Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

For

One-Pot Thiol-free Synthetic Approach to Sulfides and Sulfoxides Selectively

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General information

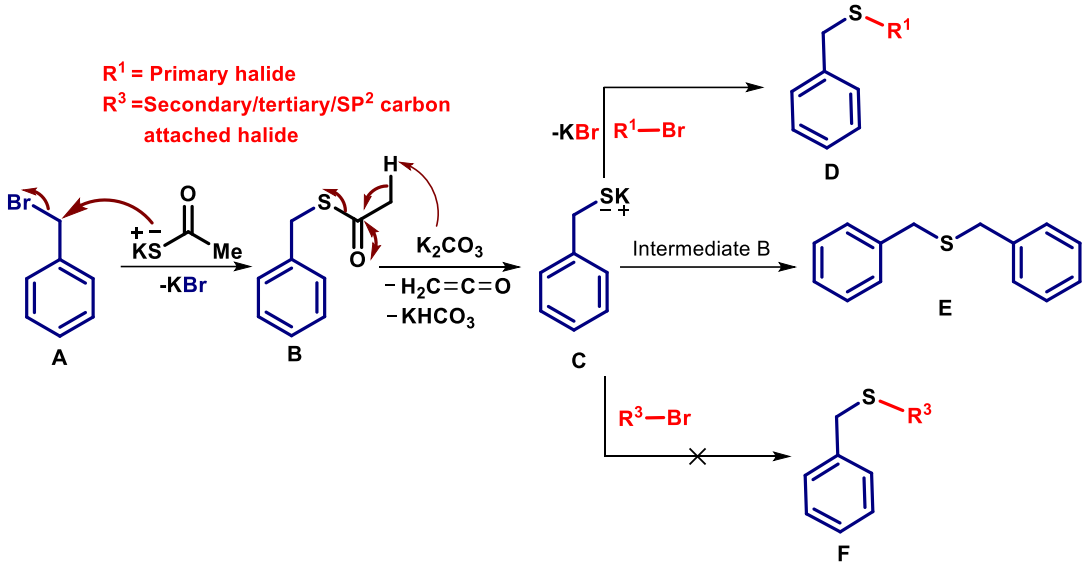
All commercially accessible reagents were used without further purification. Reagents like Potassiumthioacetate (PTA), benzyl bromide, K_2CO_3, allyl bromide, 1-bromo-3-methylbut-2-ene, butenyl bromide, pentenyl bromide, hexenyl bromide, propargyl bromide, 4-bromobut-1-yne, dibromo-derivatives, citronellol, thymol, tocopherol, estrone were obtained from commercial sources such as Aldrich, Avra, Chemscene, TCI chemicals and Spectrochem. The reaction progress was monitored by thin-layer chromatography (2.0 × 4.0 cm^2 alumina plates) using appropriate solvent systems. An iodine chamber and TLC stain solutions (prepared freshly) such as $KMnO_4$ and vanillin were used to visualize the UV-inactive spots. After successive solvent extraction, the combined organic layer was washed with brine (aqueous saturated NaCl solution), dried over oven-dried anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure using a rotary evaporator. Column chromatography was performed by using Acme's silica gel (100–200 mesh) with an appropriate mixture of EtOAc and petroleum ether. NMR spectra of all newly synthesized compounds were obtained by using Bruker (AVANCE IIITM) 500 MHz and Bruker (AVANCE IIITM) 400 MHz spectrometers and solvent residual peaks as an internal standard (^{1}H NMR: 500 and 400 MHz, $CDCl_3$ at 7.26 ppm; ^{13}C NMR: 125 and 100 MHz, $CDCl_3$ at 77.2 ppm). ^{1}H NMR data expressed in chemical shift (δ ppm), multiplicity (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet), and coupling constants (*J* in hertz). High-resolution mass spectrometry (HRMS) measurements of unknown compounds were done by using Bruker (Maxis Impact) or Micromass Q-ToF spectrometers. The melting points (mp's) of solid compounds were obtained from a Veego/Buchi 560 melting point apparatus and are uncorrected. X-ray diffraction data was collected on a Bruker D8 QUEST (APEX-II CCD) diffractometer equipped withmonochromated Mo Kα (λ = 0.71073).

General procedure for the synthesis of sulfides (thioethers)

To the solution of benzyl bromide (1 equiv.) and potassium thioacetate (1 equiv.) in methanol (10 mL) in a two-neck round-bottom flask, stirred at room temperature for 2 h. After consumption of starting material, potassium carbonate, (3 equiv.) was added and the resulting reaction mixture was allowed to stir for 10 min. Further, bromo compound (electrophile) (1 equiv.) was transferred to the reaction mixture and stirred at room temperature for 3 h. After completion of the reaction (TLC monitoring), solvent was evaporated under reduced pressure, then the reaction mixture was diluted with water and extracted with ethyl acetate (3×10 mL). The organic layer was separated, washed

with brine solution and dried over anhydrous Na_2SO_4. Then, the solution was concentrated under reduced pressure and purified by silica gel column chromatography by using petroleum ether and ethyl acetate to afford the sulfide compounds. (Reactions were carried out in 100 mg scale)

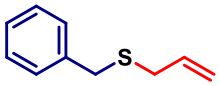
Mechanism for the Formation of Unsymmetrical and Symmetrical Sulfide (D and E)



Scheme 1. Plausible mechanism

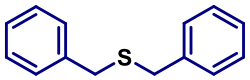
Based on the previous reports,[1] we propose the mechanism as shown in Scheme 1 for the formation of unsymmetrical sulfide as well as the dibenzyl sulfide **E** (**3** in main manuscript). In the first step, benzyl bromide (**A)** interacts with potassium thioacetate to generate compound **B.** Next, we added potassium carbonate which abstracts proton from the compound **B** and gives intermediate **C**. The intermediate **C** further reacts with primary halide to deliver the desired compound **D**. However, if intermediate sulfide **C** attacks at the benzylic carbon of **B**, it leads to the dimer **E**. Additionally, in case of secondary/tertiary/sp^2 hybridized electrophilic center of halides, unsymmetrical sulfide **F** was not delivered and only the dimer **E** was observed.

Allyl(benzyl)sulfane 2



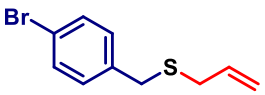
Yield 114 mg, 80%, **Appearance** colorless liquid, R_f = 0.7 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.37-7.36 (m, 4H), 7.31-7.28 (m, 1H), 5.90-5.82 (m, 1H), 5.20-5.13 (m, 2H), 3.72 (s, 2H), 3.09 (d, *J* = 7.0 Hz, 2H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 138.4, 134.3, 129.1, 128.6, 127.0, 117.4, 34.9, 34.1ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_{12}KS$ $[M+K]^+$ 203.0291, found 203.0291.

Dibenzylsulfane 3



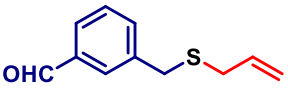
Yield 136 mg, 73%, **Appearance** colorless sticky liquid, R_f = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.36-7.25 (m, 10H), 3.62 (s, 4H), ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 137.5, 129.6, 128.7, 127.6, 43.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{14}H_{14}KS$ $[M+K]^+$ 253.0448, found 253.0447.

Allyl(4-bromobenzyl)sulfane 5a



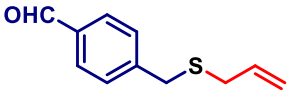
Yield 174 mg, 82%, **Appearance** colorless liquid, R_f = 0.7 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.43 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.83-5.73 (m, 1H), 5.15-5.05 (m, 2H), 3.60 (s, 2H), 3.01 (d, *J* = 7.2 Hz, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 137.5, 134.2, 131.7, 130.9, 120.9, 117.7, 34.4, 34.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_{11}BrKS$ $[M+K]^+$ 280.9396, found 280.9396.

3-((Allylthio)methyl)benzaldehyde 5b



Yield 122 mg, 73%, **Appearance** yellow liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 10.00 (s, 1H), 7.82 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 5.84-5.74 (m, 1H), 5.16-5.06 (m, 2H), 3.72 (s, 2H), 3.03 (d, *J* = 6.8 Hz, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 192.3, 139.8, 136.8, 135.3, 134.0, 130.2, 129.4, 128.7, 117.9, 34.5, 34.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{12}KOS$ $[M+K]^+$ 231.0240, found 231.0240.

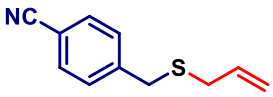
4-((Allylthio)methyl)benzaldehyde 5c



Yield 126 mg, 75%, **Appearance** yellow liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 9.98 (s, 1H), 7.82 (d,

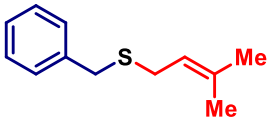
J = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 5.82-5.74 (m, 1H), 5.15-5.06 (m, 2H), 3.70 (s, 2H), 3.03 (d, *J* = 7.0 Hz, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 191.9, 145.8, 135.4, 133.9, 130.1, 129.8, 117.9, 34.8, 34.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{12}KOS$ $[M+K]^+$ 231.0240, found 231.0240.

4-((Allylthio)methyl)benzonitrile 5d



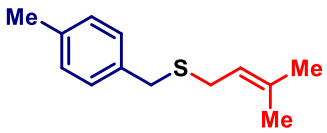
Yield 114 mg, 69%, **Appearance** yellow liquid, ***R*$_f$** = 0.5 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.59 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 5.81-5.72 (m, 1H), 5.15-5.04 (m, 2H), 3.67 (s, 2H), 3.01 (d, *J* = 7.0 Hz, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 144.3, 133.9, 132.4, 129.9, 118.9, 117.9, 110.9, 34.7, 34.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{12}NS$ $[M+H]^+$ 190.0684, found 190.0684.

benzyl(3-Methylbut-2-en-1-yl)sulfane 6a



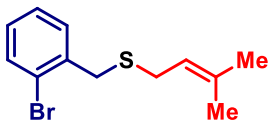
Yield 146 mg, 88%, **Appearance** colorless liquid, **R$_f$** = 0.7 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.37-7.32 (m, 4H), 7.29-7.25 (m, 1H), 5.31-5.27 (m, 1H), 3.72 (s, 2H), 3.10 (d, *J* = 7.6 Hz, 2H), 1.78 (s, 3H), 1.62 (s, 3H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$):** δ 138.7, 135.4, 128.9, 128.4, 126.9, 120.5, 35.7, 29.2, 25.8, 17.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{17}S$ $[M+H]^+$ 193.1045, found 193.1045.

(4-Methylbenzyl)(3-methylbut-2-en-1-yl)sulfane 6b



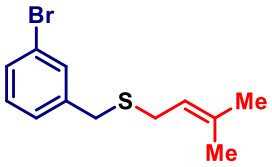
Yield 144 mg, 81%, **Appearance** colorless liquid, **R$_f$** = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl3): δ** 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.27-5.23 (m, 1H), 3.66 (s, 1H), 2.05 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H), 1.75 (s, 3H), 1.60 (s, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 136.6, 135.6, 135.5, 129.2, 128.9, 120.6, 35.5, 29.2, 25.9, 21.2, 17.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{19}S$ $[M+Na]^+$ 207.1198, found 207.1198.

(2-Bromobenzyl)(3-methylbut-2-en-1-yl)sulfane 6c



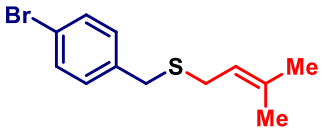
Yield 184 mg, 78%, **Appearance** colorless liquid, $\mathbf{R_f}$ = 0.7 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.28 (t, *J* = 7.8 Hz, 1H), 3.83 (s, 2H), 3.15 (d, *J* = 7.5 Hz, 2H), 1.77 (s, 3H), 1.62 (s, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 138.0, 135.9, 133.1, 130.7, 128.5, 127.5, 124.7, 120.3, 35.9, 29.6, 25.8, 17.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{15}BrKS$ $[M+K]^+$ 308.9709, found 308.9709.

(3-Bromobenzyl)(3-methylbut-2-en-1-yl)sulfane 6d



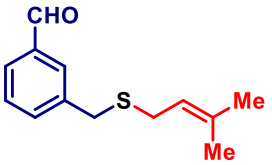
Yield 194 mg, 82%, **Appearance** colorless liquid, $\mathbf{R_f}$ = 0.9 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.46 (s, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 5.21 (t, *J* = 7.6 Hz, 1H), 3.63 (s, 2H), 3.05 (d, *J* = 8.0 Hz, 2H), 1.74 (s, 3H), 1.58 (s, 3H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 141.2, 135.9, 131.9, 130.0, 127.6, 122.5, 120.3, 35.1, 29.2, 25.8, 17.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{15}BrKS$ $[M+K]^+$ 308.9709, found 308.9709.

(4-Bromobenzyl)(3-methylbut-2-en-1-yl)sulfane 6e



Yield 214 mg, 91%, **Appearance** colorless liquid, $\mathbf{R_f}$ = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.42 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.21 (t, *J* = 7.4 Hz, 1H), 3.62 (s, 2H), 3.03 (d, *J* = 7.6 Hz, 2H), 1.73 (s, 3H), 1.57 (s, 3H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 137.9, 135.8, 131.6, 130.7, 120.7, 120.3, 35.1, 29.2, 25.8, 17.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{15}BrKS$ $[M+K]^+$ 308.9709, found 308.9709.

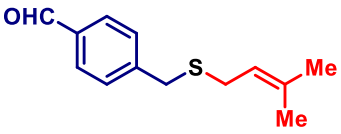
4-(((3-Methylbut-2-en-1-yl)thio)methyl)benzaldehyde 6f



Yield 146 mg, 76%, **Appearance** Yellow liquid, $\boldsymbol{R_f}$ = 0.5 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 9.99 (s, 1H), 7.81 (s, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 5.21-5.18 (m,1H), 3.72 (s, 2H), 3.04 (d, *J* = 7.6 Hz, 2H), 1.71 (s, 3H), 1.54 (s, 3H) ppm, **^{13}C**

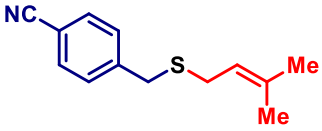
NMR (100 MHz, $CDCl_3$): δ 192.3, 140.2, 136.7, 136.0, 135.1, 129.9, 129.3, 128.5, 120.2, 35.2, 29.3, 25.8, 17.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{17}OS$ $[M+H]^+$ 221.0995, found 221.0994.

4-(((3-Methylbut-2-en-1-yl)thio)methyl)benzaldehyde 6g



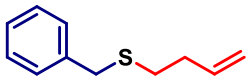
Yield 152 mg, 79%, **Appearance** yellow liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.99 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 5.23-5.18 (m,1H), 3.72 (s, 2H), 3.05 (d, *J* = 7.6 Hz, 2H), 1.72 (s, 3H), 1.56 (s, 3H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 192.0, 146.3, 136.2, 135.4, 130.1, 129.7, 120.2, 35.6, 29.4, 25.9, 18.0 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{17}OS$ $[M+H]^+$ 221.0995, found 221.0994.

4-(((3-Methylbut-2-en-1-yl)thio)methyl)benzonitrile 6h



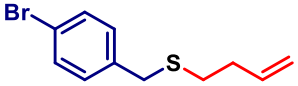
Yield 134 mg, 71%, **Appearance** yellow liquid, R_f = 0.6 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.58 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 5.18 (t, *J* = 7.8 Hz, 1H), 3.68 (s, 2H), 3.02 (d, *J* = 7.5 Hz, 2H), 1.71 (s, 3H), 1.54 (s, 3H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 144.6, 136.2, 132.3, 129.7, 119.9, 118.9, 110.7, 35.4, 29.4, 25.8, 17.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{16}NS$ $[M+H]^+$ 218.0998, found 218.0997.

Benzyl(but-3-en-1-yl)sulfane 7a



Yield 118 mg, 76%, **Appearance** colorless liquid, R_f = 0.7 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.42-7.38 (m, 4H), 7.35-7.31 (m, 1H), 5.94-5.85 (m, 1H), 5.17-5.11 (m, 2H), 3.81 (s, 2H), 2.57 (t, *J* = 7.3 Hz, 2H), 2.42-2.38 (m, 2H), ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 138.4, 136.7, 128.8, 128.4, 126.9, 115.8, 36.2, 33.5, 30.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{14}KS$ $[M+K]^+$ 217.0448, found 217.0447.

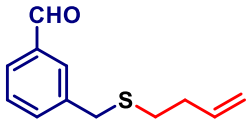
(4-Bromobenzyl)(but-3-en-1-yl)sulfane 7b



Yield 160 mg, 72%, **Appearance** colorless liquid, R_f = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.43 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.84-5.74 (m, 1H), 5.08-5.01 (m, 2H), 3.66 (s, 2H), 2.47 (t, *J* = 7.4

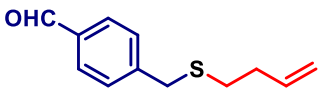
Hz, 2H), 2.33-2.27 (m, 2H), ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 137.7, 136.7, 131.7, 130.7, 120.9, 116.2, 35.9, 33.6, 30.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{13}BrKS$ $[M+K]^+$ 294.9553, found 294.9552.

3-((But-3-en-1-ylthio)methyl)benzaldehyde 7c



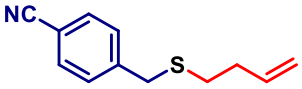
Yield 122 mg, 68%, **Appearance** yellow liquid, ***R*$_f$** = 0.3 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 9.98 (s, 1H), 7.80 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 5.79-5.72 (m, 1H), 5.04-4.98 (m, 2H), 3.76 (s, 2H), 2.46 (t, *J* = 7.3 Hz, 2H), 2.29 (t, *J* = 7.0 Hz, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 192.2, 139.9, 136.7, 136.5, 134.9, 129.9, 129.3, 128.6, 116.2, 35.9, 33.5, 30.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{14}KOS$ $[M+K]^+$ 245.0397, found 245.0396.

4-((But-3-en-1-ylthio)methyl)benzaldehyde 7d



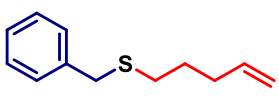
Yield 128 mg, 71%, **Appearance** yellow liquid, **R$_f$** = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$) δ** 9.98 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H) 5.82-5.72 (m, 1H), 5.06-4.99 (m, 2H), 3.76 (s, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 191.9, 145.9, 136.5, 135.4, 130.1, 129.6, 116.3, 36.3, 33.5, 30.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{14}KOS$ $[M+K]^+$ 245.0397, found 245.0397.

4-((But-3-en-1-ylthio)methyl)benzonitrile 7e



Yield 110 mg, 62%, **Appearance** colorless liquid, ***R*$_f$** = 0.3 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.61 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H) 5.81-5.73 (m, 1H), 5.07-5.02 (m, 2H), 3.74 (s, 2H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.29 (t, *J* = 7.0 Hz, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 144.4, 136.4, 132.5, 129.7, 118.9, 116.4, 110.9, 36.3, 33.5, 31.0 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{13}KS$ $[M+K]^+$ 242.0400, found 242.0400 .

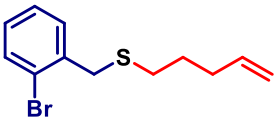
Benzyl(pent-4-en-1-yl)sulfane 8a



Yield 124 mg, 74%, **Appearance** colorless liquid, ***R*$_f$** = 0.9 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.34 (d, *J* = 4.0 Hz,

4H), 7.28-7.25 (m, 1H) 5.83-5.73 (m, 1H), 5.05-4.98 (m, 2H), 3.73 (s, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.72-1.64 (m, 2H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 138.7, 137.9, 128.9, 128.6, 127.0, 115.3, 36.3, 32.9, 30.8, 28.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{16}KS$ $[M+K]^+$ 231.0604, found 231.0604.

(2-Bromobenzyl)(pent-4-en-1-yl)sulfane 8b

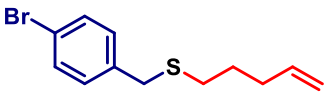


Yield 162 mg, 69%, **Appearance** colorless liquid, ***R*$_f$** = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.58 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.40 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.28 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.12 (td, *J* = 7.5, 1.6 Hz, 1H), 5.84-5.76 (m, 1H), 5.07-4.99 (m, 2H), 3.86 (s, 2H), 2.53 (t, *J* = 7.0 Hz, 2H), 2.17 (q, *J* = 6.6 Hz, 2H), 1.75-1.69 (m, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 138.1, 137.8, 133.1, 130.8, 128.6, 127.5, 124.6, 115.3, 36.5, 32.9, 31.2, 28.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{15}BrKS$ $[M+K]^+$ 308.9709, found 308.9709.

(3-Bromobenzyl)(pent-4-en-1-yl)sulfane 8c

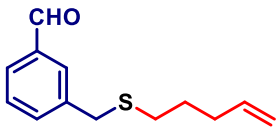
Yield 166 mg, 71%, **Appearance** colorless liquid, ***R*$_f$** = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.47 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 5.79-5.71 (m, 1H), 5.03-4.96 (m, 2H), 3.65 (s, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 2.12 (q, *J* = 7.8 Hz, 2H), 1.68-1.62 (m, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 141.1, 137.8, 131.9, 130.2, 130.1, 127.6, 122.6, 115.4, 35.8, 32.8, 30.9, 28.4 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{15}BrKS$ $[M+K]^+$ 308.9709, found 308.9709.

(4-Bromobenzyl)(pent-4-en-1-yl)sulfane 8d



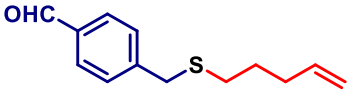
Yield 176 mg, 75%, **Appearance** colorless liquid, ***R*$_f$** = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.45 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.82-5.74 (m, 1H), 5.06-4.99 (m, 2H), 3.67 (s, 2H), 2.43 (t, *J* = 7.5 Hz, 2H), 2.14 (q, *J* = 7.3 Hz, 2H), 1.70-1.64 (m, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$) δ** 137.7, 137.7, 131.5, 130.5, 120.7, 115.3, 35.6, 32.8, 30.7, 28.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{15}BrKS$ $[M+K]^+$ 308.9709, found 308.9709 .

3-((Pent-4-en-1-ylthio)methyl)benzaldehyde 8e



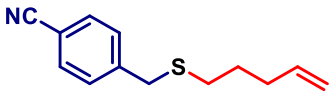
Yield 128 mg, 67%, **Appearance** colorless liquid, R_f = 0.3 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 10.01 (s, 1H), 7.82 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 5.78-5.69 (m, 1H), 5.01-4.95 (m, 2H), 3.76 (s, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 2.11 (q, *J* = 7.0 Hz, 2H), 1.68-1.62 (m, 2H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 192.4, 140.1, 137.8, 136.8, 135.1, 129.9, 129.4, 128.7, 115.5, 35.9, 32.9, 30.9, 28.4 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{16}KOS$ $[M+K]^+$ 259.0553, found 259.0553.

4-((Pent-4-en-1-ylthio)methyl)benzaldehyde 8f



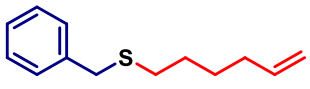
Yield 134 mg, 70%, **Appearance** yellow liquid, R_f = 0.3 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.99 (s, 1H) 7.82 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 5.78-5.68 (m, 1H), 5.02-4.94 (m, 2H), 3.74 (s, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.68-1.60 (m, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 191.9, 146.1, 137.2, 135.4, 130.2, 129.6, 115.5, 36.3, 32.9, 31.0, 28.4 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{16}KOS$ $[M+K]^+$ 259.0553, found 259.0553.

4-((Pent-4-en-1-ylthio)methyl)benzonitrile 8g



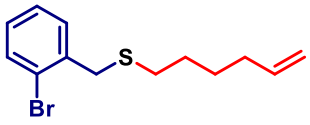
Yield 122 mg, 65%, **Appearance** colorless liquid, R_f = 0.3 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.58 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.77-5.67 (m, 1H), 5.00-4.93 (m, 2H), 3.71 (s, 2H), 2.39 (t, *J* = 7.4 Hz, 2H), 2.10 (q, *J* = 7.4 Hz, 2H), 1.66-1.59 (m, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 144.5, 137.6, 132.4, 129.6, 118.8, 115.4, 110.9, 36.1, 32.7, 30.9, 28.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{15}NNaS$ $[M+Na]^+$ 240.0817, found 240.0817.

Benzyl(hex-5-en-1-yl)sulfane 9a



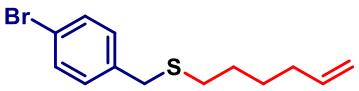
Yield 130 mg, 72%, **Appearance** yellow liquid, R_f = 0.9 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.34-7.33 (m, 4H), 7.31-7.23 (m, 1H) 5.85-5.75 (m, 1H), 5.04-4.96 (m, 2H), 3.72 (s, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.05 (q, *J* = 7.2 Hz, 2H), 1.64-1.56 (m, 2H), 1.51-1.44 (m, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 138.7, 138.6, 128.9, 128.6, 126.9, 114.8, 36.4, 33.4, 31.2, 28.7, 28.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{18}KS$ $[M+K]^+$ 245.0761, found 245.0760.

(2-Bromobenzyl)(hex-5-en-1-yl)sulfane 9b



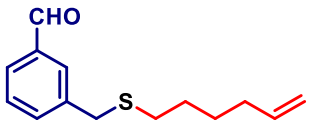
Yield 168 mg, 68%, **Appearance** colorless liquid, R_f = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.59-7.57 (m, 1H), 7.40-7.39 (m, 1H), 7.31-7.27 (m, 1H), 7.15-7.11 (m, 1H), 5.84-5.77 (m, 1H), 5.05-4.97 (m, 2H), 3.86 (s, 2H), 2.53-2.50 (m, 2H), 2.10-2.05 (m, 2H), 1.67-1.61 (m, 2H), 1.53-1.47 (m, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 138.6, 138.2, 133.2, 130.8, 128.6, 127.5, 124.6, 114.8, 36.6, 33.4, 31.7, 28.9, 28.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{17}BrKS$ $[M+K]^+$ 322.9866, found 322.9865.

(4-Bromobenzyl)(hex-5-en-1-yl)sulfane 9c



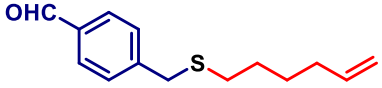
Yield 182 mg, 73%, **Appearance** colorless liquid, R_f = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.42 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.81-5.73 (m, 1H), 5.01-4.95 (m, 2H), 3.64 (s, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.03 (q, *J* = 7.8 Hz, 2H), 1.59-1.53 (m, 2H), 1.48-1.42 (m, 2H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 138.5, 137.8, 131.6, 130.6, 120.8, 114.8, 35.7, 33.3, 31.3, 28.6, 28.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{17}BrKS$ $[M+K]^+$ 322.9866, found 322.9865.

3-((Hex-5-en-1-ylthio)methyl)benzaldehyde 9d



Yield 128 mg, 63%, **Appearance** colorless liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 9.98 (s, 1H), 7.79 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 5.77-5.69 (m, 1H), 4.98-4.90 (m, 2H), 3.74 (s, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.00 (q, *J* = 7.2 Hz, 2H), 1.59-1.51 (m, 2H), 1.46-1.39 (m, 2H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 192.2, 140.1, 138.4, 136.7, 134.9, 129.9, 129.3, 128.6, 114.8, 35.9, 33.3, 31.4, 28.6, 27.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{14}H_{18}KS$ $[M+K]^+$ 273.0710, found 273.0709.

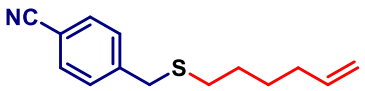
4-((Hex-5-en-1-ylthio)methyl)benzaldehyde 9e



Yield 140 mg, 69%, **Appearance** colorless liquid, R_f = 0.5 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 9.93 (s, 1H) 7.77 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 2H), 5.75-5.66 (m, 1H), 4.94-4.87 (m, 2H), 3.69 (s, 2H), 2.37-2.34 (m, 2H), 1.97-1.96 (m, 2H), 1.51-1.49 (m, 2H), 1.40-1.39 (m, 2H) ppm,

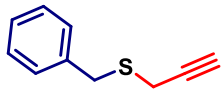
^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 145.9, 138.3, 135.2, 129.9, 129.4, 114.7, 36.1, 33.2, 31.3, 28.5, 27.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{14}H_{18}KS$ $[M+K]^+$ 273.0710, found 273.0709.

4-((Hex-5-en-1-ylthio)methyl)benzonitrile 9f



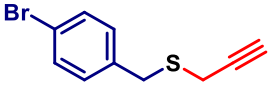
Yield 128 mg, 64%, **Appearance** colorless liquid, ***R*$_f$** = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.58 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.79-5.70 (m, 1H), 4.99-4.92 (m, 2H), 3.70 (s, 2H), 2.38 (t, *J* = 7.8 Hz, 2H), 2.01 (q, *J* = 7.3 Hz, 2H), 1.57-1.51 (m, 2H), 1.46-1.39 (m, 2H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 144.5, 138.4, 132.4, 129.6, 118.9, 114.9, 110.8, 36.2, 33.3, 31.5, 28.6, 27.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{14}H_{17}KNS$ $[M+K]^+$ 270.0713, found 270.0713.

Benzyl(prop-2-yn-1-yl)sulfane 10a



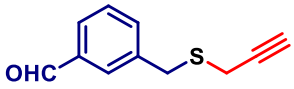
Yield 106 mg, 75%, **Appearance** yellow liquid, ***R*$_f$** = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.42-7.37 (m, 4H), 7.34-7.31 (m, 1H), 3.93 (s, 2H), 3.12 (d, *J* = 2.5 Hz, 2H), 2.36 (t, *J* = 2.8 Hz, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 137.6, 129.2, 128.7, 127.4, 80.0, 71.5, 35.4, 18.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_{11}S$ $[M+H]^+$ 163.0576, found 163.0575.

(4-Bromobenzyl)(prop-2-yn-1-yl)sulfane 10b



Yield 156 mg, 74%, **Appearance** dark brown liquid, ***R*$_f$** = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.44 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 2H), 3.07 (d, *J* = 2.4 Hz, 2H), 2.30 (t, *J* = 2.6 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 136.6, 131.8, 130.9, 121.2, 79.7, 71.7, 34.7, 18.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_9BrKS$ $[M+K]^+$ 278.9240, found 278.9240.

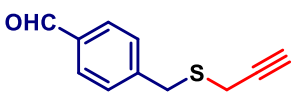
3-((Prop-2-yn-1-ylthio)methyl)benzaldehyde 10c



Yield 101 mg, 61%, **Appearance** yellow liquid, ***R*$_f$** = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 10.02 (s, 1H), 7.86 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 1H),7.63 (d, *J* = 7.5 Hz, 1H) 7.53-7.49 (m, 1H), 3.95 (s, 2H), 3.08 (d, *J* = 2.5 Hz, 2H), 2.32 (t, *J* = 2.8 Hz, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 192.3, 138.9, 136.9,

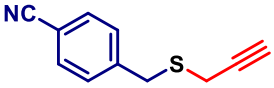
135.2, 130.3, 129.5, 128.9, 79.5, 71.9, 34.9, 18.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{10}KOS$ $[M+K]^+$ 229.0084, found 229.0084.

4-((Prop-2-yn-1-ylthio)methyl)benzaldehyde 10d



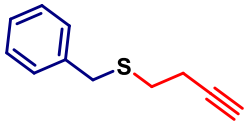
Yield 114 mg, 69%, **Appearance** brown sticky liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 10.00 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 2H), 3.08 (d, *J* = 3.0 Hz, 2H), 2.32 (t, *J* = 2.5 Hz, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 191.9, 144.9, 135.6, 130.2, 129.9, 79.5, 71.9, 35.2, 18.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{10}KOS$ $[M+K]^+$ 229.0084, found 229.0083.

4-((Prop-2-yn-1-ylthio)methyl)benzonitrile 10e



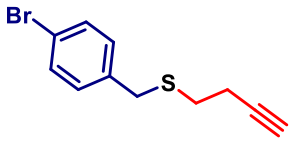
Yield 102 mg, 63%, **Appearance** brown sticky liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.62 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 2H), 3.07 (d, *J* = 2.5 Hz, 2H), 2.32 (t, *J* = 2.5 Hz, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 143.4, 132.6, 129.9, 118.9, 111.3, 79.3, 72.1, 35.0, 18.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{10}NS$ $[M+H]^+$ 188.0528, found 188.0528.

Benzyl(but-3-yn-1-yl)sulfane 11a



Yield 106 mg, 71%, **Appearance** colorless liquid, R_f = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.35-7.34 (m, 4H), 7.29-7.27 (m, 1H), 3.78 (s, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.44 (td, *J* = 7.2, 2.0 Hz, 2H), 2.05 (s, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 138.2, 128.9, 128.6, 127.2, 82.7, 69.6, 36.3, 30.0, 19.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{12}KS$ $[M+K]^+$ 215.0291, found 215.0291.

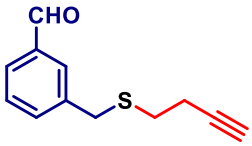
(4-Bromobenzyl)(but-3-yn-1-yl)sulfane 11b



Yield 148 mg, 67%, **Appearance** brown liquid, R_f = 0.4 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.43 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.70 (s, 2H), 2.58-2.54 (m, 2H), 2.44-2.39 (m, 2H), 2.04 (t, *J* = 2.6 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 137.2, 131.7, 130.6, 121.0,

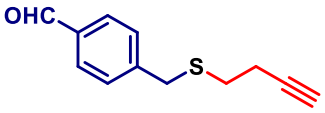
82.6, 69.7, 35.8, 30.0, 19.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{12}BrS$ $[M+H]^+$ 254.9820, found 254.9820,

3-((But-3-yn-1-ylthio)methyl)benzaldehyde 11c



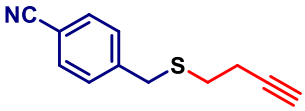
Yield 110 mg, 62%, **Appearance** yellow liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 10.00 (s, 1H), 7.83 (s, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 3.83 (s, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.46-2.42 (m, 2H), 2.03 (t, *J* = 2.8 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 192.2, 139.6, 136.8, 135.0, 129.9, 129.4, 128.8, 82.5, 69.9, 36.0, 30.2, 19.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{12}KOS$ $[M+K]^+$ 243.0240, found 243.0240.

4-((But-3-yn-1-ylthio)methyl)benzaldehyde 11d



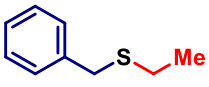
Yield 120 mg, 68%, **Appearance** brown liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 9.99 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H) 3.83 (s, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.46-2.43 (m, 2H), 2.03 (t, *J* = 2.5 Hz, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 191.9, 145.6, 135.6, 130.3, 129.7, 82.5, 69.9, 36.4, 30.3, 19.8 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{12}KOS$ $[M+K]^+$ 243.0240, found 243.0240.

4-((But-3-yn-1-ylthio)methyl)benzonitrile 11e



Yield 110 mg, 63%, **Appearance** yellow sticky liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.62 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.47-2.43 (m, 2H), 2.04 (t, *J* = 2.4 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 144.0, 132.6, 129.8, 118.9, 111.2, 82.4, 69.9, 36.3, 30.3, 19.8 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{11}KNS$ $[M+K]^+$ 240.0243, found 240.0243.

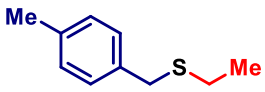
Benzyl(ethyl)sulfane 12a



Yield 102 mg, 77%, **Appearance** colorless liquid, R_f = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.37-7.34 (m, 4H), 7.30-7.28 (m, 1H), 3.77 (s, 2H), 2.48 (q, *J* = 11.3 Hz, 2H), 1.28 (t, *J* = 7.3 Hz, 3H) ppm**, ^{13}C NMR (125**

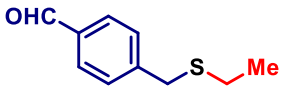
MHz, $CDCl_3$): δ 138.7, 128.9, 128.5, 126.9, 35.9, 25.3, 14.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_9H_{12}KS$ $[M+K]^+$ 191.0291, found 191.0291.

Ethyl(4-methylbenzyl)sulfane 12b



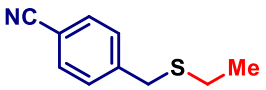
Yield 106 mg, 73%, **Appearance** colorless liquid, R_f = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.26 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.75 (s, 2H), 2.49 (q, *J* = 11.2 Hz, 2H), 2.39 (s, 3H), 1.29 (t, *J* = 7.4 Hz, 3H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 136.5, 135.6, 129.2, 128.8, 35.6, 25.2, 21.1, 14.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_{14}KS$ $[M+K]^+$ 205.0448, found 205.0447.

4-((Ethylthio)methyl)benzaldehyde 12c



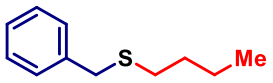
Yield 106 mg, 68%, **Appearance** colorless liquid, R_f = 0.5 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.99 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 2H), 2.42 (q, *J* = 11.2 Hz, 2H), 1.22 (t, *J* = 7.4 Hz, 3H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 191.8, 146.1, 135.3, 130.0, 129.5, 35.8, 25.5, 14.4 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_{13}OS$ $[M+H]^+$ 181.0682, found 181.0681.

4-((Ethylthio)methyl)benzonitrile 12d



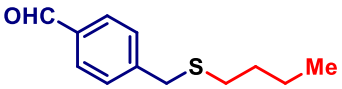
Yield 98 mg, 63%, **Appearance** colorless liquid, R_f = 0.5 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.54 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.69 (s, 2H), 2.37 (q, *J* = 11.3 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 144.3, 132.0, 129.4, 118.6, 110.4, 35.4, 25.2, 14.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_{11}KNS$ $[M+K]^+$ 216.0243, found 216.0243.

Benzyl(butyl)sulfane 13a



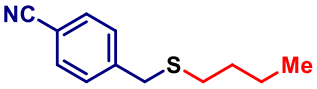
Yield 110 mg, 71%, **Appearance** colorless liquid, R_f = 0.6 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.41-7.37 (m, 4H), 7.33-7.29 (m, 1H), 3.78 (s, 2H), 2.50 (t, *J* = 7.5 Hz, 2H), 1.67-1.61 (m, 2H), 1.51-1.43 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 138.7, 128.8, 128.4, 126.8, 36.2, 31.3, 30.9, 21.9, 13.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{16}KS$ $[M+K]^+$ 219.0604, found 219.0604.

4-((Butylthio)methyl)benzaldehyde 13b



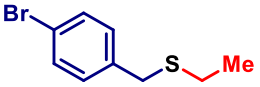
Yield 124 mg, 68%, **Appearance** yellow liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 9.96 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.54-1.48 (m, 2H) 1.37-1.30 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 191.9, 146.1, 135.3, 130.0, 129.5, 36.2, 31.3, 31.2, 21.9, 13.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{16}KOS$ $[M+K]^+$ 247.0553, found 247.0553.

4-((Butylthio)methyl)benzonitrile 13c



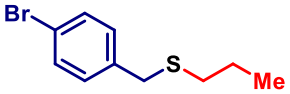
Yield 116 mg, 65%, **Appearance** colorless liquid, R_f = 0.4 (10% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.56 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.08 (s, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 1.52-1.46 (m, 2H) 1.37-1.29 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 144.4, 132.1, 129.4, 118.7, 110.5, 35.9, 31.1, 31.0, 21.8, 13.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{15}KNS$ $[M+K]^+$ 244.0557, found 244.0556.

(4-Bromobenzyl)(ethyl)sulfane 14a



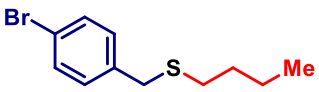
Yield 152 mg, 76%, **Appearance** colorless liquid, R_f = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.45 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 3.68 (s, 2H), 2.44 (q, *J* = 11.0 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 137.7, 131.6, 130.6, 120.7, 35.3, 25.3, 14.4 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_9H_{11}BrKS$ $[M+K]^+$ 268.9396, found 268.9398.

(4-Bromobenzyl)(propyl)sulfane 14b



Yield 156 mg, 73%, **Appearance** colorless liquid, R_f = 0.6 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.43 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 1.62-1.53 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 137.9, 131.6, 130.6, 120.8, 35.7, 33.5, 22.6, 13.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{10}H_{13}BrKS$ $[M+K]^+$ 282.9553, found 282.9552.

(4-Bromobenzyl)(butyl)sulfane 14c

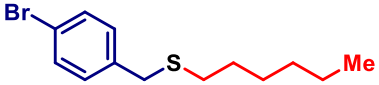


Yield 158 mg, 70%, **Appearance** colorless liquid, R_f = 0.6 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.43 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 3.64 (s, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 1.56-1.50 (m, 2H), 1.41-1.33 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 137.8, 131.6, 130.6, 120.7, 35.7, 31.3, 31.2, 22.1, 13.8 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{11}H_{15}BrKS$ $[M+K]^+$ 296.9709, found 296.9709.

(4-Bromobenzyl)(pentyl)sulfane 14d

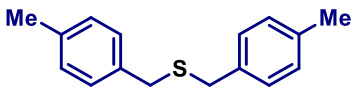
Yield 160 mg, 67%, **Appearance** colorless liquid, R_f = 0.6 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.45 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.67 (s, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.63-1.54 (m, 2H), 1.38-1.28 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm, **13C NMR (125 MHz, CDCl$_3$): δ** 137.9, 131.6, 130.6, 120.8, 35.8, 31.5, 31.1, 28.9, 22.4, 14.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{12}H_{17}BrKS$ $[M+K]^+$ 310.9866, found 310.9865.

(4-Bromobenzyl)(pentyl)sulfane 14e



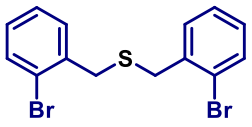
Yield 164 mg, 66%, **Appearance** colorless liquid, R_f = 0.6 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.45 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 3.67 (s, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.59-1.53 (m, 2H), 1.39-1.25 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 3H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 137.9, 131.7, 130.7, 120.8, 35.8, 31.5, 31.5, 29.3, 28.7, 22.7, 14.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{13}H_{19}BrKS$ $[M+K]^+$ 325.0022, found 325.0022.

Bis(4-methylbenzyl)sulfane 15a



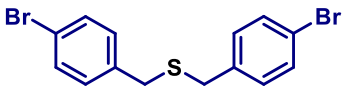
Yield 162 mg, 77%, **Appearance** colorless solid, **MP**. 72-74 °C, R_f = 0.6 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.35 (d, *J* = 8.0 Hz, 4H), 7.28 (d, *J* = 7.5 Hz, 4H), 3.72 (s, 4H), 2.49 (s, 6H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 136.5, 135.2, 129.2, 128.9, 35.3, 21.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{16}H_{19}S$ $[M+H]^+$ 243.1201, found 243.1201.

Bis(2-bromobenzyl)sulfane 15b



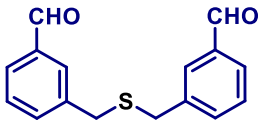
Yield 266 mg, 82%, **Appearance** white solid, **MP**. 66-68 °C, R_f = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.56 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.13-7.09 (m, 2H),3.83 (s, 4H), ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 137.4, 133.2, 130.9, 128.8, 127.6, 124.8, 36.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{14}H_{12}Br_2KS$ $[M+K]^+$ 408.8658, found 408.8658.

Bis(2-bromobenzyl)sulfane 15c



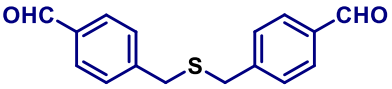
Yield 282 mg, 87%, **Appearance** colorless solid, **MP**. 78-80 °C, R_f = 0.5 (1 % EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.45 (d, *J* = 8.4 Hz, 4H), 7.09 (d, *J* = 8.8 Hz, 4H), 3.56 (s, 4H), ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 136.5, 131.8, 131.2, 121.7, 42.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{14}H_{12}Br_2KS$ $[M+K]^+$ 408.8658, found 408.8658.

3,3'-(Thiobis(methylene))dibenzaldehyde 15d



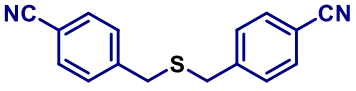
Yield 188 mg, 80 % , **Appearance** white solid, **Mp** 74-76 °C, R_f = 0.4 (15% EtOAc-petroleum ether), **^{1}HNMR (400 MHz, CDCl$_3$): δ** 9.98 (s, 2H),7.76-7.75 (m, 4H), 7.55-7.46 (m, 4H), 3.67 (s, 4H) ppm, **^{13}CNMR (100 MHz, CDCl$_3$): δ** 192.2, 139.2, 136.8, 135.1, 129.9, 129.5, 128.9, 35.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd $C_{16}H_{14}NaO_2S$ $[M+Na]^+$ 293.0607, found 293.0607.

4,4'-(Thiobis(methylene))dibenzaldehyde 15e



Yield 199 mg, 85 % , **Appearance** White solid, **Mp** 108-110 °C , R_f = 0.4 (15% EtOAc-petroleum ether), **^{1}HNMR (500 MHz, CDCl$_3$): δ** 9.99 (s, 2H), 7.83 (d, *J* = 8 Hz, 4H), 7.42 (d, *J* = 8 Hz, 4H), 3.65 (s, 4H) ppm, **^{13}CNMR (125 MHz, CDCl$_3$): δ** 191.9, 145.1, 135.6, 130.2, 129.8, 35.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{16}H_{14}NaO_2S$ $[M+Na]^+$ 293.0612, found 293.0607.

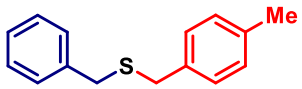
4,4'-(Thiobis(methylene))dibenzonitrile 15f



Yield 182 mg, 79%, **Appearance** colorless solid, R_f = 0.5 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.61 (d, *J* = 8.4 Hz, 4H), 7.37 (d, *J* = 8.4 Hz, 4H), 3.61 (s, 4H), ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ**

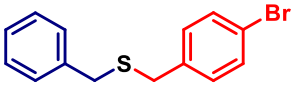
143.3, 132.5, 129.8, 118.7, 111.3, 35.6 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{20}H_{16}NaN_2S_2$ $[M+Na]^+$ 371.0652, found 371.0652.

Benzyl(4-methylbenzyl)sulfane 16a



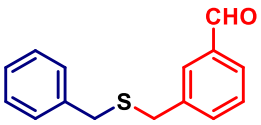
Yield 146 mg, 74%, **Appearance** colorless liquid, R_f = 0.8 (1% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 739-7.35 (m, 4H), 7.32-7.28 (m, 1H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 3.66 (s, 2H), 3.64 (s, 2H), 2.41(s, 3H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 138.4, 136.7,135.1, 129.3, 129.1, 129.0, 128.6, 127.1, 35.7, 35.4, 21.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{15}H_{17}S$ $[M+H]^+$ 229.1040, found 229.1040.

Benzyl(4-methylbenzyl)sulfane 16b



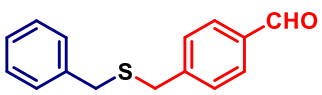
Yield 202 mg, 79%, **Appearance** colorless liquid, R_f = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.46 (d, *J* = 8.4 Hz, 2H), 7.35-7.28 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 2H), 3.56 (s, 2H) ppm, **^{13}CNMR (100 MHz, $CDCl_3$): δ** 137.9, 137.3, 131.7, 130.8, 129.1, 128.6, 127.2, 120.9, 35.7, 35.0 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{14}H_{13}BrKS$ $[M+K]^+$ 330.9553, found 330.9553.

3-((Benzylthio)methyl)benzaldehyde 16c



Yield 162 mg, 77%, **Appearance** colorless liquid, R_f = 0.5 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.99 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.34-7.23 (m, 5H), 3.65 (s, 2H), 2.02 (s, 2H), ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 192.1, 139.5, 137.7, 136.6, 135.0, 130.1, 129.2, 128.9, 128.6, 128.5, 127.2, 35.8, 35.1 sppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{15}H_{15}OS$ $[M+H]^+$ 243.0835, found 243.0835.

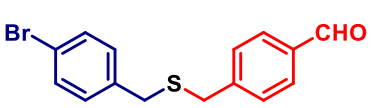
4-((Benzylthio)methyl)benzaldehyde 16d



Yield 168 mg, 80%, **Appearance** colorless liquid, R_f = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.99 (s, 1H), 7.82 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.6, 2H), 7.34-7.27 (m 5H), 3.64 (s, 2H), 3.61 (s, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 191.8, 145.6, 137.7, 135.3. 129.9, 129.7, 129.0, 128.6, 127.2,

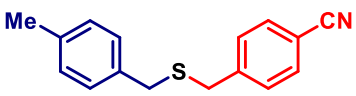
35.8, 35.5 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{15}H_{15}OS$ $[M+H]^+$ 243.0835, found 243.0835.

4-(((4-Bromobenzyl)thio)methyl)benzaldehyde 17



Yield 248 mg, 89%, **Appearance** brown solid, **MP**. 58-60 °C, ***R*$_f$** = 0.5 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.95 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0, 4H), 7.10 (d, *J* = 8.4, 2H), 3.59 (s, 2H), 3.51 (s, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 191.6, 145.1, 136.7, 135.3, 131.6, 130.6, 129.9, 129.5, 120.9, 35.4, 35.0 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{15}H_{13}BrOS$ $[M+H]^+$ 322.9925, found 322.9925.

4-(((4-Bromobenzyl)thio)methyl)benzaldehyde 18

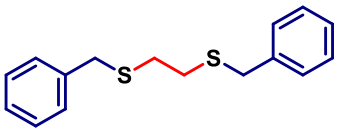


Yield 176 mg, 80%, **Appearance** white solid, **MP**. 64-66 °C, ***R*$_f$** = 0.4 (10 % EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.62 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.0, 2H), 7.18-7.14 (m, 4H), 3.63 (s, 2H), 3.59 (s, 2H), 2.37 (s, 3H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 144.1, 136.9, 134.3, 132.3, 129.7, 129.3, 128.9, 118.9, 110.8, 35.5, 35.2, 21.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{16}H_{15}NNaS$ $[M+Na]^+$ 276.0817, found 276.0816.

General procedure for the synthesis of dithio/disulfinyl compound

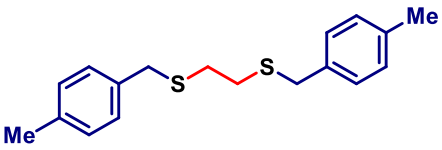
To the solution of bromomethyl benzaldehyde (1 equiv.) and potassium thioacetate (1 equiv.) in methanol (10 mL) in a two-neck round-bottom flask, stirred at room temperature for 2 h. After consumption of starting material, potassium carbonate, (3 equiv.) was added and the resulting reaction mixture was allowed to stir for 10 min. Further, dibromo compound (0.5 equiv.) was transferred to the reaction mixture and stirred at room temperature for 3 h. After completion of the reaction (TLC monitoring), solvent was evaporated under reduced pressure, then the reaction mixture was diluted with water and extracted with ethyl acetate (3×10 mL). The organic layer was separated, washed with brine solution and dried over anhydrous Na_2SO_4 then the solution was concentrated under reduced pressure and purified by silica gel column chromatography by using petroleum ether and ethyl acetate to afford the dithio/disulfinyl compounds. (Reactions were carried out in 100 mg scale)

4-(((4-Bromobenzyl)thio)methyl)benzaldehyde 19a



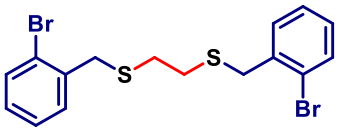
Yield 146 mg, 61%, **Appearance** colorless sticky liquid, R_f = 0.3 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.34-7.24 (m, 10H), 3.69 (s, 4H), 3.58 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 138.3, 128.9, 128.7, 127.2, 36.4, 31.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{16}H_{18}KS_2$ $[M+K]^+$ 313.0482, found 313.0481.

1,2-Bis((4-methylbenzyl)thio)ethane 19b



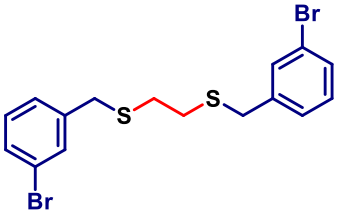
Yield 156 mg, 59%, **Appearance** colorless solid, **MP**. 96-98 °C, R_f = 0.3 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.17-7.10 (m, 8H), 3.66 (s, 4H), 2.56 (s, 4H), 2.34 (s, 6H) ppm, **13C NMR (100 MHz, $CDCl_3$) δ** 136.9, 135.2, 129.4, 128.9, 36.1, 31.2, 21.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{22}KS_2$ $[M+K]^+$ 341.0795, found 341.0794.

1,2-Bis((2-Bromobenzyl)thio)ethane 19c



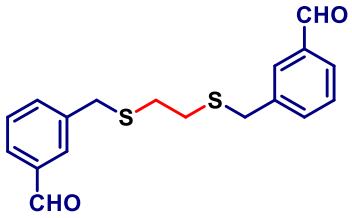
Yield 274 mg, 73%, **Appearance** colorless liquid, R_f = 0.3 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.58 (s, 2H), 7.37-7.28 (m, 4H), 7.13 (s, 2H), 3.87 (s, 4H), 2.71 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 137.7, 133.2, 130.8, 128.8, 127.7, 124.6, 36.6, 31.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{16}H_{16}Br_2KS_2$ $[M+K]^+$ 468.8692, found 468.8692.

1,2-Bis((3-bromobenzyl)thio)ethane 19d



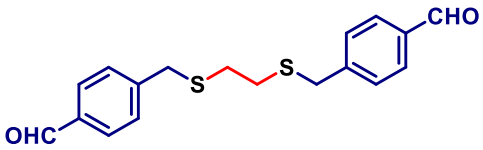
Yield 292 mg, 78%, **Appearance** colorless solid, **MP**. 72-74 °C, R_f = 0.3 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.45 (s, 2H), 7.39-7.37 (m, 2H), 7.21-7.17 (m, 4H), 3.64 (s, 4H), 2.56 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 140.6, 131.8, 130.3, 130.2, 127.5, 122.7, 35.9, 31.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{16}H_{16}Br_2KS_2$ $[M+K]^+$ 468.8692, found 468.8693.

3,3'-((Ethane-1,2-diylbis(sulfanediyl))bis(methylene))dibenzaldehyde 19e



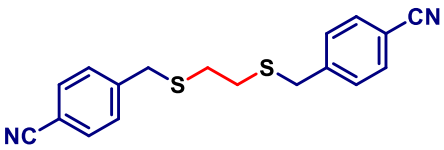
Yield 204 mg, 71%, **Appearance** colorless liquid, R_f = 0.3 (10% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.99 (s, 2H) 7.79-7.76 (m, 4H), 7.57-7.47 (m, 4H), 3.76 (s, 4H), 2.58 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 192.1, 139.5, 136.7, 134.9, 129.7, 129.4, 128.8, 35.9, 31.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** for $C_{18}H_{18}NaO_2S_2$ $[M+Na]^+$ 353.0640, found 353.0640.

4,4'-((Ethane-1,2-diylbis(sulfanediyl))bis(methylene))dibenzaldehyde 19f



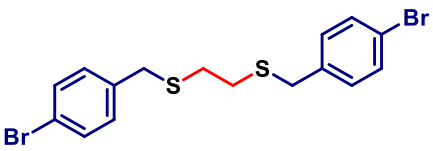
Yield 198 mg, 69%, **Appearance** colorless solid, **MP**. 106-108 °C, R_f = 0.4 (20% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 9.99 (s, 2H), 7.81 (d, *J* = 8.0 Hz, 4H), 7.42 (d, *J* = 8.0 Hz, 4H), 3.74 (s, 4H), 2.56 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 191.9, 145.4, 135.5, 130.2, 129.6, 36.4, 31.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{18}NaO_2S_2$ $[M+Na]^+$ 353.0640, found 353.0640.

4,4'-((Ethane-1,2-diylbis(sulfanediyl))bis(methylene))dibenzonitrile 19g



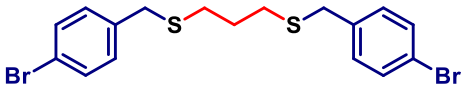
Yield 184 mg, 65%, **Appearance** colorless solid, **MP**. 104-106 °C, R_f = 0.4 (20% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.59 (d, *J* = 8.0 Hz, 4H), 7.38 (d, *J* = 8.4 Hz, 4H), 3.72 (s, 4H), 2.55 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 143.8, 132.5, 129.6, 118.7, 111.1, 36.3, 31.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{16}N_2NaS_2$ $[M+Na]^+$ 347.0647, found 347.0647.

1,2-Bis((4-bromobenzyl)thio)ethane 20a



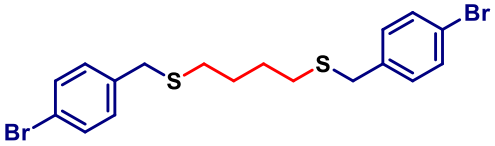
Yield 324 mg, 86%, **Appearance** colorless solid, **MP**. 94-96 °C, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.42 (d, *J* = 8.0 Hz, 4H), 7.14 (d, *J* = 8.5 Hz, 4H), 3.63 (s, 4H), 2.54 (s, 4H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 137.3, 131.8, 130.6, 121.1, 35.9, 31.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{16}H_{16}Br_2KS_2$ $[M+K]^+$ 468.8692, found 468.8691.

1,3-Bis((4-bromobenzyl)thio)propane 20b



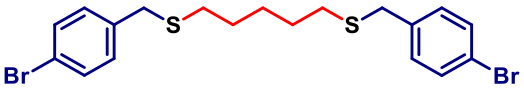
Yield 322 mg, 83%, **Appearance** colorless liquid, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.43 (d, *J* = 8.0 Hz, 4H), 7.17 (d, *J* = 8.5 Hz, 4H), 3.61 (s, 4H), 2.45 (t, *J* = 7.6 Hz, 4H), 1.79-1.72 (m, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 137.6, 131.7, 130.6, 120.9, 35.8, 30.3, 28.7 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{17}H_{18}Br_2KS_2$ $[M+K]^+$ 482.8848, found 482.8848.

1,4-Bis((4-bromobenzyl)thio)butane 20c



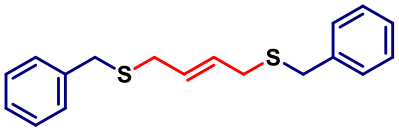
Yield 308 mg, 77%, **Appearance** colorless solid, **MP**. 74-76 °C, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.42 (d, *J* = 8.0 Hz, 4H), 7.17 (d, *J* = 8.5 Hz, 4H), 3.62 (s, 4H), 2.35 (t, *J* = 6.5 Hz, 4H), 1.61-1.58 (m, 4H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 137.7, 131.7, 130.7, 120.9, 35.8, 30.9, 28.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{20}Br_2KS_2$ $[M+K]^+$ 496.9004, found 496.9004.

1,5-Bis((4-Bromobenzyl)thio)pentane 20d



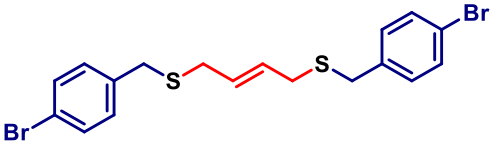
Yield 314 mg, 76%, **Appearance** colorless sticky liquid, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.44 (d, *J* = 8.0 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 3.65 (s, 4H), 2.39 (t, *J* = 7.3 Hz, 4H), 1.57-1.51 (m, 4H), 1.49-1.38 (m, 2H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 137.7, 131.6, 130.6, 120.7, 35.7, 31.2, 28.7, 27.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{19}H_{22}Br_2KS_2$ $[M+K]^+$ 510.9161, found 510.9161.

(E)-1,4-Bis(benzylthio)but-2-ene 21a



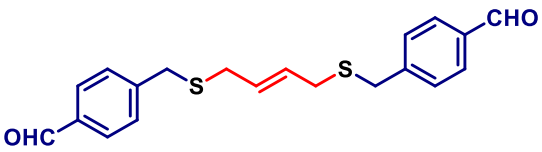
Yield 200 mg, 71%, **Appearance** colorless liquid, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.37-7.36 (m, 8H), 7.30-7.28 (m, 2H), 5.56-5.54 (m, 2H), 3.73 (s, 4H), 3.08-3.07 (m, 4H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 138.3, 129.2, 129.1, 128.6, 127.1, 35.3, 32.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{20}KS_2$ $[M+K]^+$ 339.0638, found 339.0638.

(E)-1,4-Bis((4-bromobenzyl)thio)but-2-ene 21b



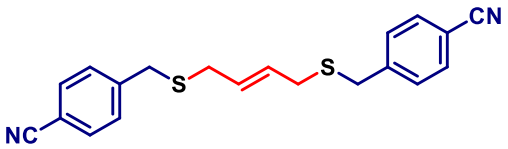
Yield 326 mg, 82%, **Appearance** white solid, **MP**. 84-86 °C, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.46 (d, *J* = 8.0 Hz, 4H), 7.21 (d, *J* = 7.5 Hz, 4H), 5.49 (s, 2H), 3.64 (s, 4H), 3.03 (d, *J* = 4.5 Hz, 4H), ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 137.4, 131.8, 130.8, 129.2, 121.0, 34.8, 32.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{18}Br_2KS_2$ $[M+K]^+$ 494.8848, found 494.8848.

(E)-4,4'-((But-2-ene-1,4-diylbis(sulfanediyl))bis(methylene))dibenzaldehyde 21c



Yield 326 mg, 72%, **Appearance** colorless solid, **MP**. 102-104 °C, R_f = 0.3 (15% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 9.99 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.47 (d, *J* = 8.0 Hz, 4H), 5.49 (t, *J* = 4.0 Hz, 2H), 3.72 (s, 4H), 3.02 (d, *J* = 5.5 Hz, 4H), ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 191.9, 145.6, 135.5, 130.2, 129.8, 129.2, 35.3, 33.1 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{20}H_{20}NaO_2S_2$ $[M+Na]^+$ 379.0797, found 379.0796.

(E)-4,4'-((But-2-ene-1,4-diylbis(sulfanediyl))bis(methylene))dibenzonitrile 21d

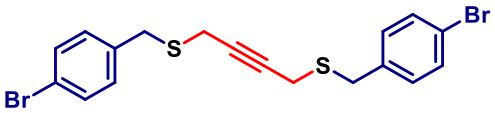


Yield 204 mg, 67%, **Appearance** white solid, **MP**. 98-100 °C, R_f = 0.3 (15% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.61 (d, *J* = 8.0 Hz, 4H), 7.43 (d, *J* = 8.4 Hz, 4H), 5.49-5.48 (m, 2H), 3.70 (s, 4H), 3.03-3.02 (m, 4H), ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 143.9, 132.4, 129.8, 129.0, 118.8, 110.9, 35.1, 32.9 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{20}H_{18}NaN_2S_2$ $[M+Na]^+$ 373.0806, found 373.0806.

1,4-Bis(benzylthio)but-2-yne 22a

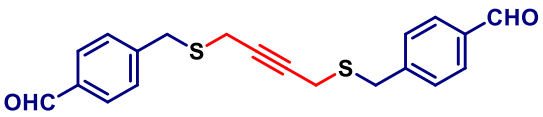
Yield 202 mg, 78%, **Appearance** dark brown liquid, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.39-7.34 (m, 8H), 7.30-7.27 (m, 2H), 3.91 (s, 4H), 3.19 (s, 4H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 137.7, 129.1, 128.7, 127.3, 79.2, 35.6, 19.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{19}S_2$ $[M+H]^+$ 299.0928, found 299.0928.

1,4-Bis((4-bromobenzyl)thio)but-2-yne 22b



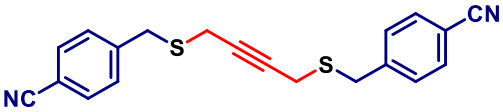
Yield 322 mg, 81%, **Appearance** colorless solid, **MP**. 104-106 °C, R_f = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.44 (d, *J* = 8.4 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 3.81 (s, 4H), 3.13 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 136.8, 131.8, 130.8, 121.2, 79.2, 35.1, 19.2 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{18}H_{17}Br_2S_2$ $[M+H]^+$ 456.9106, found 456.9107.

4,4'-((But-2-yne-1,4-diylbis(sulfanediyl))bis(methylene))dibenzaldehyde 22c



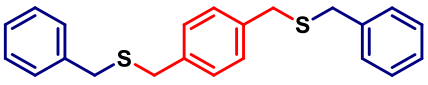
Yield 230 mg, 75%, **Appearance** brown solid, **MP**. 136-138 °C, R_f = 0.2 (15% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 10.00 (s, 2H), 7.85 (d, *J* = 8.0 Hz, 4H), 7.51 (d, *J* = 8.0 Hz, 4H), 3.92 (s, 4H), 3.16 (s, 4H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 191.9, 144.9, 135.6, 130.2, 129.8, 79.2, 35.5, 19.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{20}H_{18}NaO_2S_2$ $[M+Na]^+$ 377.0642, found 377.0643,

4,4'-((But-2-yne-1,4-diylbis(sulfanediyl))bis(methylene))dibenzonitrile 22d



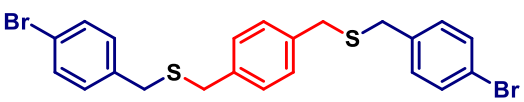
Yield 196 mg, 65%, **Appearance** white fluffy solid, **MP**. 130-132 °C, R_f = 0.2 (15% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.60 (d, *J* = 8.0 Hz, 4H), 7.44 (d, *J* = 8.5 Hz, 4H), 3.87 (s, 4H), 3.13 (s, 4H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 143.3, 132.5, 129.8, 118.8, 111.2, 79.1, 35.4, 19.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{20}H_{16}NaN_2S_2$ $[M+Na]^+$ 371.0652, found 371.0652,

1,4-Bis((benzylthio)methyl)benzene 23a



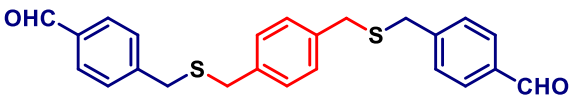
Yield 230 mg, 76%, **Appearance** colorless solid, **MP**. 60-62 °C, R_f = 0.7 (5% EtOAc-petroleum ether), **^{1}HNMR (400 MHz, $CDCl_3$): δ** 7.36-7.26 (m, 14H), 3.64 (s, 4H), 3.62 (s, 4H), ppm, **^{13}CNMR (100 MHz, $CDCl_3$): δ** 138.3, 136.9, 129.2, 129.1,128.6, 127.1, 35.8, 35.4 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{22}H_{23}S_2$ $[M+H]^+$ 351.1237, found 351.1237.

1,4-Bis(((4-bromobenzyl)thio)methyl)benzene 23b



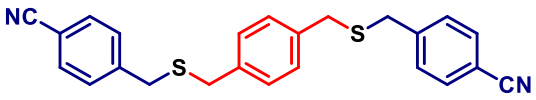
Yield 350 mg, 79%, **Appearance** brown solid, **MP**. 108-110 °C, $\mathbf{R_f}$ = 0.4 (5% EtOAc-petroleum ether), **^{1}HNMR (500 MHz, CDCl$_3$): δ** 7.43 (d, *J* = 8.5 Hz, 4H), 7.21 (s, 2H), 7.15 (d, *J* = 8.5 Hz, 4H), 3.57 (s, 4H), 3.55 (s, 4H), ppm, **^{13}CNMR (125 MHz, CDCl$_3$): δ** 137.3, 136.9, 131.7, 130.8, 129.3, 120.9, 35.5, 35.2, ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{22}H_{21}Br_2S_2$ $[M+H]^+$ 508.9424, found 508.9424.

4,4'-(((1,4-Phenylenebis(methylene))bis(sulfanediyl))bis(methylene))dibenzaldehyde 23c



Yield 258 mg, 73%, **Appearance** Colorless solid, **MP**. 134-136 °C, $\mathbf{R_f}$ = 0.4 (15% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 9.99 (s, 2H), 7.83 (d, *J* = 8.4 Hz, 4H), 7.43 (d, *J* = 8.0 Hz, 4H), 7.21 (s, 4H), 3.65 (s, 4H), 3.59 (s, 4H), ppm, **^{13}CNMR (100 MHz, CDCl$_3$): δ** 191.9, 145.6, 136.8, 135.5, 130.2, 129.8, 129.3, 35.8, 35.6, ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{24}H_{22}NaO_2S_2$ $[M+Na]^+$ 429.0953, found 429.0953.

4,4'-(((1,4-Phenylenebis(methylene))bis(sulfanediyl))bis(methylene))dibenzonitrile 23d



Yield 230 mg, 66%, **Appearance** colorless solid, **MP**. 156-158 °C, $\mathbf{R_f}$ = 0.4 (15% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$): δ** 7.59 (d, *J* = 8.0 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.19 (s, 4H), 3.62 (s, 4H), 3.58 (s, 4H), ppm, **^{13}C NMR (125 MHz, CDCl$_3$): δ** 144.0, 136.7, 132.4, 129.8, 129.3, 118.9, 111.0, 35.7(2-CH2 peaks merge) ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{24}H_{20}NaN_2S_2$ $[M+Na]^+$ 423.0963, found 423.0963.

((2,5-Dimethoxy-1,4-phenylene)bis(methylene))bis(benzylsulfane) 24a

Yield 242 mg, 68%, **Appearance** colorless solid, **MP**. 106-108 °C, $\boldsymbol{R_f}$ = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.37-7.32 (m, 8H), 7.28-7.25 (m, 2H), 6.78 (s, 2H), 3.79 (s, 6H), 3.72 (s, 4H), 3.68 (s, 4H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 151.3, 138.6, 129.1, 128.5, 127.0, 126.2, 113.5, 56.3, 36.4, 30.2 ppm, **HRMS (ESI)** m/z calcd for $C_{24}H_{26}NaO_2S_2$ $[M+Na]^+$ 433.1265, found 433.1265.

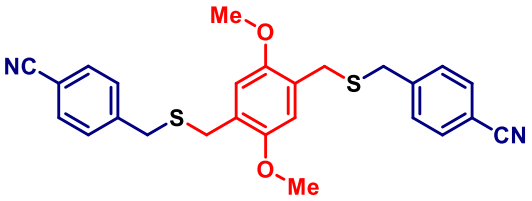
((2,5-Dimethoxy-1,4-phenylene)bis(methylene))bis((4-bromobenzyl)sulfane) 24b

Yield 346 mg, 70%, **Appearance** colorless solid, **MP**. 122-124 °C, $\mathbf{R_f}$ = 0.2 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.42 (d, *J* = 8.4 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 4H), 6.73 (s, 2H), 3.76 (s, 6H), 3.63 (s, 8H), ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 151.3, 137.7, 131.6, 130.8, 126.1, 120.7, 113.5, 56.3, 35.8, 30.2, ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{24}H_{24}NaBr_2O_2S_2$ $[M+Na]^+$ 590.9452, found 590.9453.

4,4'-((((2,5-Dimethoxy-1,4-phenylene)bis(methylene))bis(sulfanediyl))bis(methylene))dibenzaldehyde 24c

Yield 260 mg, 64%, **Appearance** yellow solid, **MP**. 136-138 °C, $\boldsymbol{R_f}$ = 0.4 (15% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 9.99 (s, 2H), 7.83 (d, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 8.0 Hz, 4H), 6.74 (s, 2H), 3.75 (s, 6H), 3.74 (s, 4H), 3.65 (s, 4H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 192.0, 151.3, 146.0, 135.4, 130.1, 129.7, 126.1, 113.5, 56.3, 36.4, 30.3 ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{26}H_{26}NaO_4S_2$ $[M+Na]^+$ 489.1165, found 489.1164.

4,4'-((((2,5-Dimethoxy-1,4-phenylene)bis(methylene))bis(sulfanediyl))bis(methylene))dibenzonitrile 24d

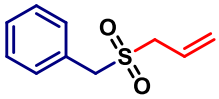


Yield 244 mg, 85%, **Appearance** colorless solid, **MP**. 150-152 °C, $\boldsymbol{R_f}$ = 0.4 (15% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$): δ** 7.59 (d, *J* = 8.0 Hz, 4H), 7.41 (d, *J* = 8.0 Hz, 4H), 6.72 (s, 2H), 3.75 (s, 6H), 3.71 (s, 4H), 3.64 (s, 4H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$): δ** 151.4, 144.5, 132.4, 129.8, 126.0, 119.0, 113.5, 110.9, 56.3, 36.3, 30.4, ppm, **HRMS (ESI,Q-ToF) *m/z*:** calcd for $C_{26}H_{25}N_2O_2S_2$ $[M+H]^+$ 461.1352, found 461.1350.

Procedure for the synthesis of sulfone 25

To the solution of sulfide **2** (1 equiv., 100 mg) in methanol (10 mL) in a two-neck round-bottom flask, we added Oxone® (2.2 equiv., 588 mg) in water dropwise in the reaction mixture at room temperature and allowed the reaction mixture to stir for 3 h. After completion of the reaction (TLC monitoring), solvent was evaporated under reduced pressure, then the reaction mixture was diluted with water and extracted with ethyl acetate (3×10 mL). The organic layer was separated, washed with brine solution and dried over anhydrous Na_2SO_4 then the solution was concentrated under reduced pressure and purified by silica gel column chromatography by using petroleum ether and ethyl acetate to afford the pure compound **25**.

((Allylsulfonyl)methyl)benzene 25

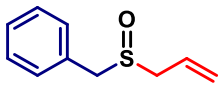


Yield 106 mg, 89% from 50 mg of compound **2**, **Appearance** yellow liquid, $\boldsymbol{R_f}$ = 0.5 (25% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (s, 5H), 5.95-5.85 (m, 1H), 5.52-5.38 (m, 2H), 4.21 (s, 2H), 3.58 (d, *J* = 7.6 Hz, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 130.8, 129.1, 129.1, 127.7, 124.9, 124.9, 57.9, 55.9 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{10}H_{12}NaO_2S$ $[M+Na]^+$ 219.0450 found 219.0451.

General procedure for the synthesis of sulfoxides

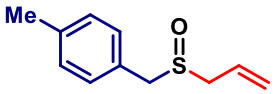
To the solution of benzylbromides (1 equiv.) and potassiumthioacetate (1 equiv.) in methanol (10 mL) in a two-neck round-bottom flask, stirred at room temperature for 2 h. After consumption of starting material, potassium carbonate, (3 equiv.) was added and the resulting reaction mixture was allowed to stir for 10 min. Further, bromo compound (1 equiv.) was transferred to the reaction mixture and stirred at room temperature for 3 h. After completion of the reaction (TLC monitoring), for sulfoxide preparation, we added Oxone® (2.2 equiv.) in water dropwise in the same reaction mixture at room temperature and further allowed the reaction mixture to stir for next 3 h. After completion of the reaction (TLC monitoring), solvent was evaporated under reduced pressure, then the reaction mixture was diluted with water and extracted with ethyl acetate (3×10 mL). The organic layer was separated, washed with brine solution and dried over anhydrous Na_2SO_4 then the solution was concentrated under reduced pressure and purified by silica gel column chromatography by using petroleum ether and ethyl acetate to afford the sulfoxide compounds. (Reactions were carried out in 100 mg scale)

((Allylsulfinyl)methyl)benzene 26a



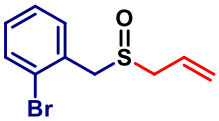
Yield 120 mg, 76% from 50 mg of compound **1**, **Appearance** colorless liquid, R_f = 0.3 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.38-7.29 (m, 5H), 5.97-5.88 (m, 1H), 5.49-5.38 (m, 2H), 4.02-3.95 (m, 2H), 3.45-3.41 (m, 1H), 3.29-3.25 (m, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 130.1, 129.9, 129.0, 128.4, 125.8, 123.8, 56.9, 54.2 ppm, **HRMS (ESI,Q-ToF)** ***m/z*:** calcd for $C_{10}H_{13}OS$ $[M+H]^+$ 181.0682 found 181.0681.

1-((Allylsulfinyl)methyl)-4-methylbenzene 26b



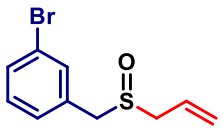
Yield 121 mg, 73%, **Appearance** colorless liquid, R_f = 0.3 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17 (s, 4H), 5.96-5.85 (m, 1H), 5.47-5.36 (m, 2H), 3.94 (d, *J* = 1.6 Hz, 2H), 3.43-3.38 (m, 1H), 3.27-3.22 (m, 1H), 2.34 (s, 3H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.4, 130.1, 129.8, 126.8, 125.9, 123.8, 56.6, 54.1, 21.3 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{11}H_{15}OS$ $[M+H]^+$ 195.0838 found 195.0838.

1-((Allylsulfinyl)methyl)-2-bromobenzene 26c



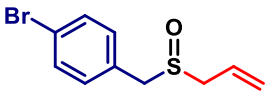
Yield 170 mg, 75%, **Appearance** colorless liquid, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.59 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.37 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.29 (td, *J* = 7.5, 1.0 Hz, 1H), 7.18 (td, *J* = 8.0, 1.5 Hz, 1H), 5.99-5.91 (m, 1H), 5.47-5.39 (m, 2H), 4.26 (d, *J* = 13.0, 1H), 4.01 (d, *J* = 12.5, 1H), 3.56-3.52 (m, 1H), 3.41-3.37 (m, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 133.3, 132.6, 130.6, 130.2, 128.0, 125.9, 125.1, 123.9, 57.9, 55.5 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{10}H_{12}BrOS$ $[M+H]^+$ 258.9787 found 258.9786.

1-((Allylsulfinyl)methyl)-3-bromobenzene 26d



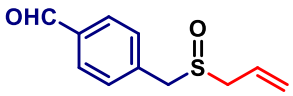
Yield 176 mg, 78%, **Appearance** colorless liquid, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.43-7.40 (m, 2H), 7.19-7.18 (m, 2H), 5.90-5.82 (m, 1H), 5.44-5.33 (m, 2H), 3.90 (d, *J* = 13.0, 1H), 3.82 (d, *J* = 13.0, 1H), 3.43-3.39 (m, 1H), 3.29-3.25 (m, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 132.9, 132.4, 131.4, 130.4, 128.8, 125.5, 123.9, 122.8, 55.9, 54.6 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{10}H_{12}BrOS$ $[M+H]^+$ 258.9787 found 258.9788.

1-((Allylsulfinyl)methyl)-4-bromobenzene 26e



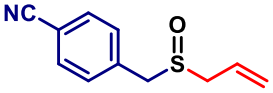
Yield 182 mg, 81%, **Appearance** white solid, **MP**. 98-100 °C, R_f = 0.2 (20% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4, Hz, 2H), 5.89-5.78 (m, 1H), 5.42-5.30 (m, 2H), 3.88 (d, *J* = 13.2, 1H), 3.79 (d, *J* = 13.2, 1H), 3.39-3.34 (m, 1H), 3.26-3.21 (m, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 131.9, 131.7, 129.0, 125.6, 123.8, 122.5, 55.8, 54.5 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{10}H_{12}BrOS$ $[M+H]^+$ 258.9787 found 258.9786.

4-((Allylsulfinyl)methyl)benzaldehyde 26f



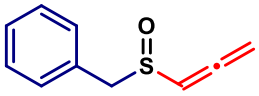
Yield 132 mg, 73%, **Appearance** white solid, **MP**. 72-74 °C, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 10.02 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 5.98-5.87 (m, 1H), 5.51-5.39 (m, 2H), 4.08 (d, *J* = 12.8, 1H), 3.98 (d, *J* = 13.2, 1H), 3.49-3.45 (m, 1H), 3.37-3.32 (m, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.7, 137.0, 136.3, 130.9, 130.2, 125.6, 124.2, 56.6, 55.0 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{11}H_{13}O_2S$ $[M+H]^+$ 209.0631 found 209.0630.

4-((Allylsulfinyl)methyl)benzonitrile 26g



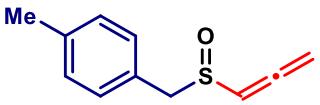
Yield 120 mg, 68%, **Appearance** white solid, **MP**. 82-84 °C, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 5.93-5.82 (m, 1H), 5.47-5.36 (m, 2H), 4.00 (d, *J* = 12.0, 1H), 3.89 (d, *J* = 12.8, 1H), 3.47-3.42 (m, 1H), 3.35-3.30 (m, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.7, 132.5, 130.9, 125.3, 124.3, 118.4, 112.2, 56.1, 55.1 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{11}H_{12}NOS$ $[M+H]^+$ 206.0634 found 206.0634.

((Propa-1,2-dien-1-ylsulfinyl)methyl)benzene 27a



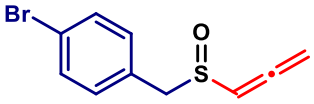
Yield 102 mg, 72%, **Appearance** yellow liquid, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40-7.34 (m, 3H), 7.31-7.29 (m, 2H), 5.90 (t, *J* = 6.2 Hz, 1H), 5.21-5.17 (m, 1H), 5.12-5.07 (m, 1H), 4.14 (d, *J* = 12.8, 1H), 4.06 (d, *J* = 12.4, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 207.1, 130.5, 129.5, 128.9, 128.5, 98.2, 82.0, 61.2 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{10}H_{10}NaOS$ $[M+Na]^+$ 201.0345 found 201.0344.

1-Methyl-4-((propa-1,2-dien-1-ylsulfinyl)methyl)benzene 27b



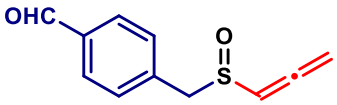
Yield 118 mg, 71%, **Appearance** brown liquid, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.17 (s, 4H), 5.89 (t, *J* = 6.5 Hz, 1H), 5.21-5.17 (m, 1H), 5.12-5.08 (m, 1H), 4.09 (d, *J* = 12.5, 1H), 4.01 (d, *J* = 12.5, 1H) 2.35 (s, 3H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 207.2, 138.5, 130.4, 129.9, 129.7, 126.3, 98.3, 82.1, 60.9, 21.4 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{11}H_{13}OS$ $[M+H]^+$ 193.0682 found 193.0681.

1-Bromo-4-((propa-1,2-dien-1-ylsulfinyl)methyl)benzene 27c



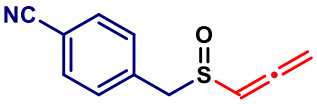
Yield 168 mg, 76%, **Appearance** yellow sticky liquid, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.87 (t, *J* = 6.2 Hz, 1H), 5.23-5.18 (m, 1H), 5.17-5.12 (m, 1H), 4.01 (s, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 207.3, 132.2, 132.1, 128.5, 122.9, 98.1, 82.4, 60.3 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{10}H_{10}BrOS$ $[M+H]^+$ 256.9630 found 256.9632.

4-((Propa-1,2-dien-1-ylsulfinyl)methyl)benzaldehyde 27d



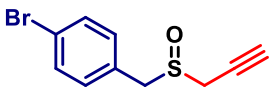
Yield 134 mg, 69%, **Appearance** yellow sticky solid, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.99 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.89 (t, *J* = 6.4 Hz, 1H), 5.21-5.16 (m, 1H), 5.15-5.09 (m, 1H), 4.15-4.08 (m, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 207.2, 191.8, 136.2, 136.2,131.2, 130.0, 98.1, 82.5, 60.6 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{11}H_{11}O_2S$ $[M+H]^+$ 207.0474 found 207.0474.

4-((Propa-1,2-dien-1-ylsulfinyl)methyl)benzonitrile 27e



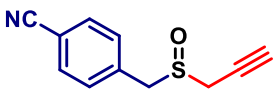
Yield 114 mg, 65%, **Appearance** yellow liquid, R_f = 0.2 (35% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.88 (t, *J* = 6.4 Hz, 1H), 5.23-5.19 (m, 1H), 5.18-5.14 (m, 1H), 4.12 (d, *J* = 12.8 Hz, 2H), 4.04(d, *J* = 12.8 Hz, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 207.2, 134.9, 132.4,131.3, 118.5, 112.4, 98.0, 82.7, 60.2 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{11}H_9NNaOS$ $[M+Na]^+$ 226.0297 found 226.0297.

1-bromo-4-((prop-2-yn-1-ylsulfinyl)methyl)benzene 28



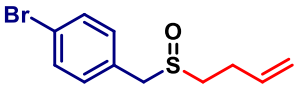
Yield 20 mg, 21%, **Appearance** brown solid, **MP**. 104-106 °C, R_f = 0.3 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.52 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 4.18 (d, *J* = 13.0 Hz, 1H), 4.03 (d, *J* = 13.5 Hz, 1H), 3.37 (d, *J* = 2.5 Hz, 2H), 2.55 (t, *J* = 2.5 Hz, 1H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 132.3, 132.1, 127.8, 123.2, 77.3, 72.6, 55.2, 40.0 ppm, **HRMS (ESI, Q-ToF) *m/z:*** calcd for $C_{10}H_{10}BrOS$ $[M+H]^+$ 256.9630 found 256.9631.

4-((Prop-2-yn-1-ylsulfinyl)methyl)benzonitrile 29



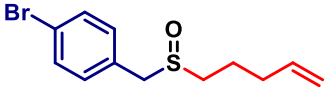
Yield 26 mg, 15%, **Appearance** yellow solid, **MP**. 146-148 °C, R_f = 0.3 (35% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.68 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 4.25 (d, *J* = 12.8 Hz, 1H), 4.11 (d, *J* = 12.8 Hz, 1H), 3.47-3.32 (m, 2H), 2.57 (t, *J* = 6.6 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 134.3, 132.7, 131.3, 118.5, 112.7, 77.6, 72.4, 55.4, 40.5 ppm, **HRMS (ESI, Q-ToF) *m/z:*** calcd for $C_{11}H_{10}NOS$ $[M+H]^+$ 204.0478 found 204.0477.

1-Bromo-4-((but-3-en-1-ylsulfinyl)methyl)benzene 30



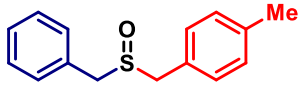
Yield 172 mg, 72%, **Appearance** colorless sticky solid, R_f = 0.4 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$): δ** 7.49 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.84-5.74 (m, 1H), 5.14-5.07 (m, 2H), 3.91 (s, 2H), 2.65-2.61 (m, 2H), 2.53-2.46 (m, 2H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$): δ** 134.9, 132.3, 131.8, 128.9, 122.8, 117.4, 57.6, 50.3, 26.8 ppm, **HRMS (ESI, Q-ToF) *m/z:*** calcd for $C_{11}H_{13}BrKOS$ $[M+K]^+$ 310.9502 found 310.9501.

1-Bromo-4-((pent-4-en-1-ylsulfinyl)methyl)benzene 31



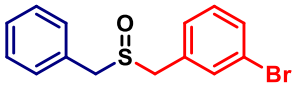
Yield 172 mg, 69%, **Appearance** yellow solid, **MP**. 164-166 °C, R_f = 0.3 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$): δ** 7.48 (d, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 5.76-5.68 (m, 1H), 5.02-4.99 (m, 2H), 3.89 (s, 2H), 2.56 (t, *J* = 7.8 Hz, 2H), 2.21-2.14 (m, 2H), 1.87-1.82 (m, 2H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$): δ** 136.8, 132.2, 131.8, 129.1, 122.7, 116.3, 57.5, 50.4, 32.7, 21.8 ppm, **HRMS (ESI, Q-ToF) *m/z:*** calcd for $C_{12}H_{15}BrNaOS$ $[M+Na]^+$ 308.9919 found 308.9919.

1-((benzylsulfinyl)methyl)-4-methylbenzene 32a



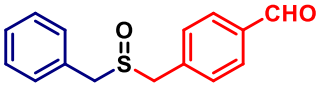
Yield 190 mg, 88 %, **Appearance** white solid, **MP**. 96-98 °C, R_f = 0.3 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41-7.35 (m, 3H), 7.32-7.29 (m, 2H),7.19 (s, 3H), 3.95-3.84 (m, 4H), 2.37 (s, 3H), ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 138.2, 130.3, 130.2, 130.0, 129.7, 128.9, 128.3, 126.9, 57.1, 56.9, 21.2 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{15}H_{17}OS$ $[M+H]^+$ 245.0995 found 245.0994.

1-((Benzylsulfinyl)methyl)-3-bromobenzene 32b



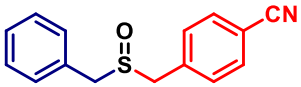
Yield 250 mg, 93%, **Appearance** white solid, **MP**. 90-92 °C, R_f = 0.3 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46-7.43 (m, 1H), 7.39-7.34 (m, 4H),7.28-7.20 (m, 4H), 3.92 (s, 2H), 3.85 (d, *J* = 13.2 Hz, 1H), 3.74 (d, *J* = 13.2 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 133.0, 132.6, 131.5, 130.4, 130.1, 129.8, 129.1, 128.9, 128.5, 122.8, 57.6, 56.4 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{14}H_{13}BrNaOS$ $[M+Na]^+$ 330.9763 found 330.9762.

4-((Benzylsulfinyl)methyl)benzaldehyde 32c



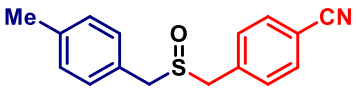
Yield 200 mg, 89%, **Appearance** white solid, **MP**. 134-136 °C, R_f = 0.2 (30% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 9.97 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.36-7.34 (m, 3H), 7.28-7.26 (m, 2H), 3.98-3.94 (m, 3H), 3.83 (d, *J* = 12.8 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 191.7, 137.2, 136.1, 130.9, 130.1, 129.7, 129.1, 128.6, 57.9, 56.8 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{15}H_{15}O_2S$ $[M+H]^+$ 259.0787 found 259.0787.

4-((Benzylsulfinyl)methyl)benzonitrile 32d



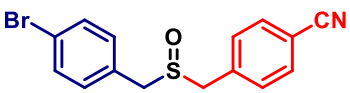
Yield 180 mg, 81%, **Appearance** white solid, **MP**. 126-128 °C, R_f = 0.2 (35% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.39-7.36 (m, 5H), 7.29-7.27 (m, 2H), 3.96-3.92 (m, 3H), 3.78 (d, *J* = 12.8 Hz, 1H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 135.9, 132.6, 131.0, 130.1, 129.5, 129.2, 128.7, 118.5, 112.3, 58.1, 56.5 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{15}H_{14}NOS$ $[M+H]^+$ 256.0791 found 256.0790.

4-(((4-Methylbenzyl)sulfinyl)methyl)benzonitrile 33a



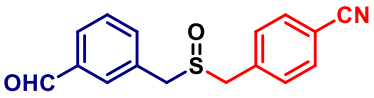
Yield 194 mg, 82%, **Appearance** white solid, **MP**. 108-110 °C, R_f = 0.1 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.20-7.16 (m, 4H), 3.98-3.89 (m, 3H), 3.77 (d, *J* = 13.0 Hz, 1H) 2.35 (s, 3H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 138.8, 136.1, 132.6, 131.1, 130.0, 129.9, 126.3, 118.5, 112.3, 57.9, 56.4, 21.3 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{16}H_{16}NOS$ $[M + H]^+$ 270.0947 found 270.0947.

4-(((4-Bromobenzyl)sulfinyl)methyl)benzonitrile 33b



Yield 246 mg, 85%, **Appearance** white solid, **MP**. 162-164 °C, R_f = 0.1 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.95-3.89 (m, 2H), 3.85-3.79 (m, 2H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 135.7, 132.6, 132.3, 131.8, 131.0, 128.6, 123.0, 118.4, 112.4, 57.2, 56.8 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{15}H_{13}BrNOS$ $[M+H]^+$ 333.9896 found 333.9895.

4-(((3-formylbenzyl)sulfinyl)methyl)benzonitrile 33c



Yield 216 mg, 87%, **Appearance** white solid, **MP**. 124-126 °C, R_f = 0.1 (30% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 9.97 (s, 1H), 7.85-7.83 (m, 1H), 7.78 (s, 1H), 7.64-7.62 (m, 2H), 7.55-7.53 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.06-3.99 (m, 2H), 3.93-3.84 (m, 2H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 191.8, 136.9, 136.1, 135.5, 132.6, 131.1, 130.9, 130.9, 130.1, 129.8, 118.4, 112.4, 57.0, 56.9 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{16}H_{13}NO_2S$ $[M+H]^+$ 284.0739 found 284.0738.

Identidication of sulfides, sulfoxides and sulfones.

The confirmation of sulfoxide as the product was confirmed by the comparison of NMR spectral and mass data of sulfur, sulfoxide and sulfone. The unique characteristic of sulfoxide is that the sulfur atom is a stereogenic centre when different groups are attached on both the sides and it assumes a tetrahedral sp^3 hybridization with a lone pair occupying one of the sp^3 orbitals.[2] Therefore, proton attached to the carbon adjacent to sulfoxide group are

diastereotopic protons and hence further splitting is observed which is absent in sulfides and sulfones (Figure 1). This property led us to the confirmation that sulfoxides indeed are obtained as the product.

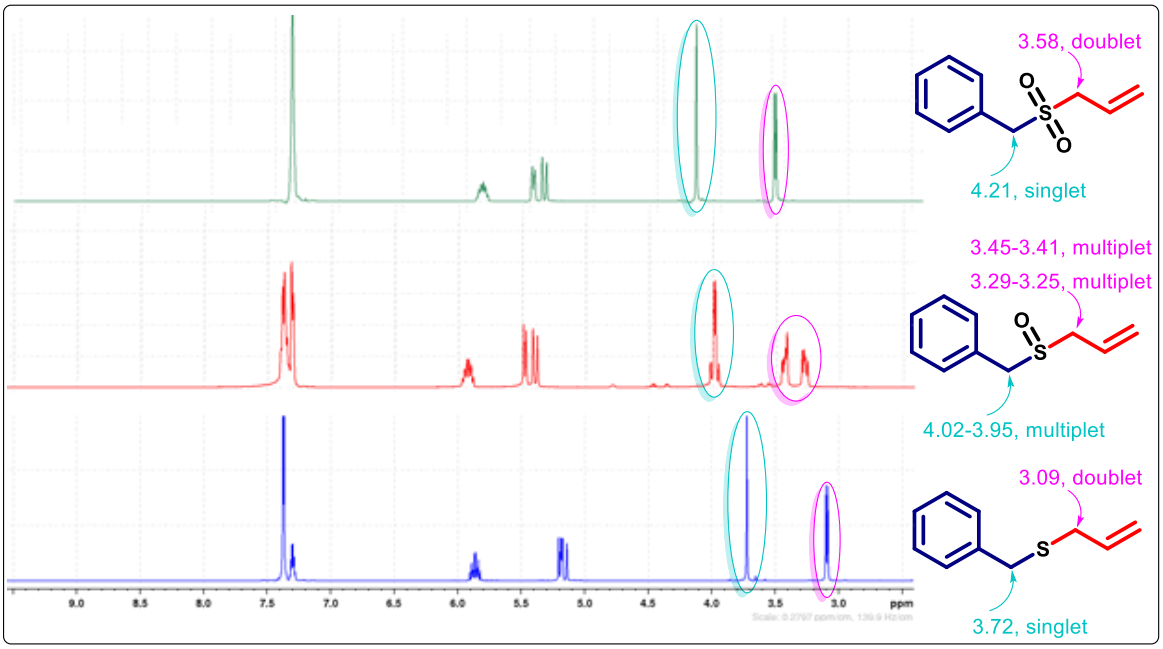
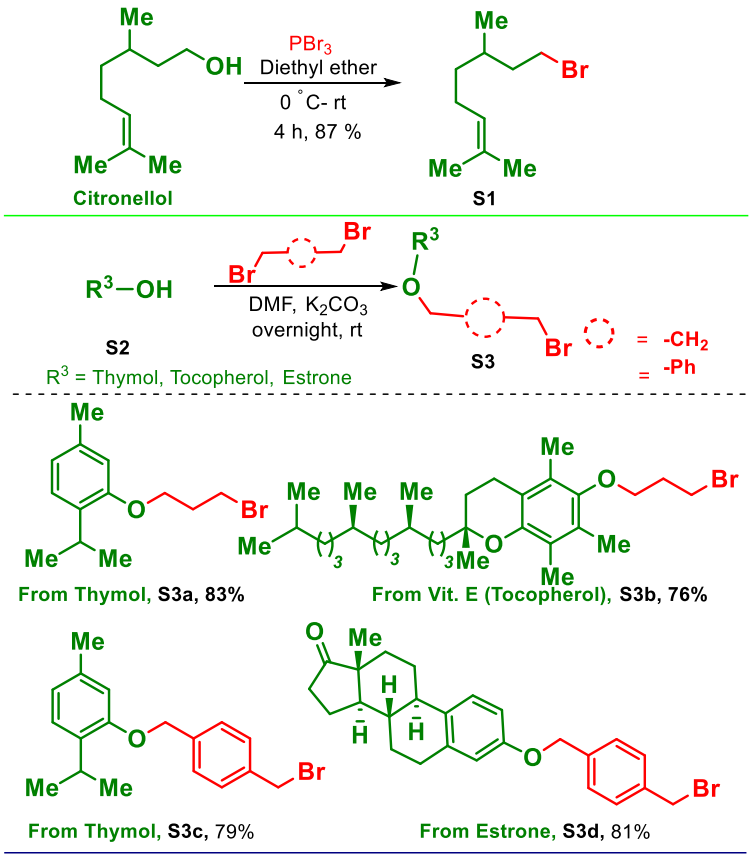


Figure 1. Comparison of chemical shift values (δ, ppm) and splitting pattern in ^{1}H NMR of sulfur, sulfoxide and sulfone derivatives.

Preparation of precursors for late-stage functionalization

We prepared bromo derivative of citronellol **S1** by using PBr_3 as a brominating agent in diethylether.[3] We prepared bromo derivatives of thymol (**37a** and **37c**), Vitamin E (**37b**) and estrone (**37d**) by using dibromo derivatives (e.g. 1, 3-dibromopropane and 1,4-bis(bromomethyl)benzene) in the presence of potassium carbonate and DMF (Scheme 2).[4]



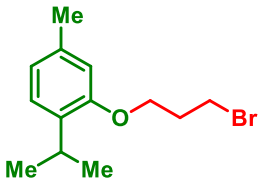
Scheme 2. Synthesis of bromo derivatives of biologically active compounds.

Synthesis and spectral data of compound **S1** has been reported.[2]

General procedure for the synthesis of bromo derivatives (S3) of biologically active compounds

To the solution of biologically active compound (1 equiv.) in DMF (10 mL) in a two-neck round-bottom flask, we added K_2CO_3 (2.5 equiv.) in reaction mixture at room temperature. Further, we allowed the reaction mixture to stir for 30 min. followed by addition of dibromoderivative (1.1 equiv.). The reaction mixture was stirred for overnight. After completion of reaction (TLC monitoring), the reaction mixture was diluted with water and extracted with ethyl acetate (3×10 mL). The organic layer was separated, washed with brine solution and dried over anhydrous Na_2SO_4 then the filterate was concentrated under reduced pressure and purified by silica gel column chromatography by using petroleum ether and ethyl acetate to afford the bromoderivative of biologically active compounds. (Reactions were carried out in 100 mg scale)

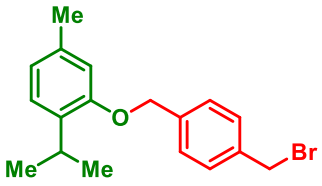
2-(3-bromopropoxy)-1-isopropyl-4-methylbenzene S3a



Yield 150 mg, 83%, **Appearance** colorless sticky solid, R_f = 0.8 (petroleum ether), **^{1}H NMR (500 MHz, CDCl$_3$):** δ 7.21 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 4.19 (t, *J* = 5.8 Hz, 2H), 3.73 (t, *J* = 6.5 Hz, 2H), 3.41-3.36 (m, 1H), 2.46-2.41 (m, 5H),1.32 (d, *J* = 7.0 Hz, 6H) ppm, **^{13}C NMR (125 MHz, CDCl$_3$):** δ 155.8, 136.5, 134.1, 126.0, 121.5, 112.4, 65.3, 32.8, 30.4, 26.7, 22.9, 21.5 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{13}H_{19}BrNaO$ $[M+Na]^+$ 293.0511 found 293.0512.

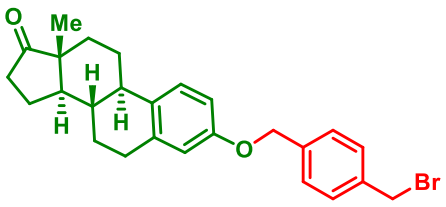
Spectral data of compound **S3b** has been reported.[3]

2-((4-(bromomethyl)benzyl)oxy)-1-isopropyl-4-methylbenzene S3c



Yield 175 mg, 79%, **Appearance** colorless solid, **MP**. 58-60 °C, R_f = 0.7 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.44 (s, 4H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.77 (s, 1H), 5.07 (s, 2H), 4.53 (s, 2H), 3.42-3.35 (m, 1H), 2.34 (s, 3H), 1.24 (d, *J* = 7.6 Hz, 6H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$):** δ 155.8, 138.2, 137.4, 136.5, 134.5, 129.4, 127.6, 126.2, 121.7, 112.8, 69.6, 33.5, 26.8, 22.9, 21.5 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{18}H_{21}BrNaO$ $[M+Na]^+$ 355.0667 found 355.0667.

(8S,9R,13R,14R)-3-((4-(bromomethyl)benzyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one S3d

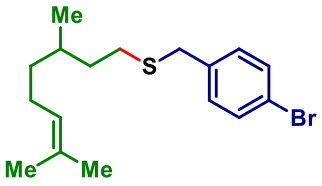


Yield 136 mg, 81%, **Appearance** colorless solid, **MP**. 112-114 °C, R_f = 0.4 (15% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.42 (s, 4H), 7.22 (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 5.04 (s, 2H), 4.52 (s, 2H), 2.93-2.89 (m, 2H), 2.55-2.49 (m, 1H), 2.43-2.39 (m, 1H), 2.29-2.24 (m, 1H), 2.20-1.95 (m, 4H), 1.67-1.45 (m, 6H), 0.92 (s, 3H) ppm, **^{13}C NMR (100 MHz, CDCl$_3$):** δ 221.1, 156.8, 138.1, 137.8, 137.5, 132.6, 129.4, 127.9, 126.5, 115.0, 112.5, 69.6, 50.5, 48.2, 44.1, 38.5, 36.0, 33.4, 31.7, 29.8, 26.7, 26.1, 21.7, 14.0 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{26}H_{30}BrO_2$ $[M+H]^+$ 453.1423 found 453.1422.

General procedure for the sulfide formation of biologically active derivatives.

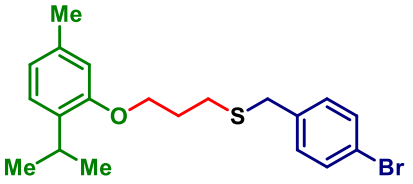
Prepared according to the general procedure mentioned on Page S2. (Reactions were carried out in 100 mg scale)

(4-Bromobenzyl)(3,7-dimethyloct-6-en-1-yl)sulfane 34a



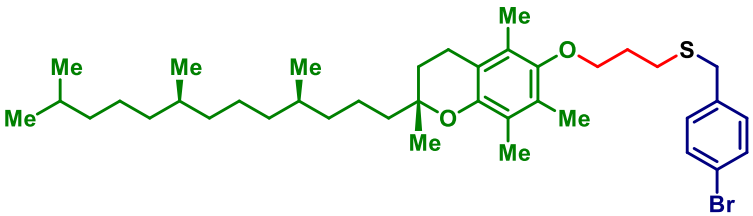
Yield 222 mg, 75%, **Appearance** colorless liquid, R_f = 0.5 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 2H), 5.12-5.08 (m, 1H), 3.67 (s, 2H), 2.49-2.35 (m, 2H), 2.01-1.93 (m, 2H), 1.71 (s, 3H), 1.62 (s, 3H), 1.59-1.48 (m, 2H), 1.42-1.36 (m, 1H), 1.33-1.27 (m, 1H), 1.19-1.12 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 3H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.9, 131.7, 131.4, 130.7, 124.8, 120.8, 36.9, 36.4, 35.8, 32.1, 29.3, 25.9, 25.6, 19.4, 17.8 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{17}H_{26}BrS$ $[M+H]^+$ 343.0912 found 343.0912.

(4-Bromobenzyl)(3-(2-isopropyl-5-methylphenoxy)propyl)sulfane 34b



Yield 280 mg, 82%, **Appearance** colorless liquid, R_f = 0.2 (2% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 4.09 (t, *J* = 6.0 Hz, 2H) 3.76 (s, 2H), 3.35-3.28 (m, 1H), 2.70 (t, *J* = 7.4 Hz, 2H),2.41 (s, 3H), 2.16-2.09 (m, 2H), 1.28 (d, *J* = 6.8 Hz, 6H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.9, 137.6, 136.4, 133.9, 131.7, 130.6, 125.9, 121.3, 120.9, 112.2, 66.1, 35.8, 29.3, 28.2, 26.7, 22.9, 21.5 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{20}H_{26}BrOS$ $[M+H]^+$ 385.0862 found 385.0863.

