Direct Synthesis of 1,3-Dithiolanes from Terminal Alkynes via Visible light Photoredox Catalysis

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Supporting Information

1. General Experimental Method

All commercially available reagents and chemicals were purchased from Sigma Aldrich, TCI, Alfa Aesar, Spectrochem and were used further without any purification. All the reactions were carried out in the oven dried round bottom flasks and anhydrous solvents were used under inert atmosphere. The reactions were carried out under the irradiation of visible light (Blue LEDs or Green LEDs or CFL light). The reactions were monitored by thin-layer chromatography on silica gel plates (60 GF_{254}) precoated aluminum backed plates (2.5 mm) and the visualization was done under UV light exposure (λ_{max} = 254 nm). Vanillin solution was used for staining TLC plates (6 g Vanillin + 1.5 mL conc. Sulfuric acid 95 mL + 96% ethanol). The compounds were purified by preparative thin-layer chromatography over silica gel. The ^{1}H NMR spectra were recorded on 400 MHz and ^{13}C decoupled NMR spectra ($^{13}C\{^{1}H\}$) were recorded on 100 MHz Brucker and Jeol spectrometers by using chloroform-D ($CDCl_3$) as a solvent containing tetramethylsilane (TMS) as an internal standard. The chemical shift was reported in parts per million (ppm) downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR or TMS (δ = 0.00 ppm) and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. The coupling constant (*J*) is given in Hz. For ^{1}H NMR, data are reported as follows: chemical shift, multiplicity as singlet (s), doublet (d), triplet (t), quartet (q), multiplate (m), doublet of doublet (dd), doublet of triplet of doublet (dtd) and broad (br). Melting points were recorded on a BUCHI M-560 melting point instrument by using an open glass capillary and are uncorrected. The exact mass of samples was analyzed by High-Resolution Mass Spectrometry (HRMS) using ESI TOF. The terminal aromatic alkynes were prepared according to the literature procedure.[1,2]

2. Appendix-I: Optimization of Solvent Screening[a]

Sr. No.	Solvent[b]	Time (h)	Yield (%)
1	Water	24	NR
2	DMSO	16	27
3	Toluene	24	Trace
4	EtOAc	12	10
5	THF	24	Trace
6	Ethanol	24	5
7	Acetone	16	23
8	DCE	24	33
9	$CHCl_3$	24	30
10	C_6H_5Cl	24	Trace
11	DCM	12	36

[a]General Reaction Conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) Eosin Y (10 mol%), Anhydrous (dry) Solvent (2 mL), Blue LEDs (5 W), under Argon balloon; [b]All the solvents were dried and degassed. We observed that the reactions did not work in moist (undried or partially pre-dried) and un-degassed solvents.

3. Appendix-II: Optimization of Catalyst loading[a] (Eosin Y- mol % screening)

Sr. No.	mol % of catalyst	Time (h)	Yield (%)
1	2	24	28
2	5	24	47
3	10	24	36
5	15	24	29
6	20	24	30

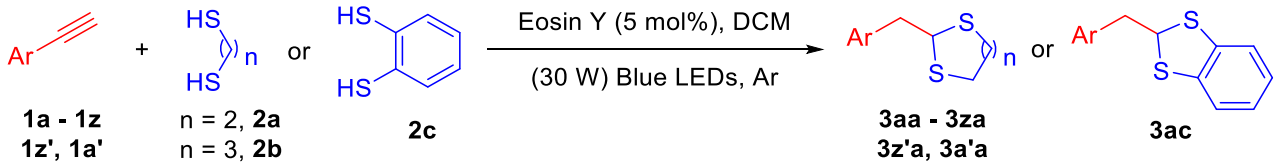
***Catalyst-Eosin Y**; [a]General Reaction Conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) Eosin Y (2-20 mol%), DCM (2 mL), Blue LEDs (5 W), under Argon balloon.

4. Appendix-III: Optimization of Light Source

Sr. No.	Light Source	Time (h)	Yield (%)
1	Green LED (15 W)	74	48
2	Blue LED (5 W)	24	47
3	Blue LED (10 W)	24	49
5	Blue LED (15 W)	24	62
6	Blue LED (30 W)	24	73
7	Blue LED (60 W)	24	54
8	CFL	1	NR
9	UV	1	NR

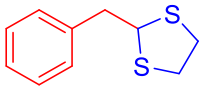
[a]General Reaction Conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) Eosin Y (5 mol%), DCM (2 mL), Light Source, under Argon balloon.

5. General Procedure A for the Synthesis of 1,3-dithiolanes (3aa-3za), (3z'a-3a'a), (3ab-3ac):



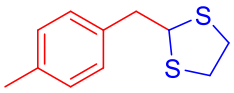
An oven-dried round bottom flask equipped with a stir bar and rubber septum is charged with aromatic acetylene derivative **1** (1 equiv., 0.2 mmol), Eosin Y (5 mol%, 6.4 mg), and 1,2-ethanedithiol **2a** (1 equiv., 0.2 mmol), DCM (2 mL) under inert atmosphere. The reaction mixture was initially purged with argon for 5 min to remove any dissolved air and the oxygen atmosphere was maintained throughout the reaction (using a balloon). The reaction mixture was stirred under the irradiation of Blue LEDs (30 W) at room temperature for 12-24 h. (Monitored by TLC, complete consumption of aromatic acetylene). After the completion of the reaction, the solvent was removed under reduced pressure and the crude residue was purified by preparative thin-layer chromatography using mixture of petroleum ether/EtOAc as an eluent to afford the 1,3-dithiolane **3** as oil or solid.

2-benzyl-1,3-dithiolane (3aa):



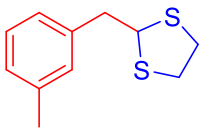
The compound **3aa** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (73% yield, 35 mg). *Rf* = 0.88 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 1H), 7.29 (m, 1H), 7.26 (m, 2H), 7.25 – 7.23 (m, 1H), 4.73 (t, *J* = 7.1 Hz, 1H), 3.30 – 3.15 (m, 4H), 3.12 (d, *J* = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$) δ 139.2, 129.2, 128.5, 126.9, 55.0, 45.4, 38.7. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{10}H_{13}S_2]^+$ 197.0453 found 197.0459.

2-(4-methylbenzyl)-1,3-dithiolane (3ba):



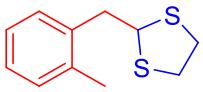
The compound **3ba** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (76% yield, 32 mg). *Rf* = 0.85 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.13 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.71 (t, *J* = 7.2 Hz, 1H), 3.22 (tdt, *J* = 14.2, 9.3, 7.0 Hz, 4H), 3.08 (d, *J* = 7.2 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.5, 136.3, 129.2, 129.1, 55.3, 45.0, 38.7, 21.2. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{15}S_2]^+$ 211.0610 found 211.0640.

2-(3-methylbenzyl)-1,3-dithiolane (3ca):



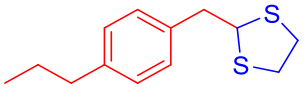
The compound **3ca** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (71% yield, 30 mg). *Rf* = 0.81 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 1H), 7.07 (m, 3H), 4.74 (t, *J* = 7.2 Hz, 1H), 3.31 – 3.17 (m, 4H), 3.09 (d, *J* = 7.2 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.2, 138.1, 130.0, 128.4, 127.7, 126.2, 55.1, 45.3, 38.7, 21.5. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{15}S_2]^+$ 211.0610 found 211.0641.

2-(2-methylbenzyl)-1,3-dithiolane (3da):



The compound **3da** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (78% yield, 33 mg). *Rf* = 0.80 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (ddd, *J* = 6.6, 4.3, 2.4 Hz, 1H), 7.16 (dd, *J* = 5.4, 4.0 Hz, 3H), 4.76 (t, *J* = 7.3 Hz, 1H), 3.36 – 3.18 (m, 4H), 3.15 (d, *J* = 7.3 Hz, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.6, 136.3, 130.5, 129.9, 127.0, 126.0, 54.0, 42.5, 38.7, 19.8. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{15}S_2]^+$ 211.0610 found 211.0633.

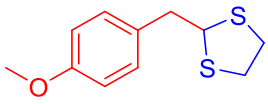
2-(4-propylbenzyl)-1,3-dithiolane (3ea):



The compound **3ea** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (73% yield, 35 mg). *Rf* = 0.86 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 4.72 (t, *J* = 7.1 Hz, 1H), 3.23 (tdt, *J* = 14.2, 9.4, 7.0 Hz, 4H), 3.09 (d, *J* = 7.1 Hz, 2H), 2.60 – 2.54 (m, 2H), 1.64 (dq, *J* = 14.8, 7.4 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.3, 136.5,

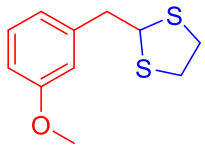
129.1, 128.6, 55.2, 45.0, 38.7, 37.8, 24.6, 14.0. HRMS (ESI TOF) *m/z* $[M]^+$ calculated for $[C_{13}H_{18}S_2]^+$ 238.0850 found 238.0868

2-(4-methoxybenzyl)-1,3-dithiolane (3fa):



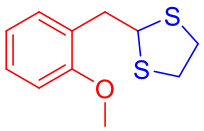
The compound **3fa** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (77% yield, 35 mg). *Rf* = 0.70 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 2H), 6.88 – 6.82 (m, 2H), 4.69 (t, *J* = 7.1 Hz, 1H), 3.79 (s, 3H), 3.28 – 3.14 (m, 4H), 3.27 – 3.05 (d, *J* =7.1, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 131.3, 130.2, 113.8, 55.3, 55.2, 44.4, 38.5. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{15}OS_2]^+$ 227.0559 found: 227.0564.

2-(3-methoxybenzyl)-1,3-dithiolane (3ga):



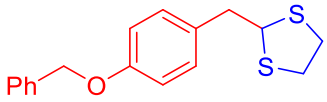
The compound **3ga** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (71% yield, 32 mg). *Rf* = 0.68 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.86 – 6.81 (m, 2H), 4.76 (t, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 3.35 – 3.18 (m, 4H), 3.13 (d, *J* = 7.1 Hz, 2H) ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 141.1, 129.8, 121.9, 115.2, 112.6, 55.6, 55.2, 45.8, 39.0. HRMS (ESI TOF) *m/z* $[M+1]^+$ calculated for $[C_{11}H_{15}OS_2]^+$ 227.0559 found: 227.0555

2-(2-methoxybenzyl)-1,3-dithiolane (3ha):



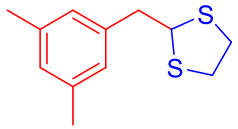
The compound **3ha** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (77% yield, 35 mg). *Rf* = 0.65 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 7.3, 3.9 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.88 (t, *J* = 7.3 Hz, 1H), 3.83 (s, 3H), 3.25 (ddq, *J* = 10.3, 8.4, 6.7 Hz, 4H), 3.11 (d, *J* = 7.3 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 131.1, 128.3, 127.7, 120.4, 110.3, 55.3, 53.2, 40.8, 38.6. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{13}OS_2]^+$ 227.0559 found: 227.0564.

2-(4-(benzyloxy)benzyl)-1,3-dithiolane (3ia):



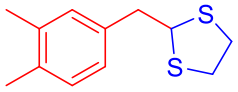
The compound **3ia** was prepared following the general procedure A for the synthesis of dithiolane. White solid (76% yield, 46 mg). MP. 70.5-73.2 ℃. *Rf* = 0.70 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.34 – 7.30 (m, 1H), 7.20 – 7.15 (m, 2H), 6.94 – 6.90 (m, 2H), 5.05 (s, 2H), 4.69 (t, *J* = 7.1 Hz, 1H), 3.27 – 3.15 (m, 4H), 3.05 (d, *J* = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.9, 137.2, 131.7, 130.3, 128.7, 128.1, 127.6, 114.8, 70.1, 55.4, 44.5, 38.7. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{17}H_{19}OS_2]^+$ 303.0872 found 303.0888.

2-(3,5-dimethylbenzyl)-1,3-dithiolane (3ja):



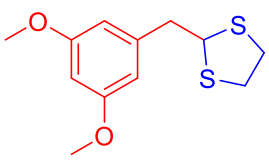
The compound **3ja** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (71% yield, 32 mg). *Rf* = 0.80 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, CDCl3) δ 6.89 (s, 1H), 6.87 (s, 2H), 4.73 (t, *J* = 7.2 Hz, 1H), 3.33 – 3.15 (m, 4H), 3.06 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.2, 138.2, 128.6, 126.9, 55.1, 45.3, 38.7, 21.4. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{12}H_{17}S_2]^+$ 225.0772 found 225.0750.

2-(3,4-dimethylbenzyl)-1,3-dithiolane (3ka):



The compound **3ka** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (78% yield, 35 mg). *Rf* = 0.74 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 7.01 – 6.97 (m, 1H), 4.72 (t, *J* = 7.2 Hz, 1H), 3.24 (tdt, *J* = 13.7, 9.2, 6.7 Hz, 4H), 3.06 (d, *J* = 7.2 Hz, 2H), 2.26 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8, 136.6, 135.1, 130.4, 129.8, 126.5, 55.3, 44.9, 38.6, 19.9, 19.5. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{12}H_{17}S_2]^+$ 225.0772 found 225.0750.

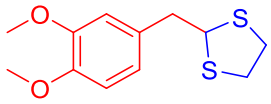
2-(3,5-dimethoxybenzyl)-1,3-dithiolane (3la):



The compound **3la** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (70% yield, 36 mg). *Rf* = 0.60 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.41 (d, *J* = 2.2 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 1H), 4.71 (t, *J* = 7.2 Hz, 1H), 3.78 (s,

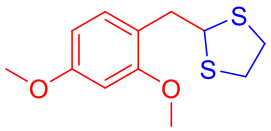
6H), 3.32 – 3.14 (m, 4H), 3.05 (d, J = 7.2 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.8, 141.5, 107.1, 98.9, 55.4, 54.8, 45.7, 38.7. HRMS (ESI TOF) *m/z* $[M]^+$ calculated for $[C_{12}H_{16}O_2S_2]^+$ 256.0592 found 256.0596.

2-(3,4-dimethoxybenzyl)-1,3-dithiolane (3ma):



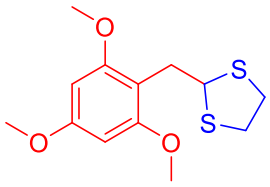
The compound **3ma** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (78% yield, 40 mg). *Rf* = 0.55 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 3H), 4.70 (t, J = 7.1 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.21 (ddq, J = 14.3, 9.4, 7.1 Hz, 4H), 3.05 (d, J = 7.1 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0, 158.4, 131.3, 120.2, 103.6, 98.4, 55.4, 55.3, 53.5, 40.0, 38.1. HRMS (ESI TOF) *m/z* $[M]^+$ calculated for $[C_{12}H_{16}S_2O_2]^+$ 256.0592 found 256.0596.

2-(2,4-dimethoxybenzyl)-1,3-dithiolane (3na):



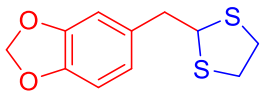
The compound **3na** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (72% yield, 37 mg). *Rf* = 0.54 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.05 (m, 1H), 6.43 (m, 1H), 6.43 – 6.41 (m, 1H), 4.83 (t, J = 7.3 Hz, 1H), 3.79 (s, 3H), 3.79 (s, 3H), 3.33 – 3.15 (m, 4H), 3.02 (d, J = 7.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0, 158.4, 131.3, 120.3, 103.7, 98.5, 55.4, 55.3, 53.5, 40.0, 38.5. HRMS (ESI TOF) *m/z* $[M]^+$ calculated for $[C_{12}H_{16}O_2S_2]^+$ 256.0592 found 256.0596.

2-(2,4,6-trimethoxybenzyl)-1,3-dithiolane (3oa):



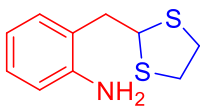
The compound **3oa** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (75% yield, 43 mg). *Rf* = 0.45 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 2H), 4.86 (t, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.80 (s, 6H), 3.35 – 3.14 (m, 4H), 3.09 (d, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 159.3, 109.0, 90.7, 55.8, 55.4, 53.7, 38.2, 31.8. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{13}H_{19}O_3S_2]^+$ 287.0776 found 287.0775.

5-((1,3-dithiolan-2-yl)methyl)benzo[d][1,3]dioxole (3pa):



The compound **3pa** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (73% yield, 35 mg). *Rf* = 0.55 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 4.7, 3.1 Hz, 2H), 6.70 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.93 (s, 2H), 4.66 (t, *J* = 7.1 Hz, 1H), 3.28 – 3.15 (m, 4H), 3.02 (d, *J* = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.6, 146.5, 133.1, 122.3, 109.6, 108.3, 101.0, 55.3, 45.1, 38.7. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{13}O_2S_2]^+$ 241.0351 found 241.0360.

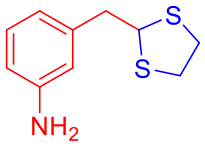
2-((1,3-dithiolan-2-yl)methyl)aniline (3qa):



The compound **3qa** was prepared following the general procedure A for the synthesis of dithiolane. Pale yellow coloured liquid (85% yield, 36 mg). *Rf* = 0.45 (petroleum ether/EtOAc 80:20) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (m, 1H), 7.07 (m, 1H), 6.77 (m, 1H), 6.69 (m, 1H), 4.83 (t, *J* = 7.0 Hz, 1H), 3.81 (br, 2H), 3.32 – 3.19 (m, 4H), 3.06 (d, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H}

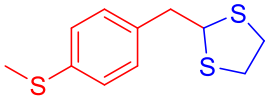
NMR (400 MHz, $CDCl_3$) δ 144.6, 131.0, 128.1, 124.3, 119.1, 116.5, 53.5, 41.3, 38.8. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{10}H_{14}NS_2]^+$ 212.0562 found 212.0563.

3-((1,3-dithiolan-2-yl)methyl)aniline (3ra):



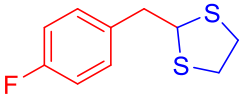
The compound **3ra** was prepared following the general procedure A for the synthesis of dithiolane. Pale yellow coloured liquid (66% yield, 28 mg). *Rf* = 0.40 (petroleum ether/EtOAc 80:20) ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (m, 1H), 6.65 (m, 1H), 6.57 (m, 2H), 4.71 (t, *J* = 7.2 Hz, 1H), 3.64 (s, 2H), 3.31 – 3.16 (m, 4H), 3.03 (d, *J* = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.5, 140.5, 129.4, 119.4, 115.9, 113.8, 55.0, 45.4, 38.7. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{10}H_{14}NS_2]^+$ 212.0562 found 212.0567.

2-(4-(methylthio)benzyl)-1,3-dithiolane (3sa):



The compound **3sa** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (83% yield, 40 mg). *Rf* = 0.90 (petroleum ether/EtOAc 99:1) ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 4H), 4.69 (t, *J* = 7.1 Hz, 1H), 3.29 – 3.14 (m, 4H), 3.07 (d, *J* = 7.1 Hz, 2H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 129.8, 128.5, 126.8, 126.6, 55.0, 44.9, 38.7, 16.1. HRMS (ESI TOF) *m/z* $[M]^+$ calculated for $[C_{11}H_{14}S_3]^+$ 242.0258 found 242.0233.

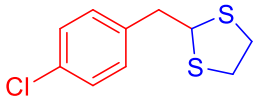
2-(4-fluorobenzyl)-1,3-dithiolane (3ta):



The compound **3ta** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (77% yield, 33 mg). *Rf* = 0.80 (petroleum ether/EtOAc 99:1) ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.02 – 6.95 (m, 2H), 4.69 (t, *J* = 7.0 Hz, 1H), 3.26 – 3.15 (m,

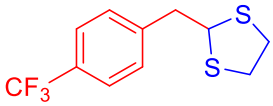
4H), 3.08 (d, J = 7.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.97 (d, J = 244.9 Hz), 134.83 (d, J = 3.2 Hz), 130.83 (d, J = 7.9 Hz), 115.27 (d, J = 21.2 Hz), 54.98 (d, J = 1.4 Hz), 44.54, 38.71. ^{19}F NMR (377 MHz, $CDCl_3$) δ -116.1. HRMS (ESI TOF) *m/z* $[M]^+$ calculated for $[C_{10}H_{11}S_2F]^+$ 214.0258 found 214.0213.

2-(4-chlorobenzyl)-1,3-dithiolane (3ua):



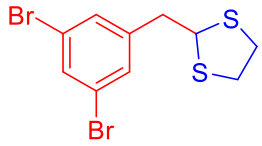
The compound **3ua** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (61% yield, 28 mg). *Rf* = 0.78 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 4.68 (t, J = 7.0 Hz, 1H), 3.26 – 3.15 (m, 4H), 3.07 (d, J = 7.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 137.5, 132.8, 130.7, 128.6, 54.7, 44.7, 38.8. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{10}H_{12}ClS_2]^+$ 231.0063 found 231.0080.

2-(4-(trifluoromethyl)benzyl)-1,3-dithiolane (3va):



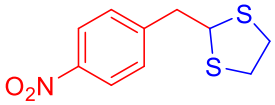
The compound **3va** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (51% yield, 27 mg). *Rf* = 0.70 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 4.72 (t, J = 7.0 Hz, 1H), 3.29 – 3.19 (m, 4H), 3.16 (d, J = 7.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.01 (d, J = 1.5 Hz), 129.75 (s), 128.47 (s), 125.44 (q, J = 4.0 Hz), 54.34 (s), 45.23 (s), 38.82 (s). ^{19}F NMR (472 MHz, $CDCl_3$) δ -62.6. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{12}F_3S_2]^+$ 265.0327 found 265.0355.

2-(3,5-dibromobenzyl)-1,3-dithiolane (3wa):



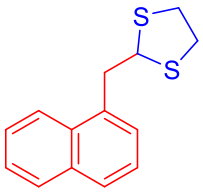
The compound **3wa** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (61% yield, 43 mg). *Rf* = 0.66 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.35 (s, 2H), 4.65 (t, *J* = 7.0 Hz, 1H), 3.33 – 3.15 (m, 4H), 3.03 (d, *J* = 7.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.5, 132.4, 131.0, 122.6, 53.8, 44.5, 38.5. HRMS (ESI TOF) *m/z* $[M]^+$ calculated for $[C_{10}H_{10}S_2Br_2]^+$ 351.8591 found 351.8595.

2-(4-nitrobenzyl)-1,3-dithiolane (3xa):



The compound **3xa** was prepared following the general procedure A for the synthesis of dithiolane. Yellow solid. (40% yield, 36 mg). MP. 72.3-74.5 °C *Rf* = 0.8 (petroleum ether/EtOAc 95:5) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.14 (m, 2H), 7.46 – 7.40 (m, 2H), 4.72 (t, *J* = 6.9 Hz, 1H), 3.23 – 3.18 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.1, 146.4, 130.4, 123.7, 53.9, 45.2, 38.9. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{10}H_{12}NO_2S_2]^+$ 242.0304 found: 242.0310.

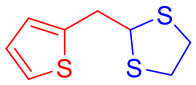
2-(naphthalen-1-ylmethyl)-1,3-dithiolane (3ya):



The compound **3ya** was prepared following the general procedure A for the synthesis of dithiolane. Pal yellow coloured liquid (73% yield, 36 mg). *Rf* = 0.80 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (m, 1H), 7.87 (m, 1H), 7.78 (m, 1H), 7.57 – 7.43 (m, 4H), 4.94

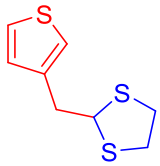
(t, J = 7.2 Hz, 1H), 3.59 (d, J = 7.2 Hz, 2H), 3.35 (ddd, J = 12.4, 8.8, 7.1 Hz, 2H), 3.23 (ddd, J = 12.4, 8.8, 7.1 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 135.3, 134.0, 131.7, 129.1, 127.9, 127.4, 126.2, 125.8, 125.5, 123.5, 54.2, 42.6, 38.8. HRMS (ESI TOF) *m/z* $[M+Na]^+$ calculated for $C_{14}H_{14}S_2$ 269.0434 found 269.0424.

2-(thiophen-2-ylmethyl)-1,3-dithiolane (3za):



The compound **3za** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (84% yield, 35 mg). *Rf* = 0.70 (petroleum ether/EtOAc 80:20) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 2.4 Hz, 1H), 7.59 (dd, J = 8.2, 2.5 Hz, 1H), 7.27 (d, J = 8.7 Hz, 2H), 4.67 (t, J = 6.7 Hz, 1H), 3.23 – 3.12 (m, 4H), 3.07 (d, J = 6.7 Hz, 2H).$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 150.7, 140.0, 133.0, 123.9, 53.9, 41.7, 38.9. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_8H_{11}S_3]^+$ 203.0023 found: 203.0023.

2-(thiophen-3-ylmethyl)-1,3-dithiolane (3z'a):

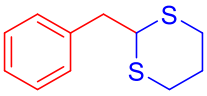


The compound **3z'a** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (89% yield, 36 mg). *Rf* = 0.75 (petroleum ether/EtOAc 80:20) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J = 4.7, 3.1 Hz, 1H), 7.02 (d, J = 2.1 Hz, 1H), 6.95 (d, J = 4.9 Hz, 1H), 4.65 (t, J = 6.9 Hz, 1H), 3.17 – 3.09 (m, 4H), 3.07 (d, J = 6.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 139.5, 128.5, 125.5, 122.4, 54.2, 40.0, 38.7. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_8H_{11}S_3]^+$ 203.0017 found: 203.0023.

2-((1,3-dithiolan-2-yl)methyl)pyridine (3a'a):

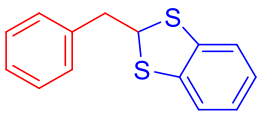
The compound **3a'a** was prepared following the general procedure A for the synthesis of dithiolane. Colourless liquid (79% yield, 31 mg). *Rf* = 0.80 (petroleum ether/EtOAc 70:30) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 – 8.46 (m, 1H), 7.54 (td, *J* = 7.7, 1.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 7.08 (ddd, *J* = 7.5, 4.9, 1.0 Hz, 1H), 4.94 (t, *J* = 7.3 Hz, 1H), 3.25 – 3.11 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.6, 149.3, 136.3, 123.5, 121.7, 52.7, 47.6, 38.5. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_9H_{12}NS_2]^+$ 198.0406 found: 198.0411.

2-benzyl-1,3-dithiane (3ab):



Synthesis of **3ab** done by following general procedure A and instead of **2a**, 1,3-propanedithiol **2b** was used for dithiolation of phenylacetylene **1a**. Colourless liquid. (20% yield, 36 mg). *Rf* = 0.4 (petroleum ether/EtOAc 98:2) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 1H), 7.34 – 7.31 (m, 1H), 7.31 – 7.26 (m, 3H), 4.28 (t, *J* = 7.4 Hz, 1H), 3.06 (d, *J* = 7.4 Hz, 2H), 2.89 – 2.84 (m, 4H), 2.18 – 2.09 (m, 1H), 1.95 – 1.83 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.4, 129.3, 128.4, 127.1, 48.7, 41.8, 30.6, 25.8. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{15}S_2]^+$ 211.0610 found: 211.0612.

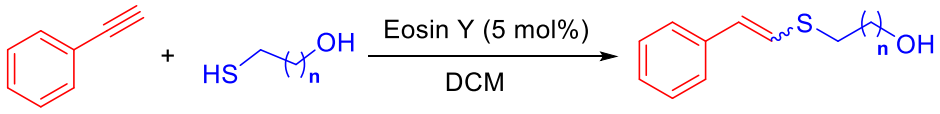
2-benzylbenzo[d][1,3]dithiole (3ac):



Synthesis of **3ac** done by following general procedure A and instead of **2a**, benzene1,2-dithiol **2c** was used for dithiolation of terminal phenylacetylene **1a**. Red coloured liquid. (74% yield, 36 mg). *Rf* = 0.8 (petroleum ether/EtOAc 95:5) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (tt, *J* = 7.9, 1.9 Hz, 2H), 7.31 (dt, *J* = 5.6, 2.3 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.08 (dd, *J* = 5.8, 3.2 Hz, 2H), 5.05 (t, *J* =

7.5 Hz, 1H), 3.26 (d, J = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 137.6, 137.2, 129.6, 128.6, 127.2, 125.6, 122.7, 55.7, 45.2. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{14}H_{13}S_2]^+$ 245.0453 found: 245.0472.

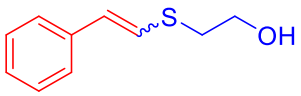
6. General procedure B for Thiol-yne reaction of 2d-2e on phenylacetylene/ Synthesis of 3ad-3ae:



1a | **2d - 2e** (**2d** n = 1, **2e** n = 2) | **3ad - 3ae** (**3ad** n = 1, **3ae** n = 2)

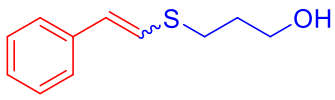
An oven-dried round bottom flask equipped with a stir bar and rubber septum is charged with phenyl acetylene **1a** (1 equiv., 0.2 mmol), 1-thioalkyl alcohol **2d-2e** (1 equiv., 0.2 mmol), Eosin Y (5 mol%, 6.4 mg), DCM (2 mL) under inert atmosphere. The reaction mixture was initially purged with argon for 5 min to remove any dissolved air and the argon atmosphere was maintained throughout the reaction (using a balloon). The reaction mixture was stirred under the irradiation of Blue LEDs (30 W) at room temperature for 24 h (Monitored by TLC, complete consumption of phenyl acetylene). After which, the solvent was evaporated under the reduced pressure and crude product was further purified by column chromatography over silica gel using mixture of petroleum ether/EtOAc as an eluent to afford respective compounds (**3ad-3ae**) as oil.

a) Synthesis of mixture of (*E*)-2-(styrylthio)ethan-1-ol and (*Z*)-2-(styrylthio)ethan-1-ol (3ad):



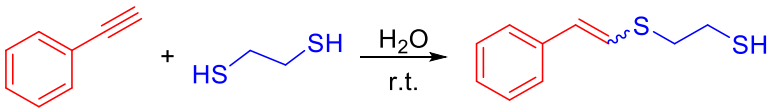
The general procedure B was followed to synthesise **3ad.** Here 2-mercapto-1-ethanol **2d** was used for dithiolation of phenyl acetylene to afford a mixture of cis and trans product 3ac. Colourless liquid (35 mg, 79%) *Rf* = 0.80 (petroleum ether/EtOAc 95:5) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 - 7.2 (5H), 6.7 - 6.2 (2H), 3.8 (2H), 3.0 - 2.9 (2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 136.7, 136.7, 129.1, 128.8, 128.8, 128.4, 127.3, 127.1, 126.9, 126.3, 125.8, 123.8, 61.6, 61.1, 38.8, 36.1. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{10}H_{13}OS]^+$ 181.0682 found: 181.0678.

b) Synthesis of mixture of (*E*)-2-(styrylthio)propa-1-ol and (*Z*)-2-(styrylthio)propa-1-ol (3ae):



Following general procedure B to synthesis of **3ae.** Here 3-mercapto-1-propanol **2e** was used for dithiolation of phenyl acetylene to afford a mixture of cis and trans product 3ad. Colourless liquid (36 mg, 76%) *Rf* = 0.81 (petroleum ether/EtOAc 95:5) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 - 7.2 (5H), 6.7 - 6.2 (2H), 3.8 - 3.7 (2H), 2.9 (2H), 2.0 - 1.9 (2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 137.1, 137.0, 128.8, 128.7, 128.4, 127.5, 127.2, 127.1, 126.8, 126.0, 125.6, 124.8, 61.4, 61.1, 32.8, 32.4, 32.1, 29.2. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{11}H_{15}OS]^+$ 195.0838 found: 195.0848.

7. Procedure for the synthesis of 3A[3]



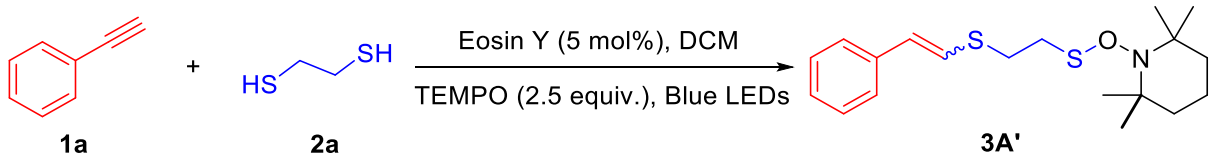
1a **2a** **3A**

An oven-dried round bottom flask equipped with a stir bar and rubber septum is charged with phenylacetylene **1a** (2 mmol, 204.3 mg), 1,2-ethanedithiane **2a** (2 mmol, 188.4 mg), H_2O (5 mL) was stirred for 3 h. After complete consumption of phenylacetylene the reaction mixture was extracted in diethyl ether two times (20 mL x 2). The combined organic layer was filtered through anhydrous sodium sulphate and was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel using mixture of petroleum ether/EtOAc as an eluent to obtain **3A** with 70% yield as a colourless oil.[3] *Rf* = 0.79 (petroleum ether/EtOAc 99:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.14 (m, 6H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.47 (d, *J* = 10.8 Hz, 1H), 6.19 (d, *J* = 10.8 Hz, 1H), 3.80 (td, *J* = 5.9, 4.6 Hz, 2H), 2.95 (dt, *J* = 7.6, 6.0 Hz, 2H), 2.03 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 136.7, 136.7, 129.1, 128.8,

128.8, 128.4, 127.3, 127.1, 126.9, 126.3, 125.8, 123.8, 77.2, 61.6, 61.1, 38.8, 36.1. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_{10}H_{13}S_2]^+$ 197.0453 found: 197.0460.

