

Disulfides turned out to be versatile S- reagents: effective sulfonylation of alkenes with disulfides under electrochemical conditions

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SUPPORTING INFORMATION

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General

NMR spectra were registered on Bruker Avance II 300 MHz instrument. Chemical shifts were measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 (CDCl₃). The TLC analyses were carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Column chromatography was performed on silica gel (60-200 mesh). Diphenyl disulfide, styrene, 1-methyl-4-vinylbenzene, 1-methyl-2-vinylbenzene, 1-methyl-3-vinylbenzene, 1-(*tert*-butyl)-4-vinylbenzene, 1-fluoro-4-vinylbenzene, 1-chloro-4-vinylbenzene, 1-bromo-4-vinylbenzene, 1-fluoro-2-vinylbenzene, 1-chloro-2-vinylbenzene, 1-chloro-3-vinylbenzene, 1-bromo-3-vinylbenzene, 1-vinyl-1*H*-1,2,4-triazole, hexene-1, cyclohexene, 4-methylbenzenethiol, 2-methylbenzenethiol, 3-methylbenzenethiol, 4-fluorobenzenethiol, 4-chlorobenzenethiol, 4-methoxybenzenethiol, 3-methoxybenzenethiol, thiophene-2-thiol, methyltriphenylphosphonium bromide, 4-nitrobenzaldehyde, 2,4-dichlorobenzaldehyde, DBU, iodine, tetrabutylammonium perchlorate, tetrabutylammonium iodide, NH₄I, KBr, KI, Na₂SO₄, NaOH, THF, DMSO, MeOH, Et₂O, petroleum ether (PE, 40/70), ethyl acetate (EA) were purchased from commercial sources and were used as is. 1-Nitro-4-vinylbenzene, 2,4-dichloro-1-vinylbenzene were synthesized according to literature through the Wittig reaction of corresponding arylaldehydes with methyltriphenylphosphonium bromide.^{1,2}

Cyclic voltammetry (CV) was implemented on an IPC-Pro M computer-assisted potentiostat manufactured by Econix (scan rate error 1.0%; potential setting 0.25 mV; scan rate 100 mV·s⁻¹). The experiments were performed in a 25 mL five-neck glass conic electrochemical cell with a water jacket for thermostating. CV curves were recorded using a three-electrode scheme. The working electrode was a disc glassy-carbon electrode (d = 3 mm). A platinum wire served as an auxiliary electrode. An Ag/Ag⁺ electrode was used as the reference electrode and was linked to the solution by a porous glass diaphragm. The solutions were kept under thermally controlled conditions at 25±0.5 °C and deaerated by bubbling argon. Electrochemical experiments were performed under an argon atmosphere. The working electrode was polished before recording each CV curve. In a typical case, 10 mL of solution was utilized. The compound concentration was 0.05 M or 0.025 M.

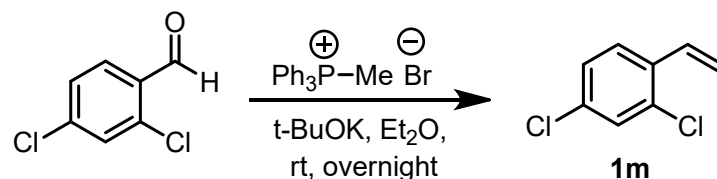
Dioxane should be purified from peroxides before use in the reaction. For the preparation of 400 mL of dioxane, it is washed with the mixture containing FeSO₄ (60

g), concentrated H_2SO_4 (6 mL), and water (100 mL). After that, NaOH is added to the organic layer to adsorb all water. The resulting mixture is filtered and distilled under air atmosphere.

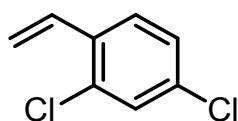
After every electrochemical experiment, the electrodes were washed with running water and then with acetone. All these procedures help to clean the electrodes from the impurities from the previous electrolysis, which can dramatically affect the reaction efficiency especially in the case of graphite electrode application.

Synthesis of the starting compounds

Synthesis of styrene 1m.

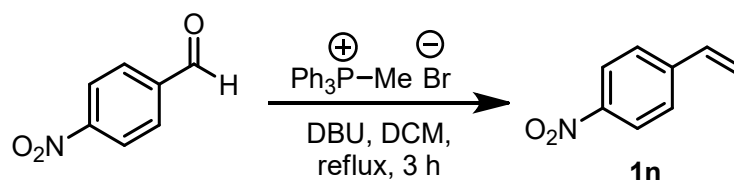


Following the literature procedure,² to a stirred suspension of methyltriphenylphosphonium bromide (6.07 g, 17 mmol) in diethyl ether (50 mL) at 0 °C potassium *tert*-butoxide (1.68 g, 15 mmol) was added. The mixture was stirred for 15 minutes and became bright yellow. The solution of 2,4-dichlorobenzaldehyde (1.75 g, 10 mmol) in diethyl ether (20 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature, cooled to 0 °C, and quenched with saturated aqueous ammonium chloride (40 mL). The aqueous layer was diluted with water (20 mL) and extracted with diethyl ether (2 x 40 mL). The combined organic layer and was washed with water (10 mL) and brine (10 mL), dried over Na₂SO₄, filtered, concentrated, and purified by flash chromatography to give the desired product.



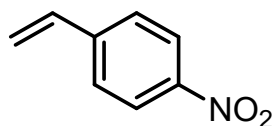
2,4-Dichloro-1-vinylbenzene (1m).³ 2,4-Dichlorobenzaldehyde (1.75 g, 10 mmol) gave the title compound as a colorless oil (1.2 g), yield 69%. ¹H NMR (CDCl₃), δ: 5.41 (dd, *J* = 11.0, 0.9 Hz, 1H), 5.73 (dd, *J* = 17.5, 0.8 Hz, 1H), 7.04 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.21 (ddd, *J* = 8.4, 2.1, 0.4 Hz, 1H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 1H). ¹³C NMR, (CDCl₃), δ: 117.2, 127.4, 127.5, 129.5, 132.4, 133.8, 133.9, 134.5.

Synthesis of styrene 1n.



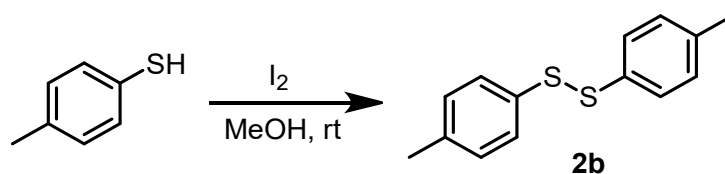
Following the literature procedure,¹ to the solution of methyltriphenylphosphonium bromide (26.8 g, 75 mmol) in DCM (250 mL) DBU (12.44 ml, 83 mmol) was added. The colorless solution was refluxed for 30 minutes. After that, the solution of 4-

nitrobenzaldehyde (5.67 g, 37.5 mmol) in DCM (50 mL) was added. The reaction mixture was refluxed for 5 hours. Then, it was cooled to room temperature, washed with water (3 × 100 mL), dried over Na₂SO₄, filtered through SiO₂ (h = 5 cm), washed with DCM (4 × 20 mL), and concentrated under reduced pressure. The residue was distilled under reduced pressure (72-74 °C, 0.1-0.2 torr) to give yellow oil.

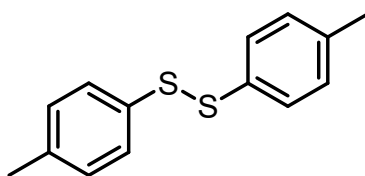


1-Nitro-4-vinylbenzene (1n).⁴ 4-Nitrobenzaldehyde (5.67 g, 37.5 mmol) gave the title compound as yellow oil (2.8 g), yield 50%. ¹H NMR (CDCl₃), δ: 5.48 (d, *J* = 10.9 Hz, 1H), 5.91 (d, *J* = 17.6 Hz, 1H), 6.76 (dd, *J* = 17.6, 10.9 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H). ¹³C NMR, (CDCl₃), δ: 118.7, 123.9, 126.9, 135.0, 143.9, 147.4.

Synthesis of disulfides 2b-2i.

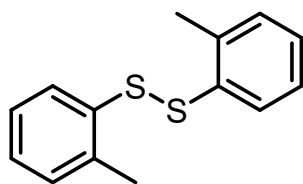


A 50 mL round-bottom flask was equipped with a magnetic stir bar. Thiol (2.5 mmol) was dissolved in methanol (10 mL). Then the solution of I₂ (317 mg, 1.25 mmol) in methanol (5 mL) was added dropwise under stirring at room temperature. The reaction mixture was stirred until the reaction completed as indicated by TLC (1-5 hours). After that, methanol was removed under reduced pressure. Subsequently, a saturated aqueous solution of NaHCO₃ (15 mL) and water (50 mL) were added. Then, the mixture was extracted with EtOAc (4×10 mL). Combined organic layer was washed with water (10 mL), brine (10 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Obtained compounds were used without any additional purification.

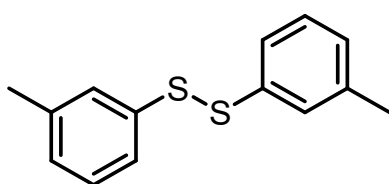


1,2-Di-*p*-tolylidysulfane (2b).⁵ 4-Methylbenzenethiol (311 mg, 2.5 mmol) gave the title compound as a white solid (301 mg), yield 98%. mp = 44.0-45.0 °C (lit. ⁵ mp = 44.0-45.0

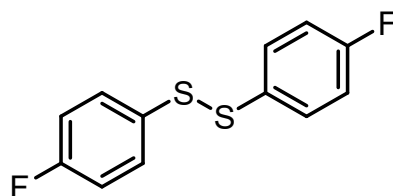
°C). ^1H NMR (CDCl_3), δ : 2.34 (s, 6H), 7.12 (d, $J = 8.0$ Hz, 4H), 7.41 (d, $J = 8.0$ Hz, 4H). ^{13}C NMR, (CDCl_3), δ : 21.2, 128.7, 129.9, 134.1, 137.6.



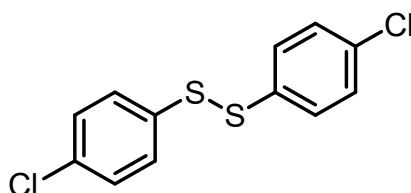
1,2-Di-*o*-tolylidysulfane (2c).⁵ 2-Methylbenzenethiol (311 mg, 2.5 mmol) gave the title compound as yellow oil (283 mg), yield 92%. ^1H NMR (CDCl_3), δ : 2.45 (s, 6H), 7.14-7.17 (m, 6H), 7.52-7.55 (m, 2H). ^{13}C NMR, (CDCl_3), δ : 20.2, 126.8, 127.5, 128.9, 130.5, 135.6, 137.6.



1,2-Di-*m*-tolylidysulfane (2d).⁶ 3-Methylbenzenethiol (311 mg, 2.5 mmol) gave the title compound as yellow oil (292 mg), yield 95%. ^1H NMR (CDCl_3), δ : 2.34 (s, 6H), 7.05 (d, $J = 7.4$ Hz, 2H), 7.20 (t, $J = 7.9$ Hz, 2H), 7.31-7.33 (m, 4H). ^{13}C NMR, (CDCl_3), δ : 21.5, 124.8, 128.2, 128.3, 129.0, 137.1, 139.1.

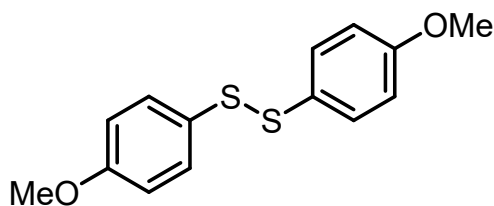


1,2-Bis(4-fluorophenyl)disulfane (2e).⁵ 4-Fluorobenzenethiol (320 mg, 2.5 mmol) gave the title compound as a yellow oil (311 mg), yield 98%. ^1H NMR (CDCl_3), δ : 7.01 (t, $J = 8.6$ Hz, 4H), 7.45 (dd, $J = 8.7, 5.2$ Hz, 4H). ^{13}C NMR, (CDCl_3), δ : 116.4 (d, $J = 22.2$ Hz), 131.5 (d, $J = 8.3$ Hz), 132.4 (d, $J = 3.4$ Hz), 162.8 (d, $J = 248.2$ Hz).

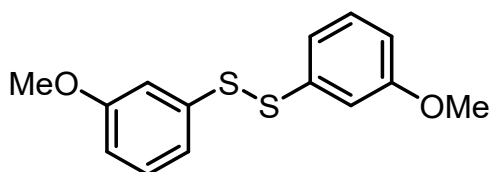


1,2-Bis(4-chlorophenyl)disulfane (2f).⁵ 4-Chlorobenzenethiol (362 mg, 2.5 mmol) gave the title compound as a yellow solid (350 mg), yield 98%. mp = 71.0-72.0 °C (lit. ⁵

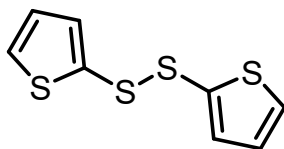
mp = 71.0-73.0 °C). ^1H NMR (CDCl_3), δ : 7.27 (d, J = 8.7 Hz, 4H), 7.40 (d, J = 8.4 Hz, 4H). ^{13}C NMR, (CDCl_3), δ : 129.4, 129.5, 133.8, 135.3.



1,2-Bis(4-methoxyphenyl)disulfane (2g).⁷ 4-Methoxybenzenethiol (351 mg, 2.5 mmol) gave the title compound as a white solid (331 mg), yield 95%. mp = 41.0-42.0 °C (lit. ⁷ mp = 41.0-43.0 °C). ^1H NMR (CDCl_3), δ : 3.80 (s, 6H), 6.84 (d, J = 8.7 Hz, 4H), 7.40 (d, J = 8.7 Hz, 4H). ^{13}C NMR, (CDCl_3), δ : 55.5, 114.7, 128.6, 132.8, 160.0.



1,2-Bis(3-methoxyphenyl)disulfane (2h).⁸ 3-Methoxybenzenethiol (351 mg, 2.5 mmol) gave the title compound as a brown oil (317 mg), yield 91%. ^1H NMR (CDCl_3), δ : 3.77 (s, 6H), 6.77 (dd, J = 7.7, 1.4 Hz, 2H), 7.08-7.10 (m, 4H), 7.21 (t, J = 8.0 Hz, 2H). ^{13}C NMR, (CDCl_3), δ : 55.4, 112.8, 113.3, 119.8, 130.0, 138.5, 160.2.

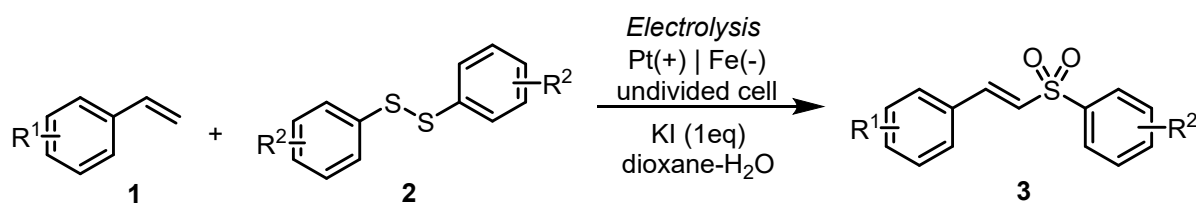


1,2-di(thiophen-2-yl)disulfane (2i). Thiophene-2-thiol (291 mg, 2.5 mmol) gave the title compound as a yellow solid (242 mg), yield 84%. mp = 52.0-53.0 °C (lit. ⁹ mp = 52.0-53.0 °C). ^1H NMR (CDCl_3), δ : 7.01 (dd, J = 5.3, 3.6 Hz, 2H), 7.16 (dd, J = 3.6, 1.1 Hz, 2H), 7.50 (dd, J = 5.3, 1.1 Hz, 2H). ^{13}C NMR, (CDCl_3), δ : 127.9, 132.4, 135.8, 135.8.