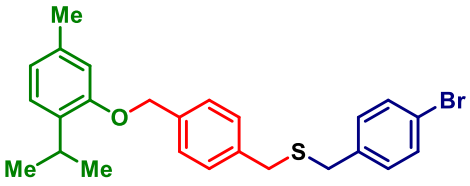
(R)-6-(3-((4-Bromobenzyl)thio)propoxy)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane 34c



Yield 419 mg, 72%, **Appearance** yellow liquid, R_f = 0.2 (1% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.72-3.69 (m, 4H), 2.69 (t, *J* = 7.2 Hz, 2H),2.59 (t, J = 6.6 Hz, 2H), 2.16 (s, 3H), 2.11 (d, J = 2.8, 6H), 2.07-2.00 (m, 2H), 1.86-1.76 (m, 2H), 1.58-1.53 (m, 3H), 1.46-

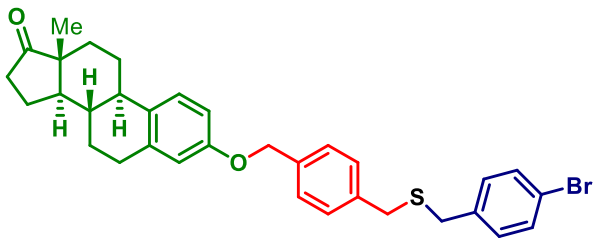
1.38 (m, 4H), 1.32-1.26 (m, 11H), 1.19-1.09 (m, 6H), 0.91-0.87 (m, 12H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 148.2, 147.9, 137.8, 131.7, 130.7, 127.9, 125.9, 122.9, 120.9, 117.7, 74.9, 71.2, 40.2, 39.5, 37.7, 37.6, 37.6, 37.5, 35.9, 32.9, 32.9, 31.4, 30.0, 28.4, 28.1, 24.9, 24.6, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.9, 12.9, 12.0, 11.9 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{39}H_{62}BrO_2S$ $[M+H]^+$ 675.3640 found 675.3641.

(4-Bromobenzyl)(4-((2-isopropyl-5-methylphenoxy)methyl)benzyl)sulfane 34d



Yield 348 mg, 88%, **Appearance** colorless sticky solid, ***R_f*** = 0.7 (5% EtOAc-petroleum ether), **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.56-7.47 (m, 4H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.24-7.21 (m, 3H), 6.87-6.83 (m, 2H), 5.13 (s, 2H), 3.67 (s, 2H), 3.62 (s, 2H), 3.49-3.43 (m, 1H), 2.41 (s, 3H), 1.31 (d, *J* =7.0 Hz, 6H) ppm, **^{13}C NMR (125 MHz, $CDCl_3$):** δ 155.9, 137.4, 137.3, 136.7, 136.5, 134.5, 131.7, 130.8, 129.3, 127.4, 127.4, 126.1, 121.6, 120.9, 112.8, 69.8, 35.4, 35.1, 26.7, 22.9, 21.5 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{25}H_{27}BrKOS$ $[M+K]^+$ 493.0598 found 493.0593.

(8S,9R,13R,14R)-3-((4-(((4-Bromobenzyl)thio)methyl)benzyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one 34e



Yield 394 mg, 79%, **Appearance** colorless sticky solid, ***R_f*** = 0.3 (5% EtOAc-petroleum ether), **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47-7.40 (m, 4H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.81 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 5.05 (s, 2H), 3.62 (s, 2H), 3.57 (s, 2H), 2.96-2.92 (m, 2H), 2.57-2.50 (m, 1H), 2.45-2.41 (m, 1H), 2.31-2.26 (m, 1H), 2.22-1.98 (m, 4H), 1.71-1.42 (m, 6H), 0.94 (s, 3H) ppm, **^{13}C NMR (100 MHz, $CDCl_3$):** δ 220.9, 156.9, 137.9, 137.6, 137.3, 136.2, 132.5, 131.6, 130.8, 129.3, 127.8, 126.5, 120.9, 115.0, 112.5, 69.8, 50.5, 48.1, 44.1, 38.4, 35.9, 35.4, 35.0, 31.7, 29.8, 26.6, 26.0, 21.7, 13.9 ppm, **HRMS (ESI, Q-ToF)** ***m/z:*** calcd for $C_{33}H_{36}BrO_2S$ $[M+H]^+$ 577.1598 found 577.1598.

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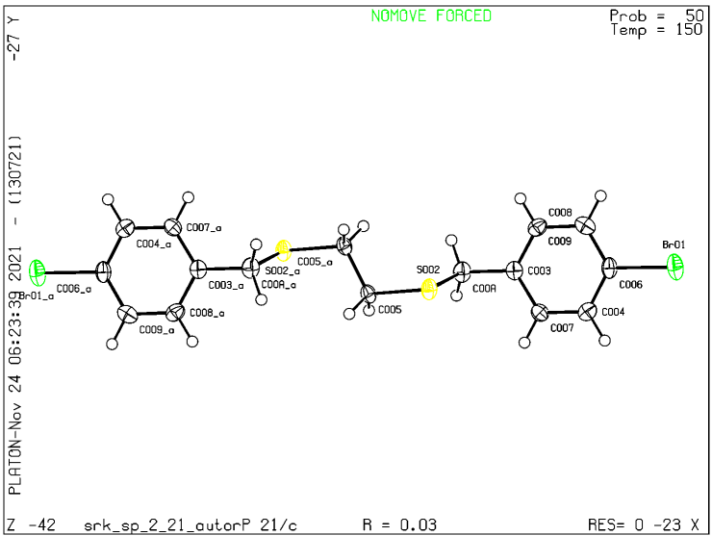
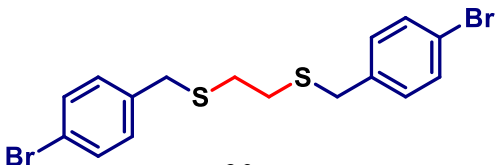
X-ray crystal data

1,2-Bis((4-bromobenzyl)thio)ethane 20a (CCDC No. 2168016)





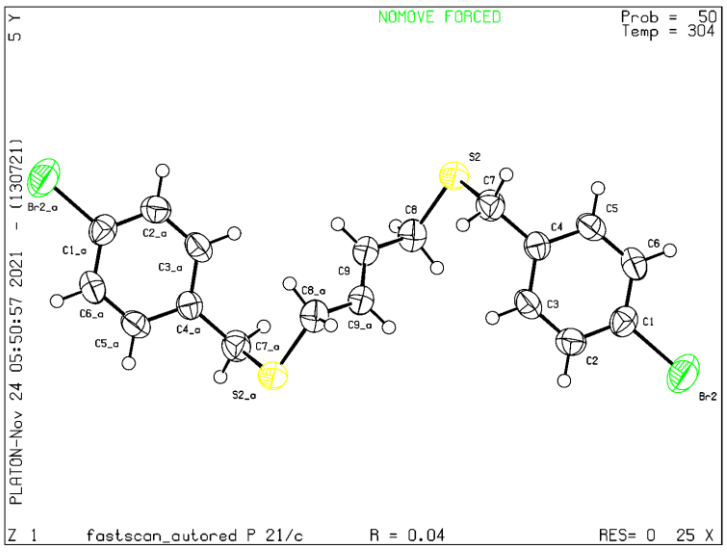
20a

Table S1. X-ray crystallographic data and refinement parameters for **20a (CCDC No. 2168016)**

Identification code	SP-2-21	
Empirical formula	C_8H_8BrS(monomer unit)	
Formula weight	216.11	
Temperature	150(2) K	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.6134(6) Å	α = 90°
	b = 5.5697(2) Å	β = 104.329(4)°
	c = 9.1693(4) Å	γ = 90°
Volume	822.06(6) $Å^3$	
Z	4	
Density (calculated)	1.746 g/cm^3	
Absorption coefficient (μ)	5.172 mm^{-1}	
Absorption correction	Multi-scan	
Max. and Min. transmission	1.000-0.283	
F (000)	428.0	
Crystal size	0.426 x 0.245 x 0.124 mm^3	

Index ranges	$-19 \leq h \leq 19, -6 \leq k \leq 6, -9 \leq l \leq 10$
Two-theta range for data collection	5.062 to 49.984°
Reflections collected	4332
Diffraction radiation wavelength	0.71073
Independent reflections	1385 [$R_{(int)}$ = 0.0317]
Completeness to θ = 24.998°	95%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1385/0/91
Goodness-of-fit on F^2	1.076
Final *R* indices [I>=2σ (I)]	*R*1 = 0.0264, *wR*2 = 0.0598
R indices (all data)	*R*1 = 0.0341, *wR*2 = 0.0631
Largest diff. peak and hole	0.34/-0.40 e $Å^{-3}$

(E)-1,4-Bis((4-bromobenzyl)thio)but-2-ene (21b) (CCDC No. 2168017)



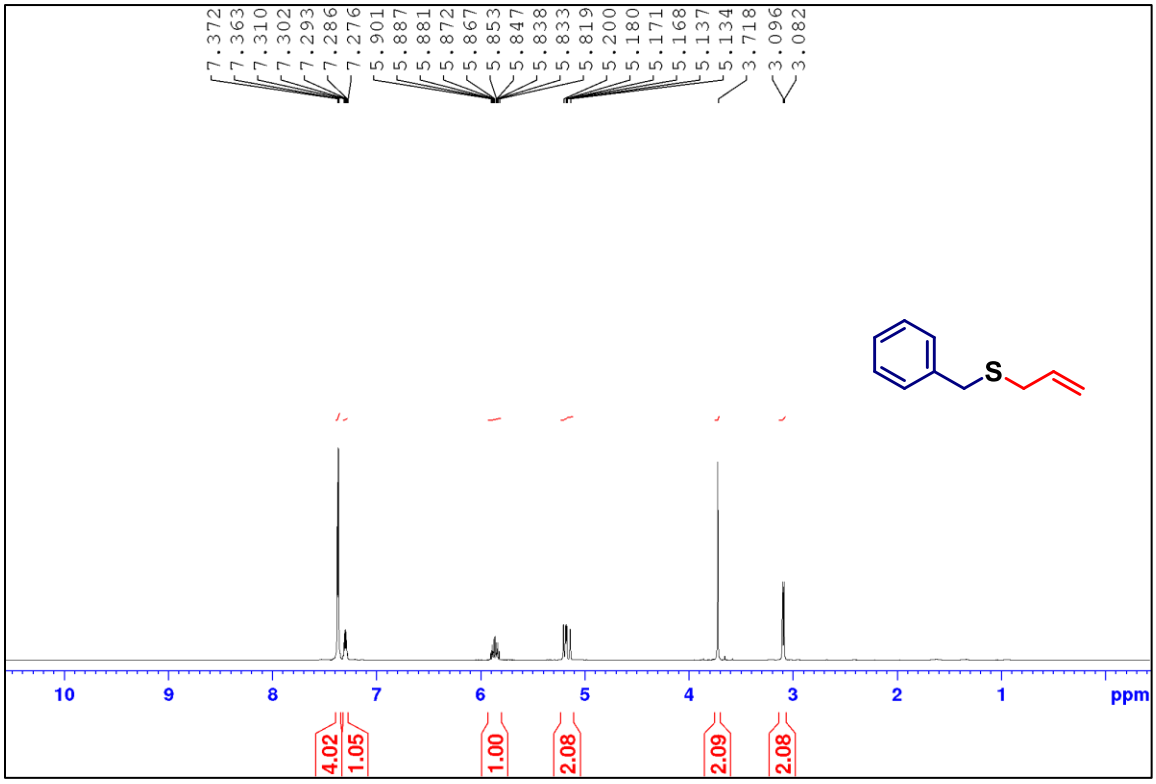
21b

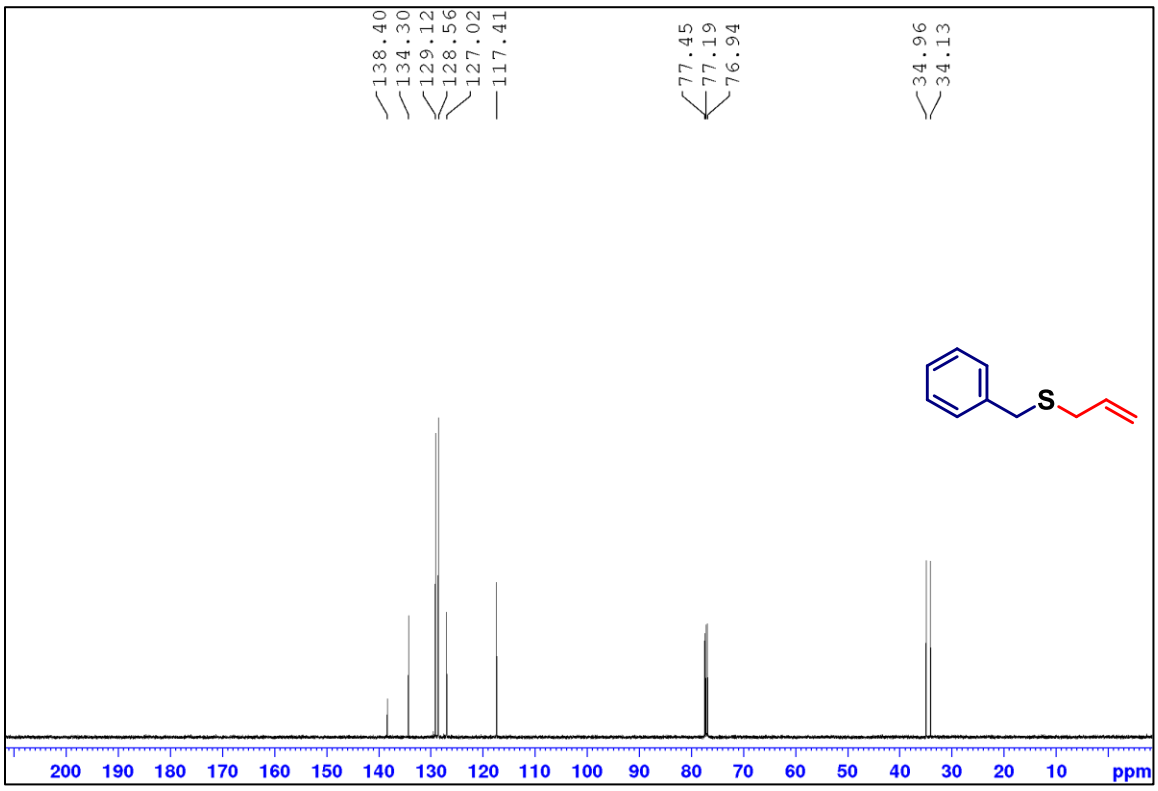
Table S1. X-ray crystallographic data and refinement parameters for **21b (CCDC No. 2168017)**

Identification code	SP-2-65
Empirical formula	C_9H_9BrS(monomer unit)
Formula weight	229.13
Temperature	304(2) K
Crystal system	monoclinic

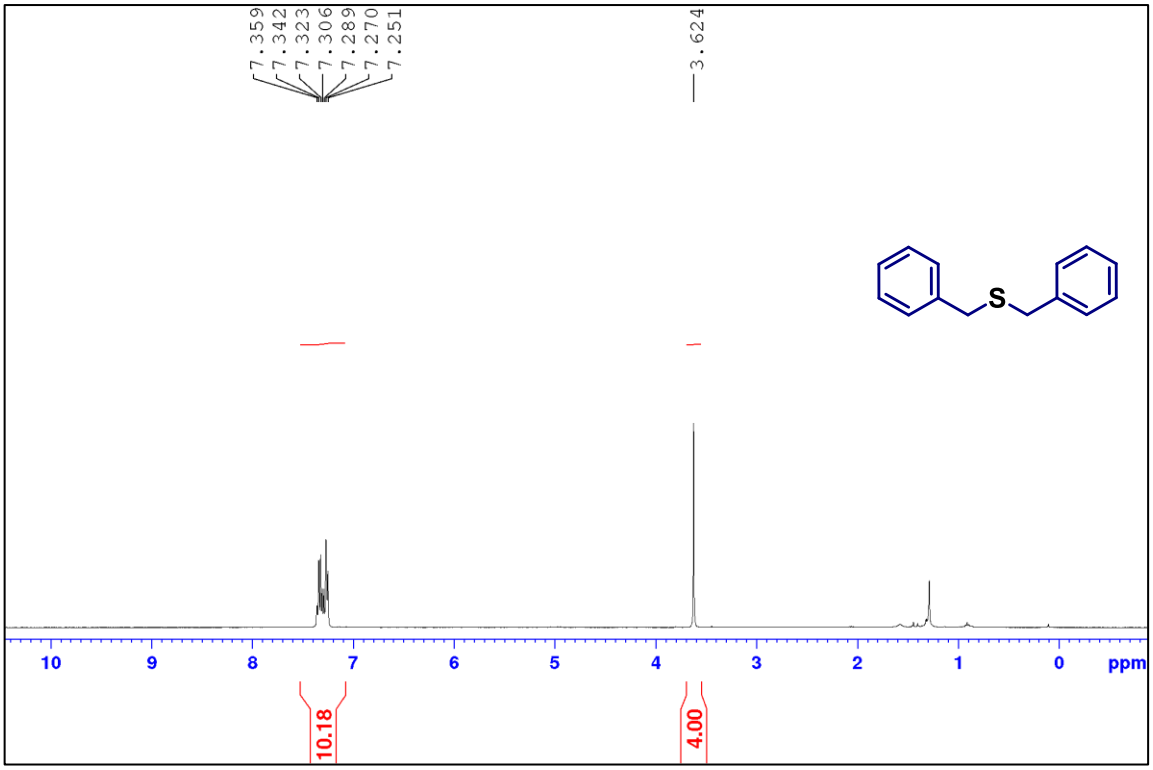
Space group	$P2_1/c$
Unit cell dimensions	a = 16.5752(12) Å α = 90°
	b = 6.3230(6) Å β = 100.622(8)°
	c = 9.1422(8) Å γ = 90°
Volume	941.73(14) $Å^3$
Z	4
Density (calculated)	1.616 g/cm^3
Absorption coefficient (μ)	4.520 mm^{-1}
Absorption correction	Multi-scan
Max. and Min. transmission	1.000-0.281
F (000)	456.0
Crystal size	0.274 x 0.270 x 0.186 mm^3
Index ranges	$-19 \leq h \leq 17$, $-7 \leq k \leq 7$, $-10 \leq l \leq 10$
Two-theta range for data collection	6.912 to 49.996°
Reflections collected	5115
Diffraction radiation wavelength	0.71073
Independent reflections	1641 [$R_{(int)}$ = 0.0379]
Completeness to θ = 24.998°	99%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1641/0/100
Goodness-of-fit on F^2	1.029
Final *R* indices [I>=2σ (I)]	*R*1 = 0.0350, *wR*2 = 0.0716
R indices (all data)	*R*1 = 0.0525, *wR*2 = 0.0800
Largest diff. peak and hole	0.40/-0.48 e $Å^{-3}$

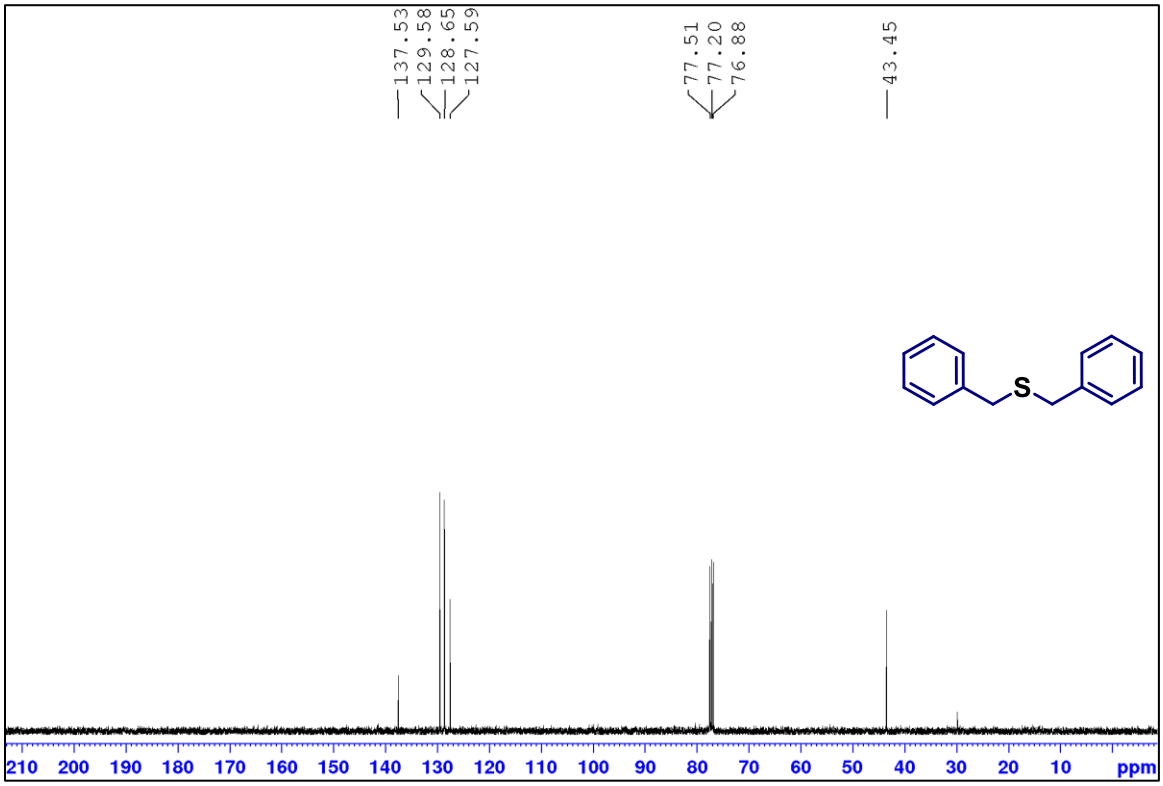
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 2 in $CDCl_3$



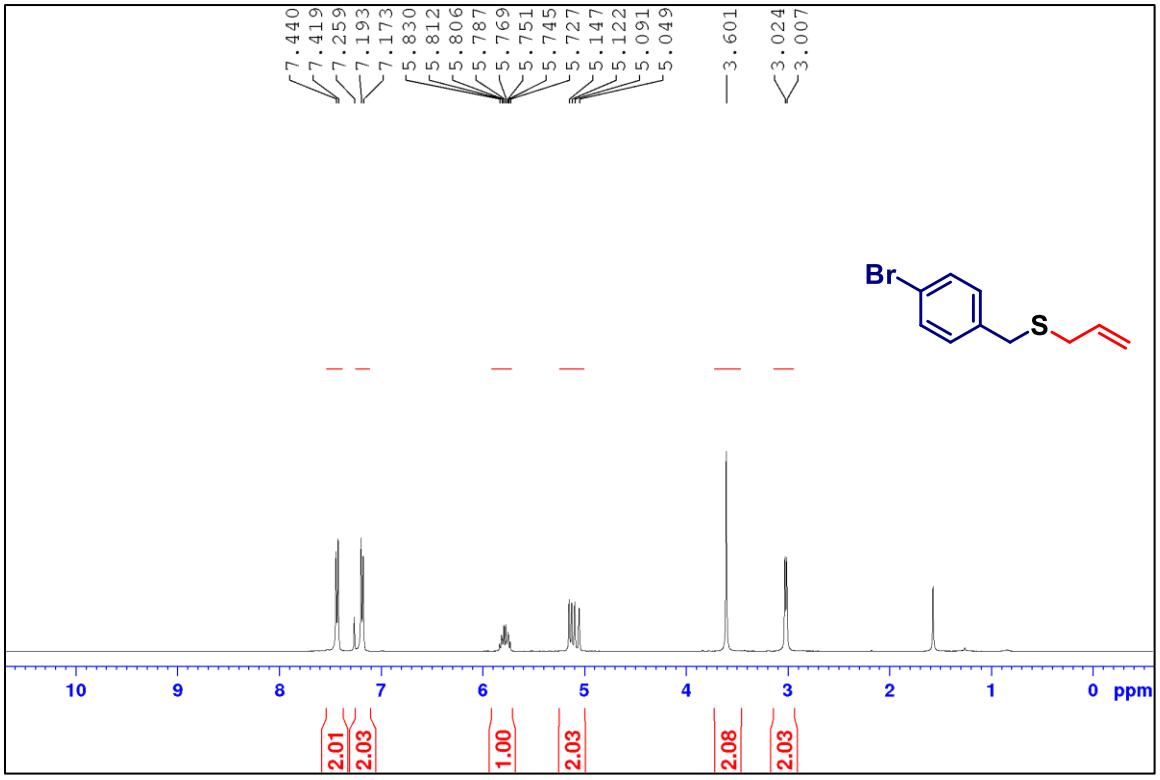


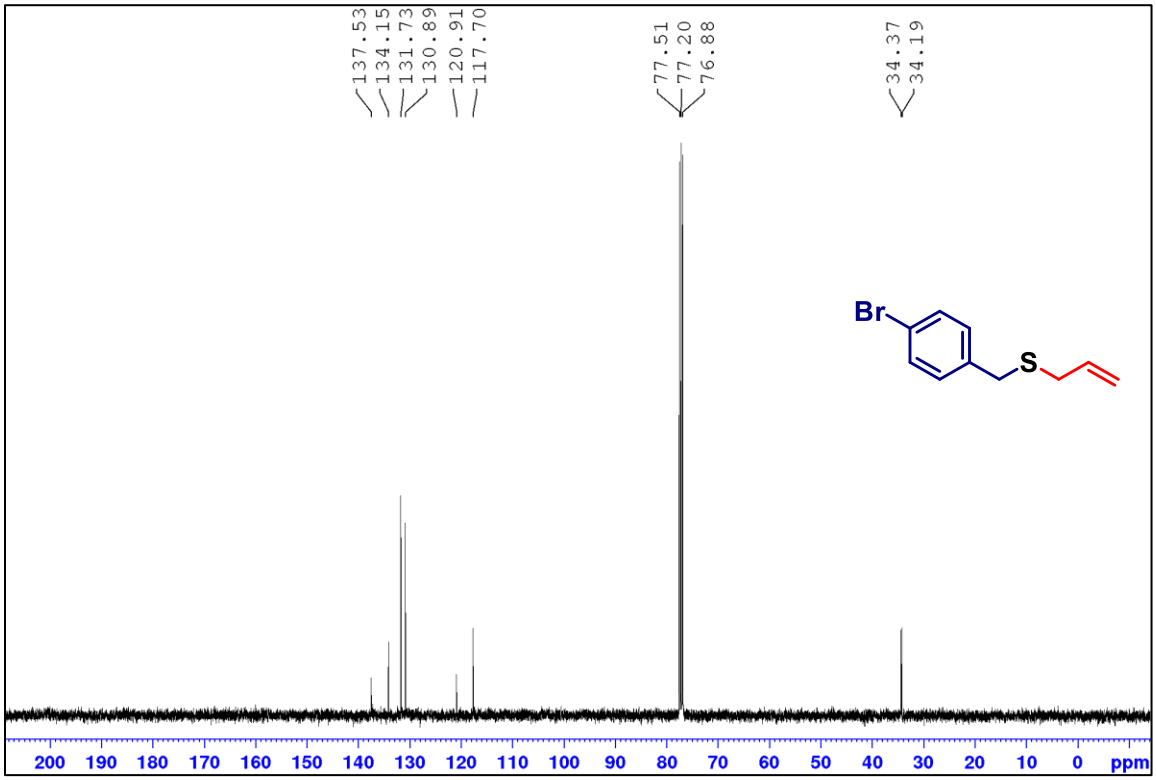
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 3 in $CDCl_3$



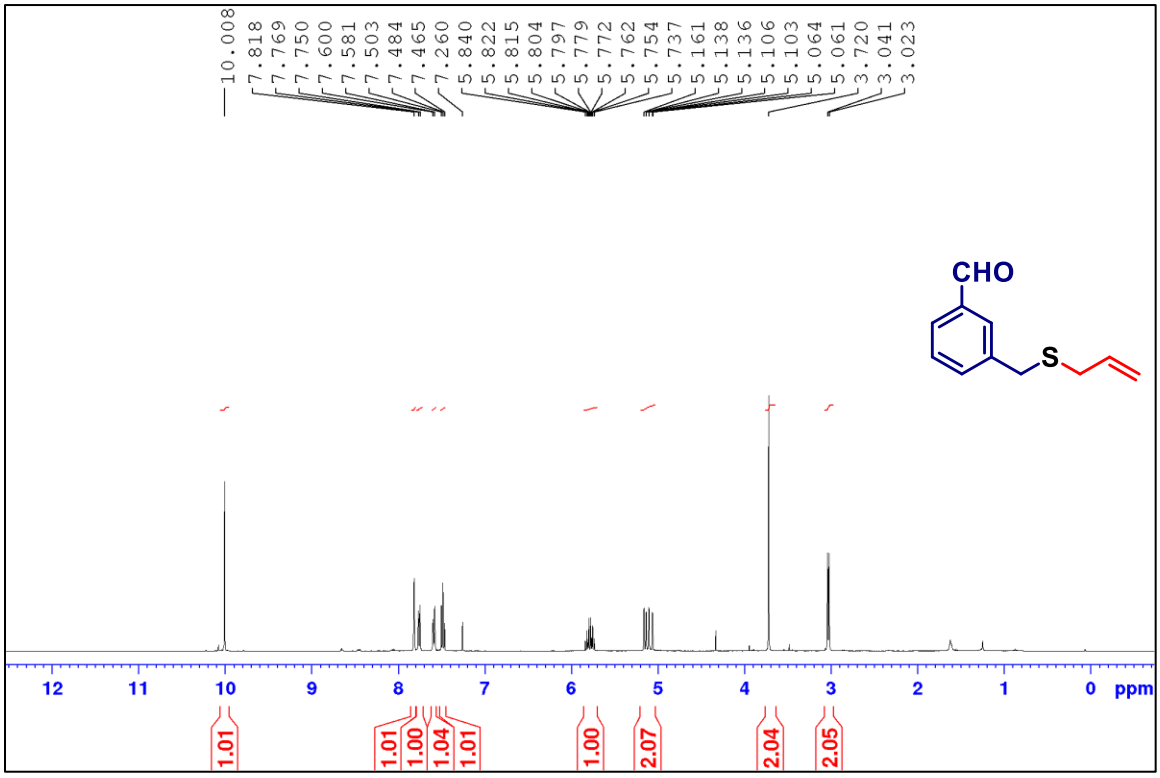


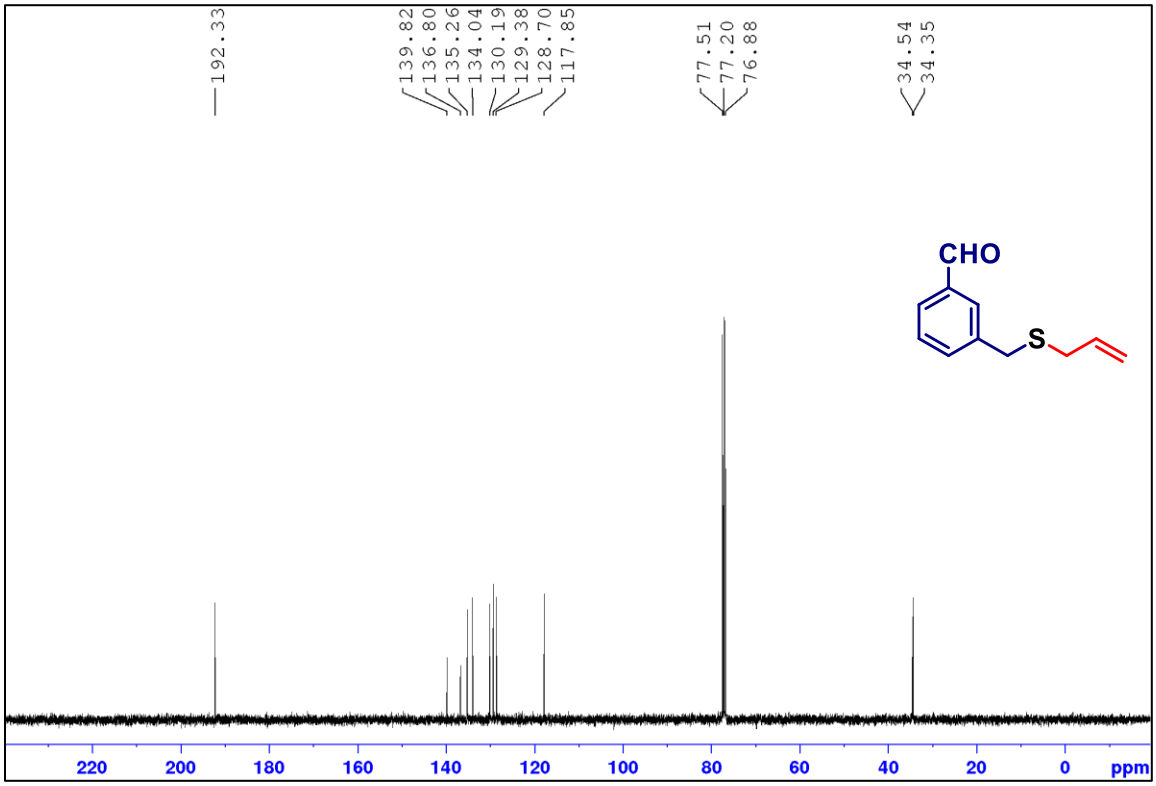
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 5a in $CDCl_3$



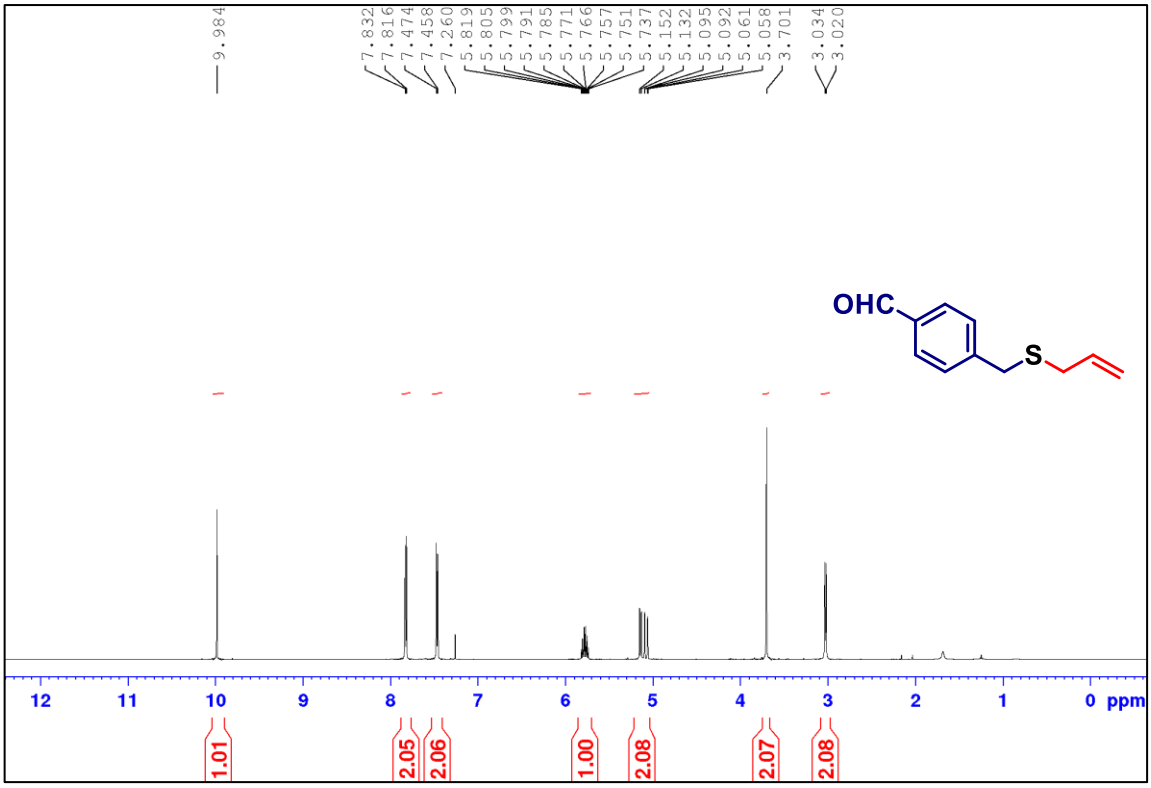


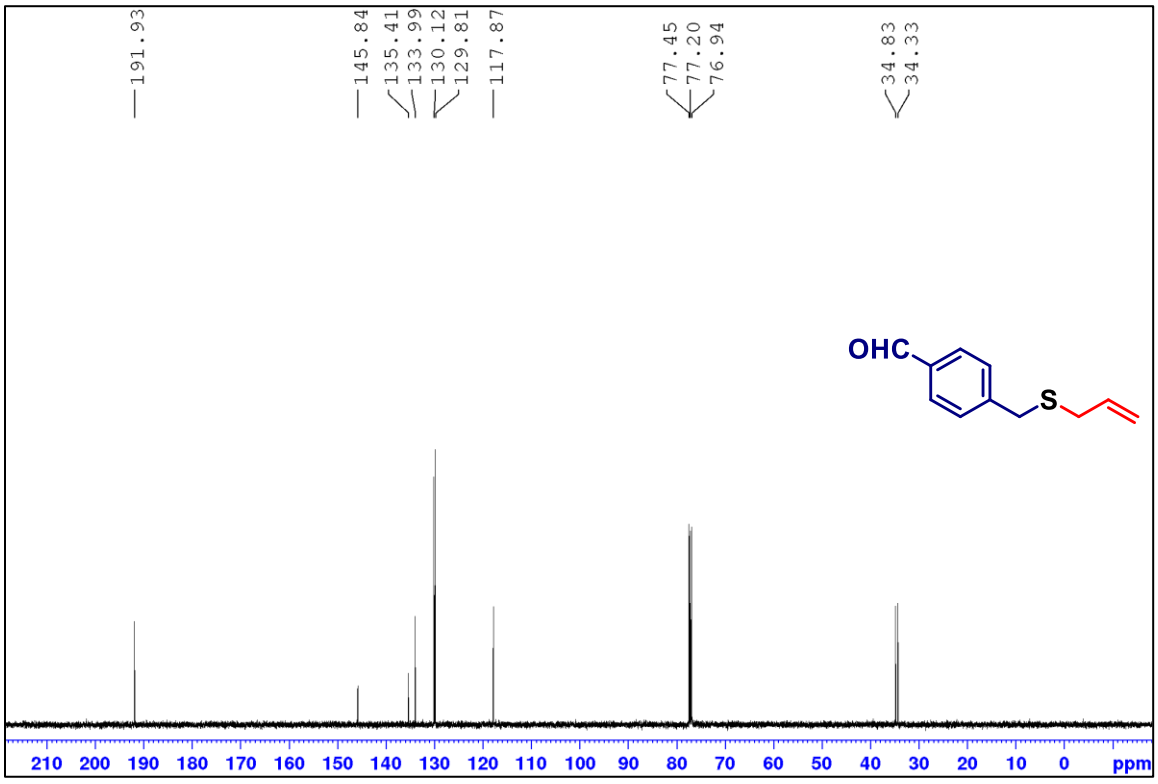
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 5b in $CDCl_3$



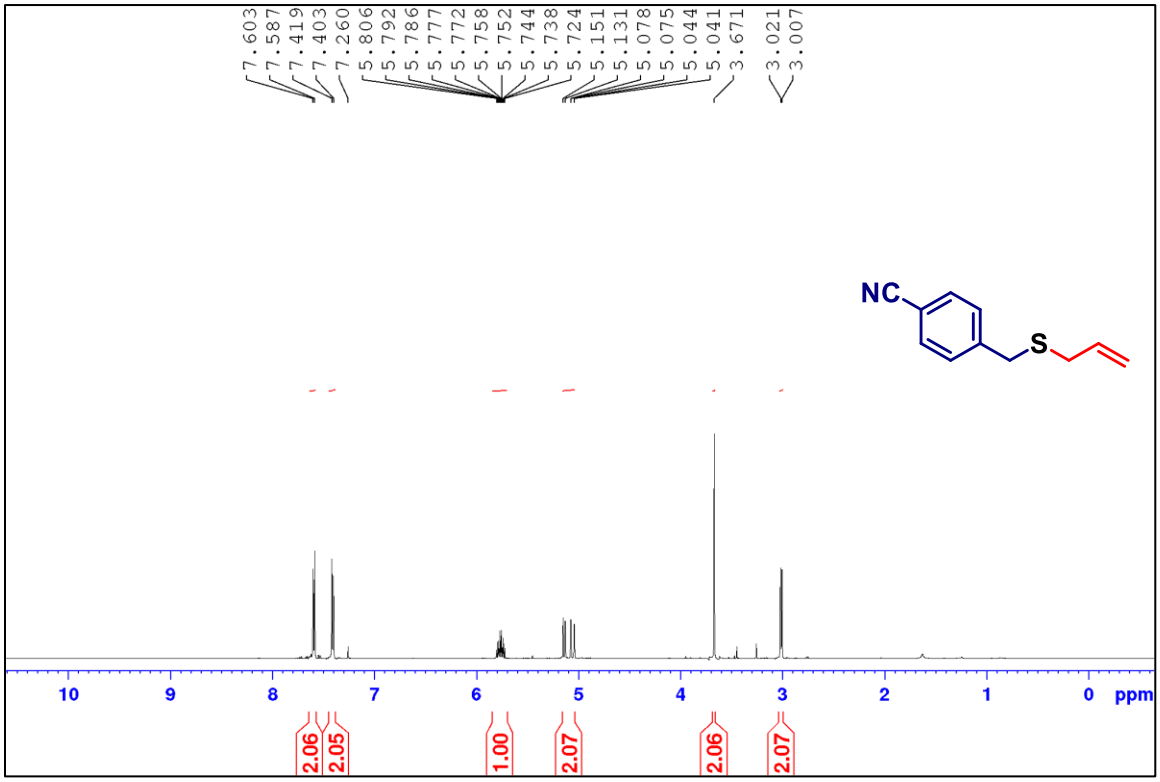


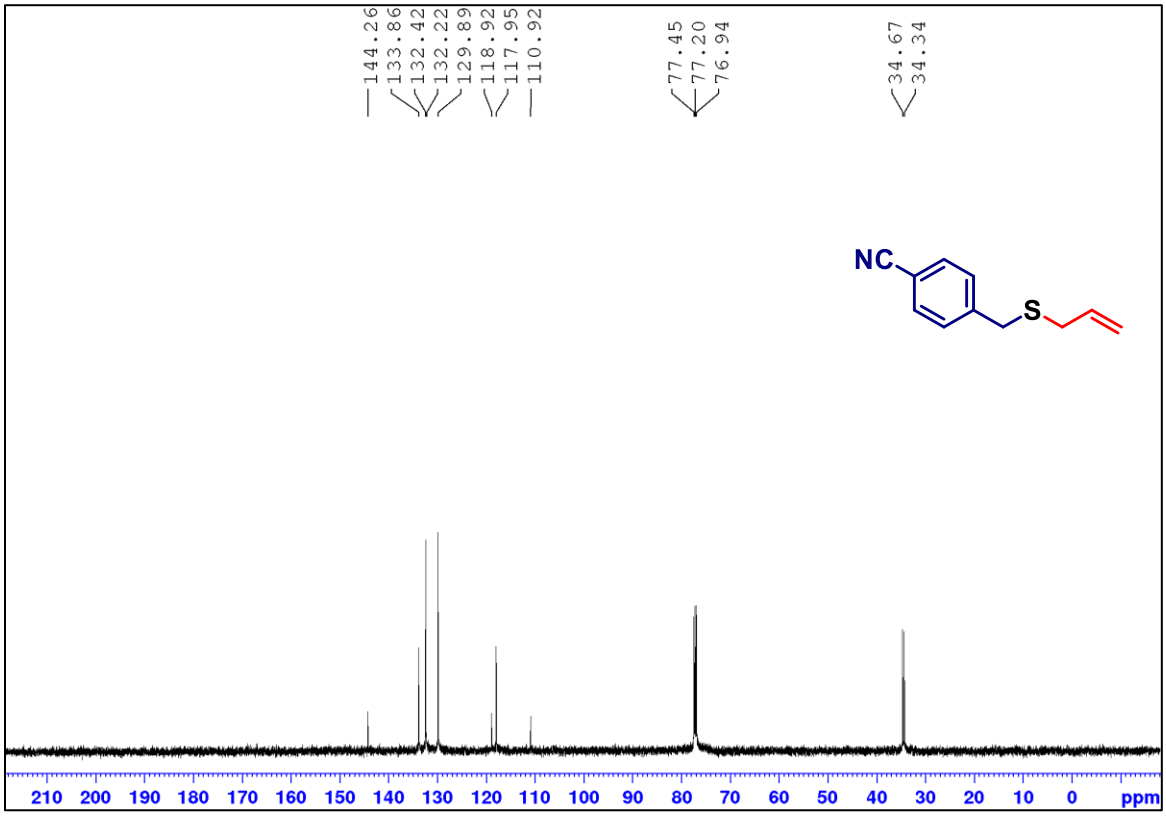
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 5c in $CDCl_3$



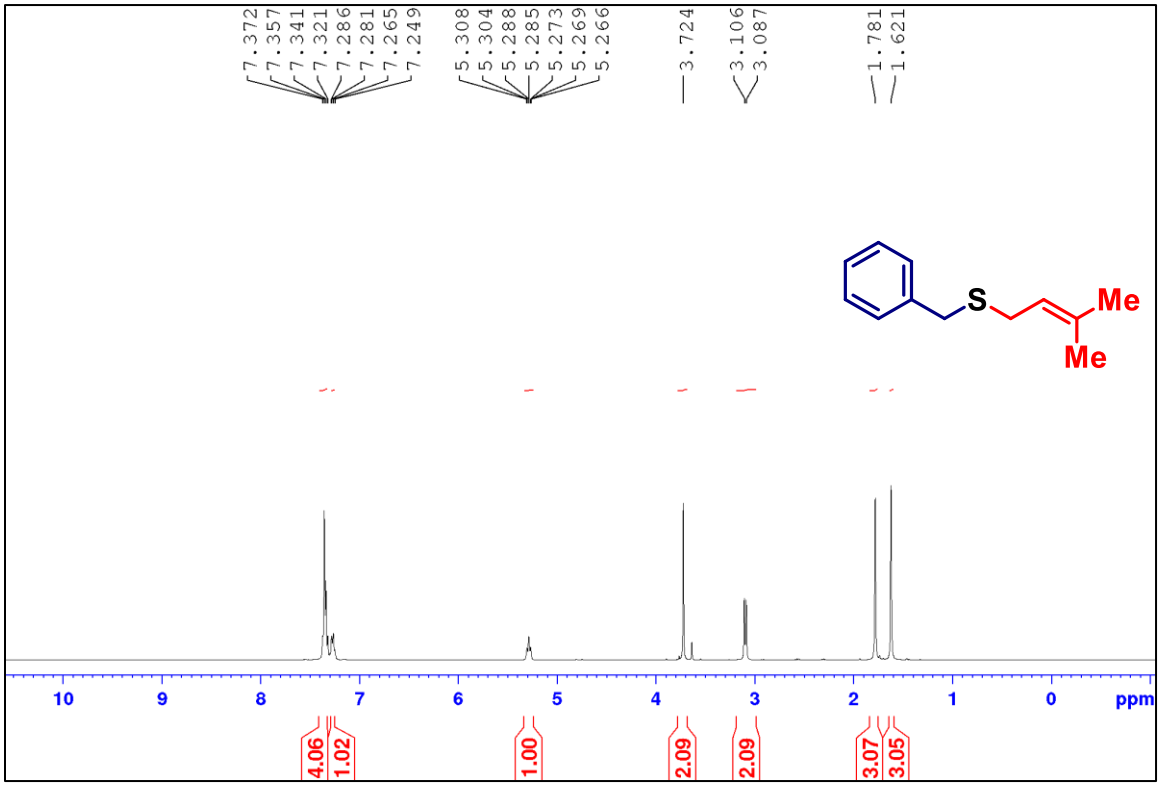


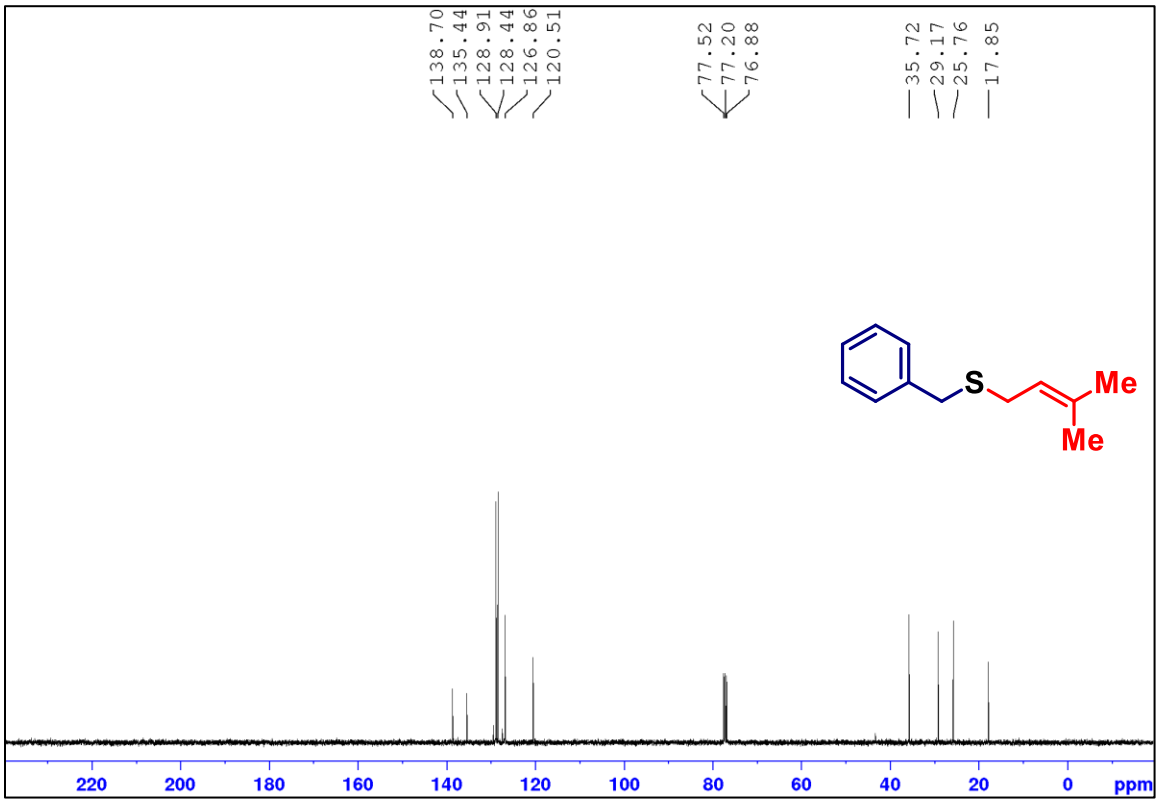
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 5d in $CDCl_3$



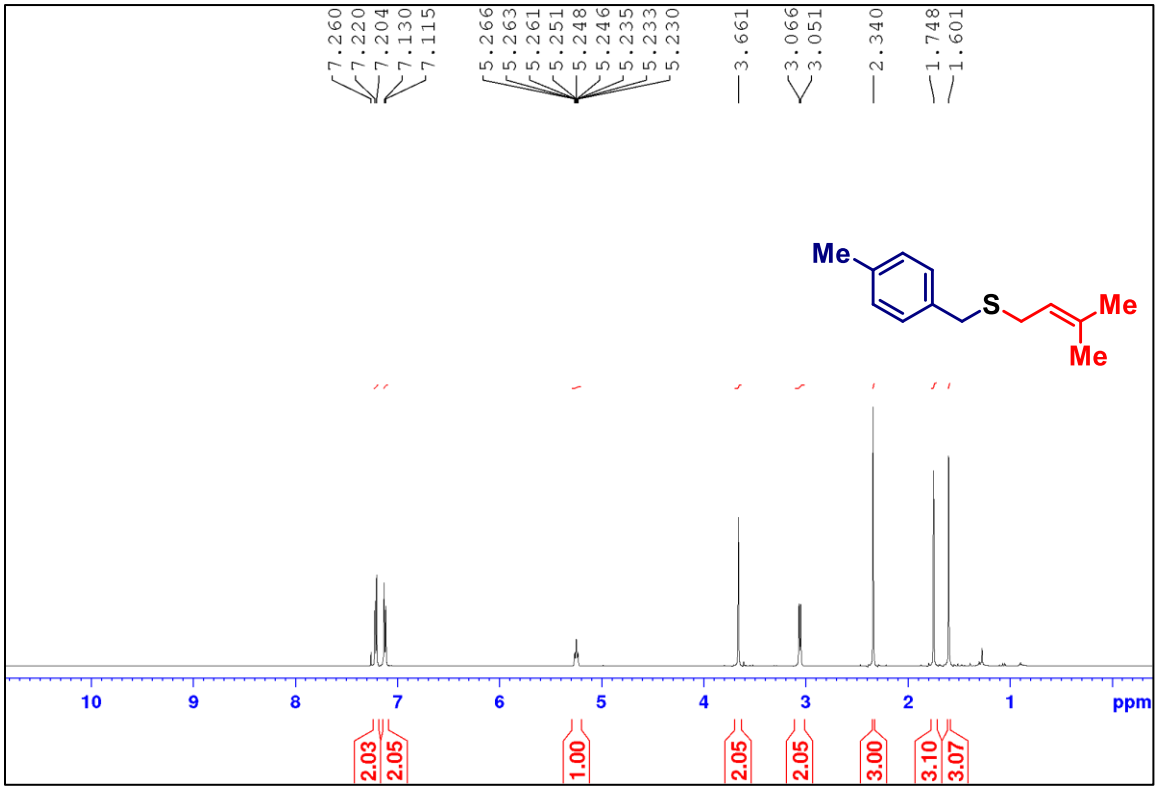


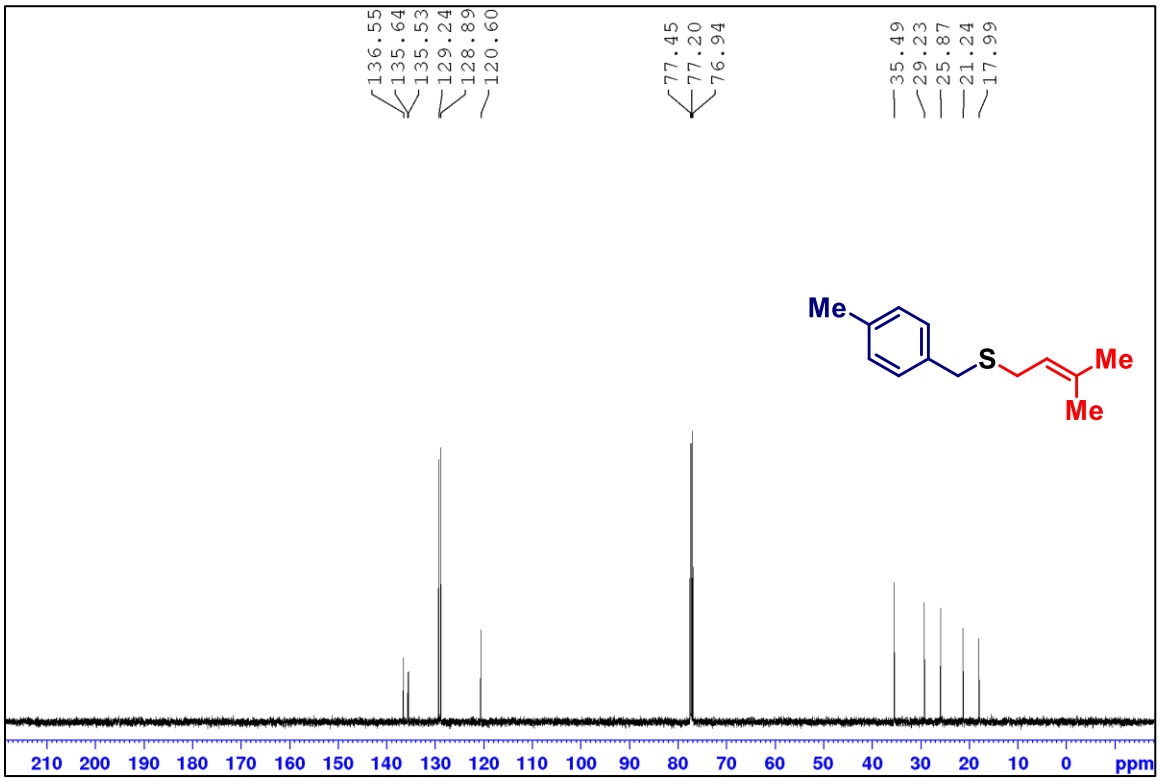
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 6a in $CDCl_3$



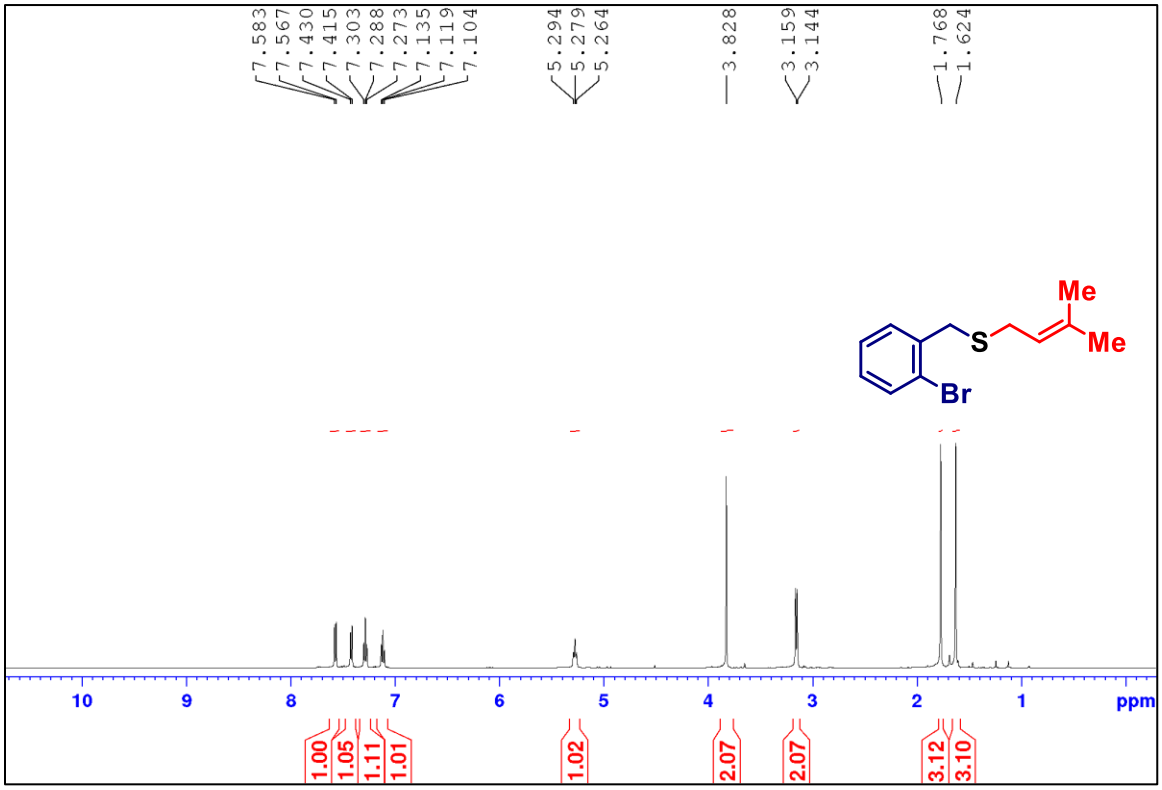


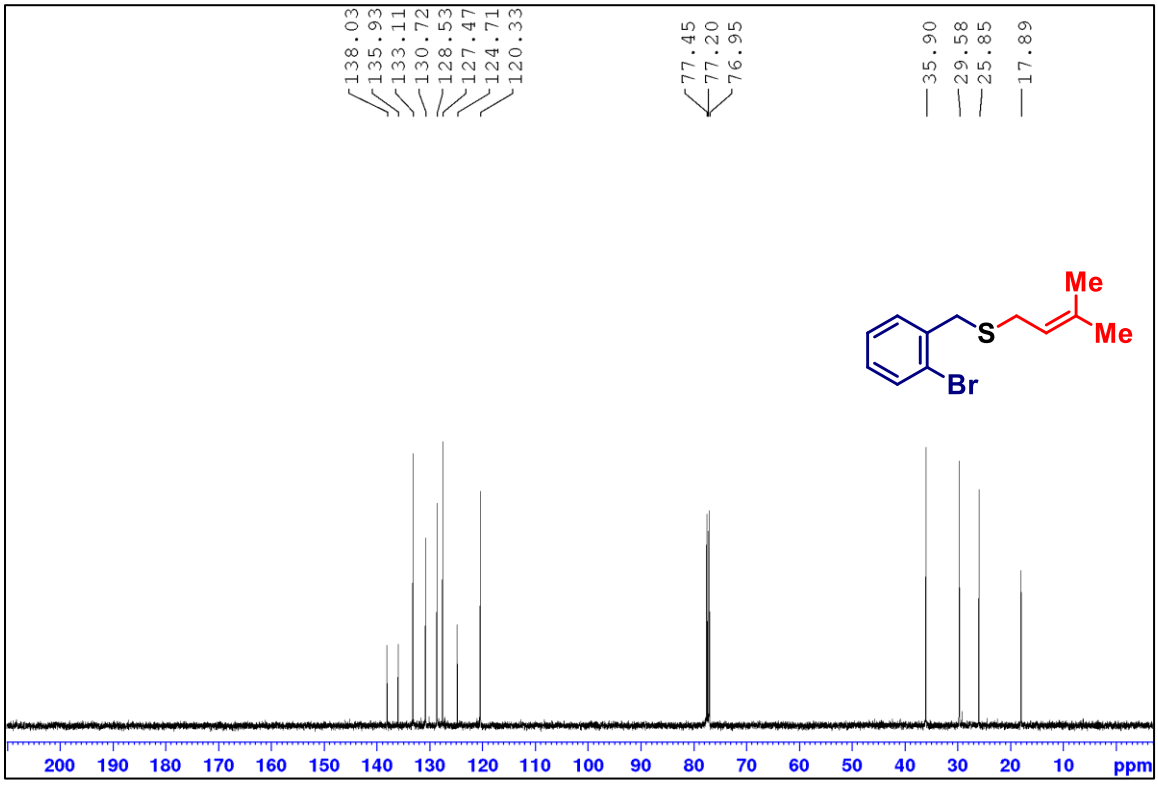
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 6b in $CDCl_3$



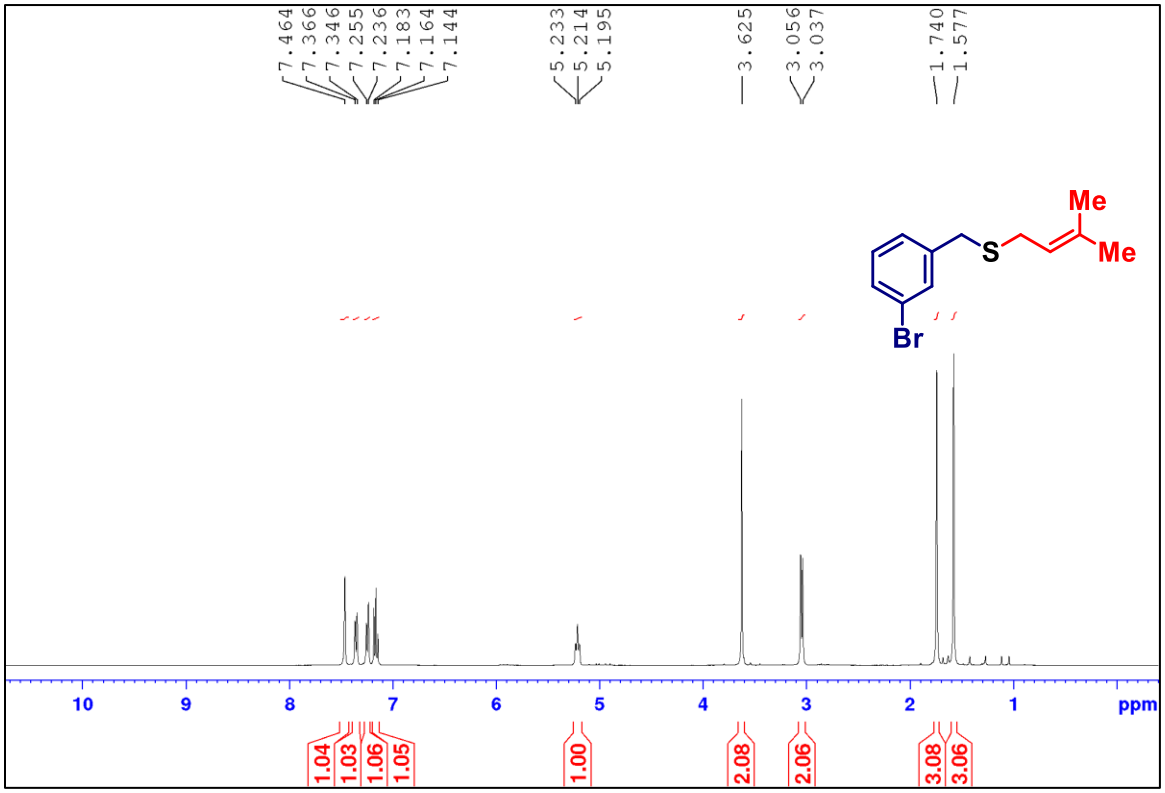


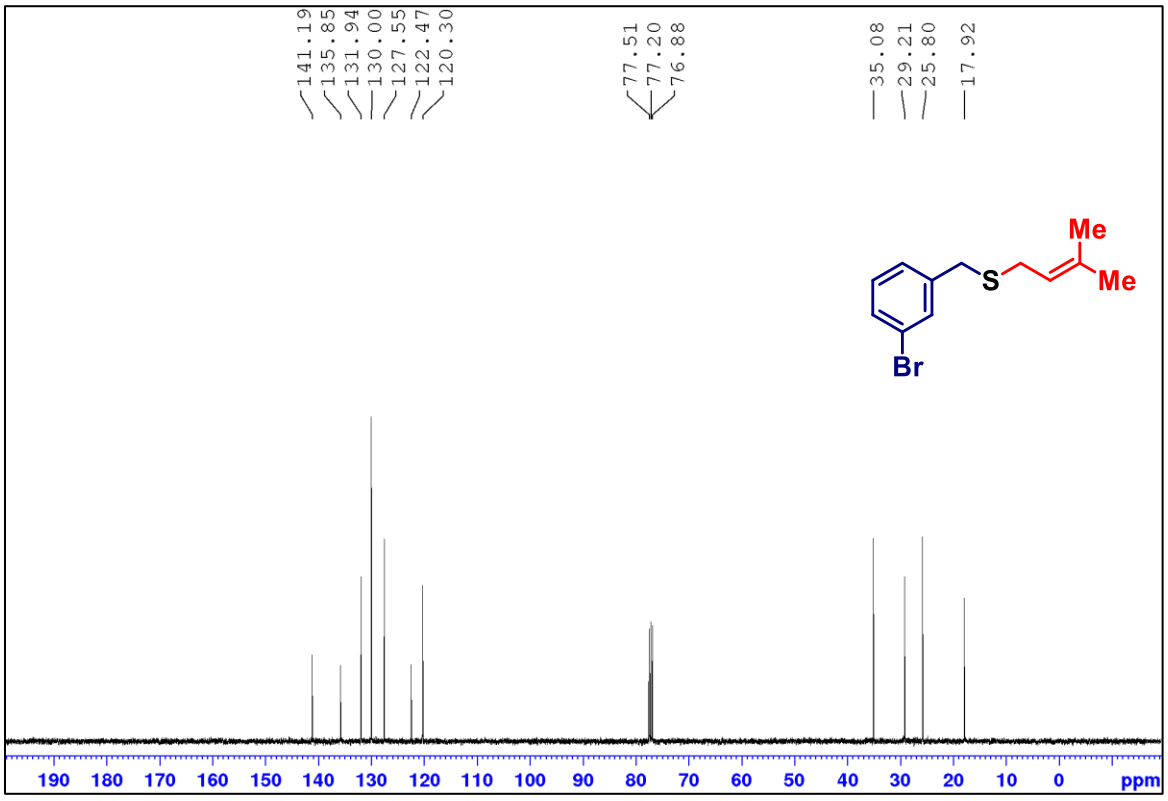
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 6c in $CDCl_3$



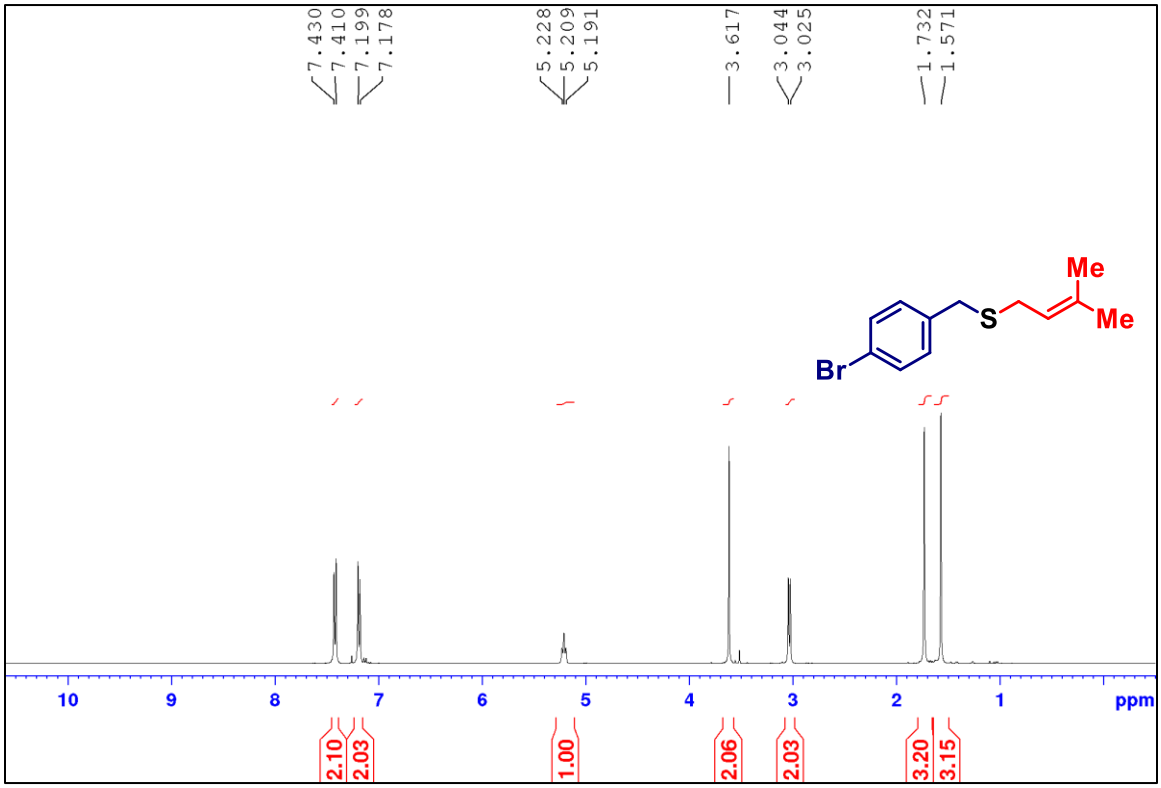


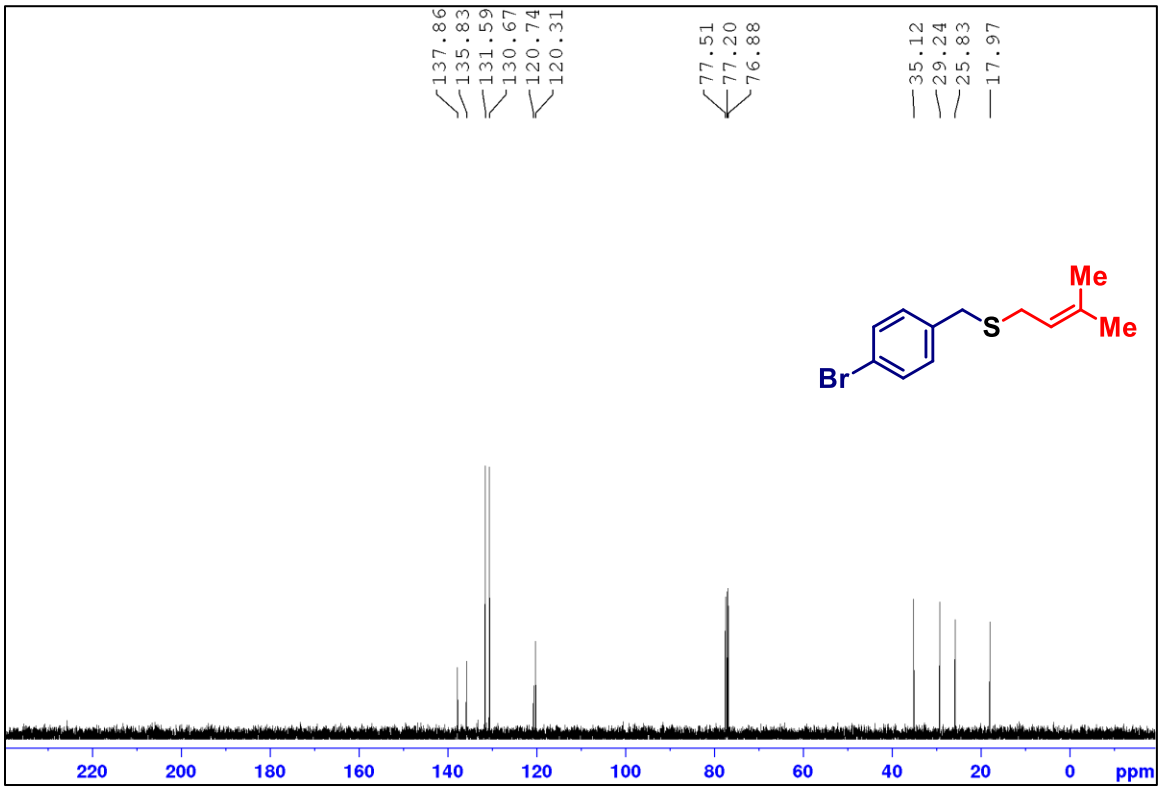
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 6d in $CDCl_3$



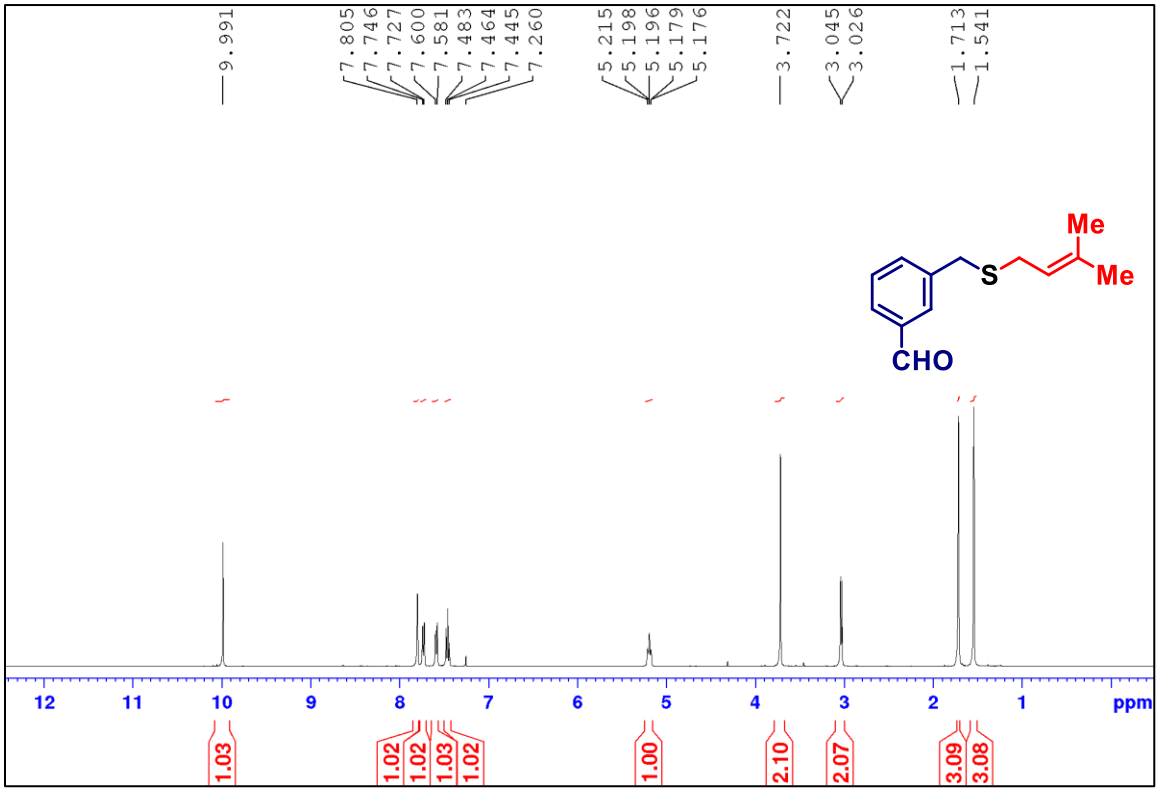


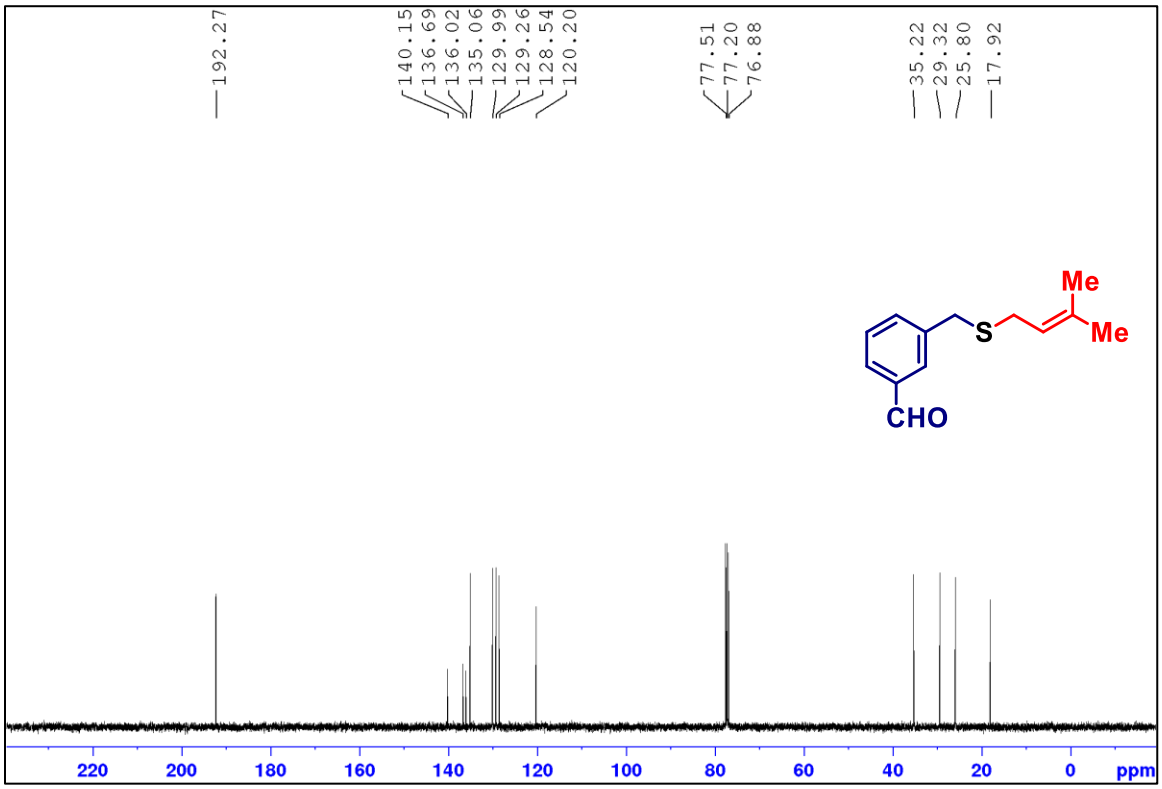
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 6e in $CDCl_3$



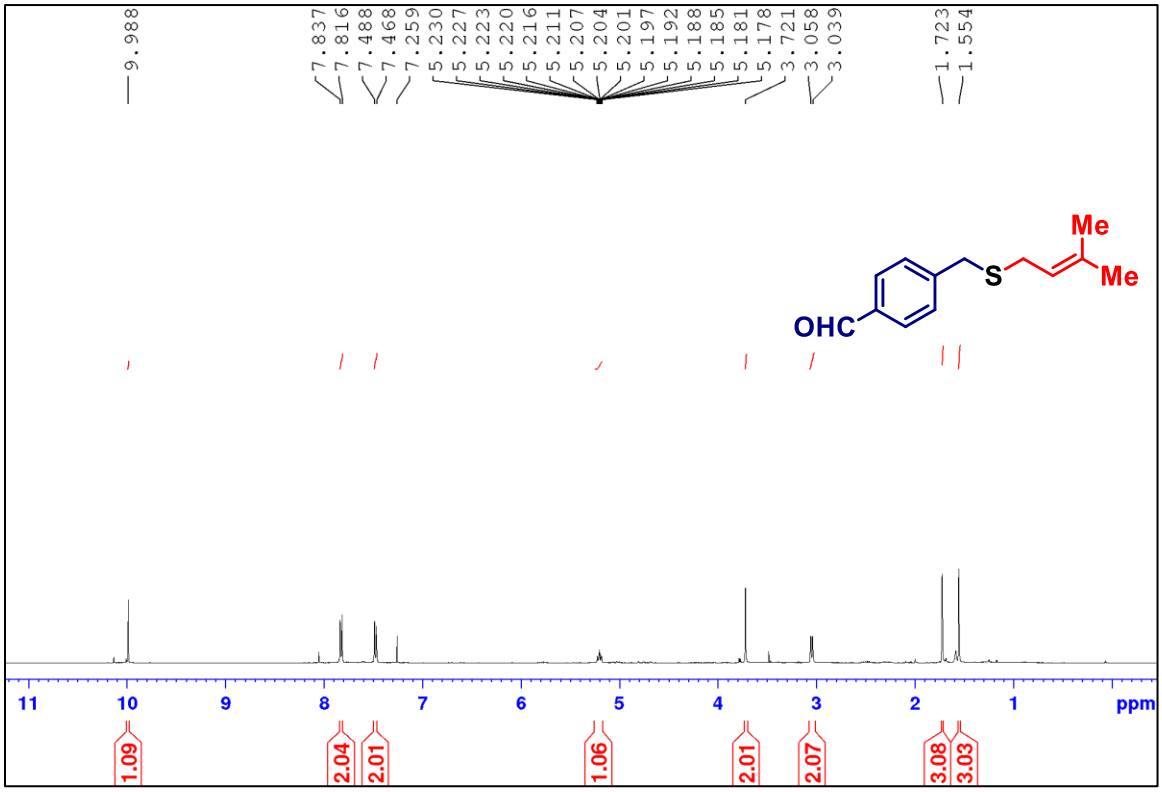


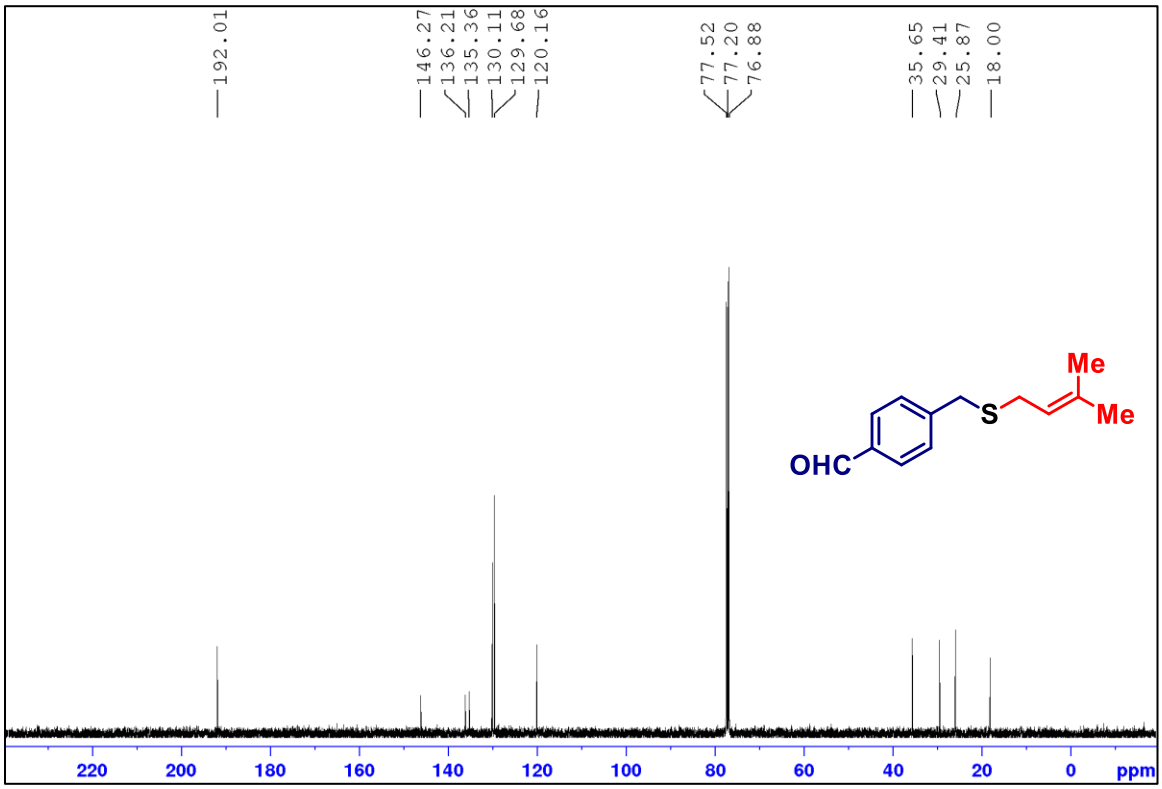
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 6f in $CDCl_3$



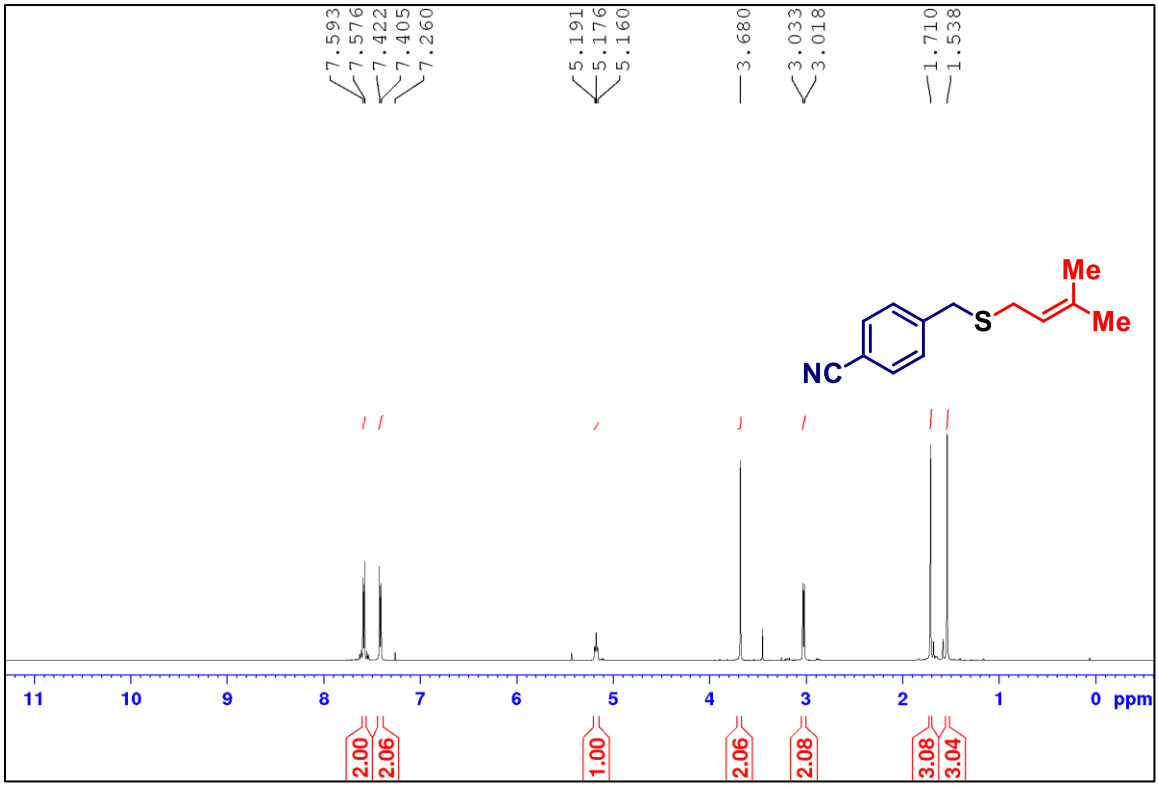


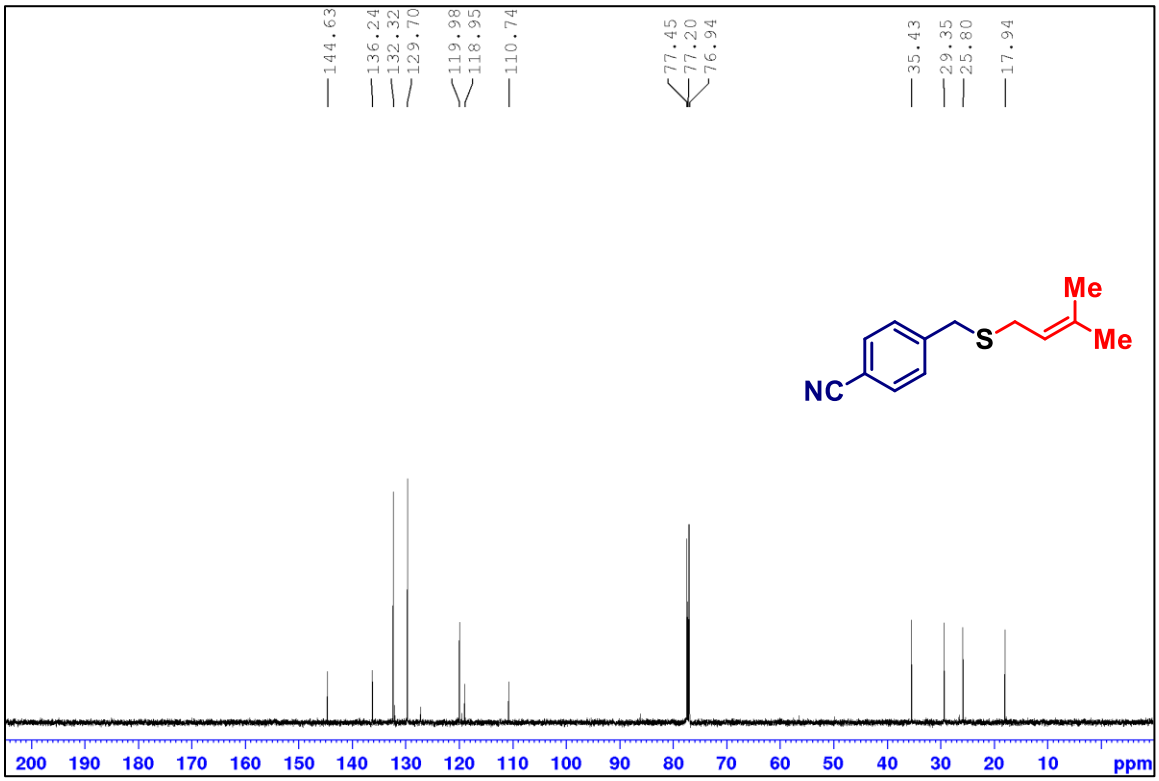
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 6g in $CDCl_3$



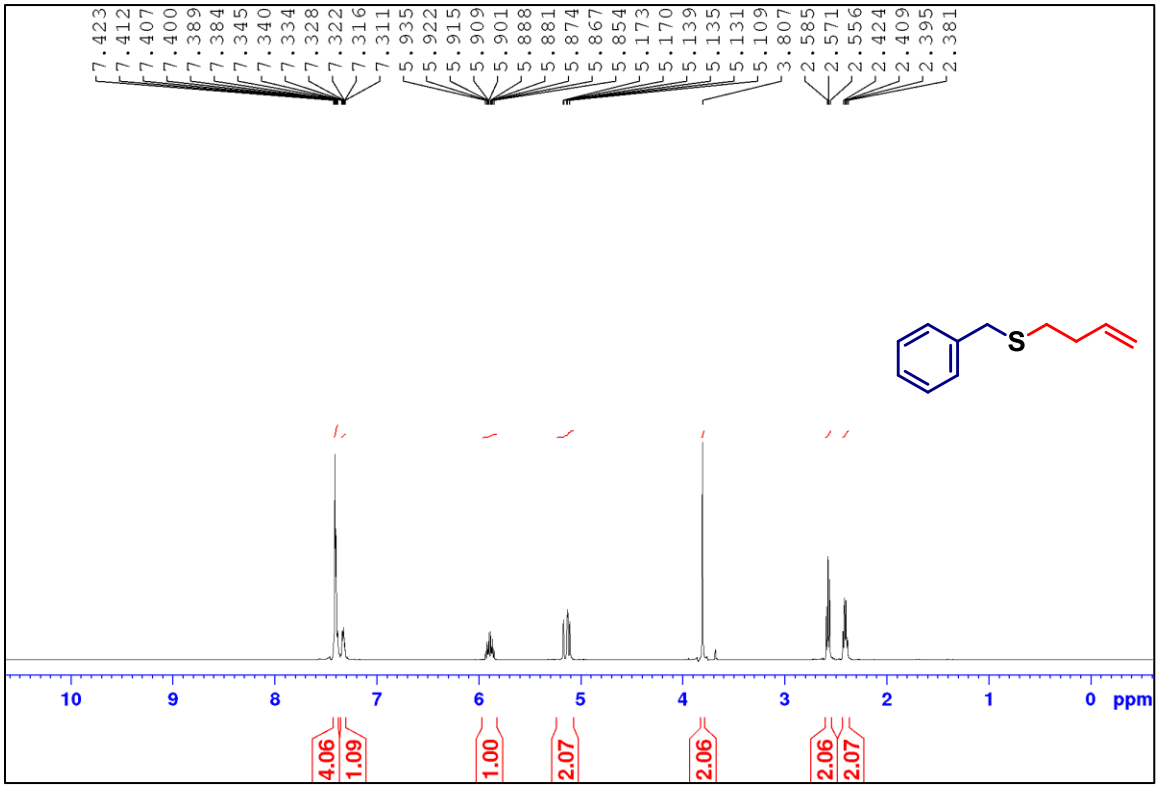


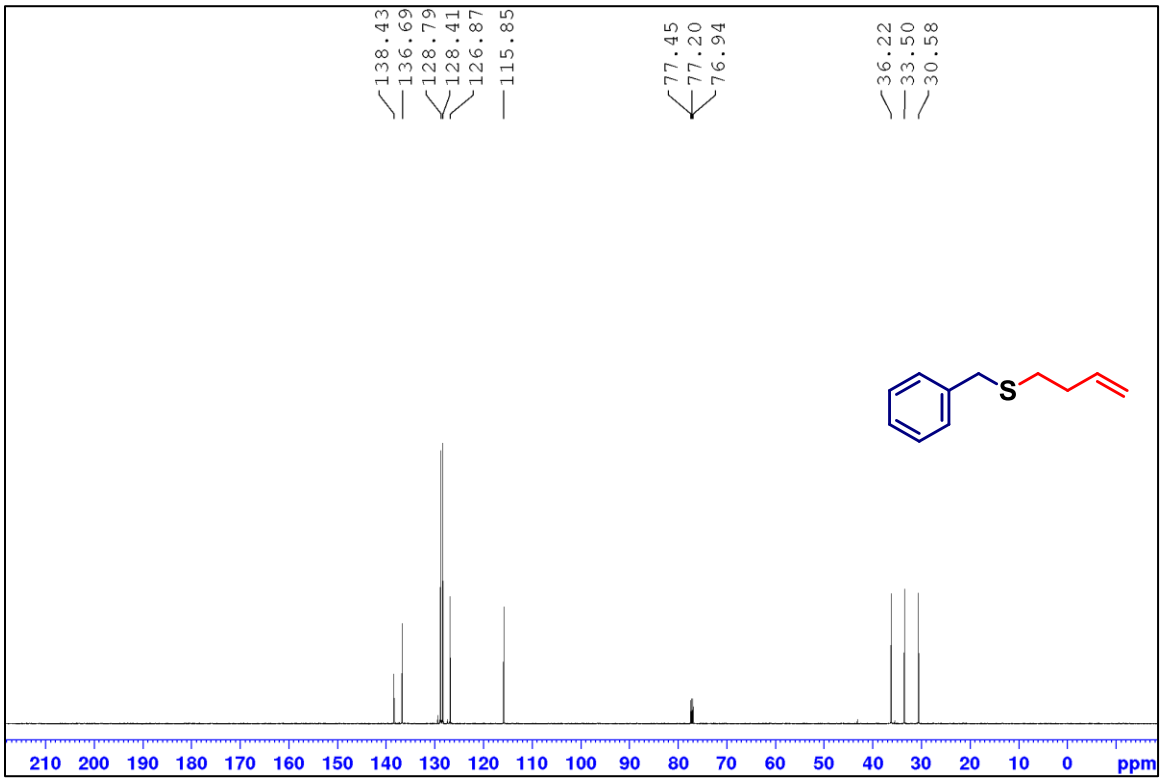
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 6h in $CDCl_3$



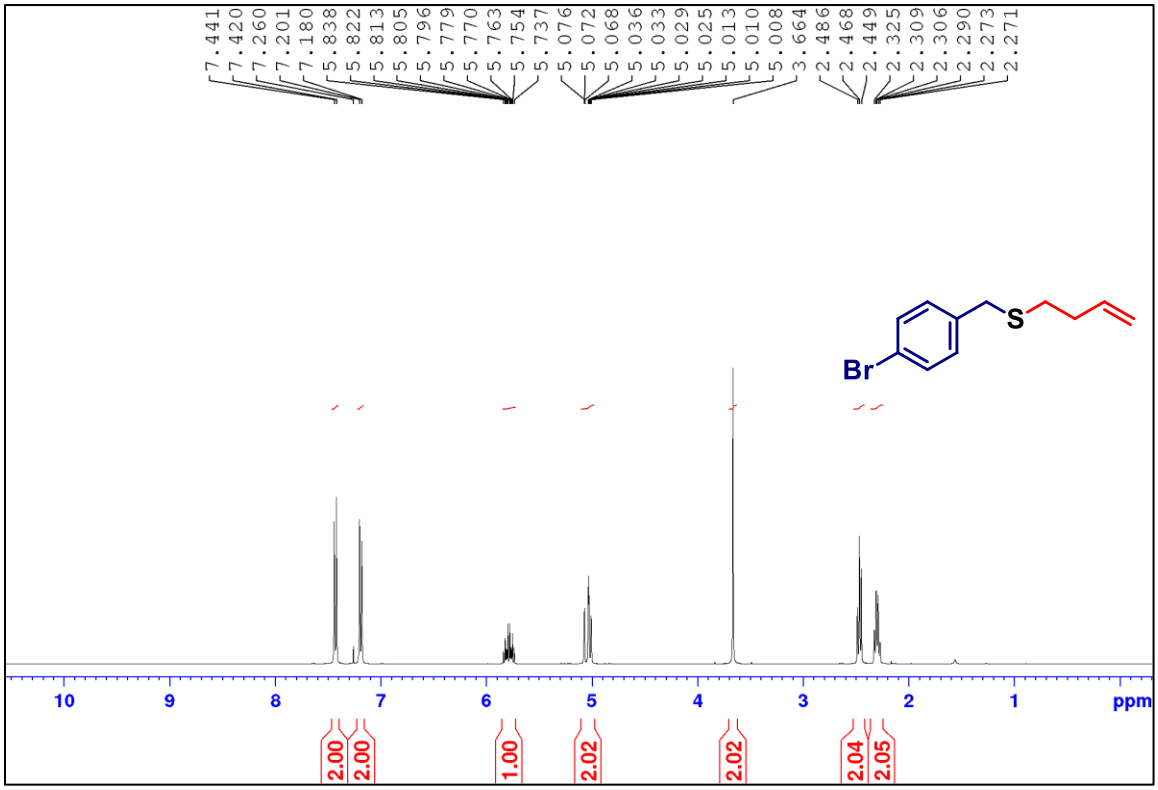


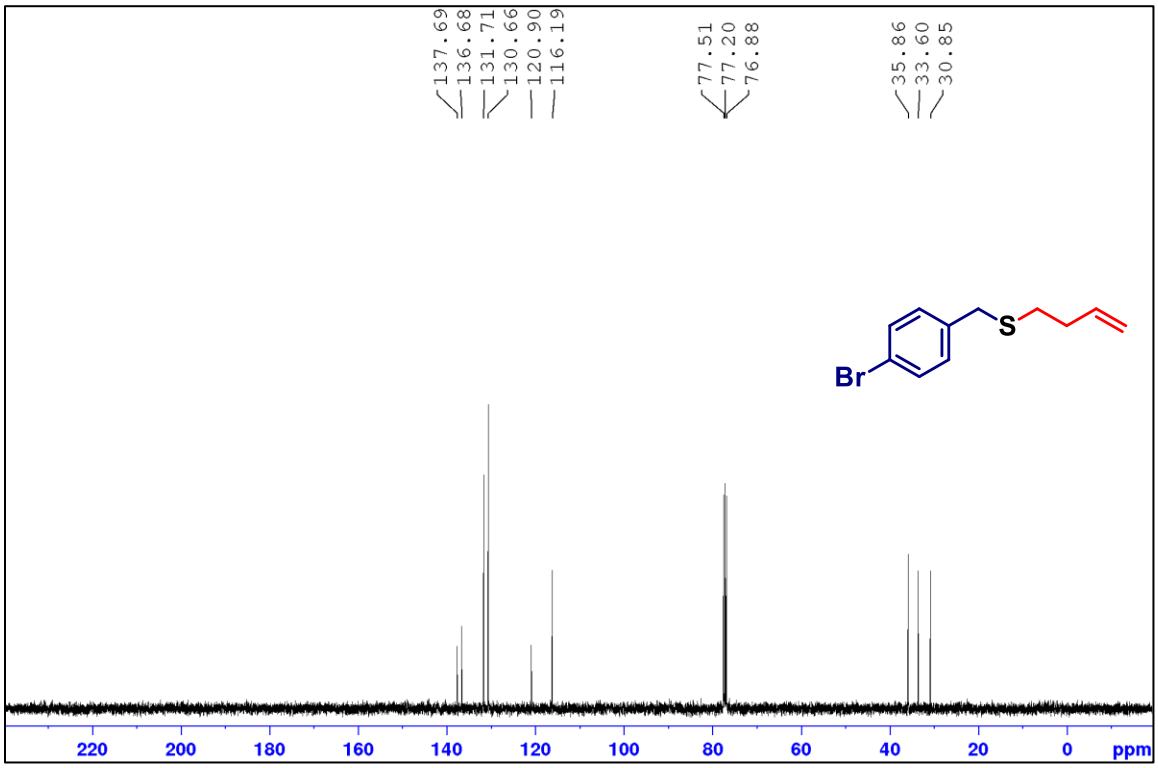
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 7a in $CDCl_3$



