

## Supporting Information

### Stereoselective Thiosulfonylation of Alkynes Using Sodium Thiosulfate as a Sulfur Transfer Agent to Access Bis-Z-Vinyl Sulfones

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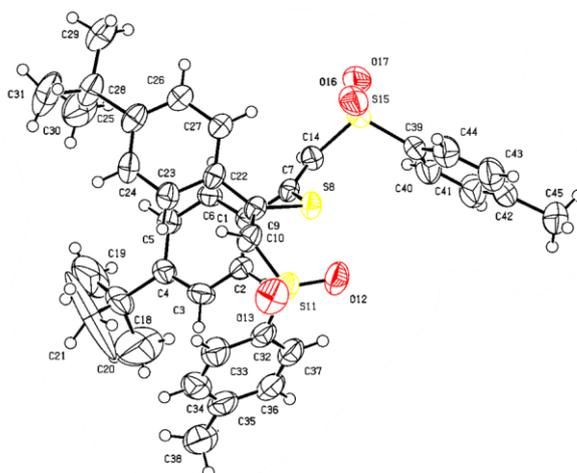
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## X-Ray Crystallographic Studies of 3cb



**Figure 1: ORTEP diagram for each molecule of the asymmetric unit of compound 3cb drawn with 50% ellipsoid probability.**

High-quality crystals of **3cb** were procured through  $\text{CHCl}_3$ . The compound **3cb** exhibited crystallization within the Monoclinic crystal system, possessing the space group P 21/c. Single-crystal X-ray data were systematically gathered using an Oxford XCalibur CCD diffractometer, employing graphite monochromated Mo  $K\alpha$  radiation. The structural elucidation was accomplished through the implementation of SIR-92, and subsequent refinement ensued via a full matrix least square technique on F<sup>2</sup>, facilitated by the SHELXL-97 program within the WinGX v 1.80.05 software package. Comprehensive data, encompassing atomic coordinates, bond lengths, bond angles, and thermal parameters for the 6aa compound, have been deposited at the Cambridge Crystallographic Data Centre. The CCDC deposit number associated with 3cb is 2495741.

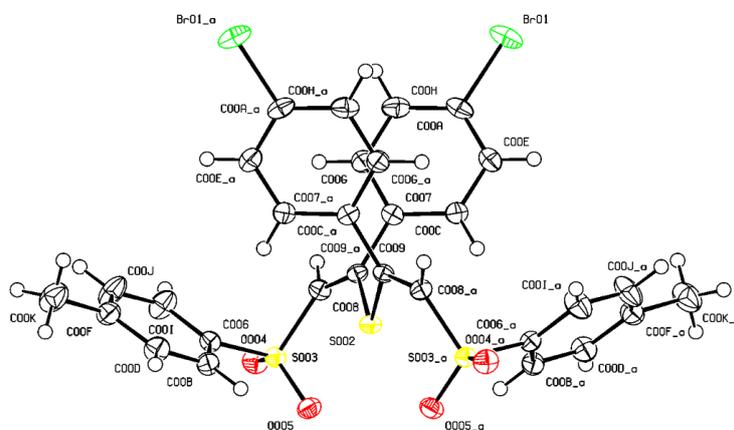
**Table S1: Crystallographic data and structure refinement for compound 3cb**

Identification code	<b>3cb</b>	
Empirical formula	$\text{C}_{38} \text{H}_{42} \text{O}_4 \text{S}_3$	
Formula weight	658.89	
Temperature	298 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	$a = 6.9287(4)$	$\alpha = 90$

	b = 24.5829(13)	$\beta = 93.895(5)$
	c = 20.8338(11)	$\gamma = 90$
Volume	3540.4(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.236 g/cm <sup>3</sup>	
Absorption coefficient	0.247 mm <sup>-1</sup>	
F(000)	1400.0	
Index ranges	h= 8, k = 28, l = 24	
Reflections collected	0.0816(4427)	
Completeness to theta = 26.37 °	99.9 %	
Final R indices [I>2 sigma(I)] <sup>a,b</sup>	R1 = 0.0816, wR2 = 0.2223	

$$^a R = \sum(|F_o| - |F_c|) / \sum |F_o| ; ^b R_w = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

### X-Ray Crystallographic Studies of **3ib**.



**Figure 2: ORTEP diagram for each molecule of the asymmetric unit of compound **3ib** drawn with 50% ellipsoid probability.**

High-quality crystals of **3ib** were procured through CHCl<sub>2</sub>/*n*-hexane. The compound **3ib** exhibited crystallization within the Monoclinic crystal system, possessing the space group I 2/a. Single-crystal X-ray data were systematically gathered using an Oxford XCalibur CCD diffractometer, employing graphite monochromated Mo K $\alpha$  radiation. The structural elucidation was accomplished through the implementation of SIR-92, and subsequent refinement ensued via a full matrix least square technique on F<sub>2</sub>, facilitated by the SHELXL-

97 program within the WinGX v 1.80.05 software package. Comprehensive data, encompassing atomic coordinates, bond lengths, bond angles, and thermal parameters for the 6aa compound, have been deposited at the Cambridge Crystallographic Data Centre. The CCDC deposit number associated with 3ib is 2495738.

**Table SII: Crystallographic data and structure refinement for compounds 3ib**

Identification code	<b>3ib</b>	
Empirical formula	C <sub>30</sub> H <sub>24</sub> Br <sub>2</sub> O <sub>4</sub> S <sub>3</sub>	
Formula weight	704.47	
Temperature	153 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 16.6288(7)	α = 90
	b = 9.5465(4)	β = 107.989(5)
	c = 19.9075(9)	γ = 90
Volume	3005.8 (2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.557 g/cm <sup>3</sup>	
Absorption coefficient	2.939 mm <sup>-1</sup>	
F(000)	1416.0	
Index ranges	h= 22, k = 12, l = 26	
Reflections collected	0.0335(3035)	
Completeness to theta = 26.37 °	79.9%	
Final R indices [I>2 sigma(I)] <sup>a,b</sup>	R1 = 0.0335, wR2 = 0.0745	

$$^a R = \sum(|F_o| - |F_c|) / \sum |F_o| ; ^b R_w = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

**References:**

1. CrysAlisPro, Agilent Technologies, Version 1.171.34.49, 2011.
2. Sheldrick, G. M., *Acta Cryst.* 2008, *A64*, 112.
3. Farrugia, L. J. WinGX Version 1.80.05, An integrated system of Windows Programs for

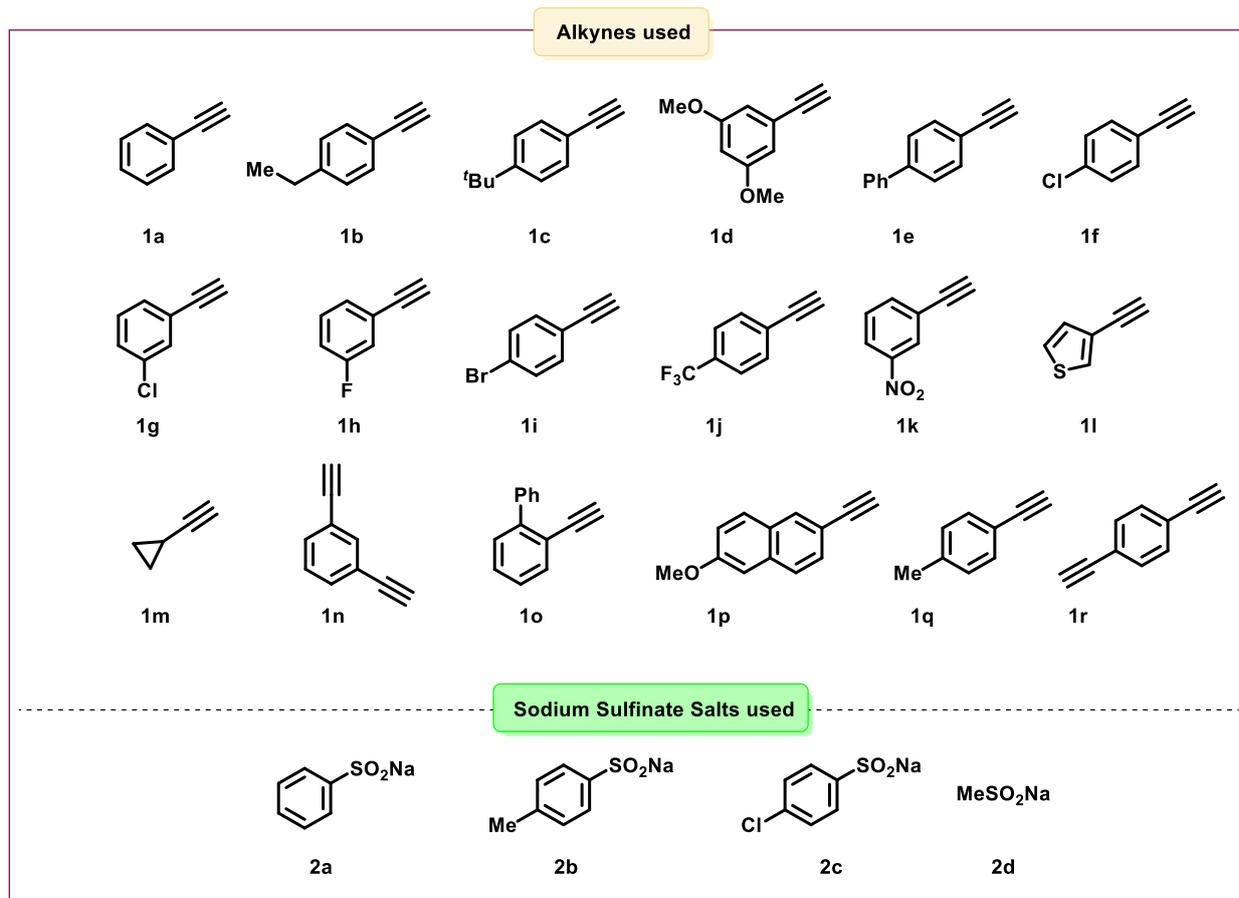
the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data; Department of Chemistry, University of Glasgow, 1997-2009.

4. (a) Foresman, J. B.; Frisch, A. E. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA. 1995. (b) Hehre, W. J., Radom, L., Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1985.

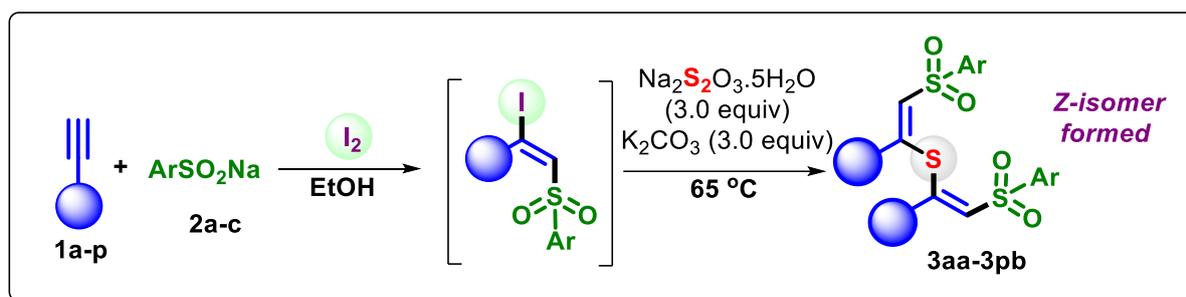
### **General Experimental**

**General Method.**  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) spectra were recorded in  $\text{CDCl}_3/(\text{CD}_3)_2\text{SO}$ . Chemical shifts for protons and carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constants in Hertz and integration. High resolution mass spectra (HRMS) were recorded on an Agilent 6500 series B5125 mass spectrometer (ESI-TOF). Crystal structure analysis was accomplished on single needles X-ray diffractometer. TLC analysis was performed on commercially prepared 60 F<sub>254</sub> silica gel plates. All purchased chemicals were used as received. All melting points are uncorrected. Starting materials 1 and 2 was purchased from Sigma-Aldrich Chemical Co. and were used without further purification unless otherwise stated.

## List of Starting substrates Used :



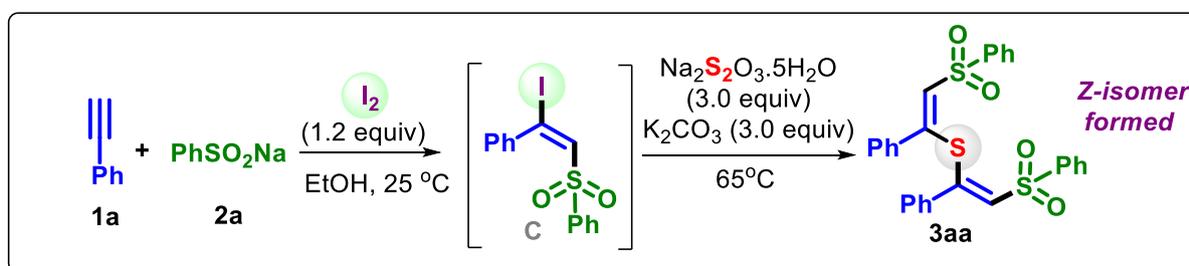
## General Procedure for the Synthesis of bis-(Z)-vinyl sulphones :



In a 10 mL oven-dried round bottom flask, phenylacetylene or its derivatives **1** (0.20 mmol, 1.0 equiv.), sodium salts of benzenesulfinic acid **2a-c** (0.30 mmol, 1.5 equiv.), 1.2 equiv of  $I_2$  in 2.0 mL EtOH was taken and stirred at room temperature for 2 h. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the solution of 3.0 eq sodium thiosulfate ( $Na_2S_2O_3 \cdot 5H_2O$ ), 3.0 equiv.  $K_2CO_3$  in 2.0 mL EtOH was added

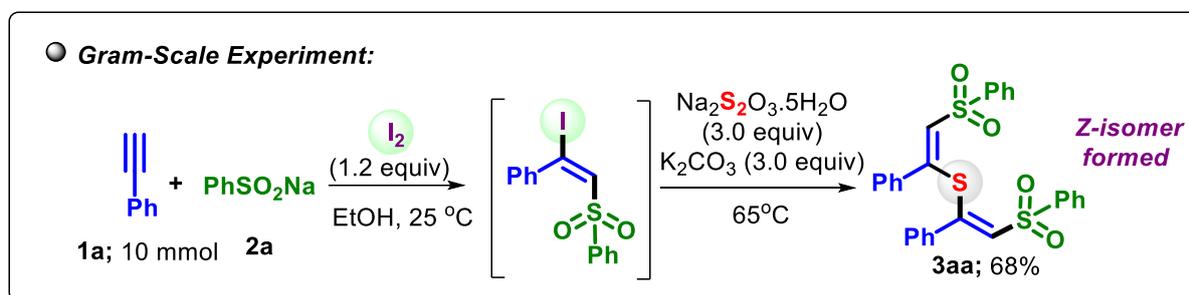
sequentially. Again, the reaction mixture was allowed to stir at 65°C for about 1 h. and progression of the reaction was monitored by TLC analysis. After the complete consumption of the starting material, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then, the organic layer was washed with an aqueous saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100–200) using hexane:ethyl acetate (80/20) as a mobile phase.

**Table SIII: Optimisation of reaction conditions:**



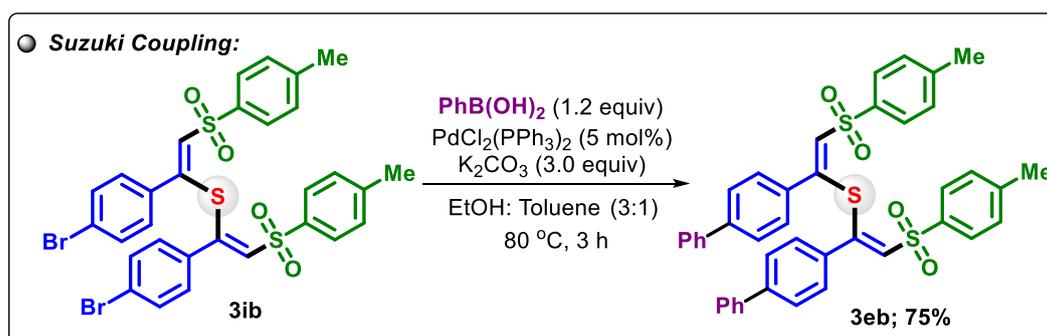
S.No.	Solvent	Base	Temp ( °C)	Yield (%)
1.	DMF	K <sub>2</sub> CO <sub>3</sub>	65	40
2.	THF	K <sub>2</sub> CO <sub>3</sub>	65	61
3.	CH <sub>3</sub> CN	K <sub>2</sub> CO <sub>3</sub>	65	55
4.	Dioxane	K <sub>2</sub> CO <sub>3</sub>	65	50
5.	Toluene	K <sub>2</sub> CO <sub>3</sub>	65	31
6.	DCM	K <sub>2</sub> CO <sub>3</sub>	65	25
7.	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	65	55
<b>8.</b>	<b>EtOH</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>65</b>	<b>70</b>
9.	EtOH	Cs <sub>2</sub> CO <sub>3</sub>	65	68
10.	EtOH	Et <sub>3</sub> N	65	44
11.	EtOH	KO <sup>t</sup> Bu	65	30
12.	EtOH	DIPEA	65	21
13.	EtOH	K <sub>2</sub> CO <sub>3</sub>	25	46
14.	EtOH	K <sub>2</sub> CO <sub>3</sub>	100	57

## General Procedure for the Gram-Scale Synthesis of bis-(Z)-vinyl sulphones :



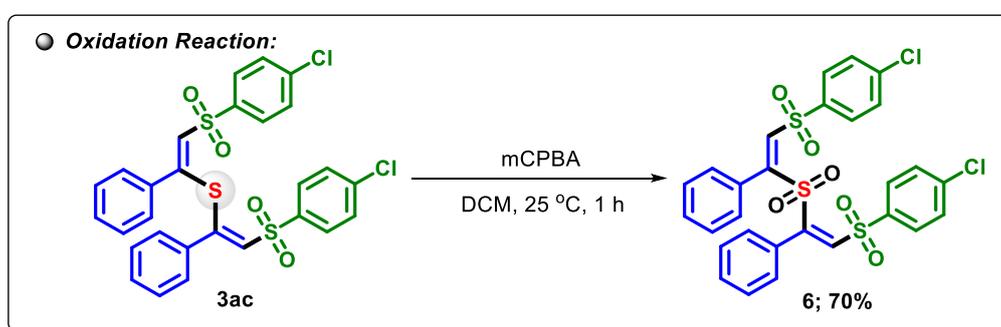
In a 100 mL oven-dried round bottom flask, phenylacetylene **1a** (10 mmol, 1.0 equiv.), sodium salts of benzenesulfonic acid **2a** (15 mmol, 1.5 equiv.), 1.2 equiv of I<sub>2</sub> in 2.0 mL EtOH was taken and stirred at room temperature for 2 h. Progression of the reaction was monitored by TLC analysis; after complete consumption of starting material, the solution of 3.0 eq sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O), 3.0 equiv. K<sub>2</sub>CO<sub>3</sub> in 2.0 mL EtOH was added sequentially. Again, the reaction mixture was allowed to stir at 65°C for about 1 h. and progression of the reaction was monitored by TLC analysis. After the complete consumption of the starting material, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then, the organic layer was washed with an aqueous saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100–200) using hexane:ethyl acetate (80/20) as a mobile phase to afford **3aa** in 68% yield.

## General Procedure for the Suzuki coupling of compound **3ib** to provide compound **3eb**:



In a 10 mL oven-dried round bottom flask, the obtained product **3ib** (0.2 mmol, 1.0 equiv), phenylboronic acid (0.26 mmol, 1.3 equiv.), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mol %), K<sub>2</sub>CO<sub>3</sub> (0.6 mmol, 3.0 equiv.) was taken in 3:1 DMF/H<sub>2</sub>O. The reactants were degassed and filled with N<sub>2</sub> for three times. Then the reaction mixture was stirred at 80 °C for 3 h. When the reaction was completed, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then organic layer was washed with aqueous saturated brine solution and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100–200) (hexane:ethyl acetate; 80/20) to afford the desired product **3eb** in 75% yield.

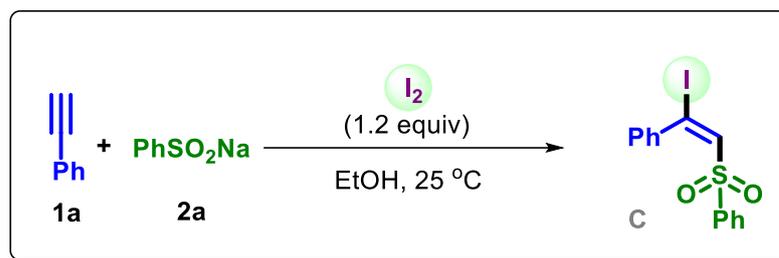
#### General Procedure for the synthesis of compound **6**:



In a 10 mL oven-dried round bottom flask, the obtained product **3ac** (0.2 mmol, 1.0 equiv), *m*-chloroperoxybenzoic acid (0.6 mmol, 3.0 equiv.), was taken in 2 mL DCM. Then the reaction mixture was stirred at 25°C for 1 h. When the reaction was completed, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then organic layer was washed with aqueous saturated brine solution and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100–200) (hexane:ethyl acetate; 80/20) to afford the desired product **6** in 70% yield.

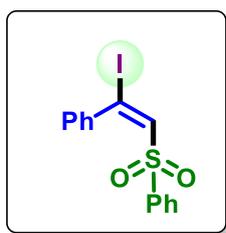
## Control Experiments

### Synthesis of Intermediate C:



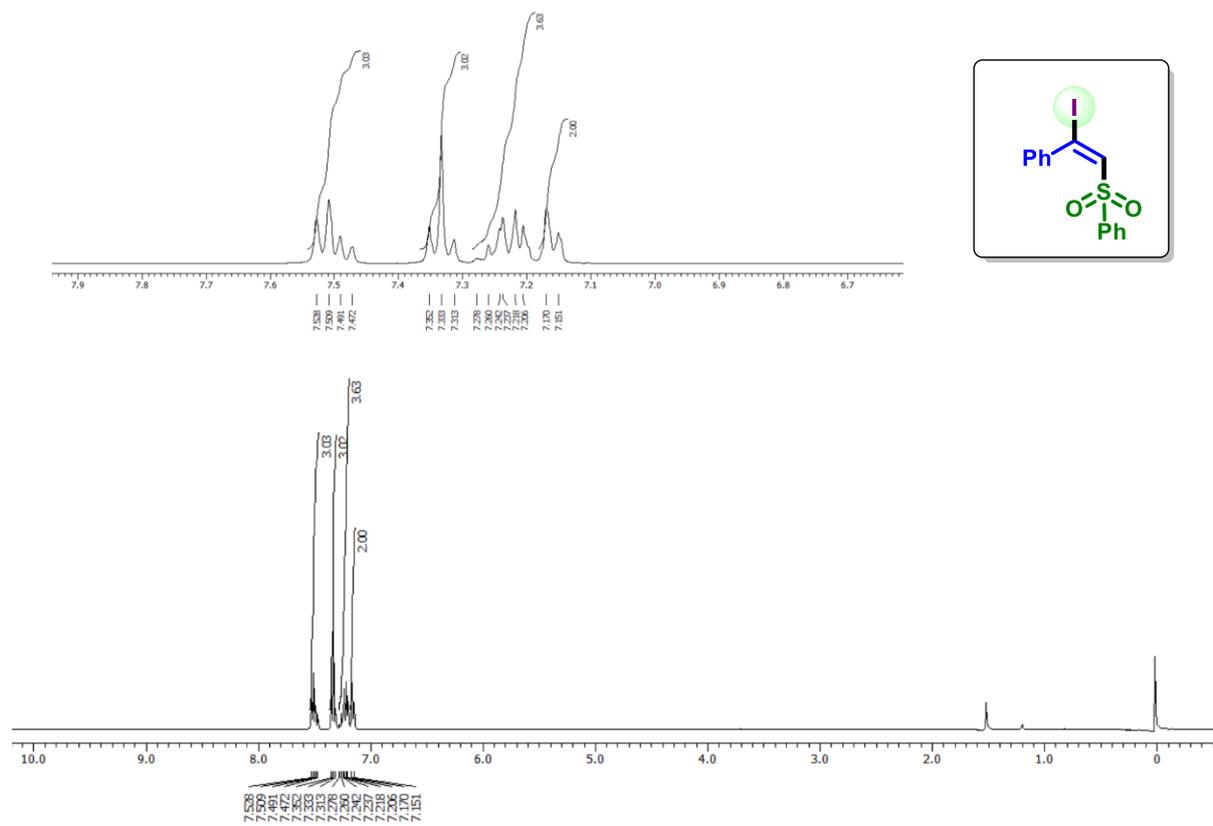
In a 10 mL oven-dried round bottom flask, phenylacetylene or its derivatives **1** (0.20 mmol, 1.0 equiv.), sodium salts of benzenesulfonic acid **2a-c** (0.30 mmol, 1.5 equiv.), 1.2 equiv of I<sub>2</sub> in 2.0 mL EtOH was taken and stirred at room temperature for 2 h and progression of the reaction was monitored by TLC analysis. After the complete consumption of the starting material, the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate. Then, the organic layer was washed with an aqueous saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude material obtained was purified by column chromatography on silica gel (100–200) using hexane:ethyl acetate (80/20) as a mobile phase to afford **C** in 75% yield.

### Characterization data for the intermediate C:

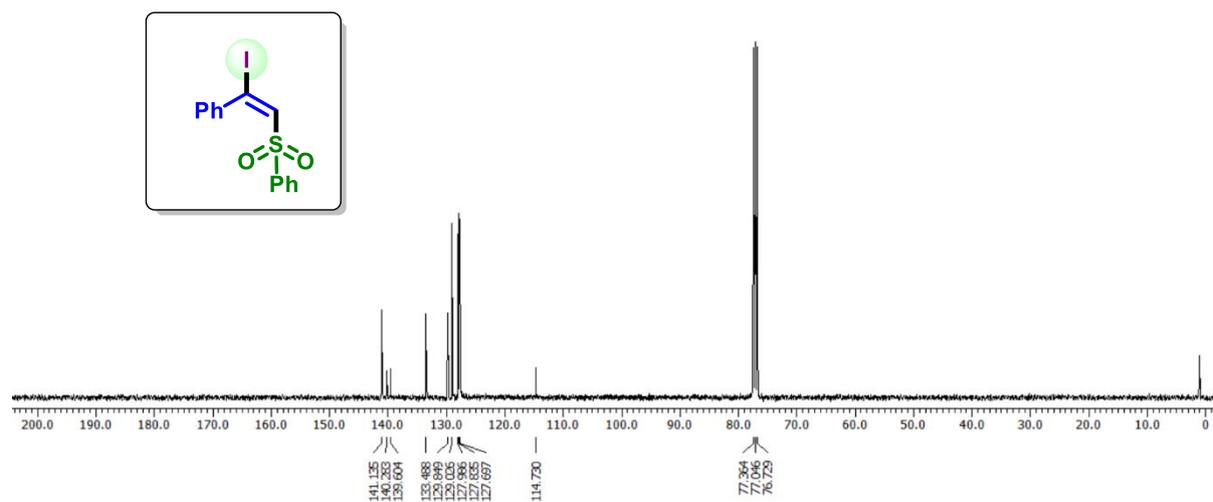


**(E)-1-iodo-2-(phenylsulfonyl)vinylbenzene (C)**. The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **C** as a white solid (Yield: 75%); m.p = 131-134 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (q, J = 7.4 Hz, 3H), 7.33 (t, J = 7.8 Hz, 3H), 7.28-7.21 (m, 3H + residual CDCl<sub>3</sub>), 7.16 (d, J = 7.5 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 141.1, 140.3, 139.6, 133.5, 129.8, 129.0, 128.0, 127.8, 127.7, 114.7; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>14</sub>H<sub>11</sub>IO<sub>2</sub>S] : 370.9603, found : 370.9612.

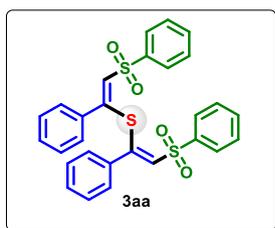
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



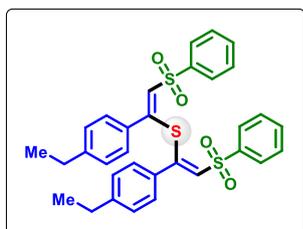
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



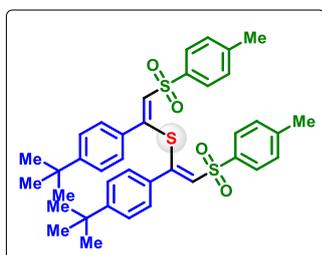
## Characterization data for the products:



**bis((Z)-1-phenyl-2-(phenylsulfonyl)vinyl)sulfane (3aa).** The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3aa** as a white solid (Yield: 70%); m.p = 120-122 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16-8.14 (m, 4H), 7.78-7.74 (m, 2H), 7.71-7.67 (m, 4H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.81-6.78 (m, 4H), 6.55 (s, 2H), 6.21 (dd, *J* = 8.3, 1.0 Hz, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 140.5, 137.5, 133.8, 131.1, 129.8, 129.2, 128.6, 128.2, 127.3; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>28</sub>H<sub>22</sub>O<sub>4</sub>S<sub>3</sub>] : 519.0758, found : 519.0731.

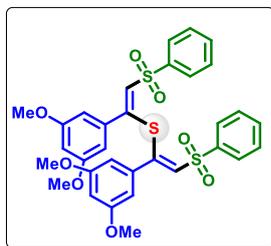


**bis((Z)-1-(4-ethylphenyl)-2-(phenylsulfonyl)vinyl)sulfane (3ba):** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **3ba** as a white solid (Yield: 72%); m.p = 112-114 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.5 Hz, 4H), 7.76-7.65 (m, 6H), 6.60 (d, *J* = 8.2 Hz, 4H), 6.51 (s, 2H), 6.12 (d, *J* = 8.1 Hz, 4H), 2.46 (q, *J* = 7.6 Hz, 4H), 1.10 (t, *J* = 7.6 Hz, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 152.9, 146.6, 140.8, 135.1, 133.7, 130.1, 129.1, 128.6, 127.8, 127.6, 127.3, 29.7, 15.6; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>32</sub>H<sub>30</sub>O<sub>4</sub>S<sub>3</sub>] : 575.1384, found : 575.1373.



