Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for

Photochemical Halogen-Bonding Assisted Generation of Vinyl and Sulfur-Centered Radicals: Stereoselective Catalyst-Free C(sp^2)-S Bond Forming Reactions

Helena F. Piedra and Dr. Manuel Plaza*

Departamento de Química Orgánica e Inorgánica and Instituto Universitario de Química Organometálica "Enrique Moles". Universidad de Oviedo. c/ Julián Clavería 8. Oviedo. 33006. Spain.

Corresponding author: plazamanuel@uniovi.es

CONTENTS

1. General considerations

All of the vinyl bromides **1** were prepared following previously reported methodologies.[1] The thiol **2g** was prepared following a known procedure.[2] The radical trapping agent **7** was synthesized through a previously reported procedure.[3] The different bases, photocatalysts and thiols **2** employed during the development of this work are commercially available from Sigma Aldrich Chemical co., Acros Organics Chemical co. and Alfa Aesar Chemical co. Dry DMSO stored with molecular sieves acquired from Sigma Aldrich Chemical co. was used for the photochemical reactions.

A Kessil® PR160 Rig equipped with different lamps (PR160-366nm, PR160-390nm, PR160-427nm, PR160-440nm and PR160-456nm) and a cooling fan was used as the photochemistry setup. A PR time controller was additionally used to select the irradiation time. 5 mL glass vials purchased in VWR® were used to run the photochemical reactions. The vials were sealed with a cap after adding the chemicals and solvent and placed at a distance of approximately 5 cm away from the lamp prior to irradiation at maximum intensity (100% power) of the Kessil lamp. Figures SI-1 to SI-3 illustrate relevant photophysical properties of the lamps.

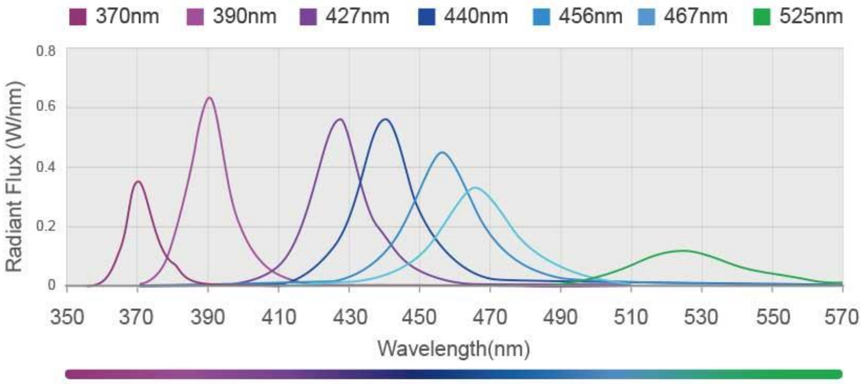


Figure SI-1. Emission spectrums of the different Kessil® lamps.

---

[1] a) For the synthesis of the vinyl bromides **1**, we followed a two-step sequence based on a dibromoolefination reaction of the corresponding aldehyde precursor (A. R. Silva, E. C. Polo, N. C. Martins, Correia, D. C. Roque. *Adv. Synth. Catal.* **2018**, *360*, 346.) followed by a dehalogenation reaction (Y. Ye, H. Chen, K. Yao, H. Gong. *Org. Lett.* **2020**, *22*, 2070.). b) The *cis*-configured vinyl bromide **1a'** was synthesized following this procedure: K. G. Tang, G. T. Kent, I. Erden, W. Wu. *Tetrahedron Lett.* **2017**, *58*, 3894.

[2] S. Mishra, A. K. Mondal, E. Z. B. Smolinsky, R. Naaman, K. Maeda, T. Nishimura, T. Taniguchi, T. Yoshida, K. Takayama, E. Yashima. *Angew. Chem. Int. Ed.* **2020**, *59*, 14671.

[3] H. Pang, Y. Wang, F. Gallou, B. H. Lipshutz. *J. Am. Chem. Soc.* **2019**, *141*, 17117.

Power Consumption	370nm (max 43W), 390nm (max 52W), 427nm & 440nm (max 45W), 456nm (max 50W), 467nm (max 44W), 525nm (max 44W)
Input Voltage	100-240 VAC
Operating Temperature	0 - 40°C / 32 - 104°F
Beam Angle	56°
Wavelength Options	370nm, 390nm, 427nm, 440nm, 456nm, 467nm, 525nm
Average Intensity of PR160 series	352mW/cm2 (measured from 1 cm distance)
Dimensions (H x D)	4.49" x 2.48" / 11.4cm x 6.3cm

Figure SI-2. Technical specifications of the Kessil® lamps.

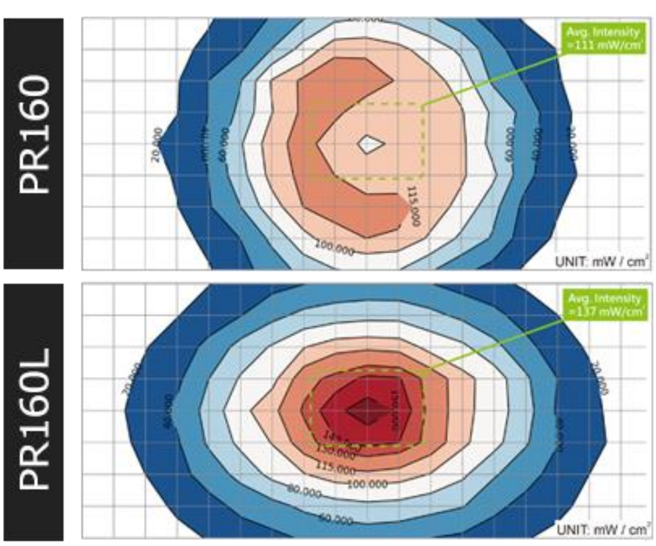


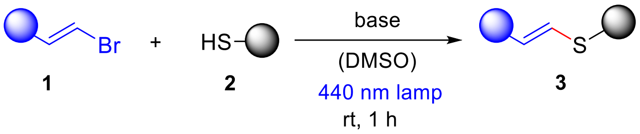
Figure SI-3. Intensity map of the Kessil® lamps.

NMR spectra were recorded in $CDCl_3$ at 600 MHz and 300 MHz for ^{1}H, 75 MHz, 100 MHz and 150 MHz for ^{13}C and 282 MHz for ^{19}F, with tetramethylsilane as internal standard for ^{1}H and the residual solvent signals as standard for ^{13}C. The data is being reported as s = singlet, bs = broad singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quatriplet, p = quintuplet and m = multiplet or unresolved, chemical shifts in ppm and coupling constant(s) in Hz. The values of the chemical shift of the signals in the NMR reports are in ppms. HRMS were measured in ESI, EI or APCI mode, and the mass analyser of the HRMS was TOF (Bruker model Impact II).

Melting points were measured in a Gallenkamp apparatus.

2. General procedures for the synthesis and characterization data for the compounds 3, 14, 15, 17 and 3aa’.

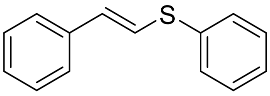
General procedure A (for the synthesis of compounds **3**)



A 5 mL glass vial was charged with the corresponding vinyl bromide **1** (0.26 mmol), thiol **2** (0.4 mmol), base (0.4 mmol) and dry DMSO (2 mL). The vial was capped and placed in front of the 440 nm Kessil® lamp at a distance of approximately 5 cm. The light and the cooling fan were turned on and the reaction was stirred at room temperature for 1 h to ensure full conversion. The reaction was quenched by adding 2 mL of water and the heterogeneous mixture was diluted with 5 mL of Et_2O and transferred to a separating funnel. The aqueous phase was extracted 3 times with 5 mL of Et_2O, and the combined organic phases were washed with 10 mL of brine and dried over Na_2SO_4. The solvents were evaporated first in the rotavapor and later in the high-vacuum pump. The crude of the reaction was analyzed by ^{1}H-NMR or GC/MS to determine the *trans*/*cis* ratio and later subjected to flash chromatography (Hex/EtOAc) to afford the corresponding vinyl sulfides **3** in a pure form.

Characterization data for the compounds 3, 14, 15, 17 and 3aa’.

(*E*)-Phenyl(styryl)sulfane (3aa)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 52 mg of **3aa** (95% isolated yield, *d.r.*: 8:1 *trans*/*cis*) as a colourless oil were obtained.

Rf = 0.46 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 8:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

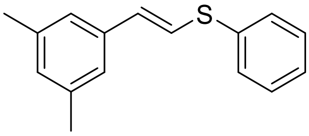
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.58 – 7.17 (m, 10H, + isom. *cis*), 6.91 (d, ^3J = 15.4 Hz, 1H), 6.76 (d, ^3J = 15.5 Hz, 1H), 6.62 (d, ^3J = 10.8 Hz, isom. *cis*), 6.52 (d, ^3J = 10.8 Hz, isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 136.5 (C), 135.2 (C), 132.9 (C), 131.8 (CH), 130.1 (CH), 129.8 (CH), 129.1 (CH), 128.7 (CH), 128.7 (CH), 128.3 (CH), 127.6 (CH), 126.9 (CH), 126.0 (CH), 123.4 (CH).

HRMS [APCI(+)]: calcd. For $([C_{14}H_{12}S]+H)^+$: 213.0732, found: 213.0736.

IR (ATR): ṽ [cm^{-1}] = 3042, 1927, 1466, 1255, 1071, 839.

(*E*)-(3,5-Dimethylstyryl)(phenyl)sulfane (3ba)



Following the **general procedure A**, a 1.5:1 *trans/cis* mixture of vinyl bromide **1b** (54.9 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 62 mg of **3ba** (99% isolated yield, *d.r.*: 8.2:1 *trans*/*cis*) as a yellow oil were obtained.

Rf = 0.31 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 8.2:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

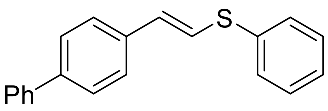
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.50 – 7.47 (m, 1H, + isom. *cis*), 7.43 – 7.29 (m, 4H, + isom. *cis*), 7.05 (s, 2H), 6.99 – 6.89 (m, 2H), 6.77 (d, ^3J = 15.4 Hz, 1H), 6.62 (d, ^3J = 10.7 Hz, isom. *cis*), 6.53 (d, ^3J = 10.7 Hz, isom. *cis*), 2.43 (s, isom. *cis*), 2.38 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 138.2 (C), 136.5 (C), 135.6 (C), 132.5 (CH), 130.1 (CH), 129.7 (CH), 129.5 (CH), 129.2 (CH), 126.9 (CH), 124.0 (CH), 122.8 (CH), 21.3 (CH_3).

HRMS [APCI(+)]: calcd. For $([C_{16}H_{17}S]+H)^+$: 241.1045, found: 241.1047.

IR (ATR): ṽ [cm^{-1}] = 3015, 2219, 1579, 1470, 1436, 1171.

(*E*)-(2-([1,1'-Biphenyl]-4-yl)vinyl)(phenyl)sulfane (3ca)



Following the **general procedure A**, a 13.4:1 *trans/cis* mixture of the vinyl bromide **1c** (67.4 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 73 mg of **3ca** (98% isolated yield, *d.r.*: 4.8:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.64 (10:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 4.8.2:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

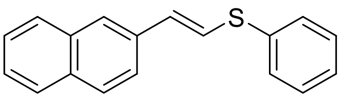
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.68 – 7.57 (m, 4H, + isom. *cis*), 7.52 – 7.28 (m, 10H, + isom. *cis*), 6.97 (d, ^3J = 15.4 Hz, 1H), 6.80 (d, ^3J = 15.5 Hz, 1H) 6.67 (d, ^3J = 10.7 Hz, isom. *cis*), 6.57 (d, ^3J = 10.8 Hz, isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 140.6 (C), 140.3 (C), 135.6 (C), 135.2 (C), 131.3 (CH), 130.2 (CH), 129.9 (CH), 129.4 (CH), 129.2 (CH), 129.1 (CH), 128.8 (CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.5 (CH), 126.3 (CH), 123.6 (CH).

HRMS [APCI(+)]: calcd. For ($[C_{20}H_{16}S]+H)^+$: 289.1045, found: 289.1047.

IR (ATR): ṽ [cm^{-1}] = 3047, 1581, 1479, 1434, 1085.

(*E*)-(2-(naphthalen-2-yl)vinyl)(phenyl)sulfane (3da)



Following the **general procedure A**, a 9.4:1 *trans/cis* mixture of vinyl bromide **1d** (61 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (25:1 Hex/EtOAc), 27 mg of **3da** (40% isolated yield, *d.r.*: 4.3:1 *trans*/*cis*) as a colourless oil were obtained.

Rf = 0.36 (25:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 5:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

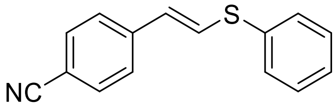
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.95 – 7.77 (m, 2H + isom. *cis*), 7.71 (s, 1H), 7.63 – 7.23 (m, 8H + isom. *cis*), 7.05 (d, ^3J = 15.4 Hz, 1H), 6.91 (d, ^3J = 15.5 Hz, 1H), 6.77 (d, ^3J = 10.6 Hz, isom. *cis*), 6.62 (d, ^3J = 10.7 Hz, isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 135.1 (C), 134.0 (C), 133.6 (C), 132.9 (C), 131.5 (CH), 130.1 (CH), 130.0 (CH), 129.2 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 127.2 (CH), 127.0 (CH), 126.4 (CH), 125.9 (CH), 125.7 (CH), 123.9 (CH), 123.2 (CH).

HRMS [APCI(+)]: calcd. For $([C_{18}H_{16}S]+H)^+$: 263.0889, found: 263.0888.

IR (ATR): ṽ [cm^{-1}] = 3047, 2366, 1579, 1472, 1439, 1024, 951.

(*E*)-4-(2-(Phenylthio)vinyl)benzonitrile (3ea)



Following the **general procedure A**, the vinyl bromide **1e** (54.1 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 46 mg of **3ea** (72% isolated yield, *d.r.*: 7.4:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.34 (20:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 7.4:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.58 (d, ^3J = 8.3 Hz, 2H, + isom. *cis*), 7.53 – 7.31 (m, 7H, + isom. *cis*), 7.10 (d, ^3J = 15.5 Hz, 1H), 6.74 (d, ^3J = 11.0 Hz, isom. *cis*), 6.57 (d, ^3J = 15.6 Hz, 1H, + isom. *cis*).

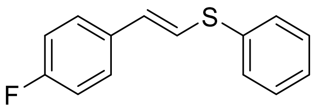
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 140.9 (C), 133.4 (C), 132.5 (CH), 132.1 (CH), 131.2 (CH), 130.5 (CH), 129.9 (CH), 129.5 (CH), 129.4 (CH), 129.1 (CH), 128.0 (CH), 127.9 (CH), 127.1 (CH), 126.2 (CH), 124.8 (CH), 119.0 (C), 110.2 (C).

HRMS [APCI(+)]: calcd. For $([C_{15}H_{12}NS]+H)^+$: 238.0685, found: 238.0688.

IR (ATR): ṽ [cm^{-1}] = 3063, 2219, 1586, 1472, 1178.

m.p.= 75.0 - 76.0 ºC

(*E*)-(4-Fluorostyryl)(phenyl)sulfane (3fa)



Following the **general procedure A**, a 5.4:1 *trans/cis* mixture of the vinyl bromide **1f** (52.3 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 58 mg of **3fa** (97% isolated yield, *d.r.*: 8.3:1 *trans*/*cis*) as a yellow oil were obtained.

Rf = 0.45 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 8.3:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

^{1}H NMR (600 MHz, $CDCl_3$, 300K) δ 7.47 – 7.43 (m, 2H), 7.38 (t, ^3J = 7.6 Hz, 2H), 7.35 – 7.30 (m, 3H, + isom. *cis*), 7.04 (t, ^3J = 8.7 Hz, 2H), 6.83 (d, ^3J = 15.4 Hz, 1H), 6.73 (d, ^3J = 15.4 Hz, 1H). 6.59 (d, ^3J = 10.7 Hz, isom. *cis*), 6.51 (d, ^3J = 10.7 Hz, isom. *cis*).

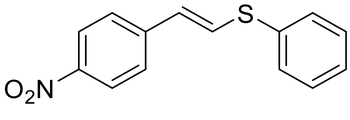
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 162.3 (d, $^1J_{C\text{-}F}$ = 247.4 Hz, C), 135.1 (C), 132.8 (C), 130.6 (CH), 129.9 (CH), 129.2 (CH), 127.6 (CH), 127.6 (CH), 127.1 (CH), 123.2 (CH), 115.6 (d, $^2J_{C\text{-}F}$ = 21.7 Hz, CH), 115.27 (d, $^2J_{C\text{-}F}$ = 21.2 Hz, CH).

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -114.1, -114.1 (isom. *cis*).

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{11}FS]+H)^+$: 231.0638, found: 231.0634.

IR (ATR): ṽ [cm^{-1}] = 3058, 1602, 1572, 1502, 1227.

(*E*)-(4-Nitrostyryl)(phenyl)sulfane (3ga)



Following the **general procedure A**, a 2.5:1 *trans/cis* mixture of the vinyl bromide **1g** (59.3 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 27 mg of **3ga** (40% isolated yield, *d.r.*: 6:1 *trans*/*cis*) as an orange solid were obtained.

Rf = 0.43 (20:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 6:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 8.17 (d, ^3J = 8.9 Hz, 2H), 7.56 – 7.47 (m, 2H), 7.47 – 7.35 (m, 5H, + isom. *cis*), 7.17 (d, ^3J = 15.5 Hz, 1H), 6.81 (d, ^3J = 10.9 Hz, isom. *cis*), 6.59 (d, ^3J = 15.6 Hz, 1H).

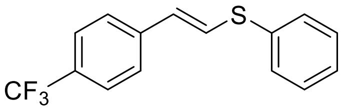
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 146.4 (C), 142.9 (C), 133.0 (C), 132.4 (CH), 131.5 (CH), 131.3 (CH), 130.6 (CH), 129.5 (CH), 128.2 (CH), 128.0 (CH), 126.3 (CH), 126.1 (CH), 124.2 (CH), 123.7 (CH).

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{12}NO_2S]+H)^+$: 258.0583, found: 258.0582.

IR (ATR): ṽ [cm^{-1}] = 3042, 1570, 1495, 1472, 1325, 1096.

m.p.= 59.0 - 60.0 ºC

(*E*)-Phenyl(4-(trifluoromethyl)styryl)sulfane (3ha)



Following the **general procedure A**, a 9.1:1 *trans/cis* mixture of the vinyl bromide **1h** (59.3 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 65 mg of **3ha** (97% isolated yield, *d.r.*: 7.6:1 *trans*/*cis*) as a white oil were obtained.

Rf = 0.62 (10:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 7.6:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.68 – 7.18 (m, 9H, + isom. *cis*), 7.03 (d, ^3J = 15.5 Hz, 1H), 6.65 (d, 1H, ^3J = 15.6 Hz, + isom. *cis*).

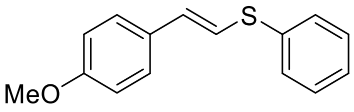
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 140.0 (C), 135.6, 134.1 (C), 130.8 (CH), 130.5 (CH), 129.7 (CH), 129.6 (CH), 129.4 (CH), 129.3 (CH), 129.2 (CH), 128.9 (CH), 128.5 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.2 (CH), 126.0 (CH), 125.6 (q, $^{2}J_{C\text{-}F}$ = 3.9 Hz, CH), 125.4 (q, $^{2}J_{C\text{-}F}$ = 3.7 Hz, CH), 123.9 (q, $^{1}J_{C\text{-}F}$ = 271.7 Hz, CF_3).

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -62.4, -62.4 (isom. *cis*).

IR (ATR): ṽ [cm^{-1}] = 3060, 1611, 1570, 1436, 1323.

m.p.= 80.0 - 81.0 ºC

(*E*)-(4-Methoxystyryl)(phenyl)sulfane (3ia)



Following the **general procedure A**, a 9.2:1 *trans/cis* mixture of the vinyl bromide **1i** (55.3 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 61 mg of **3ia** (97% isolated yield, *d.r.*: 9:1 *trans*/*cis*) as a yellow oil were obtained.

Rf = 0.36 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 9:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

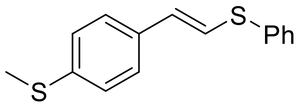
^{1}H NMR (600 MHz, $CDCl_3$, 300K) δ 7.47 – 7.43 (m, 2H), 7.40 – 7.33 (m, 4H, + isom. *cis*), 7.30 – 7.25 (m, 1H, + isom. *cis*), 6.91 (d, ^{3}J = 8.9 Hz, 2H), 6.81 (d, ^{3}J = 15.3 Hz, 1H), 6.77 (d, ^{3}J = 15.3 Hz, 1H), 6.61 (d, ^{3}J = 10.6 Hz, isom. *cis*), 6.43 (d, ^{3}J = 10.6 Hz, isom. *cis*), 3.85 (s, 3H, + isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.4 (C), 136.0 (C), 132.8 (CH), 131.1 (CH), 130.9 (CH), 130.2 (CH), 129.9 (CH), 129.7 (CH), 129.4 (CH), 129.3(C), 129.2 (CH), 129.1 (CH), 127.4 (CH), 126.6 (CH), 123.2 (CH), 120.1 (CH), 114.2 (CH), 113.8(CH), 55.3 (CH_3).

HRMS [APCI(+)]: calcd. For ([$C_{15}H_{15}OS$]+H)$^{+}$: 243.0838, found: 243.0839.

IR (ATR): ṽ [cm^{-1}] = 3024, 1604, 1565, 1504, 1246.

(*E*)-methyl(4-(2-(phenylthio)vinyl)phenyl)sulfane (3ja)



Following the **general procedure A**, a 10.6:1 *trans/cis* mixture of vinyl bromide **1j** (57 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 67 mg of **3ja** (50% isolated yield, *d.r.*: 6.8:1 *trans*/*cis*) as a colorless oil were obtained.

Rf = 0.30 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 6.8:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

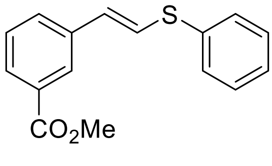
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.55 – 7.13 (m, 9H + isom. *cis*), 6.88 (d, ^3J = 15.4 Hz, 1H), 6.72 (d, ^3J = 15.5 Hz, 1H), 6.58 (d, ^3J = 10.7 Hz, isom. *cis*), 6.50 (d, ^3J = 10.7 Hz, isom. *cis*), 2.53 (s, isom. *cis*), 2.51 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.9 (C), 135.3 (C), 133.5 (C), 131.3 (CH), 130.0 (CH), 129.8 (CH), 129.1 (CH), 127.2 (CH), 126.9 (CH), 126.7 (CH), 126.4 (CH), 126.3 (CH), 125.4 (CH), 122.7 (CH), 15.8 (CH_3).

HRMS [APCI(+)]: calcd. For $([C_{15}H_{14}S_2]+H)^+$: 259.0612, found: 259.0610.

IR (ATR): ṽ [cm^{-1}] = 2925, 2346, 1586, 1486, 1434, 1096.

Methyl (*E*)-3-(2-(phenylthio)vinyl)benzoate (3ka)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1k** (63 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (8:1 Hex/EtOAc), 28 mg of **3ka** (40% isolated yield, *d.r.*: 5.4:1 *trans*/*cis*) as a colorless oil were obtained.

Rf = 0.35 (8:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 5.4:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

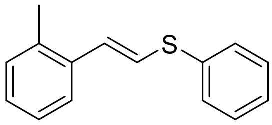
^{1}H NMR (600 MHz, $CDCl_3$, 300K) δ 8.03 (dd, *J* = 2.1, 1.4 Hz, 1H), 7.96 (dt, J = 7.8, 1.4 Hz, isom. *cis*), 7.92 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.80 – 7.76 (m, isom. *cis*), 7.55 – 7.45 (m, 2H + isom. *cis*), 7.43 – 7.37 (m, 3H + isom. *cis*), 7.35 – 7.30 (m, 1H + isom. *cis*), 7.02 (d, ^3J = 15.5 Hz, 1H), 6.72 (d, ^3J = 15.5 Hz, 1H), 6.64 (d, ^3J = 10.8 Hz, isom. *cis*), 6.62 (d, ^3J = 10.7 Hz, isom. *cis*), 3.97 (s, isom. *cis*), 3.95 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 166.9 (C), 136.9 (C), 134.4 (C), 130.6 (C), 130.4 (CH), 130.2 (CH), 129.9 (CH), 129.5 (CH), 129.2 (CH), 128.7 (CH), 128.3 (CH), 127.7 (CH), 127.3 (CH), 126.8 (CH), 125.6 (CH), 52.1 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{16}H_{14}O_2S]+H)^+$: 271.0887, found: 271.0788.

IR (ATR): ṽ [cm^{-1}] = 2949, 1724, 1581, 1436, 1289, 1105.

(*E*)-(2-Methylstyryl)(phenyl)sulfane (3la)



Following the **general procedure A**, a 8.6:1 *trans/cis* mixture of the vinyl bromide **1l** (51.2 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 36 mg of **3la** (62% isolated yield, *d.r.*: 4.8:1 *trans*/*cis*) as a yellow oil were obtained.

Rf = 0.54 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 4.8:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

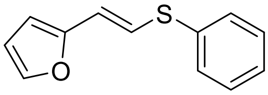
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.49 – 7.42 (m, 3H), 7.38 – 7.26 (m, 4H, + isom. *cis*), 7.20 – 7.17 (m, 2H, + isom. *cis*), 7.02 (d, ^3J = 15.3 Hz, 1H), 6.82 (d, ^3J = 15.3 Hz, 1H), 6.76 (d, ^3J = 10.4 Hz, isom. *cis*), 6.59 (d, ^3J = 10.5 Hz, isom. *cis*), 2.37 (s, 3H, + isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 135.6 (C), 135.5 (C), 135.2 (C), 133.9 (CH), 130.5 (CH), 130.1 (CH), 129.7 (CH), 129.2 (CH), 127.7 (CH), 126.9 (CH), 126.5 (CH), 126.2 (CH), 125.4 (CH), 124.3 (CH), 19.9 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{15}H_{15}S]+H)^+$: 227.0889, found: 227.0889.

IR (ATR): ṽ [cm^{-1}] = 3063, 1577, 1474, 1436, 903.

(*E*)-2-(2-(phenylthio)vinyl)furan (3ma)



Following the **general procedure A**, a 5.2:1 *trans/cis* mixture of vinyl bromide **1m** (45 mg, 0.26 mmol), thiol **2a** (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 16 mg of **3ma** (30% isolated yield, *d.r.*: 1.7:1 *trans*/*cis*) as a yellow oil were obtained.

Rf = 0.36 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 1.7:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

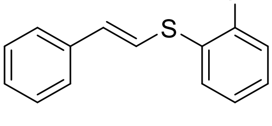
^{1}H NMR (600 MHz, $CDCl_3$, 300K) δ 7.54 – 7.47 (m, 1H + isom. *cis*), 7.54 – 7.47 (m, 1H + isom. *cis*), 7.41 – 7.24 (m, 5H + isom. *cis*), 6.86 (d, ^3J = 15.1 Hz, 1H), 6.59 (d, ^3J = 3.4 Hz, isom. *cis*), 6.54 – 6.48 (m, 2H + isom. *cis*), 6.43 (d, ^3J = 11.1 Hz, isom. *cis*), 6.21 (d, ^3J = 3.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 152.1 (C), 142.0 (CH), 141.7 (C), 134.8 (C), 130.2 (CH), 130.0 (CH), 129.1 (CH), 127.5 (CH), 127.3 (CH), 127.0 (CH), 124.2 (CH), 122.2 (CH), 119.5 (CH), 115.1 (CH), 111.6 (CH), 111.4 (CH), 109.8 (CH), 107.3 (CH).

HRMS [APCI(+)]: calcd. For ($[C_{12}H_{11}OS]+H)^+$: 203.0525, found: 203.0526.

IR (ATR): ṽ [cm^{-1}] = 2945, 1711, 1588, 1461, 1273, 1060.

(*E*)-(2-fluorophenyl)(styryl)sulfane (3ab)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2b** (43 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 59 mg of **3ab** (98% isolated yield, *d.r.*: 11.4:1 *trans*/*cis*) as a yellow oil were obtained.

Rf = 0.47 (20:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 11.4:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.63 – 7.22 (m, 8H, + isom. *cis*), 7.22 – 7.07 (m, 2H, + isom. *cis*), 6.84 (d, ^3J = 15.5 Hz, 1H), 6.76 (d, ^3J = 15.4 Hz, 1H), 6.67 (d, ^3J = 10.7 Hz, isom. *cis*), 6.42 (d, ^3J = 10.6 Hz, isom. *cis*).

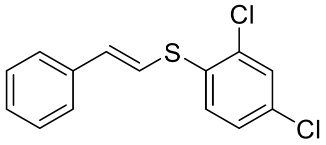
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 160.8 (d, $^1J_{C\text{-}F}$ = 246.7 Hz, C), 136.3 (C), 132.7 (CH), 132.1 (CH), 129.1 (d, $^3J_{C\text{-}F}$ = 7.7 Hz, CH), 128.7 (CH), 127.8 (CH), 126.1 (CH), 124.8 (d, $^4J_{C\text{-}F}$ = 3.7 Hz, CH), 122.2 (d, $^2J_{C\text{-}F}$ = 17.4 Hz, C), 121.6 (CH), 115.9 (d, $^2J_{C\text{-}F}$ = 22.0 Hz, CH).

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -109.5 (isom. *cis*), -109.7.

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{11}FS]+H)^+$: 231.0638, found: 231.0639.

IR (ATR): ṽ [cm^{-1}] = 3063, 1595, 1568, 1466, 1441, 1255, 942.

(*E*)-(2,4-Dichlorophenyl)(styryl)sulfane (3ac)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2c** (50.5 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (hexane), 46 mg of **3ac** (63% isolated yield, *d.r.*: 10.6:1 *trans*/*cis*) as a white oil were obtained.

Rf = 0.42 (Hexane) [UV] [$KMnO_4$].

A 10.6:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

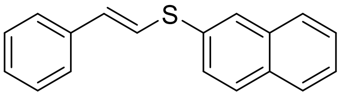
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.43 – 7.20 (m, 8H, + isom. *cis*), 6.92 (d, ^3J = 15.3 Hz, 1H), 6.77 (d, ^3J = 15.3 Hz, 1H, + isom. *cis*), 6.36 (d, ^3J = 10.5 Hz, isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 136.1 (CH), 136.0 (C), 134.2 (C), 133.7 (C), 132.6 (C), 130.0 (CH), 129.6 (CH), 128.8 (CH), 128.4 (CH), 127.6 (CH), 126.4 (CH), 119.7 (CH).

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{11}Cl_2S]+H)^+$: 280.9953, found: 280.9953.

IR (ATR): ṽ [cm^{-1}] = 3074, 1565, 1495, 1445, 1030, 803.

(*E*)-(4-Methoxyphenyl)(styryl)sulfane (3ad)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2d** (64.1 mg, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (0.32 hexane), 51 mg of **3ad** (75% isolated yield, *d.r.*: 3.5:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.32 (Hexane) [UV] [$KMnO_4$].

A 3.5:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 8.02 – 7.78 (m, 4H, + isom. *cis*), 7.70 – 7.26 (m, 8H, + isom. *cis*), 7.05 (d, ^3J = 15.4 Hz, 1H), 6.86 (d, ^3J = 15.5 Hz, 1H), 6.73 (d, ^3J = 10.8 Hz, isom. *cis*), 6.67 (d, ^3J = 10.7 Hz, isom. *cis*).

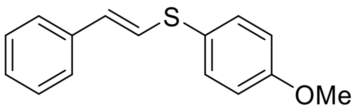
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 136.6 (C), 136.5 (C), 133.9 (C), 133.8 (C), 133.6 (C), 132.7 (C), 132.3 (CH), 128.9 (CH), 128.8 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 126.8 (CH), 126.8 (CH), 126.3 (CH), 126.2 (CH), 125.8 (CH), 123.2 (CH).

HRMS [APCI(+)]: calcd. For ($[C_{18}H_{14}S]+H)^+$: 263.0889, found: 263.0888.

IR (ATR): ṽ [cm^{-1}] = 3047, 2366, 1579, 1439, 951.

m.p.= 67.0 - 68.0 ºC.

(*E*)-(4-Methoxyphenyl)(styryl)sulfane (3ae)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2e** (49 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 48 mg of **3ae** (76% isolated yield, *d.r.*: 3.6:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.51 (20:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 3.6:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

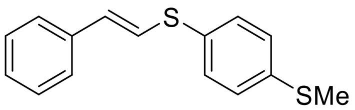
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.48 – 7.42 (m, 2H), 7.37 – 7.24 (m, 5H, + isom. *cis*), 6.97 – 6.92 (m, 2H, + isom. *cis*), 6.87 (d, ^3J = 15.5 Hz, 1H), 6.55 (d, ^3J = 15.5 Hz, 1H, + isom. *cis*), 6.44 (d, ^3J = 10.8 Hz, isom. *cis*), 3.86 (s, 3H, + isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.6 (C), 136.8 (C), 133.5 (CH), 133.0 (CH), 129.0 (CH), 128.7 (CH), 128.4 (CH), 128.3 (CH), 127.2 (CH), 127.0 (CH), 125.8 (CH), 125.8 (CH), 124.5 (C), 114.9 (CH), 55.4 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{15}H_{15}OS]+H)^+$: 243.0838, found: 243.0840.

IR (ATR): ṽ [cm^{-1}] = 3019, 1593, 1493, 1459, 1030.

(*E*)-Methyl(4-(styrylthio)phenyl)sulfane (3af)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2f** (62.5 mg, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 51 mg of **3af** (76% isolated yield, *d.r.*: 2.7:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.64 (20:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 2.7:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.58 – 7.49 (m, 1H), 7.46 – 7.18 (m, 8H, + isom. *cis*), 6.85 (d, ^3J = 15.4 Hz, 1H), 6.68 (d, ^3J = 15.4 Hz, 1H), 6.59 (d, ^3J = 10.7 Hz, isom. *cis*), 6.45 (d, ^3J = 10.7 Hz, isom. *cis*), 2.50 (s, 3H, + isom. *cis*).

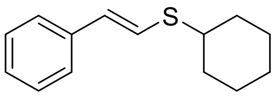
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 13C NMR (75 MHz, CDCl3) δ 138.2 (C), 137.9 (C), 136.5 (C), 131.2 (CH), 131.1 (CH), 130.9 (CH), 130.9 (CH), 128.7 (CH), 128.7 (CH), 128.3 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 127.1 (CH), 126.3 (CH), 126.0 (CH), 123.7 (CH), 15.8 (CH).

HRMS [APCI(+)]: calcd. For ([$C_{15}H_{14}S_2$]+H)$^+$: 259.0610, found: 259.0613.

IR (ATR): ṽ [cm^{-1}] = 3031, 1575, 1475, 1388, 1103, 810.

m.p.= 52.0 - 53.0 ºC

(*E*)-Cyclohexyl(styryl)sulfane (3ah)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2h** (49 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (hexane), 48 mg of **3ah** (84% isolated yield, *d.r.*: 3.2:1 *trans*/*cis*) as an orange oil were obtained.

Rf = 0.36 (Hexane) [UV] [$KMnO_4$].

A 3.2:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

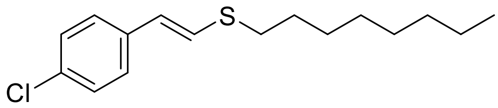
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.56 – 7.48 (m, 1H), 7.43 – 7.18 (m, 4H, + isom. *cis*), 6.80 (d, ^3J = 15.6 Hz, 1H), 6.60 (d, ^3J = 15.6 Hz, 1H), 6.46 (d, ^3J = 11.0 Hz, isom. *cis*), 6.36 (d, ^3J = 11.0 Hz, isom. *cis*), 3.12 – 2.84 (m, 1H, + isom. *cis*), 2.19 – 2.00 (m, 2H, + isom. *cis*), 1.95 – 1.75 (m, 2H, + isom. *cis*), 1.73 – 1.58 (m, 1H, + isom. *cis*), 1.58 – 1.22 (m, 5H, + isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 137.2 (C), 128.7 (CH), 128.6 (CH), 128.6 (CH), 128.2 (CH), 126.9 (CH), 126.5 (CH), 125.9 (CH), 125.6 (CH), 125.0 (CH), 124.1 (CH), 47.8 (CH), 45.3 (CH), 33.7 (CH_2), 33.6 (CH_2), 29.7 (CH_2), 26.0 (CH_2), 25.7 (CH_2), 25.6 (CH_2).

HRMS [APCI(+)]: calcd. For ($[C_{14}H_{18}S]+H)^+$: 219.1202, found: 219.1203.

IR (ATR): ṽ [cm^{-1}] = 3017, 2922, 2849, 1595, 1443, 935.

(*E*)-(4-chlorostyryl)(octyl)sulfane (3ni)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1n** (56 mg, 0.26 mmol), thiol **2i** (70 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (Hexane), 38 mg of **3ni** (50% isolated yield, *d.r.*: 3.5:1 *trans*/*cis*) as a colorless oil were obtained.

Rf = 0.60 (Hexane) [UV] [$KMnO_4$].

A 3.5:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

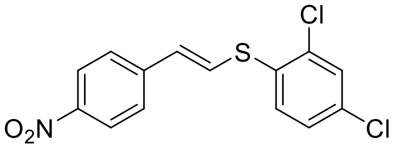
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.42 (d, ^3J = 8.5 Hz, isom. *cis*), 7.35 – 7.15 (m, 4H + isom. *cis*), 6.72 (d, ^3J = 15.6 Hz, 1H), 6.46 – 6.33 (m, 1H + isom. *cis*), 6.28 (d, ^3J = 10.9 Hz, isom. *cis*), 2.80 (t, ^3J = 7.4 Hz, 2H + isom. *cis*), 1.69 (q, J = 7.3 Hz, 2H + isom. *cis*), 1.49 – 1.24 (m, 10H + isom. *cis*), 0.94 – 0.84 (m, 3H + isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 135.7 (C), 132.2 (C), 129.8 (CH), 128.7 (CH), 128.5 (CH), 128.3 (CH), 126.5 (CH), 126.4 (CH), 125.1 (CH), 124.9 (CH), 124.0 (CH), 35.9 (CH), 32.6 (CH), 31.8 (CH_2), 30.2 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 28.5 (CH_2), 22.6 (CH_2), 14.0 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{16}H_{23}ClS]+H)^+$: 283.1282, found: 283.1284.

IR (ATR): ṽ [cm^{-1}] = 2915, 1588, 1486, 1402, 1091, 824.

(*E*)-(2,4-Dichlorophenyl)(4-nitrostyryl)sulfane (3gc)



Following the **general procedure A**, a 2.5:1 *trans/cis* mixture of the vinyl bromide **1g** (59.3 mg, 0.26 mmol), thiol **2c** (50.5 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (50:1 Hex/EtOAc), 52 mg of **3gc** (61% isolated yield, *d.r.*: 9.5:1 *trans*/*cis*) as a yellow solid were obtained.

Rf = 0.46 (50:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 9.5:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analyzed.

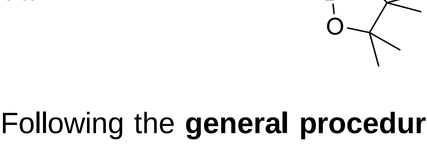
^{1}H NMR (600 MHz, $CDCl_3$, 300K) δ 8.22 – 8.17 (m, 2H, + isom. *cis*), 7.50 – 7.46 (m, 1H, + isom. *cis*), 7.41 (d, ^3J = 8.4 Hz, 1H), 7.31 – 7.28 (m, 1H, + isom. *cis*), 7.03 (d, ^3J = 15.5 Hz, 1H), 6.71 (d, ^3J = 15.4 Hz, 1H), 6.75 (d, ^3J = 10.8 Hz, isom. *cis*), 6.62 (d, ^3J = 10.8 Hz, isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 146.9 (C), 142.3 (C), 135.8 (C), 134.4 (C), 132.5 (CH), 131.5 (C), 130.1 (CH), 129.3 (CH), 128.0 (CH), 127.6 (CH), 126.4 (CH), 124.2 (CH).

