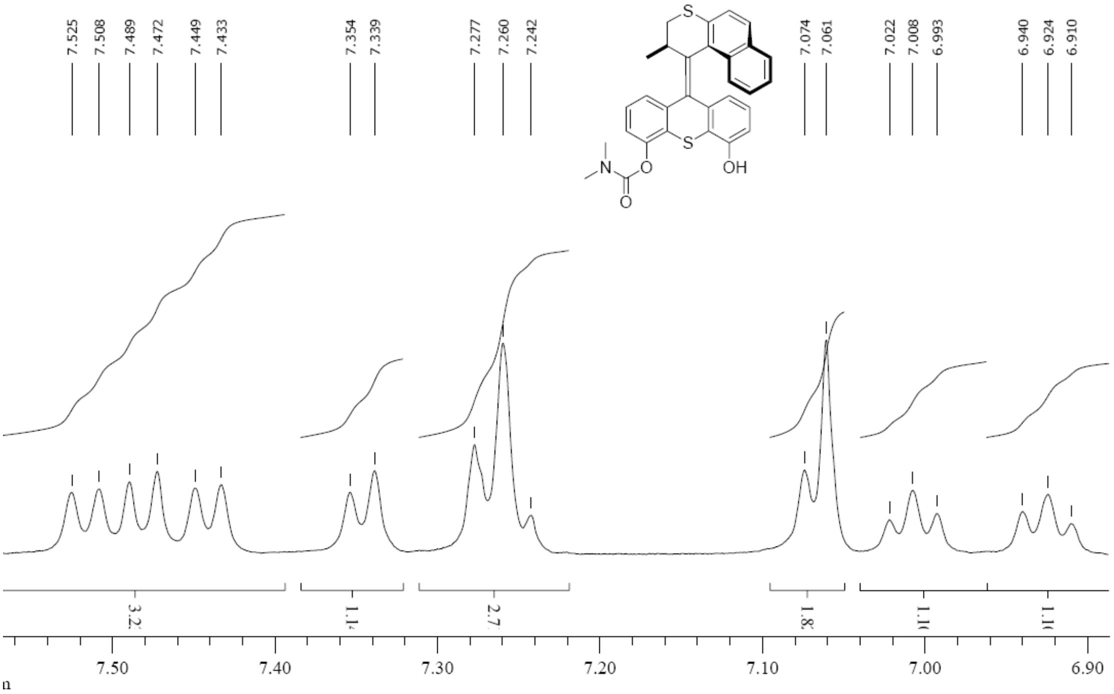


Figure 98. 400 MHz ^{1}H NMR spectrum of *trans*-**47** in CDCl$_3$ (expansion).

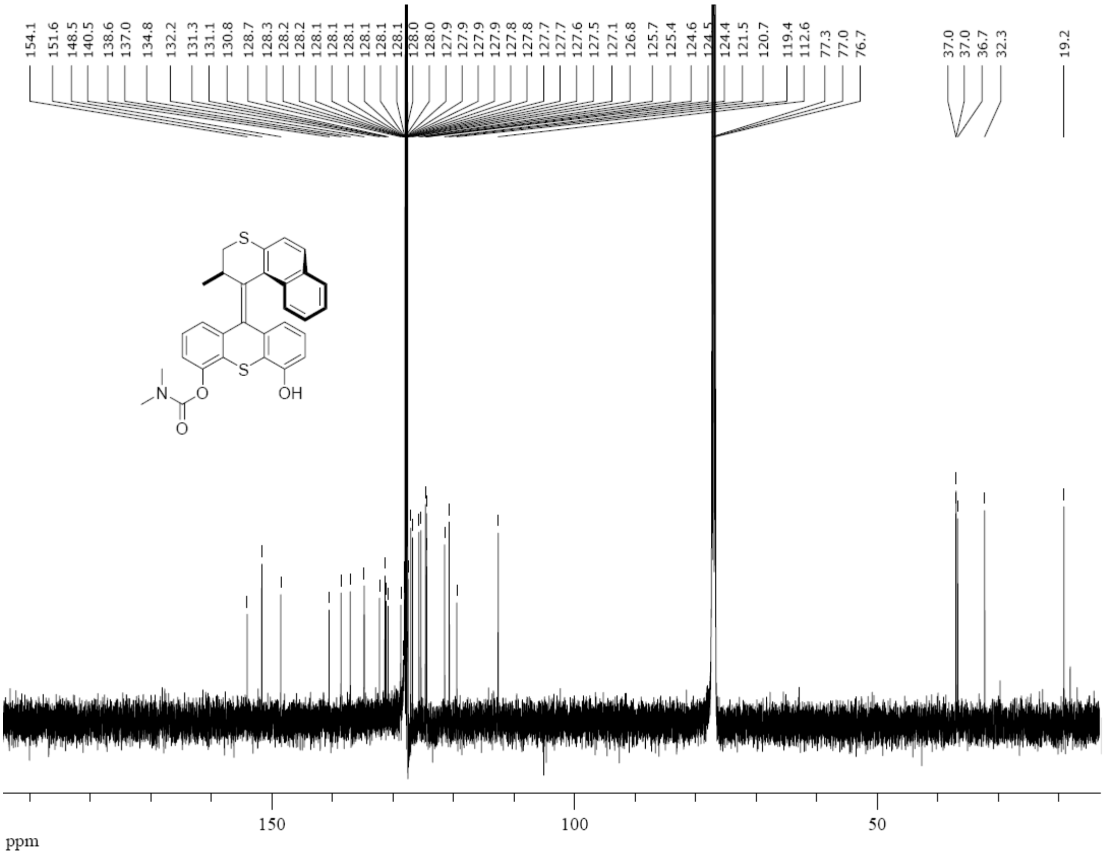


Figure 99. 125 MHz ^{13}C NMR spectrum of a sat'd sol'n of *trans*-**47** in CDCl$_3$. (nb: some benzene-D$_6$ was present, accounting for the large peak at 128 ppm, this compound was too poorly soluble in benzene d$_6$ to obtain a satisfactory ^{13}C NMR spectrum.)

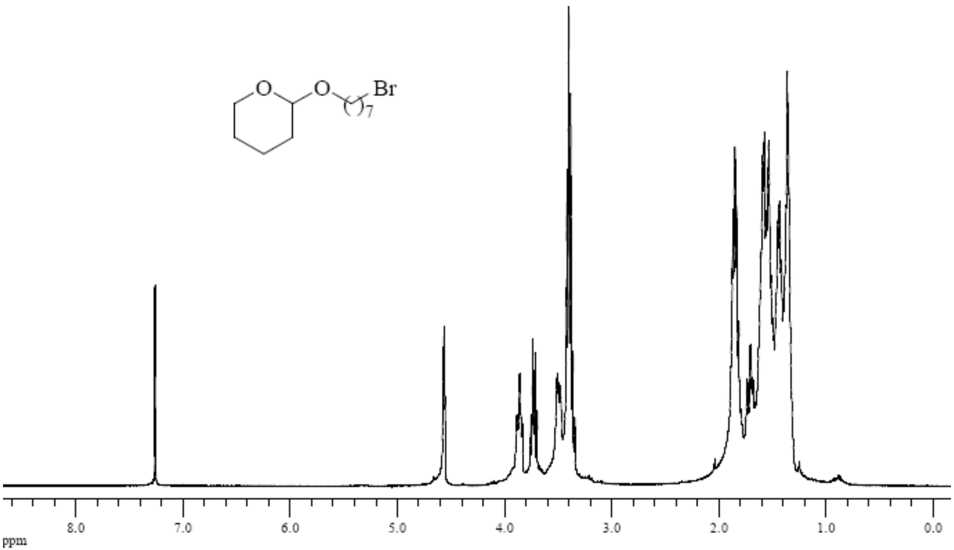


Figure 100. 400 MHz ^{1}H NMR spectrum of cyclic acetal in $CDCl_3$.

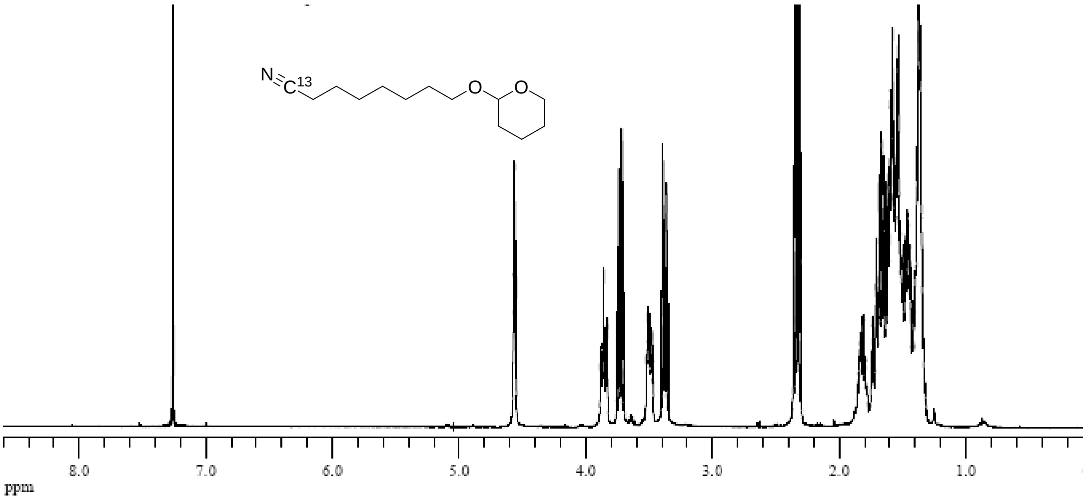


Figure 101. 400 MHz ^{1}H NMR spectrum of *8*-^{13}C-*8-(tetrahydro-pyran-2-yloxy)-octanenitrile* in $CDCl_3$.

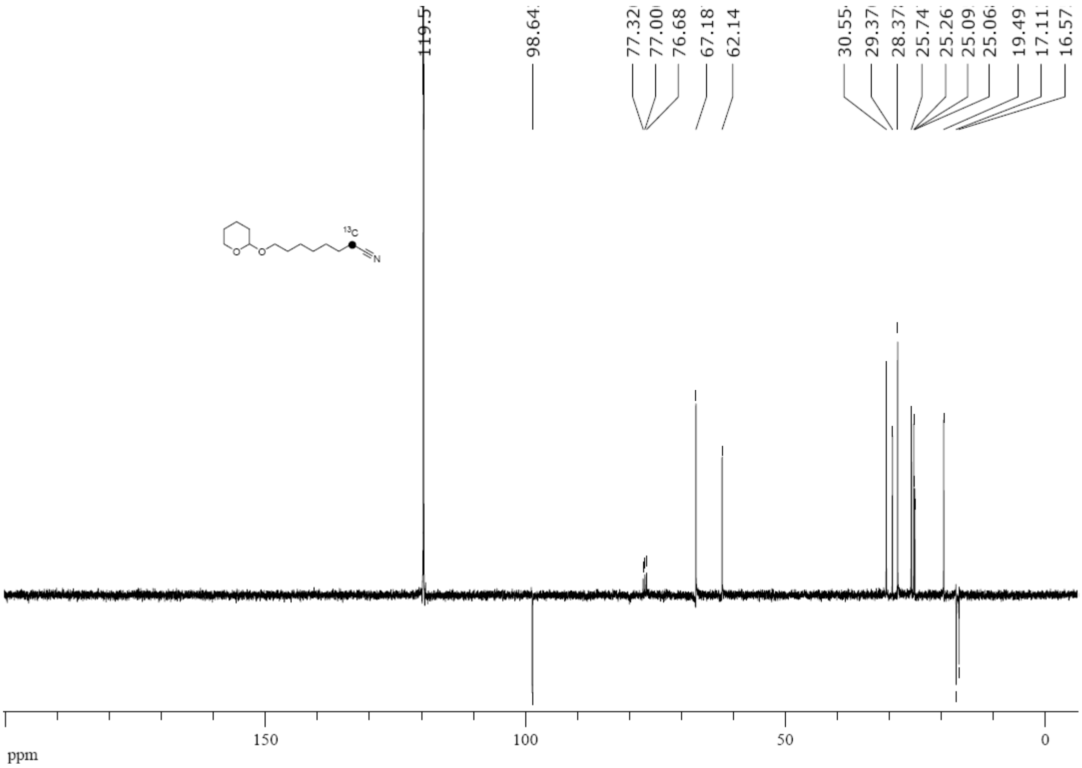


Figure 102. 100 MHz ^{13}C NMR (APT) spectrum of *8-*^{13}C*-8-(tetrahydro-pyran-2-yloxy)-octanenitrile* in $CDCl_3$.