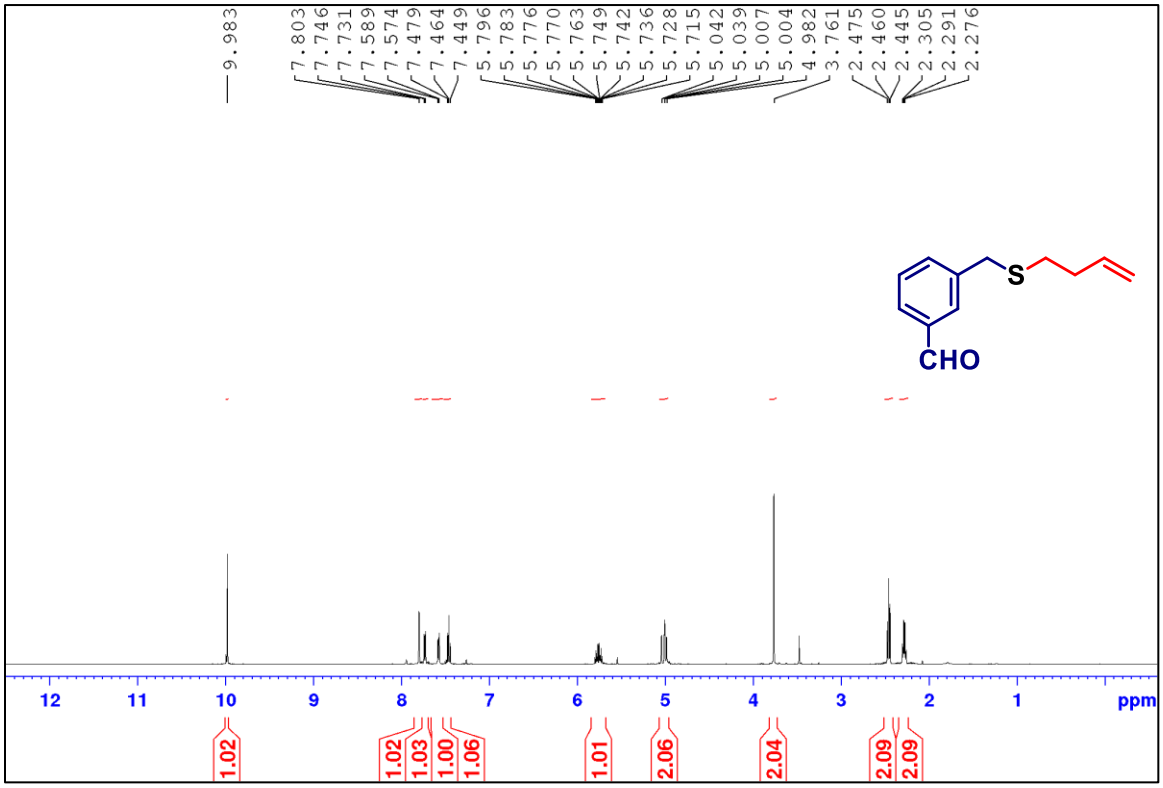


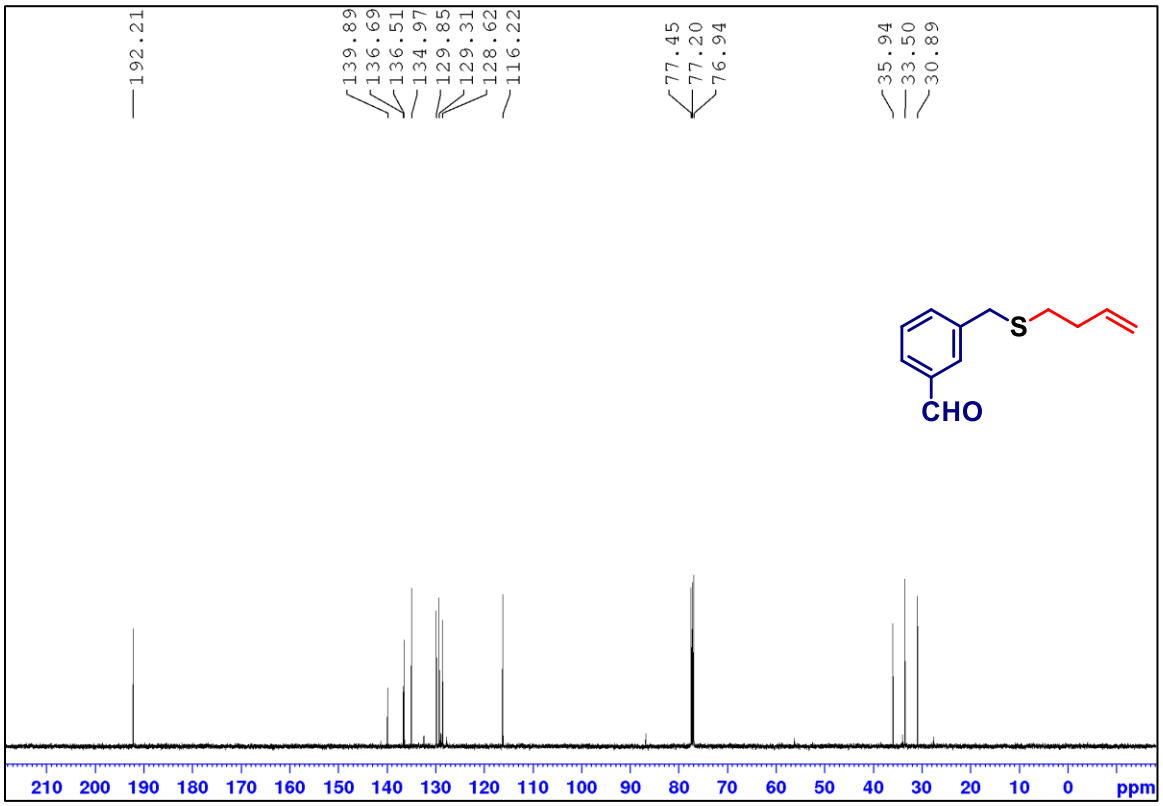
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 7b in $CDCl_3$



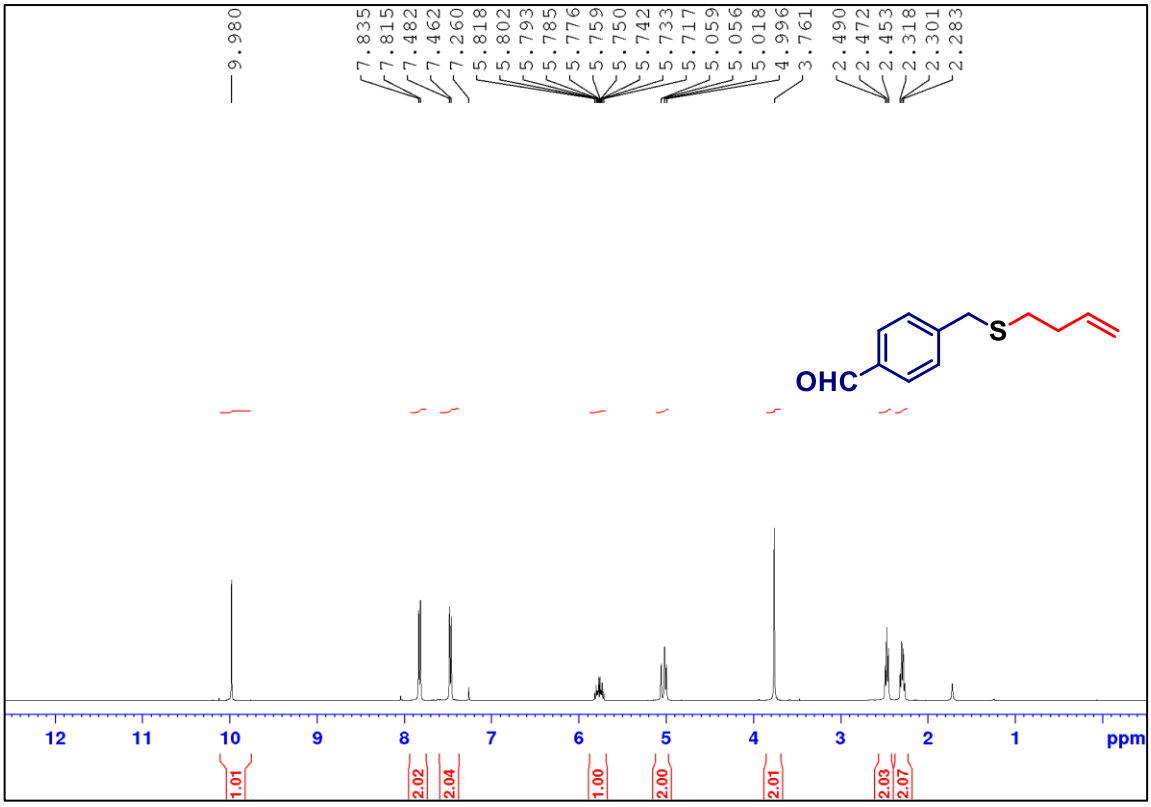


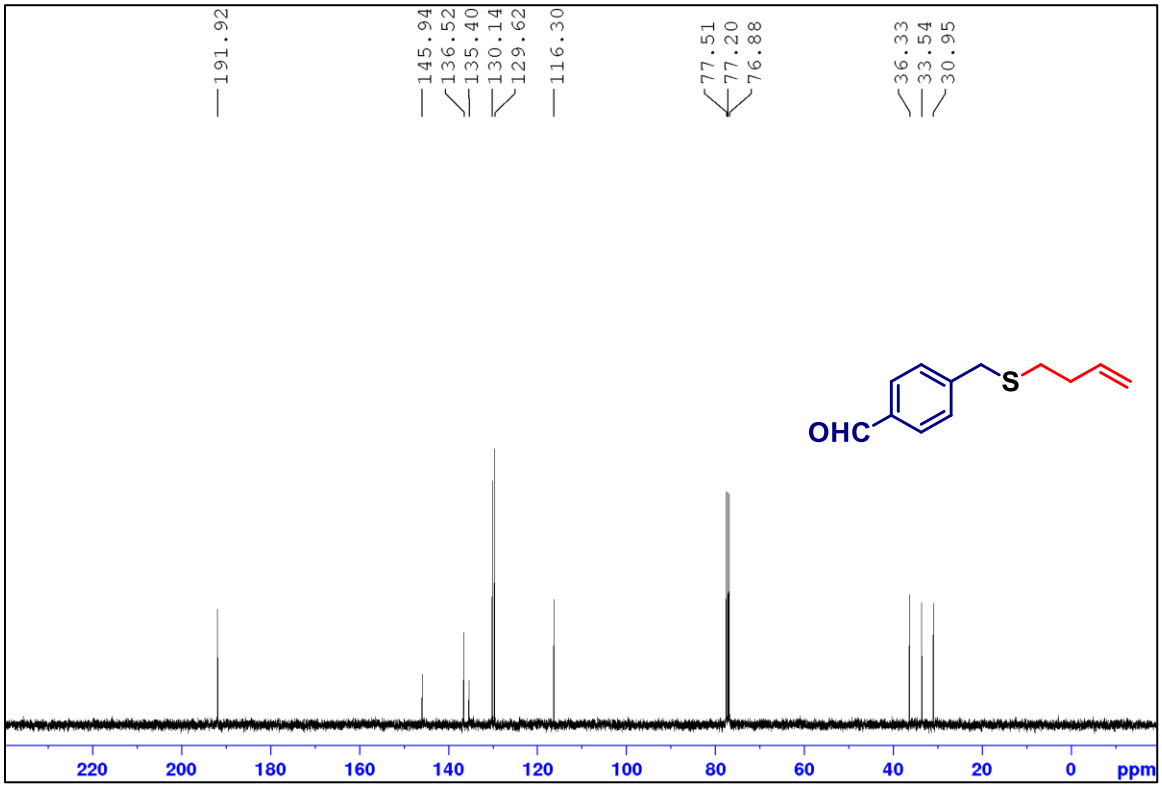
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 7c in $CDCl_3$



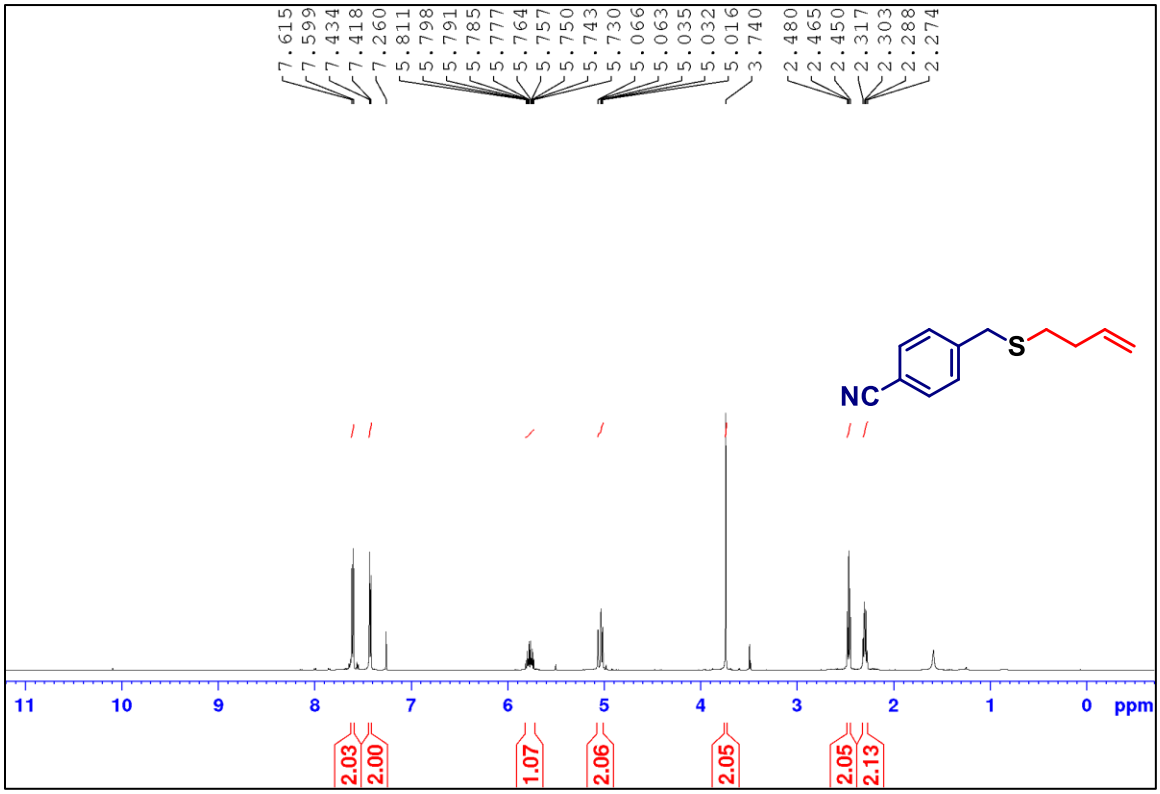


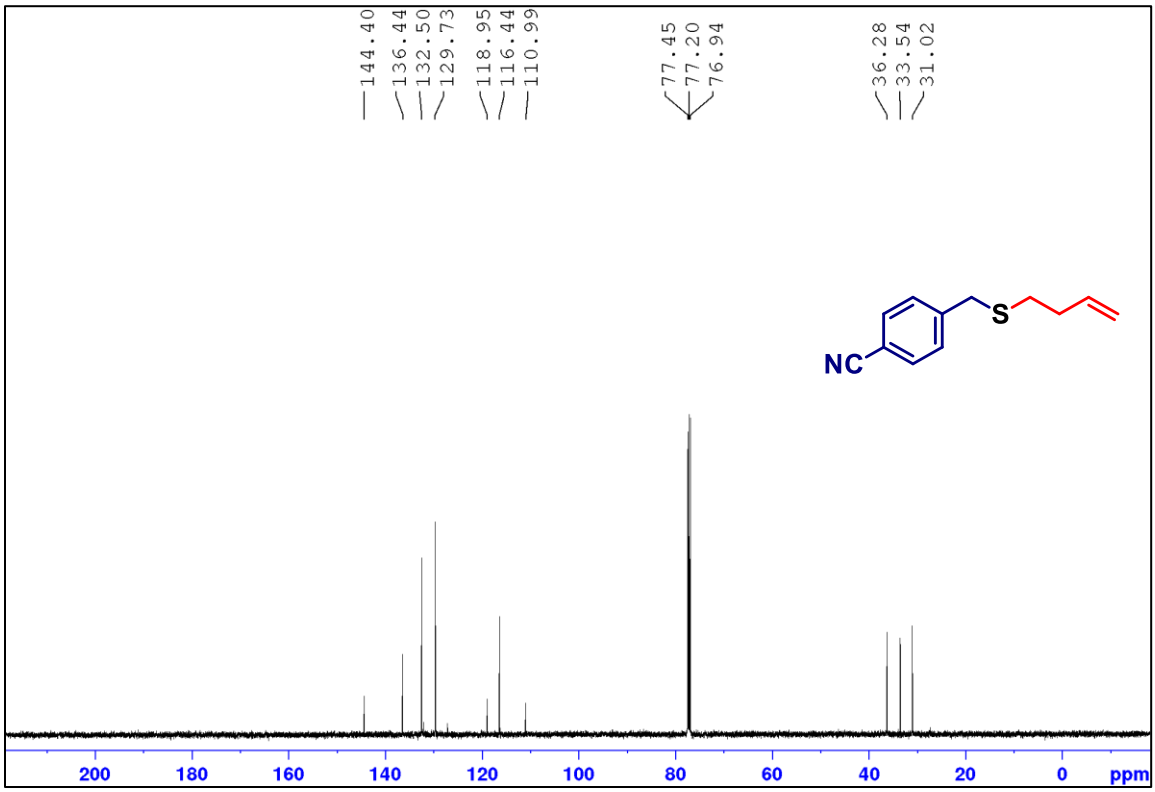
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 7d in $CDCl_3$



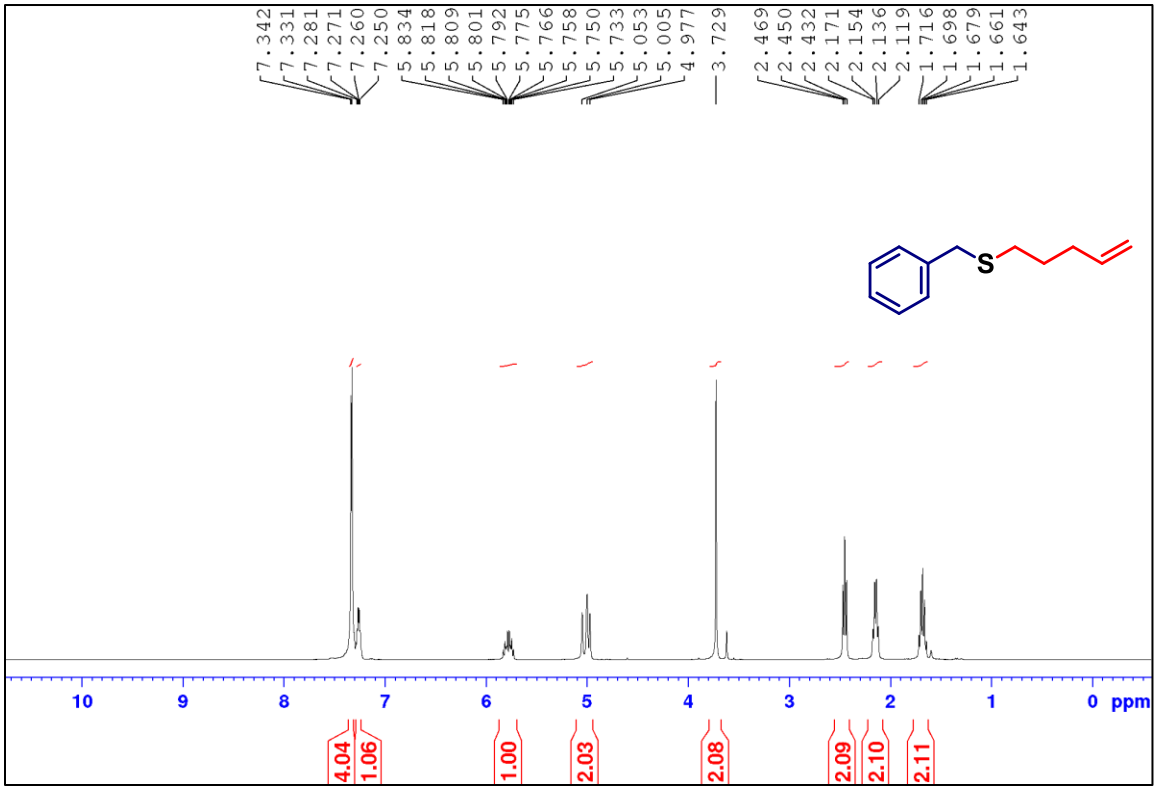


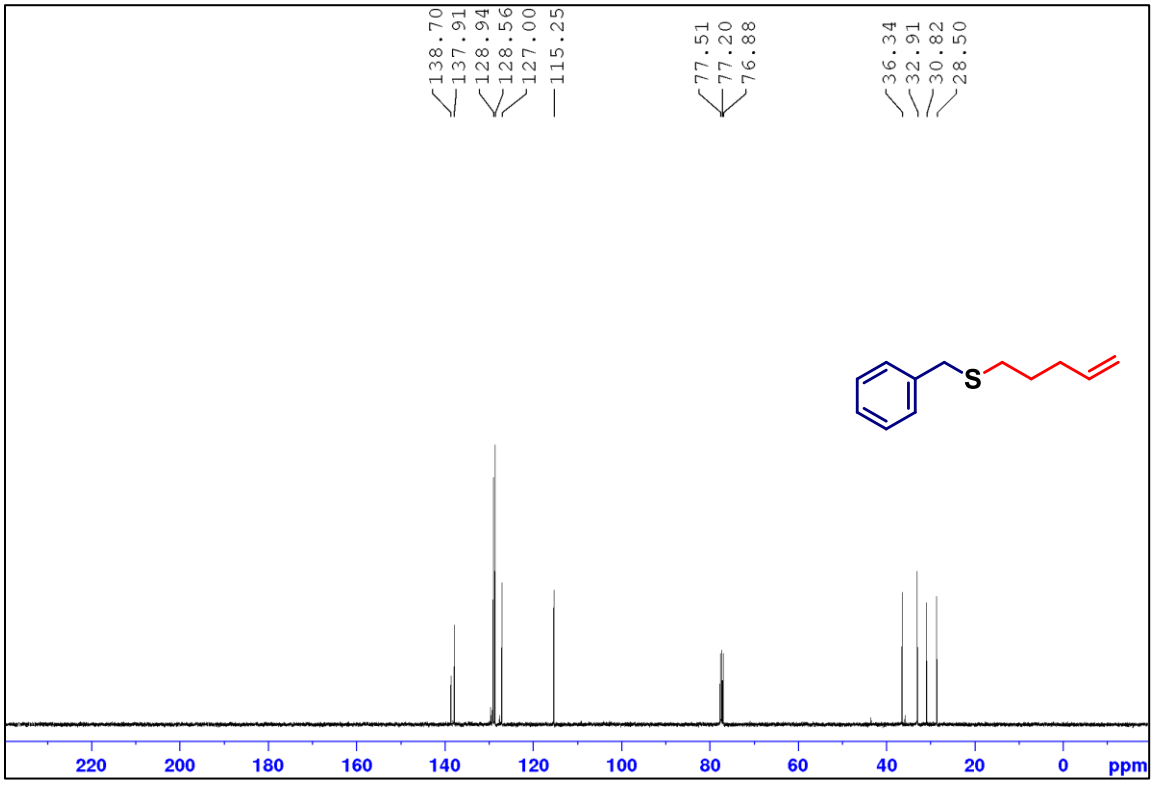
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 7e in $CDCl_3$



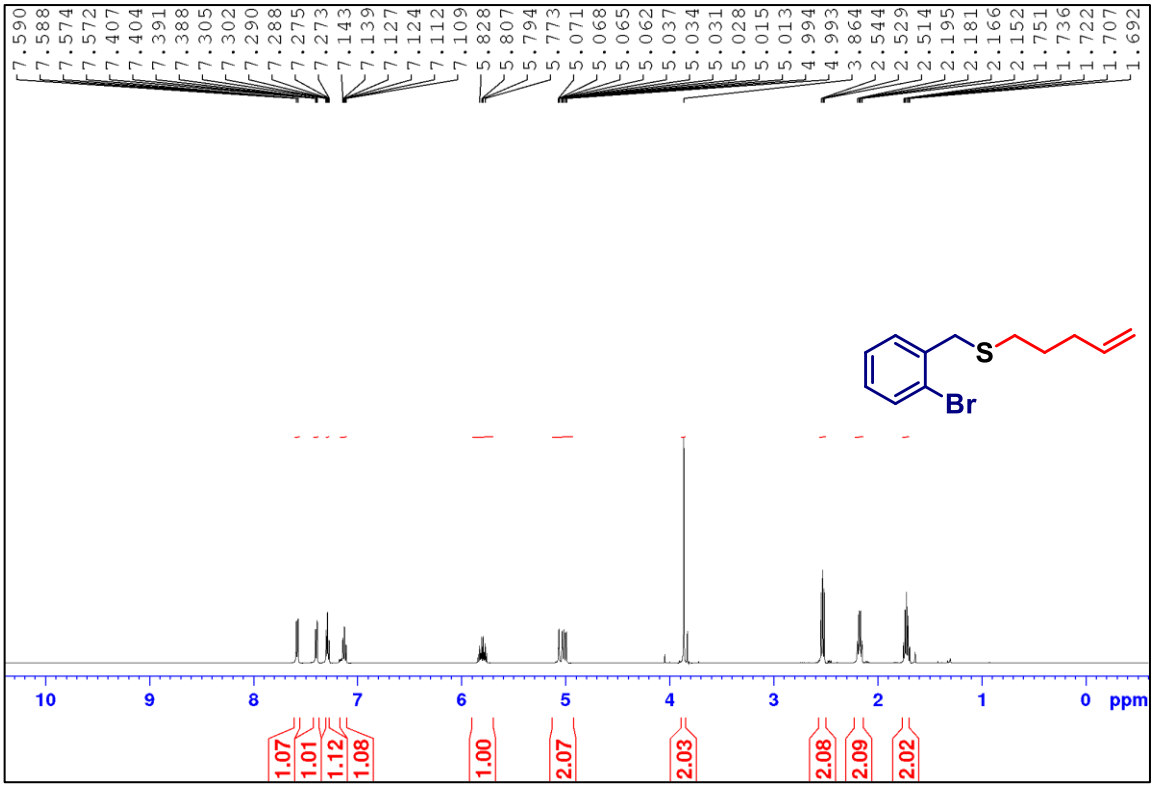


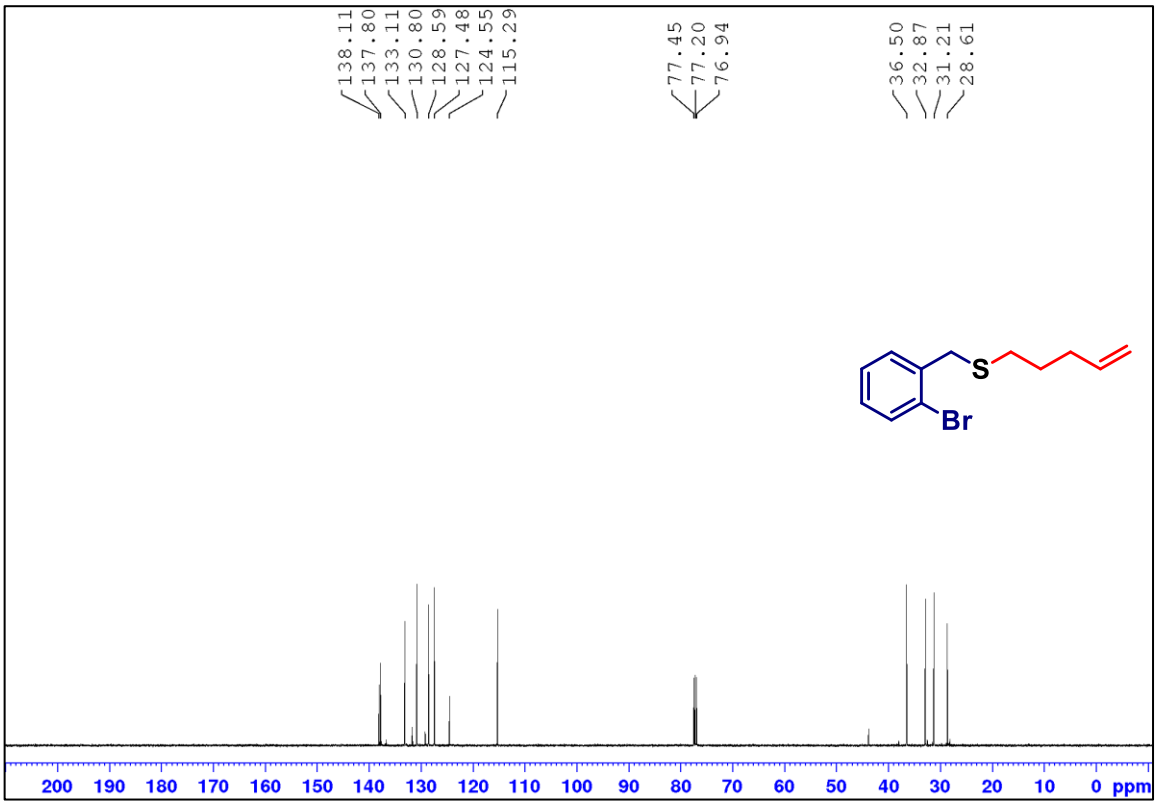
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 8a in $CDCl_3$



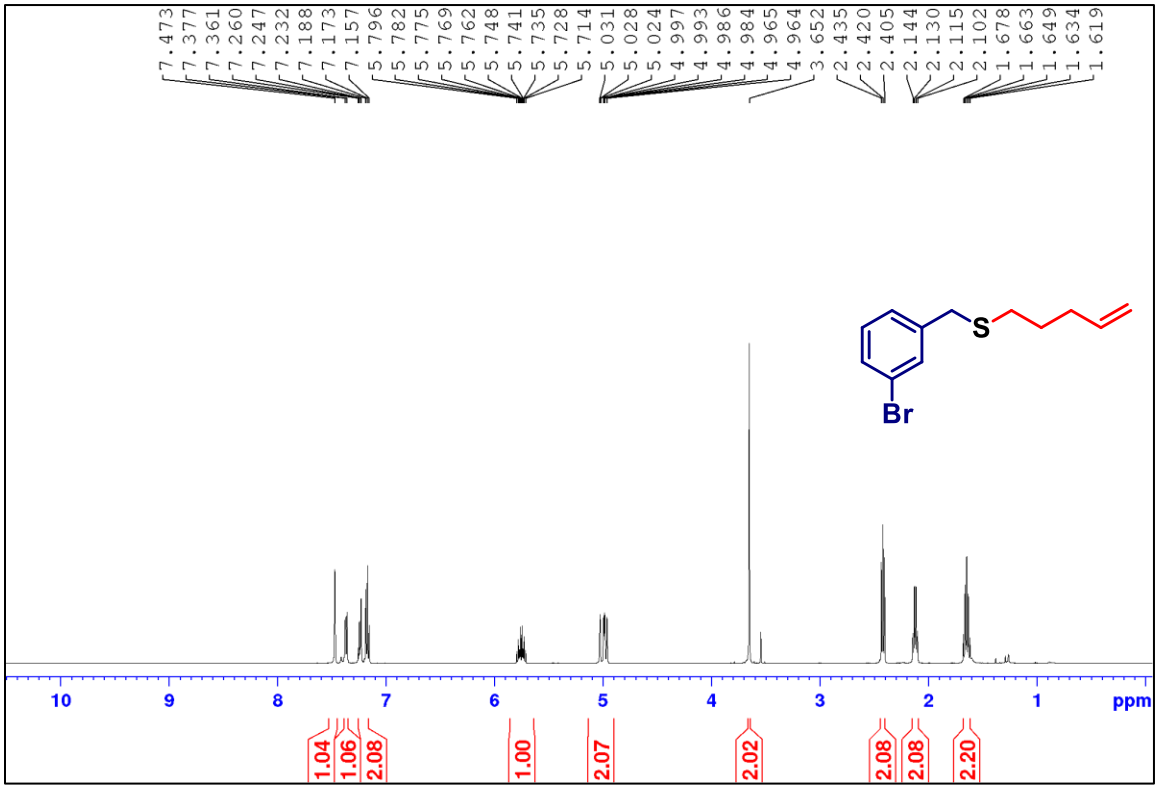


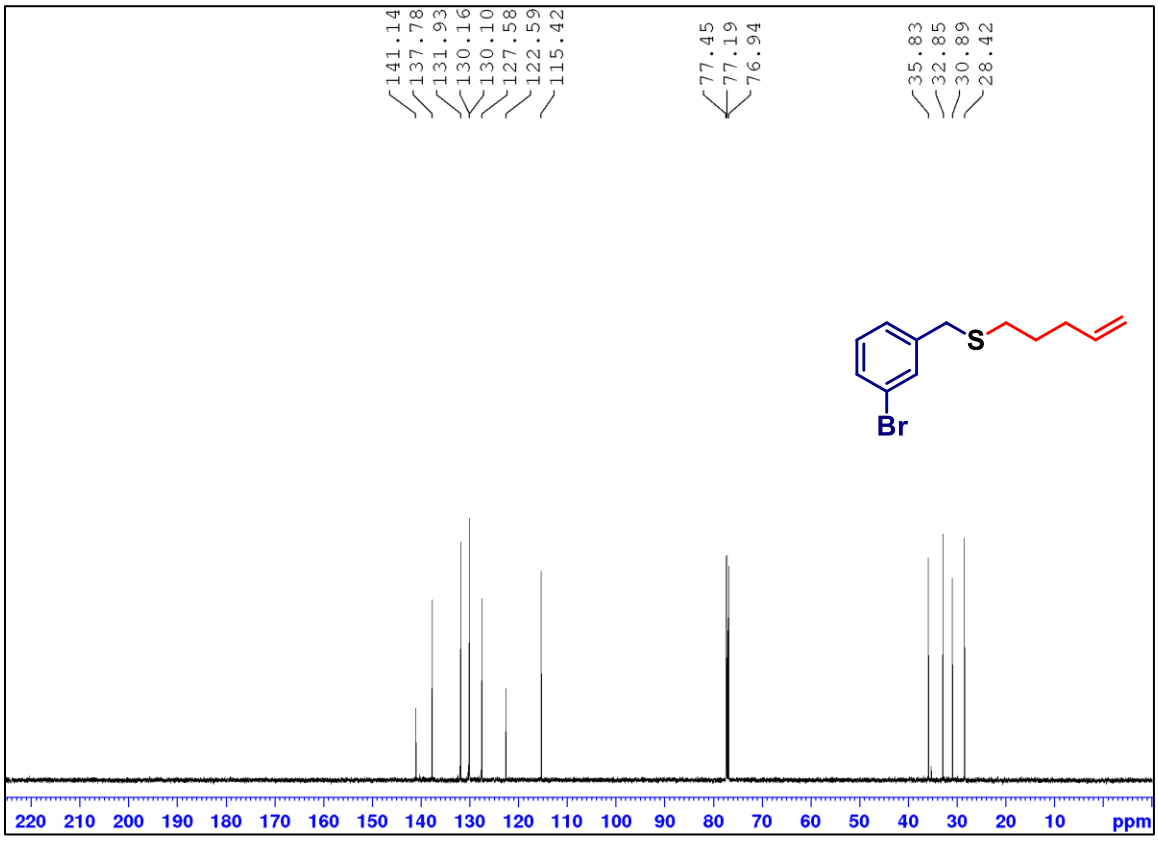
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 8b in $CDCl_3$



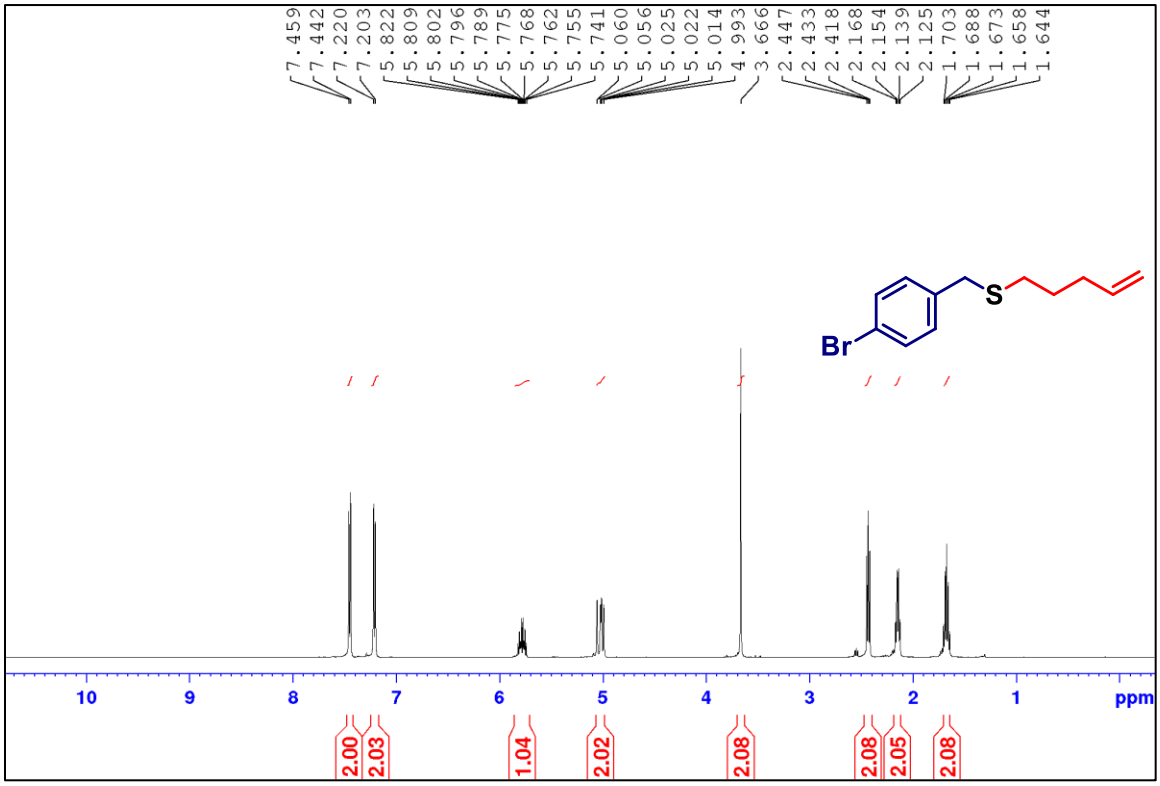


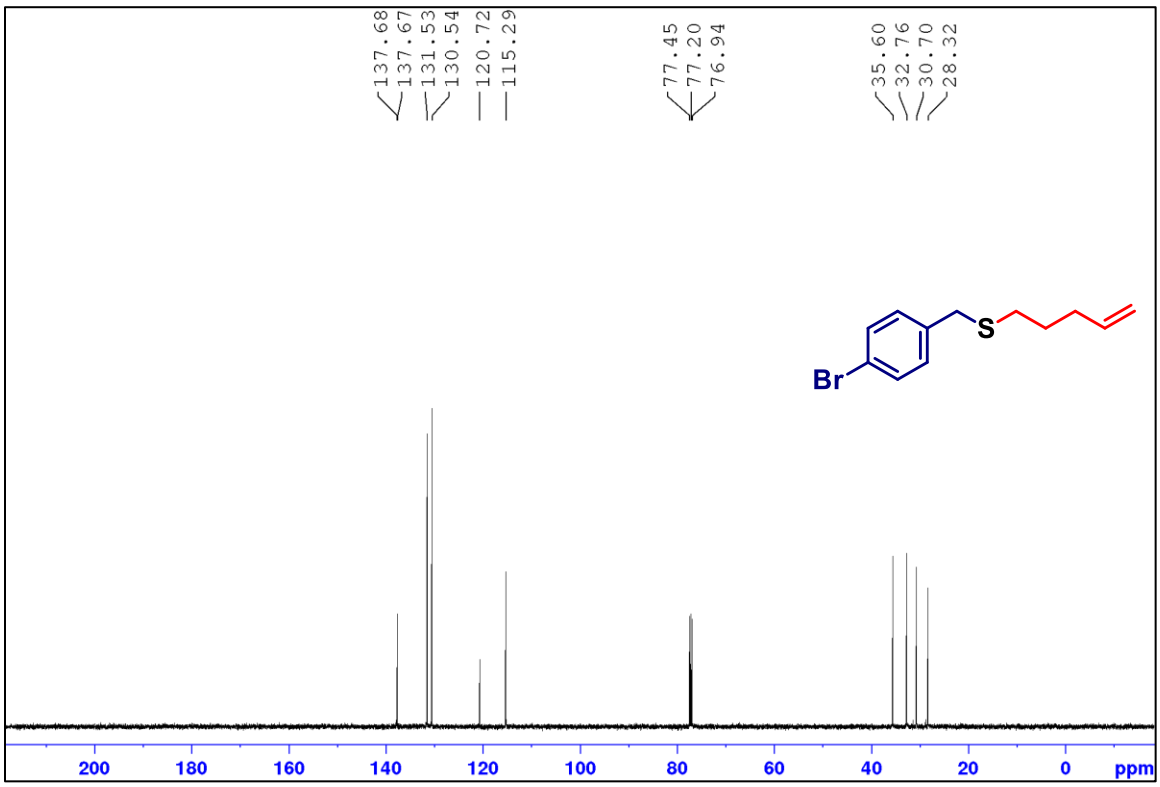
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 8c in $CDCl_3$



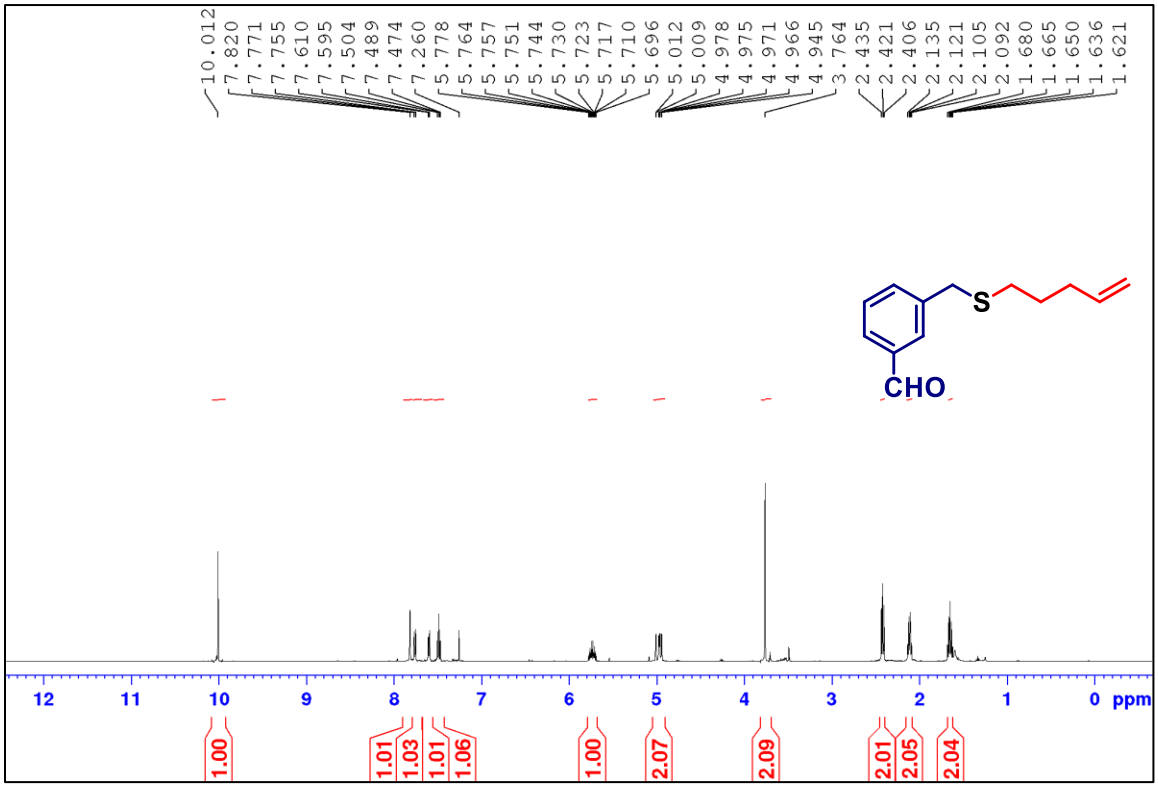


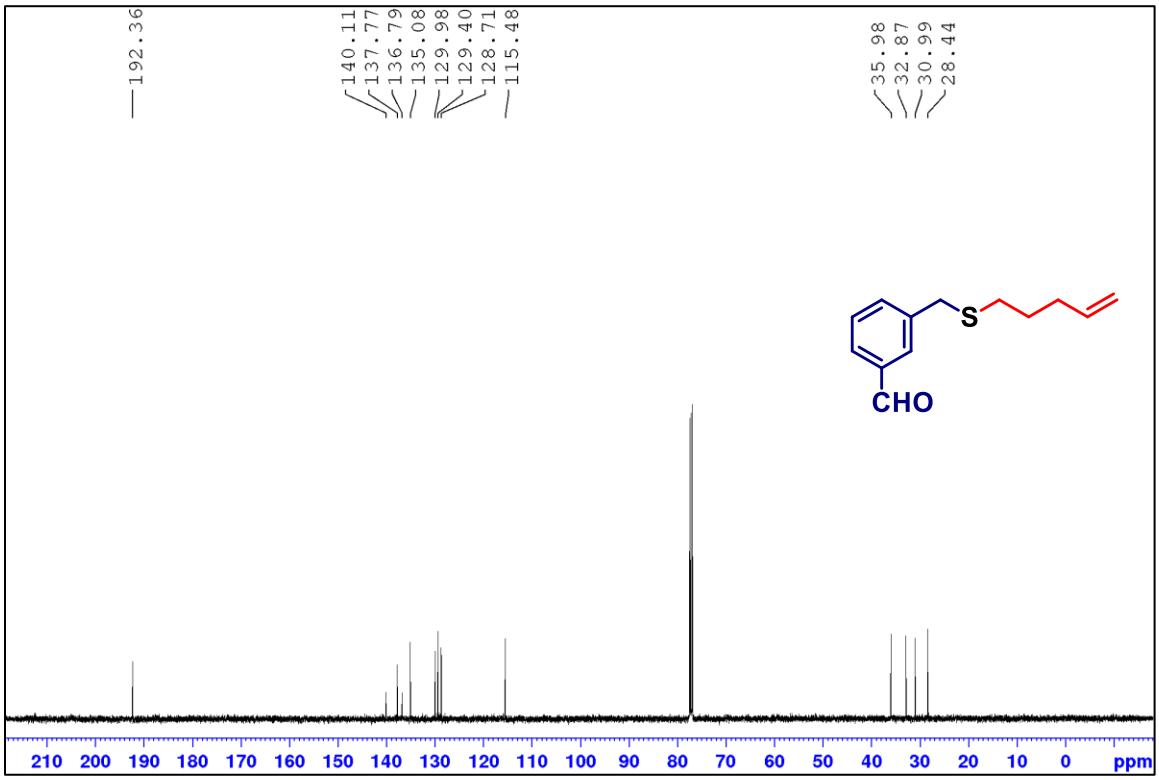
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 8d in $CDCl_3$



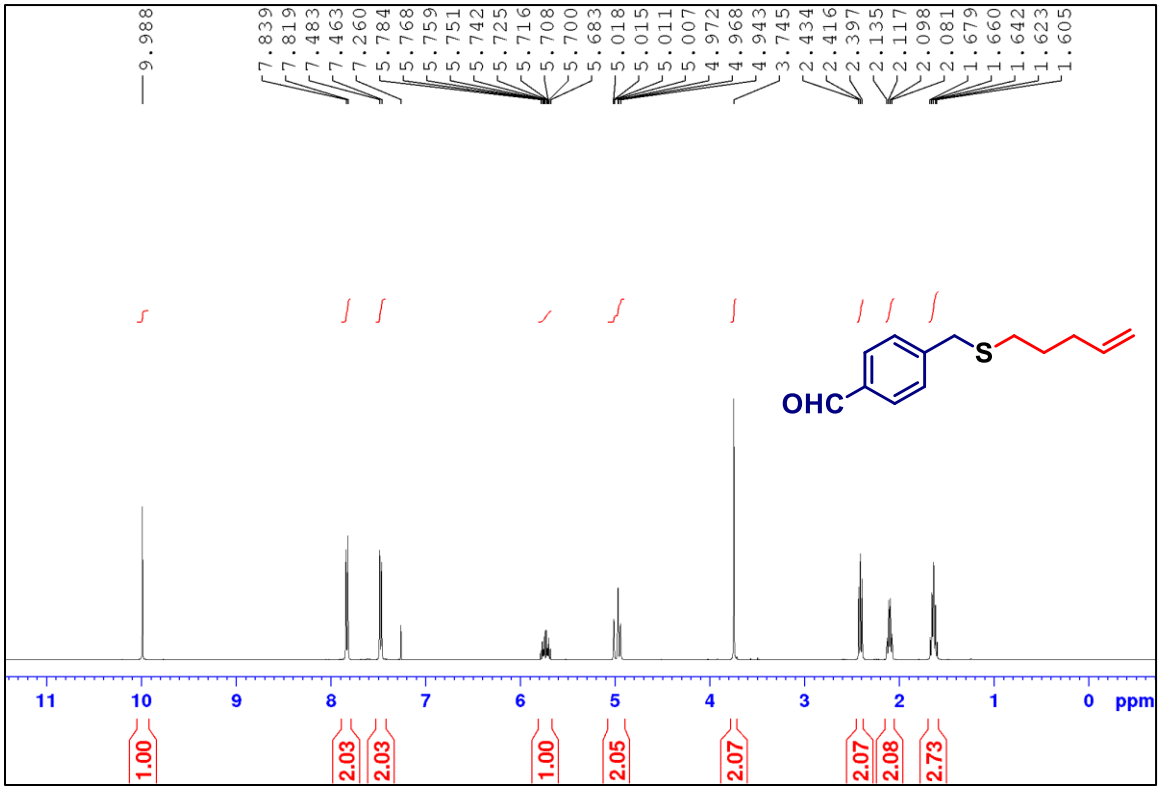


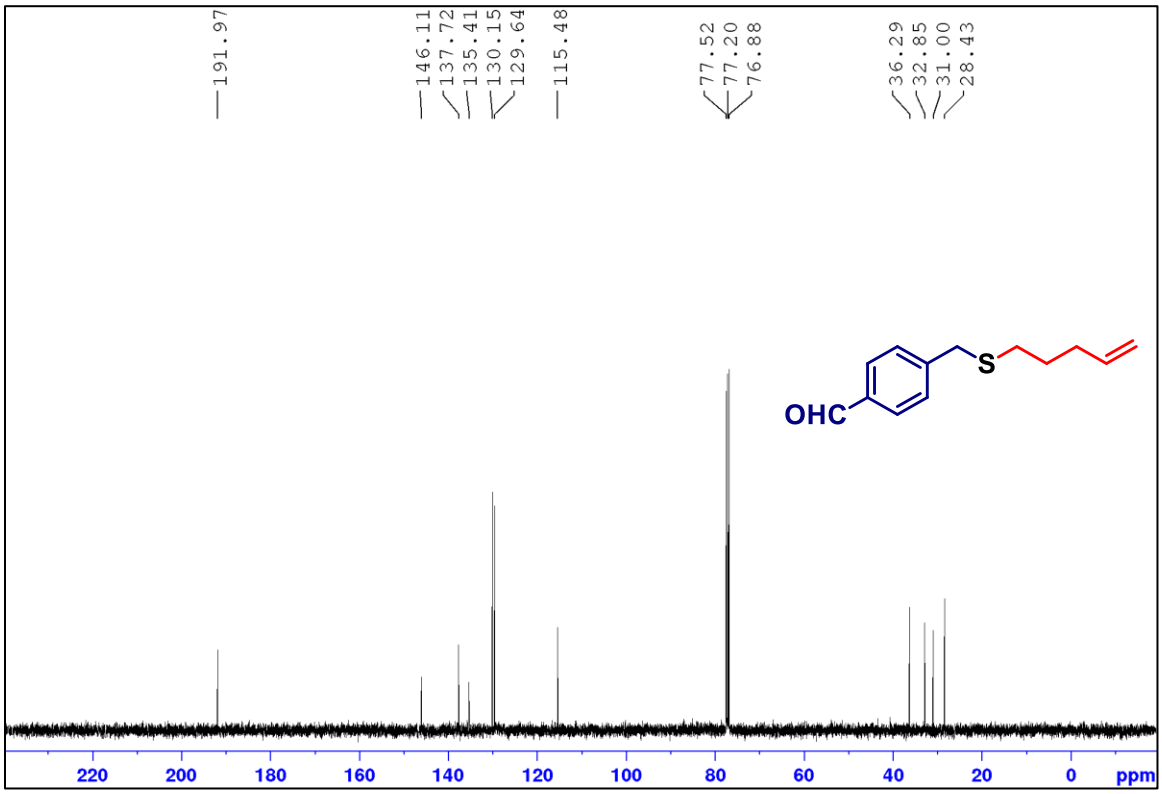
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 8e in $CDCl_3$



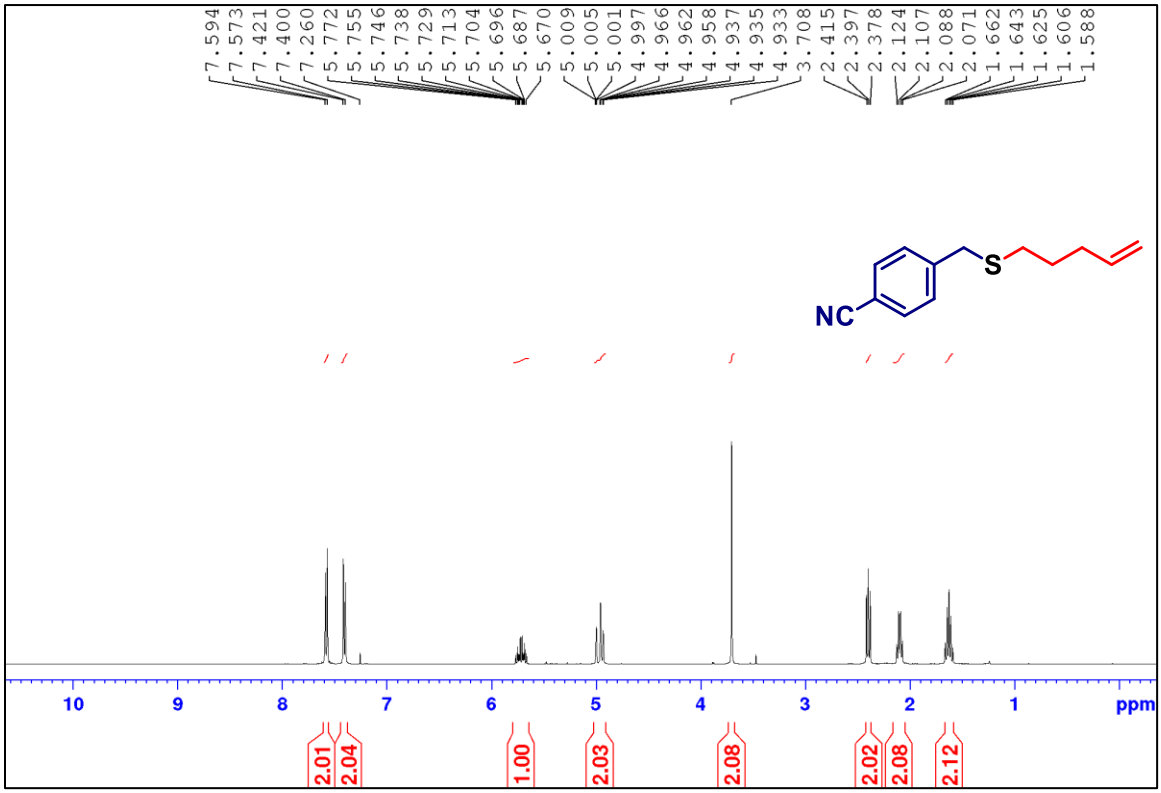


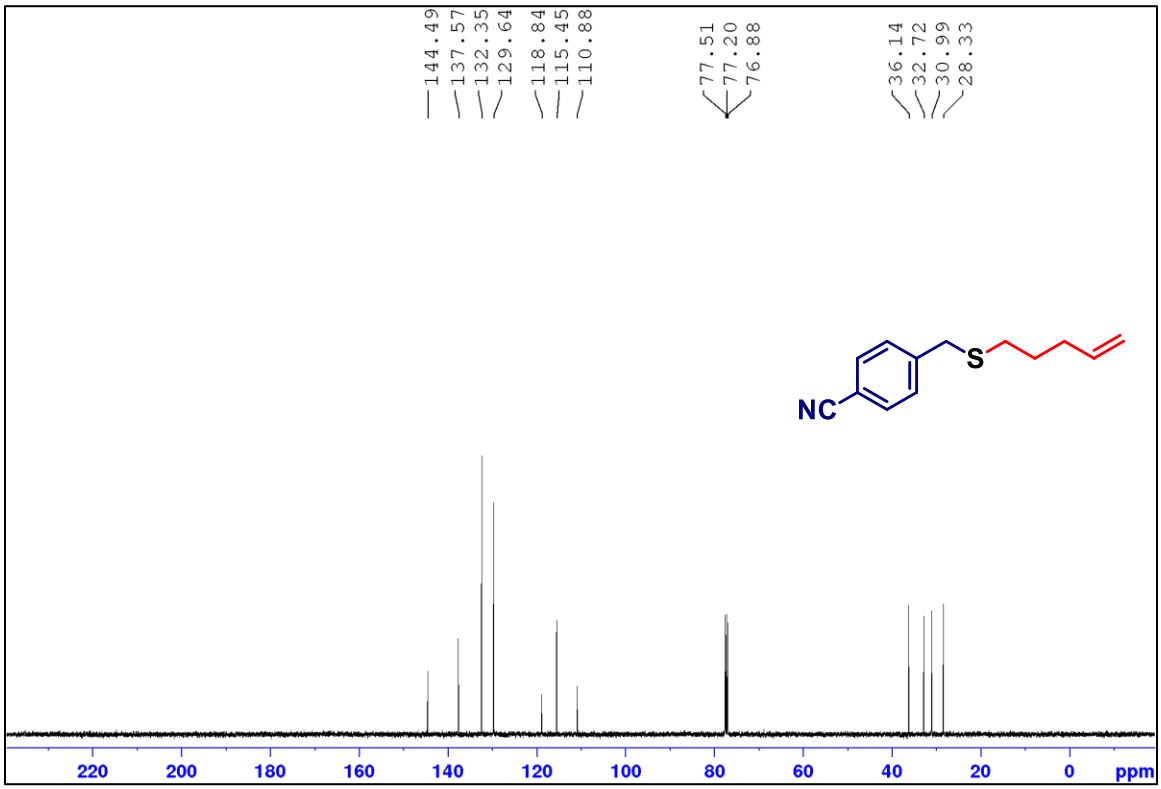
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 8f in $CDCl_3$



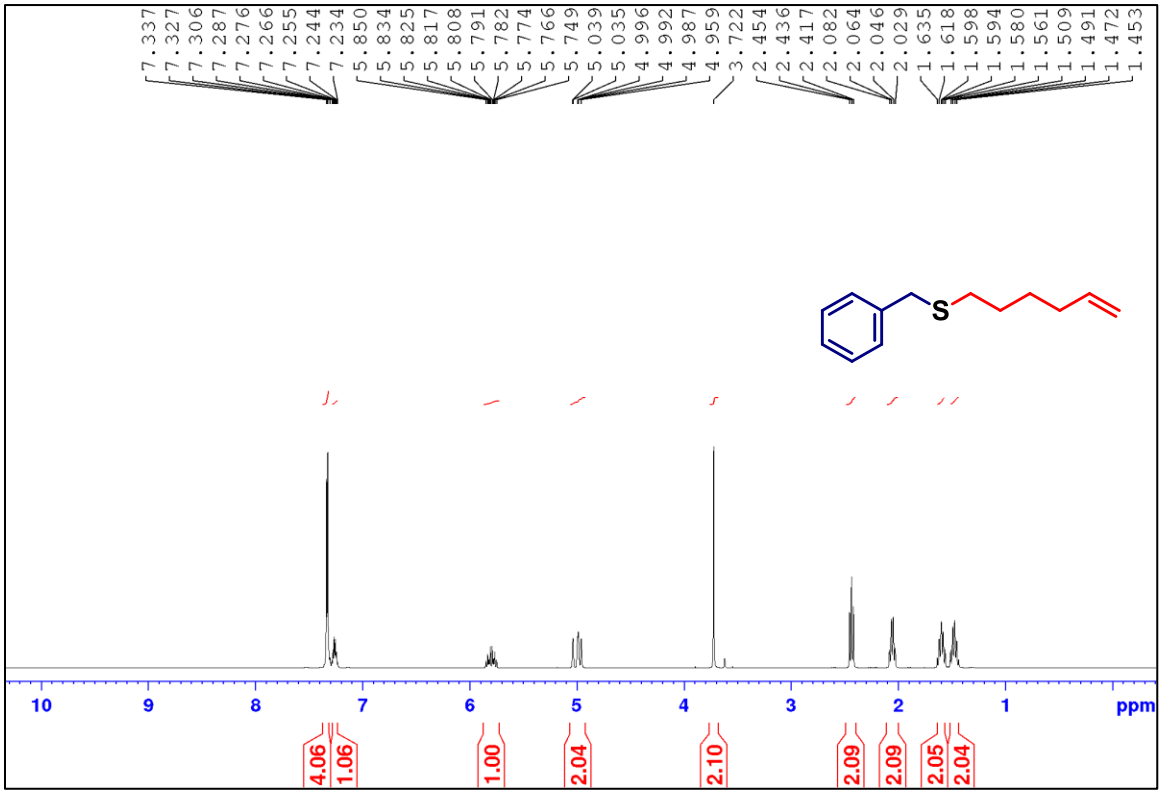


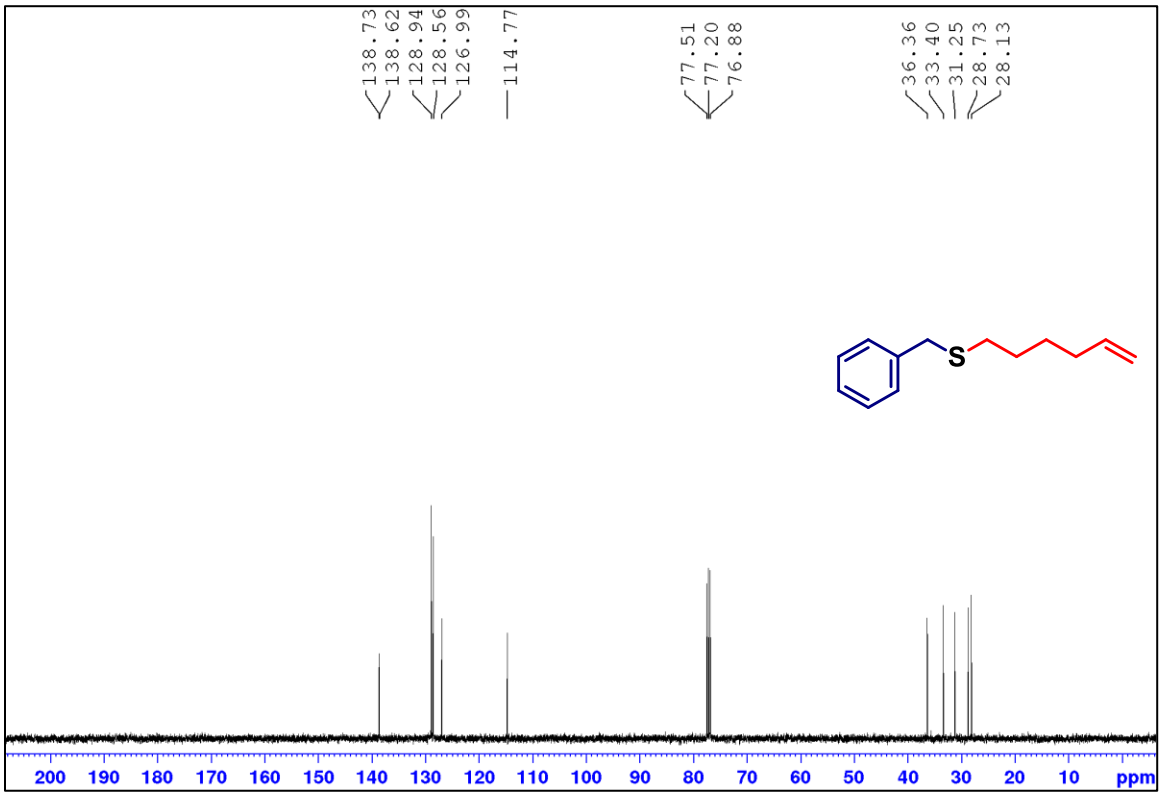
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 8g in $CDCl_3$



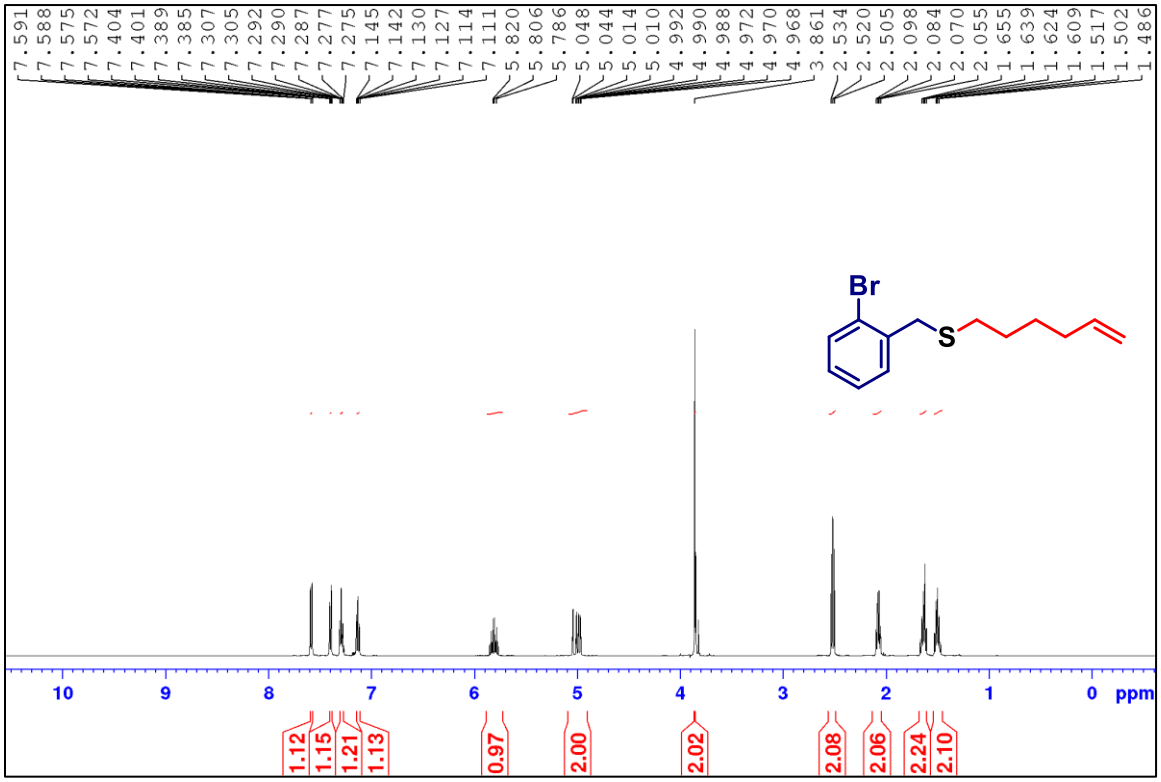


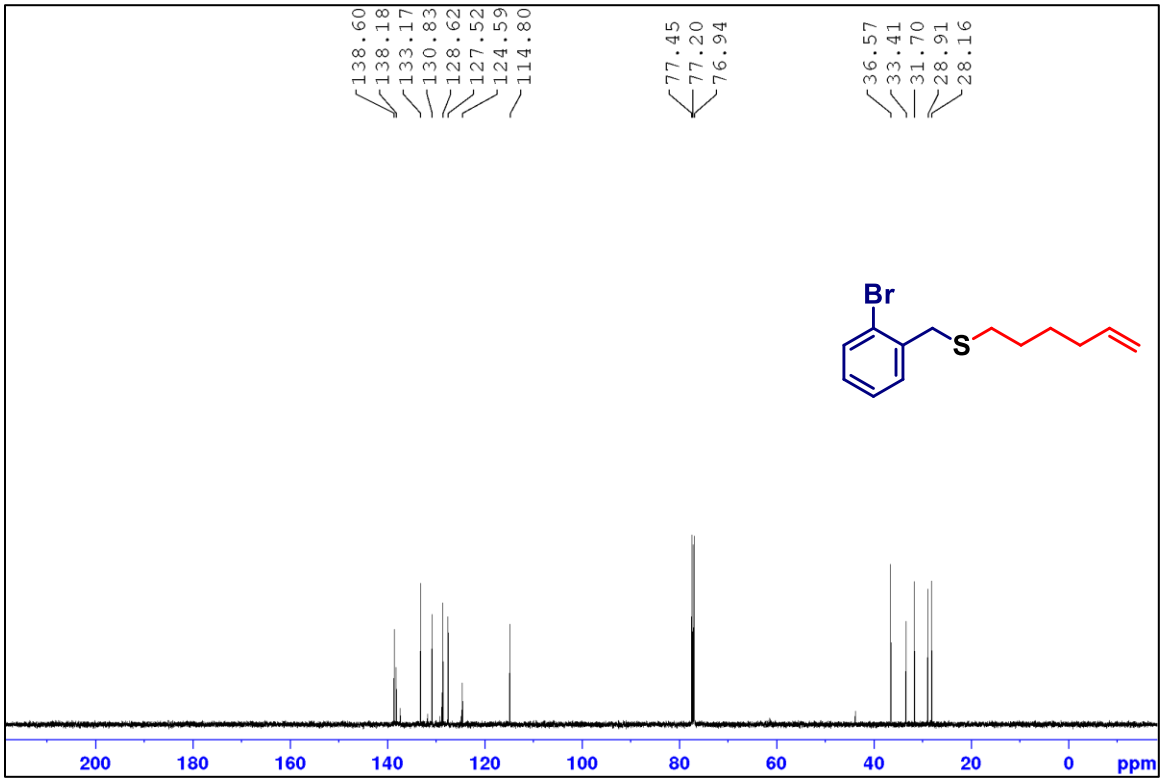
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 9a in $CDCl_3$



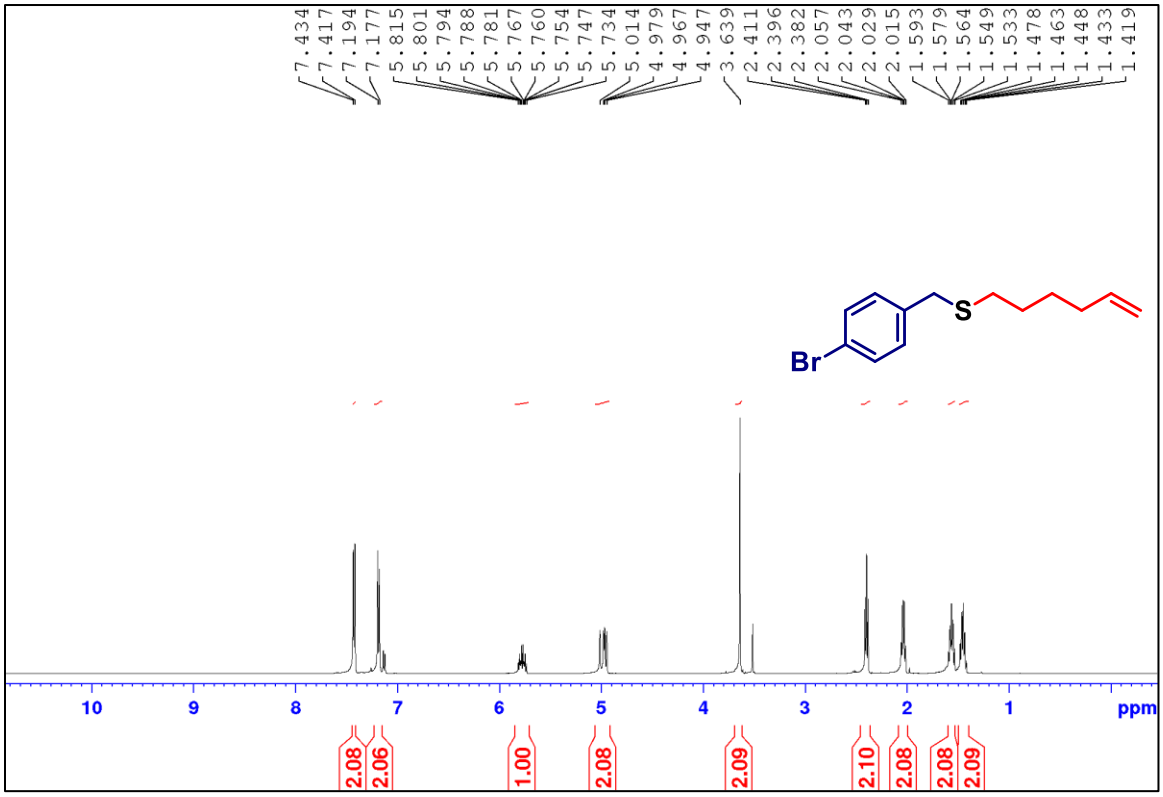


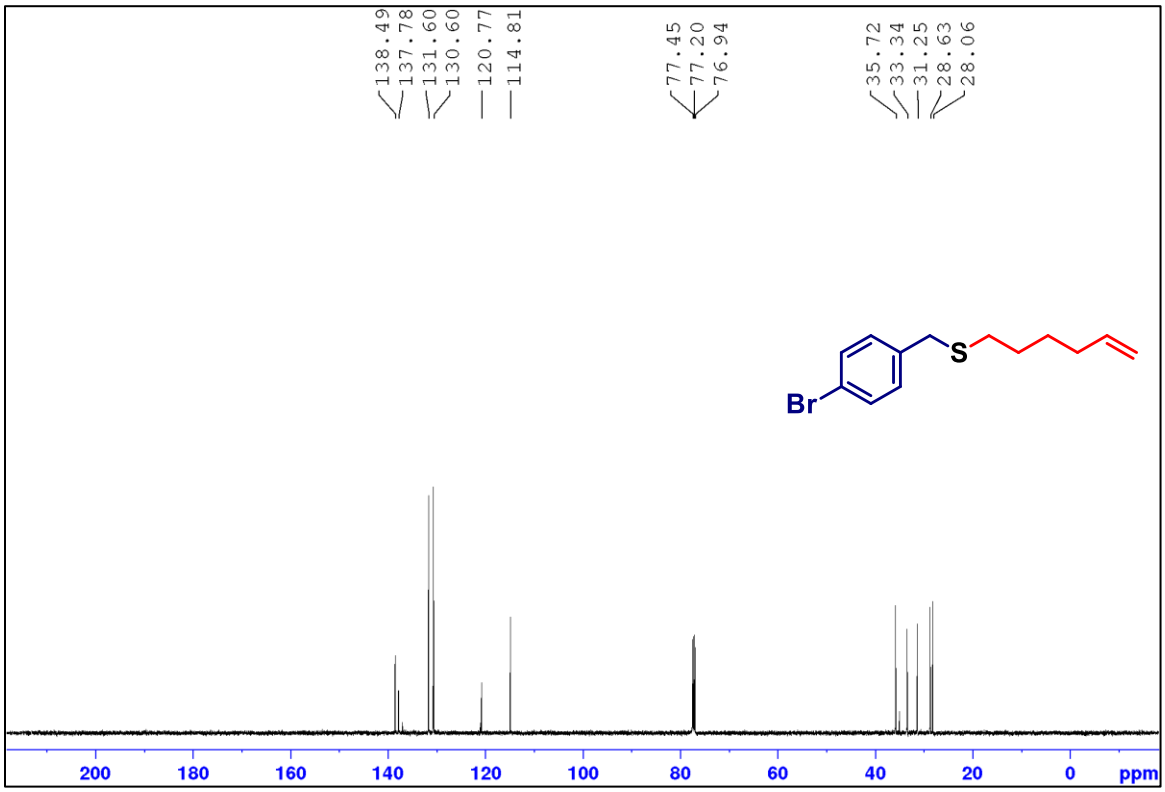
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 9b in $CDCl_3$



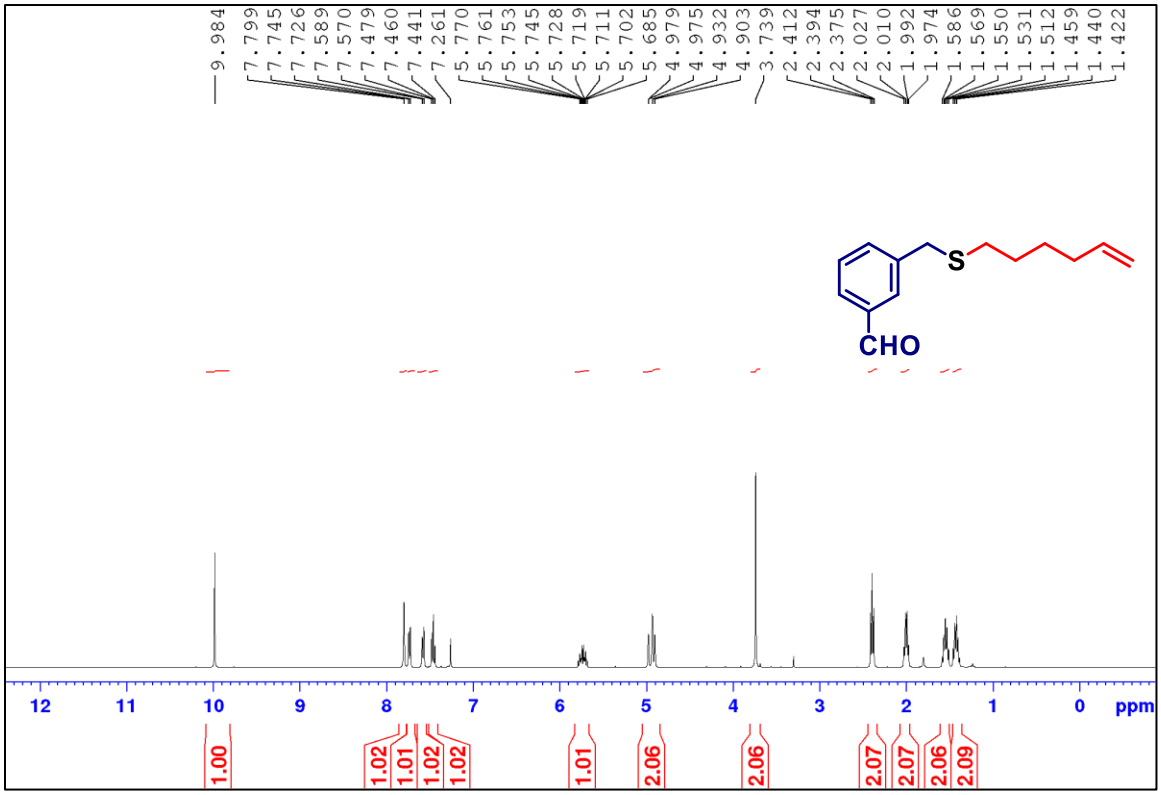


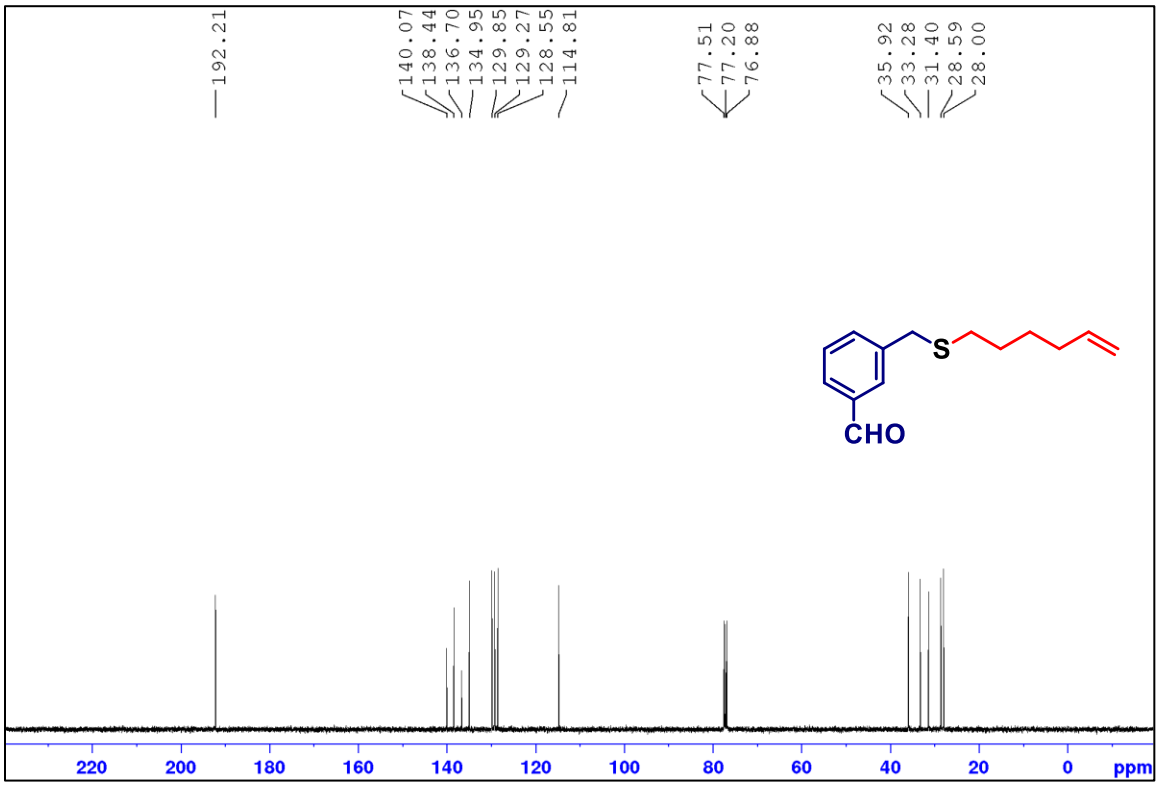
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 9c in $CDCl_3$



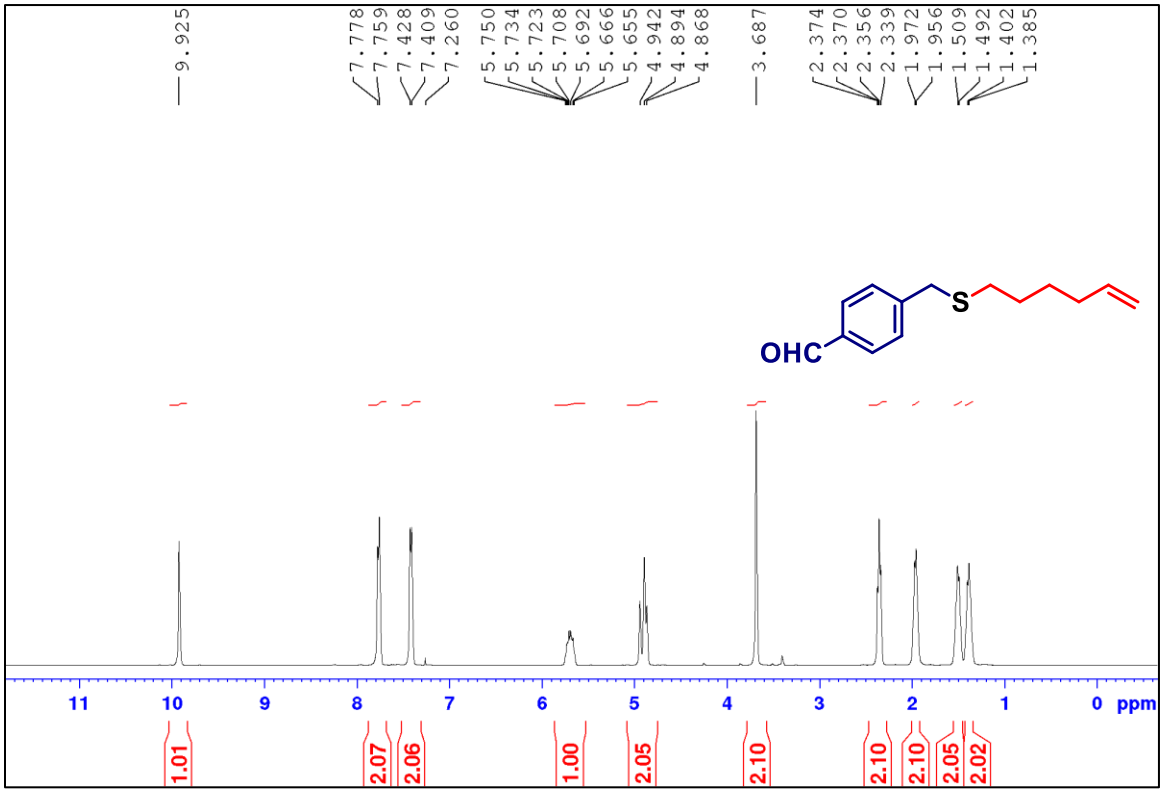


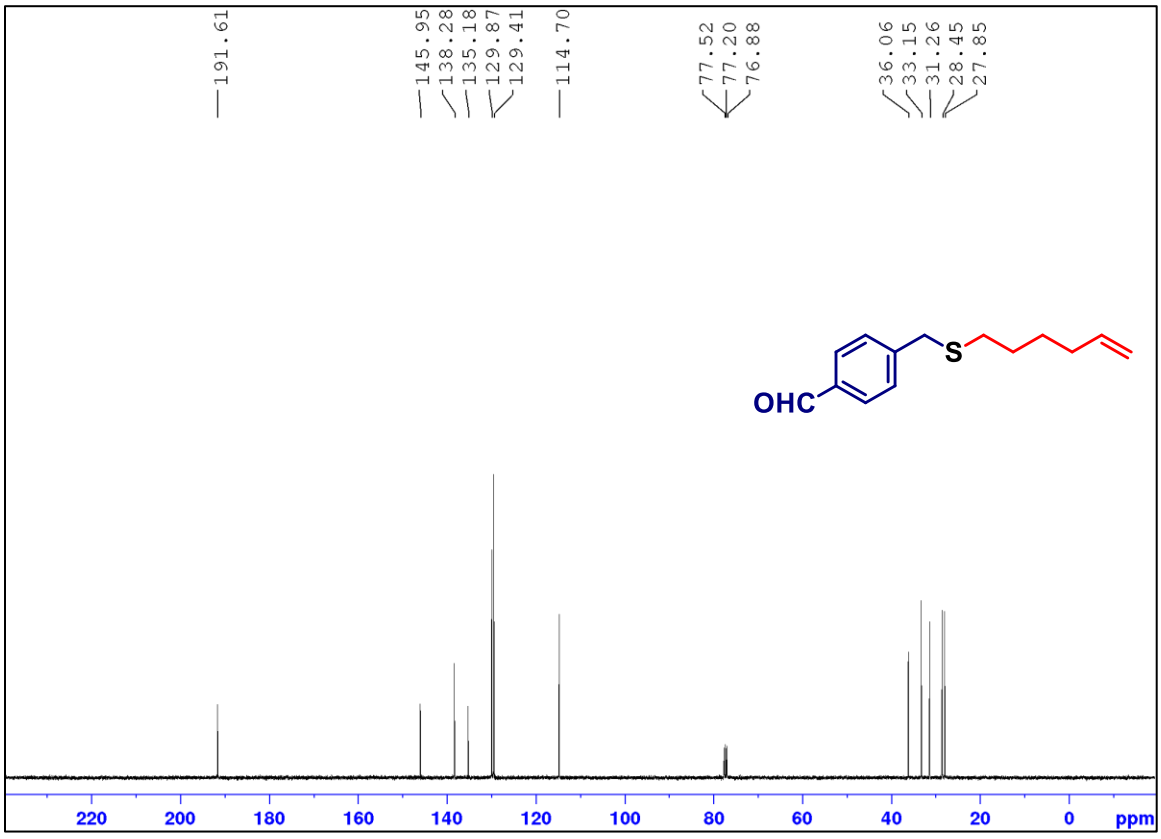
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 9d in $CDCl_3$



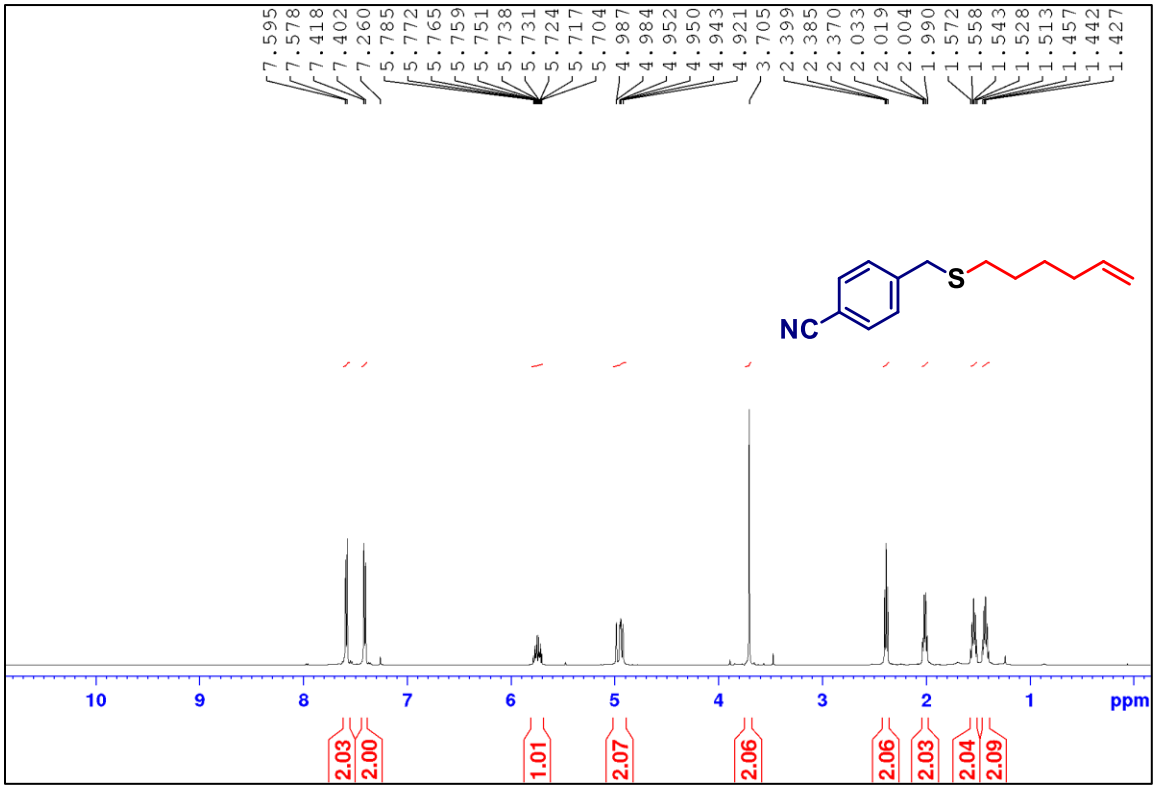


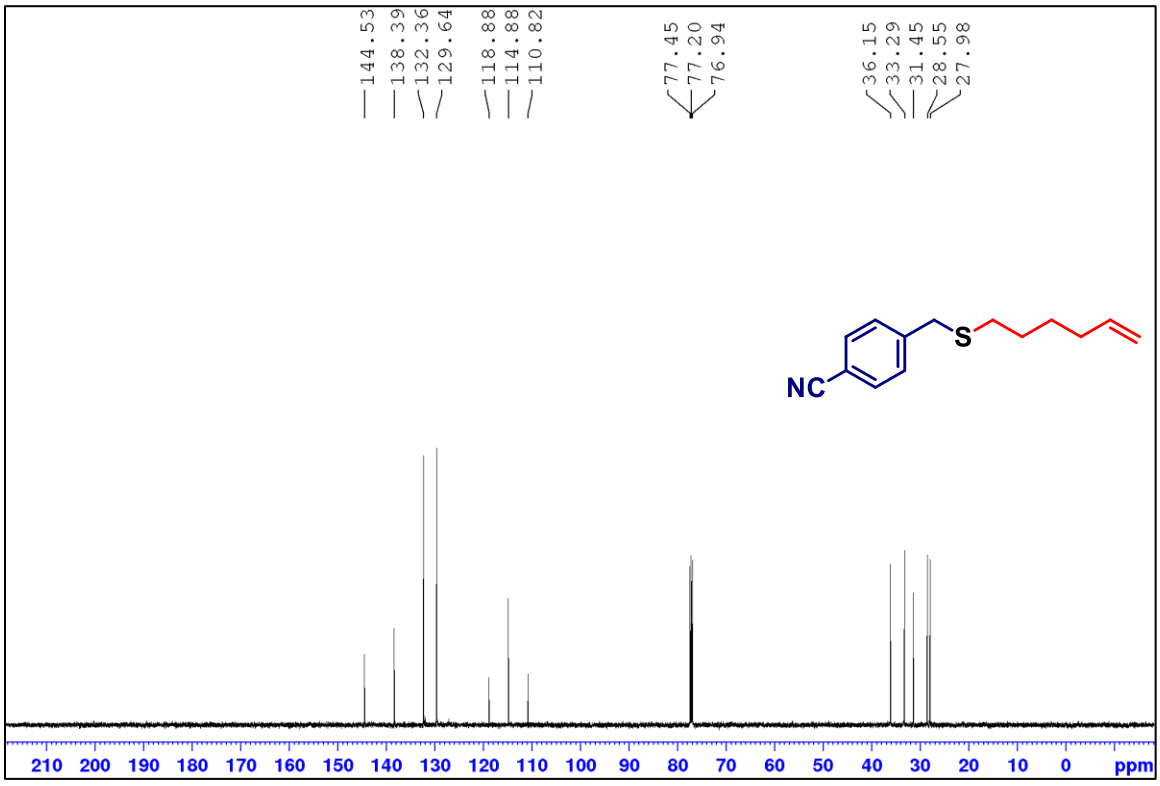
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 9e in $CDCl_3$



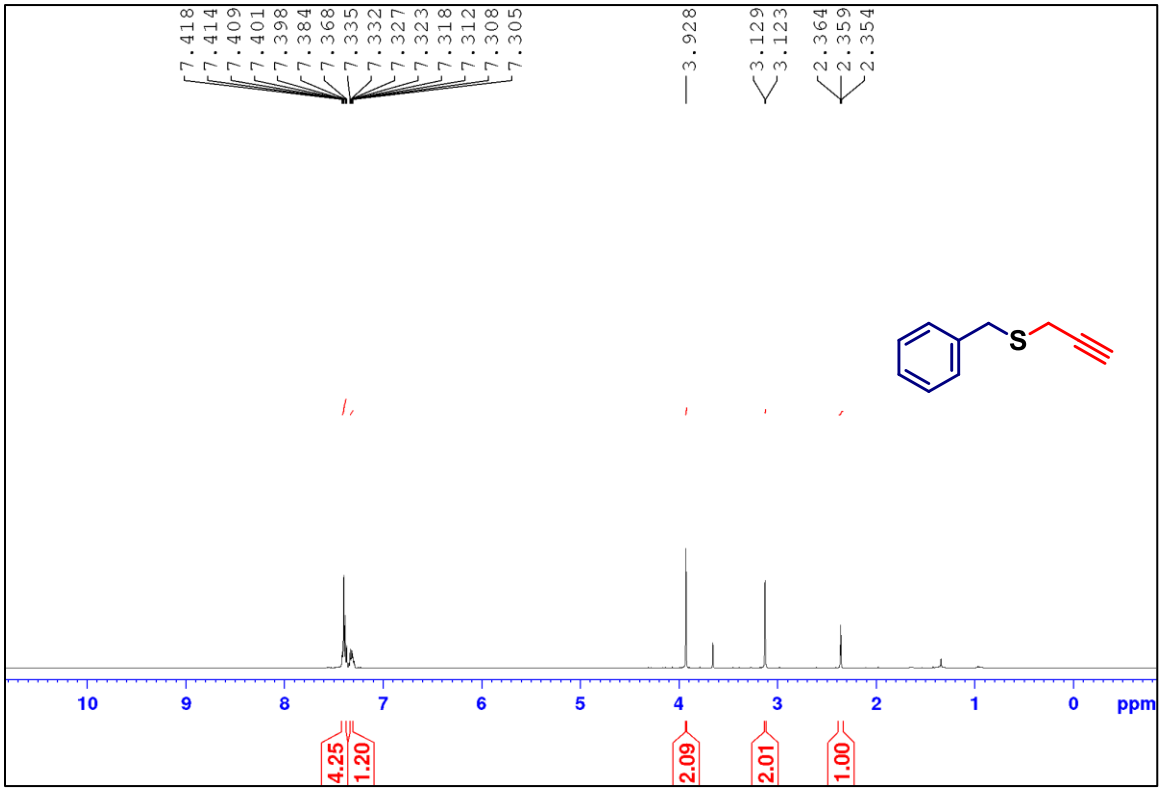


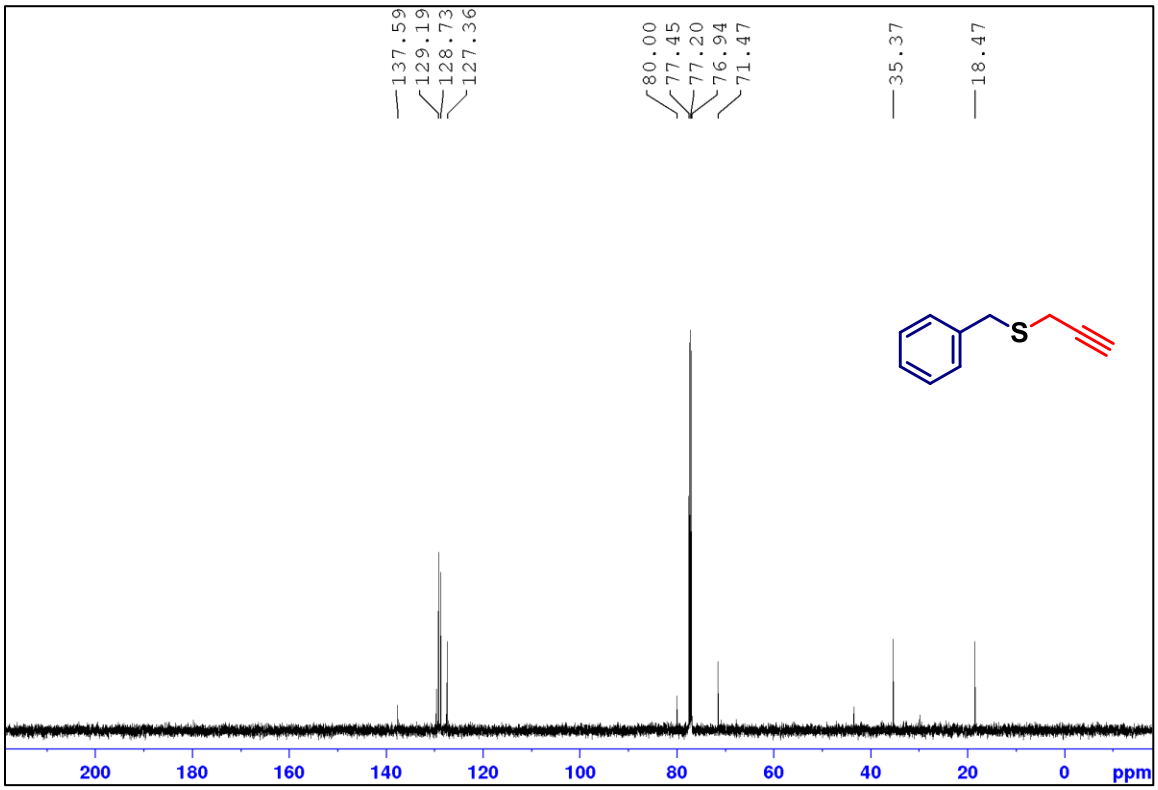
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 9f in $CDCl_3$



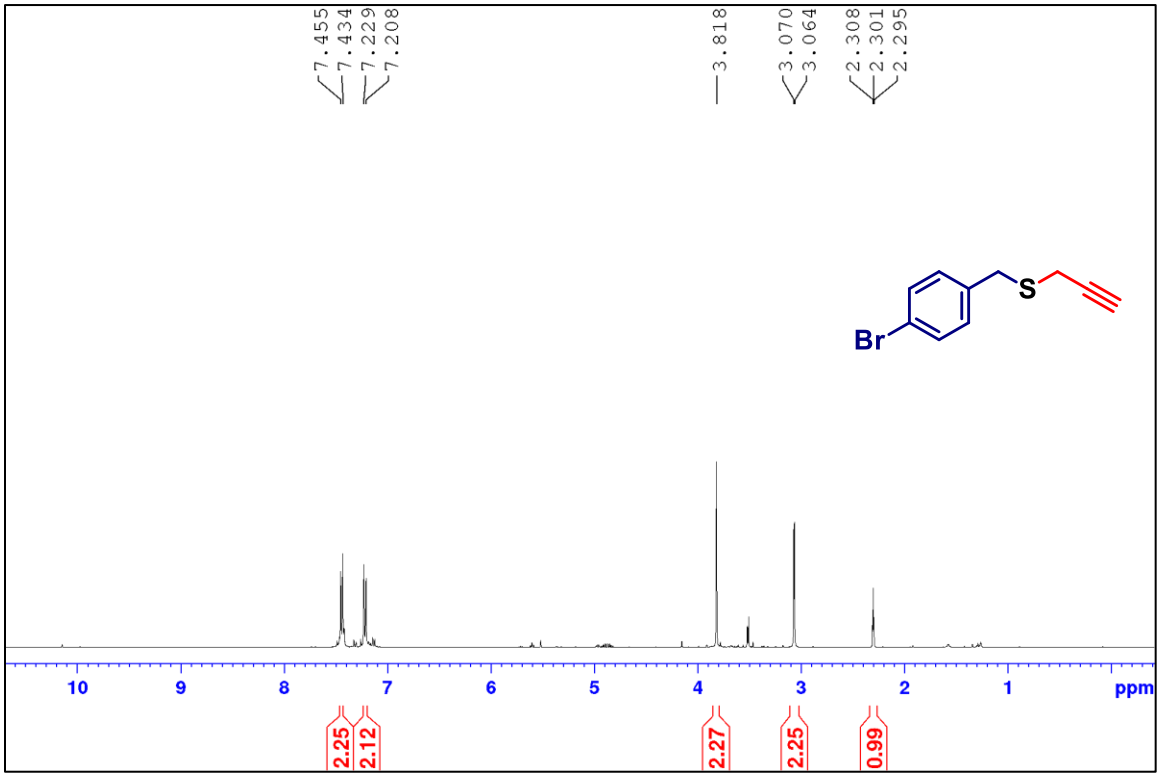


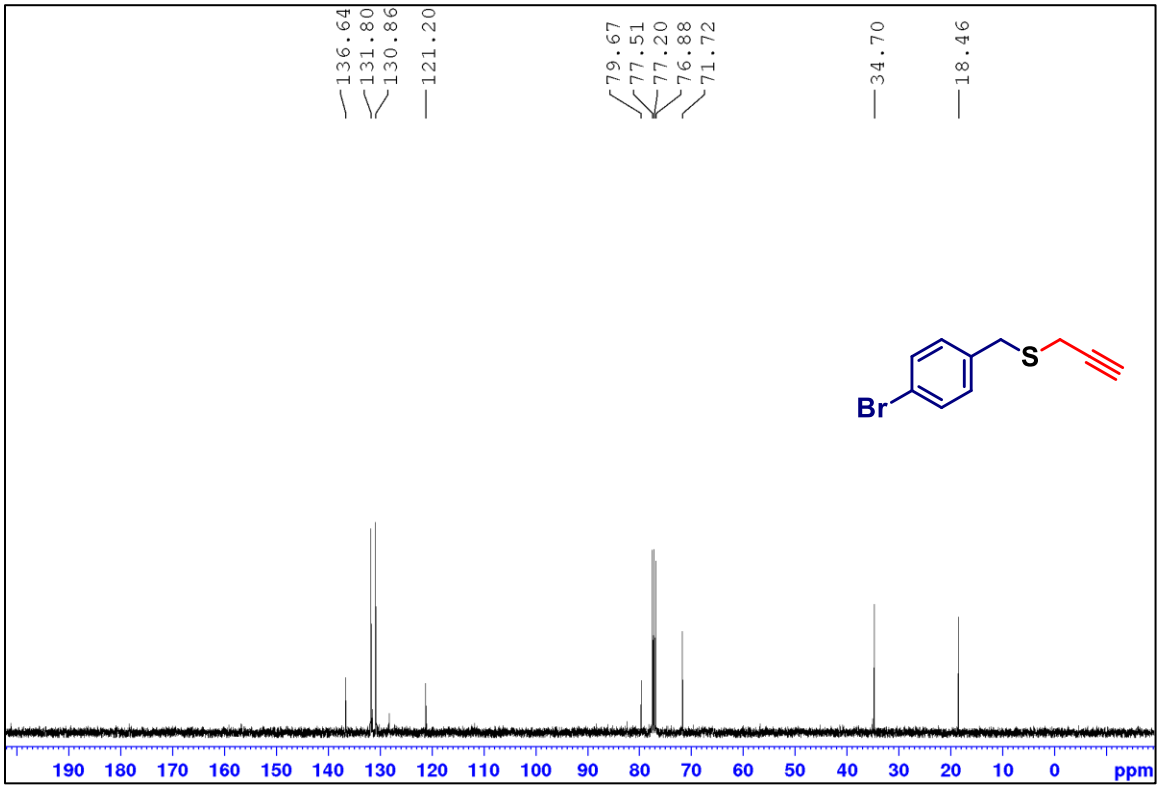
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 10a in $CDCl_3$