IR (ATR): ṽ [cm^{-1}] = 3076, 1586, 1502, 1447, 1327, 1091.

m.p.= 123.0 - 124.0 ºC.

(*E*)-2-(4-((2-([1,1'-biphenyl]-4-yl)vinyl)thio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3cg)



Following the **general procedure A**, a 13.4:1 *trans/cis* mixture of the vinyl bromide **1c** (67 mg, 0.26 mmol), thiol **2g** (95 mg, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (8:1 Hex/EtOAc), 56 mg of **3cg** (52% isolated yield, *d.r.*: 6.5:1 *trans*/*cis*) as a colorless oil were obtained.

Rf = 0.20 (8:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 6.5:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

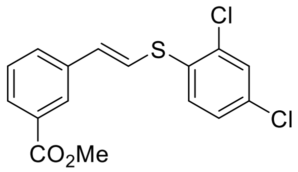
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.78 (d, ^3J = 7.9 Hz, 2H + isom. *cis*), 7.66 – 7.52 (m, 4H + isom. *cis*), 7.50 – 7.32 (m, 7H + isom. *cis*), 6.96 (d, ^3J = 15.5 Hz, 1H), 6.85 (d, ^3J = 15.5 Hz, 1H), 6.70 (d, ^3J = 10.7 Hz, isom. *cis*), 6.58 (d, ^3J = 10.7 Hz, isom. *cis*), 1.59 (s, isom. *cis*), 1.36 (s, 12H).

^{13}C NMR (75 MHz, CDCl3) δ 140.5 (C), 139.4 (C), 135.4 (CH), 135.4 (C), 132.4 (CH), 129.2 (CH), 128.8 (CH), 128.4 (CH), 128.0 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 126.5 (CH), 122.3 (C), 83.9 (C), 24.8 (CH_3).

HRMS [APCI(+)]: calcd. For ([$C_{26}H_{27}BO_2S$]+H)$^+$: 415.1898, found: 415.1909.

IR (ATR): ṽ [cm^{-1}] = 2974, 1597, 1482, 1355, 1141, 760.

Methyl (*E*)-3-(2-((2,4-dichlorophenyl)thio)vinyl)benzoate (3kc)



Following the **general procedure A**, a 8.6:1 *trans/cis* mixture of the vinyl bromide **1k** (63 mg, 0.26 mmol), thiol **2c** (51 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 88 mg of **3kc** (62% isolated yield, *d.r.*: 12.8:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.40 (20:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 12.8:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (600 MHz, $CDCl_3$, 300K) δ 8.07 (d, ^3J = 1.9 Hz, 1H), 7.96 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.56 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46 – 7.44 (m, 2H + isom. *cis*), 7.33 (d, J = 8.4 Hz, 1H), 7.25 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.89 (d, ^3J = 12.0 Hz, 1H), 6.87 (d, ^3J = 12.0 Hz, 1H), 6.79 (d, ${}^3J$ = 10.6 Hz, isom. *cis*), 6.44 (d, ${}^3J$ = 10.6 Hz, isom. *cis*), 3.96 (s, isom. *cis*), 3.95 (s, 3H).

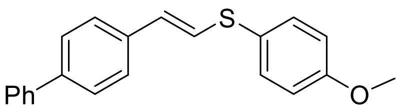
^{13}C NMR (75 MHz, CDCl3) δ 166.7 (C), 136.3 (C), 134.3 (C), 133.5 (CH), 133.3 (C), 133.1 (C), 131.6 (CH), 130.8 (CH), 130.7 (CH), 130.5 (CH), 130.1 (CH), 129.7 (CH), 129.1 (CH), 129.0 (CH), 128.8 (CH), 128.5 (CH), 127.7 (CH), 127.1 (CH), 121.9 (CH), 52.2 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{16}H_{12}Cl_2O_2S]+H)^+$: 339.0008, found: 339.0011.

IR (ATR): ṽ [cm^{-1}] = 2954, 1717, 1545, 1425, 1280.

m.p. = 88.0 - 89 ºC.

(*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)(4-methoxyphenyl)sulfane (3ce)



Following the **general procedure A**, a 13.4:1 *trans/cis* mixture of the vinyl bromide **1c** (67 mg, 0.26 mmol), thiol **2e** (49 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (25:1 Hex/EtOAc), 50 mg of **3ce** (61% isolated yield, *d.r.*: 4.3:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.25 (25:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 4.3:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.73 – 7.53 (m, 4H + isom. *cis*), 7.54 – 7.31 (m, 7H + isom. *cis*), δ 6.98 – 6.88 (m, 3H + isom. *cis*), 6.59 (d, ${}^3J$ = 15.5 Hz, 1H), 6.47 (d, ${}^3J$ = 10.8 Hz, isom. *cis*), 3.86 (s, 3H), 3.85 (s, 3H, isom. *cis*).

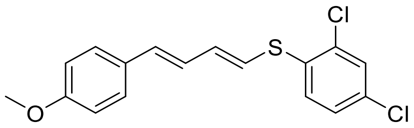
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.6 (C), 140.6 (C), 139.9 (C), 135.8 (C), 133.5 (CH), 133.0 (C), 129.1 (CH), 128.8 (CH), 128.6 (CH), 128.4 (CH), 127.3 (CH), 127.0 (CH), 126.8 (CH), 126.2 (CH), 125.9 (CH), 125.3 (CH), 124.5 (CH), 114.9 (CH), 114.8 (CH), 55.4 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{21}H_{18}OS]+H)^+$: 319.1151, found: 319.1153.

IR (ATR): ṽ [cm^{-1}] = 3035, 2931, 1586, 1572, 1404, 1291.

m.p. = 91.0 - 92 ºC.

(2,4-dichlorophenyl)((1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)sulfane (3nb)



Following the **general procedure A**, a 2.2:1 *trans/cis* mixture of the vinyl bromide **1n** (61 mg, 0.26 mmol), thiol **2b** (51 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (25:1 Hex/EtOAc), 87 mg of **3pb** (99% isolated yield, *d.r.*: 1.7:1 *trans*/*cis*) as a brown oil were obtained.

Rf = 0.25 (25:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 1.7:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

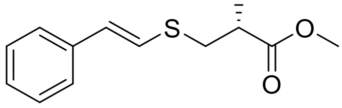
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.45 – 7.31 (m, 3H + isom. *cis*), 7.29 – 7.04 (m, 2H + isom. *cis*), 6.88 (d, ^3J = 8.8 Hz, 2H), 6.81 – 6.62 (m, 2H + isom. *cis*), 6.54 (d, ^3J = 14.8 Hz, 2H), 6.31 (d, ^3J = 14.1 Hz, 1H), 6.10 (d, ^3J = 9.1 Hz, isom. *cis*), 3.82 (s, 3H + isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 159.8 (C), 159.6 (C), 137.6 (CH), 135.5 (CH), 135.4 (C), 134.5 (CH), 133.4 (CH), 133.2 (CH), 132.3 (CH), 132.0 (CH), 129.6 (CH), 129.5 (CH), 129.4 (CH), 129.2 (CH), 128.1 (CH), 127.8 (CH), 127.5 (CH), 124.9 (CH), 121.7 (CH), 120.8 (CH), 119.0 (CH), 114.2 (CH), 114.2 (CH), 55.3 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{17}H_{15}ClO_2S]+H)^+$: 337.0215, found: 337.0215.

IR (ATR): ṽ [cm^{-1}] = 2833, 1602, 1502, 1445, 1248, 1098.

Methyl (*E*)-*N*-(tert-butoxycarbonyl)-*S*-styryl-*L*-cysteinate (3al)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2l** (50.5 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40

mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (20:1 Hex/EtOAc), 46 mg of **3al** (30% isolated yield, *d.r.*: 1.3:1 *trans*/*cis*) as a yellow solid were obtained.

Rf = 0.60 (20:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 1.3:1 *trans*/*cis* isomeric mixture was obtained. The signals of the corresponding *cis* and *trans* isomer have been analyzed.

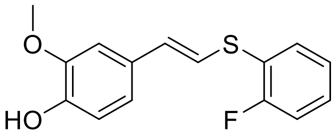
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.49 – 7.46 (m, 1H), 7.40 – 7.35 (m, 1H), 7.32 – 7.29 (m, 2H), 7.27 – 7.20 (m, 1H), 6.65 (d, ^3J = 15.5 Hz, 0.5H), 6.61 (d, ^3J = 15.5 Hz, 0.5H), 6.46 (d, ^3J = 10.8 Hz, 0.5H), 6.18 (d, ^3J = 10.8 Hz, 0.5H), 5.48 – 5.38 (m, 1H), 4.68 (q, ^3J = 6.5 Hz, 1H), 3.81 – 3.77 (m, 2H), 3.73 (s, 2H), 3.34 – 3.21 (m, 1H), 1.49 – 1.46 (m, 7H), 1.45 (s, 5H).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 171.0 (C), 170.8 (C), 155.0 (C), 136.6 (C), 129.7 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 127.3 (CH), 126.9 (CH), 126.6 (CH), 126.4 (CH), 125.7 (CH), 124.0 (CH), 80.3 (C), 53.8 (CH), 53.6 (CH), 52.6 (CH_3), 38.4 (CH_2), 35.8 (CH_2), 28.3 (CH_3).

HRMS [ESI(+)]: calcd. For ($[C_{12}H_{15}NO_2S]+H)^+$: 238.0896, found: 238.0893. (Loss of -Boc group)

IR (ATR): ṽ [cm^{-1}] = 3392, 2979, 1736, 1701, 1488, 1355, 1155.

(*E*)-4-(2-((2-fluorophenyl)thio)vinyl)-2-methoxyphenol (3pb)



Following the **general procedure A**, the vinyl bromide **1p** (59 mg, 0.26 mmol), thiol **2b** (43 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (5:1 Hex/EtOAc), 44 mg of **3pb** (61% isolated yield, *d.r.*: 11.3:1 *trans*/*cis*) as a brown oil were obtained.

Rf = 0.25 (5:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 11.3:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.41 (td, *J* = 7.5, 1.7 Hz, 1H), 7.31 – 7.01 (m, 3H + isom. *cis*), 6.96 – 6.84 (m, 3H + isom. *cis*), 6.75 (d, ^3J = 15.3 Hz, 1H + isom. *cis*), 6.61

(d, ^3J = 15.3 Hz, 1H), 6.25 (d, J = 10.6 Hz, isom. *cis*), 5.72 (s, isom. *cis*), 5.68 (s, 1H), 3.95 (s, isom. *cis*), 3.90 (s, 3H).

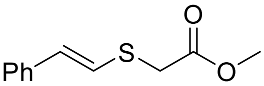
^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 160.61 (d, $^1J_{C\text{-}F}$ = 246.6 Hz, C), 146.7 (CH), 145.8 (CH), 134.0 (C), 131.5 (CH), 128.88 (d, $^3J_{C\text{-}F}$ = 21.4 Hz, C), 128.7 (CH), 124.7 (CH), 124.6 (CH), 122.9 (CH), 120.1 (CH), 118.2 (CH), 115.79 (d, $^3J_{C\text{-}F}$ = 21.6 Hz, CH), 114.6 (CH), 108.2 (CH), 55.9 (CH_3).

^{19}F NMR (282 MHz, $CDCl_3$, 300K) δ -109.62 (isom. *cis*), -110.16.

HRMS [APCI(+)]: calcd. For $([C_{15}H_{13}FO_2S]+H)^+$: 277.0693, found: 277.0692.

IR (ATR): ṽ [cm^{-1}] = 2840, 1597, 1466, 1361, 1268, 1028, 744.

Methyl (*E*)-2-(styrylthio)acetate (3an)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2n** (36 µL, 0.40 mmol) and freshly ground K_2CO_3 (55 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (5:1 Hex/EtOAc), 26 mg of **3an** (48% isolated yield, *d.r.*: 7.4:1 *trans*/*cis*) as a colourless oil were obtained.

Rf = 0.27 (5:1 Hex/EtOAc) [UV] [$KMnO_4$].

A 7.4:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

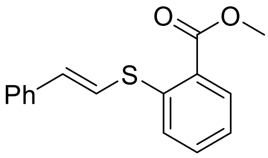
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.54 – 7.14 (m, 5H + isom. *cis*), 6.78 (d, ^3J = 15.6 Hz, 1H), 6.62 (d, ^3J = 15.6 Hz, 1H), 6.54 (d, ^3J = 10.8 Hz, isom. *cis*), 6.35 (d, ^3J = 10.8 Hz, isom. *cis*), 3.79 (s, 3H + isom. *cis*), 3.54 (s, 2H), 3.50 (s, isom. *cis*).

^{13}C NMR (75 MHz, CDCl3) δ 169.9 (C), 136.5 (C), 129.5 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 127.4 (CH), 127.0 (CH), 125.8 (CH), 124.9 (CH), 122.8 (CH), 52.6 (CH_3), 36.3 (CH_2), 34.72 (CH_3).

HRMS [APCI(+)]: calcd. For $([C_{11}H_{12}O_2S]+H)^+$: 209.0631, found: 209.0632.

IR (ATR): ṽ [cm^{-1}] = 3026, 1733, 1600, 1439, 1291, 1130, 903.

Methyl (*E*)-2-(styrylthio)benzoate (3am)



Following the **general procedure A**, a 10:1 *trans/cis* mixture of the vinyl bromide **1a** (34 µL, 0.26 mmol), thiol **2i** (55 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO_2 (9:1 Hex/acetone), 45 mg of **3am** (64% isolated yield, *d.r.*: 2.2:1 *trans*/*cis*) as a colorless oil were obtained.

Rf = 0.30 (9:1 Hex/acetone) [UV] [$KMnO_4$].

A 2.2:1 *trans*/*cis* isomeric mixture was obtained. For simplicity, the integrals in the ^{1}H-NMR spectra have been adjusted to the major (*trans*) isomer. The signals of the corresponding *cis* isomer have also been analysed.

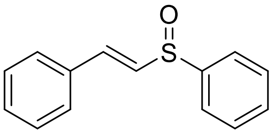
^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 8.05 – 7.97 (m, 1H), 7.95 (dd, ^3J = 7.9, 1.5 Hz, isom. *cis*), 7.64 (d, ^3J = 7.2 Hz, 1H), 7.57 – 7.18 (m, 7H + isom. *cis*), 7.05 (d, ^3J = 15.4 Hz, 1H), 6.91 (d, ^3J = 15.4 Hz, 1H), 6.82 (d, ^3J = 10.7 Hz, isom. *cis*), 6.51 (d, ^3J = 10.7 Hz, isom. *cis*), 3.95 (s, 3H), 3.94 (s, isom. *cis*).

^{13}C NMR (75 MHz, CDCl3) δ 166.7 (C), 141.1 (C), 140.1 (C), 136.8 (CH), 136.3 (CH), 136.0 (C), 132.4 (CH), 131.6 (CH), 131.2 (CH), 130.9 (CH), 129.1 (CH), 129.0 (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 127.5 (CH), 126.4 (CH), 125.5 (CH), 124.9 (CH), 123.9 (CH), 121.3 (CH), 52.2 (CH_3), 52.2 (CH_3).

HRMS [APCI(+)]: calcd. For ($[C_{16}H_{14}O_2S]+H)^+$: 271.0786, found: 271.0787.

IR (ATR): ṽ [cm^{-1}] = 2945, 1711, 1588, 1436, 1246, 1182.

(*E*)-(2-(Phenylsulfinyl)vinyl)benzene (14)



A 50 mL round-bottomed flask was charged with the phenyl vinyl sulfide **3aa** (42.5 mg, 0.2 mmol), in dichloromethane (1.5 mL) and the solution was stirred and cooled down to -78 ºC. Then, *m*-chloroperbenzoic acid (34.5 mg, 0.2 mmol) was added slowly to the solution during 30 min. The reaction mixture was later stirred for 1 h at 30 ºC. The reaction was quenched by pouring it into 10 ml of saturated sodium bicarbonate solution and was extracted 3 times with 10 mL of dichloromethane. The combined organic phases were washed with 10 mL of brine and dried over Na_2SO_4. The solvents were evaporated first in the rotavapor and later in the high-vacuum pump. The crude of the reaction was analyzed by ^{1}H-NMR to determine the *trans*/*cis* ratio and later subjected to flash chromatography in SiO_2 (1:1 Hex/EtOAc), 42 mg of **14** (92% isolated yield, *d.r.*: 100:0 *trans*/*cis*) as a white solid were obtained.

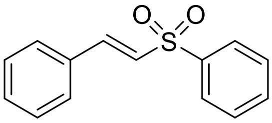
Rf = 0.5 (1:1 Hex/EtOAc) [UV] [$KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.73 – 7.64 (m, 2H), 7.58 – 7.32 (m, 9H), 6.83 (d, ^3J = 15.5 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 144.0 (C), 136.5 (CH), 133.7 (C), 133.0 (CH), 131.2 (CH), 129.9 (CH), 129.5 (CH), 128.9 (CH), 127.8 (CH), 124.7 (CH).

All of the characterization data for this compound is in agreement with that reported in the literature.[4]

(*E*)-(2-(Phenylsulfonyl)vinyl)benzene (15)



A 50 mL round-bottomed flask was charged with the phenyl vinyl sulfide **3aa** (42.5 mg, 0.2 mmol), in glacial acetic acid (1 mL) and hydrogen peroxide (30%$_{\text{aq sol}}$, 0.08 ml, 0.7 mmol) was added dropwise. The reaction mixture was stirred at reflux for 20 min. Then, the mixture was cooled down and extracted with Et_2O (10 mL) and water (10 ml). The organic phase was then washed with 10 mL of brine and dried over Na_2SO_4. The solvents were evaporated first in the rotavapor and later in the high-vacuum pump. The crude of the reaction was analyzed by ^{1}H-NMR to determine the *trans*/*cis* ratio and later subjected to flash chromatography in SiO_2 (5:1 Hex/EtOAc), 31 mg of **15** (64% isolated yield, *d.r.*: 14.4:1 *trans*/*cis*) as a white solid were obtained.

Rf = 0.28 (5:1 Hex/EtOAc) [UV] [$KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 8.04 – 7.93 (m, 2H, + isom. *cis*), 7.71 (d, ^3J = 15.4 Hz, 1H), 7.69 – 7.58 (m, 2H, + isom. *cis*), 7.58 – 7.47 (m, 3H, + isom. *cis*), 7.45 – 7.38

---

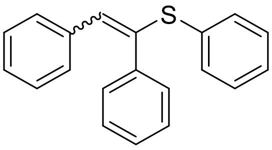
[4] Y. Li and A. Studer, *Org. Lett.*, **2017**, *19*, 666.

(m, 3H, + isom. *cis*), 7.11 (d, ^3J = 12.1 Hz, isom. *cis*), 6.89 (d, ^3J = 15.4 Hz, 1H), 6.55 (d, ^3J = 12.0 Hz, isom. *cis*).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 142.5 (CH), 140.8 (C), 133.4 (CH), 132.4 (C), 131.2 (CH), 129.4 (CH), 129.1 (CH), 128.6 (CH), 127.7 (CH), 127.3 (CH).

All of the characterization data for this compound is in agreement with that reported in the literature.[5]

(1,2-Diphenylvinyl)(phenyl)sulfane (17)



Following the **general procedure A**, the 1-bromoethene-1,2-diyldibenzene[6] (67.4 mg, 0.26 mmol), thiol 2a (41 µL, 0.40 mmol) and freshly ground NaOH (16 mg, 0.40 mmol) were dissolved in 2 mL of dry DMSO. After purification by flash chromatography in SiO2 (Hexane), 30 mg of **17** (40% isolated yield, *d.r.*: 3.9:1 *E/Z*) as a white solid were obtained.

Rf = 0.43 (Hexane) [UV] [$KMnO_4$].

^{1}H NMR (300 MHz, $CDCl_3$, 300K) δ 7.67 – 7.61 (m, 2H), 7.60 – 7.55 (m, 3H), 7.52 – 7.45 (m, 2H), 7.42 – 7.36 (m, 5H), 7.31 – 7.22 (m, 4H), 6.64 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$, 300K) δ 141.3(C), 137.4 (C), 137.3 (C), 131.6 (CH), 130.3 (CH), 128.9 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.3 (CH), 127.2 (CH), 127.1 (CH), 126.5 (CH), 123.3 (C), 89.4 (C).

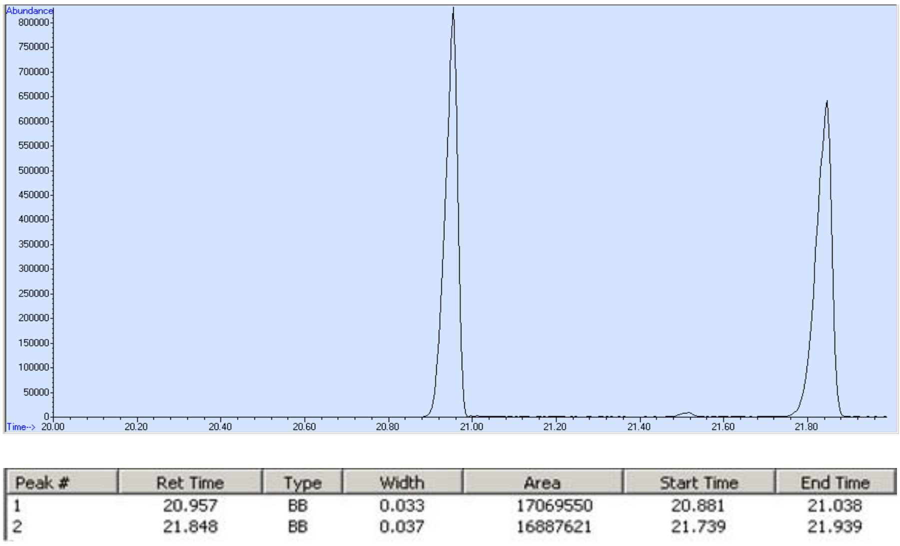
The identification of the major isomer is not possible via NMR studies.[7] The E/Z ratio was this time determined *via* GC/MS analysis, where a 1/1 E/Z ratio was observed for compound **17**.

---

[5] H.-Y. Tu, B.-L. Hu, C.-L. Denga, X.-G. Zhang, *Chem. Commun.*, **2015**, *51*, 15558.

[6] 1-Bromoethene-1,2-diyldibenzene was synthesized following the next reported procedure: M. Paraja, R. Barroso, M. P. Cabal, C. Valdés, *Adv. Synth. Catal.* **2017**, *359*, 1058.

[7] R. Pötzsch, H. Komber, B.-C. Stahl, C.-J. Hawker, B. I. Voit. *Macromol. Rapid Commun.* **2013**, *34*, 1772.



Peak #	Ret Time	Type	Width	Area	Start Time	End Time
1	20.957	BB	0.033	17069550	20.881	21.038
2	21.848	BB	0.037	16887621	21.739	21.939

Figure SI-4. GC/MS spectra of compound **17**.

3. UV/Vis spectra

All of the measurements were carried out by dissolving the corresponding reagents in DMSO at a [1.3 mM] concentration. A red-shifted bathochromic shift is observed for the mixture of **1a** + **2a** + Cs_2CO_3, which supports the formation of a HB complex between **1a** and the thiolate anion coming from deprotonation of **2a**. This allows for a selective excitation of this complex employing a 440-456 nm lamp.

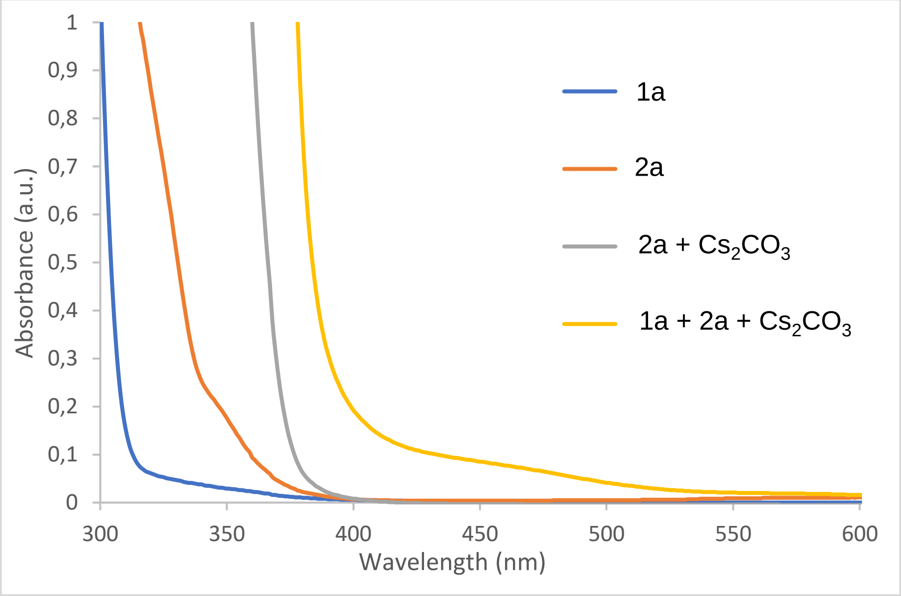


Figure SI-5. UV-Vis spectra of compounds **1a** (blue line), **2a** (orange line), **2a** + Cs_2CO_3 (grey line) and a equimolar mixture of **1a** + **2a** + Cs_2CO_3 (yellow line).

4. Radical clock experiments

The structural determination of the compound **8** was carried out by NMR studies and GC/MS experiments. An *E/Z* isomeric mixture of this compound was observed. While performing flash chromatography, this compound coeluted with the molecule **3ae** when employing a 20:1 Hex/EtOAc mixture using SiO_2 as the stationary phase. The ^{1}H-NMR signals corresponding to the compound **8** have been highlighted in purple in the figure SI-6.

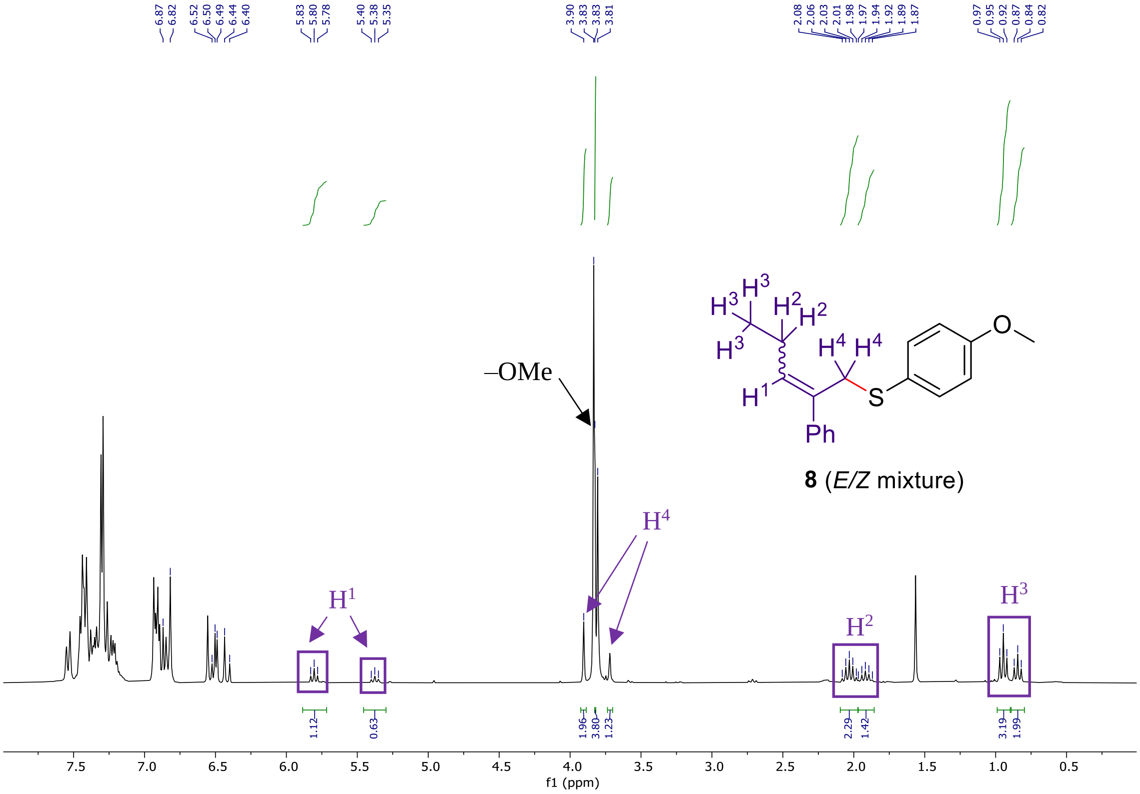


Figure SI-6. ^{1}H-NMR spectra of the mixture of the compounds **3ae** and **8**.

On the other hand, the NMR signals derived from the *trans*/*cis* mixture of the compound **3ae** have been previously described in this SI and present the same multiplicities and chemical shifts as the ones obtained in this NMR spectra. Critical signals for the structural identification of **8** are the two triplets at 5.80 (t, ^3J = 7.3 Hz) and 5.36 ppm (t, ^3J = 7.6 Hz) which correspond to the olefinic H^1 of both *E/Z* isomers. Two singlet signals overlapping at 3.83 ppm are assigned to each of the –OMe groups. The methylenic H^4 adjacent to the sulfur atom are located as singlet signals at 3.90 and 3.81 ppm for each of the *E* and *Z* isomer respectively. The allylic H^2 hydrogens show a signal for each of the isomers at 2.03 (^3J = 7.5 Hz) and 1.92 (^3J = 7.5 Hz) ppm and present the multiplicity of a quintuplet due to the coupling with H^1 and H^3. This determines unambiguously that the starting cyclopropyl moiety at compound **7** had been opened and now a linear alkylic C^2–C^3 chain is present in the molecule **8**. This is eventually confirmed by the presence of the H^3 from the methyl group, which feature a signal for each of the *E/Z* isomers at 0.95 (t, ^3J = 7.5 Hz) and 0.4 (t, ^3J = 7.5 Hz) ppm.

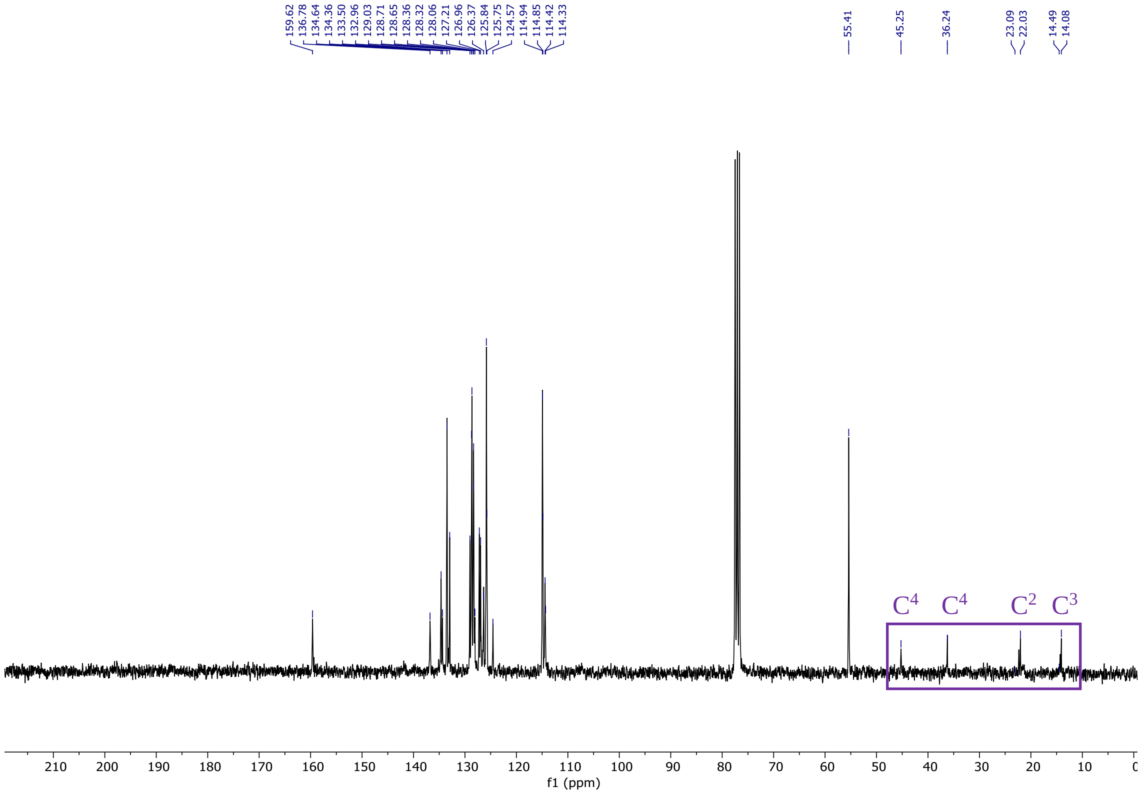


Figure SI-7. ^{13}C-NMR spectra of the mixture of the compounds **3ae** and **8**.

The critical ^{13}C-NMR signals for the aliphatic zone of the compound **8** also could be assigned to each of the C^2 (23.0 and 22.0 ppm), C^3 (14.4 and 14.0 ppm) and C^4 (45.2 and 36.4 ppm) correspondingly (Figure SI-7).

Further evidence was provided by a GC/MS analysis (Figure SI-8) of this mixture revealed the presence of each of the *trans*/*cis* isomers of **3ae** (MW = 242 g/mol) and each of the *E/Z* isomers of **8** (MW = 284 g/mol).

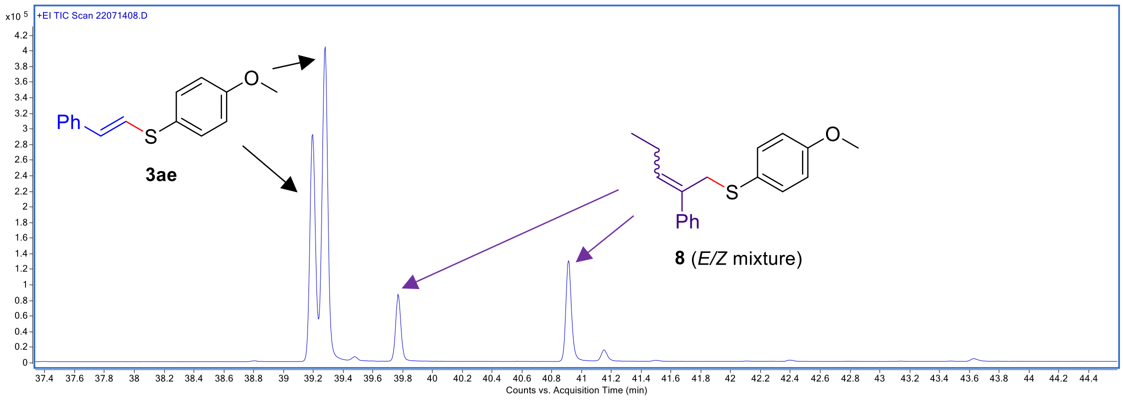
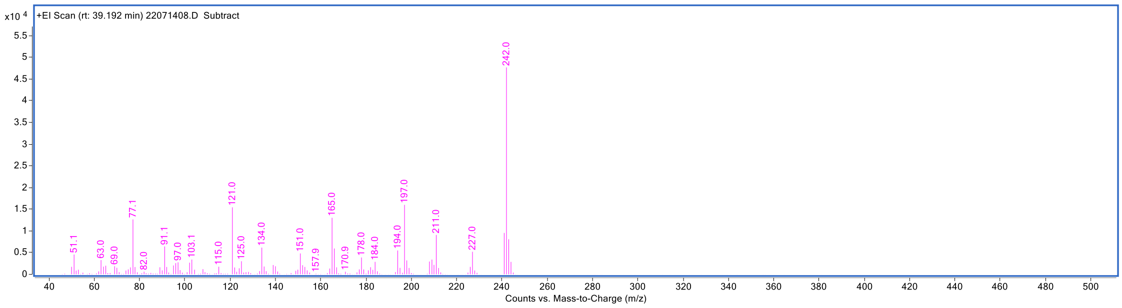
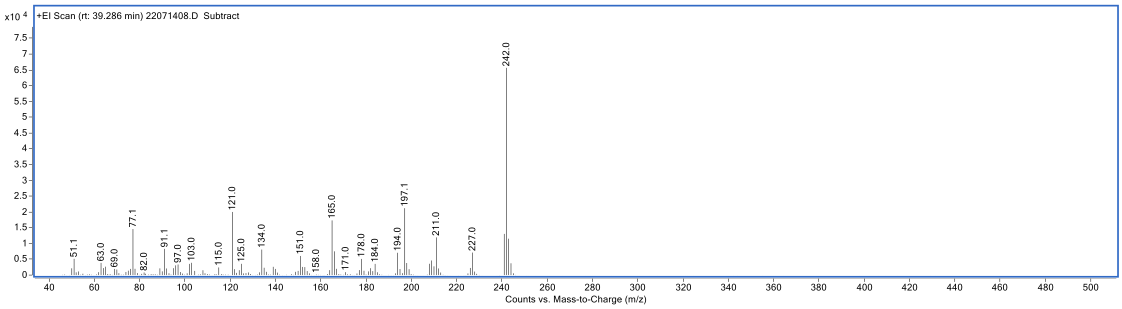


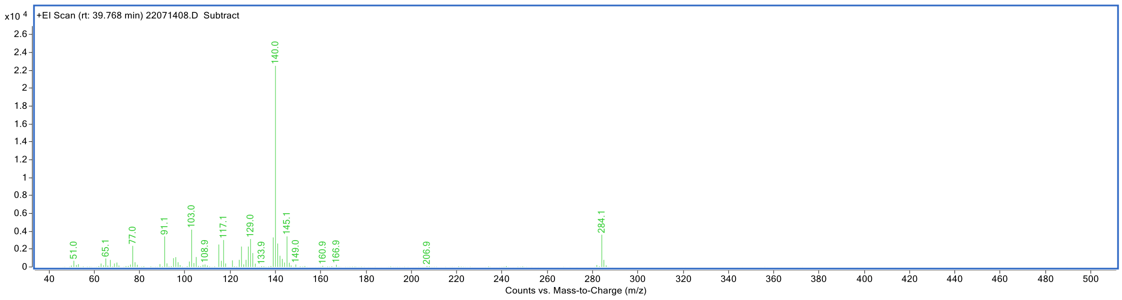
Figure SI-8. GC/MS spectra of the mixture of the compounds **3ae** and **8**.