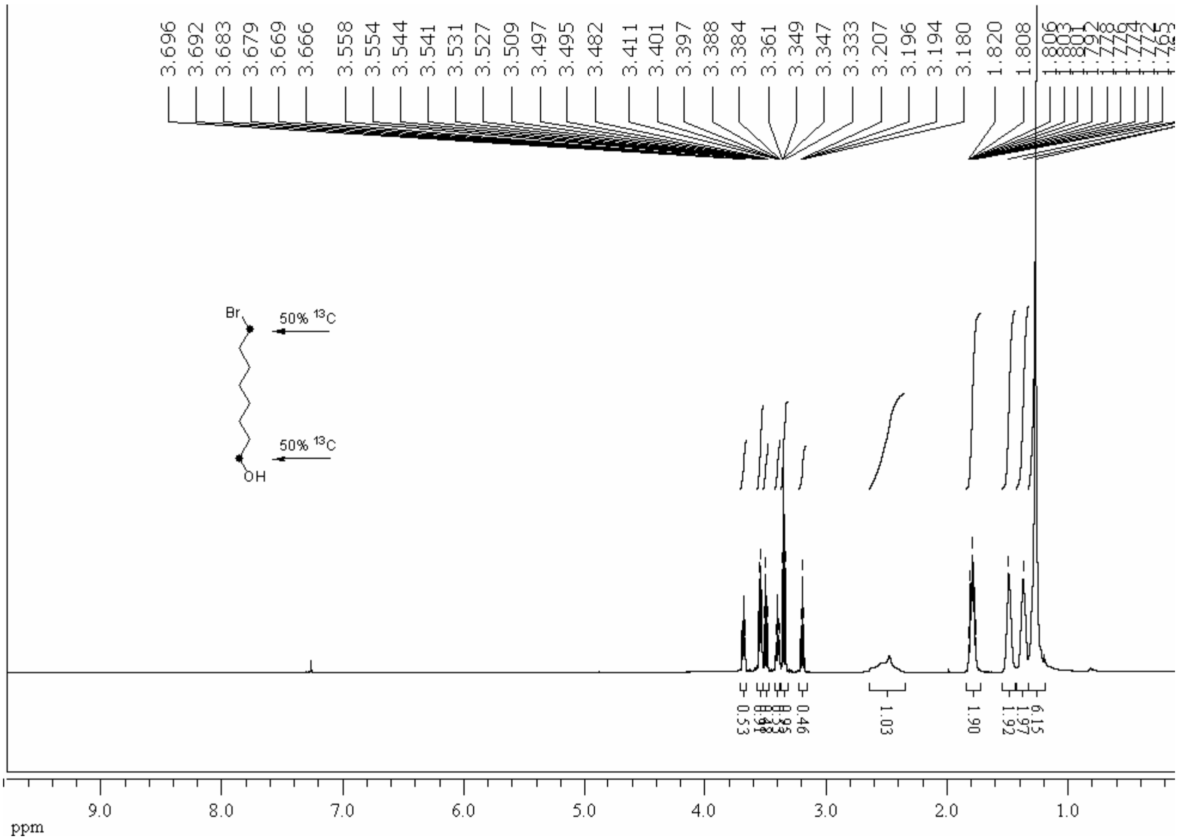


Figure 103. 400 MHz ^{1}H NMR spectrum of **48** in $CDCl_3$.

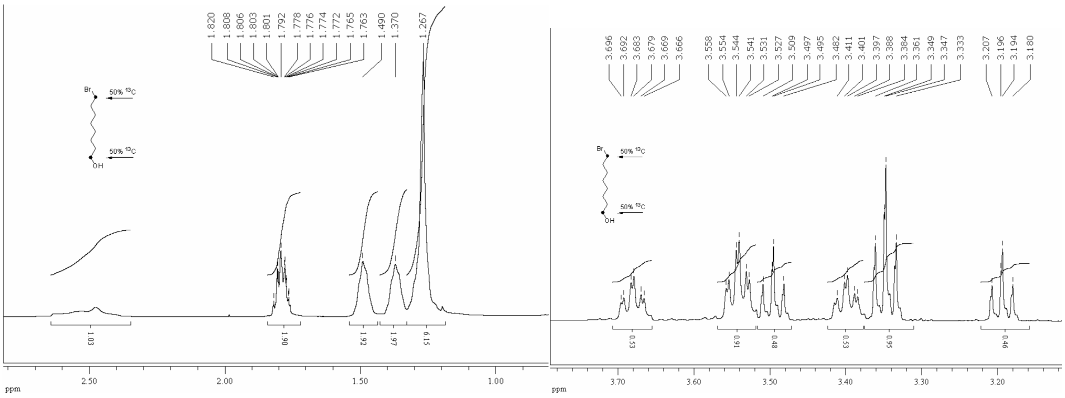


Figure 104. 400 MHz ^{1}H NMR spectrum of **48** in CDCl$_3$ (expansions).

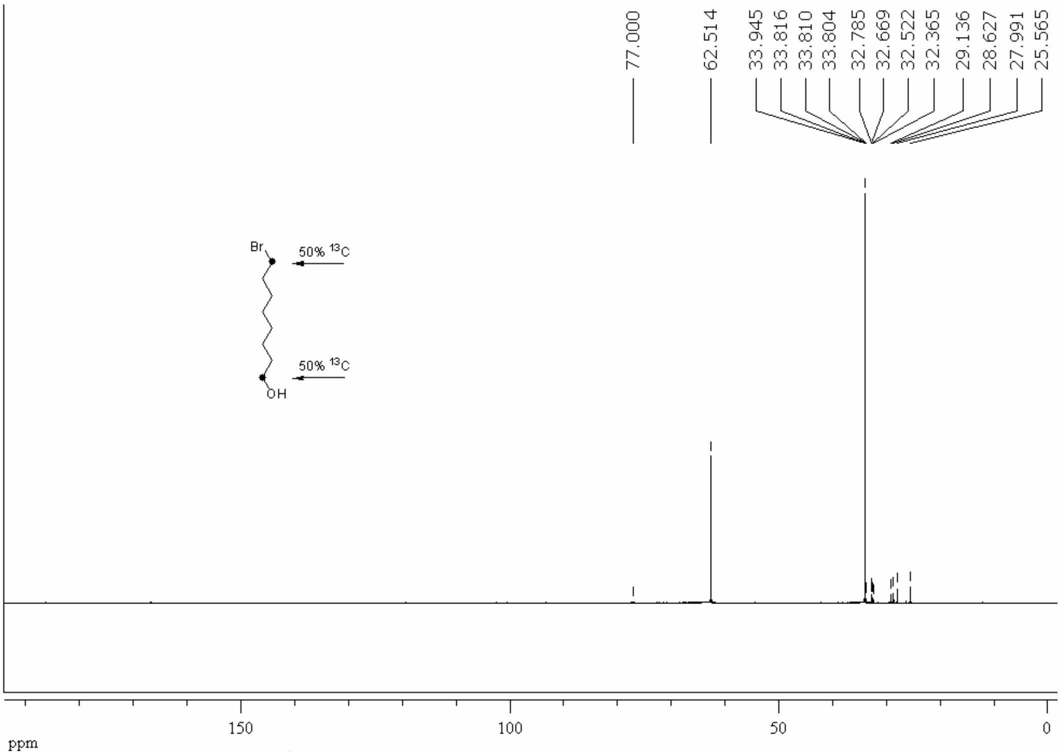


Figure 105. 100 MHz ^{13}C NMR spectrum of **48** in CDCl$_3$.

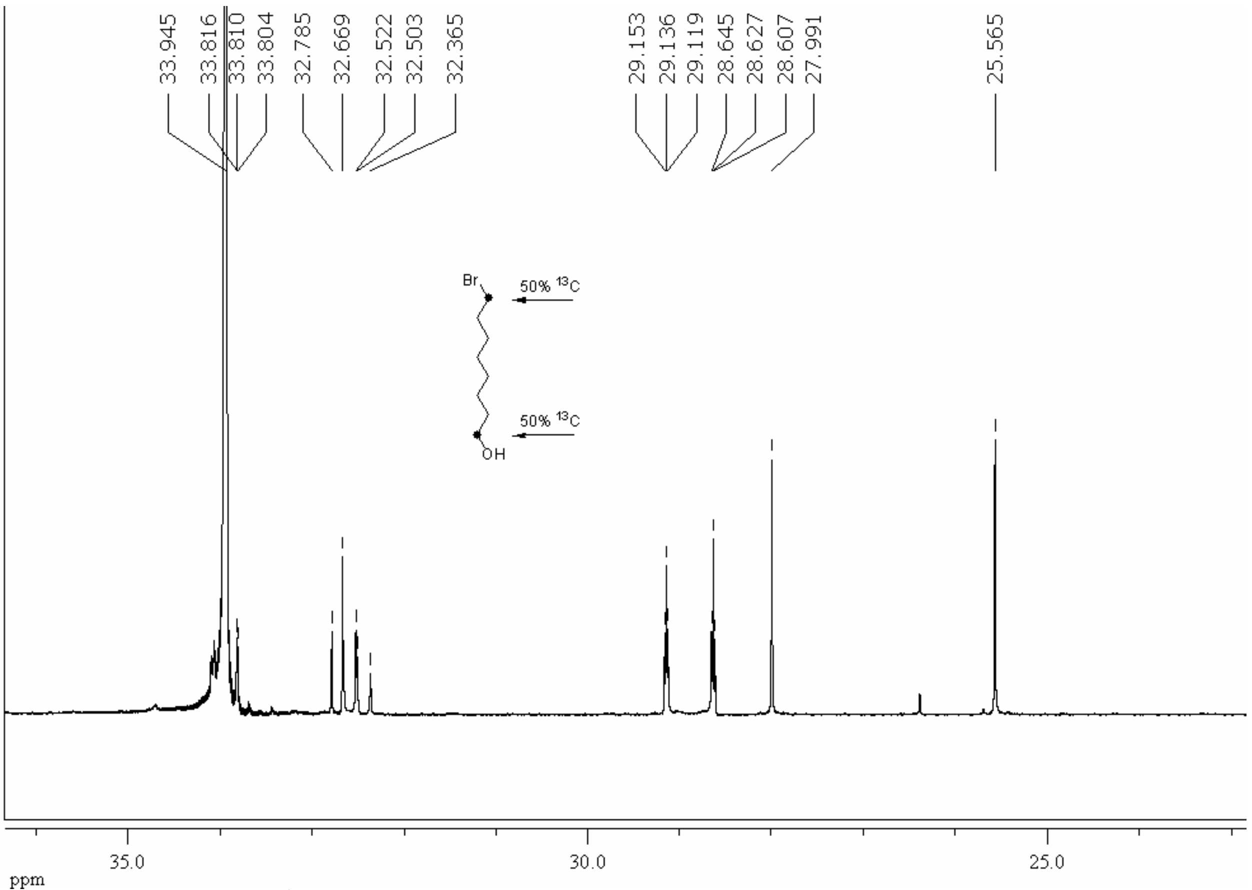


Figure 106. 100 MHz ^{13}C NMR spectrum of **48** in $CDCl_3$ (expansion).

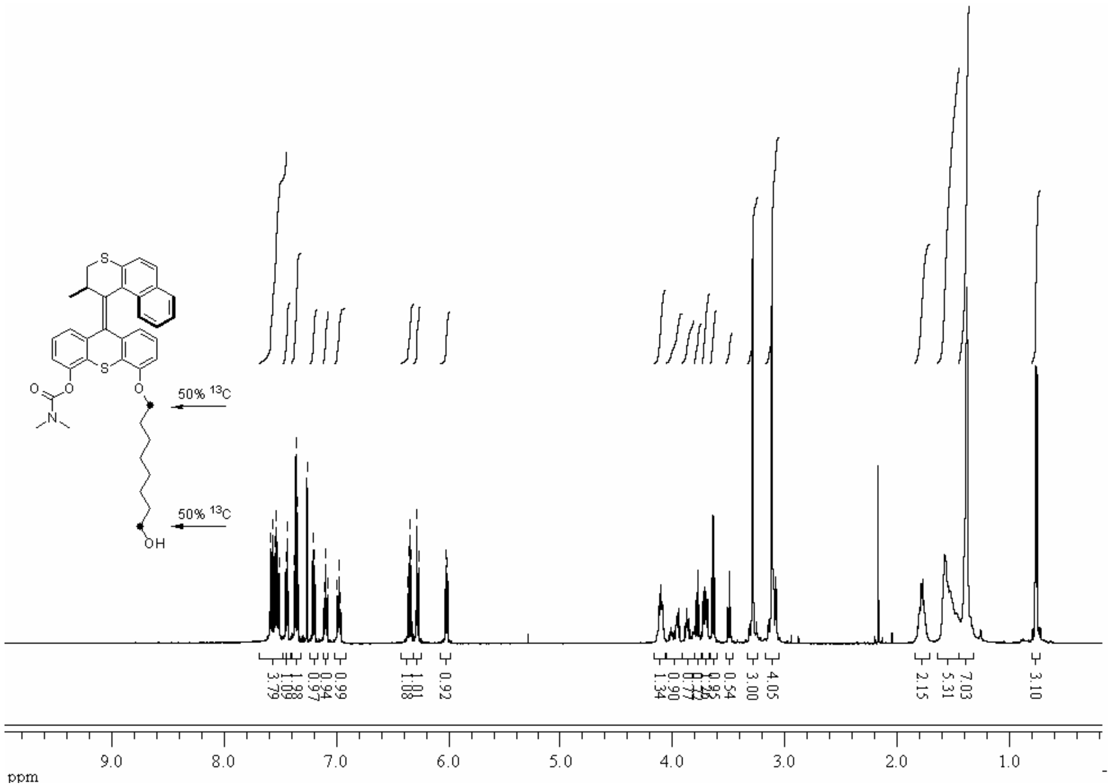


Figure 107. 400 MHz ^{1}H NMR spectrum of **49** in $CDCl_3$.