Electrochemical sulfonylation of styrenes with disulfides

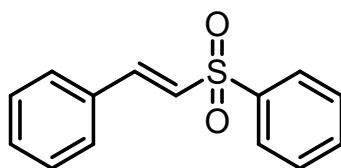
General procedure for the optimization of the reaction conditions for the synthesis of (*E*)-(2-(phenylsulfonyl)vinyl)benzene 3a from styrene 1a and diphenyl disulfide 2a (Table 1): An undivided cell was equipped with a platinum plate (3.4 cm²) or graphite anode (3.4 cm²) (entry 15) and a platinum (entries 1-11,16), graphite (entries 12,15), nickel plate (entry 13) or stainless steel plate cathode (entry 14) (5 cm² for each electrode) and connected to a DC regulated power supply. The solution of styrene **1a** (1 equiv, 1 mmol, 104 mg), diphenyl disulfide **2a** (109-218 mg, 0.5-1 mmol, 1-2 equiv), and supporting electrolyte (0.5-2 mmol, 0.5-2 equiv) in 20 mL of appropriate solvent was electrolyzed under constant current conditions for 90 min (entries 1-6), 150 min (entries 7, 9-16) or 190 min (entry 8) under magnetic stirring ($I = 50 \text{ mA}$, $j = 15 \text{ mA/cm}^2$) at 25-40 °C. After that, the reaction mixture was diluted with water (50 mL) and 1 M solution of Na₂S₂O₃ (10 mL). It was washed with EA (4×10 mL), which was used for the washing of electrodes after the reaction. Combined organic layer was washed with water (10 mL) and brine (10mL), dried over Na₂SO₄, and concentrated under reduced pressure. The yield of the desired product **3a** was determined by ¹H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

Electrosynthesis of vinyl sulfones **3** (Table 2).

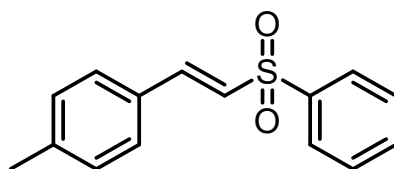


An undivided cell was equipped with a platinum plate anode (3.4 cm²) and a stainless steel plate cathode (5 cm²) and connected to a DC regulated power supply. The solution of styrene **1** (1 mmol), disulfide **2** (0.5 mmol), and KI (1 mmol) in 20 mL of 1,4-dioxane–water (1:1) was electrolyzed using constant current conditions ($I = 50 \text{ mA}$, $j = 15 \text{ mA/cm}^2$ at room temperature, $\tau = 150 \text{ min}$ or 210 min) under magnetic stirring. After that, the reaction mixture was diluted with water (50 mL) and 1 M solution of Na₂S₂O₃ (10 mL). It was washed with EA (4×10 mL), which was used for the washing of electrodes after the reaction. Combined organic layer was washed with water (10 mL) and brine (10mL), dried over Na₂SO₄, and concentrated under reduced pressure. The

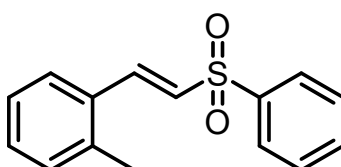
desired products **3aa-3ah** were isolated by chromatography on SiO₂ with elution using PE-EA in a gradient of the latter from 5 to 50 vol%.



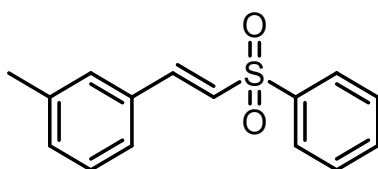
(E)-2-(phenylsulfonyl)vinylbenzene (3aa).¹⁰ White solid. 183 mg (yield 75%). R_f = 0.42 (PE:EA 5:1), mp = 70.0-71.0 °C (lit.¹⁰ mp = 71.0-73.0 °C). ¹H NMR (CDCl₃), δ: 6.86 (d, *J* = 15.4 Hz, 1H), 7.39-7.41 (m, 3H), 7.47-7.50 (m, 2H), 7.52-7.65 (m, 3H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.95-7.97 (m, 2H). ¹³C NMR (CDCl₃), δ: 127.6, 127.8, 128.7, 129.2, 129.5, 131.3, 132.6, 133.5, 140.9, 142.6



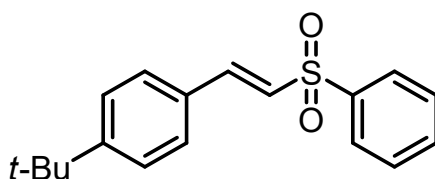
(E)-1-methyl-4-(2-(phenylsulfonyl)vinyl)benzene (3ba).¹¹ White solid. 140 mg (yield 54%). R_f = 0.46 (PE:EA 5:1), mp = 133.0-134.0 °C (lit.¹¹ mp = 134.1-136.3 °C). ¹H NMR (CDCl₃), δ: 2.36 (s, 3H), 6.81 (d, *J* = 15.4 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.51-7.61 (m, 3H), 7.66 (d, *J* = 15.3 Hz, 1H), 7.95 (d, *J* = 6.8 Hz, 2H). ¹³C NMR (CDCl₃), δ: 21.6, 126.2, 127.7, 128.7, 129.4, 129.7, 129.9, 133.4, 141.1, 141.9, 142.7.



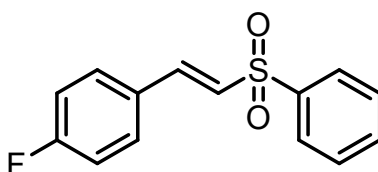
(E)-1-methyl-2-(2-(phenylsulfonyl)vinyl)benzene (3ca).¹² White solid. 196 mg (yield 76%). R_f = 0.40 (PE:EA 5:1), mp = 110.0-111.0 °C (lit.¹² mp = 112.0-115.0 °C). ¹H NMR (CDCl₃), δ: 2.45 (s, 3H), 6.79 (d, *J* = 15.3 Hz, 1H), 7.16-7.32 (m, 3H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.52-7.65 (m, 3H), 7.95-8.00 (m, 3H). ¹³C NMR, (CDCl₃) δ: 19.8, 126.6, 126.9, 127.7, 128.3, 129.4, 131.0, 131.1, 131.3, 133.4, 138.3, 140.2, 140.8.



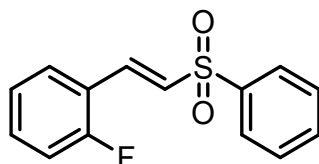
(E)-1-methyl-3-(2-(phenylsulfonyl)vinyl)benzene (3da).¹² White solid. 152 mg (yield 59%). $R_f = 0.44$ (PE:EA 5:1), mp = 104.0-105.0 °C (lit.¹² mp = 104.0-106.0 °C). ¹H NMR (CDCl₃), δ : 2.35 (s, 3H), 6.85 (d, $J = 15.4$ Hz, 1H), 7.20-7.24 (m, 1H), 7.27-7.29 (m, 3H), 7.52-7.61 (m, 3H), 7.66 (d, $J = 15.4$ Hz, 1H), 7.93-7.96 (m, 2H). ¹³C NMR (CDCl₃), δ : 21.3, 125.9, 127.2, 127.7, 129.0, 129.2, 129.4, 132.1, 132.5, 133.4, 138.9, 141.0, 142.8.



(E)-1-(tert-butyl)-4-(2-(phenylsulfonyl)vinyl)benzene (3ea).¹³ White solid. 156 mg (yield 52%). $R_f = 0.41$ (PE:EA 5:1), mp = 113.0-114.0 °C (lit.¹³ mp = 112.0-113.0 °C). ¹H NMR (CDCl₃), δ : 1.31 (s, 9H), 6.83 (d, $J = 15.4$ Hz, 1H), 7.39-7.45 (m, 4H), 7.51-7.63 (m, 3H), 7.68 (d, $J = 15.4$ Hz, 1H), 7.93-7.96 (m, 2H). ¹³C NMR (CDCl₃), δ : 31.2, 35.1, 126.2, 126.4, 127.7, 128.6, 129.4, 129.7, 133.3, 141.1, 142.6, 155.1.

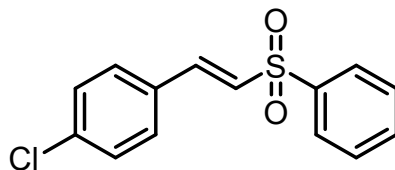


(E)-1-fluoro-4-(2-(phenylsulfonyl)vinyl)benzene (3fa).¹¹ White solid. 181 mg (yield 69%). $R_f = 0.35$ (PE:EA 5:1), mp = 107.0-108.0 °C (lit.¹¹ mp = 109.0-110.0 °C). ¹H NMR (CDCl₃), δ : 6.80 (d, $J = 15.4$ Hz, 1H), 7.04-7.10 (m, 2H), 7.45-7.67 (m, 6H), 7.93-7.95 (m, 2H). ¹³C NMR (CDCl₃), δ : 116.4 (d, $J = 22.1$ Hz), 127.2, 127.7, 128.8 (d, $J = 3.4$ Hz), 130.7 (d, $J = 8.8$ Hz), 133.5, 140.8, 141.3, 164.5 (d, $J = 253.1$ Hz).

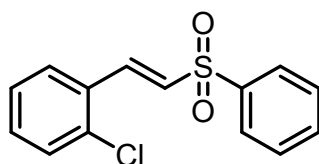


(E)-1-fluoro-2-(2-(phenylsulfonyl)vinyl)benzene (3ga).¹⁴ White solid. 158 mg (yield 60%). $R_f = 0.56$ (PE:EA 2:1), mp = 73.0-74.0 °C. ¹H NMR (CDCl₃), δ : 7.02 (d, $J = 15.6$ Hz, 1H), 7.07-7.19 (m, 2H), 7.35-7.49 (m, 2H), 7.52-7.65 (m, 3H), 7.76 (d, $J = 15.6$ Hz,

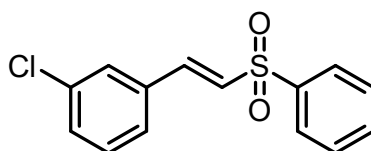
1H), 7.94-7.98 (m, 2H). ¹³C NMR (CDCl₃), δ: 116.5 (d, *J* = 21.7 Hz), 120.6 (d, *J* = 11.4 Hz), 124.8 (d, *J* = 3.7 Hz), 127.9, 129.5, 130.2 (d, *J* = 8.5 Hz), 130.4 (d, *J* = 2.6 Hz), 132.9 (d, *J* = 9.0 Hz), 133.6, 135.6 (d, *J* = 2.2 Hz), 140.6, 161.6 (d, *J* = 255.4 Hz).



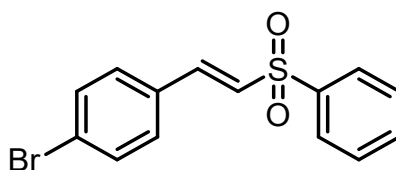
(E)-1-chloro-4-(2-(phenylsulfonyl)vinyl)benzene (3ha).¹¹ White solid. 187 mg (yield 67%). *R_f* = 0.8 (PE:EA 2:1), mp = 127.0-128.0 °C (lit.¹¹ mp = 128.0-130.0 °C). ¹H NMR (CDCl₃), δ: 6.85 (d, *J* = 15.4 Hz, 1H), 7.33-7.42 (m, 4H), 7.52-7.65 (m, 4H), 7.93-7.95 (m, 2H). ¹³C NMR (CDCl₃), δ: 127.8, 128.0, 129.5, 129.5, 129.8, 130.9, 133.6, 137.3, 140.6, 141.1.



(E)-1-chloro-2-(2-(phenylsulfonyl)vinyl)benzene (3ia).¹³ White solid. 201 mg (yield 72%). *R_f* = 0.72 (PE:EA 2:1), mp = 101.0-102.0 °C (lit.¹³ mp = 100.0-102.0 °C). ¹H NMR (CDCl₃), δ: 6.91 (d, *J* = 15.5 Hz, 1H), 7.24-7.36 (m, 2H), 7.41-7.64 (m, 1H), 7.50-7.66 (m, 4H), 7.96-7.98 (m, 2H), 8.08 (d, *J* = 15.5 Hz, 1H). ¹³C NMR (CDCl₃), δ: 127.3, 127.9, 128.4, 129.5, 130.3, 130.5, 130.8, 132.0, 133.6, 135.4, 138.5, 140.5

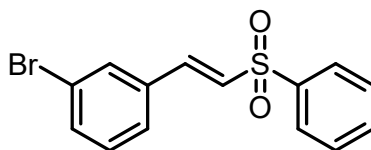


(E)-1-chloro-3-(2-(phenylsulfonyl)vinyl)benzene (3ja).¹⁵ White solid. 201 mg (yield 72%). *R_f* = 0.64 (PE:EA 2:1), mp = 100.0-101.0 °C (lit.¹⁵ mp = 98.0-100.0 °C). ¹H NMR (CDCl₃), δ: 6.88 (d, *J* = 15.4 Hz, 1H), 7.29-7.39 (m, 3H), 7.46 (s, 1H), 7.53-7.66 (m, 4H), 7.93-7.96 (m, 2H). ¹³C NMR (CDCl₃), δ: 126.9, 127.9, 128.3, 129.0, 129.5, 130.5, 131.2, 133.7, 134.2, 135.2, 140.4, 140.8.

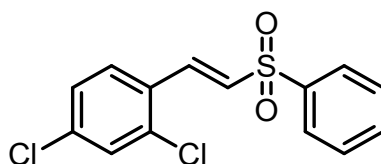


(E)-1-bromo-4-(2-(phenylsulfonyl)vinyl)benzene (3ka).¹¹ White solid. 165 mg (yield 51%). *R_f* = 0.81 (PE:EA 2:1), mp = 151.0-152.0 °C (lit.¹¹ mp = 152.0-154.0 °C). ¹H NMR

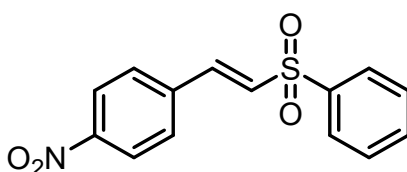
(CDCl₃), δ : 6.86 (d, J = 15.4 Hz, 1H), 7.32-7.35 (m, 2H), 7.50-7.64 (m, 6H), 7.93-7.95 (m, 2H). ¹³C NMR, (CDCl₃) δ : 125.8, 127.8, 128.3, 129.5, 130.0, 131.5, 132.5, 133.6, 140.7, 141.2.



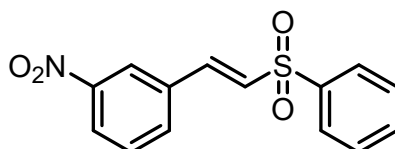
(E)-1-bromo-3-(2-(phenylsulfonyl)vinyl)benzene (3la).¹⁶ White solid. 217 mg (yield 67%). R_f = 0.74 (PE:EA 2:1), mp = 99.0-100.0 °C (lit.¹⁶ mp = 100.0-103.0 °C). ¹H NMR (CDCl₃), δ : 6.87 (d, J = 15.5 Hz, 1H), 7.23-7.29 (m, 1H), 7.39-7.41 (m, 1H), 7.51-7.66 (m, 6H), 7.93-7.96 (m, 2H). ¹³C NMR (CDCl₃), δ : 123.3, 127.4, 127.9, 129.2, 129.5, 130.7, 131.2, 133.7, 134.1, 134.6, 140.5, 140.7.



