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Supporting Information

Highly Efficient and Stereoselective Thioallylation of Alkynes: Possible Gold Redox Catalysis with No Need for a Strong Oxidant

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Supporting Information

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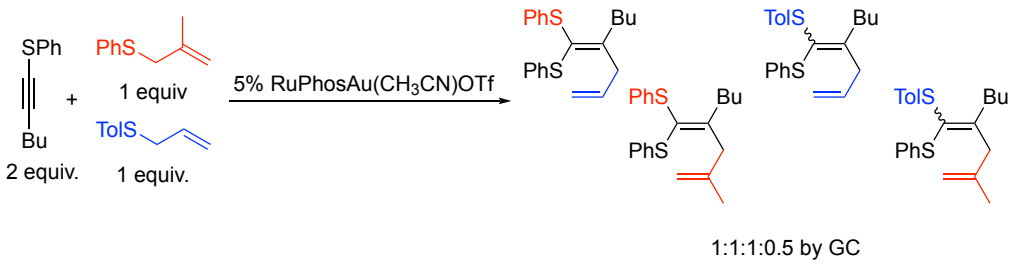
I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Allyl sulfides, bromo-alkynes and chloro-alkynes were prepared according to literature reports.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian Inova400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) for ^{1}H and $CDCl_3$ (δ 77.0 ppm) for ^{13}C. Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with pre-coated glass baked plates (250μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS data for substrates in **Table 2** were collected on an Agilent 6540 LC/QTOF spectrometer in the mass-spec facility in the University of South Florida. The rest of the HRMS data were collected in Ohio University on a Thermo Scientific Orbitrap Q Extractive Plus (Bremen, Germany) in the positive ion mode. For mechanistic studies using ESI-MS, the same MS instrument in Ohio University was used, and the samples were infused with a flow rate of 10 μL/min and sprayed at a high voltage of 5 kV. For compounds **5**, **6**, **7**, **8** and **10**, 1% $IPrAuNTf_2$ was added into a 0.01M solution of substrates in order to help the ionization for HRMS detection. The X-ray diffraction data for **3c** was measured on Bruker D8 Venture PHOTON 100 CMOS system.

II. General Procedures

2.1 Cross-over experiment for thioallylation with thioalkynes



1:1:1:0.5 by GC

To a 1mL DCE solution of thioalkyne (0.2 mmol) and two different sulfides (0.1 mmol each) was added RuPhosAu(CH_3CN)OTf catalyst (0.05 equiv.). The reaction was allowed to stir at 60 ^{o}C for 12 h. The crude mixture was analyzed using GC-MS.

Qualitative Analysis Report

Data Filename	JW-1-81.D	**Sample Name**	JW-1-81
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Comment			
Expected Barcode		**Sample Amount**	
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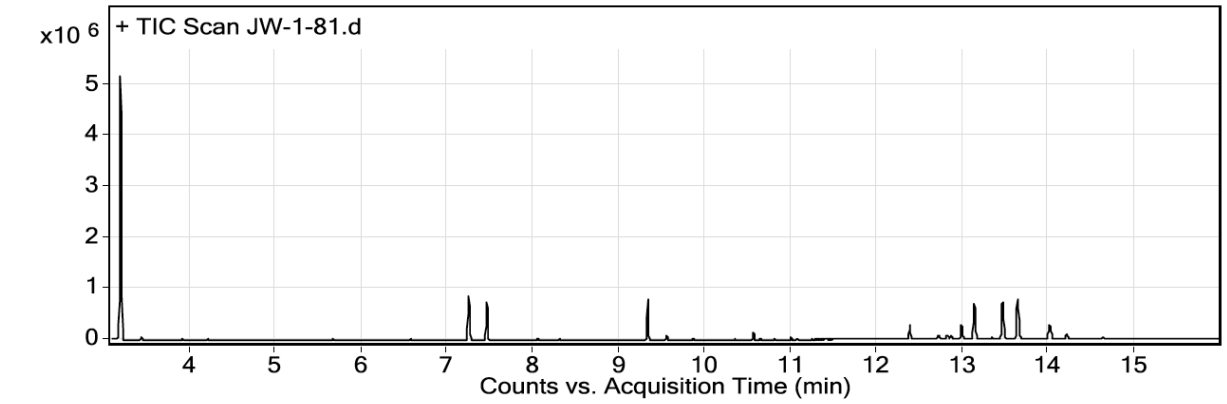
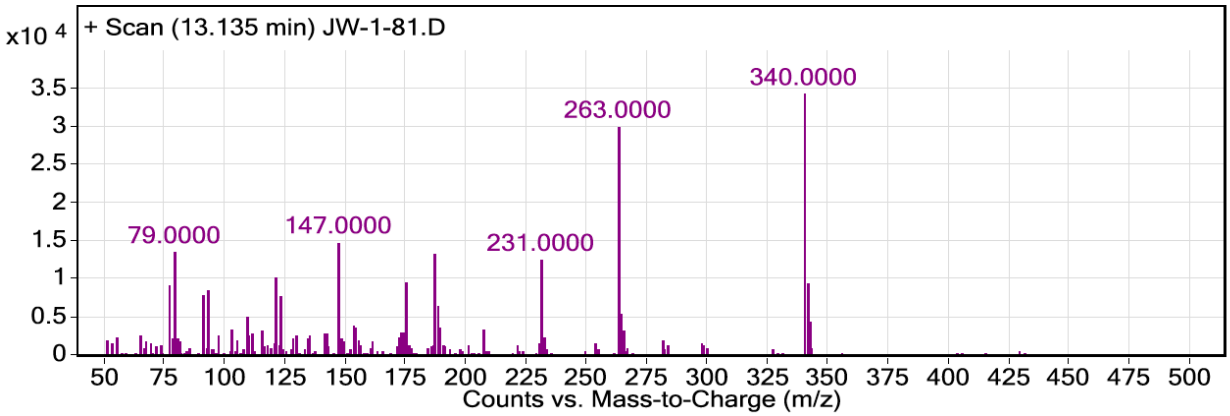
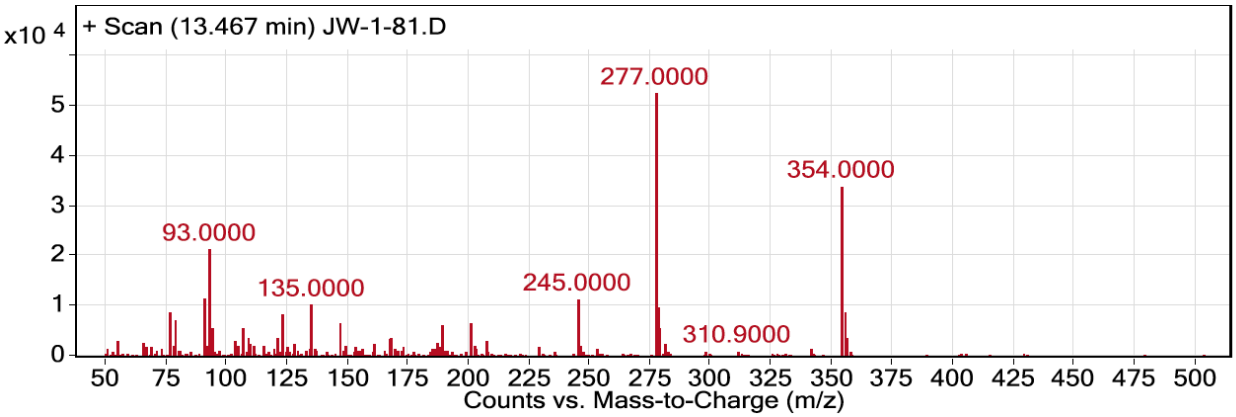
User Chromatograms

Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** Unspecified



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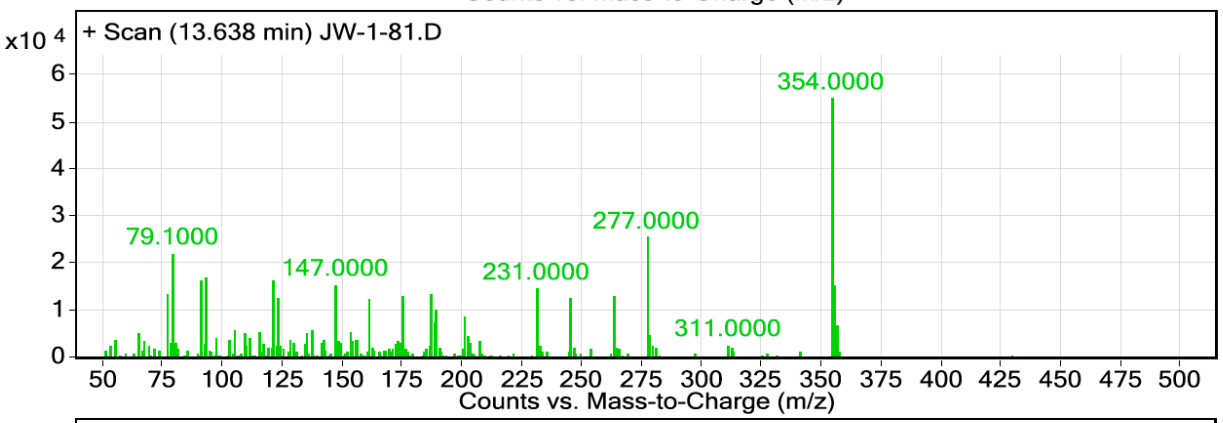
245.0000
310.9000
Counts vs. Mass-to-Charge (m/z)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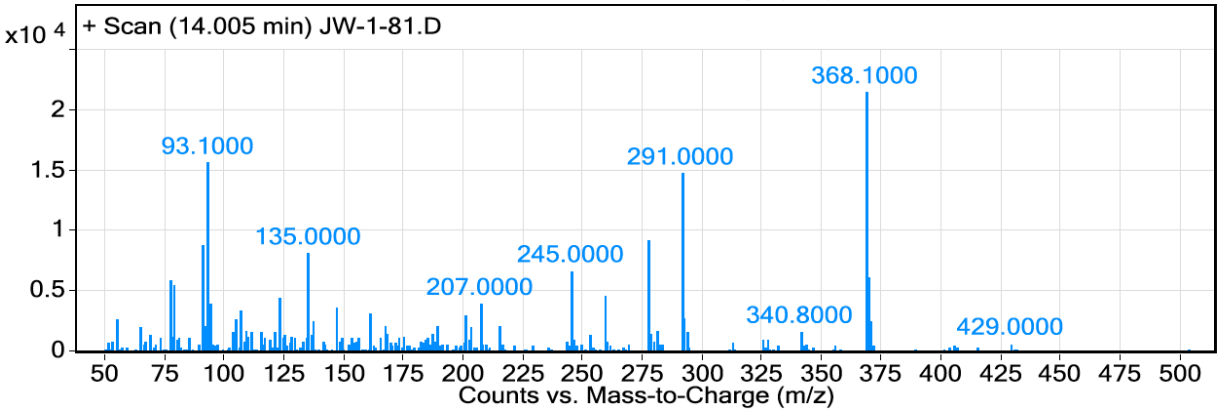
311.0000
Counts vs. Mass-to-Charge (m/z)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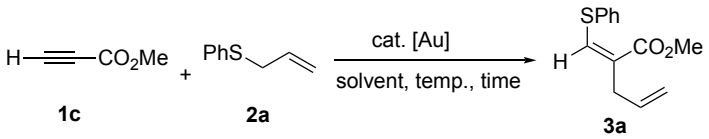
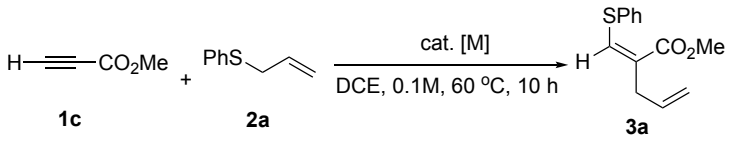
Counts vs. Mass-to-Charge (m/z)

2.2 Reaction Optimization



entry	cat.	solvent	conc.	time	conv.	yield	*E/Z*
1	5% JohnPhosAuNTf$_2$	DCE	0.1M	10 h	100%	78%	2:3
2	5% JohnPhosAu(CH$_3$CN)OTf	DCE	0.1M	10 h	100%	93%	*Z* only
3	5% RuPhosAuNTf$_2$	DCE	0.1M	10 h	100%	81%	1:3
4	5% *t*-Bu$_3$PAuNTf$_2$	DCE	0.1M	10 h	100%	92%	*Z* only
5	5% (PhO)$_3$PAu(TA-Ph))OTf	DCE	0.1M	10 h	100%	93%	*Z* only
6	5% IPrAuNTf$_2$	DCE	0.1M	10 h	100%	93%	*Z* only
7	5% IPrAuCl	DCE	0.1M	10 h	<5%	0%	-
8	5% JohnPhosAu(TA-H)OTf	DCE	0.1M	10 h	91%	87%	*Z* only
9	5% di-*t*-BuXPhosAuNTf$_2$	DCE	0.1M	10 h	100%	63%	1:2
10	5% PPh$_3$Au(TA-Me)OTf	DCE	0.1M	10 h	90%	87%	*Z* only
11	5% IPrAu(TA-H)OTf	DCE	0.1M	10 h	25%	15%	*Z* only
12	DavePhosAuNTf$_2$	DCE	0.1M	10 h	43%	33%	*Z* only
13	5% JohnPhosAuNTf$_2$	toluene	0.1M	10 h	100%	80%	2:3
14	5% JohnPhosAu(CH$_3$CN)OTf	toluene	0.1M	10 h	100%	85%	*Z* only
15	5% RuPhosAuNTf$_2$	toluene	0.1M	10 h	100%	79%	1:3
16	5% PPh$_3$AuNTf$_2$	toluene	0.1M	10 h	100%	80%	2:3
17	5% *t*-Bu$_3$PAuNTf$_2$	toluene	0.1M	10 h	100%	92%	*Z* only
18	5% IPrAuNTf$_2$	toluene	0.1M	10 h	100%	96%	*Z* only
19	5% IPrAuNTf$_2$	THF	0.1M	40 h	82%	78%	*Z* only
20	5% IPrAuNTf$_2$	CH$_3$CN	0.1M	40 h	78%	72%	*Z* only
21	2% IPrAuNTf$_2$	toluene	0.1M	20 h	88%	84%	*Z* only
22	2% IPrAuNTf$_2$	toluene	0.2M	10 h	100%	96%	*Z* only
23	1% IPrAuNTf$_2$	toluene	0.1M	20h	69%	66%	*Z* only
24	1% IPrAuNTf$_2$	toluene	0.2M	20 h	100%	96%	*Z* only
25	1% IPrAuNTf$_2$	toluene	0.5M	10 h	100%	98%	*Z* only
26	1% IPrAuNTf$_2$	toluene	1.0M	5 h	100%	92%	*Z* only
27	0.5% IPrAuNTf$_2$	toluene	1.0M	10 h	100%	95%	*Z* only
28	0.2% IPrAuNTf$_2$	toluene	1.0M	40 h	81%	73%	*Z* only
29	0.1% IPrAuNTf$_2$	toluene	1.0M	40 h	63%	60%	*Z* only
30[a]	1% IPrAuNTf$_2$	toluene	0.5M	40 h	93%	88%	*Z* only
31[b]	1% IPrAuNTf$_2$	toluene	0.5M	40 h	47%	42%	*Z* only
32[c]	1% IPrAuNTf$_2$	toluene	0.5M	20 h	100%	88%	1:17
33[d]	1% IPrAuNTf$_2$	toluene	0.5M	40 h	94%	74%	1:8

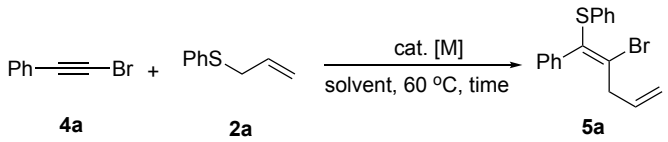
Reaction conditions: gold catalyst was added to a solution (1 mL) of alkyne **1c** (0.15 mmol) and allyl sulfide **2a** (0.1 mmol), and reaction was kept at 60 ^{o}C for specified time. Conversion and yield were determined by ^{1}H NMR spectroscopy using dimethylsulfone as internal standard. [a] reaction at 40 ^{o}C. [b] reaction at rt. [c] reaction with 1.2 eq alkyne **1c**. [d] reaction with 1.1 eq alkyne **1c**.



1c **2a** **3a**

entry	cat.	conv.	yield
1	5% $IPrAuNTf_2$	100%	93%
2	none	<5%	0%
3	TfOH	20%	0%
4	AgOTf	<5%	0%
5	$AgNTf_2$	<5%	0%
6	$Cu(OTf)_2$	<5%	0%
7	$In(OTf)_3$	<5%	trace
8	$FeCl_3$	<5%	trace
9	$Zn(OTf)_2$	<5%	0%
10	$Cp2TiCl_2$	<5%	0%
11	$La(OTf)_3$	<5%	0%
12	$Rh_2(esp)_2$	<5%	0%
13	$Pd(PPh_3)_2Cl_2$	<5%	0%
14	$Pd(OAc)_2$	<5%	0%
15	Cp_2RuCl_2	<5%	0%
16	$(cod)_2Ir_2Cl_2$	<5%	0%

Reaction conditions: metal catalyst was added to a solution (1 mL) of alkyne **1c** (0.15 mmol) and allyl sulfide **2a** (0.1 mmol), and reaction was kept at 60 °C for 10 h. Conversion and yield were determined by ^{1}H NMR spectroscopy using dimethylsulfone as internal standard.

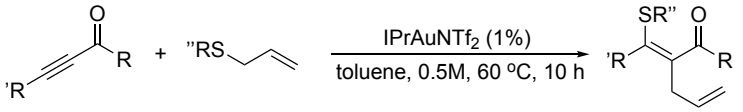


4a **2a** **5a**

entry	cat.	solvent	conc.	time	conv.	yield	*E/Z*
1	5% $JohnPhosAuNTf_2$	DCE	0.1M	24 h	<20%	7%	-
2	5% $JohnPhosAu(CH_3CN)OTf$	DCE	0.1M	24 h	<20%	<5%	-
3	5% $(PhO)_3PAu(TA\text{-}Ph))OTf$	DCE	0.1M	24 h	<20%	13%	*Z* only
4	5% AgOTf	DCE	0.1M	24 h	<5%	0%	-
5	5% $Cu(OTf)_2$	DCE	0.1M	24 h	<5%	0%	-
6	none	DCE	0.1M	24 h	<5%	0%	-
7	5% $IPrAuNTf_2$	DCE	0.1M	24 h	80%	66%	*Z* only
8	5% $IPrAuNTf_2$	toluene	0.1M	24 h	82%	74%	*Z* only
9	2% $IPrAuNTf_2$	toluene	0.3M	24 h	100%	84%	*Z* only
10	2% $IPrAuNTf_2$	toluene	0.5M	24 h	100%	97%	*Z* only

Reaction conditions: gold catalyst was added to a solution (1 mL) of alkyne **4a** (0.15 mmol) and allyl sulfide **2a** (0.1 mmol), and reaction was kept at 60 °C for specified time. Conversion and yield were determined by ^{1}H NMR spectroscopy using dimethylsulfone as internal standard.

2.3 General procedure for thioallylation of carbonyl-activated alkynes



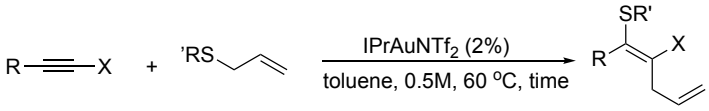
1 2 3

To a toluene solution (0.6 mL) of sulfide **2** (0.3 mmol, 1 eq) and carbonyl-activated alkyne **1** (0.45 mmol, 1.5 eq) was added $IPrAuNTf_2$ catalyst (0.003 mmol, 0.01 eq) in one portion. The reaction mixture was allowed to stir at 60 ^oC for 10 h. The reaction mixture was then concentrated by rot-vap, and purified by flash chromatography (20:1 hex/EtOAc) to obtain pure product **3**.

2.4 Gram-scale synthesis of 3a

To a toluene solution (2.5 mL) of sulfide **2a** (773 μL, 5.0 mmol, 1 eq) and carbonyl-activated alkyne **1c** (667 μL, 7.5 mmol, 1.5 eq) was added $IPrAuNTf_2$ catalyst (4.3 mg, 0.005 mmol, 0.001 eq) in one portion. The reaction mixture was allowed to stir at 60 ^oC for 48 h. The reaction mixture was then concentrated by rot-vap, and purified by flash chromatography (20:1 hex/EtOAc) to obtain pure product **3** (1.114 g, 95%).

2.5 General procedure for thioallylation of halo-alkynes

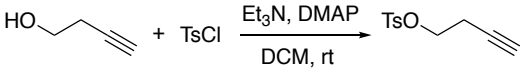


4, X = Br or Cl **2** **5**

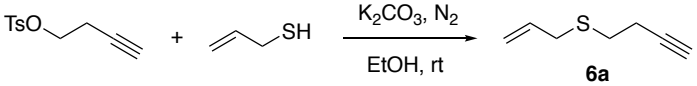
To a toluene solution (0.4 mL) of sulfide **2** (0.2 mmol, 1eq) and halo-alkyne **4** (0.3 mmol, 1.5 eq) was added $IPrAuNTf_2$ catalyst (0.004 mmol, 0.02 eq) in one portion. The reaction mixture was allowed to stir at 60 ^oC for 24 h. The reaction mixture was then concentrated by rot-vap, and purified by preparative TLC (pure hexane) to obtain pure product **5**.

2.6 General procedure for the synthesis of homopropargyl allyl sulfide 6a-6l

General Procedure for the synthesize of compound 6



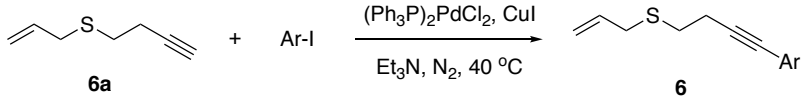
To a 500 mL round bottom flask was added 3-butyn-1-ol (7.01 g, 100 mmol, 1 eq), DCM (200 mL), DMAP (1.22 g, 10 mmol, 0.1 eq), Et_3N (42 mL, 3 eq) and TsCl (22.88 g, 120 mmol, 1.2 eq) sequentially. The reaction system was stirred vigorously at room temperature for 3h. After the reaction was completed (determined by TLC), the reaction mixture was quenched with water and extracted with DCM. Combined organic layer was dried with Na_2SO_4. The solvent was removed under reduced pressure and crude product was purified by column chromatography (5:1 hexane/EtOAc) to give the desired product as a colorless oil.



6a

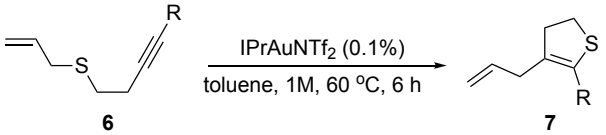
To a mixture of 3-butyn-1-yl-4-methylbenzenesulfonate (10.51 g, 50 mmol, 1 eq) and K_2CO_3 (10.35 g, 75 mmol, 1.5 eq) under argon atmosphere in 250 mL round bottom flask, ethanol (100 mL) and allyl mercaptan (5 mL, 1.2 eq) was added. The reaction mixture was stirred at room temperature for 24h. After the reaction was completed (determined by TLC), 200 mL water was added, and organic layer was collected. The water layer was extract with hexane for several times, then the combined organic layer was dried with Na_2SO_4. The solvent was removed under reduced

pressure and purified by column chromatography (40:1 hexane/EtOAc) to give the desired product **6a** as a colorless oil.



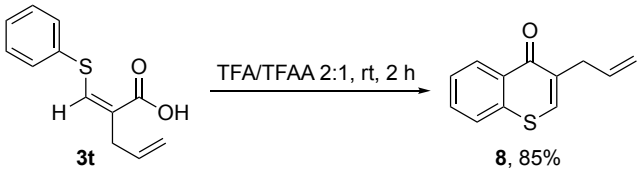
To a mixture of Pd $(PPh_3)_2Cl_2$ (42.1 mg, 0.06 mmol, 0.02 eq) and CuI (22.9 mg, 0.12 mmol, 0.04 eq) under N_2 atmosphere, Et_3N (10 mL), iodoarenes (3 mmol, 1 eq) and **6a** (378.7 mg, 3 mmol, 1 eq) was added sequentially. The reaction mixuture was stirred at 40 °C for 16 h. After the reaction was completed (determined by TLC), the reaction mixture was filtered and washed with ethyl acetate. The filtrate was evaporated under reduced pressure and purified by column chromatography to give the desired product **6b-6l**.

2.7 General procedure for intramolecular thioallylation



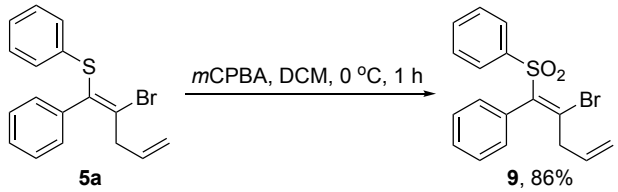
To a toluene solution (0.3 mL) of sulfide **6** (0.3 mmol, 1eq) was added $IPrAuNTf_2$ catalyst (0.0003 mmol, 0.001 eq) in one portion. The reaction mixture was allowed to stir at 60 °C for 6 h or 24 h. The reaction mixture was then concentrated by rot-vap, and purified by preparative TLC (pure hexane) to obtain pure product **7**.

2.8 General procedure for thioflavone 8 synthesis from 3t



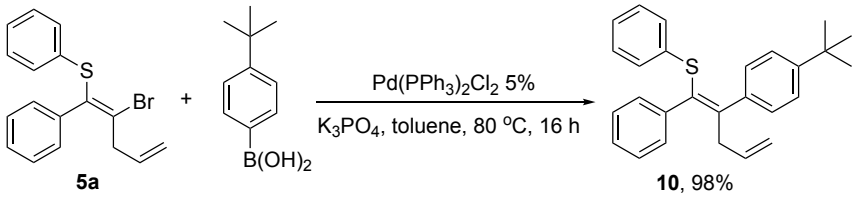
To a 2:1 TFAA/TFA mixed solution (1.5 mL) was added compound **3t** (110 mg, 0.50 mmol). The reaction mixture was allowed to stir at rt for 2 h. The reaction mixture was then concentrated by rot-vap, and purified by flash chromatography (pure hexane) to obtain pure product **8** (86 mg, 85%).

2.9 General procedure for sulfone 9 synthesis from 5a



To a DCM solution (2 mL) of sulfide **5a** (132 mg, 0.4 mmol, 1 eq) was added mCPBA (197 mg, 0.8 mmol, 2 eq) in one portion at 0 °C. After reacting at 0 °C for 1 h, the reaction mixture was diluted with DCM and washed with $NaHCO_3$ solution twice. The organic layer was dried with Na_2SO_4 and concentrated by rot-vap. The crude product was purified by flash chromatography (3:1 hexane/EtOAc) to yield the desired product **9** (118 mg, 86%).

2.10 General procedure for Suzuki coupling of 5a



5a **10**, 98%

To a Schlenk tube was added **5a** (132 mg, 0.4 mmol, 1 eq), boronic acid (214 mg, 1.2 mmol. 3 eq), $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol, 0.05 eq) and K_3PO_4 (255 mg, 1.2 mmol, 3 eq) sequentially. The reaction mixture was transferred into glove box and charged with toluene (2 mL). After reacting for 16 h at 80 ^oC, the reaction was quenched with diluted with DCM and extracted with H_2O twice. The organic layer was dried with Na_2SO_4 and concentrated. Crude mixture was purified by flash chromatography (pure hexane) to yield the desired product **10** (152 mg, 98%).

III. ORTEP Drawing for Crystal Structures

X-ray Crystallography

The X-ray diffraction data were measured on Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K_α INCOATEC ImuS micro-focus source (λ = 1.54178 Å). Indexing was performed using Apex3 [1]. Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space group was determined using XPREP implemented in APEX3 [1]. Structure was solved using SHELXT [4] and refined using SHELXL-2017 [5-7] (full-matrix least-squares on F^2) through OLEX2 interface program [8]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters**.** Crystal data and refinement conditions are shown in Table 1.

[1] Bruker (2017). *APEX3* (Version 2015.9). Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Bruker (2017) SAINT V8.35A. Data Reduction Software.
[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.
[4] Sheldrick, G. M. (2015) "SHELXT - Integrated space-group and crystal structure determination" Acta Cryst. A71, 3-8
[5] Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473
[6] Sheldrick, G. M. (2008) Acta Cryst. A64, 112-122.
[7] G.M. Sheldrick (2015) "Crystal structure refinement with SHELXL", Acta Cryst., C71, 3-8
[8] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341.
[9] A.L.Spek, Acta Cryst. 2009, D65, 148-155.
[10] R. W. W. Hooft, L. H. Straver , A. L. Spek J. Appl. Cryst. (2008), 41, 96-103

Table 1 Crystal data and structure refinement for Z1_6_4.	
Identification code	Z1_6_4
Empirical formula	$C_{13}H_{13}BrO_2S$
Formula weight	313.20
Temperature/K	100.01
Crystal system	orthorhombic
Space group	Pbca
a/Å	9.4379(4)
b/Å	7.6208(3)
c/Å	36.1062(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2596.91(18)
Z	8
ρ_{calc}g/cm^3	1.602
μ/mm^{-1}	5.716
F(000)	1264.0
Crystal size/mm^3	0.217 × 0.136 × 0.036
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.798 to 154.634
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 9, -44 ≤ l ≤ 45
Reflections collected	36169
Independent reflections	2747 [R_{int} = 0.0862, R_{sigma} = 0.0306]
Data/restraints/parameters	2747/0/155
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0704
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.0763
Largest diff. peak/hole / e Å^{-3}	0.29/-0.47

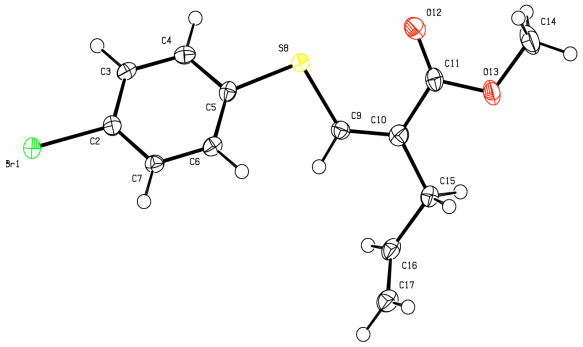
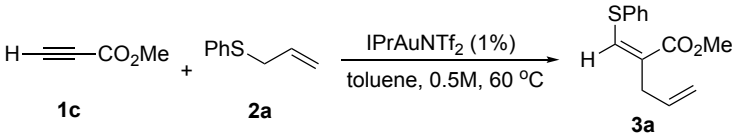


Fig.1. Asymmetric unit of **Z1_6_4**. Anisotropic displacement parameters were drawn at 50% probability. CCDC:1826391

IV. Mass Spectrometry Study

ESI-MS spectra were collected using a Thermo scientific Orbitrap Q Extractive Plus (Bremen, Germany) in the positive ion mode. Samples were infused at a flow rate of 10 µL/min and ionized at a high voltage of +5 kV.

4.1 ESI-MS analysis of 1c and 2a

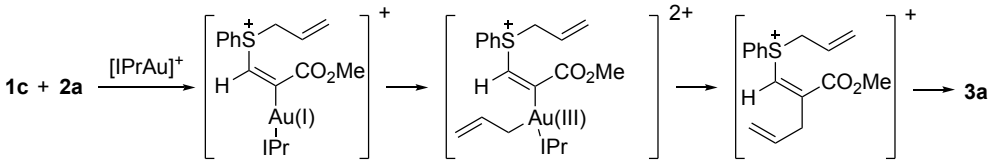


1c 2a 3a

General procedure: 200 µM $IPrAuNTf_2$ was added to 20 mM of **2a** and 30 mM **1c** in 3 mL of toluene, and the reaction mixture was stirred at 60 ^oC for 24 h. The reaction mixture was diluted in 1:20 ratio with acetonitrile, and tested on 5 min, 1 h, 2.5 h, 5 h and 24 h using ESI-MS.

Data analysis

Based on the cross-over experiment, a tentative mechanism for thioallylation is shown below:



B m/z: 819.3 C m/z: 430.2 D m/z: 275.1

Figure 4.1.1. Proposed mechanism

As shown in **Figure 4.1.2**, An ion peak at *m/z* = 819.4 showed up after 1 h, and its concentration became higher at 2.5 h then attenuated over time. At 2.5 h, another important ion peak at *m/z* = 859.3 showed up, which became stronger at 5h. *m/z* = 275.1was also detected after 2.5 h. Another very intense peak throughout the experiment was *m/z* = 735.3. For clarity, data at 2.5 h was used to analyze the peaks at *m/z* = 819.4, 859.3, 275.1, 735.3. CID analysis were performed to determine the structure of these peaks. In principle, precursor ions after CID will provide fragment ions by losing neutrals from its own structure. Common fragmentation pathways include homolysis and heterolysis of a weak chemical bond. A detailed analysis of ion peaks with their CID spectrum (819.3, 859.4, 275.1, 735.3) is discussed here to determine their exact structures. Experimental data for all the ion peaks discussed here is within an error < 5ppm with the proposed molecular formulas.

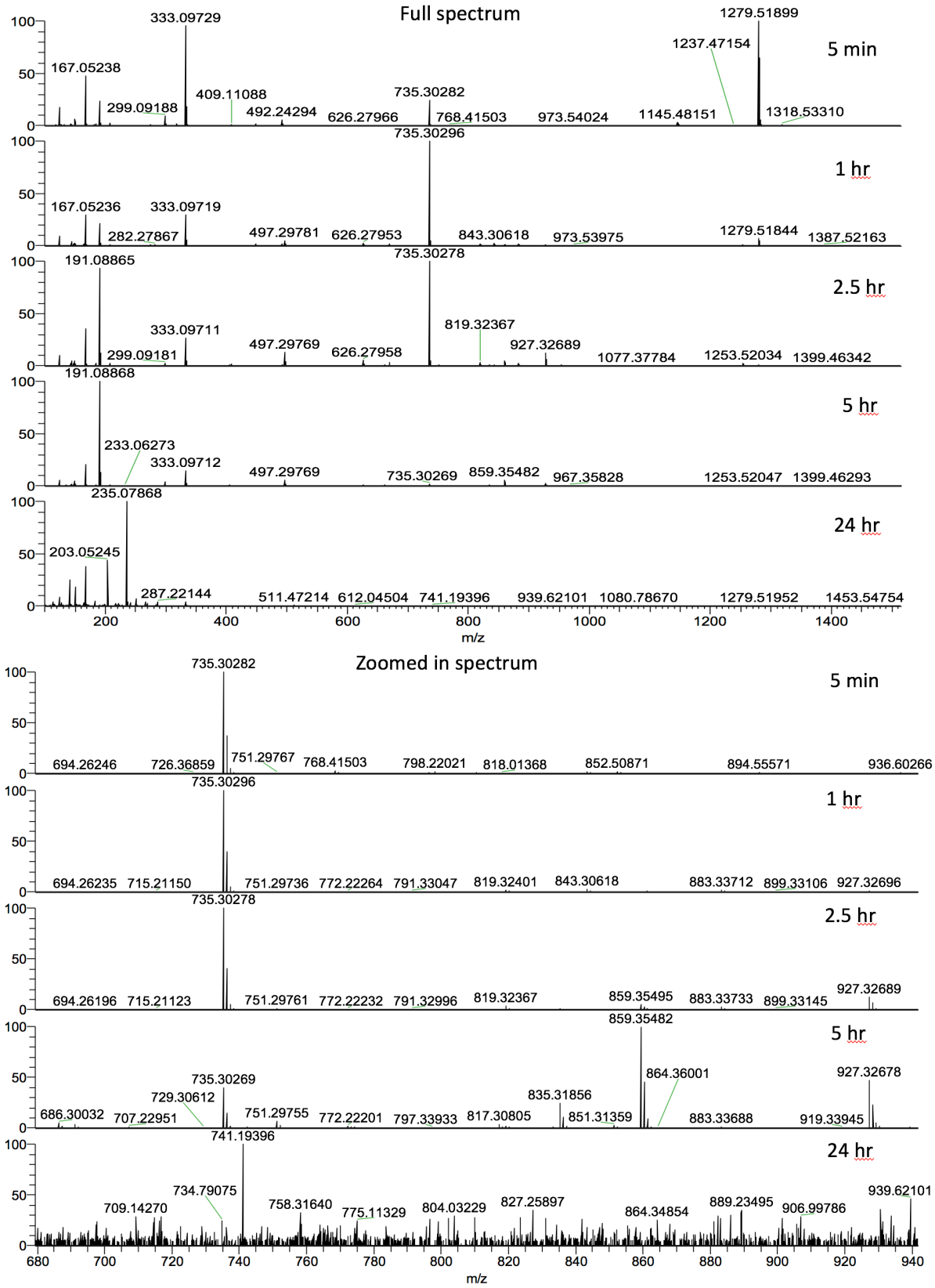


Figure 4.1.2. full and zoomed-in MS spectrum at different time intervals

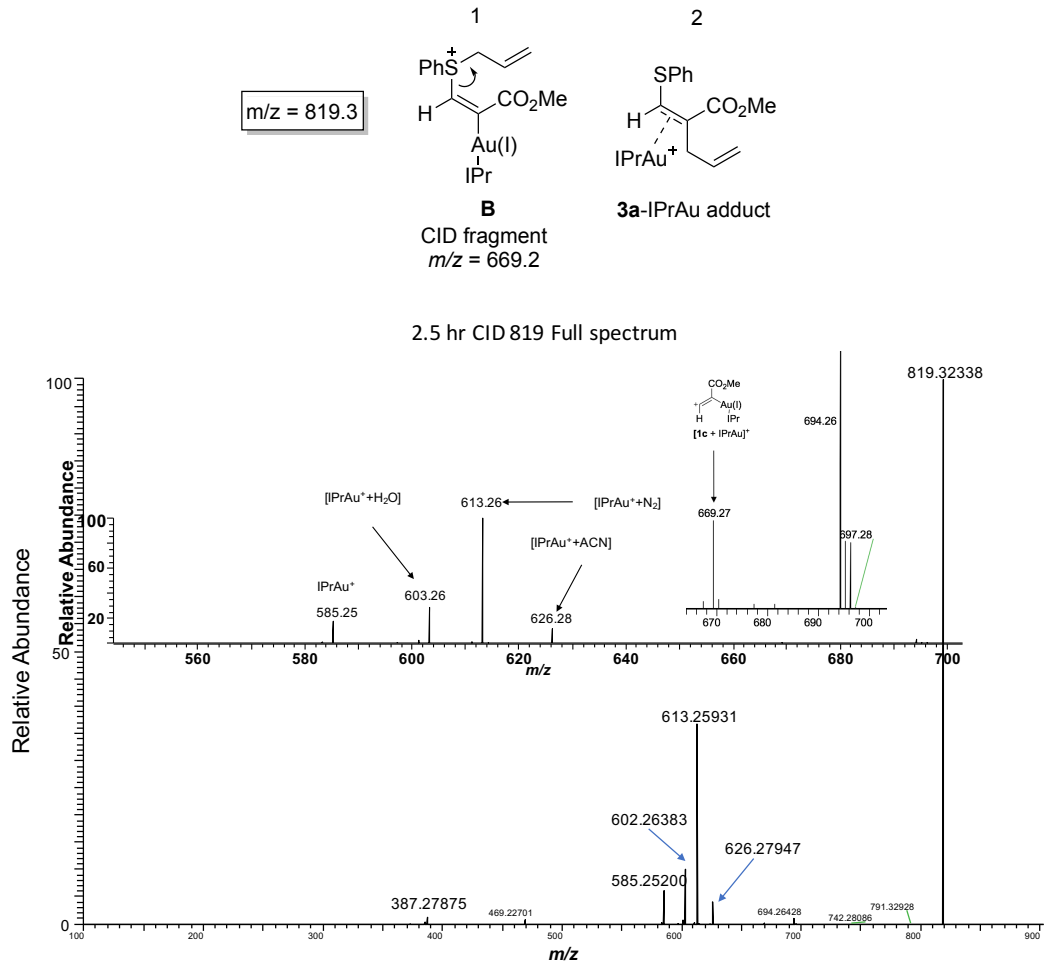


Figure 4.1.3. CID MS/MS spectrum for *m/z* = 819.3 at 2.5 h

Two possible structures for m/z = 819.3 are listed. Major $IPrAu^+$ fragment ions were detected upon CID as shown in **Figure 4.1.3**. The fact that the intensity of m/z = 819.3 reached its maximum then attenuated suggests structure 1 is more likely, because if it's structure 2, the concentration should keep increasing as the reaction goes. In addition, the ion peak at *m/z* = 669.2 represents $[\mathbf{1c}+IPrAu]^+$, which further proved structure 1 instead of structure 2 is the correct structure. **In conclusion, structure 1 which corresponds to intermediate B based on the proposed mechanism most likely accounts for m/z = 819.3.**

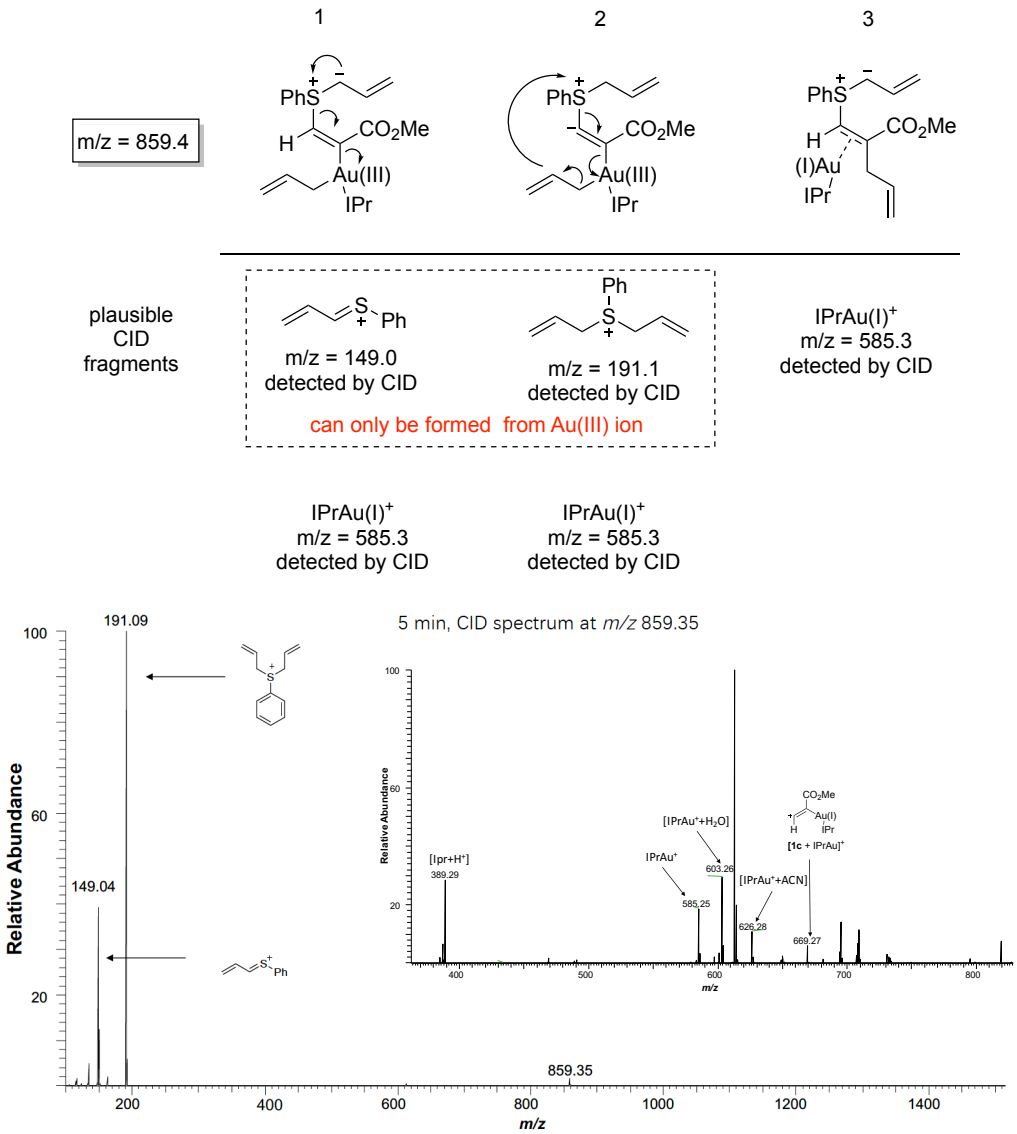


Figure 4.1.4. CID MS/MS spectrum for *m/z* = 859.4 at 2.5 h

The ion peak at *m/z* = 859.4, corresponding to intermediate **C** $[M\text{-}H]^+$ was clearly detected after 1 h. The corresponding CID data is shown in **Figure 4.1.4**. Besides $IPrAu^+$ fragments, two very intensive ion peaks *m/z* = 149.0 and 191.1 were detected. Three possible structures and their primary CID pathway are proposed. As the reviewer suggested, possible structures include Au(III) ions (1 and 2) and Au(I) ions 3. *For Au(I) ion structure 3, after CID they would primarily give* $IPrAu^+$ *ion and a neutral stable sulfonium ylide, thus is very unlikely to give the fragment ions m/z = 149.0 and 191.1. On the other hand, the Au(III) ions such as structure 1 can easily generate desired fragment m/z = 149.0 by the loss of a neutral stable propiolate and allyl-IPrAu(I) (further fragments to* $IPrAu^+$*). Likewise, structure 2 will produce m/z = 191.1 preferably by the loss of a neutral stable IPrAu(I)-acetylide upon CID.* In addition, the CID file revealed *m/z* = 669.2 corresponding to [**1c** + IPrAu]$^+$, which further proved the precursor ion cannot be a simple Au(I)-product adduct. **In conclusion, the CID data strongly supported Au(III) ions such as structures 1 and 2 existed in the m/z = 859.4 ion.**

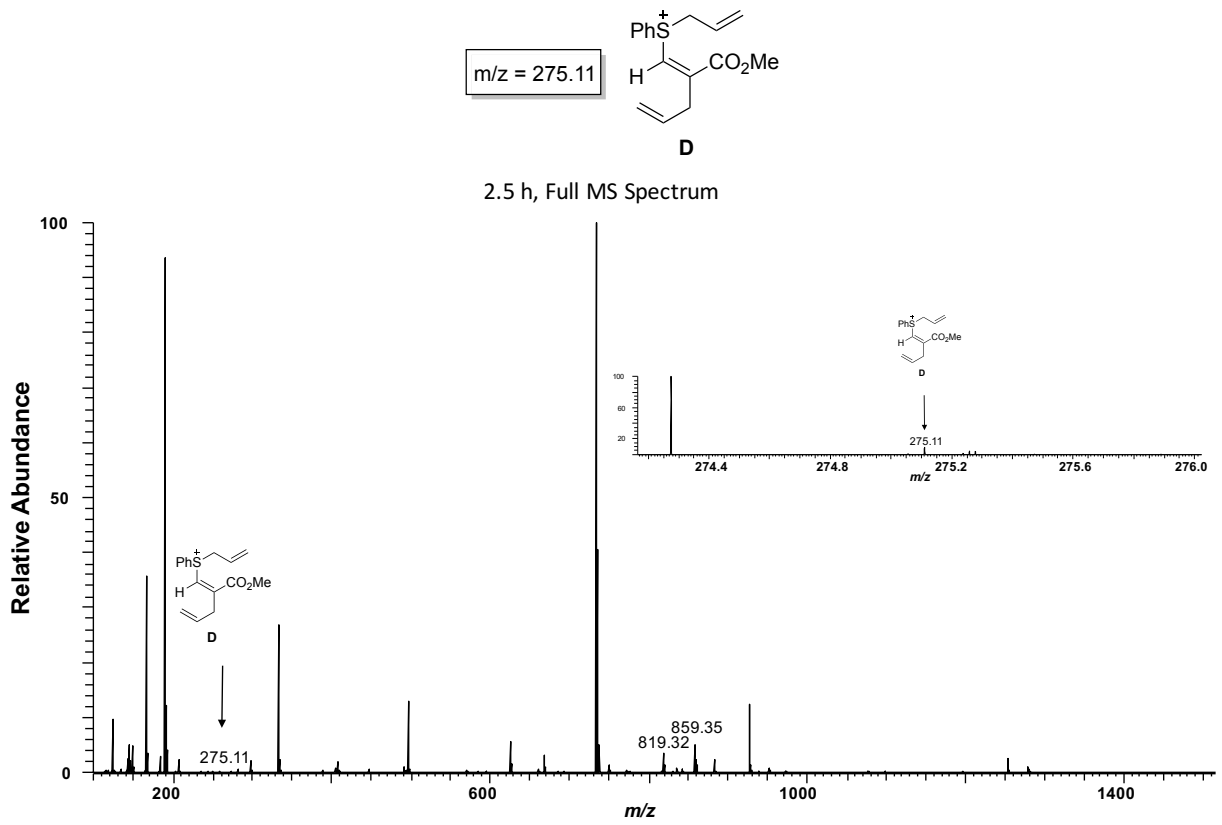


Figure 4.1.5. Intermediate **D** (m/z = 275.1) observed at 2.5 h.

Intermediate **D** have also been detected at 2.5 h (**Figure 4.1.4**). Although CID of this ion was not performed due to its low intensity, it represents an important intermediate in the intermolecular allyl transfer pathway.

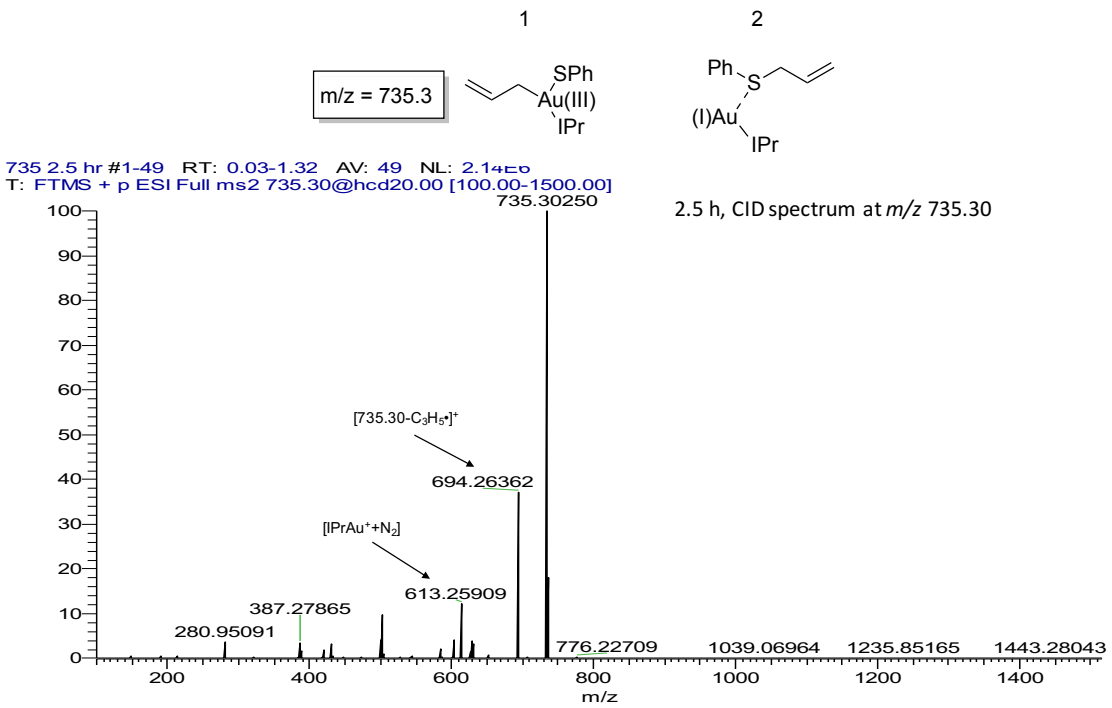


Figure 4.1.6. CID MS/MS data for *m/z* = 735.30 at 2.5 h

Another important ion peak that draw our attention was *m/z* = 735.3. The intensity of this peak was very high throughout the reaction process. Two structures are proposed. The fact that CID file clearly showed a fragment ion of *m/z* = 694.3 by the loss of an allyl radical (C_3H_5·) suggests that it is actually a Au(III) ion as shown in structure 1, because the Au(I) structure 2 is unlikely to break a C-S bond in the neutral allyl sulfide molecule. **In conclusion, structure 1 as a Au(III) ion was confirmed.**

Conclusions for chapter 4.1

Overall, we have successfully detected the ion peaks of several key intermediates to validate the reaction mechanism we proposed. The results are summarized in ***Figure 4.1.7****. The existence of Au(III) ions are strongly supported by the CID MS/MS data of two ions (m/z = 735.3 and 859.3). The fact that three key ions at m/z = 819.3, 859.4 and 275.1 were detected largely supported a Au(I/III) pathway.*

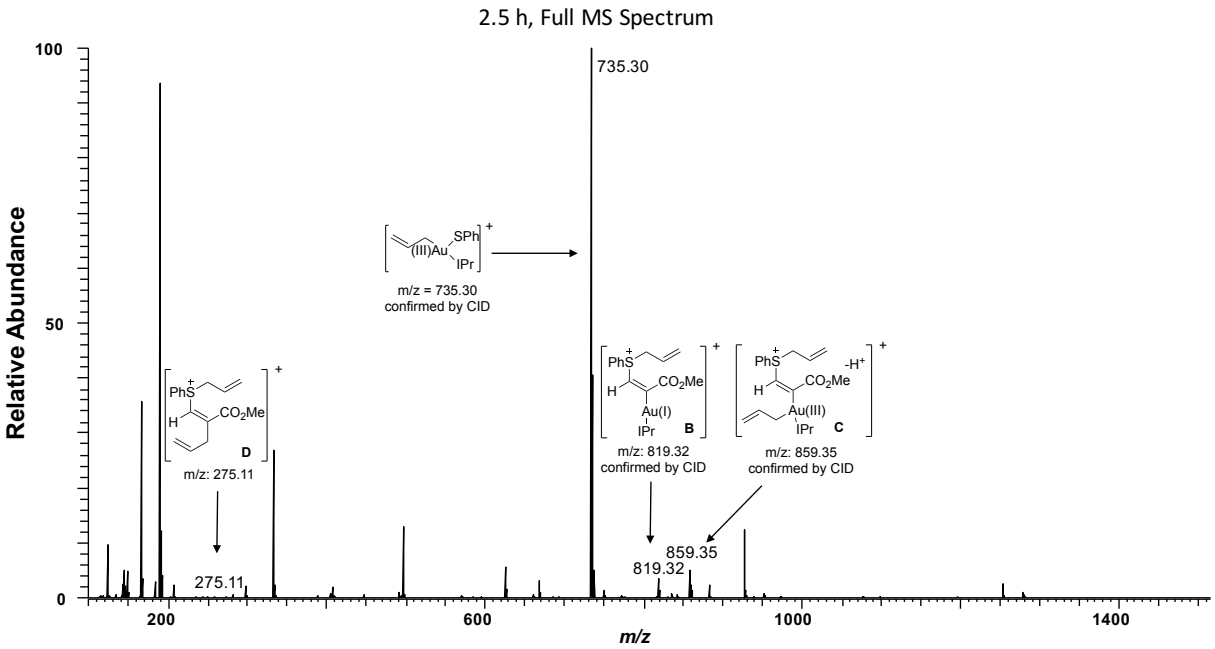
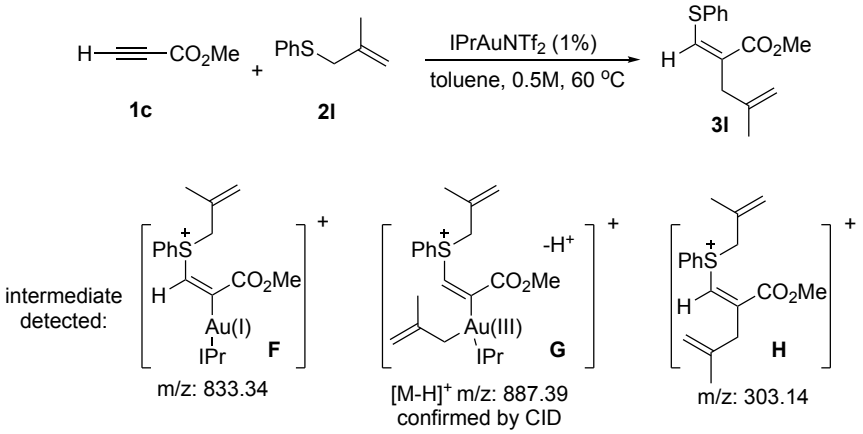


Figure 4.1.7. Summary for MS study **4.1**

4.2 ESI-MS analysis of 1c and 2l



In order to further confirm the Au (I) and Au (III) intermediates observed in **Chapter 4.1**, **1c** was mixed with another sulfide **2l** in the presence of $IPrAuNTf_2$ catalyst (**Figure 4.2**). The vinyl-Au(I) intermediate **F** at m/z = 833.34 was observed, and Au (III) intermediate **G** was observed at *m/z* = 887.4. Intermediate **H** without Au was also observed at *m/z* 303.14. The CID spectrum of Au (III) intermediate **G** displayed a very similar pattern with intermediate **C**, except for that in CID fragments of intermediate **G** the allyl group was replaced with the 2-methylallyl group (*m/z* = 219.1 and 163.1). *m/z* = 669.2 corresponding to $[\mathbf{1c} + IPrAu]^+$ was detected again, which further

proved the precursor ion *m/z* = 887.4 must be a Au(III) species instead of a simple Au(I)-product adduct.

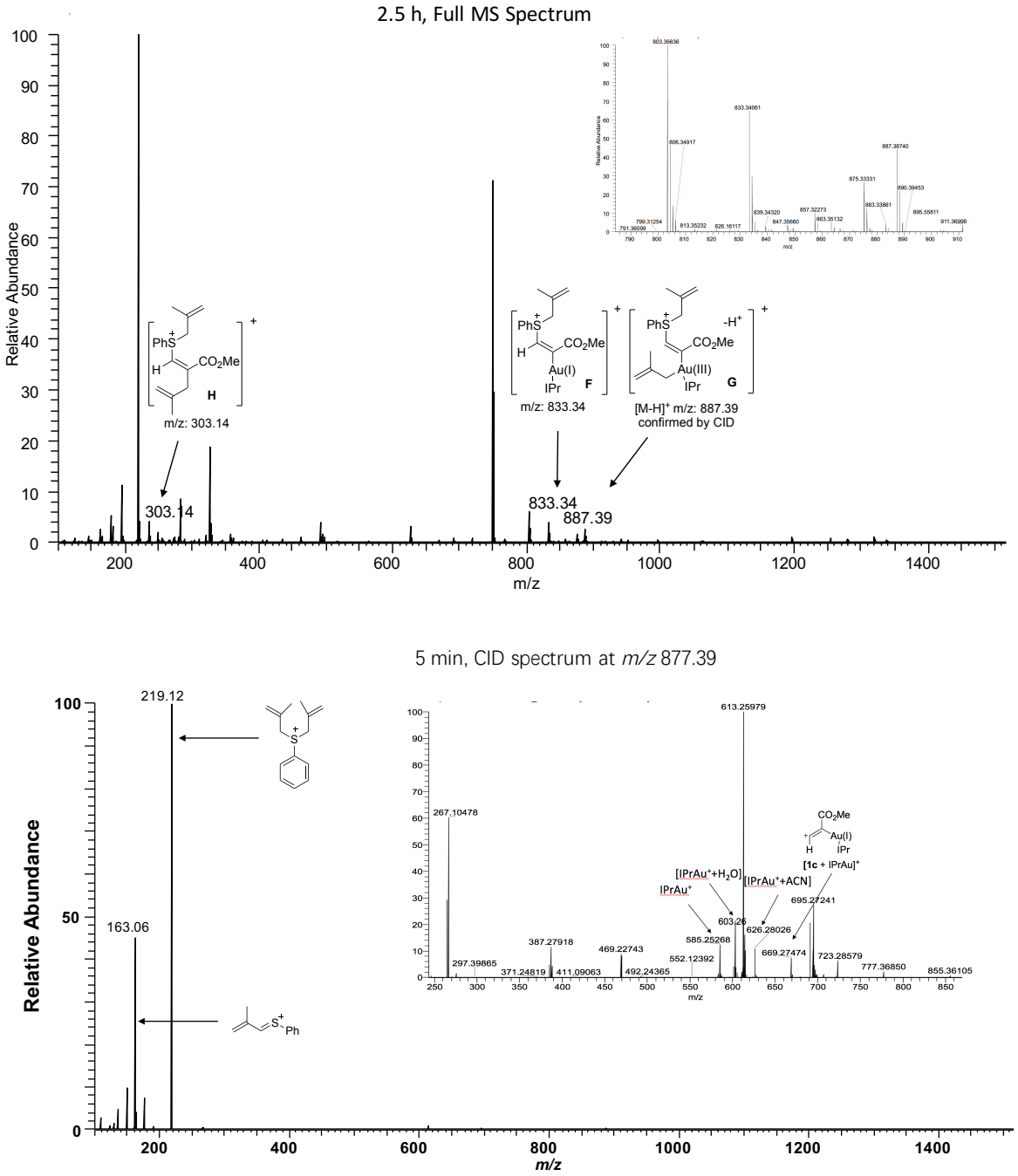
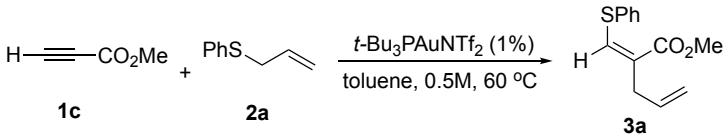


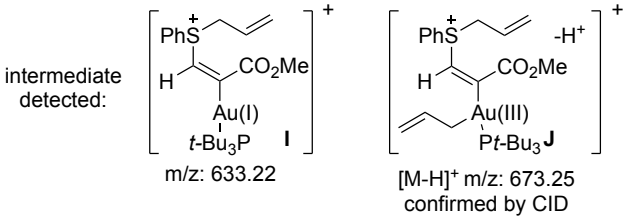
Figure 4.2. ESI-MS spectrum for **1c** and **2l** and CID analysis for *m/z* = 877.4

Conclusions for chapter 4.2

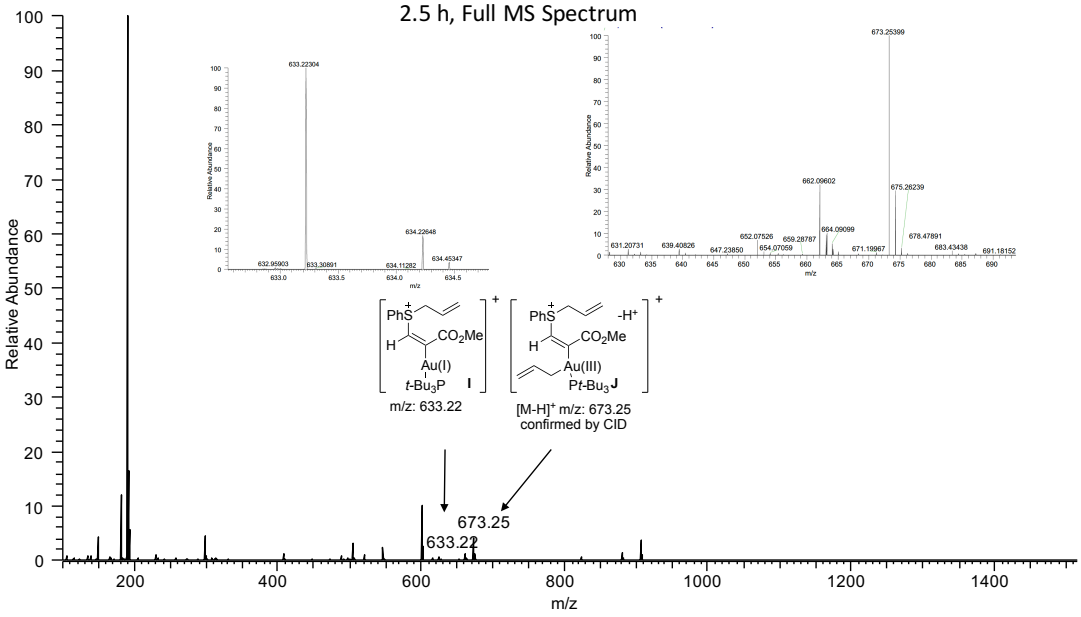
*Overall, this experiment confirmed the reaction between **1c** and **2l** underwent the same reaction pathway as **1c** and **2a**; Au(III) intermediate at m/z = 887.4 was confirmed.*

4.3 ESI-MS analysis of 1c and 2a with *t*-$Bu_3PAuNTf_2$





More investigation was conducted by replacing the $IPrAuNTf_2$ catalyst with *t*-$Bu_3PAuNTf_2$ (**Figure 4.3**). The vinyl-Au(I) intermediate **I** at m/z = 633.2 was observed, and Au (III) intermediate **J** was observed at *m/z* 673.3. The CID spectrum of Au (III) intermediate **J** displayed a very similar pattern as intermediate **C** with major fragments observed at *m/z* = 149.0 and 191.1.



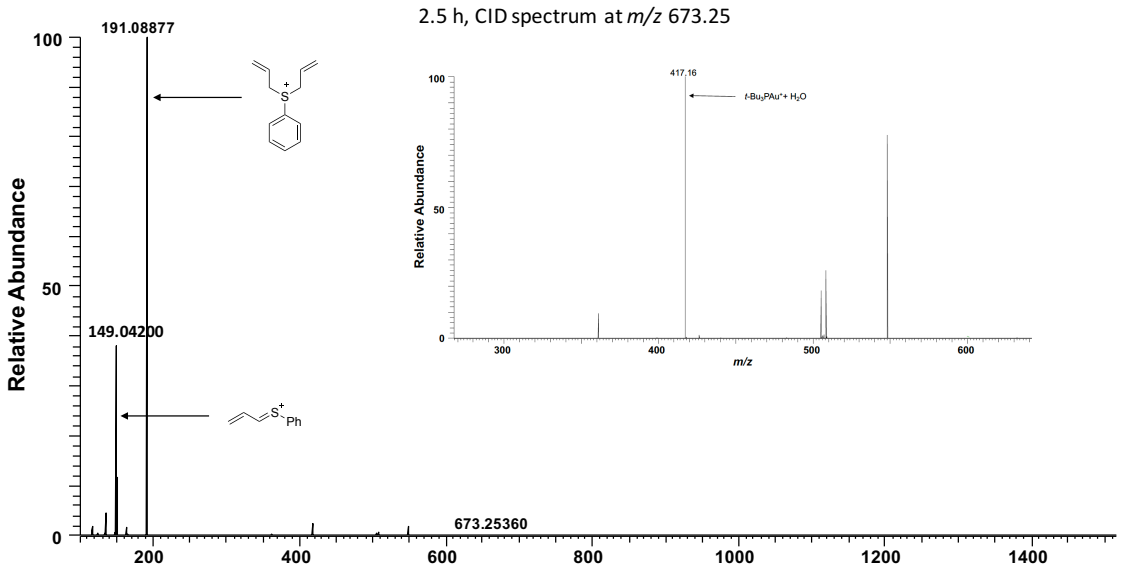


Figure 4.3. ESI-MS spectrum for **1c** and **2a** with *t*-$Bu_3PAuNTf_2$ and CID analysis *for m/z* = 673.3

Conclusions for chapter 4.3

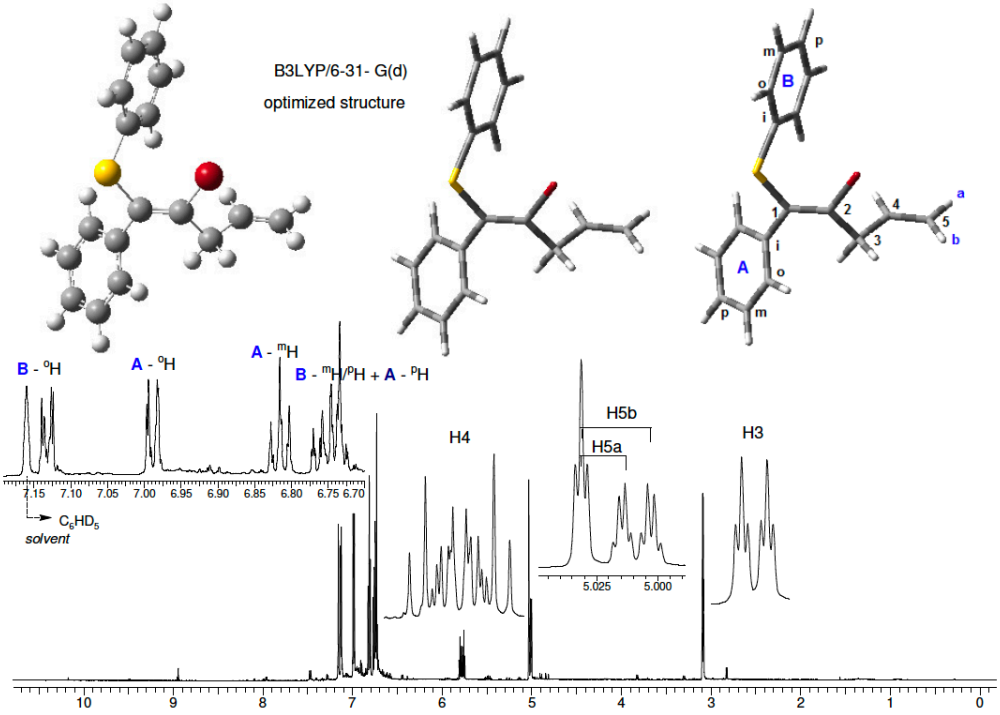
Overall, thioallylation with a phosphine-based gold catalyst t-$Bu_3PAuNTf_2$ underwent the same reaction pathway as IPrAuNTf₂. Au(III)intermediate at m/z = 673.3 was confirmed.

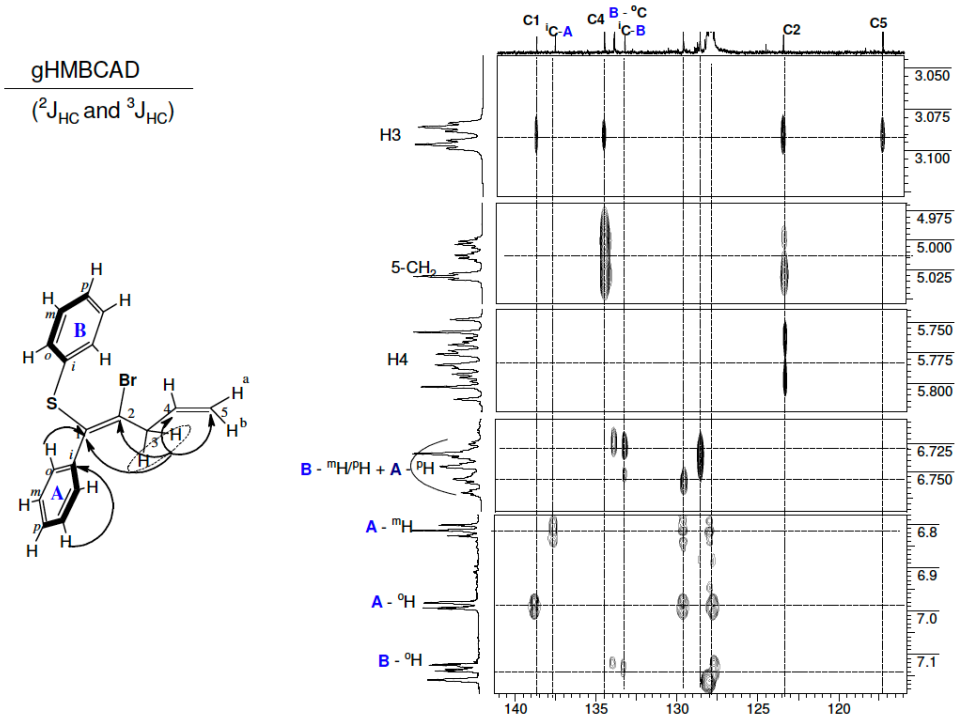
Conclusions for Mass study

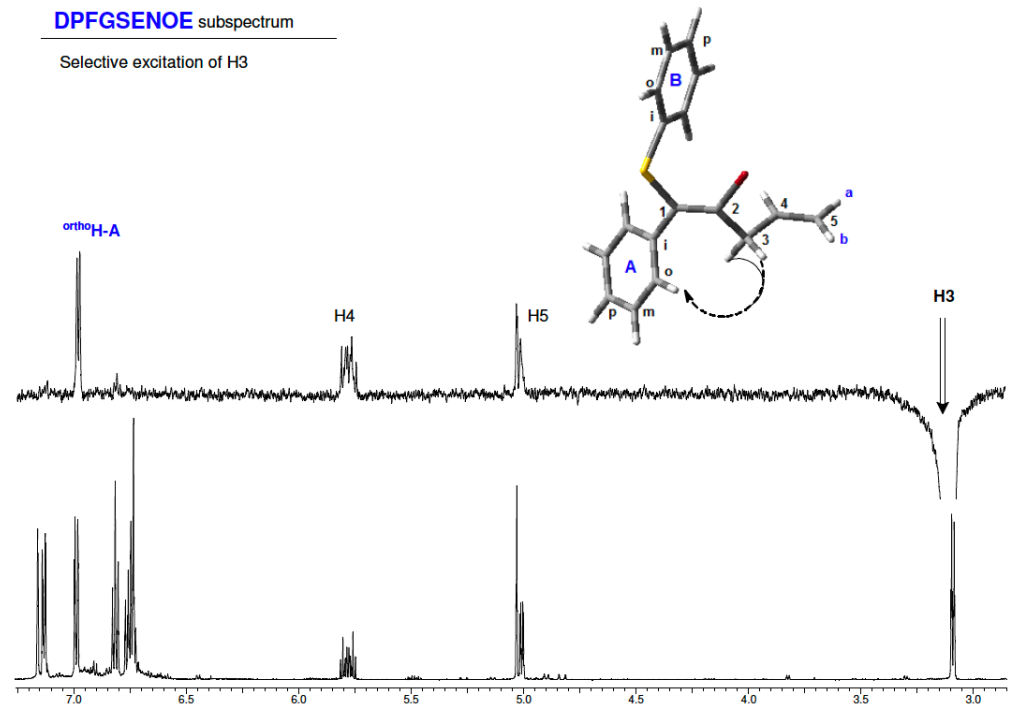
In conclusion, we have successfully identified two Au(III) intermediates by their *m/z* (859.4 and 735.3) and confirmed their structures by CID MS/MS spectrum. Several other key intermediates in our proposed mechanism were also detected, which provided sufficient proof for the reaction pathway which involves a vinyl gold formation and subsequent allyl transfer in intermolecular fashion via Au(I/III) cycle.

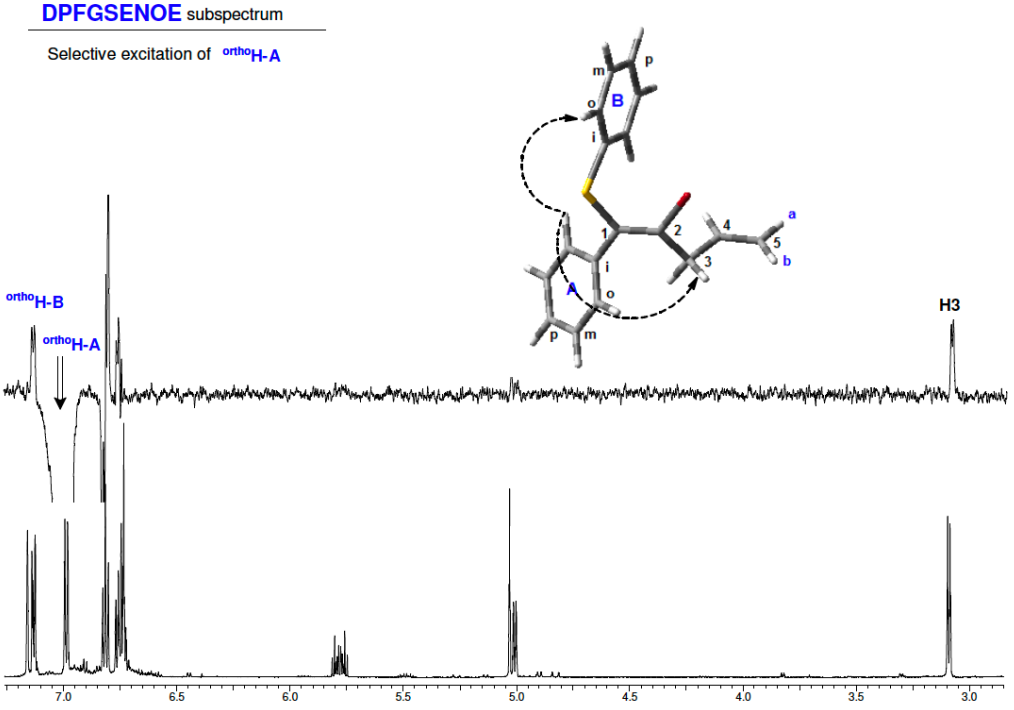
V. NMR Study

5.1 NMR study for compound 5a

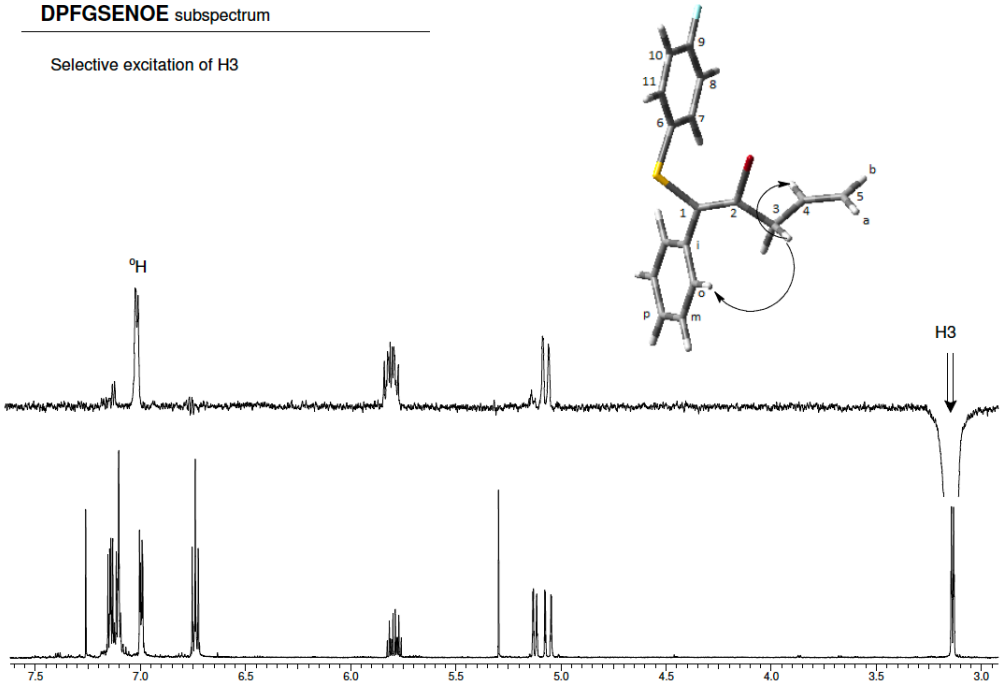


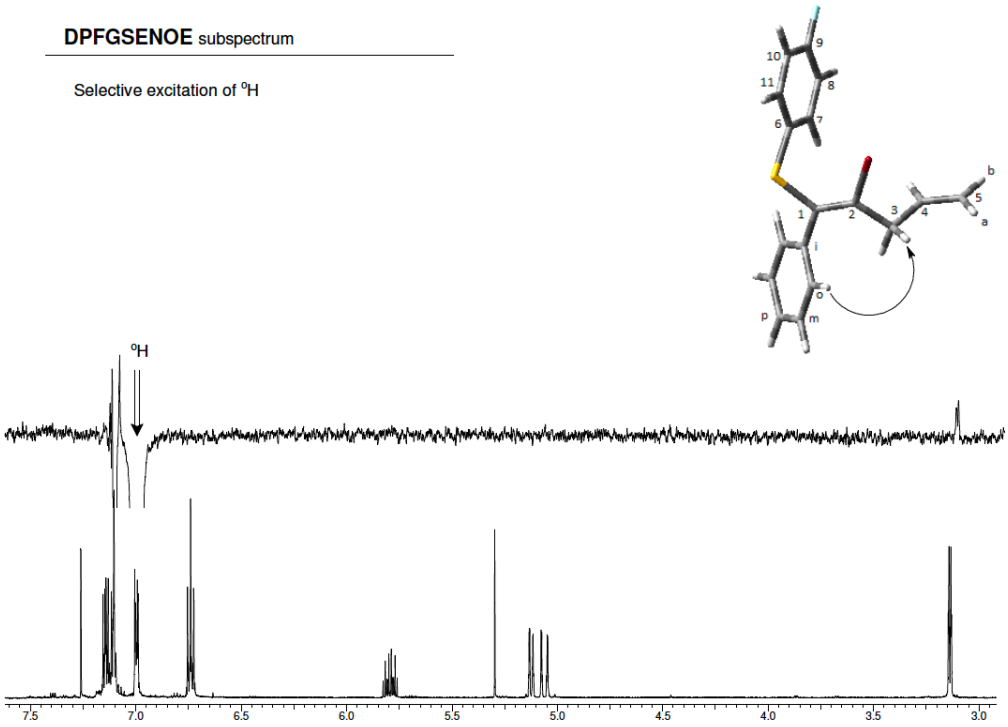



DPFGSENOE subspectrum
Selective excitation of H3
orthoH-A
H4
H5
H3
m
p
o
B
i
1
2
3
4
5
a
b
A
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

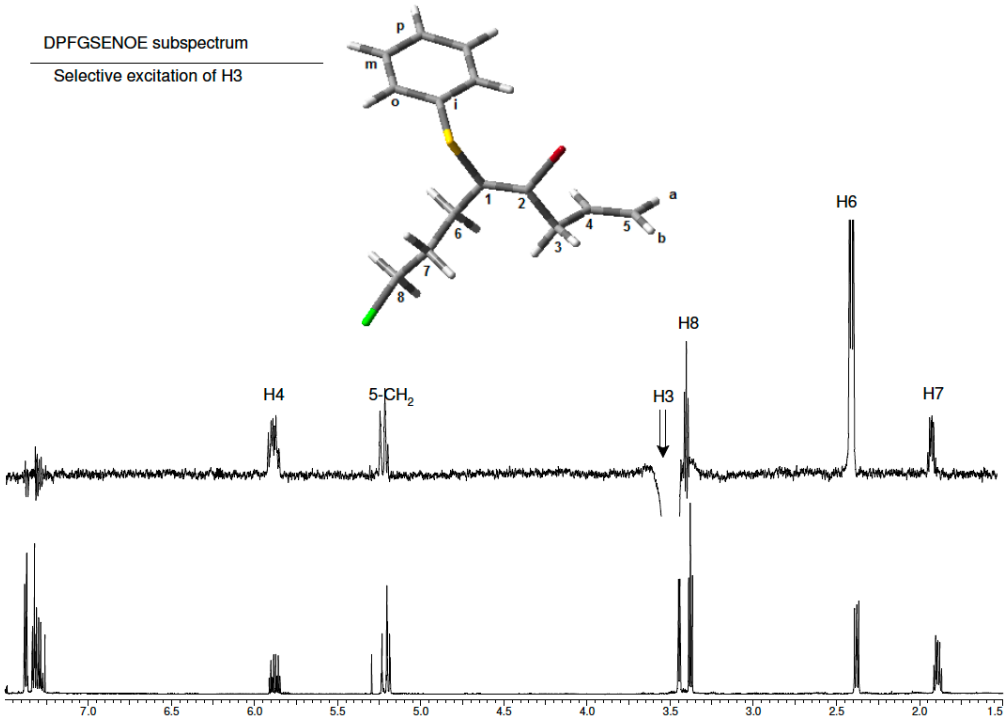

DPFGSENOE subspectrum
Selective excitation of orthoH-A
orthoH-B
orthoH-A
H3
m
p
o
B
i
1
2
3
4
5
a
b
A
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

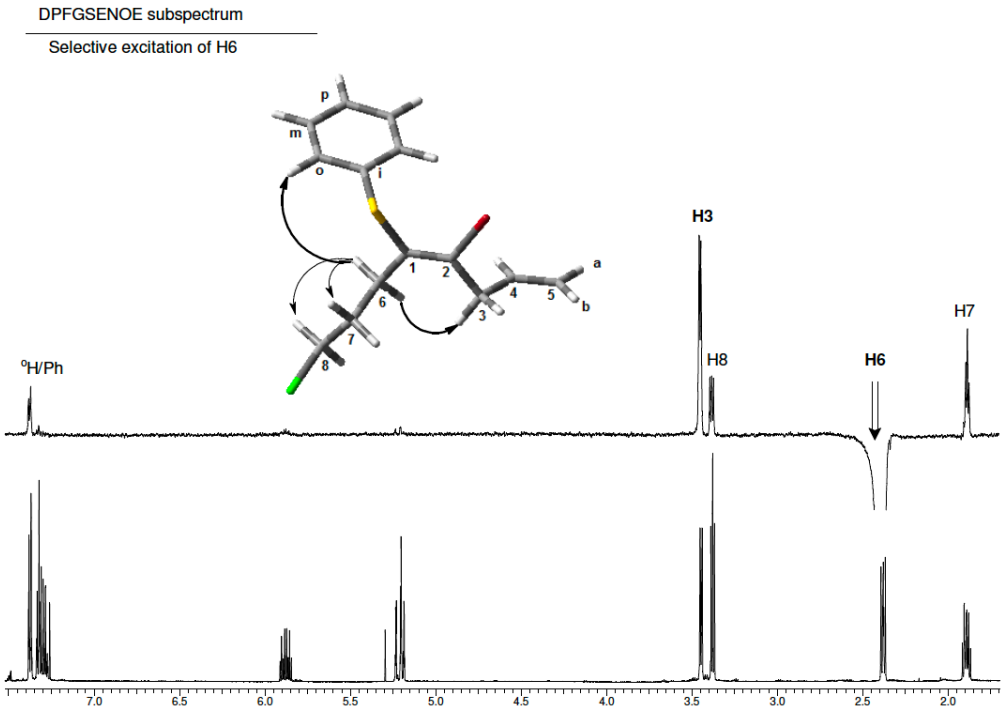
5.2 NMR study for compound 5c

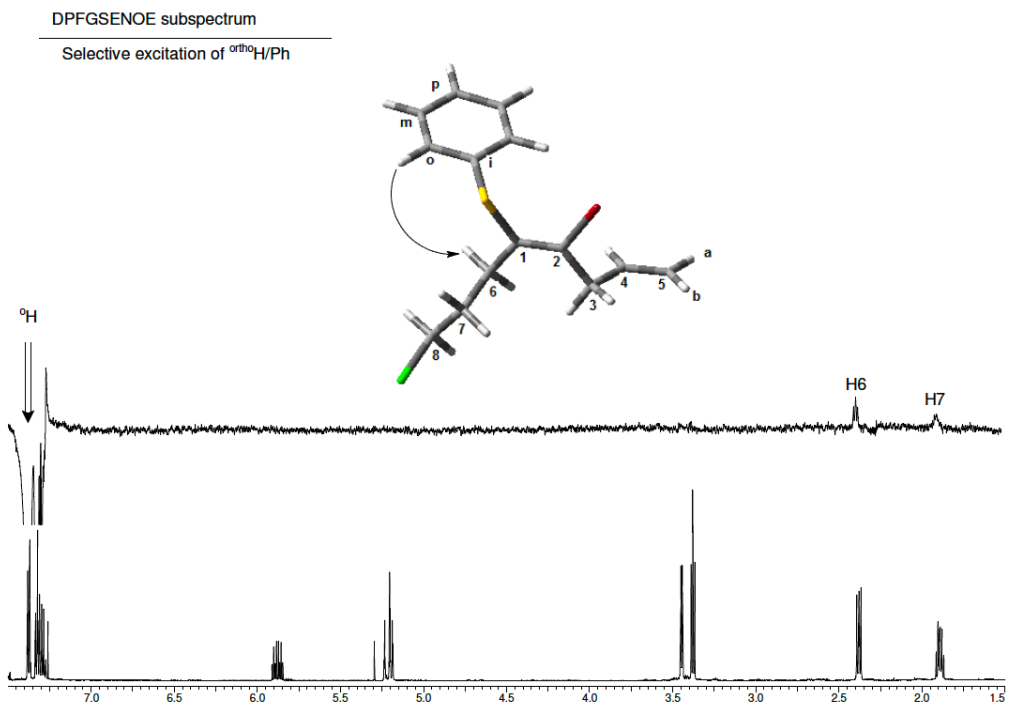




5.3 NMR study for compound 5p






DPFGSENOE subspectrum
Selective excitation of orthoH/Ph
oH
H6
H7
p
m
o
i
1
2
3
4
5
6
7
8
a
b
7.0
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3.0
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2.0
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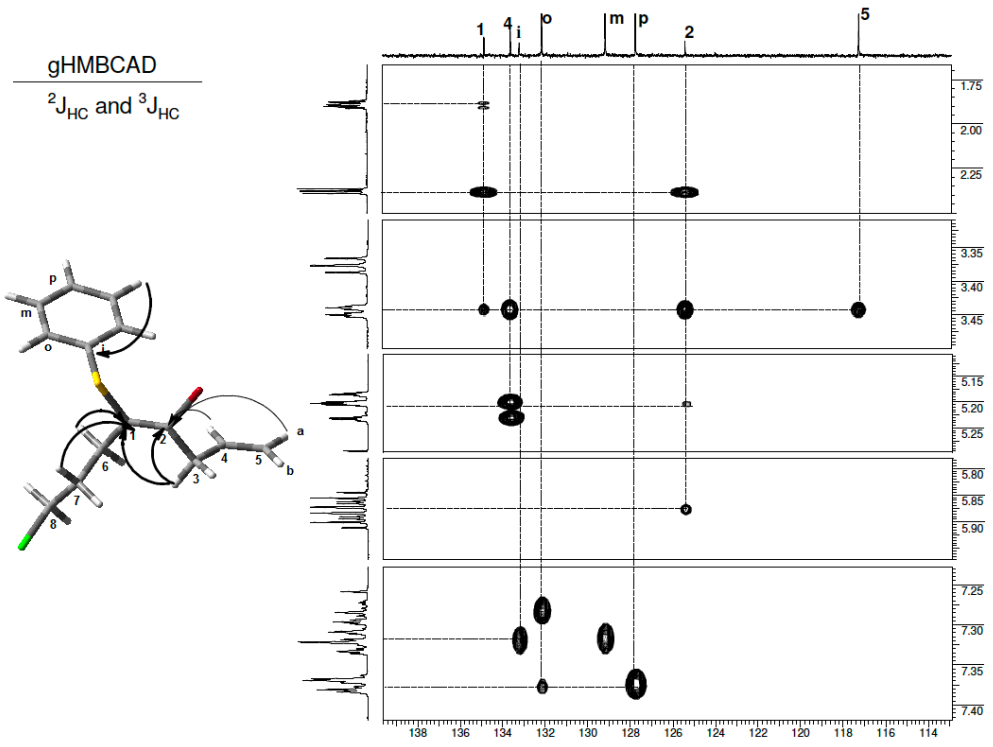
gHMBCAD
2JHC and 3JHC
1
4
i
o
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2
5
1.75
2.00
2.25
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3.40
3.45
5.15
5.20
5.25
5.80
5.85
5.90
7.25
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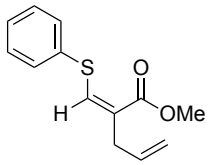
114

VI. Compound Characterization



3a

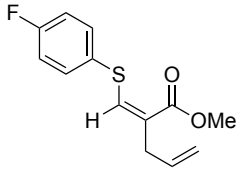
methyl (Z)-2-((phenylthio)methylene)pent-4-enoate (**3a**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (95%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.46-7.43 (m, 2H), 7.35-7.26 (m, 3H), 6.99 (t, *J* = 1.0 Hz, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07-5.00 (m, 2H), 3.78 (s, 3H), 3.06 (dq, *J* = 6.5, 1.3 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 167.0, 145.0, 136.9, 135.5, 130.9, 129.3, 127.9, 123.5, 116.6, 51.6, 36.7.