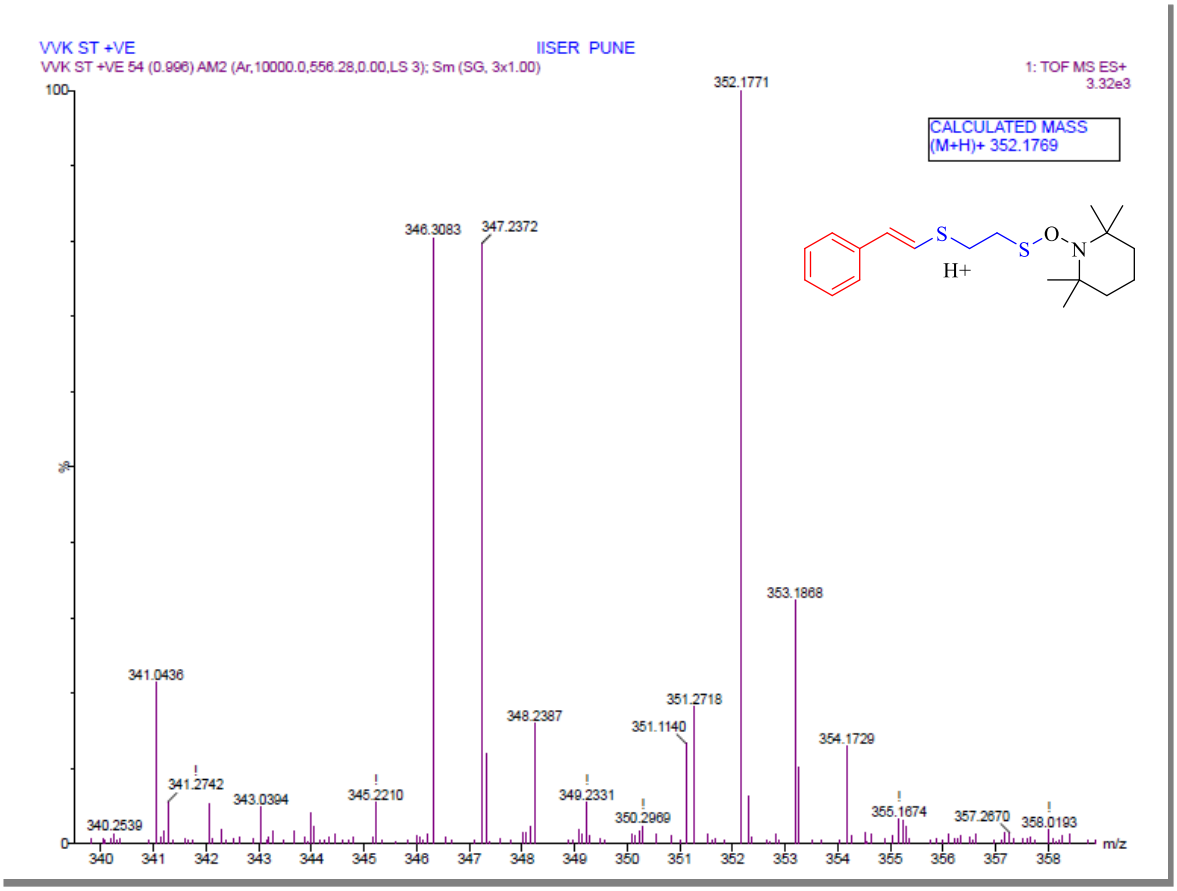
8. Control experiments:

a) Reaction with TEMPO



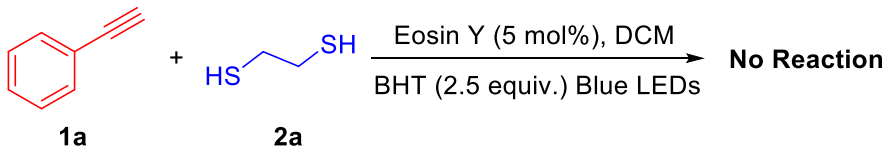
1a **2a** **3A'**

The 10 mL round bottom flask was charged a magnetic stir bar, **1a** (0.2 mmol, 20.43 mg), **2a** (0.2 mmol, 18.84 mg), Eosin Y (5 mol%, 0.06 mg) as a photoredox catalyst with TEMPO (0.5 mmol, 78.13 mg) in dichloromethane under an inert atmosphere. The reaction mixture was degassed for 5 minutes then it was subjected to the irradiation of blue light. After 24 hours we have taken the TLC of the reaction mixture and we came to know that our dithiolation type of product was not formed but starting material was completely consumed then we have given the HRMS of the reaction mixture. We notified that TEMPO trapped **3A'** product was formed and the HRMS of **3A'** shown below.



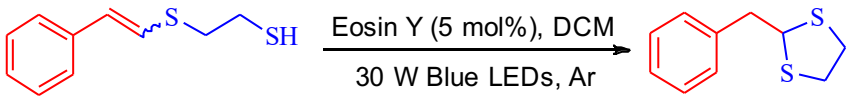
HRMS Spectrum of 3A'

b) Reaction with BHT



A 10 mL round bottom flask was charged a magnetic stir bar, **1a** (0.2 mmol, 20.43 mg), **2a** (0.2 mmol, 18.84 mg), Eosin Y (5 mol%, 0.06 mg) as a photoredox catalyst with BHT (0.5 mmol, 55.08 mg) in dichloromethane under an inert atmosphere. The reaction mixture was degassed for 5 minutes then it was subjected to the irradiation of blue light. After 24 hours we have taken TLC of the reaction mixture and we came to know that our dithiolation type of product was not formed.

c) Reaction of 3A under optimized reaction condition:

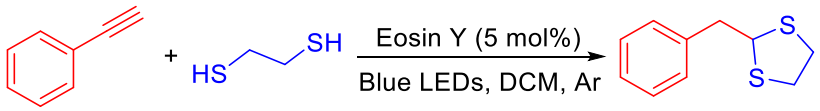


3A **3aa, 70%**

A 10 mL round bottom flask was charged a magnetic stir bar, **3A** (0.2 mmol, 39.26 mg), Eosin Y (5 mol%, 0.06 mg) as a photoredox catalyst in dichloromethane (2 mL) solvent under an inert atmosphere. The reaction mixture was degassed for 5 minutes then it was kept under the irradiation of blue LED (30 W). The reaction was monitored by TLC, after completion of reaction solvent was evaporated and **3aa** was purified by preparative thin-layer chromatography (70% yield).

9. Applications of 2-benzyl-1,3-dithiol

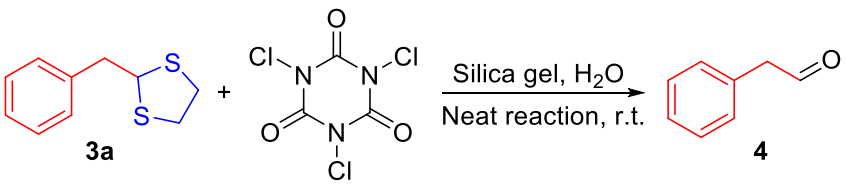
a) Gram scale synthesis of (3aa):



1a **2a** **3aa**

An oven-dried round bottom flask (100 mL) equipped with a stir bar and rubber septum is charged with phenyl acetylene **1a** (9.79 mmol, 1 equiv., 1 g), ethane-1,2-dithiol **2a** (9.79 mmol, 0.922 g, 1 equiv.), Eosin Y (5 mol%, 0.308 g), DCM (80 mL). The reaction mixture was initially purged with argon for 5 min to remove any dissolved air and the argon atmosphere was maintained throughout the reaction (using a balloon). After which, the solvent was evaporated under the reduced pressure and crude product was further purified by column chromatography over silica gel using mixture of petroleum ether/EtOAc as an eluent to afford **3aa** as colourless oil (73% yield, 1.4 g).

b) Deprotection (4):



3a **4**

A mixture of 2-benzyl-1,3-dithiol **3aa** (2 mmol, 39.26 mg), trichloro isocyanuric acid (3 mmol, 69.72 mg) and silica gel (2 g) was graded ground in a mortar with the help of a piston. Water (10-15 drops) was added with constant stirring and the resultant mixture was extracted in 5ml of hexane/ethyl acetate (5:1). The organic layer was filtered through sodium sulphate and evaporated under reduced pressure to afford phenyl acetaldehyde **4** as a colourless liquid. (80%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 2.4 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.32 (dt, *J* = 9.7, 4.4 Hz, 1H), 7.25 – 7.21 (m, 2H), 3.70 (d, *J* = 2.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.6, 132.0, 129.7, 129.1, 127.5, 50.7. HRMS (ESI TOF) *m/z* $[M+H]^+$ calculated for $[C_8H_9O]^+$ 121.0648 found: 121.0644.

10. Cyclic Voltammetry:

Cyclic voltammetry was performed using a glassy carbon as a working electrode, a platinum-plated counter electrode and Ag/AgCl as a reference electrode. We prepared 3 mM concentation of substrates (**3aa** and **3A** independently) in dry and degassed acetonitrile along with 100 mM of tetra-*n*-butylammonium hexafluorophosphate in a dry, degassed acetonitrile as electrolyte solution. The data was recorded with a scan rate of 50 mV/S. Reductions were measured by scanning potentials in the negative direction and oxidations in the positive direction and the glassy carbon electrode was polished before each scan. The cyclic voltammetry of phenylacetylene **1a** was previously reported and the obtained value was referenced to Ag/AgCl and converted to SCE by subtracting 0.03 V.[4]

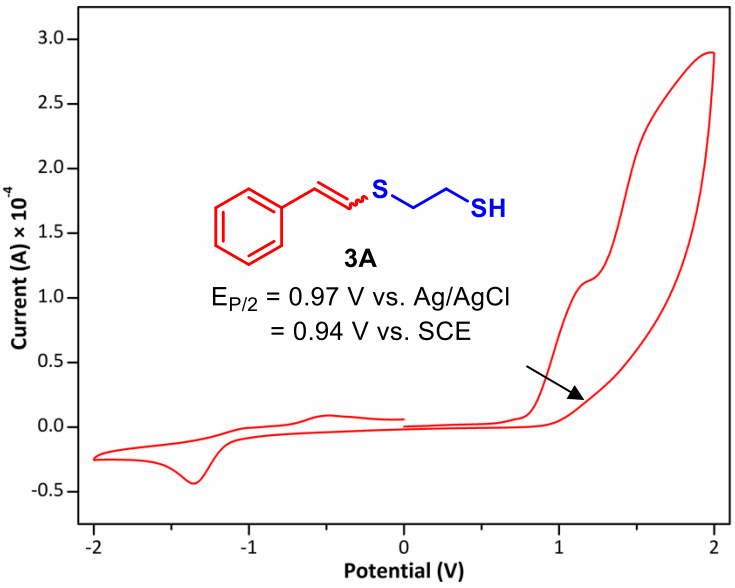


Fig. 10.1. Cyclic voltammetry of **3A**

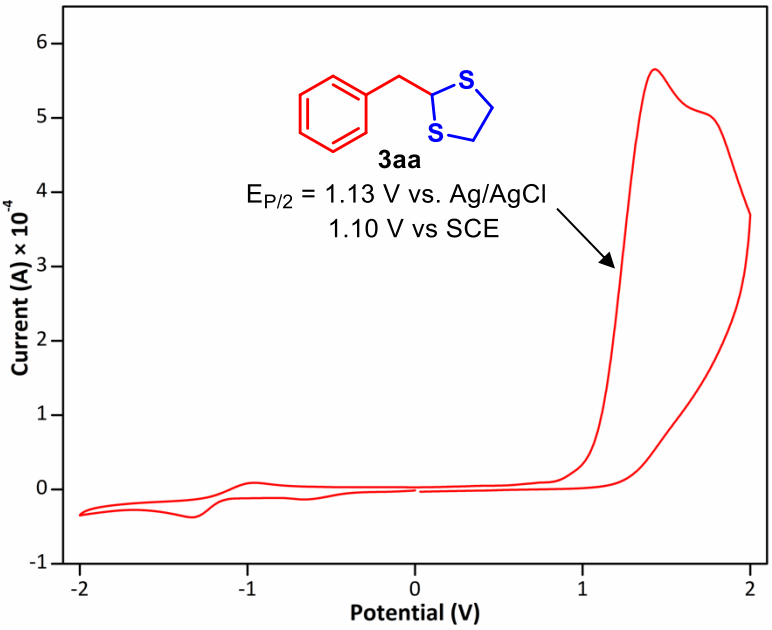


Fig. 10.2. Cyclic voltammetry of **3aa**

11. Emission quenching of EY (Eosin Y) with 3A/1a/3aa.

Emission spectra were collected on Fluoromax-4 spectrophotometer from Horiba Jobin-Yvon, with xenon light source with excitation and emission slit widths of 1 and 2 nm respectively. Experiments were carried out using 1 μM solution of **EY** in acetonitrile and variable concentrations of compounds (**3A/1a/3aa**) as quenchers in Hellma fluorescence cuvette (path length 1.0 cm, 3 mL). All the samples were excited at 490 nm and the intensity of emission was monitored at 547 nm and expressed as the I_0/I as a function of the quencher concentration was measured. I_0 is the emission intensity of **EY** at 547 nm in the absence of a quencher and I is the observed intensity in presence of quencher.

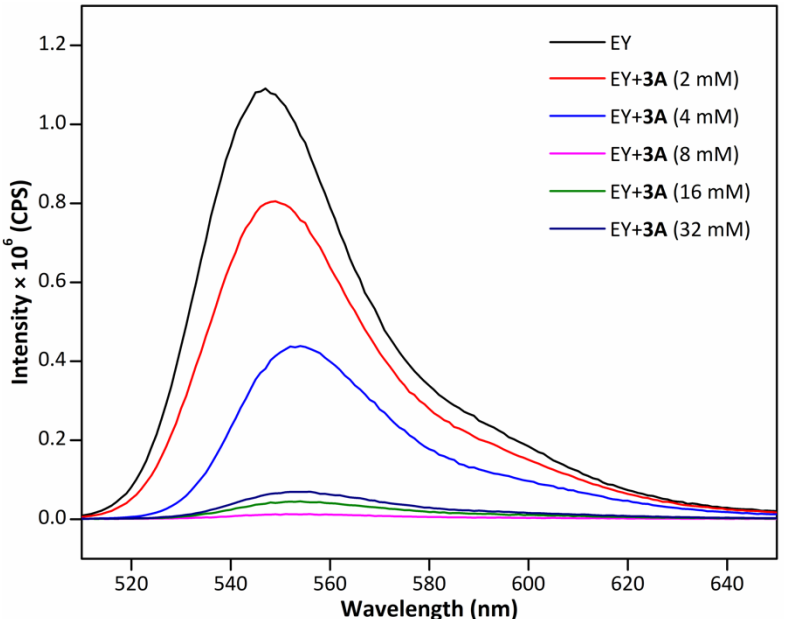


Fig. 11.1 Emission quenching of Eosin Y with **3A**

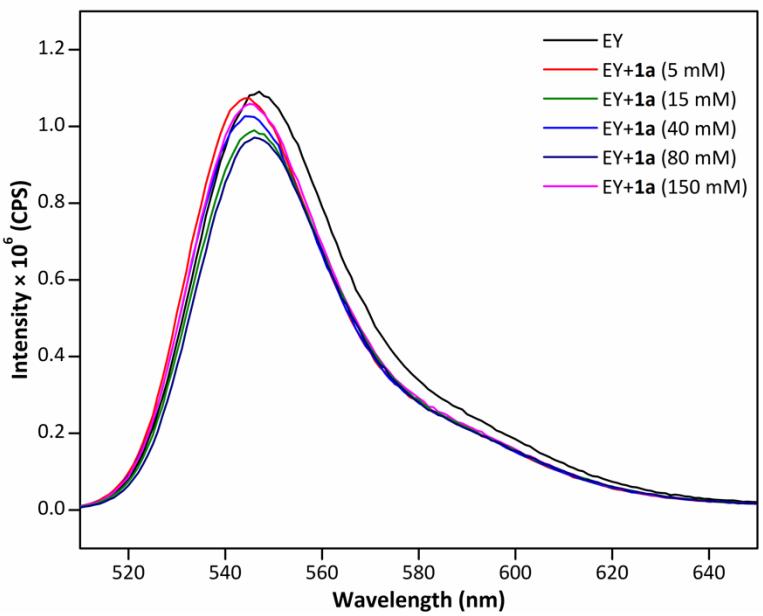


Fig. 11.1 Emission quenching of Eosin Y with **1a**

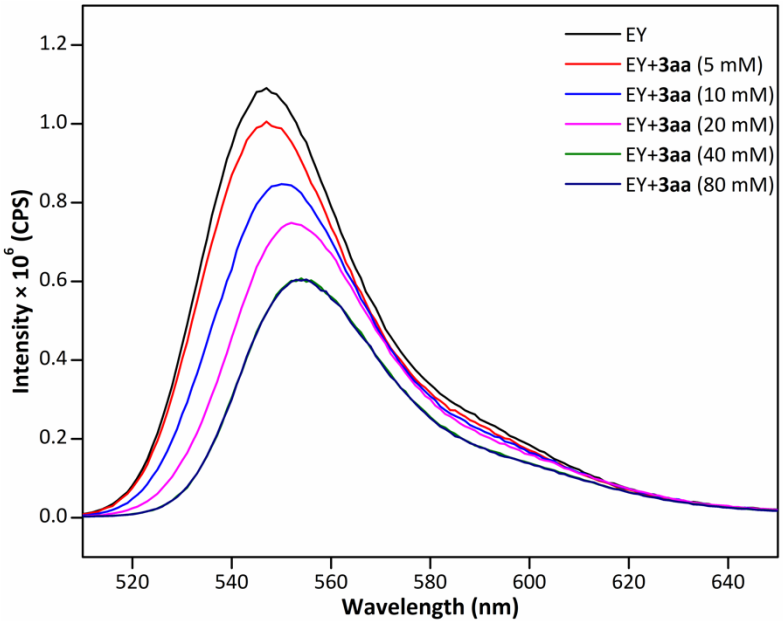
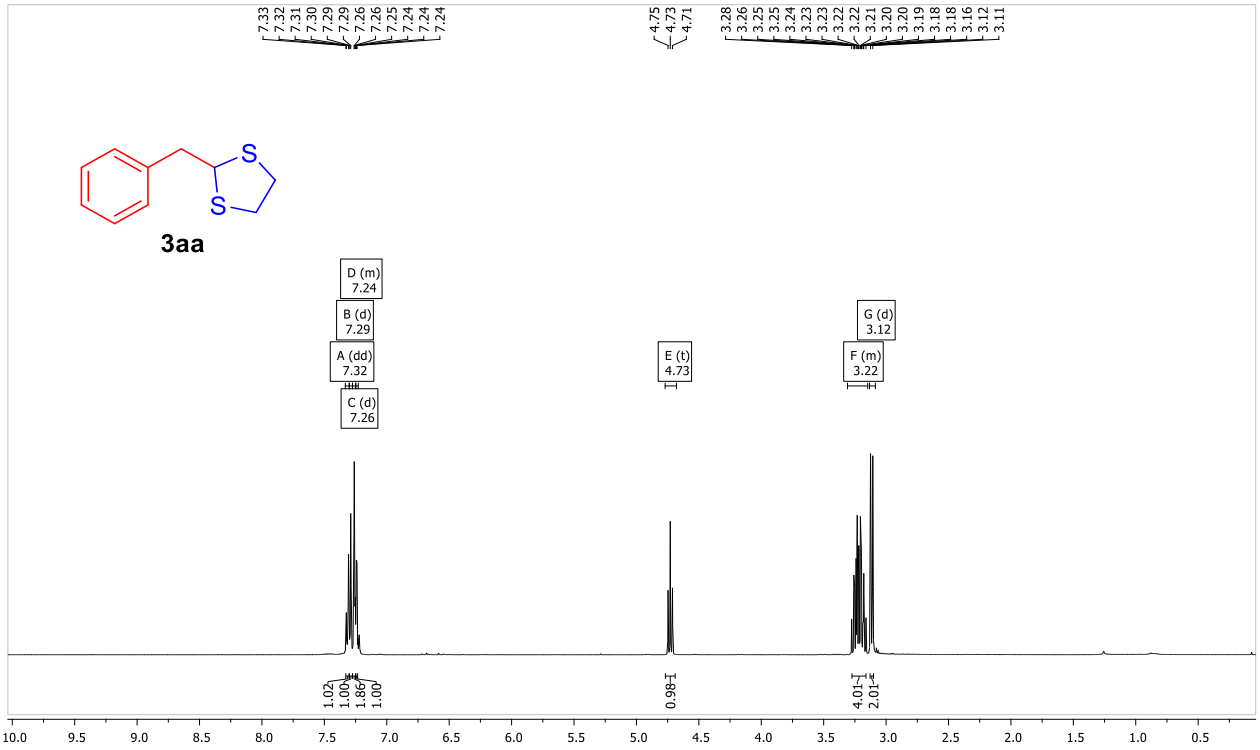
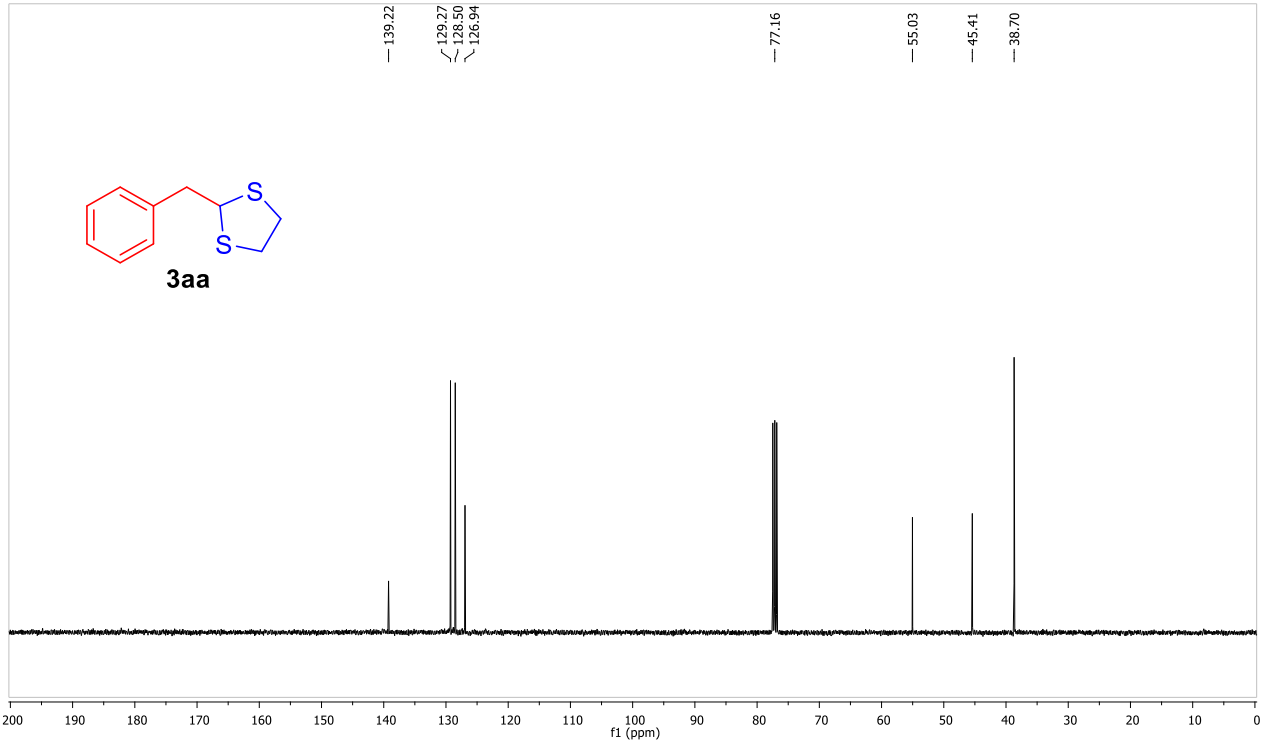


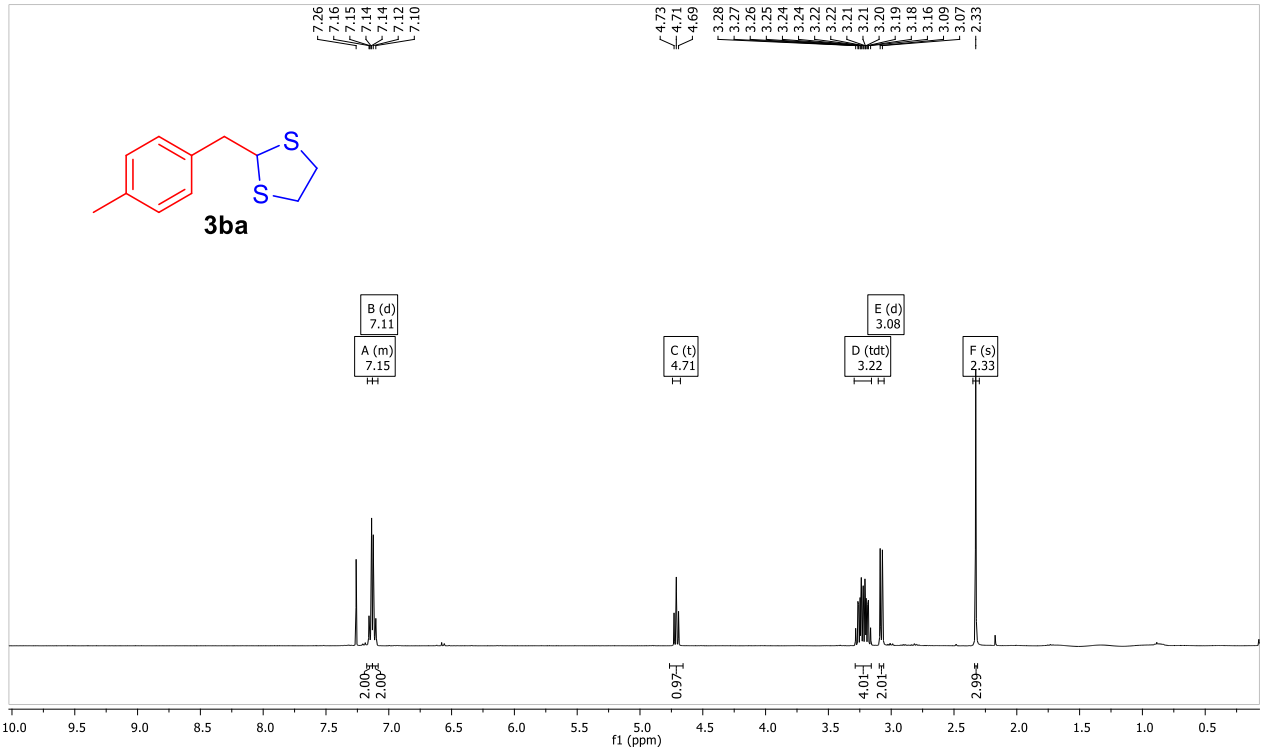
Fig. 11.1 Emission quenching of Eosin Y with **3aa**