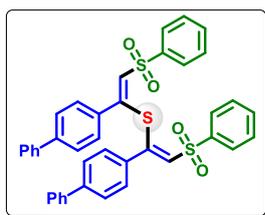
**bis((Z)-1-(4-(tert-butyl)phenyl)-2-(tosyl)vinyl)sulfane (3cb):** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **3cb** as a white solid (Yield: 70%); m.p = 144-146 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.4 Hz, 4H), 7.38 (d, *J* = 8.1 Hz, 4H), 6.69 (d, *J* = 8.4 Hz, 4H), 6.42 (s, 2H), 6.08 (d, *J* = 8.5 Hz, 4H), 2.43 (s, 6H), 1.13 (s, 18H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 153.0, 152.2, 144.6, 137.9,

134.8, 129.9, 129.6, 128.4, 127.0, 124.8, 34.4, 30.9, 21.6; HRMS (ESI)  $[M+H]^+$  Calcd for  $[C_{38}H_{42}O_4S_3]$  : 659.2323, found : 659.2312.



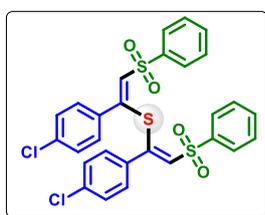
**bis((Z)-1-(3,5-dimethoxyphenyl)-2-(phenylsulfonyl)vinyl)sulfane**

**(3da).** The crude product was purified by column chromatography (hexane/EtOAc =70/30) to afford **3da** as a white solid (Yield: 80%); m.p = 172-174 °C;  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.07 (d,  $J$  = 5.3 Hz, 4H), 7.72-7.64 (m, 6H), 6.58 (s, 2H), 6.30 (s, 2H), 5.95-5.94 (s, 4H), 3.63 (s, 12H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  160.5, 152.5, 141.1, 139.6, 133.8, 130.0, 129.4, 128.1, 107.6, 106.1, 105.9, 102.9, 55.5; HRMS (ESI)  $[M+H]^+$  Calcd for  $[C_{32}H_{30}O_8S_3]$  : 639.1181, found : 639.1164.



**bis((Z)-1-([1,1'-biphenyl]-4-yl)-2-(phenylsulfonyl)vinyl)sulfane (3ea).**

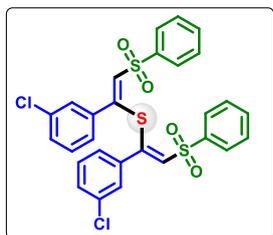
The crude product was purified by column chromatography (hexane/EtOAc =75/25) to afford **3ea** as a white solid (Yield: 73%); m.p = 153-156 °C;  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.18 (d,  $J$  = 7.3 Hz, 4H), 7.78 (t,  $J$  = 7.3 Hz, 2H), 7.71 (t,  $J$  = 7.5 Hz, 4H), 7.45-7.37 (m, 10H), 7.04 (d,  $J$  = 8.3 Hz, 4H), 6.62 (s, 2H), 6.37 (d,  $J$  = 8.3 Hz, 4H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  152.2, 142.8, 140.7, 139.5, 136.5, 133.9, 130.9, 129.3, 129.0, 128.6, 128.1, 127.9, 126.9, 126.8; HRMS (ESI)  $[M+H]^+$  Calcd for  $[C_{40}H_{30}O_4S_3]$  : 671.1384, found : 671.1392.



**bis((Z)-1-(4-chlorophenyl)-2-tosylvinyl)sulfane (3fa).**

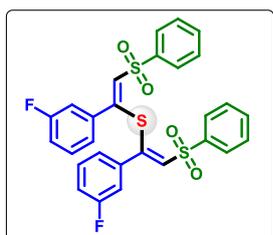
The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3fa** as a white solid (Yield: 60%); m.p = 148-150 °C;  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.04 (d,  $J$  = 7.5 Hz, 4H), 7.58 (dt,  $J$  = 27.5, 7.3 Hz, 6H), 7.37 (dd,  $J$  = 20.3, 8.5 Hz, 8H), 6.12 (s, 2H);  $^{13}C$ -

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.8, 137.5, 133.0, 130.3, 129.3, 129.2, 128.8, 127.7, 114.2; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>28</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>4</sub>S<sub>3</sub>] : 586.9979, found : 586.9982.



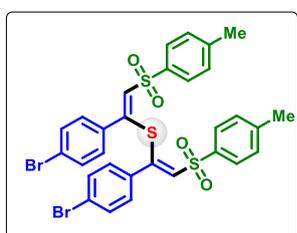
**bis((Z)-1-(3-chlorophenyl)-2-(phenylsulfonyl)vinyl)sulfane (3ga):**

The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3ga** as a white solid (Yield: 62%); m.p = 122-124 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, *J* = 7.5 Hz, 4H), 7.77 (t, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 4H), 7.13 (d, *J* = 7.3 Hz, 2H), 6.82 (t, *J* = 7.9 Hz, 2H), 6.57 (s, 2H), 6.22 (t, *J* = 7.8 Hz, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.1, 140.3, 139.1, 134.5, 134.1, 132.3, 130.0, 129.7, 129.5, 128.5, 127.3, 125.6 ; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>28</sub>H<sub>20</sub>Cl<sub>2</sub>O<sub>4</sub>S<sub>3</sub>] : 586.9979, found : 586.9965.



**bis((Z)-1-(3-fluorophenyl)-2-(phenylsulfonyl)vinyl)sulfane (3ha):**

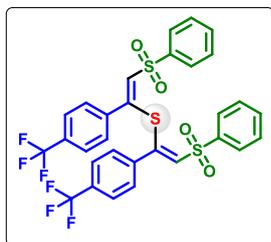
The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3ha** as a white solid (Yield: 60%); m.p = 130-132 °C <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, *J* = 7.8 Hz, 4H), 7.73 (dt, *J* = 29.9, 7.4 Hz, 6H), 6.83 (t, *J* = 5.4 Hz, 4H), 6.60 (s, 2H), 6.10 (t, *J* = 13.0 Hz, 2H), 5.95 (d, *J* = 9.3 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.2, 140.2, 139.5, 139.4, 134.1, 132.4, 130.1, 130.0, 129.4, 128.5, 123.2, 117.1, 116.9, 114.4, 114.2, 112.1; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [ C<sub>28</sub>H<sub>20</sub>F<sub>2</sub>O<sub>4</sub>S<sub>3</sub>] : 555.0570, found : 555.0582.



**bis((Z)-1-(4-bromophenyl)-2-(4-methylphenylsulfonyl)vinyl)sulfane (3ib).**

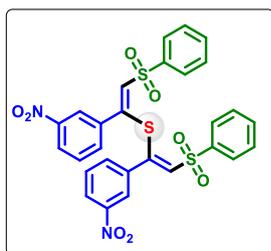
The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3ib** as a white solid (Yield: 65%); m.p = 168-170 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (d, *J* = 7.8 Hz, 4H), 7.47 (d, *J* = 7.8 Hz, 4H), 7.01 (d, *J* = 8.0 Hz, 4H), 6.56 (s, 2H), 6.20 (d, *J* = 8.0 Hz, 4H), 2.52 (s, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.1, 145.2, 137.5, 136.4, 132.3, 131.5,

129.9, 128.9, 128.6, 124.6, 21.8; HRMS (ESI)  $[M+H]^+$  Calcd for  $[C_{30}H_{24}Br_2O_4S_3]$  : 702.9282, found : 702.9276.



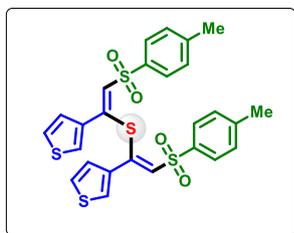
**bis((Z)-2-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)vinyl)**

**sulfane (3ja):** The crude product was purified by column chromatography (hexane/EtOAc =75/25) to afford **3ja** as a white solid (Yield: 58%); m.p = 202-206 °C;  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.08 (d,  $J$  = 7.6 Hz, 4H), 7.75-7.71 (m, 2H), 7.65 (d,  $J$  = 7.8 Hz, 4H), 7.03 (d,  $J$  = 8.2 Hz, 4H), 6.57 (s, 2H), 6.34 (d,  $J$  = 8.1 Hz, 4H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  149.6, 140.6, 140.1, 134.2, 133.3, 132.4, 132.1, 131.7, 131.4, 129.4, 128.5, 127.8, 125.3, 125.2; HRMS (ESI)  $[M+H]^+$  Calcd for  $[C_{30}H_{20}F_6O_4S_3]$  : 655.0506, found : 655.0515.



**bis((Z)-1-(3-nitrophenyl)-2-(phenylsulfonyl)vinyl)sulfane (3ka):** The

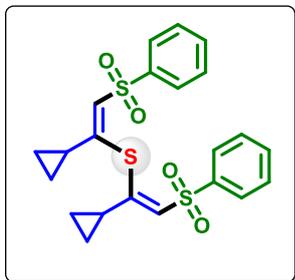
crude product was purified by column chromatography (hexane/EtOAc = 75/25) to afford **3ka** as a white solid (Yield: 60%); m.p = 190-192 °C  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.17 (d,  $J$  = 7.3 Hz, 4H), 8.03 (dd,  $J$  = 8.3, 1.3 Hz, 2H), 7.82 (t,  $J$  = 7.5 Hz, 2H), 7.74 (t,  $J$  = 7.5 Hz, 4H), 7.25-7.20 (m, 4H), 6.95 (d,  $J$  = 7.8 Hz, 2H), 6.70 (s, 2H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  148.0, 147.7, 139.9, 138.9, 134.5, 134.4, 133.3, 129.9, 129.7, 128.5, 124.8, 122.1; HRMS (ESI)  $[M+H]^+$  Calcd for  $[C_{28}H_{20}N_2O_8S_3]$  : 609.0460, found : 609.0457.



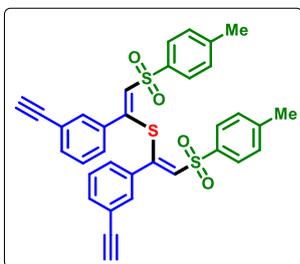
**bis((Z)-1-(thiophen-3-yl)-2-tosylvinyl)sulfane (3lb):** The crude

product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3lb** as a white solid (Yield: 70%); m.p = 135-137 °C;  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.96 (d,  $J$  = 8.2 Hz, 4H), 7.43 (d,  $J$  = 8.2 Hz, 4H), 6.94 (dd,  $J$  = 5.0, 3.0 Hz, 2H), 6.68 (q,  $J$  = 1.4 Hz, 2H), 6.61

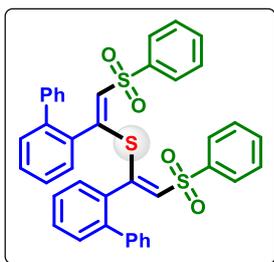
(s, 2H), 6.34 (dd,  $J = 5.0, 1.3$  Hz, 2H), 2.50 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 144.9, 138.7, 138.1, 129.9, 128.4, 126.4, 126.2, 126.0, 21.7; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{26}\text{H}_{22}\text{O}_4\text{S}_5]$  : 559.0200, found : 559.0212.



**bis((Z)-1-cyclopropyl-2-(phenylsulfonyl)vinyl)sulfane (3ma)**. The crude product was purified by column chromatography (hexane/EtOAc = 85/15) to afford **3ma** as a white solid (Yield: 67%); m.p = 113-115 °C;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J = 7.8$  Hz, 4H), 7.62 (t,  $J = 7.4$  Hz, 2H), 7.54-7.49 (m, 4H), 6.44 (s, 2H), 1.48-1.40 (m, 2H), 0.83-0.78 (m, 4H), 0.65-0.61 (m, 4H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 141.2, 133.5, 129.0, 128.4, 128.1, 29.7, 19.5, 10.9.; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{22}\text{H}_{22}\text{O}_4\text{S}_3]$  : 447.0758, found : 447.0767.

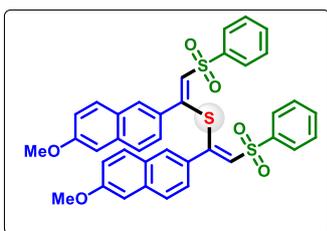


**bis((Z)-1-(3-ethynylphenyl)-2-tosylvinyl)sulfane (3nb)**: The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **3nb** as a white solid (Yield: 64%); m.p = 125-127 °C;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.3$  Hz, 4H), 7.49 (d,  $J = 8.0$  Hz, 4H), 7.28-7.25 (m, 2H), 6.85 (t,  $J = 7.8$  Hz, 2H), 6.56 (s, 2H), 6.41 (s, 2H), 6.32 (d,  $J = 8.0$  Hz, 2H), 3.02 (s, 2H), 2.53 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2, 145.0, 137.9, 137.5, 133.3, 132.3, 130.7, 130.0, 128.6, 128.4, 127.8, 125.0, 122.7, 82.0, 78.2, 21.8; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{34}\text{H}_{26}\text{O}_4\text{S}_3]$  : 595.1071, found : 595.1055.



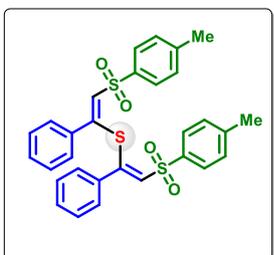
**bis((Z)-1-([1,1'-biphenyl]-2-yl)-2-(phenylsulfonyl)vinyl)sulfane**

**(30a).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **30a** as a white solid (Yield: 70%); m.p = 165-167 °C;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (dd,  $J = 18.8, 7.5$  Hz, 6H), 7.54 (t,  $J = 7.6$  Hz, 4H), 7.32 (t,  $J = 7.3$  Hz, 2H), 7.15-7.06 (m, 8H), 6.96 (t,  $J = 7.6$  Hz, 4H), 6.39 (d,  $J = 7.3$  Hz, 4H), 6.21 (s, 2H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7, 139.3, 136.0, 133.4, 130.9, 130.6, 129.8, 129.1, 128.6, 128.2, 128.0, 127.5, 127.1; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{40}\text{H}_{30}\text{O}_4\text{S}_3]$  : 671.1384, found : 671.1392.



**bis((Z)-1-(6-methoxynaphthalen-2-yl)-2-**

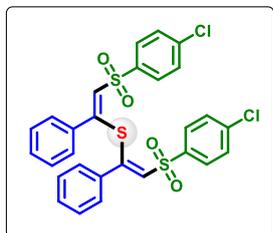
**(phenylsulfonyl)vinyl)sulfane (3pa):** The crude product was purified by column chromatography (hexane/EtOAc = 70/30) to afford **3pa** as a white solid (Yield: 75%); m.p = 232-234 °C;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 7.1$  Hz, 4H), 7.75-7.71 (m, 2H), 7.68-7.63 (m, 4H), 6.92 (d,  $J = 8.7$  Hz, 2H), 6.85 (s, 4H), 6.79 (s, 2H), 6.58 (d,  $J = 1.4$  Hz, 2H), 6.49 (s, 2H), 6.10 (dd,  $J = 8.6, 1.9$  Hz, 2H), 3.79 (s, 6H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.7, 153.0, 141.0, 134.7, 133.7, 132.7, 130.1, 129.5, 129.3, 128.5, 127.7, 127.5, 126.6, 124.4, 119.3, 105.1, 55.3; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{38}\text{H}_{30}\text{O}_6\text{S}_3]$ : 679.1283, found : 679.1253.



**bis((Z)-1-phenyl-2-(4-methylphenyl)sulfonyl)vinyl)sulfane (3ab):** The crude product was

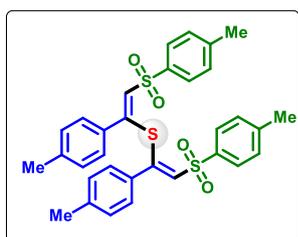
purified by column chromatography (hexane/EtOAc = 80/20) to afford **3ab** as a white solid (Yield: 73%); m.p = 119-121 °C;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.2$  Hz, 4H), 7.47-7.43 (m, 6H), 7.06 (d,  $J = 8.4$  Hz, 4H), 6.63 (s, 2H), 6.41 (d,  $J = 8.2$  Hz, 4H), 2.54 (s, 6H);

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.6, 144.9, 142.6, 139.5, 137.7, 136.5, 129.7, 128.9, 128.6, 127.9, 126.8, 126.6, 21.7; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{30}\text{H}_{26}\text{O}_4\text{S}_3]$  : 547.1071, found : 547.1066.



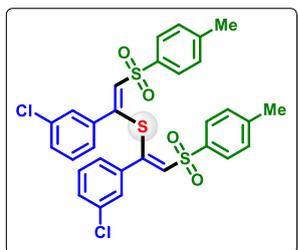
**bis((Z)-2-((4-chlorophenyl)sulfonyl)-1-phenylvinyl)sulfane (3ac):**

The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3ac** as a white solid (Yield: 70%); m.p = 152-154 °C  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J$  = 8.5 Hz, 4H), 7.65 (d,  $J$  = 8.5 Hz, 4H), 7.13 (t,  $J$  = 7.3 Hz, 2H), 6.86 (t,  $J$  = 7.6 Hz, 4H), 6.53 (s, 2H), 6.31 (d,  $J$  = 7.8 Hz, 4H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.7, 140.6, 139.2, 137.4, 130.8, 130.1, 129.9, 129.5, 128.3, 127.4; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{28}\text{H}_{20}\text{Cl}_2\text{O}_4\text{S}_3]$  : 586.9979, found : 586.9954.



**bis((Z)-1-(p-tolyl)-2-tosylvinyl)sulfane (3qb).** The crude product was

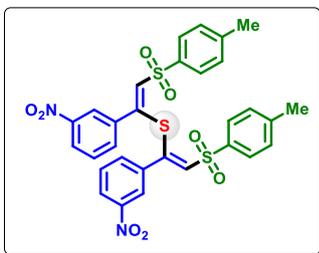
purified by column chromatography (hexane/EtOAc =80/20) to afford **3qb** as a white solid (Yield: 74%); m.p = 143-145 °C  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J$  = 8.3 Hz, 4H), 7.46 (d,  $J$  = 8.0 Hz, 4H), 6.59 (d,  $J$  = 8.0 Hz, 4H), 6.49 (s, 2H), 6.13 (d,  $J$  = 8.0 Hz, 4H), 2.52 (s, 6H), 2.19 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  152.3, 144.8, 140.1, 137.9, 135.0, 130.6, 129.7, 128.7, 128.7, 127.4, 21.8, 21.2; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{32}\text{H}_{30}\text{O}_4\text{S}_3]$  : 575.1384, found : 575.1377.



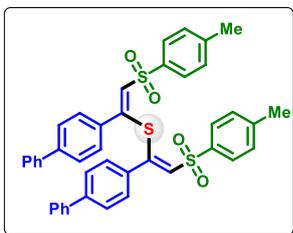
**bis((Z)-1-(3-chlorophenyl)-2-tosylvinyl)sulfane (3gb):** The crude

product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **3gb** as a white solid (Yield: 64%); m.p = 136-140 °C;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J$  = 8.3

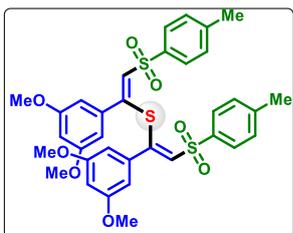
Hz, 4H), 7.49 (d,  $J = 8.3$  Hz, 4H), 7.14 (d,  $J = 8.0$  Hz, 2H), 6.83 (t,  $J = 7.9$  Hz, 2H), 6.57 (s, 2H), 6.26-6.23 (m, 4H), 2.53 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 145.3, 139.2, 137.4, 134.4, 132.6, 130.0, 129.9, 129.6, 128.6, 127.3, 125.7, 21.8; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{O}_4\text{S}_3]$  : 615.0292, found : 615.0291.



**bis((Z)-1-(3-nitrophenyl)-2-tosylvinyl)sulfane(3kb):** The crude product was purified by column chromatography (hexane/EtOAc =75/25) to afford **3kb** as a white solid (Yield: 62%); m.p = 206-208 °C;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.3$  Hz, 4H), 7.47 (d,  $J = 8.0$  Hz, 4H), 7.01 (d,  $J = 8.5$  Hz, 4H), 6.55 (s, 2H), 6.22 (d,  $J = 8.5$  Hz, 4H), 2.52 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.1, 145.2, 137.6, 136.4, 132.3, 131.5, 129.9, 128.9, 128.6, 128.5, 124.6, 21.8; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{30}\text{H}_{24}\text{N}_2\text{O}_8\text{S}_3]$  : 637.0773, found : 637.0776.

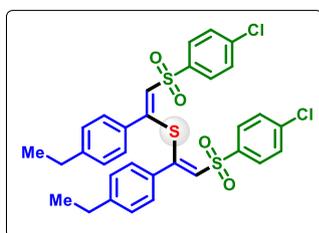


**bis((Z)-1-([1,1'-biphenyl]-4-yl)-2-tosylvinyl)sulfane (3eb):** The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **3eb** as a white solid (Yield: 70%); m.p = 210-212 °C;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.2$  Hz, 4H), 7.41-7.26 (m, 14H + residual  $\text{CDCl}_3$ ), 6.95 (d,  $J = 8.4$  Hz, 4H), 6.52 (s, 2H), 6.30 (d,  $J = 8.2$  Hz, 4H), 2.43 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.6, 144.9, 142.7, 139.6, 137.9, 136.6, 131.2, 129.8, 129.0, 128.7, 128.1, 128.0, 126.9, 126.7, 21.8; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{42}\text{H}_{34}\text{O}_4\text{S}_3]$  : 699.1697, found : 699.1689.



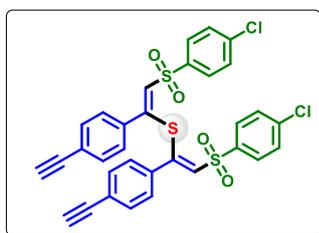
**bis((Z)-1-(3,5-dimethoxyphenyl)-2-tosylvinyl)sulfane (3db).** The crude product was purified by column chromatography (hexane/EtOAc =70/30) to afford **3db** as a white solid (Yield: 80%); m.p = 215-217 °C;  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J =$

8.3 Hz, 4H), 7.41 (d,  $J = 8.0$  Hz, 4H), 6.54 (s, 2H), 6.28 (t,  $J = 2.1$  Hz, 2H), 5.92 (d,  $J = 2.4$  Hz, 4H), 3.62 (s, 12H), 2.49 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 152.0, 144.8, 139.7, 138.3, 130.4, 130.0, 128.1, 105.9, 103.0, 55.5, 21.7; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{34}\text{H}_{34}\text{O}_8\text{S}_3]$  : 667.1494, found : 667.1467.



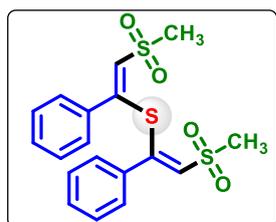
**bis((Z)-2-((4-chlorophenyl)sulfonyl)-1-(4-**

**ethylphenyl)vinyl)sulfane (3bc):** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **3bc** as a white solid (Yield: 76%); m.p = 152-154 °C  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.5$  Hz, 4H), 7.57 (d,  $J = 8.8$  Hz, 4H), 6.59 (d,  $J = 8.0$  Hz, 4H), 6.43 (s, 2H), 6.16 (d,  $J = 8.3$  Hz, 4H), 2.41 (q,  $J = 7.7$  Hz, 4H), 1.04 (t,  $J = 7.6$  Hz, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 159.2, 153.0, 146.9, 140.4, 139.3, 134.8, 129.8, 129.6, 129.4, 127.6, 127.3, 28.4, 15.2; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{32}\text{H}_{28}\text{Cl}_2\text{O}_4\text{S}_3]$  : 643.0605, found : 643.0613.



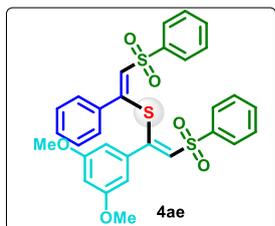
**bis((Z)-2-((4-chlorophenyl)sulfonyl)-1-(4-**

**ethynylphenyl)vinyl)sulfane (3rc):** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **3rc** as a white solid (Yield: 68%); m.p = 141-143 °C  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.5$  Hz, 4H), 7.65 (d,  $J = 8.5$  Hz, 4H), 7.02 (d,  $J = 8.0$  Hz, 4H), 6.55 (s, 2H), 6.36 (d,  $J = 8.3$  Hz, 4H), 3.18 (s, 2H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2, 140.8, 138.9, 137.3, 132.0, 131.6, 129.9, 129.6, 127.3, 124.2, 82.2, 80.1; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{32}\text{H}_{20}\text{Cl}_2\text{O}_4\text{S}_3]$  : 634.9979, found : 634.9987.



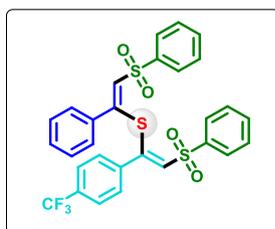
**bis((Z)-2-(methylsulfonyl)-1-phenylvinyl)sulfane (3ad).** The crude product was purified by column chromatography (hexane/EtOAc = 80/20) to afford **3ad** as a

white solid (Yield: 65%); m.p = 121-124 °C <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 (t, *J* = 7.4 Hz, 2H + residual CDCl<sub>3</sub>), 7.12 (t, *J* = 7.8 Hz, 4H), 6.97 (d, *J* = 7.5 Hz, 4H), 6.47 (s, 2H), 3.22 (s, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 152.5, 137.3, 130.3, 129.8, 128.6, 127.9, 44.3.; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>S<sub>3</sub>] : 395.0445, found : 395.0436.



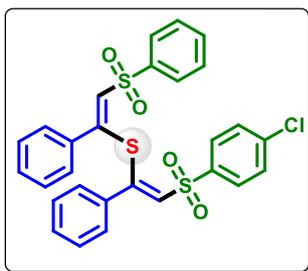
**((Z)-1-(3,5-dimethoxyphenyl)-2-(phenylsulfonyl)vinyl)((Z)-1-**

**phenyl-2-(phenylsulfonyl)vinyl)sulfane (4aa).** The crude product was purified by column chromatography (hexane/EtOAc =75/25) to afford **4aa** as a white solid (Yield: 67%); m.p = 172-174 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (t, *J* = 6.9 Hz, 4H), 7.76-7.62 (m, 6H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 2H), 6.59 (s, 1H), 6.51 (s, 1H), 6.43 (d, *J* = 7.6 Hz, 2H), 6.25 (t, *J* = 2.2 Hz, 1H), 5.79 (d, *J* = 2.1 Hz, 2H), 3.57 (s, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 160.4, 152.6, 152.3, 141.0, 140.7, 139.4, 137.7, 133.8, 130.6, 130.4, 129.8, 129.4, 129.2, 128.4, 128.2, 128.1, 127.7, 105.6, 102.9, 55.4.; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>30</sub>H<sub>26</sub>O<sub>6</sub>S<sub>3</sub>] : 579.0970, found : 579.0965.

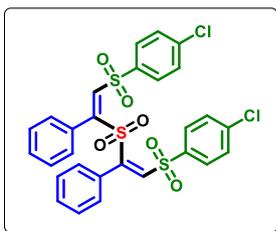


**(Z)-1-(4-((difluoro-1,3-methyl)-1,2-fluoranyl)phenyl)-2-**

**(phenylsulfonyl)vinyl)((Z)-1-phenyl-2-(phenylsulfonyl)vinyl)sulfane (4ab):** The crude product was purified by column chromatography (hexane/EtOAc =75/25) to afford **4ab** as a white solid (Yield: 65%); m.p = 159-161 °C; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 6.0 Hz, 4H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.67-7.62 (m, 4H), 7.07-7.03 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 7.8 Hz, 2H), 6.52 (d, *J* = 1.2 Hz, 2H), 6.28 (d, *J* = 8.2 Hz, 2H), 6.17 (d, *J* = 7.7 Hz, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 151.4, 150.8, 140.8, 140.2, 137.3, 134.2, 134.1, 134.0, 133.3, 132.5, 131.8, 130.1, 129.4, 129.3, 129.3, 128.9, 128.6, 128.4, 127.8, 127.7, 127.3, 125.3, 125.1; HRMS (ESI) [M+H]<sup>+</sup> Calcd for [C<sub>29</sub>H<sub>21</sub>F<sub>3</sub>O<sub>4</sub>S<sub>3</sub>] : 587.0632, found : 587.0651.