HRMS: *m/z* (ESI) calculated for $C_{13}H_{14}O_2S$ $(M+Na)^+$: 257.0607, found 257.0610.



3b

methyl (Z)-2-(((4-fluorophenyl)thio)methylene)pent-4-enoate (**3b**)

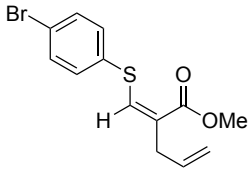
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (90%).

^{1}H NMR (400 MHz; CDCl3): δ 7.49-7.45 (m, 2H), 7.09-7.05 (m, 2H), 6.91 (t, *J* = 1.1 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09-5.04 (m, 2H), 3.83 (s, 3H), 3.08 (dq, *J* = 6.5, 1.3 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 167.0, 162.7 (d, J = 247.3), 145.3, 135.4, 133.4 (d, *J* = 8.7 Hz), 132.1 (d, *J* = 4.3 Hz), 123.5, 116.6, 116.4 (d, *J* = 21.8 Hz), 51.7, 36.6.

^{19}F NMR (376 MHz; $CDCl_3$): δ -113.1 (tt, *J* = 8.5, 5.3 Hz, 1F)

HRMS: *m/z* (ESI) calculated for $C_{13}H_{13}FO_2S$ $(M+Na)^+$: 275.0512, found 275.0509.

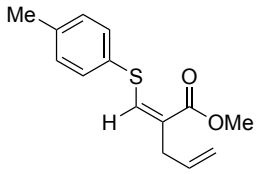


3c

methyl (Z)-2-(((4-bromophenyl)thio)methylene)pent-4-enoate (**3c**)

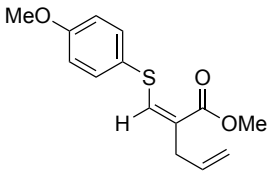
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as white solid (89%).

^{1}H NMR (400 MHz; CDCl3): δ 7.50-7.46 (m, 2H), 7.35-7.31 (m, 2H), 6.92 (t, *J* = 1.1 Hz, 1H), 5.87-5.77 (m, 1H), 5.10-5.04 (m, 2H), 3.81 (s, 3H), 3.08 (dq, *J* = 6.5, 1.3 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 166.9, 143.9, 136.0, 135.2, 132.4, 132.3, 124.1, 122.2, 116.8, 51.7, 36.7.
HRMS: *m*/*z* (ESI) calculated for $C_{13}H_{13}BrO_2S$ $(M+H)^+$: 314.9872, found 314.9864.



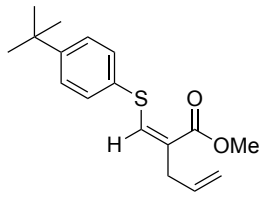
3d

methyl (*Z*)-2-((*p*-tolylthio)methylene)pent-4-enoate (**3d**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (92%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.38-7.35 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.97 (t, *J* = 1.0 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.08-5.01 (m, 2H), 3.81 (s, 3H), 3.07 (dq, *J* = 6.5, 1.3 Hz, 2H), 2.35 (s, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.1, 146.0, 138.1, 135.6, 133.4, 131.2, 130.0, 123.0, 116.5, 51.6, 36.7, 21.1.
HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}O_2S$ $(M+Na)^+$: 271.0763, found 271.0768.



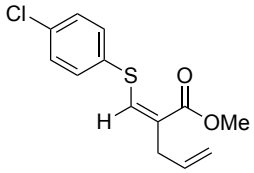
3e

methyl (*Z*)-2-(((4-methoxyphenyl)thio)methylene)pent-4-enoate (**3e**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (10:1 hexane/EtOAc) to yield the desired product as colorless oil (86%). *Cation: this product is prone to E/Z isomerization over time with Au catalyst or on column. Fast purification is required.*
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.44-7.40 (m, 2H), 6.91-6.88 (m, 3H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.08-5.01 (m, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.05 (dq, *J* = 6.5, 1.3 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.1, 159.8, 147.0, 135.6, 133.4, 127.6, 122.6, 116.4, 114.8, 77.3, 77.0, 76.7, 55.4, 51.6, 36.7
HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}O_3S$ $(M+Na)^+$: 287.0719, found 287.0706.



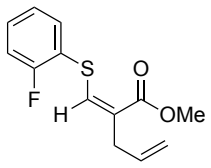
3f

methyl (*Z*)-2-(((4-(*tert*-butyl)phenyl)thio)methylene)pent-4-enoate (**3f**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (94%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.42-7.37 (m, 4H), 7.02 (t, *J* = 1.1 Hz, 1H), 5.83 (dd, *J* = 17.1, 10.1 Hz, 1H), 5.08-5.02 (m, 2H), 3.81 (s, 3H), 3.07 (dq, *J* = 6.5, 1.3 Hz, 2H), 1.32 (s, 9H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.1, 151.3, 145.9, 135.6, 133.4, 130.9, 126.3, 123.0, 116.4, 51.6, 36.8, 34.6, 31.2.
HRMS: *m/z* (ESI) calculated for $C_{17}H_{22}O_2S$ $(M+H)^+$: 291.1414, found 291.1212.



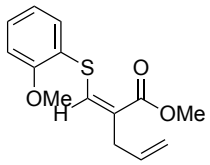
3g

methyl (*Z*)-2-(((4-chlorophenyl)thio)methylene)pent-4-enoate (**3g**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (92%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.42-7.38 (m, 2H), 7.34-7.31 (m, 2H), 6.92 (t, *J* = 1.1 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.10-5.04 (m, 2H), 3.82 (s, 3H), 3.08 (dq, *J* = 6.5, 1.3 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 166.9, 144.1, 135.4, 135.3, 134.2, 132.2, 129.4, 124.0, 116.7, 51.7, 36.7.
HRMS: *m/z* (ESI) calculated for $C_{13}H_{13}ClO_2S$ $(M+Na)^+$: 291.0217, found 291.0221.



3h

methyl (*Z*)-2-(((2-fluorophenyl)thio)methylene)pent-4-enoate (**3h**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (90%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.50 (ddd, *J* = 7.6, 7.6, 1.7 Hz, 1H), 7.35 (dddd, *J* = 8.1, 7.5, 5.1, 1.8 Hz, 1H), 7.18-7.11 (m, 2H), 6.88 (q, *J* = 1.1 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.10-5.03 (m, 2H), 3.83 (s, 3H), 3.08 (dt, *J* = 6.5, 1.3 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.0, 161.4 (d, *J* = 246.2 Hz), 143.9, 135.3, 133.9, 130.5 (d, *J* = 7.8 Hz), 124.7 (d, *J* = 3.9 Hz), 124.1, 123.5 (d, *J* = 17.6 Hz), 116.6, 116.3 (d, *J* = 22.4 Hz), 51.7, 36.6.
^{19}F NMR (376 MHz; $CDCl_3$): δ -108.7 (m, 1F)
HRMS: *m/z* (ESI) calculated for $C_{13}H_{13}FO_2S$ $(M+Na)^+$: 275.0512, found 275.0507.



3i

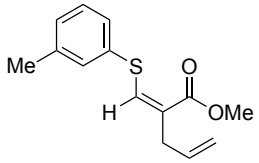
methyl (*Z*)-2-(((2-methoxyphenyl)thio)methylene)pent-4-enoate (**3i**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (90%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.45 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.32 (ddd, *J* = 7.8, 7.8, 1.6 Hz, 1H), 6.98-6.91 (m, 3H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.08-5.01 (m, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 3.06 (qd, *J* = 6.5, 1.2 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 167.1, 158.2, 145.5, 135.7, 133.2, 129.9, 124.2, 123.0, 121.1, 116.3, 111.3, 55.8, 51.5, 36.7.

HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}O_3S$ $(M+Na)^+$: 287.0719, found 287.0707.



3j

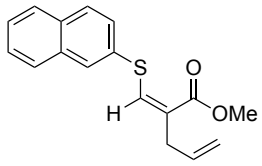
methyl (*Z*)-2-((*m*-tolylthio)methylene)pent-4-enoate (**3j**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (95%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.29-7.24 (m, 3H), 7.13-7.11 (m, 1H), 7.02 (t, *J* = 0.9 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.3, 6.6 Hz, 1H), 5.09-5.02 (m, 2H), 3.81 (s, 3H), 3.08 (dq, *J* = 6.5, 1.2 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 167.0, 145.3, 139.1, 136.6, 135.6, 131.6, 129.1, 128.8, 128.0, 123.2, 116.5, 51.6, 36.8, 21.3.

HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}O_2S$ $(M+Na)^+$: 271.0763, found 271.0777.



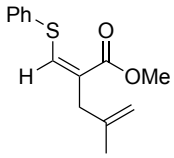
3k

methyl (*Z*)-2-((naphthalen-2-ylthio)methylene)pent-4-enoate (**3k**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (70%).

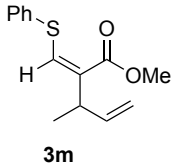
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.96-7.96 (m, 1H), 7.84-7.79 (m, 3H), 7.55-7.49 (m, 3H), 7.11 (t, *J* = 1.1 Hz, 1H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.11-5.03 (m, 2H), 3.84 (s, 3H), 3.11 (dq, *J* = 6.5, 1.3 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 167.1, 144.9, 135.5, 134.0, 133.5, 132.6, 130.0, 129.1, 128.3, 127.7, 127.6, 126.8, 126.6, 123.7, 116.6, 51.7, 36.8.
HRMS: *m*/*z* (ESI) calculated for $C_{17}H_{16}O_2S$ $(M+Na)^+$: 307.0763, found 307.0758.



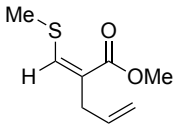
3l

methyl (*Z*)-4-methyl-2-((phenylthio)methylene)pent-4-enoate (**3l**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (88%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.47 (dq, *J* = 6.3, 2.0 Hz, 2H), 7.38-7.29 (m, 3H), 7.01 (t, *J* = 0.9 Hz, 1H), 4.81-4.71 (m, 2H), 3.80 (s, 3H), 3.03 (s, 2H), 1.72 (s, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.3, 145.3, 143.4, 136.9, 130.9, 129.3, 127.9, 123.1, 112.1, 51.6, 40.4, 22.3.
HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}O_2S$ $(M+H)^+$: 249.0944, found 249.0944.



3m

methyl (*Z*)-3-methyl-2-((phenylthio)methylene)pent-4-enoate (**3m**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (91%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.46 (dq, *J* = 6.3, 1.9 Hz, 2H), 7.38-7.29 (m, 3H), 7.00 (d, *J* = 0.6 Hz, 1H), 5.87 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.08-5.01 (m, 2H), 3.82 (s, 3H), 3.52-3.45 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.0, 143.7, 141.2, 137.1, 130.7, 129.3, 129.1, 127.8, 114.0, 51.6, 38.9, 19.1.
HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}O_2S$ $(M+Na)^+$: 271.0763, found 271.0772.

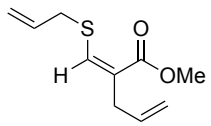


3n

methyl (*Z*)-2-((methylthio)methylene)pent-4-enoate (**3n**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (86%). *Cation: this product is volatile. Careful rot-vap and vacuum is required.*

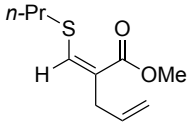
^{1}H NMR (400 MHz; $CDCl_3$): δ 6.77 (t, *J* = 1.0 Hz, 1H), 5.88-5.78 (m, 1H), 5.09-5.04 (m, 2H), 3.77 (s, 3H), 3.06-3.03 (dq, *J* = 6.4, 1.2 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 167.1, 147.3, 135.8, 122.9, 116.3, 51.4, 36.8, 19.3.
HRMS: *m/z* (ESI) calculated for $C_8H_{12}O_2S$ $(M+Na)^+$:195.0450, found 195.0453.



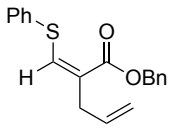
3o

methyl (*Z*)-2-((allylthio)methylene)pent-4-enoate (**3o**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (64%). *Cation: this product is volatile. Careful rot-vap and vacuum is required.*
^{1}H NMR (400 MHz; CDCl3): δ 6.78 (t, *J* = 1.0 Hz, 1H), 5.90-5.76 (m, 2H), 5.23-5.15 (m, 2H), 5.08-5.03 (m, 2H), 3.77 (s, 3H), 3.33 (dt, *J* = 7.1, 1.1 Hz, 2H), 3.04 (dq, *J* = 6.5, 1.3 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.1, 143.8, 135.7, 134.0, 123.5, 118.0, 116.3, 51.5, 38.2, 36.8.
HRMS: *m/z* (ESI) calculated for $C_{10}H_{14}O_2S$ $(M+Na)^+$: 221.0607, found 221.0604.



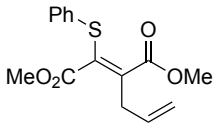
3p

methyl (*Z*)-2-((propylthio)methylene)pent-4-enoate (**3p**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (75%). *Cation: this product is volatile. Careful rot-vap and vacuum is required.*
^{1}H NMR (400 MHz; $CDCl_3$): δ 6.80 (t, *J* = 1.0 Hz, 1H), 5.88-5.78 (m, 1H), 5.08-5.04 (m, 2H), 3.77 (s, 3H), 3.05 (dq, *J* = 6.5, 1.3 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H), 1.69 (sextet, *J* = 7.3 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 167.2, 145.9, 135.9, 122.8, 116.2, 51.4, 38.1, 36.9, 23.6, 13.1.
HRMS: *m/z* (ESI) calculated for $C_{10}H_{16}O_2S$ $(M+Na)^+$: 223.0763, found 223.0760.



3q

benzyl (*Z*)-2-((phenylthio)methylene)pent-4-enoate (**3q**)
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (90%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.47 (dq, *J* = 6.2, 2.0 Hz, 2H), 7.42-7.29 (m, 8H), 7.04 (t, *J* = 1.1 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.26 (s, 2H), 5.08-5.01 (m, 2H), 3.10 (dq, *J* = 6.5, 1.3 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 166.4, 145.6, 136.9, 136.0, 135.5, 131.0, 129.3, 128.5, 128.2, 128.1, 128.0, 123.4, 116.7, 66.4, 36.8.
HRMS: *m/z* (ESI) calculated for $C_{19}H_{18}O_2S$ $(M+H)^+$: 311.1101, found 311.1095.



3r

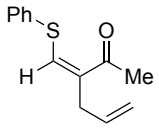
dimethyl 2-allyl-3-(phenylthio)fumarate (**3r**)

This compound was prepared following a modified general procedure **2.3** (2% cat. was used), and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (74%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.54-7.51 (m, 2H), 7.38-7.30 (m, 3H), 5.83-5.73 (m, 1H), 5.07-5.00 (m, 2H), 3.83 (s, 3H), 3.24 (s, 3H), 3.10 (dt, J = 6.4, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 166.8, 164.4, 144.6, 135.3, 134.4, 131.3, 129.4, 128.7, 125.3, 116.5, 52.0, 51.9, 35.6.

HRMS: m/z (ESI) calculated for $C_{15}H_{16}O_4S$ $(M+Na)^+$: 315.0661, found 315.0658.



3s

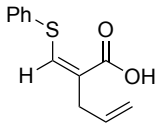
(*Z*)-3-((phenylthio)methylene)hex-5-en-2-one (**3s**)

This compound was prepared following a modified general procedure **2.3** (2% cat. was used), and crude mixture was purified using flash chromatography (10:1 hexane/EtOAc) to yield the desired product as colorless oil (57%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.49-7.46 (m, 2H), 7.38-7.29 (m, 3H), 6.99 (s, 1H), 5.91-5.81 (m, 1H), 5.14-5.07 (m, 2H), 3.19-3.17 (m, 2H), 2.30 (s, 3H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 198.1, 145.4, 137.9, 135.7, 130.8, 129.8, 129.2, 127.9, 117.0, 37.7, 27.8.

HRMS: m/z (ESI) calculated for $C_{13}H_{14}OS$ $(M+H)^+$: 219.0838, found 219.0841.



3t

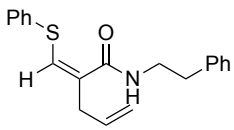
(*Z*)-2-((phenylthio)methylene)pent-4-enoic acid (**3t**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (5:1 hexane/EtOAc) to yield the desired product as white solid (90%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.46 (dq, J = 6.2, 2.0 Hz, 2H), 7.38-7.30 (m, 3H), 7.14 (d, J = 0.9 Hz, 1H), 5.86 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.11-5.04 (m, 2H), 3.10 (dq, J = 6.5, 1.3 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 172.2, 148.2, 136.7, 135.4, 131.0, 129.3, 128.1, 122.9, 116.7, 36.7.

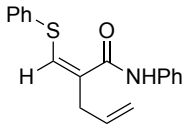
HRMS: m/z (ESI) calculated for $C_{12}H_{12}O_2S$ $(M+Na)^+$: 243.0450, found 243.0450.



3u

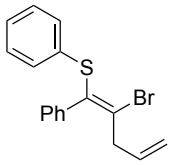
(*Z*)-*N*-phenethyl-2-((phenylthio)methylene)pent-4-enamide (**3u**)

This compound was prepared following a modified general procedure **2.3** (0.3 mmol alkyne and 0.45 mmol sulfide were used), and crude mixture was purified using flash chromatography (3:1 hexane/EtOAc) to yield the desired product as colorless oil (66%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.48-7.45 (m, 2H), 7.35-7.25 (m, 5H), 7.24-7.19 (m, 3H), 6.79 (s, 1H), 5.89 br, 1H), 5.72 (dt, *J* = 17.8, 7.3 Hz, 1H), 5.01-4.95 (m, 2H), 3.62 (q, *J* = 6.4 Hz, 2H), 2.97 (dd, *J* = 6.3, 1.2 Hz, 2H), 2.86 (t, *J* = 6.9 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 166.9, 140.8, 138.9, 137.8, 135.6, 130.8, 129.1, 128.8, 128.6, 127.6, 126.5, 124.9, 117.5, 40.6, 37.8, 35.5.
HRMS: *m*/*z* (ESI) calculated for $C_{20}H_{21}NOS$ $(M+Na)^+$: 346.1236, found 346.1236.



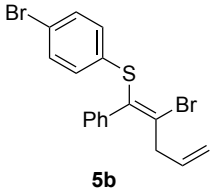
3v

(*Z*)-*N*-phenyl-2-((phenylthio)methylene)pent-4-enamide (**3v**)
This compound was prepared following a modified general procedure **2.3** (0.3 mmol alkyne and 0.45 mmol sulfide were used), and crude mixture was purified using flash chromatography (3:1 hexane/EtOAc) to yield the desired product as white solid (63%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.70 (br, 1H), 7.57-7.54 (m, 2H), 7.50-7.47 (m, 2H), 7.37-7.28 (m, 5H), 7.11-7.07 (m, 1H), 6.97 (t, *J* = 0.9 Hz, 1H), 6.00-5.90 (m, 1H), 5.36-5.25 (m, 2H), 3.21(dq, *J* = 6.4, 1.2 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 165.0, 143.0, 137.8, 137.5, 136.2, 130.8, 129.2, 128.9, 127.8, 124.6, 124.3, 119.9, 118.1, 38.2.
HRMS: *m*/*z* (ESI) calculated for $C_{18}H_{17}NOS$ $(M+H)^+$: 318.0923, found 318.0921.



5a

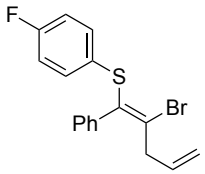
(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(phenyl)sulfane (**5a**)
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as white solid (97%).
^{1}H NMR (400 MHz; CDCl3): δ 7.18-7.14 (m, 2H), 7.11-7.01 (m, 8H), 5.81 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.12 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.07 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.16 (dt, *J* = 6.3, 1.5 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 138.2, 137.0, 134.3, 133.7, 132.6, 129.3, 128.3, 127.8, 127.6, 127.5, 122.7, 117.1, 43.4.
HRMS: *m*/*z* (ESI) calculated for $C_{17}H_{15}BrS$ $(M+IPrAu)^+$: 915.2617, found 915.2613.



5b

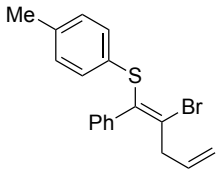
(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(4-bromophenyl)sulfane (**5b**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (94%).
^{1}H NMR (400 MHz; CDCl3): δ 7.20-7.12 (m, 5H), 7.08-7.00 (m, 4H), 5.81 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.14 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.08 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.17 (dt, *J* = 6.3, 1.5 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 137.4, 136.8, 134.8, 134.1, 131.9, 131.5, 129.3, 128.0, 127.9, 123.8, 121.9, 117.3, 43.4.
HRMS: *m/z* (ESI) calculated for $C_{17}H_{14}Br_2S$ $(M+IPrAu)^+$: 993.1722, found 993.1711.



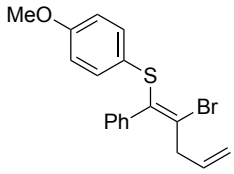
5c

(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(4-fluorophenyl)sulfane (**5c**)
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (89%).
^{1}H NMR (400 MHz; CDCl3): δ 7.17-7.09 (m, 5H), 7.01-6.98 (m, 2H), 6.76-6.72 (m, 2H), 5.79 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.12 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.06 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.14 (dt, *J* = 6.3, 1.5 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 162.5 (d, *J* = 247.2 Hz), 138.3 (d, *J* = 1.2 Hz), 136.7, 136.3 (d, *J* = 8.4 Hz), 134.2, 129.3, 127.8, 127.7, 127.6, 121.7, 117.1, 115.6, 115.3, 43.3.
^{19}F-NMR (376 MHz; $CDCl_3$): δ -113.1 (tt, *J* = 8.3, 5.3 Hz, 1F).
HRMS: *m/z* (ESI) calculated for $C_{17}H_{14}BrFS$ $(M+IPrAu)^+$: 933.2523, found 933.2503.



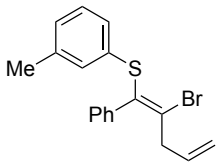
5d

(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(2-fluorophenyl)sulfane (**5d**)
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (73%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.13-7.01 (m, 7H), 6.86-6.84 (m, 2H), 5.80 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.12 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.07 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.14 (dt, *J* = 6.3, 1.5 Hz, 2H), 2.18 (s, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 138.6, 137.7, 137.1, 134.3, 133.9, 129.3, 129.1, 128.8, 127.7, 127.5, 121.9, 117.0, 43.4, 21.0.
HRMS: *m/z* (ESI) calculated for $C_{18}H_{17}BrS$ $(M+IPrAu)^+$: 929.2773, found 929.2760.



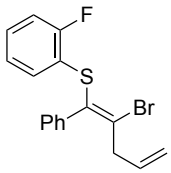
5e

(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(4-methoxyphenyl)sulfane (**5e**)
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as colorless oil (73%). *Cation: this product is prone to E/Z isomerization over time on column. Fast purification is required.*
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.11-7.07 (m, 5H), 6.98-6.96 (m, 2H), 6.58-6.55 (m, 2H), 5.78 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.11 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.05 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.68 (s, 3H), 3.11 (dt, *J* = 6.3, 1.5 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 159.6, 139.2, 136.9, 136.4, 134.3, 129.3, 127.7, 127.5, 122.9, 120.2, 117.0, 113.9, 55.1, 43.3.
HRMS: *m*/*z* (ESI) calculated for $C_{18}H_{17}BrOS$ $(M+IPrAu)^+$: 945.2722, found 945.2699.



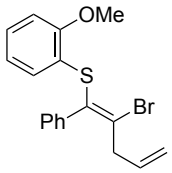
5f

(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(*m*-tolyl)sulfane (**5f**)
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (81%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.13-7.03 (m, 5H), 6.98-6.91 (m, 3H), 6.87-6.85 (m, 1H), 5.87-5.77 (m, 1H), 5.13 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.08 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.17 (dt, *J* = 6.3, 1.5 Hz, 2H), 2.14 (s, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 138.2, 138.0, 137.1, 134.30, 134.26, 132.2, 130.5, 129.3, 128.3, 128.1, 127.7, 127.6, 122.6, 117.1, 43.4, 21.0.
HRMS: *m*/*z* (ESI) calculated for $C_{18}H_{17}BrS$ $(M+IPrAu)^+$: 929.2773, found 929.2745.



5g

(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(2-fluorophenyl)sulfane (**5g**)
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (92%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.21 (td, *J* = 7.5, 1.8 Hz, 1H), 7.11-7.05 (m, 6H), 6.86-6.76 (m, 2H), 5.84-5.74 (m, 1H), 5.13 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.08 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.14 (dt, *J* = 6.3, 1.5 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 162.2 (d, *J* = 246.3 Hz), 137.5, 136.5, 134.2, 130.6 (d, *J* = 8.0 Hz), 129.1, 127.7, 123.8 (d, *J* = 3.9 Hz), 121.6, 119.7 (d, *J* = 18.0 Hz), 117.1, 115.4 (d, *J* = 22.8 Hz), 43.3.
^{19}F-NMR (376 MHz; $CDCl_3$): δ -105.7 (m, 1F).
HRMS: *m*/*z* (ESI) calculated for $C_{17}H_{14}BrFS$ $(M+IPrAu)^+$: 933.2523, found 933.2509.



5h

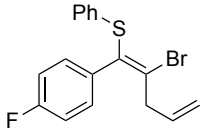
(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(2-methoxyphenyl)sulfane (**5h**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as colorless oil (75%). *Cation: this product is prone to E/Z isomerization over time on column. Fast purification is required.*

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.23 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.10-7.02 (m, 6H), 6.70-6.66 (m, 1H), 6.55 (dd, *J* = 8.3, 1.0 Hz, 1H), 5.85-5.76 (m, 1H), 5.15-5.06 (m, 2H), 3.71 (s, 3H), 3.15 (dt, *J* = 6.2, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 158.8, 138.4, 136.9, 135.9, 134.5, 129.9, 129.1, 127.41, 127.24, 121.0, 120.34, 120.30, 116.8, 110.4, 55.4, 43.3, 36.4.

HRMS: *m/z* (ESI) calculated for $C_{18}H_{17}BrOS$ $(M+IPrAu)^+$: 945.2722, found 945.2703.



5i

(*Z*)-(2-bromo-1-(4-fluorophenyl)penta-1,4-dien-1-yl)(phenyl)sulfane (**5i**)

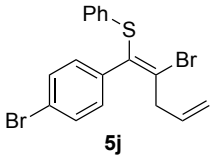
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (94%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.17-7.15 (m, 2H), 7.10-7.01 (m, 4H), 6.81-6.77 (m, 2H), 5.86-5.76 (m, 1H), 5.14 (dt, *J* = 10.1, 1.4 Hz, 1H), 5.10-5.05 (m, 1H), 3.15 (dt, *J* = 6.3, 1.4 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 161.9 (d, *J* = 246.6 Hz), 137.3, 134.1, 133.8, 132.9 (d, *J* = 3.4 Hz), 132.4, 131.0 (d, *J* = 8.2 Hz), 128.5, 127.8, 122.8, 117.2, 114.8 (d, *J* = 21.6 Hz), 43.4.

^{19}F-NMR (376 MHz; $CDCl_3$): δ -113.5 (tt, *J* = 9.0, 5.3 Hz, 1F).

HRMS: *m/z* (ESI) calculated for $C_{17}H_{14}BrFS$ $(M+IPrAu)^+$: 933.2523, found 933.2511.



5j

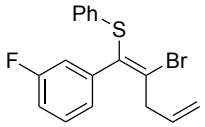
(*Z*)-(2-bromo-1-(4-bromophenyl)penta-1,4-dien-1-yl)(phenyl)sulfane (**5j**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (91%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.24-7.21 (m, 2H), 7.16-7.12 (m, 2H), 7.10-7.05 (m, 3H), 6.94-6.91 (m, 2H), 5.79 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.13 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.06 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.14 (dt, *J* = 6.2, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 137.0, 136.1, 133.9, 133.5, 132.2, 131.0, 130.9, 128.6, 127.9, 123.7, 121.8, 117.3, 43.4.

HRMS: *m/z* (ESI) calculated for $C_{17}H_{14}Br_2S$ $(M+IPrAu)^+$: 993.1722, found 993.1689.



5k

(*Z*)-(2-bromo-1-(3-fluorophenyl)penta-1,4-dien-1-yl)(phenyl)sulfane (**5k**)

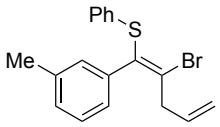
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (87%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.20-7.16 (m, 2H), 7.12-7.04 (m, 4H), 6.84 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.81-6.76 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.15 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.08 (dq, *J* = 17.0, 1.5 Hz, 1H), 3.17 (dt, *J* = 6.3, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 162.1 (d, *J* = 245.6 Hz), 139.1 (d, *J* = 7.9 Hz), 137.0 (d, *J* = 2.1 Hz), 133.9, 133.8, 132.2, 129.3 (d, *J* = 8.4Hz), 128.5, 127.9, 125.2 (d, *J* = 2.9 Hz), 123.5, 117.3, 116.3 (d, *J* = 22.2 Hz), 114.6 (d, *J* = 20.9 Hz), 43.4.

^{19}F-NMR (376 MHz; $CDCl_3$): δ -113.4 (dt, *J* = 9.0, 5.6 Hz, 1F).

HRMS: *m*/*z* (ESI) calculated for $C_{17}H_{14}BrFS$ $(M+IPrAu)^+$: 933.2523, found 933.2494.



5l

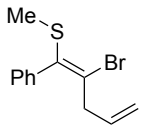
(*Z*)-(2-bromo-1-(*m*-tolyl)penta-1,4-dien-1-yl)(phenyl)sulfane (**5l**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (76%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.16 (dt, *J* = 4.8, 2.4 Hz, 2H), 7.06-7.03 (m, 3H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.88-6.84 (m, 3H), 5.81 (ddt, *J* = 16.8, 10.3, 6.4 Hz, 1H), 5.14-5.05 (m, 2H), 3.17 (dt, *J* = 6.3, 1.1 Hz, 2H), 2.16 (s, 3H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 138.2, 137.3, 136.9, 134.4, 133.6, 132.7, 130.0, 128.3, 128.2, 127.6, 127.5, 126.4, 122.8, 117.1, 43.5, 21.1.

HRMS: *m*/*z* (ESI) calculated for $C_{18}H_{17}BrS$ $(M+IPrAu)^+$: 929.2773, found 929.2761.



5m

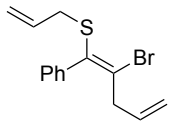
(*Z*)-(2-bromo-1-phenylpenta-1,4-dien-1-yl)(methyl)sulfane (**5m**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (74%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.41-7.31 (m, 3H), 7.21-7.18 (m, 2H), 5.79-5.69 (m, 1H), 5.08 (dq, *J* = 10.1, 1.5 Hz, 1H), 5.02 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.07 (dt, *J* = 6.3, 1.5 Hz, 2H), 1.79 (s, 3H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 138.4, 136.6, 134.4, 129.0, 128.6, 128.1, 119.3, 116.8, 43.1, 16.0.

HRMS: *m*/*z* (ESI) calculated for $C_{12}H_{13}BrS$ $(M+IPrAu)^+$: 853.2460, found 853.2449.



5n

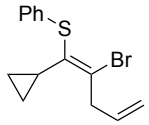
(*Z*)-allyl(2-bromo-1-phenylpenta-1,4-dien-1-yl)sulfane (**5n**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (64%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.30 (m, 3H), 7.24-7.22 (m, 2H), 5.75 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.64 (tt, *J* = 12.2, 4.6 Hz, 1H), 5.09 (dq, *J* = 10.1, 1.4 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.98-4.96 (m, 1H), 4.91 (dq, *J* = 16.9, 1.3 Hz, 1H), 3.09 (dt, *J* = 6.3, 1.3 Hz, 2H), 3.09 (dt, *J* = 6.3, 1.3 Hz, 2H), 2.89 (dt, *J* = 6.7, 1.1 Hz, 2H), 2.89 (dt, *J* = 6.7, 1.1 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 137.4, 136.9, 134.3, 133.6, 129.2, 128.4, 128.2, 121.7, 117.5, 116.9, 43.1, 35.7.

HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{15}BrS$ $(M+IPrAu)^+$: 879.2617, found 879.2602.



5o

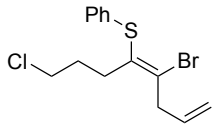
(*Z*)-(2-bromo-1-cyclopropylpenta-1,4-dien-1-yl)(phenyl)sulfane (**5o**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (67%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.29-7.24 (m, 4H), 7.20-7.16 (m, 1H), 5.96-5.86 (m, 1H), 5.25-5.18 (m, 2H), 3.63 (dt, *J* = 6.2, 1.5 Hz, 2H), 1.68-1.61 (m, 1H), 0.68-0.65 (m, 4H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 136.0, 135.3, 133.4, 130.1, 129.0, 128.8, 126.1, 117.1, 43.0, 14.8, 8.1.

HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{15}BrS$ $(M+IPrAu)^+$: 879.2617, found 879.2603.



5p

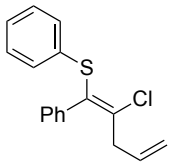
(*Z*)-(5-bromo-1-chloroocta-4,7-dien-4-yl)(phenyl)sulfane (**5p**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (80%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.38-7.28 (m, 5H), 5.87 (ddt, *J* = 17.0, 10.1, 6.2 Hz, 1H), 5.24-5.17 (m, 2H), 3.44 (dt, *J* = 6.2, 1.5 Hz, 2H), 3.37 (t, *J* = 6.2 Hz, 2H), 2.39-2.36 (m, 2H), 1.92-1.85 (m, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 134.8, 133.6, 133.2, 132.1, 129.1, 127.7, 125.4, 117.2, 44.1, 42.8, 31.3, 29.5.

HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}BrClS$ $(M+IPrAu)^+$: 915.2384, found 915.2364.



5q

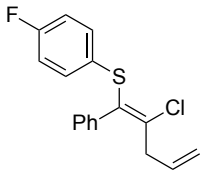
(*Z*)-(2-chloro-1-phenylpenta-1,4-dien-1-yl)(phenyl)sulfane (**5q**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (92%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.18-7.16 (m, 2H), 7.13-7.04 (m, 8H), 5.83 (ddt, *J* = 16.8, 10.3, 6.4 Hz, 1H), 5.14-5.06 (m, 2H), 3.07 (dt, *J* = 6.3, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 136.8, 134.7, 133.7, 133.3, 132.5, 130.7, 129.5, 128.4, 127.8, 127.6, 127.4, 117.3, 41.4.

HRMS: *m/z* (ESI) calculated for $C_{17}H_{15}ClS$ $(M+IPrAu)^+$: 871.3122, found 871.3207.



5r

(*Z*)-(2-chloro-1-phenylpenta-1,4-dien-1-yl)(4-fluorophenyl)sulfane (**5r**)

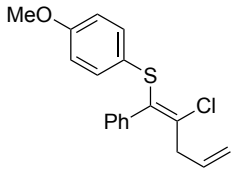
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (90%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.16-7.09 (m, 5H), 7.03-7.01 (m, 2H), 6.77-6.71 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.13-5.04 (m, 2H), 3.03 (dt, *J* = 6.3, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 162.4 (d, *J* = 247Hz), 136.5, 136.1 (d, *J* = 8.3 Hz), 134.9, 133.6, 129.56, 129.51, 127.9, 127.7, 127.5 (d, *J* = 3.4 Hz), 117.3, 115.4 (d, *J* = 21.9 Hz), 41.4.

^{19}F-NMR (376 MHz; $CDCl_3$): δ -113.4 (tt, *J* = 9.0, 6.0 Hz, 1F).

HRMS: *m/z* (ESI) calculated for $C_{17}H_{14}ClFS$ $(M+IPrAu)^+$: 889.3028, found 889.3013.



5s

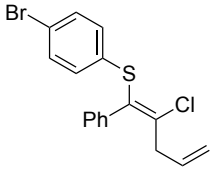
(*Z*)-(2-chloro-1-phenylpenta-1,4-dien-1-yl)(4-methoxyphenyl)sulfane (**5s**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (92%). *Cation: this product is prone to E/Z isomerization over time on column. Fast purification is required.*

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.12-7.08 (m, 5H), 7.02-6.99 (m, 2H), 6.60-6.56 (m, 2H), 5.81 (ddt, *J* 16.9, 10.3, 6.5 Hz, 1H), 5.12-5.04 (m, 2H), 3.68 (s, 3H), 3.01 (dt, *J* = 6.3, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 159.5, 136.7, 136.2, 135.9, 133.8, 129.5, 128.0, 127.8, 127.5, 122.7, 117.1, 113.9, 55.2, 41.4.

HRMS: *m/z* (ESI) calculated for $C_{18}H_{17}ClOS$ $(M+IPrAu)^+$: 901.3228, found 901.3215.



5t

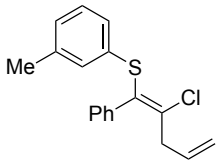
(*Z*)-(4-bromophenyl)(2-chloro-1-phenylpenta-1,4-dien-1-yl)sulfane (**5t**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (91%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.19-7.12 (m, 5H), 7.09-7.06 (m, 2H), 7.02 (t, *J* = 2.2 Hz, 1H), 7.00 (t, *J* = 2.3 Hz, 1H), 5.82 (ddt, *J* = 16.8, 10.3, 6.4 Hz, 1H), 5.12 (dq, *J* = 10.1, 1.3 Hz, 1H), 5.07 (dq, *J* = 17.0, 1.5 Hz, 1H), 3.06 (dt, *J* = 6.3, 1.4 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 136.6, 134.4, 133.9, 133.5, 131.92, 131.79, 131.5, 129.5, 128.0, 127.9, 121.7, 117.4, 41.4.

HRMS: *m*/*z* (ESI) calculated for $C_{17}H_{14}BrClS$ $(M+IPrAu)^+$: 949.2227, found 949.2210.



5u

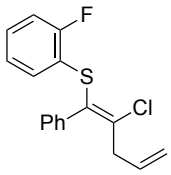
(*Z*)-(2-chloro-1-phenylpenta-1,4-dien-1-yl)(*m*-tolyl)sulfane (**5u**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (87%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.14-7.06 (m, 5H), 6.98-6.92 (m, 3H), 6.87-6.84 (m, 1H), 5.88-5.78 (m, 1H), 5.14-5.05 (m, 2H), 3.07 (dt, *J* = 6.3, 1.5 Hz, 2H), 2.14 (s, 3H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 138.0, 136.9, 134.7, 133.85, 133.75, 132.2, 130.6, 130.1, 129.5, 128.16, 128.14, 127.7, 127.6, 117.2, 41.4, 21.0.

HRMS: *m*/*z* (ESI) calculated for $C_{18}H_{17}ClS$ $(M+IPrAu)^+$: 885.3278, found 885.3170.



5v

(*Z*)-(2-chloro-1-phenylpenta-1,4-dien-1-yl)(2-fluorophenyl)sulfane (**5v**)

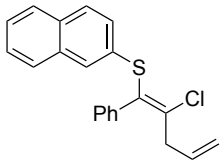
This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (90%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.19 (td, *J* = 7.5, 1.8 Hz, 1H), 7.09-7.03 (m, 6H), 6.85-6.76 (m, 2H), 5.80 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.12-5.04 (m, 2H), 3.02 (dt, *J* = 6.3, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 162.1 (d, *J* = 246.2 Hz), 136.3, 134.0, 133.6, 130.4 (d, *J* = 7.9 Hz), 129.6, 129.3, 127.7, 123.9 (d, *J* = 3.9 Hz), 119.5 (d, *J* = 17.9 Hz), 117.2, 115. 4 (d, *J* = 22.8 Hz), 41.3.

^{19}F-NMR (376 MHz; $CDCl_3$): δ -106.1 (m, 1F).

HRMS: *m*/*z* (ESI) calculated for $C_{17}H_{14}ClFS$ $(M+IPrAu)^+$: 889.3028, found 889.3021.



5w

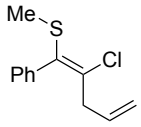
(*Z*)-(2-chloro-1-phenylpenta-1,4-dien-1-yl)(naphthalen-2-yl)sulfane (**5w**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (83%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.70-7.69 (m, 1H), 7.66-7.60 (m, 2H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.40-7.32 (m, 2H), 7.19 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.16-7.12 (m, 2H), 7.08-6.98 (m, 3H), 5.86 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.16-5.08 (m, 2H), 3.11 (dt, *J* = 6.3, 1.5 Hz, 2H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 137.0, 134.4, 133.7, 133.2, 132.2, 131.9, 131.7, 130.2, 130.0, 129.5, 127.90, 127.85, 127.76, 127.55, 127.36, 126.26, 126.17, 117.4, 41.5.

HRMS: *m*/*z* (ESI) calculated for $C_{21}H_{17}ClS$ $(M+IPrAu)^+$: 921.3278, found 921.3271.



5x

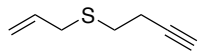
(*Z*)-(2-chloro-1-phenylpenta-1,4-dien-1-yl)(methyl)sulfane (**5x**)

This compound was prepared following general procedure **2.5**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (84%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.41-7.36 (m, 2H), 7.35-7.31 (m, 1H), 7.22-7.19 (m, 2H), 5.81-5.71 (m, 1H), 5.09-4.99 (m, 2H), 2.96 (dt, *J* = 6.3, 1.4 Hz, 2H), 1.80 (s, 3H).

^{13}C NMR (100 MHz; $CDCl_3$): δ 136.2, 135.1, 133.8, 129.2, 128.5, 128.1, 126.9, 116.9, 41.1, 15.4.

HRMS: *m*/*z* (ESI) calculated for $C_{12}H_{13}ClS$ $(M+IPrAu)^+$: 809.2965, found 809.2959.



6a

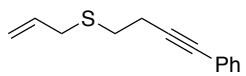
allyl(but-3-yn-1-yl)sulfane (**6a**)

This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as colorless oil (70%). *Cation: this product is volatile. Careful rot-vap and vacuum is required.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (ddt, *J* = 17.0, 9.9, 7.2 Hz, 1H), 5.03-4.99 (m, 2H), 3.07 (d, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.35 (dt, *J* = 7.2, 2.4 Hz, 2H), 1.92 (t, *J* = 2.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.98, 117.14, 82.51, 69.20, 34.61, 29.15, 19.46.

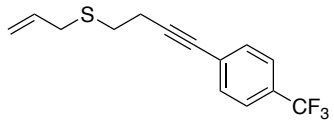
HRMS: *m*/*z* (ESI) calculated for $C_7H_{10}S$ $(M+IPrAu)^+$: 711.3042, found 711.3019.



6b

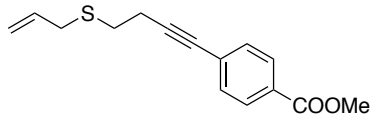
allyl(4-phenylbut-3-yn-1-yl)sulfane (**6b**)

This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as colorless oil (76%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.36 (m, 2H), 7.32-7.20 (m, 3H), 5.80 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.23-5.00 (m, 2H), 3.21 (d, *J* = 7.2 Hz, 2H), 2.76-2.49 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 131.6, 128.2, 127.8, 123.5, 117.3, 88.3, 81.5, 34.9, 29.5, 20.8.
HRMS: *m/z* (ESI) calculated for $C_{13}H_{14}S$ (M+IPrAu)$^+$: 787.3355, found 787.3335.



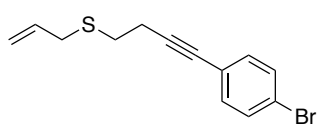
6c

allyl(4-(4-(trifluoromethyl)phenyl)but-3-yn-1-yl)sulfane (**6c**)
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as pale yellow oil (75%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 19.2, 8.4 Hz, 4H), 5.80 (ddt, *J* = 17.1, 10.0, 7.2 Hz, 1H), 5.26-4.75 (m, 2H), 3.20 (d, *J* = 7.2 Hz, 2H), 2.69 (dd, *J* = 5.9, 4.1 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 131.8, 129.5 (q, *J* = 32.5 Hz), 126.3 (q, *J* = 210.3 Hz), 125.1 (q, *J* = 3.5 Hz), 117.3, 91.0, 80.3, 34.8, 29.3, 20.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 3F).
HRMS: *m/z* (ESI) calculated for $C_{14}H_{13}F_3S$ (M+IPrAu)$^+$: 855.3229, found 855.3202.



6d

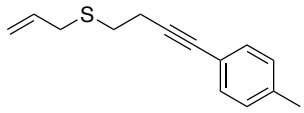
methyl 4-(4-(allylthio)but-1-yn-1-yl)benzoate (**6d**)
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as pale yellow oil (70%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 5.78 (ddt, *J* = 17.0, 9.9, 7.2 Hz, 1H), 5.25-4.96 (m, 2H), 3.87 (s, 3H), 3.19 (d, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 3.9 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 134.1, 131.5, 129.4, 129.1, 128.3, 117.3, 91.6, 80.9, 52.1, 34.8, 29.3, 20.8.
HRMS: *m/z* (ESI) calculated for $C_{15}H_{16}O_2S$ (M+IPrAu)$^+$: 845.3410, found 845.3381.



6e

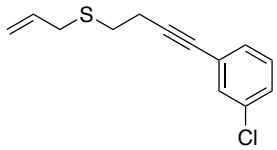
allyl(4-(4-bromophenyl)but-3-yn-1-yl)sulfane (**6e**)

This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as pale yellow oil (62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.79 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.20-4.91 (m, 2H), 3.19 (d, *J* = 7.2 Hz, 2H), 2.80-2.54 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 133.0, 131.4, 122.5, 121.9, 117.3, 89.5, 80.5, 34.8, 29.4, 20.7.
HRMS: *m*/*z* (ESI) calculated for $C_{13}H_{13}BrS$ $(M+IPrAu)^+$: 865.2460, found 865.2431.



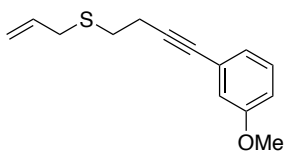
6f

allyl(4-(*p*-tolyl)but-3-yn-1-yl)sulfane (**6f**)
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as pale yellow oil (78%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.80 (ddt, *J* = 17.0, 9.9, 7.2 Hz, 1H), 5.23-4.87 (m, 2H), 3.21 (d, *J* = 7.1 Hz, 2H), 2.67 (dt, *J* = 12.1, 6.1 Hz, 4H), 2.32 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 134.2, 131.4, 128.9, 120.4, 117.2, 87.5, 81.5, 34.8, 29.6, 21.4, 20.8.
HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}S$ $(M+IPrAu)^+$: 801.3512, found 801.3489.



6g

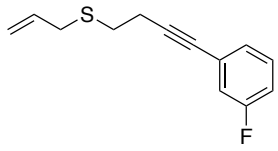
allyl(4-(3-chlorophenyl)but-3-yn-1-yl)sulfane (**6g**)
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as pale yellow oil (69%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.22 (dq, *J* = 24.5, 7.6 Hz, 3H), 5.79 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.13 (dd, *J* = 13.9, 5.2 Hz, 2H), 3.20 (d, *J* = 7.1 Hz, 2H), 2.77-2.55 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 134.0, 131.5, 129.7, 129.4, 128.1, 125.2, 117.3, 89.7, 80.2, 34.8, 29.4, 20.6.
HRMS: *m*/*z* (ESI) calculated for $C_{13}H_{13}ClS$ $(M+IPrAu)^+$: 821.2965, found 821.2940.



6h

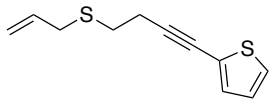
allyl(4-(3-methoxyphenyl)but-3-yn-1-yl)sulfane (**6h**)

This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as pale yellow oil (65%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 7.9 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.83 (dd, *J* = 8.3, 2.1 Hz, 1H), 5.80 (ddt, *J* = 17.0, 9.9, 7.2 Hz, 1H), 5.23-4.99 (m, 2H), 3.77 (s, 3H), 3.21 (d, *J* = 7.1 Hz, 2H), 3.00-2.54 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 134.2, 129.2, 124.5, 124.1, 117.3, 116.4, 114.4, 88.1, 81.4, 55.2, 34.8, 29.5, 20.8.
HRMS: *m/z* (ESI) calculated for $C_{14}H_{16}OS$ $(M+IPrAu)^+$: 817.3461, found 817.3438.



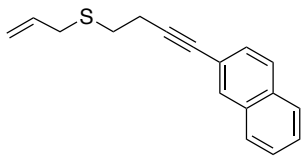
6i

allyl(4-(3-fluorophenyl)but-3-yn-1-yl)sulfane (**6i**)
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as pale yellow oil (57%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (td, *J* = 7.8, 1.6 Hz, 1H), 7.27-7.19 (m, 1H), 7.08-6.90 (m, 2H), 5.80 (ddt, *J* = 17.0, 9.9, 7.2 Hz, 1H), 5.22-4.97 (m, 2H), 3.22 (d, *J* = 7.1 Hz, 2H), 2.72 (s, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 250.5 Hz), 134.2, 133.6, 129.4 (d, *J* = 7.7 Hz), 123.8 (d, *J* = 3.2 Hz), 117.3, 115.3 (d, *J* = 21.0 Hz), 112.0 (d, *J* = 16.1 Hz), 93.6, 74.8, 34.9, 29.4, 21.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -110.8 (m, 1F).
HRMS: *m/z* (ESI) calculated for $C_{13}H_{13}FS$ $(M+IPrAu)^+$: 805.3261, found 805.3239.



6j

2-(4-(allylthio)but-1-yn-1-yl)thiophene (**6j**)
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as pale yellow oil (46%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.00 (m, 2H), 6.92 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.79 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.19-5.03 (m, 2H), 3.20 (d, *J* = 7.2 Hz, 2H), 2.68 (s, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 131.3, 126.8, 126.3, 123.6, 117.3, 92.3, 74.7, 34.9, 29.3, 21.0.
HRMS: *m/z* (ESI) calculated for $C_{11}H_{12}S_2$ $(M+IPrAu)^+$: 793.2919, found 793.2896.

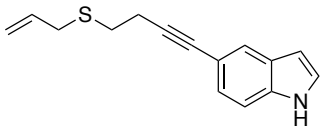


6k

allyl(4-(naphthalen-2-yl)but-3-yn-1-yl)sulfane (**6k**)

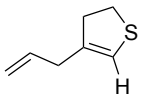
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (40:1 hexane/EtOAc) to yield the desired product as pale yellow oil (74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.87-7.65 (m, 3H), 7.65-7.36 (m, 3H), 5.83 (ddt, *J* = 17.1, 9.9, 7.2 Hz, 1H), 5.26-5.03 (m, 2H), 3.24 (d, *J* = 7.1 Hz, 2H), 2.74 (h, *J* = 6.7 Hz, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 133.0, 132.6, 131.2, 128.6, 127.8, 127.7, 127.6, 126.4, 120.8, 117.3, 88.6, 81.8, 34.9, 29.6, 20.9.
HRMS: *m/z* (ESI) calculated for $C_{17}H_{16}S$ $(M+IPrAu)^+$: 837.3512, found 837.3489.



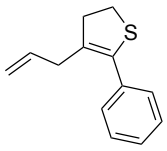
6l

5-(4-(allylthio)but-1-yn-1-yl)-1*H*-indole (**6l**)
This compound was prepared following general procedure **2.6**, and crude mixture was purified using flash chromatography (3:1 hexane/EtOAc) to yield the desired product as brown oil (75%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.72 (s, 1H), 7.23 (ddd, *J* = 18.8, 17.7, 5.3 Hz, 3H), 6.50 (s, 1H), 5.82 (ddt, *J* = 17.0, 9.9, 7.2 Hz, 1H), 5.15 (dd, *J* = 21.4, 5.6 Hz, 2H), 3.24 (d, *J* = 7.2 Hz, 2H), 2.83-2.58 (m, 4H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.3, 127.7, 125.6, 124.9, 124.4, 117.3, 114.6, 110.9, 102.7, 85.5, 82.7, 34.9, 29.8, 20.9.
HRMS: *m/z* (ESI) calculated for $C_{15}H_{15}NS$ $(M+IPrAu)^+$: 826.3464, found 826.3436.



7a

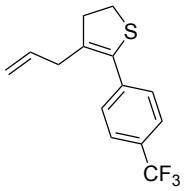
4-allyl-2,3-dihydrothiophene (**7a**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (88%).
Cation: this product is volatile. Careful rot-vap and vacuum is required.
^{1}H NMR (400 MHz; $CDCl_3$): δ 5.86-5.74 (m, 2H), 5.10-5.03 (m, 2H), 3.23 (t, *J* = 8.7 Hz, 2H), 2.85 (d, *J* = 6.7 Hz, 2H), 2.68-2.63 (m, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 135.4, 135.2, 118.5, 116.2, 37.9, 35.9, 32.1.
HRMS: *m/z* (ESI) calculated for $C_7H_{10}S$ $(M+IPrAu)^+$: 711.3042, found 711.3034.



7b

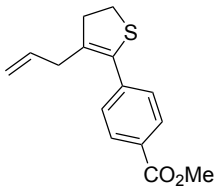
4-allyl-5-phenyl-2,3-dihydrothiophene (**7b**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.37-7.30 (m, 4H), 7.28-7.24 (m, 1H), 5.81 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H), 5.12-5.04 (m, 2H), 3.24(t, *J* = 8.8 Hz, 2H), 2.96-2.90 (m, 4H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 135.8, 135.0, 133.7, 128.7, 128.43, 128.24, 127.7, 115.9, 40.8, 34.3, 30.5.
HRMS: *m*/*z* (ESI) calculated for $C_{13}H_{14}S$ (M+IPrAu)$^+$: 787.3355, found 787.3349.



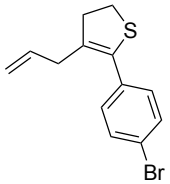
7c

4-allyl-5-(4-(trifluoromethyl)phenyl)-2,3-dihydrothiophene (**7c**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (80%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 5.84-5.74 (m, 1H), 5.11-5.05 (m, 2H), 3.26 (t, *J* = 8.6 Hz, 2H), 2.95 (t, *J* = 8.6 Hz, 2H), 2.88 (d, *J* = 6.1 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 138.7, 135.2, 132.6, 130.6, 129.9 (q, *J* = 32.3 Hz), 128.7, 124.0 (q, *J* = 270.5 Hz), 125.2 (q, *J* = 3.7 Hz), 116.2, 40.9, 34.1, 30.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7 (s, 3F).
HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{13}F_3S$ (M+IPrAu)$^+$: 855.3229, found 855.3220.



7d

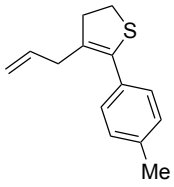
methyl 4-(3-allyl-4,5-dihydrothiophen-2-yl)benzoate (**7d**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (96%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.02-7.99 (m, 2H), 7.44-7.41 (m, 2H), 5.86-5.76 (m, 1H), 5.13-5.07 (m, 2H), 3.91 (s, 3H), 3.27(t, *J* = 8.5 Hz, 2H), 2.97 (t, *J* = 8.5 Hz, 2H), 2.92 (d, *J* = 6.2 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 166.7, 139.7, 135.3, 133.0, 130.6, 129.5, 129.2, 128.4, 116.1, 52.1, 41.0, 34.2, 30.6.
HRMS: *m*/*z* (ESI) calculated for $C_{15}H_{16}O_2S$ (M+IPrAu)$^+$: 845.3410, found 845.3400.



7e

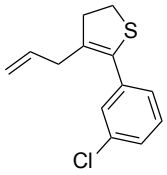
4-allyl-5-(4-bromophenyl)-2,3-dihydrothiophene (**7e**)

This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (90%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.45-7.42 (m, 2H), 7.19 (d, *J* = 2.4 Hz, 2H), 5.82-5.73 (m, 1H), 5.09-5.04 (m, 2H), 3.22 (t, *J* = 8.5 Hz, 2H), 2.91 (t, *J* = 8.6 Hz, 2H), 2.86 (d, *J* = 6.1 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 135.4, 133.9, 132.7, 131.4, 130.1, 129.5, 121.6, 116.0, 40.9, 34.2, 30.5.
HRMS: *m*/*z* (ESI) calculated for $C_{13}H_{13}BrS$ (M+IPrAu)$^{+}$: 856.2460, found 856.2450.



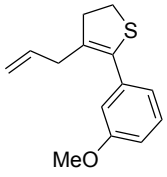
7f

4-allyl-5-(*p*-tolyl)-2,3-dihydrothiophene (**7f**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (91%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.23 (m, 2H), 7.14-7.12 (m, 2H), 5.80 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1H), 5.11-5.03 (m, 2H), 3.22 (t, *J* = 8.6 Hz, 2H), 2.94-2.90 (m, 4H), 2.33 (s, 3H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 137.5, 135.8, 133.6, 132.0, 128.9, 128.3, 128.1, 115.8, 40.8, 34.3, 30.4, 21.2.
HRMS: *m*/*z* (ESI) calculated for $C_{14}H_{16}S$ (M+IPrAu)$^{+}$: 801.3512, found 801.3502.



7g

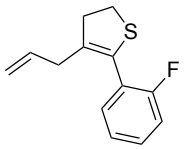
4-allyl-5-(3-chlorophenyl)-2,3-dihydrothiophene (**7g**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (90%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.34 (t, *J* = 2.0 Hz, 1H), 7.25-7.20 (m, 3H), 5.84-5.74 (m, 1H), 5.11-5.05 (m, 2H), 3.23 (t, *J* = 8.5 Hz, 2H), 2.95-2.88 (m, 4H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 136.8, 135.3, 134.1, 132.5, 129.9, 129.5, 128.5, 127.8, 126.6, 116.1, 40.8, 34.2, 30.6.
HRMS: *m*/*z* (ESI) calculated for $C_{13}H_{13}ClS$ (M+IPrAu)$^{+}$: 821.2965, found 821.2955.



7h

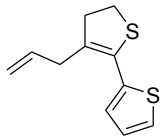
4-allyl-5-(3-methoxyphenyl)-2,3-dihydrothiophene (**7h**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (95%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.24 (t, *J* = 7.9 Hz, 1H), 6.96-6.91 (m, 2H), 6.82 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.12-5.05 (m, 2H), 3.79 (s, 3H), 3.24 (t, *J* = 8.6 Hz, 2H), 2.96-2.92 (m, 4H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 159.4, 136.3, 135.8, 133.6, 129.3, 128.8, 120.9, 115.9, 113.73, 113.62, 55.2, 40.8, 34.3, 30.5.
HRMS: *m/z* (ESI) calculated for $C_{14}H_{16}OS$ $(M+IPrAu)^+$: 817.3461, found 817.3450.



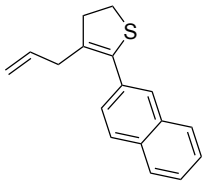
7i

4-allyl-5-(2-fluorophenyl)-2,3-dihydrothiophene (**7i**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (73%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.32-7.23 (m, 2H), 7.11-7.03 (m, 2H), 5.73 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05-4.98 (m, 2H), 3.28 (t, *J* = 8.6 Hz, 2H), 2.91 (t, *J* = 8.5 Hz, 2H), 2.75 (d, *J* = 6.6 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 159.6 (d, J = 246.8 Hz), 135.4, 132.1, 131.3 (d, *J* = 3.2 Hz), 129.6, 126.7 (d, *J* = 8.1 Hz), 123.9 (d, *J* = 3.5 Hz), 122.6 (d, *J* = 15.8 Hz), 116.08, 115.8 (d, *J* = 22.2 Hz), 39.8, 34.6, 31.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8 (dt, *J* = 9.0, 6.6 Hz, 1F).
HRMS: *m/z* (ESI) calculated for $C_{13}H_{13}FS$ $(M+IPrAu)^+$: 805.3261, found 805.3240.



7j

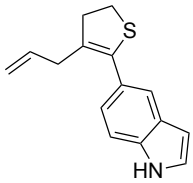
3-allyl-4,5-dihydro-2,2'-bithiophene (**7j**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (99%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.26-7.24 (m, 1H), 7.07 (d, *J* = 3.6 Hz, 1H), 6.99 (ddd, *J* = 3.1, 2.9, 2.2 Hz, 1H), 5.87-5.77 (m, 1H), 5.13-5.05 (m, 2H), 3.22 (t, *J* = 8.4 Hz, 2H), 3.14-3.13 (d, J = 6.0 Hz, 2H), 2.95 (t, *J* = 8.4 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 136.3, 134.8, 129.7, 126.9, 126.8, 126.6, 125.4, 116.1, 41.5, 34.7, 30.5.
HRMS: *m/z* (ESI) calculated for $C_{11}H_{12}S_2$ $(M+IPrAu)^+$: 793.2919, found 793.2916.



7k

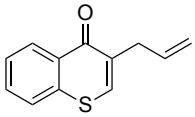
4-allyl-5-(naphthalen-2-yl)-2,3-dihydrothiophene (**7k**)

This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (91%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.83-7.78 (m, 4H), 7.49-7.43 (m, 3H), 5.84 (ddt, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.14-5.07 (m, 2H), 3.27 (t, *J* = 8.6 Hz, 2H), 2.99-2.95 (m, 4H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 135.8, 133.8, 133.2, 132.8, 132.5, 129.3, 128.1, 127.9, 127.6, 127.5, 126.5, 126.21, 126.13, 116.0, 40.9, 34.4, 30.7.
HRMS: *m/z* (ESI) calculated for $C_{17}H_{16}S$ (M+IPrAu)$^+$: 837.3512, found 837.3504.



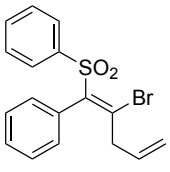
7l

5-(3-allyl-4,5-dihydrothiophen-2-yl)-1*H*-indole (**7l**)
This compound was prepared following general procedure **2.7**, and crude mixture was purified using flash chromatography (3:1 hexane/EtOAc) to yield the desired product as yellow solid (62%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.12 (br, 1H), 7.64 (t, *J* = 0.8 Hz, 1H), 7.29-7.27 (m, 1H), 7.20 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.14 (dd, *J* = 3.0, 2.6 Hz, 1H), 6.51 (ddd, *J* = 3.1, 2.1, 1.0 Hz, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.12-5.04 (m, 2H), 3.24 (t, *J* = 8.5 Hz, 2H), 2.95 (m, 4H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 136.2, 135.3, 134.6, 127.7, 127.2, 126.5, 124.8, 122.9, 120.8, 115.7, 110.8, 102.8, 40.7, 34.4, 30.4.
HRMS: *m/z* (ESI) calculated for $C_{15}H_{15}NS$ (M+IPrAu)$^+$: 826.3464, found 826.3444.



8

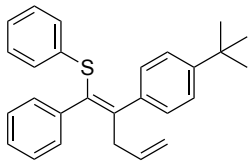
3-allyl-4*H*-thiochromen-4-one (**8**)
This compound was prepared following general procedure **2.8**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (85%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.57-8.55 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.63 (t, *J* = 1.0 Hz, 1H), 7.55 (m, 2H), 7.50 (m, 1H), 6.01-5.91 (m, 1H), 5.21-5.16 (m, 2H), 3.42 (dq, *J* = 6.8, 1.2 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 178.9, 137.2, 135.2, 134.9, 133.4, 131.5, 130.9, 128.9, 127.4, 126.4, 117.6, 35.7.
HRMS: *m/z* (ESI) calculated for $C_{12}H_{10}OS$ (M+IPrAu)$^+$: 787.2991, found 787.2973.



9

(*Z*)-(2-bromo-1-(phenylsulfonyl)penta-1,4-dien-1-yl)benzene (**9**)

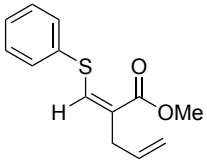
This compound was prepared following general procedure **2.9**, and crude mixture was purified using flash chromatography (10:1 hexane/EtOAc) to yield the desired product as white solid (86%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.83-7.80 (m, 2H), 7.59 (ddt, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.48-7.44 (m, 2H), 7.39-7.31 (m, 3H), 7.11-7.09 (m, 2H), 5.67 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.10 (dq, *J* = 10.1, 1.3 Hz, 1H), 4.95 (dq, *J* = 17.0, 1.5 Hz, 1H), 3.08 (dt, *J* = 6.5, 1.5 Hz, 2H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 143.8, 140.0, 135.0, 133.5, 133.42, 132.1, 130.1, 129.2, 128.7, 128.6, 128.5, 118.7, 46.0
HRMS: *m*/*z* (ESI) calculated for $C_{17}H_{15}BrO_2S$ $(M+H)^+$: 365.0029, found 365.0027.



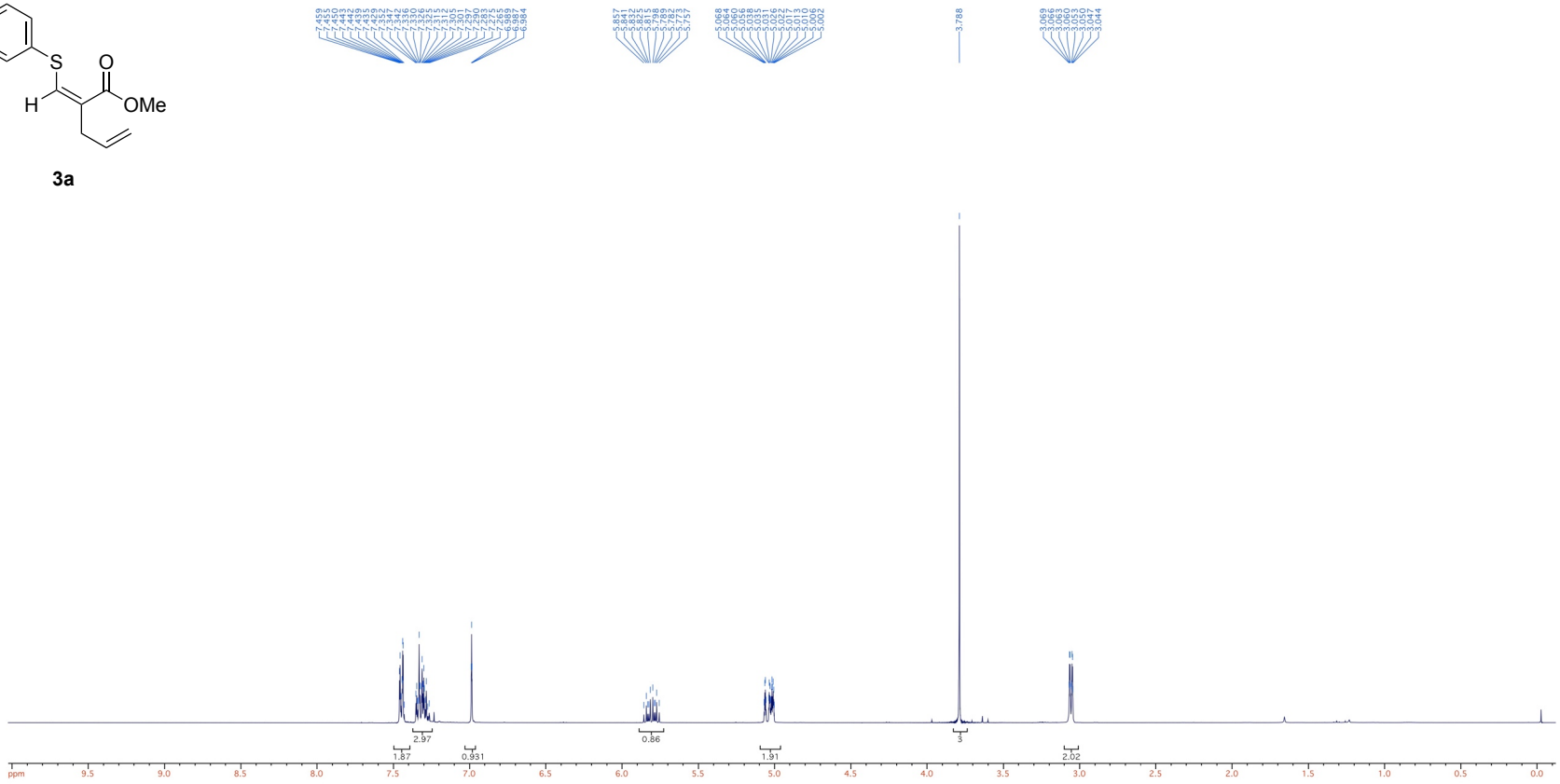
10

(*Z*)-(2-(4-(*tert*-butyl)phenyl)-1-phenylpenta-1,4-dien-1-yl)(phenyl)sulfane (**10**)
This compound was prepared following general procedure **2.10**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as yellow solid (98%).
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35 (ddt, *J* = 7.5, 5.6, 1.8 Hz, 4H), 7.31-7.28 (m, 2H), 7.20-7.16 (m, 2H), 7.12-7.08 (m, 3H), 7.05-6.97 (m, 3H), 5.68 (dd, *J* = 16.9, 10.3 Hz, 1H), 4.94-4.88 (m, 2H), 3.15 (dt, *J* = 6.5, 1.4 Hz, 2H), 1.33 (s, 10H).
^{13}C NMR (100 MHz; $CDCl_3$): δ 149.8, 143.5, 139.4, 138.8, 135.6, 135.4, 132.7, 130.9, 129.8, 128.3, 128.2, 127.6, 127.1, 126.0, 124.9, 116.0, 41.2, 34.6, 31.4
HRMS: *m*/*z* (ESI) calculated for $C_{27}H_{28}S$ $(M+IPrAu)^+$: 969.4459, found 969.4457.