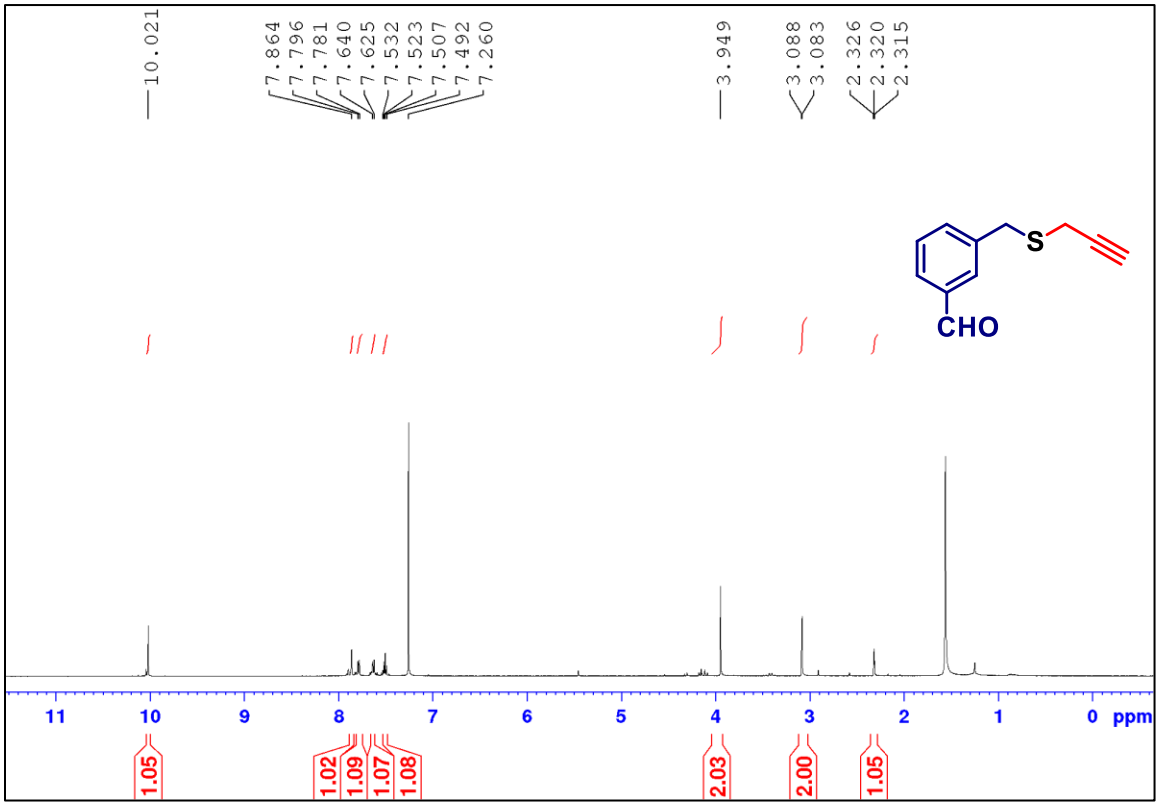


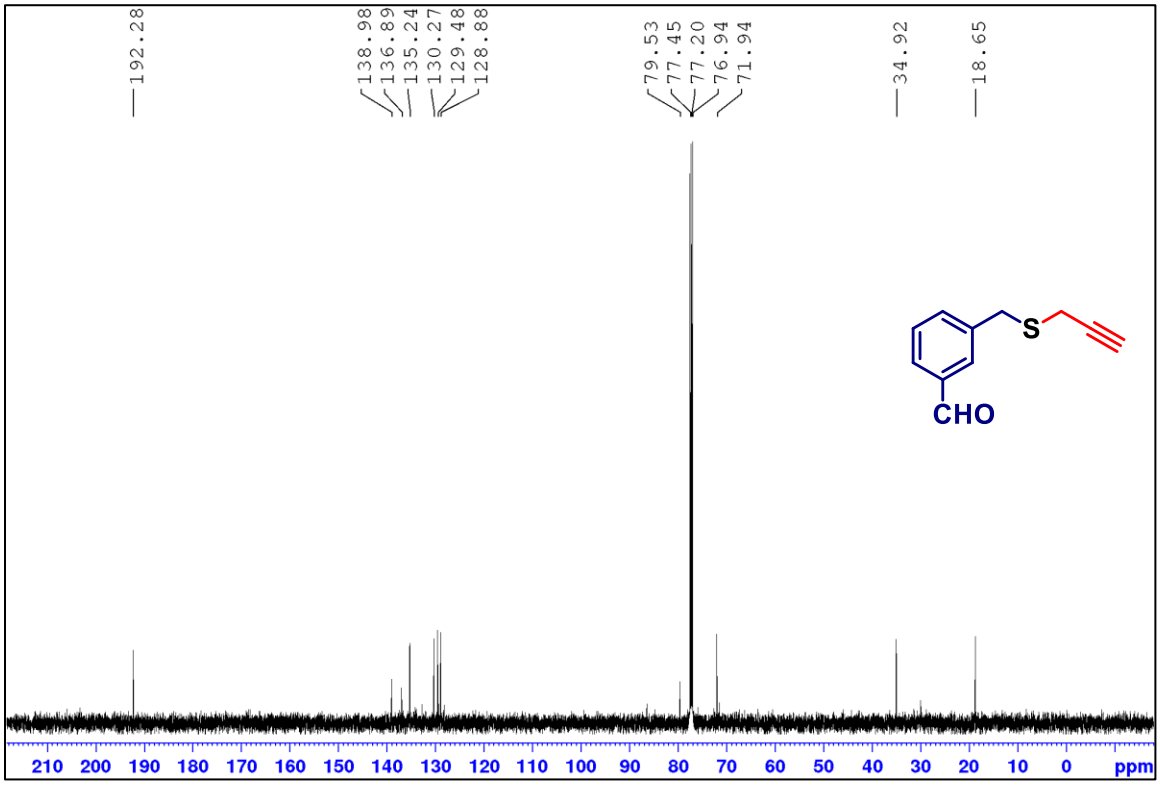
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 10b in $CDCl_3$



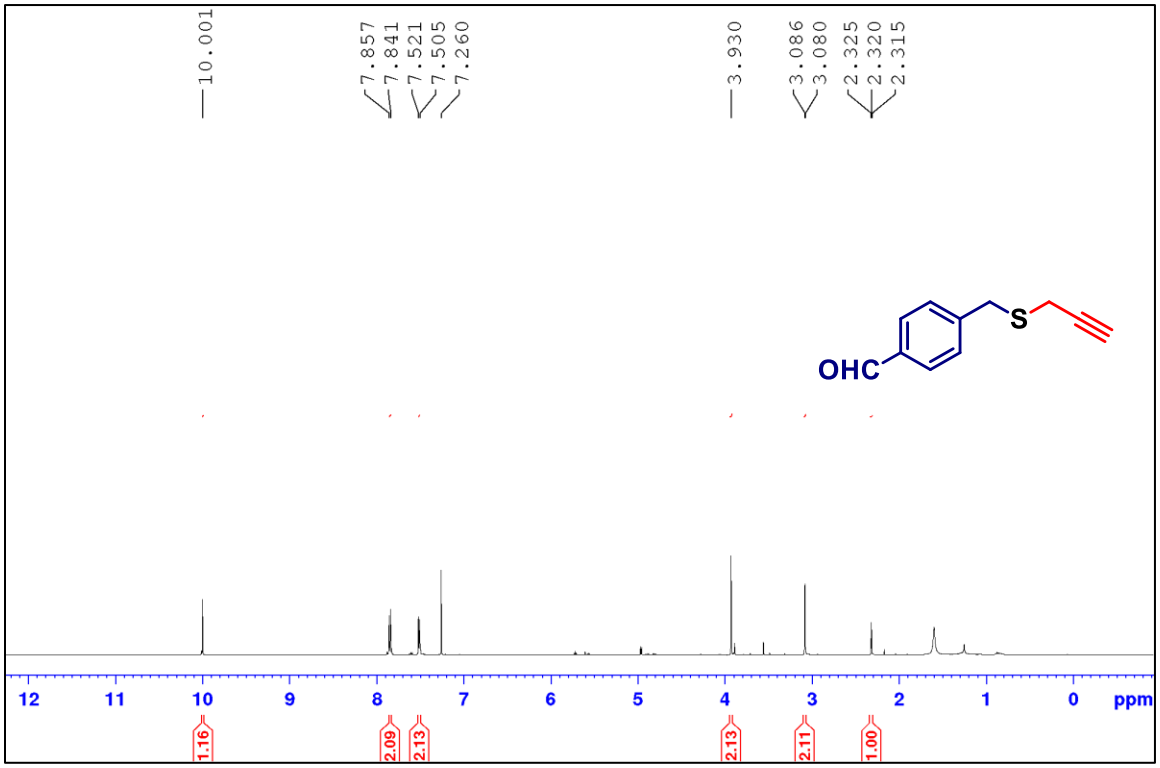


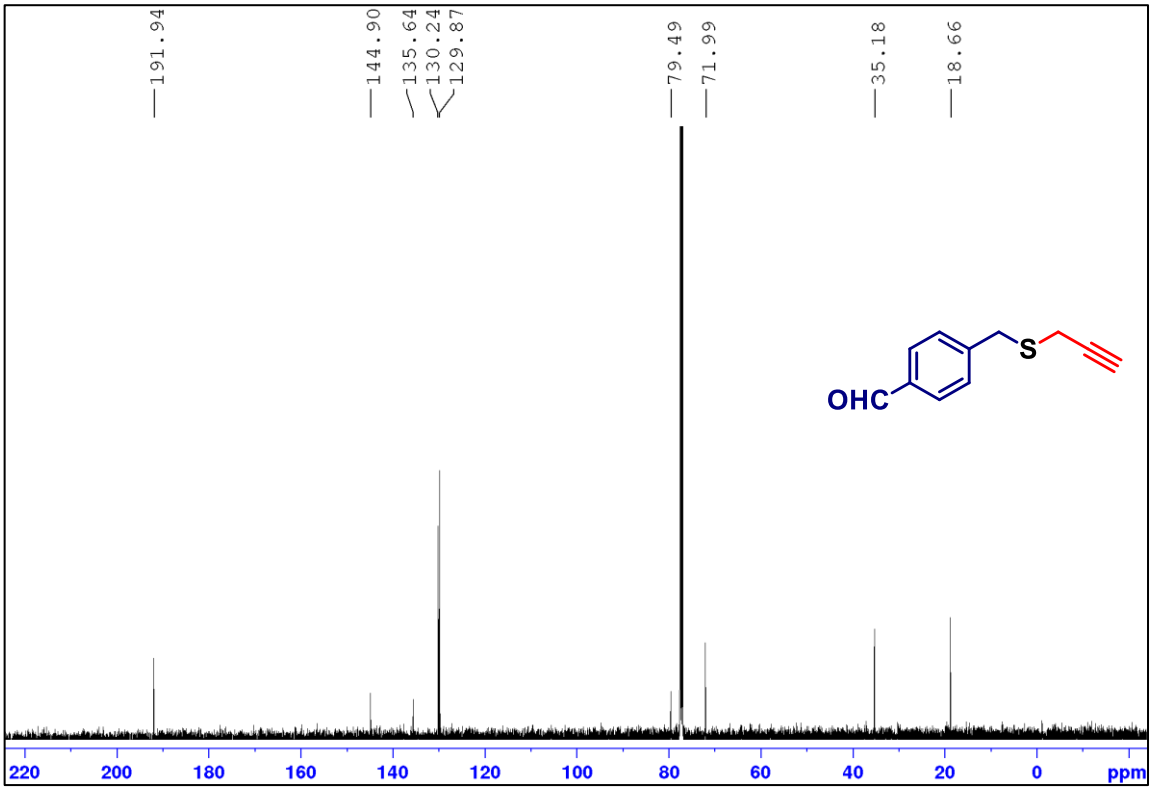
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 10c in $CDCl_3$



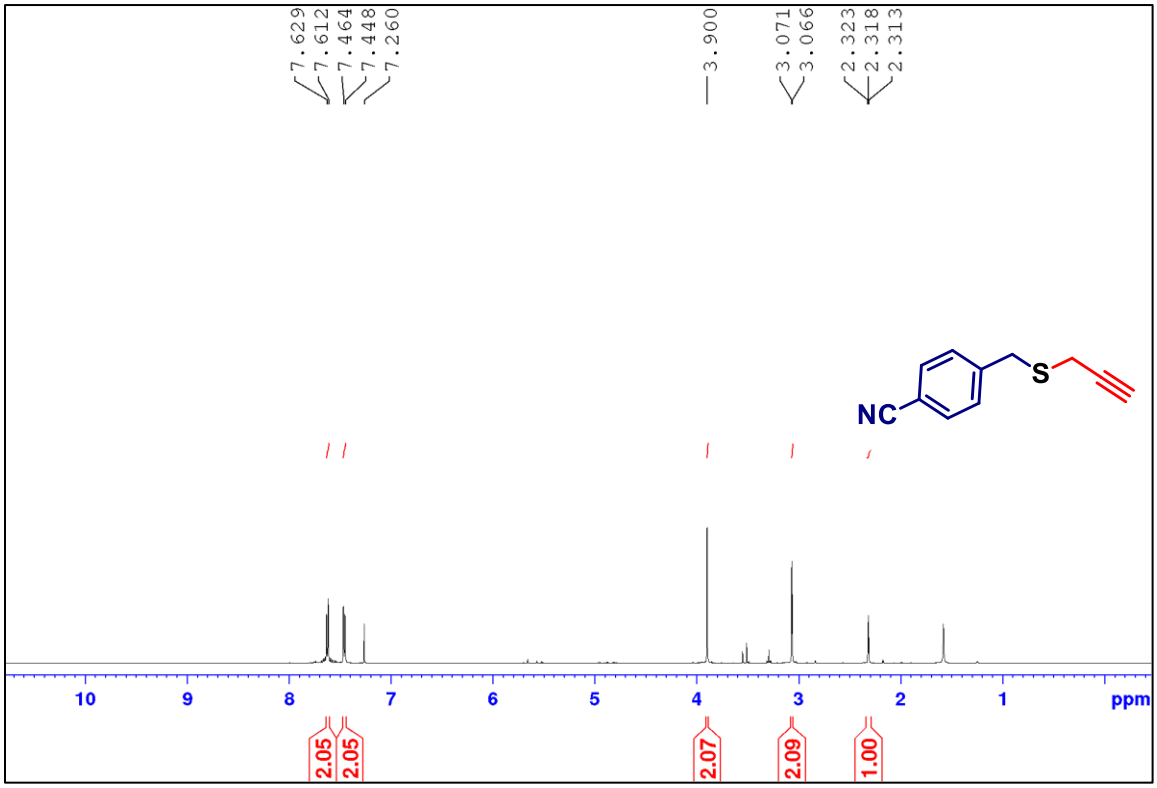


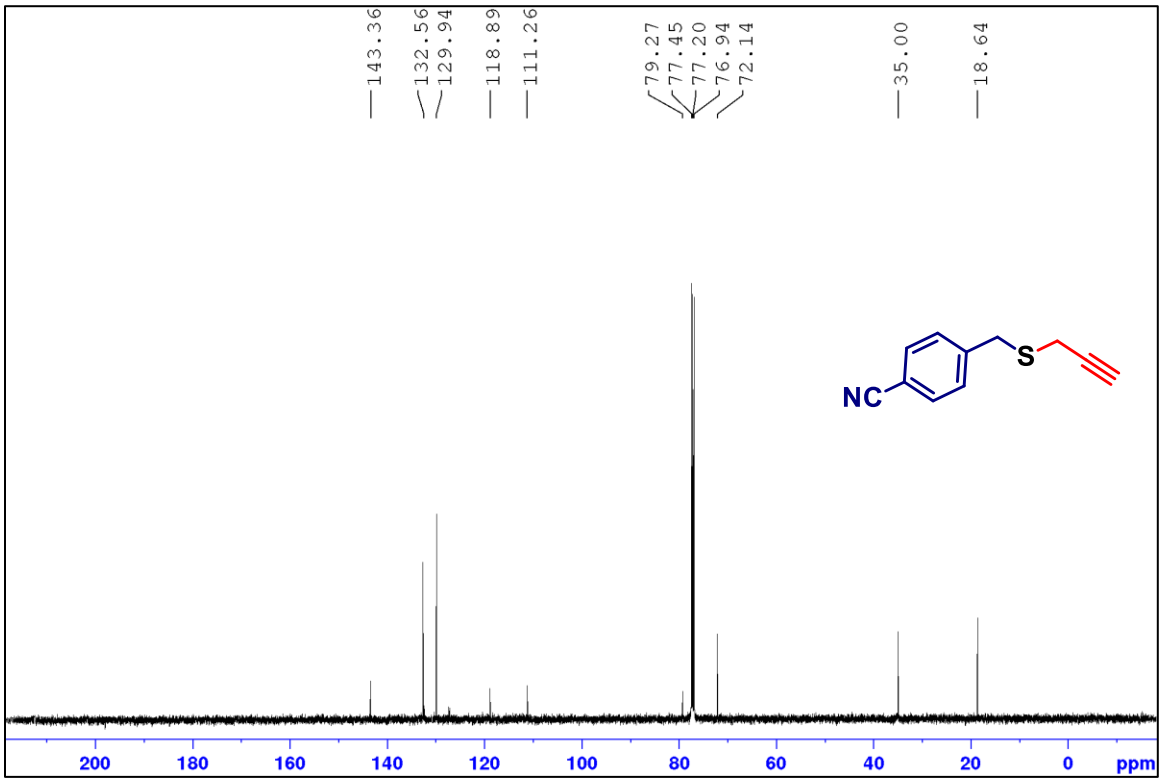
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 10d in $CDCl_3$



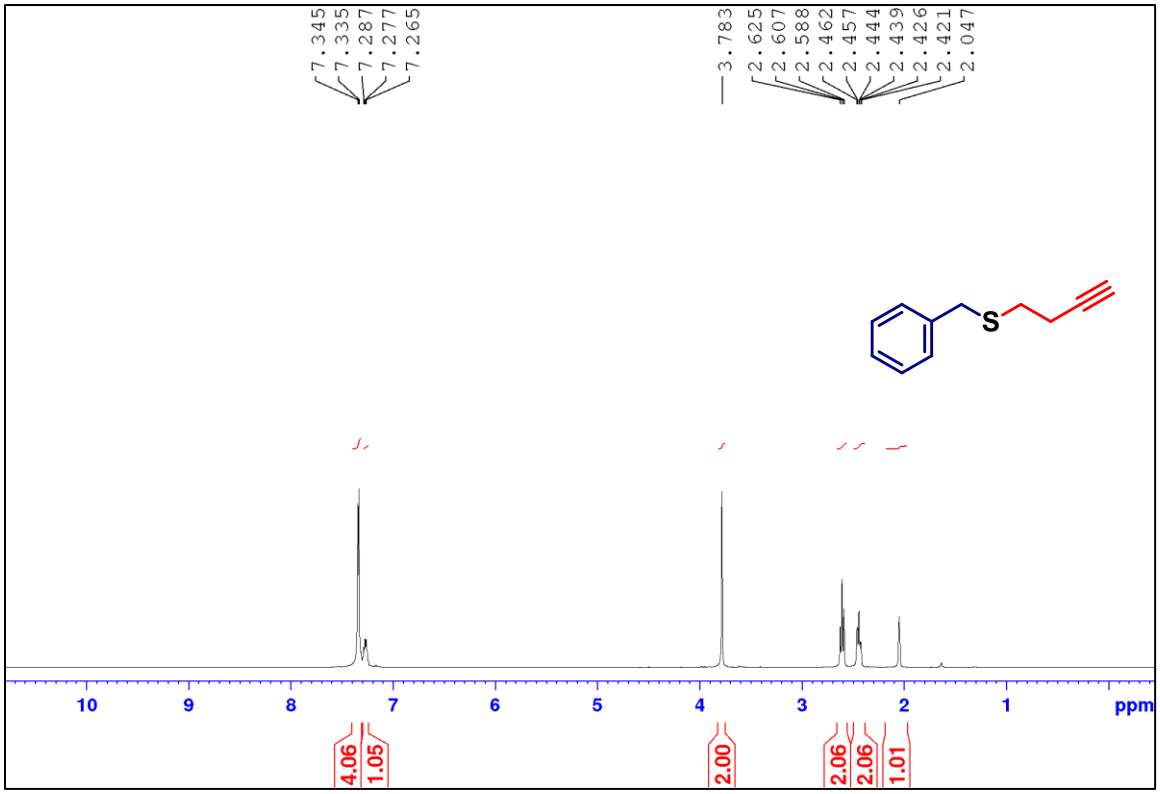


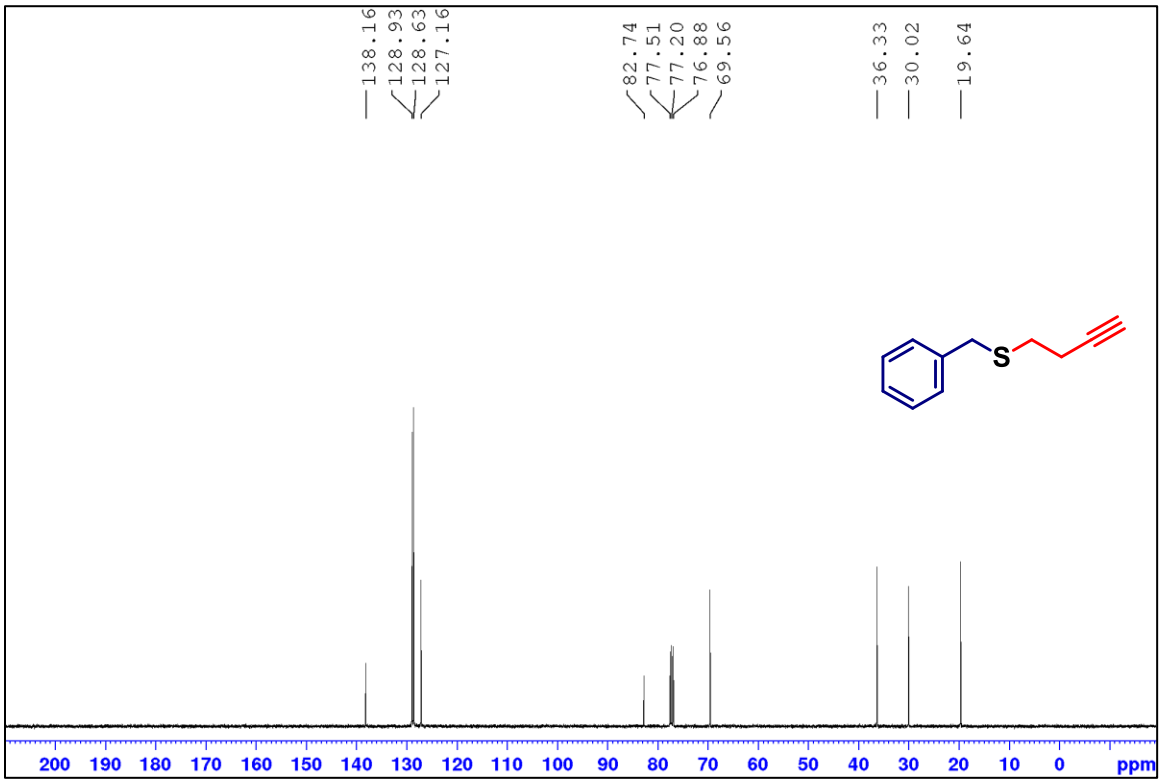
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 10e in $CDCl_3$



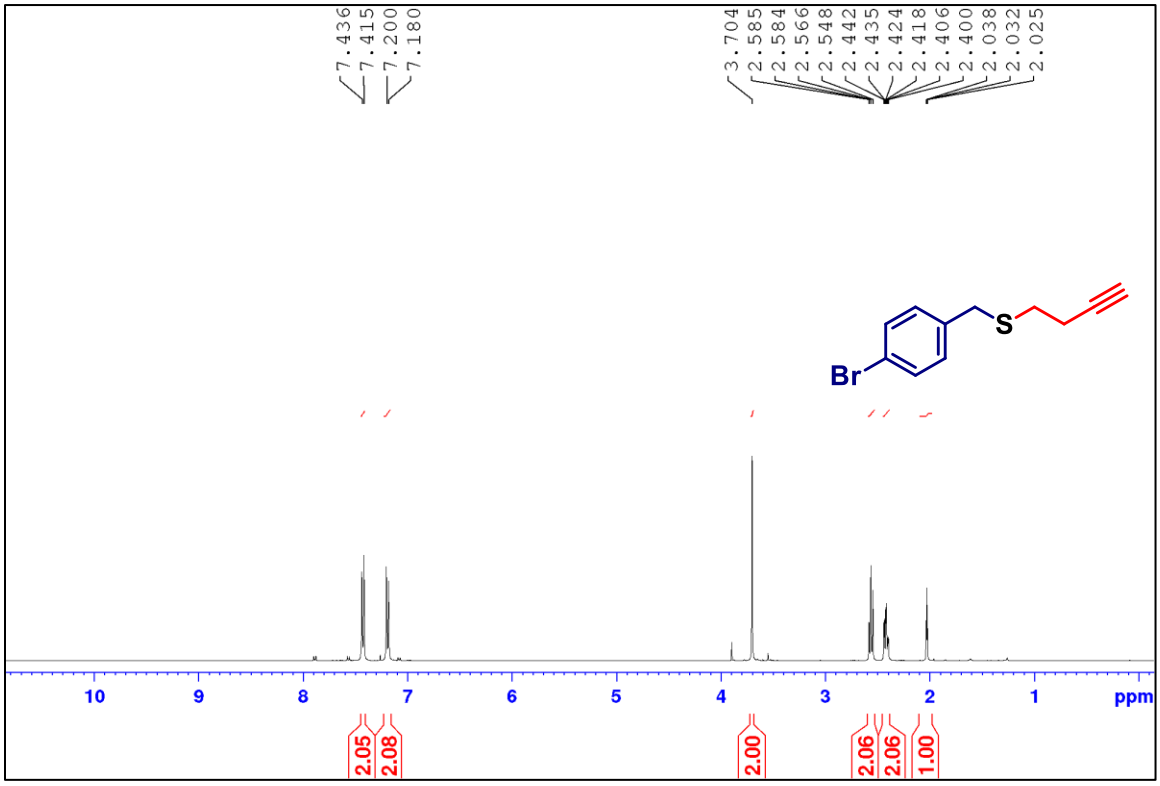


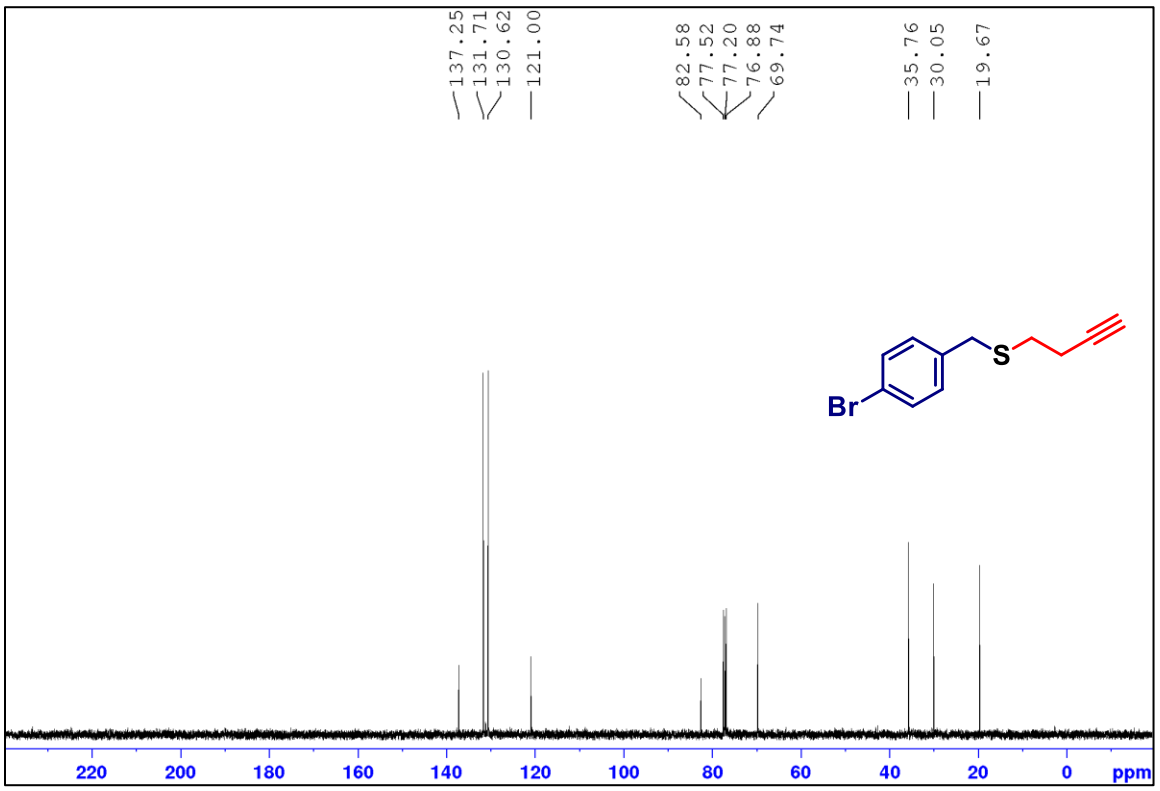
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 11a in $CDCl_3$



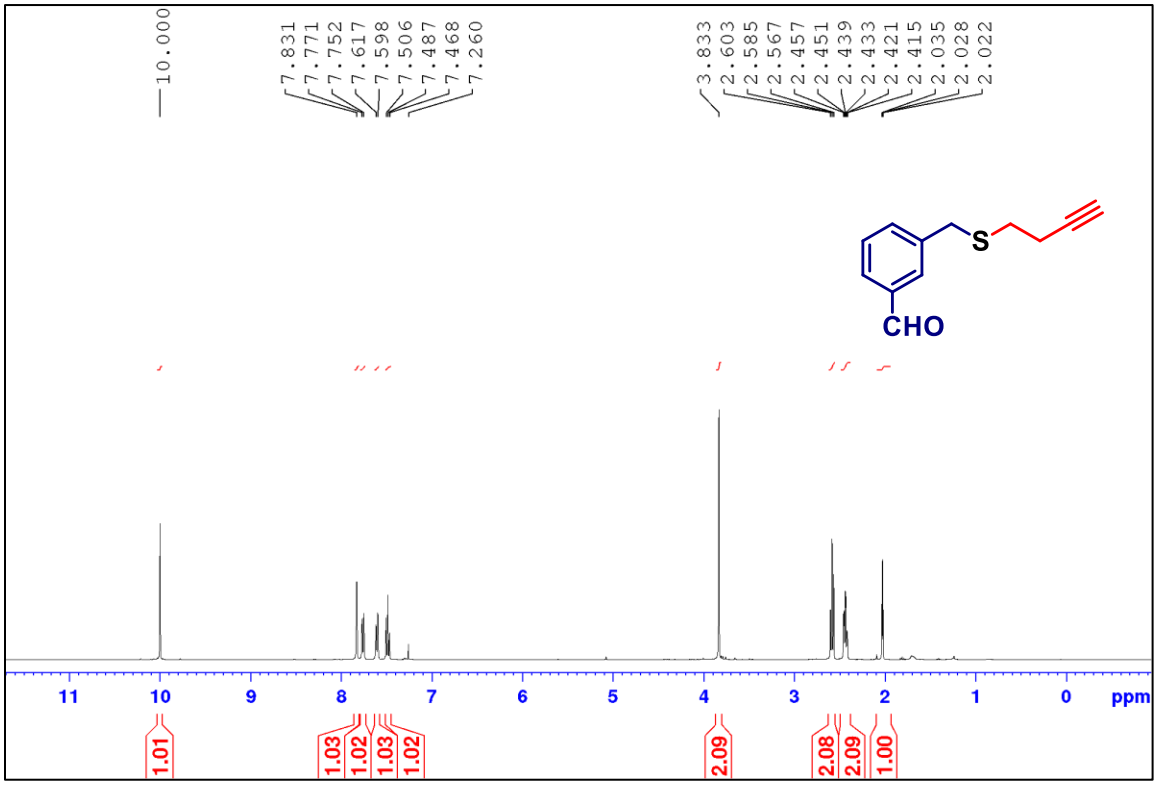


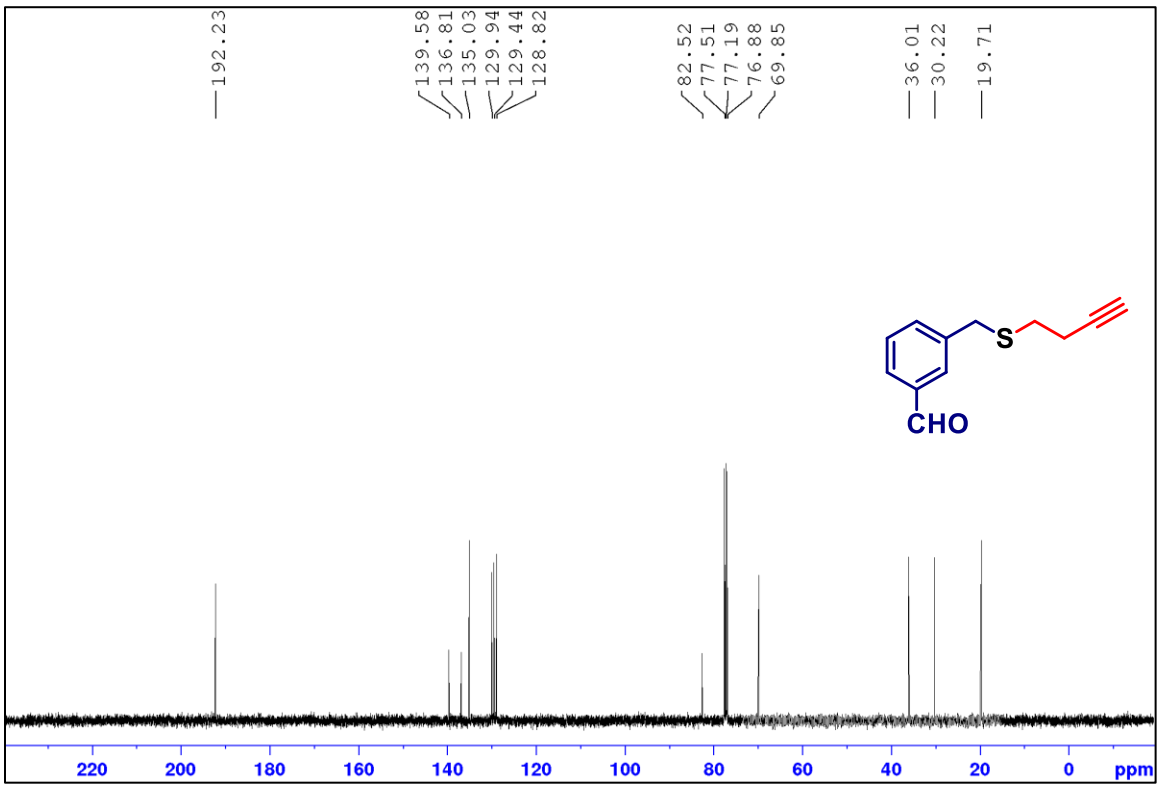
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 11b in $CDCl_3$



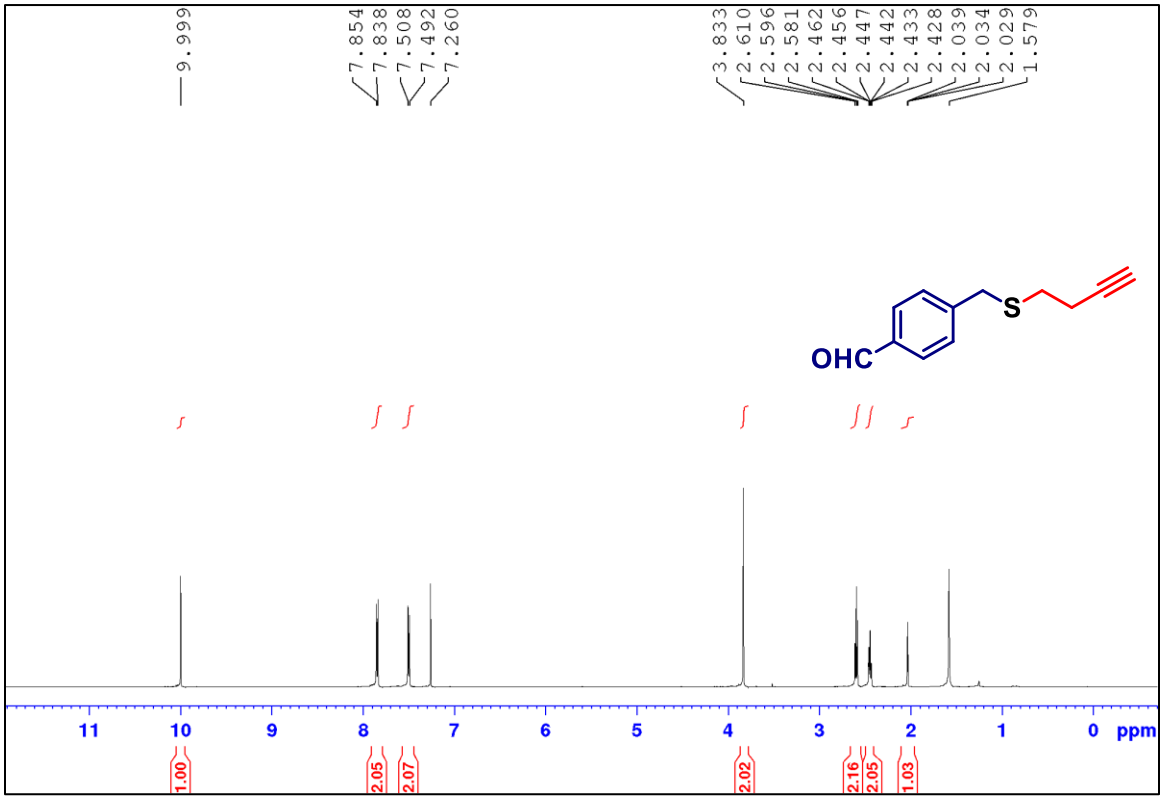


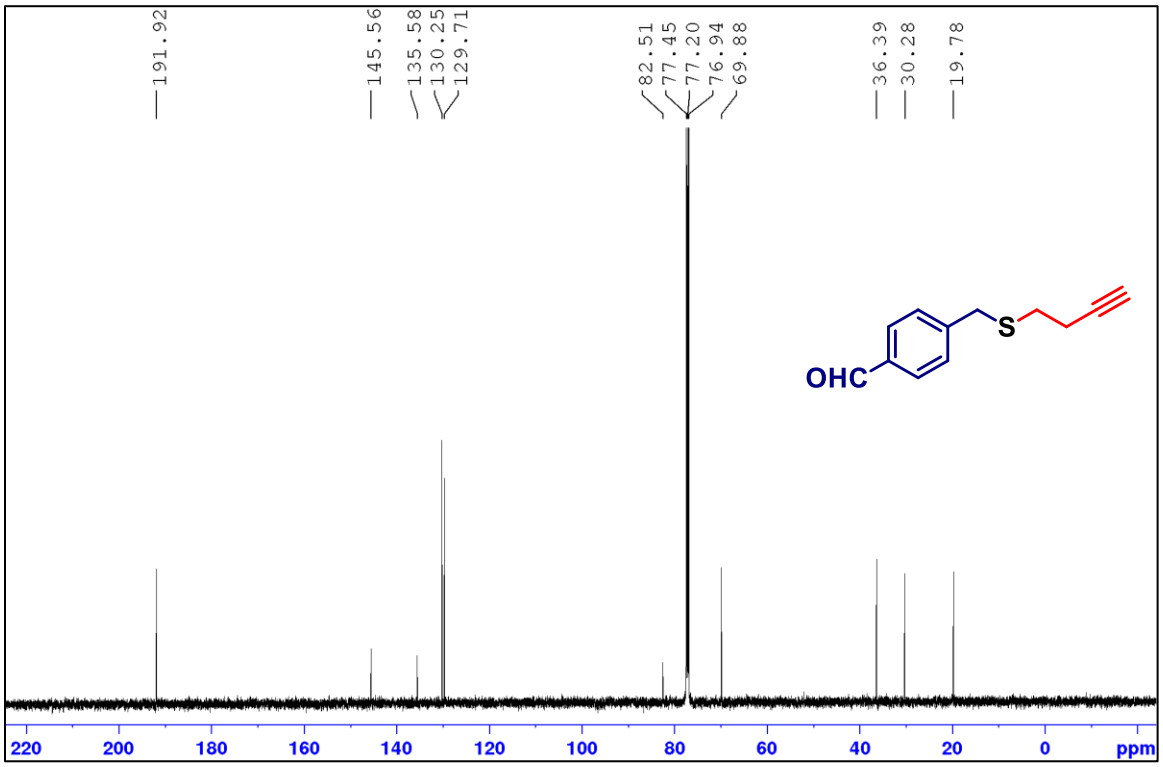
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 11c in $CDCl_3$



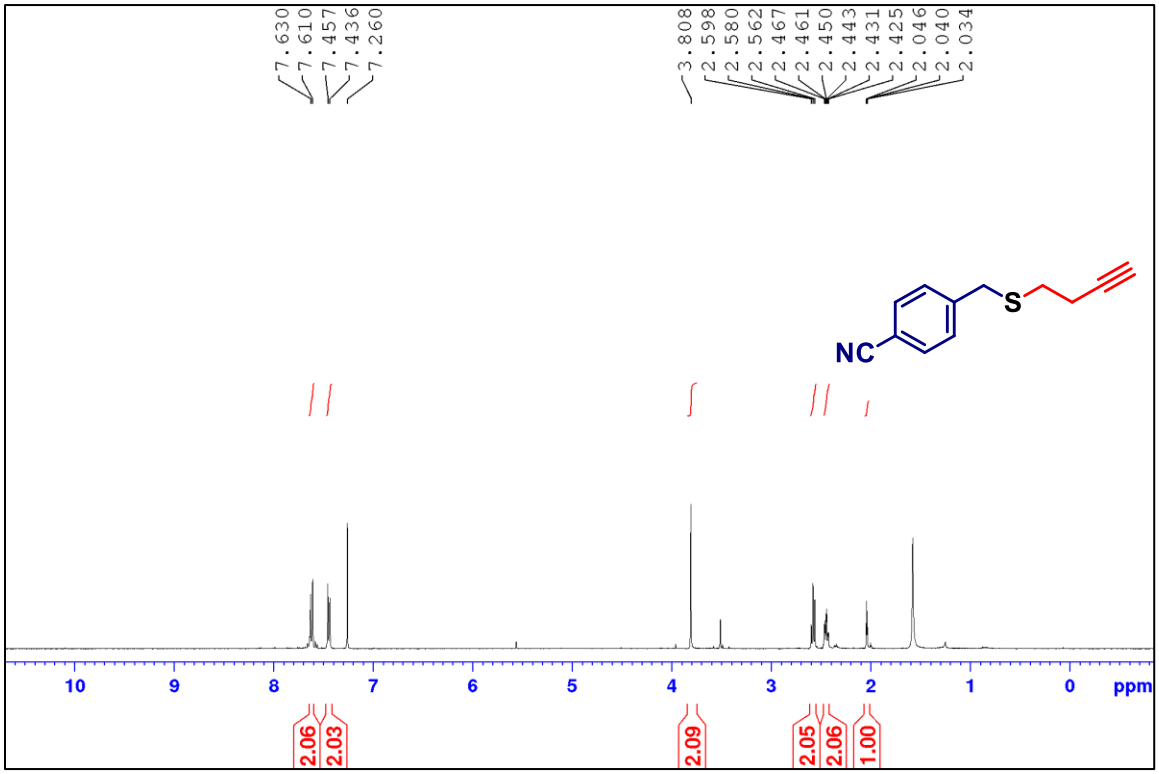


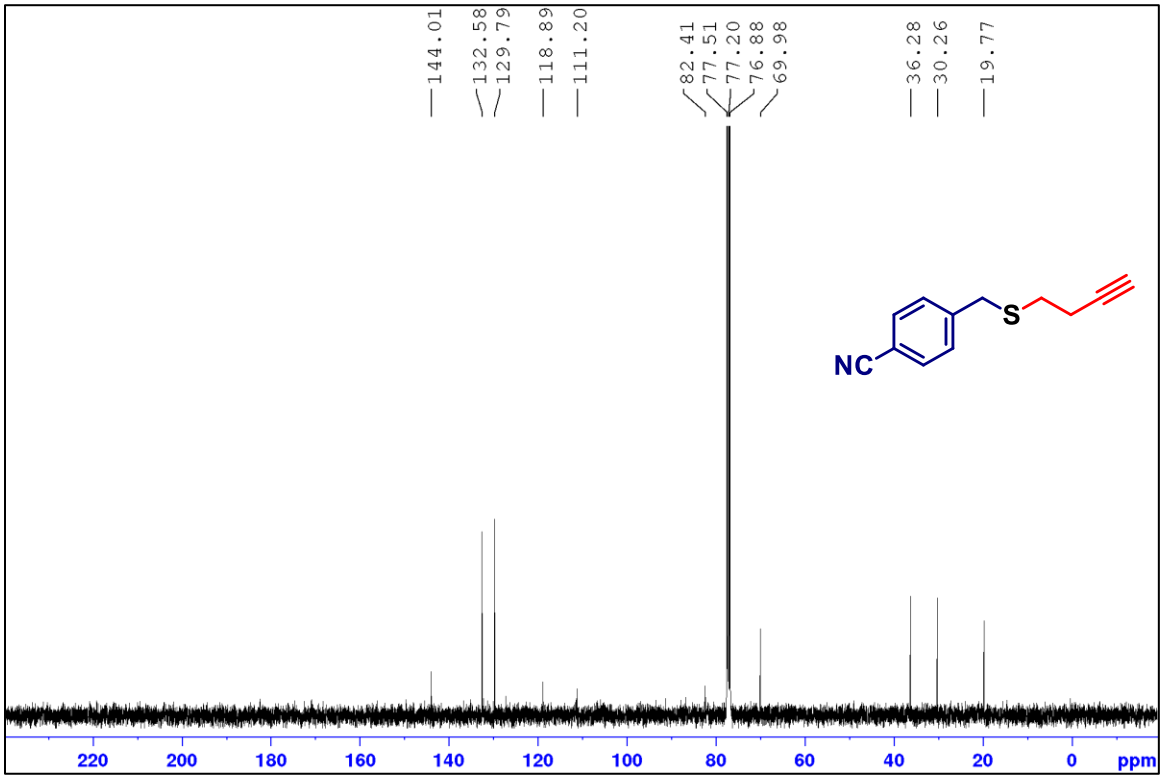
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 11d in $CDCl_3$



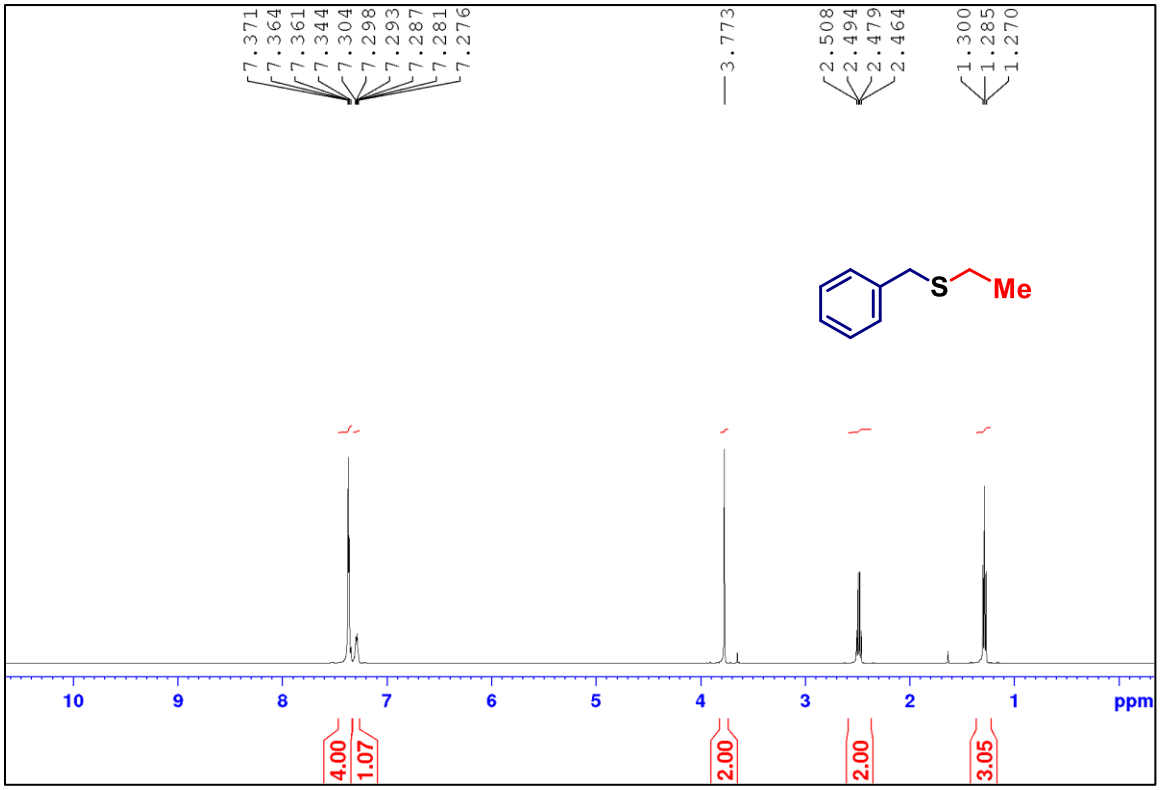


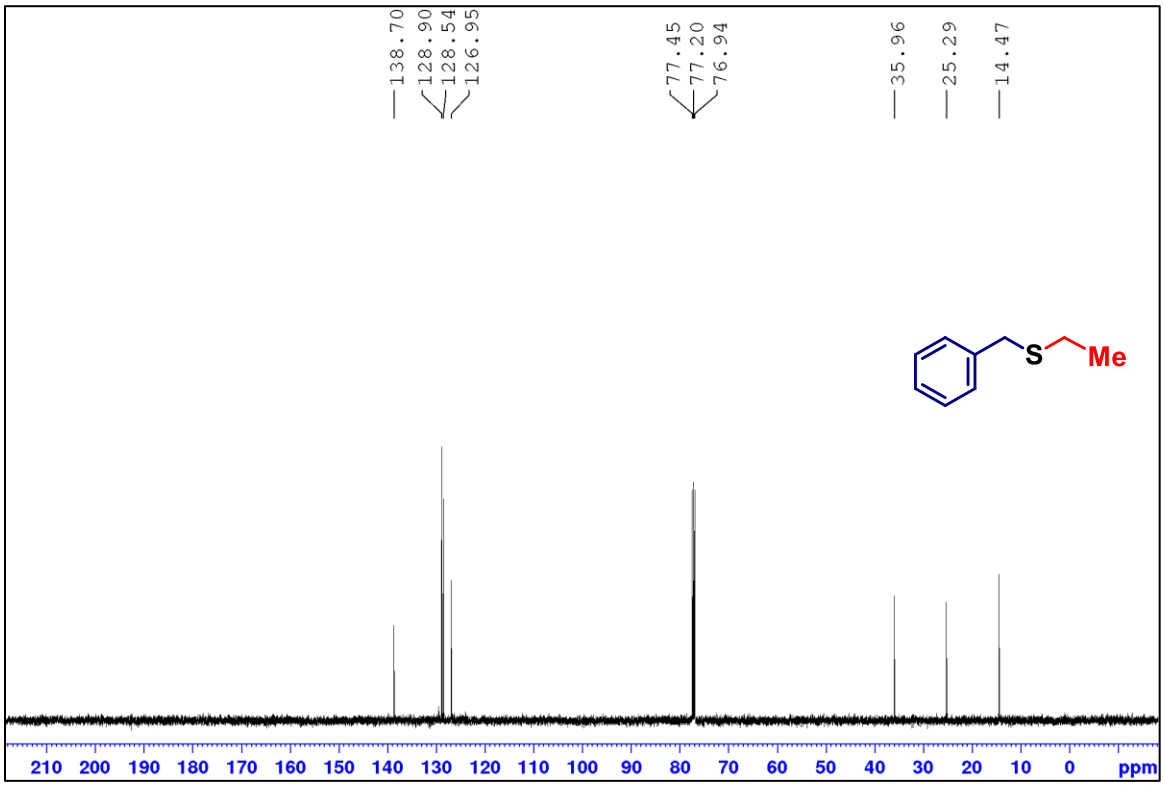
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 11e in $CDCl_3$



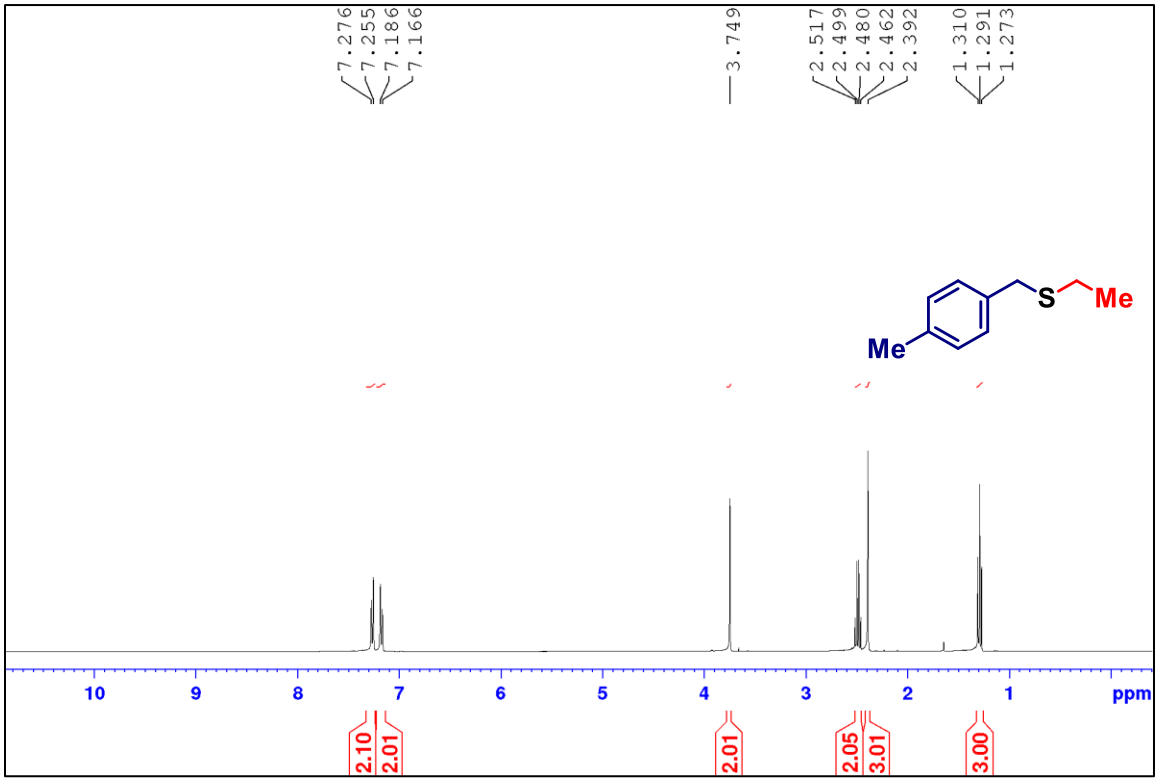


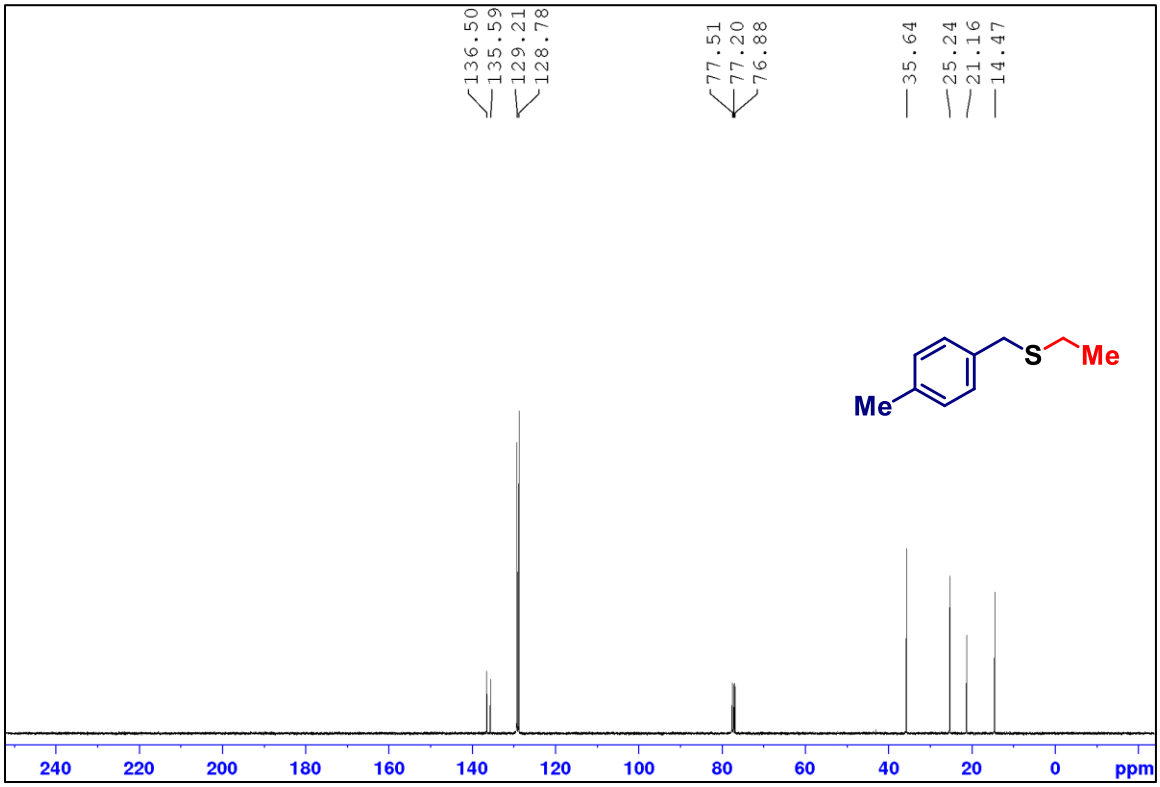
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 12a in $CDCl_3$



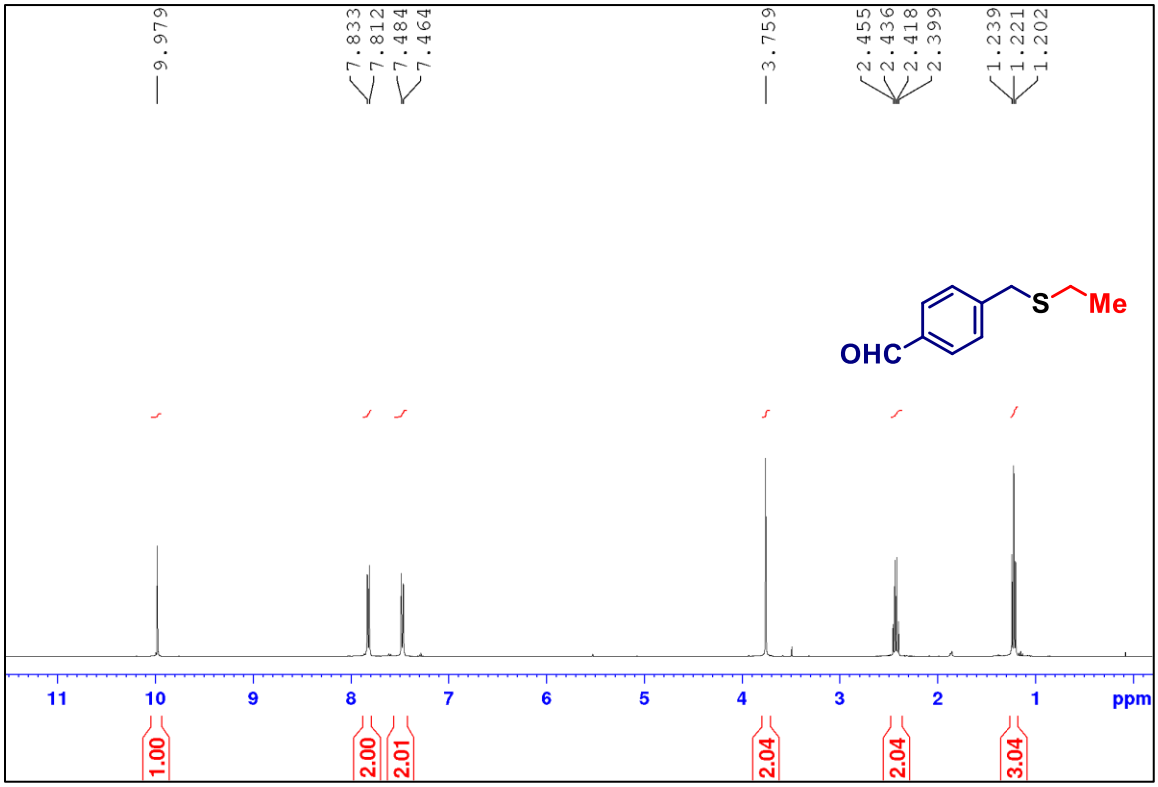


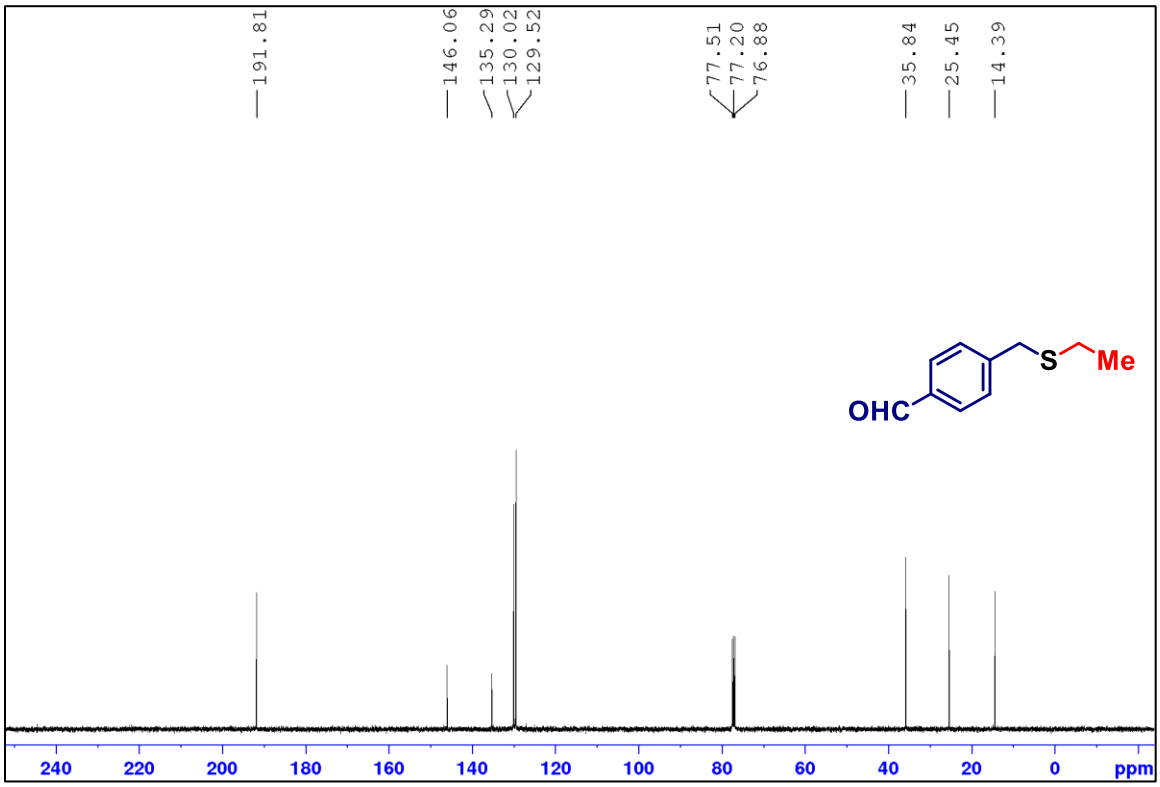
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 12b in $CDCl_3$



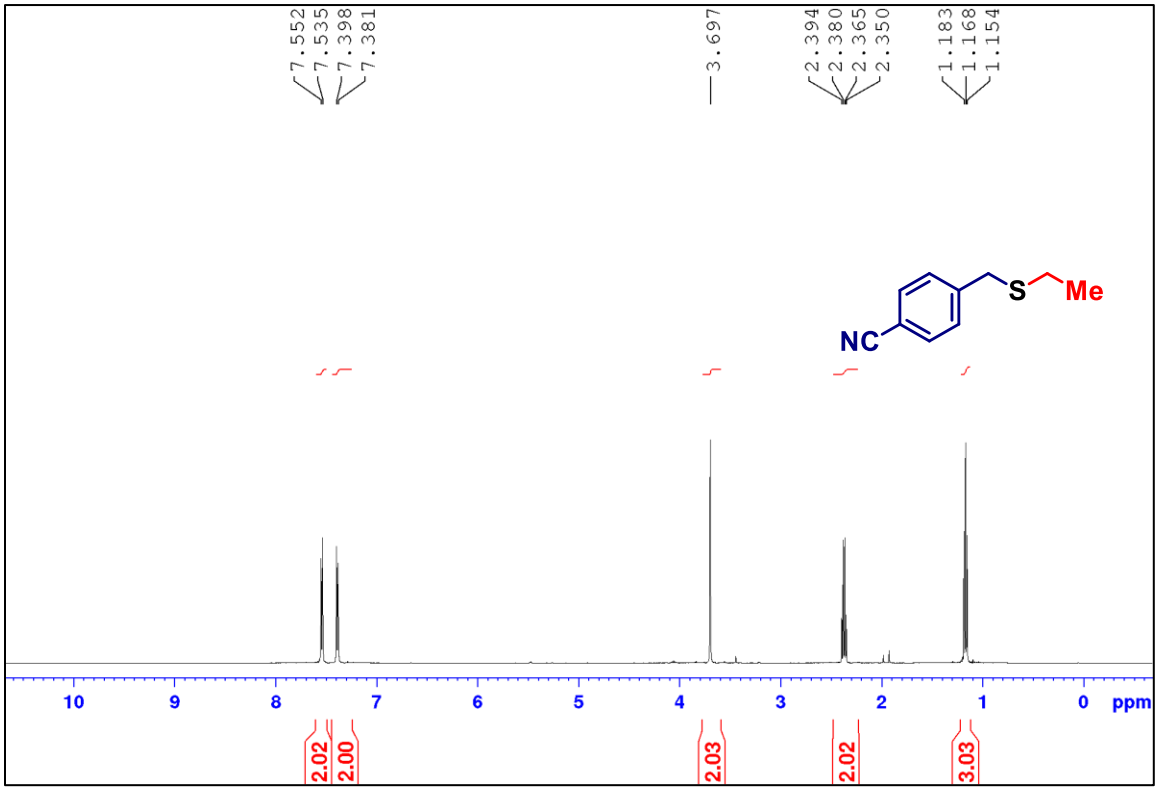


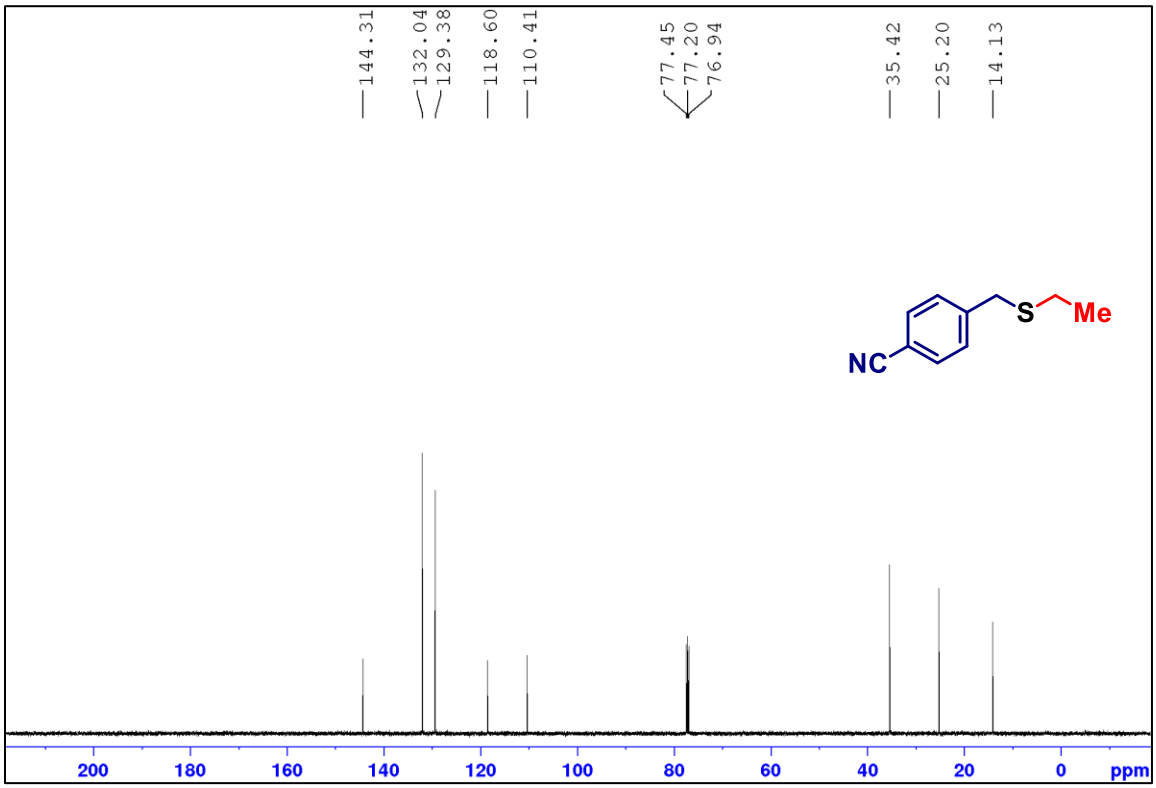
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 12c in $CDCl_3$



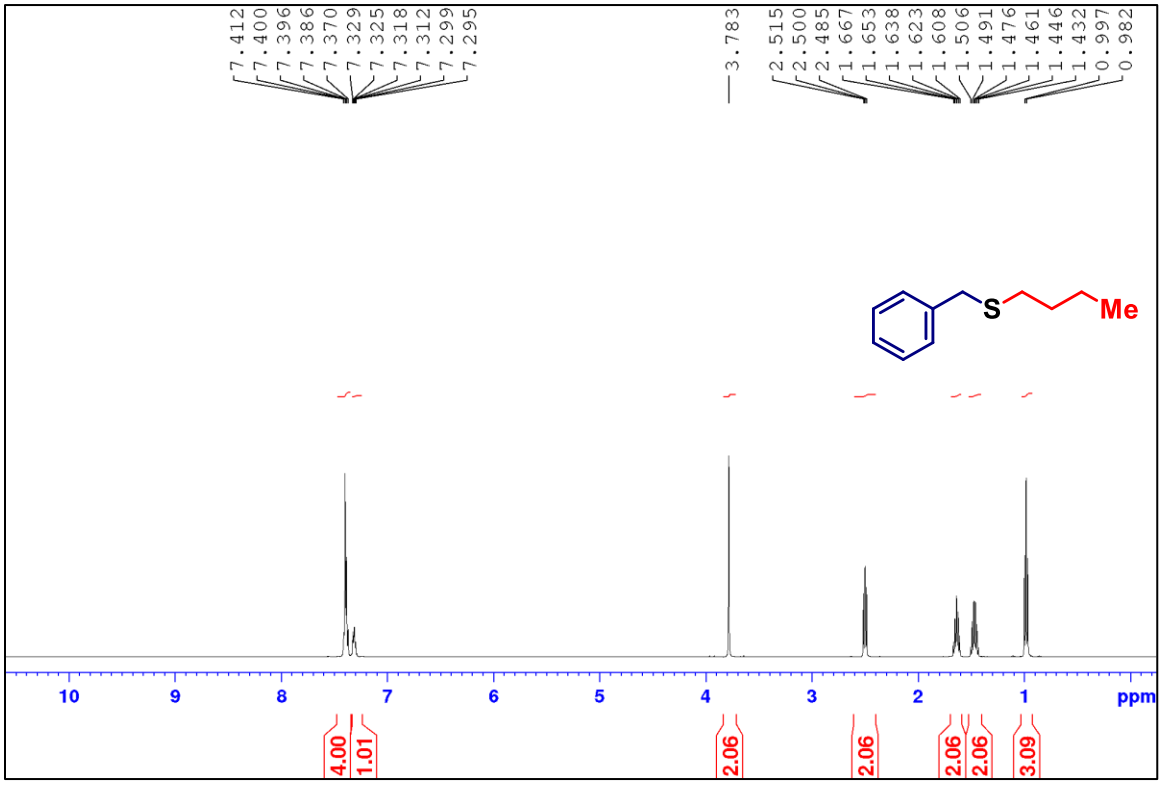


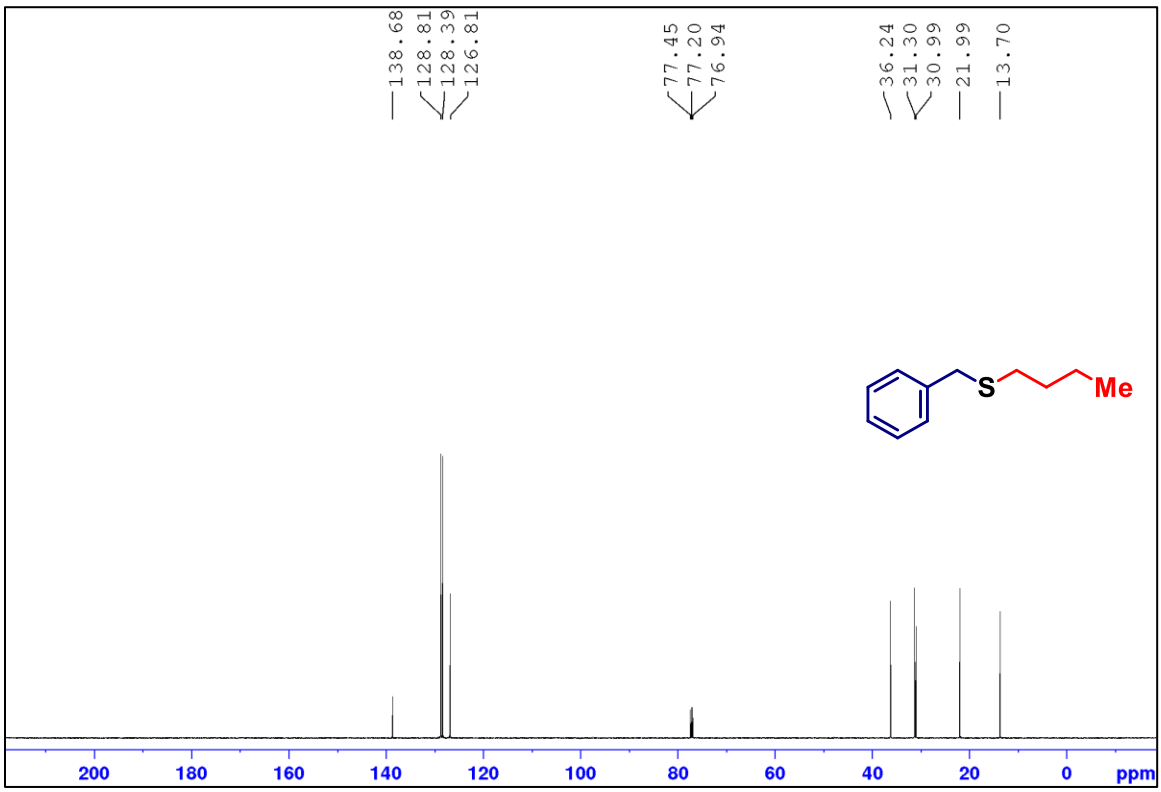
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 12d in $CDCl_3$



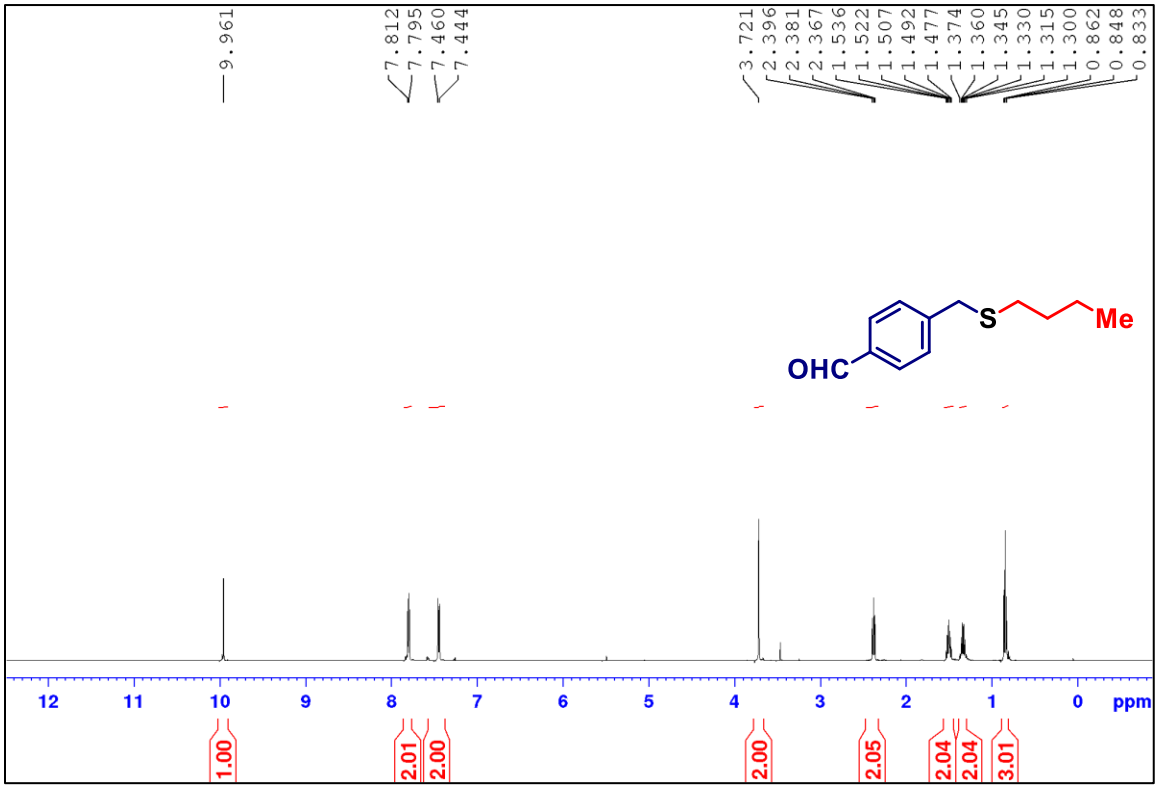


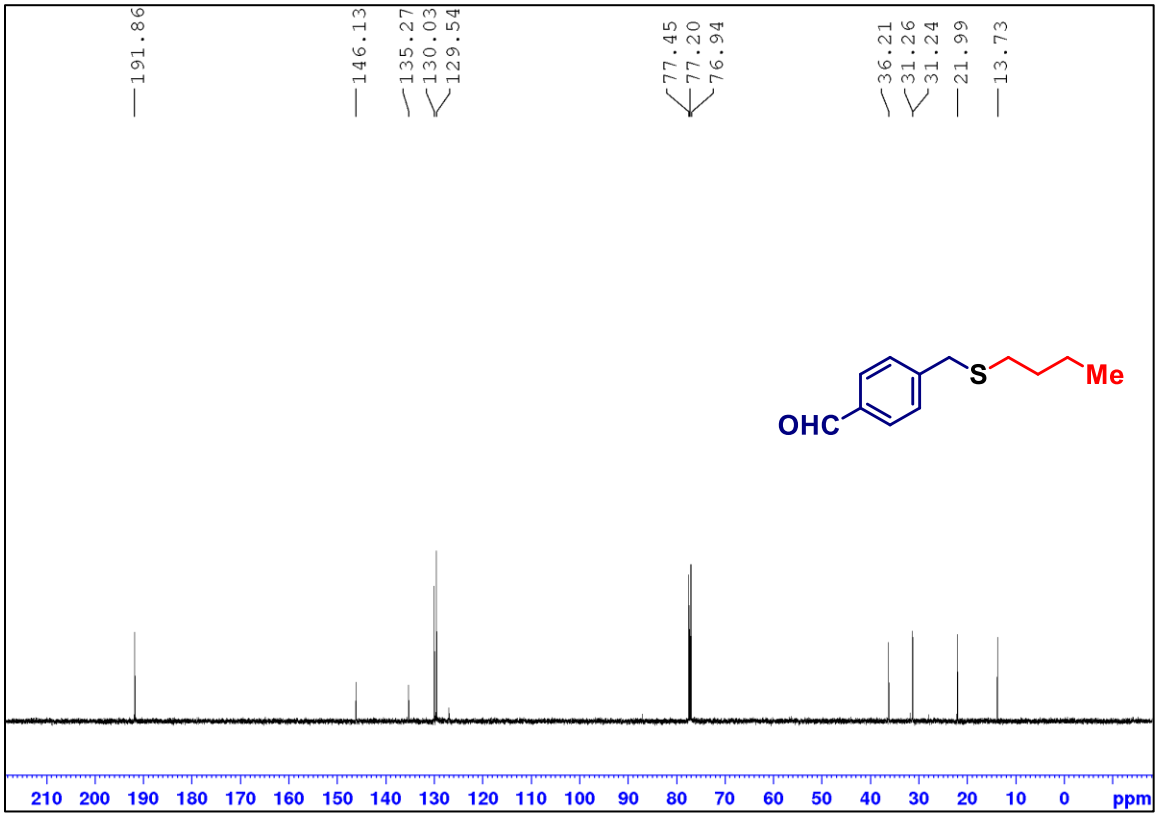
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 13a in $CDCl_3$



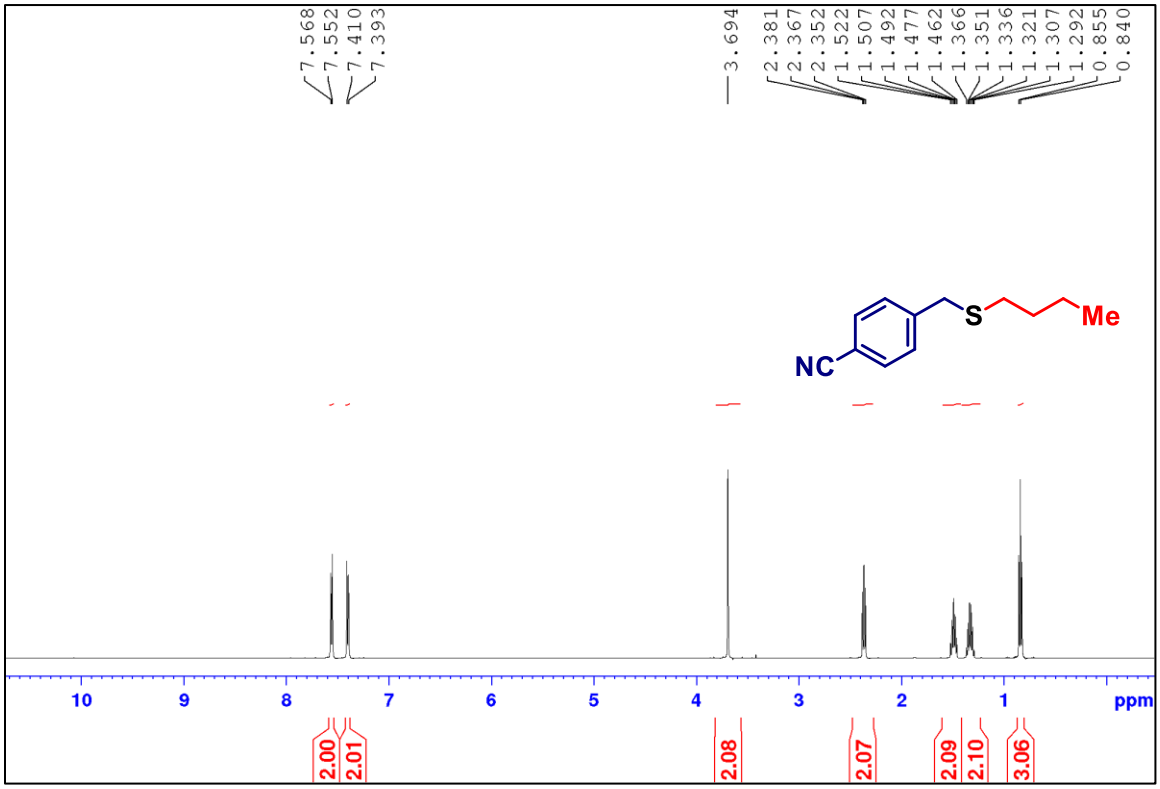


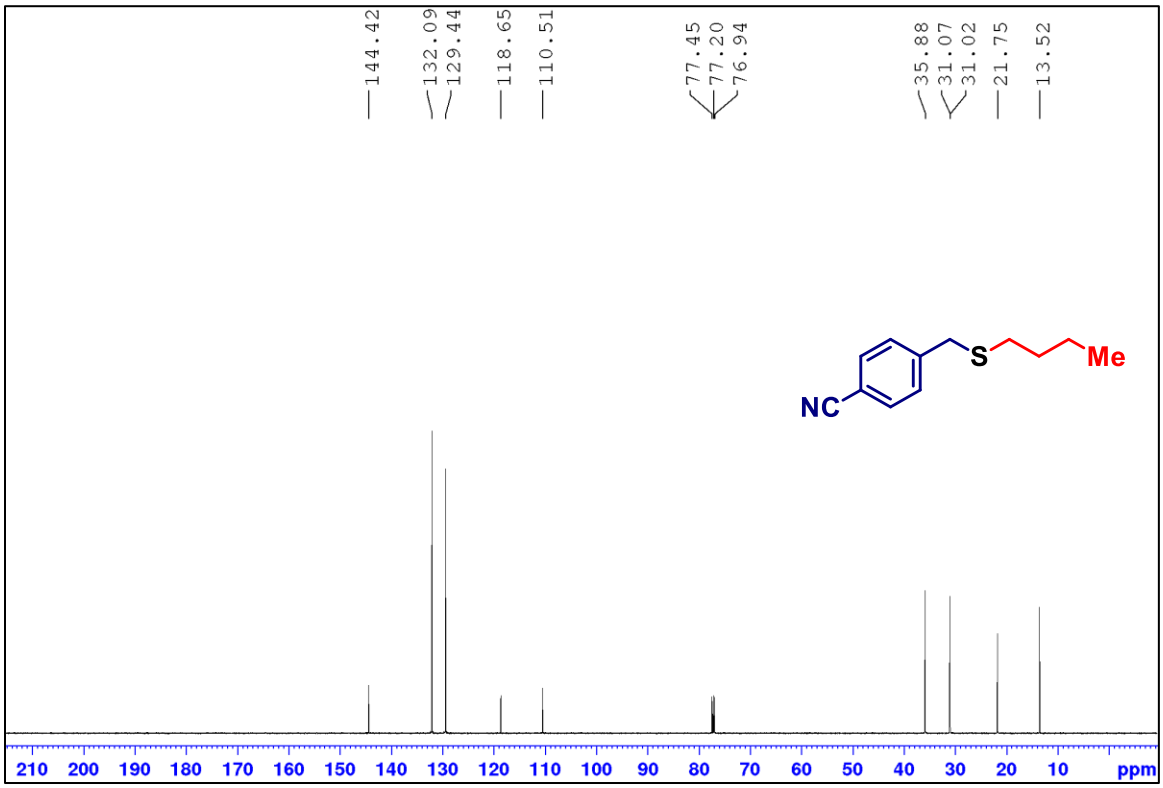
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 13b in $CDCl_3$



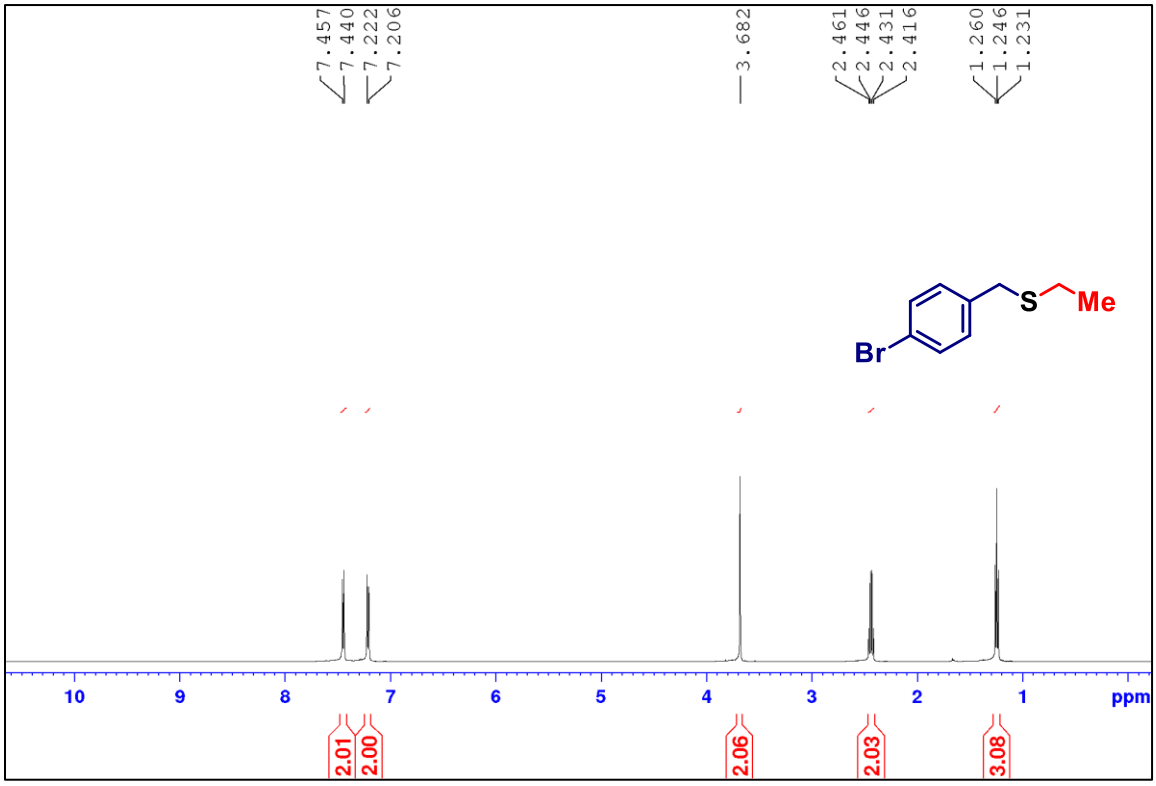


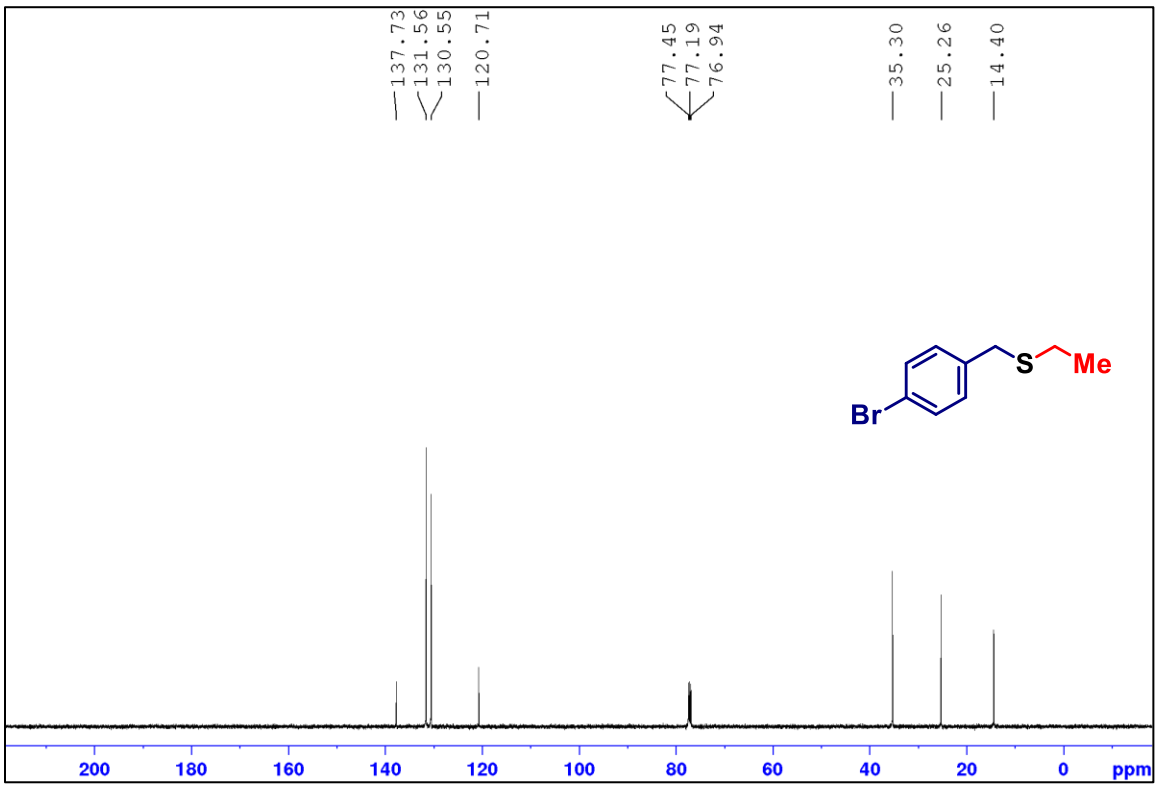
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 13c in $CDCl_3$



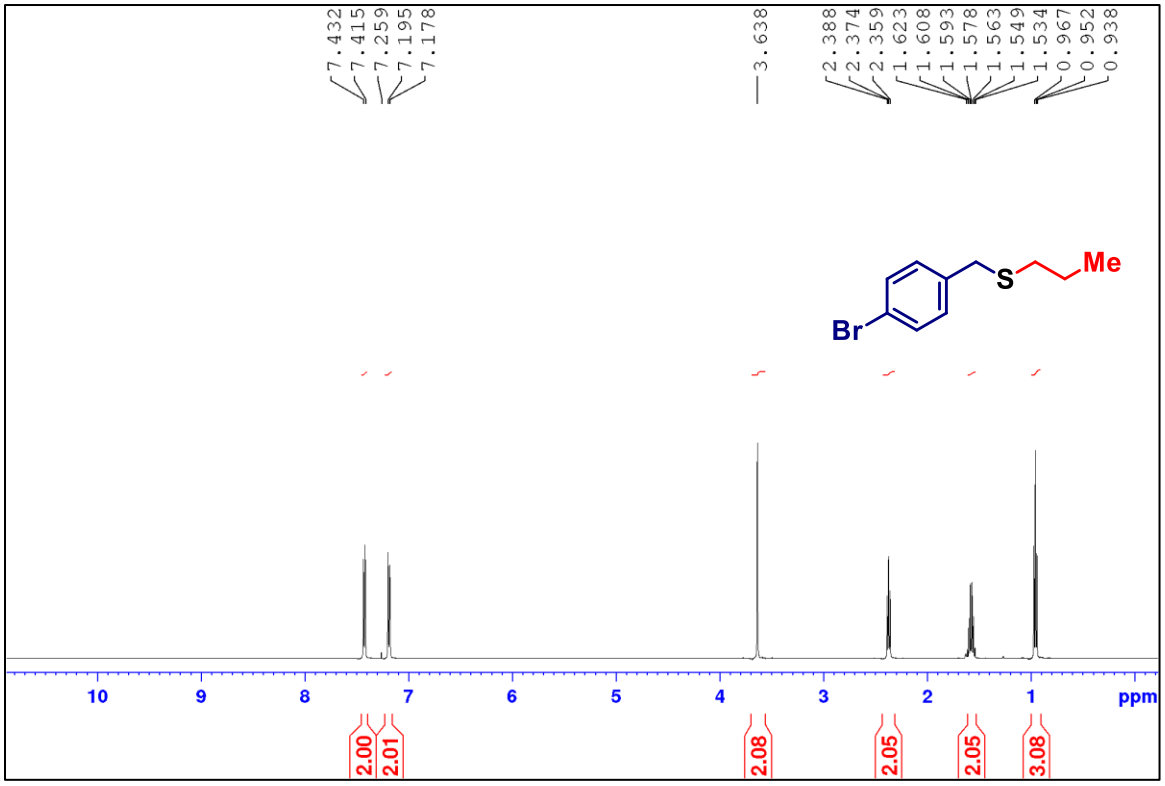


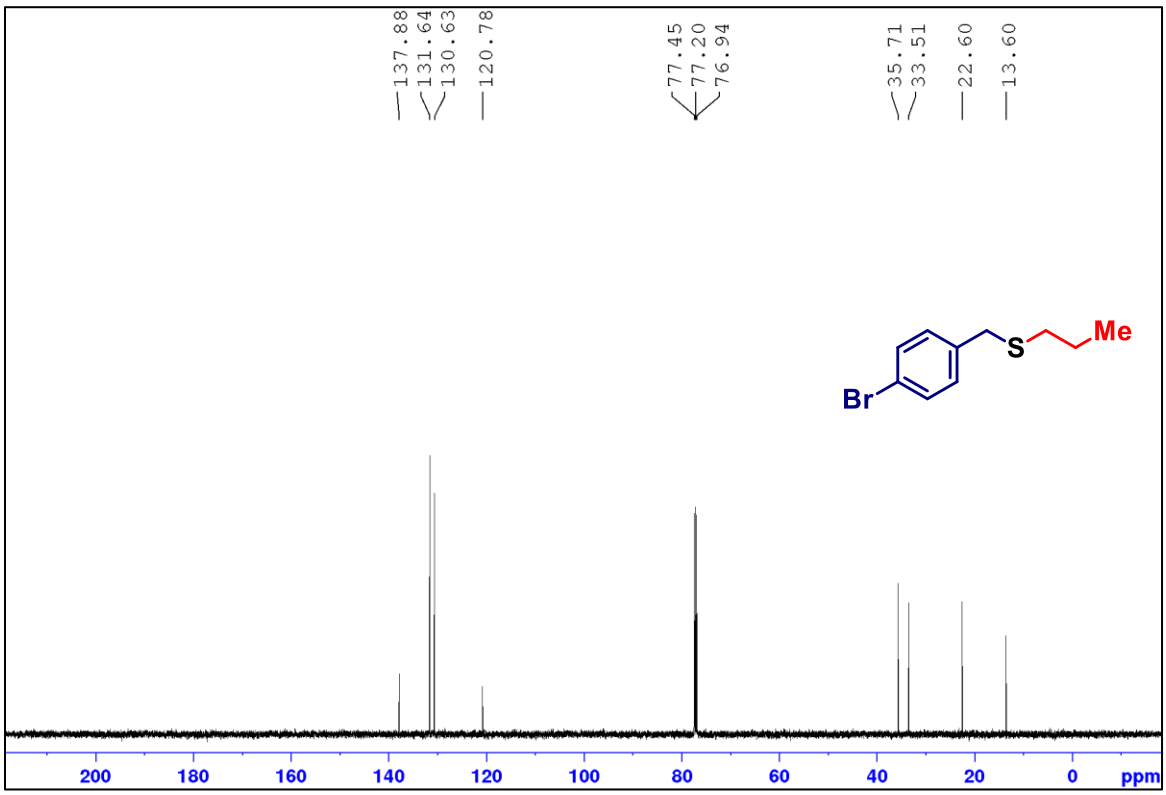
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 14a in $CDCl_3$



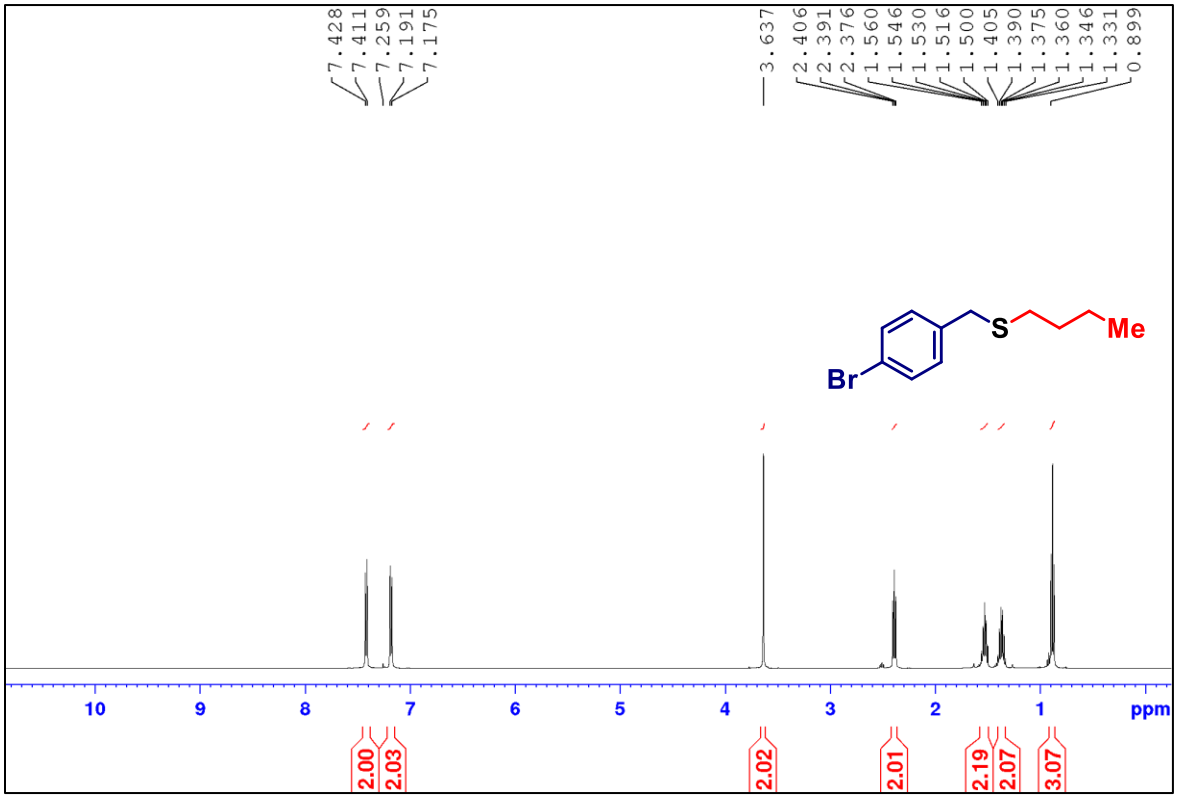


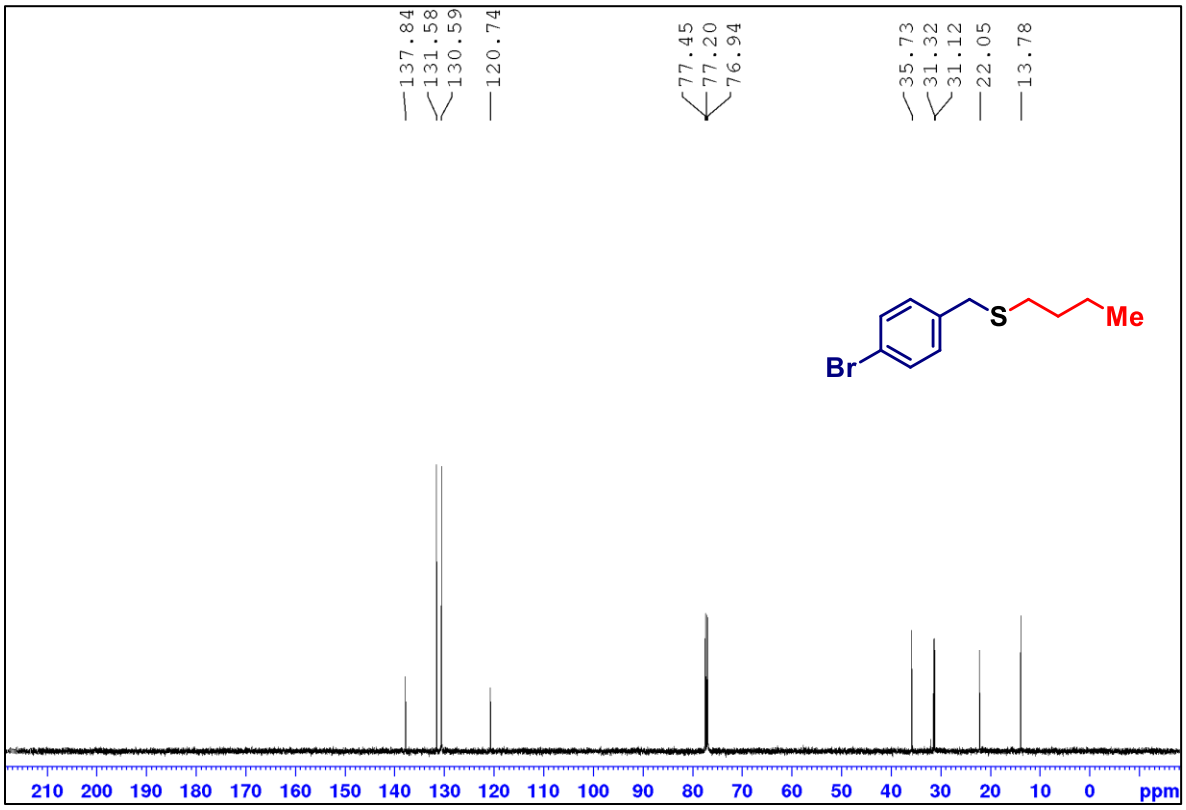
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 14b in $CDCl_3$