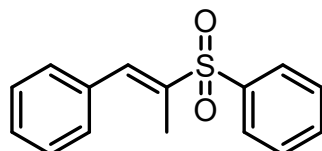
(E)-2,4-dichloro-1-(2-(phenylsulfonyl)vinyl)benzene (3ma).¹⁷ White solid. 213 mg (yield 68%). R_f = 0.74 (PE:EA 2:1), mp = 126.0-127.0 °C. ¹H NMR (CDCl₃), δ : 6.89 (d, J = 15.4 Hz, 1H), 7.23-7.26 (m, 1H), 7.43-7.45 (m, 2H), 7.54-7.67 (m, 3H), 7.94-8.02 (m, 3H). ¹³C NMR, (CDCl₃) δ : 127.9, 128.0, 129.1, 129.5, 129.6, 130.4, 130.8, 133.8, 136.1, 137.2, 137.5, 140.3. HRMS (ESI) m/z (M+H⁺) calculated for [C₁₄H₁₁³⁵Cl₂O₂S]⁺: 312.9850. Found: 312.9851.



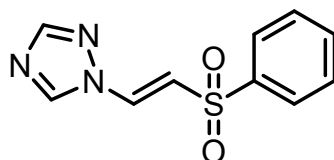
(E)-1-nitro-4-(2-(phenylsulfonyl)vinyl)benzene (3na).¹¹ White solid. 191 mg (yield 66%). R_f = 0.67 (PE:EA 2:1), mp = 170.0-171.0 °C (lit.¹¹ mp = 170.0-172.0 °C). ¹H NMR (CDCl₃), δ : 7.03 (d, J = 15.5 Hz, 1H), 7.55-7.60 (m, 2H), 7.64-7.66 (m, 3H), 7.72 (d, J = 15.5 Hz, 1H), 7.94-7.97 (m, 2H), 8.22-8.25 (m, 2H). ¹³C NMR (CDCl₃), δ : 124.4, 128.0, 129.4, 129.7, 131.8, 134.0, 138.5, 139.4, 139.8, 149.1.



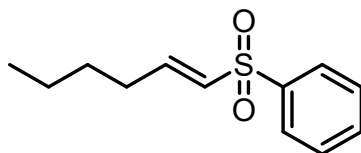
(E)-1-nitro-3-(2-(phenylsulfonyl)vinyl)benzene (30a).¹¹ White solid. 217 mg (yield 75%). $R_f = 0.49$ (PE:EA 2:1), mp = 136.0-137.0 °C (lit.¹¹ mp = 136.0-138.0 °C). ¹H NMR (CDCl₃), δ : 7.04 (d, $J = 15.5$ Hz, 1H), 7.55-7.81 (m, 6H), 7.95-7.97 (m, 2H), 8.23-8.26 (m, 1H), 8.33 (s, 1H). ¹³C NMR, (CDCl₃) δ : 122.9, 125.4, 127.9, 129.6, 130.4, 130.9, 133.9, 134.3, 134.4, 139.5, 140.0, 148.8.



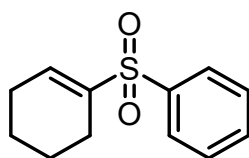
(E)-((1-phenylprop-1-en-2-yl)sulfonyl)benzene (3pa).¹⁸ White solid. 83 mg (yield 32%). $R_f = 0.43$ (PE:EA 5:1), mp = 85.0-86.0 °C (lit. ¹⁸ mp = 84.0-86.0 °C). ¹H NMR (CDCl₃), δ : 2.12 (s, 3H), 7.34-7.45 (m, 5H), 7.52-7.65 (m, 3H), 7.83 (s, 1H), 7.92-7.94 (m, 2H). ¹³C NMR, (CDCl₃) δ : 13.3, 128.3, 128.8, 128.9, 129.2, 129.3, 129.7, 133.4, 133.9, 137.4, 137.6.



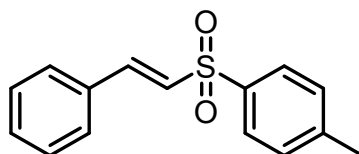
(E)-1-(2-(phenylsulfonyl)vinyl)-1H-1,2,4-triazole (3qa). White solid. 96 mg (yield 41%). $R_f = 0.36$ (PE:EA 1:1), mp = 168.0-169.0 °C. ¹H NMR (CDCl₃), δ : 7.12 (d, $J = 13.2$ Hz, 1H), 7.54-7.59 (m, 2H), 7.63-7.68 (m, 1H), 7.93-7.95 (m, 2H), 8.05 (s, 1H), 8.10 (d, $J = 13.3$ Hz, 1H), 8.40 (s, 1H). ¹³C NMR, (CDCl₃) δ : 120.5, 127.8, 129.7, 133.1, 134.1, 140.1, 145.7, 154.2. HRMS (ESI) m/z ($M+H^+$) calculated for [C₁₀H₁₀N₃O₂S]⁺: 236.0488. Found: 236.0492.



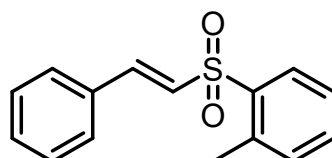
(E)-(hex-1-en-1-ylsulfonyl)benzene (3ra).¹⁹ Colorless oil. 47 mg (yield 21%). $R_f = 0.55$ (PE:EA 5:1). ¹H NMR (CDCl₃), δ : 0.88 (t, $J = 7.2$ Hz, 3H), 1.30-1.48 (m, 4H), 2.19-2.27 (m, 2H), 6.30 (d, $J = 15.1$ Hz, 1H), 6.94 (td, $J = 14.9$ Hz, 6.9 Hz 1H), 7.49-7.62 (m, 3H), 7.85-7.93 (m, 2H). ¹³C NMR, (CDCl₃) δ : 13.8, 22.2, 29.8, 31.3, 127.6, 129.3, 129.3, 130.4, 133.3, 140.9, 147.4.



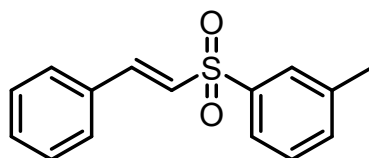
(Cyclohex-1-en-1-ylsulfonyl)benzene (3sa).¹⁹ Colorless oil. 22 mg (yield 10%). $R_f = 0.37$ (PE:EA 5:1). $^1\text{H NMR}$ (CDCl_3), δ : 1.53-1.68 (m, 4H), 2.16-2.28 (m, 4H), 7.06 (s, 1H), 7.50-7.63 (m, 3H), 7.84-7.87 (m, 2H). $^{13}\text{C NMR}$, (CDCl_3) δ : 20.9, 21.9, 22.9, 25.6, 128.1, 129.2, 133.2, 138.6, 139.6, 139.9.



(E)-1-methyl-4-(styrylsulfonyl)benzene (3ab).¹⁰ White solid. 158 mg (yield 61%). $R_f = 0.71$ (PE:EA 2:1), mp = 125.0-126.0 °C (lit.¹⁰ mp = 124.0-124.9 °C). $^1\text{H NMR}$ (CDCl_3), δ : 2.43 (s, 3H), 6.85 (d, $J = 15.4$ Hz, 1H), 7.33-7.40 (m, 5H), 7.46-7.48 (m, 2H), 7.66 (d, $J = 15.4$ Hz, 1H), 7.82-7.84 (m, 2H). $^{13}\text{C NMR}$ (CDCl_3), δ : 21.7, 127.9, 128.6, 129.2, 130.1, 131.2, 132.6, 137.9, 142.1, 144.5.

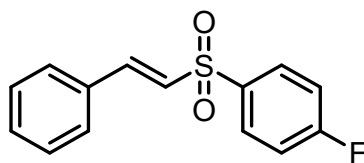


(E)-1-methyl-2-(styrylsulfonyl)benzene (3ac).¹⁰ Yellow oil. 202 mg (yield 78%). $R_f = 0.78$ (PE:EA 2:1). $^1\text{H NMR}$ (CDCl_3), δ : 2.64 (s, 3H), 6.85 (d, $J = 15.4$ Hz, 1H), 7.29-7.32 (m, 1H), 7.37-7.41 (m, 4H), 7.48-7.53 (m, 3H), 7.69 (d, $J = 15.4$ Hz, 1H), 8.10-8.13 (m, 1H). $^{13}\text{C NMR}$ (CDCl_3), δ : 20.4, 126.8, 127.0, 128.7, 129.2, 129.6, 131.3, 132.6, 132.7, 133.7, 138.2, 138.6, 142.9.

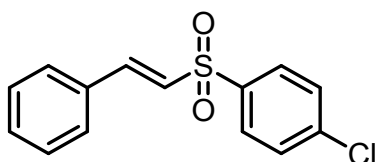


(E)-1-methyl-3-(styrylsulfonyl)benzene (3ad).¹⁰ Yellow oil. 98 mg (yield 38%). $R_f = 0.78$ (PE:EA 2:1). $^1\text{H NMR}$ (CDCl_3), δ : 2.42 (s, 3H), 6.87 (d, $J = 15.4$ Hz, 1H), 7.37-7.43 (m, 5H), 7.46-7.49 (m, 2H), 7.67 (d, $J = 15.4$ Hz, 1H), 7.74-7.76 (m, 2H). $^{13}\text{C NMR}$

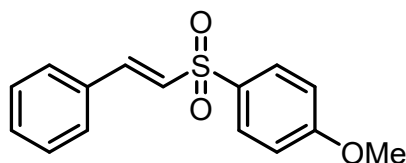
(CDCl₃), δ : 21.4, 124.8, 127.6, 128.0, 128.6, 129.1, 129.3, 131.2, 132.2, 134.2, 139.7, 140.7, 142.3.



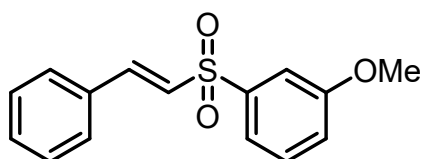
(E)-1-fluoro-4-(styrylsulfonyl)benzene (3ae).¹⁰ White solid. 168 mg (yield 64%). R_f = 0.77 (PE:EA 2:1), mp = 78.0-79.0 °C (lit.¹⁰ mp = 78.8-80.1 °C). ¹H NMR (CDCl₃), δ : 6.85 (d, J = 15.4 Hz, 1H), 7.22 (t, J = 8.5 Hz, 2H), 7.39-7.41 (m, 3H), 7.47-7.50 (m, 3H), 7.68 (d, J = 15.4 Hz, 1H), 7.97 (dd, J = 8.7, 5.1 Hz, 2H). ¹³C NMR (CDCl₃), δ : 116.8 (d, J = 22.7 Hz), 127.3, 128.7, 129.3, 130.6 (d, J = 9.5 Hz), 131.5, 132.4, 137.0 (d, J = 2.2 Hz), 142.8, 165.8 (d, J = 255.9 Hz).



(E)-1-chloro-4-(styrylsulfonyl)benzene (3af).¹⁰ White solid. 162 mg (yield 58%). R_f = 0.77 (PE:EA 2:1), mp = 85.0-86.0 °C (lit.¹⁰ mp = 83.4-84.5 °C). ¹H NMR (CDCl₃), δ : 6.84 (d, J = 15.4 Hz, 1H), 7.39-7.44 (m, 3H), 7.45-7.53 (m, 4H), 7.69 (d, J = 15.4 Hz, 1H), 7.88 (d, J = 8.6 Hz, 2H). ¹³C NMR (CDCl₃), δ : 127.1, 128.8, 129.3, 129.3, 129.8, 131.5, 132.4, 139.5, 140.2, 143.2.



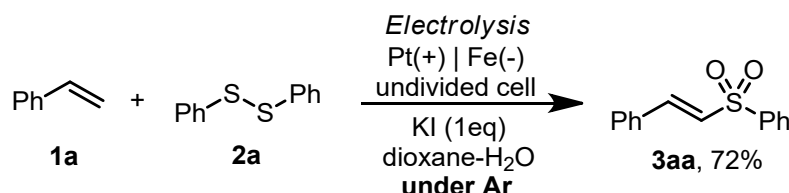
(E)-1-methoxy-4-(styrylsulfonyl)benzene (3ag).¹³ White solid. 168 mg (yield 62%). R_f = 0.56 (PE:EA 2:1), mp = 73.0-74.0 °C (lit.¹³ mp = 74.0-75.0 °C). ¹H NMR (CDCl₃), δ : 3.87 (s, 3H), 6.84 (d, J = 15.4 Hz, 1H), 7.00 (d, J = 8.7 Hz, 2H), 7.38-7.39 (m, 3H), 7.45-7.48 (m, 2H), 7.63 (d, J = 15.4 Hz, 1H), 7.87 (d, J = 8.7 Hz, 2H). ¹³C NMR (CDCl₃), δ : 55.8, 114.7, 128.2, 128.6, 129.2, 130.0, 131.1, 132.4, 132.7, 141.5, 163.7.



conditions ($I = 100 \text{ mA}$, $j = 15 \text{ mA/cm}^2$ at room temperature, $\tau = 2 \text{ h}$ and 30 min) under magnetic stirring. After that, the reaction mixture was diluted with water (100 mL) and 1 M solution of $\text{Na}_2\text{S}_2\text{O}_3$ (20 mL). It was washed with EA (4×20 mL), which was used for the washing of electrodes after the reaction. Combined organic layer was washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The desired product **3aa** was isolated by chromatography on SiO_2 with elution using PE-EA in a gradient of the latter from 5 to 50 vol%. Yield 72% (352 mg).

Experimental details for control experiments (Scheme 3).

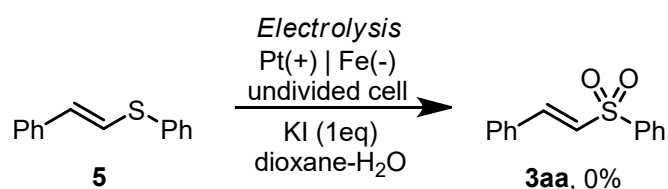
Electrosynthesis of (*E*)-(2-(phenylsulfonyl)vinyl)benzene **3aa** from styrene **1a** and diphenyl disulfide **2a** under an inert atmosphere (Scheme 3a).



An undivided cell was equipped with a platinum plate anode (3.4 cm²) and a stainless steel plate cathode (5 cm²) and connected to a DC regulated power supply. Argon was bubbled through the solution of styrene **1** (1 mmol), disulfide **2** (0.5 mmol), and KI (1 mmol) in 20 mL of 1,4-dioxane–water (1:1). Electrolysis was conducted with argon bubbling using constant current conditions ($I = 50 \text{ mA}$, $j = 15 \text{ mA/cm}^2$ at room temperature, $\tau = 150 \text{ min}$) under magnetic stirring. After that, the reaction mixture was diluted with water (50 mL) and 1 M solution of $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL). It was washed with EA (4×10 mL), which was used for the washing of electrodes after the reaction. Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The yield of the desired product **3aa** was determined by ¹H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

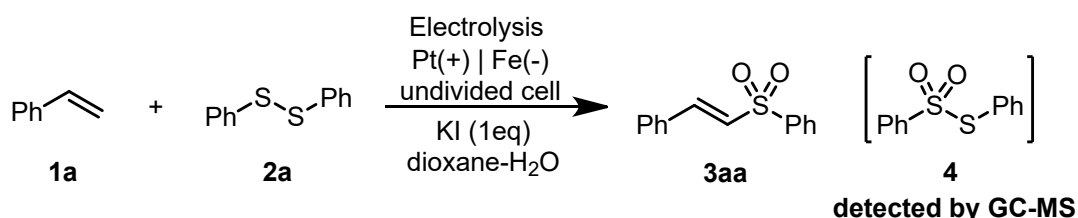
Attempt of conversion of (*E*)-phenyl(styryl)sulfane **5** into (*E*)-(2-(phenylsulfonyl)vinyl)benzene **3aa** (Scheme 3b).