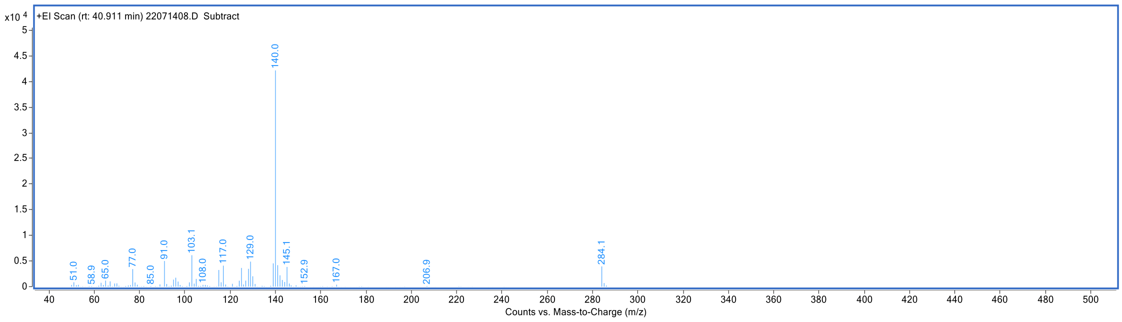
+EI Scan (rt: 39.192 min) 22071408.D Subtract
x10 4
51.1
63.0
69.0
77.1
82.0
91.1
97.0
103.1
115.0
121.0
125.0
134.0
151.0
157.9
165.0
170.9
178.0
184.0
194.0
197.0
211.0
227.0
242.0
Counts vs. Mass-to-Charge (m/z)



+EI Scan (rt: 39.286 min) 22071408.D Subtract
x10 4
51.1
63.0
69.0
77.1
82.0
91.1
97.0
103.0
115.0
121.0
125.0
134.0
151.0
158.0
165.0
171.0
178.0
184.0
194.0
197.1
211.0
227.0
242.0
Counts vs. Mass-to-Charge (m/z)



+EI Scan (rt: 39.768 min) 22071408.D Subtract
x10 4
51.0
65.1
77.0
91.1
103.0
108.9
117.1
129.0
133.9
140.0
145.1
149.0
160.9
166.9
206.9
284.1
Counts vs. Mass-to-Charge (m/z)



+EI Scan (rt: 40.911 min) 22071408.D Subtract
x10 4
51.0
58.9
65.0
77.0
85.0
91.0
103.1
108.0
117.0
129.0
140.0
145.1
152.9
167.0
206.9
284.1
Counts vs. Mass-to-Charge (m/z)

5. Optimization for the *E*/*Z* photochemical isomerization of the compound 1a

For this purpose, the *trans* configured compound **3aa** (*d.r.*: 8:1 trans/cis) was selected as the model substrate for the optimization and the photochemical conversion to **3aa’** was explored. First of all, the UV-vis absorption profiles of the the vinyl sulfides **3aa** and **3aa’** were analysed (Figure SI-9).

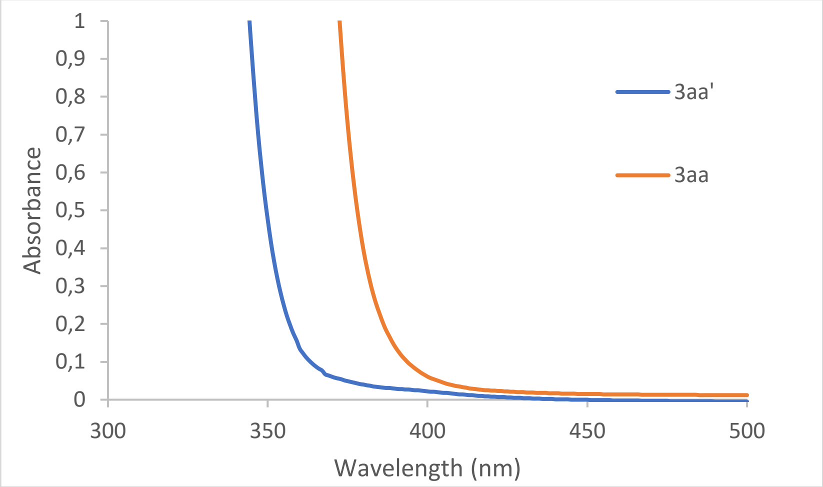


Figure SI-9. Overlap of the UV/vis absorption spectra of the compounds **3aa** (orange line) and **3aa’** (blue line).

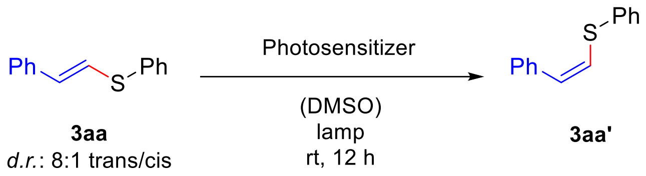
In this diagram, it is observed that direct irradiation at 390 nm could potentially convert compound **3aa** into **3aa’**. Thus, we performed an experiment in which **3aa** (0,2 mmol) was dissolved in DMSO (2 mL), and direct irradiation at nm gave access to a photostationary state after 48 hours in which a 1:1 *trans/cis* mixture was obtained. Irradiation at lower waveleghts than 390 nm did not improve the diastereomeric ratio in favour of the *cis* isomer **3aa’**. This is not surprising, given that normally the intersystem crossing to access the triplet state of organic molecules, from which the isomerization takes place, is a slow process.[8] As an alternative, we decided to follow a photosensitization strategy, in which a photocatalyst is expected to transfer its triplet energy to a target molecule (in this case, the compound **3aa**). For an efficient triplet energy transfer to occur from the photocatalyst to the *trans* isomer **3aa**, it is required that E_T (*cis* isomer) > E_T (photosensitizer) > E_T (*trans* isomer).

Given the lack of reports on photochemical *E/Z* isomerization of vinyl sulfides and triplet energy values,[9] we ran a screening of photosensitizers in order to find a photostationary state in which the cis isomer **1a’** prevailed as the major stereoisomer. In the table SI-1, the most representative experiments have been gathered:

---

[8] D. Sasikumar, A. T. John, J. Sunny, M. Hariharan. *Chem. Soc. Rev.* **2020**, *49*, 6122.

[9] For a recent review on photochemical *E/Z* isomerizations, see: T. Neveselý, M. Wienhold, J. J. Molloy, R. Gilmour. *Chem. Rev.* **2022**, *122*, 2650.



3aa
d.r.: 8:1 trans/cis

3aa'

Entry	**Photocatalyst**	**E_T (KJ·mol^{-1})**	**λ_{max} (nm)**	**lamp (nm)**	**P.S (h)**	**Ratio Trans/cis**
1	**-**	**-**	**-**	**427**	**48**	**1:1**
2	**Xanthone**	**310**	**350**	**366**	**12**	**1:1.8**
3	**Thioxanthone**	**265**	**390**	**427**	**12**	**1:1**
4	**Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6**	**251**	**389**	**427**	**12**	**1:1**
5	**9-Fluorenone**	**211**	**230**	**366**	**12**	**1:1.2**
6	**[Ru(bpy)$_3$][PF_6]$_2$**	**205**	**451**	**427**	**12**	**1:4.8**
7	**Ru(bpy)$_3$$Cl_2$**	**194**	**452**	**427**	**12**	**1:4.4**
8	**Eosin Y**	**190**	**539**	**525**	**12**	**9:1**

Table SI-1. Screening of photosensitizers for the photochemical E/Z isomerization of **1a.**

We observed that irradiation at 427 nm employing 5% mol of the photosensitizer [Ru(bpy)$_3$][PF_6]$_2$ (entry 6), a photostationary state is reached after 12 h in most of the *trans* isomer **3aa** had been converted into the *cis* configured compound **3aa’** (1:5 *trans/cis*) with a 95% yield. This determination of the stereochemistry was done by ^{1}H-NMR spectroscopy, as shown in the figure SI-10.

In light of these results, we expect the triplet energy of the compound **3aa** to be close to the one of the photosensitizer (205 KJ·mol^{-1}). Photosensitizers presenting a higher triplet energy, such as xanthone (E_T = 205 KJ·mol^{-1}), which require irradiation at shorter wavelengths (366 nm) for the excitation of the photocatalyst, fail to provide a better stereoselectivity in favour of the cis isomer for the reasons previously pointed out. On the other hand, the employment of photosensitizers with low triplet energy values like Eosin Y (E_T = 190 KJ·mol^{-1}) result in no energy transfer to the alkenyl bromide **1a**.

Motivated by these preliminary results, we are currently investigating in-depth potential applications and extension of this isomerization to other substrates in our research group.

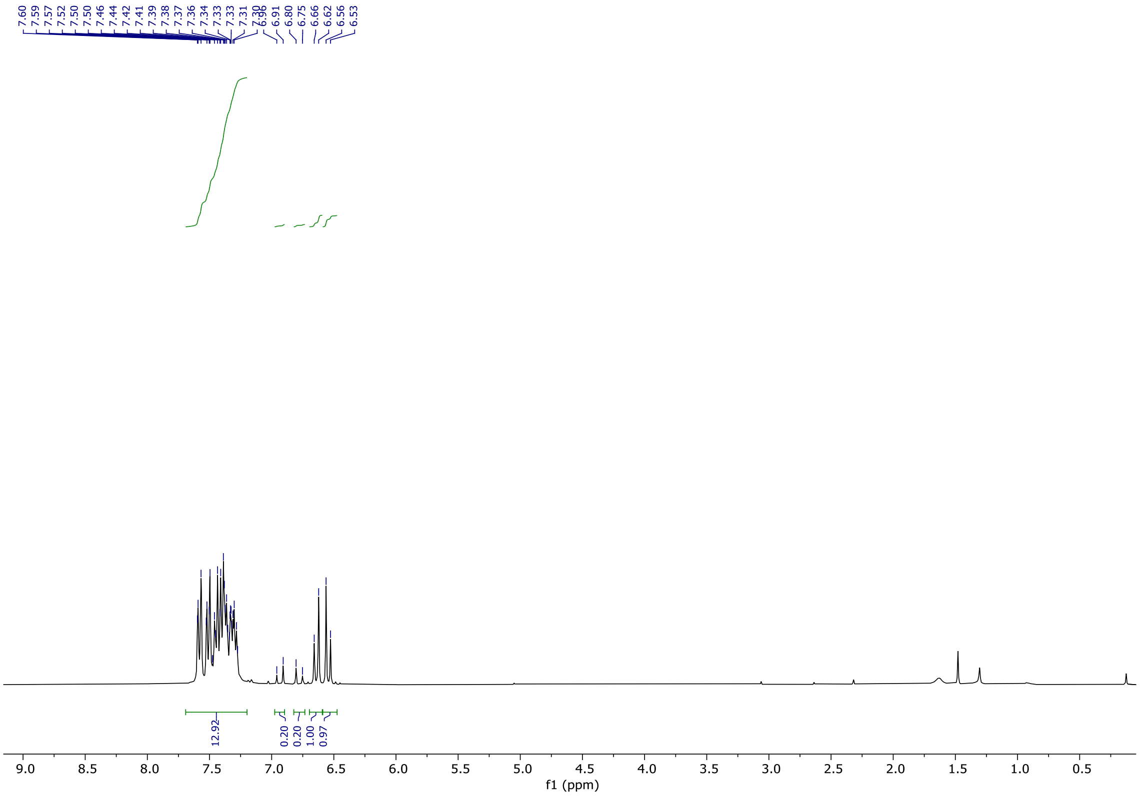


Figure SI-10. ^{1}H-NMR spectra of the compound **3aa’.**

6. Computational studies

The computational calculations were performed using the ORCA 5.0.3 software.[10] The geometry optimizations were conducted employing the wB97x-D3 functional, which features dispersion corrections and has been shown to give reliable results for non-bonding interactions.[11] The triple z basis set with polarization correction Def2-TZVPP was employed for all atoms. Analytical frequency calculations were computed to characterize the optimized structures as minima in the potential energy surface. Single point energy calculations on the optimized structures were computed at the CMCD(dmso) model at the same theory level to account for the solvation effects. The 3D model has been represented with Cylview 2.0.[12] The electrostatic potential map representation was rendered with Gaussview 5.0 from a model obtained with Gaussian 09 at the wB97x/ Def2-TZVPP level. The electrostatic potential was mapped over a $4x10^{-4}$ au isodensity surface.

The modeling studies indicate the existence of a minimum in the potential energy surface corresponding to the halogen bonded complex **HB-complex** between **1a** and the thiophenolate **2a**. The halogen bond interaction between the bromine and sulfur atom presents a great directionality, displaying a dihedral angle of 173.4 º between the Csp^2–Br–S bonds, which results in a nearly linear structure for the halogen-bonding complex. Indeed, in the electrostatic potential surface it is observed that positively charged bromine σ–hole zone is located at almost the center of the C–Br axis (Scheme 4, b of the manuscript). This linear geometry with dihedral angles between 160 º and 180 º for the HB complex is in agreement with previously reported observations on parent complexes (reference 26 in the manuscript). Furthermore, we found that in the halogen-bonding complex the distance between the bromine and sulfur atoms was 3.21 Å, which is shorter than the sum of the Van der Waals radii of the sulfur and bromine atoms (3.65 Å). This fact supports the existence of a non-covalent weak interaction between these atoms, which is most likely due to the halogen bond formation. According to the calculations the complexation process is exothermic $\Delta H = -4.88$ kcal· mol^{-1}, but endergonic. Nevertheless, the ΔG value overestimates the entropic effects in complexation process.

---

[10] F. Neese, W. Wennmohs, U. Becker, C. Riplinger, The ORCA quantum chemistry program package, *J. Chem. Phys.* **2020**, *152*, 224108.

[11] Y.-S. Lin, G.-D. Li, S. P. Mao, J.-D. Chai Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections *J. Chem. Theory Comput.* **2013**, *9*, 1, 263.

[12] CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org).

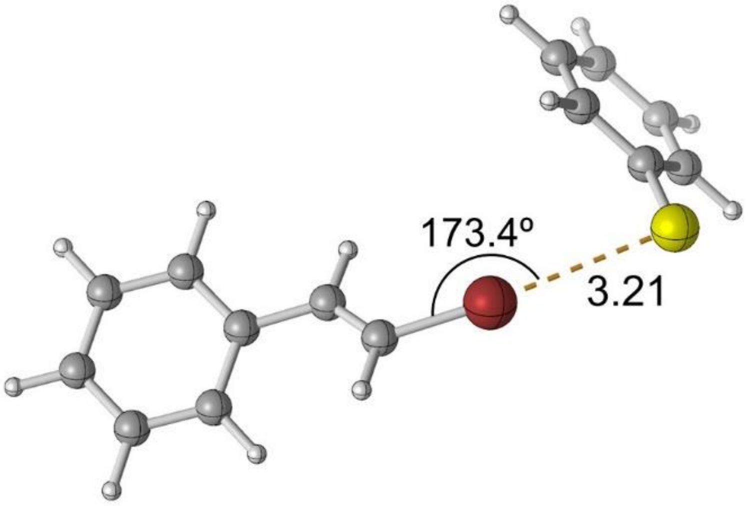


Figure SI-11: HB complex between **1a** and the anionic form of **2a** calculated at the wB97x-D3/Def2TZVPP.

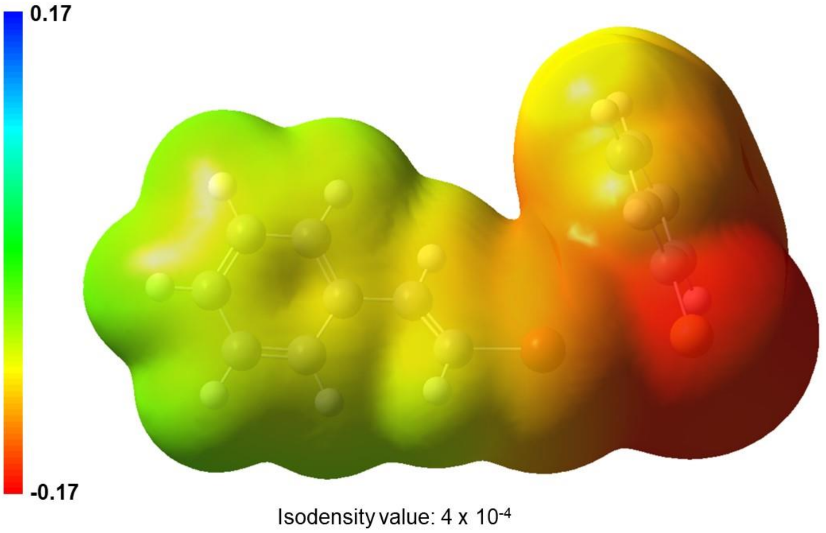
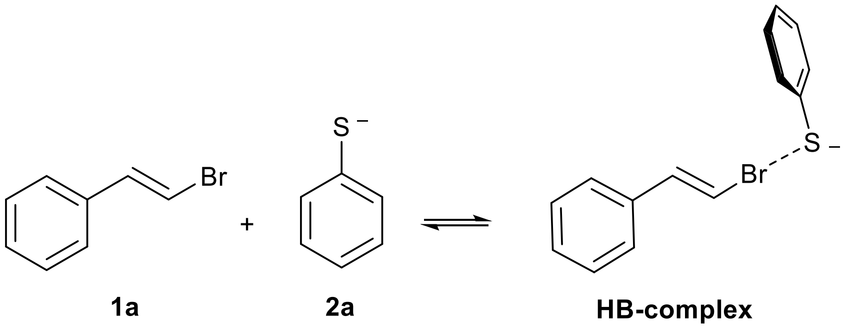


Figure SI-12: Calculated electrostatic potential map (red = negative electrostatic potential) on the 0.0004 au isodensity surface.



$$\Delta H = -4.9\ kcal \cdot mol^{-1};\ \Delta G(solv) = 13.4\ kcal \cdot mol^{-1}$$

Cartesian Coordinates and energy data

β-bromostyrene 1a

C	-4.63546818435086	1.34655300852485	0.41022761699868
C	-3.25036516181254	1.37089149724193	0.40199920944765
C	-2.51592635779114	0.23086291807249	0.08076353924522
C	-3.20858577022248	-0.93126644365324	-0.26002709063971
C	-4.59187990442767	-0.95682528836676	-0.25088080340643
C	-5.31164423066023	0.18056854067149	0.08807480917014
H	-5.18772718251069	2.24104255465535	0.66883763665657
H	-2.72580278172333	2.28408213078950	0.65740692949911
H	-2.66230341808630	-1.81872614710356	-0.55436096732489
H	-5.11322006577966	-1.86669264051637	-0.52017533595197
H	-6.39380714697929	0.15883806799089	0.09157326919565
C	-1.04588253641666	0.29932262723883	0.11649405304985
H	-0.60867939903231	1.29040087880289	0.06190457187367
C	-0.24439247938492	-0.74692541119409	0.24299581962614
H	-0.58669879210334	-1.76677633370668	0.34088593175248
Br	1.62928341128143	-0.59514995944752	0.29198081080784

SCF energy: -2883.282915428244 Hartree

Gibbs free energy: -2883.19187950 Hartree

SCF energy (CPCM-dmso): -2883.289725376402 Hartree

Gibbs free energy (CPCM-dmso): -2883.198689 Hartree

Thiophenolate 2a

S	4.80622810944030	-0.07188404792749	0.34257531510327
C	4.47107398438478	1.57703959307068	-0.05105514741972
C	3.69597285613138	2.41295653041389	0.78378702389091
C	4.95285459925418	2.18566419456068	-1.23192429915407
C	3.42563974558027	3.73225209371156	0.46499656231788
H	3.30767833128029	1.98675514049827	1.70164792542955
C	4.68209251543060	3.50526603736859	-1.54846771034451
H	5.55397282061170	1.57918376871518	-1.89945290646206
C	3.91314745175782	4.30242886814360	-0.70663504544615
H	2.82232159308970	4.32950227939201	1.14276411666475
H	5.07759856036545	3.92098502931653	-2.47096222324010
H	3.69871943267353	5.33535051273650	-0.95567361133975

SCF energy: -629.907074 Hartree

Gibbs free energy: -629.846127 Hartree

SCF energy (CPCM-dmso): -630.004074 Hartree

Gibbs free energy (CPCM-dmso): -629,943127 Hartree

HB-Complex

C	-4.63764345688228	1.33966229157699	0.42053414167993
C	-3.25257039728649	1.37015014152489	0.40184275867356
C	-2.50861061917325	0.23785812165342	0.06704653866893
C	-3.20588291762364	-0.92167888614133	-0.27951349324764
C	-4.58939602175370	-0.95557408886765	-0.25635968466545
C	-5.31490477259037	0.17374627339633	0.09733907606277

H	-5.19038236394007	2.23119923189652	0.69124306620055
H	-2.72918283789402	2.28295187748378	0.66138657136511
H	-2.65536499104704	-1.80194499284559	-0.58727541376420
H	-5.10665441219142	-1.86758252566846	-0.52936231035185
H	-6.39735940284189	0.14634035986925	0.11164619546699
C	-1.03874984527497	0.30500859081137	0.09340885146102
H	-0.59546496537591	1.29198545705080	0.00580152717304
C	-0.23845656710509	-0.74182918828353	0.26015714473635
H	-0.63010623702264	-1.74353262322307	0.39107950872343
Br	1.63790307514906	-0.62671243975164	0.31901310662771
S	4.80056474711480	-0.07435620475627	0.33793193319476
C	4.47224873515092	1.58412566115405	-0.05135027066807
C	3.69800719354010	2.41339225752640	0.78557119415041
C	4.95489812784137	2.18601236365533	-1.23095750794277
C	3.42379279855134	3.73215965395578	0.46467389316142
H	3.31322628466224	1.98829752349995	1.70505964667631
C	4.68438144589644	3.50587505708107	-1.54792621899193
H	5.55312902024856	1.57747230776403	-1.89883615295947
C	3.91249993127963	4.29943087632162	-0.70652919213865
H	2.81842493290053	4.32890672157859	1.14033130439167
H	5.07805060562339	3.92197144743720	-2.47046876720289
H	3.69810291004437	5.33216473430010	-0.95588744648104

SCF energy: -3513.199547 Hartree

Gibbs free energy: -3513.02663693 Hartree

SCF energy (CPCM-dmso): -3513.293334274013 Hartree

Gibbs free energy (CPCM-dmso): -3513.12042 Hartree

7. Quantum yield measurement

The quantum yield measurement was performed following a procedure described by Dell' Amico and coworkers.[13] This method involves a ferrioxalate actinometry solution where the decomposition of ferric ions to ferrous ions, by irradiation at a particular wavelength, is measured.[14] To achieve this, the ferrous ions are complexed with 1,10-phenanthroline and its absorbance at 510 nm by UV/Vis is determined.[15] Finally, the moles of iron-phenanthroline complex formed are associated to the moles of photons absorbed.

Actinometry measurements:

Preparation of the solutions:

- Potassium ferrioxalate solution: 294.7 mg of potassium ferrioxalate, 139 µl of sulfuric acid (96 %) were added to a 50 ml volumetric flask and filled with distilled water.
- Phenanthroline solution: 0.2 % by weight of 1,10-phenanthroline in water was prepared in a 50 ml volumetric flask.
- Buffer solution: 2.47 g of NaOAc and 0.5 ml of sulfuric acid (96 %) were added to a 50 ml volumetric flask and filled with distilled water.
- Reaction solution: Following the general procedure A, a 9.4:1 trans/cis mixture of vinyl bromide **1d** (91 mg, 0.39 mmol), thiol **2a** (61 µL, 0.60 mmol) and freshly ground NaOH (24 mg, 0.60 mmol) were dissolved in 3 mL of dry DMSO. To this mixture, 1,3,5-trimethoxybenzene (11.2 mg, 0.066 mmol) was added as the internal standard.

These solutions were stored in the dark.

Procedure:

Although our reaction was performed irradiating at 440 nm, the quantum yield calculations have been completed by irradiating with a 456 nm LED Kessil lamp at 25% intensity. This way, monitoring the reaction is easier as it proceeds slower.

1) A 5 mL glass vial was charged with 1 ml of the potassium ferrioxalate solution and placed 9 cm away from the 456 nm LED lamp. To monitor the decomposition reaction, this step was performed six different times varying only the irradiation time for each sample: 0, 2, 4, 6, 10 and 20 seconds. All were irradiated at 25% intensity of the 456 nm LED Kessil lamp.

---

[13] S. Cuadros, C. Rosso, G. Barison, P. Costa, M. Kurbasic, M. Bonchio, M. Prato, G. Filippini and L. Dell'Amico, *Org. Lett.*, 2022, **24**, 2961.

[14] S. L. Murov, *Handbook of Photochemistry*, Marcel Dekker, New York, 1973.

[15] H. J. Kuhn, S. E. Braslavsky, R. Schmidt, Chemical Actinometry (IUPAC Technical Report), *Pure Appl. Chem.*, 2004, **76**, 2105.

2) Once the sample was irradiated, it was transferred from the vial to a 10 ml volumetric flask. To this flask, 0.5 ml of the phenanthroline solution and 2 ml of the buffer solution were added and the flask was filled with distilled water.
3) The reaction was stirred in the dark for 1 hour to achieve complete complexation between the phenanthroline and Fe^{2+}.
4) For each time interval sample a UV/Vis spectra was recorded. An overlap of these spectra is shown in the Figure SI-13.

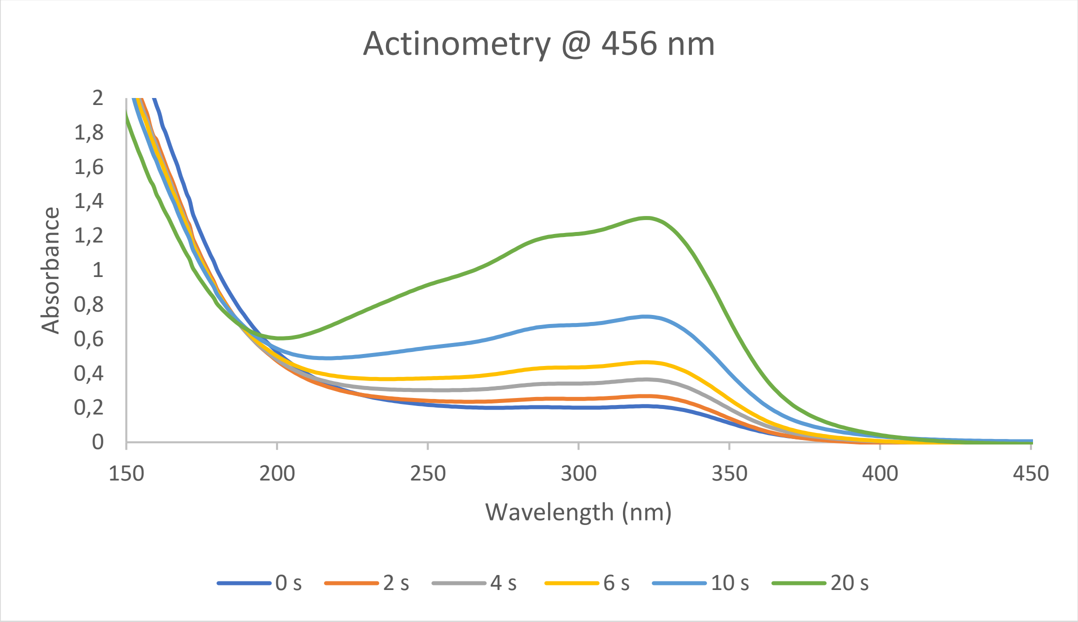


Figure SI-13. Actinometry UV/Vis spectra of samples irradiated at 456 nm LED during different time periods.

5) After measurement of all samples, the moles of Fe^{2+} formed (N) can be determined by using Beer's Law.

$$\mathrm{mmolFe}^{2+} = \frac{V_1 V_3 \Delta A_{(510nm)}}{10^3 V_2 l \varepsilon_{(510nm)}}$$

Equation SI-1. Lambert-Beer's law.

In this equation: V_1 is the irradiated volume (1 ml), V_2 is the aliquot of the irradiated potassium ferrioxalate solution (1 ml), V_3 is the final volume after complexation (10 ml), $\Delta A_{(510\ nm)}$ is the difference in absorbance between the irradiated solution and the one at 0 seconds, l is the optical path-length of the irradiation cell (1 cm), and $\varepsilon_{(510\ nm)}$ is the molar extinction coefficient of the complex (11100 L mol^{-1} cm^{-1}).

6) The photon flux (F) was obtained by plotting the moles of Fe^{2+} formed (N) versus the time (t) (Figure SI-14).

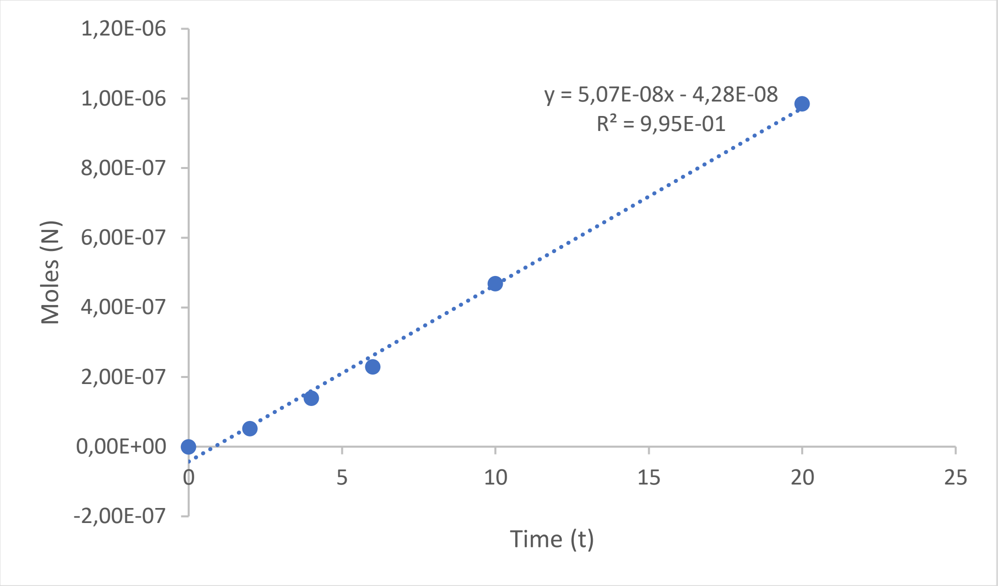


Figure SI-14. Actinometry UV/Vis spectra of samples irradiated at 456 nm LED during different time periods.

Knowing that the slope follows the equation F=N/ ϕFe^{2+} t; and that ϕFe^{2+} = 0.9 at λ = 456 nm[13]:

F = **5.63 10^{-8} einstein s^{-1}**

7) Finally, a correction factor (C) must be considered. The absorbance of the ferrioxalate solution at 510 nm using the 456 nm LED lamp is 0.21. Only if this value is higher than 2 it can be said that all the incident light is absorbed, as in our case this value is lower, a correction factor is needed to recalculate the photon flux ($F_{corrected}$).

$$\phi \mathrm{Fe}^{2+} = \frac{\left(\frac{\delta_{molesFe^{2+}}}{\delta_{time}}\right)}{FC_{Fe^{3+}}} \qquad\qquad C_{Fe^{3+}} = \left[1 - 10^{-A(\lambda)}\right]$$

Equation SI-2. Relationship between the correction factor (C) and the quantum yield equation.

As A_{456nm} = 0.21; C = 0.383 and $F_{corrected}$ = **1.47 10^{-7} einstein s^{-1}**.

8) The reaction solution previously described was irradiated in the same was as in the actinometry experiment. The moles of product formed (compound **3da**) were determined by taking aliquots of the reaction of 300 µL and following conversion via ^{1}H-NMR at different intervals of time (30, 60, 120 and 180 min). Once this was done, the moles of product formed were related to the number of photons per unit of time (Figure SI-15).

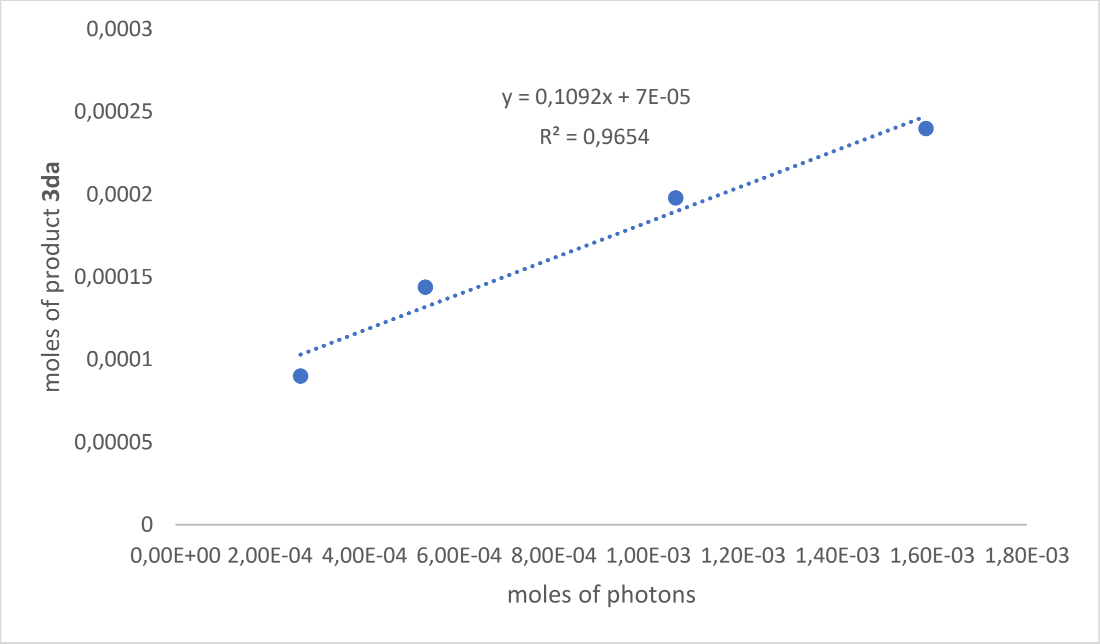


Figure SI-15. Representation of the moles of product **3da** formed related to the number of total incident photons.

Given that the absorbance of the irradiation mixture at that wavelength is higher than 2 (A_{456}>2), no correction factor needs to be applied in this case since it can be assumed that all of the incident light is absorbed. **The registered slope is the value of the quantum yield of our reaction. ϕ = 0.11.**

8. NMR titration experiments.

To carry out these experiments, we prepared different solutions with increasing amount of the sodium thiophenolate, maintaining the same amount of vinyl bromide **1a** in each of them. All of the samples were prepared in d^6-DMSO to enable direct NMR analysis. During the performance of this titration, an increasing downfield shift of the signal of the carbon in α position to the phenyl group at the vinyl bromide **1a** (marked with a red dot) was detected. A depiction of the composition of each sample and its ^{13}C-NMR spectra will be shown:

- <u>Sample 1</u>

Preparation: In a 5 mL vial, **1a** (34 µL, 0.26 mmol) was dissolved in 0.6 mL of d^6-DMSO.

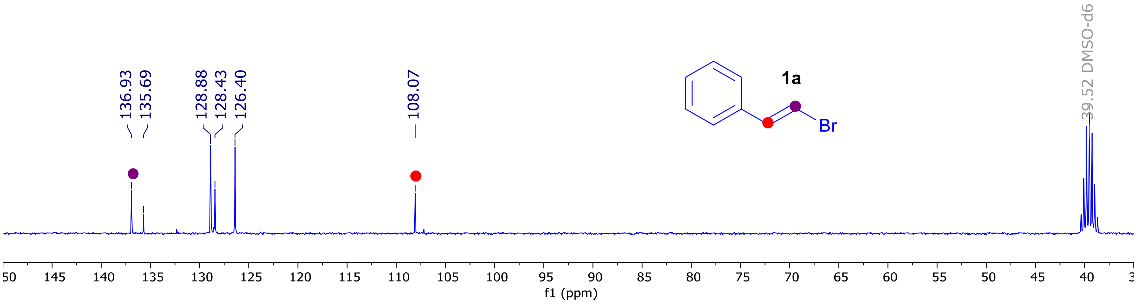


Figure SI-16. ^{13}C-NMR spectra recorded for the Sample 1 in d^6-DMSO.

Chemical shifts: (●) = 108. 07 ppm; (●) = 136.93 ppm.

- <u>Sample 2</u>

Preparation: In a 5 mL vial, **1a** (34 µL, 0.26 mmol), **2a** (0.26 mmol, 26 µL) and NaOH (0.26 mmol, 10 mg) were dissolved in 0.6 mL of d^6-DMSO. The mixture was stirred at room temperature for 20 minutes to ensure full deprotonation of the thiol in the basic media.

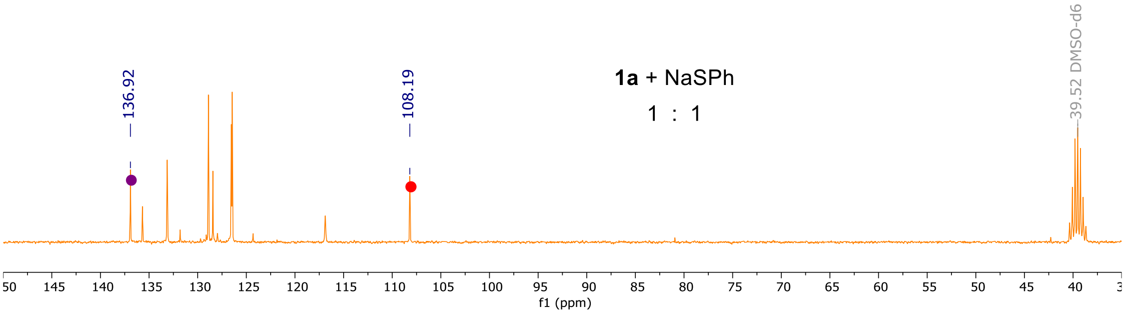


Figure SI-17. ^{13}C-NMR spectra recorded for the Sample 2 in d^6-DMSO.

Chemical shifts: (●) = 108. 19 ppm; (●) = 136.92 ppm.

- <u>Sample 3</u>

Preparation: In a 5 mL vial, **1a** (34 µL, 0.26 mmol), **2a** (0.52 mmol, 52 µL) and NaOH (0.52 mmol, 21 mg) were dissolved in 0.6 mL of d^6-DMSO. The mixture was stirred at room temperature for 20 minutes to ensure full deprotonation of the thiol in the basic media.

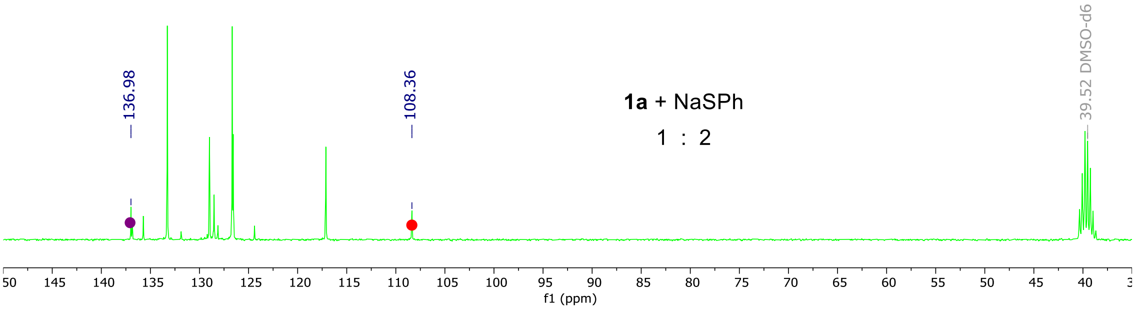


Figure SI-18. ^{13}C-NMR spectra recorded for the Sample 2 in d^6-DMSO. Chemical shifts: (🔴) = 108. 36 ppm; (🟣) = 136.98 ppm.

- <u>Sample 4</u>

Preparation: In a 5 mL vial, **1a** (34 µL, 0.26 mmol), **2a** (1.30 mmol, 130 µL) and NaOH (1.30 mmol, 52 mg) were dissolved in 0.6 mL of d^6-DMSO. The mixture was stirred at room temperature for 20 minutes to ensure full deprotonation of the thiol in the basic media.

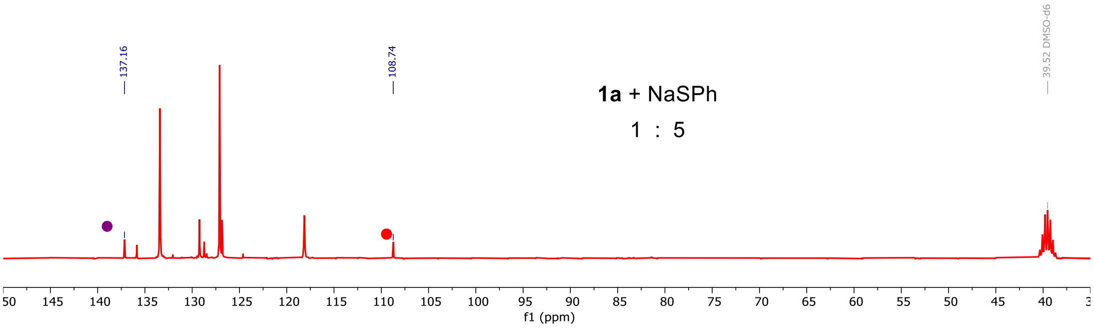


Figure SI-19. ^{13}C-NMR spectra recorded for the Sample 4 in d^6-DMSO. Chemical shifts: (🔴) = 108. 74 ppm; (🟣) = 137.16 ppm.