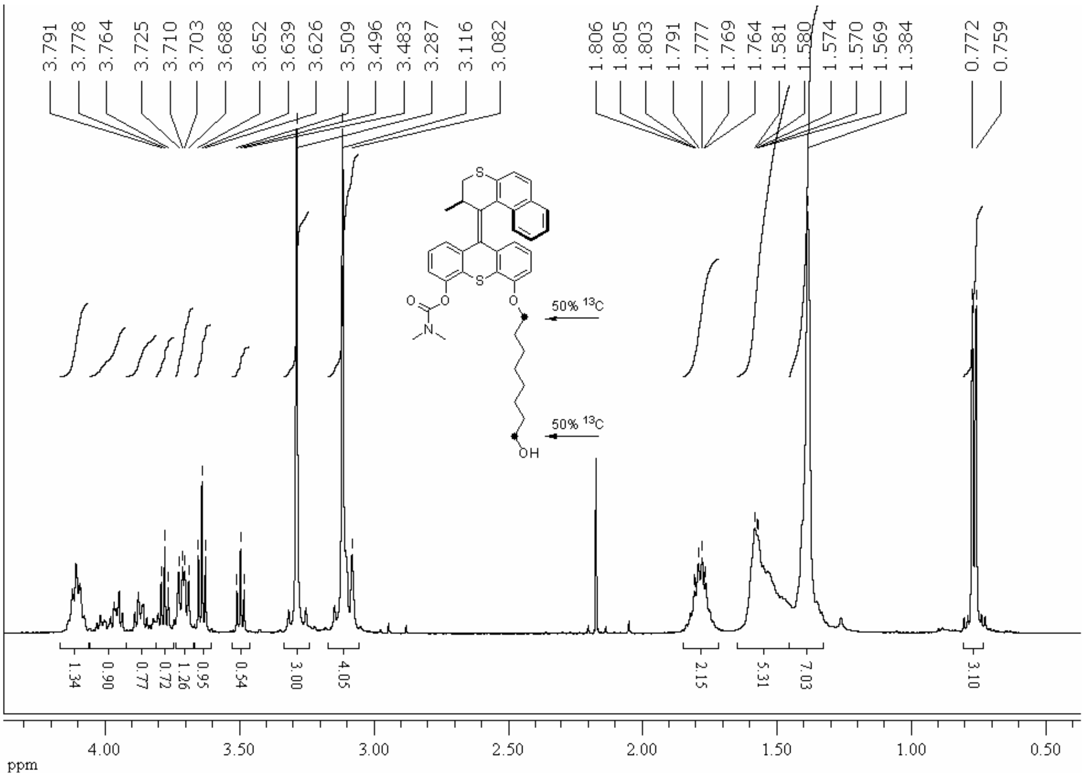


Figure 108. 400 MHz ^{1}H NMR spectrum of **49** in CDCl$_3$.

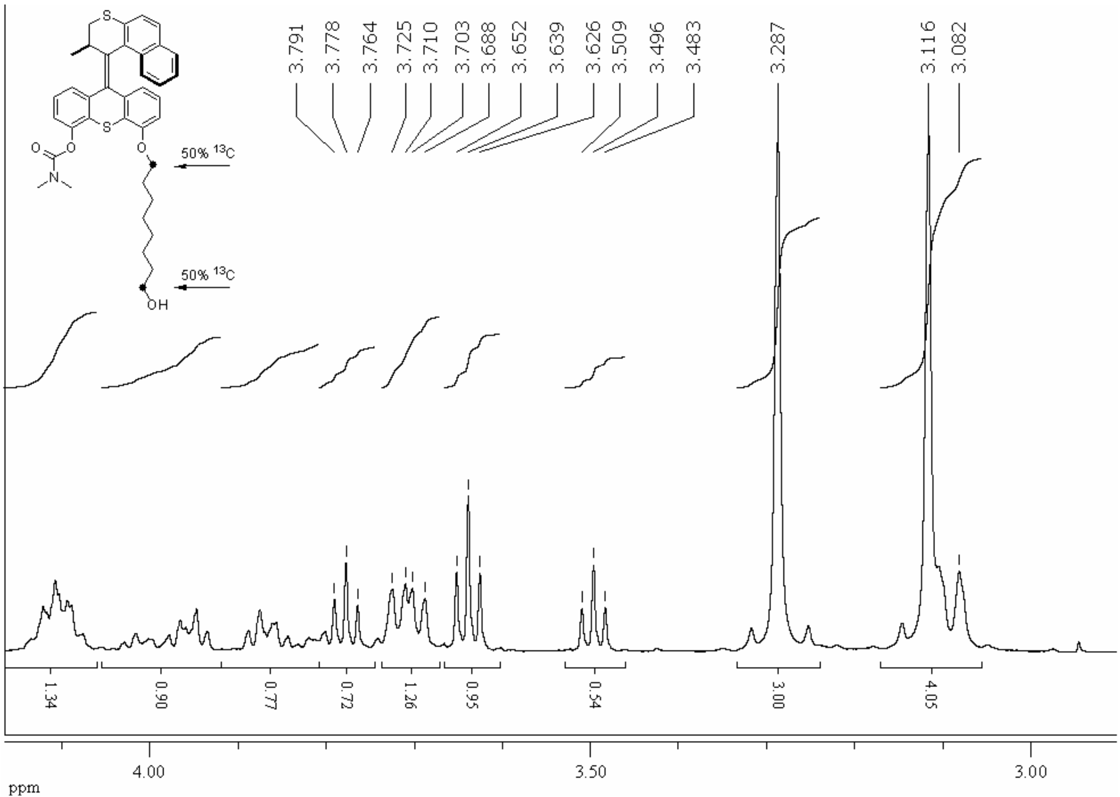


Figure 109. 400 MHz ^{1}H NMR spectrum of **49** in CDCl$_3$ (expansion).

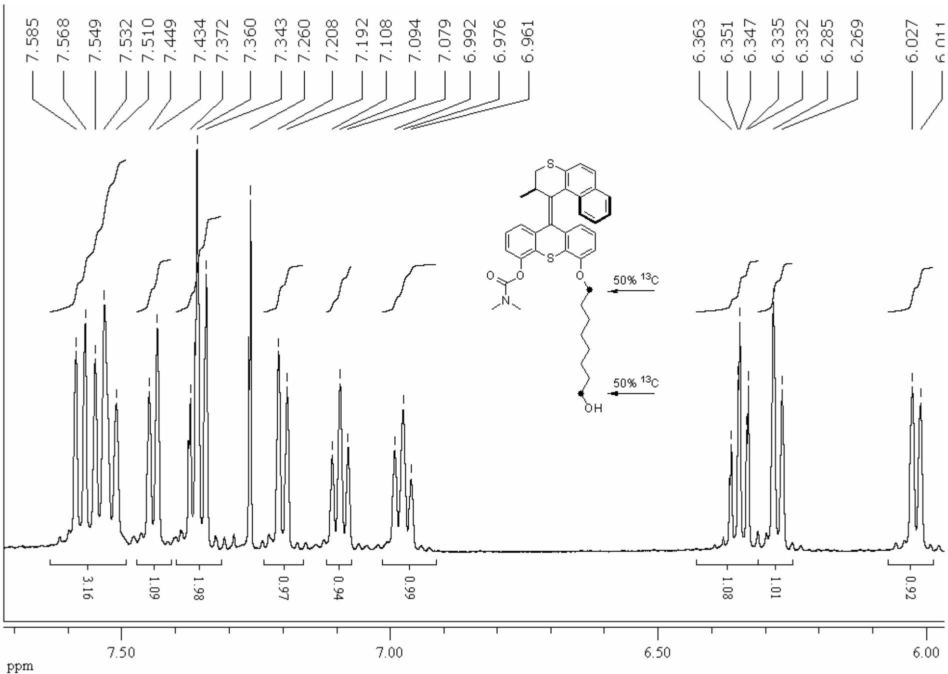


Figure 110. 400 MHz ^{1}H NMR spectrum of **49** in CDCl$_3$ (expansion).

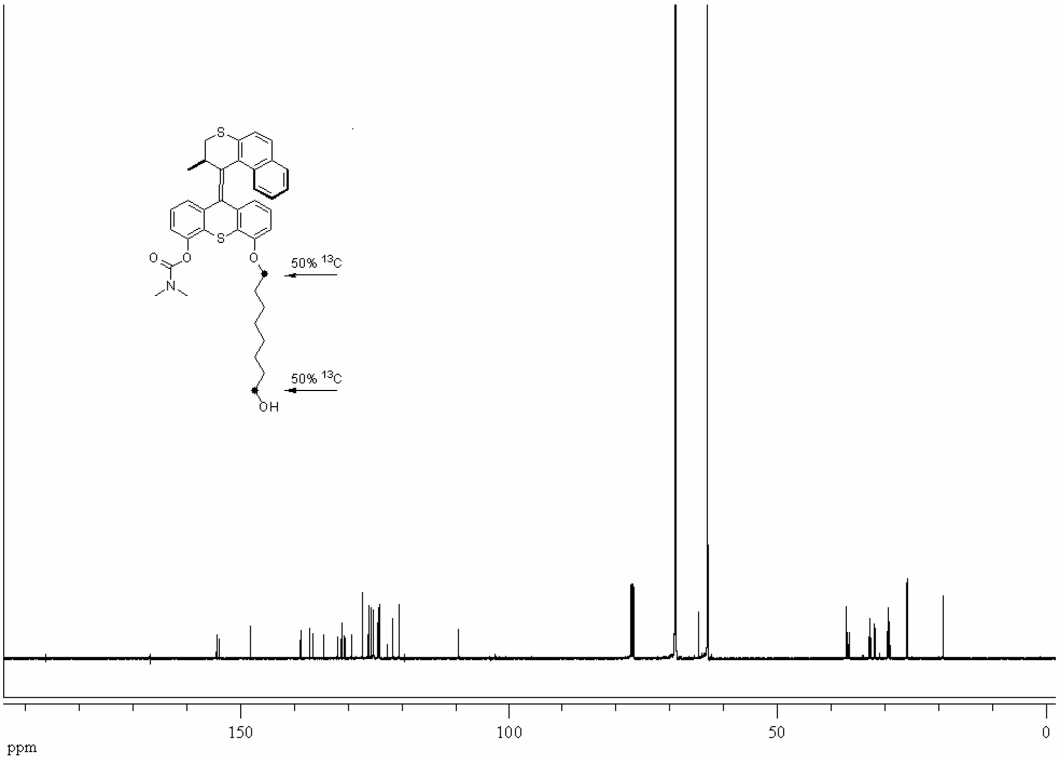


Figure 111. 100 MHz ^{13}C NMR spectrum of **49** in CDCl$_3$.

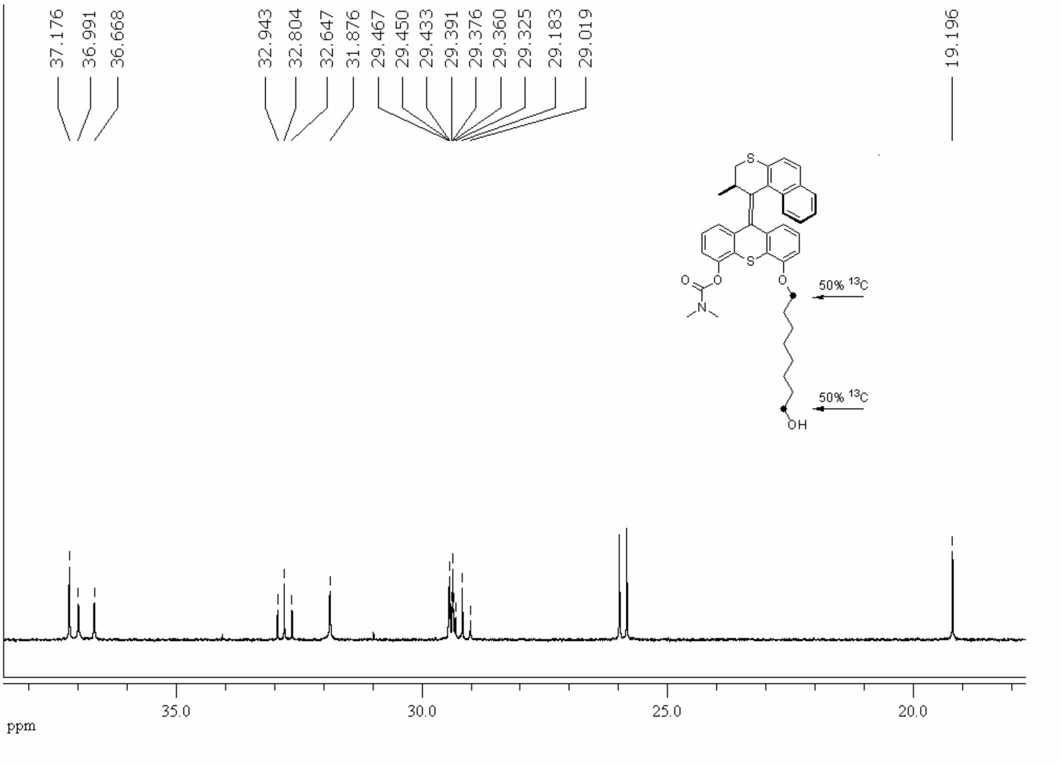


Figure 112. 400 MHz ^{1}H NMR spectrum of **49** in $CDCl_3$ (expansion).