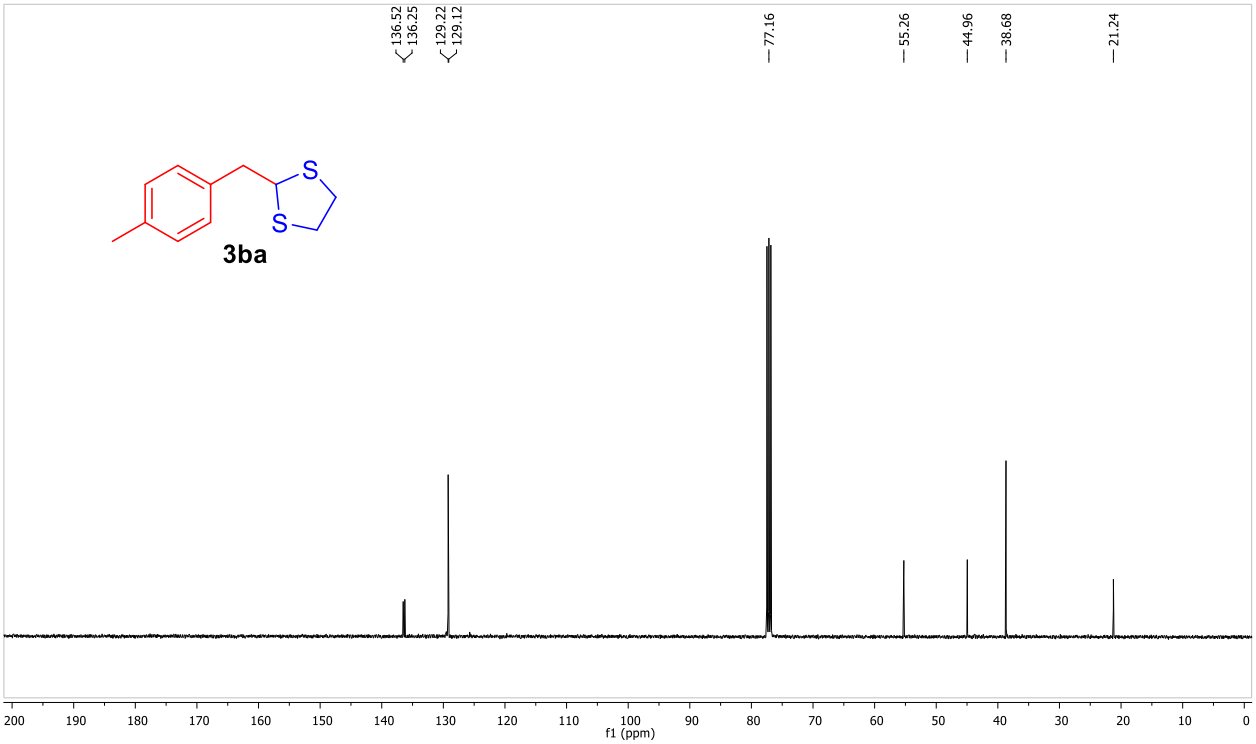
^{1}H & ^{13}C Spectra of 3aa



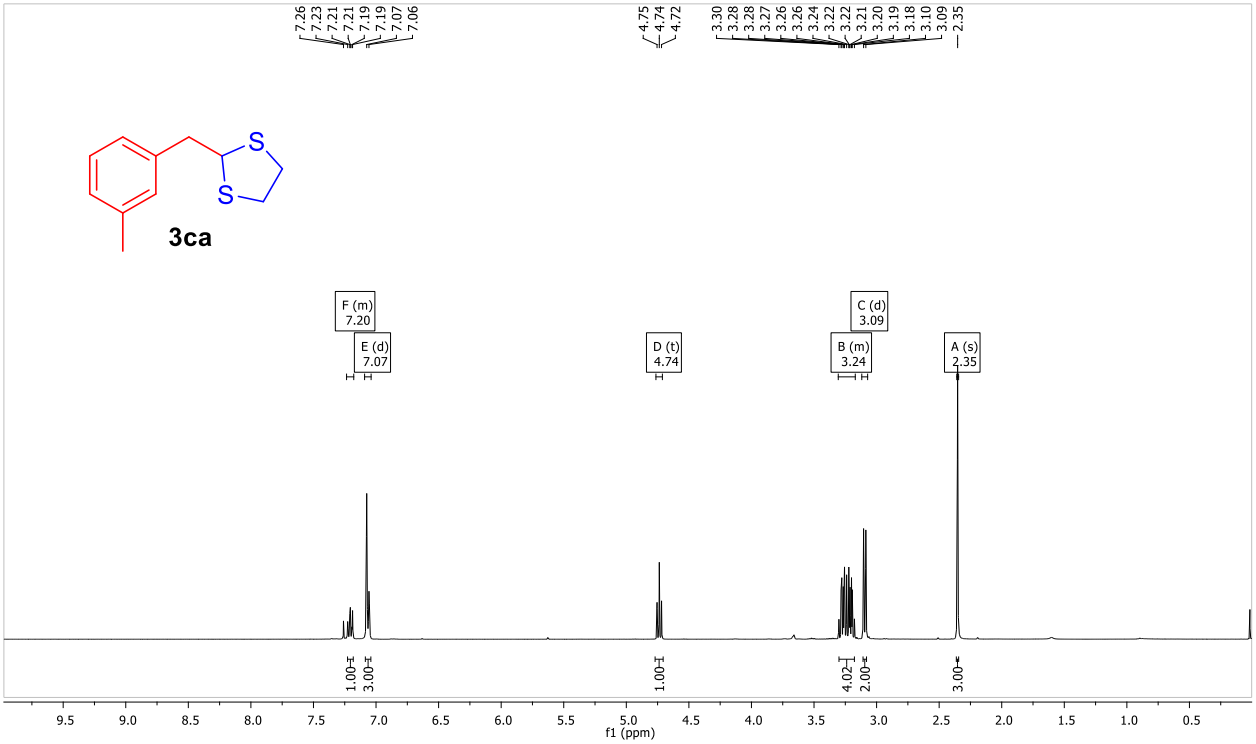


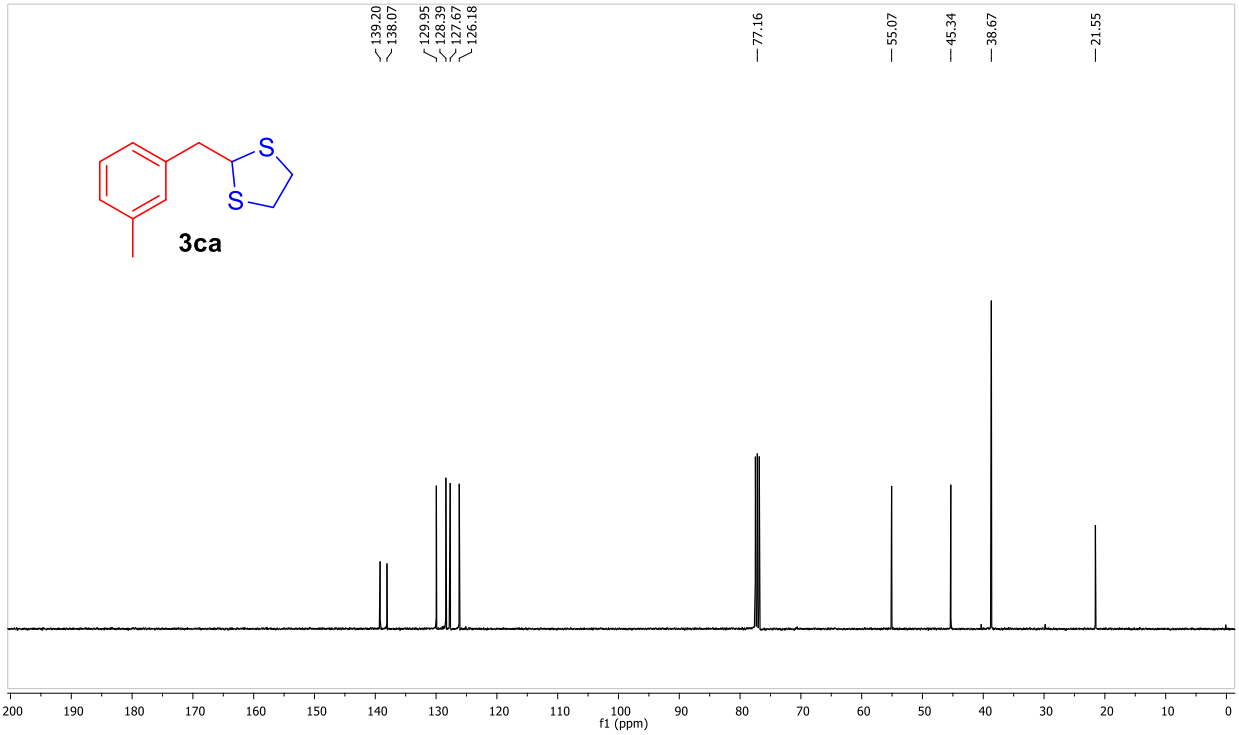
^{1}H & ^{13}C Spectra of 3ba



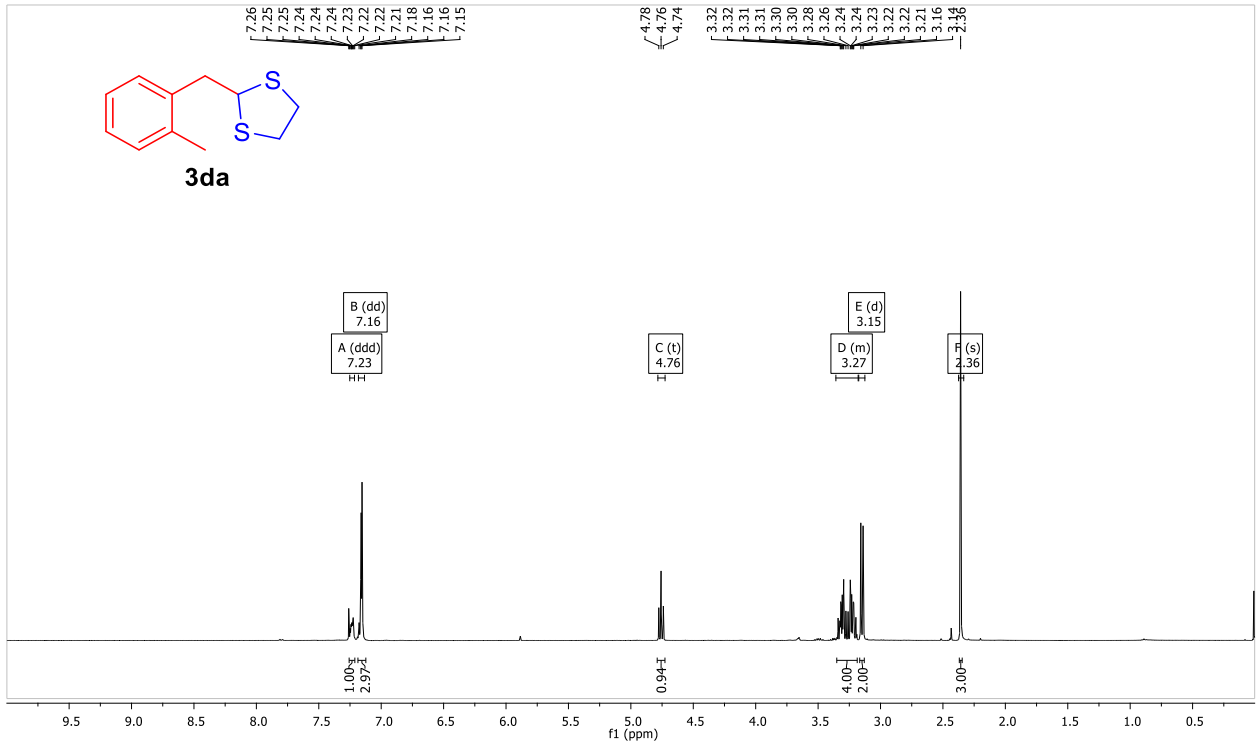


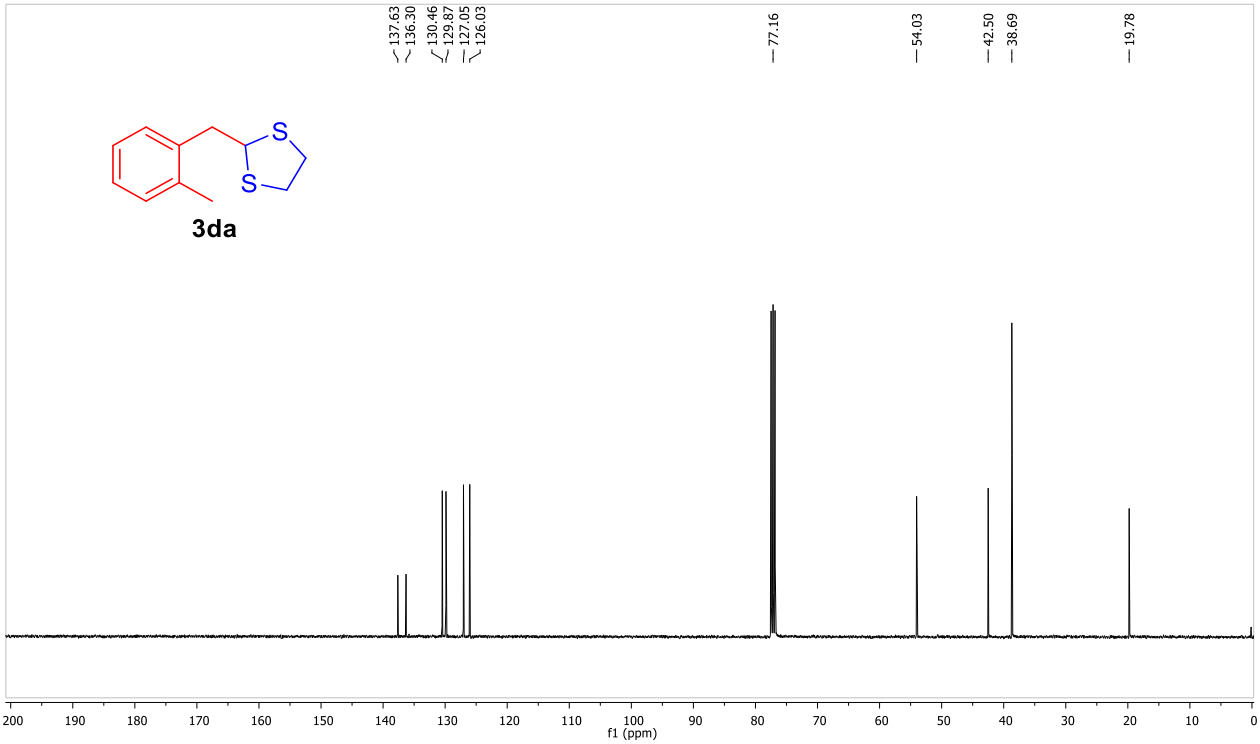
^{1}H & ^{13}C Spectra of 3ca



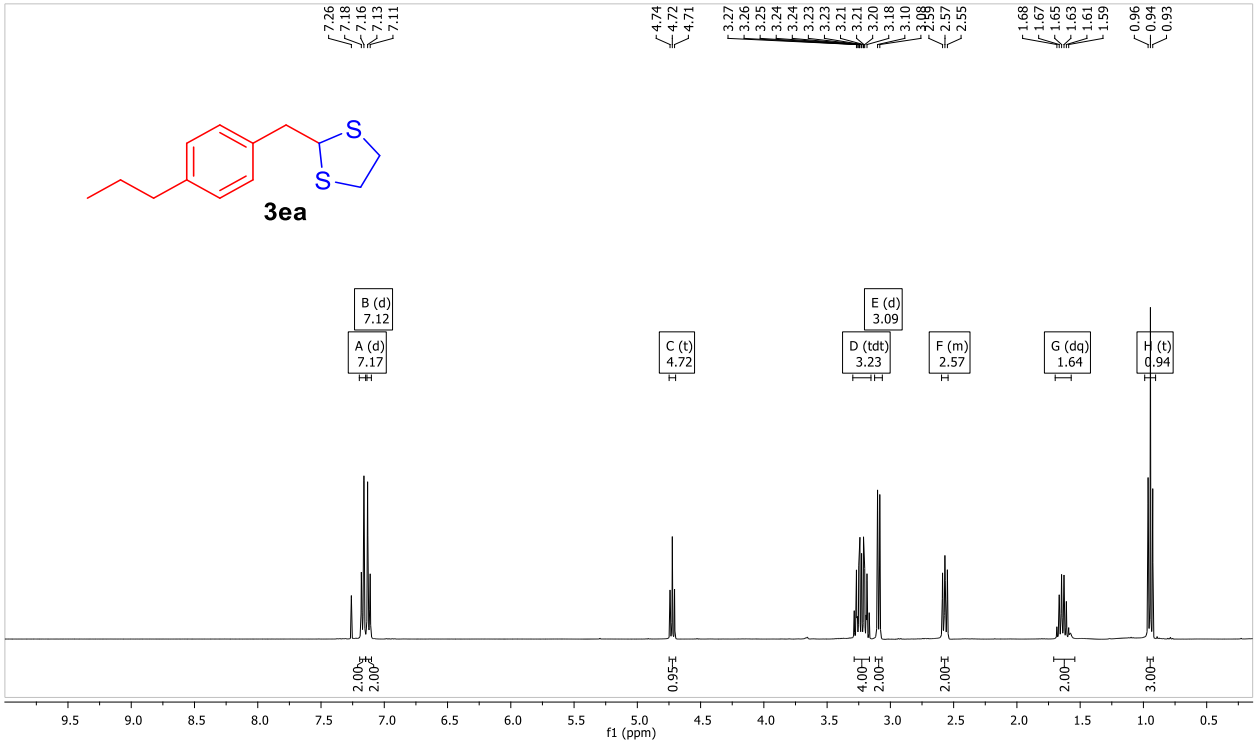


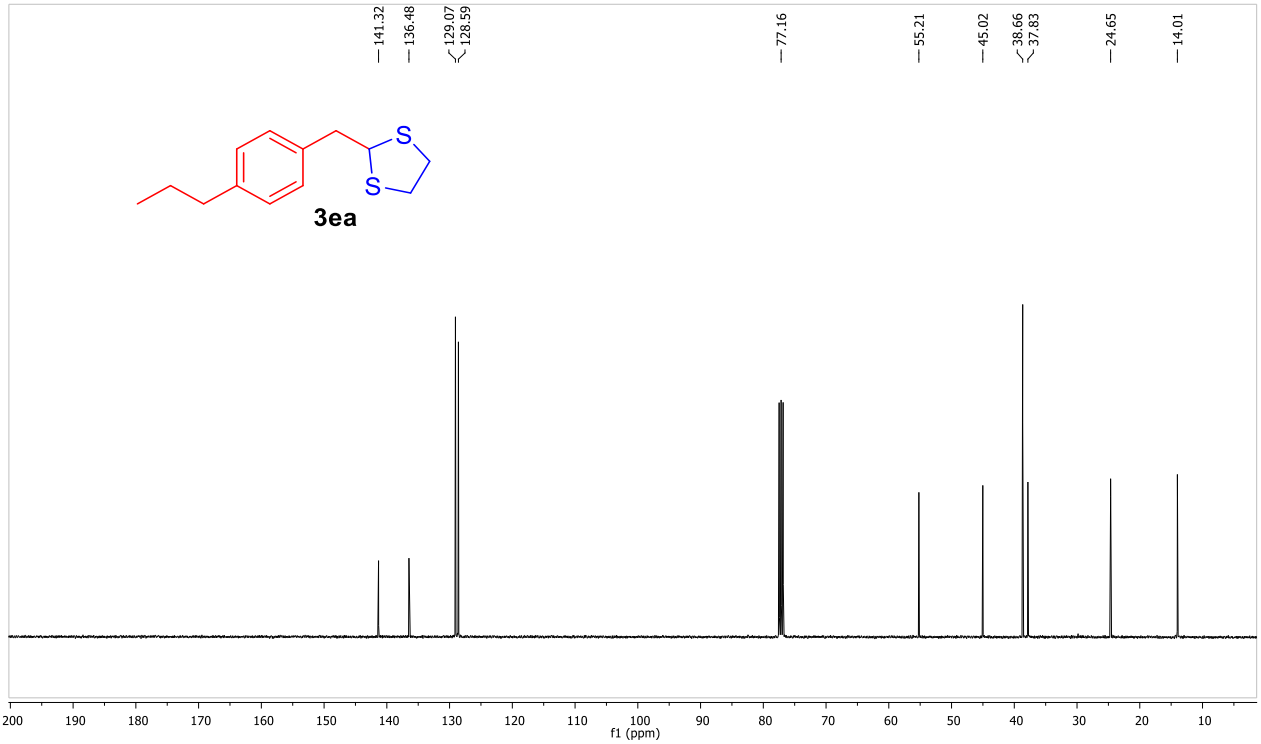
^{1}H & ^{13}C Spectra of 3da



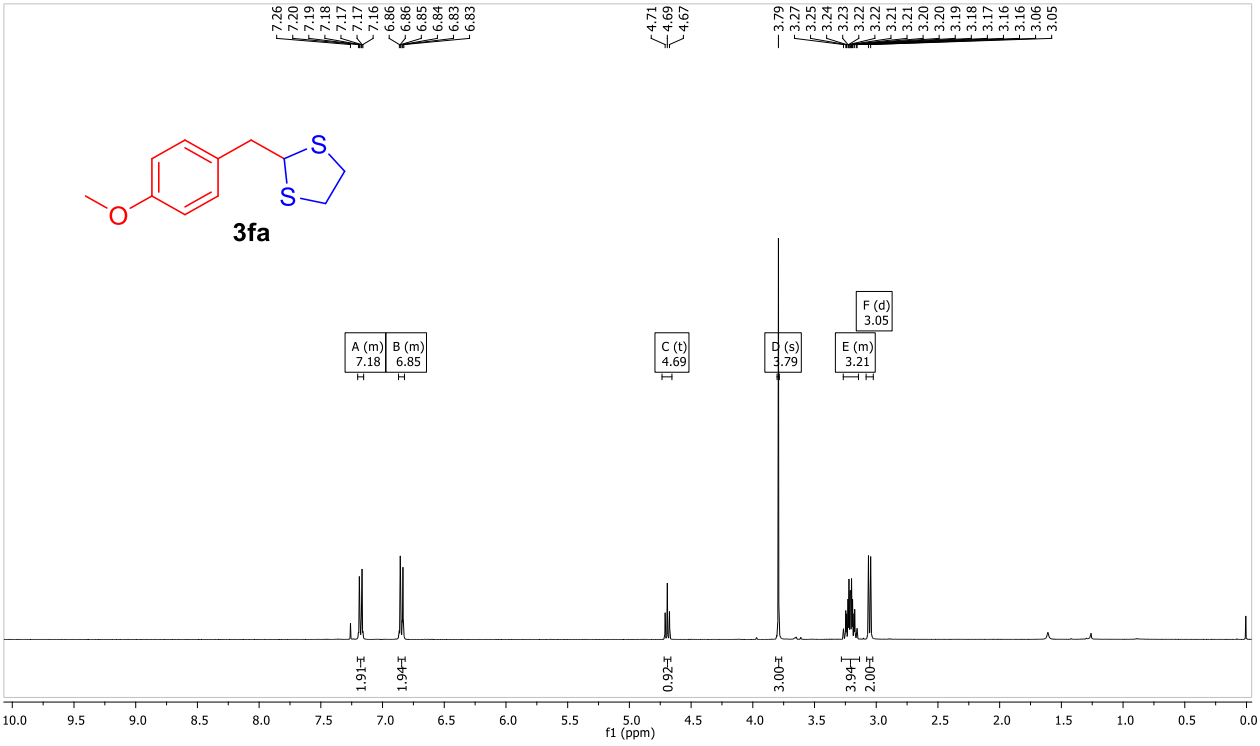


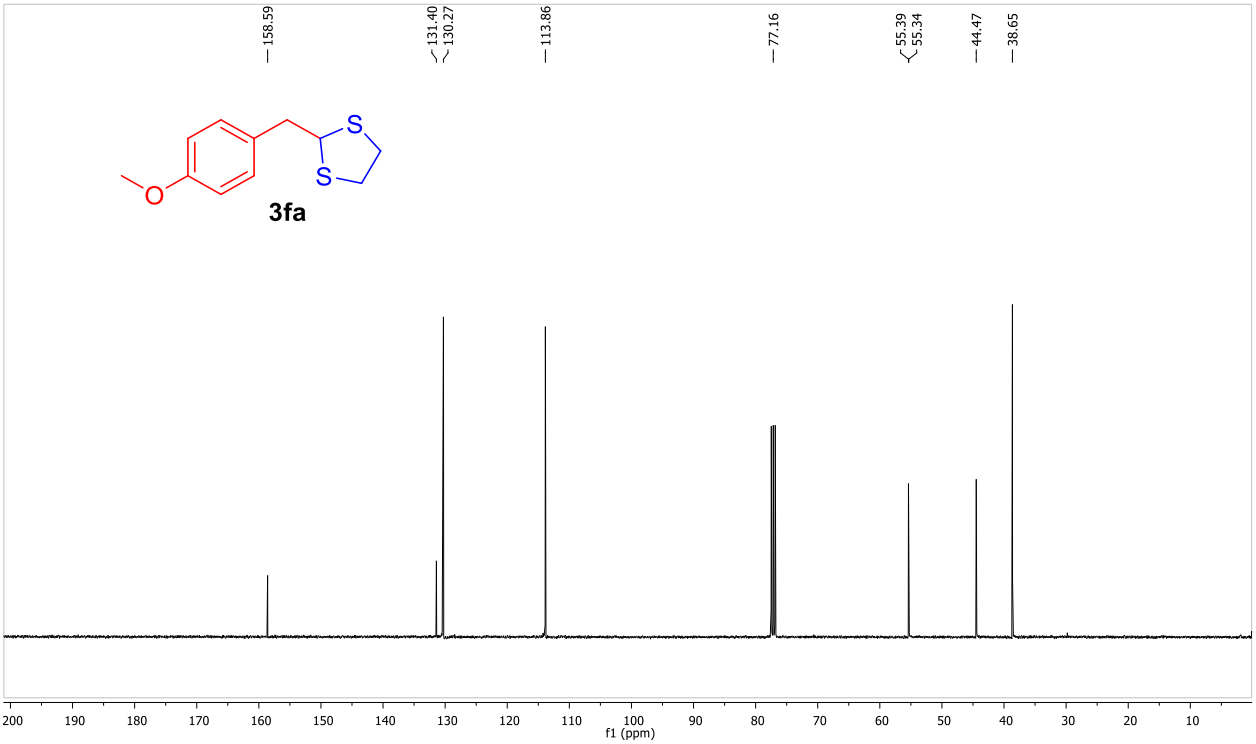
^{1}H & ^{13}C Spectra of 3ea



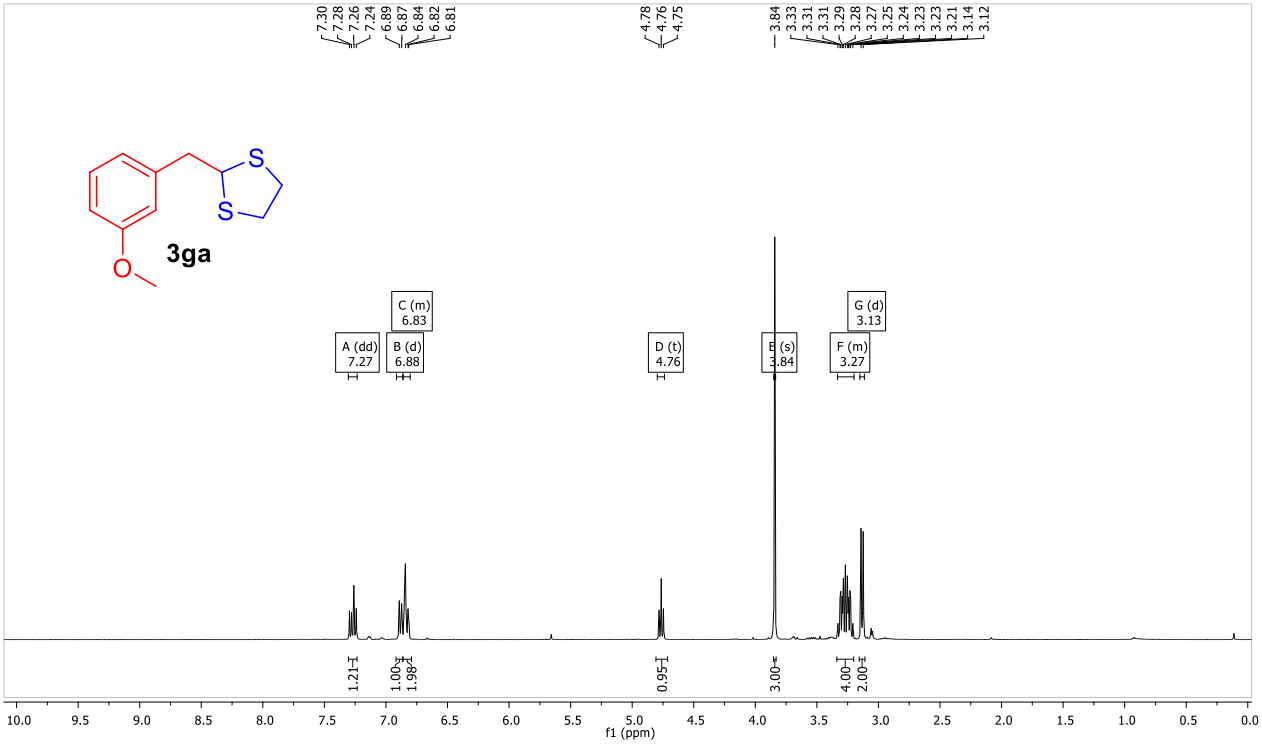


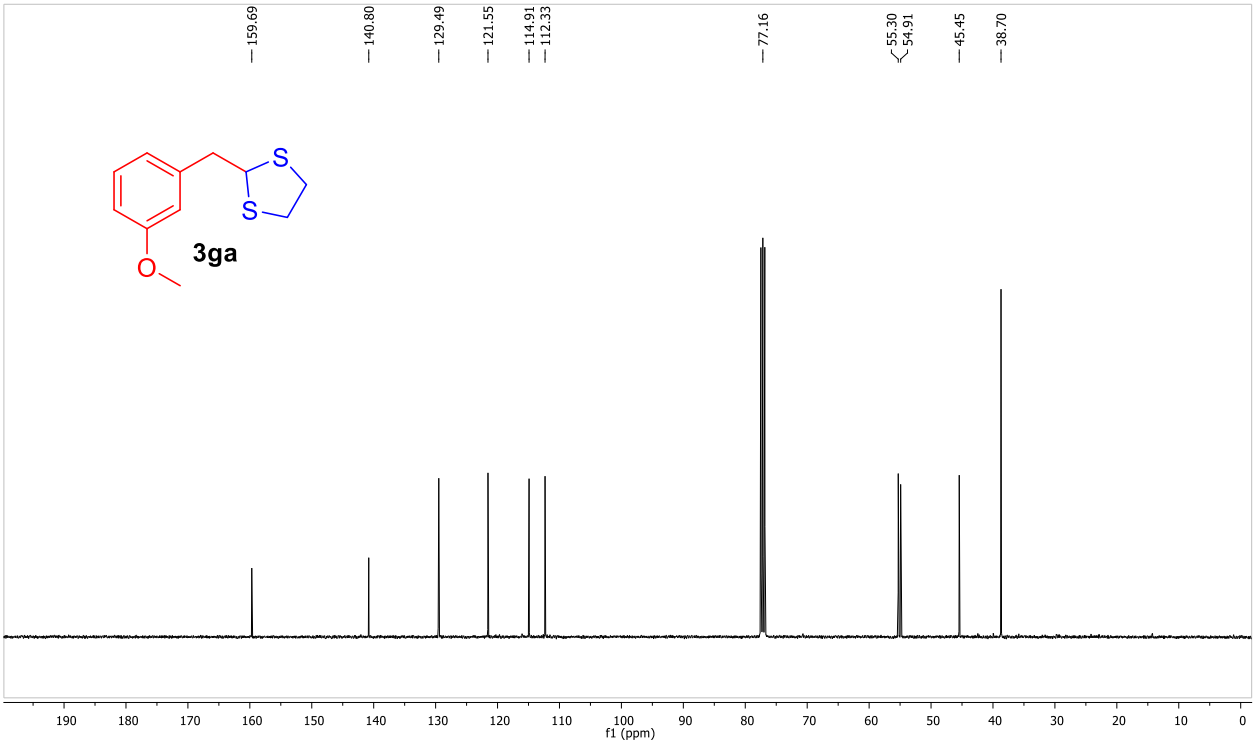
^{1}H & ^{13}C Spectra of 3fa



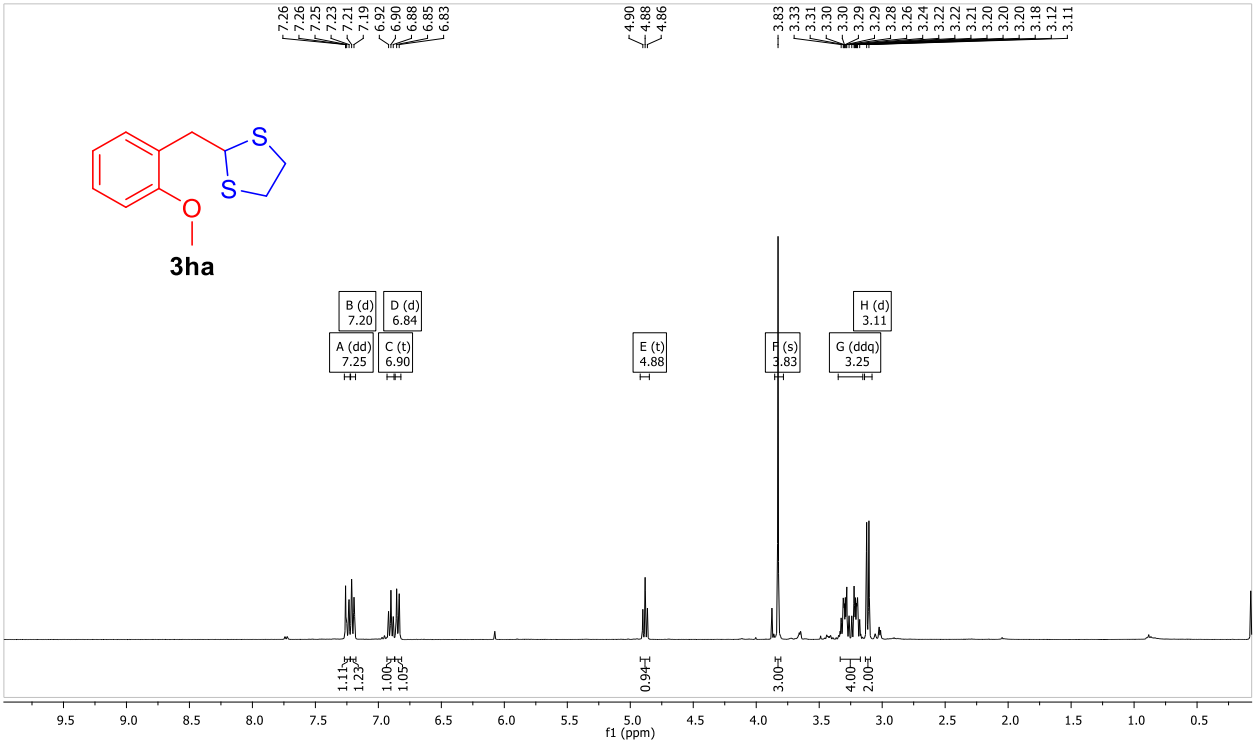


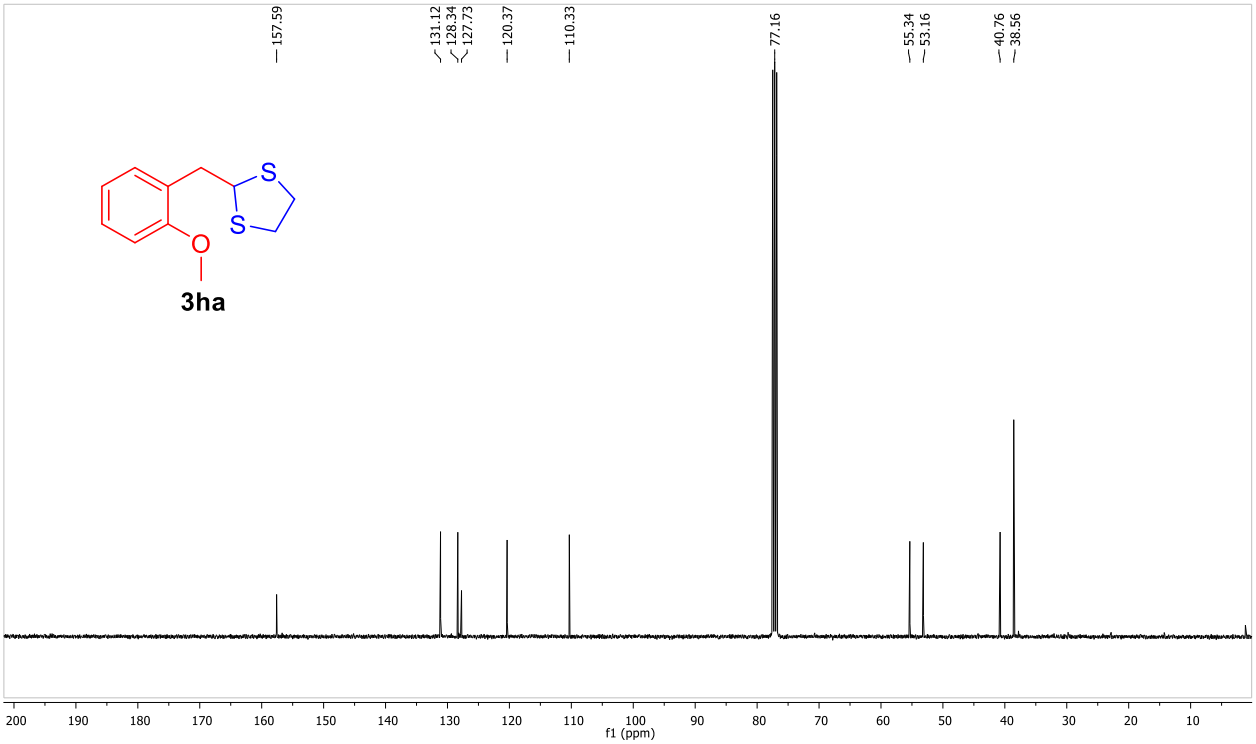