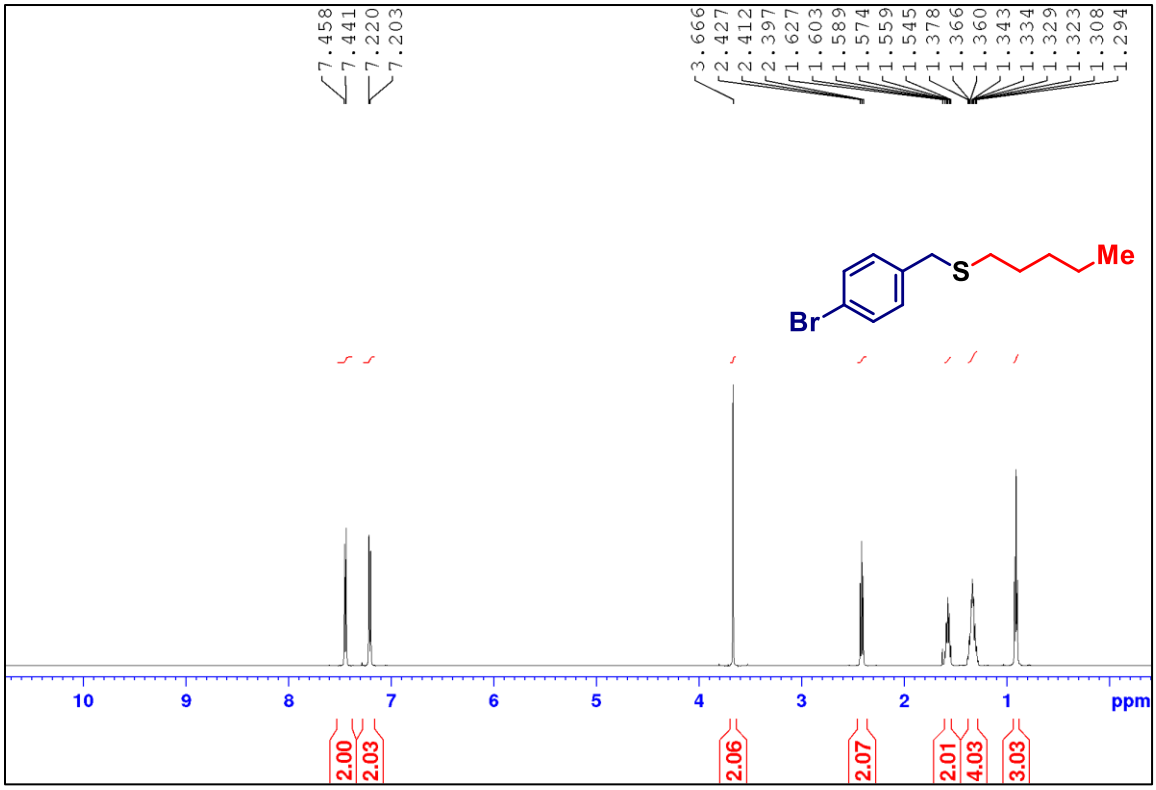


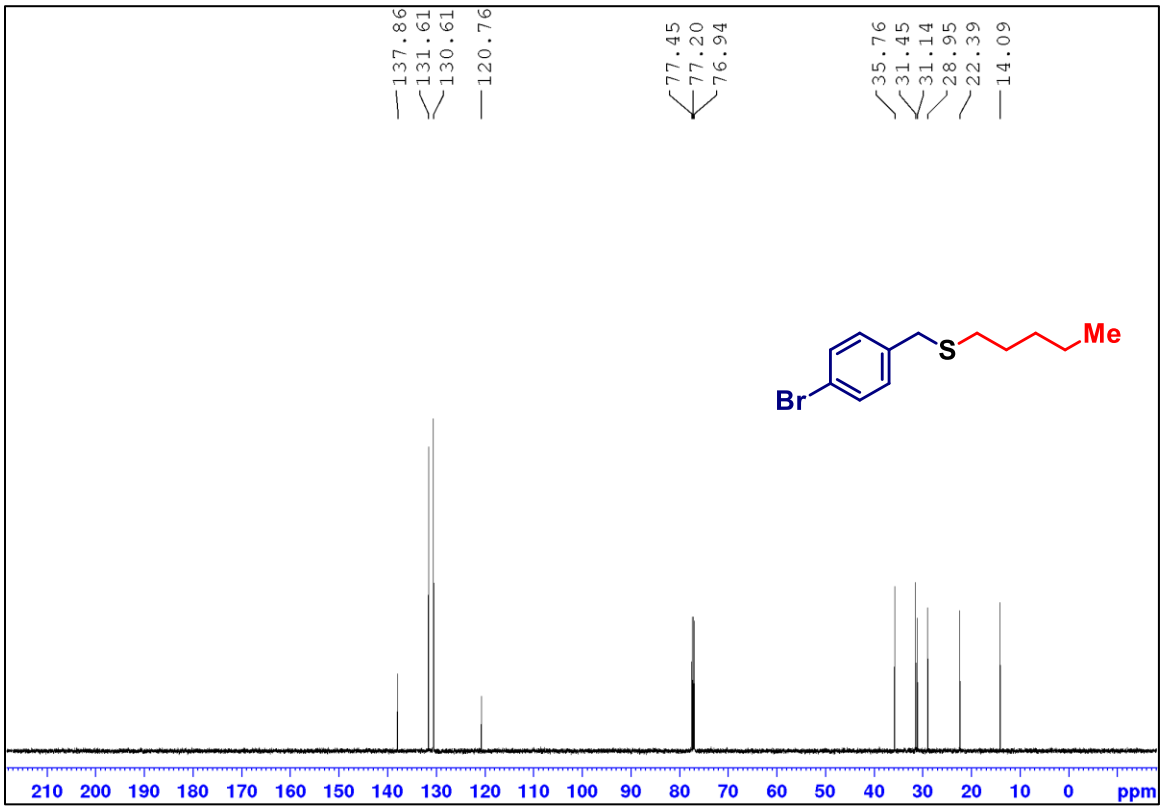
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 14c in $CDCl_3$



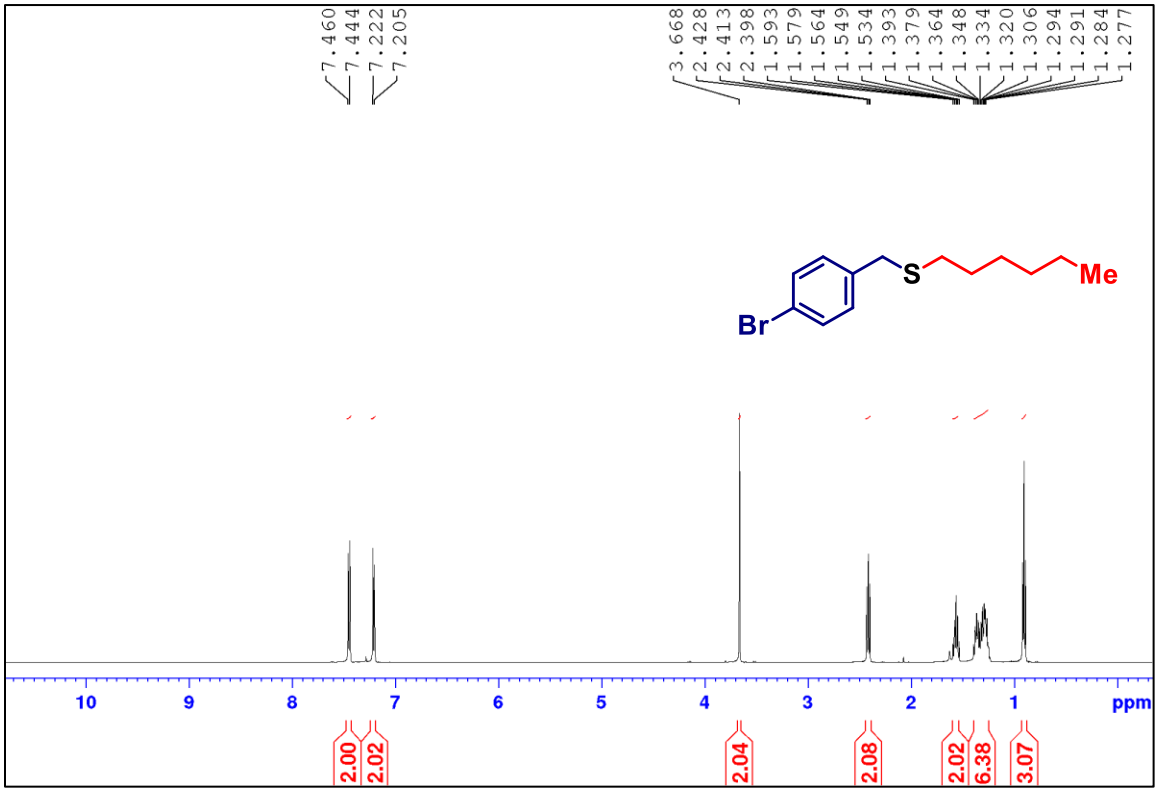


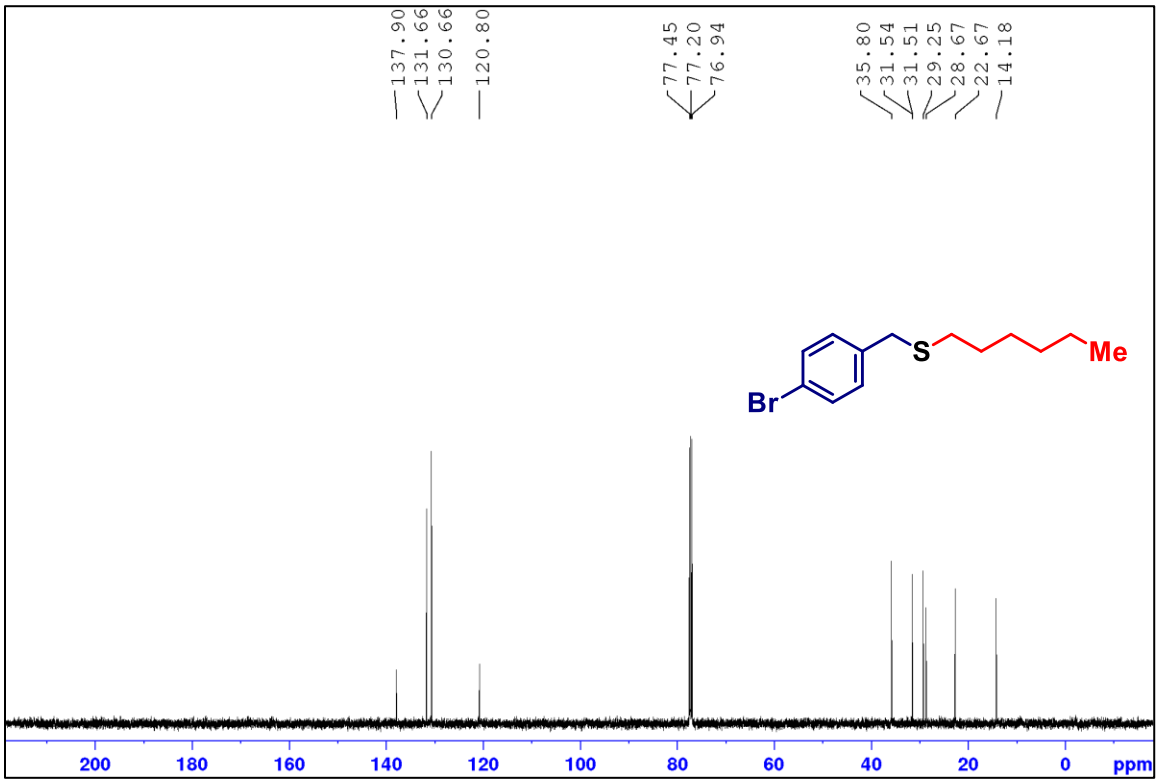
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 14d in $CDCl_3$



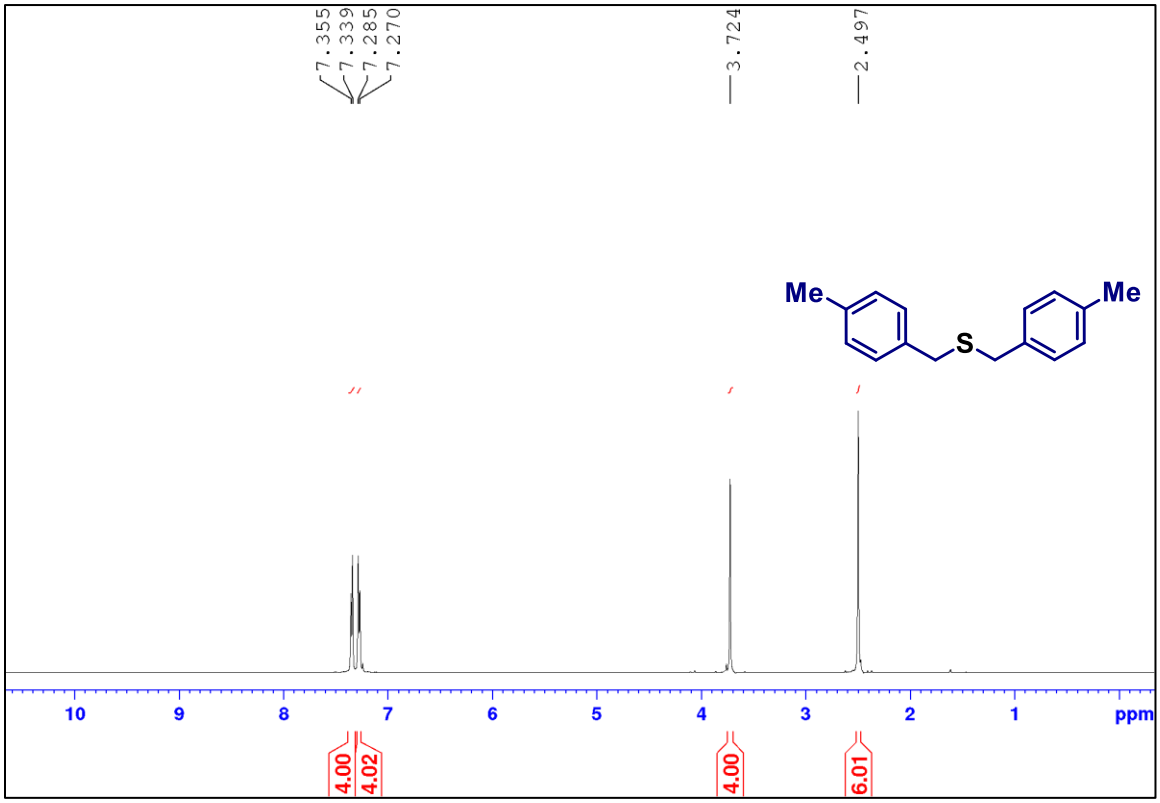


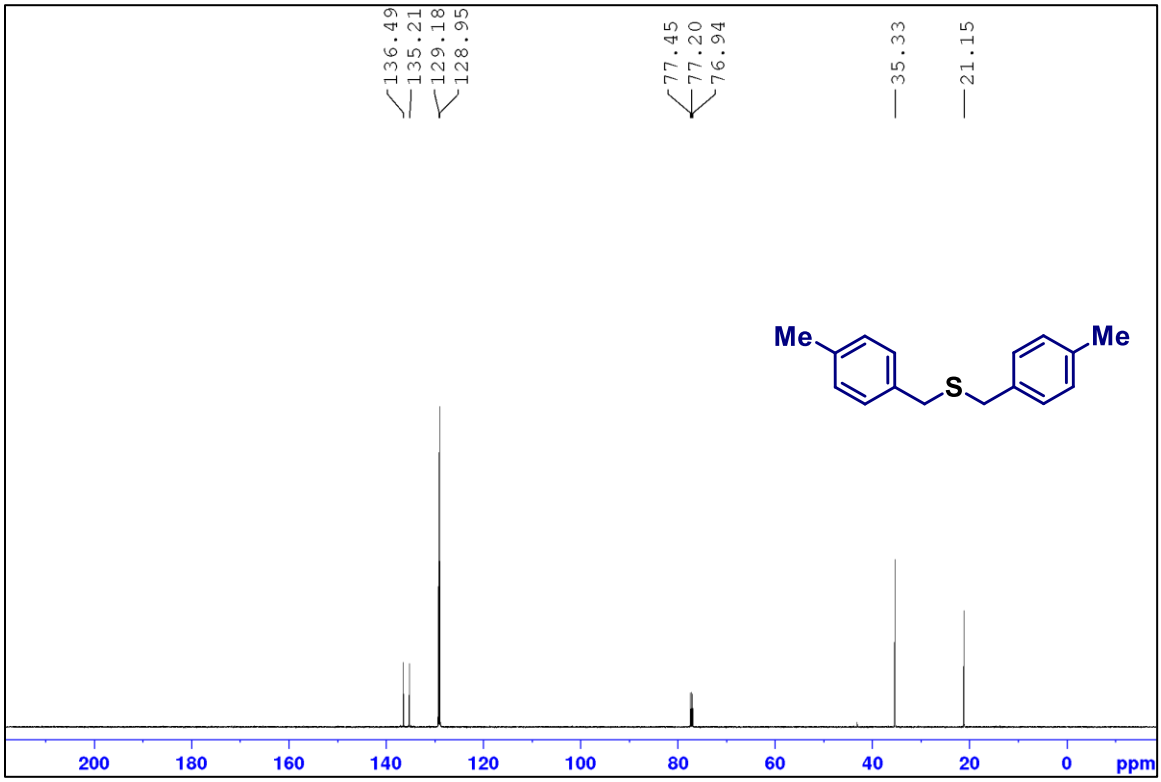
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 14e in $CDCl_3$



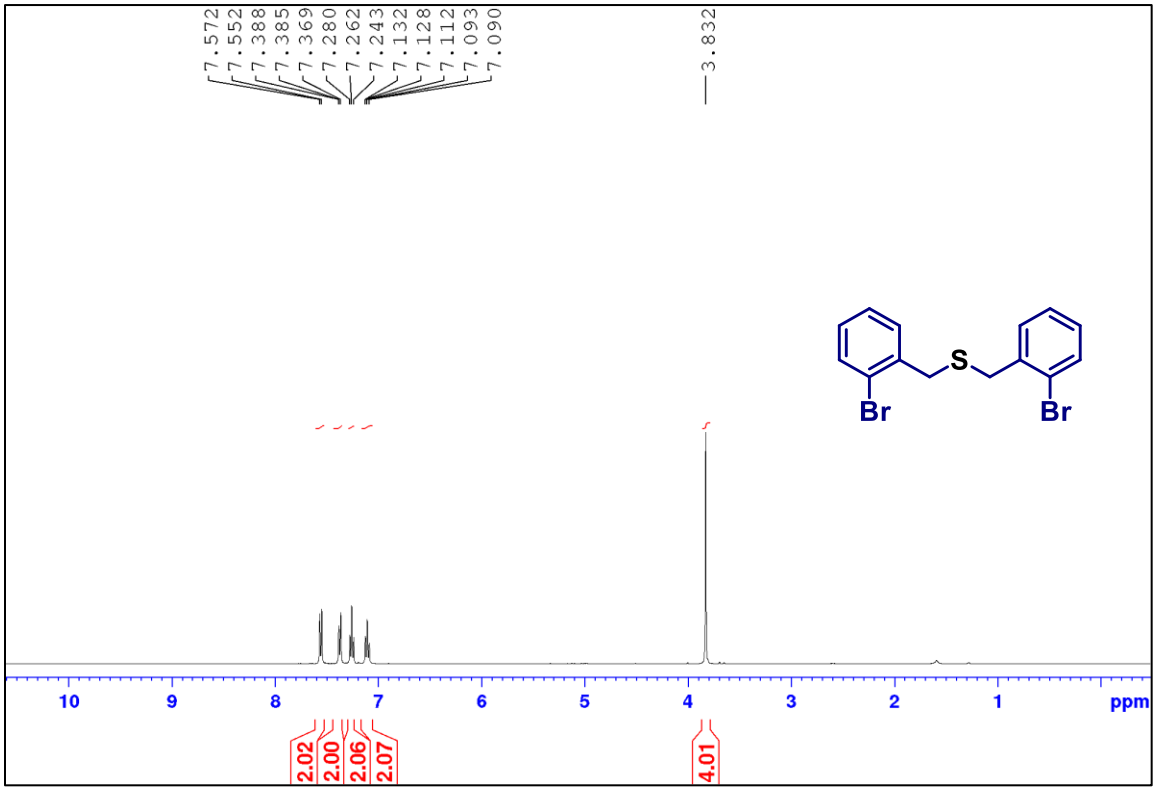


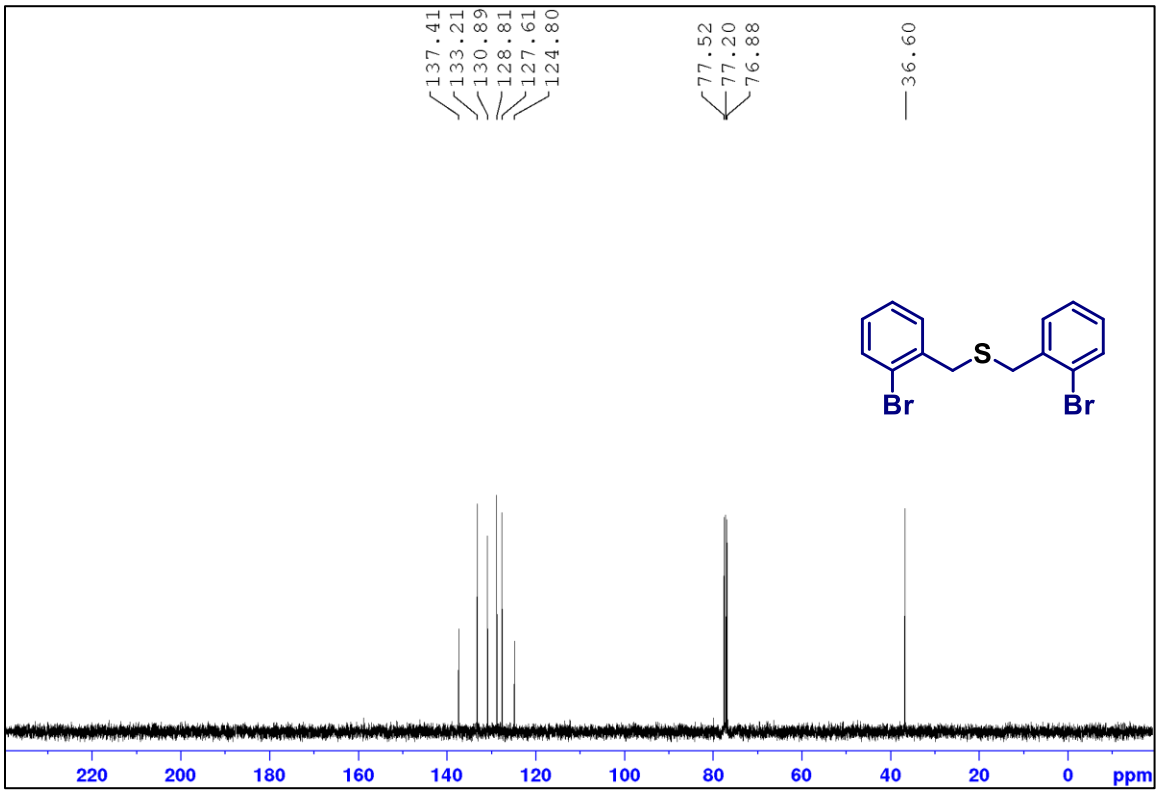
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 15a in $CDCl_3$



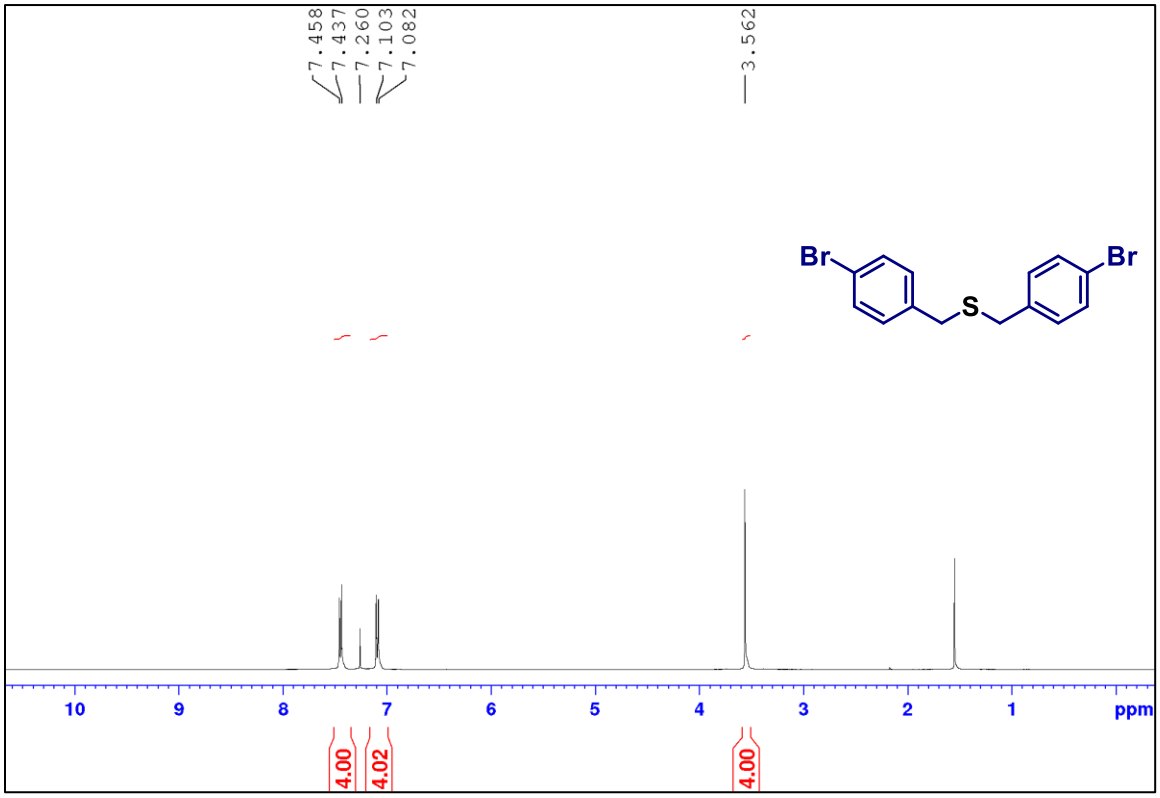


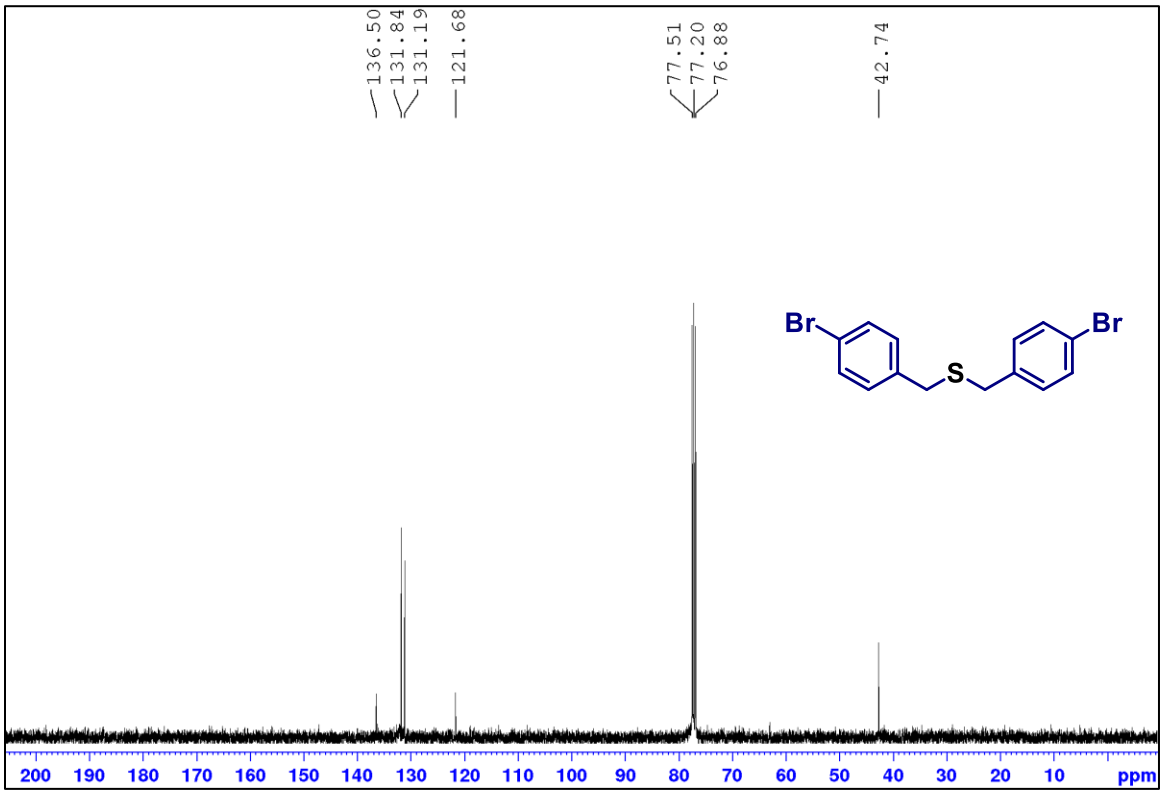
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 15b in $CDCl_3$



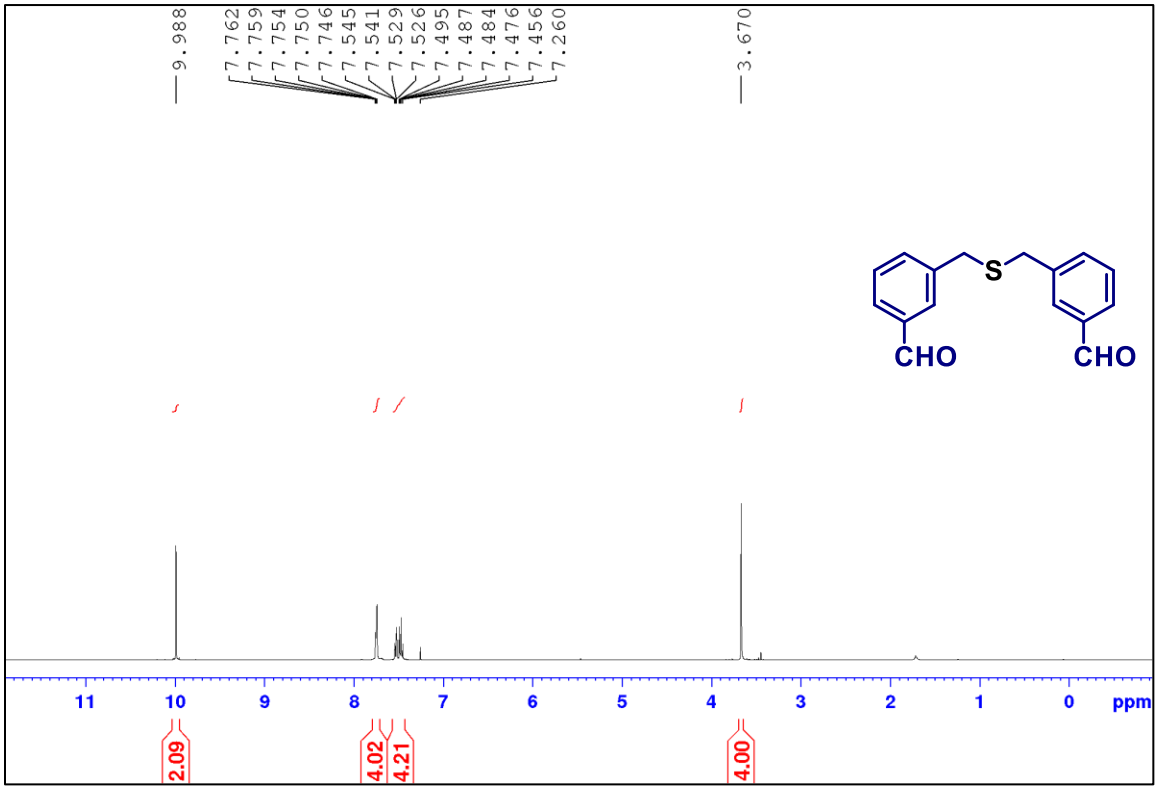


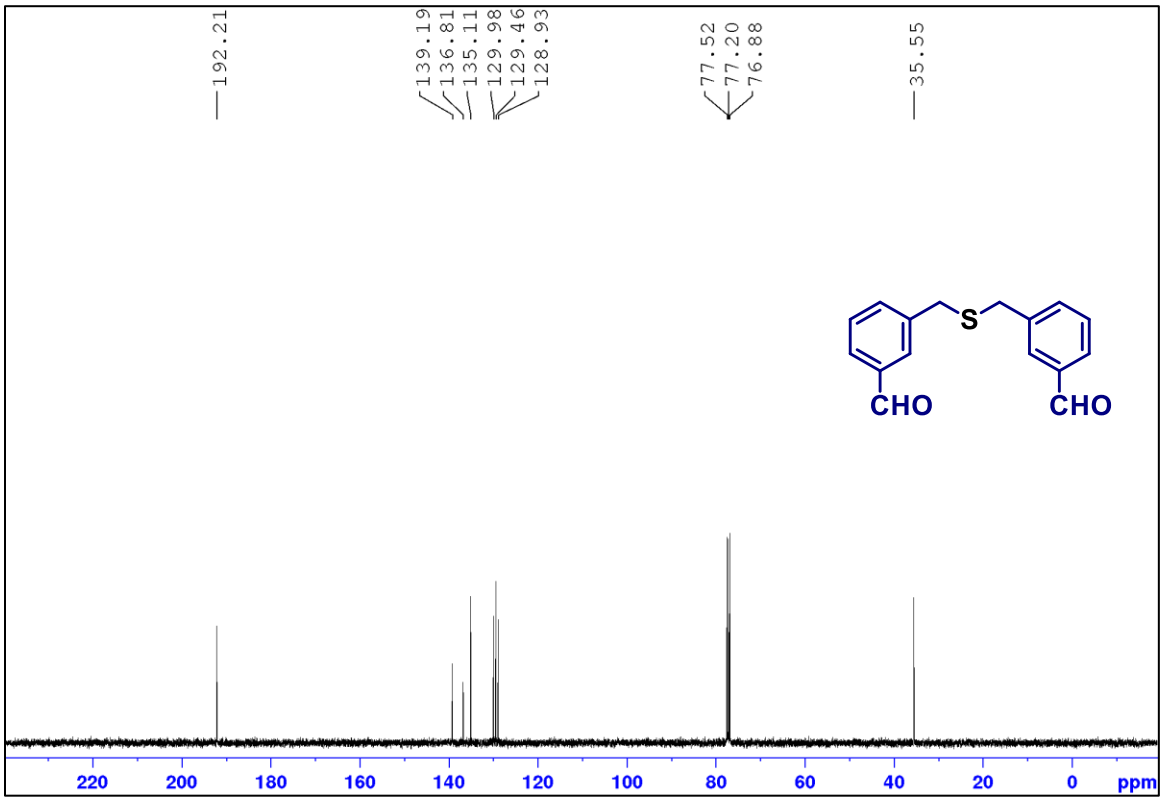
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 15c in $CDCl_3$



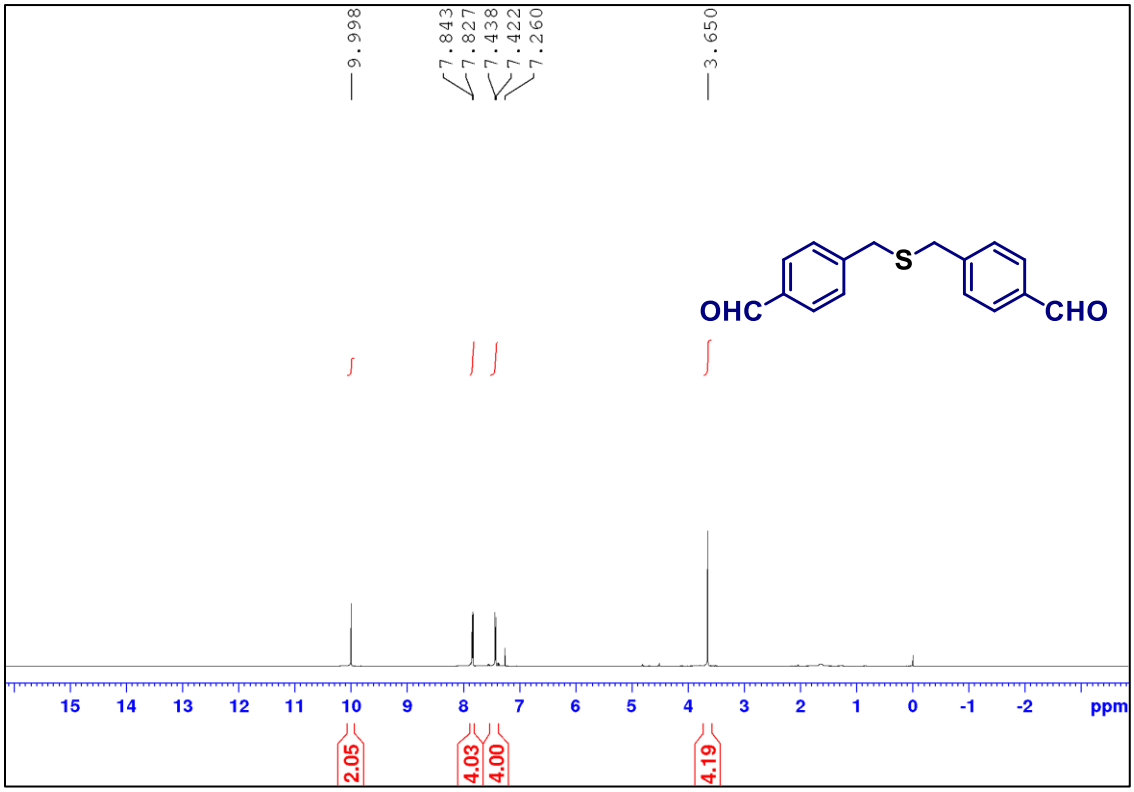


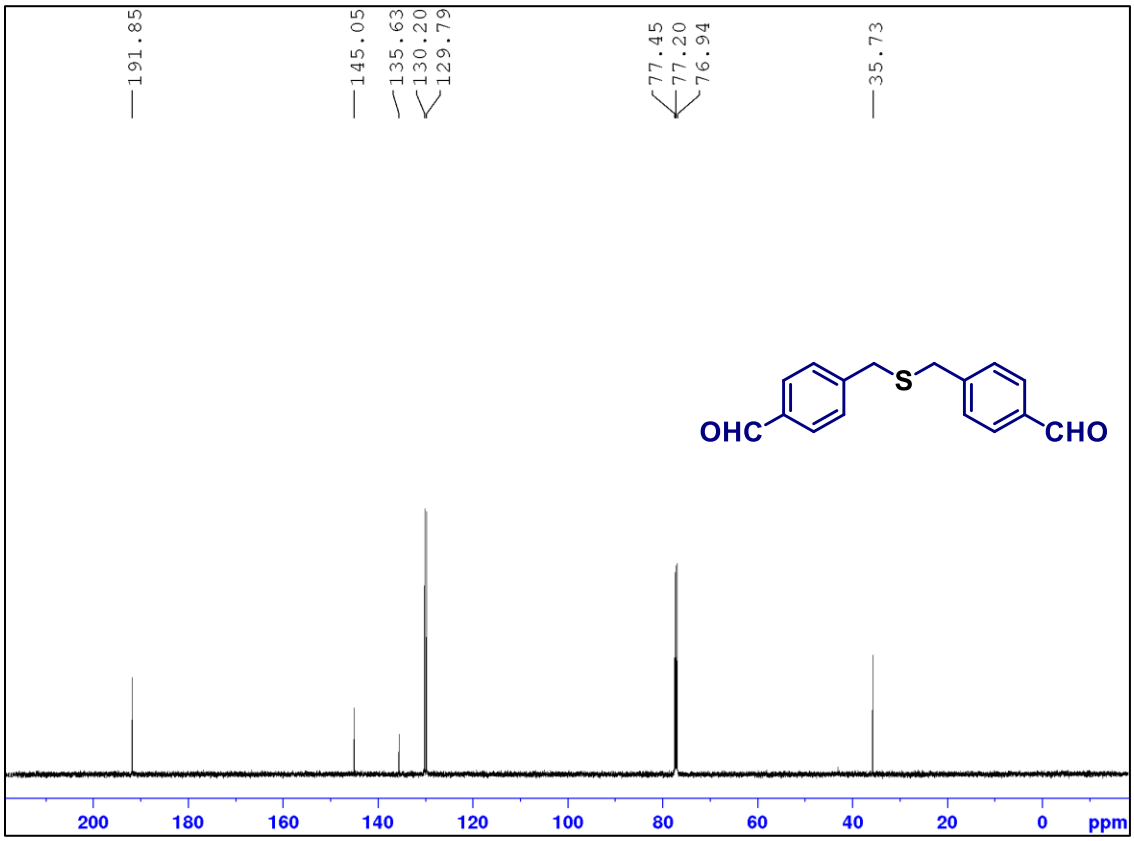
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 15d in $CDCl_3$



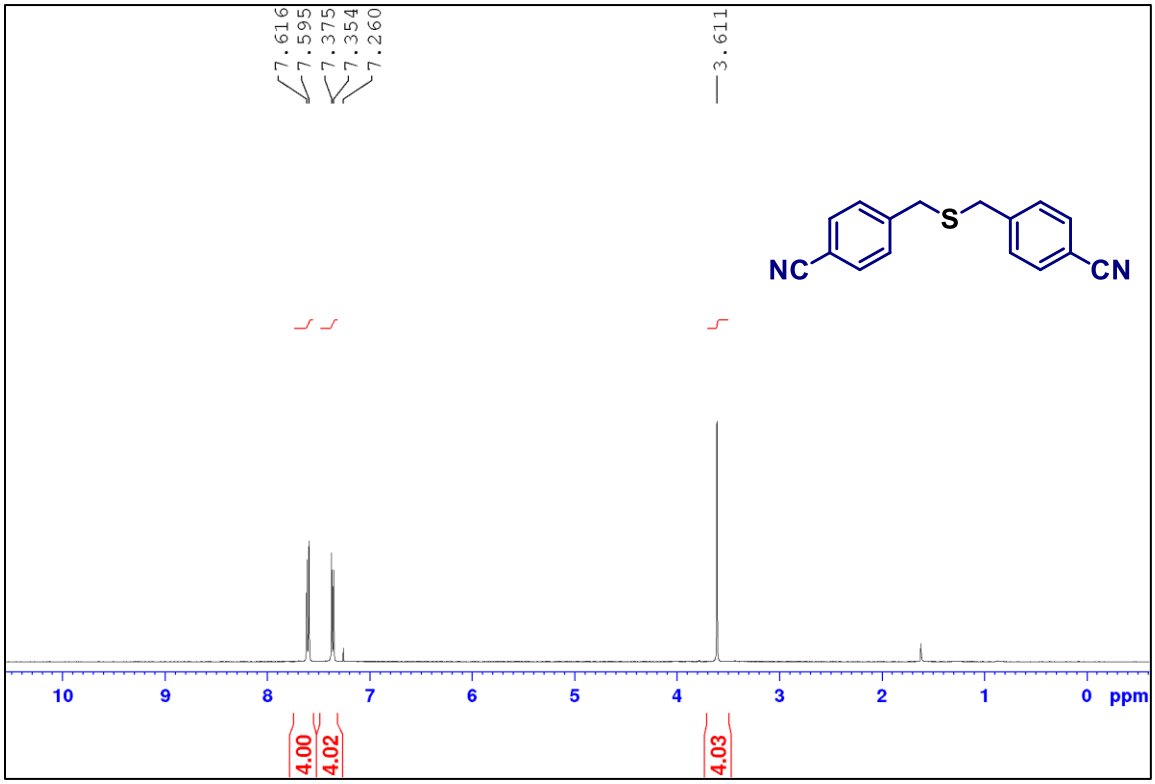


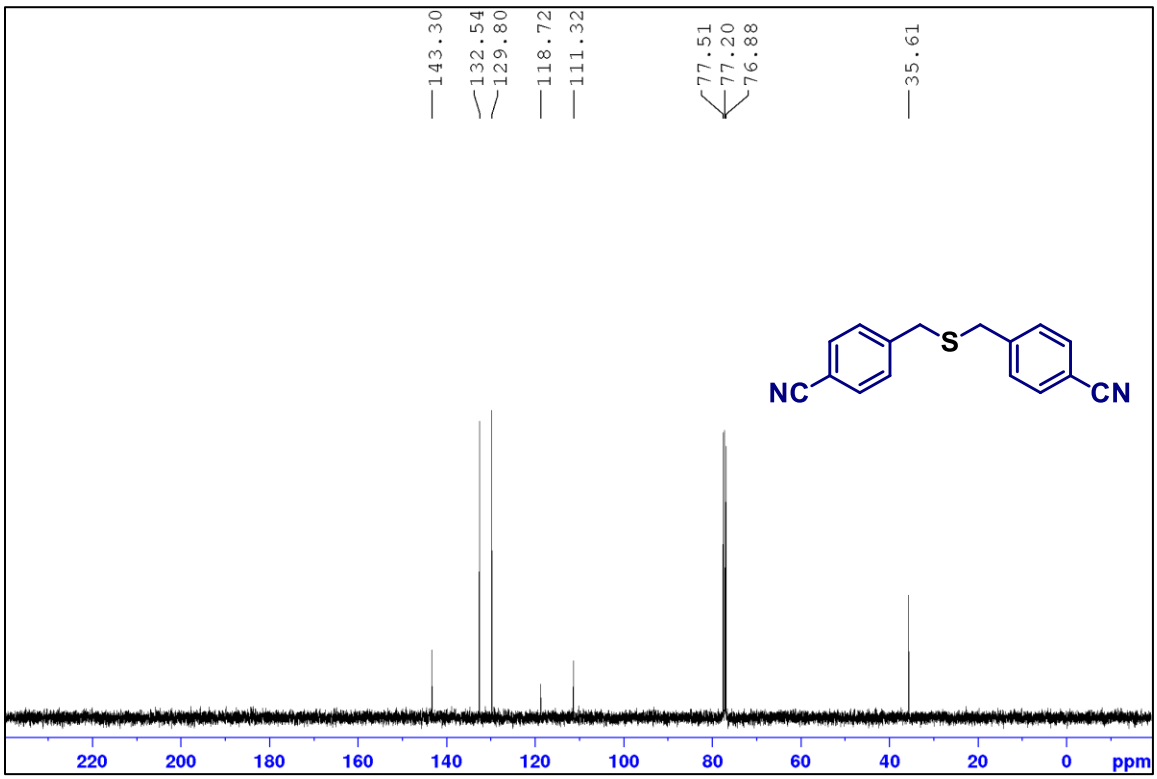
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 15e in $CDCl_3$



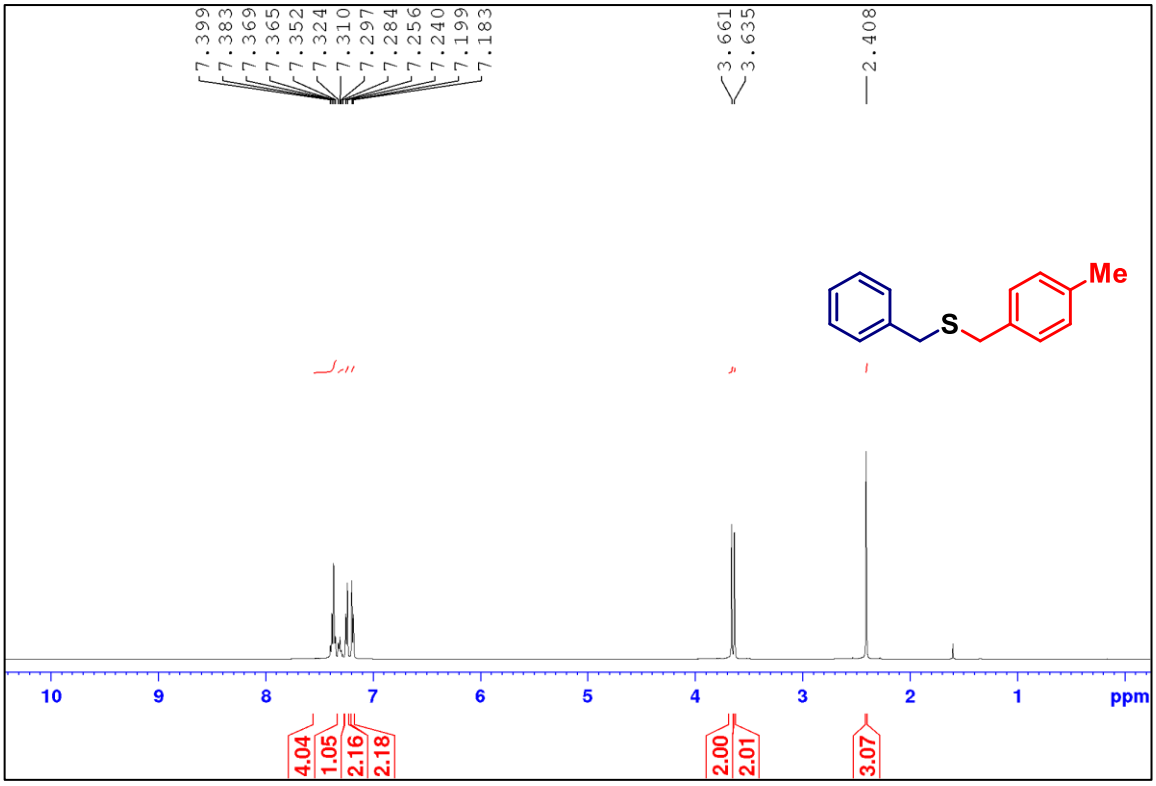


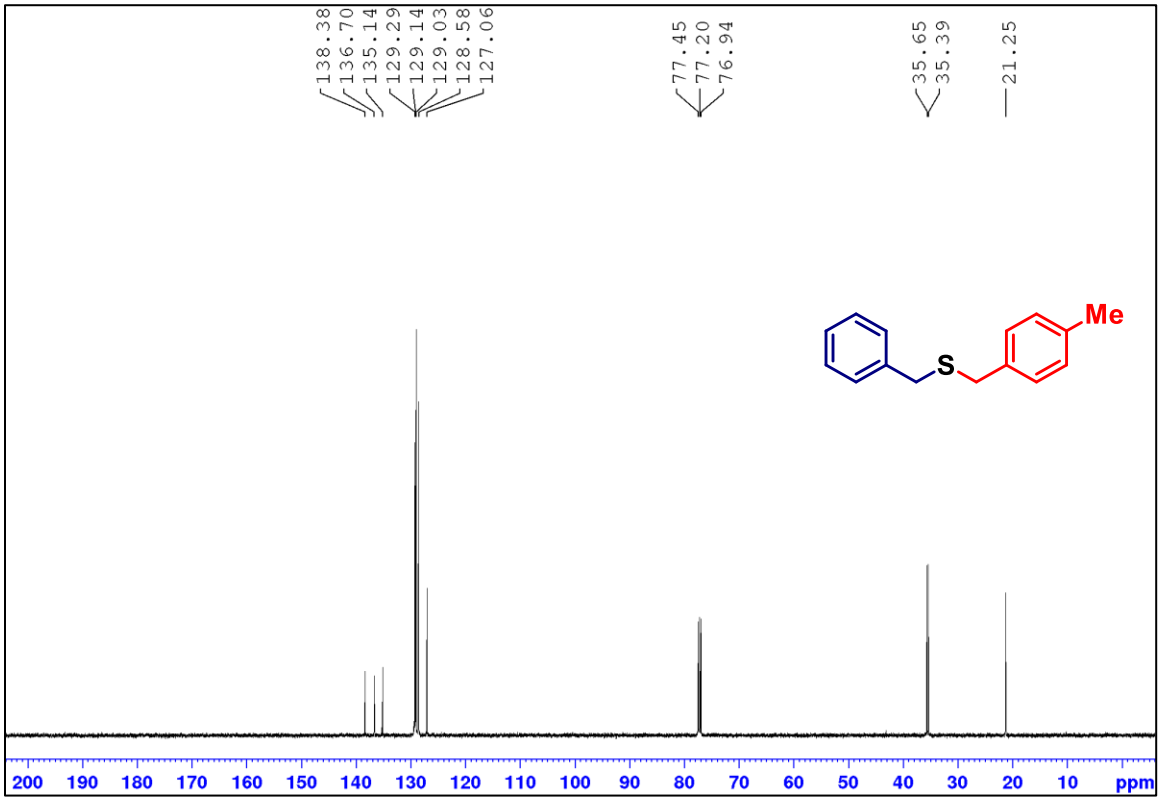
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 15f in $CDCl_3$



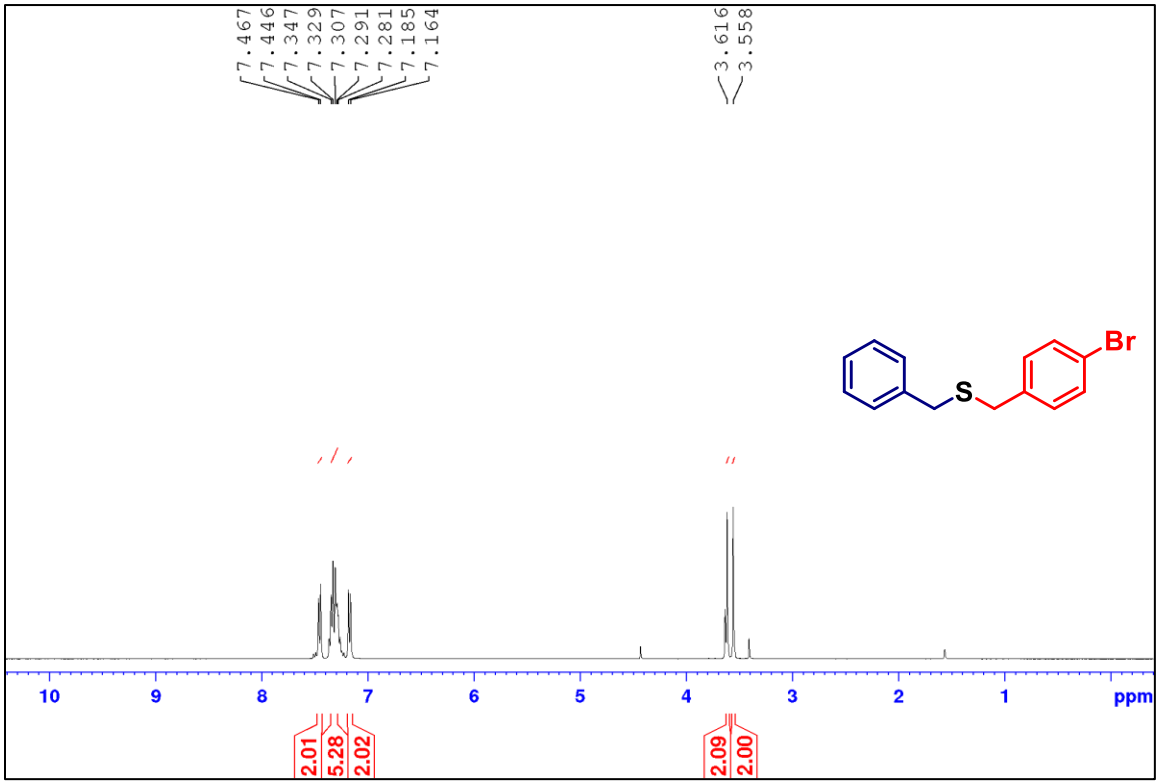


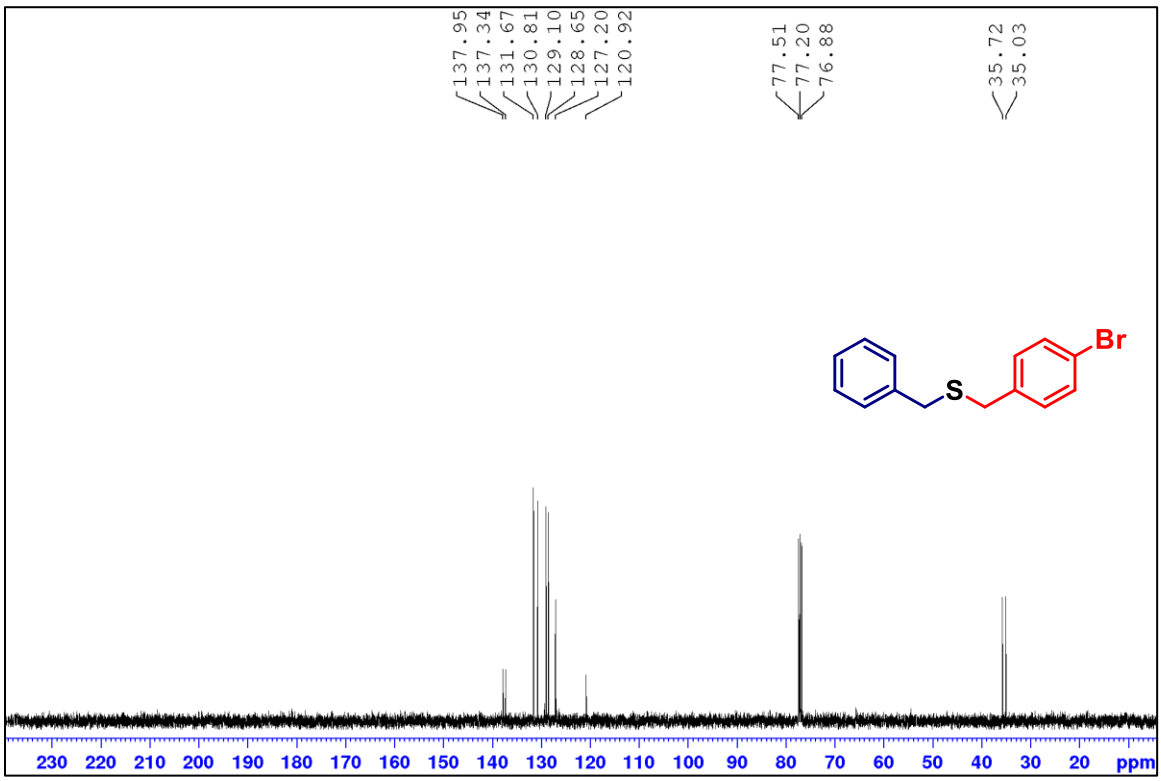
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 16a in $CDCl_3$



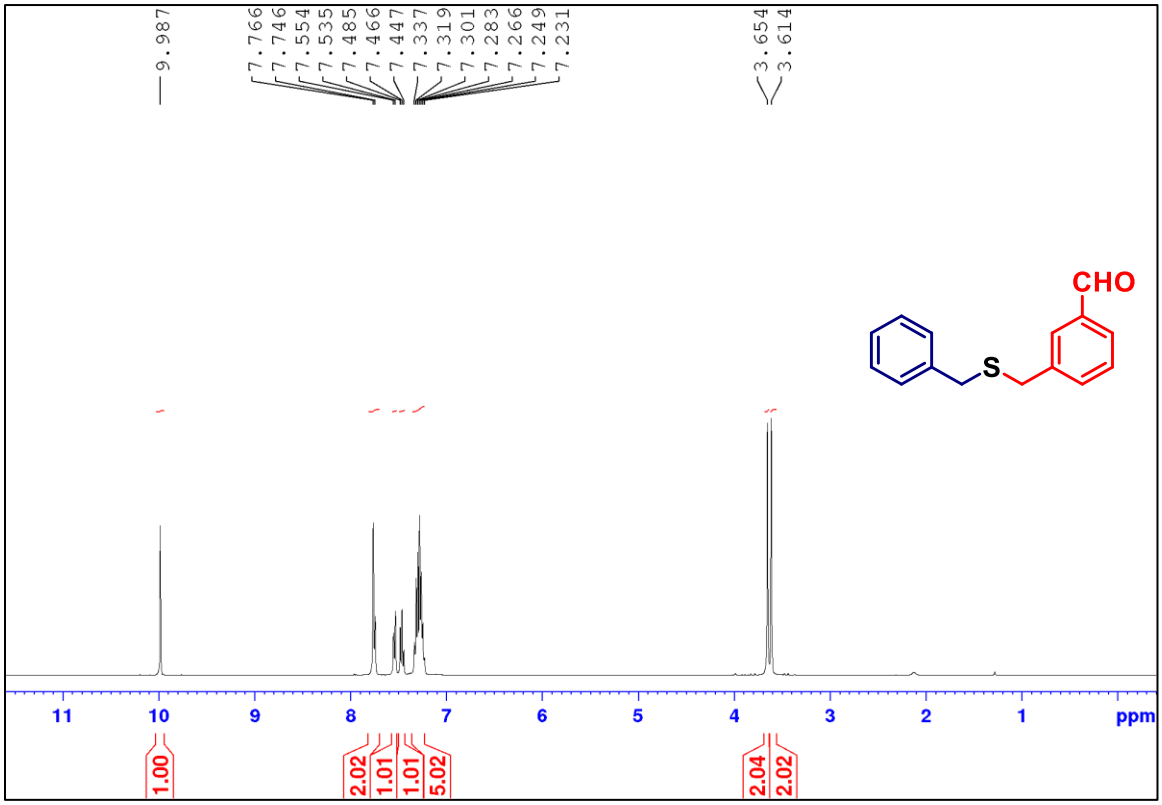


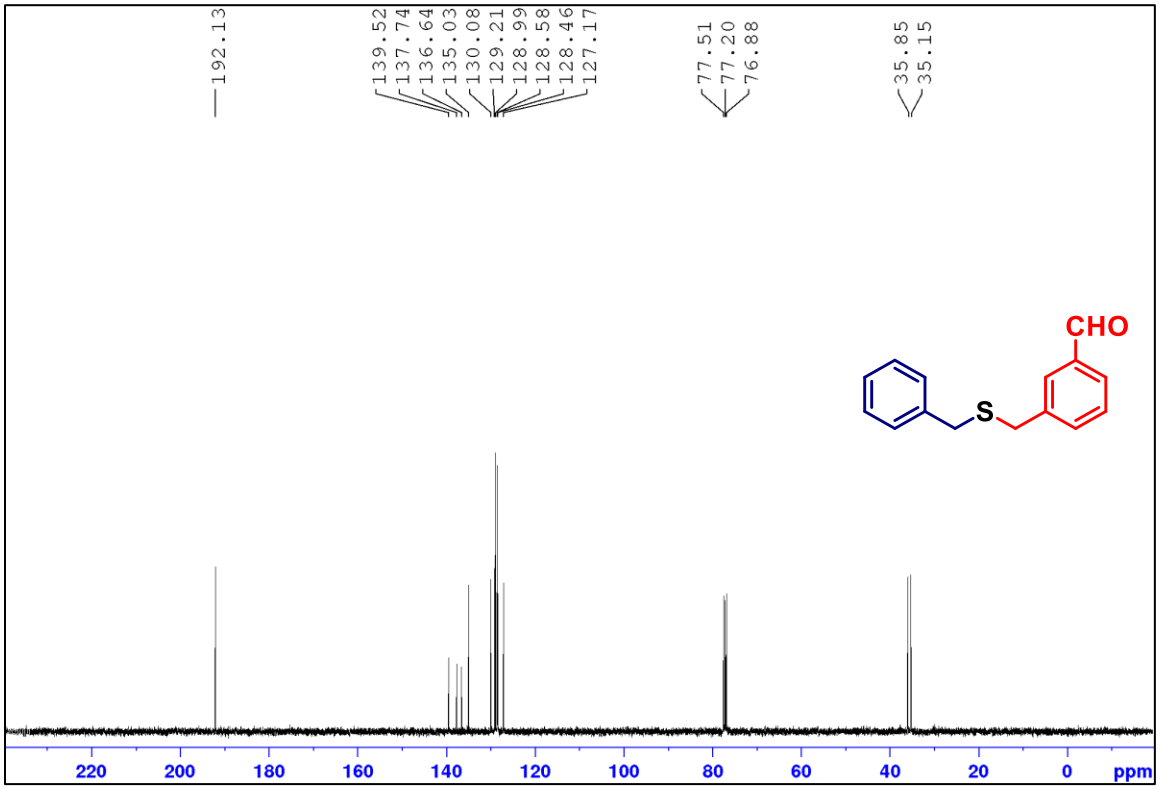
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 16b in $CDCl_3$



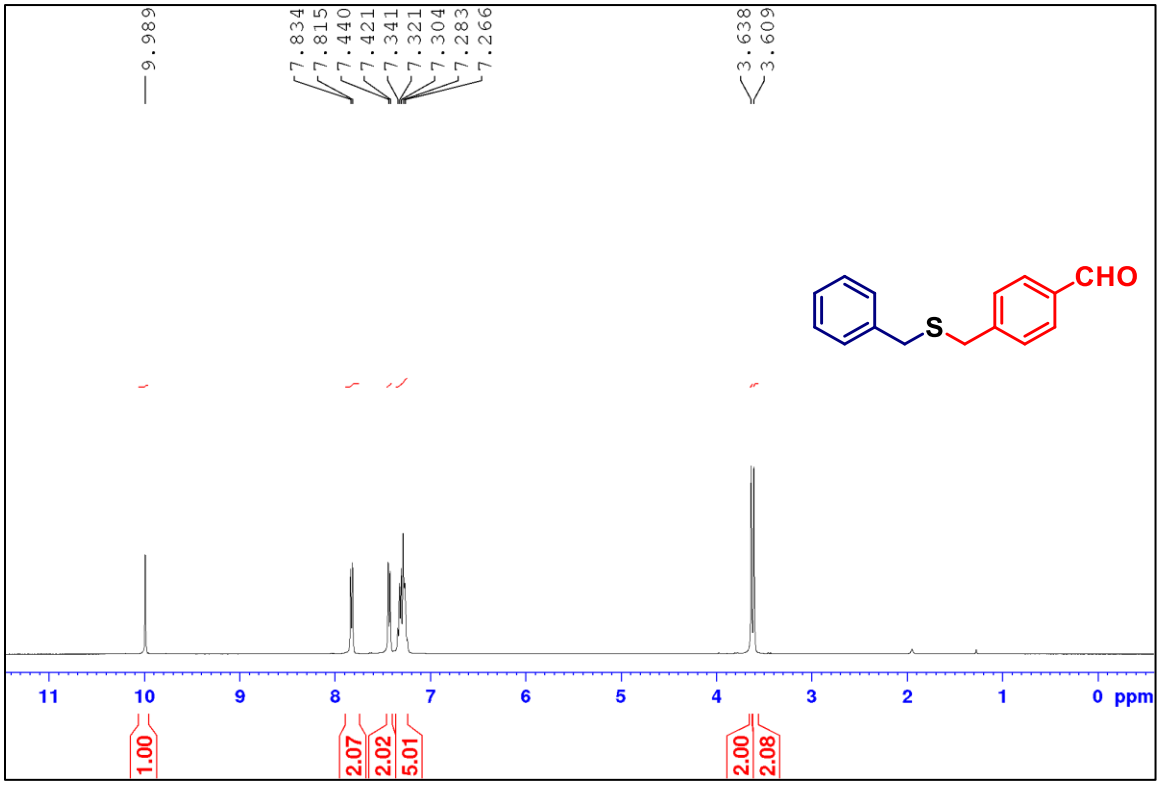


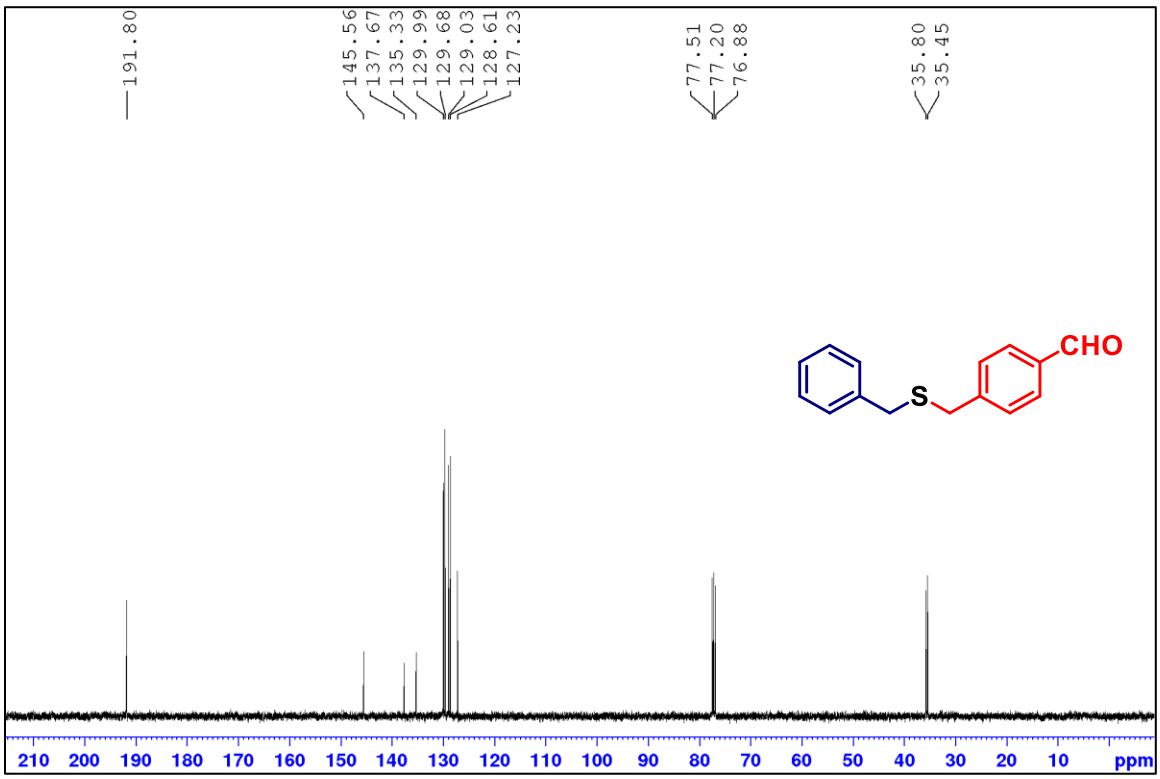
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 16c in $CDCl_3$



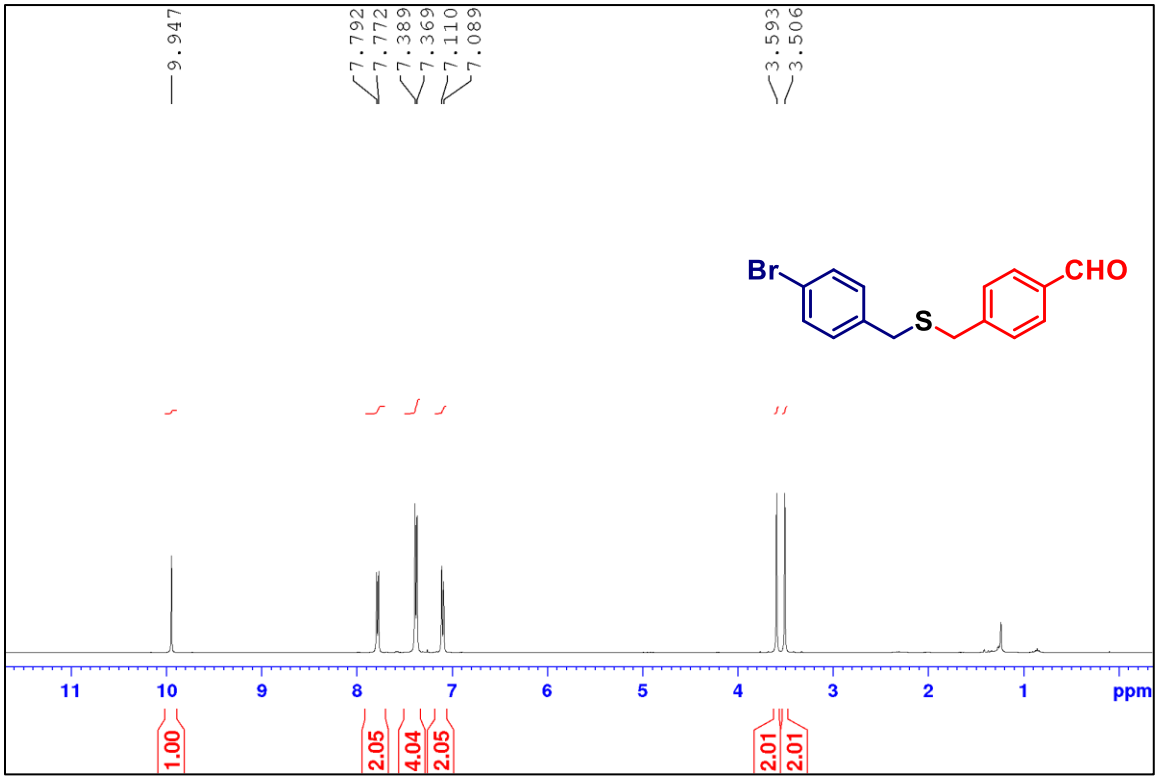


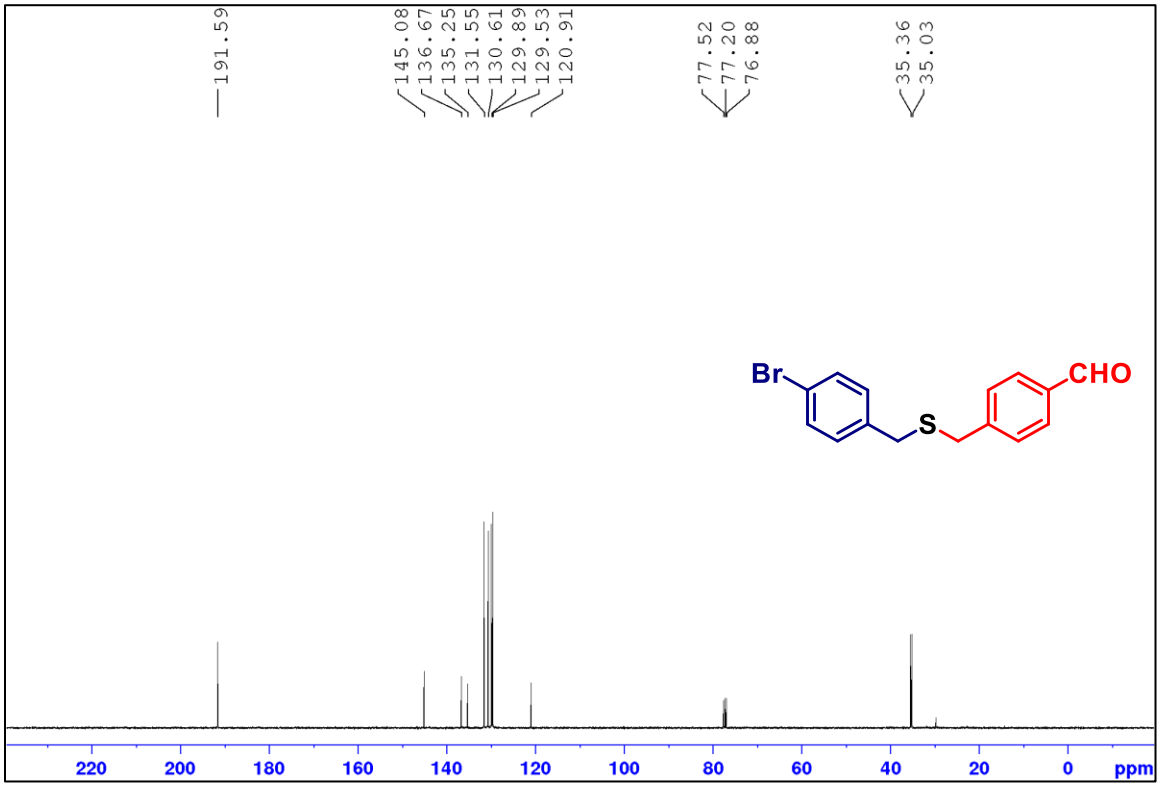
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 16d in $CDCl_3$



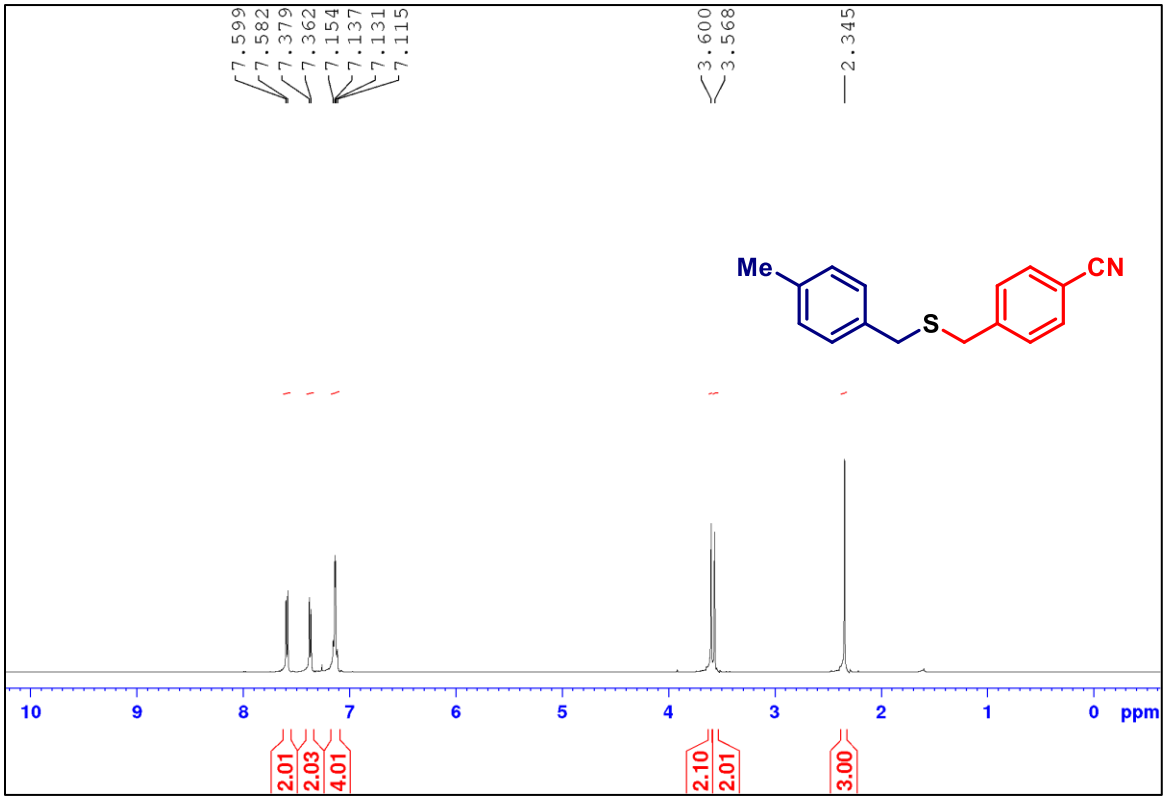


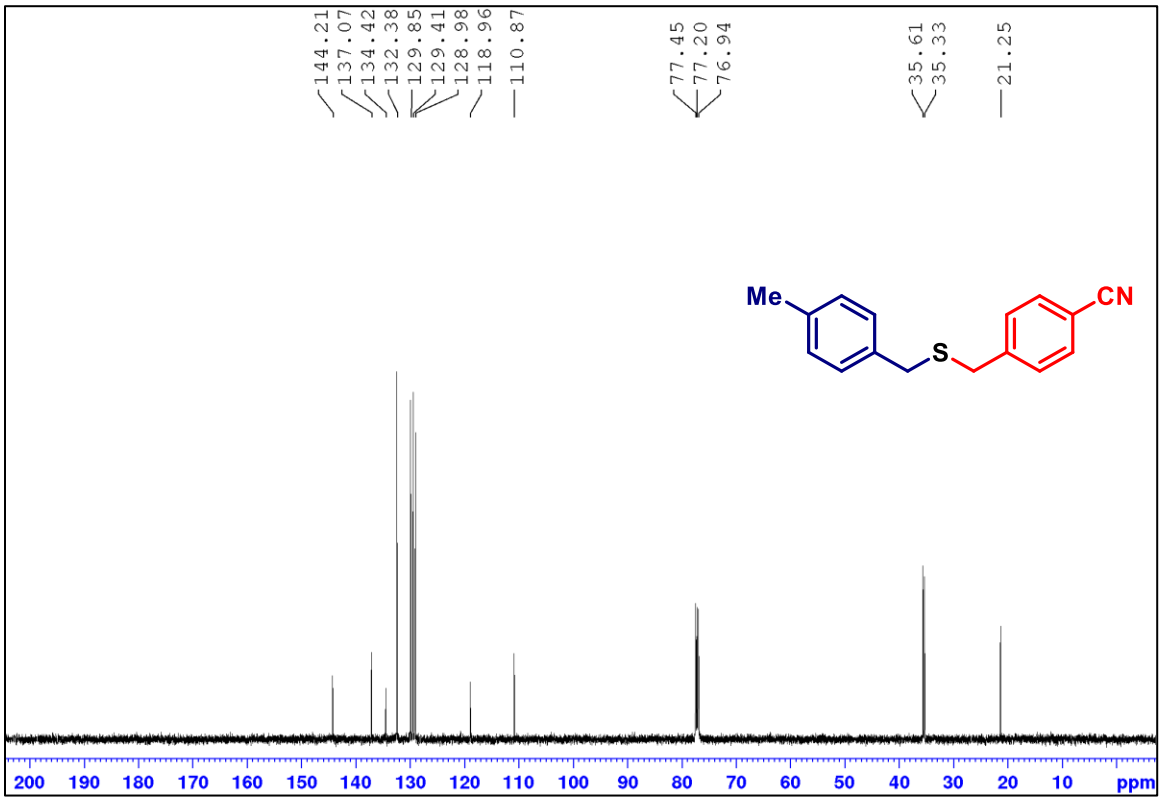
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 17 in $CDCl_3$



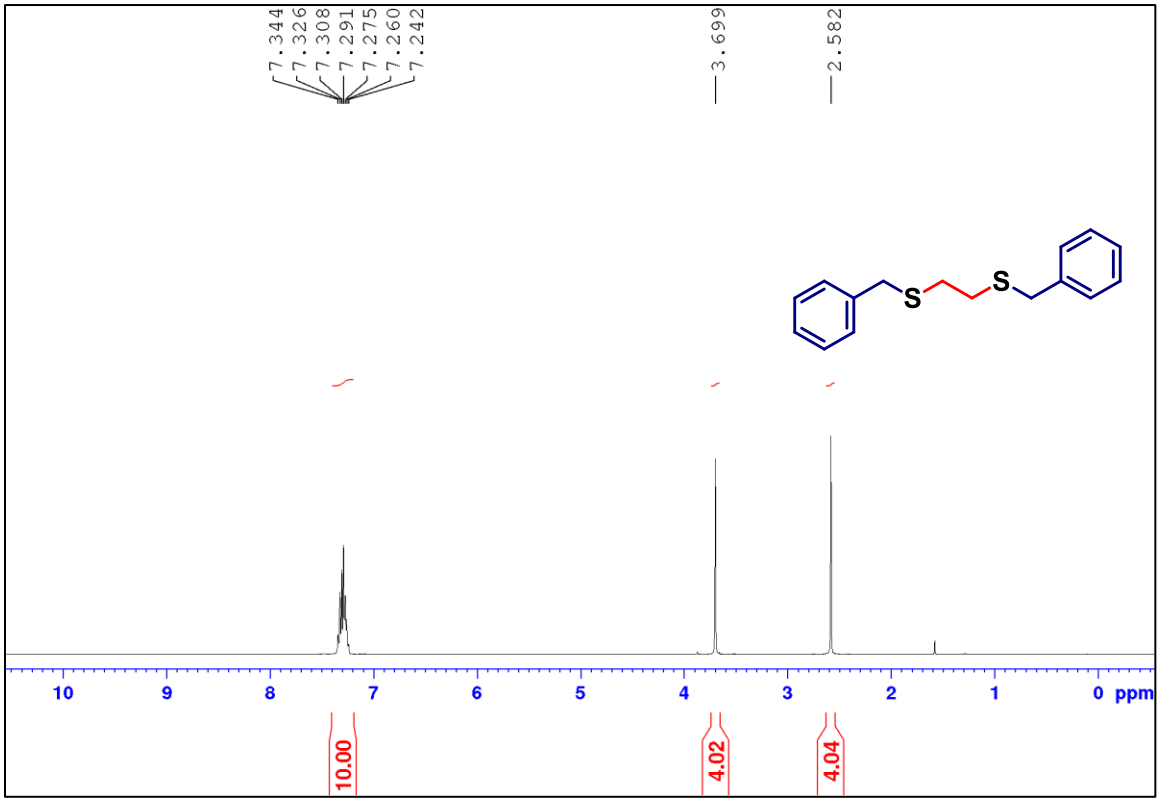


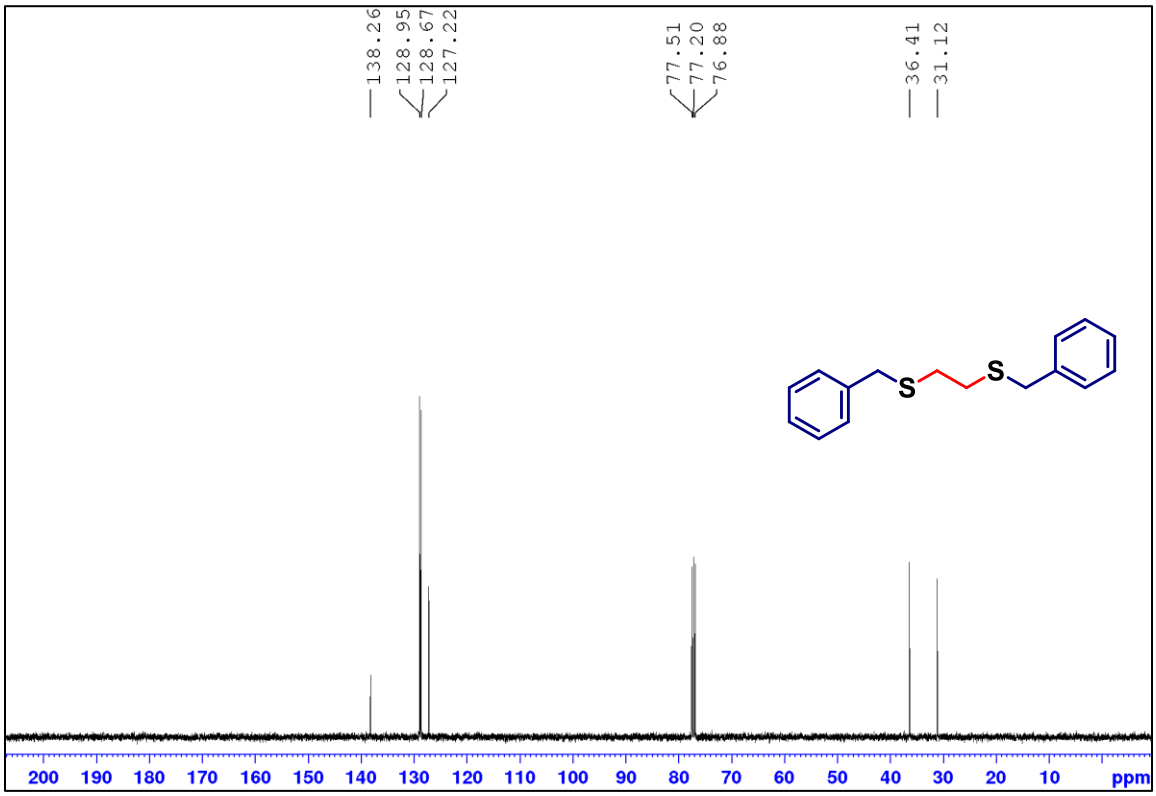
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 18 in $CDCl_3$



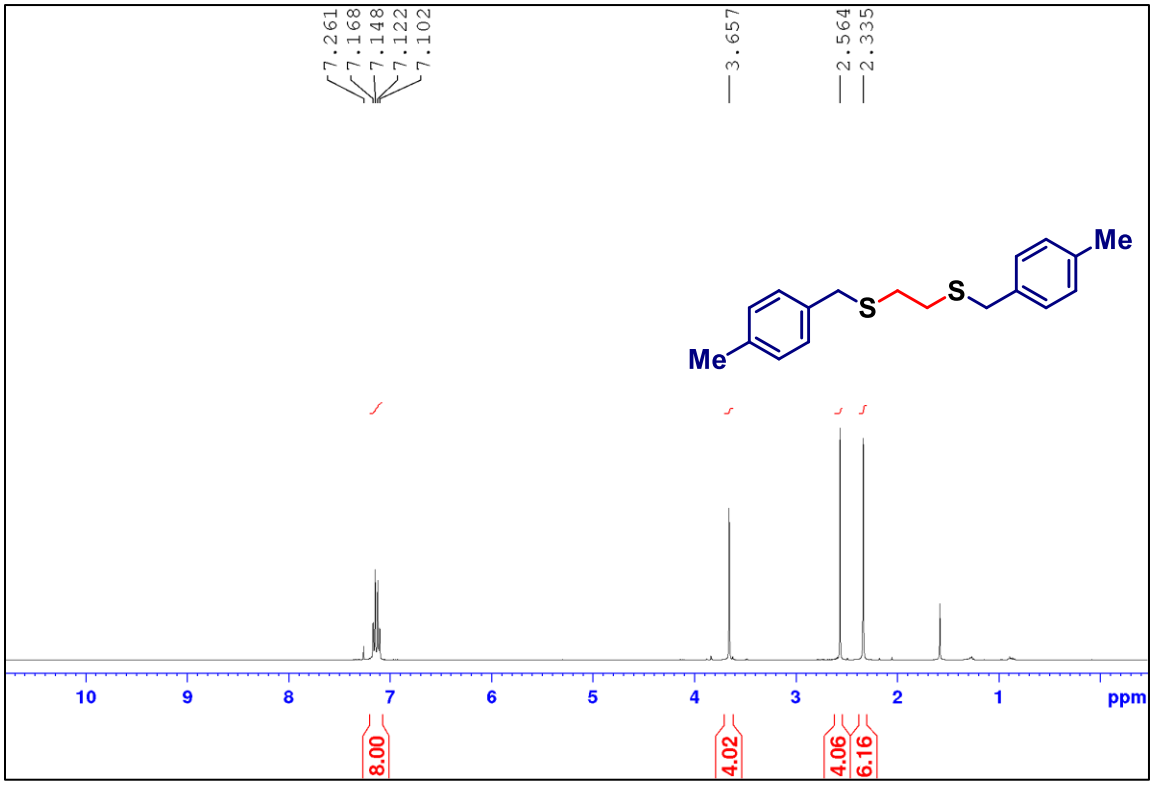


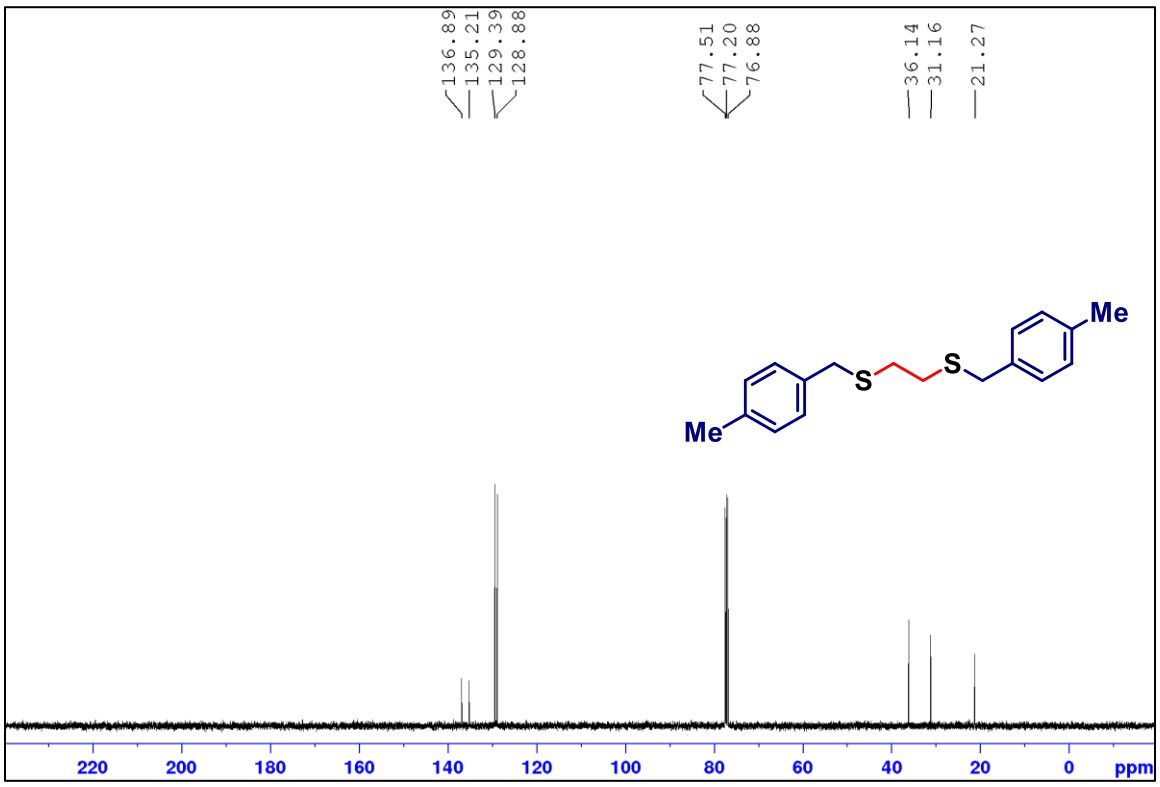
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 19a in $CDCl_3$



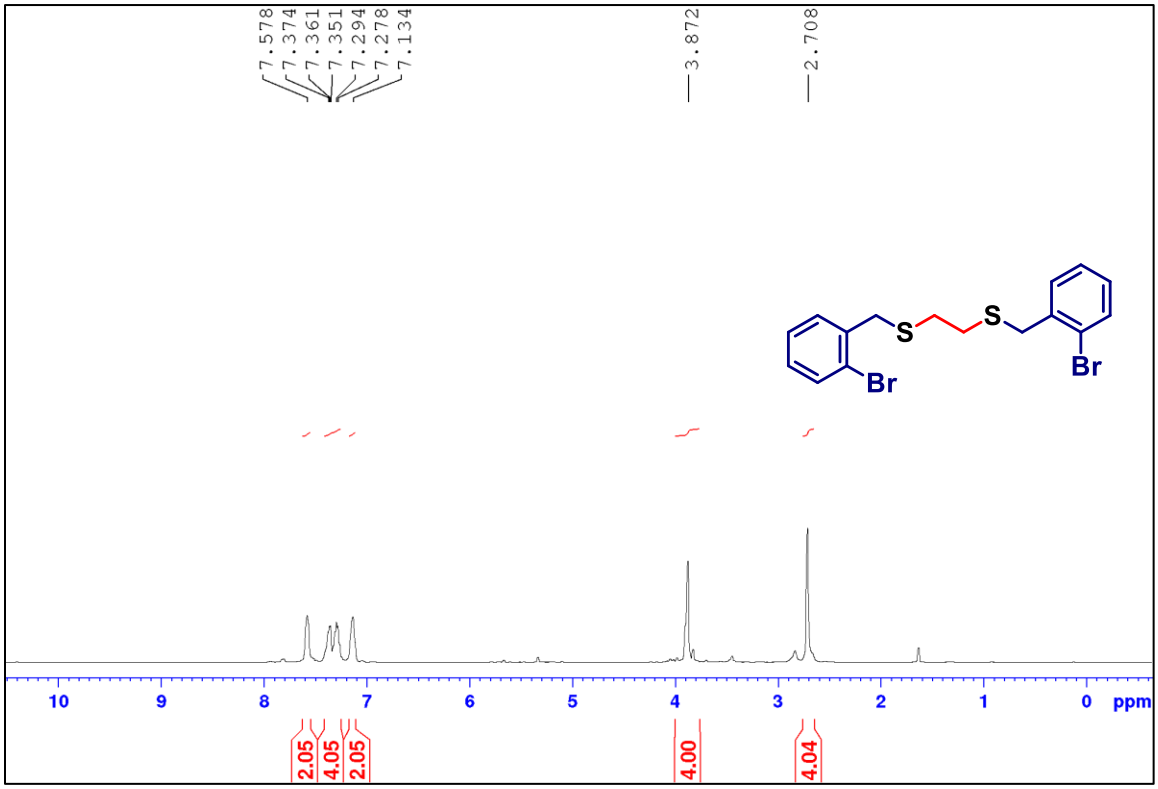


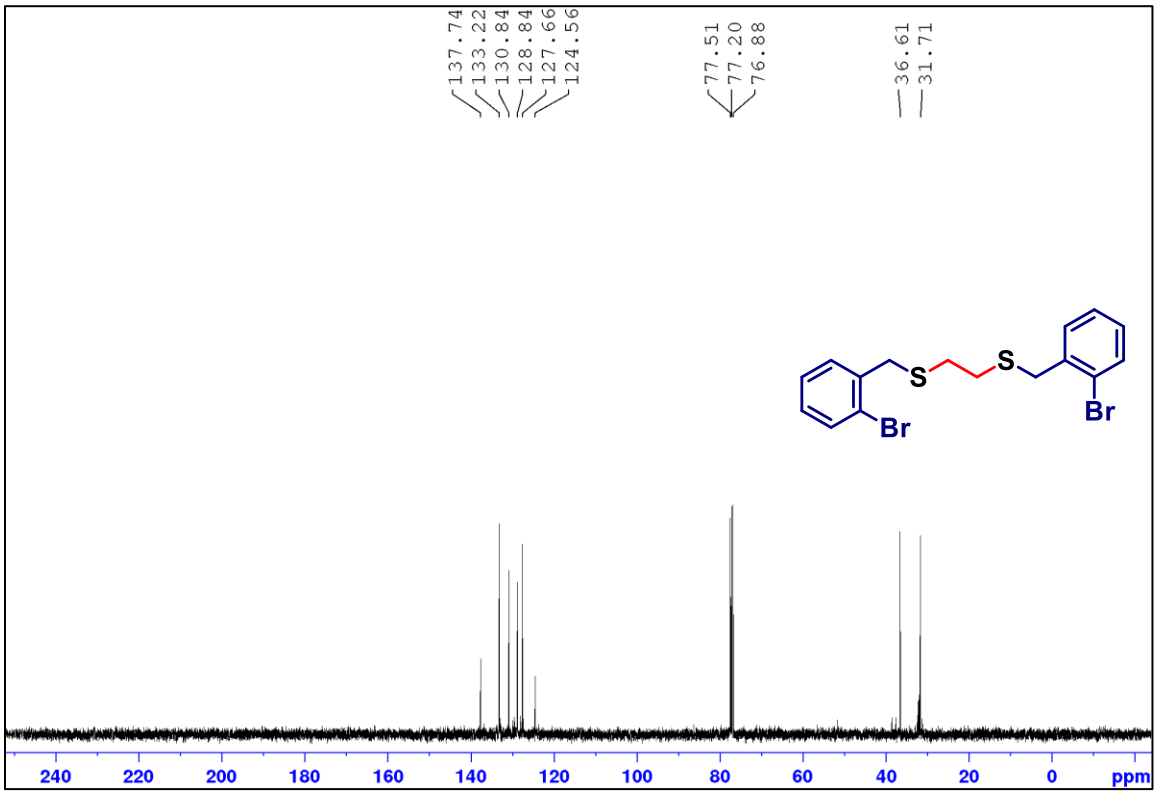
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 19b in $CDCl_3$



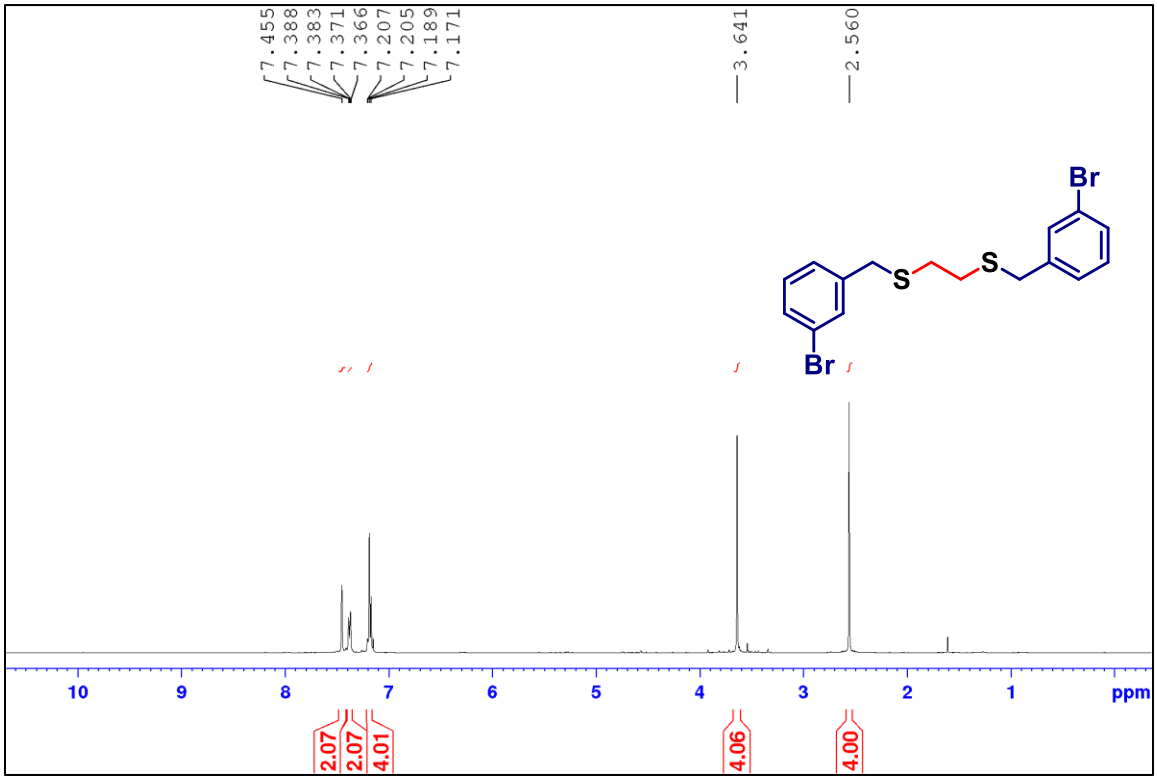


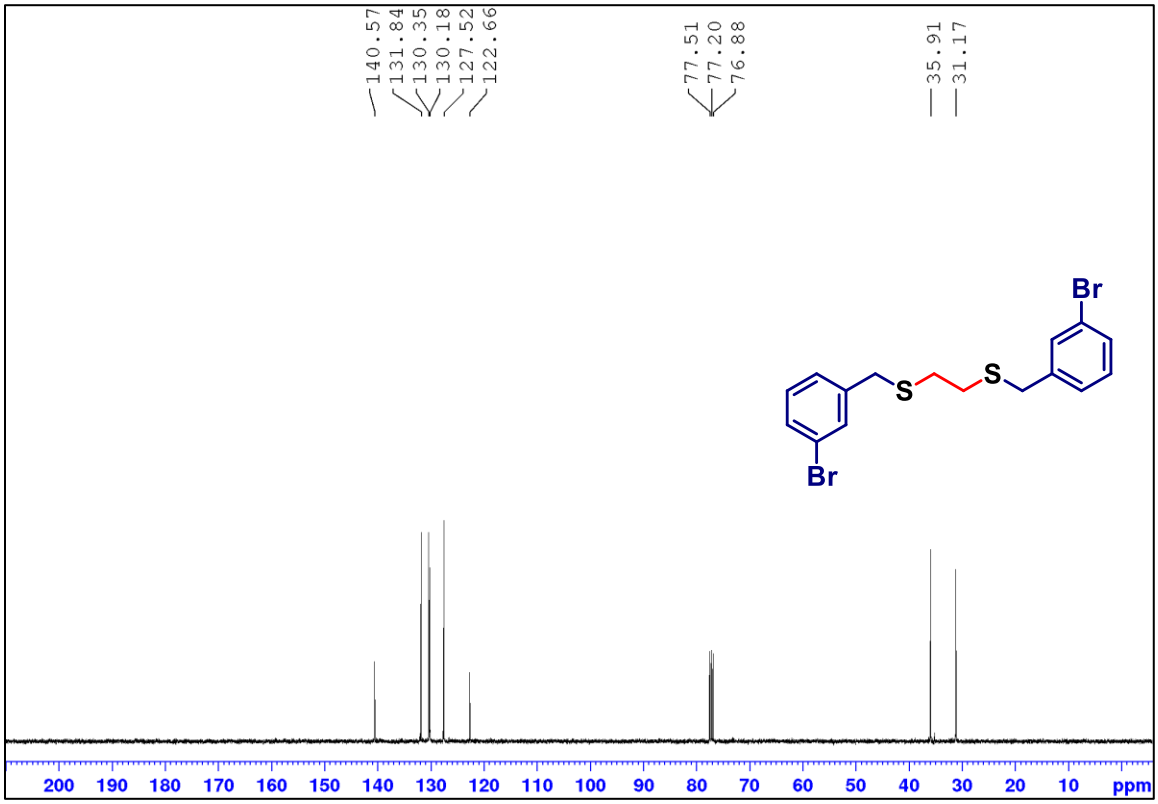
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 19c in $CDCl_3$