- <u>Sample 5</u>

Preparation: In a 5 mL vial, **1a** (34 µL, 0.26 mmol), **2a** (2.60 mmol, 264 µL) and NaOH (2.60 mmol, 104 mg) were dissolved in 0.6 mL of d^6-DMSO. The mixture was stirred at room temperature for 20 minutes to ensure full deprotonation of the thiol in the basic media.

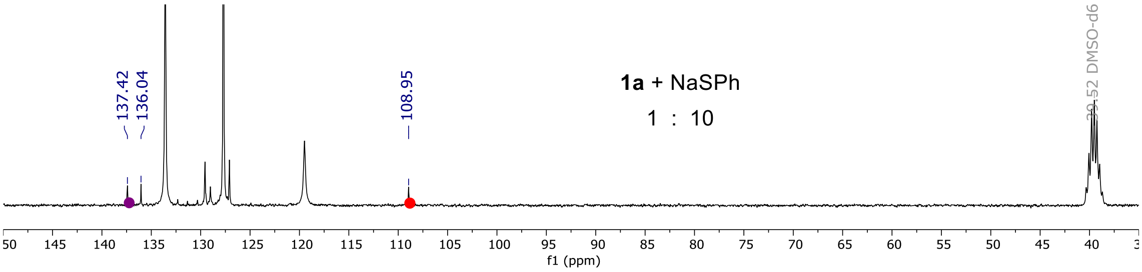
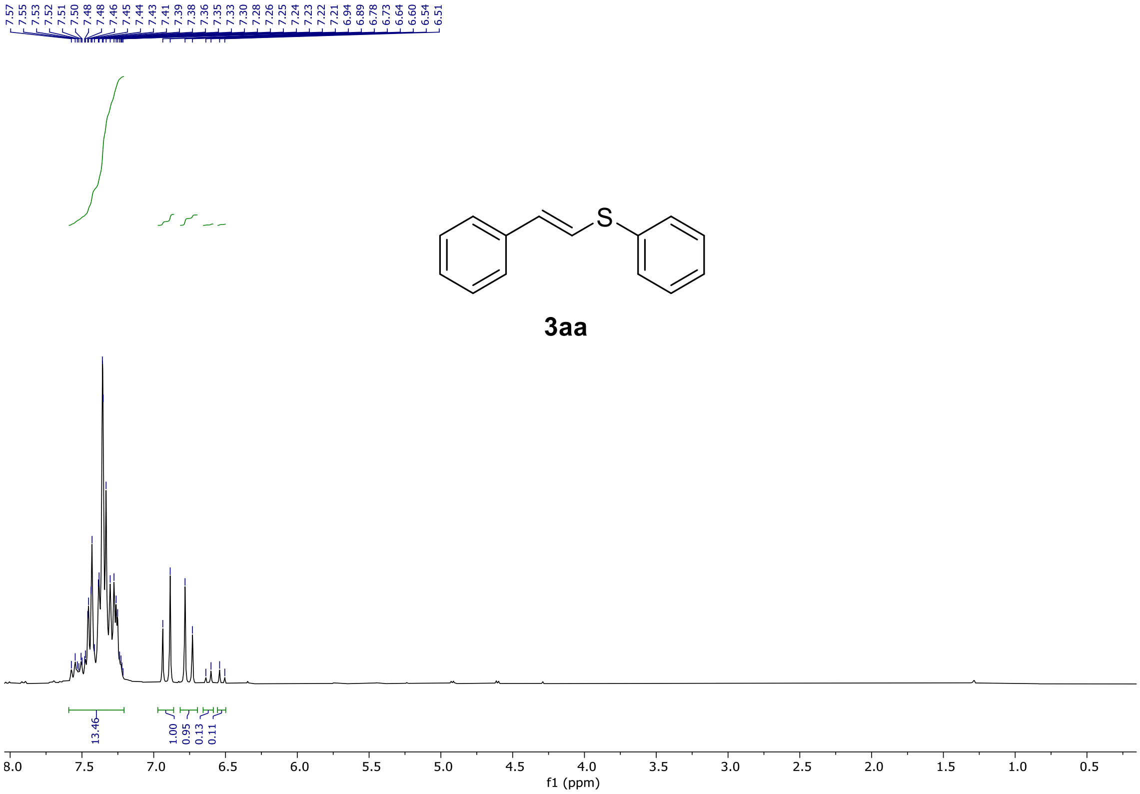
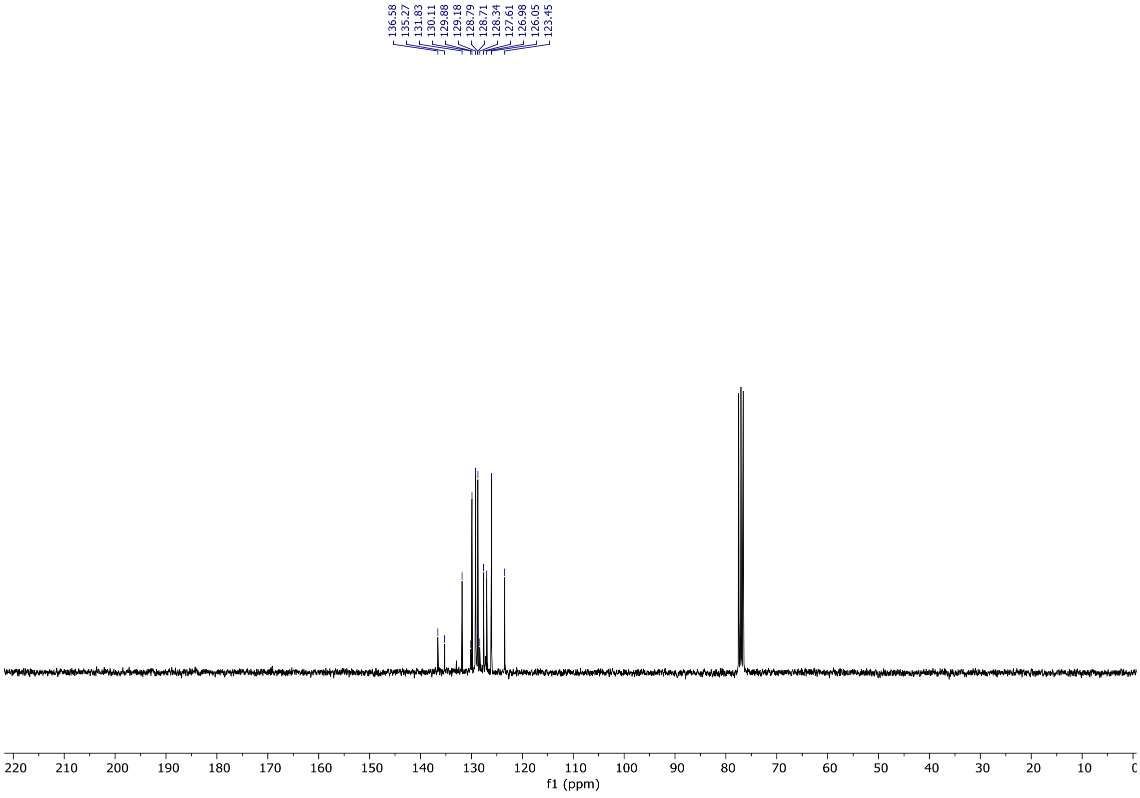


Figure SI-20. ^{13}C-NMR spectra recorded for the Sample 5 in d^6-DMSO. Chemical shifts: (🔴) = 108. 95 ppm; (🟣) = 137.42 ppm.

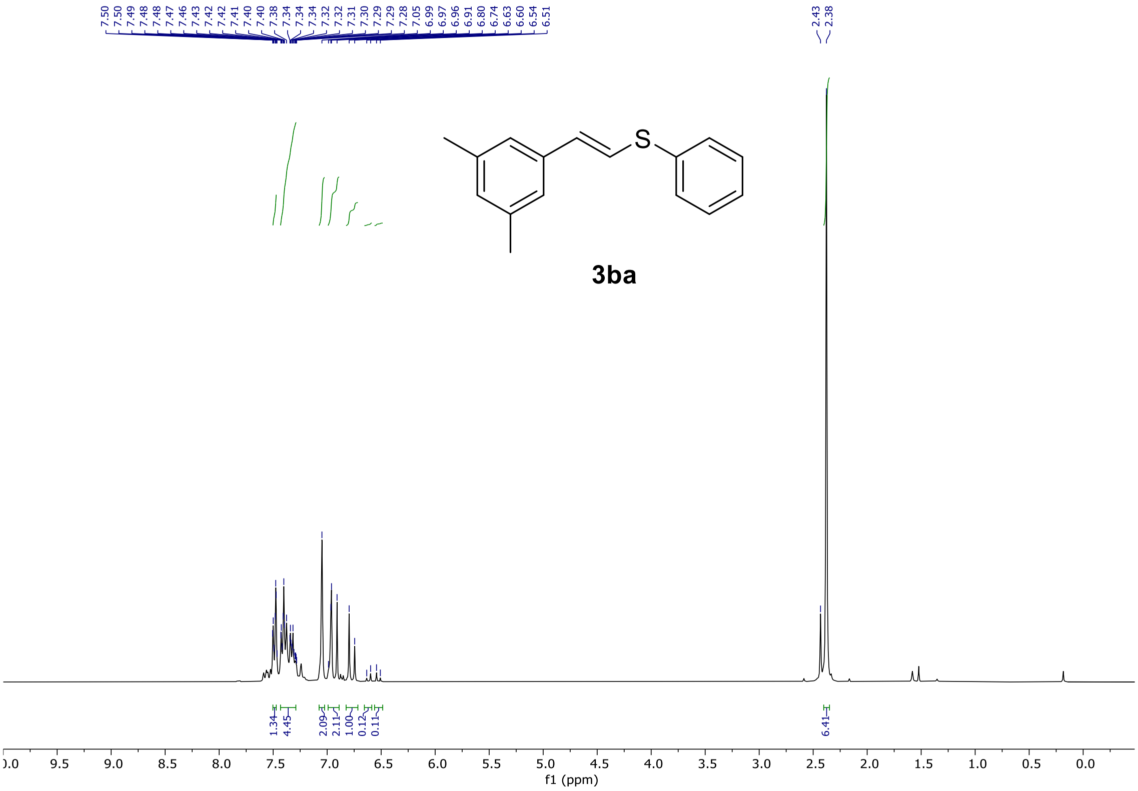
9. Copies of the NMR spectra

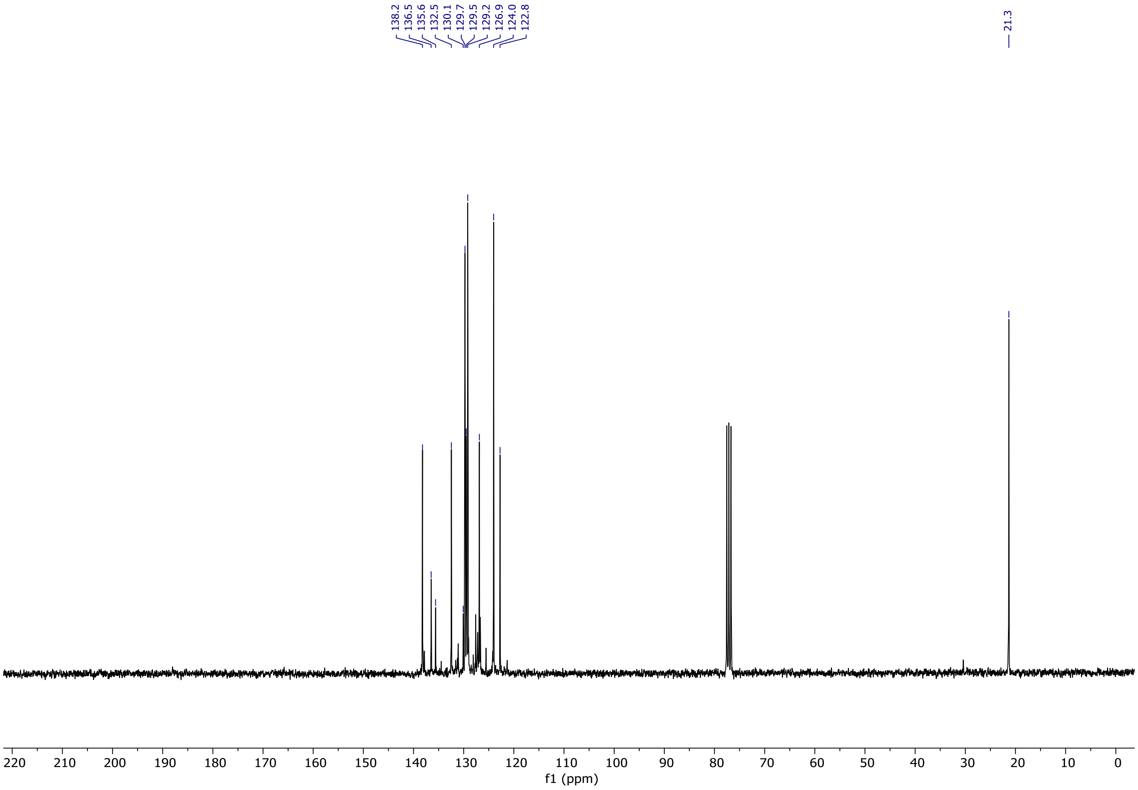
(*E*)-Phenyl(styryl)sulfane (3aa)



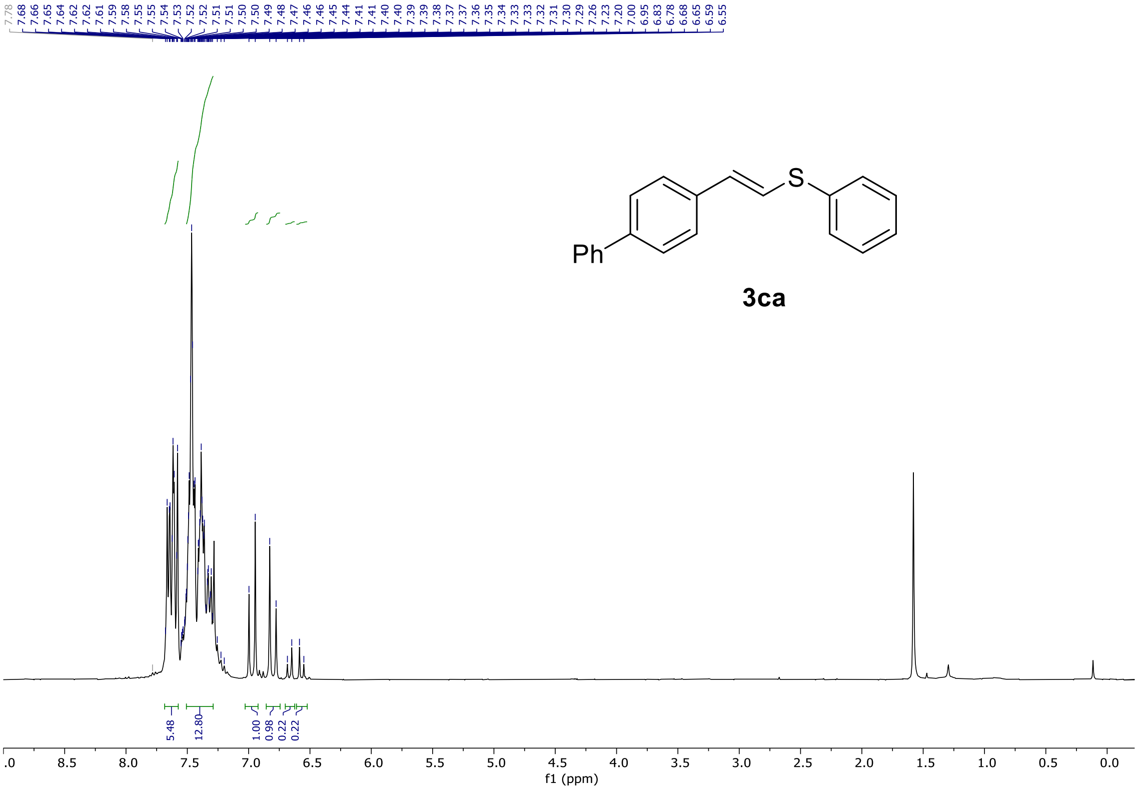


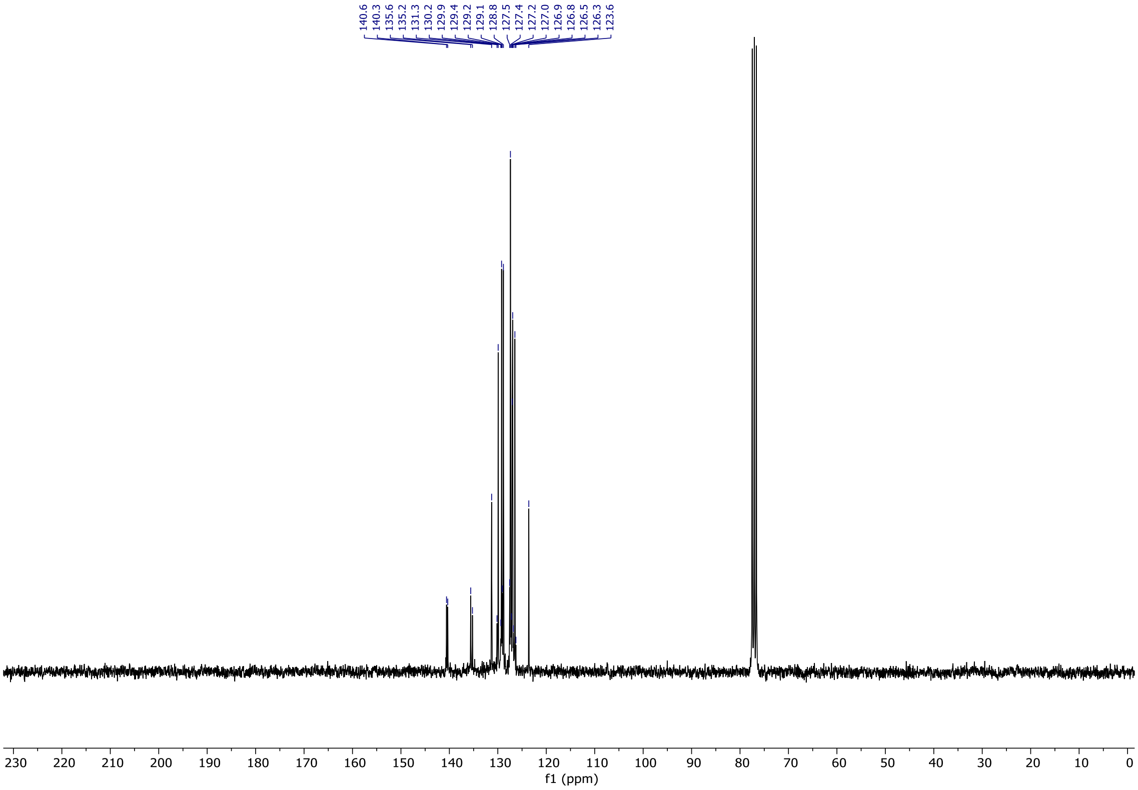
(*E*)-(3,5-Dimethylstyryl)(phenyl)sulfane (3ba)



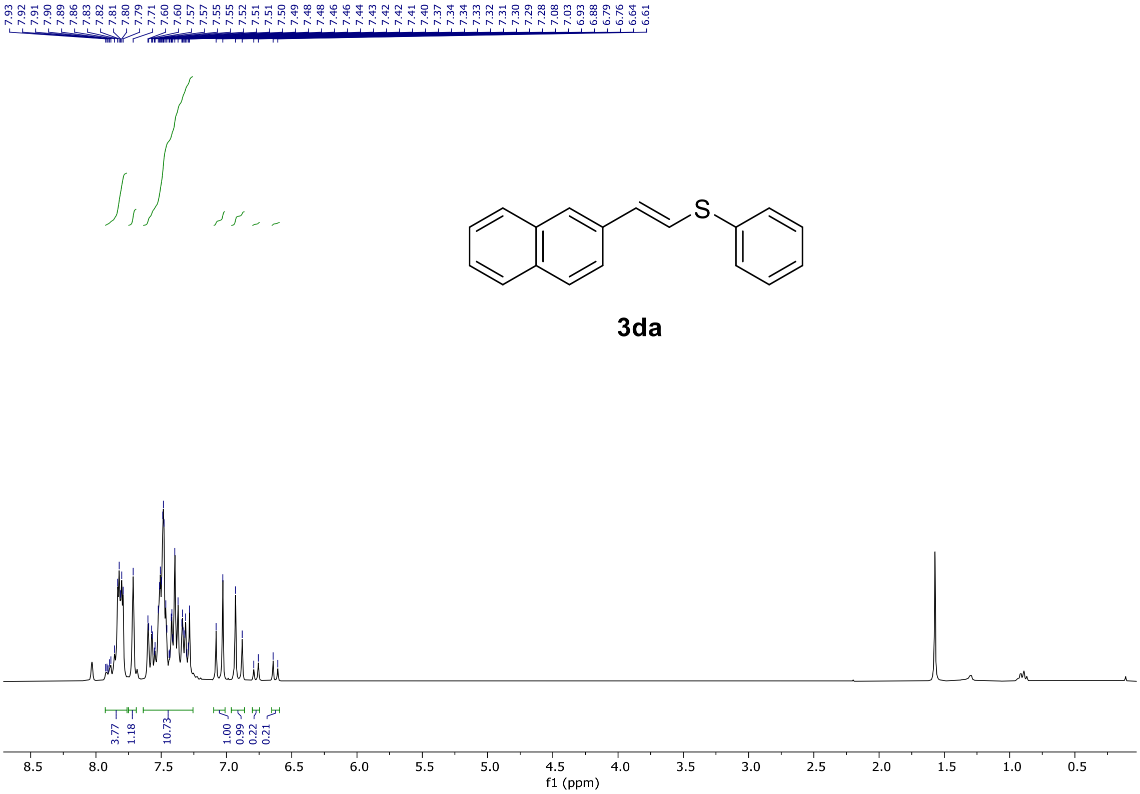


(*E*)-(2-([1,1'-Biphenyl]-4-yl)vinyl)(phenyl)sulfane (3ca)

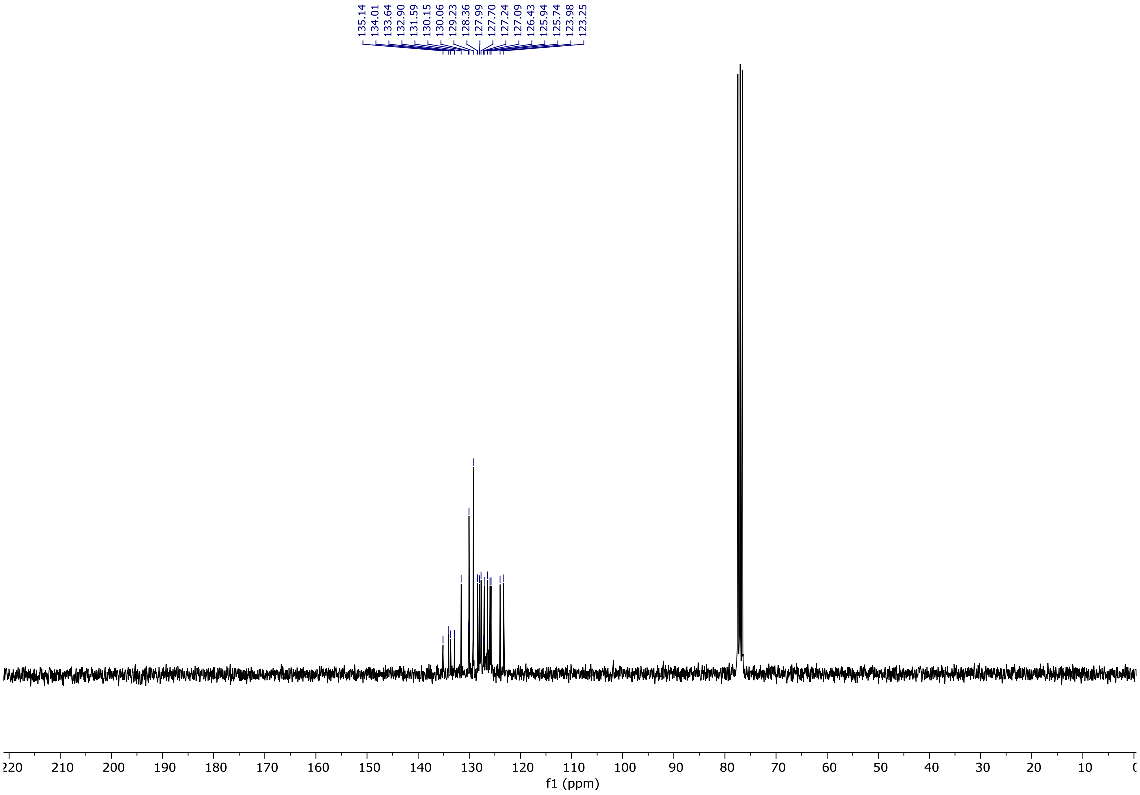




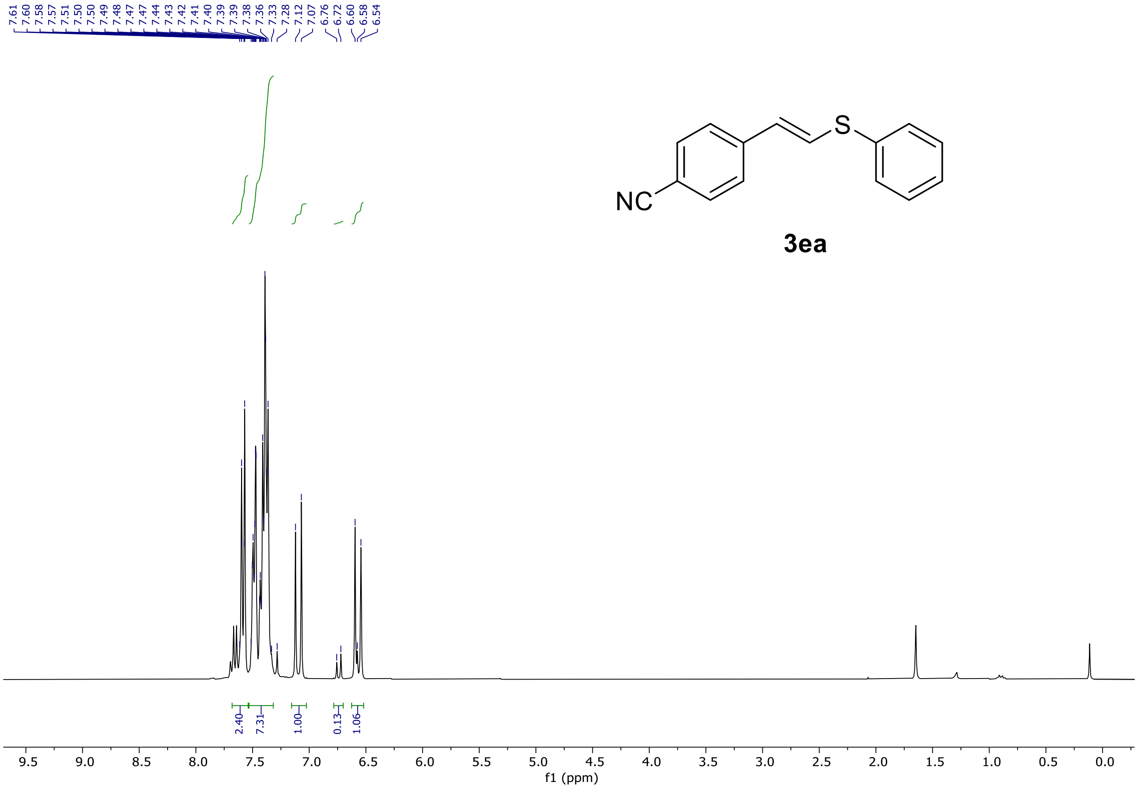
(*E*)-(2-(naphthalen-2-yl)vinyl)(phenyl)sulfane (3da)



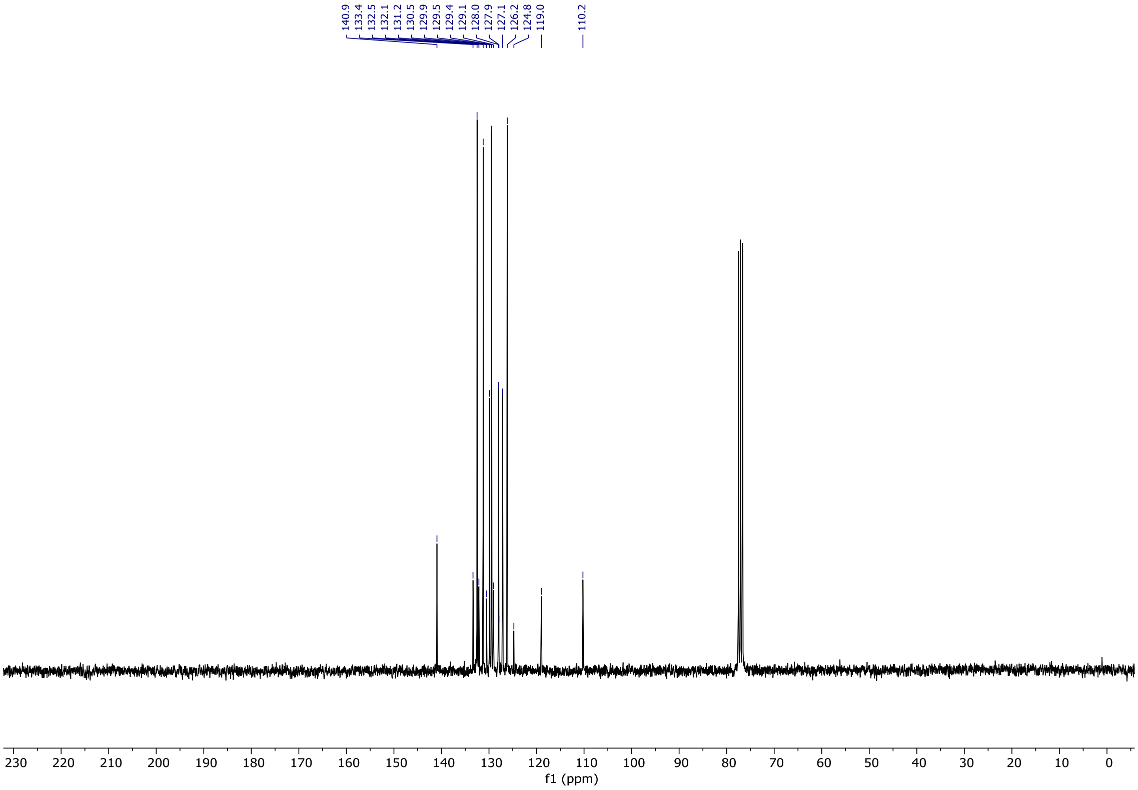
3da



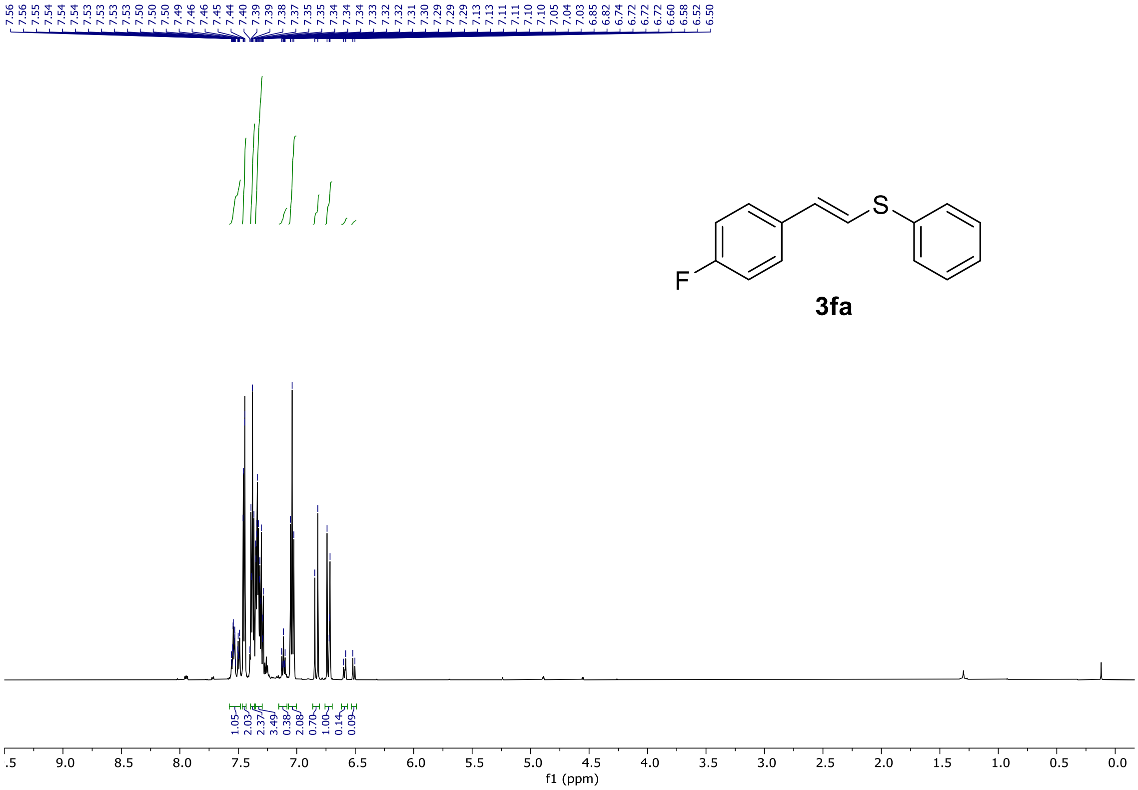
(*E*)-4-(2-(Phenylthio)vinyl)benzonitrile (3ea)



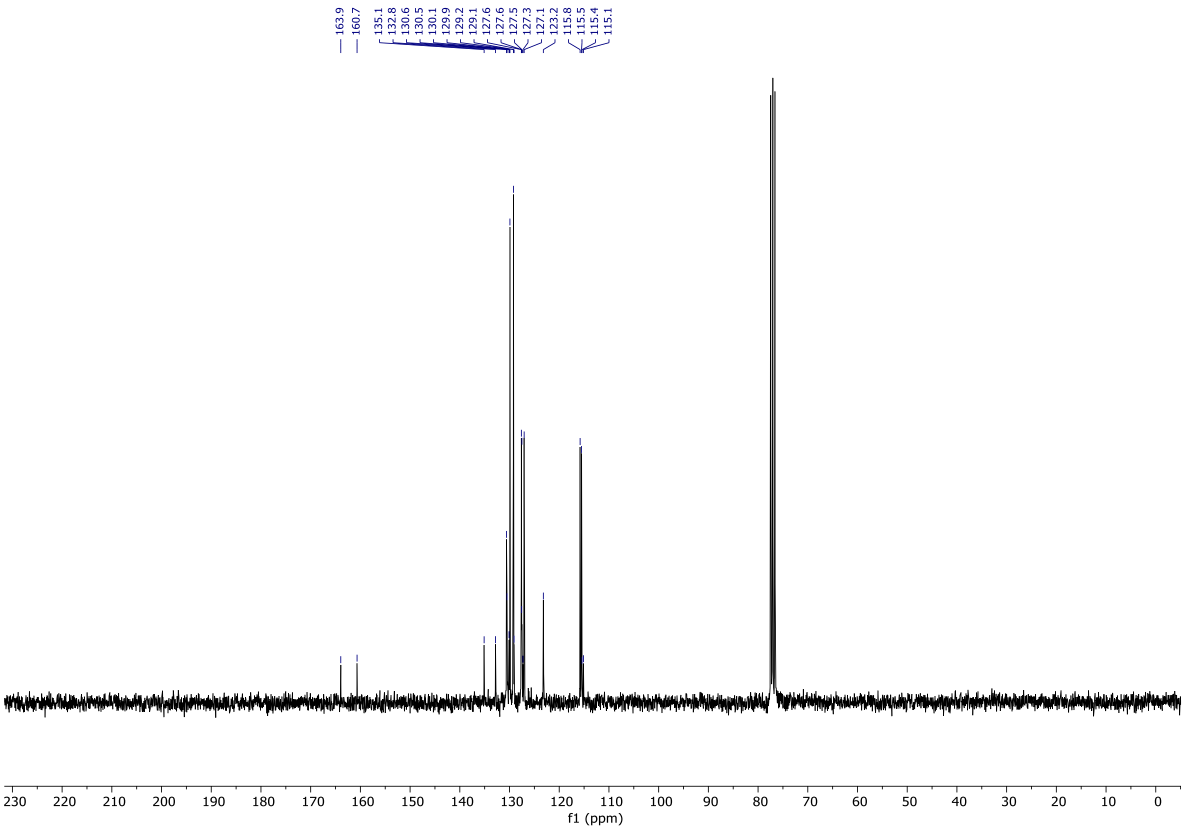
3ea

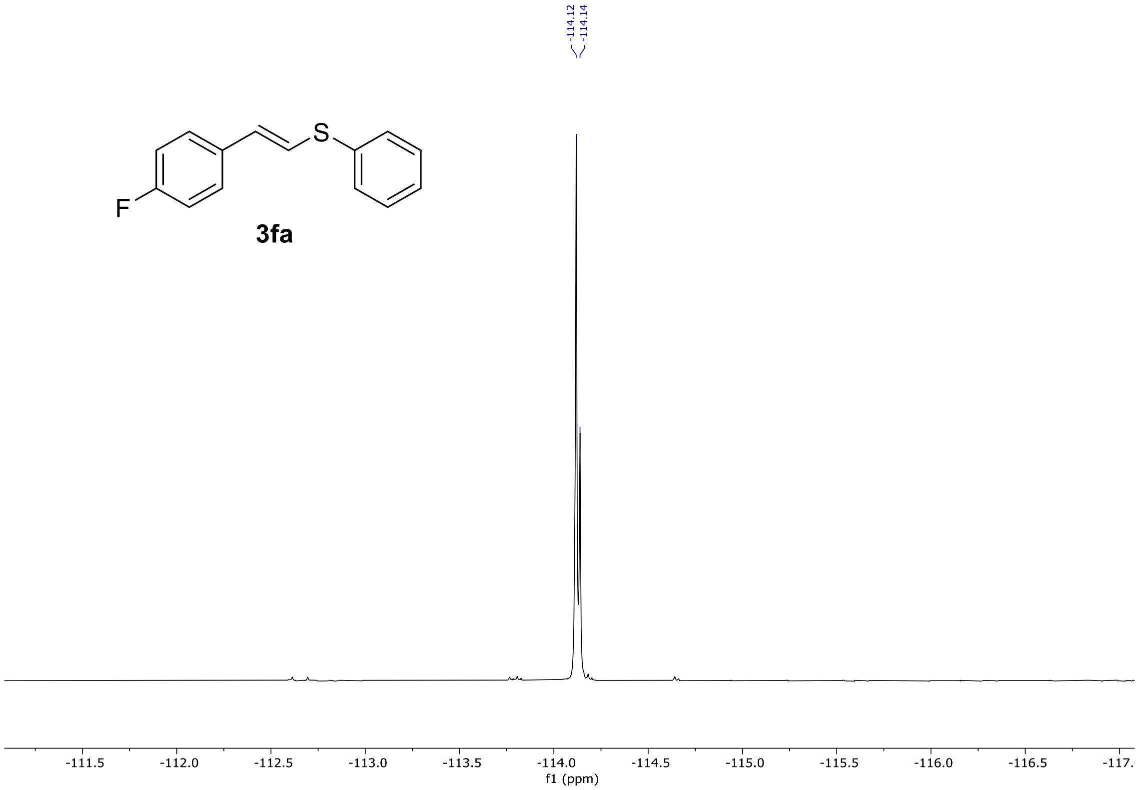


(*E*)-(4-Fluorostyryl)(phenyl)sulfane (3fa)