VII. NMR Spectra


S
O
H
OMe

3a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7.330
7.325
7.315
7.312
7.305
7.301
7.297
7.290
7.283
7.275
7.265
7.089
7.087
6.984
5.857
5.841
5.832
5.825
5.798
5.789
5.782
5.773
5.757
5.068
5.064
5.060
5.056
5.038
5.035
5.031
5.026
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5.017
5.013
5.010
5.009
5.002
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3.069
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3.044
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1.91
3
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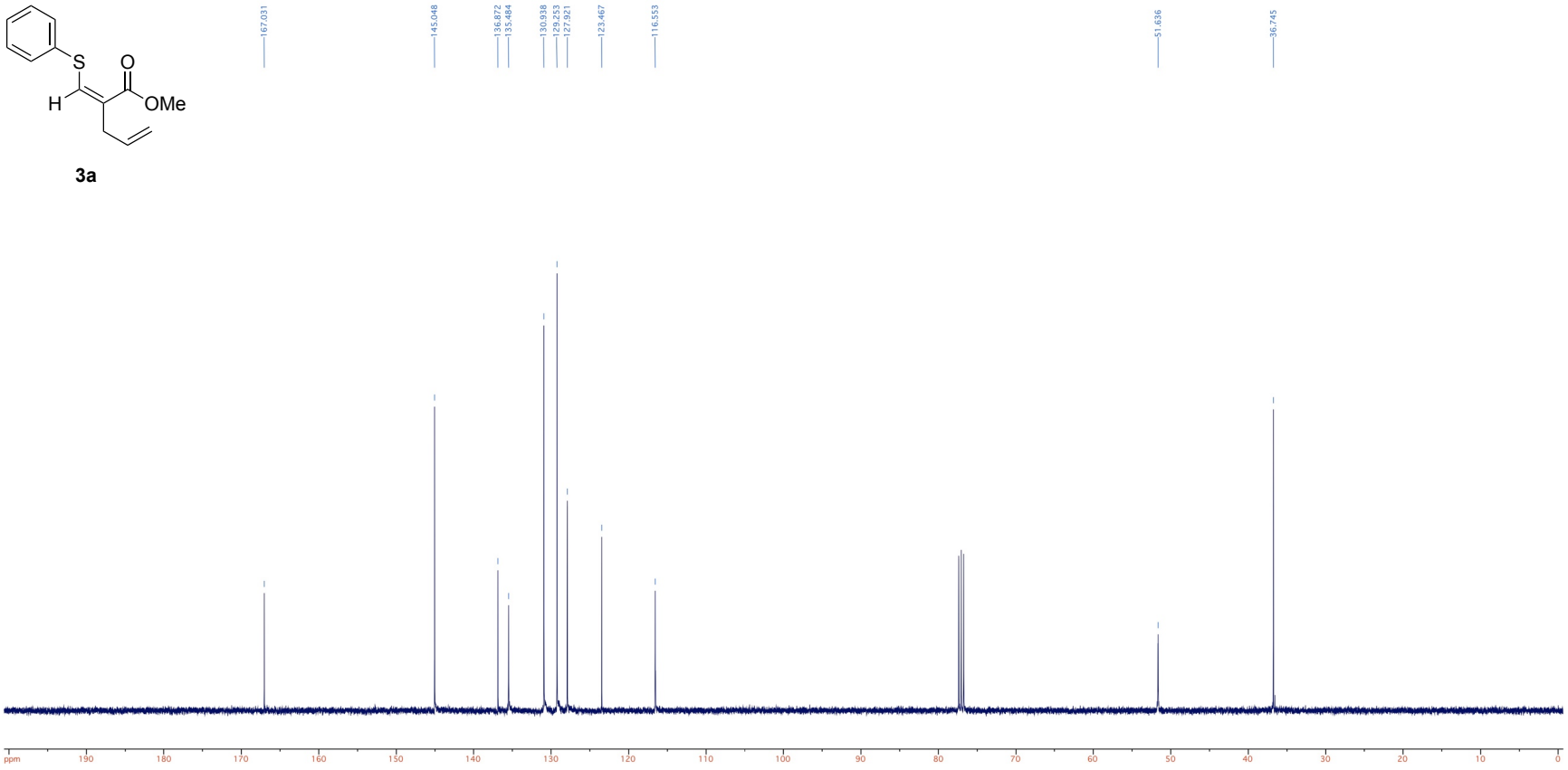
0.0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50
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10
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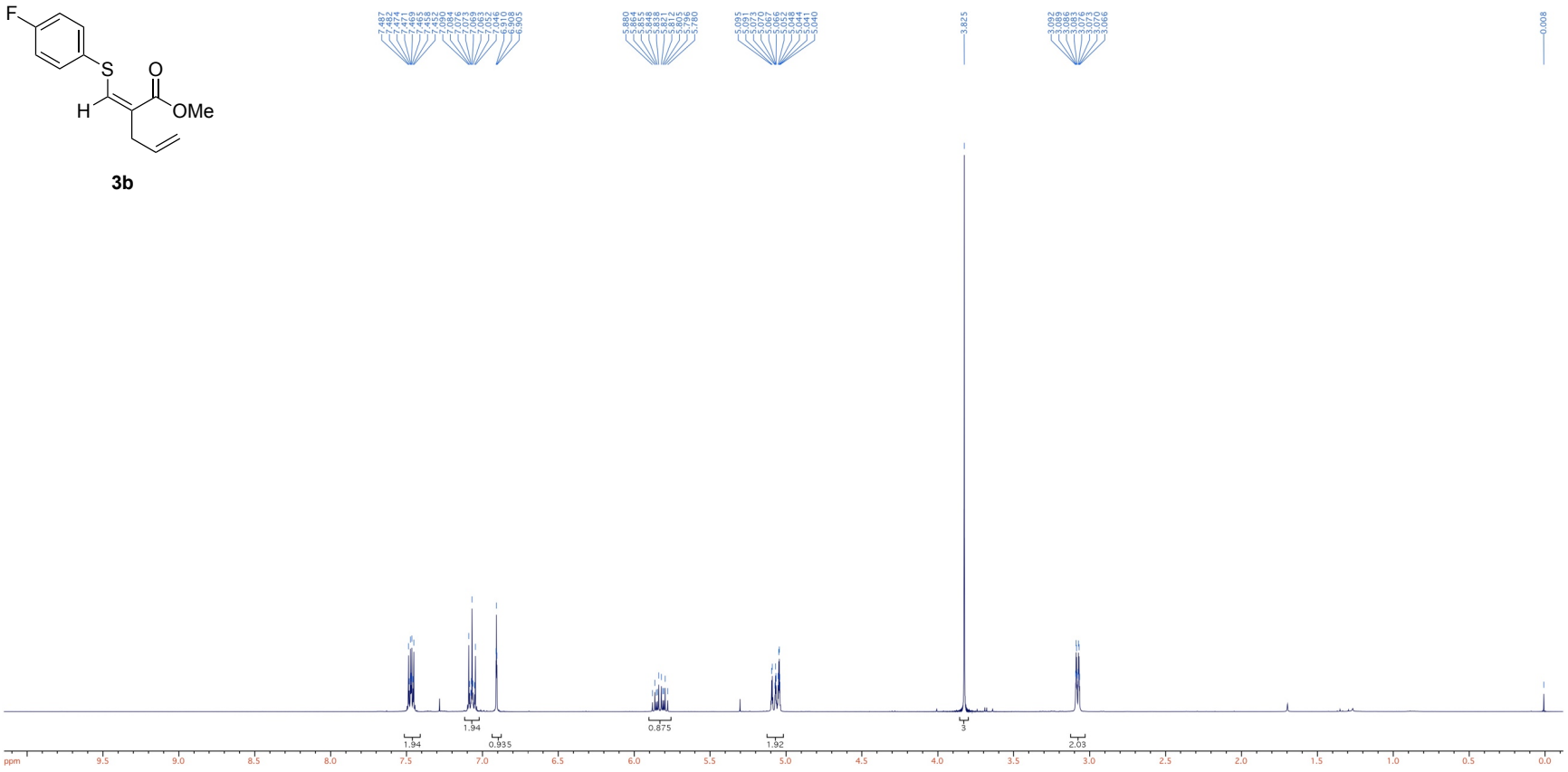
3a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7.084
7.073
7.069
7.063
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5.855
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5.812
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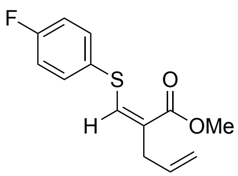
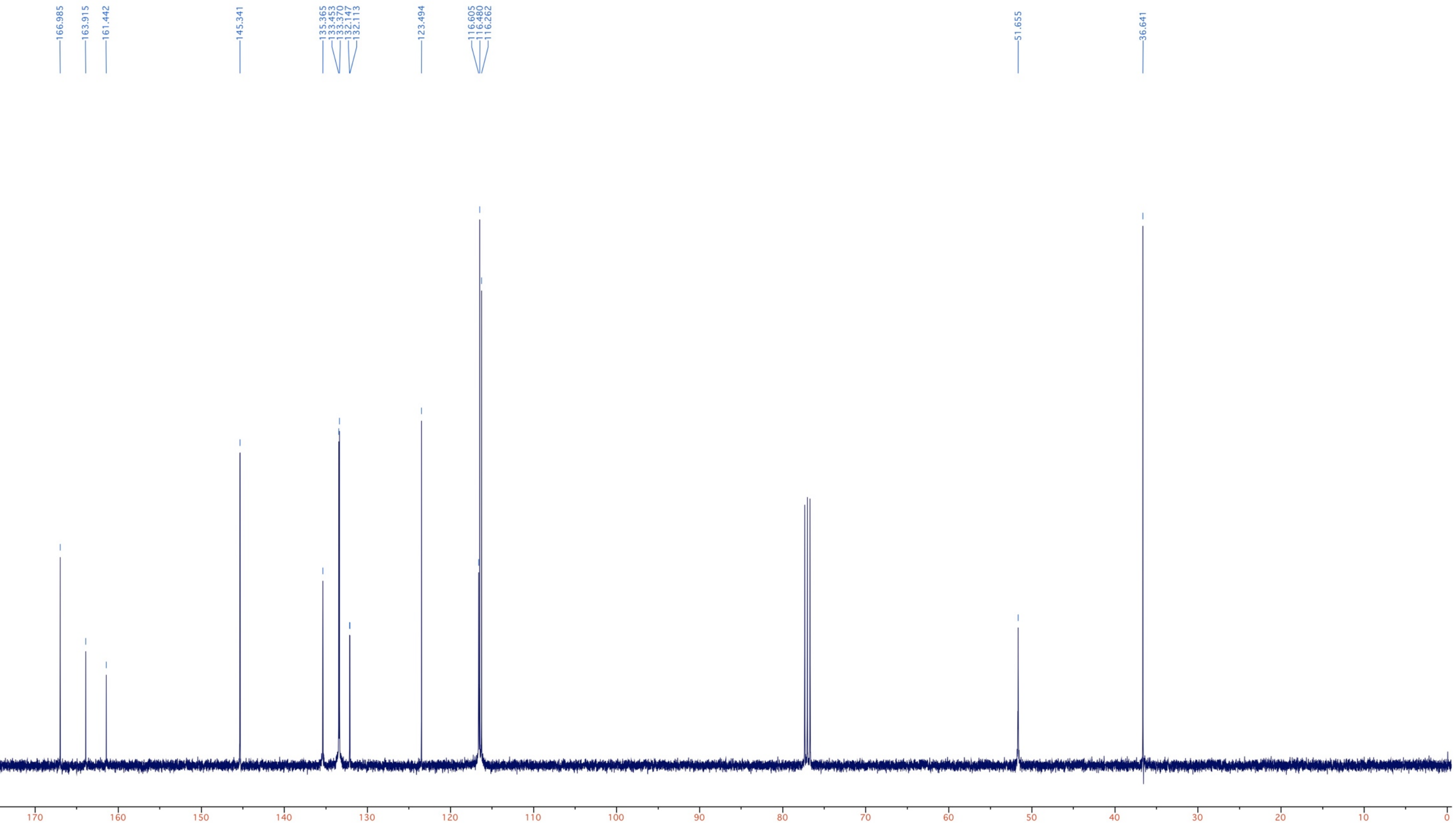
3b


F
S
O
H
OMe

3b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10
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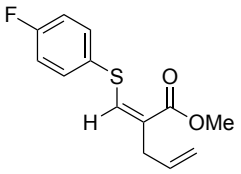
F
S
O
H
OMe

3b


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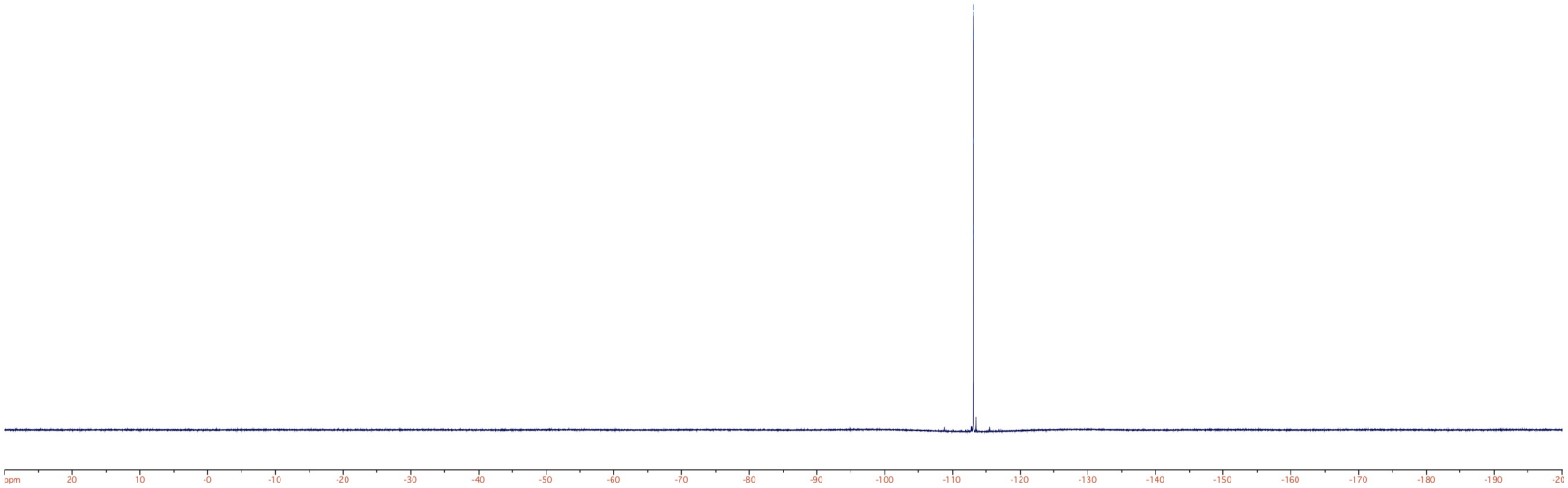
-113.098
-113.110
-113.121
-113.135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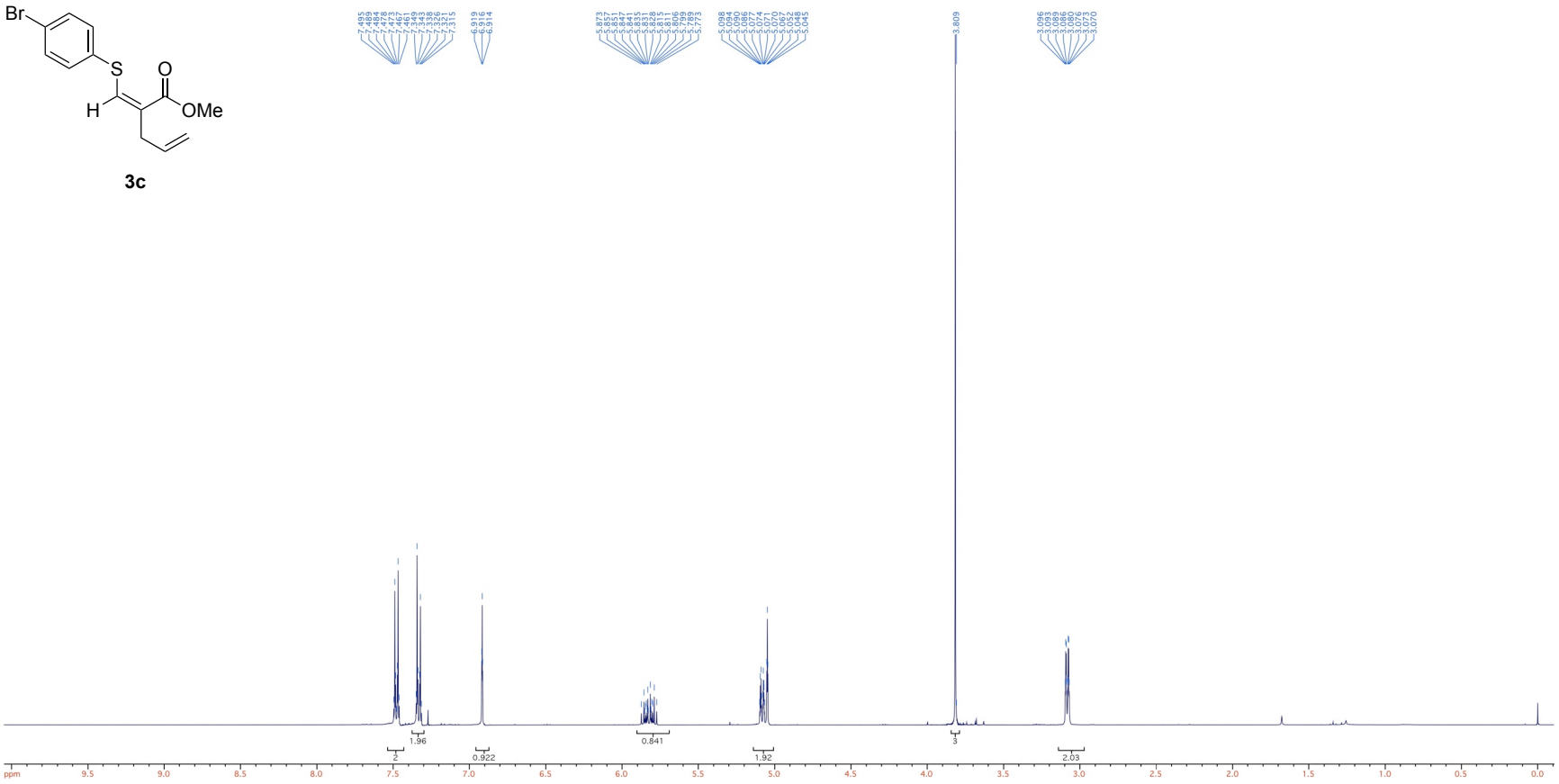
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O
H
OMe
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6.914
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5.815
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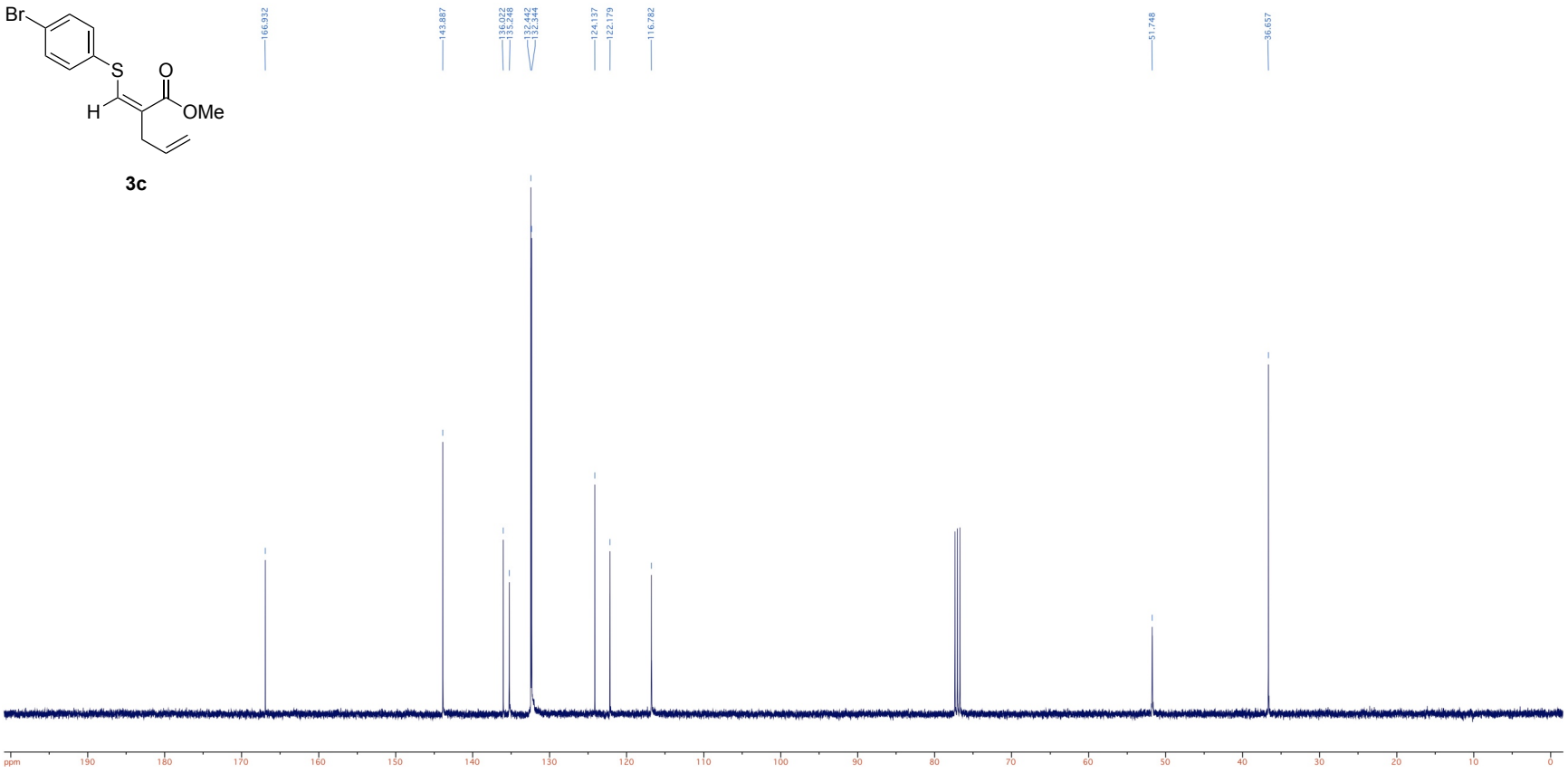
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H
OMe
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20
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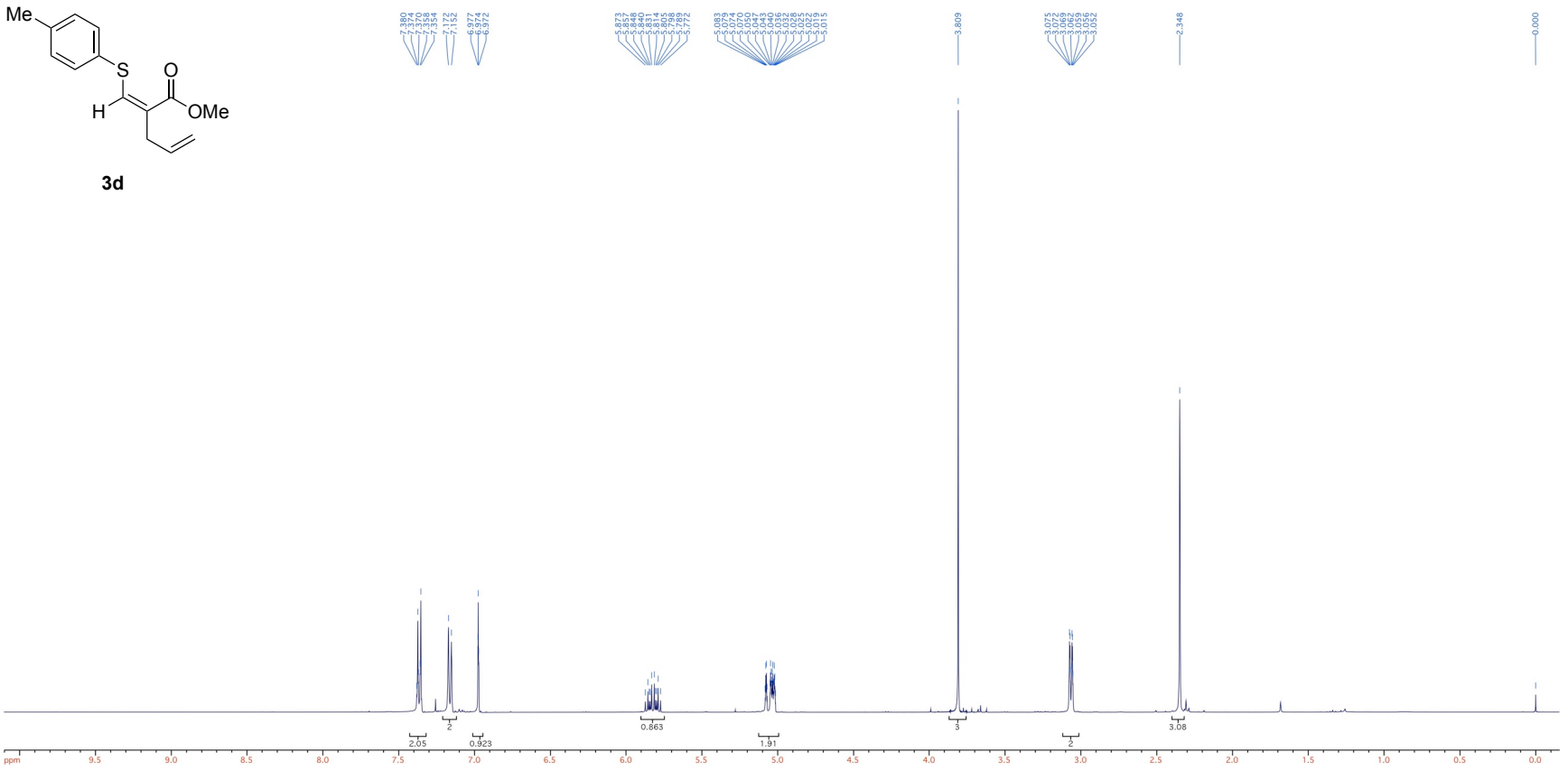
3c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O
H
OMe
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6.972
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5.789
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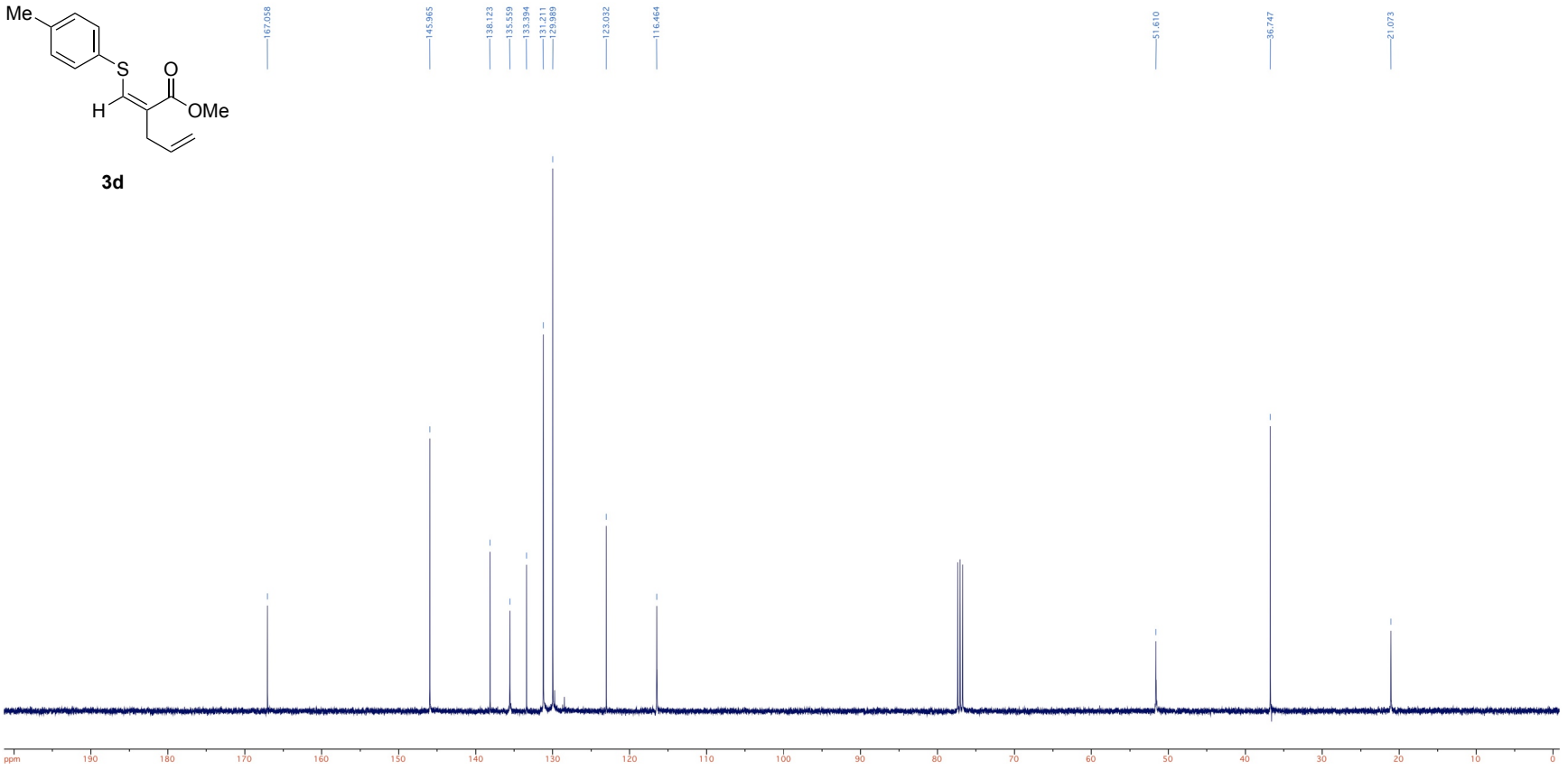
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20
10
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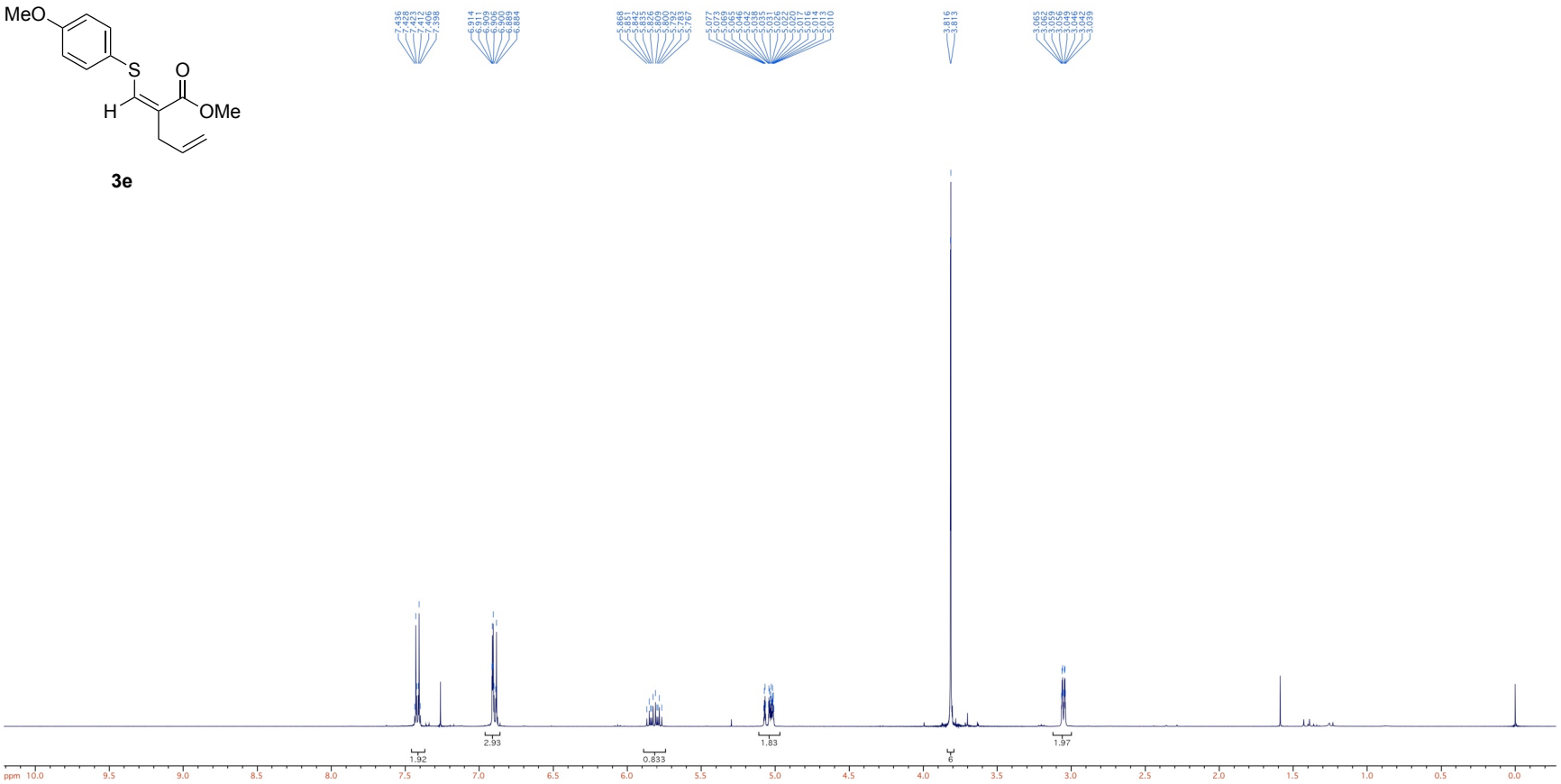
3d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O
H
OMe
3e
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6.908
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6.900
6.898
6.884
5.868
5.851
5.842
5.835
5.826
5.820
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5.783
5.767
5.077
5.073
5.069
5.065
5.046
5.042
5.038
5.035
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5.026
5.022
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5.017
5.016
5.014
5.011
5.010
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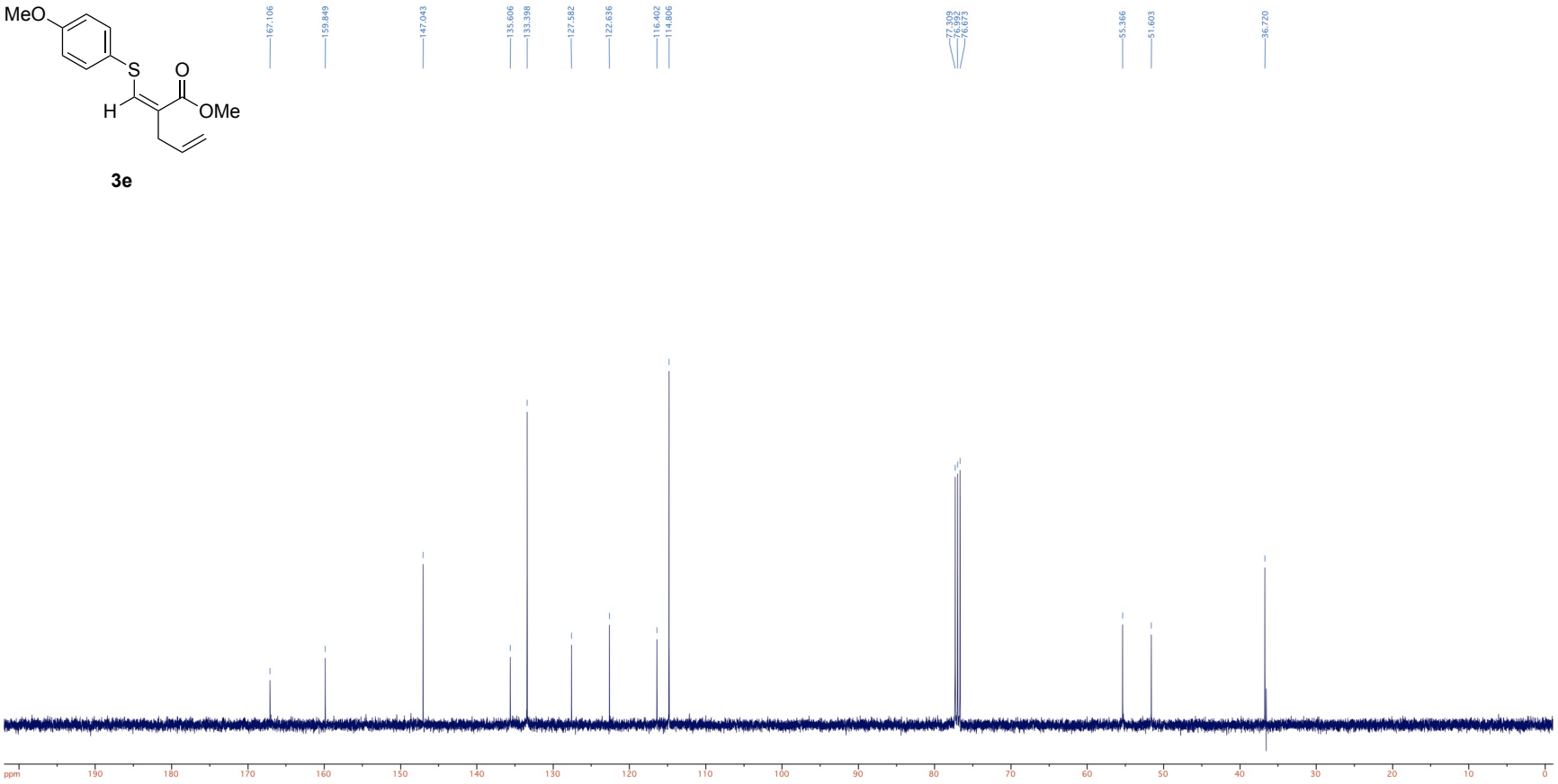
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H
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76.992
76.673
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160
150
140
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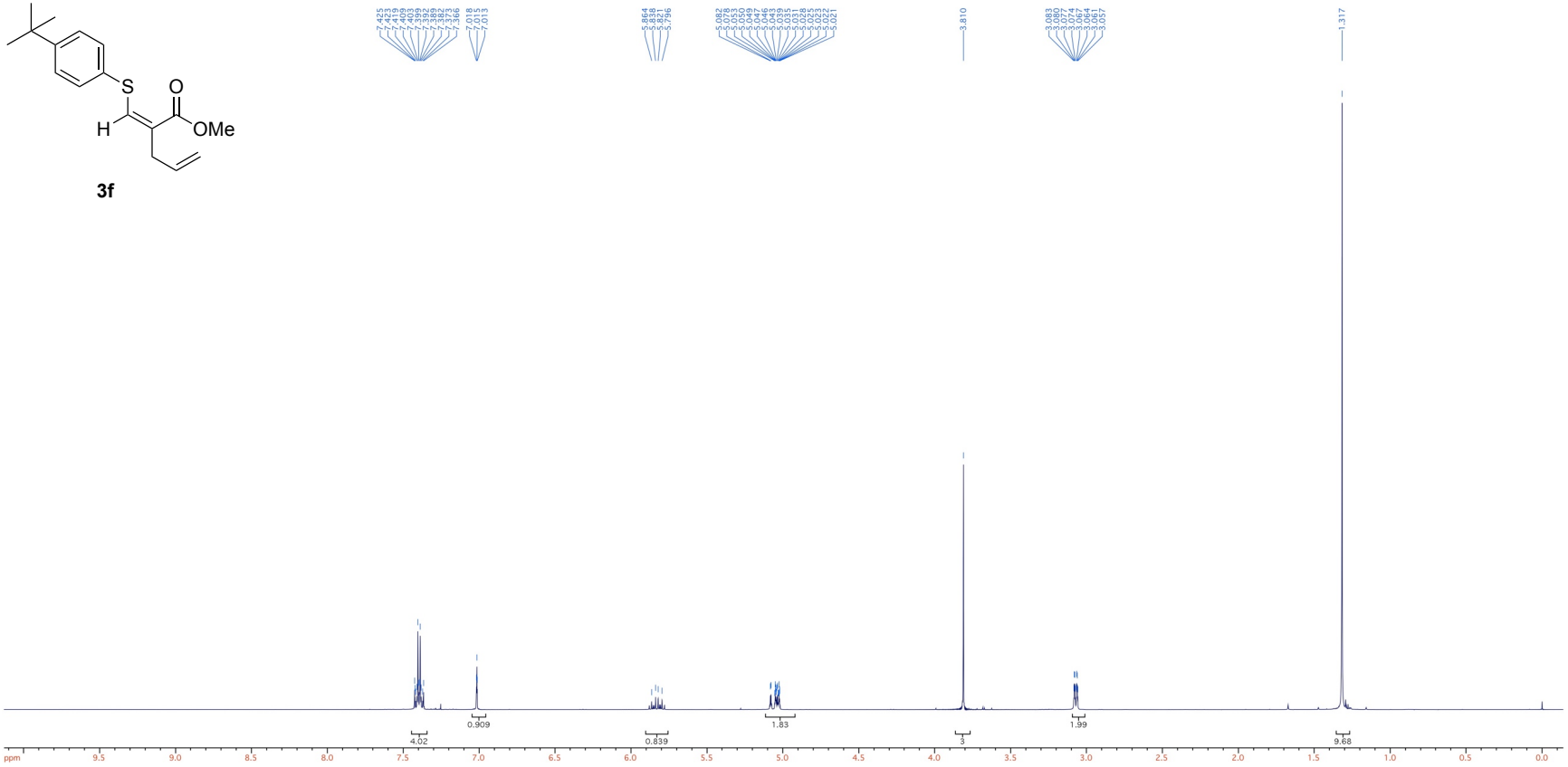
80
70
60
50
40
30
20
10
0

3e

S
O
H
OMe

3f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9.68
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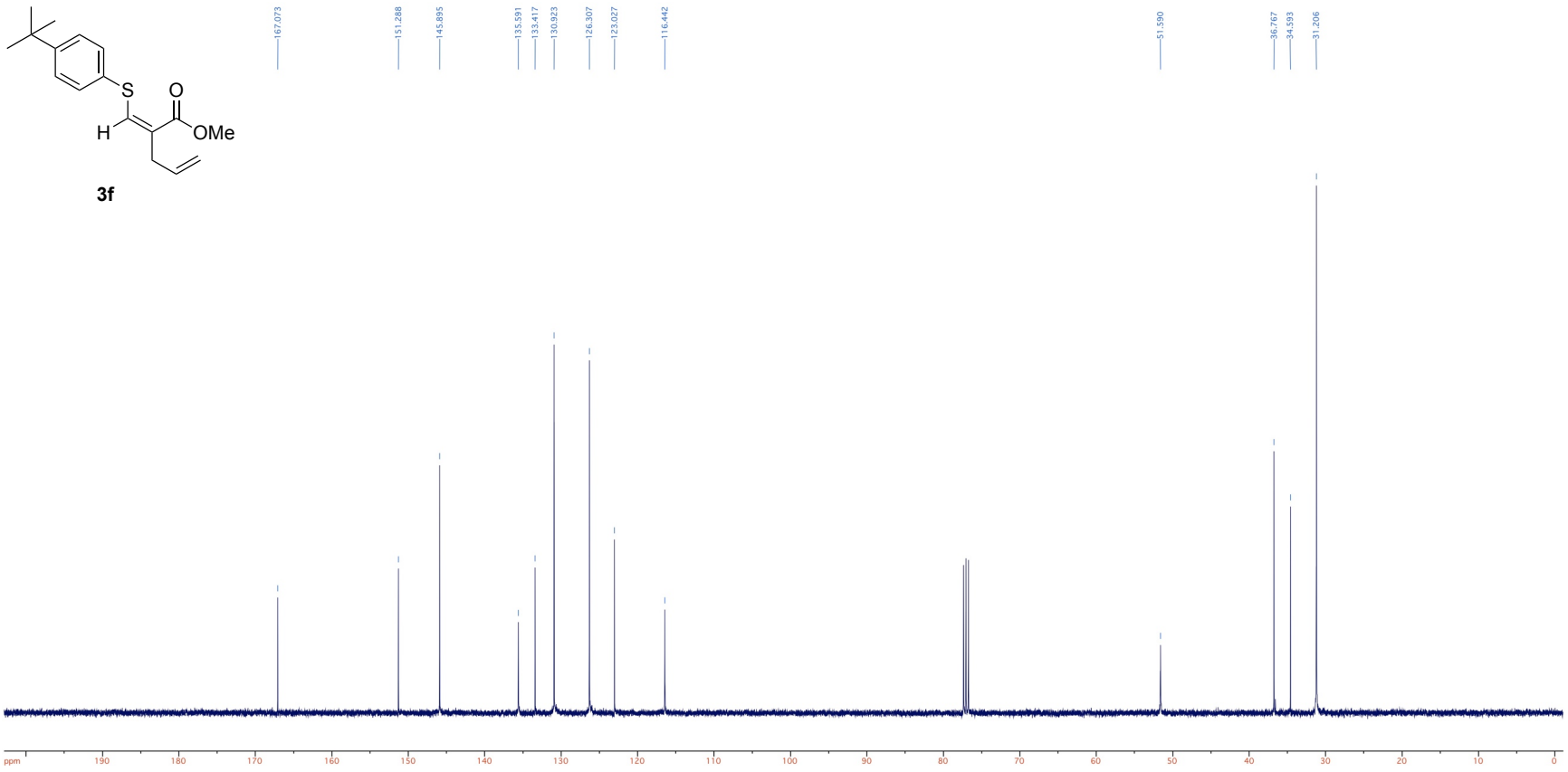
S
O
H
OMe

3f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31.206
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150
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110
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70
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30
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10
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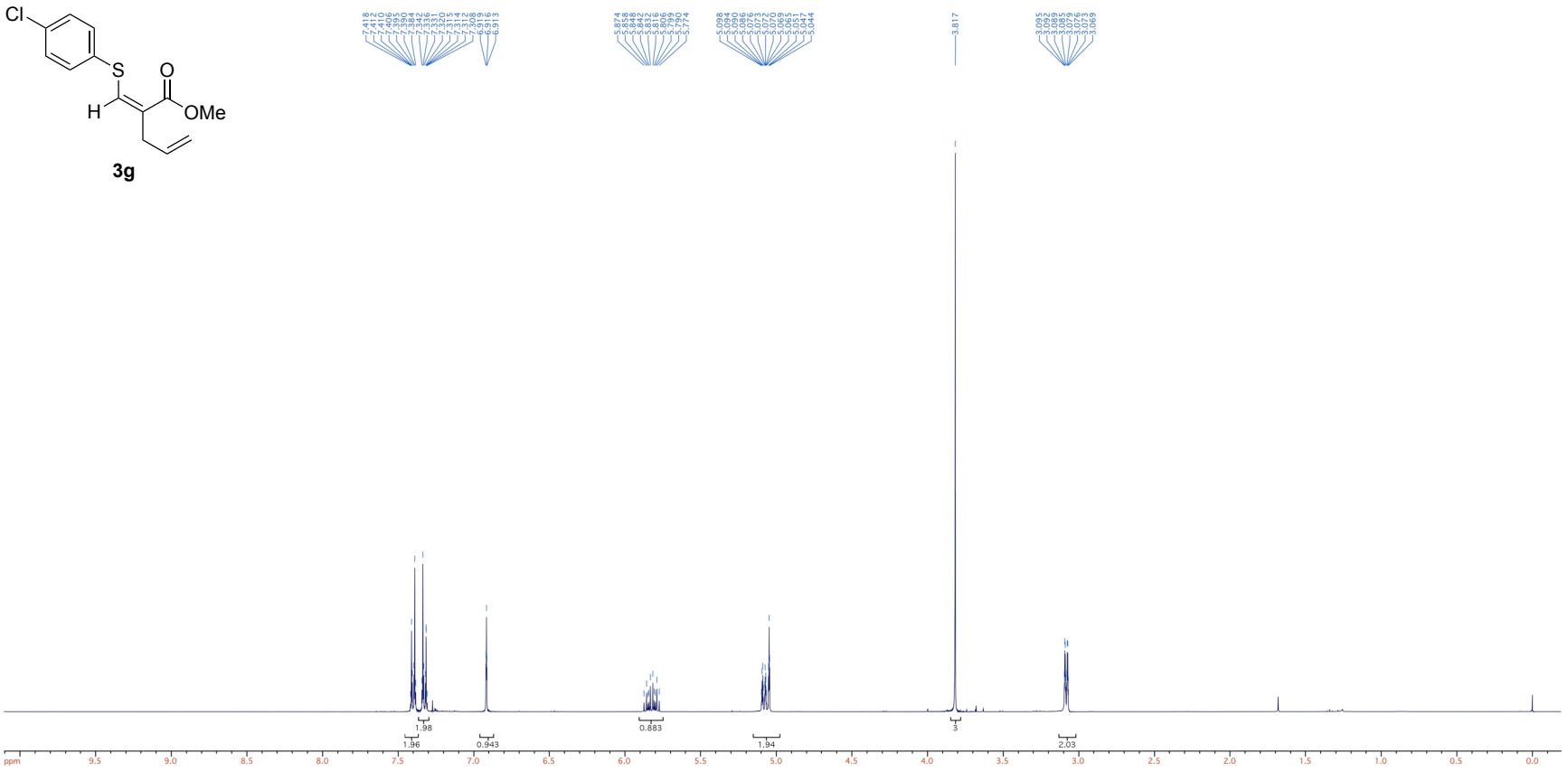
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O
H
OMe
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6.913
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5.072
5.070
5.069
5.065
5.051
5.047
5.044
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3.092
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7.5
7.0
6.5
6.0
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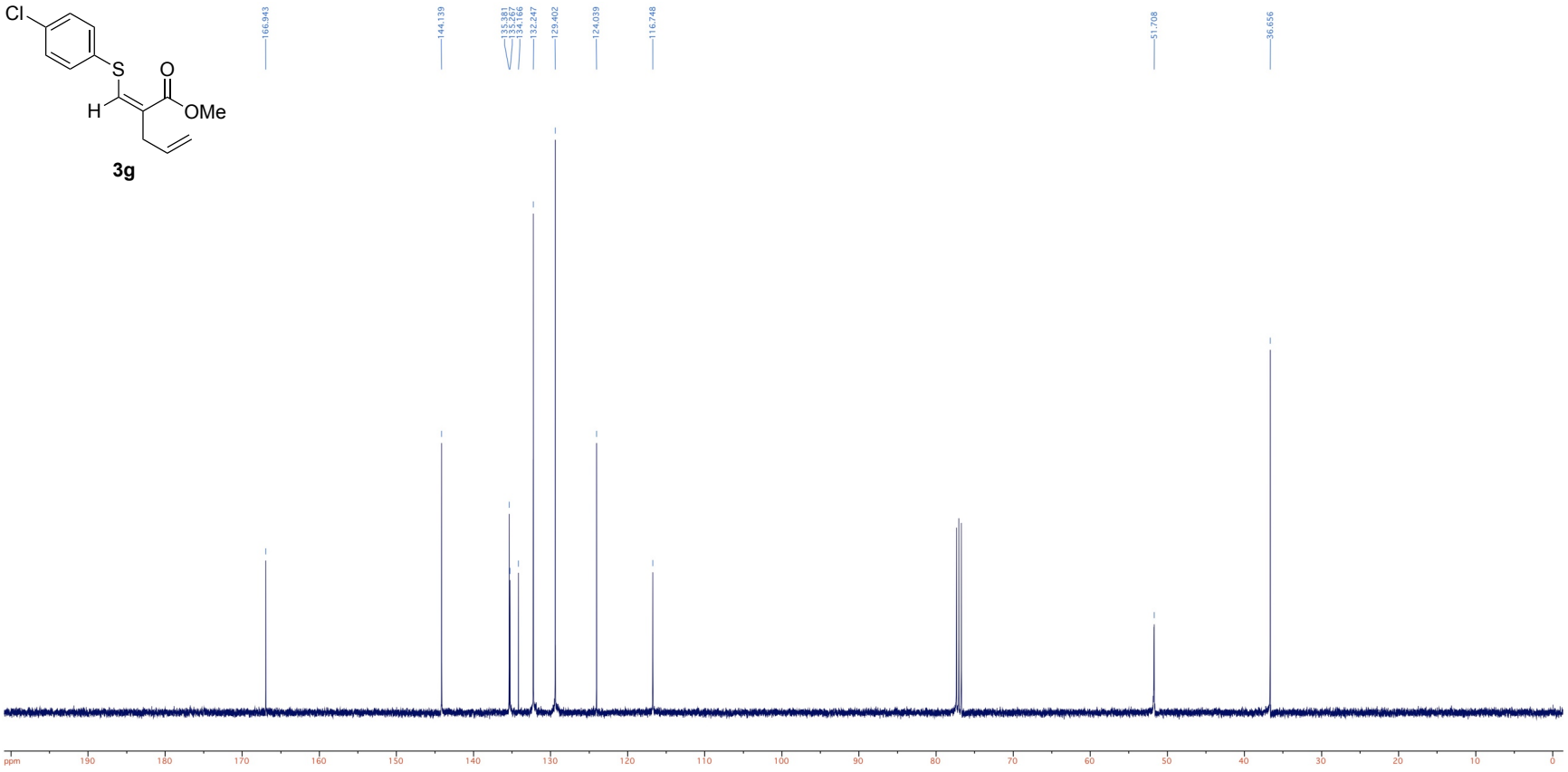
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H
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OMe
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120
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80
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60
50
40
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20
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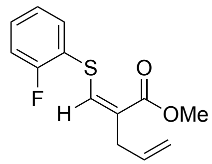
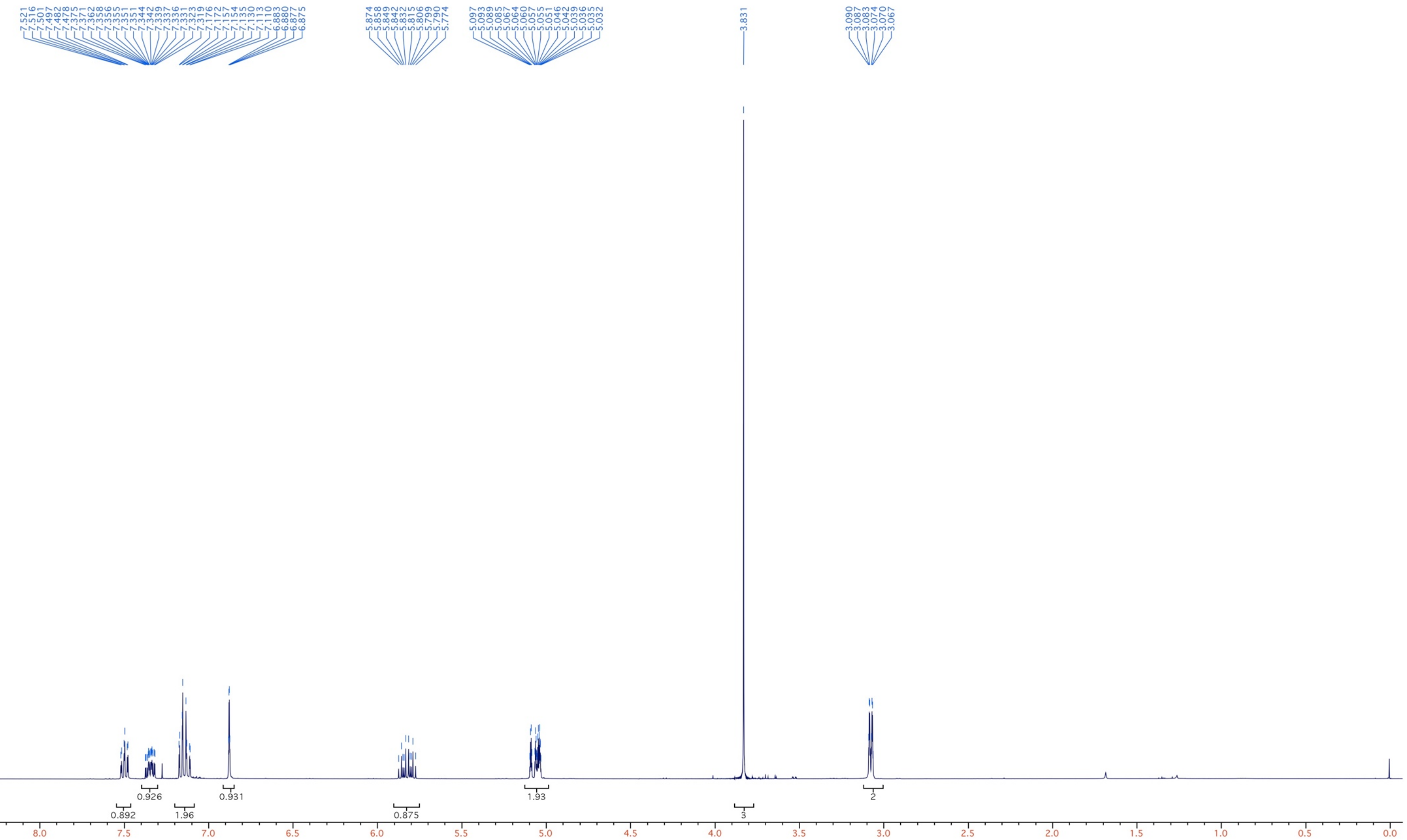
0

3g


S
O
F
H
OMe

3h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0.931
0.875
1.93
3
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ppm
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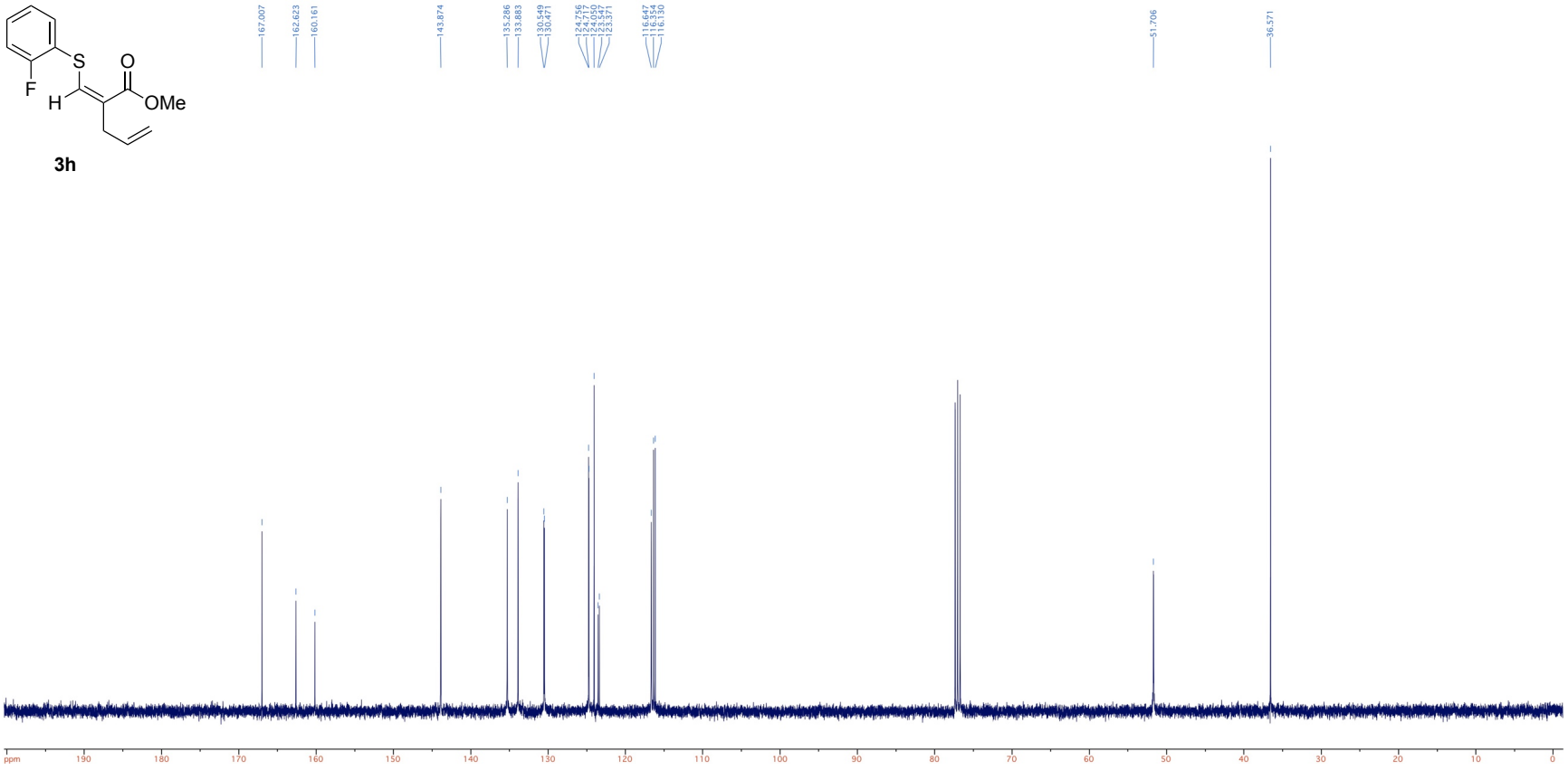
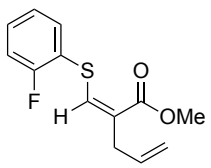
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

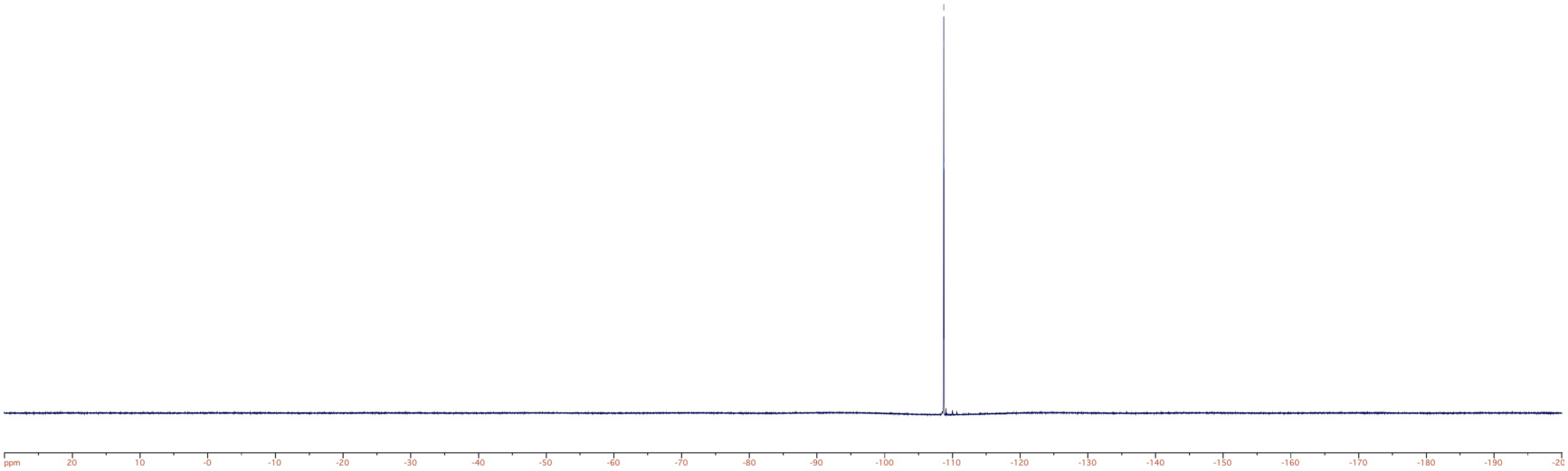

F
S
H
O
OMe
167.007
162.623
160.161
143.874
135.286
133.883
130.549
130.471
124.716
124.717
124.050
124.047
123.371
116.647
116.544
116.130
51.706
36.571
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3h


S
O
F
H
OMe

3h


-108.692
-108.714
-108.729
-108.749


ppm
20
10
-0
-10
-20
-30
-40
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-60
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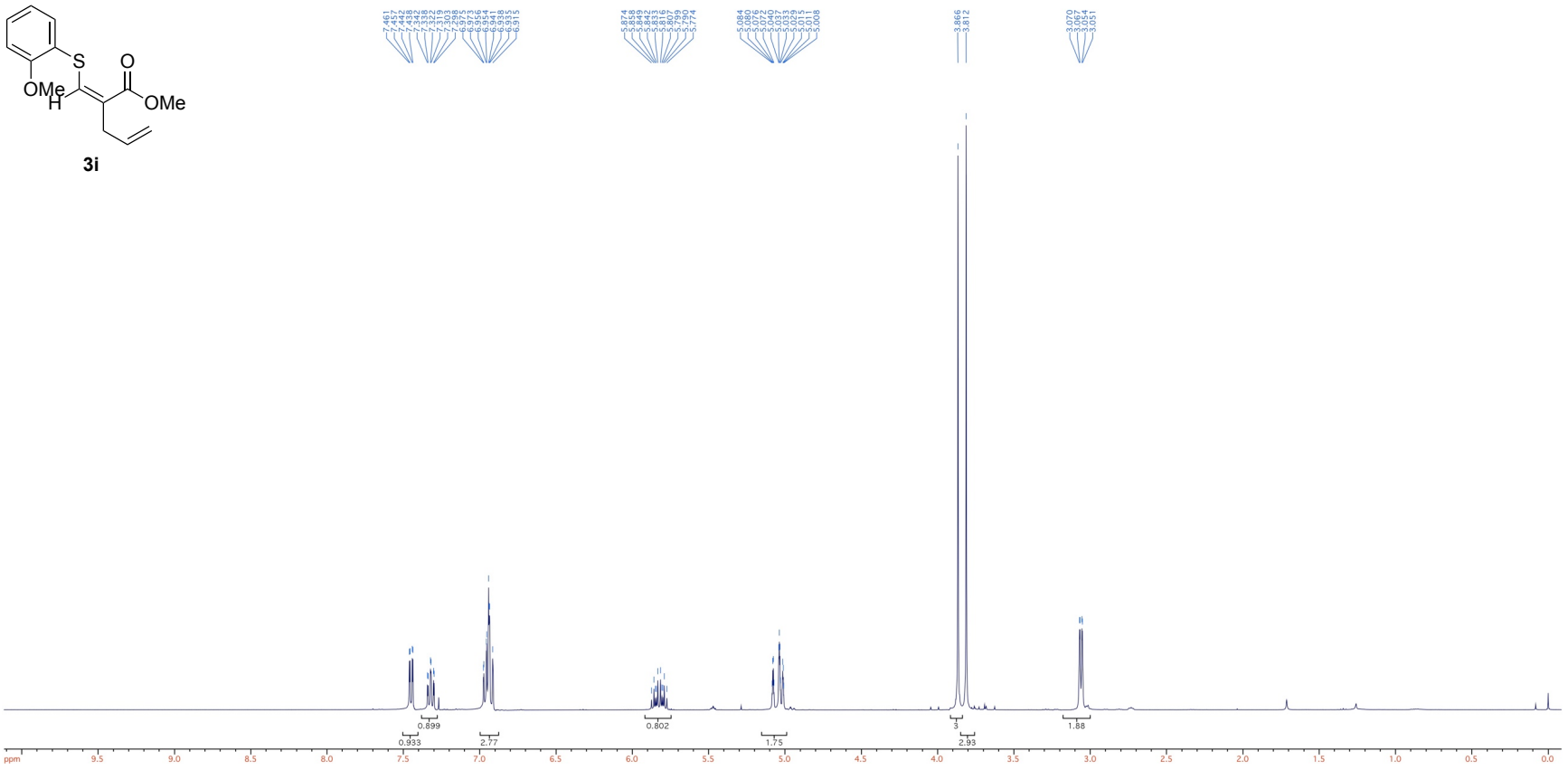
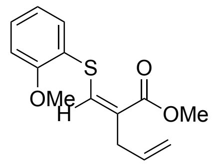
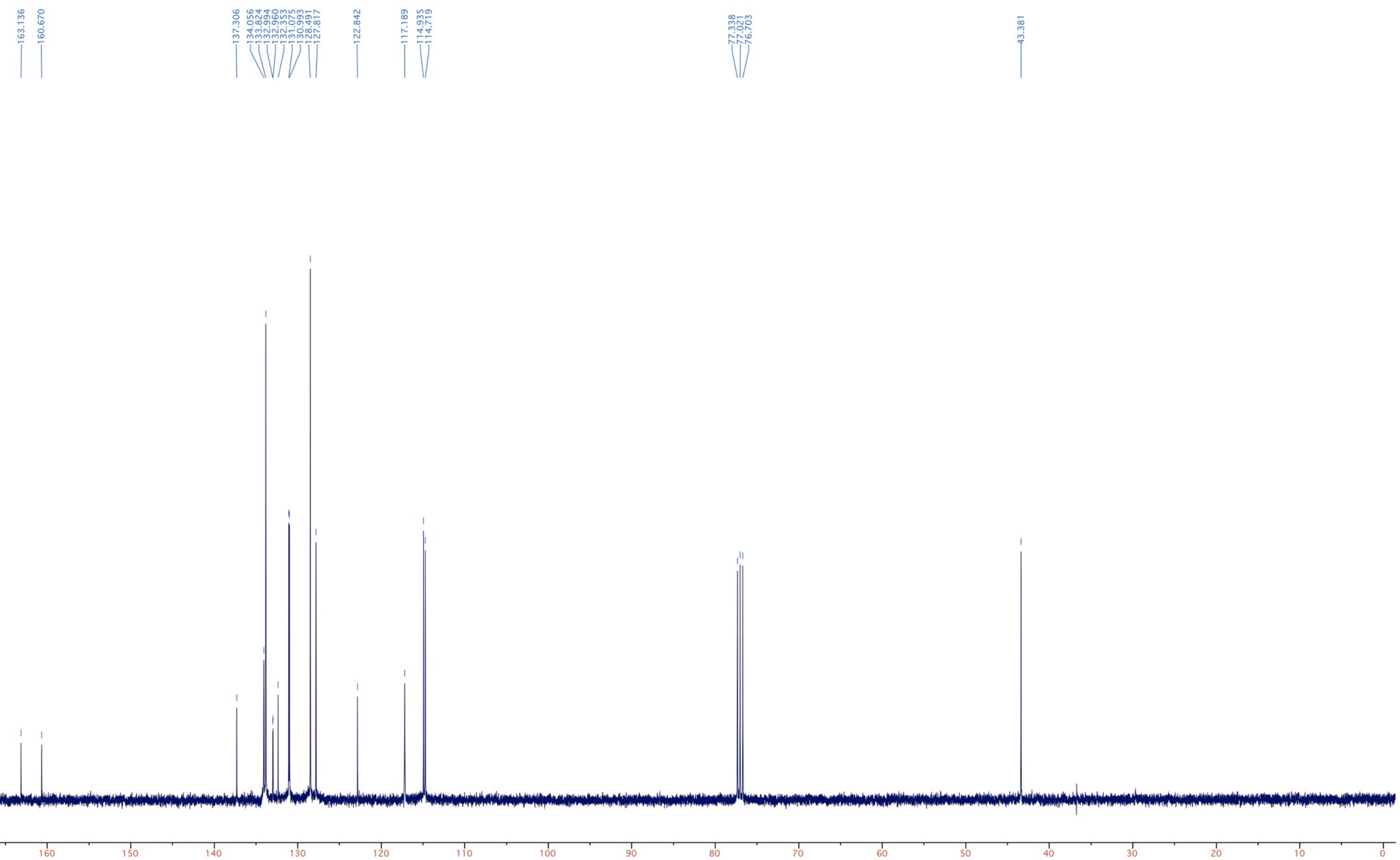
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190


OMe
S
O
H
OMe
7.461
7.457
7.442
7.441
7.348
7.342
7.326
7.319
7.303
7.298
6.973
6.956
6.954
6.941
6.938
6.935
6.915
5.874
5.858
5.849
5.842
5.833
5.816
5.807
5.799
5.790
5.774
5.084
5.080
5.076
5.072
5.040
5.037
5.033
5.029
5.015
5.011
5.008
3.866
3.812
3.070
3.067
3.054
3.051
0.933
0.899
2.77
0.802
1.75
3
2.93
1.88
ppm

3i


S
O
OMe
H
OMe

3i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160.670
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134.056
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132.960
132.353
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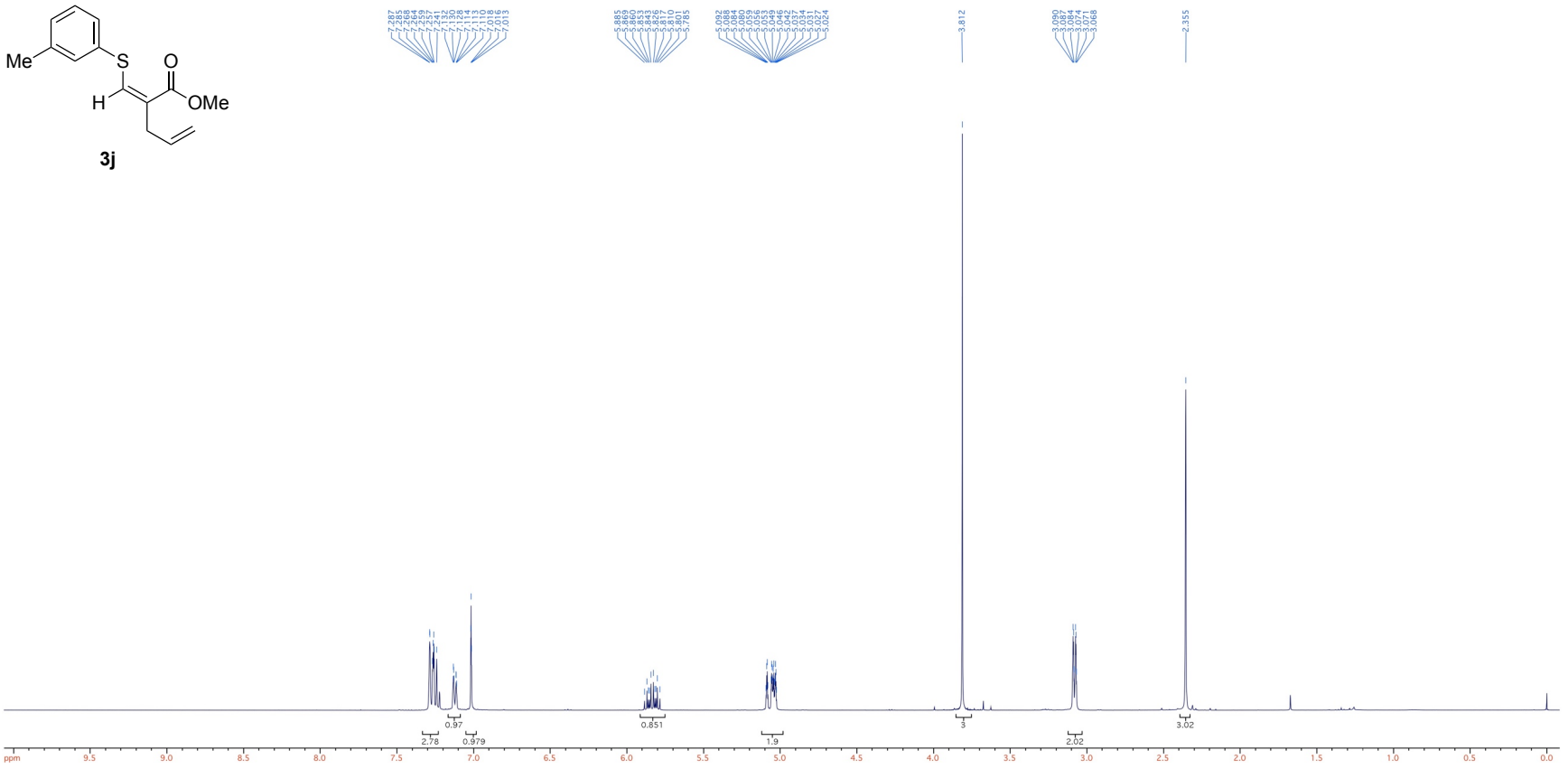
130.993
128.491
127.817
122.842
117.189
114.935
114.719
77.338
77.021
76.703
43.381
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me
S
O
H
OMe
3j
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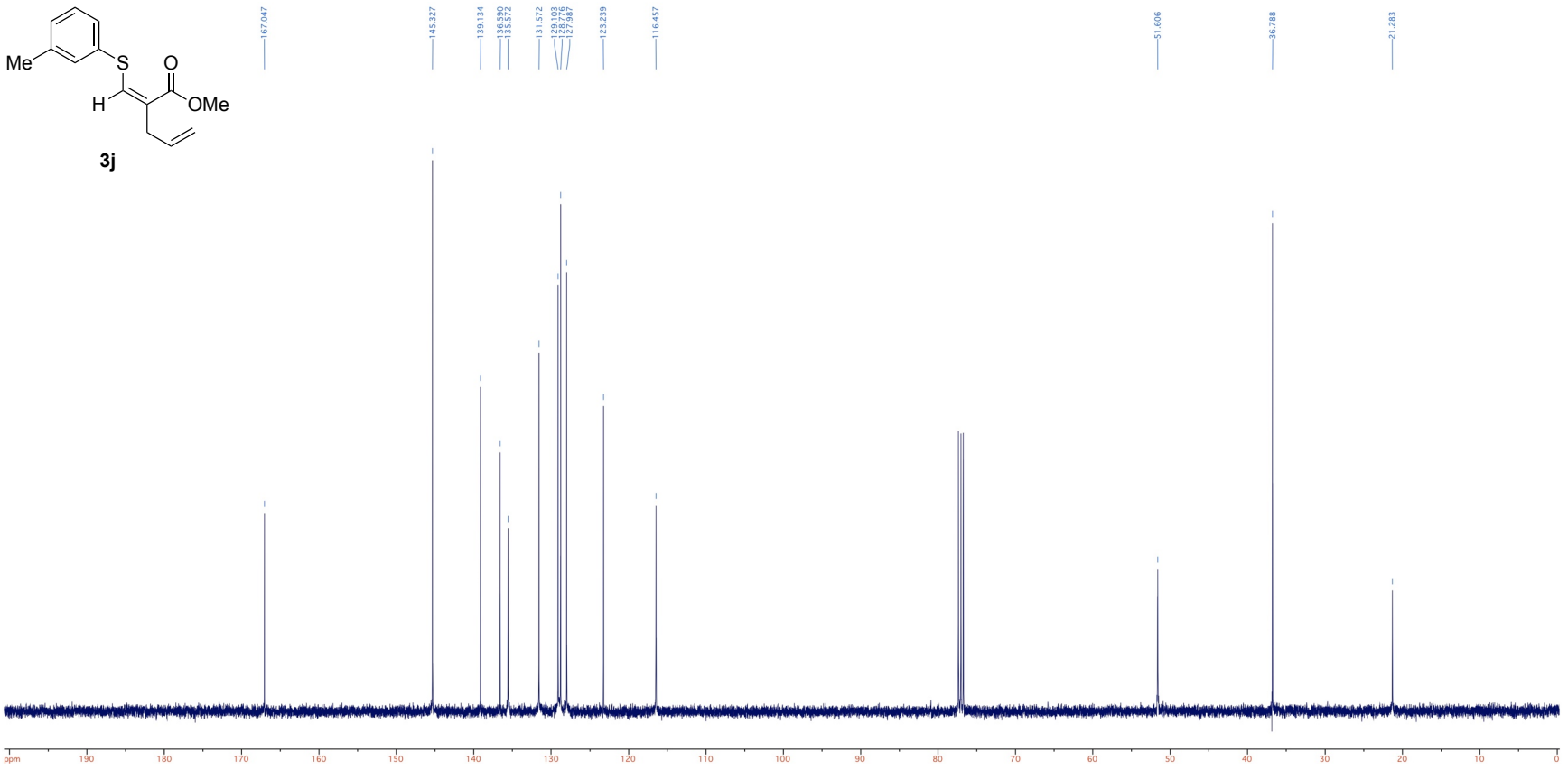
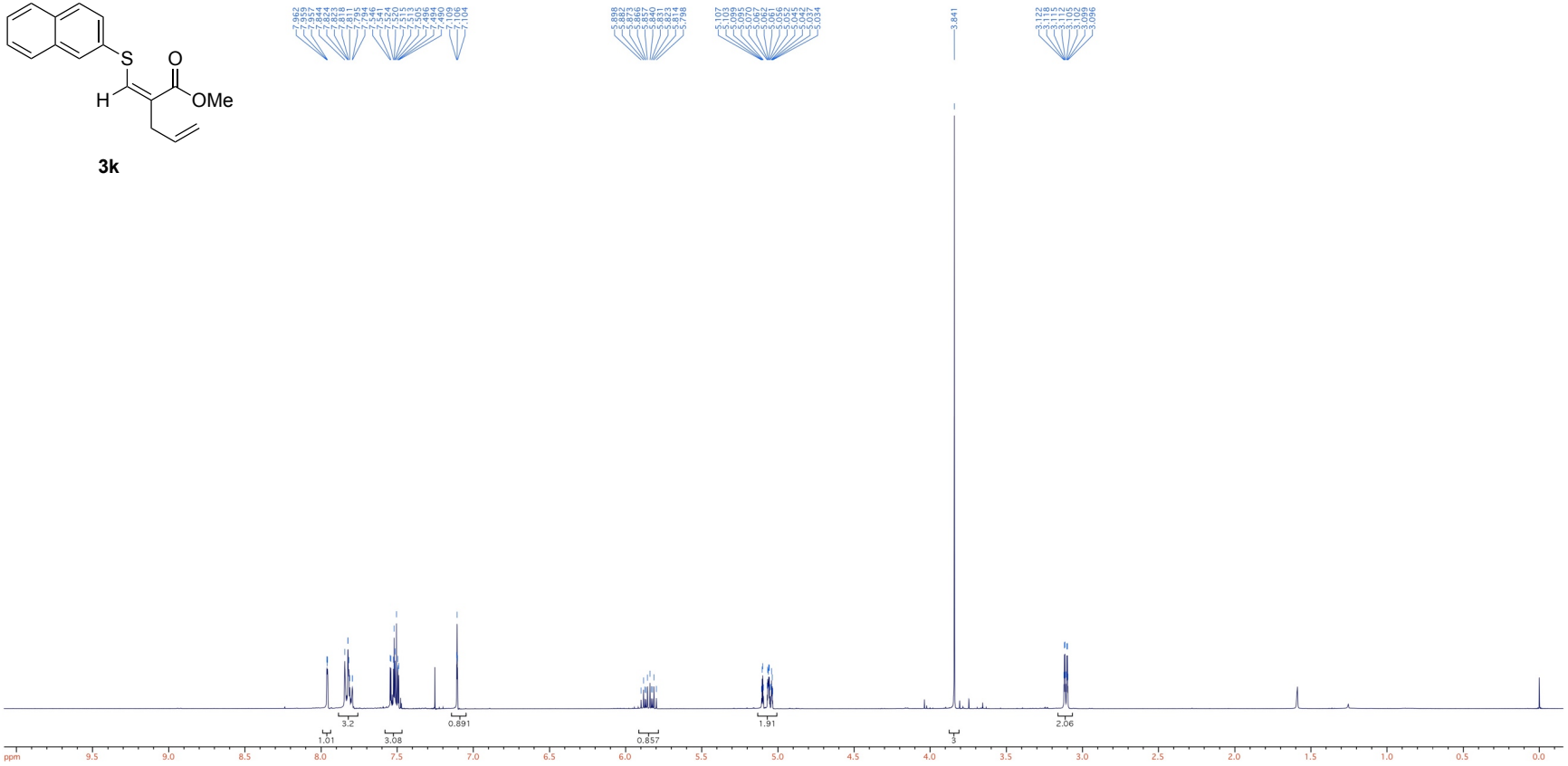
7.285
7.268
7.264
7.259
7.257
7.241
7.131
7.130
7.128
7.114
7.113
7.110
7.018
7.016
7.013
5.885
5.869
5.860
5.853
5.843
5.826
5.817
5.810
5.691
5.685
5.092
5.088
5.084
5.080
5.059
5.056
5.053
5.049
5.046
5.042
5.037
5.034
5.031
5.027
5.024
3.812
3.090
3.087
3.084
3.074
3.071
3.068
2.355
2.78
0.97
0.979
0.851
1.9
3
2.02
3.02
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Me
S
O
H
OMe
3j
167.047
145.327
139.134
136.590
135.572
131.572
129.103
128.176
127.987
123.239
116.457
51.606
36.788
21.283
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

S
O
H
OMe

3k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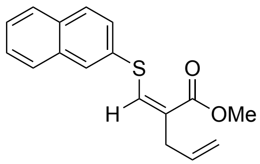
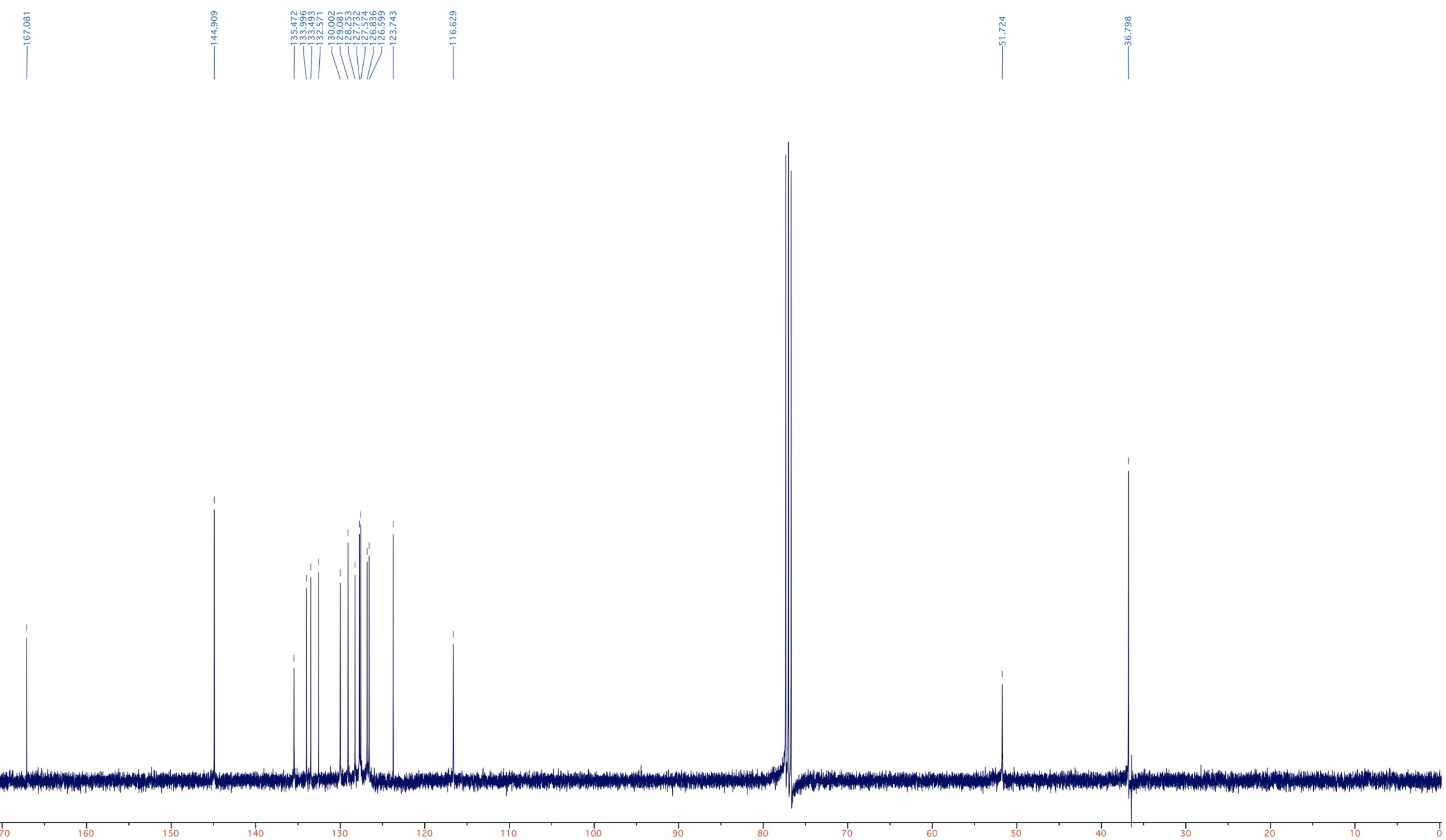
7.957
7.847
7.844
7.824
7.823
7.820
7.818
7.791
7.791
7.790
7.546
7.541
7.524
7.520
7.515
7.513
7.505
7.496
7.494
7.490
7.109
7.106
7.104
5.898
5.882
5.873
5.866
5.857
5.840
5.831
5.823
5.814
5.798
5.107
5.105
5.099
5.095
5.070
5.067
5.062
5.061
5.056
5.045
5.042
5.037
5.034
3.841
3.122
3.118
3.113
3.112
3.105
3.102
3.098
3.096
3.091
1.01
3.2
3.08
0.891
0.857
1.91
3
2.06
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


S
O
H
OMe

3k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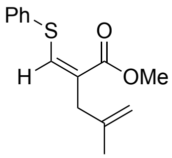
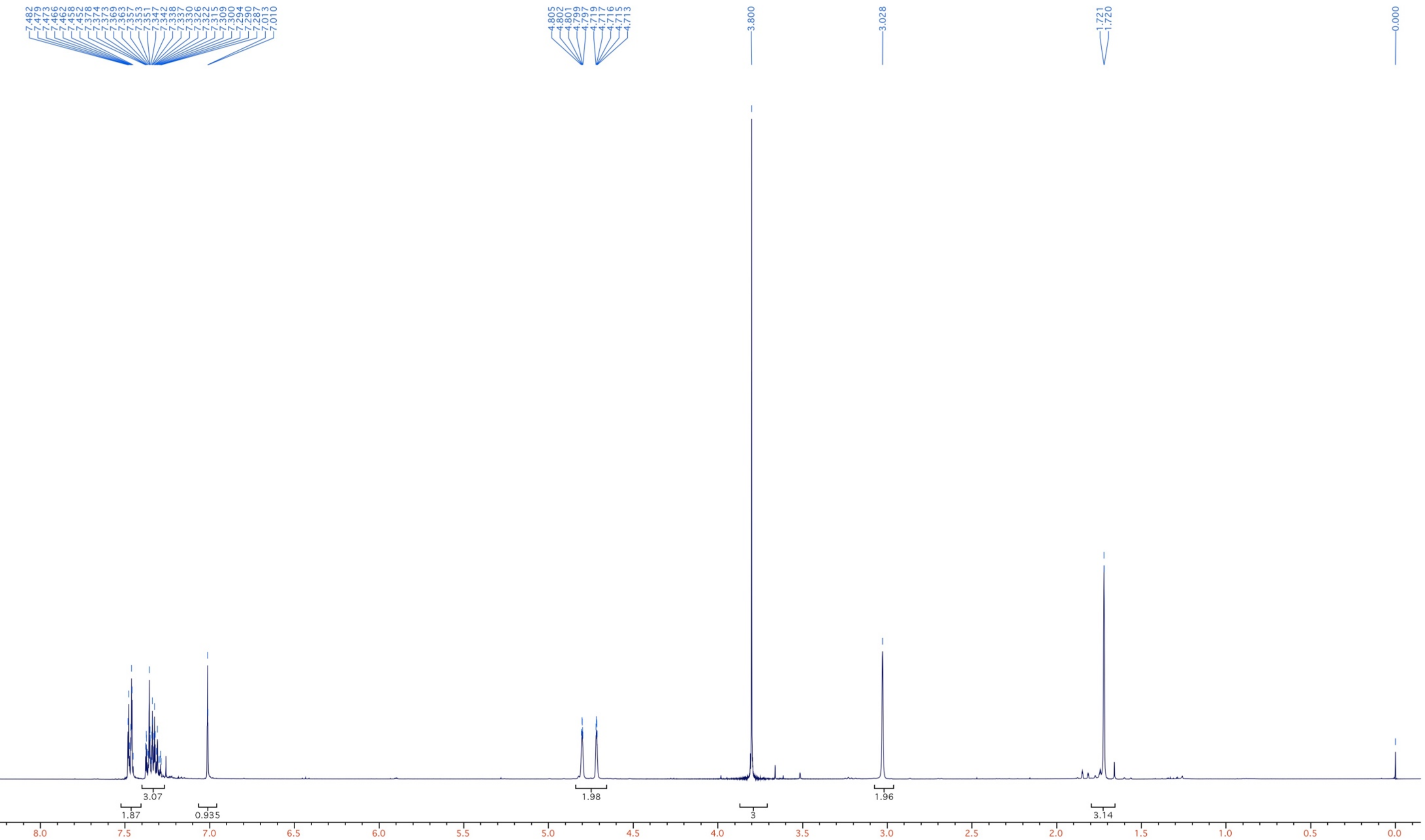
135.472
133.996
133.493
132.571
130.002
129.081
128.253
127.732
127.574
126.836
126.599
123.743
116.629
51.724
36.798
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ph
S
O
OMe
H

3l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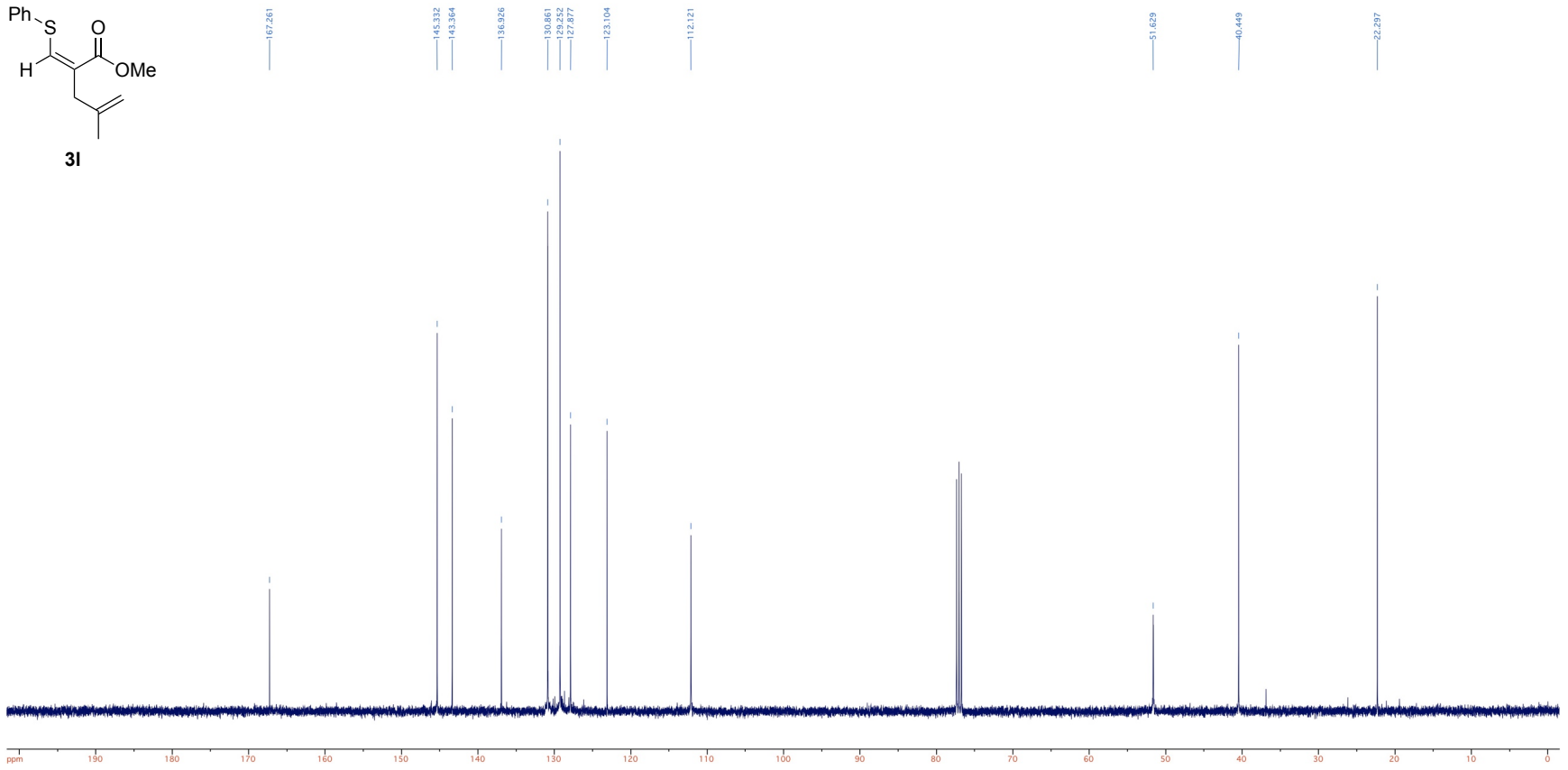
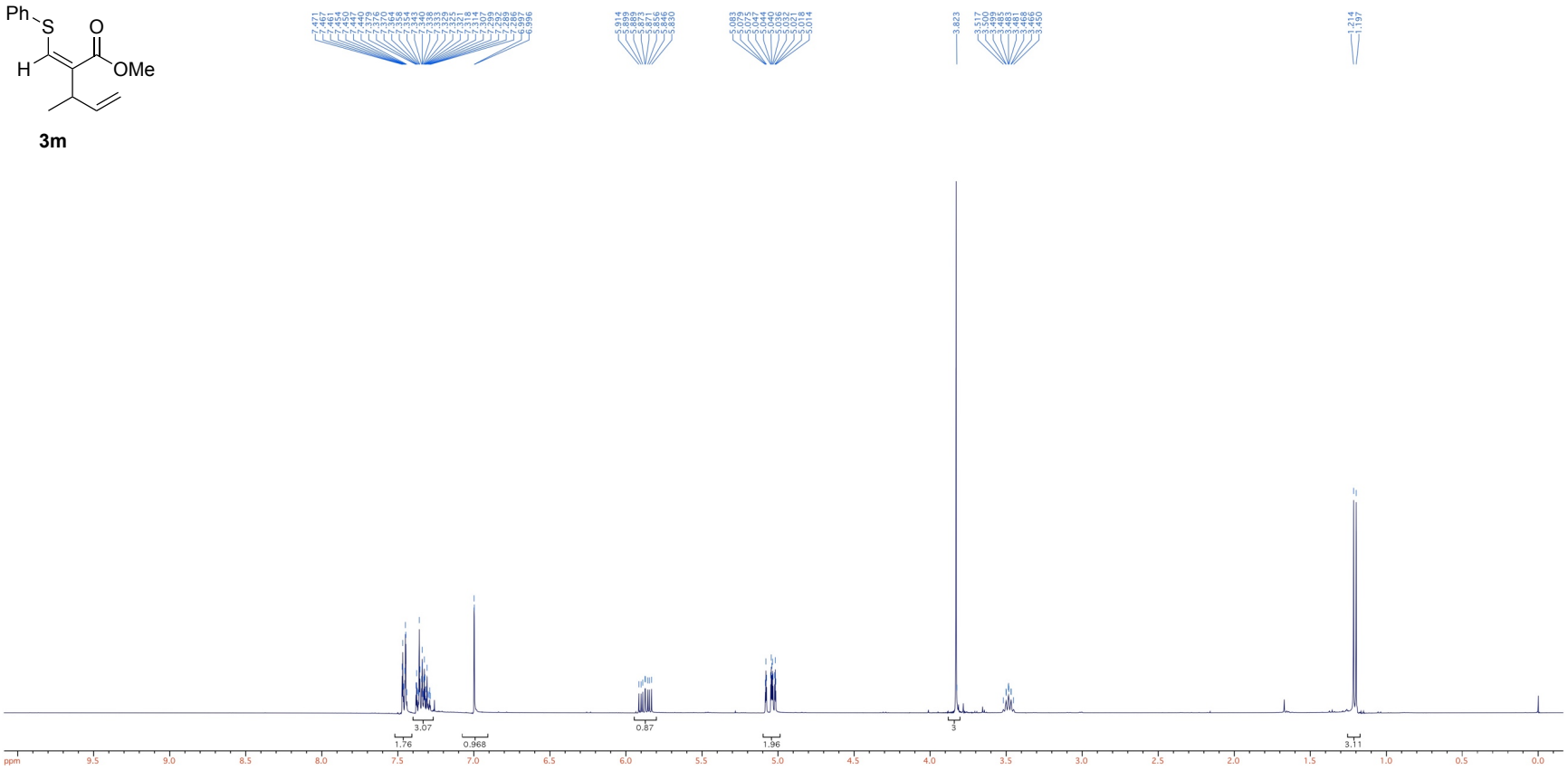
7.462
7.458
7.452
7.378
7.374
7.373
7.369
7.363
7.357
7.353
7.351
7.347
7.342
7.338
7.337
7.330
7.326
7.322
7.315
7.309
7.300
7.294
7.290
7.287
7.013
7.010
4.805
4.802
4.801
4.799
4.797
4.719
4.717
4.716
4.715
4.713
3.800
3.028
1.721
1.720
0.000
1.87
3.07
0.935
1.98
3
1.96
3.14
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Ph
S
O
H
OMe
3l
167.261
145.332
143.364
136.926
130.861
129.252
127.877
123.104
112.121
51.629
40.449
22.297
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Ph
S
O
H
OMe