^{1}H & ^{13}C Spectra of 3ga



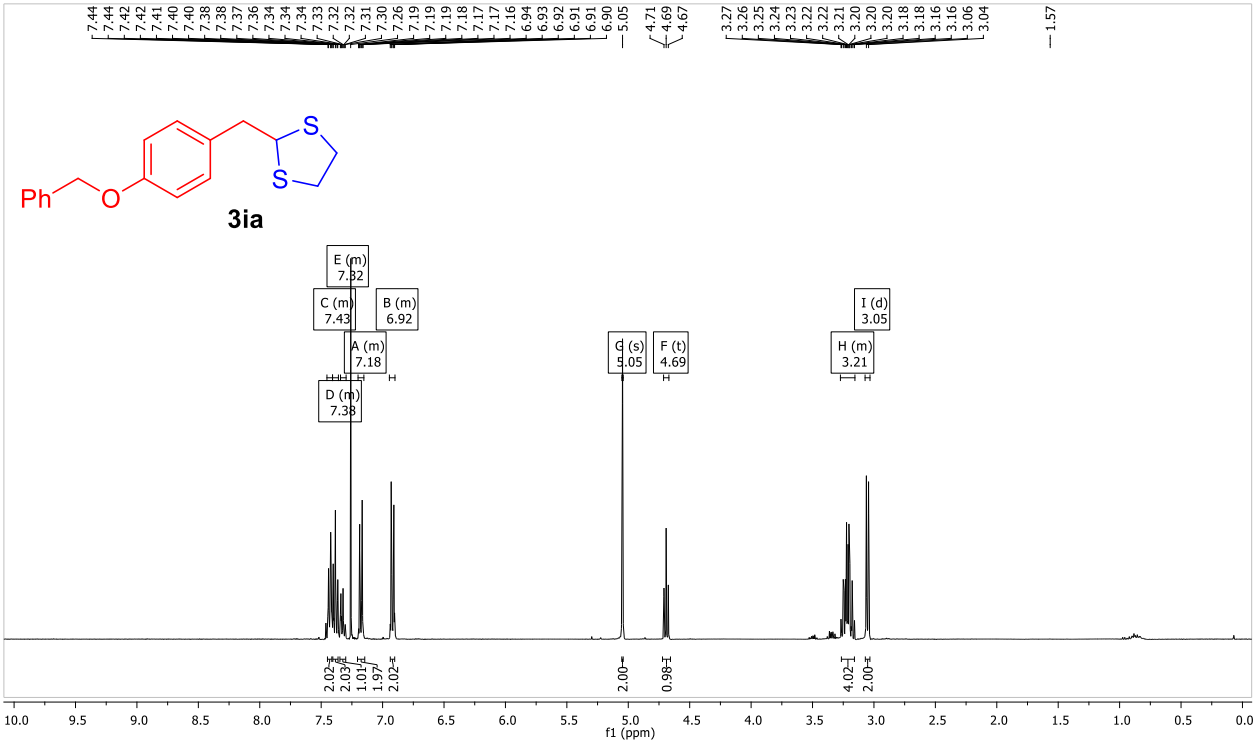


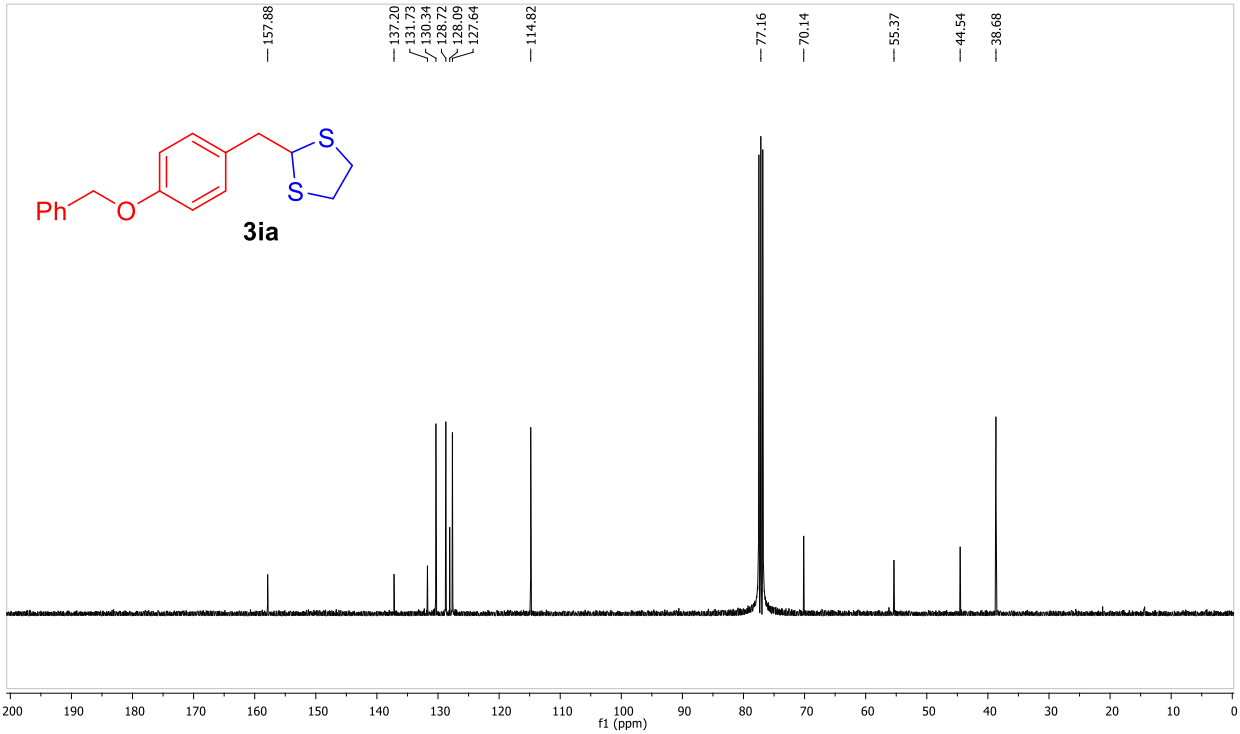
^{1}H & ^{13}C Spectra of 3ha



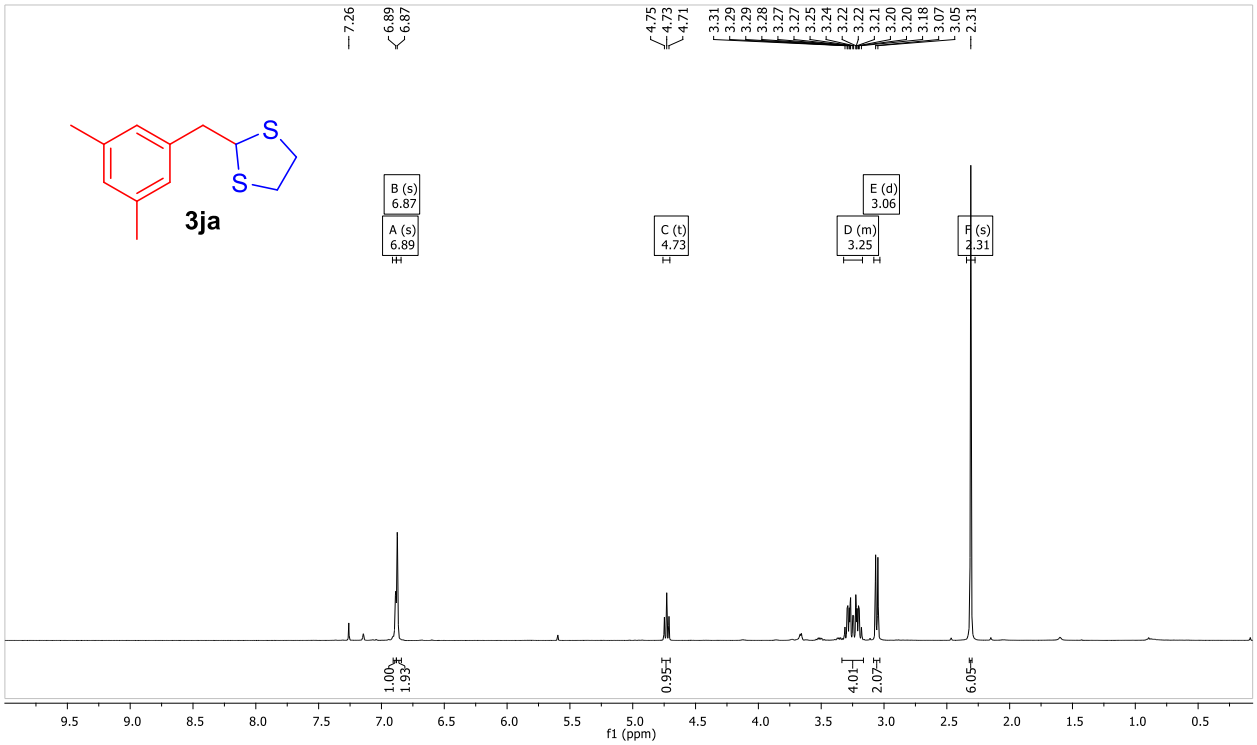


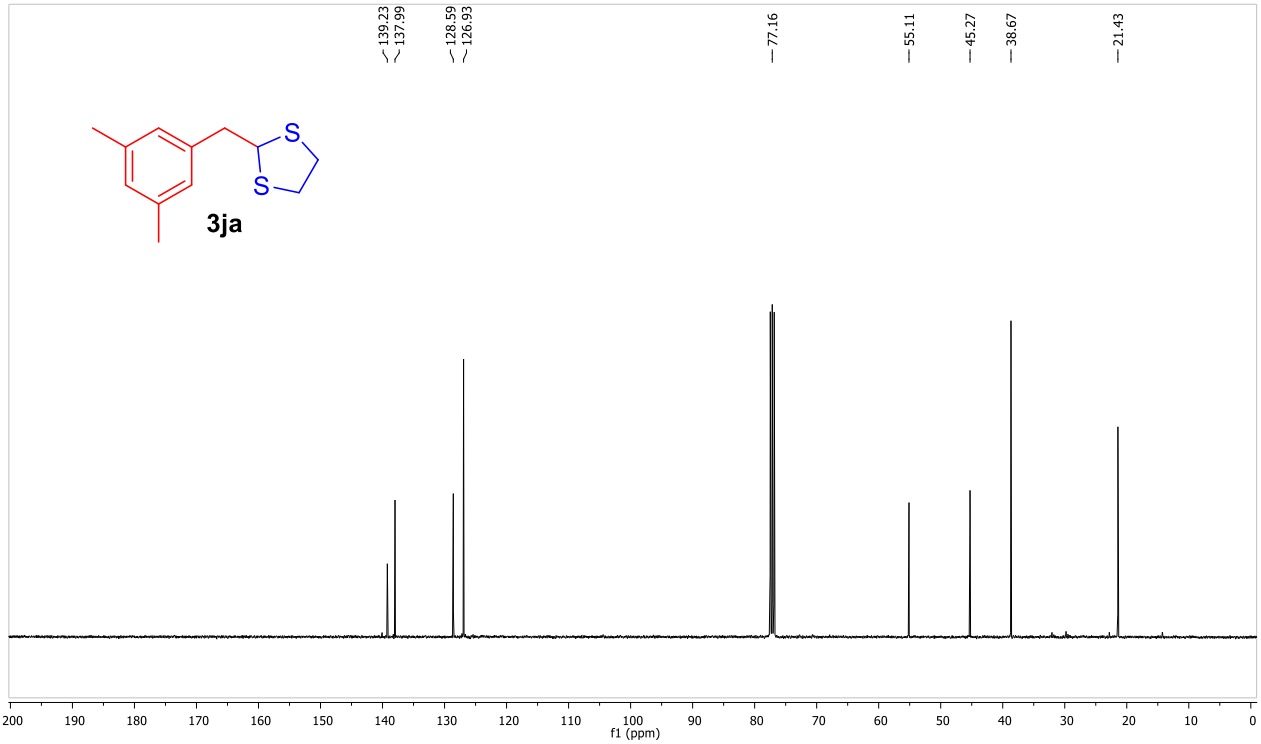
^{1}H & ^{13}C Spectra of 3ia



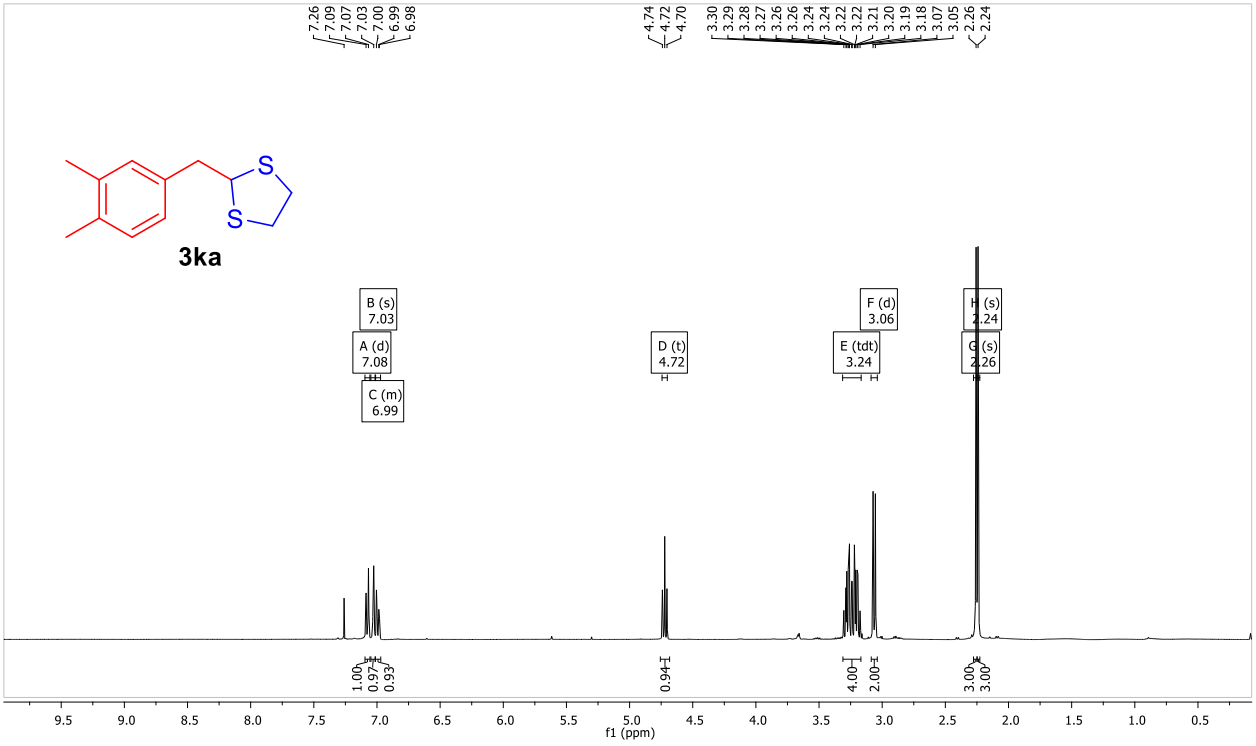


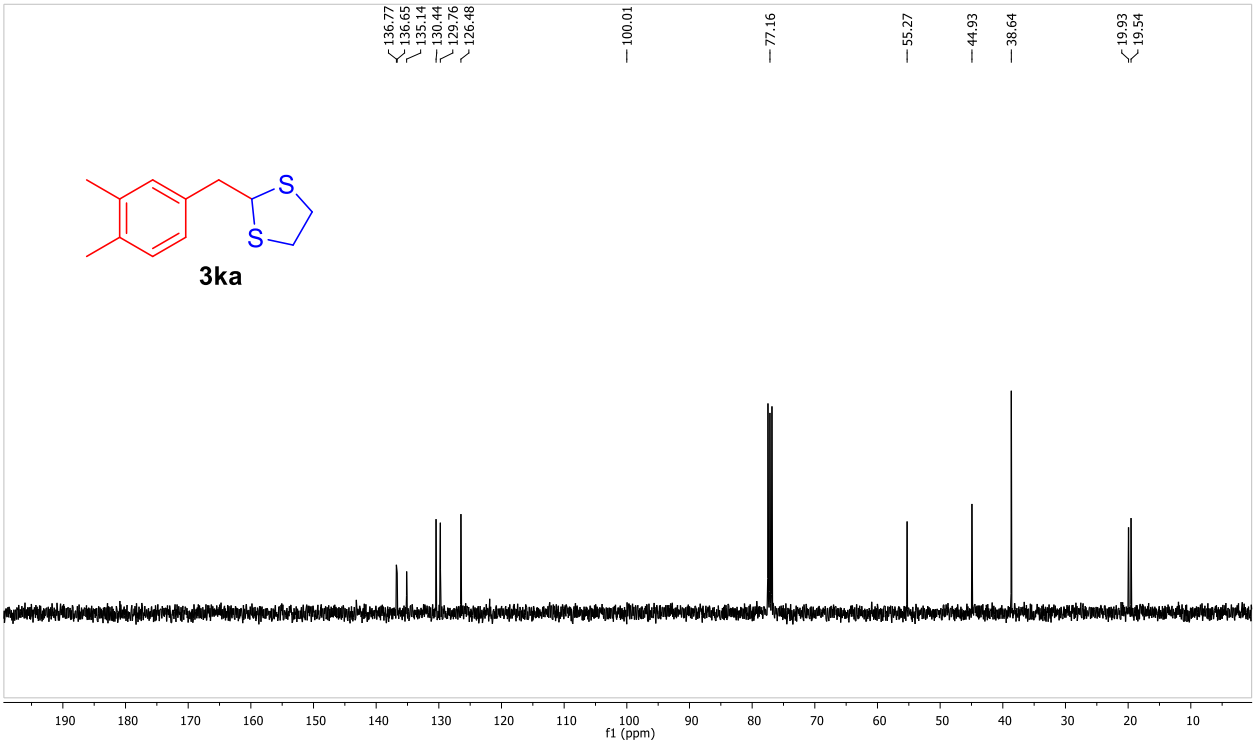
^{1}H & ^{13}C Spectra of 3ja



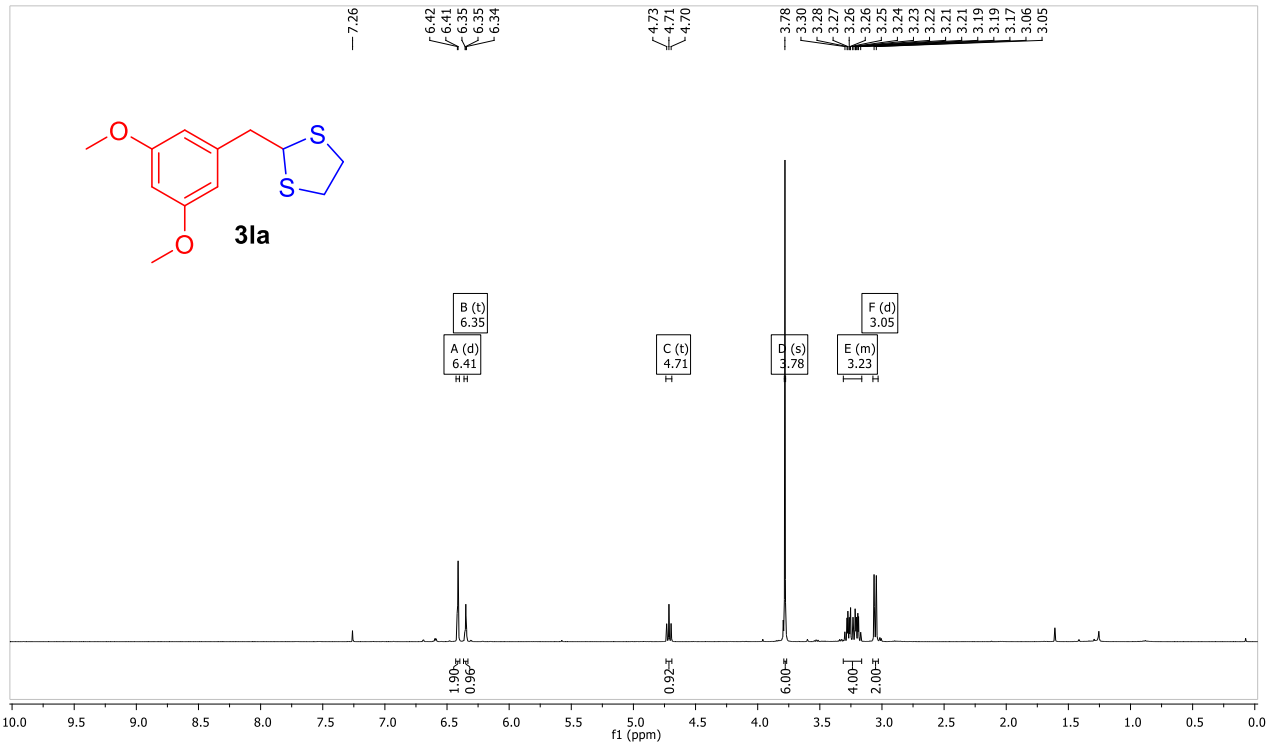


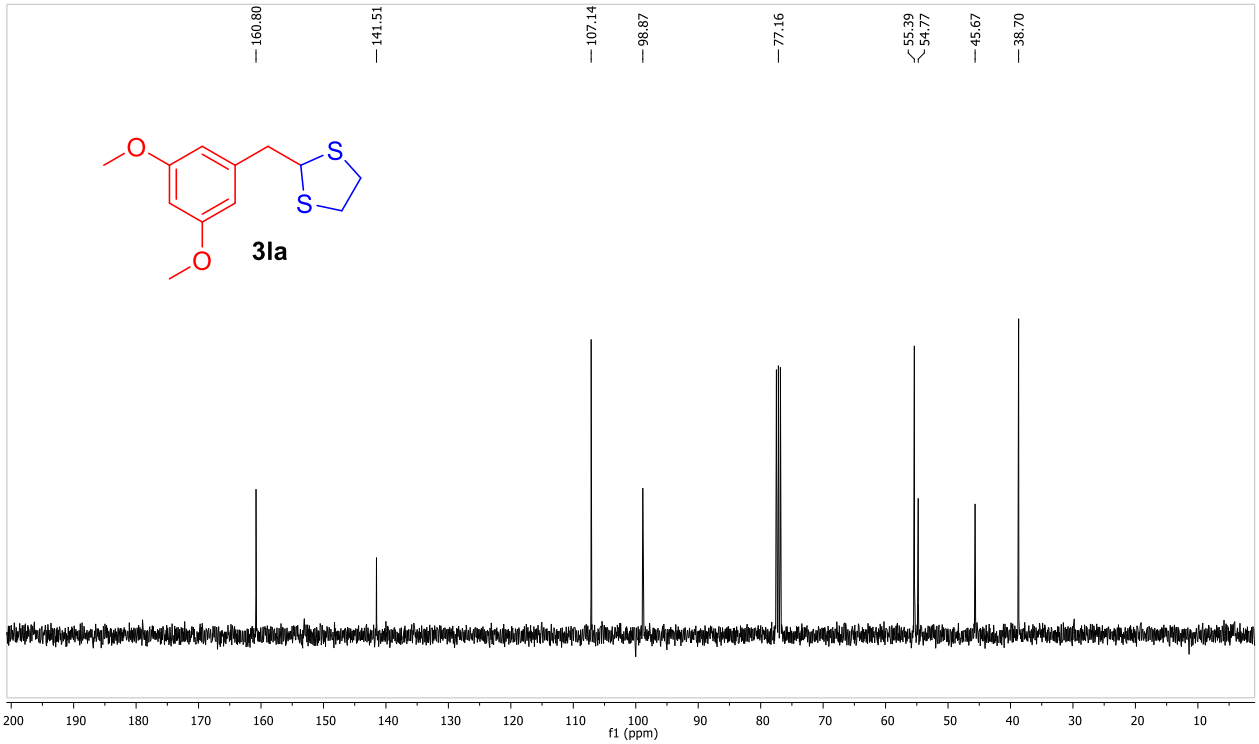
^{1}H & ^{13}C Spectra of 3ka



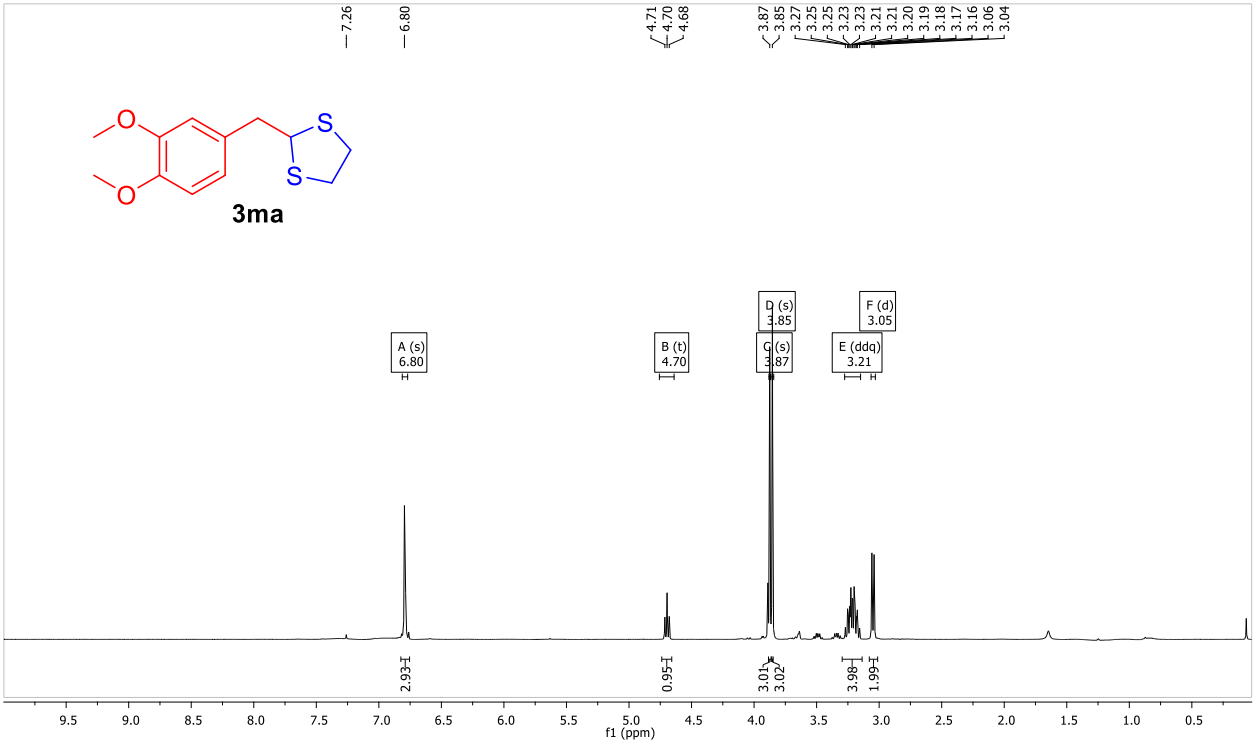


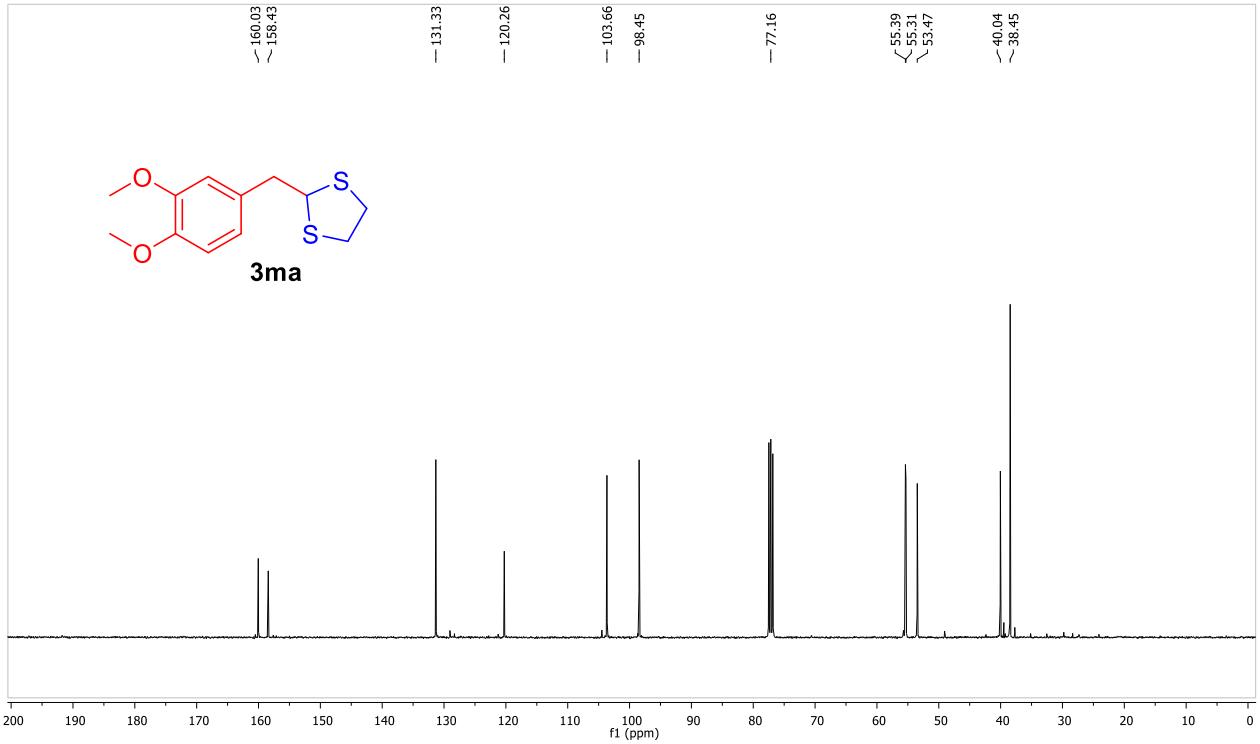
^{1}H & ^{13}C Spectra of 3la



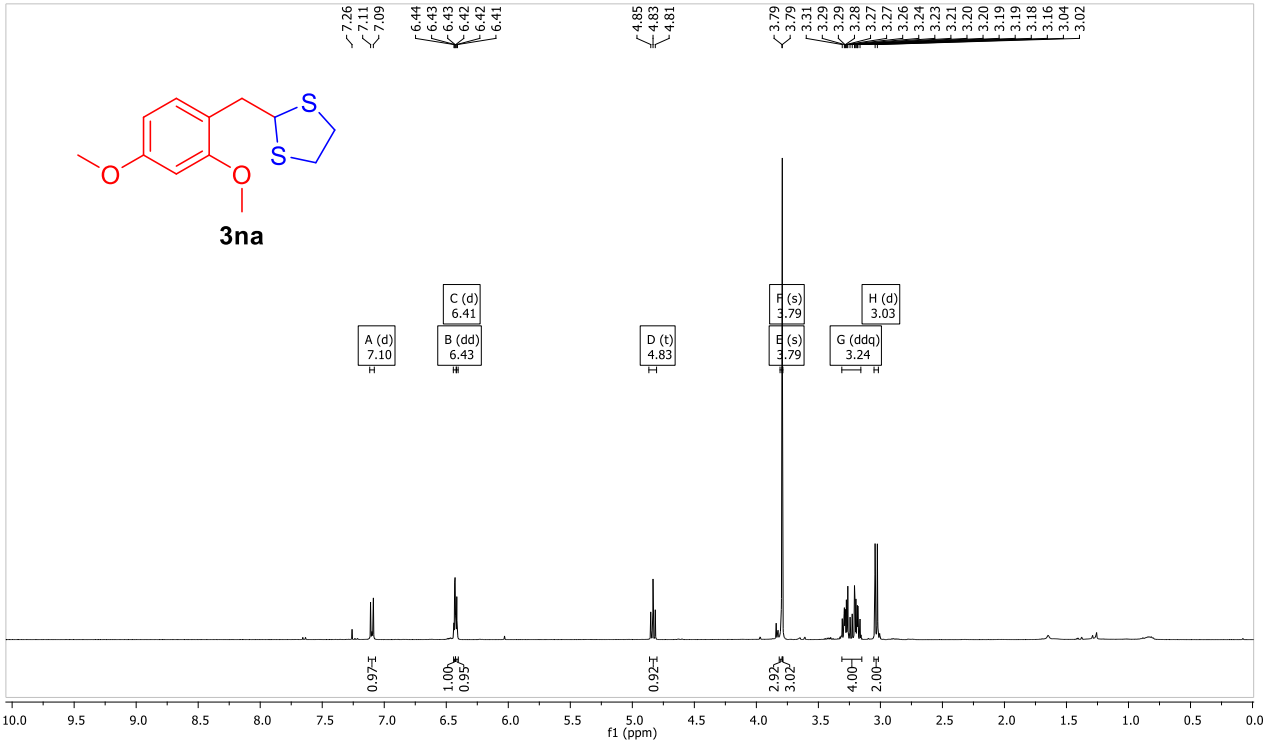


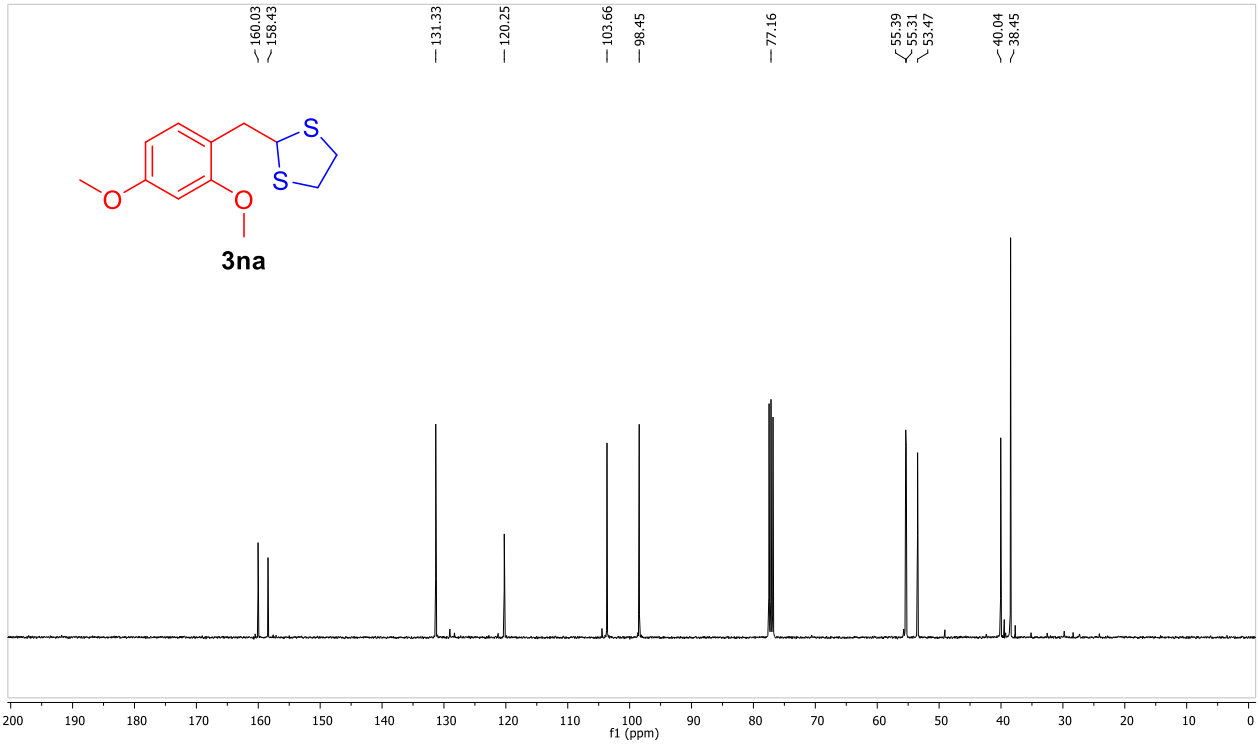
^{1}H & ^{13}C Spectra of 3ma



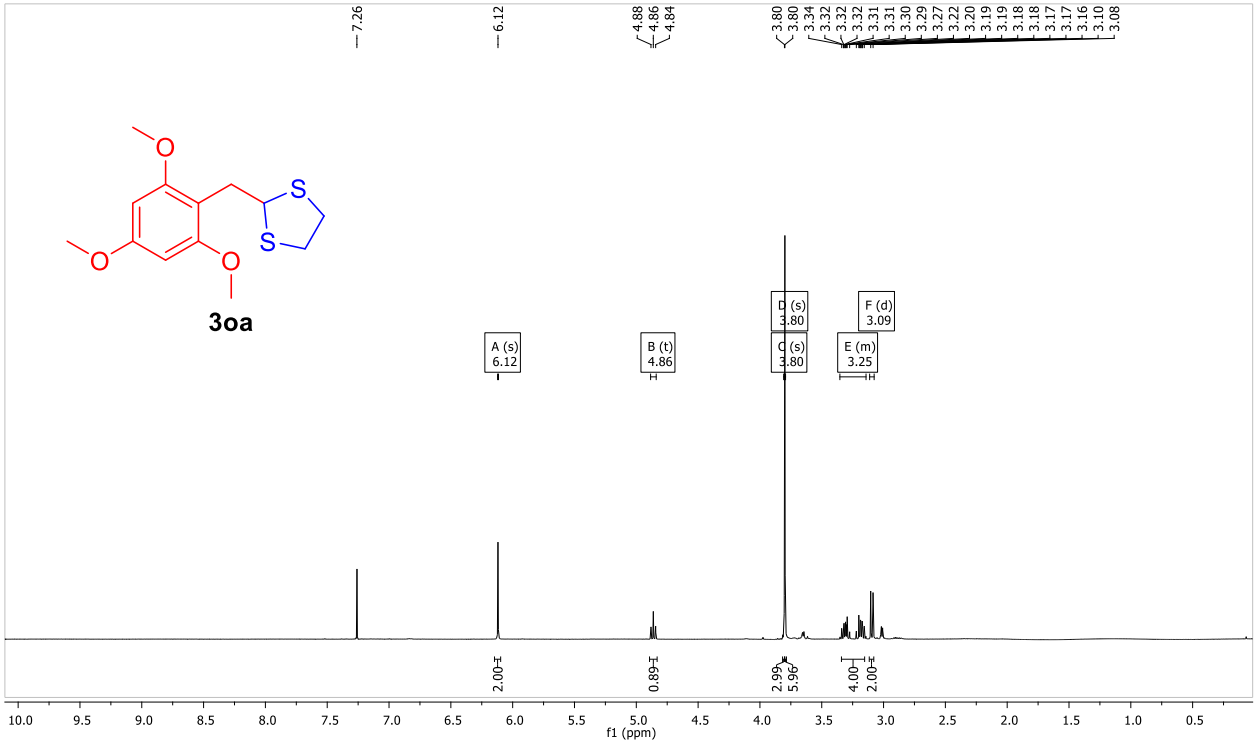