(*E*)-phenyl(styryl)sulfane **5** was prepared according to the literature.²¹



An undivided cell was equipped with a platinum plate anode (3.4 cm²) and a stainless steel plate cathode (5 cm²) and connected to a DC regulated power supply. The solution of (*E*)-phenyl(styryl)sulfane **5** (1 mmol) and KI (1 mmol) in 20 mL of 1,4-dioxane–water (1:1) was electrolyzed using constant current conditions (*I* = 50 mA, *j* = 15 mA/cm² at room temperature, τ = 150 min). After that, the reaction mixture was diluted with water (50 mL) and 1 M solution of Na₂S₂O₃ (10 mL). It was washed with EA (4×10 mL), which was used for the washing of electrodes after the reaction. Combined organic layer was washed with water (10 mL) and brine (10mL), dried over Na₂SO₄, and concentrated under reduced pressure. The analysis of the reaction mixture with ¹H NMR spectroscopy (1,4-dinitrobenzene as an internal standard) demonstrated full recovery of the starting sulfide **5**. The desired sulfone **3aa** was not formed.

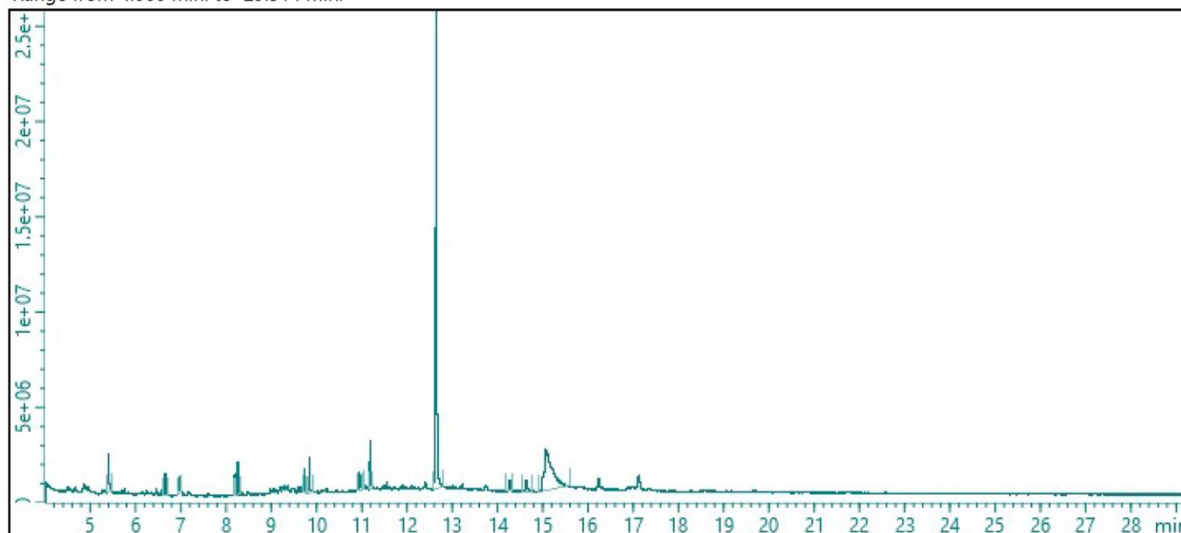
GC-MS analysis of the reaction mixture after electrosynthesis of (*E*)-(2-(phenylsulfonyl)vinyl)benzene **3aa**



An undivided cell was equipped with a platinum plate anode (3,4 cm²) and a stainless-steel plate cathode (5 cm²) and connected to a DC regulated power supply. The solution of styrene **1a** (1 mmol), disulfide **2a** (0.5 mmol) and electrolyte KI (1 mmol) in 20 mL of 1,4-dioxane–water (1:1) was electrolyzed using constant current conditions (*I* = 50 mA, *j* = 15 mA/cm² at room temperature, τ = 150 min or 210 min) under magnetic stirring. After that the reaction mixture was analyzed as is with GC-MS to detect key intermediates.

Chromatogram:

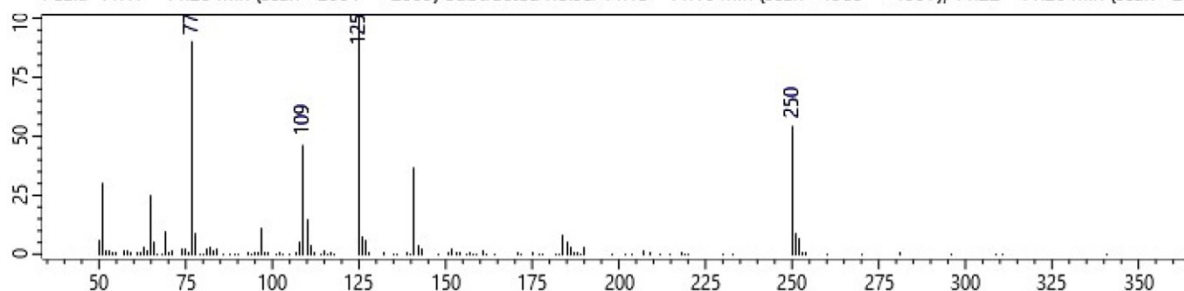
Range from 4.000 min. to 29.314 min.



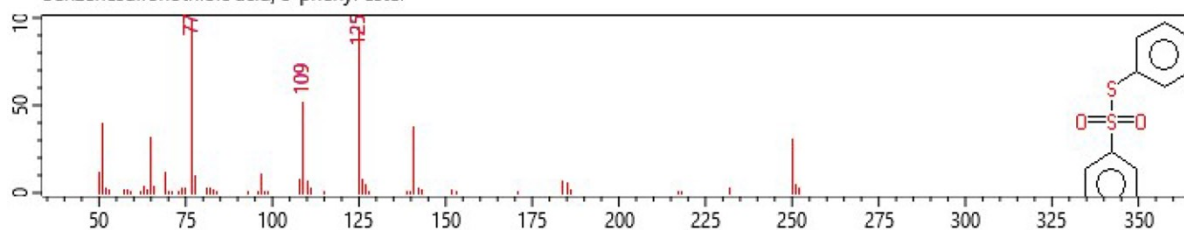
Formation of the intermediate 4

Benzenesulfonothioic acid, S-phenyl ester

Peak: 11.17 - 11.20 min (scan #2001 - #2009) Subtracted noise: 11.13 - 11.16 min (scan #1989 - #1997), 11.22 - 11.26 min (scan #20



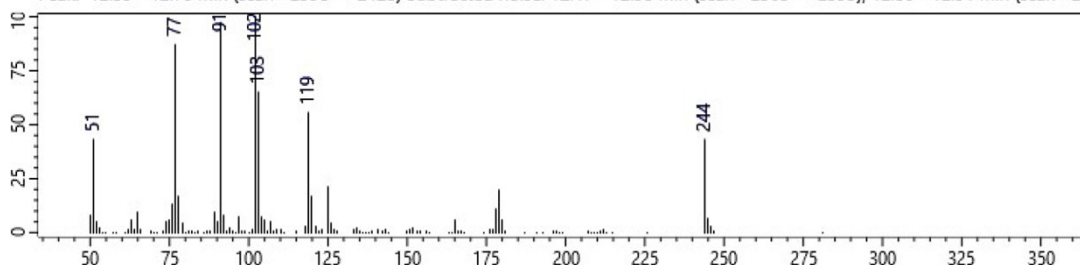
Benzenesulfonothioic acid, S-phenyl ester



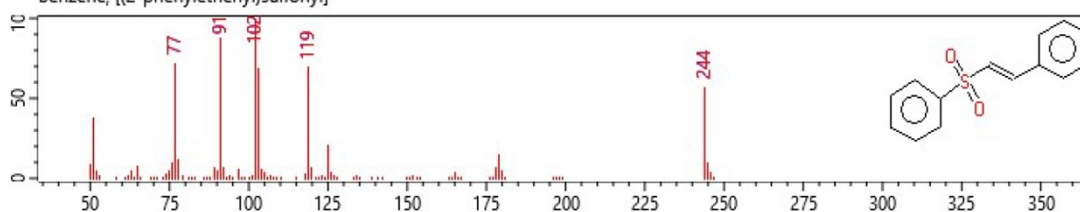
Formation of the final product 3aa:

Benzene, [(2-phenylethenyl)sulfonyl]-

Peak: 12.59 - 12.70 min (scan #2398 - #2428) Subtracted noise: 12.47 - 12.58 min (scan #2363 - #2393), 12.80 - 12.91 min (scan #24

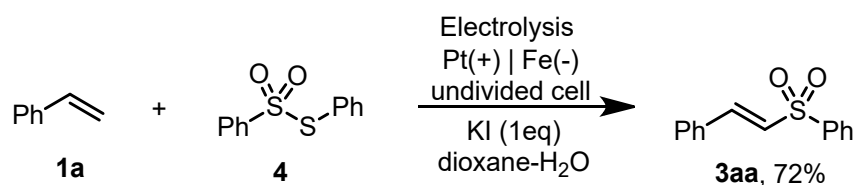


Benzene, [(2-phenylethenyl)sulfonyl]-



Electrosynthesis of (*E*)-(2-(phenylsulfonyl)vinyl)benzene **3aa** from styrene **1a** and *S*-phenyl benzenesulfonothioate **4** (Scheme 3d).

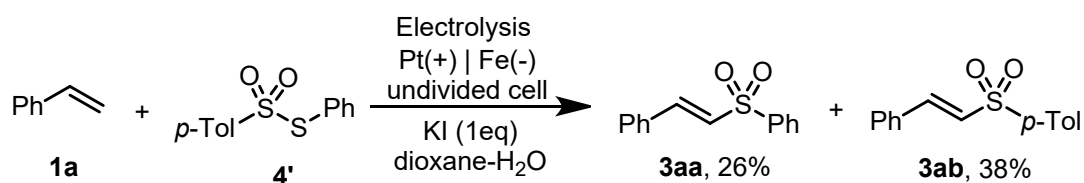
S-phenyl benzenesulfonothioate **5** was prepared according to the literature.²²



An undivided cell was equipped with a platinum plate anode (3.4 cm²) and a stainless steel plate cathode (5 cm²) and connected to a DC regulated power supply. The solution of styrene **1a** (1 mmol), *S*-phenyl benzenesulfonothioate **4** (0.5 mmol), and KI (1 mmol) in 20 mL of 1,4-dioxane–water (1:1) was electrolyzed using constant current conditions ($I = 50$ mA, $j = 15$ mA/cm² at room temperature, $\tau = 150$ min). After that, the reaction mixture was diluted with water (50 mL) and 1 M solution of Na₂S₂O₃ (10 mL). It was washed with EA (4×10 mL), which was used for the washing of electrodes after the reaction. Combined organic layer was washed with water (10 mL) and brine (10 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The yield of the desired product **3aa** was determined by ¹H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

Electrolysis of styrene **1a** and *S*-phenyl 4-methylbenzenesulfonothioate **4'** (Scheme 3e).

S-phenyl 4-methylbenzenesulfonothioate **4'** was prepared according to the literature.²³



An undivided cell was equipped with a platinum plate anode (3.4 cm²) and a stainless steel plate cathode (5 cm²) and connected to a DC regulated power supply. The solution of styrene **1a** (1 mmol), *S*-phenyl 4-methylbenzenesulfonothioate **4'** (0.5 mmol), and KI (1 mmol) in 20 mL of 1,4-

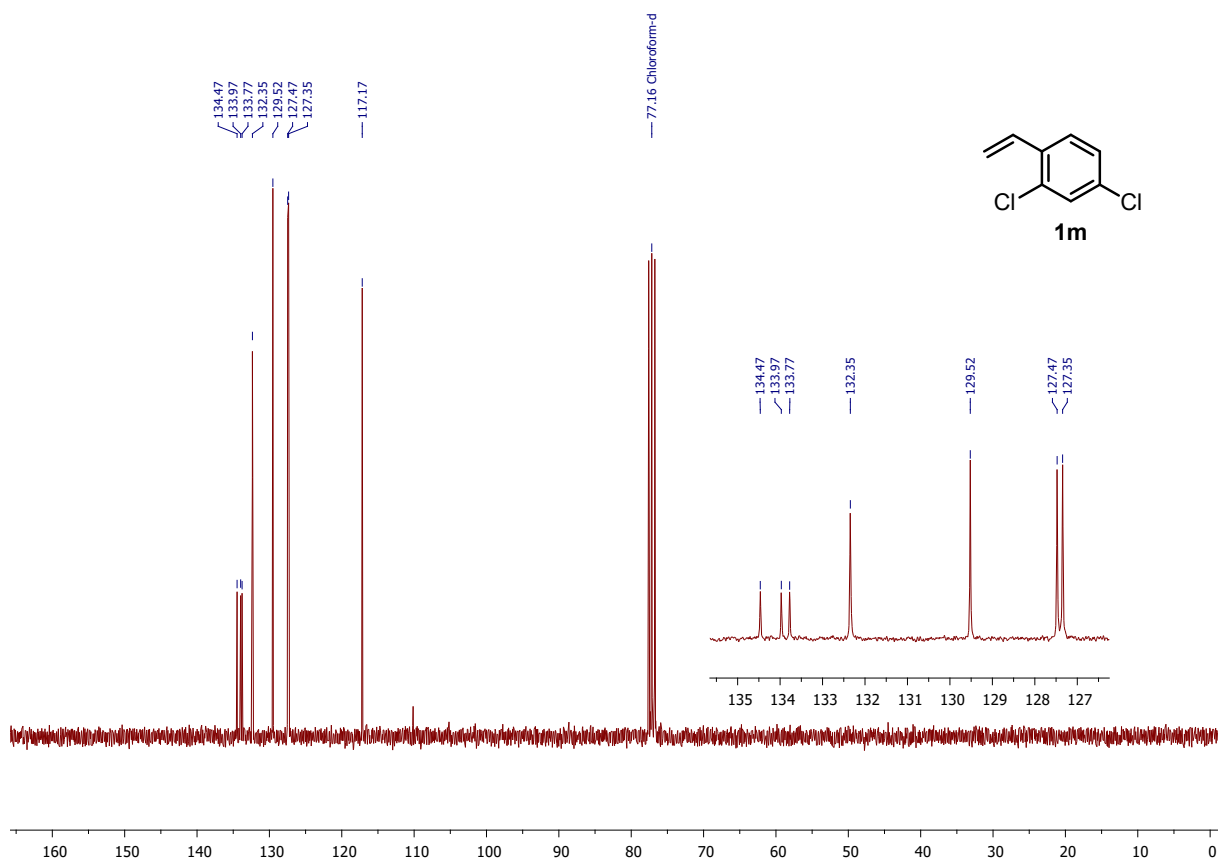
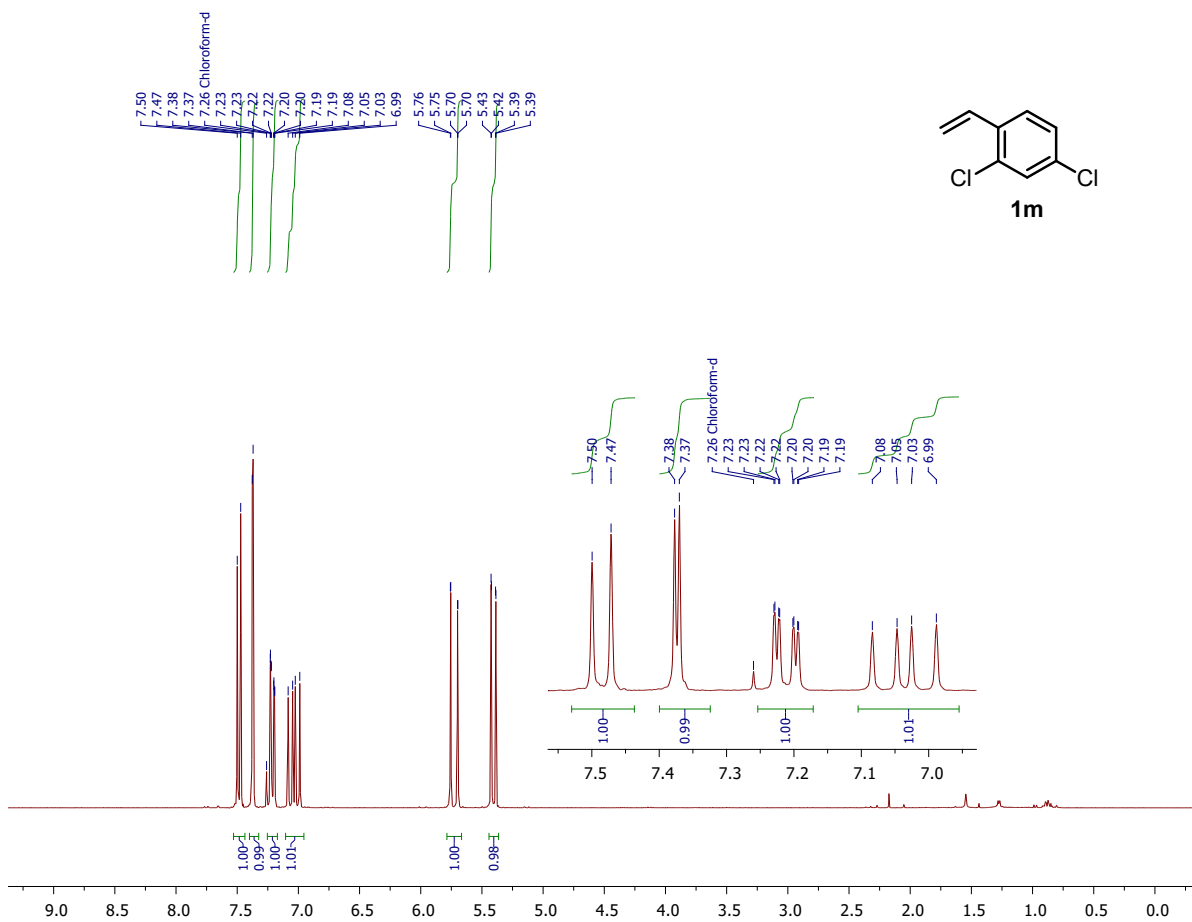
dioxane–water (1:1) was electrolyzed using constant current conditions ($I = 50 \text{ mA}$, $j = 15 \text{ mA/cm}^2$ at room temperature, $\tau = 150 \text{ min}$). After that, the reaction mixture was diluted with water (50 mL) and 1 M solution of $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL). It was washed with EA (4×10 mL), which was used for the washing of electrodes after the reaction. Combined organic layer was washed with water (10 mL) and brine (10mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The yield of the desired products **3aa** and **3ab** was determined by ^1H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard.