3m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7.461
7.454
7.450
7.447
7.440
7.379
7.376
7.370
7.364
7.354
7.343
7.340
7.338
7.333
7.329
7.325
7.321
7.318
7.314
7.307
7.299
7.292
7.289
6.997
6.996
5.914
5.889
5.873
5.871
5.856
5.846
5.830
5.083
5.079
5.075
5.047
5.044
5.040
5.036
5.032
5.028
5.018
5.014
3.823
3.517
3.500
3.489
3.485
3.481
3.468
3.466
3.450
1.214
1.197
3.07
1.76
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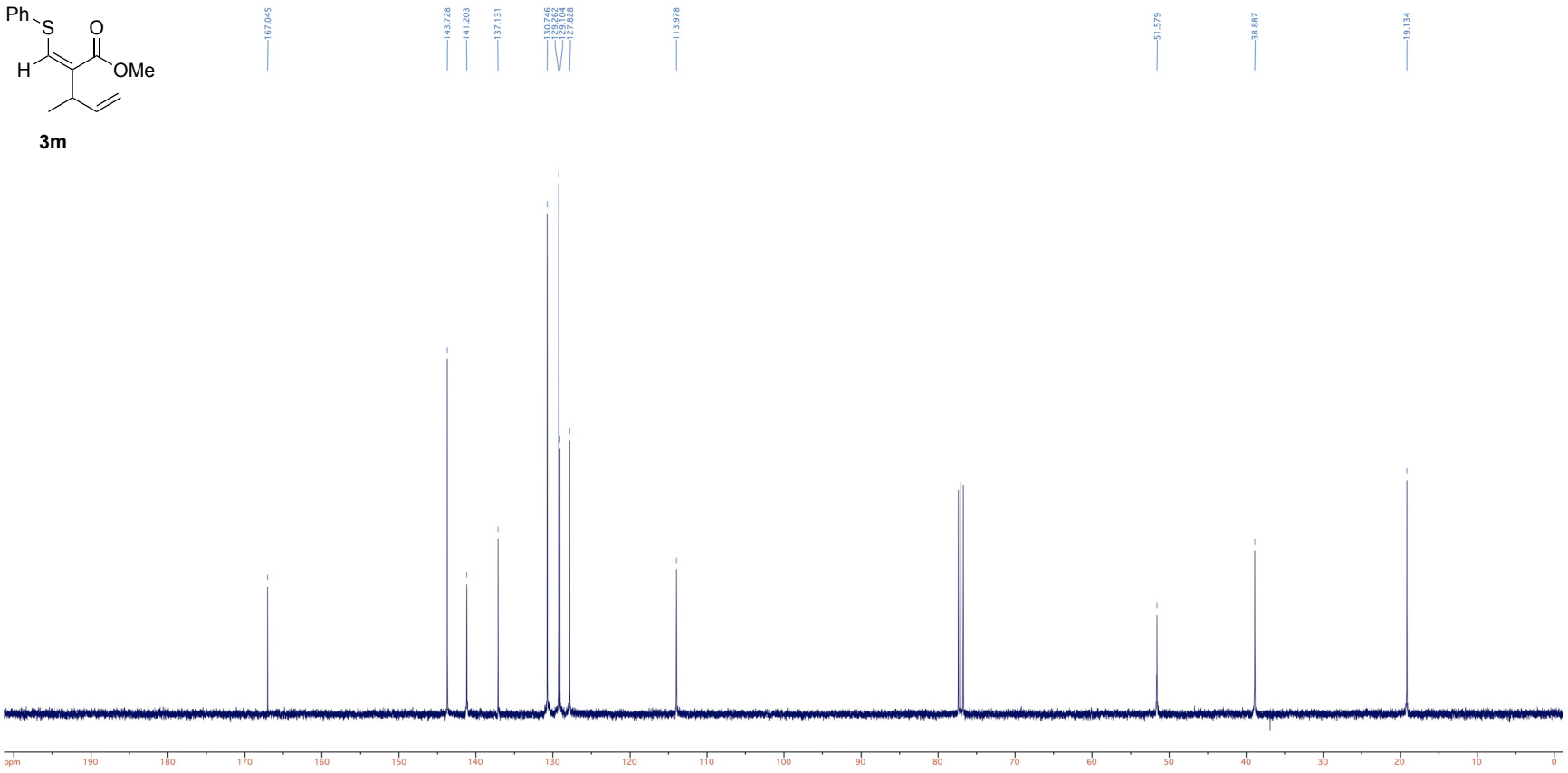
0.87
1.96
3
3.11
ppm


Ph
S
O
H
OMe
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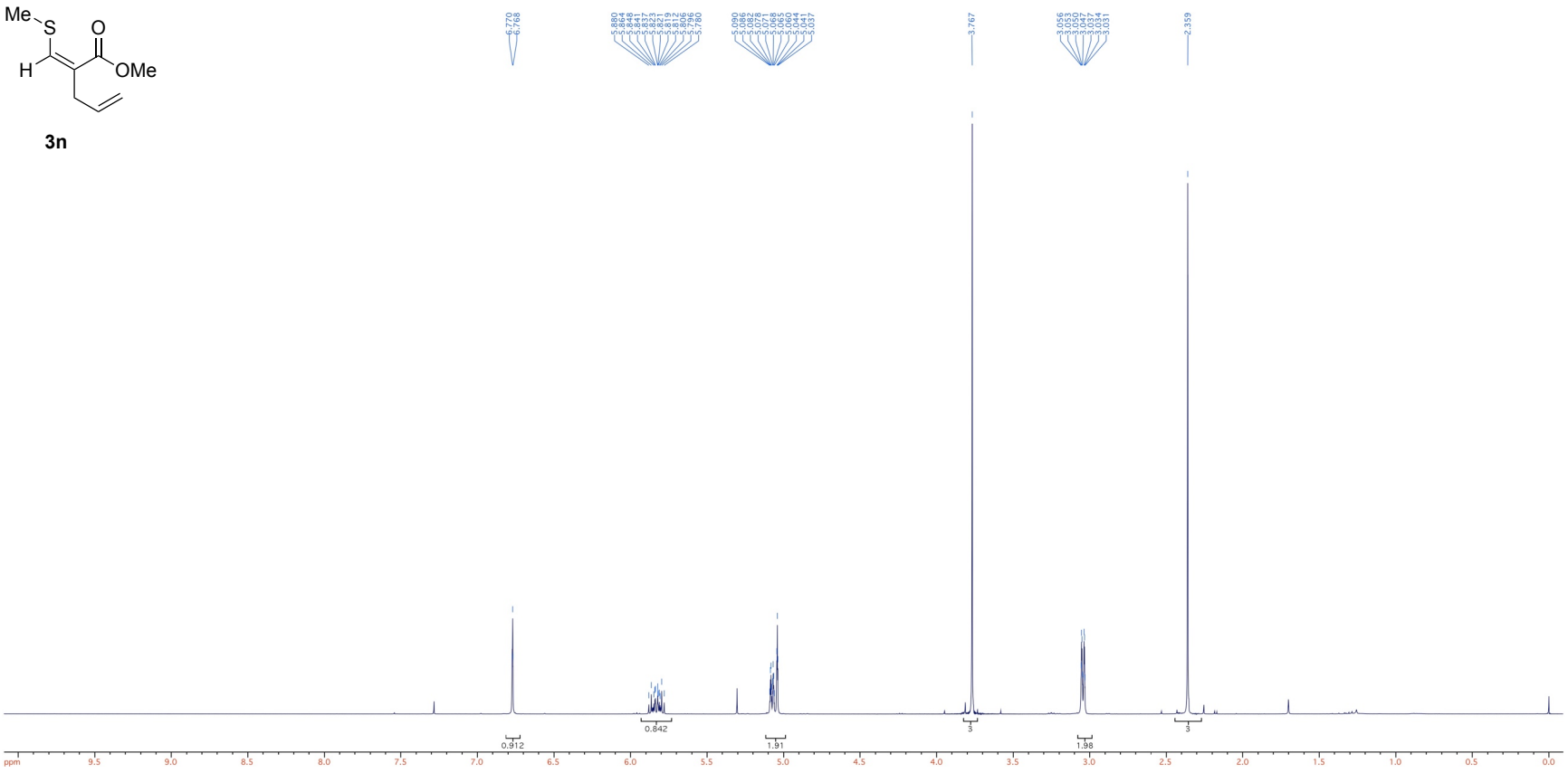
137.131
130.746
129.262
128.164
127.828
113.978
51.579
38.887
19.134
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3m


Me
S
O
H
OMe
6.770
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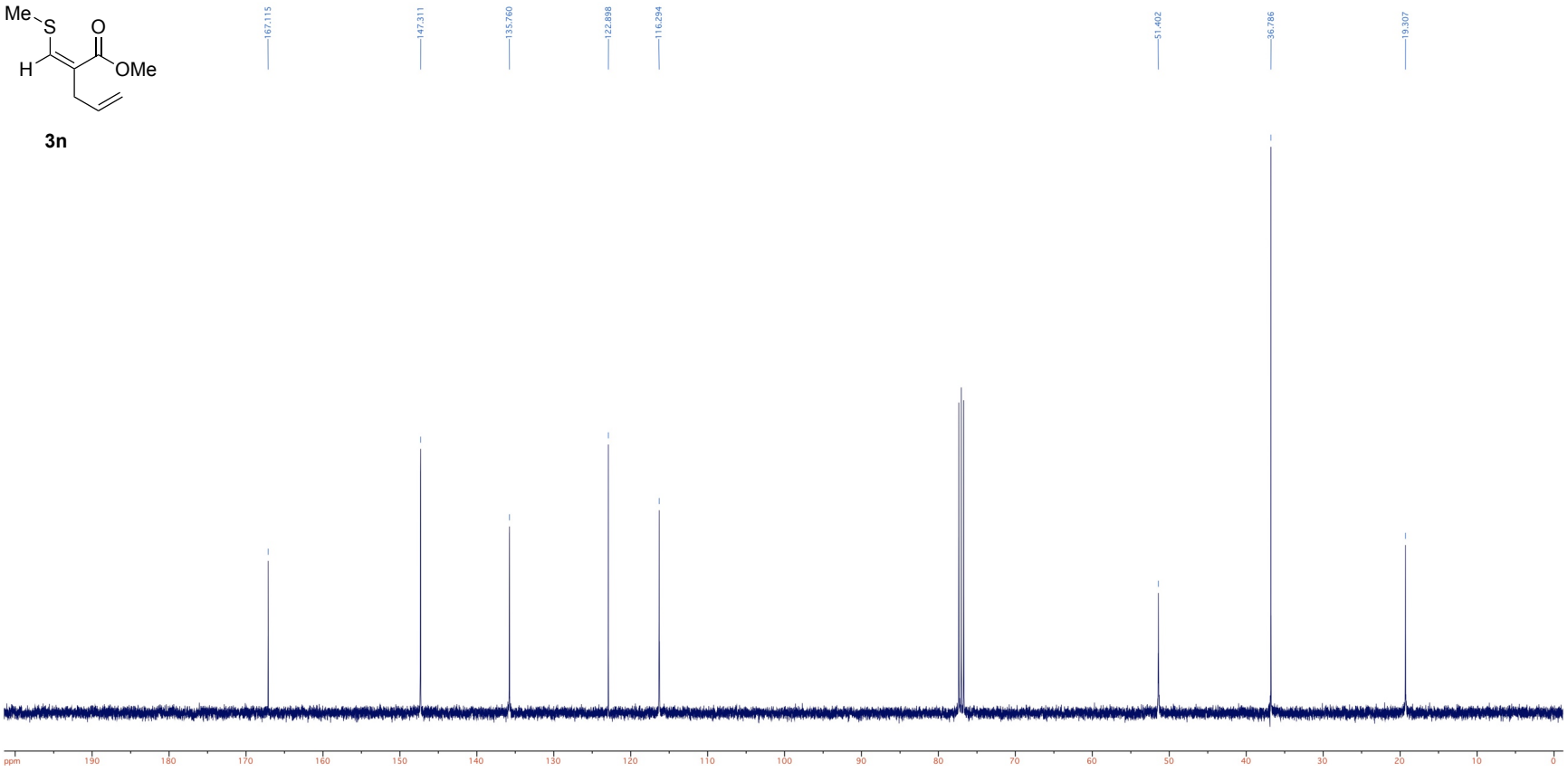
5.848
5.841
5.837
5.833
5.821
5.819
5.812
5.806
5.786
5.780
5.090
5.086
5.082
5.077
5.071
5.068
5.065
5.060
5.044
5.041
5.037
3.767
3.056
3.053
3.050
3.047
3.037
3.034
3.031
2.359
0.912
0.842
1.91
3
1.98
3
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3n


Me
S
O
H
OMe
167.115
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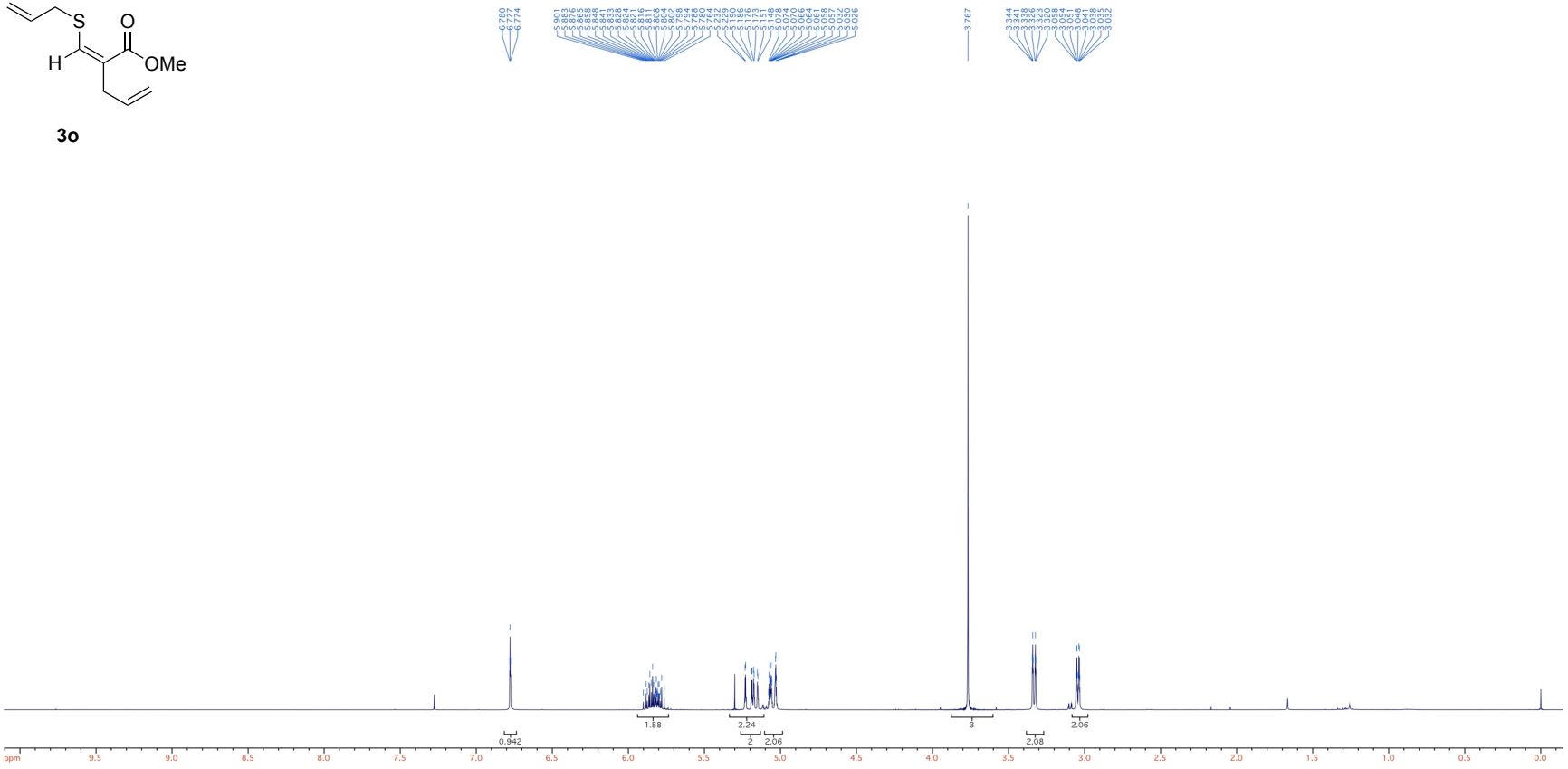
135.760
122.898
116.294
51.402
36.786
19.307
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3n

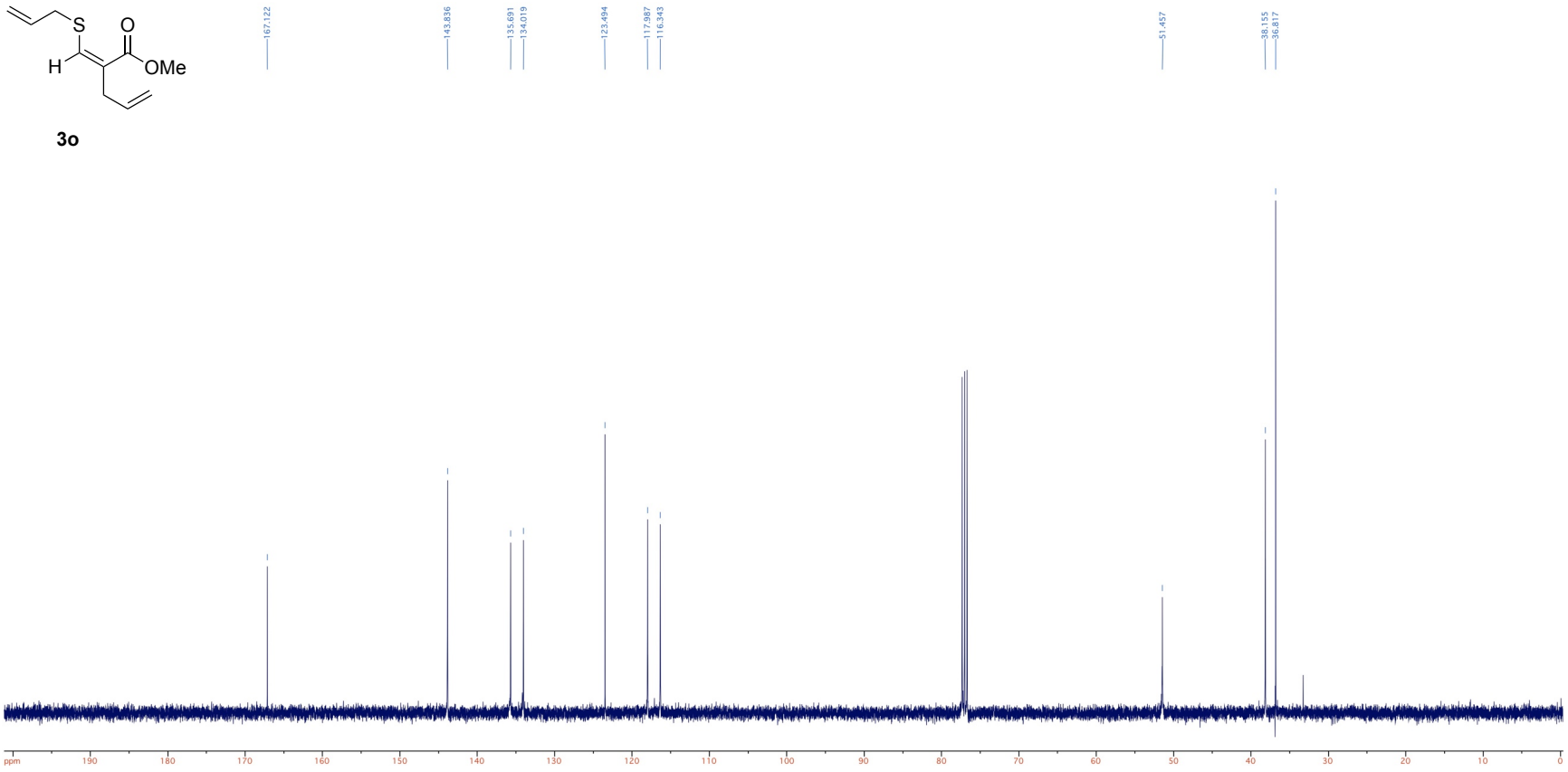
S
O
H
OMe

3o


6.790
6.777
6.774
5.901
5.893
5.883
5.865
5.858
5.848
5.841
5.831
5.828
5.824
5.821
5.816
5.811
5.808
5.804
5.802
5.798
5.794
5.788
5.780
5.764
5.232
5.225
5.190
5.186
5.176
5.173
5.151
5.148
5.078
5.074
5.070
5.066
5.061
5.058
5.057
5.052
5.030
5.026
3.767
3.344
3.341
3.338
3.326
3.323
3.320
3.060
3.054
3.051
3.048
3.041
3.038
3.035
3.032
0.942
1.88
2.24
2
2.06
3
2.08
2.06
ppm

S
O
H
OMe

3o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134.019
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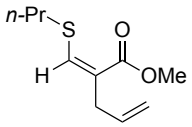
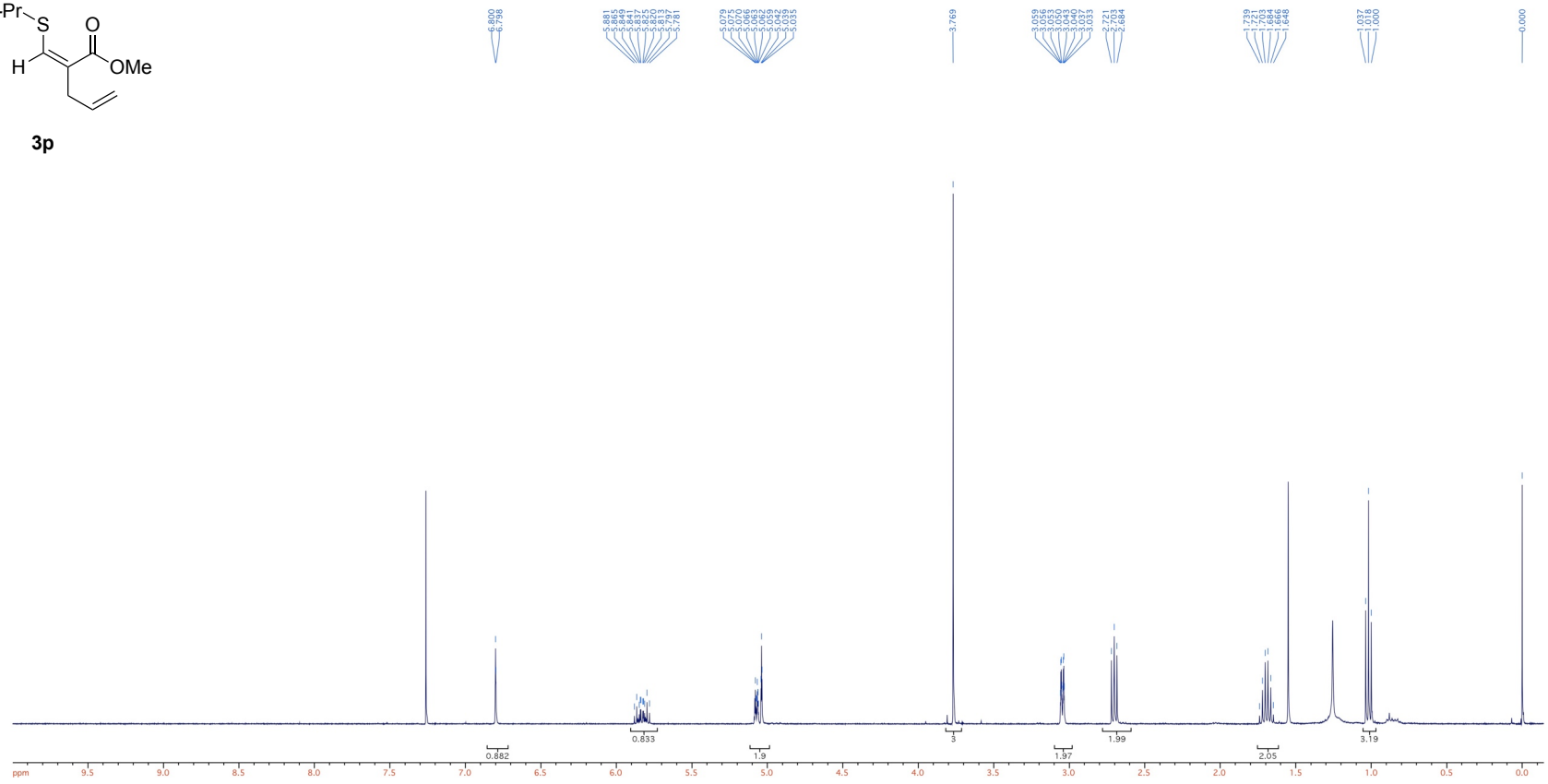
117.987
116.343
51.457
38.155
36.817
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


n-Pr
S
O
H
OMe

3p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6.798
5.881
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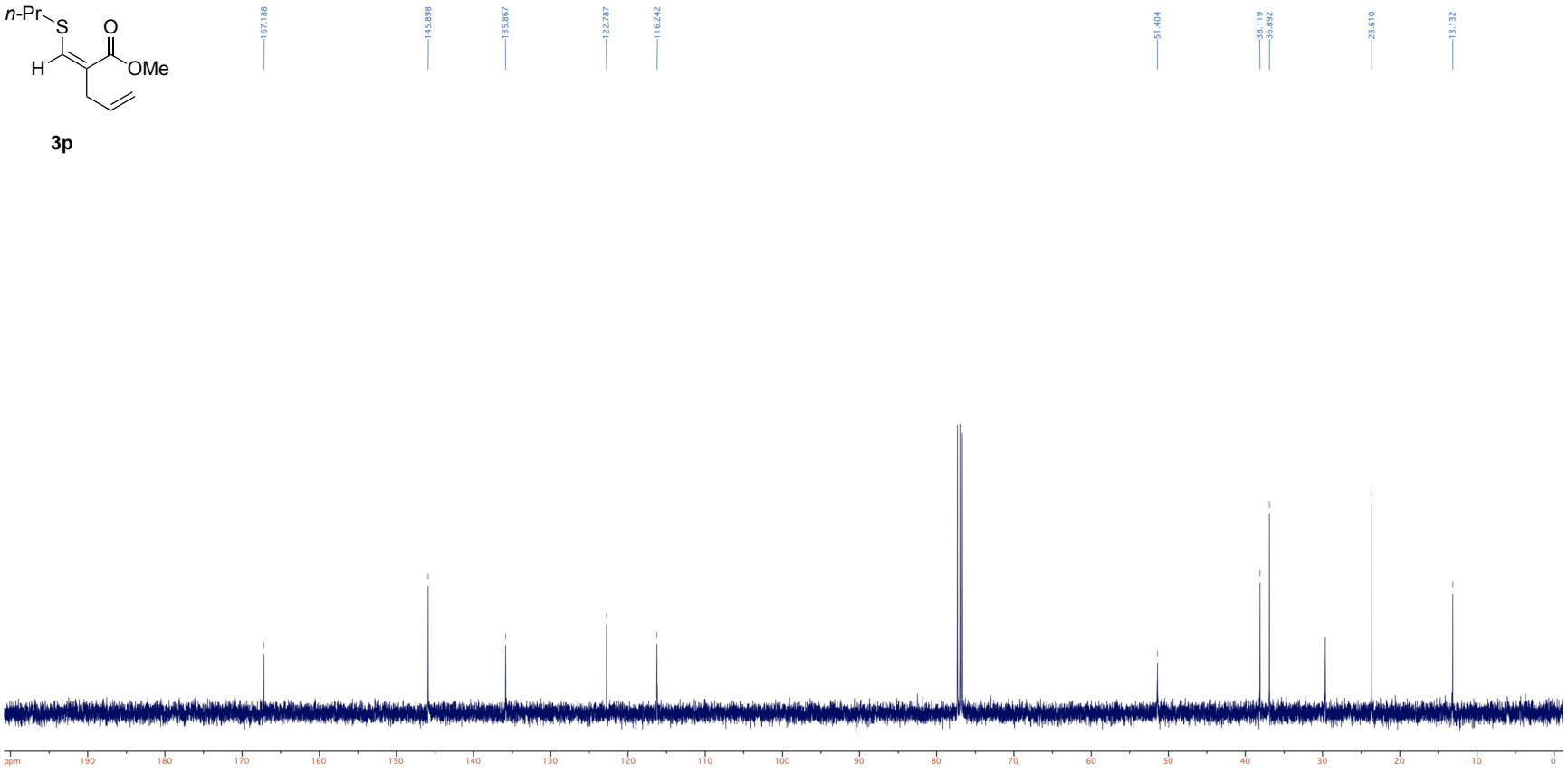
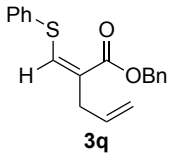
5.849
5.841
5.837
5.825
5.820
5.813
5.797
5.781
5.079
5.077
5.070
5.066
5.063
5.062
5.052
5.042
5.039
5.035
3.769
3.059
3.056
3.053
3.049
3.043
3.040
3.037
3.033
2.721
2.703
2.684
1.739
1.721
1.703
1.684
1.666
1.648
1.037
1.018
1.000
0.000
0.882
0.833
1.9
3
1.97
1.99
2.05
3.19
ppm

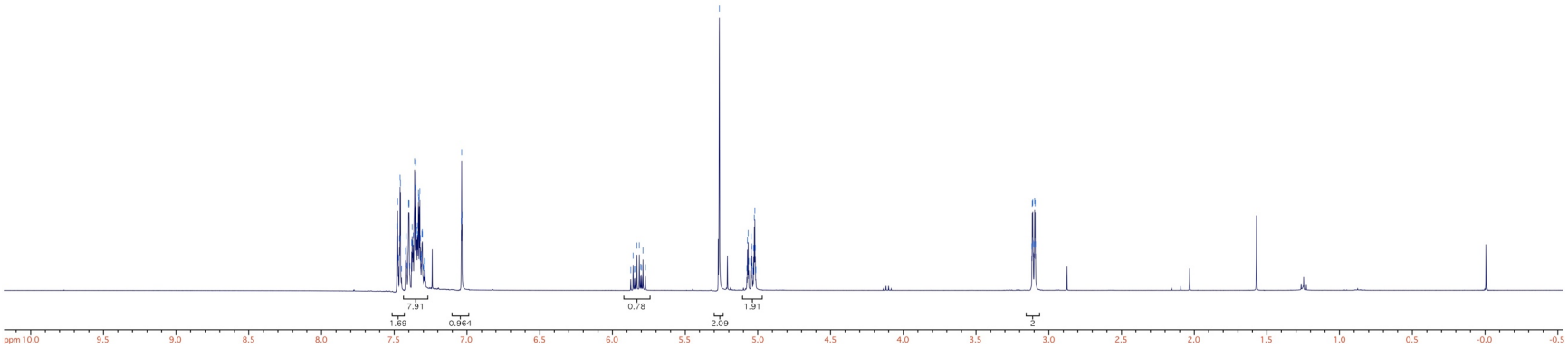
n-Pr
S
O
H
OMe

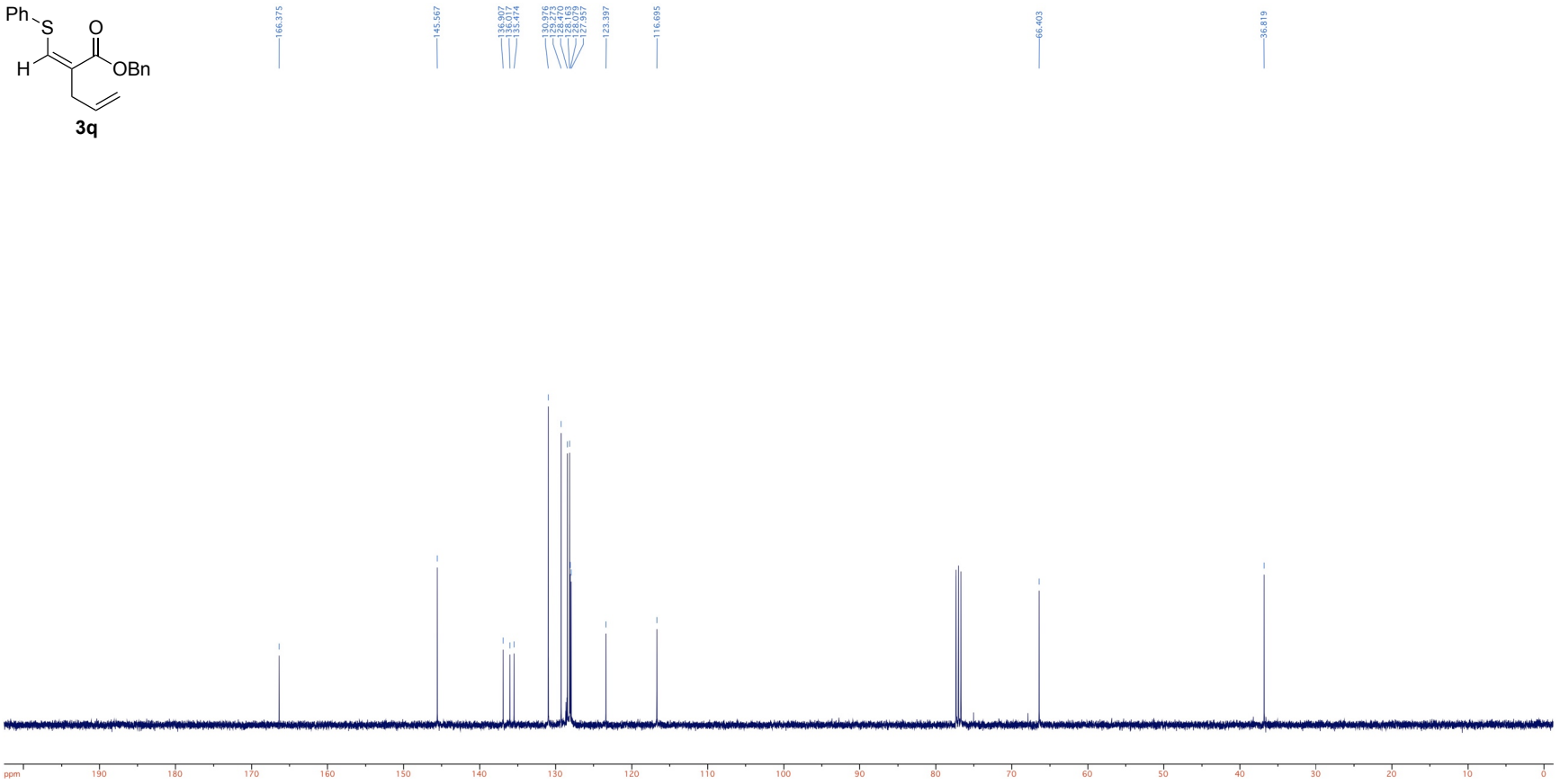
3p


167.188
145.898
135.867
122.787
116.242
51.404
38.119
36.892
23.610
13.132
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ph
S
O
H
OBn

3q


7.91
1.89
0.964
0.78
2.09
1.91
2
ppm 10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
-0.5


Ph
S
O
H
OBn
3q
166.375
145.567
136.907
136.677
135.474
130.976
129.273
129.170
128.163
128.079
127.937
123.397
116.695
66.403
36.819
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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30
20
10
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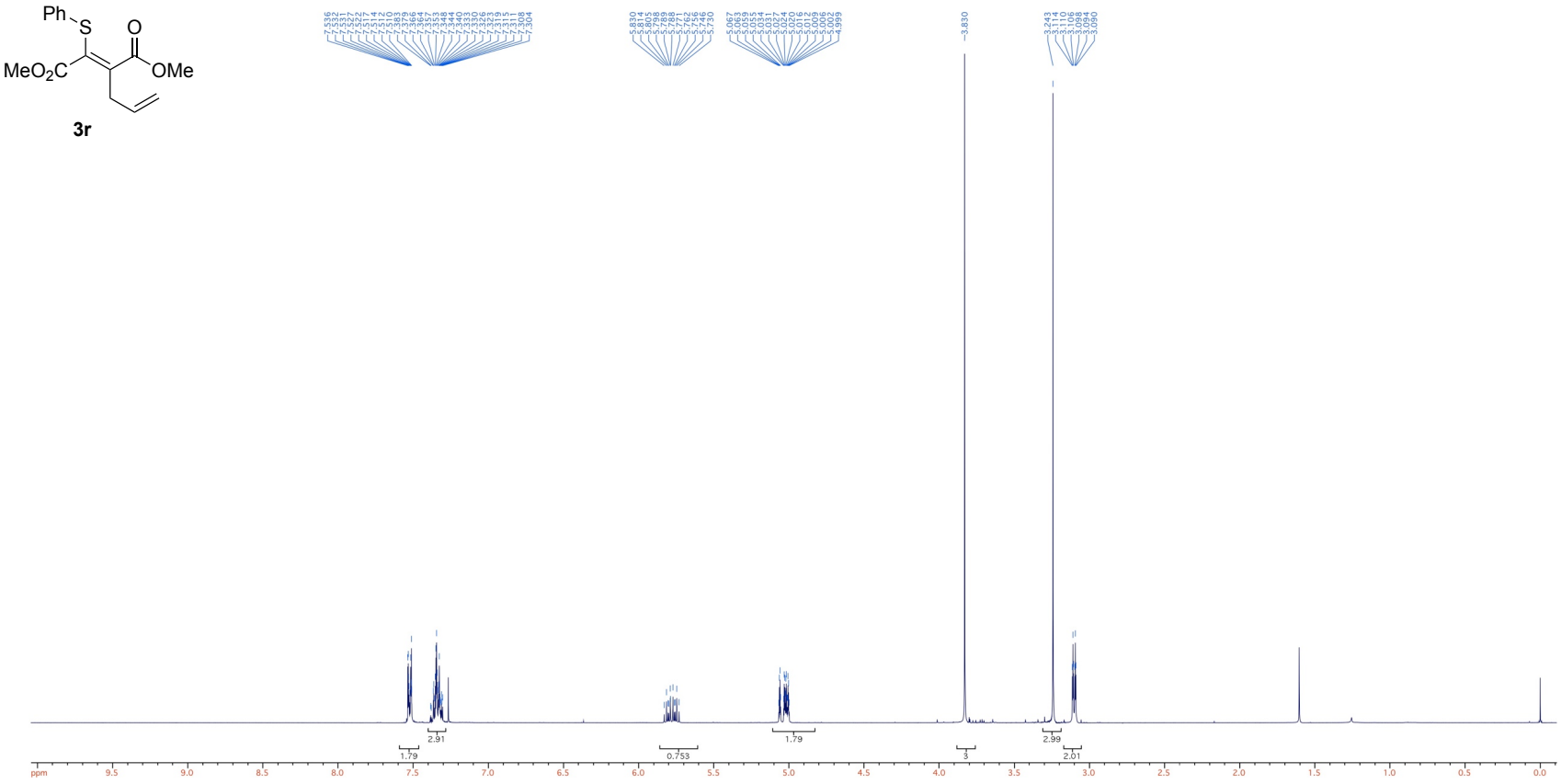
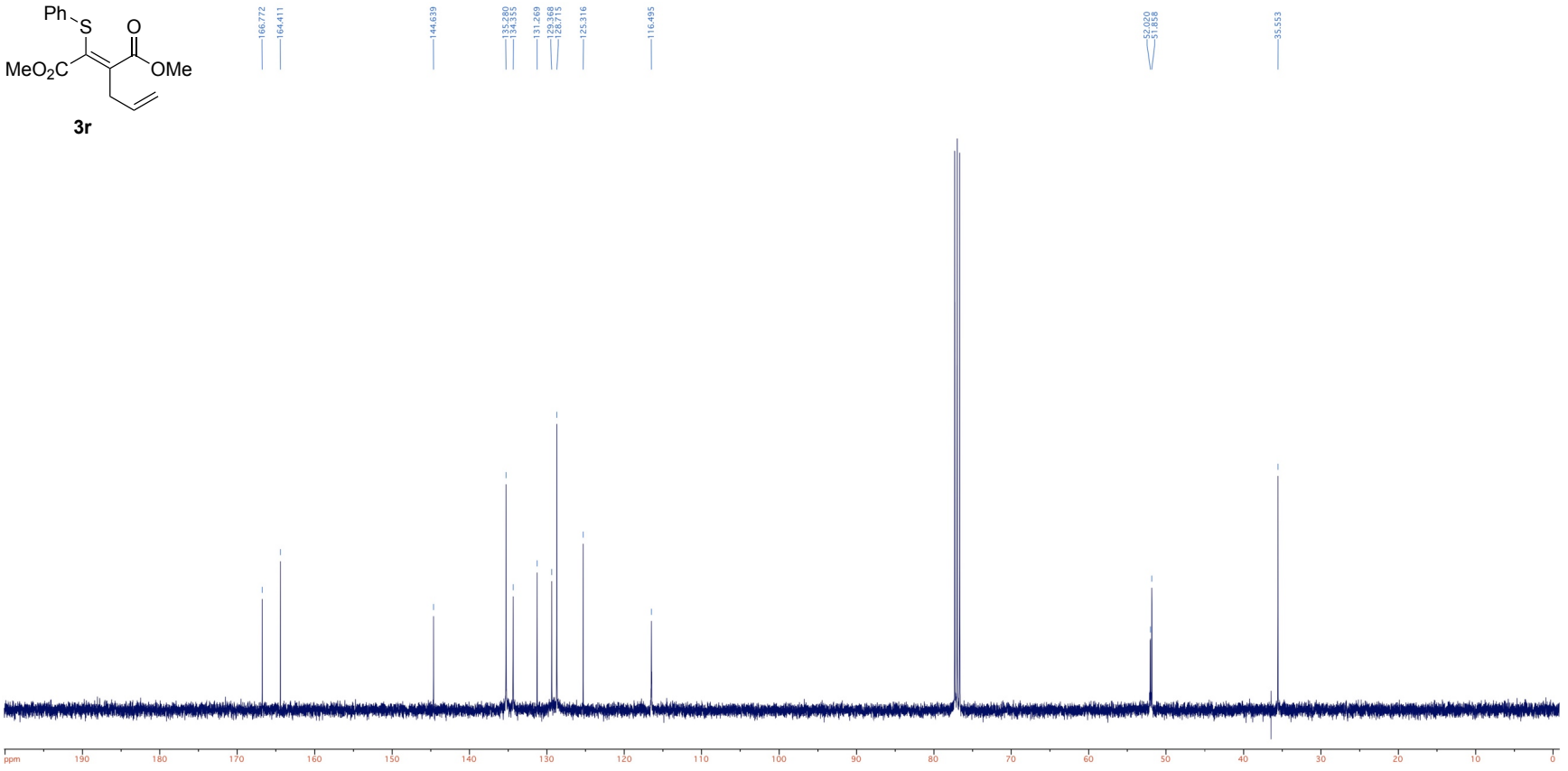

Ph
S
O
MeO2C
OMe
3r
3.830
1.79
2.91
0.753
1.79
3
2.99
2.01
ppm


Ph
S
O
MeO2C
OMe
3r
166.772
164.411
144.639
135.280
134.355
131.269
129.468
128.715
125.316
116.495
52.020
51.858
35.553
ppm
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150
140
130
120
110
100
90
80
70
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30
20
10
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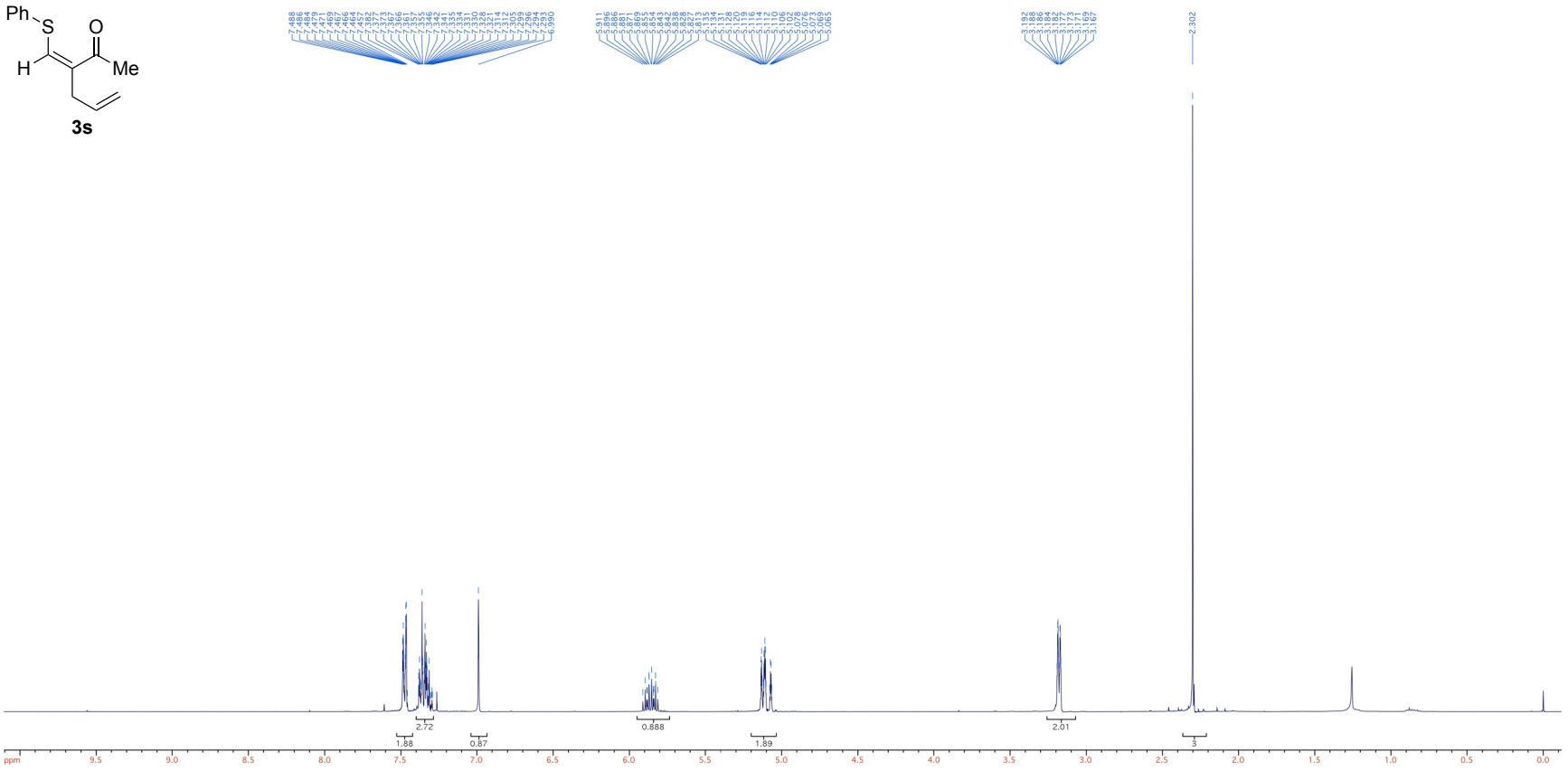
Ph
S
O
H
Me
3s
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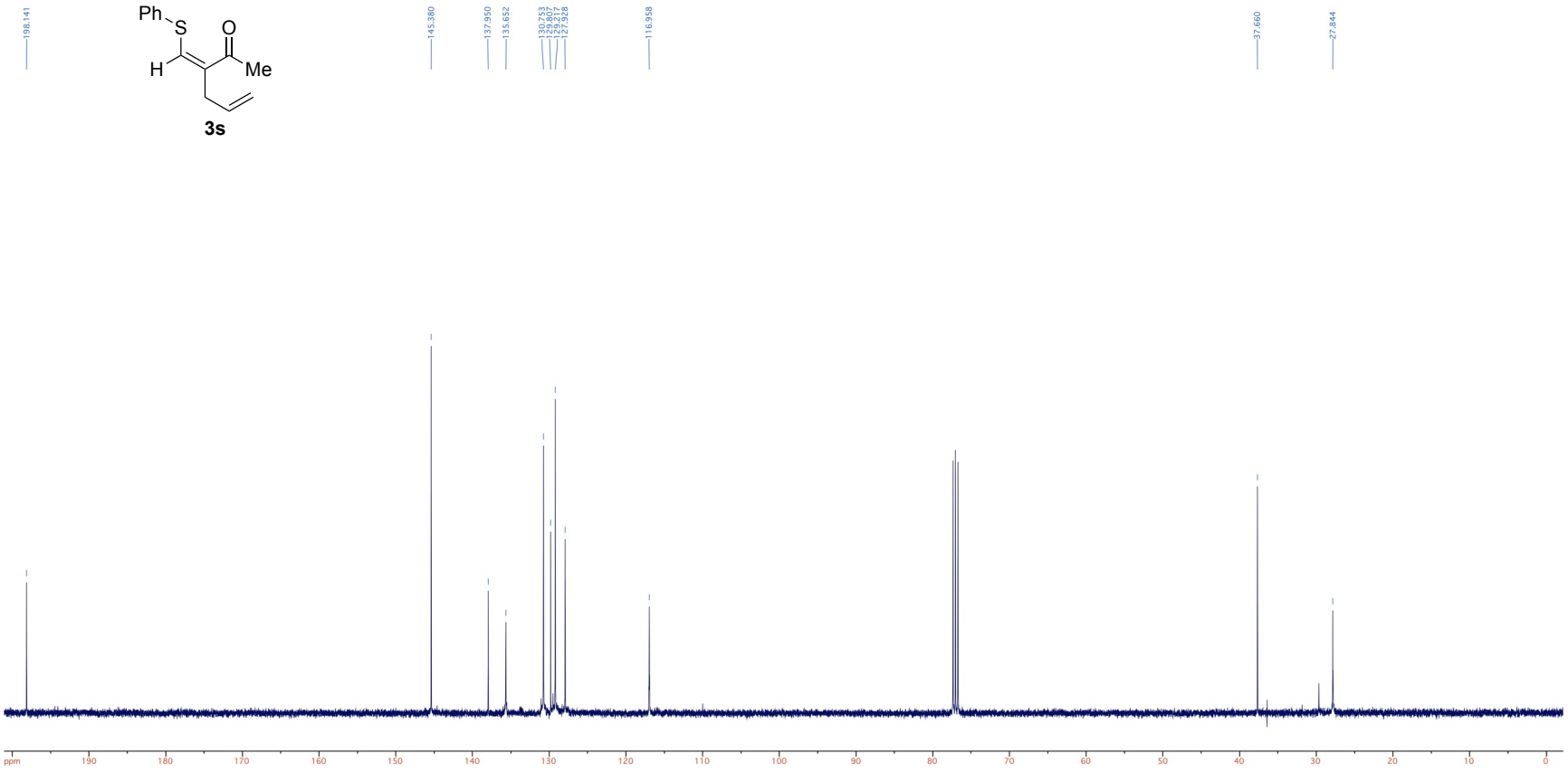
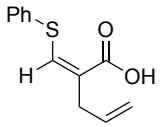
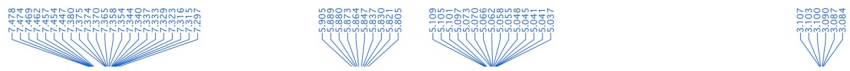
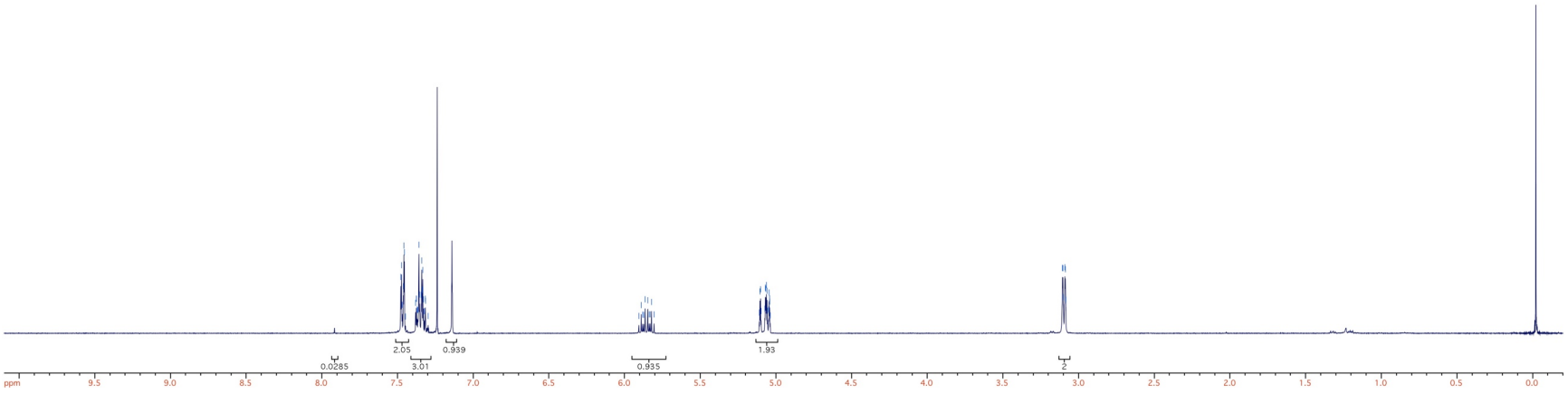
1.88
0.87
0.888
1.89
2.01
3
ppm

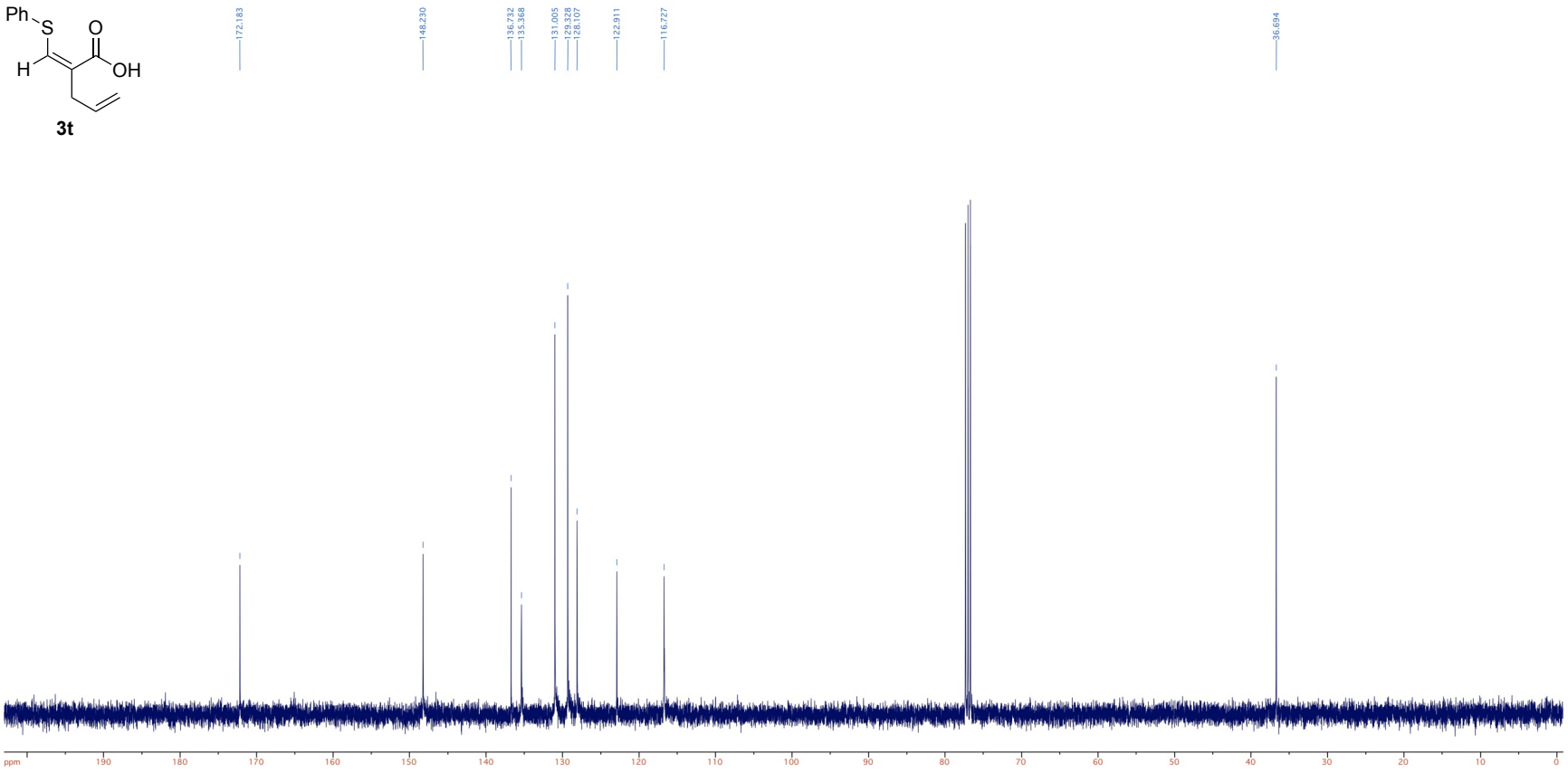

198.141
145.380
137.950
135.652
130.753
128.857
128.217
127.928
116.958
37.660
27.844
Ph
S
O
H
Me
3s
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



3t






Ph
S
O
H
OH
3t
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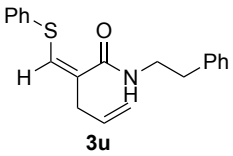
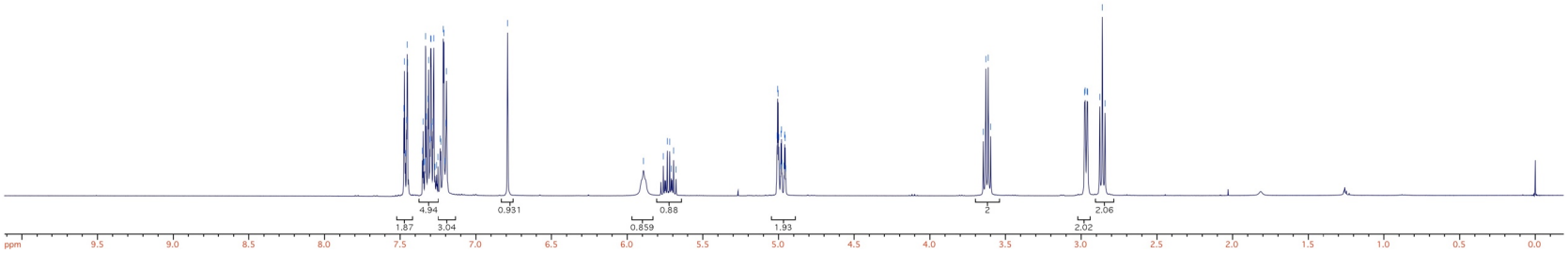
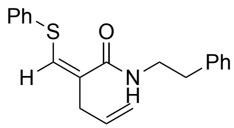
148.230
136.732
135.368
131.005
129.328
128.107
122.911
116.727
36.694
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

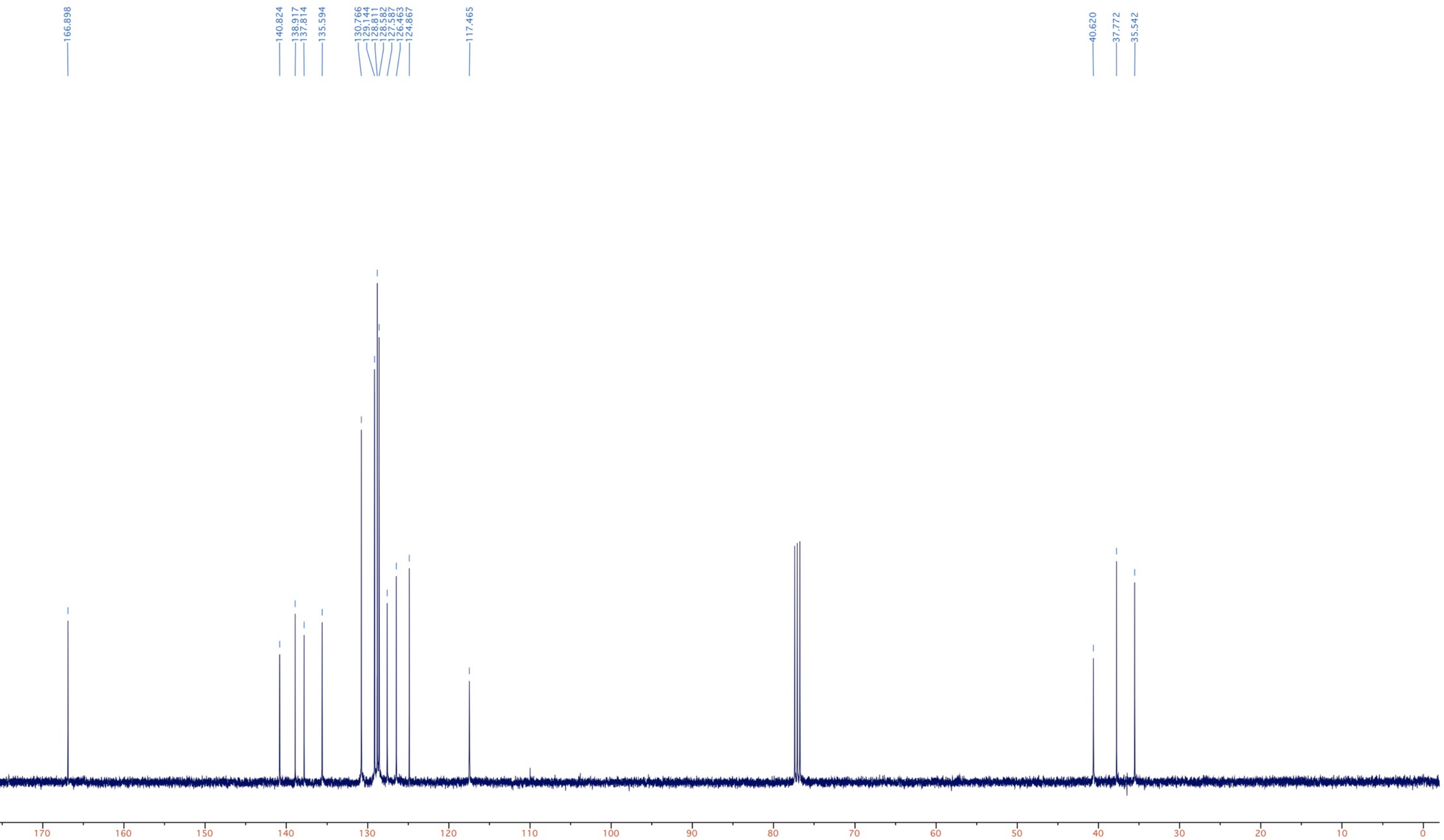


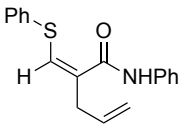
3u



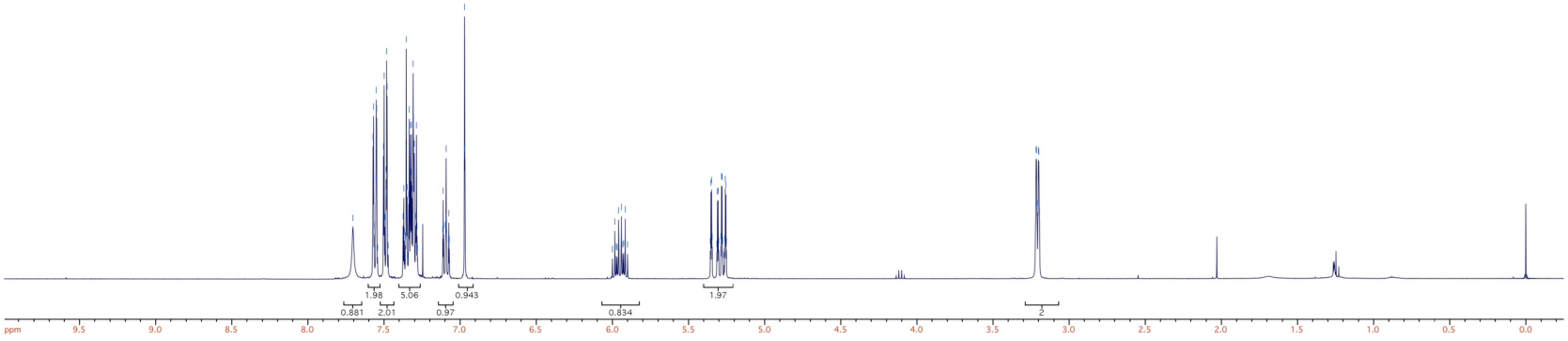

Ph
S
O
H
N
H
Ph

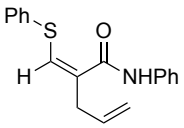
3u


166.898
140.824
138.917
137.814
135.594
130.766
129.144
128.811
128.582
127.587
126.463
124.867
117.465
40.620
37.772
35.542
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

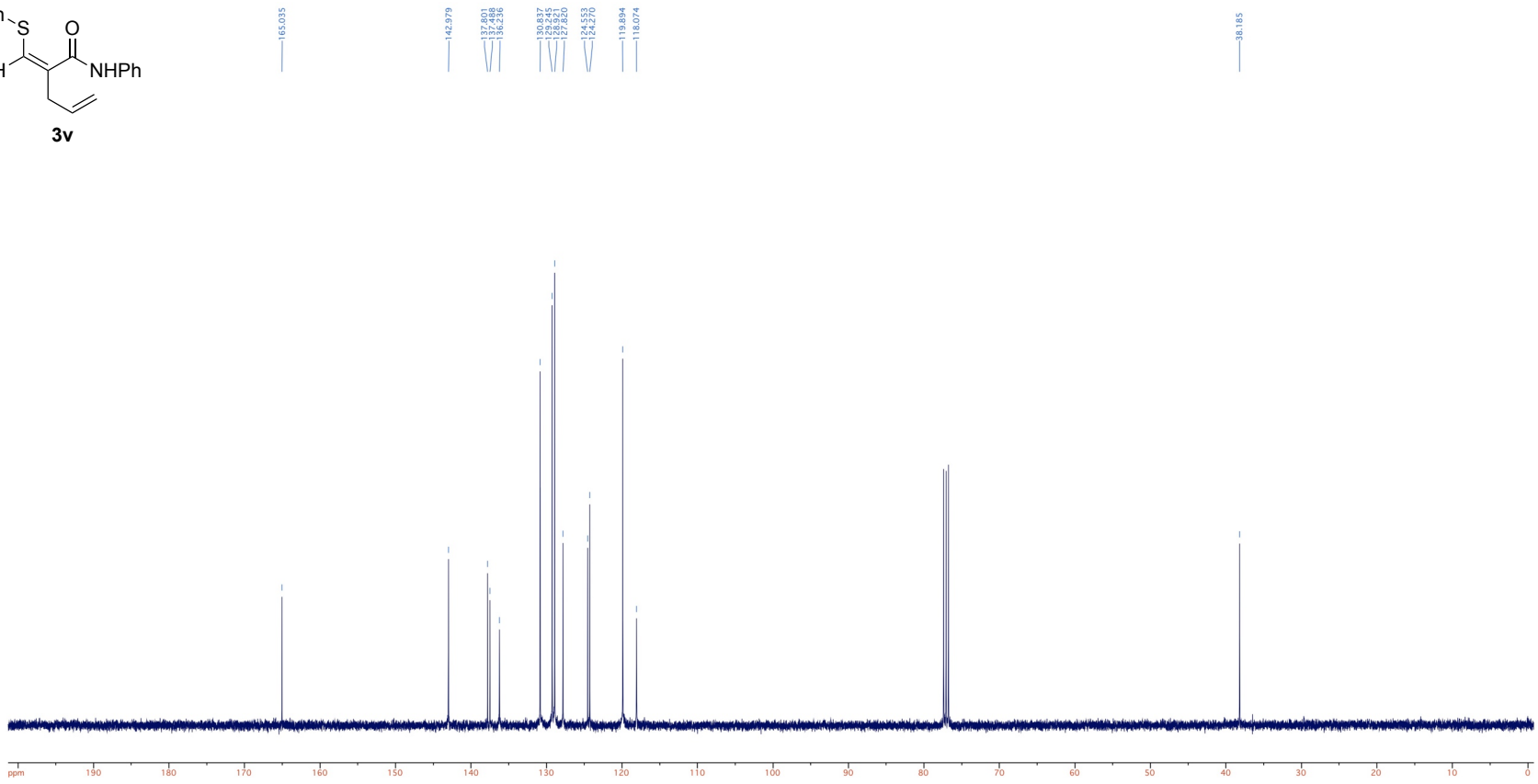


3v



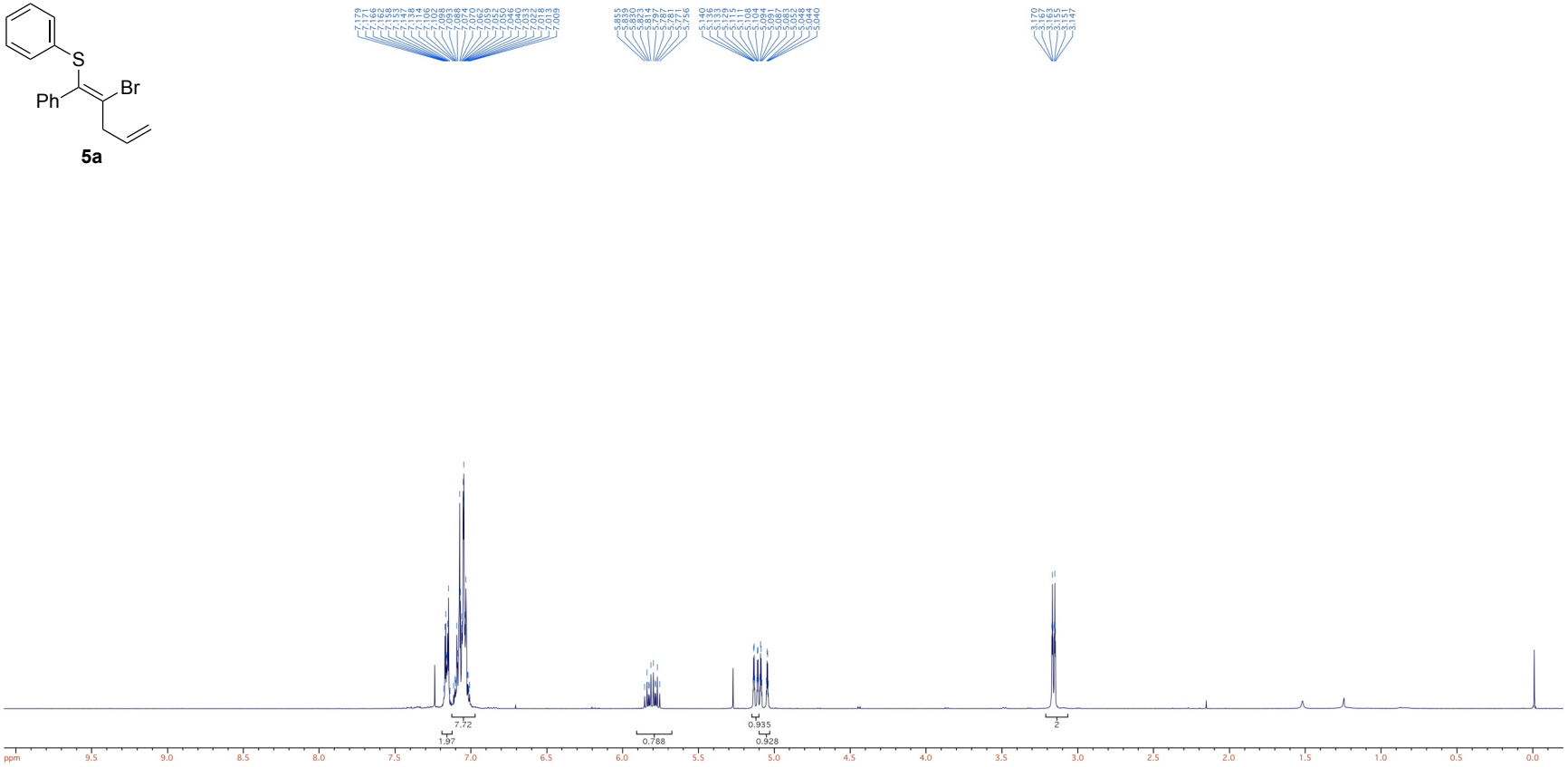

Ph
S
O
H
NHPh

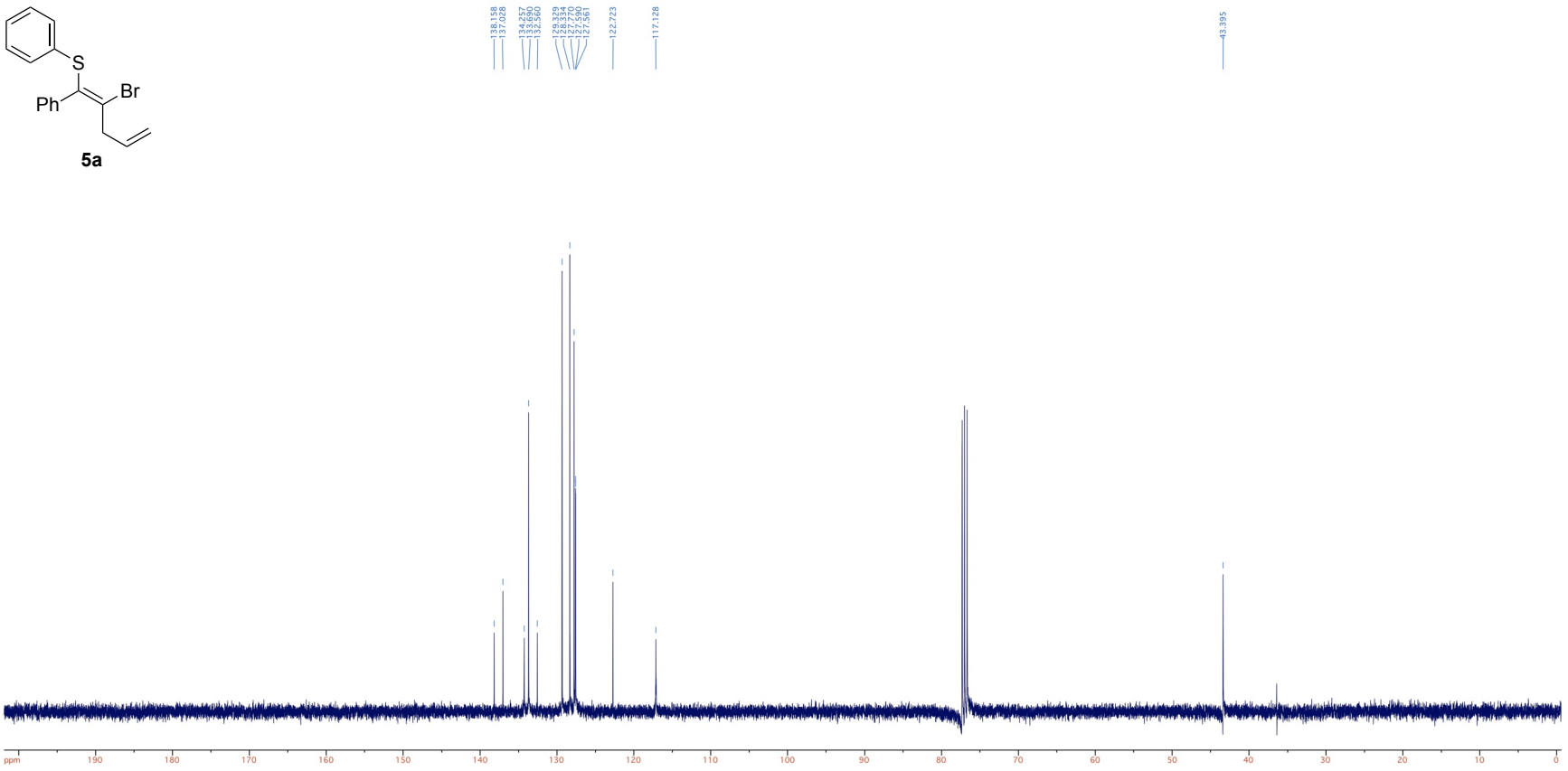
3v


165.035
142.979
137.801
137.488
136.236
130.837
129.345
128.241
127.820
124.553
124.270
119.894
118.074
38.185
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

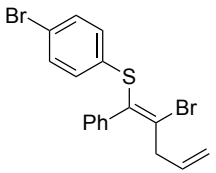
S
Ph
Br

5a

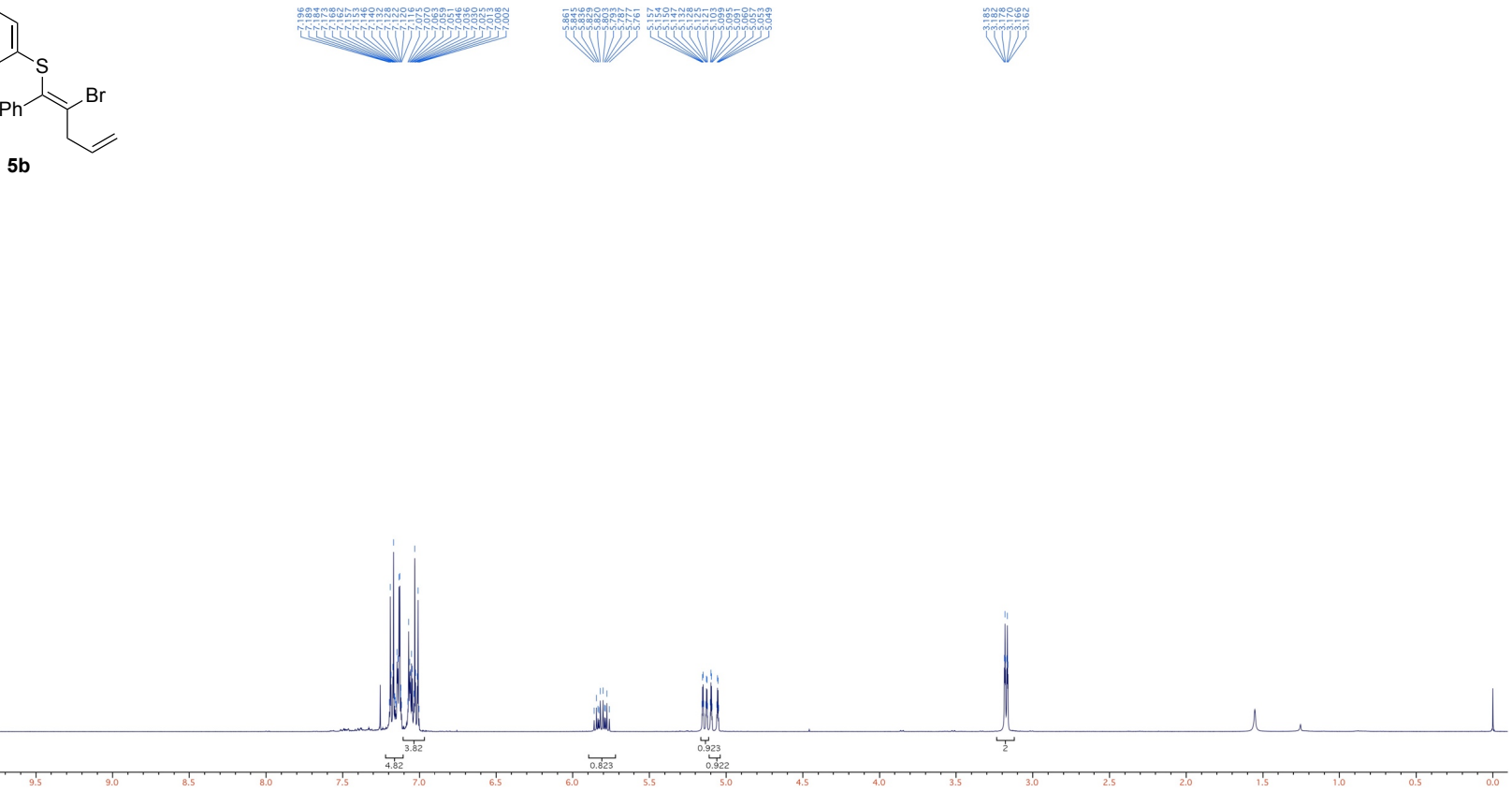

7.179
7.176
7.166
7.162
7.158
7.155
7.147
7.118
7.114
7.106
7.102
7.098
7.093
7.088
7.074
7.070
7.062
7.059
7.052
7.050
7.046
7.040
7.032
7.023
7.018
7.013
7.009
6.855
6.839
6.830
6.823
6.814
6.797
6.787
6.781
5.756
5.140
5.136
5.133
5.131
5.115
5.111
5.108
5.104
5.094
5.091
5.087
5.083
5.052
5.048
5.044
5.040
3.170
3.167
3.163
3.155
3.151
3.147
7.72
1.97
0.788
0.935
0.928
2
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

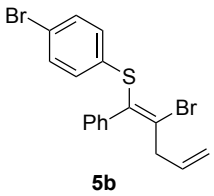

S
Ph
Br
138.158
137.028
134.257
133.690
132.560
129.329
129.134
127.770
127.590
127.561
122.723
117.128
43.395
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

5a

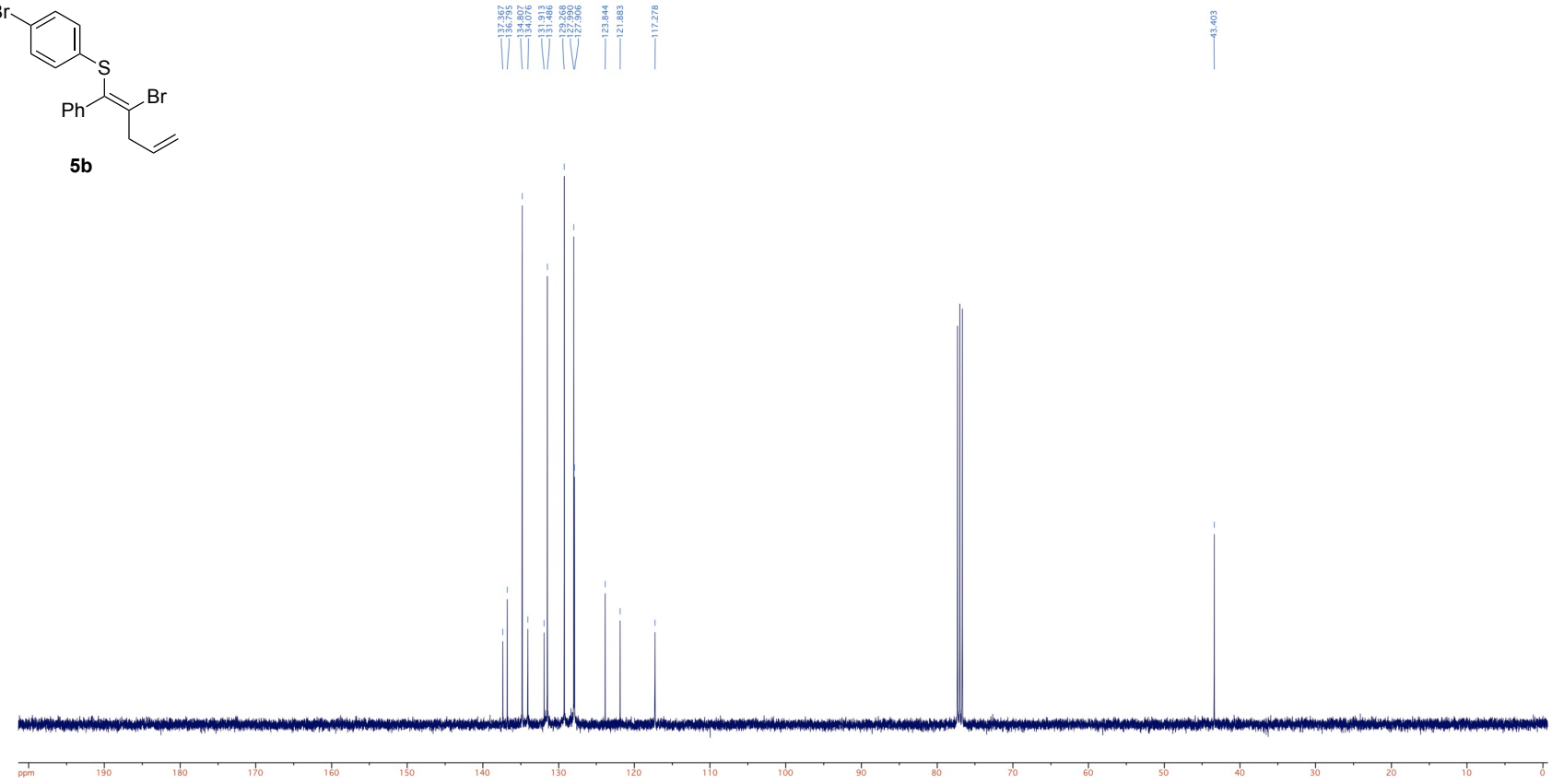

Br
S
Ph
Br

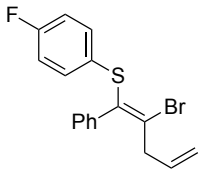
5b


7.196
7.189
7.184
7.178
7.173
7.168
7.162
7.157
7.151
7.146
7.140
7.132
7.128
7.125
7.120
7.116
7.075
7.070
7.065
7.059
7.051
7.046
7.036
7.030
7.025
7.013
7.008
7.002
5.861
5.845
5.836
5.829
5.820
5.793
5.787
5.777
5.761
3.185
3.182
3.178
3.170
3.166
3.162
4.82
3.82
0.823
0.923
0.922
2
ppm

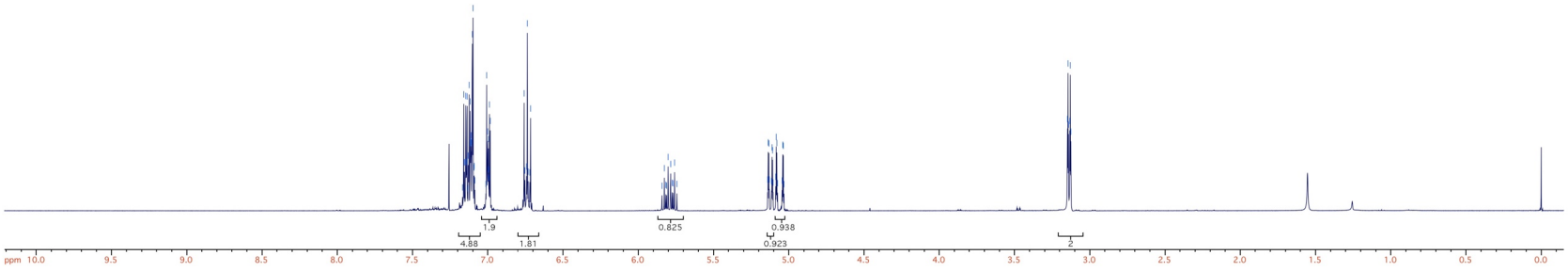

Br
S
Ph
Br

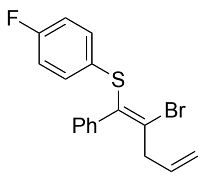
5b


137.367
136.795
134.877
134.076
131.913
131.486
129.268
129.060
127.906
123.844
121.883
117.278
43.403
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