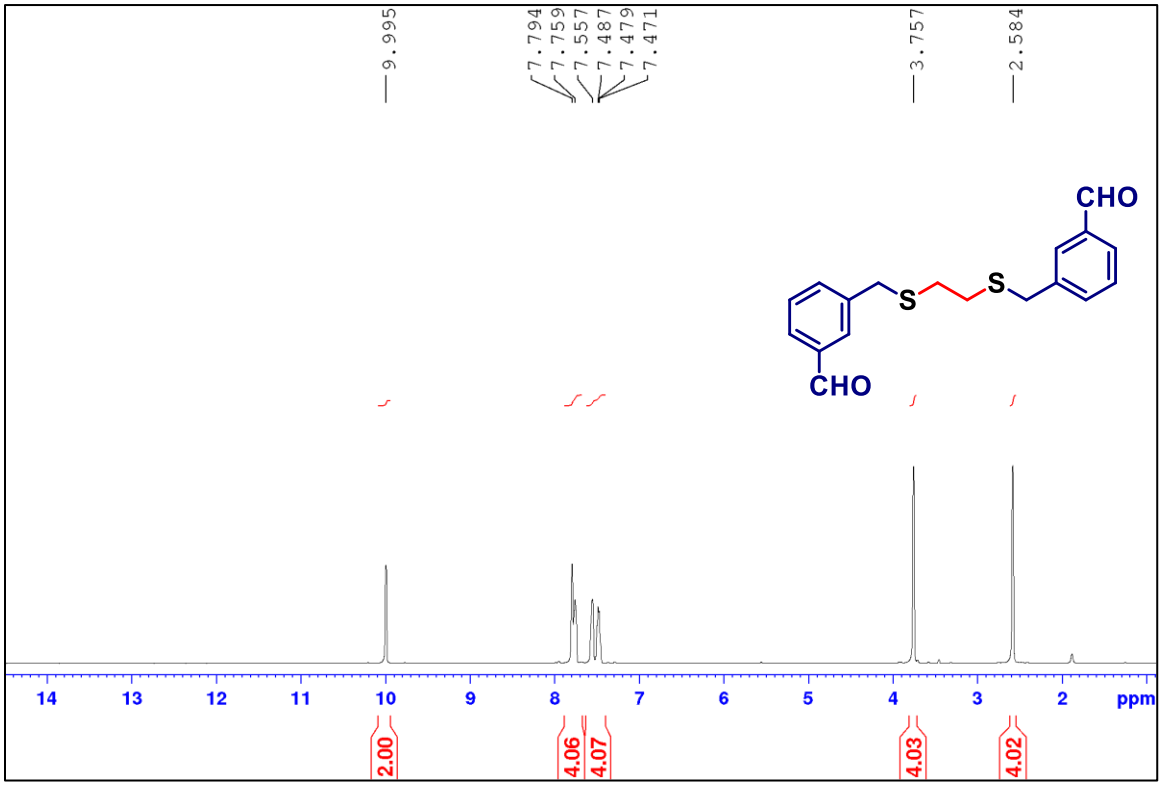


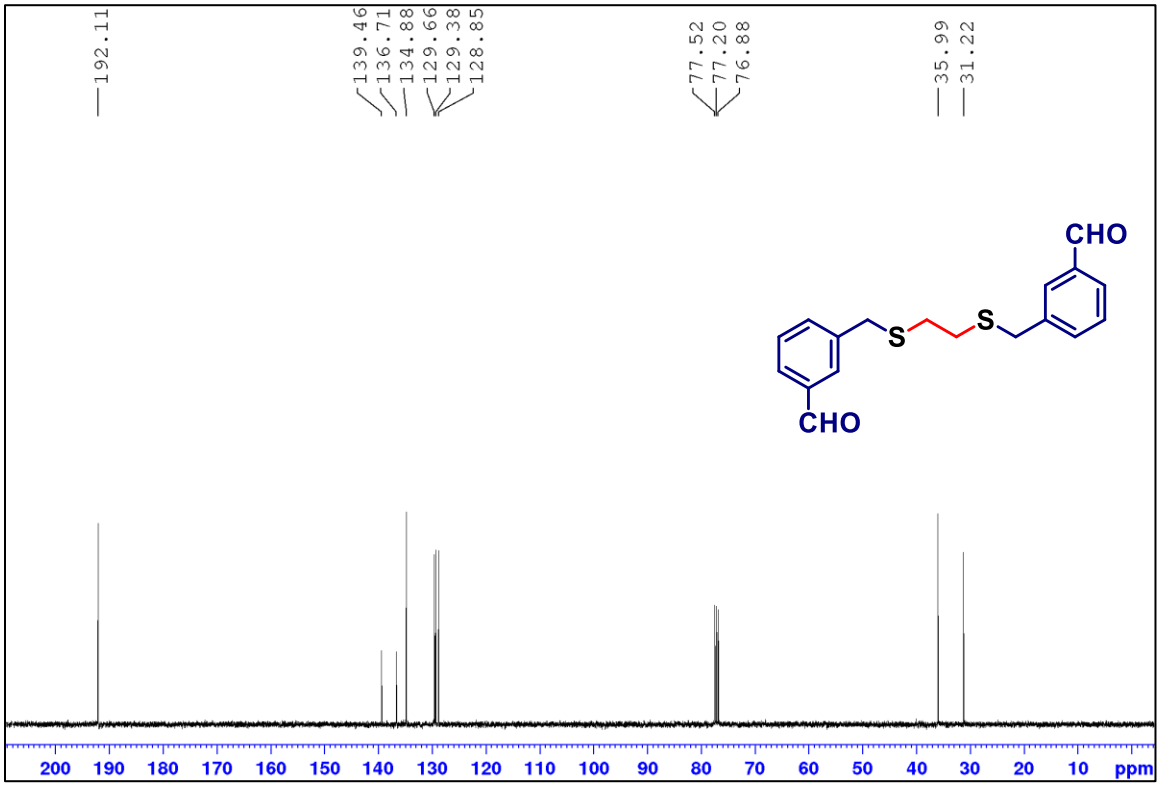
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 19d in $CDCl_3$



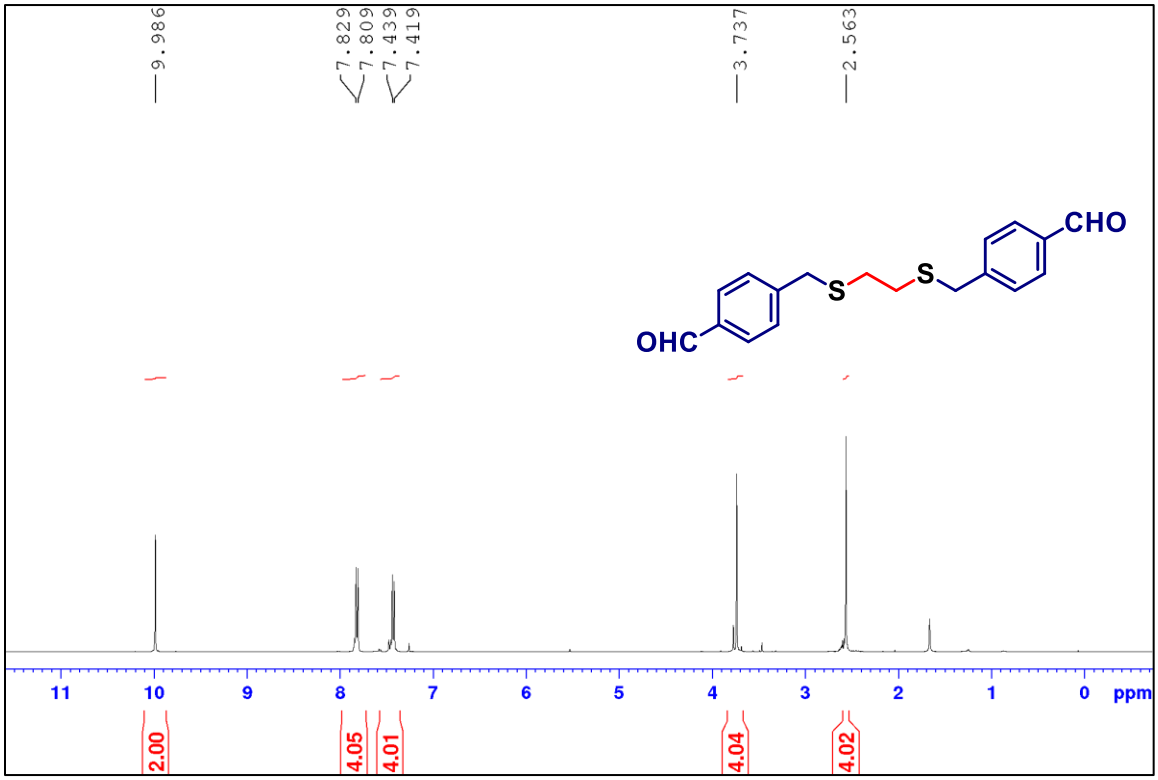


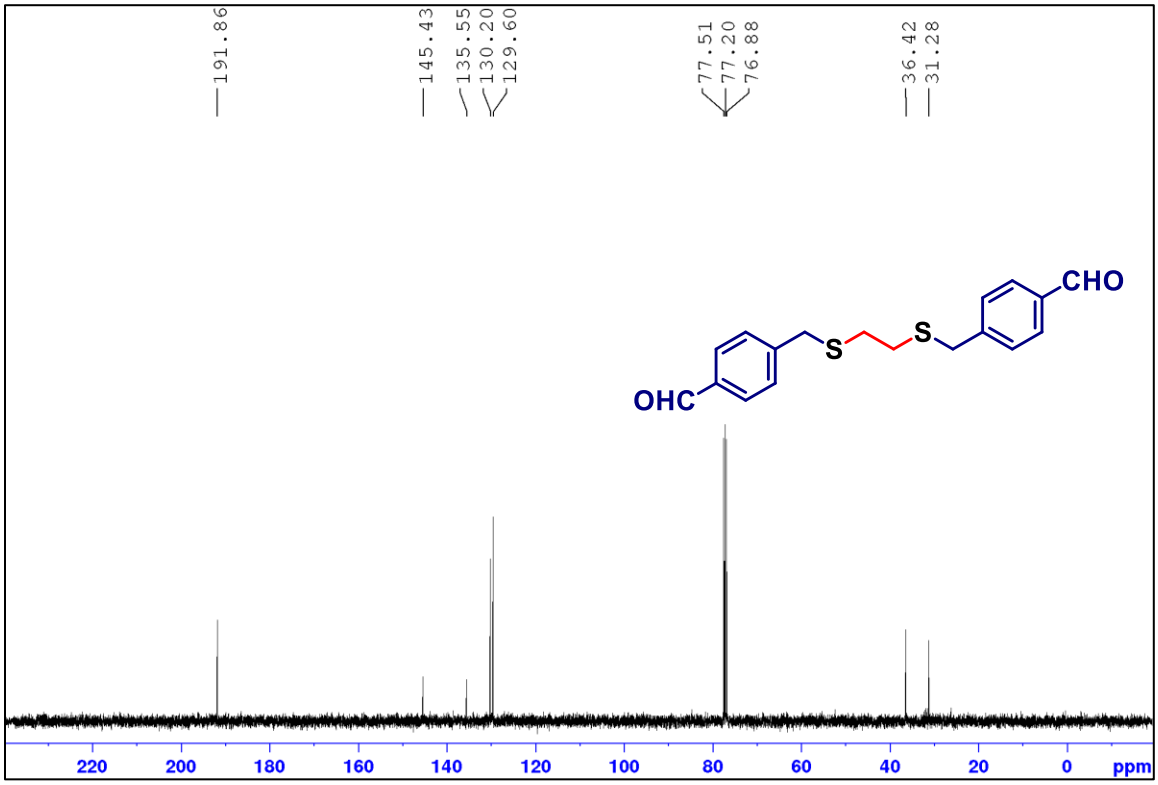
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 19e in $CDCl_3$



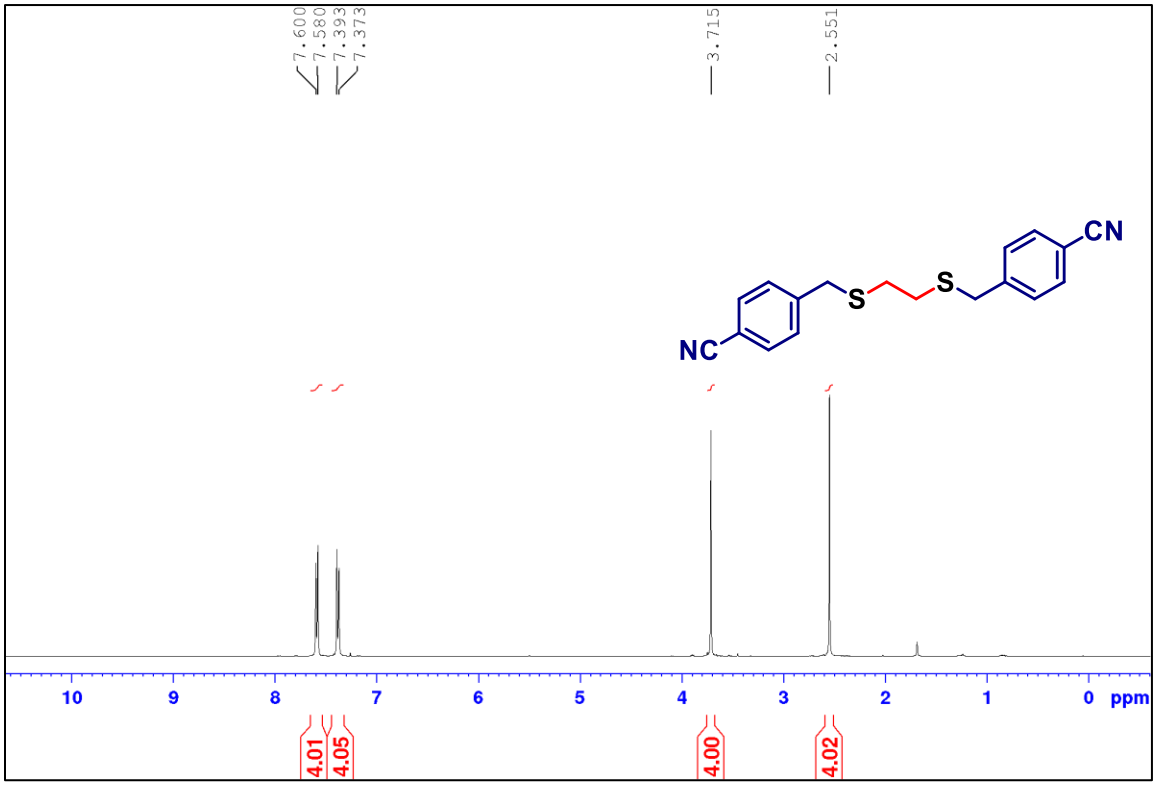


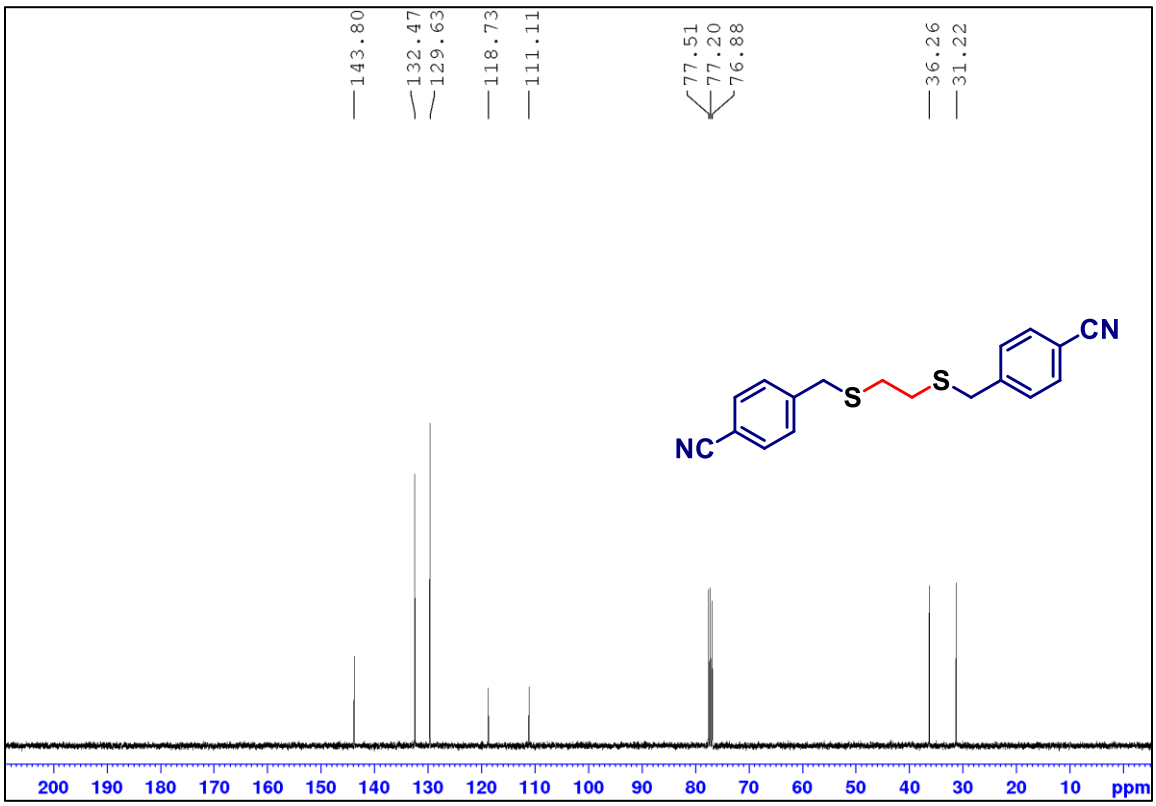
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 19f in $CDCl_3$



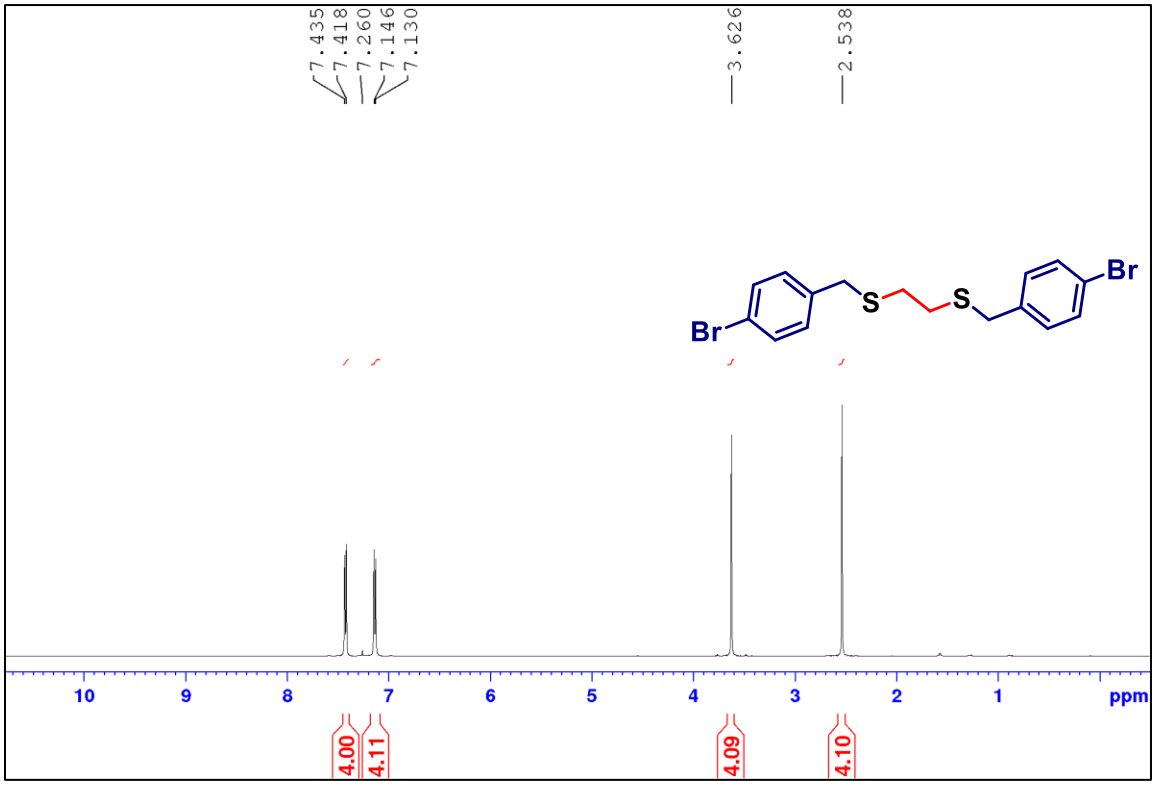


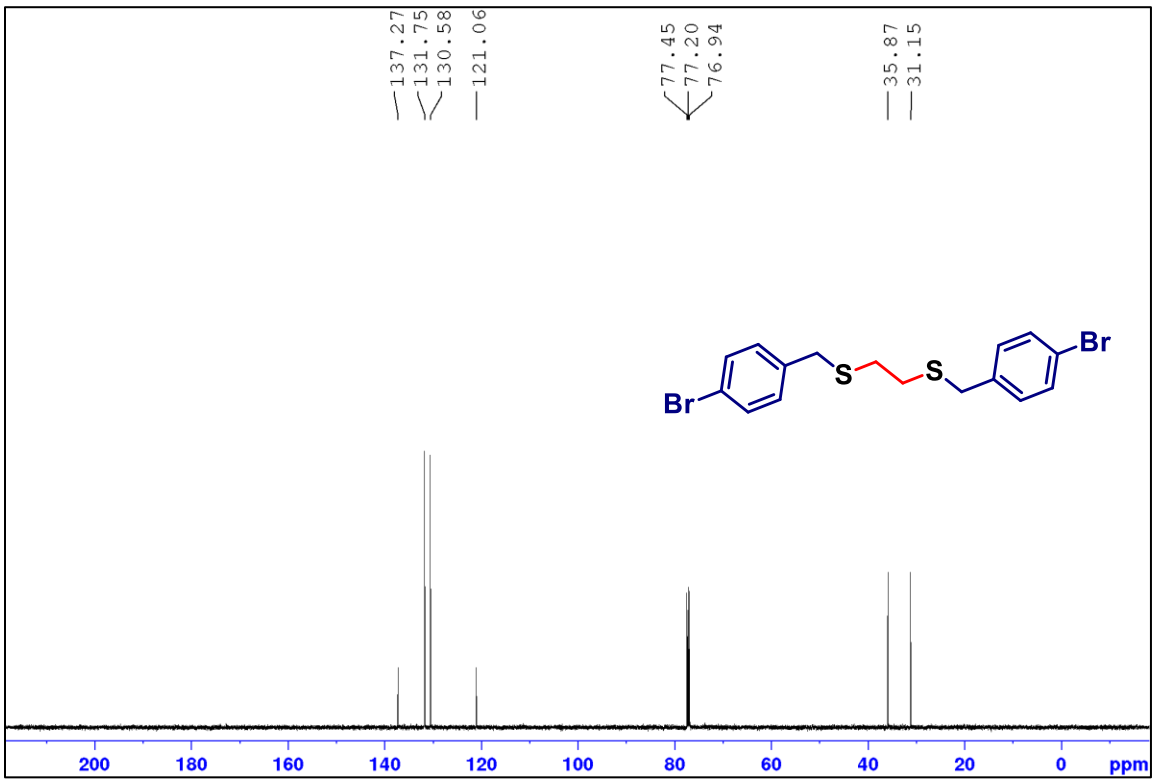
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 19g in $CDCl_3$



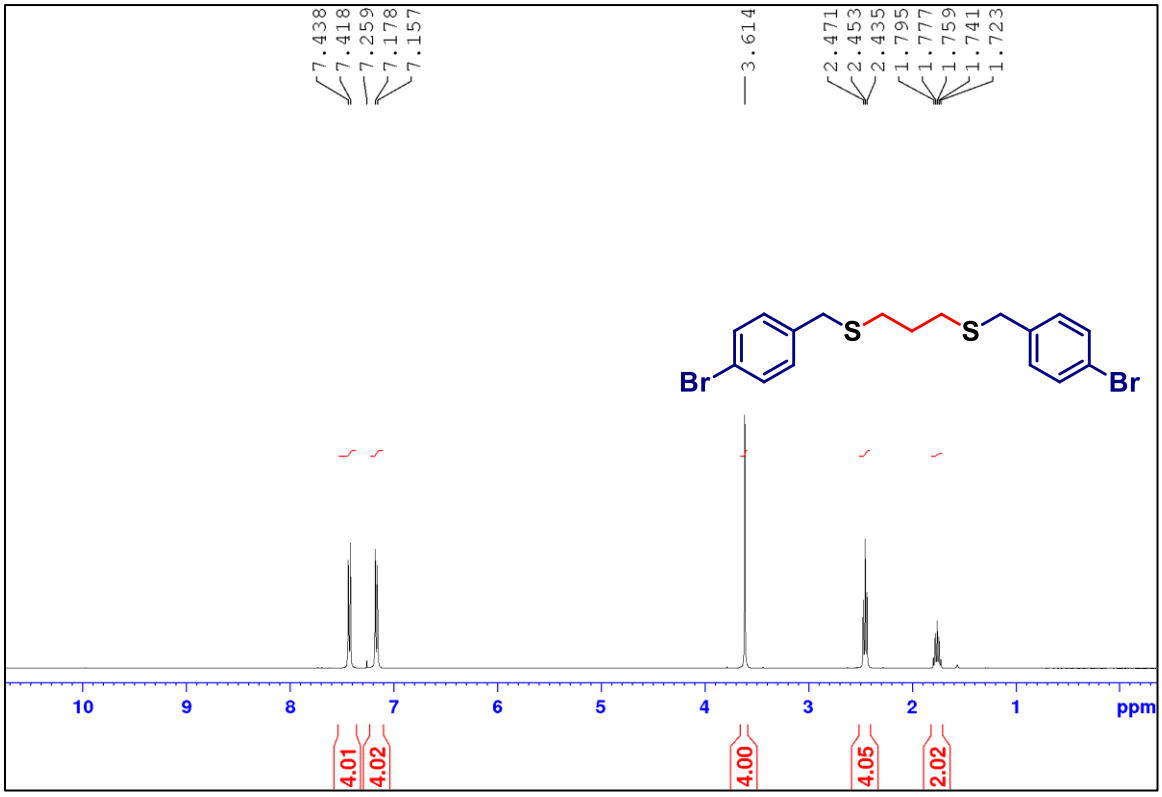


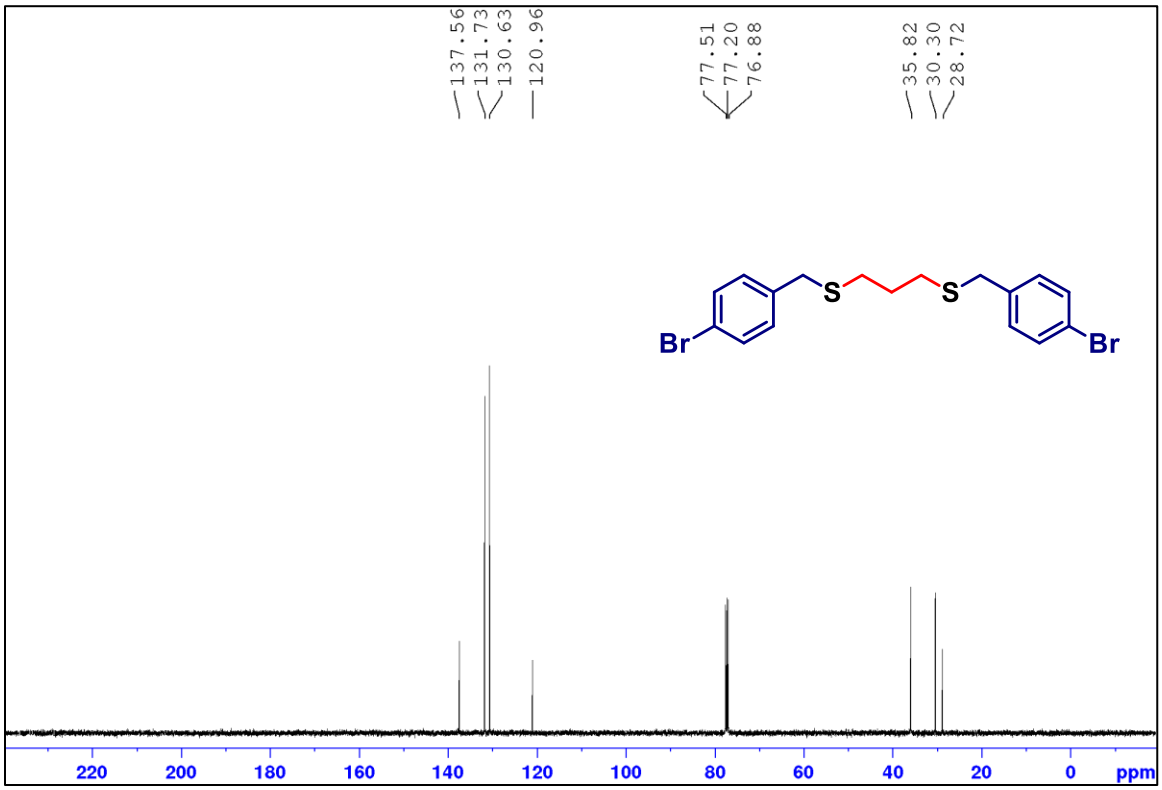
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 20a in $CDCl_3$



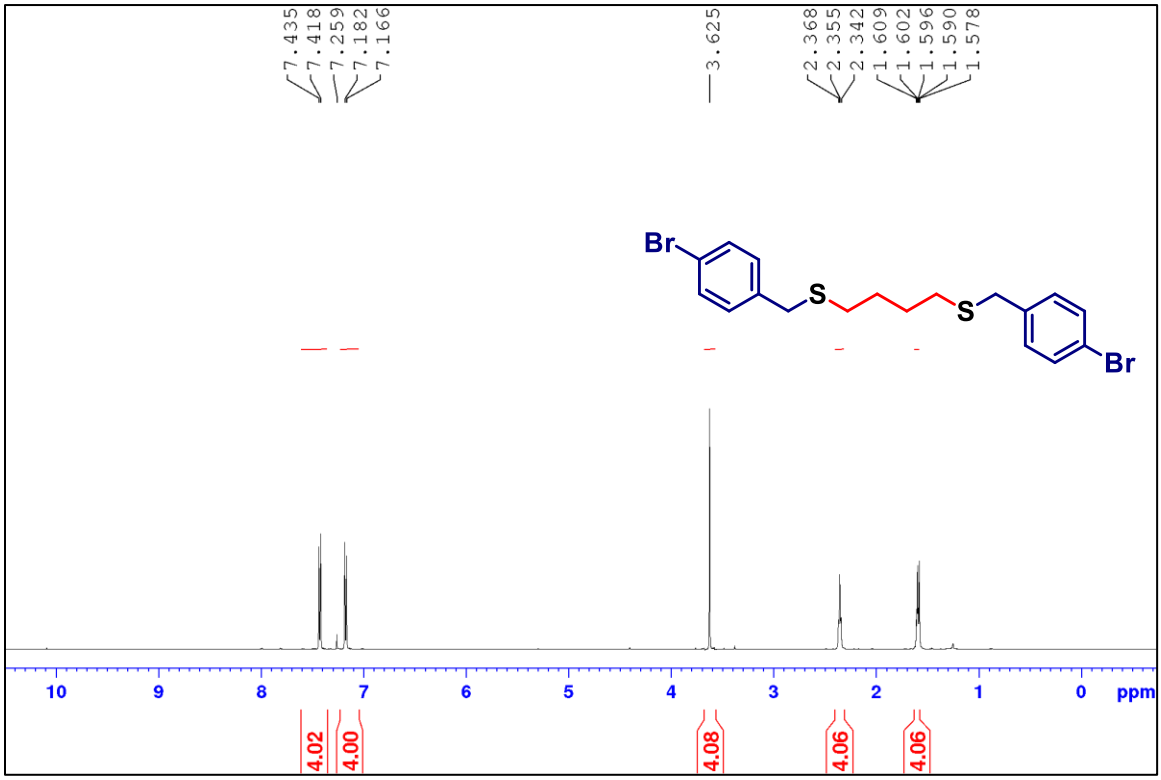


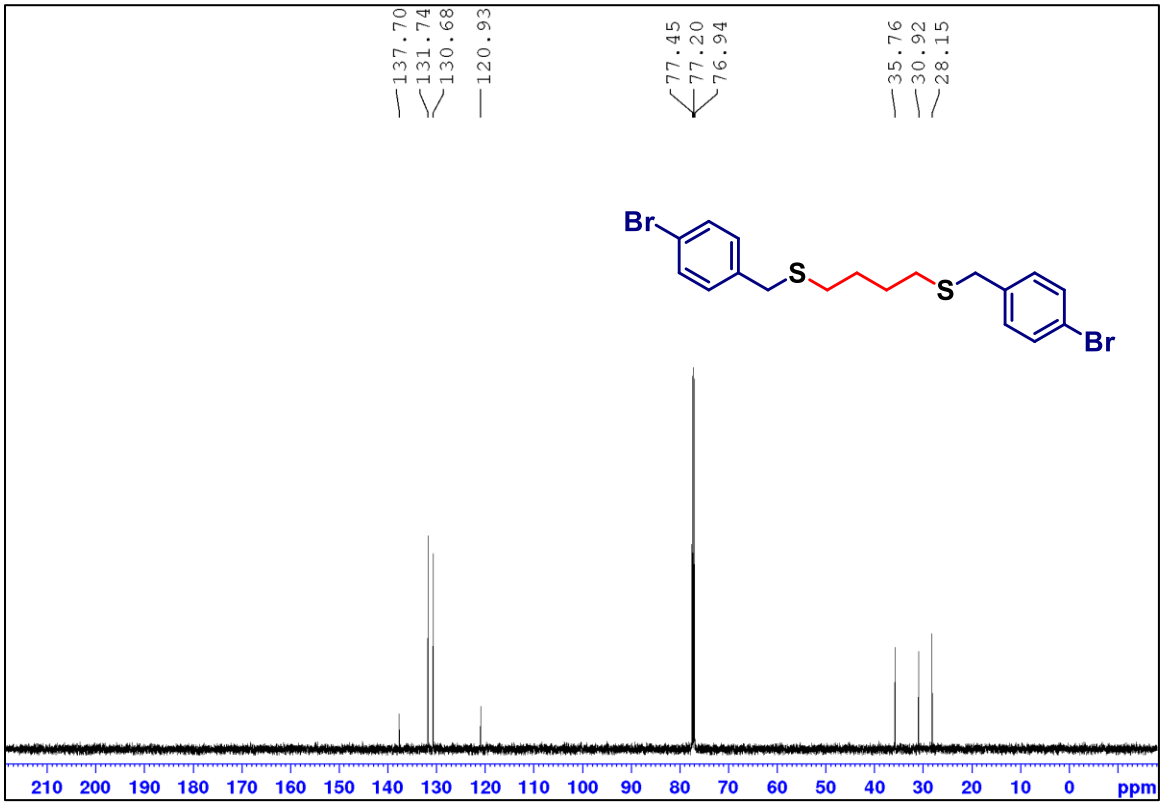
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 20b in $CDCl_3$



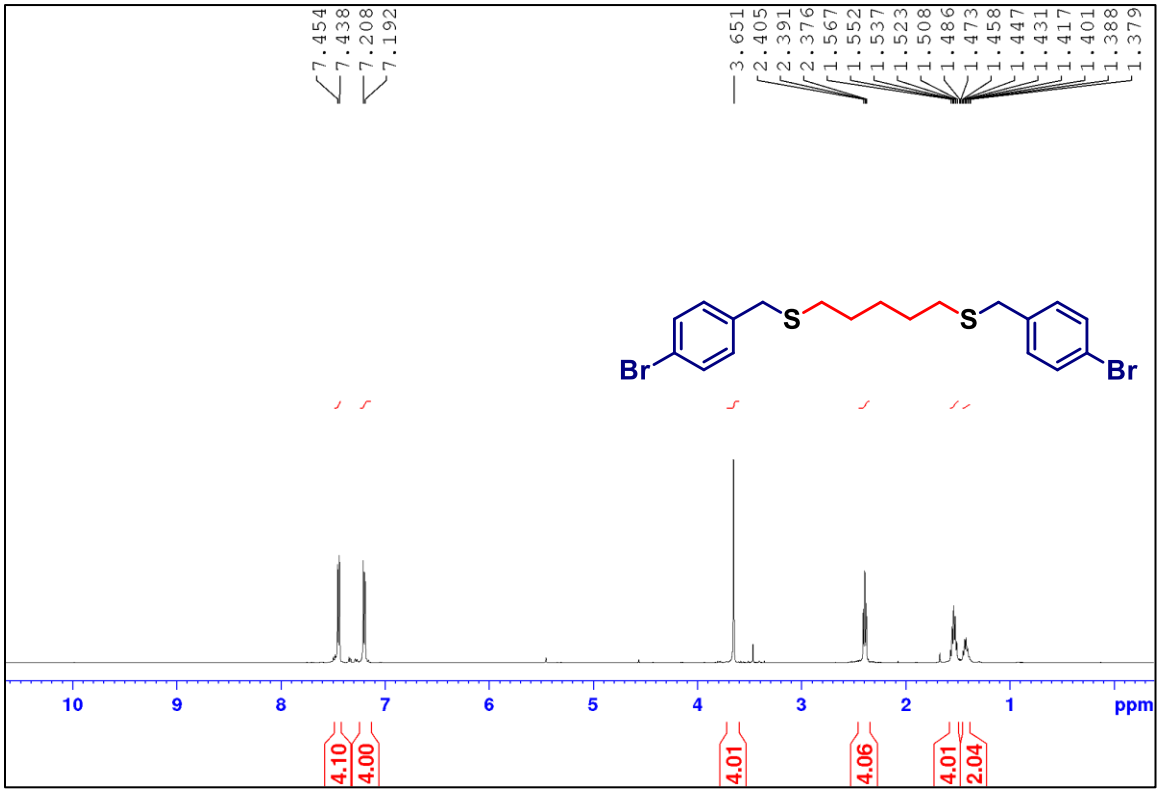


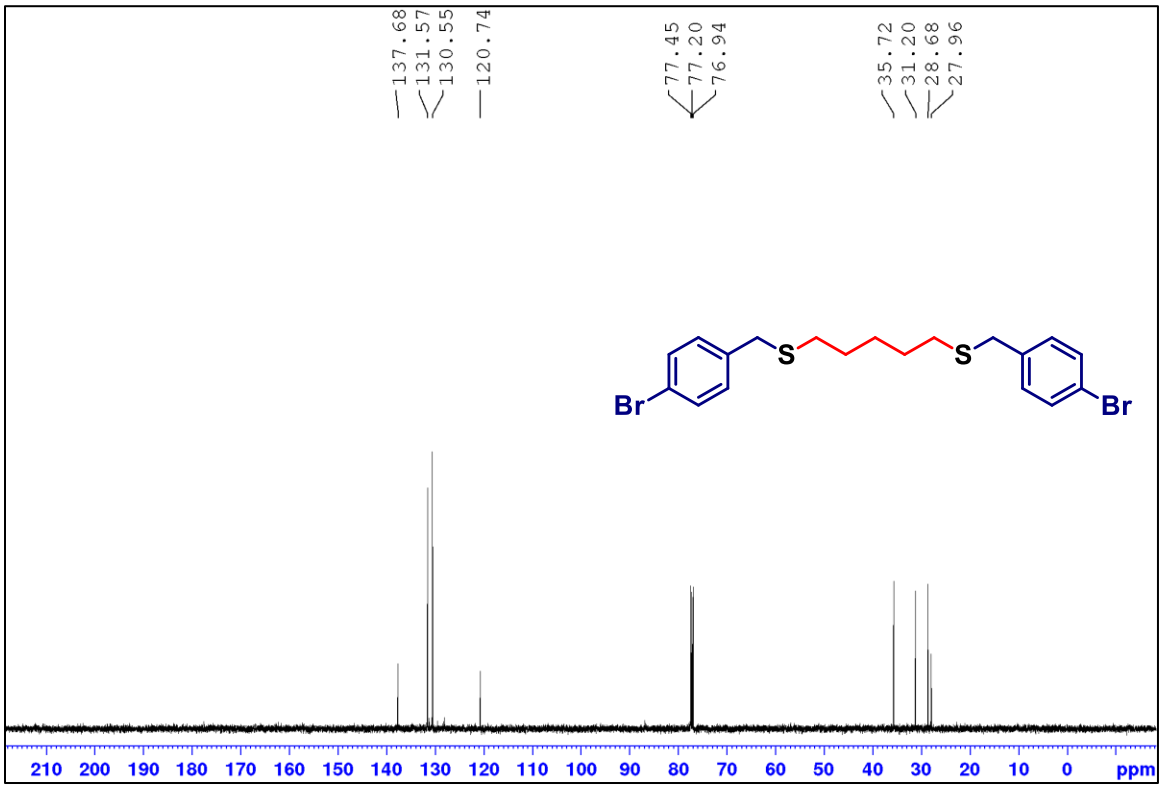
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 20c in $CDCl_3$



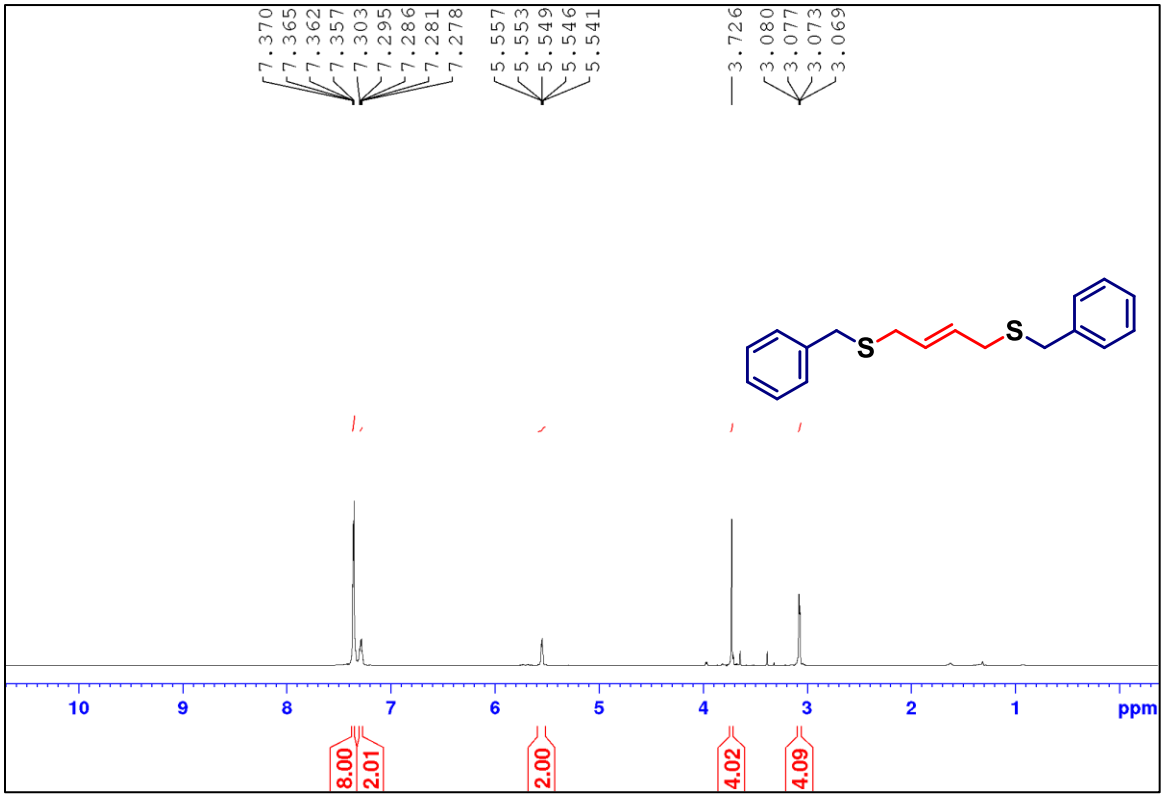


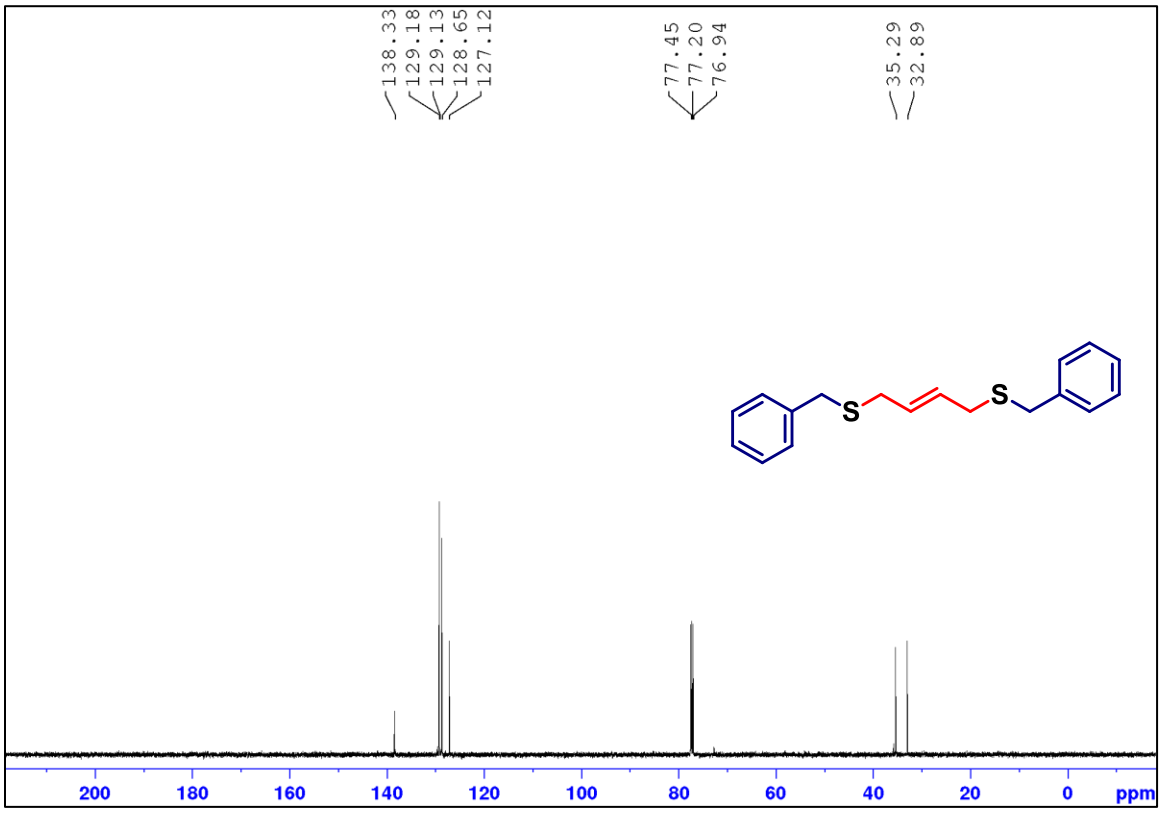
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 20d in $CDCl_3$



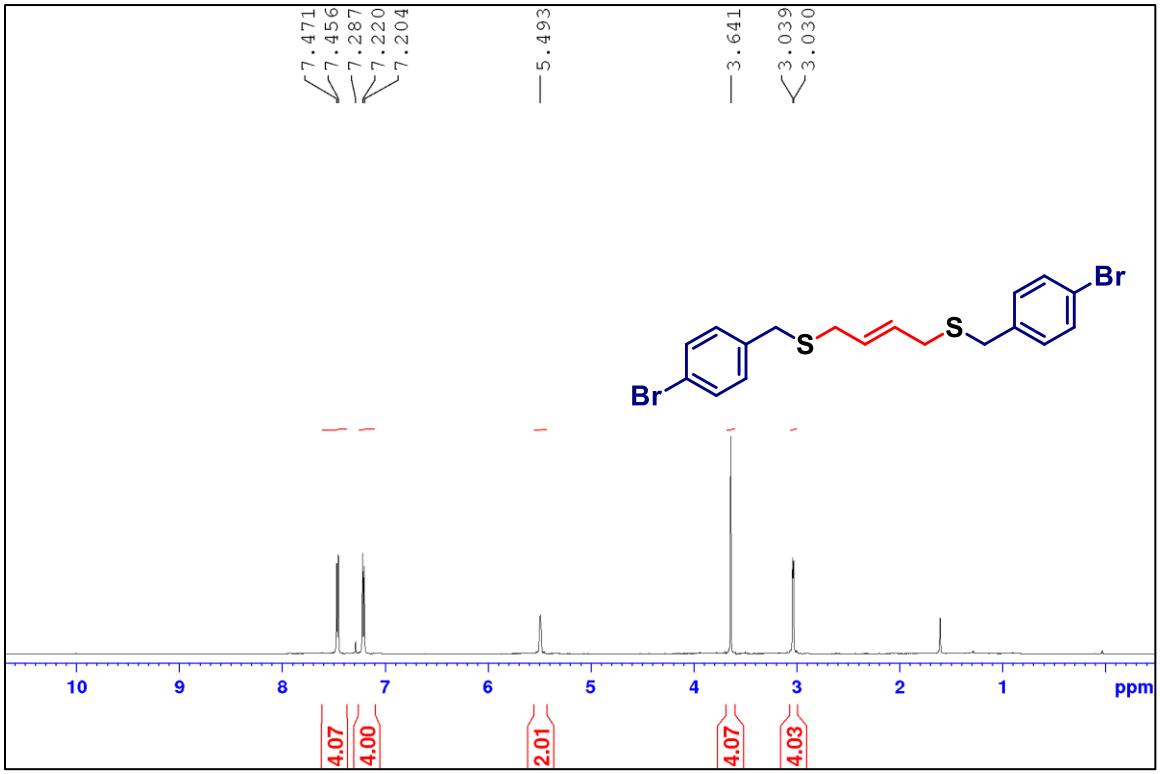


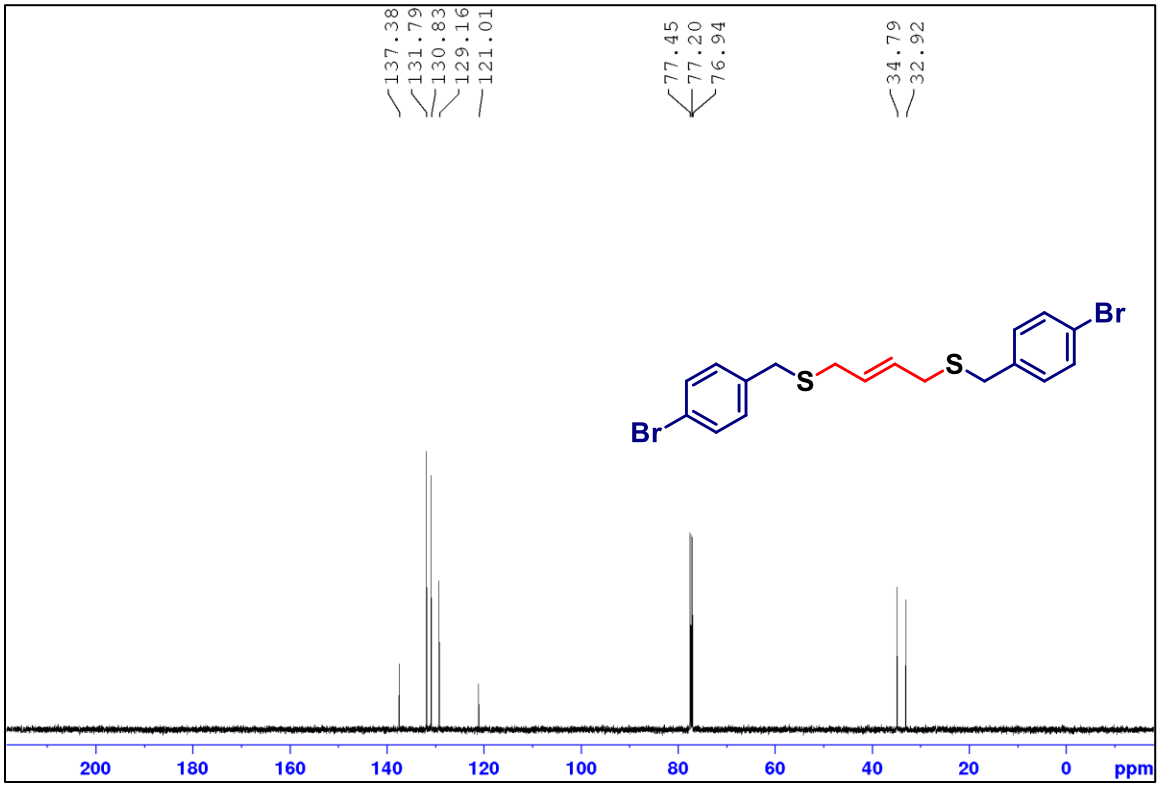
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 21a in $CDCl_3$



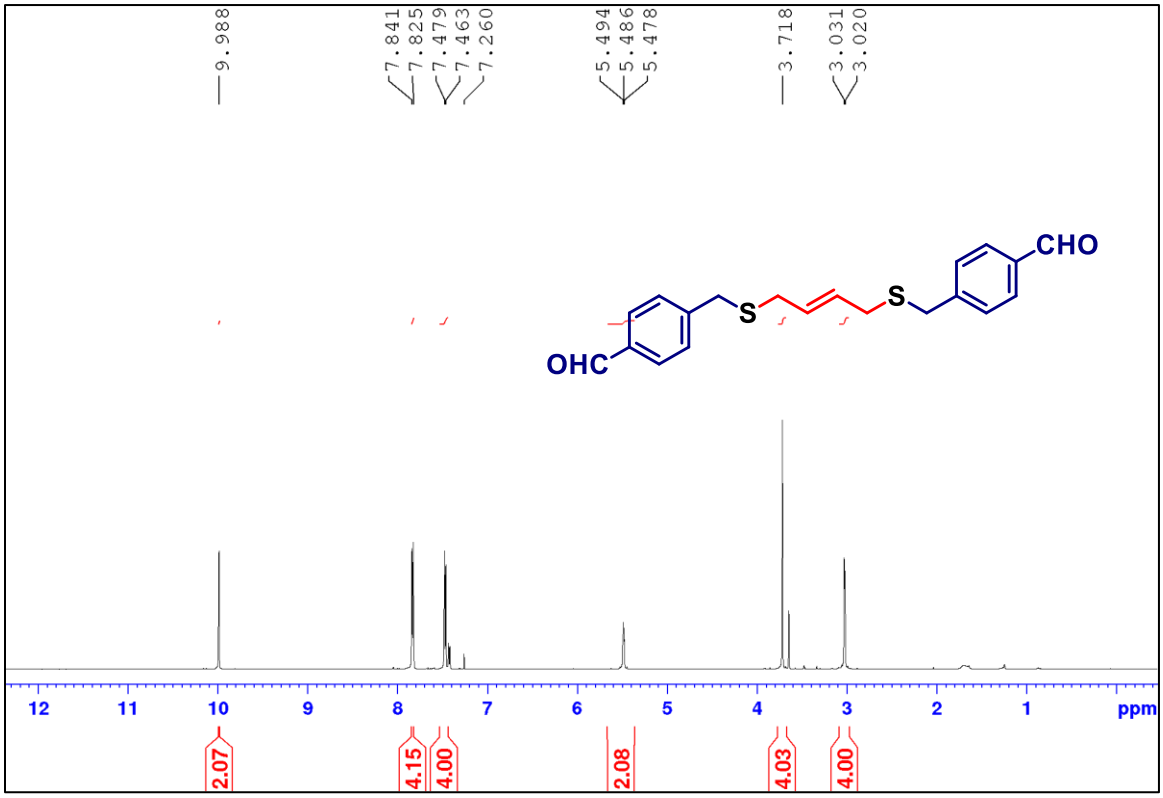


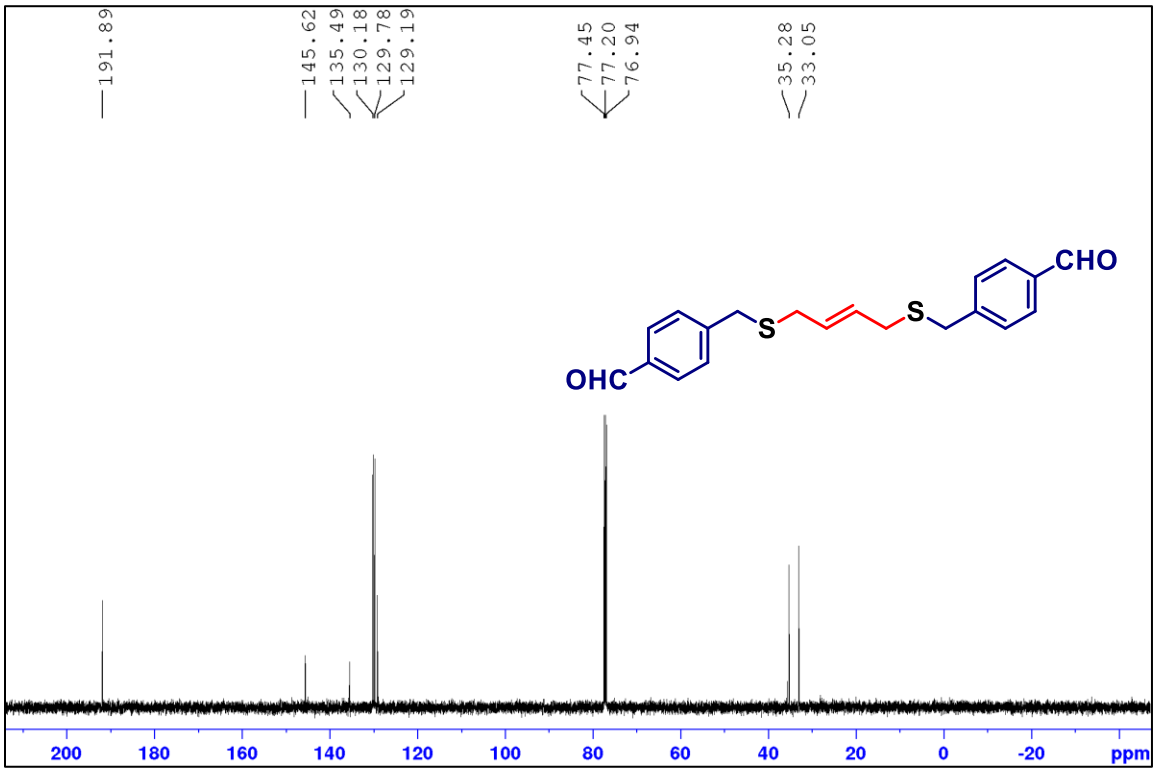
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 21b in $CDCl_3$



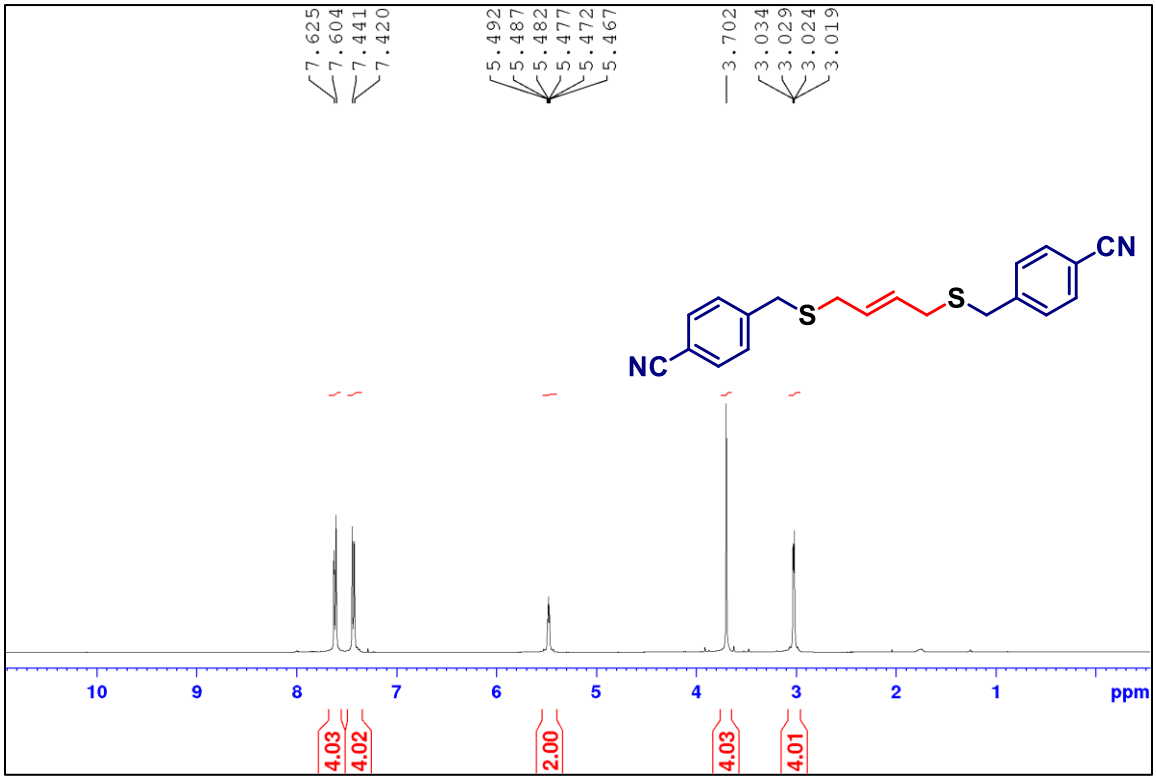


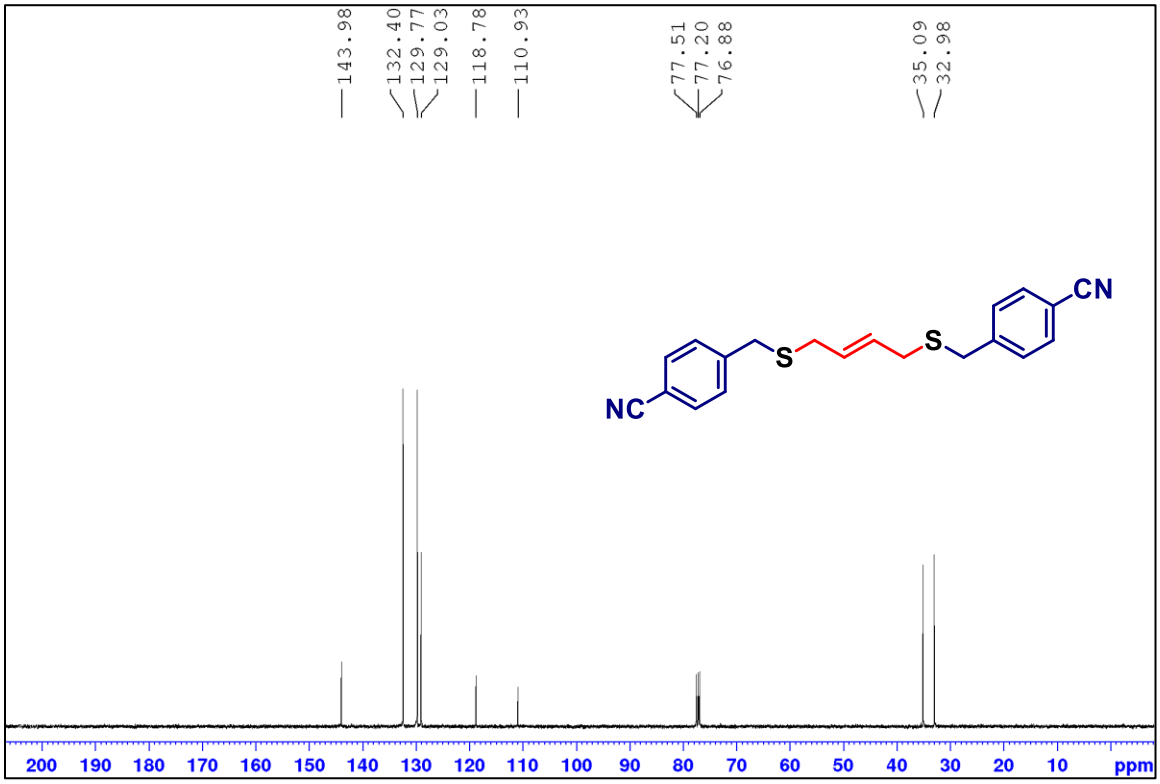
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 21c in $CDCl_3$



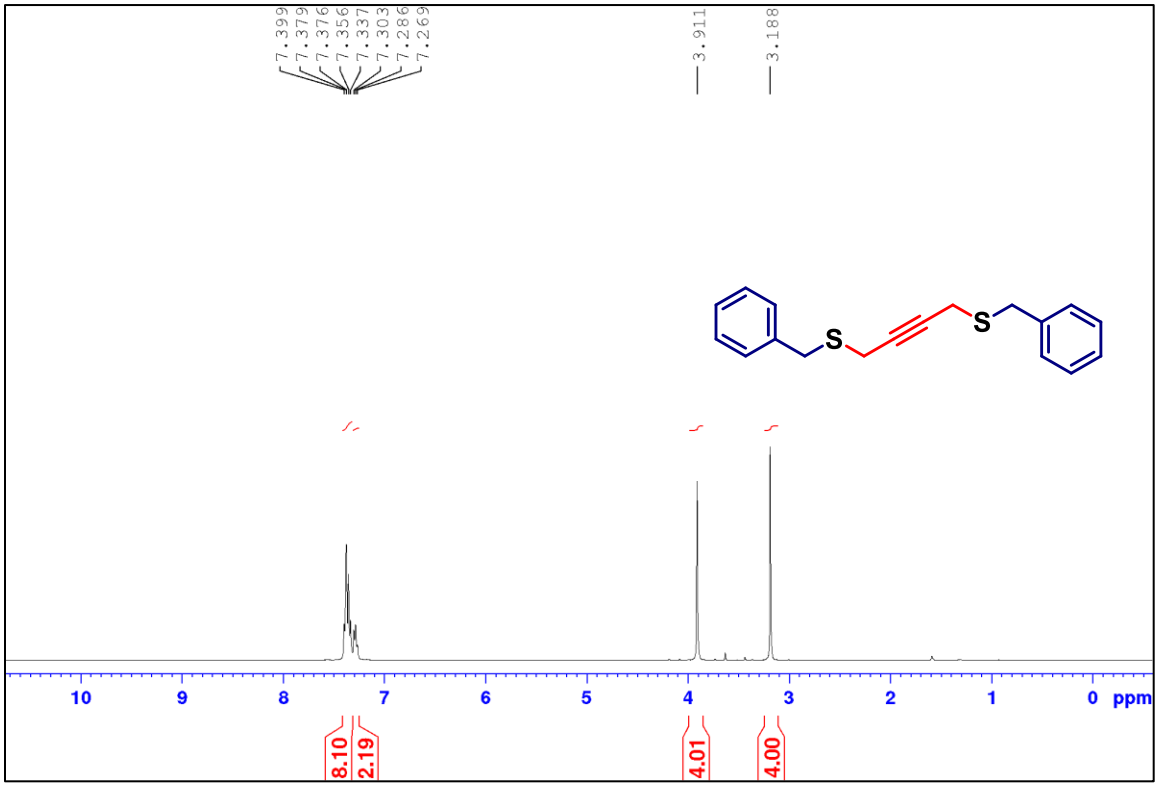


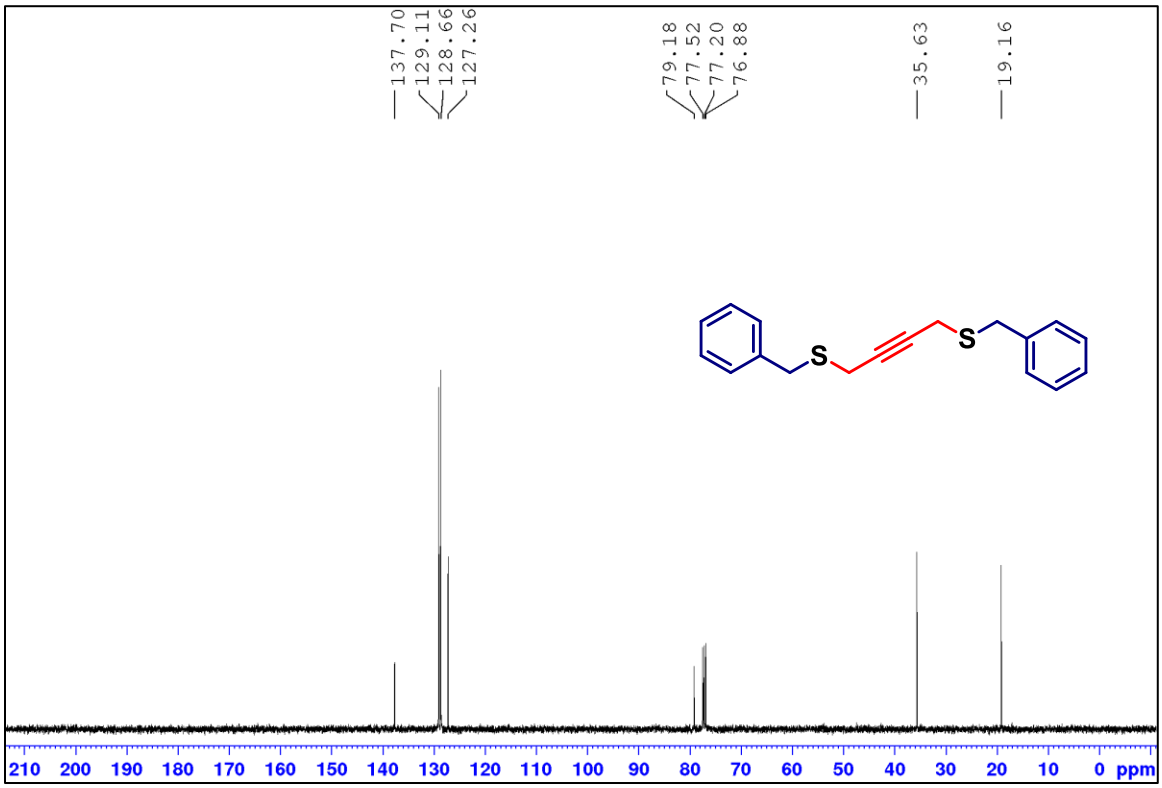
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 21d in $CDCl_3$



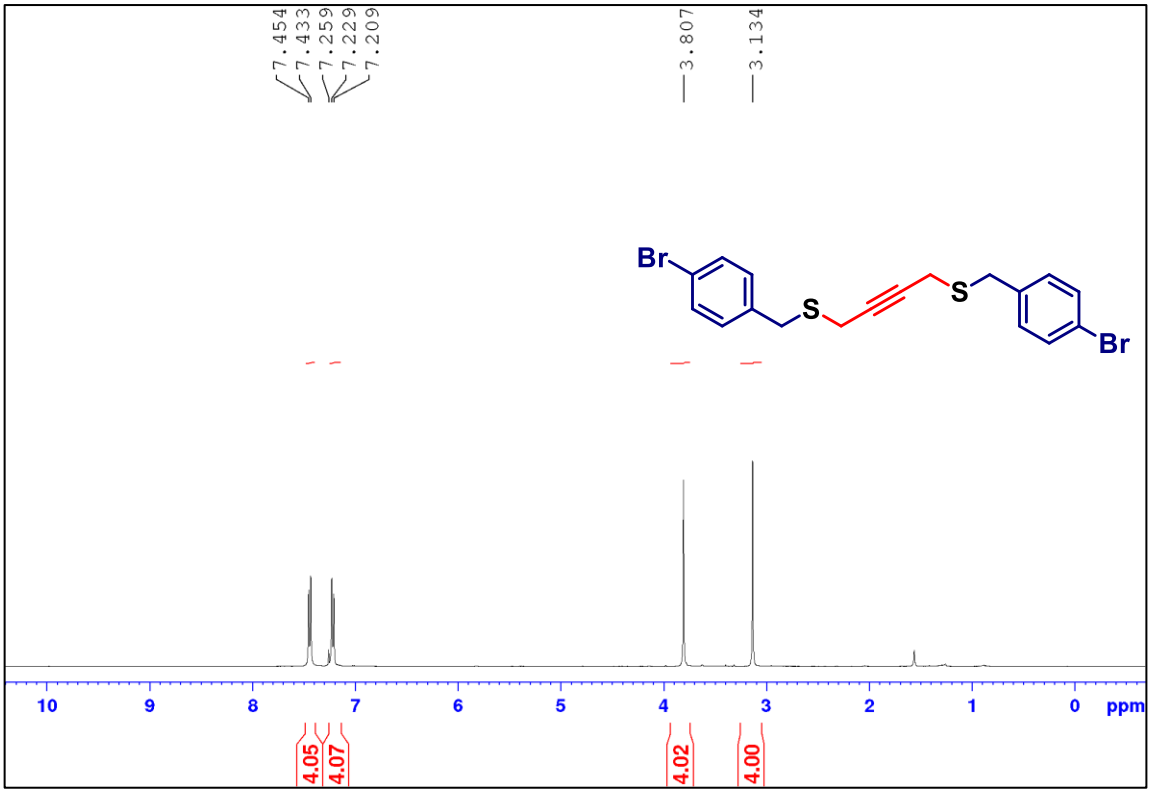


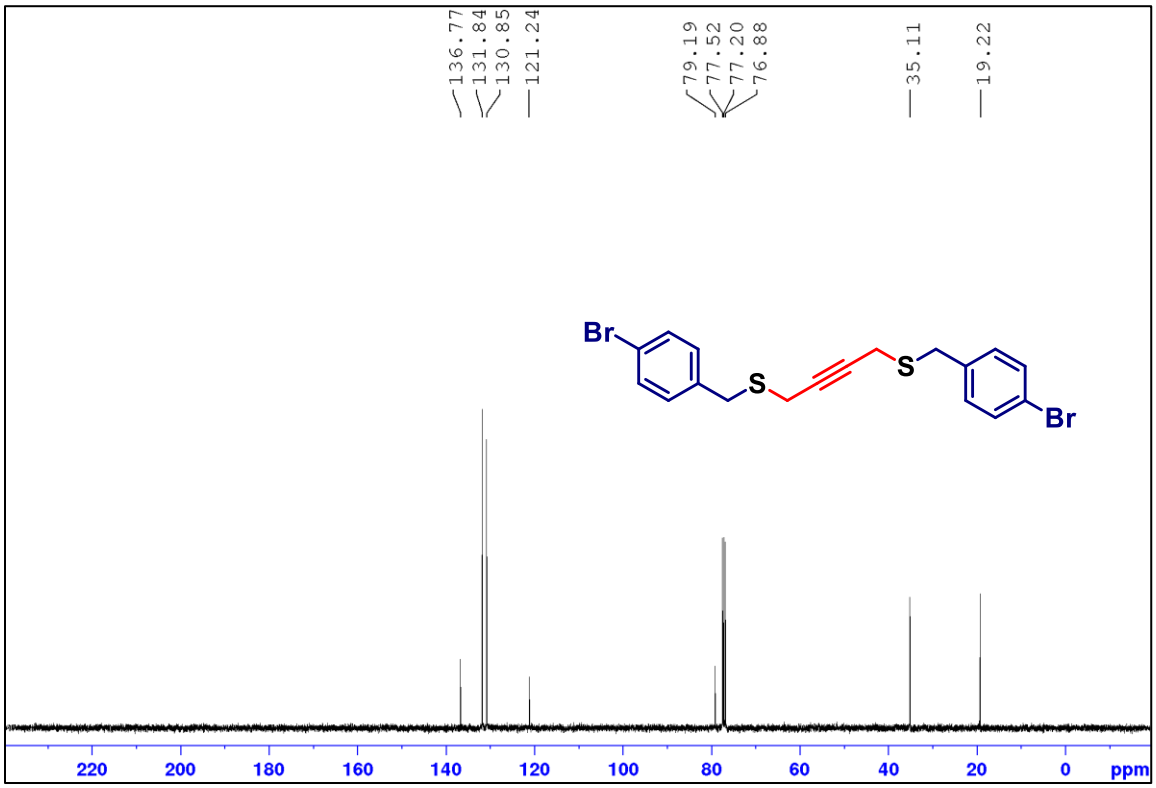
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 22a in $CDCl_3$



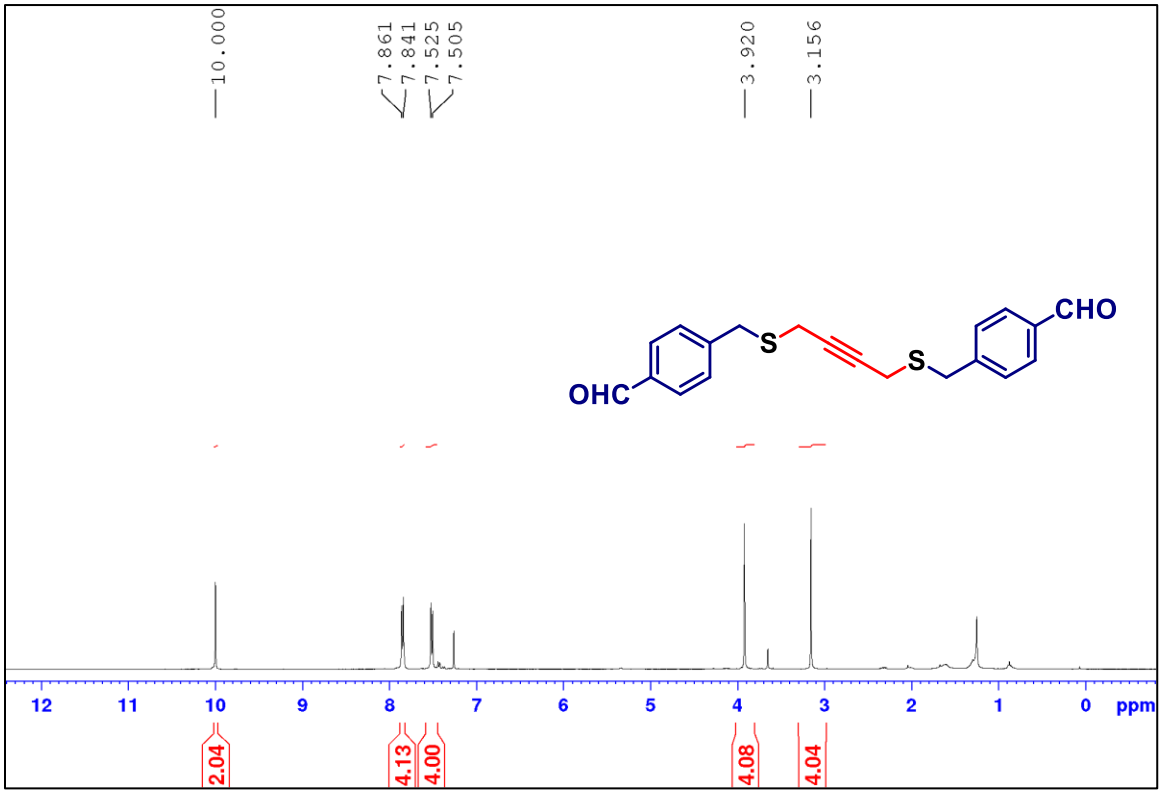


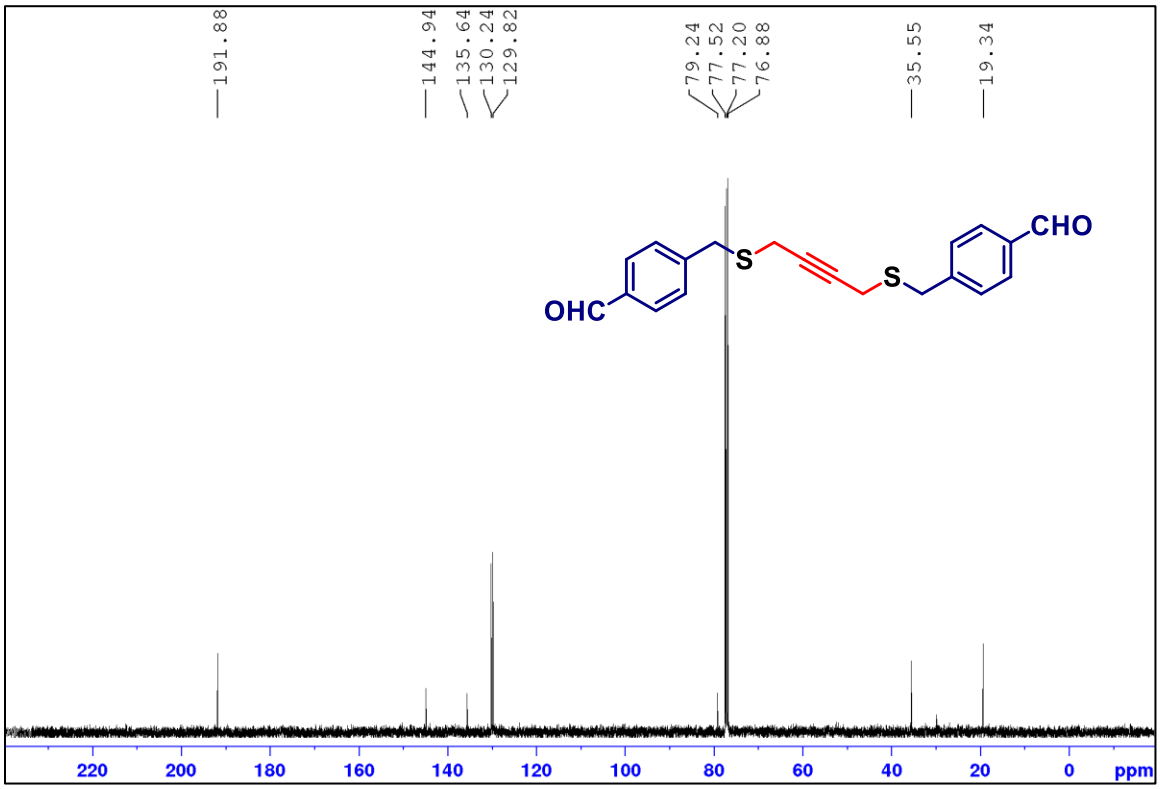
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 22b in $CDCl_3$



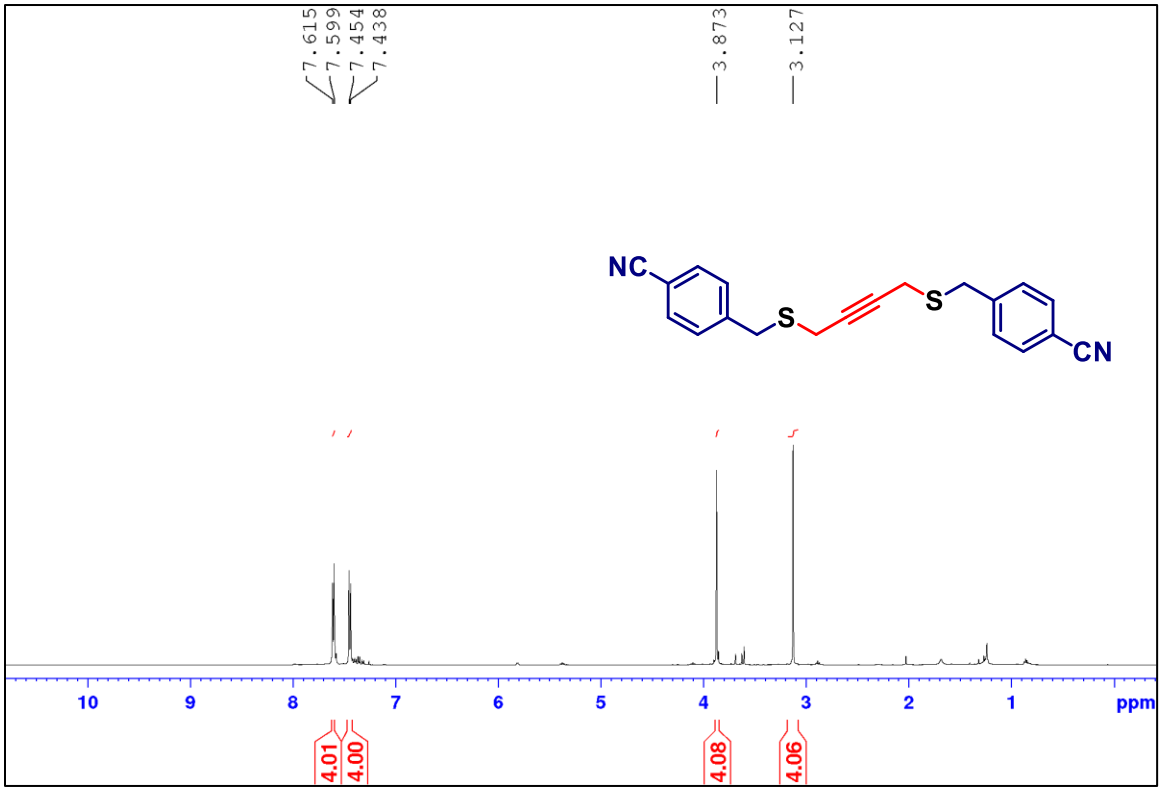


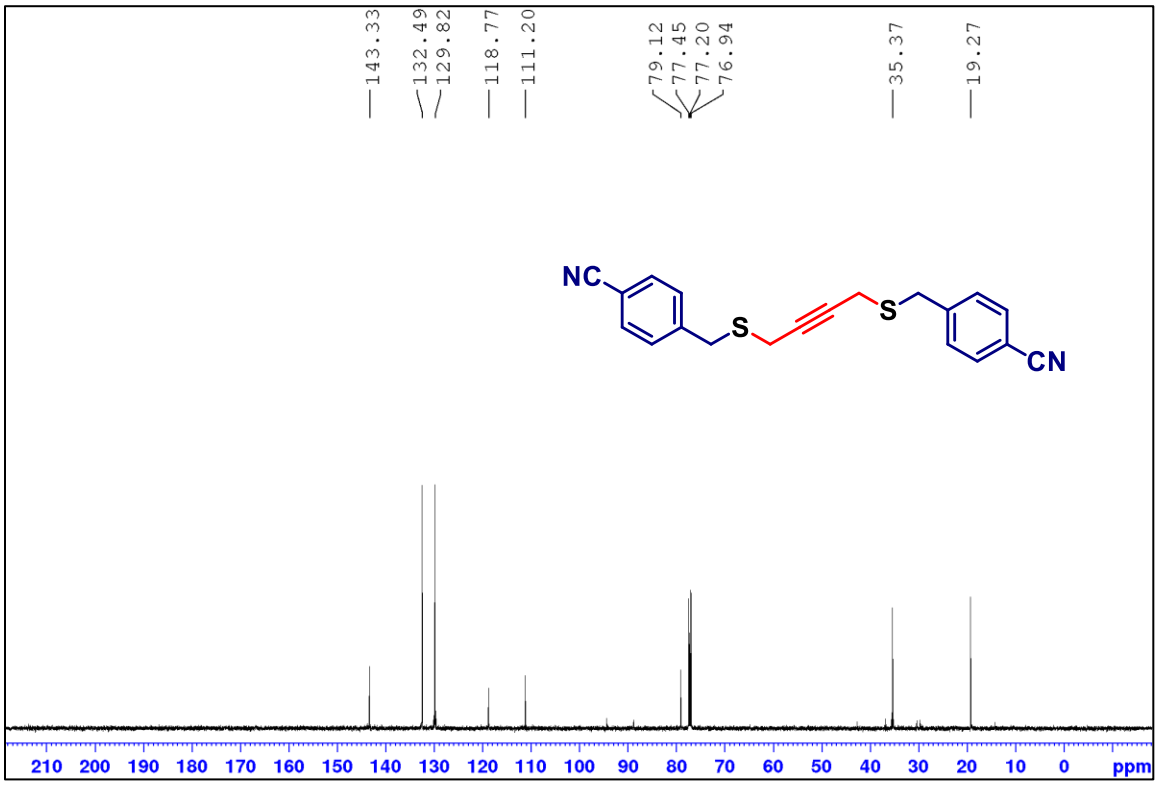
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 22c in $CDCl_3$



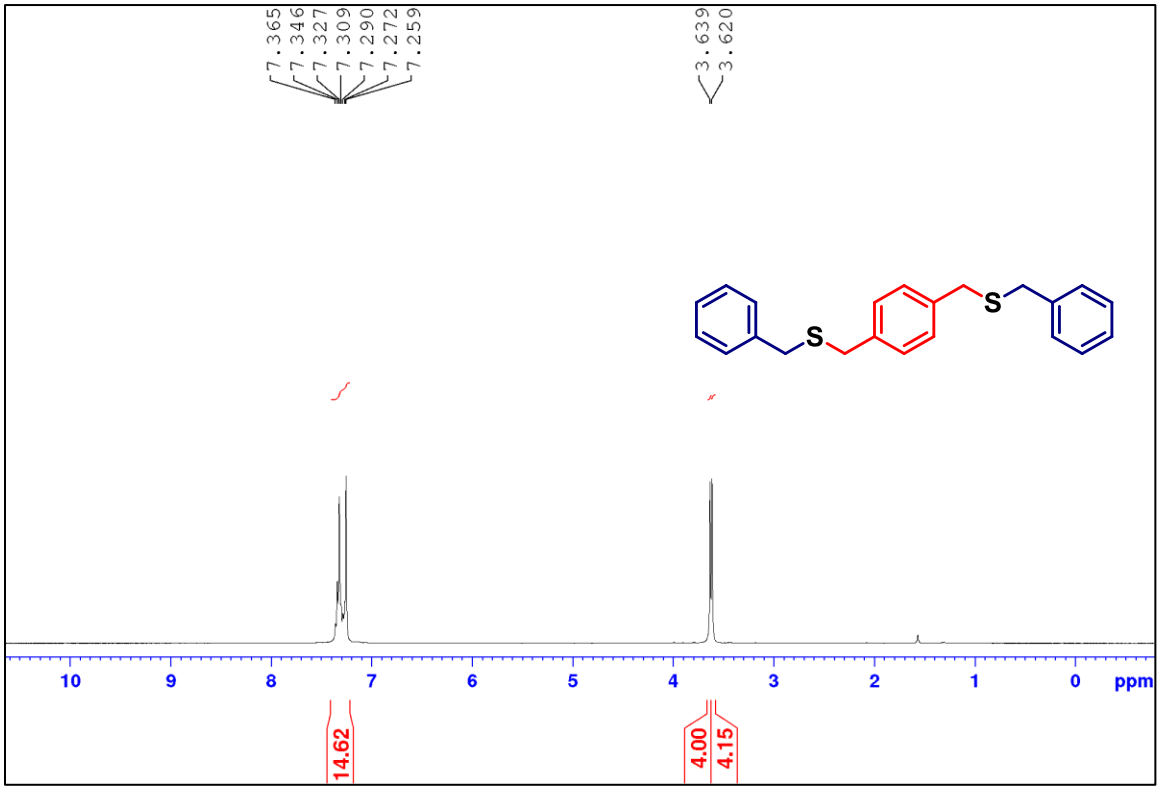


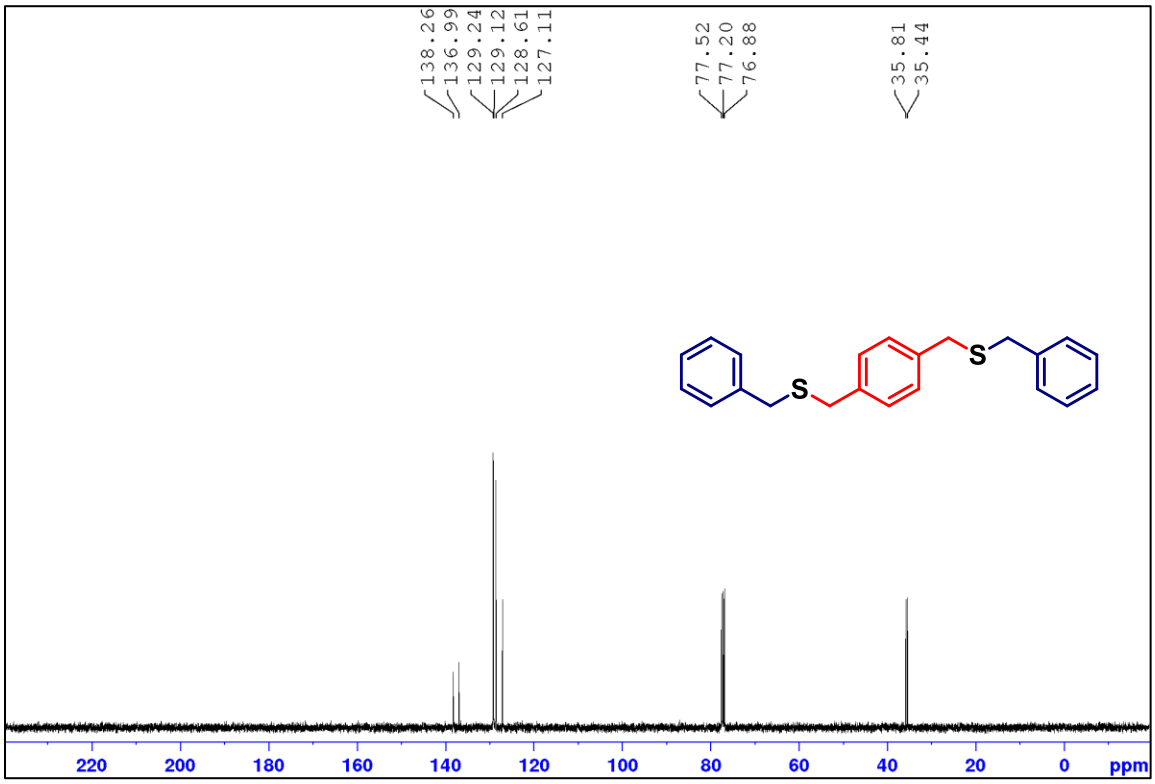
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 22d in $CDCl_3$



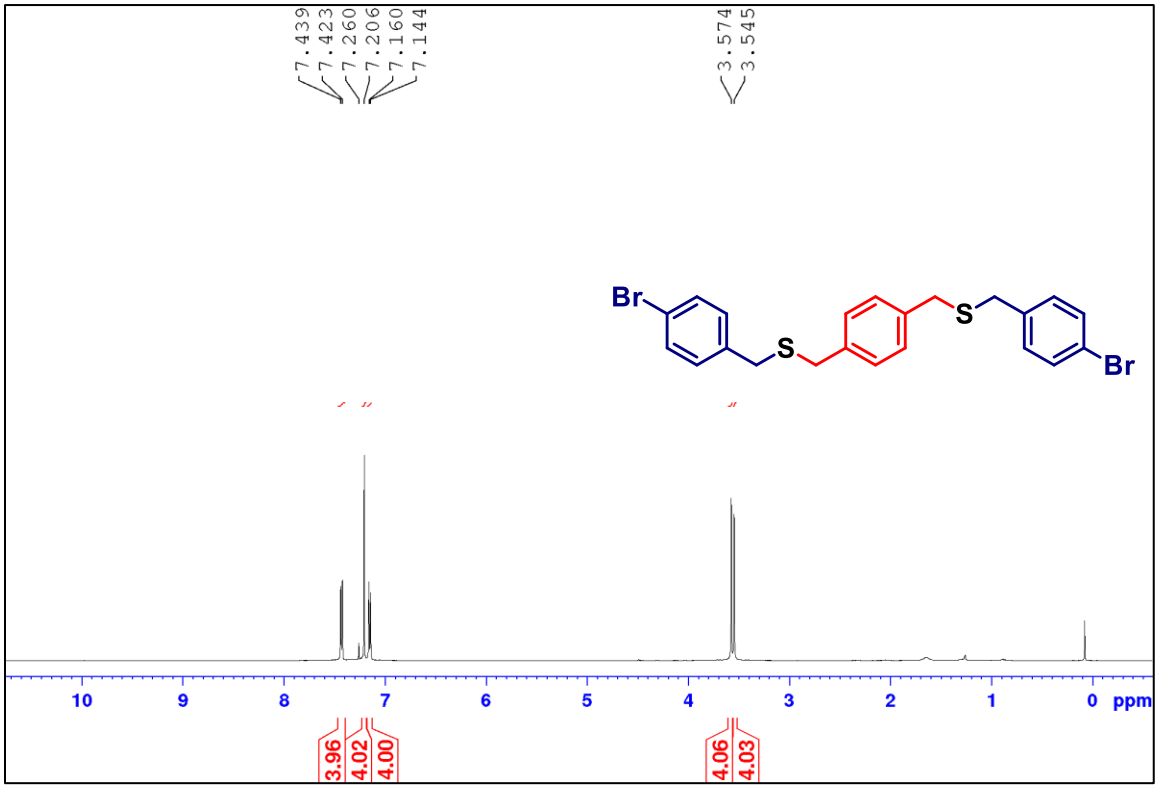


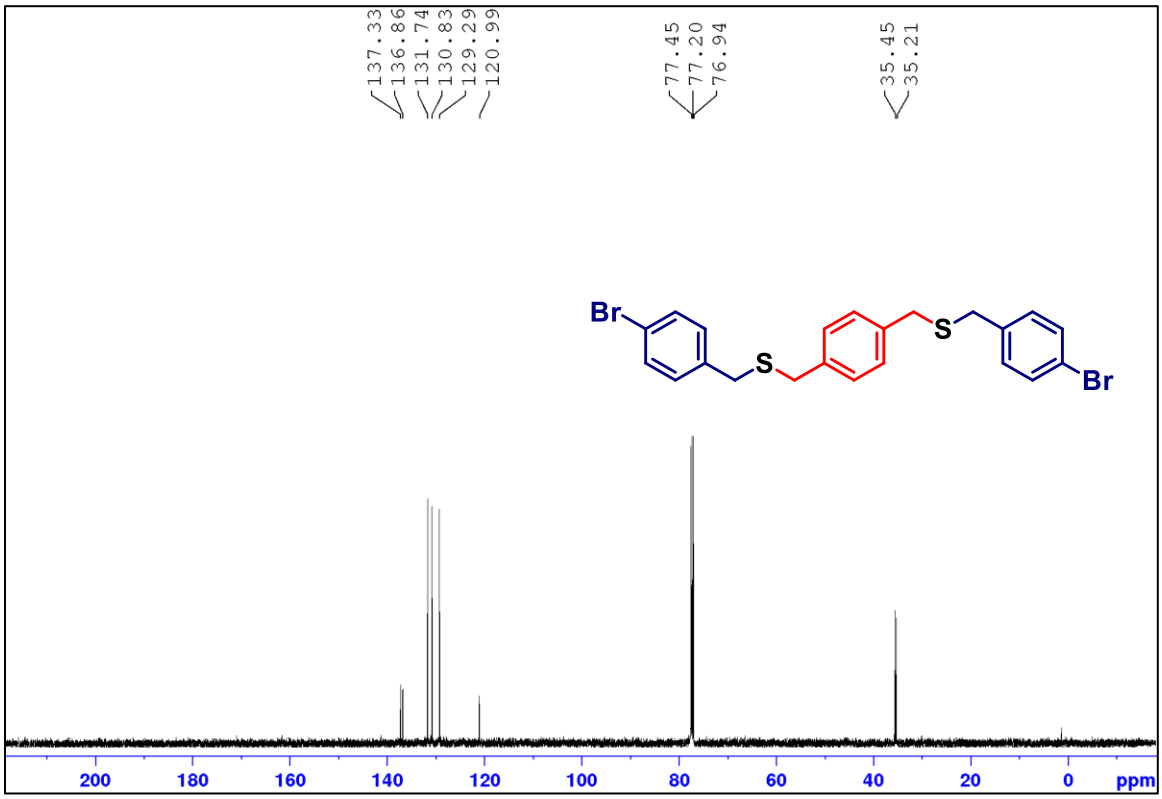
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 23a in $CDCl_3$



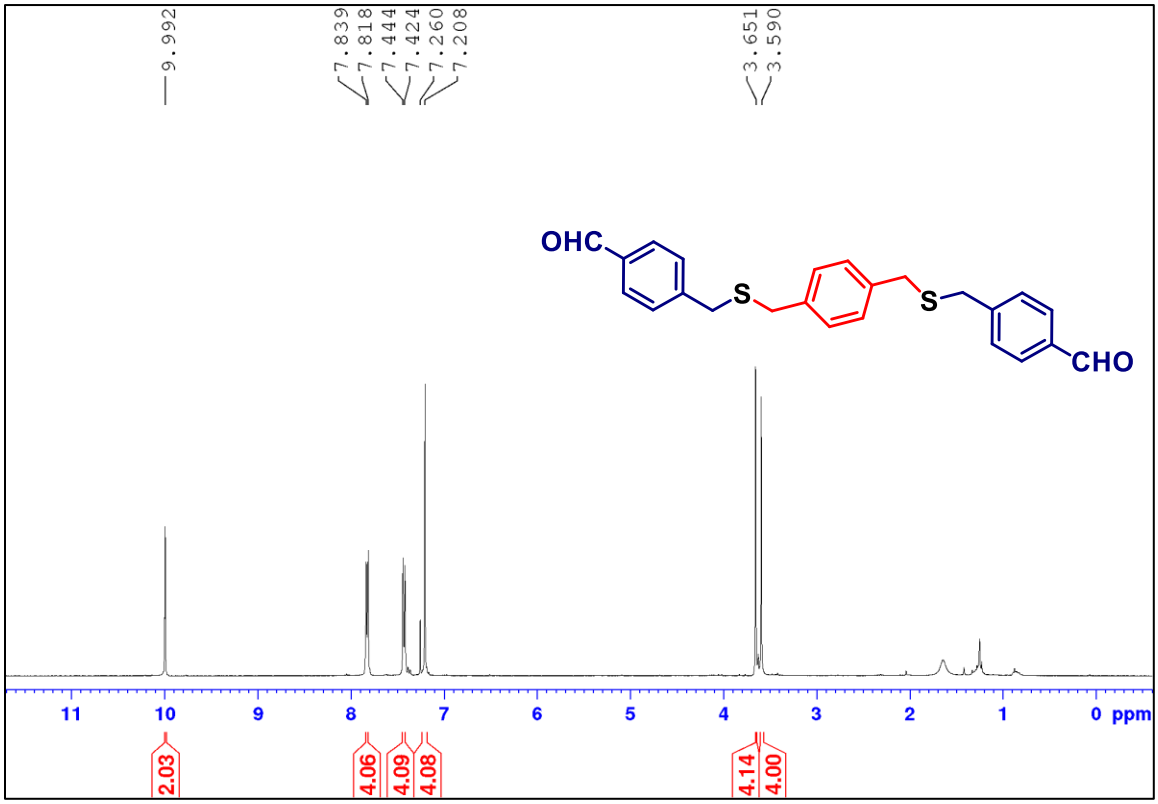


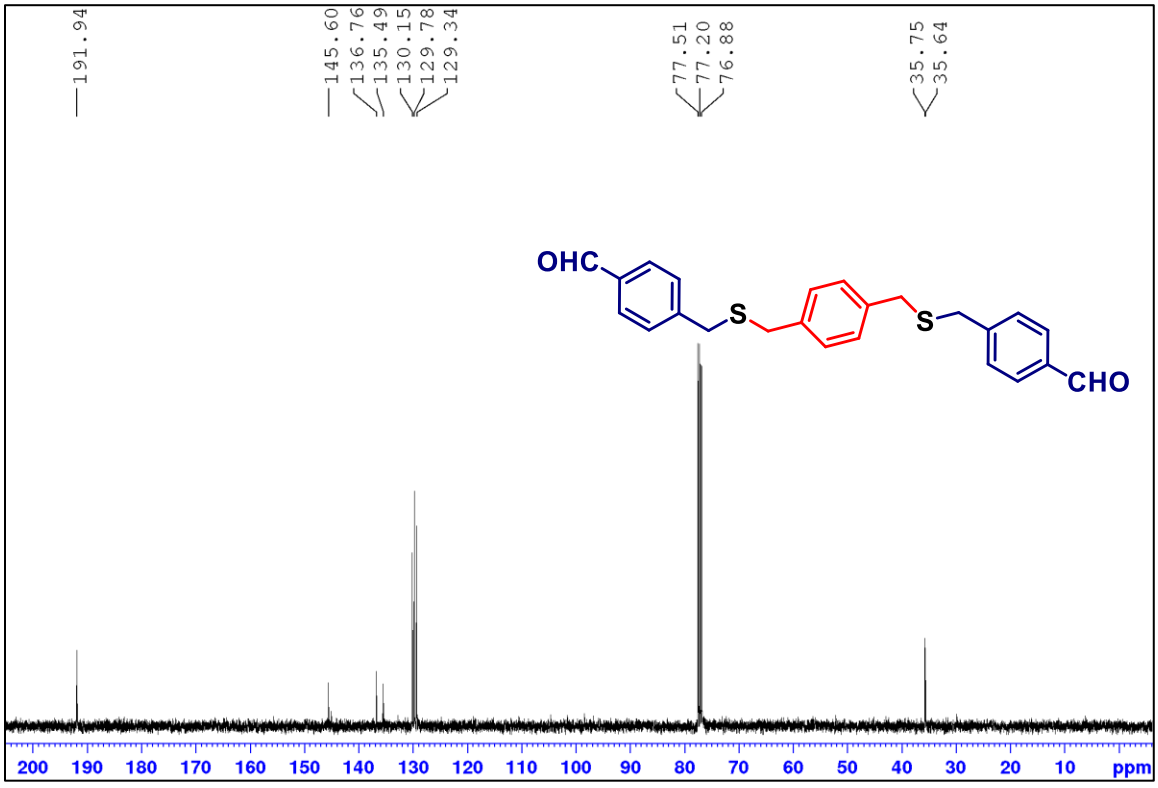
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 23b in $CDCl_3$