3fa

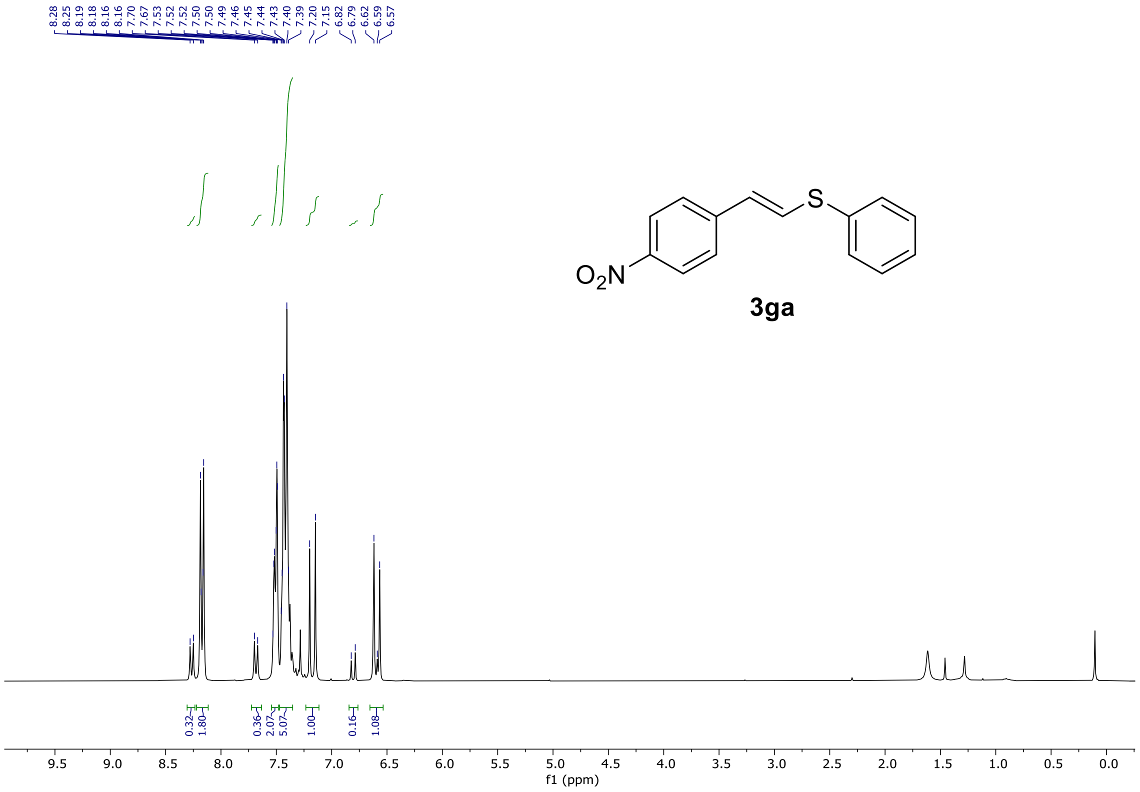


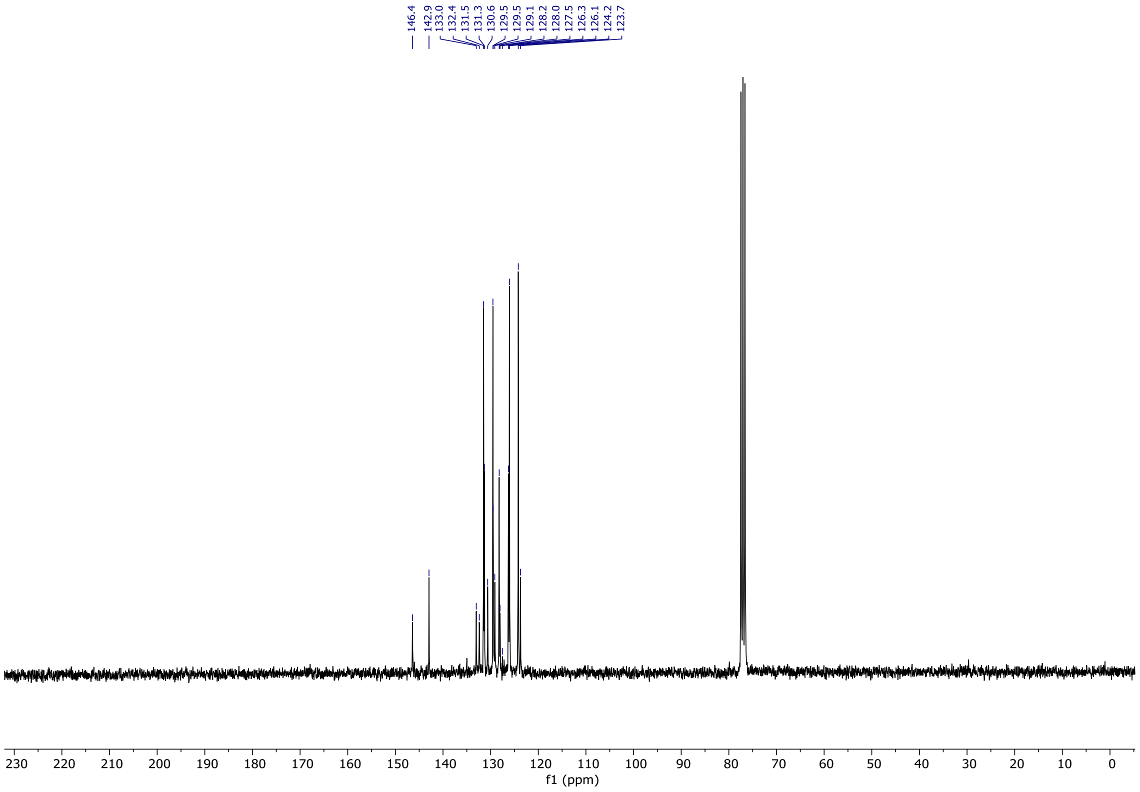


3fa

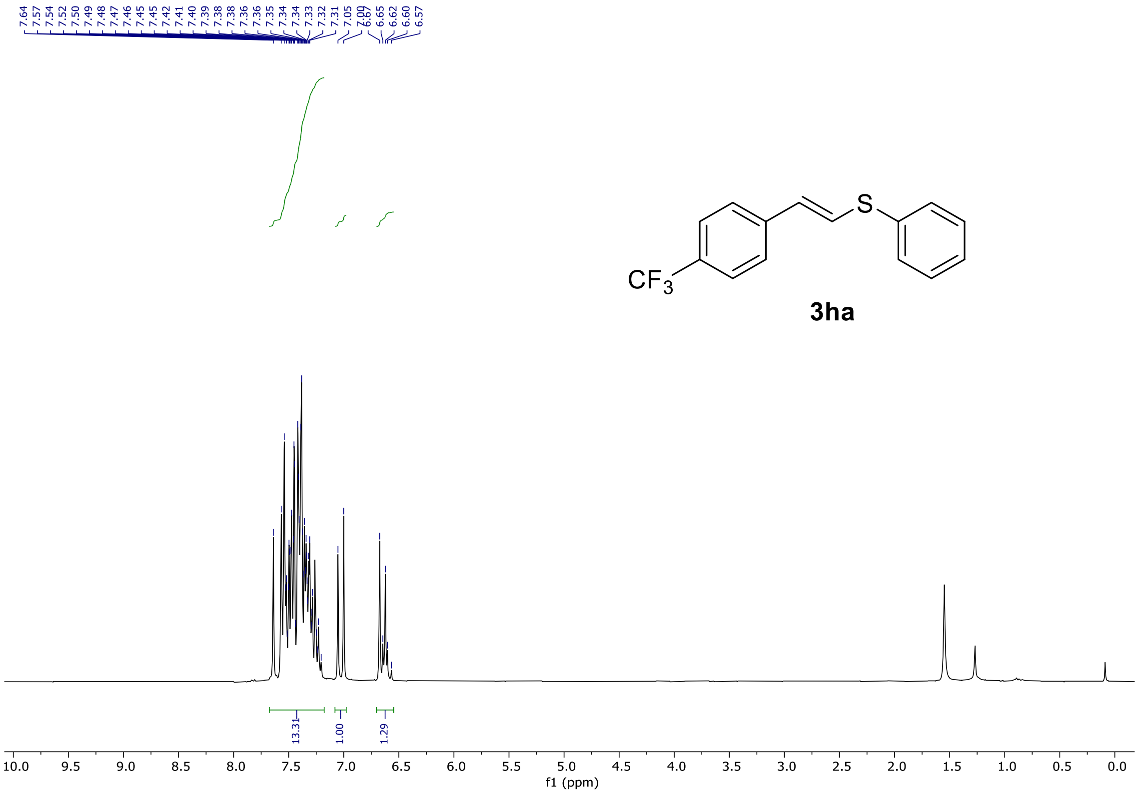
-114.12
-114.14
F
S
-111.5
-112.0
-112.5
-113.0
-113.5
-114.0
-114.5
-115.0
-115.5
-116.0
-116.5
f1 (ppm)

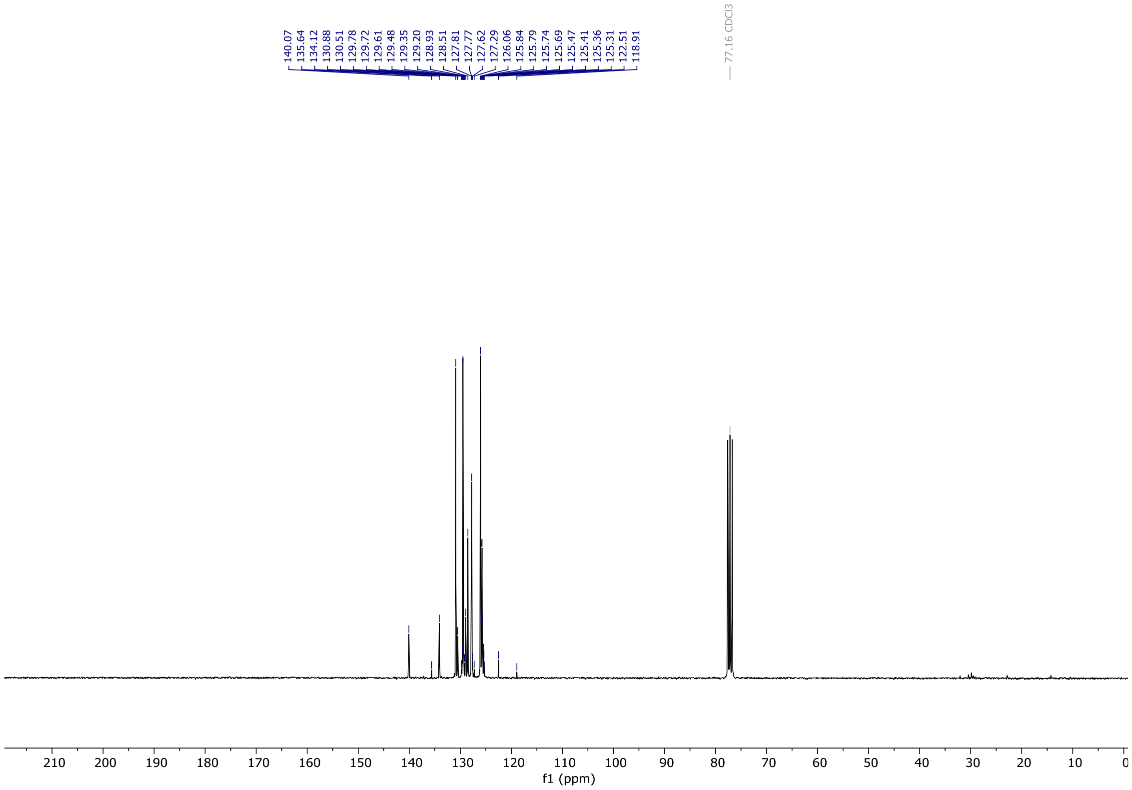
(*E*)-(4-Nitrostyryl)(phenyl)sulfane (3ga)

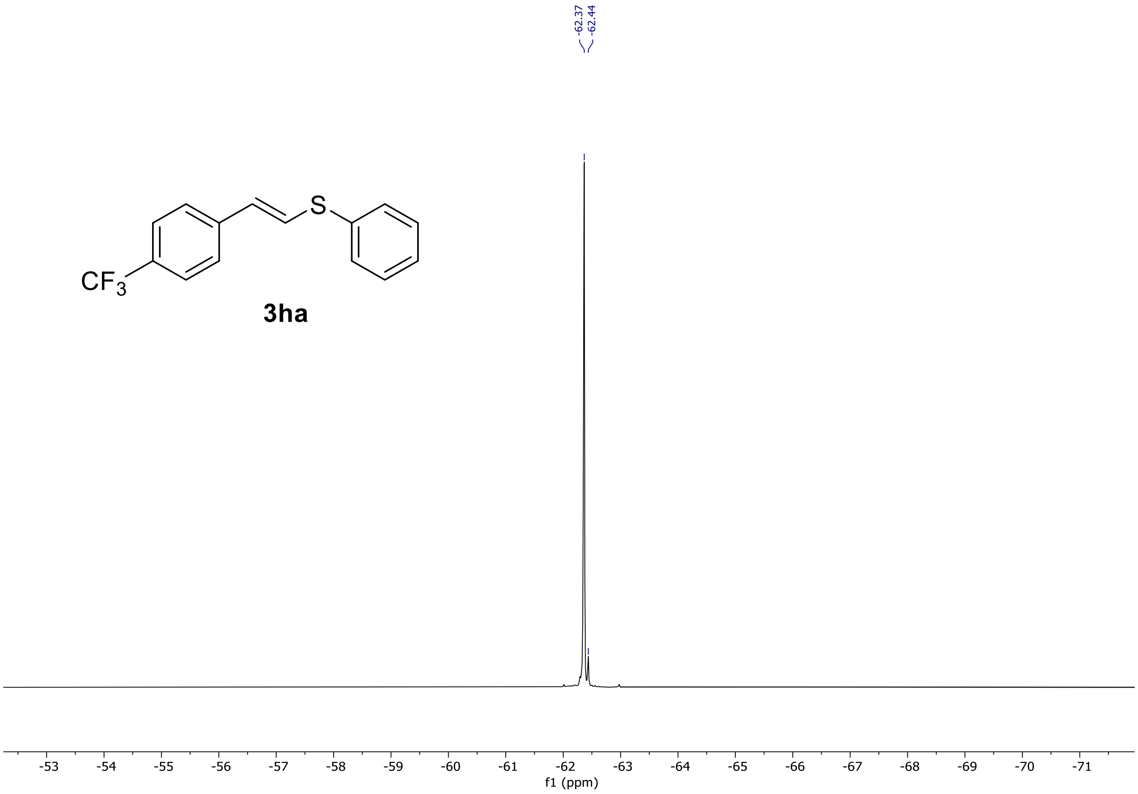




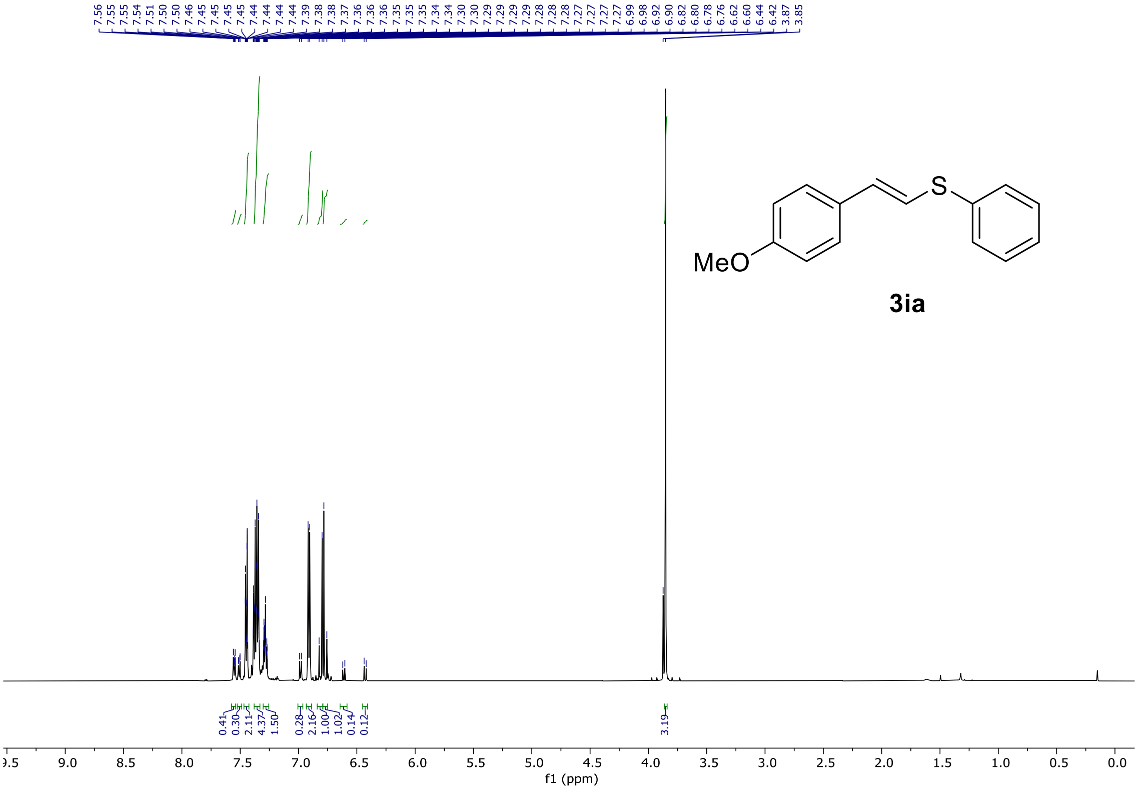
(*E*)-Phenyl(4-(trifluoromethyl)styryl)sulfane (3ha)



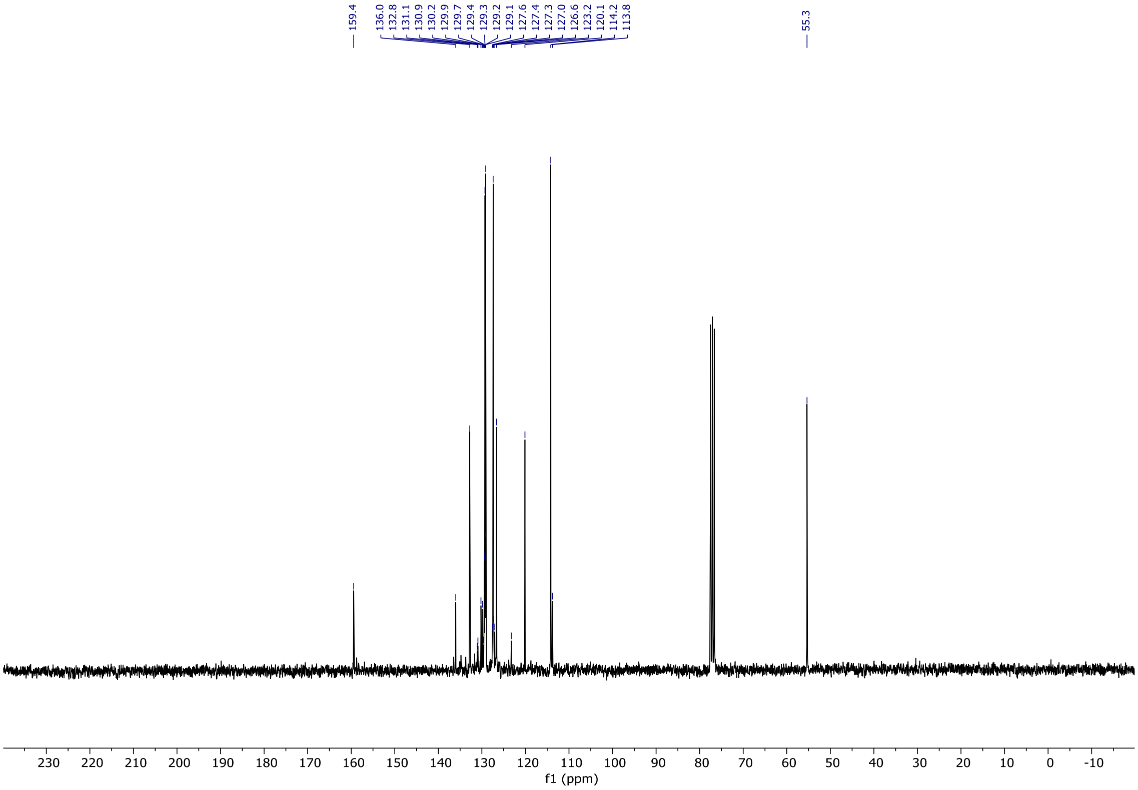



-62.37
-62.44
CF3
S
3ha
-53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
f1 (ppm)

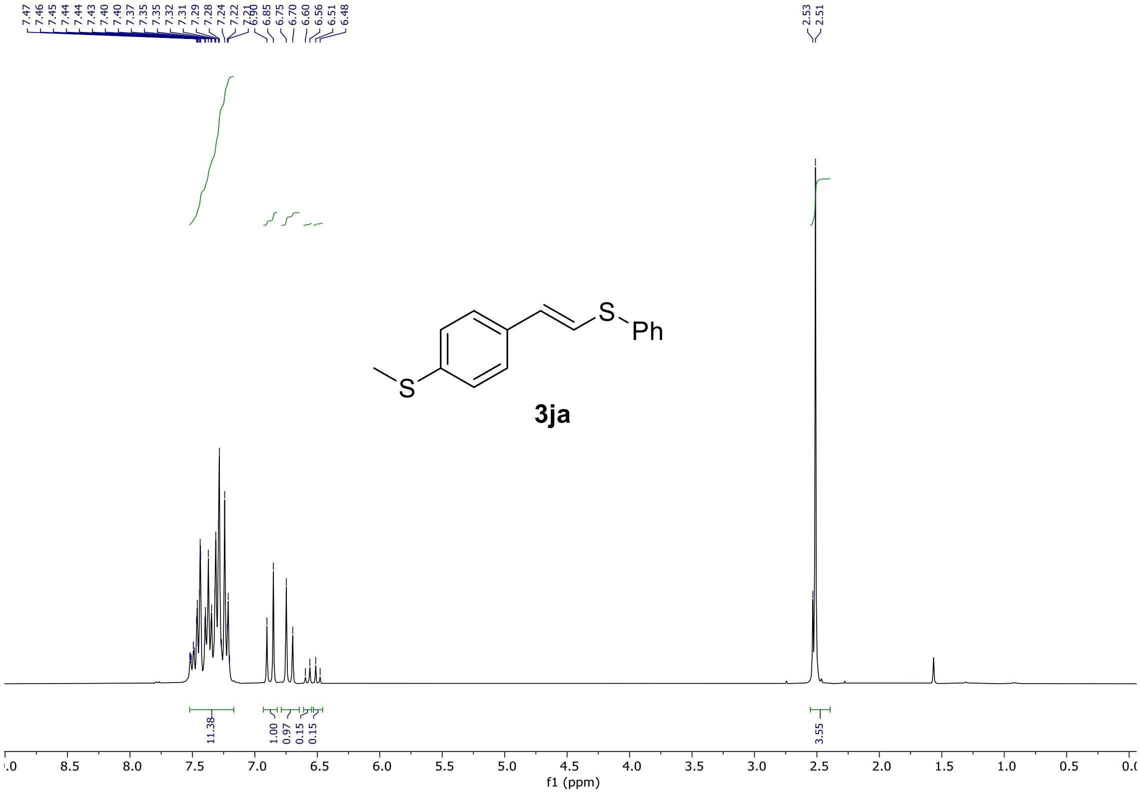
(*E*)-(4-Methoxystyryl)(phenyl)sulfane (3ia)

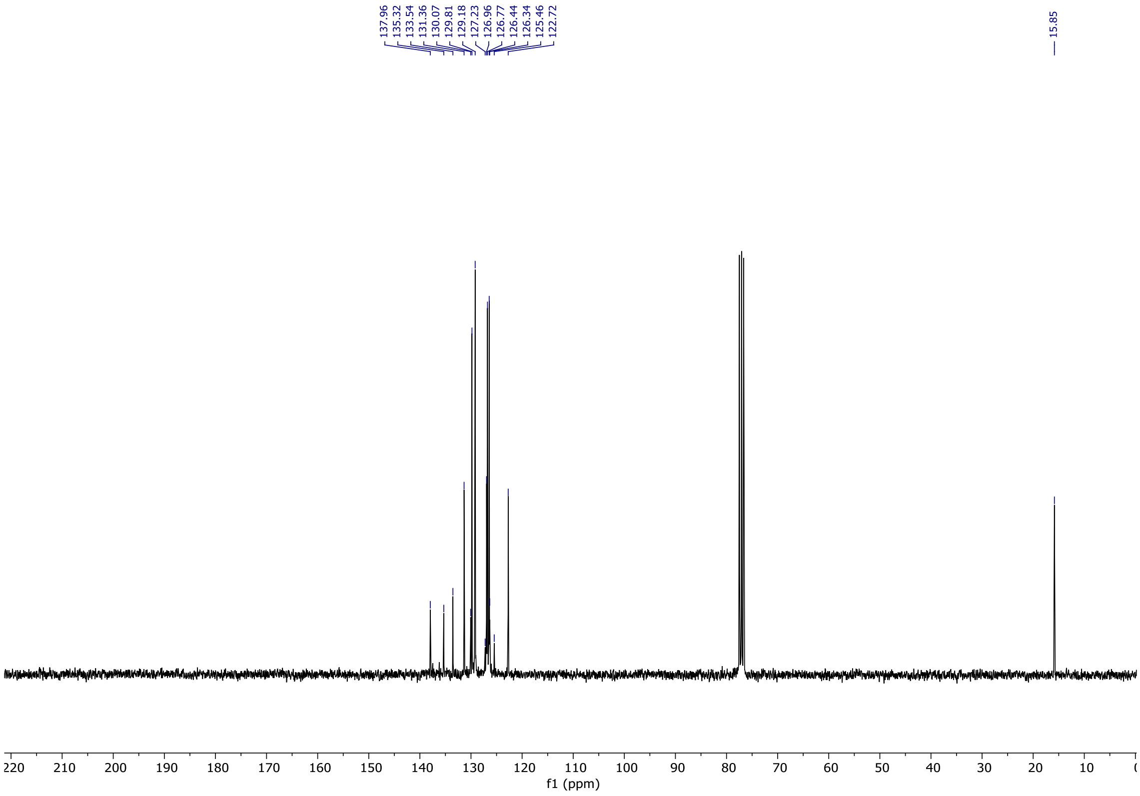


3ia

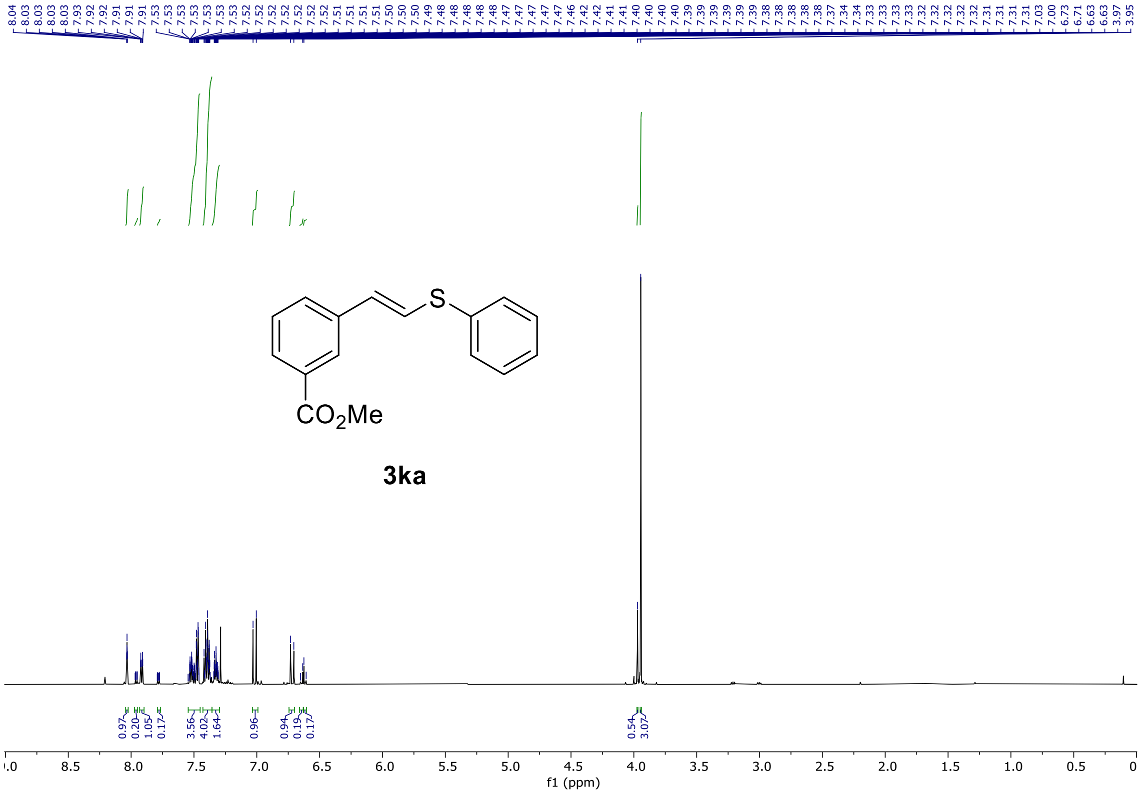


(*E*)-methyl(4-(2-(phenylthio)vinyl)phenyl)sulfane (3ja)

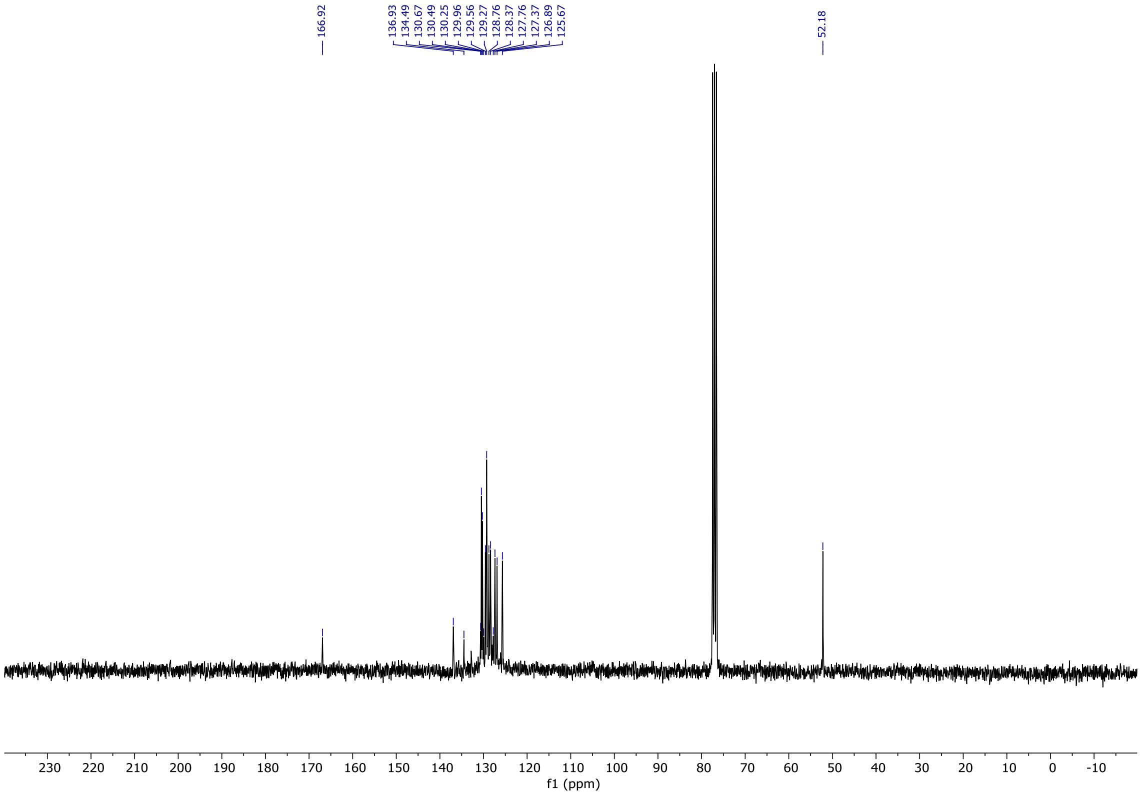




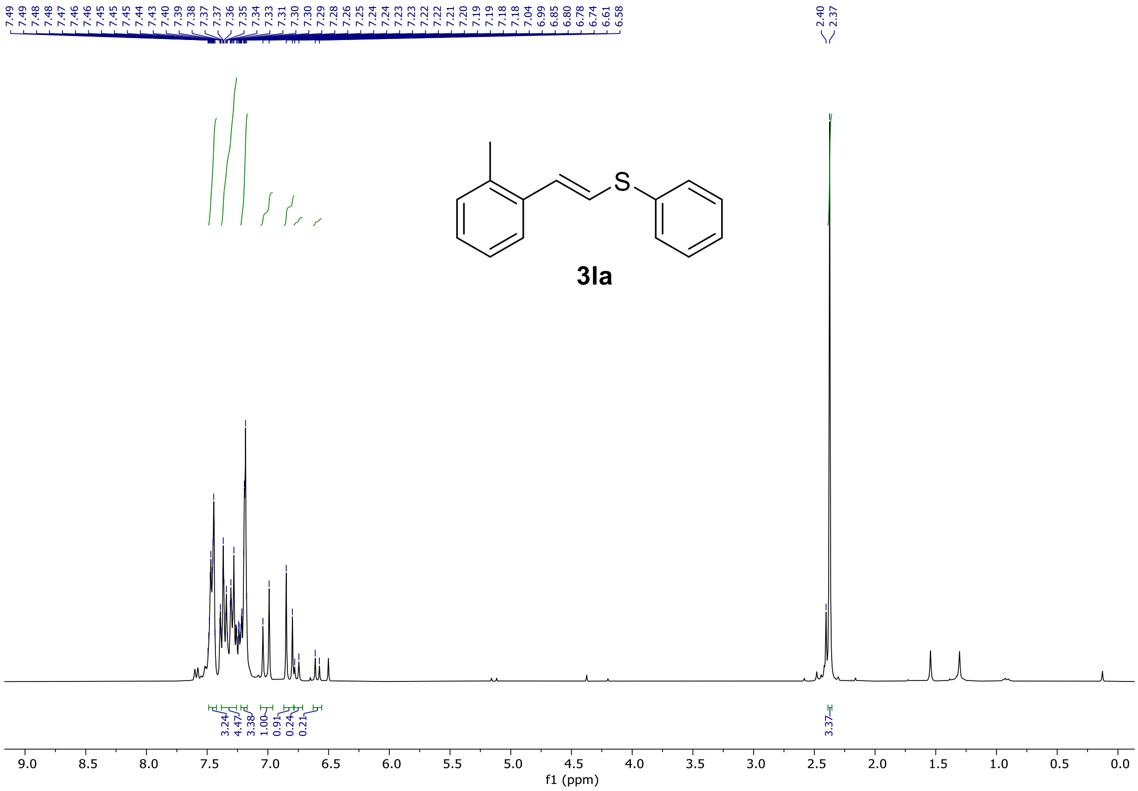
Methyl (*E*)-3-(2-(phenylthio)vinyl)benzoate (3ka)

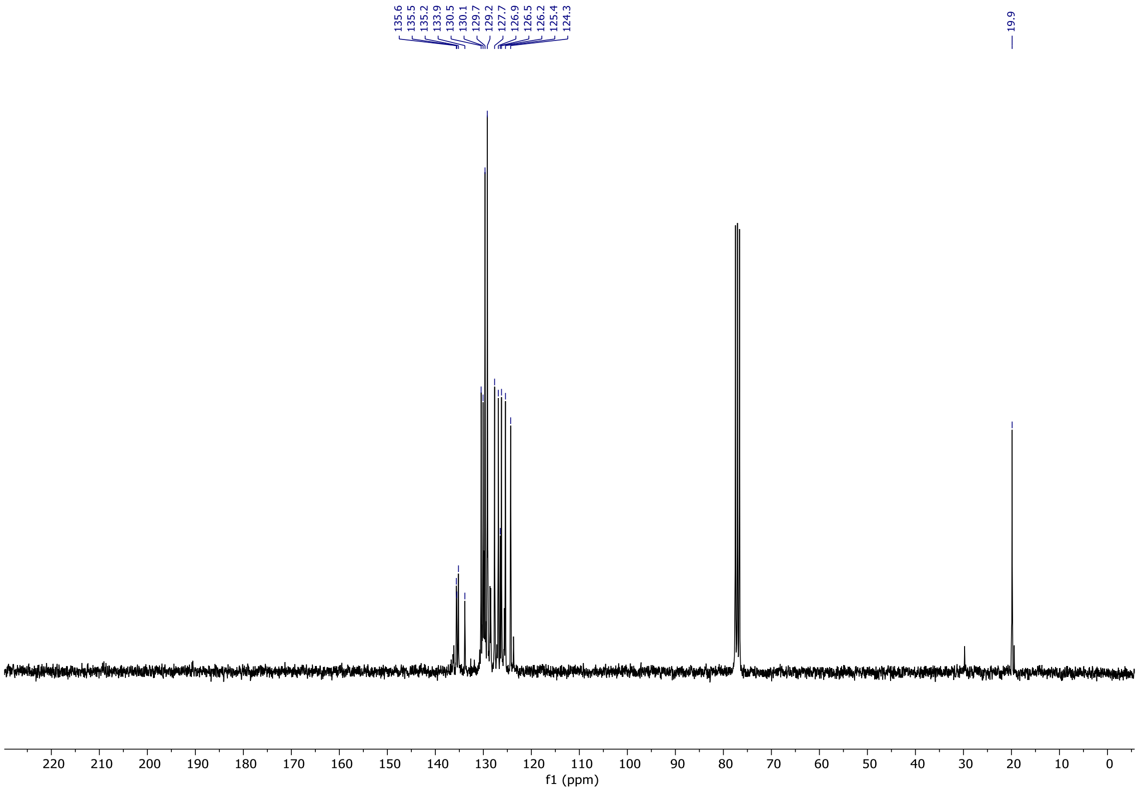


3ka



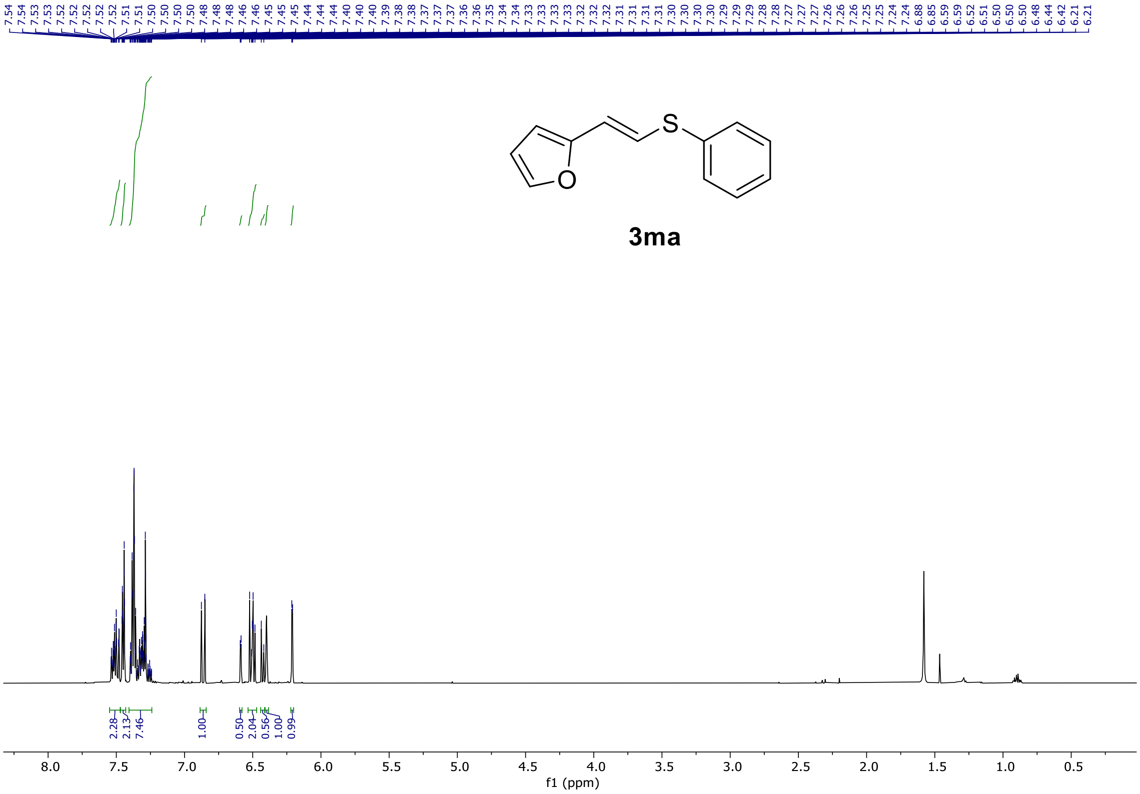
(*E*)-(2-Methylstyryl)(phenyl)sulfane (3la)