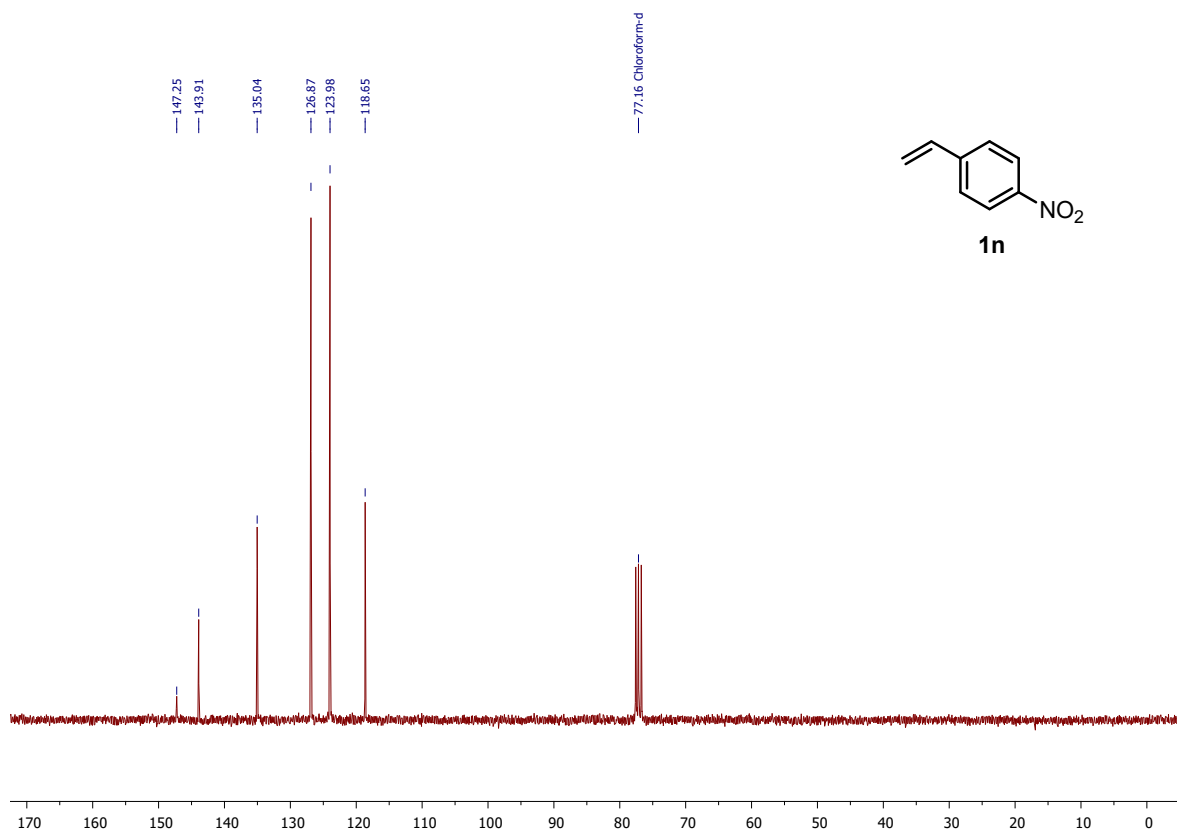
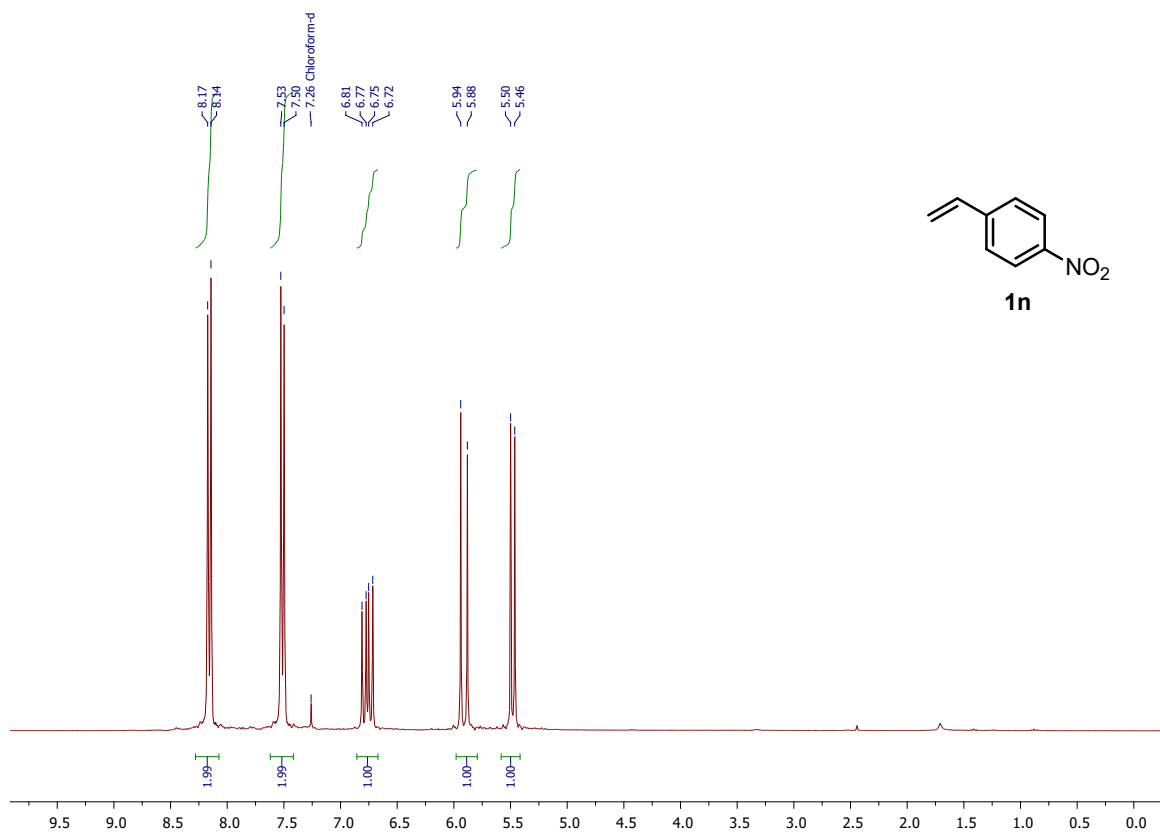
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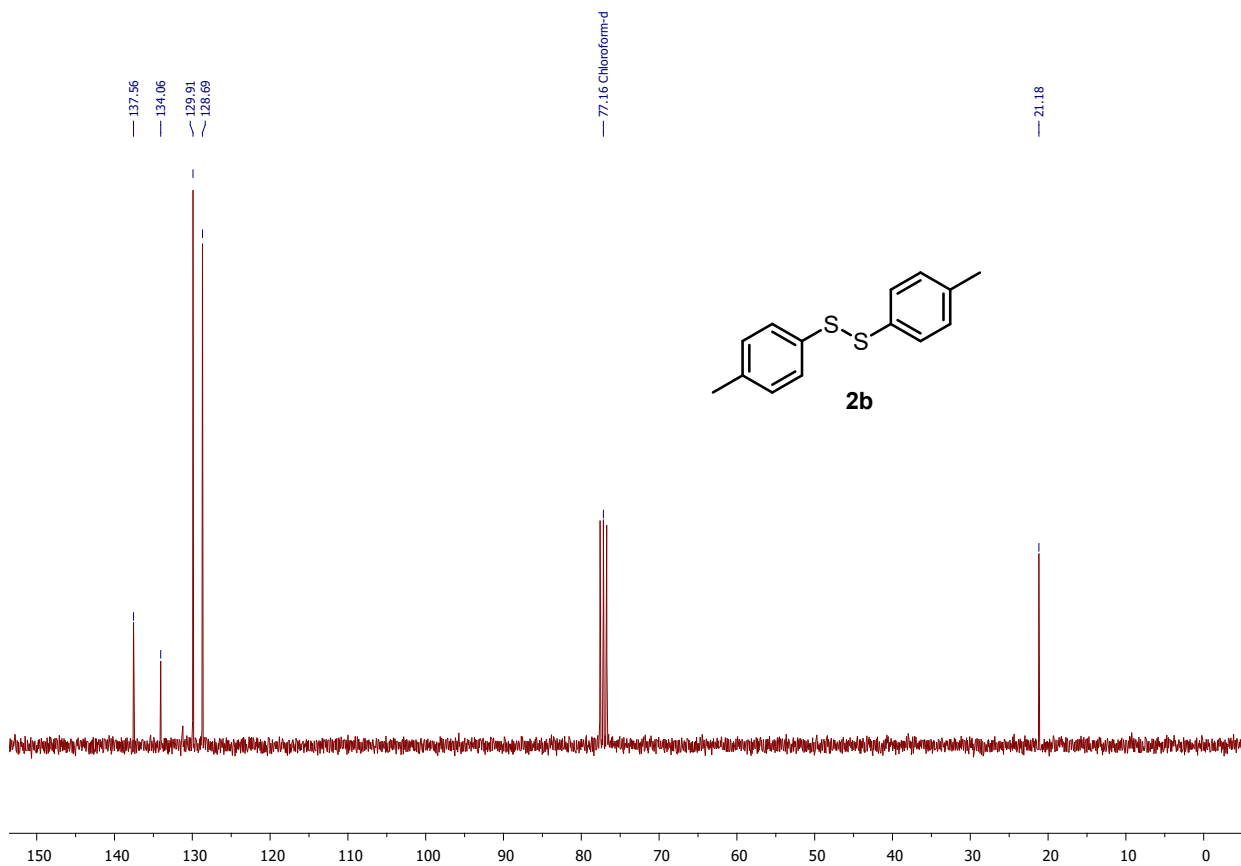
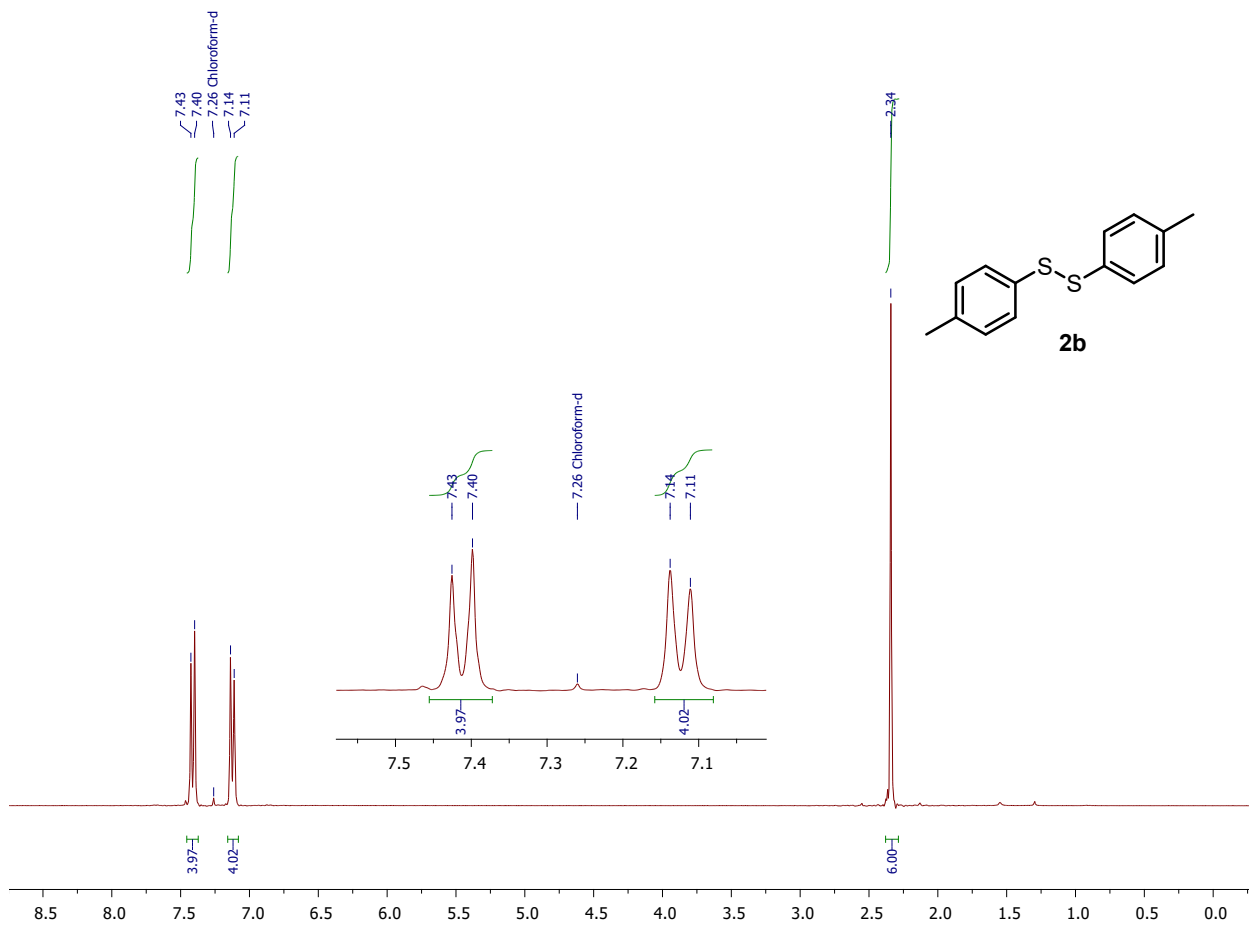
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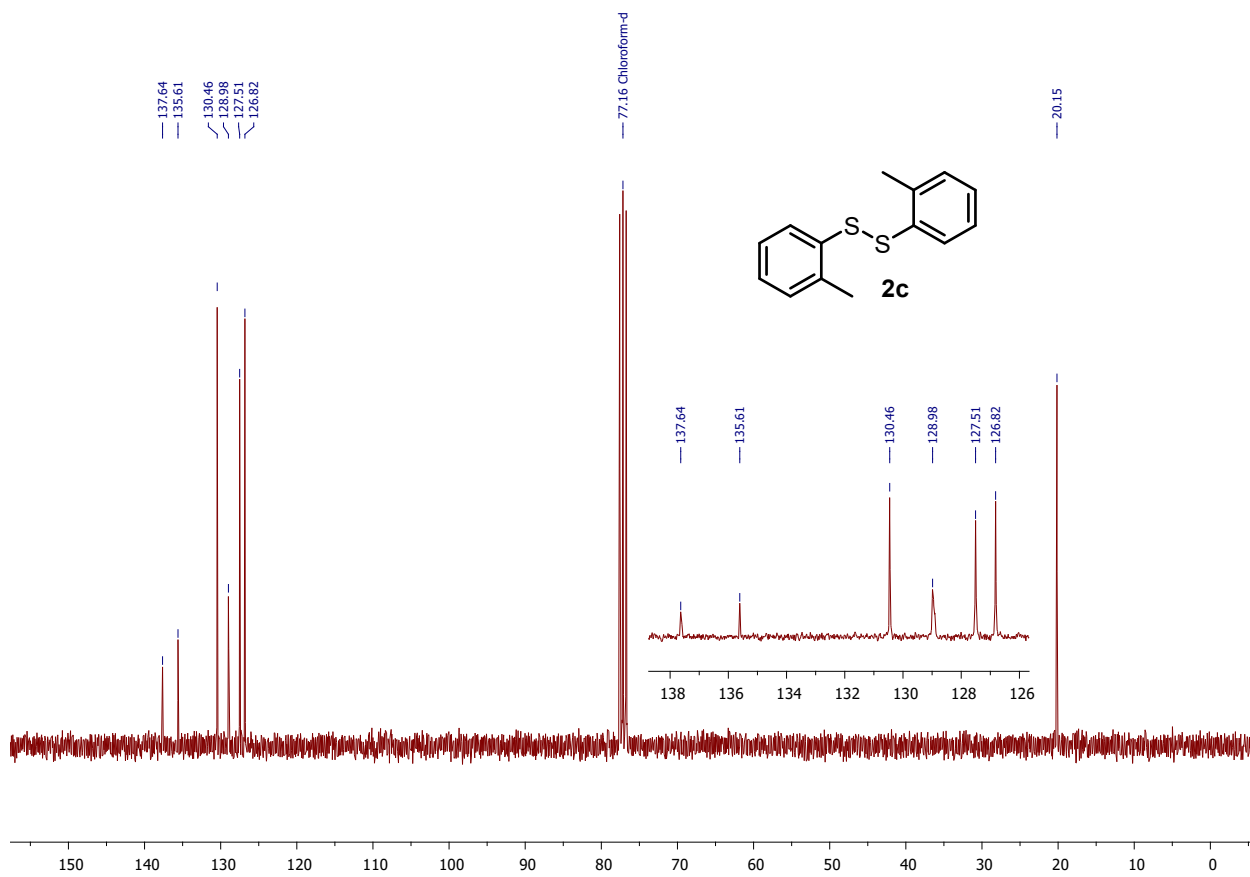
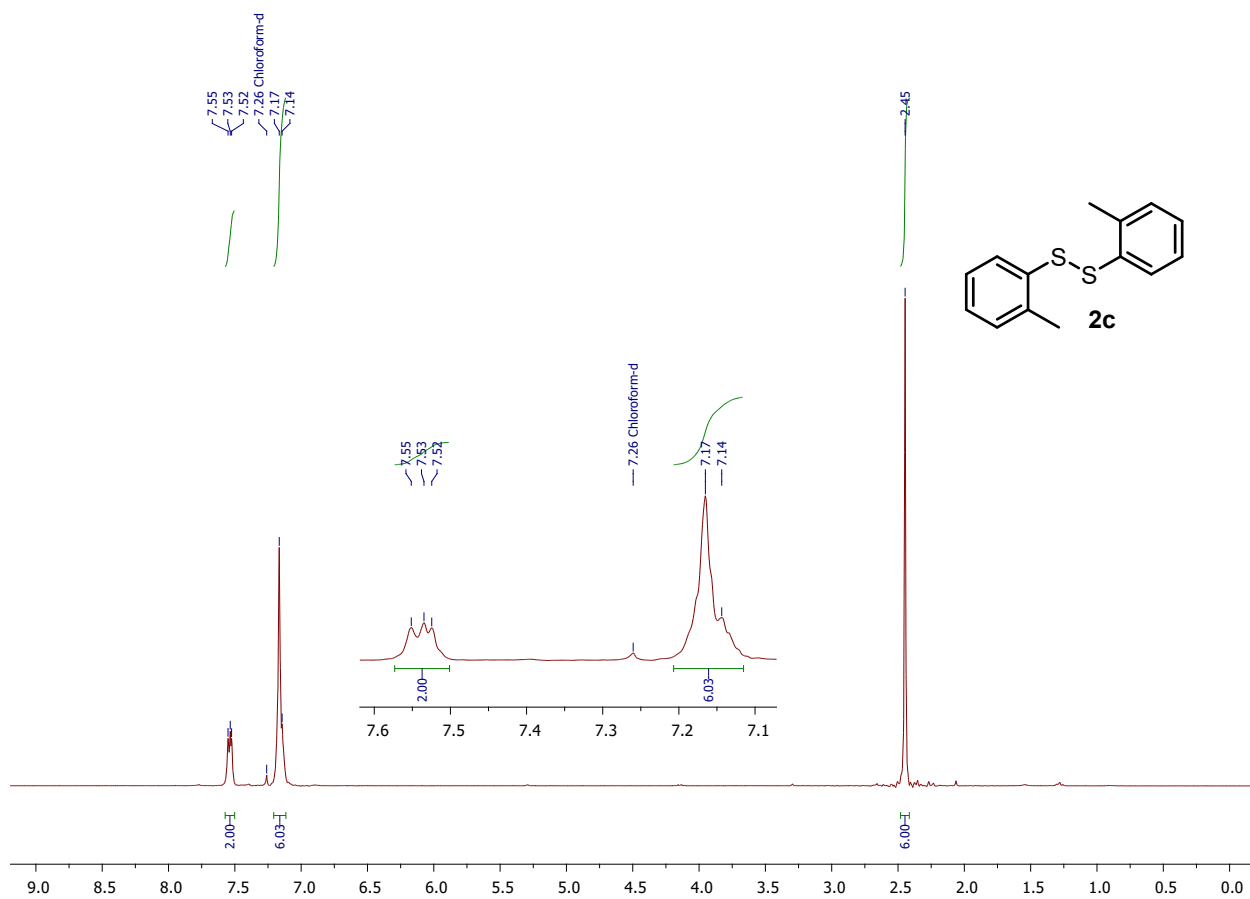
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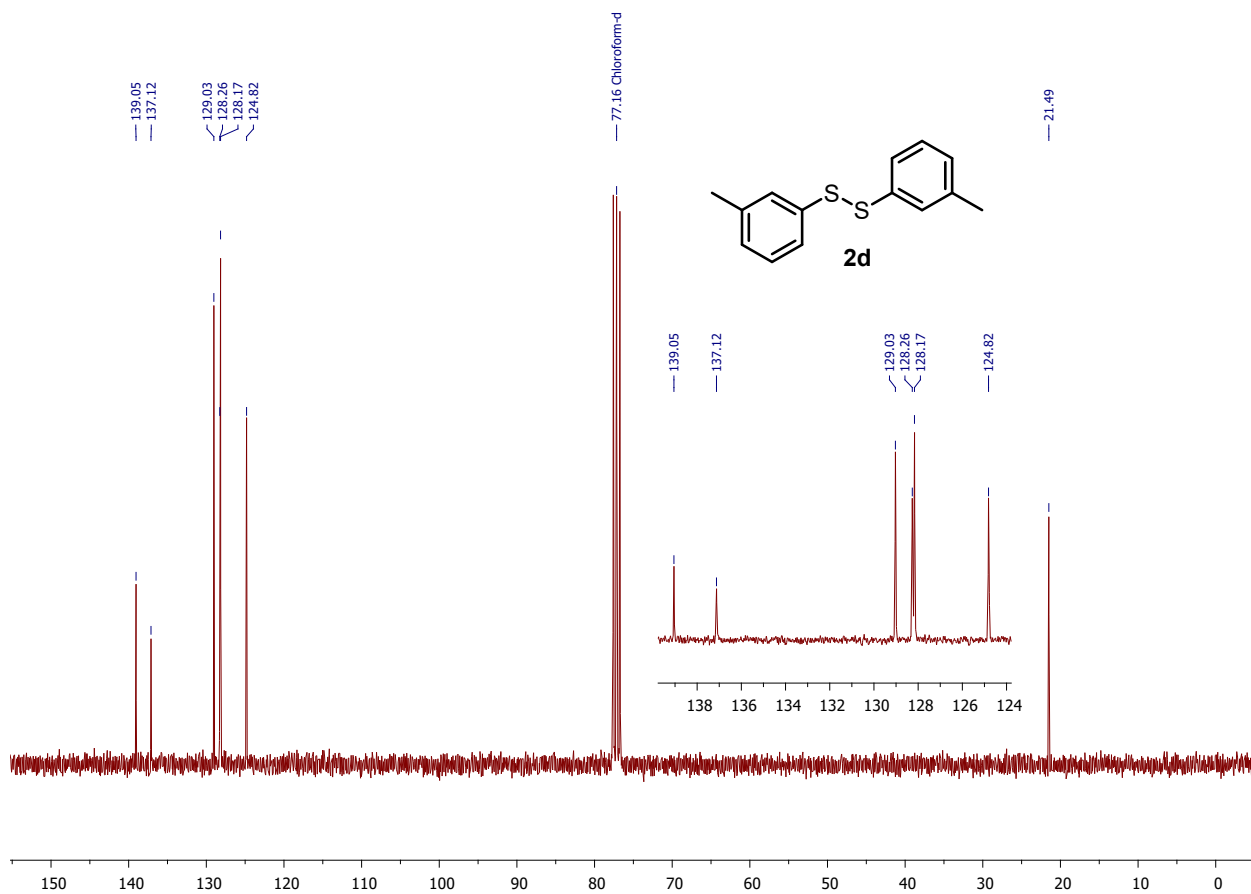
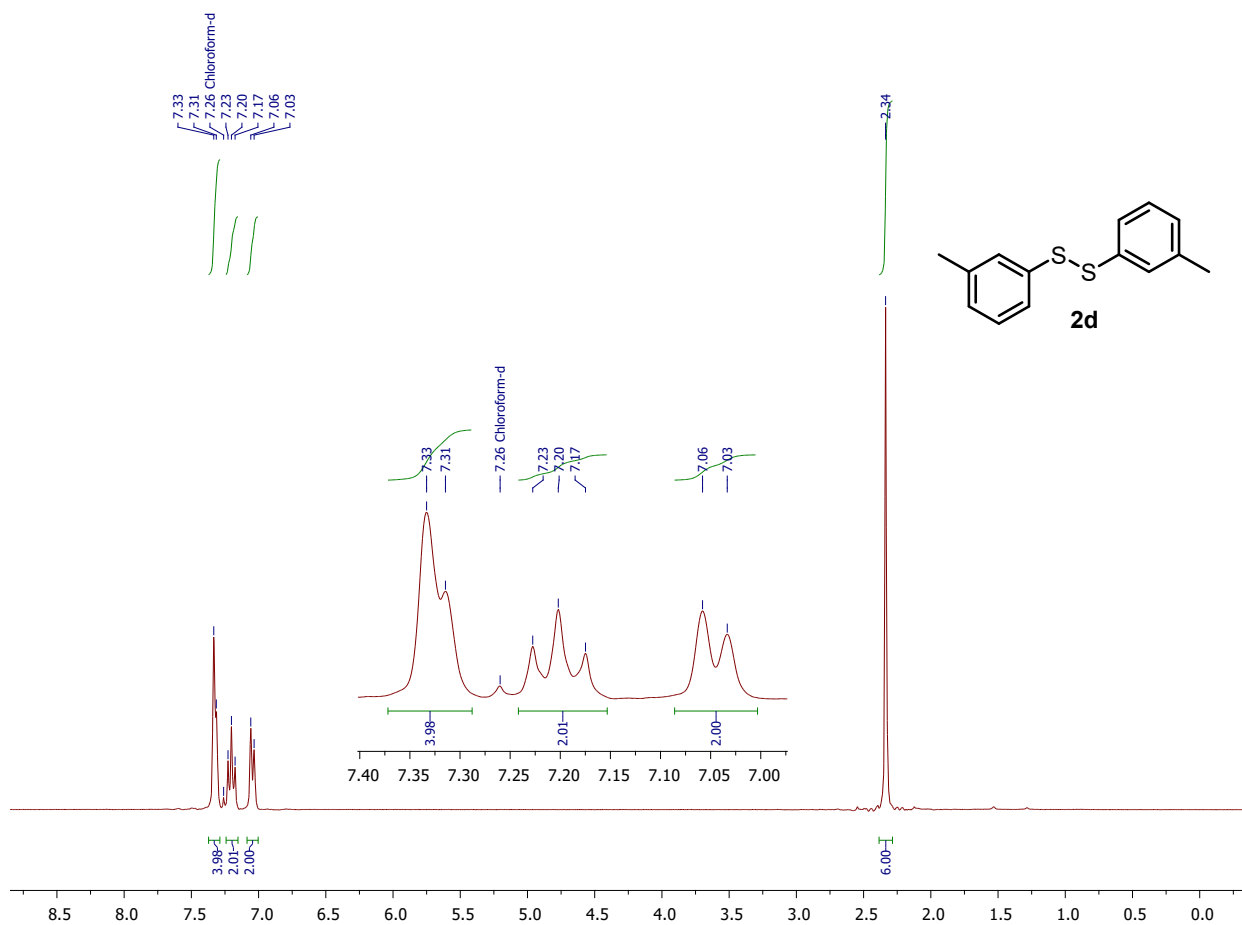
NMR spectra of synthesized compounds