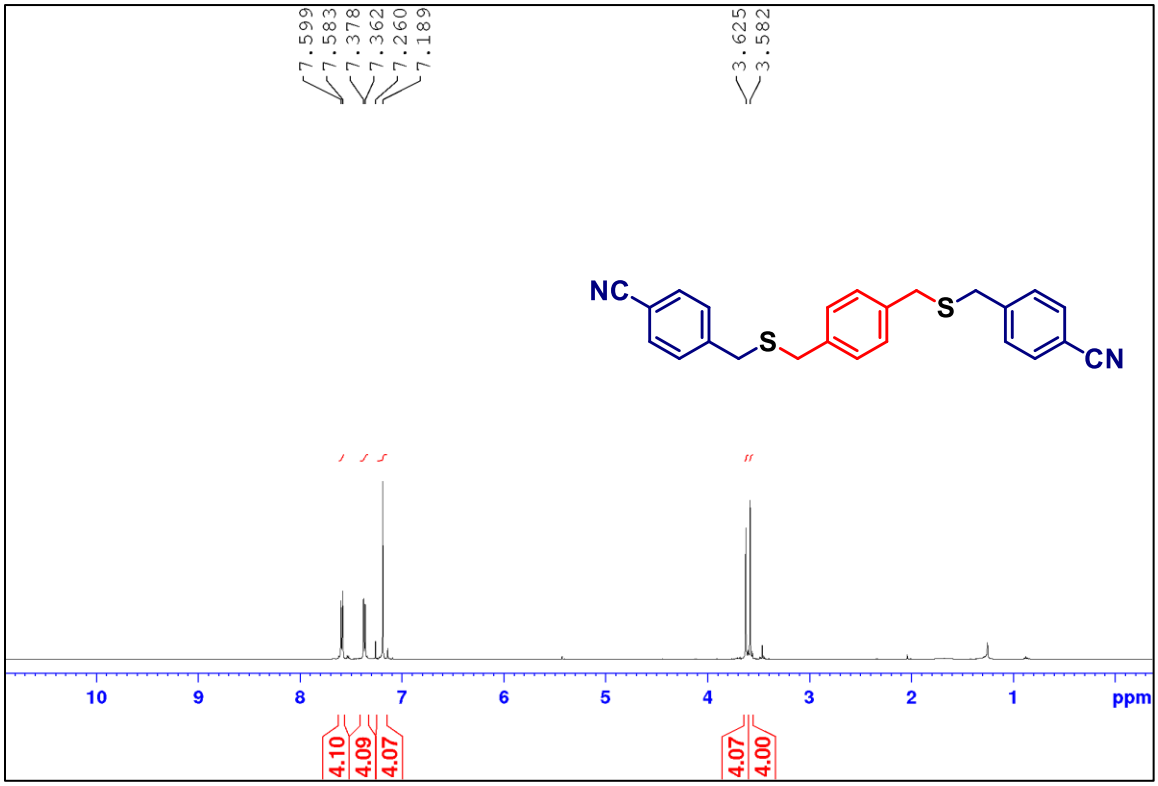


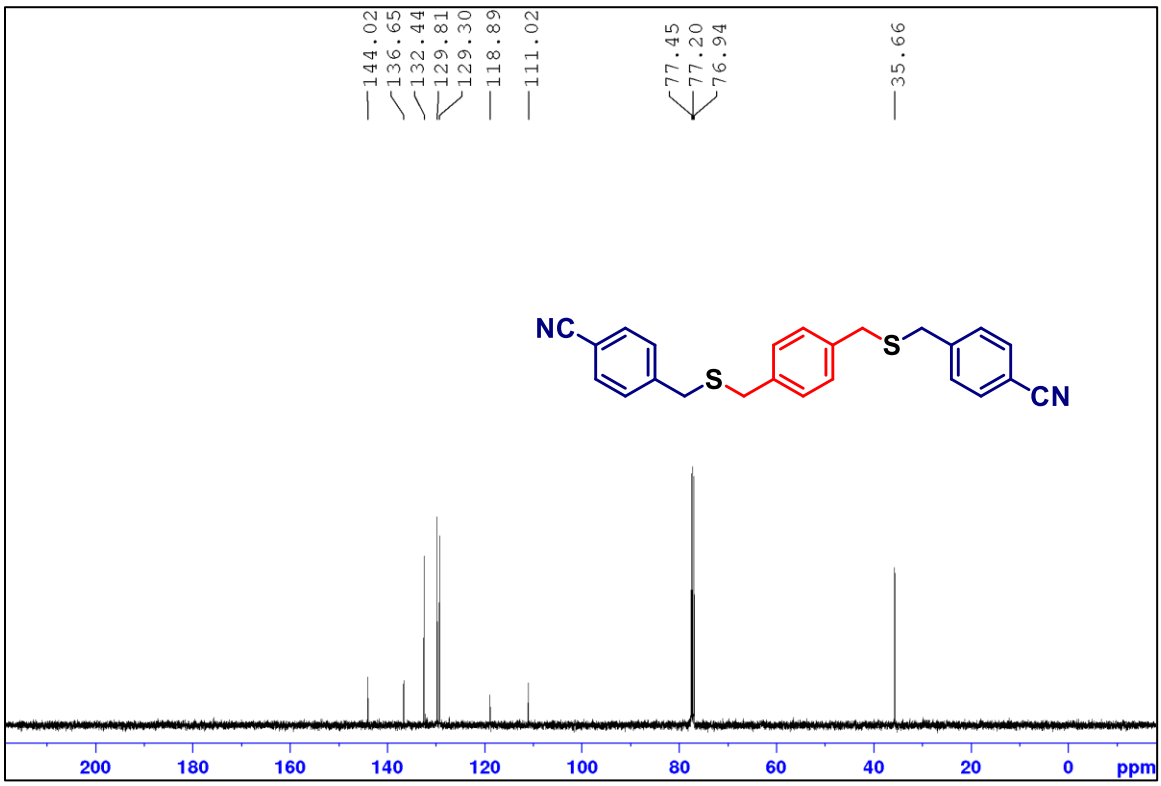
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 23c in $CDCl_3$



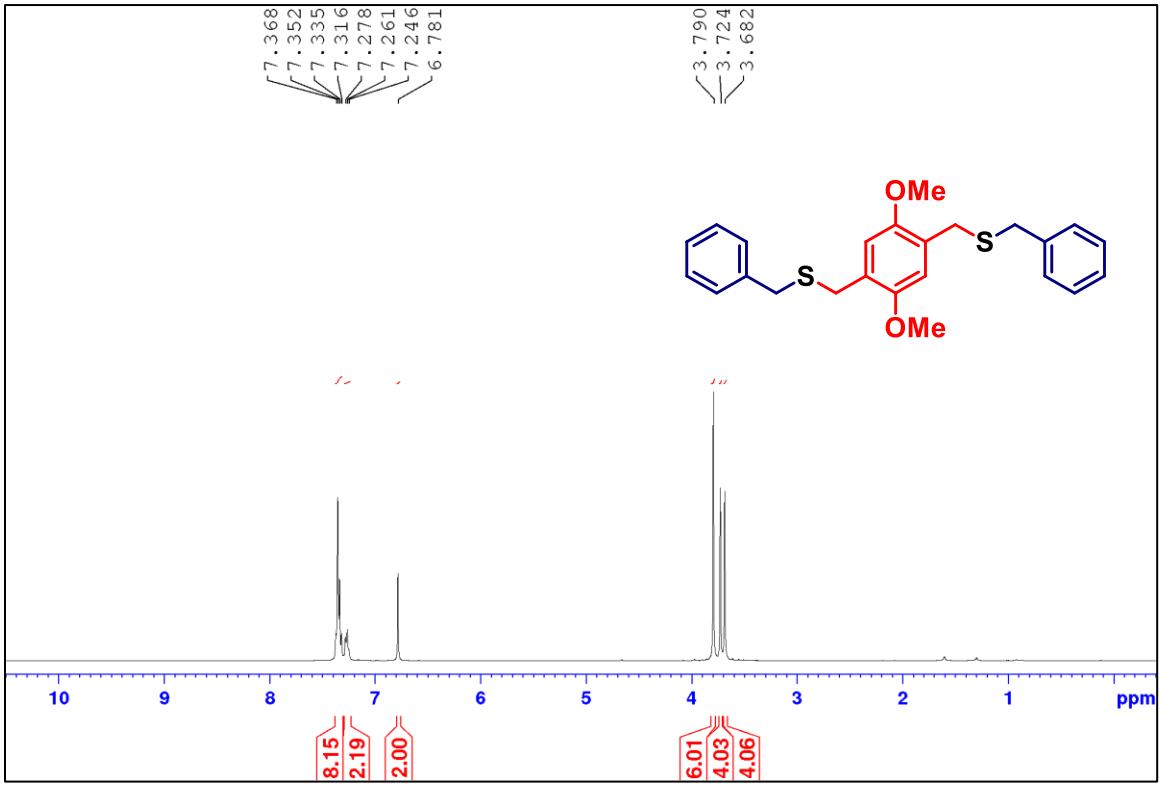


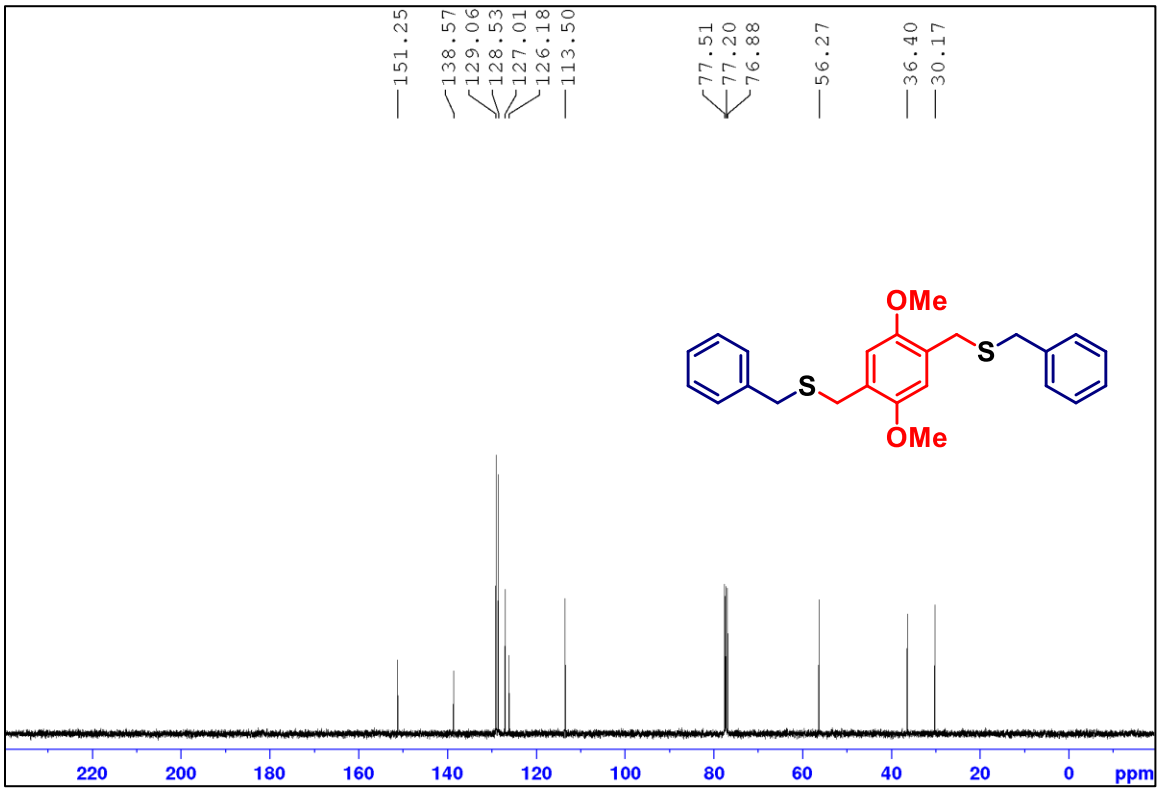
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 23d in $CDCl_3$



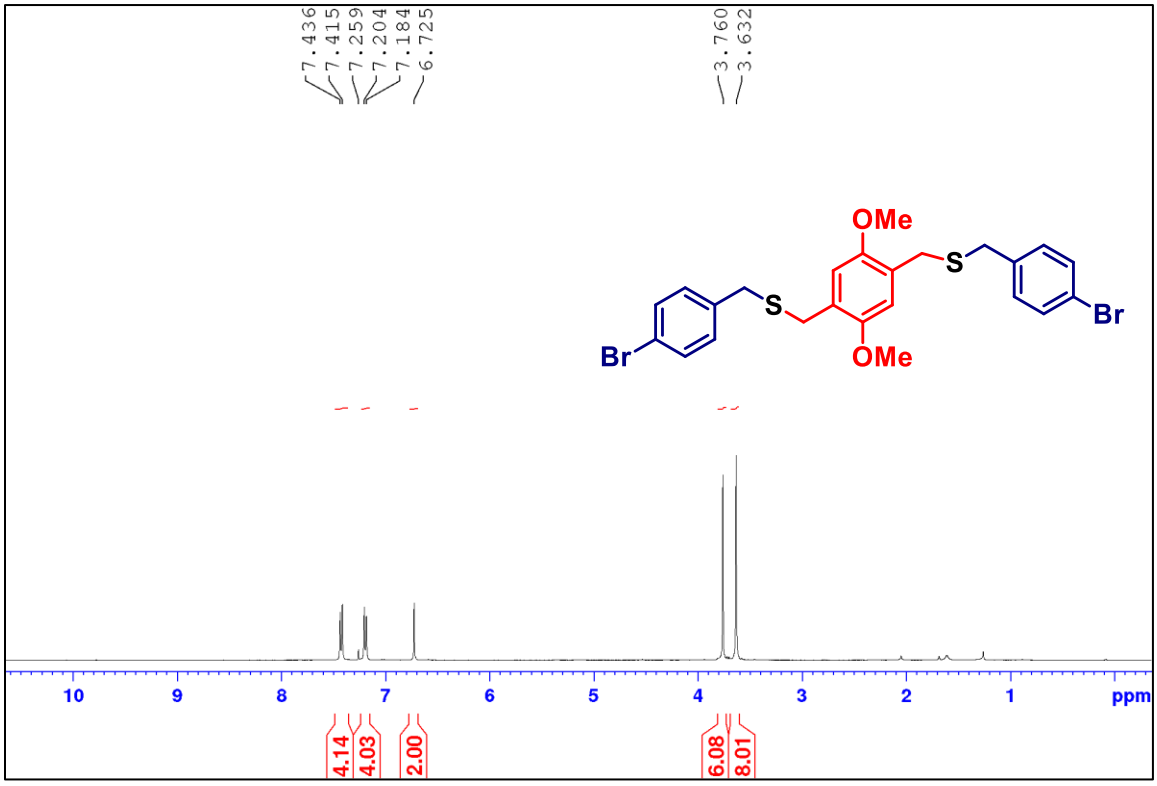


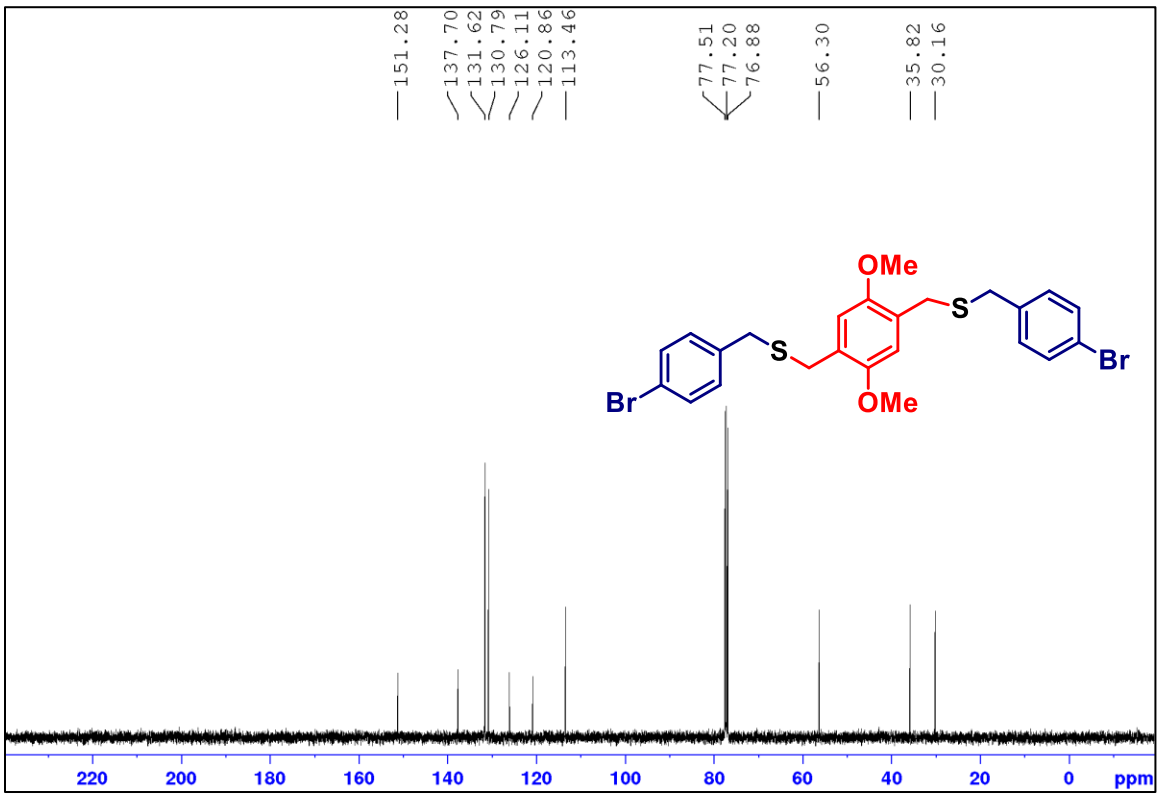
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 24a in $CDCl_3$



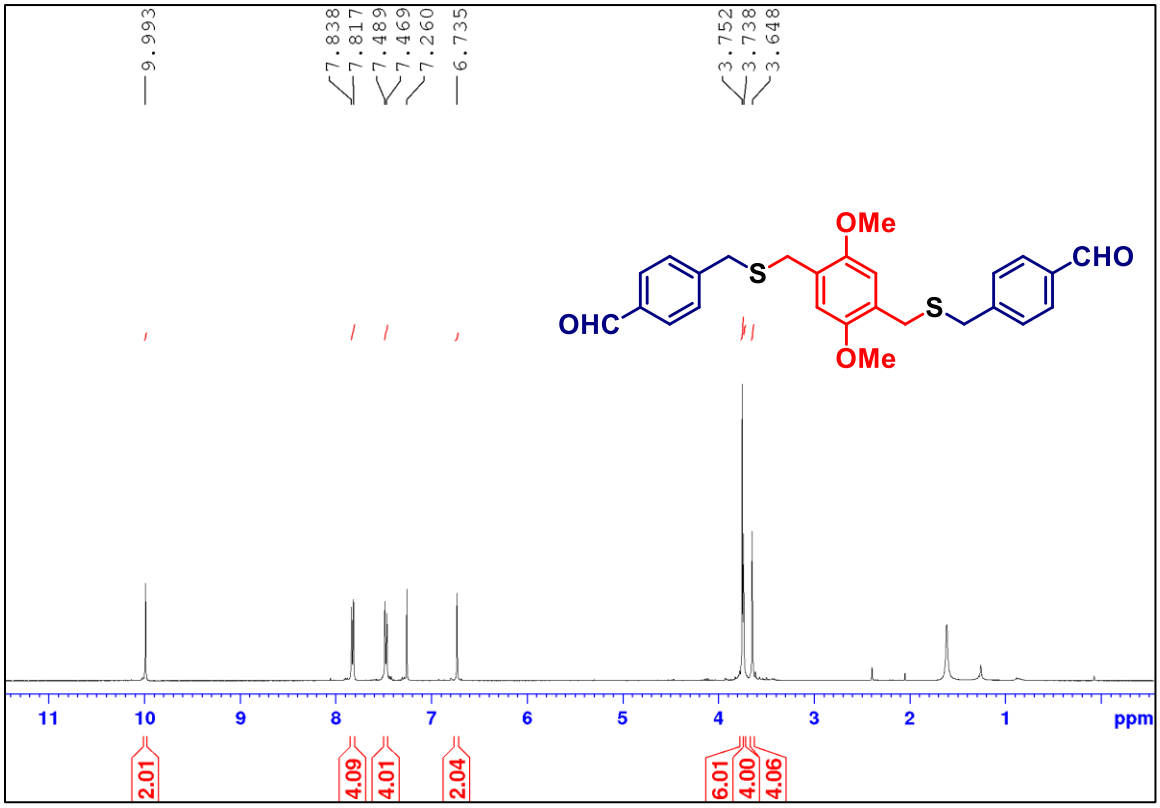


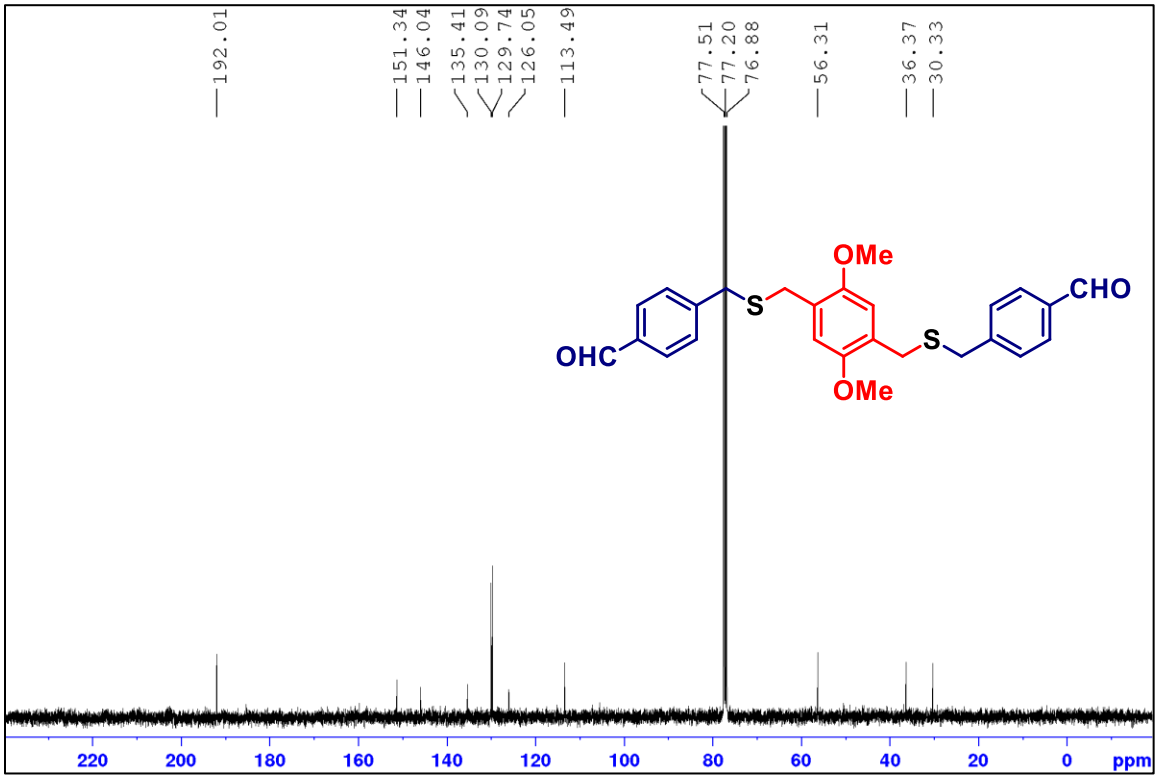
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 24b in $CDCl_3$



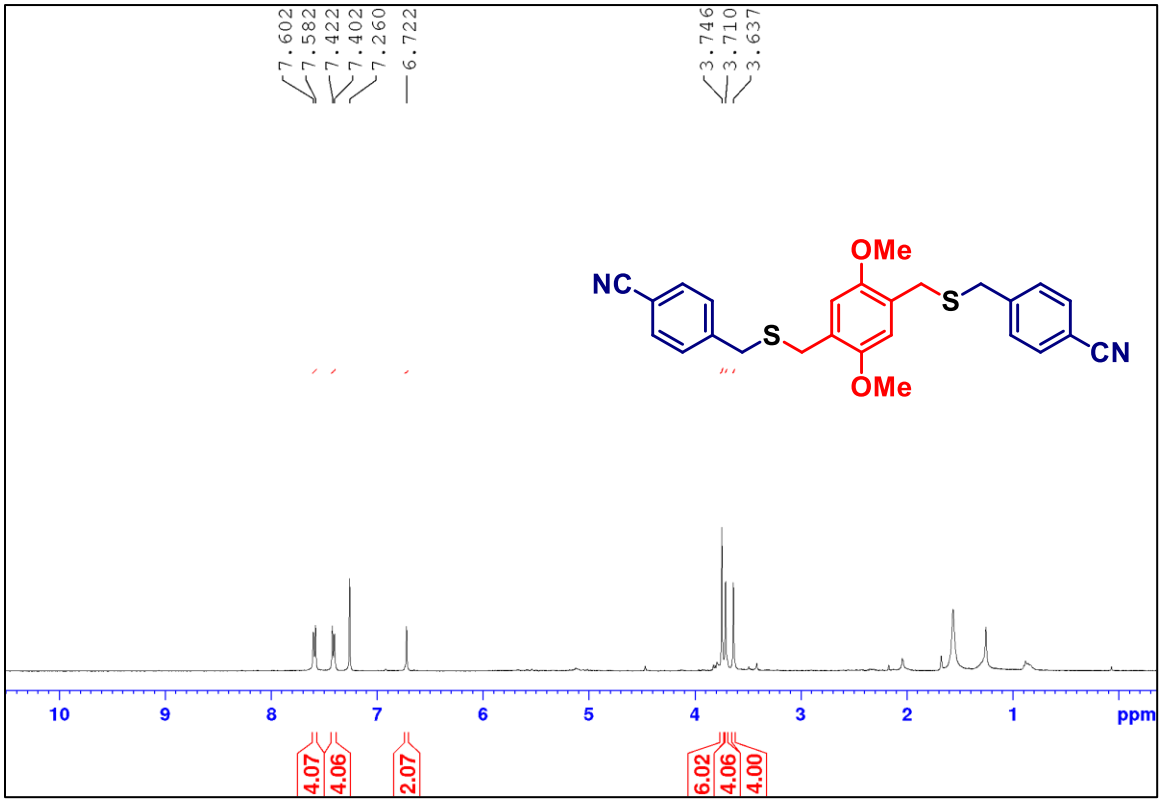


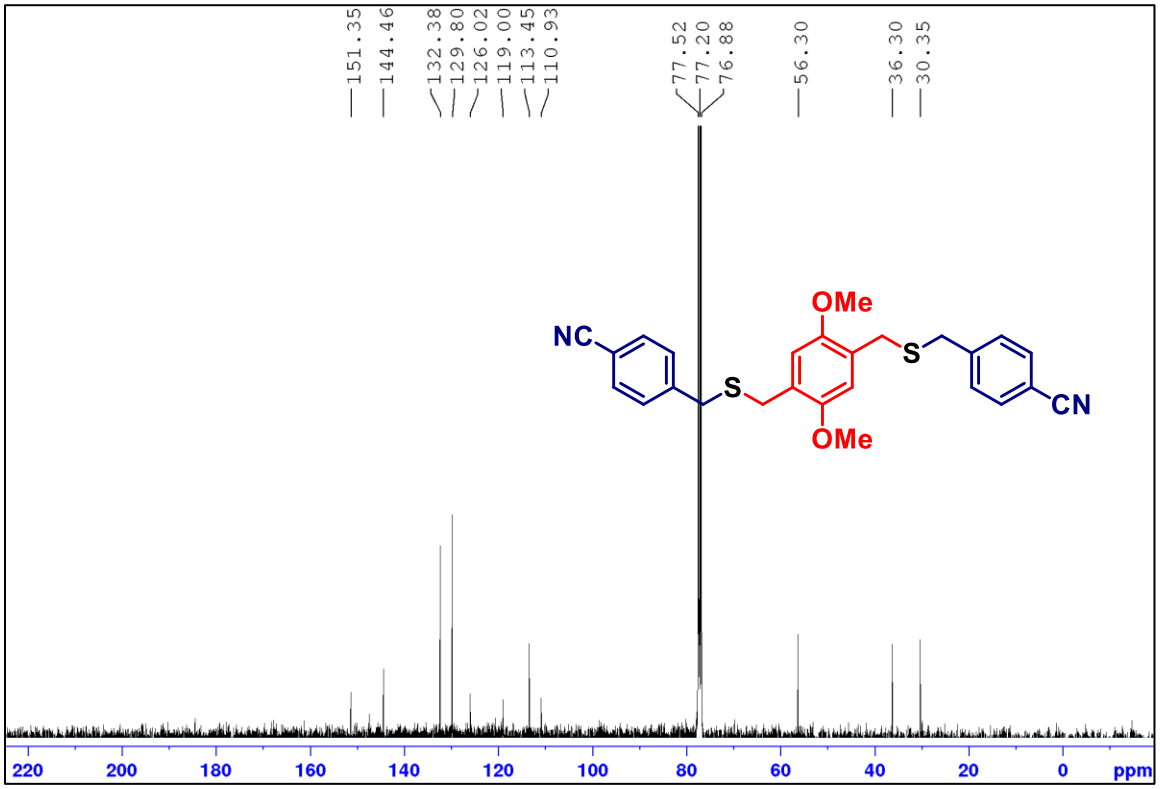
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 24c in $CDCl_3$



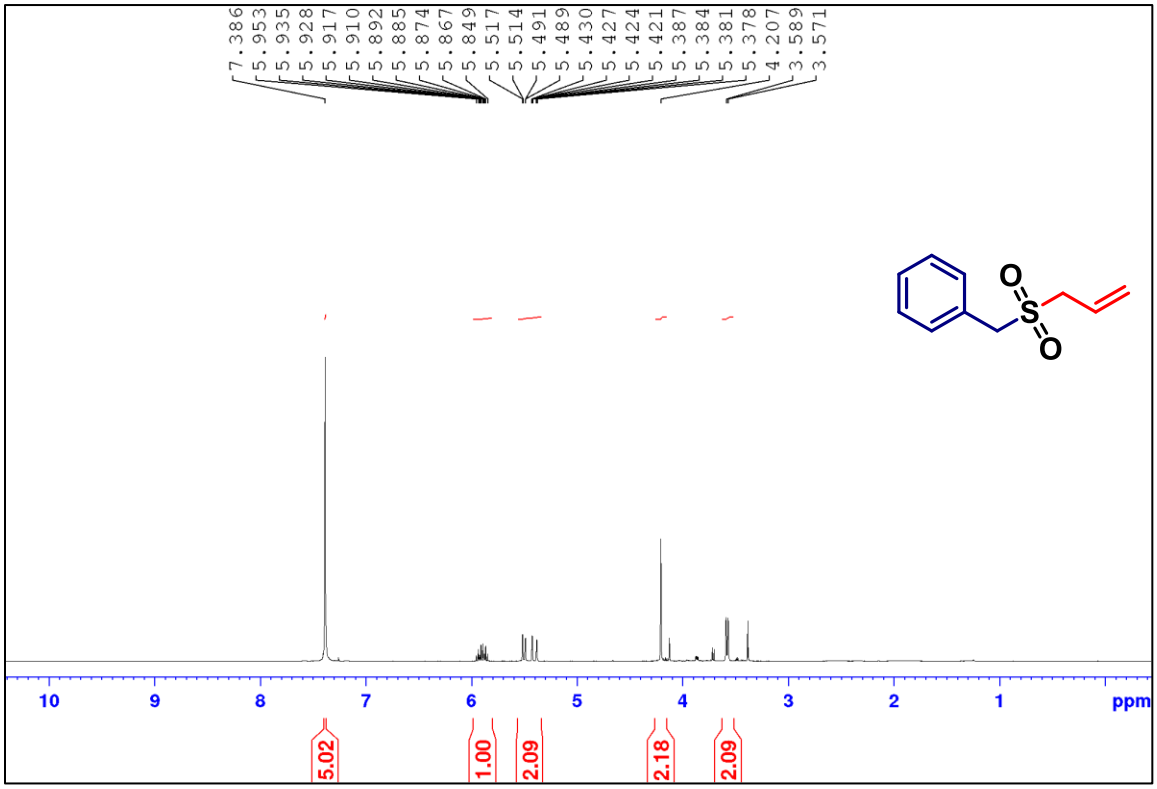


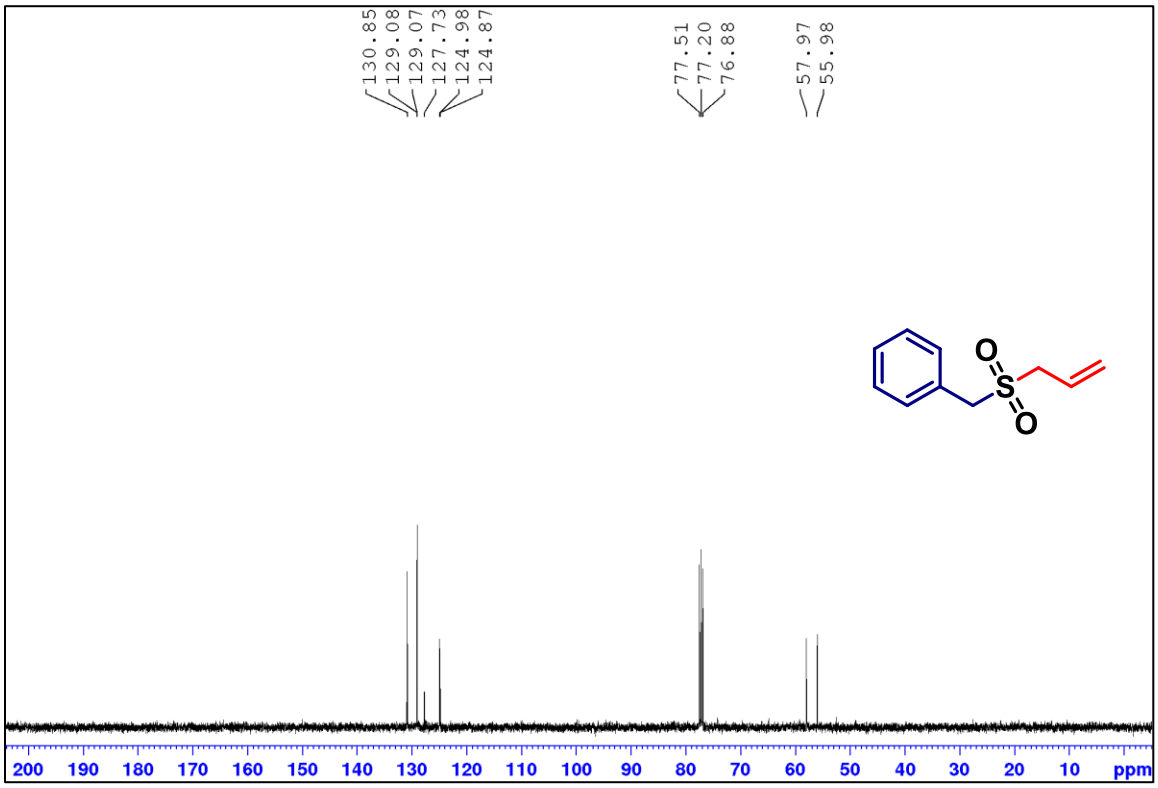
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 24d in $CDCl_3$



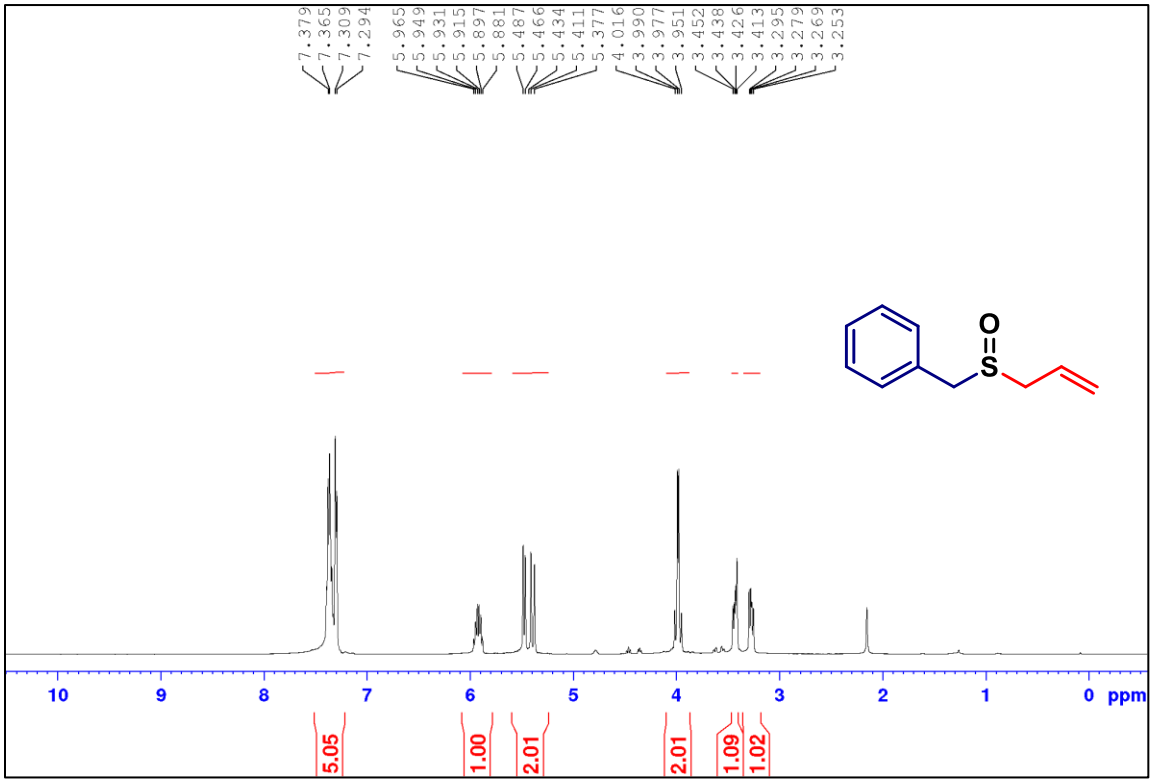


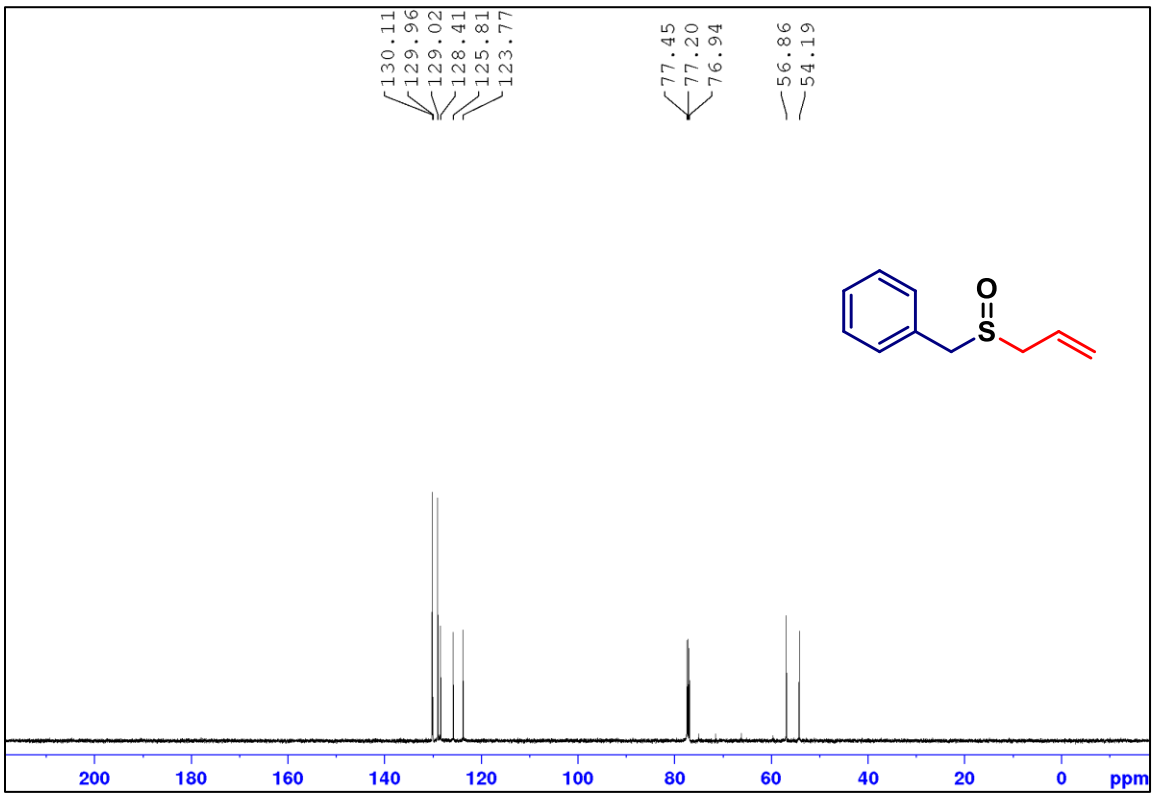
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 25 in $CDCl_3$



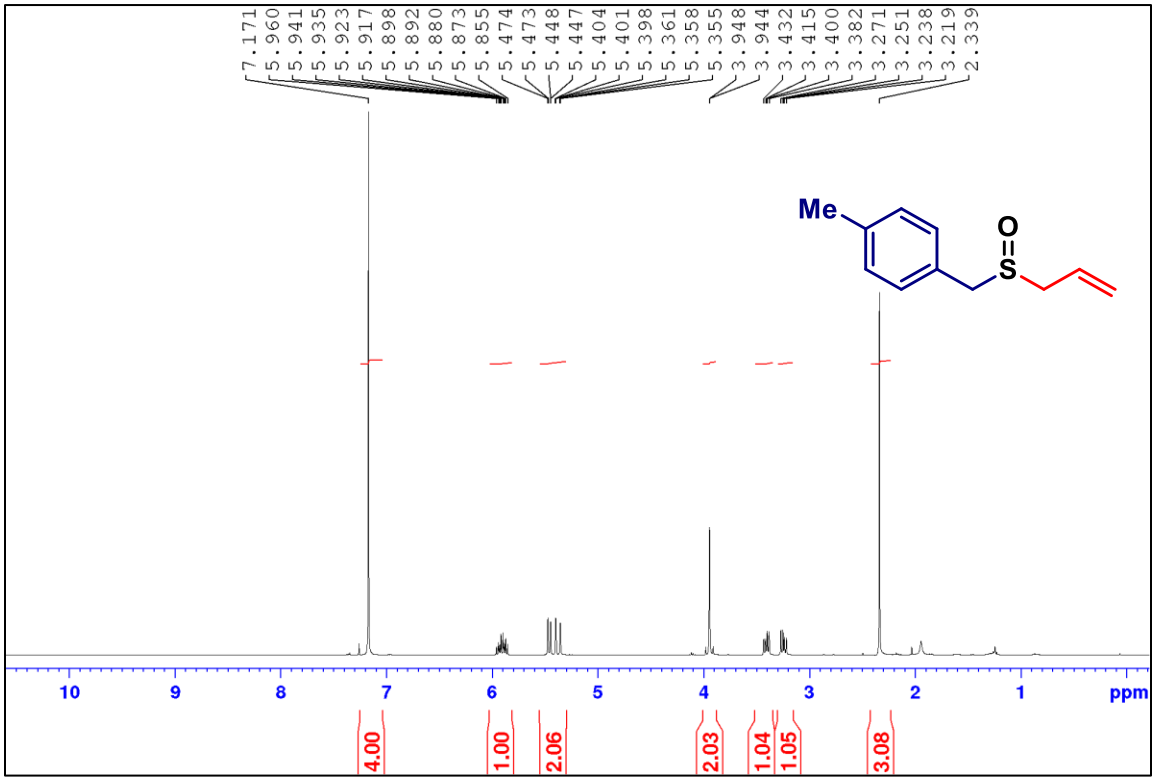


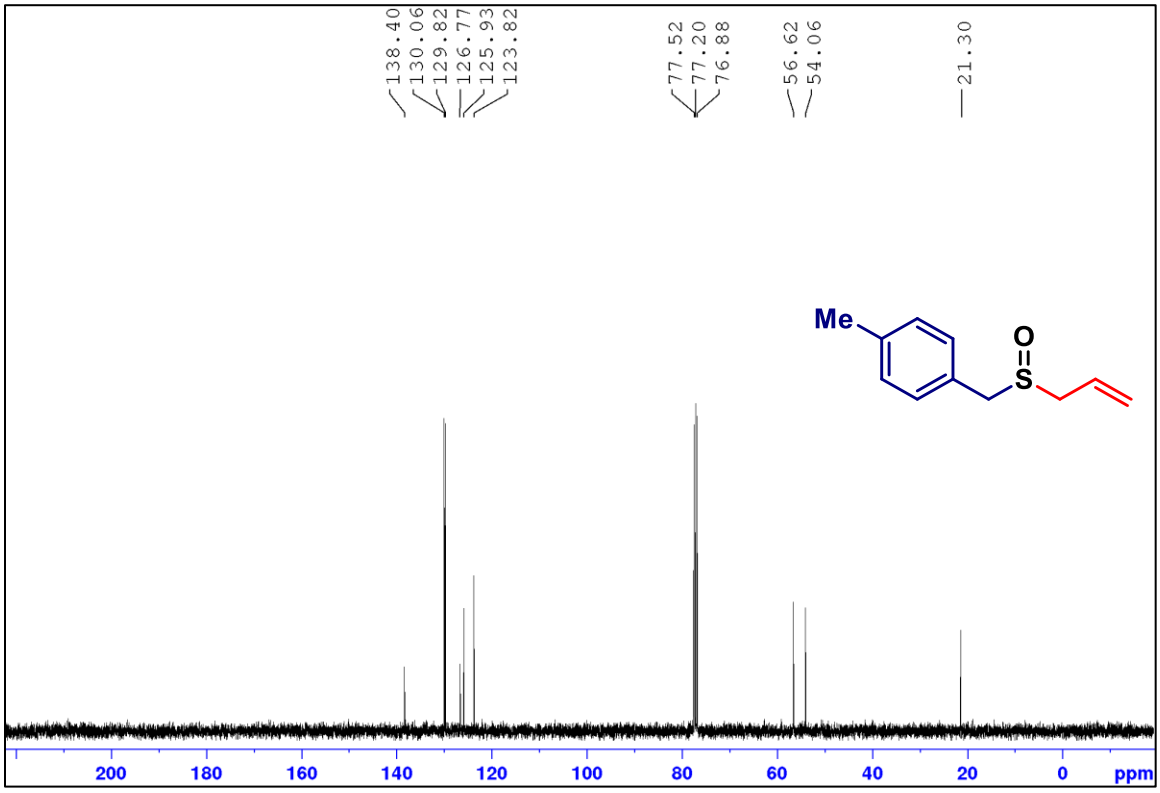
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 26a in $CDCl_3$



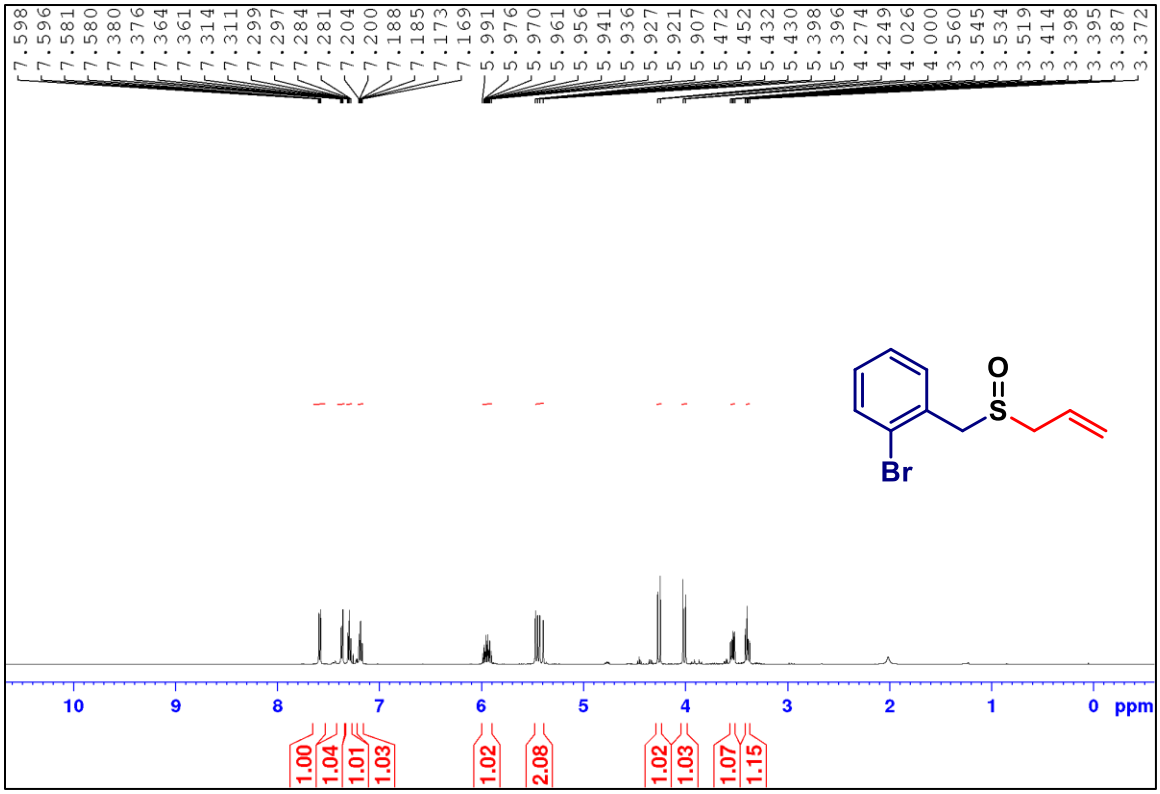


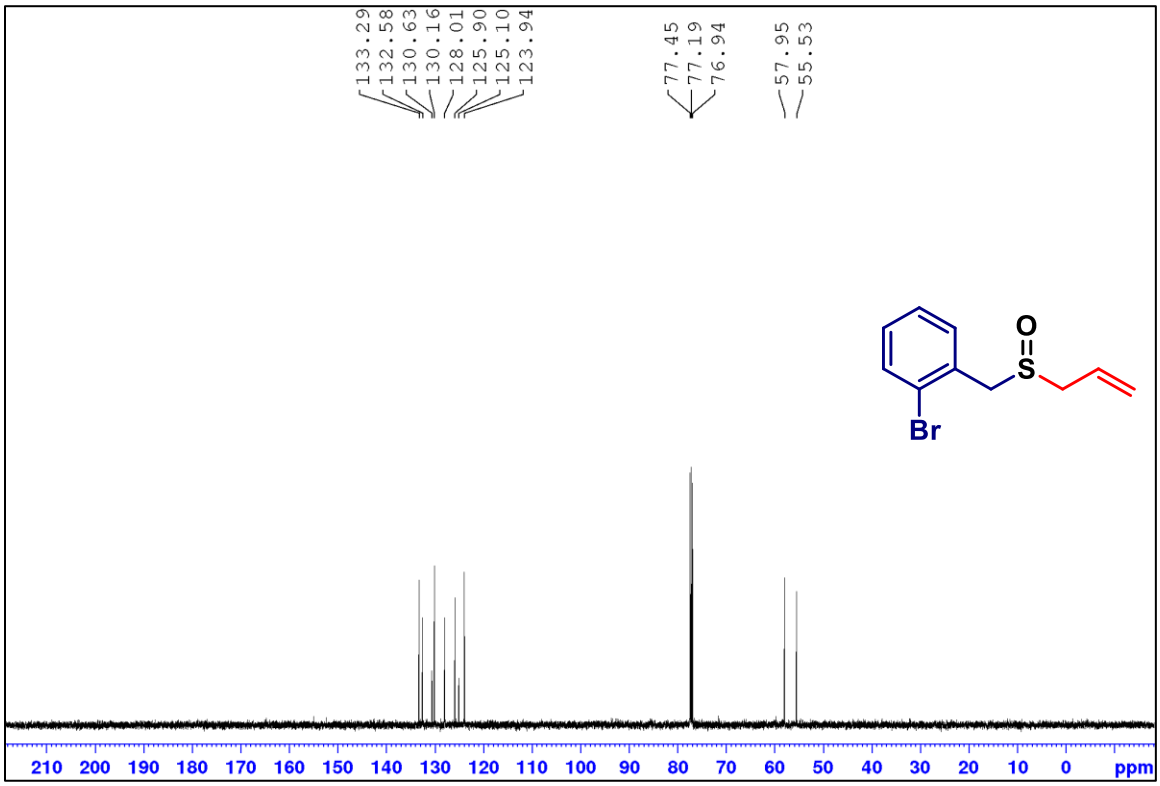
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 26b in $CDCl_3$



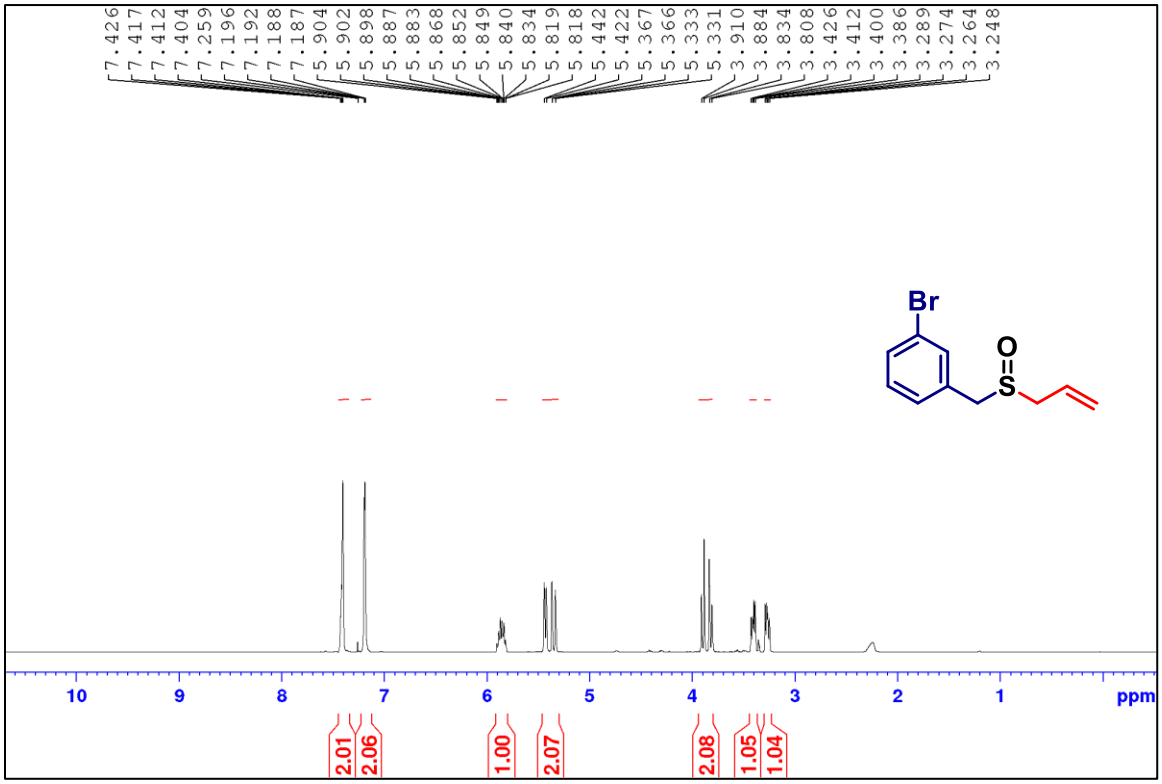


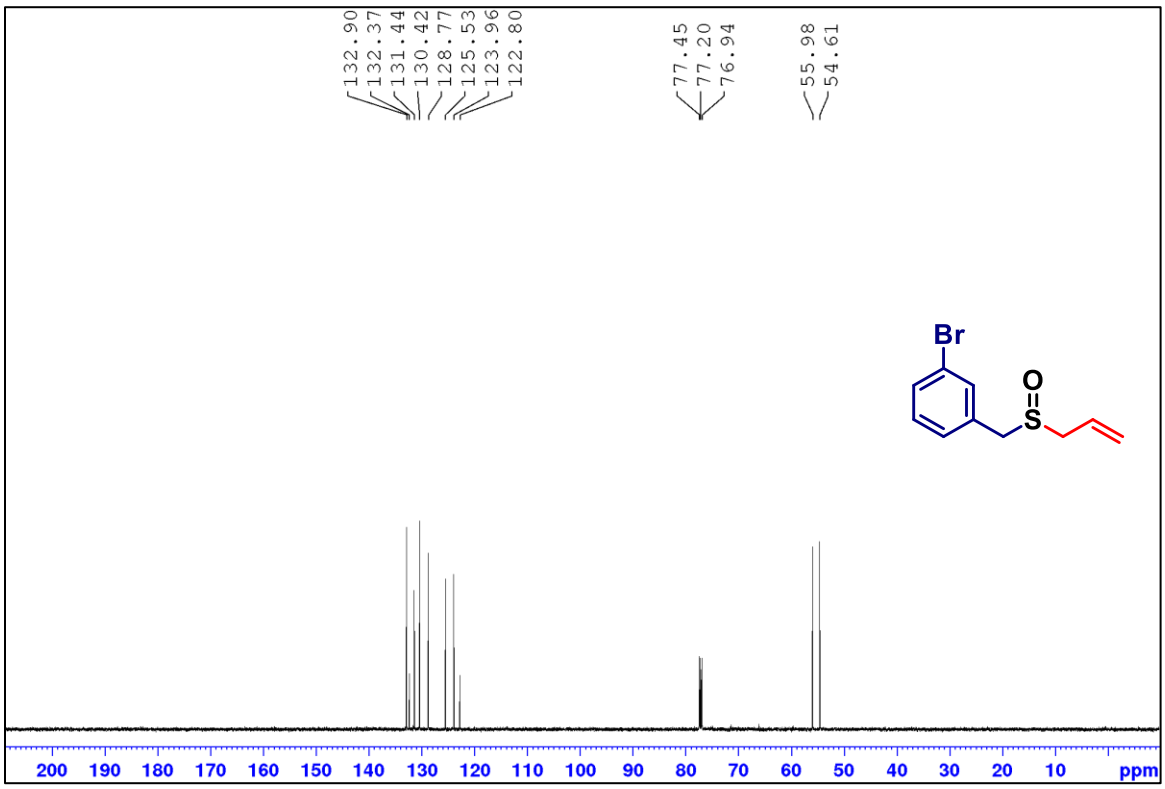
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 26c in $CDCl_3$



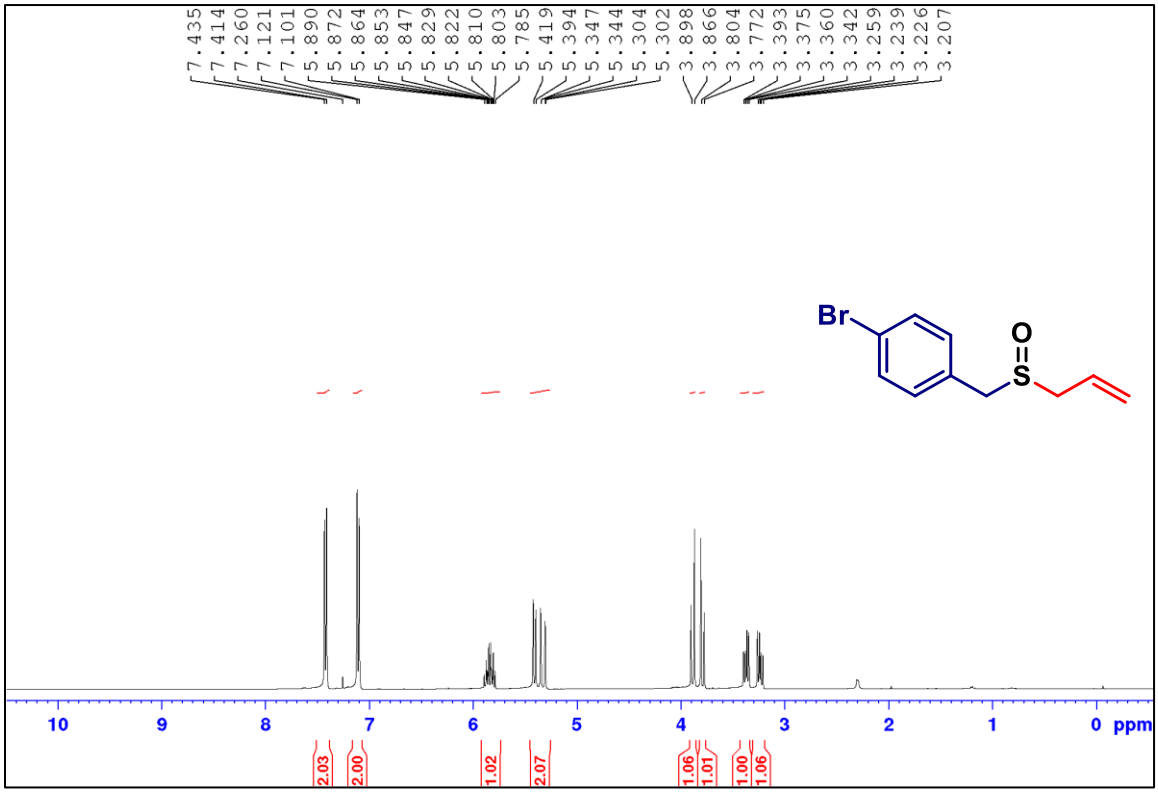


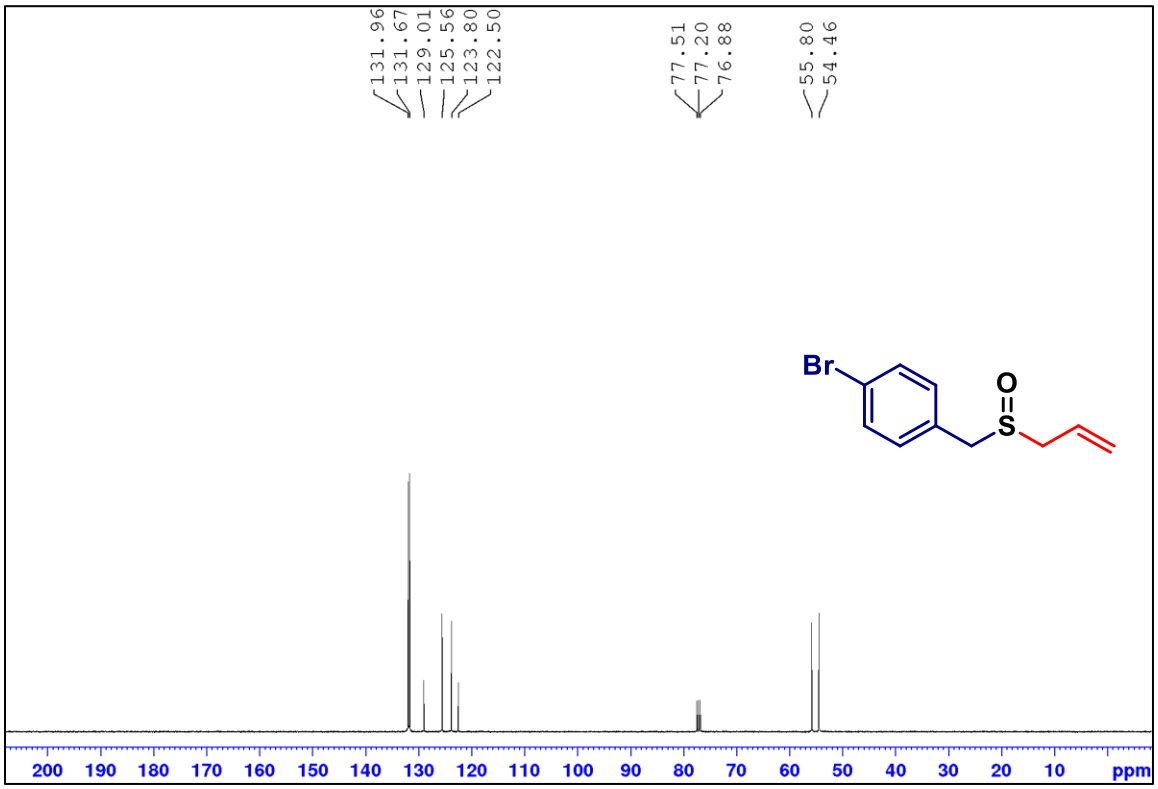
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 26d in $CDCl_3$



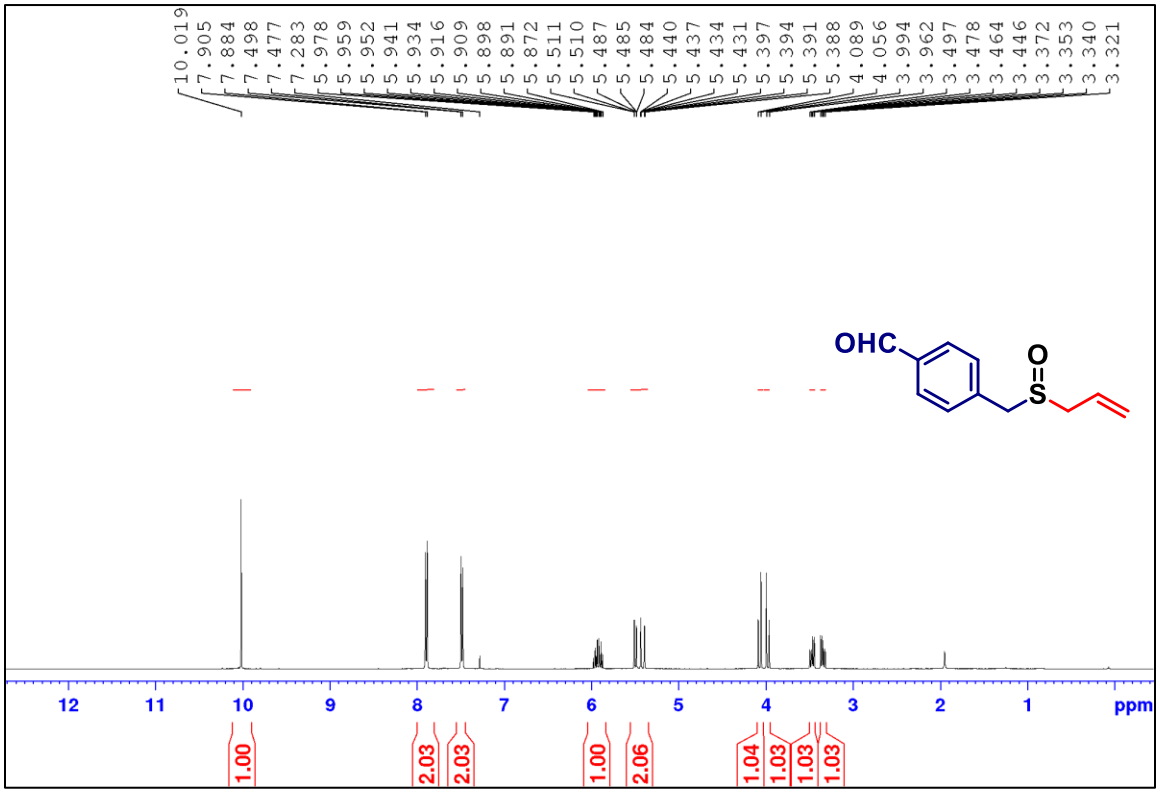


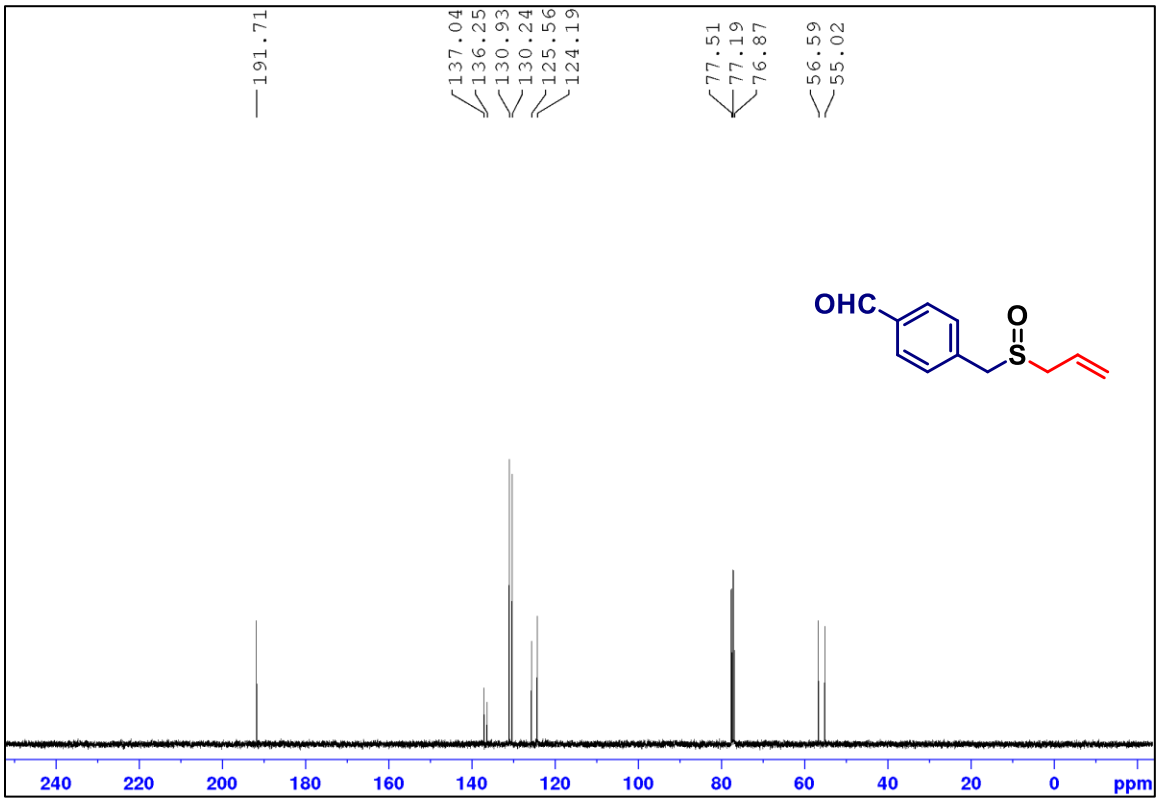
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 26e in $CDCl_3$



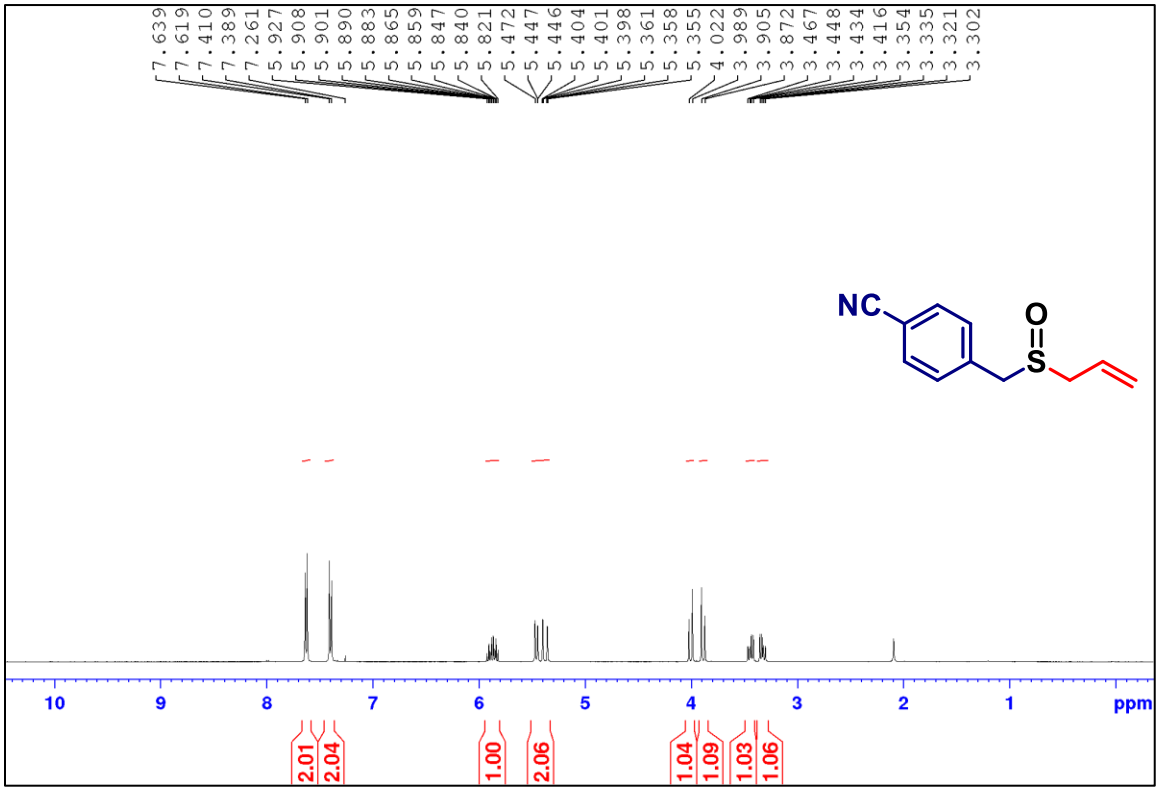


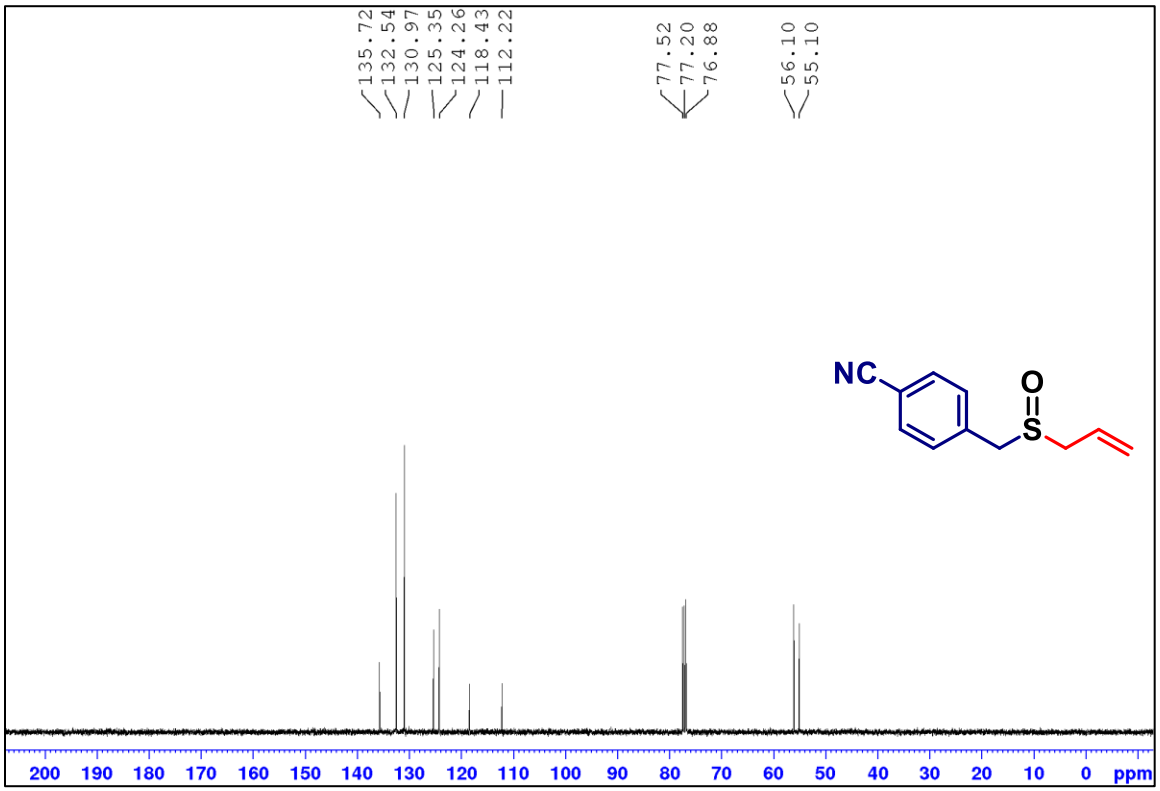
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 26f in $CDCl_3$



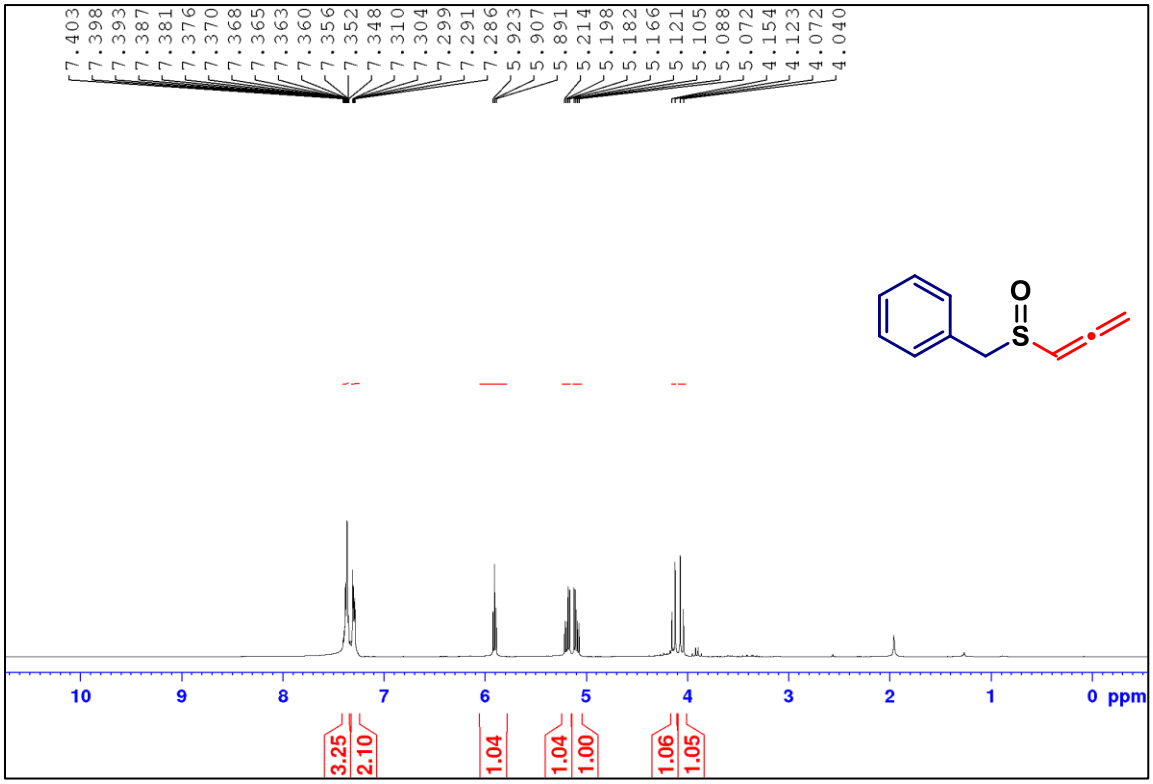


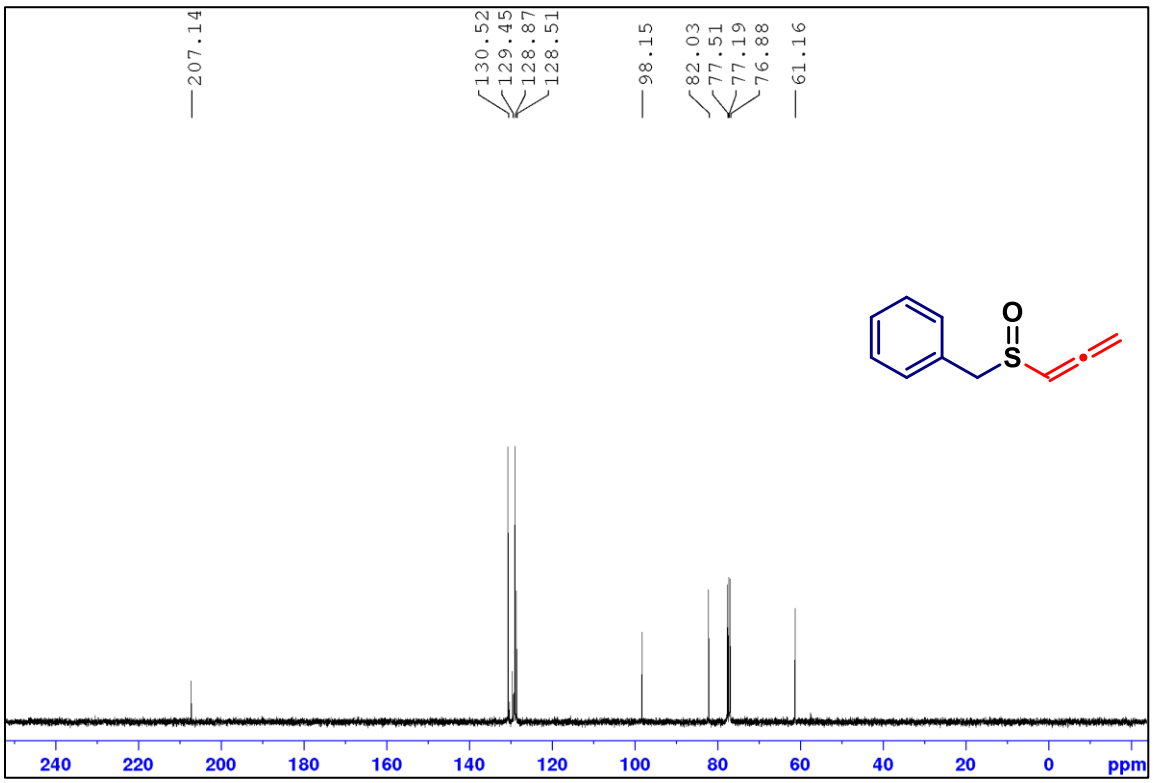
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 26g in $CDCl_3$



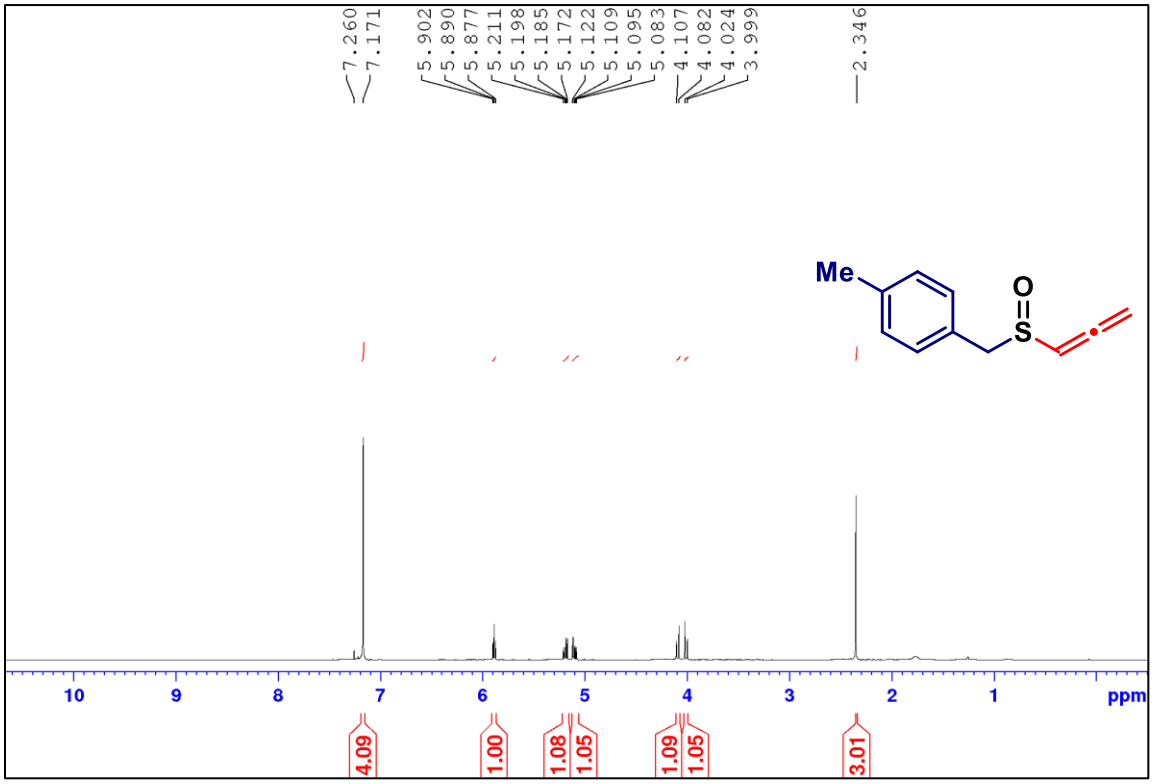


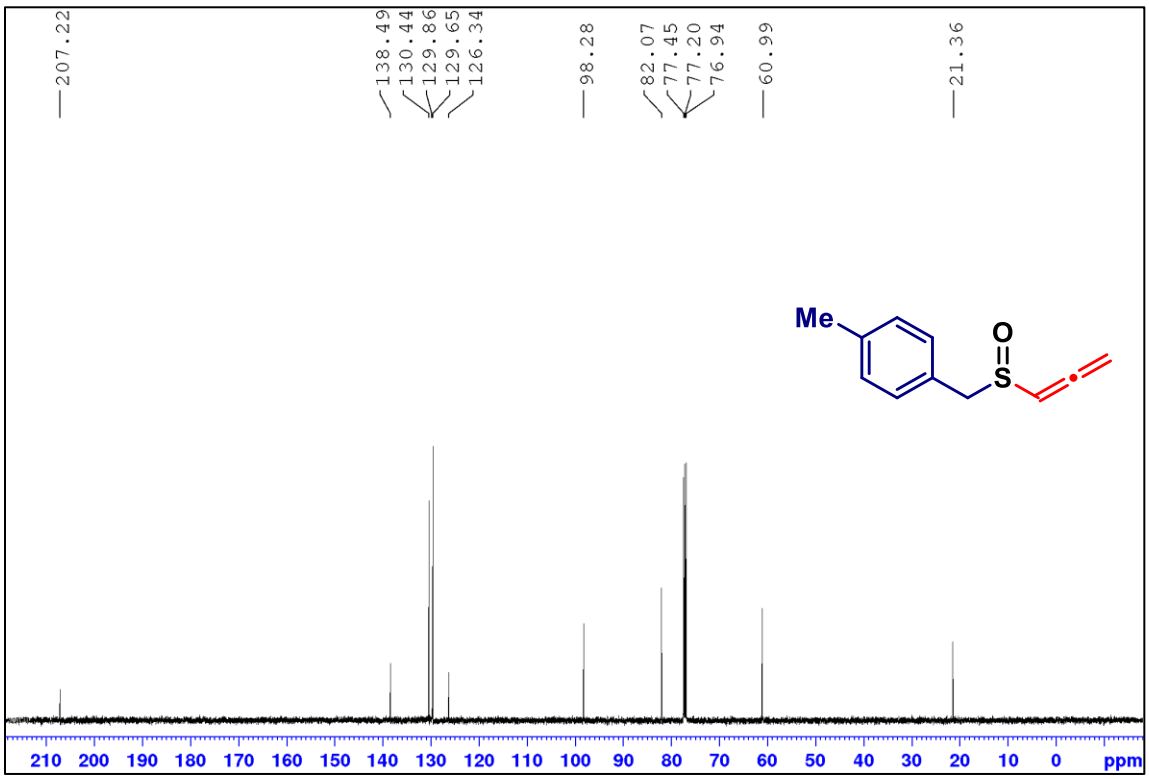
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 27a in $CDCl_3$



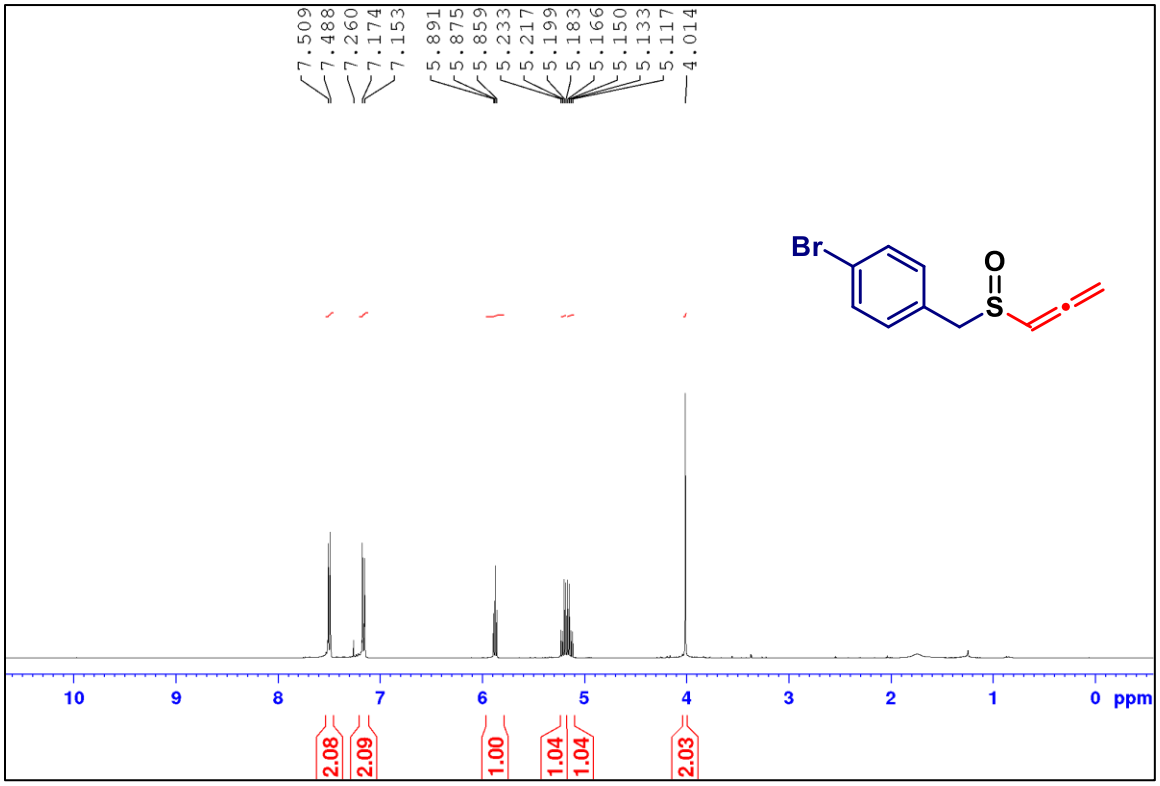


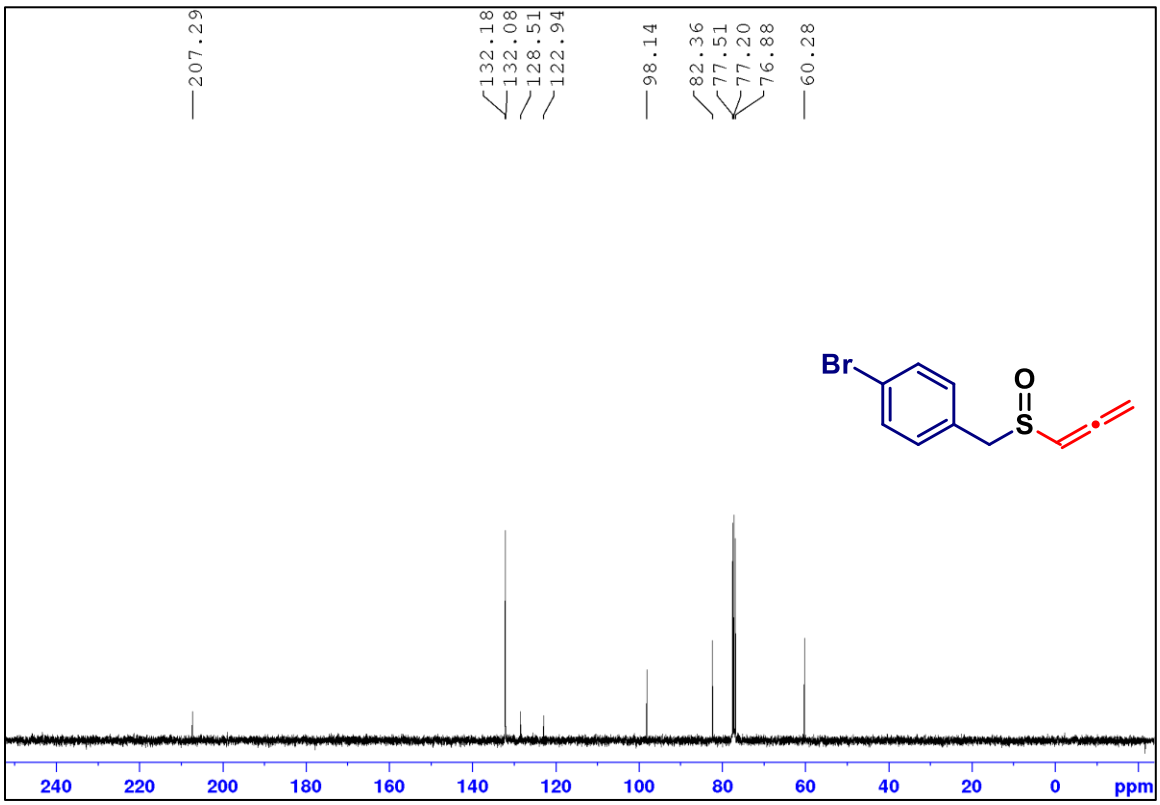
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 27b in $CDCl_3$



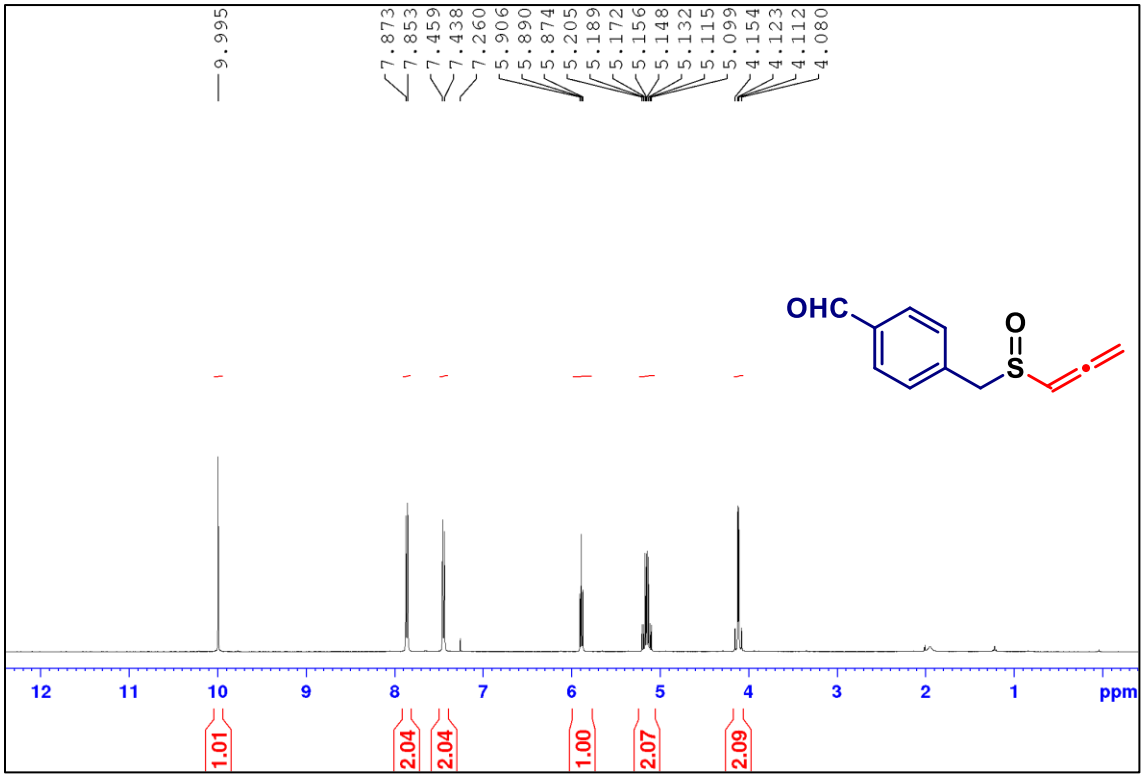


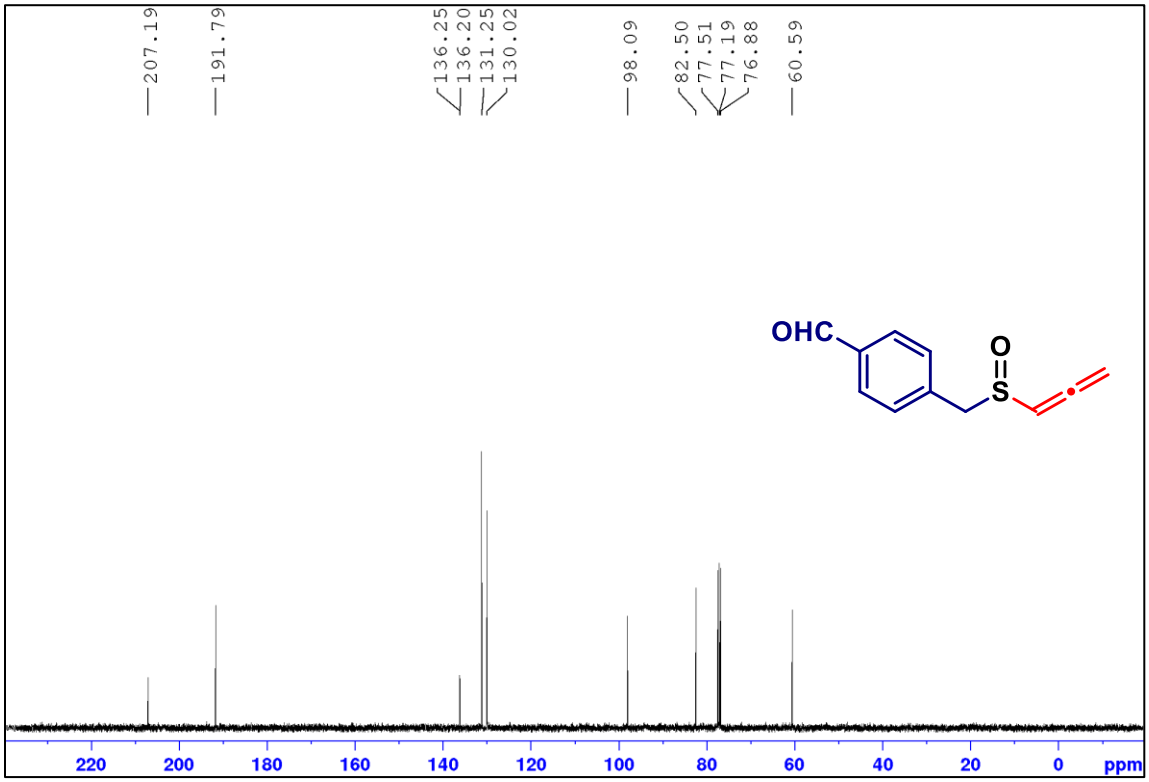
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 27c in $CDCl_3$



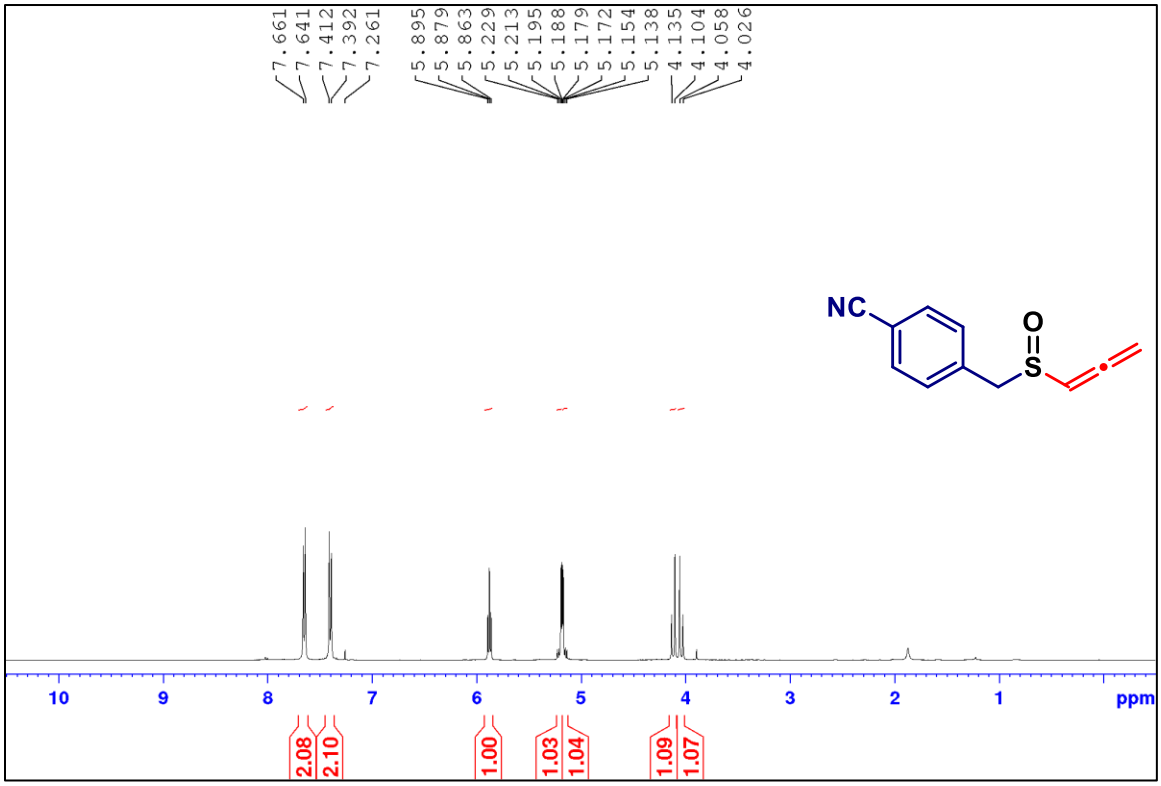


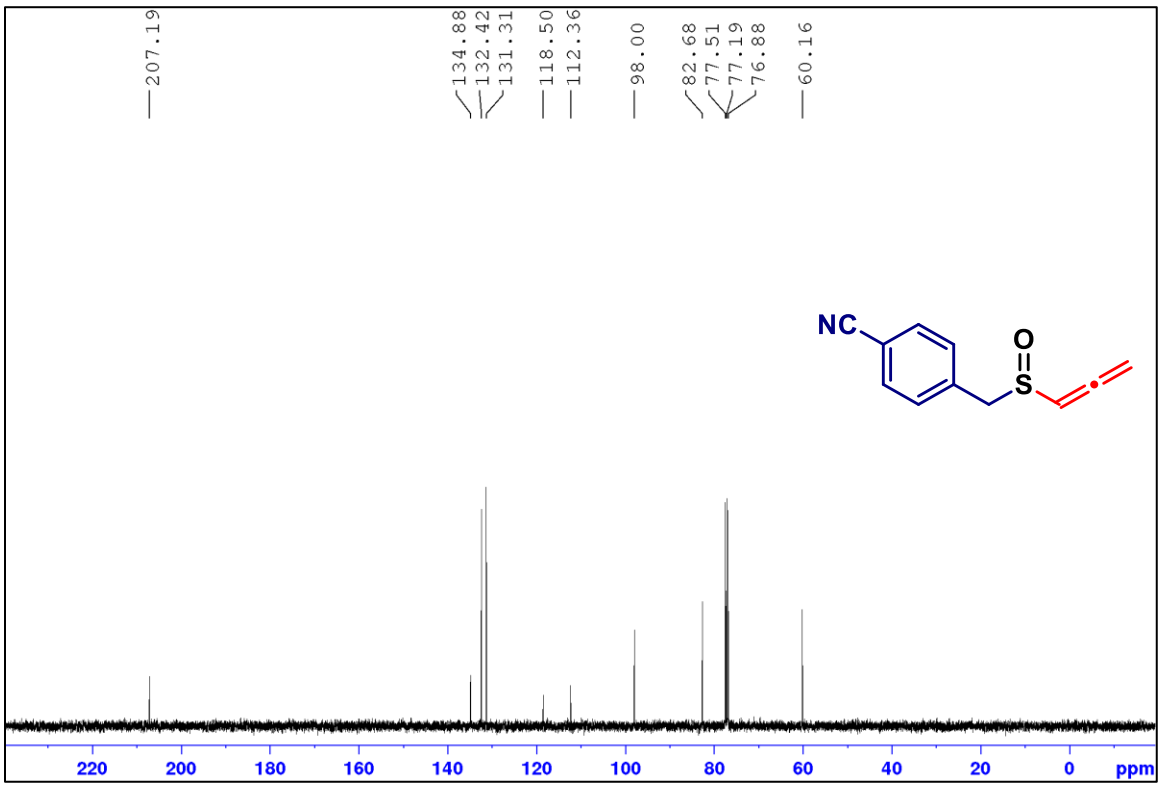
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 27d in $CDCl_3$