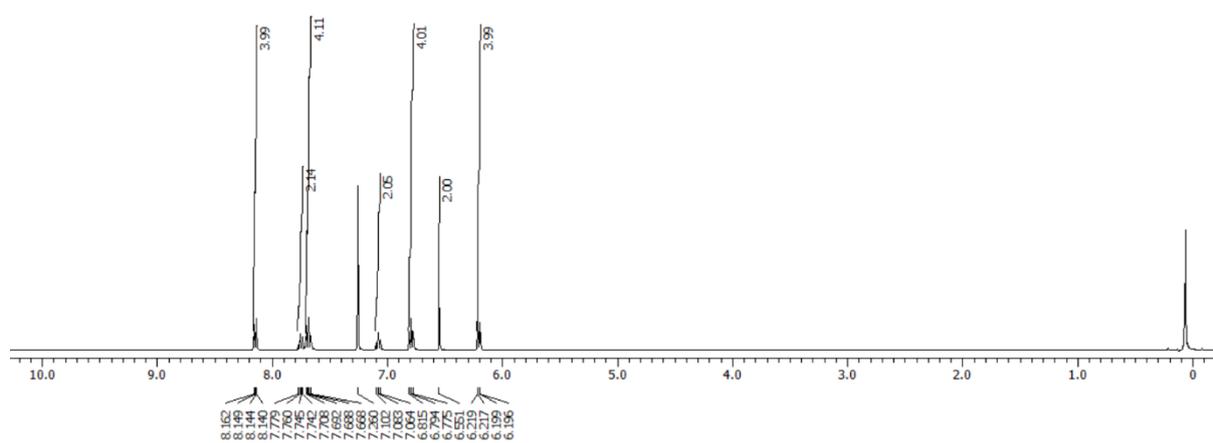
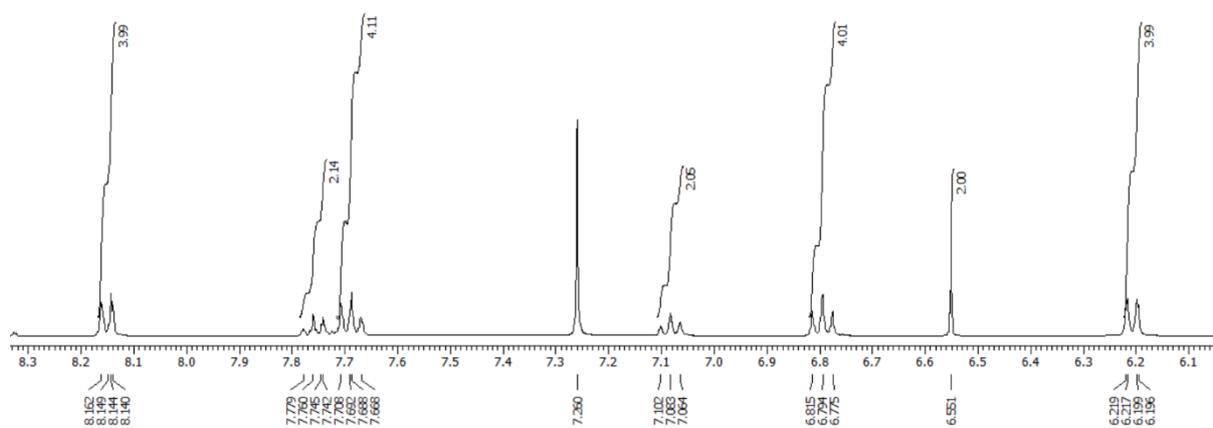
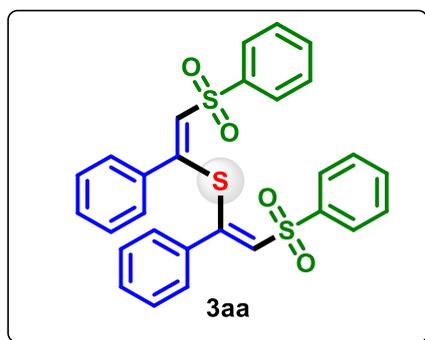
**((Z)-2-((4-chlorophenyl)sulfonyl)-1-phenylvinyl)((Z)-1-phenyl-2-phenylsulfonyl)vinyl)sulfane (5aa).** The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford **5aa** as a white solid (Yield: 62%); m.p = 168-170 °C;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (s, 2H), 8.11 (s, 2H), 7.79 (t,  $J = 7.3$  Hz, 1H), 7.73-7.67 (m, 4H), 7.13 (dd,  $J = 12.9, 7.1$  Hz, 2H), 6.85 (dd,  $J = 18.1, 7.9$  Hz, 4H), 6.59 (s, 1H), 6.54 (s, 1H), 6.29 (dd,  $J = 13.4, 7.6$  Hz, 4H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.1, 152.1, 140.7, 140.6, 139.2, 137.5, 137.4, 133.9, 131.4, 130.6, 130.0, 129.5, 129.2, 128.5, 128.3, 127.4, 127.3; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{28}\text{H}_{21}\text{ClO}_4\text{S}_3]$ : 553.0369, found: 553.0354.



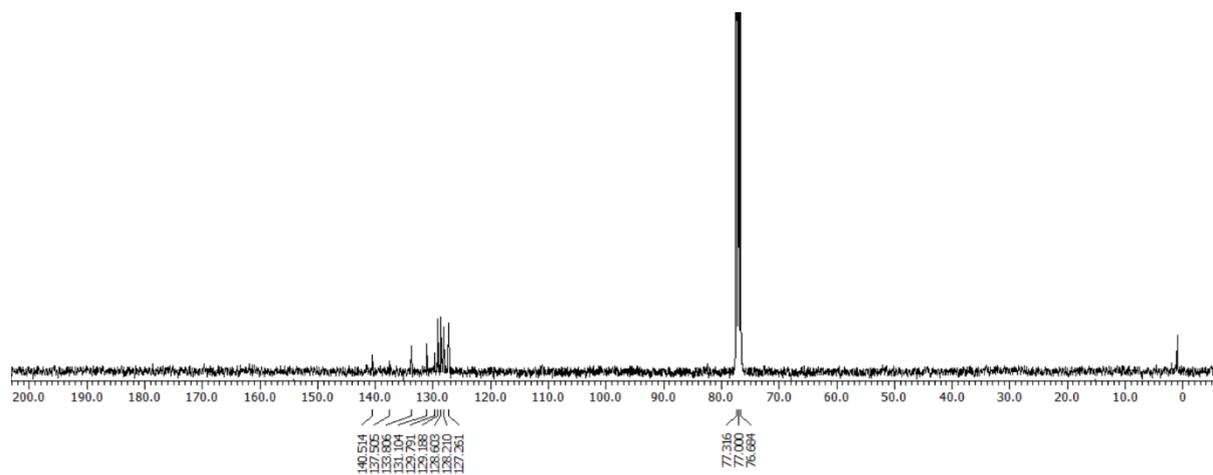
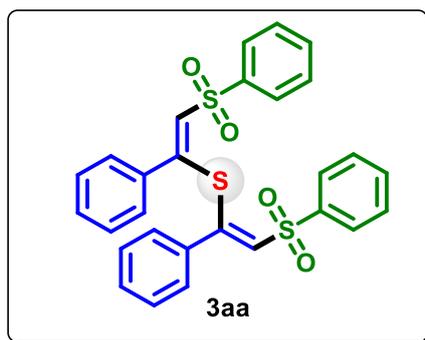
**4,4'-((Z)-2-(((Z)-2-hydrosulfonyl-1-phenylvinyl)sulfonyl)-2-phenylvinyl)sulfonyl)bis(chlorobenzene) (6).** The crude product was purified by column chromatography (hexane/EtOAc =80/20) to afford as a white solid (Yield: 70%); m.p = 192-194 °C;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 8.3$  Hz, 4H), 7.54 (d,  $J = 8.0$  Hz, 4H), 7.42 (t,  $J = 6.8$  Hz, 2H), 7.27 (d,  $J = 10.5$  Hz, 4H + residual  $\text{CDCl}_3$ ), 7.10 (d,  $J = 7.3$  Hz, 4H), 6.63 (s, 2H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 141.1, 138.4, 137.5, 131.4, 130.8, 130.4, 129.5, 129.4, 128.6.; HRMS (ESI)  $[\text{M}+\text{H}]^+$  Calcd for  $[\text{C}_{28}\text{H}_{20}\text{Cl}_2\text{O}_6\text{S}_3]$  : 618.9877, found : 618.9881.

# $^1\text{H}$ and $^{13}\text{C}$ spectra of compounds

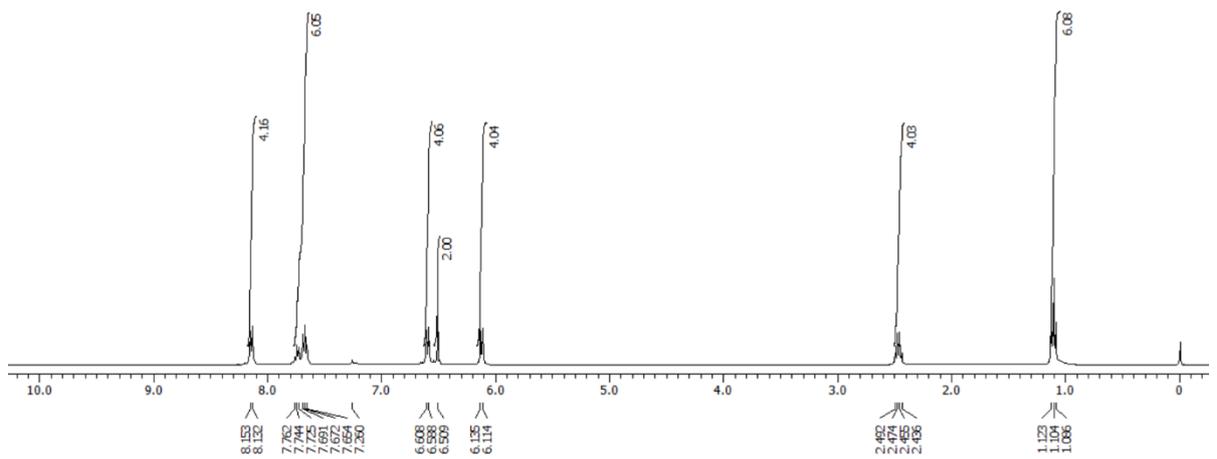
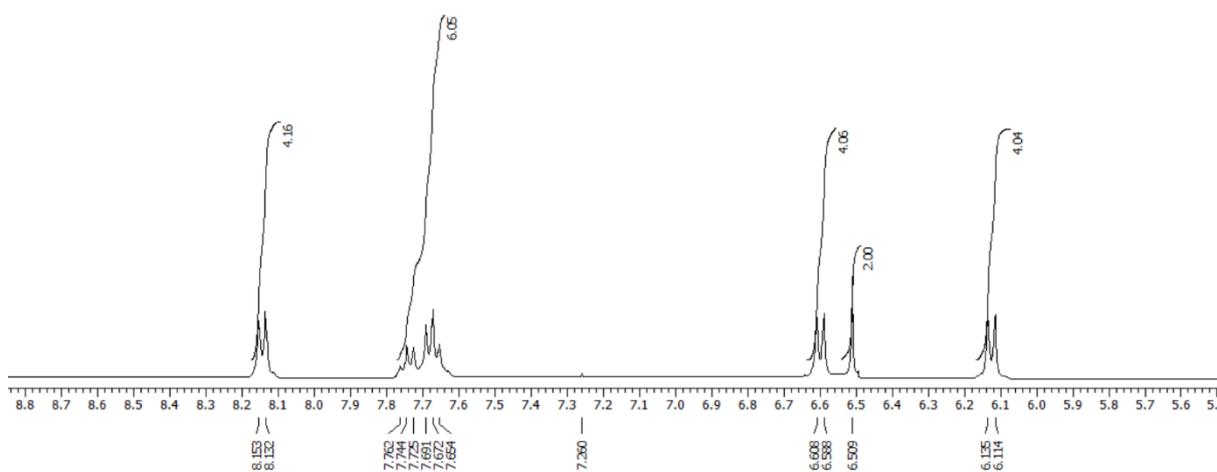
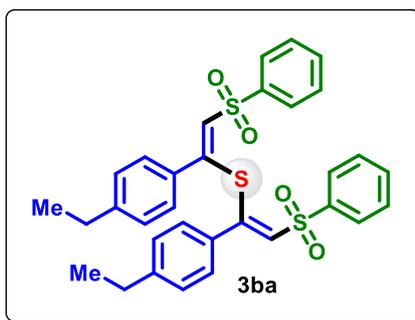
## $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



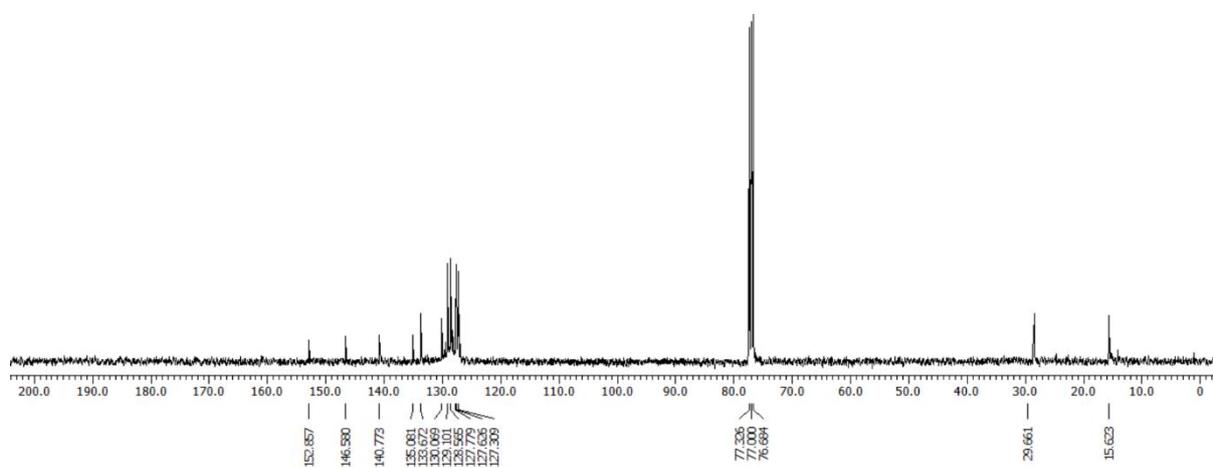
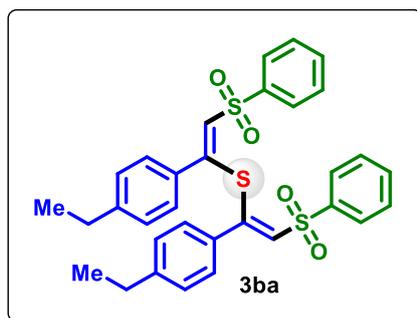
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



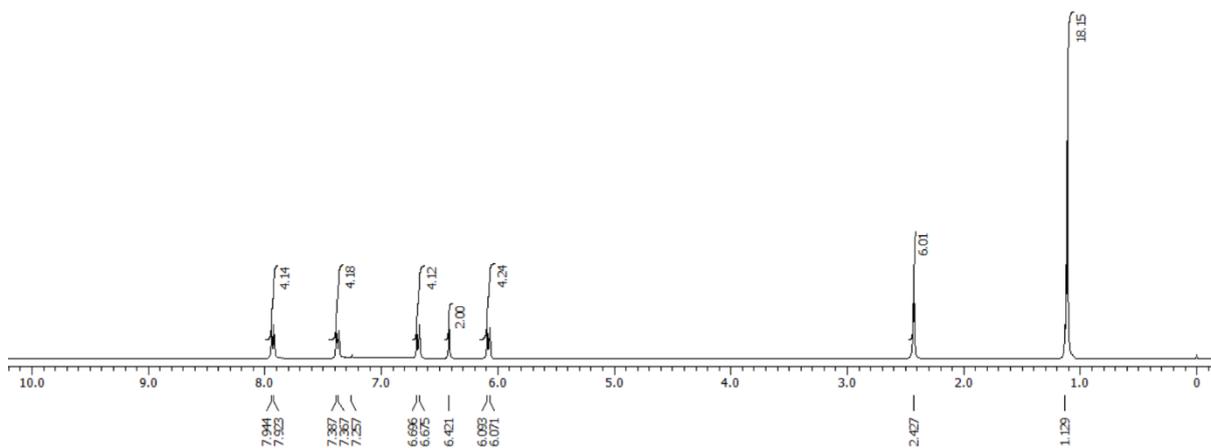
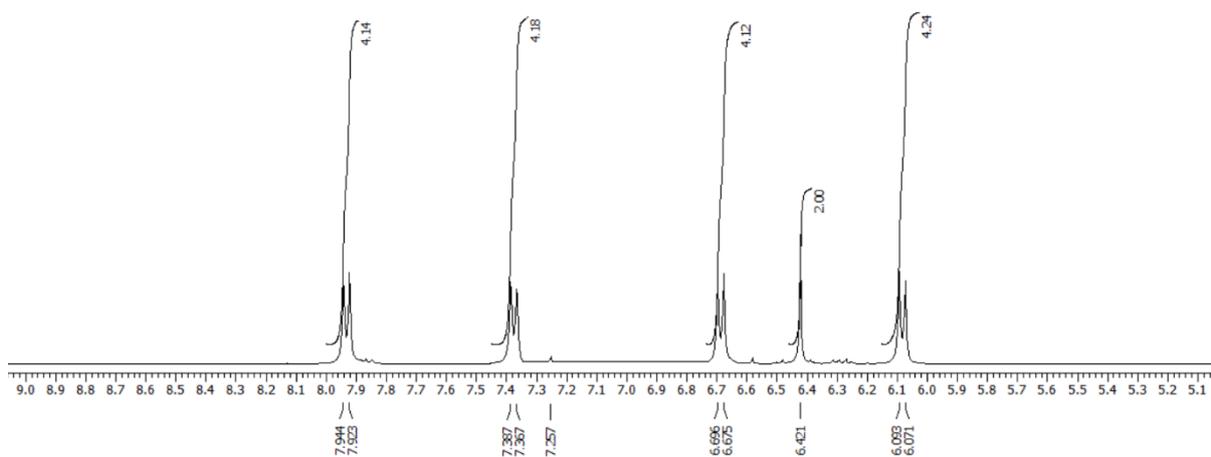
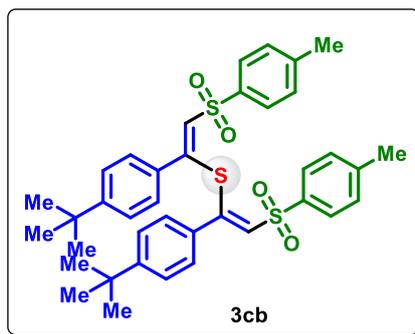
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



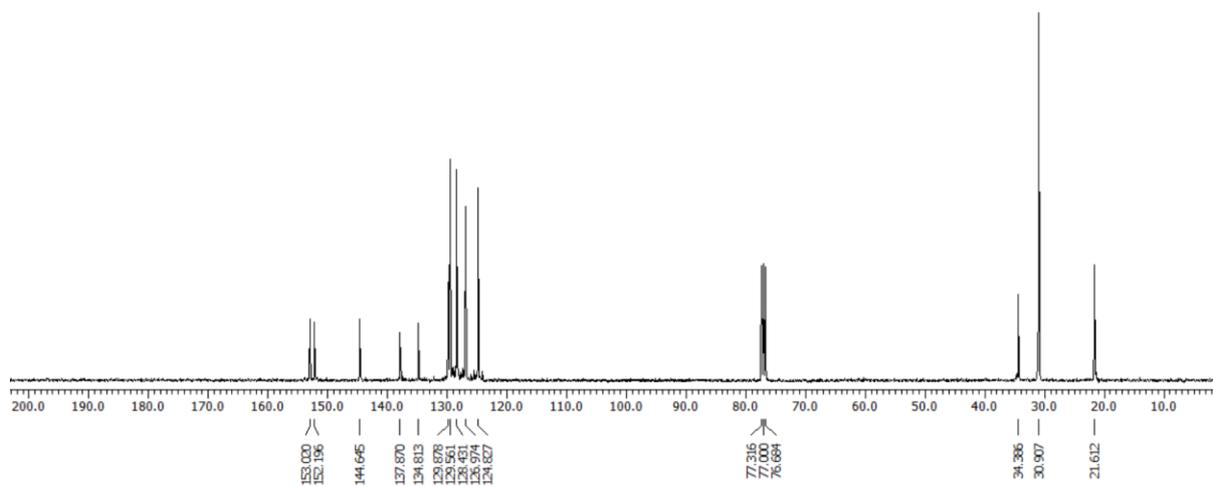
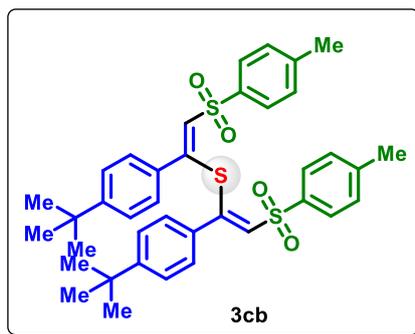
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



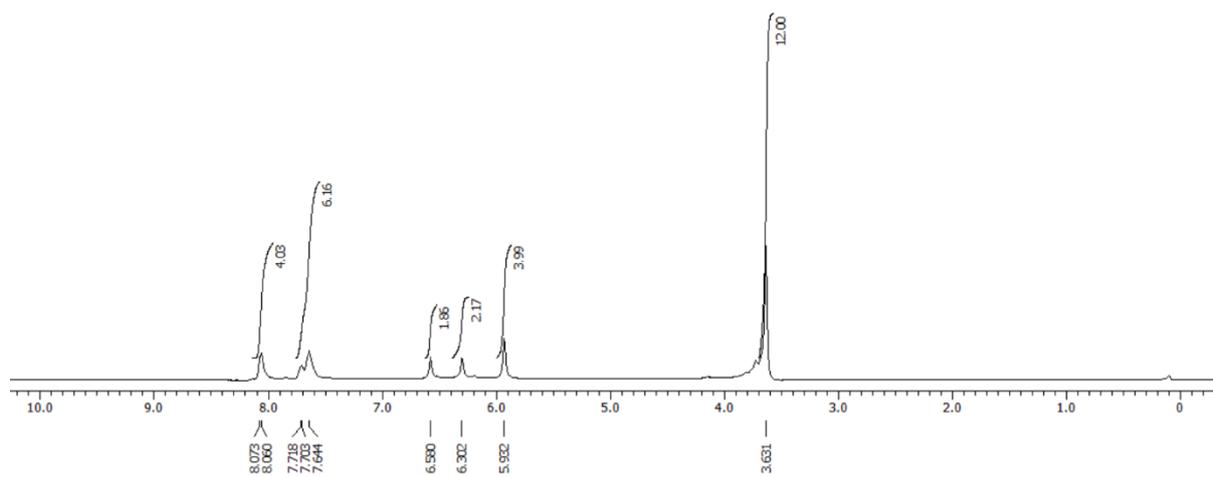
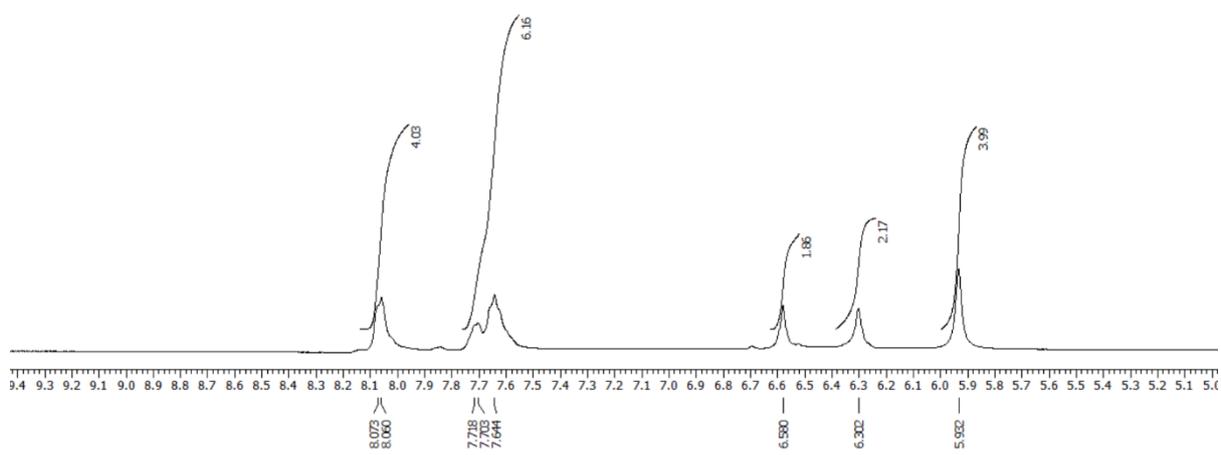
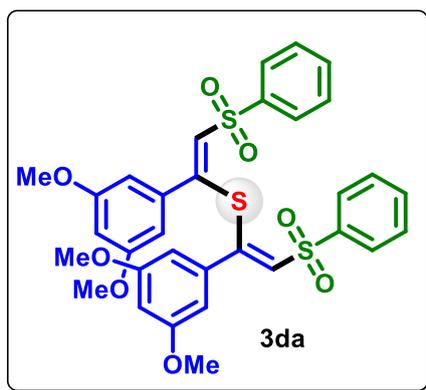
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



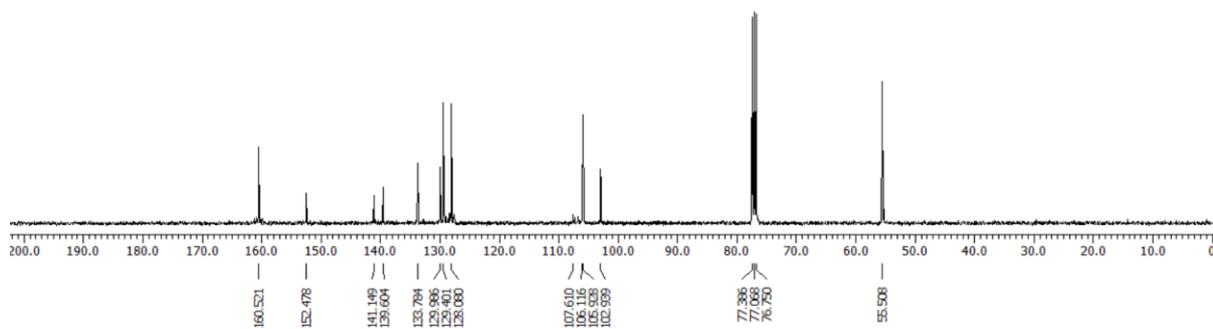
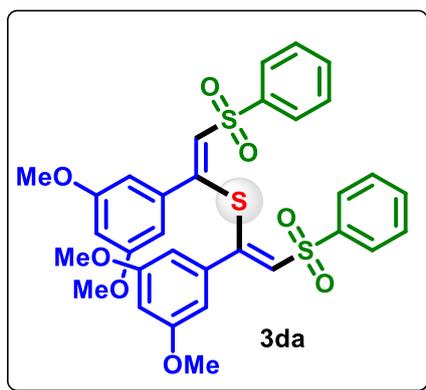
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



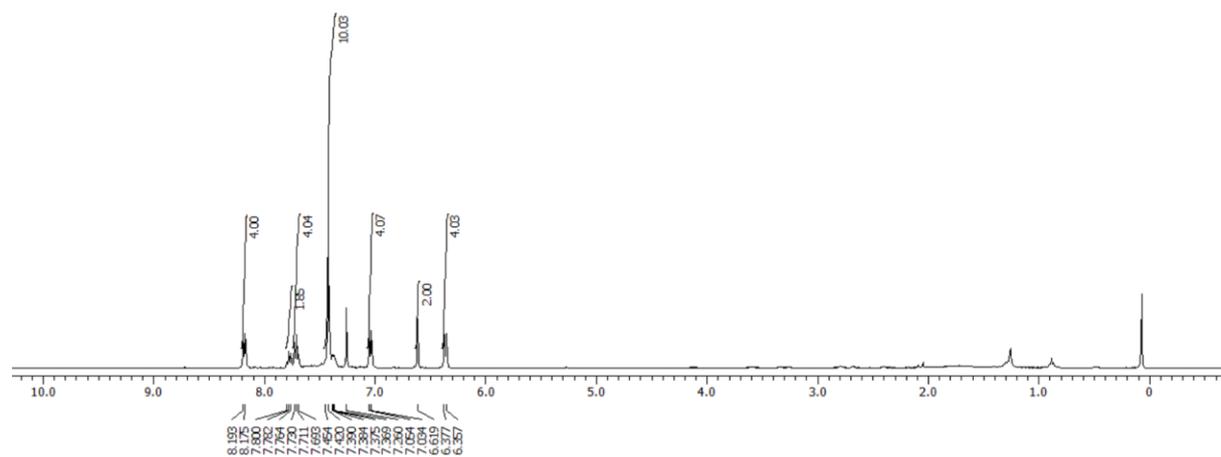
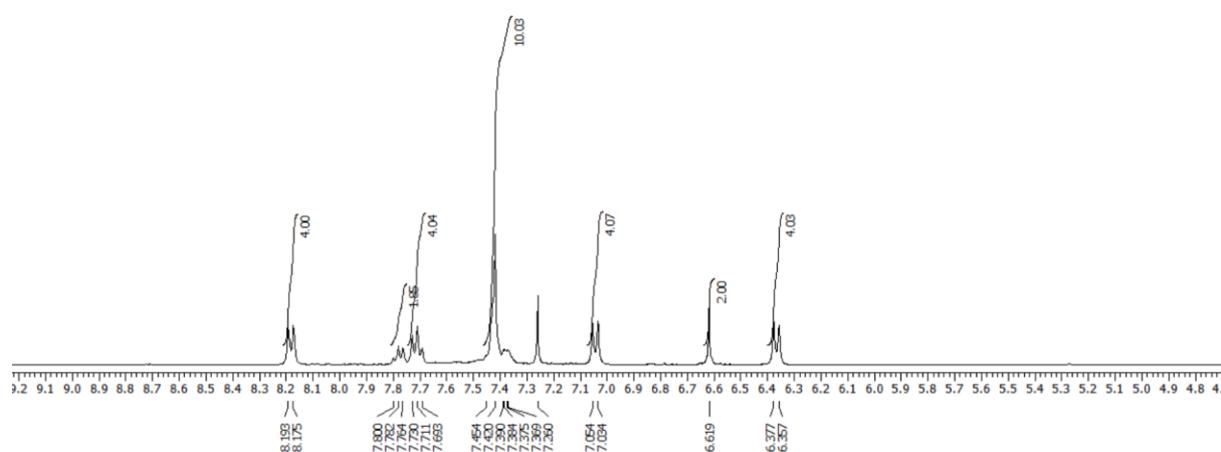
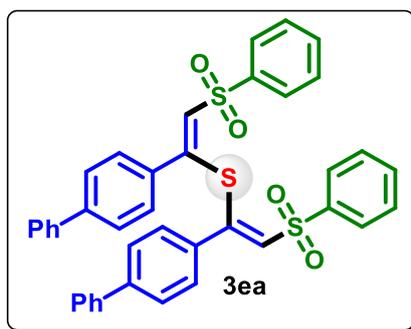
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



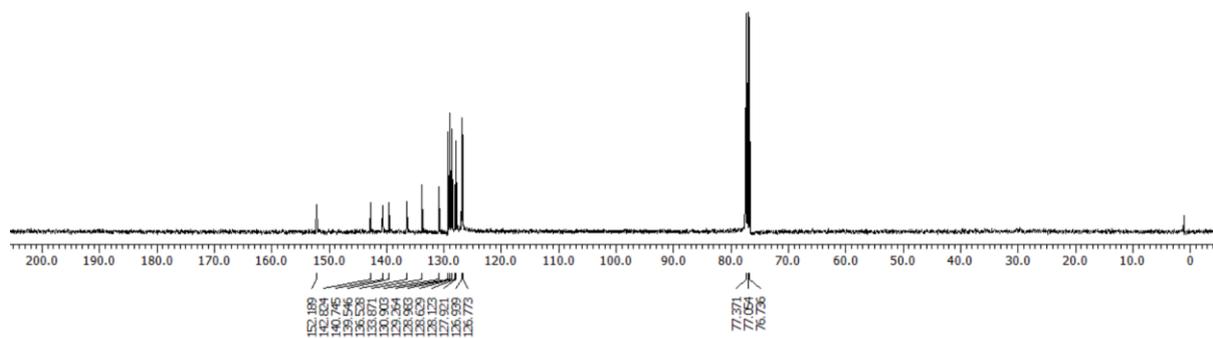
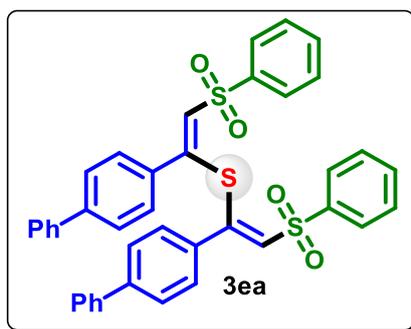
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



