Electronic Supplementary Material (ESI) for ChemComm.

Synthesis of highly substituted 1,3-dienes through halonium promoted 1,2-sulfur migration of propargylic thioethers.

Electronic Supplementary Information

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General Methods

All reactions involving air-sensitive compounds were carried out under a N_2 atmosphere (99.99%). All glassware was oven-dried (120 °C), evacuated, and purged with nitrogen. Temperatures were reported as bath temperatures. All common reagents and solvents were obtained from commercial suppliers and used without further purification. Solvents were dried following standard methods. Hexane and ethyl acetate were purchased as extra pure grade reagents and used as received. TLC was performed on alumina-backed plates coated with silica gel 60 with the F254 indicator; the chromatograms were visualized by UV light (254 nm) and/or by staining with a Ce/Mo reagent or phosphomolybdic acid solution and subsequent heating. Rf values refer to silica gel. Flash column chromatography was carried out on silica gel 60, 230–400 mesh. GC-MS spectra were recorded on an Agilent 6890N/5973 Network GC System, equipped with an HP-5MS column or a Thermo 1300GC instrument equipped with an MS 7000ISQ STDNOVPI MS detector, using Chromeleon software. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a mass spectrometer, and only the molecular ions and/or base peaks, as well as significant peaks in MS, are given. High-resolution mass spectrometry (HRMS) was carried out on a 6545 Q-TOF (Agilent) mass spectrometer (ESI or APCI as ion source) as specified. Melting points were measured on a Gallenkamp apparatus using open capillary tubes and are uncorrected. Reactions were carried out in common Pyrex round-bottom flasks or Schlenk flasks. Absorption UV-Vis spectra were recorded on a Shimadzu 2501 PC or Hitachi U-3900/3900H UV-visible spectrophotometers. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD (300 MHz for ^{1}H, 75.4 MHz for ^{13}C, 282 MHz for ^{19}F) or Bruker Advance Neo (500 MHz for ^{1}H, 125 MHz for ^{13}C, 470 MHz for ^{19}F) spectrometer at room temperature. NMR splitting pattern abbreviations are as follows: s, singlet; br s, broad singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; ddd, doublet of doublet of doublets; t, triplet; td, triplet of doublets; q, quartet; quint, quintet; sext, sextet; m, multiplet. Chemical shifts are reported in parts per million using the residual solvent peak as a reference ($CDCl_3$, ^{1}H δ 7.26 and ^{13}C δ 77.16), and the multiplicities of ^{13}C signals were determined by DEPT experiments.

1. Experimental Procedures and Characterization Data of Starting materials

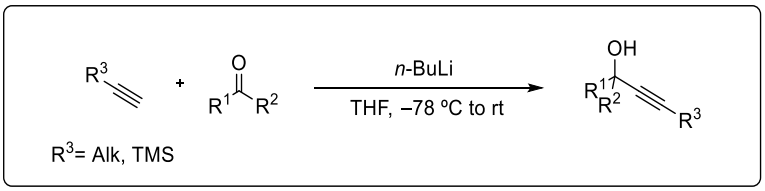
Propargylic thioethers **1** were prepared following a procedure previously described in the literature based on *p*-toluenesulfonic acid (PTSA) catalyzed thiolation reaction of the corresponding propargylic alcohols **S1**.[1]

1.1. Experimental Procedures or the Synthesis of Propargylic Alcohols

Non-commercially available alcohols **S1** were synthesized according to well-established protocols found in the literature based on the addition of alkynyllithium to ketones according to the general procedure **1** described in the following section. The previously reported alkynols 2-methyl-3-octyn-2-ol[2] (**S1a**), 1-(hex-1-yn-1-yl)cyclopentan-1-ol[3] (**S1l**), 1-(hex-1-yn-1-yl)cyclohexan-1-ol[4] (**S1m**), 1-(hex-1-yn-1-yl)cycloheptane-1-ol[5, 6] (**S1n**), 2,2,3-trimethylnon-4-yn-3-ol[4] (**S1o**), 4-propyldec-5-yn-4-ol[7] (**S1p**), 2-phenyl-4-(trimethylsilyl)but-3-yn-2-ol[8] (**S1r**), 2,5,5-trimethylhex-3-yn-ol[9, 10] (**S1s**), 2-methyl-6-phenylhex-3-yn-2-ol[11] (**S1t**), 5-methoxy-2-methylpent-3-yn-2-ol[12] (**S1v**) were prepared according this procedure and the NMR spectra are in accordance with the literature described data.

1.1.1. General Procedure 1 for the Synthesis of Propargylic Alcohols from ketones

Propargylic alcohols were prepared according to a modification of a known procedure found in the literature.[2]

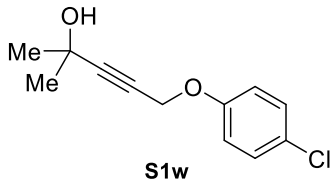


A Schlenk flask equipped with a stirring bar was charged with a solution of the alkyne (1.3 equiv., 13 mmol) in anhydrous THF (20 mL, 0.5 M), under nitrogen atmosphere. The reaction mixture was cooled down to –78 °C. The mixture was allowed to stir for a few minutes, then *n*-BuLi (4.8 mL, 12 mmol, 1.2 equiv., 2.5 M) was added dropwise. The obtained solution was allowed to stir for 45 minutes prior to the addition of ketone (1 equiv., 10 mmol) at –78 °C; after 20 min at this temperature, it was allowed to warm up to room temperature. Then, the reaction mixture was allowed to stir until full depletion of starting materials was observed by TLC chromatography and GC-MS. Then, the reaction was

quenched by the addition of NH_4Cl aqueous saturated solution (20 mL). The separated aqueous phase was extracted with Et_2O (3 × 20 mL). The organic layers were washed with saturated NaCl (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo,* affording the crude propargyl alcohol. The crude was purified by column chromatography on silica gel (eluent: hexane/AcOEt), affording the pure propargyl alcohols.

Characterization Data of Alcohol S1w:

5-(4-chlorophenoxy)-2-methylpent-3-yl-2-ol (S1w)

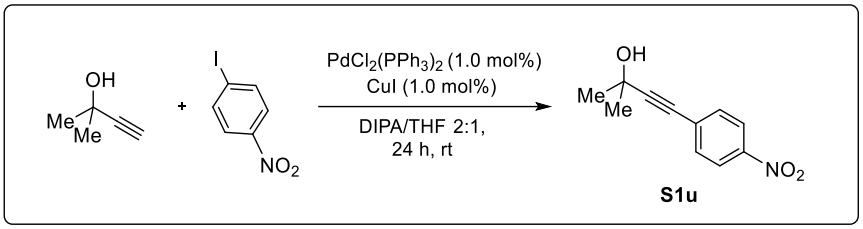


S1w

General procedure **1** was followed using propan-2-one (580 mg, 1 equiv., 10 mmol), 1-chloro-4-(prop-2-yn-1-yloxy)benzene (1660 mg, 1 equiv., 10 mmol), *n*-BuLi (4.8 mL, 12 mmol, 1.2 equiv., 2.5 M) and THF (20 mL, 0.5 M). Crude alkynol **S1w** (1.59 g, 70 %) was obtained as a yellow oil which was used in the next step without performing column chromatography purification. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.31 – 7.20 (m, 2H), 6.95 – 6.82 (m, 2H), 4.67 (s, 2H), 2.12 (br s, 1H), 1.50 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 156.4 (C), 129.4 (2 × CH), 126.5 (C), 116.4 (2 × CH), 92.5 (C), 76.6 (C), 65.3 (C), 56.6 (CH_2), 31.3 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 43 (100), 128 (22), 224 (M^+, 3). **HRMS (ESI+) *m/z*: [M + Na]$^+$** calcd for $C_{12}H_{13}ClO_2Na$, 247.0496; found 247.0497.

1.1.2. Procedure for the Synthesis of Propargylic Alcohol S1u

Propargylic alcohol **S1u** was prepared according to the following procedure:



S1u

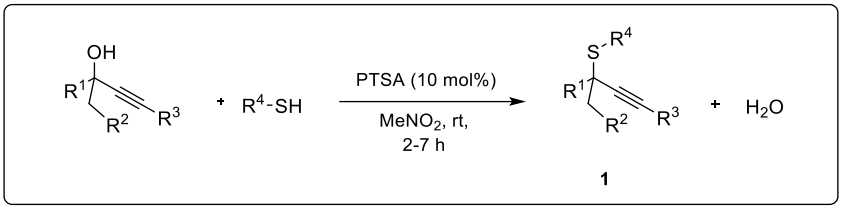
A Schlenk flask was charged with bis(triphenylphosphine)palladium (II) dichloride (42 mg, 0.01 equiv., 0.06 mmol) and diisopropylamine (12 mL, 0.5 M), in anhydrous THF (6 mL, 1 M) under nitrogen atmosphere. After 5 minutes, 1-iodo-4-nitrobenzene (1.49 g, 1 equiv., 6 mmol), 2-methyl-3-butyn-2-ol (655 mg, 1.3 equiv., 7.8 mmol) and copper iodide (11 mg, 0.01 equiv., 0.06 mmol) were sequentially added. The reaction mixture was allowed to stir at room temperature over-night (12 h), until full depletion of starting material was observed by TLC and GC-MS. Then, Et_2O (30 mL) was added and the reaction mixture was filtered through a celite plug, washing with Et_2O. The filtrate was washed with water (20 mL) and HCl (1M, 2 × 20 mL). The organic layer was dried over Na_2SO_4, filtered and

concentrated *in vacuo,* affording the crude propargyl alcohol. It was purified by column chromatography on silica gel (eluent: hexane/AcOEt = 2:1), affording the pure propargyl alcohol **S1u** (1.01 g, 82%) whose NMR spectra goes in accordance with the previously reported data.[13]

1.2. Experimental Procedures and Characterization Data of Propargylic Thioethers 1

1.2.1. General Procedure A1 for the Synthesis of Propargylic Thioethers 1 by Thiolation of Alcohols.

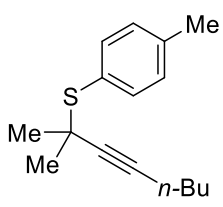
Propargylic thioethers **1** were prepared by the reaction of the corresponding propargylic alcohols with thiols according to known procedures found in the literature.[1]



Thiol (1.3 equiv., 4.5 mmol) and *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) were sequentially added to a solution of propargylic alcohol (1 equiv., 3 mmol) in nitromethane (6 mL, 0.5 M). The mixture was allowed to stir at room temperature for 2-7 hours; until full depletion of the alcohol was determined by TLC; spots were visualized by using phosphomolybdic acid solution and heat as staining agent. Then, the reaction mixture was quenched by the addition of aqueous NaOH and NaCl. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: mixtures of hexane/ CH_2Cl_2), affording the corresponding propargylic sulfides **1**.

Characterization Data of Propargylic Thioethers 1:

(2-methyloct-3-yn-2-yl) (*p*-tolyl)sulfide[1] (1a)

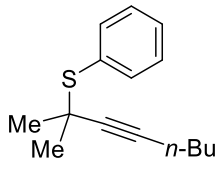


1a

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1a** (521 mg, 70%) as colourless oil; *Rf* = 0.28 (hexane). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.51 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.4 Hz,

2H), 2.37 (s, 3H), 2.17 (t, *J* = 6.9 Hz, 2H), 1.50 (s, 6H), 1.47 – 1.26 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 139.1 (C), 137.0 (2 × CH), 129.4 (2 × CH), 129.3 (C), 84.8 (C), 83.6 (C), 42.4 (C), 31.0 (CH_2), 30.9 (2 × CH_3), 22.1 (CH_2), 21.4 (CH_3), 18.6 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 125 (36), 246 (M^+, 3). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{23}S$, 247.1515; found, 247.1518.

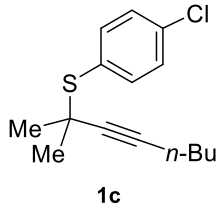
(2-methyloct-3-yn-2-yl) (phenyl)sulfide (1b)



1b

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), benzenethiol (495 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1b** (452 mg, 64%) as colourless liquid; *Rf* = 0.11 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.67 – 7.61 (m, 2H), 7.38 – 7.30 (m, 3H), 2.17 (t, *J* = 6.9 Hz, 2H), 1.52 (s, 6H), 1.49 – 1.27 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 136.8 (2 × CH), 133.0 (C), 128.9 (CH), 128.5 (2 × CH), 84.7 (C), 83.7 (C), 42.5 (C), 31.0 (2 × CH_3), 22.0 (CH_2), 18.6 (CH_2), 13.8 (CH_3) ppm. One peak missing due to overlapping. **LRMS (EI) *m/z* (%)** 81 (100), 79 (40), 232 (M^+,1). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{21}S$, 233.1358; found, 233.1359.

(4-chlorophenyl) (2-methyloct-3-yn-2-yl)sulfide (1c)

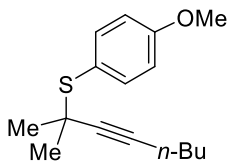


1c

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), 4-chlorobenzenethiol (648 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1c** (421 mg, 53%) as pale yellow liquid; *Rf* = 0.25 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.58 – 7.52 (m, 2H), 7.33 – 7.28 (m, 2H), 2.16 (t, *J* = 6.9 Hz, 2H), 1.50 (s, 6H), 1.47 – 1.23 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 138.0 (2 × CH), 135.4 (C), 131.6 (C), 128.7 (2 × CH), 84.4 (C), 84.1 (C), 42.8 (C), 31.0 (CH_2), 31.0 (2 × CH_3), 22.1 (CH_2), 18.6 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 79 (33), 266 (M^+,1). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{20}ClS$, 267.0969; found, 267.0968.

(4-methoxyphenyl) (2-methyloct-3-yn-2-yl)sulfide (1d)

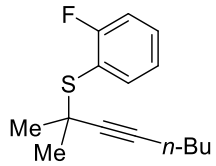
The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), 4-methoxybenzenethiol (630 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by



1d

column chromatography yielded **1d** (439 mg, 56%) as pale yellow liquid; *Rf* = 0.37 (hexane/CH_2Cl_2 = 2:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.57 – 7.52 (m, 2H), 6.89 – 6.84 (m, 2H), 3.81 (s, 3H), 2.16 (t, *J* = 6.9 Hz, 2H), 1.48 (s, 6H), 1.46 – 1.30 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 160.6 (C), 138.7 (2 × CH), 123.8 (C), 114.0 (2 × CH), 84.8 (C), 83.6 (C), 55.4 (CH_3), 42.5 (C), 31.0 (CH_2), 30.8 (2 × CH_3), 22.0 (CH_2), 18.6 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 140 (71), 262 (M^+,11). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{23}OS$, 263.1464 ; found, 263.1466.

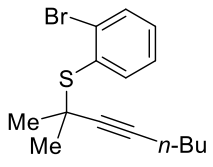
(2-fluorophenyl) (2-methyloct-3-yn-2-yl)sulfide (1e)



1e

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), 2-fluorobenzenethiol (576 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1e** (368 mg, 49%) as colourless liquid; *Rf* = 0.23 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.68 (td, *J* = 7.6, 1.9 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.16 – 7.05 (m, 2H), 2.13 (t, *J* = 6.9 Hz, 2H), 1.54 (s, 6H), 1.47 – 1.21 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 163.9 (d, $J_{C\text{-}F}$ = 247.2 Hz, C), 139.7 (CH), 131.4 (d, $J_{C\text{-}F}$ = 8.1 Hz, CH), 124.0 (d, $J_{C\text{-}F}$ = 4.0 Hz, CH), 119.9 (d, $J_{C\text{-}F}$ = 18.3 Hz, C), 115.8 (d, $J_{C\text{-}F}$ = 24.1 Hz, CH), 84.1 (C), 84.0 (C), 43.6 (C), 31.1 (2 × CH_3), 30.9 (CH_2), 22.0 (CH_2), 18.5 (CH_2), 13.7 (CH_3) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = -105.3 ppm. **LRMS (EI) *m/z* (%)** 81 (100), 79 (43), 250 (M^+,1). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{20}FS$, 251.1264; found, 251.1268.

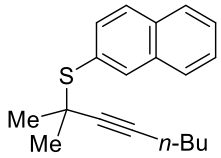
(2-bromophenyl) (2-methyloct-3-yn-2-yl)sulfide (1f)



1f

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), 2-bromobenzenethiol (845 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1f** (475 mg, 51%) as colourless liquid; *Rf* = 0.12 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.98 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.71 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.23 (td, *J* = 7.8, 1.7 Hz, 1H), 2.25 (t, *J* = 7.0 Hz, 2H), 1.67 (s, 6H), 1.61 – 1.31 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 137.2 (CH), 135.0 (C), 133.3 (CH), 130.3 (C), 129.6 (CH), 127.3 (CH), 84.3 (2 × C), 44.0 (C), 31.1 (2 × CH_3), 30.9 (CH_2), 22.1 (CH_2), 18.6 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 67 (39), 310 (M^+,1). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{20}BrS$, 311.0464; found, 311.0464.

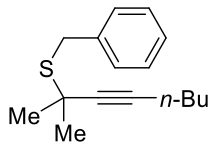
(2-methyloct-3-yn-2-yl) (naphthalen-2-yl)sulfide (1g)



1g

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), naphthalene-2-thiol (720 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1g** (340 mg, 40%) as pale yellow oil; *Rf* = 0.25 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 8.18 (s, 1H), 7.88 – 7.78 (m, 3H), 7.73 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.56 – 7.43 (m, 2H), 2.18 (t, *J* = 7.0 Hz, 2H), 1.58 (s, 6H), 1.49 – 1.40 (m, 2H), 1.37 – 1.22 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 136.4 (CH), 133.48 (C), 133.45 (CH), 133.3 (C), 130.5 (C), 128.1 (CH), 127.8 (2 × CH), 126.8 (CH), 126.3 (CH), 84.8 (C), 83.9 (C), 42.8 (C), 31.1 (2 × CH_3), 31.0 (CH_2), 22.1 (CH_2), 18.7 (CH_2), 13.7 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 115 (62), 282 (M^+,8). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{23}S$, 283.1515; found, 283.1520.

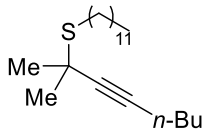
Benzyl (2-methyloct-3-yn-2-yl)sulfide (1h)



1h

The general procedure **A1** was followed 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), phenylmethanethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1h** (378 mg, 51%) as colourless liquid; *Rf* = 0.23 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.40 – 7.36 (m, 2H), 7.30 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 2H), 7.27 – 7.22 (m, 1H), 3.98 (s, 2H), 2.26 (t, *J* = 6.9 Hz, 2H), 1.55 (s, 6H), 1.53 – 1.39 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 138.4 (C), 129.3 (2 × CH), 128.6 (2 × CH), 127.0 (CH), 84.2 (C), 83.3 (C), 39.9 (C), 35.8 (CH_2), 31.3 (2 × CH_3), 31.2 (CH_2), 22.1 (CH_2), 18.6 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 67 (38), 246 (M^+,2). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{23}S$, 247.1515; found, 247.1519.

Dodecyl(2-methyloct-3-yn-2-yl)sulfane (1i)

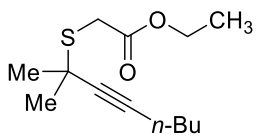


1i

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), dodecane-1-thiol (909 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and a mixture (2:1) nitromethane/CH_2Cl_2 (6 mL, 0.5 M). Purification by column chromatography yielded **1i** (471 mg, 48%) as colourless liquid; *Rf* = 0.30 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 2.75 – 2.64 (m, 2H), 2.19 (t, *J* = 6.9 Hz, 2H), 1.68 – 1.54 (m, 2H), 1.52 (s, 6H), 1.49 – 1.33 (m, 6H), 1.34 – 1.22 (m, 16H), 0.94 – 0.82 (m, 6H). ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 84.5 (C), 82.4 (C), 38.8 (C), 32.1

(CH_2), 31.5 (2 × CH_3), 31.2 (CH_2), 30.8 (CH_2), 29.81 (CH_2), 29.78 (2 × CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (2 × CH_2), 22.8 (CH_2), 22.1 (CH_2), 18.6 (CH_2), 14.2 (CH_3), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 55 (23), 324 (M^+,2). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{21}H_{41}S$, 325.2929 ; found, 325.2926.

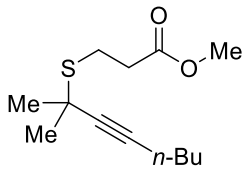
Ethyl 2-((2-methyloct-3-yn-2-yl)thio)acetate (1j)



1j

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), ethyl 2-mercaptoacetate (540 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1j** (390 mg, 54%) as colourless liquid; *Rf* = 0.42 (hexane/AcOEt = 10:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 4.16 (q, *J* = 7.1 Hz, 2H), 3.49 (s, 2H), 2.18 (t, *J* = 6.9 Hz, 2H), 1.52 (s, 6H), 1.50 – 1.32 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 170.8 (C), 83.9 (C), 83.3 (C), 61.4 (CH_2), 40.1 (C), 33.7 (CH_2), 31.2 (2 × CH_3), 31.0 (CH_2), 22.0 (CH_2), 18.5 (CH_2), 14.2 (CH_3), 13.7 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 155 (40), 242 (M^+, 1). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{13}H_{23}O_2S$, 243.1413; found, 243.1414.

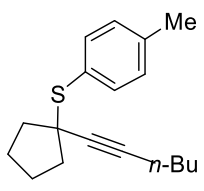
methyl 3-((2-methyloct-3-yn-2-yl)thio)propanoate (1k)



1k

The general procedure **A1** was followed using 2-methyl-3-octyn-2-ol[2] (420 mg, 1 equiv., 3 mmol), methyl 3-mercaptopropanoate (540 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1k** (476 mg, 65%) as colourless liquid; *Rf* = 0.35 (hexane/AcOEt = 10:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 3.68 (s, 3H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.18 (t, *J* = 6.8 Hz, 2H), 1.51 (s, 6H), 1.49 – 1.30 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 172.6 (C), 84.1 (C), 83.0 (C), 51.8 (CH_3), 39.2 (C), 34.8 (CH_2), 31.4 (2 × CH_3), 31.1 (CH_2), 25.7 (CH_2), 22.0 (CH_2), 18.5 (CH_2), 13.7 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 155 (26), 242 (M^+, 1). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{13}H_{23}O_2S$, 243.1413; found, 243.1414.

(1-(hex-1-yn-1-yl)cyclopentyl) (*p*-tolyl)sulfide (1l)

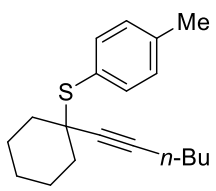


1l

The general procedure **A1** was followed using 1-(hex-1-yn-1-yl)cyclopentan-1-ol[3] (**S1l**) (498 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1l** (332 mg, 41%) as pale yellow oil; *Rf* = 0.16

(hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.56 – 7.50 (m, 2H), 7.17 – 7.10 (m, 2H), 2.36 (s, 3H), 2.19 (t, *J* = 6.9 Hz, 2H), 1.99 – 1.89 (m, 4H), 1.89 – 1.73 (m, 4H), 1.52 – 1.25 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 138.6 (C), 135.9 (2 × CH), 130.4 (C), 129.3 (2 × CH), 84.5 (C), 83.7 (C), 52.0 (C), 41.3 (2 × CH_2), 31.1 (CH_2), 23.9 (2 × CH_2), 22.1 (CH_2), 21.4 (CH_3), 18.7 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 79 (100), 67 (70), 272 (M^+,8). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{18}H_{25}S$, 273.1671; found, 273.1675.

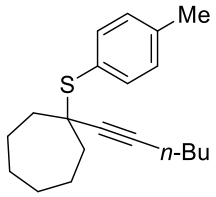
(1-(hex-1-yn-1-yl)cyclohexyl) (*p*-tolyl)sulfide (1m)



1m

The general procedure **A1** was followed using 1-(hex-1-yn-1-yl)cyclohexan-1-ol[4] (**S1m**) (540 mg, mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1m** (412 mg, 48%) as colourless oil; *Rf* = 0.16 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.54 – 7.48 (m, 2H), 7.16 – 7.10 (m, 2H), 2.36 (s, 3H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.70 – 1.51 (m, 7H), 1.51 – 1.32 (m, 4H), 1.28 – 1.12 (m, 1H) 0.90 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 138.9 (C), 137.2 (2 × CH), 129.2 (2 × CH), 128.4 (C), 85.8 (C), 82.8 (C), 48.0 (CH_2), 39.0 (2 × CH_2), 31.2 (CH_2), 25.7 (CH_2), 23.7 (2 × CH_2), 22.1 (CH_2), 21.4 (C), 18.7 (CH_3), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 79 (100), 91 (54), 286(M^+, 10). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{27}S$, 287.1828; found, 287.1831.

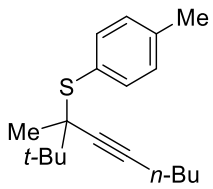
(1-(hex-1-yn-1-yl)cycloheptyl) (*p*-tolyl)sulfide (1n)



1n

The general procedure **A1** was followed using 1-(hex-1-yn-1-yl)cycloheptane-1-ol[5, 6] (**S1n**) (582 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1n** (309 mg, 34%) as colourless oil; *Rf* = 0.16 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.52 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 2.21 (t, *J* = 6.9 Hz, 2H), 2.01 – 1.95 (m, 2H), 1.81 – 1.70 (m, 2H), 1.69 – 1.51 (m, 8H), 1.49 – 1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 139.0 (C), 137.1 (2 × CH), 129.5 (C), 129.2 (2 × CH), 85.2 (C), 84.0 (C), 51.0 (C), 41.4 (2 × CH_2), 31.2 (CH_2), 28.3 (2 × CH_2), 23.8 (2 × CH_2), 22.1 (CH_2), 21.4 (CH_3), 18.7 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 79 (100), 91 (55), 300 (M^+,19). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{29}S$, 301.1984 ; found, 301.1978.

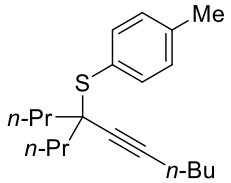
(2,2,3-trimethylnon-4-yn-3-yl) (*p*-tolyl)sulfide (1o)



1o

The general procedure **A1** was followed using 2,2,3-trimethylnon-4-yn-3-ol[4] (**S1o**) (546 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1o** (351 mg, 40%) as colourless oil; *Rf* = 0.21 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.52 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 2.15 (t, 2H), 1.48 – 1.38 (m, 4H), 1.36 (s, 3H), 1.21 (s, 9H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 138.8 (C), 137.8 (2 × CH), 129.9 (C), 129.1 (2 × CH), 85.8 (C), 83.3 (C), 56.4 (C), 38.5 (C), 31.1 (CH_2), 26.7 (3 × CH_3), 25.0 (CH_3), 22.1 (CH_2), 21.4 (CH_3), 18.7 (CH_2), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 57 (100), 123 (65), 288 (M^+,8). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{29}S$, 289.1984; found, 289.1985.

(4-propyldec-5-yn-4-yl) (*p*-tolyl)sulfide (1p)

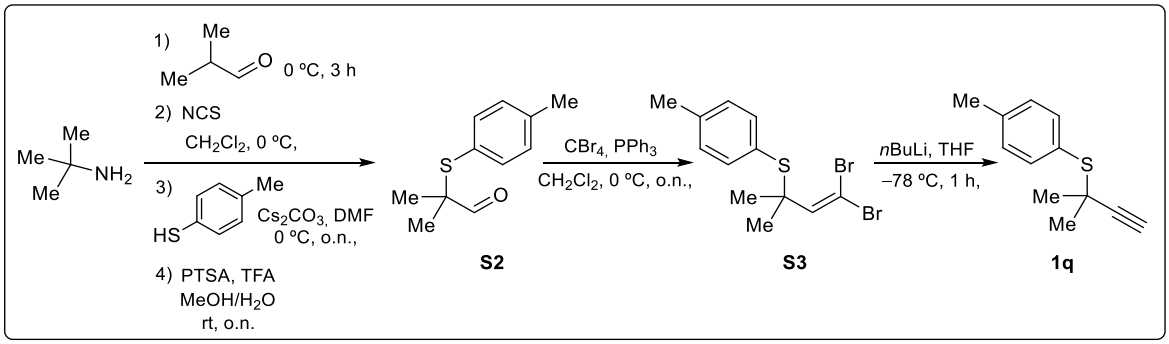


1p

The general procedure **A1** was followed using 4-propyldec-5-yn-4-ol[7] (**S1p**) (588 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1p** (302mg, 33%) as colourless oil; *Rf* = 0.19 (hexane/DCM = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.46 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.19 (t, *J* = 6.9 Hz, 2H), 1.66 – 1.51 (m, 8H), 1.49 – 1.31 (m, 4H), 0.94 – 0.85 (m, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 138.9 (C), 137.2 (2 × CH), 129.2 (2 × CH), 128.9 (C), 86.1 (C), 82.7 (C), 51.7 (C), 41.9 (2 x CH_2), 31.1 (CH_2), 22.1 (CH_2), 21.4 (CH_3), 18.7 (CH_2), 18.5 (2 × CH_2), 14.3 (2 × CH_3), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 95 (61), 302 (M^+,7). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{31}S$, 303.2141; found, 303.2141.

Procedure for the Synthesis of (2-methylbut-3-yn-2-yl) (*p*-tolyl)sulfide (1q)

Compound **1q** was prepared according to the following synthetic sequence:[14,15]



A mixture of 2-methylpropan-2-amine (731 mg, 1 equiv., 10 mmol) and isobutyraldehyde (721 mg, 1 equiv., 10 mmol) was stirred at 0 °C for 3 hours until full depletion of the aldehyde or amine was determined by GC-MS. The reaction mixture was diluted in dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

The resulting crude *N*-(*tert*-butyl)-2-methylpropan-1-imine was dissolved in dichloromethane (10 mL, 1M) at 0 °C under N_2. Then, *N*-chlorosuccinimide (NCS) (1.34 g, 1 equiv., 10 mmol) was added at once and stirred until full depletion of the imine was determined by GC-MS. The reaction mixture was diluted in Et_2O and was washed with $Na_2S_2O_3$ and NaOH. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure affording crude *N*-(*tert*-butyl)-2-chloro-2-methylpropan-1-imine.[14]

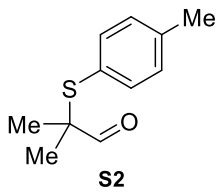
Cs_2CO_3 (6.52 g, 2 equiv., 20 mmol) was added to a solution of 4-methylbenzenethiol (1.24 g, 1 equiv., 10 mmol) in DMF (20 mL, 0.5 M) at 0 °C under N_2. The mixture was allowed to stir for 1 hour and then, crude *N*-(*tert*-butyl)-2-chloro-2-methylpropan-1-imine dissolved in DMF (5 ml) and generated in the previous step was added dropwise to the mixture and was allowed to stir at room temperature overnight. Then, the reaction mixture was quenched by addition of H_2O at 0 °C. The separated aqueous phase was extracted with Et_2O (3 × 30 mL) and washed with NaCl. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Then, *p*-toluensulfonic acid (PTSA) (34 mg, 0.02 equiv., 0.2 mmol) and trifluoroacetic acid (TFA) (2.28 g, 2 equiv., 20 mmol) were sequentially added to a solution of crude thioimine dissolved in a 1:1 mixture of MeOH/H_2O (33 mL, 0.3 M). The mixture was allowed to stir at room temperature overnight until full depletion of the imine was determined by GC-MS. Then, the reaction mixture was quenched by the addition of aqueous NaCl and H_2O. The separated aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, affording the corresponding aldehyde **S2**.

The transformation of the aldehyde into the corresponding terminal alkyne is carried out through the well-known Corey-Fuchs synthesis. The first step of the procedure involved the conversion of the aldehyde to the corresponding homologated dibromoolefin through the addition of the 2-methyl-2-(*p*-tolylthio)propanal (1.16 g, 1 equiv., 6 mmol) to a mixture of triphenylphosphine (6.29 g, 4 equiv., 24 mmol) and carbon tetrabromide (3.98 g, 2 equiv., 12 mmol) in CH_2Cl_2 (24 mL, 0.25 M), at 0 °C under N_2 for 2 hours. Then, the reaction mixture was filtered through a celite plug. The filtrate was washed with CH_2Cl_2. The organic layer

was dried over Na_2SO_4, filtered and concentrated *in vacuo*. It was purified by column chromatography on silica gel affording the pure dibromoolefin **S3**.

In the second step, the conversion of the prepared (4,4-dibromo-2-methylbut-3-en-2-yl)(*p*-tolyl)sulfane **S3** (1043 mg, 1 equiv., 3 mmol) to the corresponding terminal alkyne is accomplished by treatment with *n*-BuLi (2.64 mL, 2.5 M, 2.2 equiv., 6.6 mmol) at −78 °C in THF (12 mL, 0.25 M) under N_2 followed by simple hydrolysis with H_2O. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, affording the corresponding alkyne **1q**.

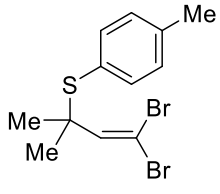
2-methyl-2-(*p*-tolylthio)propanal (S2)



S2

Purification by column chromatography yielded **S2** (1.32 g, 68%) as yellow oil; *Rf* = 0.33 (hexane/AcOEt 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 9.33 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 2.33 (s, 3H), 1.31 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 195.5 (CH), 140.0 (C), 137.1 (2 × CH), 129.9 (2 × CH), 126.4 (C), 55.4 (C), 21.4 (CH_3), 21.2 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 165 (100), 73 (86), 194 (M^+, 14). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{11}H_{15}SO$, 195.0838 ; found, 195.0839.

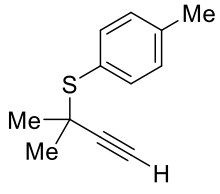
(4,4-dibromo-2-methylbut-3-en-2-yl) (*p*-tolyl)sulfide (S3)



S3

Purification by column chromatography yielded **S3** (1.35 g, 64%) as yellow oil; *Rf* = 0.50 (hexane/AcOEt 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.40 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.58 (s, 1H), 2.38 (s, 3H), 1.52 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 142.9 (CH), 139.6 (C), 137.4 (2 × CH), 129.6 (2 × CH), 128.3 (C), 87.7 (C), 51.2 (C), 28.8 (2 × CH_3), 21.5 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 124 (100), 269 (23), 352 (M^+, 1). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{12}H_{15}Br_2S$, 347.9183 ; not found.

(2-methylbut-3-yn-2-yl) (*p*-tolyl)sulfide (1q)

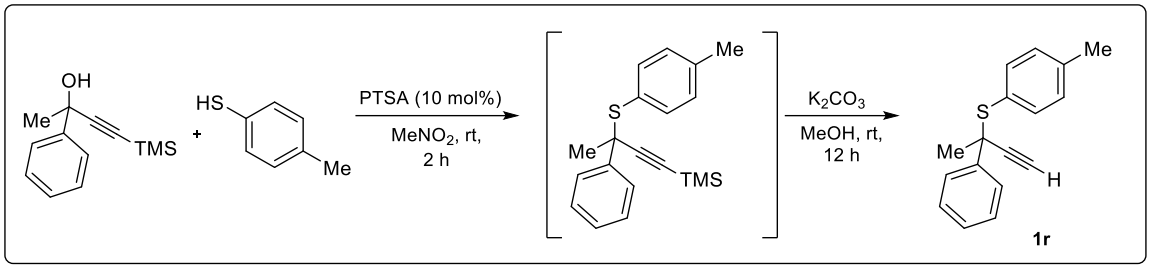


1q

Purification by column chromatography yielded **1q** (396 mg, 69%) as colourless liquid; *Rf* = 0.28 (hexane/CH_2Cl_2 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.58 – 7.52 (m, 2H), 7.20 – 7.14 (m, 2H), 2.40 (s, 1H), 2.38 (s, 3H), 1.54 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 139.5 (C), 136.9 (2 × CH), 129.5 (2 × CH), 128.7 (C), 88.7 (C), 70.9 (CH), 41.4 (CH), 30.3 (2 × CH_3), 21.4 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 124 (100), 175 (59), 190 (M^+, 18). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{12}H_{15}S$, 191.0889 ; found, 191.0892.

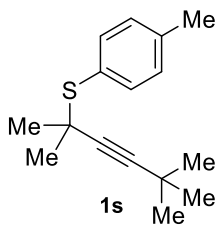
(2-phenylbut-3-yn-2-yl)(*p*-tolyl)sulfide (1r)

Compound **1r** was prepared according to the following synthetic sequence:



4-Methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol) and *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) were sequentially added to a solution of 2-phenyl-4-(trimethylsilyl)but-3-yn-2-ol[10] (654 mg, 1 equiv., 3 mmol) in nitromethane (6 mL, 0.5 M). The mixture was allowed to stir at room temperature for 2 hours until full depletion of the alcohol was determined by TLC; spots were visualized by using phosphomolybdic acid solution and heat as the staining agent. Then, the reaction mixture was quenched by the addition of aqueous NaOH and NaCl. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Then, K_2CO_3 (1.24 g, 3 equiv., 9 mmol) was added to a solution of the reaction crude (1 equiv., 3 mmol) in methanol (15 mL, 0.2 M). The mixture was allowed to stir at room temperature overnight. Then, the reaction mixture was quenched by the addition of aqueous NaCl and H_2O. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by column chromatography yielded **1r** (539 mg, 71%) as white solid; m.p. =68–70 °C; *Rf* = 0.16 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.67 – 7.62 (m, 2H), 7.38 – 7.24 (m, 5H), 7.08 (d, *J* = 8.1 Hz, 2H), 2.74 (s, 1H), 2.37 (s, 3H), 1.98 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 142.1 (C), 139.5 (C), 136.7 (2 × CH), 129.3 (2 × CH), 129.0 (C), 128.2 (2 × CH), 127.5 (CH), 126.9 (2 × CH), 86.4 (C), 74.7 (CH), 49.4 (C), 30.0 (CH_3), 21.4 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 73 (100), 105 (48), 252 (M^+,6). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{17}H_{17}S$, 253.1045; found, 253.1049.

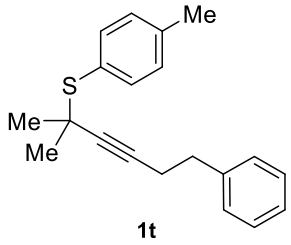
***p*-tolyl(2,5,5-trimethylhex-3-yn-2-yl)sulfide (1s)**



The general procedure **A1** was followed using 2,5,5-trimethylhex-3-yn-ol[9, 10] (**S1s**) (420 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1s** (464 mg, 64%) as white solid; m.p.= 54–56

°C; *Rf* = 0.41 (hexane/ CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.53 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 1.49 (s, 6H), 1.17 (s, 9H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 139.0 (C), 137.0 (2 × CH), 129.5 (C), 129.2 (2 × CH), 91.7 (C), 83.2 (C), 42.3 (C), 31.3 (3 × CH_3), 31.0 (2 × CH_3), 27.4 (C), 21.4 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 81 (100), 124 (42), 246 (M^+, 6). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{23}S$, 247.1515; found, 247.1516.

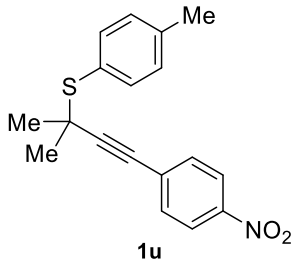
(2-methyl-6-phenylhex-3-yn-2-yl)(*p*-tolyl)sulfide (1t)



1t

The general procedure **A1** was followed using 2-methyl-6-phenylhex-3-yn-2-ol[11] (**S1t**) (564 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1t** (505 mg, 57%) as colourless liquid; *Rf* = 0.18 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.53 – 7.47 (m, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.13 (m, 3H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.49 (t, *J* = 7.7 Hz, 2H), 2.40 (s, 3H), 1.52 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 140.8 (C), 139.1 (C), 136.9 (2 × CH), 129.2 (2 × CH), 129.2 (CH), 128.5 (2 × CH), 128.3 (2 × CH), 126.2 (C), 85.5 (C), 82.7 (C), 42.2 (C), 35.3 (CH_2), 30.7 (2 × CH_3), 21.3 (CH_2), 21.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 91 (100), 129 (43), 294 (M^+,7). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{23}S$, 295.1515; found, 295.1526.

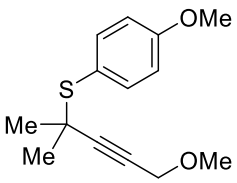
(2-methyl-4-(4-nitrophenyl)but-3-yn-2-yl)(*p*-tolyl)sulfide (1u)



1u

The general procedure **A1** modified at 80 °C overnight was followed using 2-methyl-4-(4-nitrophenyl)but-3-yn-2-ol[11] **S1u** (615 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1u** (533 mg, 56%) as yellow solid; m.p.= 58–60 °C; *Rf* = 0.38 (hexane/CH_2Cl_2 = 2:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 8.16 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H), 1.63 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 146.9 (C), 139.8 (C), 137.2 (2 × CH), 132.3 (2 × CH), 130.4 (C), 129.5 (2 × CH), 128.6 (C), 123.6 (2 × CH), 99.9 (C), 81.7 (C), 42.3 (C), 30.1 (2 × CH_3), 21.4 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 188 (100), 141 (34), 311 (M^+, 6). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{18}H_{18}NO_2S$, 312.1053; found, 312,1058.

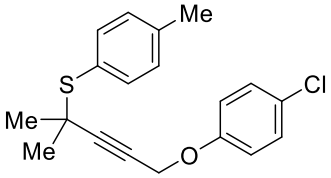
(5-methoxy-2-methylpent-3-yn-2-yl)(4-methoxyphenyl)sulfide (1v)



1v

The general procedure **A1** was followed using 5-methoxy-2-methylpent-3-yn-2-ol[12] (**S1v**) (384 mg, 3 mmol), 4-methoxybenzenethiol (630 mg, 4.5 mmol), *p*-toluensulfonic acid (PTSA) (mg, mmol) and nitromethane (mL). Purification by column chromatography yielded **1v** (278 mg, 37%) as yellow liquid; *Rf* = 0.28 (hexane/AcOEt 5:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.58 – 7.50 (m, 2H), 6.90 – 6.83 (m, 2H), 4.09 (s, 2H), 3.81 (s, 3H), 3.31 (s, 3H), 1.51 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 160.8 (C), 138.7 (2 × CH), 123.3 (C), 114.1 (2 × CH), 91.2 (C), 78.7 (C), 60.2 (CH_2), 57.5 (CH_3), 55.4 (CH_3), 42.0 (C), 30.3 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 140 (100), 187 (12), 250 (M^+, 10). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{14}H_{19}O_2S$, 251.1100; found, 251.1101.

(5-(4-chlorophenoxy)-2-methylpent-3-yn-2-yl)(*p*-tolyl)sulfide (1w)

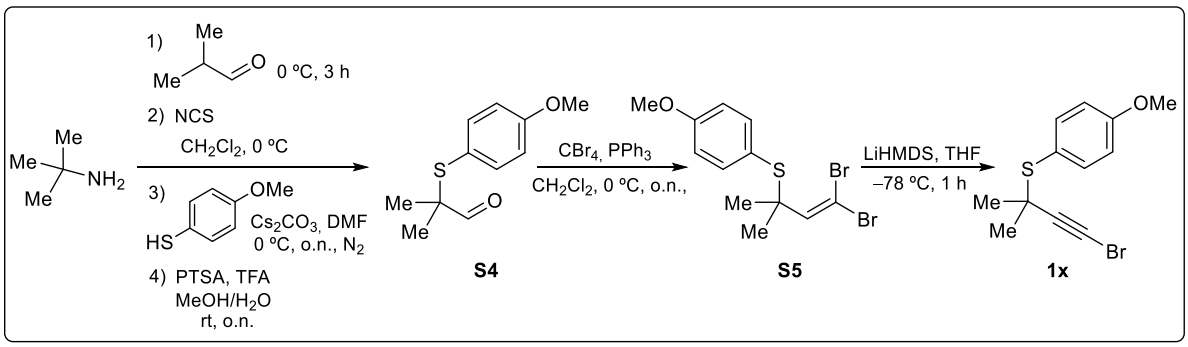


1w

The general procedure **A1** modified at 60 °C was followed using 5-(4-chlorophenoxy)-2-methylpent-3-yn-2-ol **S1w** (672 mg, 3 mmol), 4-methylbenzenethiol (558 mg, 1.5 equiv., 4.5 mmol), *p*-toluensulfonic acid (PTSA) (52 mg, 0.1 equiv., 0.3 mmol) and nitromethane (6 mL, 0.5 M). Purification by column chromatography yielded **1w** (294 mg, 30%) as yellow oil; *Rf* = 0.38 (hexane/CH_2Cl_2 = 20:1); Yield = 14%. **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.44 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.88 – 6.81 (m, 2H), 4.66 (s, 2H), 2.36 (s, 3H), 1.50 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 156.5 (C), 139.5 (C), 137.0 (2 × CH), 129.4 (2 × CH), 129.4 (2 × CH), 128.6 (C), 126.3 (C), 116.5 (2 × CH), 92.5 (C), 77.4 (C), 56.7 (CH_2), 41.7 (C), 30.2 (2 × CH_3), 21.4 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 77 (100), 124 (52), 330 (M^+, 4). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{20}ClOS$, 331.0918; found, 331.0921.

Procedure for the Synthesis of (4-bromo-2-methylbut-3-yn-2-yl)(4-methoxyphenyl)sulfide (1x)

Compound **1x** was prepared according to the following synthetic sequence:[14,15]



A mixture of 2-methylpropan-2-amine (0.73 mg, 1 equiv., 10 mmol) and isobutyraldehyde (0.72 mg, 1 equiv., 10 mmol) was stirred at 0 °C for 3 hours until full depletion of the aldehyde or amine was determined by GC-MS. The reaction mixture was diluted in dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure.

The resulting crude imine was dissolved in dichloromethane (10 mL, 1M) at 0 °C under N_2. Then, *N*-chlorosuccinimide (NCS) (1.34 g, 1 equiv., 10 mmol) was added at once and was stirred until full depletion of the imine was determined by GC-MS. The reaction mixture was diluted in Et_2O and was washed with $Na_2S_2O_3$ and NaOH. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude *N*-(*tert*-butyl)-2-chloro-2-methylpropan-1-imine was immediately used in the next step.

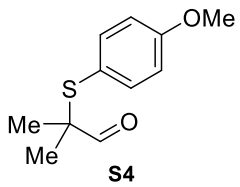
Cs_2CO_3 (6.52 g, 2 equiv., 20 mmol) was added to a solution of 4-methoxybenzenethiol (1.40 g, 1 equiv., 10 mmol) in DMF (20 mL, 0.5 M) at 0 °C under N_2. The mixture was allowed to stir for 1 hour, and then, crude *N*-(*tert*-butyl)-2-chloro-2-methylpropan-1-imine generated in the previous step and dissolved in DMF (5 ml), was added dropwise and the mixture was allowed to stir at room temperature overnight. Then, the reaction was quenched by addition of H_20 at 0 °C. The separated aqueous phase was extracted with Et_2O (3 × 20 mL) and washed with NaCl. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was dissolved in a 1:1 mixture of MeOH/H_2O (33 mL, 0.3 M) and then *p*-toluensulfonic acid (PTSA) (34 mg, 0.02 equiv., 0.2 mmol) and trifluoroacetic acid (TFA) (2.28 g, 2 equiv., 20 mmol) were sequentially added. The obtained mixture was allowed to stir at room temperature overnight until full depletion of the imine was determined by GC-MS. Then, the reaction mixture was quenched by the addition of saturated aqueous NaCl and H_2O. The separated aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, affording the corresponding aldehyde **S4**.

The transformation of the aldehyde into the corresponding terminal alkyne is carried out through the well-known Corey-Fuchs reaction. The first step of the procedure involved the conversion of the aldehyde to the corresponding dibromoalkene through the addition of the 2-((4-methoxyphenyl)thio)-2-methylpropanal (1.26 g, 1 equiv., 6 mmol) to a mixture of triphenylphosphine (6.29 g, 4 equiv., 24 mmol) and carbon tetrabromide (3.98 g, 2 equiv., 12 mmol) in CH_2Cl_2 (24 mL, 0.25 M), at 0 °C under N_2 for 2 hours. Then, the reaction mixture was filtered through a celite plug. The filtrate was washed with CH_2Cl_2. The organic layer

was dried over Na_2SO_4, filtered and concentrated *in vacuo*. It was purified by column chromatography on silica gel, affording the pure dibromoolefin **S5**.

In the second step, the conversion of the prepared (4,4-dibromo-2-methylbut-3-en-2-yl)(4-methoxyphenyl)sulfane **S5** (1.09 g, 1 equiv., 3 mmol) dissolved in THF (10 mL, 0.3 M) to the corresponding terminal alkyne is accomplished by treatment with LiHMDS (5.4 mL, 1 M, 1.8 equiv., 5.4 mmol) at −78 °C under N_2 followed by subsequent hydrolysis with NH_4Cl. The separated aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel, affording the corresponding alkyne **1x**.

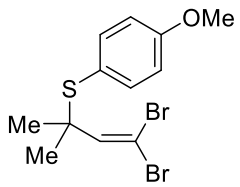
2-((4-methoxyphenyl)thio)-2-methylpropanal (S4)



S4

Purification by column chromatography yielded **S4** (1.54 g, 73%) as yellow oil; *Rf* = 0.36 (hexane/AcOEt 10:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 9.31 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 1.30 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 195.4 (CH), 161.0 (C), 138.8 (2 × CH), 120.6 (C), 114.6 (2 × CH), 55.5 (C), 55.4 (CH_3), 21.1 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 181 (100), 139 (51), 210 (M^+, 34). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{11}H_{15}SO_2$, 211.0787 ; found, 211.0786.

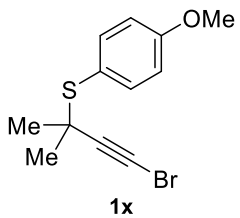
(4,4-dibromo-2-methylbut-3-en-2-yl)(4-methoxyphenyl)sulfane (S5)



S5

Purification by column chromatography yielded **S5** (1.85 g, 82%) as yellow oil; *Rf* = 0.29 (hexane/AcOEt 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.43 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.55 (s, 1H), 3.83 (s, 3H), 1.50 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 160.9 (C), 142.8 (CH), 139.0 (2 × CH), 122.7 (C), 114.4 (2 × CH), 87.6 (C), 55.5 (C), 51.3 (CH_3), 28.6 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 140 (100), 125 (18), 366 (M^+, 1). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{12}H_{15}Br_2SO$, 364.9205 ;not found.

(4-bromo-2-methylbut-3-yn-2-yl) (4-methoxyphenyl)sulfide (1x)

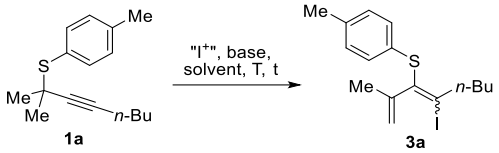


1x

Purification by column chromatography yielded **1x** (721 mg, 84%) as yellow oil; *Rf* = 0.32 (hexane/AcOEt 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.54 – 7.48 (m, 2H), 6.92 – 6.86 (m, 2H), 3.82 (s, 3H), 1.50 (s, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 160.9 (C), 138.7 (2 × CH), 122.9 (C), 114.2 (2 × CH), 84.3 (C), 55.4 (CH_3), 43.1 (C), 43.0 (C_{sp}-Br), 29.9 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 140 (100), 205 (46), 286 (M^+, 7). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{12}H_{14}BrOS$, 284.9943; found, 284.9940.

2. Optimization studies and structure elucidation of *E*-3a

2.1. Optimization table for the Synthesis of 1-iodo-1,3-diene 3a

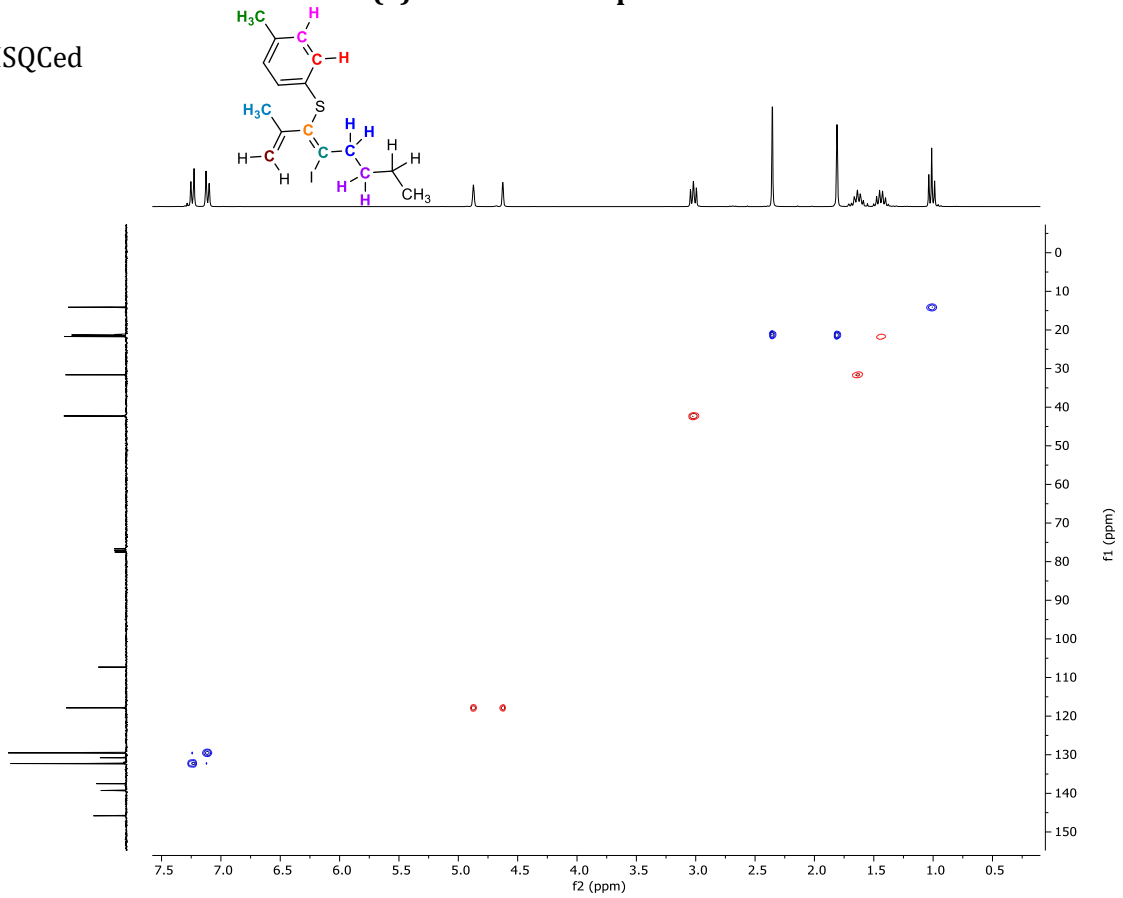


entry	solvent	I^+ source	Equiv.	base	Equiv.	T	t (h)	Conversion (%)	**3a** yield[b] (%) (*E*:*Z*)
1	$MeNO_2$	I_2	1.5	K_2CO_3	1.5	rt	6	90	16 (4:1)
2	$MeNO_2$	I_2	1.5	Cs_2CO_3	1.5	rt	6	90	10 (3:1)
3	$MeNO_2$	I_2	1.5	Na_2CO_3	1.5	rt	6	90	13 (3:1)
4	$MeNO_2$	NIS	1.5	K_2CO_3	1.5	rt	3	80	24 (3:1)
5	CH_2Cl_2	I_2	1.5	K_2CO_3	1.5	rt	6	>95	15 (>20:1)
6	CH_2Cl_2	I_2	1.5	Cs_2CO_3	1.5	rt	6	>95	15 (>20:1)
7	CH_2Cl_2	I_2	1.5	–		rt	24	5<	–
8	CH_2Cl_2	NIS	1.5	K_2CO_3	1.0	rt	24	>95	92 (4.4:1)
9	CH_2Cl_2	NIS	1.5	K_2CO_3	1.5	rt	24	>95	84 (4:1)
10	CH_2Cl_2	NIS	1.5	K_2CO_3	2.0	rt	24	>95	90 (3:1)
11	toluene	NIS	1.5	K_2CO_3	1.0	rt	24	34	–
12	THF	NIS	1.5	K_2CO_3	1.0	rt	24	5<	–
13	CH_2Cl_2	NIS	1.5	K_2CO_3	0.1	rt	24	>95	88 (2:1)
14	CH_2Cl_2	NIS	1.5	DBU	0.1	rt	24	>95	>95 (2:1)
15	CH_2Cl_2	NIS	1.5	DBU	1.0	rt	24	5<	–
16	CH_2Cl_2	NIS	1.5	DABCO	0.1	rt	24	30	–
17	CH_2Cl_2	NIS	1.5	–		rt	0.5	>95	79 (2:1)
18	toluene	NIS	1.5	–		rt	24	>95	77 (2:1)
19	THF	NIS	1.5	–		rt	24	>95	56 (4:1)
20	MeCN	NIS	1.5	–		rt	24	>95	54 (3:2)
21	CH_2Cl_2	NIS	1.5	–		0 °C	2	>95	>95 (90)[c] (20:1)
22	CH_2Cl_2	NIS	1.5	–		–20 °C	24	5<	–
23	toluene	NIS	1.5	–		0 °C	48	85	58 (8:1)
24	THF	NIS	1.5	–		0 °C	24	5<	–
25	CH_2Cl_2	NIS	1.5	K_2CO_3		0 °C	24	86	81 (7:1)
26	CH_2Cl_2	NIP	1.5	–		0 °C	2	>95	82 (10:1)
27	CH_2Cl_2	DIDMH	1.5	–		0 °C	2	>95	74 (10:1)
28	CH_2Cl_2	NIS	2.0	–		0 ºC	2	>95	78 (20:1)
29	CH_2Cl_2	NIS	1.1	–		0 ºC	3	>95	84 (20:1)

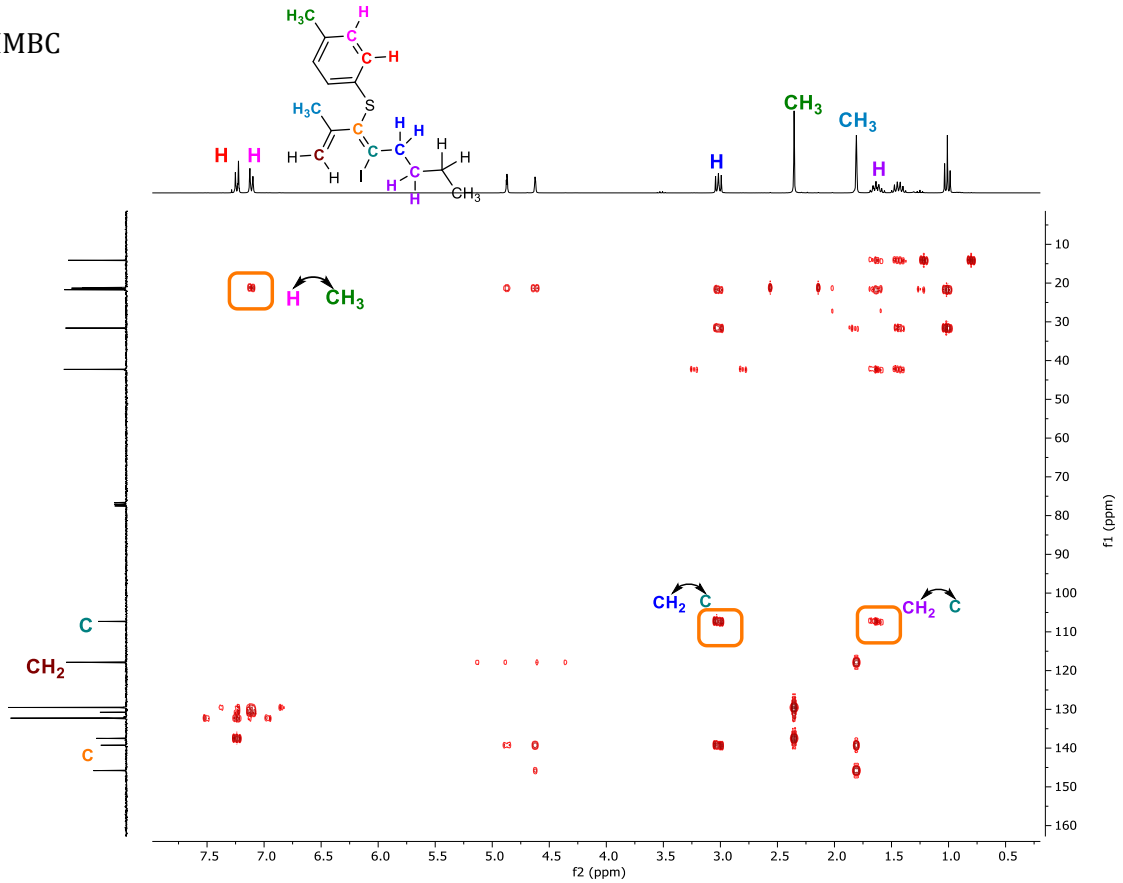
[a]Reaction conditions: thioether **1a** (0.1 mmol), I^+ source (0.15 mmol), base (0.1 mmol), temperature (T), and reaction time (t). [b]Yield determined by 1H NMR using CH_2Br_2 as internal standard and referred to starting **1a**. [c]Yield of isolated product after column chromatography referred to starting product 1**a**.

2.2. Structure elucidation (*E*)-3a: 2D NMR experiments

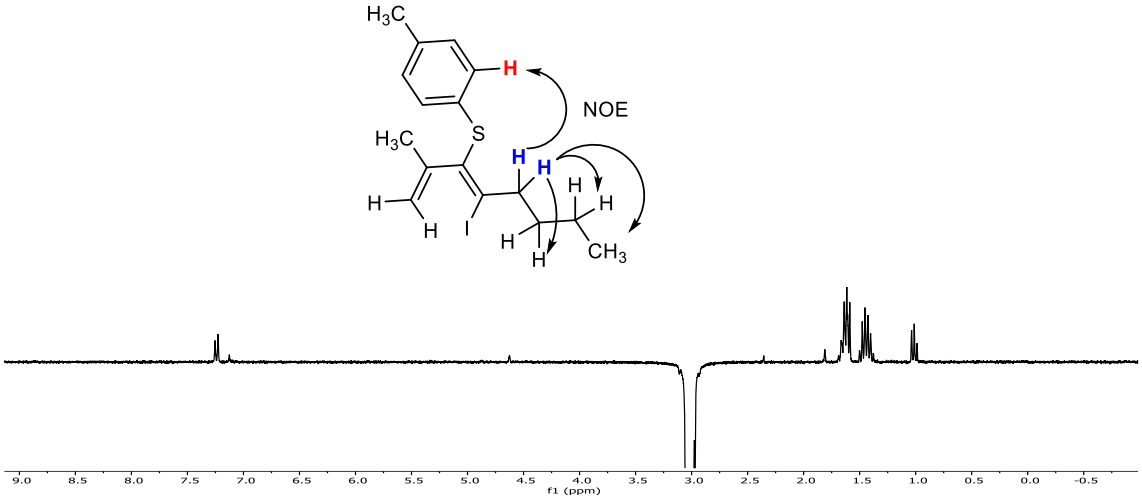
HSQCed



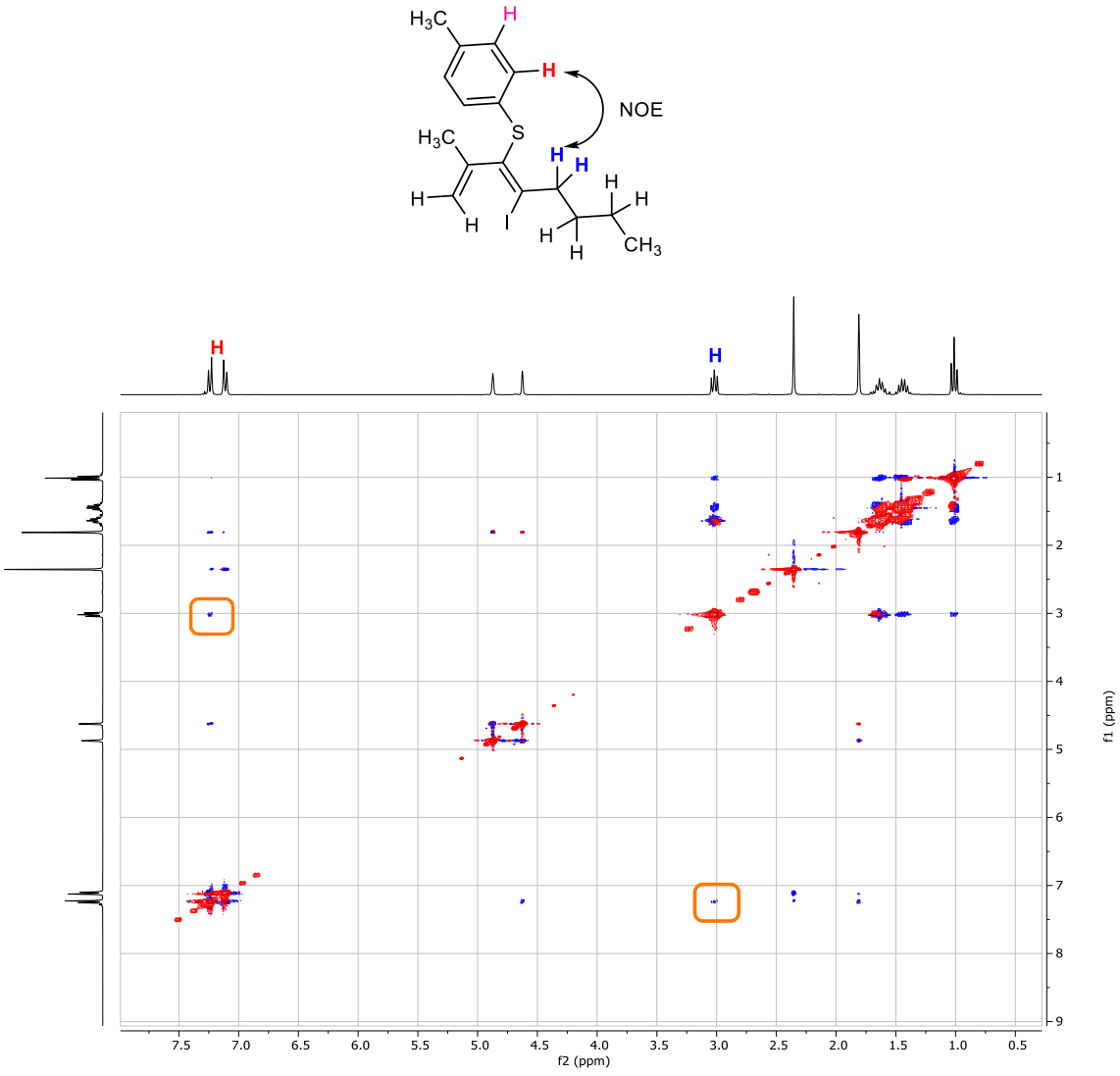
HMBC



NOE 1D



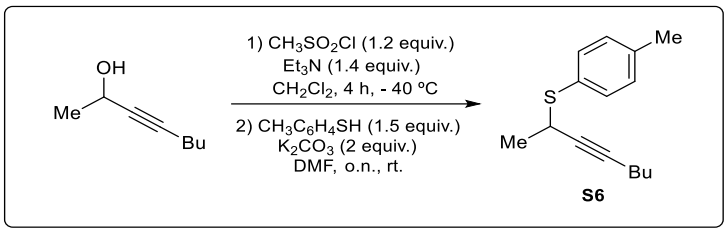
NOESY experiment



2.3. Control experiments with primary and secondary thioethers

2.3.1. Experimental Procedure for the Synthesis of Secondary Thioether S6

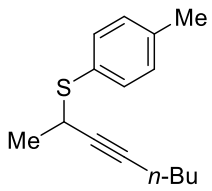
Secondary thioether **S6** was prepared by the reaction of the corresponding secondary alcohol.



Oct-3-yn-2-ol (1 equiv., 10 mmol, 1261 mg) was dissolved in dichloromethane (30 mL, 0.3 M) under nitrogen atmosphere. The reaction mixture was cooled down to –40 °C. The mixture was allowed to stir for a few minutes, then triethylamine (1.4 equiv., 14 mmol, 1416 mg) and methanesulfonyl chloride (1.2 equiv., 12 mmol, 1374 mg) were added sequentially dropwise. The obtained solution was allowed to stir until full depletion or starting materials was observed by TLC and GC-MS. Then, the reaction was quenched by the addition of water. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The organic layers were washed with saturated NH_4Cl and NaCl (20 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mesylate was immediately used in the next step without column purification.

4-methylbenzenethiol (1.5 equiv., 6 mmol, 745 mg) was dissolved in dimethylformamide (8 mL, 0.5 M). Then K_2CO_3 (2 equiv., 8 mmol, 1105 mg) was added to the solution. The reaction mixture was allowed to stir for 30 minutes. Then, the resulting crude mesylate (1 equiv., 4 mmol, 816 mg) was added and the reaction was allowed to stir overnight until full depletion or starting materials was observed by TLC. Then, the reaction was quenched by the addition of water at 0 °C. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The organic layers were washed with saturated $NaHCO_3$ and NaCl (20 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (eluent: mixtures of hexane/CH_2Cl_2) to afford the corresponding thioether **S6**.

Oct-3-yn-2-yl(p-tolyl)sulfide (S6)

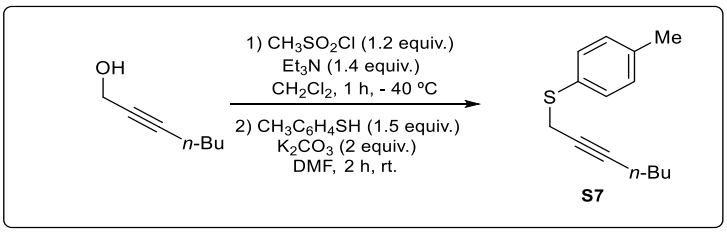


S6

Purification by column chromatography yielded **S6** (658 mg, 71%) as yellow oil; *Rf* = 0.28 (hexane/CH_2Cl_2 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.42 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.86 (qt, *J* = 7.0, 2.2 Hz, 1H), 2.35 (s, 3H), 2.17 (td, *J* = 6.9, 2.2 Hz, 2H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.44 – 1.26 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 137.9 (C), 133.7 (2 × CH), 130.6 (C), 129.6 (2 × CH), 84.2 (C), 80.9 (C), 34.3 (CH), 30.9 (CH_2), 22.4 (CH_3), 22.0 (CH_2), 21.3 (CH_3), 18.6 (CH_2), 13.7 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 124 (100), 175 (49), 232 (M^+, 32). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{21}S$, 233.1358; found, 233.1355.

2.3.2. Experimental Procedure for the Synthesis of Primary Thioether S7

Primary thioether **S7** was prepared by the reaction of the corresponding primary alcohol.

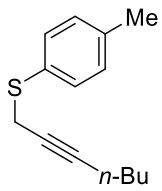


Hept-2-yn-1-ol (1 equiv., 6 mmol, 670 mg) was dissolved in dichloromethane (20 mL, 0.3 M) under nitrogen atmosphere. The reaction mixture was cooled down to –40 °C. The mixture was allowed to stir for a few minutes, then triethylamine (1.4 equiv., 8.4 mmol, 849 mg) and methanesulfonyl chloride (1.2 equiv., 7.2 mmol, 824 mg) were added sequentially dropwise. The obtained solution was allowed to stir until full depletion or starting materials was observed by TLC and GC-MS. Then, the reaction was quenched by the addition of water. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The organic layers were washed with saturated NH_4Cl and NaCl (20 mL) and dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mesylate was immediately used in the next step without column purification.

4-methylbenzenethiol (1.5 equiv., 7.5 mmol, 931 mg) was dissolved in dimethylformamide (10 mL, 0.5 M). Then K_2CO_3 (2 equiv., 10 mmol, 1382 mg) was added to the solution. The reaction mixture was allowed to stir for 30 minutes. Then, the resulting crude mesylate (1 equiv., 5 mmol, 950 mg) was added and the reaction was allowed to stir until full depletion or starting materials was observed by TLC. Then, the reaction was quenched by the addition of water at 0 °C. The separated aqueous phase was extracted with Et_2O (3 × 10 mL). The organic layers were washed with saturated $NaHCO_3$ and NaCl (20 mL) and dried over

anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (eluent: mixtures of hexane/CH_2Cl_2) to afford the corresponding thioether **S7**.

