Sulfur Mediated Propargylic C−H Alkylation of Alkynes

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Electronic Supplementary Information

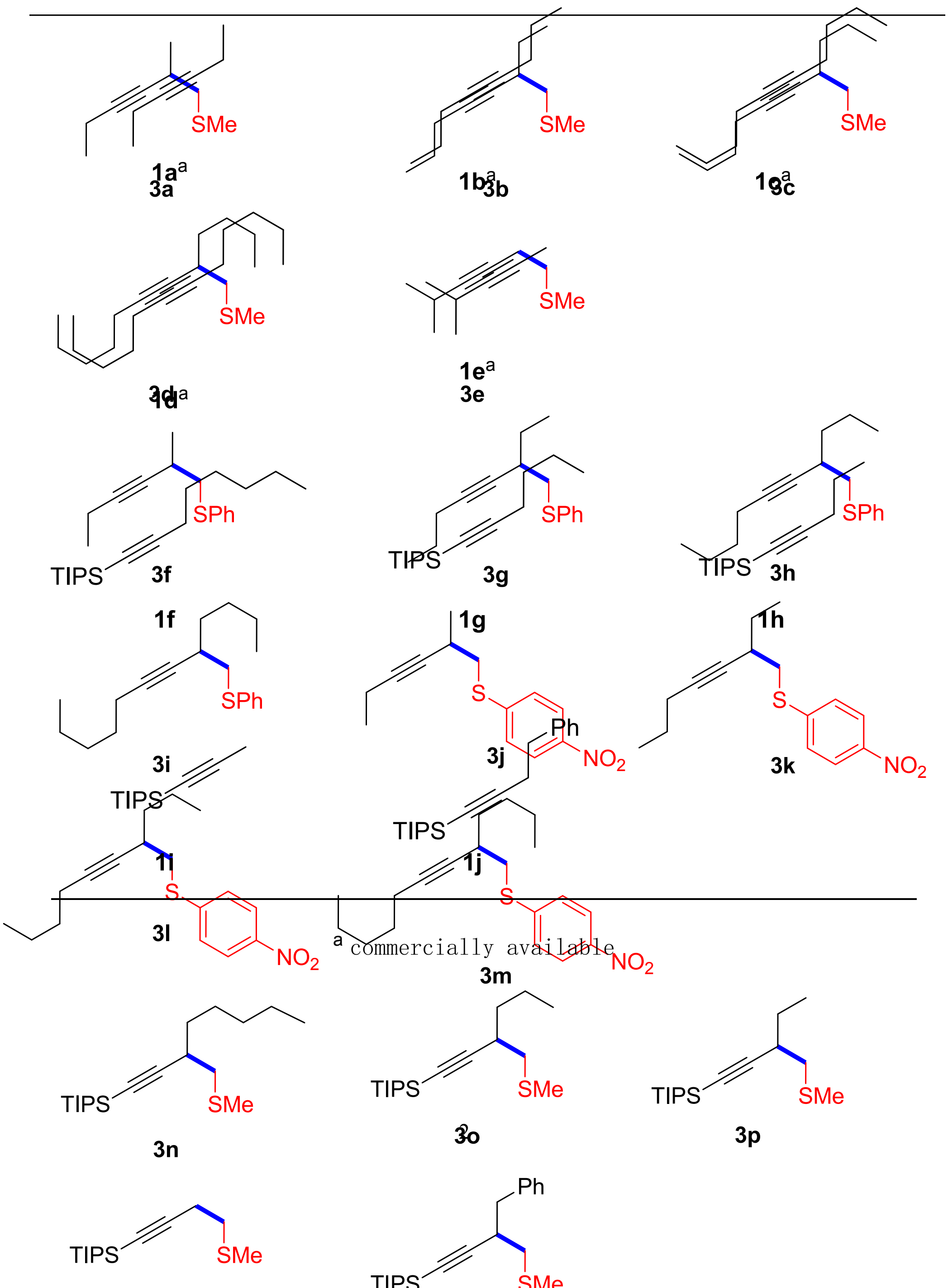
Content

I. General Information

Unless otherwise noted, all materials were purchased from commercial suppliers. Dichloromethane was refluxed over CaH_2, and freshly distilled prior to use. Tetrahydrofuran (THF) and toluene were refluxed with sodium/benzophenone, and freshly distilled prior to use. Potassium *tert*-butoxide was sublimed under reduce pressure prior to use. *tert*-Butanol was refluxed over CaH_2, and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200-300 mesh) from Branch of Qingdao Haiyang Chemical. Petroleum ether used for column chromatography were 60-90 ^{o}C fraction, and the removal of residue solvent was accomplished under rotovap with repeated azeotrope with chloroform, and then evaporation under vacuum (< 1 mmHg pressure). Reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates from Yantai Chemical Industry Research Institute. The plates were visualized under UV light, as well as other TLC stains (phosphomolybdic acid: 10% in ethanol; potassium permanganate: 1% in water; iodine: 10 g iodine absorbed on 30g silica gel). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer, usually in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) were reported in parts per million (ppm). The IR spectra (KBr pellets, ν [cm^{-1}]) were taken on a Nicolet 5700 FTIR spectrometer. HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. LRMS measurements were carried out on Thermo Fisher TRACE 1300 GC System with an Thermo Fisher ISQ Mass Selective Detector. Melting points were obtained on a Yanaco MP-500 melting point apparatus and were uncorrected.

II. Compounds Chart

The substrates used in propargylic alkylation reaction



1a[a] **3a** **1b**[a] **3b** **1c**[a] **3c**

3d **1d**[a] **1e**[a] **3e**

3f **3g** **3h**

1f **1g** **1h**

3i **3j** **3k**

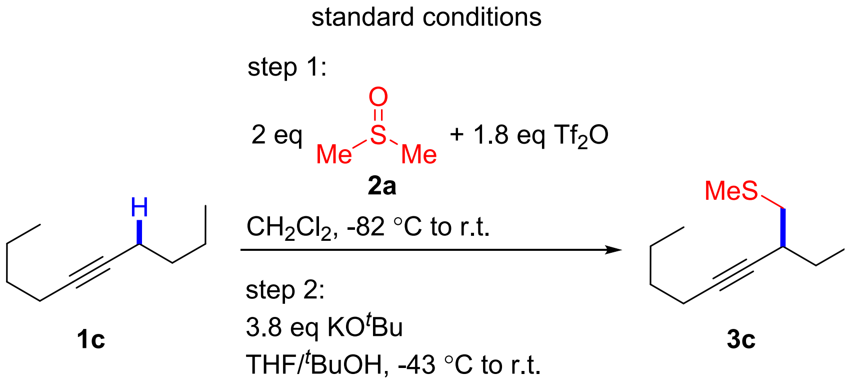
1l **1j**

3l **3m**

[a] commercially available

3n **3o** **3p**

III. Optimization of Reaction Conditions



Entry	variation from standard conditions	yield of **3c** (%)[a]
1	none	50
2	use 1.3 eq DMSO (**2a**), 1.2 eq Tf$_2$O in step 1	48
3	use LiO^{t}Bu instead of KO^{t}Bu as base in step 2	30
4	use NaO^{t}Bu instead of KO^{t}Bu as base in step 2	45
5	use DBU instead of KO^{t}Bu as base in step 2	10
6	use LiH instead of KO^{t}Bu as base in step 2	0
7	use triethylamine instead of KO^{t}Bu as base in step 2	0
8	use $(CF_3CO)_2O$ instead of Tf$_2$O in step 1	0
9	reaction conducted from -43 °C to room temperature in step 1	41
10	reaction conducted from 0 °C to room temperature in step 1	27
11	reaction conducted at room temperature in step 1	39

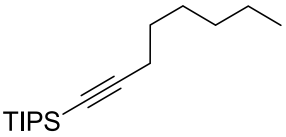
[a] Isolated yield for 0.2 mmol scale reactions.

IV. Experimental Procedures and Characterization Data

A. Preparation of alkyne substrates

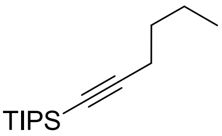
General Procedure 1[1]:

Under a nitrogen atmosphere, to a flame-dried 50 mL flask, 1 eq 1-octyne (2.2 g, 20 mmol) was added, and then dissolved with tetrahydrofuran (30 mL) before cooling down to -82 °C. 1.1 eq *n*-BuLi (2.6 M, 8.5 mL) was added dropwise, after 2 hours at -82°C, the reaction was stirred at 0 °C for 2 hours. and then 1.1 eq tris-isopropylchlorosilane 4.7 mL was added, warming up to room temperature over 5 hours. The reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with petro ether, dried over sodium sulfate, and purified with flash column chromatography to give 1.91 g product **1f** as an oil in 36% yield.



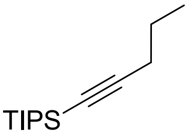
1f

Triisopropyl(oct-1-yn-1-yl)silane (**1f**) was synthesized according to General Procedure 1 from 1- octyne (2.2 g, 20 mmol), eluted by petroleum ether, to give 1.91 g product **1f** as an oil in 36% yield.



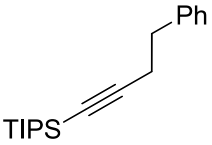
1g

Hex-1-yn-1-yltriisopropylsilane (**1g**) was synthesized according to General Procedure 1 from 1- hexyne (1.476 g, 18 mmol), eluted by petroleum ether, to give 2.175 g product **1g** as an oil in 51% yield.



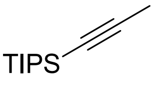
1h

Triisopropyl(pent-1-yn-1-yl)silane (**1h**) was synthesized according to General Procedure 1 from 1- pentyne (1.224 g, 18 mmol), eluted by petroleum ether, to give 2.060 g product **1h** as an oil in 51% yield.



1j

Triisopropyl(4-phenylbut-1-yn-1-yl)silane(**1j**) was synthesized according to General Procedure 1 from but-3-yn-1-ylbenzene (1 g, 7.7 mmol), eluted by petroleum ether, to give 1.995 g product **1j** as an oil in 90% yield.



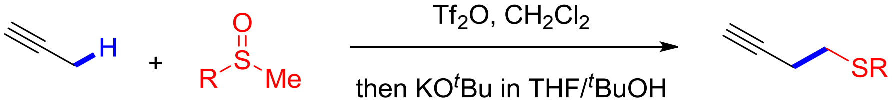
1i

Triisopropyl(prop-1-yn-1-yl)silane **1i**

Under a nitrogen atmosphere, to a flame-dried 50 mL flask, 1 eq ethynyltriisopropylsilane (1.82 g, 10 mmol) was added, and then dissolved with tetrahydrofuran (30 mL) before cooling down to -82 ºC. 1.1 eq n-BuLi (2.6 M, 8.5 mL) was added dropwise, after 2 hours at -82ºC, and then 1.3 eq iodomethane was added, warming up to room temperature. The reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with petro ether, dried over sodium sulfate, and purified with flash column chromatography to give 1.225 g product **1i** as an oil in 62% yield.

B. Sulfur mediated propargylic C-H alkylation reactions

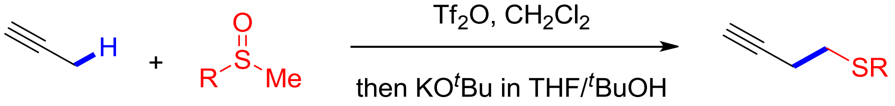
（1）General Procedure A:



1 **2** **3**

To a flame-dried Schlenk tube, 1 eq 5-decyne (**1c**) (28 mg, 0.20 mmol) and 2 eq dimethyl sulfoxide(**2a**) (32 mg, 0.4 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC. 1.8 eq Tf$_2$O (62 μL, 0.36 mmol) was added dropwise, and then gradually warming up to room temperature over 24 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 3.8 eq potassium *tert*-butoxide (87 mg, 0.77 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (3.7 mL) dropwise. After gradually warming up to room temperature overnight for about 10 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with dichloromethane, washed with brine, dried over sodium sulfate, and purified with flash column chromatography (petroleum ether to 40:1 petroleum ether/dichloromethane) to give 19 mg product **3c** as an oil in 50% yield.

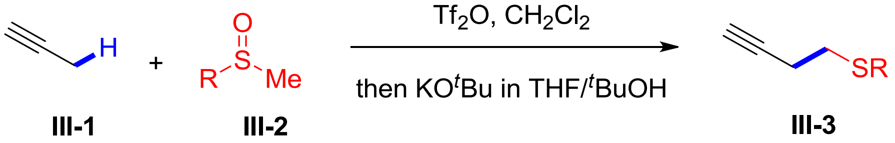
（2）General Procedure B:



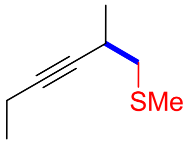
1 **2** **3**

To a flame-dried Schlenk tube, 1 eq alkyne (**1b**) (20 mg, 0.18 mmol), 1.5 eq methyl phenyl sulfoxide (**2b**) (42 mg, 0.30 mmol) and 3 eq 2-fluoropyridine (58 mg, 0.6 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N$_2$/ethyl acetate bath). 1.5 eq Tf$_2$O (50 μL, 0.3 mmol) was added dropwise, and then gradually warmed up to room temperature over 12 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 3.4 eq potassium *tert*-butoxide in 10:1 (v/v) tetrahydrofuran/*tert*-butanol dropwise (3.4 eq, 76 mg, 0.68 mmol). After gradually warming up to room temperature overnight for about 10 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with petroleum ether, washed with brine, dried over sodium sulfate, and purified with flash column chromatography (petroleum ether/dichloromethane = 40/1) to give 9 mg product **3g** as an oil in 21% yield.

（3）General Procedure C:



To a flame-dried Schlenk tube, 1 eq alkeyne (**1f**) (66 mg, 0.25 mmol) and 1.3 eq methyl phenyl sulfoxide (**2b**) (48 mg, 0.33 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N_2/ethyl acetate bath). 1.2 eq Tf_2O (41 µL, 0.24 mmol) was added dropwise, After 30 min at -82ºC, the reaction was stirred at 0 ºC for 2 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 2.6 eq potassium *tert*-butoxide (73 mg, 0.65 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (4.4 mL) dropwise. After gradually warming up to room temperature overnight for about 10 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with petroleum ether, washed with brine, dried over sodium sulfate, and purified with flash column chromatography (petroleum ether to 40:1 petroleum ether/dichloromethane) to give 49 mg product **3p** as an oil in 66% yield.



3a

Methyl(2-methylhex-3-yn-1-yl) sulfide (**3a**) was synthesized according to General Procedure A from 3-hexyne (**1a**) (15 mg, 0.18 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 6 mg product **3a** as an oil in 22% yield.

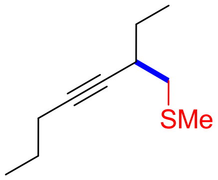
3a: R_f = 0.29 (petroleum ether/dichloromethane 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.69 – 2.61 (m, 2H), 2.51 (dd, J = 15.2 Hz, 9.5 Hz, 1H), 2.21 – 2.14 (td, J = 7.5, 1.9 Hz, 2H), 2.16 (s, 3H), 1.23 (d, J = 6.7 Hz, 3H), 1.12 (t, J = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 82.7, 77.2, 41.7, 26.6, 20.7, 16.4, 14.2, 12.4.

IR (KBr) ν (cm^{-1}) 2917, 2849, 1142, 1075, 1024, 800,760.

MS (EI) calcd for C8H14S: 142, found: 142.



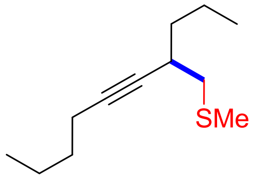
3b

(2-Ethylhept-3-yn-1-yl)(methyl) sulfide (**3b**) was synthesized according to General Procedure A from 4-octyne (**1b**) (19 mg, 0.17 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 15 mg product **3b** as an oil in 51% yield.

3b: R_f = 0.31 (petroleum ether/ dichloromethane 5:1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (dd, *J* = 12.8, 7.0 Hz, 1H), 2.56 (dd, *J* = 12.8, 6.7 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.19 – 2.13 (dt, *J* = 2.2 Hz, 7.1Hz, 2H), 2.16 (s, 3H), 1.66 (dqd, *J* = 14.8, 7.4, 4.6 Hz, 1H), 1.53 (qt, *J* = 7.1, 7.4 Hz, 2H), 1.48 – 1.40 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 82.2, 82.1, 39.8, 33.8, 27.4, 22.5, 20.8, 16.4, 13.4, 11.5.

IR (KBr) ν (cm^{-1}) 2962,2917, 2849, 1142, 1075, 1024, 800,760.
MS (EI) calcd for C10H18S: 170, found: 170.

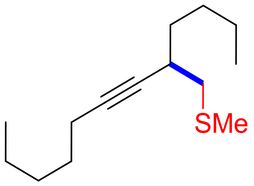


3c

Methyl(2-propyloct-3-yn-1-yl) sulfide (**3c**) was synthesized according to General Procedure A from 5-decyne (**1c**) (28 mg, 0.2 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 19 mg product **3c** as an oil in 50% yield.

3c: R_f = 0.31 (petroleum ether/ dichloromethane 5:1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (dd, *J* = 14.8, 9.3 Hz, 1H), 2.59 – 2.52 (m, 2H), 2.18 (dt, *J* = 6.8, 1.7 Hz, 2H), 2.16 (s, 3H), 1.60 – 1.35 (m, 8H), 0.95 – 0.87 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 82.20, 82.13, 40.2, 36.6, 32.1, 31.2, 21.9, 20.4, 18.5, 16.4, 13.9, 13.6.
IR (KBr) ν (cm^{-1}) 2922,2853, 1180, 1142, 1075, 1030, 802.

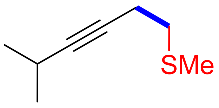
MS (EI) calcd for C12H22S: 198, found: 198.



3d

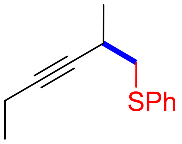
(2-Butylnon-3-yn-1-yl)(methyl) sulfide (**3da**) was synthesized according to General Procedure A from 6-dodecyne (**1d**) (34 mg, 0.20 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 27 mg product **3d** as an oil in 60% yield.
3d: R_f = 0.37 (petroleum ether/ dichloromethane 5:1)
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (dd, *J* = 14.8, 9.3 Hz, 1H), 2.59 – 2.51 (m, 2H), 2.18 (t, *J* = 6.9 Hz, 2H), 2.16 – 2.14 (s, 3H), 1.63 – 1.25 (m, 12H), 0.95 – 0.87 (m, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 82.28, 82.23, 40.2, 34.1, 32.3, 31.0, 29.4, 28.7, 22.5, 22.2, 18.7, 16.4, 14.04, 14.00.
IR (KBr) ν (cm^{-1}) 2957, 2931, 2871, 2860, 1466, 1437, 1075.
MS (EI) calcd for C14H26S: 226, found: 226.



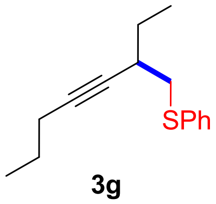
3e

(2-Butylnon-3-yn-1-yl)(methyl) sulfide (**3e**) was synthesized according to General Procedure A from 4-methylpent-2-yne (**1e**) (31 mg, 0.38 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 28 mg product **3e** as an oil in 52% yield.
3e: R_f = 0.29 (petroleum ether/ dichloromethane 5:1)
^{1}H NMR (400 MHz, CDCl$_3$) δ 2.63 (t, J = 7.5 Hz, 2H), 2.57 – 2.49 (m, 1H), 2.45 (td, J = 7.4, 2.1 Hz, 2H), 2.15 (s, 3H), 1.14 (d, J = 6.8 Hz, 6H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 87.1, 77.2, 33.7, 23.3, 20.5, 19.9, 15.7.
IR (KBr) ν (cm^{-1}) 2958, 2921, 2851, 1731, 1463, 1269, 1122, 1074.
MS (EI) calcd for C8H14S: 142, found: 142.



3f

(2-Methylhex-3-yn-1-yl)(phenyl) sulfide (**3f**) was synthesized according to General Procedure B from 3-hexyne (**1a**) (15 mg, 0.18 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 9 mg product **3f** as an oil in 23% yield.
3f: R_f = 0.47 (petroleum ether/ dichloromethane 5:1)
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (s, 1H), 7.22 – 7.17 (m, 3H), 7.09 (t, J = 7.3 Hz, 1H), 3.05 (dd, J = 13.0, 6.3 Hz, 1H), 2.79 (dd, J = 13.0, 7.7 Hz, 1H), 2.56 (dd, J = 13.8, 6.9 Hz, 1H), 2.07 (qd, J = 7.5, 2.0 Hz, 2H), 1.18 (d, J = 6.8 Hz, 4H), 1.02 (t, J = 7.5 Hz, 3H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 136.5, 129.5, 128.9, 126.0, 83.2, 82.2, 41.1, 26.3, 20.5, 14.2, 12.4.
IR (KBr) ν (cm^{-1}) 2973, 2919, 1480, 1439, 1142, 1090, 1026, 738, 690.
MS (EI) calcd for C13H16S: 204, found: 204.



3g

(2-Ethylhept-3-yn-1-yl)(phenyl) sulfide (**3g**) was synthesized according to General Procedure B from 4-octyne (**1b**) (20 mg, 0.18 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 9 mg product **3g** as an oil in 21% yield.

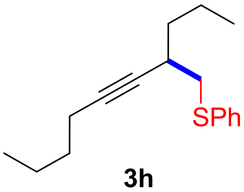
3g: R_f = 0.5 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.22 – 7.16 (m, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 3.02 (dd, *J* = 12.9, 6.8 Hz, 1H), 2.86 (dd, *J* = 12.9, 7.2 Hz, 1H), 2.48 – 2.37 (m, 1H), 2.06 (td, *J* = 7.0, 2.1 Hz, 2H), 1.67 – 1.57 (m, 1H), 1.47 – 1.35 (m, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 129.4, 128.9, 126.0, 82.7, 81.7, 39.2, 33.5, 27.3, 22.5, 20.8, 13.5, 11.4.

IR (KBr) ν (cm^{-1}) 2962, 2922, 2873, 1084, 1026, 737, 691.

MS (EI) calcd for C15H20S: 232, found: 232.



3h

Phenyl(2-propyloct-3-yn-1-yl) sulfide (**3h**) was synthesized according to General Procedure B from 5-decyne (**1c**) (28 mg, 0.2 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 9 mg product **3h** as an oil in 17% yield.

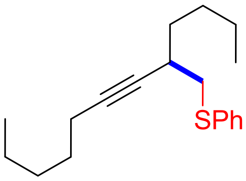
3h: R_f = 0.5 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.30 – 7.25 (m, 2H), 7.20 – 7.13 (m, 1H), 3.09 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.94 (dd, *J* = 12.8, 7.1 Hz, 1H), 2.57 (m, 1H), 2.15 (td, *J* = 6.9, 2.2 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.49 – 1.34 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 129.4, 128.8, 125.9, 82.7, 81.7, 39.6, 36.5, 31.8, 31.1, 21.9, 20.3, 18.4, 13.7, 13.6.

IR (KBr) ν (cm^{-1}) 2957, 2929, 2871, 1089, 1025, 802, 737, 690.

MS (EI) calcd for C17H24S: 260, found 260.



3i

(2-Butylnon-3-yn-1-yl)(phenyl) sulfide (**3i**) was synthesized according to General Procedure B from 6-dodecyne (**1d**) (33 mg, 0.2 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 20 mg product **3i** as an oil in 35% yield.

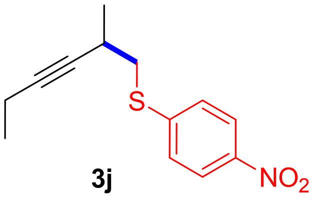
3i: R_f = 0.55 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 3.09 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.94 (dd, *J* = 12.8, 7.1 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.19 – 2.12 (m, 2H), 1.52 – 1.43 (m, 4H), 1.40 – 1.24 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 136.8, 129.4 128.8, 125.9, 82.8, 81.8, 39.6, 34.0, 32.0, 31.0, 29.3, 28.9, 28.7, 22.5, 22.2, 18.7, 14.0.

IR (KBr) ν (cm^{-1}) 2956, 2929, 2858, 1439, 1085, 1026, 737, 690.

MS (EI) calcd for C19H28S: 288, found 288.



3j

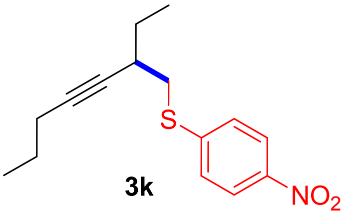
(2-methylhex-3-yn-1-yl)(4-nitrophenyl) sulfide **3j**

To a flame-dried Schlenk tube, 1 eq 3-hexyne (**1a**) (18 mg, 0.2 mmol) and 1.3 eq sulfoxide (**2c**) (48 mg, 0.26 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N$_2$/ethyl acetate bath). 1.2 eq Tf$_2$O (41 μL, 0.24 mmol) was added dropwise, and then gradually warmed up to room temperature over 24 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 2.6 eq potassium *tert*-butoxide (59mg, 0.52 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (2.6 mL) dropwise. After gradually warming up to room temperature overnight for about 7 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with dichloromethane, washed with brine, dried over sodium sulfate, concentrated for NMR test, then purified with flash column chromatography, eluted by 20:1 petroleum ether/dichloromethane to 5:1 petroleum ether/dichloromethane to give 18 mg crude product **3**, then PTLC (petroleum ether/ethyl acetate 20:1) give **3j** 14 mg in 28% yield.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.37 (d, *J* = 8.9 Hz, 2H), 3.20 (dd, *J* = 12.9, 6.7 Hz, 1H), 3.02 (dd, *J* = 12.9, 7.0 Hz, 1H), 2.76 (ddtq, *J* = 7.0, 6.7, 2.0, 7.5 Hz, 1H), 2.15 (qd, *J* = 7.5, 2.1 Hz, 2H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.09 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 147.6, 145.0, 126.5, 123.9, 84.0, 81.3, 39.1, 26.2, 20.8, 14.1, 12.3.

IR (KBr) ν (cm^{-1}) 2919, 2849, 1594, 1578, 1511, 1384, 1337, 1180, 1142, 1090, 852.

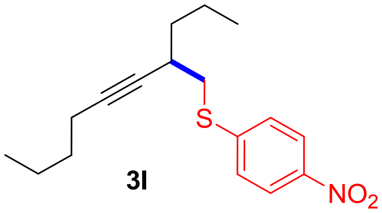


3k

(2-ethylhept-3-yn-1-yl)(4-nitrophenyl) sulfide **3k**

To a flame-dried Schlenk tube, 1 eq 4-octyne (**1b**) (21 mg, 0.18 mmol) and 1.3 eq sulfoxide (**2c**) (48 mg, 0.26 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N_2/ethyl acetate bath). 1.2 eq Tf_2O (41 µL, 0.24 mmol) was added dropwise, and then gradually warmed up to room temperature over 24 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 2.6 eq potassium *tert*-butoxide (59mg, 0.52 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (2.6 mL) dropwise. After gradually warming up to room temperature overnight for about 7 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with dichloromethane, washed with brine, dried over sodium sulfate, concentrated for NMR test, then purified with flash column chromatography, eluted by 20:1 petroleum ether/dichloromethane to 5:1 petroleum ether/dichloromethane to give 38 mg crude product **3**, then PTLC (petroleum ether/ethyl acetate 20:1) give **3k** 18 mg in 34% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.40 – 7.32 (m, 2H), 3.18 (dd, *J* = 12.7, 7.2 Hz, 1H), 3.07 (dd, *J* = 12.7, 6.6 Hz, 1H), 2.66 – 2.56 (m, 1H), 2.14 (td, *J* = 7.0, 2.2 Hz, 2H), 1.75 – 1.64 (m, 1H), 1.60 – 1.44 (m, 3H), 1.04 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.0, 126.4, 123.9, 83.6, 37.3, 33.4, 27.7, 22.3, 20.7, 13.4, 11.5.
IR (KBr) ν (cm^{-1}) 2962, 2921, 1594, 1578, 1512, 1459, 1337, 1181, 1091, 853, 742.



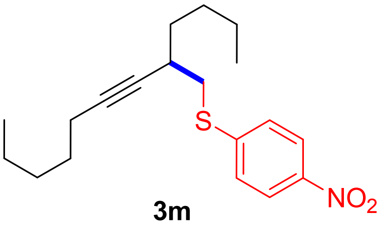
3l

(4-Nitrophenyl)(2-propyloct-3-yn-1-yl) sulfide **3l**

To a flame-dried Schlenk tube, 1 eq 5-decyne (**1c**) (55 mg, 0.40 mmol) and 1.3 eq sulfoxide (**2c**) (95 mg, 0.52 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N_2/ethyl acetate bath). 1.2 eq Tf_2O (82 µL, 0.48 mmol) was added dropwise, and then gradually warmed up to room temperature over 24 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 2.6 eq potassium *tert*-butoxide (117 mg, 1.04 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (5.2 mL) dropwise. After gradually warming up to room temperature overnight for about 7 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with dichloromethane, washed with brine, dried over sodium sulfate, concentrated for NMR test, then purified with flash column chromatography, eluted by 20:1 petroleum ether/dichloromethane to 5:1 petroleum ether/dichloromethane to give crude product **3j**, then PTLC (petroleum ether/ethyl acetate 20:1) give **3l** 40 mg in 33% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 3.17 (dd, *J* = 12.7, 7.2 Hz, 1H), 3.07 (dd, *J* = 12.7, 6.5 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.15

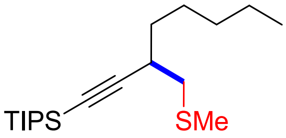
(td, J = 6.9, 2.1 Hz, 2H), 1.63 – 1.51 (m, 3H), 1.49 – 1.36 (m, 5H), 0.96 – 0.86 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.0, 126.4, 123.9, 83.6, 80.8, 37.7, 36.8, 31.6, 31.0, 21.9, 20.3, 18.4, 13.8, 13.6.
IR (KBr) ν (cm^{-1}) 2957, 2930, 2871, 1511, 1578, 1337, 1090, 852, 741.