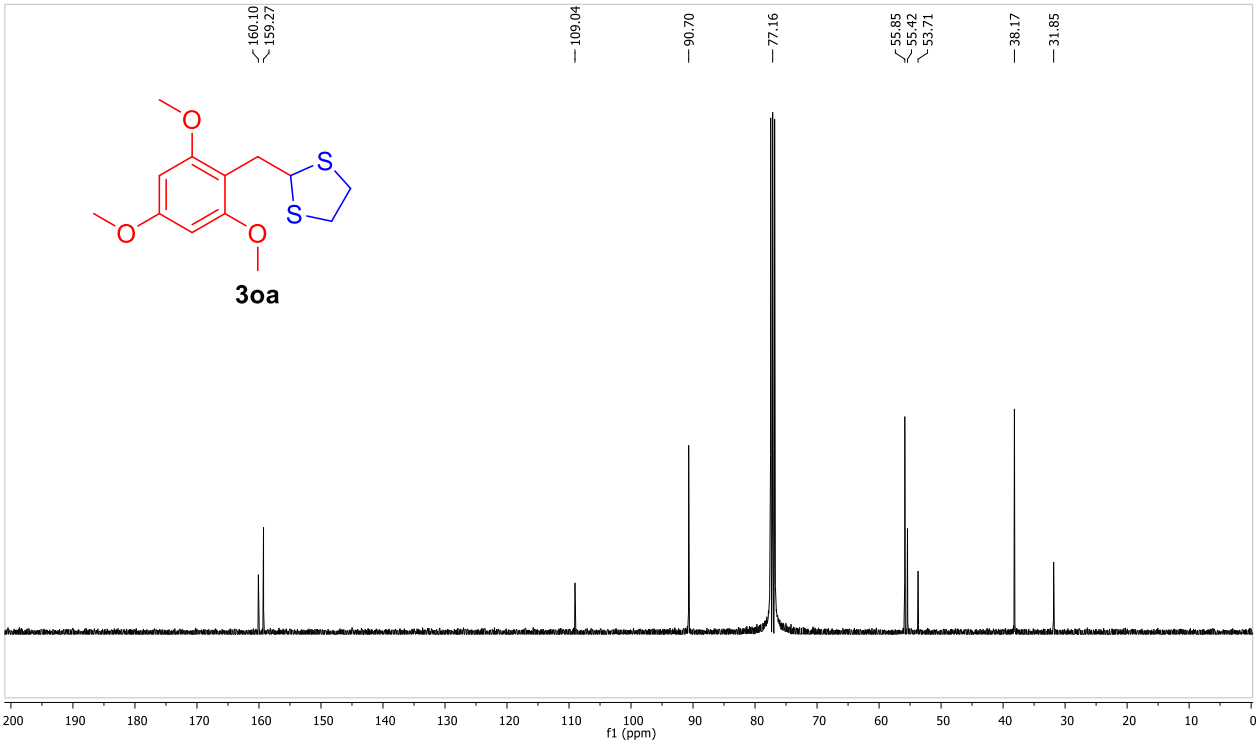
^{1}H & ^{13}C Spectra of 3na



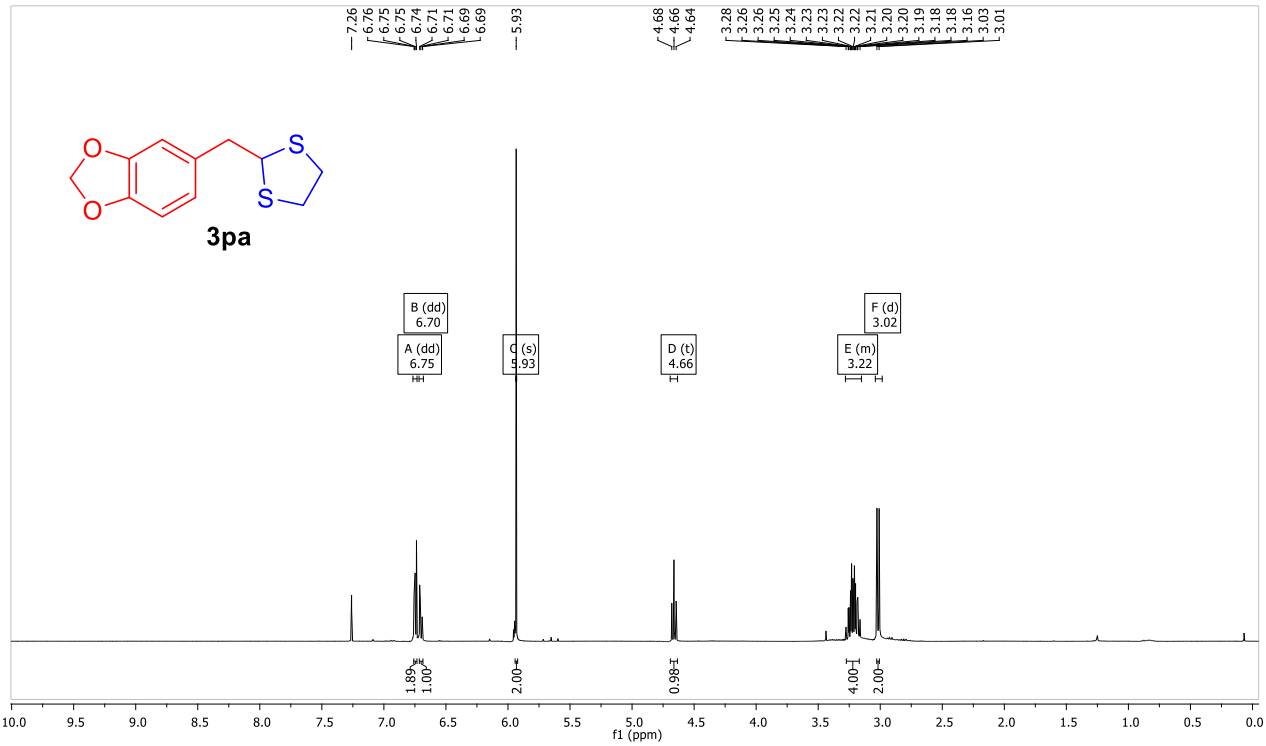


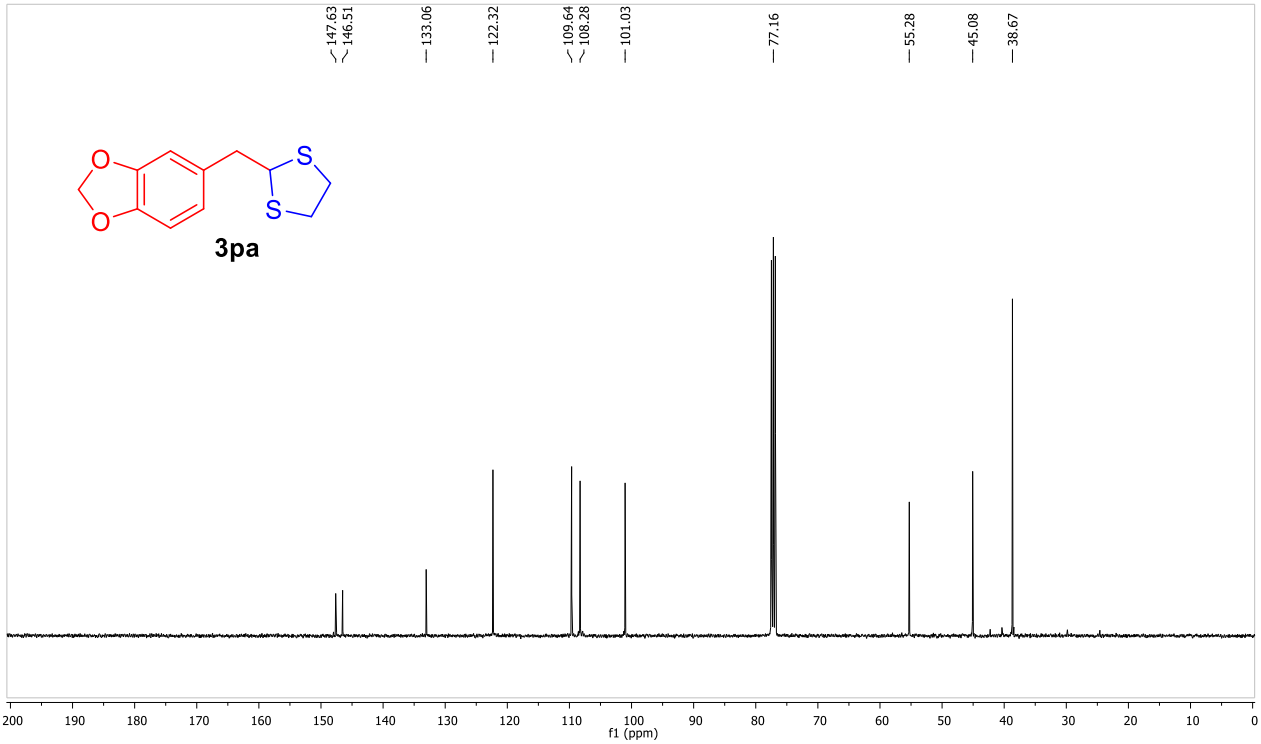
^{1}H & ^{13}C Spectra of 3oa



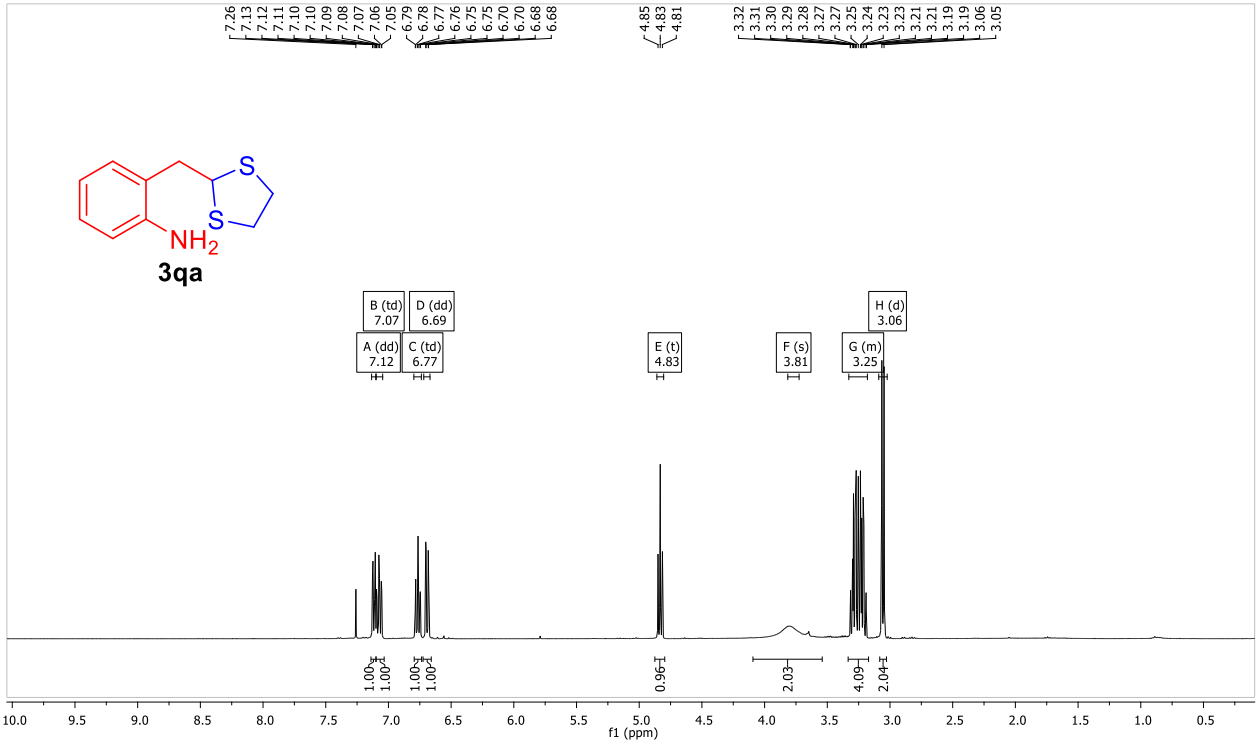


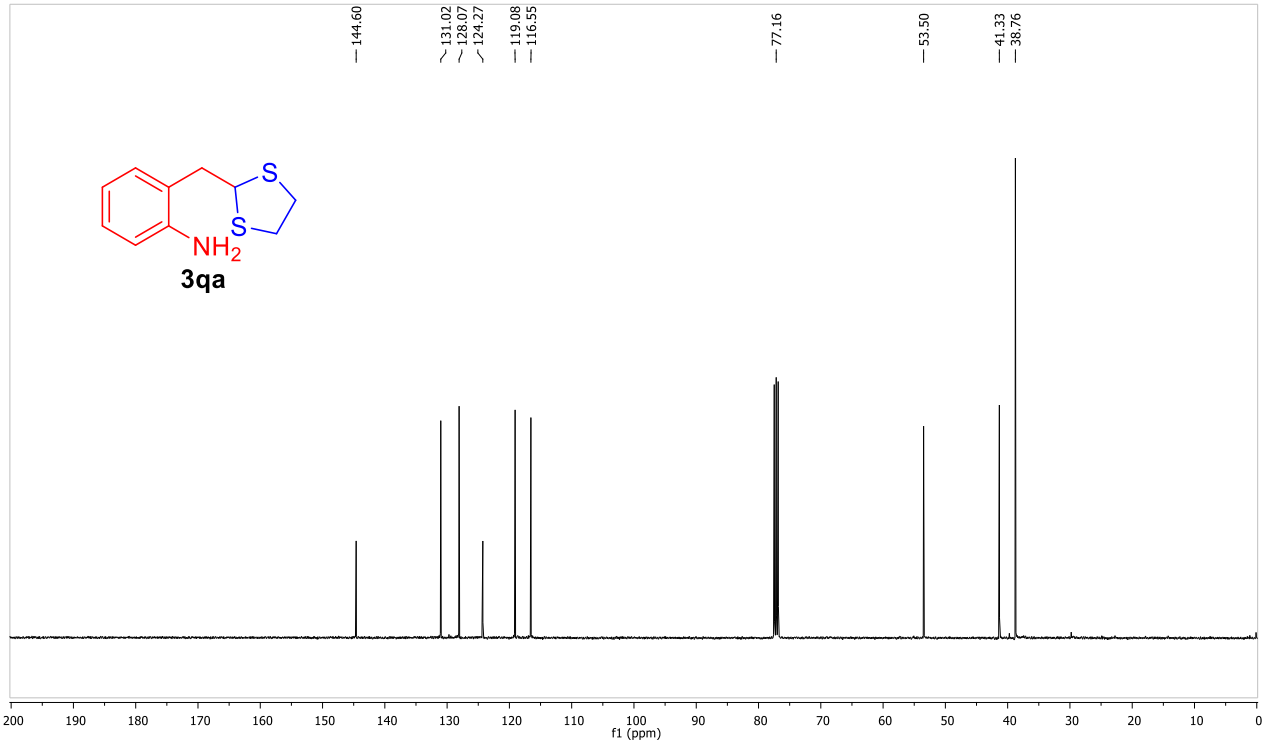
^{1}H & ^{13}C Spectra of 3pa



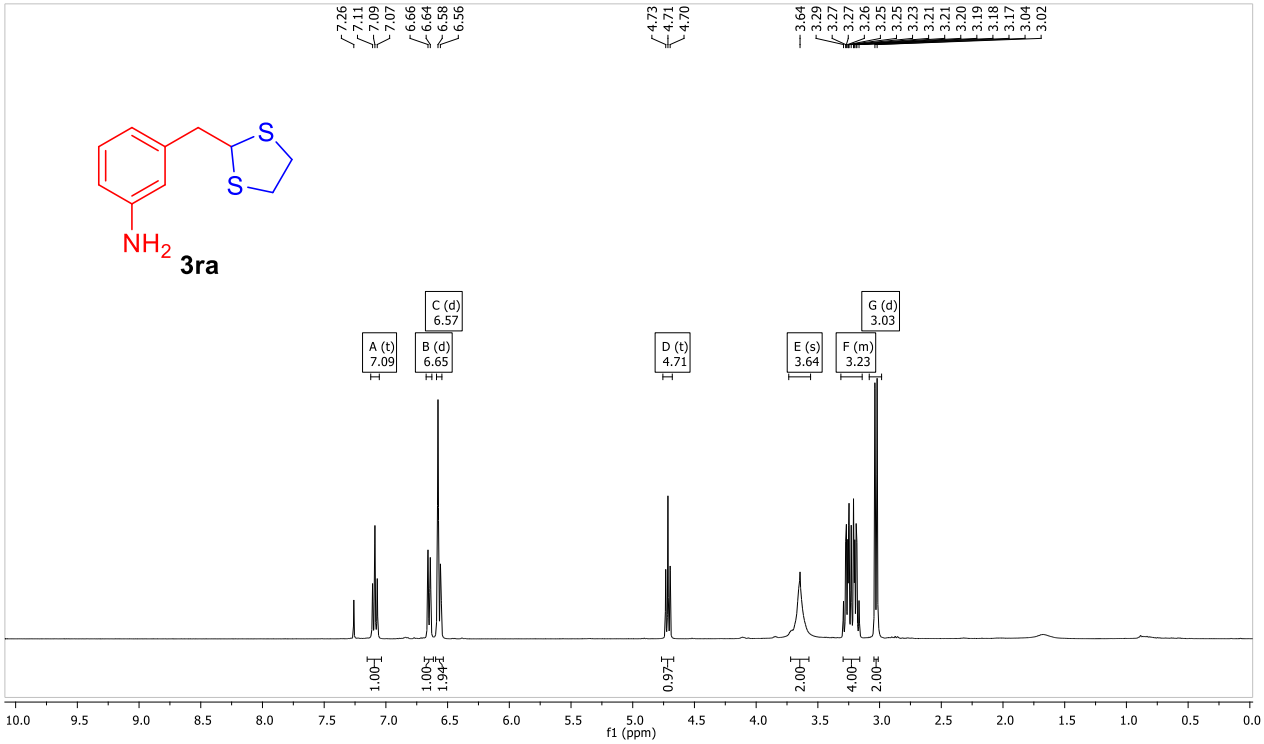


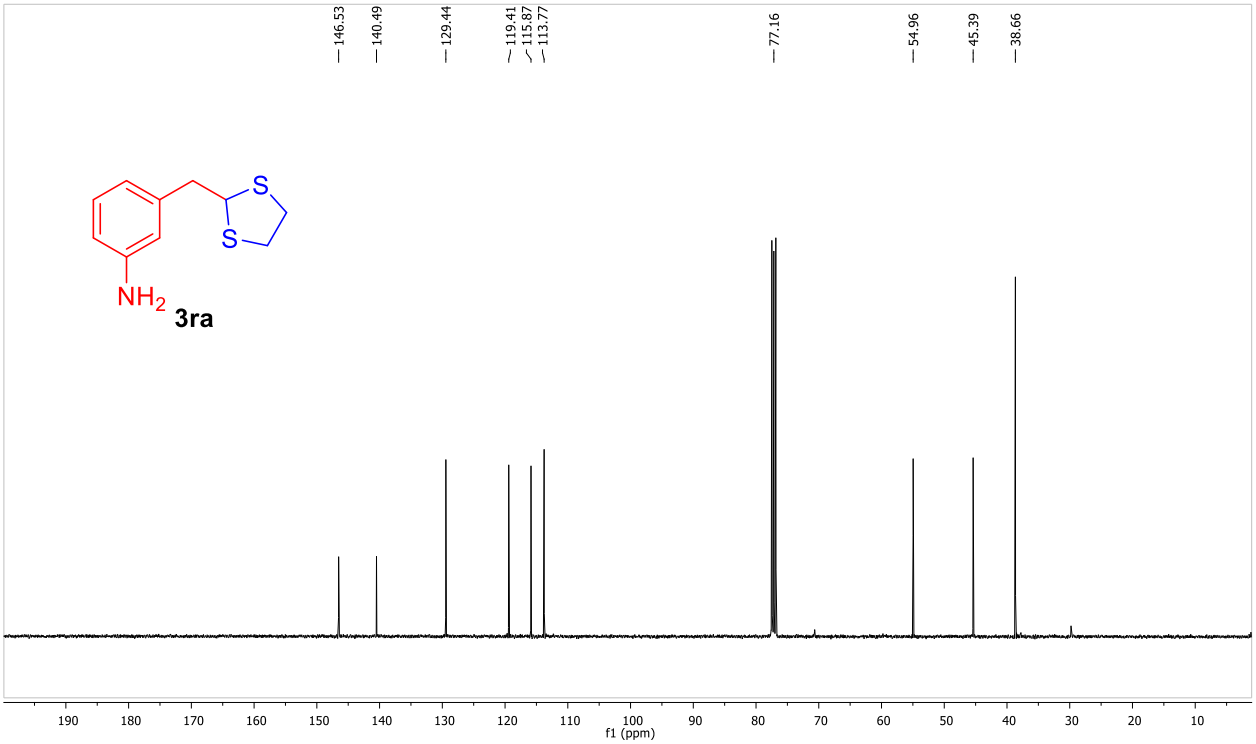
^{1}H & ^{13}C Spectra of 3qa



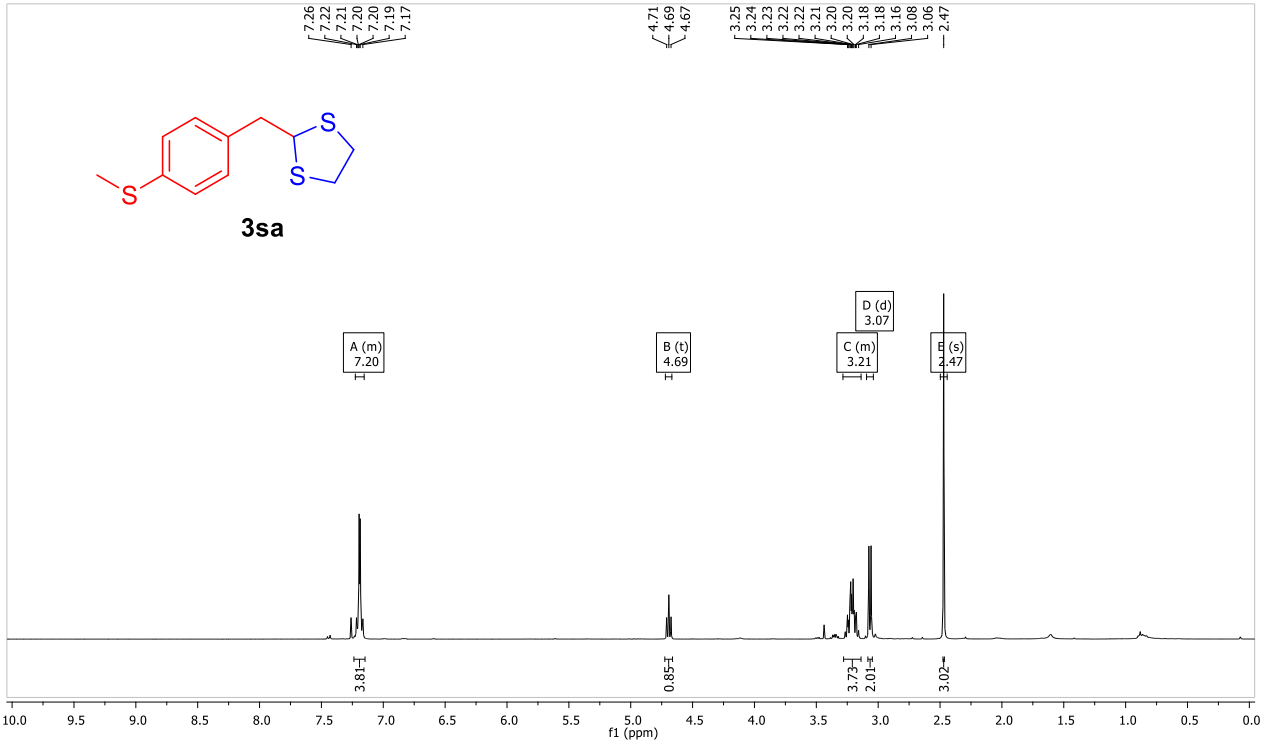


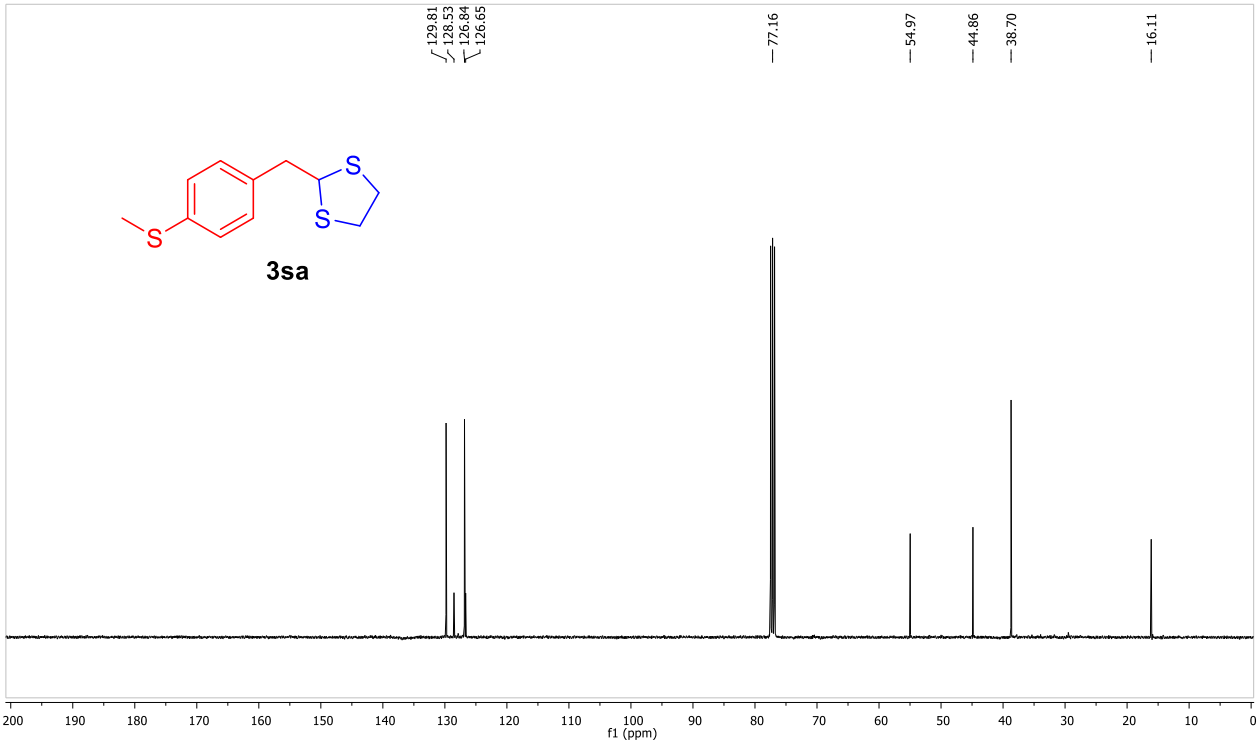
^{1}H & ^{13}C Spectra of 3ra



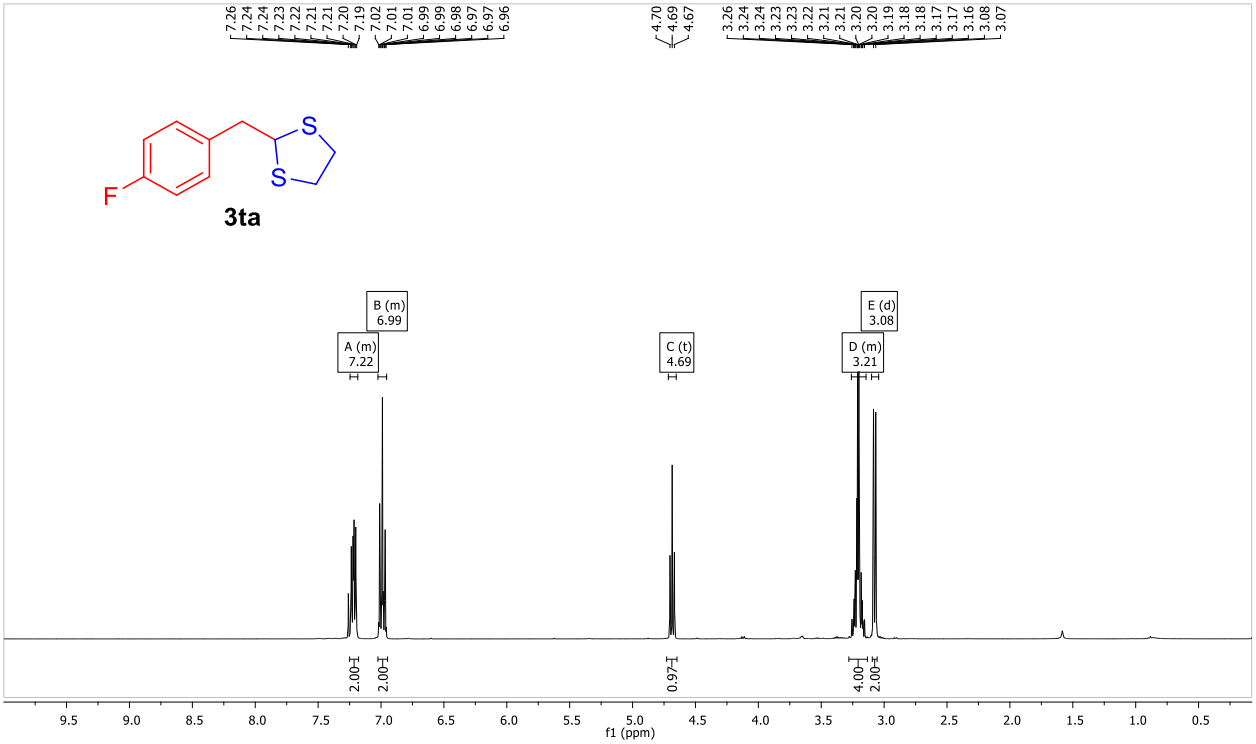


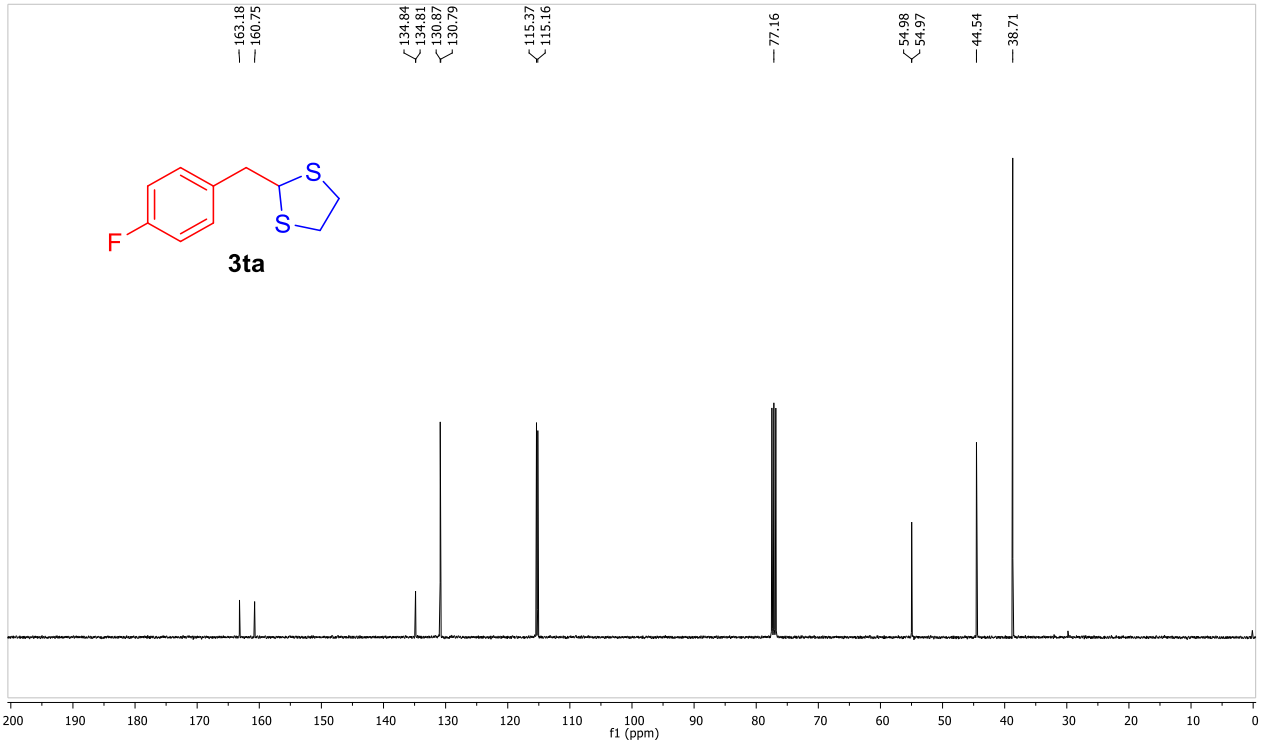
^{1}H & ^{13}C Spectra of 3sa

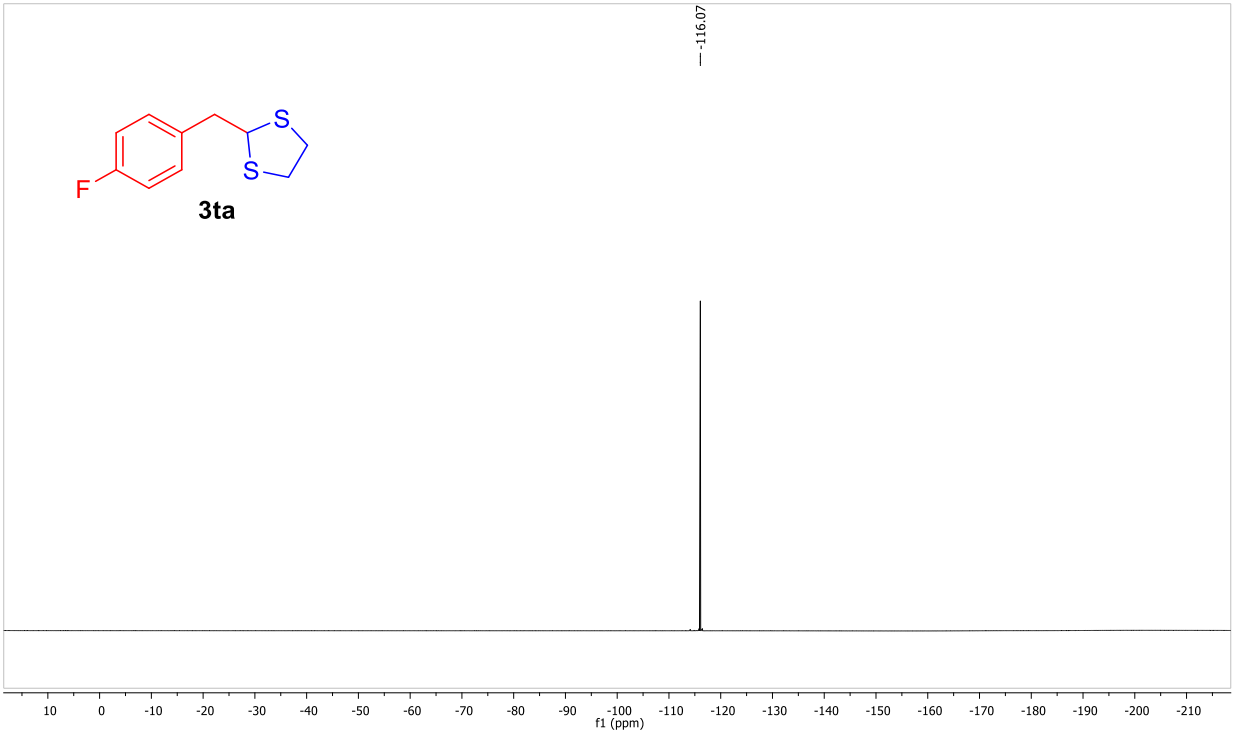




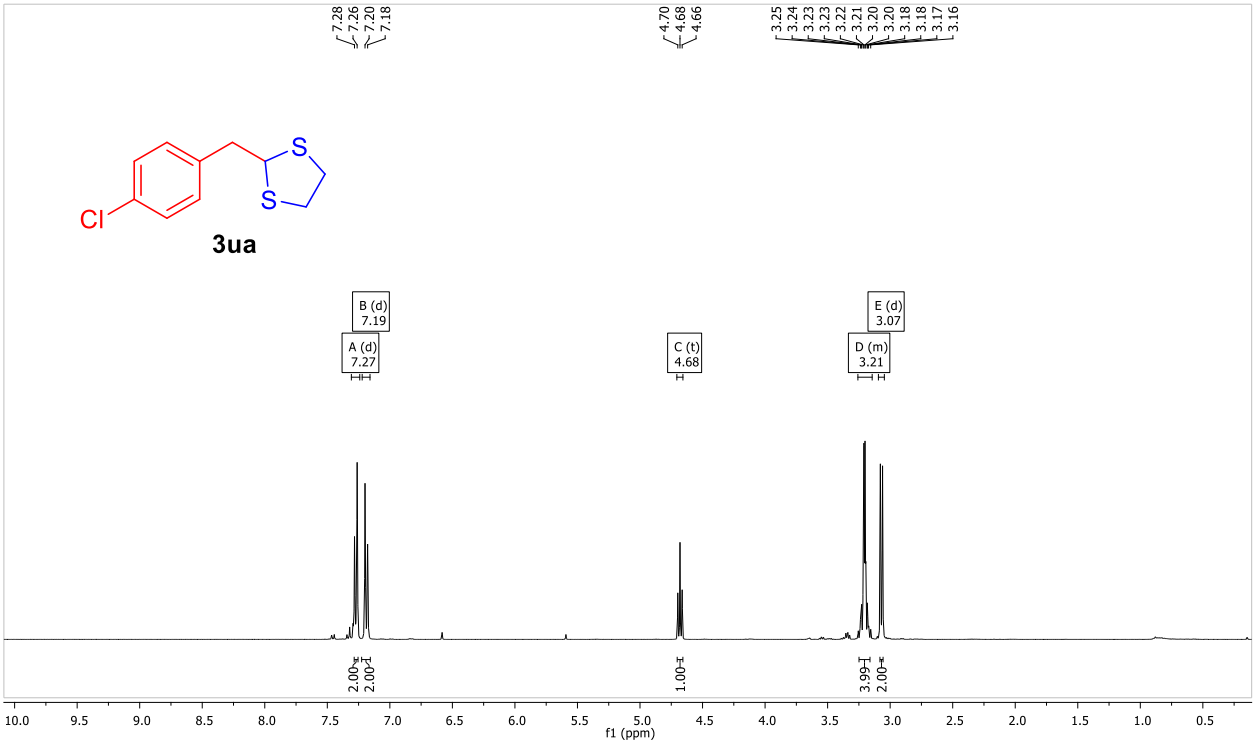