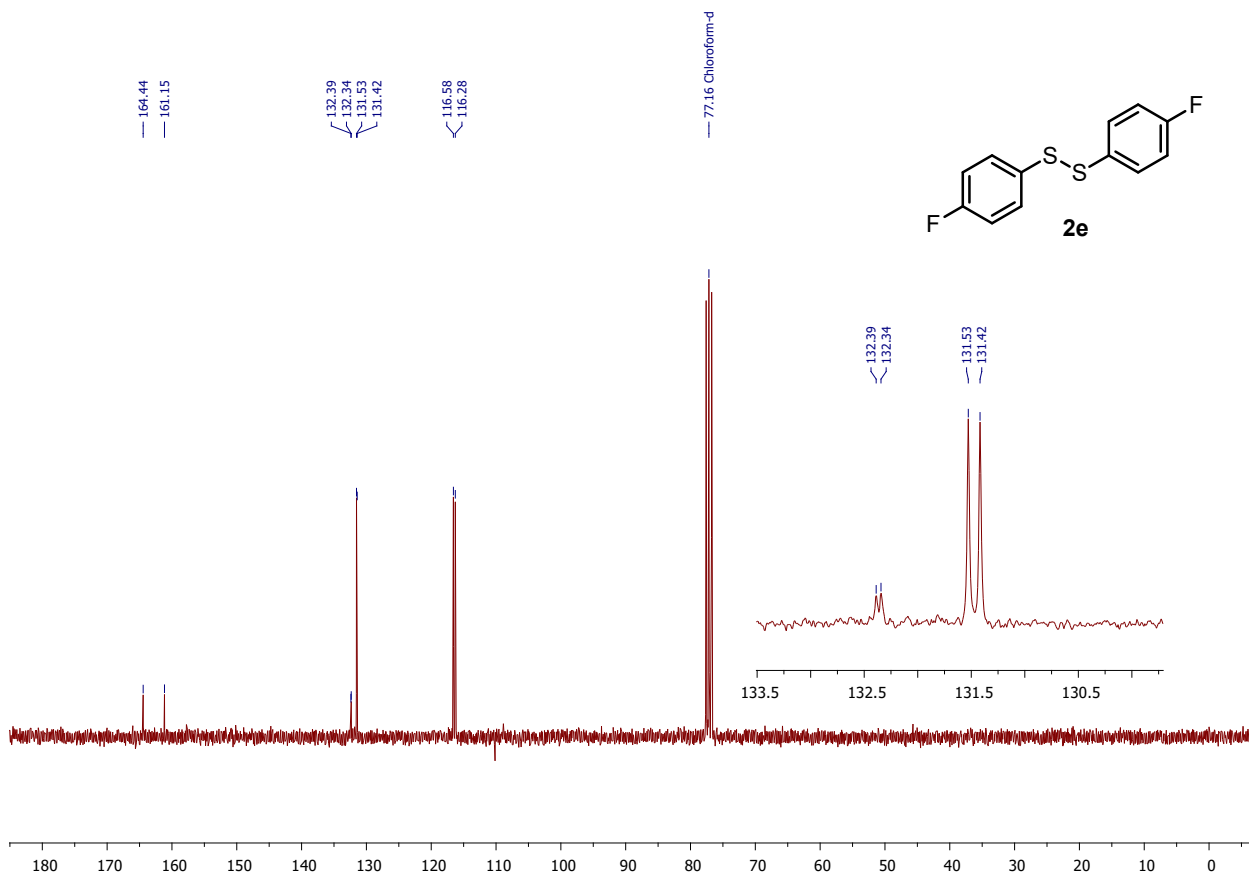
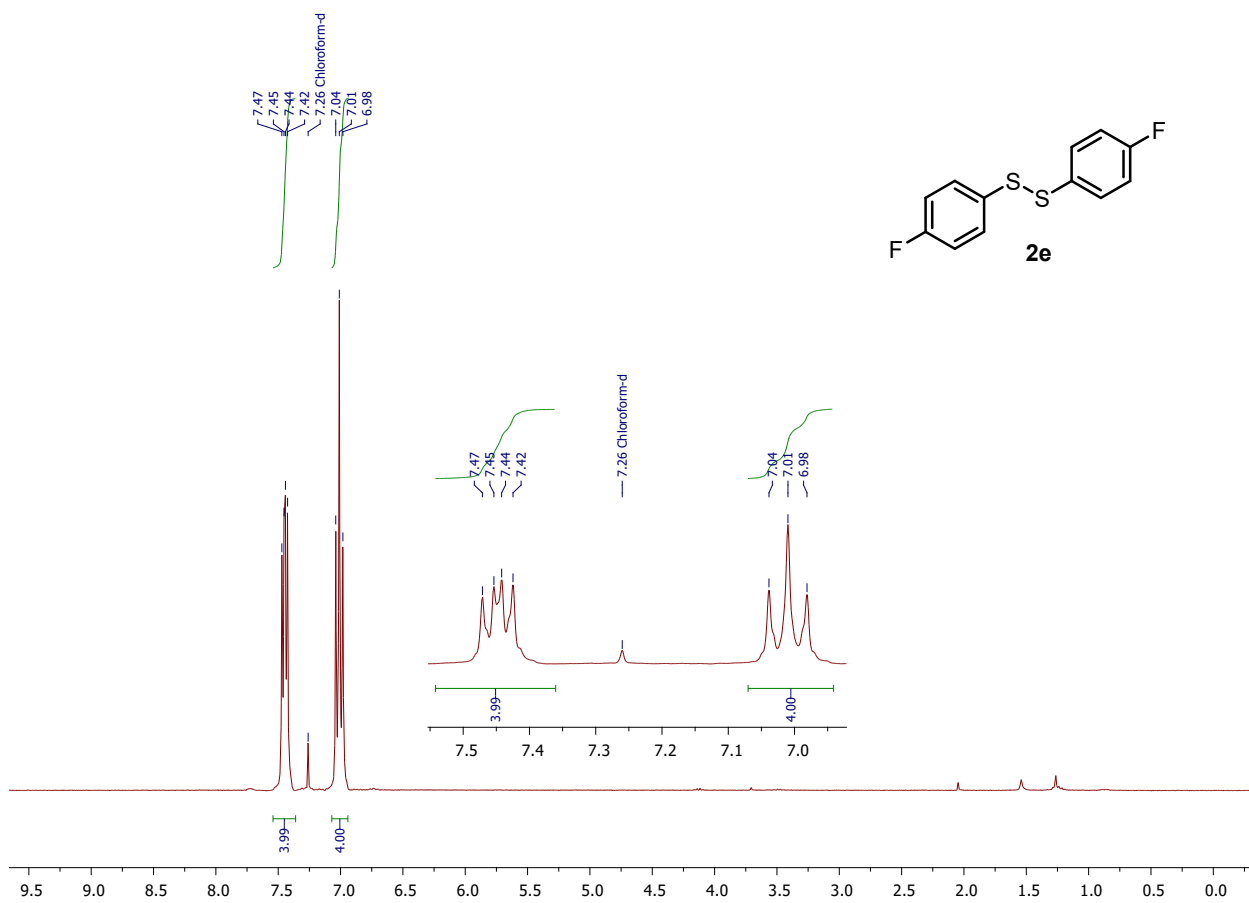