3m

(2-butylnon-3-yn-1-yl)(4-nitrophenyl) sulfide **3m**
To a flame-dried Schlenk tube, 1 eq 6-dodecyne (**1d**) (33 mg, 0.2 mmol) and 1.3 eq sulfoxide (**2c**) (48 mg, 0.26 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N_2/ethyl acetate bath). 1.2 eq Tf_2O (41 μL, 0.24 mmol) was added dropwise, and then gradually warmed up to room temperature over 24 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 2.6 eq potassium *tert*-butoxide (59mg, 0.52 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (2.6 mL) dropwise. After gradually warming up to room temperature overnight for about 7 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with dichloromethane, washed with brine, dried over sodium sulfate, concentrated for NMR test, then purified with flash column chromatography, eluted by 20:1 petroleum ether/dichloromethane to 5:1 petroleum ether/dichloromethane to give 37 mg crude product **3**, then PTLC (petroleum ether/ethyl acetate 20:1) give **3m** 19 mg in 29% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 8.9 Hz, 2H), 3.17 (dd, J = 12.7, 7.2 Hz, 1H), 3.07 (dd, J = 12.7, 6.5 Hz, 1H), 2.71 – 2.61 (m, 1H), 2.14 (td, J = 7.0, 2.1 Hz, 2H), 1.69 – 1.59 (m, 1H), 1.56 – 1.42 (m, 4H), 1.40 – 1.27 (m, 7H), 0.90 (q, J = 7.3 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 145.0, 126.4, 123.9, 83.6, 80.9, 37.7, 34.4, 31.8, 31.0, 29.3, 28.6, 22.4, 22.2, 18.7, 13.99, 13.96.
IR (KBr) ν (cm^{-1}) 2924, 2855, 1742, 1511, 1459, 1337, 1180, 1090, 852, 741.



3n

Triisopropyl(3-((methylthio)methyl)oct-1-yn-1-yl)silane (**3n**) was synthesized according to General Procedure A from triisopropyl(oct-1-yn-1-yl)silane (**1f**) (54 mg, 0.20 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 39 mg product **3n** as an oil in 64% yield.

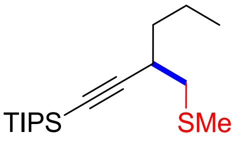
3n: R$_f$ = 0.50 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 2.71 (dd, *J* = 11.5, 5.3 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.17 (s, 3H), 1.68 – 1.60 (m, 1H), 1.59 – 1.53 (m, 1H), 1.49 – 1.43 (m, 2H), 1.35 – 1.28 (m, 4H), 1.11 – 1.03 (m, 24H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 111.0, 82.0, 39.8, 34.0, 33.3, 31.5, 26.7, 22.6, 18.6, 16.5, 14.0, 11.3.

IR (KBr) ν (cm^{-1}) 2921, 2864, 2164, 1665, 1637, 660.

MS (EI) calcd for C19H38SSi: 326, found: 326.



3o

Triisopropyl(3-((methylthio)methyl)hex-1-yn-1-yl)silane (**3o**) was synthesized according to General Procedure A from triisopropyl(hex-1-yn-1-yl)silane (**1g**) (47 mg, 0.19 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 29 mg product **3o** as an oil in 49% yield.

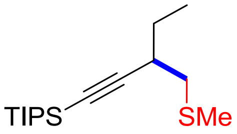
3o: R$_f$ = 0.50 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 2.71 (dd, *J* = 11.6, 5.6 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.58 (dd, *J* = 11.6, 6.5 Hz, 1H), 2.17 (s, 3H), 1.64 – 1.56 (m, 2H), 1.51 – 1.42 (m, 2H), 1.12 – 1.02 (m, 21H), 0.94 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 110.9, 82.0, 39.8, 36.2, 33.0, 20.3, 18.6, 16.5, 13.8, 11.3.

IR (KBr) ν (cm^{-1}) 2940, 2865, 2164, 1075, 882.

MS (EI) calcd for C17H34SSi: 298, found: 298.



3p

Triisopropyl(3-((methylthio)methyl)pent-1-yn-1-yl)silane (**3p**) was synthesized according to General Procedure A from triisopropyl(pent-1-yn-1-yl)silane (**1h**) (44 mg, 0.20 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 43 mg product **3p** as an oil in 77% yield.

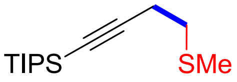
3p: R$_f$ = 0.50 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 2.71 (dd, *J* = 15.6, 9.2 Hz, 1H), 2.61 – 2.53 (m, 2H), 2.16 (s, 3H), 1.76 – 1.65 (m, 1H), 1.54 – 1.43 (m, 1H), 1.11 – 1.00 (m, 24H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 110.7, 82.1, 39.4, 34.8, 27.0, 18.6, 16.4, 11.4, 11.3.

IR (KBr) ν (cm^{-1}) 2960, 2921, 2864, 2165, 1460, 1017, 996, 882, 676, 660.

MS (EI) calcd for C16H32SSi: 284, found: 284.



3q

Triisopropyl(4-(methylthio)but-1-yn-1-yl)silane (**3q**) was synthesized according to General Procedure A from triisopropyl(prop-1-yn-1-yl)silane (**1i**) (36 mg, 0.18 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 7 mg product **3q** as an oil in 15% yield.

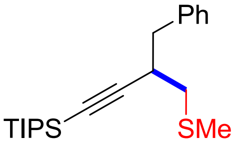
3q: R_f = 0.4 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 2.69 (t, *J* = 7.3 Hz, 2H), 2.55 (t, *J* = 7.3 Hz, 2H), 2.16 (s, 3H), 1.07 (d, *J* = 4.3 Hz, 21H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 106.9, 81.6, 33.4, 21.1, 18.6, 15.6, 11.2.

IR (KBr) ν (cm^{-1}) 2920, 2849, 2172, 1180, 1075, 626.

MS (EI) calcd for C14H28SSi: 256, found: 256.



3r

(3-Benzyl-4-(methylthio)but-1-yn-1-yl)triisopropylsilane (**3r**) was synthesized according to General Procedure A from triisopropyl(4-phenylbut-1-yn-1-yl)silane (**1j**) (58 mg, 0.2 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 17 mg product **3r** as an oil in 24% yield.

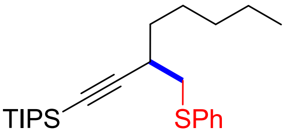
3r: R_f = 0.4 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22 – 7.18 (m, 4H), 7.15 – 7.12 (m, 1H), 2.92 (dd, *J* = 12.7, 5.2 Hz, 1H), 2.83 (dddd, *J* = 5.2, 6.6, 8.1, 6.2 Hz, 1H), 2.73 (dd, *J* = 12.7, 8.1 Hz, 1H), 2.62 (dd, *J* = 13.2, 6.2 Hz, 1H), 2.54 (dd, *J* = 13.2, 7.0 Hz, 1H), 2.10 (s, 3H), 0.98 – 0.92 (m, 21H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 138.9, 129.4, 128.1, 126.3, 110.0, 83.3, 39.9, 39.1, 35.0, 18.6, 16.4, 11.2.

IR (KBr) ν (cm^{-1}) 2920, 2863, 2168, 1180, 1075, 882, 700.

MS (EI) calcd for C21H34SSi: 346, found: 346.



3s

Triisopropyl(3-((phenylthio)methyl)oct-1-yn-1-yl)silane (**3s**) was synthesized according to General Procedure C from triisopropyl(oct-1-yn-1-yl)silane (**1f**) (66 mg, 0.25 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 49 mg product **3s** as an oil in 66% yield.

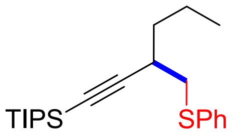
3s: R$_f$ = 0.66 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.14 (m, 1H), 3.13 (dd, *J* = 12.9, 6.6 Hz, 1H), 2.96 (dd, *J* = 12.9, 7.4 Hz, 1H), 2.62 (ddd, *J* = 8.9, 7.2, 3.6 Hz, 1H), 1.73 – 1.63 (m, 1H), 1.58 – 1.38 (m, 3H), 1.34 – 1.22 (m, 4H), 1.09 – 1.00 (m, 21H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 136.6, 129.7, 128.9, 126.1, 110.3, 82.4, 39.5, 33.9, 32.9, 31.5, 26.6, 22.5, 18.6, 14.0, 11.3.

IR (KBr) ν (cm^{-1}) 2957, 2940, 2864, 2165, 1460, 1074, 882, 736, 676.

MS (EI) calcd for C24H40SSi: 388, found: 388.



3t

Triisopropyl(3-((phenylthio)methyl)hex-1-yn-1-yl)silane (**3t**) was synthesized according to General Procedure C from triisopropyl(hex-1-yn-1-yl)silane (**1g**) (47mg, 0.20 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 27 mg product **3t** as an oil in 37% yield.

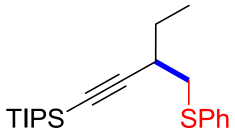
3t: R$_f$ = 0.59 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.23 – 7.18 (m, 1H), 3.16 (dd, *J* = 12.9, 6.7 Hz, 1H), 2.99 (dd, *J* = 12.9, 7.4 Hz, 1H), 1.73 – 1.65 (m, 1H), 1.63 – 1.57 (m, 1H), 1.54 – 1.40 (m, 2H), 1.14 – 1.06 (m, 22H), 0.93 (d, *J* = 7.0 Hz, 2H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 136.6, 129.7, 128.9, 126.1, 110.3, 82.4, 39.5, 36.1, 32.7, 20.2, 18.6, 13.8, 11.34, 11.25.

IR (KBr) ν (cm^{-1}) 2941, 2864, 2166, 1667, 1585, 1074, 1025, 882, 737, 676.

MS (EI) calcd for C22H36SSi: 360, found: 360.



3u

Triisopropyl(3-((phenylthio)methyl)pent-1-yn-1-yl)silane (**3u**) was synthesized according to General Procedure C from triisopropyl(pent-1-yn-1-yl)silane (**1h**) (45 mg, 0.20 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 45 mg product **3u** as an oil in 65% yield.

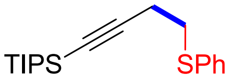
3u: R$_f$ = 0.61 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.22 (m, 10H), 3.14 (dd, *J* = 13.0, 6.2 Hz, 1H), 3.08 – 2.98 (m, 2H), 2.96 – 2.80 (m, 2H), 1.08 – 0.98 (m, 21H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 136.5, 129.7, 128.9, 126.1, 110.1, 82.6, 39.1, 34.4, 27.0, 18.7, 11.33, 11.27.

IR (KBr) ν (cm^{-1}) 2961, 2941, 2864, 2165, 1075, 1025, 736, 627.

MS (EI) calcd for C21H34SSi: 346, found: 346.



3v

Triisopropyl(4-(phenylthio)but-1-yn-1-yl)silane(**3v**) was synthesized according to General Procedure C from triisopropyl(prop-1-yn-1-yl)silane (**1i**) (38 mg, 0.19 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 37 mg product **3v** as an oil in 55% yield.

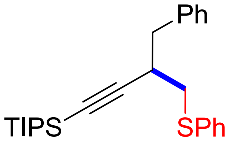
3v: R_f = 0.43 (petroleum ether/ dichloromethane 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 1H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.09 – 1.02 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 130.1, 129.0, 126.4, 106.3, 82.0, 33.4, 20.9, 18.6, 11.2.

IR (KBr) ν (cm^{-1}) 2920, 2864, 2171, 1633, 1462, 1075, 882, 676, 661.

MS (EI) calcd for C19H30SSi: 318, found: 318.



3w

(3-Benzyl-4-(phenylthio)but-1-yn-1-yl)triisopropylsilane (**3w**) was synthesized according to General Procedure B from triisopropyl(4-phenylbut-1-yn-1-yl)silane (57 mg, 0.20 mmol), eluted by petroleum ether to 40:1 petroleum ether/dichloromethane, to give 13 mg product **3w** as an oil in 16% yield.

3w: R_f = 0.46 (petroleum ether/ dichloromethane 5:1)

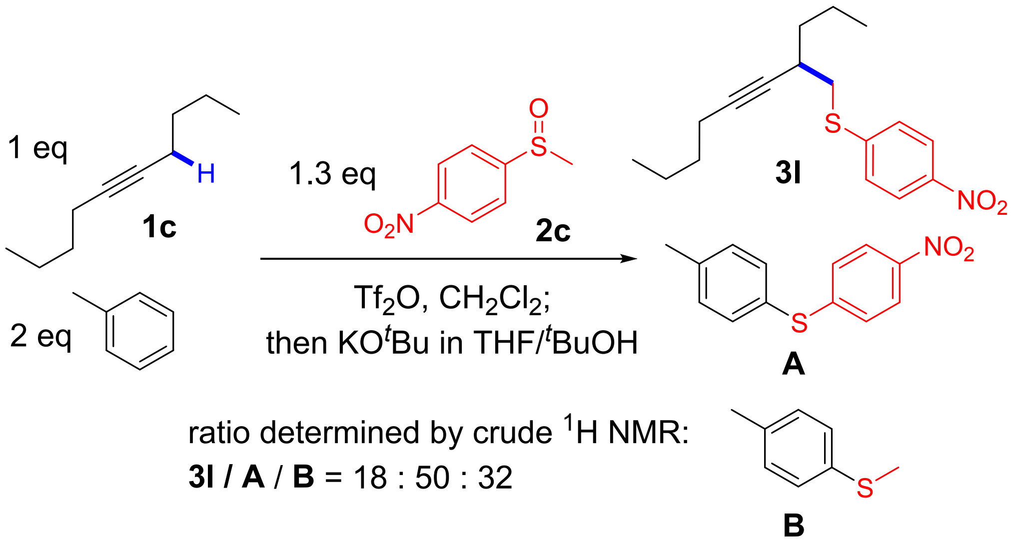
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 10H), 3.14 (dd, *J* = 13.0, 6.2 Hz, 1H), 3.08 – 2.98 (m, 2H), 2.96 – 2.80 (m, 2H), 1.08 – 0.98 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.2, 129.7, 129.5, 128.9, 128.1, 126.4, 126.2, 109.4, 83.7, 39.8, 38.7, 34.7, 18.6, 11.2.

IR (KBr) ν (cm^{-1}) 2918, 2850, 2167, 1180, 1142, 1074, 882, 737.

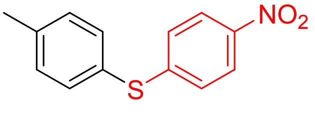
MS (EI) calcd for C26H36SSi: 408, found: 408.

C. Competition experiment



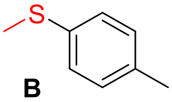
ratio determined by crude ^{1}H NMR:
3l / A / B = 18 : 50 : 32

To a flame-dried Schlenk tube, 1 eq 5-decyne (**1c**) (28 mg, 0.2 mmol), 2 eq toluene (37 mg, 0.4 mmol) and 1.3 eq sulfoxide (**2c**) (49 mg, 0.26 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N_2/ethyl acetate bath). 1.2 eq Tf_2O (41 μL, 0.24 mmol) was added dropwise, and then gradually warmed up to room temperature over 24 hours. The reaction mixture was cooled down to -43 ºC, and then added a solution of 2.6 eq potassium *tert*-butoxide (59mg, 0.52 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (2.6mL) dropwise. After gradually warming up to room temperature overnight for about 7 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with petroleum ether, washed with brine, dried over sodium sulfate, concentrated for NMR test to determine the ratio of products **3l**, **A** and **B**, then purified with flash column chromatography to give **3l** in 19% yield (corrected for impurities).



A

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 9.0 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.13 (d, J = 9.0 Hz, 2H), 2.42 (s, 3H).

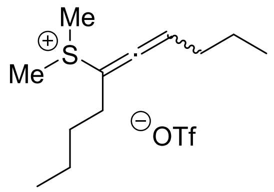


B

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H), 2.31 (s, 3H).

D. Isolation and reaction of an allenyl sulfonium salt

V-int:

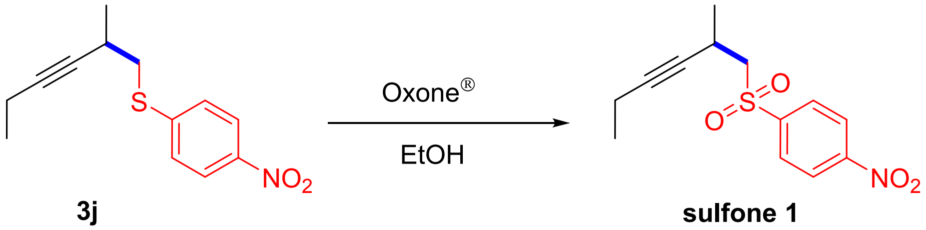


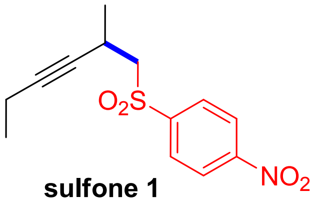
V-int

To a flame-dried Schlenk tube, 1 eq 5-decyne (**1c**) (41 mg, 0.3 mmol) and 2 eq dimethyl sulfoxide (**2a**) (41 mg, 0.6 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC. 1.2 eq Tf_2O (62 μL, 0.36 mmol) was added dropwise. After gradually warming up to room temperature over 24 hours, the liquid phase was washed with saturated aqueous sodium bicarbonate solution, extracted with dichloromethane, dried over sodium sulfate, and purified with flash column chromatography (1:1 petroleum ether/ethyl acetate to 10:1 dichloromethane /methanol) to give 79 mg product **V-int** in 77% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20- 6.05 (m, 1H), 2.993 (s, 3H), 2.983 (s, 3H), 2.25 – 2.14 (m, 2H), 1.55 – 1.26 (m, 8H), 0.95 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 120.5 (q, $J_{C\text{-}F}$ = 320.0 Hz), 105.8, 99.2, 40.7, 30.2, 29.6, 29.0, 26.9, 26.9, 21.9, 21.7, 13.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -78.41.
IR (KBr) ν (cm^{-1}) 2962, 2934, 1259, 1225, 1159, 1031, 639.
HRMS (ESI) calcd for C12H23S$^+$ [M]$^+$ *m/z* 199.1515, found 199.1523.

The sulfonium salt **V-int** (43 mg, 0.12 mmol) was dissolved in 1 mL dichloromethane, then cooled down to -43 ºC, and then added a solution of 1.3 eq potassium *tert*-butoxide (18 mg, 0.76 mmol) in 10:1 (v/v) tetrahydrofuran/*tert*-butanol (1 mL) dropwise. After gradually warming up to room temperature overnight for about 10 hours, the reaction was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with dichloromethane, washed with brine, dried over sodium sulfate, and purified with flash column chromatography (petroleum ether to 40:1 petroleum ether/dichloromethane) to give 18 mg product **3c** as an oil in 74% yield.

E. Product derivatization





sulfone 1

To a 5 mL flask, sulfide **3j** (10 mg, 0.04 mmol), 1.5 eq Oxone (40 mg, 0.06 mmol), and ethanol (2.0 mL) were added, and the mixture was stirred at 60 °C for 4 hours. The mixture was cooled to room temperature, added with brine (5 mL), and then extracted by ethyl acetate (8 mL × 3). After drying with anhydrous sodium sulfate, it was concentrated and purified with flash column chromatography, eluted by petroleum ether/ethyl acetate (10/1), to give 6 mg product as a white solid in 53% yield.

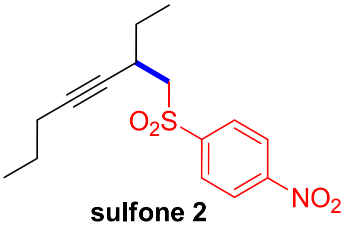
mp 97-98 °C

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 3.37 (dd, *J* = 14.4, 8.1 Hz, 1H), 3.19 (dd, *J* = 14.4, 5.3 Hz, 1H), 3.10 – 2.98 (m, 1H), 1.87 (qd, *J* = 7.5, 2.1 Hz, 2H), 1.31 (d, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 150.9, 145.3, 130.0, 124.1, 84.7, 79.6, 62.1, 21.9, 21.8, 13.7, 12.1.

IR (KBr) ν (cm^{-1}) 2919, 2849, 1655, 1648, 1533, 1350, 1298, 1180, 1143,1084, 1076, 853, 743.

HRMS (ESI) calcd for C13H16NO4S$^+$ [M+H]$^+$ *m/z* 282.0800, found 282.0798.



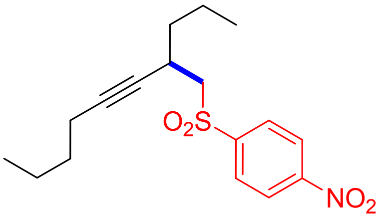
sulfone 2

Sulfone 2 was synthesized by the same method as **sulfone 1** from sulfide (**3k**) (10 mg, 0.036 mmol), eluted by petroleum ether/ethyl acetate (10/1), to give 5 mg product as a white solid in 45% yield.

mp 90-91 °C

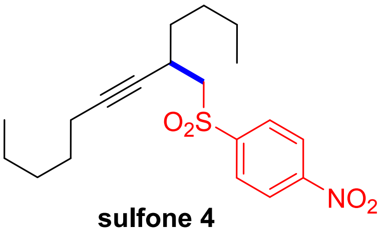
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 3.36 (dd, *J* = 14.4, 8.8 Hz, 1H), 3.22 (dd, *J* = 14.4, 4.4 Hz, 1H), 2.94 – 2.81 (m, 1H), 1.81 (tt, *J* = 6.9, 2.3 Hz, 2H), 1.72 – 1.61 (m, 1H), 1.34 – 1.25 (m, 3H), 1.00 (t, *J* = 7.3 Hz,

3H), 0.84 (t, J = 7.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 145.4, 130.1, 124.1, 84.3, 79.1, 60.8, 28.69, 28.64, 22.0, 20.5, 13.3, 11.1.
IR (KBr) ν (cm^{-1}) 2919, 2850, 1653, 1635, 1533, 1384, 1262, 1181, 1142,1075, 747, 698.
HRMS (ESI) calcd for C15H20NO4S$^+$ $[M+H]^+$ *m/z* 10.1113, found 310.1111.



sulfone 3

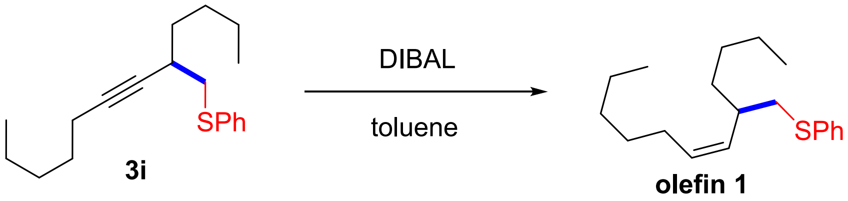
To a 5 mL flask, sulfide **3l** (31 mg, 0.1 mmol), 1.5 eq Oxone (94 mg, 0.15 mmol), and ethanol (2.0 mL) were added, and the mixture was stirred at 60 °C for 4 hours. The mixture was cooled to room temperature, added with brine (5 mL), and then extracted by ethyl acetate (8 mL × 3). After drying with anhydrous sodium sulfate, it was concentrated and purified with flash column chromatography, eluted by petroleum ether/ethyl acetate (10/1), to give 22 mg product as a white solid in 64% yield.
R_f = 0.60 (petroleum ether/ethyl acetate = 5/1).
mp 89-90 ^{o}C
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H), 3.36 (dd, J = 14.4, 8.9 Hz, 1H), 3.21 (dd, J = 14.4, 4.2 Hz, 1H), 2.94 (s, 1H), 1.82 (s, 2H), 1.59 – 1.39 (m, 4H), 1.24 (M, 4H), 0.91 (t, J = 6.8 Hz, 3H), 0.83 (t, J = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 145.4, 130.1, 124.1, 84.3, 79.0, 61.1, 37.5, 30.7, 27.0, 21.8, 19.9, 18.2, 13.5, 13.5.
IR (KBr) ν (cm^{-1}) 2920, 1628, 1578, 1531, 1475, 1459, 1179, 1142,1094, 1044, 853, 820.
HRMS (ESI) calcd for C17H24NO4S$^+$ $[M+H]^+$ *m/z* 338.1426, found 328.1420.

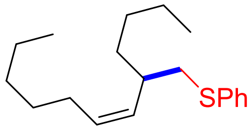


sulfone 4

Sulfone 4 was synthesized by the same method as **sulfone 1** from sulfide (**3m**) (6 mg, 0.018 mmol), eluted by petroleum ether/ethyl acetate (10/1), to give 4 mg product as a white solid in 61% yield.
mp 88-89 ^{o}C
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, J = 8.8 Hz, 2H), 8.15 (d, J = 8.8 Hz, 2H), 3.36

(dd, *J* = 14.4, 8.9 Hz, 1H), 3.22 (dd, *J* = 14.4, 4.3 Hz, 1H), 2.97 – 2.88 (m, 1H), 1.85 – 1.77 (m, 2H), 1.37 – 1.20 (m, 12H), 0.91 – 0.85 (m, 6H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 150.8, 145.4, 130.1, 124., 84.4, 79.1, 61.1, 35.1, 30.96, 28.8, 28.3, 27.2, 22.2, 22.1, 18.5, 13.92, 13.91.
IR (KBr) ν (cm^{-1}) 2920, 2849, 1647, 1531, 1346, 1289, 1262, 1181, 1142,1074, 798, 775, 740.
HRMS (ESI) calcd for C19H28NO4S^{+} [M+H]$^{+}$ *m/z* 366.1739, found 366.1736.





olefin 1

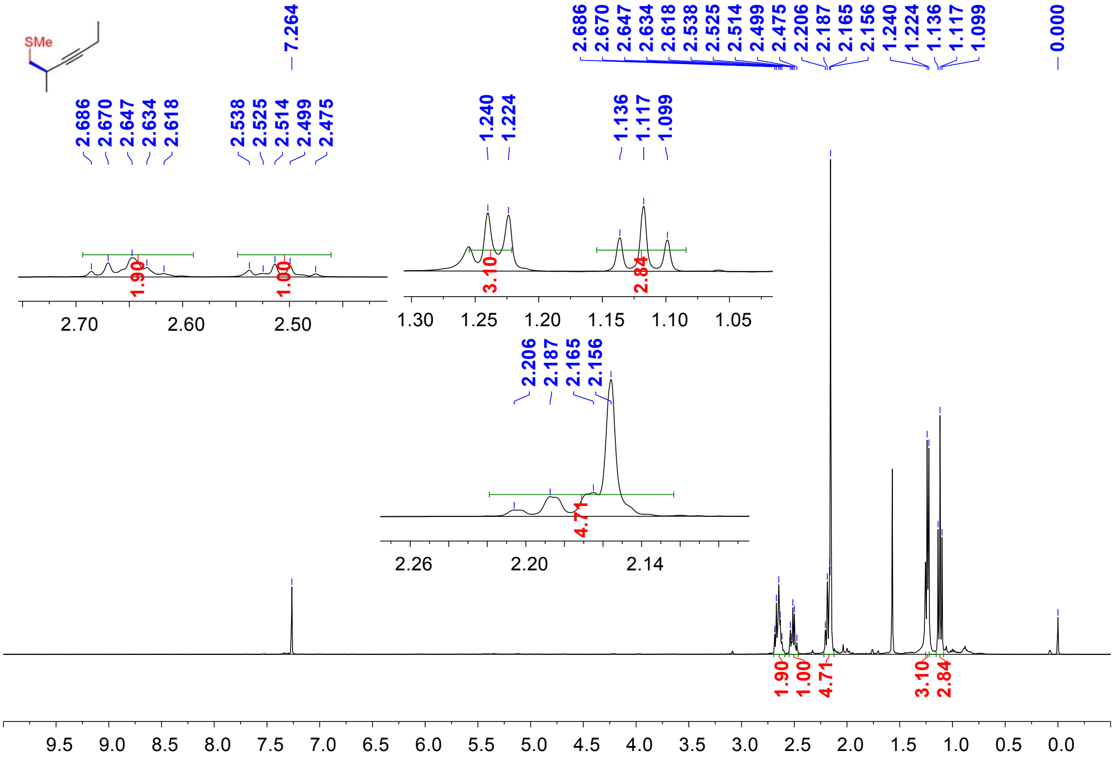
To a flame-dried 5 mL flask, sulfide **3i** (25 mg, 0.087 mmol), toluene (2.0 mL) and 1.2 eq DIBAL-H in hexane (1 M, 0.1 mL) were added, and the mixture was stirred at 50 °C for 24 hours. The mixture was cooled to to-50 °C before dropwise addition of saturated aqueous ammonium chloride solution, and then extracted by dichloromethane (8 mL × 3). After drying with anhydrous sodium sulfate, it was concentrated and purified with flash column chromatography, eluted by petroleum ether/dichloromethane (40/1), to give 16 mg product (**olefin 1**) as a liquid in 63% yield[2].
R$_f$ = 0.26 (petroleum ether).
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.50 (dt, *J* = 10.4, 7.4 Hz, 1H), 5.15 (dd, *J* = 10.4 Hz, 10.4 Hz, 1H), 2.94 (dd, *J* = 12.3, 6.6 Hz, 1H), 2.87 (dd, *J* = 12.3, 7.3 Hz, 1H), 2.63 (s, 1H), 1.96 (m, 2H), 1.36 – 1.27 (m, 12H), 0.91 (t, *J* = 6.1 Hz, 6H).
^{13}C NMR (100 MHz, CDCl$_3$) δ 137.4, 132.4, 131.6, 128.8, 128.7, 125.5, 39.7, 36.8, 34.6, 31.6, 29.7, 29.42, 29.36, 27.7, 22.8, 22.5, 14.0.
IR (KBr) ν (cm^{-1}) 2920, 2852, 1662, 1653, 1260, 1180, 1142, 1075, 876, 801, 689.
MS (EI) calcd for C19H30S^{+} [M]$^{+}$ *m/z* 290, found 290.