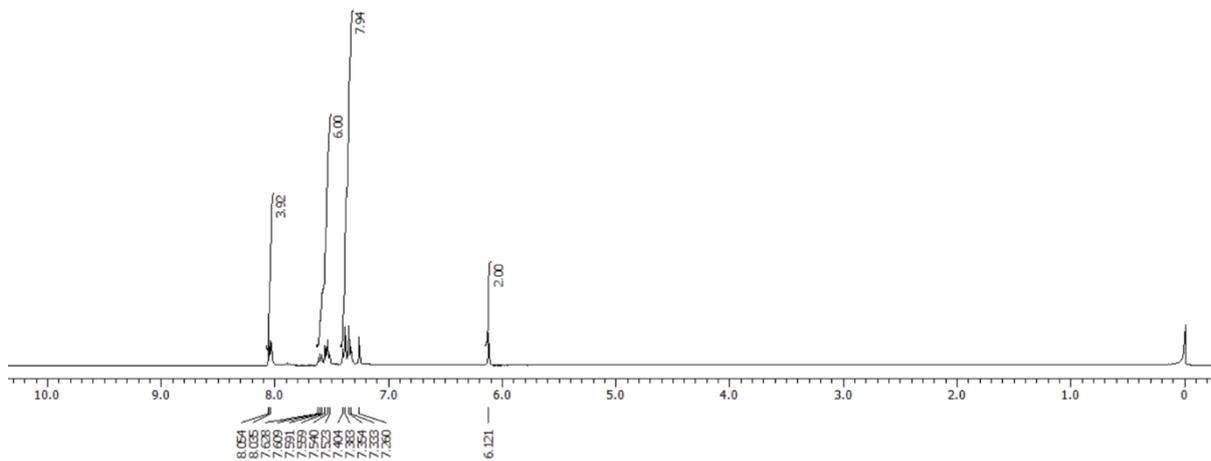
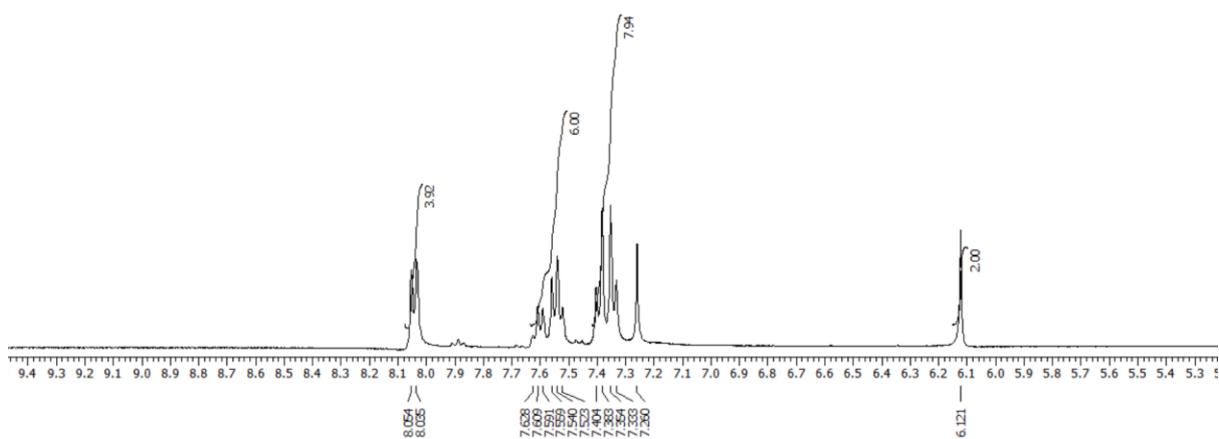
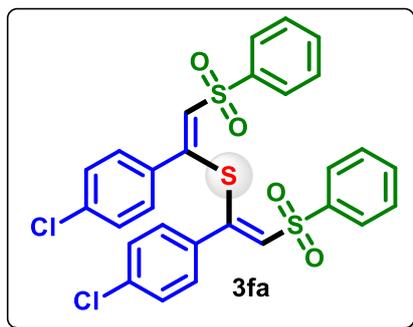
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



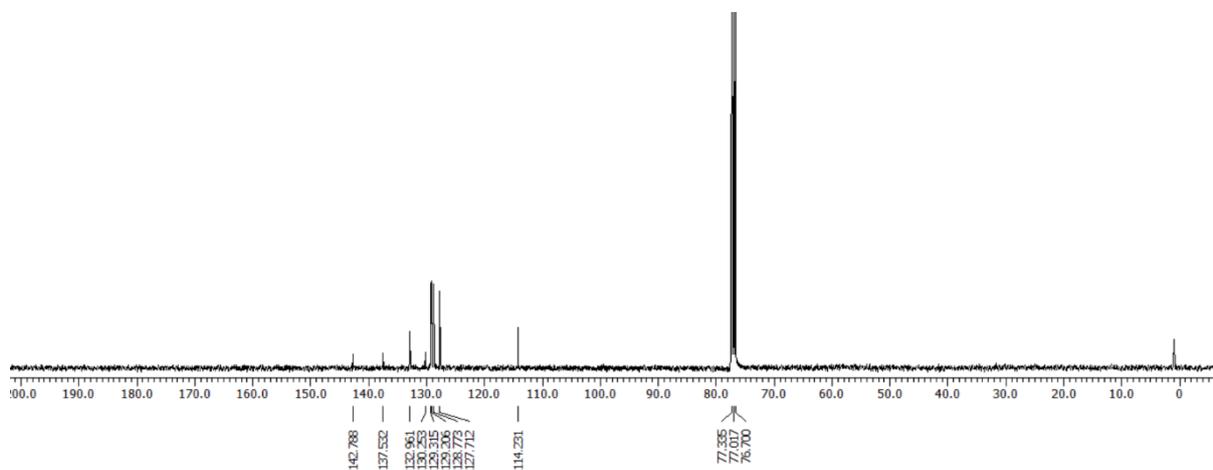
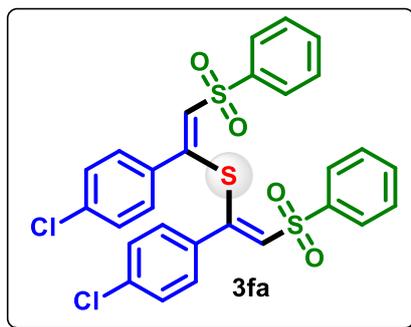
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



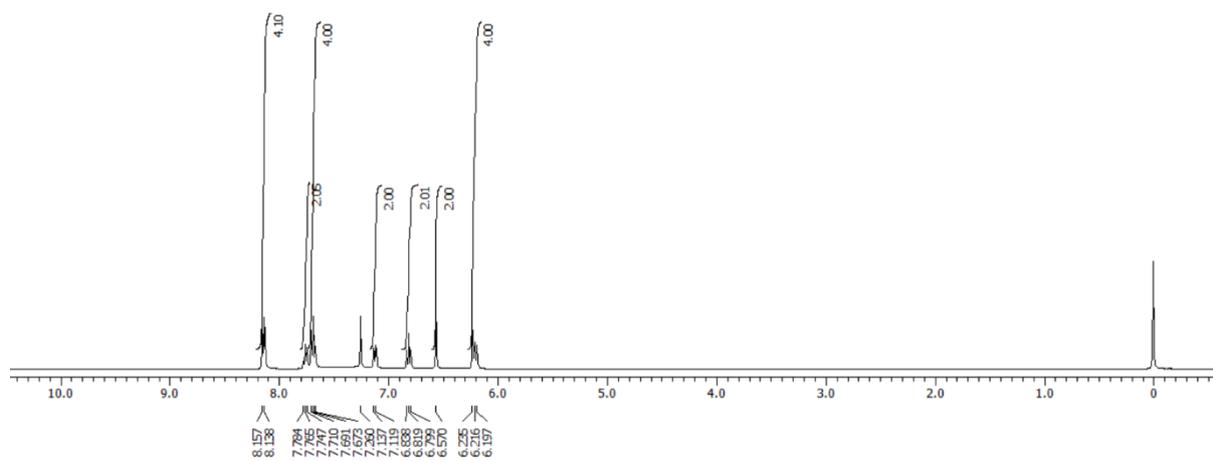
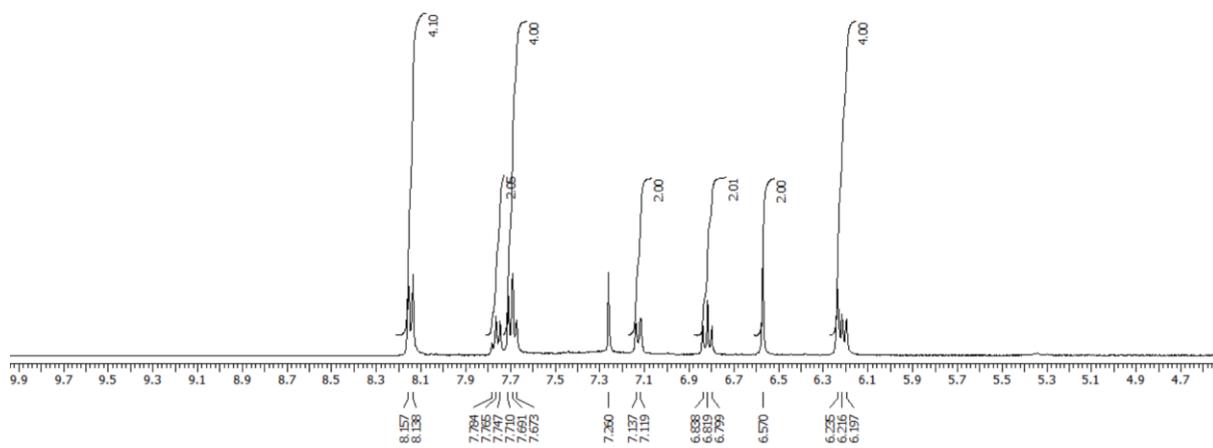
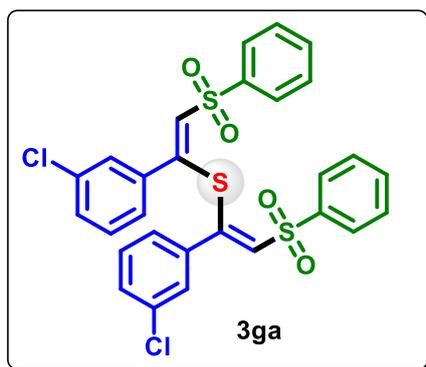
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



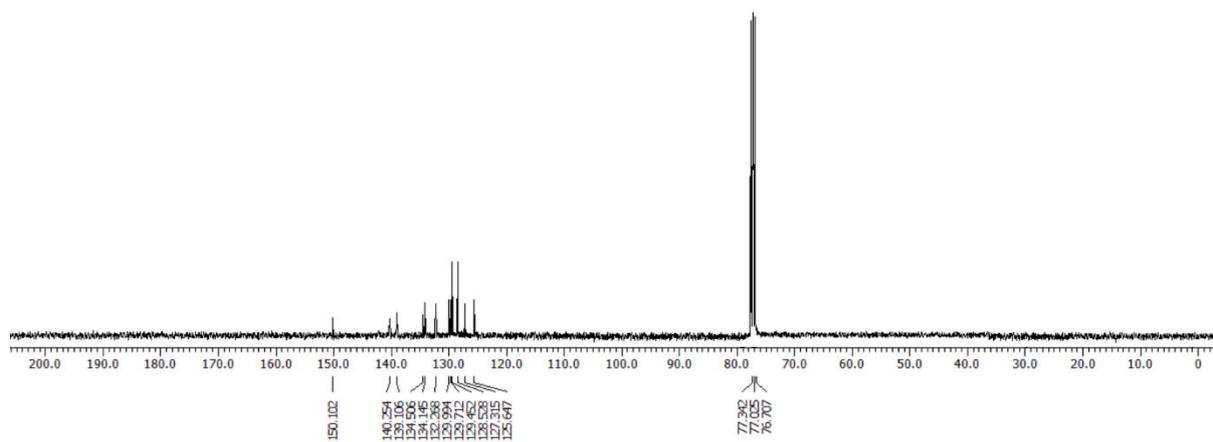
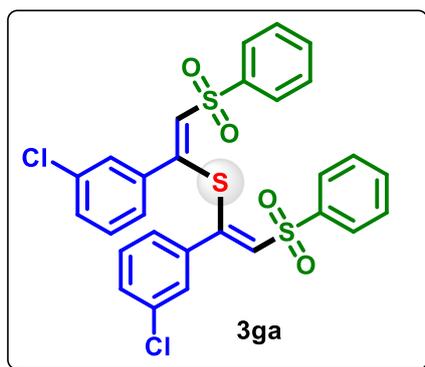
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



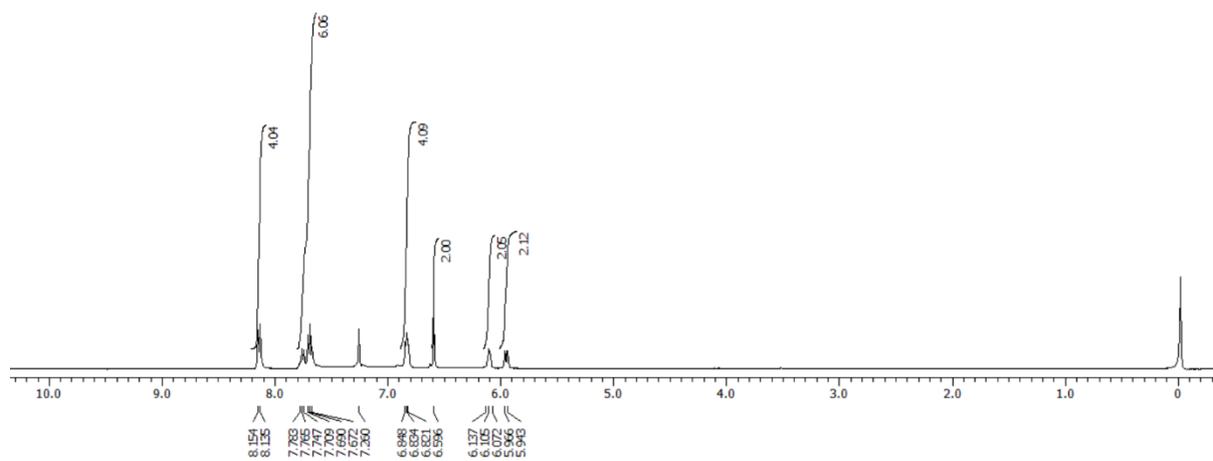
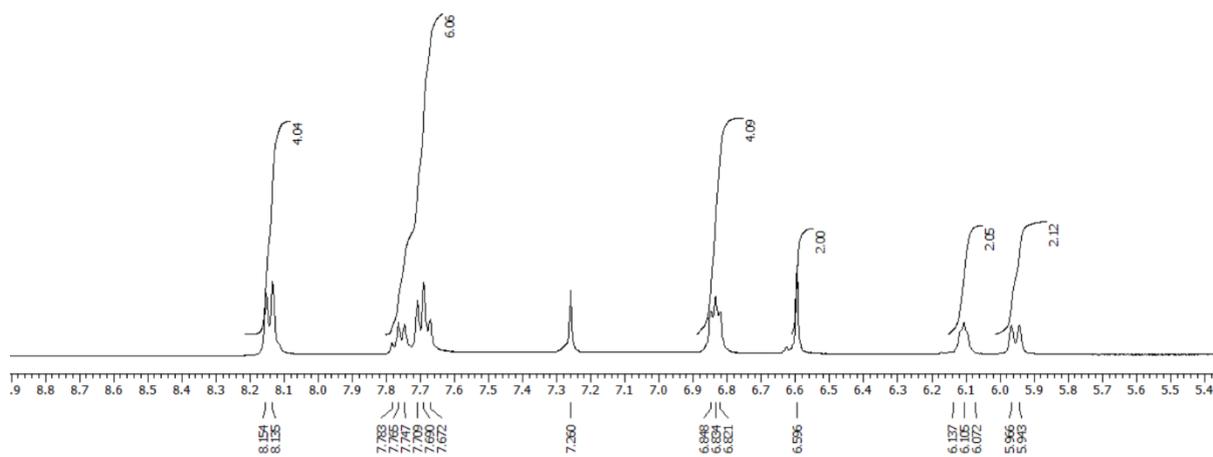
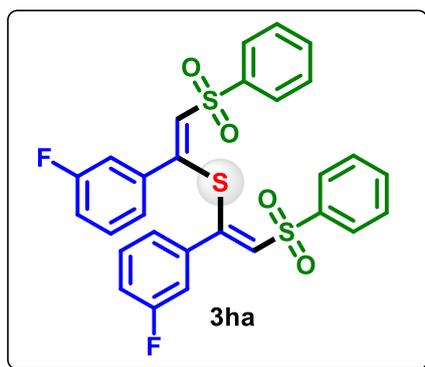
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



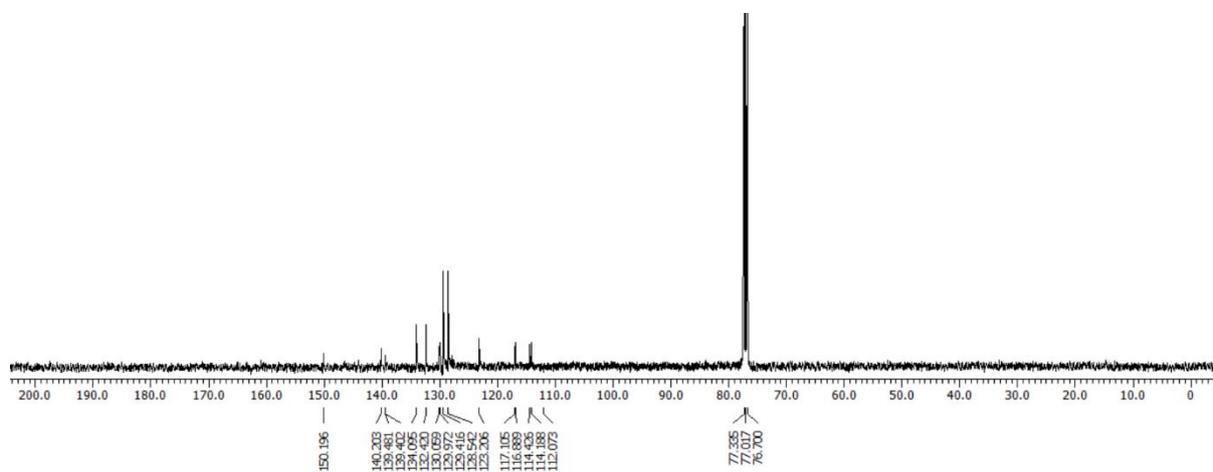
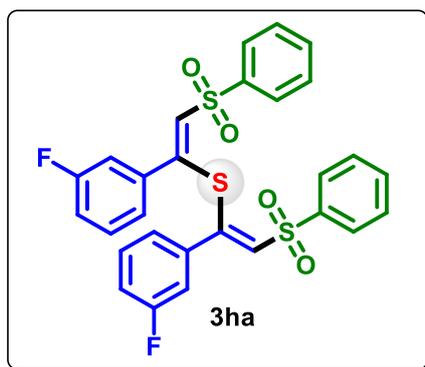
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



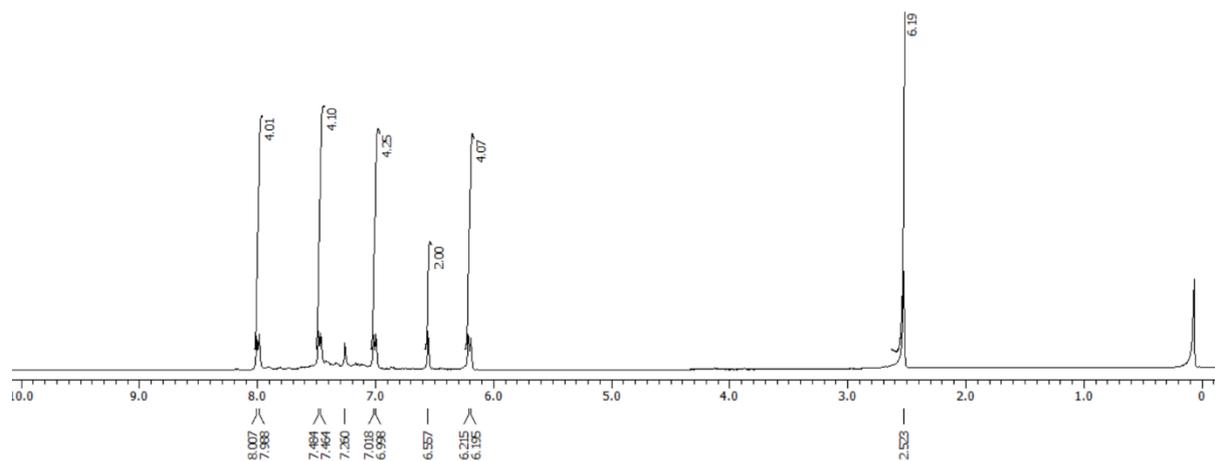
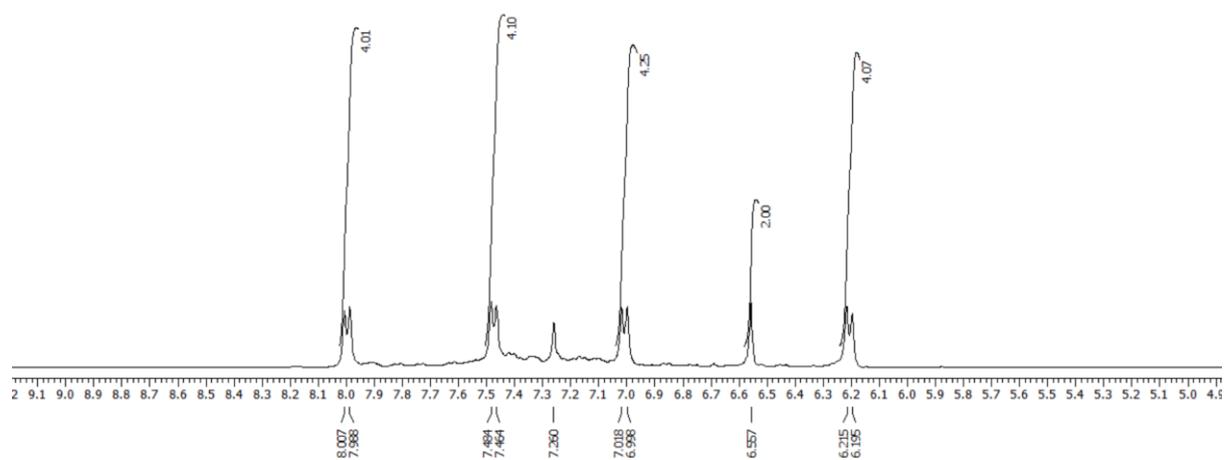
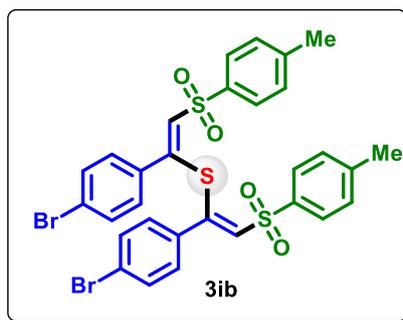
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



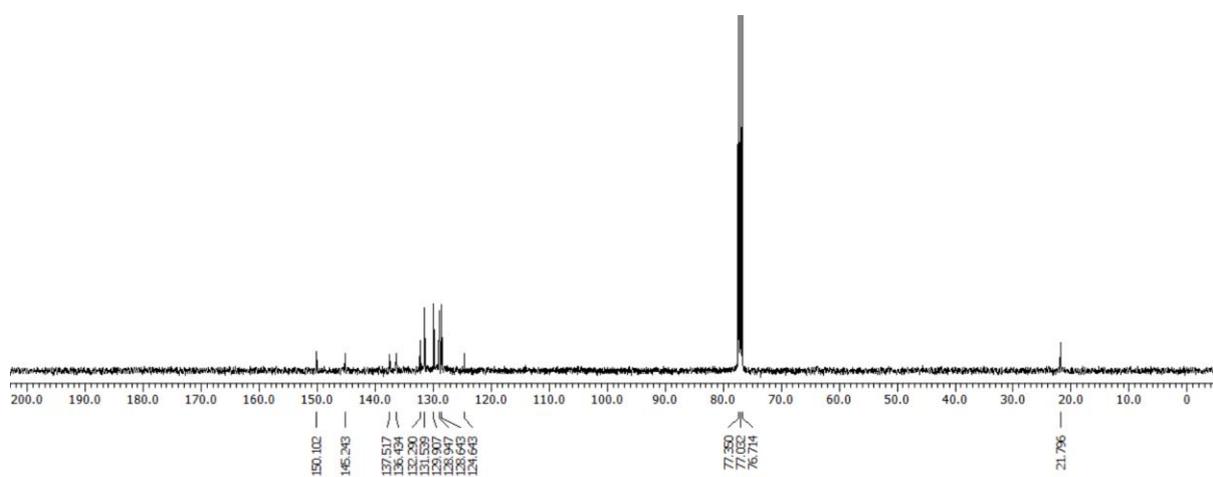
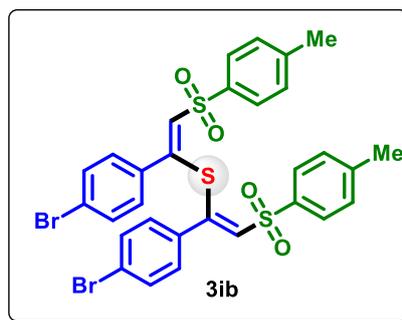
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



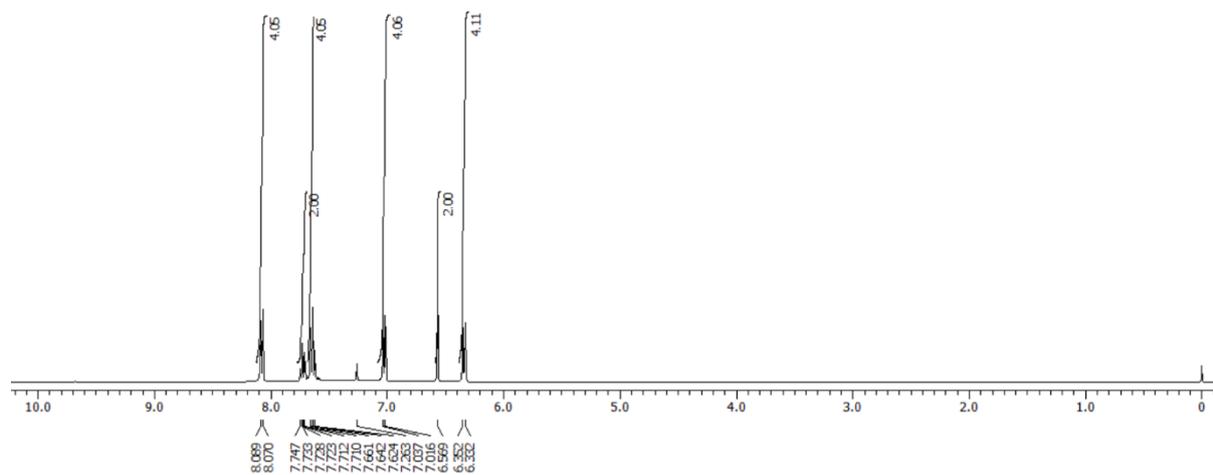
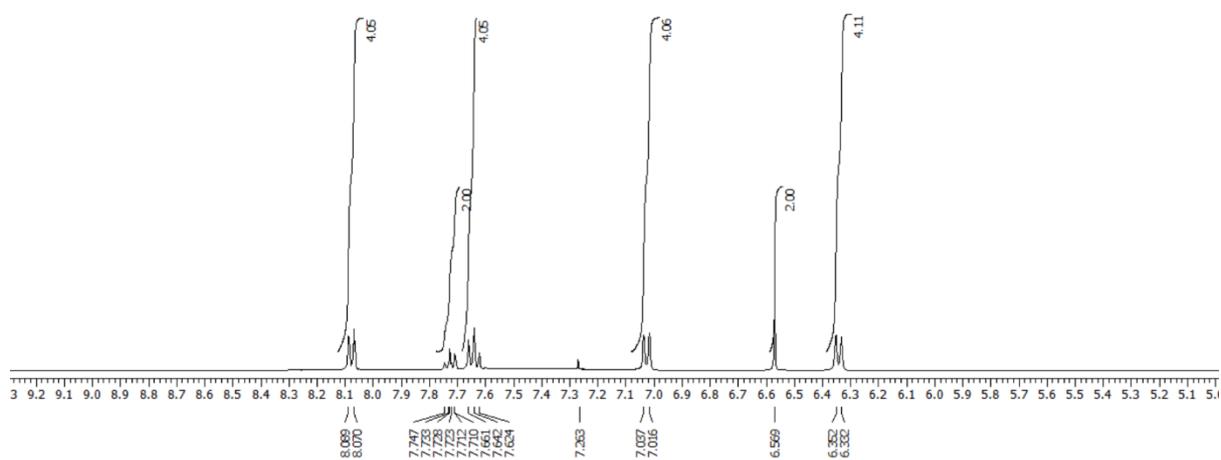
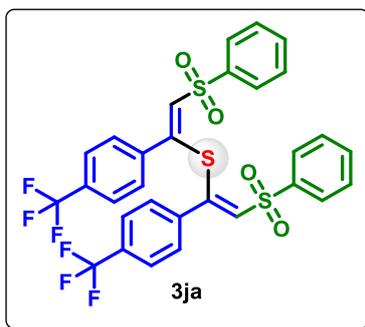
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