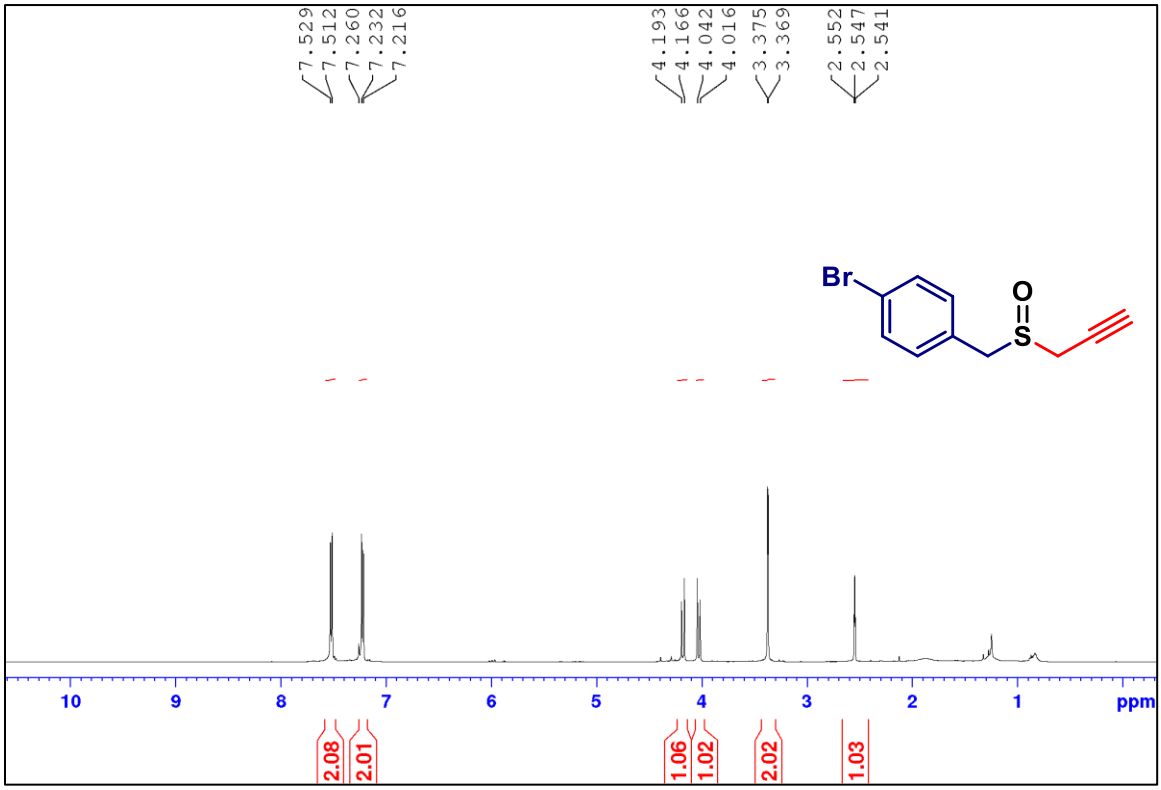


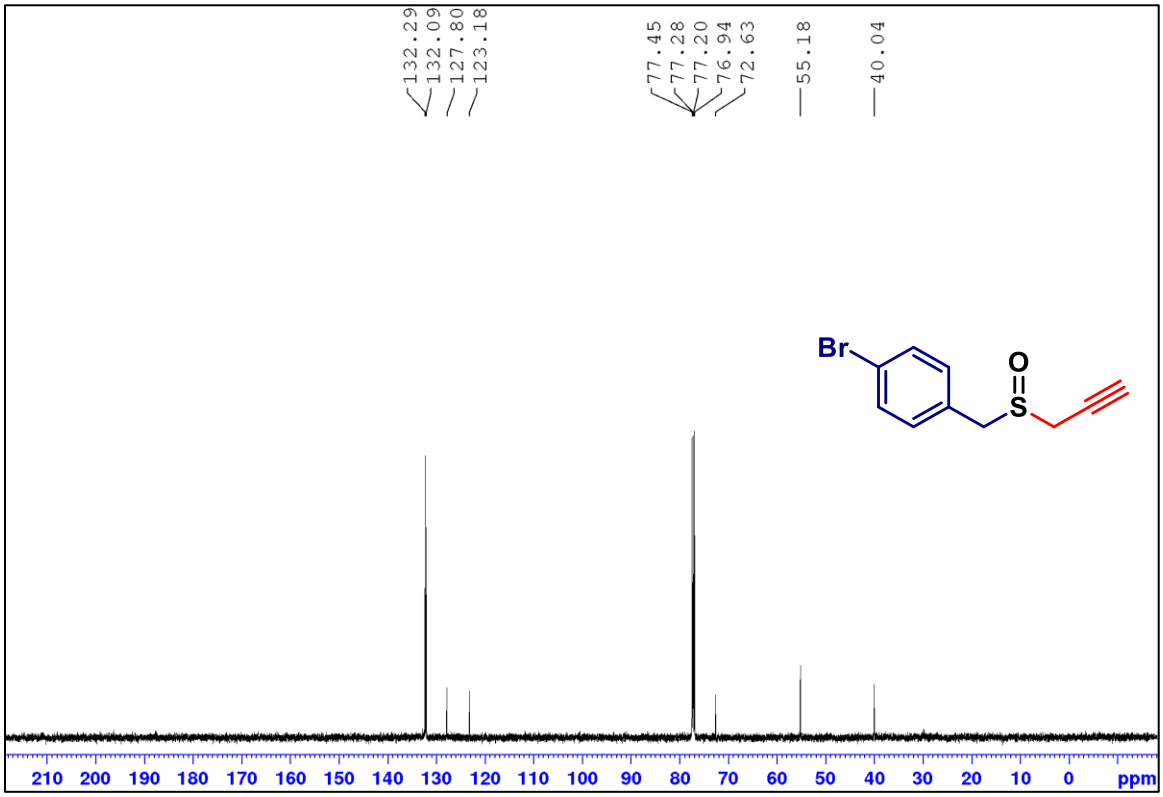
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 27e in $CDCl_3$



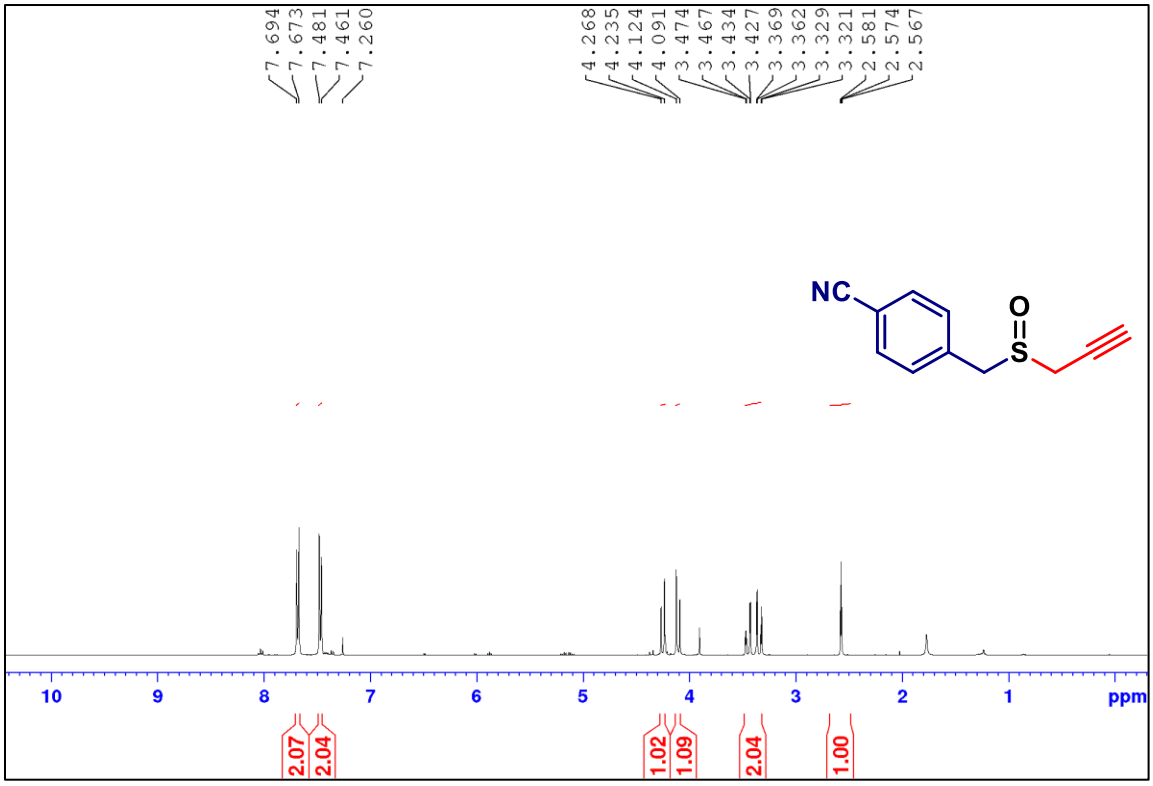


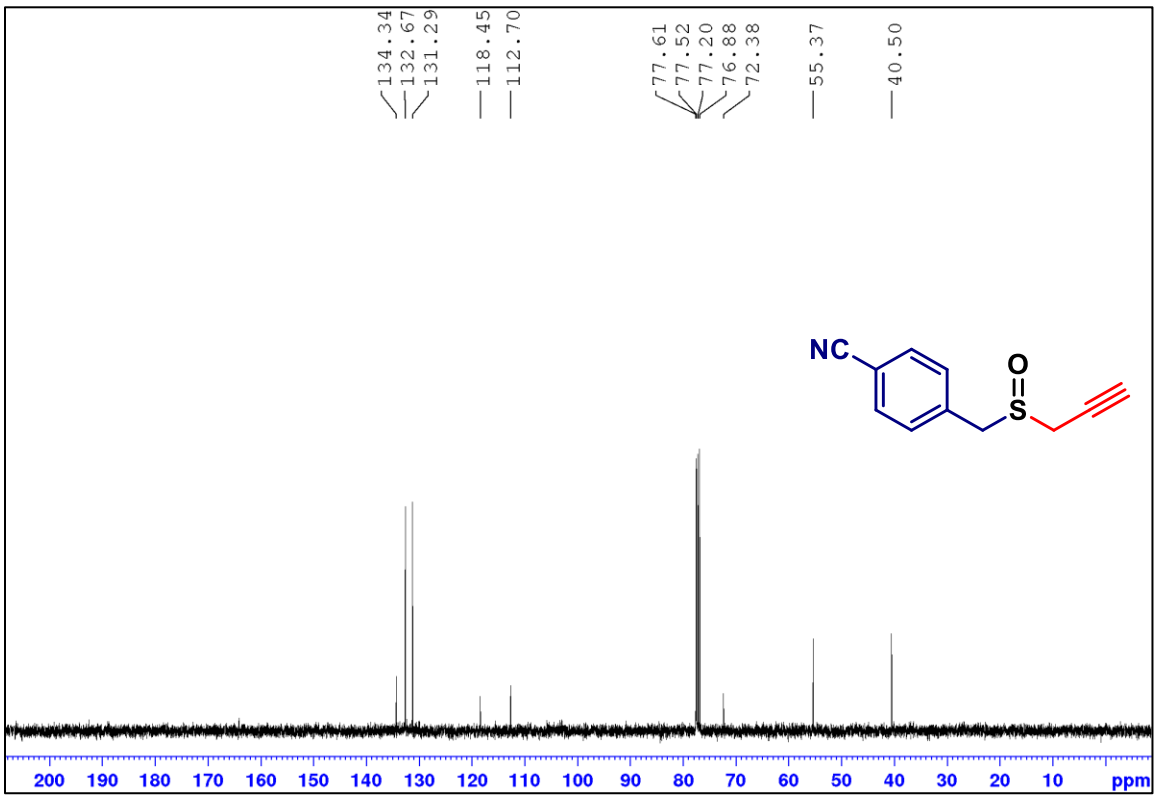
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 28 in $CDCl_3$



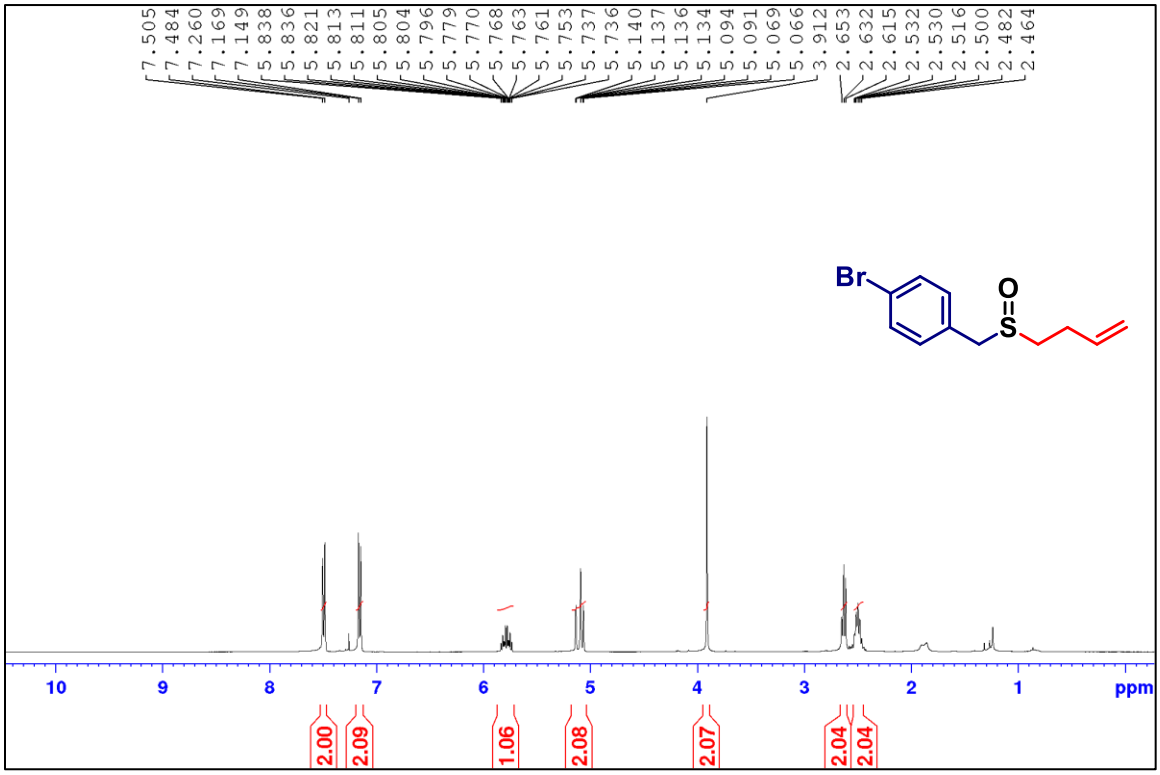


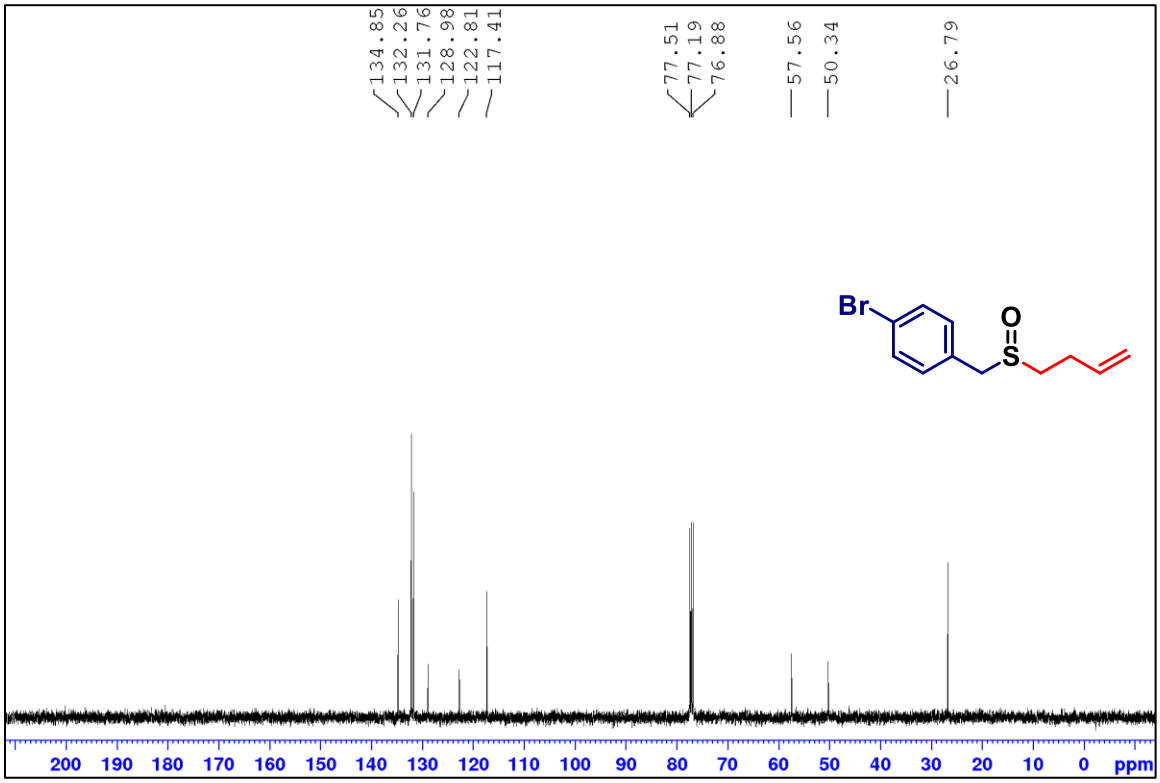
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 29 in $CDCl_3$



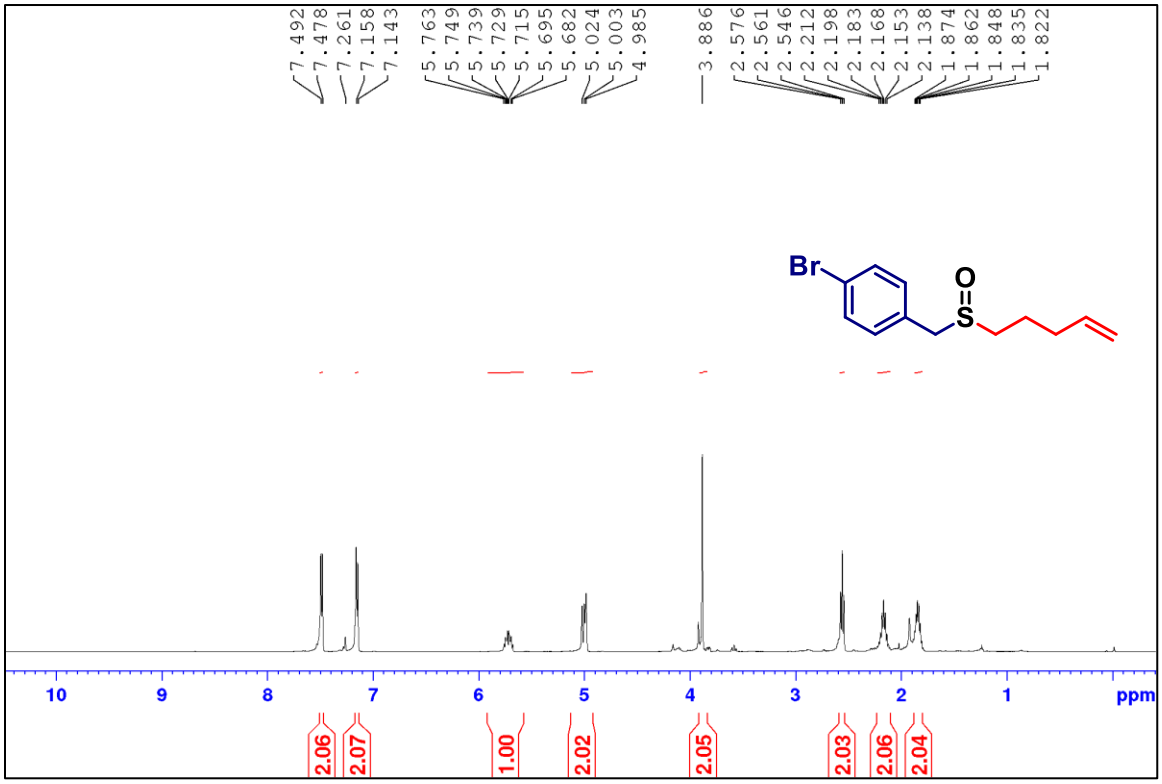


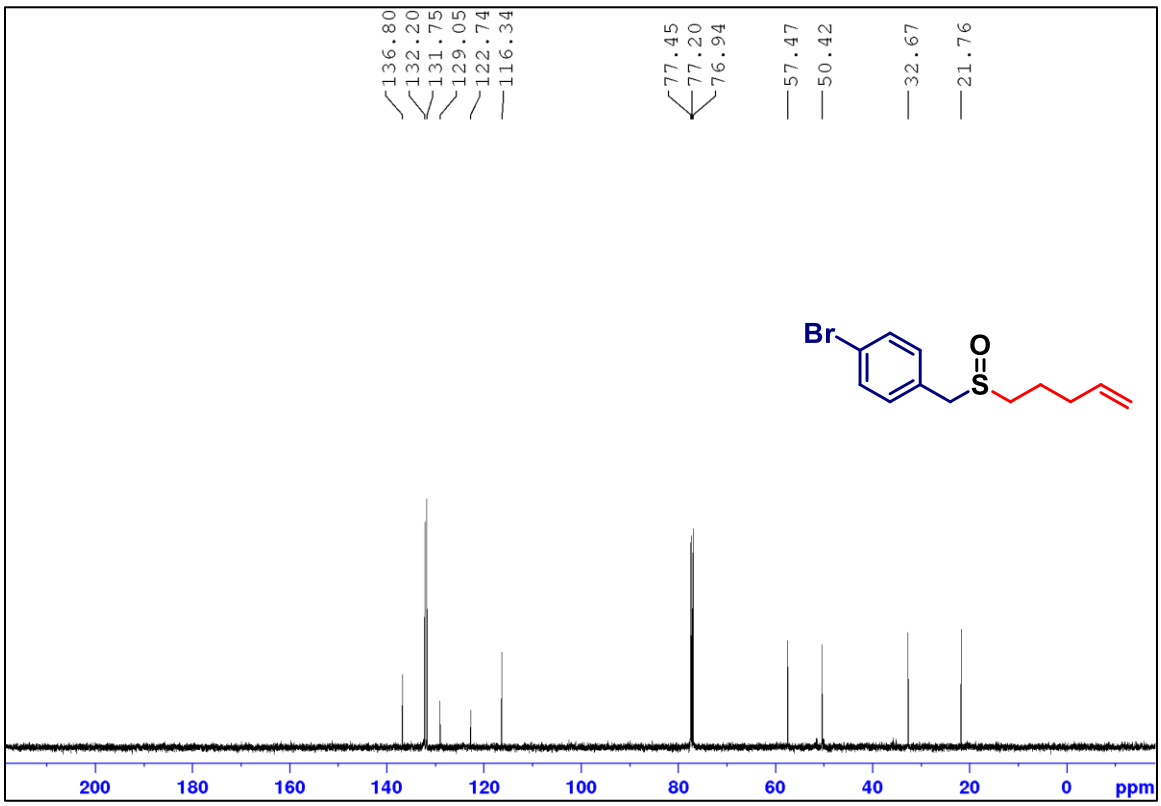
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 30 in $CDCl_3$



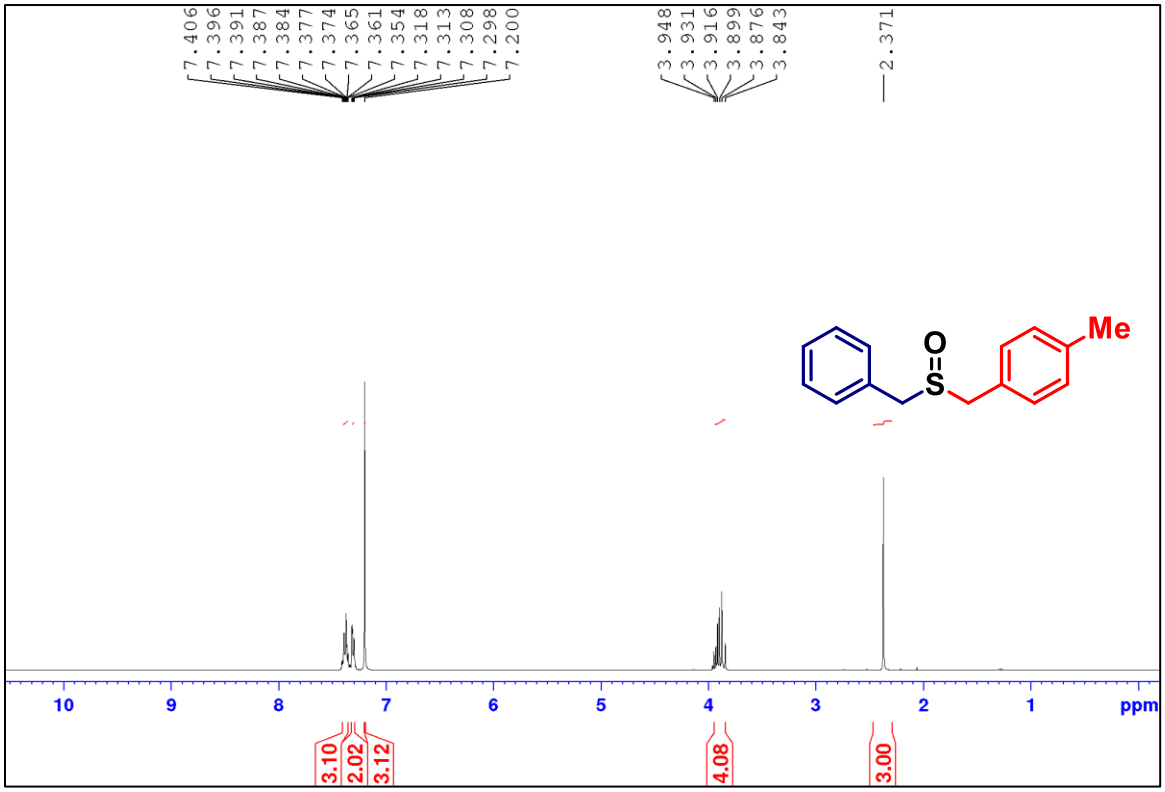


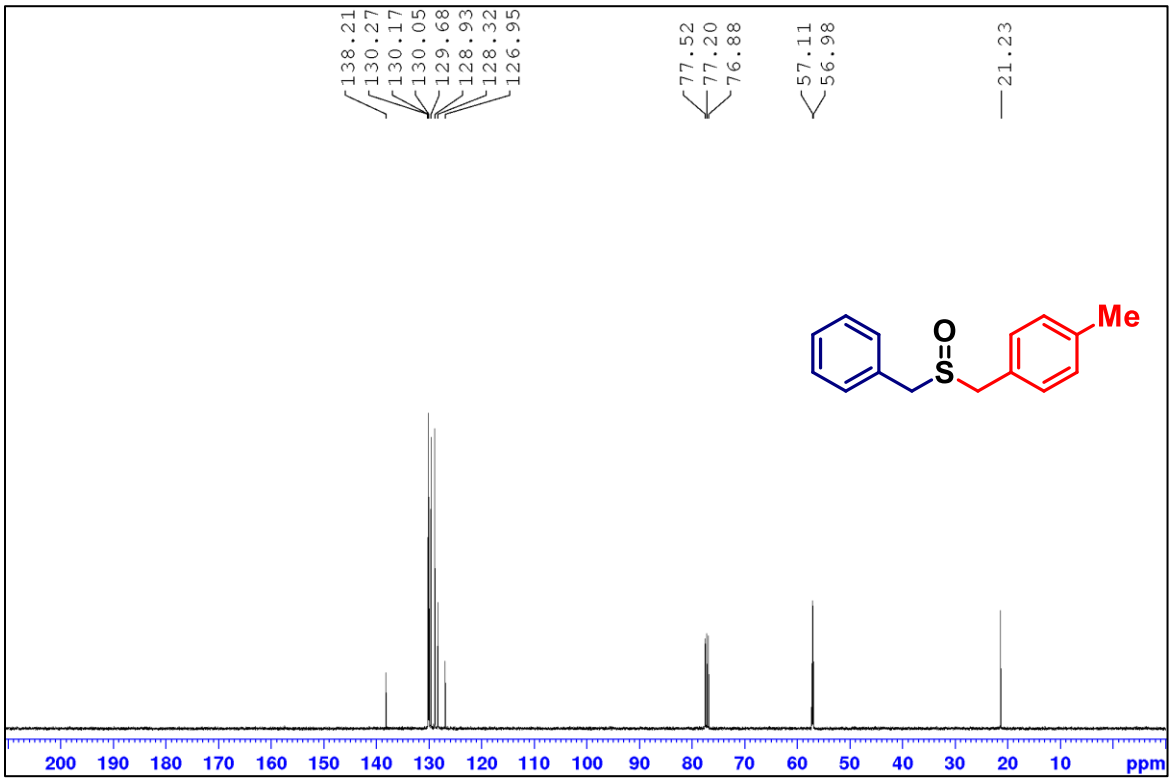
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 31 in $CDCl_3$



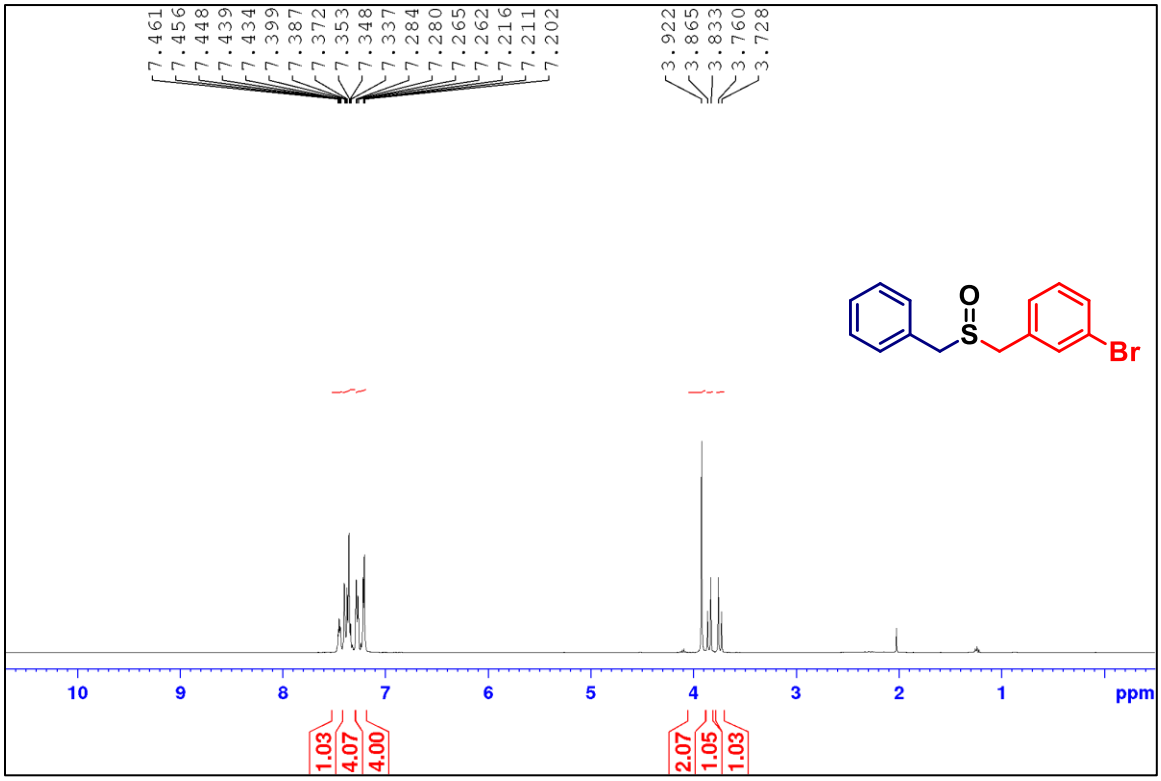


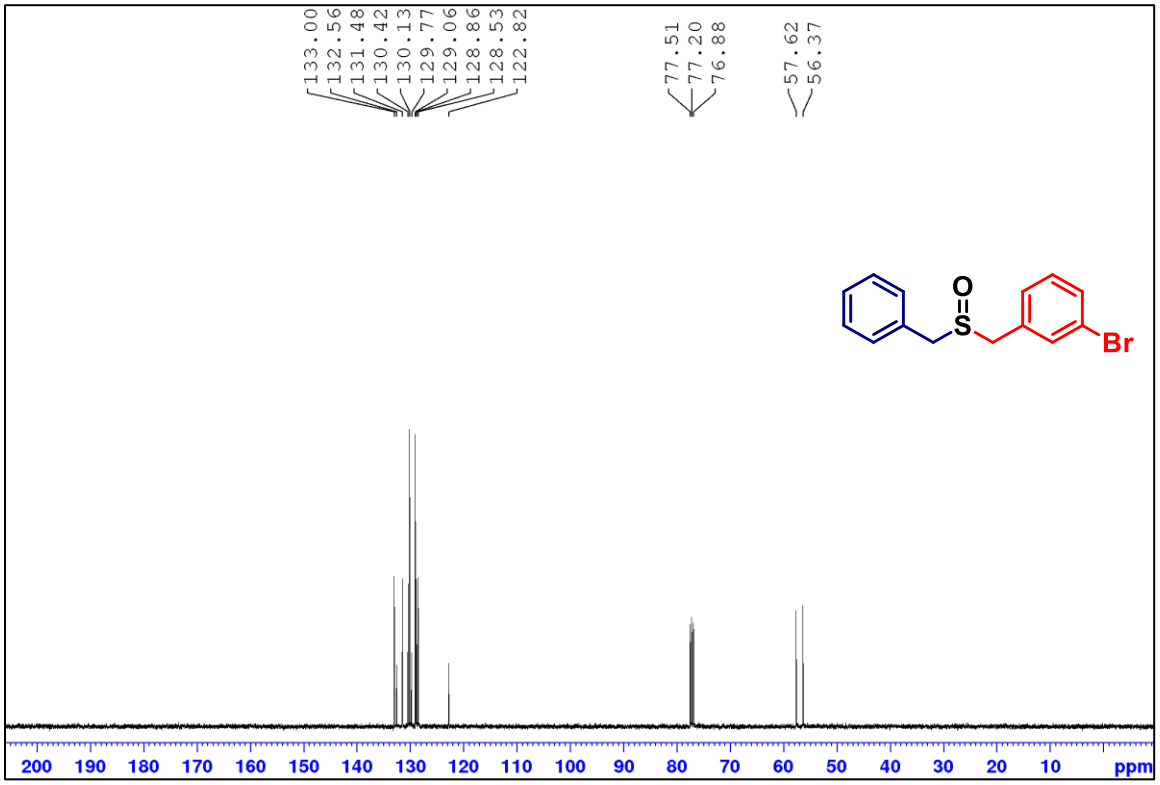
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 32a in $CDCl_3$



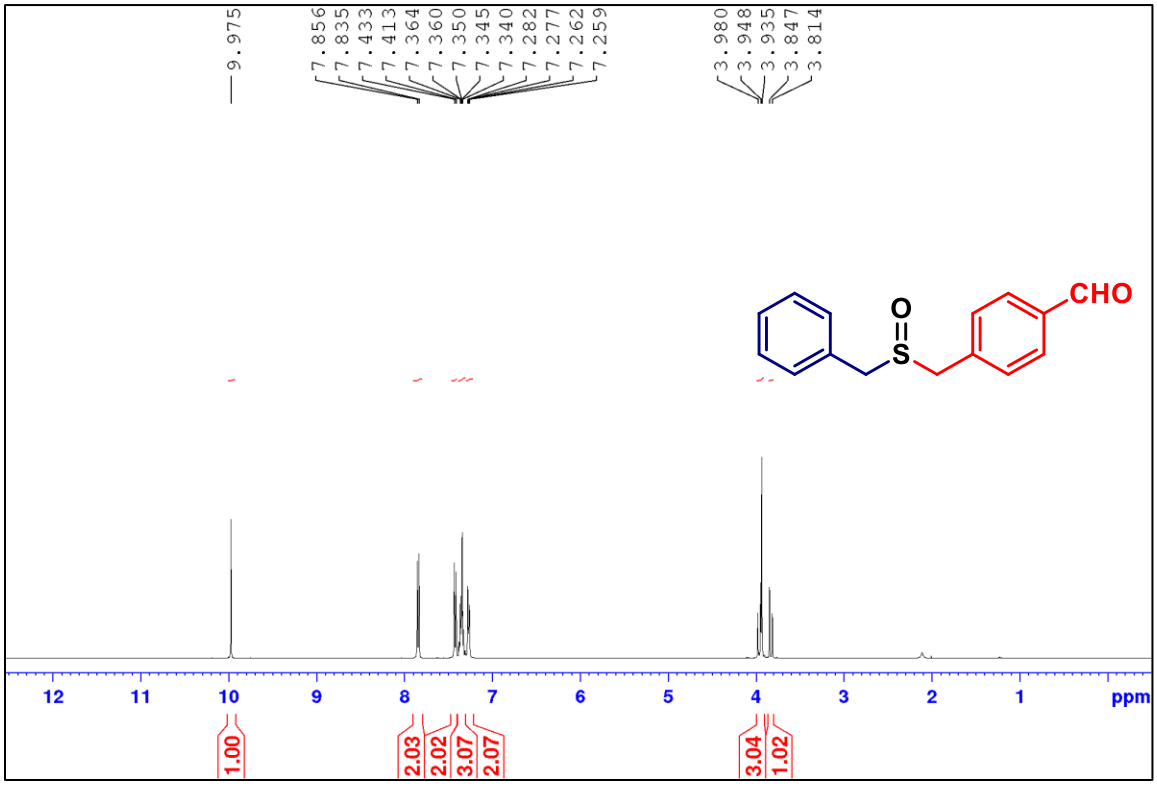


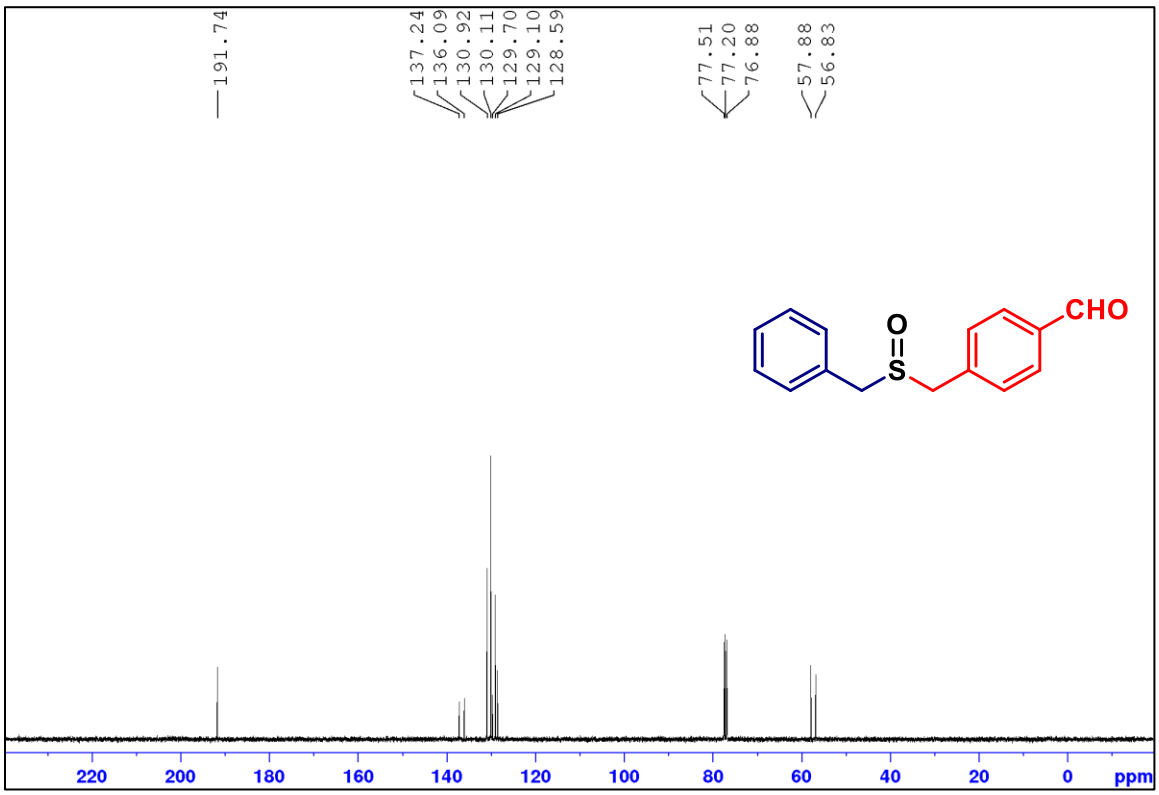
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 32b in $CDCl_3$



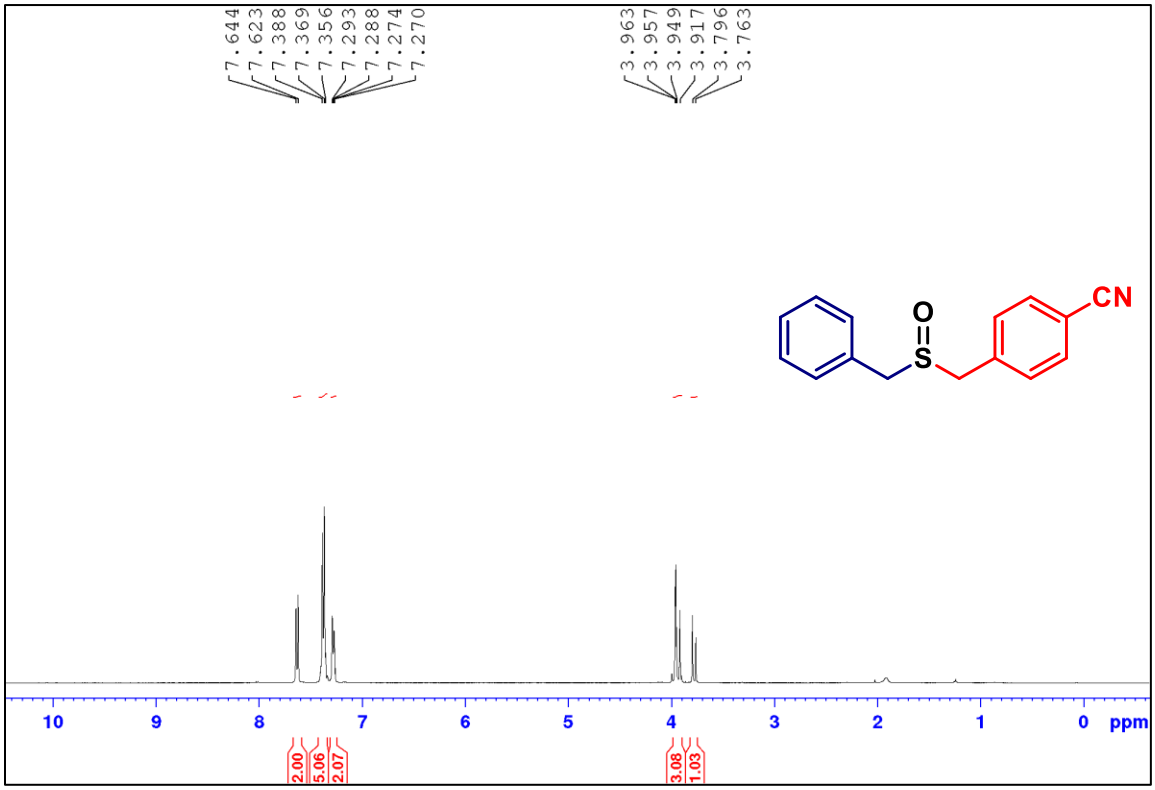


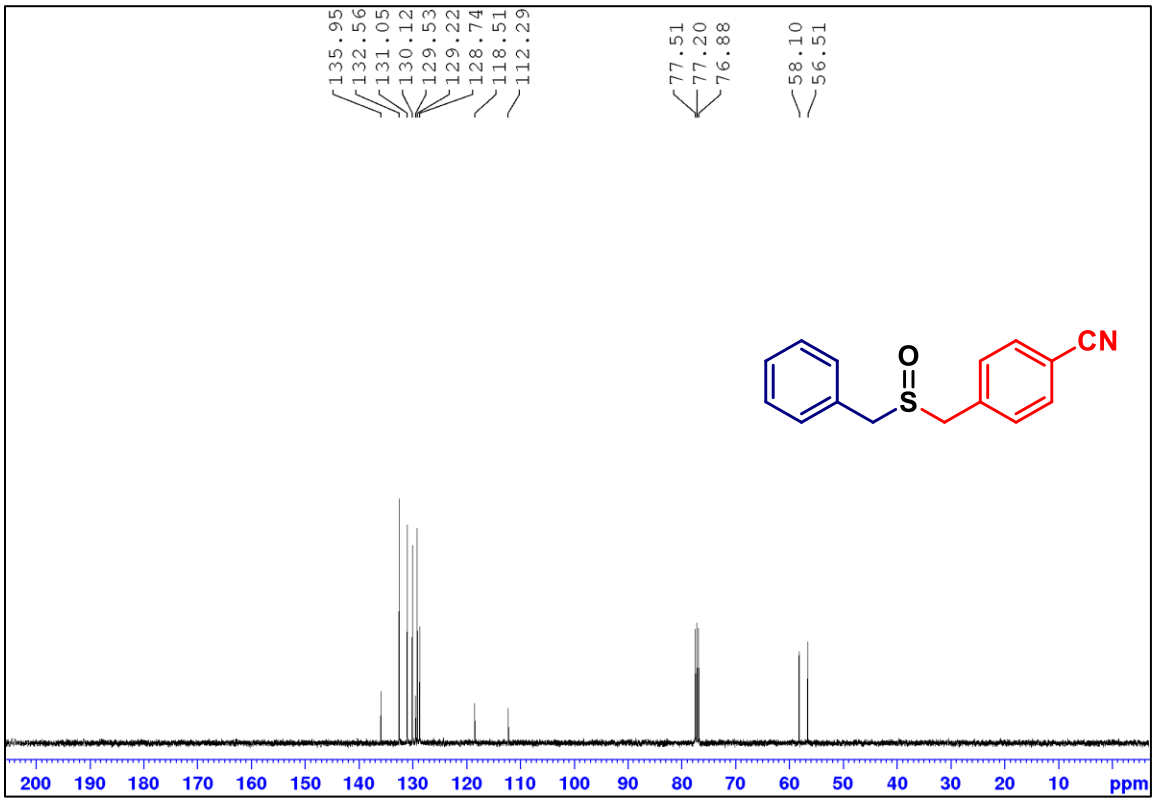
^{1}H NMR (400 MHz) and ^{13}C NMR (100MHz) of 32c in $CDCl_3$



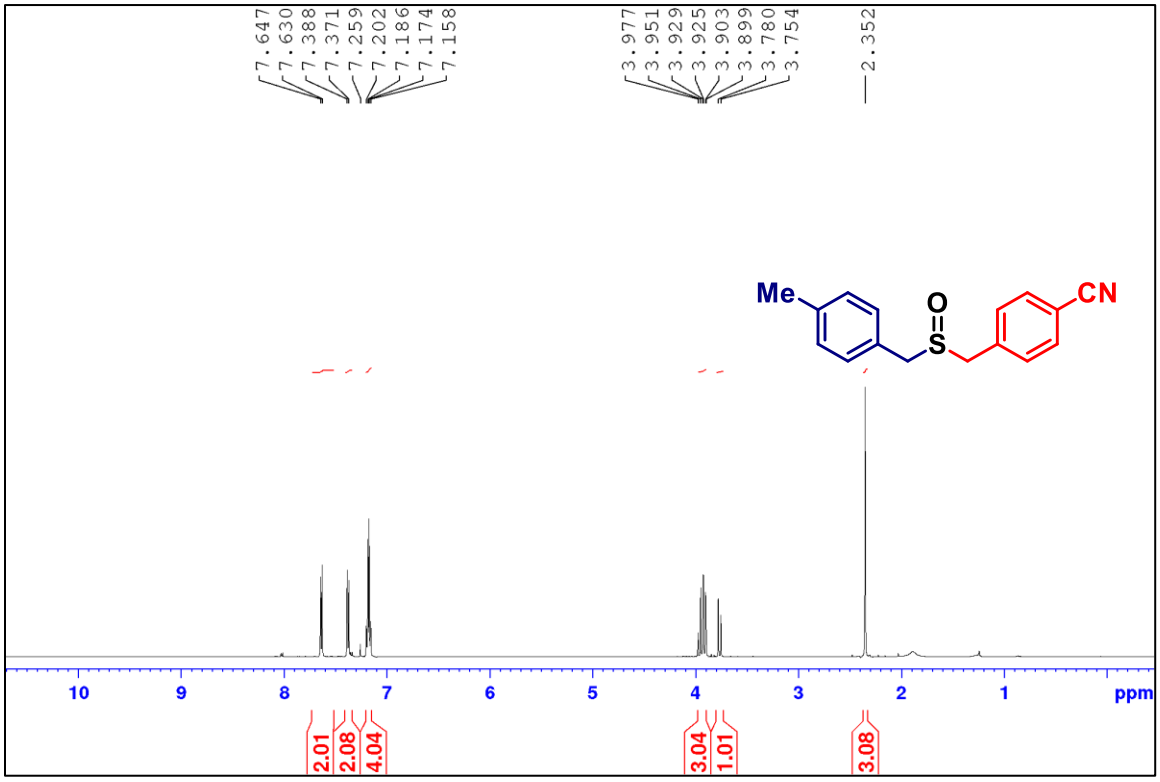


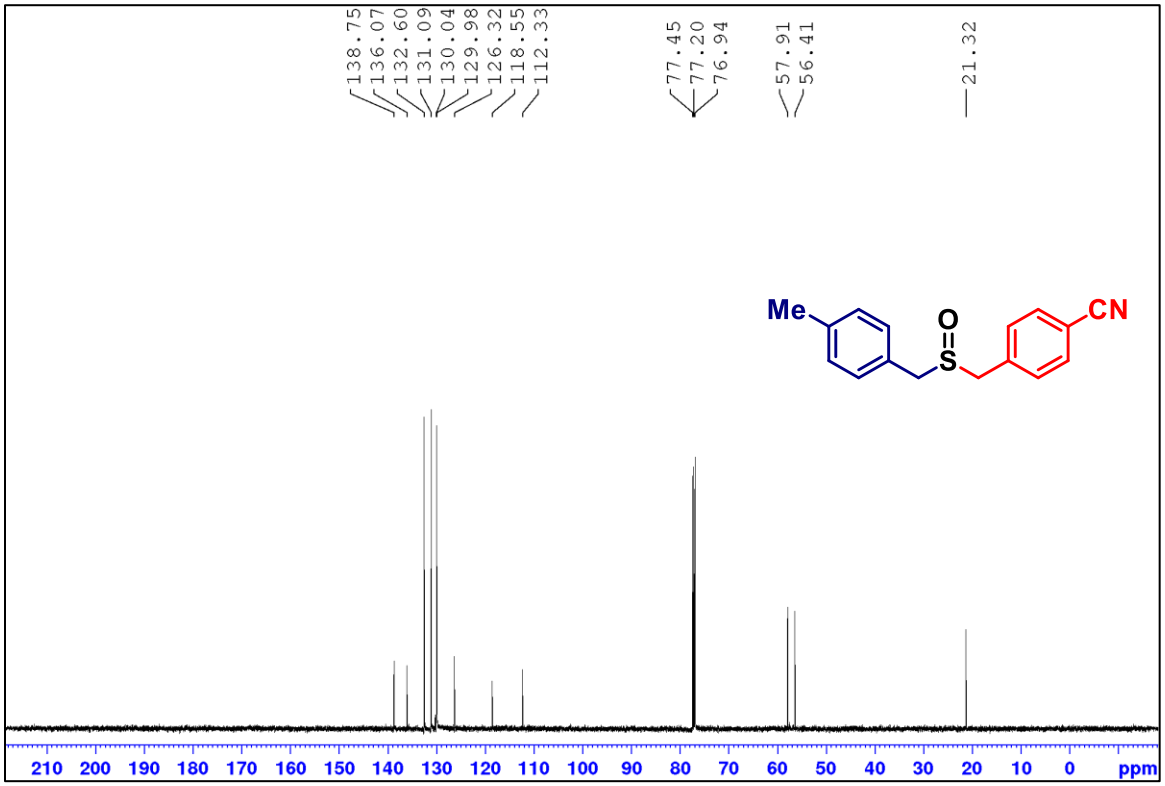
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 32d in $CDCl_3$



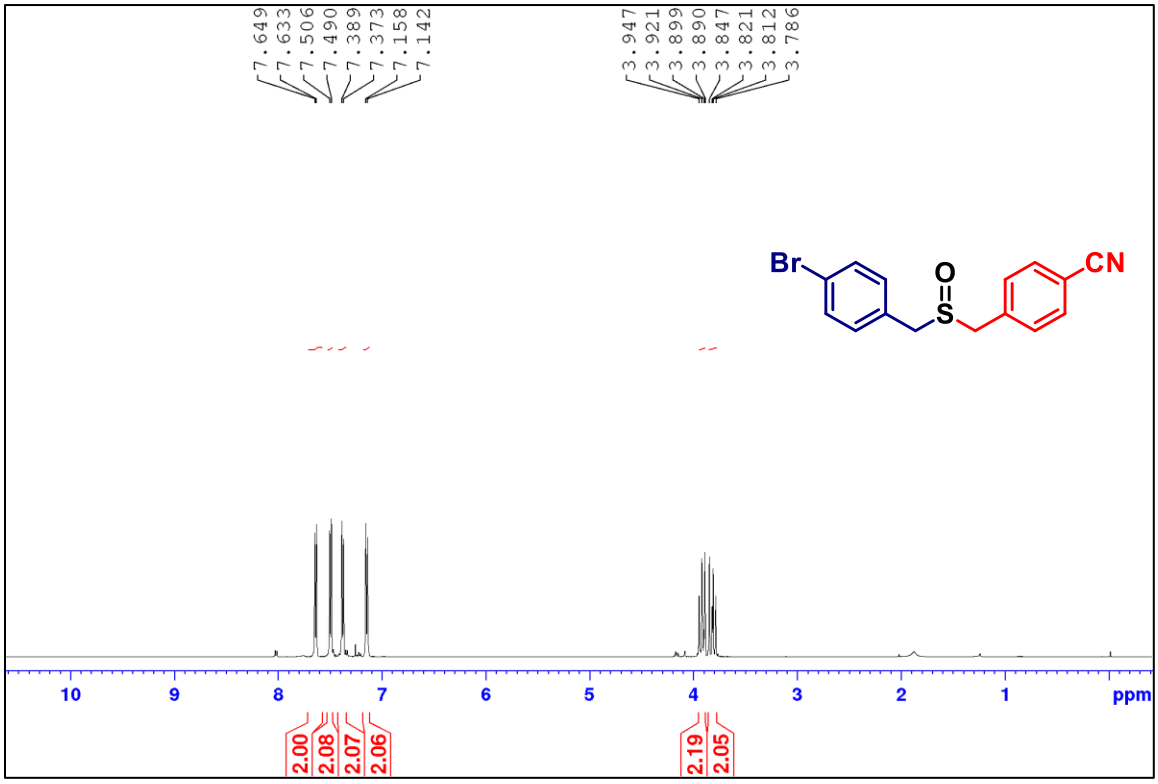


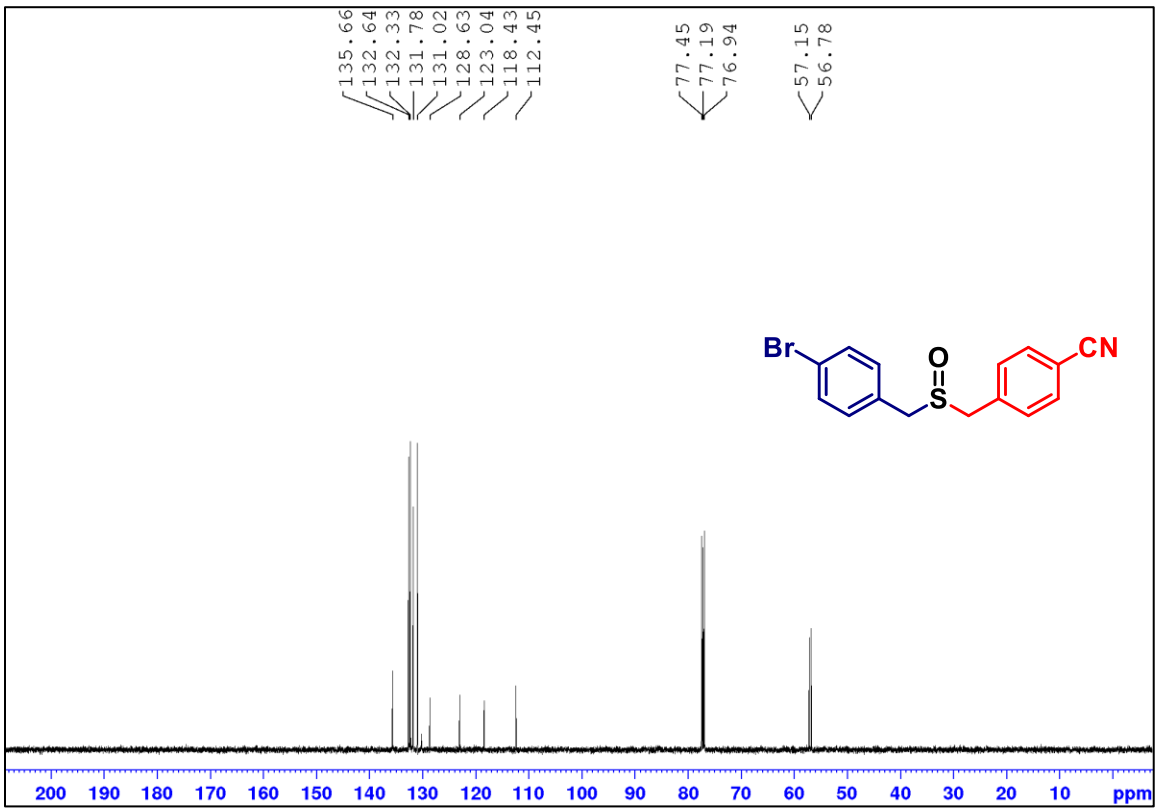
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 33a in $CDCl_3$



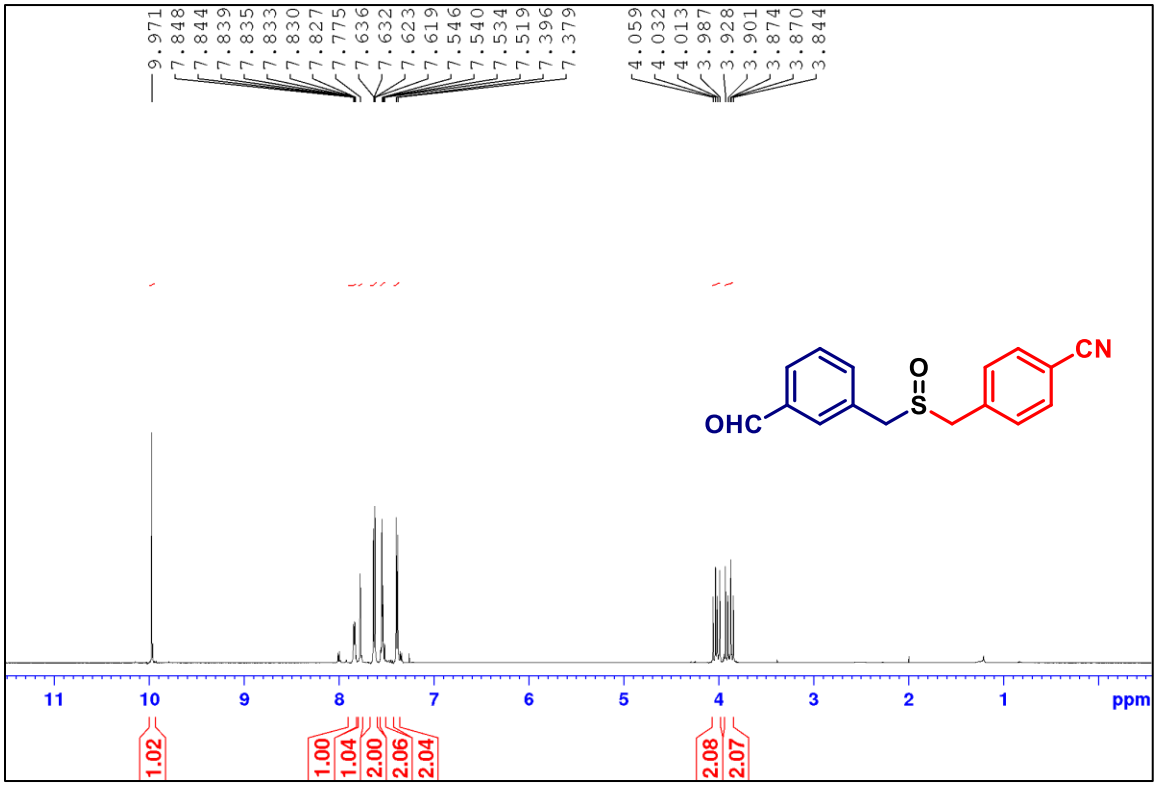


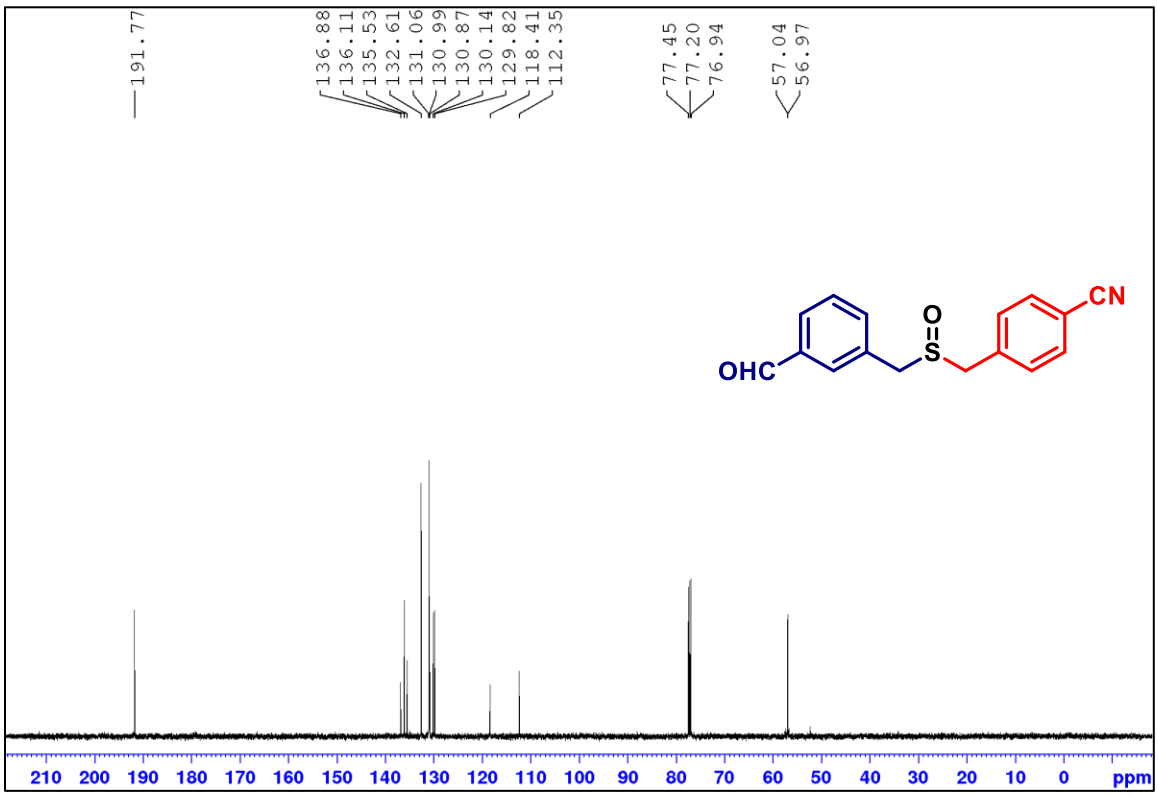
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 33b in $CDCl_3$



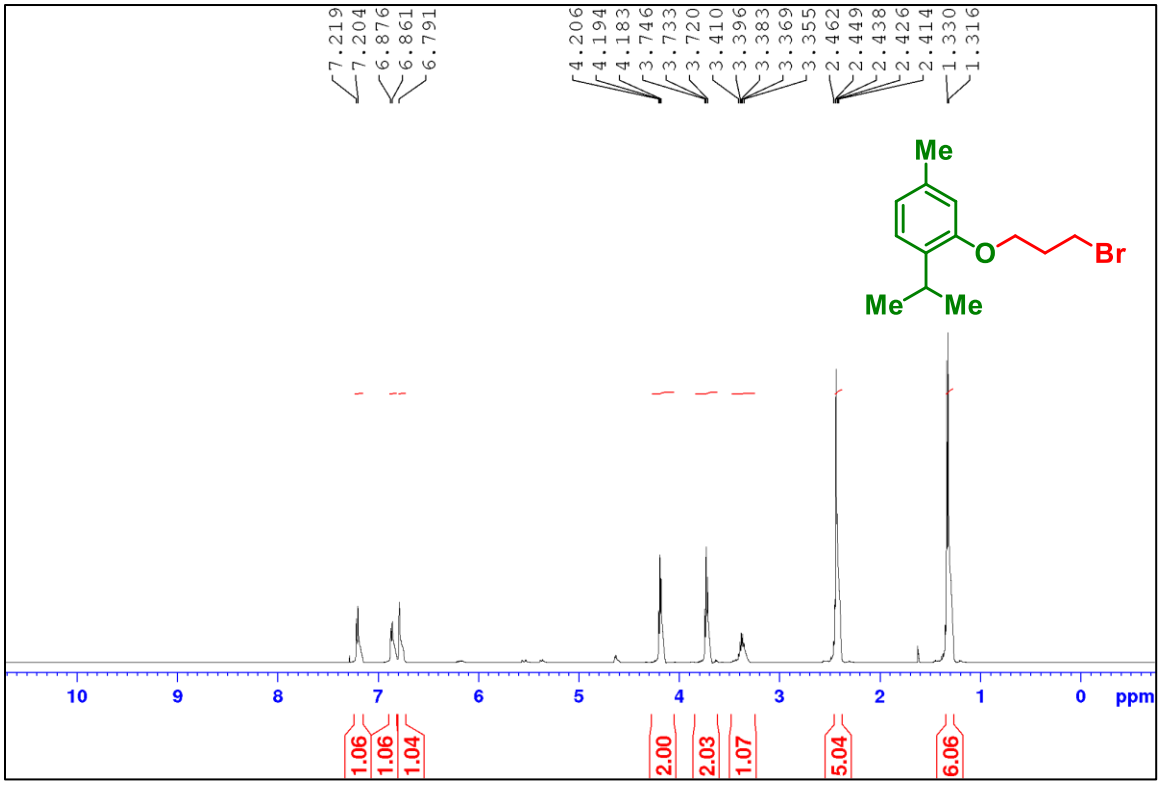


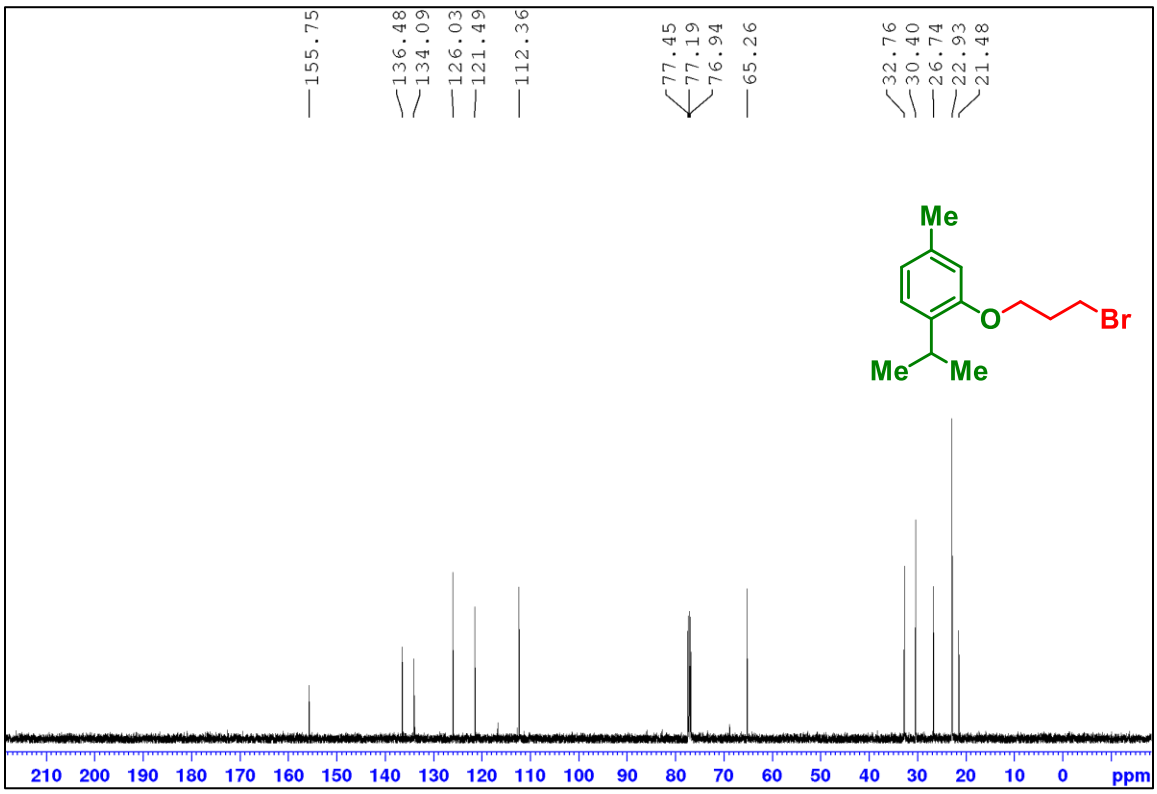
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 33c in $CDCl_3$



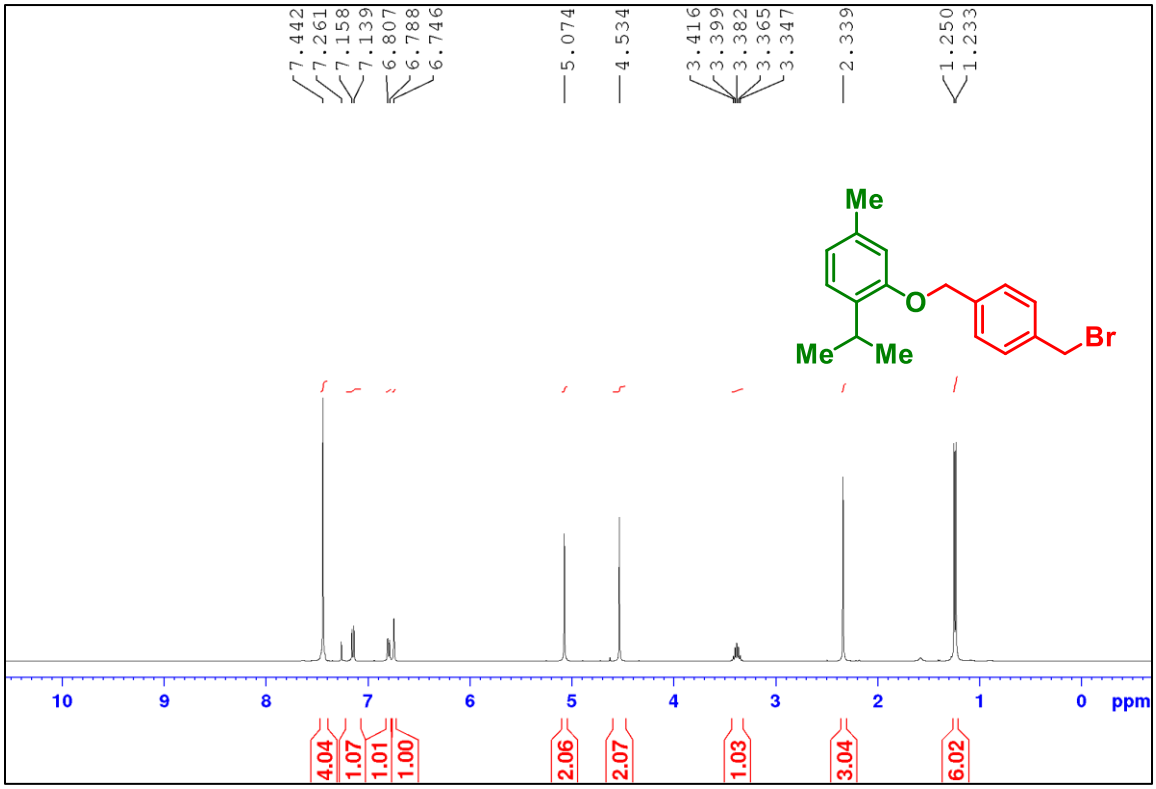


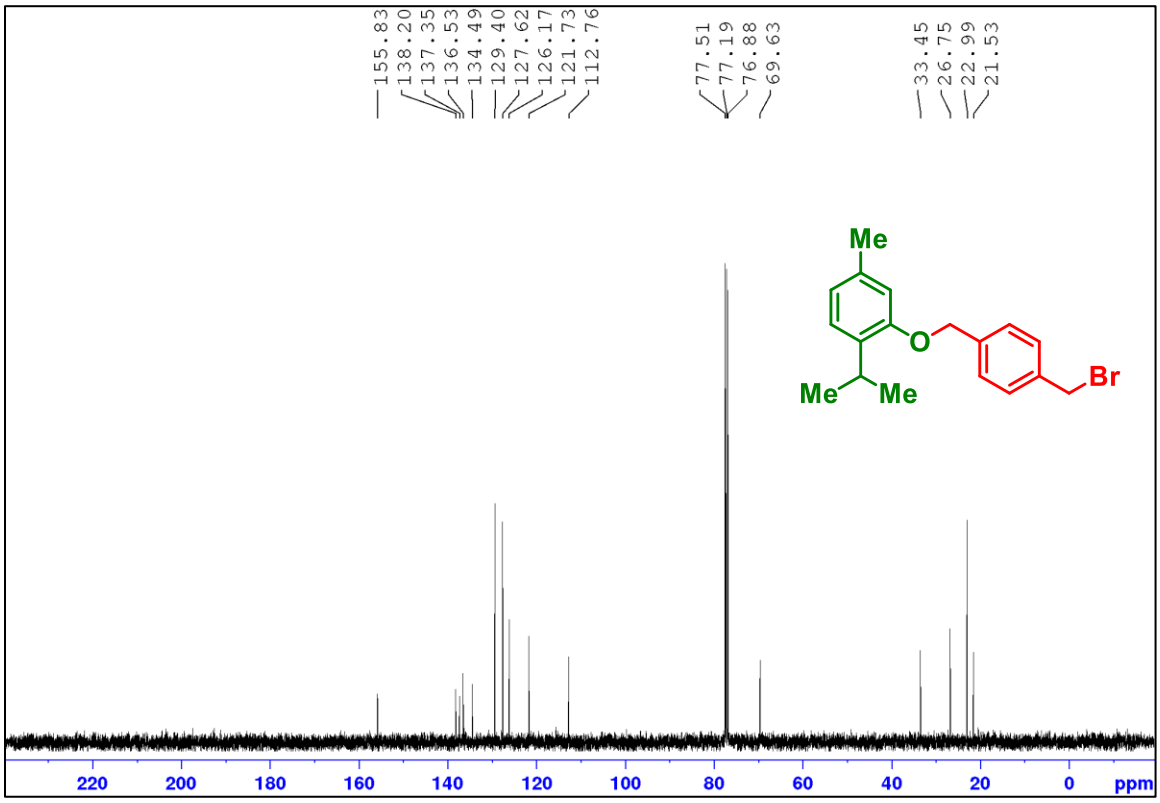
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of S3a in $CDCl_3$



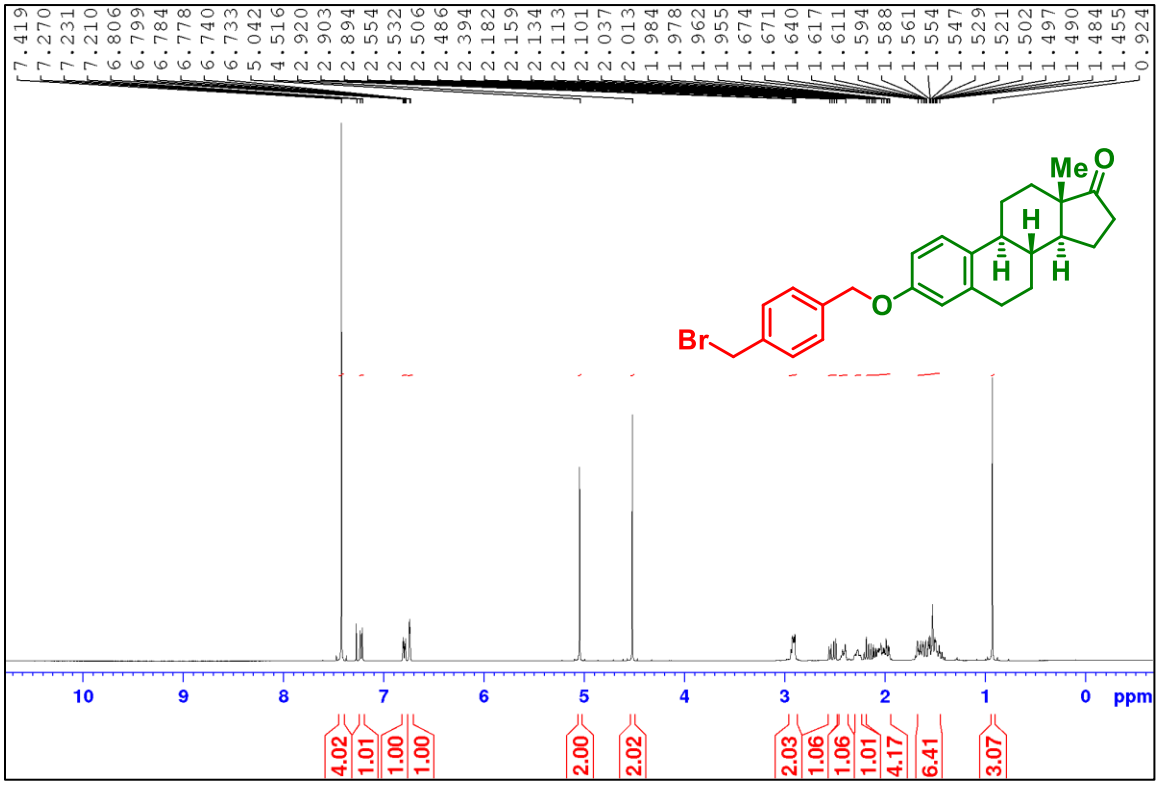


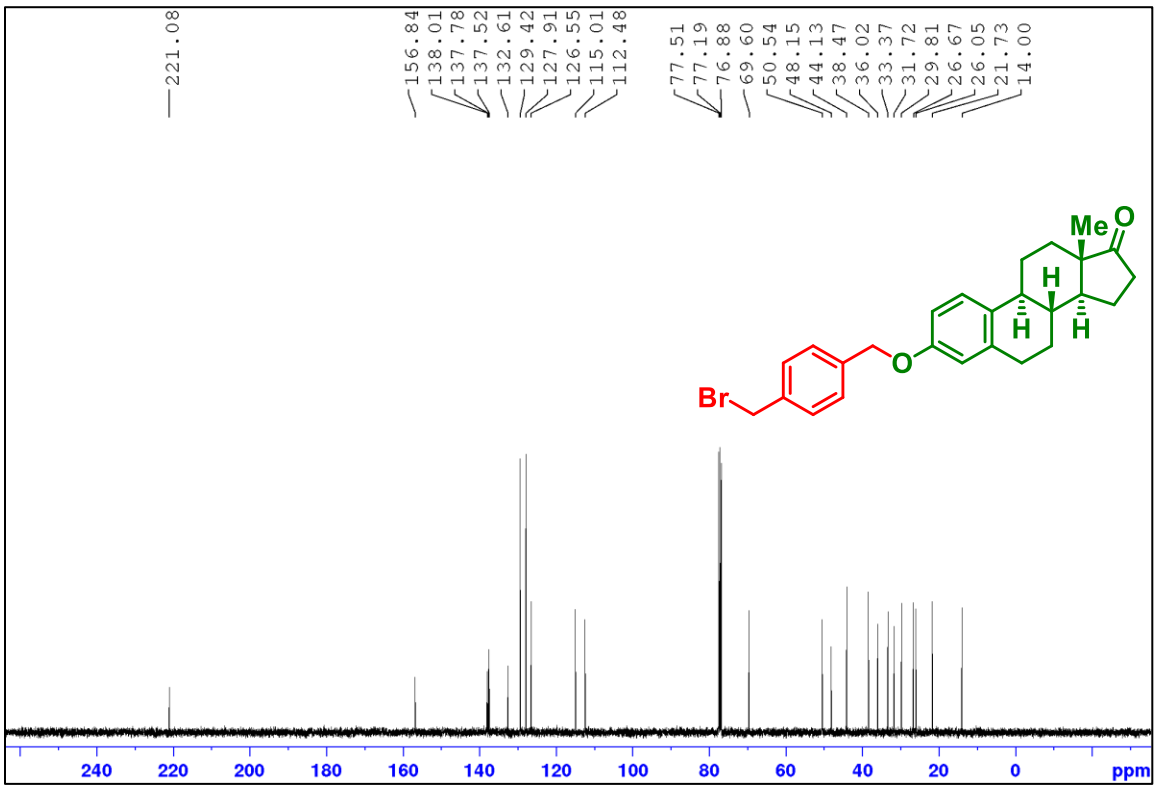
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of S3c in $CDCl_3$



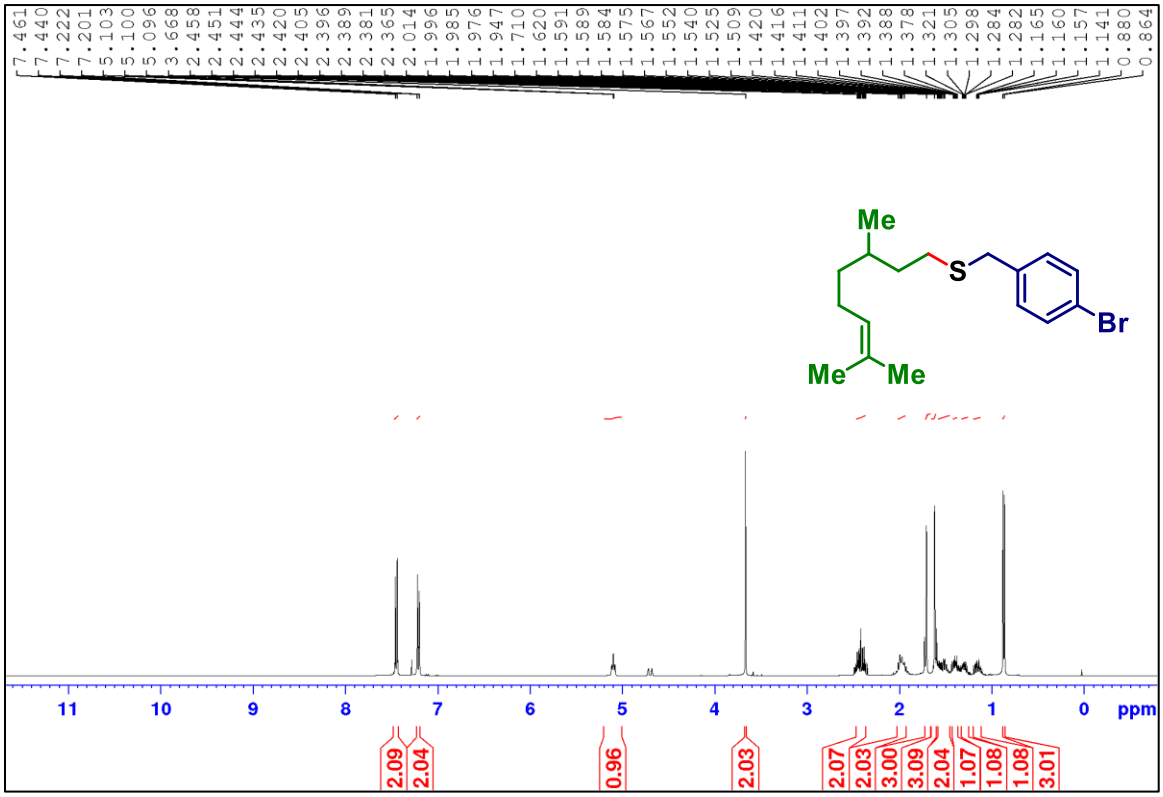


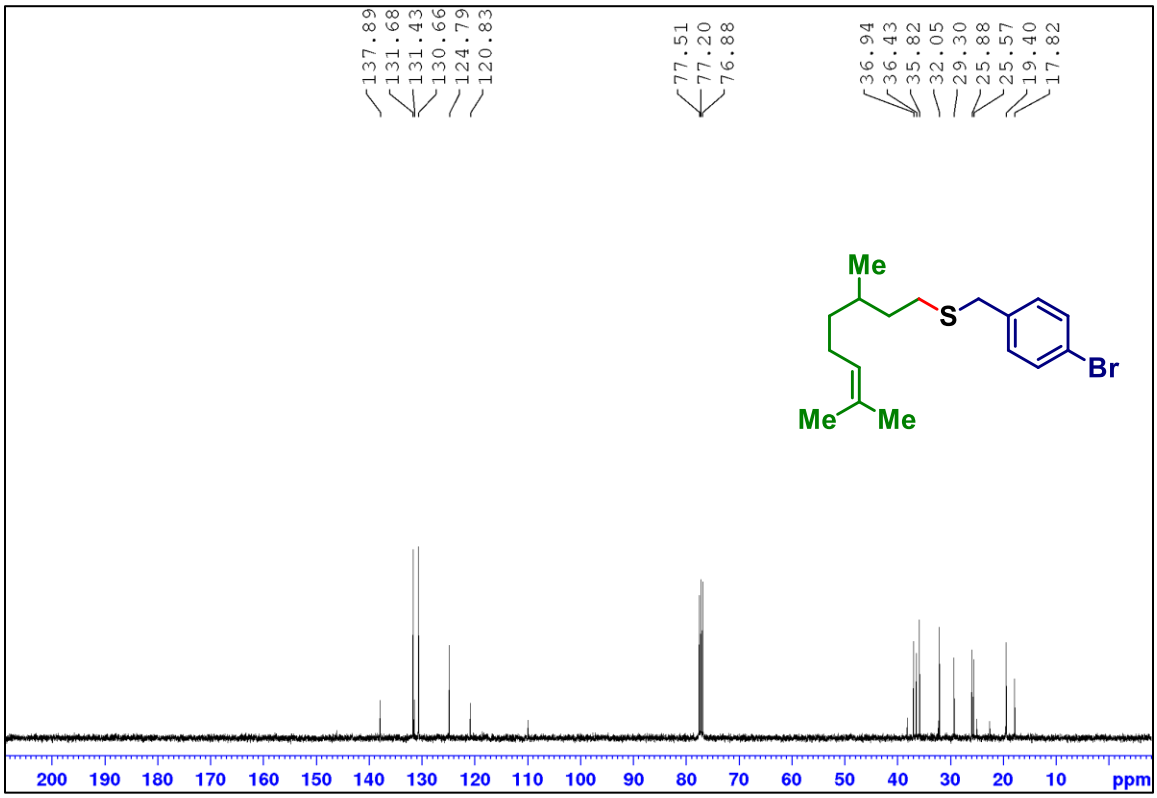
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of S3d in $CDCl_3$



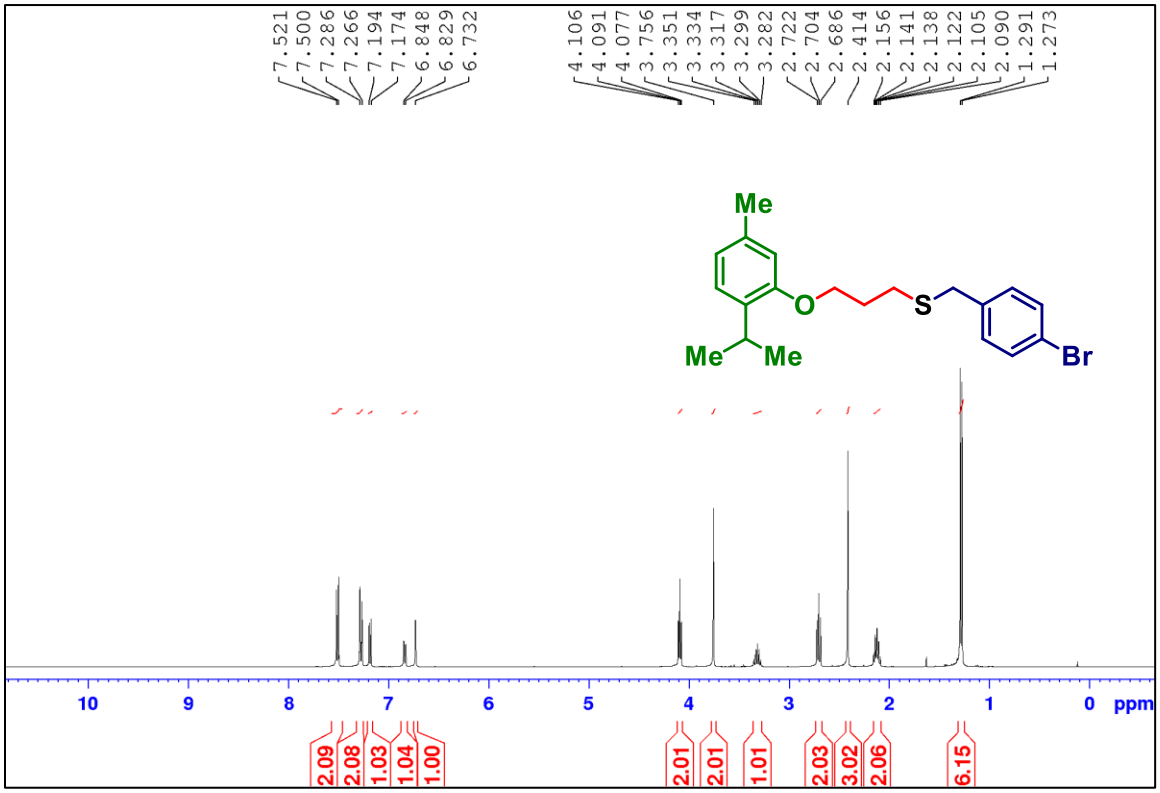


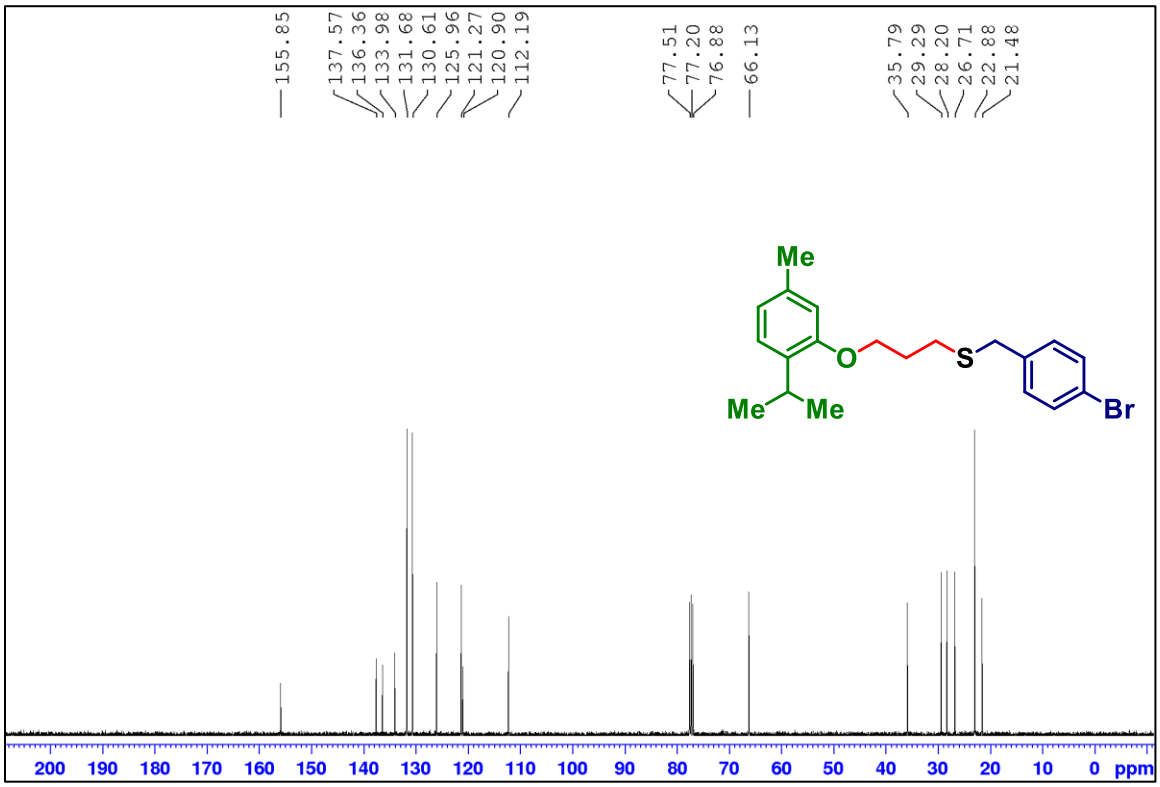
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 34a in $CDCl_3$



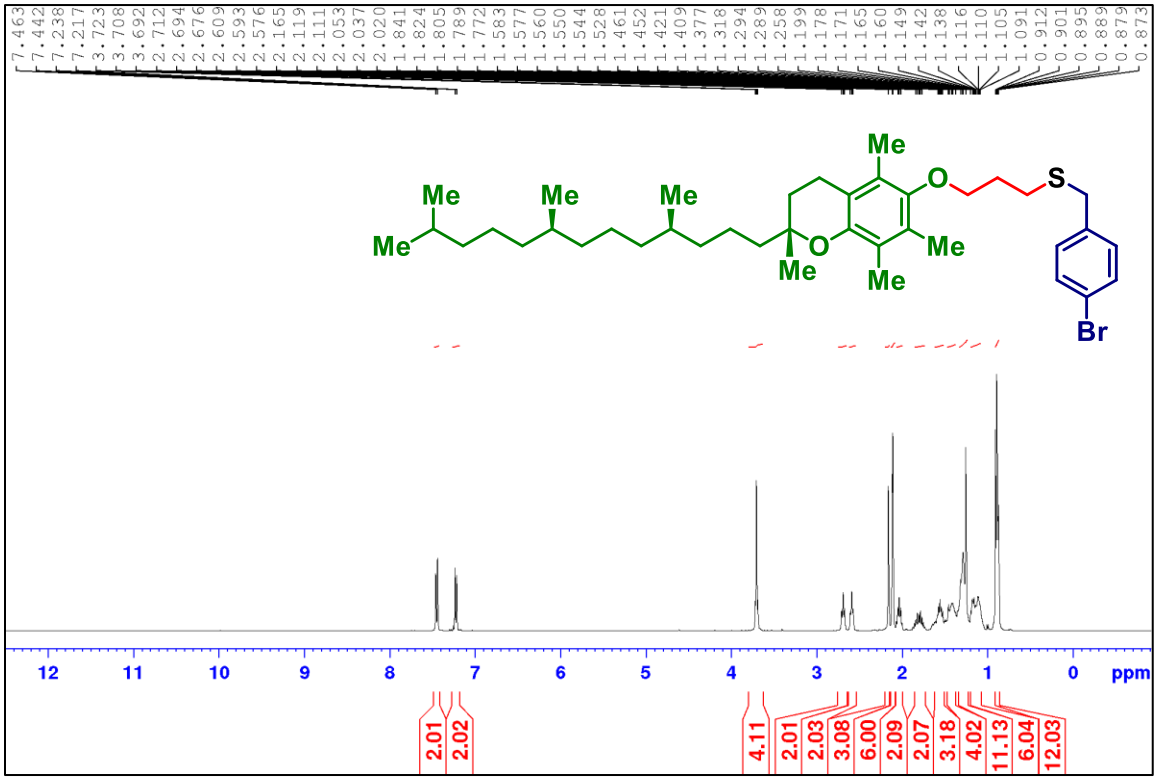


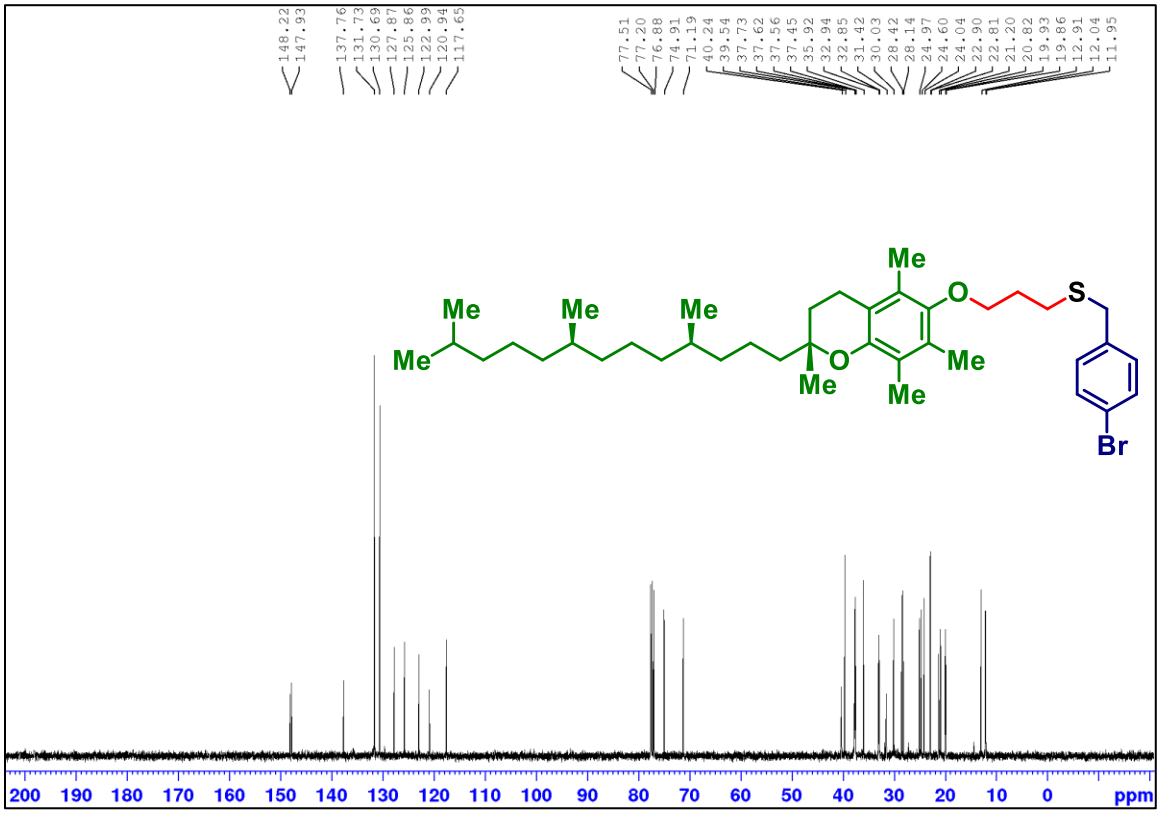
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 34b in $CDCl_3$



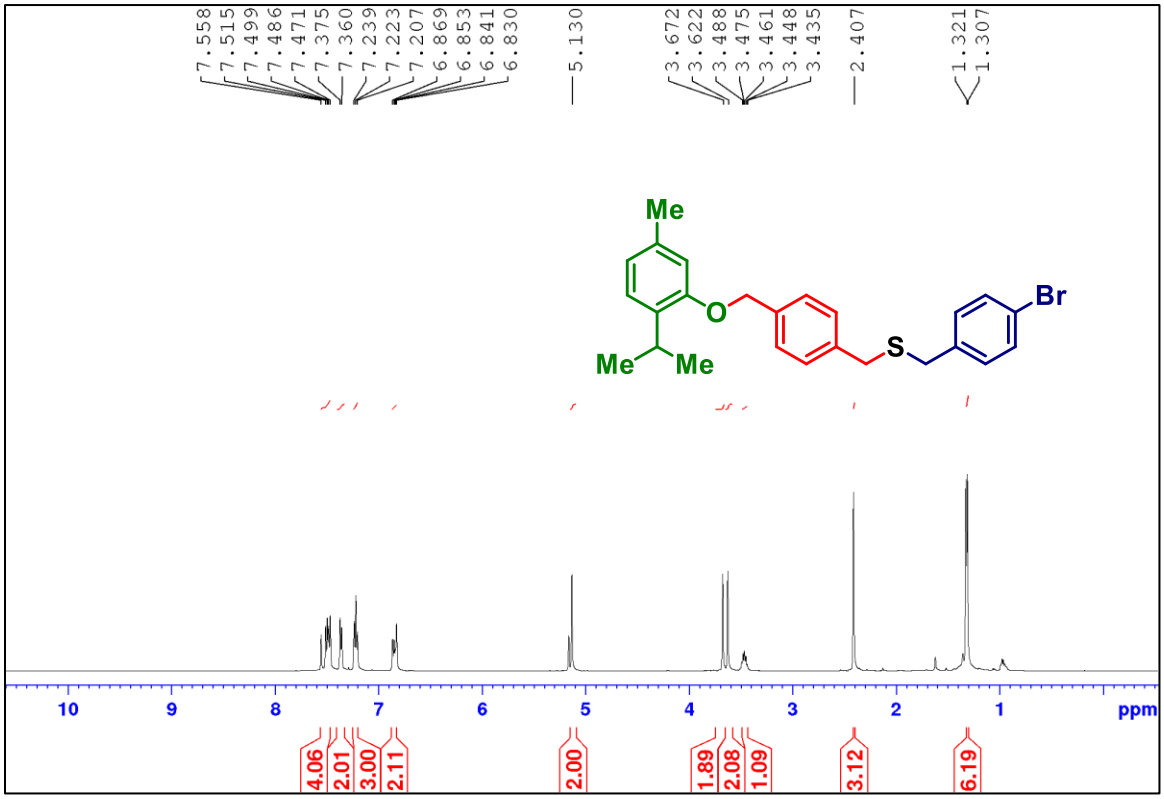


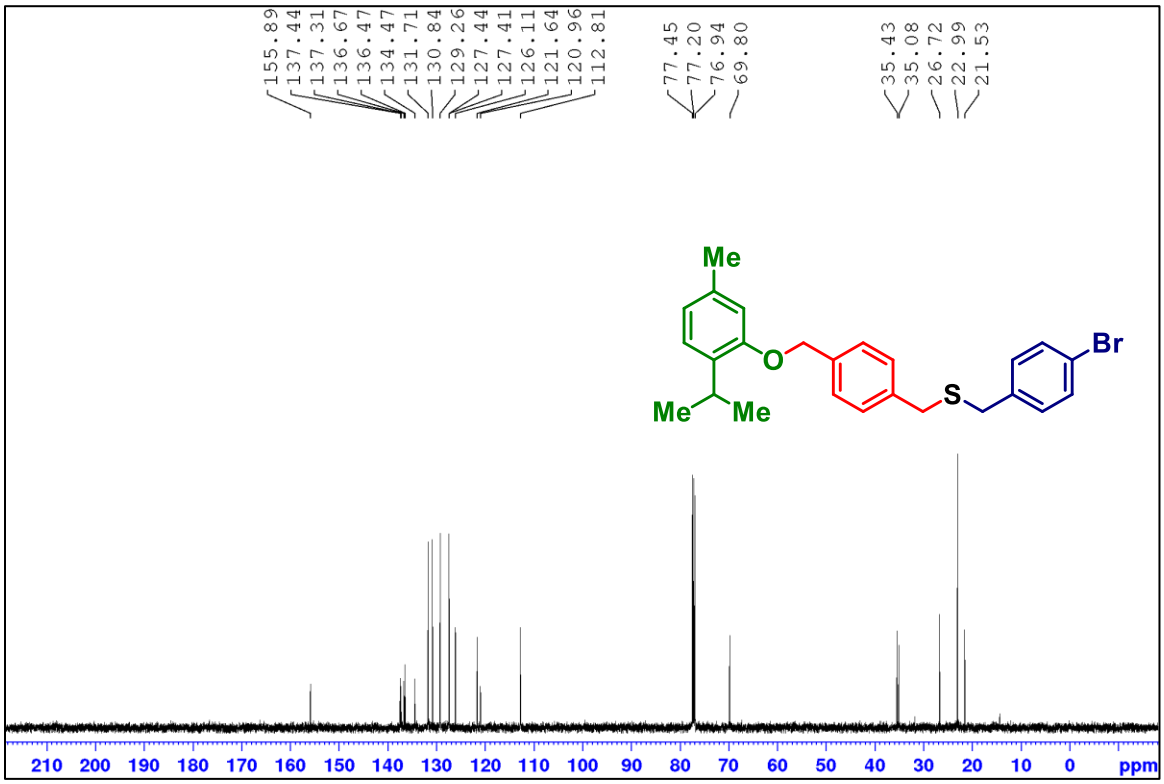
^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 34c in $CDCl_3$





^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) of 34d in $CDCl_3$





^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) of 34e in $CDCl_3$