References

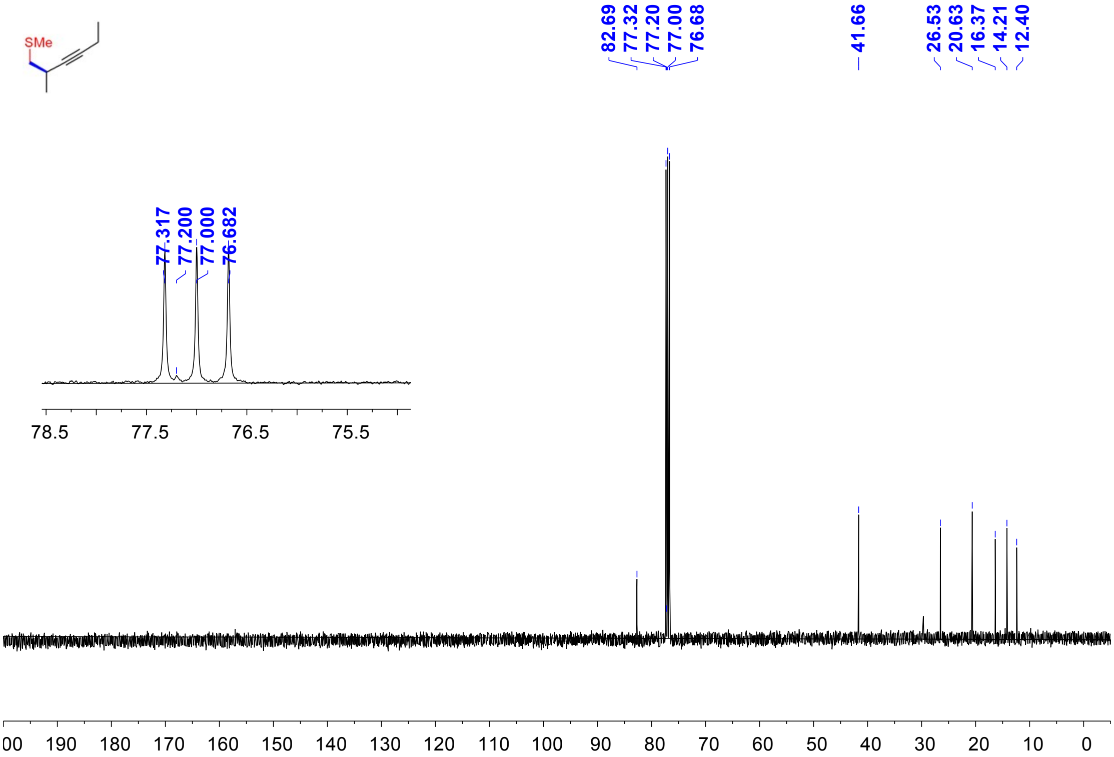
[1] Dunetz, J. R.; Danheiser, R. L. *J. Am. Chem. Soc.*, **2005**, *127*, 5776
[2] Bailey, W. F.; Luderer, M. R.; Uccello, D. P.; Bartelson, A. L. *J. Org. Chem.* **2010**, *75*, 2661.

V. Copies of ^{1}H and ^{13}C NMR Spectra

compounds 3a ^{1}H NMR spectra, 400 MHz, $CDCl_3$.



compounds 3a ^{13}C NMR spectra, 100 MHz, $CDCl_3$.



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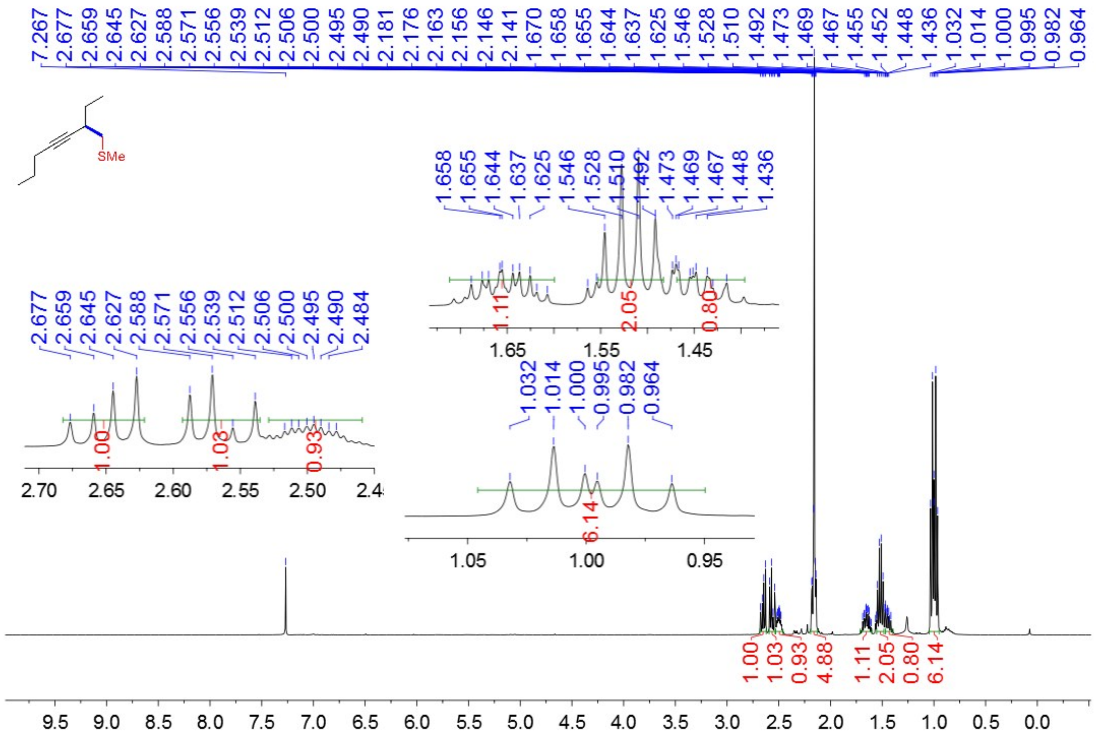

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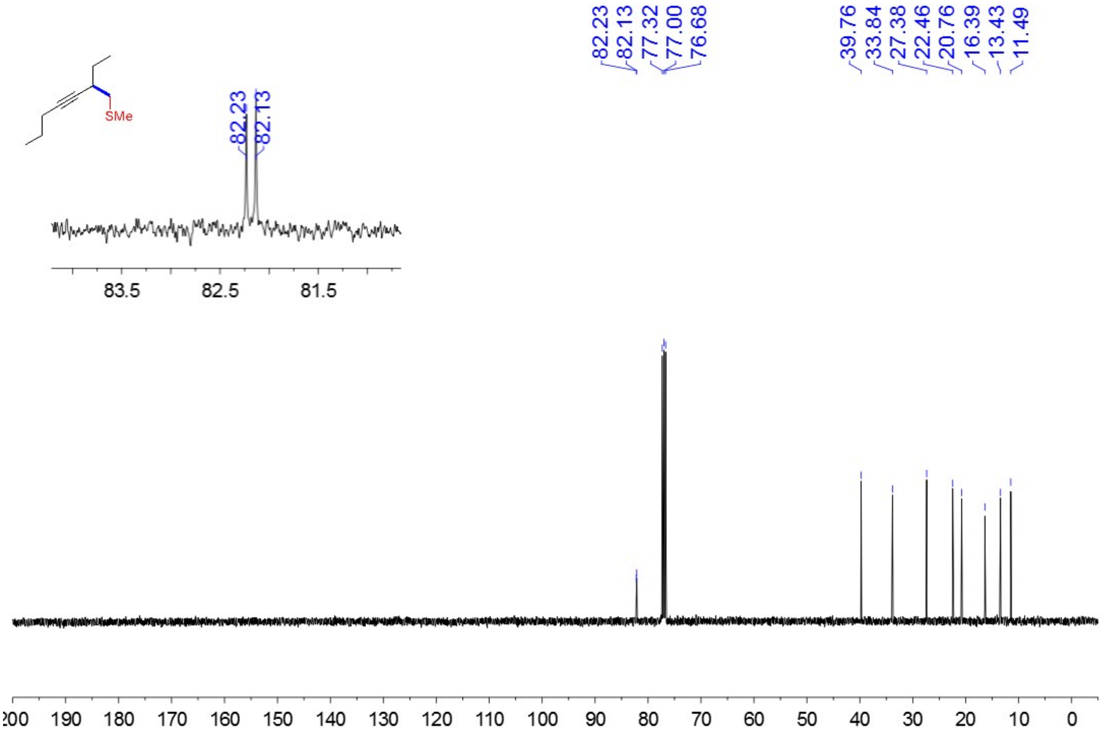
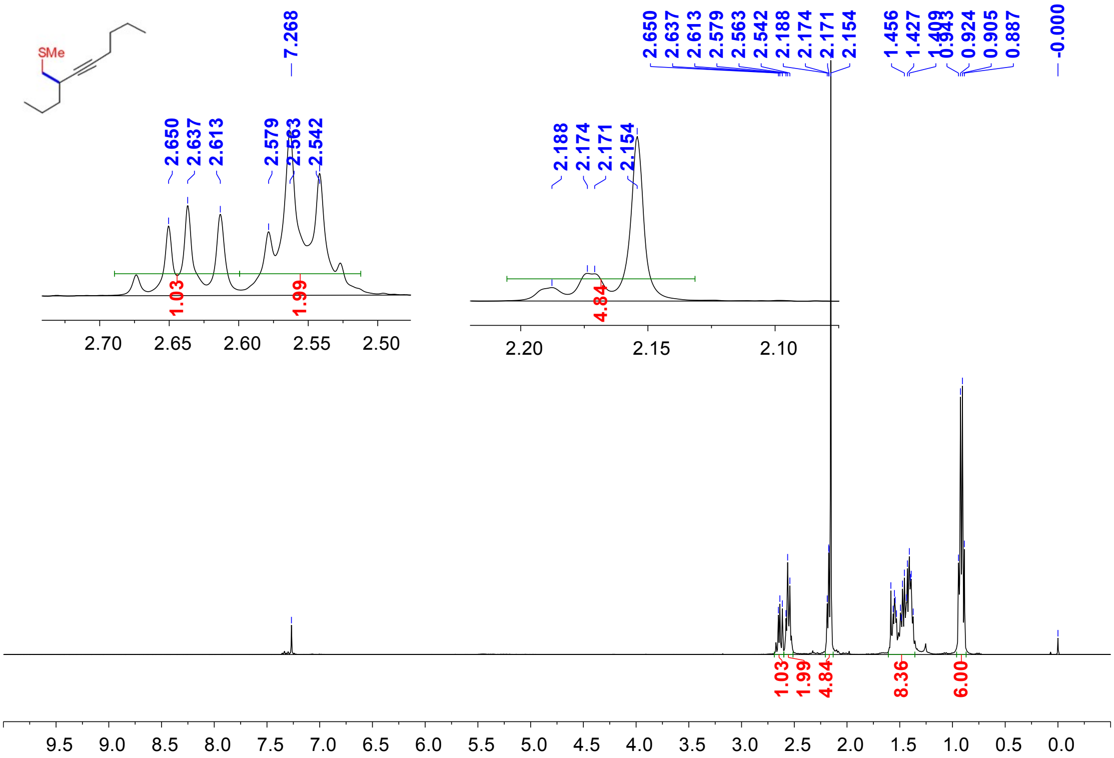


compounds 3c ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



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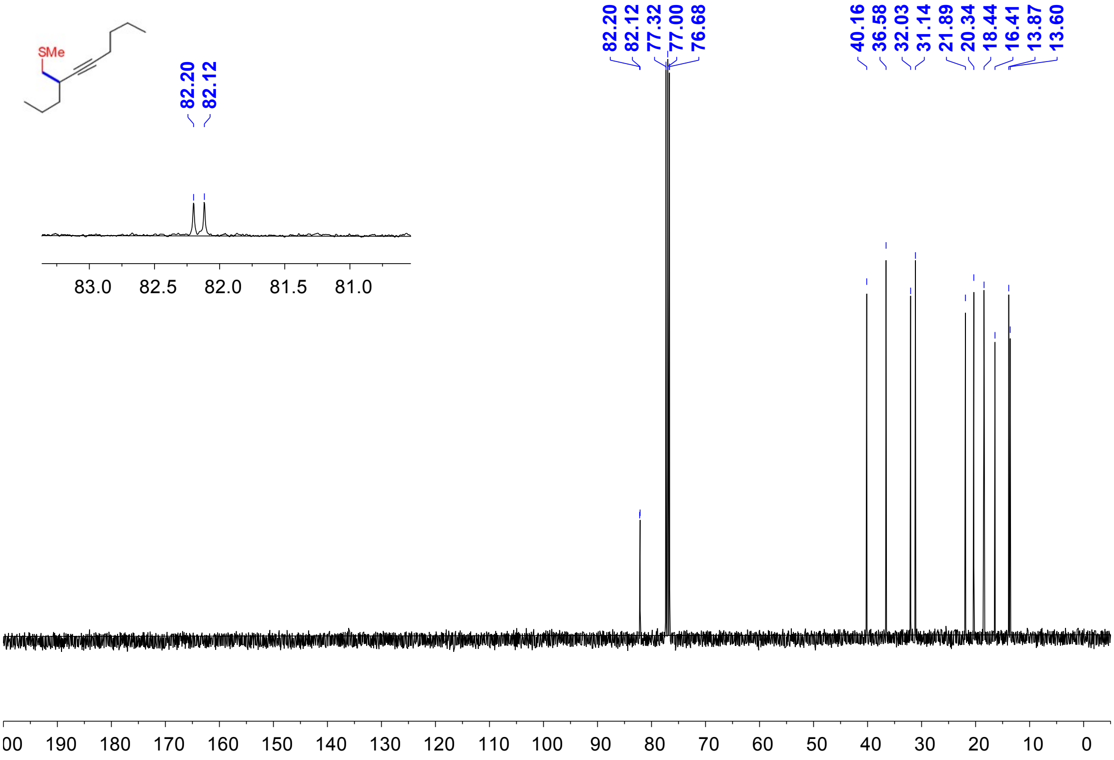

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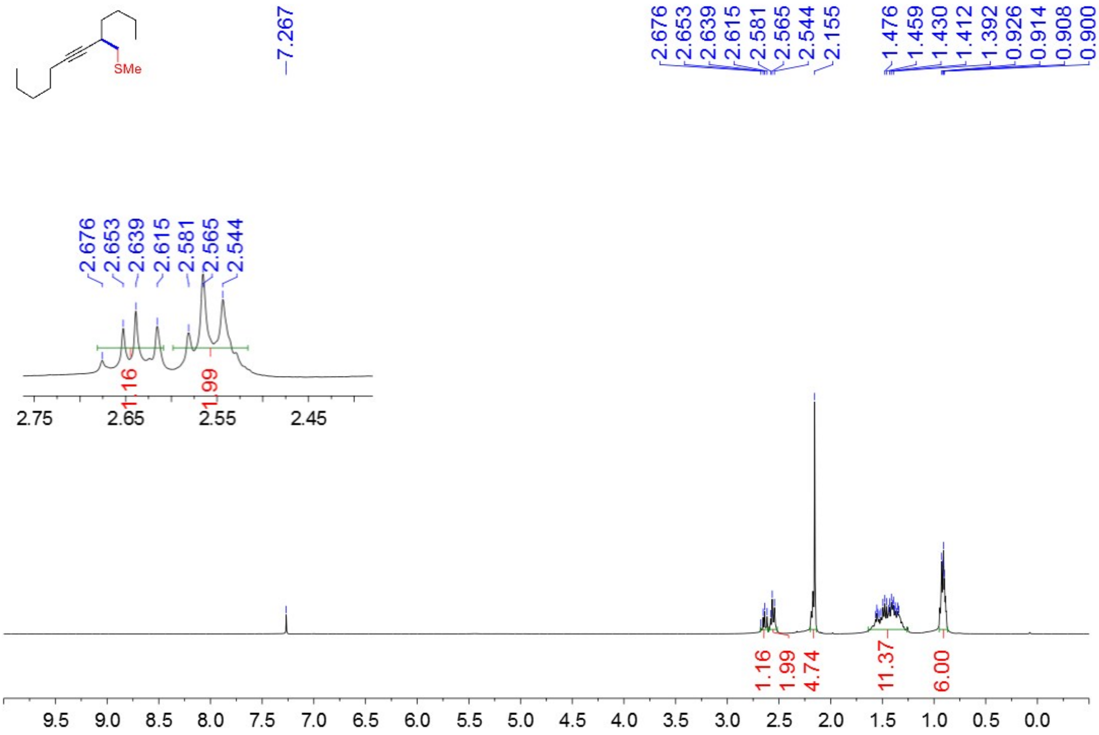

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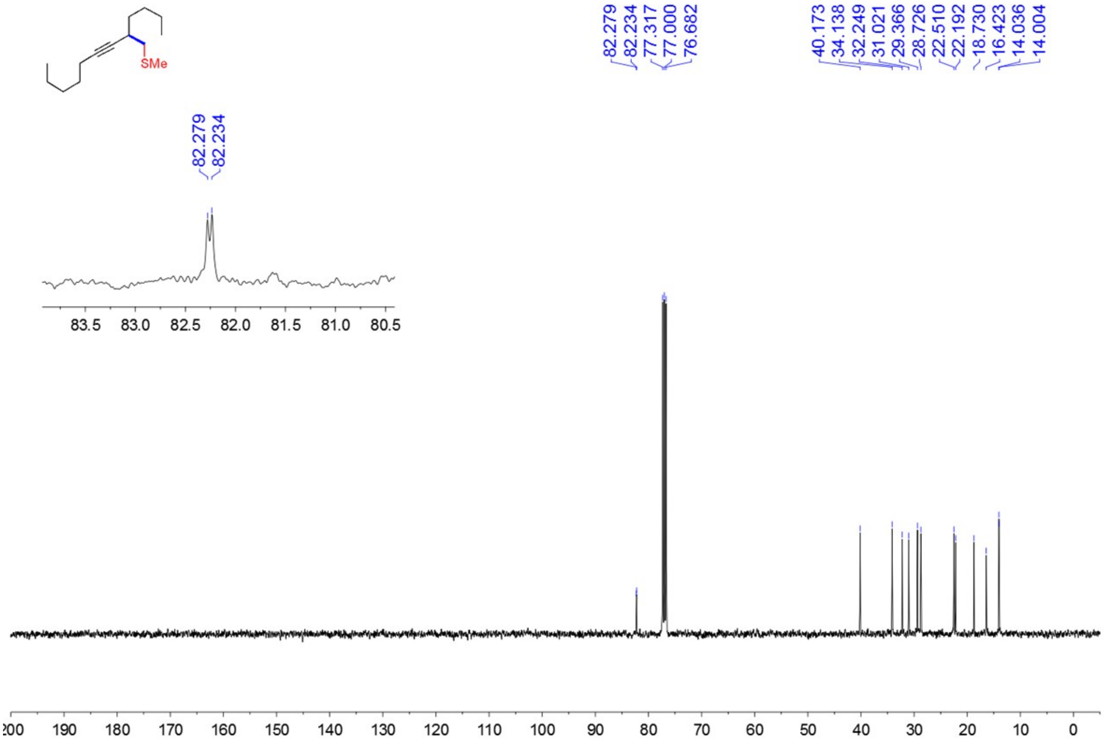

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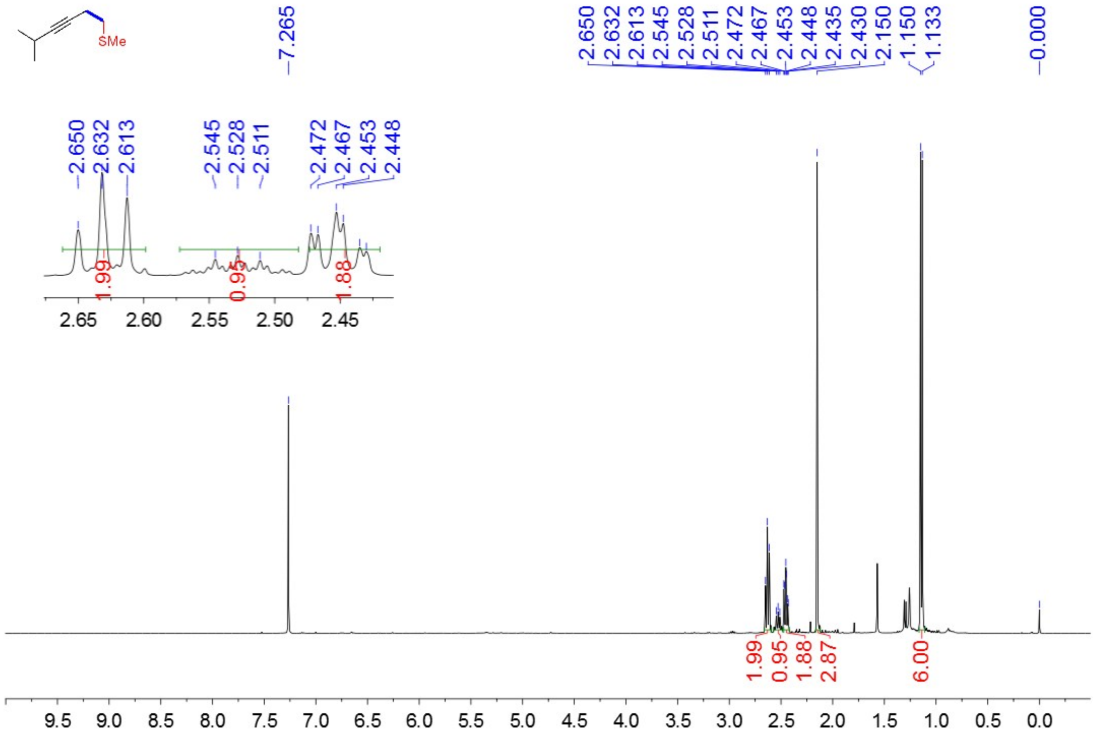
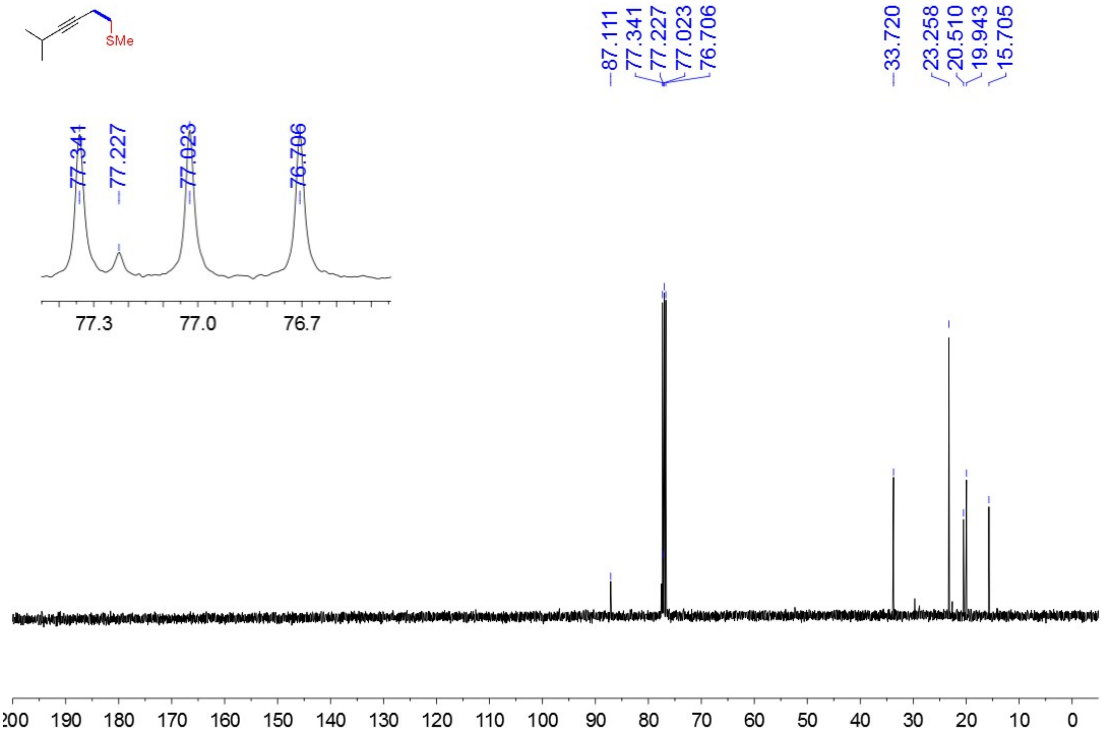


compounds 3e ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



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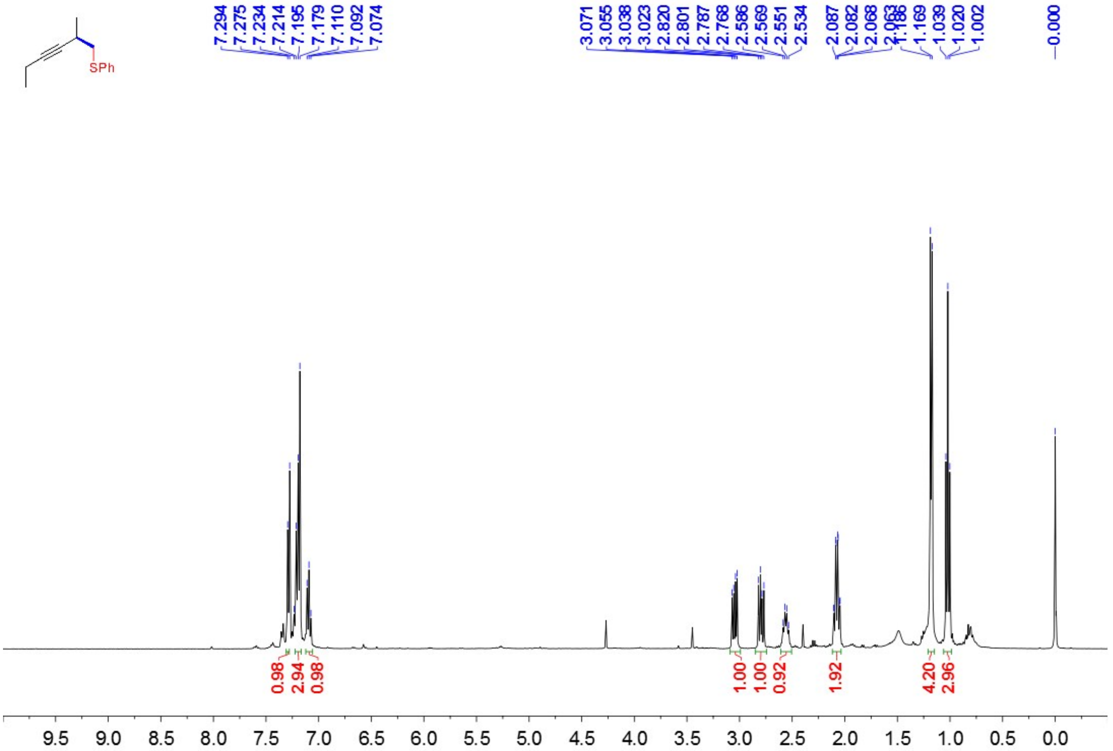

