Electronic Supplementary Information

Visible Light-Driven Photocatalytic Thiol-ene/yne Reactions using Anisotropic 1D Bi_2S_3 Nanorods: A Green Synthetic Approach

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Section 1: FTIR and Energy-dispersive X-rays (EDX) analysis and elemental mapping:

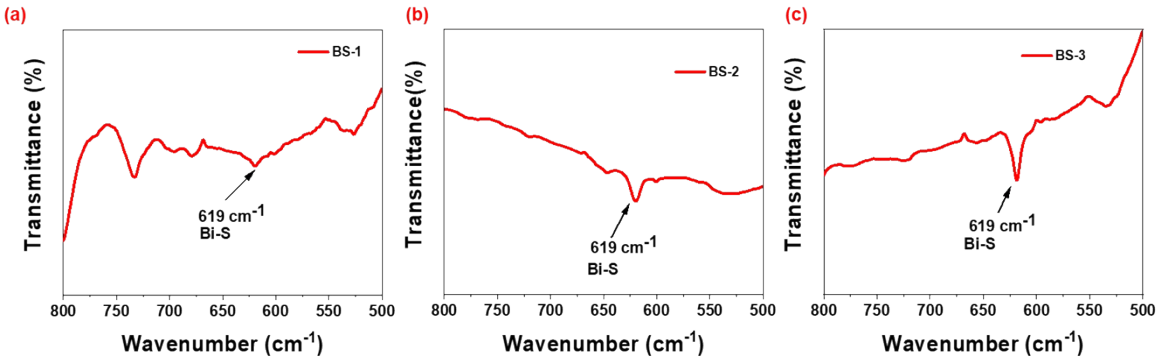
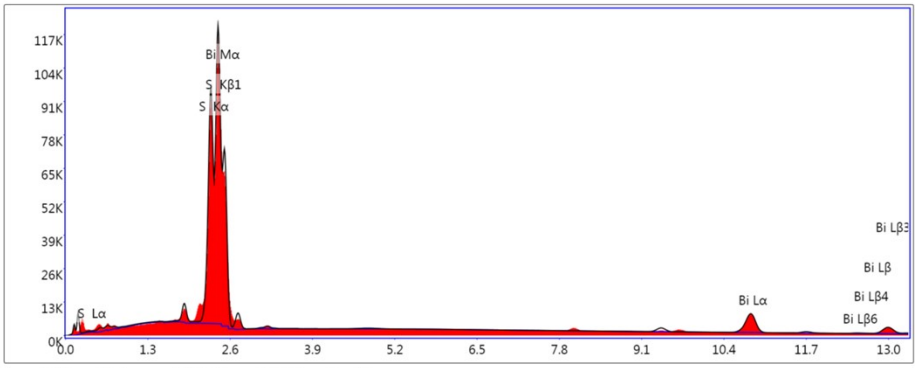


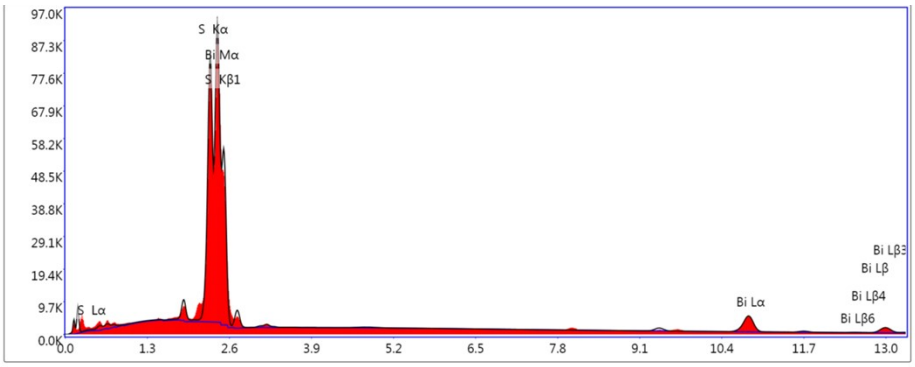
Fig. S1 Enlarged FTIR spectra of (a) BS-1, (b) BS-2, and (c) BS-3 in the range 500-800 cm^{-1}.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Error %
S K	21.25	63.76	3.48
BiM	78.75	36.24	1.30

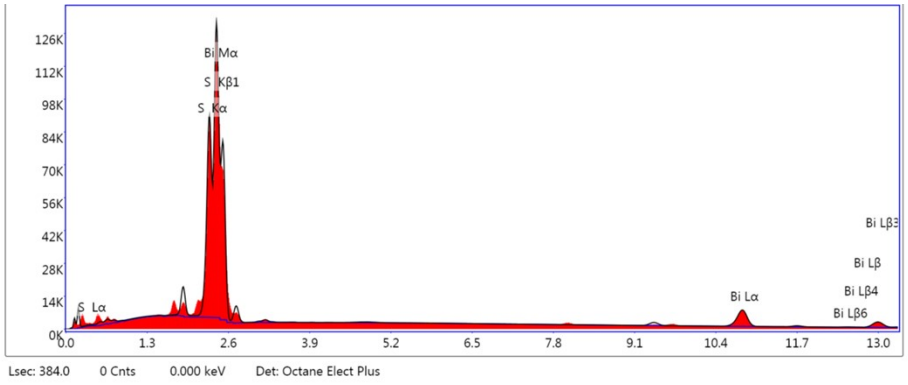
Fig. S2 EDX of BS-1.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Error %
S K	23.27	66.40	3.42
BiM	76.73	33.60	1.33

Fig. S3 EDX of BS-2.



eZAF Smart Quant Results

Element	Weight %	Atomic %	Error %
S K	19.04	60.51	3.54
BiM	80.96	39.49	1.27

Fig. S4 EDX of BS-3.

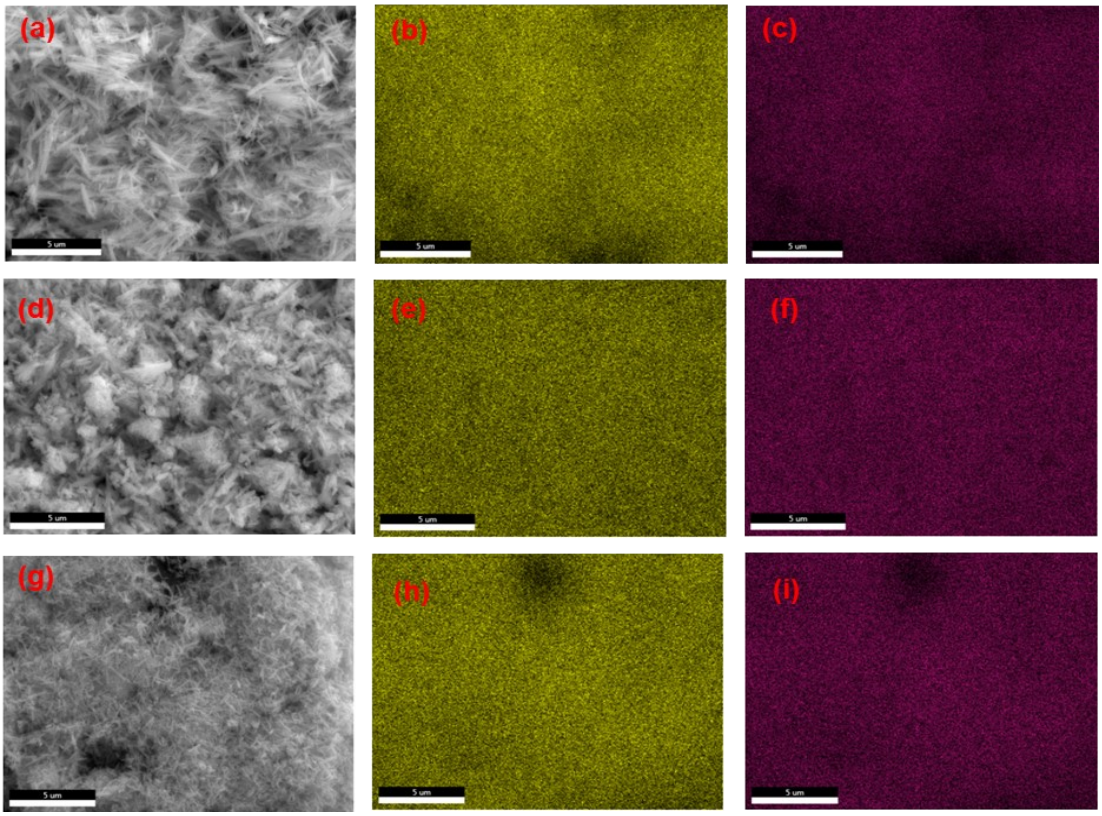


Fig. S5 EDX elemental mapping (a), (b), (c) of BS-1; (d), (e), (f) of BS-2; and (g), (h), (i) of BS-3.

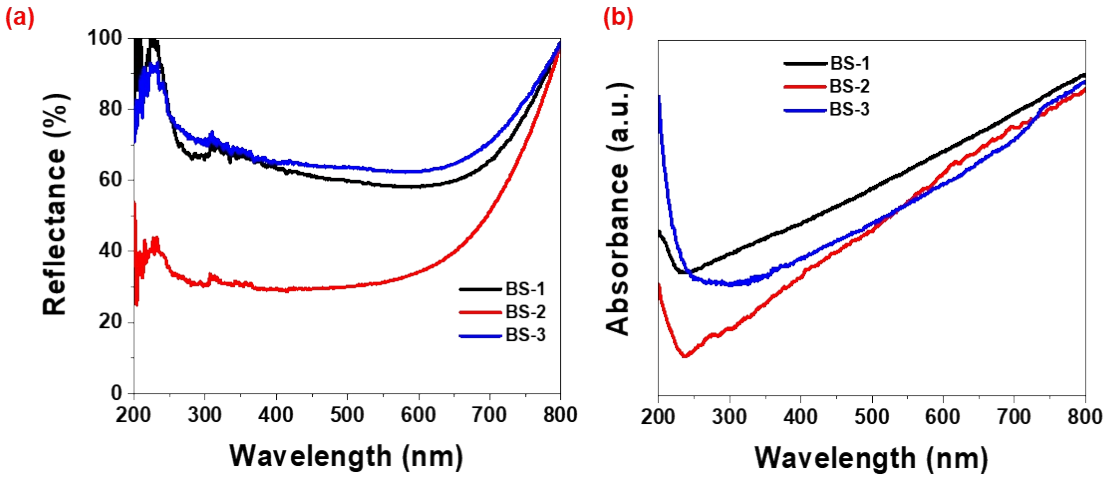


Fig. S6 (a) UV-Vis DRS spectra and (b) UV-Vis absorption spectra of BS-1, BS-2, and BS-3.

Section 2: ^{1}H NMR spectrum of the product of the model reaction:

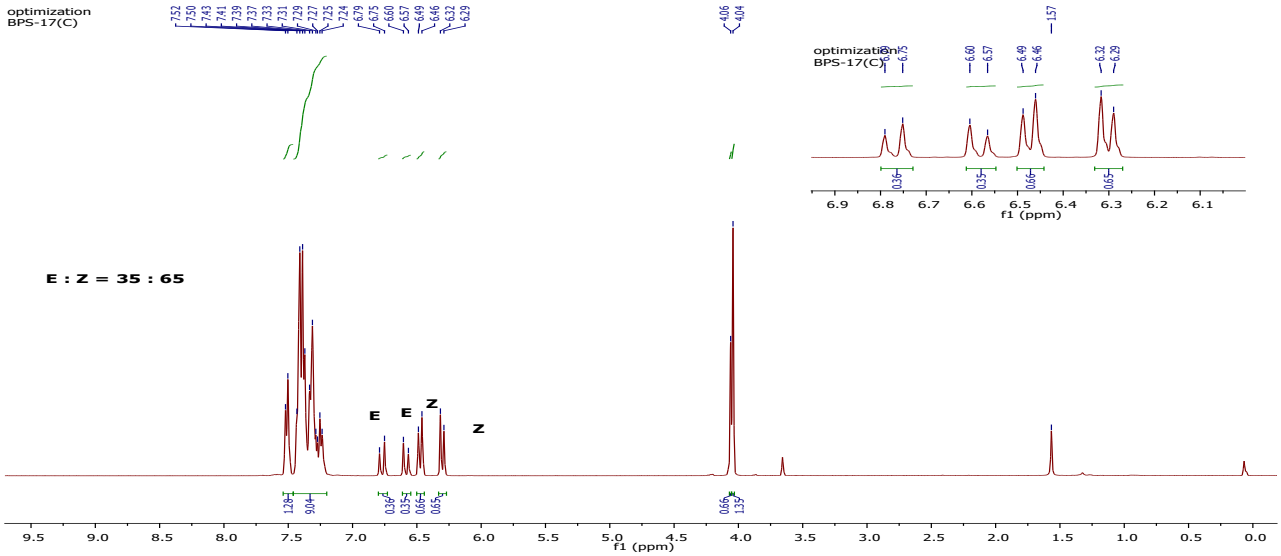
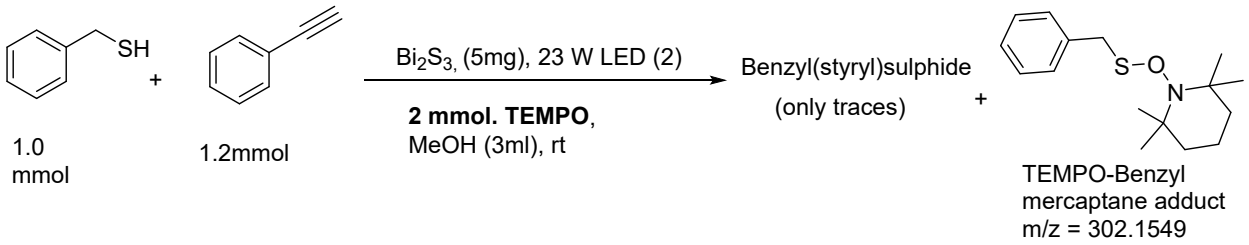


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2a)**.

Section 3: Reaction scheme for trapping thiyl free radical and characterization of the trapped products:

(a)



(b)

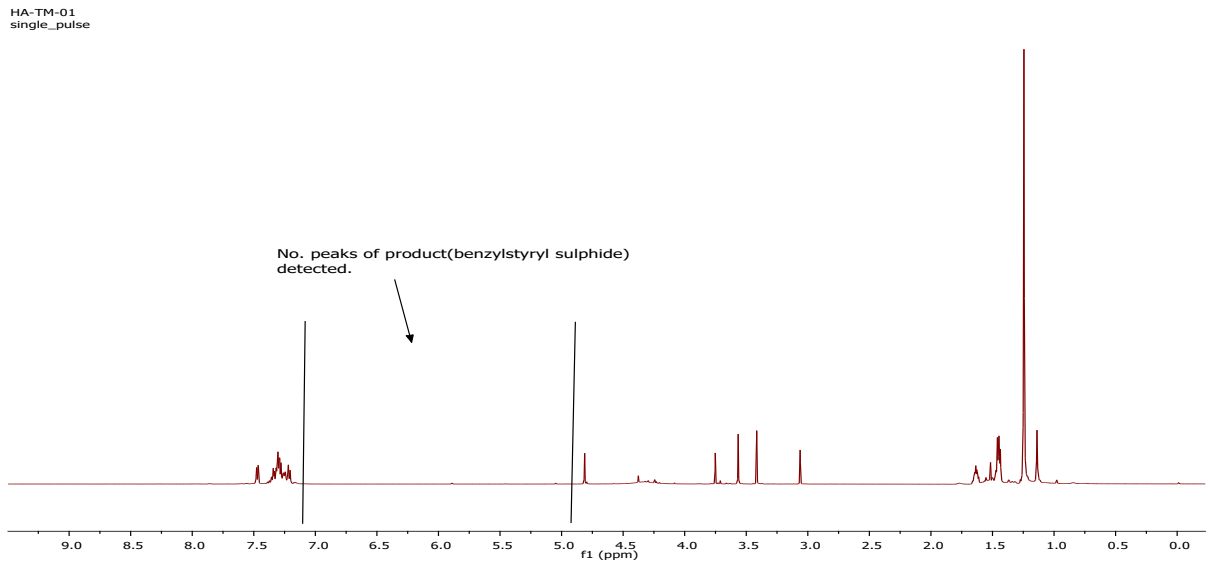


Fig. S8 (a) Reaction scheme for hydrothiolation of alkyne in the presence of TEMPO**, (b)** ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the product derived from 1D Bi_2S_3 photocatalyzed hydrothiolation in the presence of TEMPO.

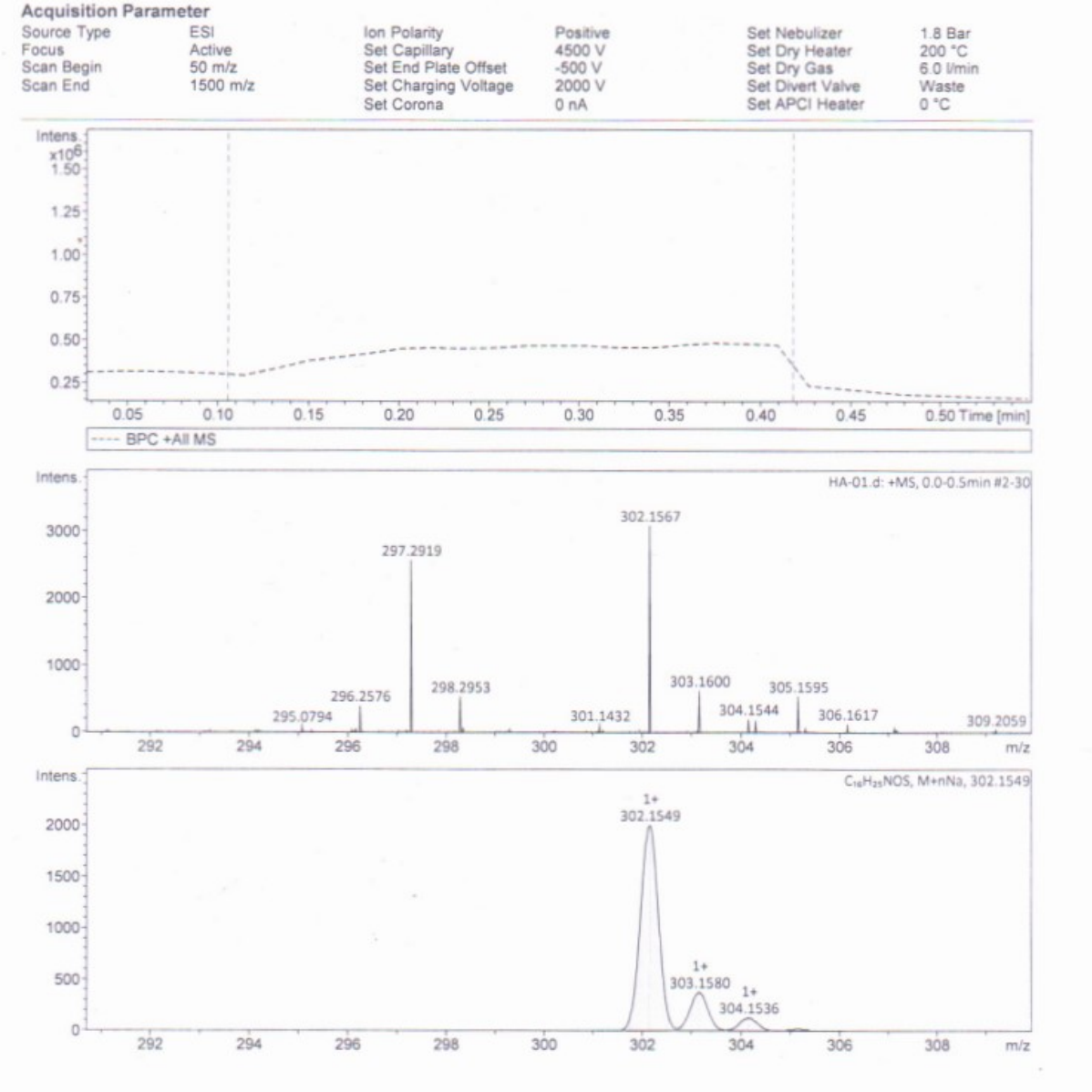


Fig. S9 ESI-MS spectrum of thiol adduct. Calculated for [**M+nNa**]: 302.1549; Found: 302.1567.

Section 4: Characterization of products of thiol-yne reaction performed in deuterated methanol:

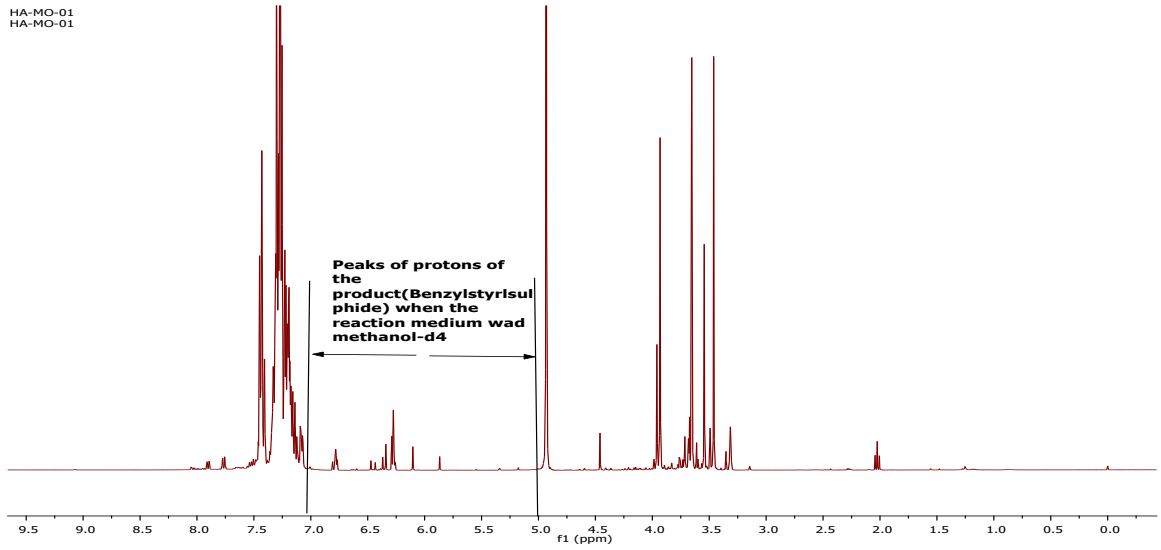


Fig. S10 ^{1}H NMR (400 MHz, CD_3OD) spectrum of 1D Bi_2S_3 photocatalyzed hydrothiolation in deuterated methanol.