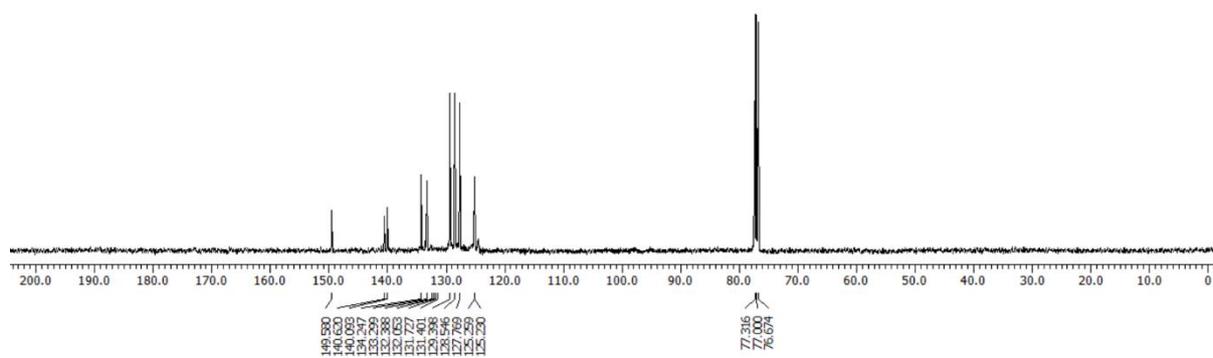
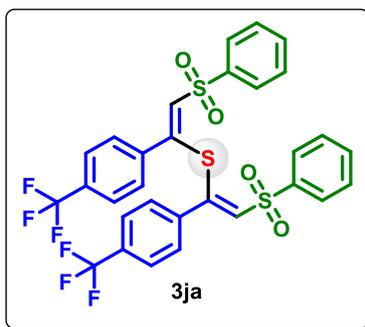
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



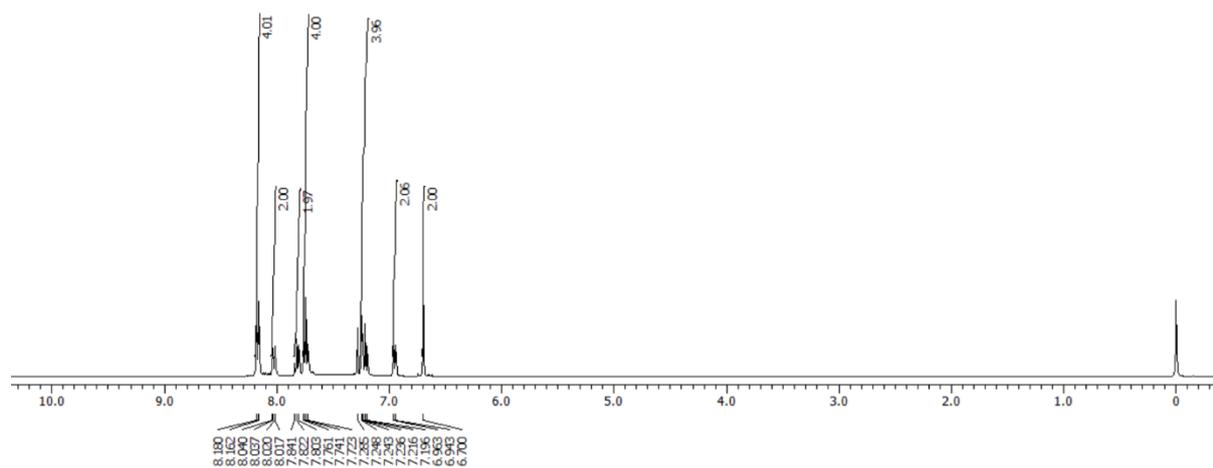
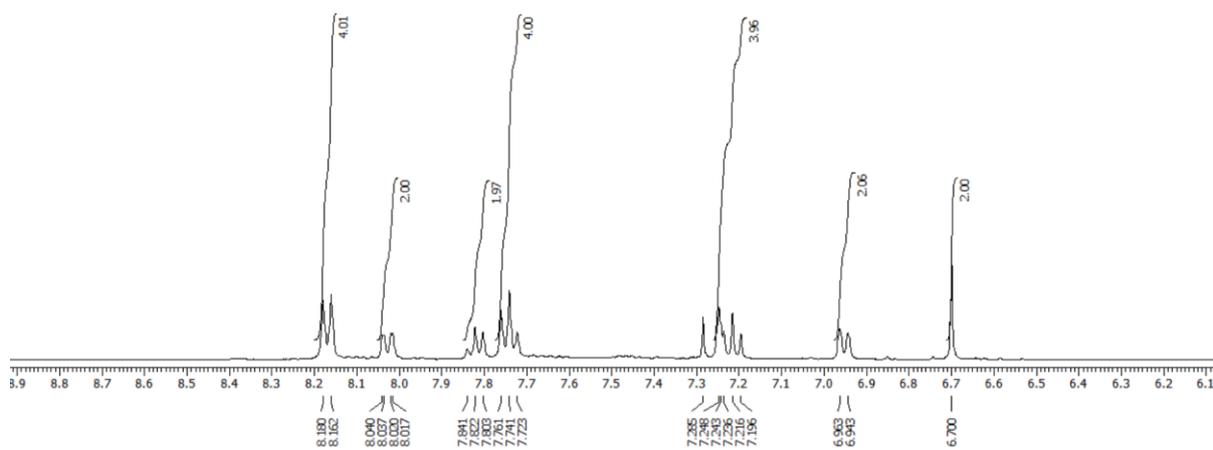
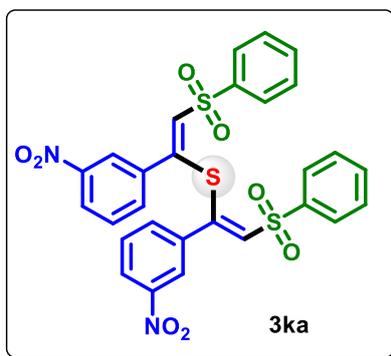
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



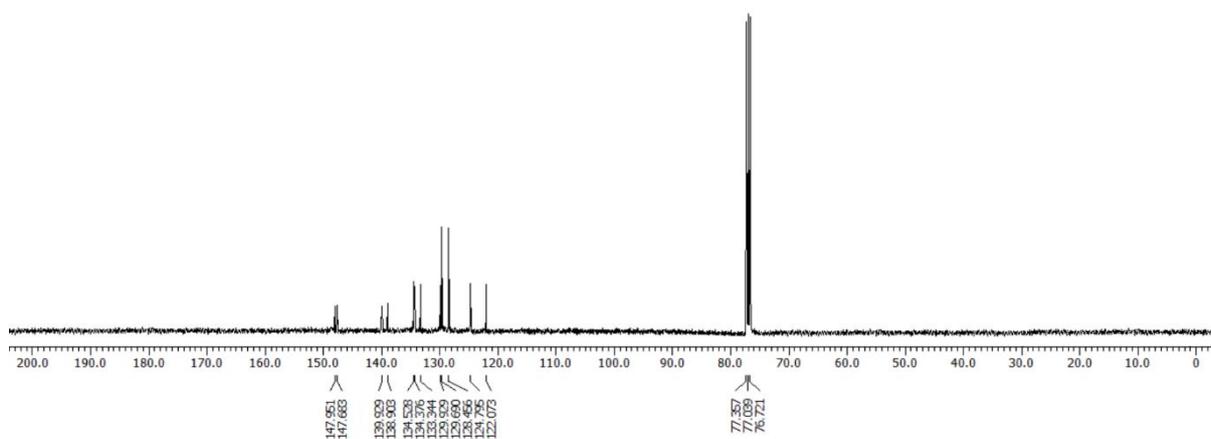
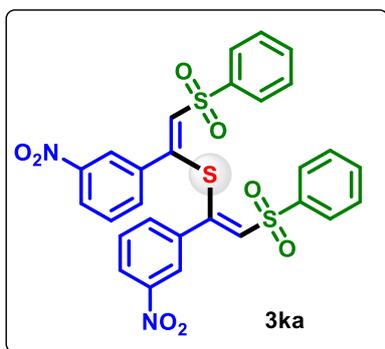
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



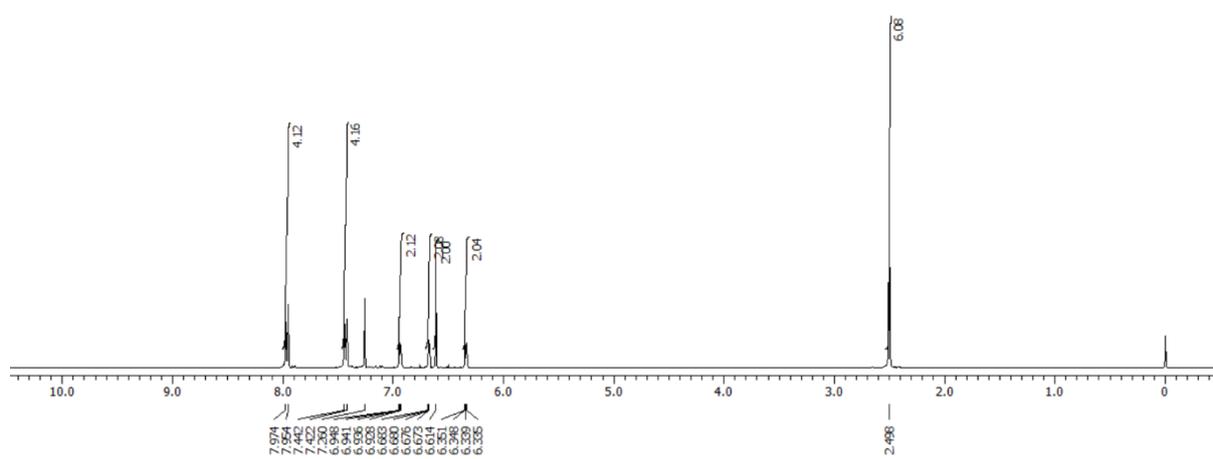
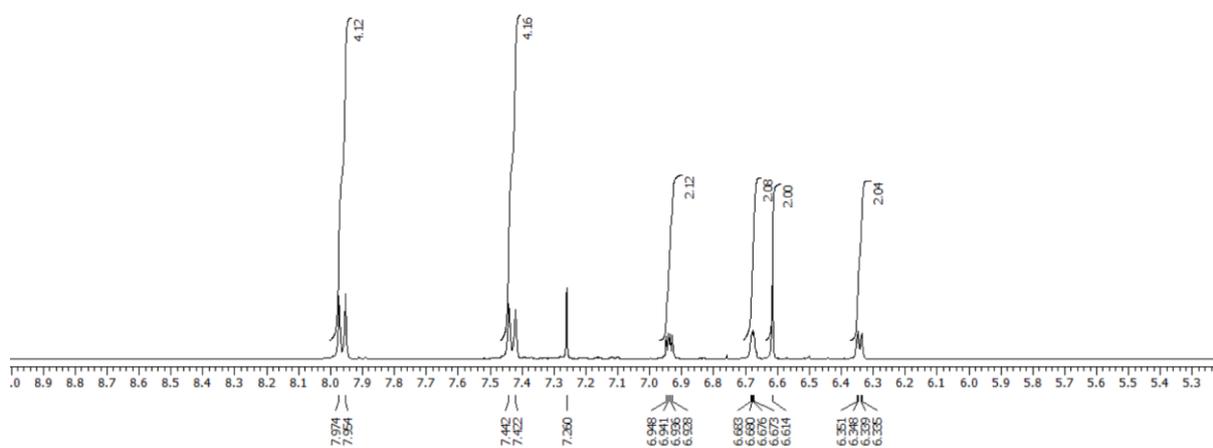
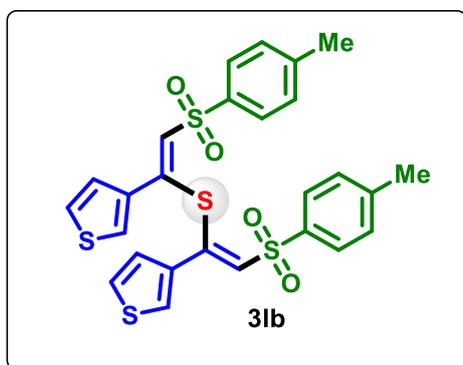
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



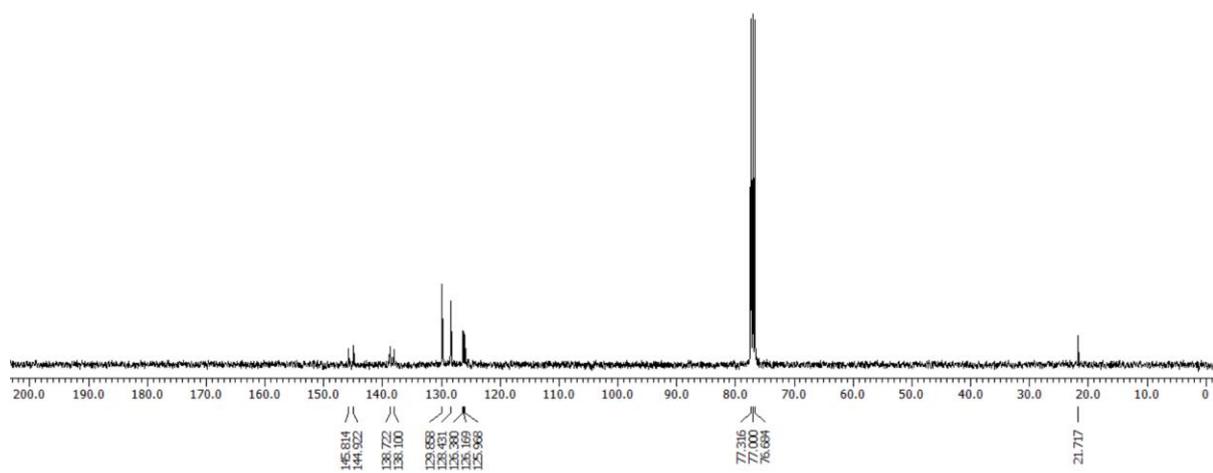
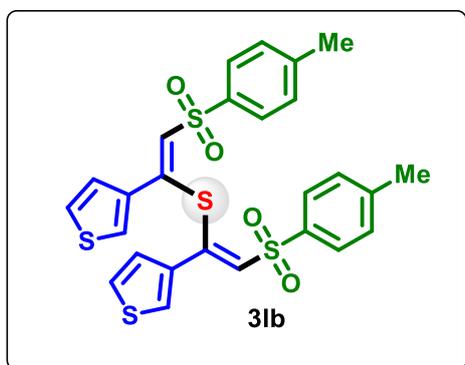
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



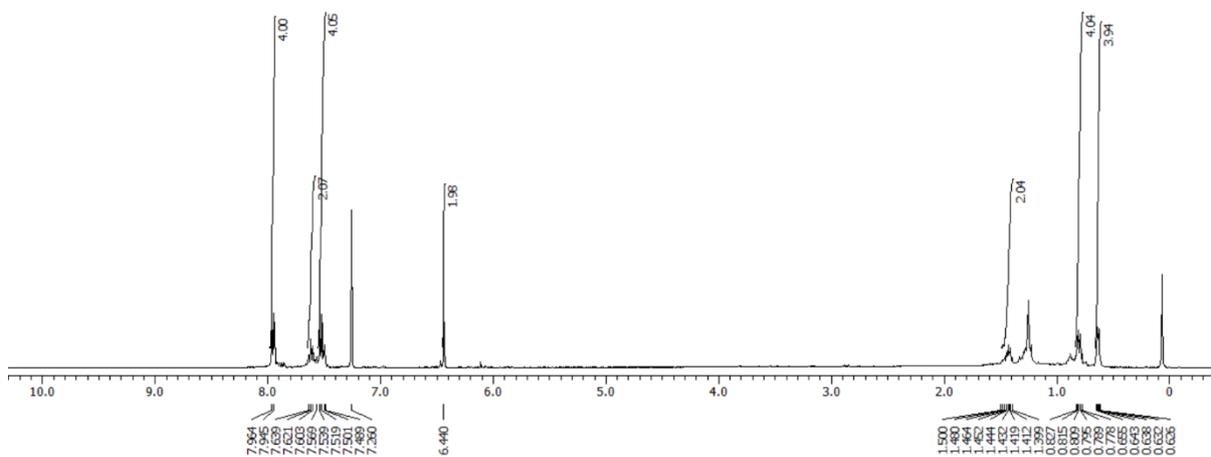
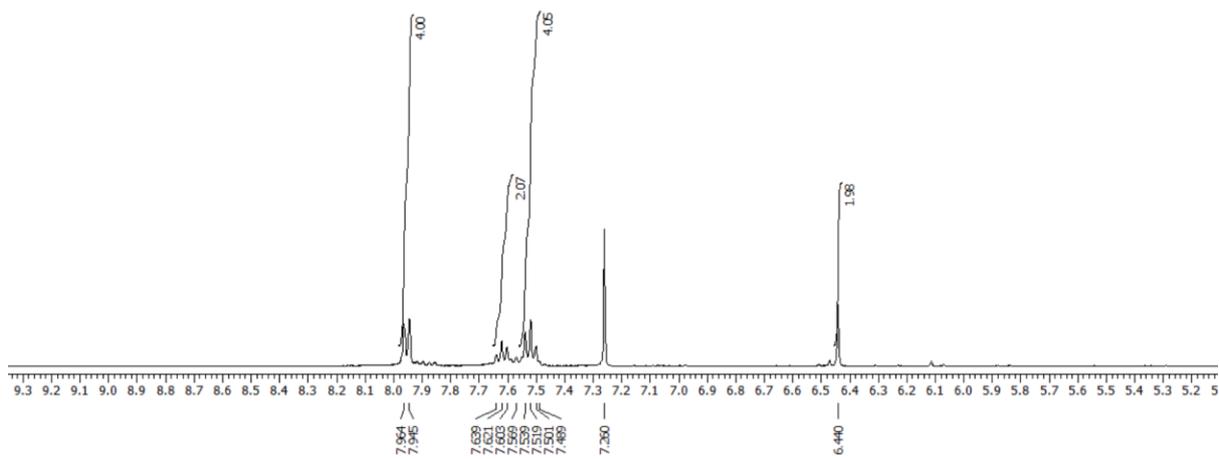
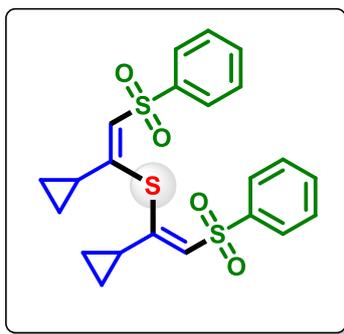
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



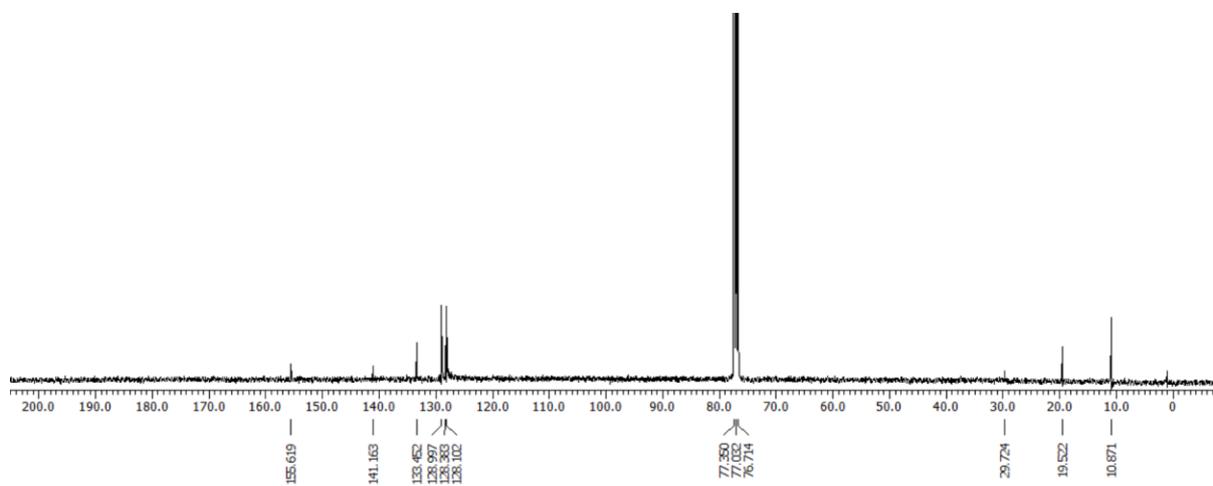
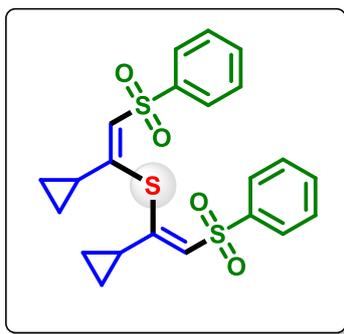
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



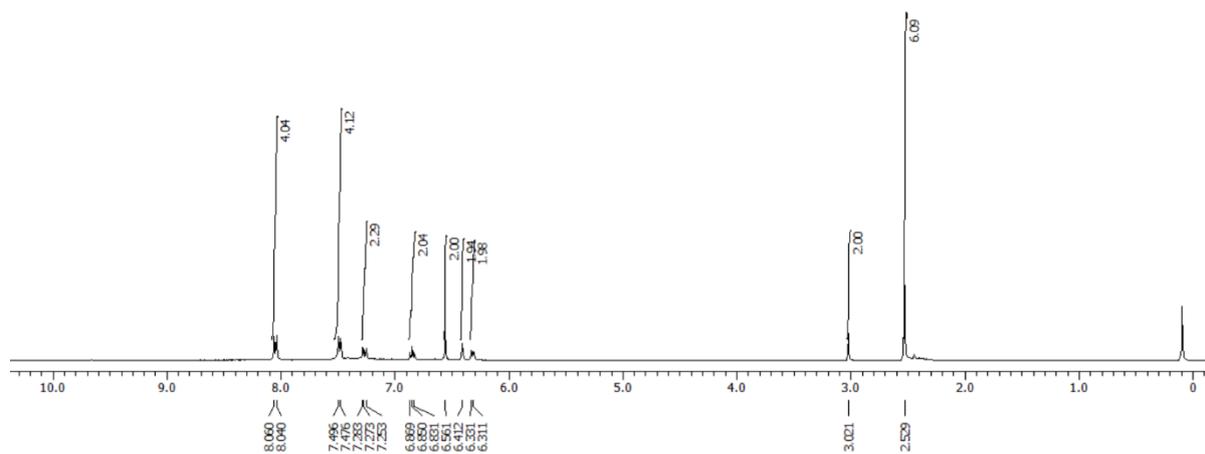
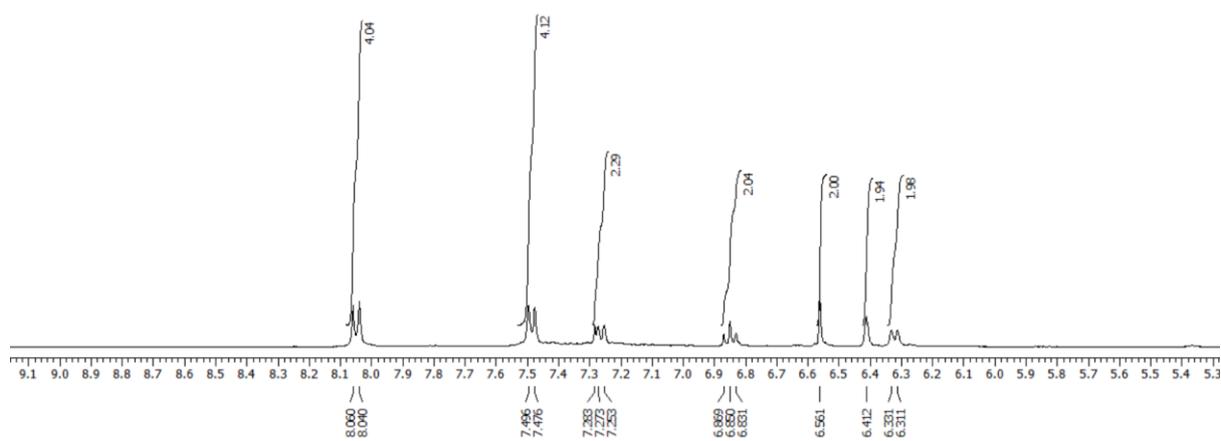
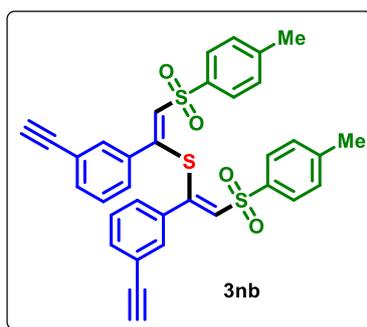
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**



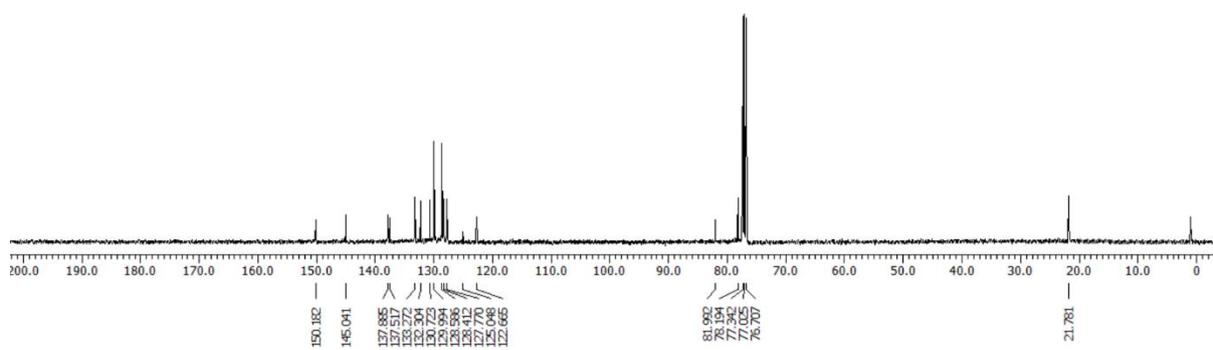
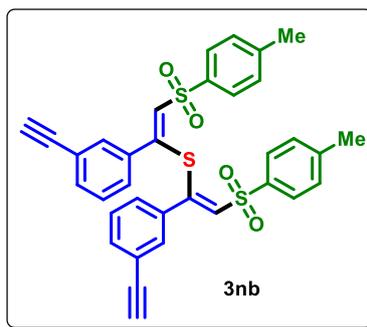
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



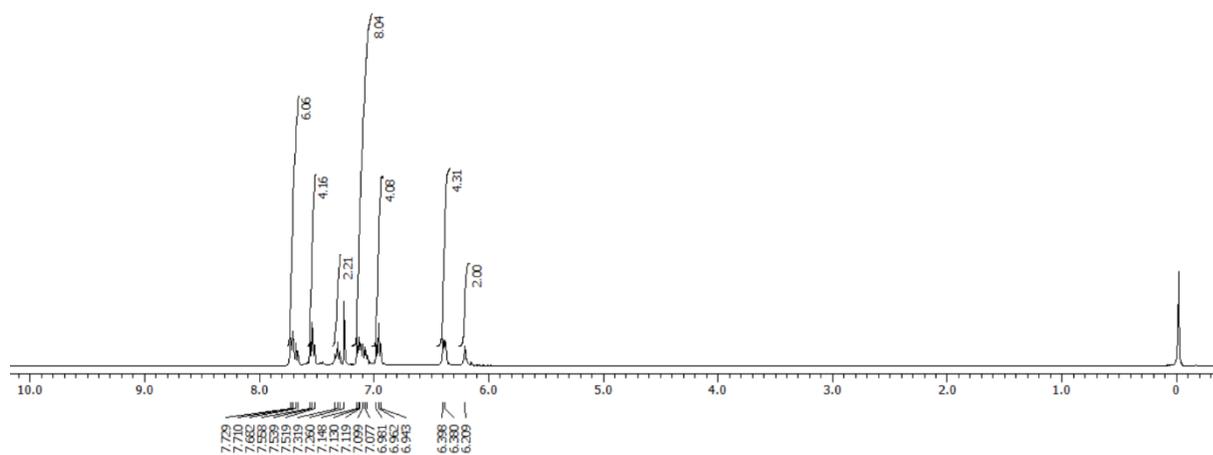
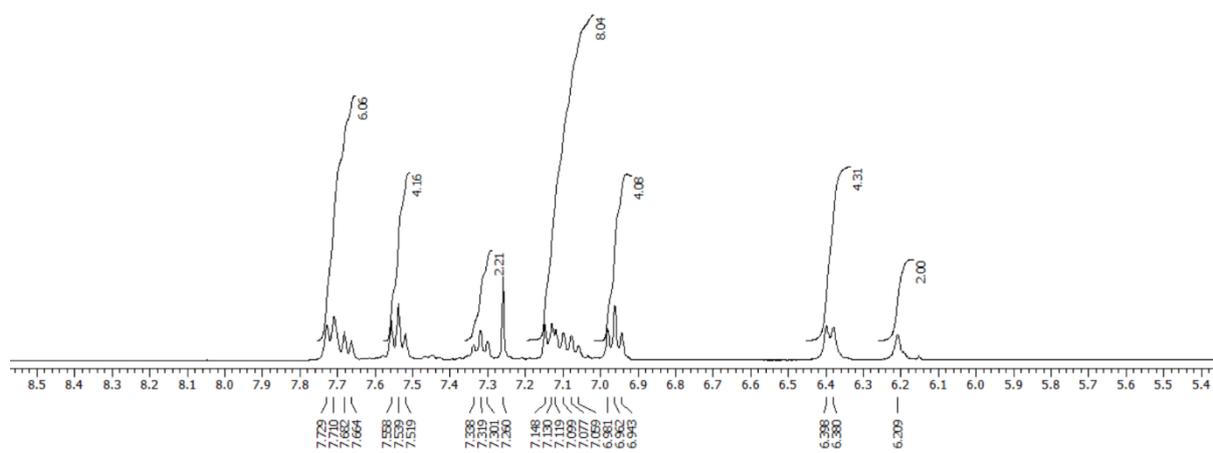
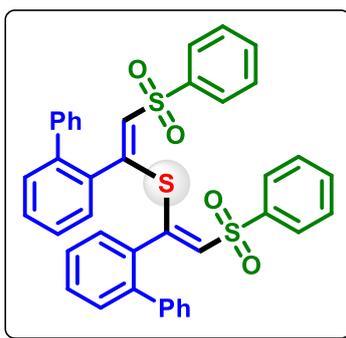
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