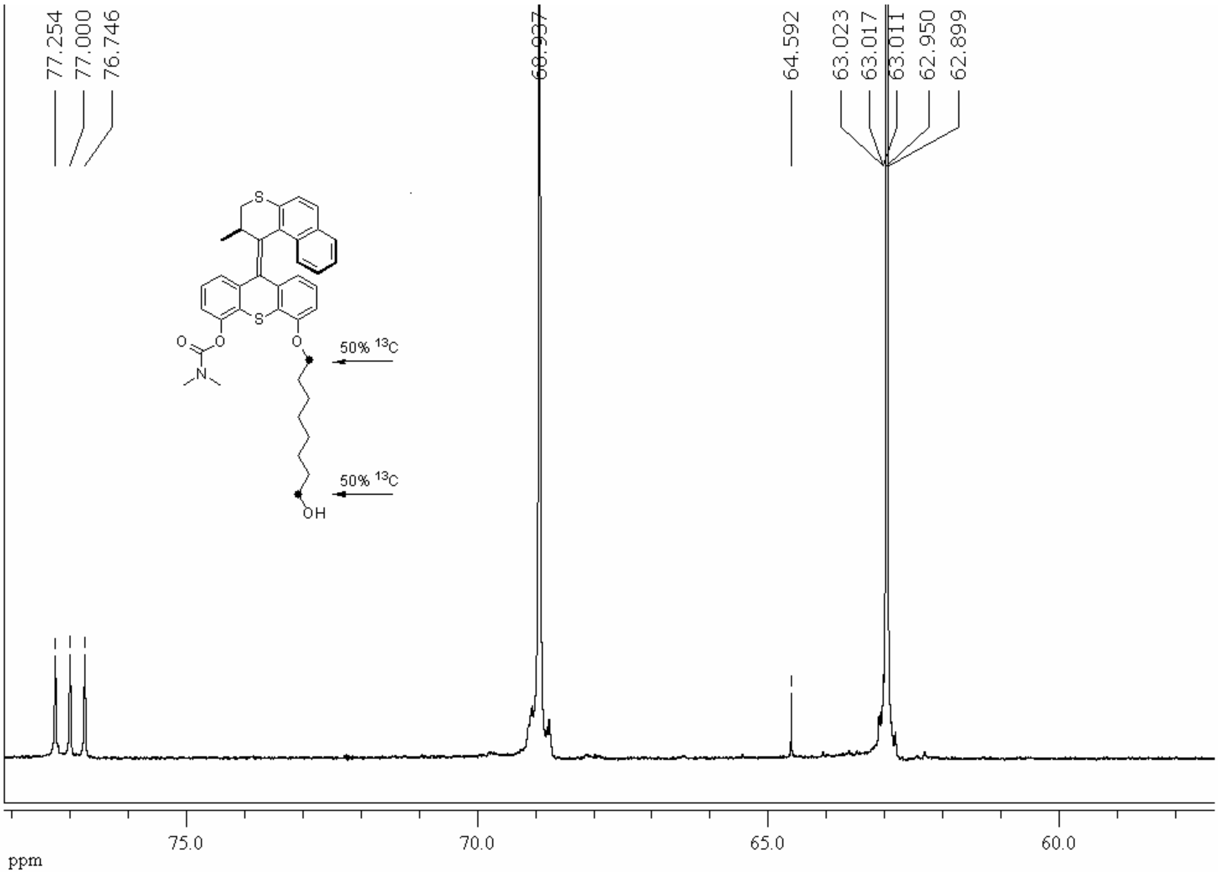


Figure 113. 400 MHz ^{1}H NMR spectrum of **49** in $CDCl_3$ (expansion).

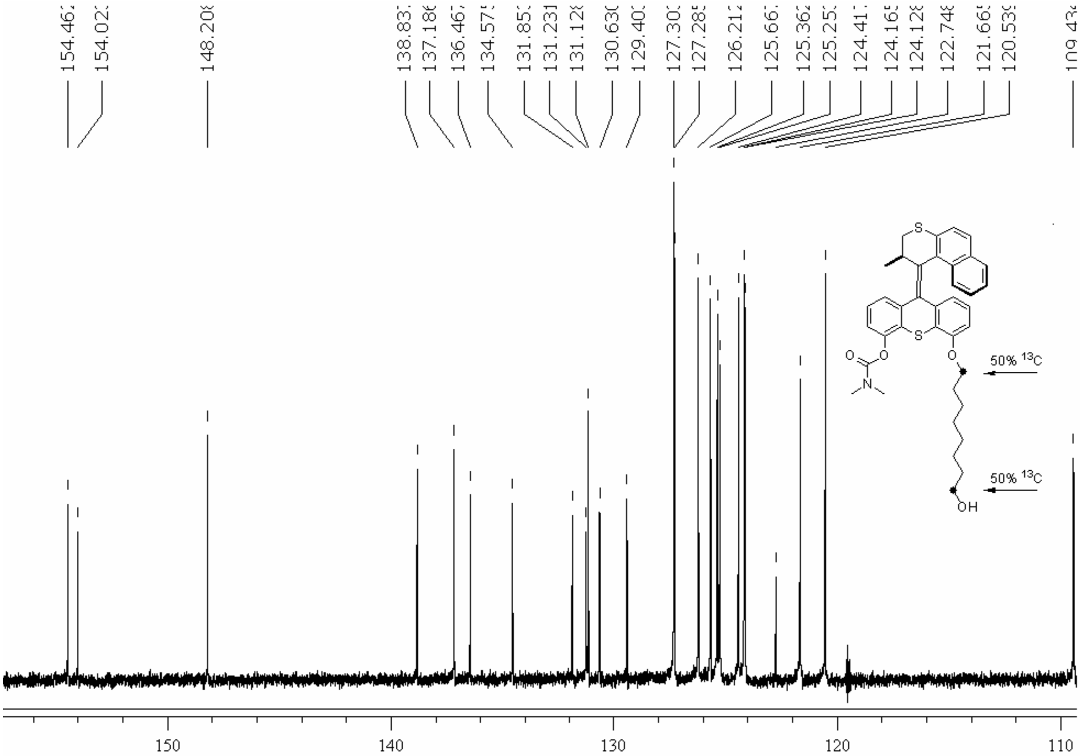


Figure 114. 400 MHz ^{1}H NMR spectrum of **49** in CDCl$_3$ (expansion).

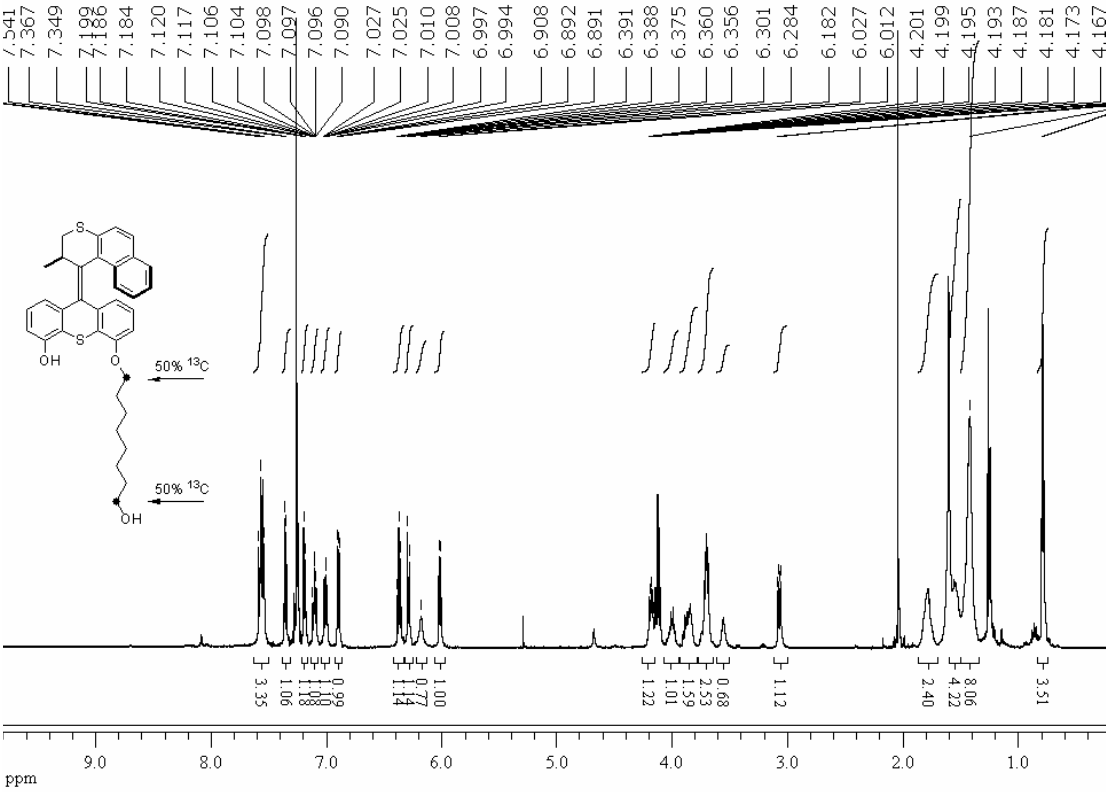


Figure 115. 400 MHz ^{1}H NMR spectrum of **51** in CDCl$_3$.

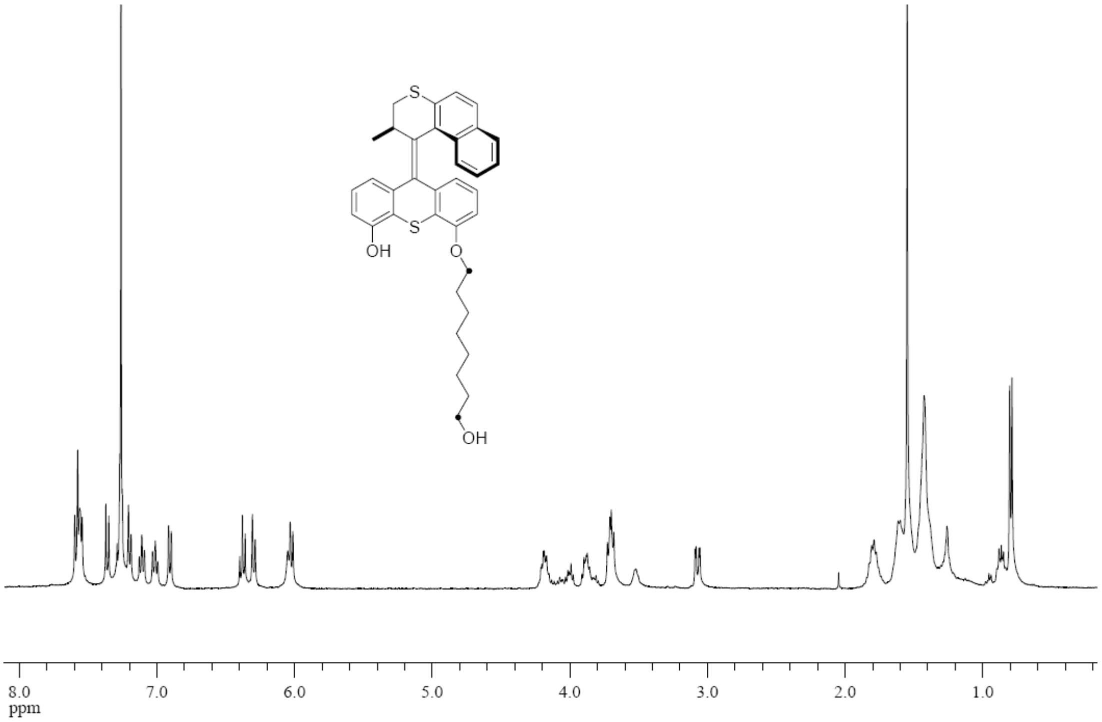
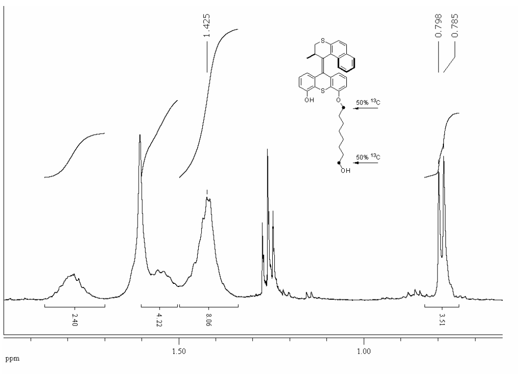
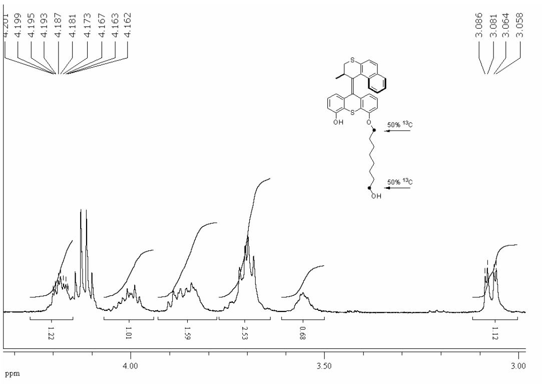


Figure 116. 400 MHz ^{1}H NMR spectrum of **50** in CDCl$_3$.





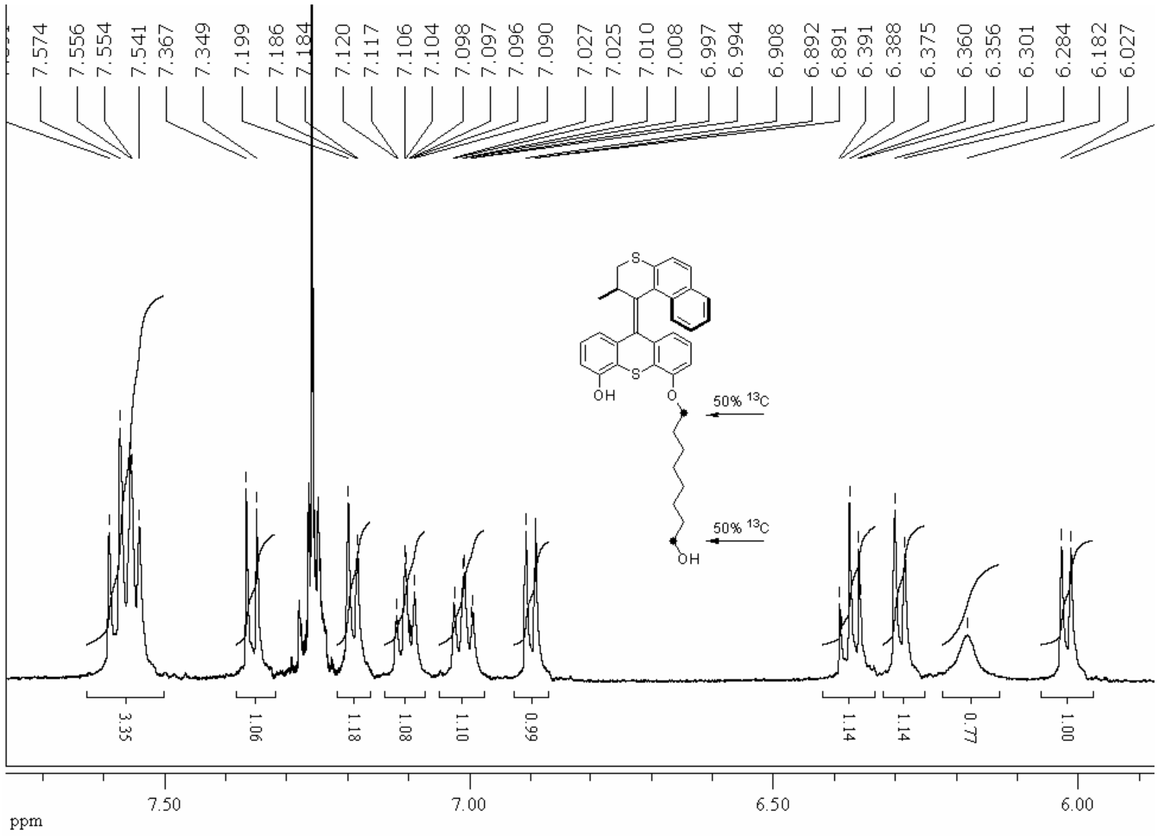


Figure 117. 400 MHz ^{1}H NMR spectrum of **50** in $CDCl_3$ (expansions).