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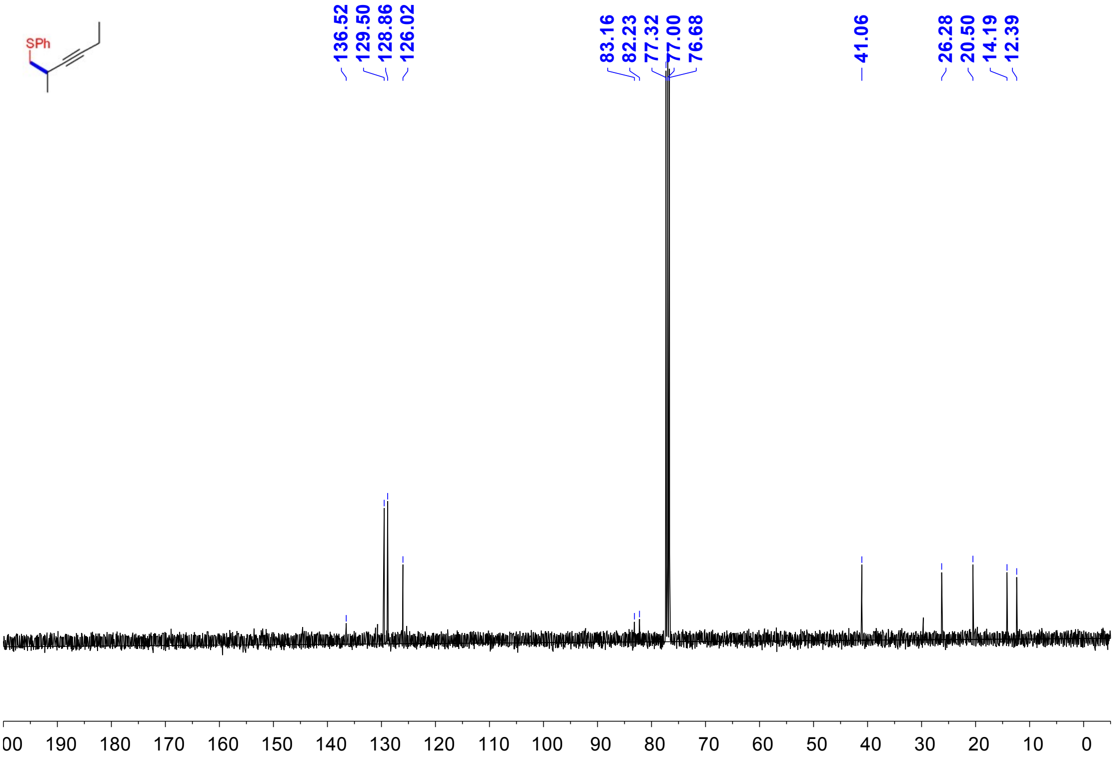
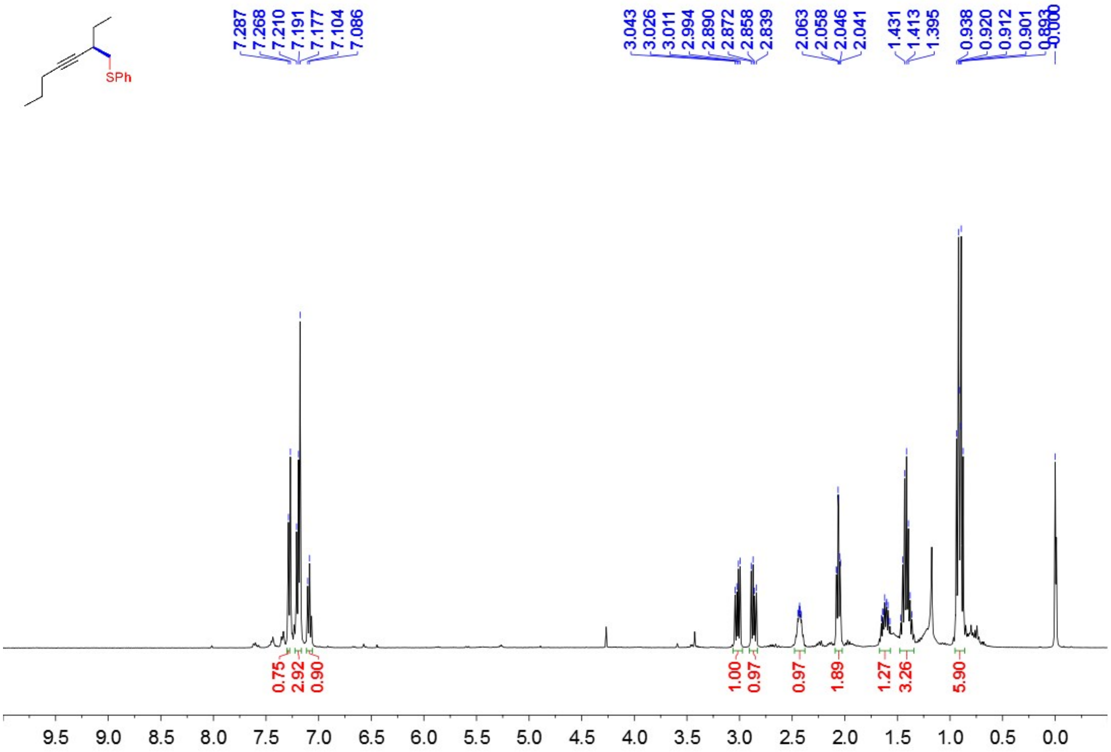
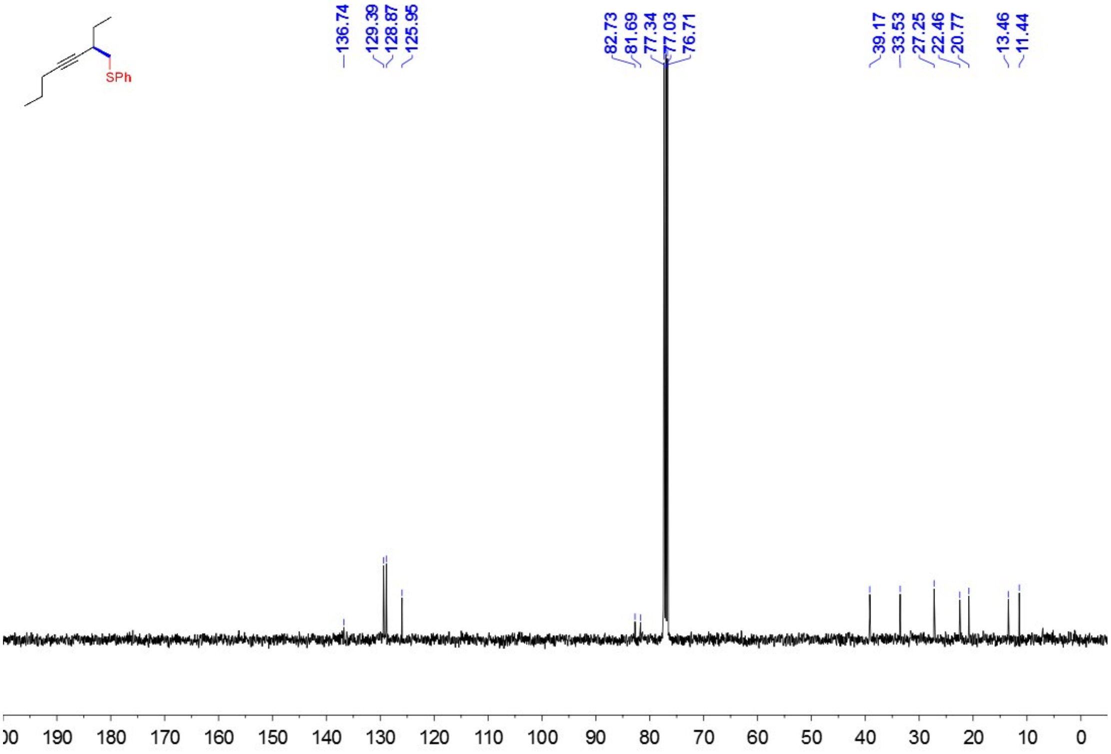


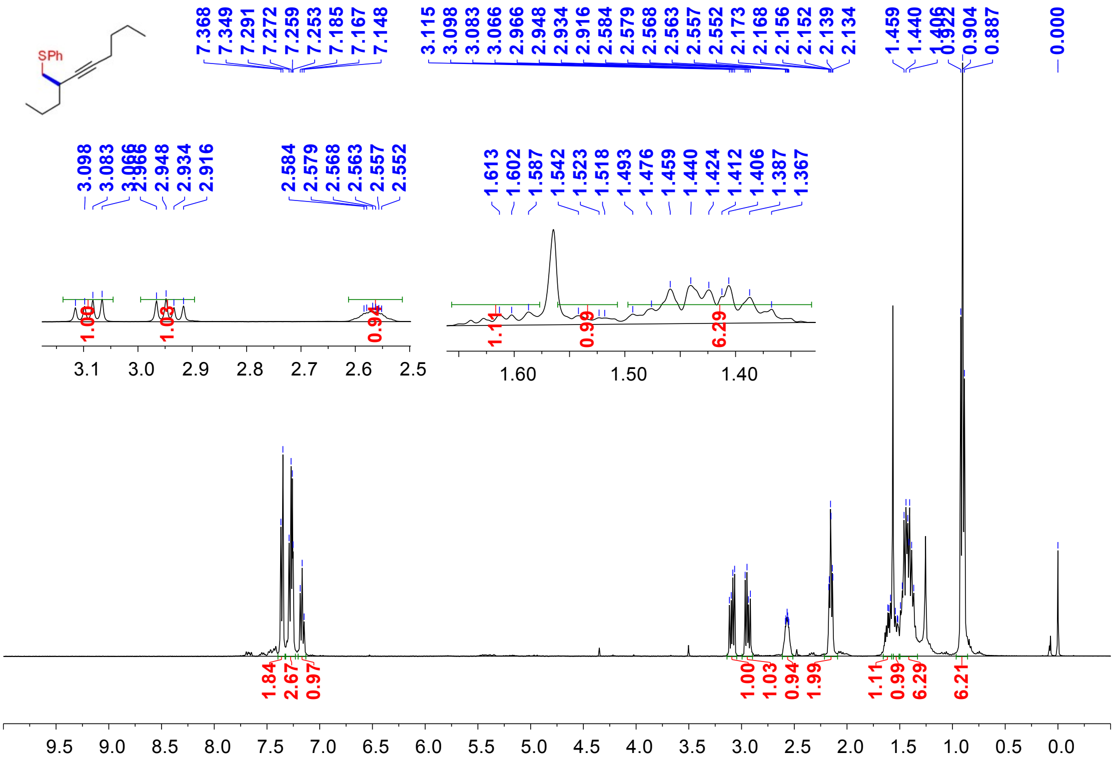
compounds 3g ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



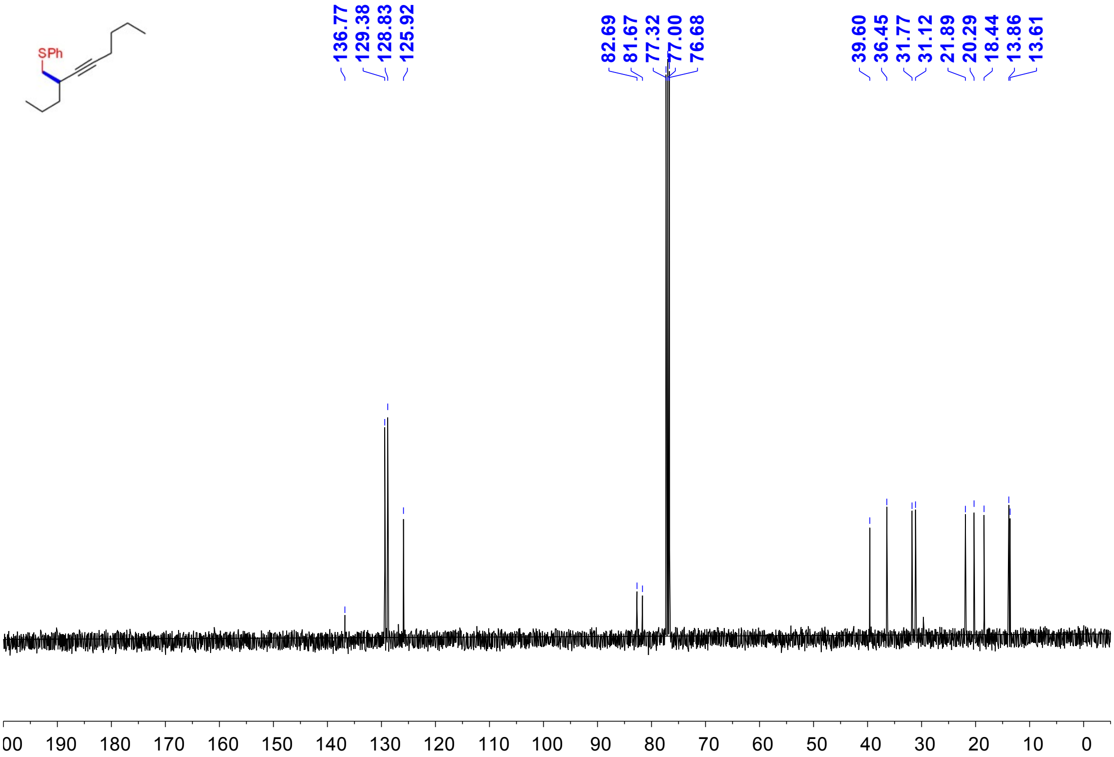
compounds 3g ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



compounds 3h ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



compounds 3h ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



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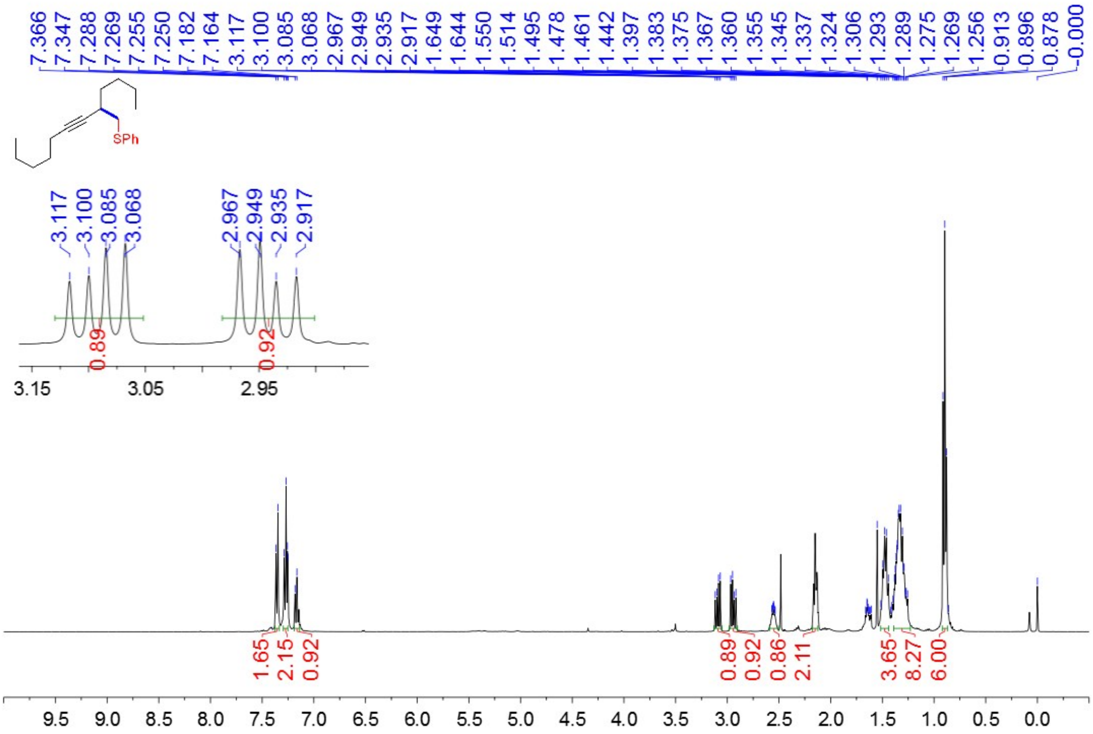

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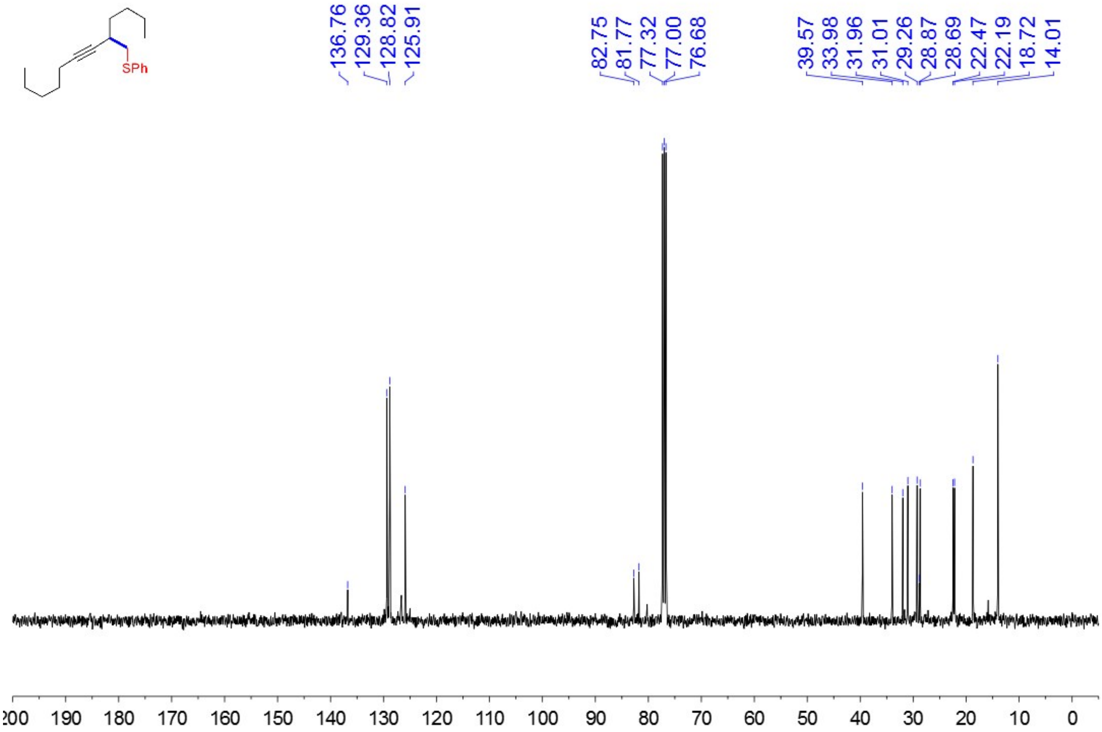

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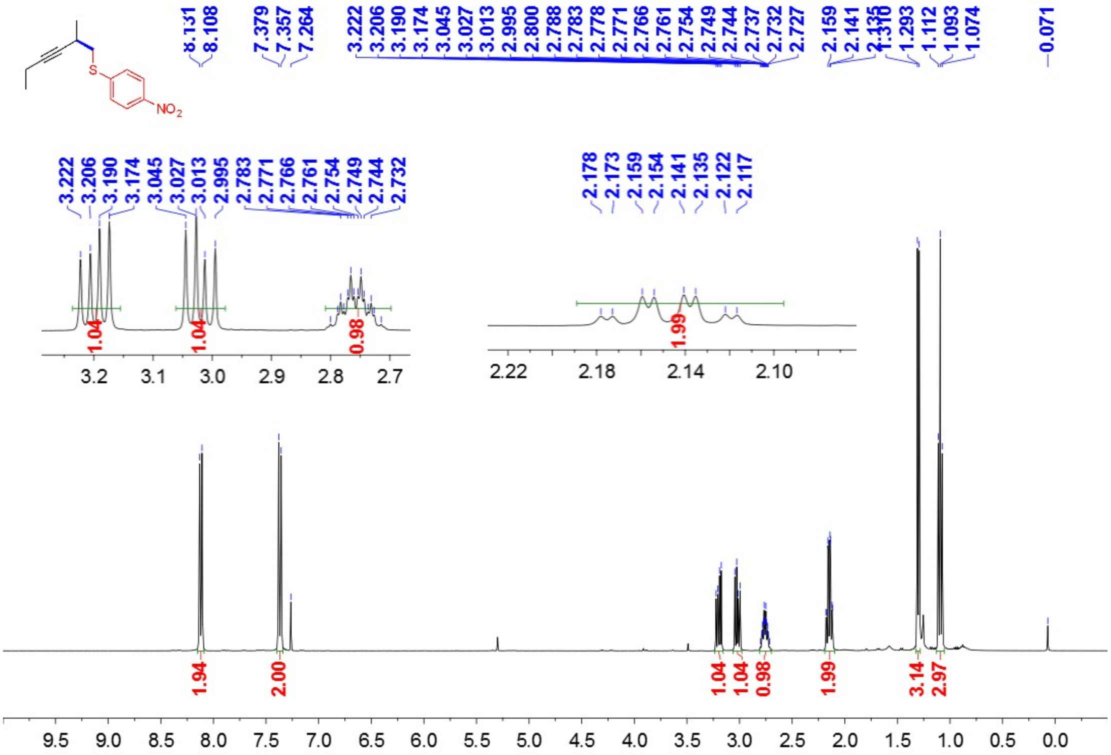
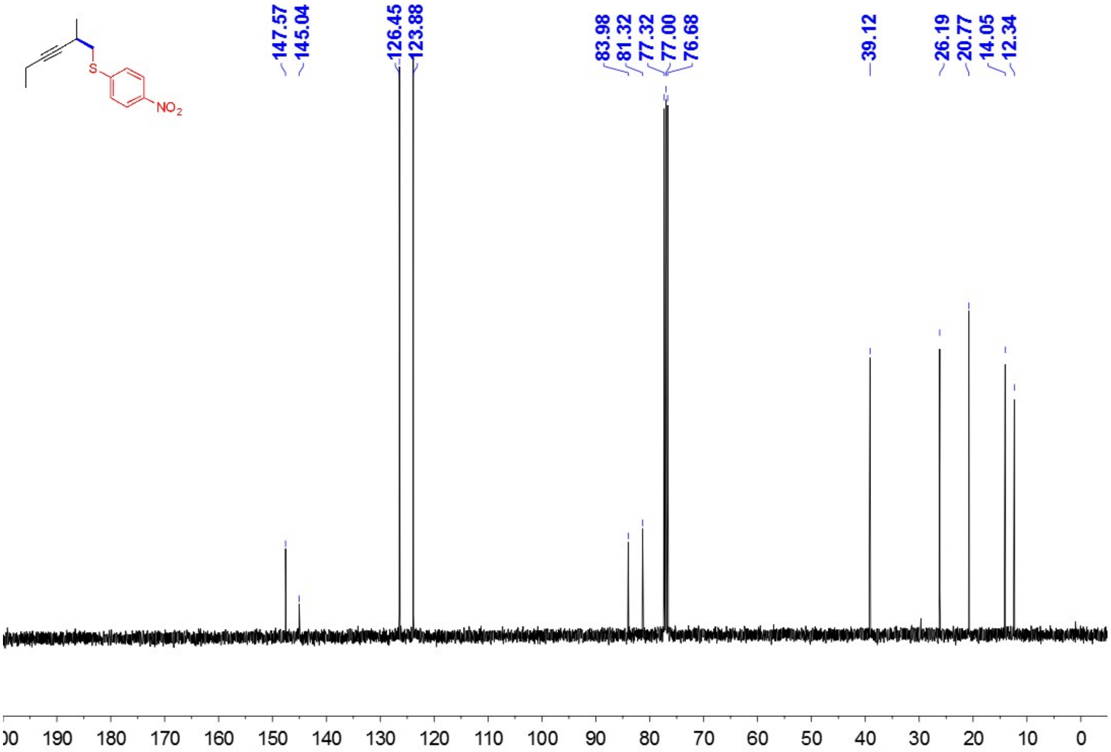


compounds 3j ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



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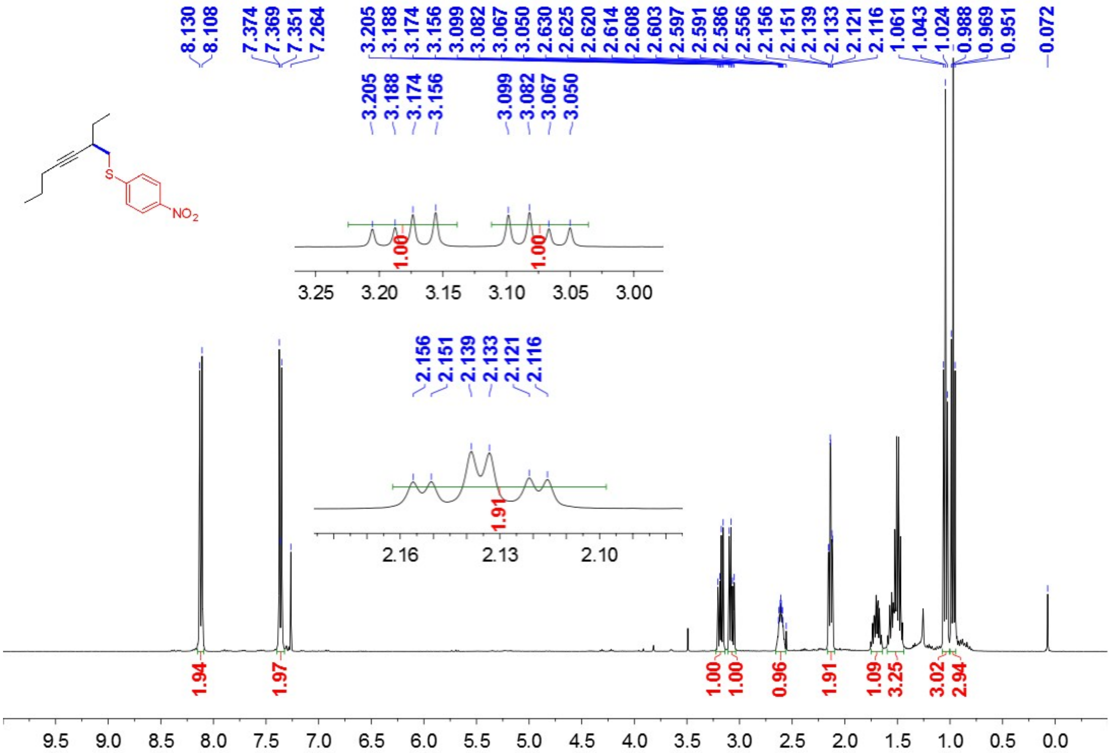
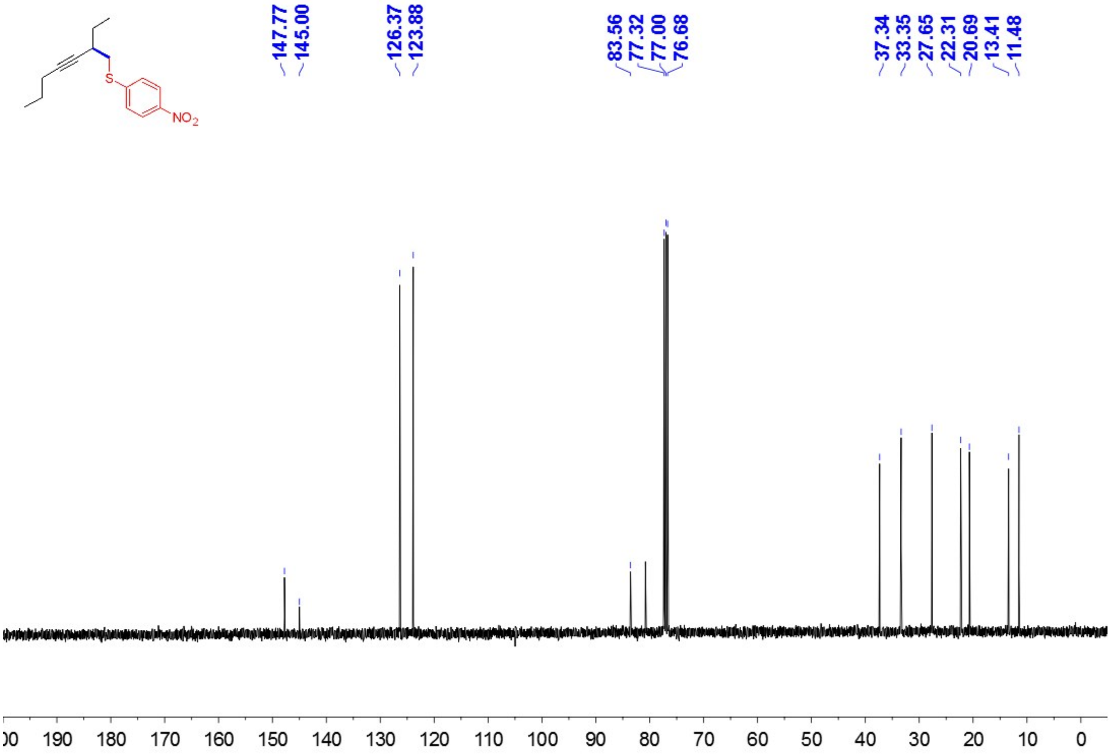


compounds 3k ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



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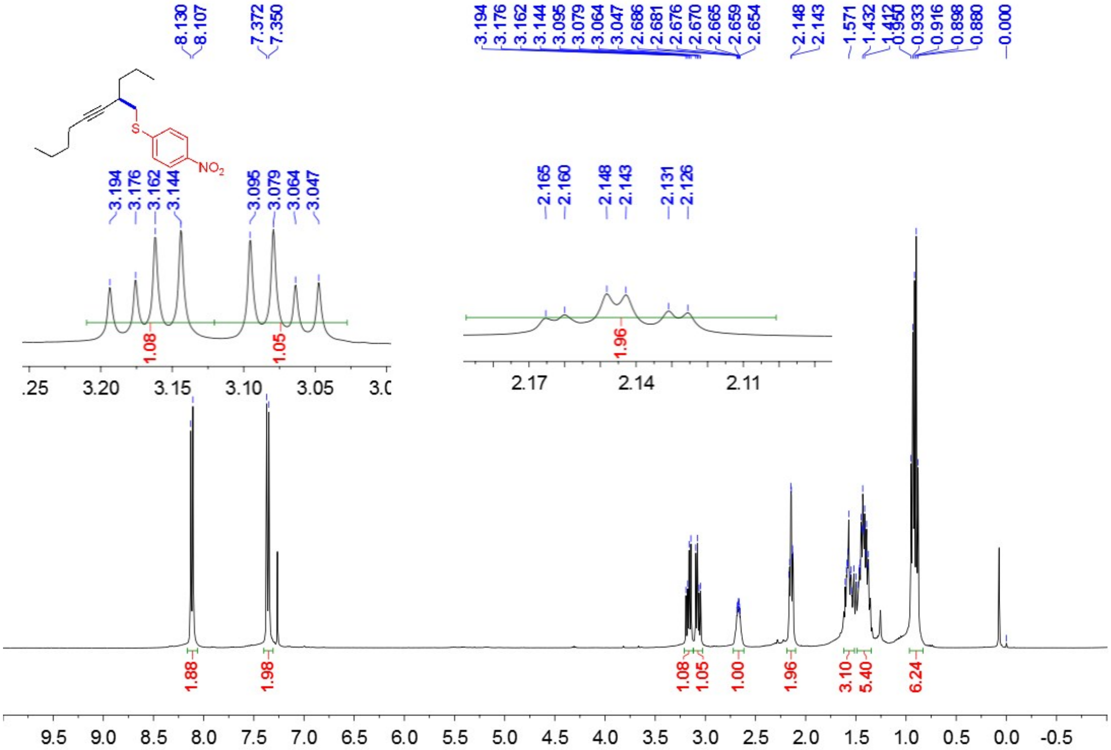
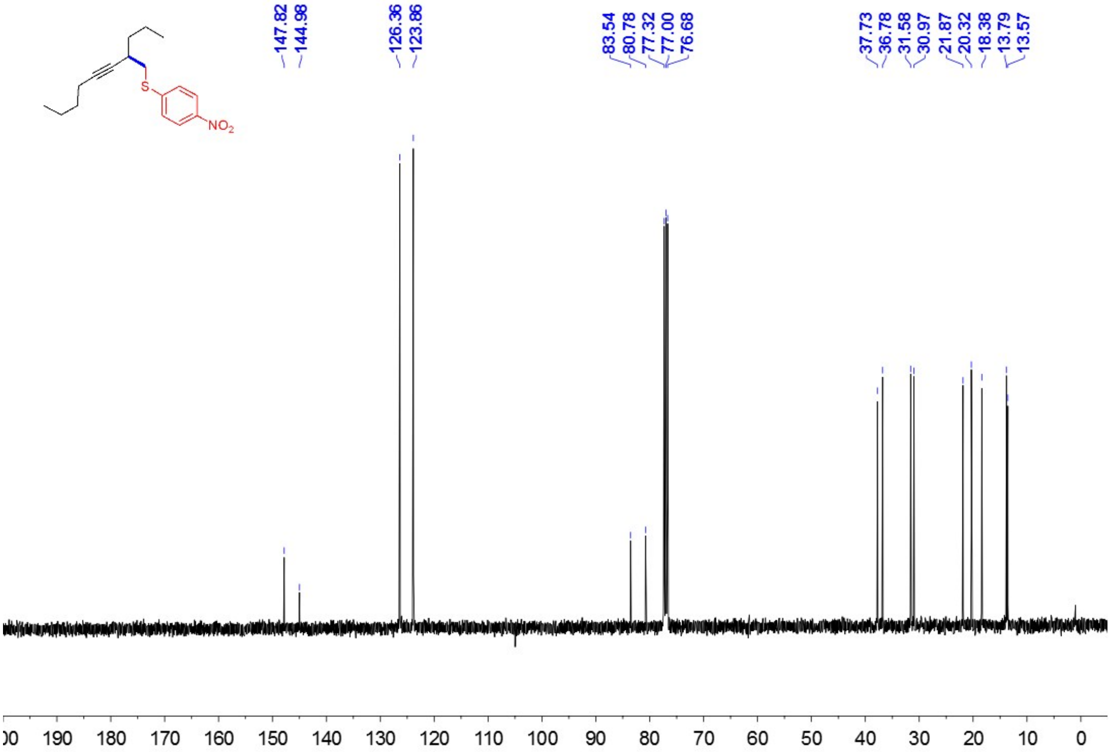
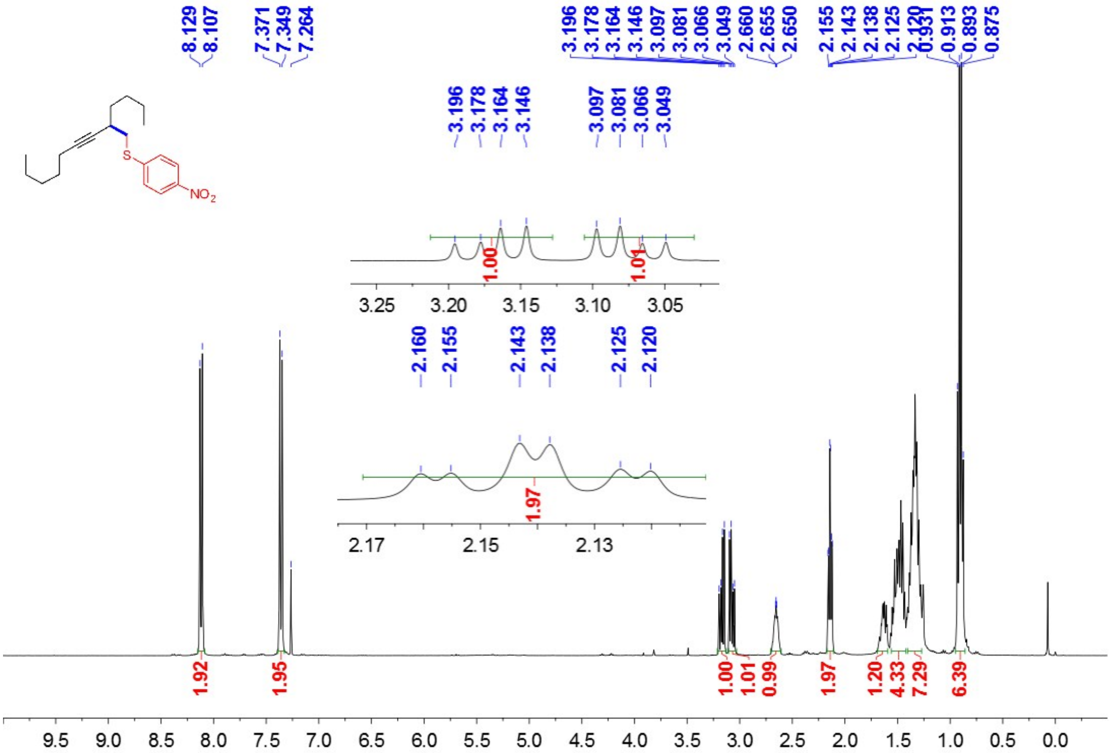