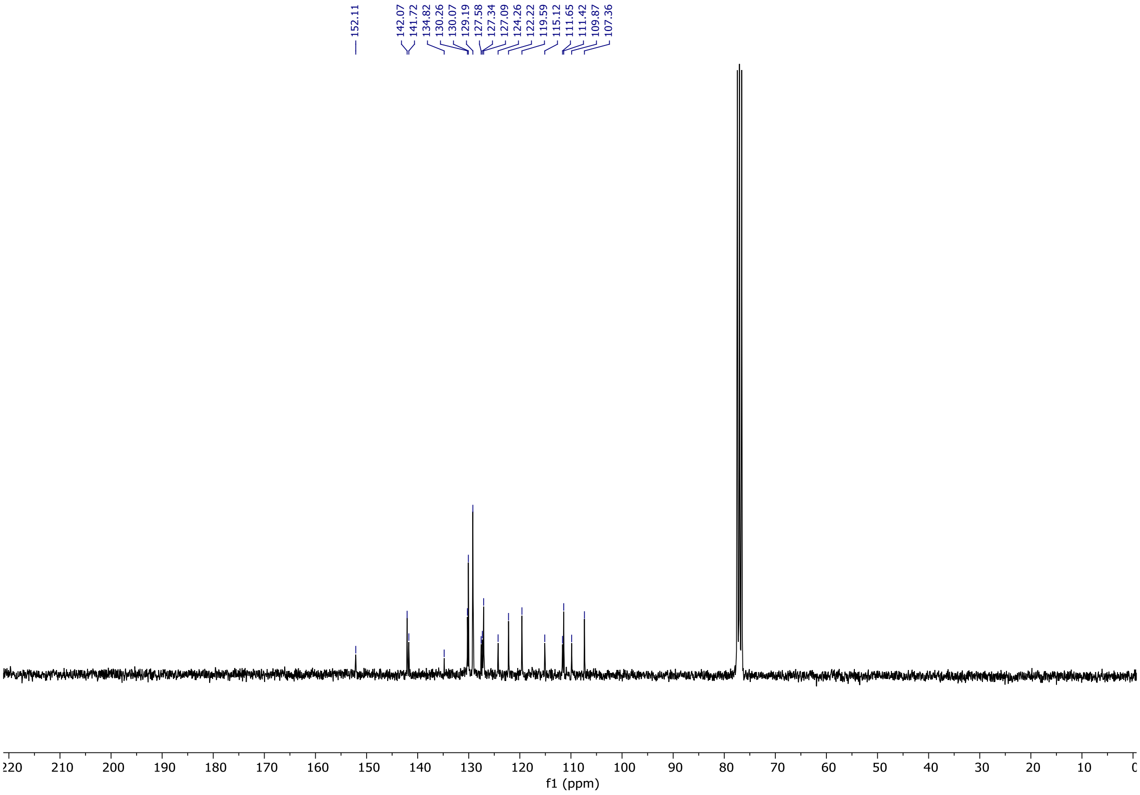




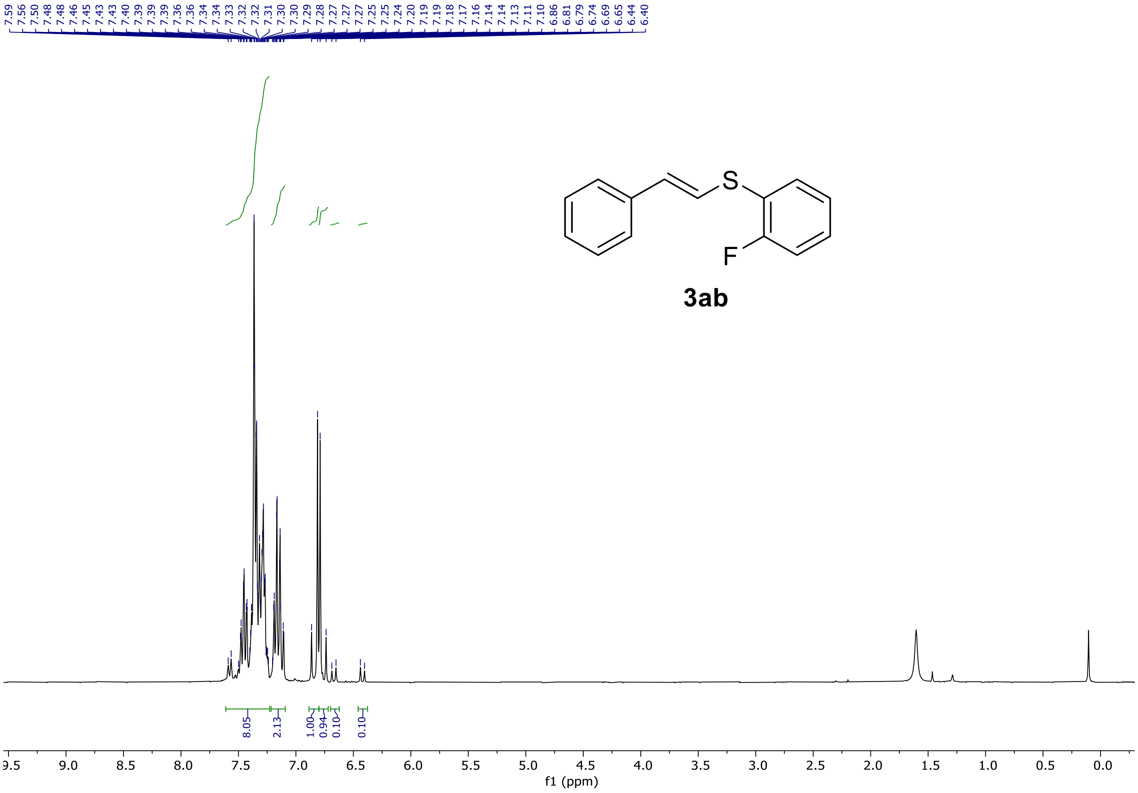
(*E*)-2-(2-(phenylthio)vinyl)furan (3ma)

3ma

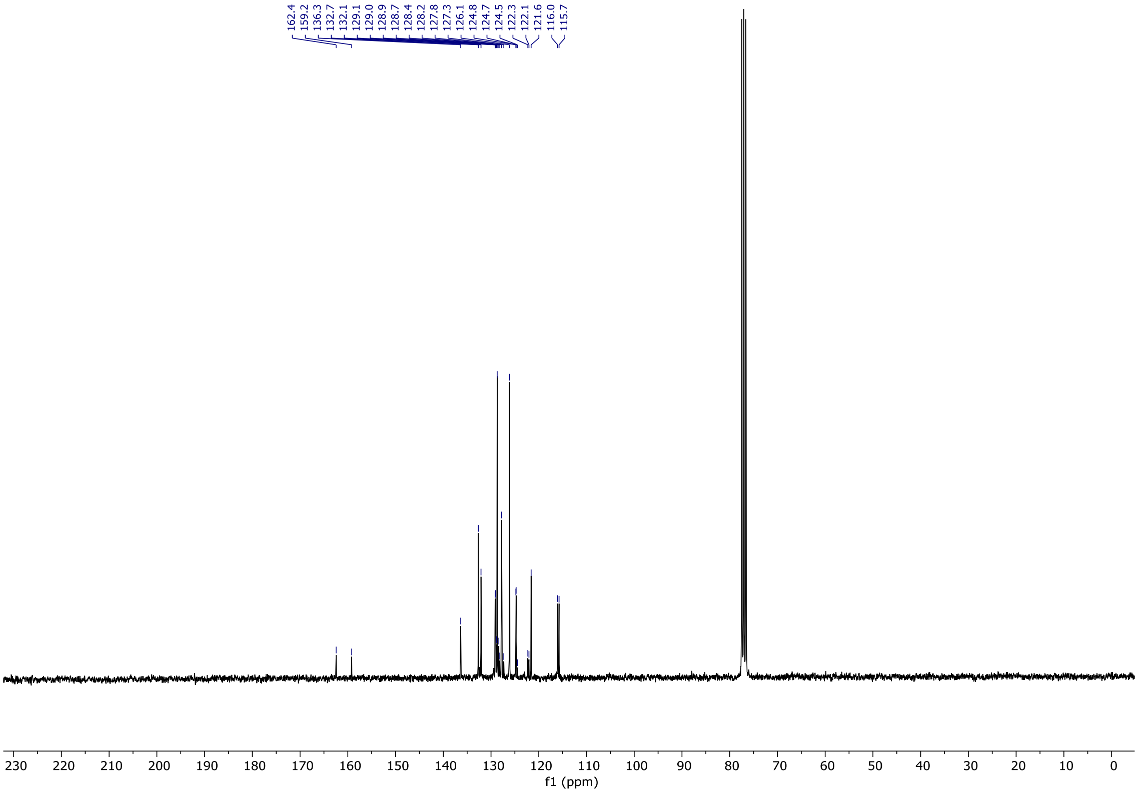


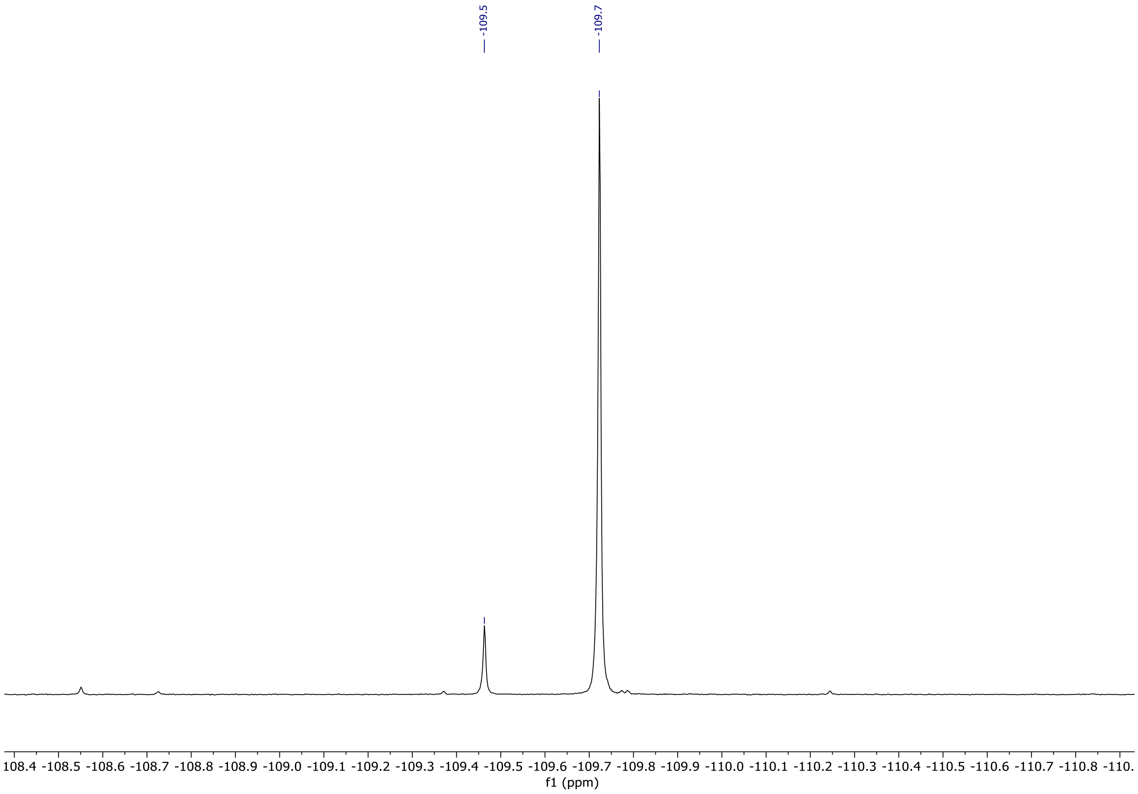


(*E*)-(2-fluorophenyl)(styryl)sulfane (3ab)



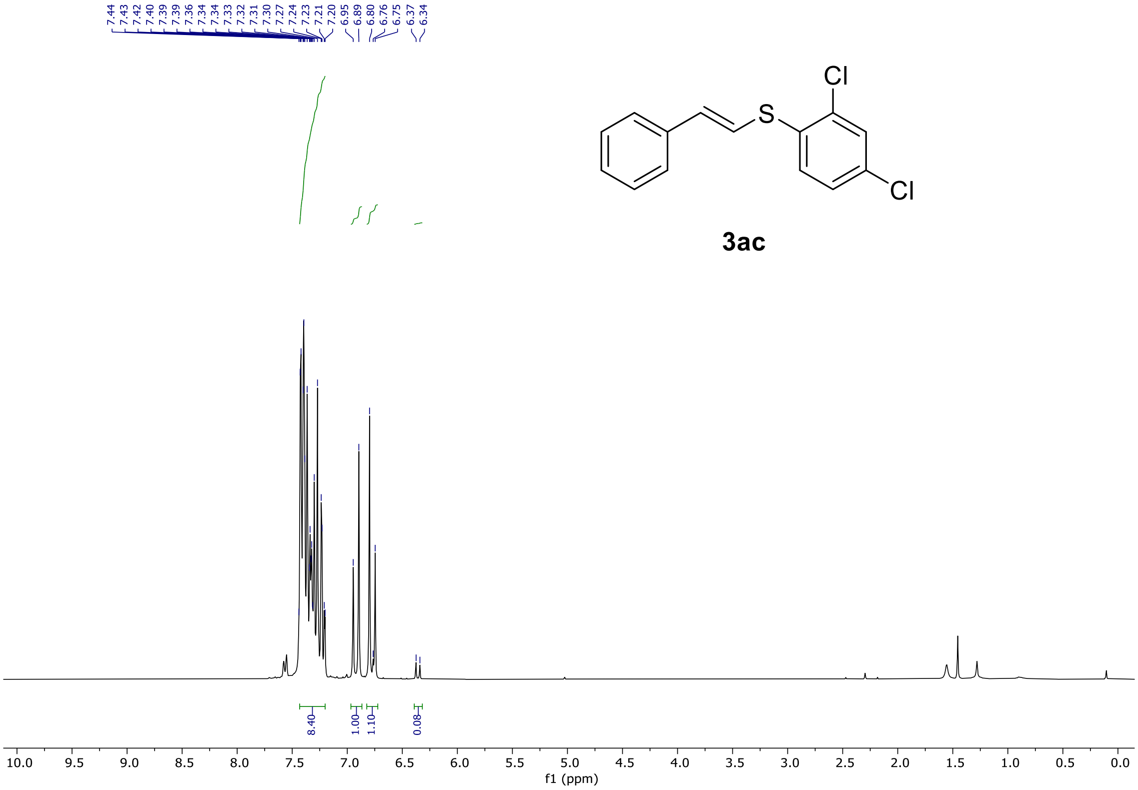
3ab

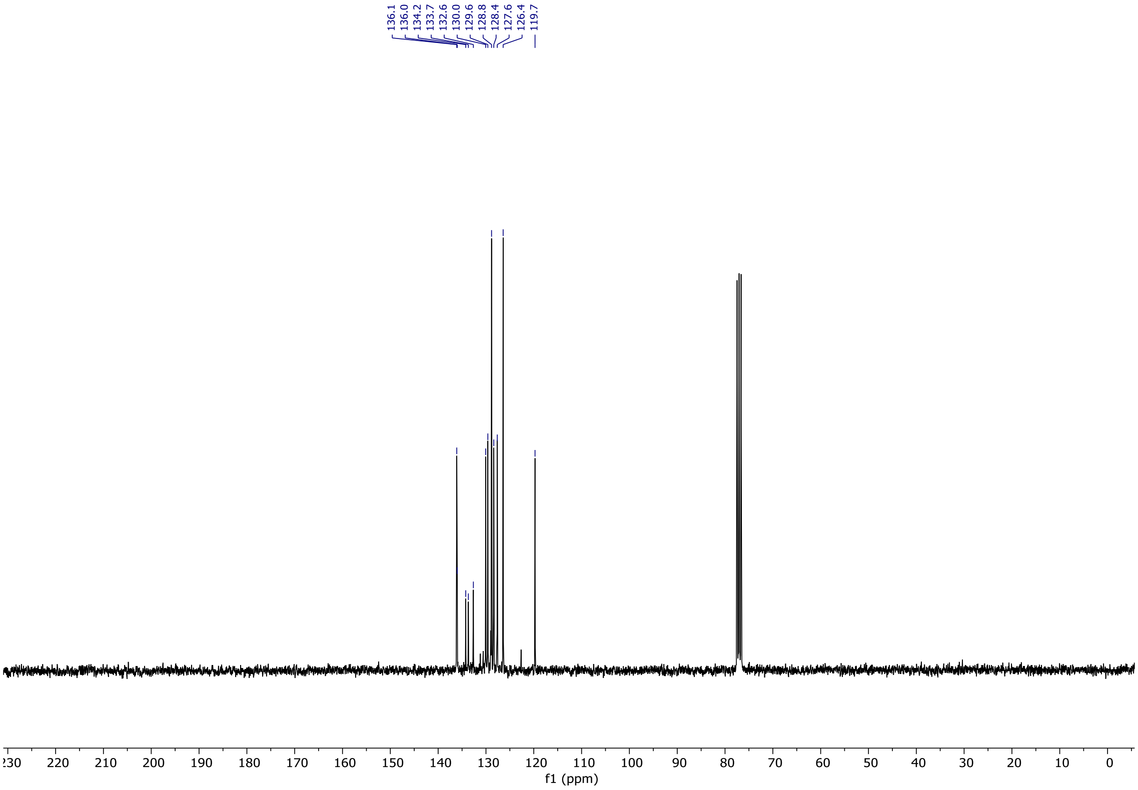



-109.5
-109.7
108.4 -108.5 -108.6 -108.7 -108.8 -108.9 -109.0 -109.1 -109.2 -109.3 -109.4 -109.5 -109.6 -109.7 -109.8 -109.9 -110.0 -110.1 -110.2 -110.3 -110.4 -110.5 -110.6 -110.7 -110.8 -110.
f1 (ppm)

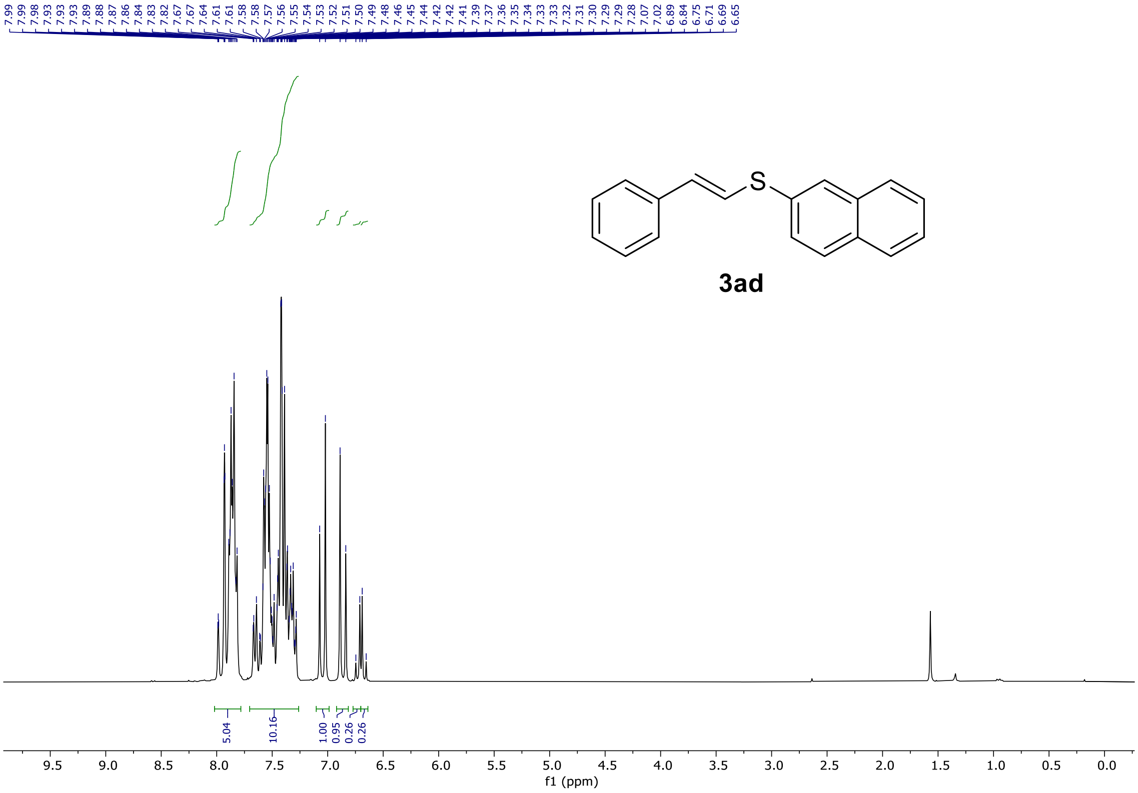
(*E*)-(2,4-Dichlorophenyl)(styryl)sulfane (3ac)

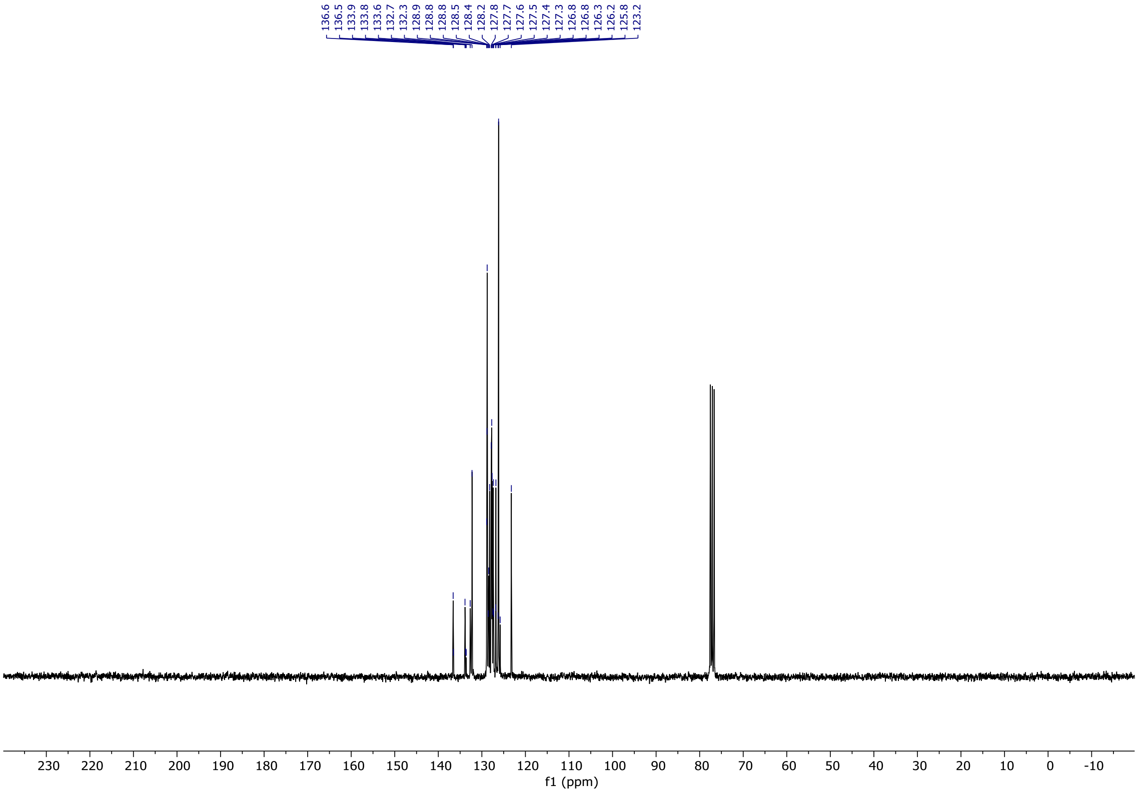
3ac



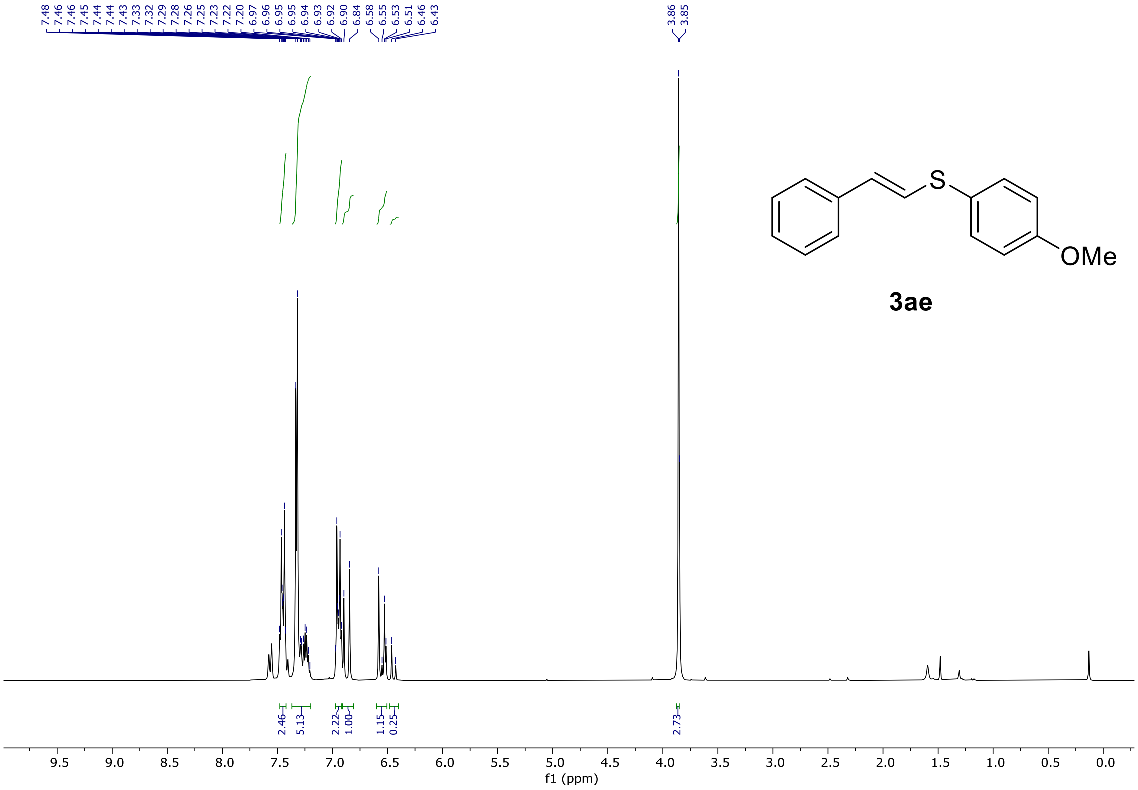


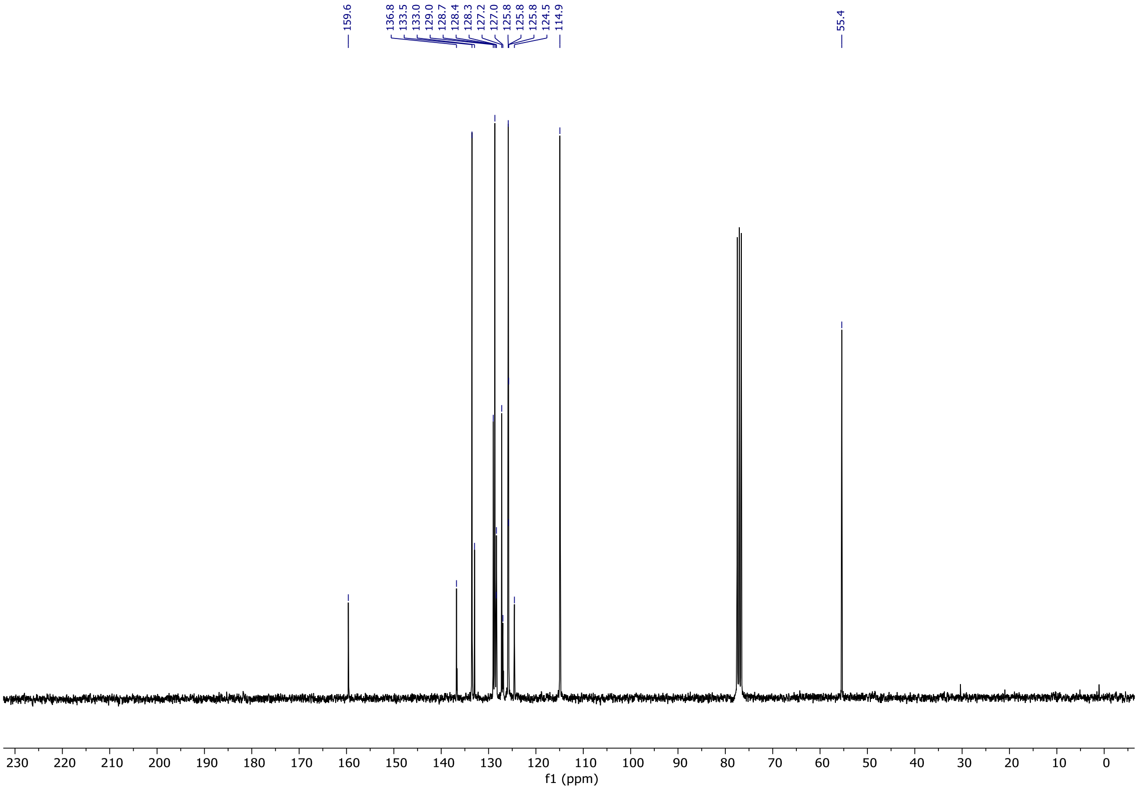
(*E*)-(4-Methoxyphenyl)(styryl)sulfane (3ad)



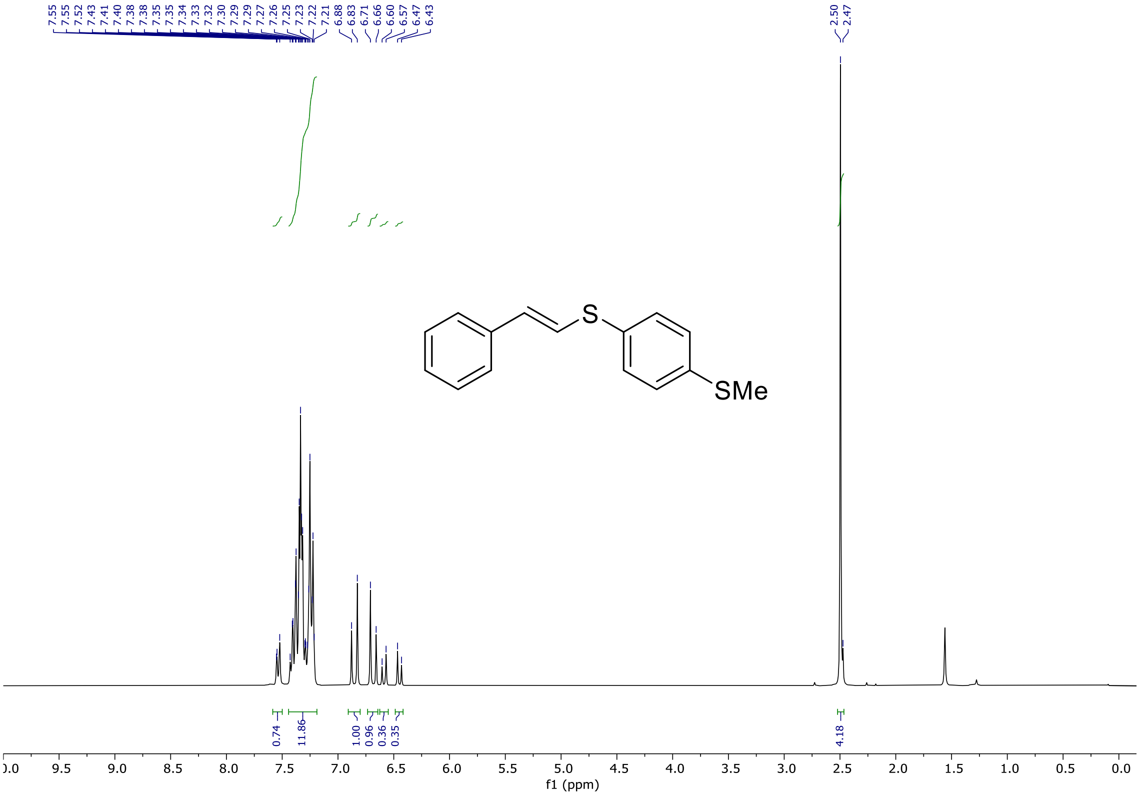


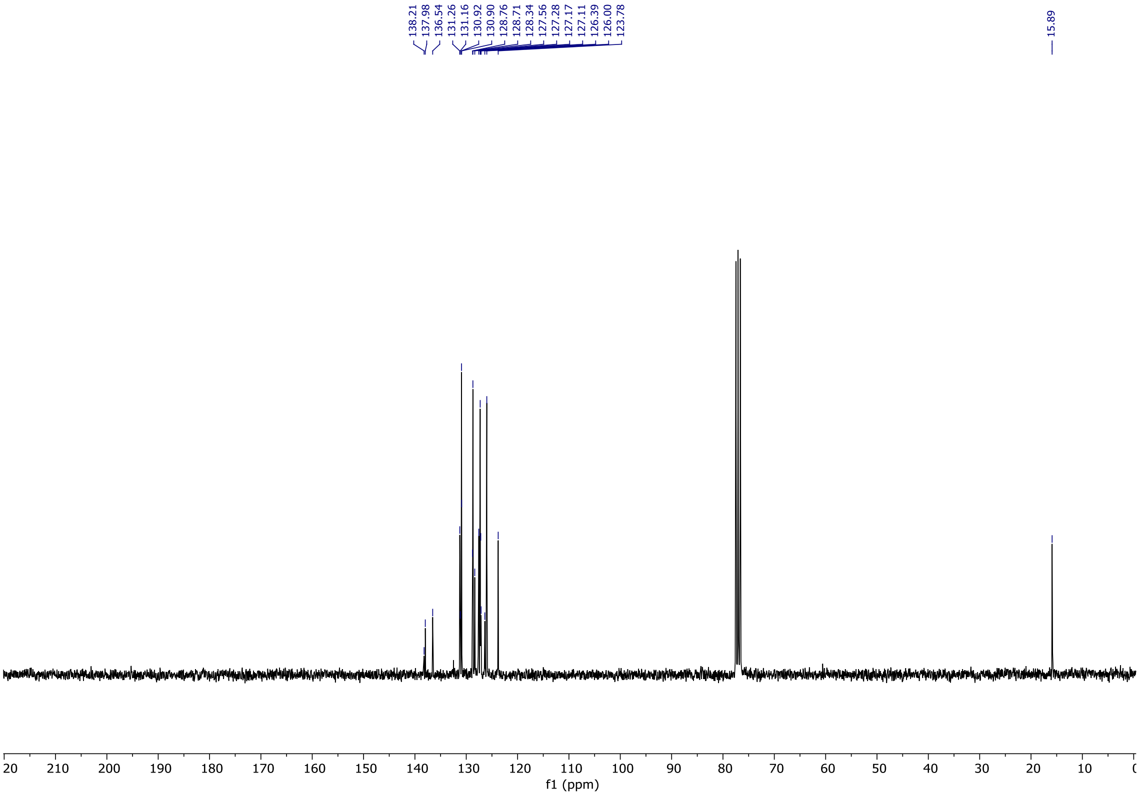
(*E*)-(4-Methoxyphenyl)(styryl)sulfane (3ae)