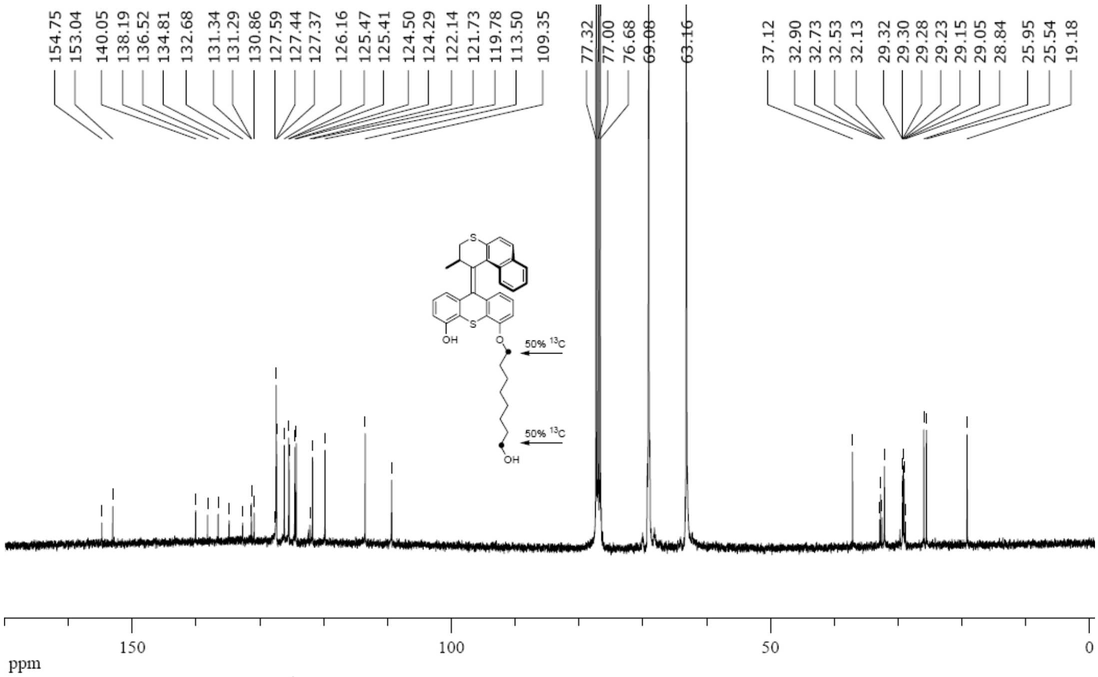


Figure 118. 100 MHz ^{13}C NMR spectrum of **51** in $CDCl_3$.

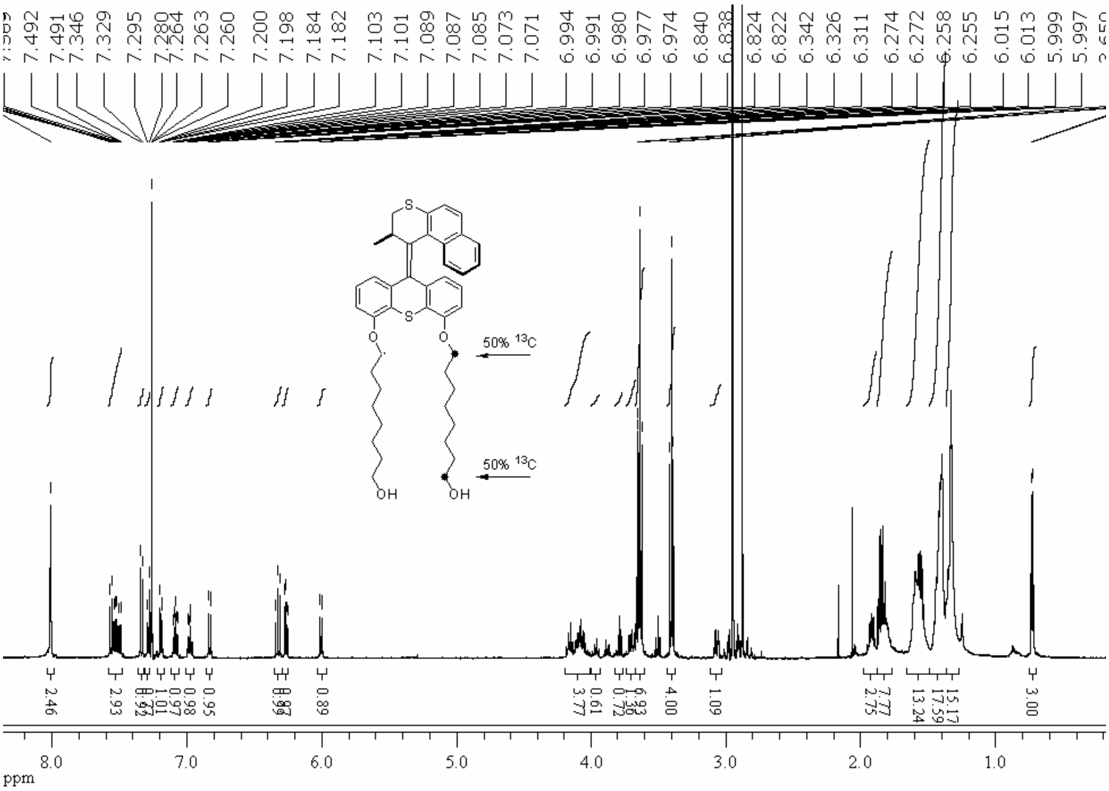


Figure 119. 400 MHz ^{1}H NMR spectrum of **52** in $CDCl_3$.

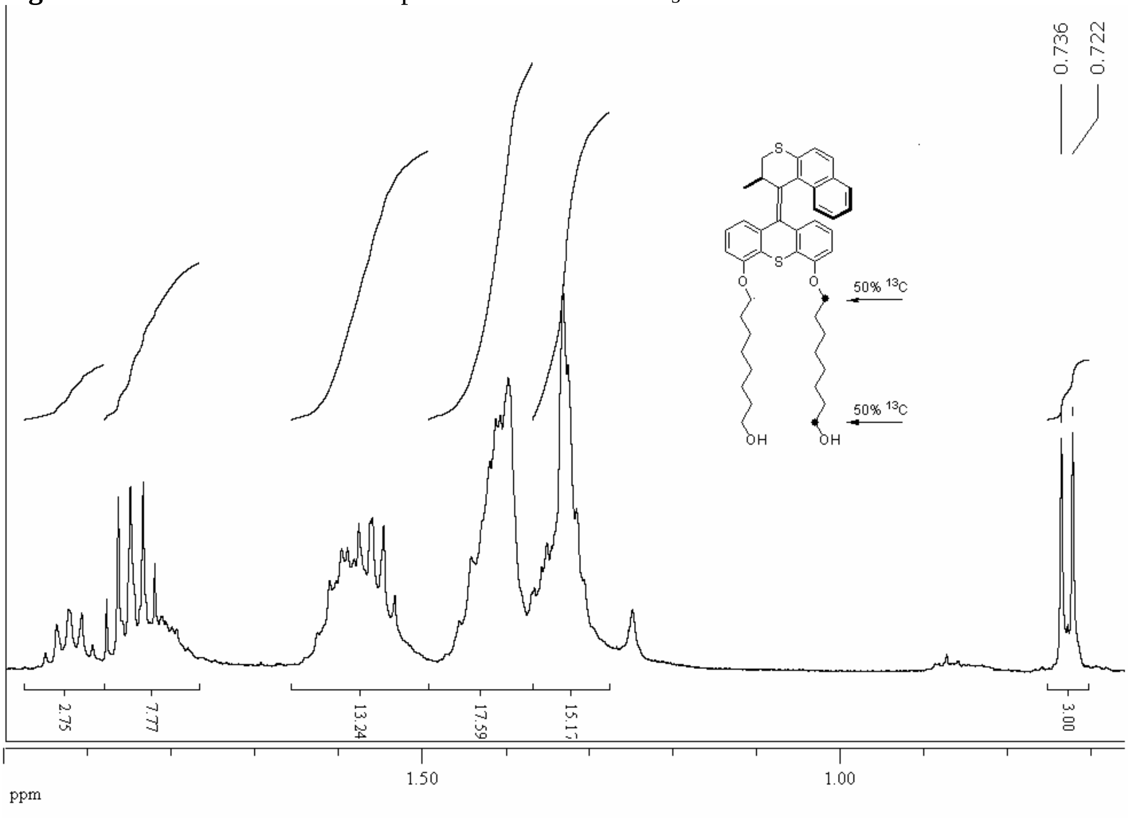


Figure 120. 400 MHz ^{1}H NMR spectrum of **52** in $CDCl_3$ (expansion).

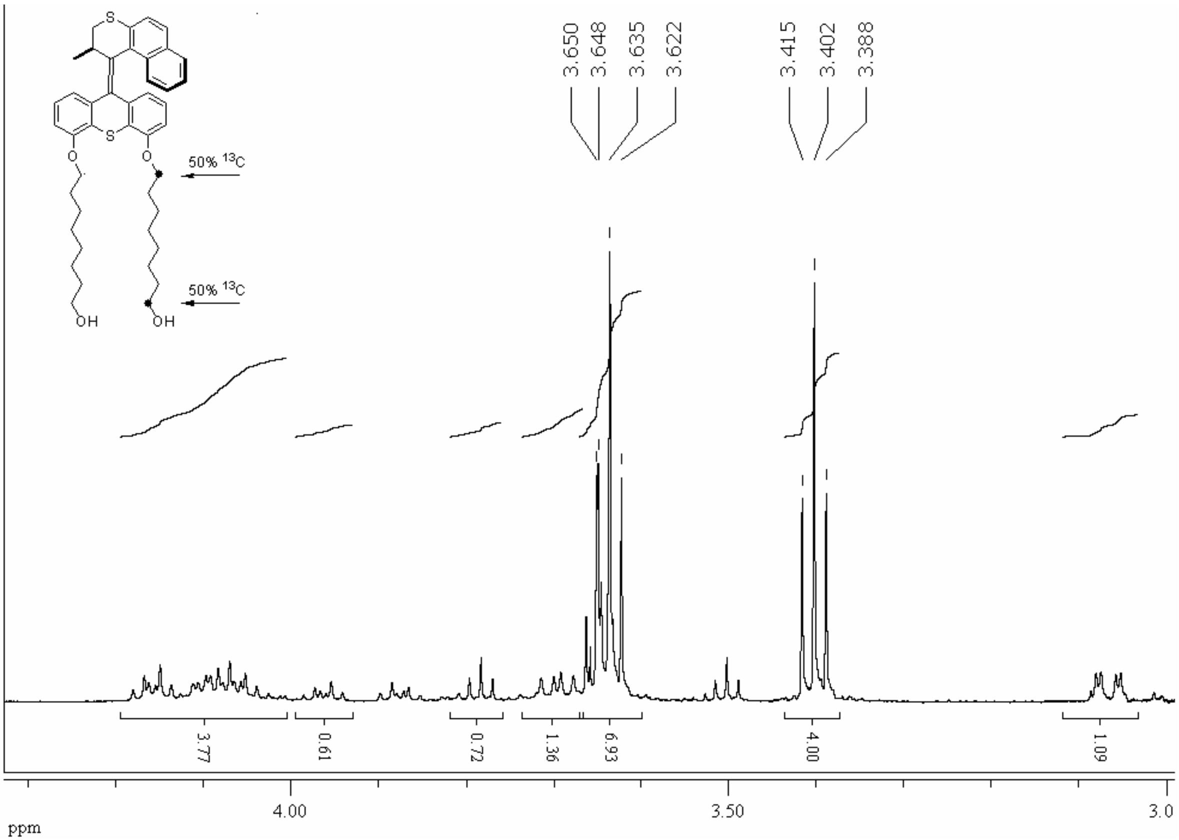


Figure 121. 400 MHz ^{1}H NMR spectrum of **52** in CDCl$_3$ (expansion).