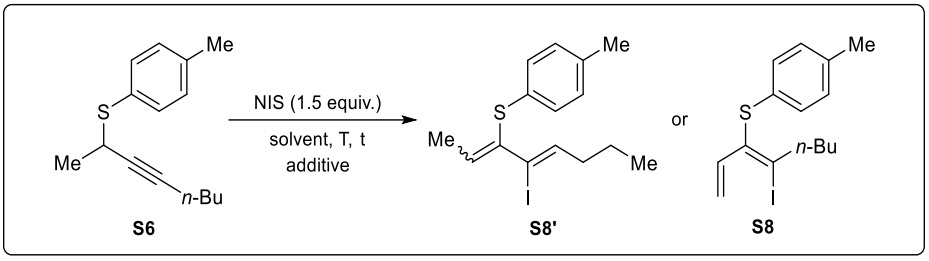
Hept-2-yn-1-yl(p-tolyl)sulfide (*S7*)



S7

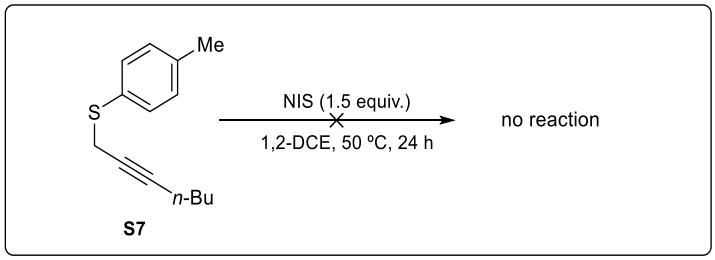
Purification by column chromatography yielded **S7** (793 mg, 71%) as yellow liquid; *Rf* = 0.33 (hexane/CH_2Cl_2 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.36 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 3.58 (t, *J* = 2.4 Hz, 2H), 2.34 (s, 3H), 2.17 (ddd, *J* = 6.9, 4.5, 2.3 Hz, 2H), 1.61 – 1.22 (m, 4H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 137.0 (C), 132.0 (C), 131.0 (2 × CH), 129.7 (2 × CH), 84.2 (C), 75.8 (C), 30.9 (CH_2), 24.0 (CH_2), 22.0 (CH_2), 21.2 (CH_3), 18.6 (CH_2), 13.7 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 161 (100), 218 (M^+, 72), 91 (33). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{14}H_{19}S$, 292.1202; found 292.1202.

2.3.3. Control experiments with Secondary and Primary Thioethers



Entry[a]	solvent	additive	equiv.	T (°C)	t (h)	conversion (%)	Yield **S8**/**S8'** (%)[b]
1	CH_2Cl_2	-	-	0	24	5<	-
2	DCE	-	-	60	1	95>	-[c]
3	toluene	-	-	60	24	5<	-
4	DCE	K_2CO_3	1.3	50	3	95>	10 (1:2)<[d]

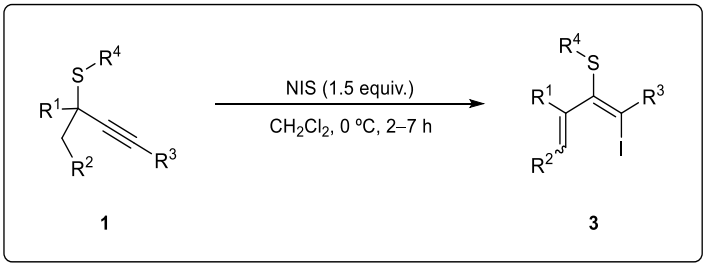
[a]Reaction conditions: thioether **S6** (0.4 mmol), I^+ source (0.6 mmol), additive (0.52 mmol), temperature (T), and reaction time (t).[b]Yield determined by 1H NMR using CH_2Br_2 as internal standard and referred to starting **S6**. [c]Complex mixtures of multiple byproducts was observed. [d]Obtained as an inseparable mixture of products, yield of isolated product after column chromatography referred to starting product S6.



3. Experimental Procedures and Characterization Data of 1-iodo-1,3-dienes (3) and 1-bromo-1,3-dienes (4)

3.1. Experimental Procedure and Characterization Data of 1-iodo-1,3-dienes

3.1.1. General Procedure B for the Synthesis of 1-iodo-1,3-dienes (3)



Propargylic sulfide **1** (1 equiv., 0.5 mmol) was dissolved in dichloromethane (5 mL, 0.1 M) in the dark. Then, iodonium ion source, *N*-iodosuccinimide (168 mg, 1.5 equiv., 0.75 mmol) was added at once. The obtained suspension was allowed to stir at 0 °C in a precooled bath until full depletion of the propargyl thioether was determined by GC-MS. Then, saturated aqueous $Na_2S_2O_3$ (0.05 mL) was added to quench the reaction. The mixture was allowed to warm to rt, and then the mixture was dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The crude was purified by column chromatography on deactivated silica gel (eluent: mixtures of hexane/CH_2Cl_2) to afford the corresponding diene **3**.

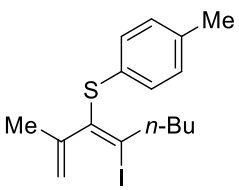
3.1.2. Procedure for the multigram-scale Synthesis of (*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl)(*p*-tolyl)sulfide (3a)

Following the general procedure **B**, propargyl sulfide **1a** (3.81 mg, 1 equiv., 15.47 mmol) was dissolved in dichloromethane (154 ml, 0.1 M) in the dark. Then iodonium ion source, *N*-iodosuccinimide (5.21 mg, 1.5 equiv., 23.20 mmol) was added at once. The obtained suspension was allowed to stir at 0 °C in a precooled bath until full depletion of the propargyl thioether was determined by GC-MS (2 h). Then, saturated aqueous $Na_2S_2O_3$ (2 mL) was added to quench the reaction. The mixture was allowed to warm to rt, dried with anhydrous Na_2SO_4 and filtered. Filtrate was concentrated under reduced pressure. The crude was purified by column chromatography on deactivated silica gel (eluent: mixtures of hexane/ CH_2Cl_2) to afford the corresponding diene **3a** (5.41g, 94%).

Characterization Data of 1-iodo-1,3-dienes 3:

(*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide (3a)

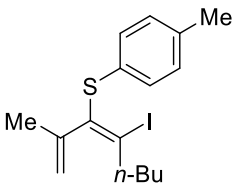
The general procedure **B** was followed using (2-methyloct-3-yn-2-yl)(*p*-tolyl)sulfide **1a** (123 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL).



3a

Purification by column chromatography yielded **3a** (168 mg, 90%) as pale yellow oil; *Rf* = 0.38 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.20 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 4.84 (t, *J* = 1.6 Hz, 1H), 4.59 (dd, *J* = 1.8, 1.0 Hz, 1H), 2.98 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 1.77 (s, 3H), 1.68 – 1.52 (m, 2H), 1.52 – 1.32 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.9 (C), 139.8 (C), 137.6 (C), 132.4 (2 × CH), 130.9 (C), 129.6 (2 × CH), 118.0 (CH_2), 107.4 (C), 42.3 (CH_2), 31.7 (CH_2), 21.8 (CH_3), 21.4 (CH_2), 21.3 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 77 (100), 245 (70), 372 (M^+,21). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{22}IS$, 373.0481; found, 373.0481.

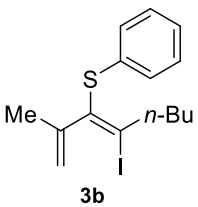
(*Z*)-(4-iodo-2-methylocta-1,3-dien-3-yl)(*p*-tolyl)sulfide (3a')



3a'

In a Schlenk flask under nitrogen atmosphere, (*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide **3a** (149 mg, 0.4 mmol), were dissolved in anhydrous freshly degassed CH_2Cl_2 (4 mL). The mixture as allowed to stir at room temperature under sunlight irradiation for 12 h. The reaction was monitored by GC-MS and TLC. After 12 h the reaction was concentrated and the crude was analyzed by NMR; no complete isomerization was observed, although a mixture (1:1) of both *E*:*Z* diastereoisomers was detected. The crude was purified by column chromatography on silica gel affording pure ***Z*-3a** (34 mg, 45%) as pale yellow oil; *Rf* = 0.34 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.27 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 4.89 – 4.82 (m, 1H), 4.70 – 4.62 (m, 1H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 1.69 (s, 3H), 1.65 – 1.49 (m, 2H), 1.33 (h, *J* = 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 144.5 (C), 141.0 (C), 137.8 (C), 133.5 (2 × CH), 130.4 (C), 129.5 (2 × CH), 117.8 (CH_2), 109.1 (C), 42.4 (CH_2), 33.0 (CH_2), 22.9 (CH_3), 21.8 (CH_2), 21.3 (CH_3), 14.1 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 77 (100), 245 (12), 372 (M^+,6). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{22}IS$, 373.0481; found, 373.0483.

(*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (phenyl)sulfide (3b)

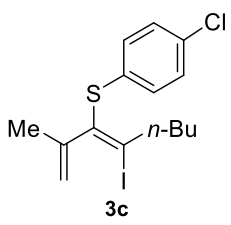


3b

The general procedure **B** was followed using (2-methyloct-3-yn-2-yl) (phenyl)sulfide **1b** (116 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3b** (130 mg, 72%) as colourless liquid; *Rf* = 0.38 (hexane/CH_2Cl_2= 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.38 – 7.19 (m, 5H), 4.88 (p, *J* = 1.6 Hz, 1H), 4.66 (dq, *J* = 1.8, 0.9 Hz, 1H), 3.02 (t, *J* = 7.5, Hz, 2H), 1.82 (t, *J* = 1.2 Hz, 3H), 1.70 – 1.58 (m, 2H), 1.43 (h, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.9 (C), 138.7 (C), 134.6 (C), 131.8 (2 × CH), 128.8 (2 × CH), 127.4 (CH), 118.0 (CH_2), 108.8 (C), 42.5 (CH_2), 31.7 (CH_2), 21.8 (CH_2), 21.4 (CH_3), 14.2 (CH_3)

ppm. **LRMS (EI) *m/z* (%)** 77 (100), 93 (74), 358 (M^+,66). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{20}IS$, 359.0325; found, 359.0325.

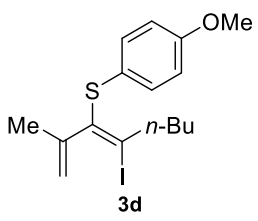
(*E*)-(4-chlorophenyl)(4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3c)



3c

The general procedure **B** was followed using (4-chlorophenyl) (2-methyloct-3-yn-2-yl)sulfide **1c** (133 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3c** (125 mg, 63%) as colourless oil; *Rf* = 0.54 (hexane). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.29 – 7.17 (m, 4H), 4.89 – 4.84 (m, 1H), 4.64 – 4.59 (m, 1H), 2.97 (t, *J* = 7.5 Hz, 2H), 1.77 (s, 3H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.39 (h, *J* = 7.2 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.6 (C), 138.2 (C), 133.6 (C), 133.1 (2 × CH), 129.0 (2 × CH), 118.4 (CH_2), 109.1 (C), 42.5 (CH_2), 31.7 (CH_2), 21.8 (CH_2), 21.3 (CH_3), 14.2 (CH_3) ppm, one peak missing due to overlapping. **LRMS (EI) *m/z* (%)** 392 (M^+,100), 41 (60), 93 (46). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{19}ClIS$, 392.9935; found, 392.9940.

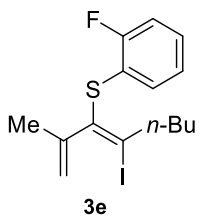
(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (4-methoxyphenyl)sulfide (3d)



3d

The general procedure **B** was followed using (4-methoxyphenyl) (2-methyloct-3-yn-2-yl)sulfide **1d** (131 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3d** (171 mg, 88%) as pale yellow liquid; *Rf* = 0.37 (hexane/CH_2Cl_2 = 5:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.33 – 7.22 (m, 2H), 6.88 – 6.77 (m, 2H), 4.82 (p, *J* = 1.6 Hz, 1H), 4.51 (dq, *J* = 1.8, 0.9 Hz, 1H), 3.80 (s, 3H), 2.99 (t, *J* = 7.5 Hz, 2H), 1.77 (t, *J* = 1.6 Hz, 3H), 1.70 – 1.53 (m, 2H), 1.43 (h, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 159.7 (C), 145.8 (C), 140.3 (C), 135.1 (2 × CH), 124.7 (C), 117.4 (CH_2), 114.4 (2 × CH), 105.3 (C), 55.4 (CH_3), 42.1 (CH_2), 31.7 (CH_2), 21.8 (CH_2), 21.4 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 340 (M^+,100), 261 (78), 139 (63). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{22}IOS$, 389.0431; found, 389.0434.

(*E*)-(2-fluorophenyl) (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3e)

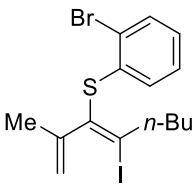


3e

The general procedure **B** was followed using (2-fluorophenyl)(2-methyloct-3-yn-2-yl)sulfide **1e** (125 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3e** (138 mg, 72%) as colourless liquid; *Rf* = 0.51 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.35 (td, *J* = 7.3, 1.6 Hz, 1H), 7.34 – 7.21 (m, 1H), 7.14 – 7.01 (m, 2H), 4.84 – 4.79 (m, 1H), 4.63 – 4.56

(m, 1H), 3.01 (t, *J* = 7.6 Hz, 2H), 1.80 (s, 3H), 1.70 – 1.55 (m, 2H), 1.43 (h, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.3 Hz, 3H). ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 162.1 (d, J_{C-F} = 247.5 Hz, C), 145.6 (C), 137.6 (C), 135.1 (CH), 130.2 (d, J_{C-F} = 7.9 Hz, CH), 124.3 (d, J_{C-F} = 3.9 Hz, CH), 121.2 (d, J_{C-F} = 17.9 Hz, C), 117.9 (CH_2), 115.9 (d, J_{C-F} = 22.6 Hz, CH), 107.1 (C), 42.4 (CH_2), 31.6 (CH_2), 21.8 (CH_2), 21.1 (CH_3), 14.2 (CH_3) ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ = –107.5 ppm. **LRMS (EI) *m/z* (%)** 376 (M^+,100), 93 (42), 121 (29). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{19}FIS$, 377.0231; found, 377.0232.

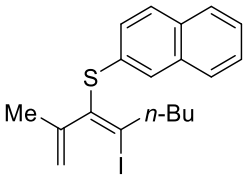
(*E*)-(2-bromophenyl) (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3f)



3f

The general procedure **B** was followed using (2-bromophenyl) (2-methyloct-3-yn-2-yl)sulfide **1f** (155 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3f** (160 mg, 73%) as colourless oil; *Rf* = 0.37 (hexane/ CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.57 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.26 (td, *J* = 7.5, 1.4 Hz, 1H), 7.10 (td, *J* = 7.6, 1.7 Hz, 1H), 44.87 (p, *J* = 1.5 Hz, 1H), 4.78 – 4.73 (m, 1H), 3.00 (t, *J* = 7.5, 2H), 1.85 (t, *J* = 1.3 Hz, 3H), 1.63 (p, *J* = 7.5 Hz, 2H), 1.42 (h, *J* = 7.3 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.8 (C), 137.1 (C), 135.7 (C), 133.2 (CH), 132.8 (CH), 128.5 (CH), 127.6 (CH), 125.8 (C), 118.1 (CH_2), 110.7 (C), 42.7 (CH_2), 31.8 (CH_2), 21.9 (CH_2), 21.4 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 77 (100), 230 (91), 436 (M^+,9). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{15}H_{19}BrIS$, 436.9430; found, 436.9433.

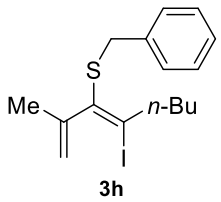
(*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (naphthalen-2-yl)sulfide (3g)



3g

The general procedure **B** was followed using (2-methyloct-3-yn-2-yl) (naphthalen-2-yl)sulfide **1g** (141 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3g** (197 mg, 96%) as colourless liquid; *Rf* = 0.41 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.85 – 7.70 (m, 4H), 7.54 – 7.45 (m, 2H), 7.39 (dd, *J* = 8.6, 1.8 Hz, 1H), 4.87 – 4.82 (m, 1H), 4.73 – 4.70 (m, 1H), 3.08 (t, *J* = 7.8 Hz, 2H), 1.84 (s, 3H), 1.68 (p, *J* = 7.1 Hz, 1H), 1.46 (h, *J* = 7.3 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.9 (C), 138.6 (C), 133.6 (C), 132.4 (C), 132.0 (C), 130.5 (CH), 129.2 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 126.6 (CH), 126.3 (CH), 118.2 (CH_2), 109.0 (C), 42.6 (CH_2), 31.8 (CH_2), 21.8 (CH_2), 21.4 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 281 (100), 408 (M^+,99), 115 (58). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{22}IS$, 409.0481 ; found, 409.0485.

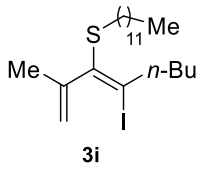
(*E*)-benzyl (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3h)



3h

The general procedure **B** was followed using benzyl (2-methyloct-3-yn-2-yl)sulfide **1h** (123 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3h** (126 mg, 67%) as colourless liquid; *Rf* = 0.46 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.37 – 7.23 (m, 5H), 5.11 (br s, 1H), 4.73 (br s, 1H), 3.72 (s, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 1.86 (br s, 3H), 1.42 – 1.27 (m, 2H), 1.26 – 1.14 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.8 (C), 139.1 (C), 137.9 (C), 129.0 (2 × CH), 128.6 (2 × CH), 127.2 (CH), 117.7 (CH_2), 106.4 (C), 41.8 (CH_2), 38.7 (CH_2), 31.5 (CH_2), 21.7 (CH_2), 21.4 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 91 (100), 372 (M^+,39), 65 (24). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{22}IS$, 373.0481; found, 373.0483.

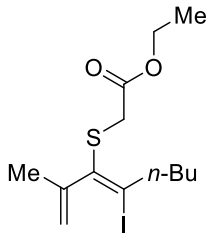
(*E*)-dodecyl (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3i)



3i

The general procedure **B** was followed using dodecyl (2-methyloct-3-yn-2-yl)sulfide **1i** (162 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3i** (183 mg, 81%) as colourless liquid; *Rf* = 0.57 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 5.10 (p, *J* = 1.6 Hz 1H), 4.74 (dq, *J* = 1.9, 1.0 Hz 1H), 2.86 (t, *J* = 7.3 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.87 (s, 3H), 1.67 – 1.43 (m, 4H), 1.42 – 1.22 (m, 20H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.8 (C), 139.6 (C), 117.0 (CH_2), 104.8 (C), 41.8 (CH_2), 34.0 (CH_2), 32.1 (CH_2), 31.5 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.73 (CH_2), 29.67 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.8 (CH_2), 22.8 (CH_2), 21.8 (CH_2), 21.4 (CH_3), 14.3 (CH_3), 14.2 (CH_3) ppm, one peak missing due to overlapping. **LRMS (EI) *m/z* (%)** 450 (M^+,100), 323 (87), 123 (37). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{21}H_{40}IS$, 451.1890; found, 451.1894.

Ethyl (*E*)-2-((4-iodo-2-methylocta-1,3-dien-3-yl)thio)acetate (3j)

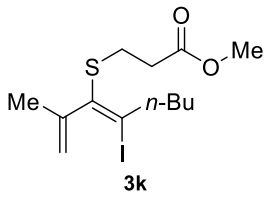


3j

The general procedure **B** was followed using Ethyl 2-((2-methyloct-3-yn-2-yl)thio)acetate **1j** (121 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3j** (101 mg, 54%) as colourless liquid; *Rf* = 0.51 (hexane/AcOEt = 10:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 5.14 (t, *J* = 1.6 Hz, 1H), 4.81 (dd, *J* = 1.9, 0.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.31 (s, 2H), 2.92 – 2.81 (m, 2H), 1.86 (d, *J* = 0.6 Hz, 3H), 1.57 – 1.43 (m, 2H), 1.39 – 1.29 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 169.6 (C),

144.8 (C), 137.5 (C), 118.4 (CH_2), 107.4 (C), 61.5 (CH_2), 42.1 (CH_2), 35.8 (CH_2), 31.5 (CH_2), 21.7 (CH_2), 21.1 (CH_3), 14.3 (CH_3), 14.1 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 93 (100), 121 (88), 368 (M^+,2). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{13}H_{22}IO_2S$, 369.0380; found, 369.0383.

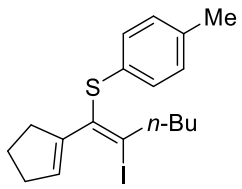
Methyl (*E*)-3-((4-iodo-2-methylocta-1,3-dien-3-yl)thio)propanoate (3k)



3k

The general procedure **B** was followed using methyl 3-((2-methyloct-3-yn-2-yl)thio)propanoate **1k** (121 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3k** (148 mg, 80%) as colourless liquid; *Rf* = 0.51 (hexane/ CH_2Cl_2 = 1:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 5.14 (p, *J* = 1.6 Hz, 1H), 4.81 (dq, *J* = 1.9, 0.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.31 (s, 2H), 2.87 (t, *J* = 7.6 Hz, 2H), 1.86 (t, *J* = 1.2 Hz, 4H), 1.56 – 1.43 (m, 2H), 1.42 – 1.24 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 172.2 (C), 145.4 (C), 138.2 (C), 117.5 (CH_2), 106.4 (C), 51.9 (CH_3), 41.9 (CH_2), 34.7 (CH_2), 31.4 (CH_2), 28.7 (CH_2), 21.7 (CH_2), 21.2 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 121 (100), 241 (20), 368 (M^+,9). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{13}H_{22}IO_2S$, 369.0380; found, 369.0385.

(*E*)-(1-(cyclopent-1-en-1-yl)-2-iodohex-1-en-1-yl) (*p*-tolyl)sulfide (3l)

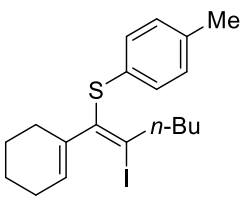


3l

The general procedure **B** was followed using (1-(hex-1-yn-1-yl)cyclopentyl (*p*-tolyl)sulfide **1l** (136 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3l** (154 mg, 77%) as brown oil (*E*:*Z*/20:1); *Rf* = 0.46 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.20 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.47 (d, *J* = 2.1 Hz, 1H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.39 – 2.28 (m, 5H), 2.27 – 2.12 (m, 2H), 1.74 (p, *J* = 7.4 Hz, 2H), 1.62 (h, *J* = 7.4, 6.4 Hz, 2H), 1.49 – 1.28 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 144.7 (C), 137.2 (C), 135.0 (C), 133.3 (C), 131.9 (2 × CH), 131.3 (C), 129.4 (2 × CH), 107.4 (CH), 42.5 (CH_2), 34.8 (CH_2), 32.9 (CH_2), 31.7 (CH_2), 23.6 (CH_2), 21.8 (CH_2), 21.3 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 398 (M^+,100), 67 (30), 271 (23). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{18}H_{24}IS$, 399.0638; found, 399.0644.

(*E*)-(1-cyclohex-1-en-1-yl)-2-iodohex-1-en-1-yl (*p*-tolyl)sulfide (3m)

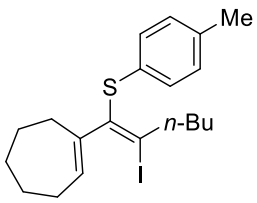
The general procedure **B** was followed using (1-(hex-1-yn-1-yl)cyclohexyl) (*p*-tolyl)sulfide **1m** (143 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5



3m

mL). Purification by column chromatography yielded **3m** (186 mg, 89%) as orange oil; *Rf* = 0.43 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.25 – 7.15 (m, 1H), 7.11 – 7.02 (m, 1H), 5.26 (tt, *J* = 3.7, 1.7 Hz, 1H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 2.02 – 1.91 (m, 1H), 1.91 – 1.78 (m, 1H), 1.66 – 1.50 (m, 2H), 1.50 – 1.29 (m, 6H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 140.0 (C), 139.5 (C), 137.6 (C), 133.3 (2 × CH), 130.7 (C), 129.9 (C), 129.2 (2 × CH), 105.0 (CH), 42.1 (CH_2), 31.5 (CH_2), 27.1 (CH_2), 25.0 (CH_2), 22.5 (CH_2), 21.82 (CH_2), 21.77 (CH_2), 21.2 (CH_3), 14.1 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 285 (100), 412 (M^+,98), 91 (84). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{26}IS$, 413.0794; found, 413.0796.

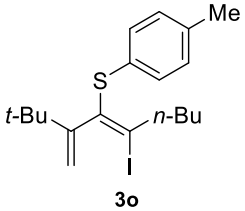
(*E*)-(1-(cyclohept-1-en-1-yl)-2-iodohex-1-en-1-yl) (*p*-tolyl)sulfide (3n)



3n

The general procedure **B** was followed using (1-(hex-1-yn-1-yl)cycloheptyl (*p*-tolyl)sulfide **1n** (150 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3n** (182 mg, 85%) as pale yellow oil; *Rf* = 0.43 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.21– 7.13 (m, 2H), 7.10– 7.05 (m, 2H), 5.49 (t, *J* = 6.4 Hz, 1H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.19 – 2.09 (m, 2H), 2.03 – 1.90 (m, 2H), 1.65 – 1.50 (m, 4H), 1.48 – 1.38 (m, 2H), 1.39 – 1.24 (m, 4H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 144.4 (C), 142.4 (C), 137.5 (C), 135.3 (C), 133.0 (2 × CH), 131.0 (CH), 129.3 (2 × CH), 105.3 (C), 42.3 (CH_2), 32.9 (CH_2), 32.0 (CH_2), 31.7 (CH_2), 28.6 (CH_2), 26.4 (CH_2), 21.8 (CH_3), 21.3 (CH_2), 14.2 (CH_3) ppm one peak missing due to overlapping. **LRMS (EI) *m/z* (%)** 91 (100), 41 (50), 426 (M^+,5). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{28}IS$, 427.0951; found, 427.0957.

(*E*)-(5-iodo-2,2-dimethyl-3-methylenenon-4-en-4-yl) (*p*-tolyl)sulfide (3o)

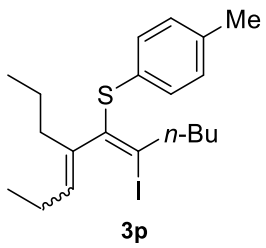


3o

The general procedure **B** was followed using (2,2,3-trimethylnon-4-yn-3-yl) (*p*-tolyl)sulfide **1o** (144 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3o** (170 mg, 82%) as pale yellow oil; *Rf* = 0.50 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.16 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 4.96 (s, 1H), 4.53 (s, 1H), 3.34 (ddd, *J* = 13.7, 8.8, 6.8 Hz, 1H), 2.87 (ddd, *J* = 14.0, 8.7, 5.6 Hz, 1H), 2.32 (s, 3H), 1.69 – 1.54 (m, 2H), 1.41 (h, *J* = 7.3 Hz, 2H), 1.20 (s, 9H), 0.98 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 157.0 (C), 138.9 (C), 137.2 (C), 131.8 (2 × CH), 131.1 (C), 129.6 (2 × CH), 116.7 (CH_2), 114.6 (C), 42.8 (CH_2), 35.6 (C), 32.0 (CH_2), 31.4 (3 × CH_3), 21.9 (CH_3), 21.3 (CH_2), 14.2 (CH_3)

ppm. **LRMS (EI) *m/z* (%)** 57 (100), 287 (70), 414 (M^+,34). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{28}IS$, 415.0951; found, 415.0951.

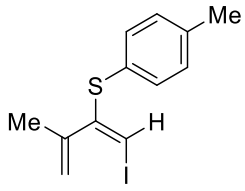
((3*E*,5*E*)-6-iodo-4-propyldeca-3,5-dien-5-yl) (*p*-tolyl)sulfide (3p)



3p

The general procedure **B** was followed using (4-propyldec-5-yn-4-yl) (*p*-tolyl)sulfide **1p** (151 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3p** (mg, 85%) as pale yellow solid; m.p.= 50–52 °C; Rf = 0.50 (hexane/CH_2Cl_2 = 100:1). Obtained as a mixture of two diastereoisomers (*E*,*E*:*E*,*Z*/3:1; **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.29 – 7.22 (m, 2H), 7.18 – 7.11 (m, 0.7H, *minor*), 7.09 – 7.02 (m, 2.7H), 5.09 (t, J = 7.4 Hz, 0.34H, *minor*), 4.98 (ddt, J = 7.7, 6.3, 1.4 Hz, 1H, *major*), 3.12 – 2.88 (m, 2.7H), 2.32 (s, 3H, *major*), 2.31 (s, 1H, *minor*), 2.12 – 1.77 (m, 3.6H), 1.70 – 1.53 (m, 4.64H), 1.51 – 1.32 (m, 5.46H), 1.04 – 0.86 (m, 8H), 0.74 (t, J = 7.5 Hz, 1H, *minor*), 0.72 (t, J = 7.5 Hz, 3H, *major*) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 140.5 (C), 139.5 (C), 139.2 (C), 138.3 (C), 138.0 (C), 137.2 (C), 136.6 (C), 134.0 (2 × CH), 132.3 (C), 131.2 (2 × CH), 129.9 (2 × C), 129.5 (2 × CH), 129.3 (2 × CH), 108.5 (CH), 107.5 (CH), 43.0 (CH_2), 42.5 (CH_2), 38.1 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 23.1 (CH_2), 21.9 (CH_2), 21.4 (CH_2), 21.3 (CH_3), 21.2 (CH_3), 20.6 (CH_2), 14.9 (2 × CH_2), 14.5 (CH_3), 14.3 (CH_3), 13.4 (2 × CH_3), 13.2 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 301 (100), 55 (75), 428 (M^+,38). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{30}IS$, 429.1107; found, 429.1112.

(*E*)-(1-iodo-3-methylbuta-1,3-dien-2-yl) (*p*-tolyl)sulfide (3q)

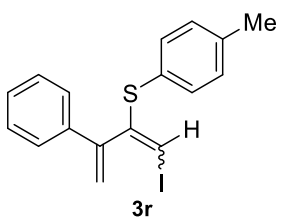


3q

The general procedure **B** was followed using (2-methylbut-3-yn-2-yl) (*p*-tolyl)sulfide **1q** (95 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3q** (69 mg, 43%) as pale yellow oil; *Rf* = 0.53 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.33 – 7.28 (m, 2H), 7.17 – 7.12 (m, 2H), 6.10 (s, 1H), 5.12 (p, *J* = 1.6 Hz, 1H), 4.95 (dq, *J* = 1.9, 1.0 Hz, 1H), 2.35 (s, 3H), 1.91 (t, *J* = 1.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 146.9 (C), 142.9 (C), 138.8 (C), 133.5 (2 × CH), 130.2 (2 × CH), 129.0 (C), 118.8 (CH_2), 72.4 (CH), 21.4 (CH_3), 21.3 (CH_3) ppm. **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{12}H_{14}IS$, 316.9855; found, 316.9857.

(1-iodo-3-phenylbuta-1,3-dien-2-yl) (*p*-tolyl)sulfide (3r)

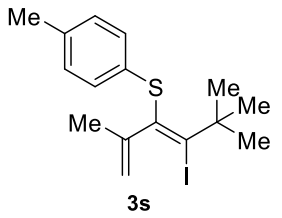
The general procedure **B** was followed using (2-phenylbut-3-yn-2-yl) (*p*-tolyl)sulfide **1r** (126 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL).



3r

Purification by column chromatography yielded **3r** (111 mg, 51%) as brown oil mixture of diastereisomers (*E*:*Z*/1:1); *Rf* = 0.31 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.45 – 7.38 (m, 2H), 7.38 – 7.30 (m, 5H), 7.25 – 7.13 (m, 5H), 7.07 – 7.00 (m, 2H), 6.99 – 6.90 (m, 4H), 6.71 (br s, 1H), 6.26 (br s, 1H), 5.70 (br s, 1H), 5.35 (d, *J* = 1.3 Hz, 1H), 5. 28 – 5.21 (m, *J* = 1.1 Hz, 2H), 2.37 (s, 3H), 2.28 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 150.8 (C), 148.3 (C), 146.4 (C), 145.9 (C), 139.9 (C), 139.4 (C), 138.4 (C), 138.0 (C), 136.8 (C), 134.7 (2 × CH), 134.1 (2 × CH), 131.0 (C), 130.3 (2 × CH), 129.2 (2 × CH), 128.6 (2 × CH), 128.3 (CH), 128.0 (3 × CH), 127.1 (2 × CH), 126.7 (2 × CH), 118.4 (CH_2), 117.9 (CH_2), 80.2 (CH), 74.1 (CH), 21.4 (CH_3), 21.3 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 128 (100), 251 (67), 378 (M^+,10). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{17}H_{16}IS$, 379.0012; found, 379.0015.

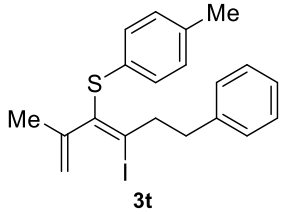
(4-iodo-2,5,5-trimethylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (3s)



3s

The general procedure **B** was followed using *p*-tolyl (2,5,5-trimethylhex-3-yn-2-yl)sulfide **1s** (123 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3s** (146 mg, 78%) as orange solid mixture of diastereoisomers (*E*:*Z*/5:1); m.p. = 59–61 °C; *Rf* = 0.41 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.30 – 7.24 (m, 2.4H), 7.20 (d, *J* = 8.1 Hz, 0.4H, *minor*), 7.10 – 7.05 (m, 2H, *major*), 4.68 – 4.63 (m, 1.2H), 4.60 – 4.56 (m, 1H, *major*), 4.45 – 4.41 (m, 0.2H, *minor*), 2.32 (s, 4H), 1.80 – 1.74 (m, 0.6H), 1.72 – 1.66 (m, 3H), 1.58 (s, 1.75H), 1.39 (s, 9H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.2 (*minor*, C), 144.7 (C), 141.5 (C), 138.9 (*minor*, C), 138.1 (C), 137.6 (*minor*, C), 134.5 (2 × CH), 132.5 (*minor*, 2 × CH), 131.6 (C), 131.4 (*minor*, C), 129.5 (*minor*, 2 × CH), 129.4 (2 × CH), 122.9 (C), 120.8 (*minor*, C), 118.7 (CH_2), 116.9(*minor*, CH_2), 43.5 (C), 41.2 (*minor*, C), 33.6 (*minor*, 3 × CH_3), 33.2 (3 × CH_3), 24.0 (CH_3), 21.5 (*minor*, CH_3), 21.4 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 57 (100), 107 (61), 372 (M^+,2). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{22}IS$, 373.0481; found, 373.0484.

(*E*)-(4-iodo-2-methyl-6-phenylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (3t)

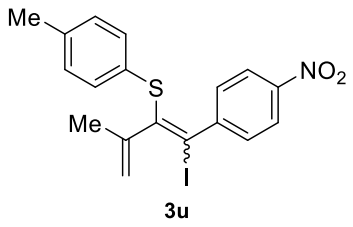


3t

The general procedure **B** was followed using (2-methyl-6-phenylhex-3-yn-2-yl) (*p*-tolyl)sulfide **1t** (147 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3t** (188 mg, 89%) as colourless liquid; *Rf* = 0.20 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.40 – 7.19 (m, 5H), 7.08 – 6.95 (m, 4H), 4.81 (p, *J* = 1.6

Hz, 1H), 4.54 – 4.47 (m, 1H), 7.01 (d, *J* = 2.8 Hz, 4H), 4.81 (s, 1H), 4.51 (s, 1H), 3.29 (t, *J* = 7.5 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.31 (s, 3H), 1.73 (t, *J* = 1.2 Hz, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 145.7 (C), 140.9 (C), 140.5 (C), 137.7 (C), 132.6 (2 × CH), 130.5 (C), 129.5 (2 × CH), 129.1 (2 × CH), 128.5 (2 × CH), 126.3 (CH_3), 118.0 (CH_2), 105.4 (C), 44.3 (CH_2), 35.5 (CH_2), 21.3 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 91 (100), 187 (22), 420 (M^+,9). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{22}IS$, 421.0481; found, 421.0485.

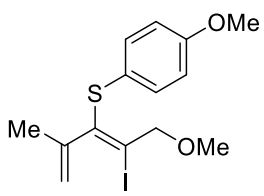
(1-iodo-3-methyl-1-(4-nitrophenyl)buta-1,3-dien-2-yl) (*p*-tolyl)sulfide (3u)



3u

The general procedure **B** was followed using (2-methyl-4-(4-nitrophenyl)but-3-yn-2-yl) (*p*-tolyl)sulfide **1u** (155 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3u** (157 mg, 73%) as yellow solid as a mixture of diastereoisomers 2:1; m.p.= 59–61 °C *Rf* = 0.40 (hexane/CH_2Cl_2 = 2:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 8.23 – 8.17 (m, 1H, *minor*), 8.11 (d, *J* = 8.8 Hz, 2H, *major*), 7.57 – 7.49 (m, 1H, *minor*), 7.44 (d, *J* = 8.8 Hz, 2H, *major*), 7.32 (d, *J* = 8.1 Hz, 2H, *major*), 7.19 – 7.02 (m, 4H), 5.01 (p, *J* = 1.5 Hz, 0.5H, *minor*), 4.86 – 4.83 (m, 0.5H, *minor*), 4.70 (p, *J* = 1.5 Hz, 1H, *major*), 4.63 – 4.59 (m, 1H, *major*), 2.33 (s, 3H, *major*), 2.31 (s, 1.5H, *minor*), 1.87 (t, *J* = 1.2 Hz, 1.5H, *minor*), 1.51 (t, *J* = 1.1 Hz, 3H, *major*) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 151.8 (C), 151.1 (C), 150.1 (C), 146.8 (C), 145.8 (C), 144.7 (C), 140.0 (2 × CH), 138.8 (2 × CH), 138.6 (C), 137.2 (C), 134.3 (2 × CH), 133.3 (2 × CH), 130.3 (2 × CH), 130.0 (2 × CH), 129.7 (4 × CH), 129.6 (C), 129.2 (C), 123.7 (CH_2), 123.4 (CH_2), 121.7 (C), 119.4 (C), 91.6 (C), 90.3 (C), 30.1 (CH_3), 23.2 (CH_3), 21.4 (CH_3), 21.3 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 309 (100), 139 (78), 91 (37). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{18}H_{17}INO_2S$, 438.0019; found, 437.9996.

(*E*)-(4-iodo-5-methoxy-2-methylpenta-1,3-dien-3-yl) (4-methoxyphenyl)sulfide (3v)

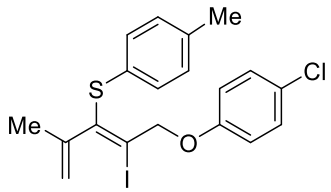


3v

The general procedure **B** was followed using (5-methoxy-2-methylpent-3-yn-2-yl) (4-methoxyphenyl)sulfide **1v** (125 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3v** (154 mg, 82%) as pale yellow oil ; *Rf* = 0.47 (hexane/AcOEt = 5:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.35 – 7.07 (m, 2H), 6.89 – 6.58 (m, 2H), 4.82 (p, *J* = 1.5 Hz, 1H), 4.55 (s, 2H), 4.54 – 4.48 (m, 1H), 3.75 (s, 3H), 3.39 (s, 3H), 1.73 (t, *J* = 1.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 159.9 (C), 145.7 (C), 144.8 (C), 135.4 (2 × CH), 123.5 (C), 118.1 (CH_2), 114.3 (2 × CH), 98.7 (C), 75.9 (CH_2), 57.3 (CH_3), 55.2

(CH_3), 21.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 139 (100), 45 (68), 376 (M^+,52). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{14}H_{18}IO_2S$, 377.0067; found, 377.0067.

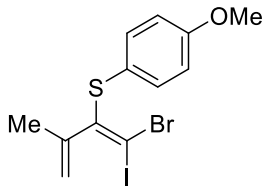
(*E*)-(5-(4-chlorophenoxy)-4-iodo-2-methylpenta-1,3-dien-3-yl) (*p*-tolyl)sulfide (3w)



3w

The general procedure **B** was followed using (5-(4-chlorophenoxy)-2-methylpent-3-yn-2-yl) (*p*-tolyl)sulfide **1w** (165 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3w** (152 mg, 66%) as pale yellow oil; *Rf* = 0.32 (hexane/CH_2Cl_2 = 5:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.29 – 7.21 (m, 2H), 7.21 – 7.16 (m, 2H), 7.12 – 7.05 (m, 2H), 7.01 – 6.94 (m, 2H), 5.10 (s, 2H), 4.88 (p, *J* = 1.5 Hz, 1H), 4.64 – 4.57 (m, 1H), 2.32 (s, 3H), 1.79 – 1.72 (m, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 156.5 (C), 146.0 (C), 144.5 (C), 138.6 (C), 133.1 (2 × CH), 129.8 (2 × CH), 129.4 (2 × CH), 129.3 (C), 126.6 (C), 119.0 (CH_2), 117.3 (2 × CH), 97.2 (C), 72.3 (CH_2), 21.3 (2 × CH_3) ppm. **LRMS (EI) *m/z* (%)** 187 (100), 202 (76), 456 (M^+,1). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{19}ClIOS$, 456.9884; found, 456.9871.

(1-bromo-1-iodo-3-methylbuta-1,3-dien-2-yl) (4-methoxyphenyl)sulfide (3x)

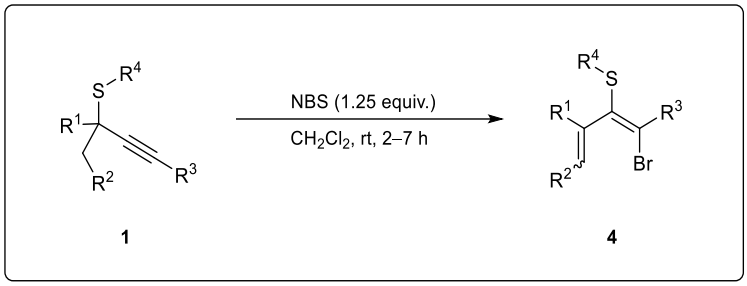


3x

The general procedure **B** was followed using (4-bromo-2-methylbut-3-yn-2-yl) (4-methoxyphenyl)sulfide **1x** (141 mg, 0.5 mmol), *N*-iodosuccinimide (168 mg, 0.75 mmol) and dichloromethane (5 mL). Purification by column chromatography yielded **3x** (200 mg, 97%) as white solid mixture of diastereoisomers (4:1); m.p = 62–64 °C; *Rf* = 0.27 (hexane/AcOEt = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.33 (d, *J* = 8.9 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.96 – 4.87 (m, 1H), 4.70 (bs, 0.75H, *major*), 4.65 (bs, 0.25H, *minor*), 3.79 (s, 3H), 1.67 (s, 0.7H, *minor*) 1.63 (s, 2.3H, *major*) ppm. *Major* **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 160.4 (C), 149.4 (C), 144.2 (C), 136.9 (2 × CH), 123.0 (C), 120.0 (CH_2), 118.9 (C), 114.4 (2 × CH), 55.4 (CH_3), 21.6 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 139 (100), 204 (35), 410 (M^+,7). **HRMS (APCI+) *m/z*: [M + H]$^+$** calcd for $C_{12}H_{13}BrIOS$, 410.8910; found, 410.8901.

3.2. Experimental Procedure and Characterization Data of 1-bromo-1,3-dienes

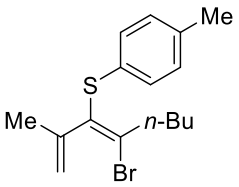
3.2.1. General Procedure C for the Synthesis of 1-bromo-1,3-dienes (4)



Propargyl sulfide **1** (1 equiv., 0.4 mmol) was dissolved in dichloromethane (4 mL, 0.1 M) at rt. Then, bromonium ion source, *N*-bromosuccinimide (88 mg, 1.25 equiv., 0.5 mmol) was added at once. The obtained suspension was allowed to stir at room temperature until full depletion of the propargyl thioether was determined by GC-MS. Then, $Na_2S_2O_3$ (0.05 mL) was added to quench the reaction. The mixture was allowed to warm to rt, dried with anhydrous Na_2SO_4 and filtered. Filtrate was concentrated under reduced pressure. The crude was purified by column chromatography on silica gel (eluent: mixtures of hexane/ CH_2Cl_2) to afford the corresponding diene **4**.

Characterization Data of 1-bromo-1,3-dienes (4):

(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide (4a)

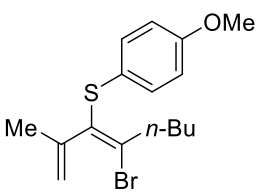


4a

The general procedure **C** was followed using (2-methyloct-3-yn-2-yl)(*p*-tolyl)sulfide **1a** (98 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4a** (115 mg, 88%) as colourless liquid; *Rf* = 0.47 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.27 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.12 (m, 2H), 4.92 (p, *J* = 1.6 Hz, 1H), 4.69 (dq, *J* = 1.8, 0.9 Hz, 1H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 1.83 (dd, *J* = 1.5, 0.9 Hz, 3H), 1.78 – 1.62 (m, 2H), 1.44 (h, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 142.9 (C), 137.4 (C), 134.9 (C), 132.0 (2 × CH), 130.6 (C), 129.6 (2 × CH), 128.2 (C), 117.5 (CH_2), 38.7 (CH_2), 30.8 (CH_2), 22.0 (CH_2), 21.6 (CH_3), 21.2 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 326 (100), 324 (M^+,96), 79 (84). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{16}H_{22}BrS$, 325.0620; found, 325.0626.

(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (4-methoxyphenyl)sulfide (4d)

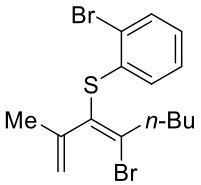
The general procedure **C** was followed using (4-methoxyphenyl)(2-methyloct-3-yn-2-yl)sulfide **1d** (104 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4d** (96 mg, 70%)



4d

as pale yellow liquid; *Rf* = 0.37 (hexane/CH_2Cl_2 = 5:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.30 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.89 (p, *J* = 1.6 Hz, 1H), 4.62 – 4.55 (m, 1H), 3.82 (s, 3H), 3.05 – 2.92 (m, 2H), 1.80 (s, 3H), 1.73 – 1.59 (m, 2H), 1.44 (h, *J* = 7.3 Hz, 2H), 1.01 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 159.7 (C), 142.9 (C), 135.9 (C), 134.8 (2 × CH), 126.4 (C), 124.4 (C), 117.4 (CH_2), 114.4 (2 × CH), 55.4 (CH_3), 38.5 (CH_2), 30.8 (CH_2), 22.0 (CH_2), 21.6 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 340 (M^+,100), 261 (78), 139 (63). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{16}H_{22}BrOS$, 341.0569; found, 341.0582.

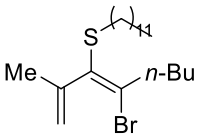
(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (2-bromophenyl)sulfide (4f)



4f

The general procedure **C** was followed using (2-bromophenyl)(2-methyloct-3-yn-2-yl)sulfide **1f** (124 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4f** (112 mg, 72%) as colourless liquid; *Rf* = 0.52 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.57 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.20 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 4.96 (br s, 1H), 4.84 (br s, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.87 (s, 3H), 1.66 (p, *J* = 7.0 Hz, 2H), 1.41 (h, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 142.8 (C), 135.6 (C), 133.2 (CH), 132.8 (C), 132.3 (CH), 131.3 (C), 128.3 (CH), 127.6 (CH), 125.3 (C), 117.8 (CH_2), 39.1 (CH_2), 30.8 (CH_2), 22.0 (CH_2), 21.6 (CH_3), 14.1 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 77 (100), 93 (80), 390 (M^+,62). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{15}H_{19}Br_2S$, 388.9569; found, 388.9584.

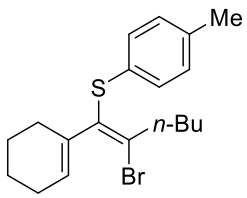
(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (dodecyl)sulfide (4i)



4i

The general procedure **C** was followed using dodecyl(2-methyloct-3-yn-2-yl)sulfide **1i** (129 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4i** (93 mg, 57%) as colourless liquid; *Rf* = 0.60 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 5.12 (p, *J* = 1.7 Hz, 1H), 4.78 – 4.76 (m, 1H), 2.83 (t, *J* = 7.3 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 1.89 (s, 3H), 1.65 – 1.43 (m, 4H), 1.41 – 1.30 (m, 6H), 1.29 – 1.22 (m, 14H), 0.94 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 6.4 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 142.7 (C), 135.0 (C), 125.5 (C), 116.6 (CH_2), 38.2 (CH_2), 33.3 (CH_2), 32.1 (CH_2), 30.6 (CH_2), 29.9 (2 × CH_2), 29.8 (2 × CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 22.9 (CH_2), 21.9 (CH_2), 21.5 (CH_3), 14.3 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 404 (100), 402 (M^+,94), 323 (68). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{21}H_{40}BrS$, 403.2029; found, 403.2046.

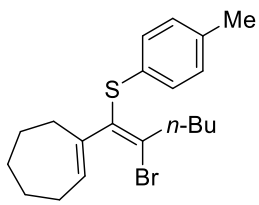
(*E*)-(2-bromo-1-(cyclohex-1-en-1-yl)hex-1-en-1-yl) (*p*-tolyl)sulfide (4m)



4m

The general procedure **C** was followed using (1-(hex-1-yn-1-yl)cyclohexyl)(*p*-tolyl)sulphide **1m** (114 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4m** (76 mg, 52%) as colourless liquid; *Rf* = 0.50 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.20 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 5.34 (tt, *J* = 3.8, 1.7 Hz, 1H), 2.95 – 2.79 (m, 2H), 2.33 (s, 3H), 2.03 – 1.95 (m, 2H)., 1.91 – 1.76 (m, 2H), 1.69 – 1.53 (m, 2H), 1.50 – 1.30 (m, 6H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 137.5 (C), 136.4 (C), 135.9 (C), 133.0 (2 × CH), 130.7 (C), 129.4 (CH), 129.4 (2 × CH), 126.1 (C), 38.6 (CH_2), 30.8 (CH_2), 27.4 (CH_2), 25.2 (CH_2), 22.6 (CH_2), 21.9 (CH_2), 21.9 (CH_2), 21.3 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 91 (100), 79 (50), 364 (M^+,12). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{19}H_{26}BrS$, 365.0933; found, 365.0944.

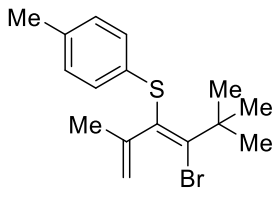
(*E*)-(2-bromo-1-(cyclohept-1-en-1-yl)hex-1-en-1-yl) (*p*-tolyl)sulfide (4n)



4n

The general procedure **C** was followed using (1-(hex-1-yn-1-yl)cycloheptyl(*p*-tolyl)sulfide **1n** (120 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4n** (99 mg, 65%) as colourless oil; *Rf* = 0.59 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.19 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 5.62 (t, *J* = 6.5 Hz, 1H), 2.99 – 2.85 (m, 2H), 2.33 (s, 3H), 2.23 – 2.12 (m, 2H), 2.05 – 1.94 (m, 2H), 1.70 – 1.52 (m, 4H), 1.48 – 1.22 (m, 6H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 141.7 (C), 137.9 (C), 137.3 (C), 134.9 (CH), 132.6 (2 × CH), 130.9 (C), 129.4 (2 × CH), 125.9 (C), 38.8 (CH_2), 33.3 (CH_2), 32.2 (CH_2), 30.8 (CH_2), 28.7 (CH_2), 26.6 (CH_2), 26.5 (CH_2), 22.0 (CH_2), 21.3 (CH_3), 14.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 299 (100), 91 (42), 380 (M^+,38). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{20}H_{28}BrS$, 379.1090; found, 379.1104.

(4-bromo-2,5,5-trimethylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (4s)

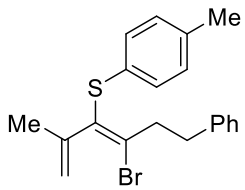


4s

The general procedure **C** was followed using *p*-tolyl (2,5,5-trimethylhex-3-yn-2-yl)sulfide **1s** (98 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **3s** (146 mg, 64%) as orange oil mixture of diastereoisomers (*E*:*Z* = 3:1); *Rf* = 0.74 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)** δ = 7.23 – 7.17 (m, 2.7H), 7.13 – 7.10 (m, 0.7 H, *minor*), 7.10 – 7.05 (m, 2H, *major*), 5.67 (q, *J* = 1.4 Hz, 0.3H, *minor*), 4.71 (p,

J = 1.5 Hz, 1H, *major*), 4.47 (dq, *J* = 1.8, 0.9 Hz, 1.3H), 2.34 (s, 1 H, *minor*), 2.32 (s, 3H, *major*), 1.79 – 1.74 (m, 4H), 1.55 (s, 9H, *major*), 1.54 (s, 3H, *minor*) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 145.1(*major*, C), 141.8 (*minor*, C), 138.7 (*minor*, C), 138.5 (*minor*, C), 137.6 (*major*, C), 137.6 (*major*, C), 135.2 (*minor*, C), 134.6 (*major*, C), 133.6 (*minor*, C), 133.3 (*minor*, 2 × CH), 132.4 (*major*, 2 × CH), 131.0 (*major*, C), 129.8 (*minor*, 2 × CH), 129.6 (*major*, 2 × CH), 129.3 (*minor*, C), 116.0 (*major*, CH_2), 108.7 (*minor*, CH_2), 41.0 (*minor*, C), 40.9 (*major*, C), 32.2 (*major*, 3 × CH_3), 32.0 (*minor*, 3 × CH_3), 21.7 (*major*, CH_3), 21.3 (*minor*, CH_3), 21.2 (*major*, CH_3) 19.4 (*minor*, CH_3). ppm. **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{22}BrS$, 325.0620; found, 325.0626.

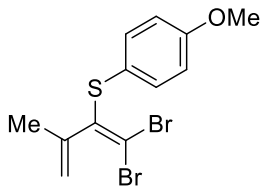
(*E*)-(4-bromo-2-methyl-6-phenylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (4t)



4t

The general procedure **C** was followed using (2-methyl-6-phenylhex-3-yn-2-yl) (*p*-tolyl)sulfide **1t** (117 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4t** (121 mg, 81%) as colourless liquid; *Rf* = 0.44 (hexane/CH_2Cl_2 = 5:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.43 – 7.21 (m, 5H), 7.15 – 6.90 (m, 4H), 4.89 (p, *J* = 1.6, 1H), 4.61 (dq, *J* = 1.8, 0.9 Hz, 1H), 3.30 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 1.78 (t, *J* = 1.5 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 142.7 (C), 140.5 (C), 137.5 (C), 136.5 (C), 132.3 (2 × CH), 130.3 (C), 129.5 (2 × CH), 129.1 (2 × CH), 128.5 (2 × CH), 126.3 (CH), 126.2 (C), 117.6 (CH_2), 40.6 (CH_2), 34.6 (CH_2), 21.5 (CH_3), 21.2 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 91 (100), 372 (M^+,70), 65 (65). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{20}H_{22}BrS$, 373.0620; found, 373.0626.

(1,1-dibromo-3-methylbuta-1,3-dien-2-yl) (4-methoxyphenyl)sulfide (4x)



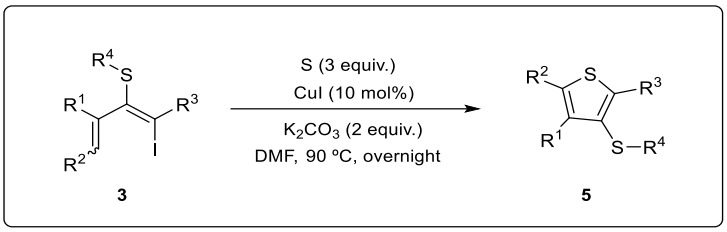
4x

The general procedure **C** was followed using (4-bromo-2-methylbut-3-yn-2-yl)(4-methoxyphenyl)sulfide **1x** (113 mg, 0.4 mmol), *N*-bromosuccinimide (88 mg, 0.5 mmol) and dichloromethane (4 mL). Purification by column chromatography yielded **4x** (119 mg, 82%) as pale yellow oil; *Rf* = 0.37 (hexane/AcOEt = 10:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.34 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 4.93 – 4.92 (m, 1H), 4.70 (p, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 1.66 (t, *J* = 1.2 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 160.4 (C), 145.2 (C), 141.6 (C), 136.8 (2 × CH), 122.6 (C), 119.4 (CH_2), 114.5 (2 × CH), 82.4 (C), 55.4 (CH_3), 21.5 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 364 (M^+,7), 204 (88), 139 (100). **HRMS (ESI+) *m/z*: [M + H]$^+$**, calcd for $C_{12}H_{13}Br_2OS$, 362.9048; found, 362.9042.

4. Experimental Procedure and Characterization Data of Thiophenes (5) and Selenophenes (6)

4.1. Experimental Procedure and Characterization Data of Thiophenes (5)

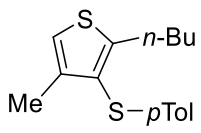
4.1.1. General Procedure D for the Synthesis of Thiophenes (5) by cyclization reaction of dienes



A mixture of 1-iodo-1,3-diene (1 equiv., 0.2 mmol), sulfur powder (3 equiv., 0.6 mmol), K_2CO_3 (2 equiv., 0.4 mmol), CuI (0.1 equiv., 0.02 mmol) and DFM (1 mL, 0.2 M) was stirred at 90 °C under N_2 (2-12h). Upon cooling to room temperature, the reaction mixture was diluted with diethyl ether (50 mL) and washed with water (3 × 20 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: mixtures of hexane/ CH_2Cl_2) to afford the desired product.

Characterization Data of Thiophenes (5):

2-butyl-4-methyl-3-(*p*-tolylthio)thiophene (5a)

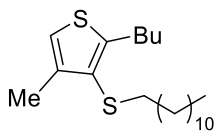


5a

The general procedure **D** was followed using (*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide **3a** (74 mg, 0.2 mmol), sulfur powder (153 mg, 0.6 mmol), K_2CO_3, (80 mg, 0.6 mmol), CuI (3.8 mg, 0.02 mmol) and DMF (1 mL) after 2 h. Purification by column chromatography yielded **5a** (43 mg, 78%) as yellow oil; *Rf* = 0.44 (hexane/CH_2Cl_2 = 50:1). **^{1}H NMR (500 MHz, $CDCl_3$, 25 °C)** δ = 7.01 (d, *J* = 0.9 Hz, 2H), 6.89 – 6.85 (m, 3H), 2.95 – 2.92 (m, 2H), 2.28 (s, 3H), 2.12 (d, *J* = 1.2 Hz, 3H), 1.67 – 1.57 (m, 2H), 1.37 (h, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (125 MHz, $CDCl_3$)** δ = 151.5 (C), 140.7 (C), 134.9 (C), 134.7 (C), 129.7 (2 × CH), 126.0 (2 × CH), 124.4 (C), 117.8 (CH), 33.9 (CH_2), 29.4 (CH_2), 22.4 (CH_2), 21.0 (CH_3), 15.7 (CH_3),

13.9 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 276 (M^+, 100), 233 (70), 199 (85). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{16}H_{21}S_2$, 277.1079; found, 277.1084.

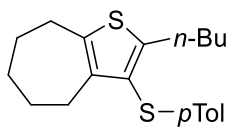
2-butyl-3-(dodecylthio)-4-methylthiophene (5i)



5i

The general procedure **D** was followed using dodecyl (2-methyloct-3-yn-2-yl)sulfide **1i** (64 mg, 0.2 mmol), sulfur powder (153 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and DMF (1 mL) after 12 h. Purification by column chromatography yielded **5i** (54 mg, 76%) as colourless oil; *Rf* = 0.6 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 6.80 (d, *J* = 1.1 Hz, 1H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 1.71 – 1.58 (m, 2H), 1.56 – 1.32 (m, 6H), 1.30 – 1.21 (m, 16H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.93 – 0.87 (m, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.8 (C), 140.5 (C), 127.5 (C), 117.1 (CH), 36.2 (CH_2), 34.2 (CH_2), 32.1 (CH_2), 30.1 – 29.3 (m, 8 × CH_2), 28.9 (CH_2), 22.8 (CH_2), 22.6 (CH_2), 16.0 (CH_3), 14.3 (CH_3), 14.0 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 354 (M^+, 100), 43 (41), 143 (35). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{21}H_{39}S_2$, 355.2488; found, 355.2493.

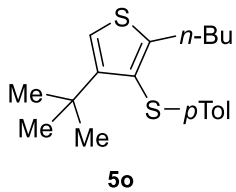
2-butyl-3-(*p*-tolylthio)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene (5n)



5n

The general procedure **D** was followed using (*E*)-(1-(cyclohept-1-en-1-yl)-2-iodohex-1-en-1-yl) (*p*-tolyl)sulfide **3n** (85 mg, 0.2 mmol), sulfur powder (153 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and DMF (1 mL) after 12 h. Purification by column chromatography yielded **5n** (37 mg, 56%) as colourless oil; *Rf* = 0.44 (hexane CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.02 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.85 – 2.79 (m, 2H), 2.71 – 2.64 (m, 2H), 2.29 (s, 3H), 1.89 – 1.76 (m, 2H), 1.75 – 1.65 (m, 2H), 1.63 – 1.46 (m, 4H), 1.36 (h, *J* = 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 146.4 (C), 142.5 (C), 136.8 (C), 135.7 (C), 134.4 (C), 129.6 (2 × CH), 125.8 (2 × CH), 124.3 (C), 34.0 (CH_2), 32.7 (CH_2), 30.6 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.4 (CH_2), 27.7 (CH_2), 22.5 (CH_2), 21.0 (CH_3), 14.0 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 287 (100), 330 (M^+, 72), 91 (23). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{27}S_2$, 331.1549; found, 331.1554.

4-(*tert*-butyl)-2-butyl-3-(*p*-tolylthio)thiophene (5o)

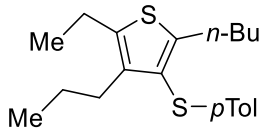


5o

The general procedure **D** was followed using (*E*)-(5-iodo-2,2-dimethyl-3-methylenenon-4-en-4-yl) (*p*-tolyl)sulfide **3o** (82 mg, 0.2 mmol), sulfur powder (153 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and DMF (1 mL) after 20 h. Purification by column chromatography yielded **5o** (52 mg, 81%) as colourless oil; *Rf*

= 0.48 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.02 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), 2.80 (t, *J* = 7.8 Hz, 2H), 2.28 (s, 3H), 1.58 (p, *J* = 7.7 Hz, 2H), 1.40 (s, 9H), 1.38 – 1.27 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 154.1 (C), 153.4 (C), 136.2 (C), 134.1 (C), 129.6 (2 × CH), 125.1 (2 × CH), 122.2 (C), 115.8 (CH), 35.0 (C), 33.1 (CH_2), 30.4 (3 × CH_3), 29.3 (CH_2), 22.6 (CH_2), 21.0 (CH_3), 14.0 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 318 (M^+, 100), 57 (26), 303 (24). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{19}H_{27}S_2$, 319.1549; found, 319.1552.

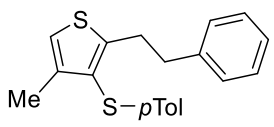
2-butyl-5-ethyl-4-propyl-3-(*p*-tolylthio)thiophene (5p)



5p

The general procedure **D** was followed using ((5*E*)-6-iodo-4-propyldeca-3,5-dien-5-yl) (*p*-tolyl)sulfide **3p** (85 mg, 0.2 mmol), sulfur powder (153 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and DMF (1 mL) after 20 h. Purification by column chromatography yielded **5p** (34 mg, 51%) as colourless oil; *Rf* = 0.54 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.01 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.79 (q, *J* = 7.5 Hz, 2H), 2.51 – 2.43 (m, 2H), 2.28 (s, 3H), 1.67 – 1.52 (m, 2H), 1.47 – 1.34 (m, 4H), 1.30 (t, *J* = 7.5 Hz, 3H), 0.93 – 0.83 (m, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 148.0 (C), 139.4 (C), 138.1 (C), 135.8 (C), 134.4 (C), 129.6 (2 × CH), 125.8 (2 × CH), 123.6 (C), 33.8 (CH_2), 30.1 (CH_2), 29.1 (CH_2), 24.1 (CH_2), 22.5 (CH_2), 22.0 (CH_2), 21.0 (CH_3), 16.3 (CH_3), 14.3 (CH_3), 14.0 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 332 (M^+, 100), 289 (56), 290 (11). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{29}S_2$, 333.1705; found, 333.1709.

4-methyl-2-phenethyl-3-(*p*-tolylthio)thiophene (5t)



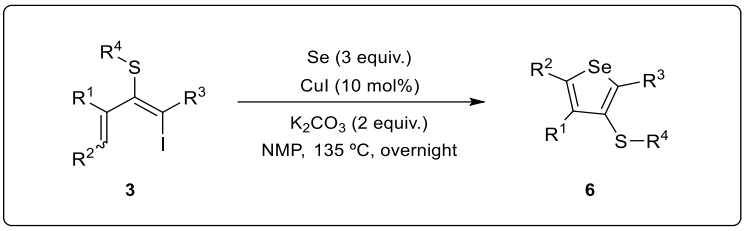
5t

The general procedure **D** was followed using (*E*)-(4-iodo-2-methyl-6-phenylhexa-1,3-dien-3-yl)(*p*-tolyl)sulfide **3t** (84 mg, 0.2 mmol), sulfur powder (153 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and DMF (1 mL) after 12 h. Purification by column chromatography yielded **5t** (46 mg, 70%) as orange oil; *Rf* = 0.25 (hexane/CH_2Cl_2 = 20:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.38 – 7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 7.11 – 7.05 (m, 2H), 6.97 – 6.88 (m, 3H), 3.38 – 3.29 (m, 2H), 3.04 – 2.94 (m, 2H), 2.35 (s, 3H), 2.20 (d, *J* = 1.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 149.8 (C), 141.0 (C), 140.8 (C), 134.8 (C), 134.6 (C), 129.8 (2 × CH), 128.6 (2 × CH), 128.5 (2 × CH), 126.2 (CH), 126.1 (2 × CH), 125.1 (C), 118.2 (CH), 37.9 (CH_2), 31.6 (CH_2), 21.0 (CH_3), 15.7 (CH_3) ppm. **LRMS (EI) *m/z***

(%) 233 (100), 324 (M^+, 94), 199 (67). **HRMS (ESI+) *m/z*: [M + H]$^+$** calcd for $C_{20}H_{21}S_2$, 325.1079; found, 325.1083.

4.2. Experimental Procedure and Analytical Data of Selenophenes (6)

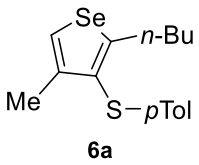
4.2.1. General Procedure *E* for the Synthesis of Selenophenes (6) by heterocyclization reaction of dienes



A mixture of 1-iodo-1,3-diene (1 equiv., 0.2 mmol), selenium powder (3 equiv., 0.6 mmol), K_2CO_3 (2 equiv., 0.4 mmol), CuI (0.1 equiv., 0.02 mmol) and *N*-methylpyrrolidone (NMP) (1 mL, 0.2 M) was stirred at 135 °C under N_2 overnight (12 h). Upon cooling to room temperature, the reaction mixture was diluted with diethyl ether (50 mL) and washed with water (3 × 20 mL). The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: mixtures of hexane/ CH_2Cl_2) to afford the desired product.

Characterization Data of Selenophenes (6):

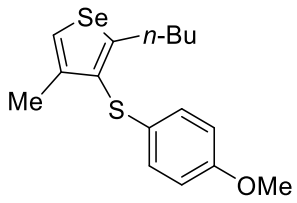
(2-butyl-4-methylselenophen-3-yl) (*p*-tolyl)sulfide (6a)



6a

The general procedure **E** was followed using (*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide **3a** (74 mg, 0.2 mmol), selenium powder (47.3 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and NMP (1 mL). Purification by column chromatography yielded **6a** (46 mg, 71%) as colourless solid; m.p.= 54–56 °C; *Rf* = 0.32 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.48 (q, *J* = 1.2 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 2.12 (d, *J* = 1.2 Hz, 3H), 1.74 – 1.57 (m, 2H), 1.41 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 159.2 (C), 142.3 (C), 134.9 (C), 134.6 (C), 129.7 (2 × CH), 126.1 (C), 125.9 (2 × CH), 121.4 (CH), 34.9 (CH_2), 31.8 (CH_2), 22.5 (CH_2), 21.0 (CH_3), 18.0 (CH_3), 14.0 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 324 (M^+,100), 199 (42), 77 (28). **HRMS (APCI+) *m/z*: [M + H]$^+$,** calcd for $C_{16}H_{21}SSe$, 325.0524; found, 325.0525.

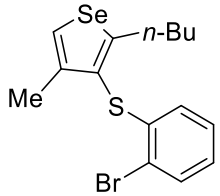
(2-butyl-4-methylselenophen-3-yl)(4-methoxyphenyl)sulfide (6d)



6d

The general procedure **E** was followed using (*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (4-methoxyphenyl)sulfide **3d** (77 mg, 0.2 mmol), selenium powder (47.3 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and NMP (1 mL). Purification by column chromatography yielded **6d** (35 mg, 52%) as pale yellow oil; *Rf* = 0.25 (hexane/CH_2Cl_2 = 5:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.43 (q, *J* = 1.1 Hz, 1H6.97 – 6.91 (m, 2H), 6.80 – 6.74 (m, 2H). 3.76 (s, 3H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.08 (d, , *J* = 1.2 Hz, 3H), 1.80 – 1.49 (m, 2H), 1.39 (h, *J* = 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 158.7 (C), 157.6 (C), 142.1 (C), 128.9 (C), 127.9 (2 × CH), 126.8 (C), 121.2 (CH), 114.6 (2 × CH), 55.3 (CH_3), 34.8 (CH_2), 31.7 (CH_2), 22.4 (CH_2), 17.9 (CH_3), 13.9 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 340 (M^+,100), 216 (48), 77 (41). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{16}H_{21}OSSe$, 341.0473; found, 341.0473.

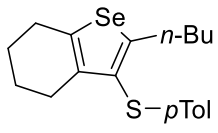
(2-bromophenyl) (2-butyl-4-methylselenophen-3-yl)sulfide (6f)



6f

The general procedure **E** was followed using (*E*)-(2-bromophenyl) (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide **3f** (87 mg, 0.2 mmol), selenium powder (47.3 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and NMP (1 mL). Purification by column chromatography yielded **6f** (37 mg, 48%) as colourless liquid; *Rf* = 0.43 (hexane/CH_2Cl_2= 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.57 – 7.42 (m, 2H), 7.08 (td, *J* = 7.6, 1.4 Hz, 1H), 6.93 (td, *J* = 7.6, 1.6 Hz, 1H), 6.42 (dd, *J* = 8.0, 1.6 Hz, 1H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.08 (s, 3H), 1.71 – 1.51 (m, 2H), 1.45 – 1.28 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 160.5 (C), 141.9 (C), 139.6 (C), 132.7 (CH), 127.7 (CH), 125.7 (2 × CH), 125.1 (C), 121.9 (CH), 120.0 (C), 34.6 (CH_2), 31.7 (CH_2), 22.3 (CH_2), 17.6 (CH_3), 13.8 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 265 (100), 388 (M^+,83), 77 (76). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{15}H_{18}BrSSe$, 386.9482; found, 386.9484.

(2-butyl-4,5,6,7-tetrahydrobenzo[*b*]selenophen-3-yl) (*p*-tolyl)sulfide (6m)



6m

The general procedure **E** was followed using (*E*)-(1-cyclohex-1-en-1-yl)-2-iodohex-1-en-1-yl (*p*-tolyl)sulfide **3m** (82 mg, 0.2 mmol), selenium powder (47.3 mg, 0.6 mmol), K_2CO_3, (55 mg, 0.4 mmol), CuI (3.8 mg, 0.02 mmol) and NMP (1 mL). Purification by column chromatography yielded **6m** (33 mg, 45%) as colourless liquid; *Rf* = 0.39 (hexane/CH_2Cl_2 = 100:1). **^{1}H NMR (300 MHz, $CDCl_3$, 25 °C)** δ = 7.03 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 3.02 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 6.0 Hz, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 2.29 (s, 3H), 1.87 – 1.67 (m, 4H), 1.67

– 1.54 (m, 2H), 1.40 (h, *J* = 7.6, 7.2 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ = 155.3 (C), 138.8 (C), 138.2 (C), 135.1 (C), 134.5 (C), 129.7 (2 × CH), 125.9 (2 × CH), 124.9 (C), 35.0 (CH_2), 31.1 (CH_2), 27.8 (CH_2), 26.9 (CH_2), 24.1 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 21.0 (CH_3), 14.0 (CH_3) ppm. **LRMS (EI) *m/z* (%)** 364 (M^+,100), 321 (82), 91 (53). **HRMS (APCI+) *m/z*: [M + H]$^+$**, calcd for $C_{19}H_{25}SSe$, 365.0837; found, 365.0837.