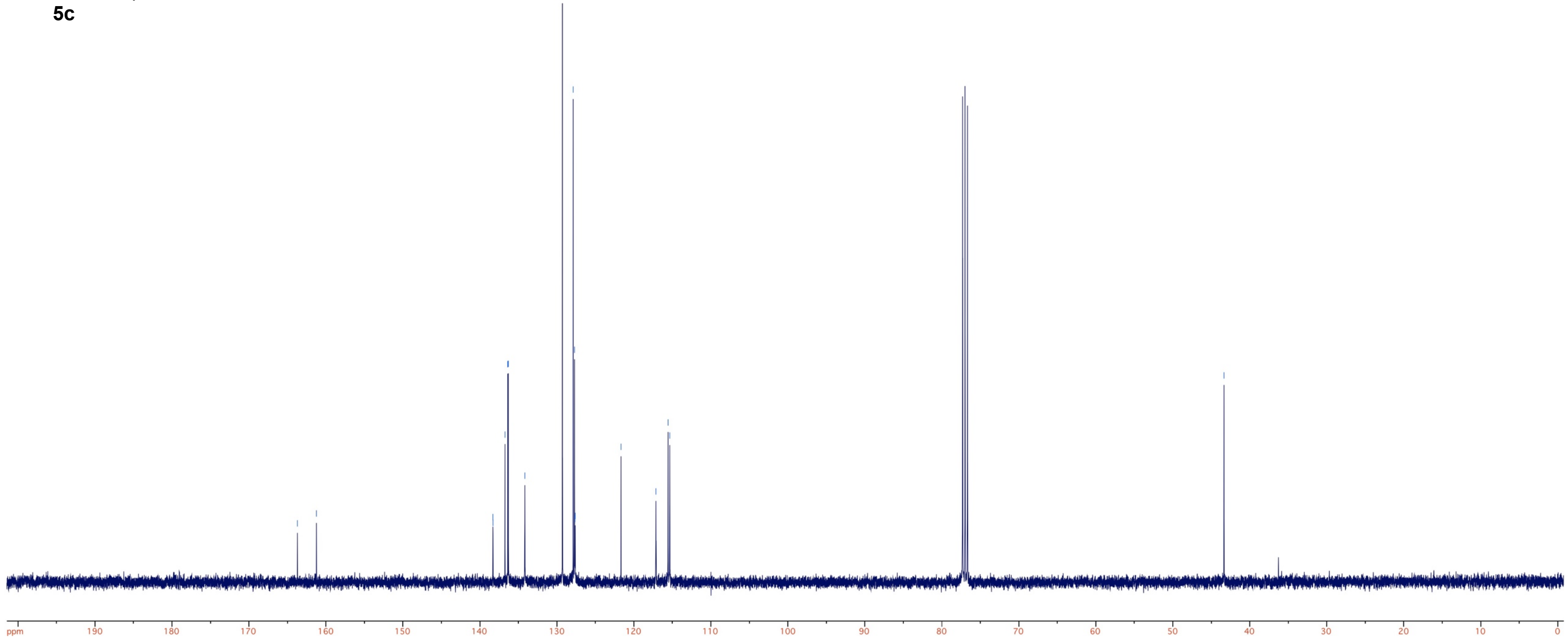


5c





5c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134.160
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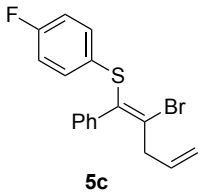
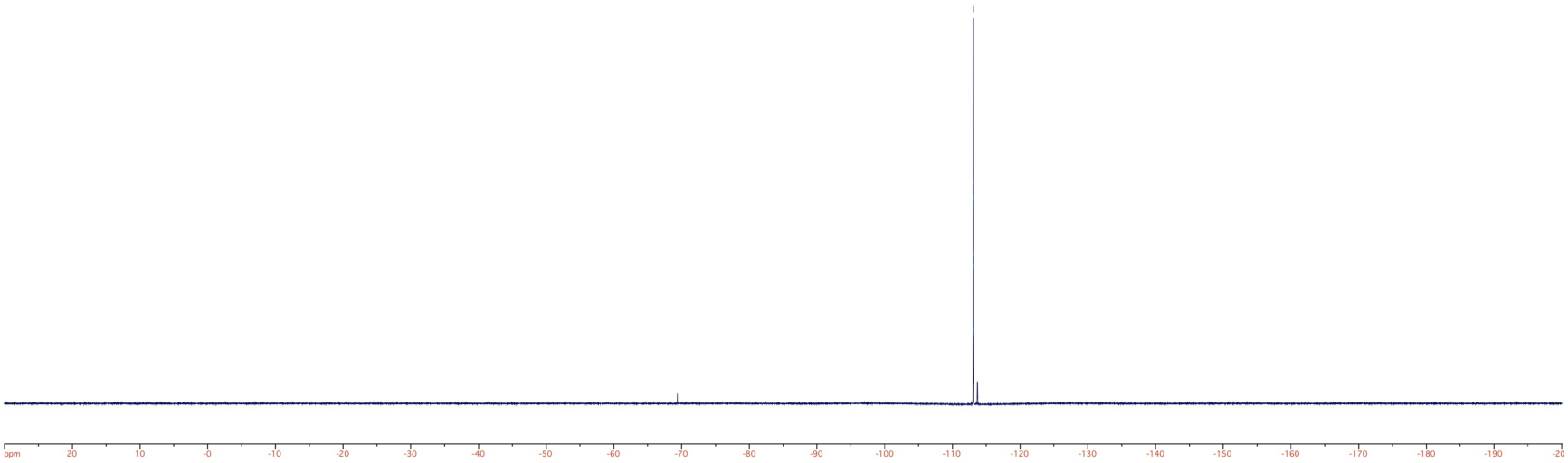
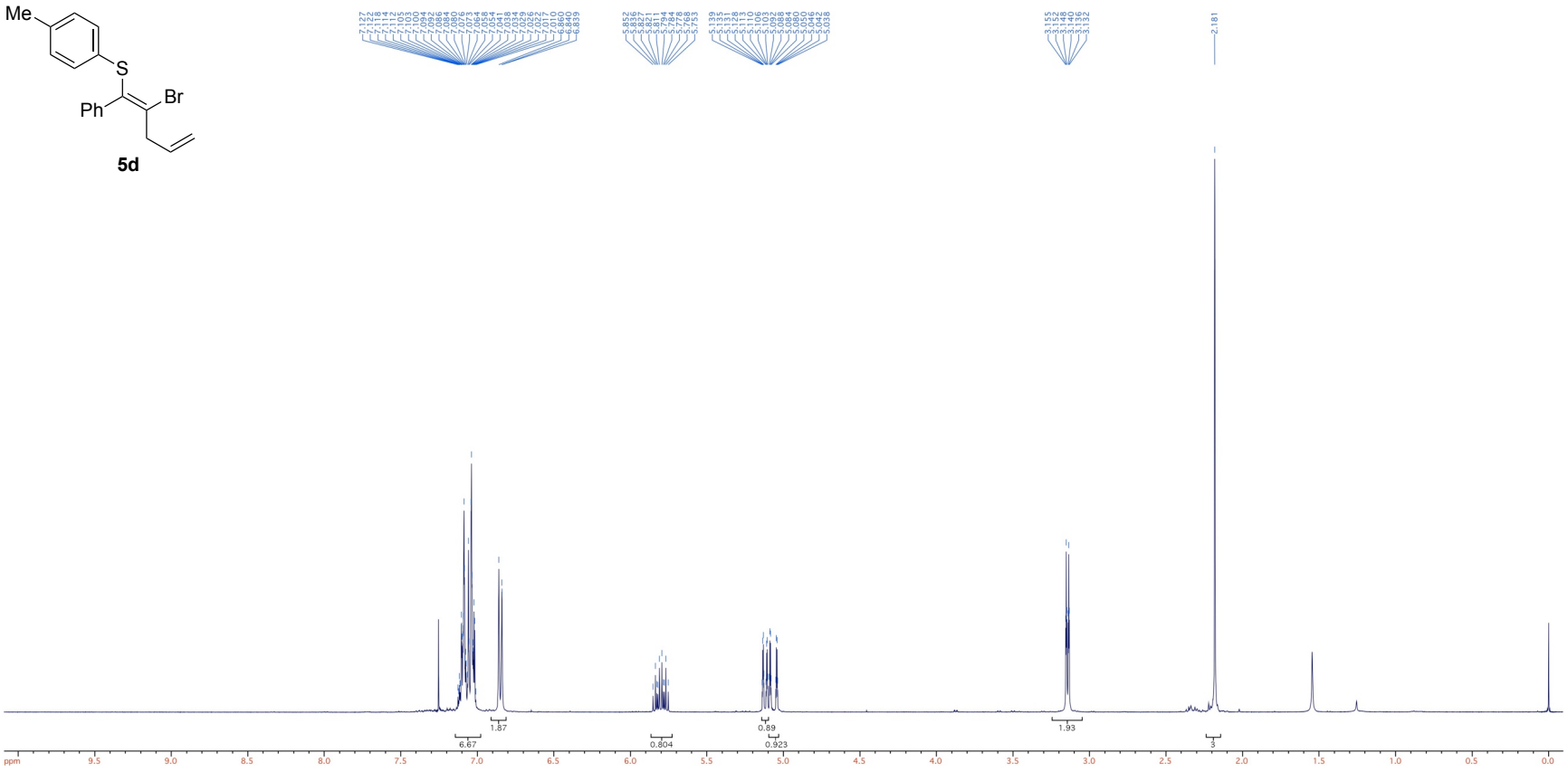
127.710
127.654
127.620
121.670
117.138
115.558
115.339
43.349
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


F
S
Ph
Br

5c


113.055
113.069
113.080
113.093
113.107
113.115
113.129


ppm
20
10
-0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190


Me
S
Ph
Br
5d
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7.118
7.114
7.112
7.105
7.103
7.100
7.094
7.092
7.086
7.084
7.080
7.076
7.073
7.064
7.056
7.054
7.041
7.038
7.034
7.029
7.026
7.017
7.010
6.860
6.840
6.839
5.852
5.836
5.827
5.821
5.811
5.794
5.784
5.778
5.768
5.753
5.139
5.135
5.131
5.128
5.113
5.110
5.106
5.103
5.092
5.088
5.084
5.080
5.050
5.046
5.042
5.038
3.155
3.152
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0.89
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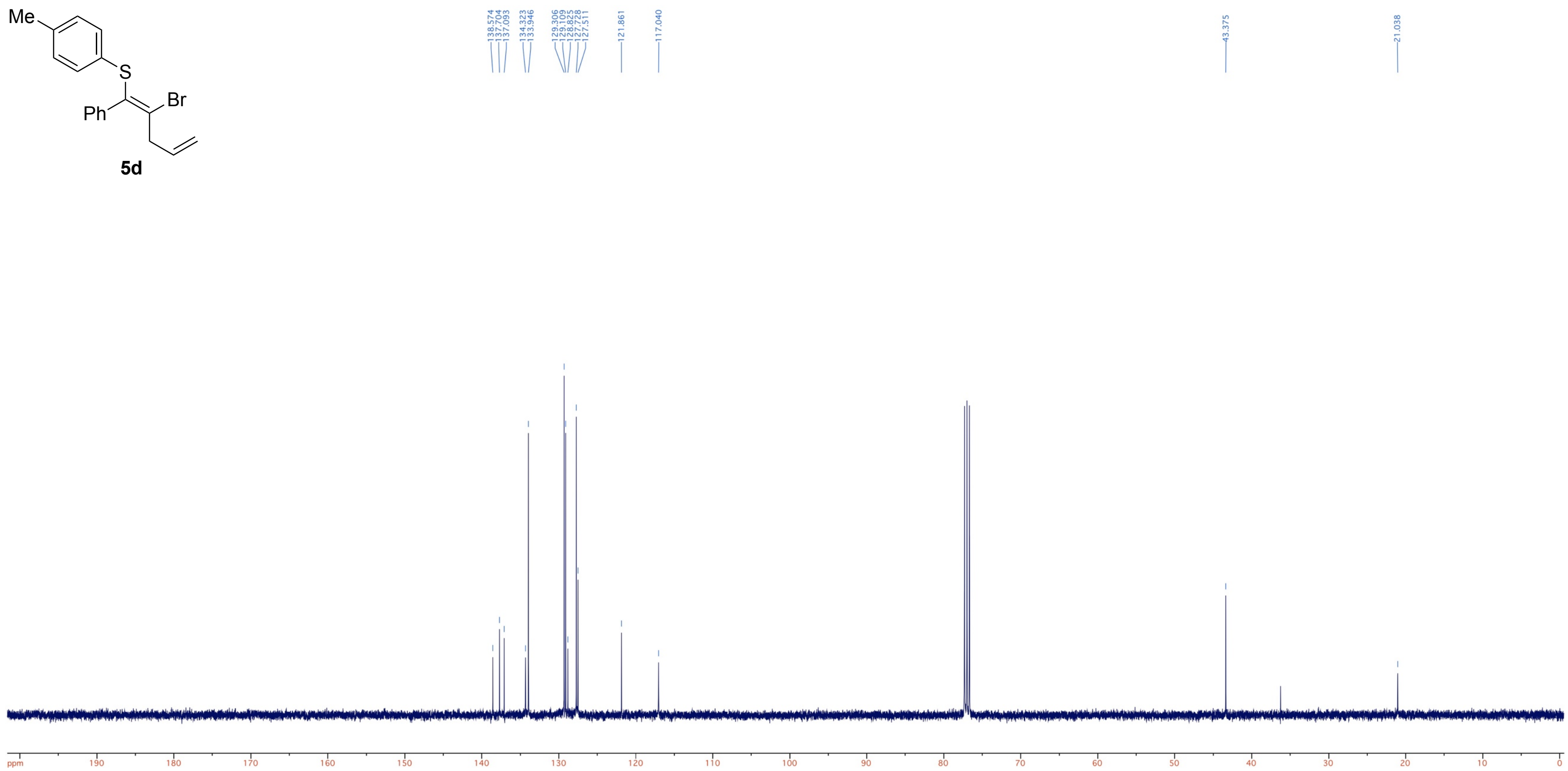
1.93
3
ppm


Me
S
Br
Ph
5d
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133.946
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129.109
128.825
127.728
127.511
121.861
117.040
43.375
21.038
ppm
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150
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110
100
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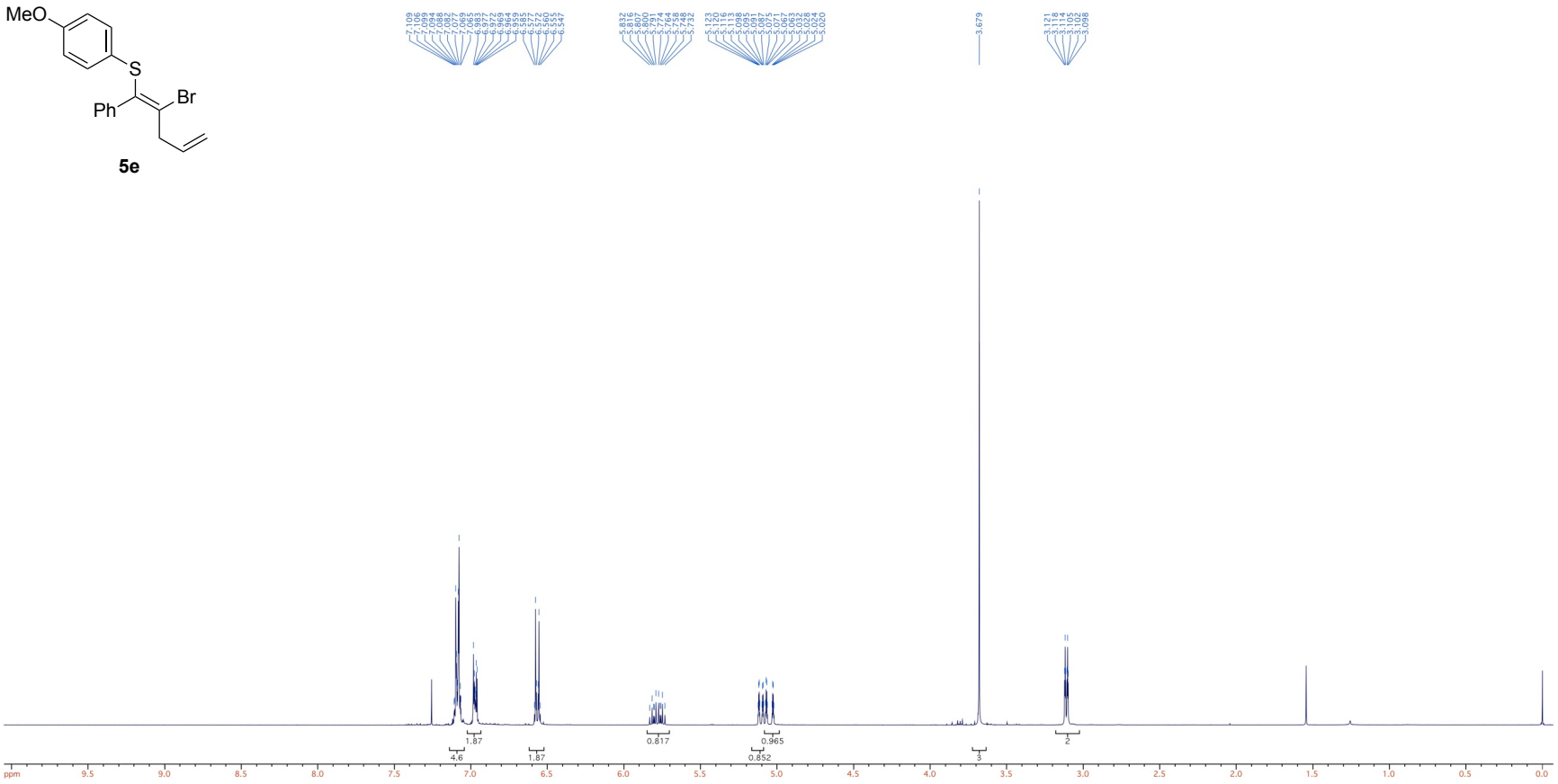
80
70
60
50
40
30
20
10
0


MeO
S
Ph
Br
5e
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7.106
7.099
7.094
7.088
7.082
7.072
7.069
7.065
6.983
6.977
6.972
6.669
6.664
6.659
6.577
6.572
6.560
6.555
6.547
5.832
5.816
5.807
5.800
5.791
5.764
5.758
5.749
5.732
5.123
5.120
5.115
5.098
5.095
5.091
5.087
5.075
5.071
5.067
5.063
5.031
5.028
5.024
5.020
3.679
3.121
3.118
3.114
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0.852
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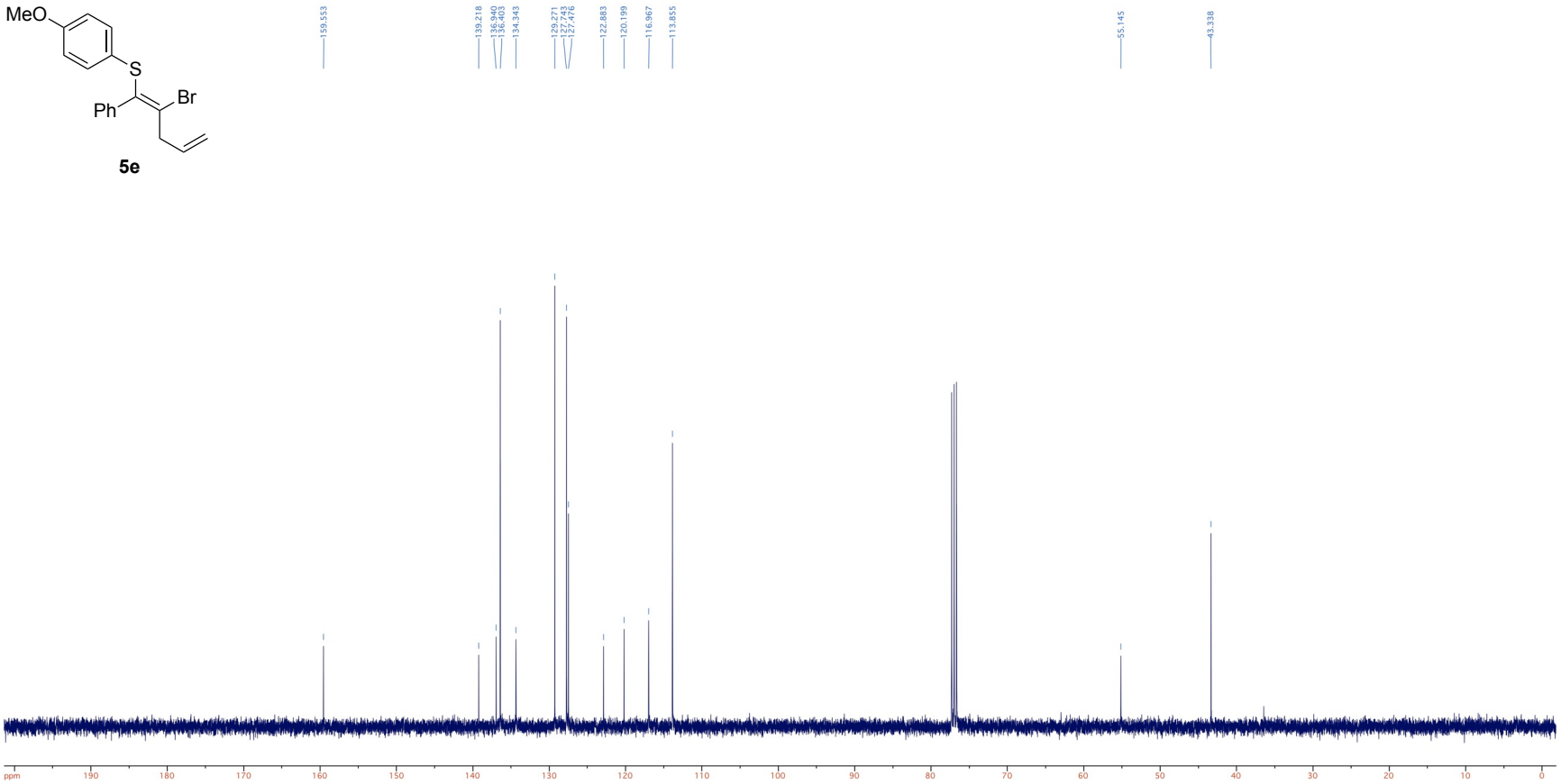
2
ppm


MeO
S
Ph
Br
5e
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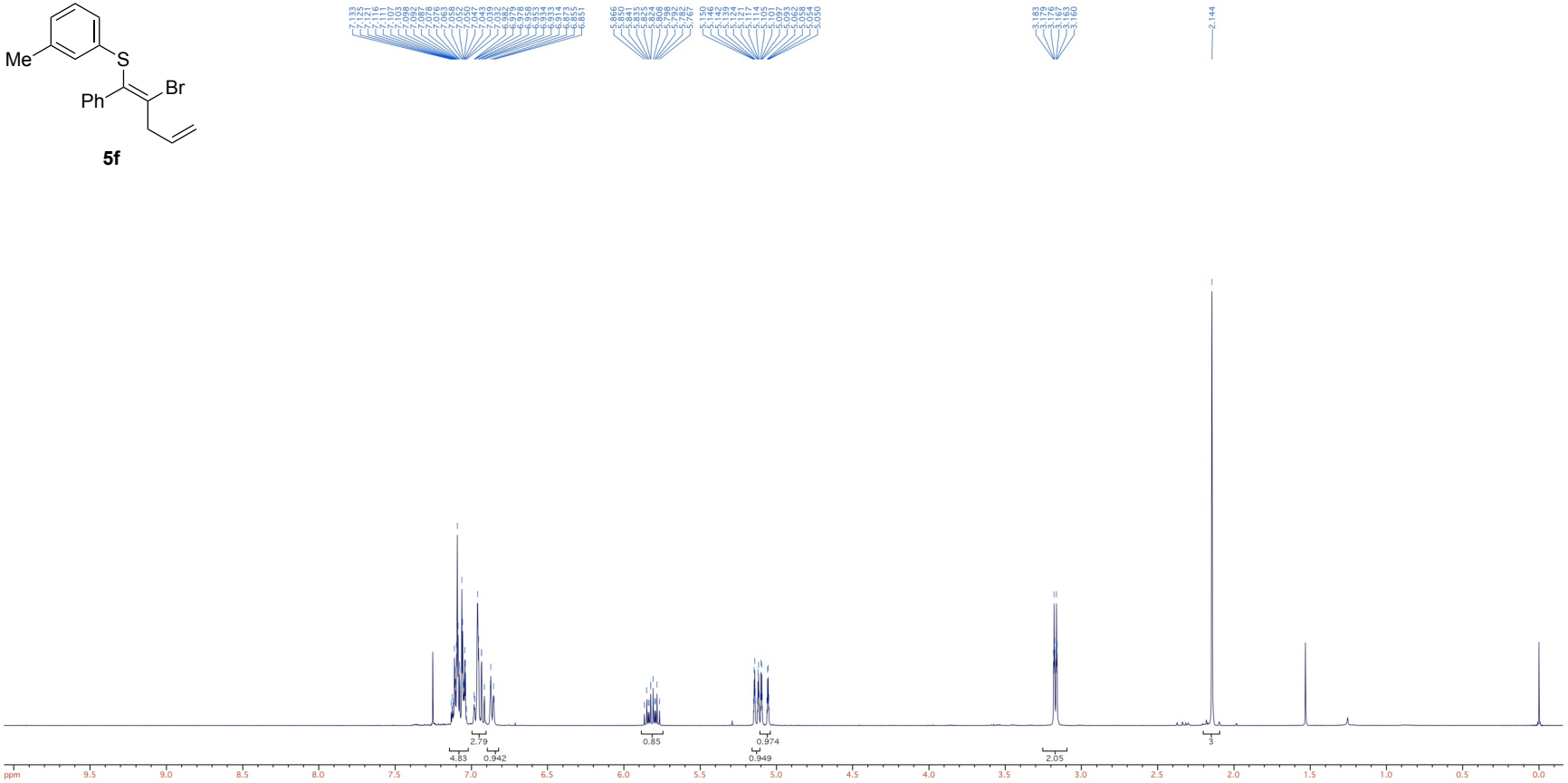
136.940
136.403
134.343
129.271
127.748
127.476
122.883
120.199
116.967
113.655
55.145
43.338
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Me
S
Ph
Br

5f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7.125
7.121
7.116
7.111
7.107
7.103
7.098
7.092
7.087
7.078
7.076
7.063
7.058
7.052
7.050
7.047
7.043
7.039
7.032
6.982
6.979
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6.958
6.955
6.934
6.933
6.914
6.873
6.857
6.851
5.866
5.850
5.841
5.835
5.825
5.824
5.808
5.798
5.792
5.782
5.767
5.150
5.146
5.142
5.139
5.124
5.121
5.117
5.114
5.105
5.101
5.097
5.093
5.062
5.058
5.054
5.050
3.193
3.189
3.176
3.167
3.163
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2.144
2.79
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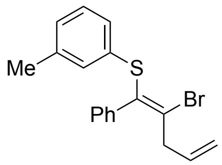
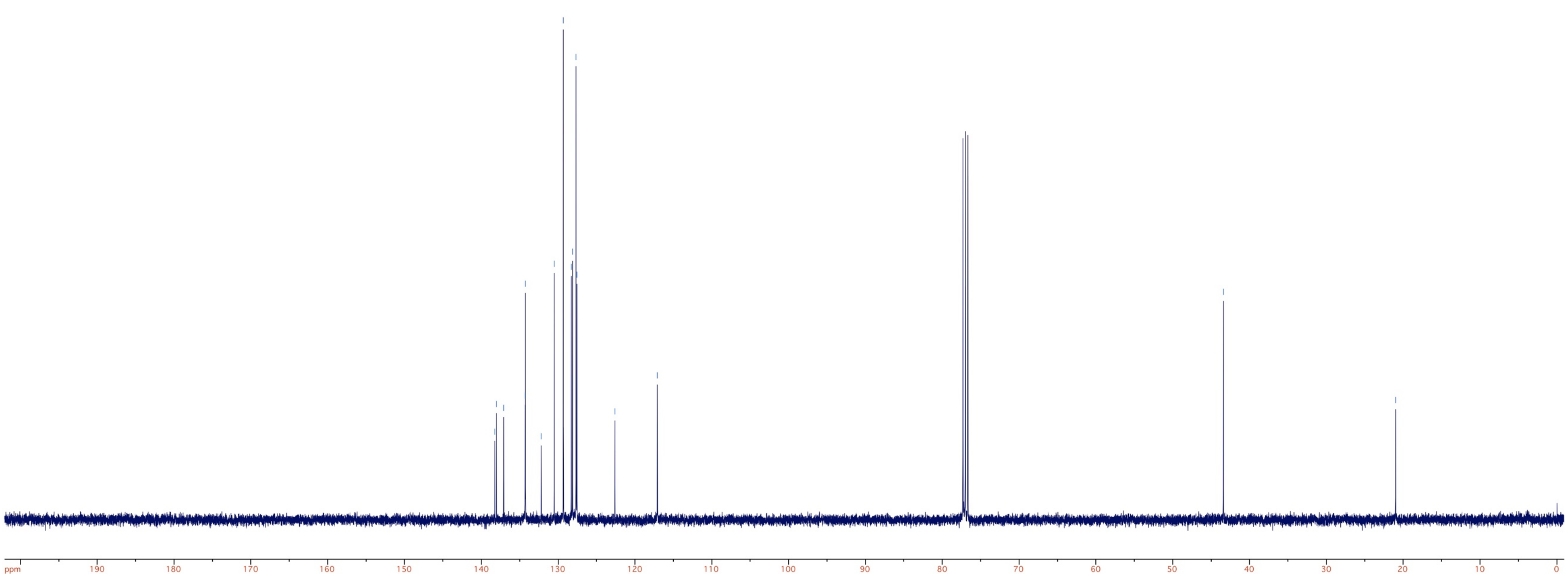
0.85
0.974
0.949
2.05
3
ppm



5f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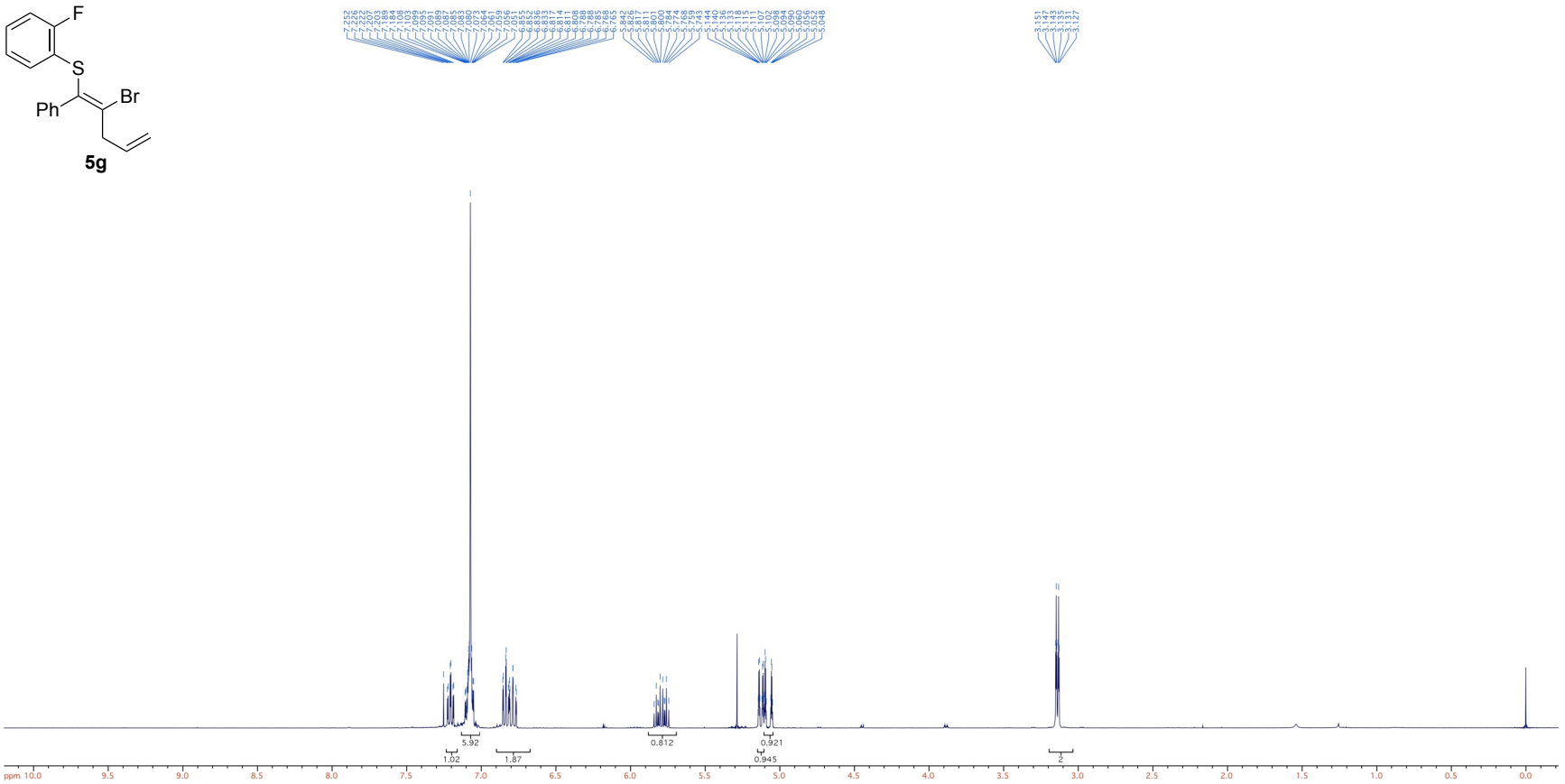
137.082
134.299
134.259
132.206
130.510
129.325
128.292
128.123
127.671
127.552
122.602
117.083
43.402
20.977
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


F
S
Ph
Br
5g
5.92
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1.87
0.812
0.921
0.945
2
ppm 10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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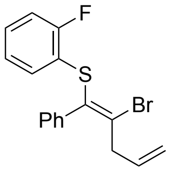
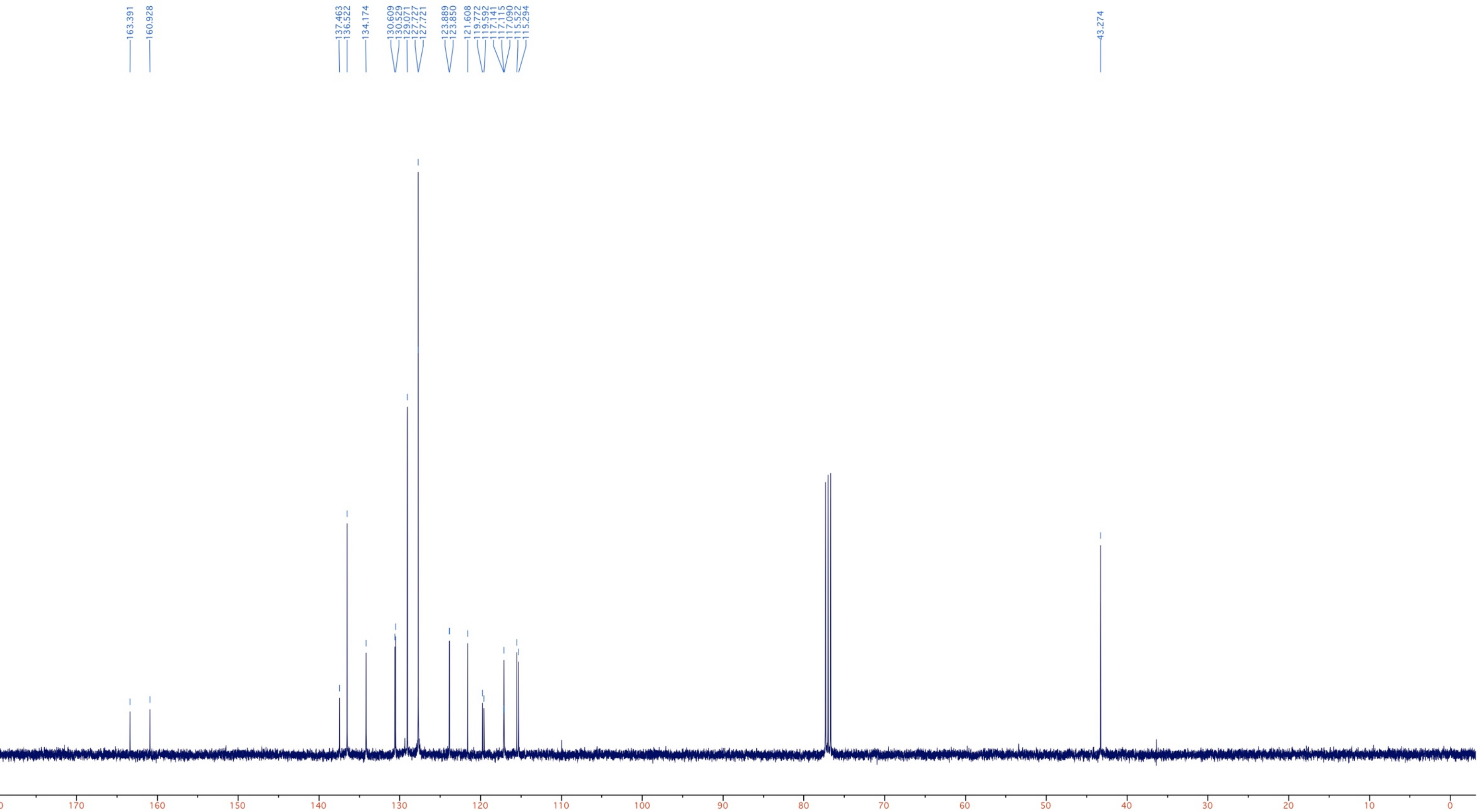
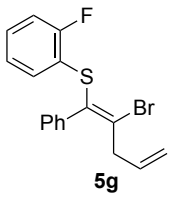
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



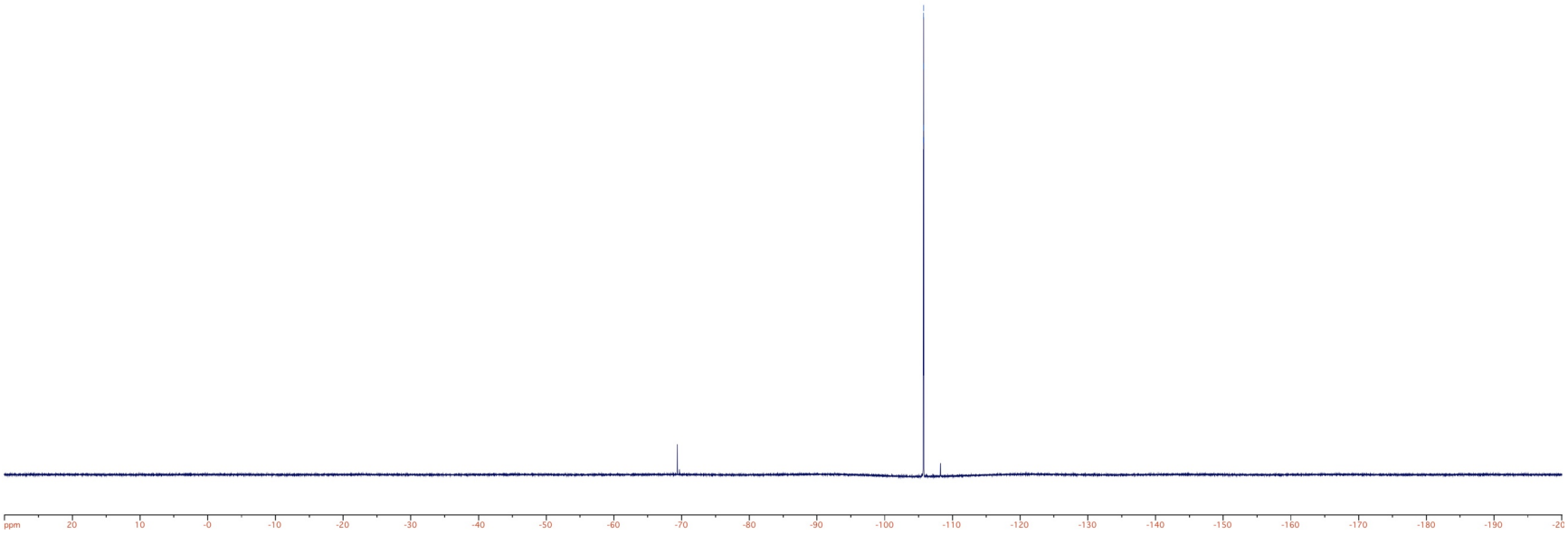
5g




F
S
Ph
Br

5g


105.705
105.727
105.735
105.739
105.746
105.761


ppm
20
10
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-10
-20
-30
-40
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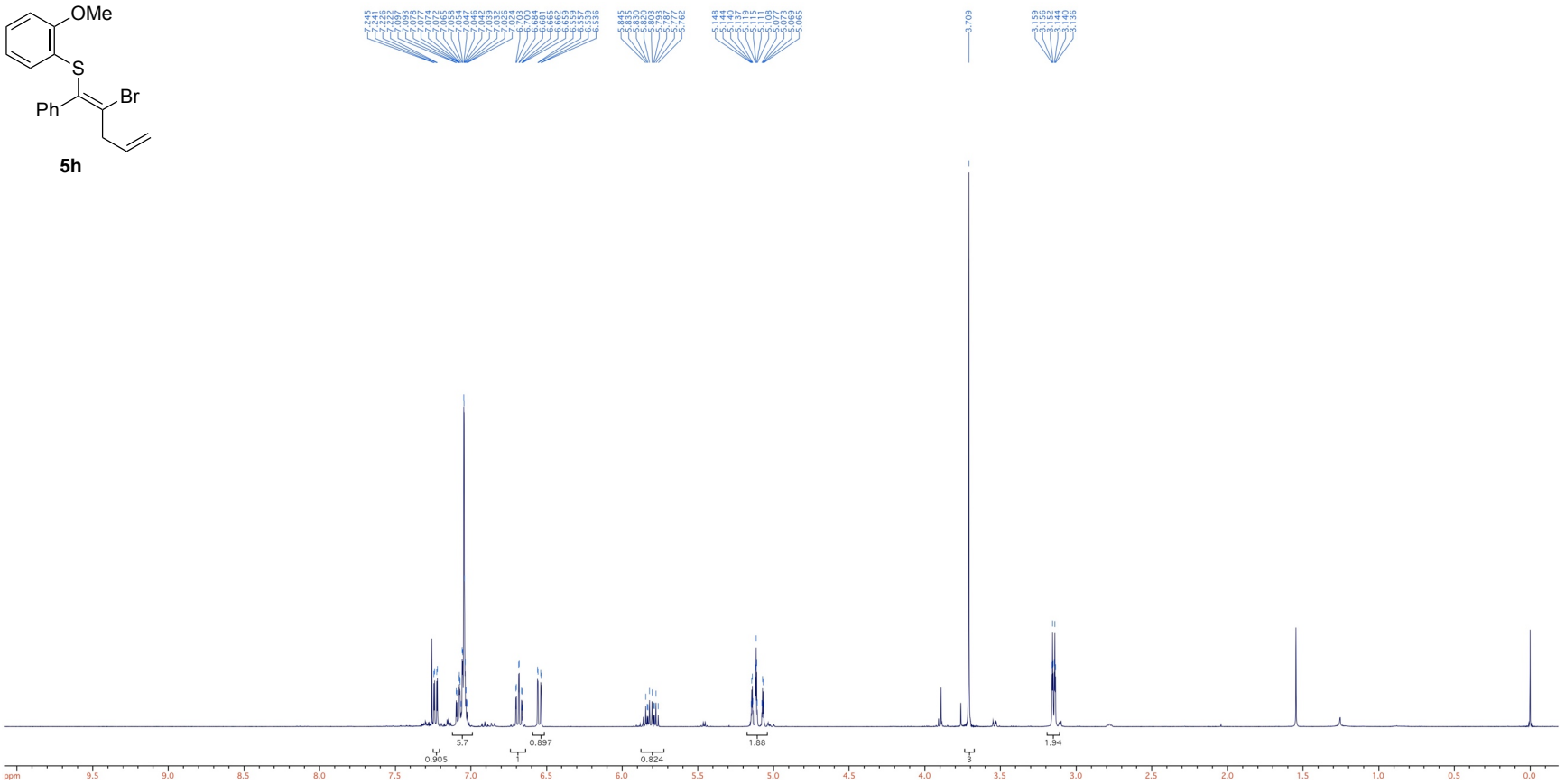
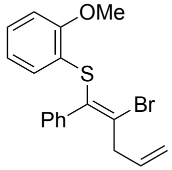
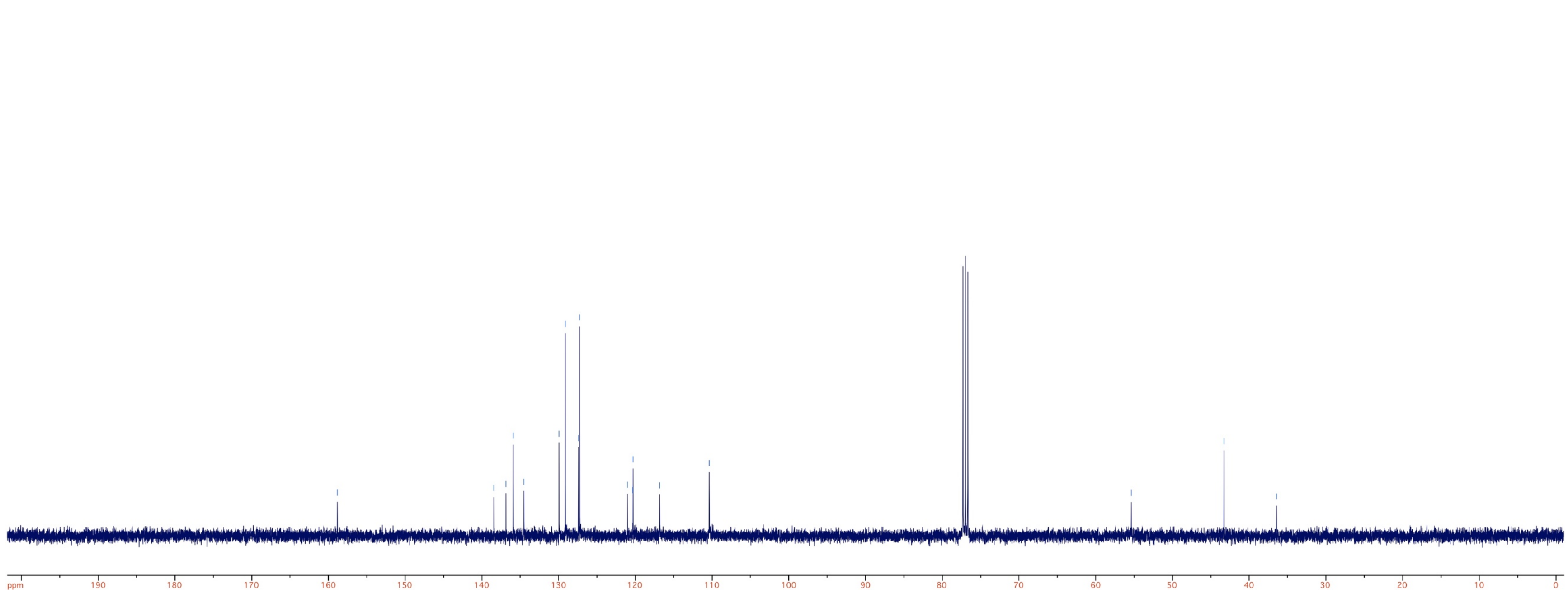
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190


OMe
S
Ph
Br
5h
7.245
7.241
7.236
7.227
7.222
7.093
7.079
7.077
7.074
7.072
7.065
7.058
7.054
7.047
7.044
7.042
7.039
7.032
7.026
7.024
6.704
6.700
6.684
6.681
6.665
6.659
6.559
6.557
6.538
5.845
5.835
5.820
5.803
5.793
5.787
5.762
5.148
5.144
5.140
5.137
5.119
5.115
5.111
5.108
5.077
5.073
5.069
5.065
3.709
3.159
3.156
3.152
3.144
3.140
3.136
0.905
5.7
1
0.897
0.824
1.88
3
1.94
ppm


OMe
S
Br
Ph

5h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136.869
135.907
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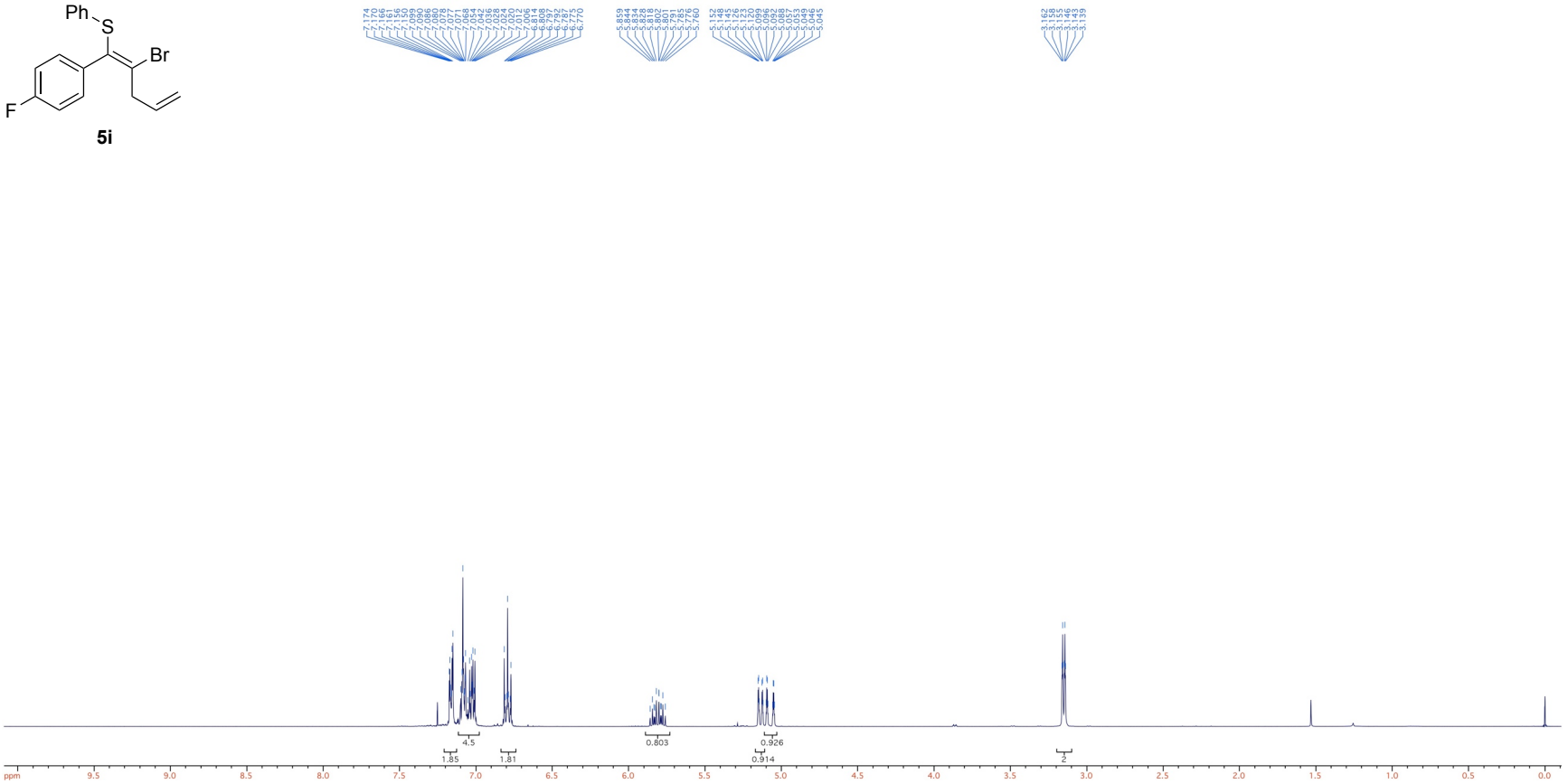
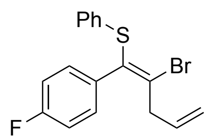
127.409
127.243
121.024
120.340
120.299
116.839
110.371
55.355
43.284
36.438
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

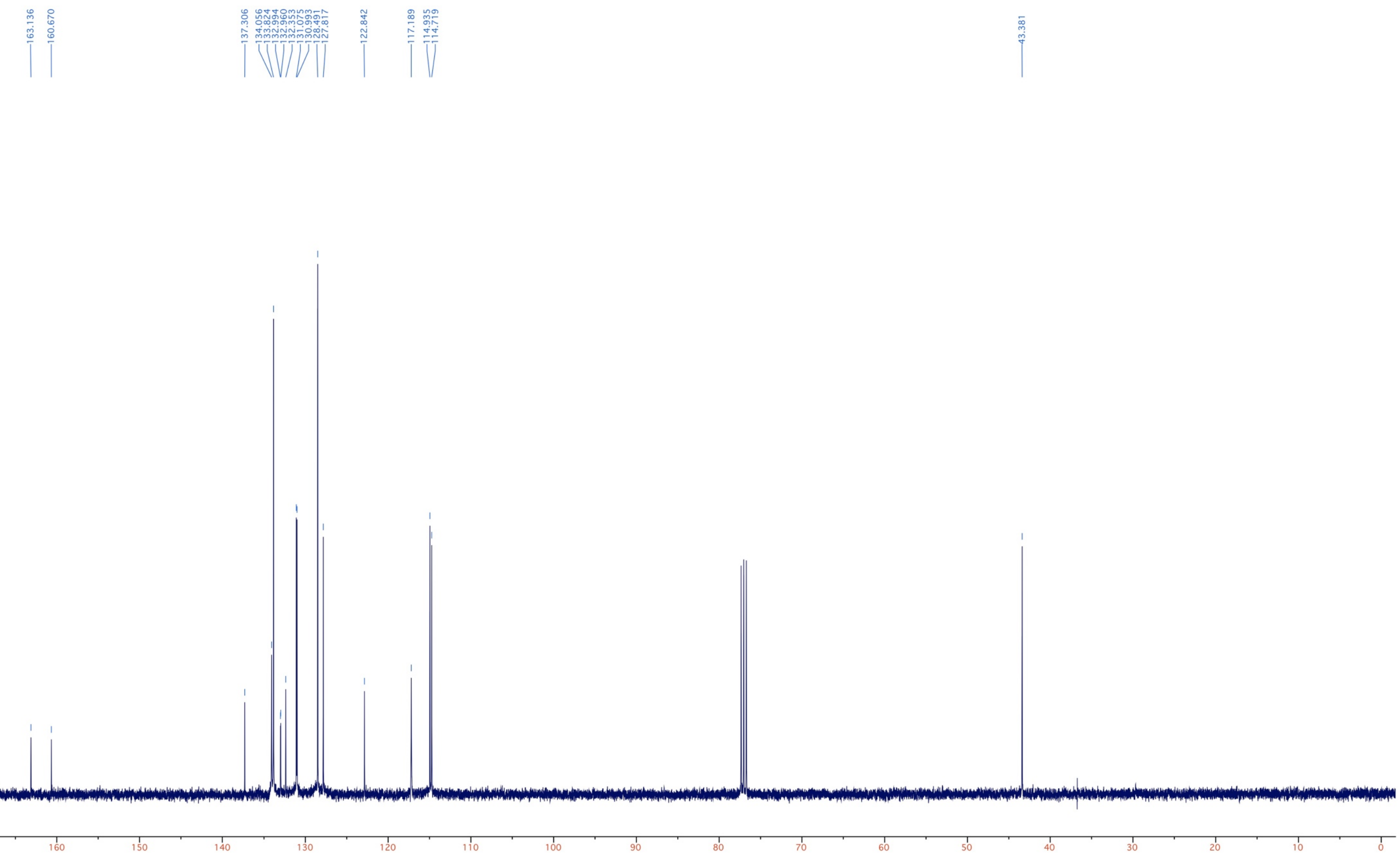
Ph
S
Br
F

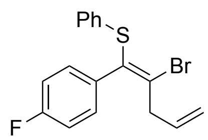
5i


7.174
7.170
7.166
7.161
7.155
7.150
7.099
7.095
7.086
7.080
7.078
7.077
7.071
7.068
7.064
7.042
7.036
7.030
7.024
7.020
7.012
7.006
7.004
6.808
6.807
6.792
6.757
6.755
6.770
5.859
5.854
5.844
5.828
5.818
5.802
5.801
5.791
5.785
5.776
5.760
5.152
5.148
5.145
5.126
5.123
5.120
5.099
5.096
5.089
5.088
5.077
5.053
5.049
5.048
5.045
3.162
3.156
3.155
3.146
3.143
3.139
4.5
1.85
1.81
0.803
0.926
0.914
2
ppm

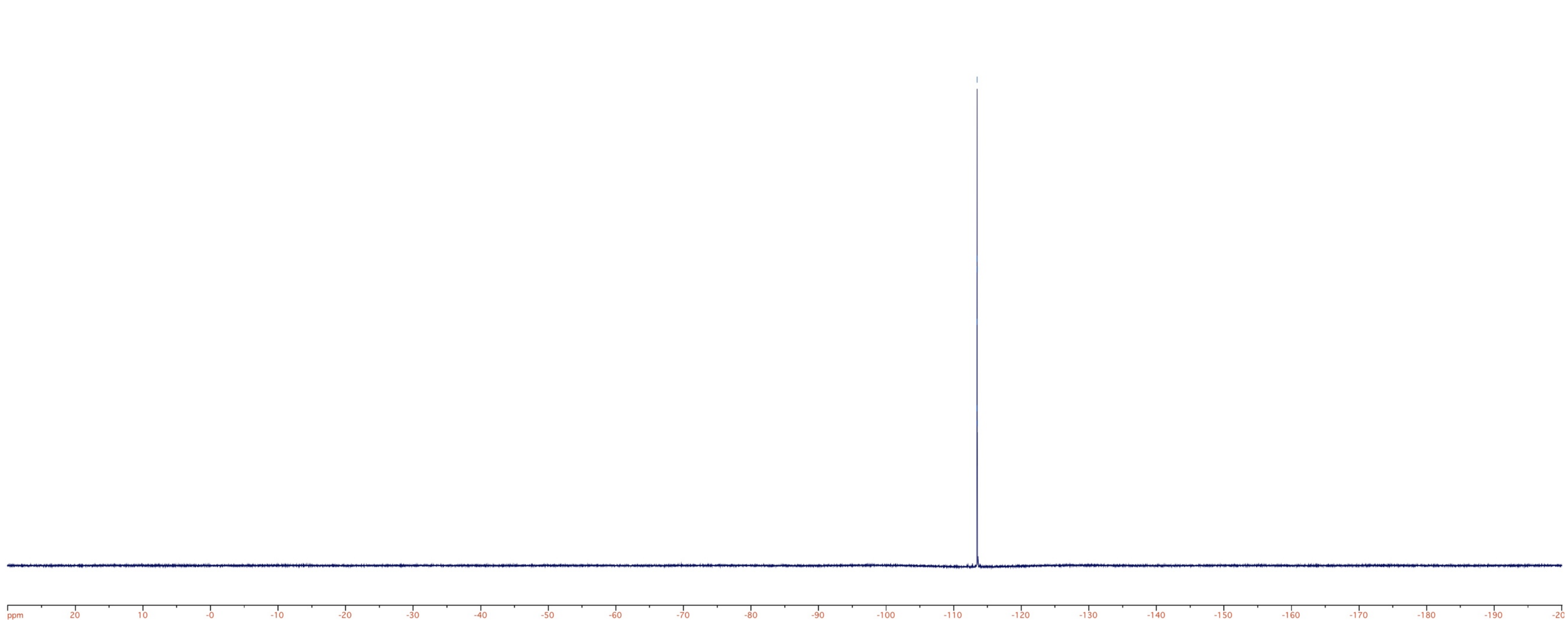


5i

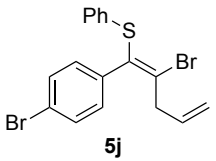

163.136
160.670
137.306
134.056
133.824
132.994
132.960
132.353
131.075
130.993
128.491
127.817
122.842
117.189
114.935
114.719
43.381
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



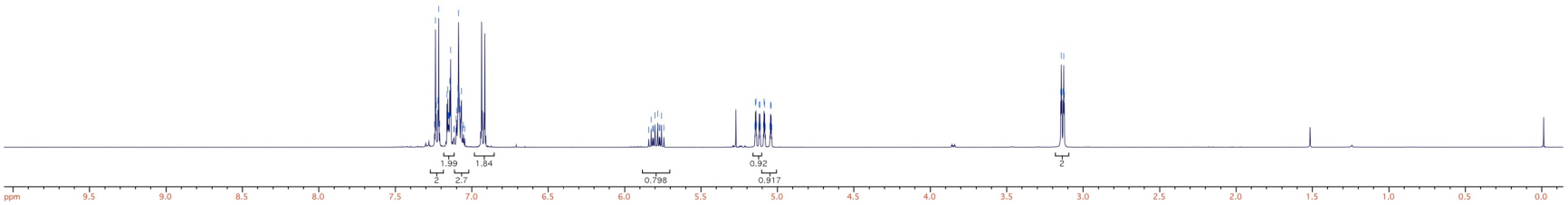
5i

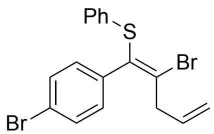


-113.438
-113.452
-113.463
-113.476
-113.497
-113.512
ppm
20
10
-0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20

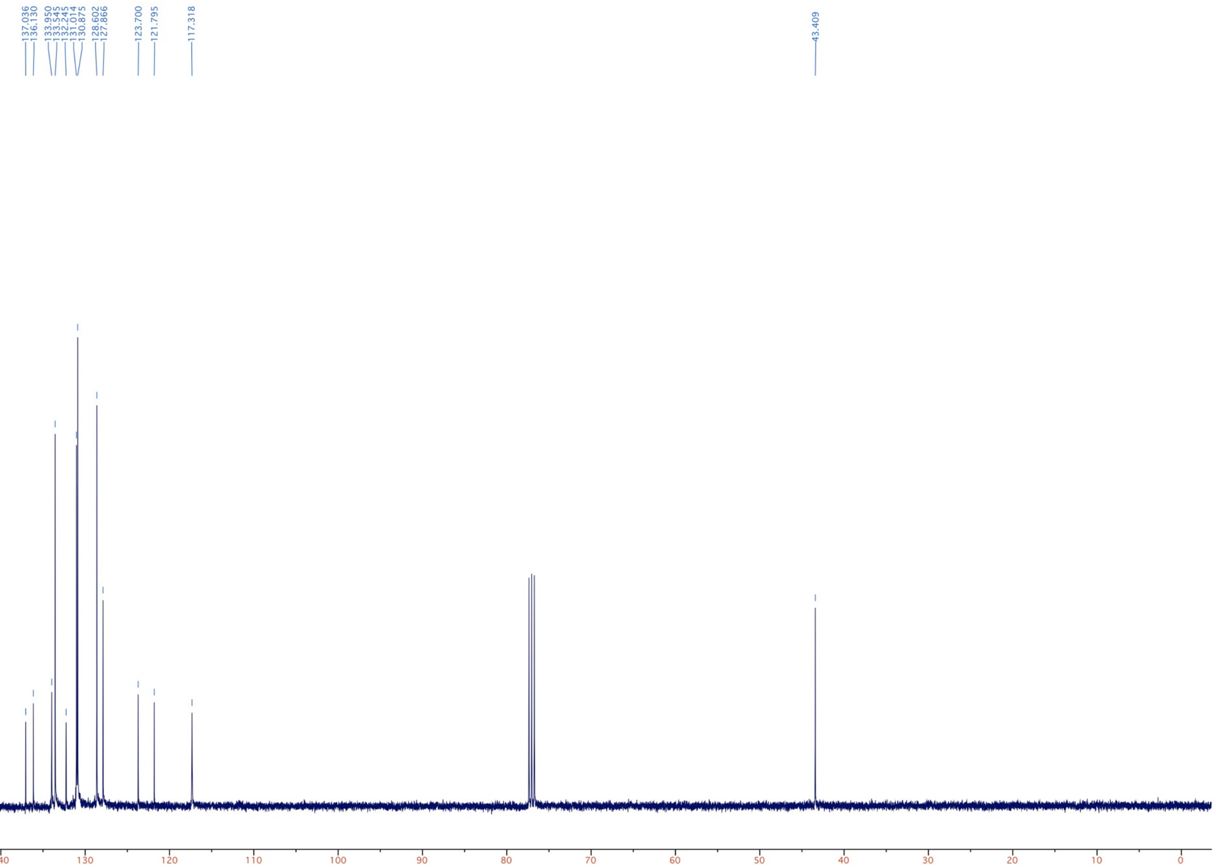


5j




Ph
S
Br
Br

5j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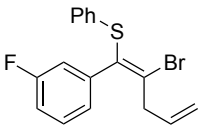
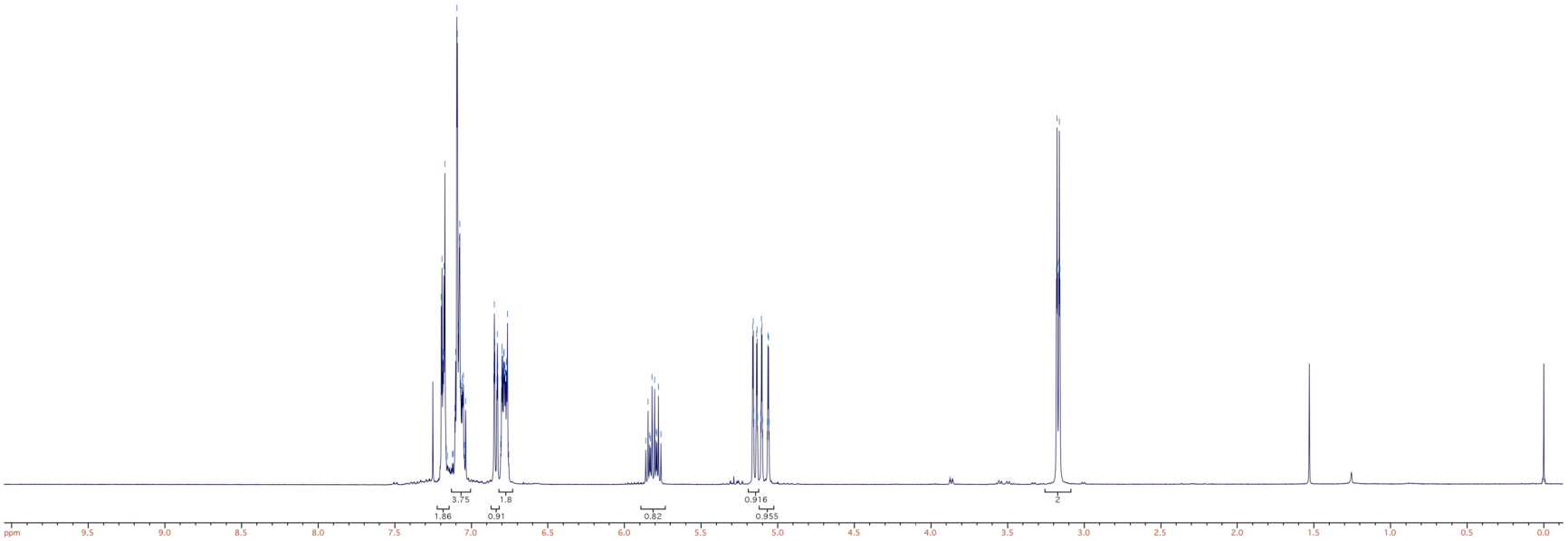
133.545
132.245
131.014
130.875
128.602
127.866
123.700
121.795
117.318
43.409
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

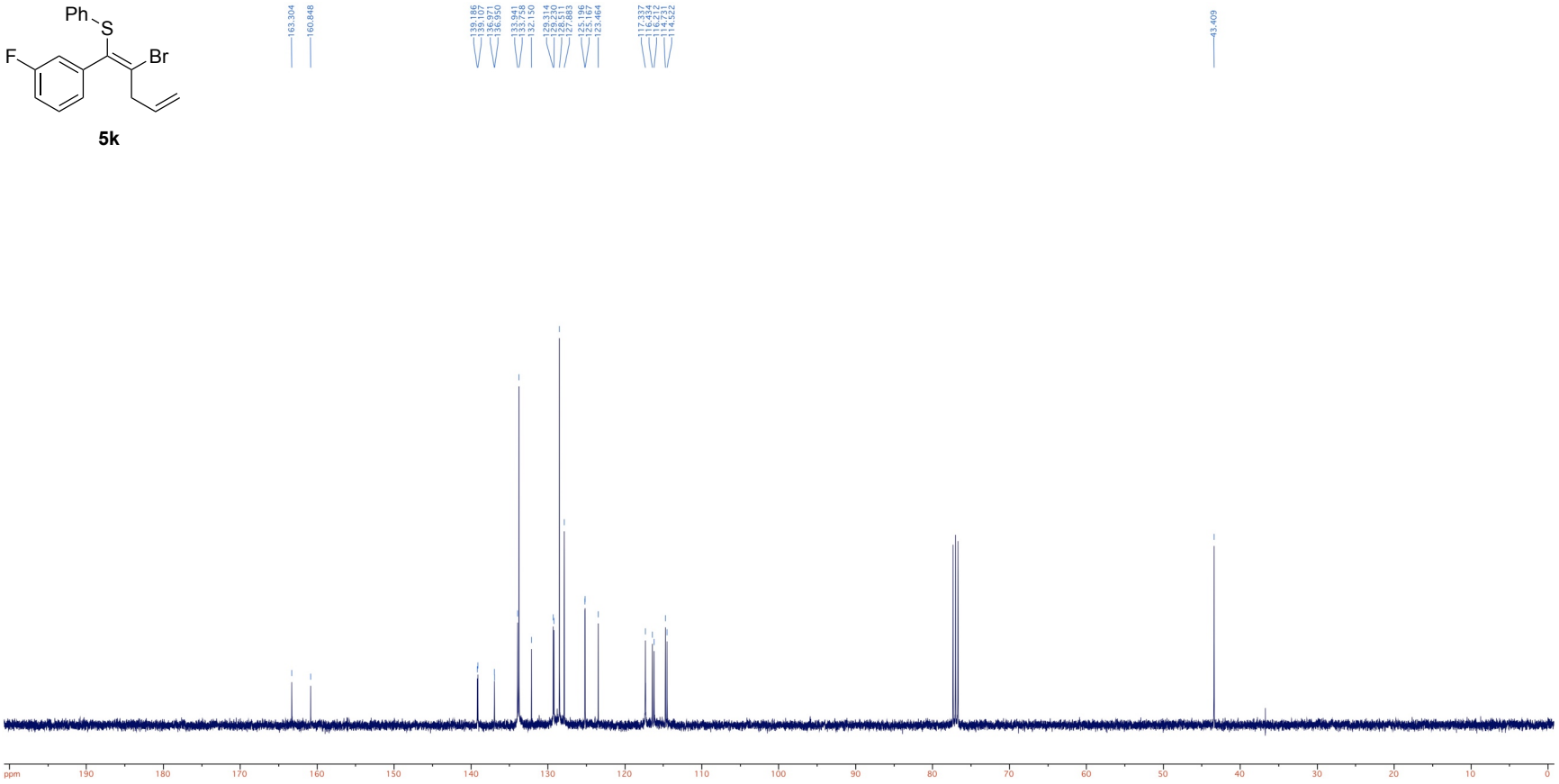


5k



Ph
S
F
Br

5k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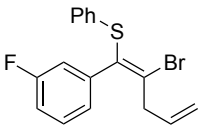
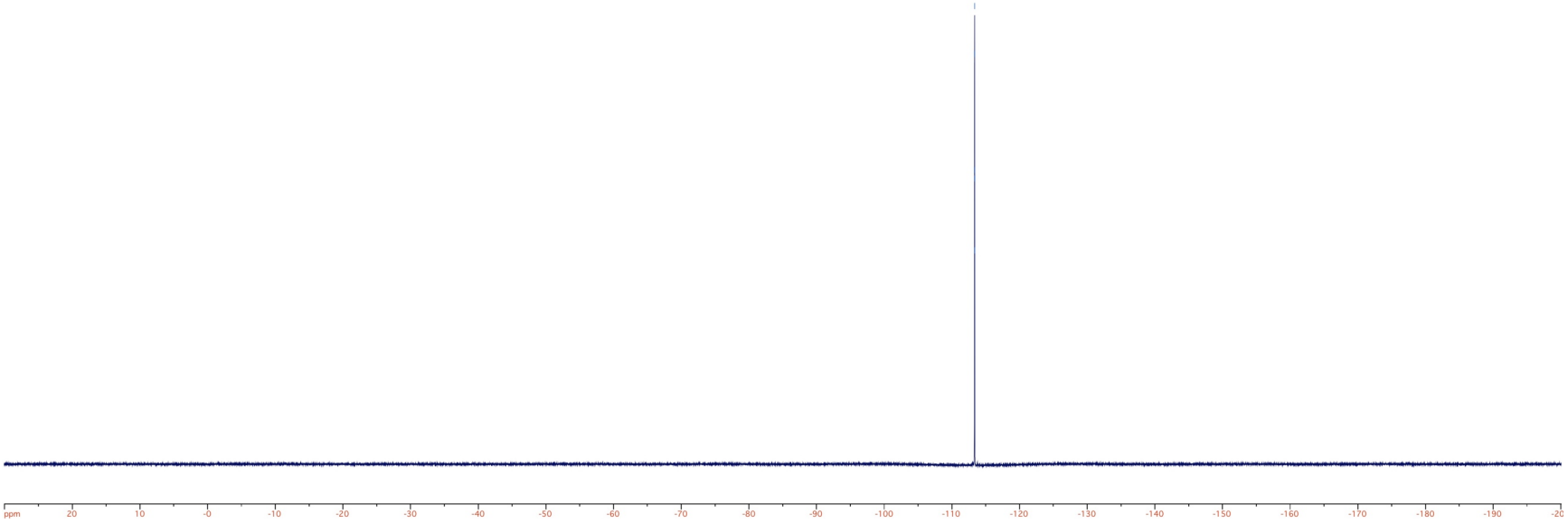
139.107
136.971
136.950
133.941
133.798
132.150
129.314
129.230
128.811
127.883
125.196
125.167
123.464
117.337
117.244
116.212
116.121
114.231
114.222
43.409
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Ph
S
F
Br

5k


-113.332
-113.356
-113.371
-113.381
-113.395


ppm
20
10
0
-10
-20
-30
-40
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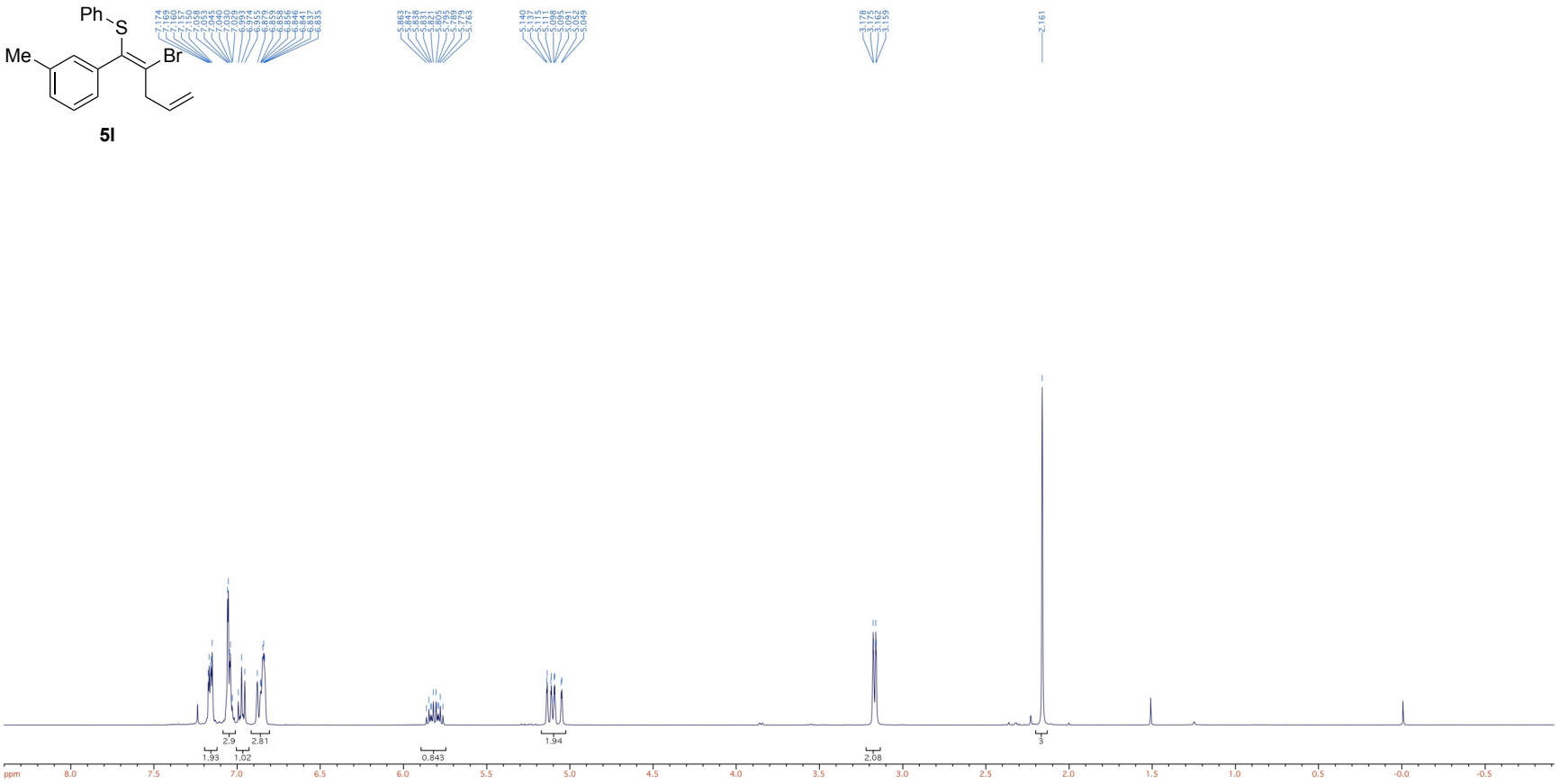
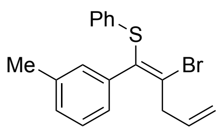
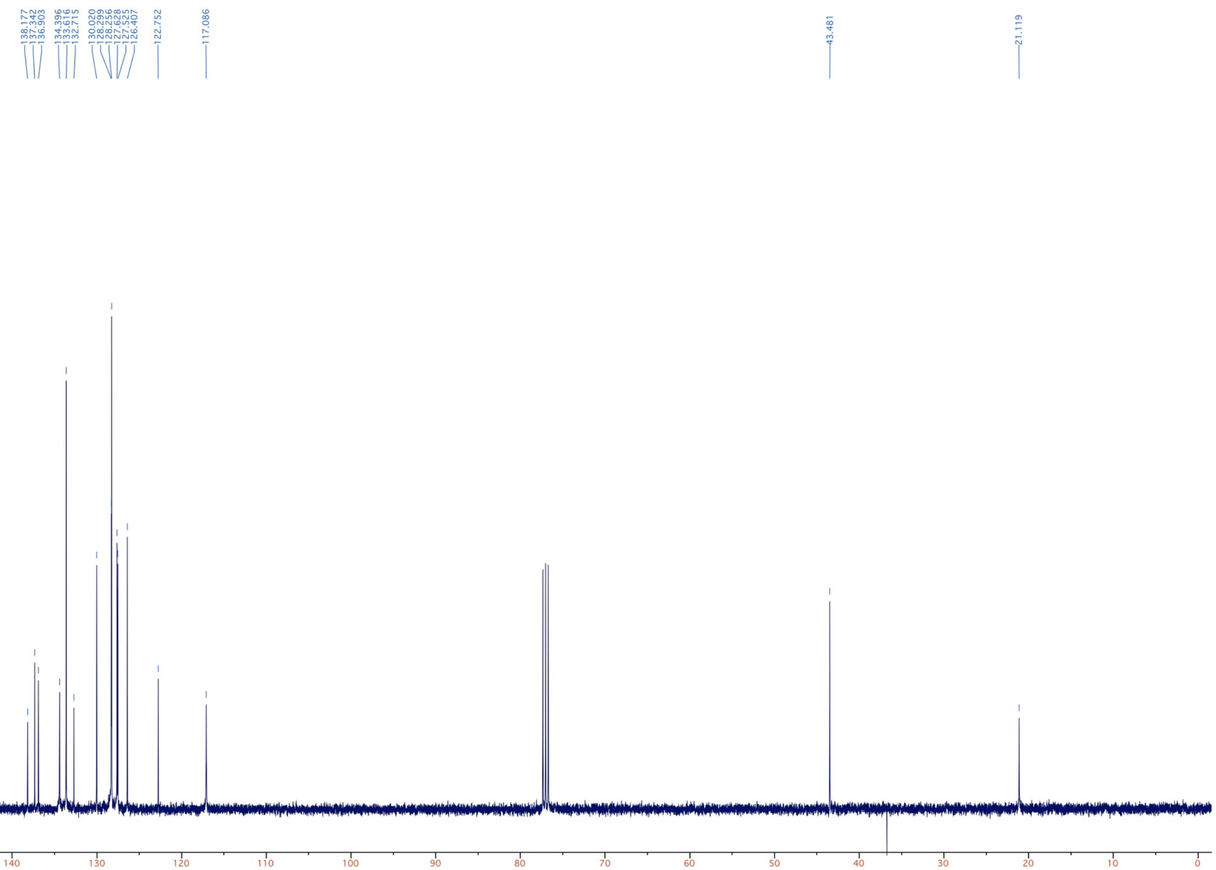
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190


Ph
S
Me
Br
7.174
7.169
7.160
7.157
7.150
7.058
7.054
7.045
7.040
7.030
7.029
7.023
6.975
6.974
6.879
6.859
6.856
6.856
6.841
6.837
6.835
5.863
5.857
5.838
5.831
5.821
5.810
5.805
5.795
5.789
5.779
5.763
5.140
5.137
5.115
5.111
5.098
5.095
5.091
5.052
5.049
3.178
3.175
3.162
3.159
2.161
2.9
1.93
1.02
2.81
0.843
1.94
2.08
3
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0
-0.5