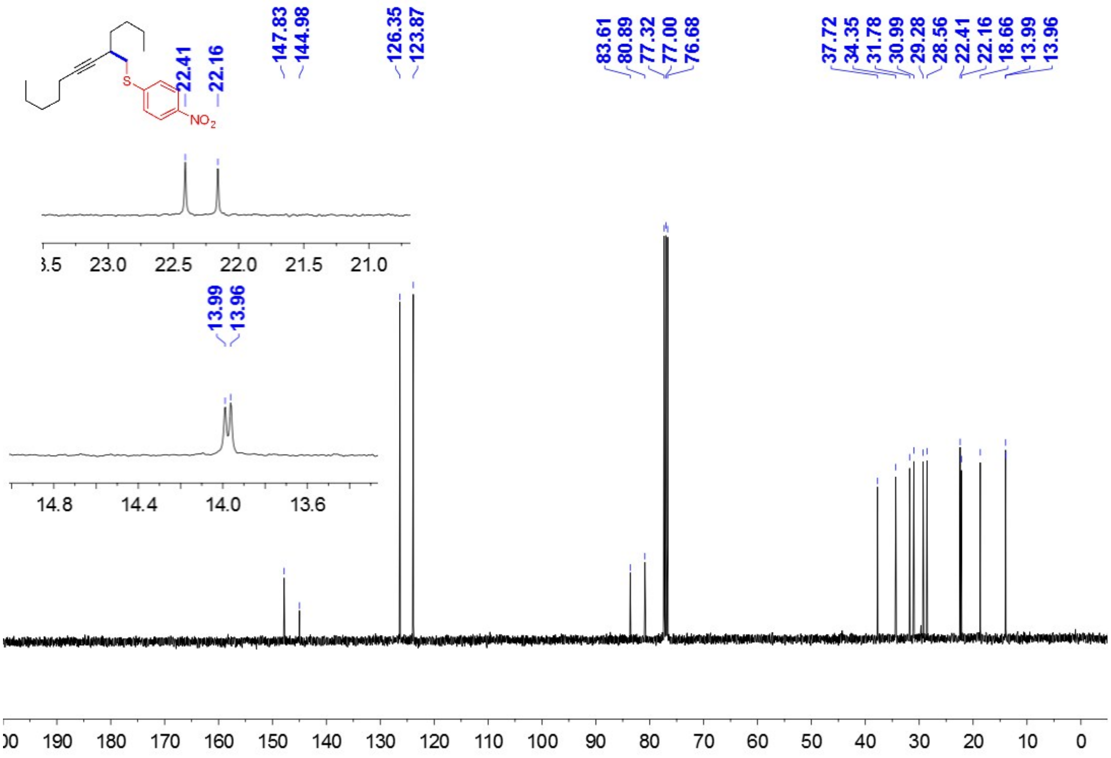
compounds 3l ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



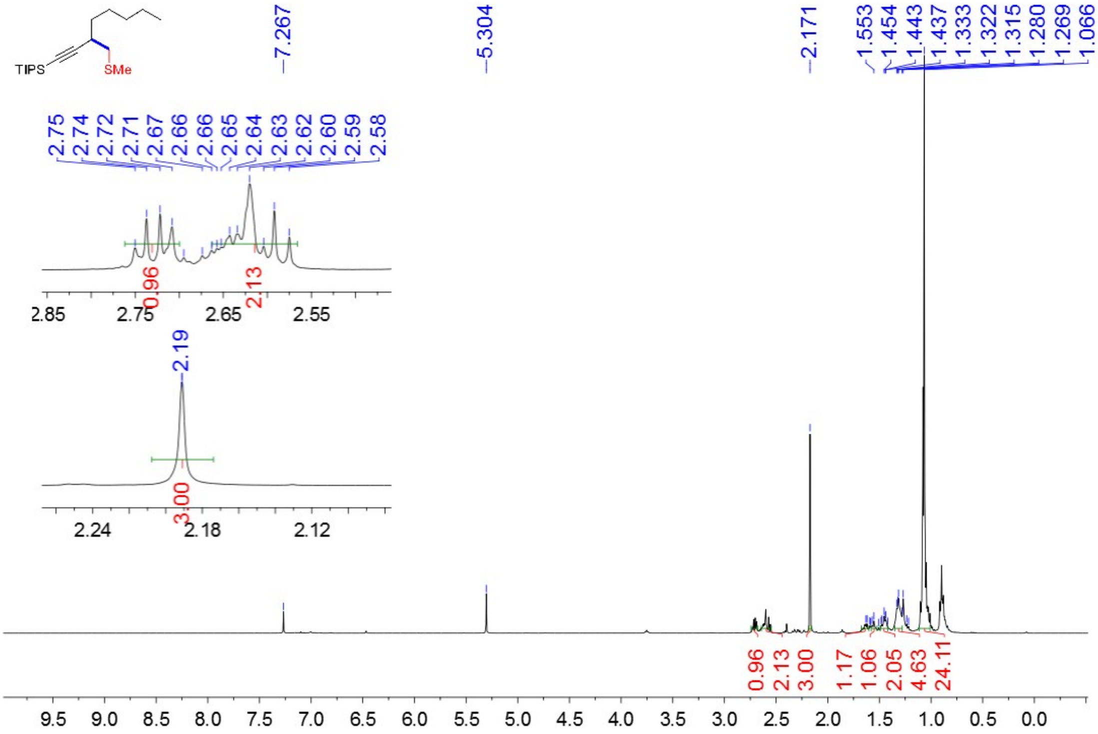
compounds 3m ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



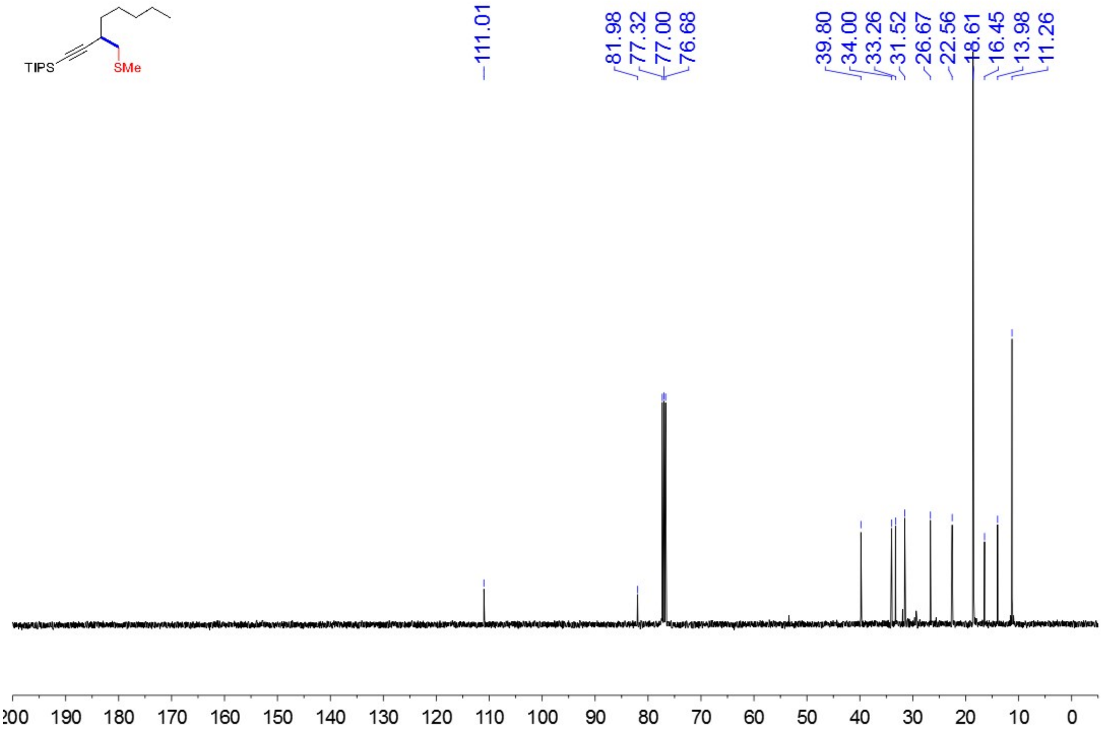
compounds 3m ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



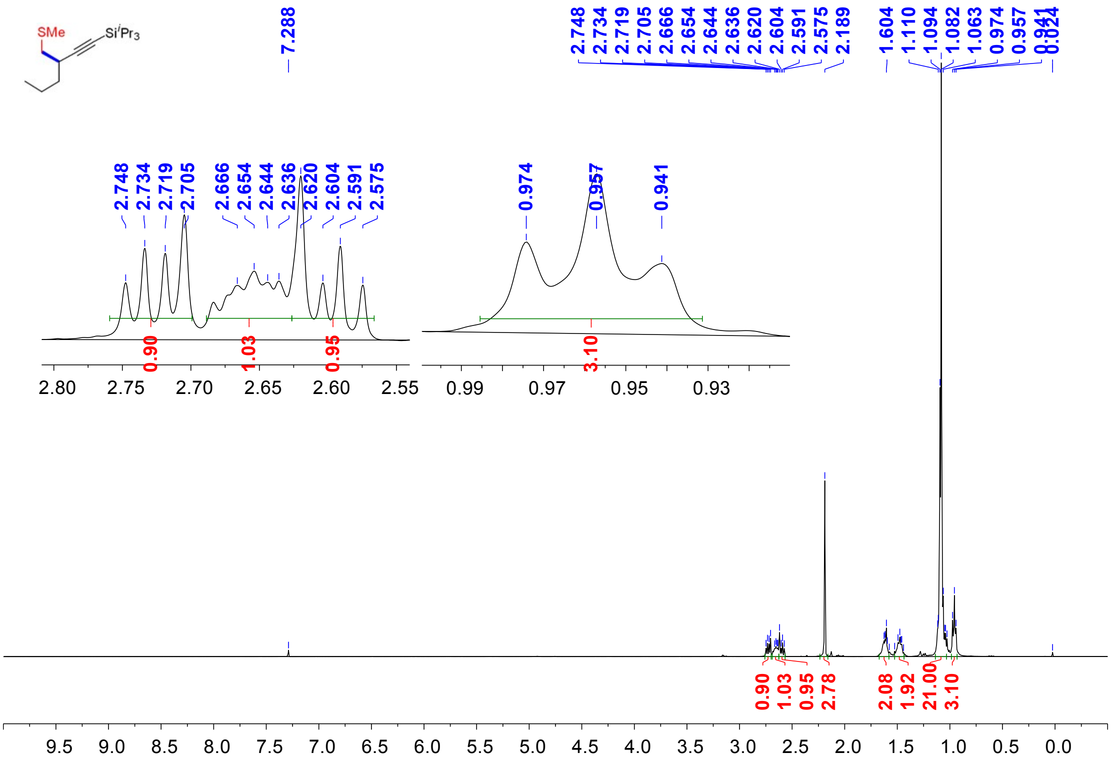
compounds 3n ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



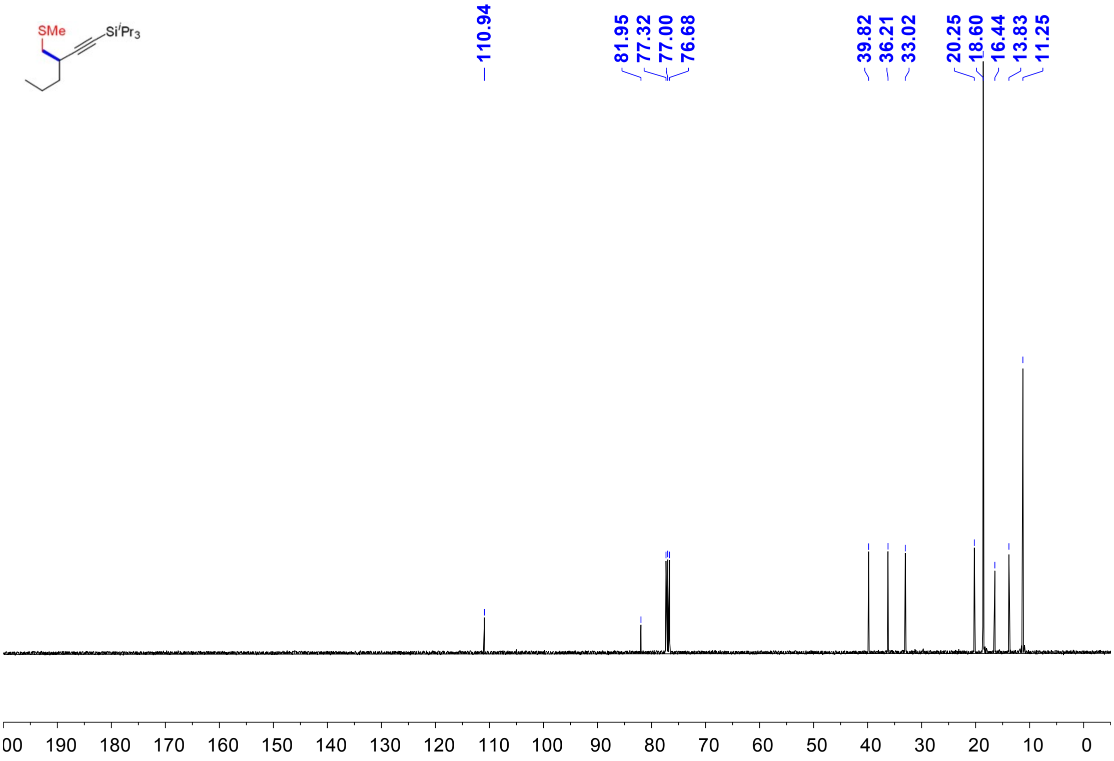
compounds 3n ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



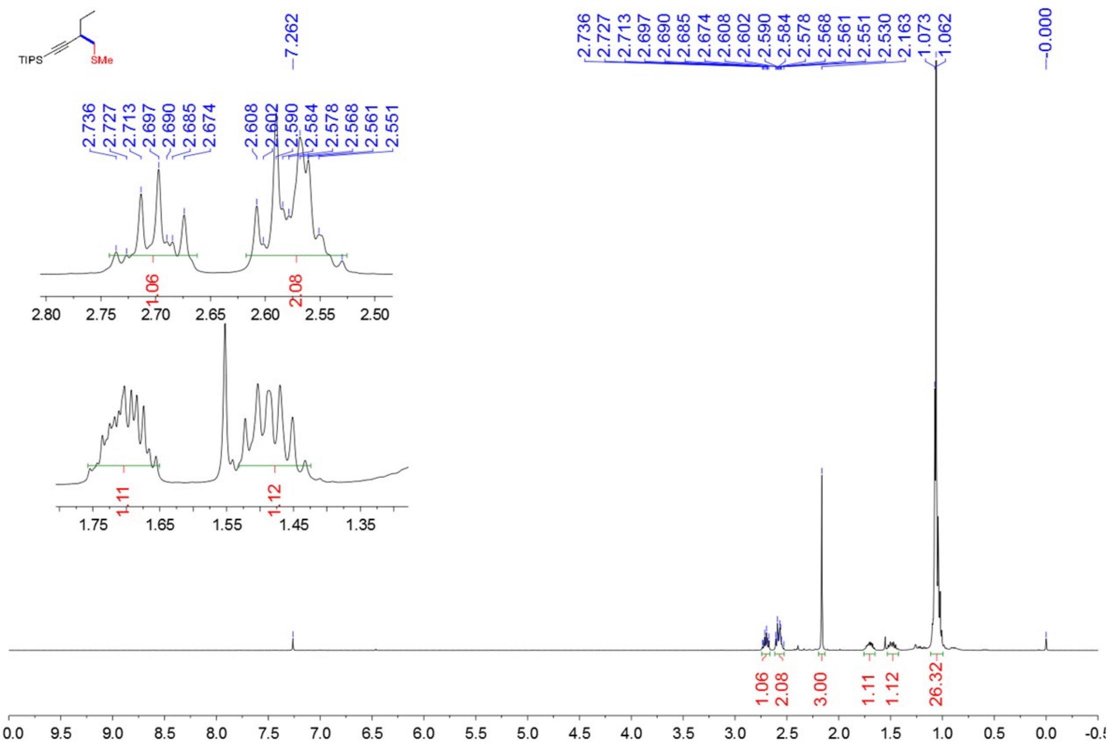
compounds 3o ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



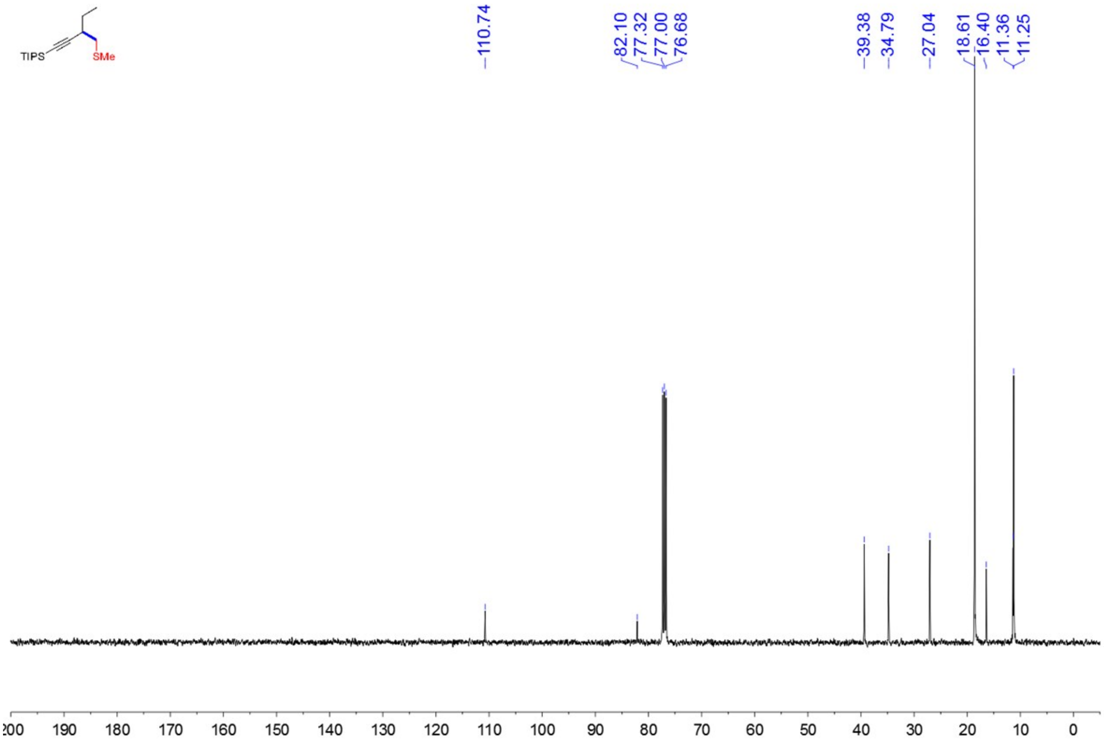
compounds 3o ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



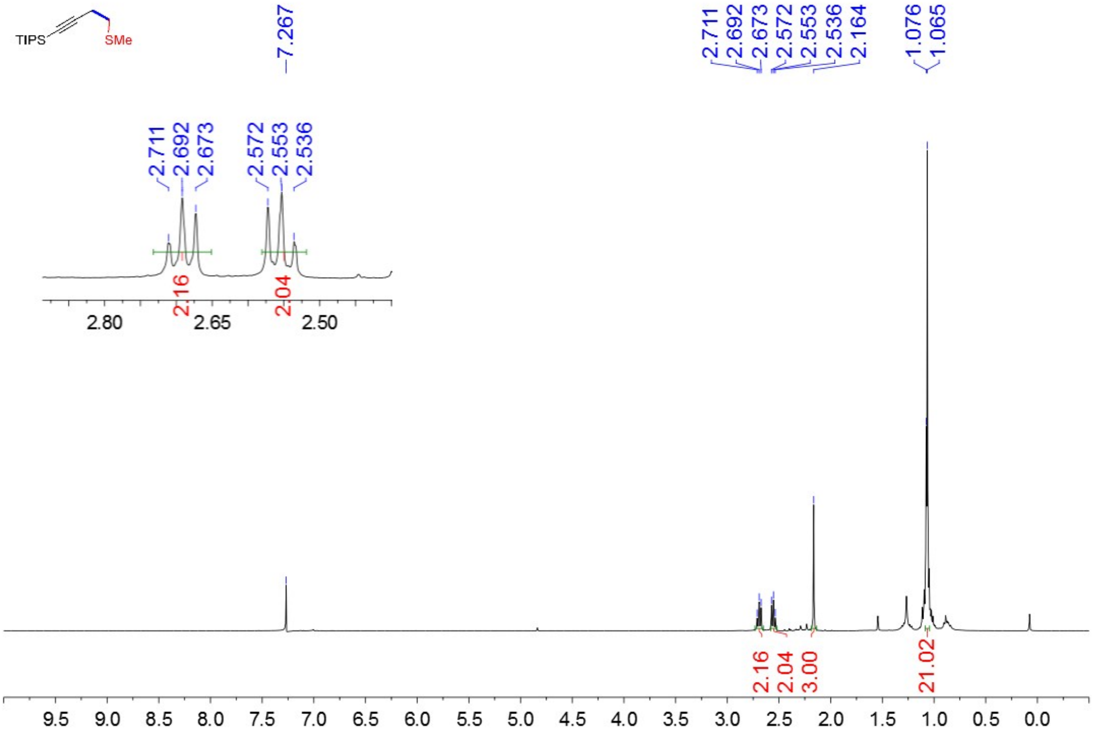
compounds 3p ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



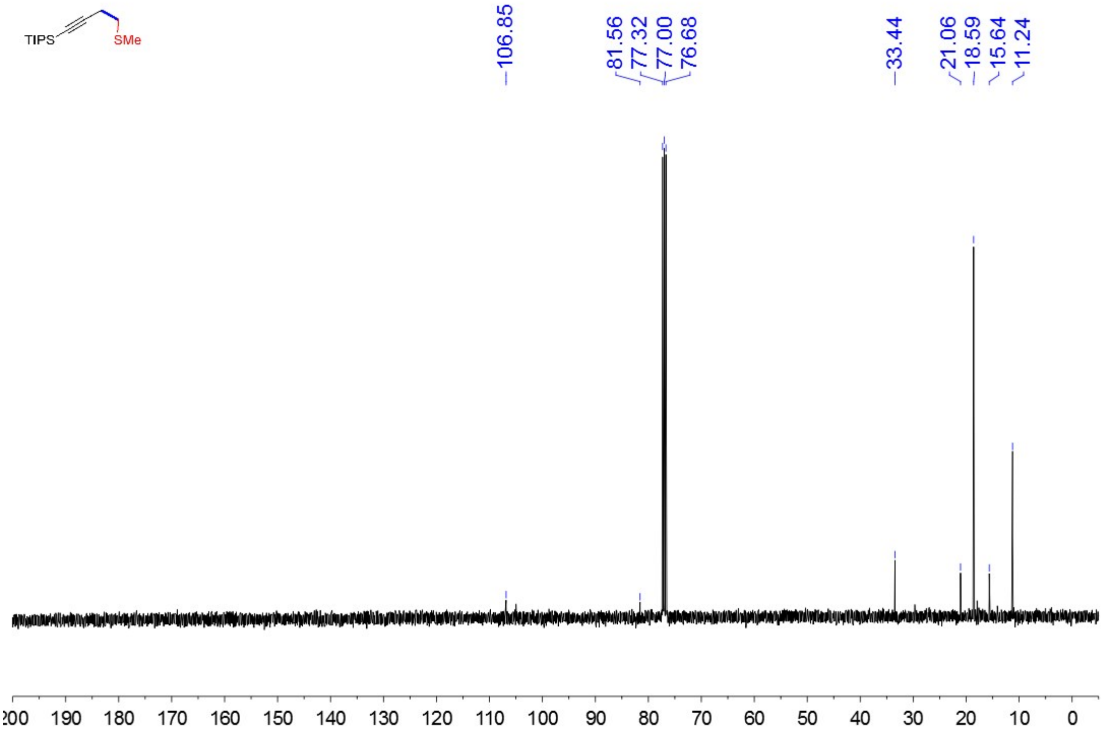
compounds 3p ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



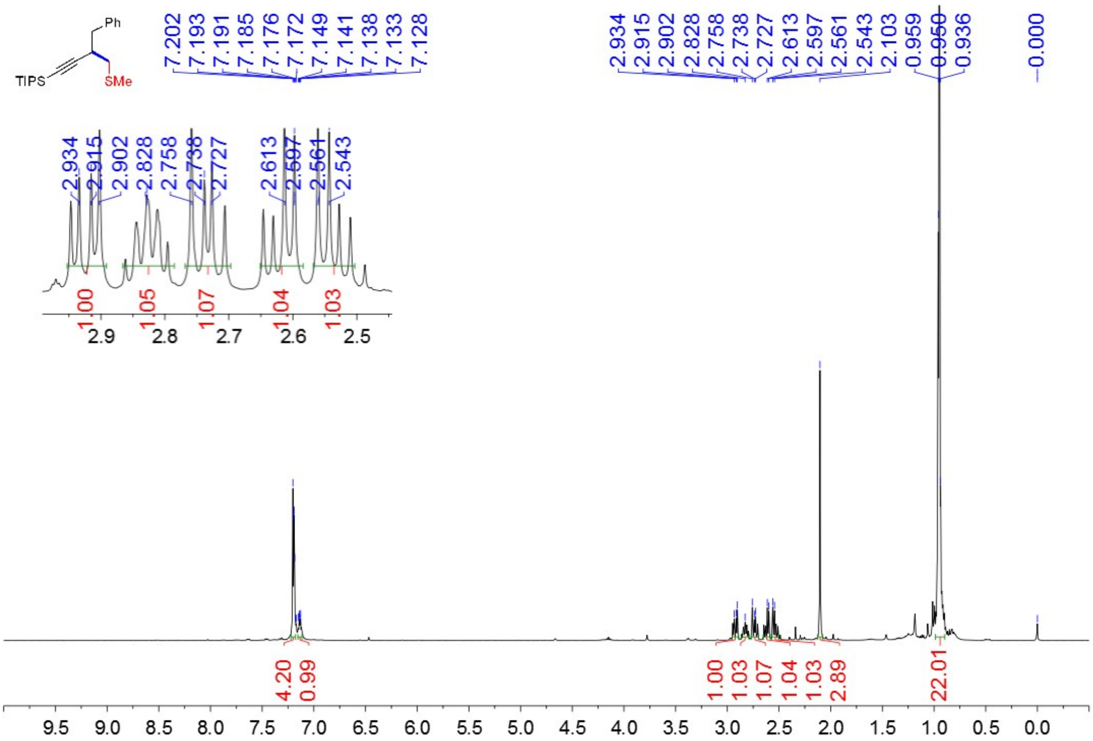
compounds 3q ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