Section 5: Comparison of different photocatalysts utilized in thio-ene/yne reactions:

Table S1: Aspect ratio of BS-1, BS-2, and BS-3

	BS-1	**BS-2**	**BS-3**
The number of Bi_2S_3 nanorods measured	40	40	40
Average length (nm)	318.4	142.6	137.6
Average width (nm)	21.2	27.8	29.3
Aspect ratio (length/width)	~15	5.1	4.7

Table S2. Comparison of different photocatalysts for thiol-ene/yne reactions.

Catalyst	Solvent	Light source	Yield (%)	Reference
Bi_2S_3	**MeOH**	**White light**	**92**	**This work**
$ZnIn_2S_4$	MeOH	Visible light	90	[1]
$Ir_2S_3/ZnIn_2S_4$	MeOH	Visible light	95	[2]
TiO_2	MeCN	Visible light	92	[3]
Bi_2O_3 and $BrCCl_3$	DMF	Visible light	95	[4]
$Ru(bpy)_3Cl_2$	DMF	Blue LED	89	[5]
Rose Bengal	Toluene	Blue LED	69	[6]
g-C_3N_4	MeCN	Visible light	93	[7]

Section 6: Calculation of turnover number (TON), E:Z ratio of products, and recyclability study:

Calculation of turnover number (TON):

The turnover number of 1D-Bi_2S_3 photocatalyzed reactions was calculated using the following expression[8,9]:

$$\textbf{Turnover number (TON)} = \frac{No.\ of\ Moles\ of\ the\ products\ formed}{No.\ of\ \ Moles\ of\ catalysed\ used}$$

Calculation of the ratio of E and Z products:

The E and Z products ratio was calculated from the NMR peaks' integrated values.

The % of E- Benzyl(styryl)sulphide in the product formation = 0.35 / (0.35 + 0.65) × 100

= 35%

The % of Z- Benzyl(styryl)sulphide in the product formation = 0.65 / (0.65 + 0.35) × 100

= 65%

Hence, the ratio of E and Z benzyl (styryl)sulphide would be = 35:65.

Recyclability of the 1D Bi_2S_3 photocatalyst

In a 5 mL glass vial, 5 mg of Bi_2S_3, 1.0 mmol (1.0 equiv.) of benzyl mercaptan, 1.2 mmol (1.0 equiv.) of phenylacetylene, and 3.0 mL of CH_3OH were taken and magnetically stirred for homogeneous mixing. The vial was positioned approximately 7 cm away from a light source and irradiated from two 23 W white LEDs for 6 h. After completion of the reaction, the resulting mixture was diluted with ethyl acetate. The catalyst Bi_2S_3 was separated from the mixture through centrifugation at 10000 rpm for 10 minutes. Further, the settled catalyst in the centrifuge tube was washed thrice with ethanol. After washing, the catalyst was dried overnight in a hot air oven and reused in the subsequent catalytic cycle.

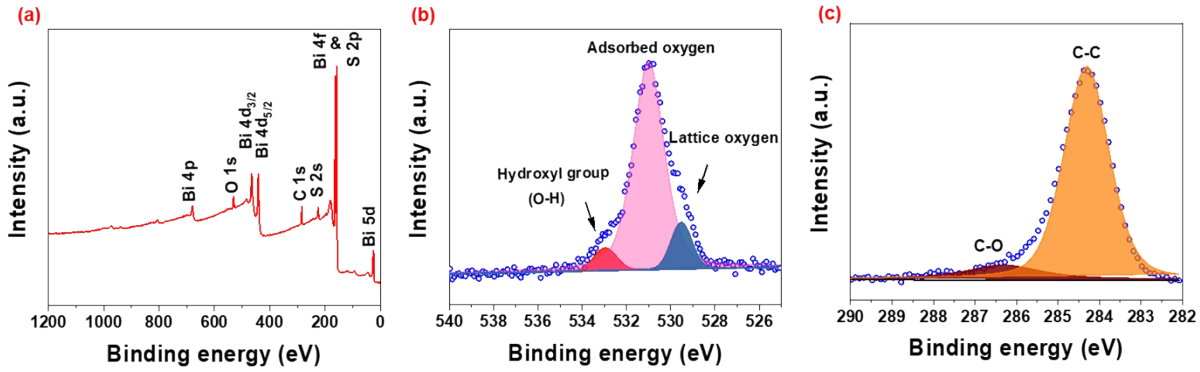
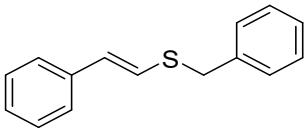


Fig. S11 (a) XPS survey spectrum of recycled BS-1. Core level spectrum of (b) O 1s, and (c) C 1s of recycled catalyst BS-1.

<u>Section 7: Synthetic procedure and analysis of the compounds:</u>



Benzyl(styryl)sulphide (2a)

The above compound was synthesized using the standard process involving phenylacetylene (1.2 mmol) and benzyl thiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2a)** in the form of a light-yellow oil (208.20 mg, 92%, E: Z ratio: 35:65). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 – 7.24 (m, 10H), 6.77 (d, 0.35 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.58 (d, 0.35 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.47 (d, 0.65 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.30 (d, 0.65 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 4.06 (s, 0.35 × 2H), 4.04 (s, 0.65 × 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.4, 137.2, 136.9, 129.0, 128.8, 128.7, 128.6, 128.2, 128.0, 127.4, 127.0, 126.7, 126.0, 125.9, 125.6, 124.4, 39.7, 37.3.

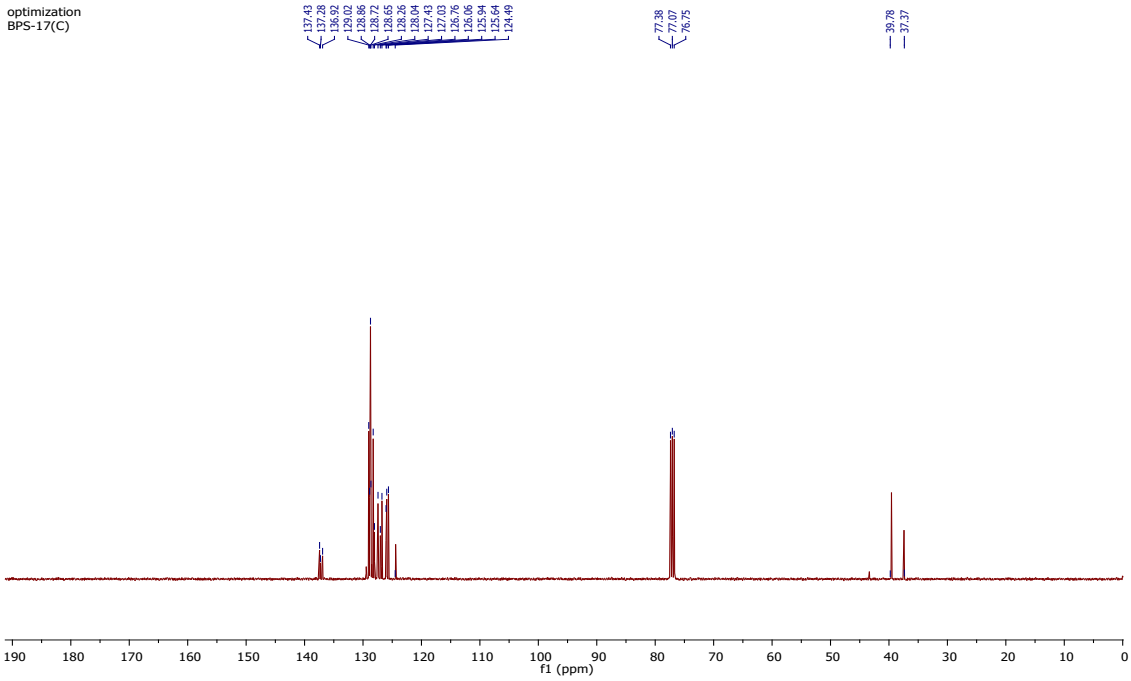
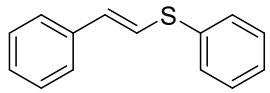


Fig. S12 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2a)**.



Phenyl(styryl)sulfane (2b)

The above compound was synthesized using the standard process involving phenylacetylene (1.20 mmol) and thiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2b)** in the form of light-yellow oil (193.55 mg, 91%, E: Z ratio: 70:30). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.25 (m, 10H), 6.92 (d, 0.70 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.77 (d, 0.70 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.63 (d, 0.30 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.54 (d, 0.30 × 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.5, 136.2, 135.3, 135.2, 131.9, 130.1, 129.8, 129.1, 128.7, 128.3, 127.6, 127.2, 127.1, 126.9, 126.0, 123.4.

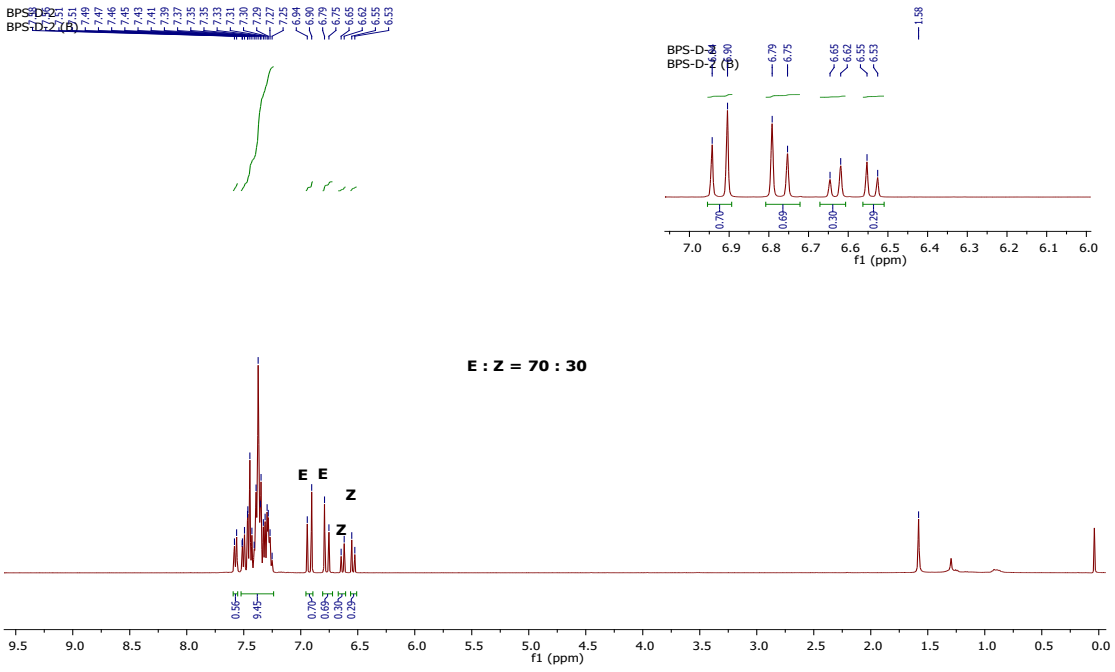


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2b)**.

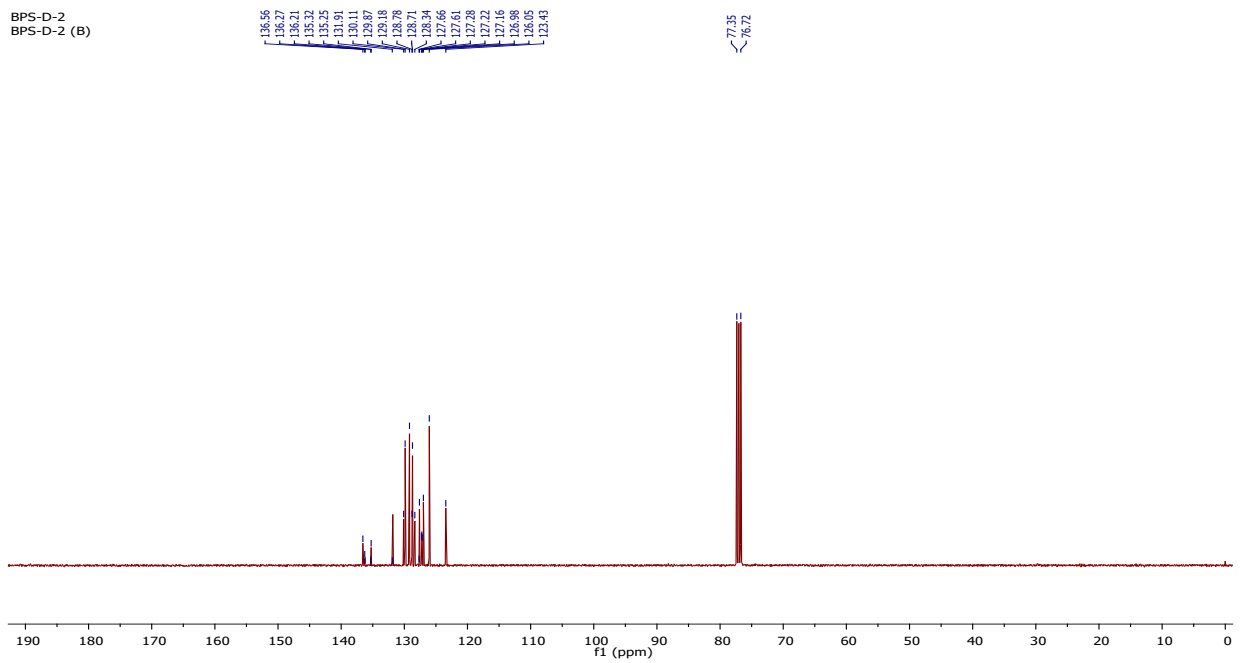
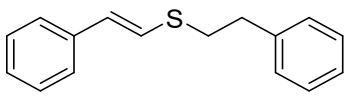


Fig. S14 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2b)**.



Phenethyl(styryl)sulfane (2c)

The above compound was synthesized using the standard process involving phenylacetylene (1.20 mmol) and 2-phenylethanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2c)** in the form of light-yellow oil (203.50 mg, 85%, E: Z ratio: 32:68). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.19 (m, 11H), 6.69 (d, 0.32 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.50 (d, 0.32 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.46 (d, 0.68 × 1H, $^3J_{H\text{-}H}$ = 8.00 Hz), 6.24 (d, 0.68 × 1H, $^3J_{H\text{-}H}$ = 8.00 Hz), 3.07 – 2.92 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 136.9, 128.6, 128.2, 127.4, 126.7, 126.4, 125.9, 125.5, 124.7, 40.2, 37.2, 36.8, 35.7.

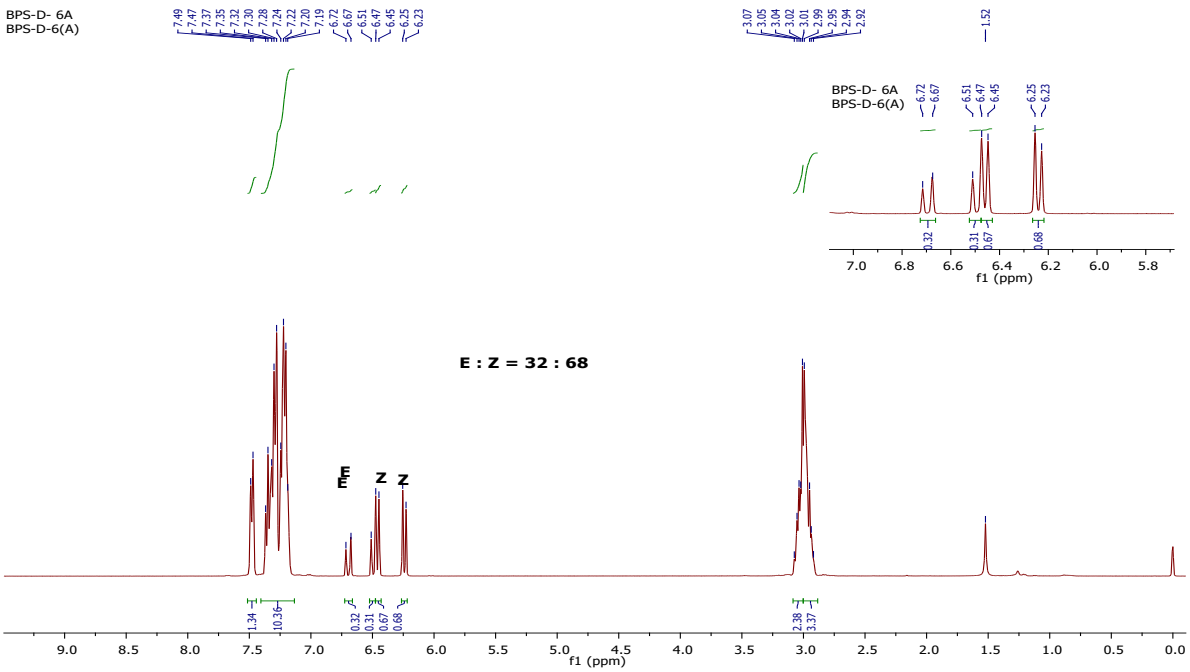


Fig. S15 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2c)**.

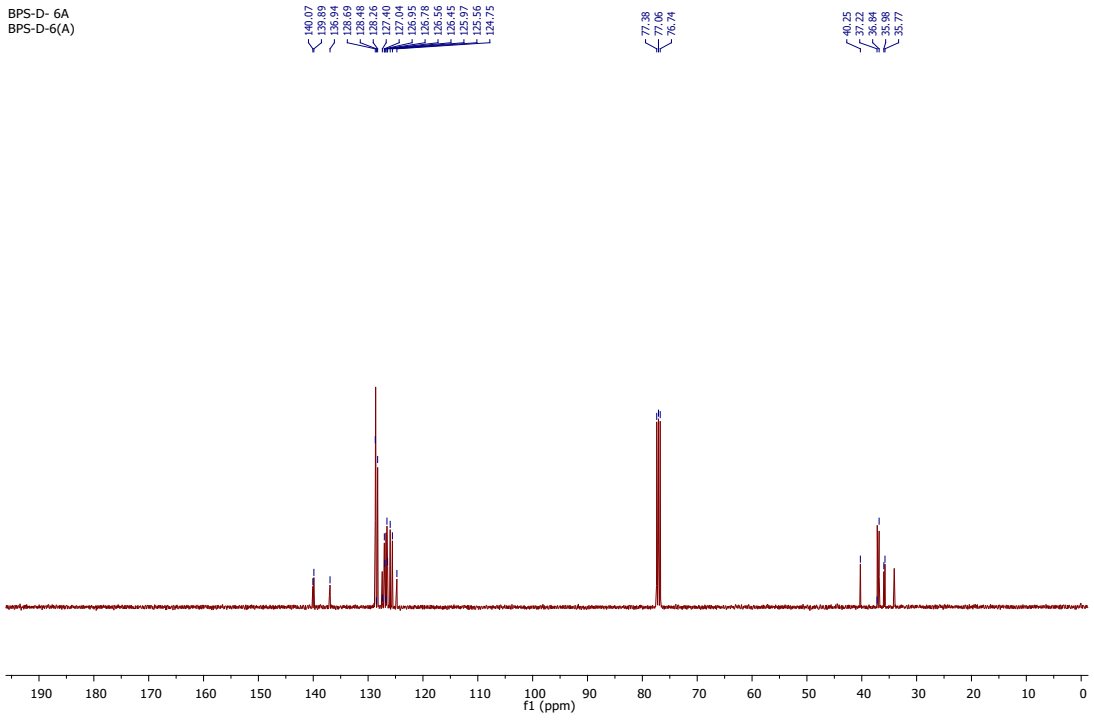
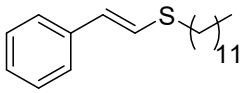


Fig. S16 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2c)**.



Dodecyl(styryl)sulfane (2d)

The above compound was synthesized using the standard process involving phenylacetylene (1.20 mmol) and dodecanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2d)** in the form of light-yellow oil (215.50 mg, 71%, E: Z ratio: 23:77). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.20 (m, 5H), 6.76 (d, 0.23 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.51 (d, 0.23 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.46 (d, 0.77 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.28 (d, 0.77 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 2.81 (t, 2H), 1.72 (m, 2H), 1.45 (t, 2H), 1.30 (broad s, 16H), 0.92 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 128.6, 128.2, 127.7, 126.7, 126.5, 125.4, 125.2, 35.9, 32.6, 31.9, 30.2, 29.6, 29.3, 29.2, 28.8, 28.6, 28.5, 22.7, 14.1.

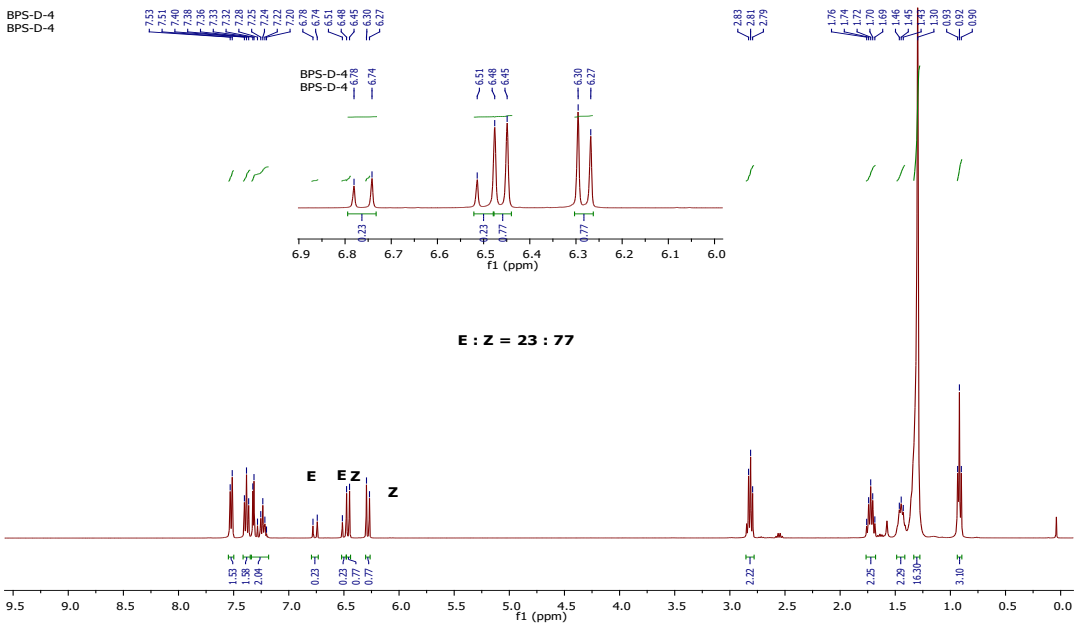


Fig. S17 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2d)**.