5. References

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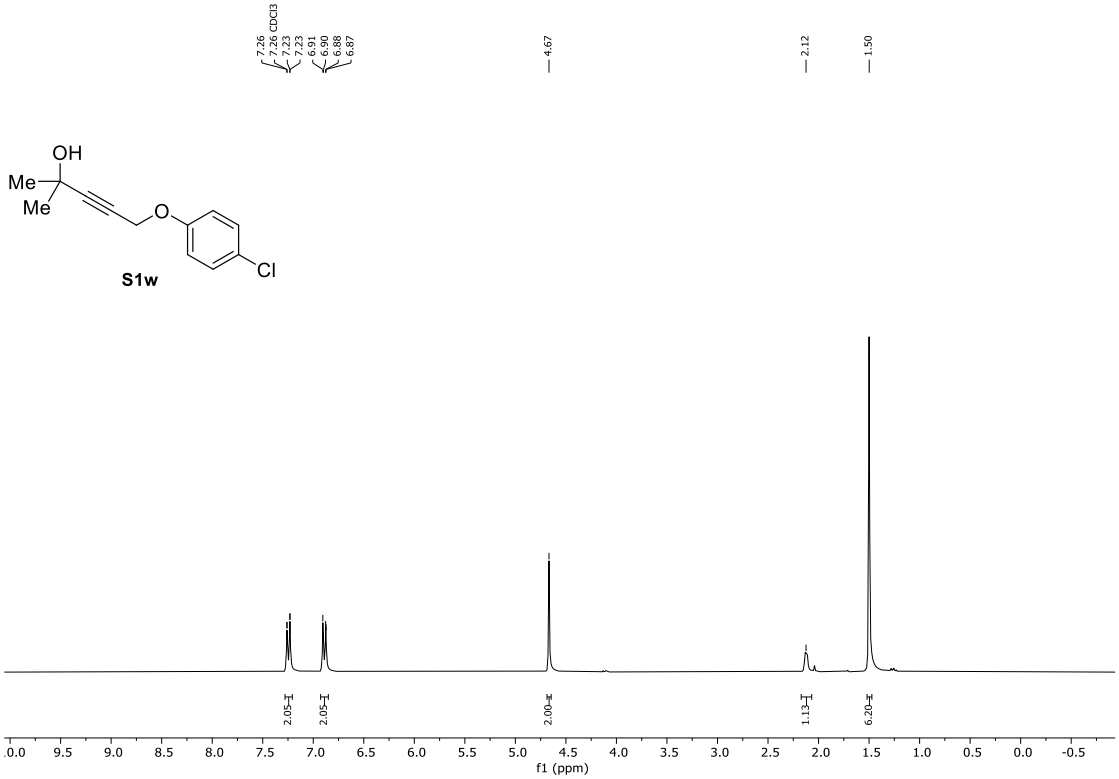
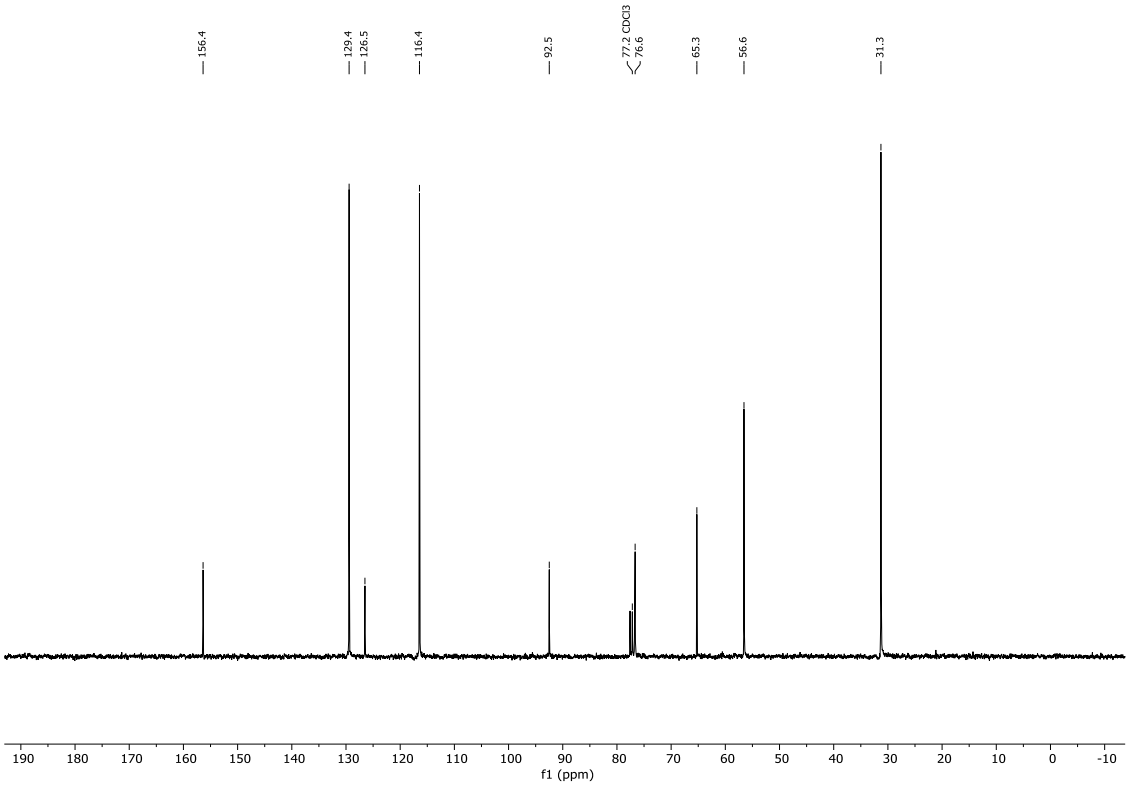
NMR SPECTRA

5-(4-chlorophenoxy)-2-methylpent-3-yl-2-ol (S1w)

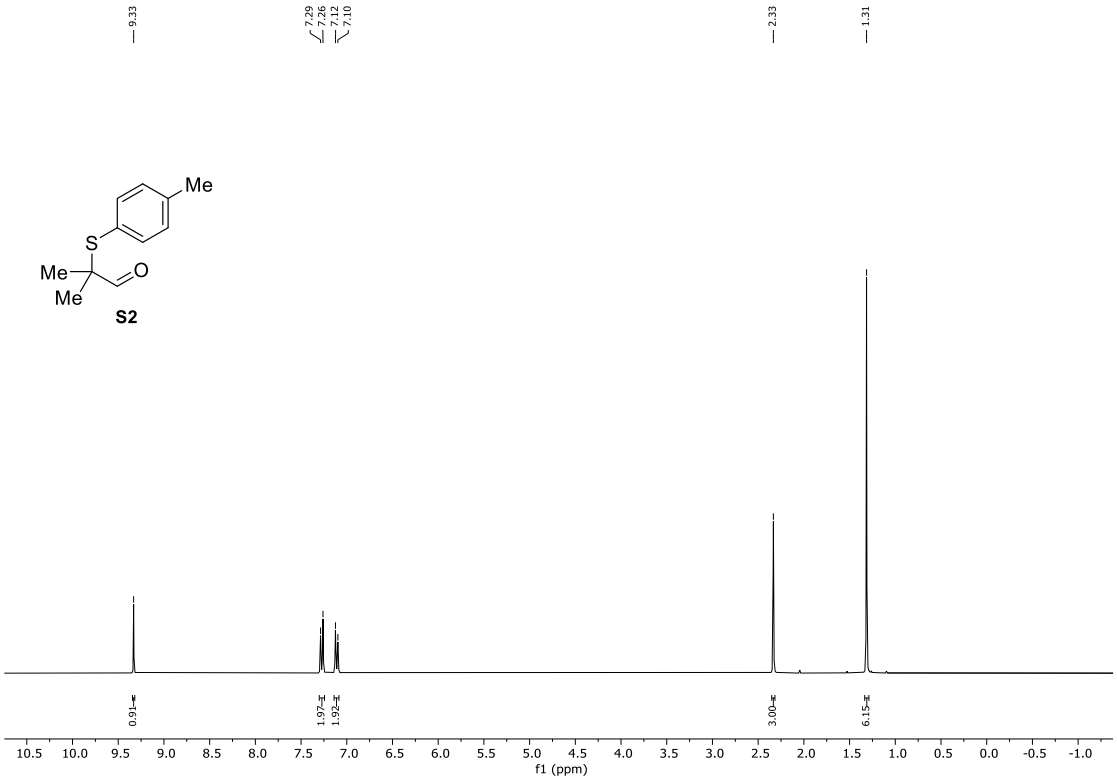


^{1}H-NMR (300 MHz, $CDCl_3$)

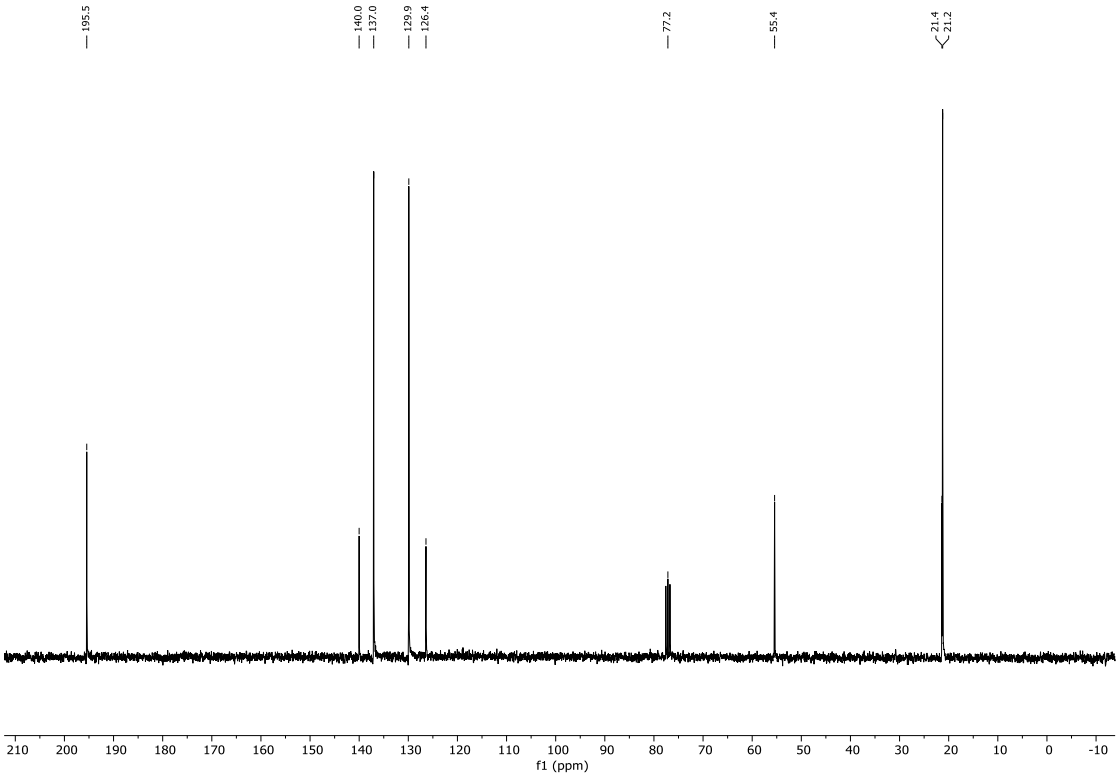


^{13}C-NMR (75 MHz, $CDCl_3$)

2-methyl-2-(*p*-tolylthio)propanal (S2)

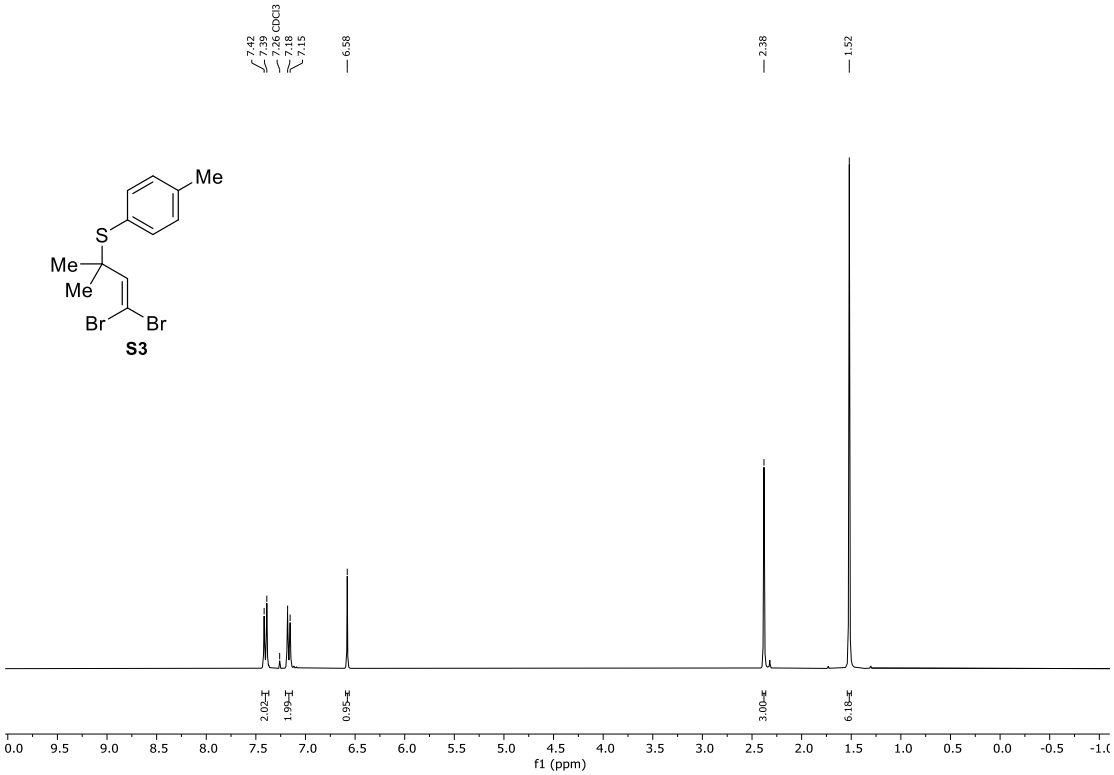


^{1}H-NMR (300 MHz, $CDCl_3$)

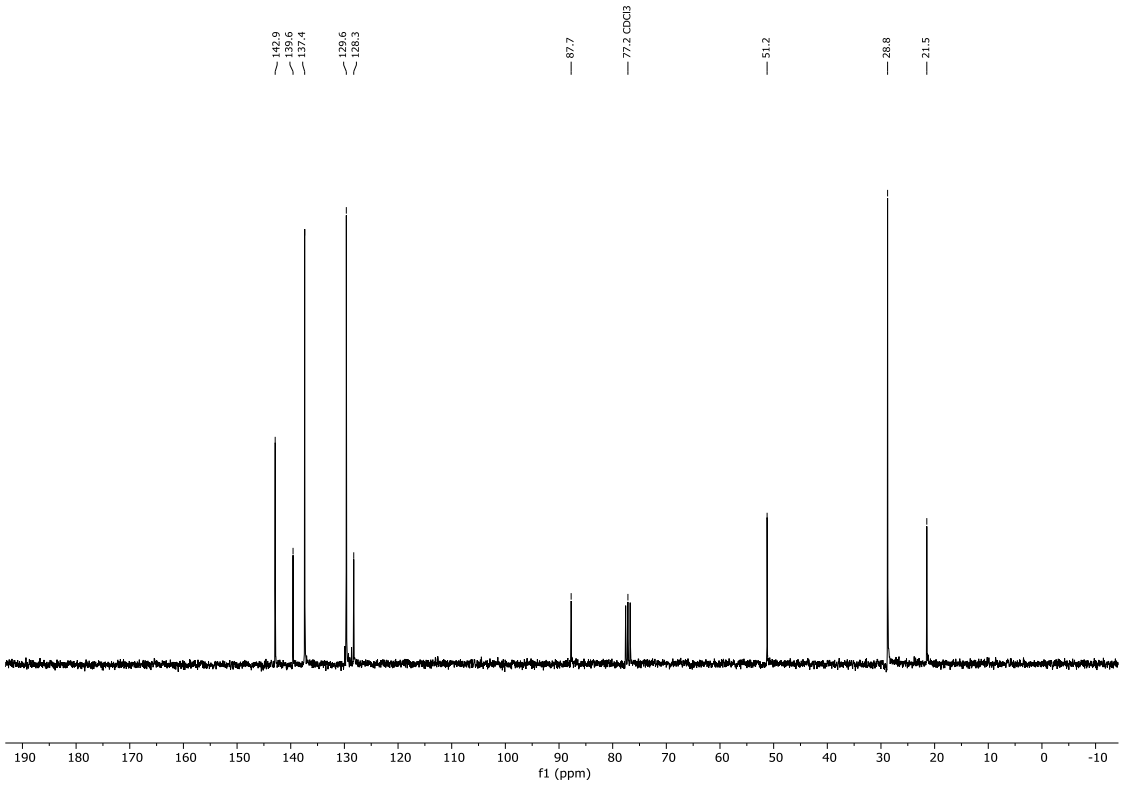


^{13}C-NMR (75 MHz, $CDCl_3$)

(4,4-dibromo-2-methylbut-3-en-2-yl)(*p*-tolyl)sulfane (S3)

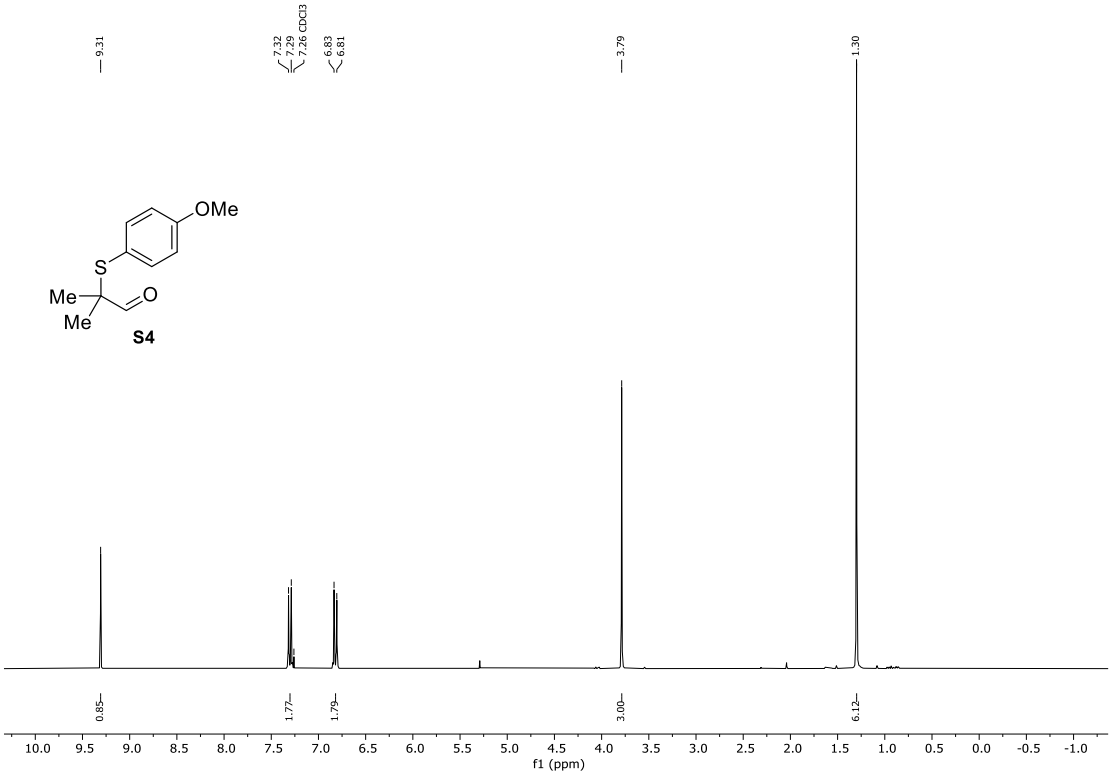


^{1}H-NMR (300 MHz, $CDCl_3$)

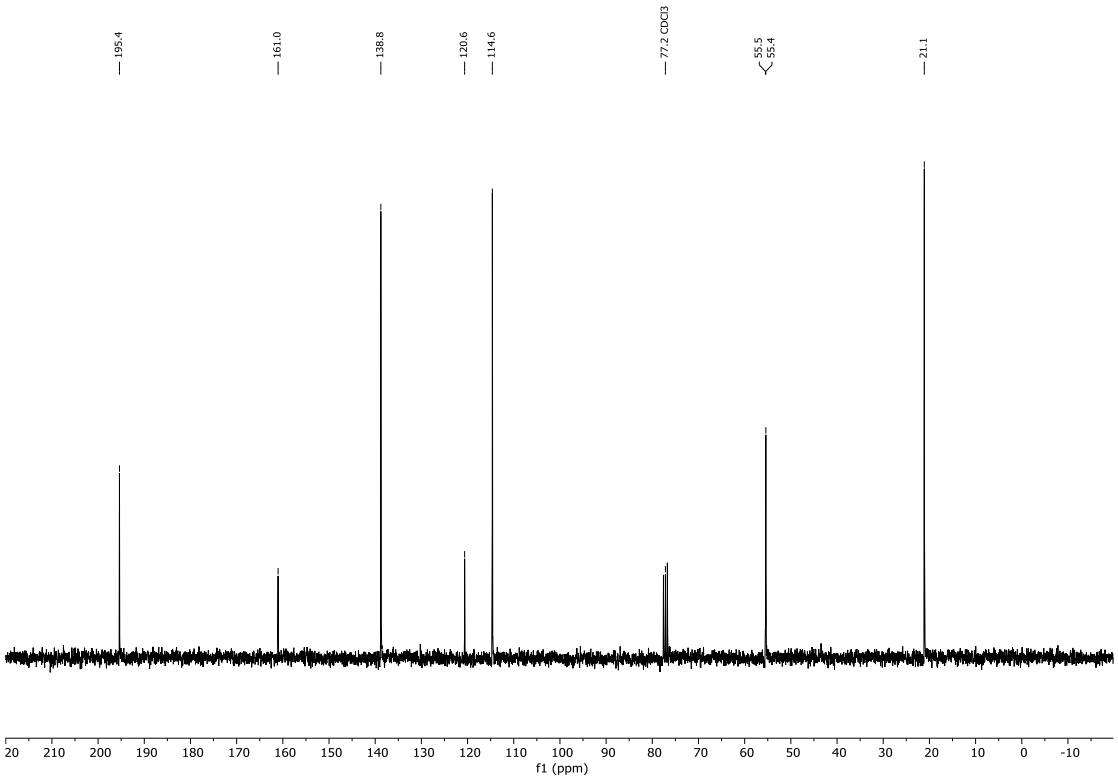


^{13}C-NMR (75 MHz, $CDCl_3$)

2-((4-methoxyphenyl)thio)-2-methylpropanal (S4)

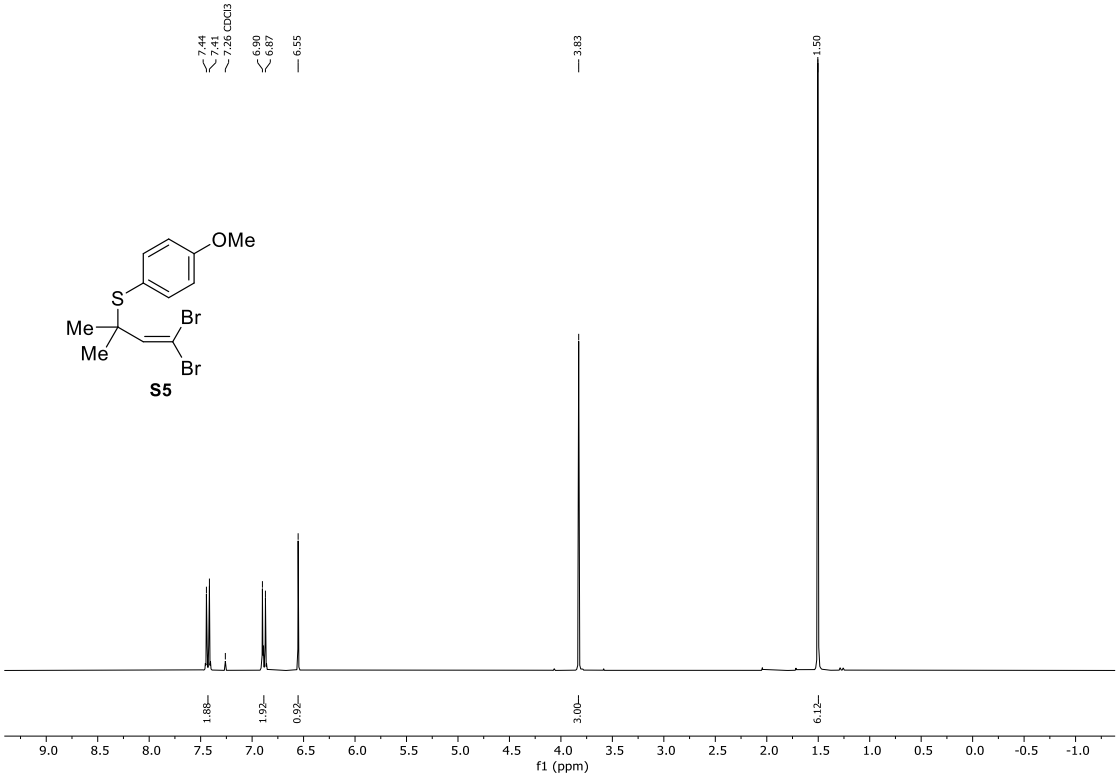


^{1}H-NMR (300 MHz, $CDCl_3$)

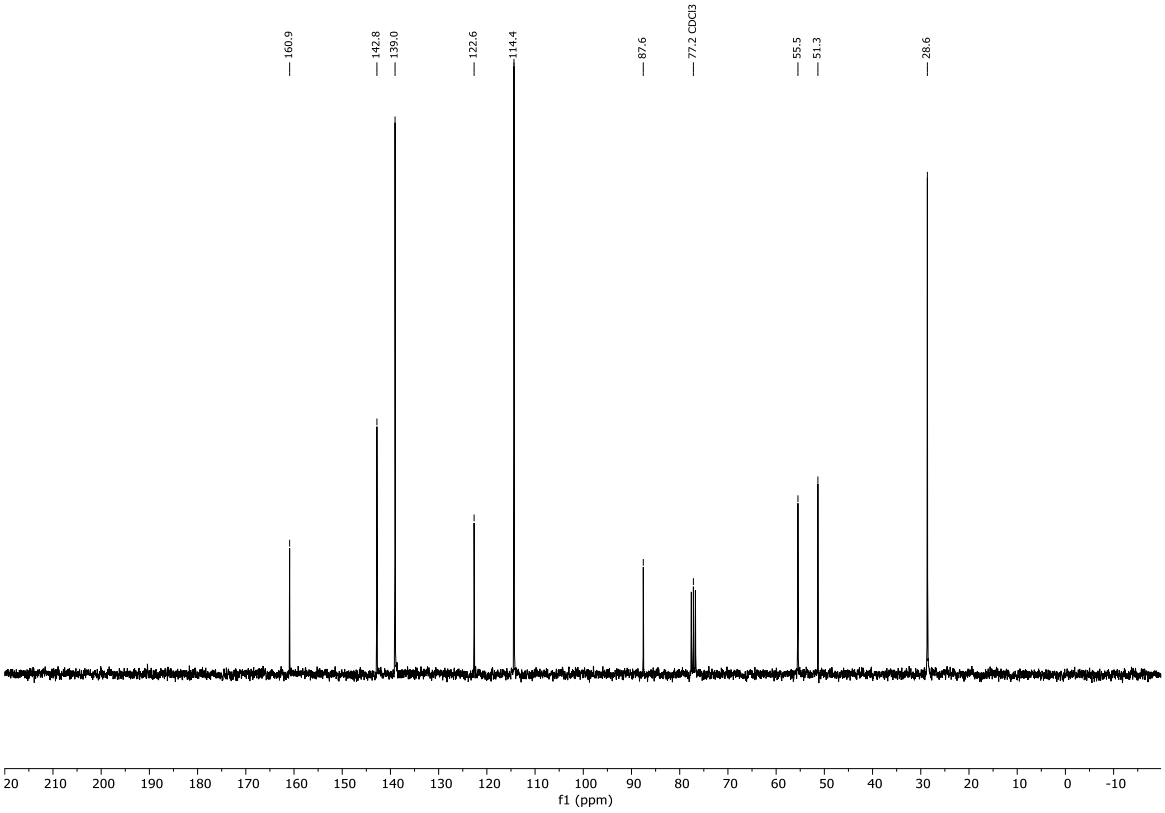


^{13}C-NMR (75 MHz, $CDCl_3$)

(4,4-dibromo-2-methylbut-3-en-2-yl)(4-methoxyphenyl)sulfane (S5)

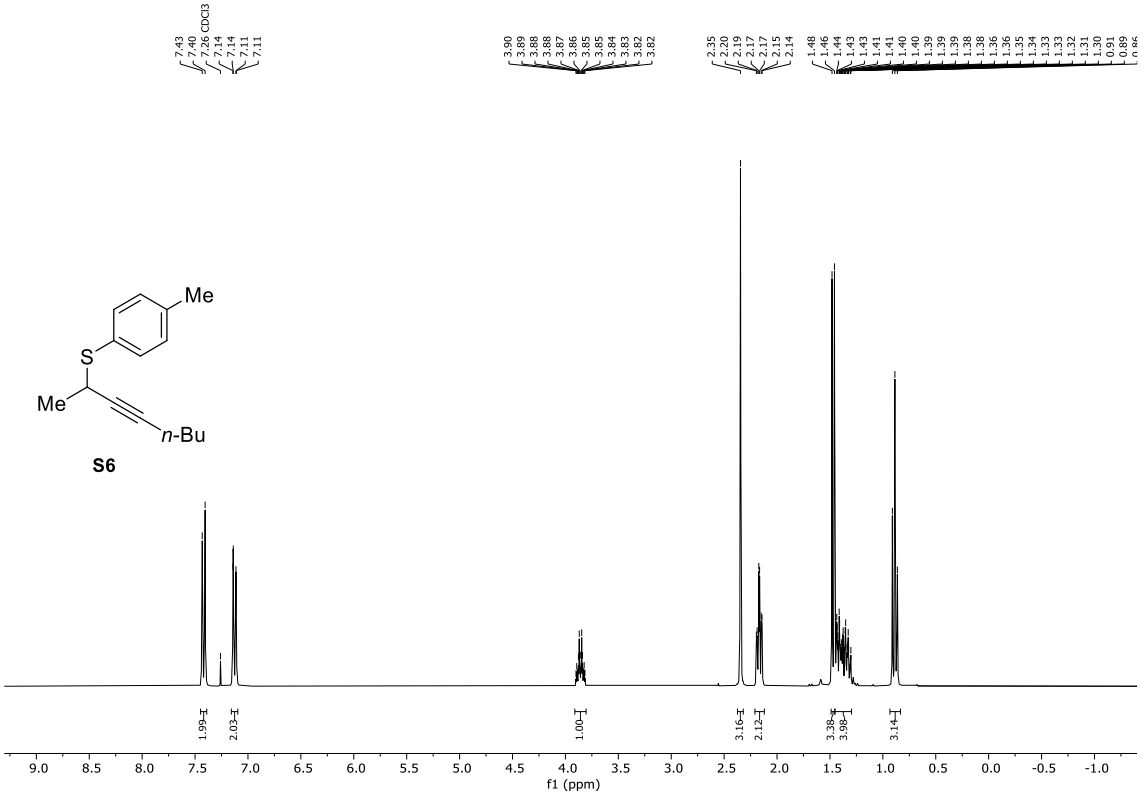


^{1}H-NMR (300 MHz, $CDCl_3$)

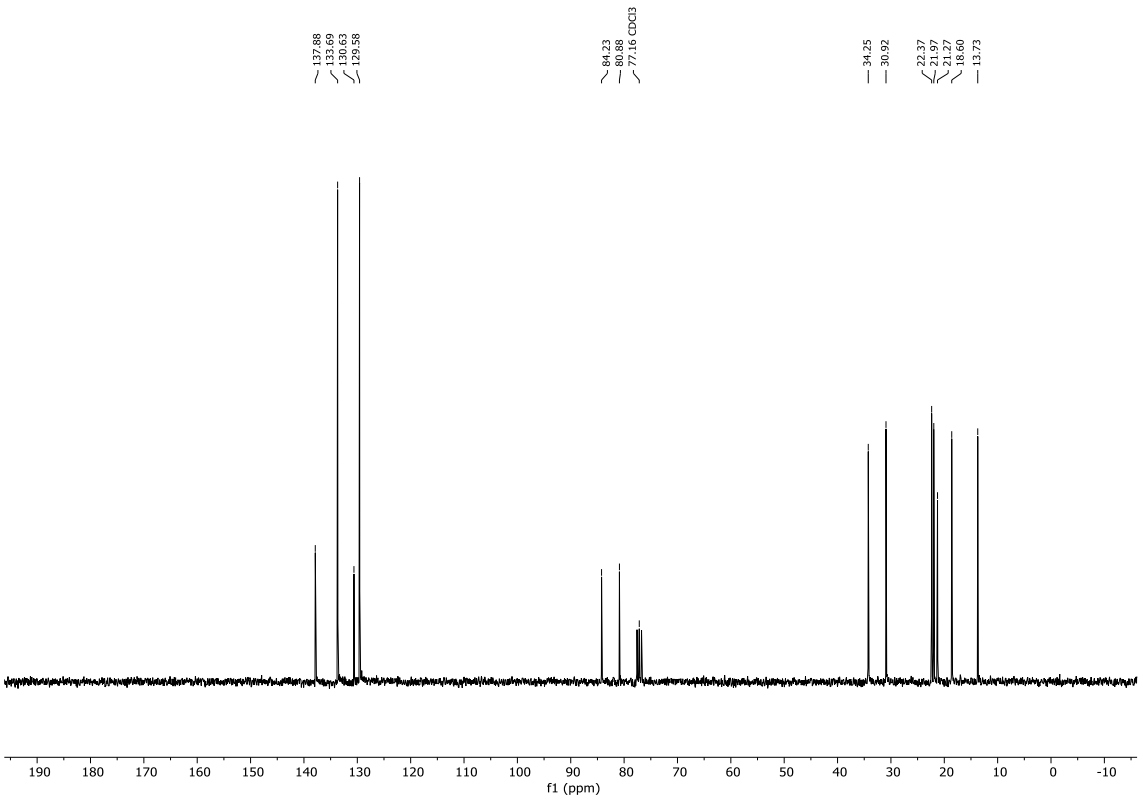


^{13}C-NMR (75 MHz, $CDCl_3$)

Oct-3-yn-2-yl(p-tolyl)sulfide (S6)

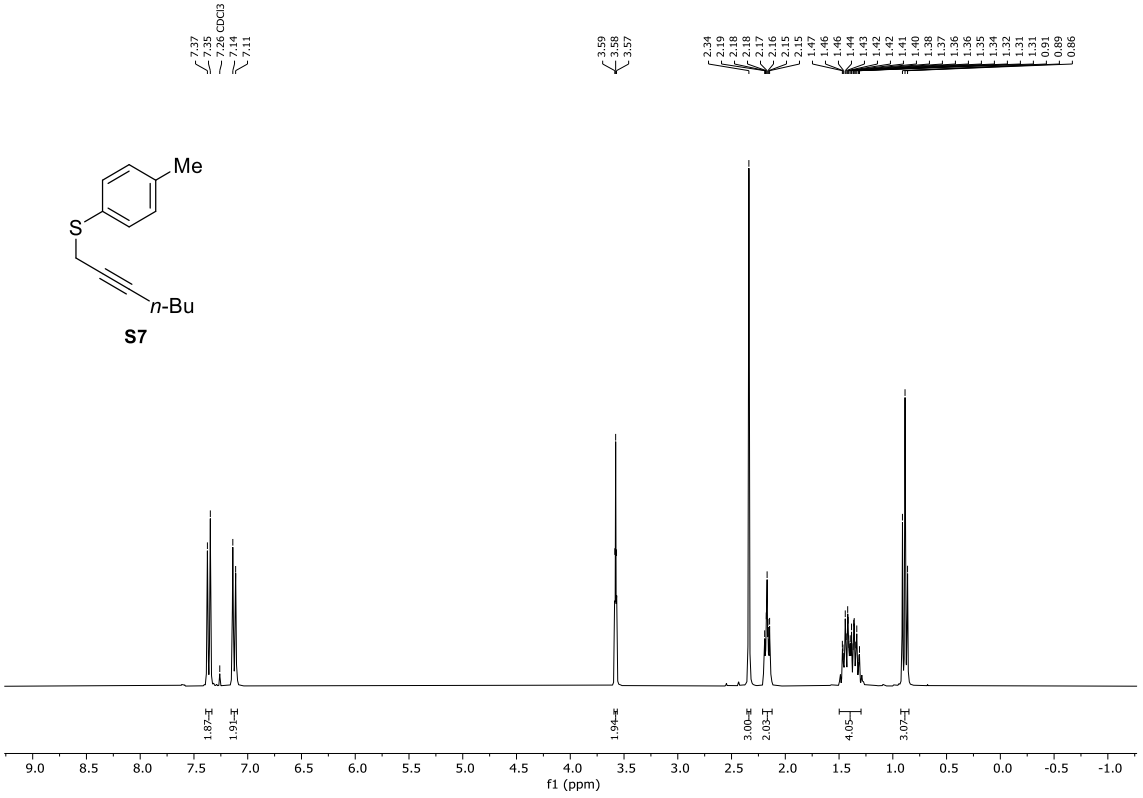


^{1}H-NMR (300 MHz, $CDCl_3$)

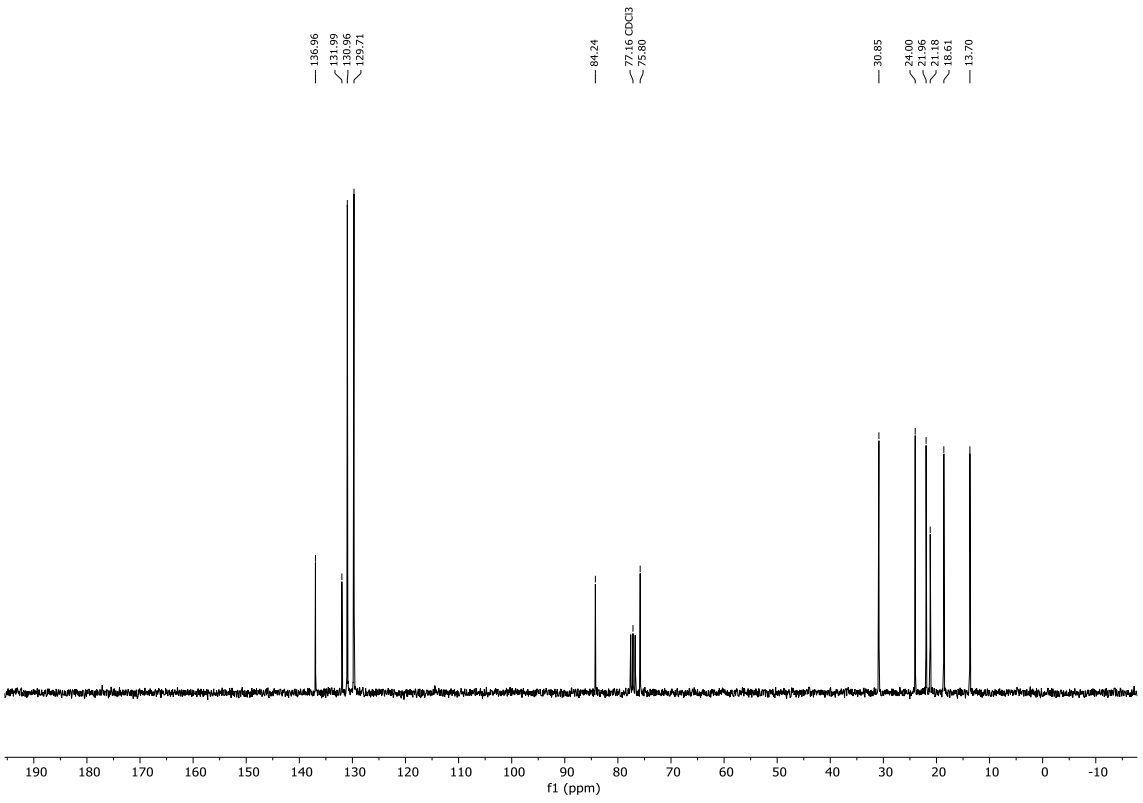


^{13}C-NMR (75 MHz, $CDCl_3$)

Hept-2-yn-1-yl(p-tolyl)sulfide (S7)

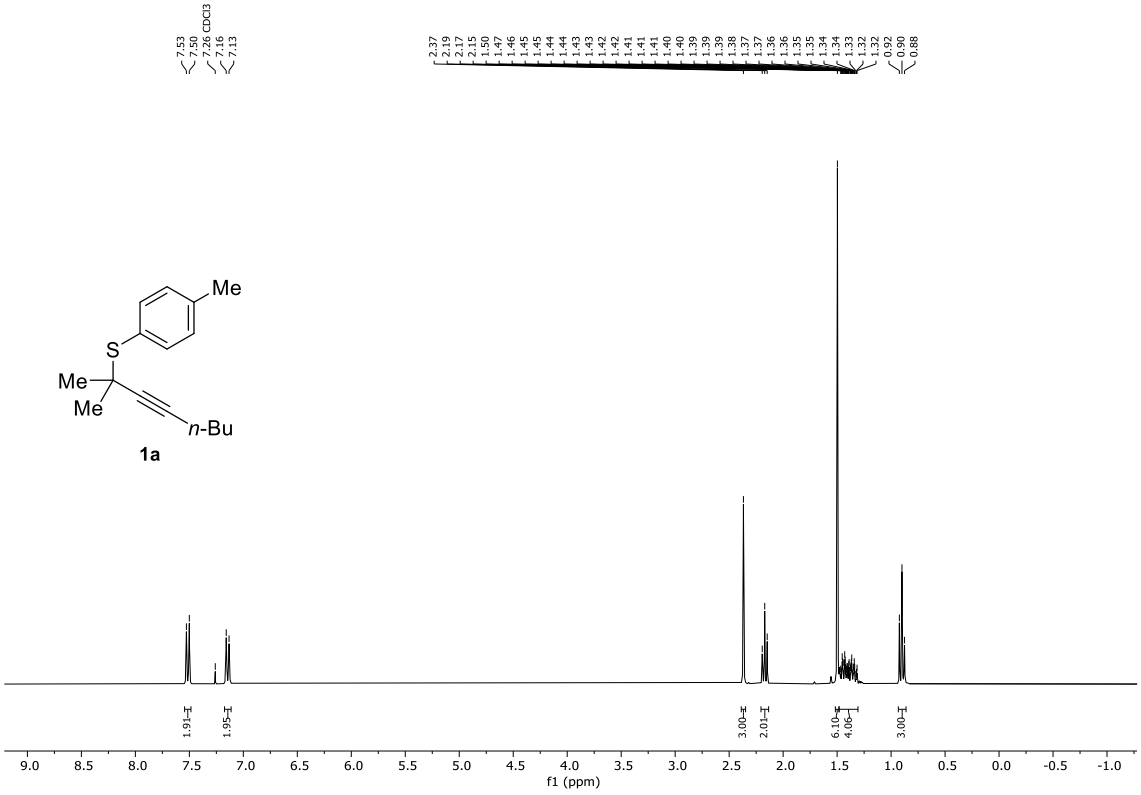


^{1}H-NMR (300 MHz, $CDCl_3$)

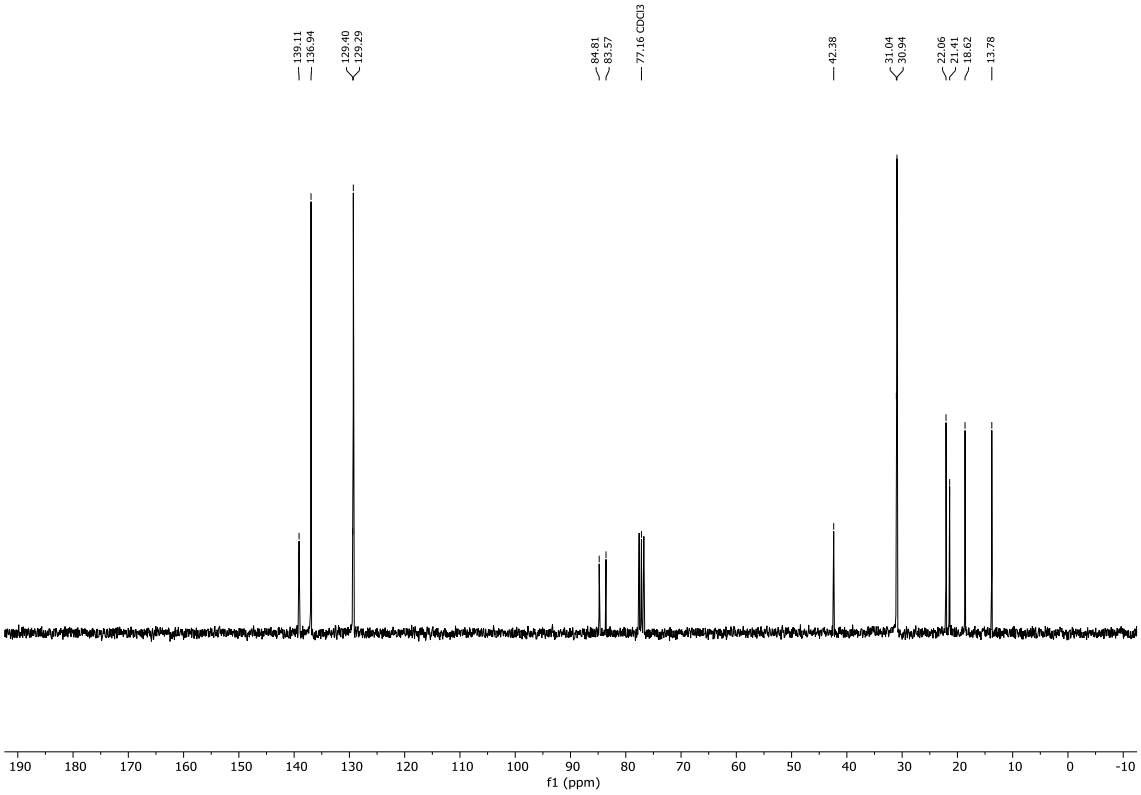


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-methyloct-3-yn-2-yl) (*p*-tolyl)sulfide (1a)

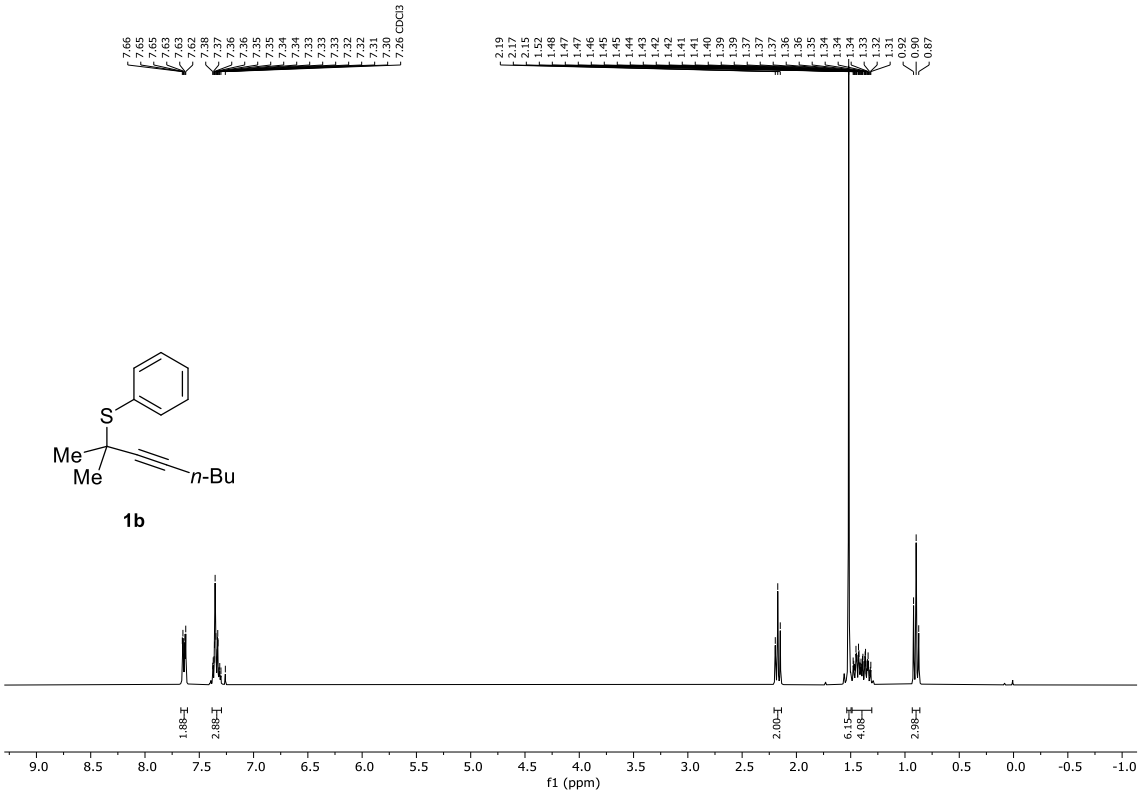


^{1}H-NMR (300 MHz, $CDCl_3$)

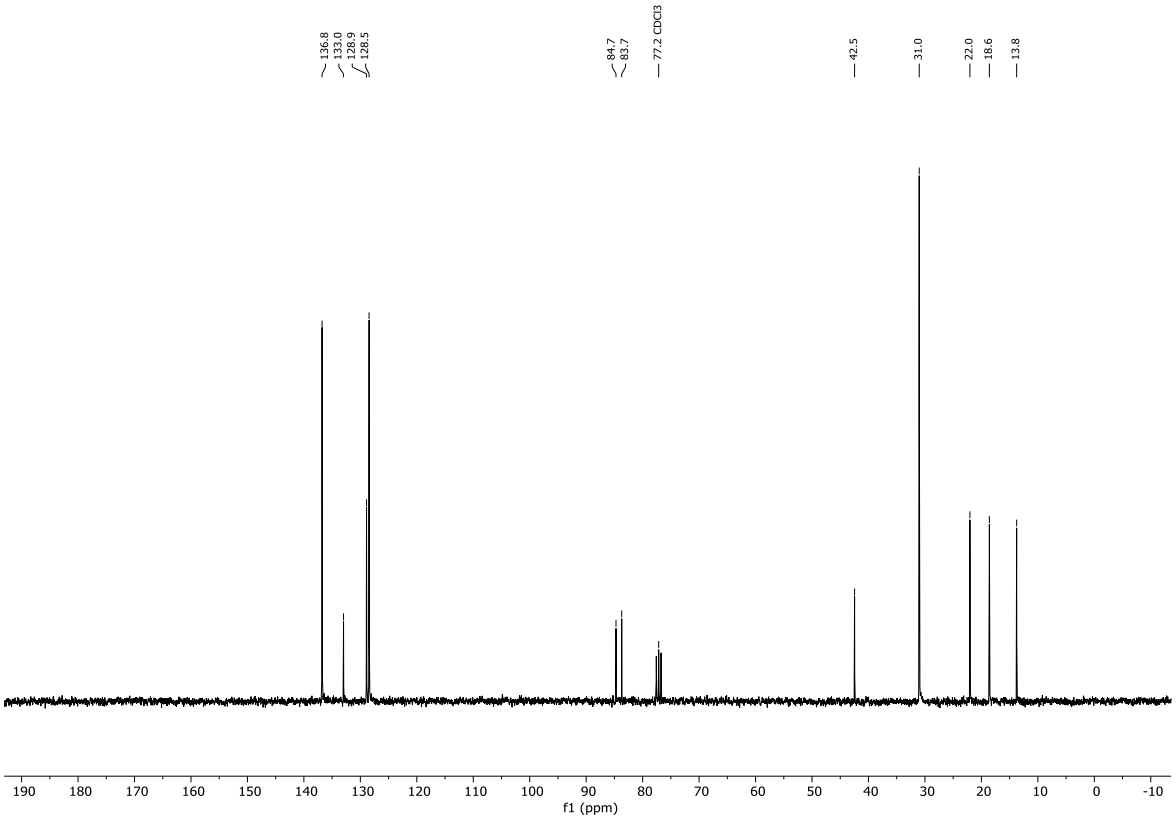


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-methyloct-3-yn-2-yl) (phenyl)sulfide (1b)

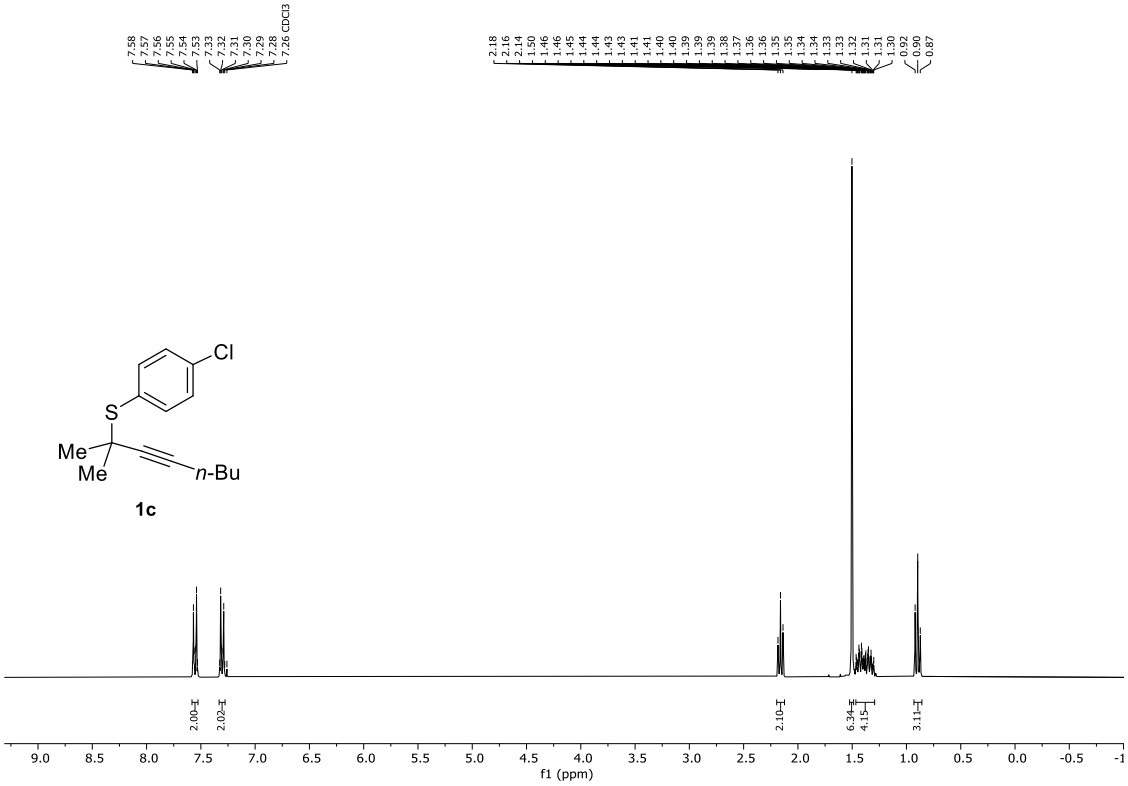


^{1}H-NMR (300 MHz, $CDCl_3$)

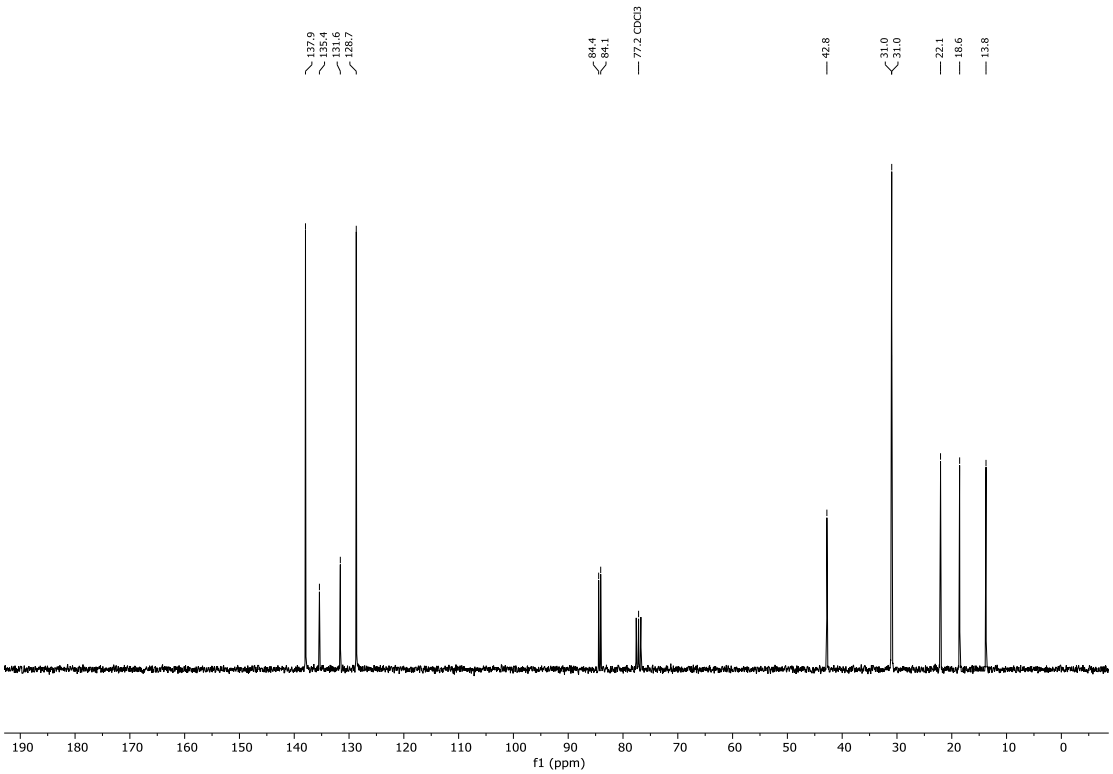


^{13}C-NMR (75 MHz, $CDCl_3$)

(4-chlorophenyl) (2-methyloct-3-yn-2-yl)sulfide (1c)

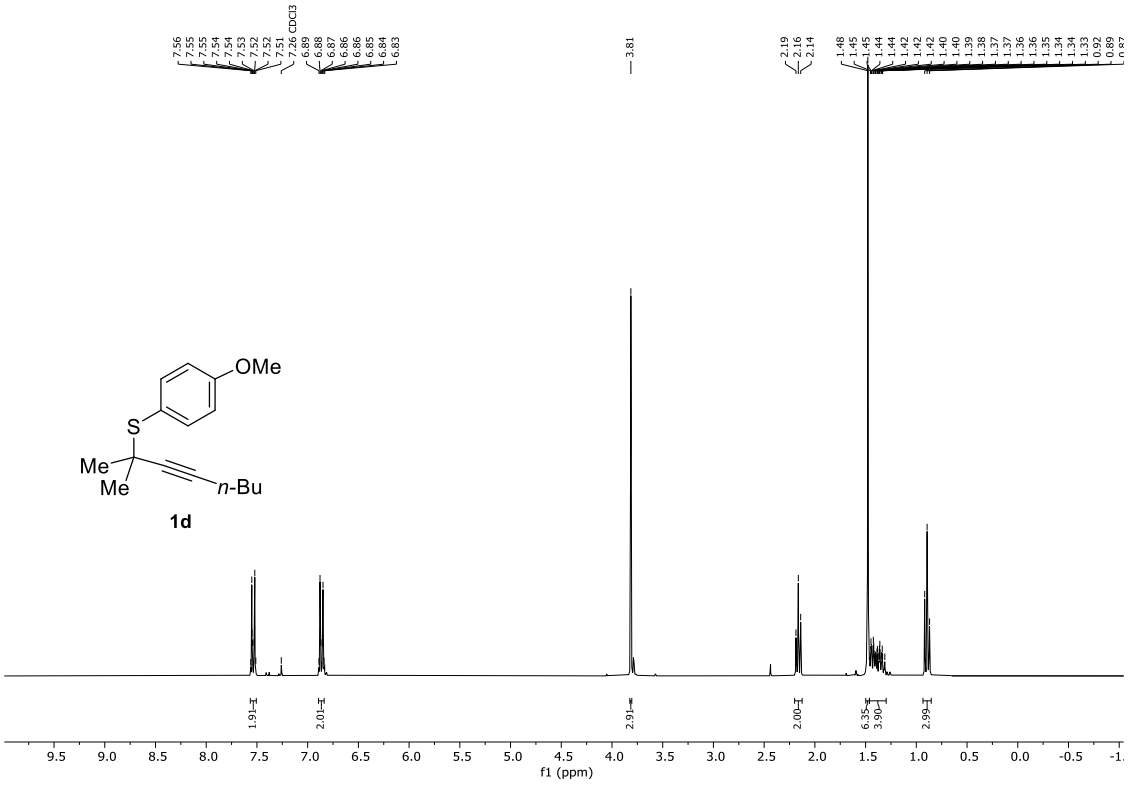


^{1}H-NMR (300 MHz, $CDCl_3$)

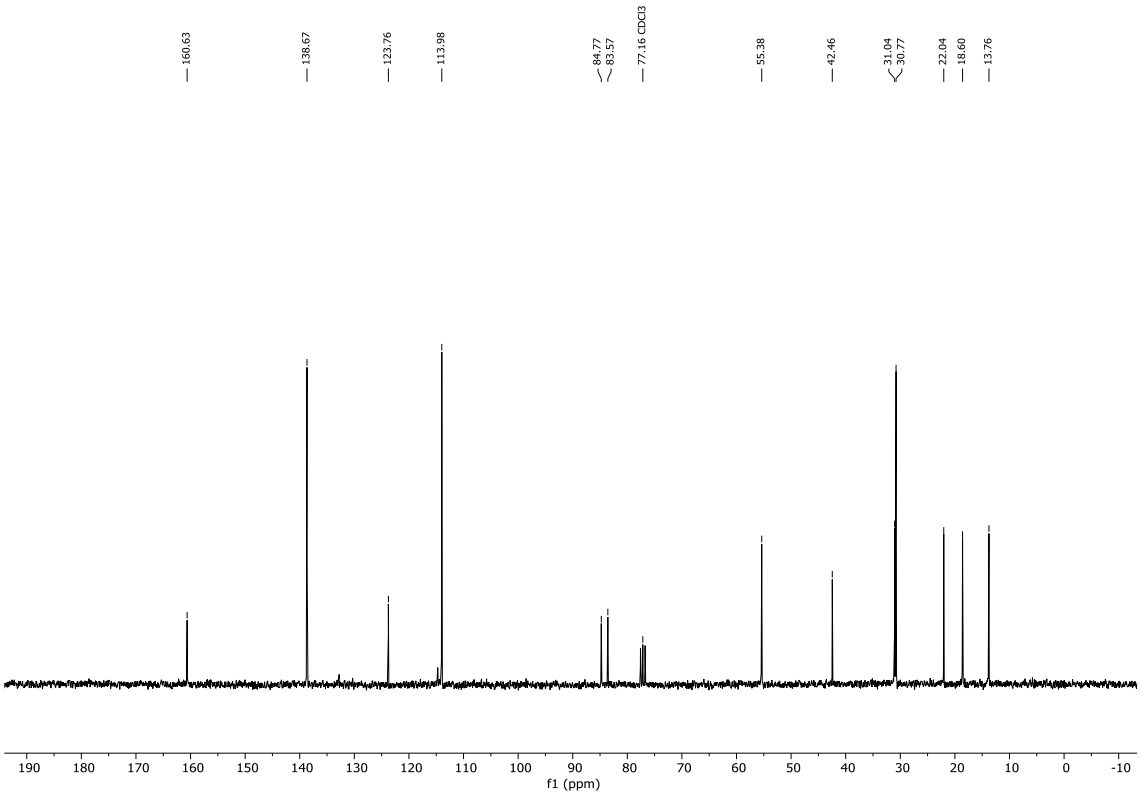


^{13}C-NMR (75 MHz, $CDCl_3$)

(4-methoxyphenyl) (2-methyloct-3-yn-2-yl)sulfide (1d)

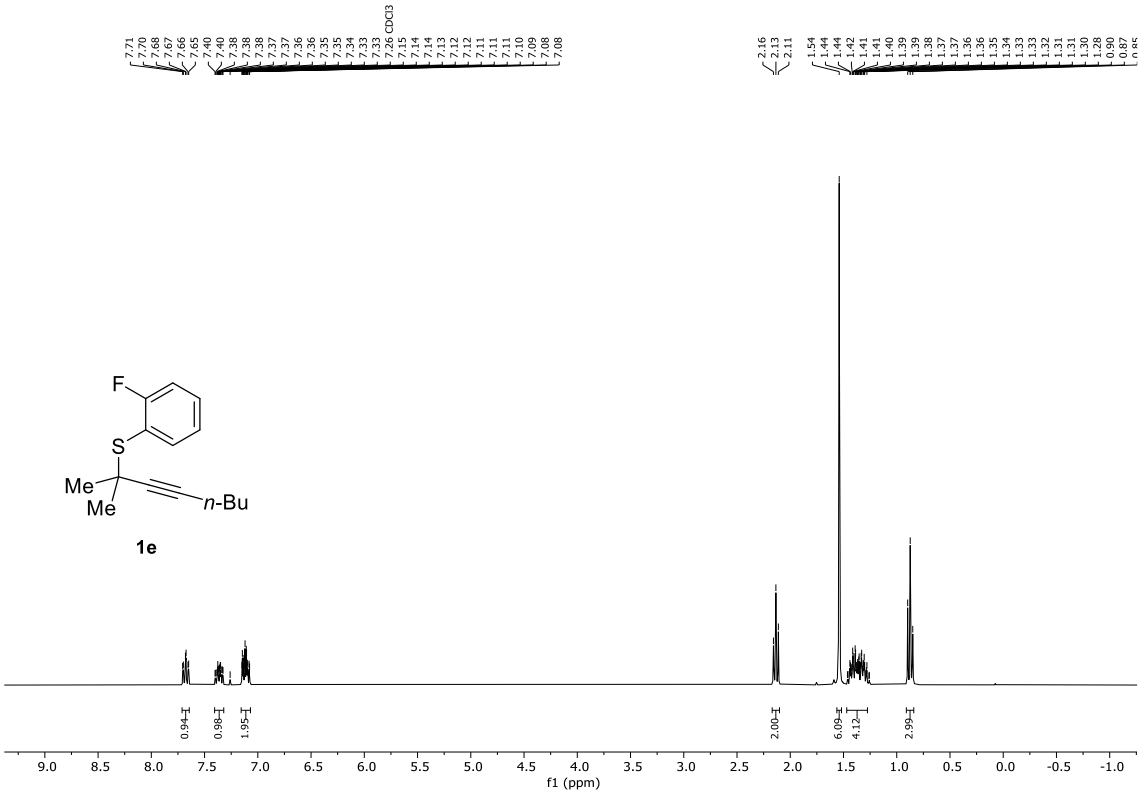


^{1}H-NMR (300 MHz, $CDCl_3$)

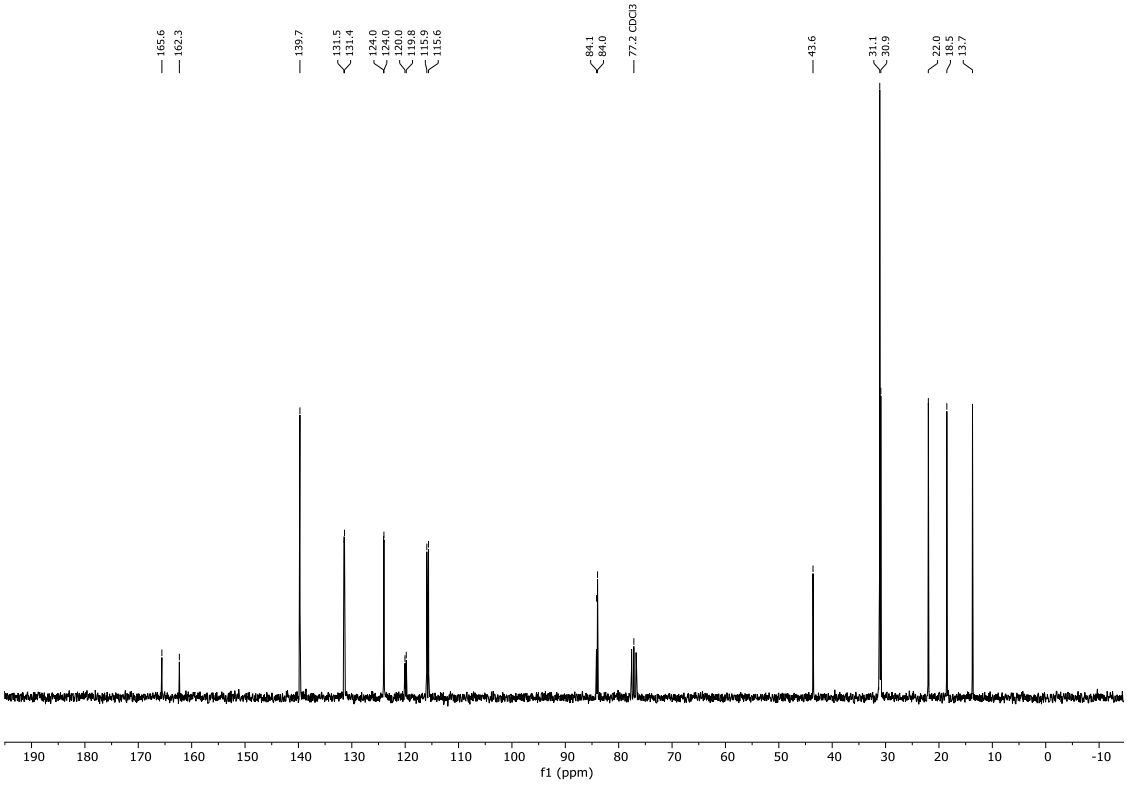


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-fluorophenyl) (2-methyloct-3-yn-2-yl)sulfide (1e)

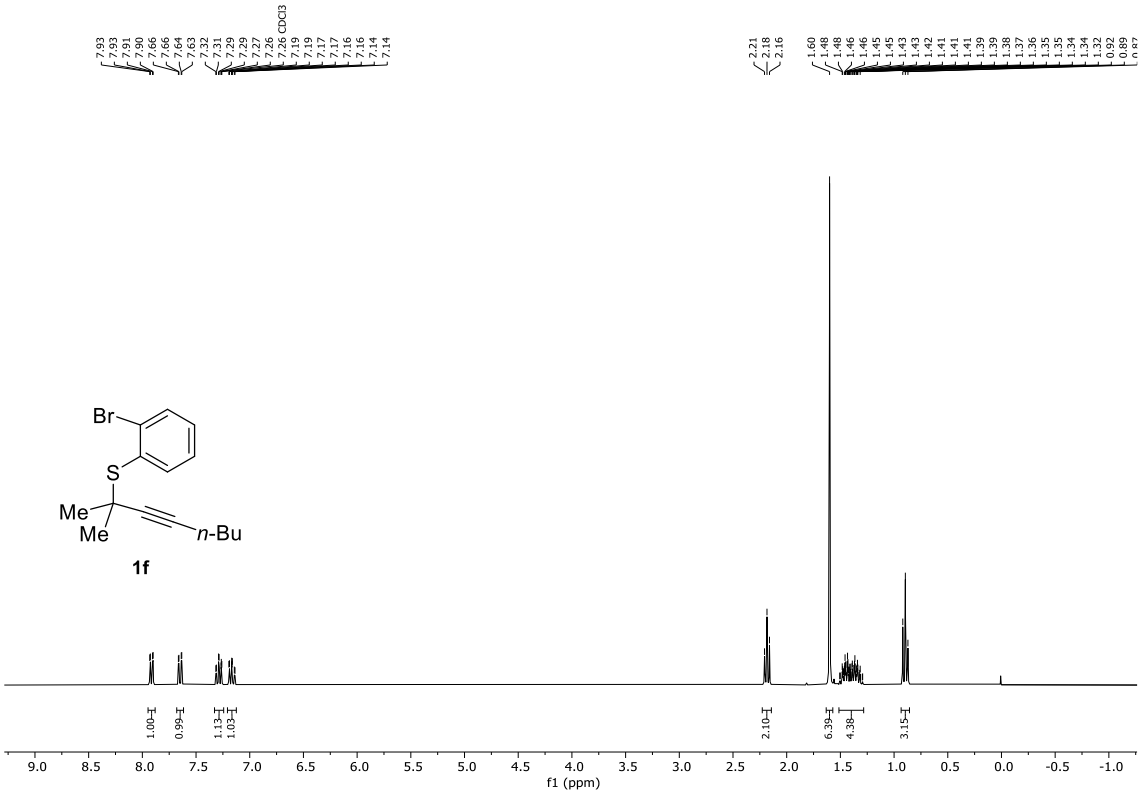


^{1}H-NMR (300 MHz, $CDCl_3$)

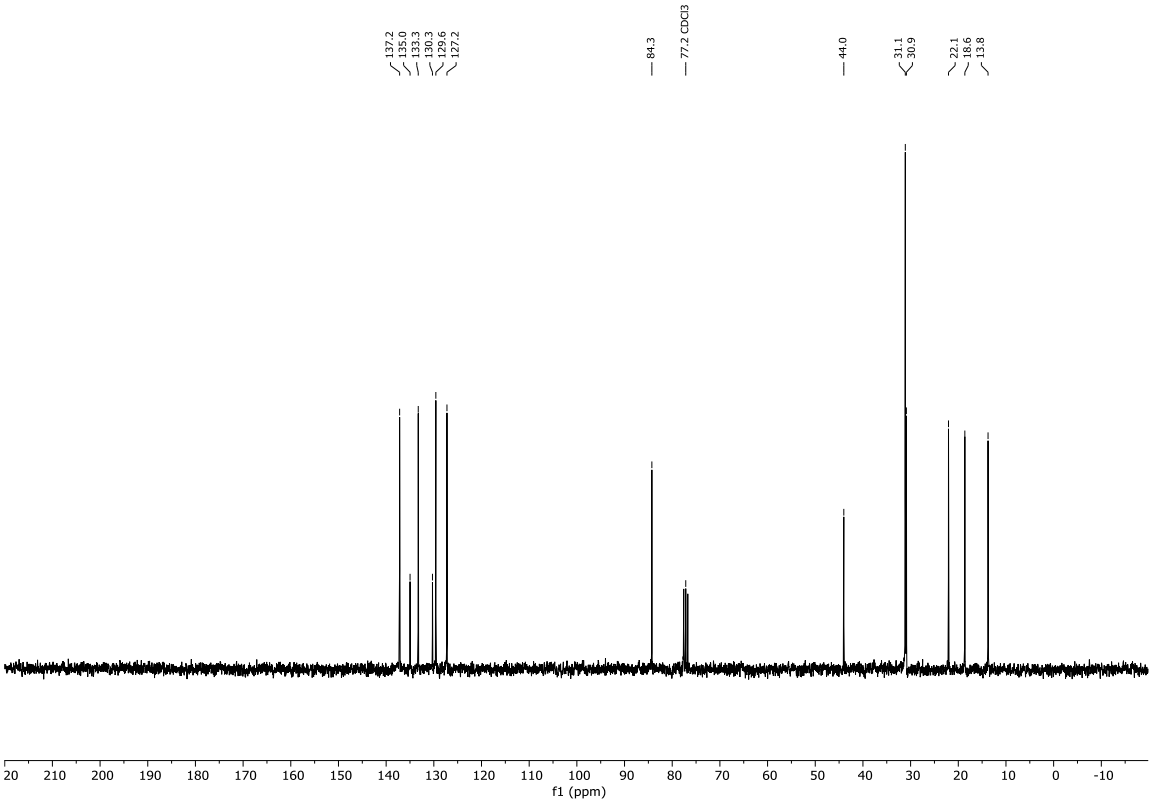


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-bromophenyl) (2-methyloct-3-yn-2-yl)sulfide (1f)