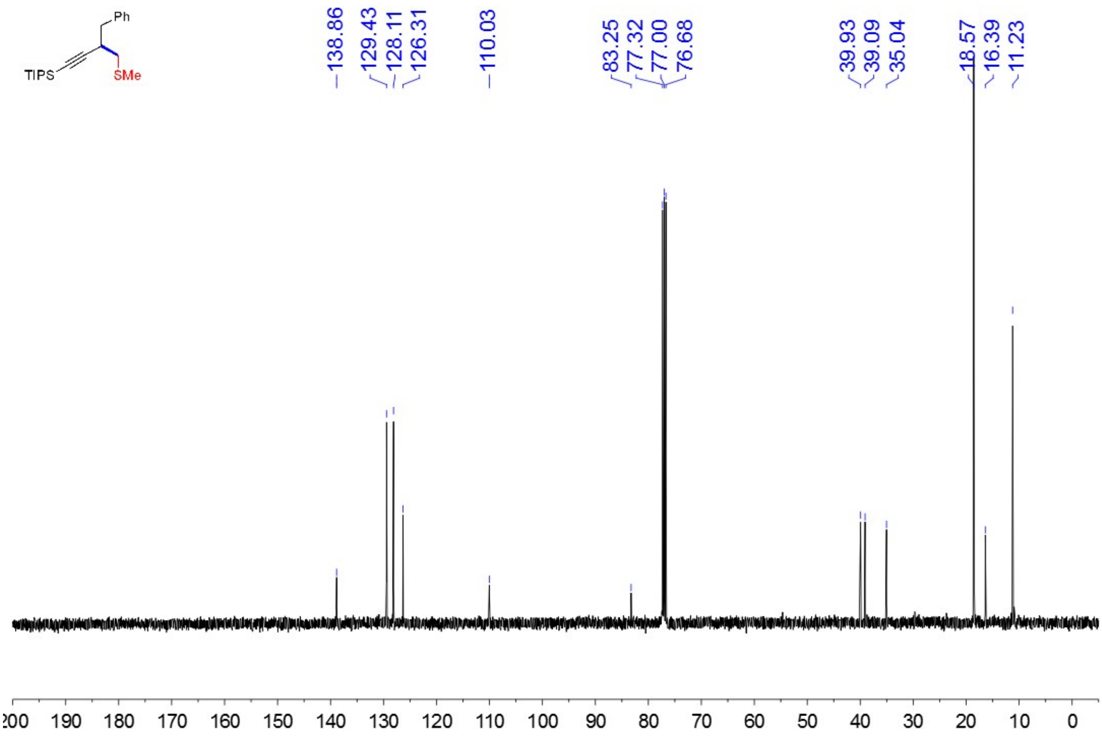
compounds 3q ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



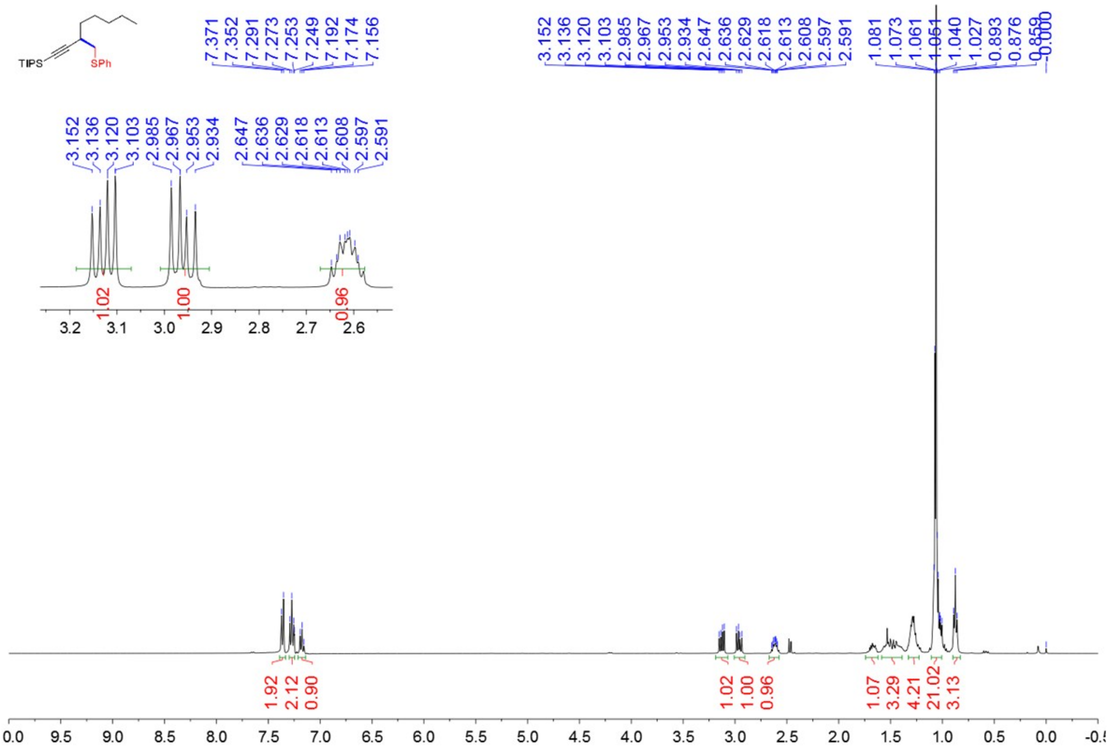
compounds 3r ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



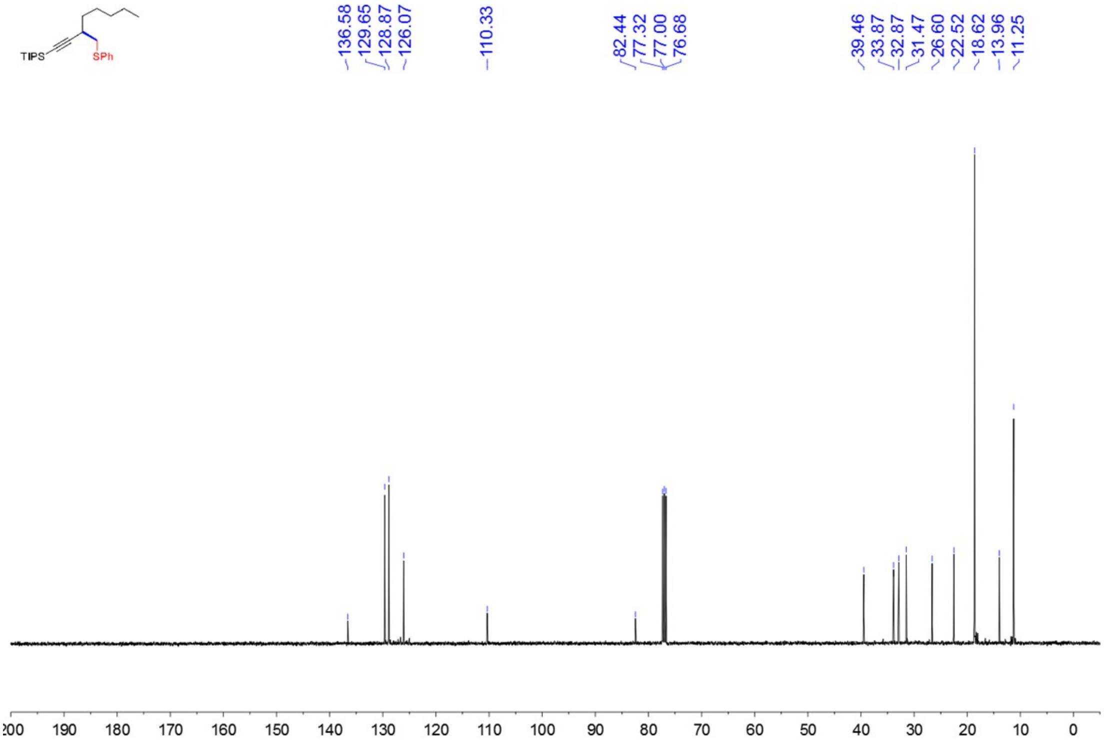
compounds 3r ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



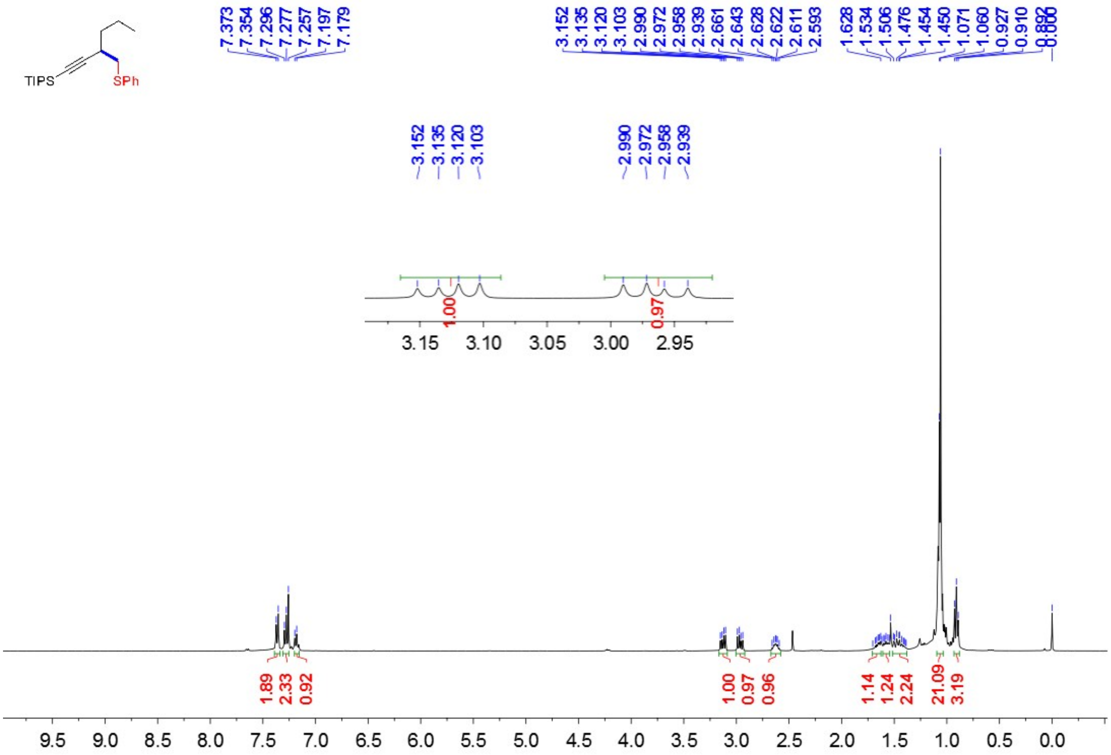
compounds 3s ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



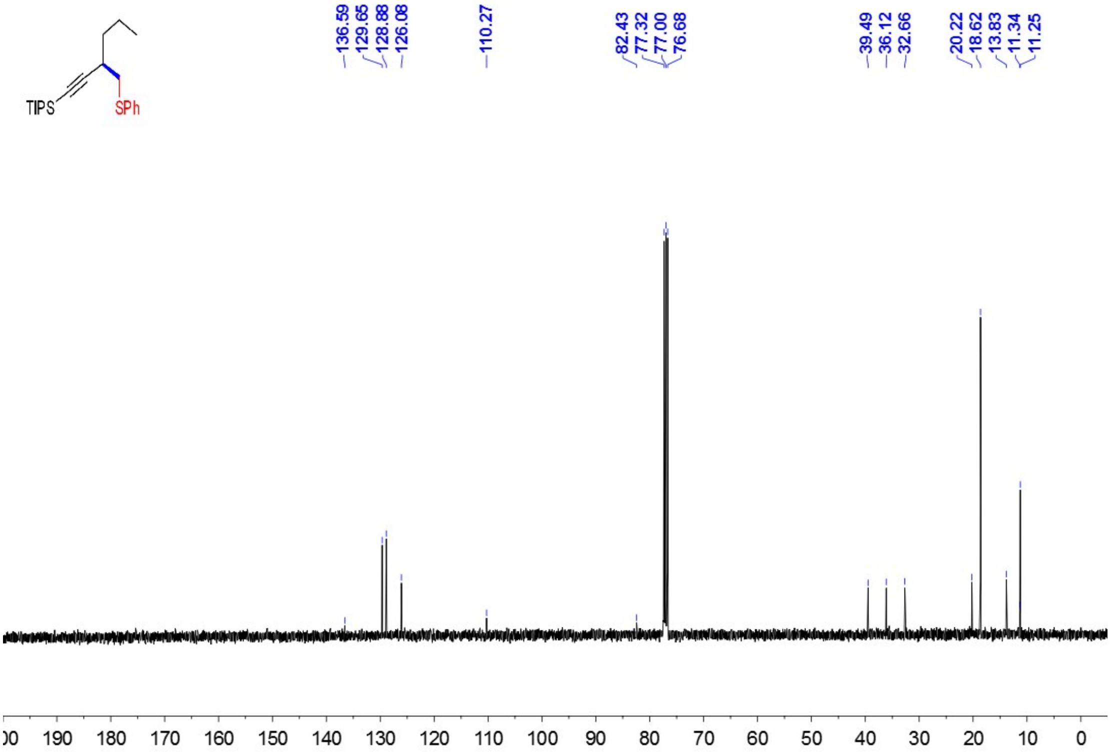
compounds 3s ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



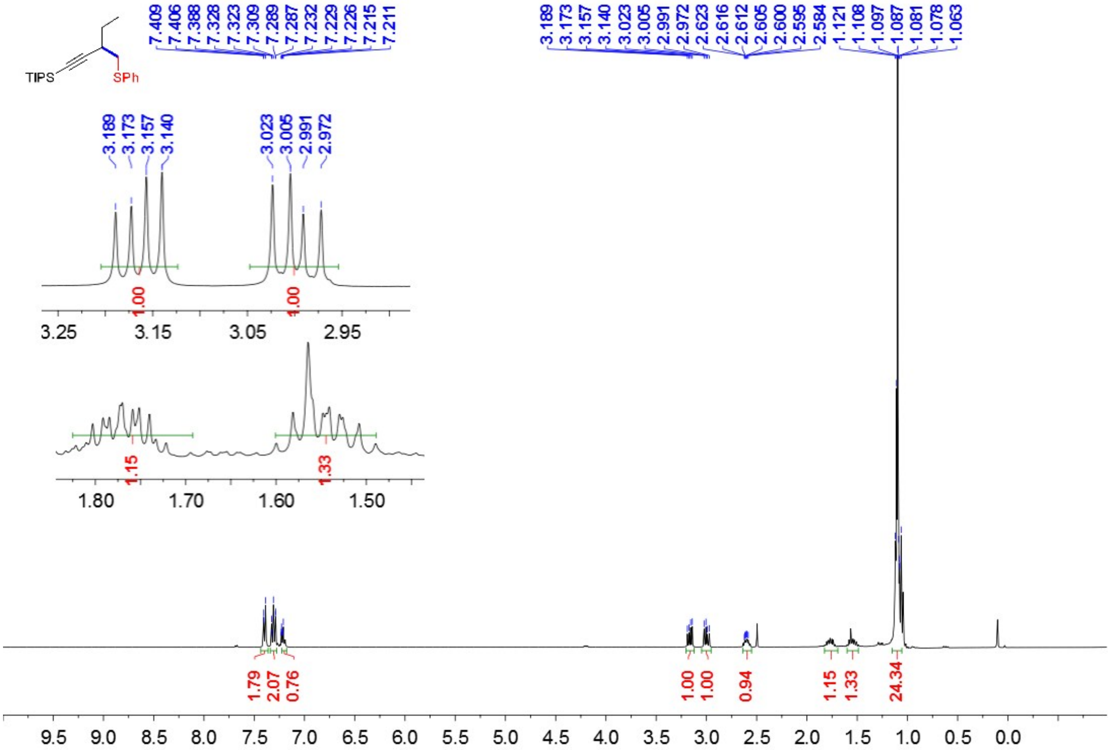
compounds 3t ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



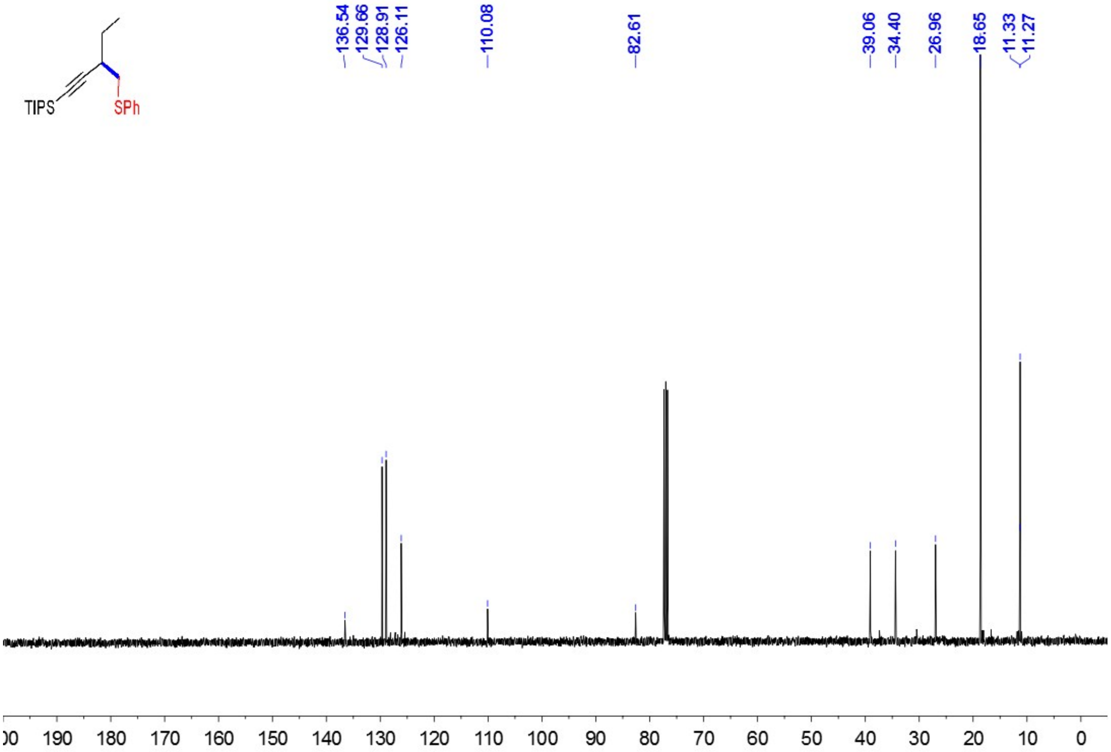
compounds 3t ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



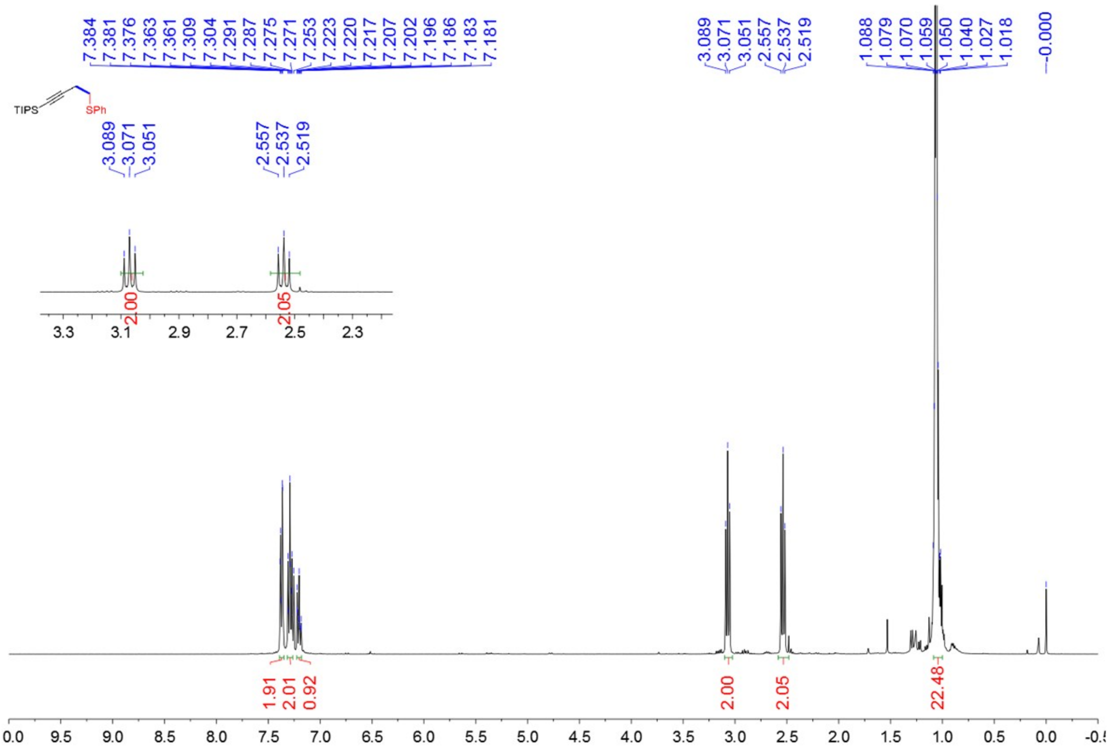
compounds 3u ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



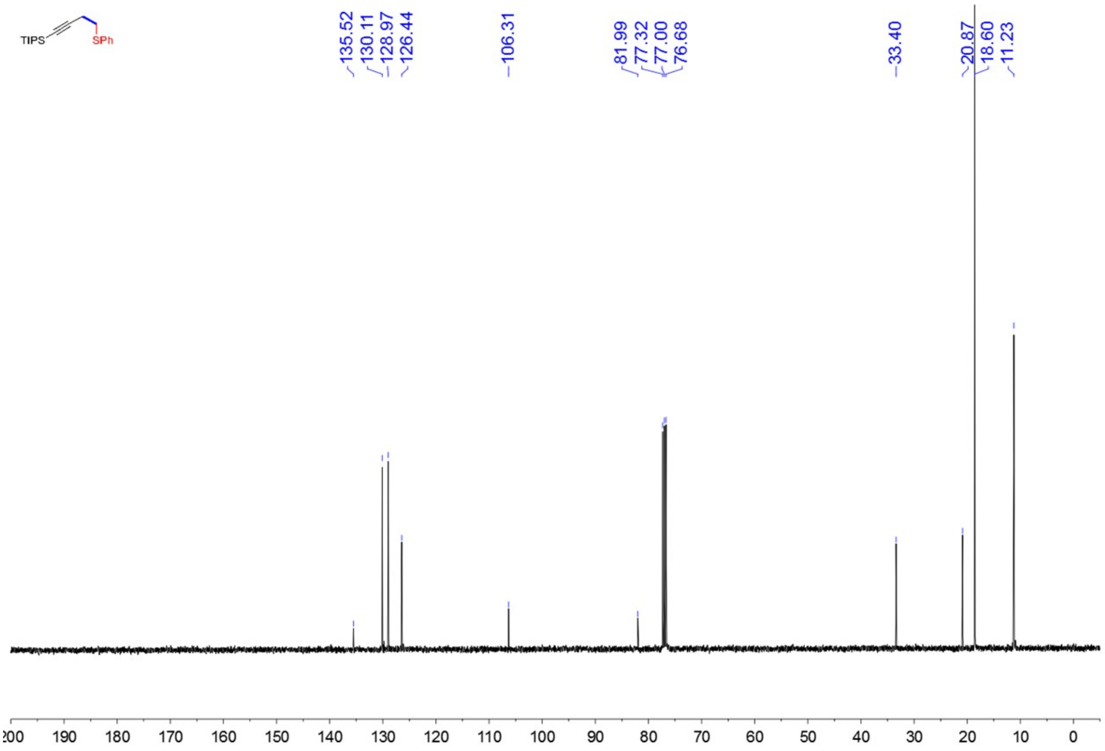
compounds 3u ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



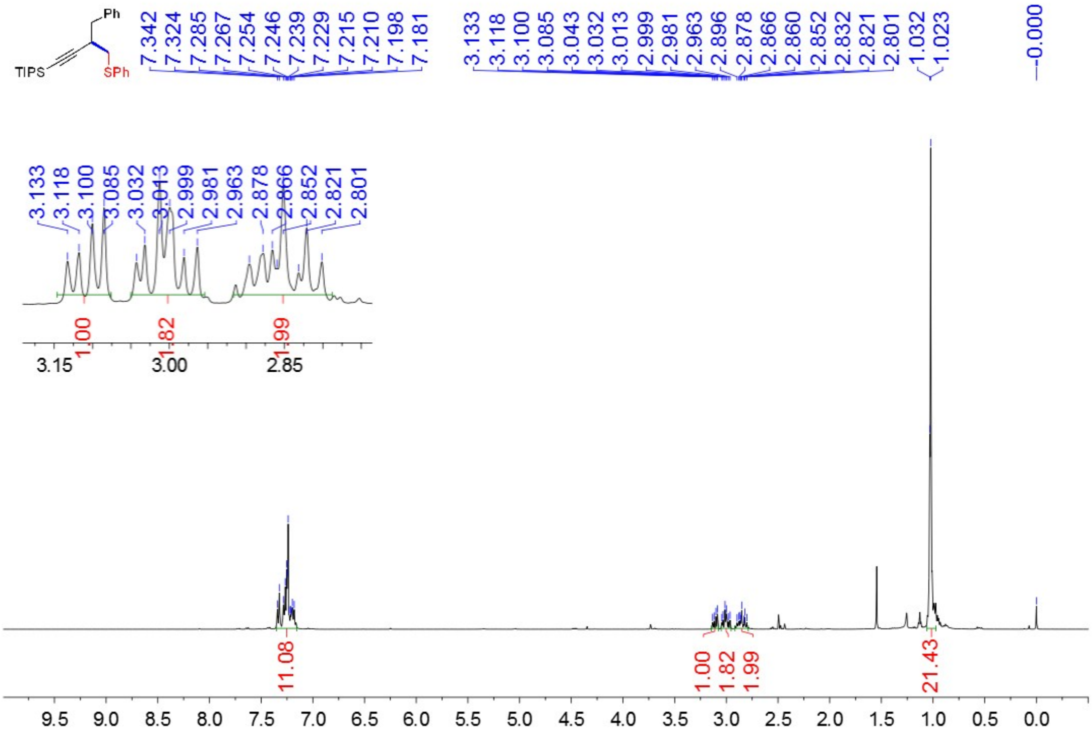
compounds 3v ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



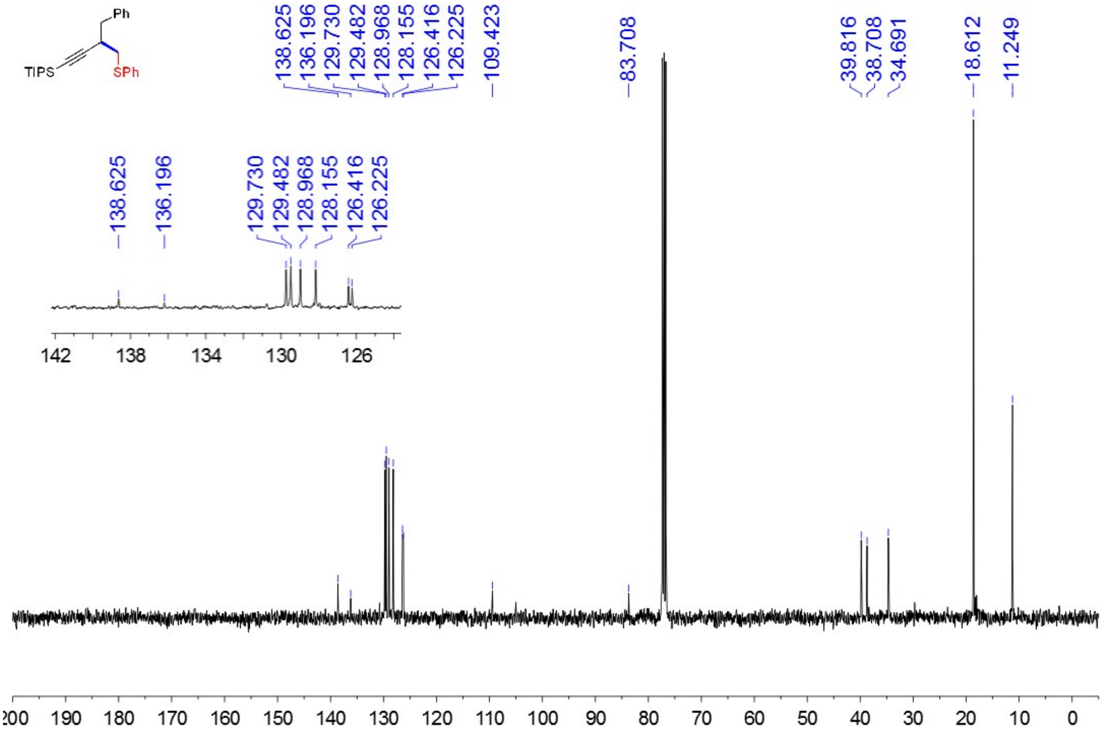
compounds 3v ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