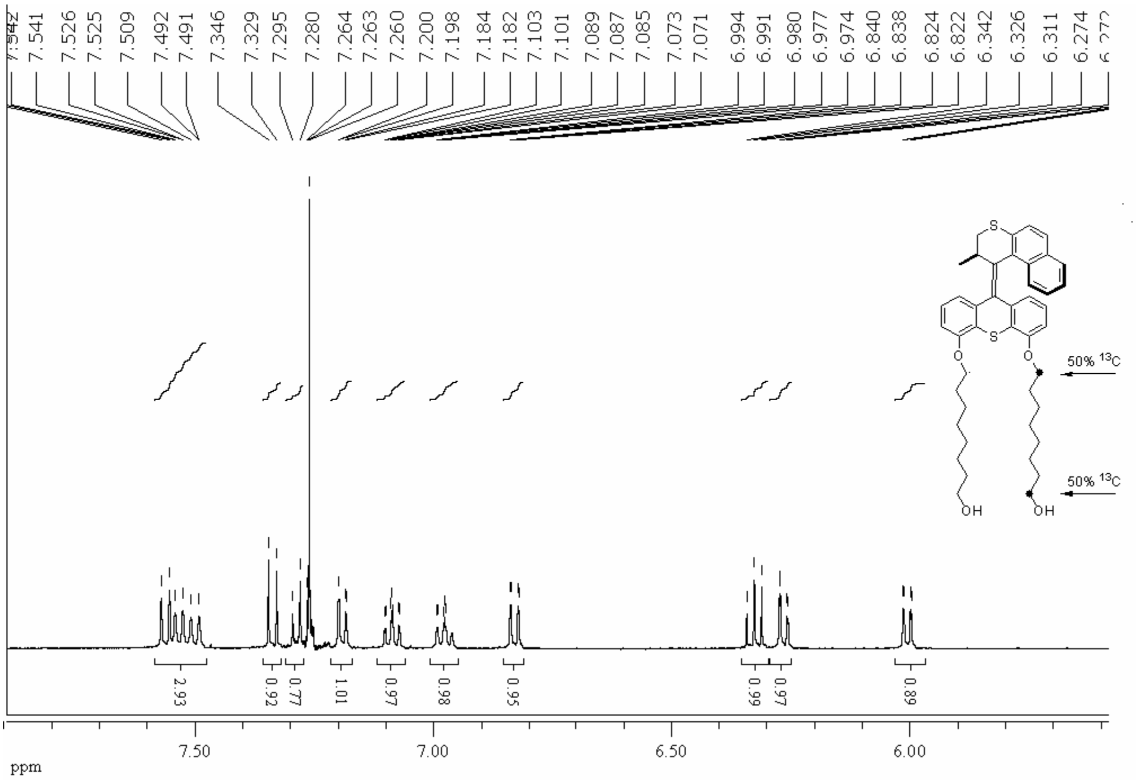


Figure 122. 400 MHz ^{1}H NMR spectrum of **52** in CDCl$_3$ (expansion).

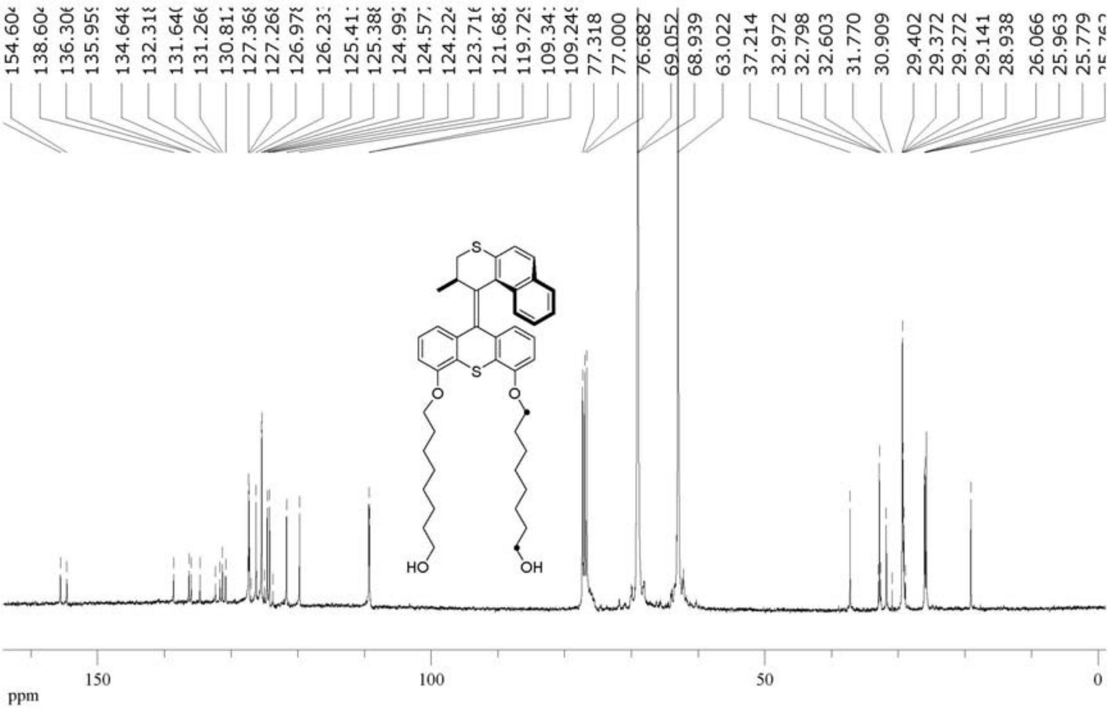


Figure 123. 100 MHz ^{13}C NMR spectrum of **52** in CDCl$_3$ (expansion).

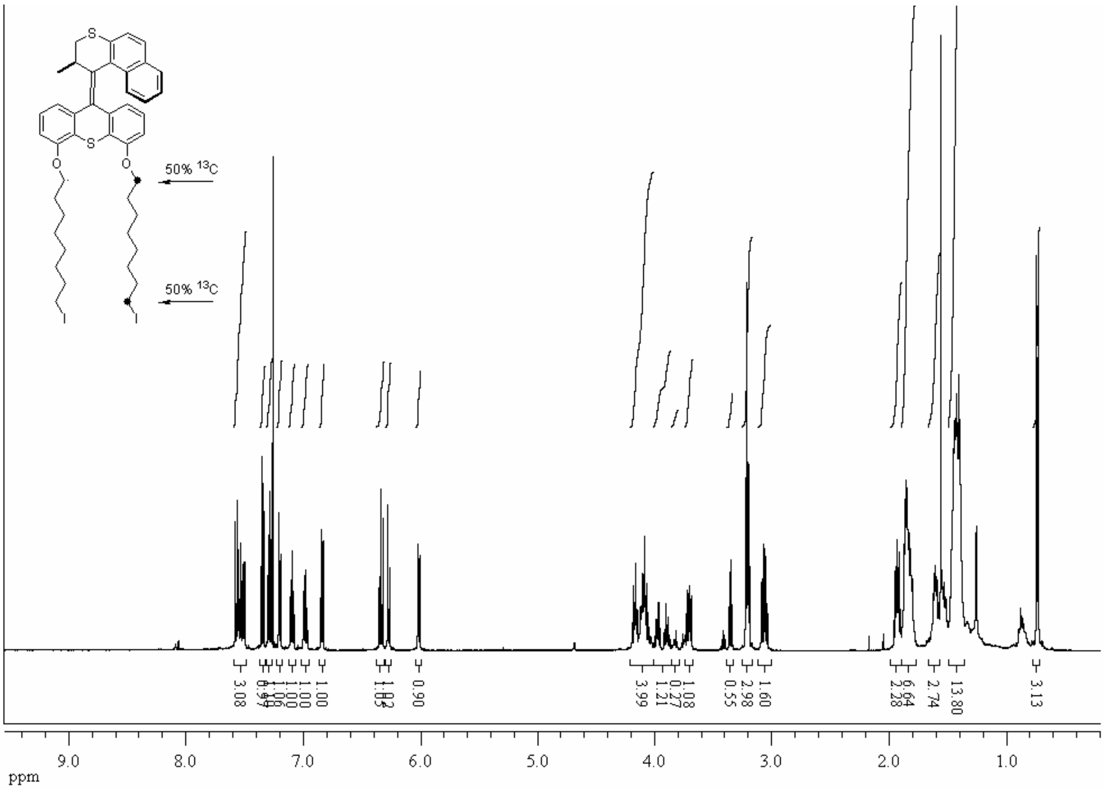


Figure 124. 400 MHz ^{1}H NMR spectrum of **53** in CDCl$_3$.

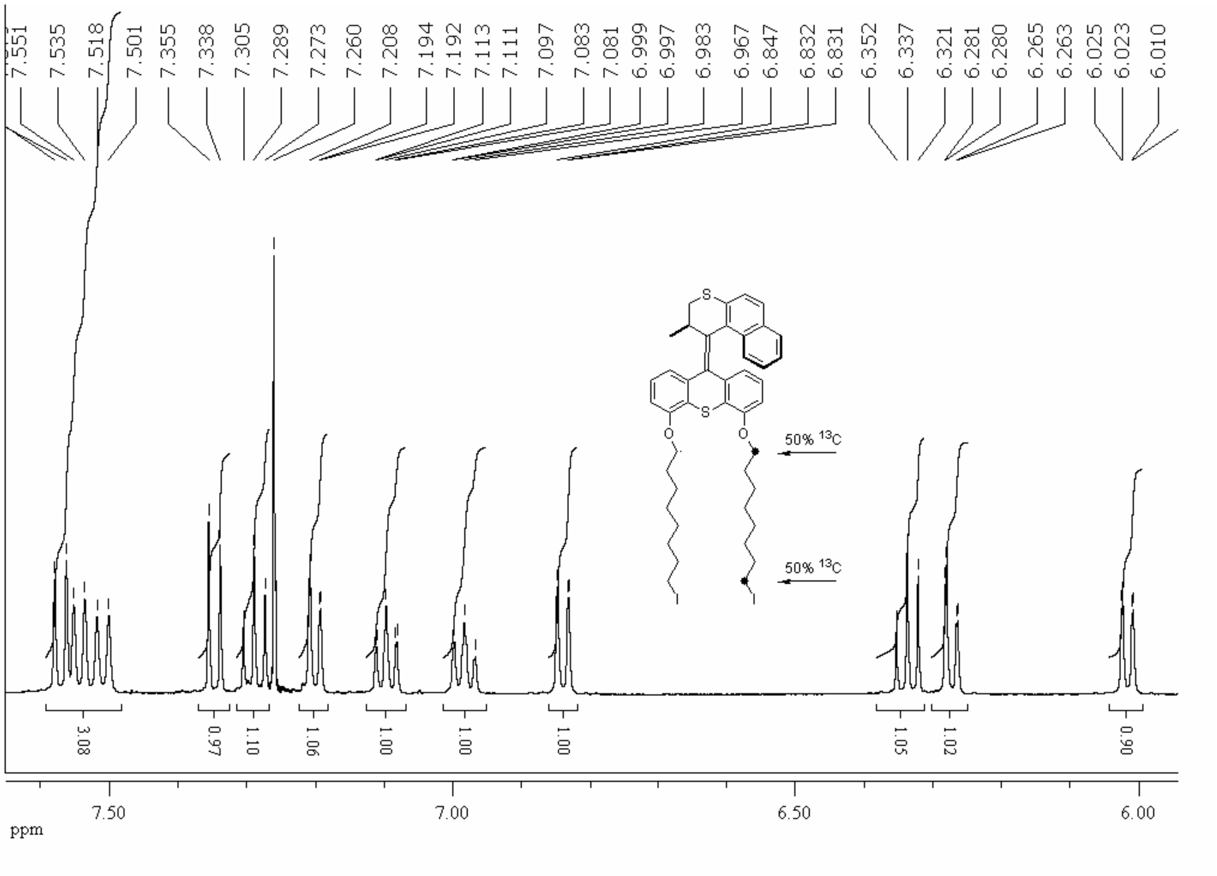


Figure 125. 400 MHz ^{1}H NMR spectrum of **53** in $CDCl_3$ (expansion).

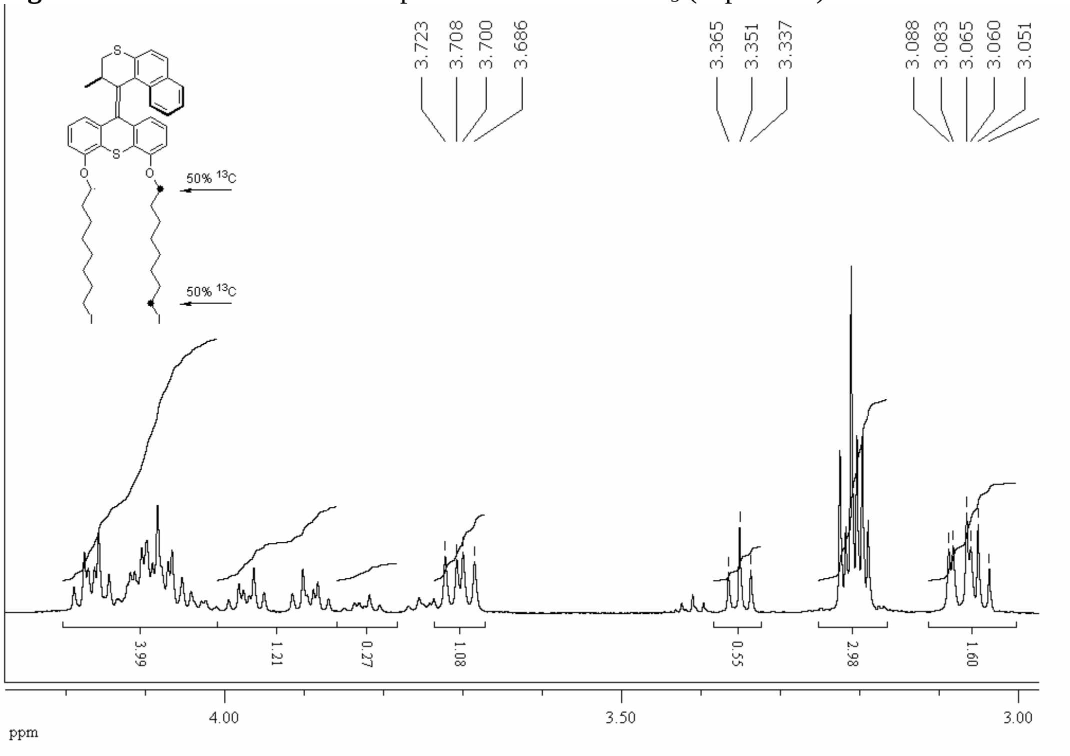


Figure 126. 400 MHz ^{1}H NMR spectrum of **53** in $CDCl_3$ (expansion).