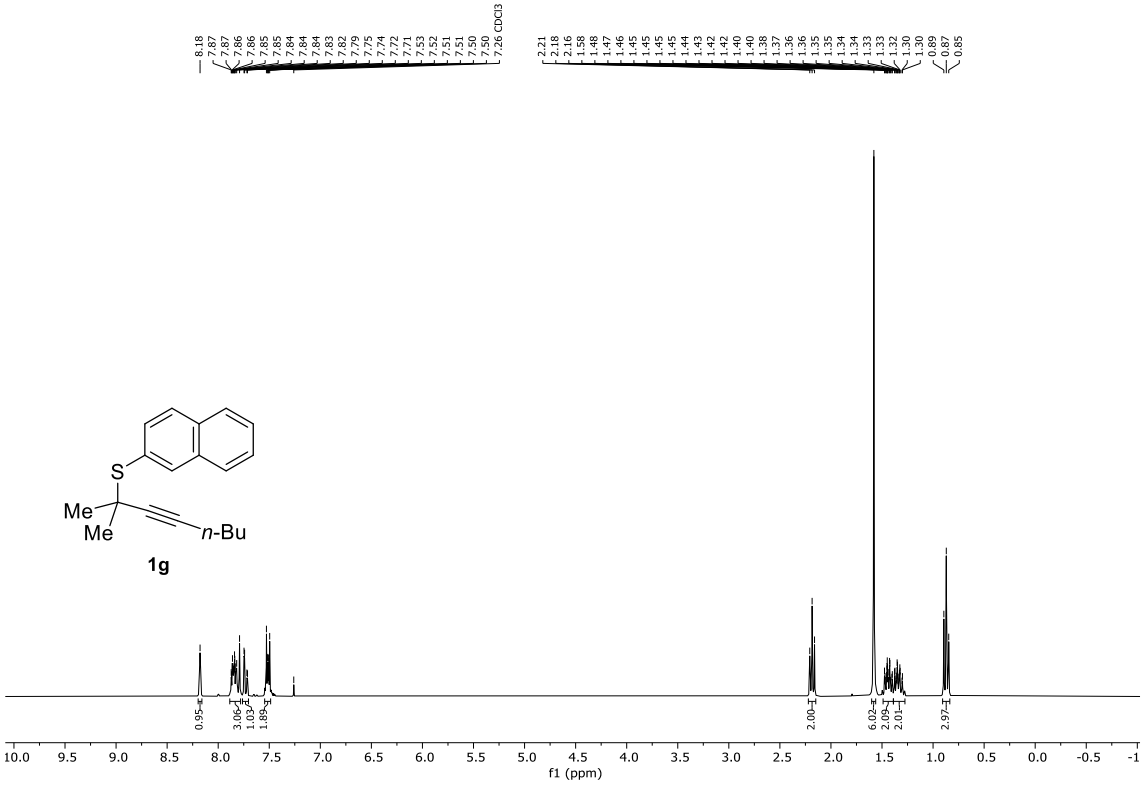


^{1}H-NMR (300 MHz, $CDCl_3$)

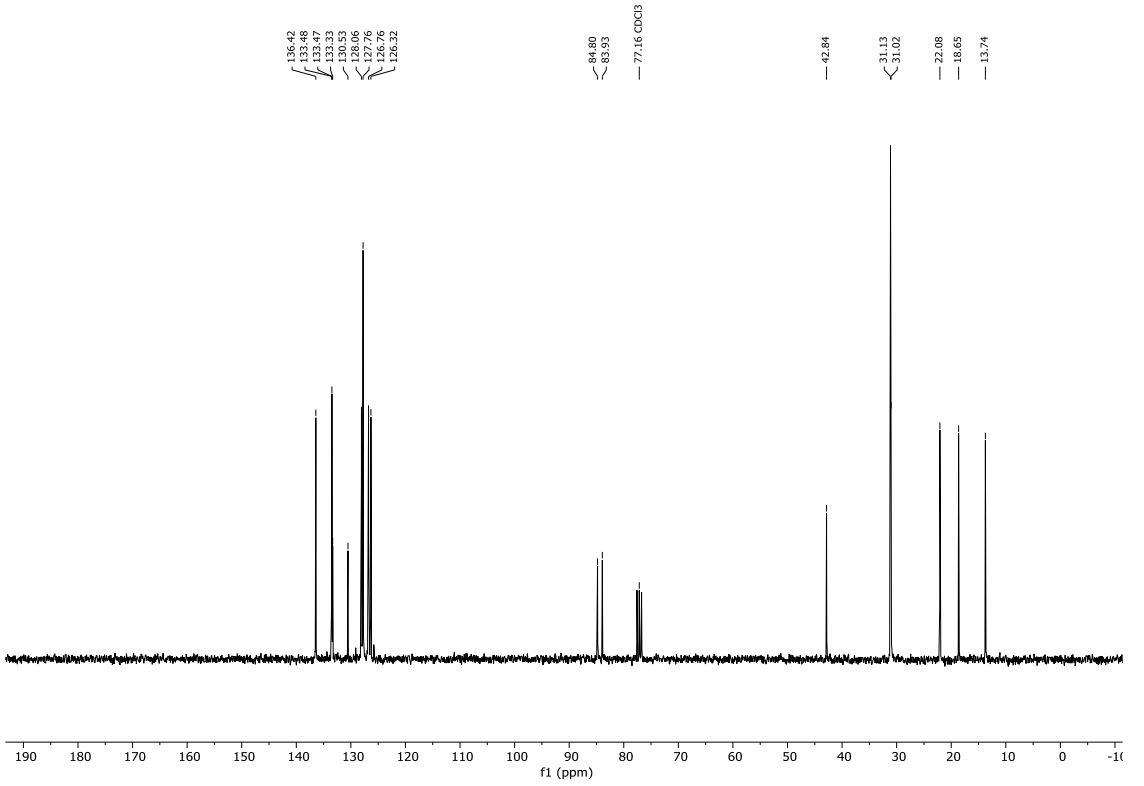


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-methyloct-3-yn-2-yl) (naphthalen-2-yl)sulfide (1g)

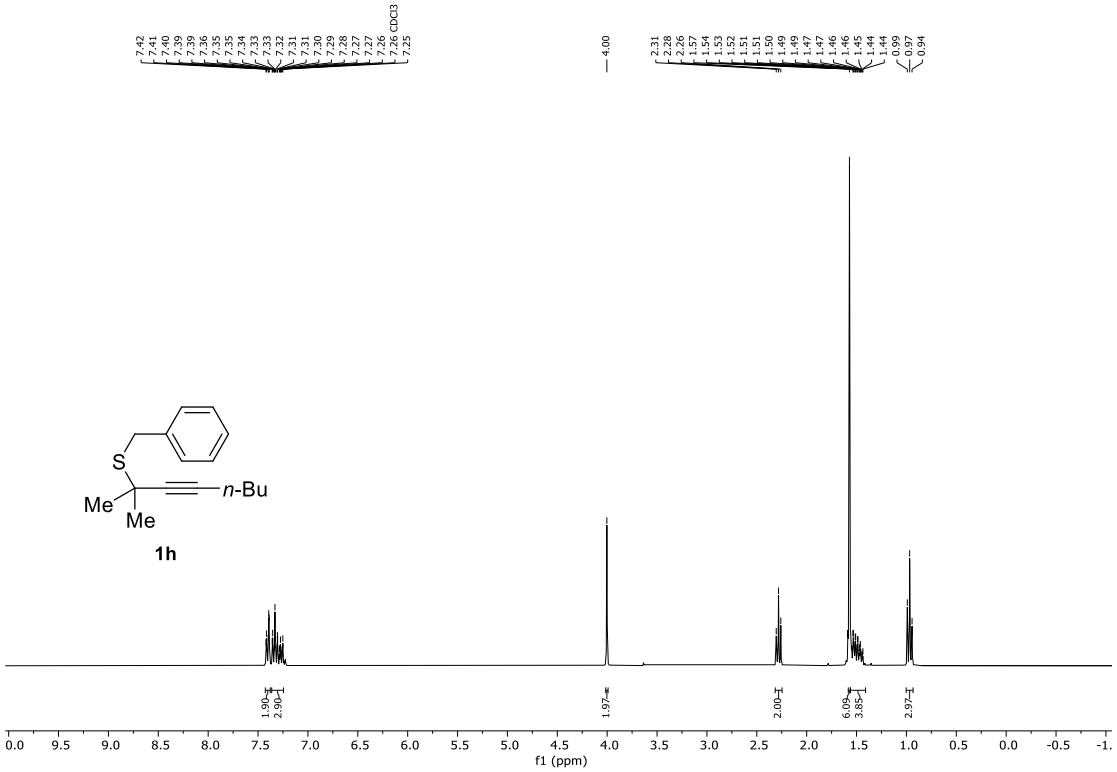


^{1}H-NMR (300 MHz, $CDCl_3$)

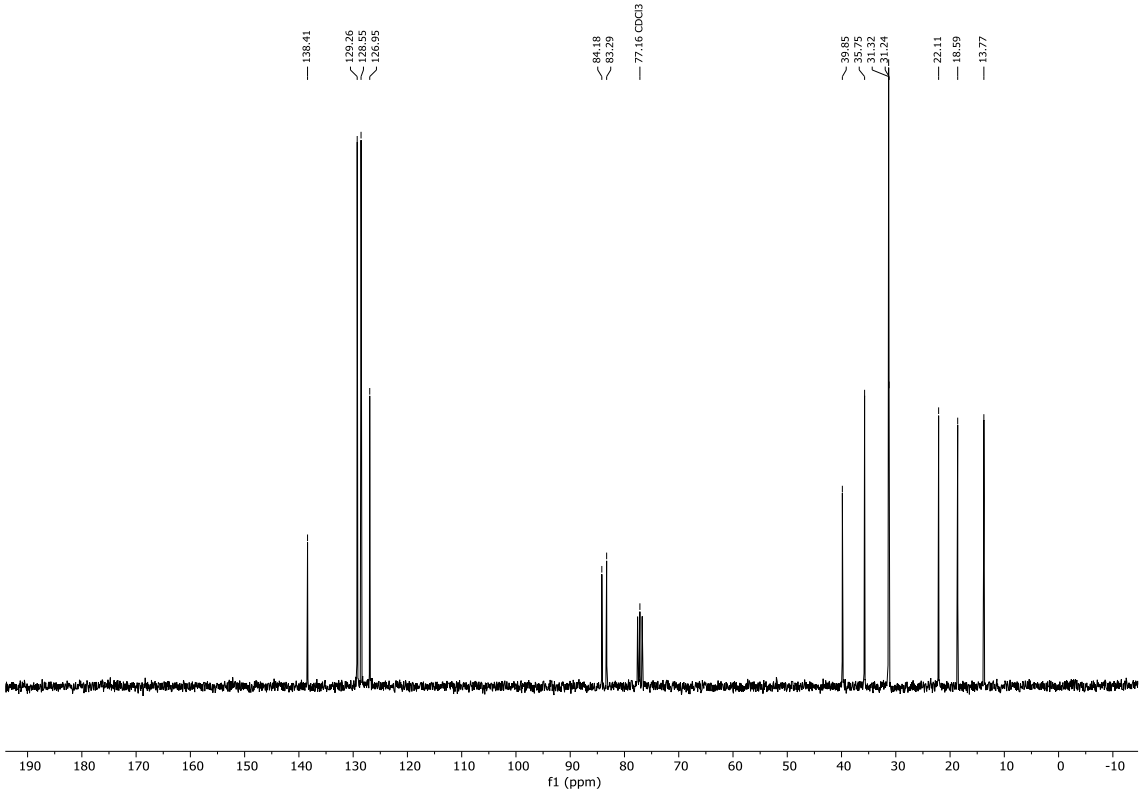


^{13}C-NMR (75 MHz, $CDCl_3$)

Benzyl (2-methyloct-3-yn-2-yl)sulfide (1h)

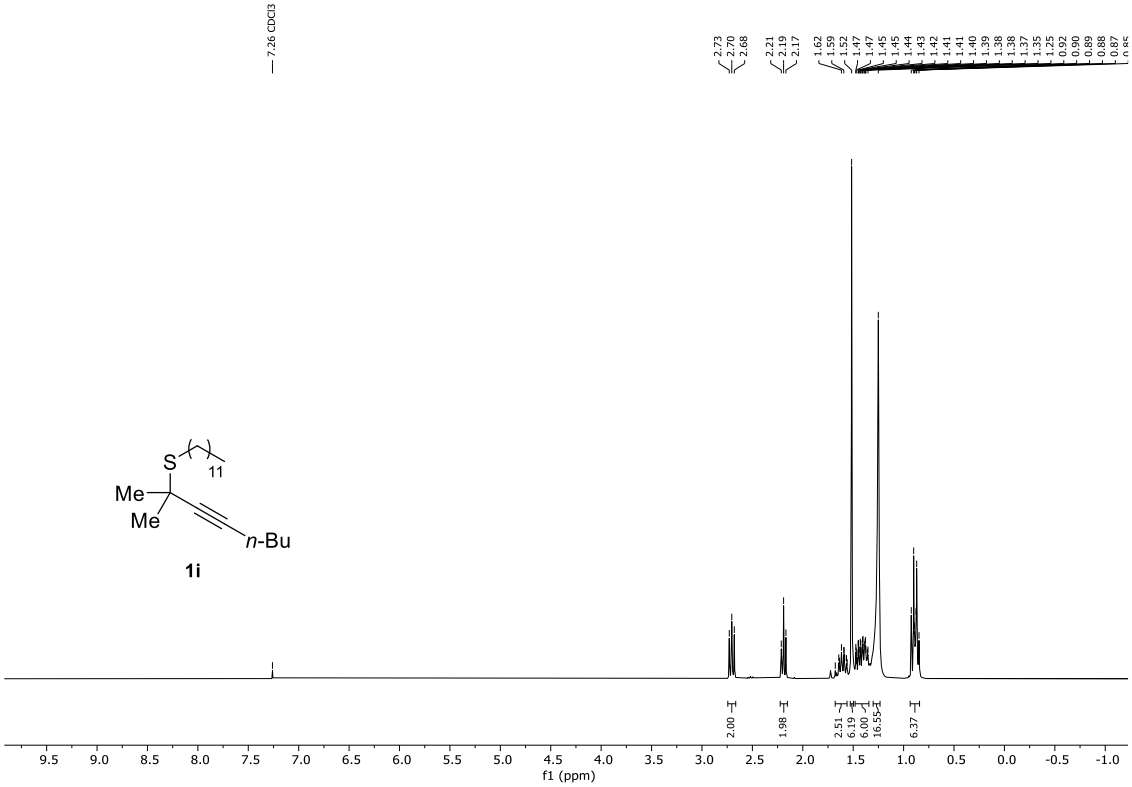


^{1}H-NMR (300 MHz, $CDCl_3$)

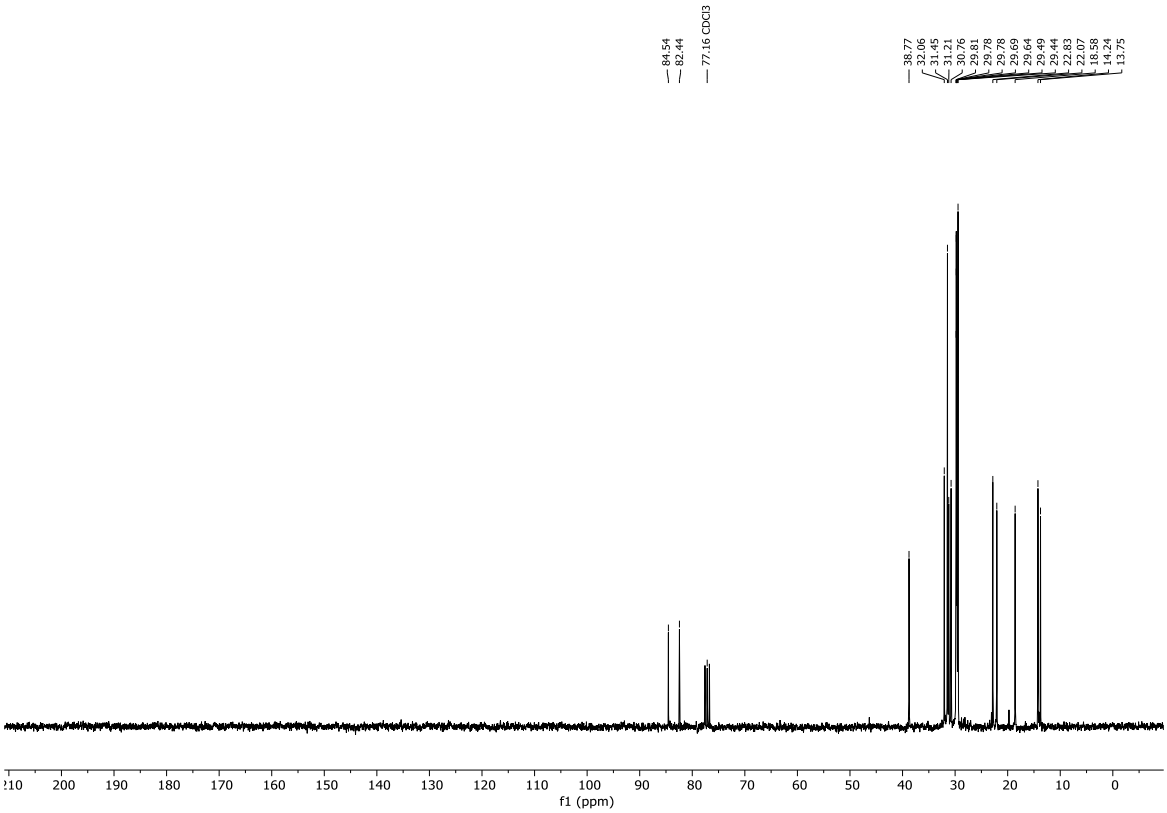


^{13}C-NMR (75 MHz, $CDCl_3$)

Dodecyl (2-methyloct-3-yn-2-yl)sulfide (1i)

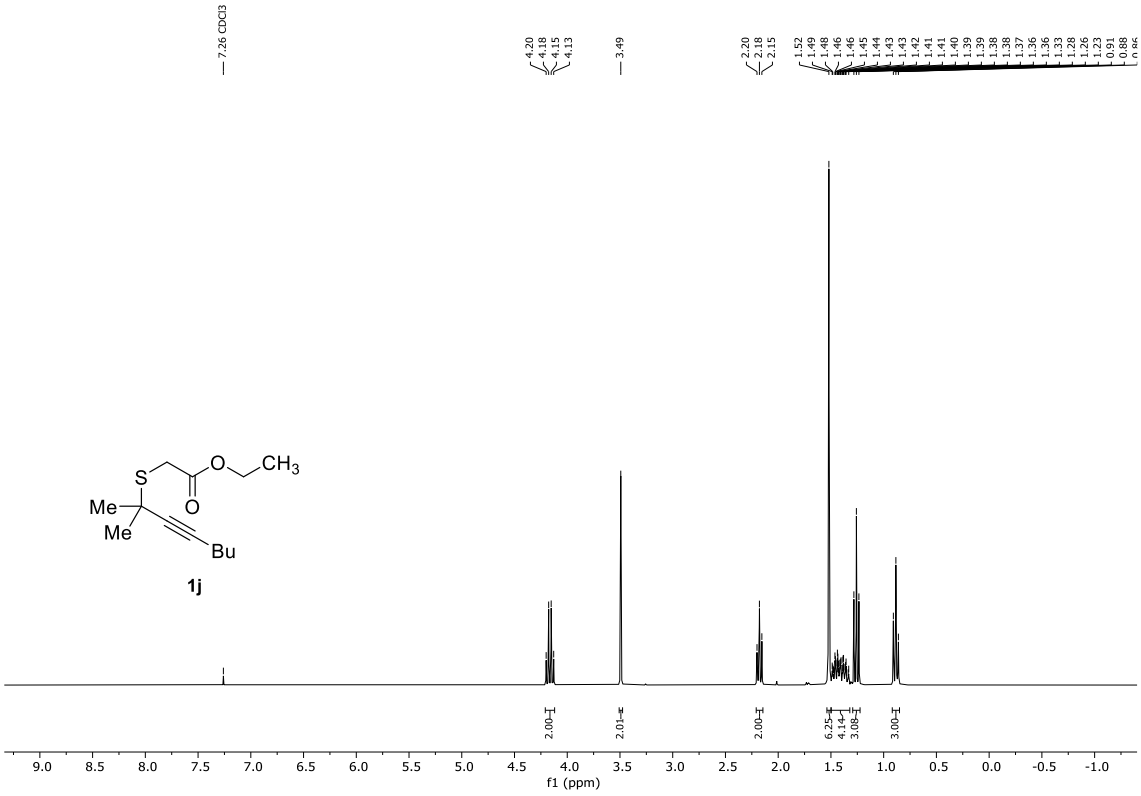


^{1}H-NMR (300 MHz, $CDCl_3$)

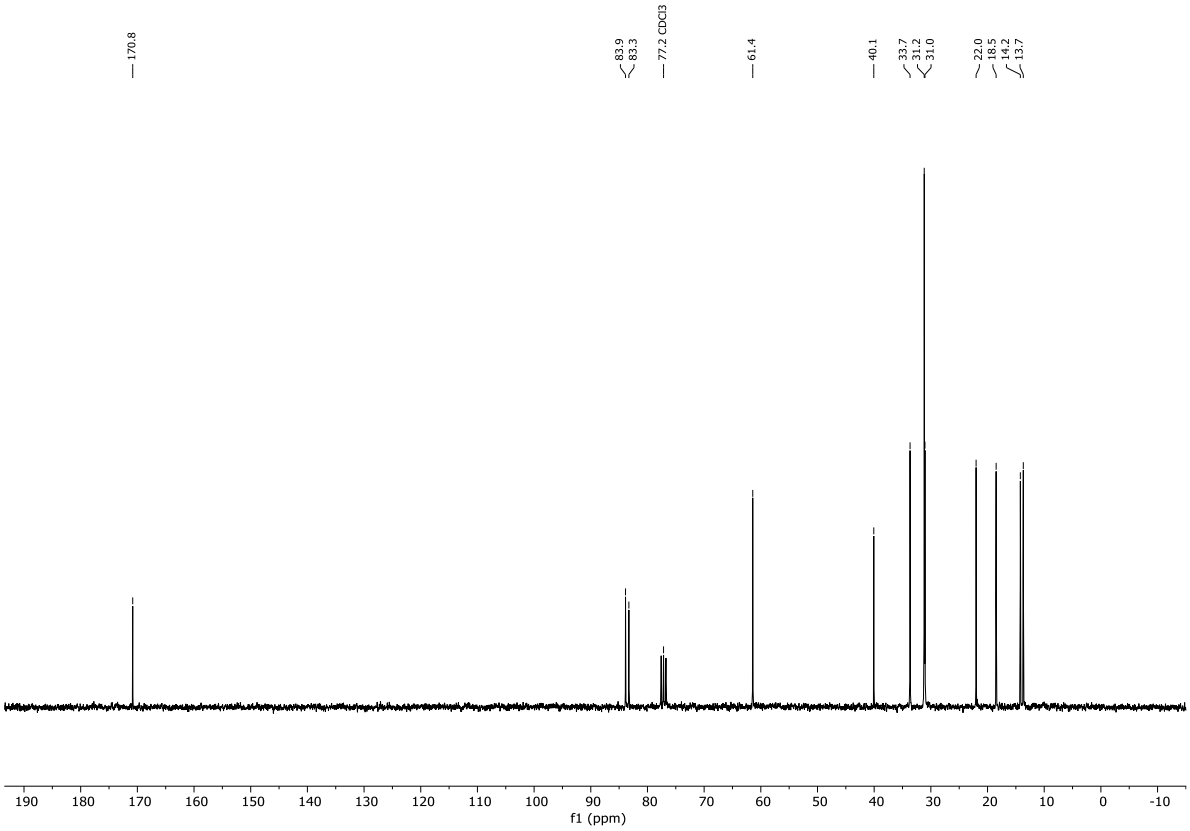


^{13}C-NMR (75 MHz, $CDCl_3$)

Ethyl 2-((2-methyloct-3-yn-2-yl)thio)acetate (1j)

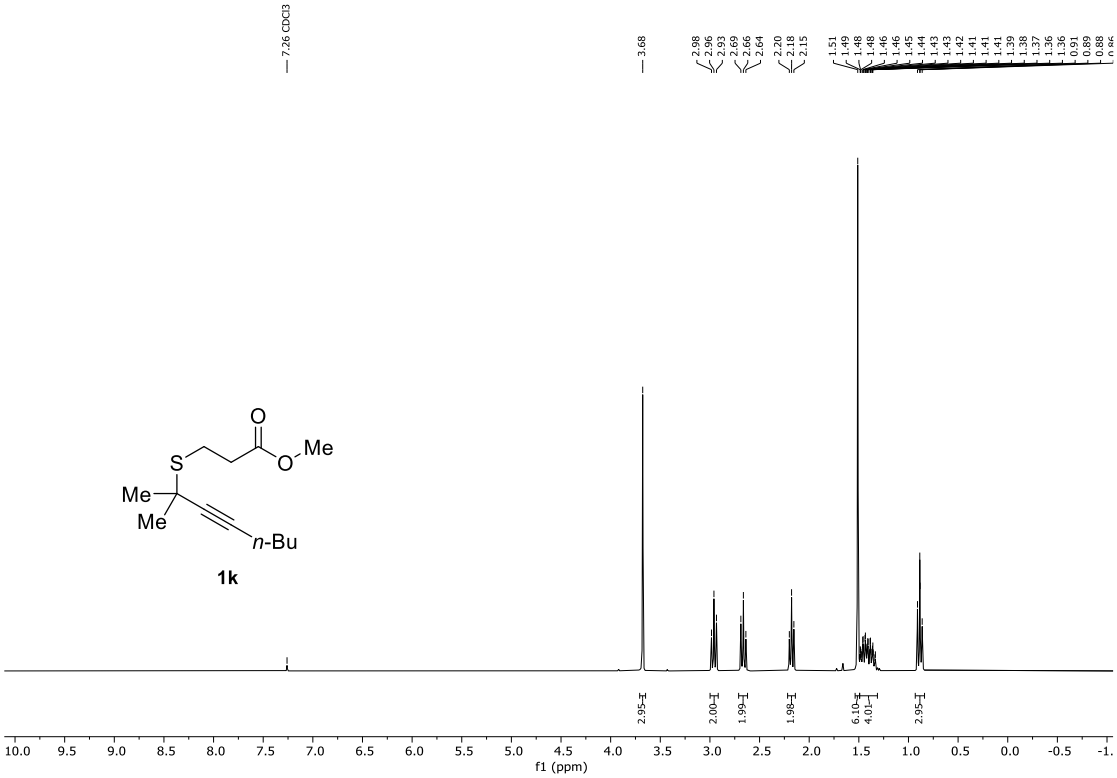


^{1}H-NMR (300 MHz, $CDCl_3$)

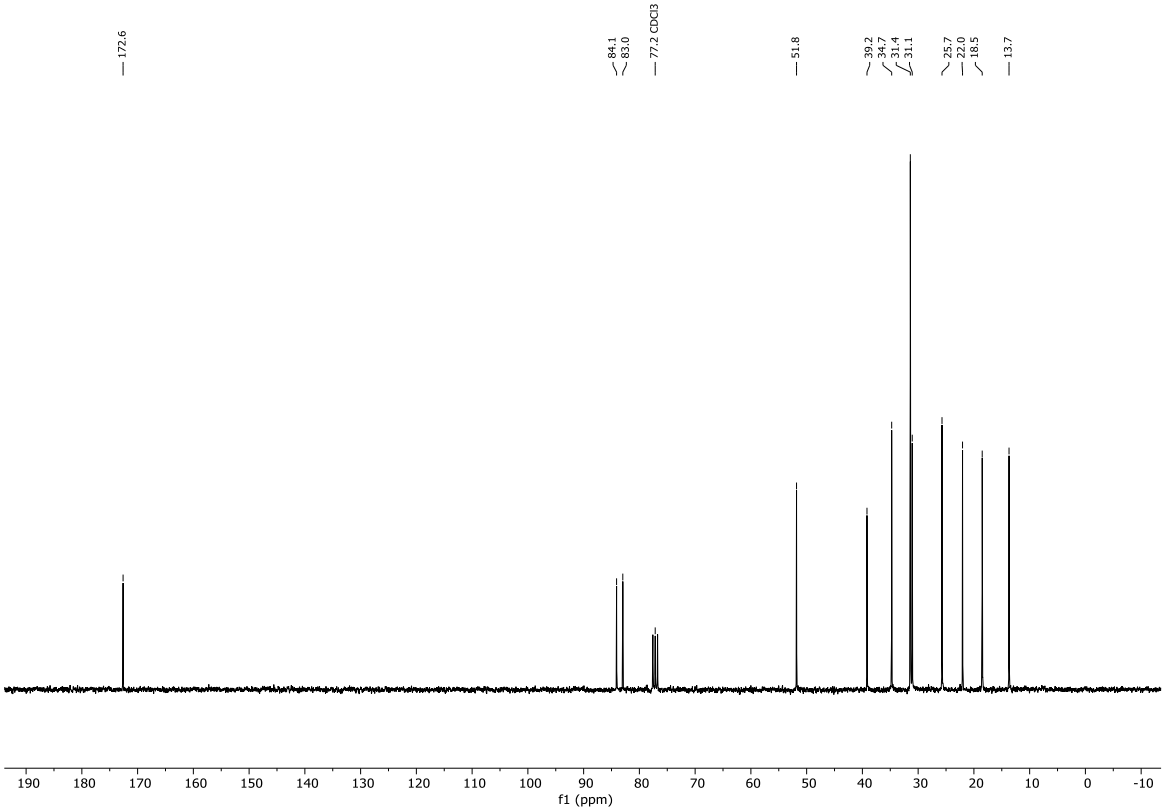


^{13}C-NMR (75 MHz, $CDCl_3$)

methyl 3-((2-methyloct-3-yn-2-yl)thio)propanoate (1k)

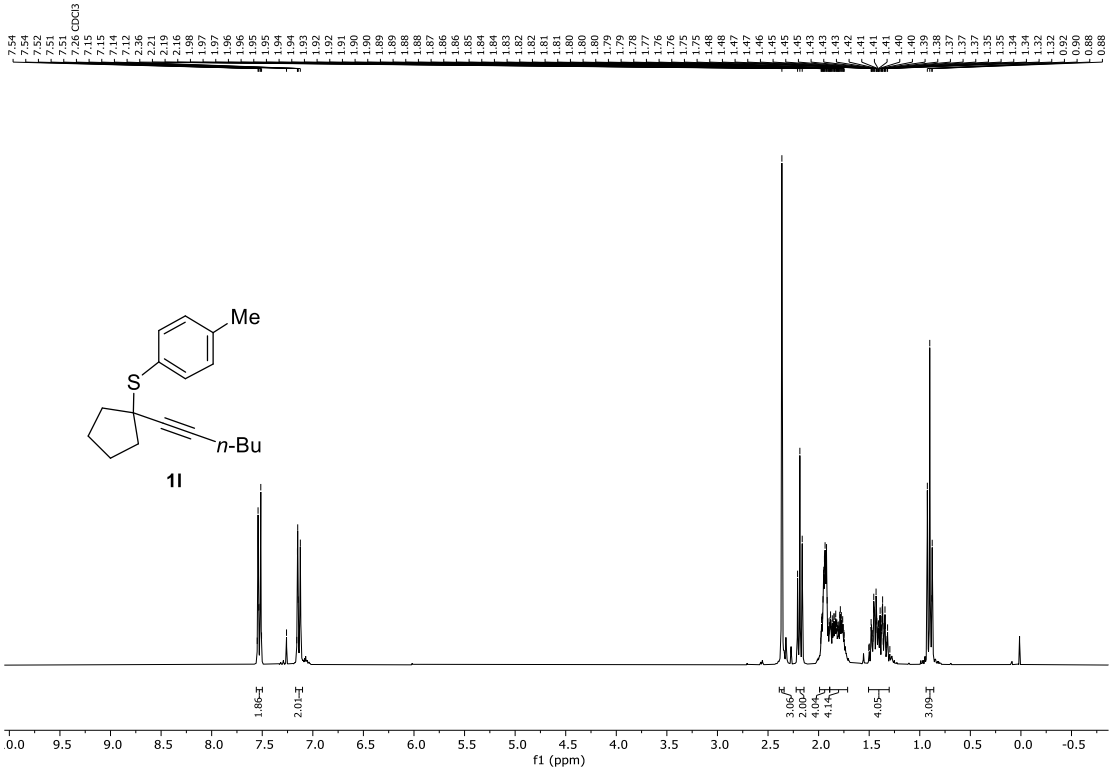


^{1}H-NMR (300 MHz, $CDCl_3$)

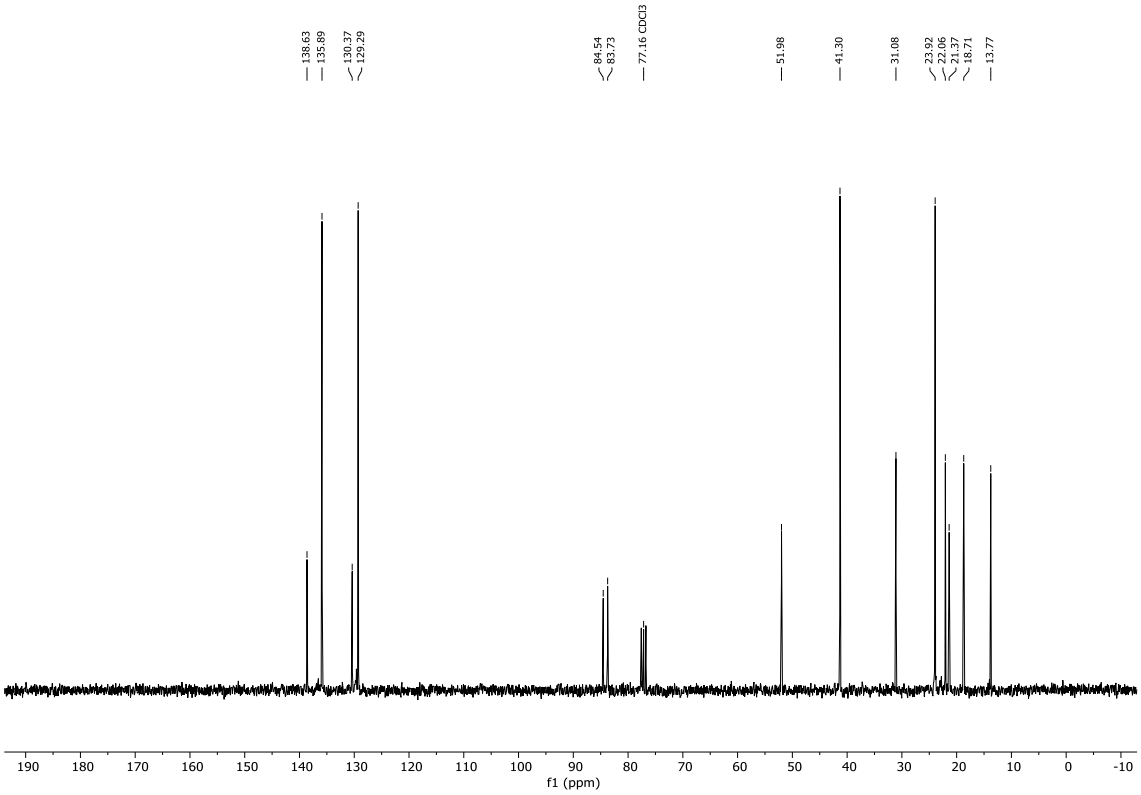


^{13}C-NMR (75 MHz, $CDCl_3$)

(1-(hex-1-yn-1-yl)cyclopentyl) (*p*-tolyl)sulfide (1l)

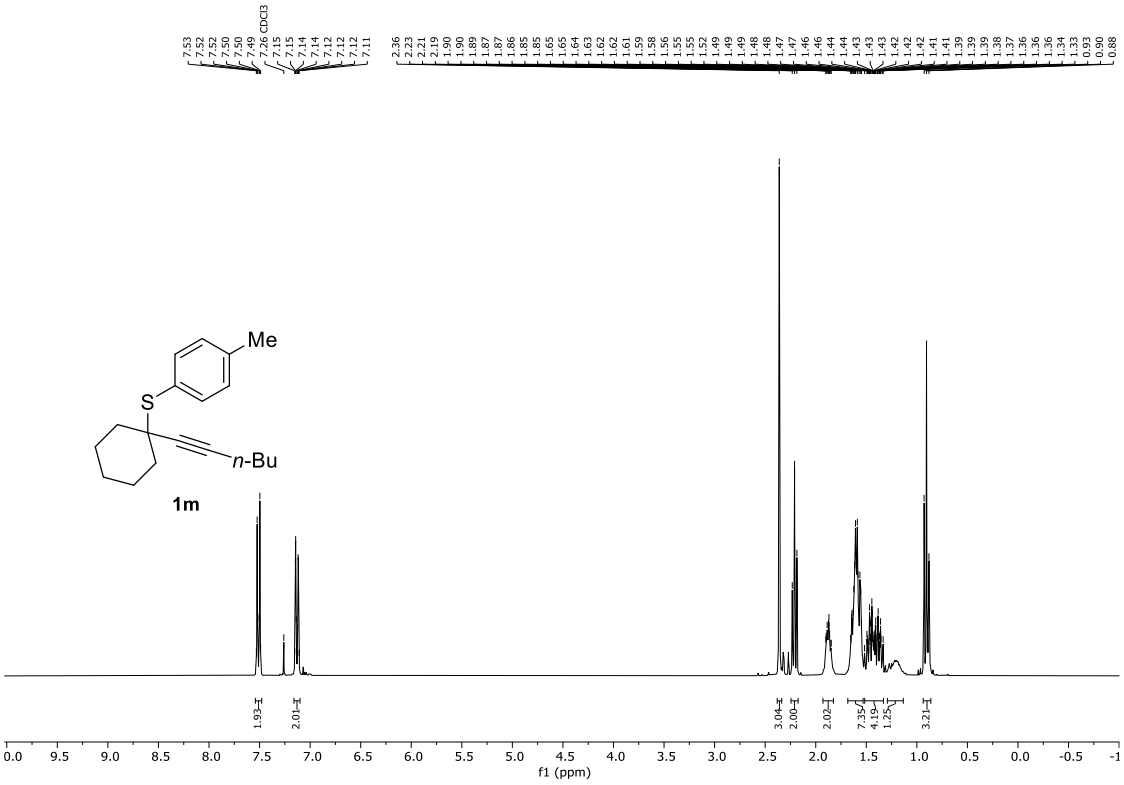


^{1}H-NMR (300 MHz, $CDCl_3$)

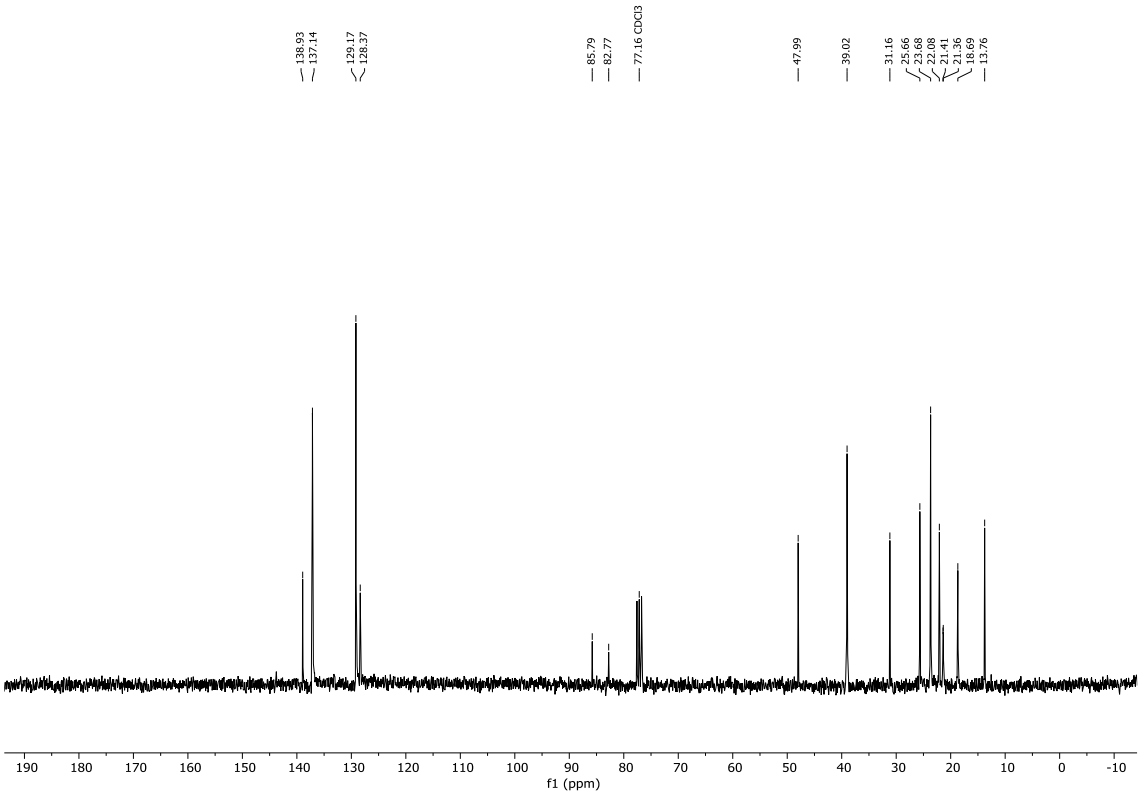


^{13}C-NMR (75 MHz, $CDCl_3$)

(1-(hex-1-yn-1-yl)cyclohexyl) (*p*-tolyl)sulfide (1m)

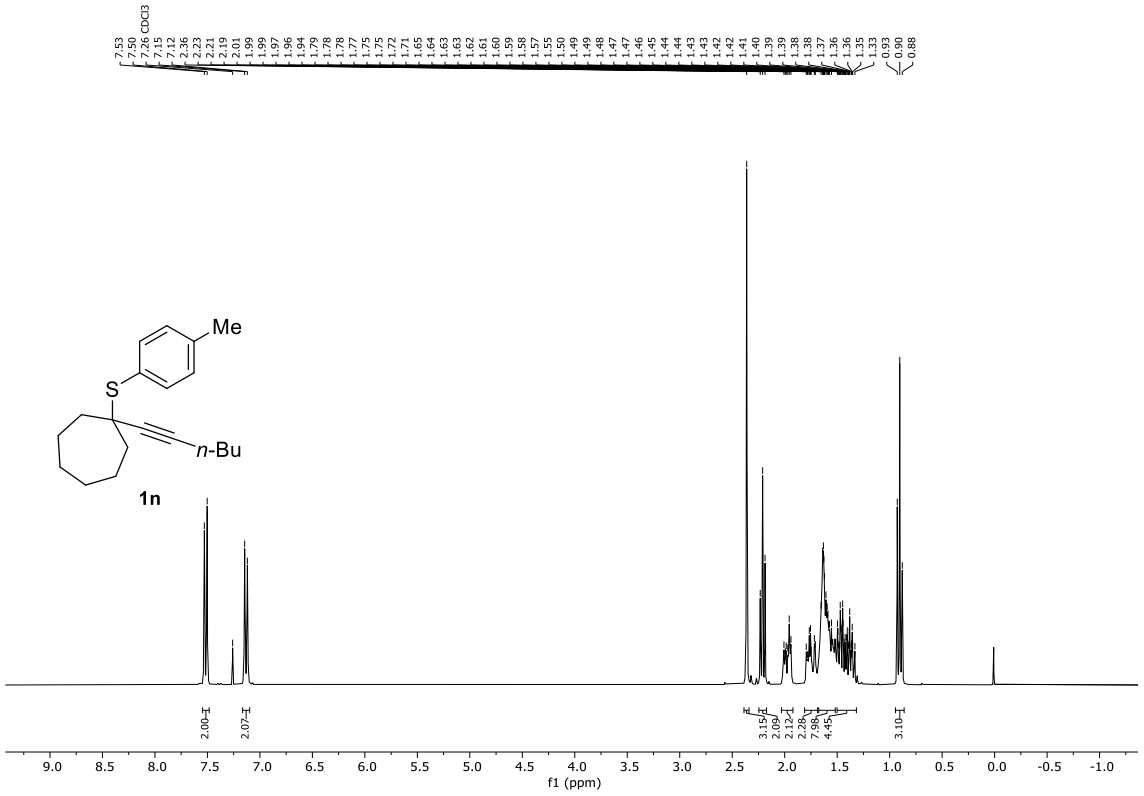


^{1}H-NMR (300 MHz, $CDCl_3$)

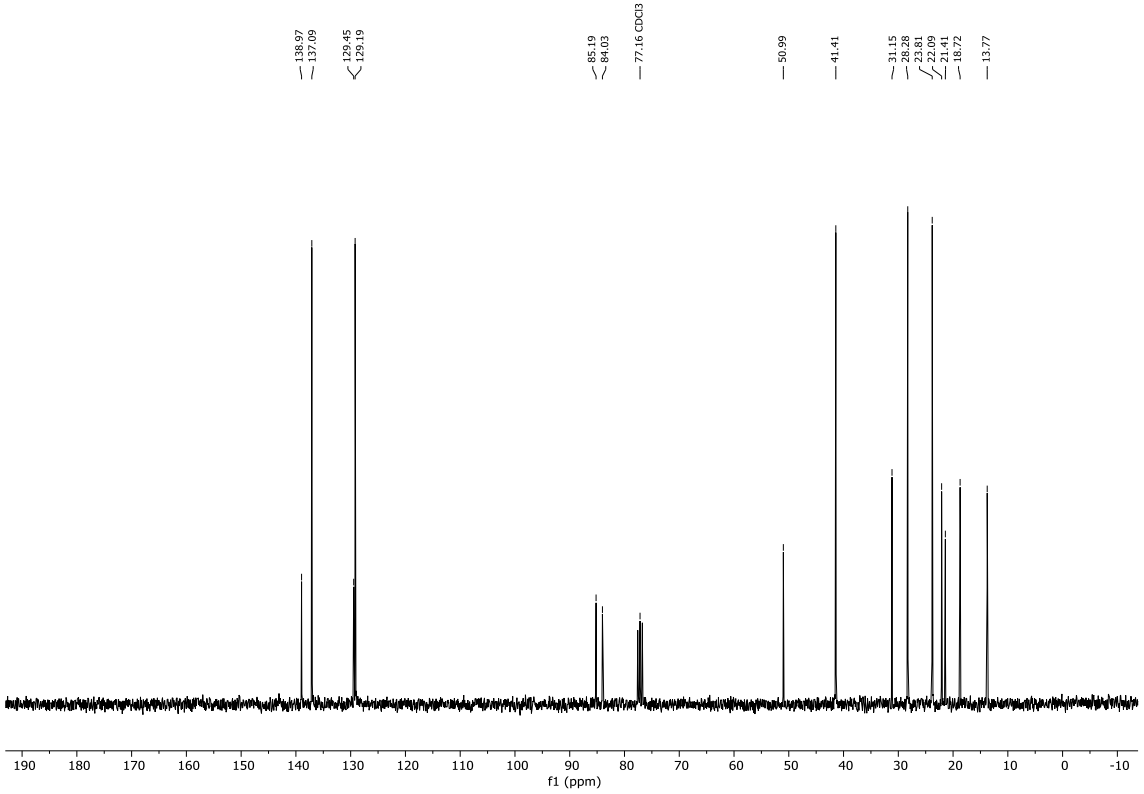


^{13}C-NMR (75 MHz, $CDCl_3$)

(1-(hex-1-yn-1-yl)cycloheptyl) (*p*-tolyl)sulfide (1n)

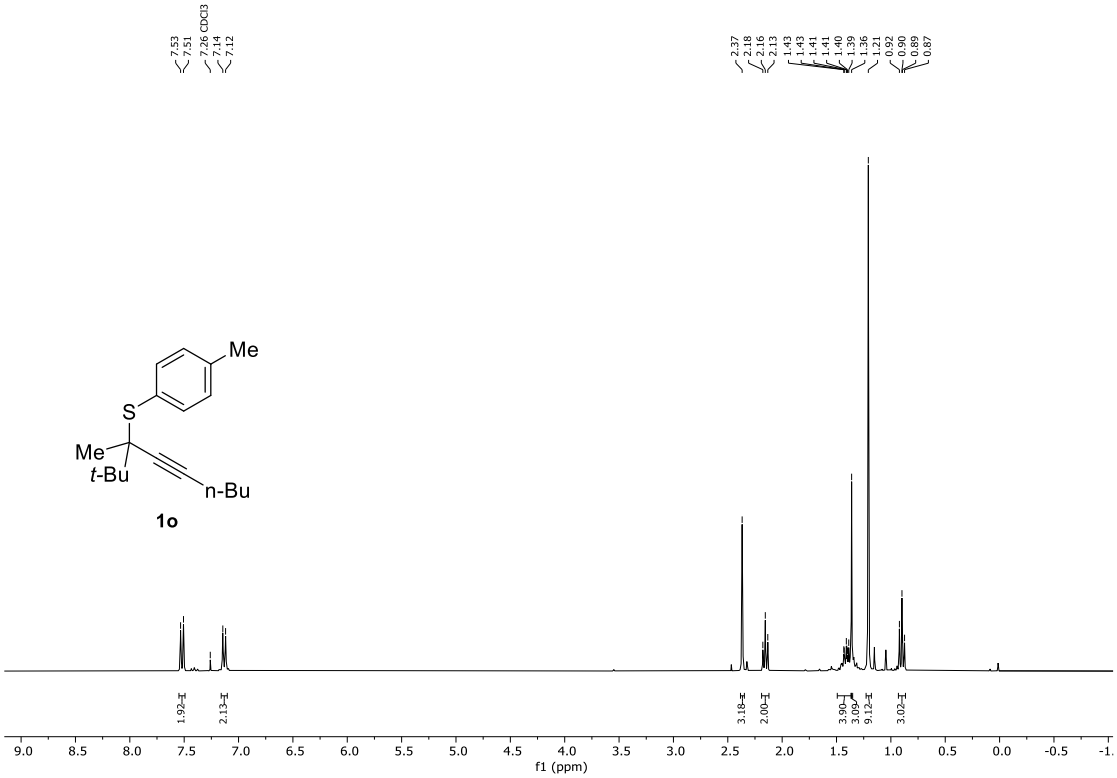


^{1}H-NMR (300 MHz, $CDCl_3$)

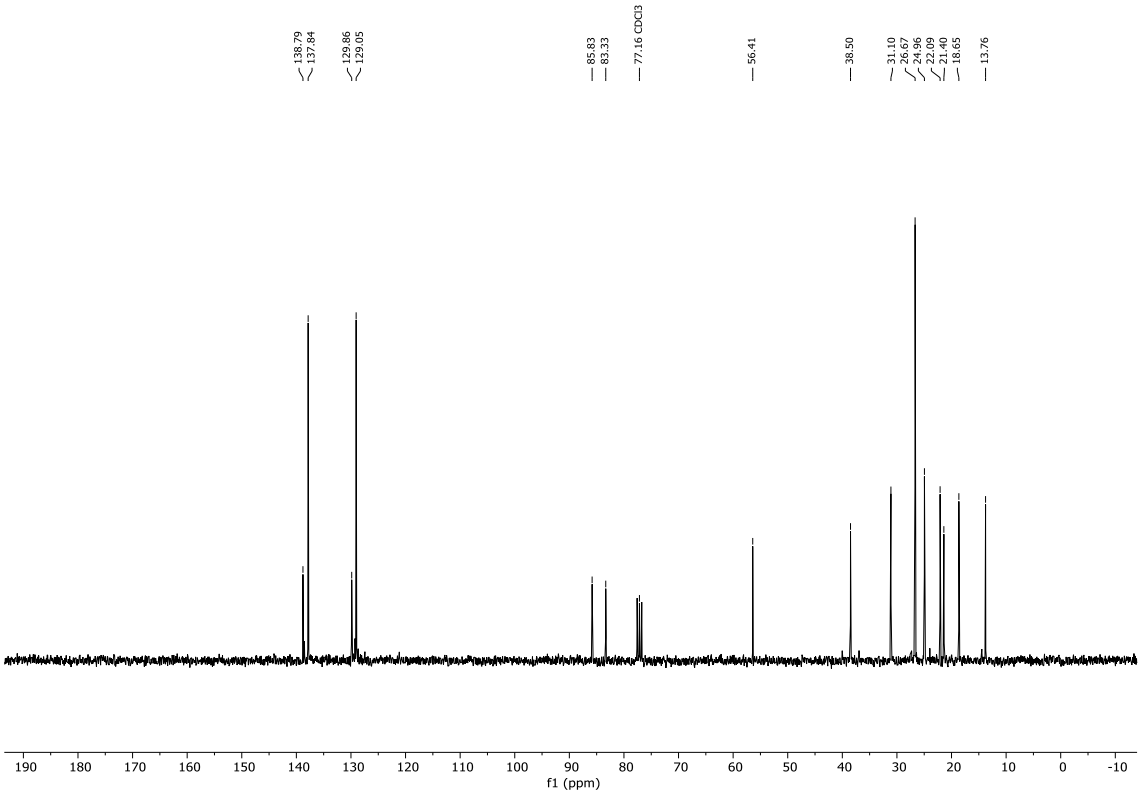


^{13}C-NMR (75 MHz, $CDCl_3$)

(2,2,3-trimethylnon-4-yn-3-yl) (*p*-tolyl)sulfide (1o)

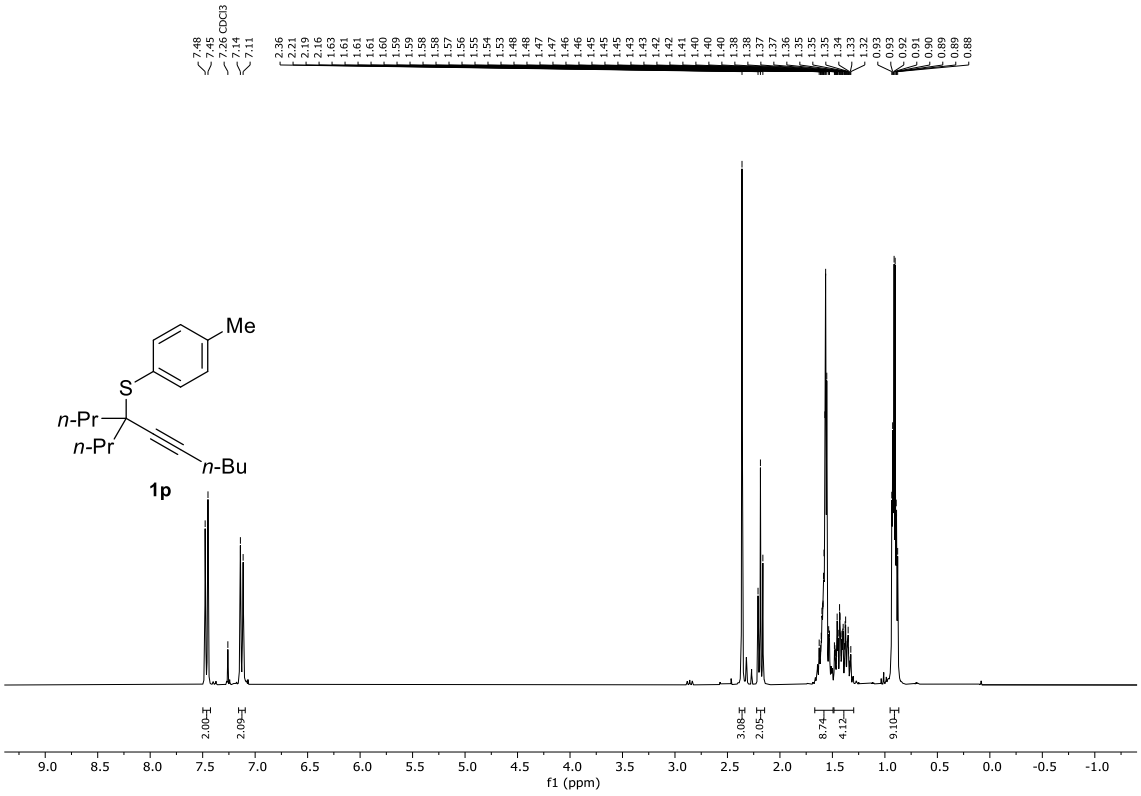


^{1}H-NMR (300 MHz, $CDCl_3$)

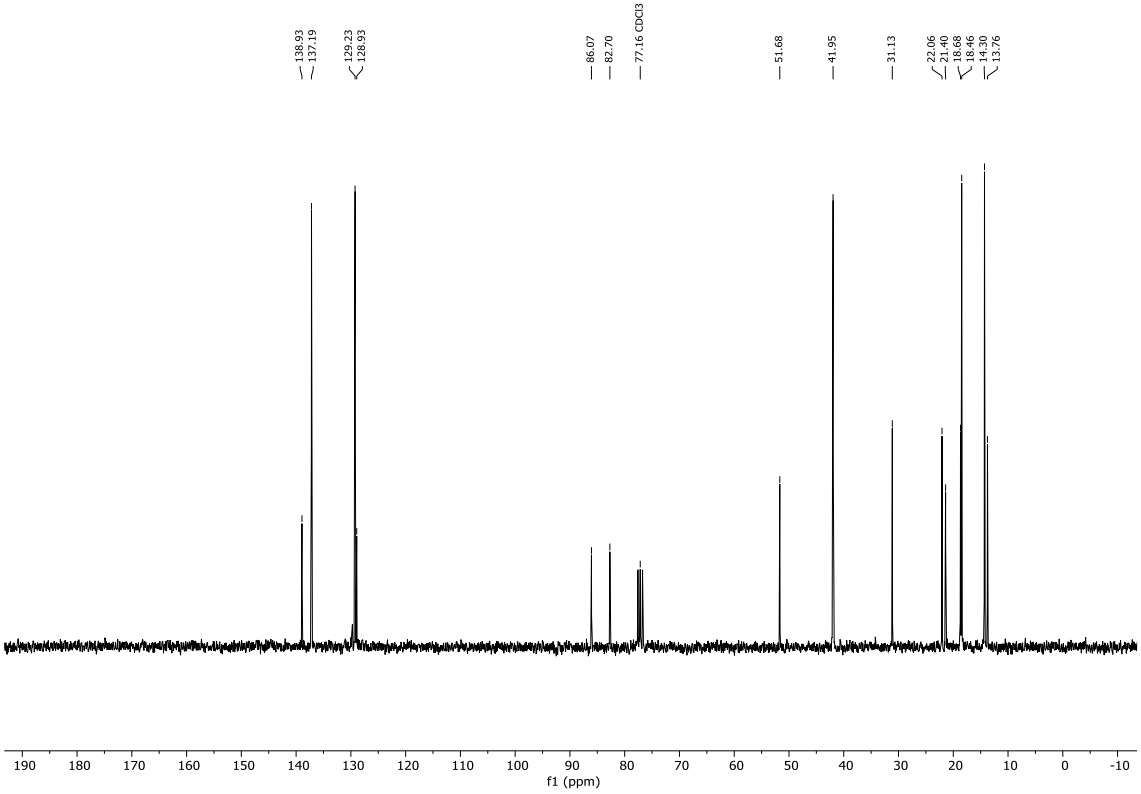


^{13}C-NMR (75 MHz, $CDCl_3$)

(4-propyldec-5-yn-4-yl) (*p*-tolyl)sulfide (1p)

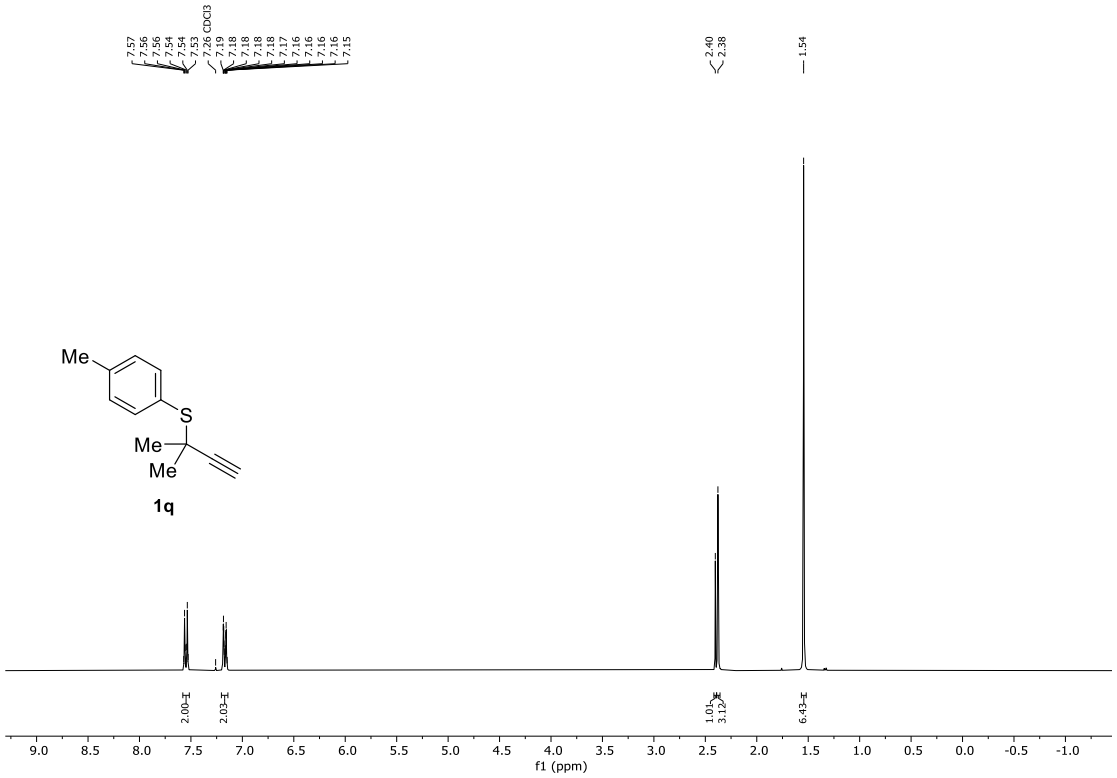


^{1}H-NMR (300 MHz, $CDCl_3$)

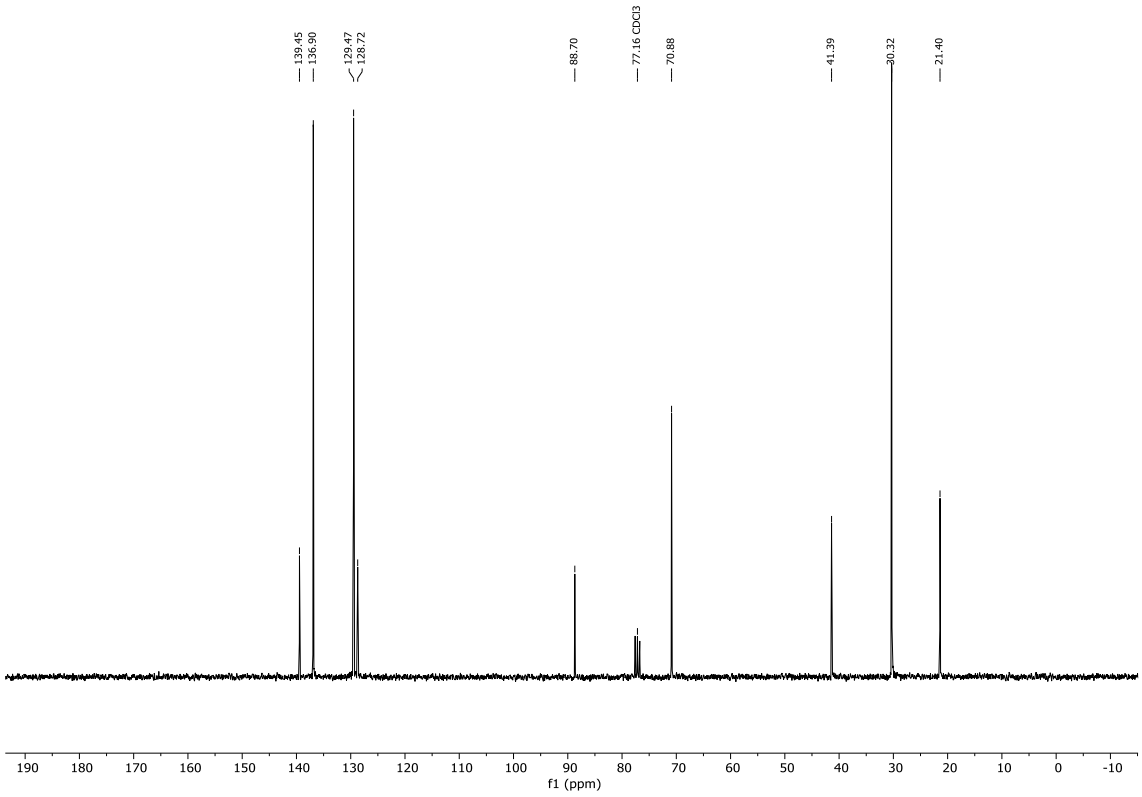


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-methylbut-3-yn-2-yl) (*p*-tolyl)sulfide (1q)

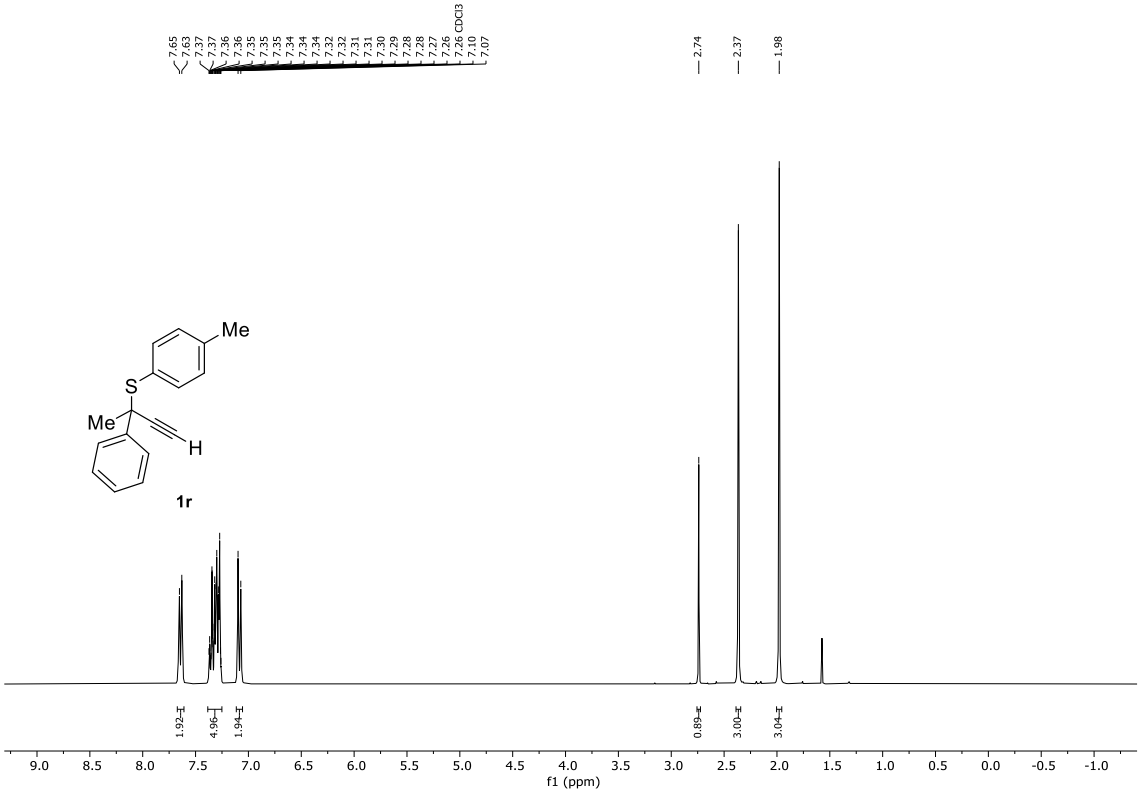


^{1}H-NMR (300 MHz, $CDCl_3$)

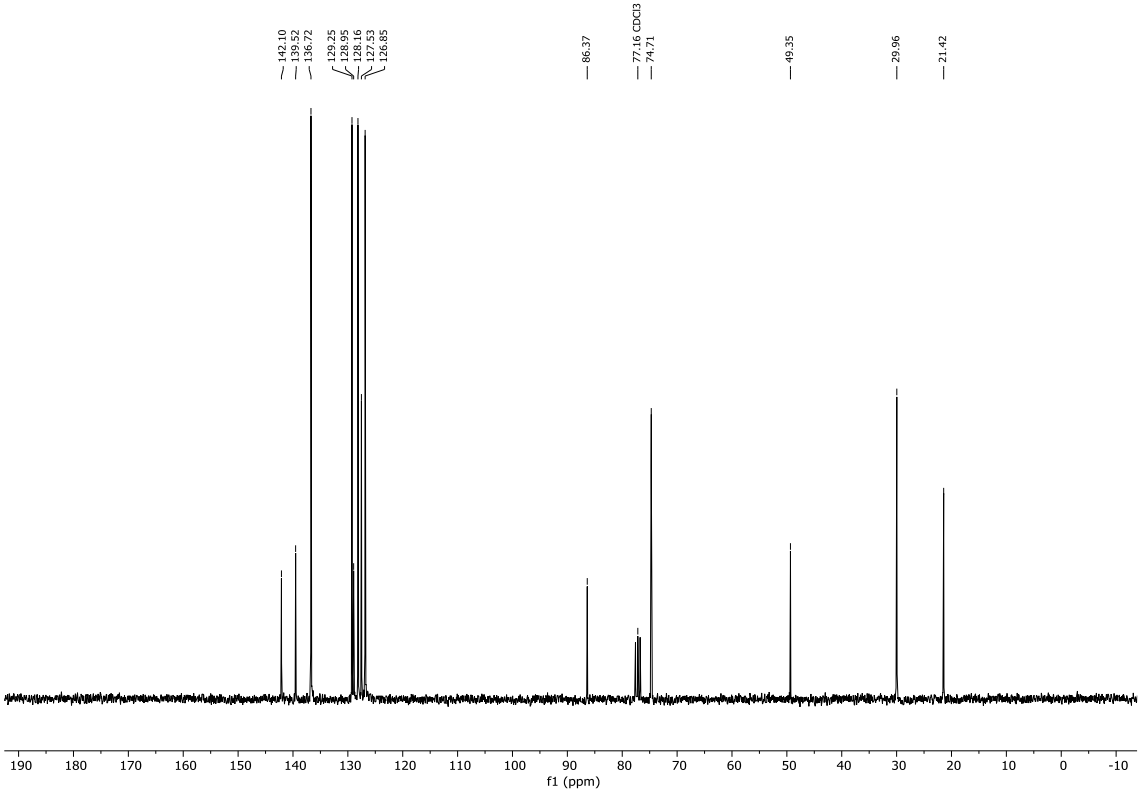


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-phenylbut-3-yn-2-yl) (*p*-tolyl)sulfide (1r)