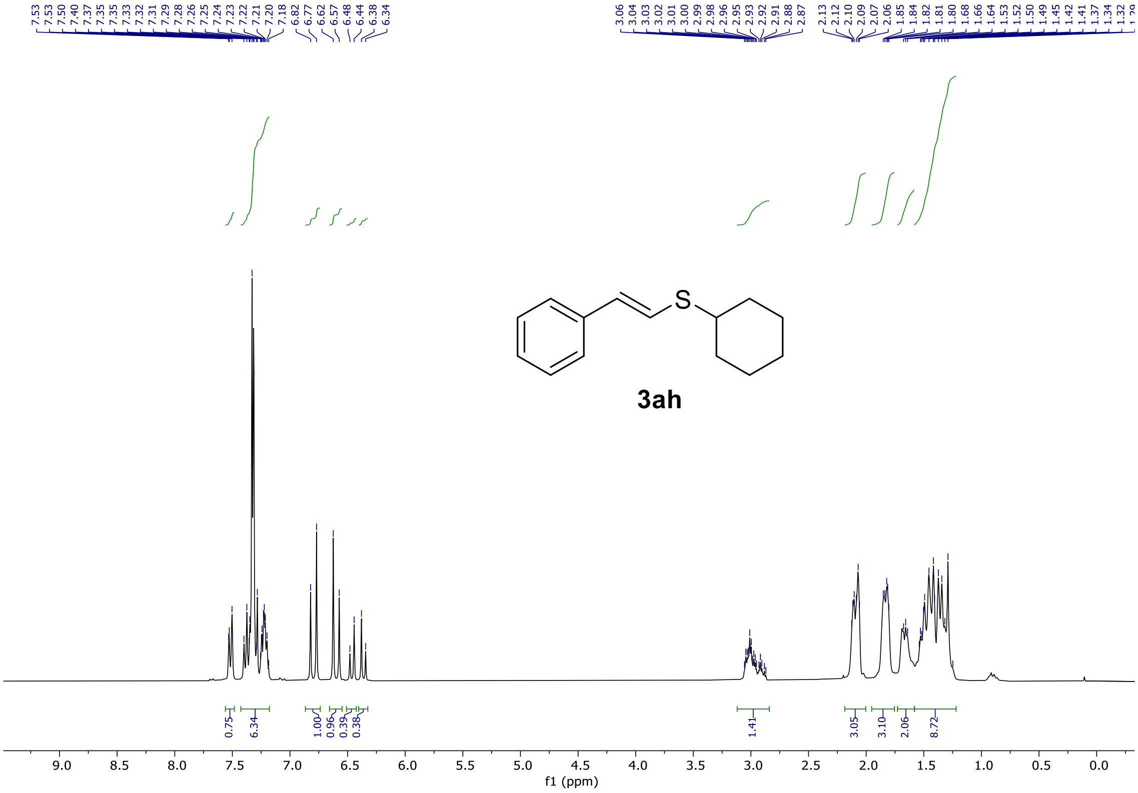


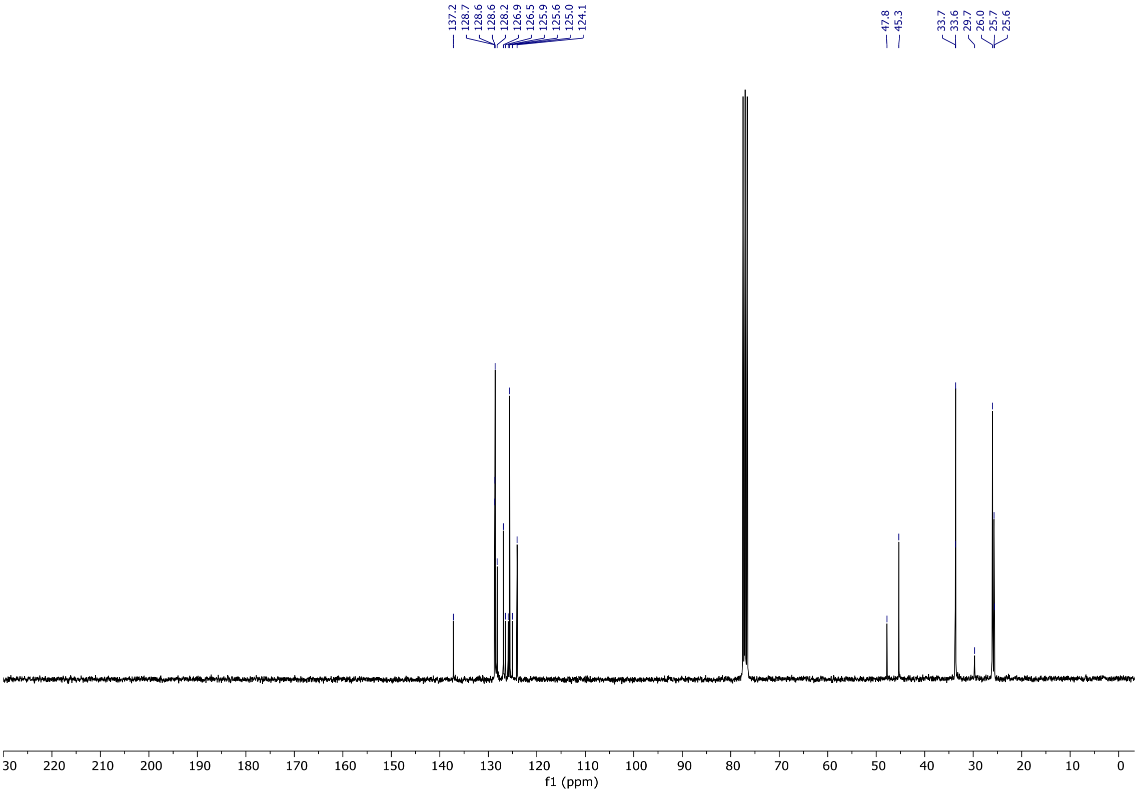
(*E*)-Methyl(4-(styrylthio)phenyl)sulfane (3af)



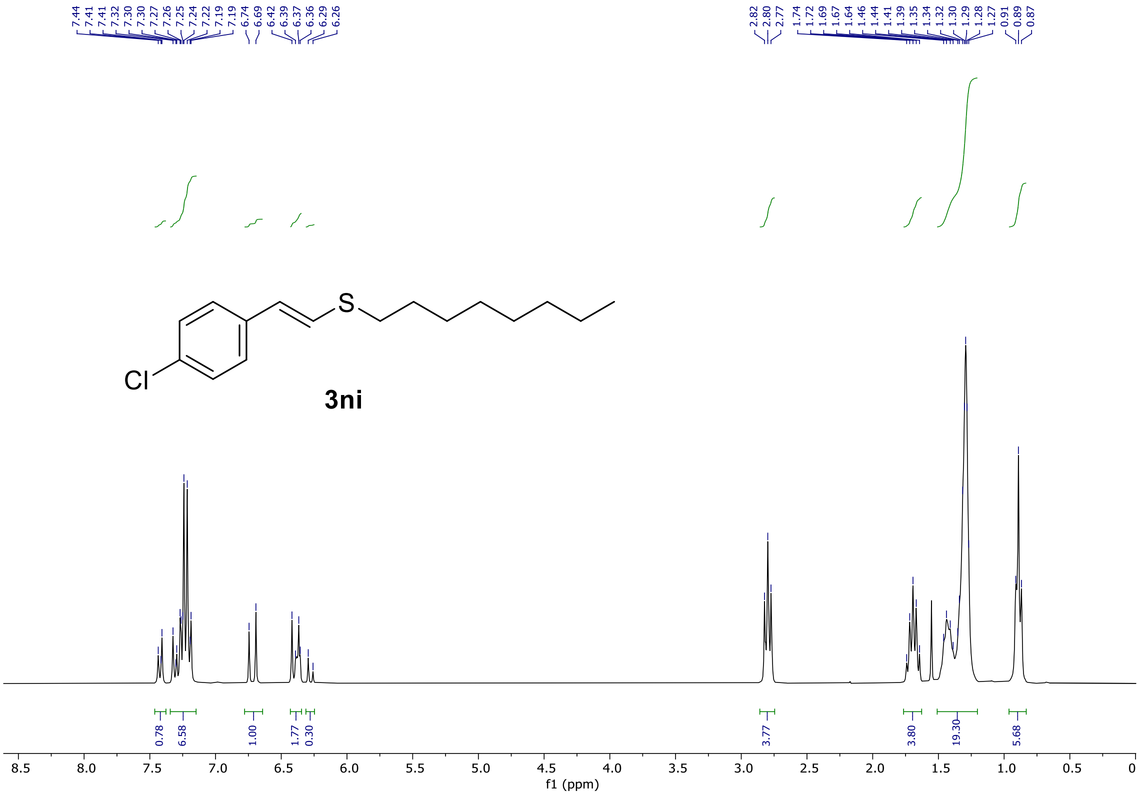


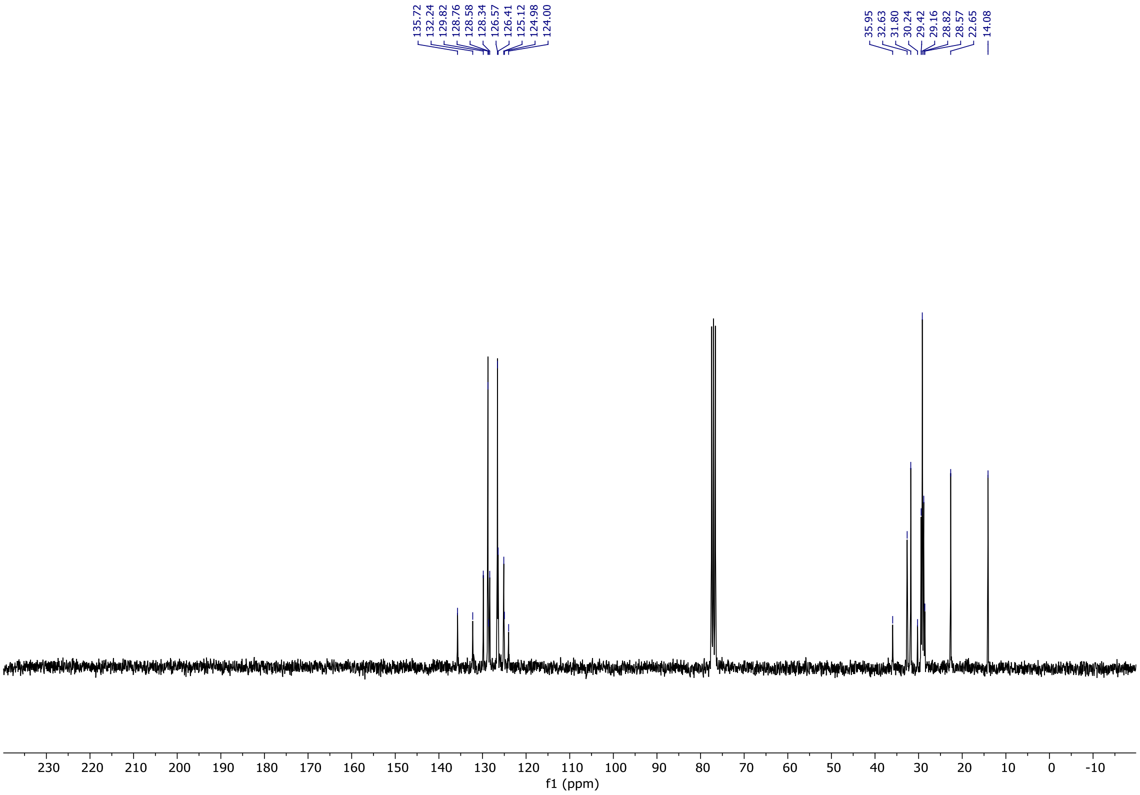
(*E*)-Cyclohexyl(styryl)sulfane (3ah)



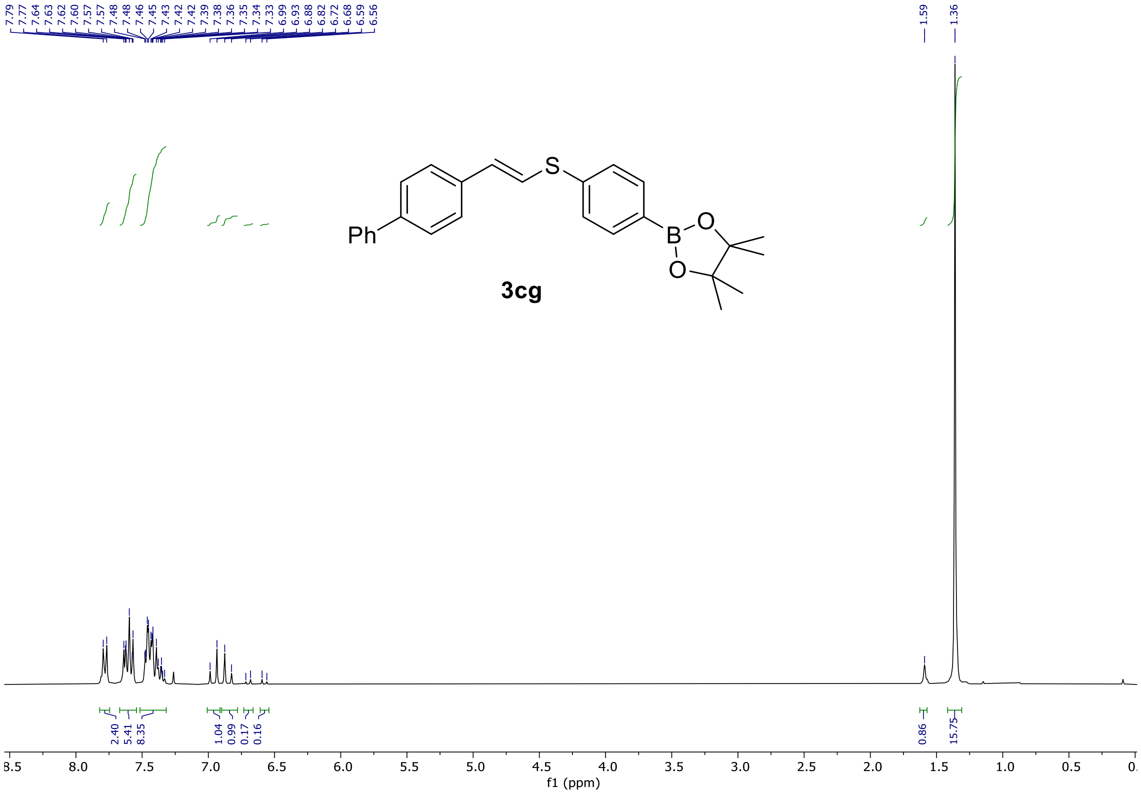


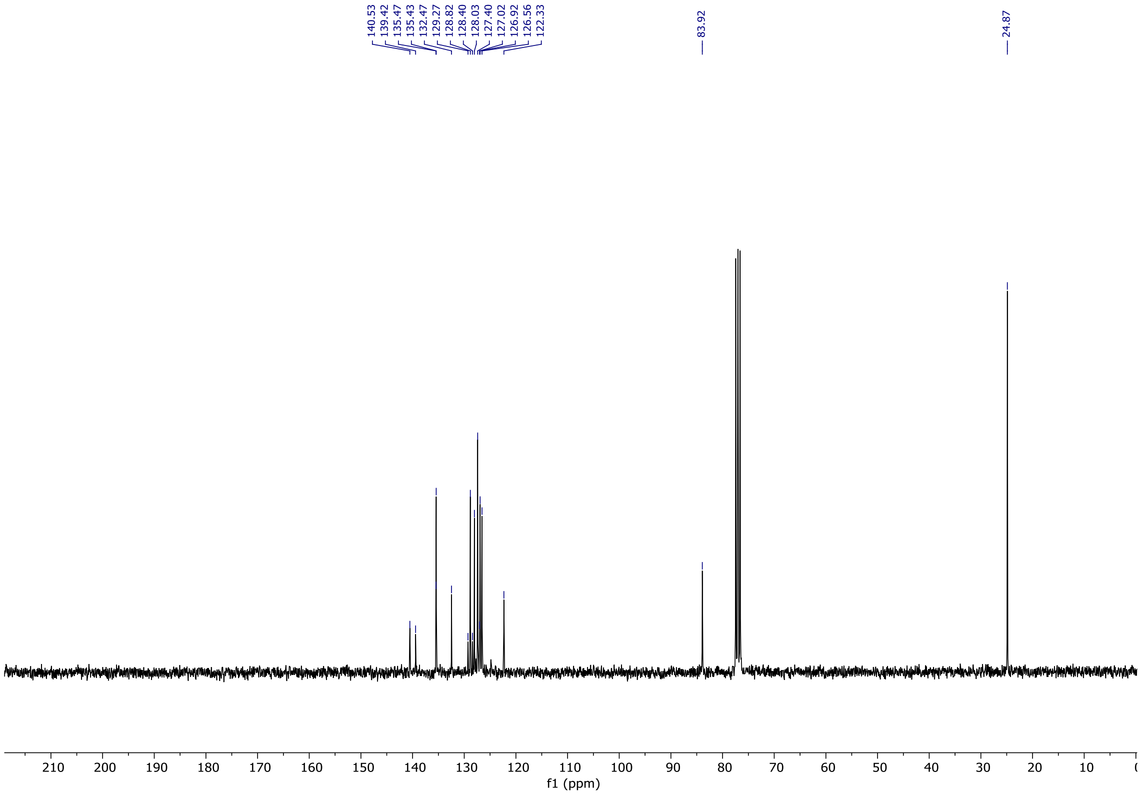
(*E*)-(4-chlorostyryl)(octyl)sulfane (3ni)



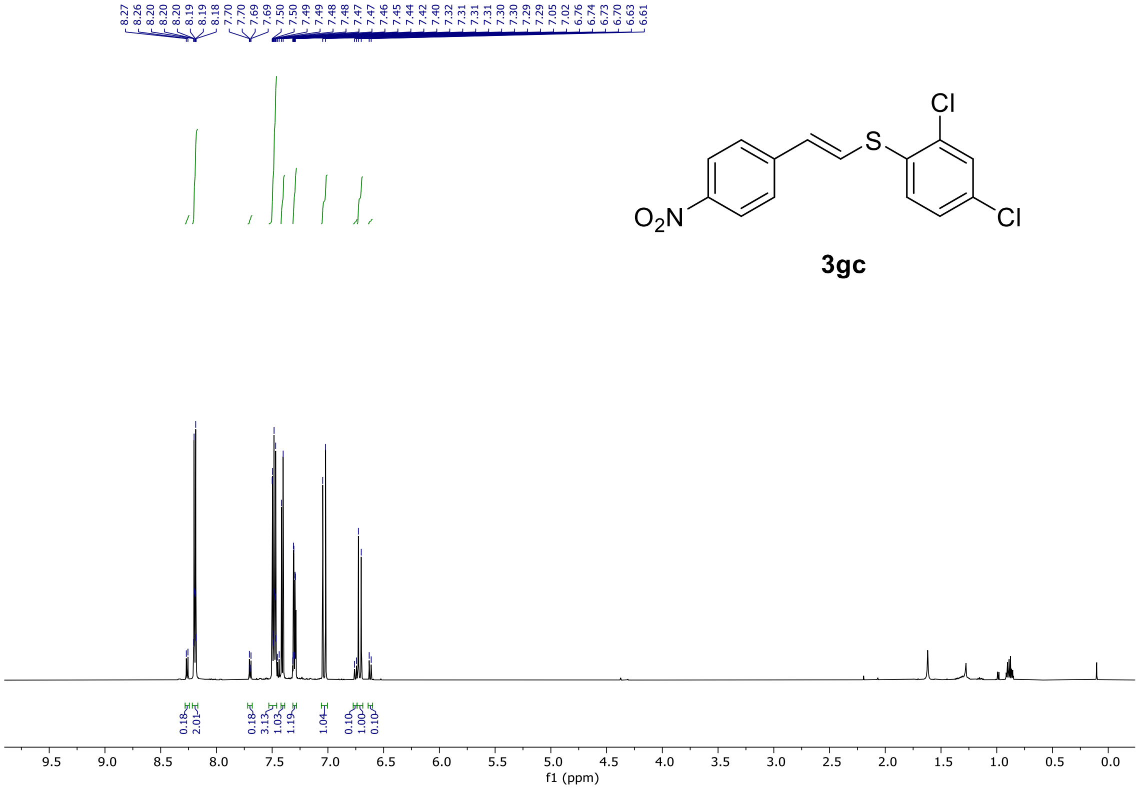


(*E*)-2-(4-((2-([1,1'-biphenyl]-4-yl)vinyl)thio)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3cg)

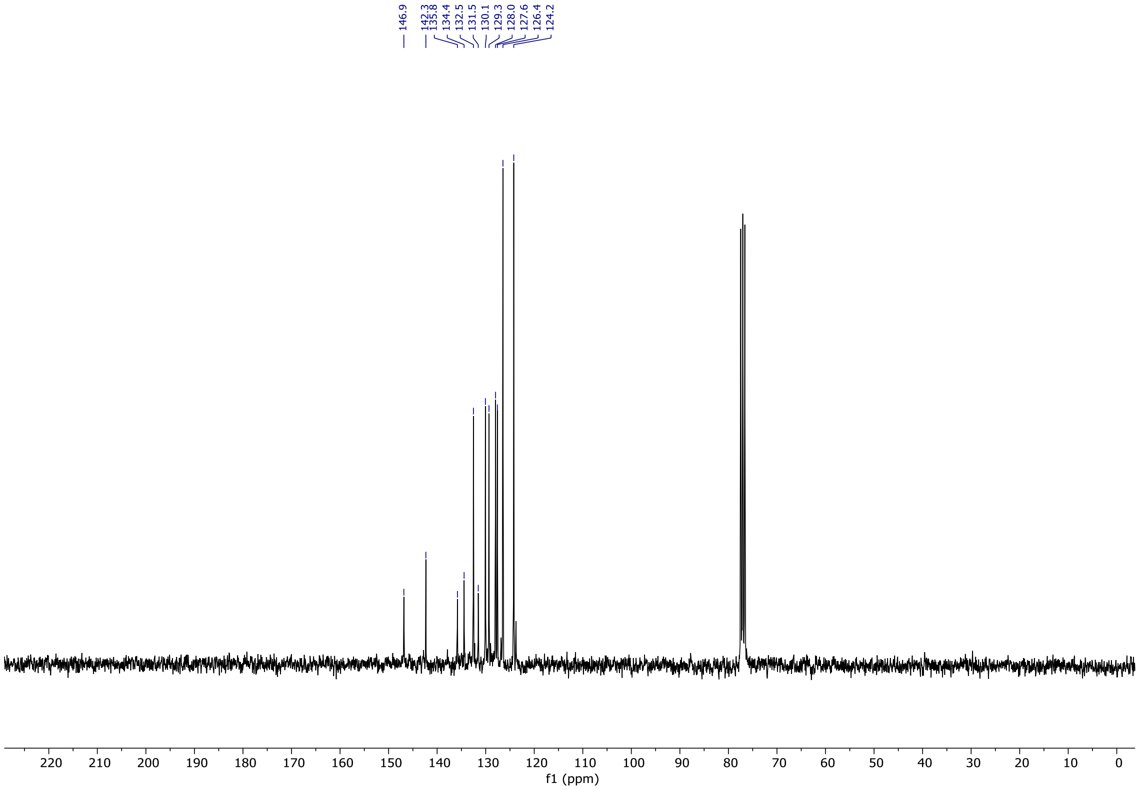




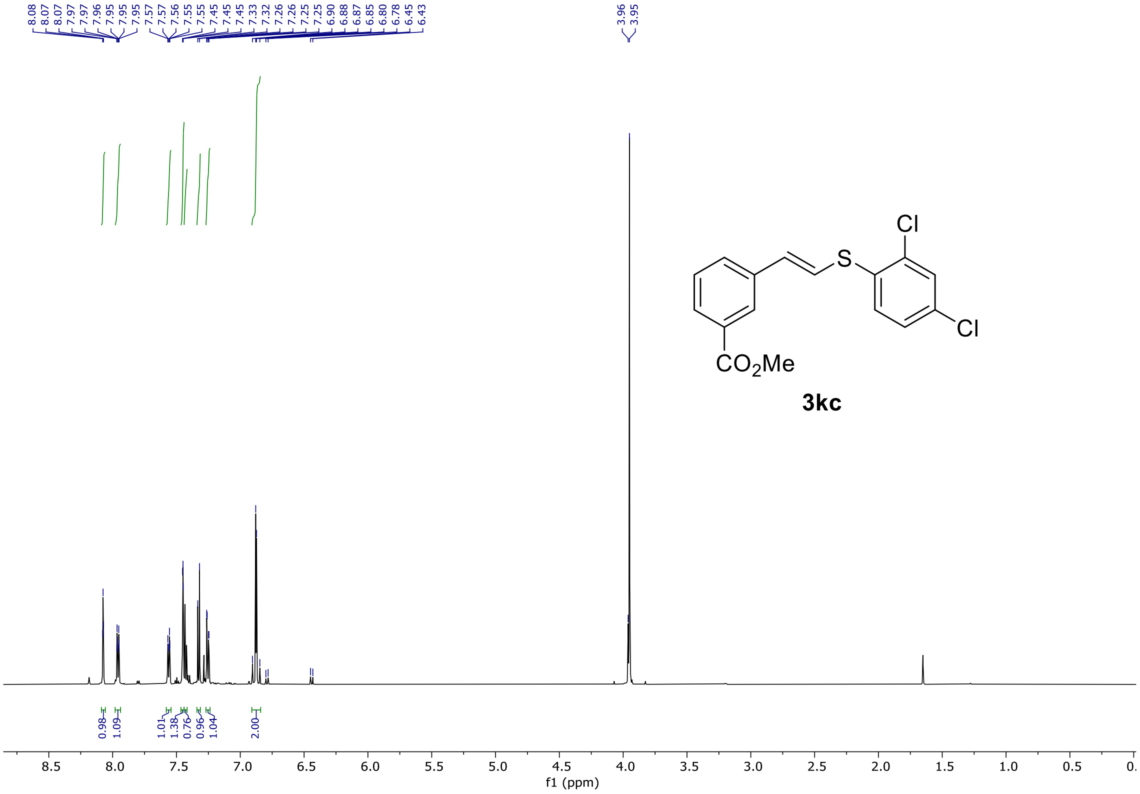
(*E*)-(2,4-Dichlorophenyl)(4-nitrostyryl)sulfane (3gc)

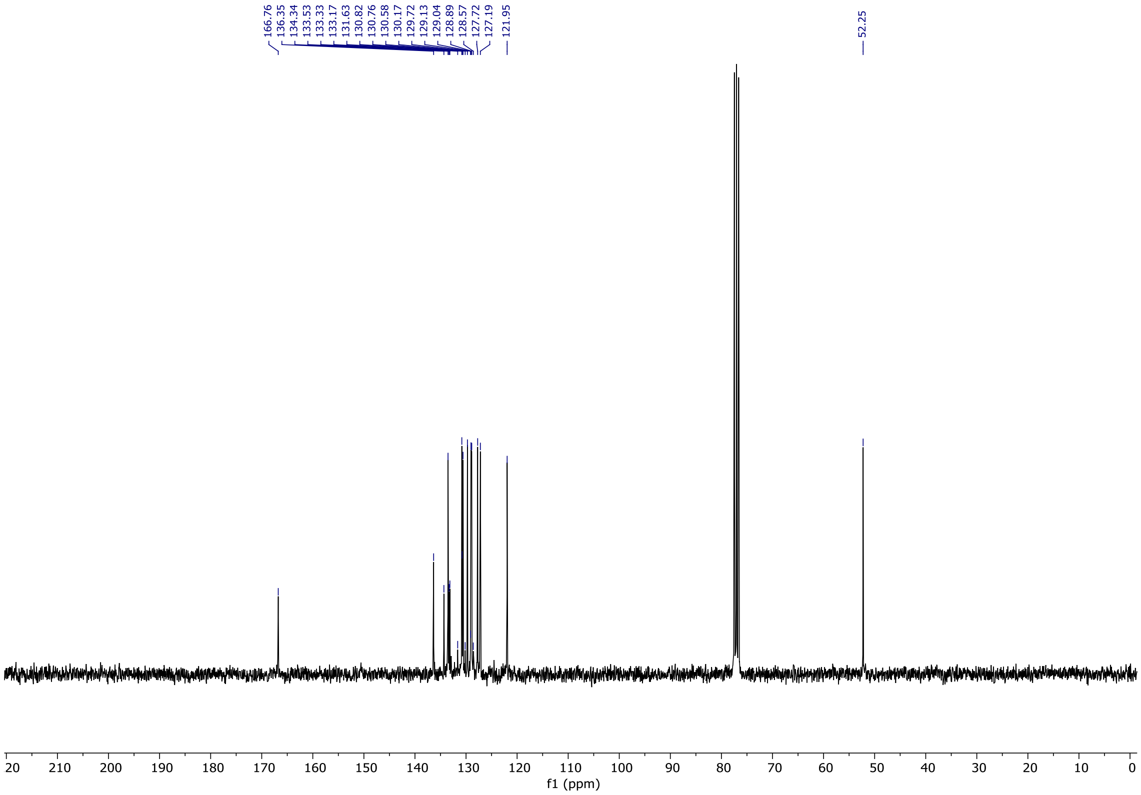


3gc

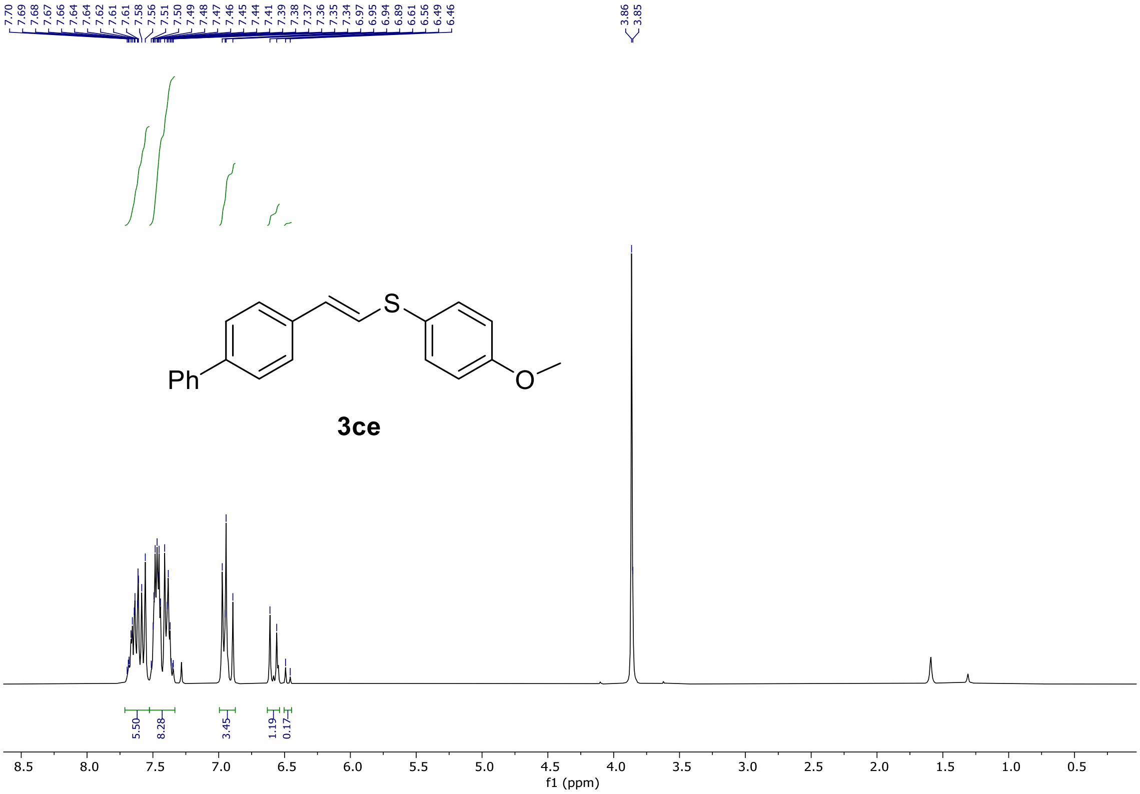


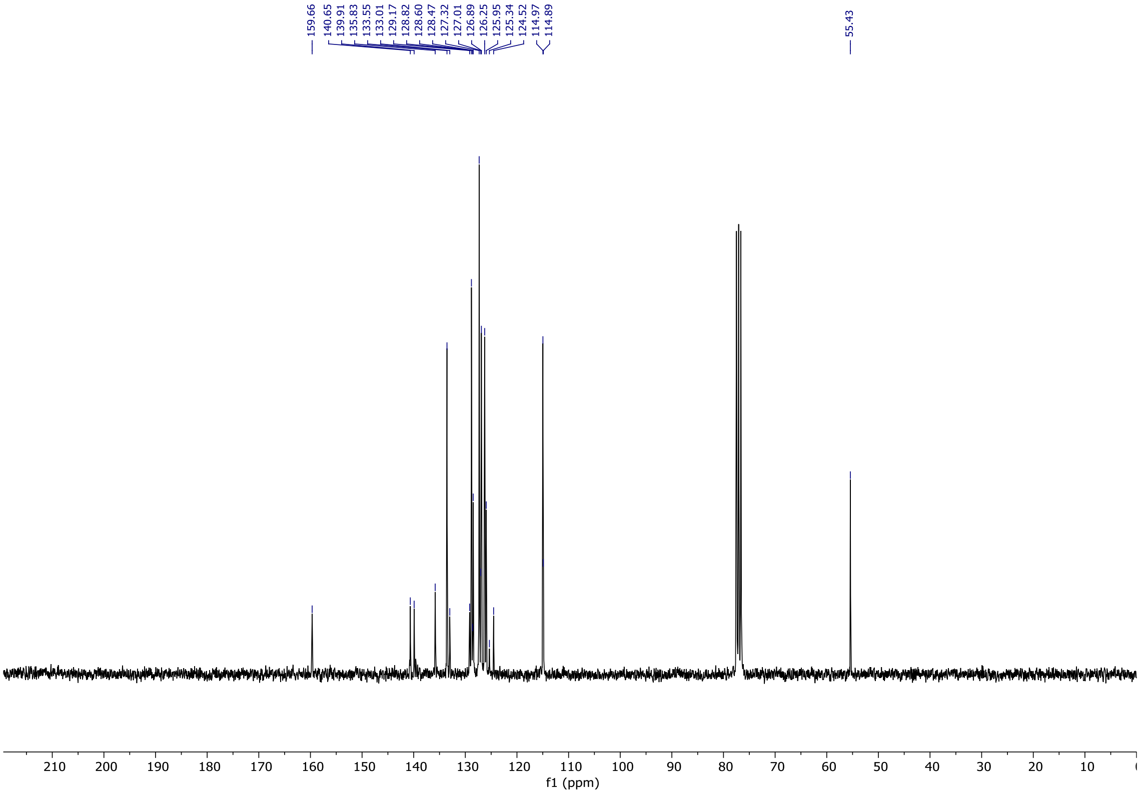
Methyl (*E*)-3-(2-((2,4-dichlorophenyl)thio)vinyl)benzoate (3kc)



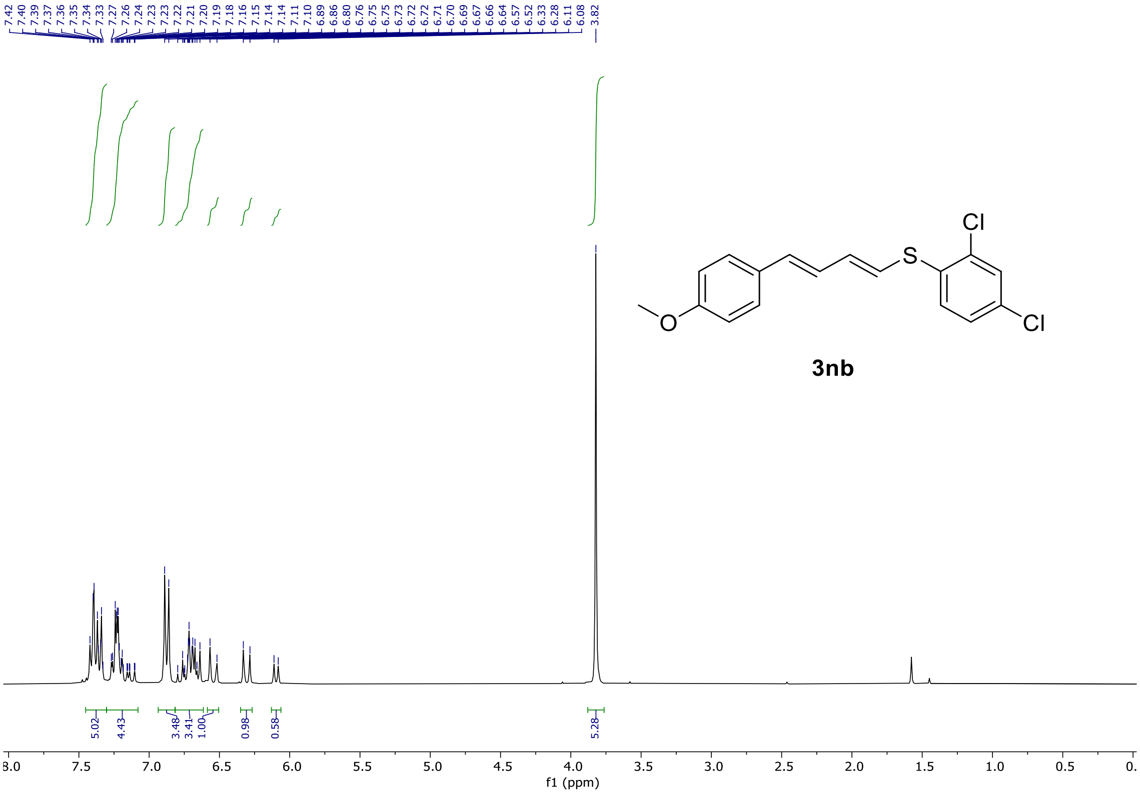


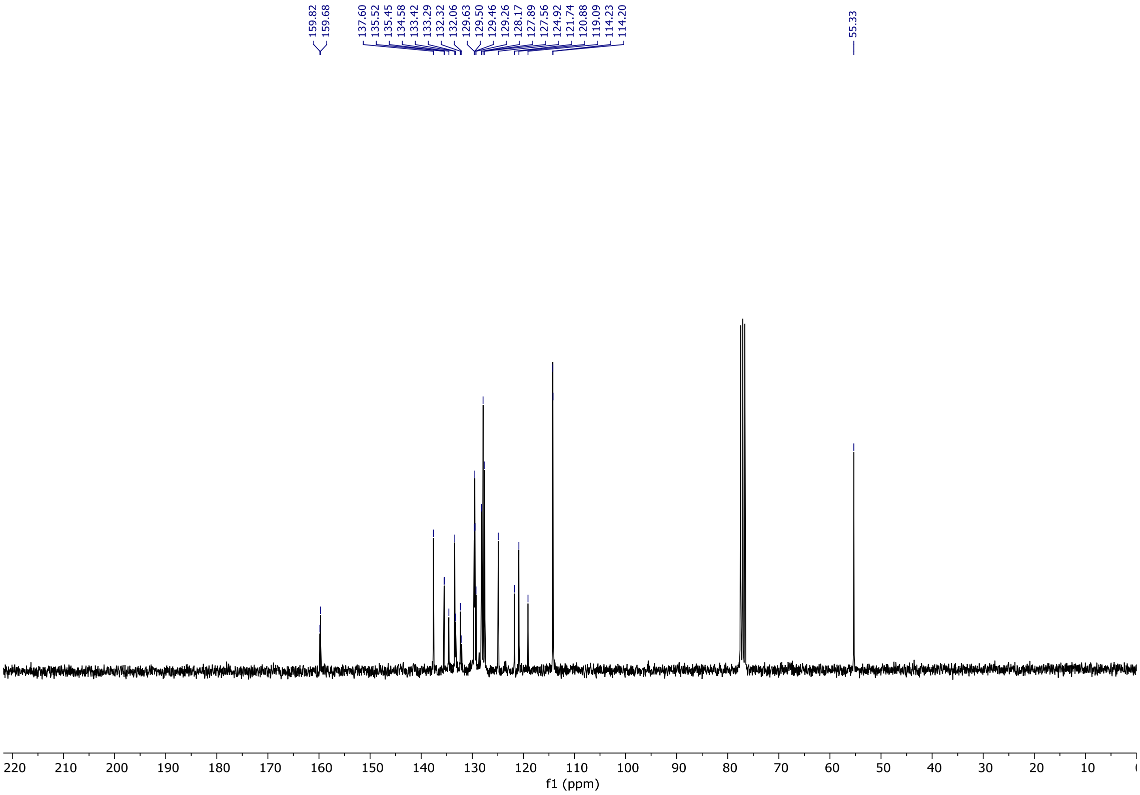
(*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)(4-methoxyphenyl)sulfane (3ce)