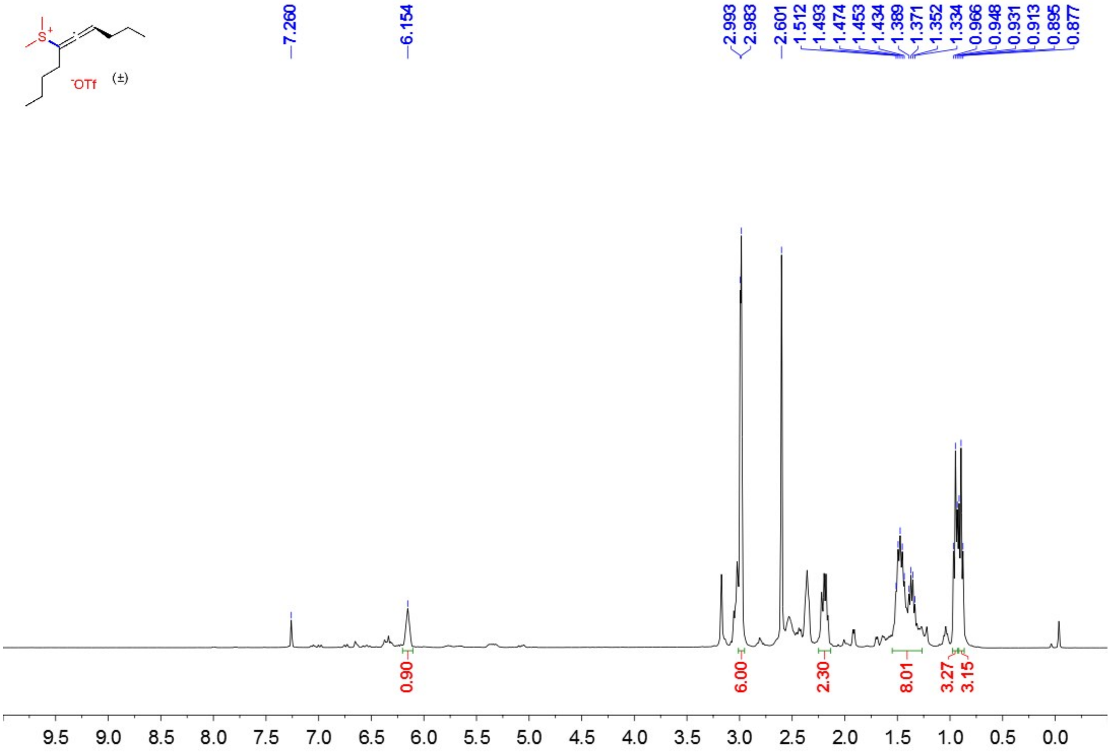
compounds 3w ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



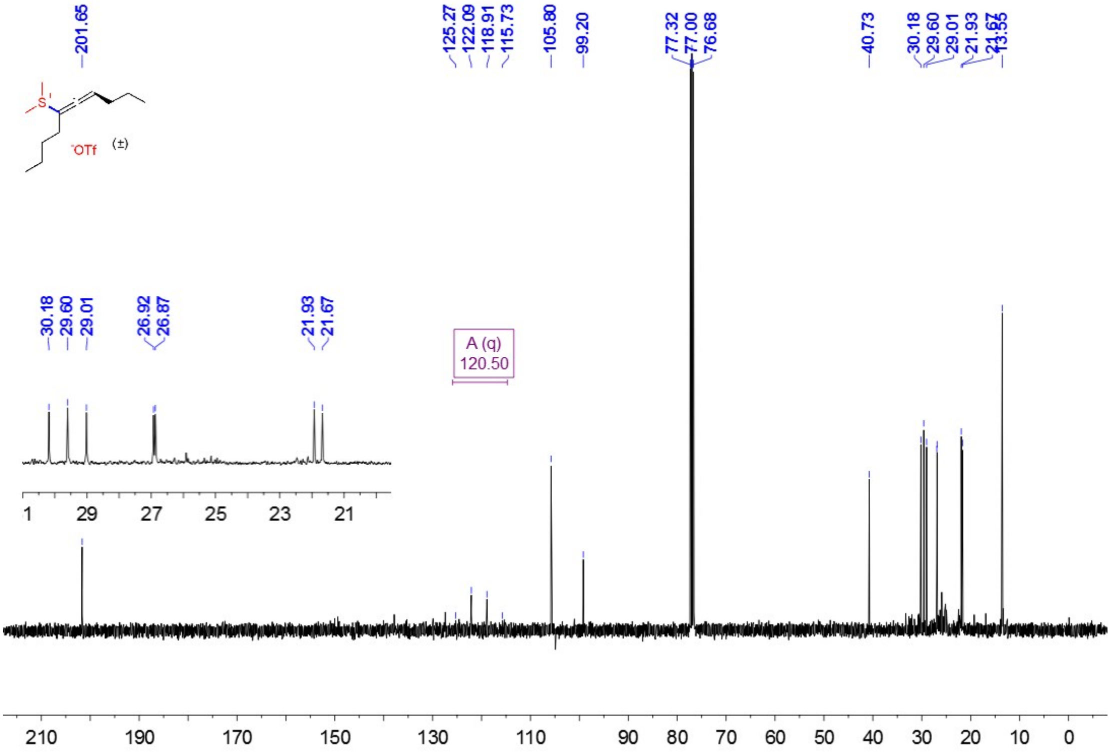
compounds 3w ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



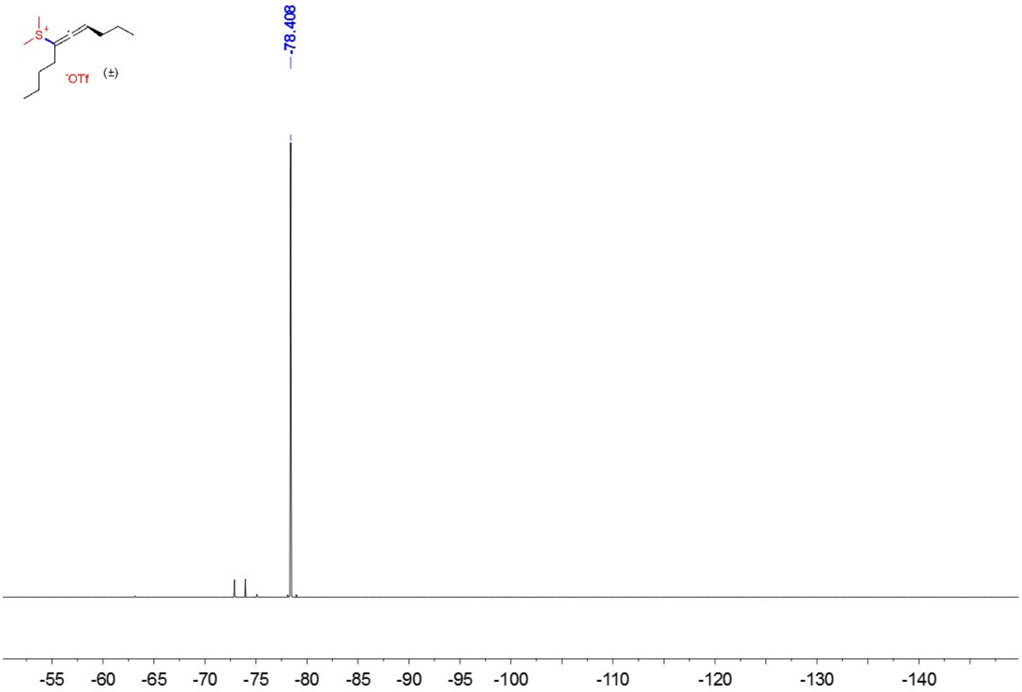
V-int ^{1}H NMR spectra, 400 MHz, CDCl$_3$



V-int ^{13}C NMR spectra, 100 MHz, CDCl$_3$

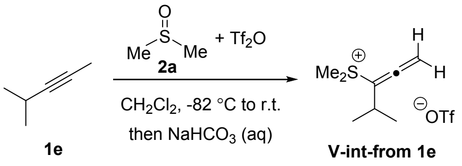


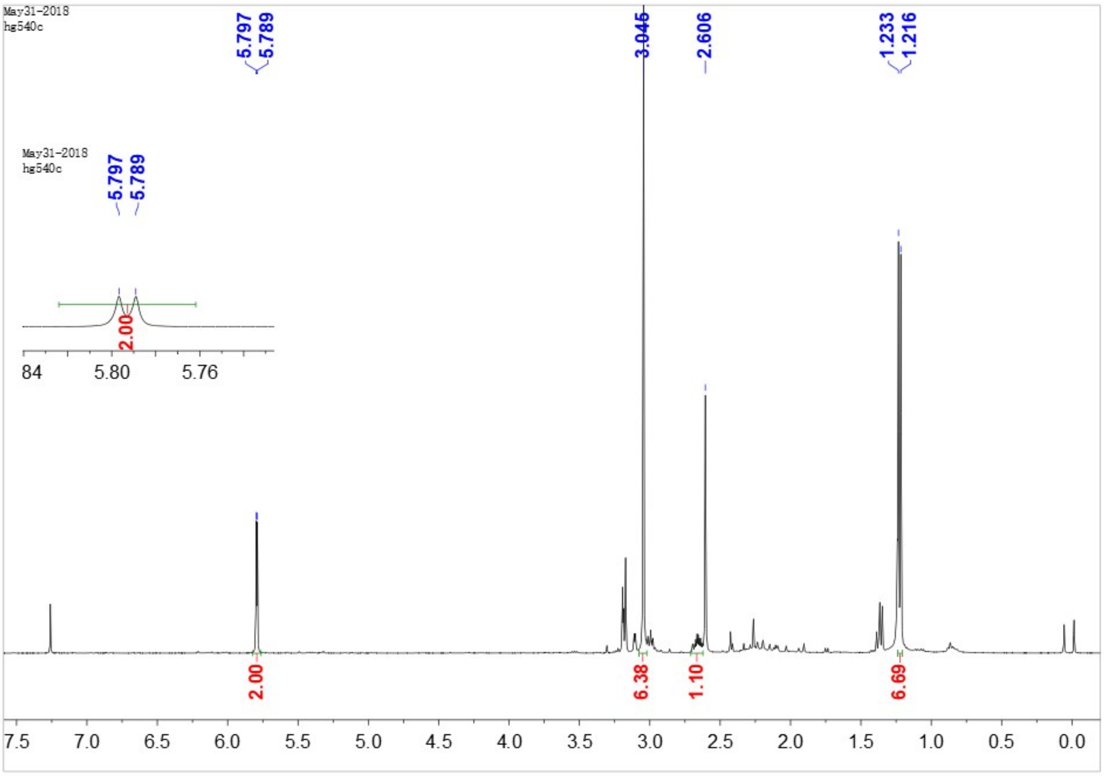
V-int ^{19}F NMR spectra, 376 MHz, $CDCl_3$.



V-int-from 1e crude ^{1}H NMR spectra, 400 MHz, $CDCl_3$

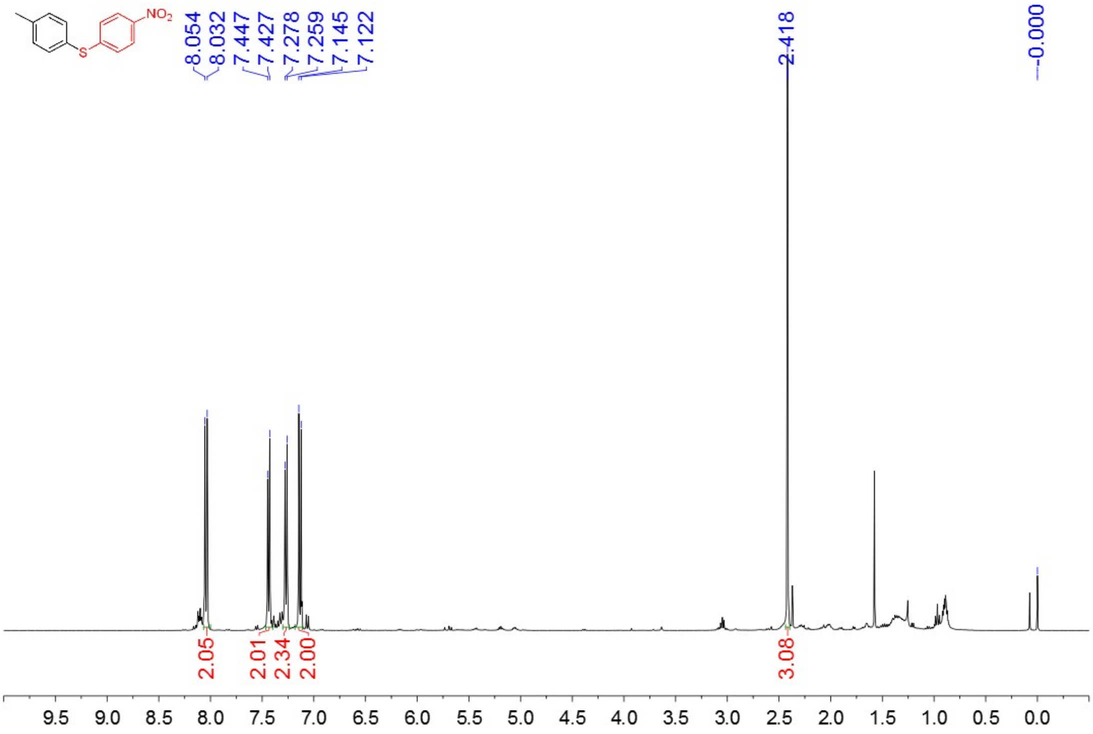
Isolated similarly as **V-Int** from the reaction between alkyne **1e**, DMSO (**2a**), and Tf_2O.

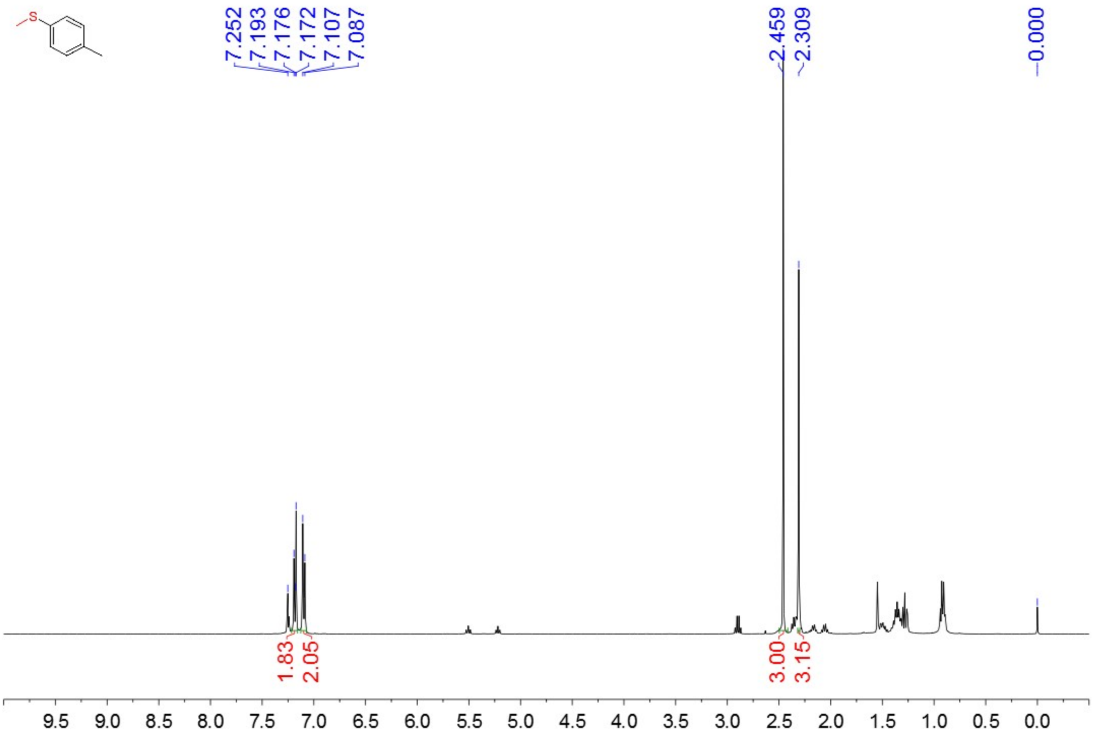




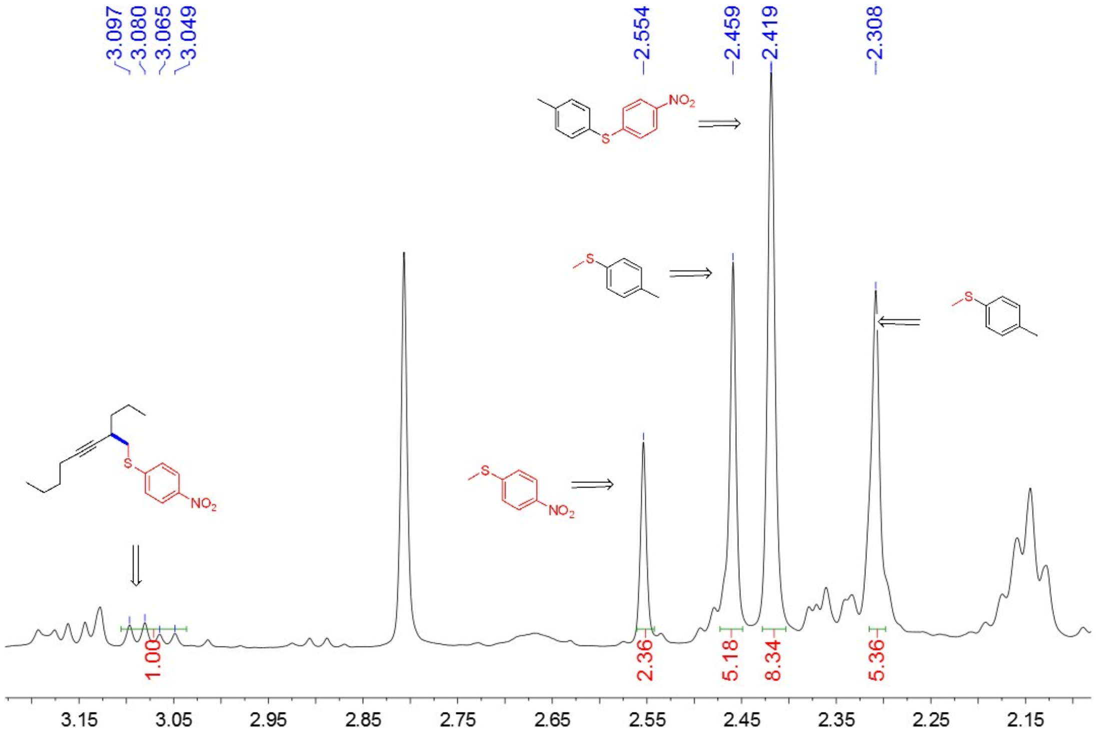
Arylthiolation product A and methylthiolation product B

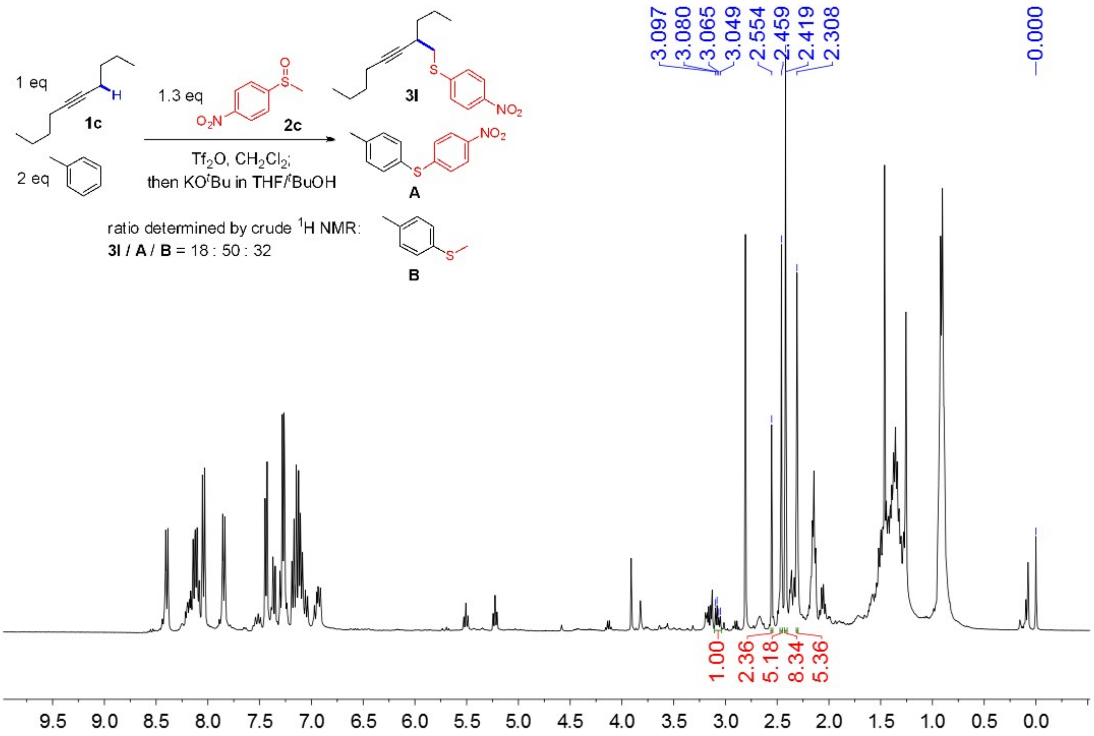
^{1}H NMR spectra, 400 MHz, $CDCl_3$.



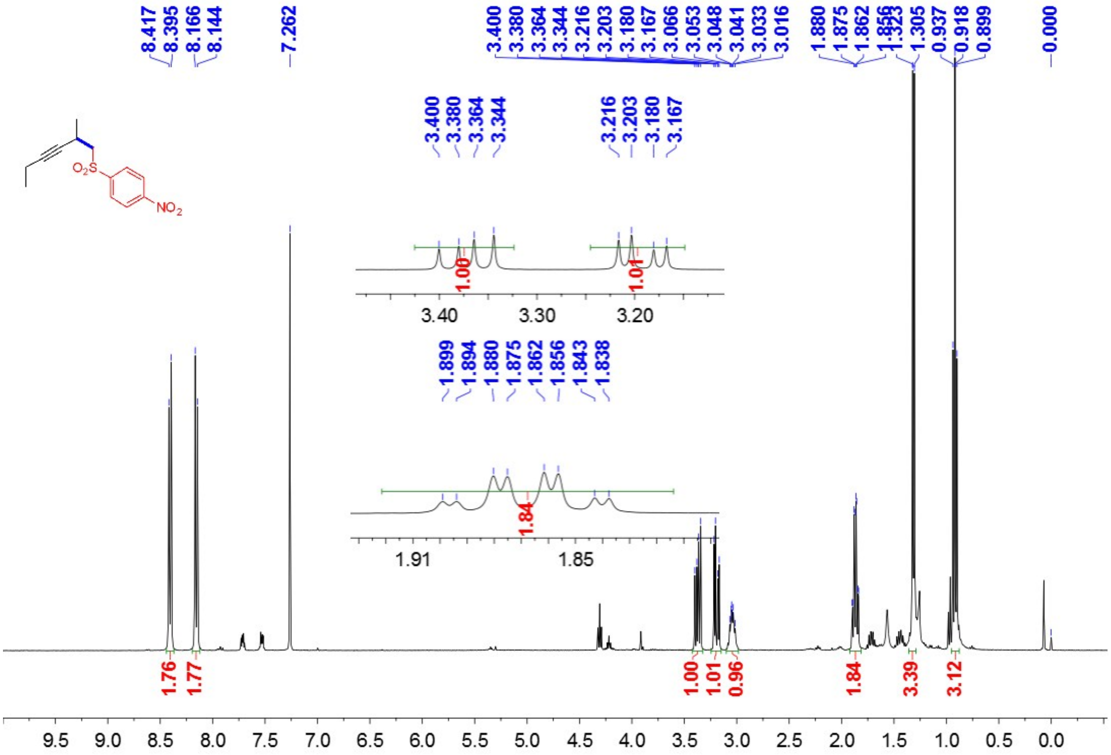


^1H NMR spectra, 400 MHz, $CDCl_3$.

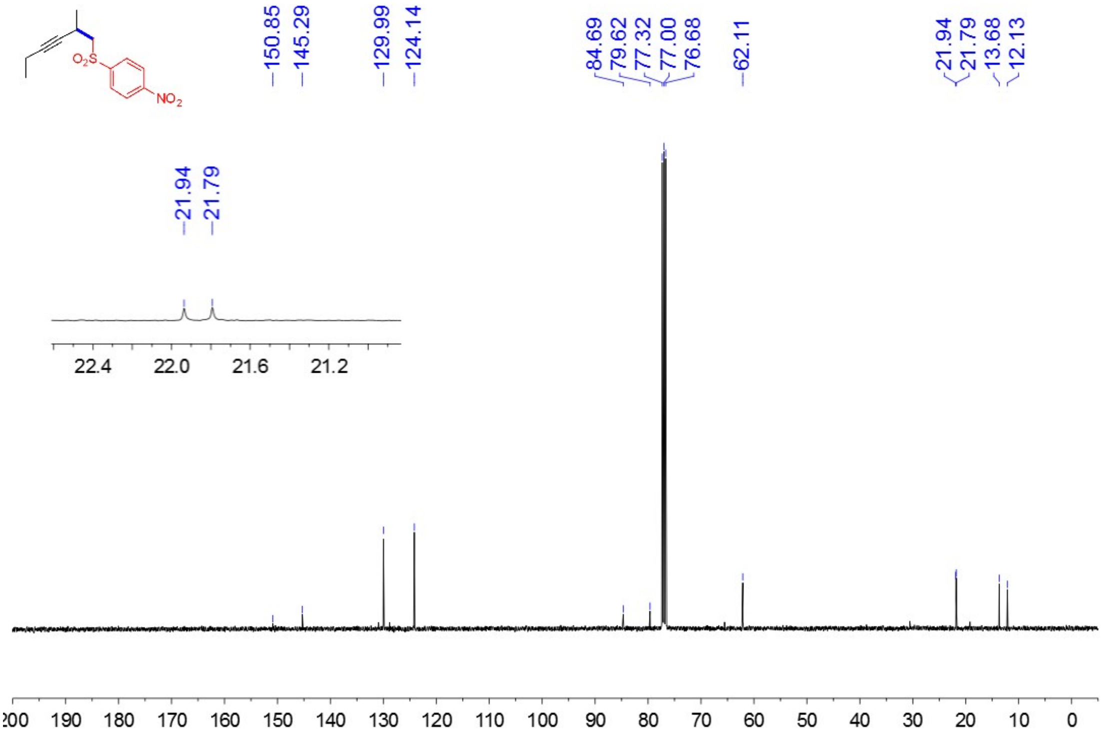




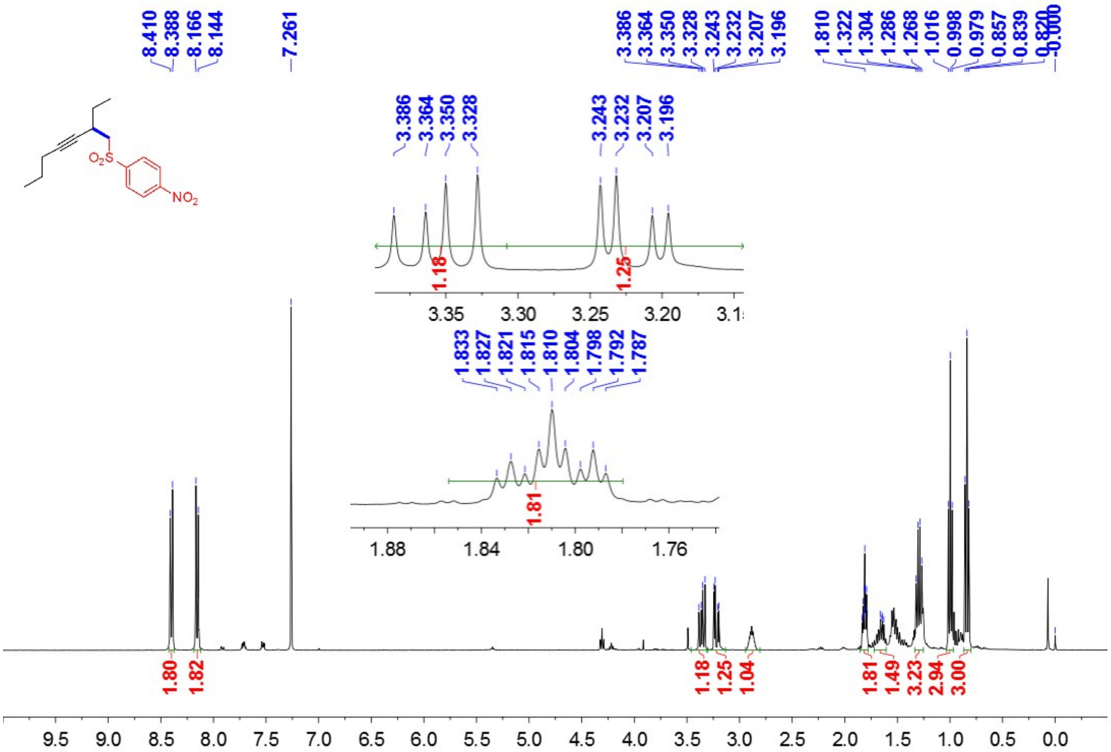
Sulfone 1 ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