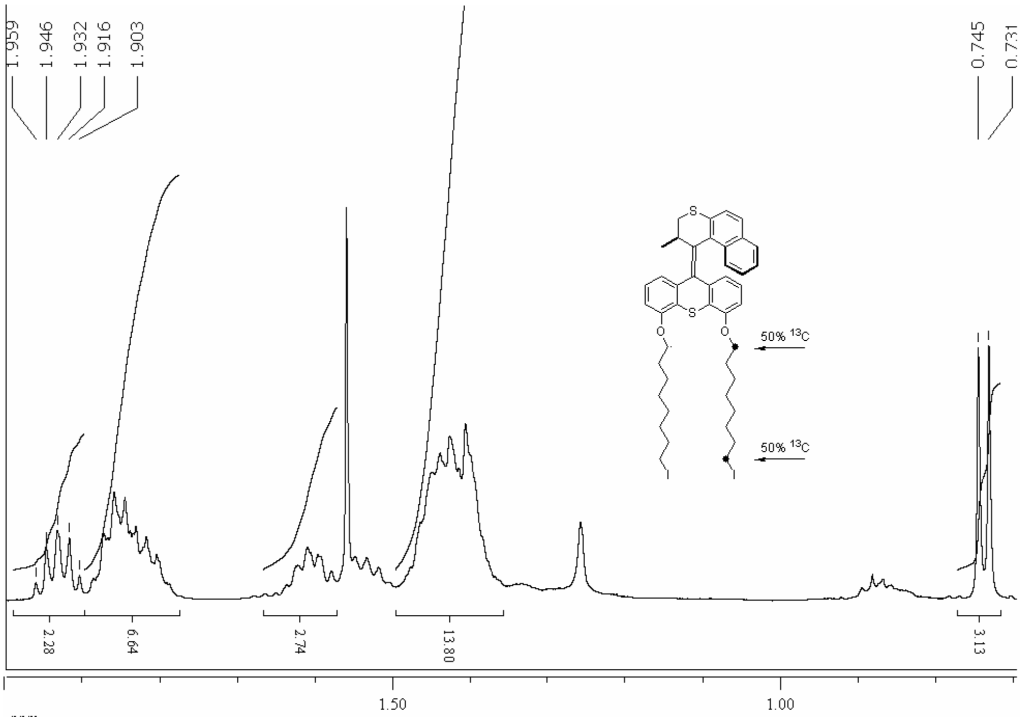


Figure 127. 400 MHz ^{1}H NMR spectrum of **53** in $CDCl_3$ (expansion).

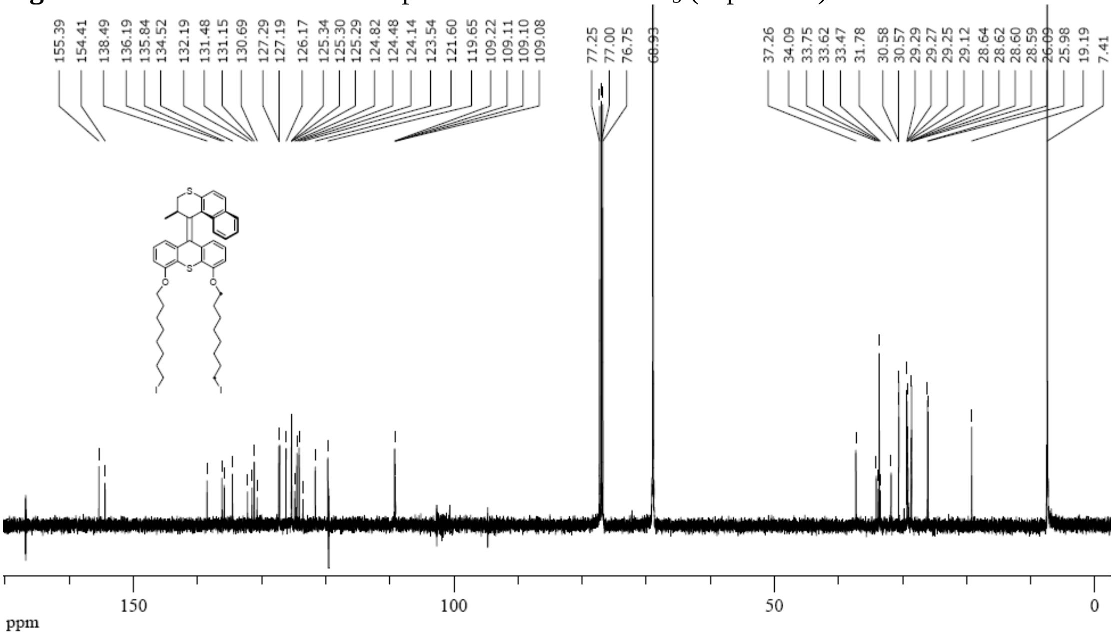


Figure 128. 125 MHz ^{13}C NMR spectrum of **53** in $CDCl_3$.

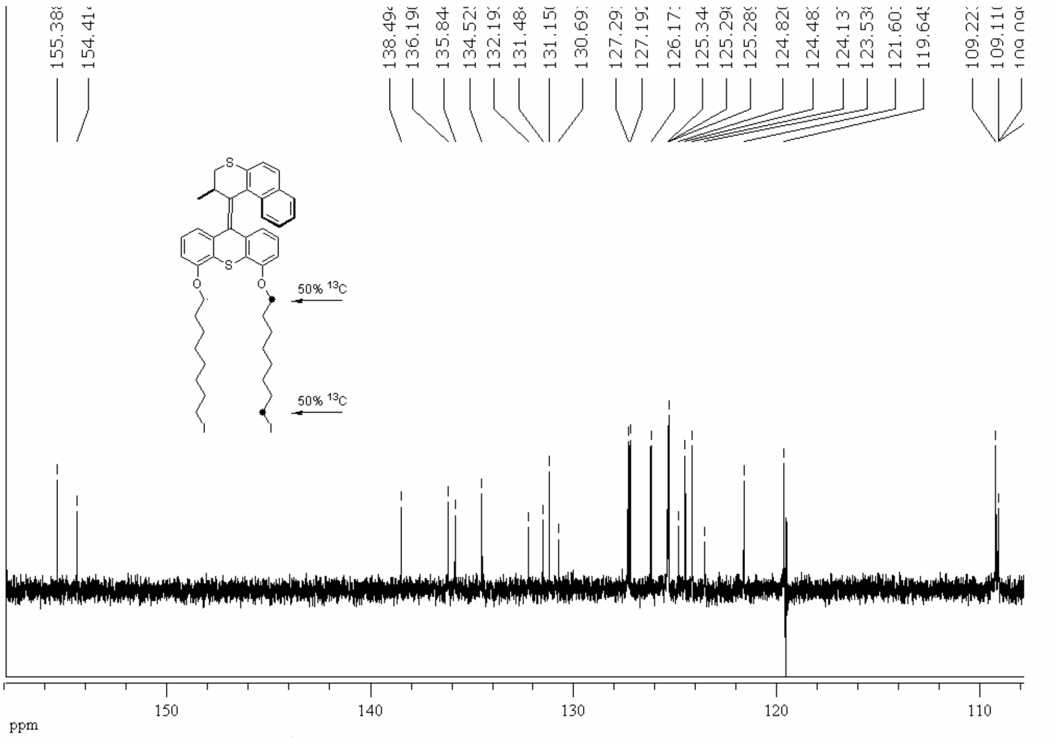


Figure 129. 125 MHz ^{13}C NMR spectrum of **53** in $CDCl_3$ (expansion).

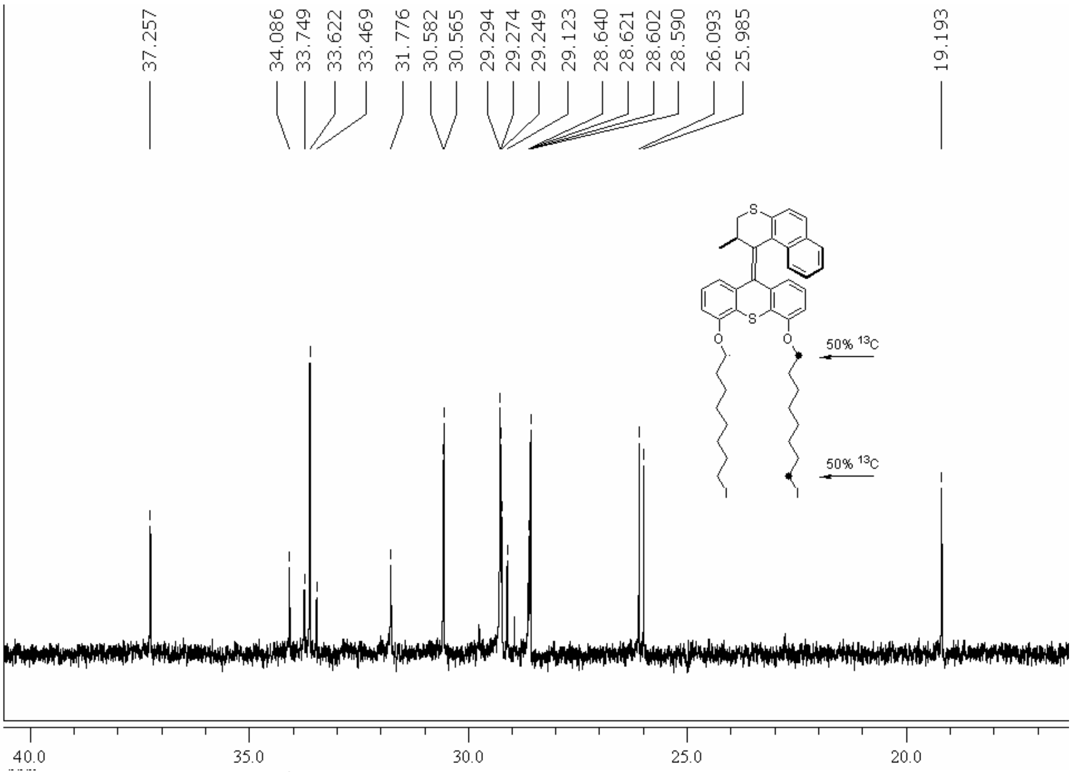


Figure 130. 125 MHz ^{13}C NMR spectrum of **53** in $CDCl_3$ (expansion).

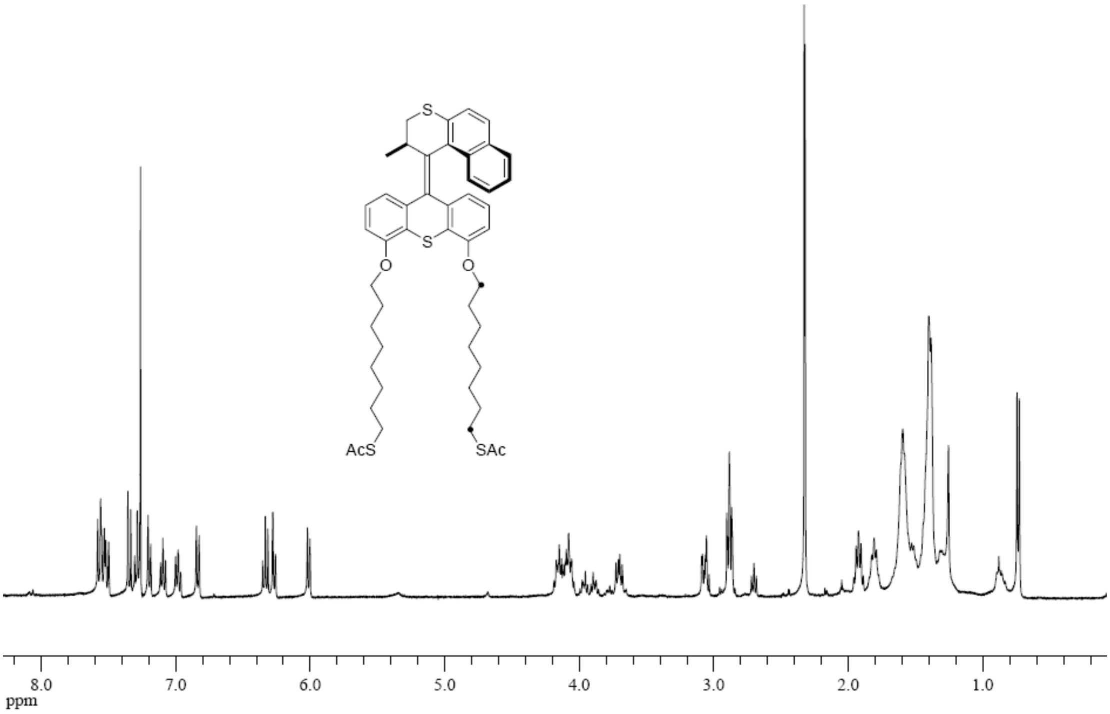


Figure 131. 400 MHz ^{1}H NMR spectrum of **54** in CDCl$_3$.