^{1}H, ^{13}C and ^{19}F Spectra of 3ta

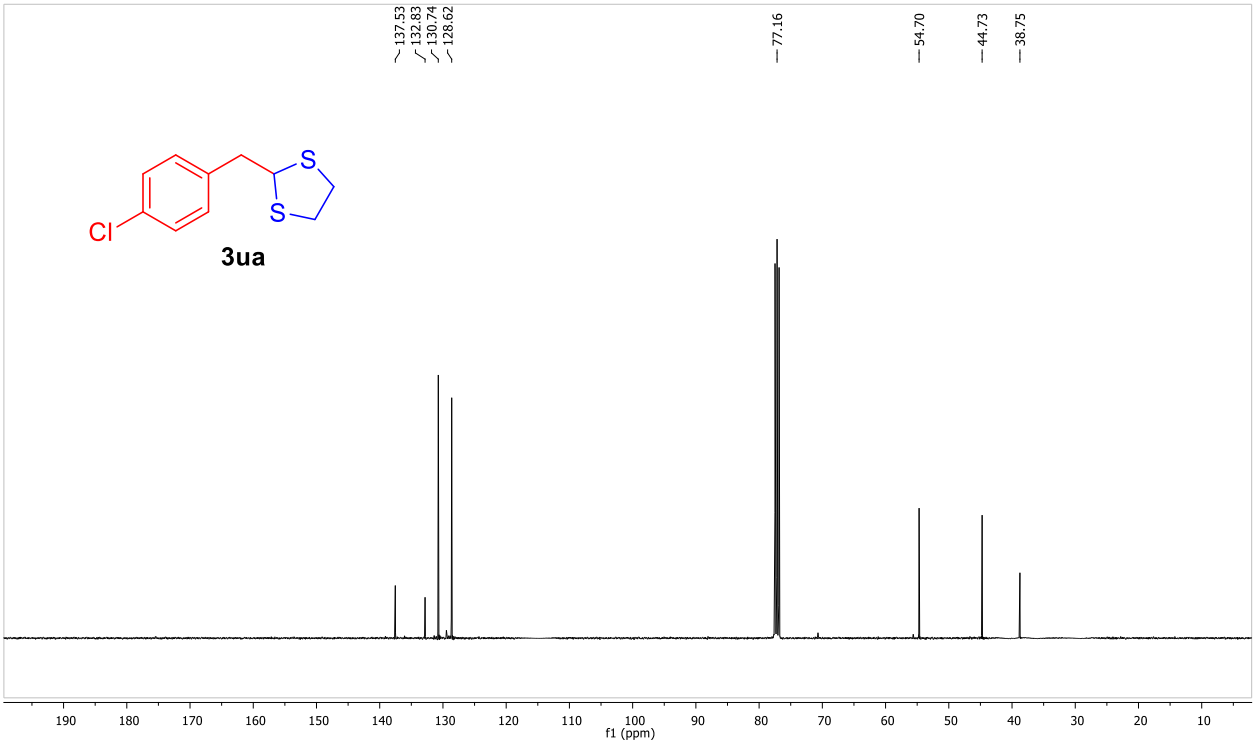



163.18
160.75
134.84
134.81
130.87
130.79
115.37
115.16
77.16
54.98
54.97
44.54
38.71
S
S
F
3ta
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

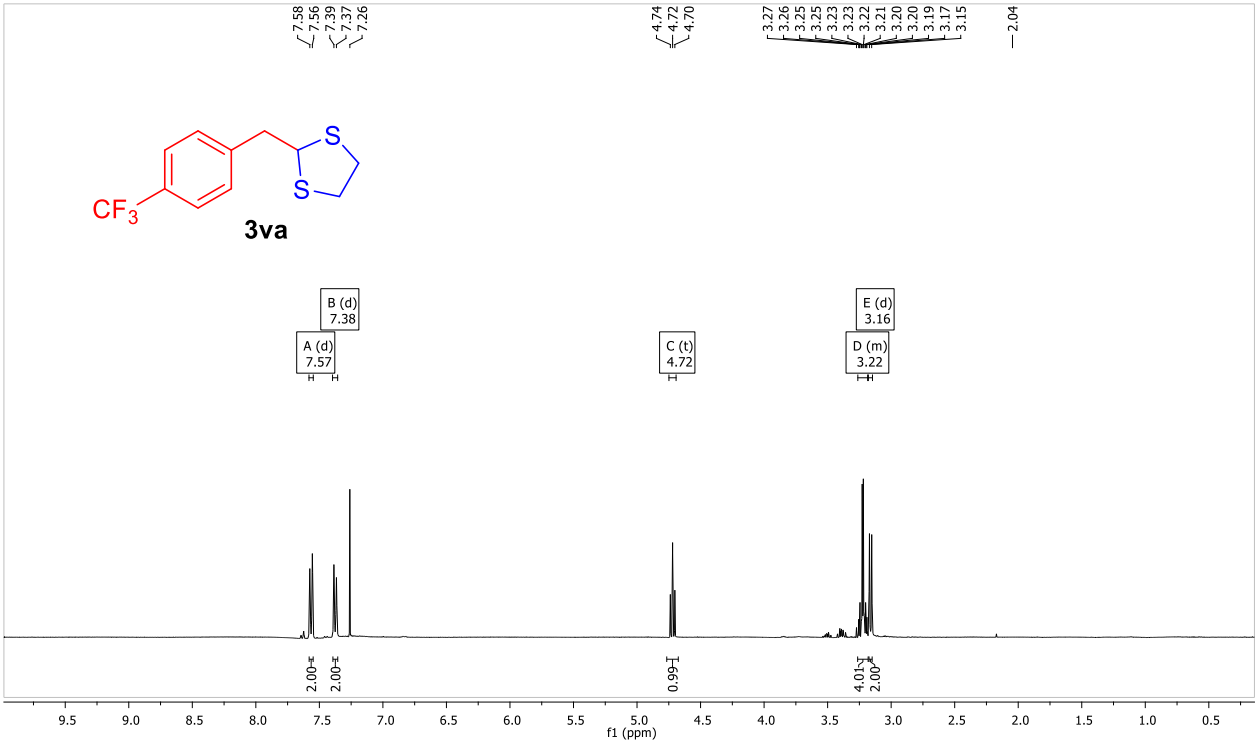

-116.07
S
S
F
3ta
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

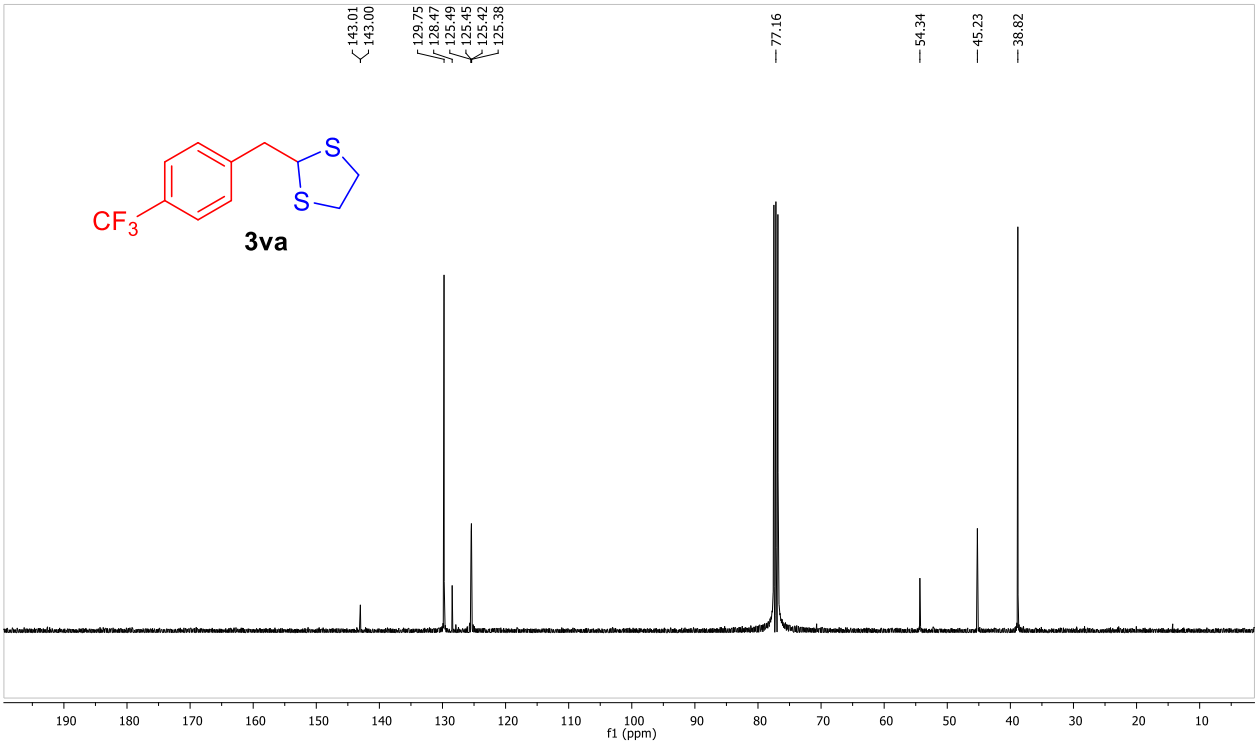
^{1}H and ^{13}C Spectra of 3ua

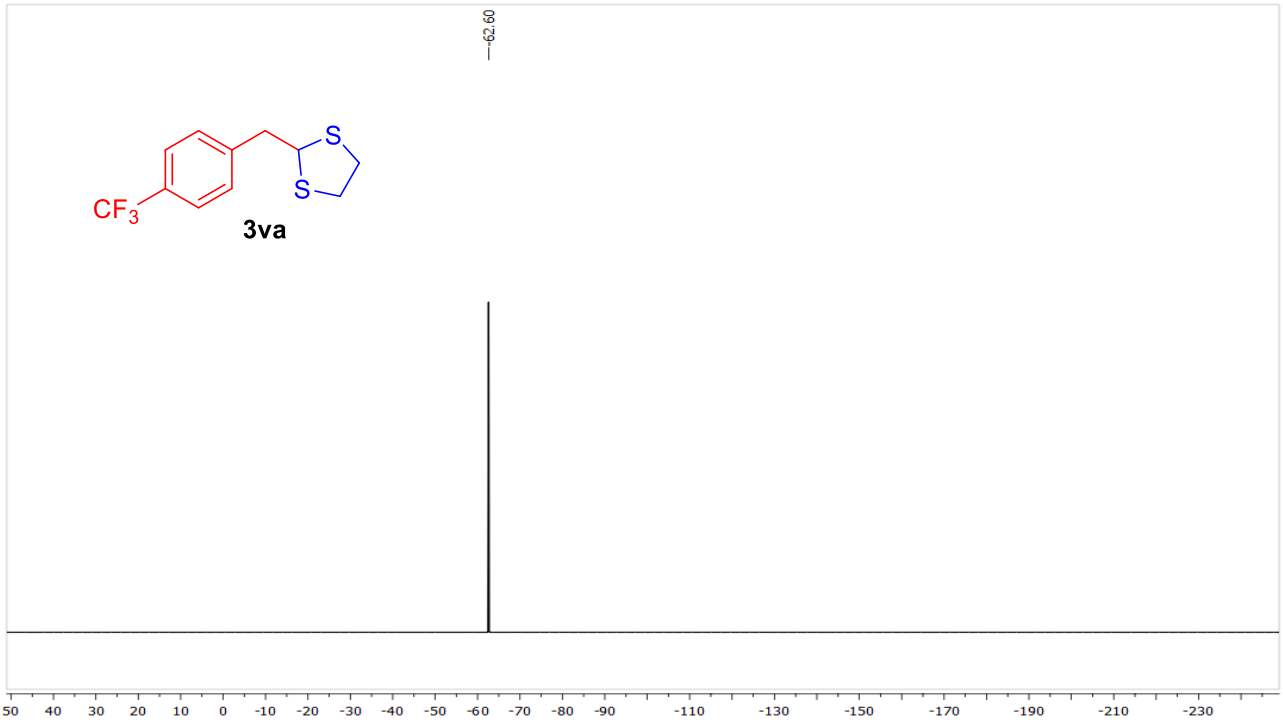




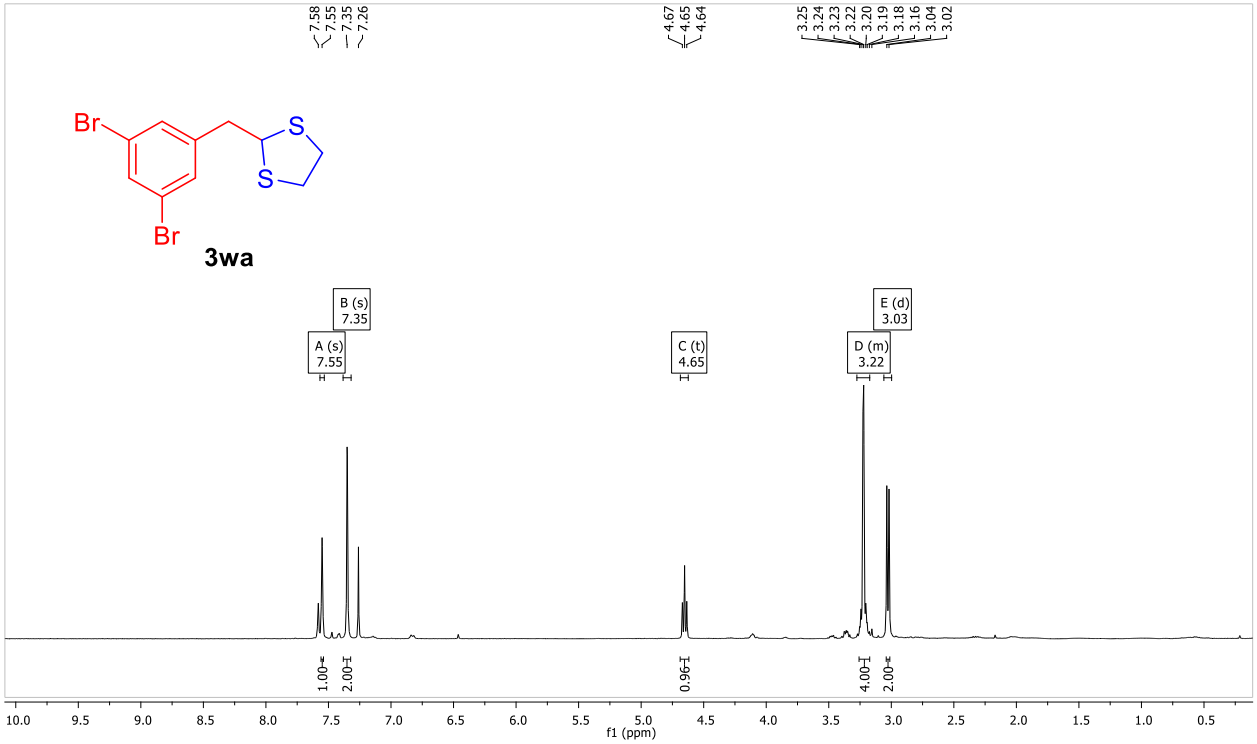
^{1}H, ^{13}C and ^{19}F Spectra of 3va

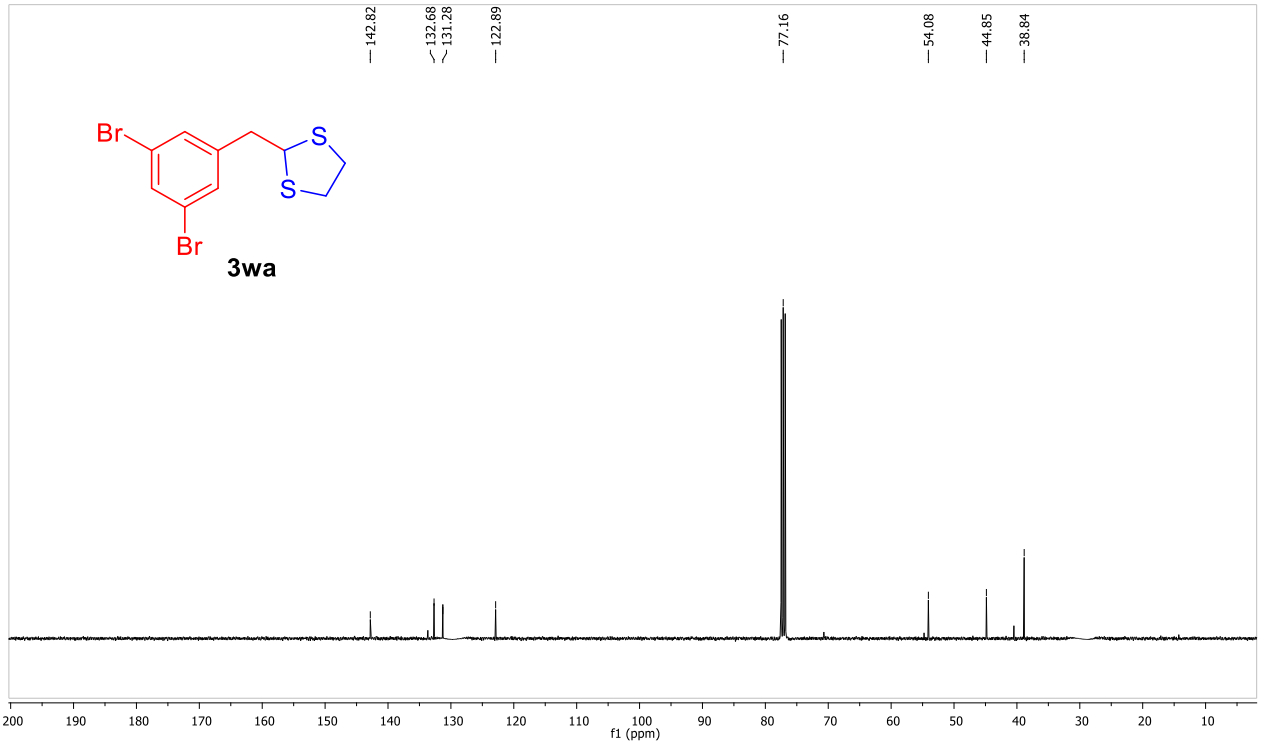



143.01
143.00
129.75
128.47
125.49
125.45
125.42
125.38
77.16
54.34
45.23
38.82
S
S
CF3
3va
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