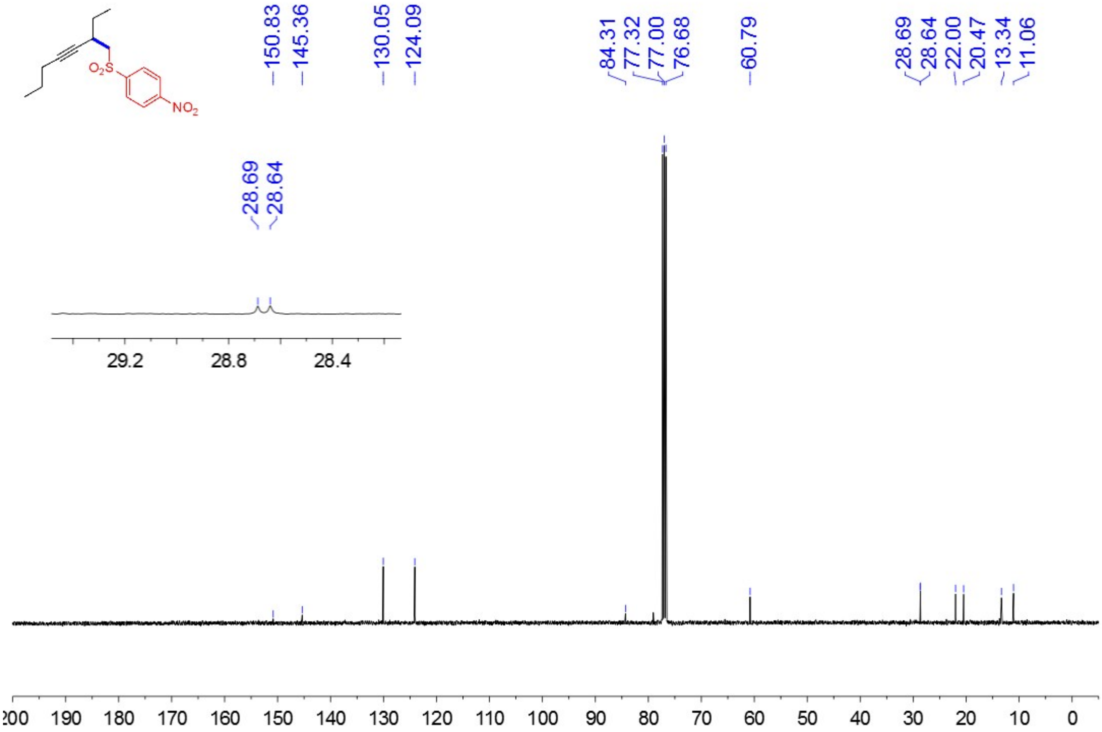
Sulfone 1 ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



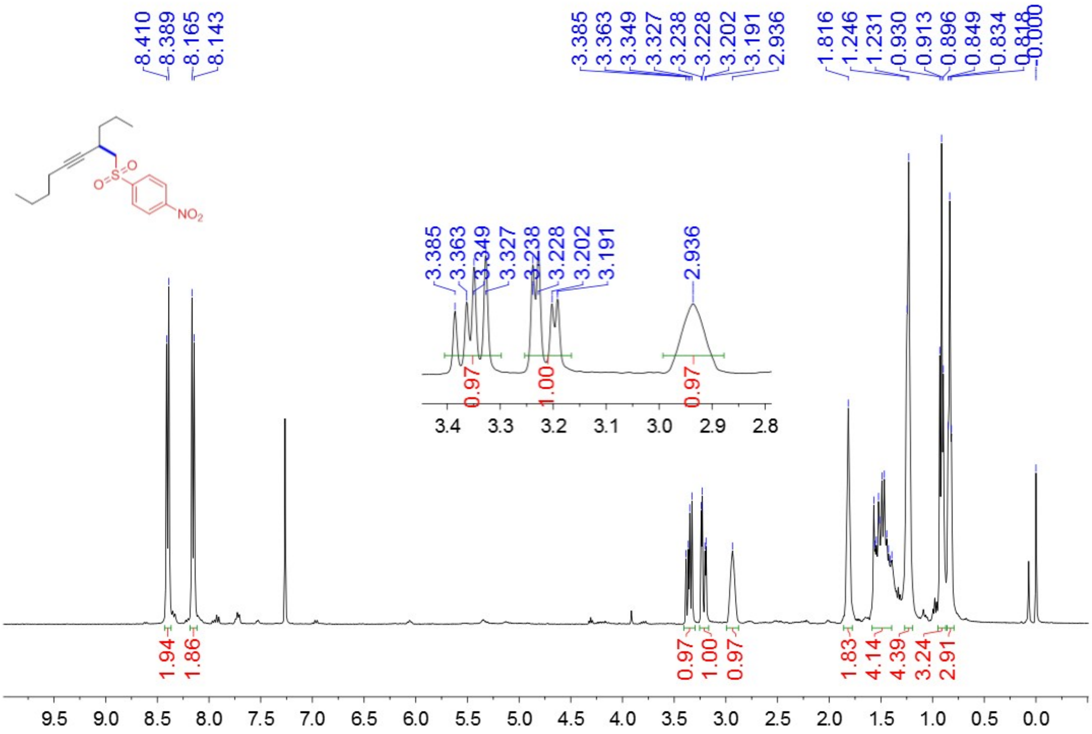
Sulfone 2 ^{1}H NMR spectra, 400 MHz, $CDCl_3$.



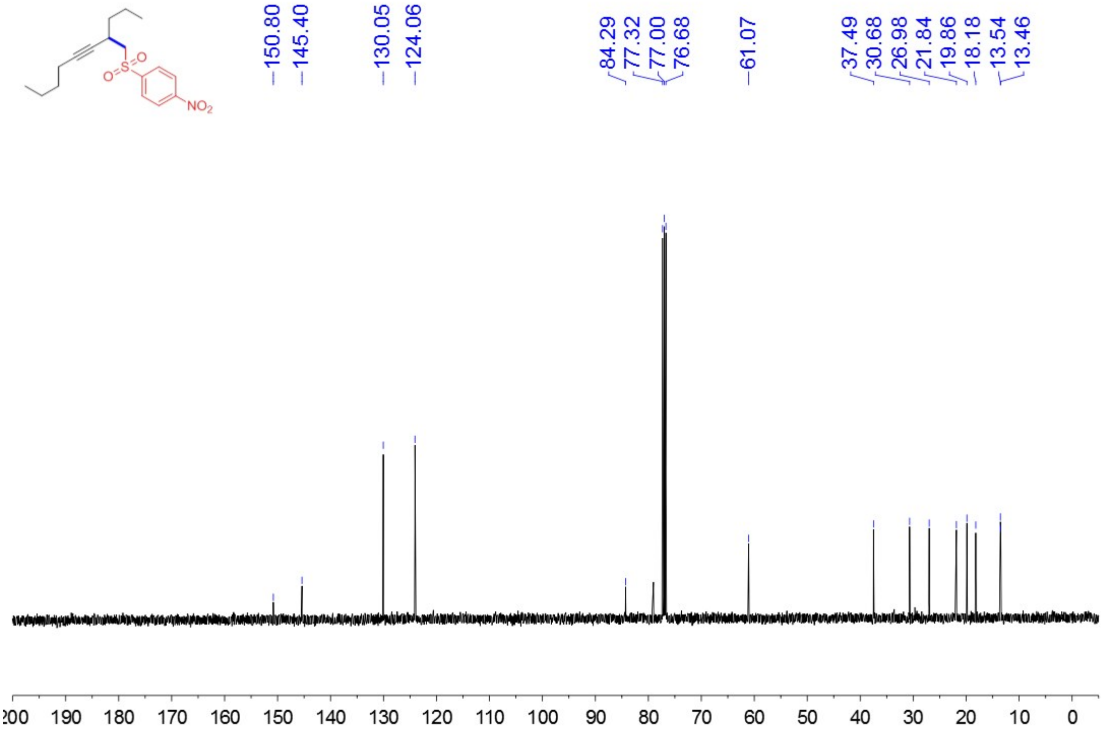
Sulfone 2 ^{13}C NMR spectra, 100 MHz, $CDCl_3$.



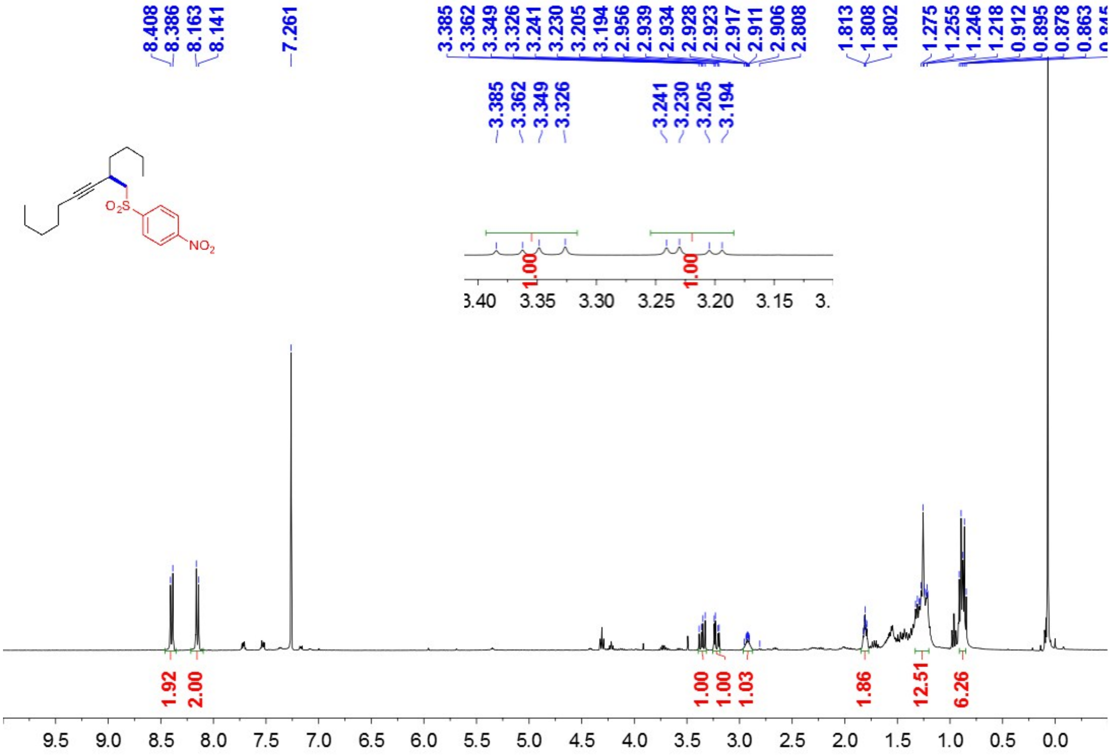
Sulfone 3 ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



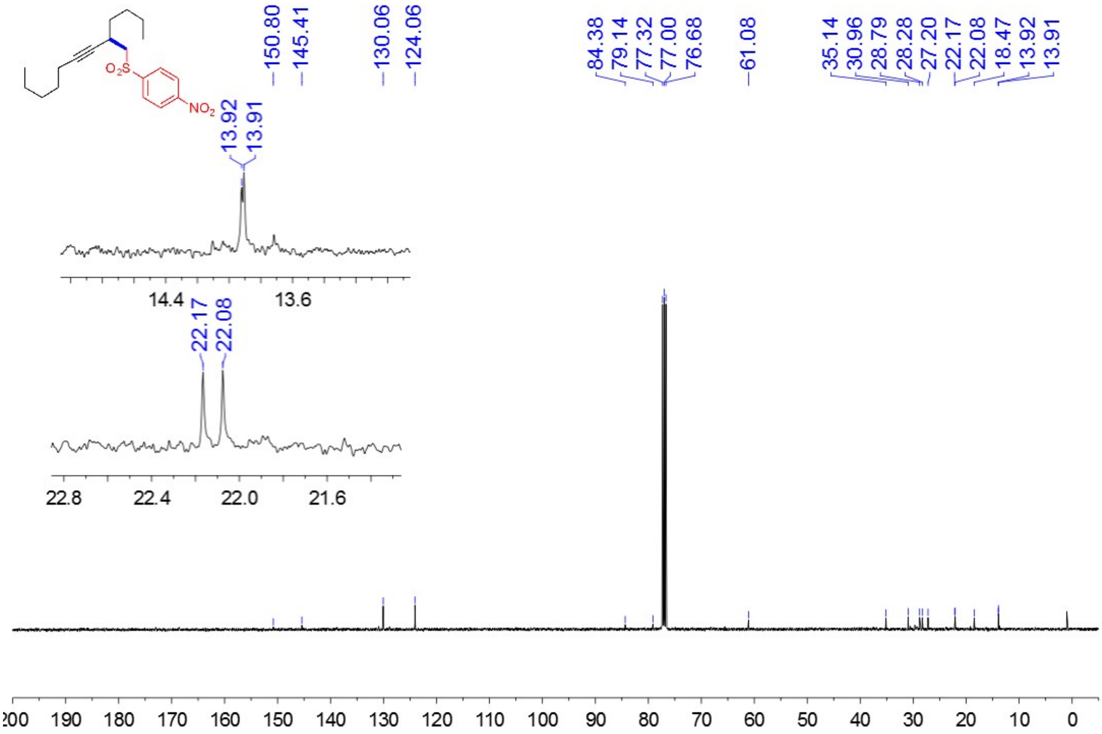
Sulfone 3 ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



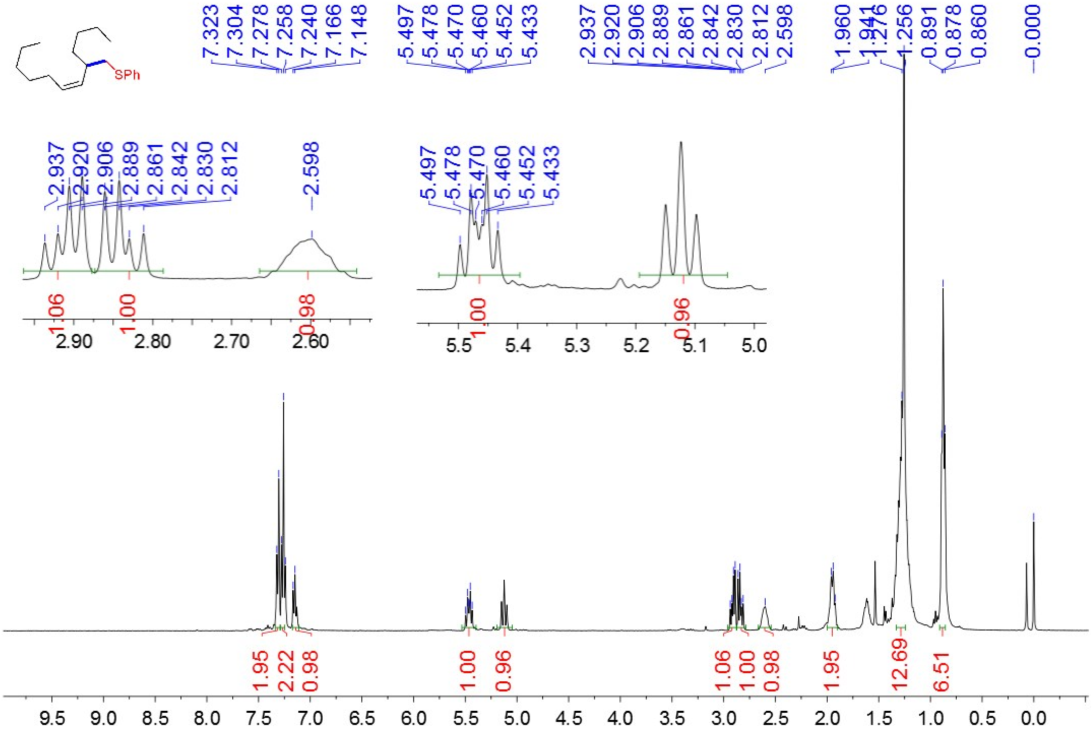
Sulfone 4 ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



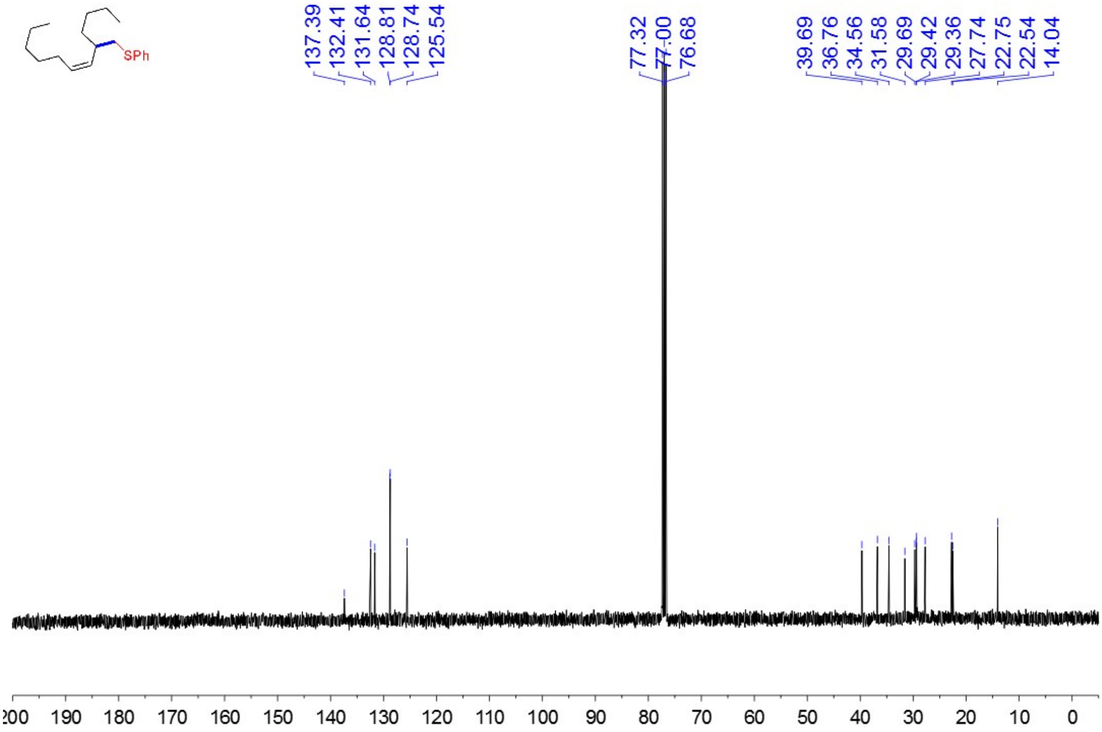
Sulfone 4 ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



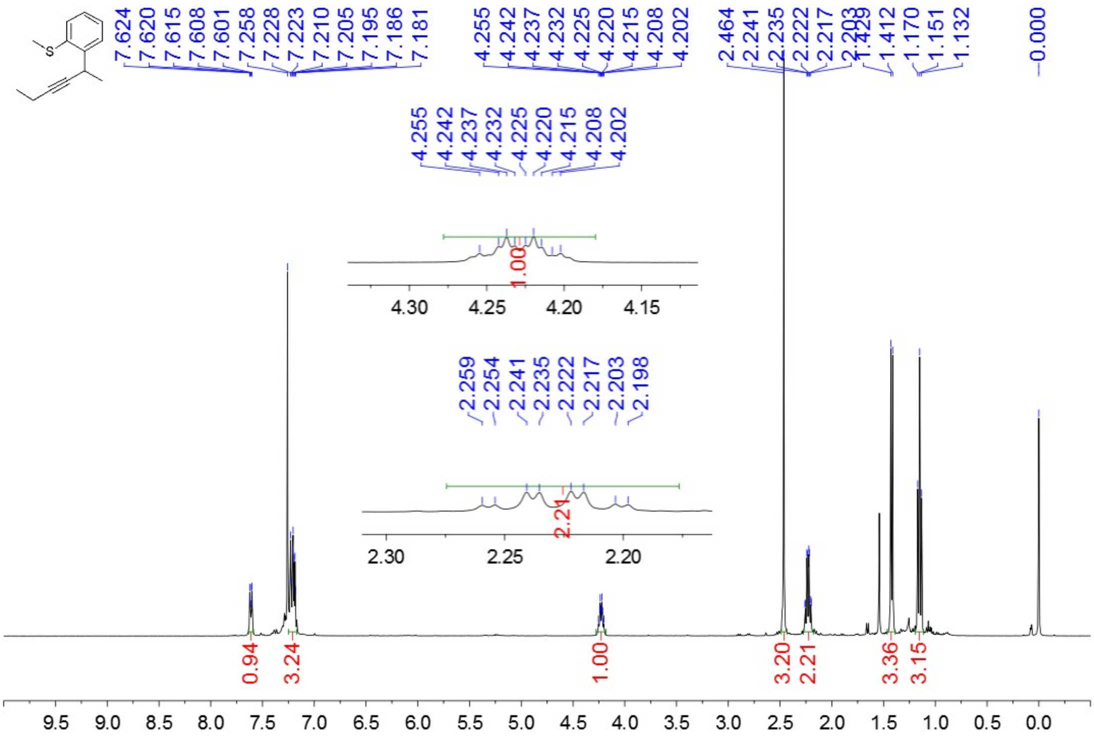
Olefin 1 ^{1}H NMR spectra, 400 MHz, CDCl$_3$.



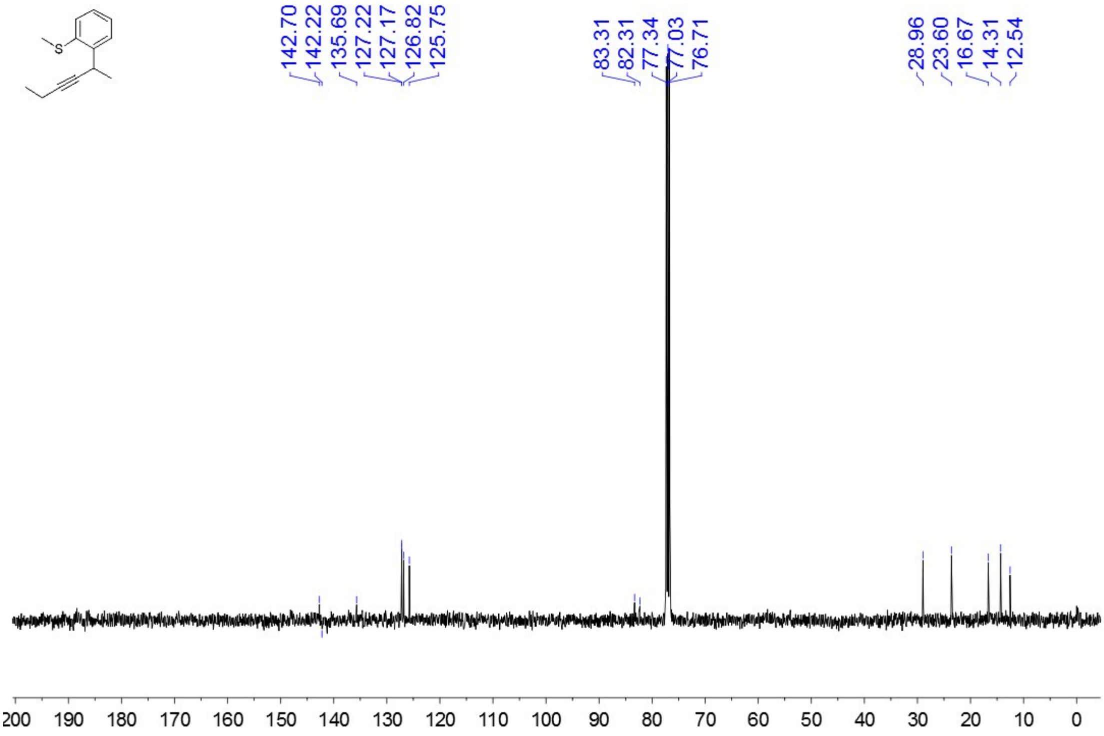
Olefin 1 ^{13}C NMR spectra, 100 MHz, CDCl$_3$.



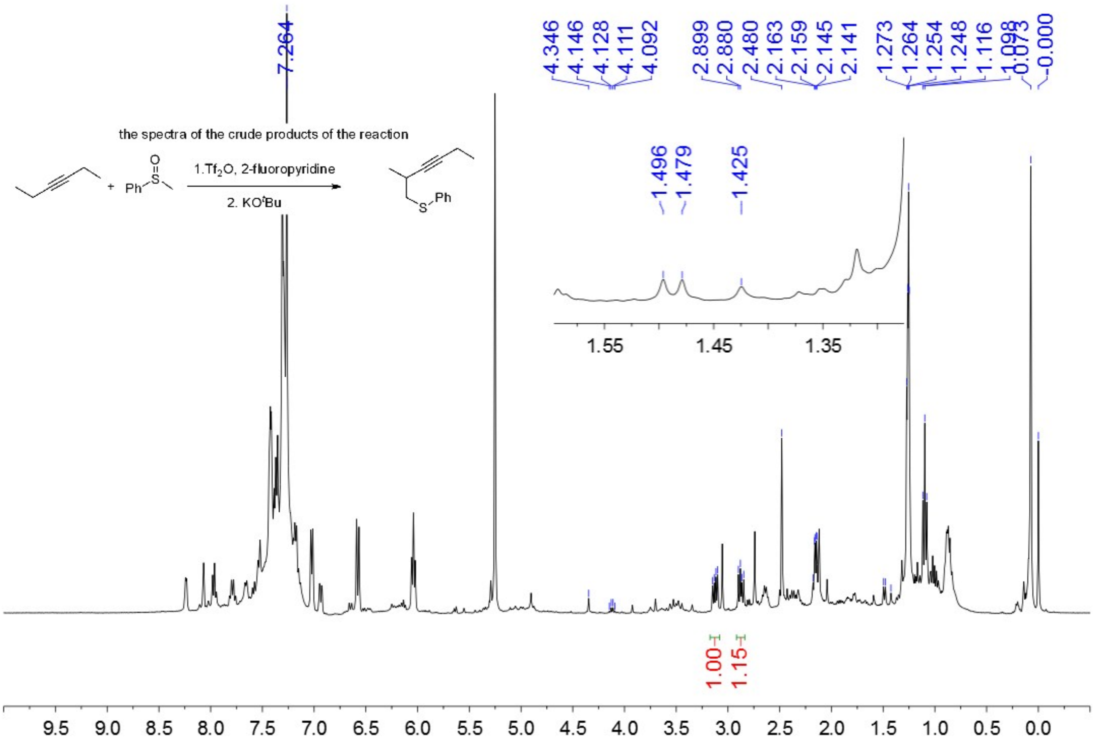
^{1}H NMR spectra, 400 MHz, CDCl$_3$.



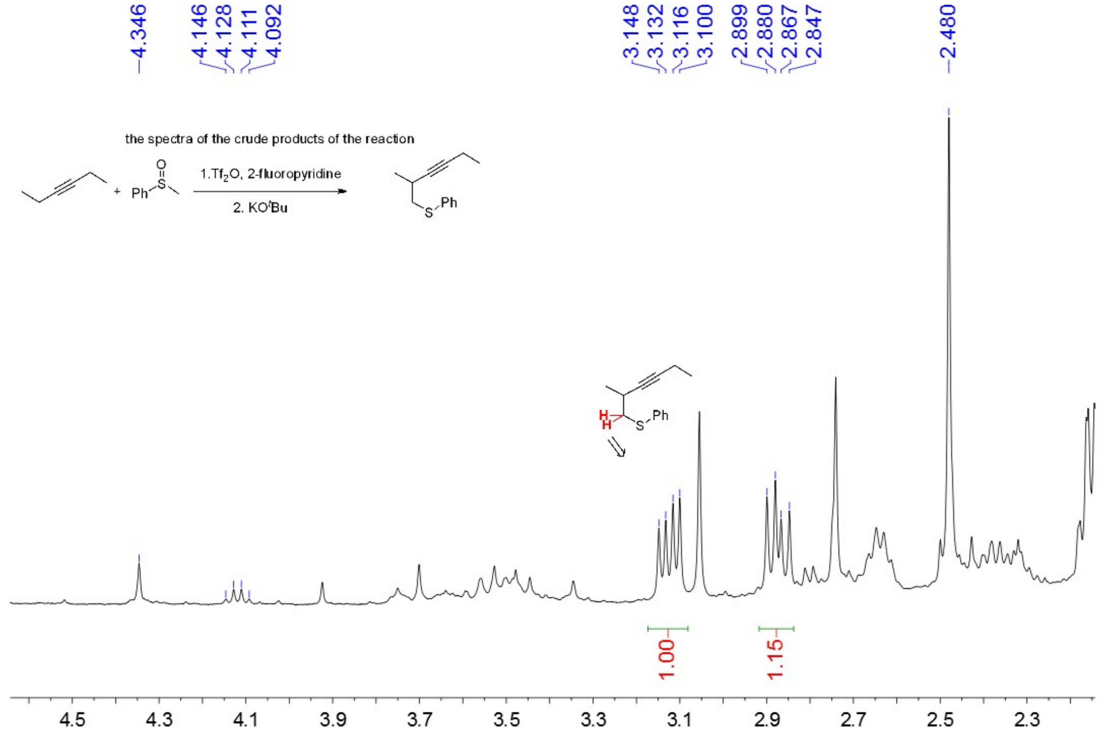
^{13}C NMR spectra, 100 MHz, CDCl$_3$



crude 3f ^{1}H NMR spectra, 400 MHz, $CDCl_3$



crude 3f ^{1}H NMR spectra, 400 MHz, $CDCl_3$



The second step of reaction at Procter's reaction temperature (65 °C)

To a flame-dried Schlenk tube, 1 eq alkyne (**1a**) (15 mg, 0.18 mmol), 1.5 eq methyl phenyl sulfoxide (**2b**) (42 mg, 0.30 mmol) and 3 eq 2-fluoropyridine (58 mg, 0.6 mmol) were added, and then dissolved with dichloromethane (2 mL) before cooling down to -82 ºC (liquid N_2/ethyl acetate bath). 1.5 eq Tf_2O (50 µL, 0.3 mmol) was added dropwise, and then gradually warmed up to room temperature over 12 hours. Then added a solution of 3.4 eq potassium *tert*-butoxide in 10:1 (v/v) tetrahydrofuran/*tert*-butanol dropwise (3.4 eq, 76 mg, 0.68 mmol) at room temperature. After that the reaction mixture was heated to 65ºC in a microwave reactor for 1 hour, then the mixture was quenched with saturated aqueous ammonium chloride solution, diluted with water, extracted with dichloromethane, concentrated for NMR test. From the ^{1}H NMR spectra of the mixture, the ratio for [2,3] product and [3,3] product was about 8:1.

^{1}H NMR spectra, 400 MHz, $CDCl_3$