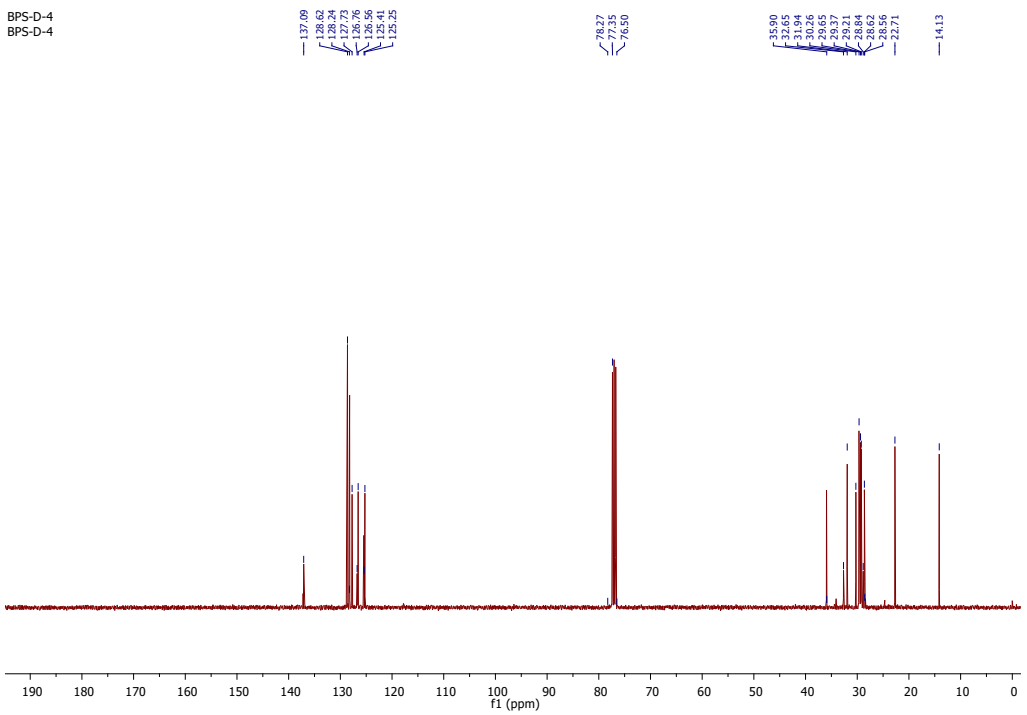
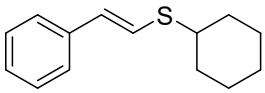


Fig. S18 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2d)**.



Cyclohexyl(styryl)sulfane (2e)

The above compound was synthesized using the standard process involving phenylacetylene (1.20 mmol) and cyclohexenethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2e)** in the form of light-yellow oil (131.50 mg, 60%, E: Z ratio: 12:88). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.22 (m, 5H), 6.81 (d, 0.12 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.62 (d, 0.12 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.47 (d, 0.88 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), 6.38 (d, 0.88 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), 3.05 – 2.89 (m, 1H), 2.12 – 2.09 (m, 2H), 1.86 – 1.83 (m, 2H), 1.69 – 1.67 (m, 1H), 1.55 – 1.30 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 128.6, 128.2, 126.5, 125.9, 125.0, 123.9, 47.8, 45.5, 33.6, 26.1, 25.6.

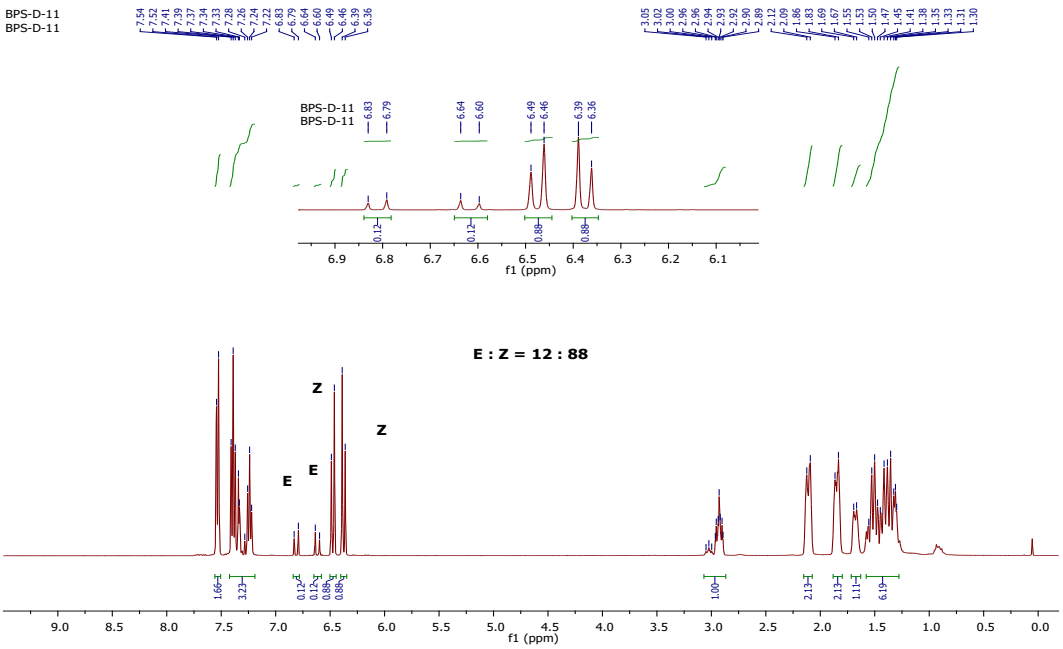


Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2e)**.

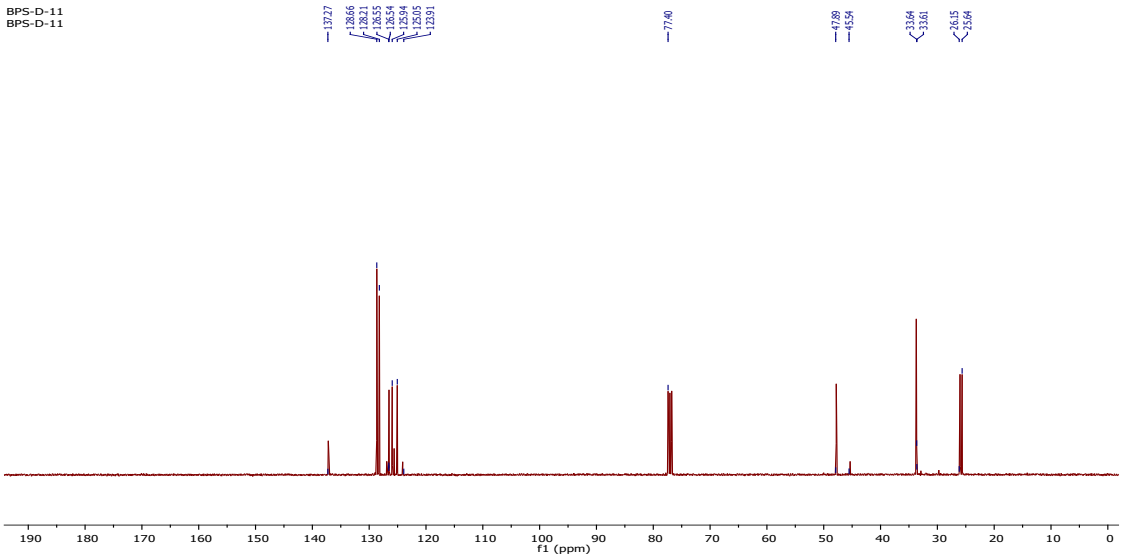
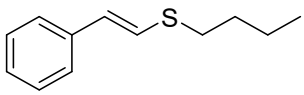


Fig. S20 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2e)**.



Butyl(styryl)sulfane (2f)

The above compound was synthesized using the standard process involving phenylacetylene (1.20 mmol) and 1-butanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2f)** in the form of a colorless oil (172.89 mg, 80 %, E: Z ratio: 30:70). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.15 (m, 5H), 6.71 (d, 0.30 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.44 (d, 0.30 × 1H, $^{3}J_{H\text{-}H}$ = 16.00 Hz), 6.41 (d, 0.70 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.22 (d, 0.70 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 2.78-2.72 (m, 2H), 1.68-1.60 (m, 2H), 1.46-1.37 (m, 2H), 0.89-0.94 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.1, 128.7, 128.3, 127.8, 126.8, 125.5, 35.6, 32.4, 21.8, 13.7.

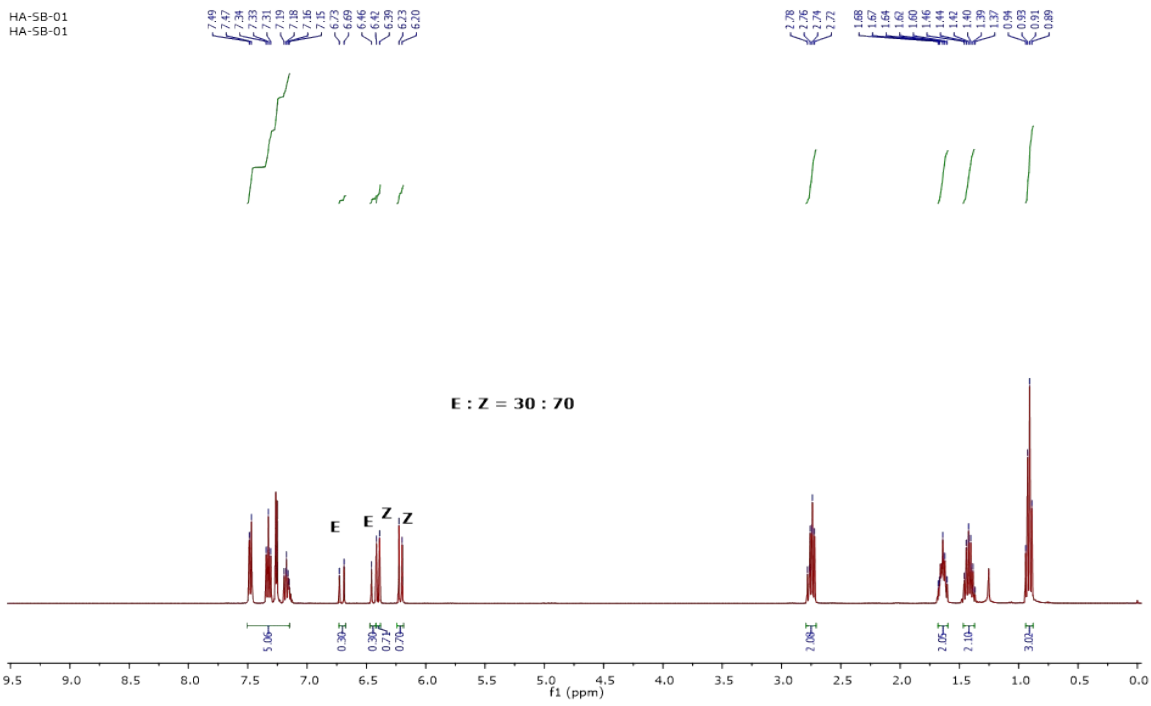


Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2f)**.

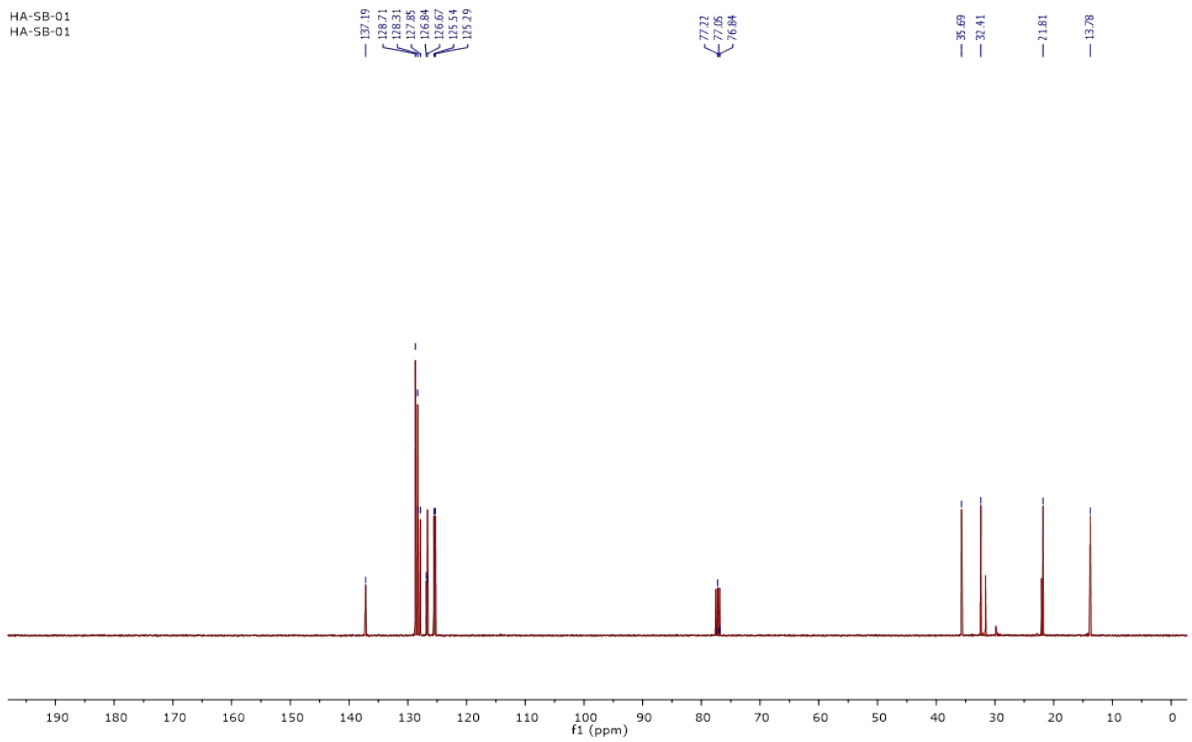
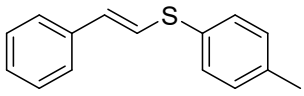


Fig. S22 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2f)**.



1-Methyl-4-[[2-phenylethenyl]thio]benzene (2g)

The above compound was synthesized using the standard process involving phenylacetylene (1.20 mmol) and 4-methylthiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2g)** in the form of a yellow oil (187.59 mg, 83 %, E: Z ratio: 62:38). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 6.51 (m, 9H), 6.92(d, 0.62 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.71 (d, 0.62× 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.60 (d, 0.38 × 1H, $^3J_{H\text{-}H}$ =12.00 Hz), 6.53 (d, 0.0.38 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), 2.40 (s, 3H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.4, 136.8, 130.8, 130.6, 130.1, 128.9, 128.8, 128.7, 128.4, 127.5, 127.2, 126.6, 126.0, 124.6, 21.0.

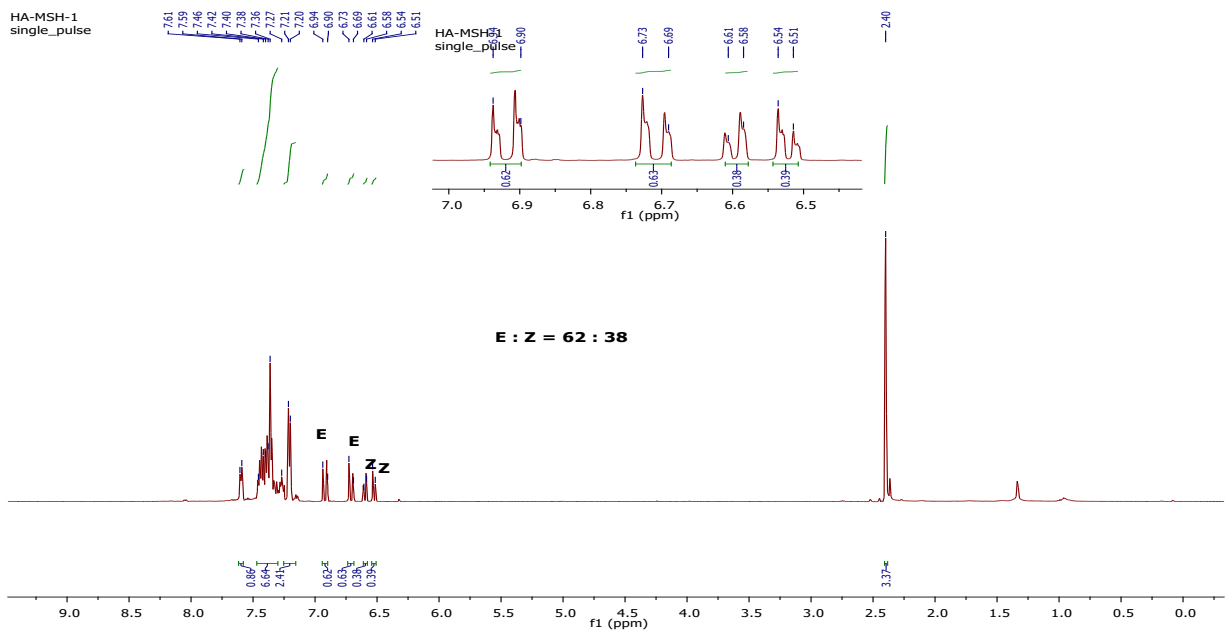


Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound (**2g**).

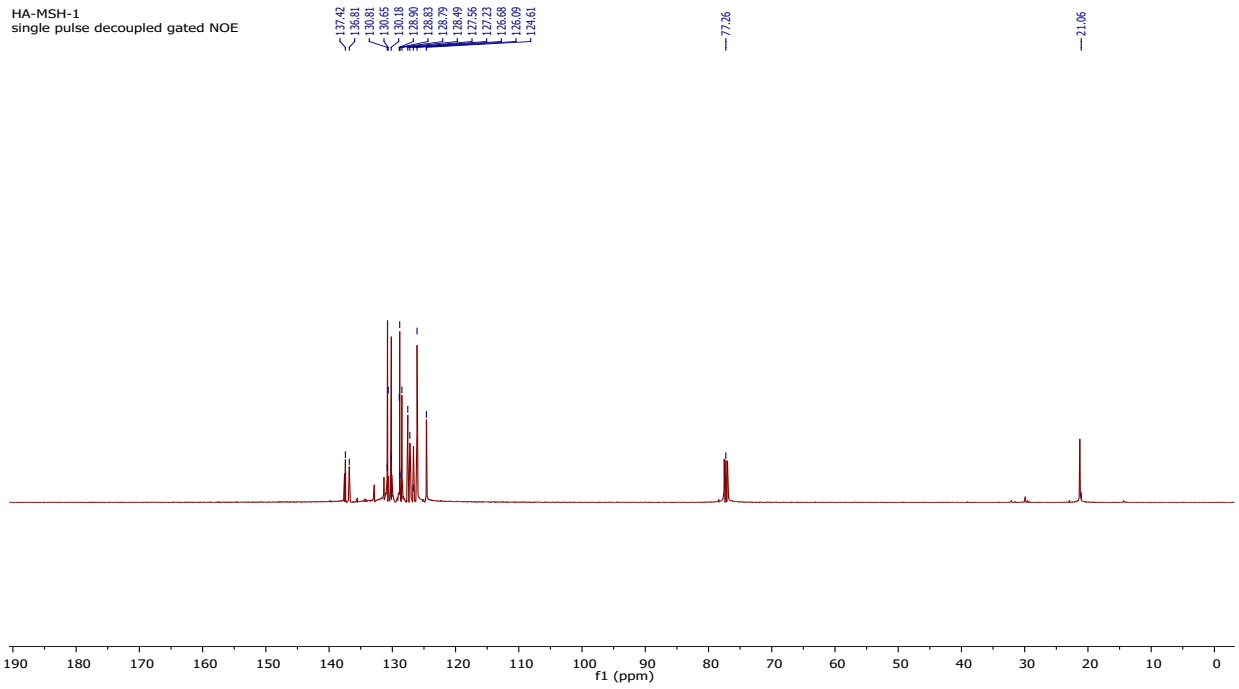
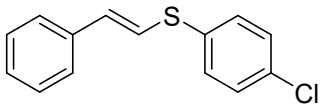


Fig. S24 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound (**2g**).



4-Chlorophenyl(styryl)sulfane (2h)

The above compound was synthesized using the standard process involving phenylacetylene (1.20 mmol) and 4-chlorothiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2h)** in the form of white solid (208.60 mg, 80%, E: Z ratio: 34: 66). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.55 (m, 1H), 7.45-7.26 (m, 8H), 6.86 (d, 0.34 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.78 (d, 0.34 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.66 (d, 0.66 × 1H, $^{3}J_{H\text{-}H}$ =12.00 Hz), 6.45 (d, 0.66 × 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 134.9, 133.4, 132.9, 131.4, 131.1, 129.5, 128.9, 128.5, 128.1, 127.4, 126.2, 125.3, 122.6.