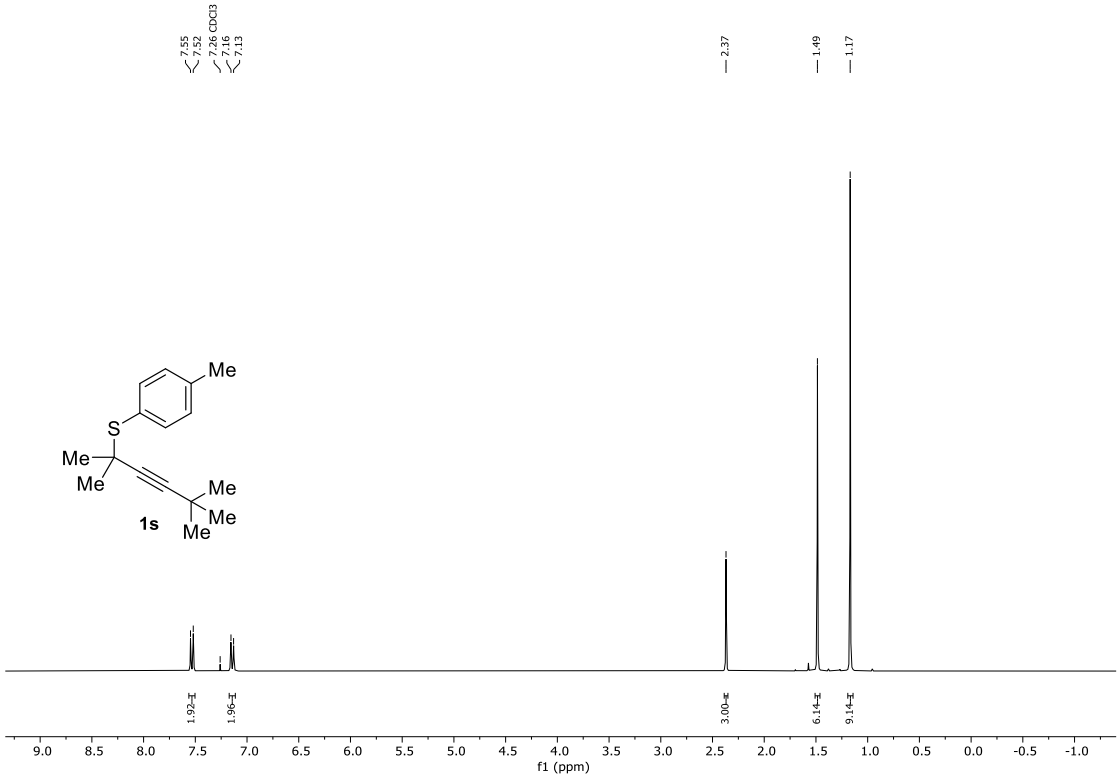


^{1}H-NMR (300 MHz, $CDCl_3$)

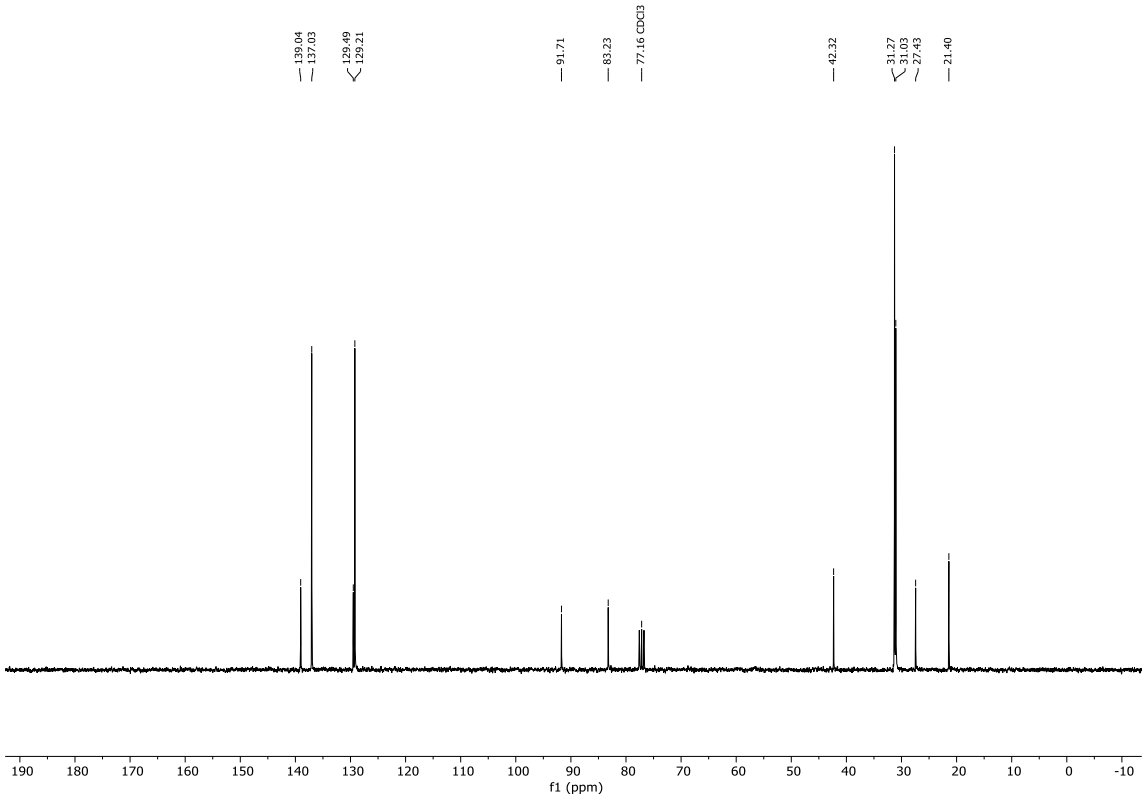


^{13}C-NMR (75 MHz, $CDCl_3$)

***p*-tolyl (2,5,5-trimethylhex-3-yn-2-yl)sulfide (1s)**

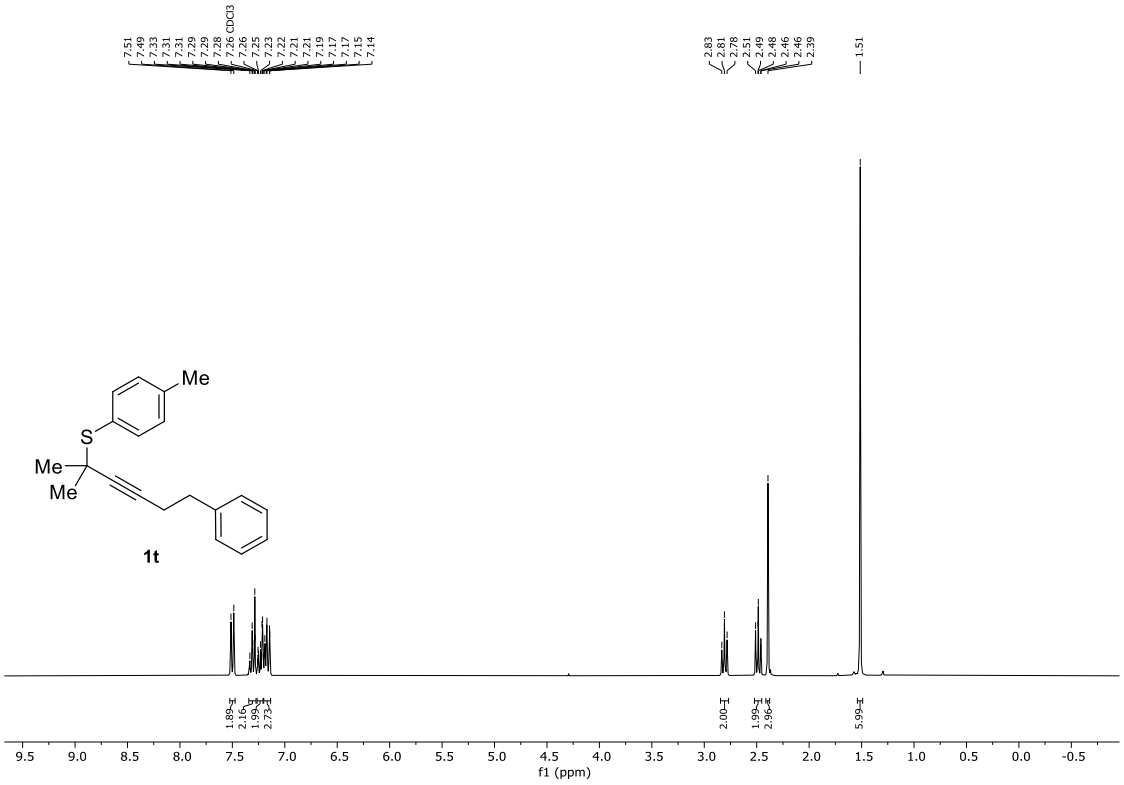


^{1}H-NMR (300 MHz, $CDCl_3$)

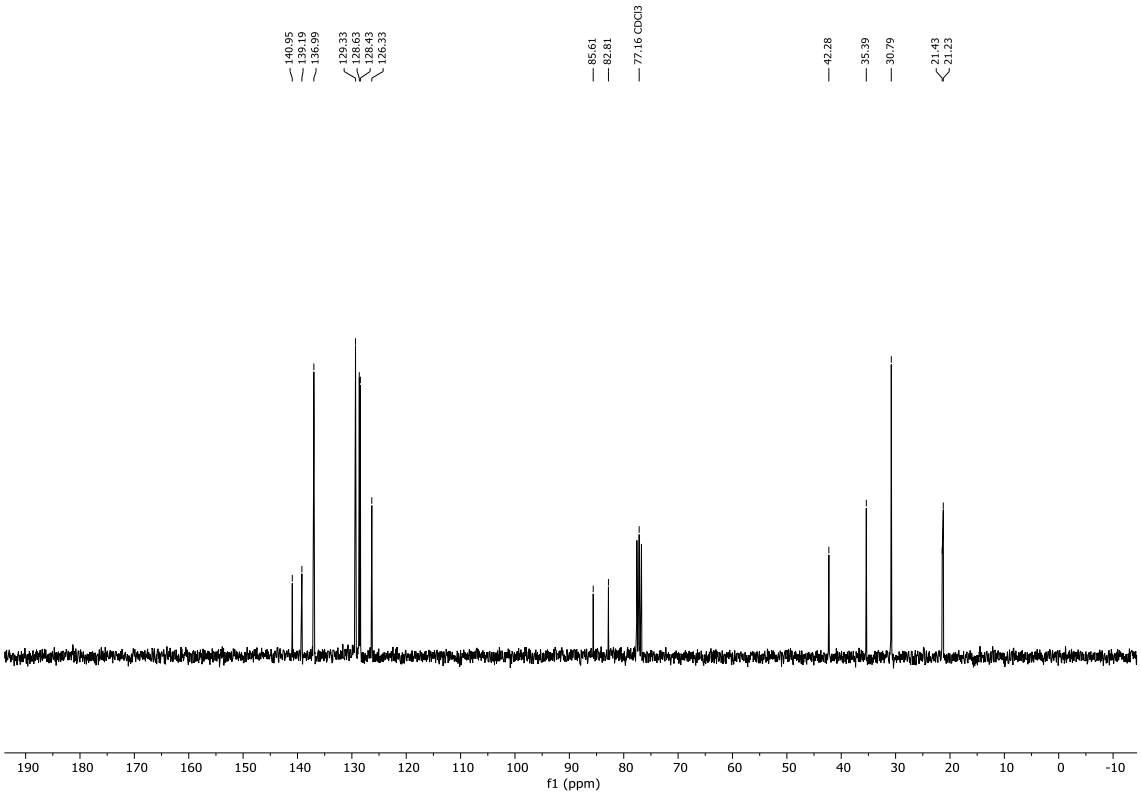


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-methyl-6-phenylhex-3-yn-2-yl) (*p*-tolyl)sulfide (1t)

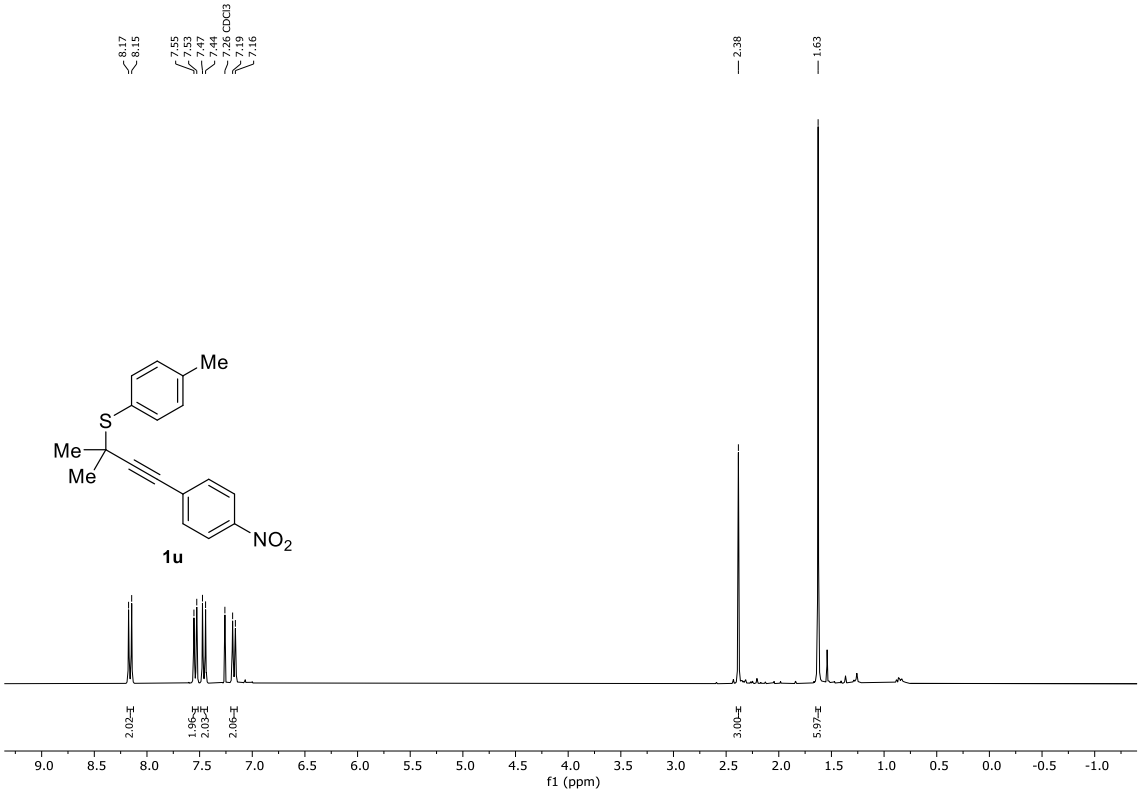


^{1}H-NMR (300 MHz, $CDCl_3$)

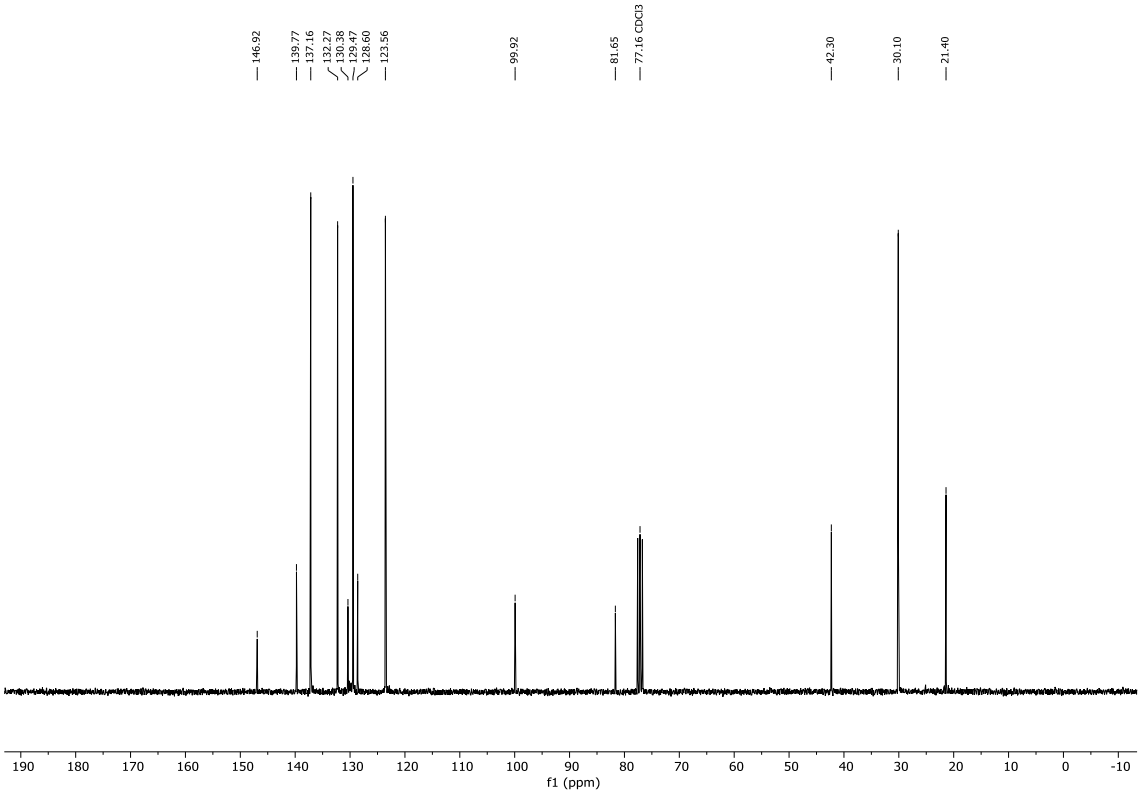


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-methyl-4-(4-nitrophenyl)but-3-yn-2-yl) (*p*-tolyl)sulfide (1u)

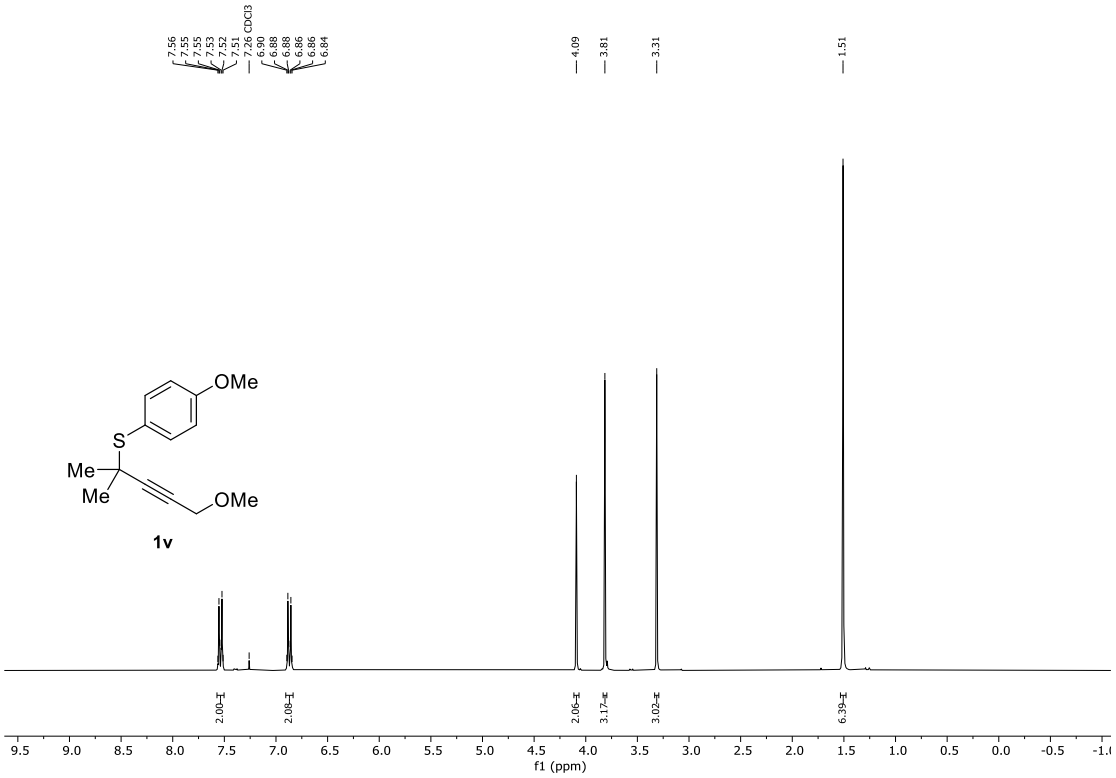


^{1}H-NMR (300 MHz, $CDCl_3$)

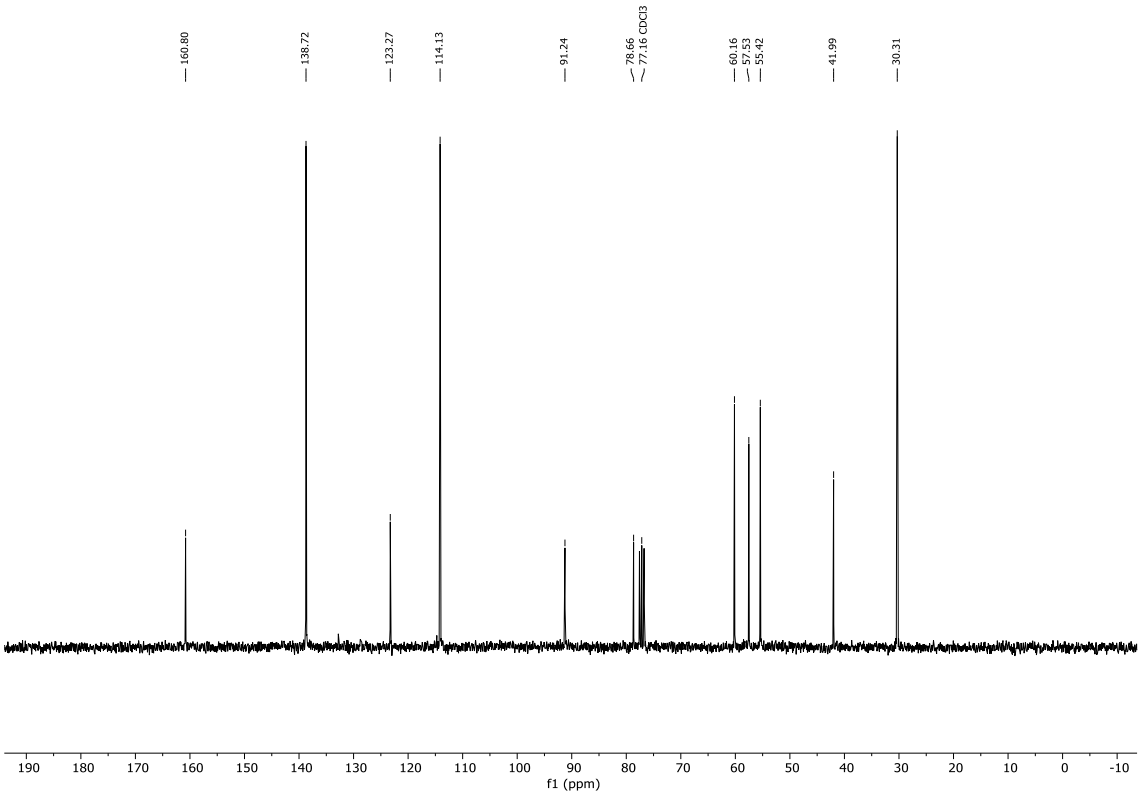


^{13}C-NMR (75 MHz, $CDCl_3$)

(5-methoxy-2-methylpent-3-yn-2-yl) (4-methoxyphenyl)sulfide (1v)

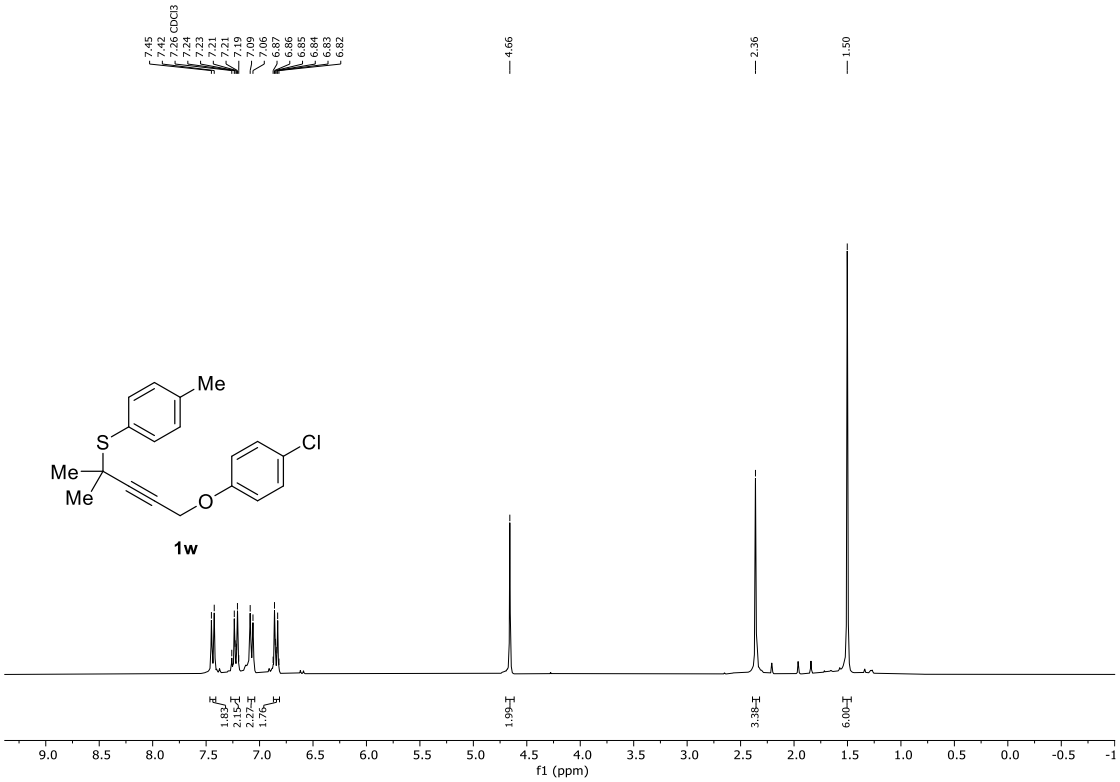


^{1}H-NMR (300 MHz, $CDCl_3$)

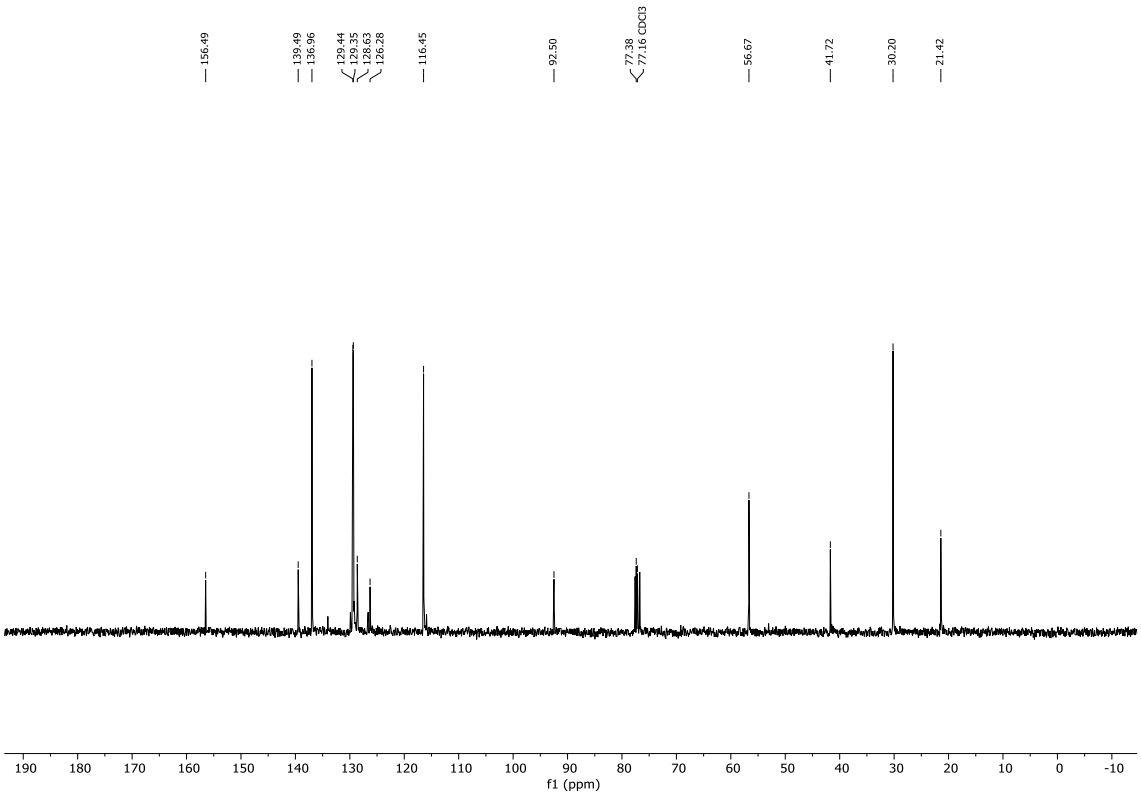


^{13}C-NMR (75 MHz, $CDCl_3$)

(5-(4-chlorophenoxy)-2-methylpent-3-yn-2-yl) (*p*-tolyl)sulfide (1w)

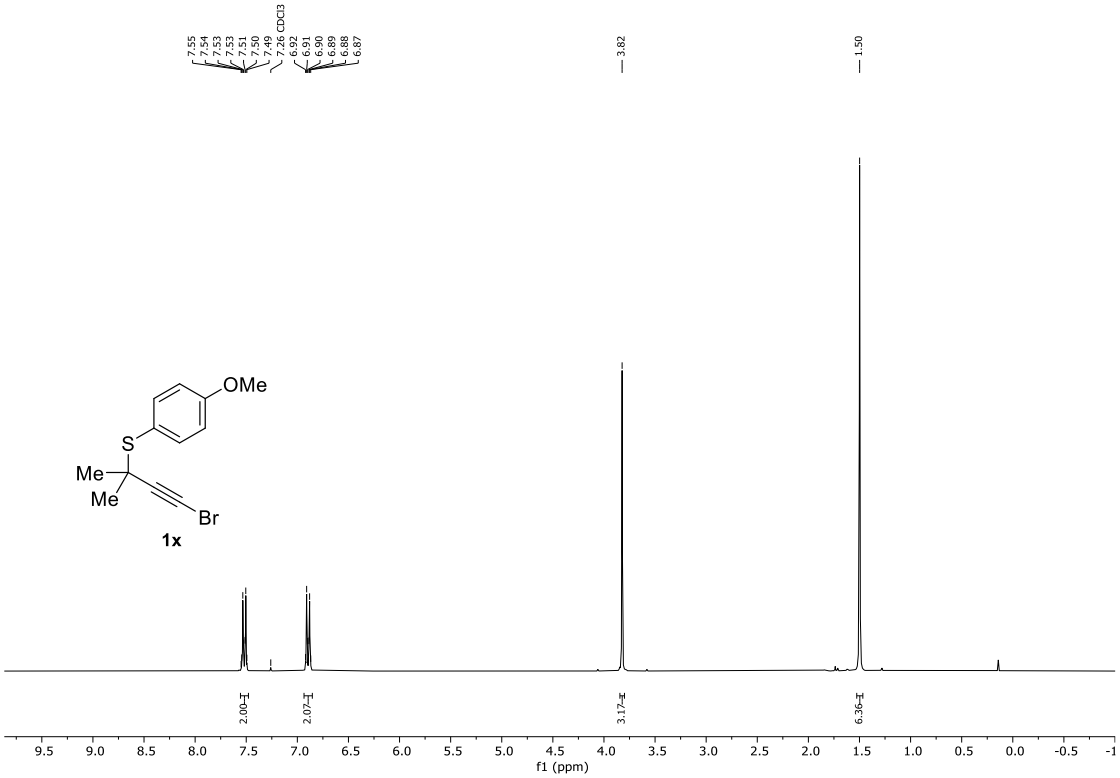


^{1}H-NMR (300 MHz, $CDCl_3$)

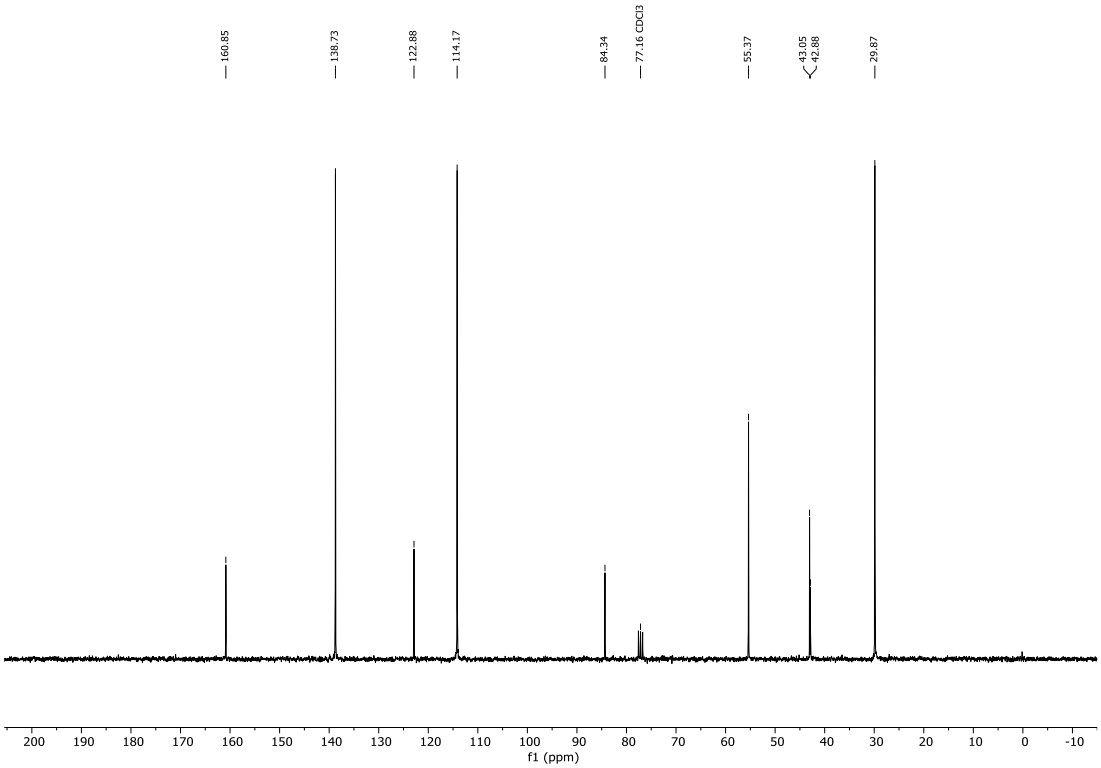


^{13}C-NMR (75 MHz, $CDCl_3$)

(4-bromo-2-methylbut-3-yn-2-yl) (4-methoxyphenyl)sulfide (1x)

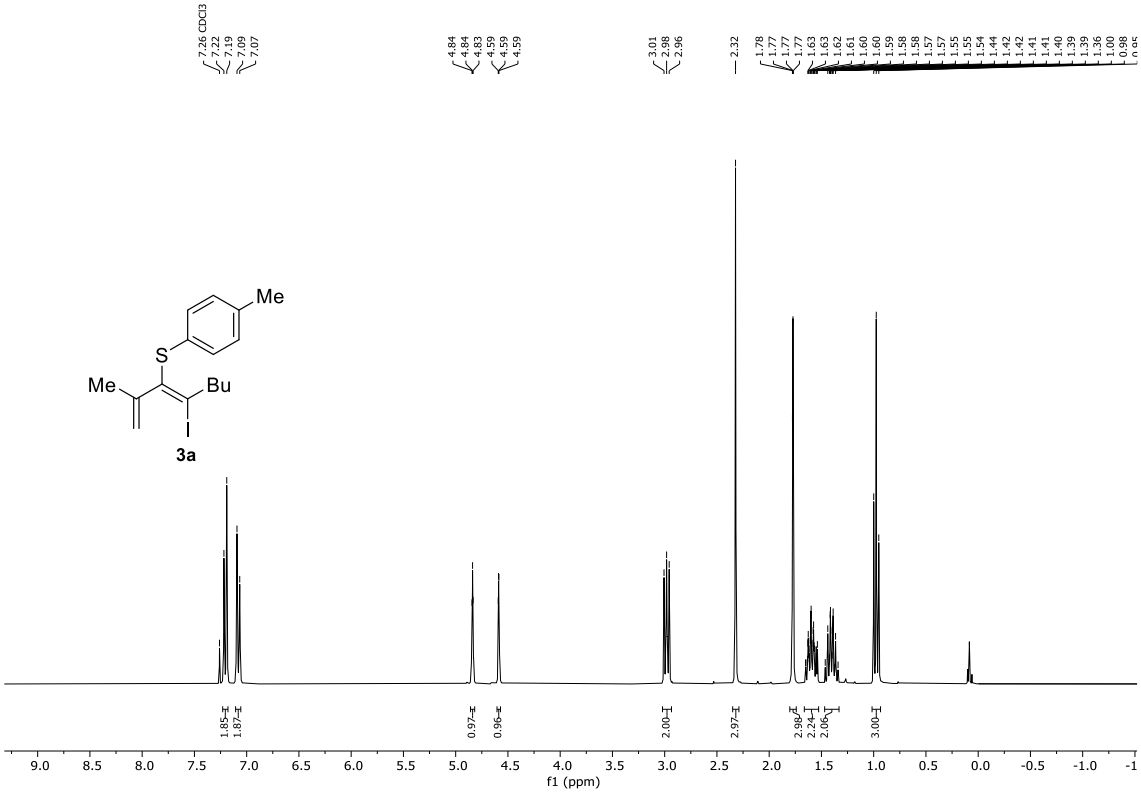


^{1}H-NMR (300 MHz, $CDCl_3$)

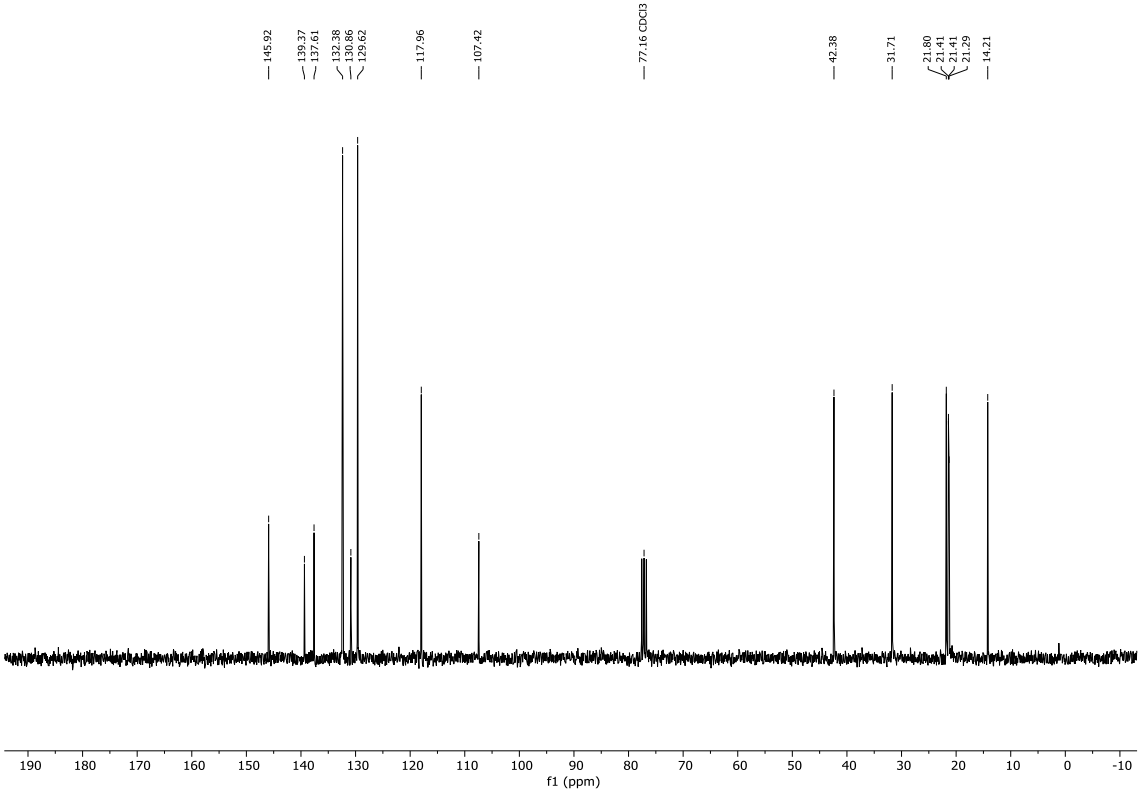


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide (3a)

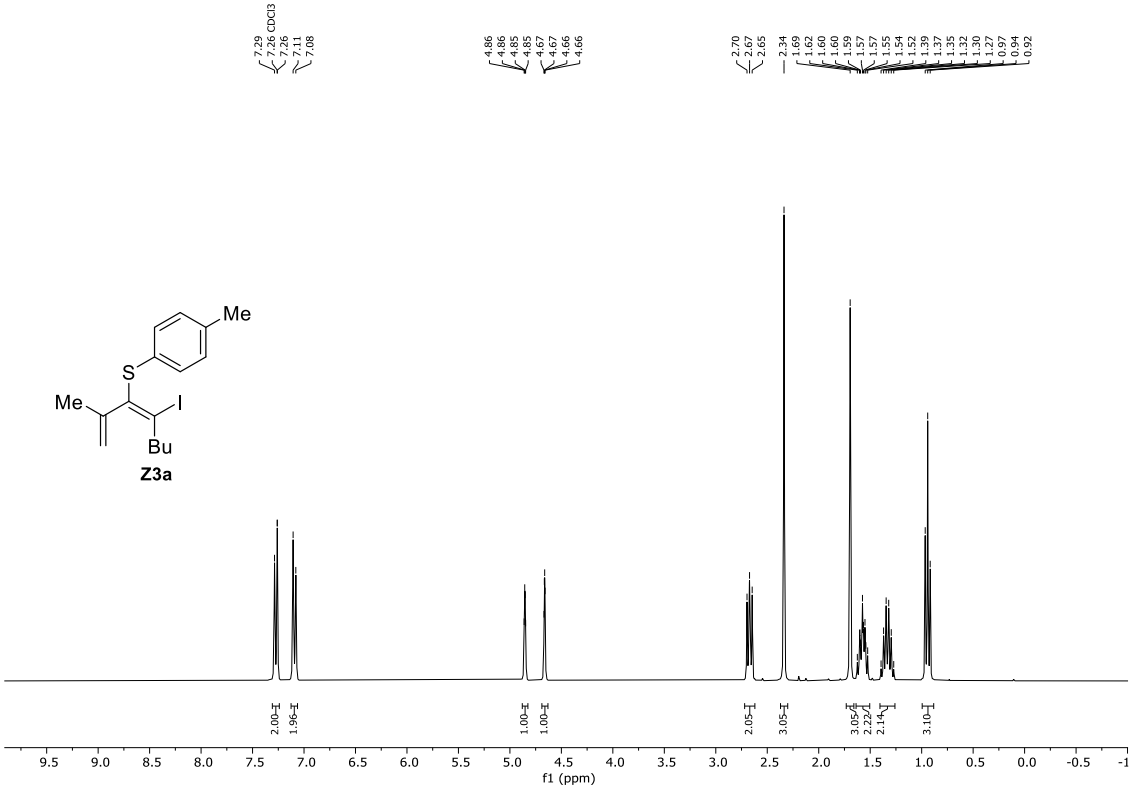


^{1}H-NMR (300 MHz, $CDCl_3$)

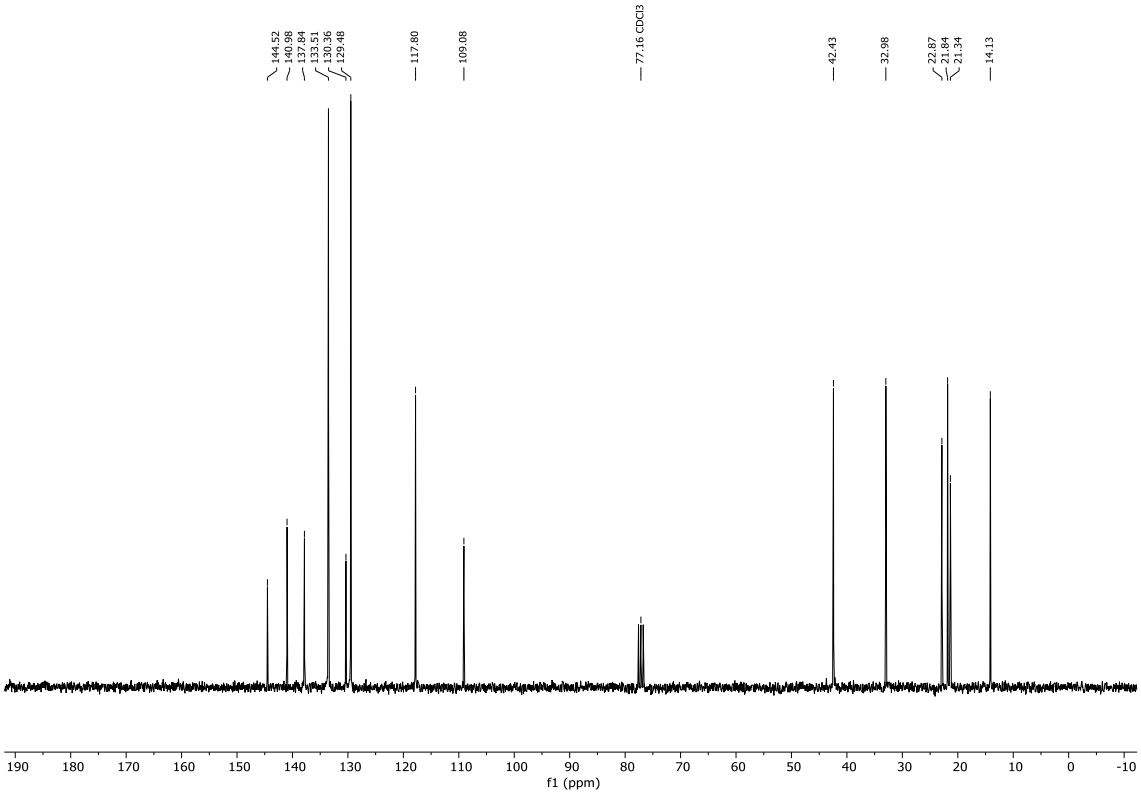


^{13}C-NMR (75 MHz, $CDCl_3$)

(*Z*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide (*Z*-3a)

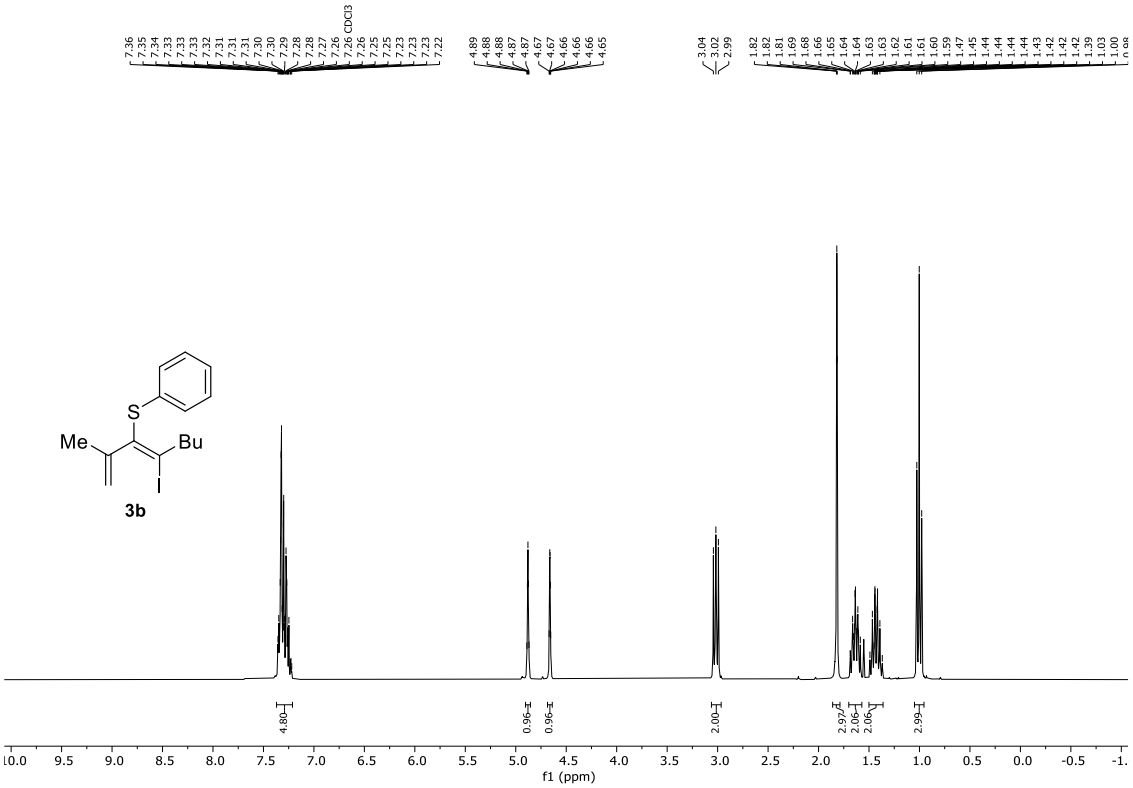


^{1}H-NMR (300 MHz, $CDCl_3$)

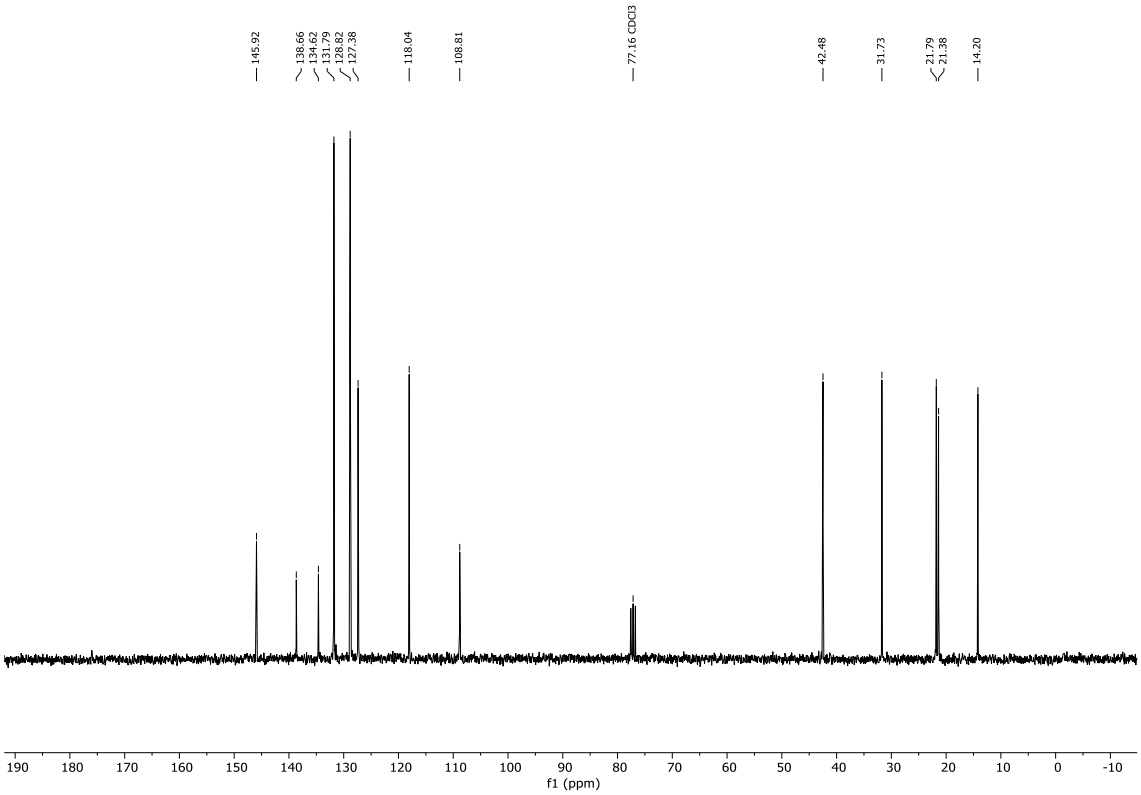


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (phenyl)sulfide (3b)

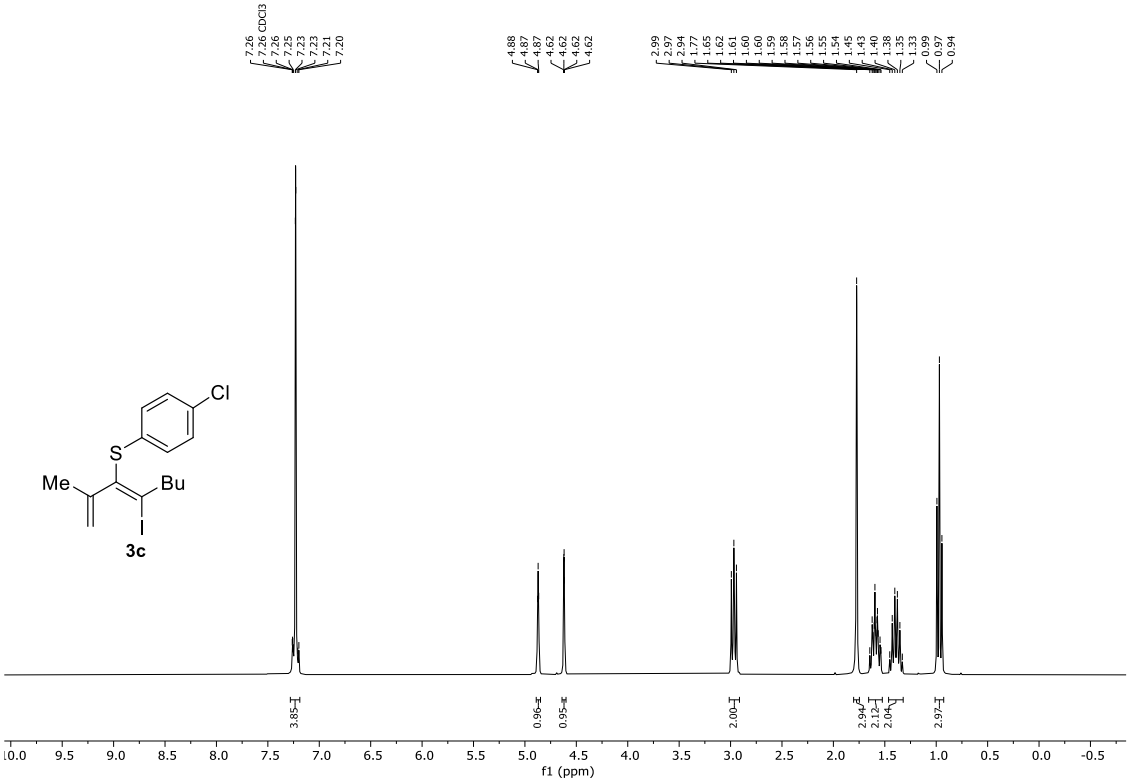


^{1}H-NMR (300 MHz, $CDCl_3$)

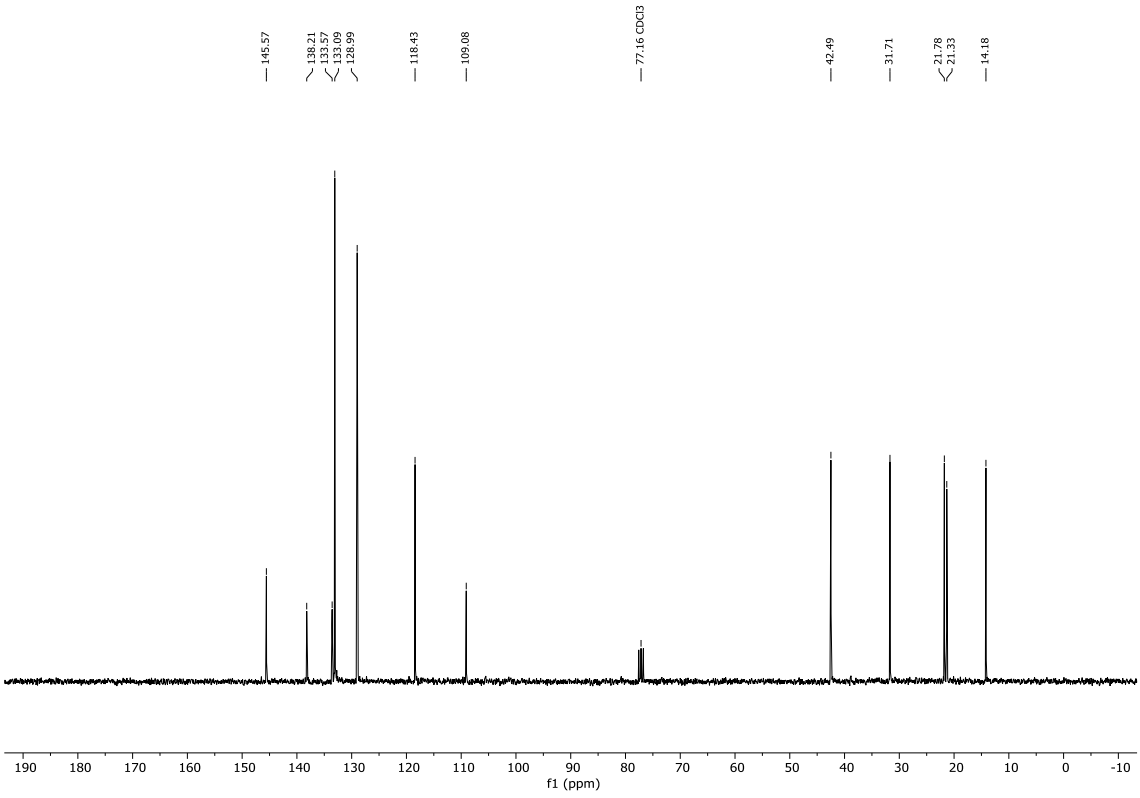


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-chlorophenyl) (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3c)

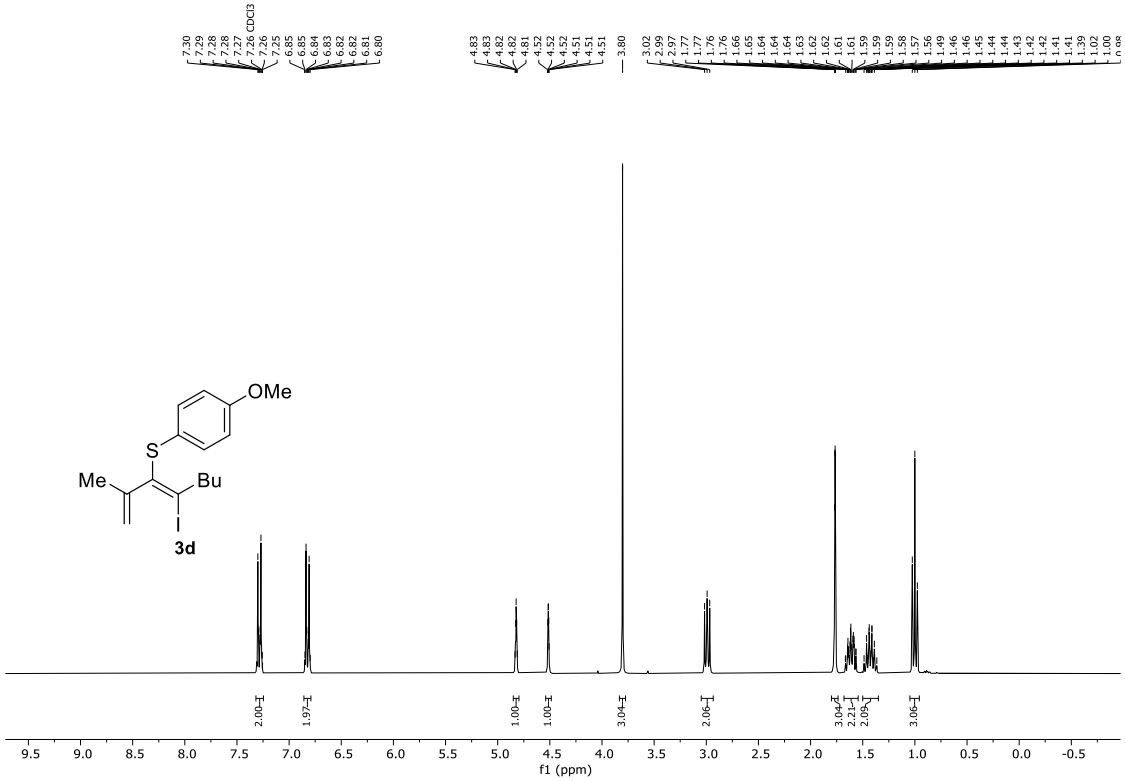


^{1}H-NMR (300 MHz, $CDCl_3$)

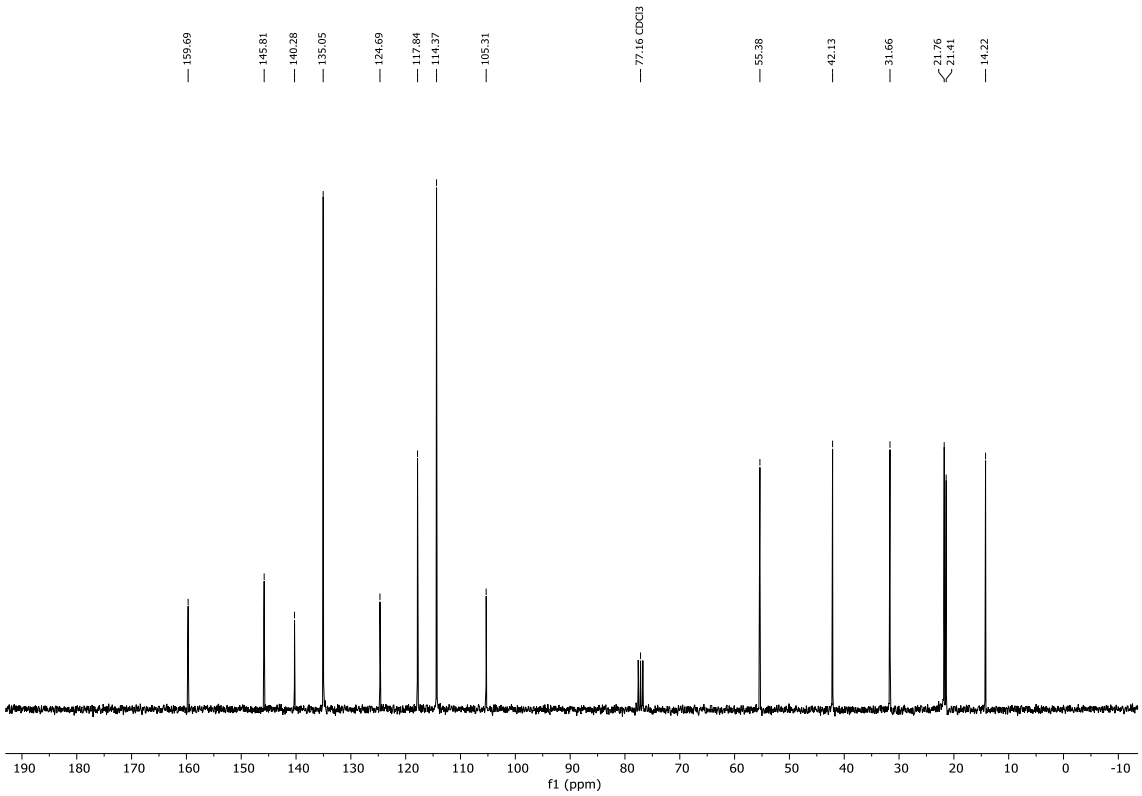


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (4-methoxyphenyl)sulfide (3d)

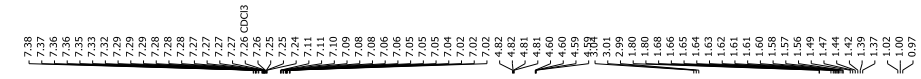


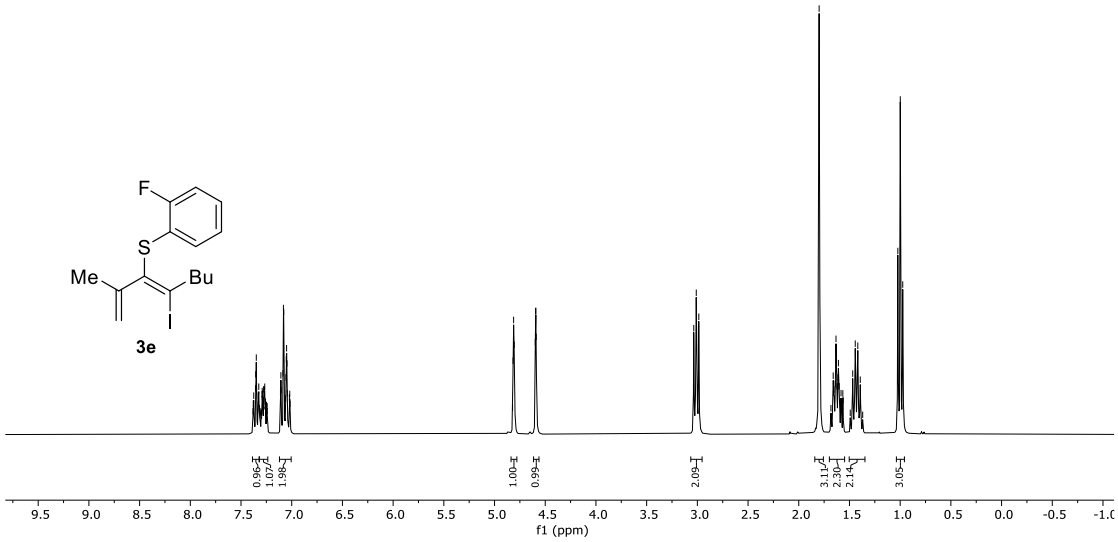
^{1}H-NMR (300 MHz, $CDCl_3$)



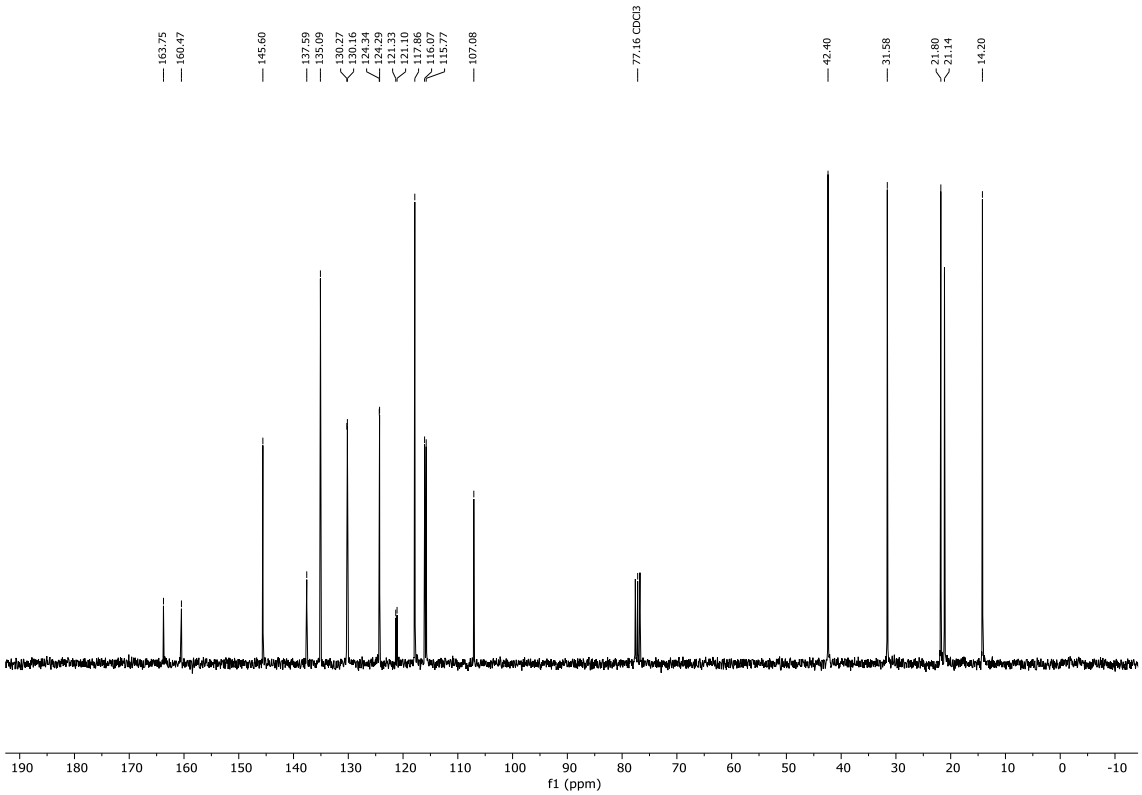
^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(2-fluorophenyl) (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3e)



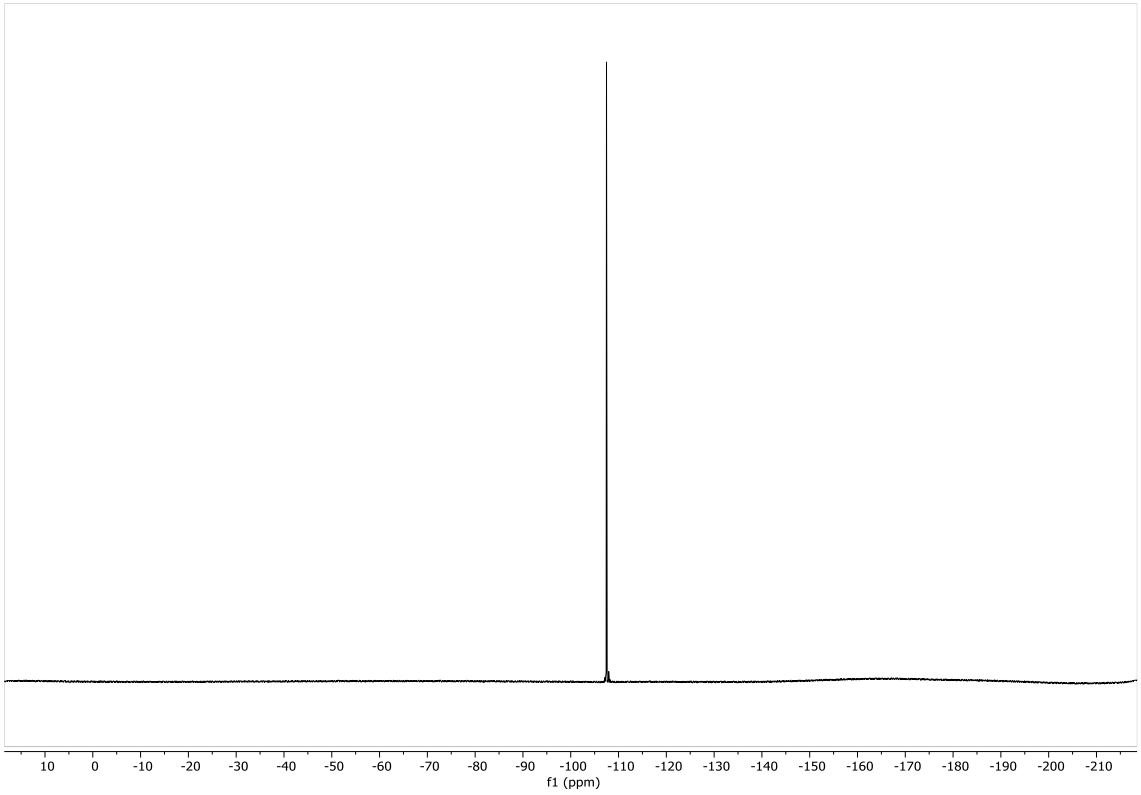


^{1}H-NMR (300 MHz, $CDCl_3$)



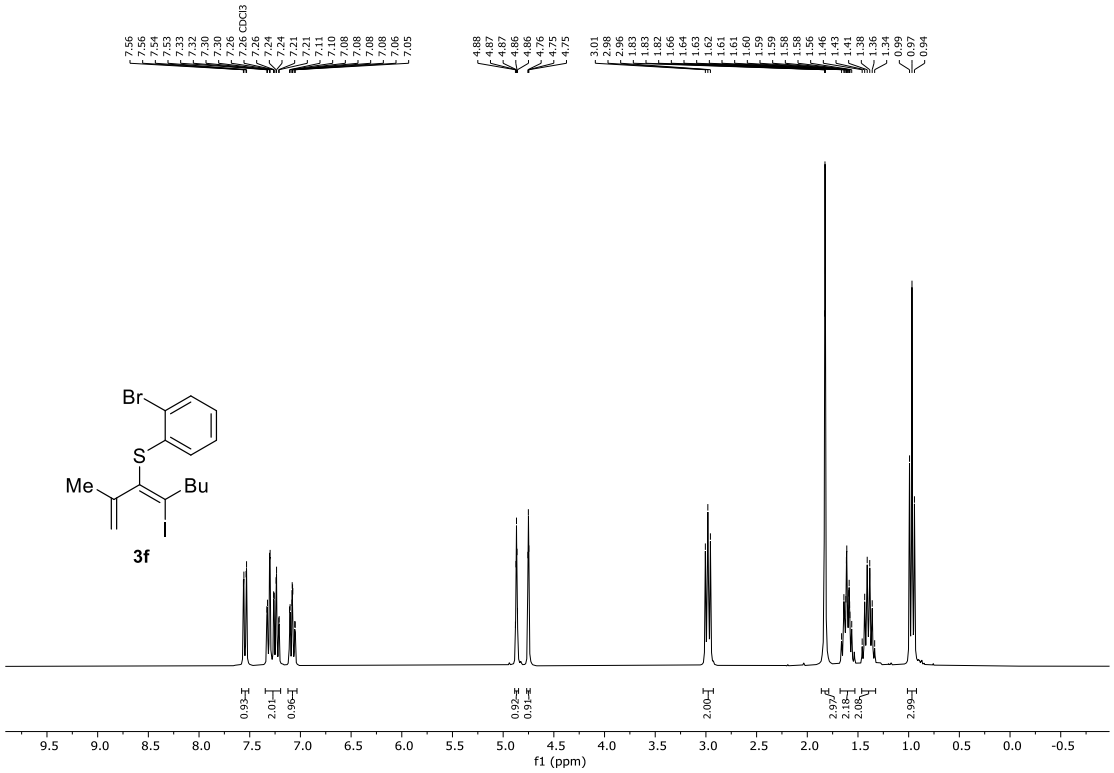
^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(2-fluorophenyl) (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3e)