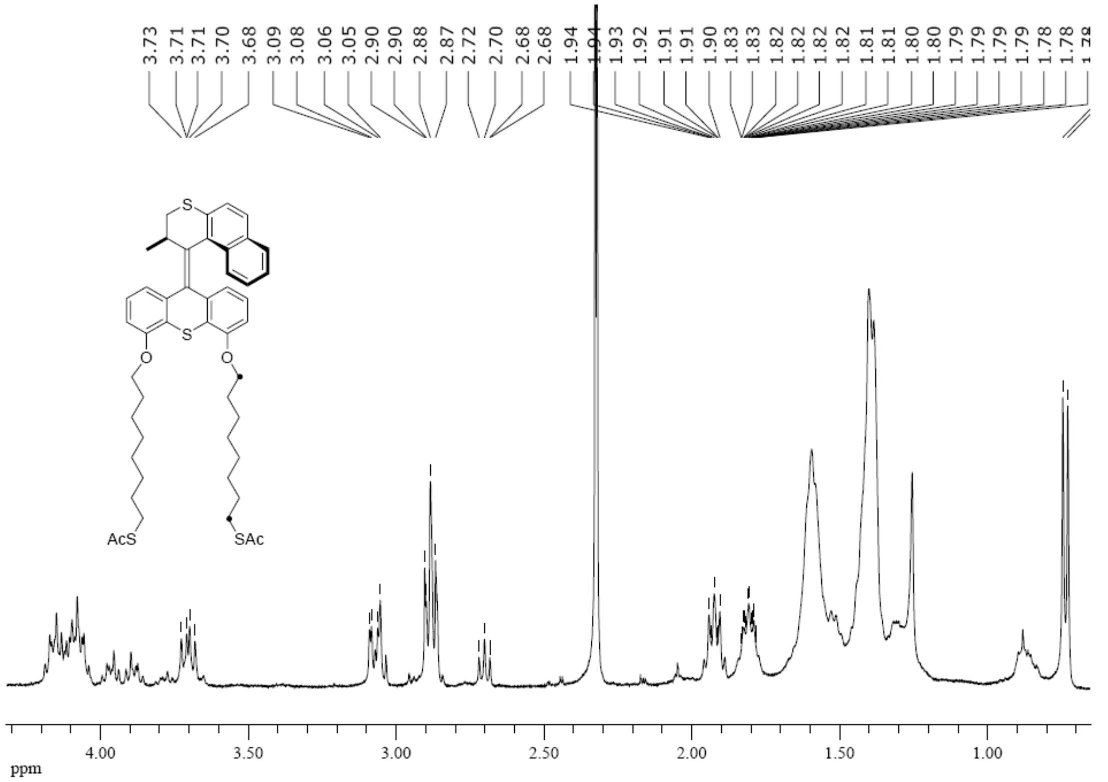


Figure 132. 400 MHz ^{1}H NMR spectrum of **54** in CDCl$_3$ (expansion).

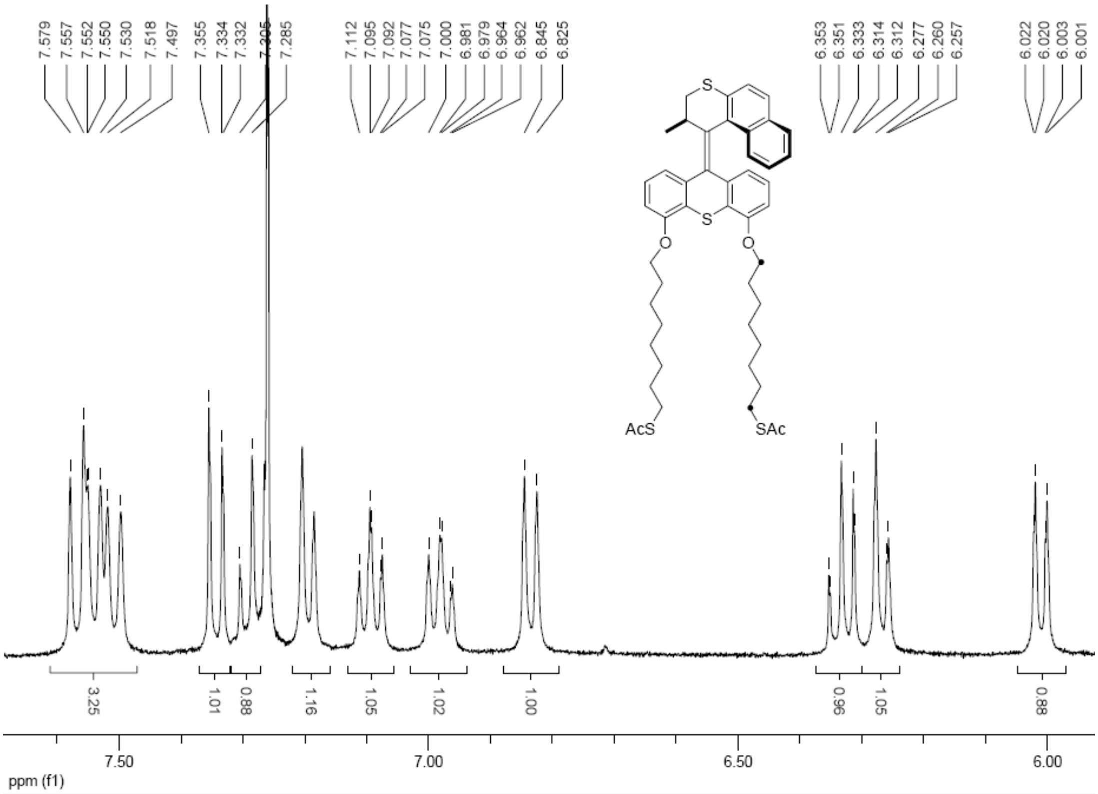


Figure 133. 400 MHz ^{1}H NMR spectrum of **54** in $CDCl_3$ (expansion).

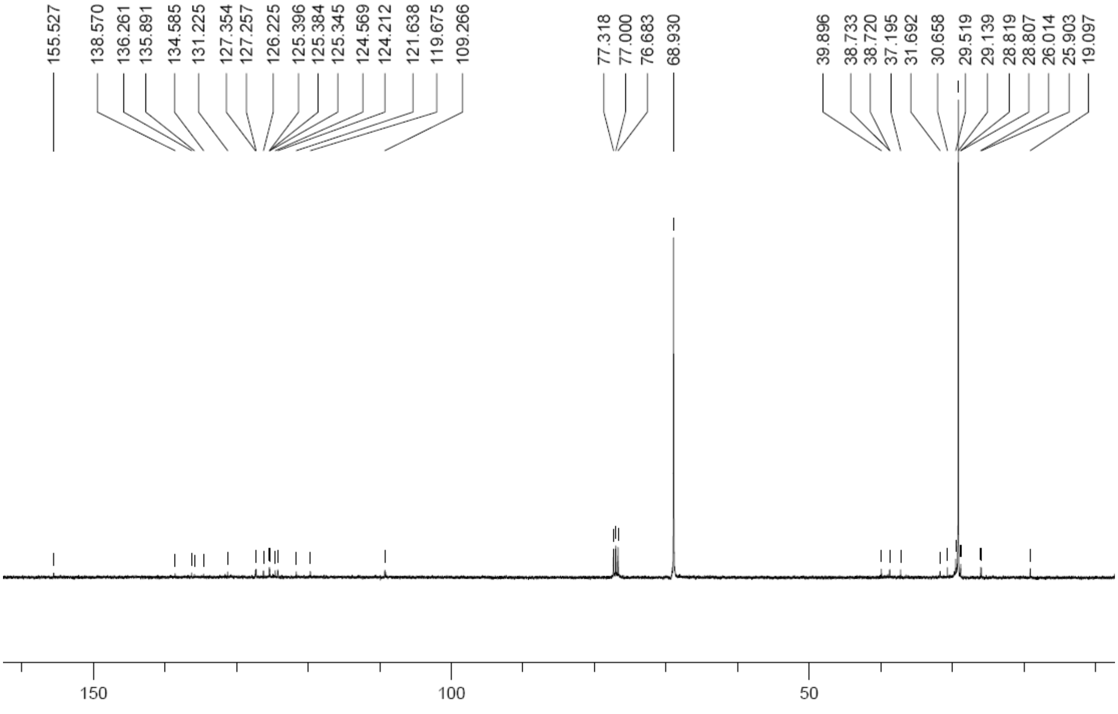


Figure 134. 100 MHz ^{13}C NMR spectrum of **54** in $CDCl_3$.

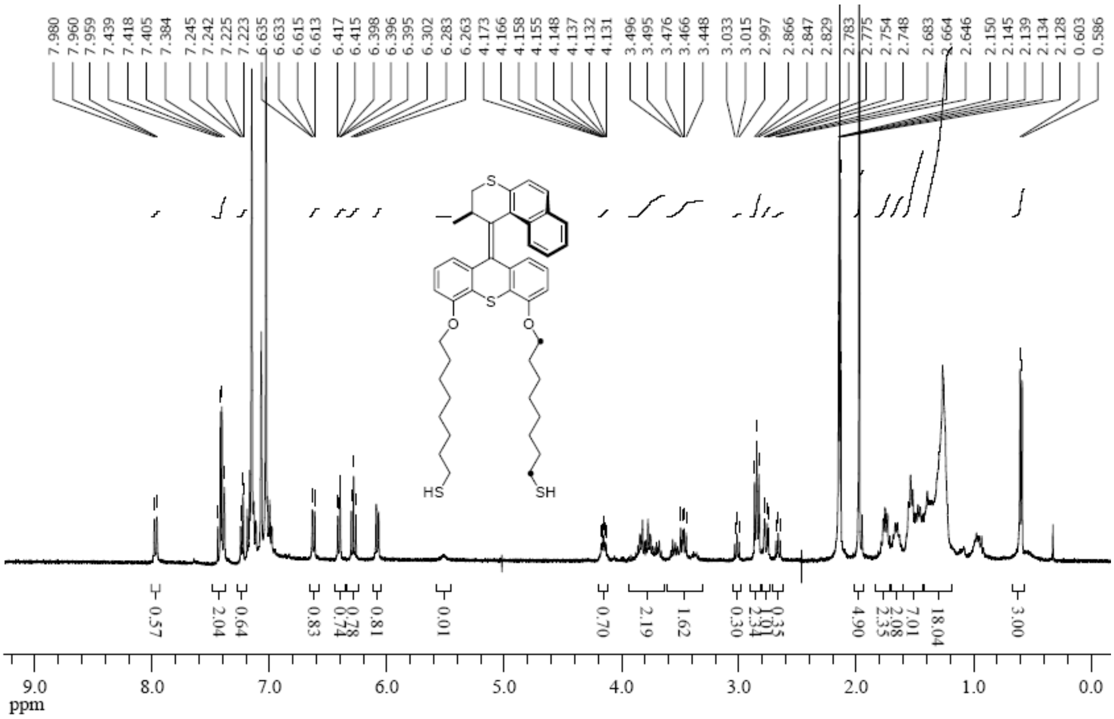


Figure 135. 500 MHz ^{1}H NMR spectrum of **55** in Toluene-D$_8$.

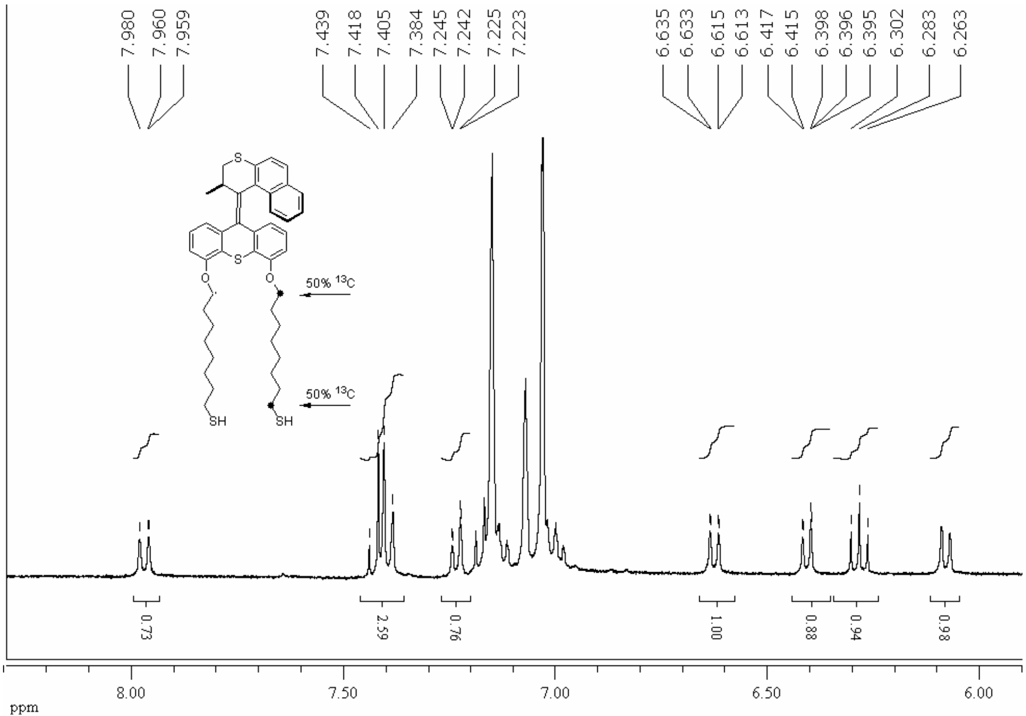


Figure 136. 500 MHz ^{1}H NMR spectrum of **55** in Toluene-D$_8$ (expansion).

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[*11] Supplementary Material Available: Tables of crystal data, anisotropic displacement parameters, atomic coordinates, bond lengths, bond angles, and torsion angles (as a CIF[14] file) and an ORTEP[12] plot; a listing of observed and calculated structure factors (also as a CIF file). Supplementary data for this paper are available from the IUCr electronic archives (Reference: CCDCxxxxxxx). Services for accessing these data are described at the back of the journal. (Acta Cryst. C)