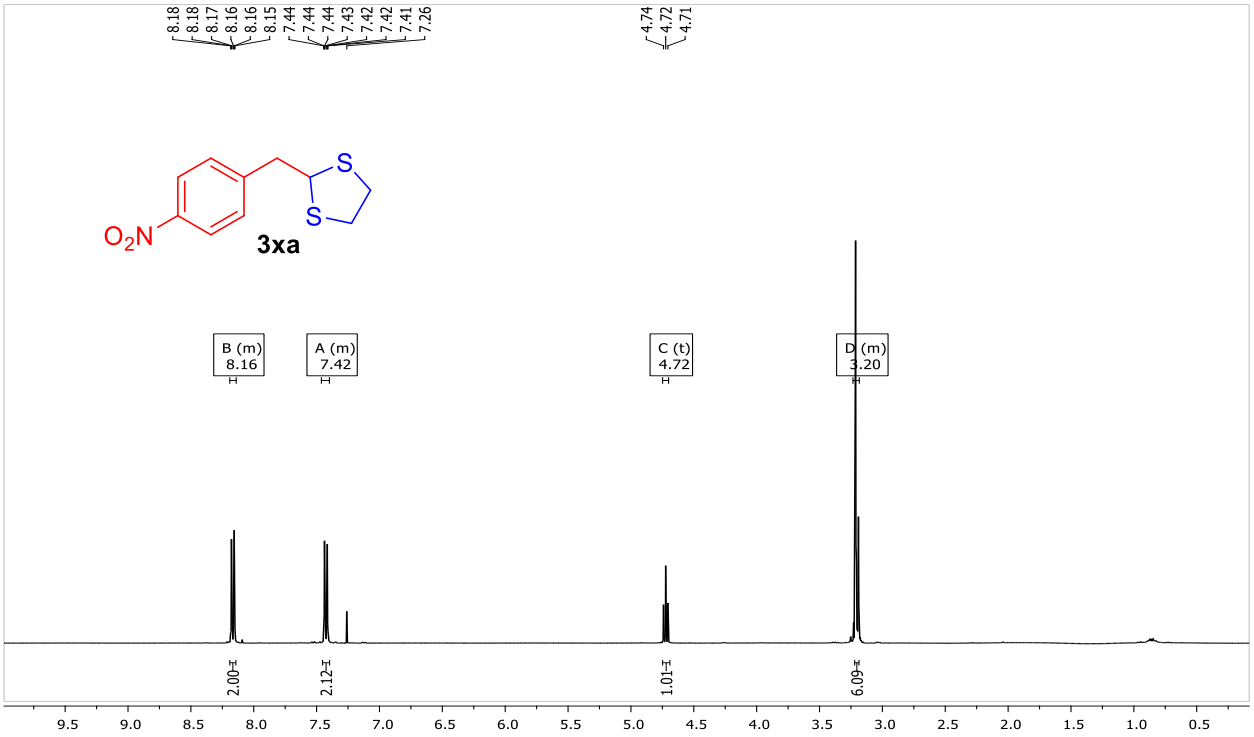

62.60
S
S
CF3
3va
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210 -230

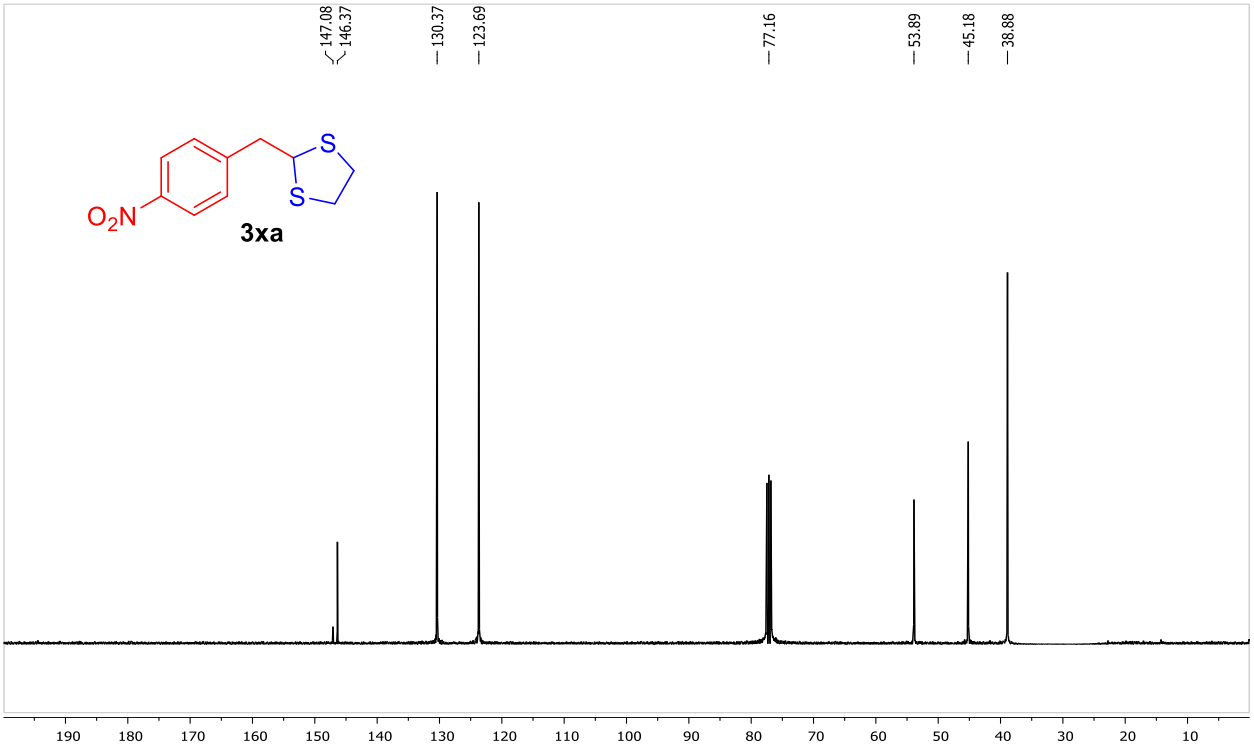
^{1}H & ^{13}C Spectra of 3wa



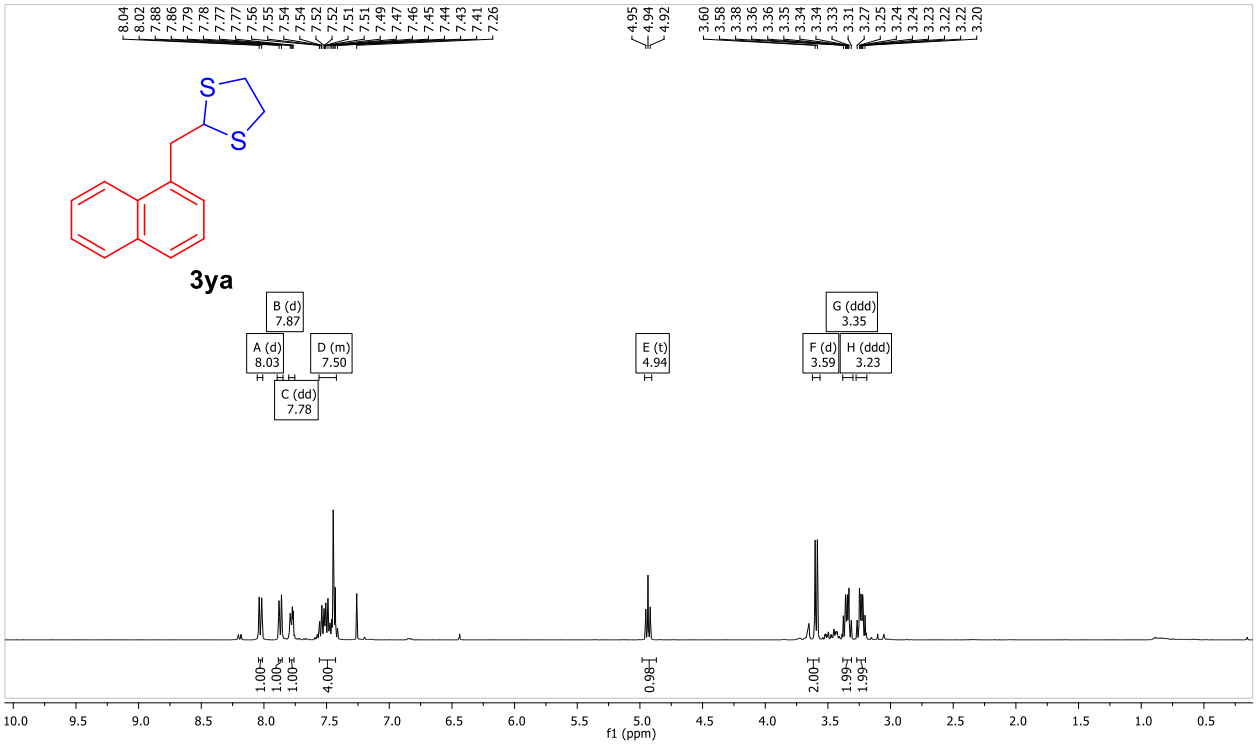


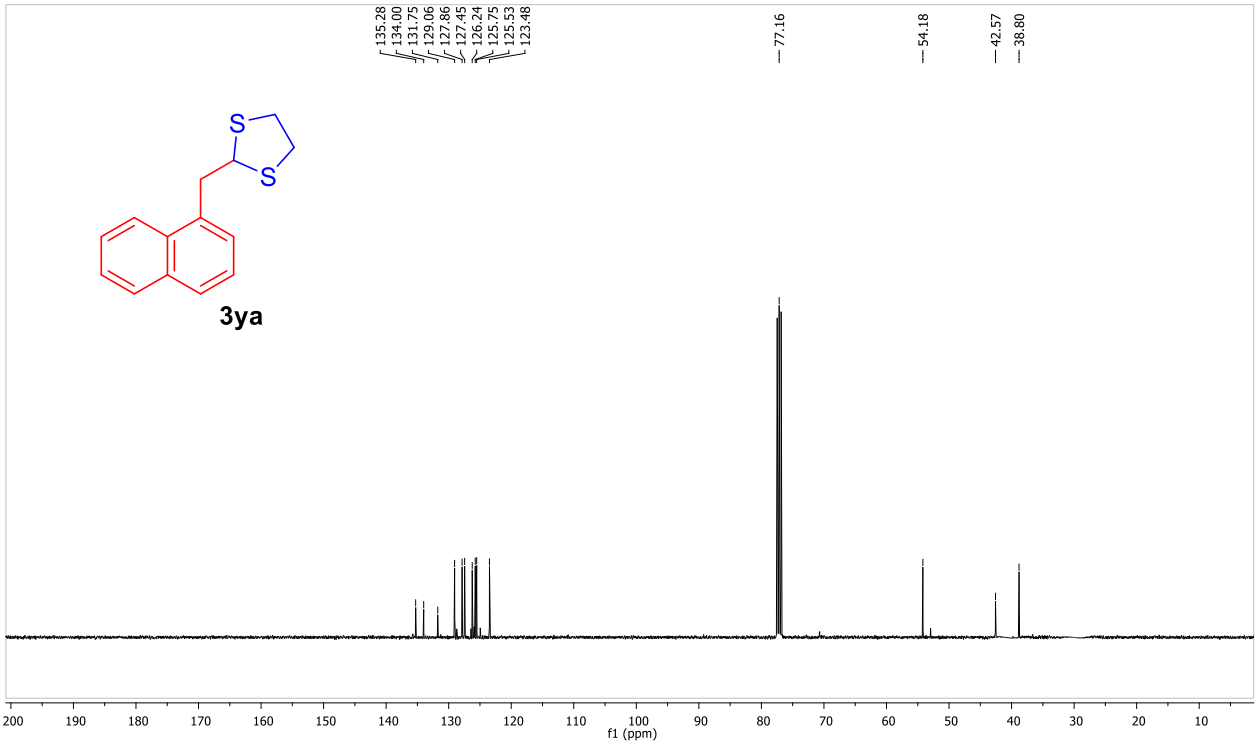
^{1}H and ^{13}C NMR of 3xa



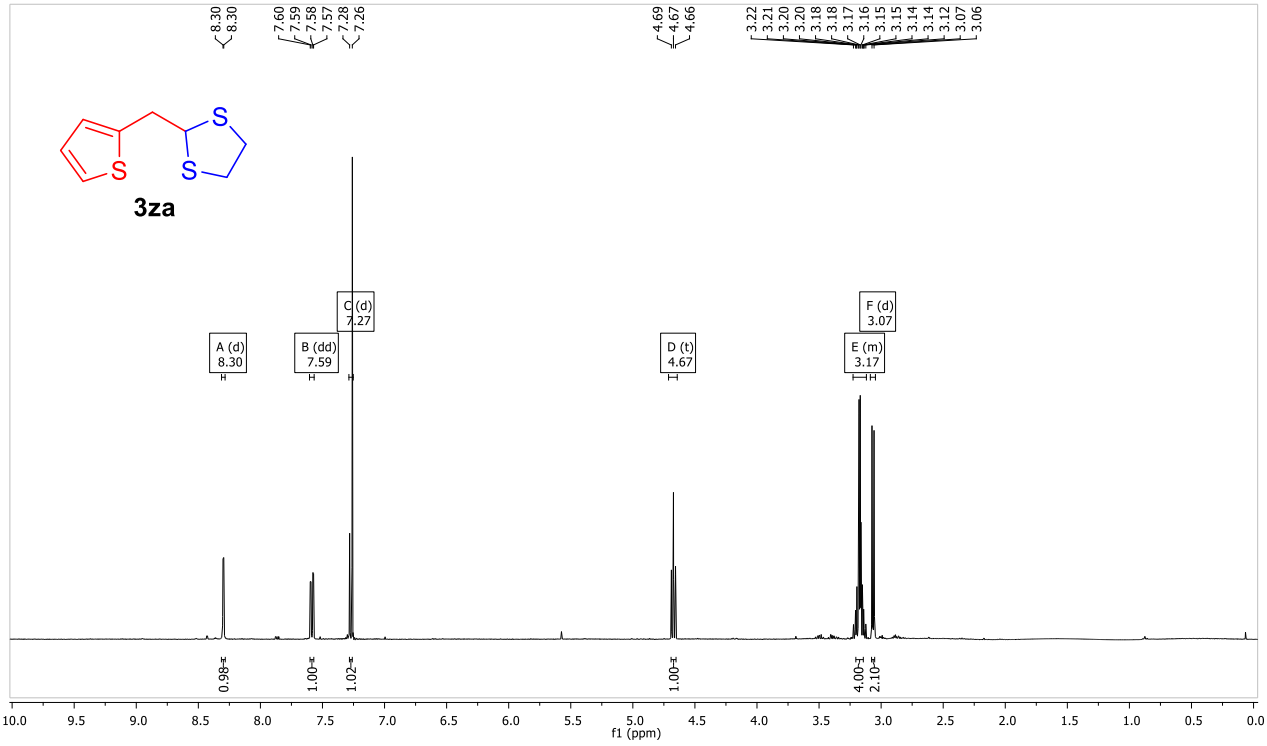


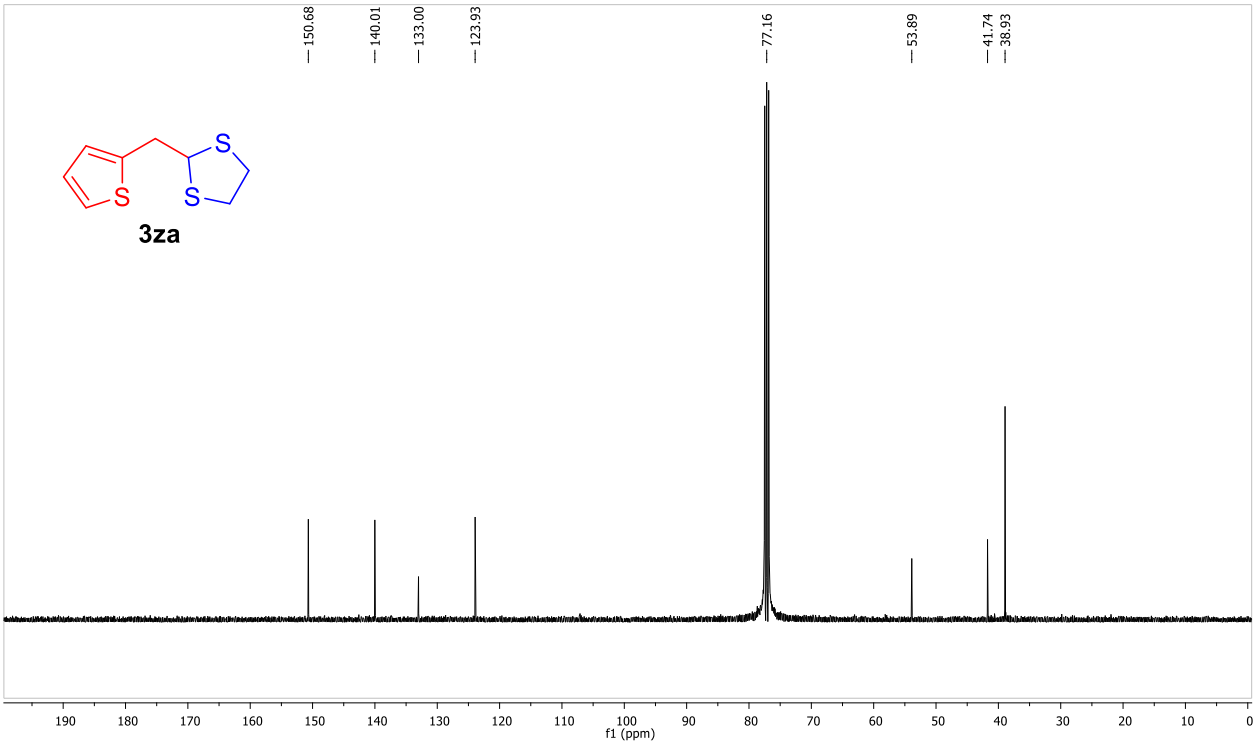
^{1}H & ^{13}C Spectra of 3ya



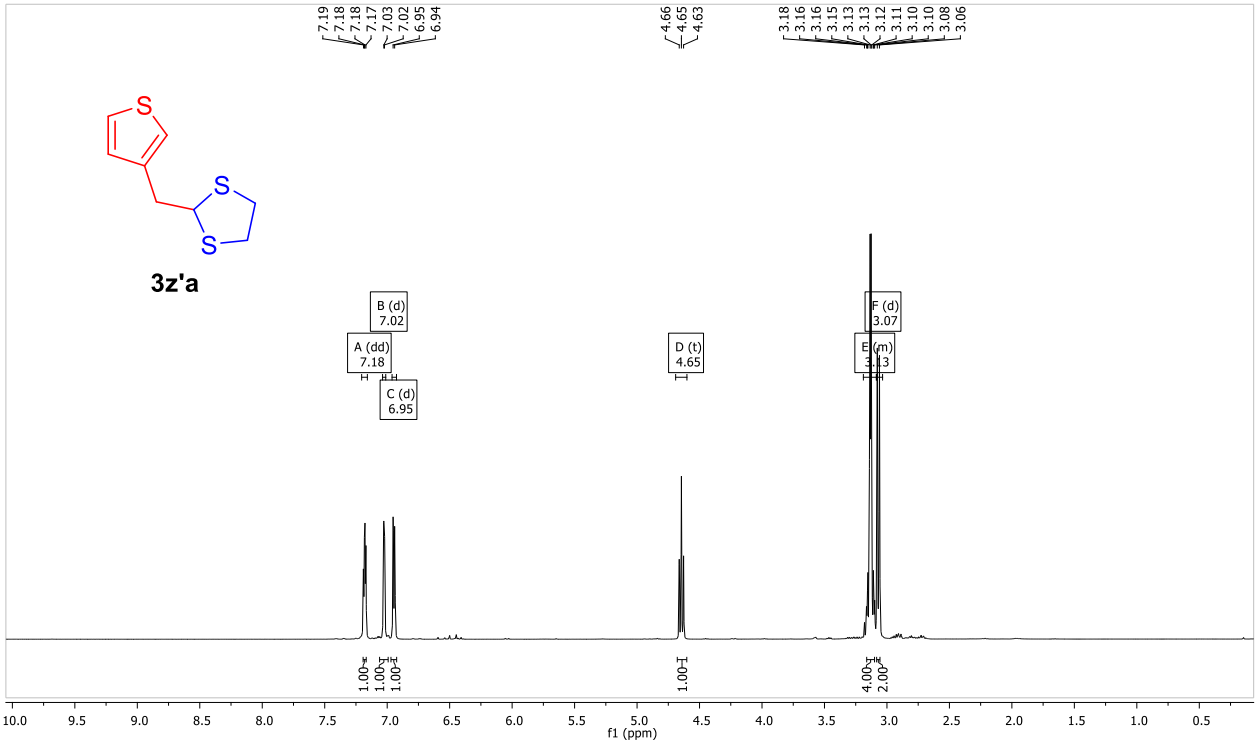


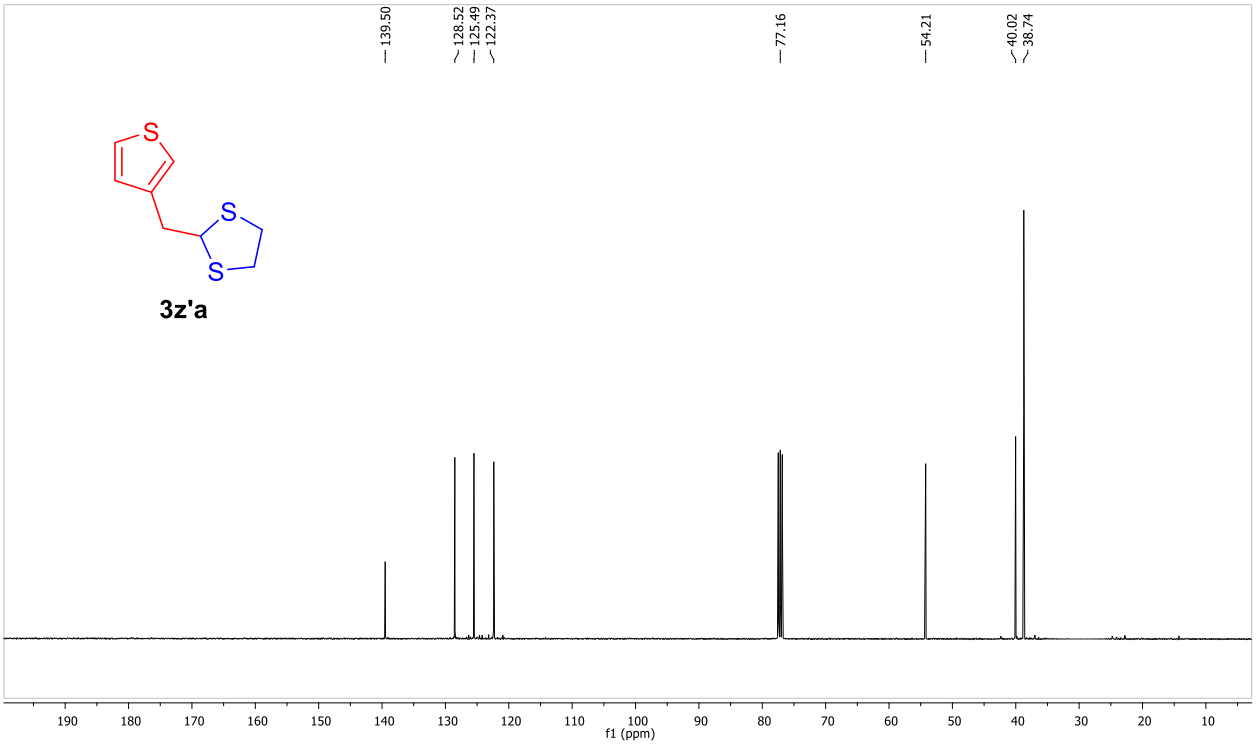
^{1}H and ^{13}C Spectra of 3za



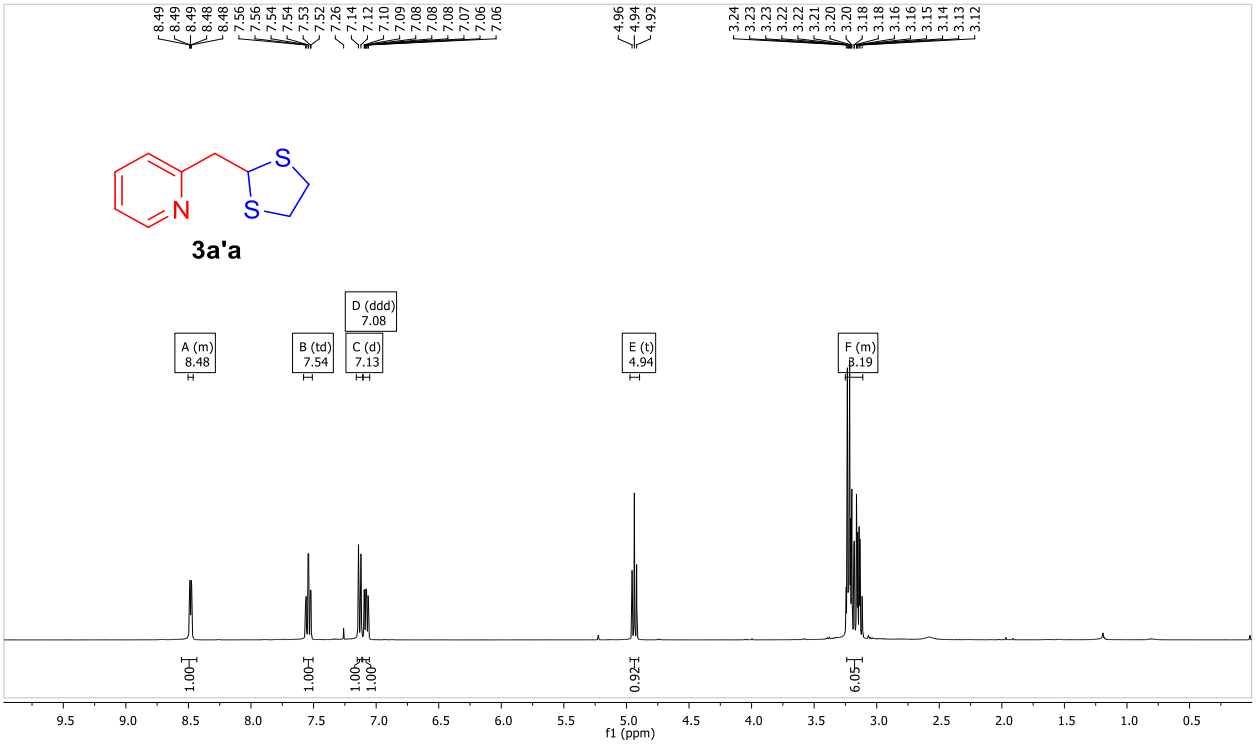


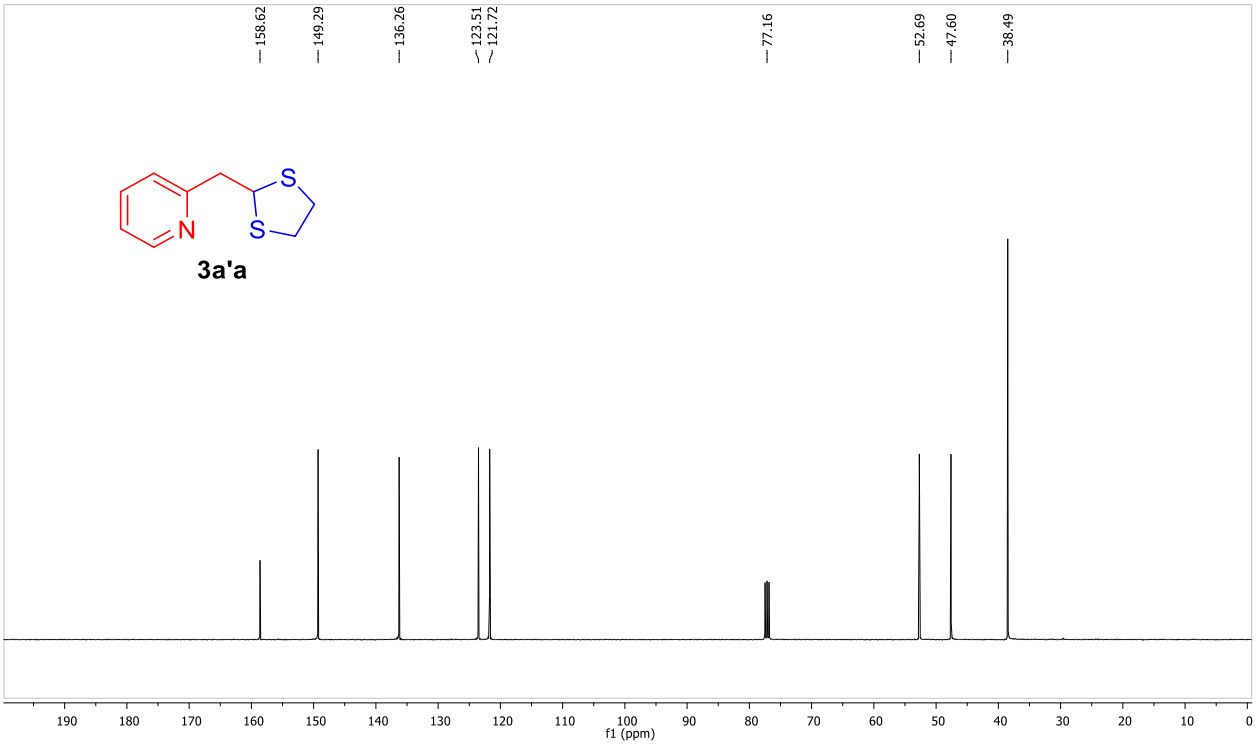
^{1}H & ^{13}C Spectra of 3z'a



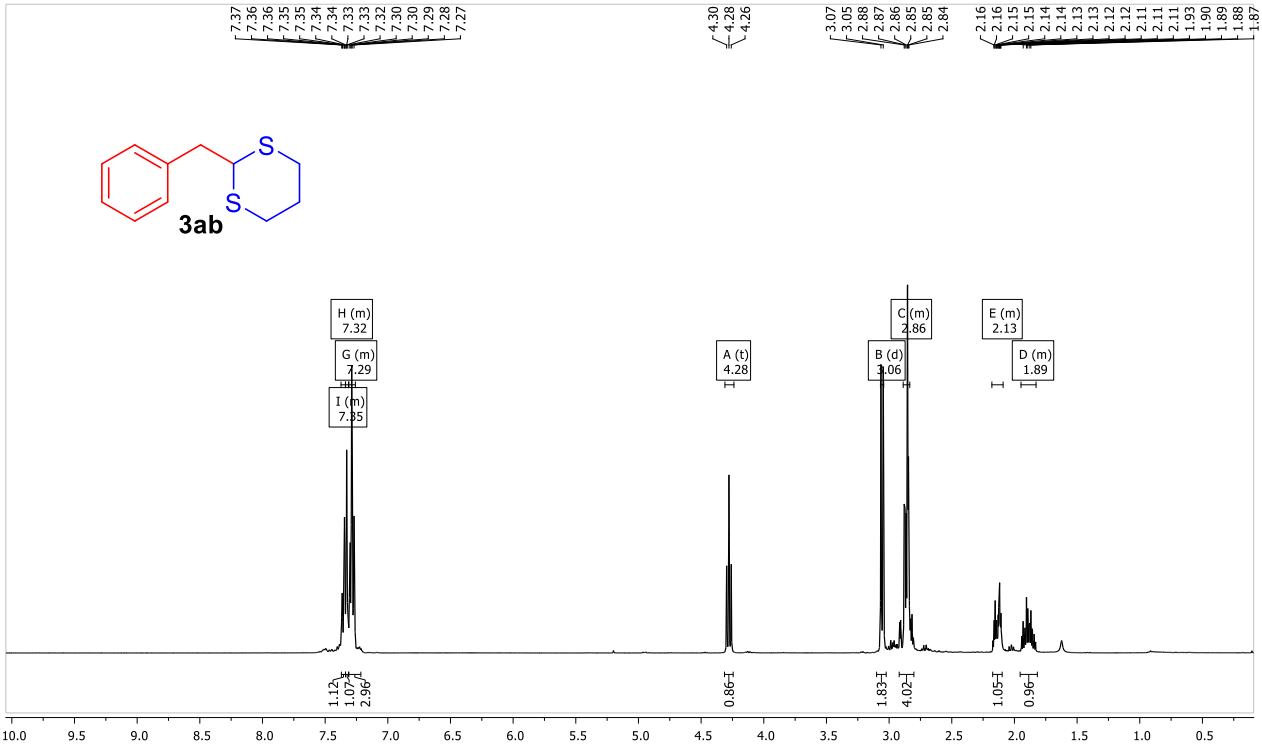


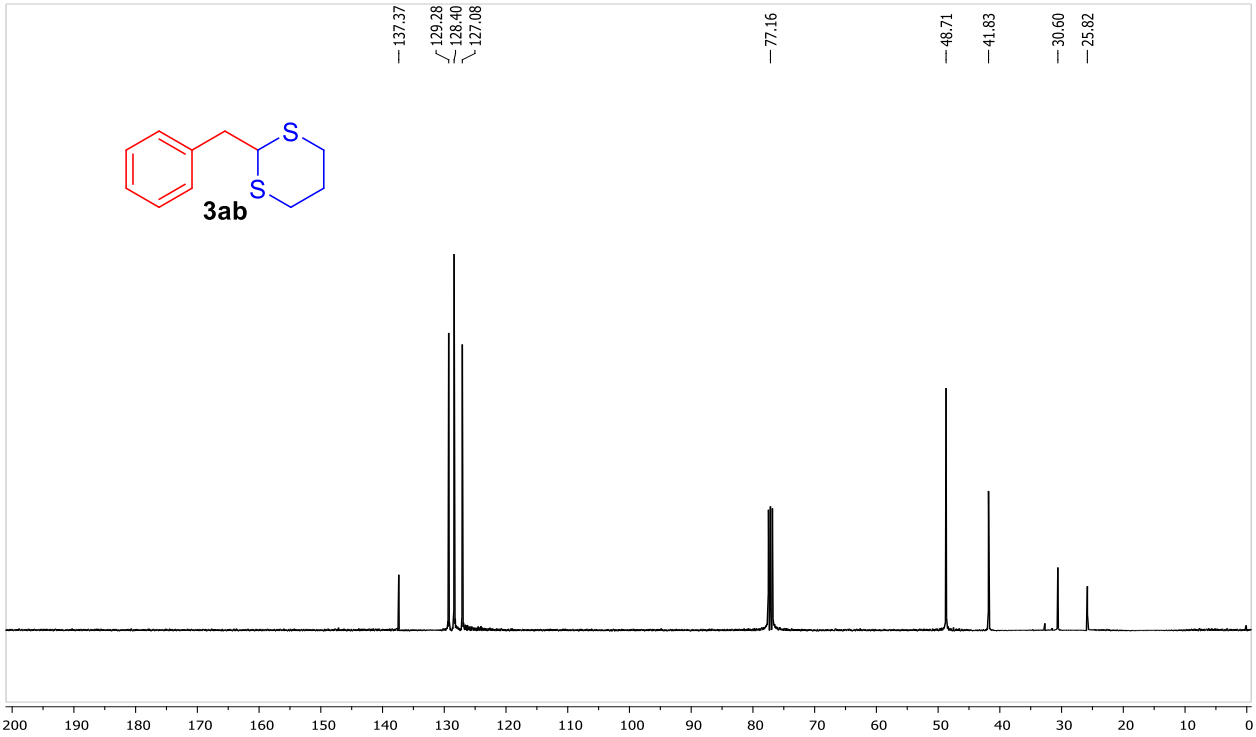
^{1}H and ^{13}C Spectra of 3a'a