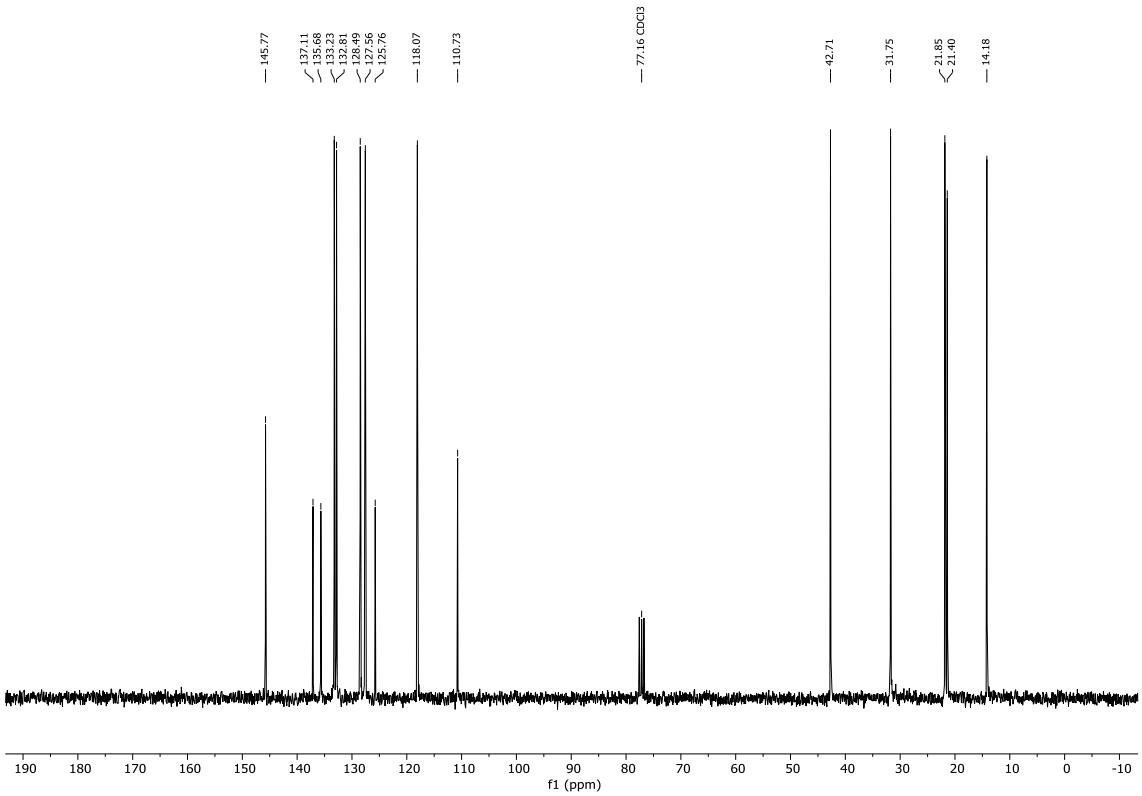


^{19}F-NMR (282 MHz, $CDCl_3$)

(*E*)-(2-bromophenyl) (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3f)

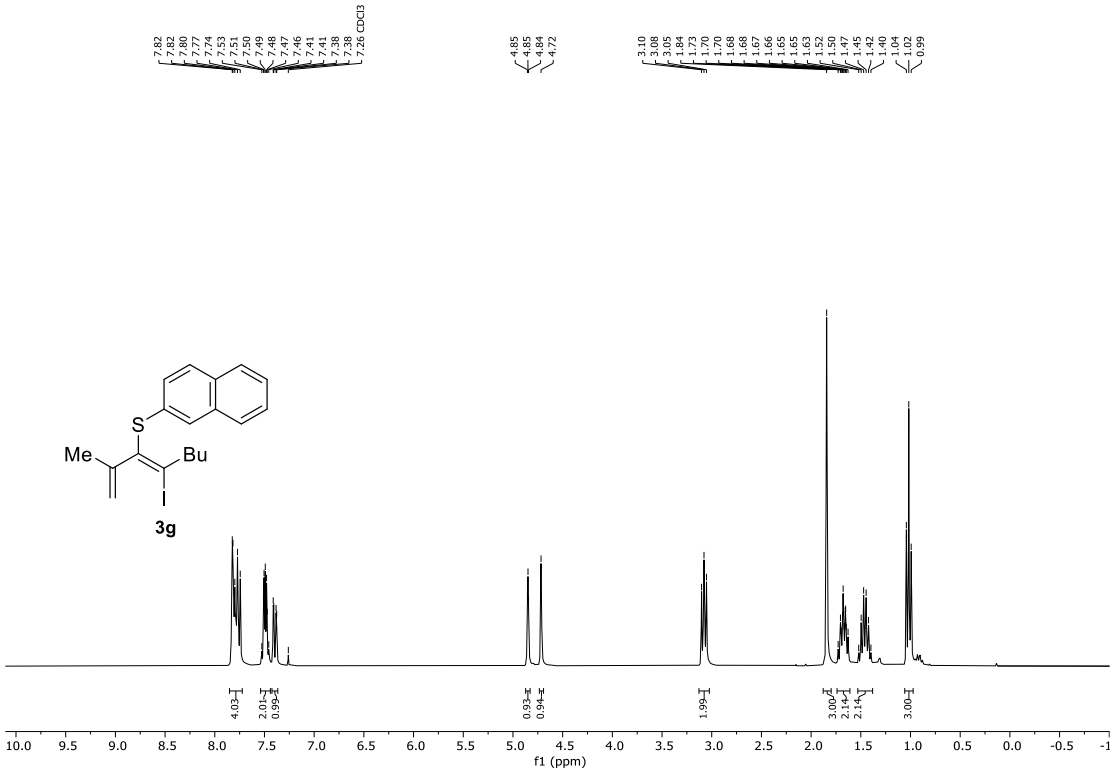


^{1}H-NMR (300 MHz, $CDCl_3$)

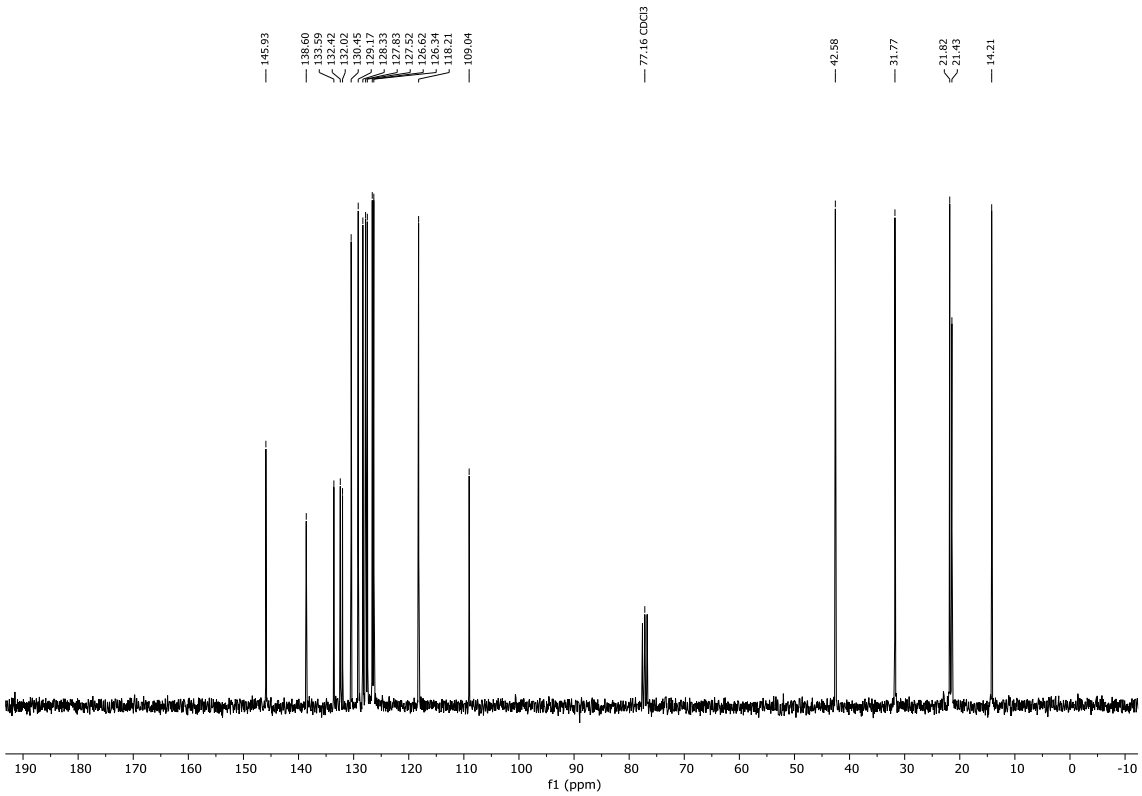


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-iodo-2-methylocta-1,3-dien-3-yl) (naphthalen-2-yl)sulfide (3g)

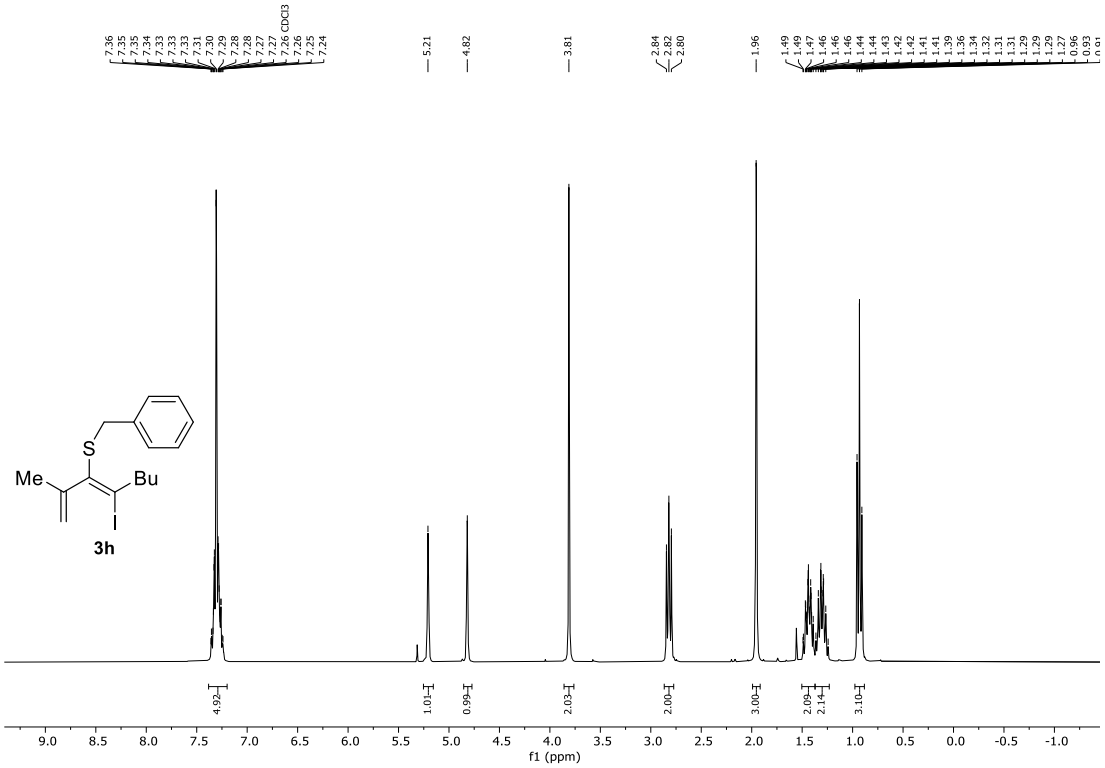


^{1}H-NMR (300 MHz, $CDCl_3$)

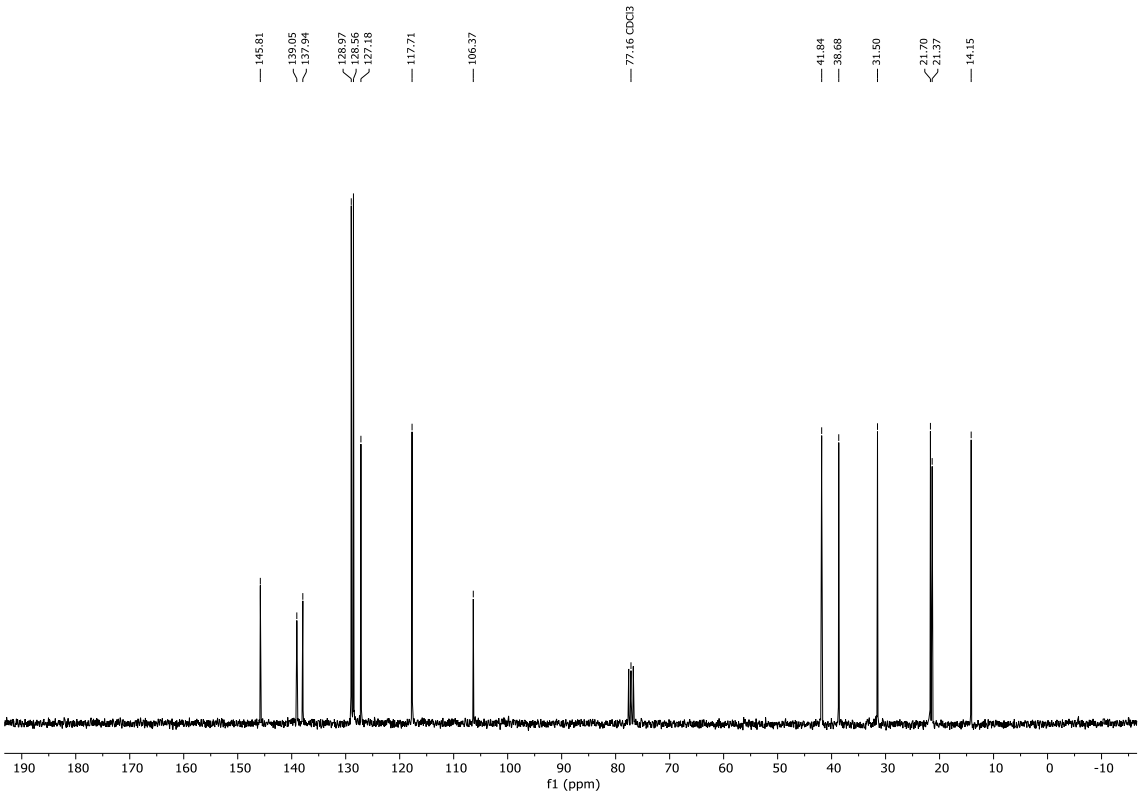


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-benzyl (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3h)

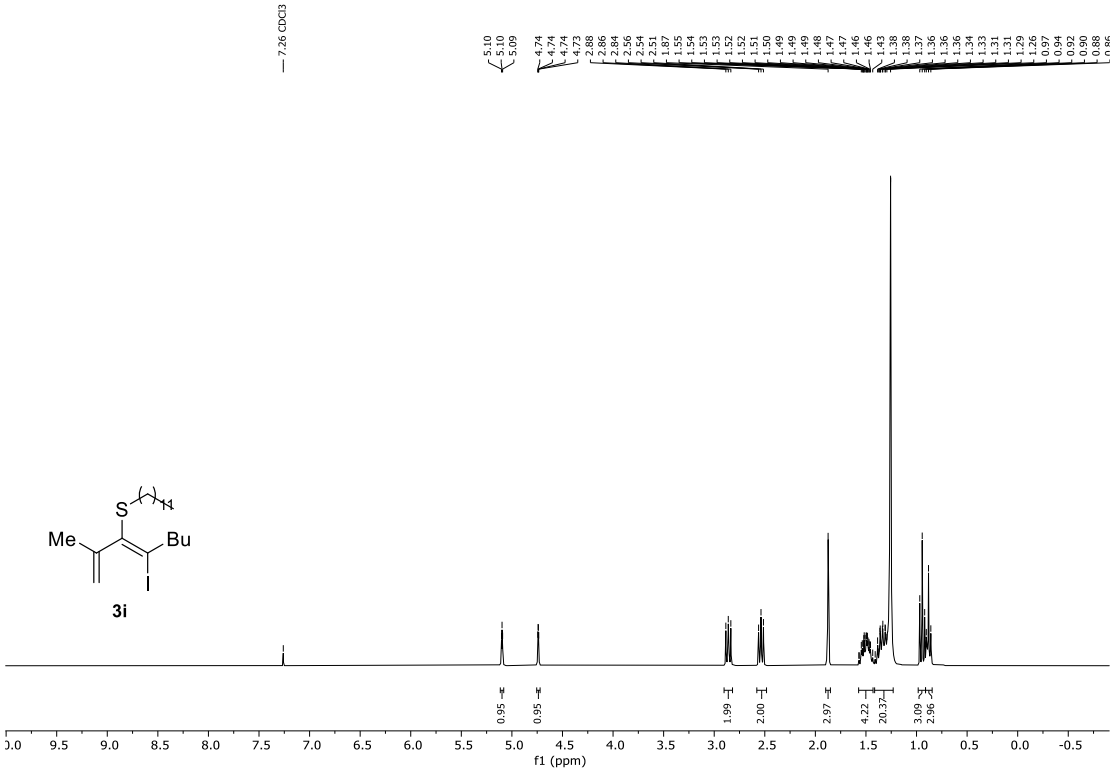


^{1}H-NMR (300 MHz, $CDCl_3$)

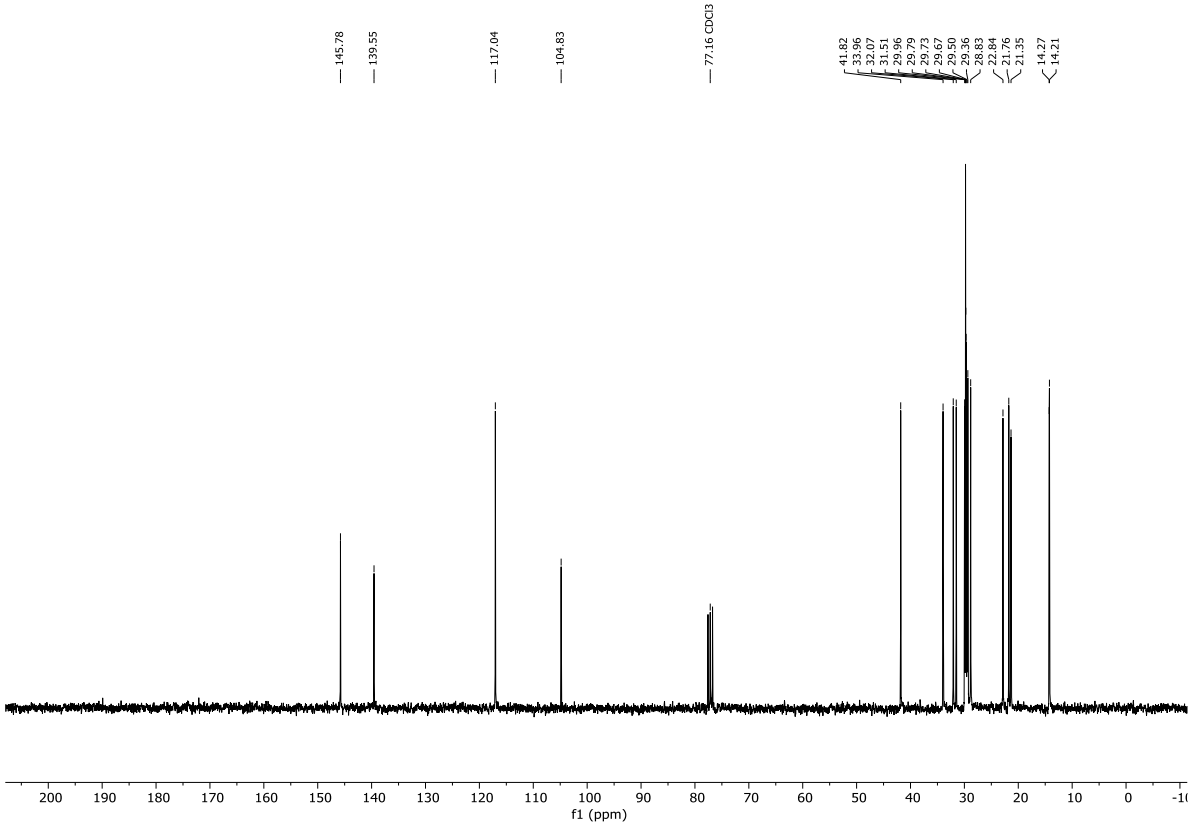


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-dodecyl (4-iodo-2-methylocta-1,3-dien-3-yl)sulfide (3i)

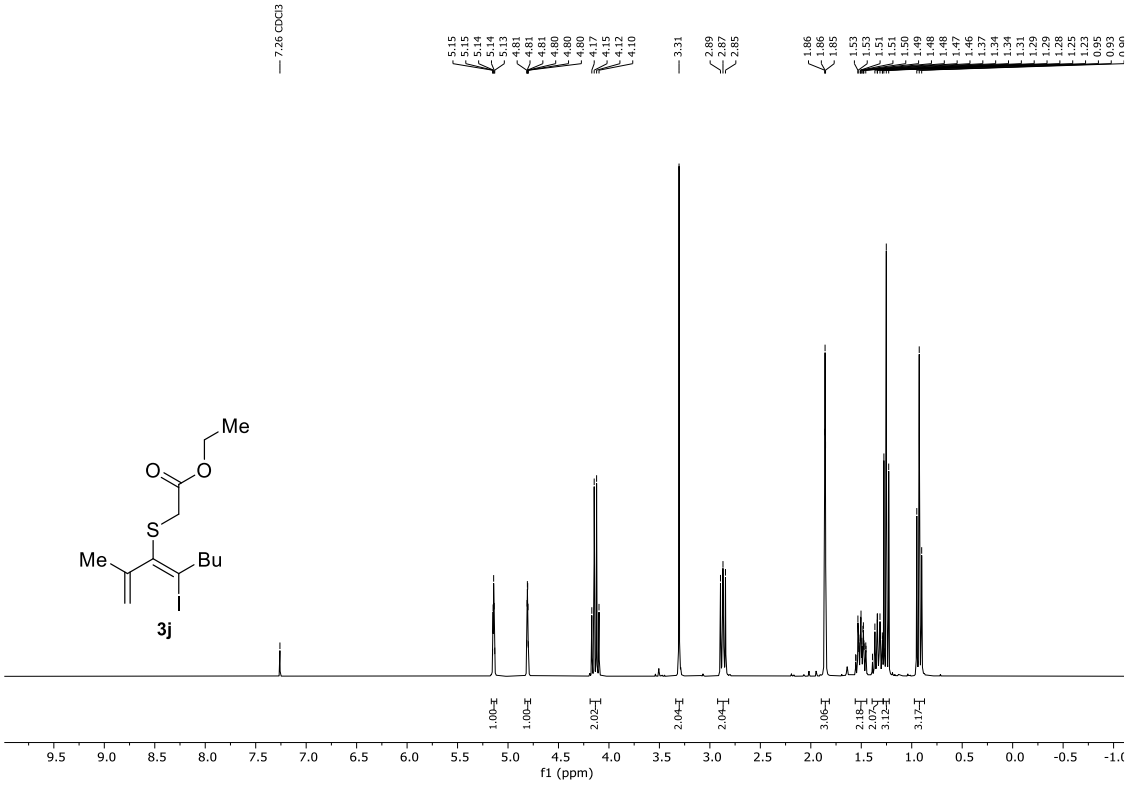


^{1}H-NMR (300 MHz, $CDCl_3$)

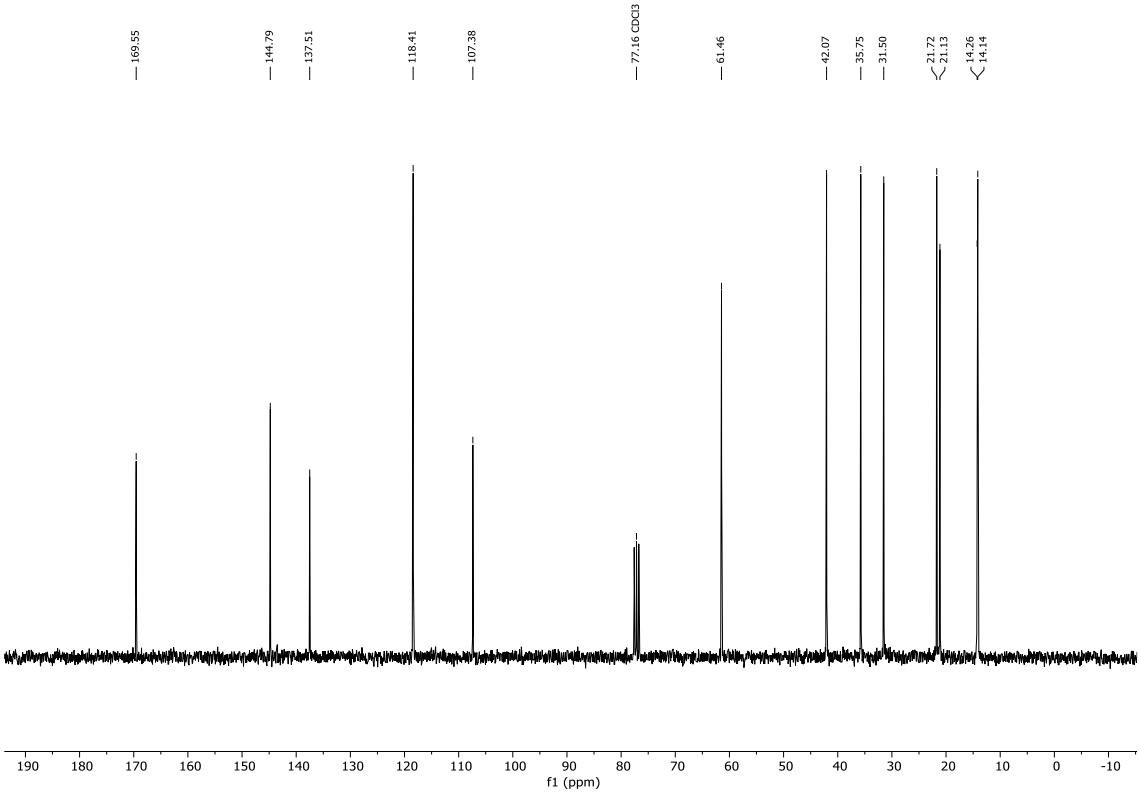


^{13}C-NMR (75 MHz, $CDCl_3$)

Ethyl (*E*)-2-((4-iodo-2-methylocta-1,3-dien-3-yl)thio)acetate (3j)

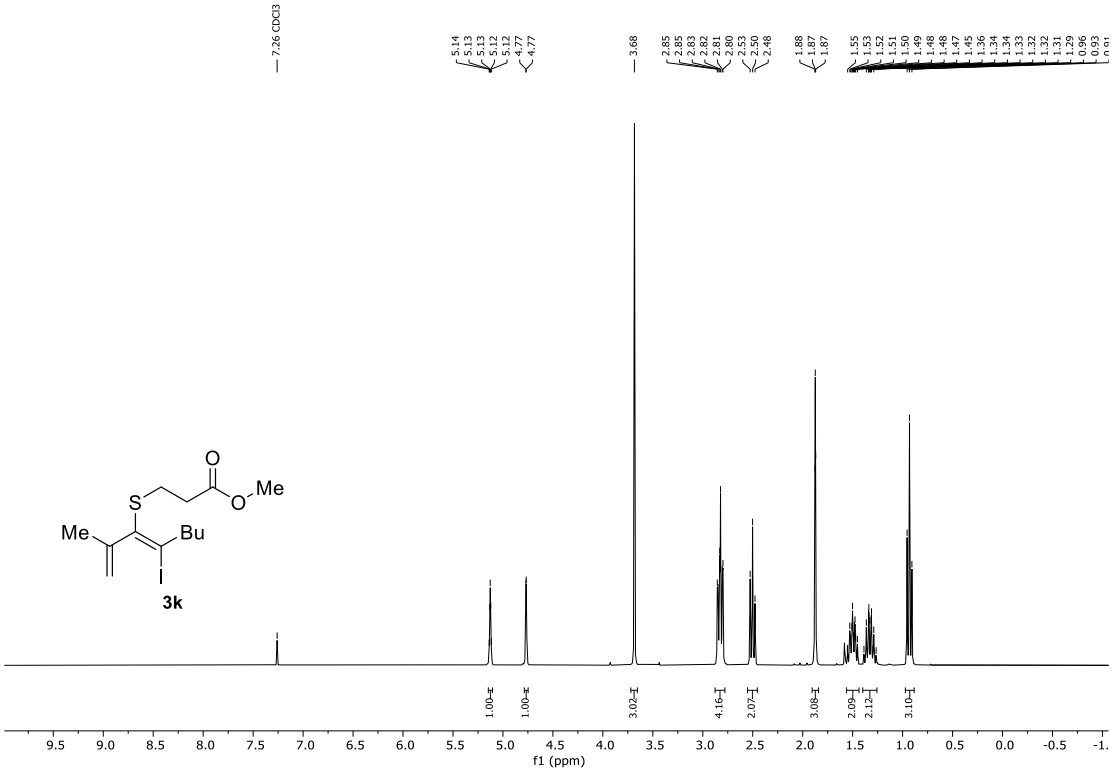


^{1}H-NMR (300 MHz, $CDCl_3$)

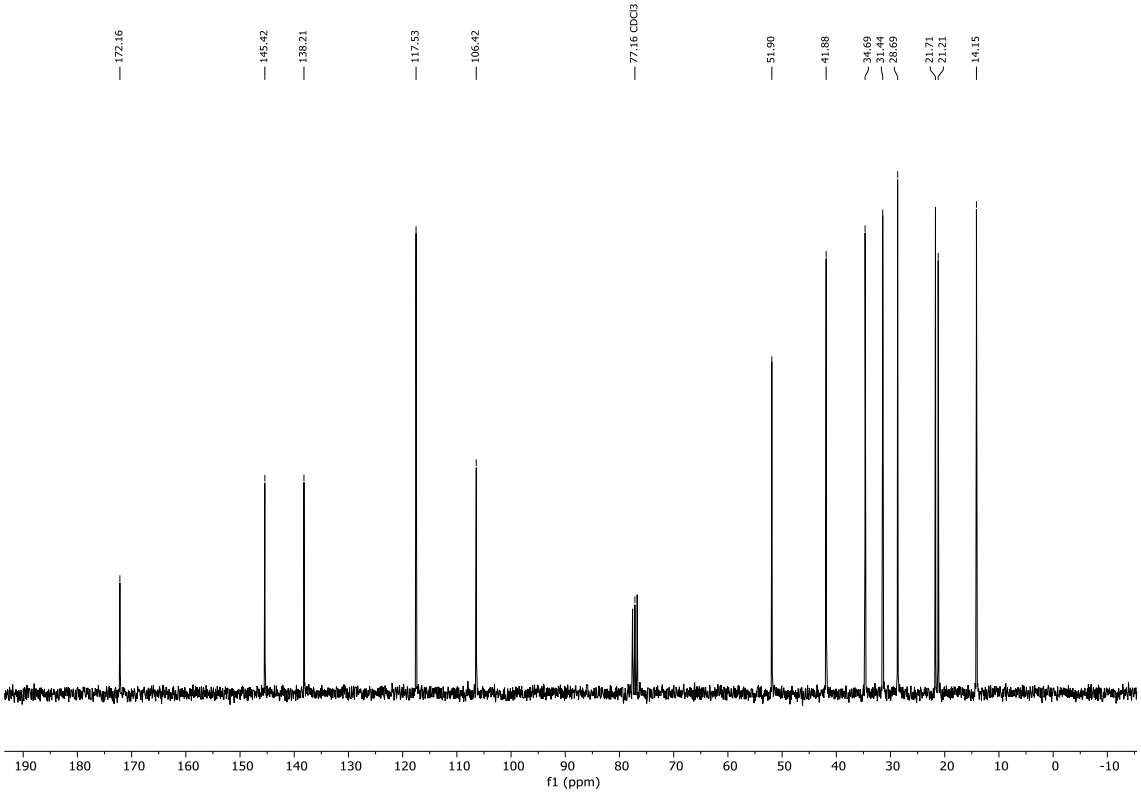


^{13}C-NMR (75 MHz, $CDCl_3$)

Methyl (*E*)-3-((4-iodo-2-methylocta-1,3-dien-3-yl)thio)propanoate (3k)

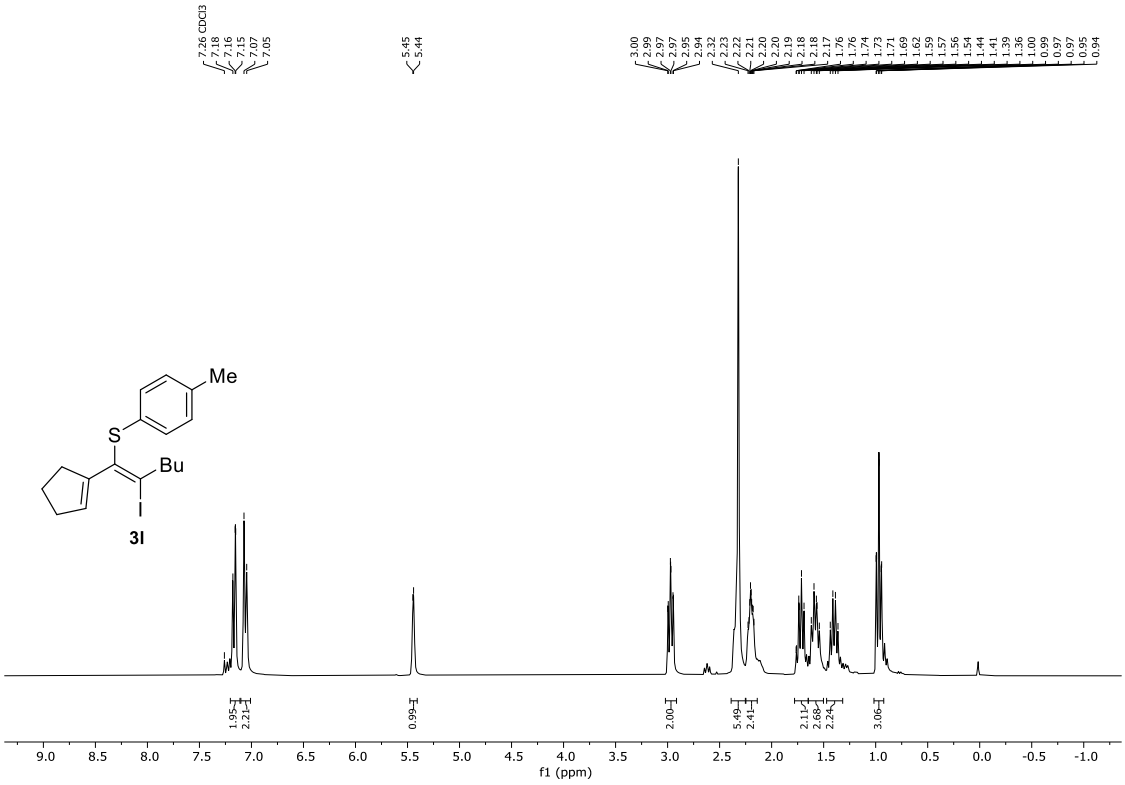


^{1}H-NMR (300 MHz, $CDCl_3$)

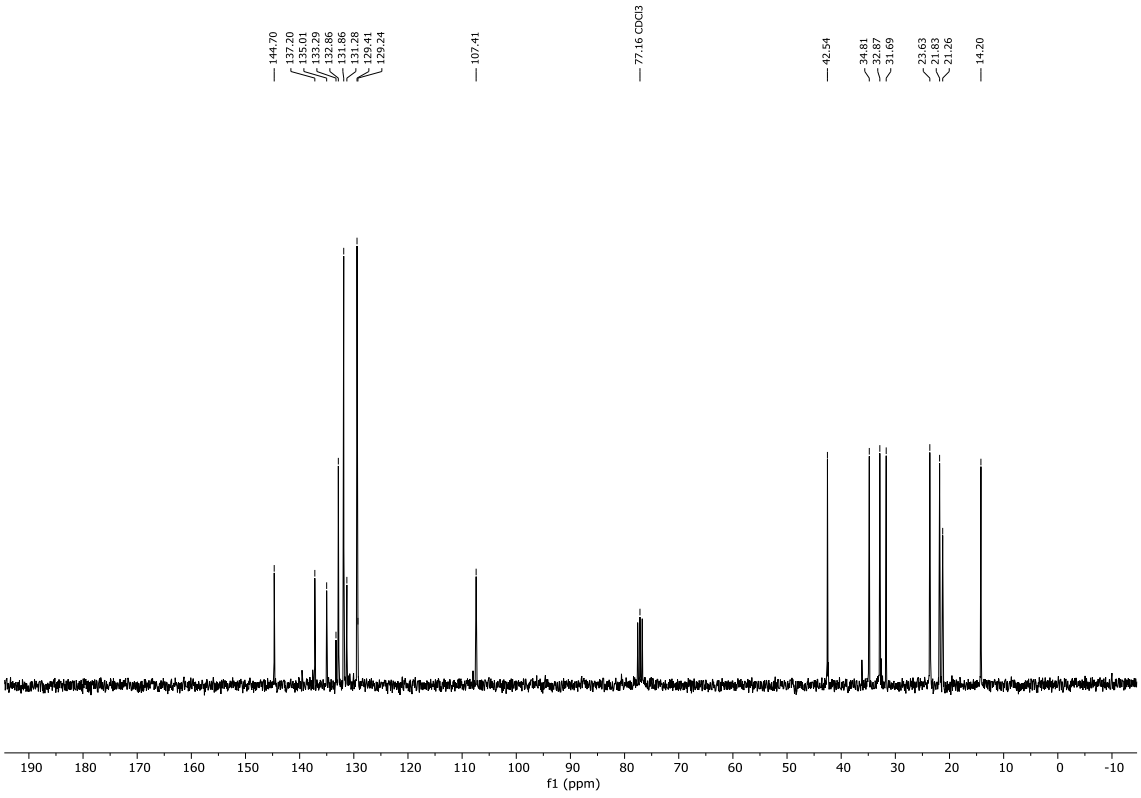


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(1-(cyclopent-1-en-1-yl)-2-iodohex-1-en-1-yl) (*p*-tolyl)sulfide (3l)

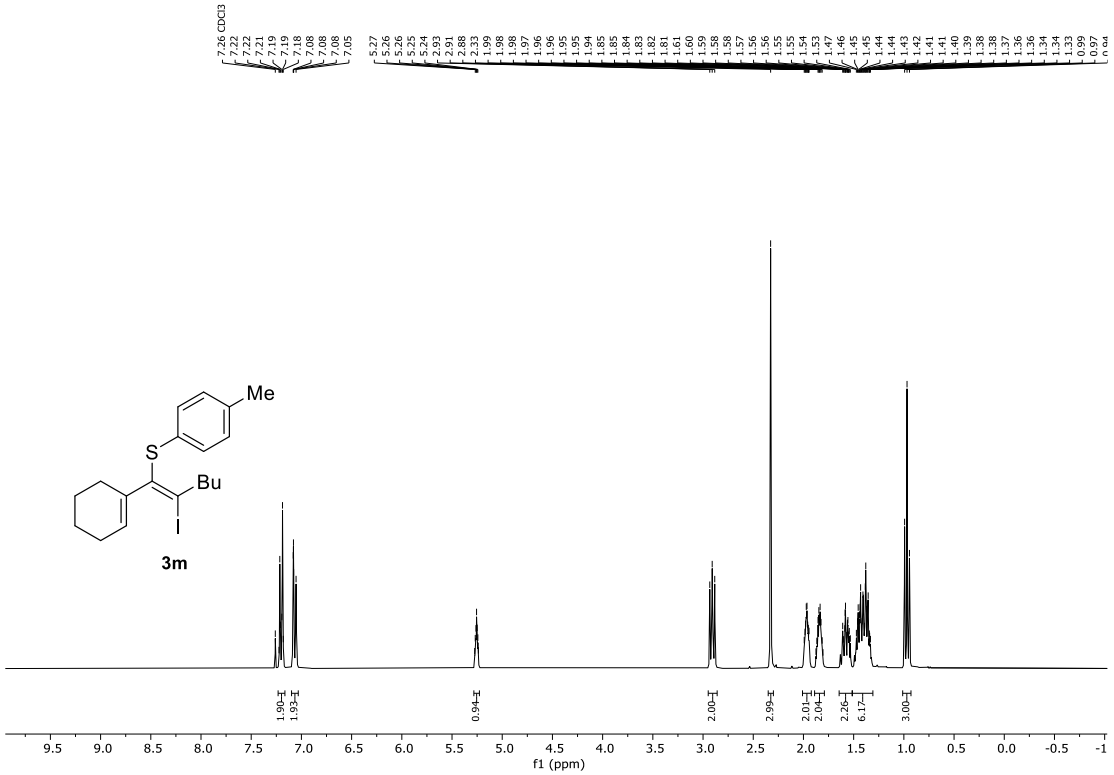


^{1}H-NMR (300 MHz, $CDCl_3$)

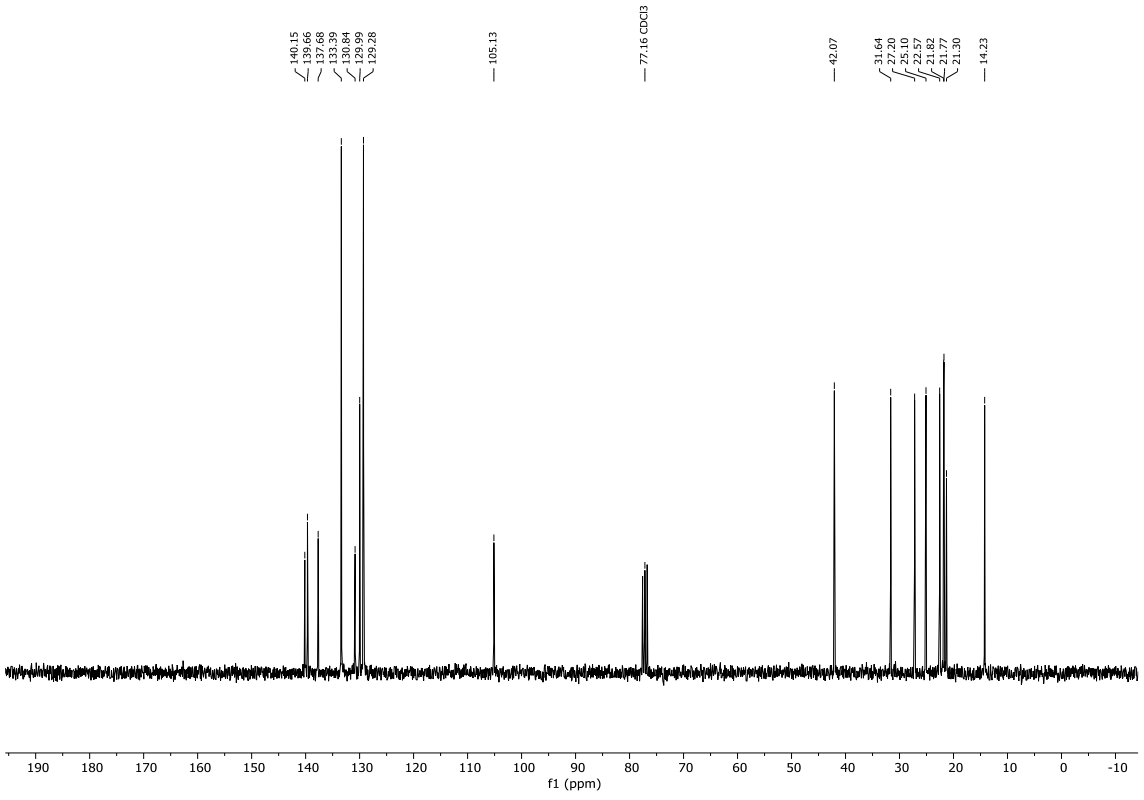


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(1-(cyclohex-1-en-1-yl)-2-iodohex-1-en-1-yl) (*p*-tolyl)sulfide (3m)

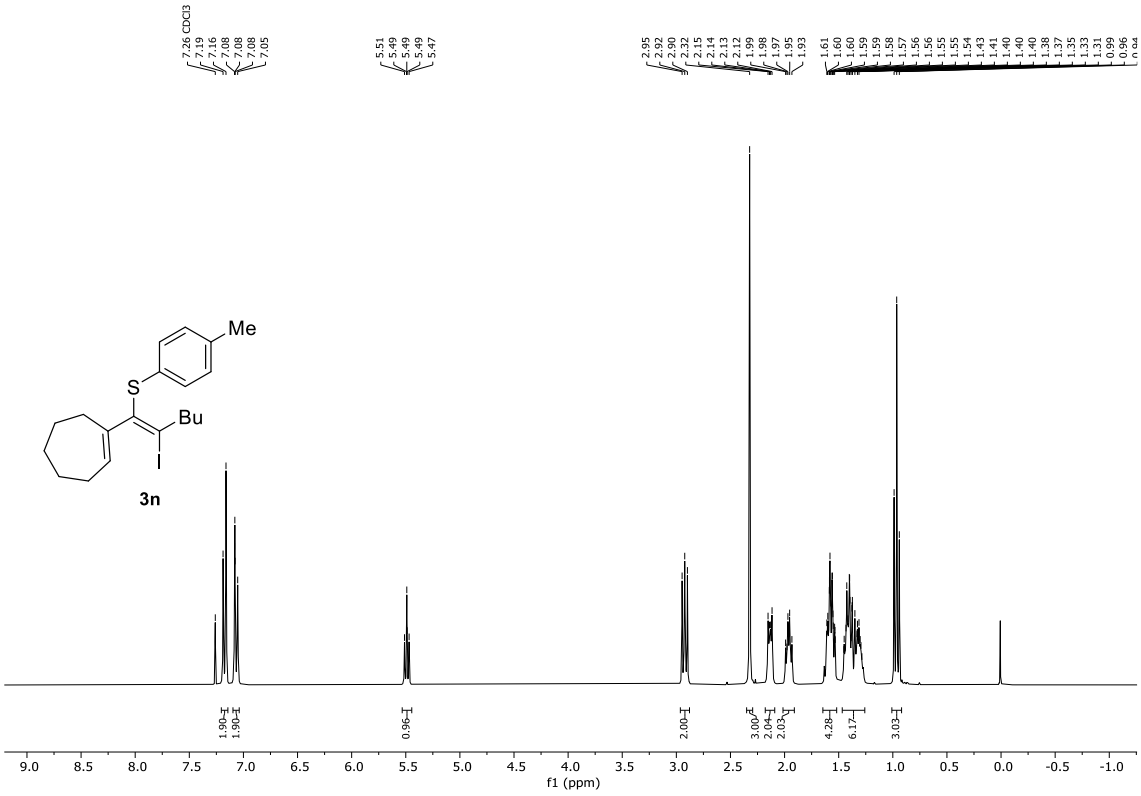


^{1}H-NMR (300 MHz, $CDCl_3$)

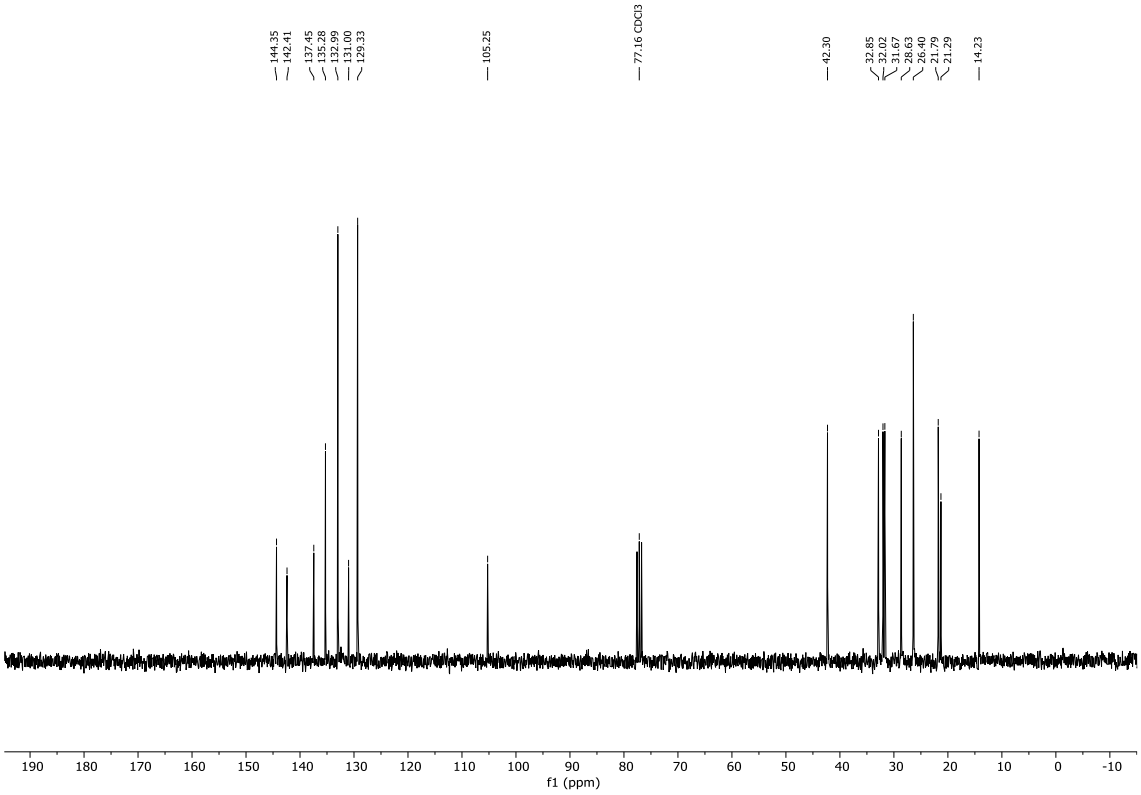


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(1-(cyclohept-1-en-1-yl)-2-iodohex-1-en-1-yl) (*p*-tolyl)sulfide (3n)

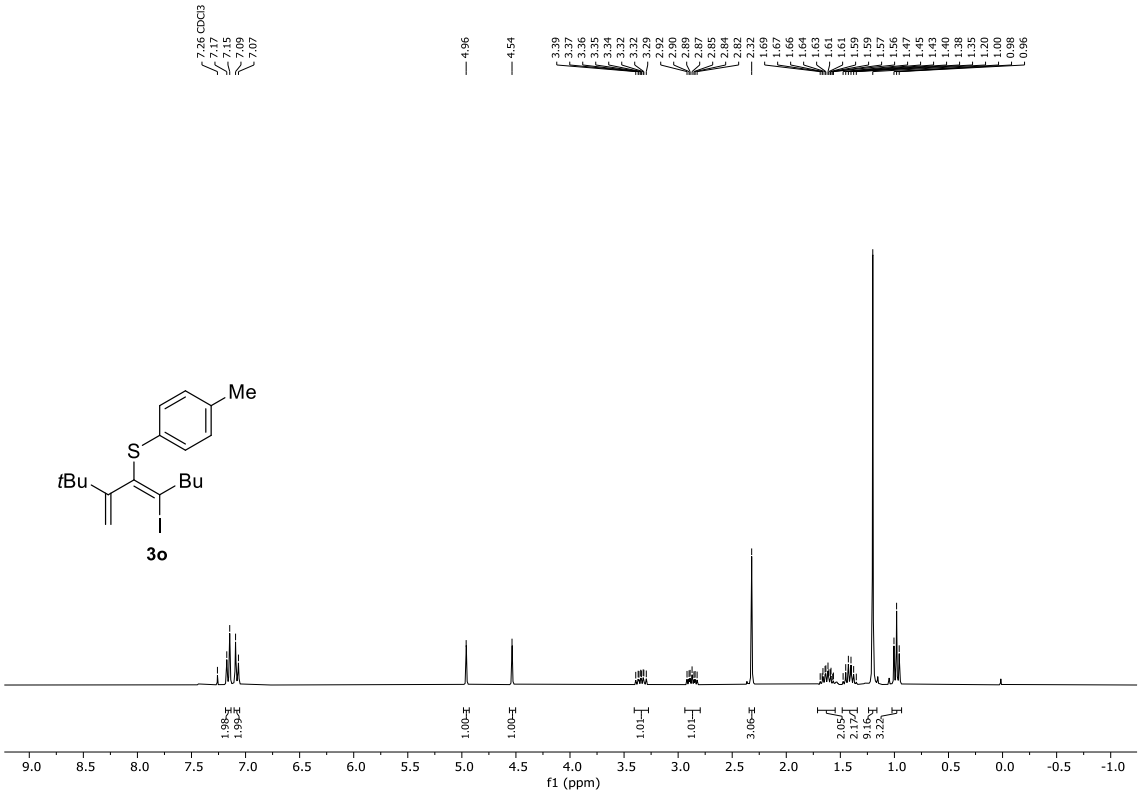


^{1}H-NMR (300 MHz, $CDCl_3$)

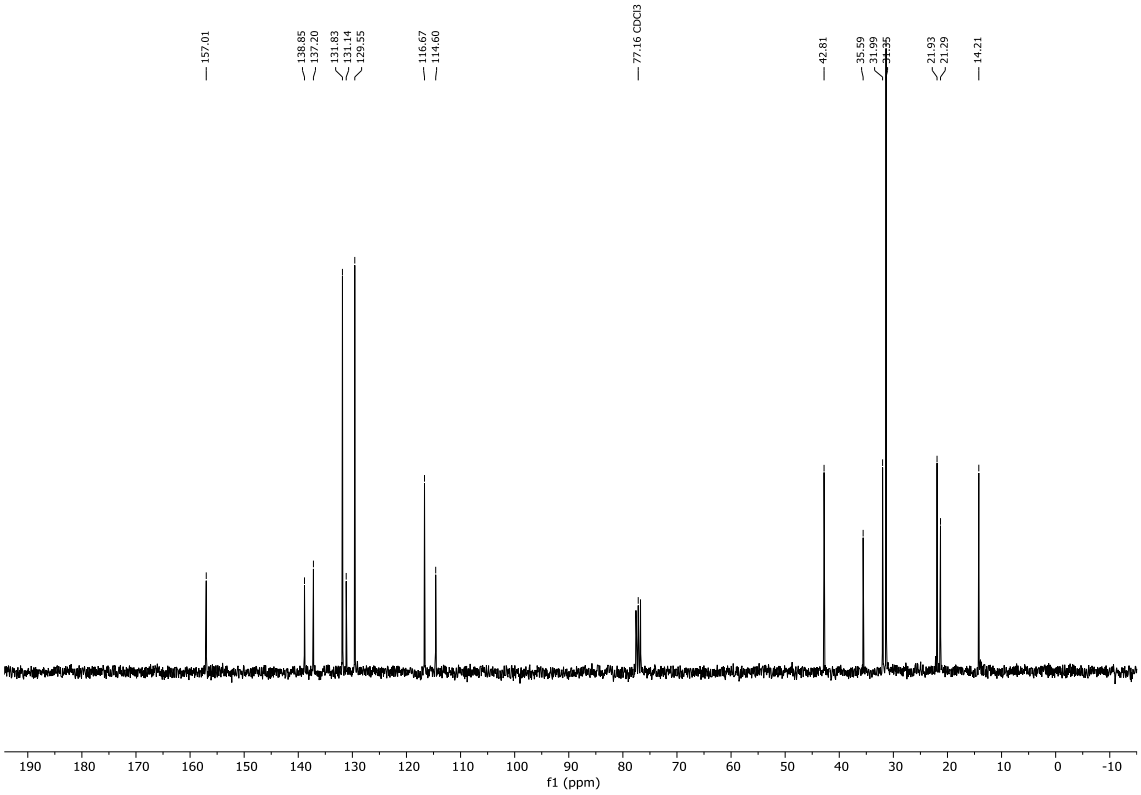


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(5-iodo-2,2-dimethyl-3-methylenenon-4-en-4-yl) (*p*-tolyl)sulfide (3o)

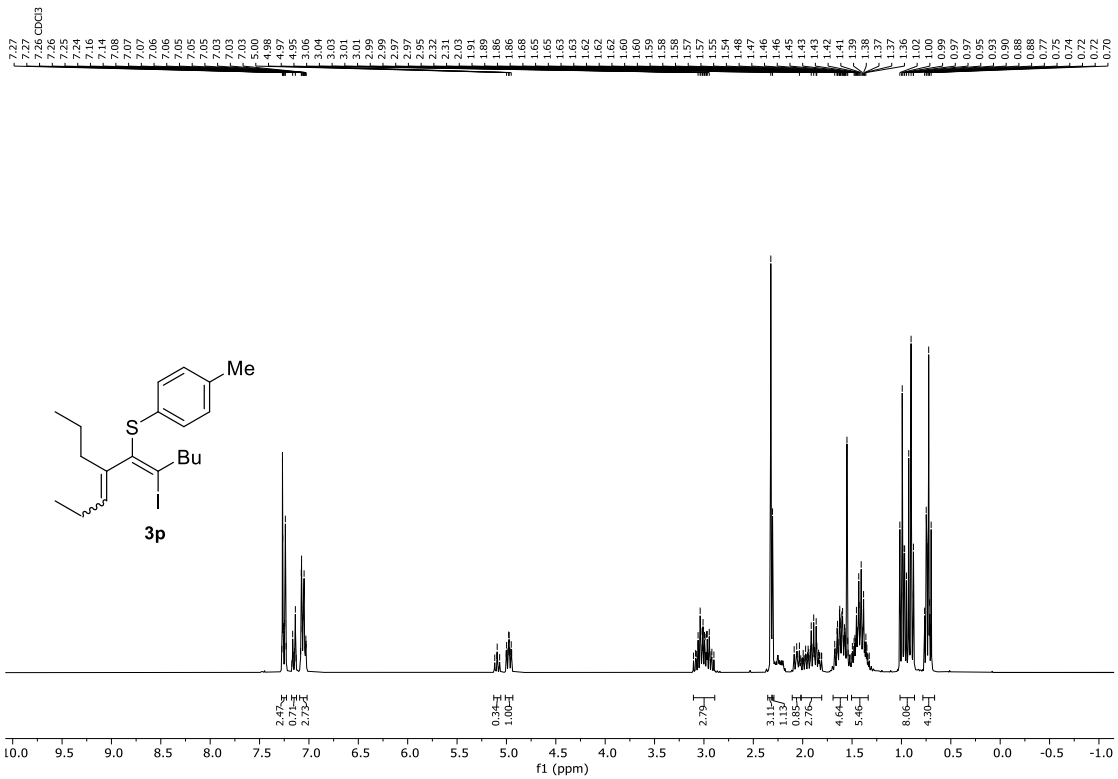


^{1}H-NMR (300 MHz, $CDCl_3$)

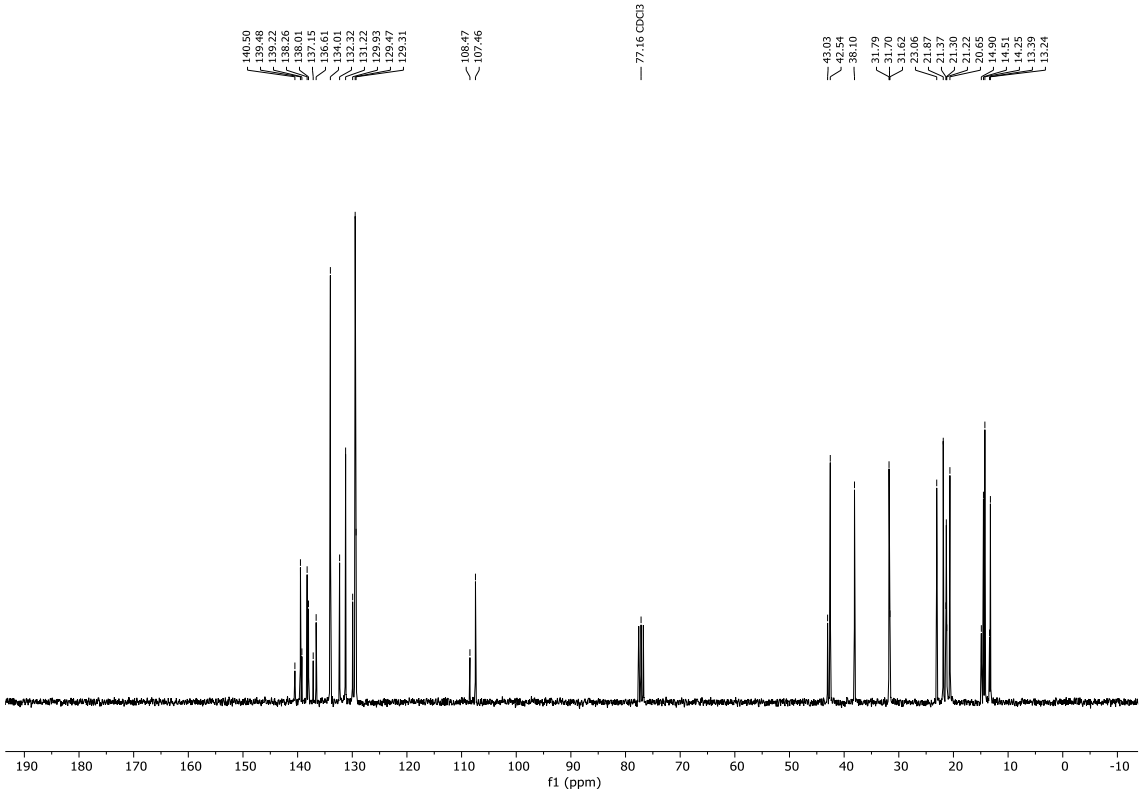


^{13}C-NMR (75 MHz, $CDCl_3$)

((3*E*,5*E*)-6-iodo-4-propyldeca-3,5-dien-5-yl) (*p*-tolyl)sulfide (3p)

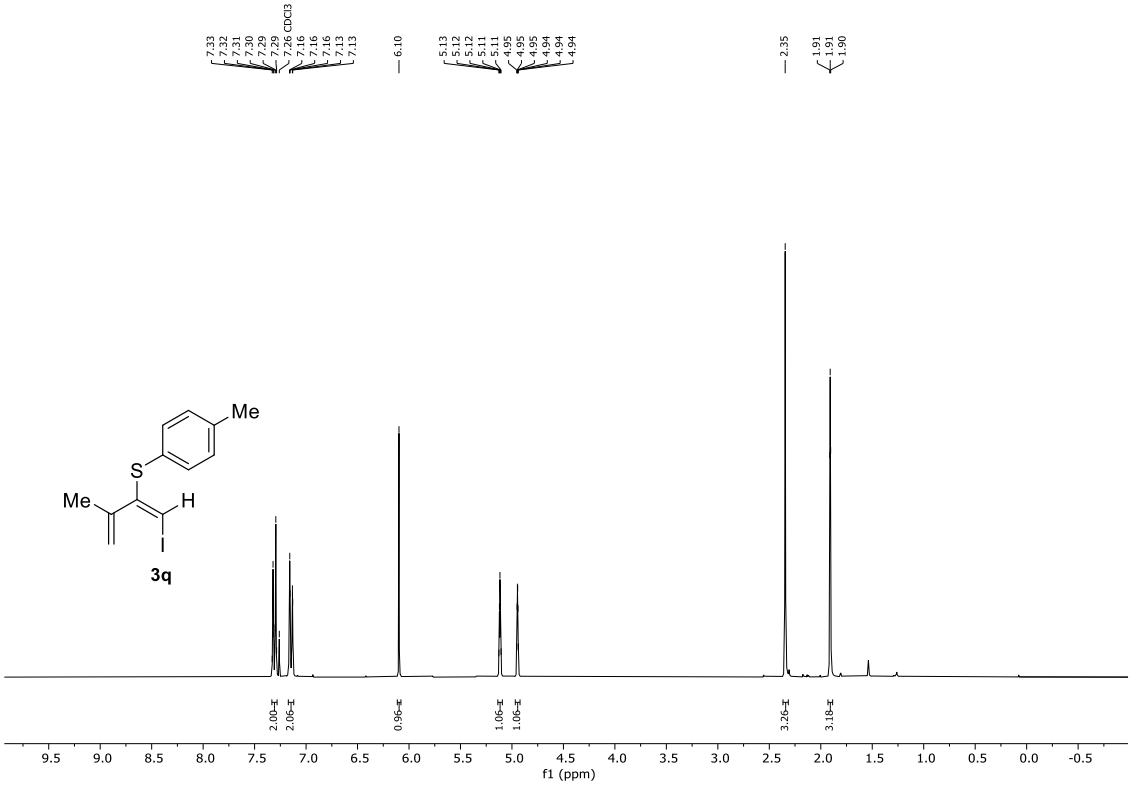


^{1}H-NMR (300 MHz, $CDCl_3$)

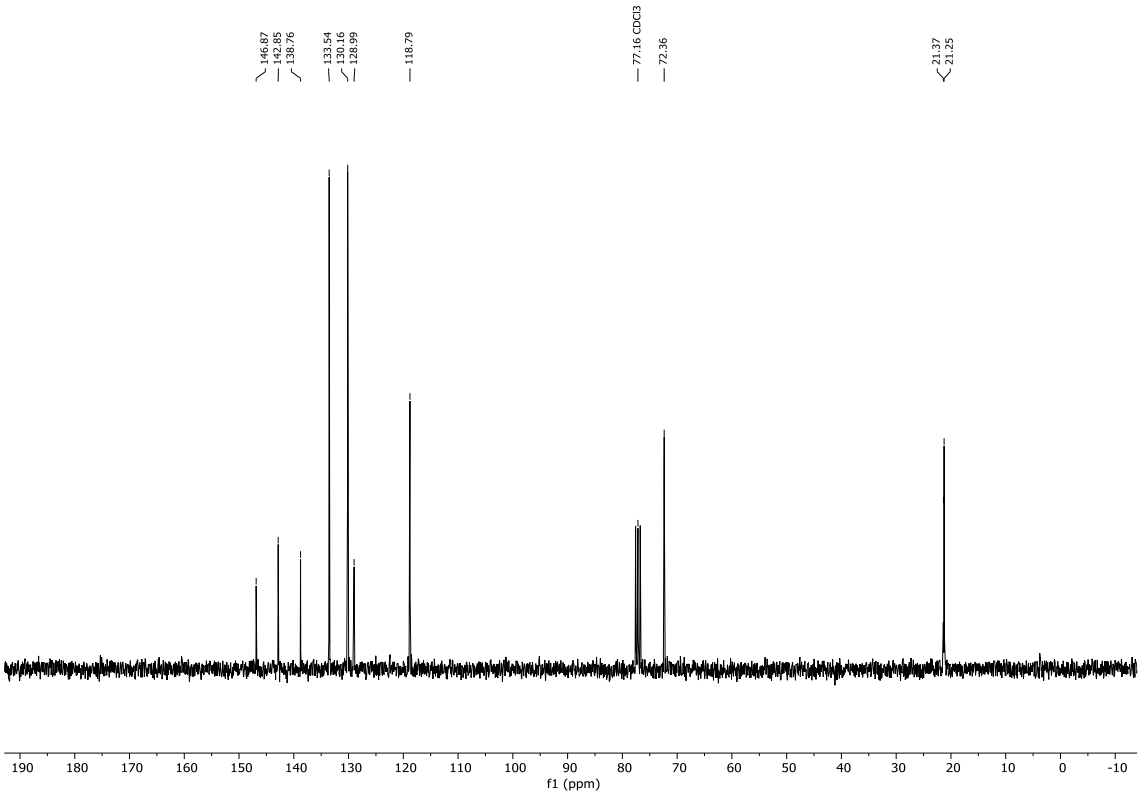


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(1-iodo-3-methylbuta-1,3-dien-2-yl) (*p*-tolyl)sulfide (3q)

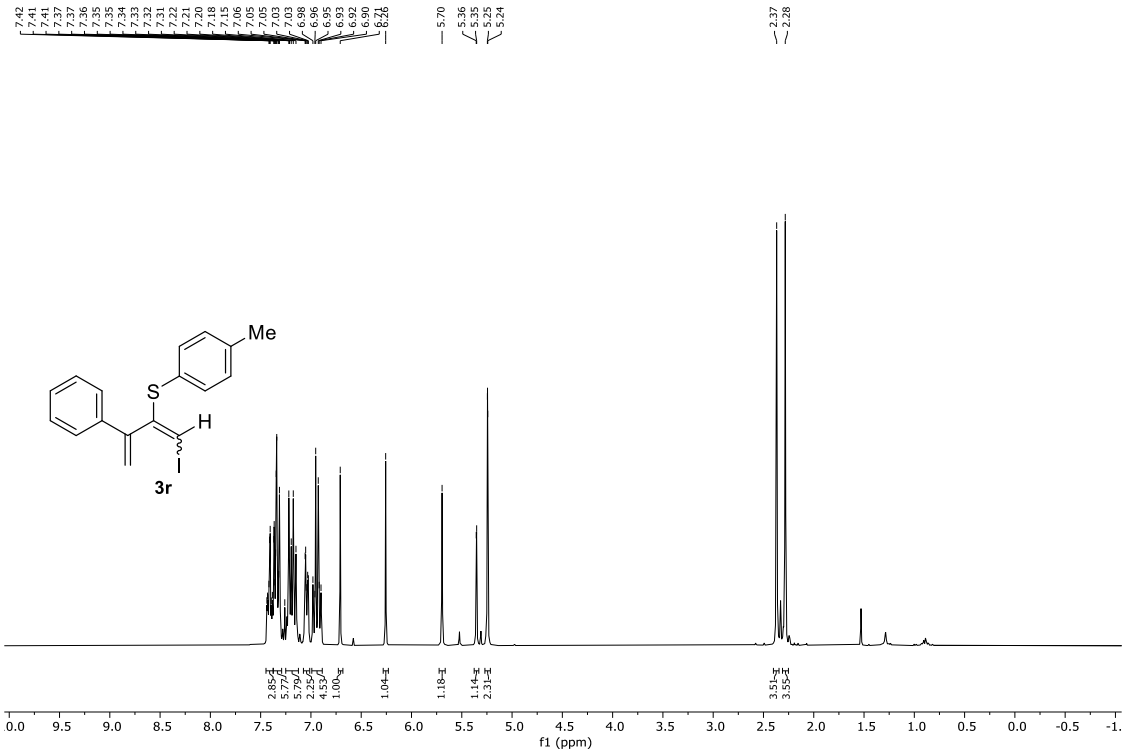


^{1}H-NMR (300 MHz, $CDCl_3$)

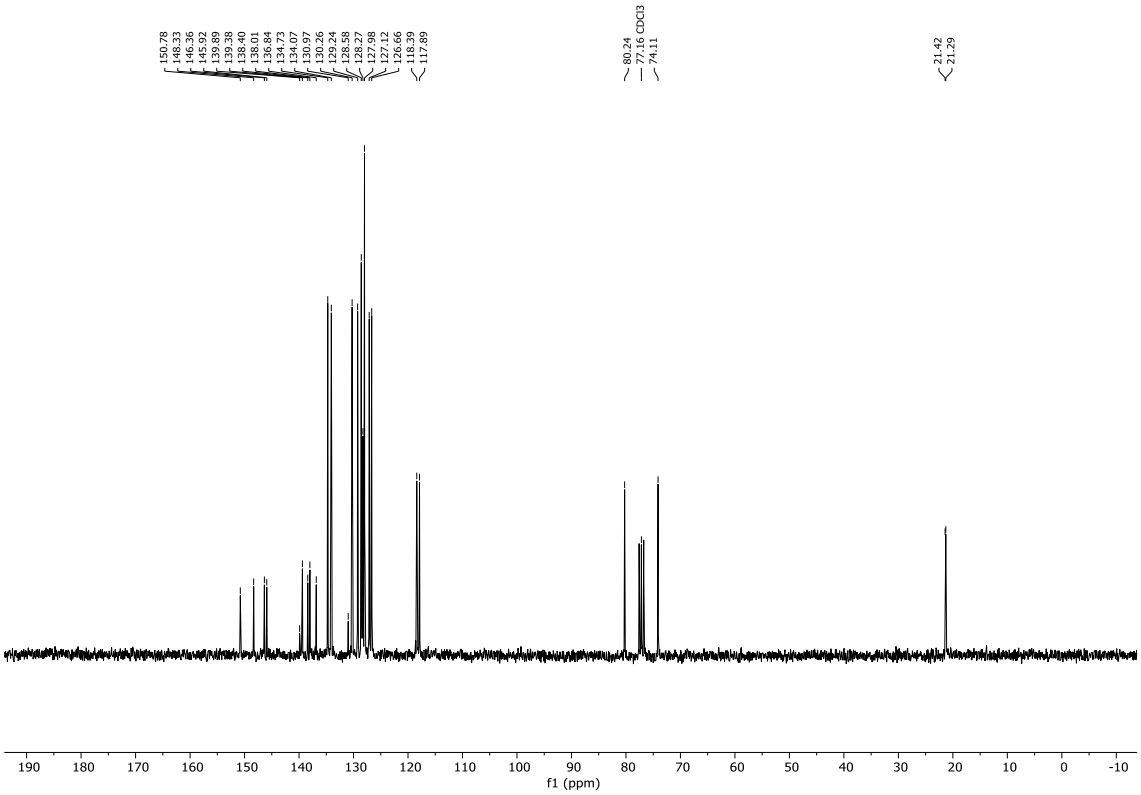


^{13}C-NMR (75 MHz, $CDCl_3$)