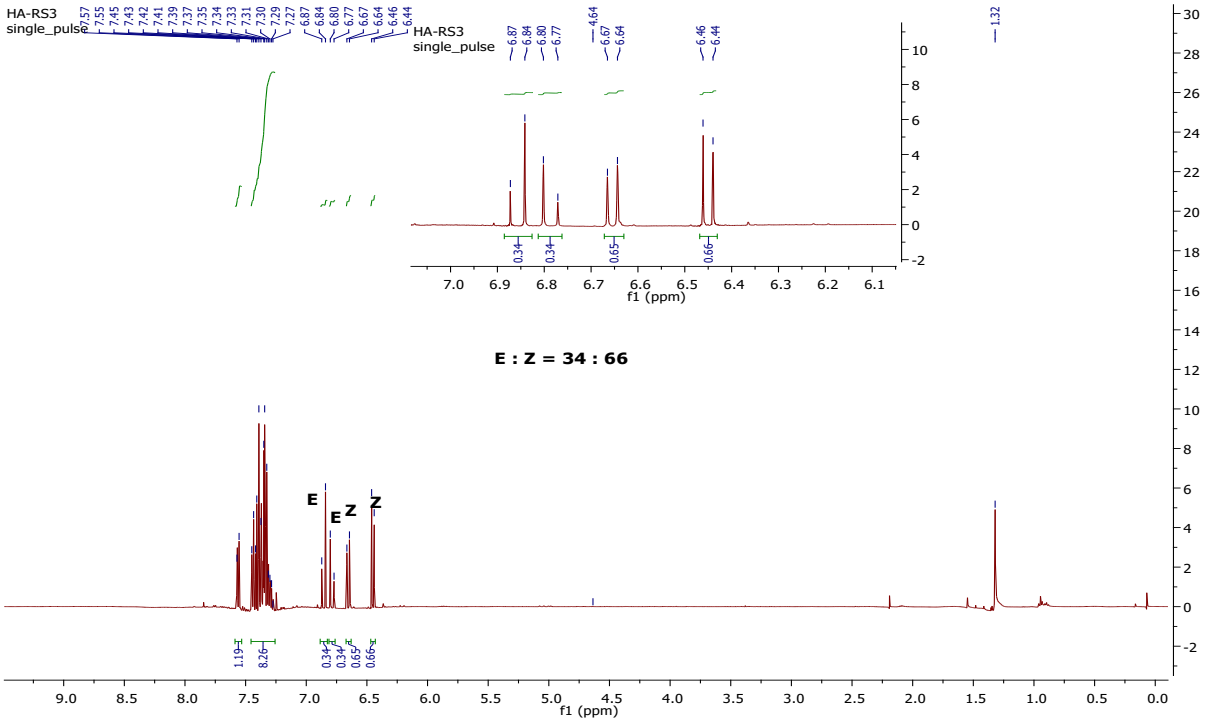


Fig. S25 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2h)**.

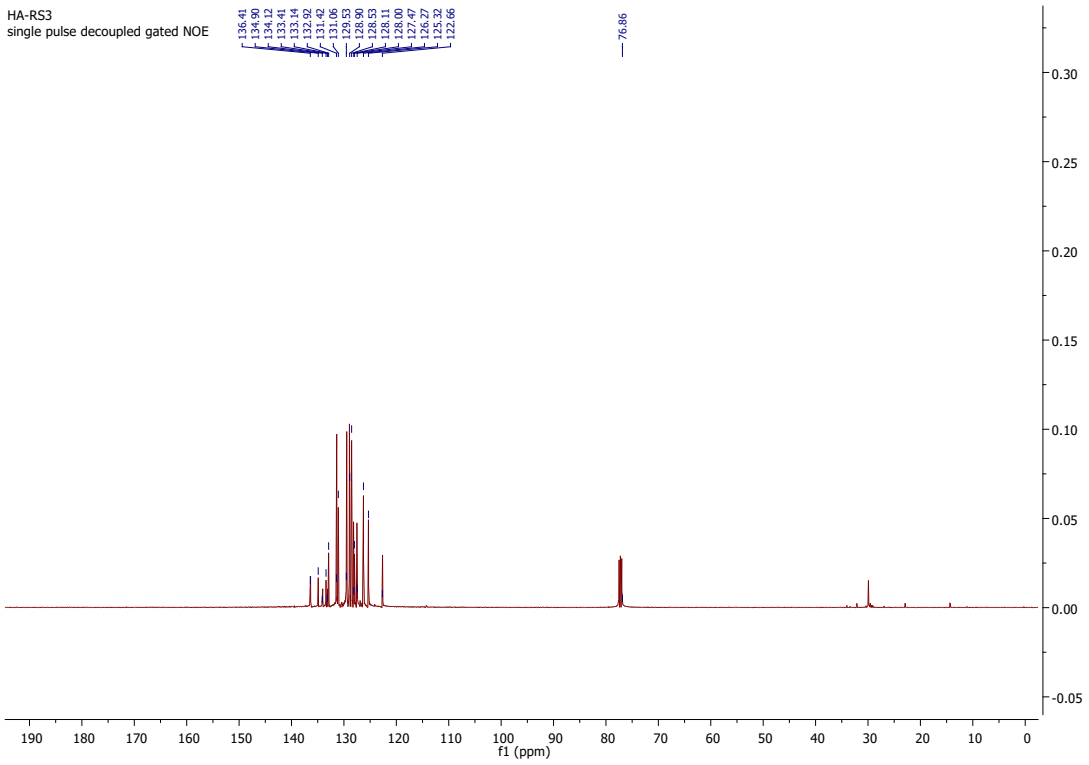
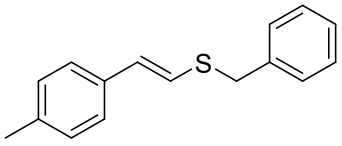


Fig. S26 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2h)**



1-Methyl-4-[2-[(phenylmethyl)thio]ethenyl]benzene (2i)

The above compound was synthesized using the standard process involving 4-ethynyltoluene (1.20 mmol) and benzyl thiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2i)** in the form of light-yellow oil (208.54 mg, 87%, E: Z ratio: 21:79). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.11 (m, 10H), 6.68 (d, 0.21 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.55 (d, 0.21 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.43 (d, 0.79 × 1H, $^3J_{H\text{-}H}$ = 8.00 Hz), 6.22 (d, 0.79 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), 4.03 (s, 2H), 2.36 (s, 3H), ^{13}C NMR

(100 MHz, $CDCl_3$): δ 137.5, 129.3, 129.0, 128.9, 128.8, 128.6, 128.3, 127.4, 125.9, 125.5, 124.8, 123.1, 39.7, 21.0.

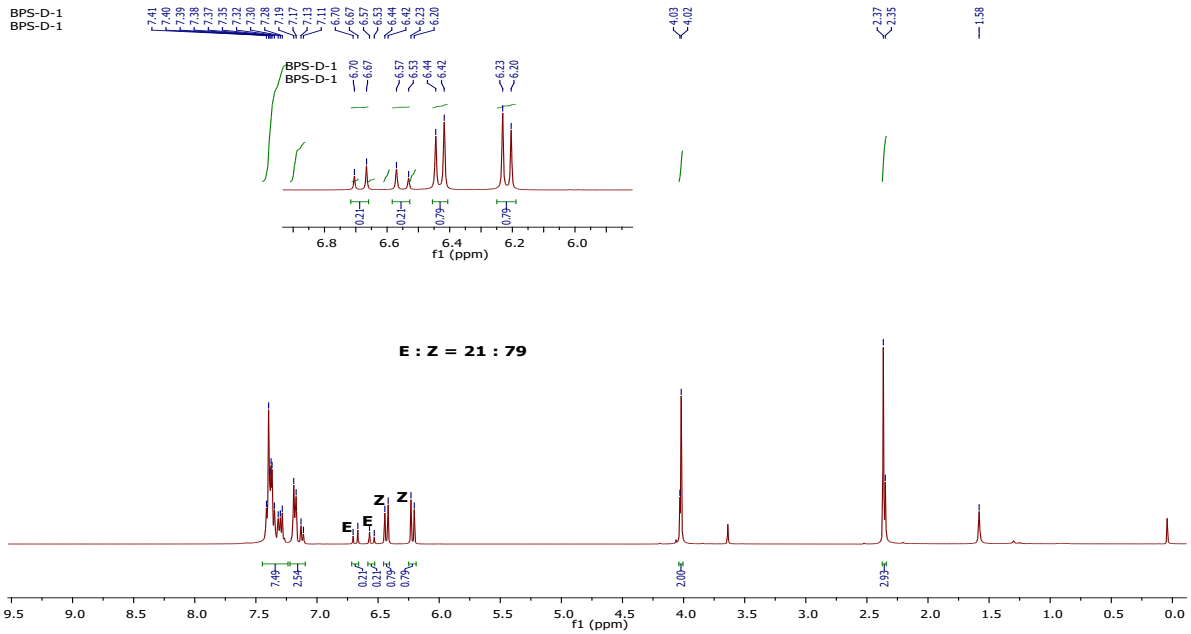


Fig. S27 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2i)**.

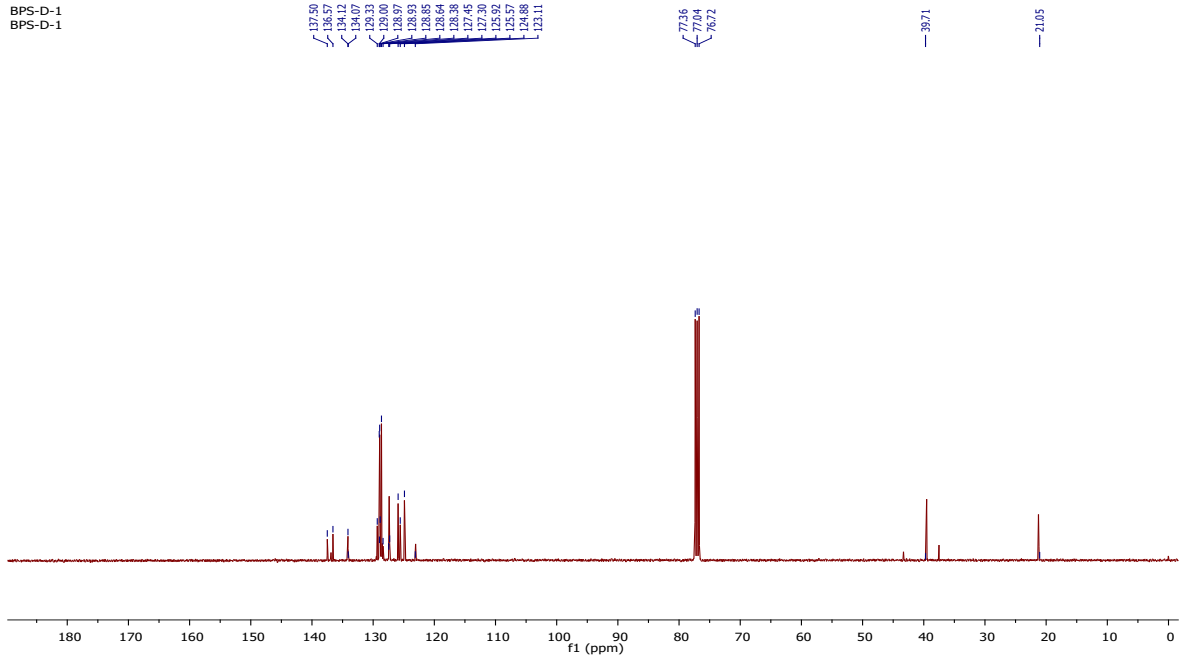
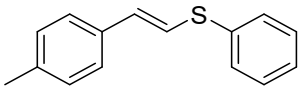


Fig. S28 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2i).**



(4-Methylstyryl) (phenyl)sulfane (2j)

The above compound was synthesized using the standard process involving 4-ethynyltoluene (1.20 mmol) and thiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2j)** in the form of light-yellow oil (201.20 mg, 89%, E: Z ratio: 52:48). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.16 (m, 9H), 6.87 (d, 0.52 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.76 (d, 0.52 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.62 (d, 0.48 × 1H, $^3J_{H\text{-}H}$ =8.00 Hz), 6.48 (d, 0.48 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.0, 136.4, 135.6, 133.8, 132.4, 130.0, 129.5, 129.0, 128.7, 127.4, 126.0, 124.8, 121.8, 21.1.

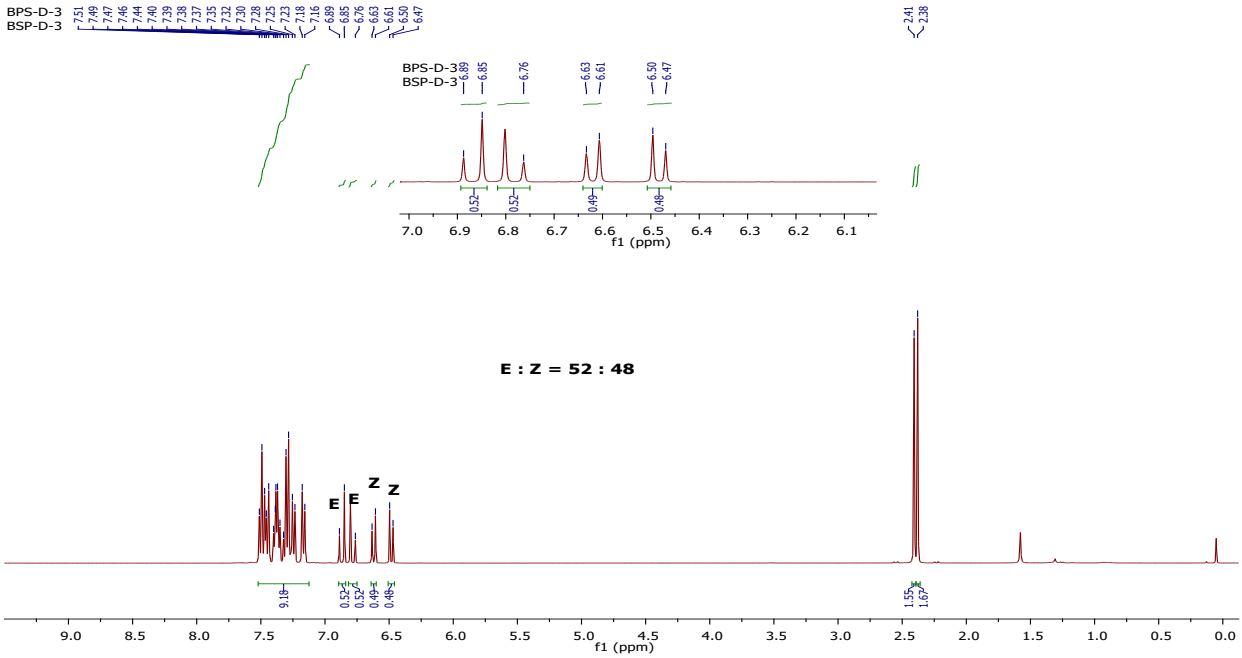


Fig. S29 ^1H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2j)**.

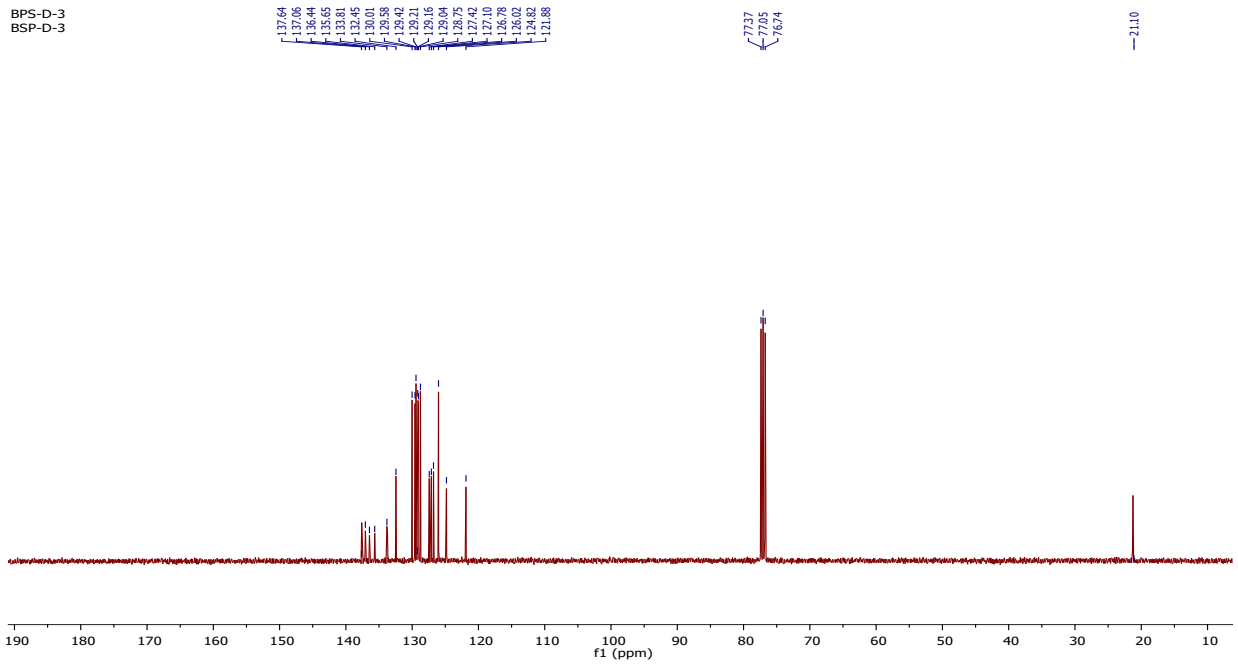
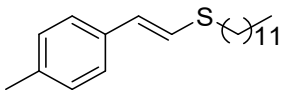


Fig. S30 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2j)**.



4-Methyl-1-[2-(dodecylthio)ethenyl]benzene (2k)

The above compound was synthesized using the standard process involving 4-ethynyltoluene (1.20 mmol) and dodecanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2k)** in the form of light-yellow oil (208.54 mg, 61%, E: Z ratio: 11:89). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.12 (m, 4H), 6.69 (d, 0.11 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.50 (d, 0.11 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.44 (d, 0.89 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), 6.21 (d, 0.89 × 1H, $^3J_{H\text{-}H}$ = 8.00 Hz), 2.80 (t, 2H), 2.36 (s, 3H), 1.72 (m, 2H), 1.44 (t, 2H), 1.30 (broad s, 16H), 0.92 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 134.3, 129.3, 128.8, 128.5, 126.5, 125.4, 125.2, 35.8, 31.9, 29.6, 29.4, 28.6, 22.7, 21.1, 14.0.

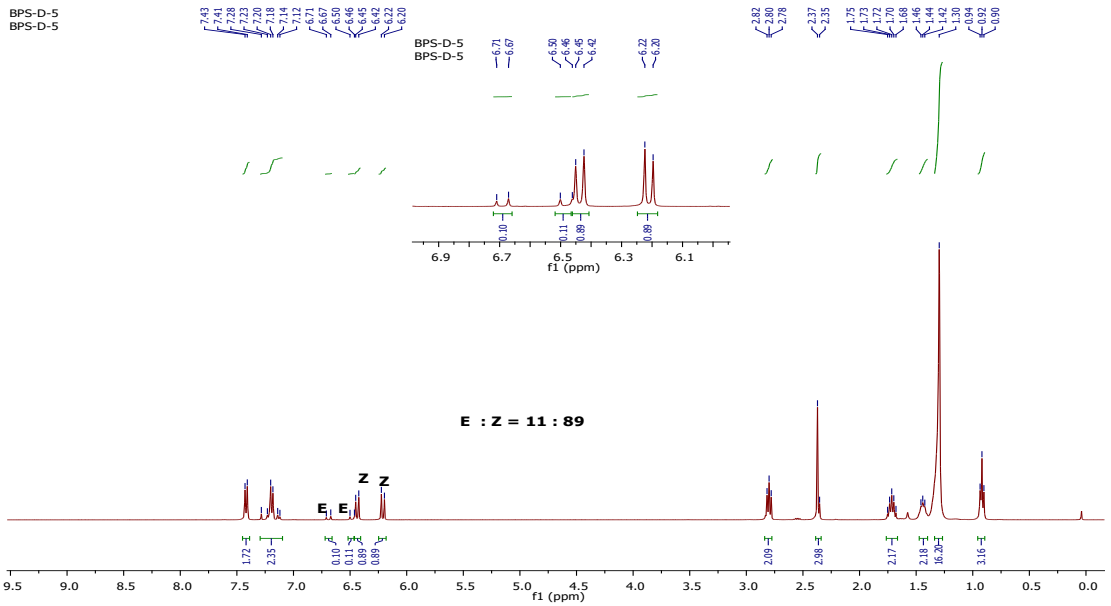


Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2k)**.

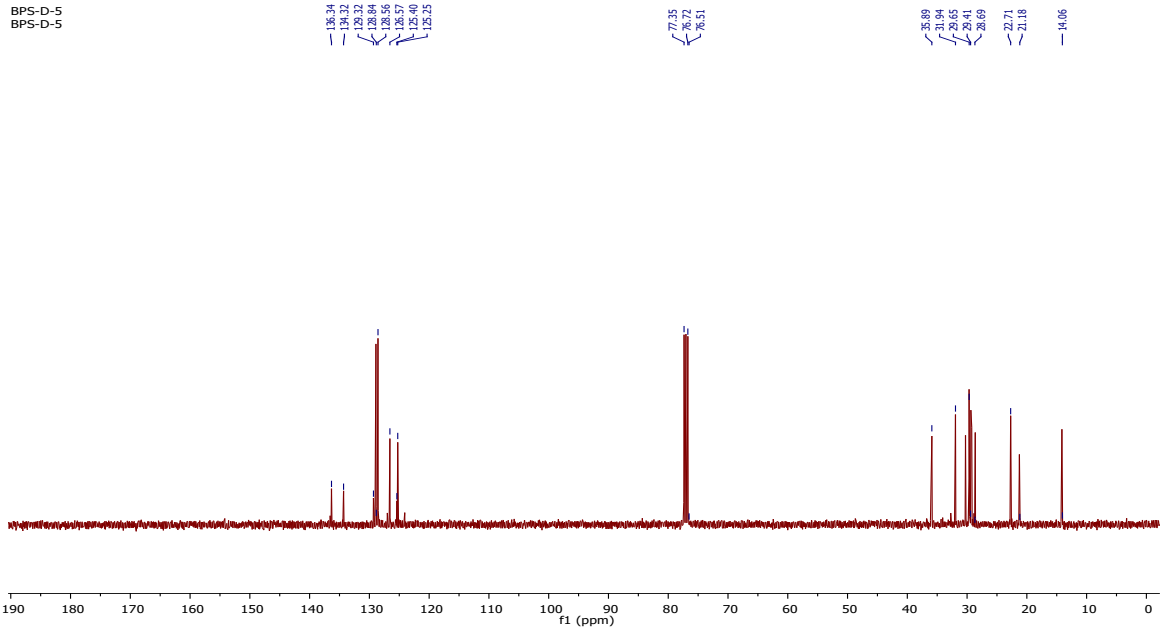
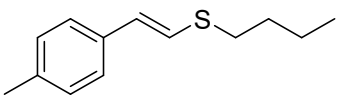


Fig. S32 ^{13}**C** NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2k)**



1-[2-(Butylthio)ethenyl]-4-methylbenzene (2l)

The above compound was synthesized using the standard process involving 4-ethynylene toluene (1.20 mmol) and 1-butanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of (**2l**) in the form of white solid (171.30 mg, 83%, E: Z ratio: 47: 53). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 1H), 7.20-7.09 (m, 3H), 6.66 (d, 0.47 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.45 (d, 0.47 × 1H, $^{3}J_{H\text{-}H}$ = 12.00 Hz), 6.41 (d, 0.53 × 1H, $^{3}J_{H\text{-}H}$ =8.00 Hz), 6.18 (d, 0.53 × 1H, $^{3}J_{H\text{-}H}$ = 8.00 Hz), 2.81-2.76 (m, 2H), 2.34-2.32 (m, 3H), 1.69-1.49(m, 2H), 1.47-1.43 (m, 2H), 0.96-0.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 134.4, 129.5, 128.7, 126.8, 124.4, 35.7, 32.5, 31.6, 29.8, 13.5.