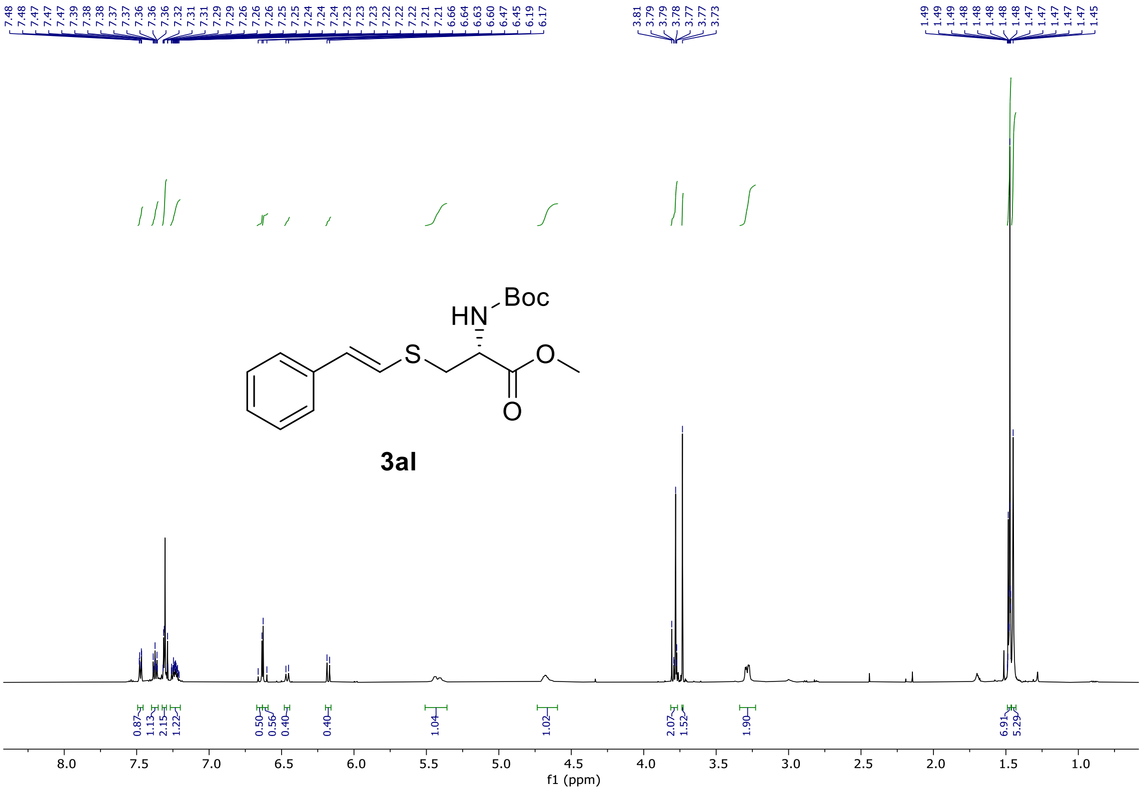


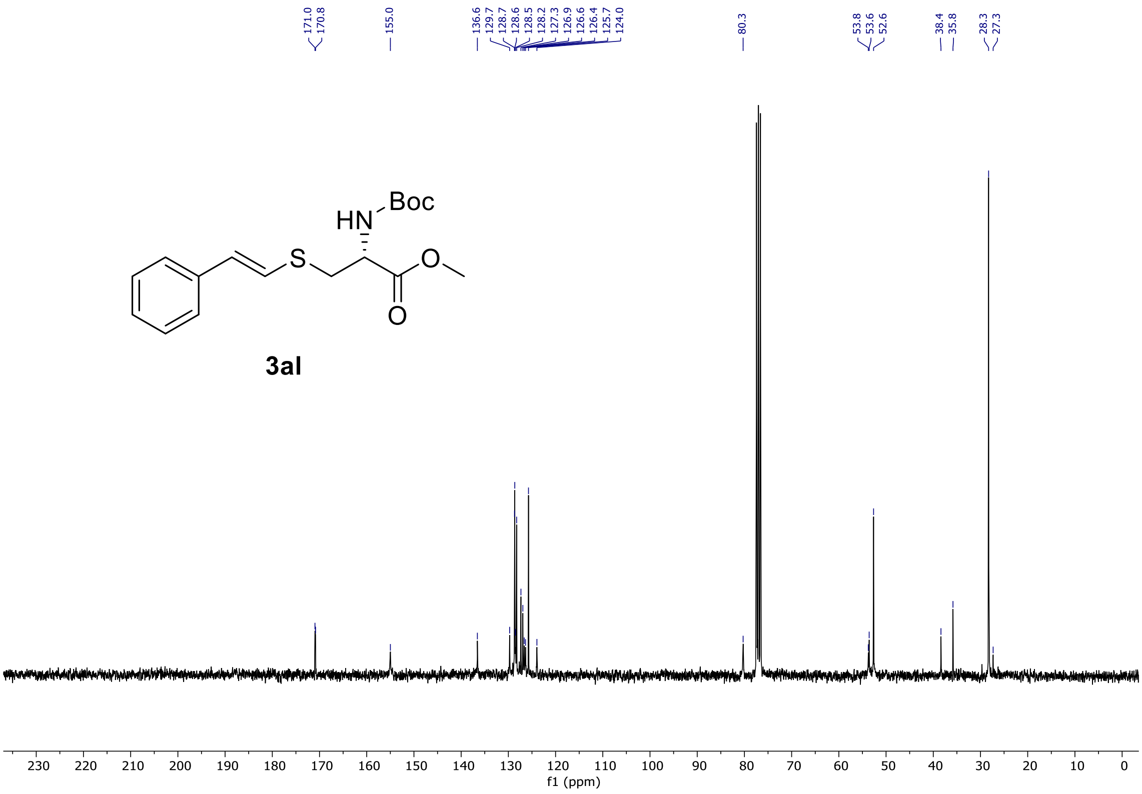
(2,4-dichlorophenyl)((1*E*,3*E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)sulfane (3nb)



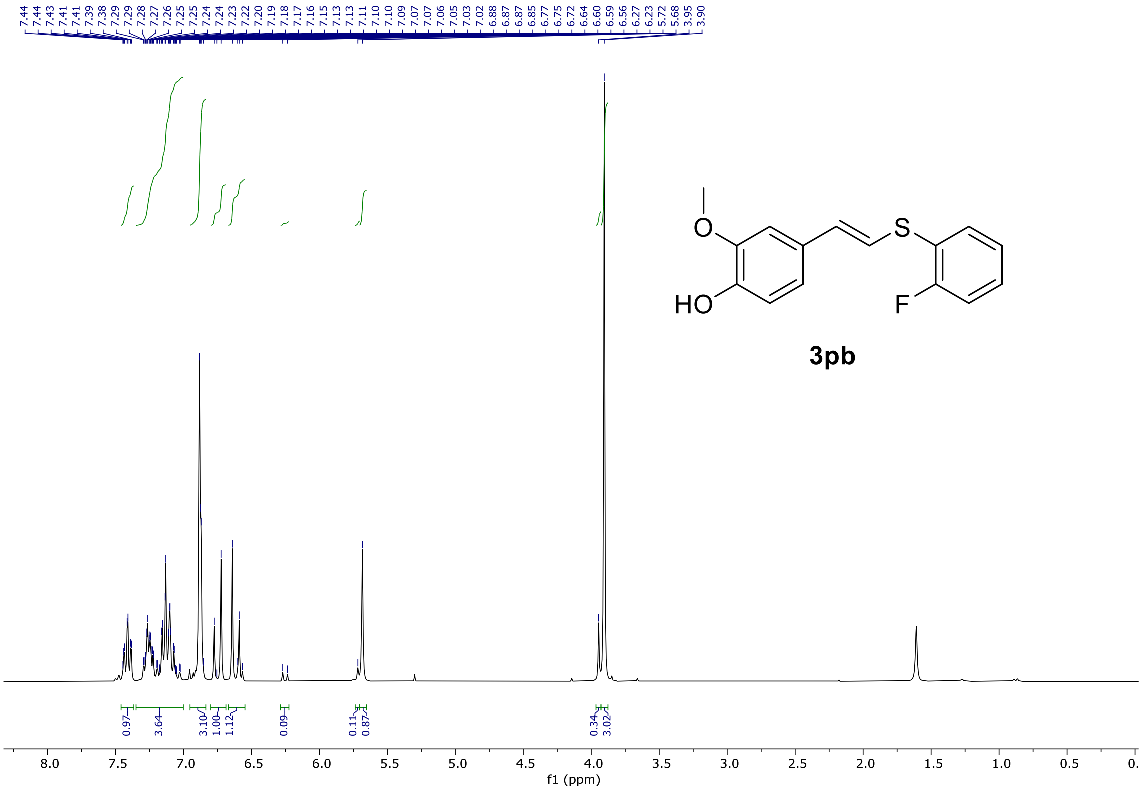


Methyl (*E*)-*N*-(tert-butoxycarbonyl)-*S*-styryl-*L*-cysteinate (3al)

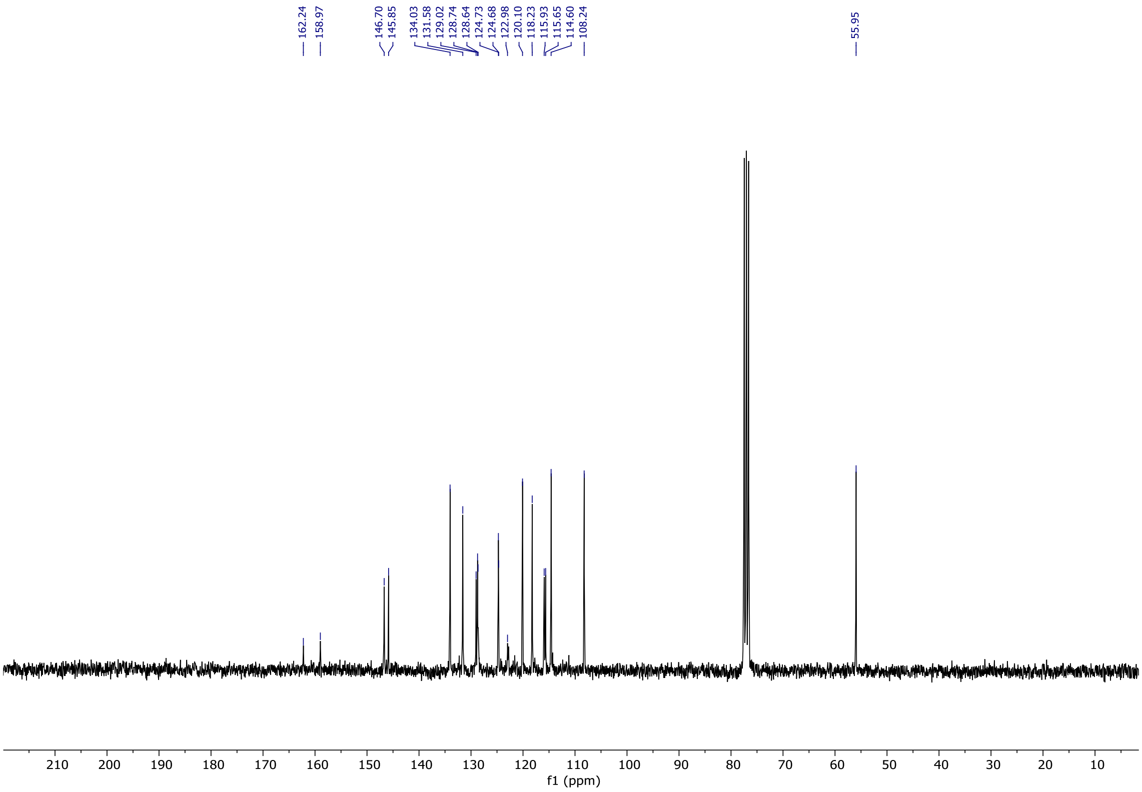


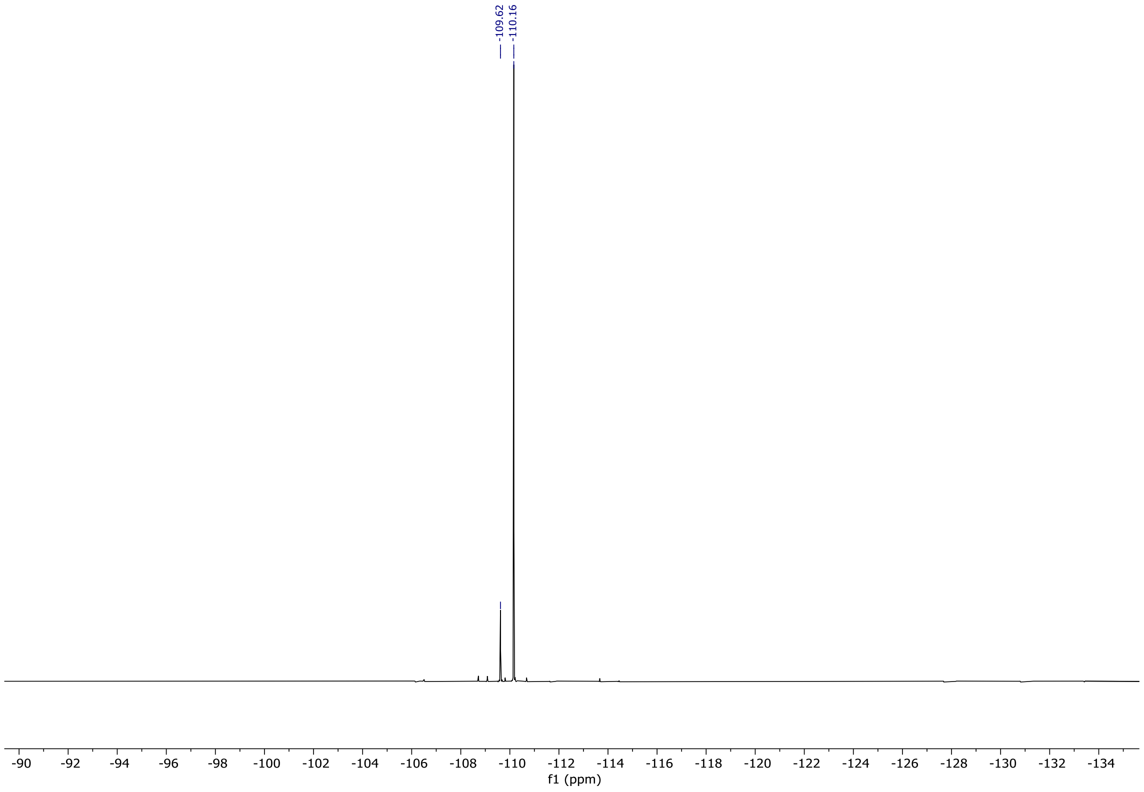


(*E*)-4-(2-((2-fluorophenyl)thio)vinyl)-2-methoxyphenol (3pb)

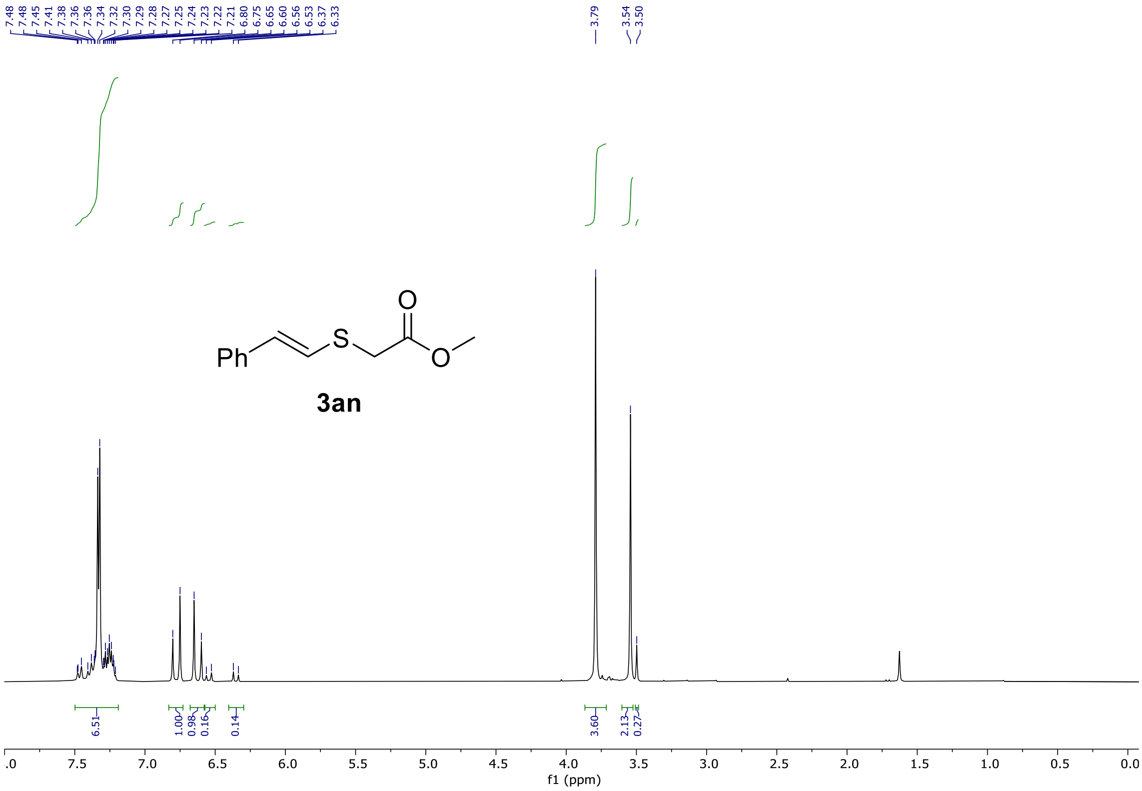


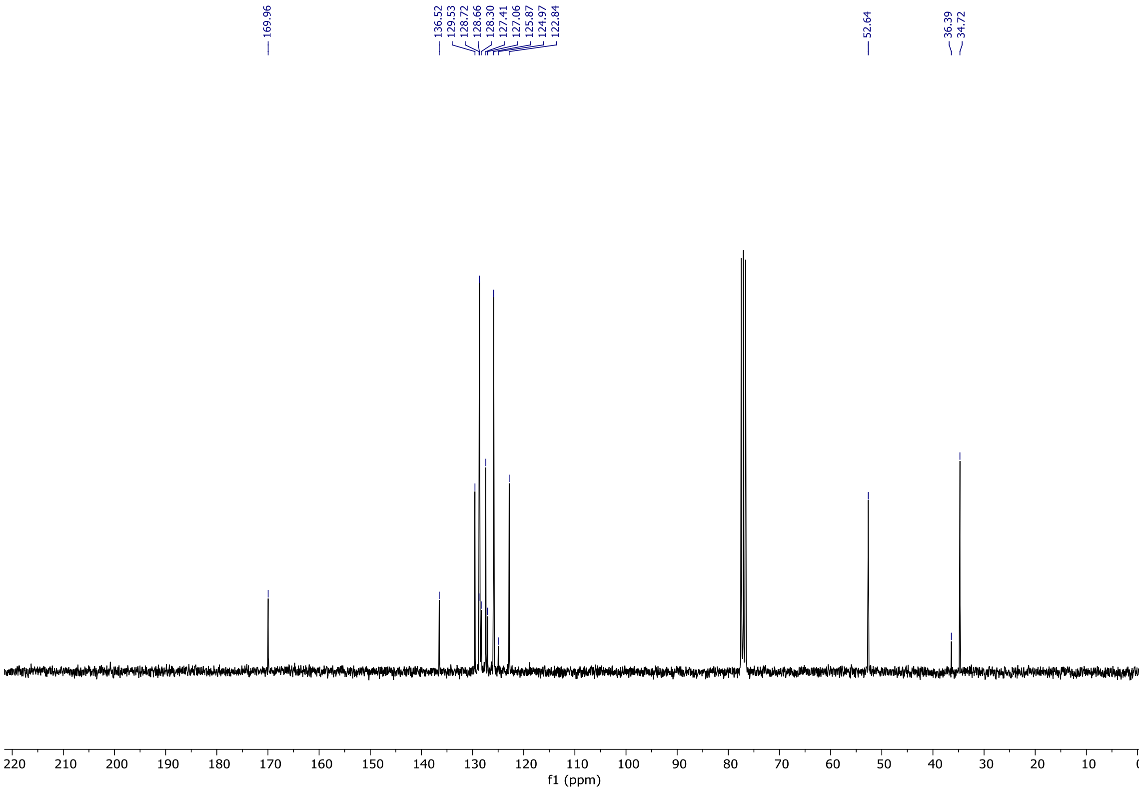
3pb



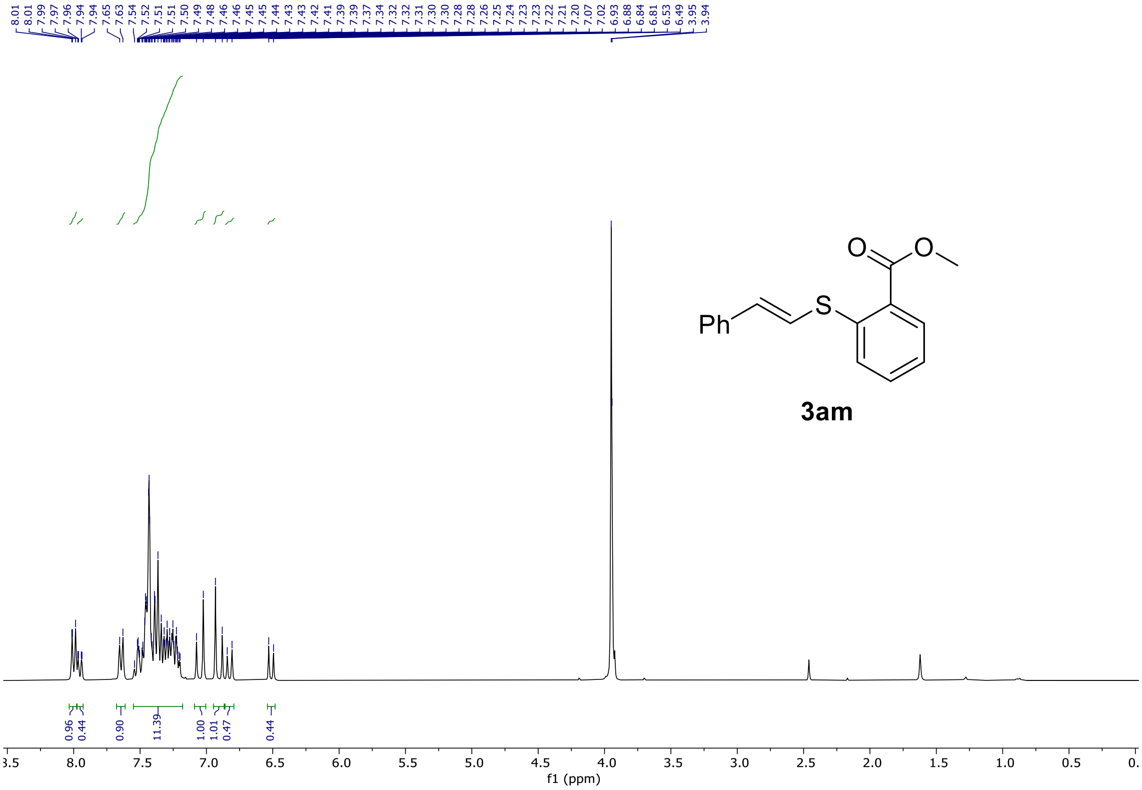

-109.62
-110.16
-90
-92
-94
-96
-98
-100
-102
-104
-106
-108
-110
-112
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
f1 (ppm)

Methyl (*E*)-2-(styrylthio)acetate (3an)

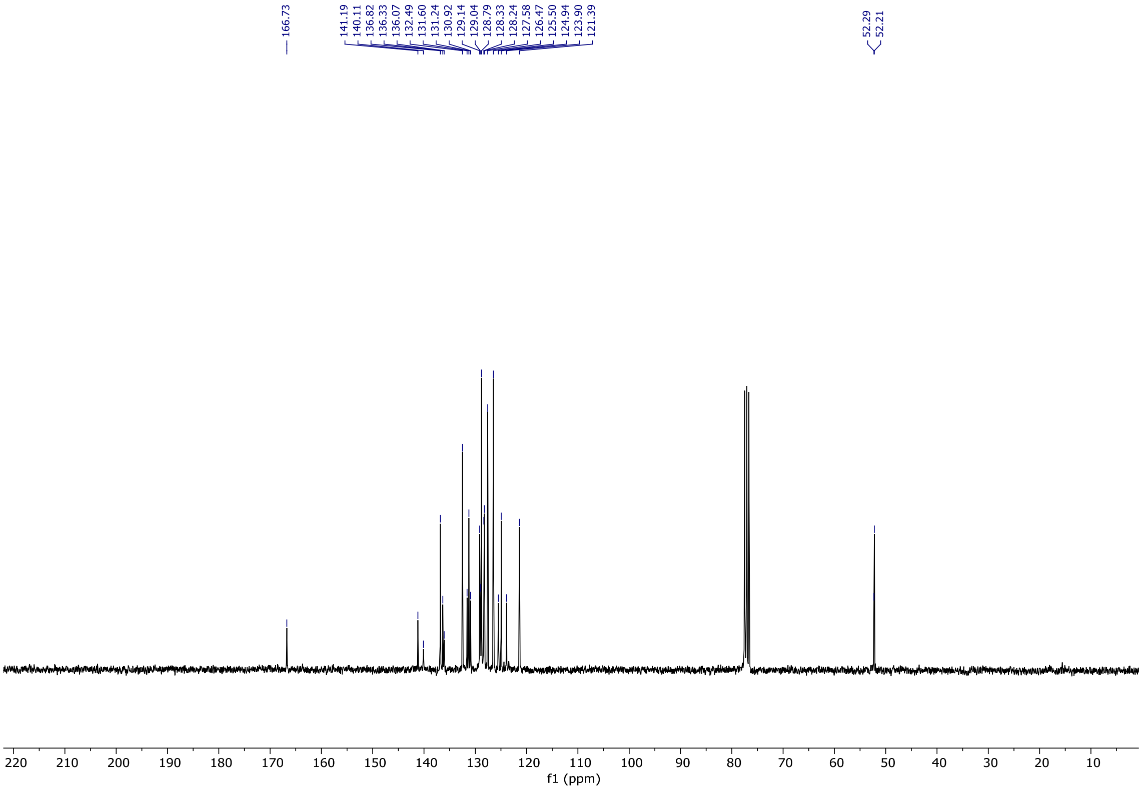




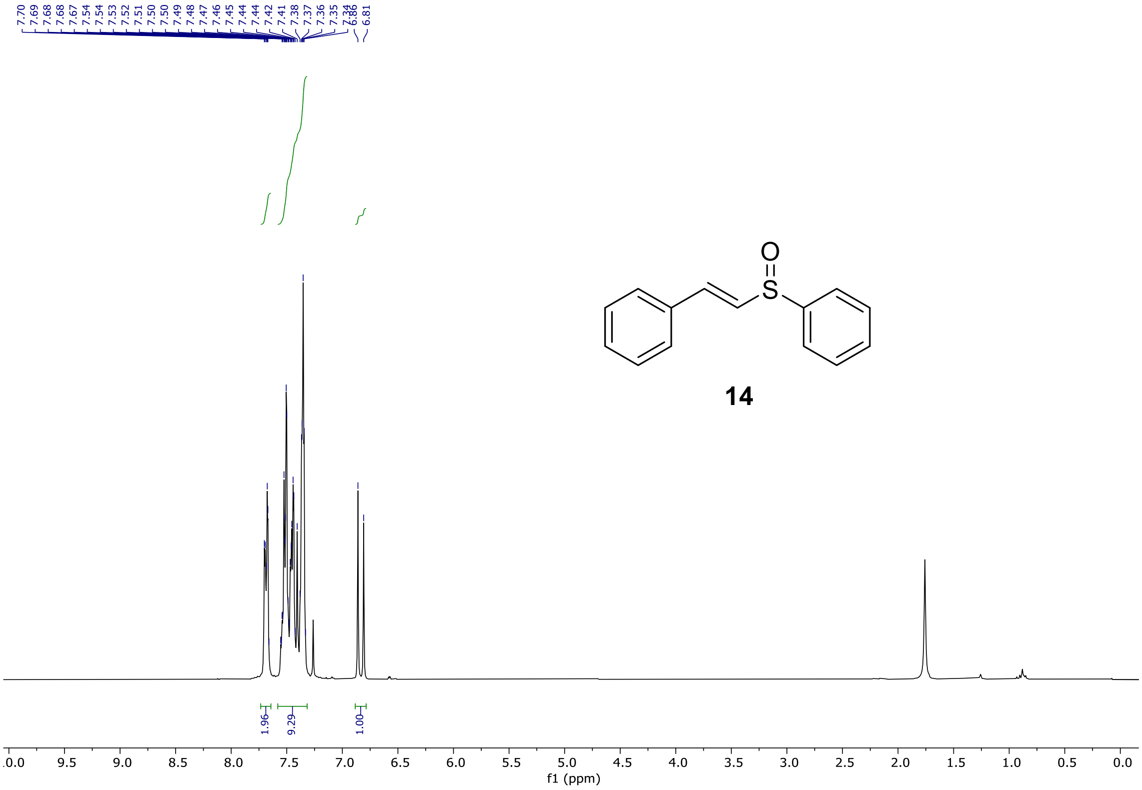
Methyl (*E*)-2-(styrylthio)benzoate (3am)

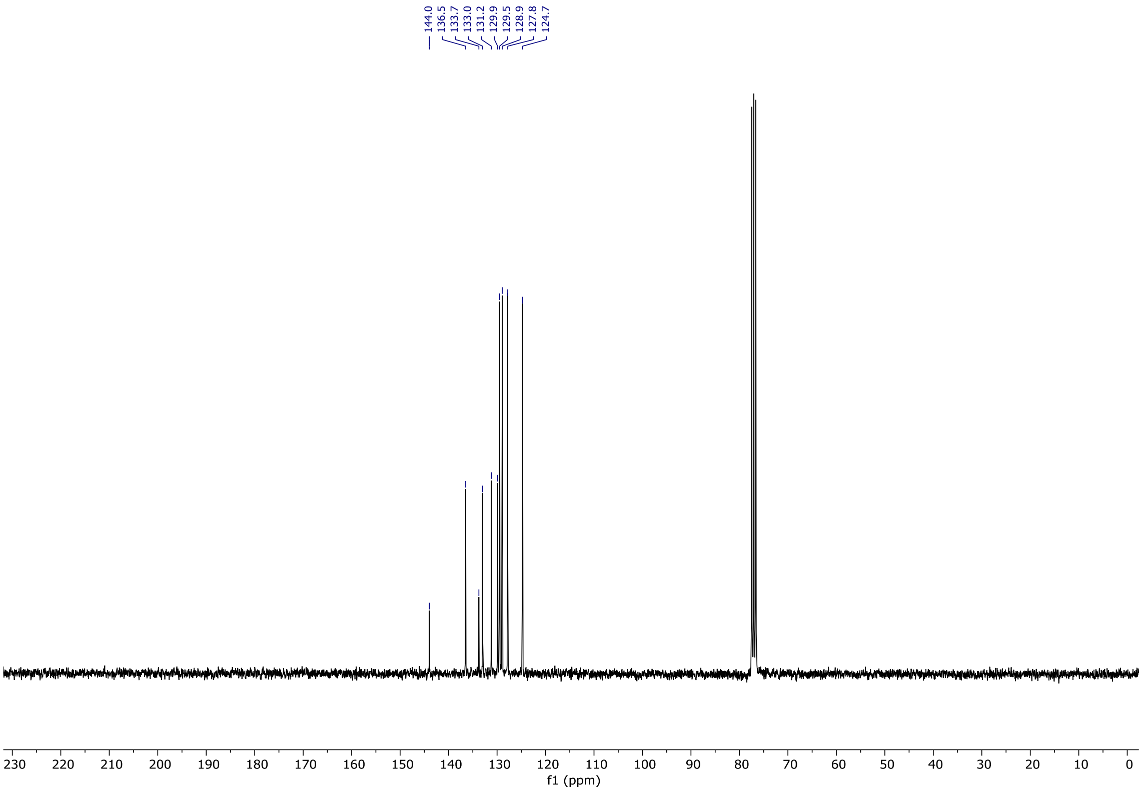


3am

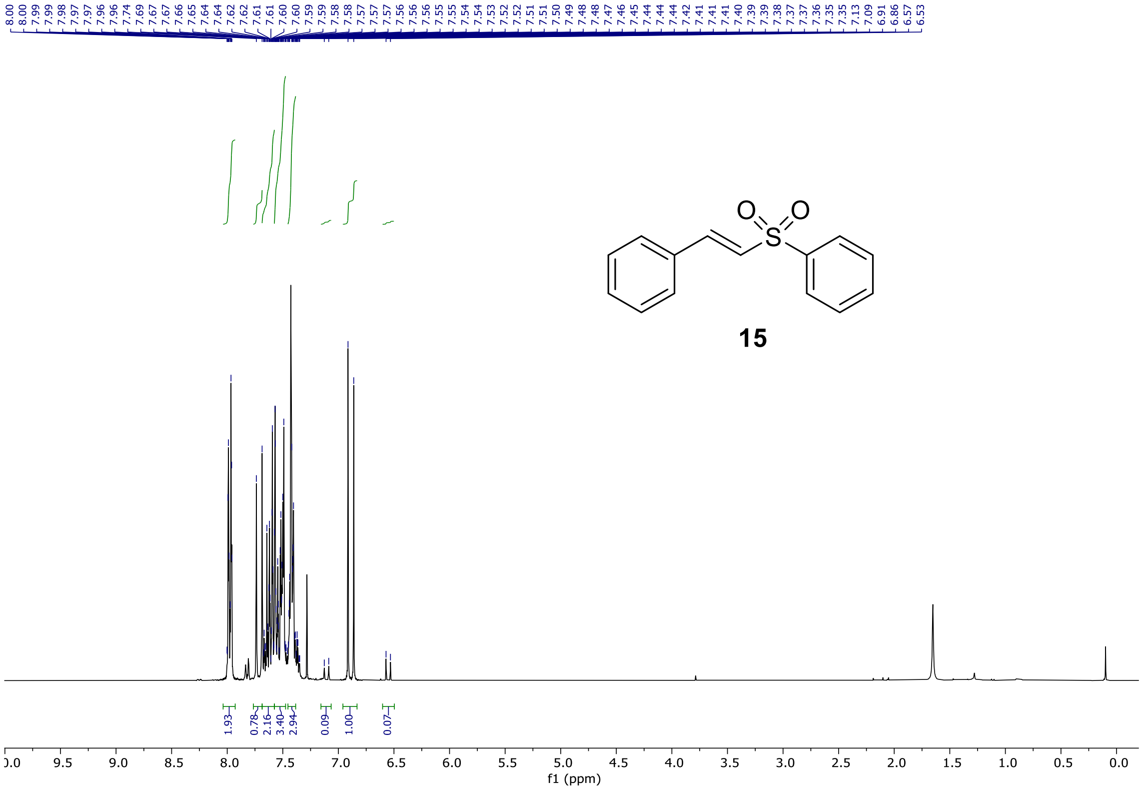


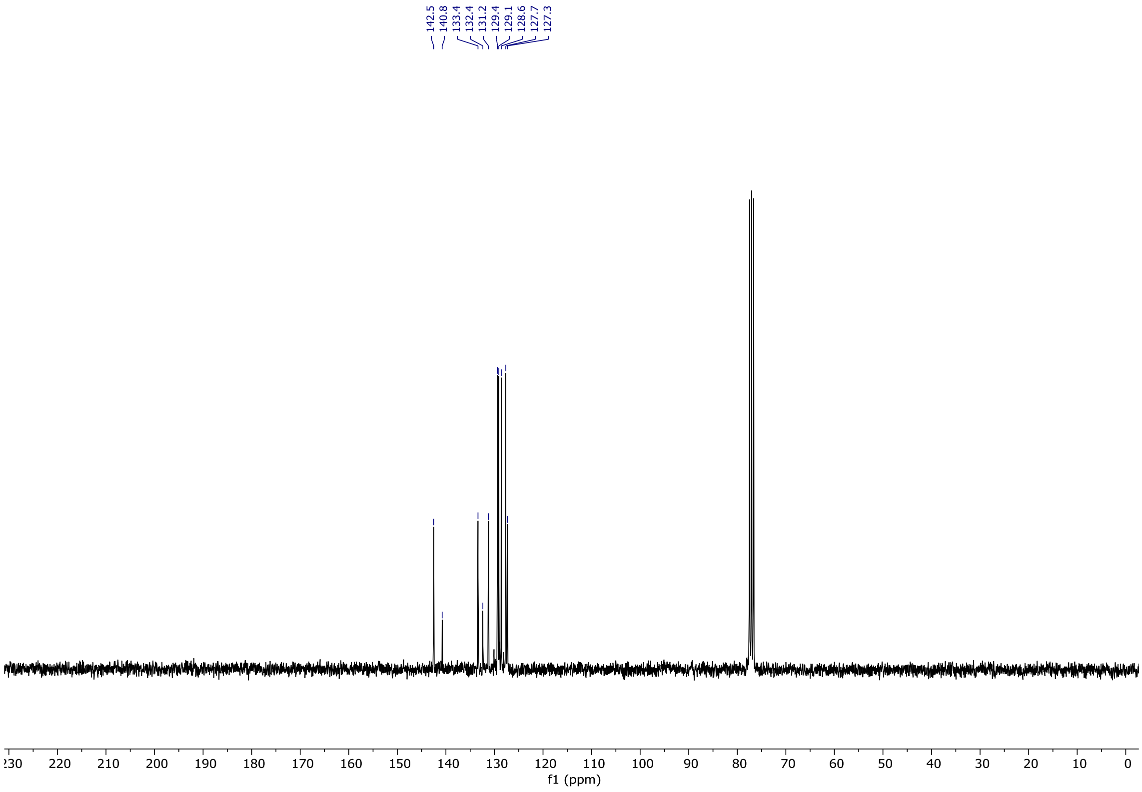
(*E*)-(2-(Phenylsulfinyl)vinyl)benzene (14)



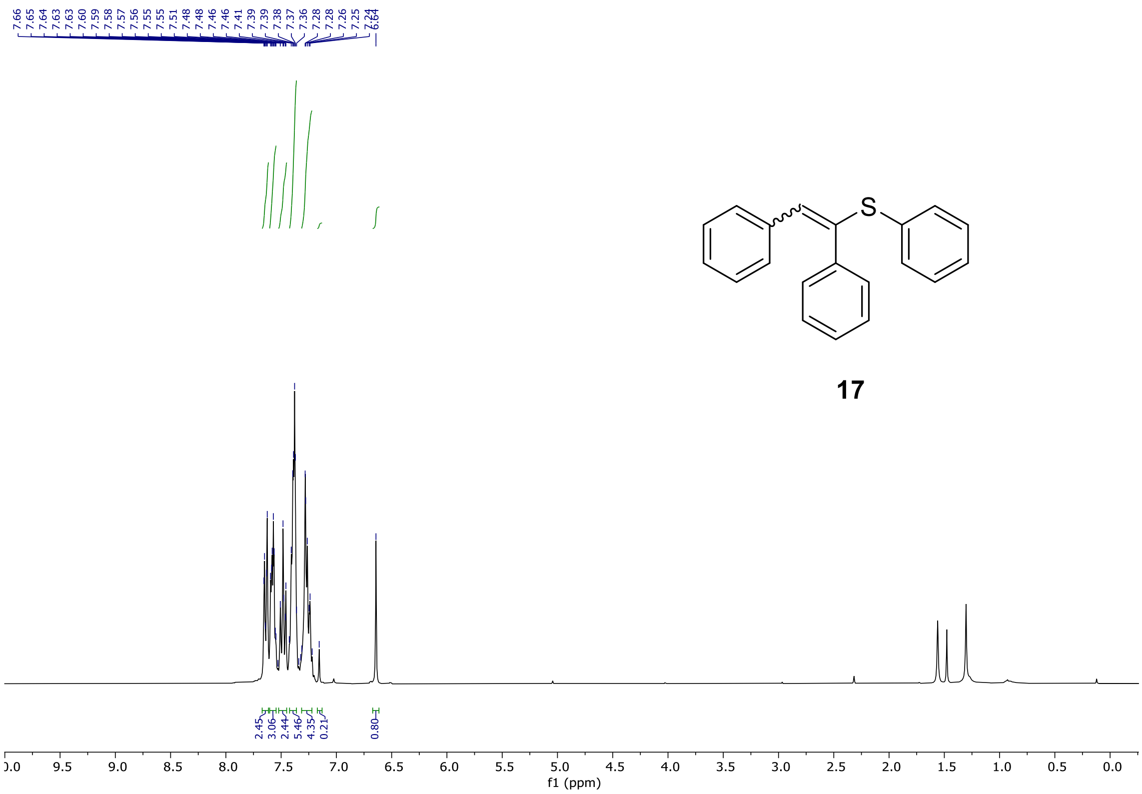


(*E*)-(2-(Phenylsulfonyl)vinyl)benzene (15)





(1,2-Diphenylvinyl)(phenyl)sulfane (17)



17