(1-iodo-3-phenylbuta-1,3-dien-3-yl) (*p*-tolyl)sulfide (3r)

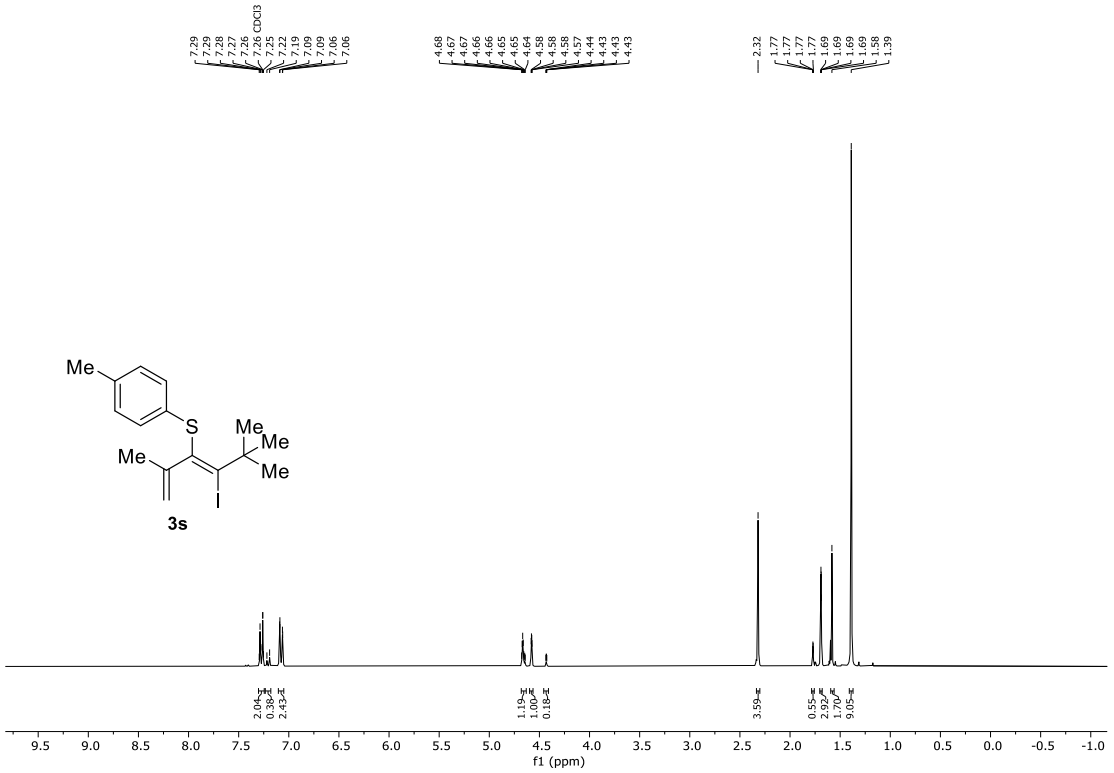


^{1}H-NMR (300 MHz, $CDCl_3$)

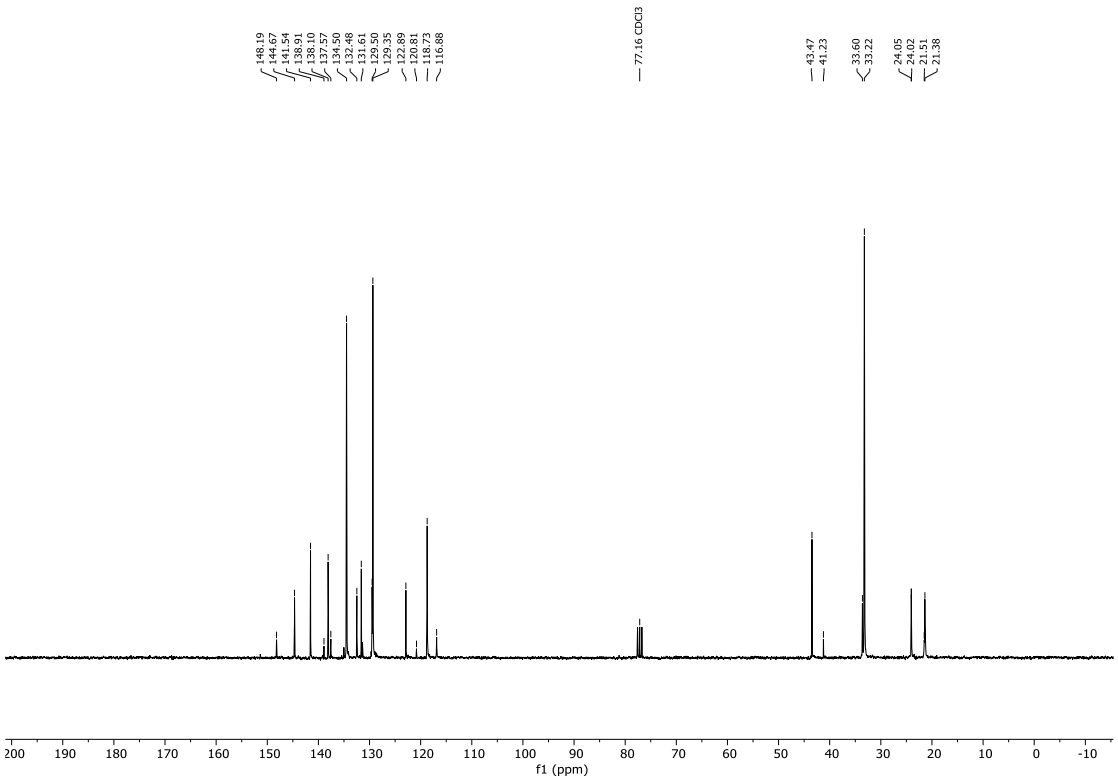


^{13}C-NMR (75 MHz, $CDCl_3$)

(4-iodo-2,5,5-trimethylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (3s) (E:Z/5:1)

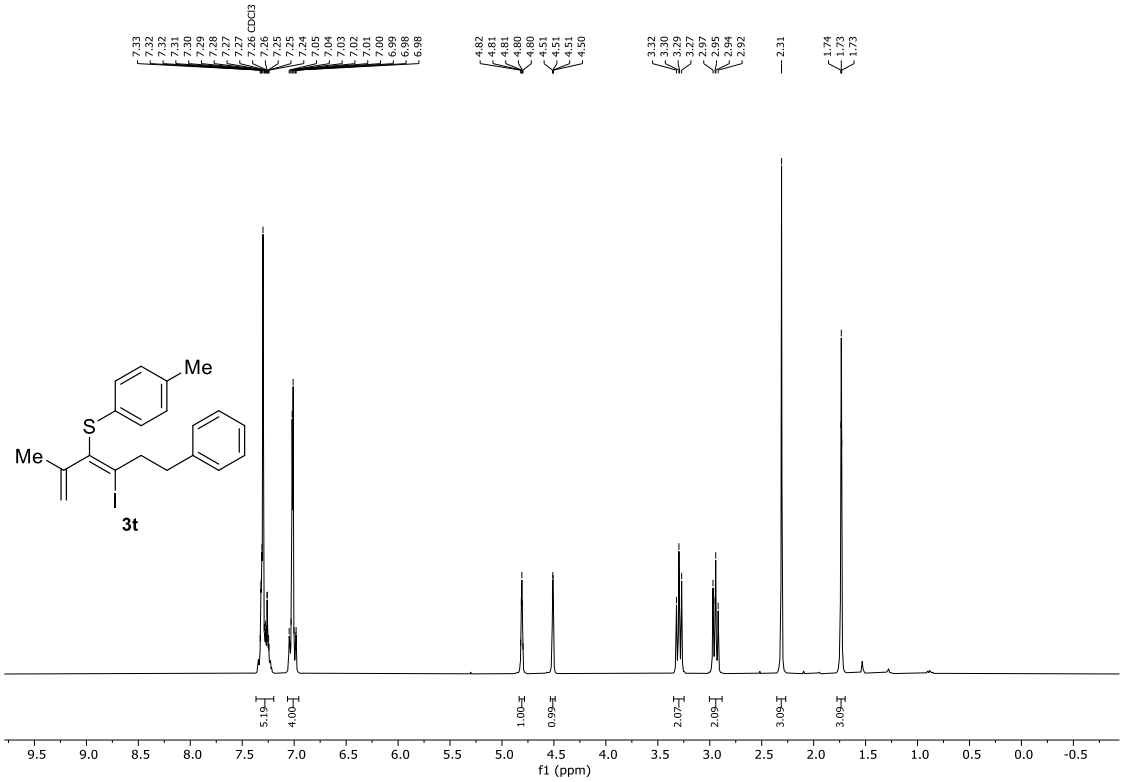


^{1}H-NMR (300 MHz, $CDCl_3$)

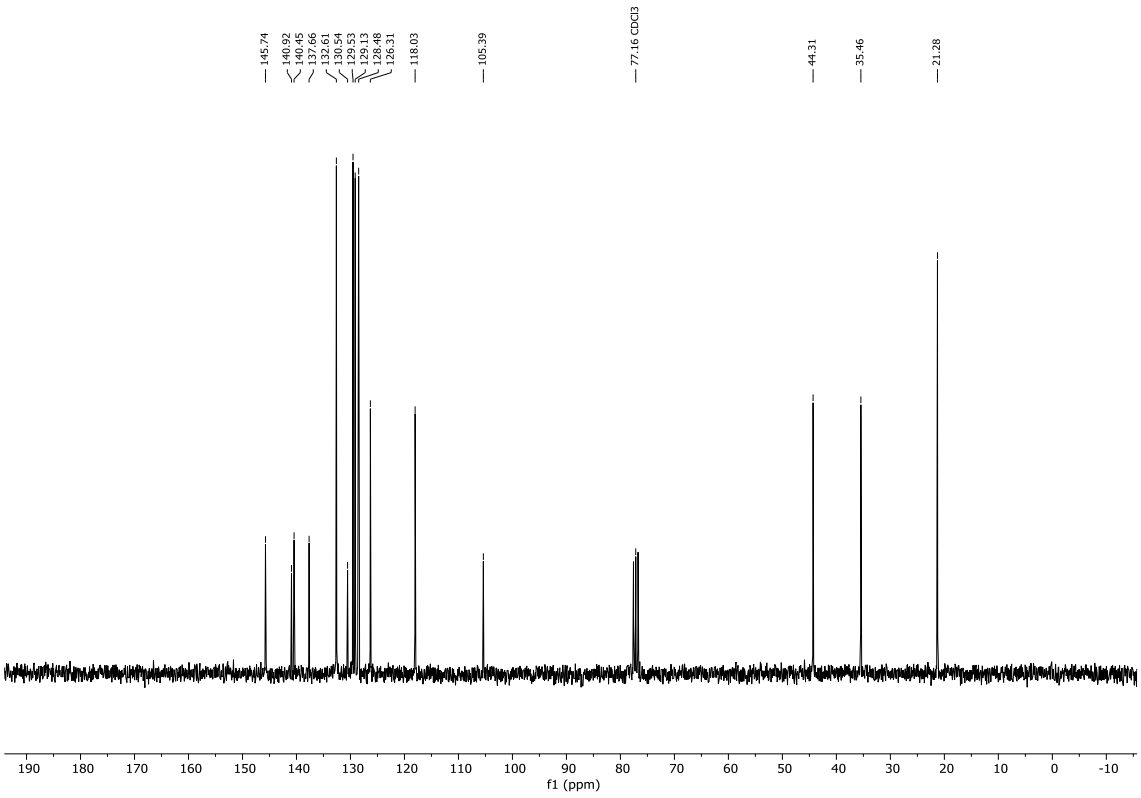


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-iodo-2-methyl-6-phenylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (3t)

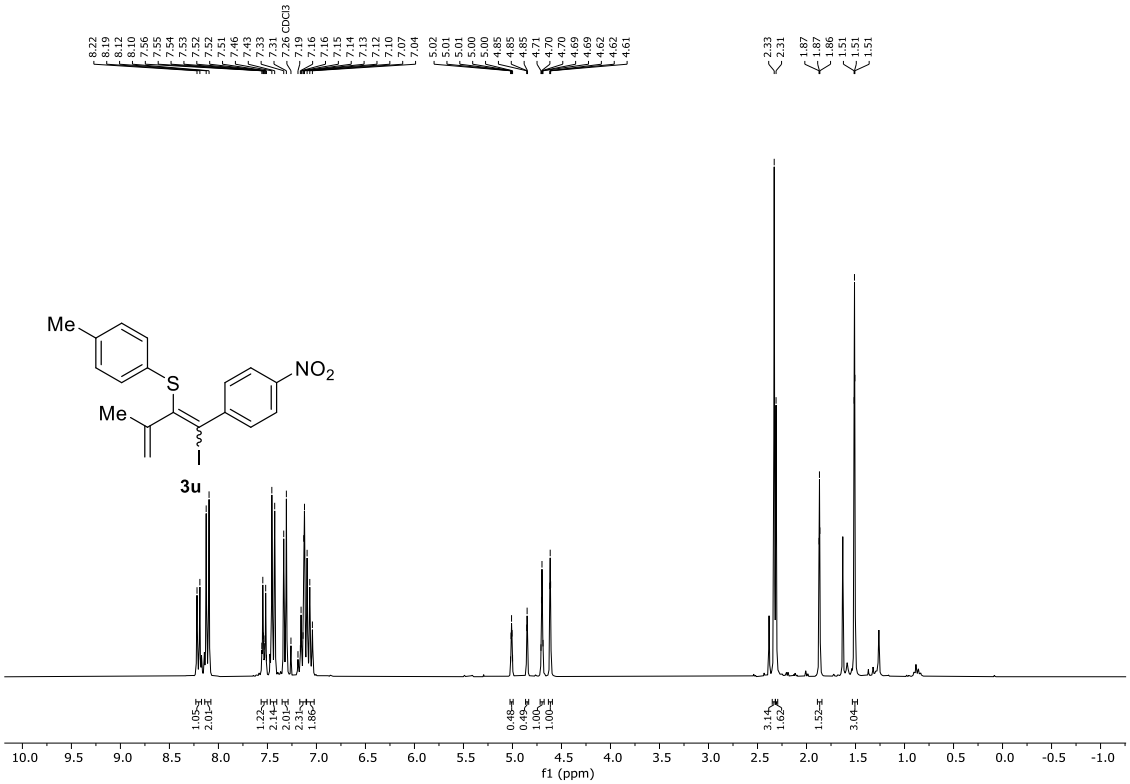


^{1}H-NMR (300 MHz, $CDCl_3$)

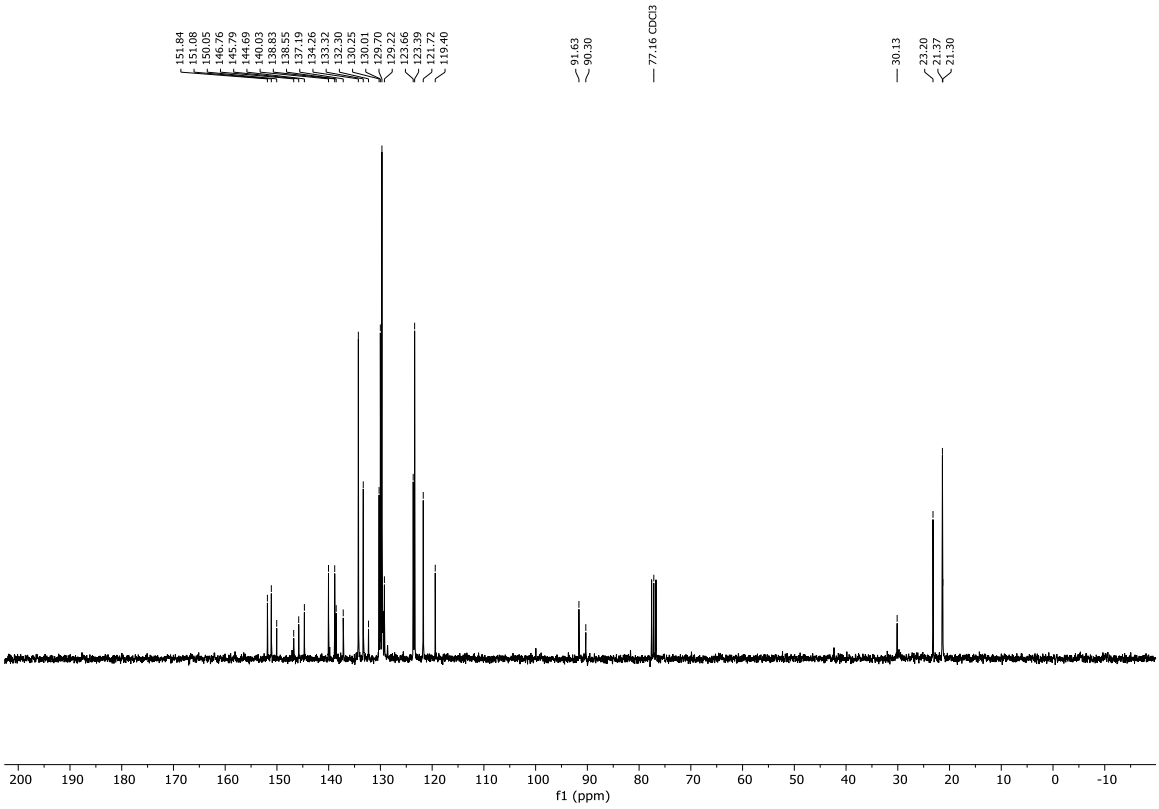


^{13}C-NMR (75 MHz, $CDCl_3$)

(1-iodo-3-methyl-1-(4-nitrophenyl)buta-1,3-dien-2-yl) (*p*-tolyl)sulfide (3u)

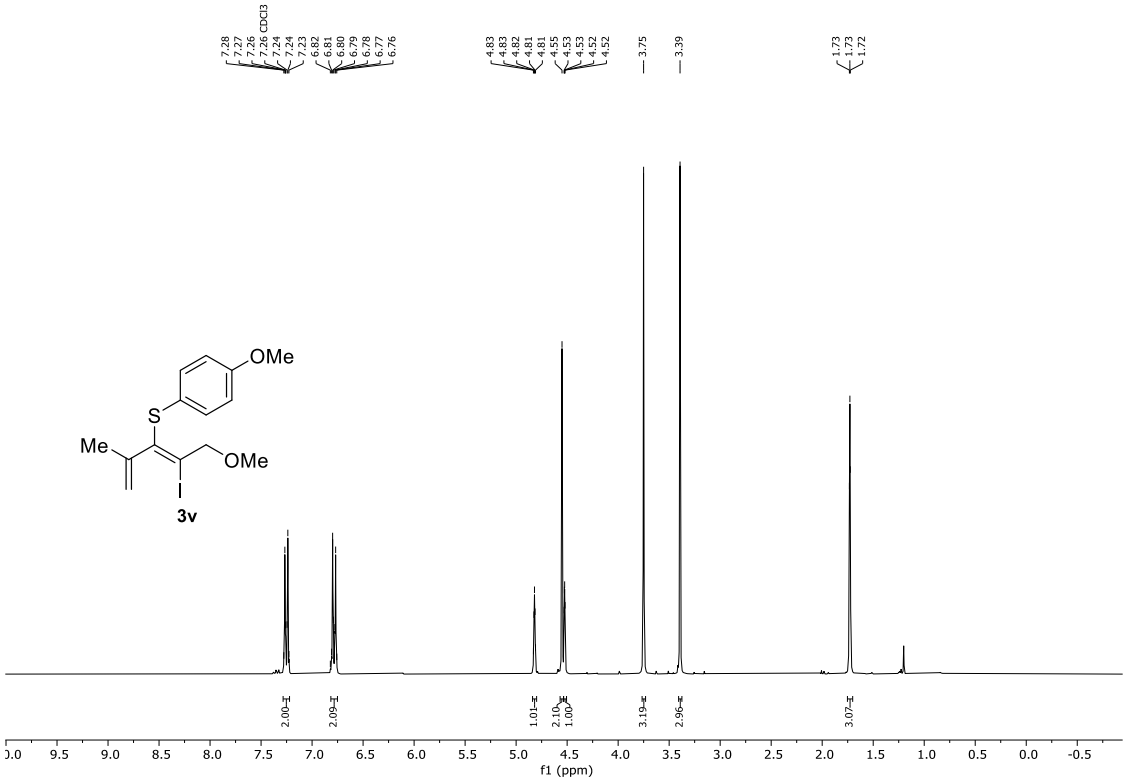


^{1}H-NMR (300 MHz, $CDCl_3$)

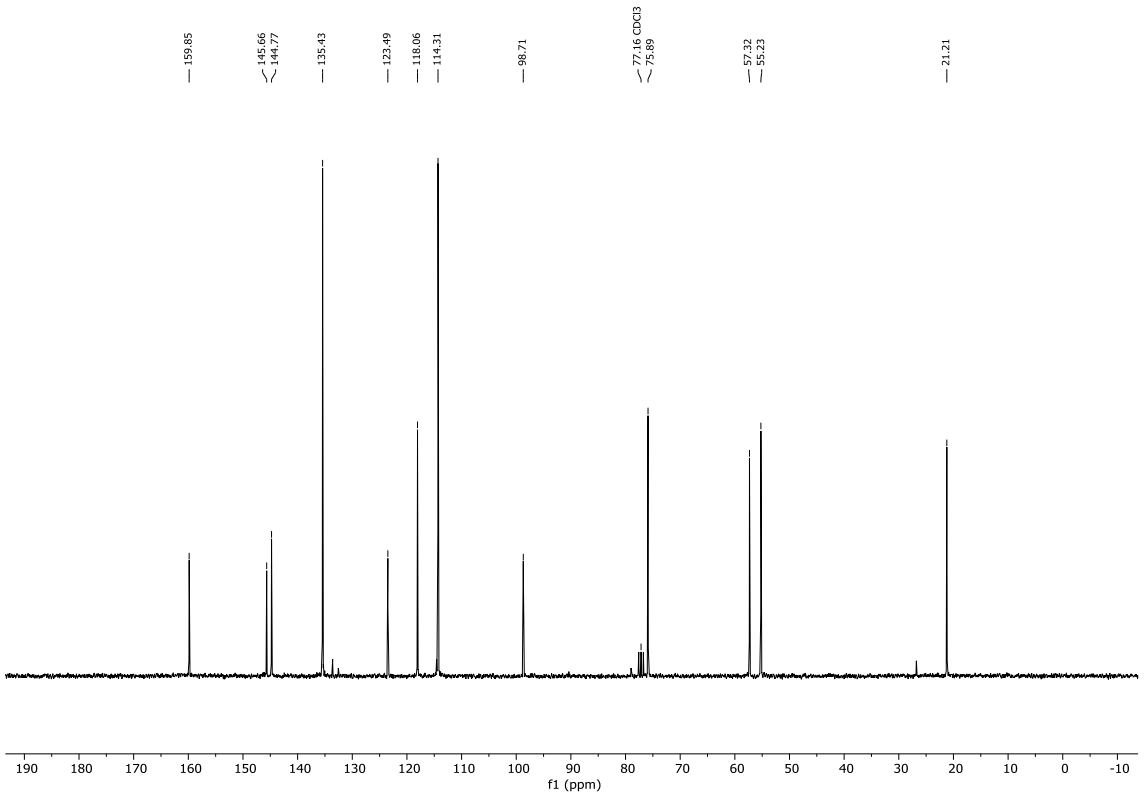


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-iodo-5-methoxy-2-methylpenta-1,3-dien-3-yl) (4-methoxyphenyl)sulfide (3v)

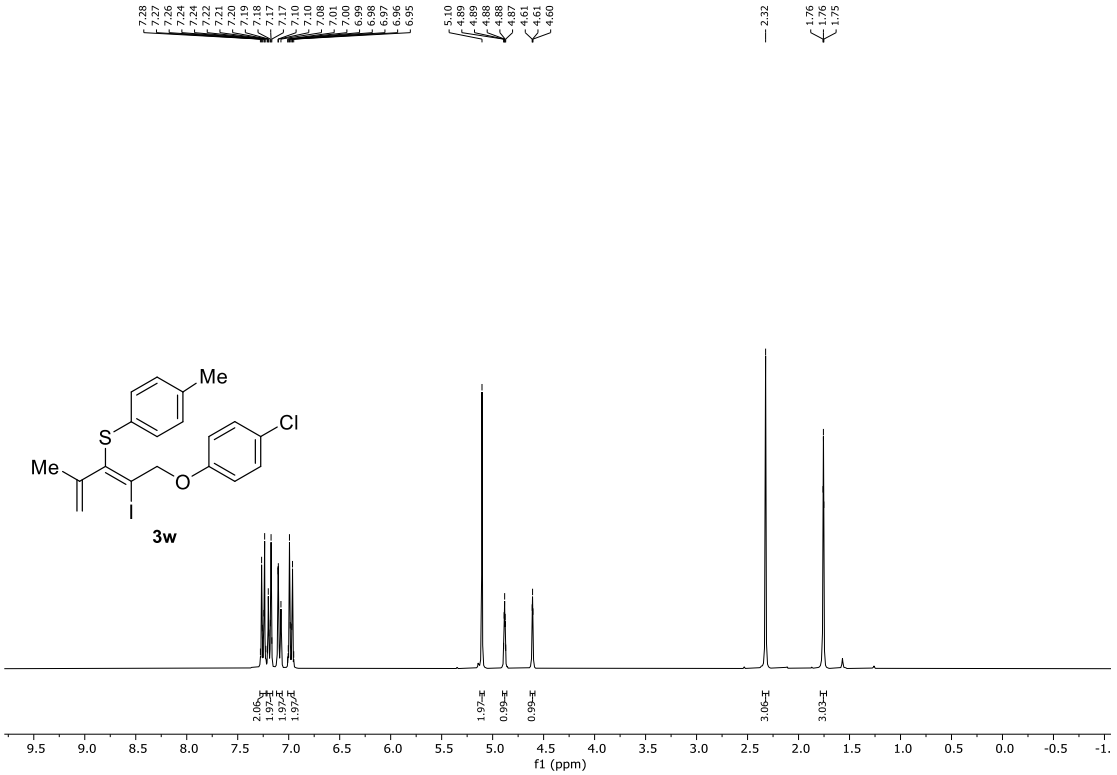


^{1}H-NMR (300 MHz, $CDCl_3$)

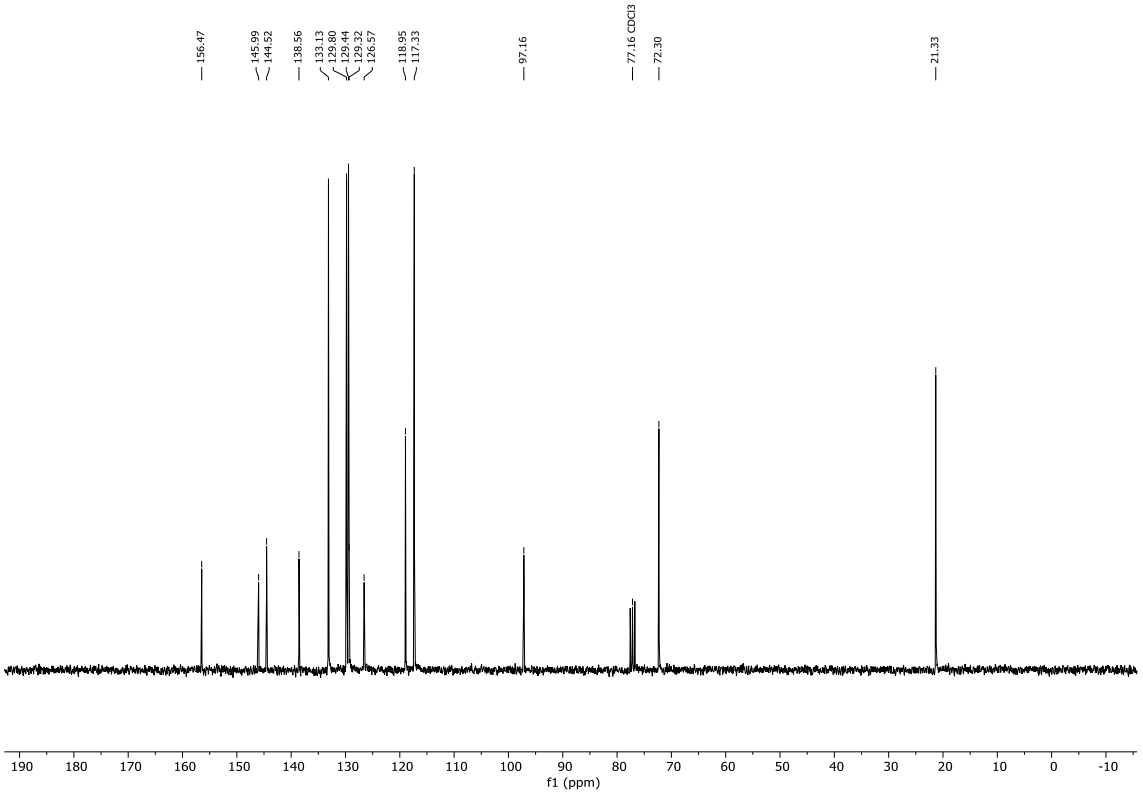


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(5-(4-chlorophenoxy)-4-iodo-2-methylpenta-1,3-dien-3-yl) (*p*-tolyl)sulfide (3w)

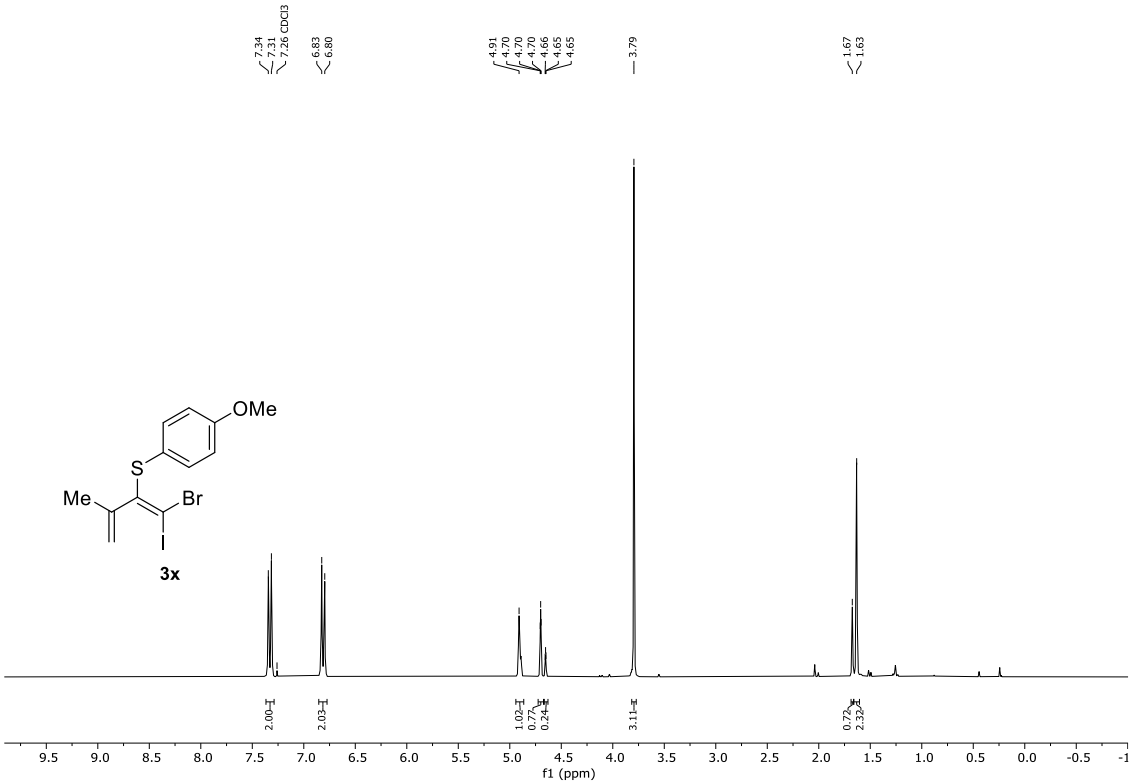


^{1}H-NMR (300 MHz, $CDCl_3$)

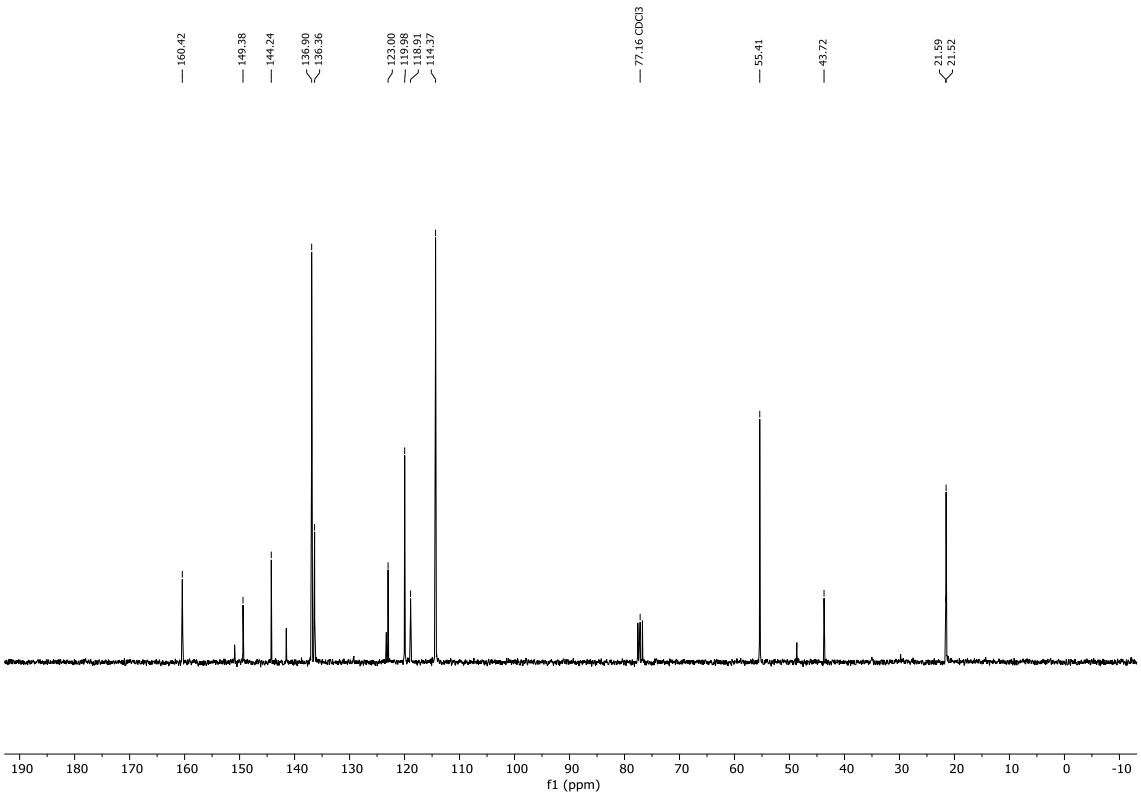


^{13}C-NMR (75 MHz, $CDCl_3$)

(1-bromo-1-iodo-3-methylbuta-1,3-dien-2-yl) (4-methoxyphenyl)sulfide (3x)

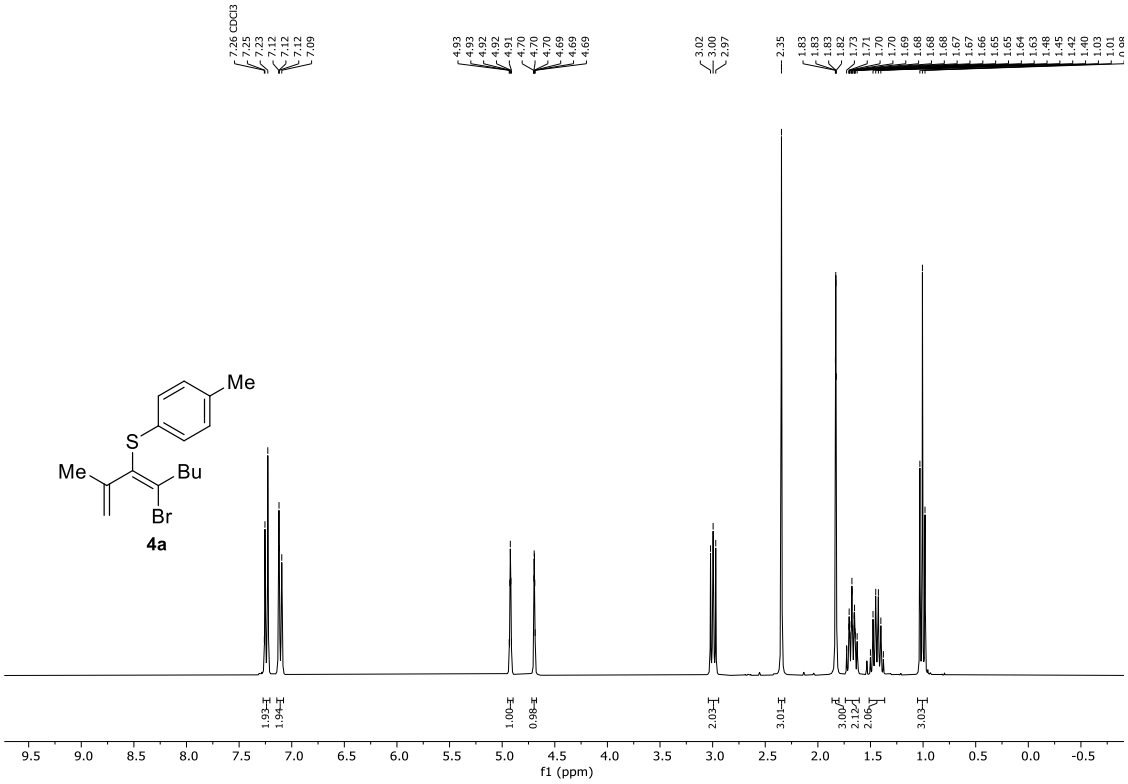


^{1}H-NMR (300 MHz, $CDCl_3$)

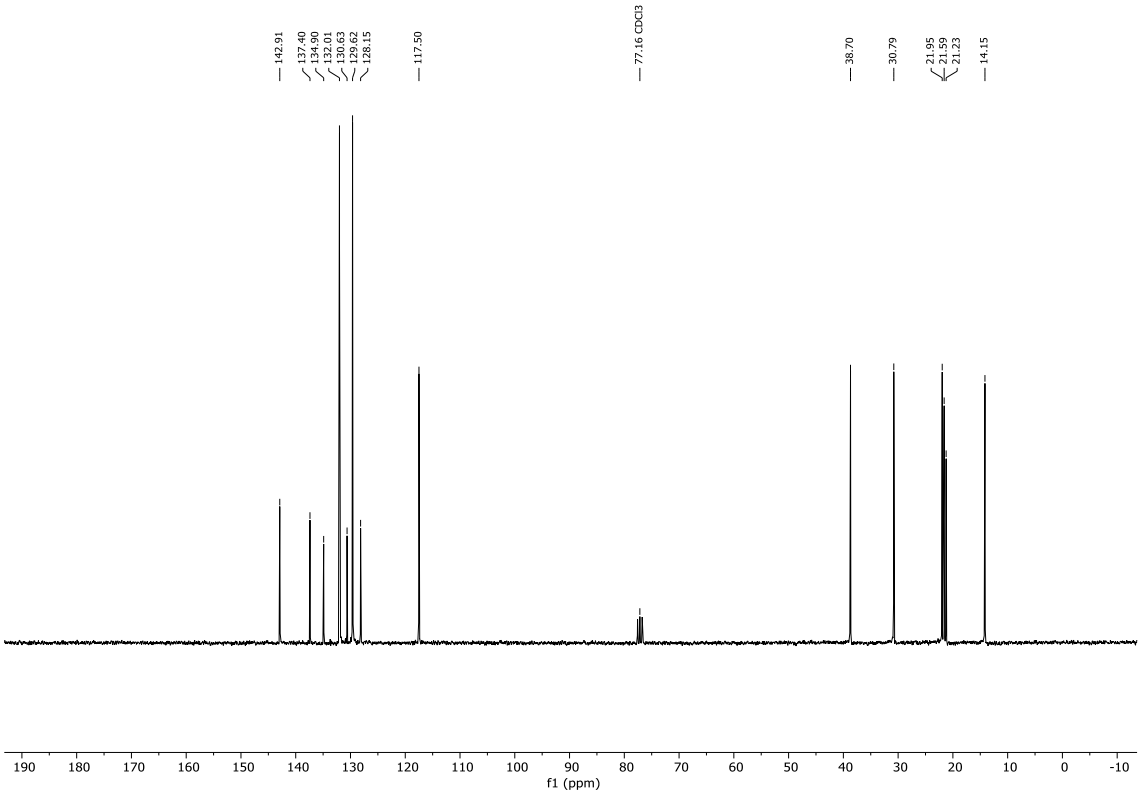


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (*p*-tolyl)sulfide (4a)

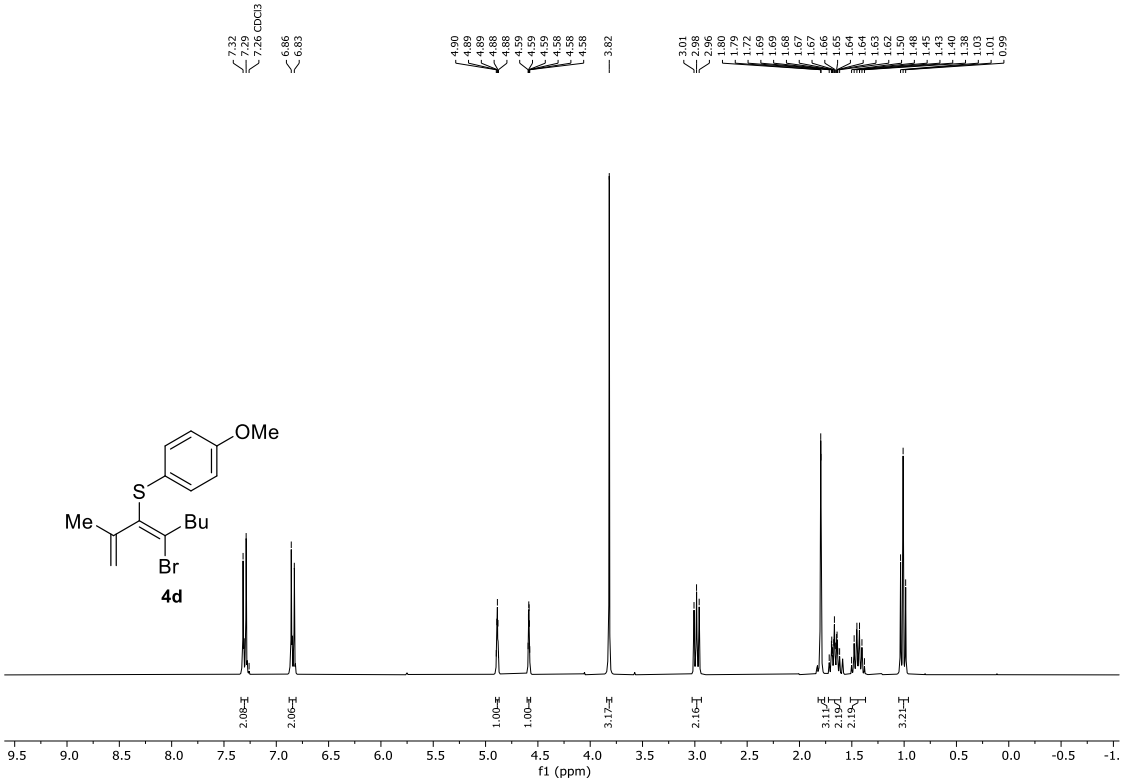


^{1}H-NMR (300 MHz, $CDCl_3$)

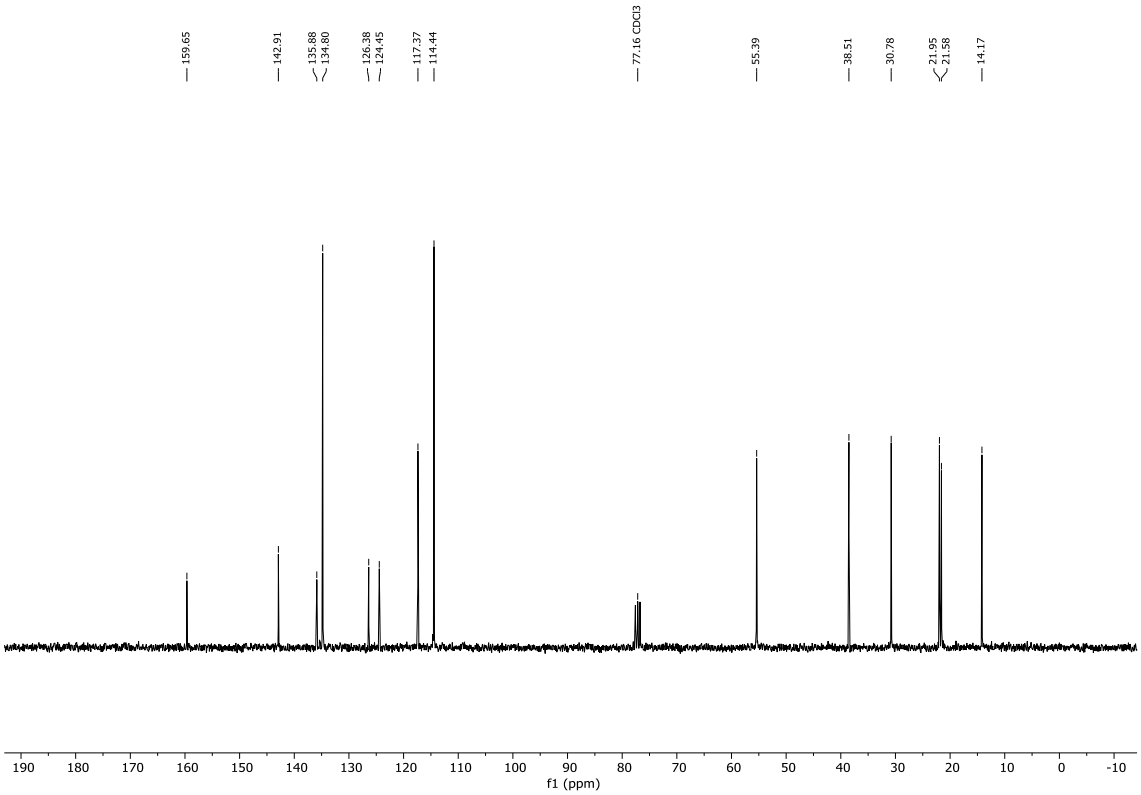


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (4-methoxyphenyl)sulfide (4d)

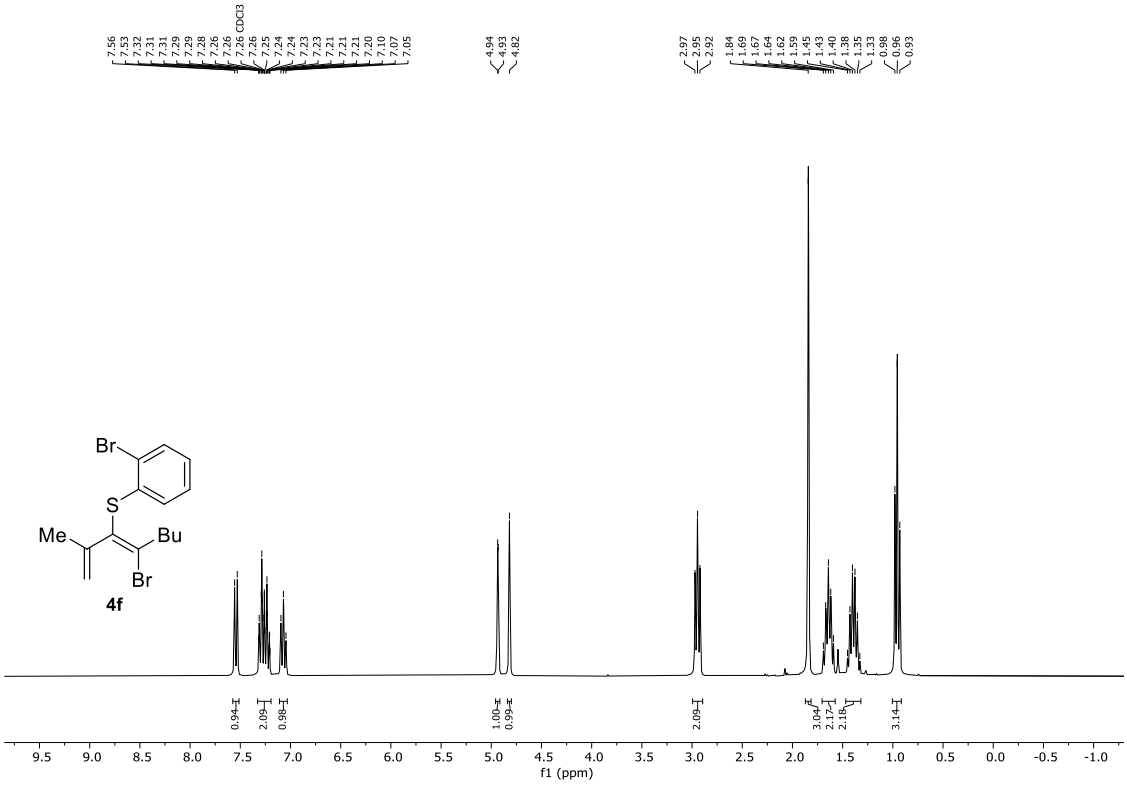


^{1}H-NMR (300 MHz, $CDCl_3$)

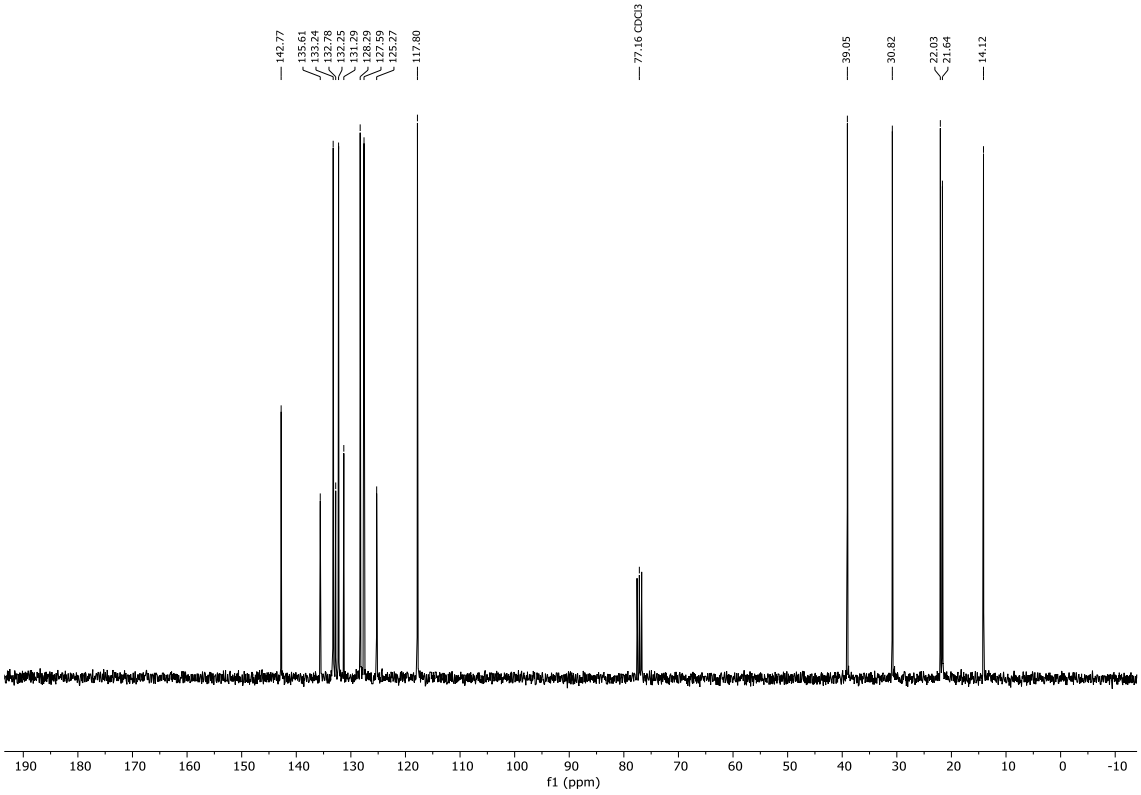


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (2-bromophenyl)sulfide (4f)

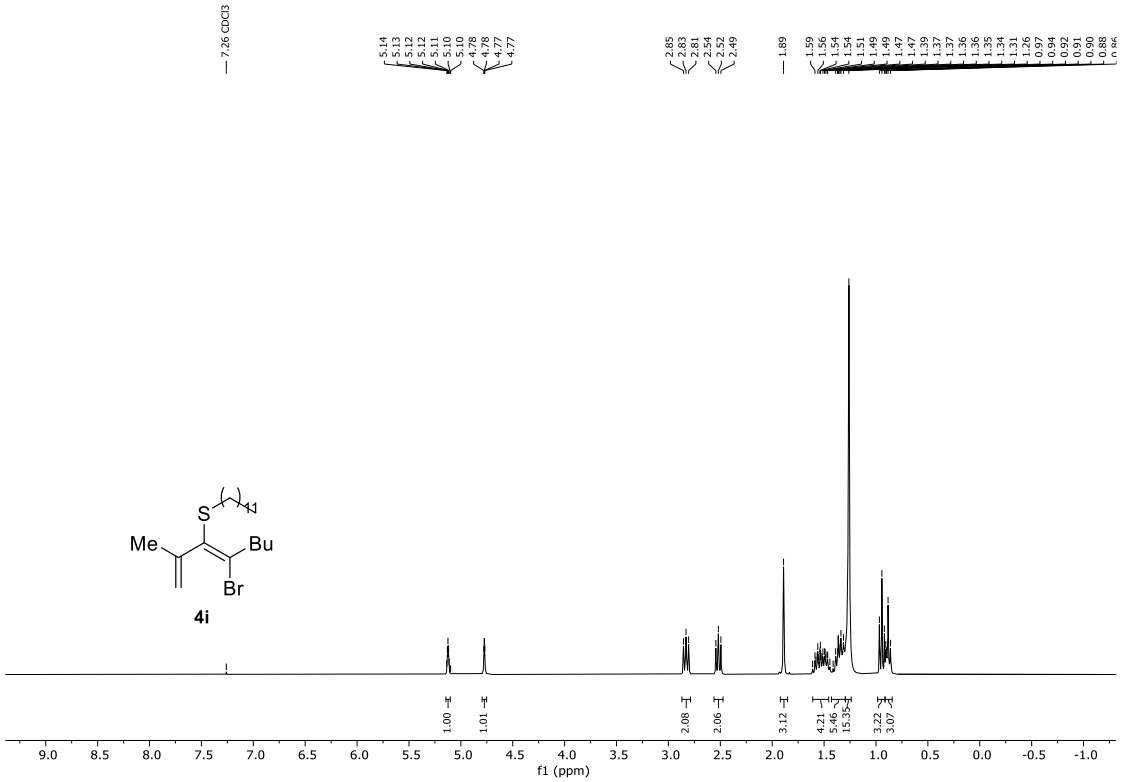


^{1}H-NMR (300 MHz, $CDCl_3$)

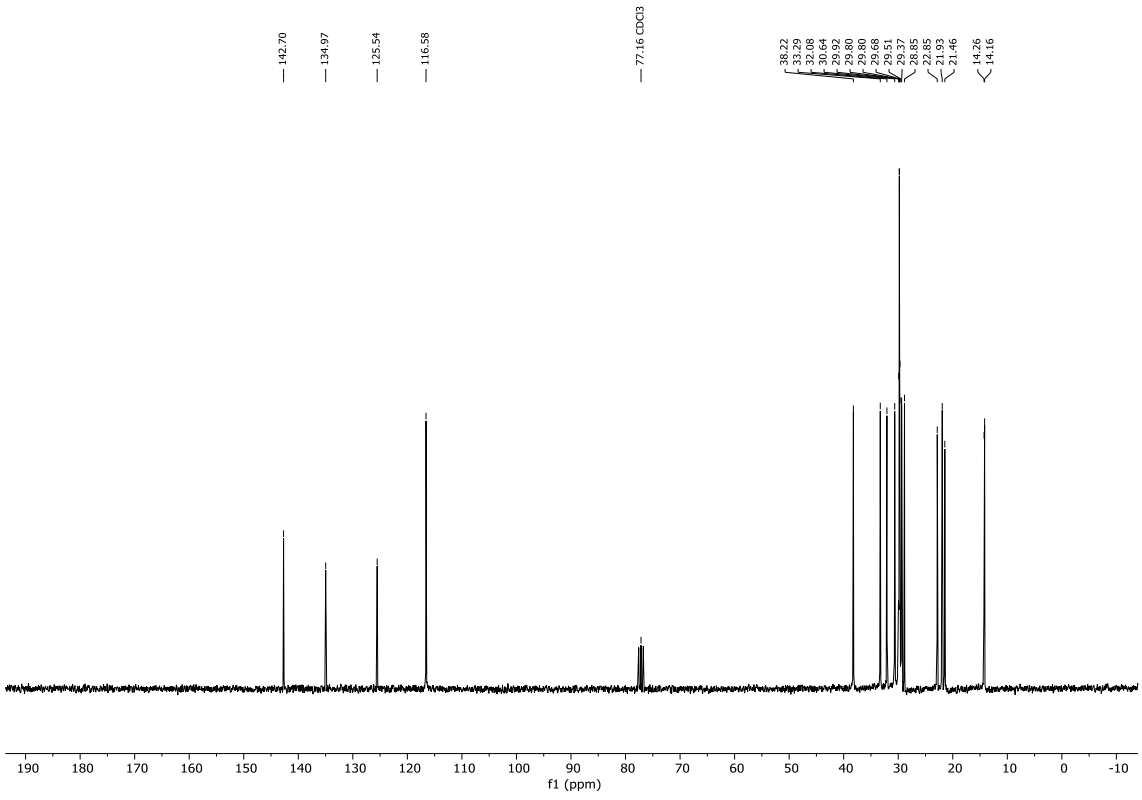


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-bromo-2-methylocta-1,3-dien-3-yl) (dodecyl)sulfide (4i)

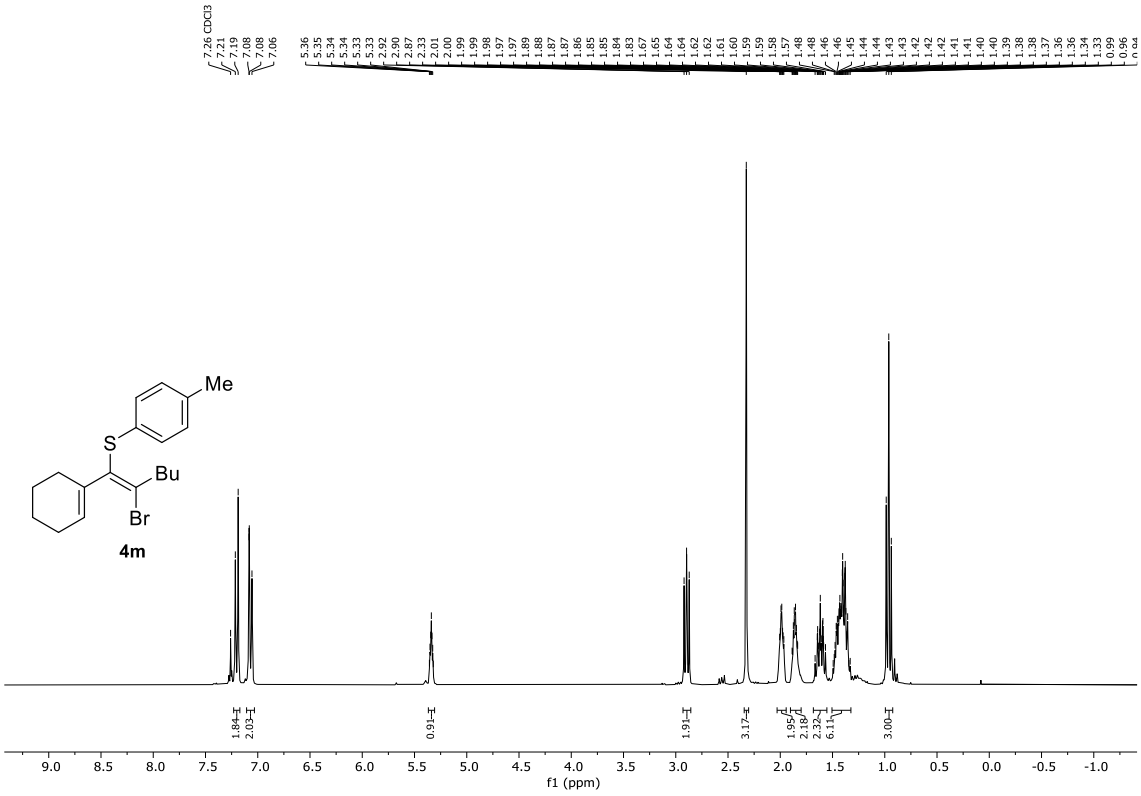


^{1}H-NMR (300 MHz, $CDCl_3$)

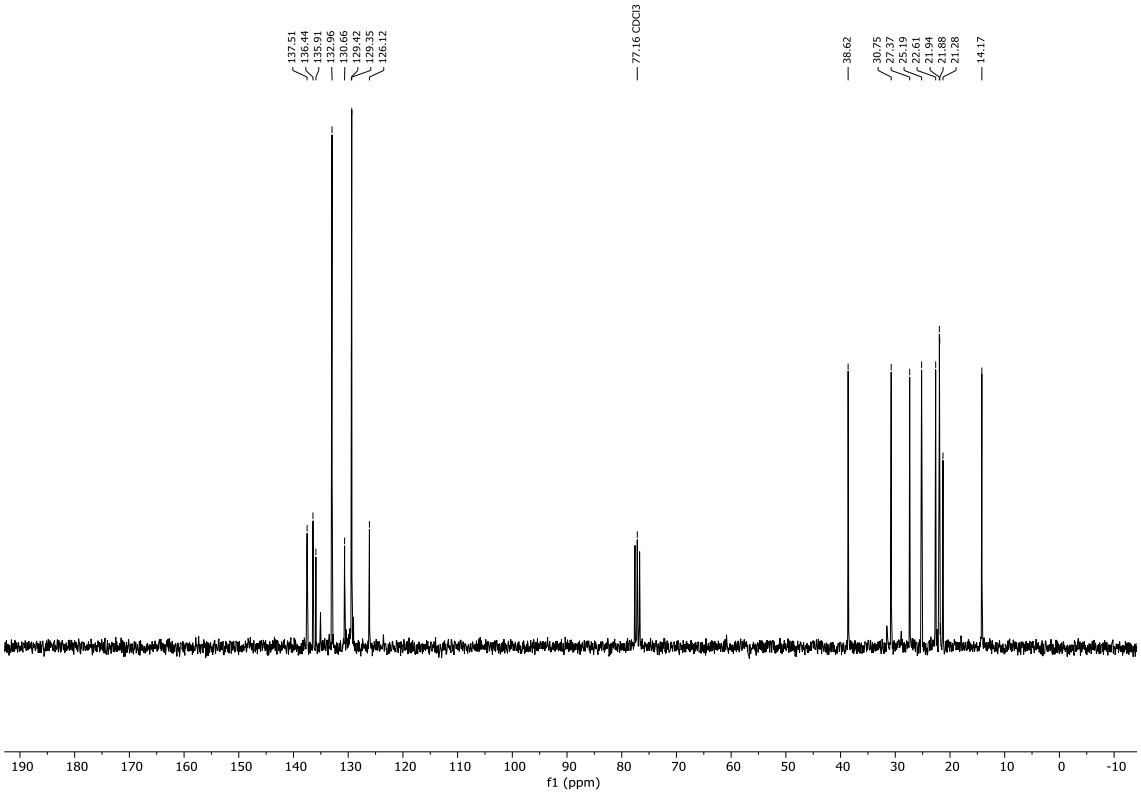


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(2-bromo-1-(cyclohex-1-en-1-yl)hex-1-en-1-yl) (*p*-tolyl)sulfide (4m)

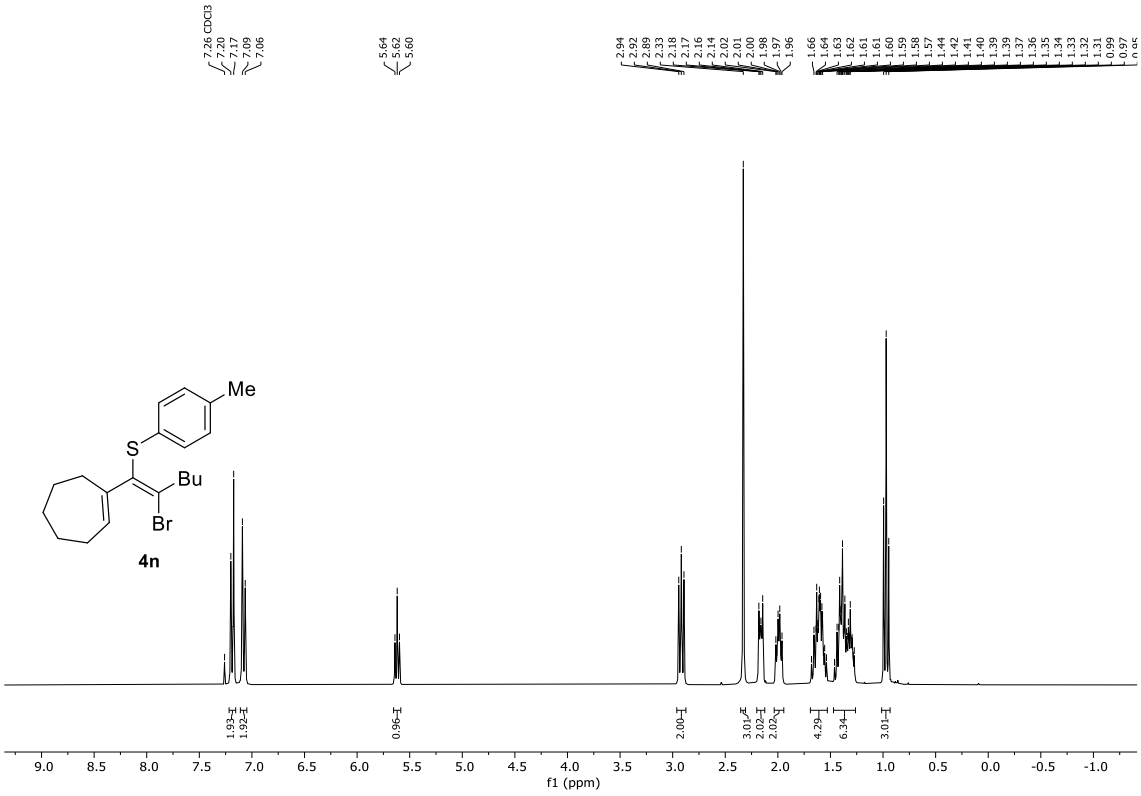


^{1}H-NMR (300 MHz, $CDCl_3$)

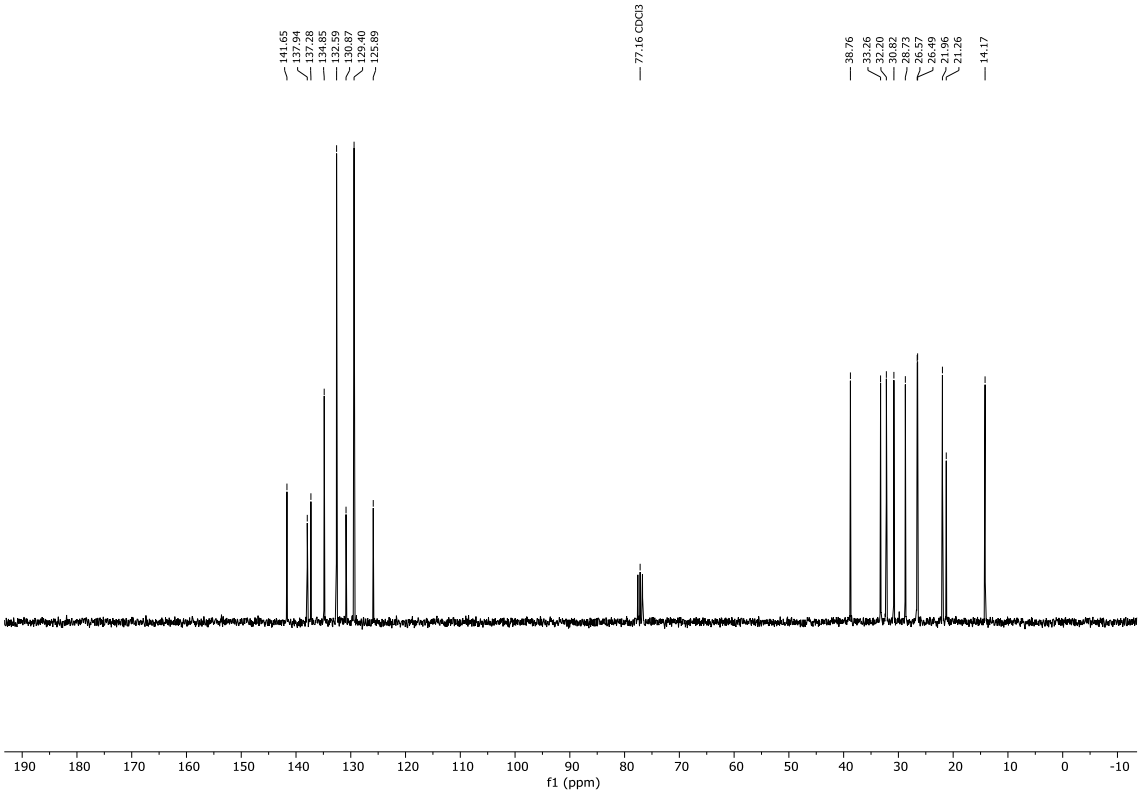


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(1-(cyclohept-1-en-1-yl)-2-bromohex-1-en-1-yl) (*p*-tolyl)sulfide (4n)

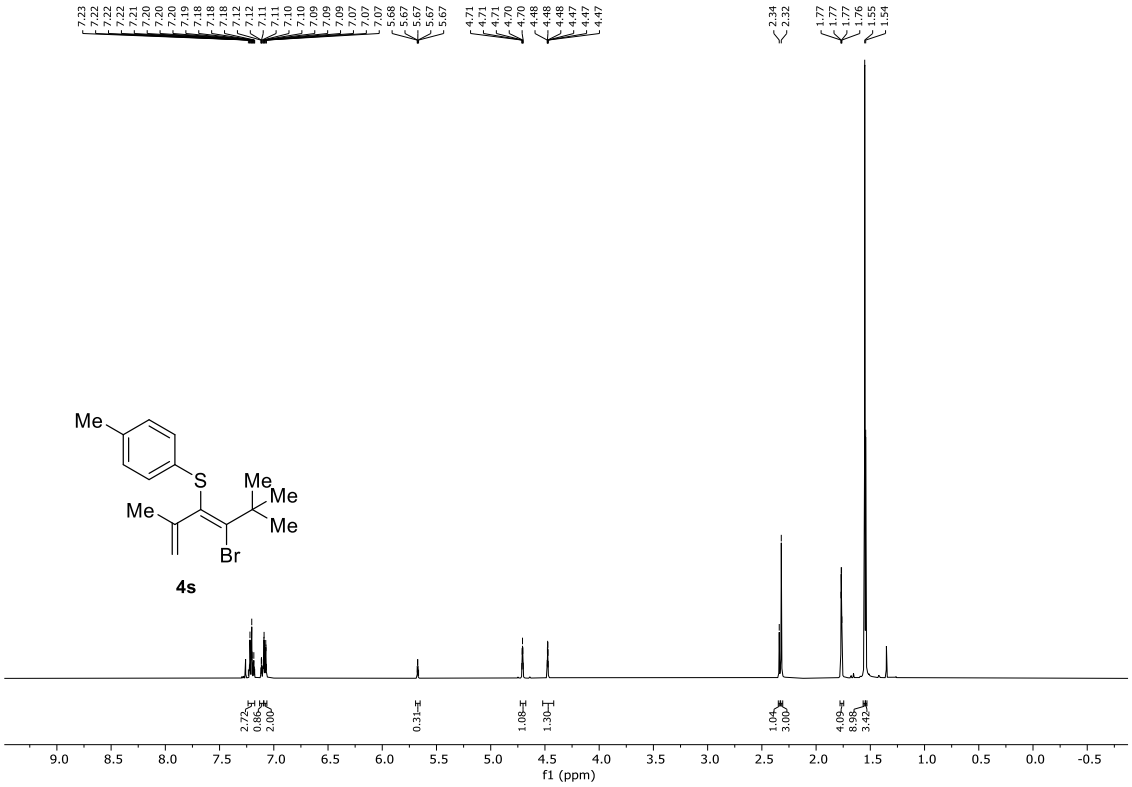


^{1}H-NMR (300 MHz, $CDCl_3$)