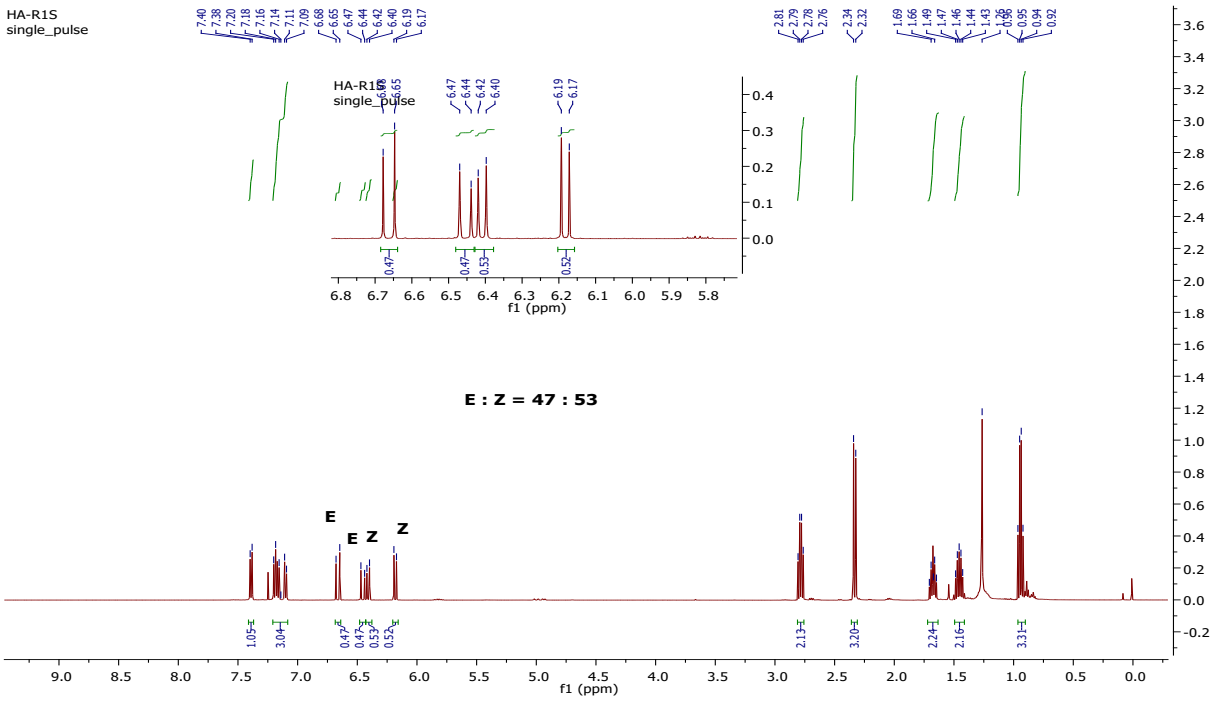


Fig. S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2l)**.

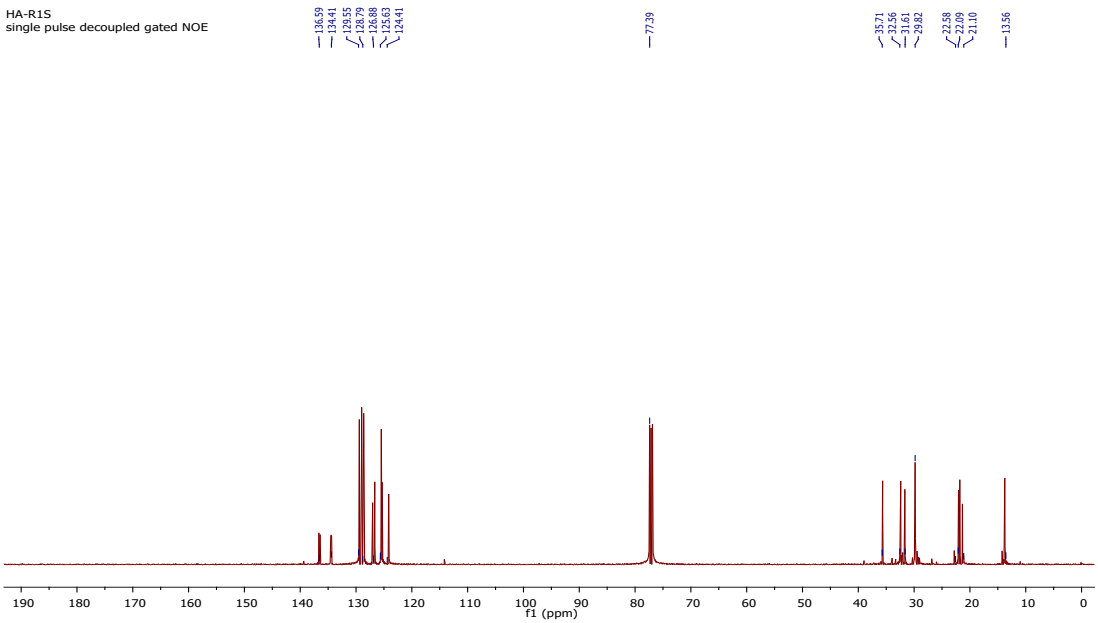
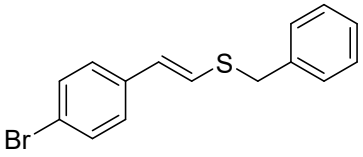


Fig. S34 ^{13}**C** NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2l**



1-Bromo-4-[2-[(phenylmethyl)thio]ethenyl]benzene (2m)

The above compound was synthesized using the standard process involving 1-bromo-4-ethynylbenzene (1.20 mmol) and benzyl thiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2m)** in the form of a pale-yellow solid (236.10 mg, 77%, E: Z ratio: 30:70). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.09 (m, 9H), 6.71 (d, 0.30 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.43 (d, 0.30 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.33 (d, 0.70 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), 6.28 (d, 0.70 × 1H, $^3J_{H\text{-}H}$ = 8.00 Hz). 4.0 (s, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 135.8, 135.7, 131.7, 131.3, 130.2, 129.4, 129.0, 128.7.128.5, 127.5, 127.4, 127.1, 126.4, 125.5, 124.6, 120.3, 39.5.

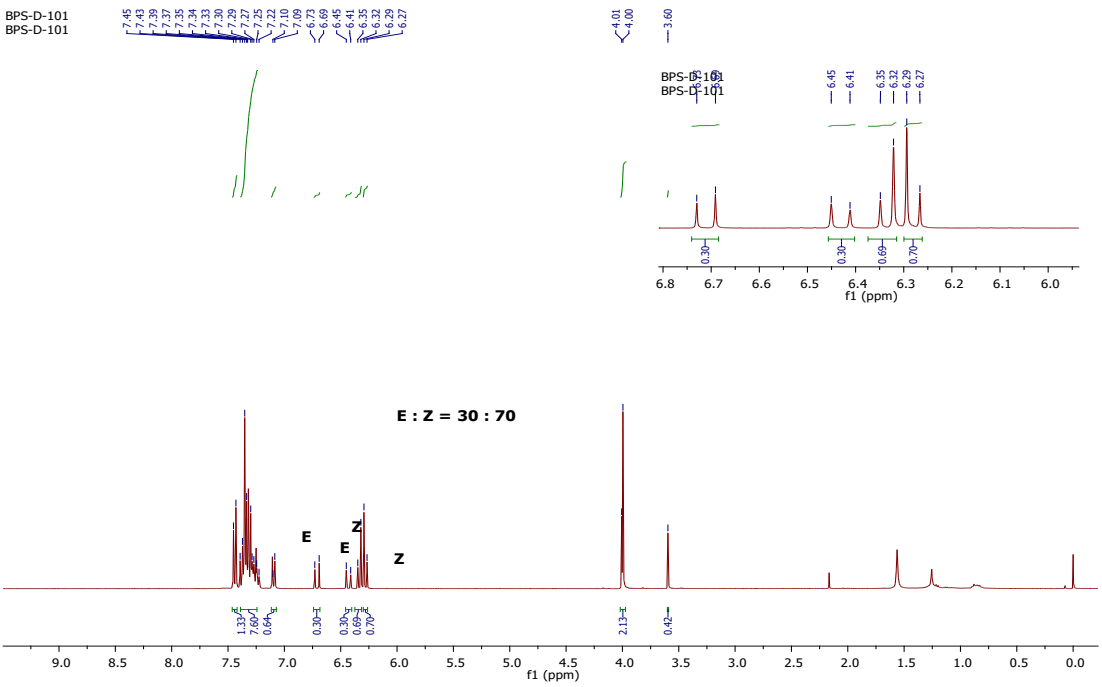


Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2m)**.

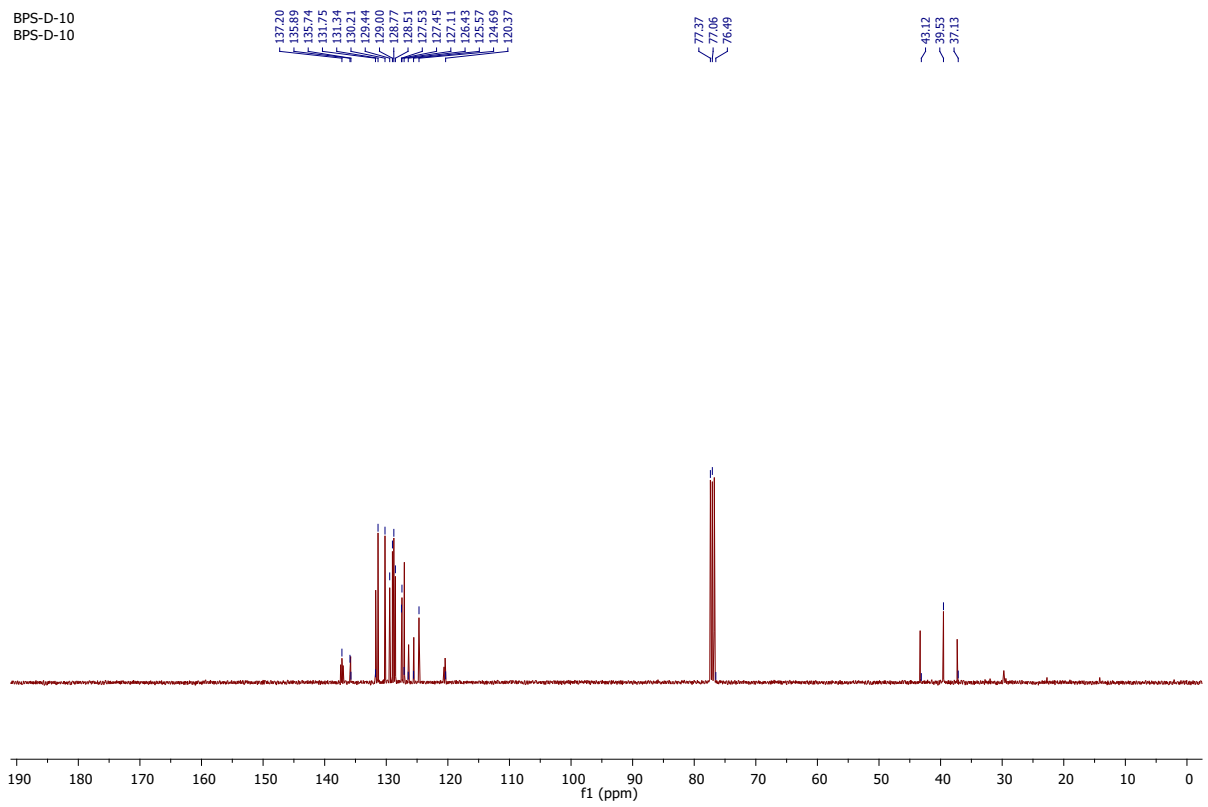
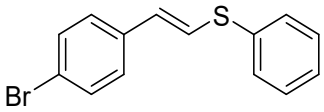


Fig. S36 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2m)**.



(4-Bromostyryl)(phenyl)sulfane (2n)

The above compound was synthesized using the standard process involving 1-bromo-4-ethynylbenzene (1.20 mmol) and thiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(2n)** in the form of a pale-yellow solid (265.10 mg, 81%, E: Z ratio: 25:75). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.21 (m, 9H), 6.92 (d, 0.25 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.65 (d, 0.25 × 1H, $^3J_{H\text{-}H}$ = 16.00 Hz), 6.58 (d, 0.75 × 1H, $^3J_{H\text{-}H}$ = 8.00 Hz), 6.53 (d, 0.75 × 1H, $^3J_{H\text{-}H}$ = 12.00 Hz), ^{13}C NMR

(100 MHz, $CDCl_3$): δ 135.8, 135.4, 135.3, 131.8, 131.5, 130.3, 130.1, 129.7, 129.2, 127.4, 127.3, 127.2, 127.1, 125.9, 124.9, 121.2, 120.9.

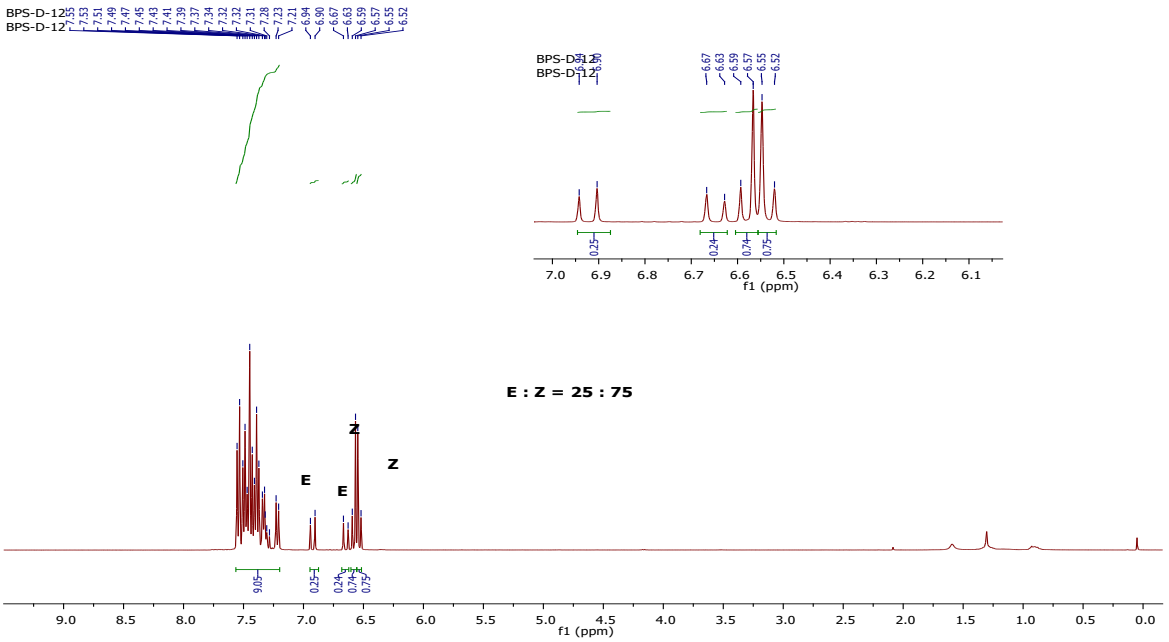


Fig. S37 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(2n)**.

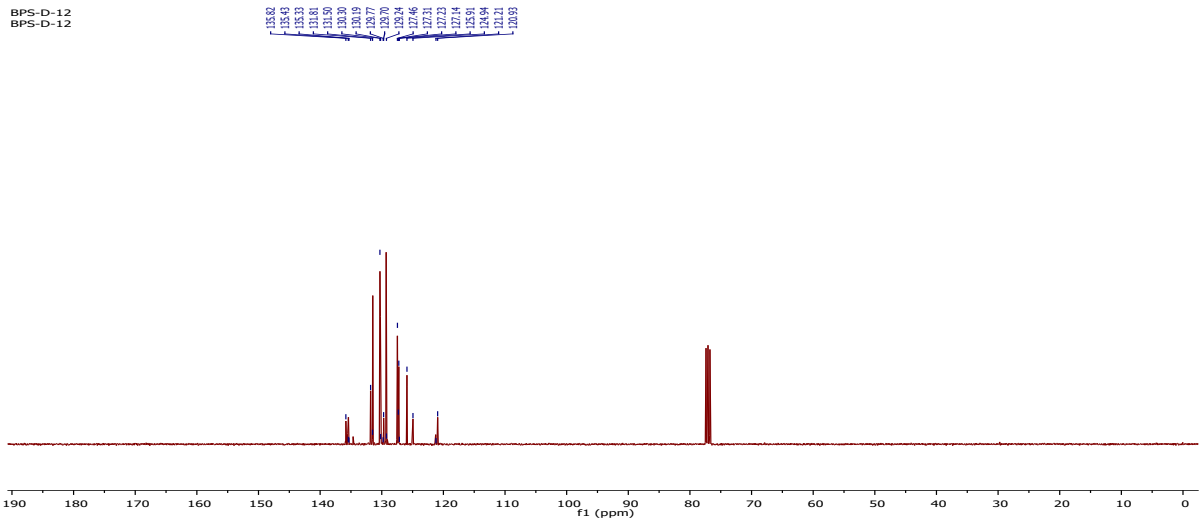
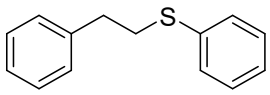


Fig. S38 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(2n)**.



Phenethyl(phenyl)sulfane (3a)

The above compound was synthesized using the standard process involving styrene (1.20 mmol) and thiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3a)** in the form of colorless oil (182.40 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.31 (m, 2H), 7.28-7.23 (m, 4H), 7.20-7.10 (m, 4H), 3.10 (t, 2 H), 2.88 (t, 2 H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 136.5, 129.3, 129.2, 129.1, 128.6, 126.5, 126.0, 35.9,35.1.