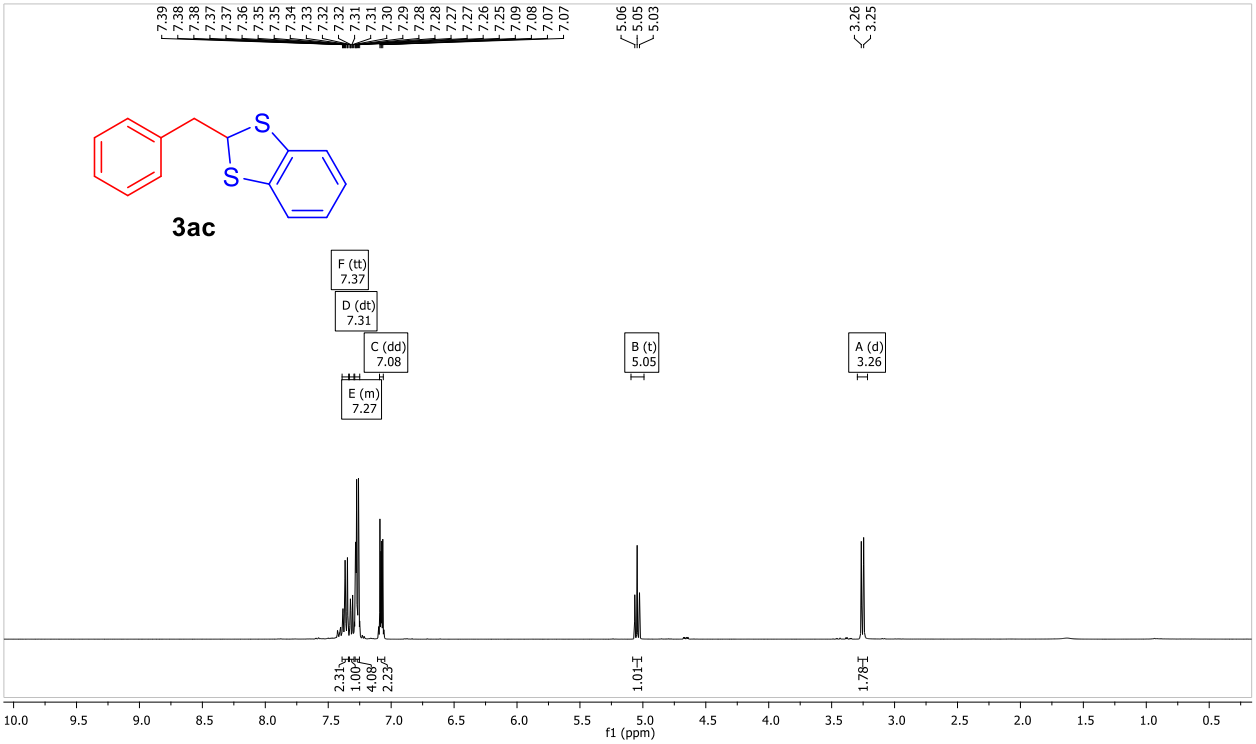


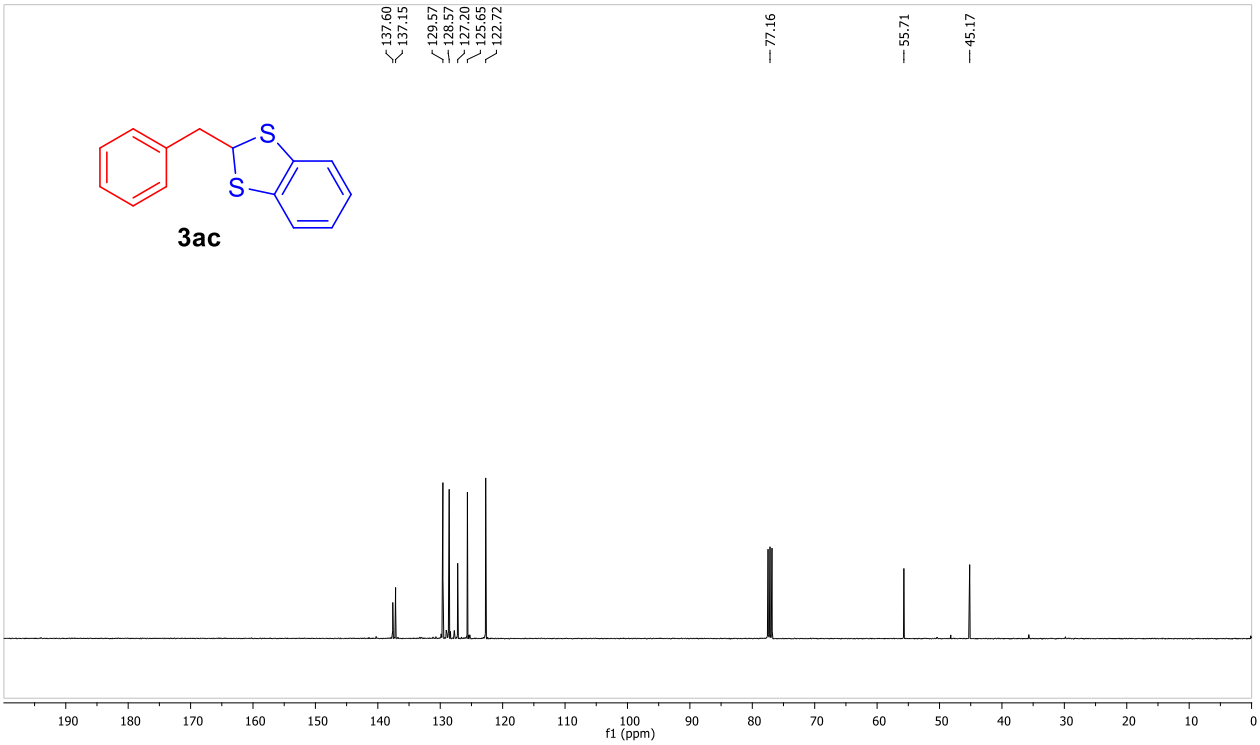
^{1}H and ^{13}C NMR of 3ab



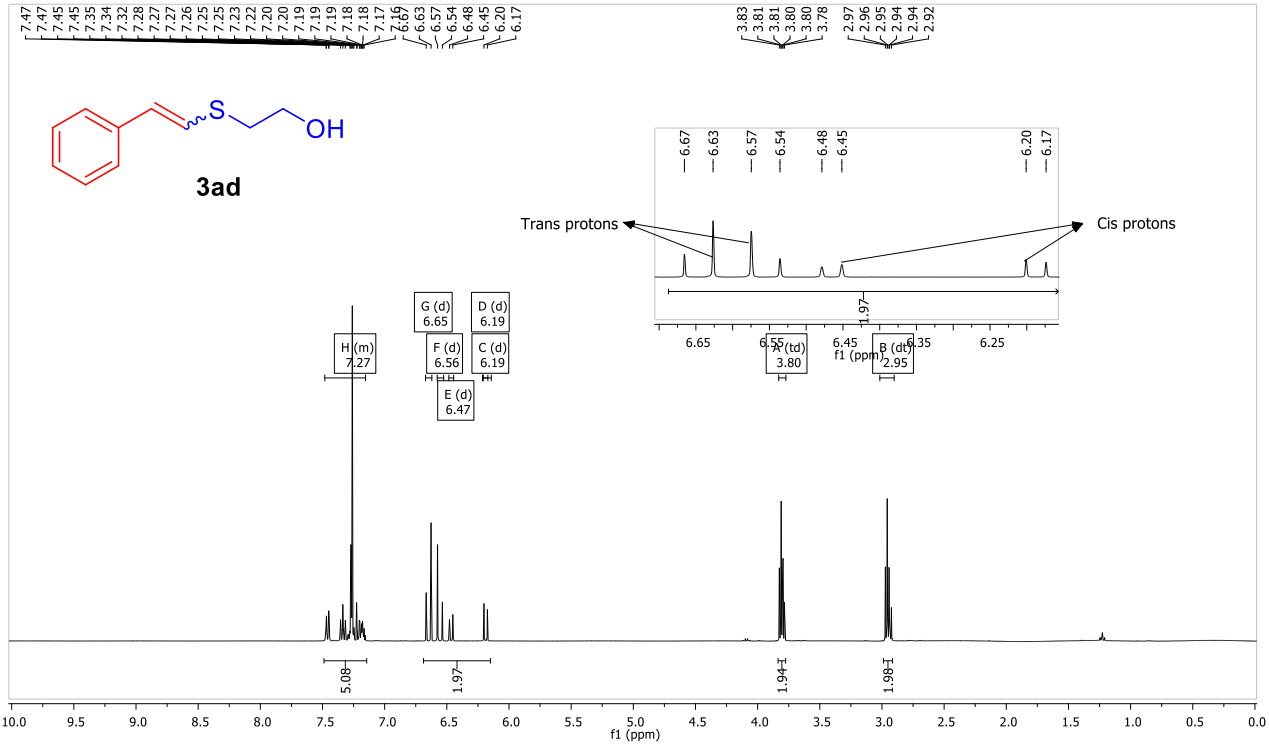


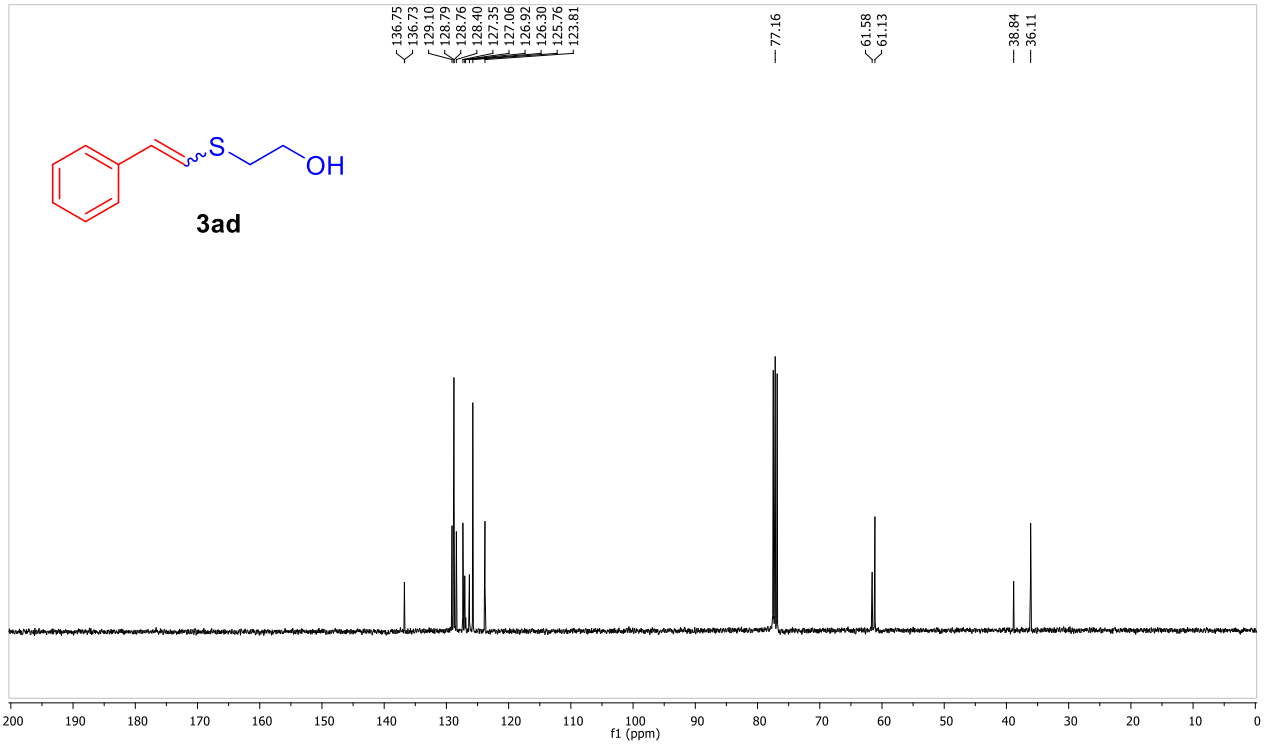
^{1}H and ^{13}C Spectra of 3ac



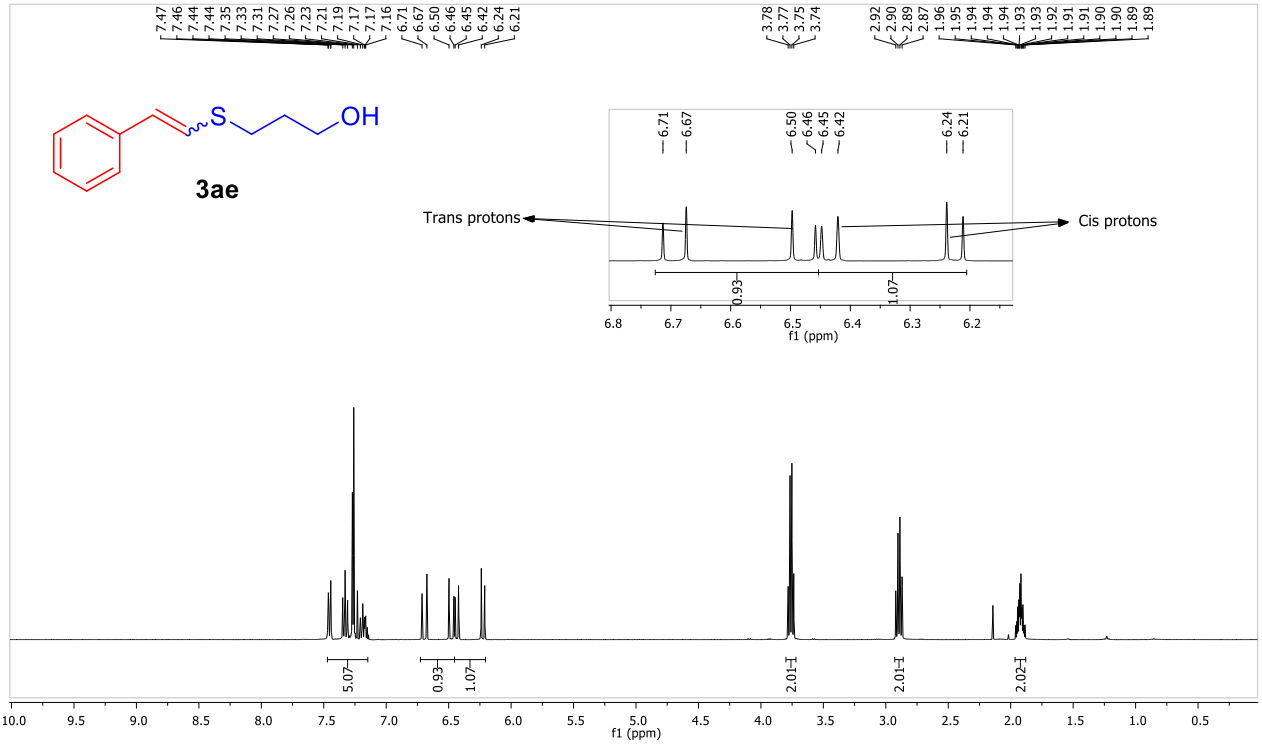


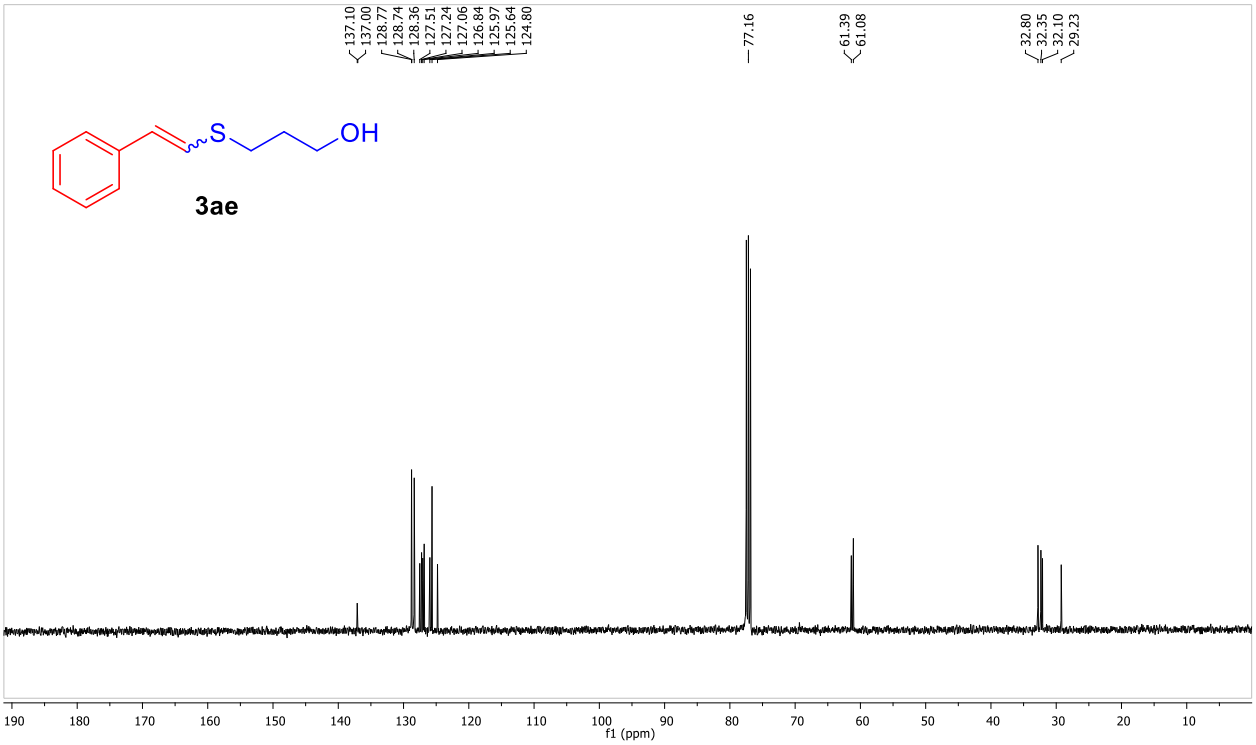
^{1}H and ^{13}C NMR of 3ad



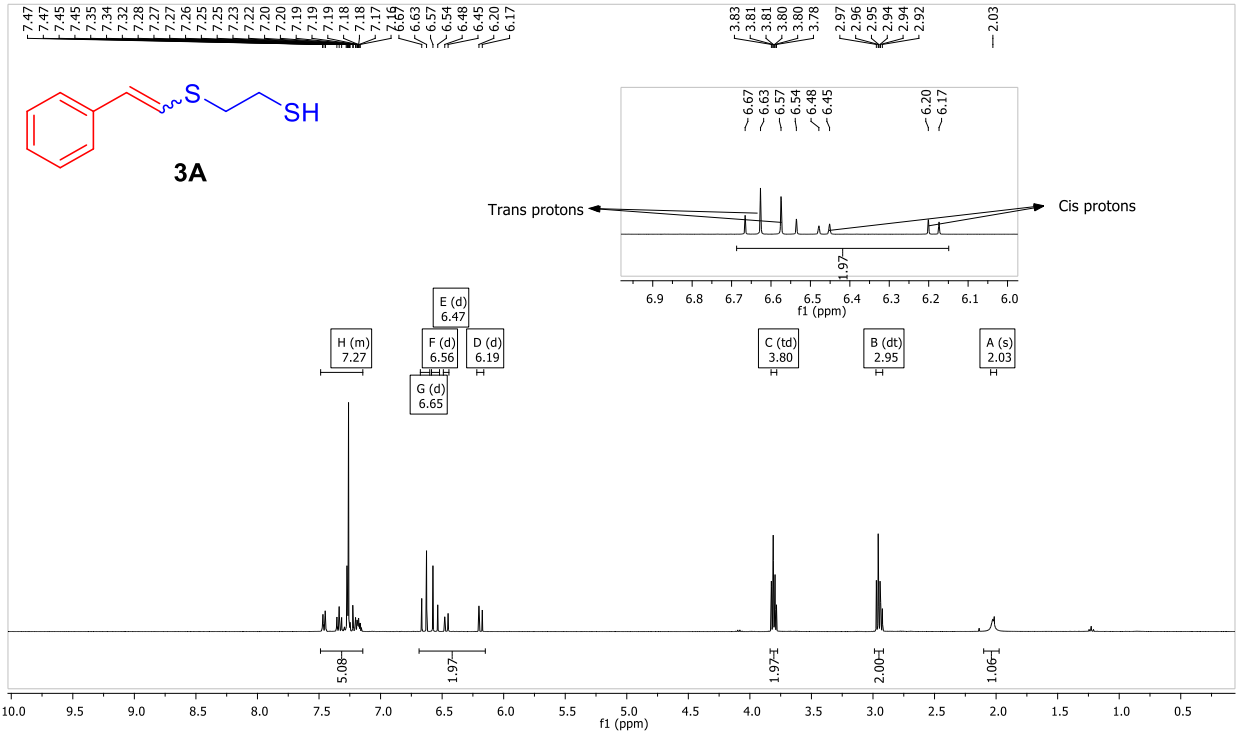


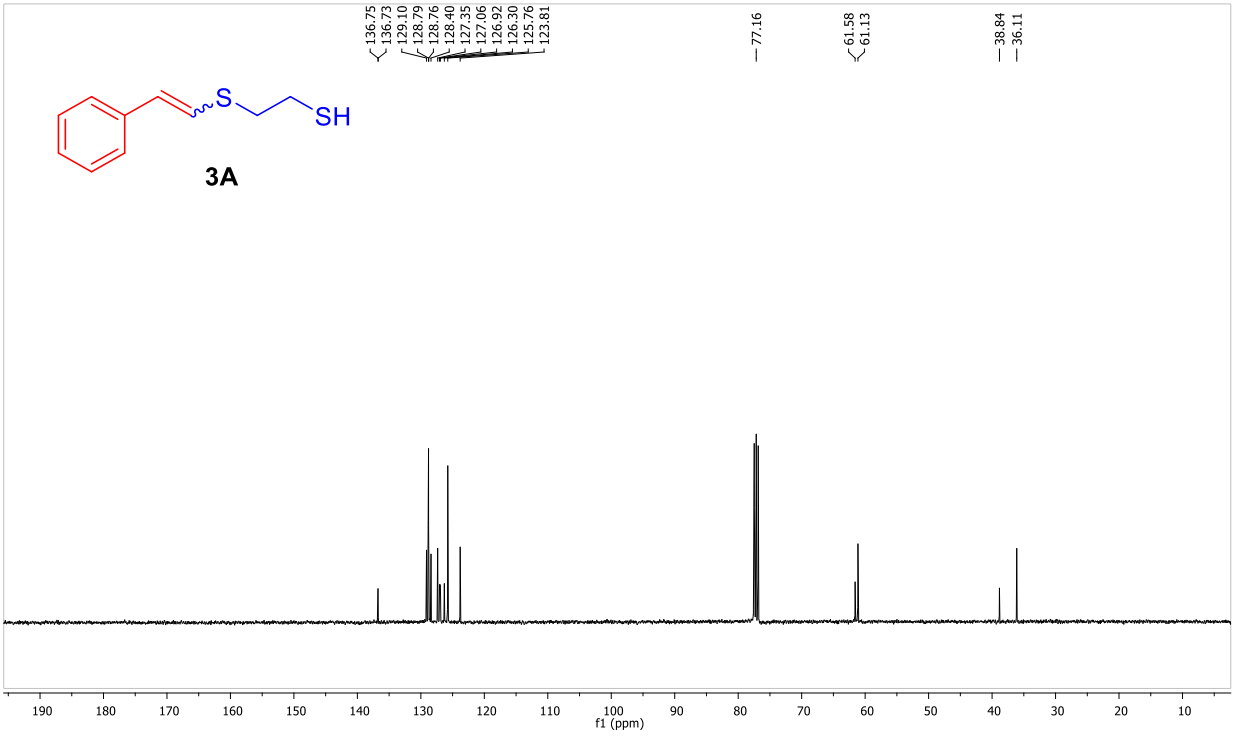
^{1}H and ^{13}C NMR of 3ae



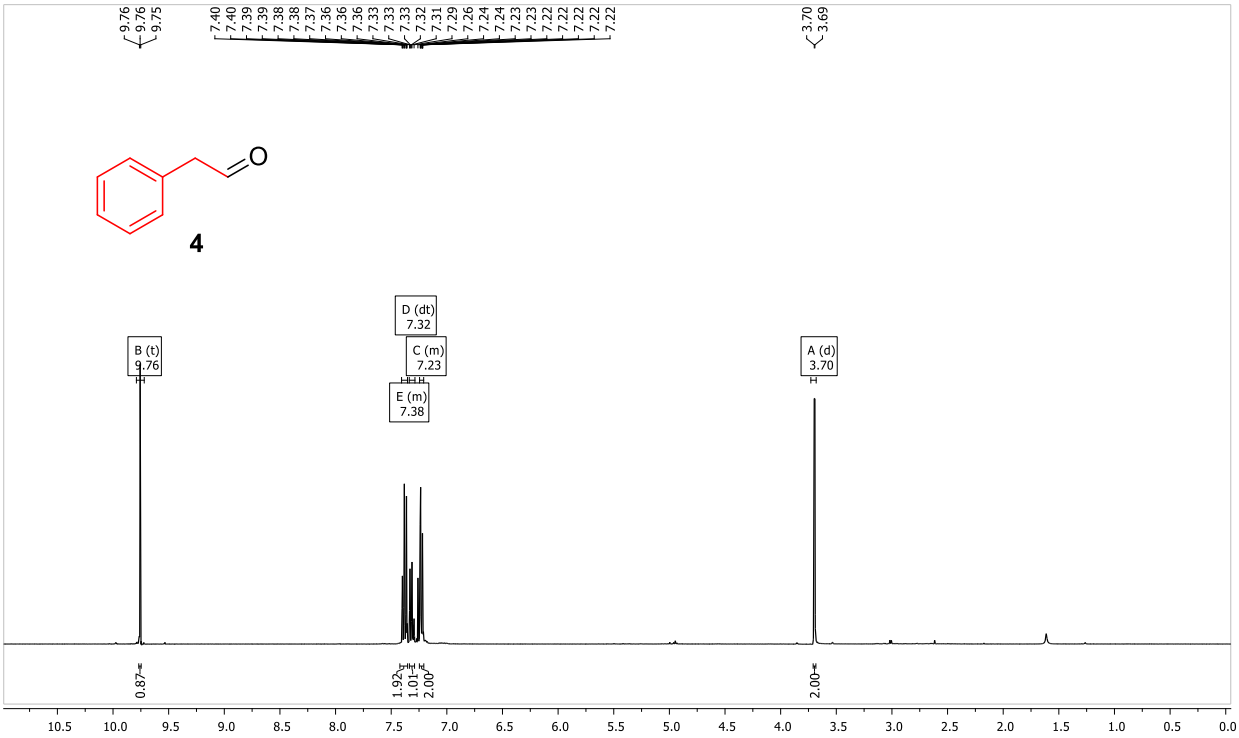


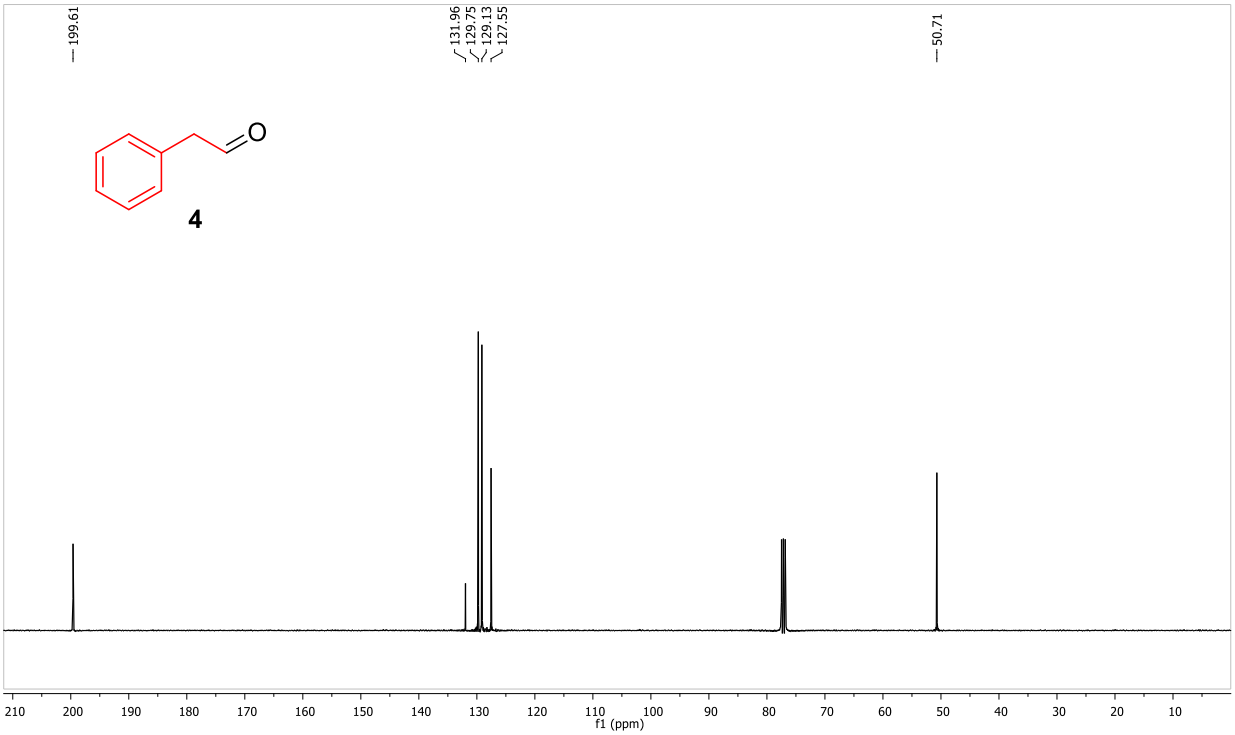
^{1}H and ^{13}C NMR of 3A





^{1}H and ^{13}C NMR of 4





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4. H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett*, **2016**, *27*, 714–723.