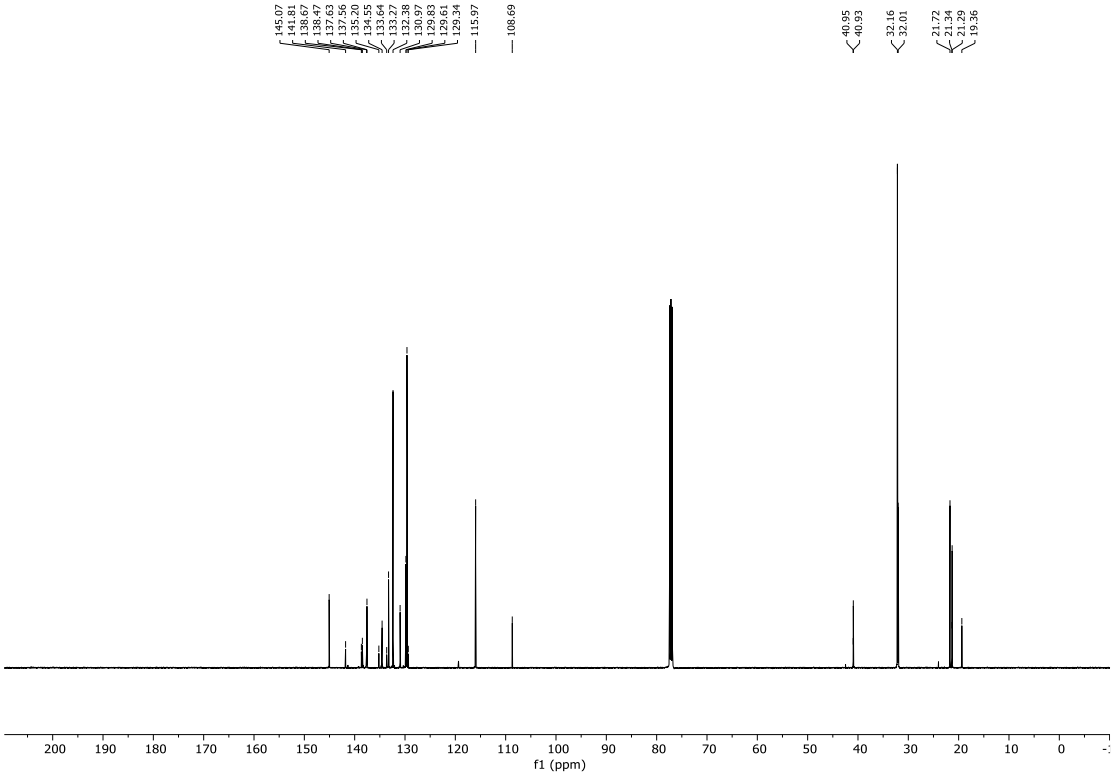


^{13}C-NMR (75 MHz, $CDCl_3$)

(4-bromo-2,5,5-trimethylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (4s) (*E*:*Z* 3:1)

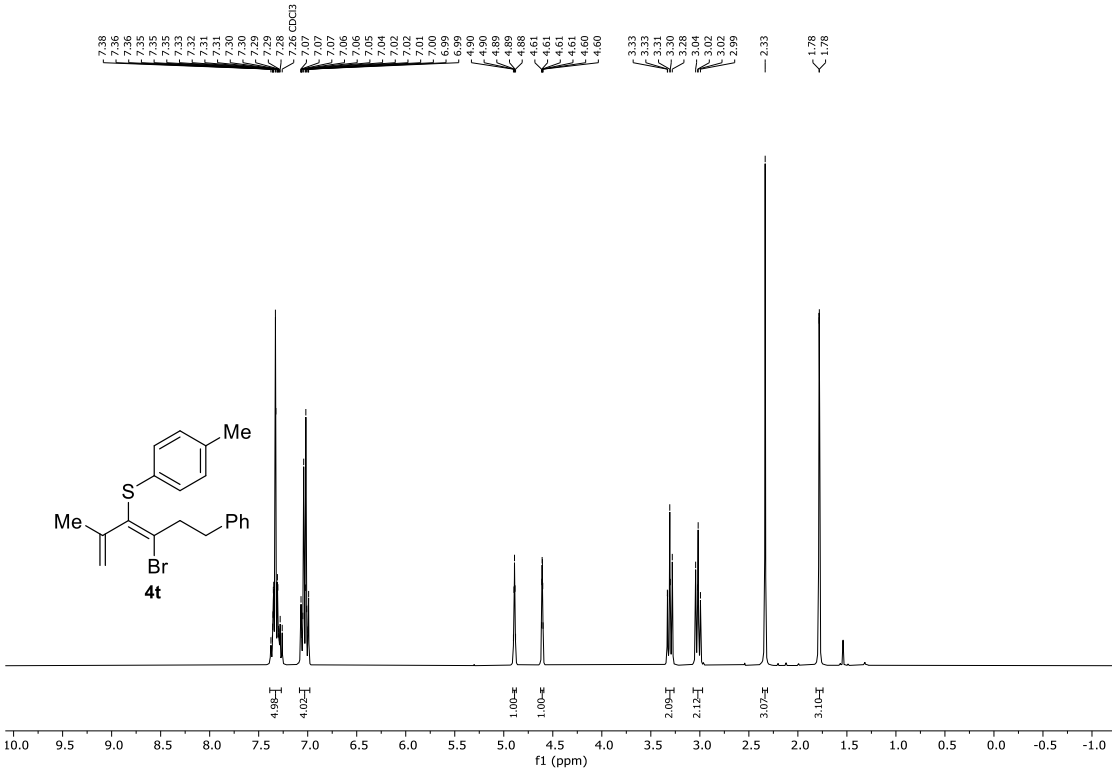


^{1}H-NMR (300 MHz, $CDCl_3$)

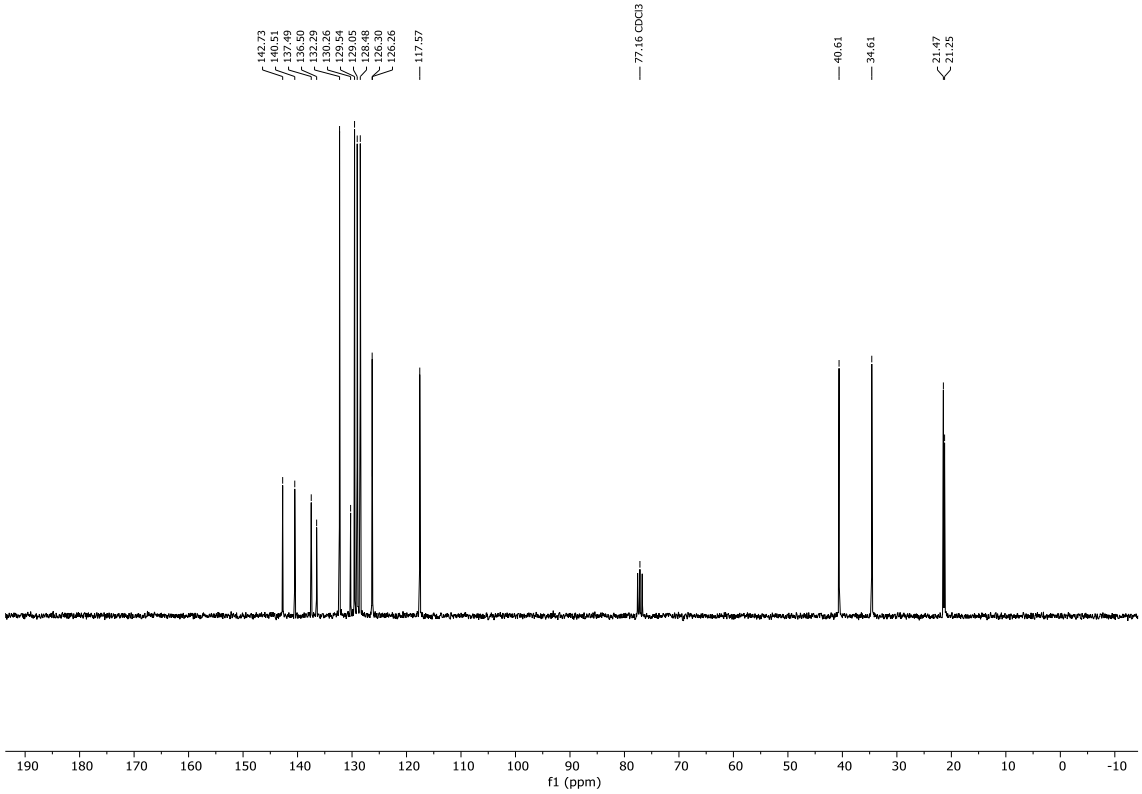


^{13}C-NMR (75 MHz, $CDCl_3$)

(*E*)-(4-bromo-2-methyl-6-phenylhexa-1,3-dien-3-yl) (*p*-tolyl)sulfide (4t)

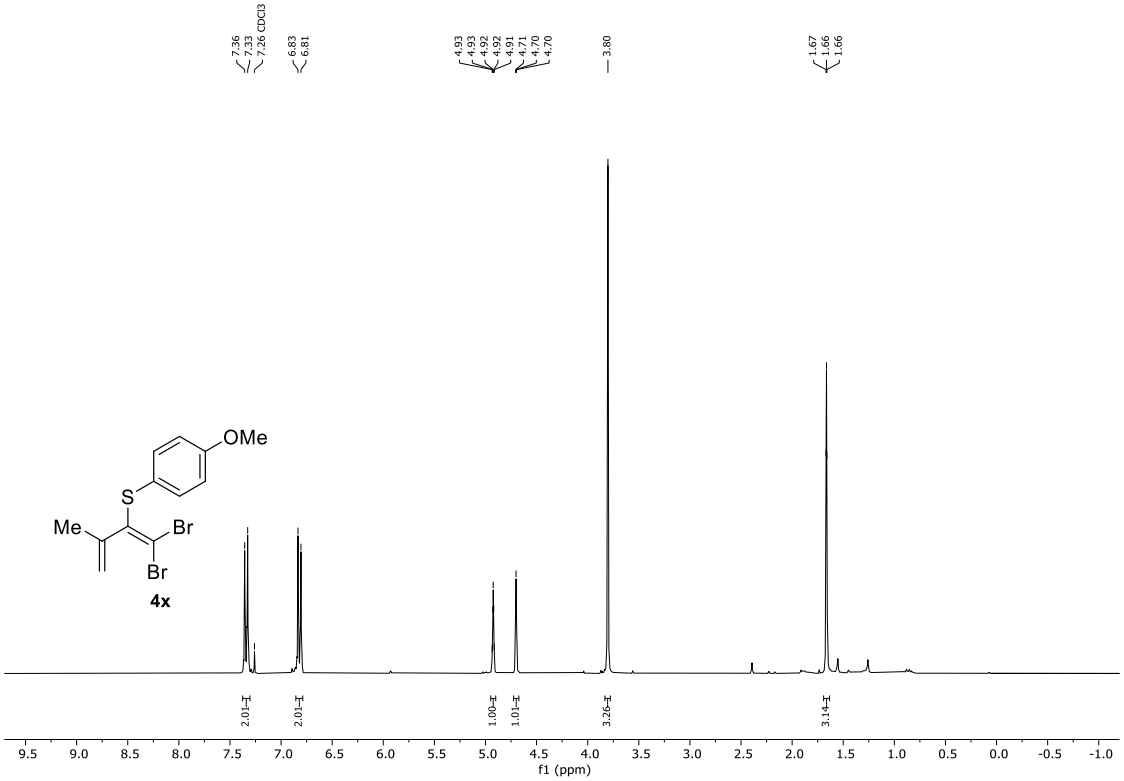


^{1}H-NMR (300 MHz, $CDCl_3$)

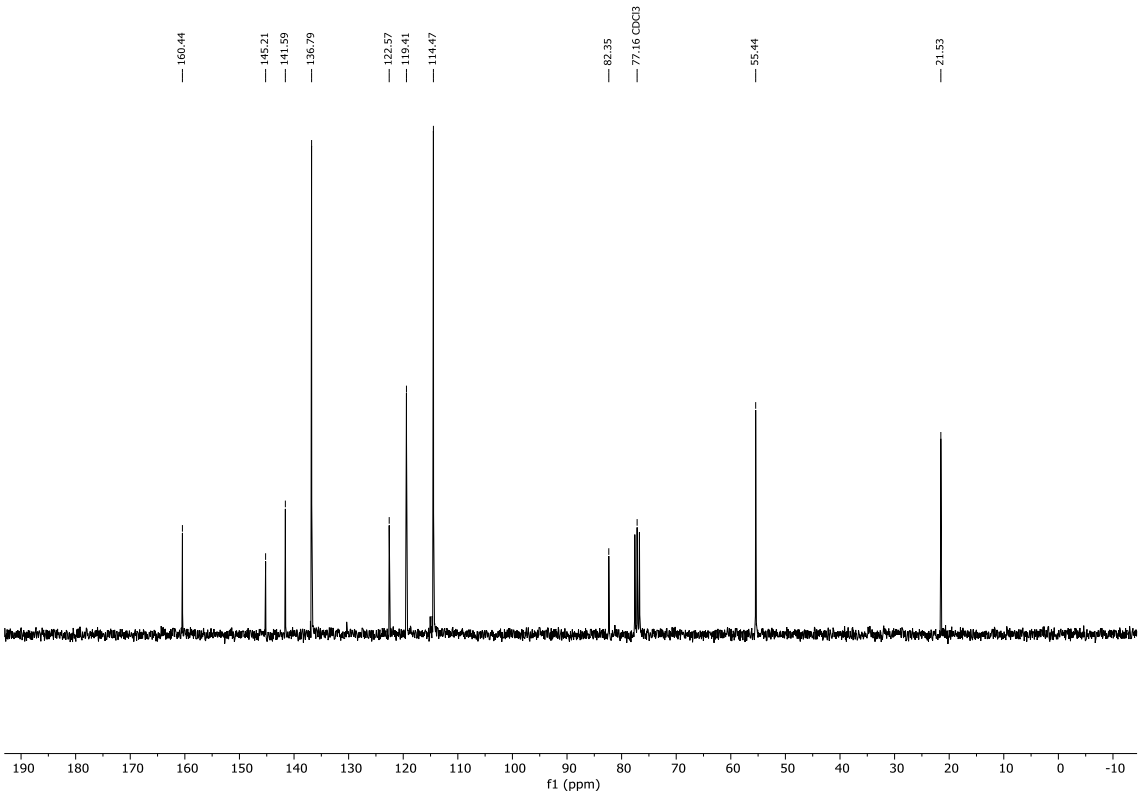


^{13}C-NMR (75 MHz, $CDCl_3$)

(1,1-dibromo-3-methylbuta-1,3-dien-2-yl) (4-methoxyphenyl)sulfide (4x)

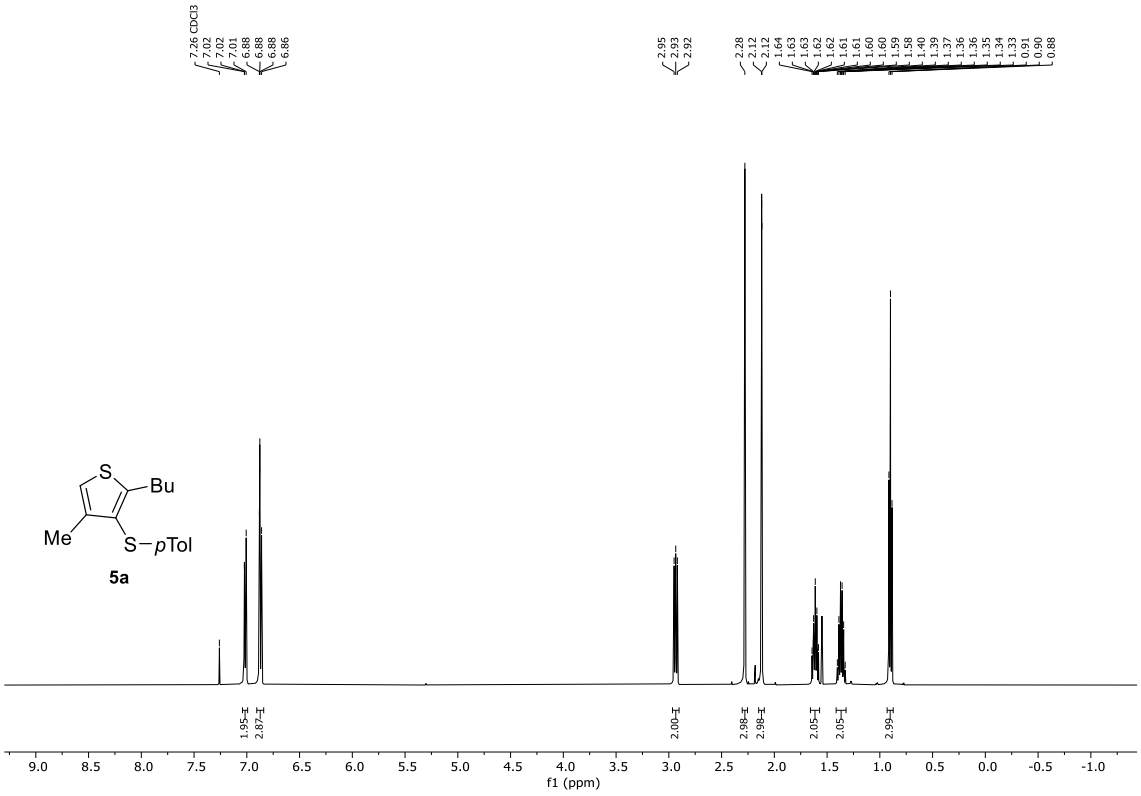


^{1}H-NMR (300 MHz, $CDCl_3$)

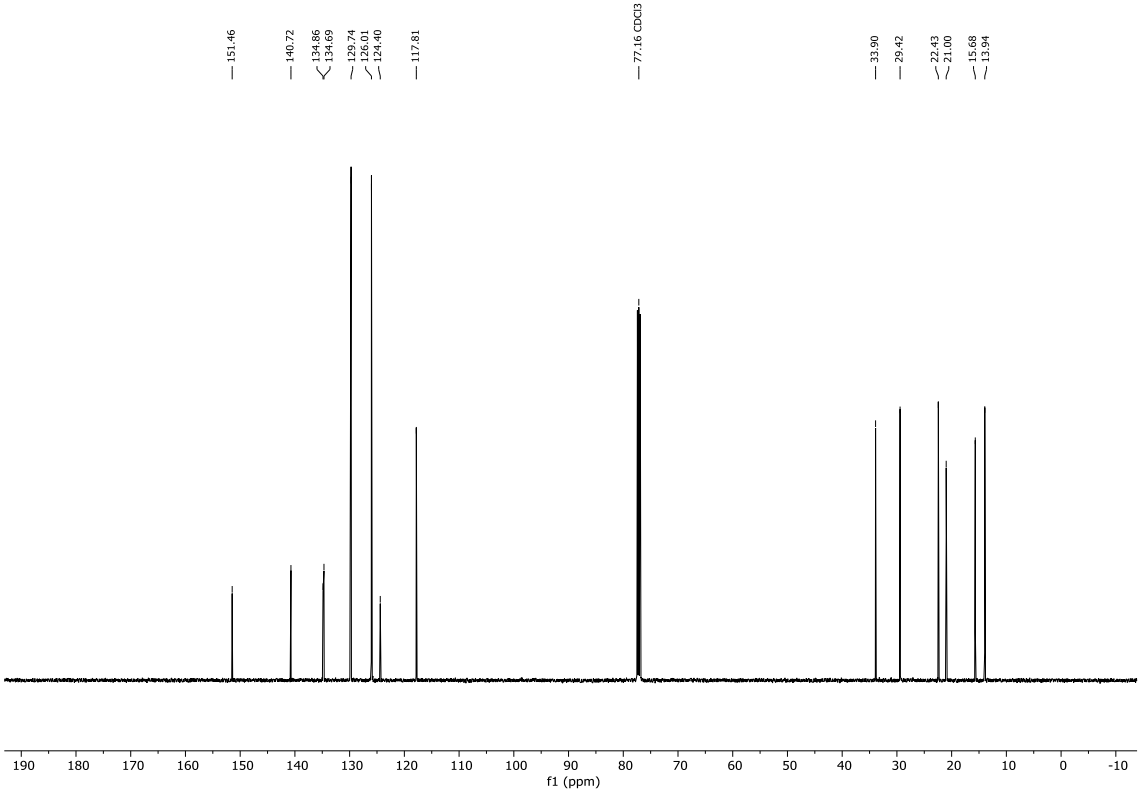


^{13}C-NMR (75 MHz, $CDCl_3$)

2-butyl-4-methyl-3-(*p*-tolylthio)thiophene (5a)

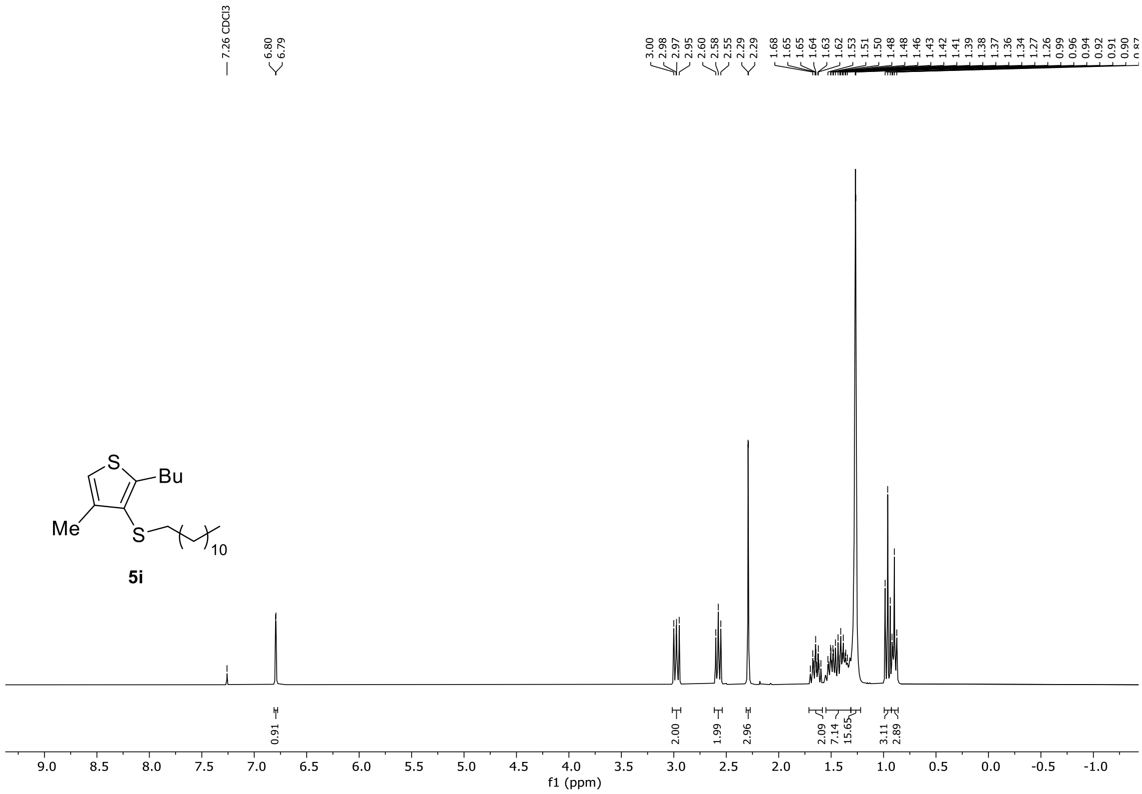


^{1}H-NMR (500 MHz, $CDCl_3$)

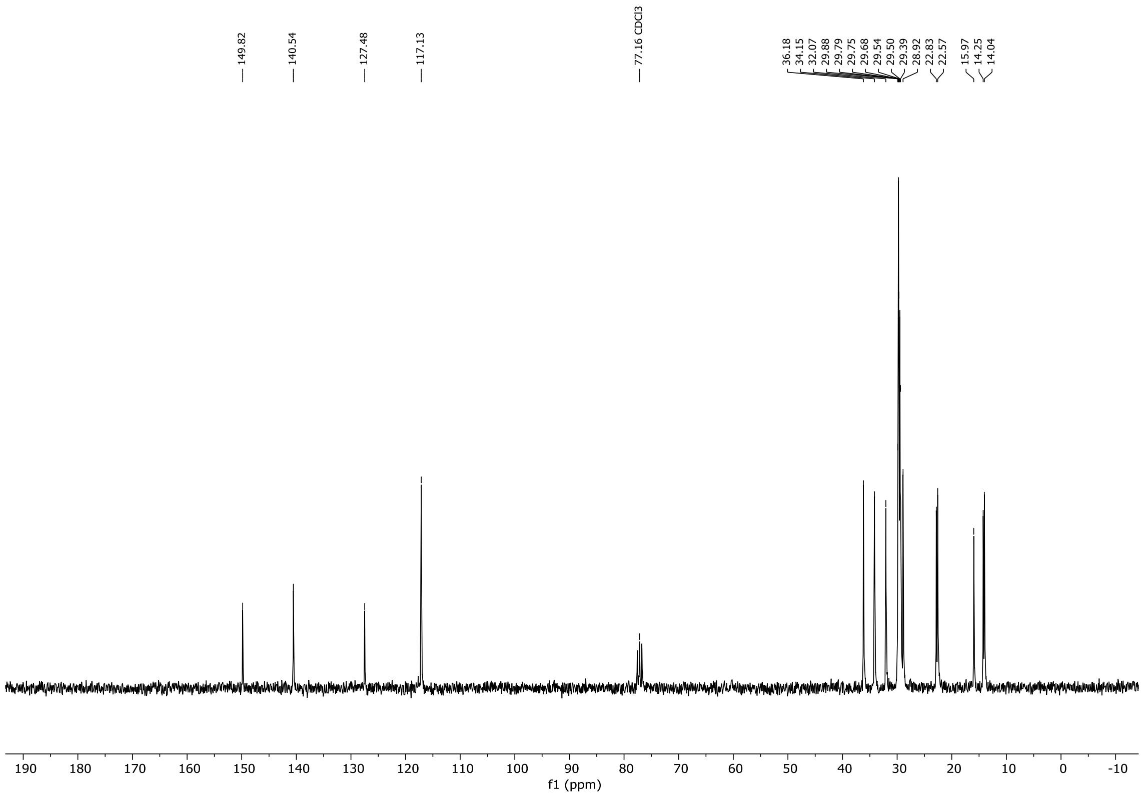


^{13}C-NMR (125 MHz, $CDCl_3$)

2-butyl-3-(dodecylthio)-4-methylthiophene (5i)

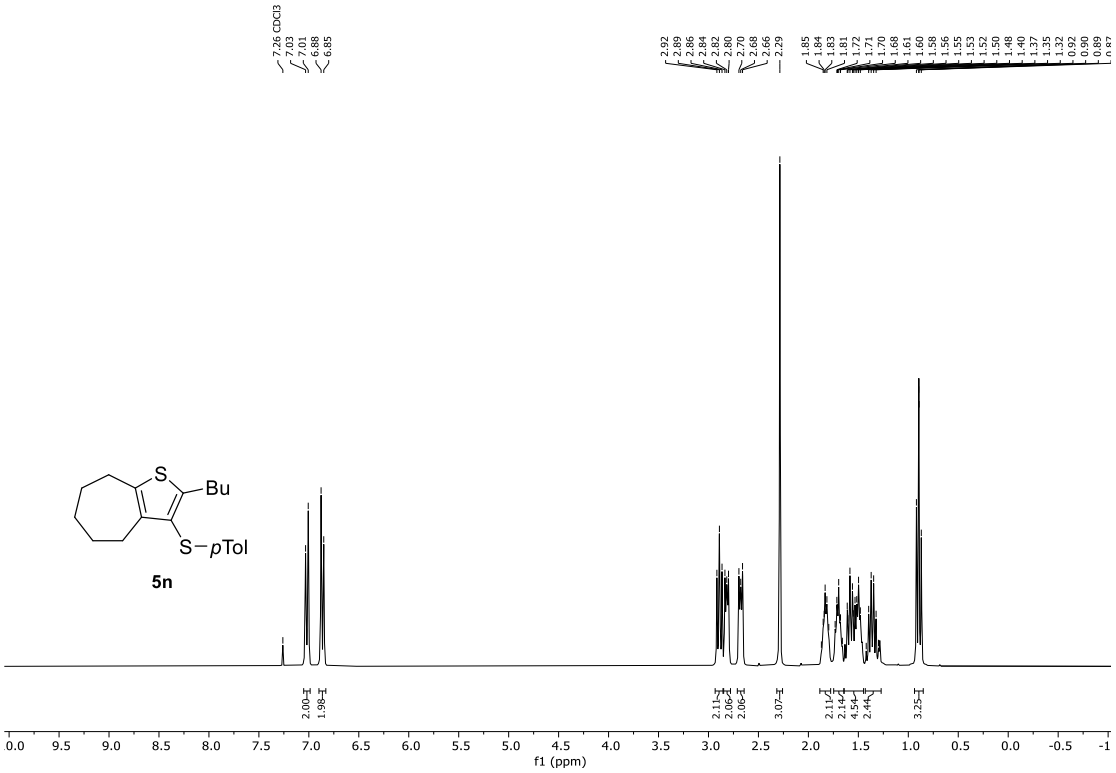


^{1}H-NMR (300 MHz, $CDCl_3$)

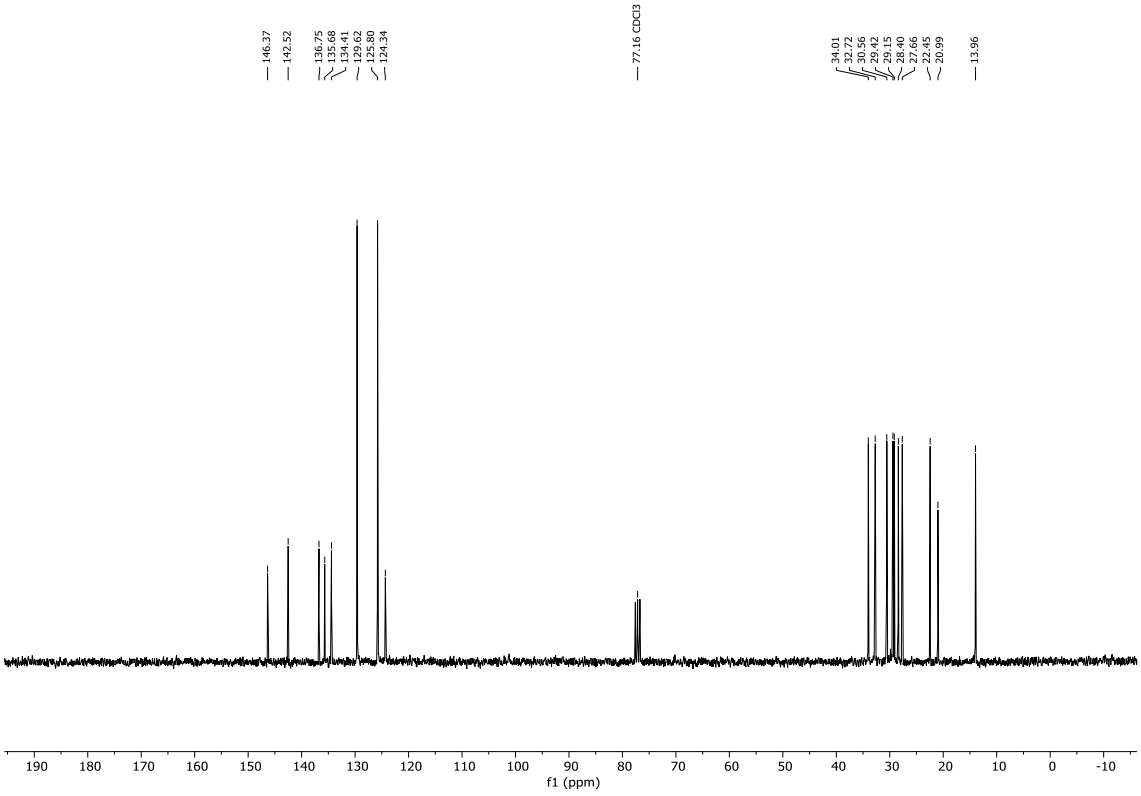


^{13}C-NMR (75 MHz, $CDCl_3$)

2-butyl-3-(*p*-tolylthio)-5,6,7,8-tetrahydro-4*H*-cyclohepta[*b*]thiophene (5n)

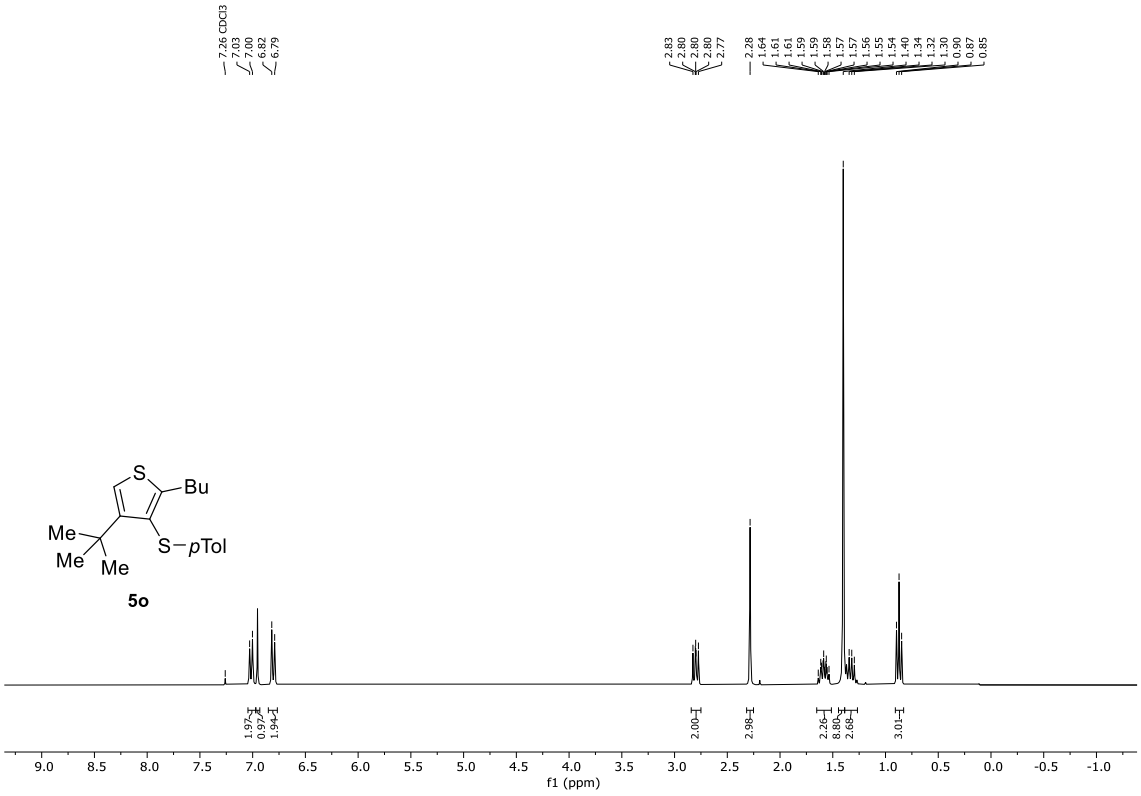


^{1}H-NMR (300 MHz, $CDCl_3$)

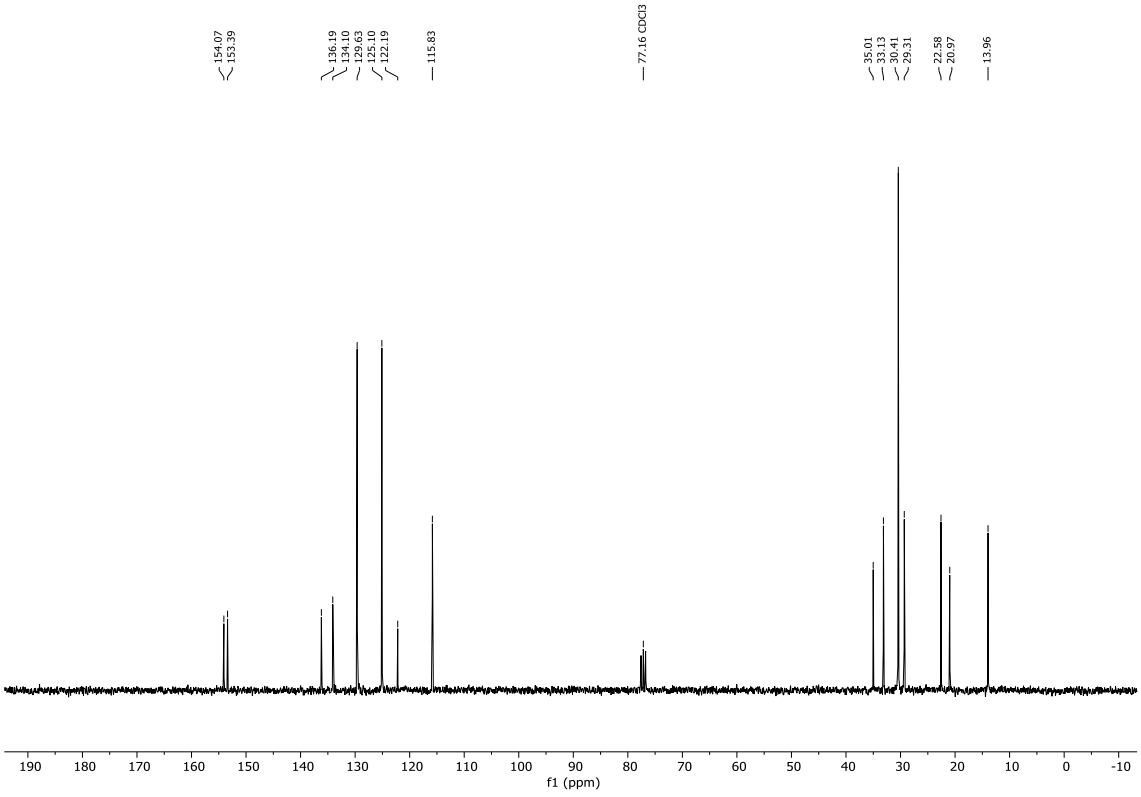


^{13}C-NMR (75 MHz, $CDCl_3$)

4-(*tert*-butyl)-2-butyl-3-(*p*-tolylthio)thiophene (5o)

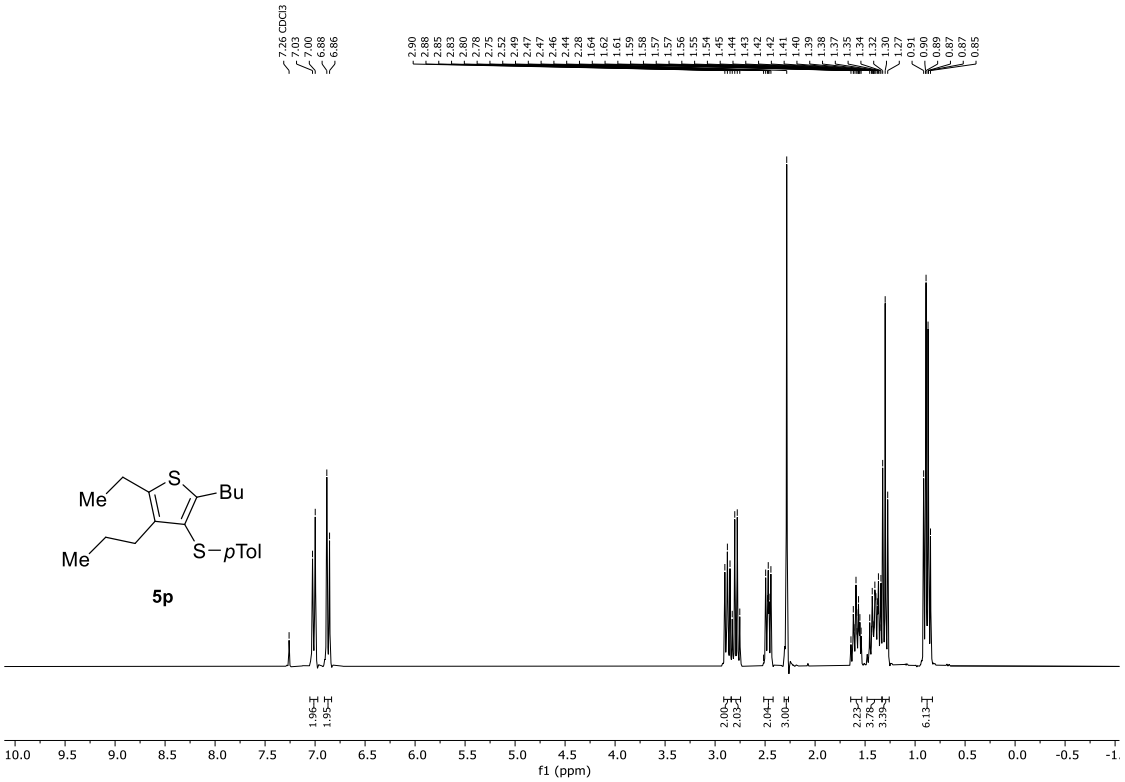


^{1}H-NMR (300 MHz, $CDCl_3$)

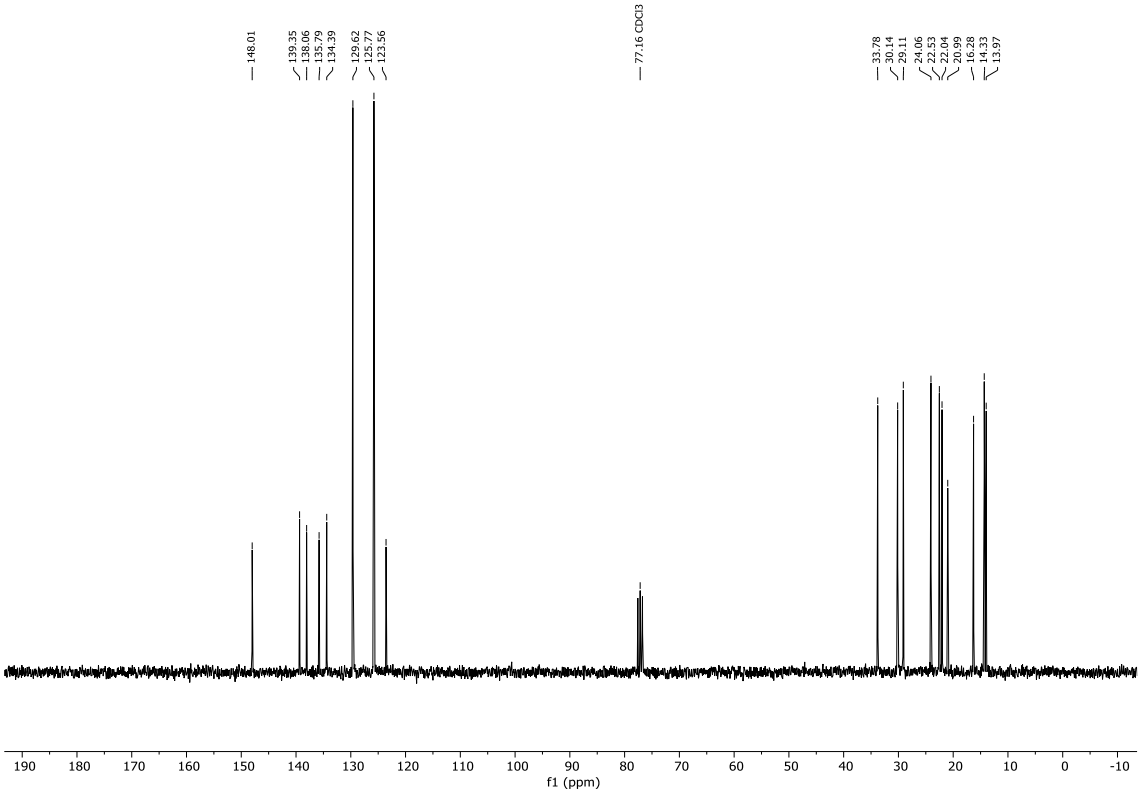


^{13}C-NMR (75 MHz, $CDCl_3$)

2-butyl-5-ethyl-4-propyl-3-(*p*-tolylthio)thiophene (5p)

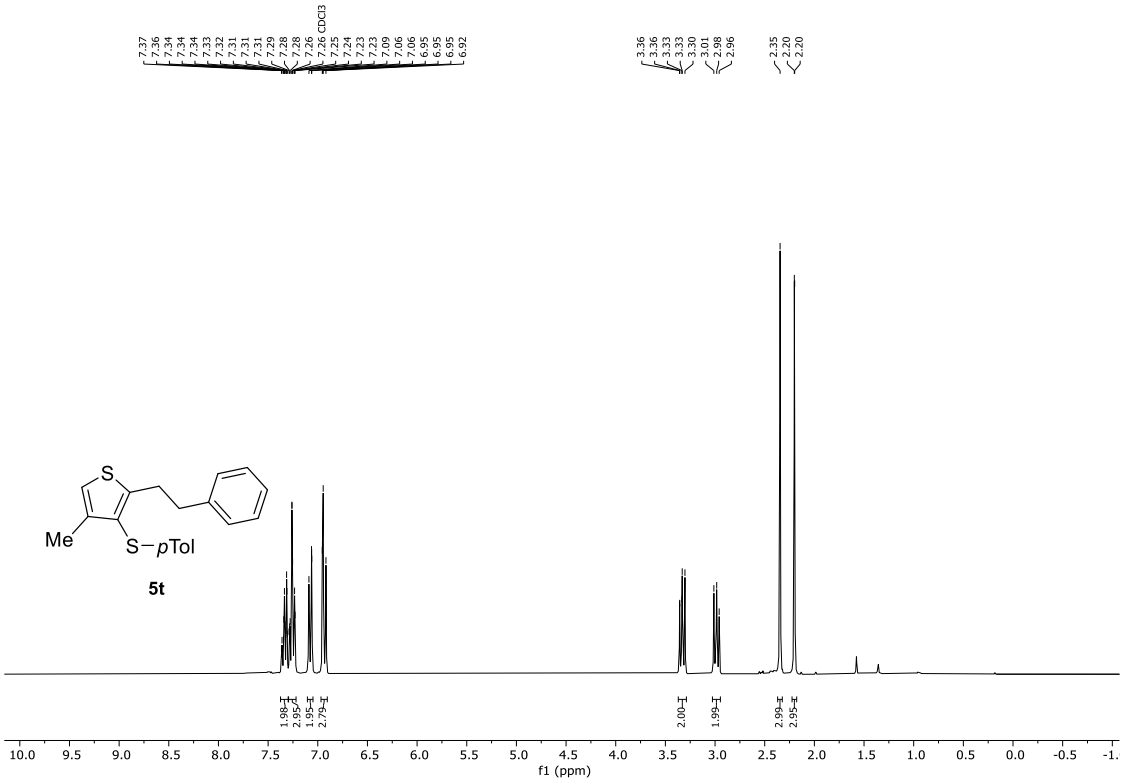


^{1}H-NMR (300 MHz, $CDCl_3$)

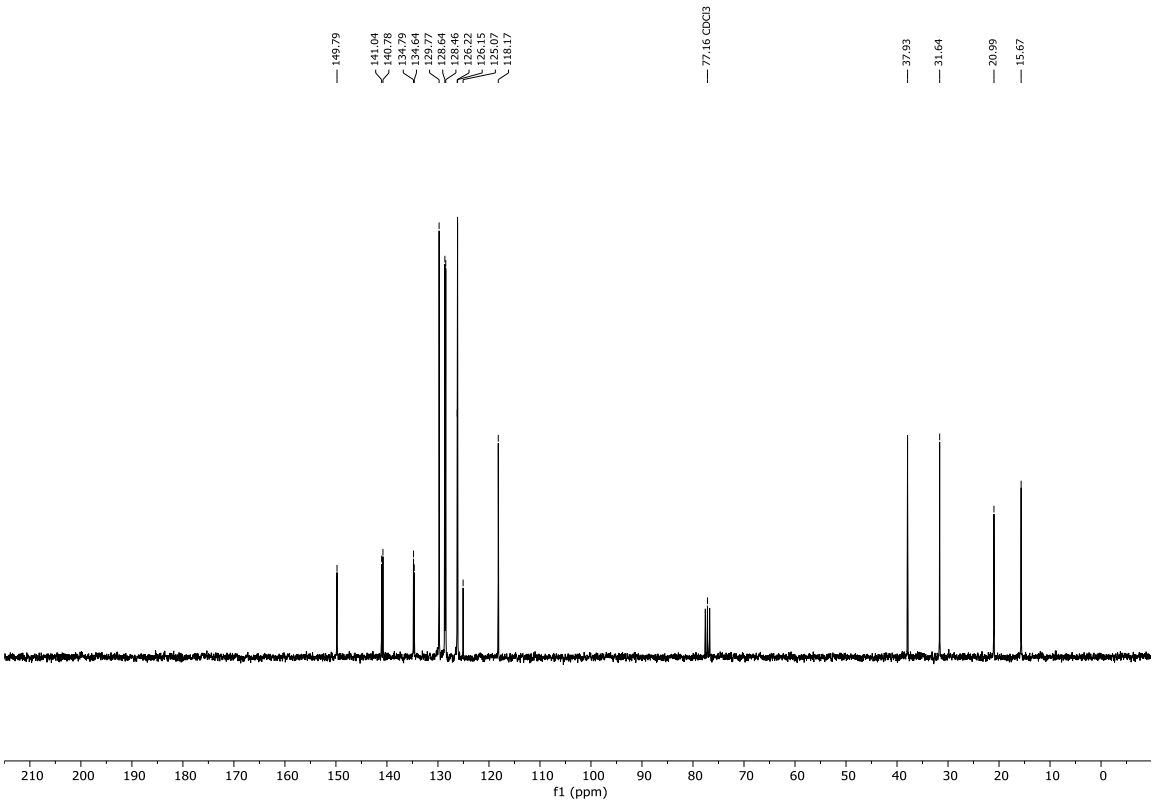


^{13}C-NMR (75 MHz, $CDCl_3$)

4-methyl-2-phenethyl-3-(*p*-tolylthio)thiophene (5t)

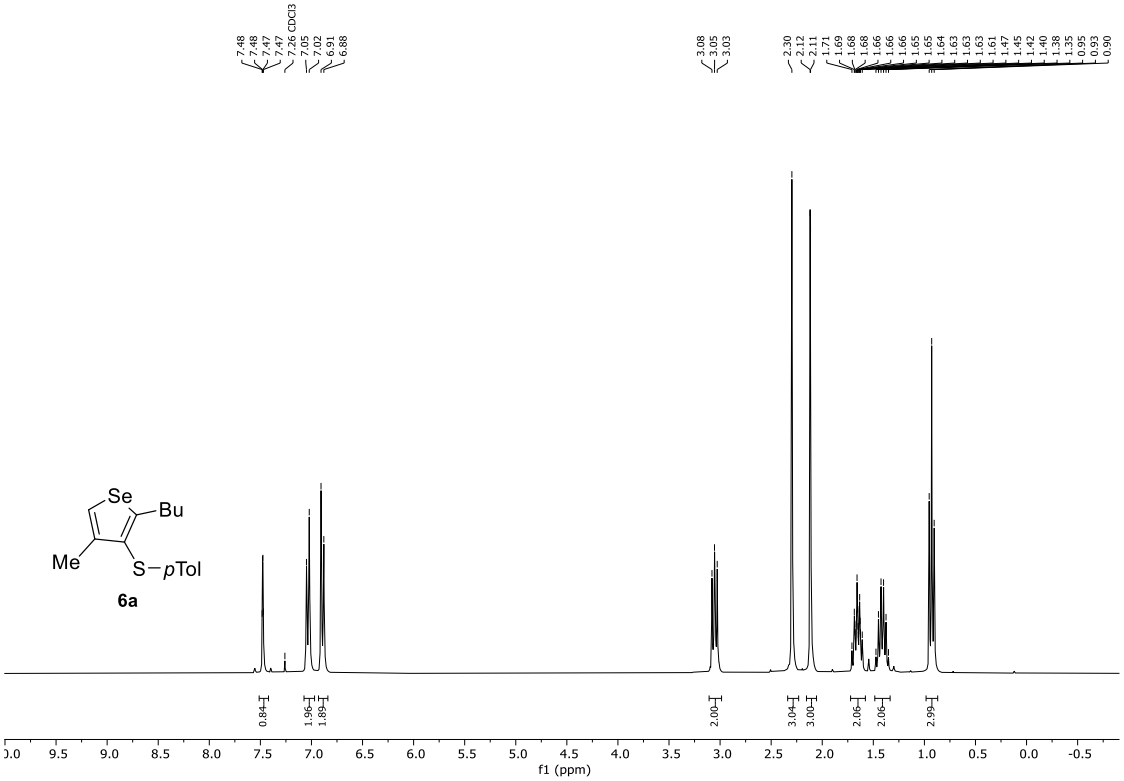


^{1}H-NMR (300 MHz, $CDCl_3$)

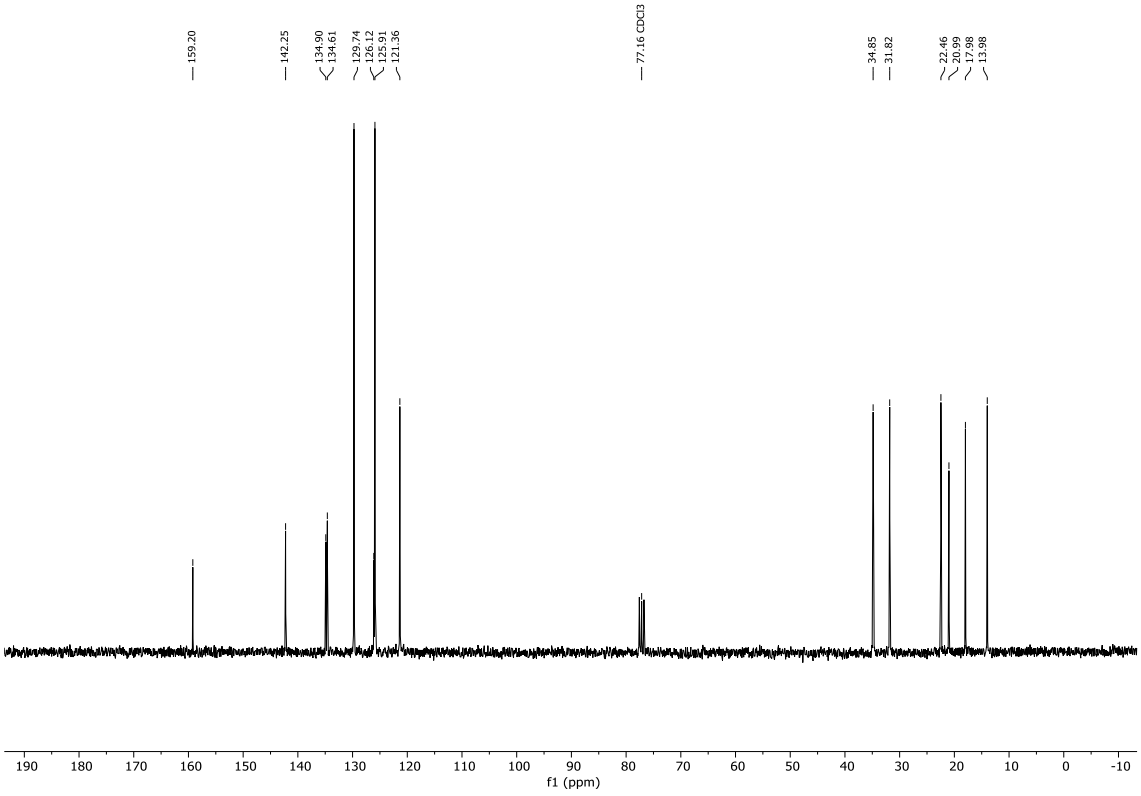


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-butyl-4-methylselenophen-3-yl) (*p*-tolyl)sulfide (6a)

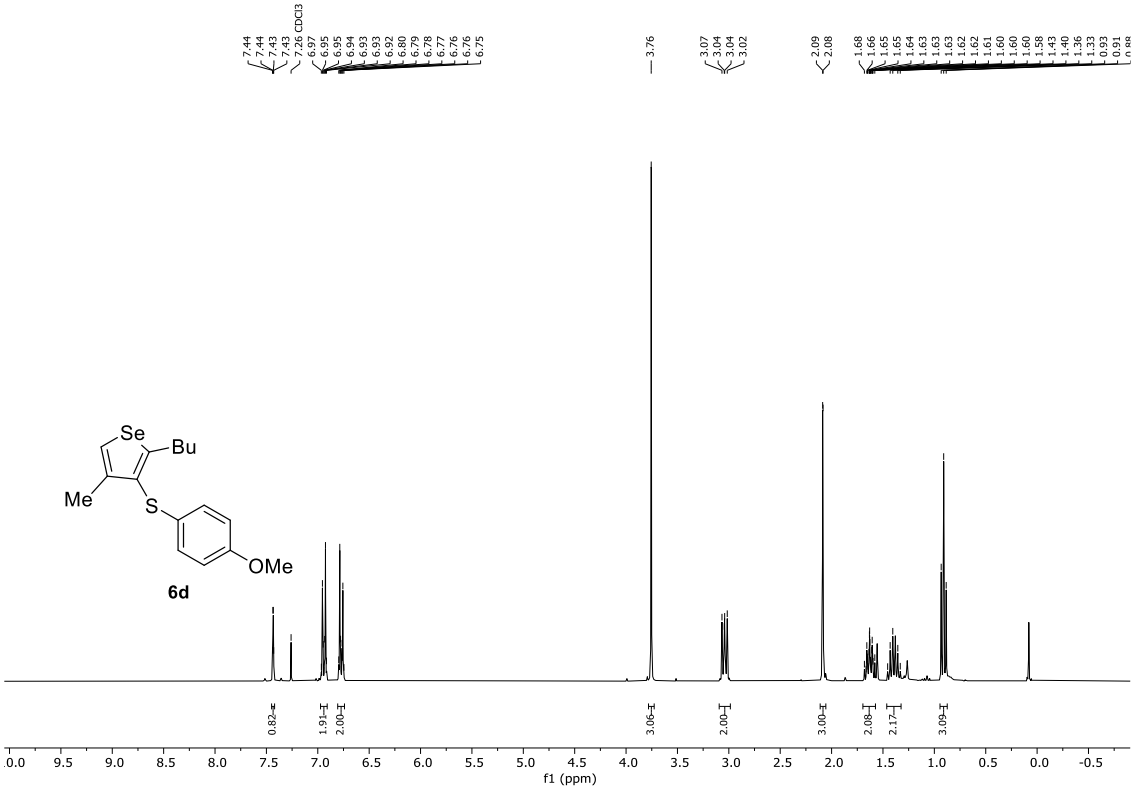


^{1}H-NMR (300 MHz, $CDCl_3$)

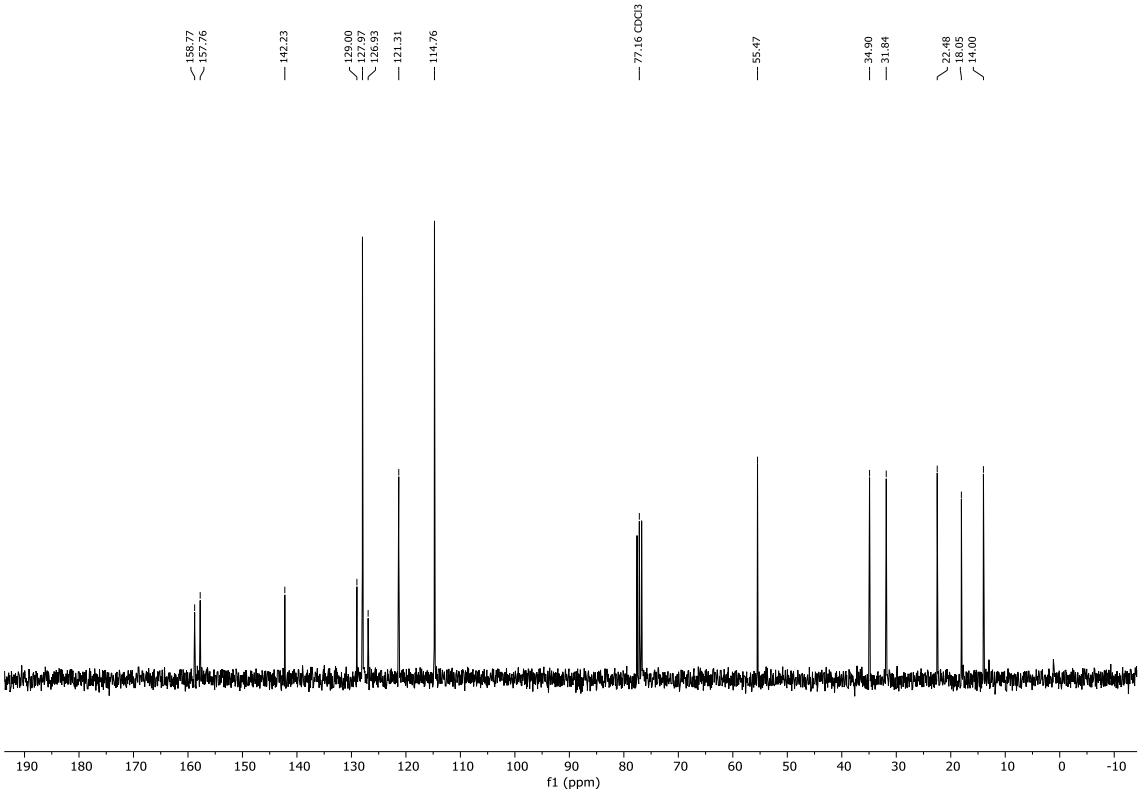


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-butyl-4-methylselenophen-3-yl) (4-methoxyphenyl)sulfide (6d)

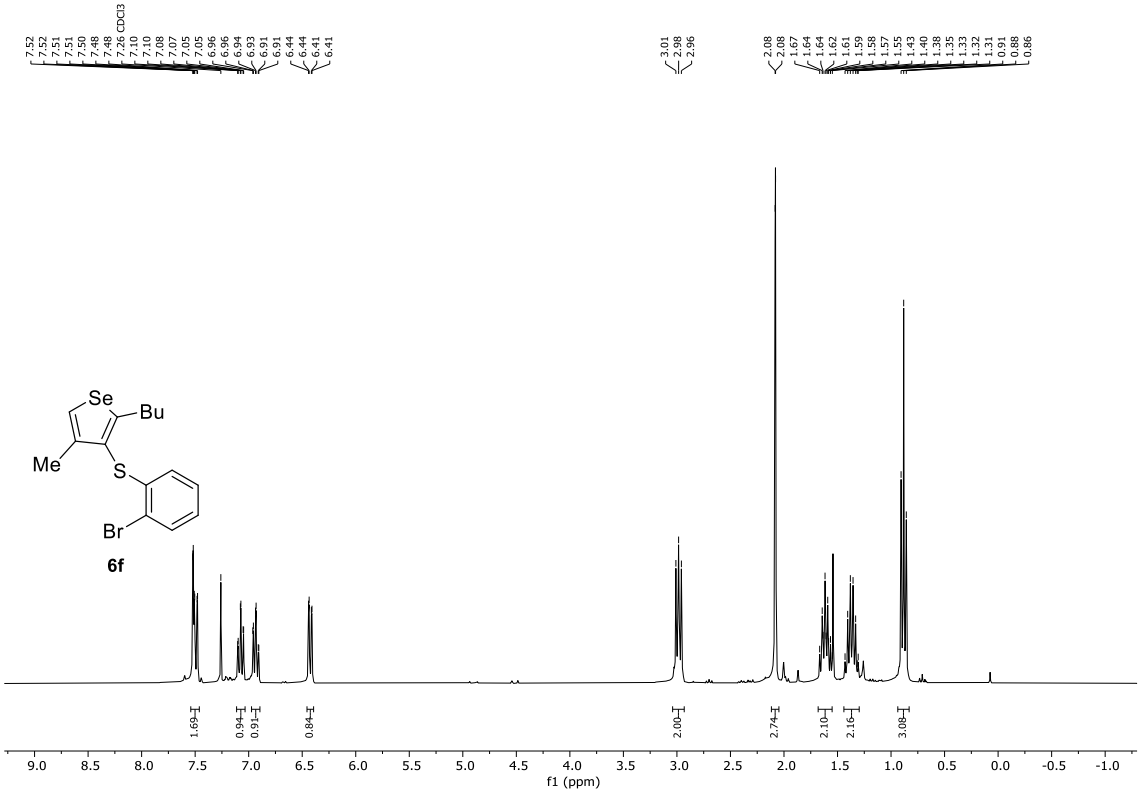


^{1}H-NMR (300 MHz, $CDCl_3$)

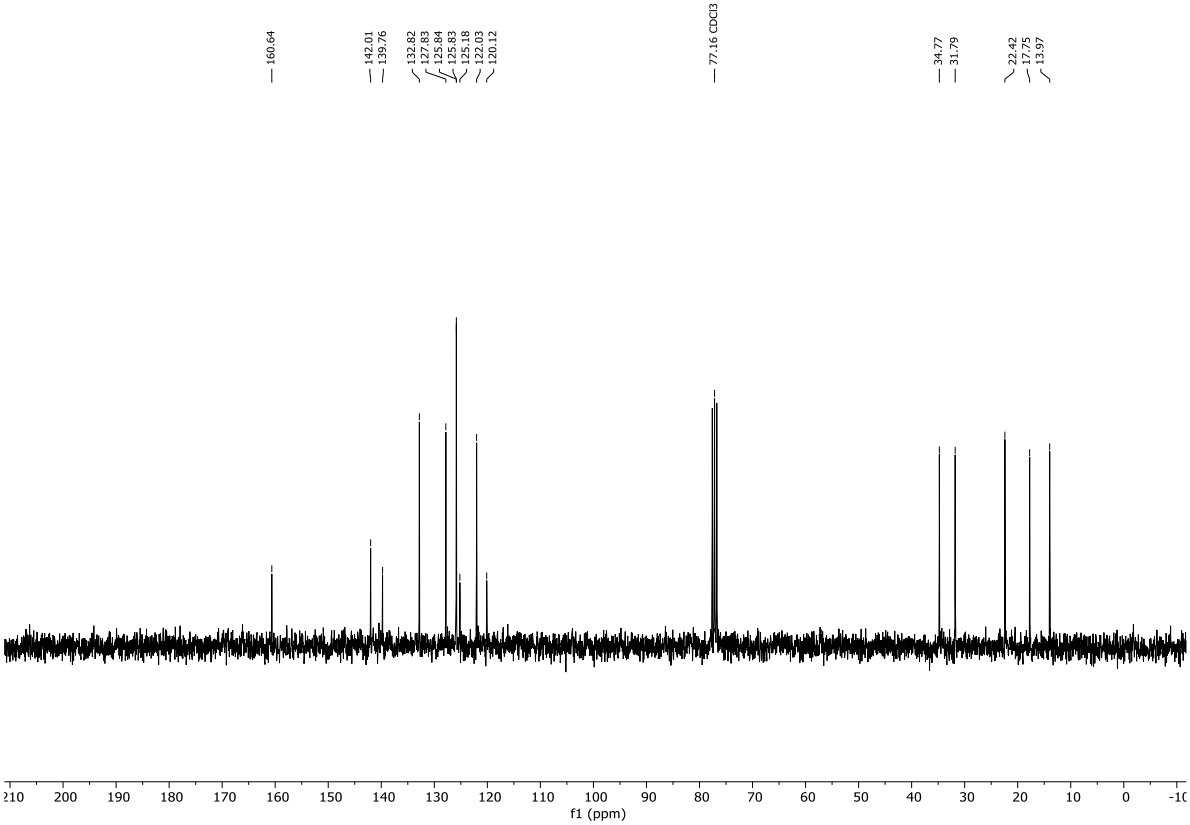


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-bromophenyl) (2-butyl-4-methylselenophen-3-yl)sulfide (6f)

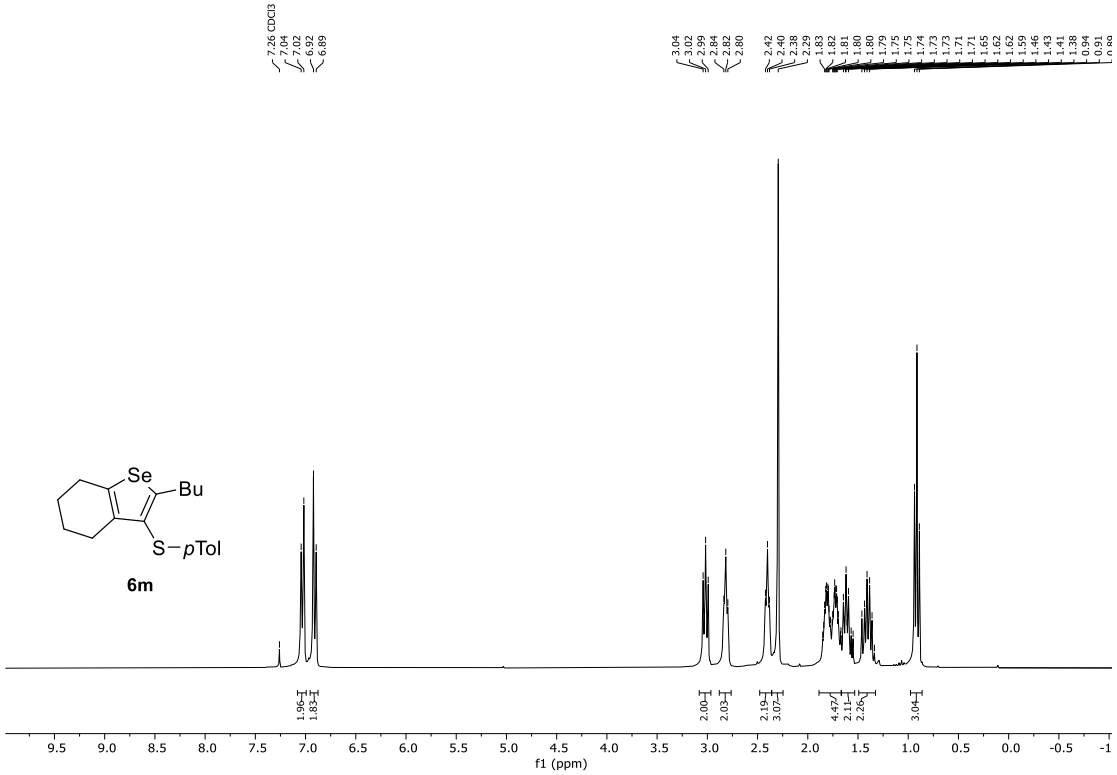


^{1}H-NMR (300 MHz, $CDCl_3$)

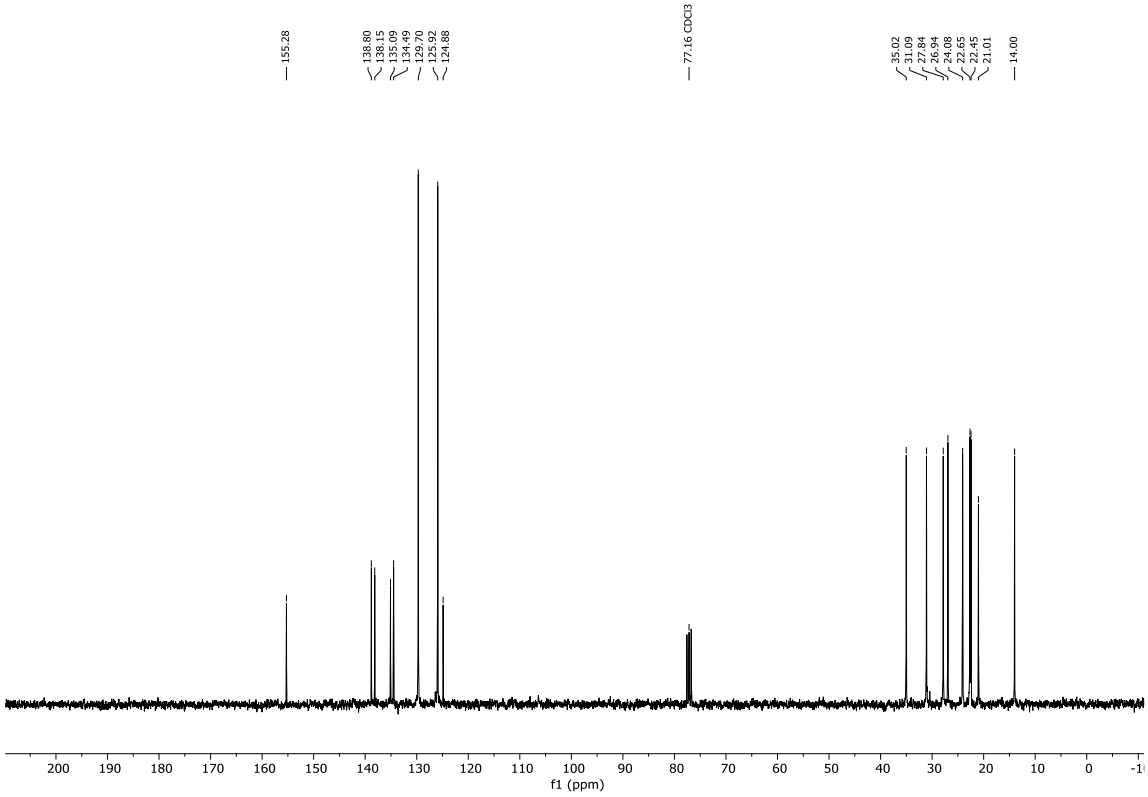


^{13}C-NMR (75 MHz, $CDCl_3$)

(2-butyl-4,5,6,7-tetrahydrobenzo[*b*]selenophen-3-yl) (*p*-tolyl)sulfide (6m)



^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (75 MHz, $CDCl_3$)