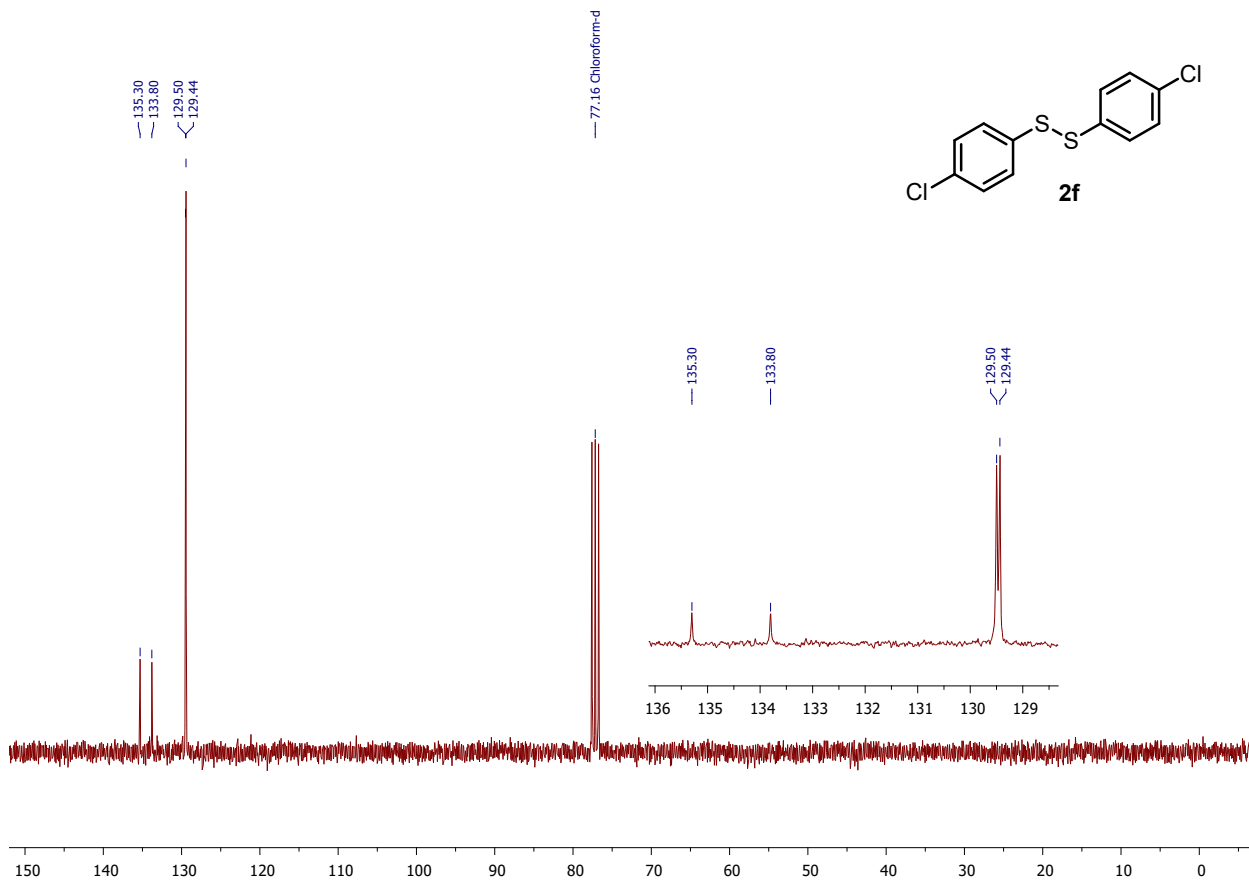
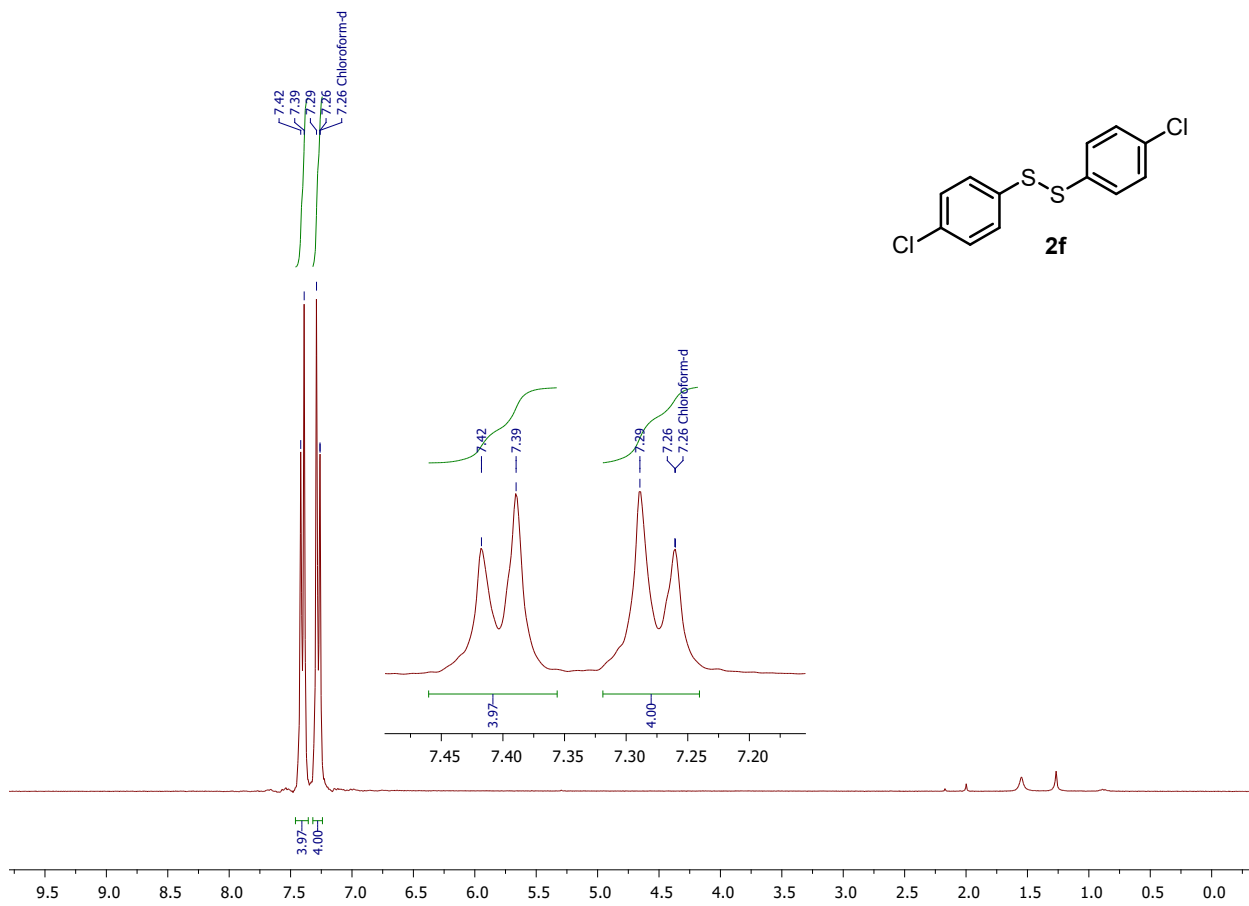