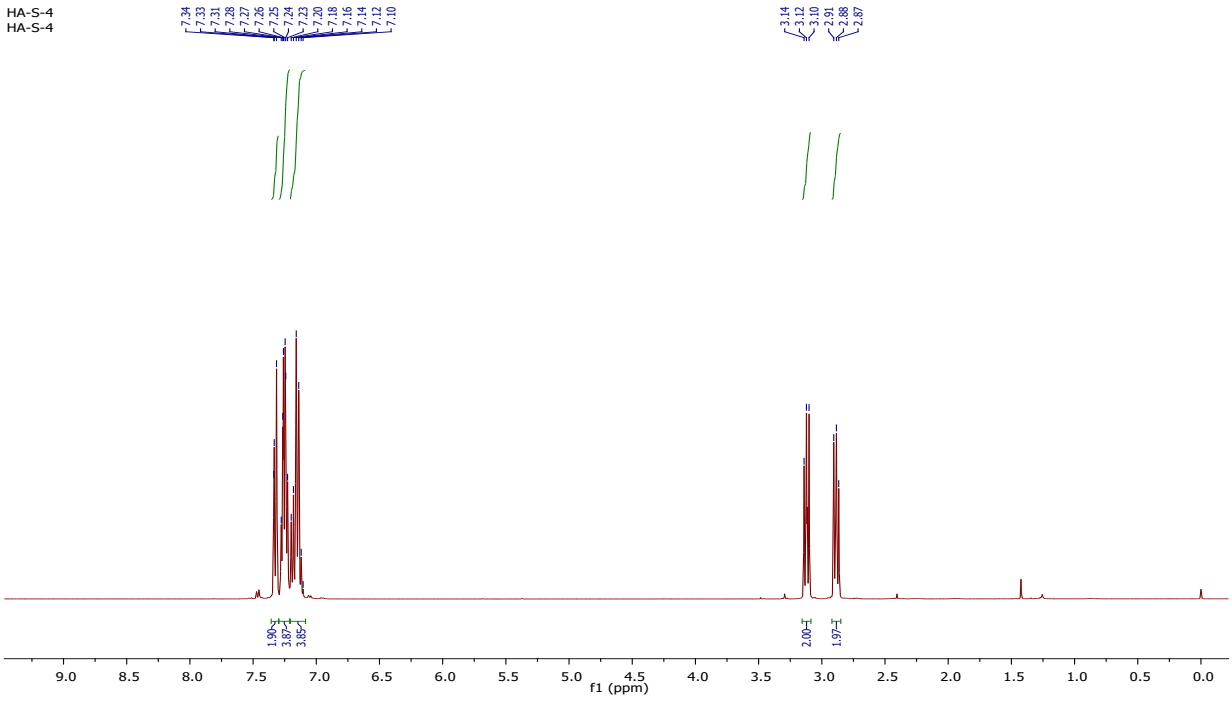


Fig. S39 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3a).**

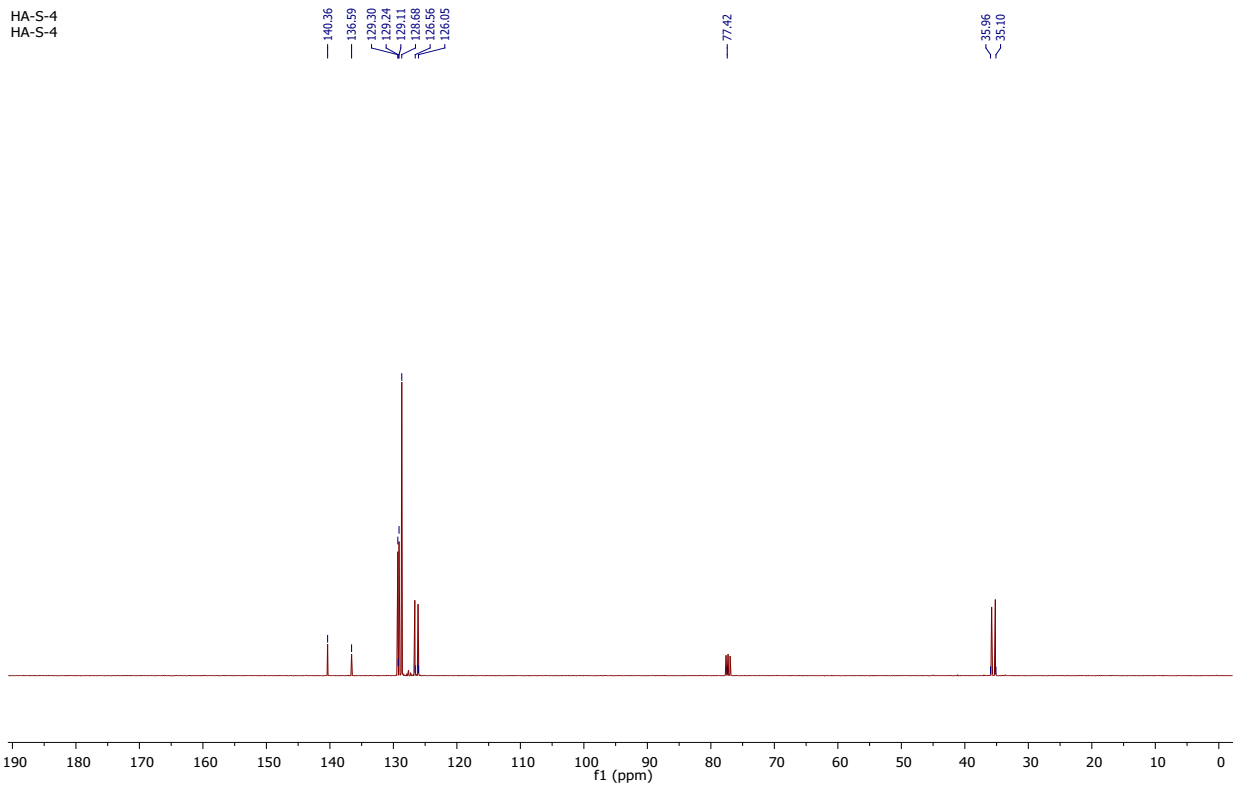
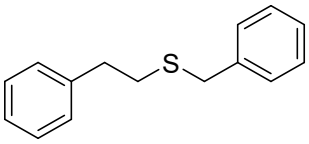


Fig. S40 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3a).**



Benzyl(phenethyl)sulfane (3b)

The above compound was synthesized using the standard process involving styrene (1.20 mmol) and benzyl thiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3b)** in the form of colorless oil (187.25 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47-7.43 (m, 4H), 7.41-7.32 (m, 5H), 7.29-7.27 (m, 1H), 3.83 (s, 2H), 2.96 (d, 2H), 2.79 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 138.6, 129.3, 129.1, 128.8, 127.1, 126.5, 36.5, 36.2, 33.2.

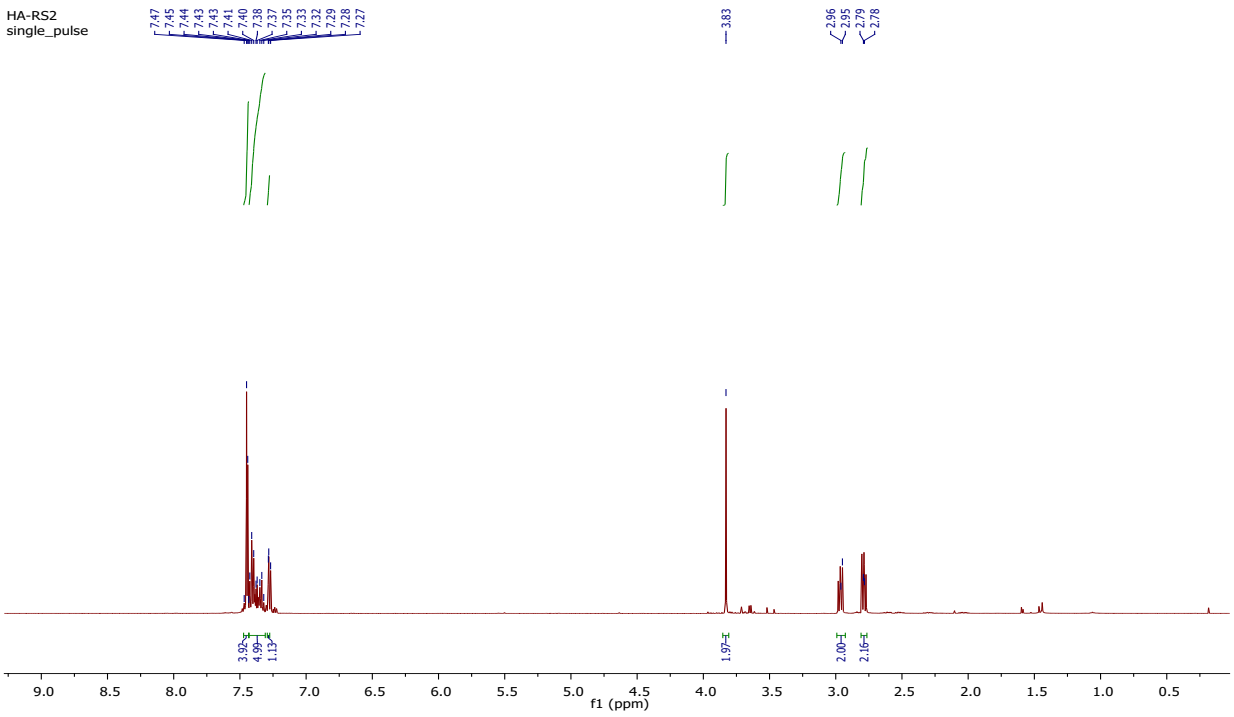


Fig. S41 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3b)**.

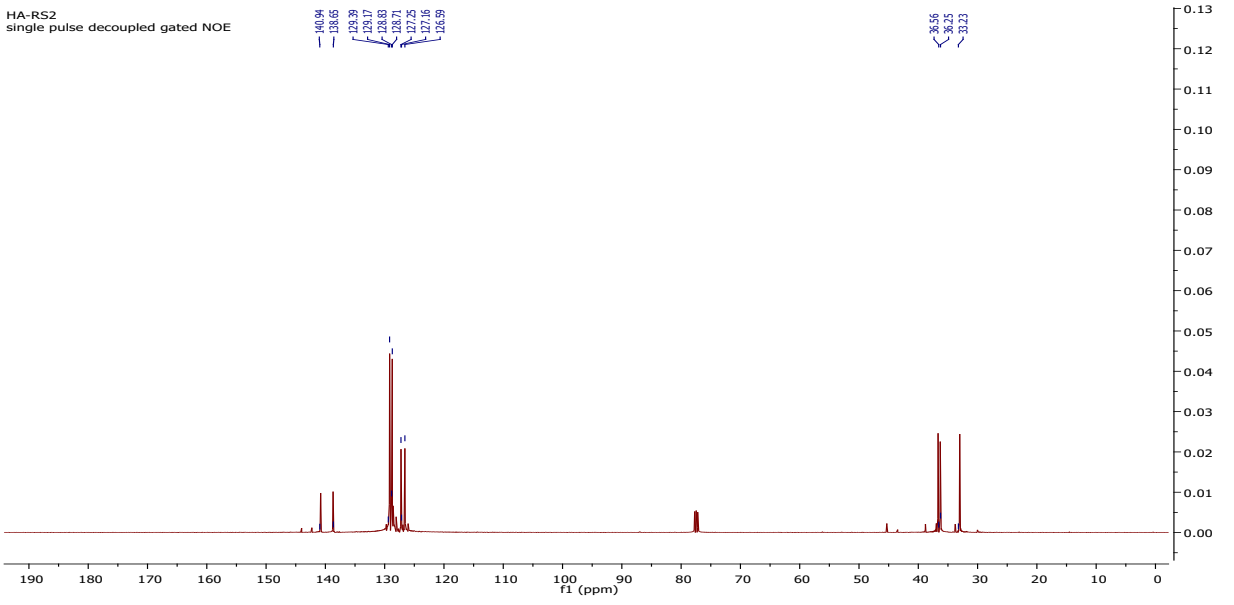
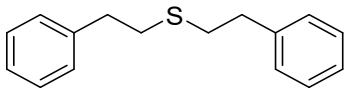


Fig. S42 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3b)**



Diphenethylsulfane (3c)

The above compound was synthesized using the standard process involving styrene (1.20 mmol) and 2-phenylethanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3c)** in the form of colorless oil (195.75 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29– 7.26 (m, 2 H), 7.21– 7.08 (m, 3 H), 2.96– 2.84 (m, 2H), 2.77-2.73 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.5, 128.6, 126.5, 40.4, 36.7.

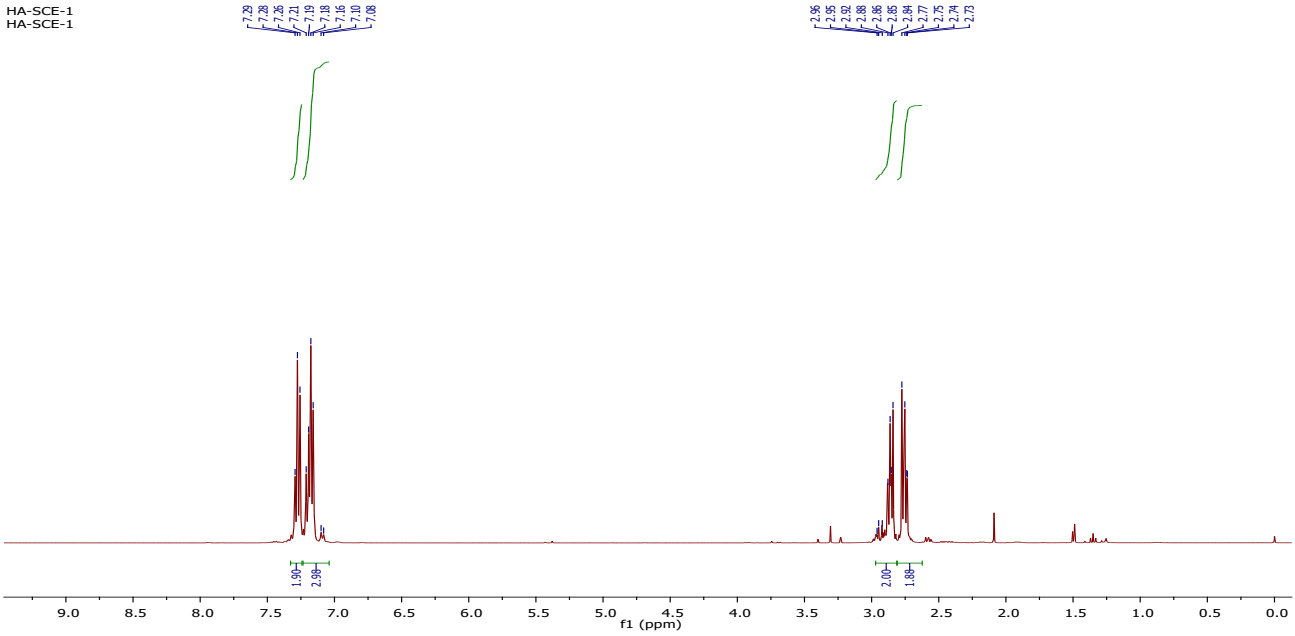


Fig. S43 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3c)**.

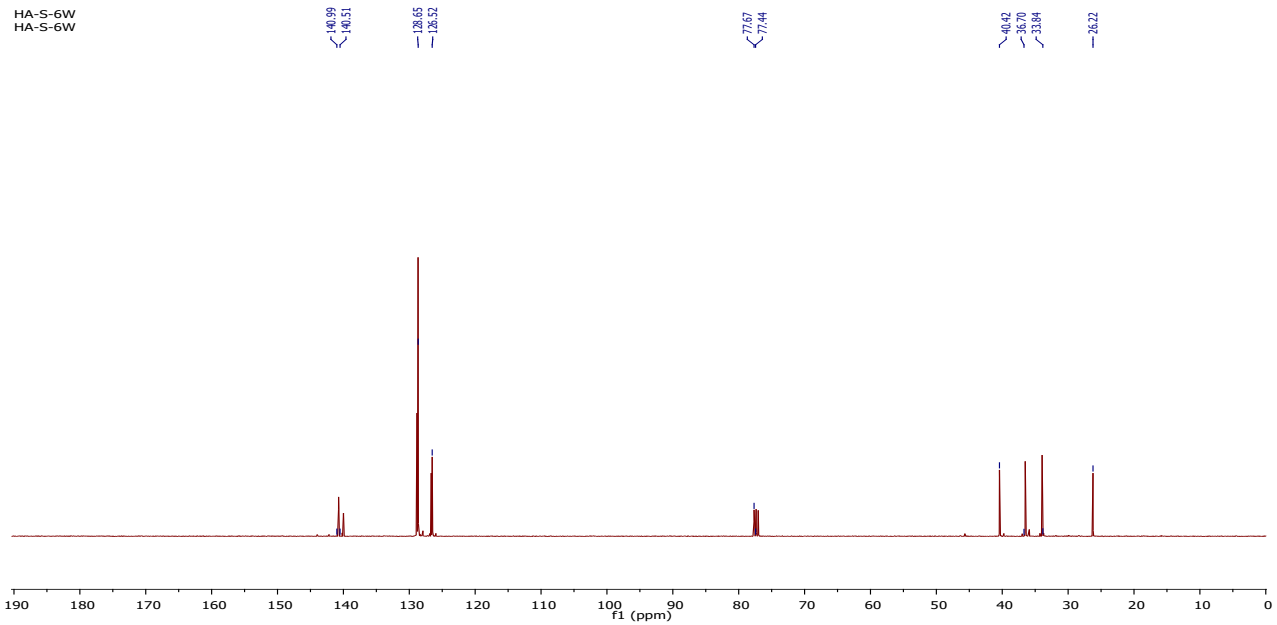
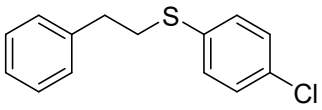


Fig. S44 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3c).**



1-Chloro-4-[(2-phenylethyl)thio]benzene (3d)

The above compound was synthesized using the standard process involving styrene (1.20 mmol) and 4-chloro thiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of (**3d**) in the form of colorless oil (196.26 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.37 (m, 2H), 7.33-7.31(m, 5H), 7.27 (d, 2H), 3.21(d, 2H), 2.99 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 135.2, 132.1, 130.6, 129.4, 129.1, 128.7, 126.7, 35.7, 35.4.

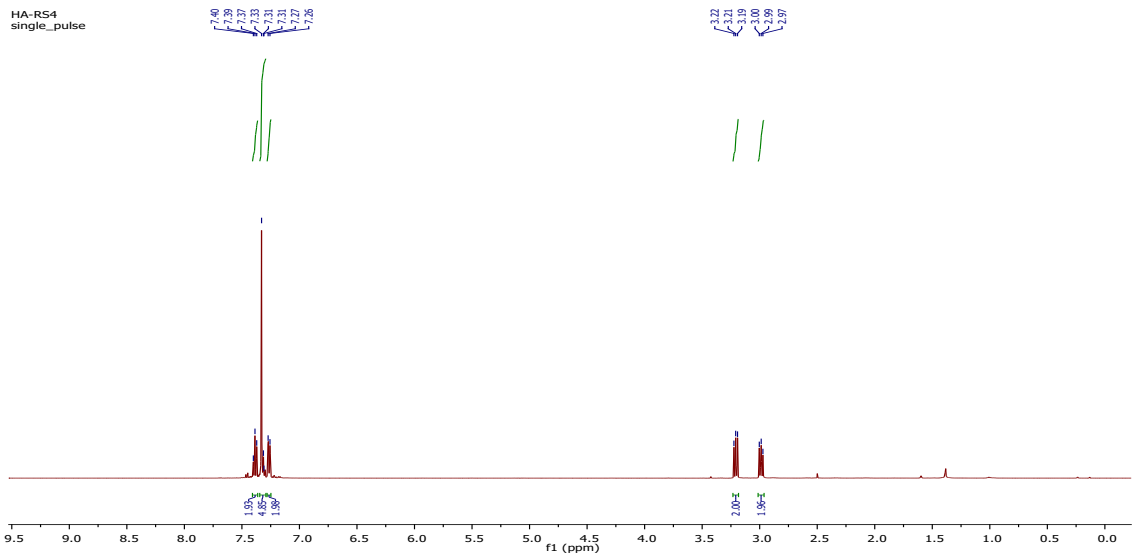


Fig. S45 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3d)**.

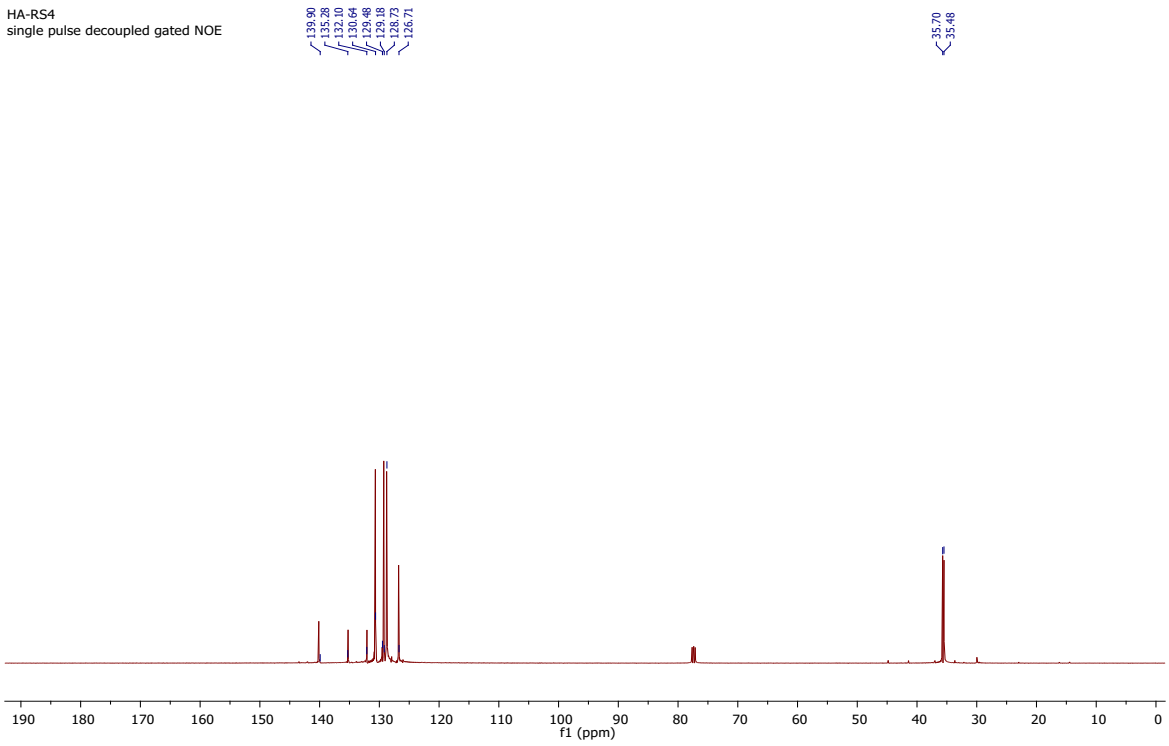
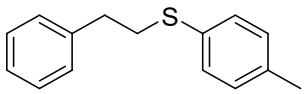


Fig. S46 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3d)**



1-Methyl-4-[(2-phenylethyl)thio]benzene (3e)

The above compound was synthesized using the standard process involving styrene (1.20 mmol) and 4-methyl thiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of (**3e**) in the form of colorless oil (194.09 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.22(m, 4H), 7.17-7.11(m, 3H), 7.05 (d, 2H), 3.07(t, 2H), 2.85(t, 2H), 2.27(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 136.2, 130.0, 132.8, 130.2, 129.9, 128.7, 126.6, 36.0, 35.9, 21.2.

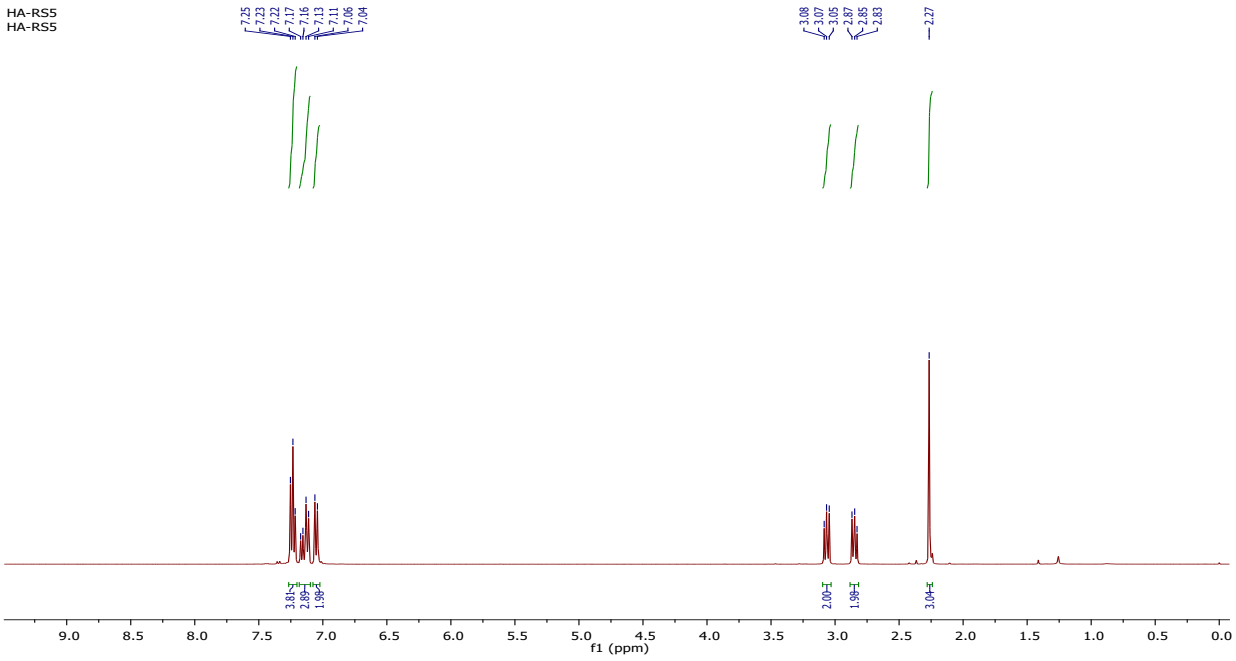


Fig. S47 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3e)**.