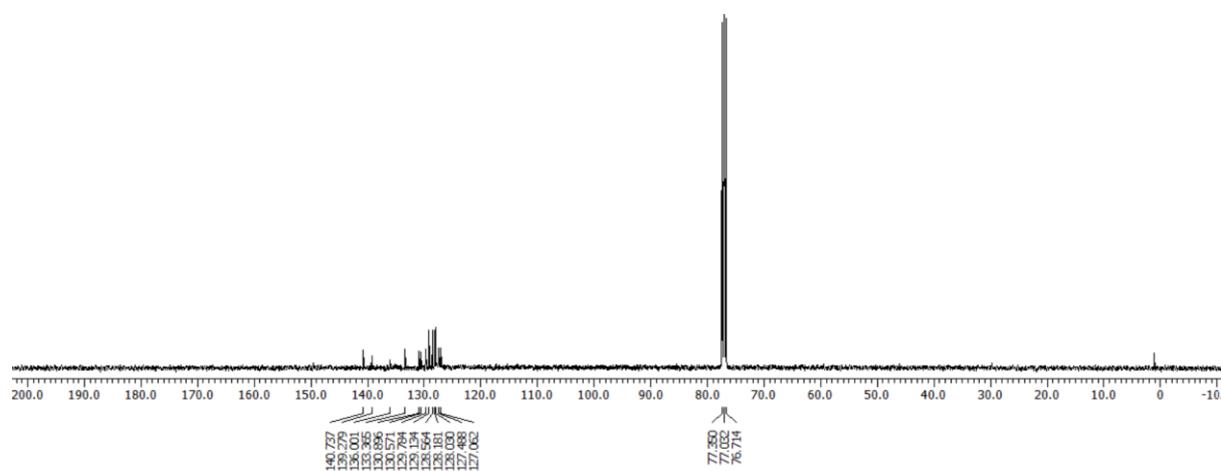
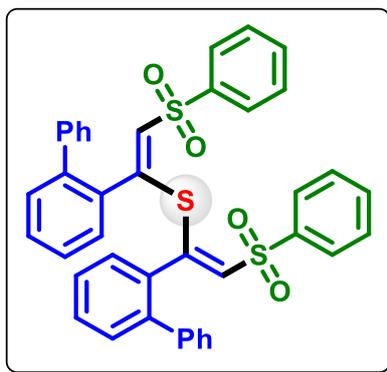
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



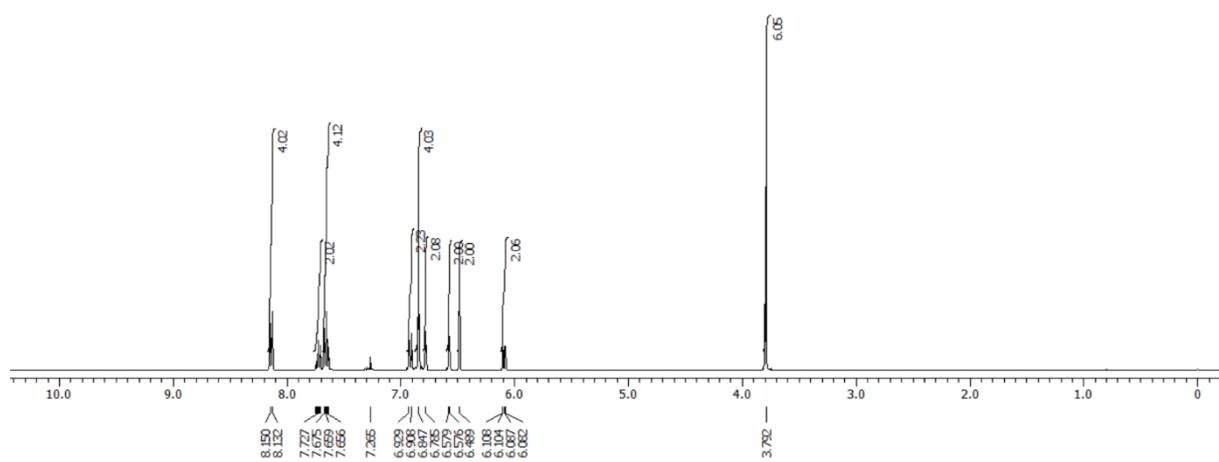
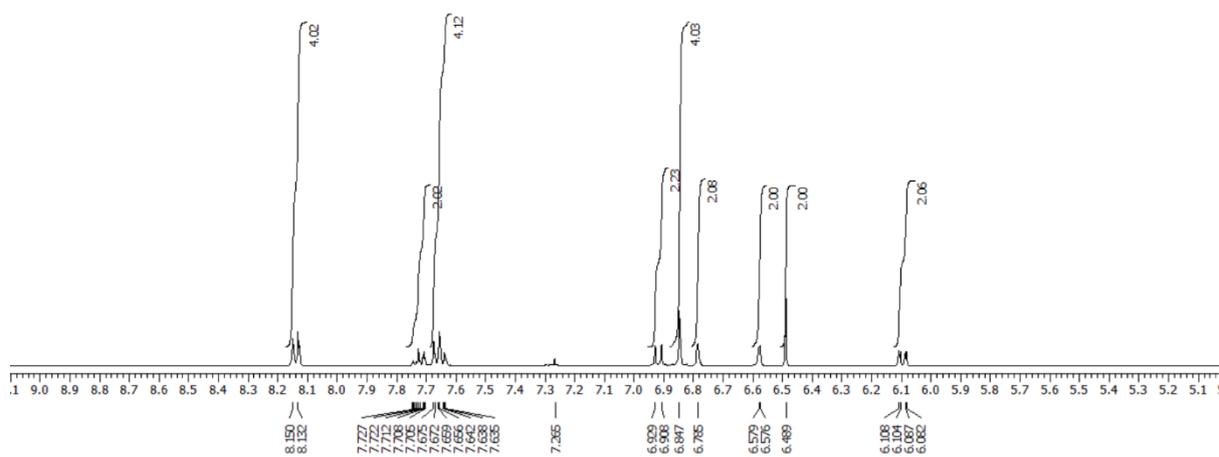
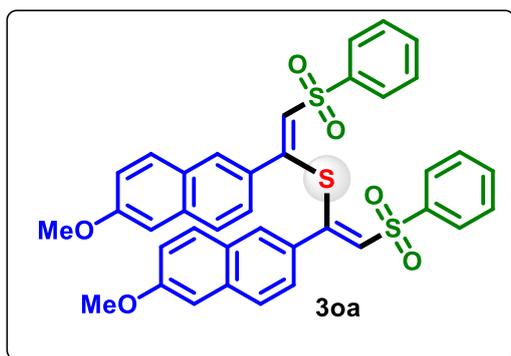
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



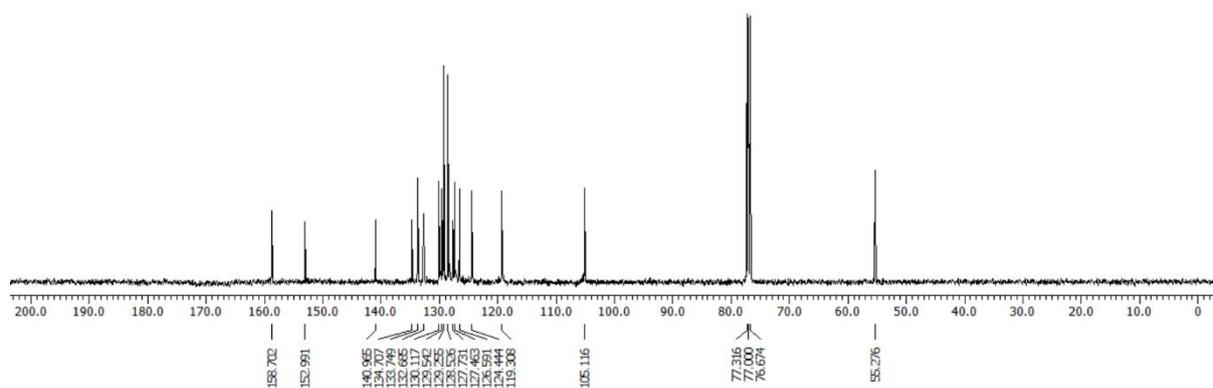
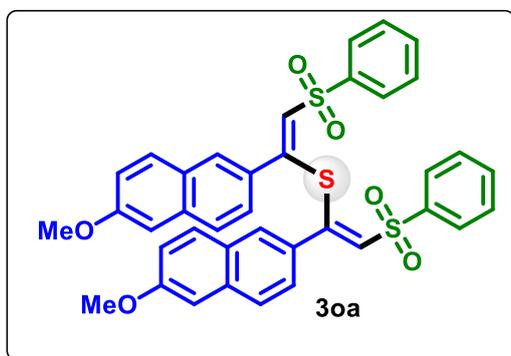
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



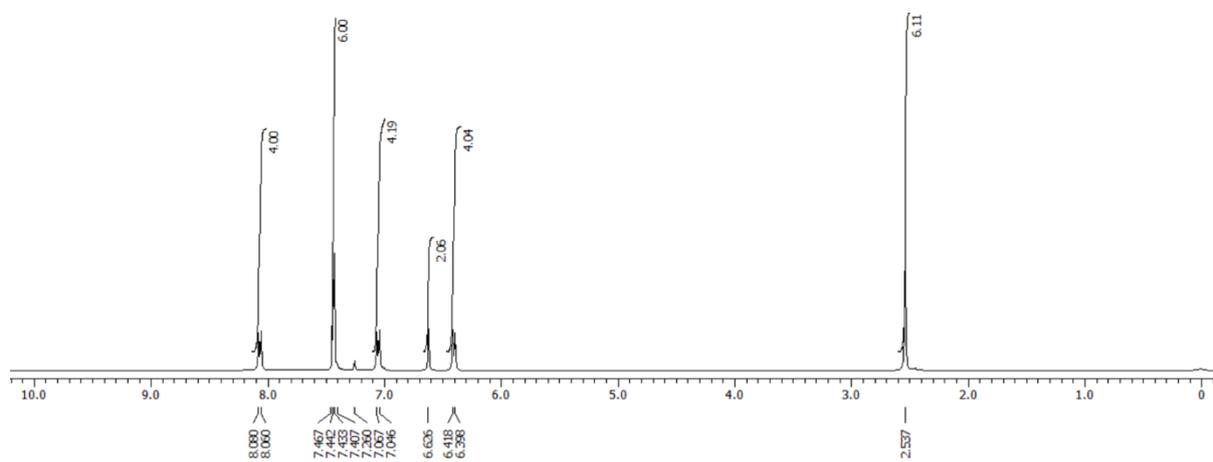
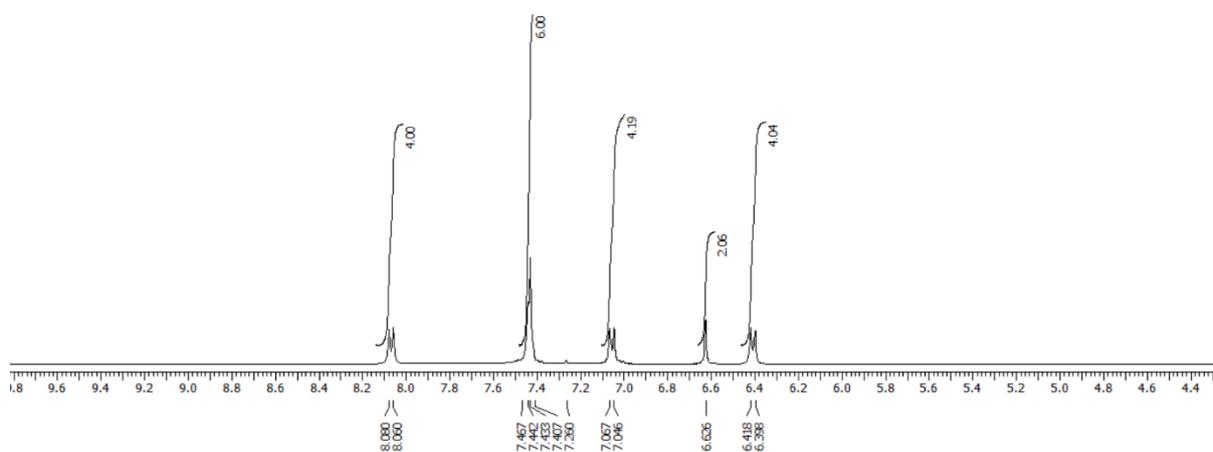
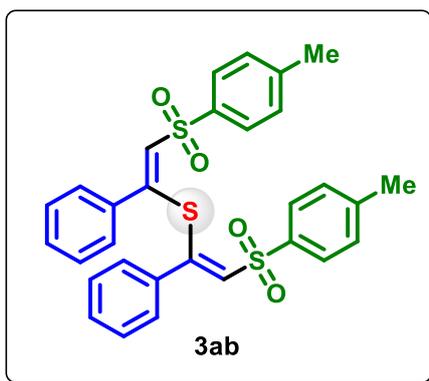
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



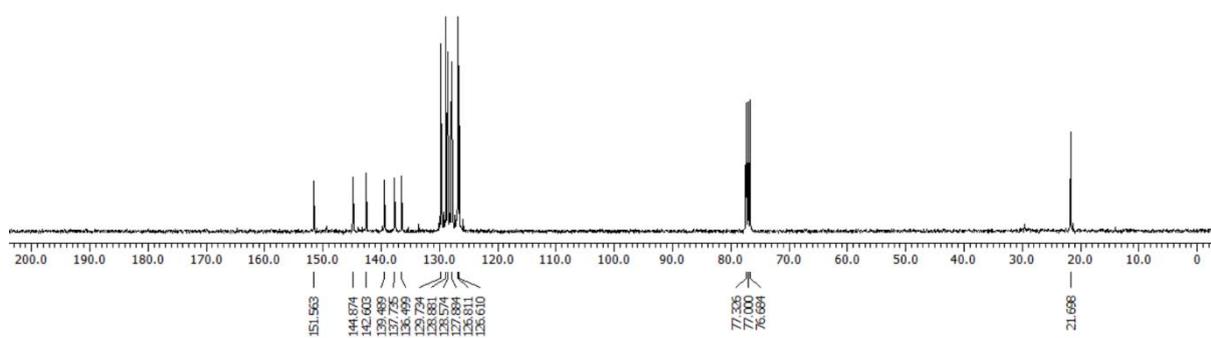
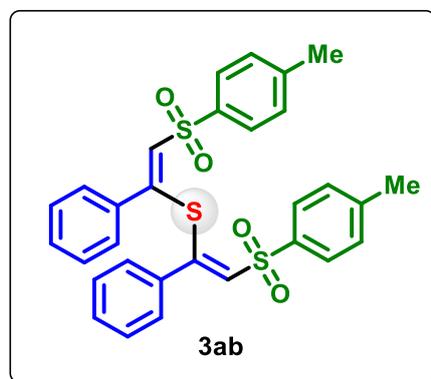
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



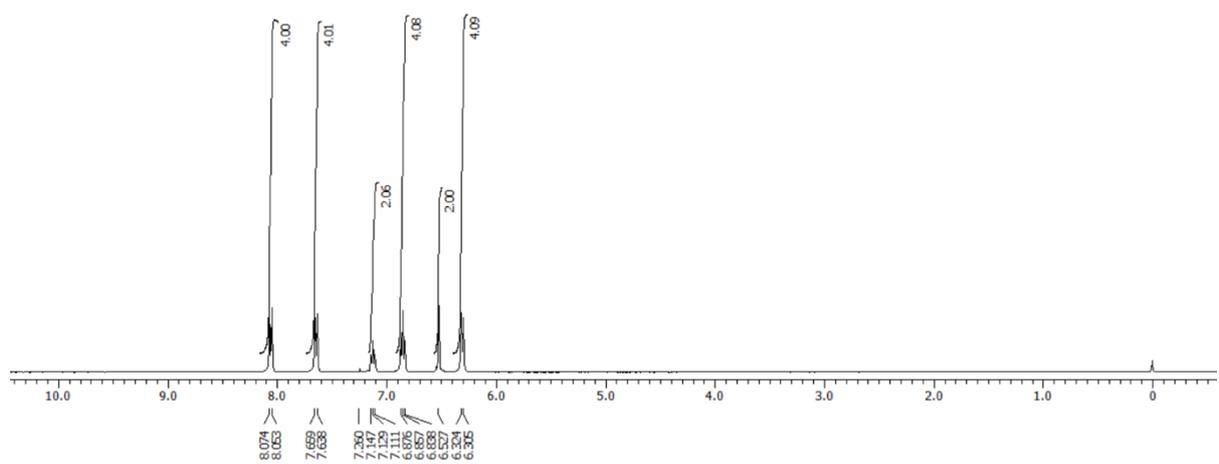
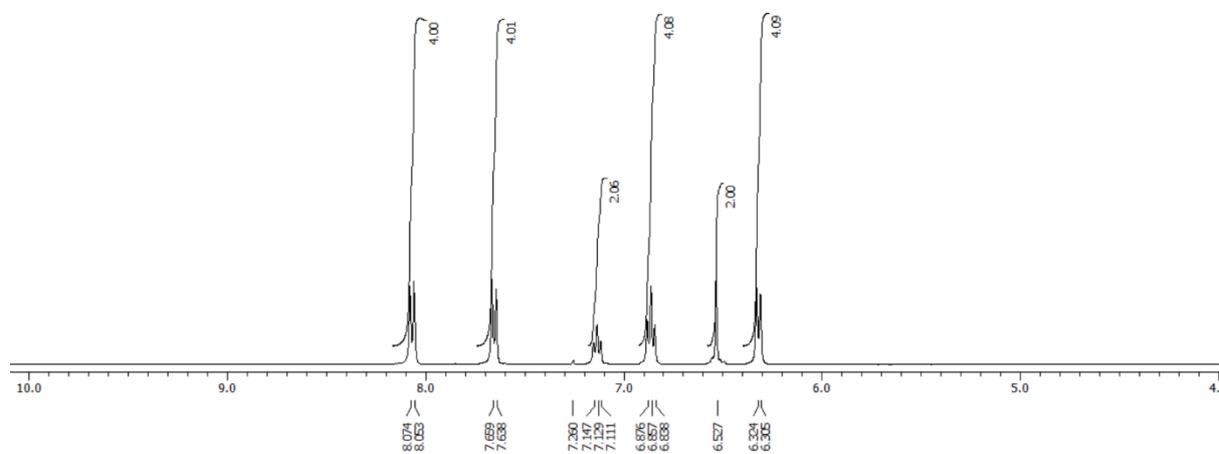
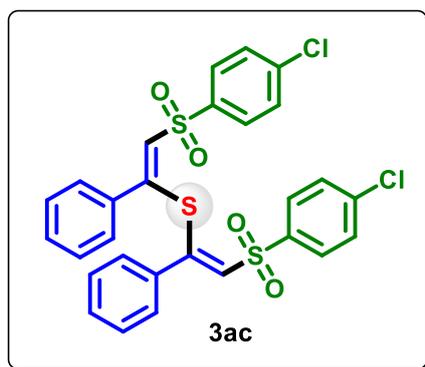
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



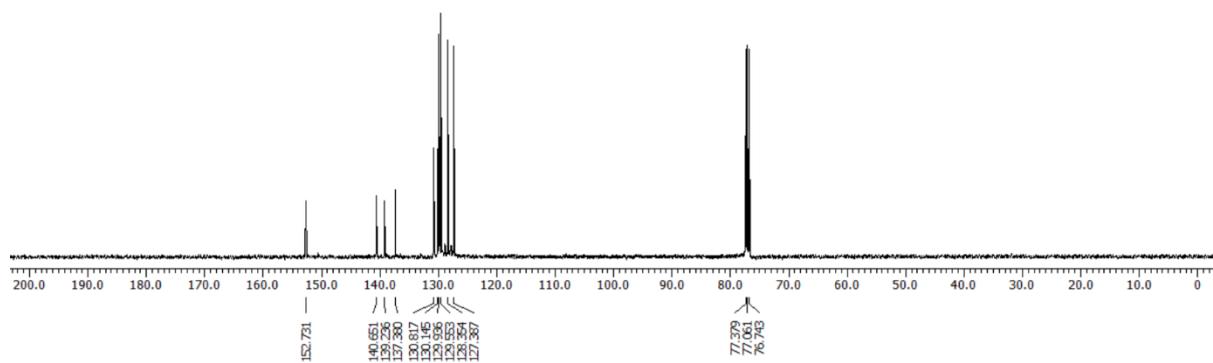
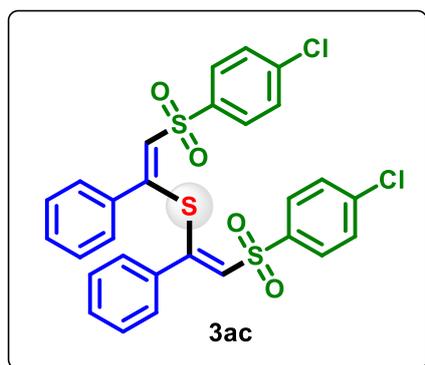
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



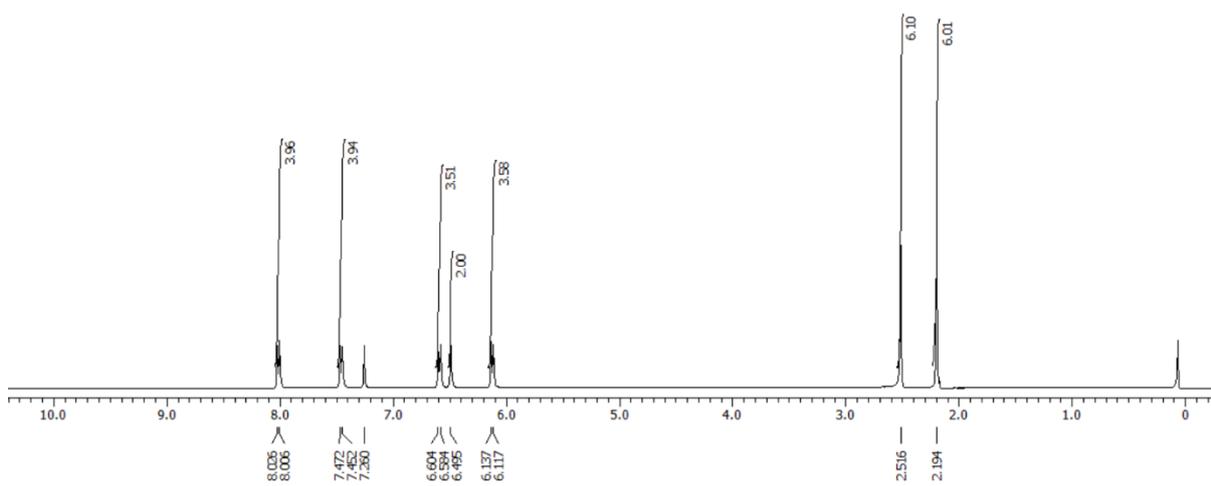
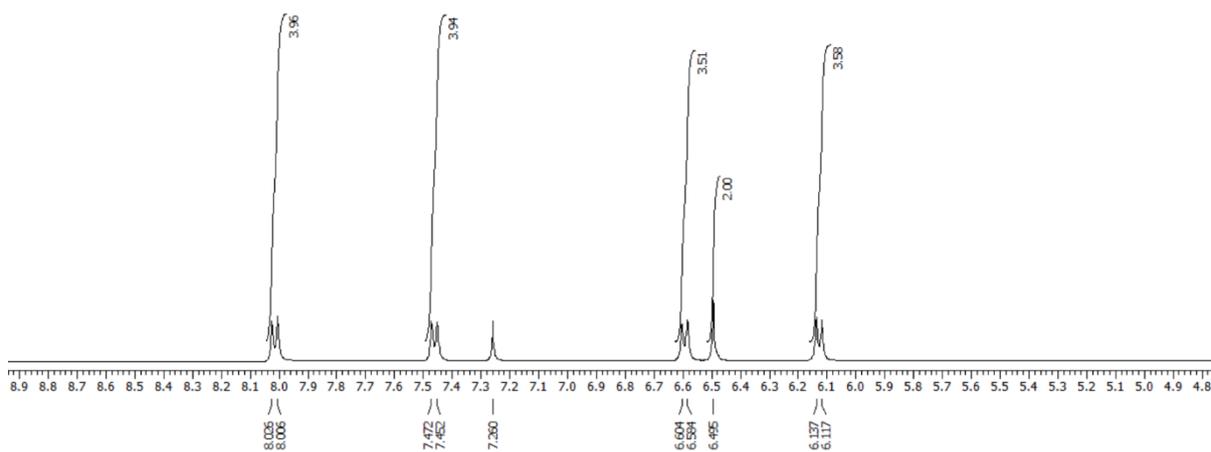
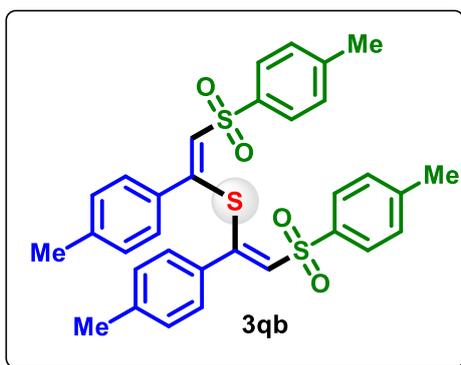
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



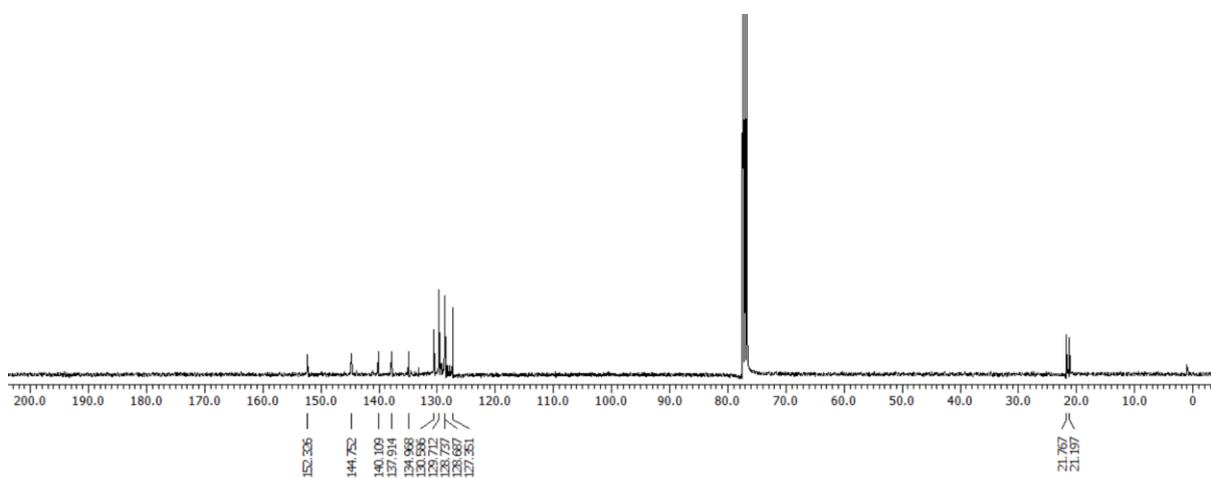
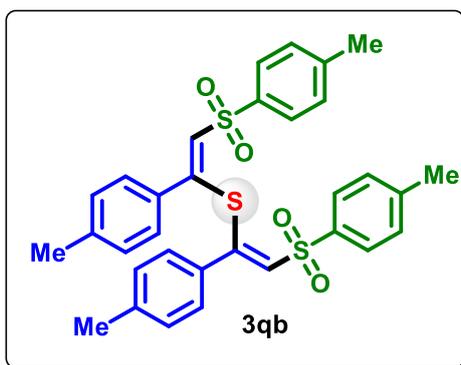
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



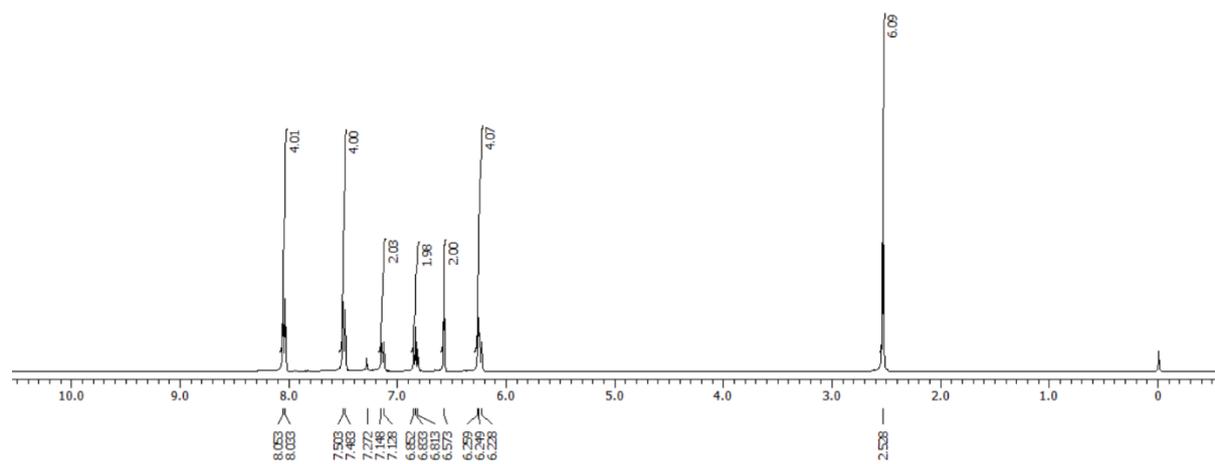
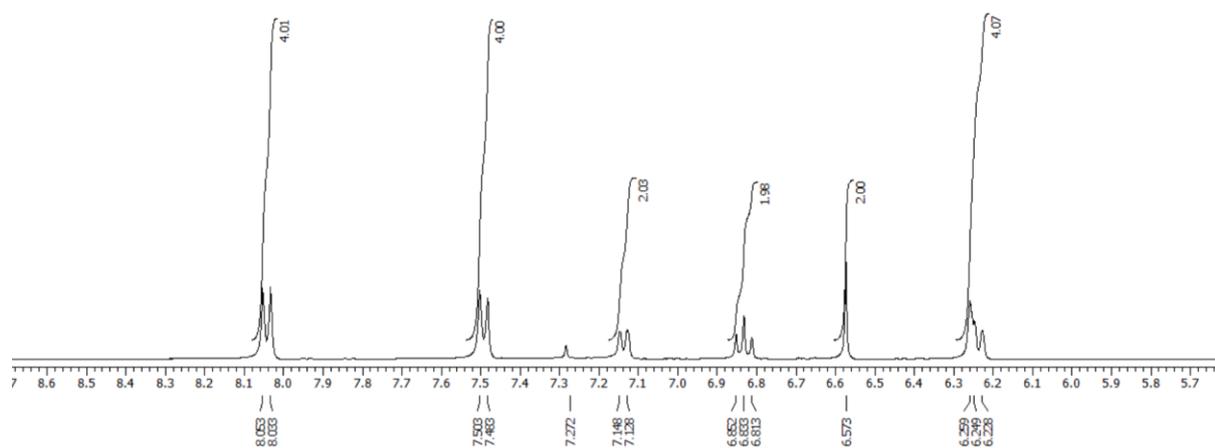
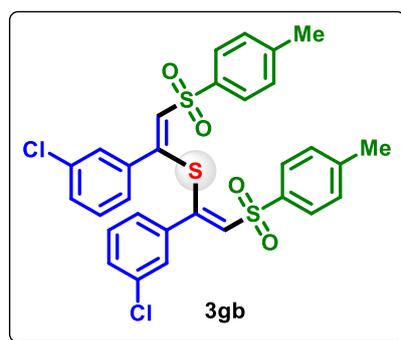
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