5l



5l



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132.715
130.020
128.299
128.256
127.628
127.525
126.407
122.752
117.086
43.481
21.119
ppm
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180
170
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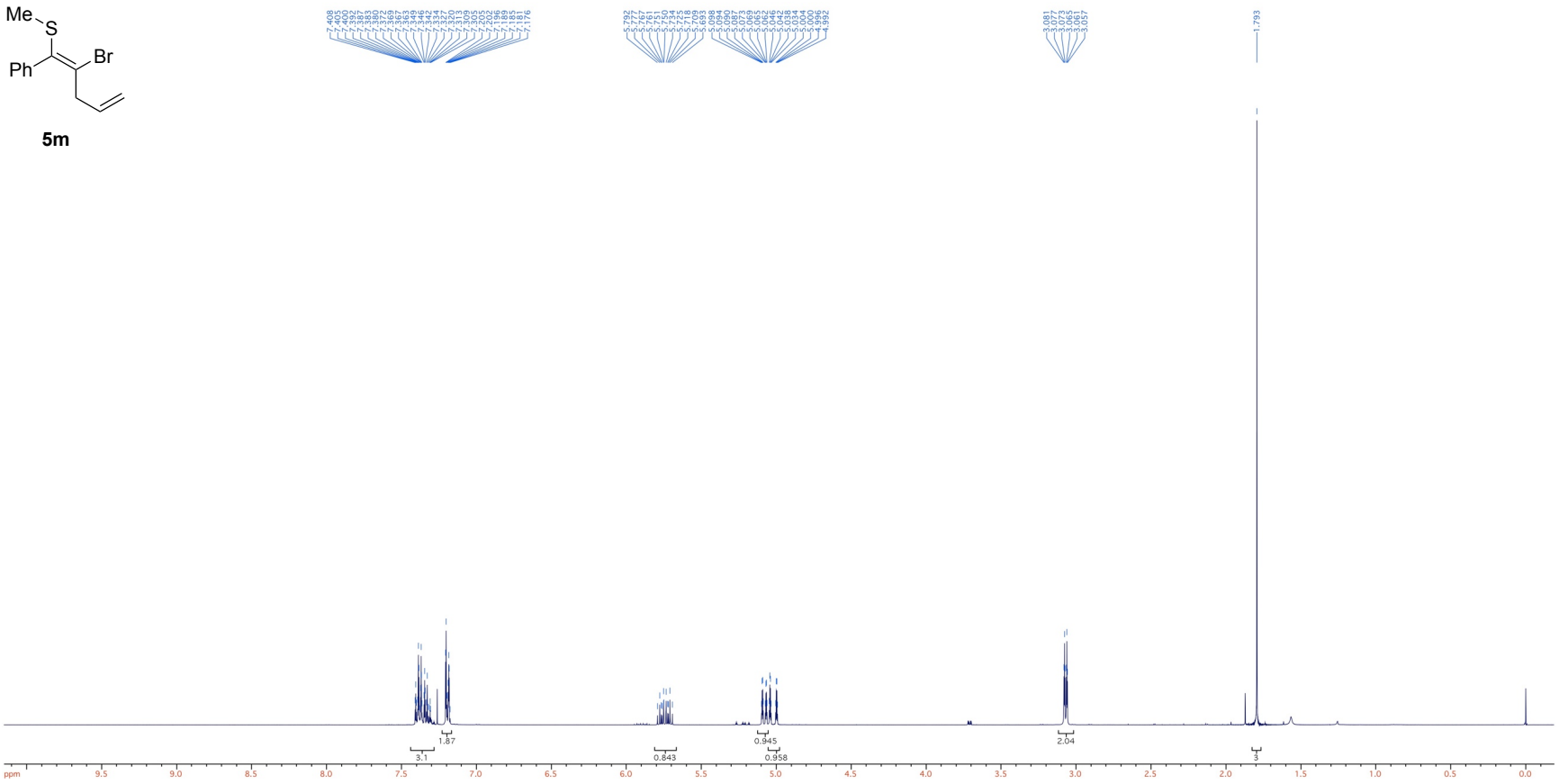
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Me
S
Ph
Br
5m
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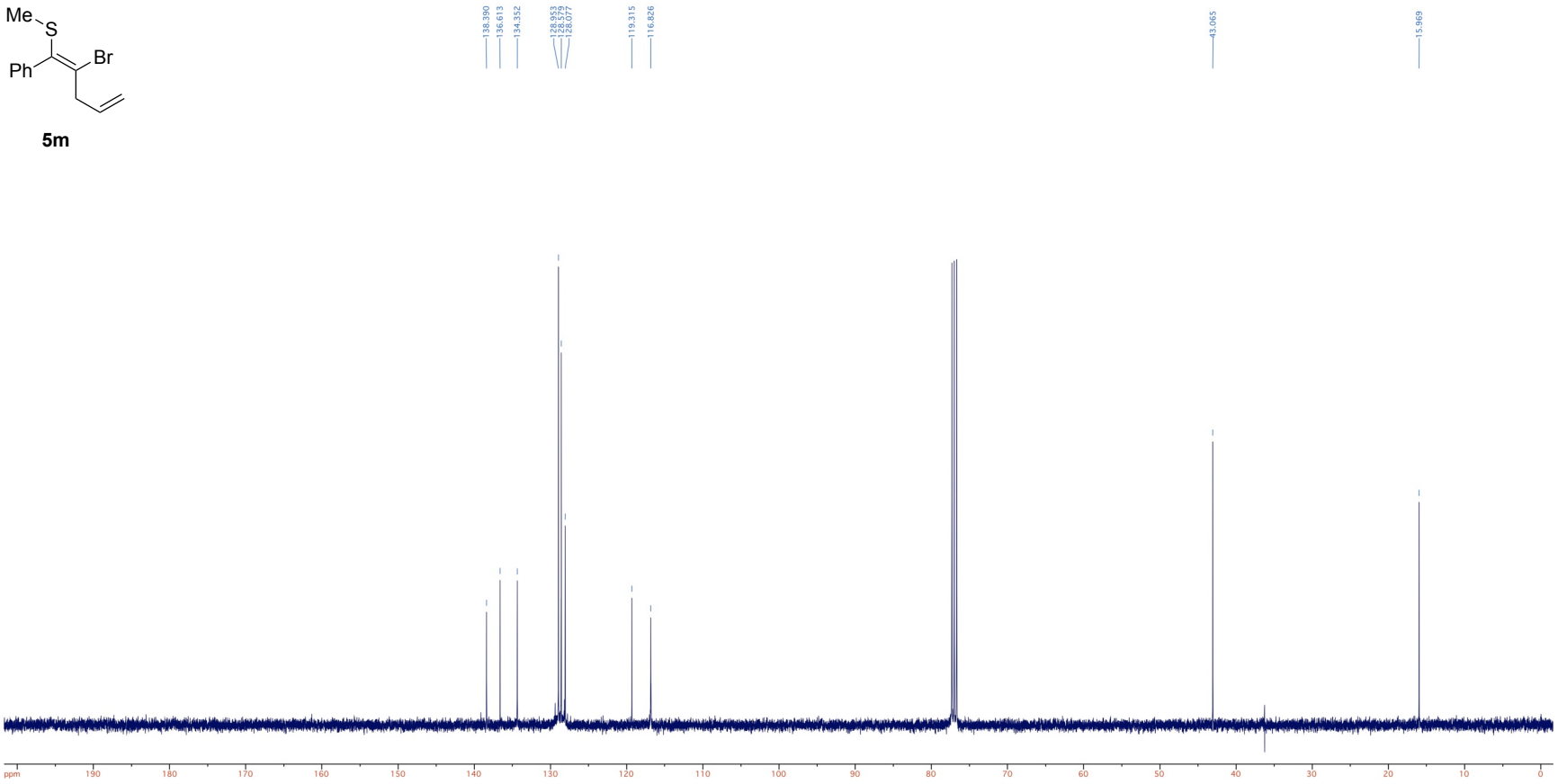
7.405
7.400
7.392
7.383
7.380
7.369
7.367
7.365
7.349
7.346
7.342
7.334
7.331
7.313
7.309
7.305
7.205
7.202
7.196
7.189
7.185
7.181
7.176
5.792
5.767
5.751
5.750
5.734
5.725
5.718
5.703
5.693
5.098
5.094
5.090
5.087
5.073
5.069
5.062
5.046
5.042
5.038
5.034
5.004
5.000
4.996
4.992
3.081
3.077
3.073
3.065
3.061
3.057
1.793
1.87
3.1
0.945
0.958
0.643
2.04
3
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Me
S
Ph
Br
5m
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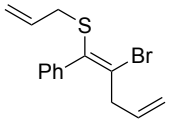
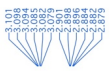
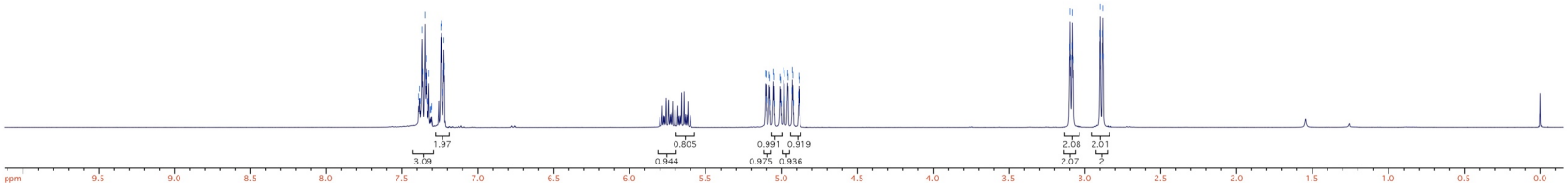
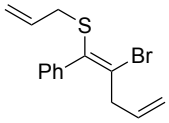
128.853
128.579
128.077
119.315
116.826
43.065
15.969
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


S
Br
Ph

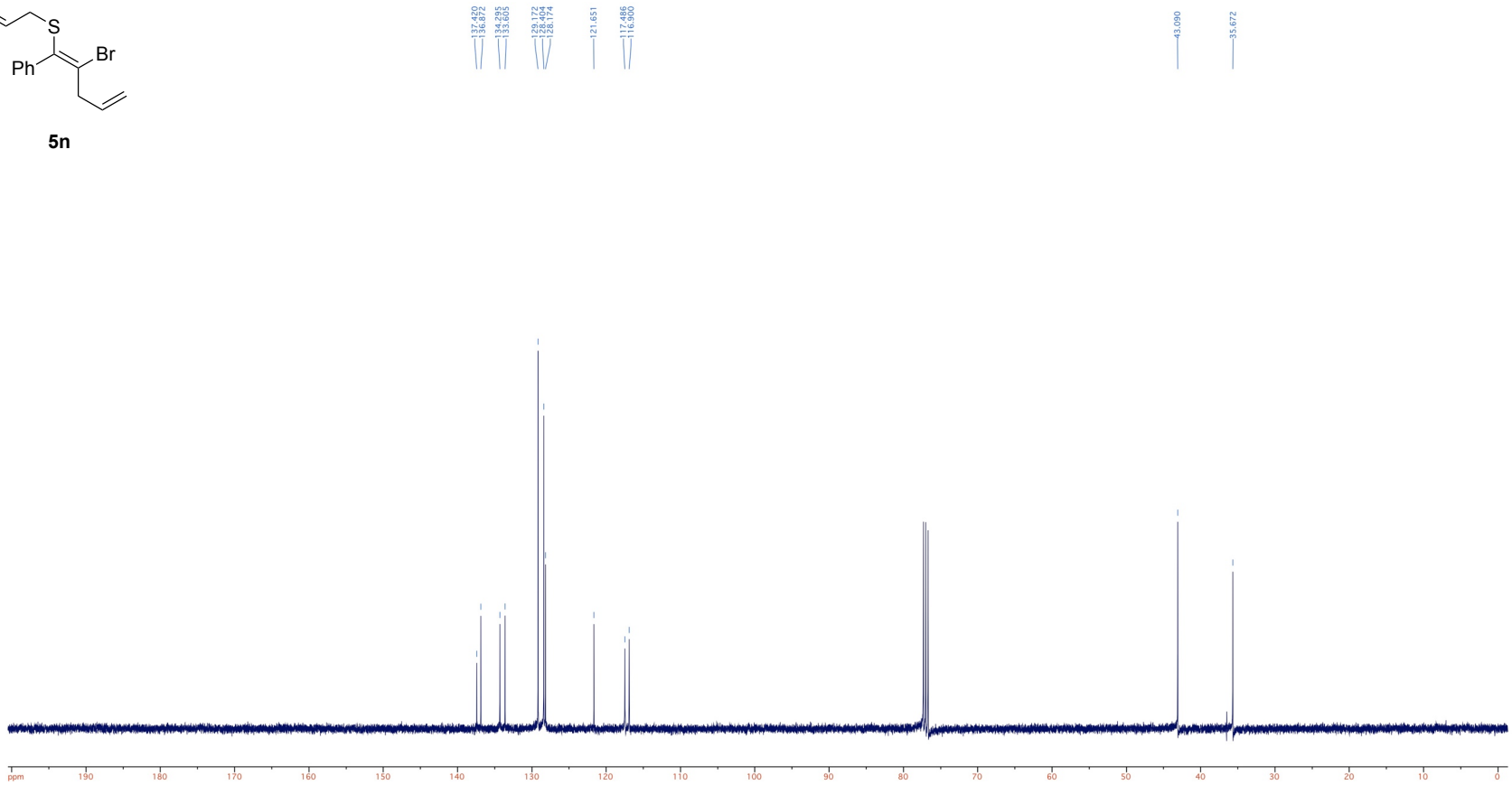
5n




1.97
3.09
0.805
0.944
0.991
0.975
0.919
0.936
2.08
2.07
2.01
2
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


S
Br
Ph

5n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134.295
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128.404
128.174
121.651
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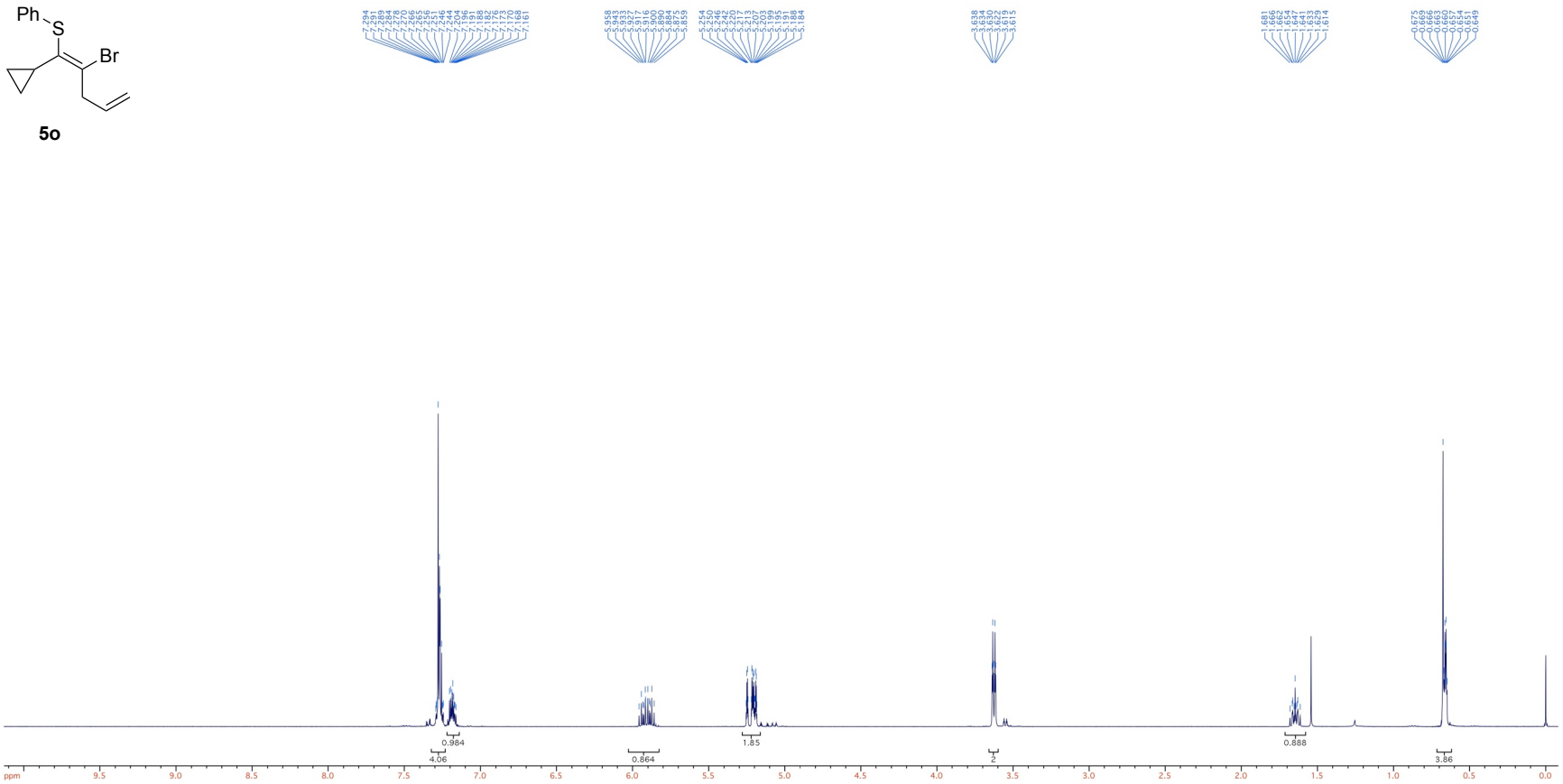
116.900
43.090
35.672
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Ph
S
Br

5o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7.291
7.289
7.287
7.284
7.278
7.270
7.265
7.260
7.256
7.251
7.246
7.244
7.204
7.196
7.191
7.188
7.182
7.172
7.173
7.170
7.168
7.161
5.958
5.943
5.933
5.927
5.917
5.900
5.890
5.884
5.875
5.859
5.254
5.250
5.246
5.242
5.220
5.217
5.213
5.207
5.203
5.199
5.195
5.191
5.188
5.184
3.638
3.634
3.631
3.622
3.619
3.615
1.681
1.666
1.662
1.654
1.647
1.641
1.633
1.629
1.614
0.675
0.669
0.666
0.663
0.660
0.657
0.654
0.651
0.649
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4.06
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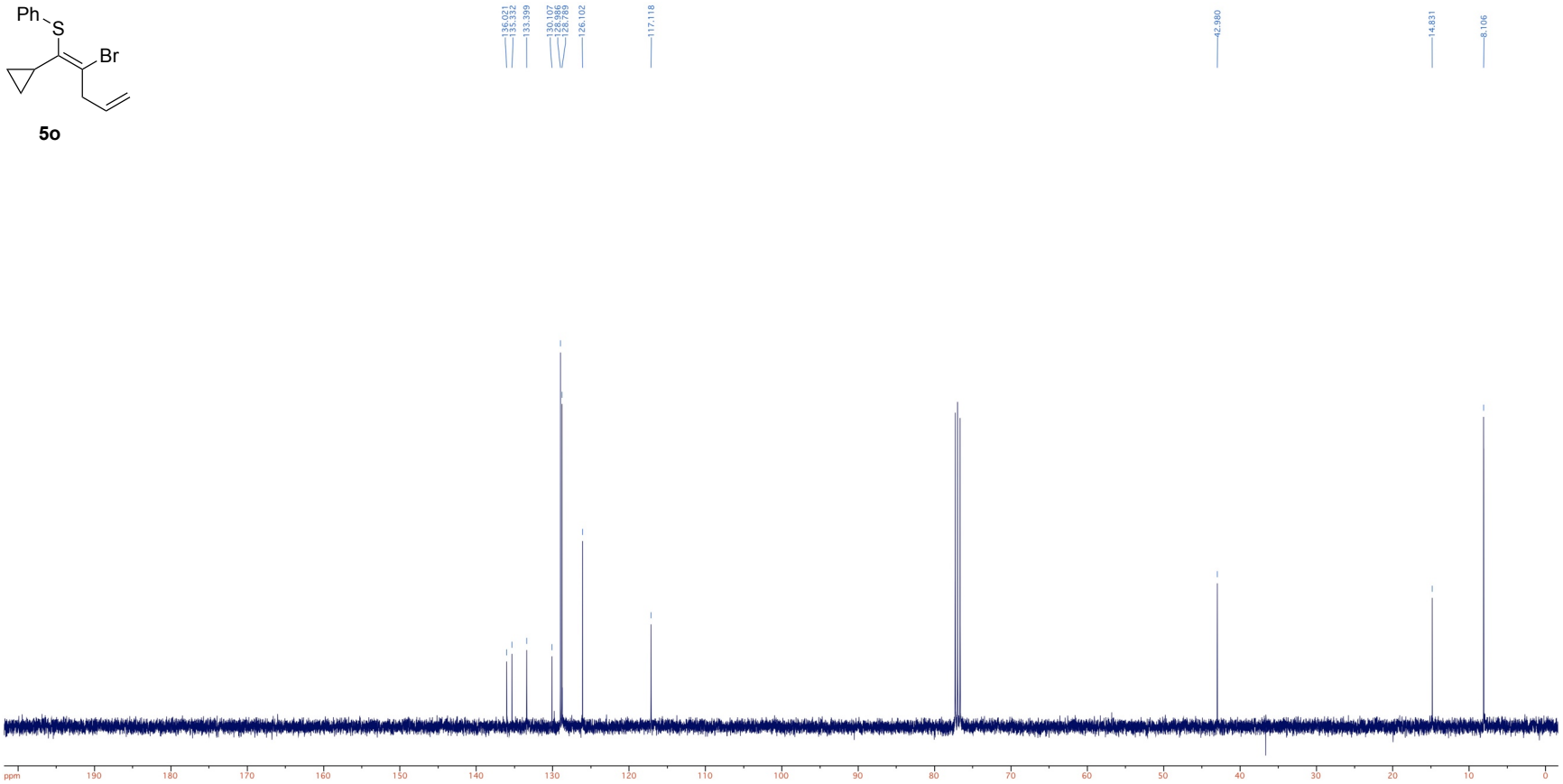
1.85
2
0.888
3.86
ppm

Ph
S
Br

5o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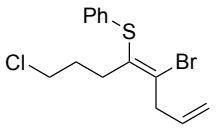
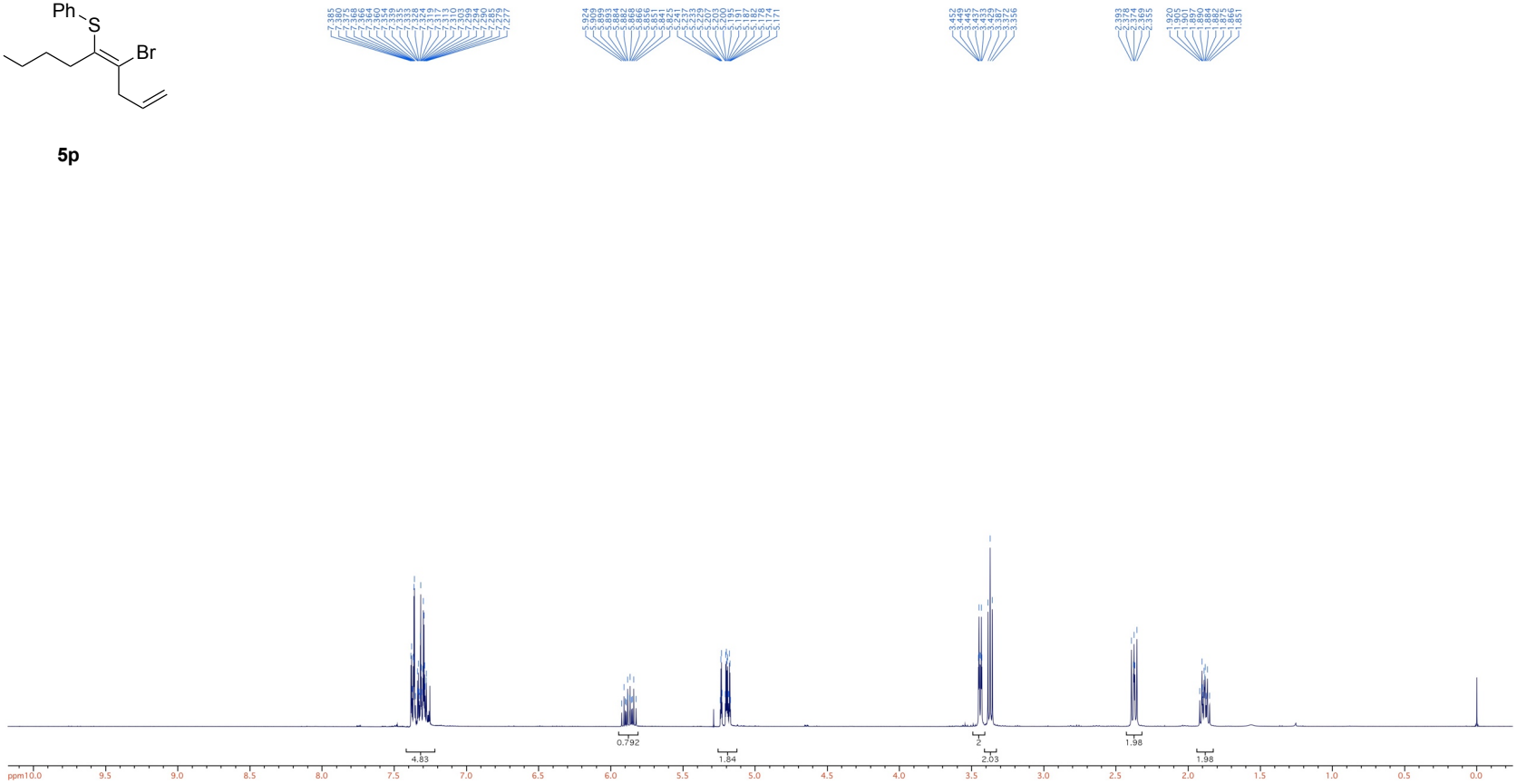
128.789
126.102
117.118
42.980
14.831
8.106
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

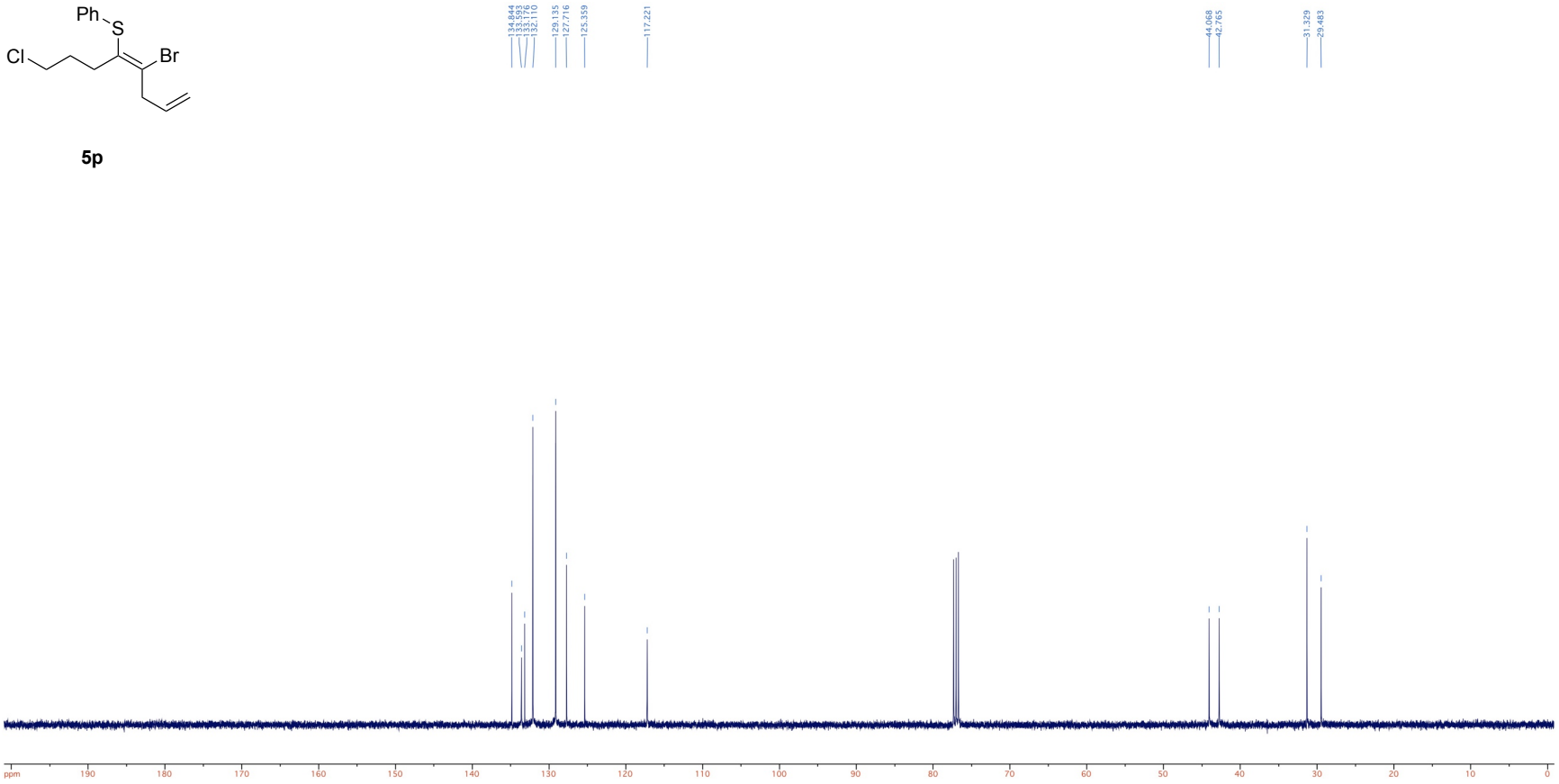

Ph
S
Cl
Br

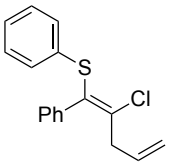
5p


4.83
0.792
1.84
2
2.03
1.98
1.98
ppm10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

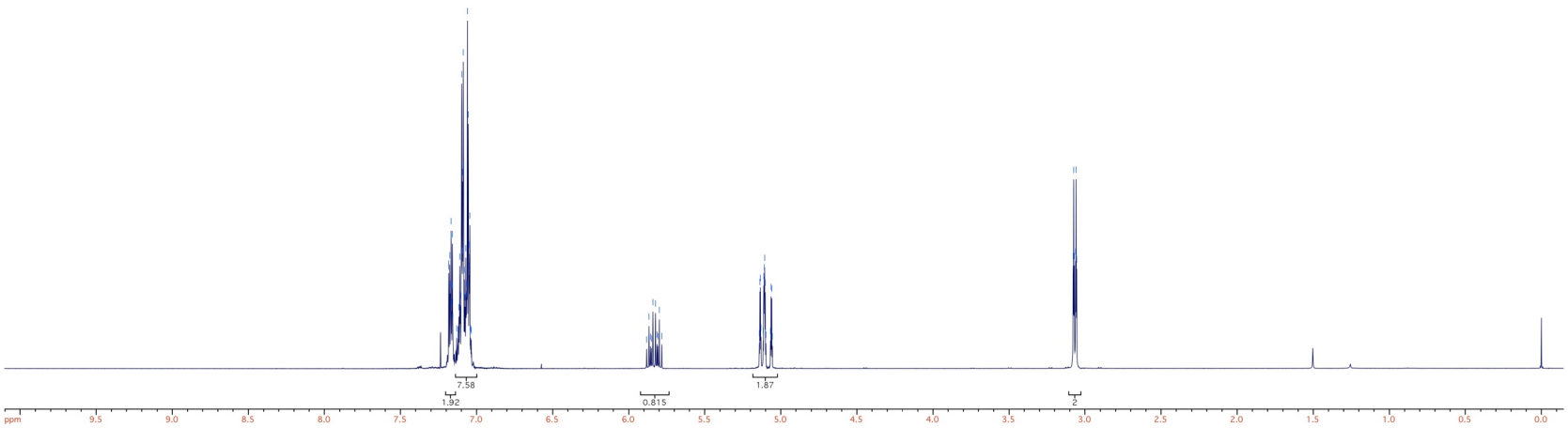
Ph
S
Cl
Br

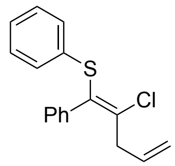
5p


134.644
134.393
133.176
132.110
129.135
127.716
125.359
117.221
44.068
42.765
31.329
29.483
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

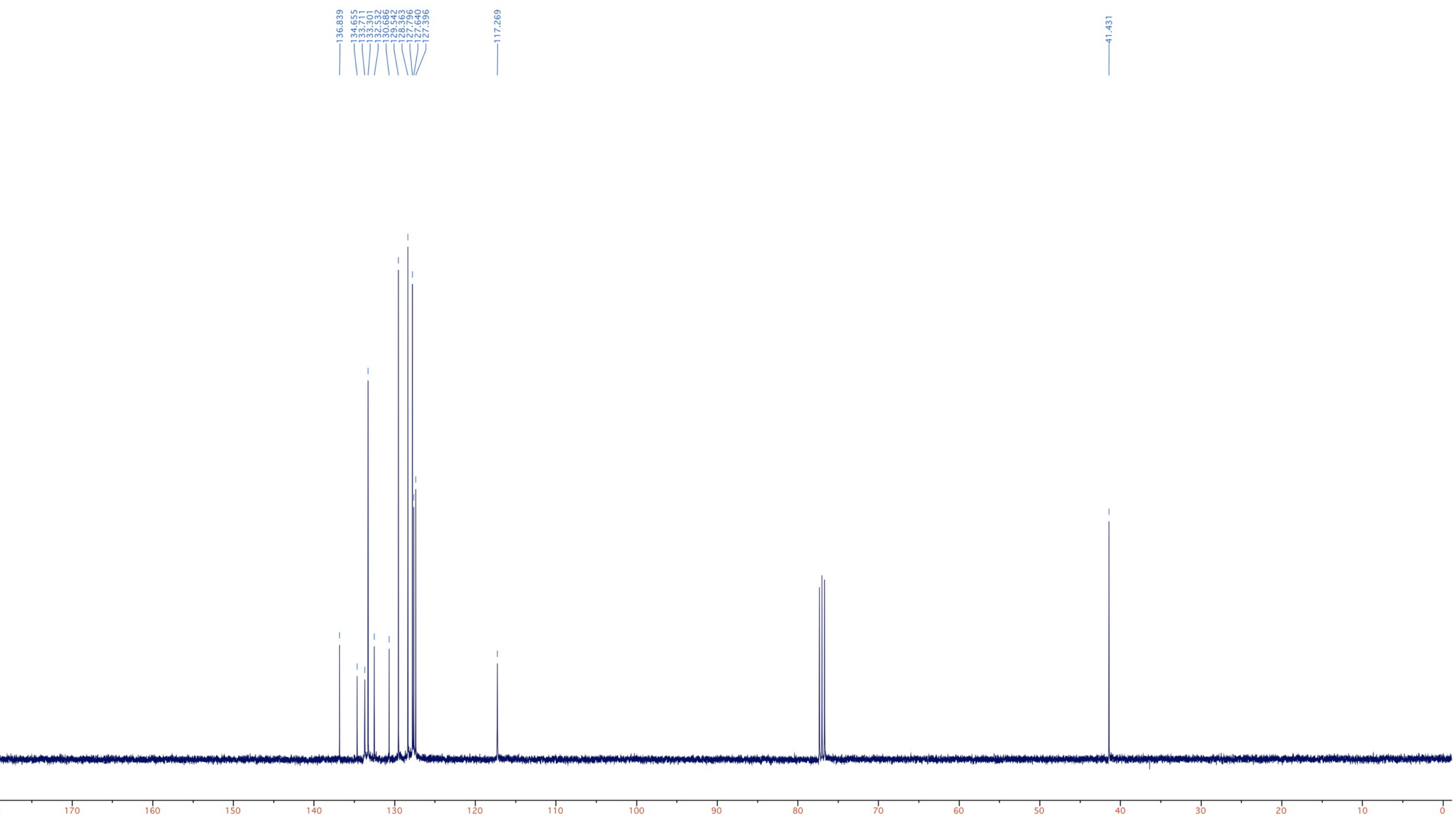


5q





5q



136.839
134.655
133.711
133.301
132.532
130.686
129.542
128.363
127.796
127.640
127.396
117.269
41.431
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
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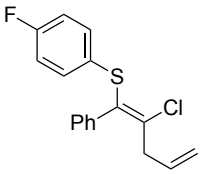
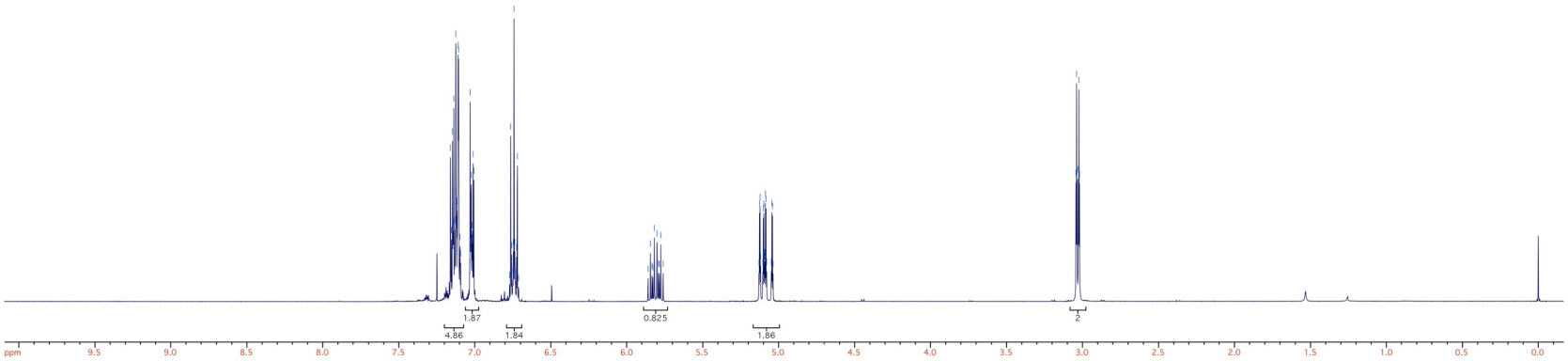
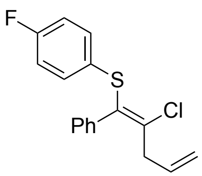
30
20
10
0

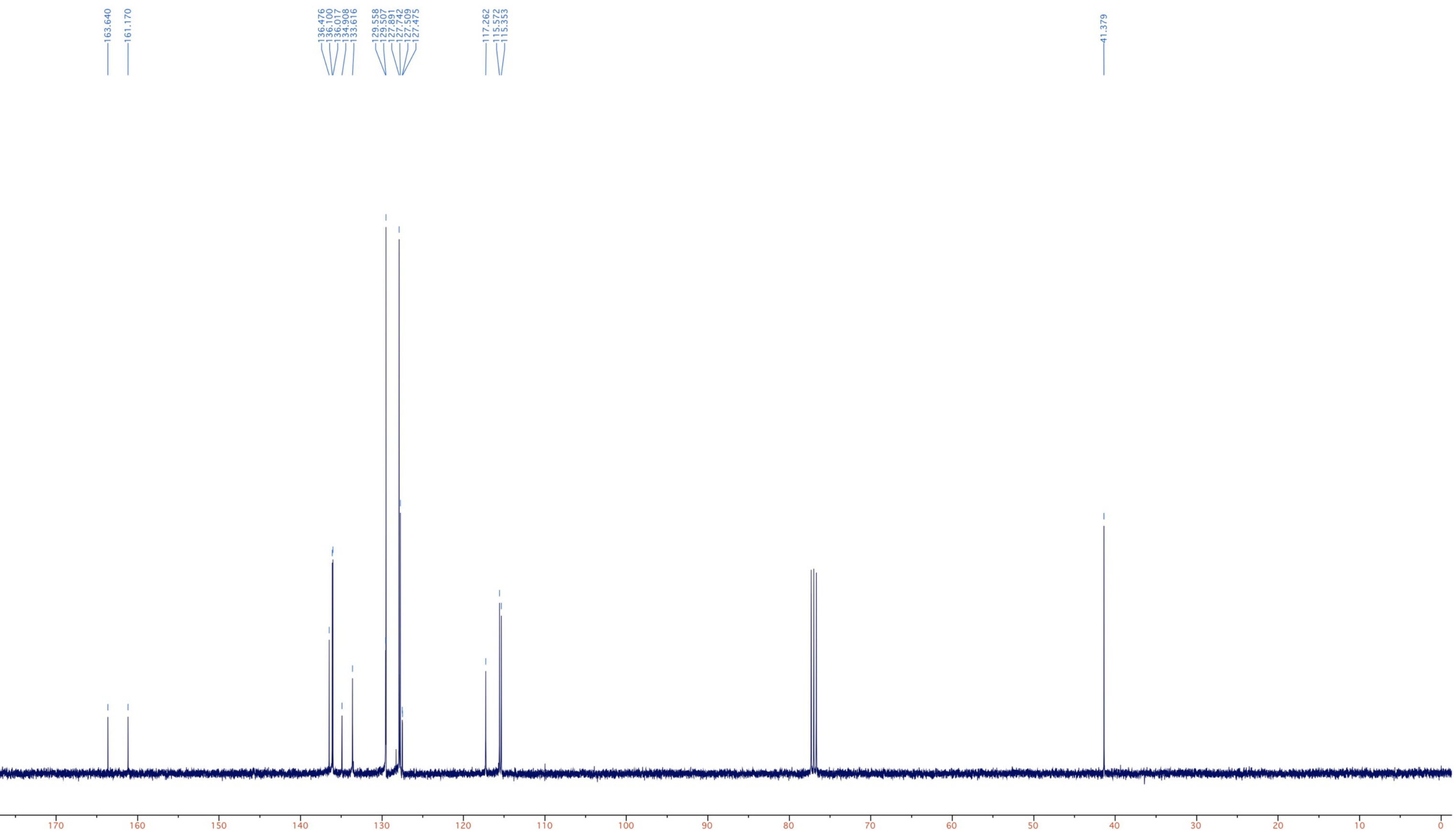


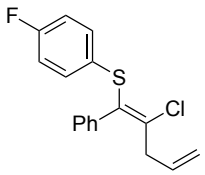
5r





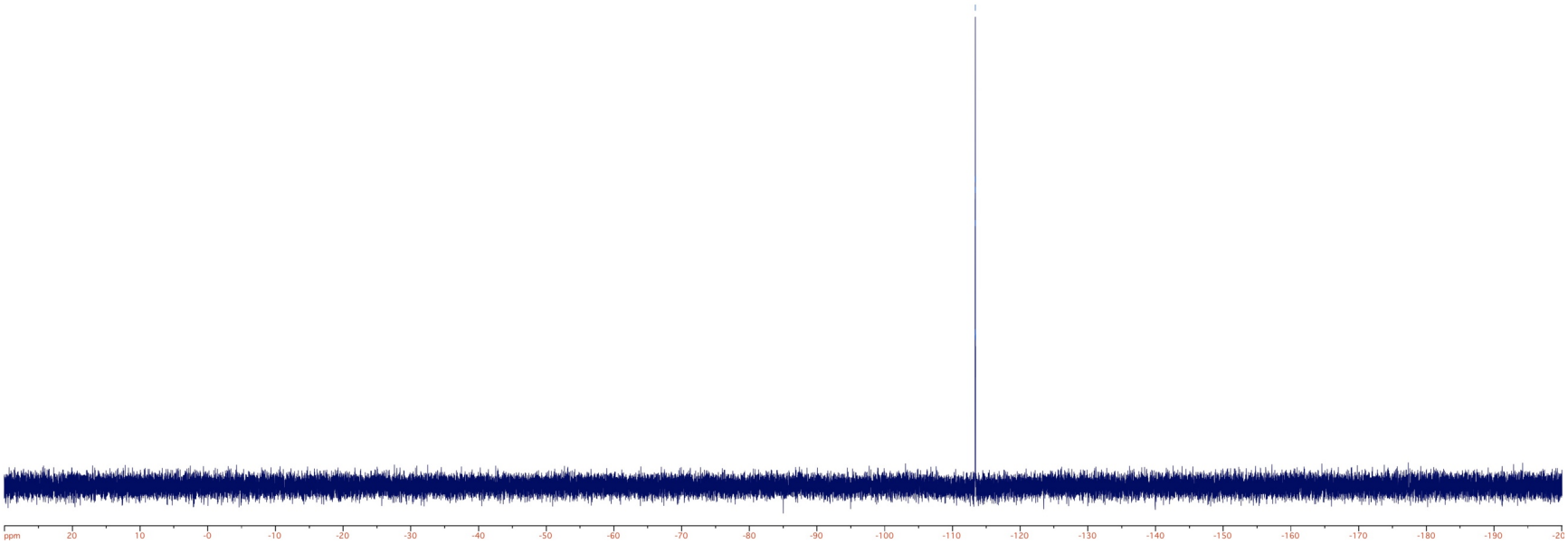
5r

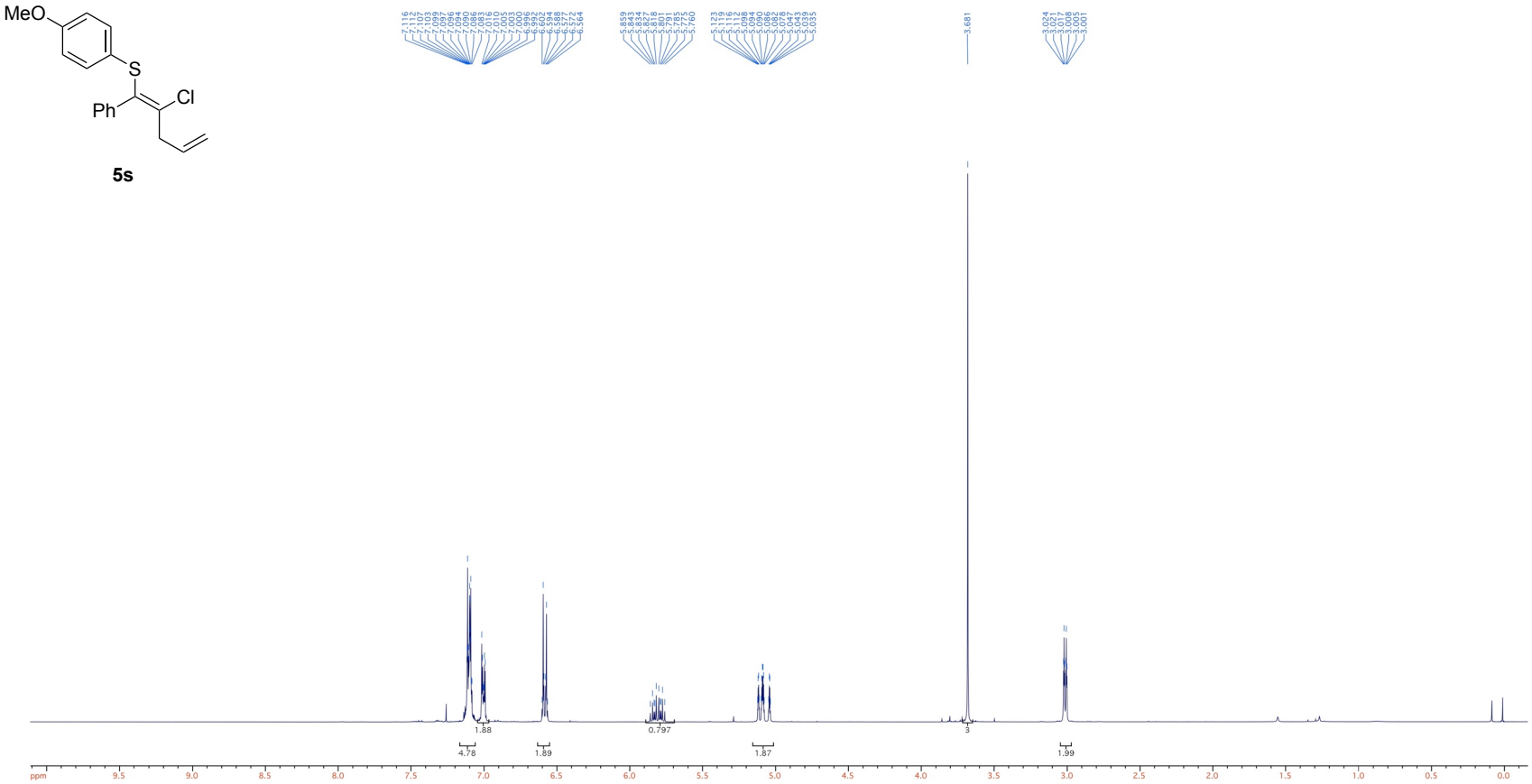


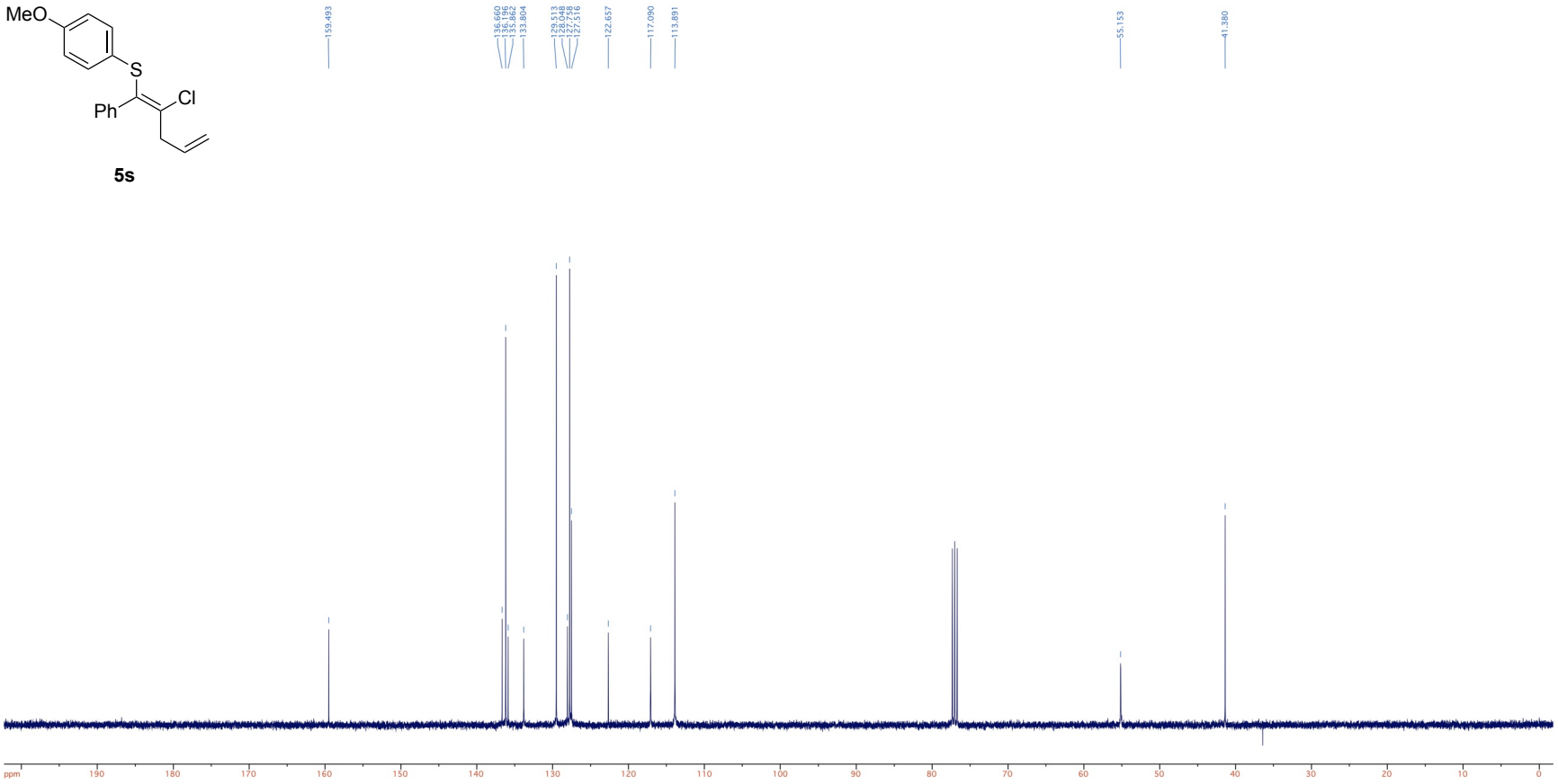

F
S
Ph
Cl

5r


-113.354
-113.368
-113.379
-113.392
-113.414
-113.427

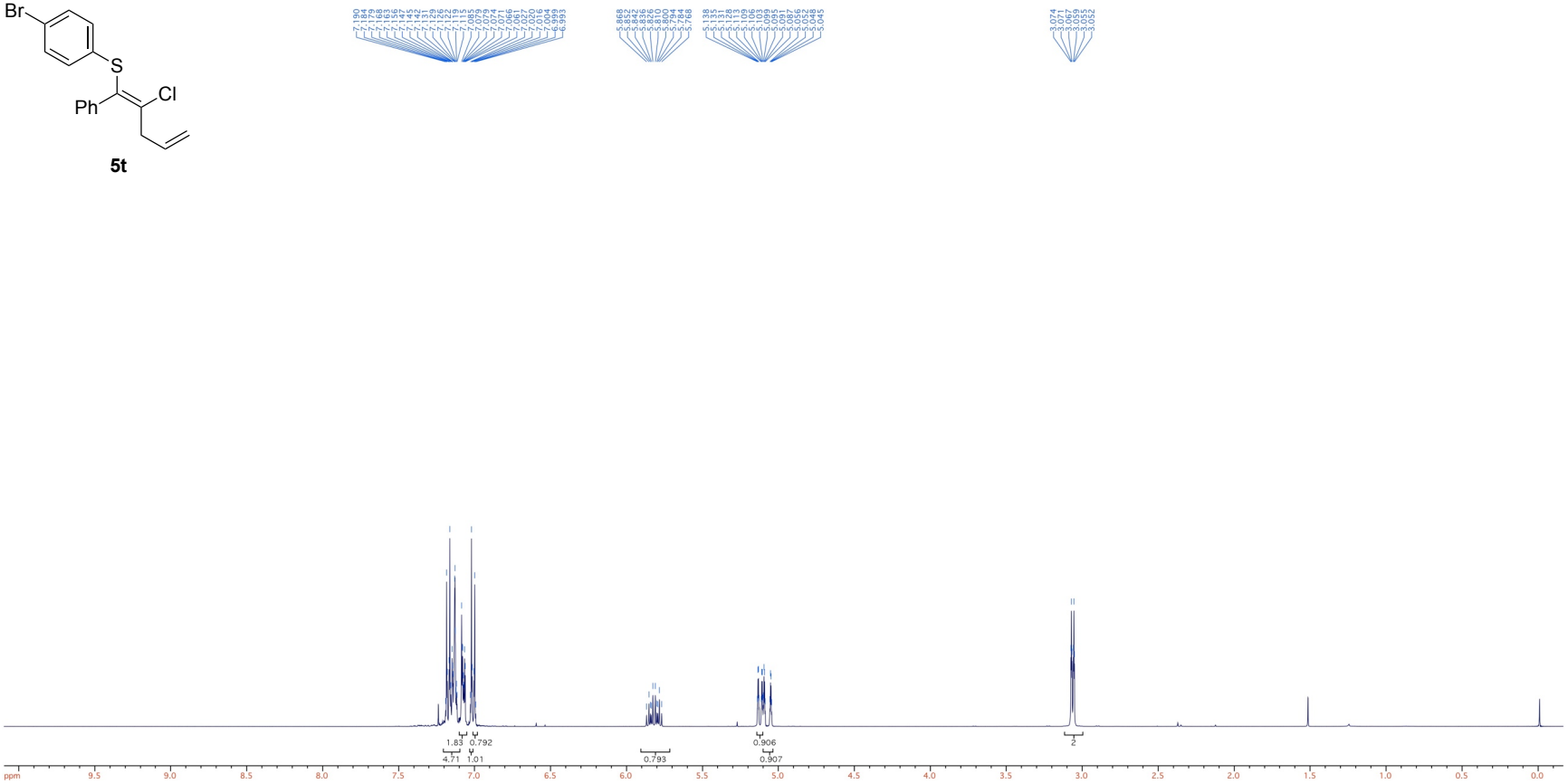

ppm
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

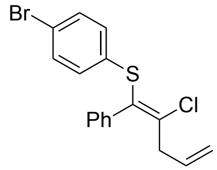

MeO
S
Ph
Cl
5s
7.116
7.112
7.107
7.103
7.099
7.097
7.096
7.094
7.090
7.086
7.085
7.016
7.010
7.005
7.003
7.000
6.996
6.992
6.602
6.584
6.580
6.577
6.573
6.564
5.859
5.843
5.834
5.827
5.818
5.791
5.785
5.760
5.123
5.119
5.116
5.112
5.098
5.094
5.090
5.086
5.082
5.078
5.047
5.043
5.039
5.035
3.681
3.024
3.017
3.011
3.008
3.005
3.001
1.88
4.78
1.89
0.797
1.87
3
1.99
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


MeO
S
Cl
Ph
159.493
136.660
136.196
135.862
133.804
129.513
128.048
127.760
127.516
122.657
117.090
113.891
55.153
41.380
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

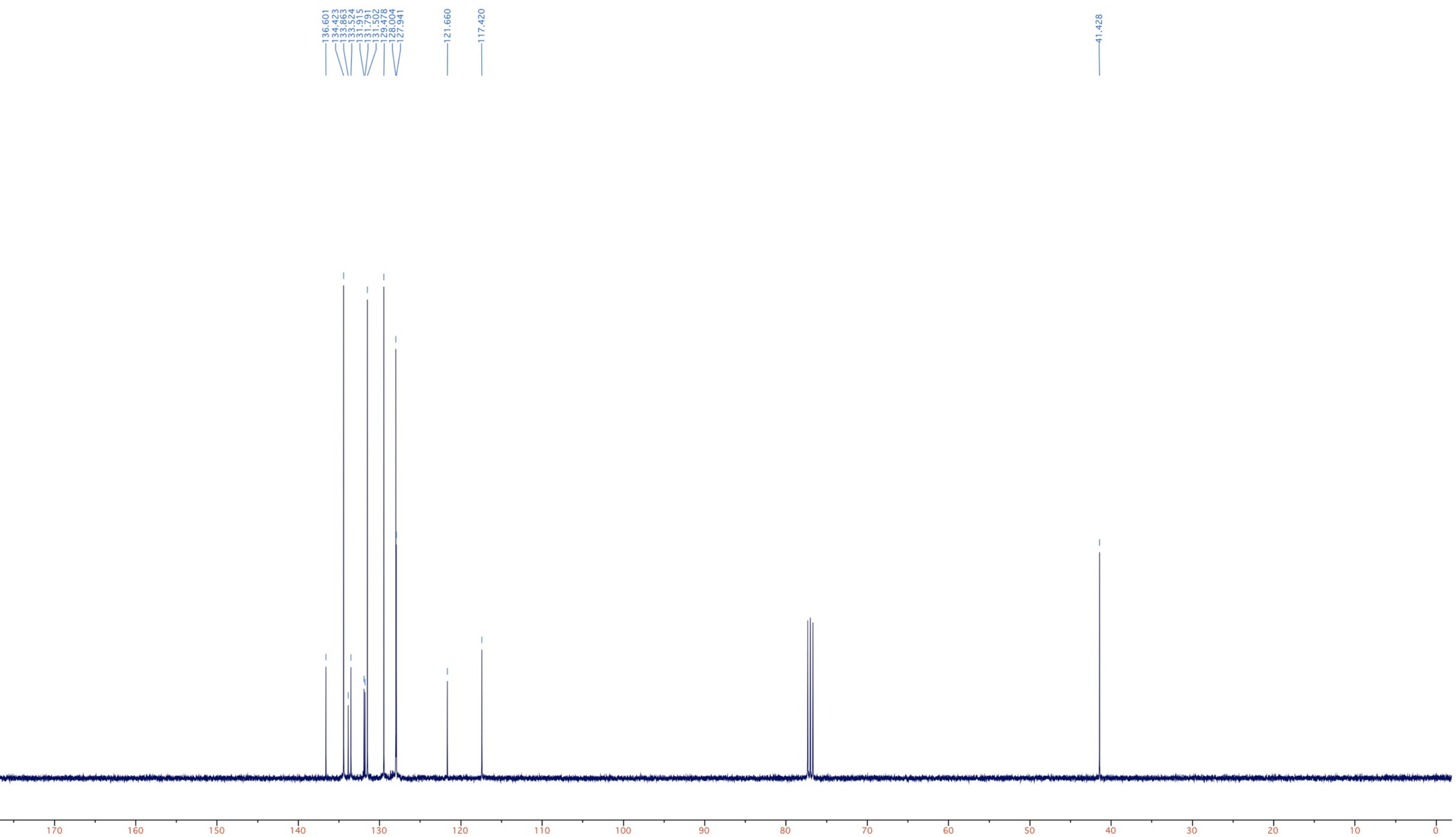
5s

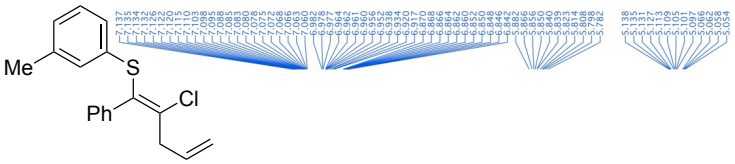
5t



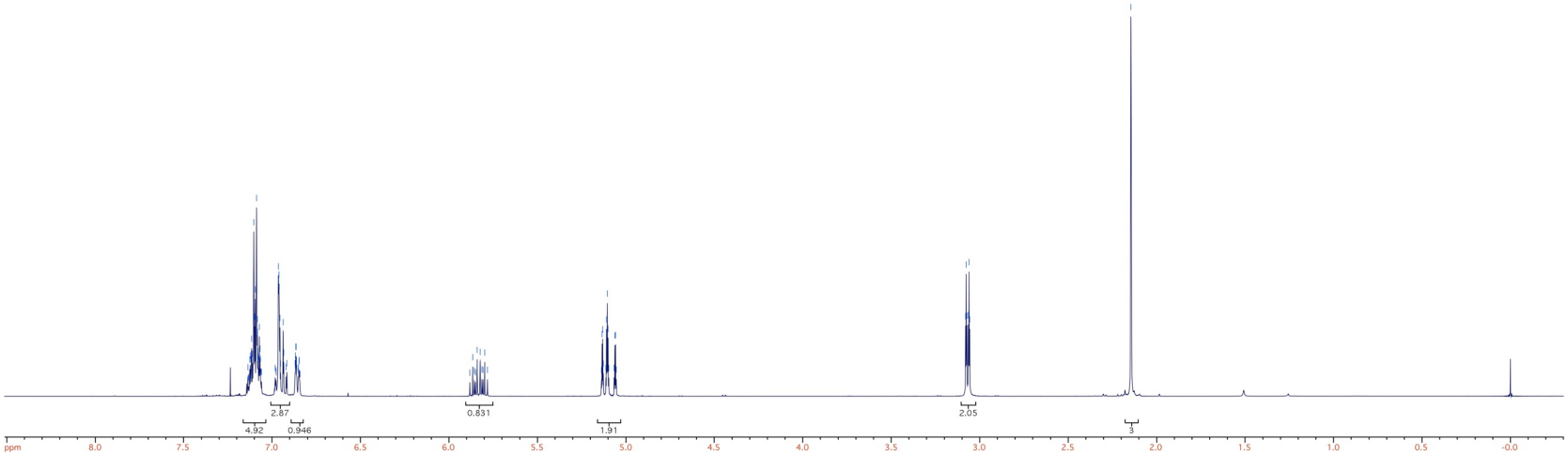

Br
S
Cl
Ph

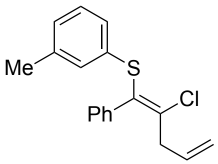
5t


136.601
134.423
133.863
133.524
131.915
131.791
131.502
129.478
128.004
127.941
121.660
117.420
41.428
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

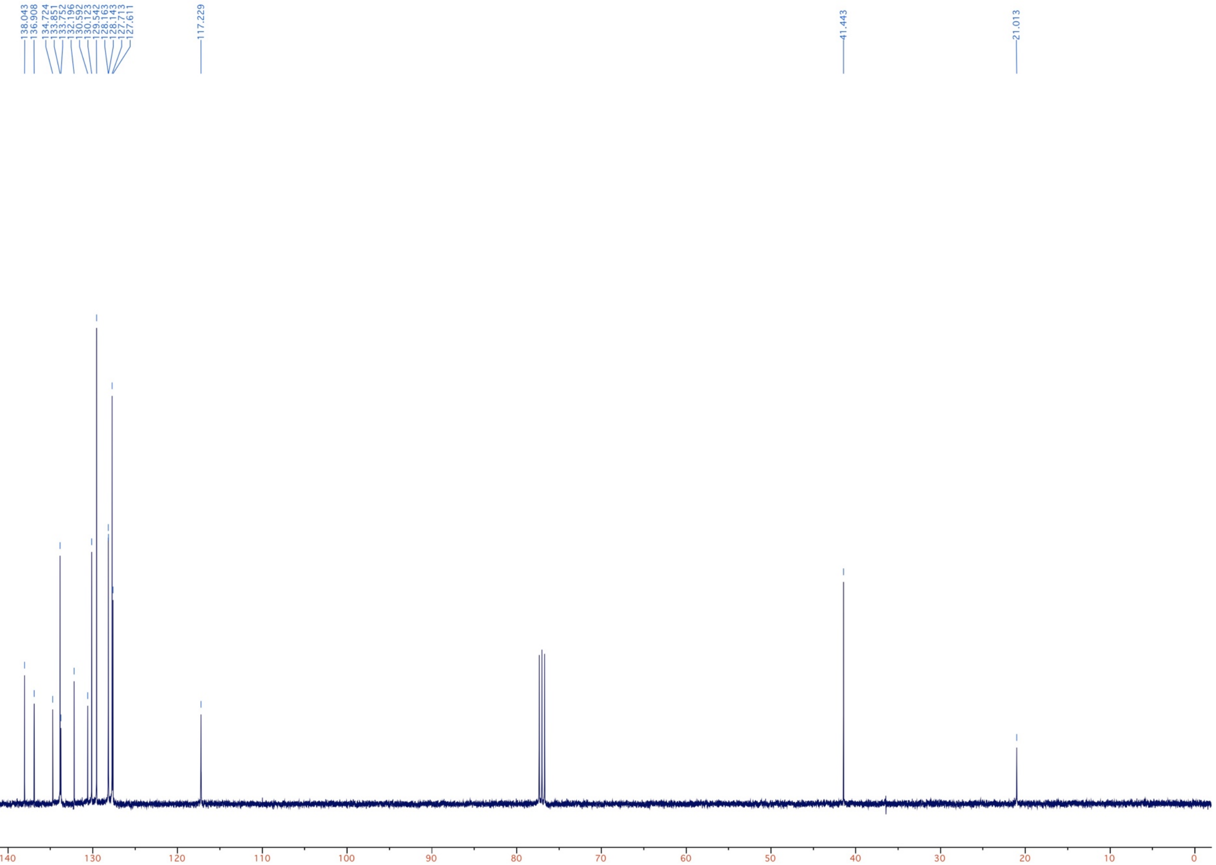


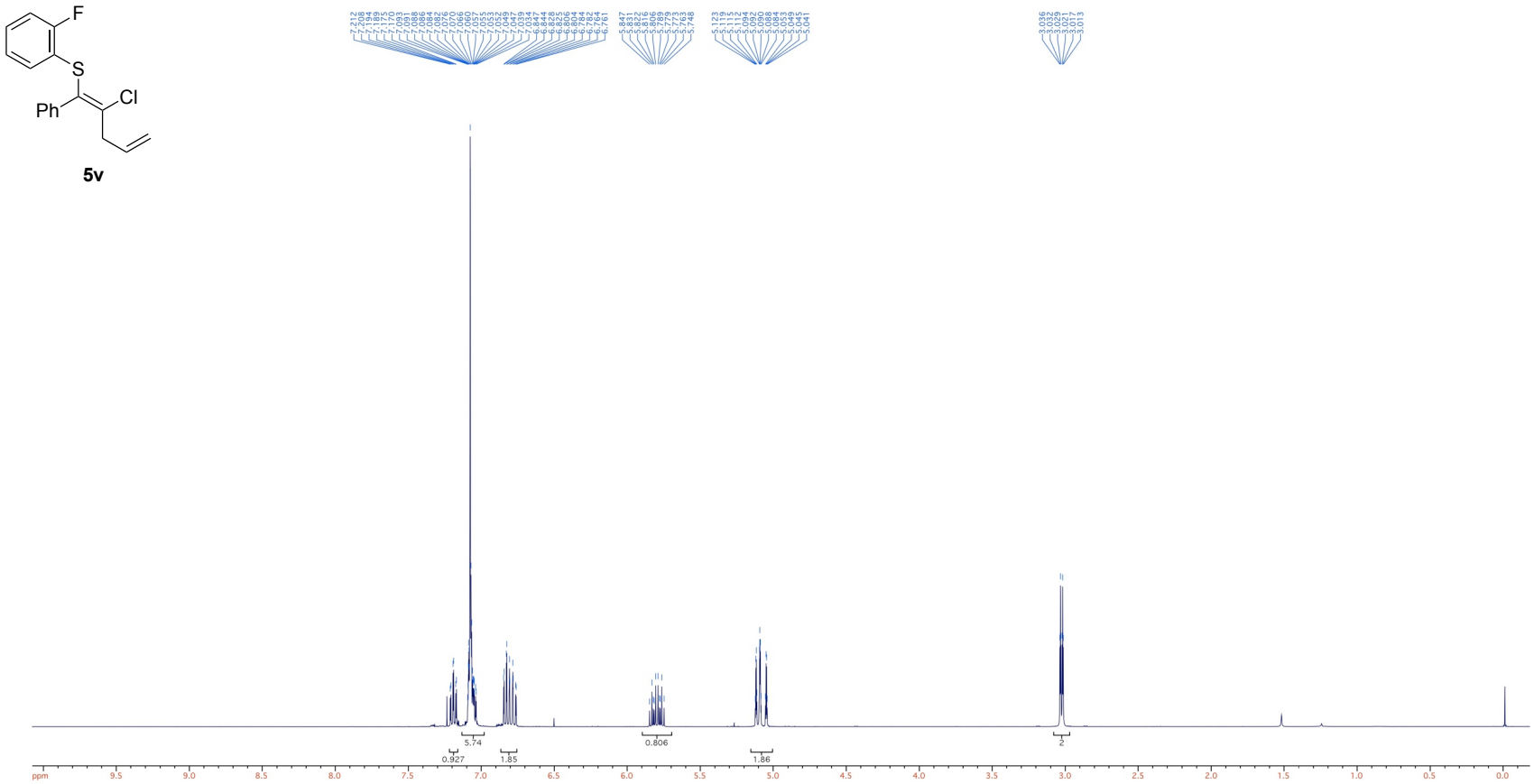
5u

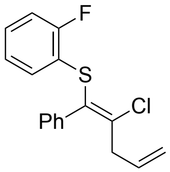




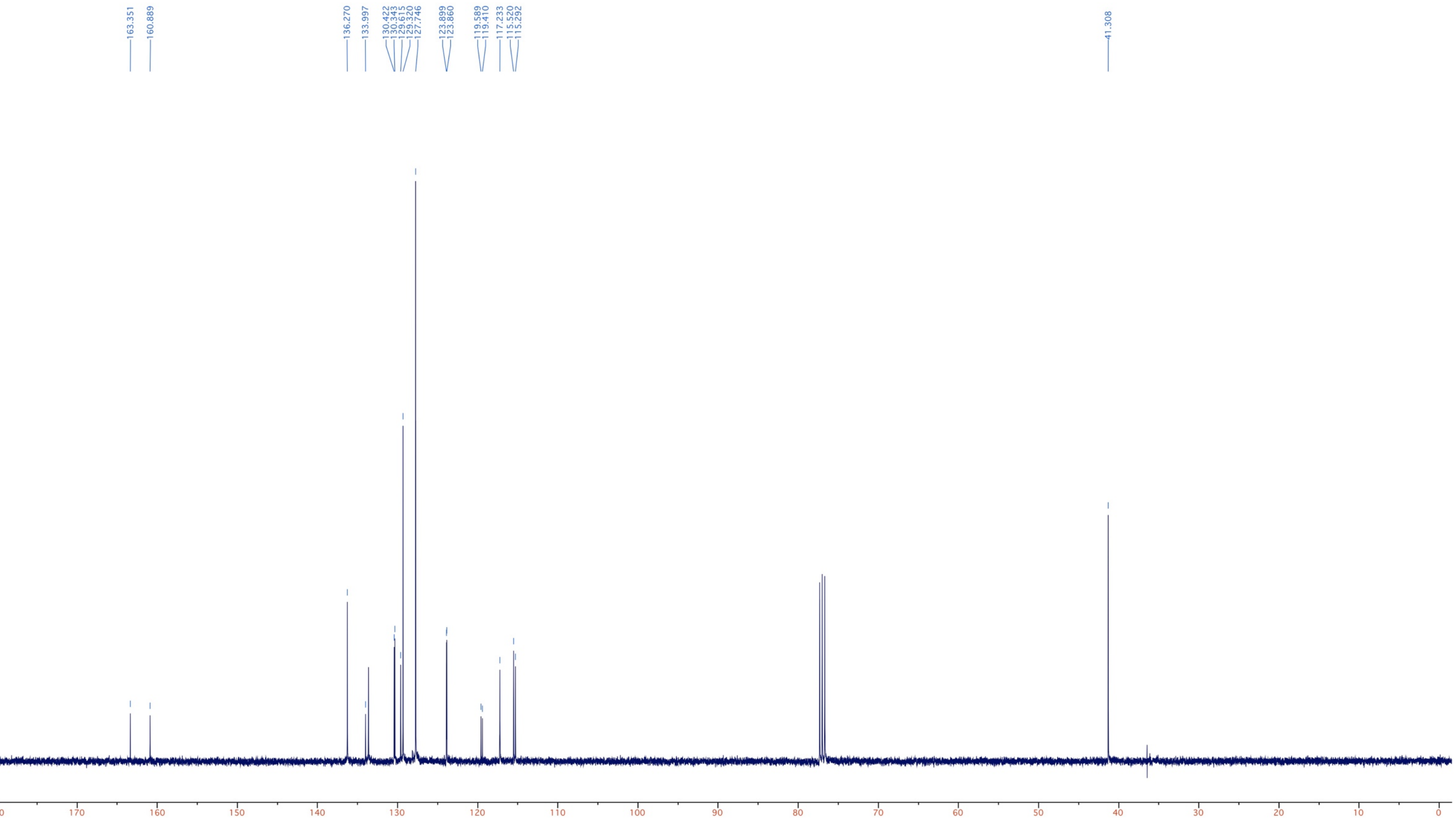
5u

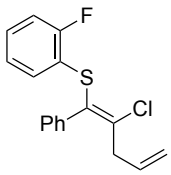



F
S
Ph
Cl
5v
5.74
0.927
1.85
0.806
1.86
2
ppm


F
S
Cl
Ph

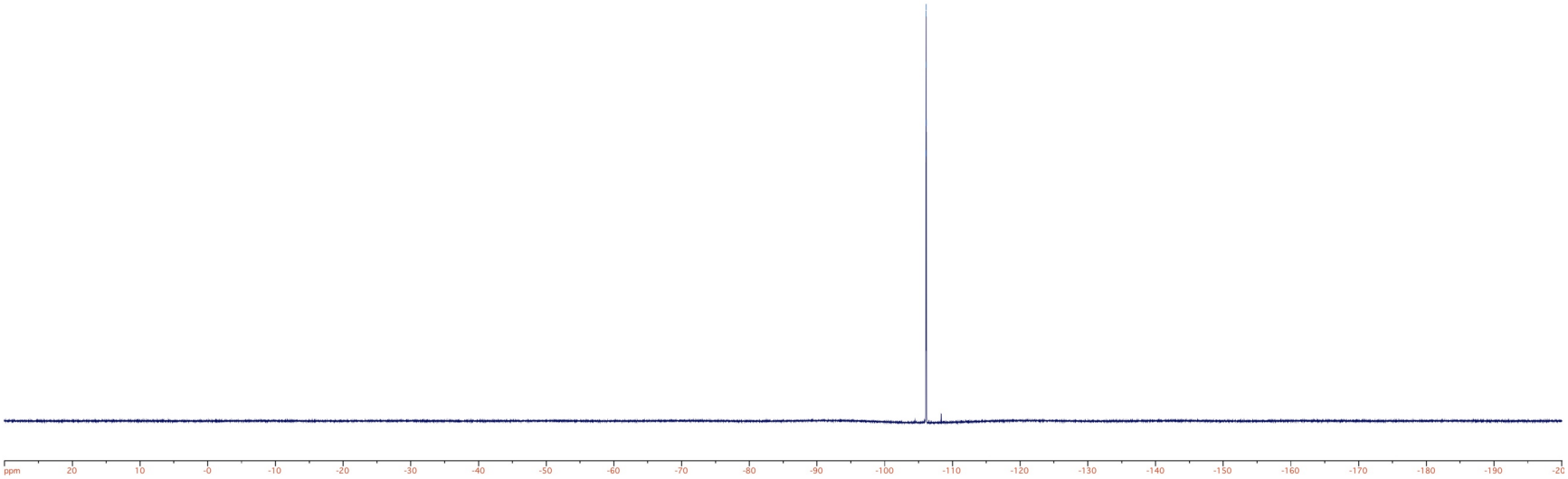
5v

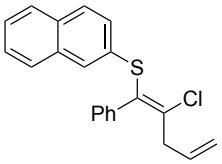

163.351
160.889
136.270
133.997
130.422
130.343
129.615
129.320
127.746
123.899
123.860
119.589
119.410
117.233
115.520
115.292
41.308
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


F
S
Ph
Cl

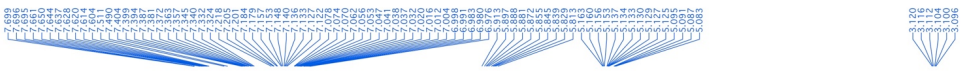
5v

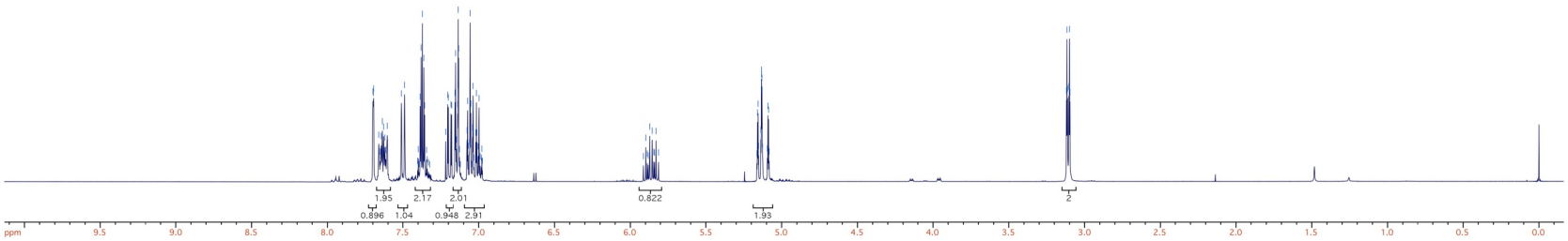

-106.098
-106.112
-106.132
-106.140
-106.154

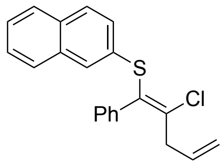

ppm
20
10
-0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190


S
Ph
Cl

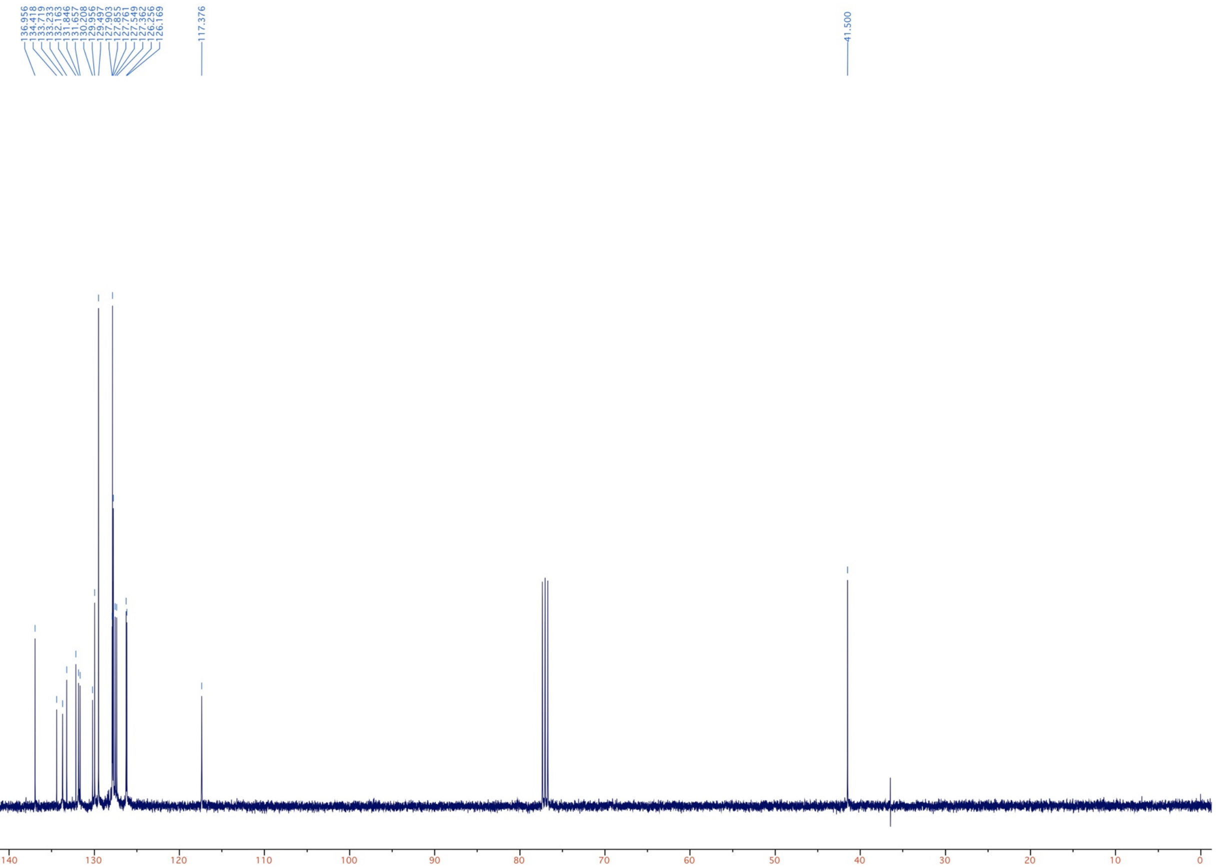
5w

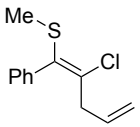



1.95
0.896
1.04
2.17
2.01
0.948
2.91
0.822
1.93
2
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

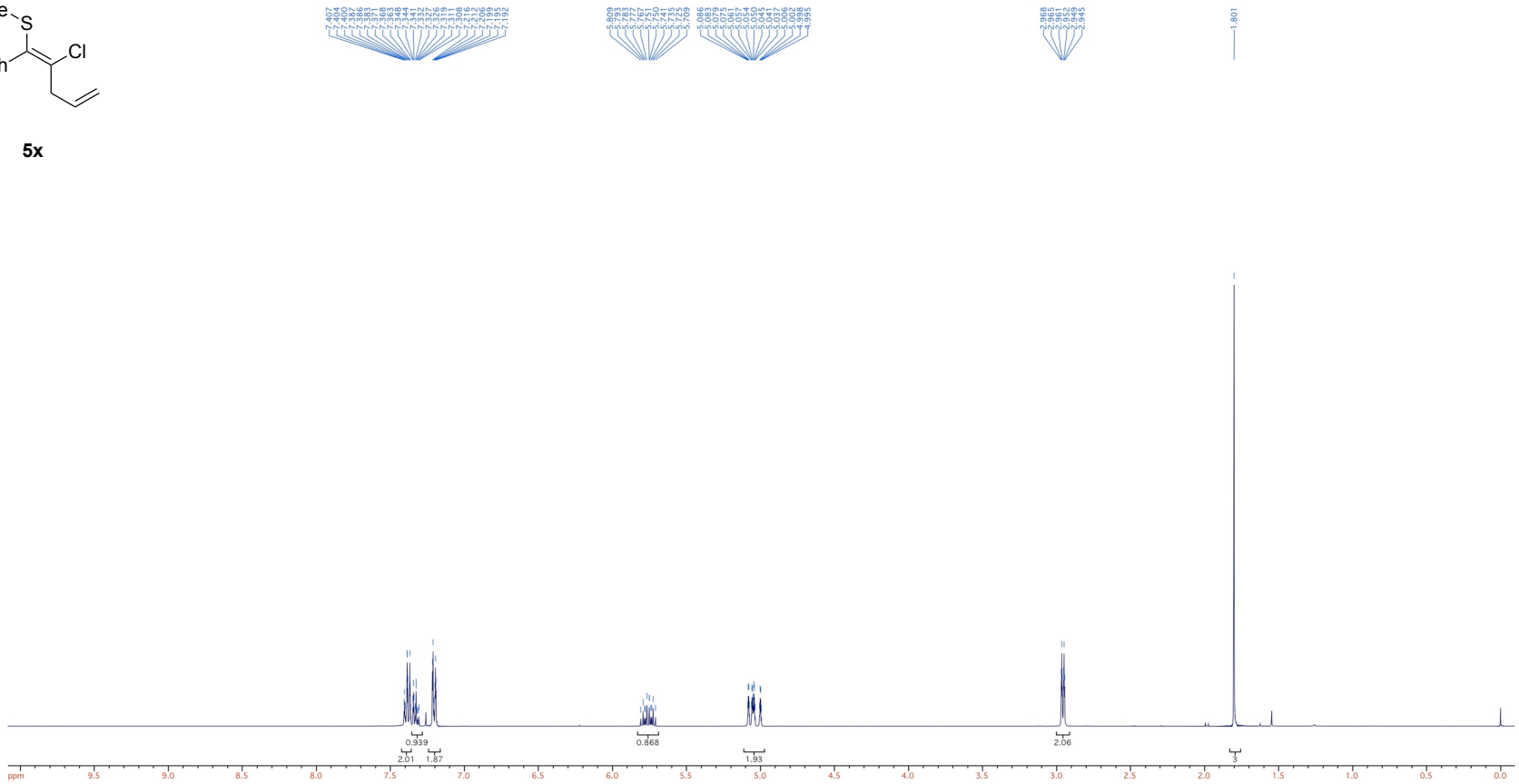

S
Cl
Ph

5w


136.956
134.418
133.719
133.233
132.163
131.846
131.657
130.208
129.956
129.497
127.903
127.855
127.761
127.549
127.362
126.256
126.169
117.376
41.500
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

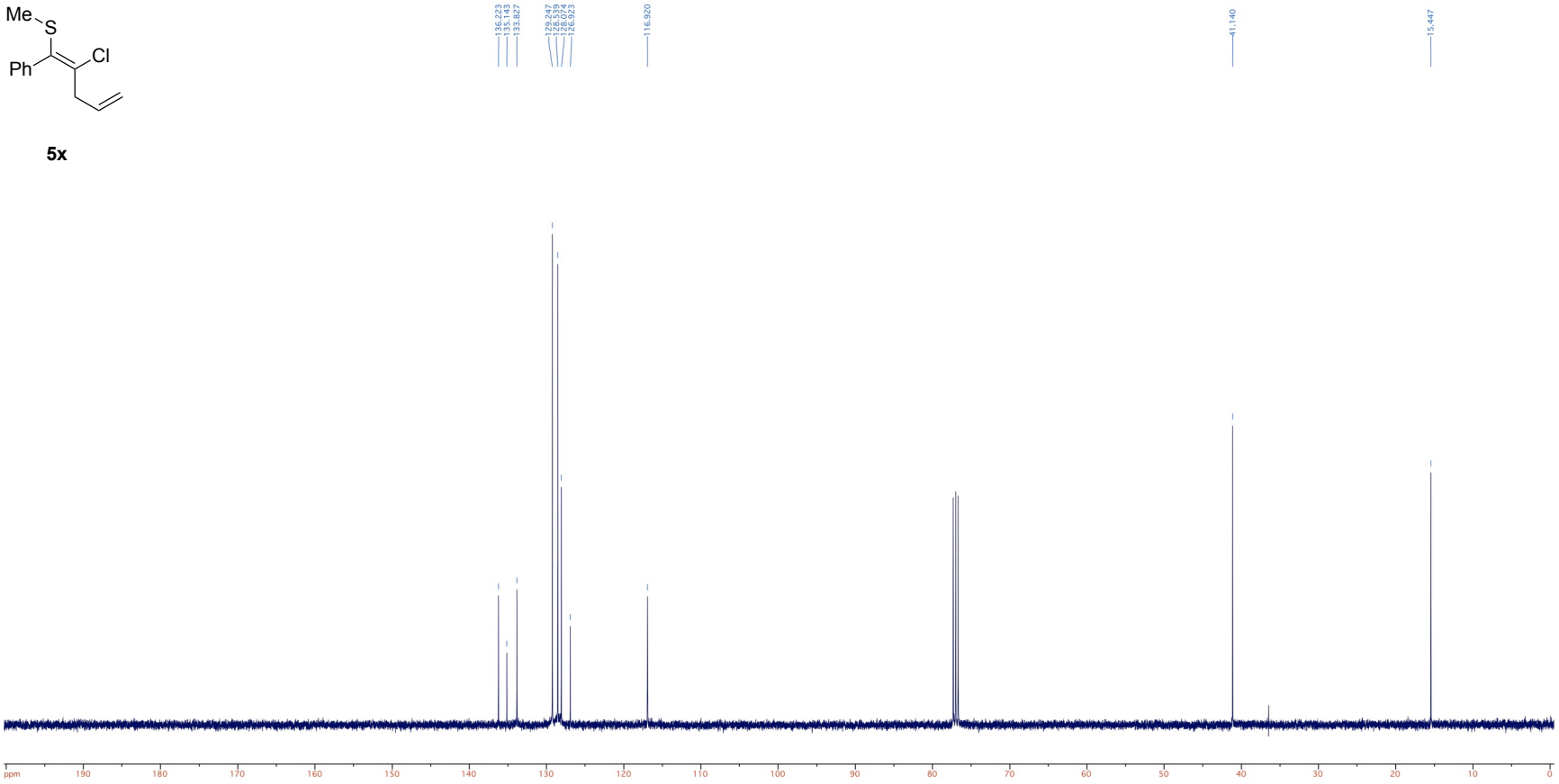


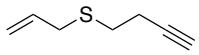
5x



Me
S
Ph
Cl

5x

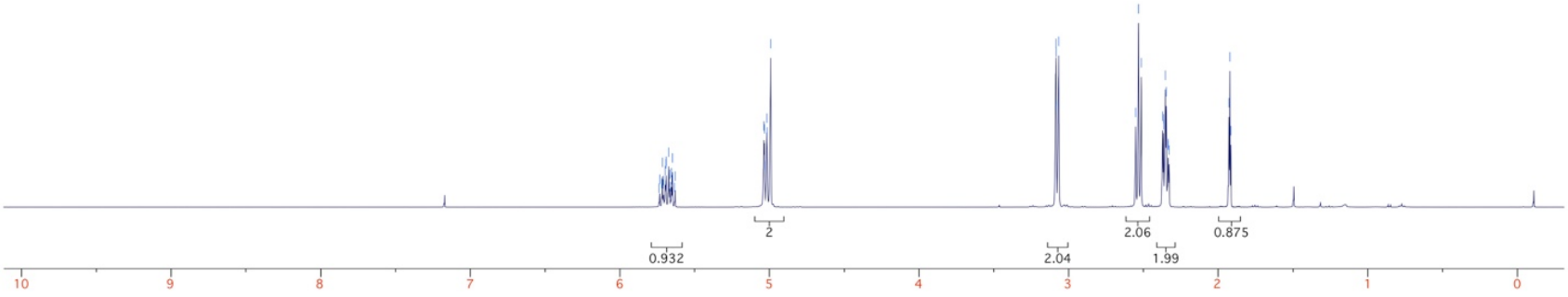

136.223
135.143
133.827
129.247
128.539
128.074
126.923
116.920
41.140
15.447
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