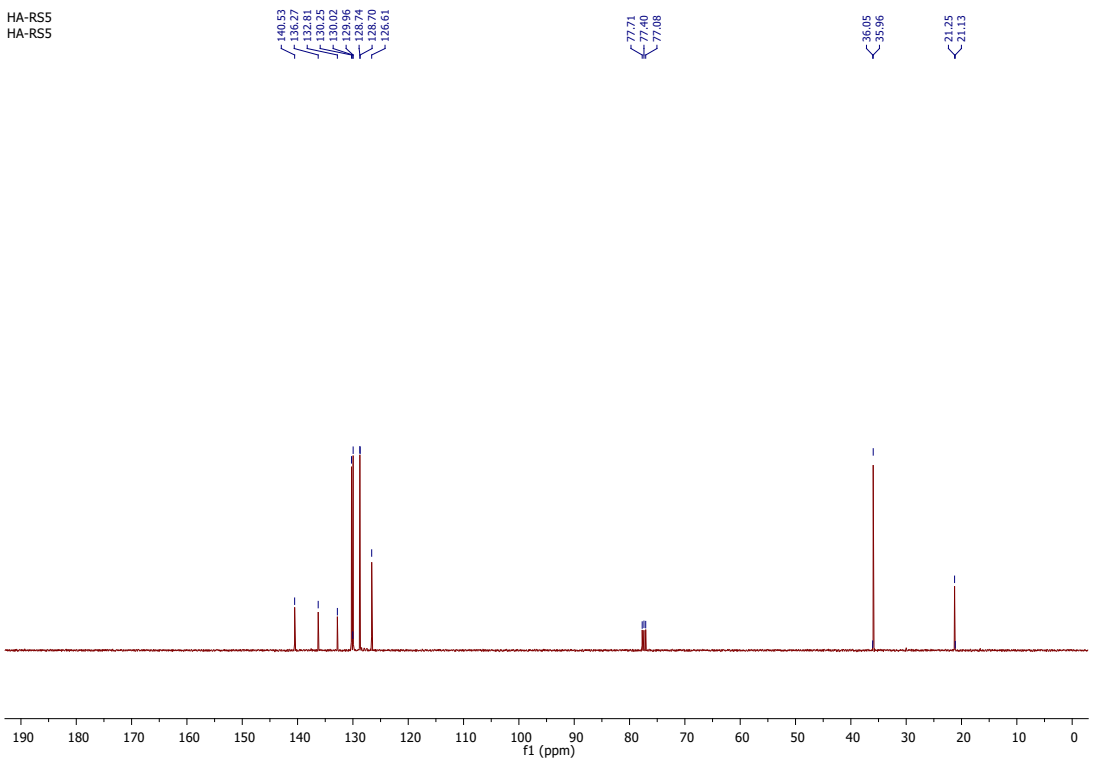
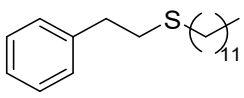


Fig. S48 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3e)**



[2-(Dodecylthio)ethyl]benzene (3f)

The above compound was synthesized using the standard process involving styrene (1.20 mmol) and dodecanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3f)** in the form of colorless oil (186.35 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.26 (m, 2H), δ 7.20 – 7.08 (m, 3H), δ 2.89 – 2.85 (m, 2H), δ 2.77 – 2.73 (m, 2H), δ 2.53 – 2.49 (m, 2H), 1.61-1.50 (m, 3H), 1.26 (broad s, 17H), 0.90-0.86 (t, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 128.6, 128.3, 126.0, 36.4, 34.0, 32.5, 32.1, 30.1,29.8, 29.7, 29.6, 29.4, 29.3, 29.2, 29.0, 22.5, 14.1.

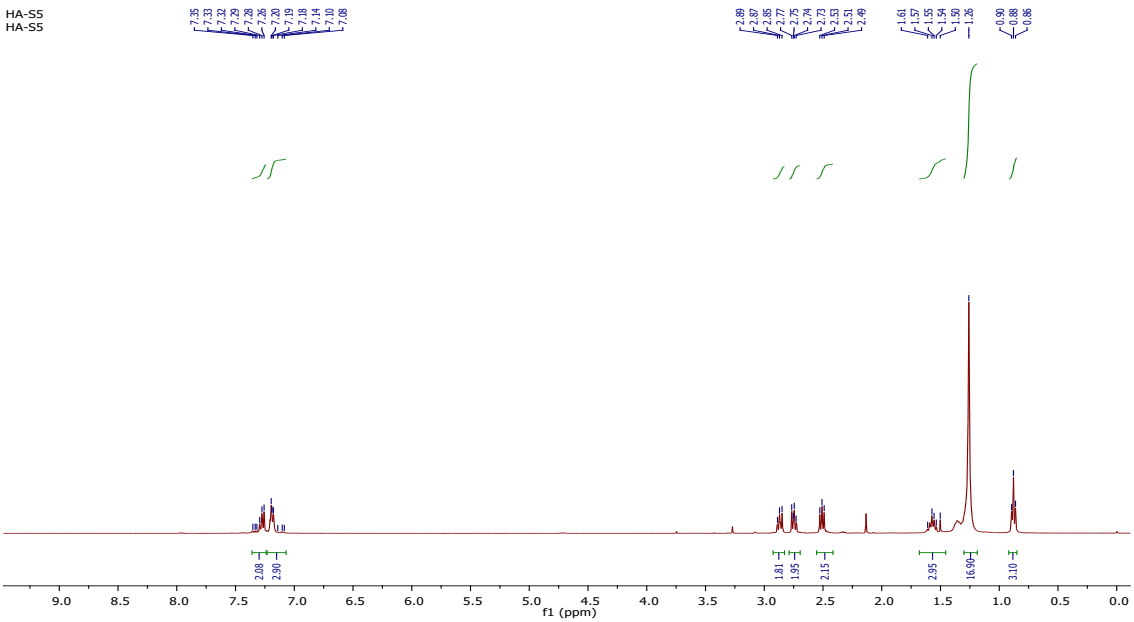


Fig. S49 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3f)**.

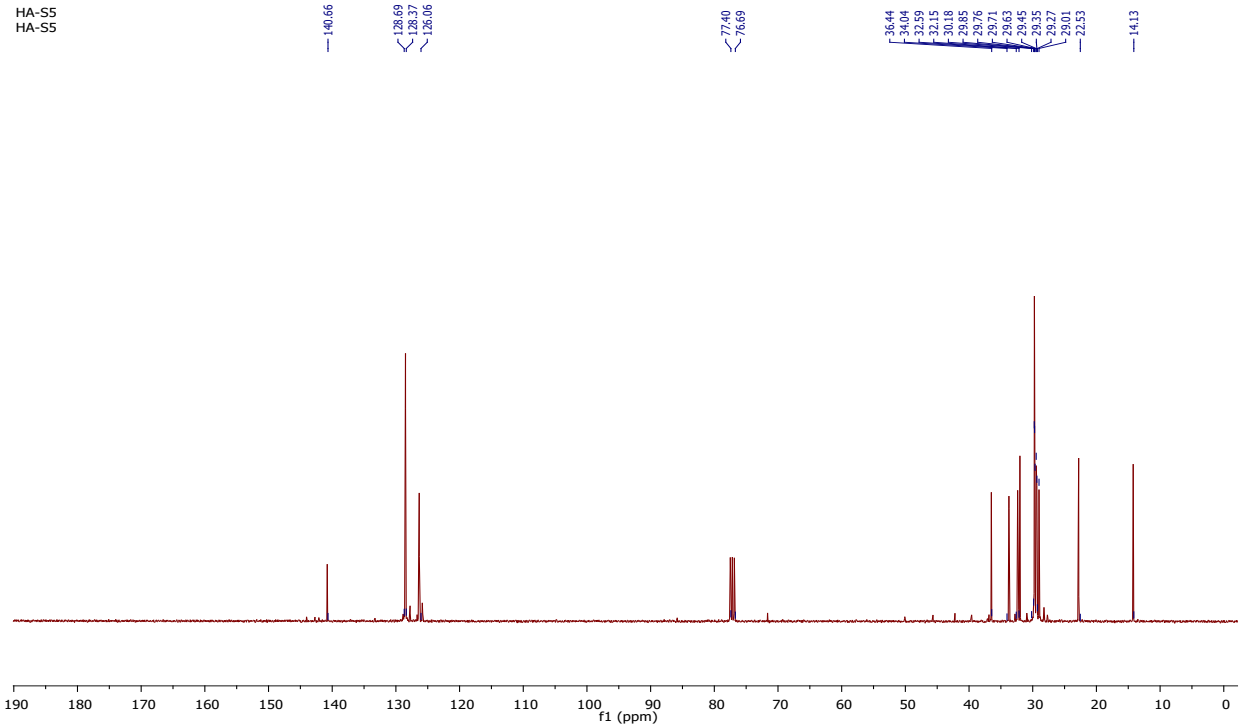
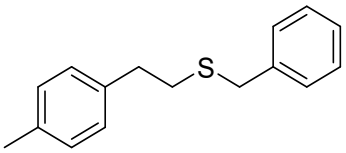


Fig. S50 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3f)**.



1-Methyl-4-[2-[(phenyl methyl)thiol]ethyl]benzene (3g)

The above compound was synthesized using the standard process involving 4-methylstyrene (1.20 mmol) and benzyl thiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3g)** in the form of colorless oil (208.69 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.16 (m, 5H), 7.05-6.98 (m, 4H), 2.65 (s, 2H), 2.75 (t, 2H), 2.59 (t, 2H), 2.27 (s, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 137.6, 135.9, 129.3, 129.1, 128.6, 128.5, 127.1, 36.5, 35.7, 33.1. 21.2.

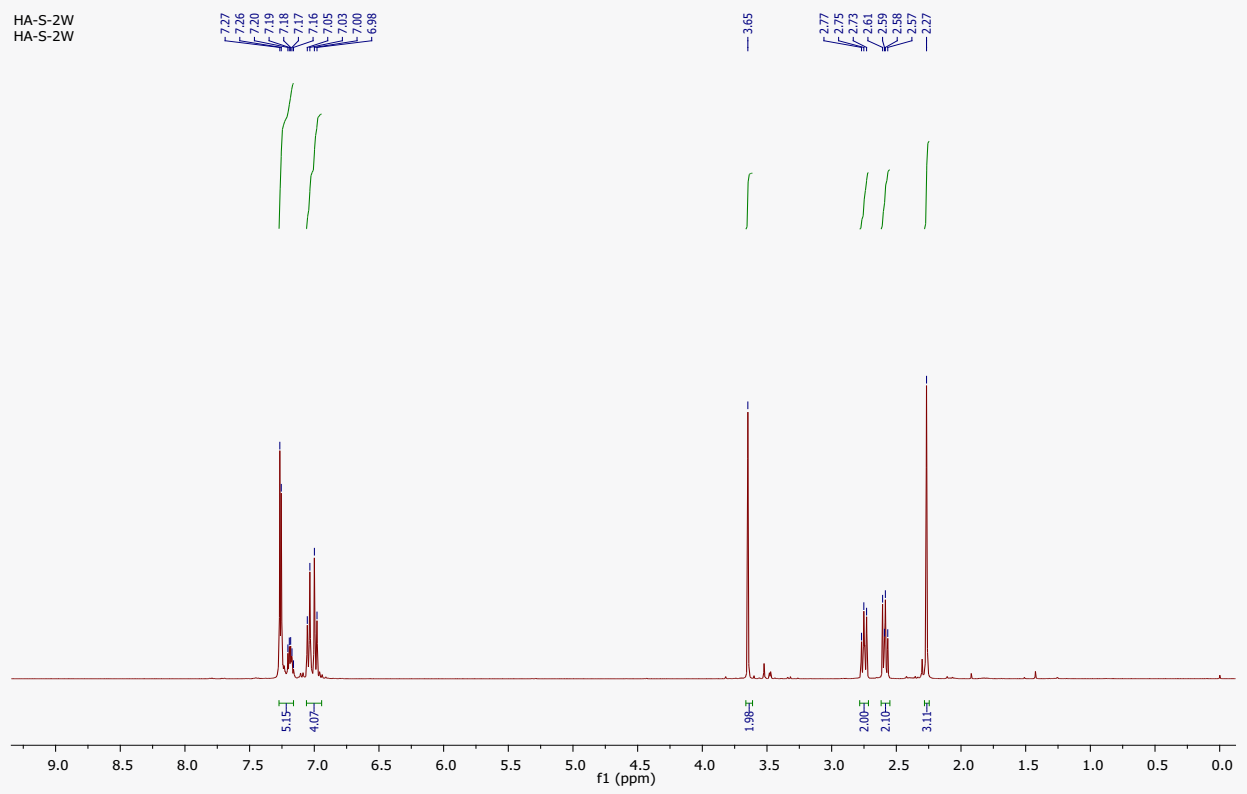


Fig. S51 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3g)**.

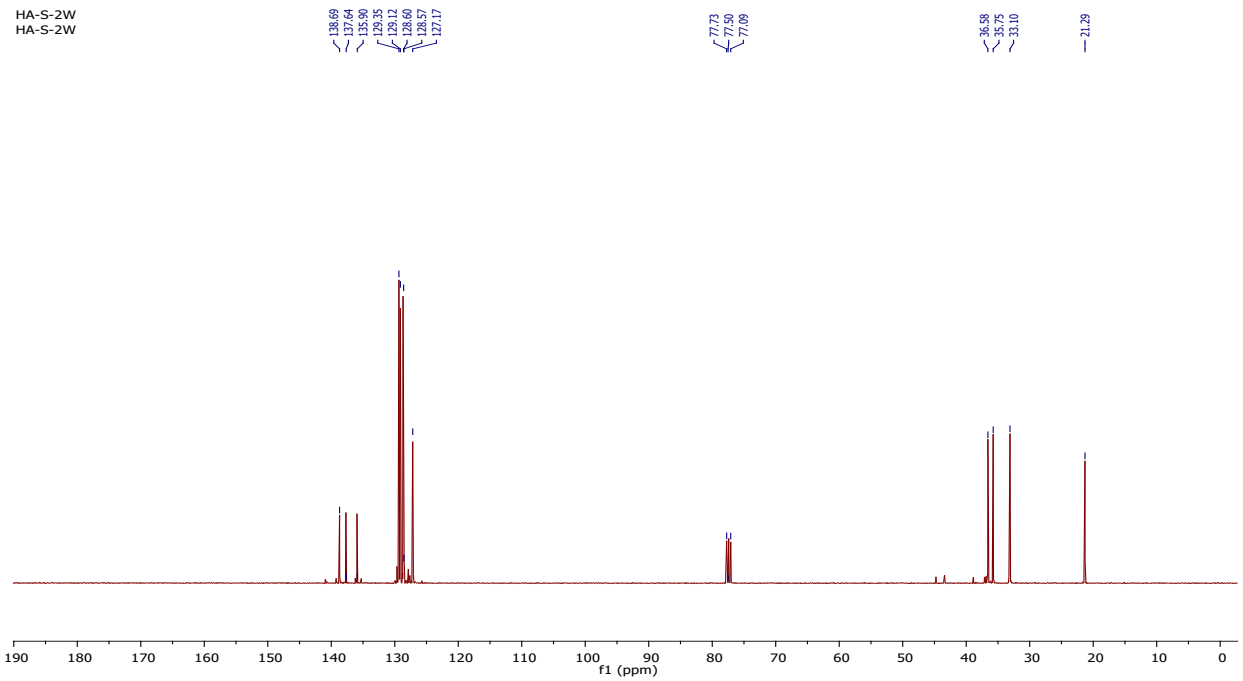
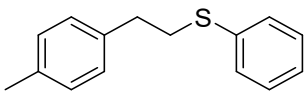


Fig. S52 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3g)**.



1-Methyl-4-[2-(phenylthio) ethyl] benzene (3h)

The above compound was synthesized using the standard process involving 4-methylstyrene (1.20 mmol) and thiophenol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3h)** in the form of colorless oil (205.65 mg, 90 %). ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.31 (m, 2H), 7.26–7.22 (m, 2H), 7.16–6.96 (m, 5H), 2.58–2.53 (m, 1H), 3.90 (t, 2H), 2.85 (t, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 136.7, 136.1, 129.4, 129.2, 129.0, 128.5, 126.0. 35.3, 21.4, 21.3.

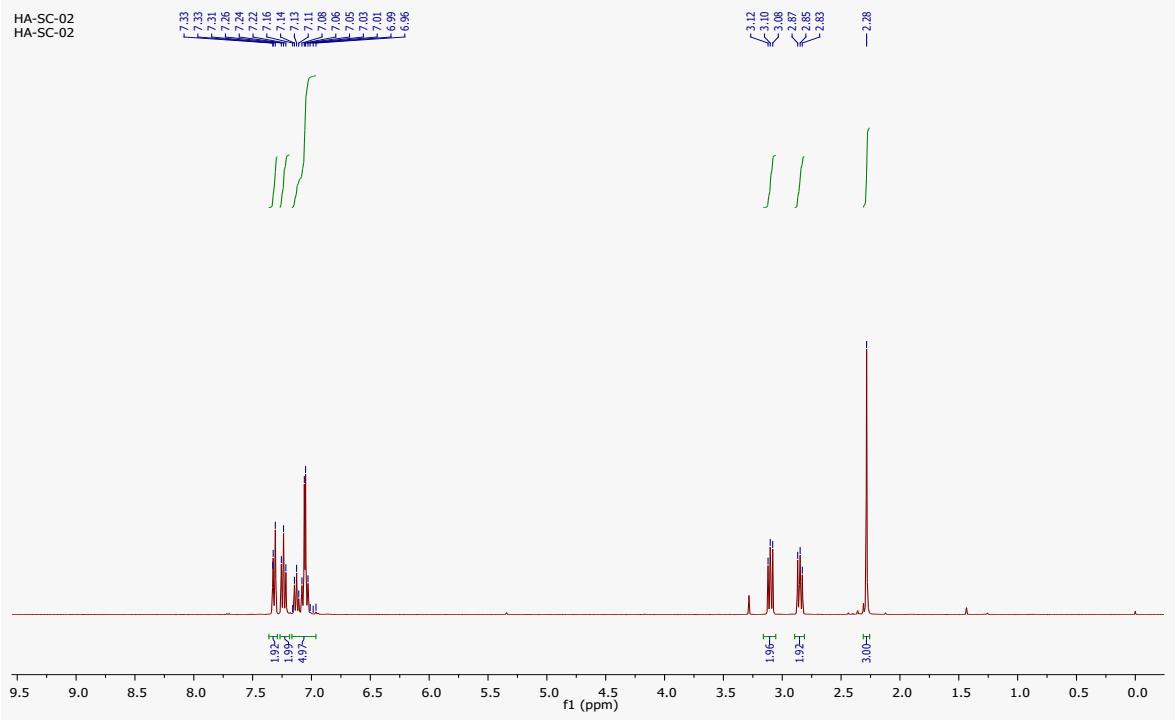


Fig. S53 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3h)**.

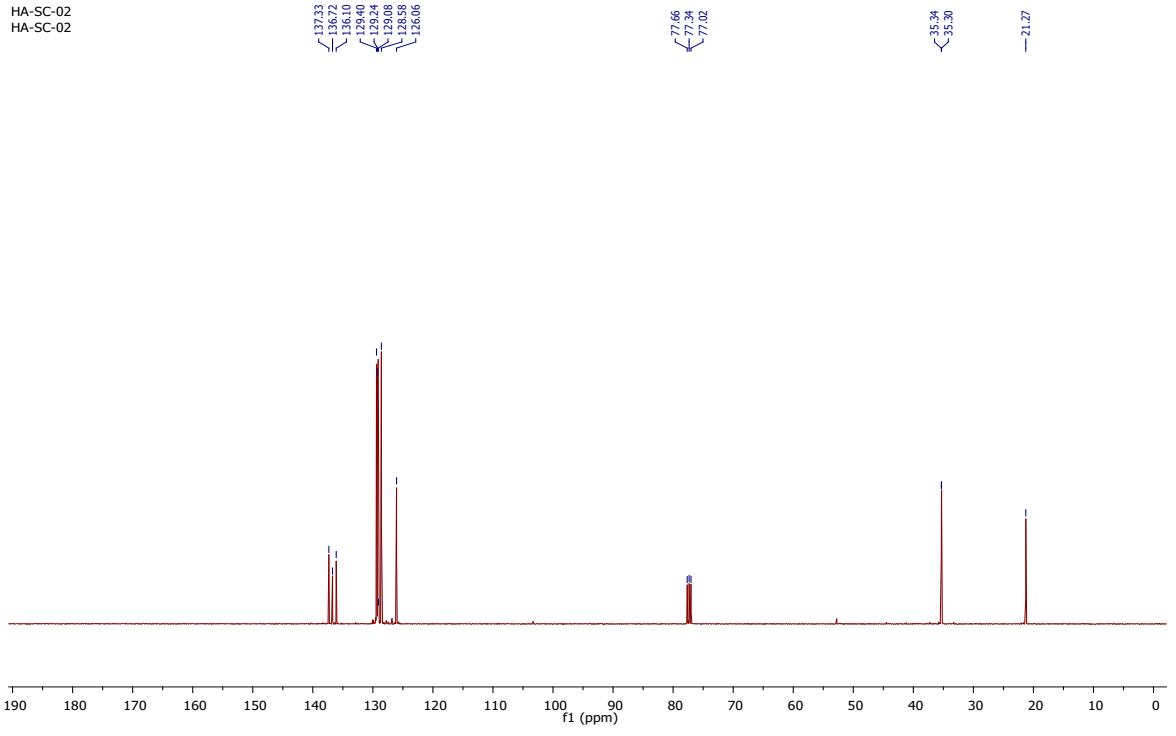
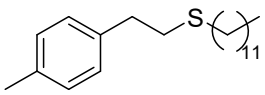


Fig. S54 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3h)**.