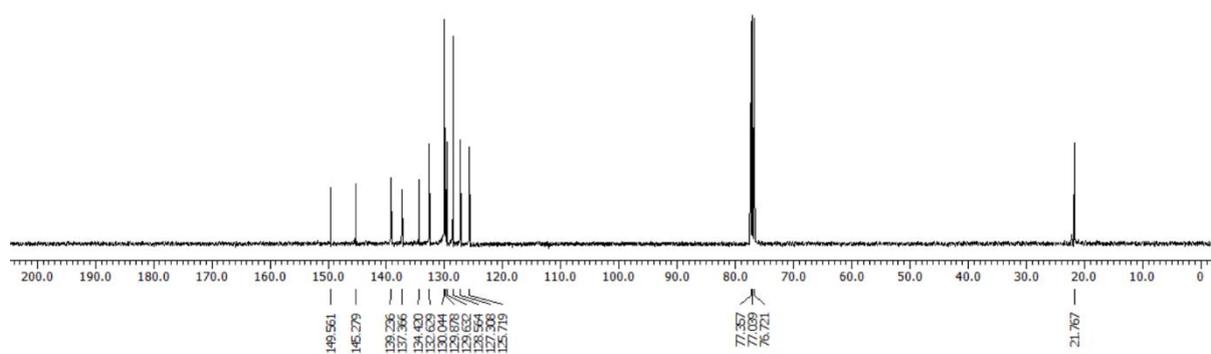
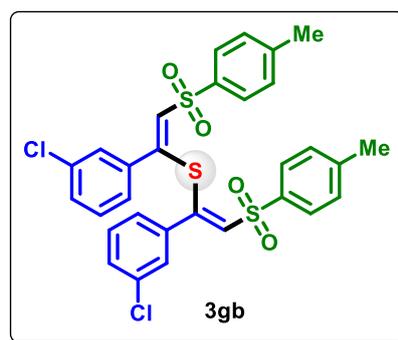
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



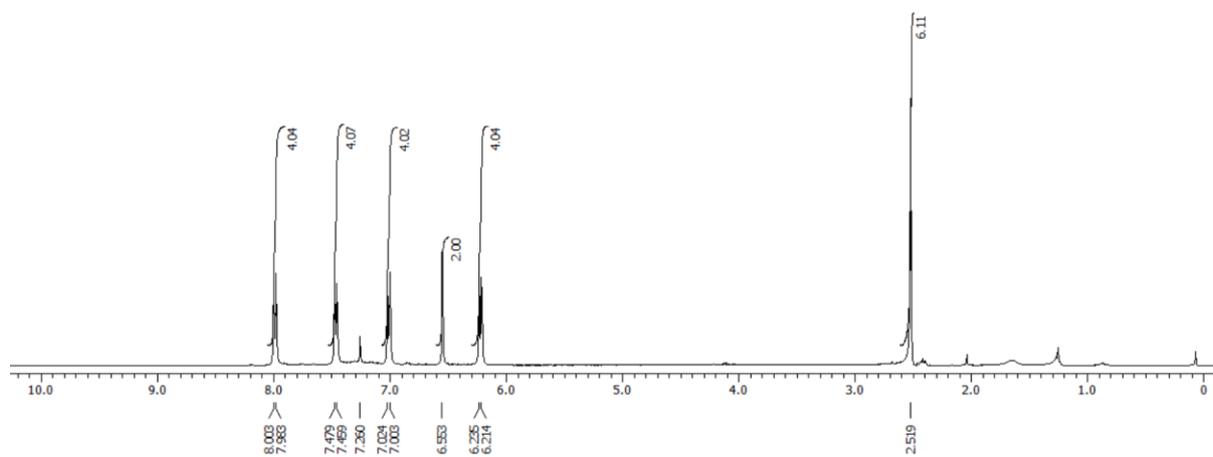
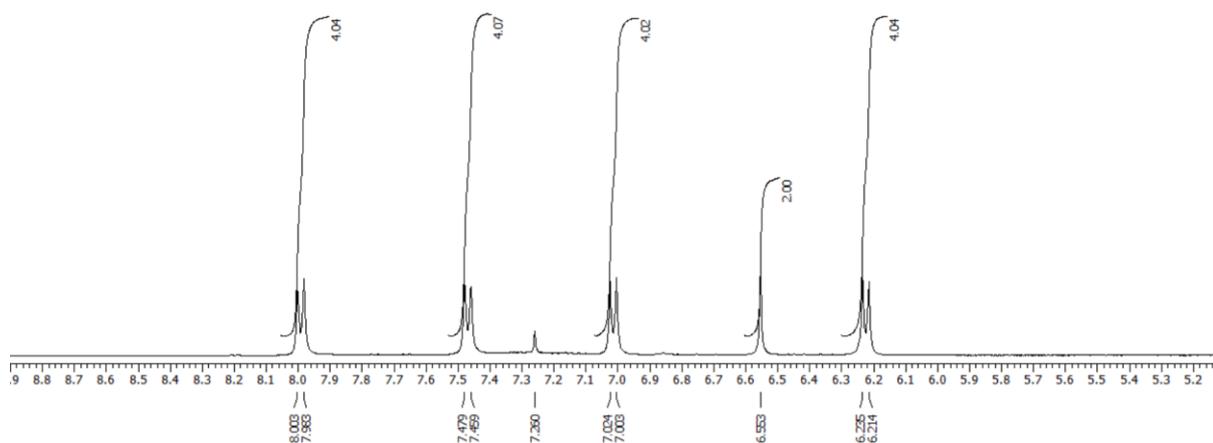
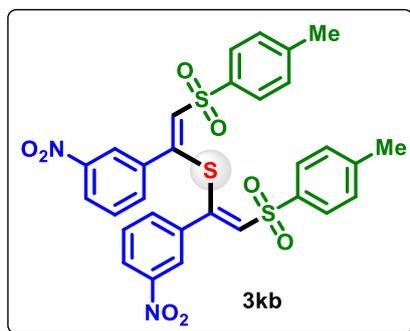
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) NKR-43



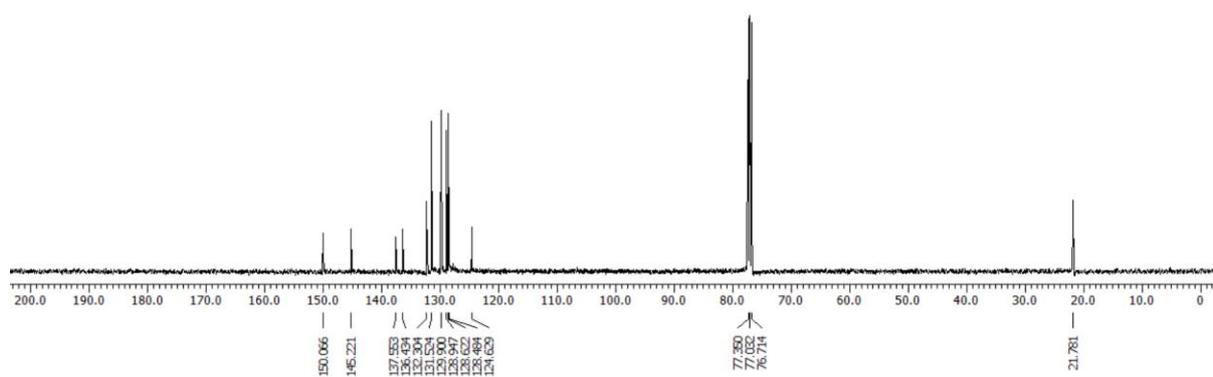
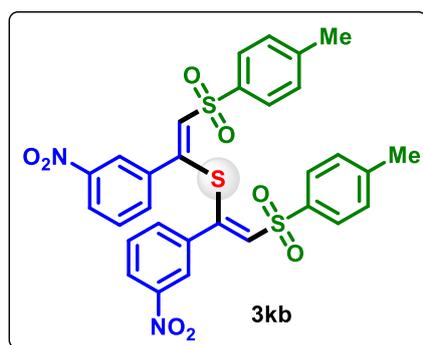
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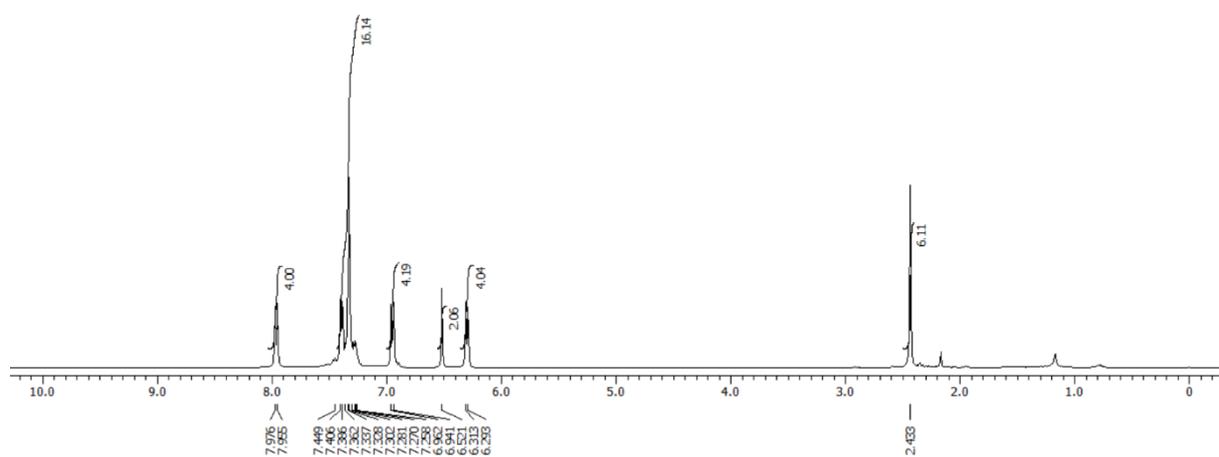
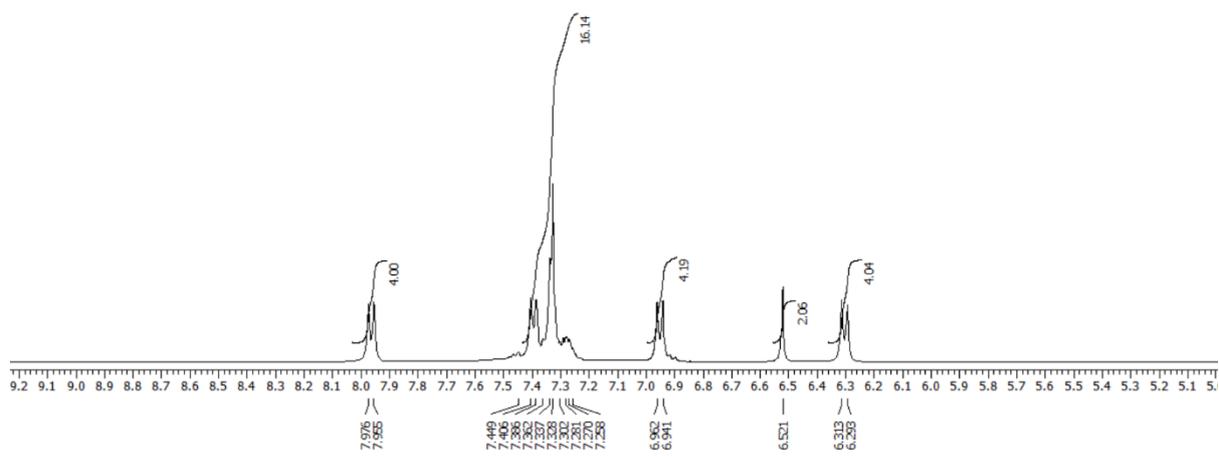
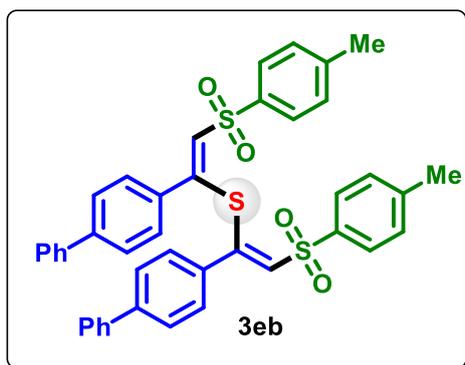
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



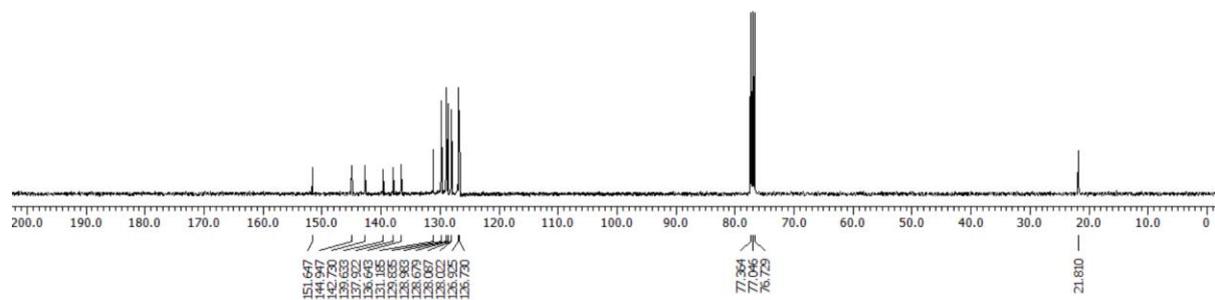
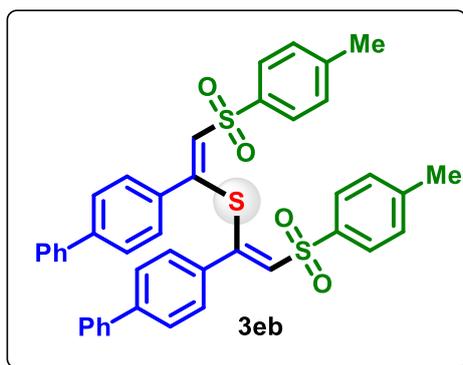
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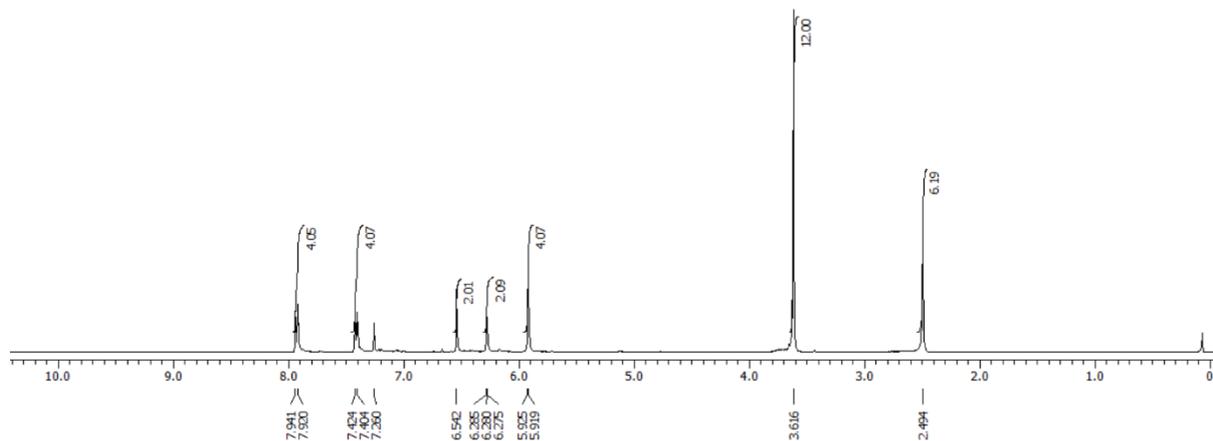
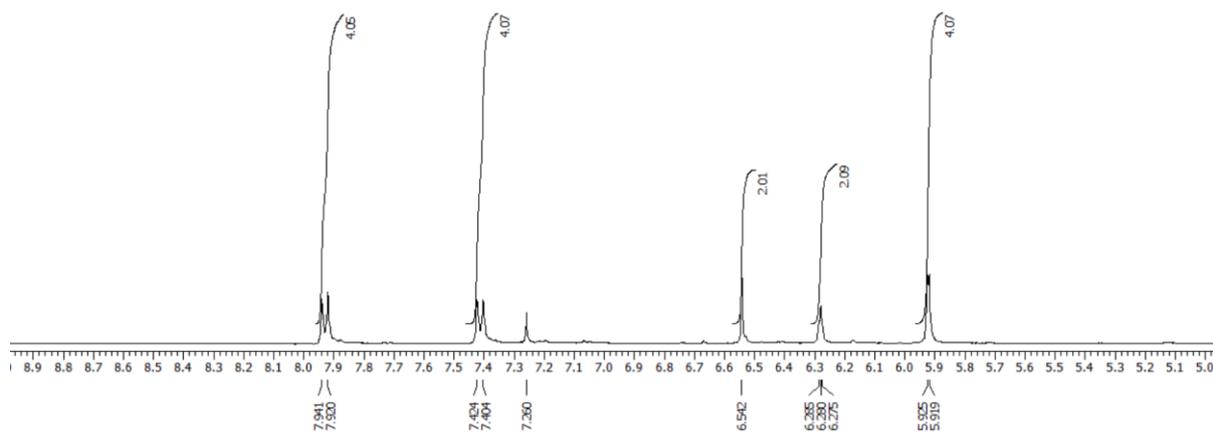
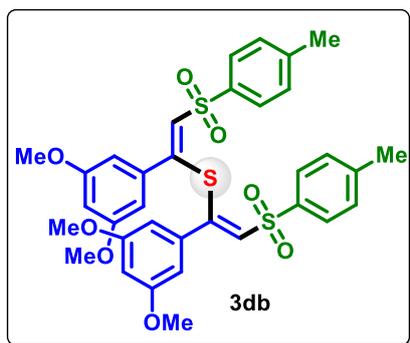
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



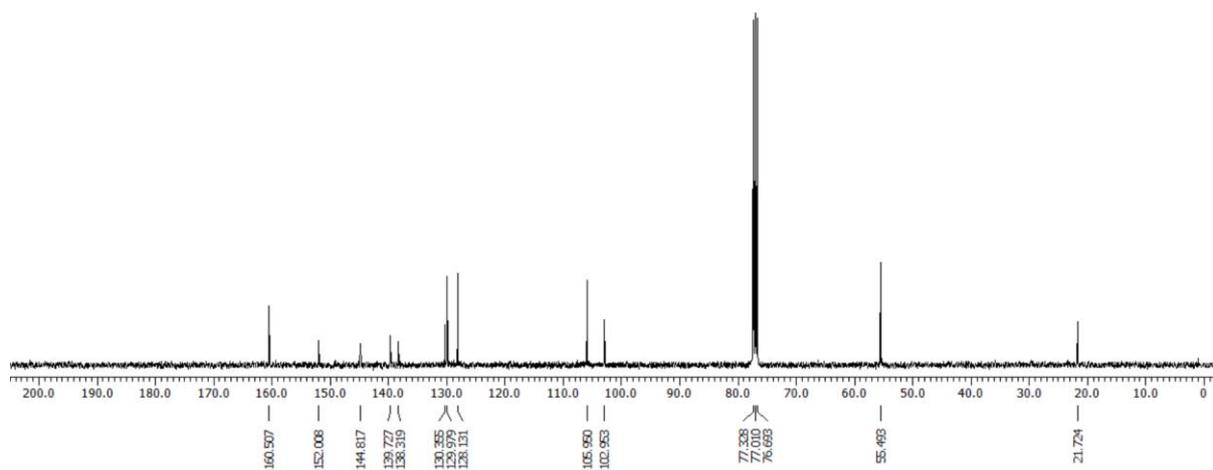
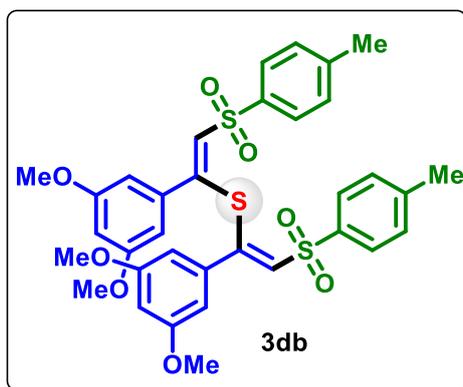
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



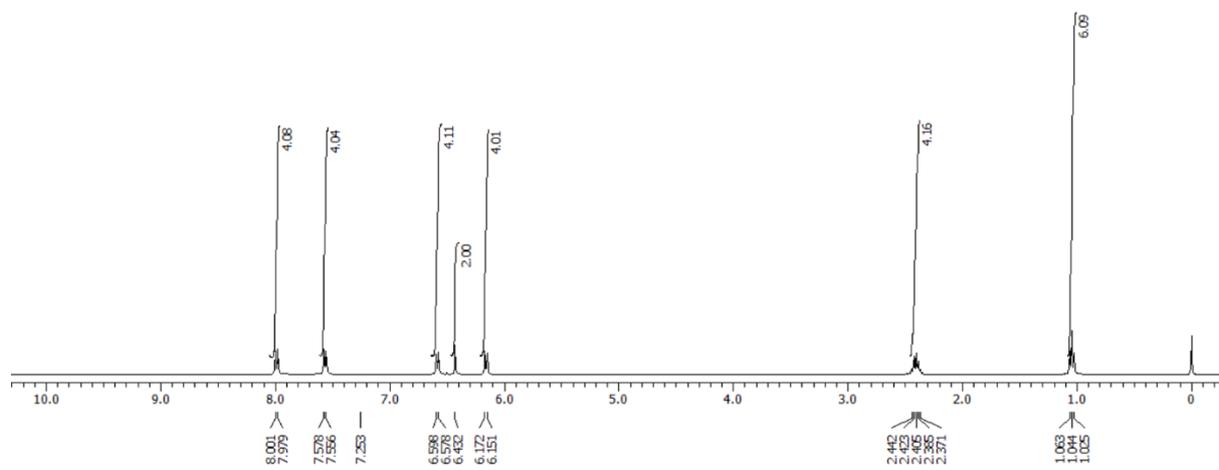
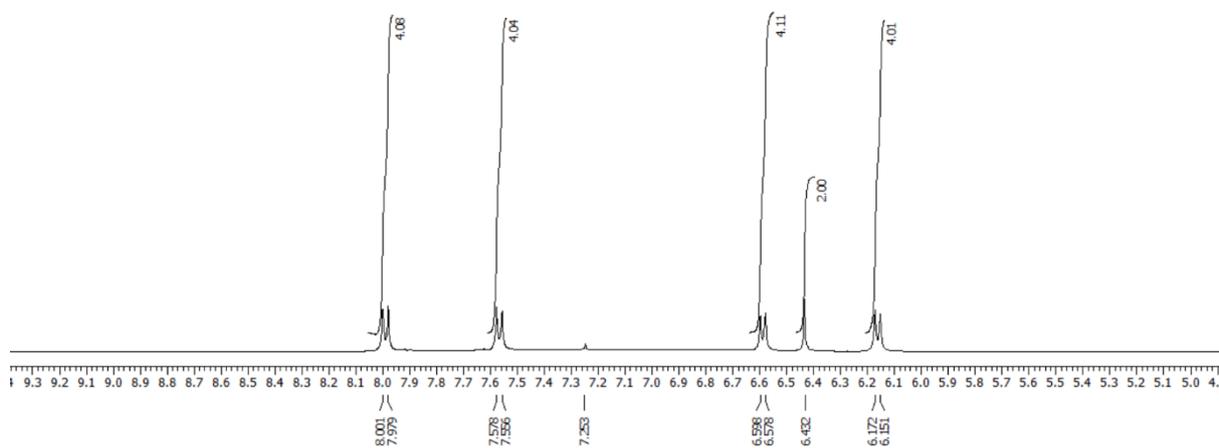
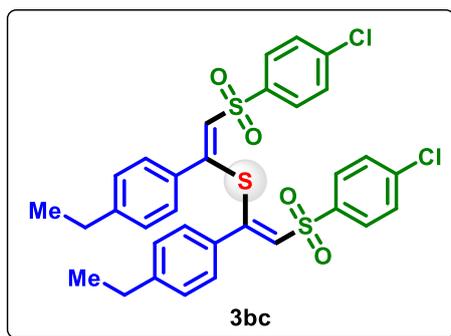
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



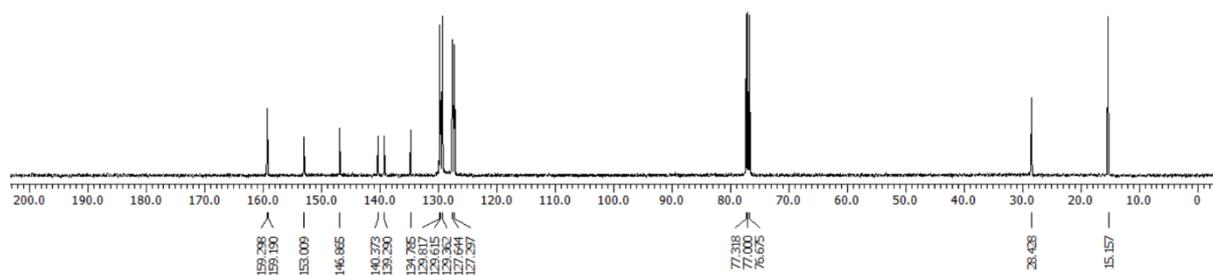
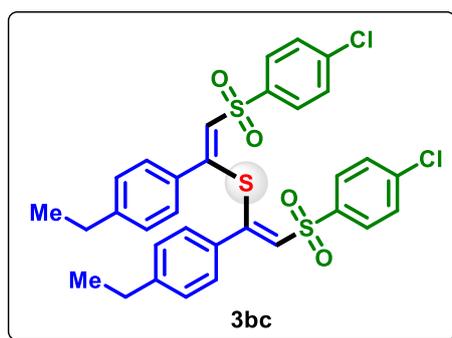
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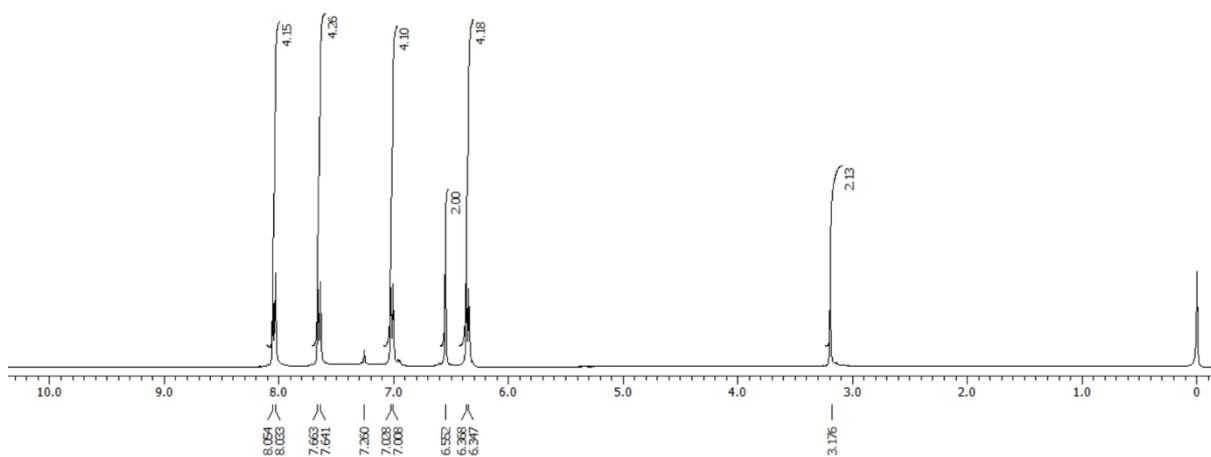
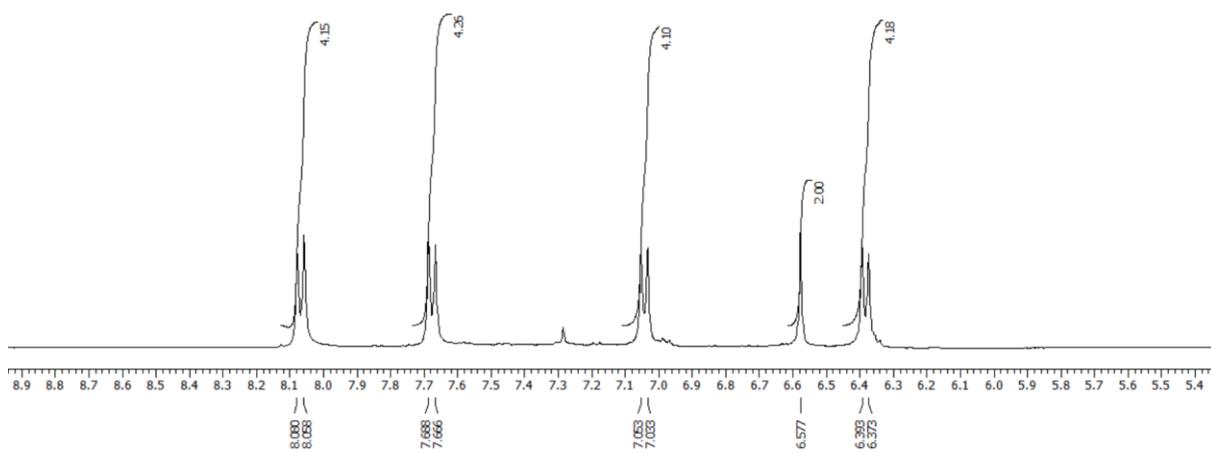
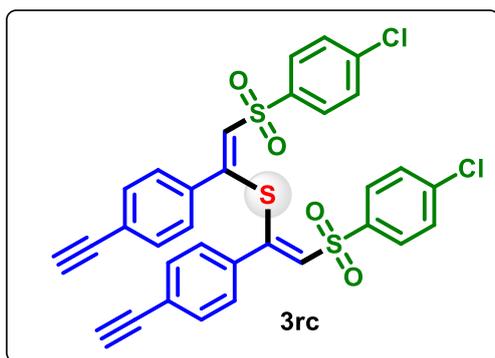
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