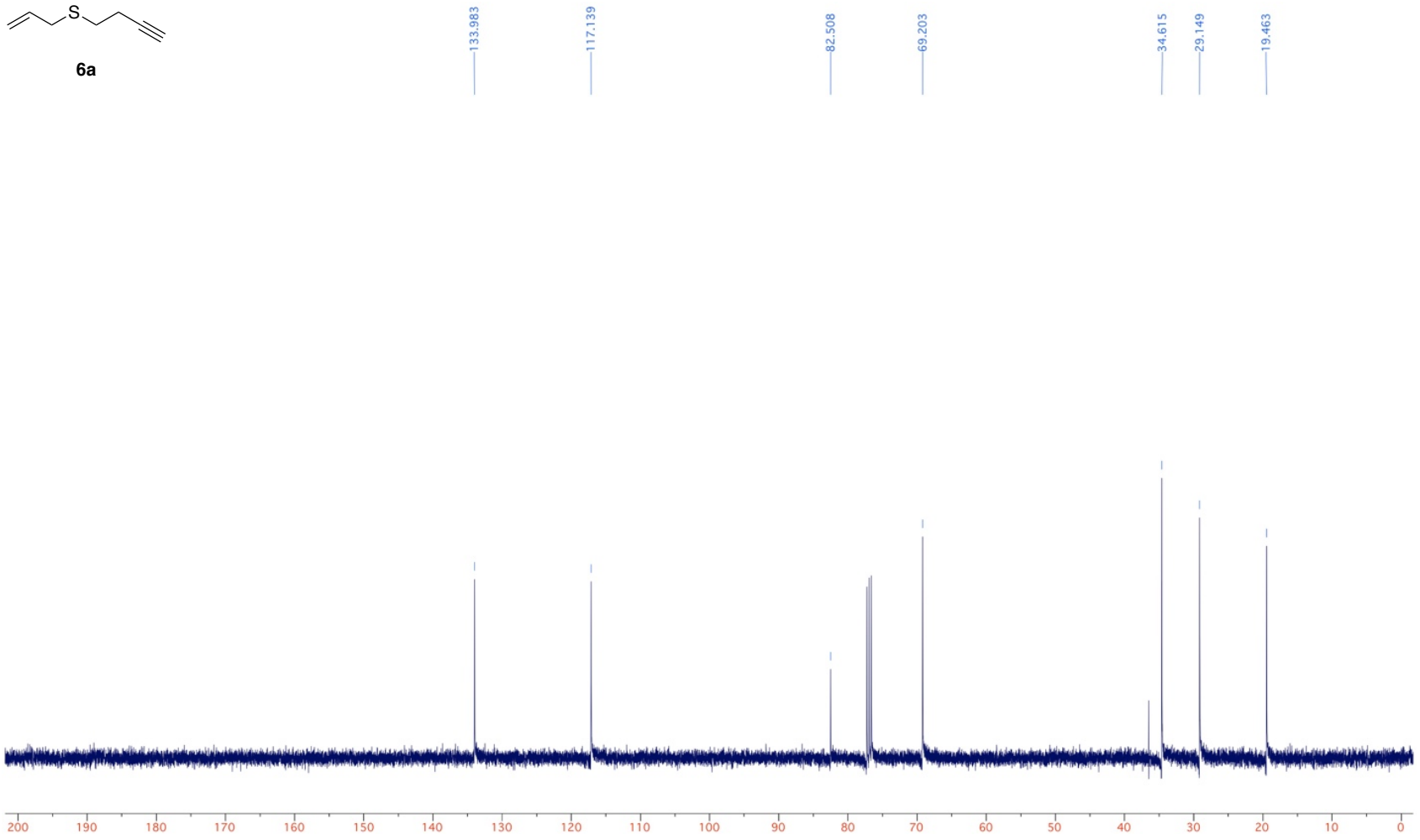
6a

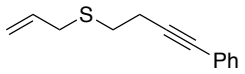

5.738
5.734
5.720
5.716
5.711
5.708
5.697
5.692
5.690
5.674
5.666
5.660
5.655
5.653
5.648
5.635
5.630
5.037
5.034
5.030
5.017
5.016
4.992


3.085
3.084
3.082
3.066
2.552
2.533
2.515
2.371
2.366
2.365
2.353
2.347
2.335
2.334
2.329
1.928
1.922
1.915


0.932
2
2.04
2.06
1.99
0.875
10
9
8
7
6
5
4
3
2
1
0

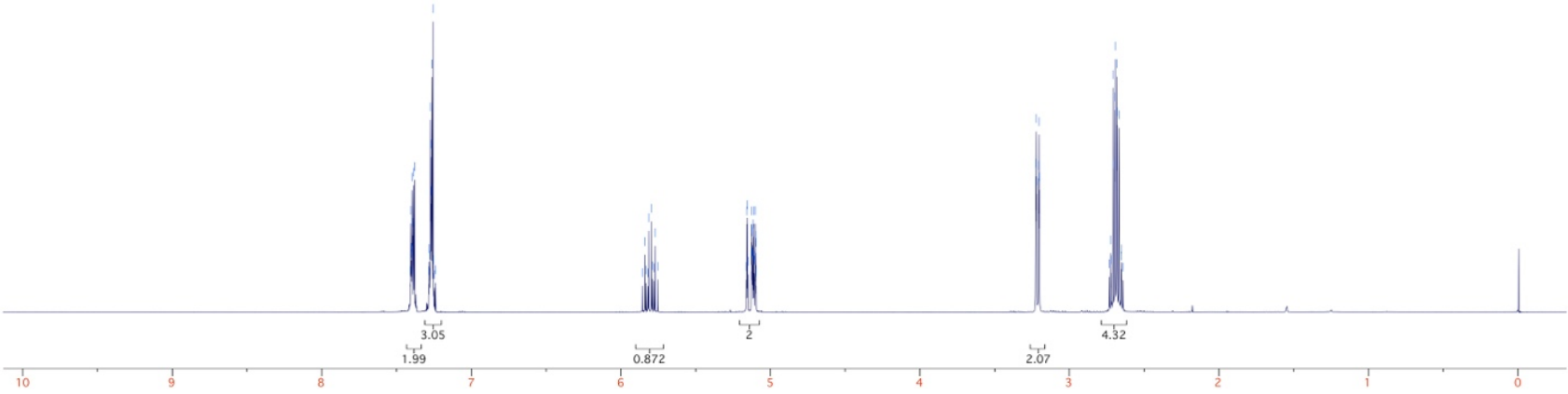
6a

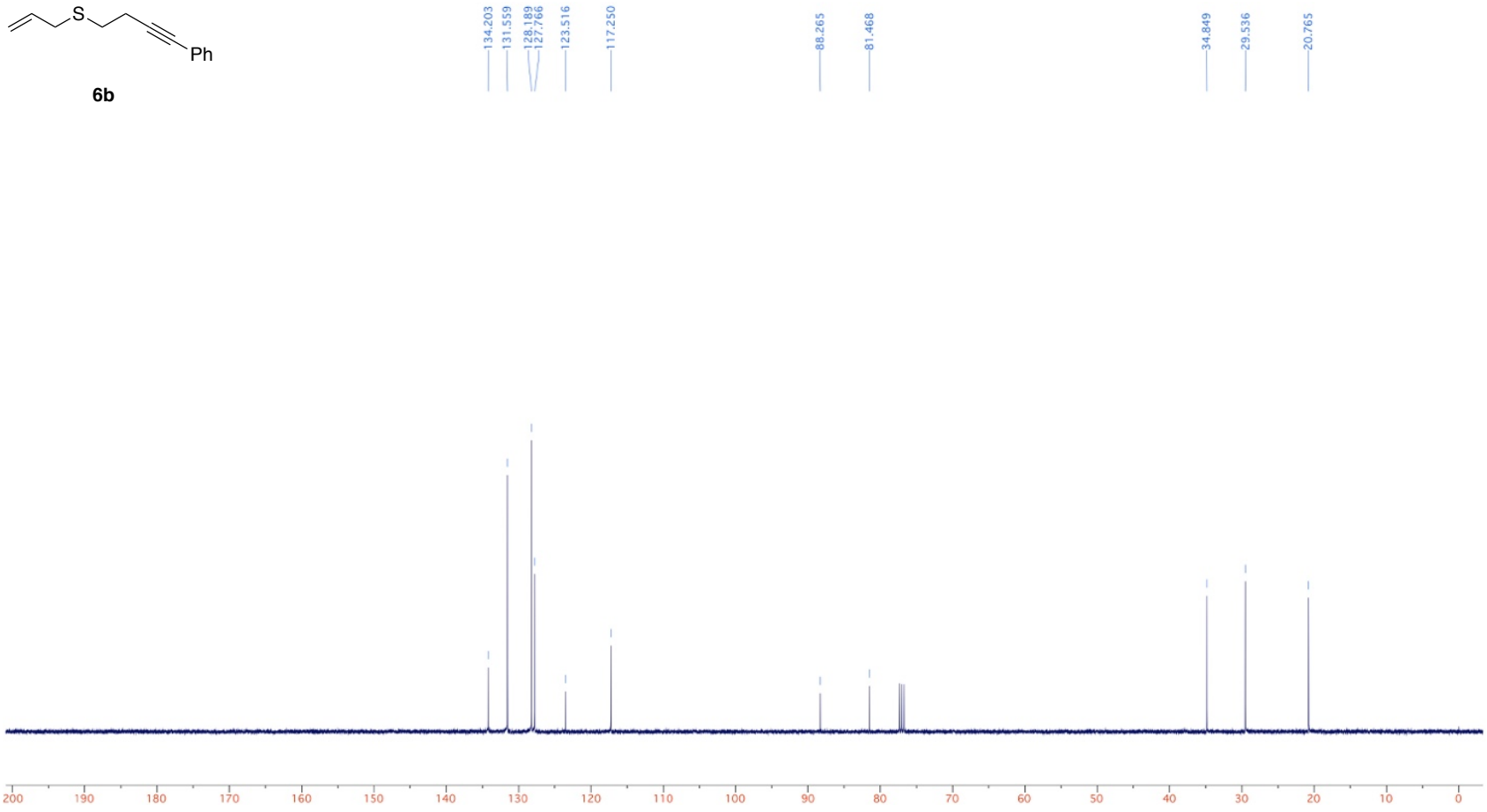

133.983
117.139
82.508
69.203
34.615
29.149
19.463
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


S
Ph

6b


7.408
7.405
7.401
7.399
7.396
7.393
7.386
7.380
7.284
7.281
7.278
7.273
7.270
7.267
7.263
7.256
7.253
7.246
7.239
5.856
5.838
5.831
5.820
5.814
5.796
5.789
5.778
5.771
5.753
5.751
5.157
5.154
5.150
5.127
5.125
5.123
5.121
5.119
5.115
5.111
5.108
5.103
5.100
5.098
5.096
5.094
3.223
3.221
3.218
3.205
3.203
3.200
2.733
2.723
2.721
2.707
2.706
2.695
2.693
2.683
2.680
2.668
2.655
2.652
2.643


3.05
1.99
0.872
2
2.07
4.32
10
9
8
7
6
5
4
3
2
1
0


S
Ph
6b
134.203
131.559
128.189
127.766
123.516
117.250
88.265
81.468
34.849
29.536
20.765
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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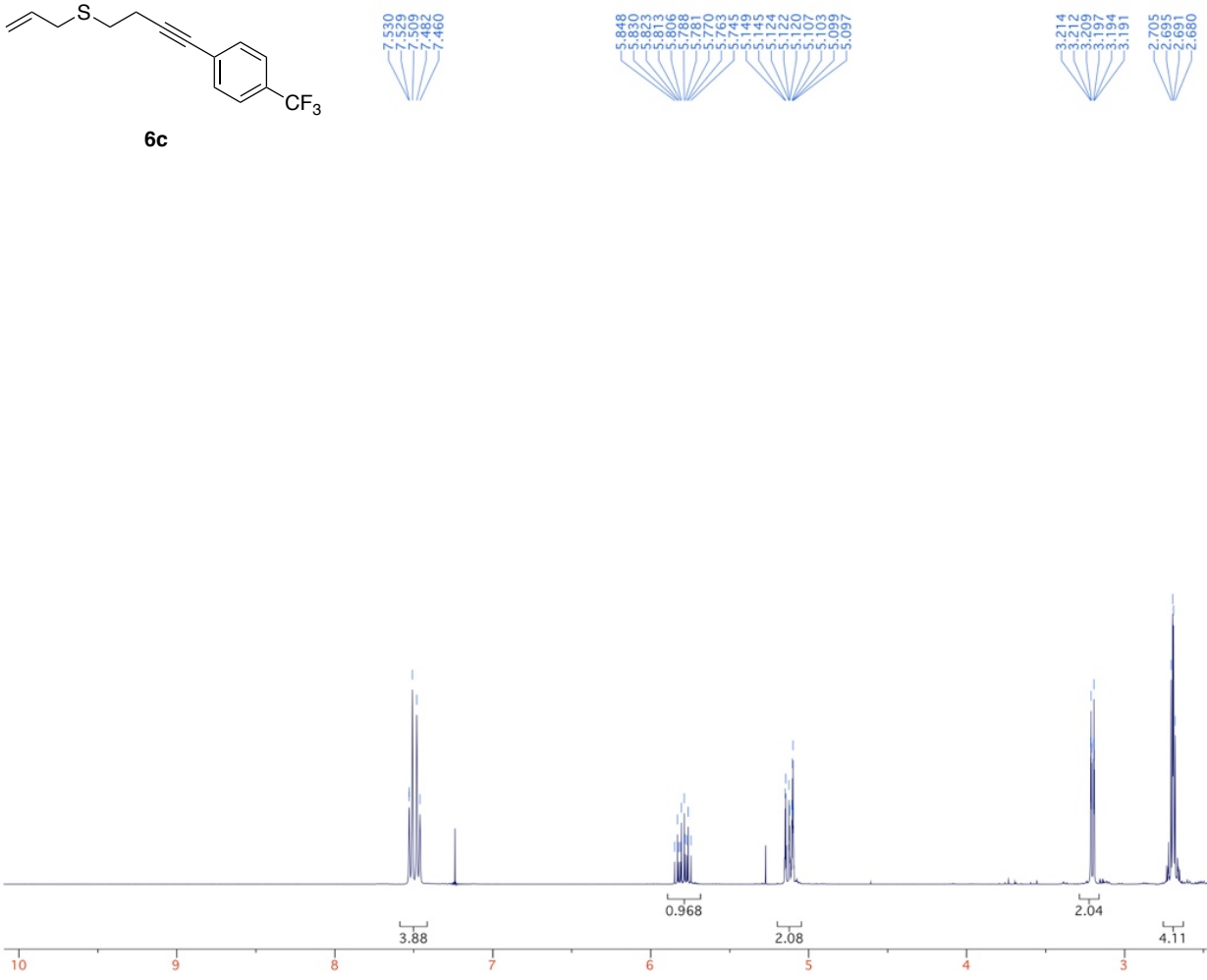
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CF3
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5.763
5.745
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5.122
5.120
5.107
5.103
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5.097
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3.212
3.209
3.197
3.194
3.191
2.705
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2.691
2.680
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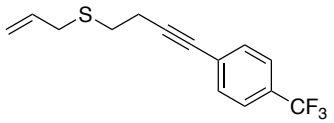
6c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CF3

6c


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125.039
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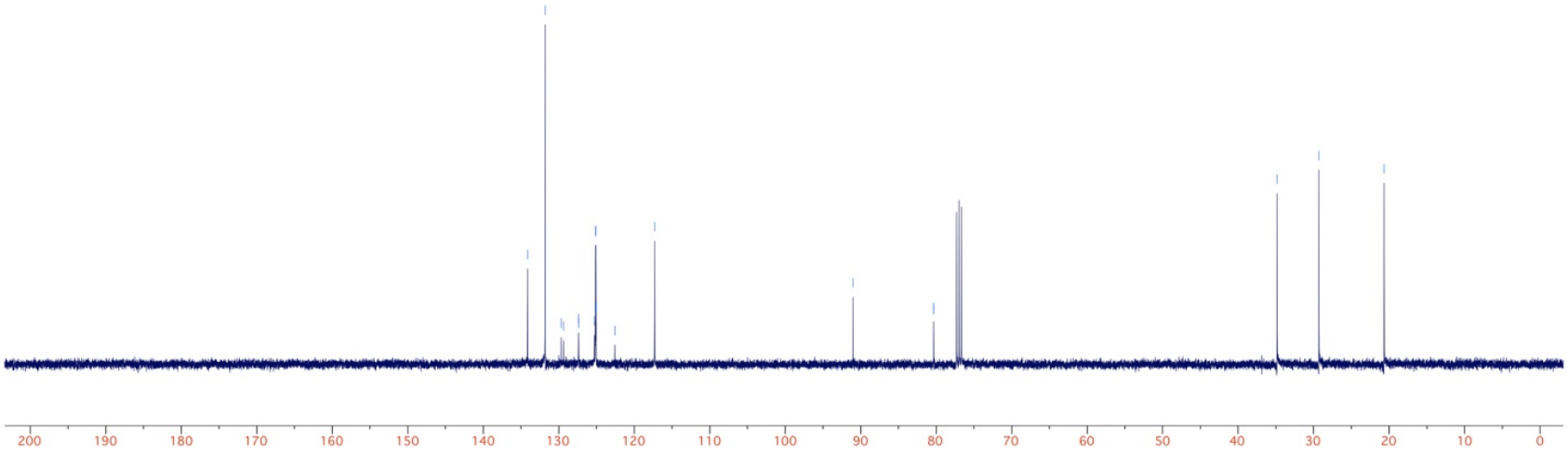
20.669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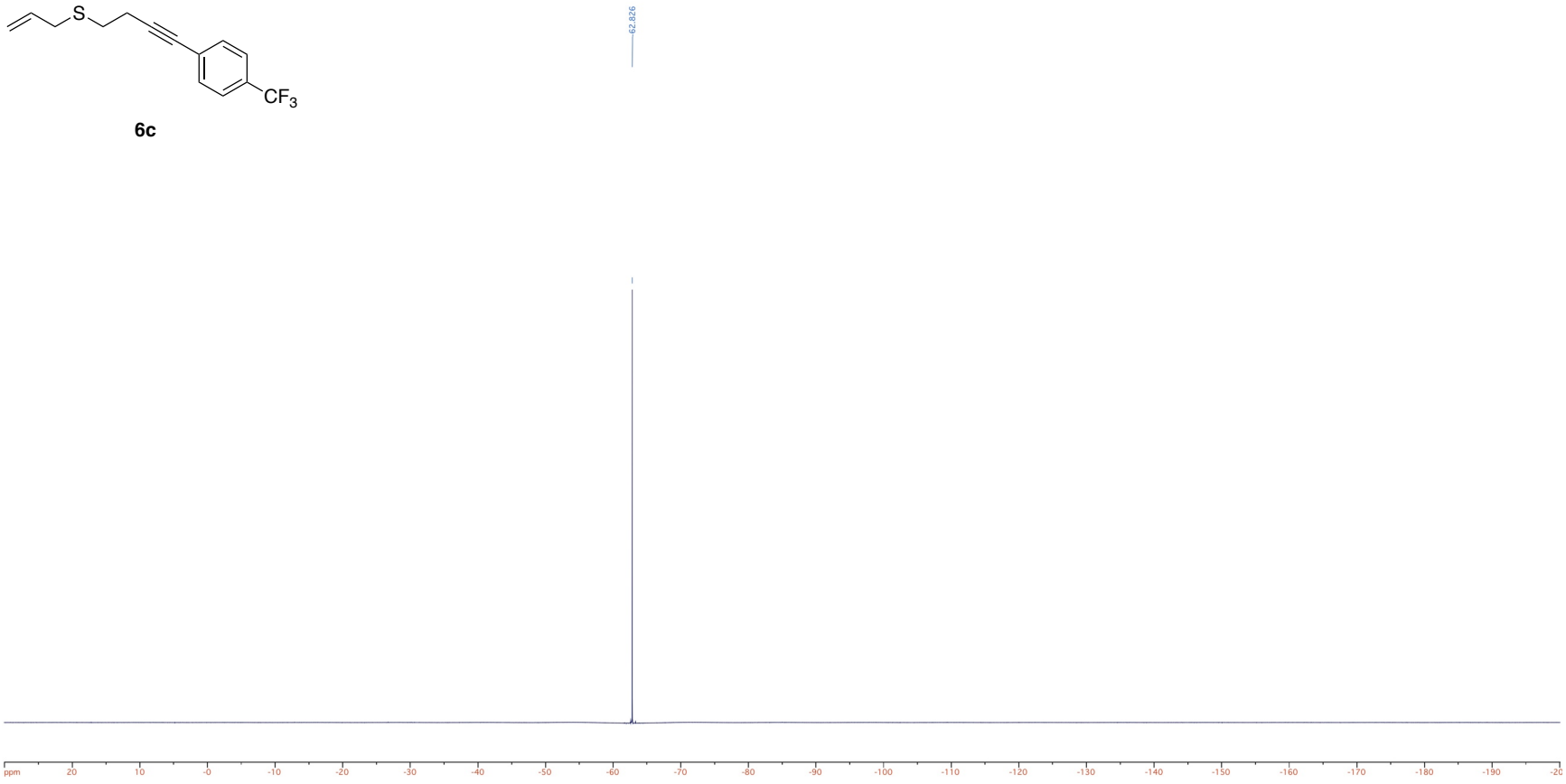
0

S
CF3

6c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-170
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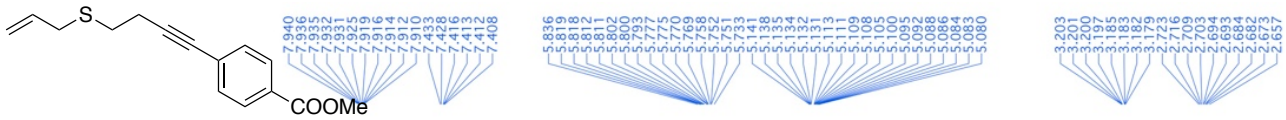
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COOMe
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7.910
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7.428
7.416
7.413
7.412
7.408
5.836
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5.818
5.812
5.811
5.802
5.800
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5.132
5.131
5.113
5.109
5.108
5.105
5.100
5.095
5.092
5.088
5.086
5.084
5.083
5.080
3.203
3.201
3.200
3.197
3.185
3.183
3.182
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2.709
2.703
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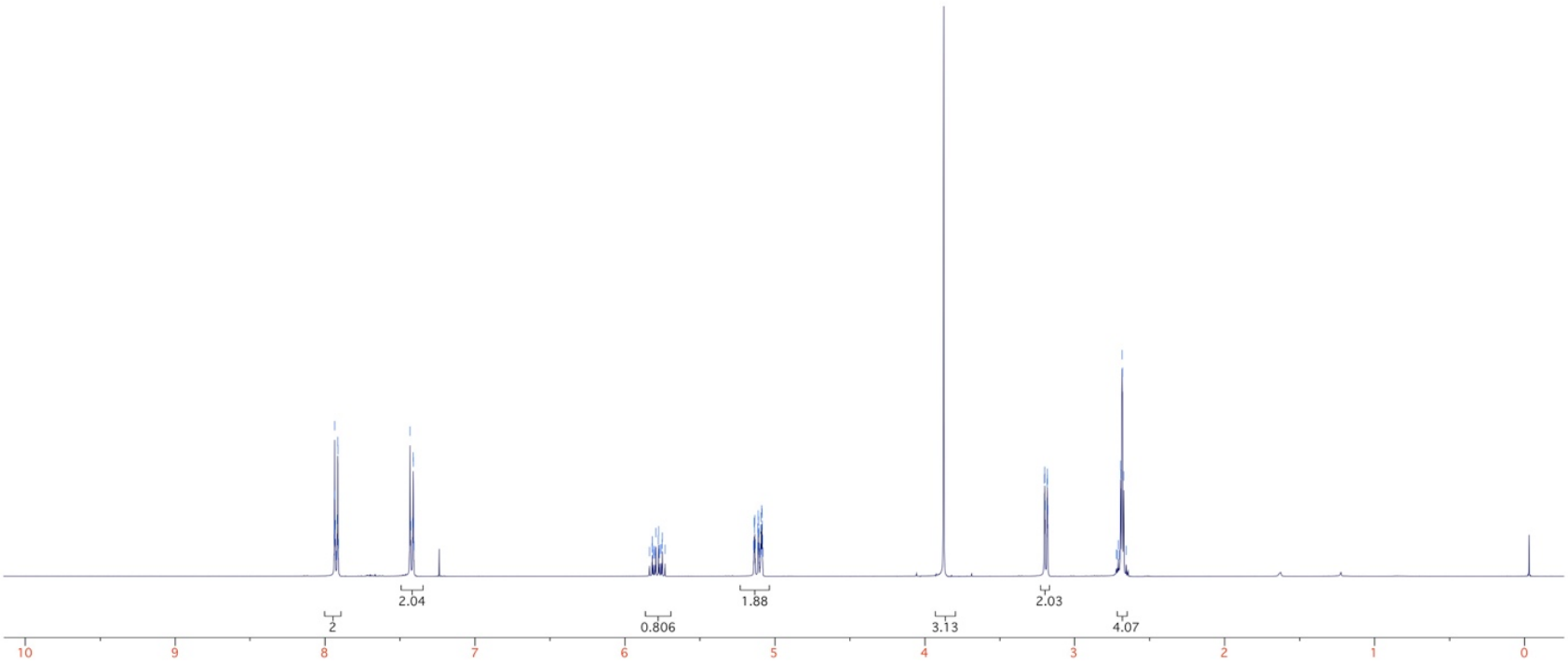
2.684
2.682
2.673
2.657

6d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3.13
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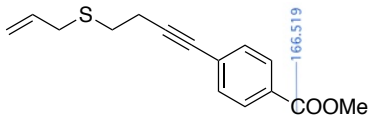
S
COOMe

6d


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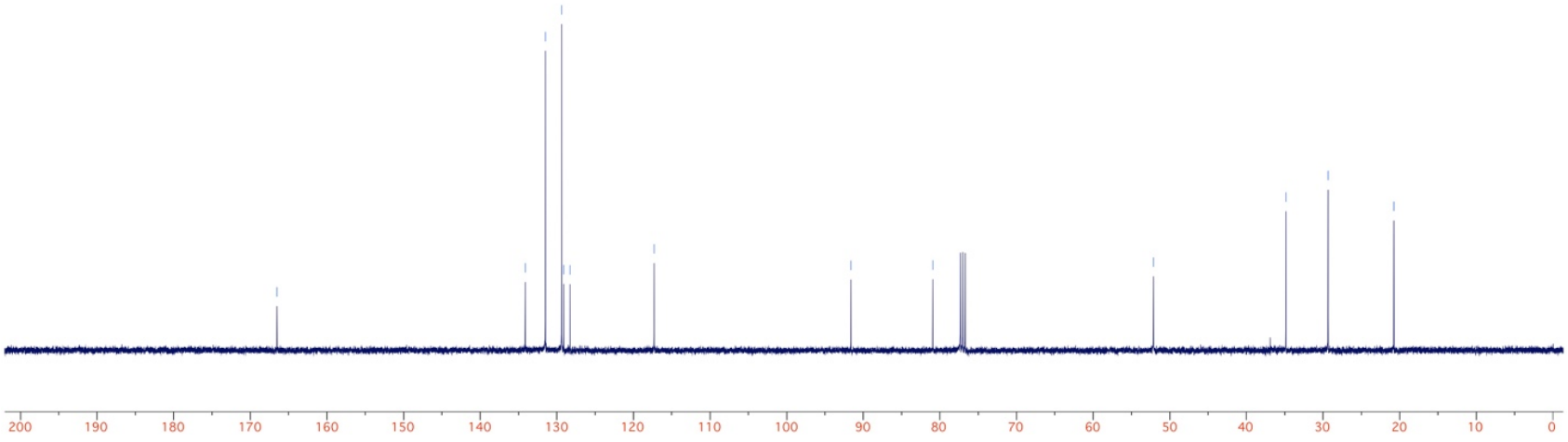
117.291
91.605
80.926
52.124
34.837
29.334
20.751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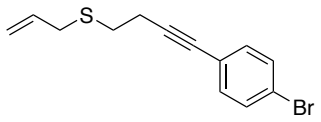
0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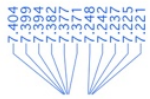
Br

6e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7.371
7.248
7.242
7.237
7.225
7.221


5.821
5.796
5.779
5.754
5.142
5.139
5.135
5.132
5.116
5.114
5.112
5.110
5.108
5.096
5.093
5.091
5.089
5.087
5.085


3.203
3.200
3.198
3.185
3.182
3.180
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2.695
2.684
2.683
2.671
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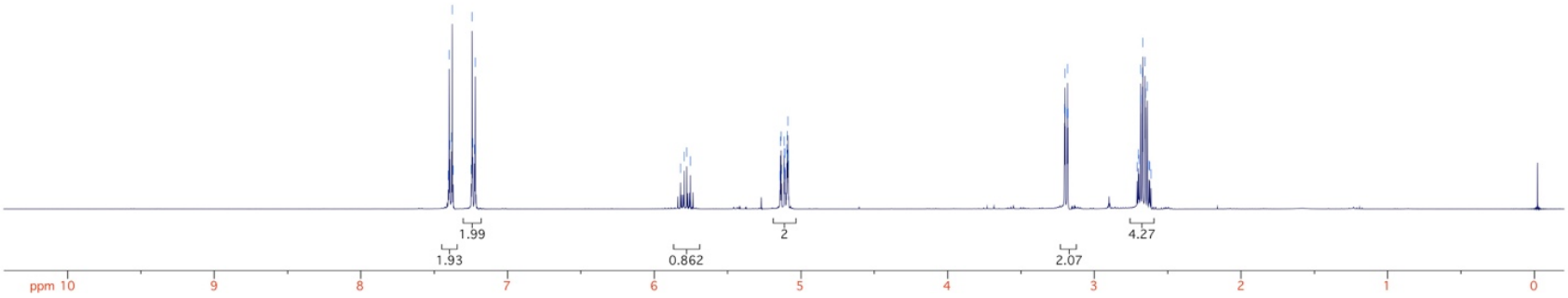
2.651
2.638
2.637
2.622
2.614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4.27
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8
7
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4
3
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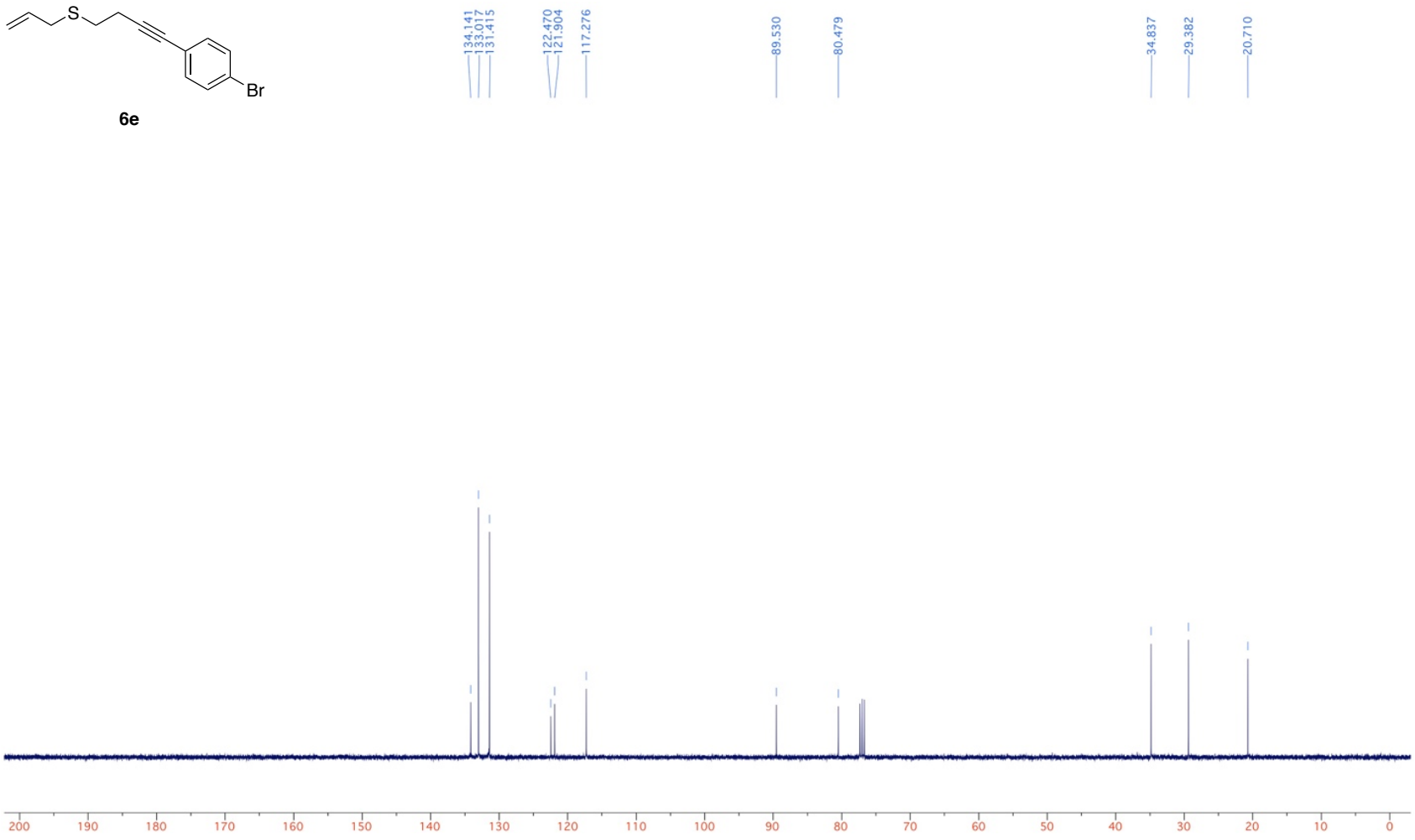
0

S
Br

6e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121.904
117.276
89.530
80.479
34.837
29.382
20.710
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150
140
130
120
110
100
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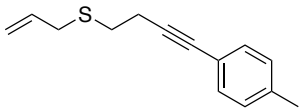
80
70
60
50
40
30
20
10
0



6f


7.296
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7.065
7.064
5.838
5.814
5.796
5.795
5.771
5.161
5.160
5.157
5.154
5.150
5.124
5.123
5.120
5.119
5.115
5.111
5.108
5.107
5.099
5.098
5.095
5.094
3.220
3.202
3.719
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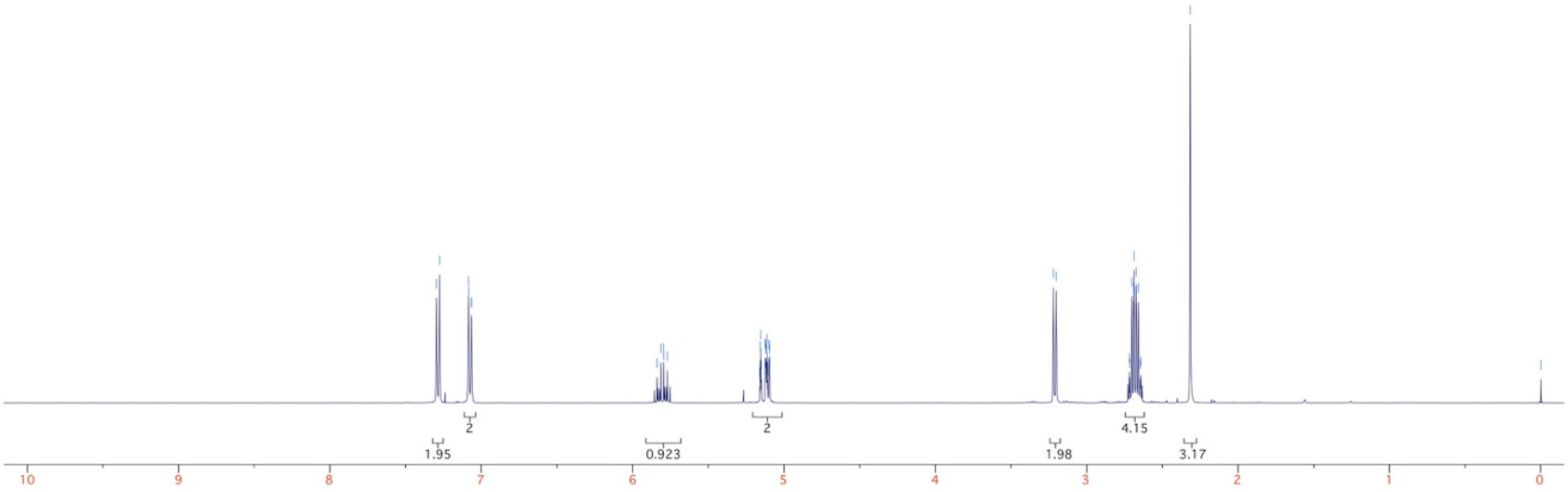
2.690
2.689
2.687
2.674
2.671
2.659
2.647
2.642
2.316
0.002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9
8
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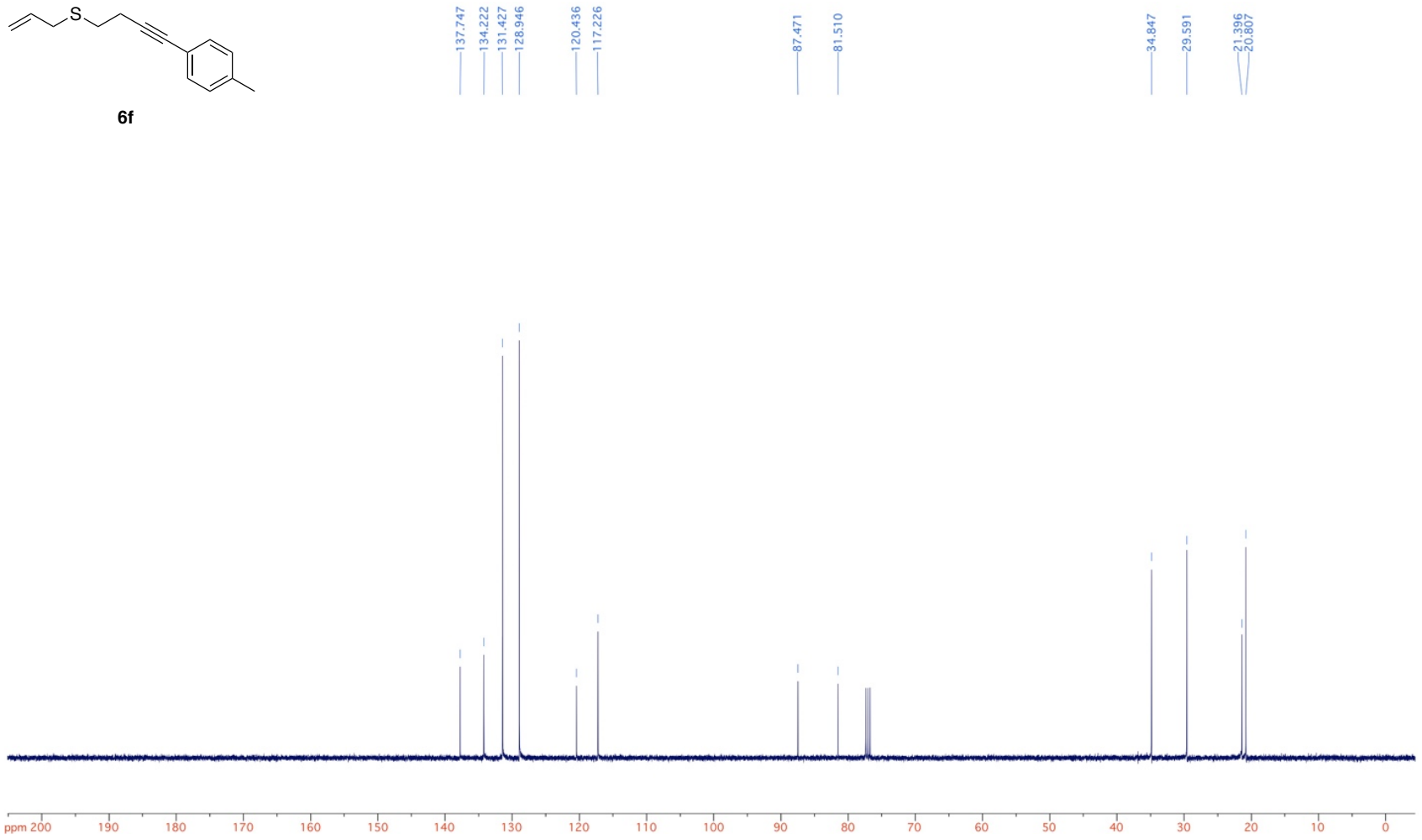
6
5
4
3
2
1
0

6f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81.510
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29.591
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20.807
ppm 200
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150
140
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110
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70
60
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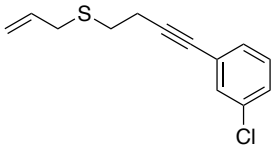
30
20
10
0


S
Cl

6g


7.372
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7.259
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7.240
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7.223
7.219
7.201
7.200
7.183
7.163
7.162
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5.826
5.819
5.808
5.801
5.794
5.766
5.759
5.741
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5.142
5.139
5.121
5.121
5.119
5.103
5.093
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3.187
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2.704
2.688
2.674
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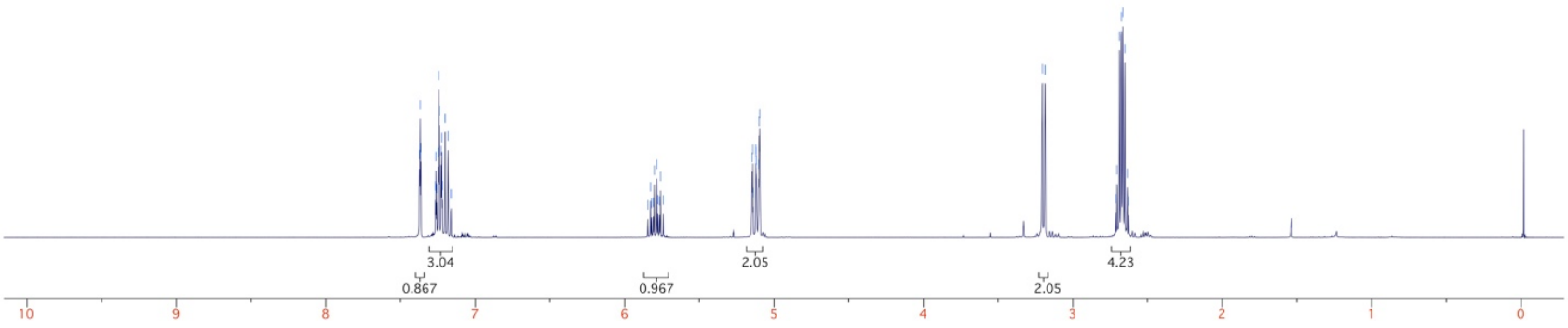
2.652
2.637
2.626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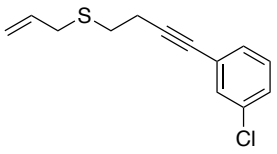
S
Cl

6g


134.130
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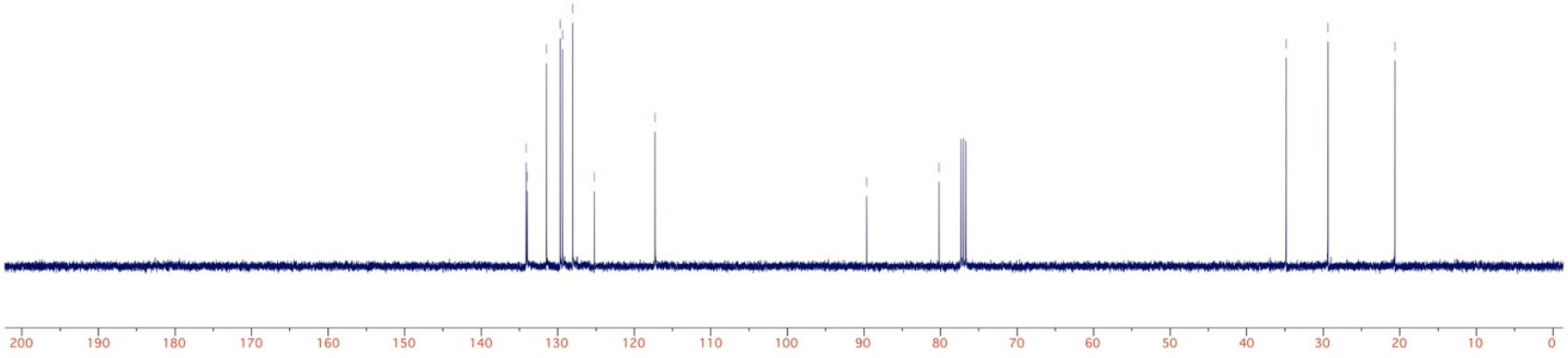
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90
80
70
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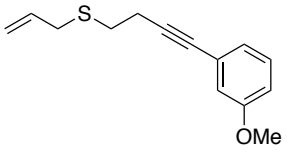
50
40
30
20
10
0


S
OMe

6h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6.995
6.992
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6.976
6.973
6.927
6.923
6.920
6.917
6.841
6.838
6.834
6.832
6.820
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6.813
6.811
5.855
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5.155
5.132
5.128
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5.124
5.122
5.120
5.116
5.113
5.109
5.104
5.101
5.100
5.098
5.096
3.769
3.225
3.222
3.219
3.207
3.204
3.201
3.192
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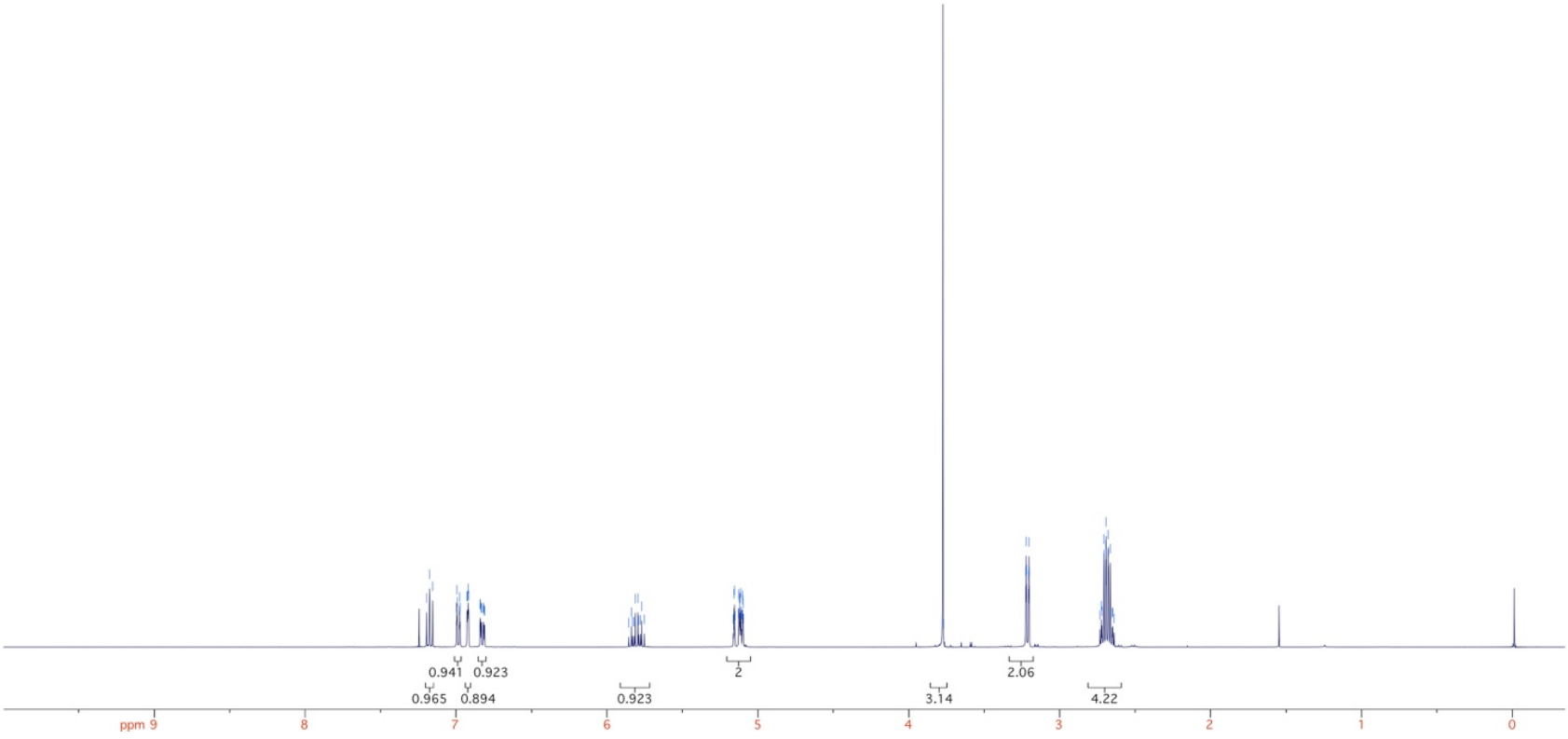
2.640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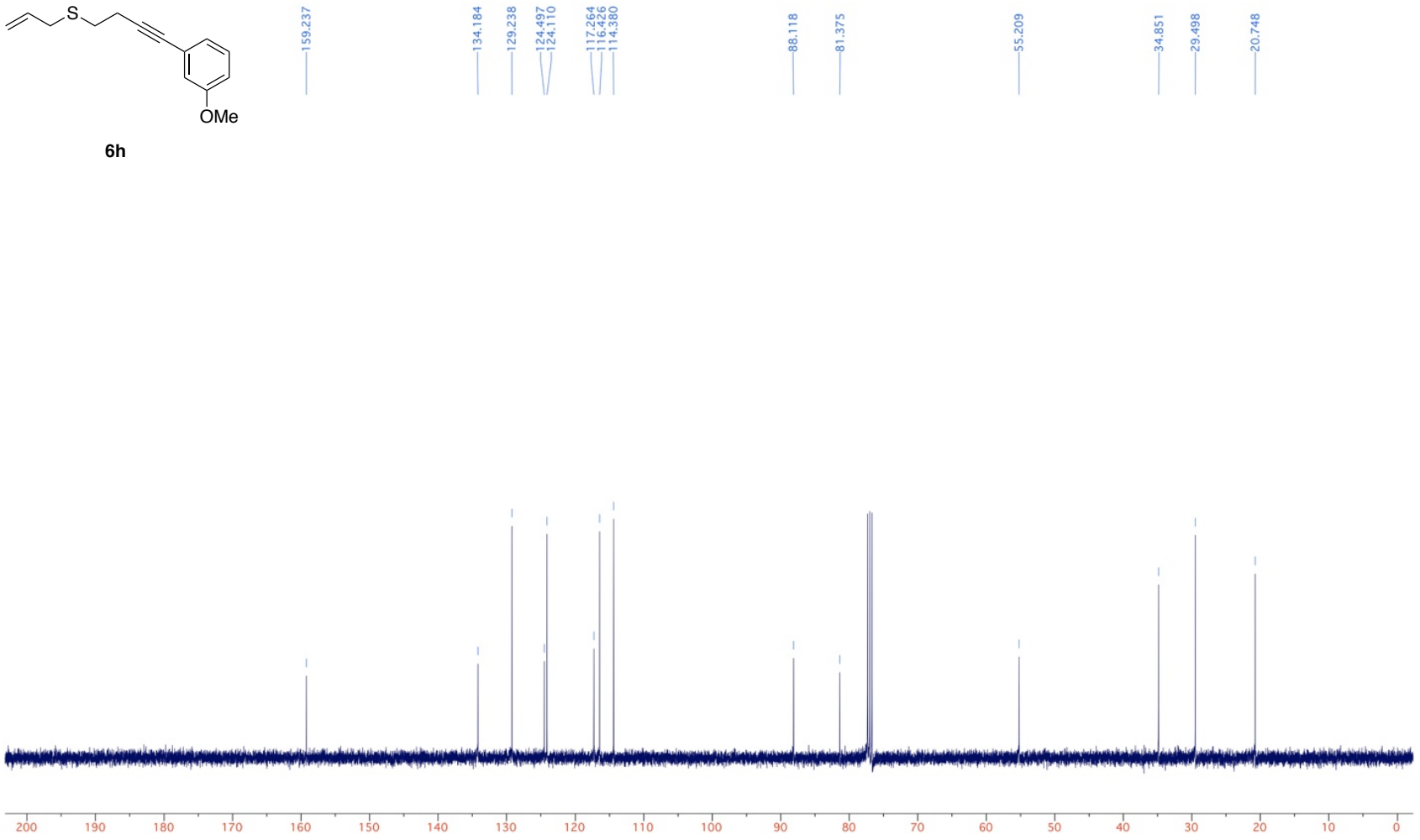
3
2
1
0

S
OMe

6h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124.110
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114.380
88.118
81.375
55.209
34.851
29.498
20.748
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150
140
130
120
110
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70
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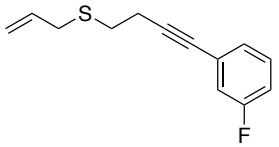
30
20
10
0


S
F

6i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7.382
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7.363
7.267
7.262
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7.241
7.234
7.228
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7.210
7.066
7.063
7.051
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7.045
7.027
7.006
7.004
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5.828
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5.793
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5.775
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5.750
5.164
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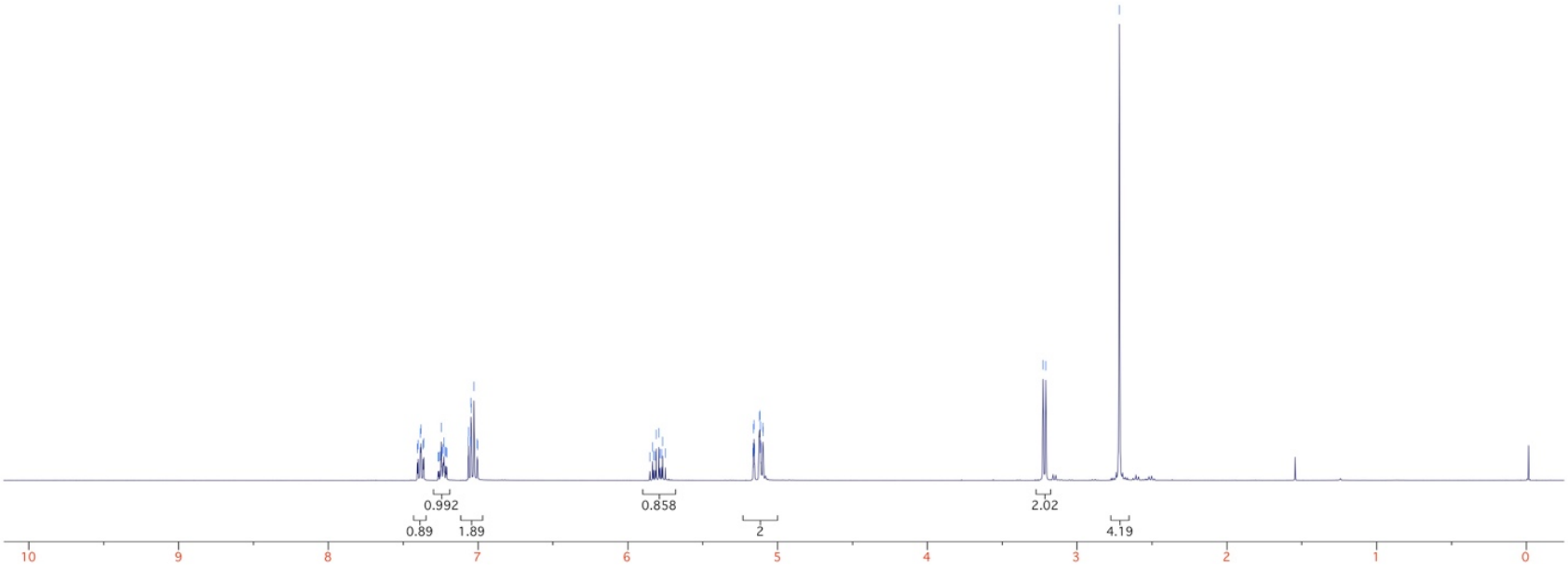
2.718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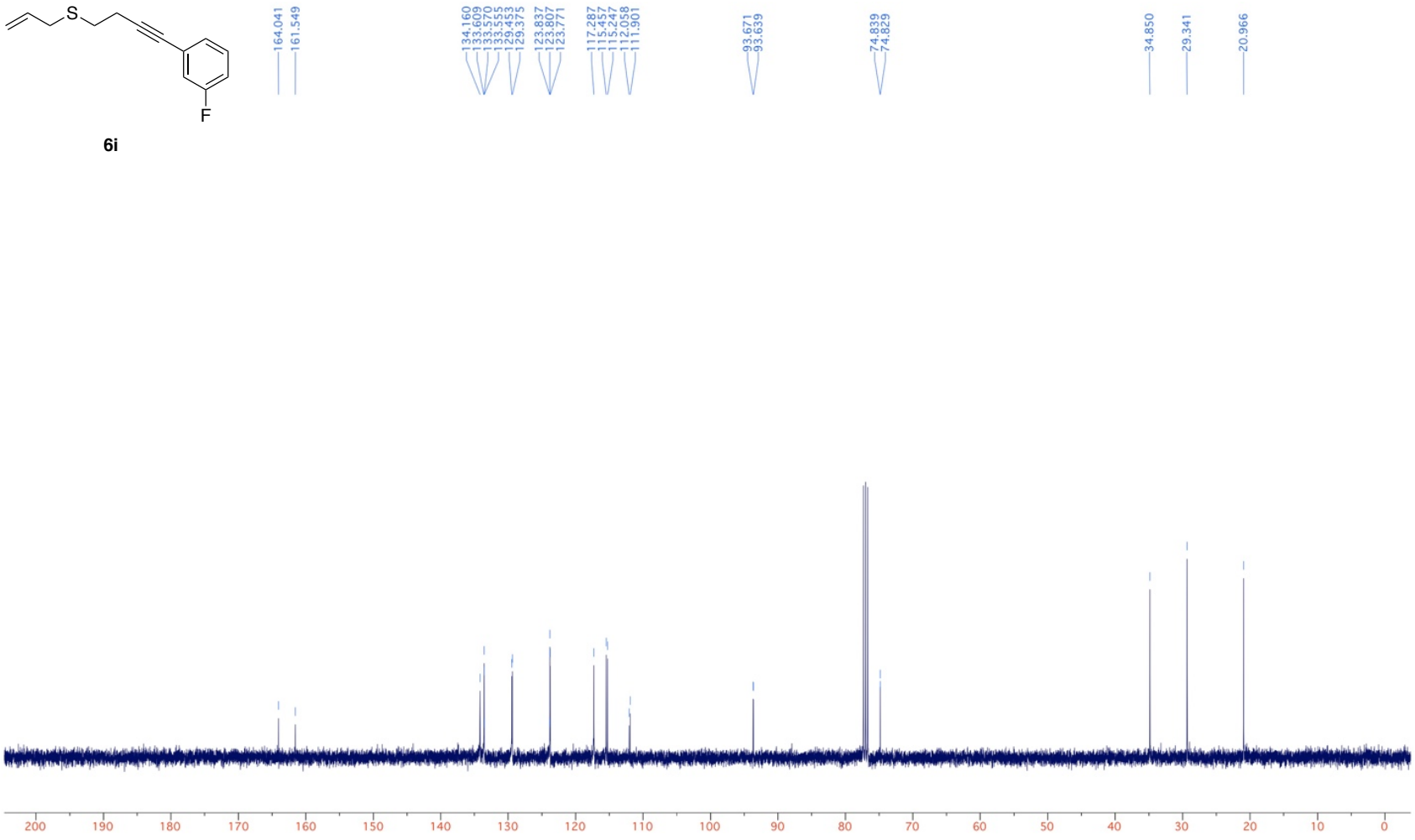
S
F
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123.807
123.771
117.287
115.457
115.247
112.058
111.901
93.671
93.639
74.839
74.829
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29.341
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200
190
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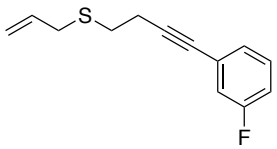
0

6i


S
F

6i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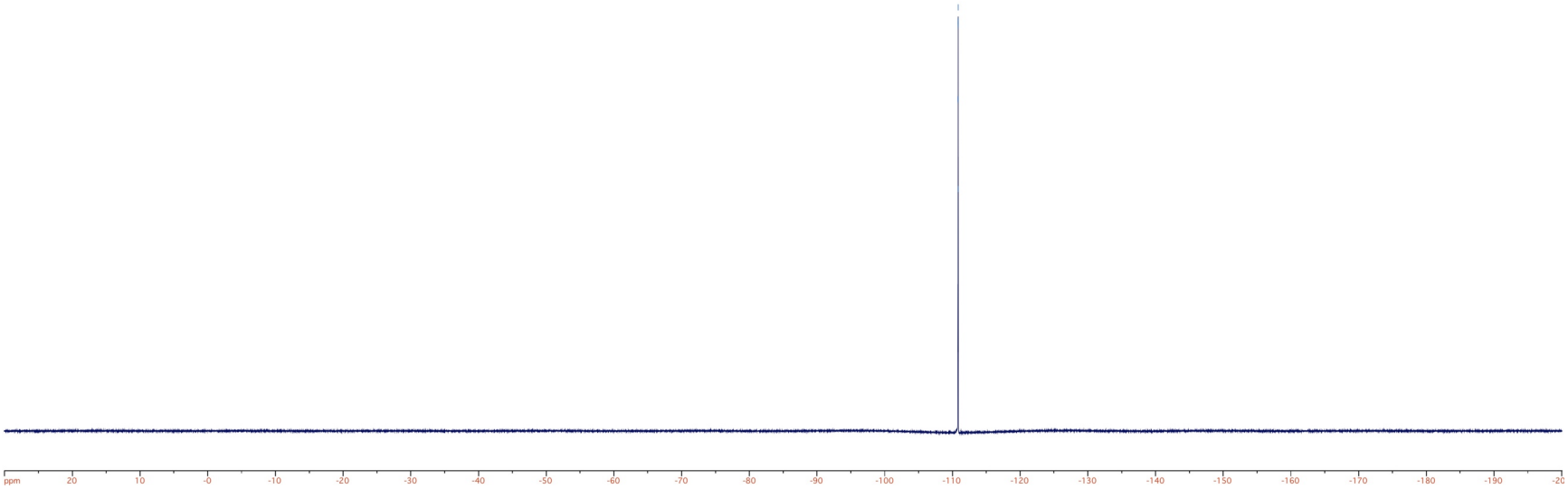
-110.842
-110.847
-110.876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-100
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-120
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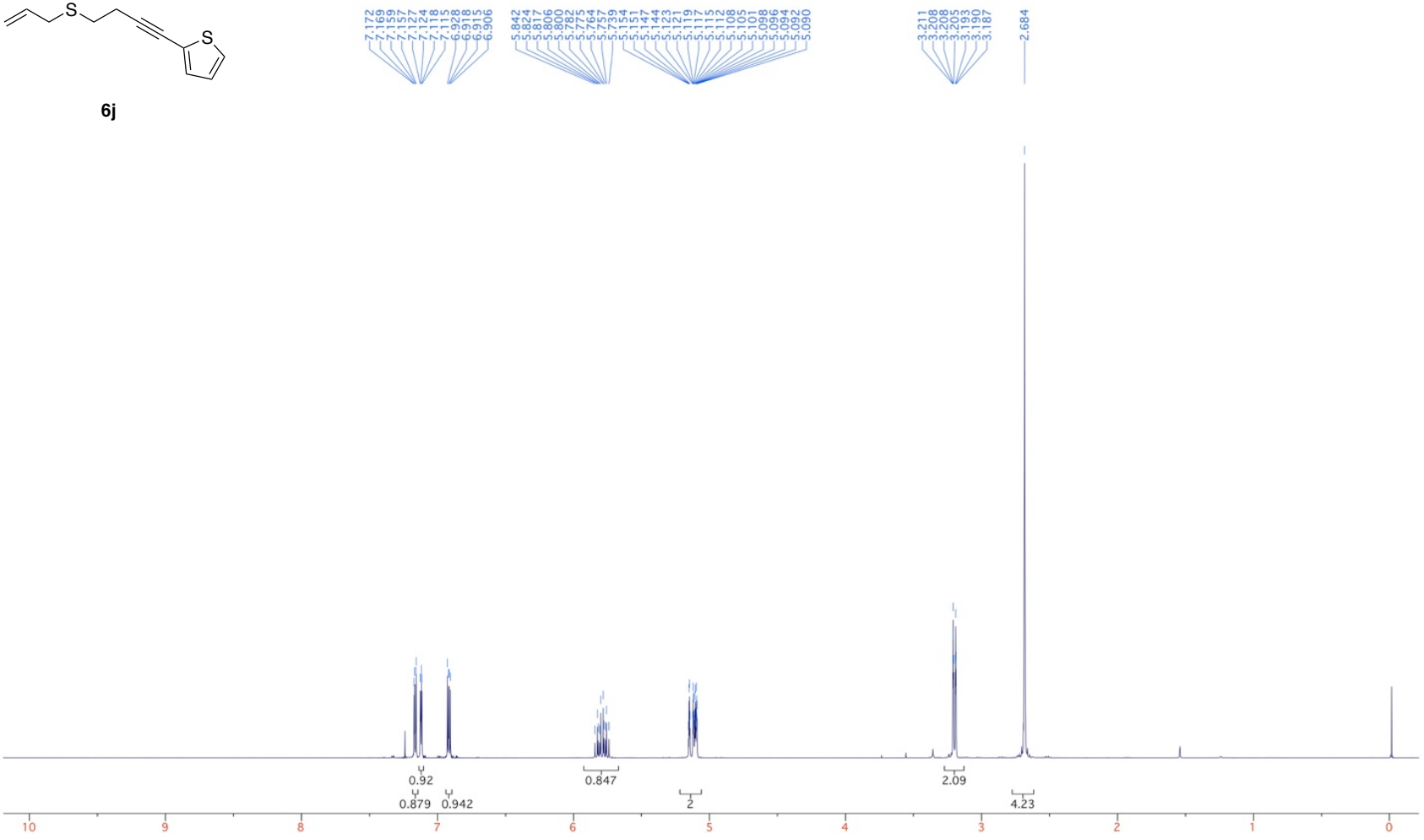
-150
-160
-170
-180
-190

6j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7.124
7.118
7.115
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6.918
6.915
6.906
5.842
5.824
5.817
5.806
5.800
5.782
5.775
5.764
5.757
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5.154
5.151
5.147
5.144
5.123
5.121
5.119
5.115
5.112
5.108
5.105
5.101
5.098
5.096
5.094
5.092
5.090
3.211
3.208
3.208
3.205
3.193
3.190
3.187
2.684
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0.879
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2.09
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5
4
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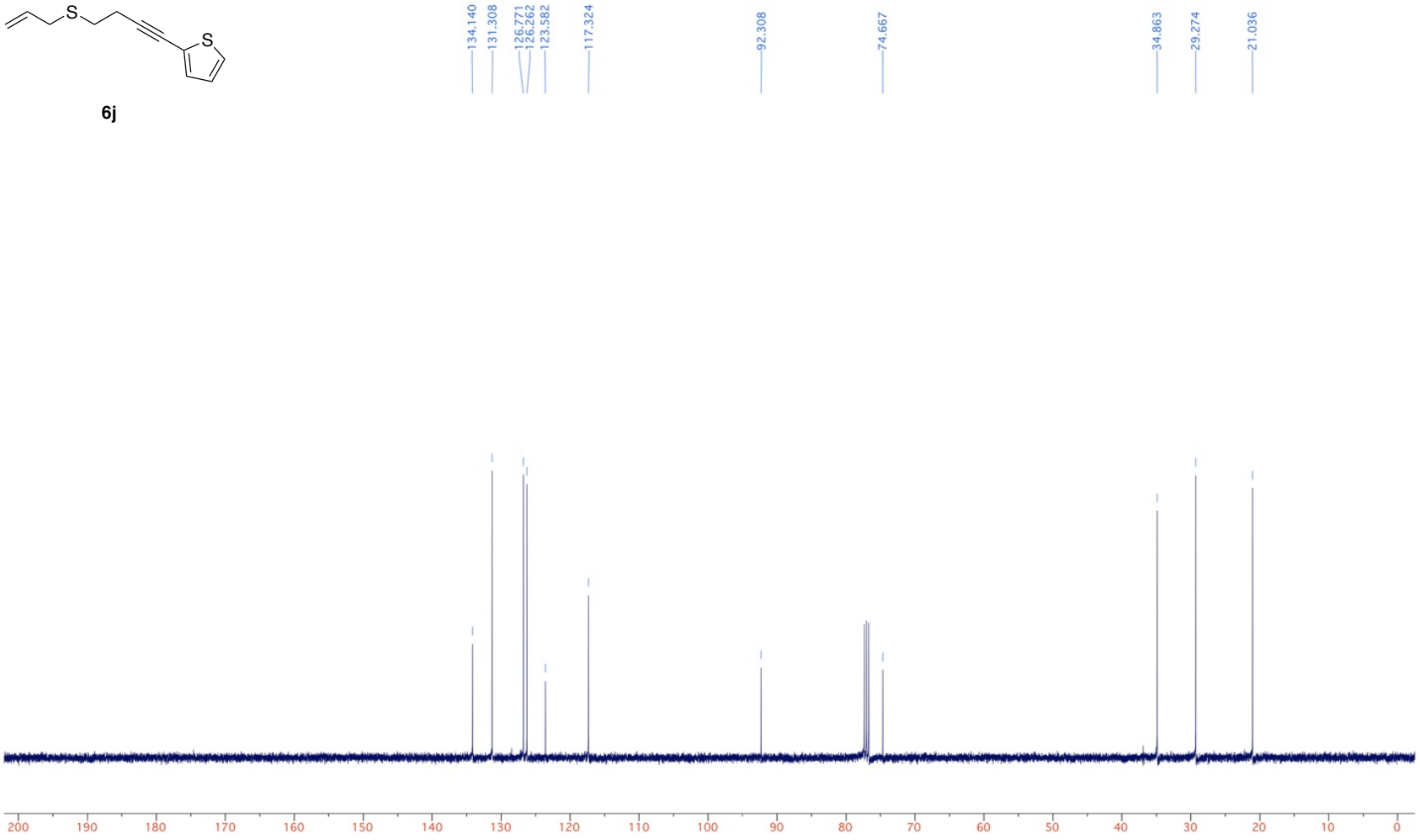
2
1
0

6j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74.667
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29.274
21.036
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150
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10
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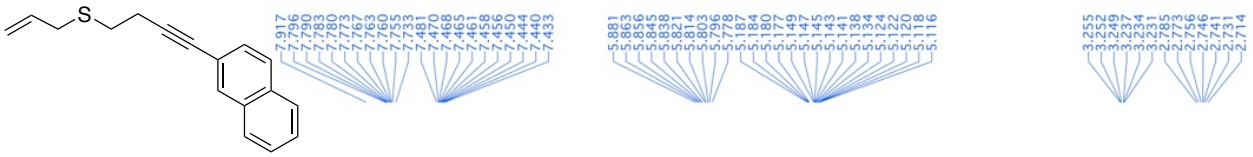
S
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7.760
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7.481
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7.468
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7.461
7.458
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5.821
5.814
5.803
5.796
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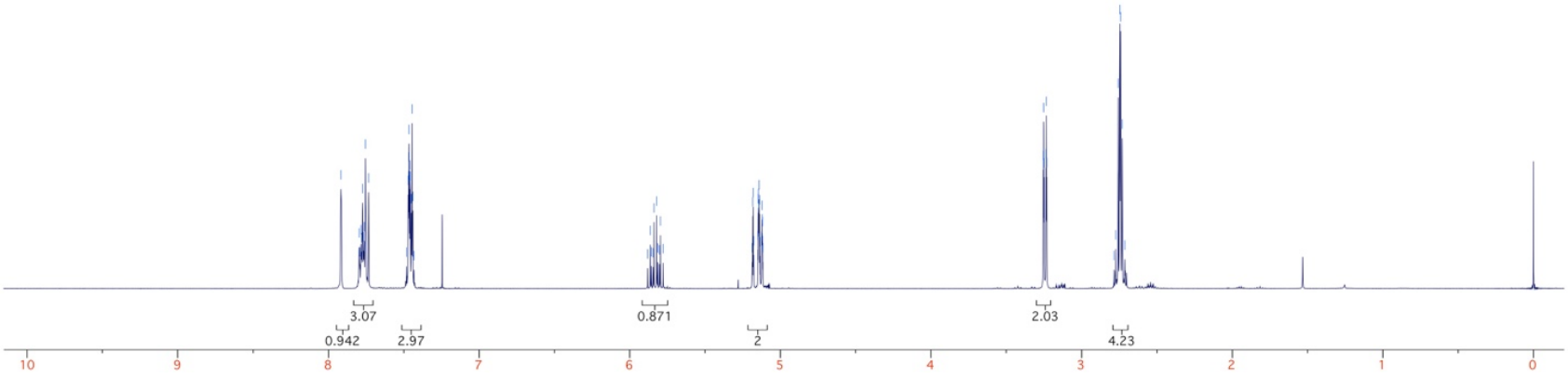
5.187
5.184
5.180
5.177
5.149
5.147
5.145
5.143
5.141
5.138
5.134
5.124
5.122
5.120
5.118
5.116
3.255
3.252
3.249
3.237
3.234
3.231
3.228
2.775
2.756
2.746
2.741
2.731
2.714

6k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2.97
0.871
2
2.03
4.23
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9
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3
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1
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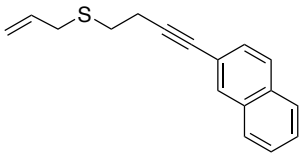
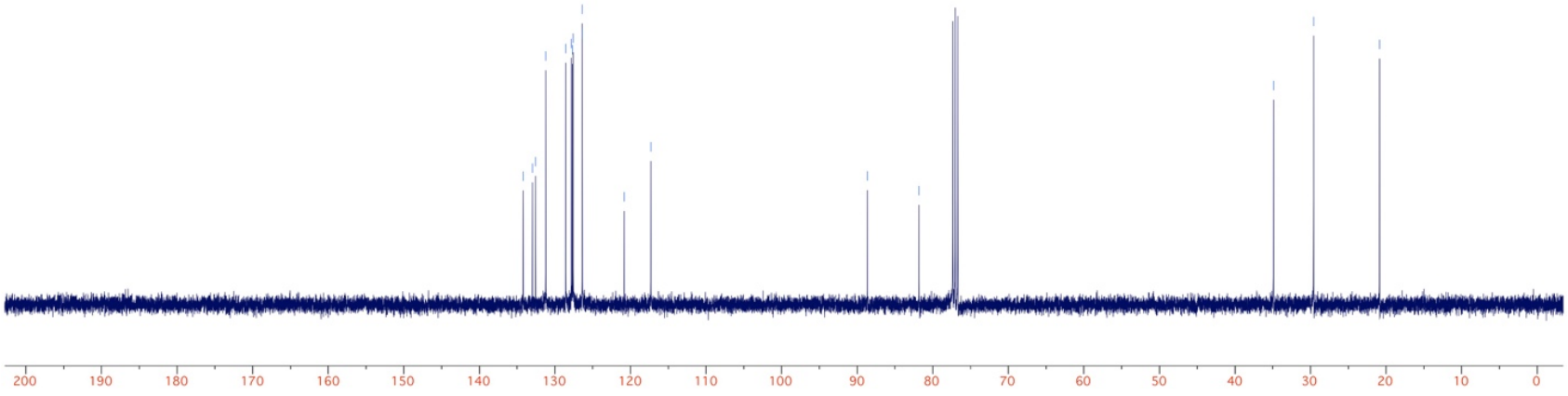

S

6k


134.206
132.974
132.559
131.214
128.570
128.371
127.676
127.590
126.388
126.370
120.830
117.300
88.640
81.824
34.888
29.582
20.860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100
90
80
70
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30
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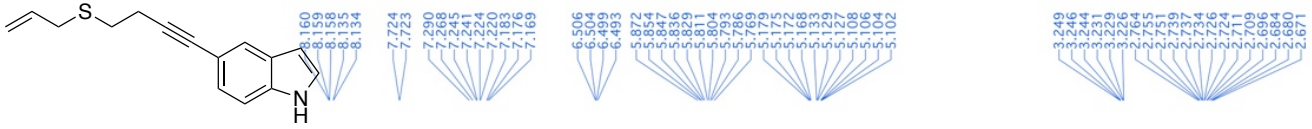
S
N
H
8.160
8.159
8.158
8.135
8.134
7.724
7.723
7.290
7.268
7.245
7.241
7.224
7.220
7.183
7.176
7.169
6.506
6.504
6.499
6.493
5.872
5.854
5.847
5.836
5.829
5.811
5.804
5.793
5.786
5.769
5.179
5.175
5.172
5.168
5.129
5.127
5.108
5.106
5.104
5.102
3.249
3.246
3.244
3.231
3.229
3.226
2.764
2.755
2.751
2.739
2.737
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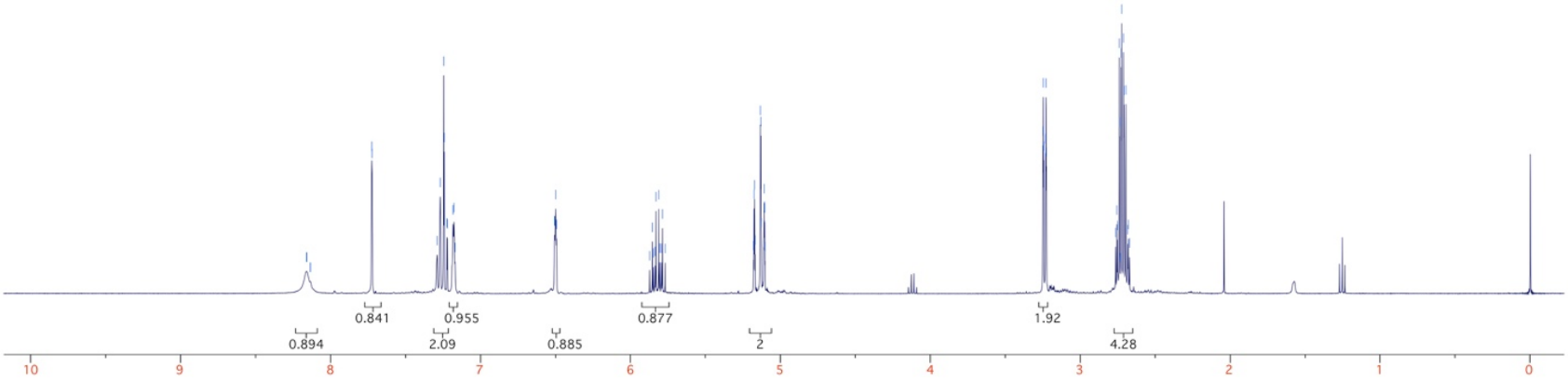
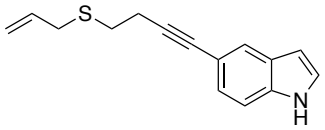
2.726
2.724
2.711
2.709
2.696
2.684
2.680
2.671

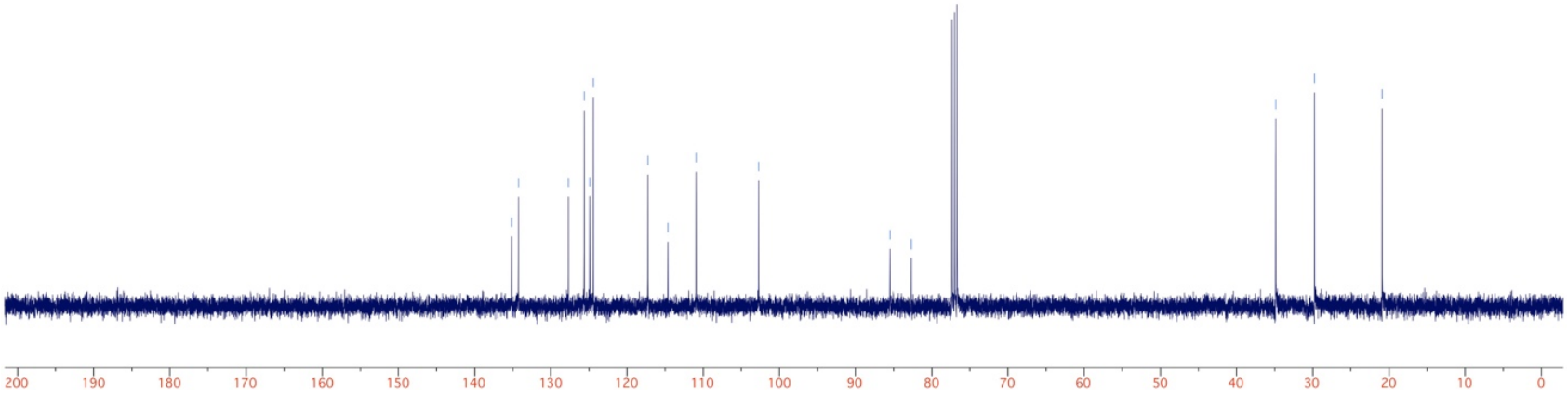
6l

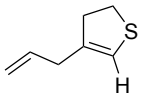

0.894
0.841
2.09
0.955
0.885
0.877
2
1.92
4.28
10
9
8
7
6
5
4
3
2
1
0


S
N
H

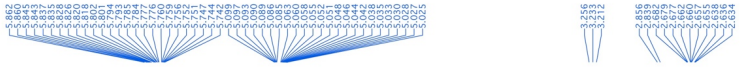
6l

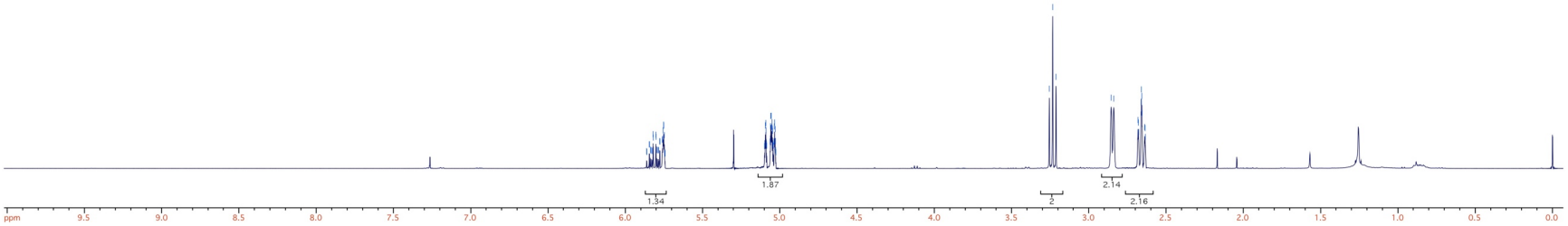

135.159
134.245
127.685
125.623
125.483
124.418
117.257
114.634
110.950
102.719
85.475
82.694
82.689
34.860
29.771
20.894


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


S
H

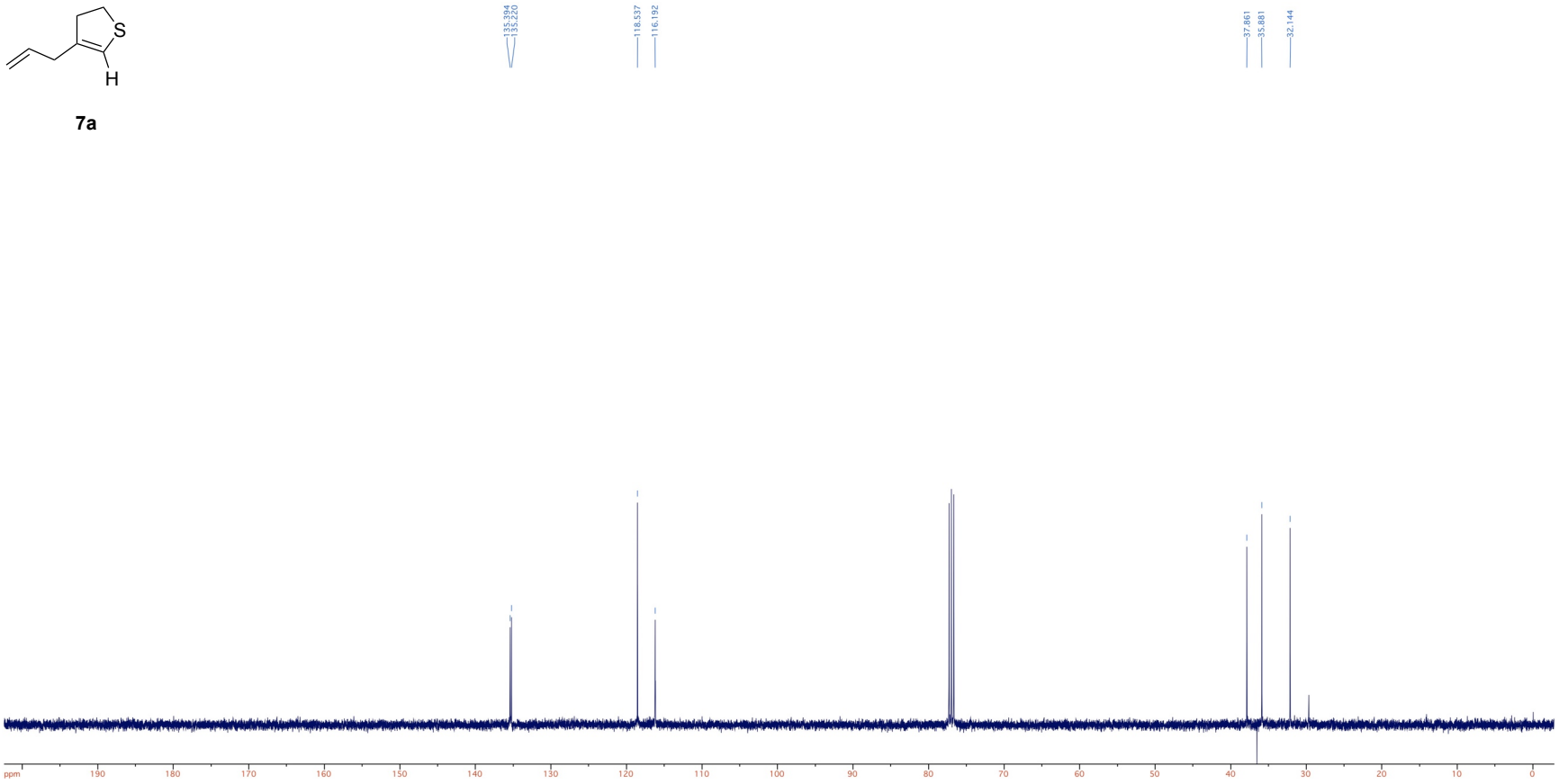
7a

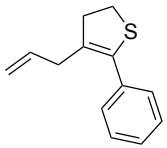



1.34
1.87
2
2.14
2.16
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

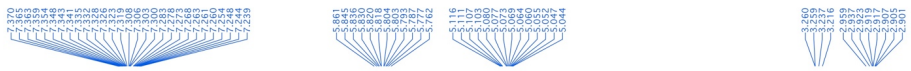
S
H

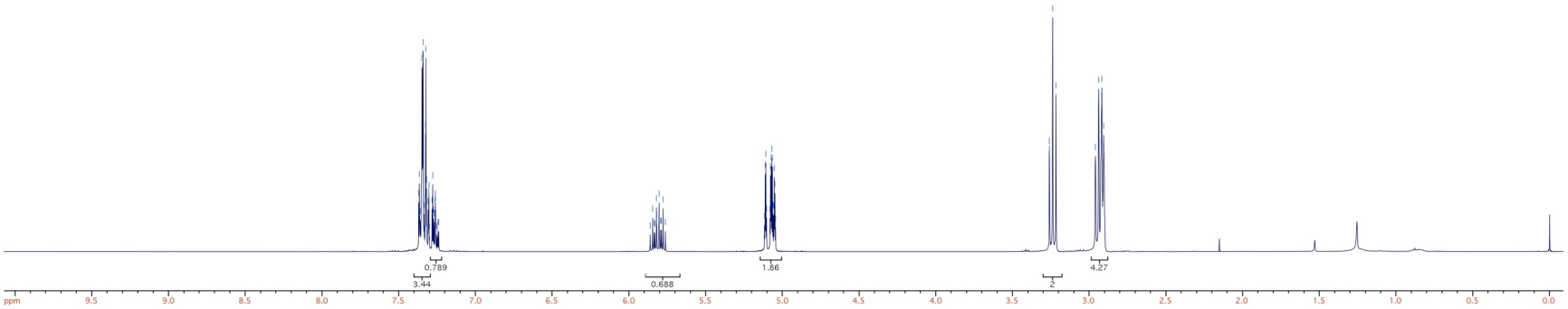
7a


135.394
135.220
118.537
116.192
37.861
35.881
32.144
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