1-[2-(Dodecylthio)ethyl]-4-methylbenzene (3i)

The above compound was synthesized using the standard process involving 4-methylstyrene (1.20 mmol) and dodecanethiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3i)** in the form of colorless oil (189.58 mg, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.29 (m, 2H), 7.22-7.20 (m, 2H), 2.94-2.85 (m, 2H), 2.81-2.72 (m, 2H), 2.73-2.70 (m, 2H), 2.17 (s, 1H), 2.06-1.96 (m, 4H), 1.80-1.77 (m, 4H), 1.67-1.57 (m, 3H), 1.36-0.82 (m, 14H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 128.6, 127.6, 126.4, 49.9, 49.7, 44.1, 43.5, 43.2, 36.7, 33.7, 32.8, 31.6, 30.8, 30.0, 29.7, 26.1, 25.8, 25.7.

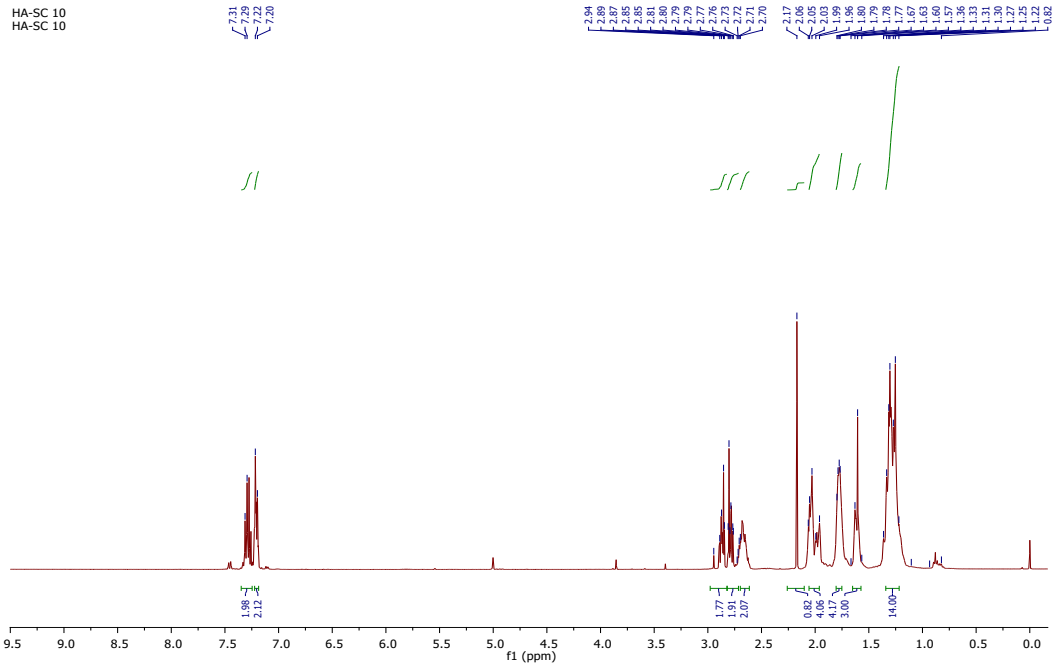


Fig. S55 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3i)**.

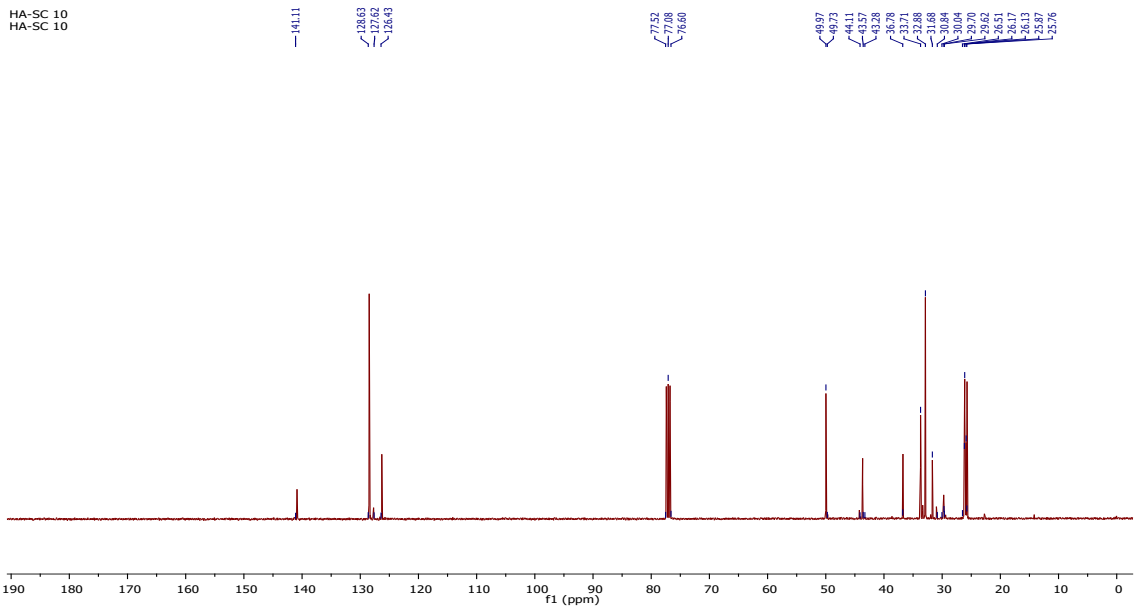
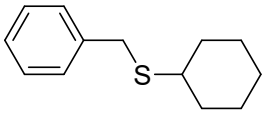


Fig. S56 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3i)**.



Cyclohexylsulfanylmethyl-benzene (3j)

The above compound was synthesized using the standard process involving cyclohexene (1.20 mmol) and benzyl thiol (1.0 mmol). Column chromatography was used to purify the raw product, and hexane was used as eluting solvent. This resulted in the production of **(3j)** in the form of colorless oil (171.40 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.18 (m, 5H), 3.76 (s, 2H), 2.58-2.53 (m, 1H), 1.92-1.75 (m, 2H), 1.74-1.73 (m, 2H), 1.59-1.54 (m, 1H), 1.36-1.18 (m, 5H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 129.4, 128.8, 126.8, 43.1, 34.8, 33.3, 26.1, 25.9.

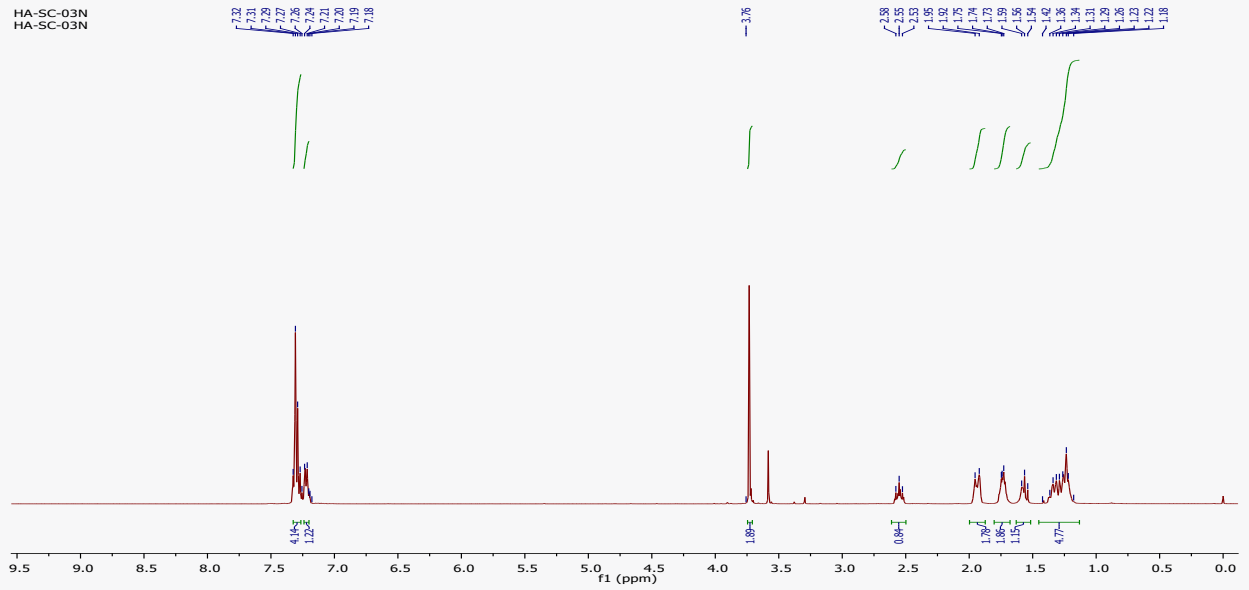


Fig. S57 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **(3j)**.

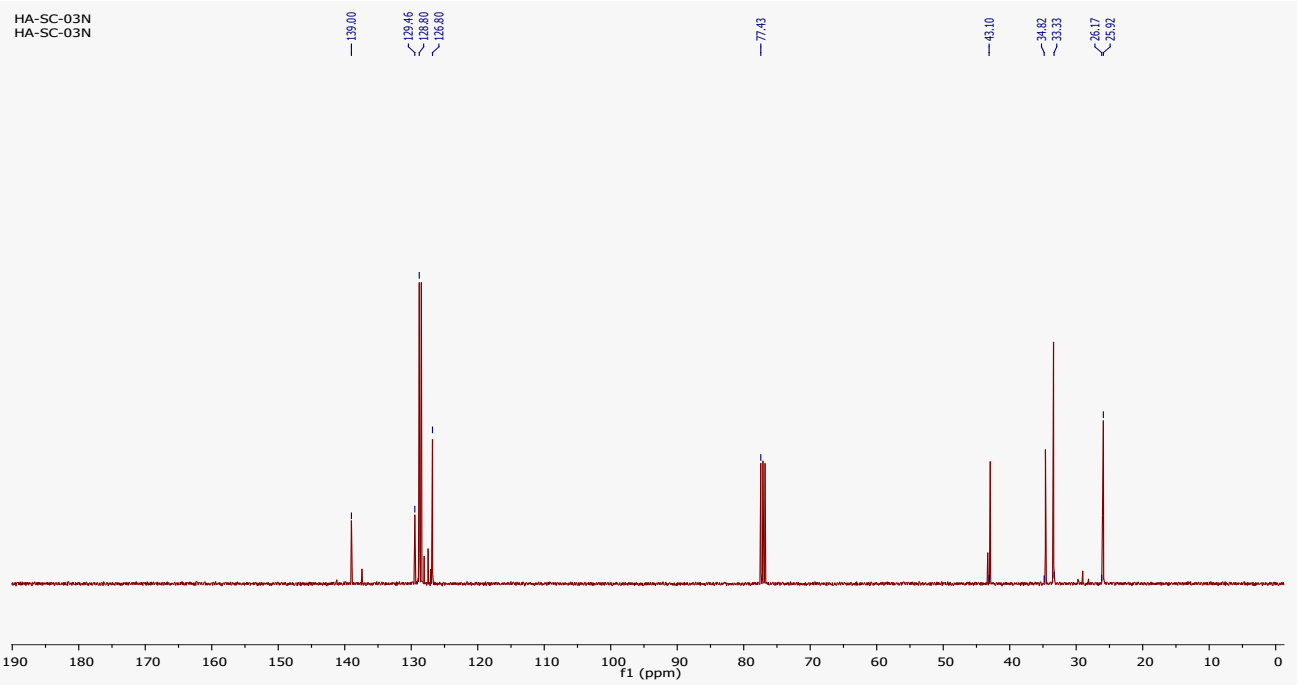


Fig. S58 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **(3j)**.

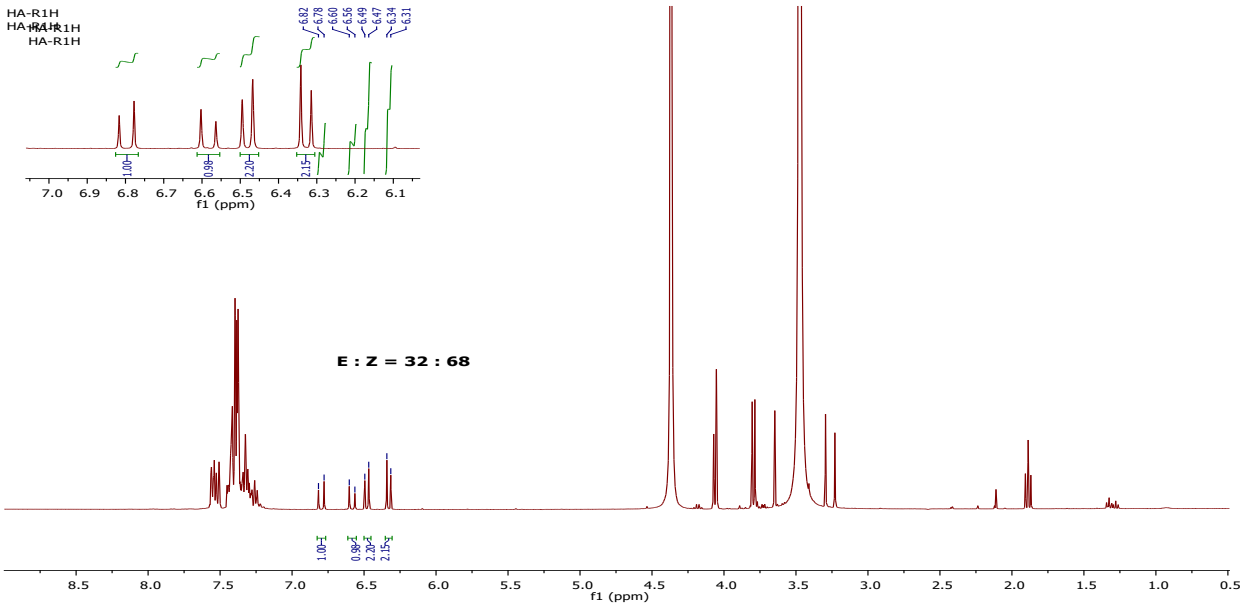


Fig. S59 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the crude product at 60℃.

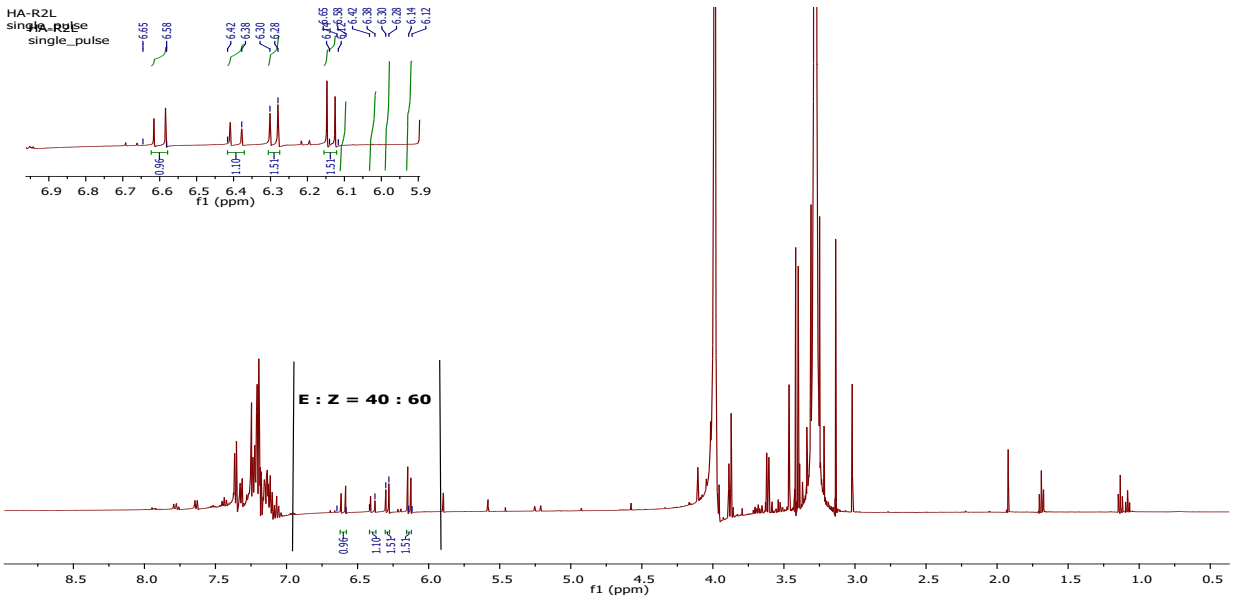


Fig. S60 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the crude product at 0℃.

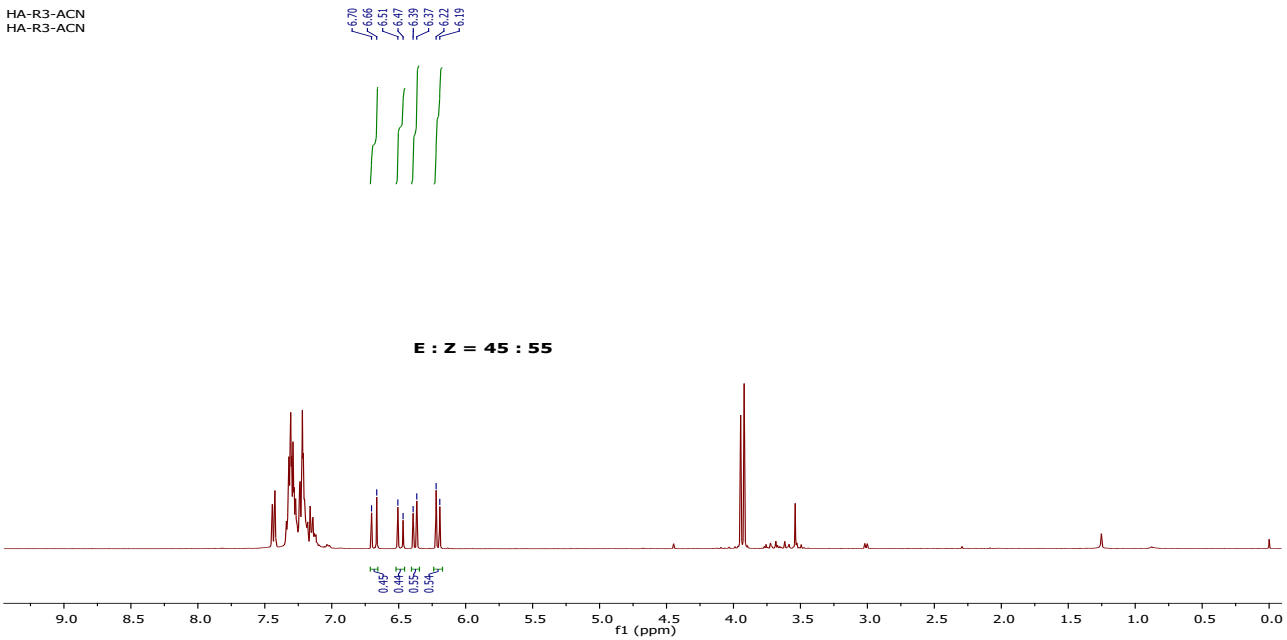


Fig. S61 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of benzylstyrysulphide using acetonitrile as reaction media.

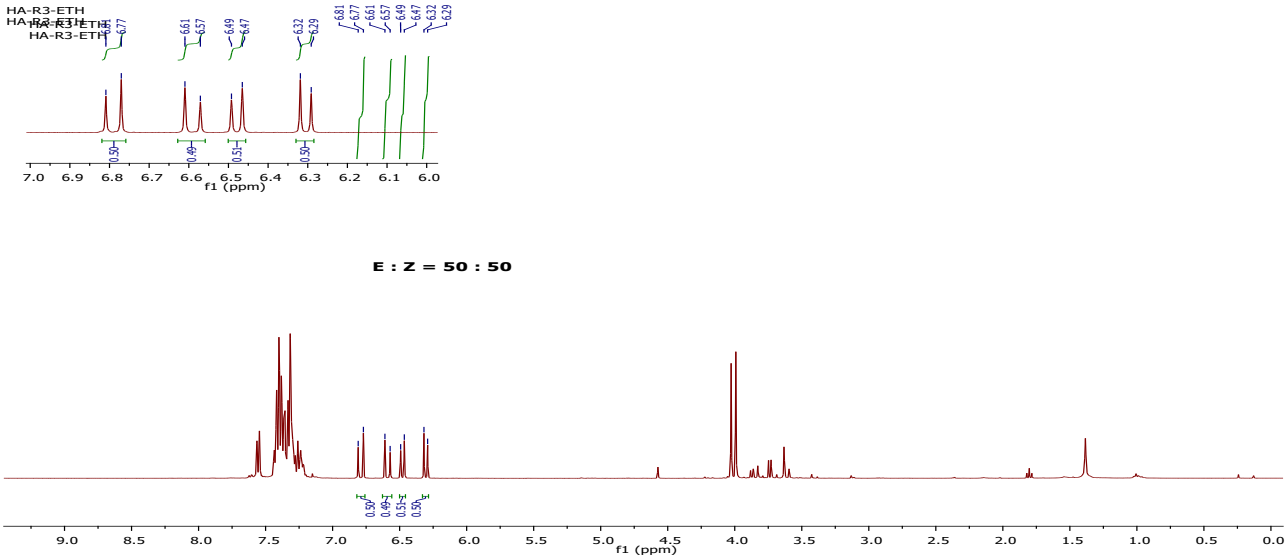


Fig. S62 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of benzylstyrysulphide using ethylacetate as reaction media.

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