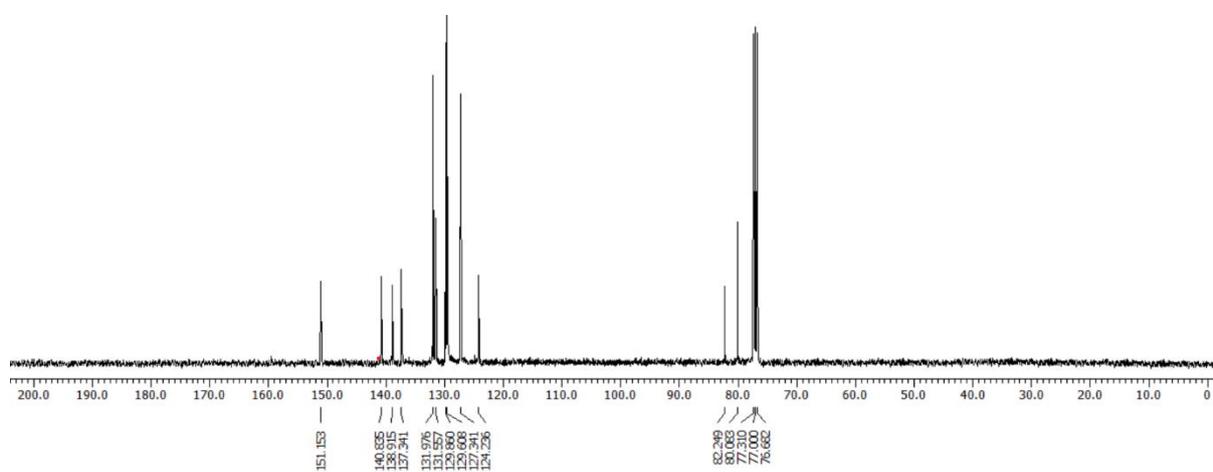
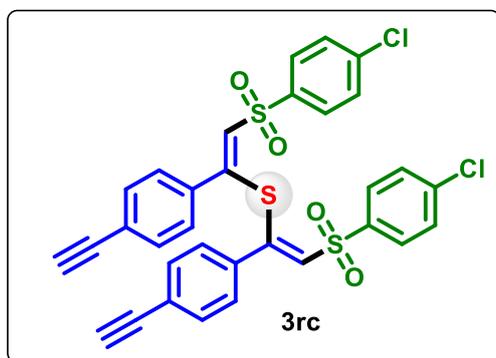
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



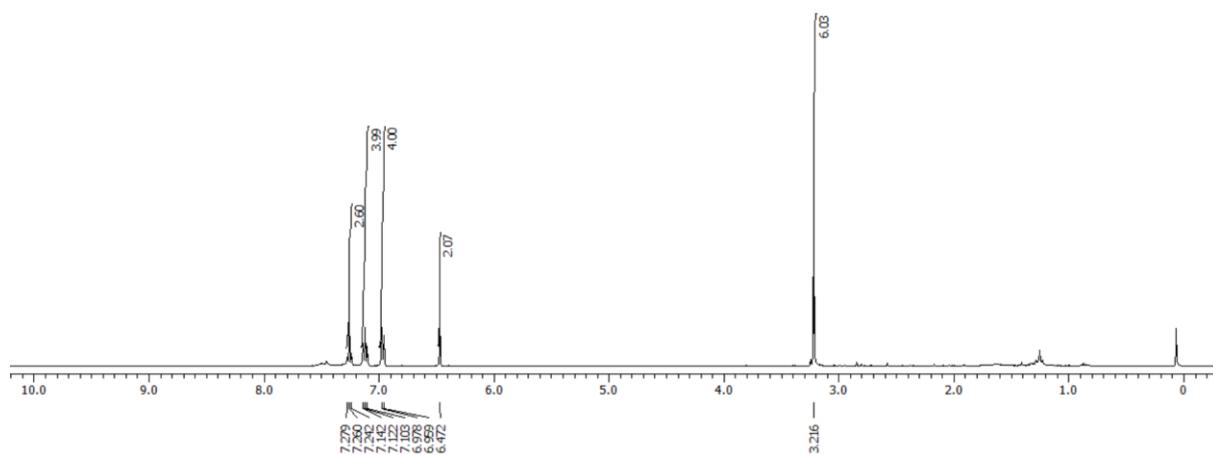
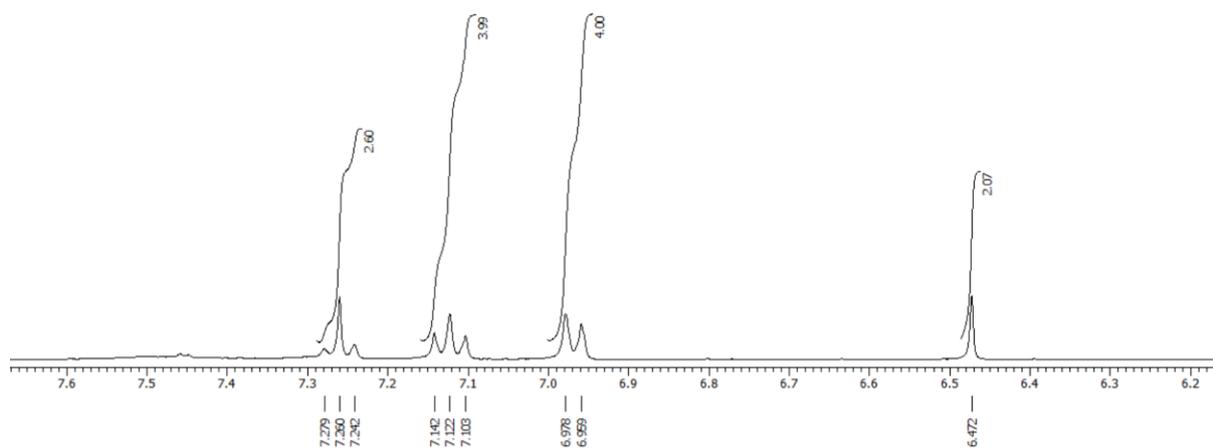
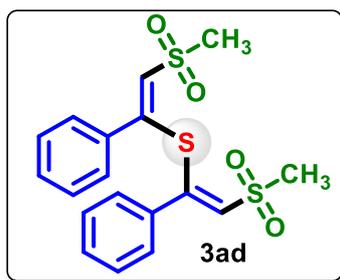
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



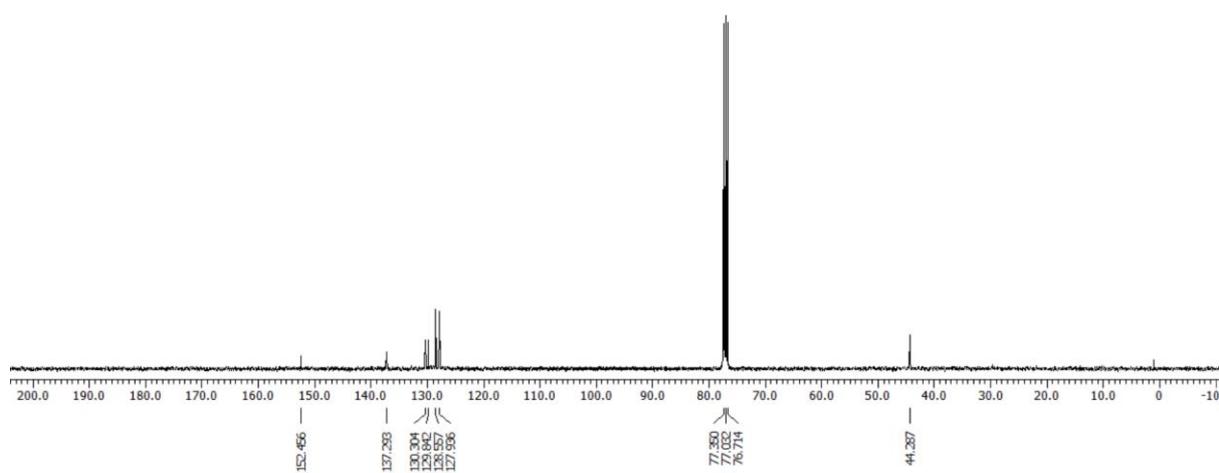
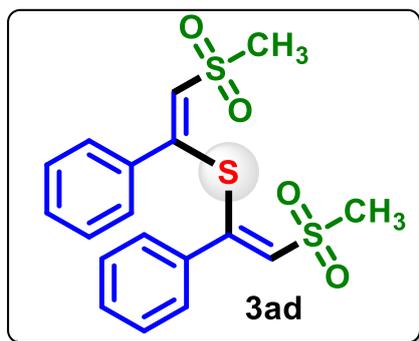
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )



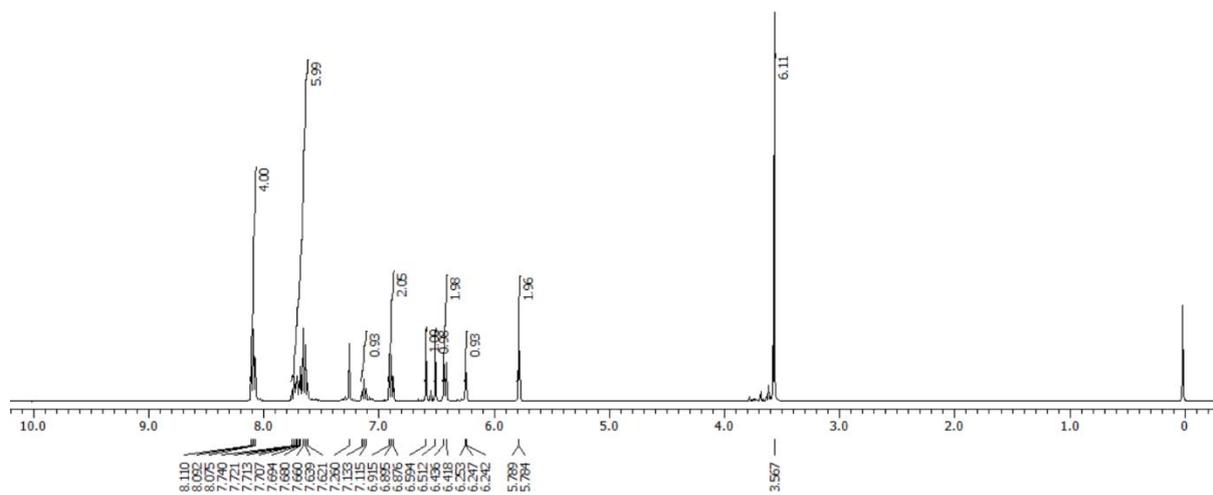
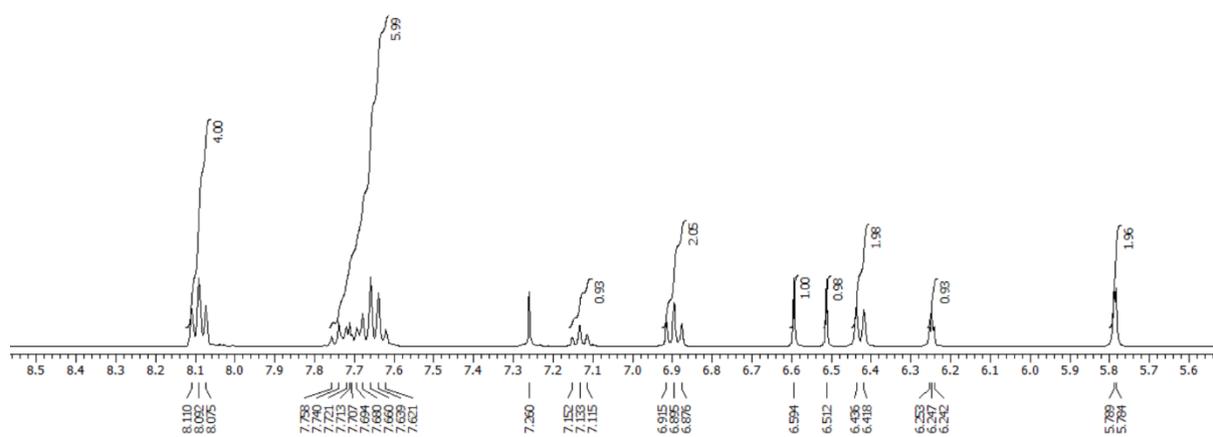
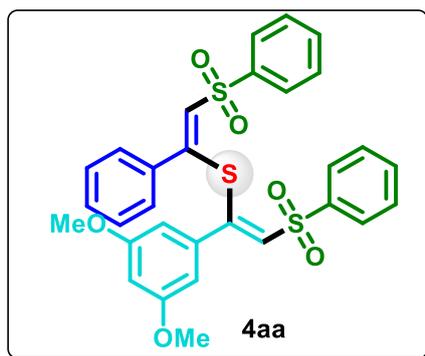
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



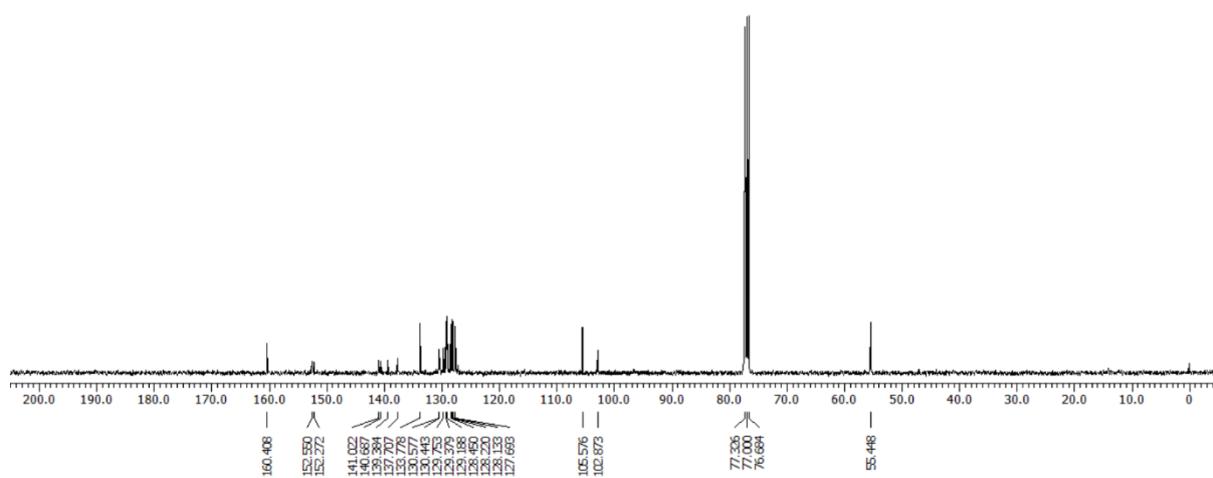
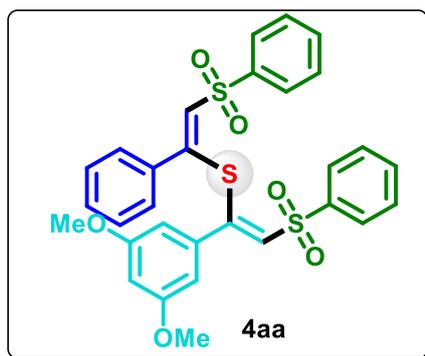
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



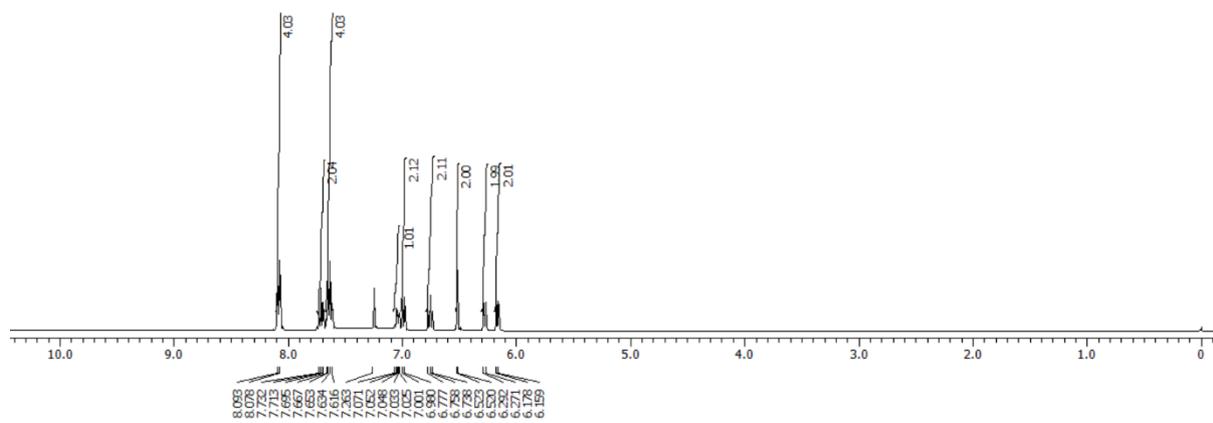
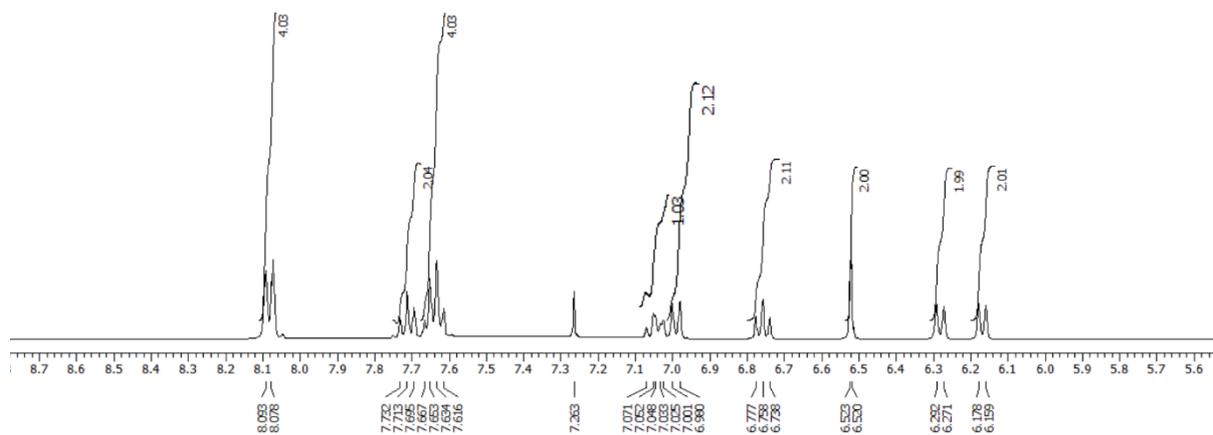
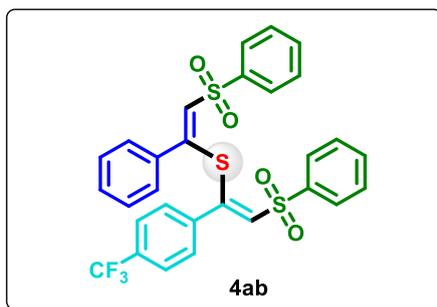
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



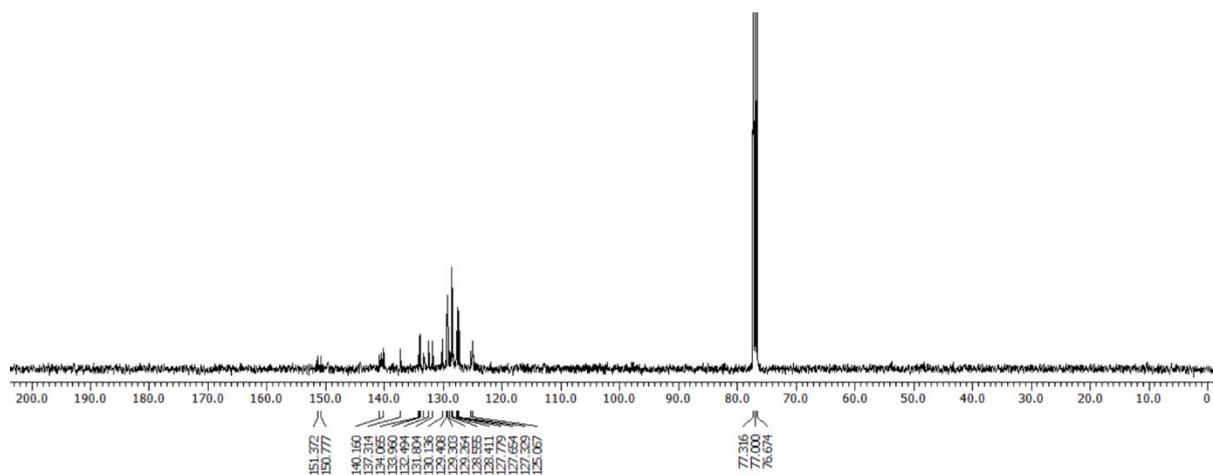
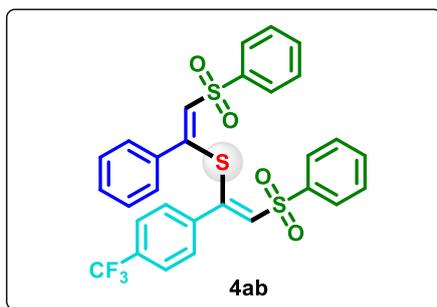
$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ ) NKR-52



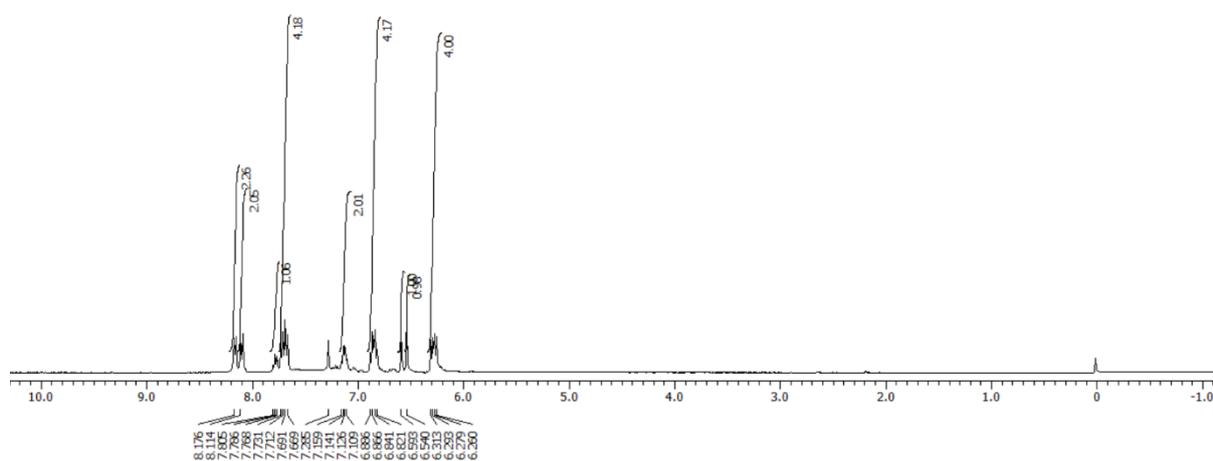
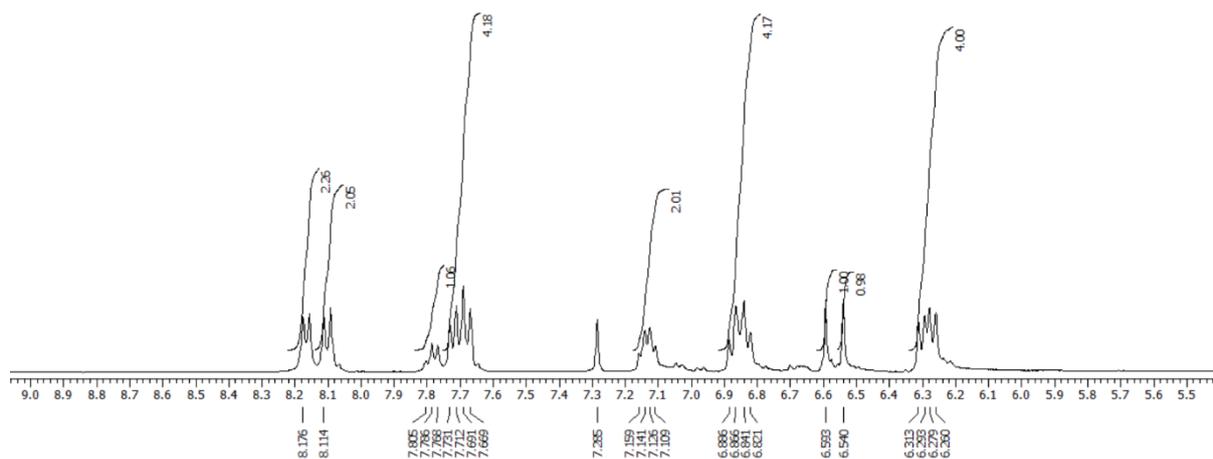
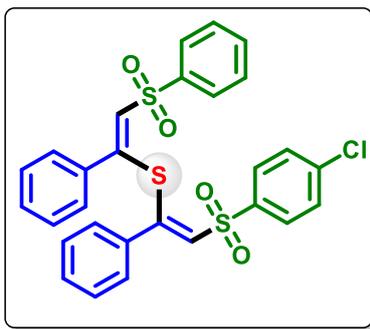
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )

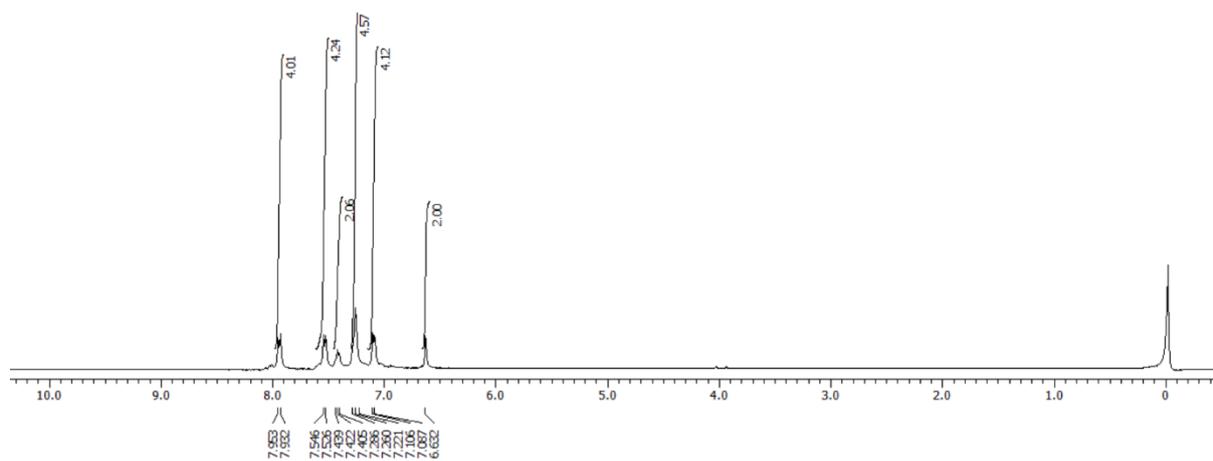
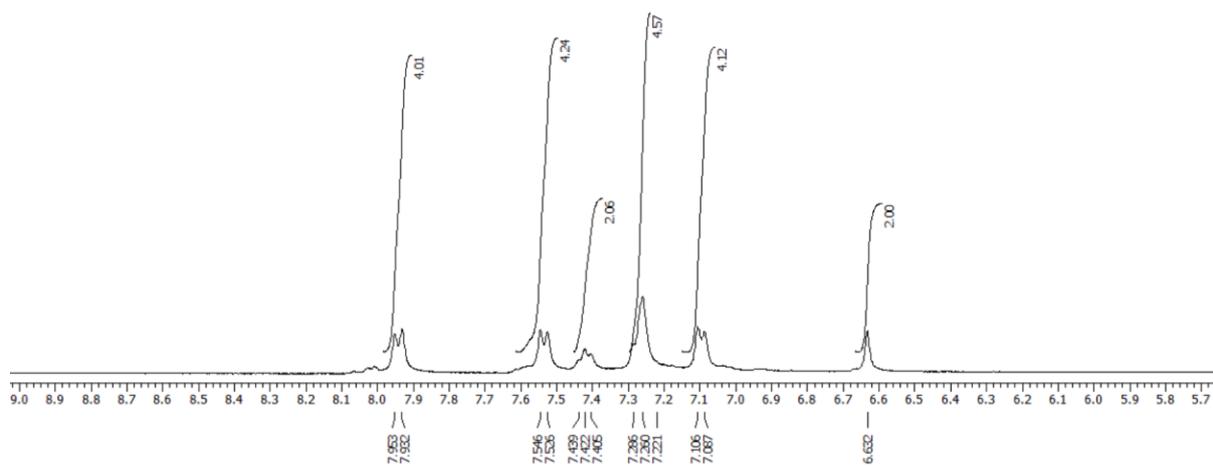
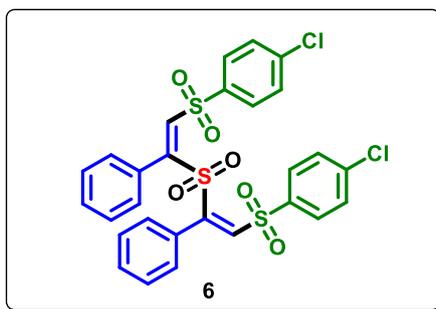


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



$^{13}\text{C}$  { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ )