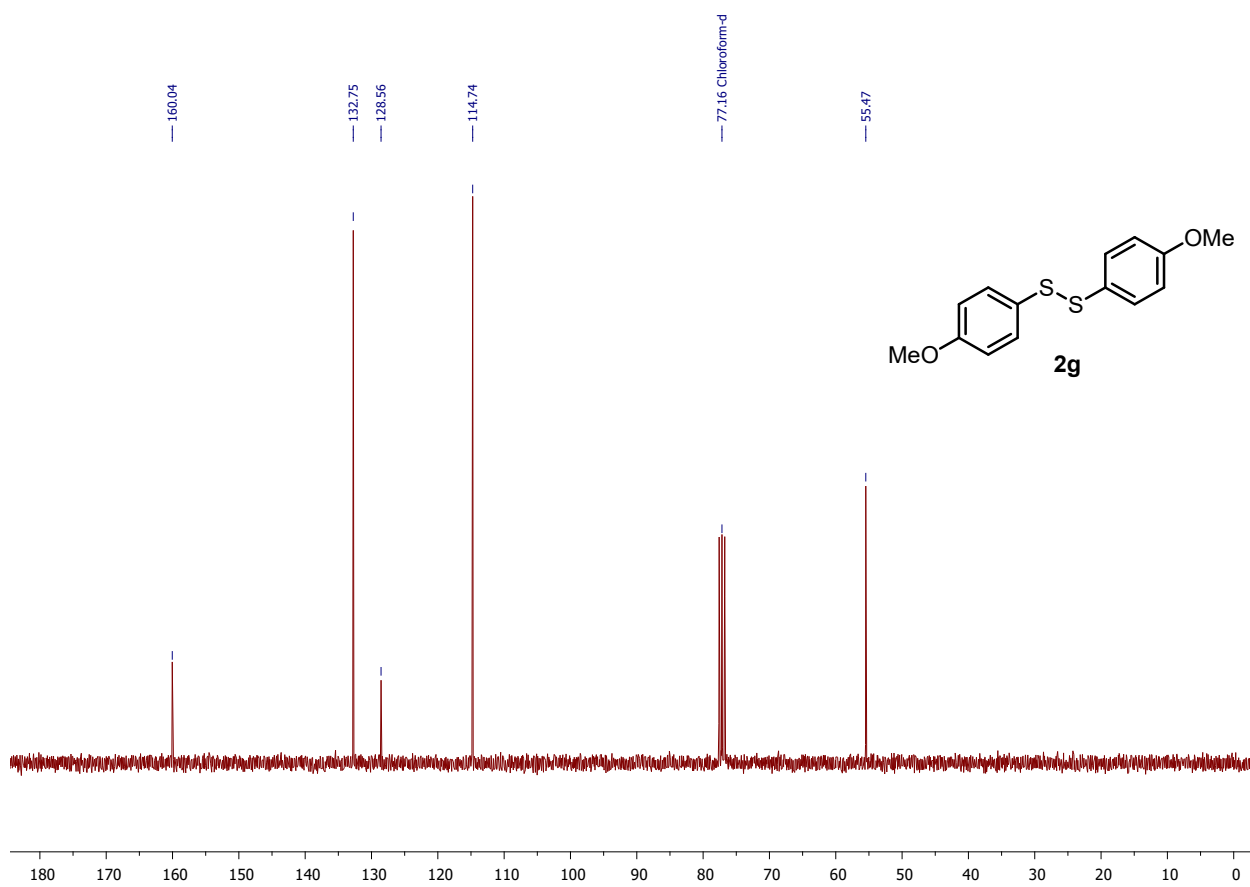
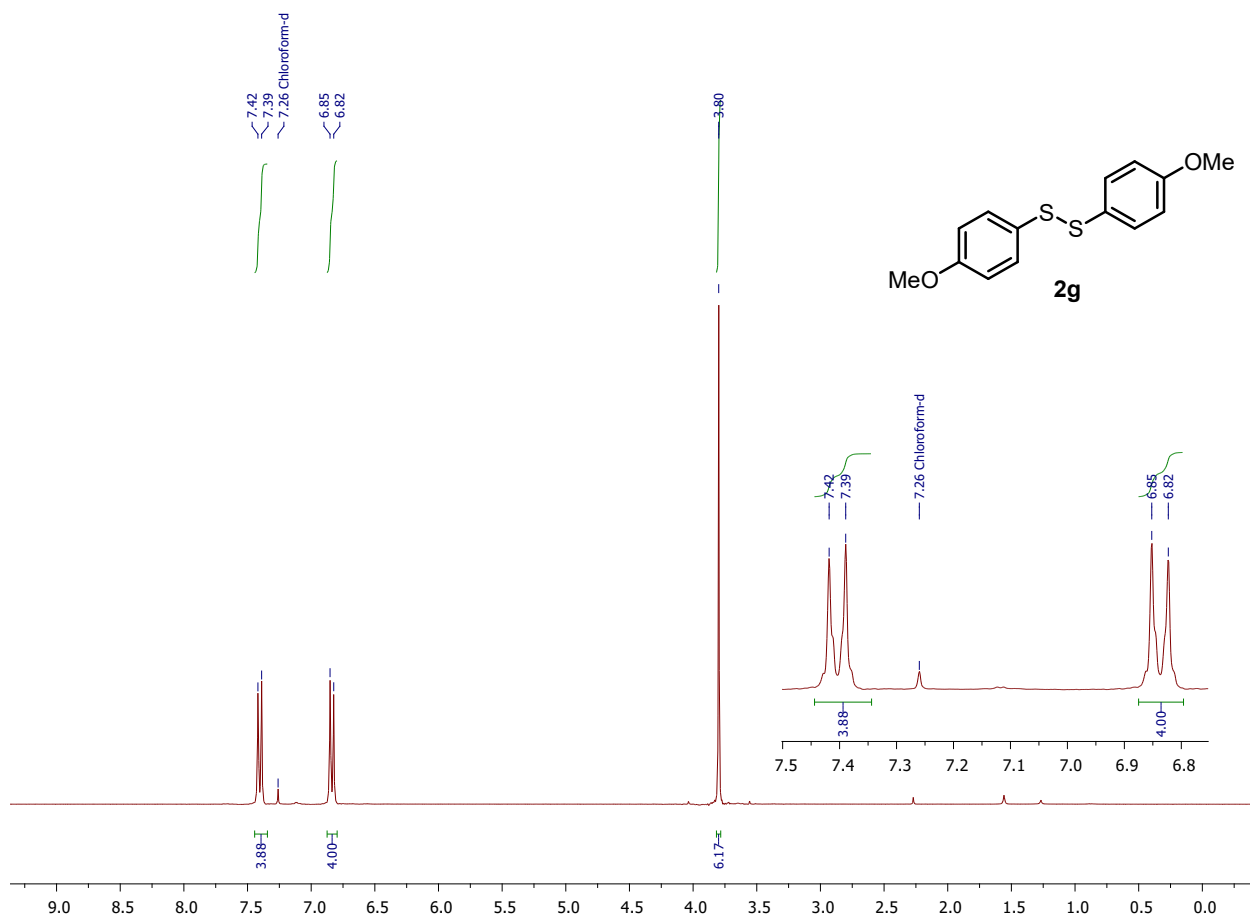


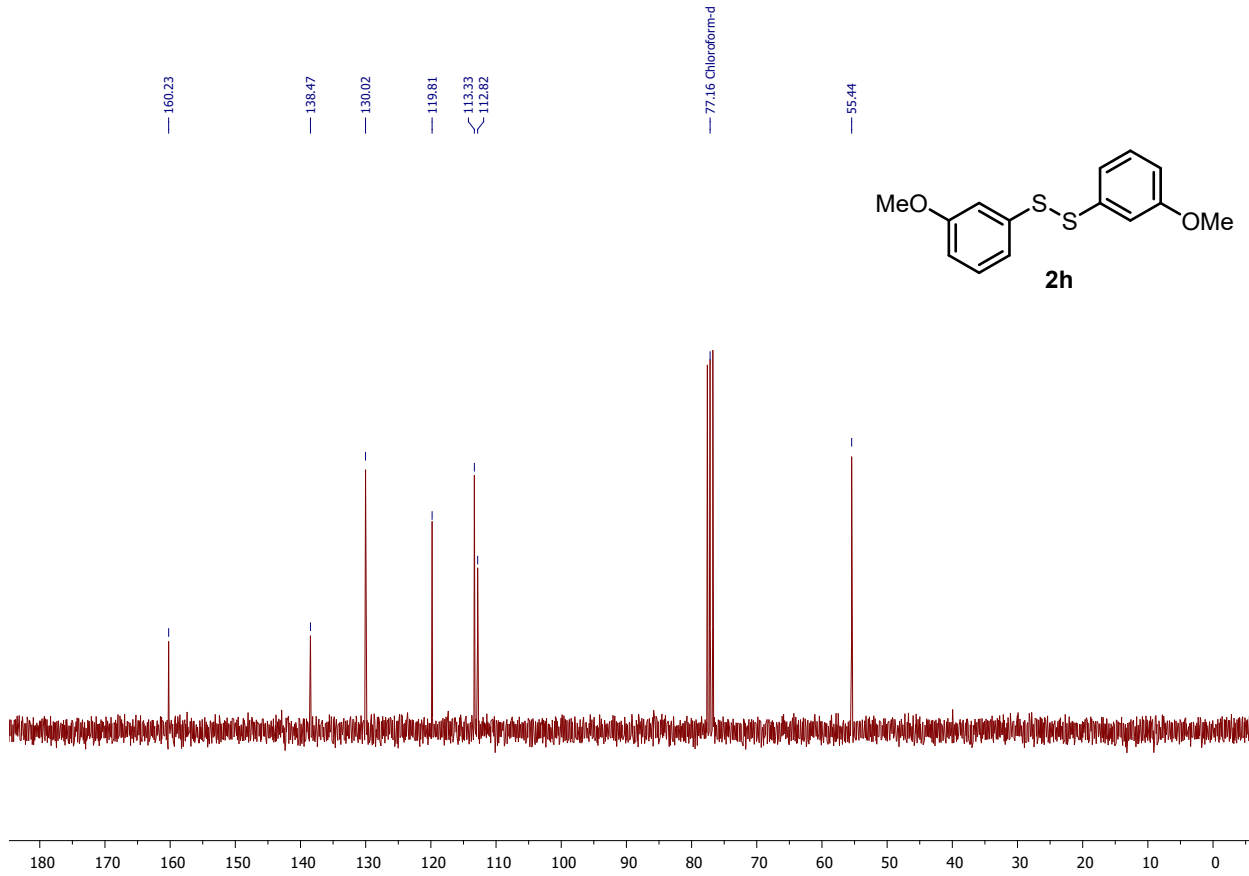
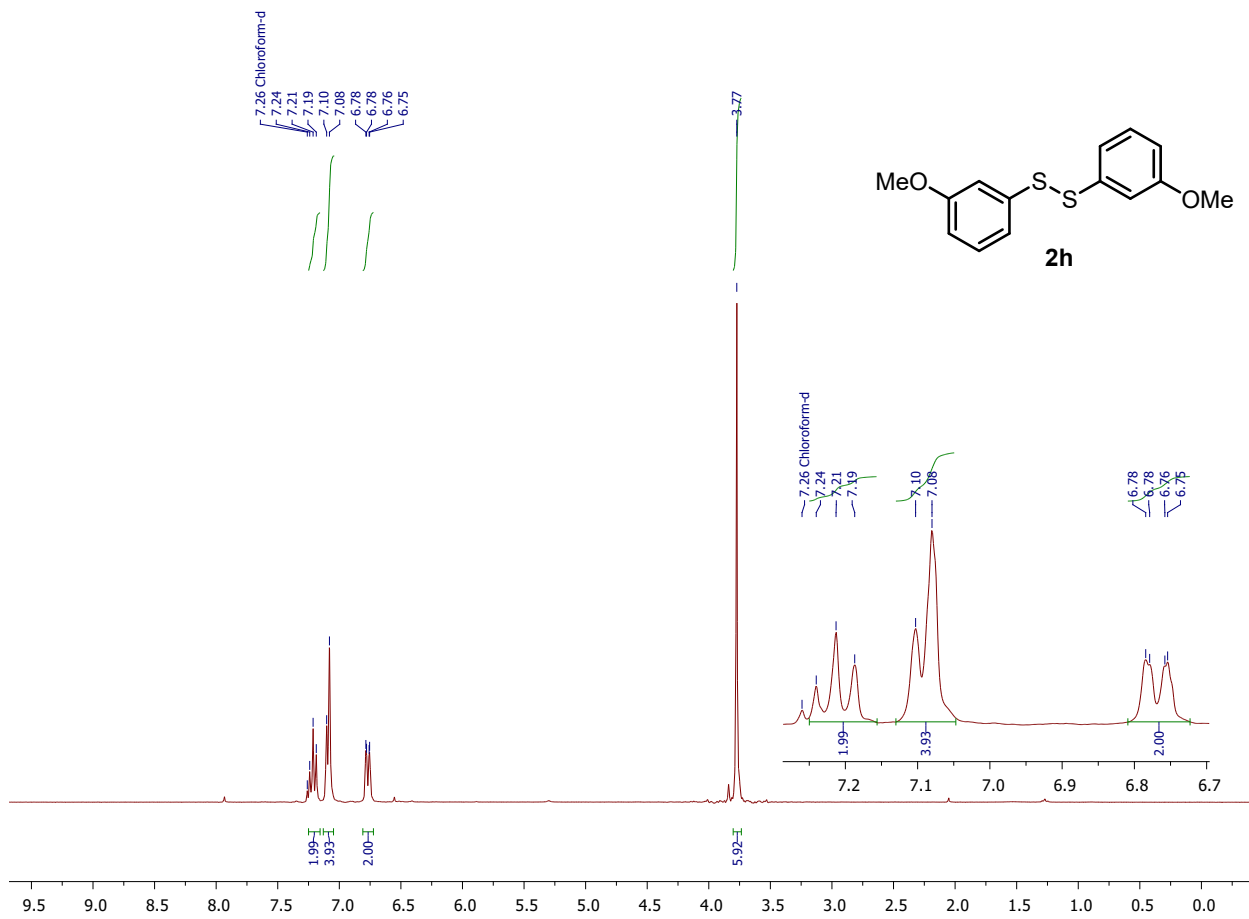


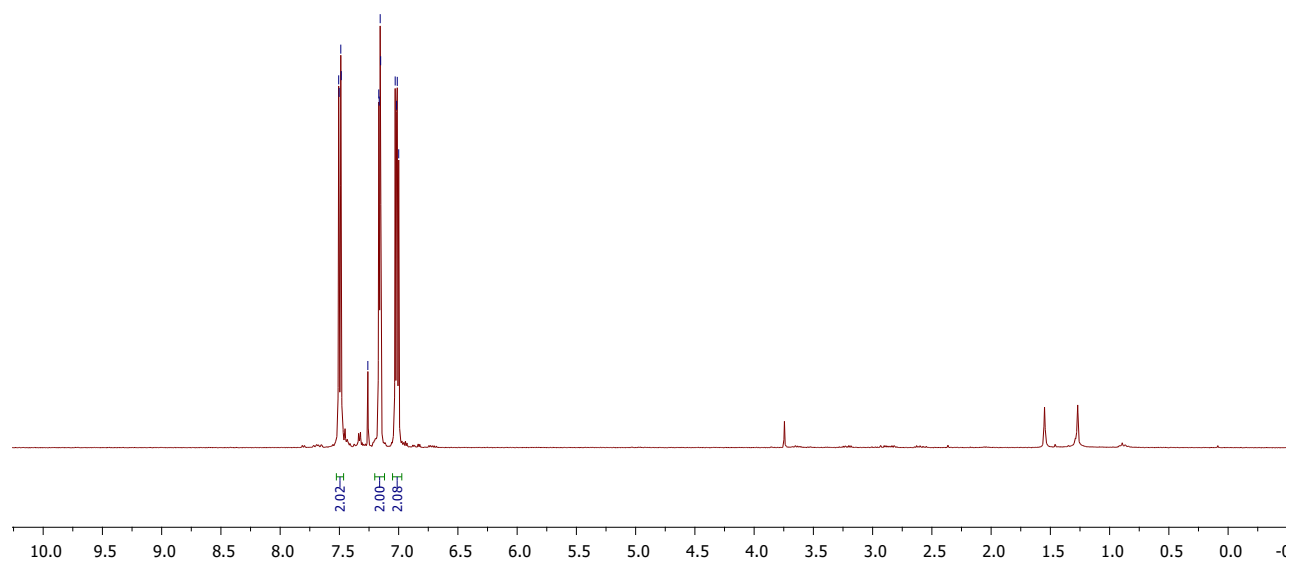
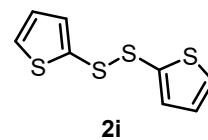
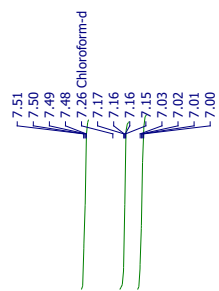












135.84
135.75
132.39
127.88

77.16 Chloroform-d