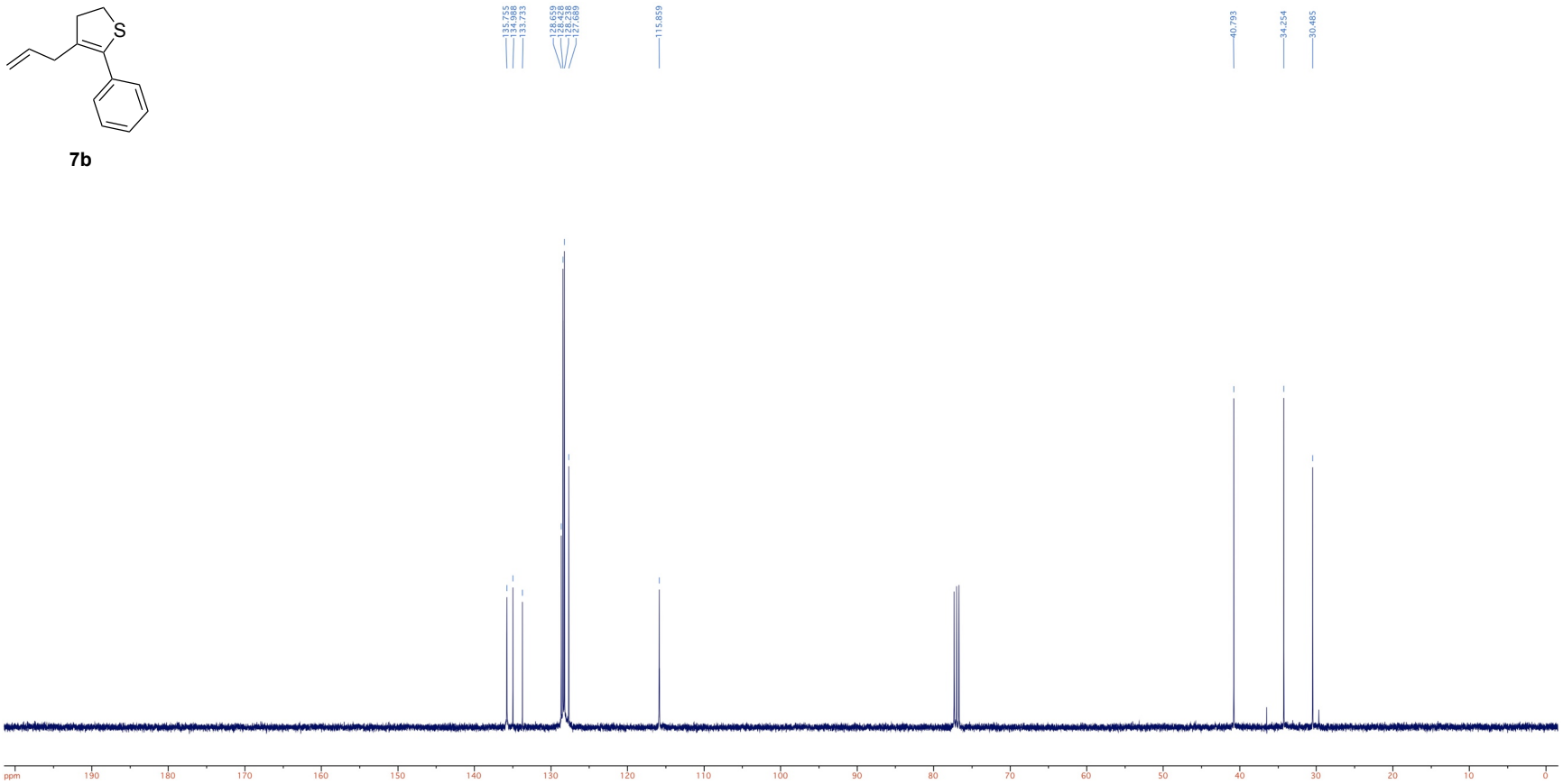
7b





S

7b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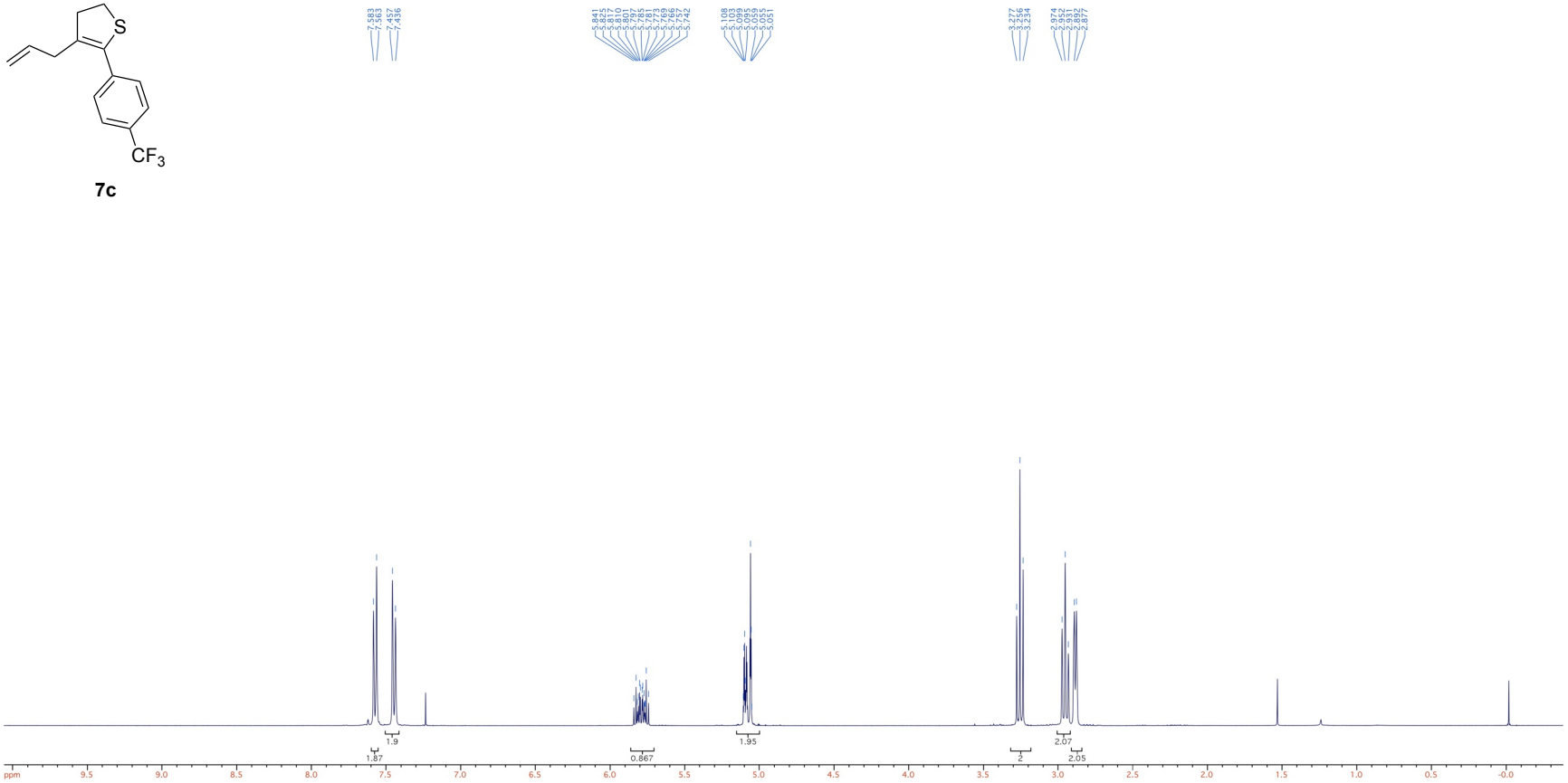
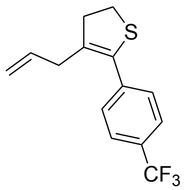
134.988
134.498
133.733
128.659
128.488
128.238
127.689
115.859
40.793
34.254
30.485
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

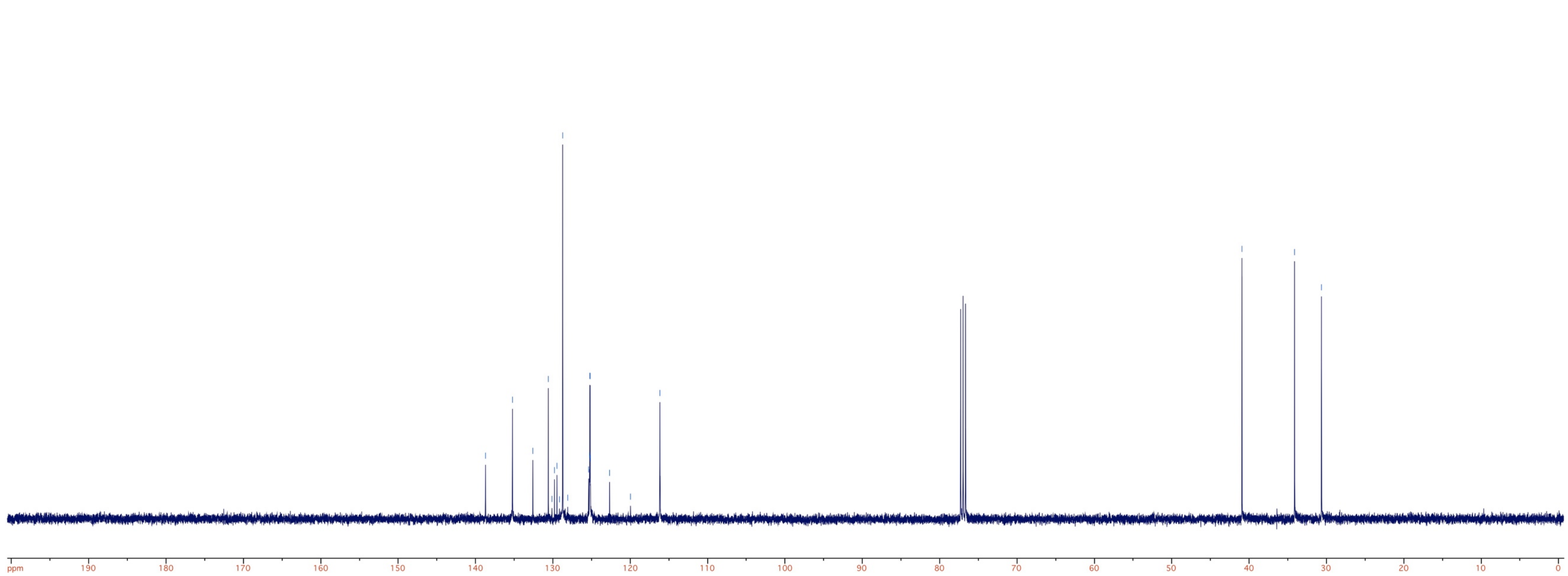
S
CF3

7c


7.583
7.563
7.457
7.436
5.841
5.817
5.810
5.801
5.797
5.785
5.773
5.769
5.766
5.757
5.752
5.108
5.103
5.099
5.095
5.059
5.055
5.051
3.277
3.256
3.234
2.974
2.952
2.931
2.892
2.877
1.87
1.9
0.867
1.95
2
2.07
2.05
ppm


S
CF3

7c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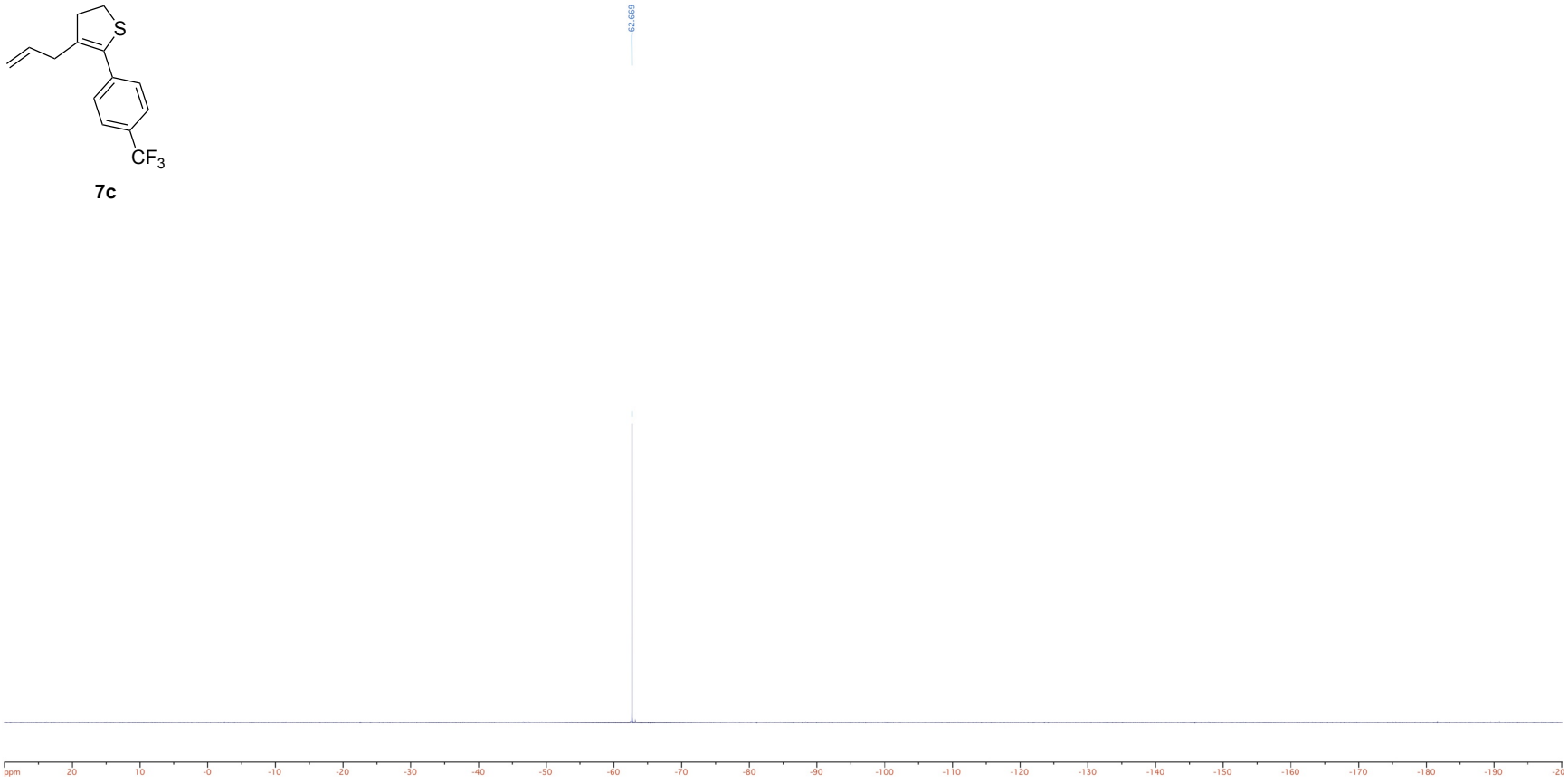
132.589
130.587
130.118
129.794
129.470
129.149
128.730
128.081
125.375
125.260
125.223
125.185
125.149
122.670
119.966
116.163
40.926
34.131
30.650
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

S
CF3

7c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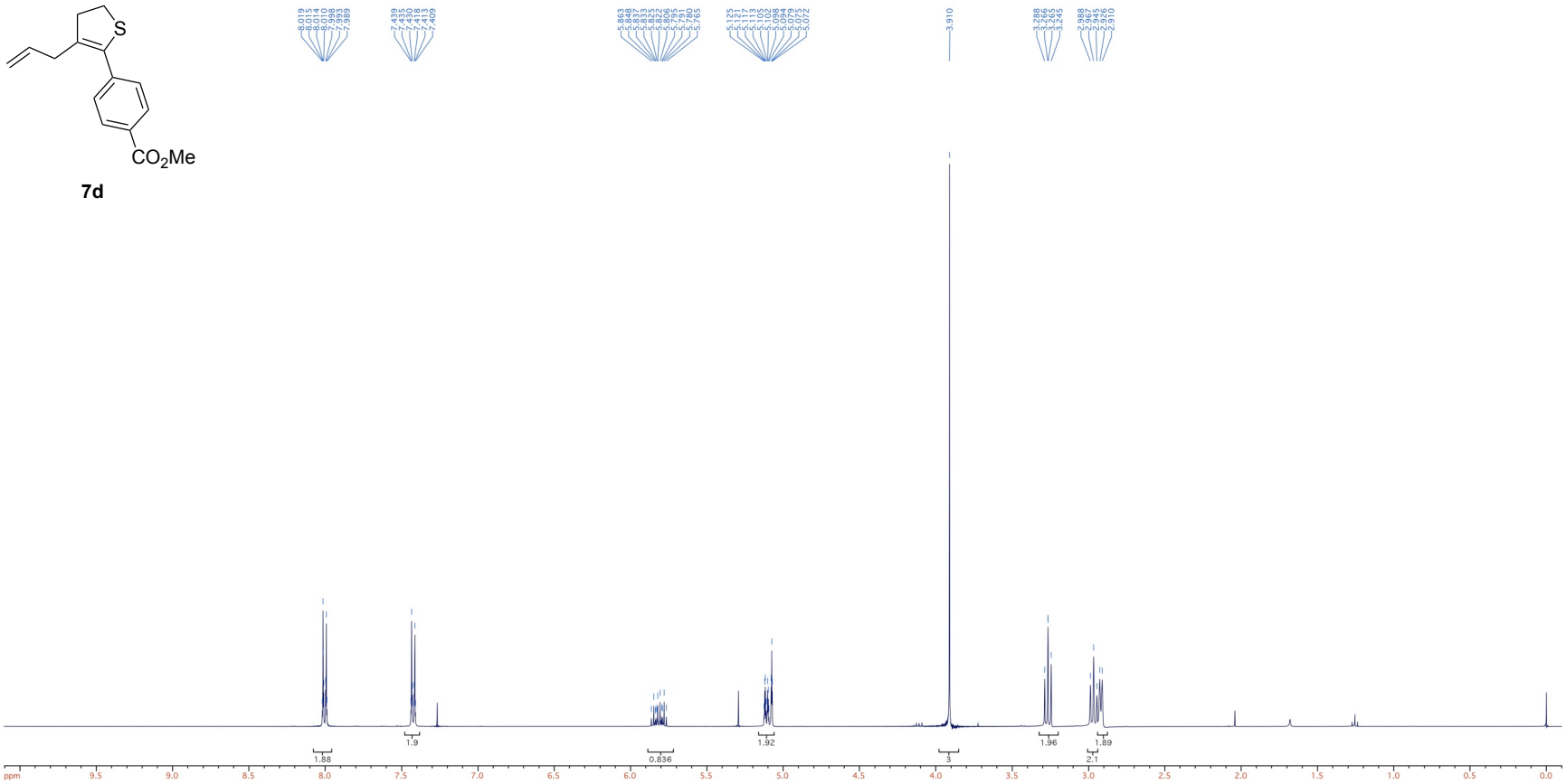
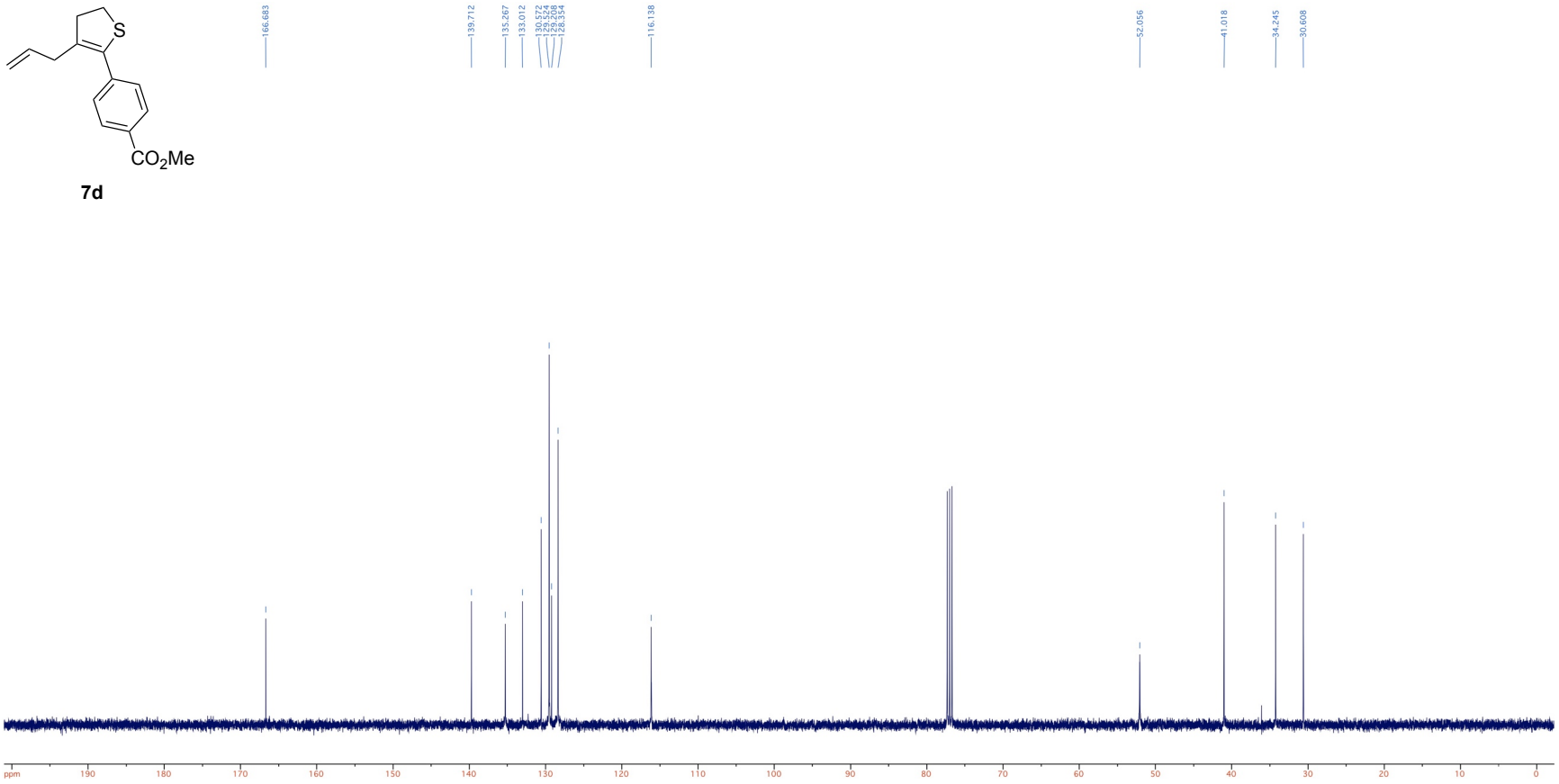
ppm
20
10
-0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

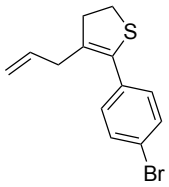

S
CO2Me
8.019
8.015
8.014
7.990
7.988
7.983
7.989
7.439
7.435
7.430
7.418
7.413
7.409
5.863
5.848
5.837
5.833
5.822
5.806
5.795
5.791
5.780
5.765
5.125
5.121
5.117
5.113
5.105
5.102
5.099
5.094
5.079
5.075
5.072
3.910
3.288
3.266
3.262
3.245
2.988
2.967
2.955
2.926
2.910
1.88
1.9
0.836
1.92
3
1.96
1.89
2.1
ppm

7d

S
CO2Me

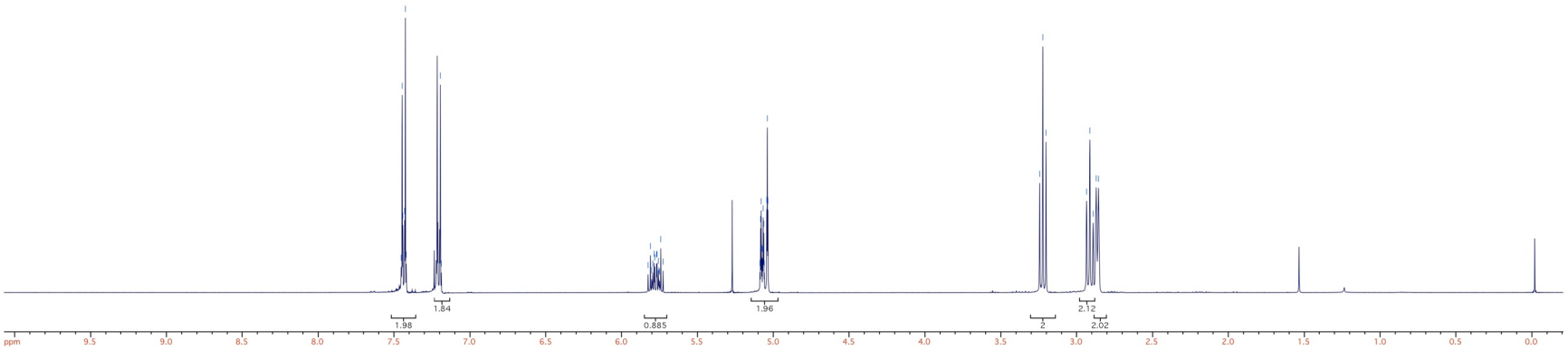
7d

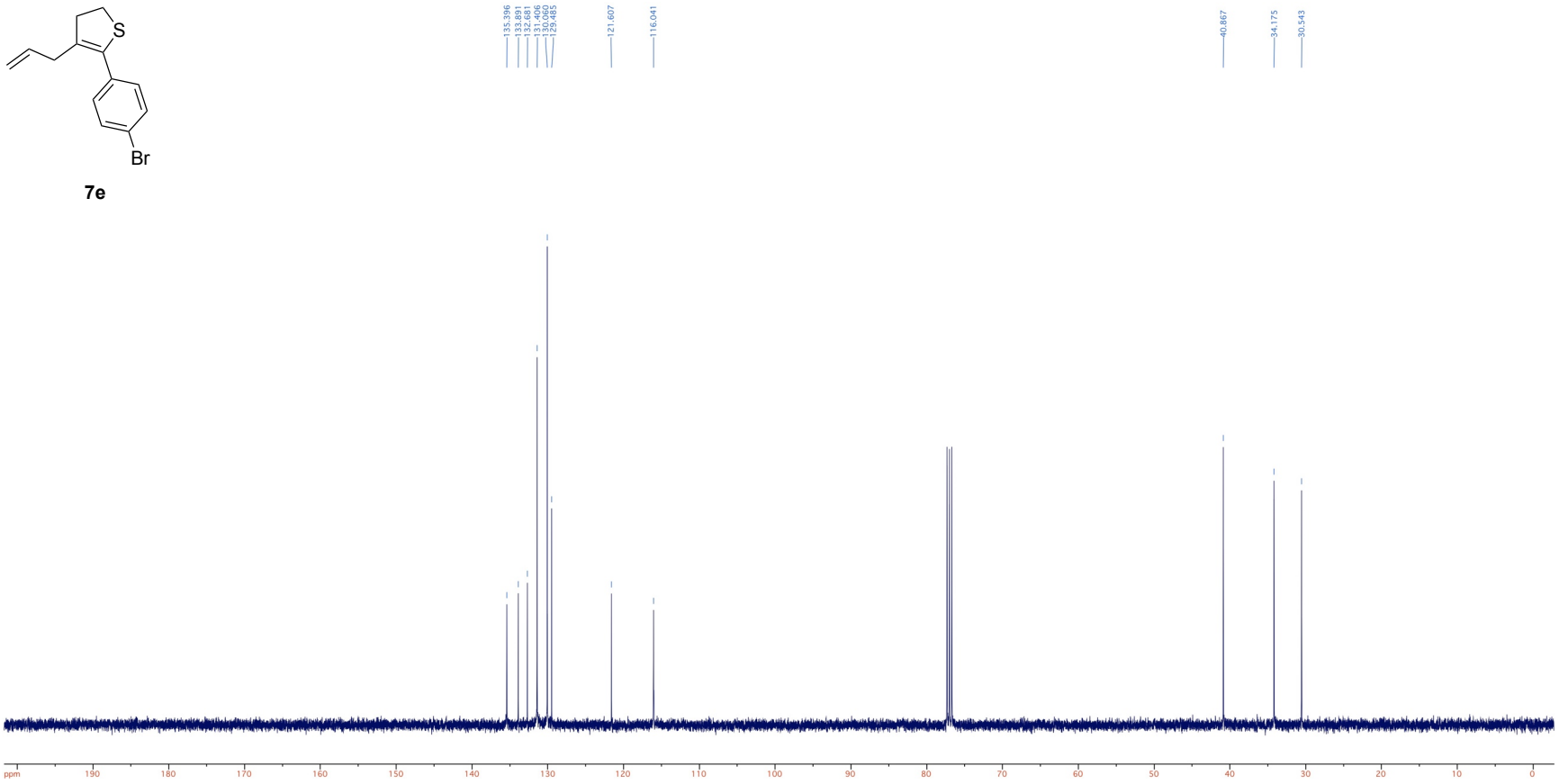

166.683
139.712
135.267
133.012
130.572
129.948
129.206
128.354
116.138
52.056
41.018
34.245
30.608
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


S
Br

7e


7.453
7.446
7.442
7.432
7.425
7.419
7.414
7.194
7.188
5.825
5.810
5.801
5.794
5.786
5.781
5.769
5.765
5.757
5.754
5.750
5.742
5.726
5.088
5.084
5.079
5.075
5.070
5.067
5.063
5.059
5.043
5.039
5.035
3.244
3.237
3.202
2.935
2.913
2.901
2.892
2.871
2.856

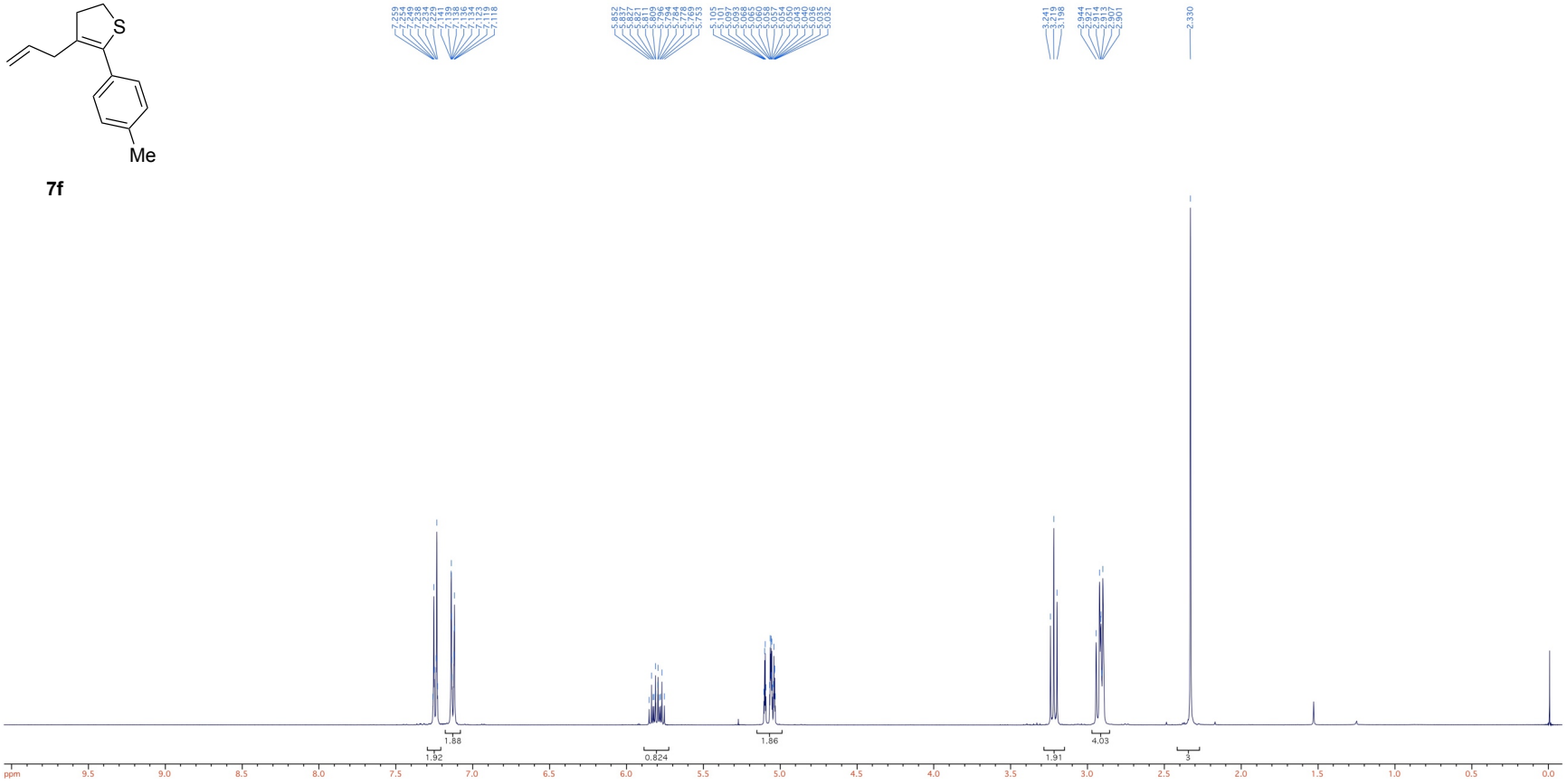

1.98
1.84
0.885
1.96
2
2.12
2.02
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


S
Br
135.396
133.891
132.681
131.406
130.040
129.485
121.607
116.041
40.867
34.175
30.543
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

7e

S
Me

7f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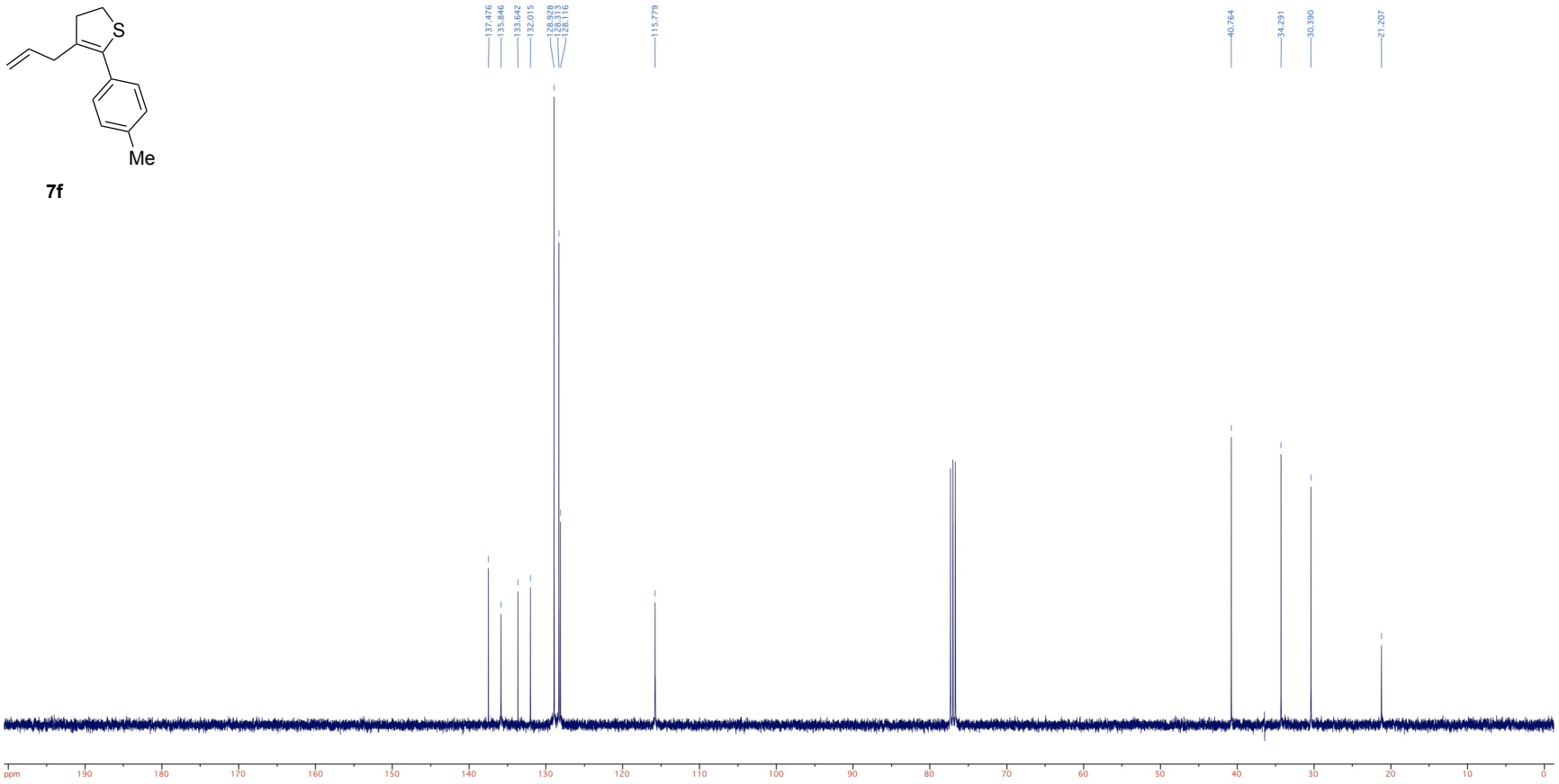
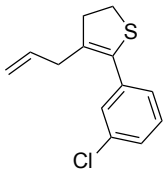
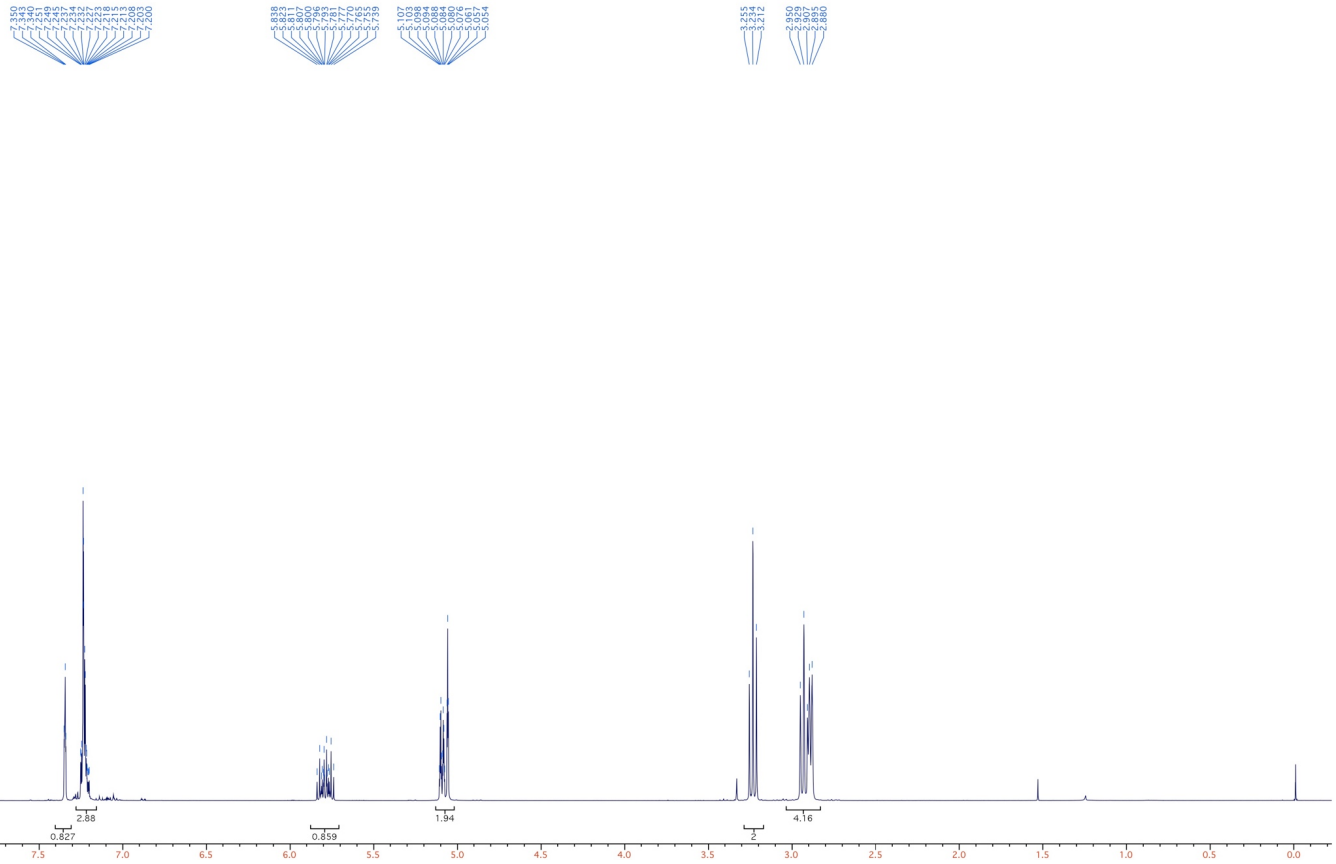
7.249
7.238
7.224
7.141
7.139
7.138
7.136
7.133
7.122
7.119
7.118
5.852
5.837
5.827
5.821
5.811
5.796
5.789
5.784
5.778
5.763
5.759
5.105
5.101
5.097
5.093
5.068
5.065
5.060
5.055
5.029
5.027
5.054
5.050
5.043
5.040
5.036
5.035
5.032
3.241
3.219
3.198
2.944
2.921
2.914
2.911
2.907
2.901
2.330
1.88
1.92
0.824
1.86
1.91
4.03
3
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


S
Me
137.476
135.846
133.642
132.015
128.938
128.353
128.116
115.779
40.764
34.291
30.390
21.207
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

7f


S
Cl

7g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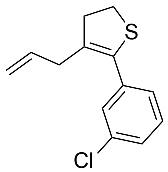
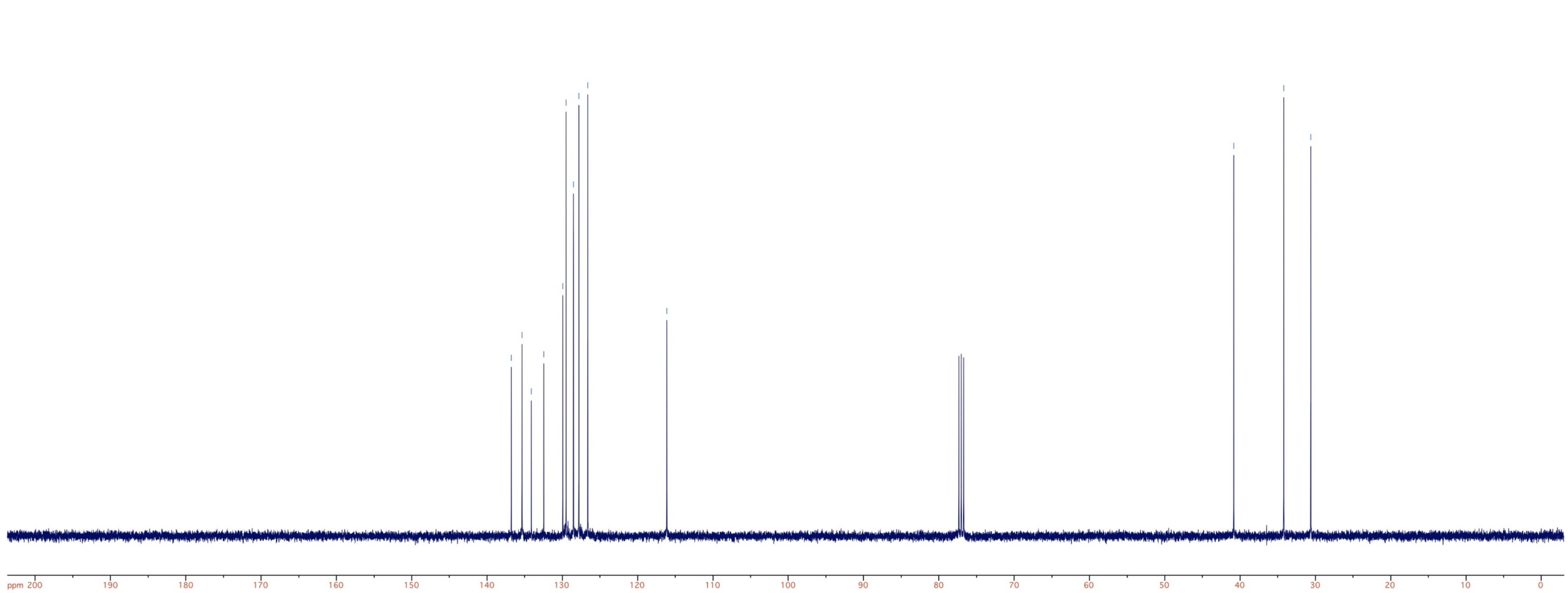
7.251
7.249
7.245
7.237
7.234
7.232
7.227
7.225
7.218
7.215
7.213
7.208
7.203
7.200
6.838
6.823
6.811
6.807
6.800
6.796
6.793
6.781
5.777
5.770
5.765
5.739
5.107
5.103
5.098
5.094
5.088
5.084
5.080
5.076
5.061
5.057
5.054
3.255
3.234
3.212
2.939
2.927
2.907
2.895
2.880
2.827
2.88
0.859
1.94
2
4.16
ppm


S
Cl

7g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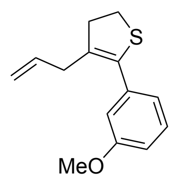
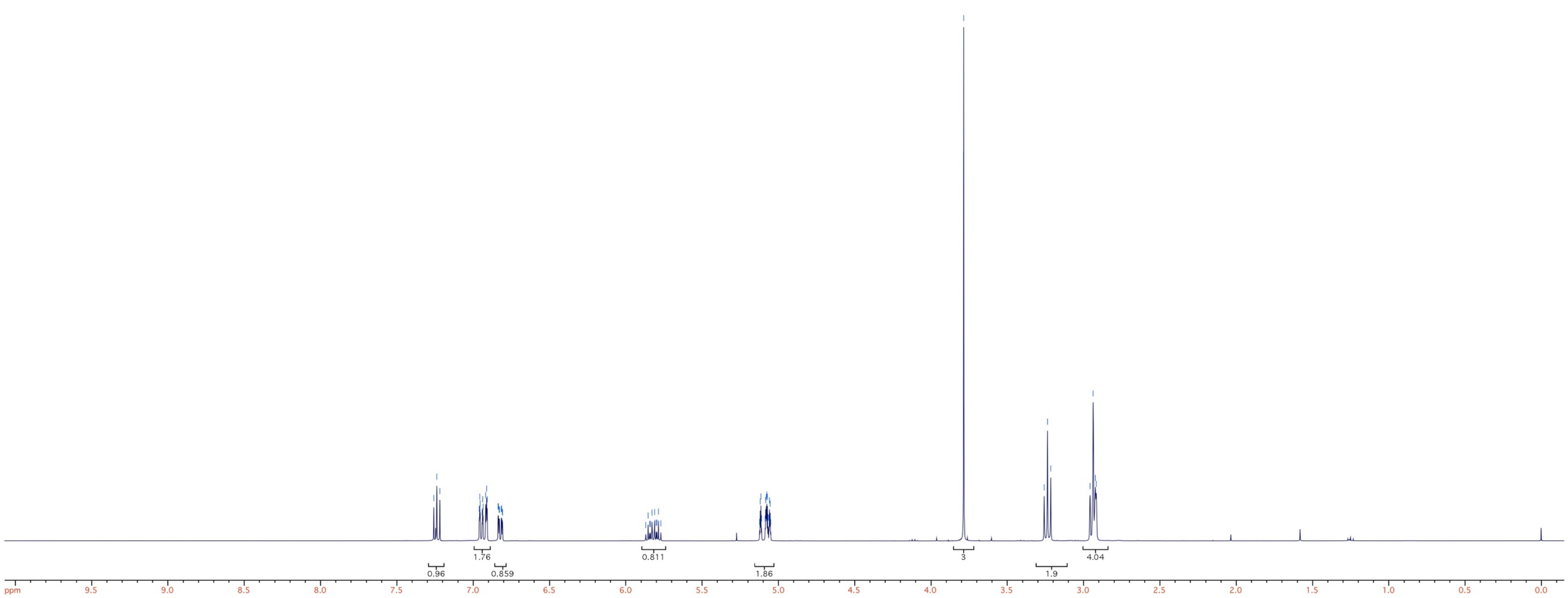
135.349
134.119
132.467
129.942
129.500
128.523
127.803
126.625
116.124
40.838
34.200
30.615
ppm 200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


S
MeO

7h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7.218
6.960
6.957
6.954
6.941
6.938
6.935
6.912
6.908
6.837
6.835
6.830
6.828
6.816
6.814
6.810
6.807
5.869
5.854
5.844
5.838
5.828
5.811
5.801
5.796
5.786
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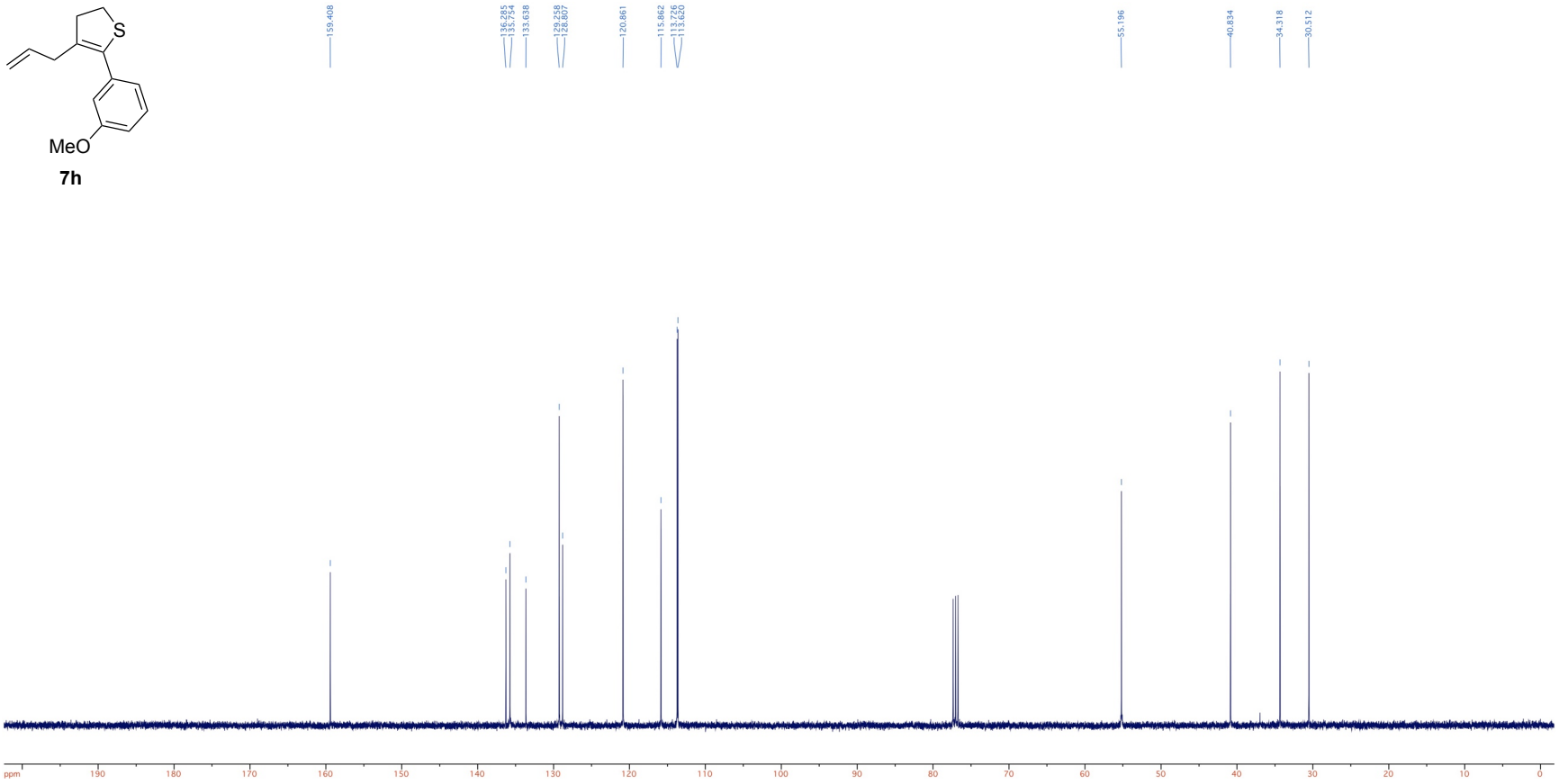
5.123
5.119
5.115
5.110
5.087
5.083
5.079
5.076
5.072
5.068
5.062
5.058
5.054
5.050
3.786
3.258
3.237
3.215
2.958
2.938
2.923
2.917
0.96
1.76
0.859
0.811
1.86
3
1.9
4.04
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


S
MeO
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136.285
135.754
133.638
129.258
128.807
120.661
115.962
113.620
55.196
40.834
34.318
30.512
ppm
190
180
170
160
150
140
130
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110
100
90
80
70
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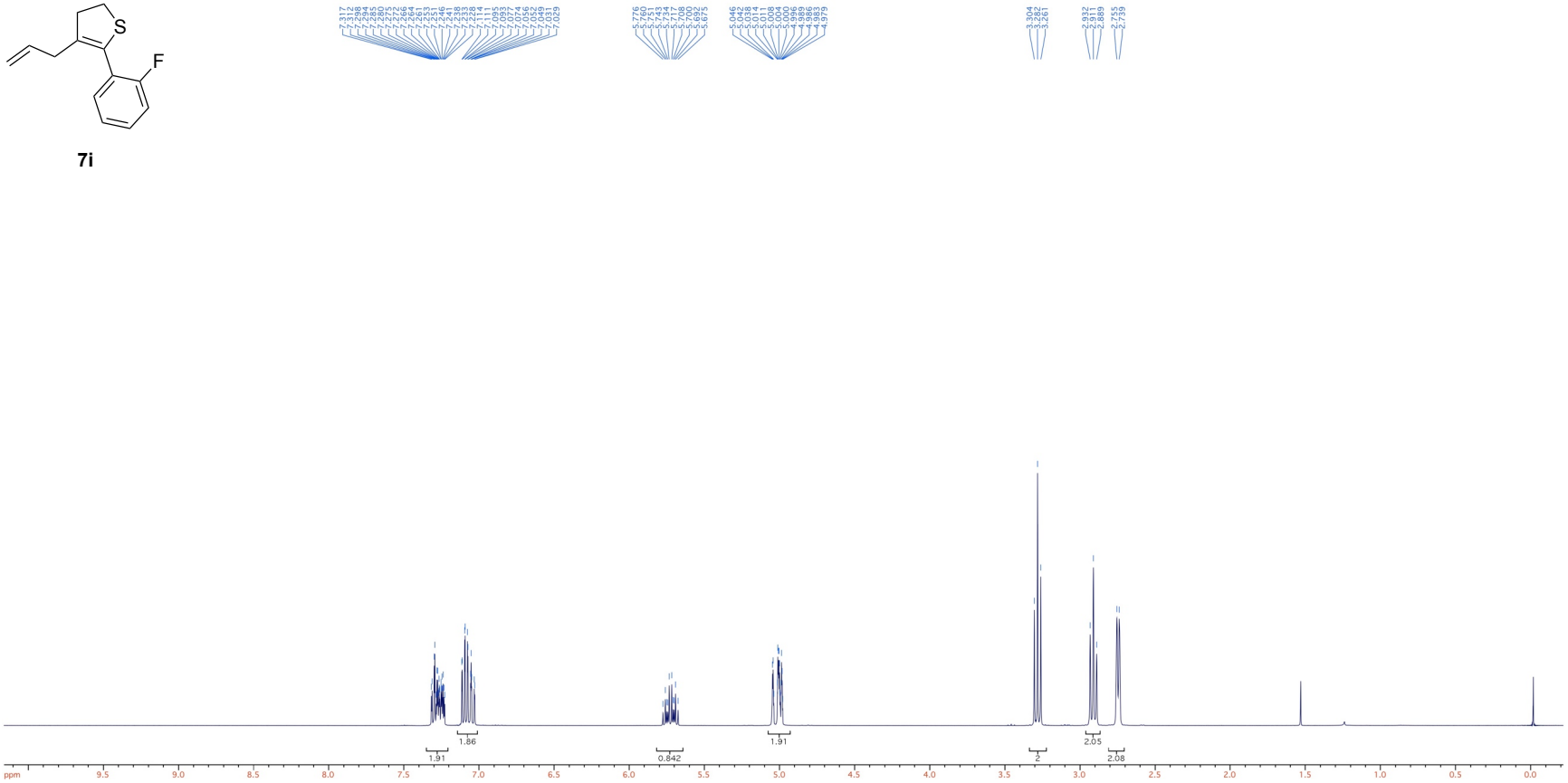
50
40
30
20
10
0

7h

S
F

7i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7.309
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7.275
7.272
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7.264
7.261
7.253
7.251
7.246
7.241
7.238
7.233
7.230
7.114
7.111
7.095
7.093
7.077
7.074
7.056
7.052
7.049
7.041
7.029
5.776
5.760
5.751
5.743
5.717
5.714
5.708
5.700
5.692
5.675
5.046
5.042
5.038
5.014
5.011
5.008
5.004
5.000
4.996
4.988
4.986
4.983
4.979
3.304
3.282
3.261
2.912
2.911
2.891
2.889
2.755
2.739
1.91
1.86
0.842
1.91
2
2.05
2.08
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
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1.0
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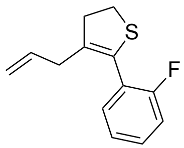
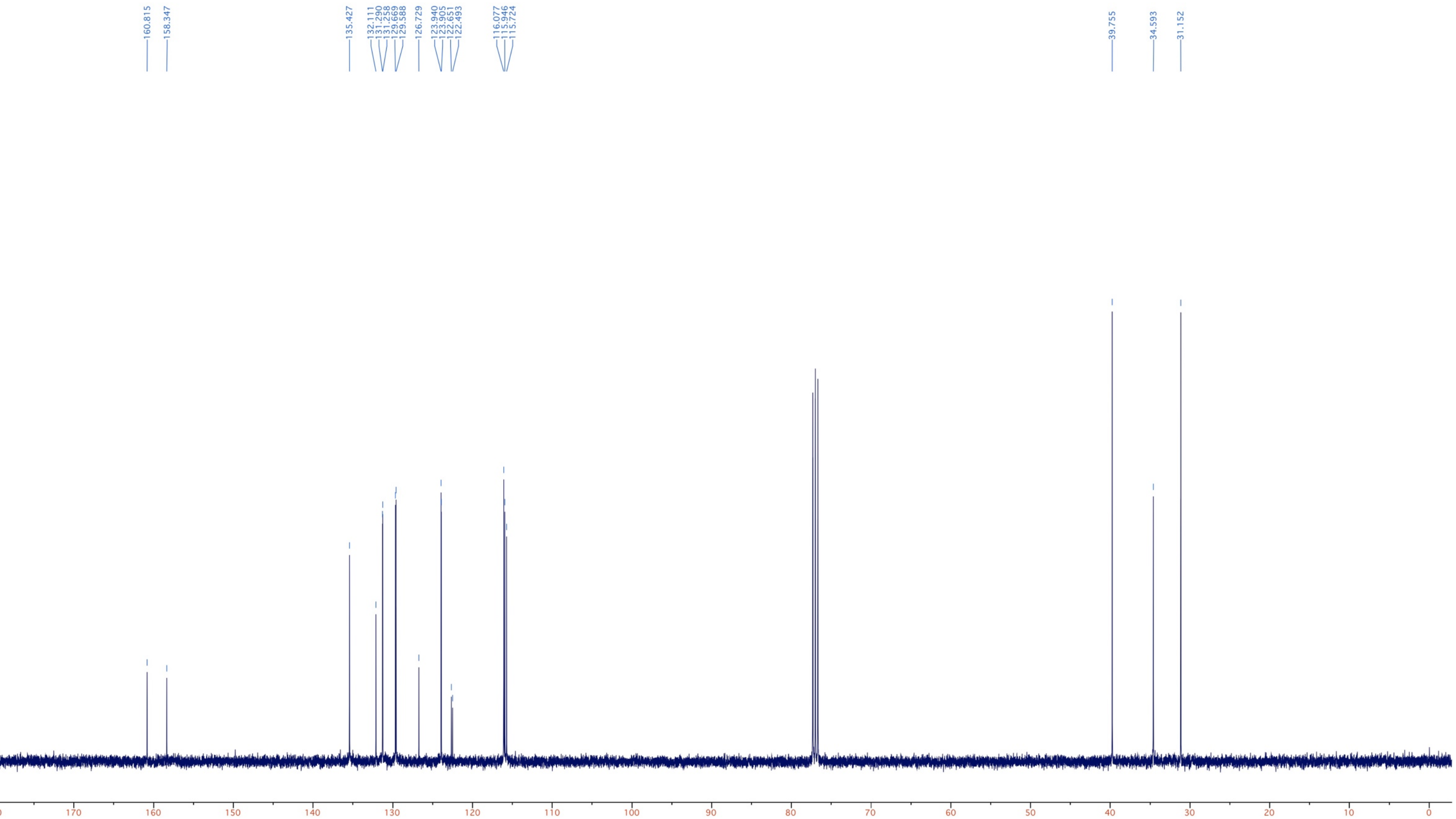
0.0


S
F

7i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135.427
132.111
131.290
131.258
129.669
129.588
126.729
123.940
123.905
122.651
122.493
116.077
115.946
115.724
39.755
34.593
31.152
ppm
190
180
170
160
150
140
130
120
110
100
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70
60
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40
30
20
10
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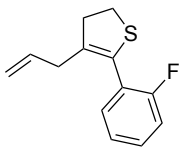
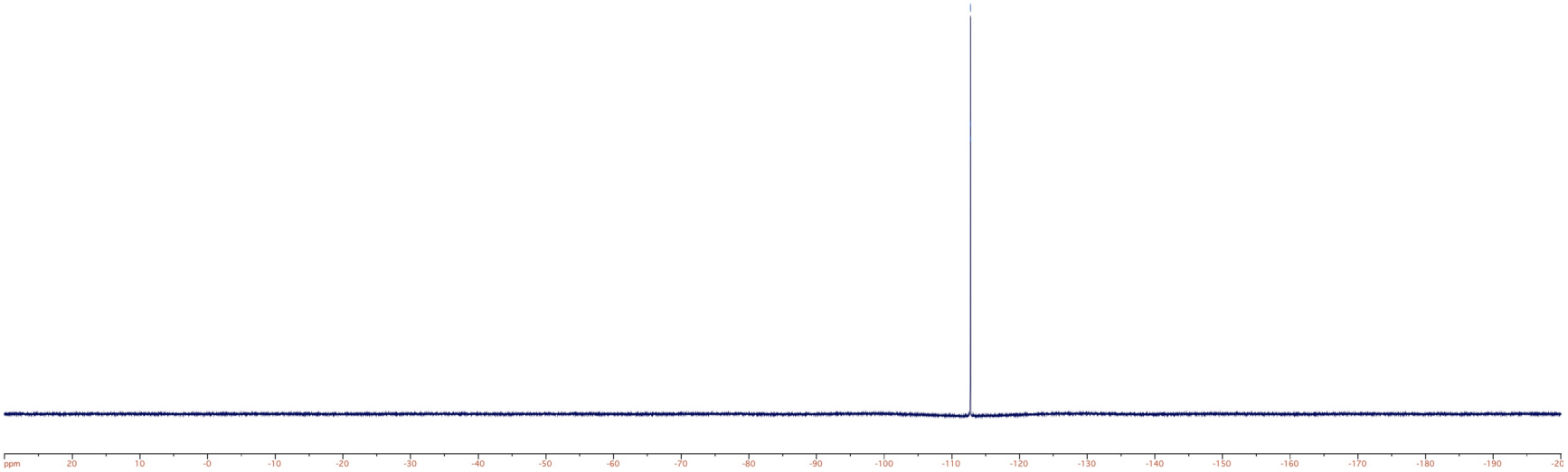

S
F

7i


-112.717
-112.734
-112.758
-112.776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20
10
0
-10
-20
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-40
-50
-60
-70
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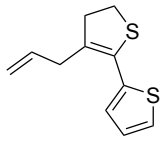
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190


S
S

7j


7.260
7.258
7.248
7.246
7.245
7.243
7.074
7.072
7.065
7.063
6.988
6.986
6.984
6.982
6.980
6.978
6.976
5.868
5.852
5.835
5.836
5.827
5.826
5.809
5.800
5.794
5.784
5.769
5.128
5.124
5.120
5.085
5.081
5.077
5.074
5.060
5.056
5.052
5.049
3.239
3.218
3.197
3.176
3.162
3.140
3.077
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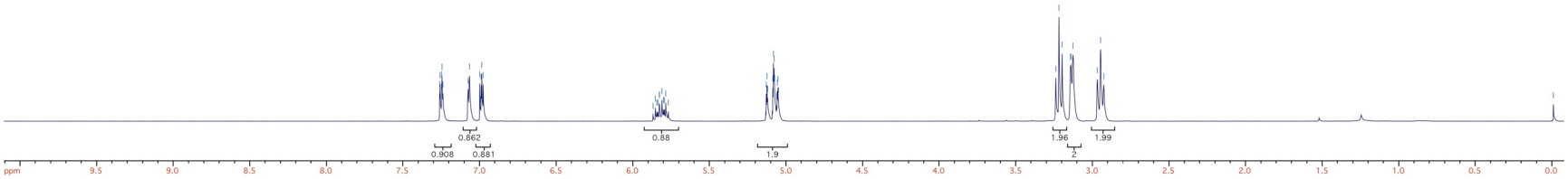
2.946
2.925
0.009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0.862
0.881
0.88
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1.96
2
1.99
ppm
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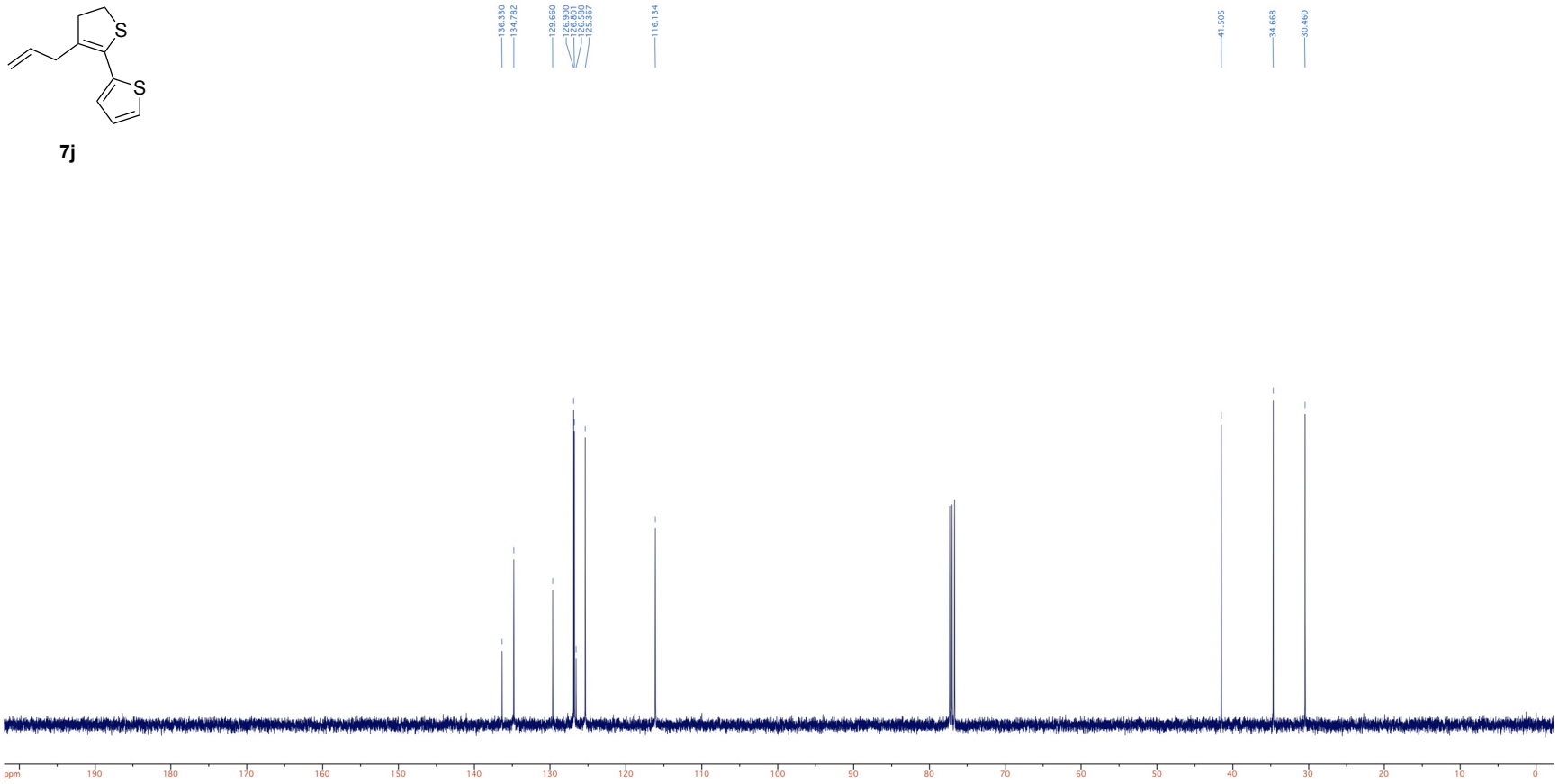
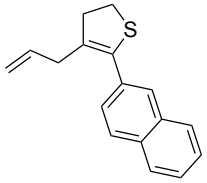
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

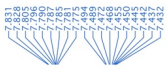
S
S

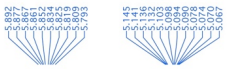
7j


136.330
134.782
129.660
126.900
126.680
126.580
125.367
116.134
41.505
34.668
30.460
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


S

7k

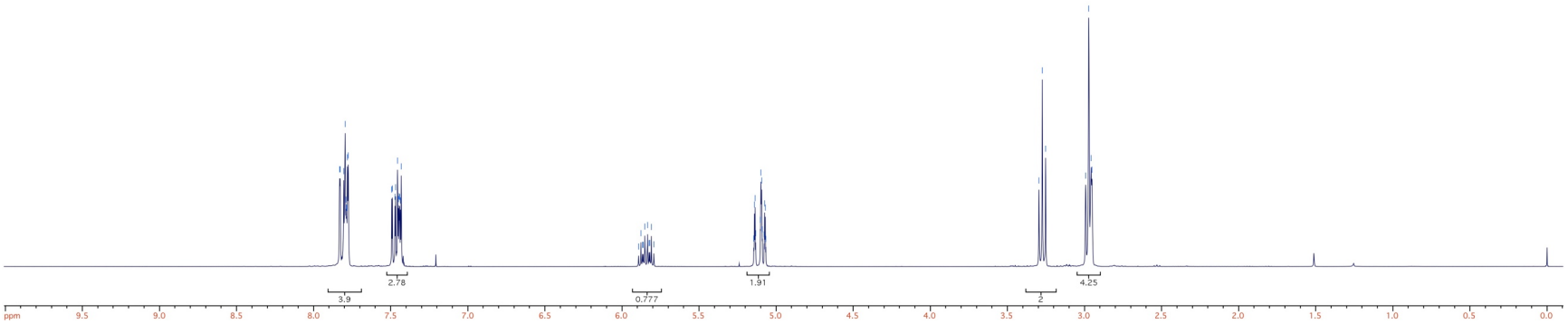

7.831
7.808
7.805
7.796
7.790
7.787
7.785
7.781
7.775
7.774
7.489
7.487
7.462
7.455
7.450
7.445
7.442
7.441
7.437
7.432


5.892
5.877
5.861
5.852
5.851
5.825
5.819
5.809
5.793

5.145
5.141
5.136
5.132
5.103
5.094
5.084
5.080
5.078
5.074
5.070
5.067


3.255
3.254
3.252

2.993
2.972
2.957
2.951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2.78
0.777
1.91
2
4.25
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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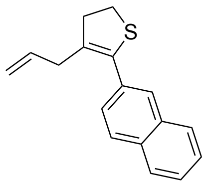
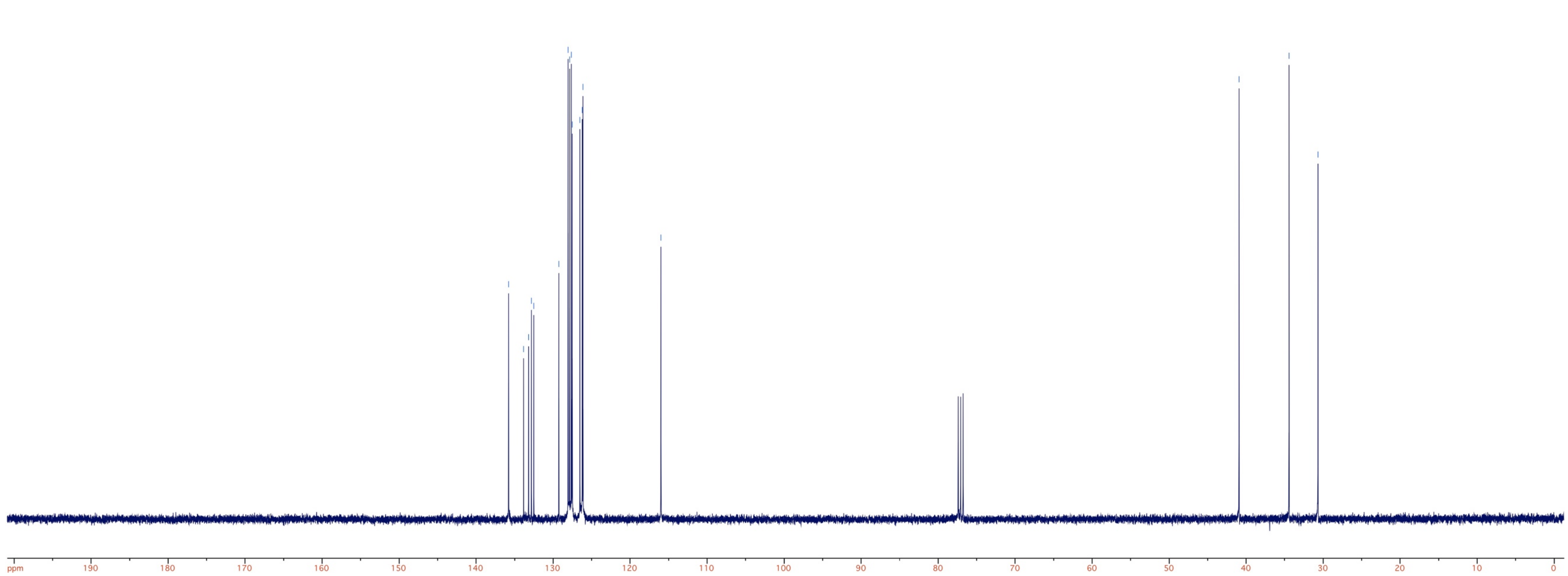
2.0
1.5
1.0
0.5
0.0


S

7k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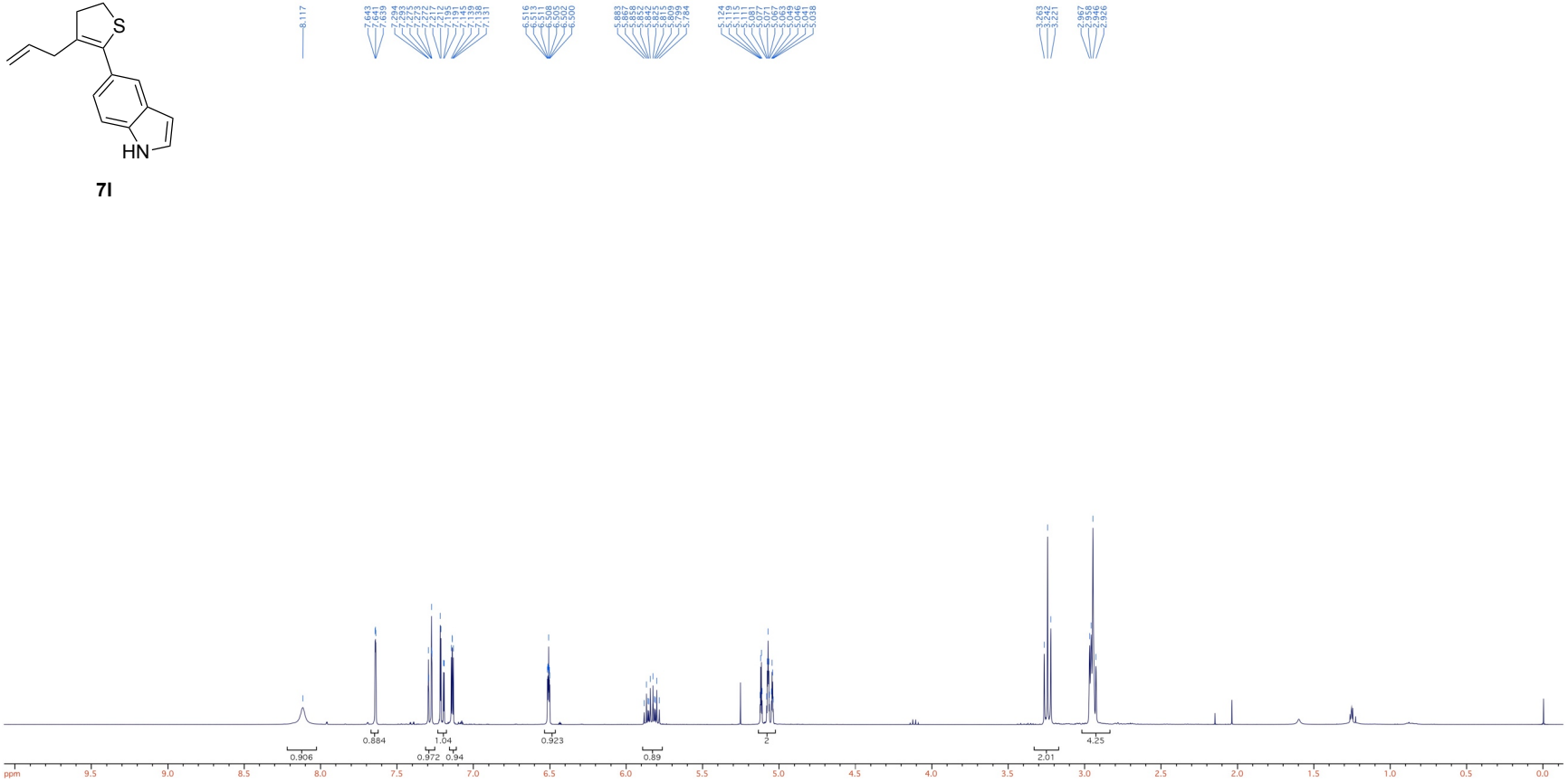
133.826
133.182
132.815
132.509
129.252
128.055
127.856
127.635
127.515
126.525
126.214
126.126
116.000
40.919
34.425
30.663
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

S
HN

7l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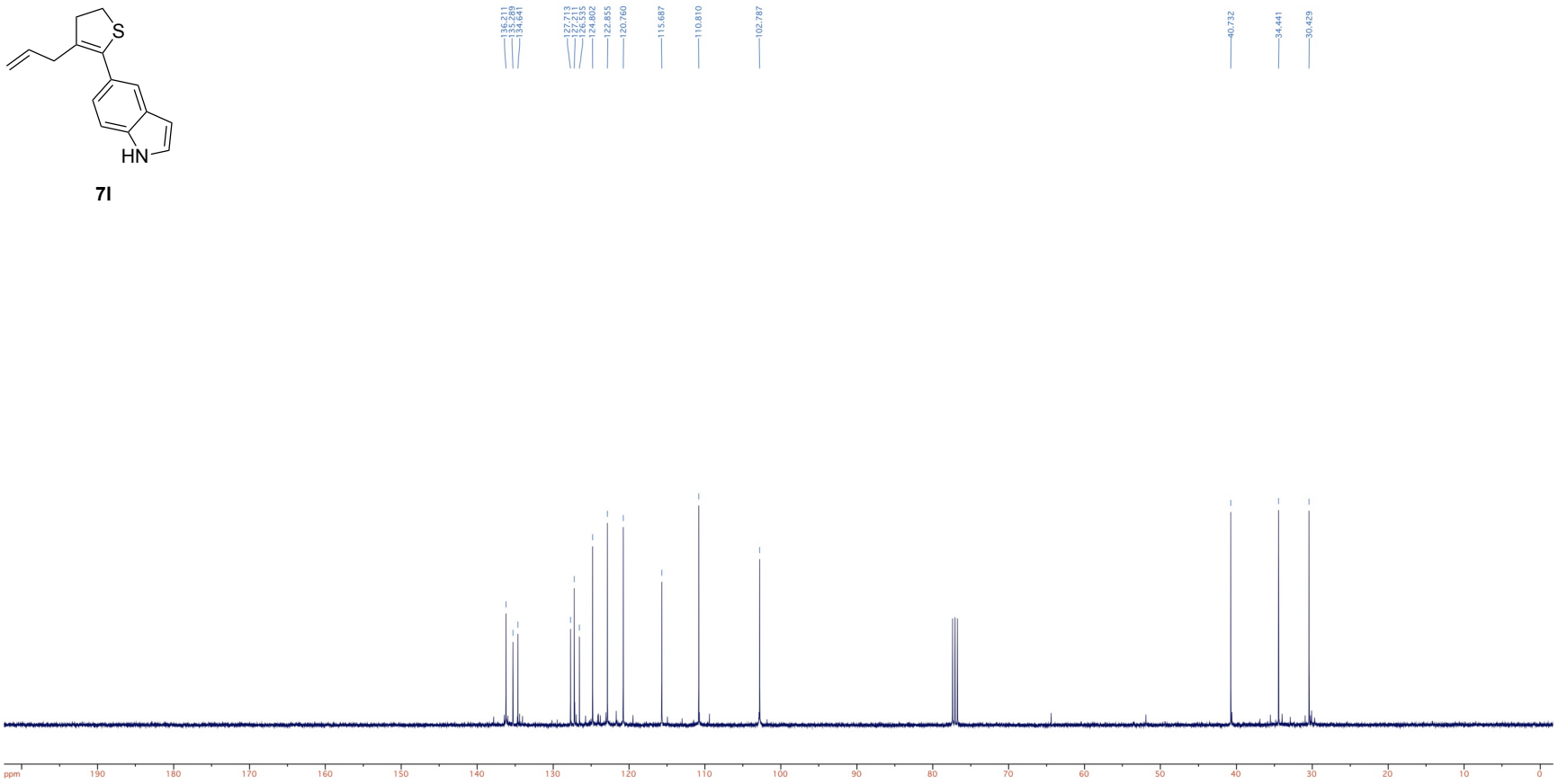
7.619
7.294
7.293
7.275
7.273
7.217
7.217
7.212
7.210
7.195
7.191
7.155
7.139
7.138
7.131
6.516
6.511
6.511
6.508
6.505
6.502
6.500
5.883
5.867
5.858
5.842
5.841
5.825
5.815
5.809
5.784
5.124
5.119
5.115
5.111
5.101
5.077
5.071
5.067
5.063
5.059
5.046
5.041
5.038
3.263
3.252
3.241
2.967
2.958
2.946
2.926
0.906
0.884
1.04
0.972
0.94
0.923
0.89
2
2.01
4.25
ppm

S
HN

7l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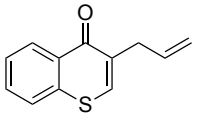
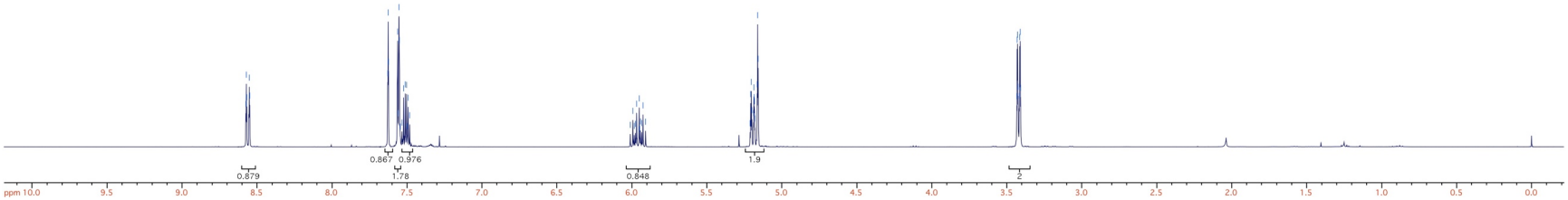
135.289
134.641
127.713
127.511
126.515
124.802
122.855
120.760
115.687
110.810
102.787
40.732
34.441
30.429
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



8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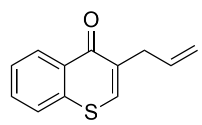
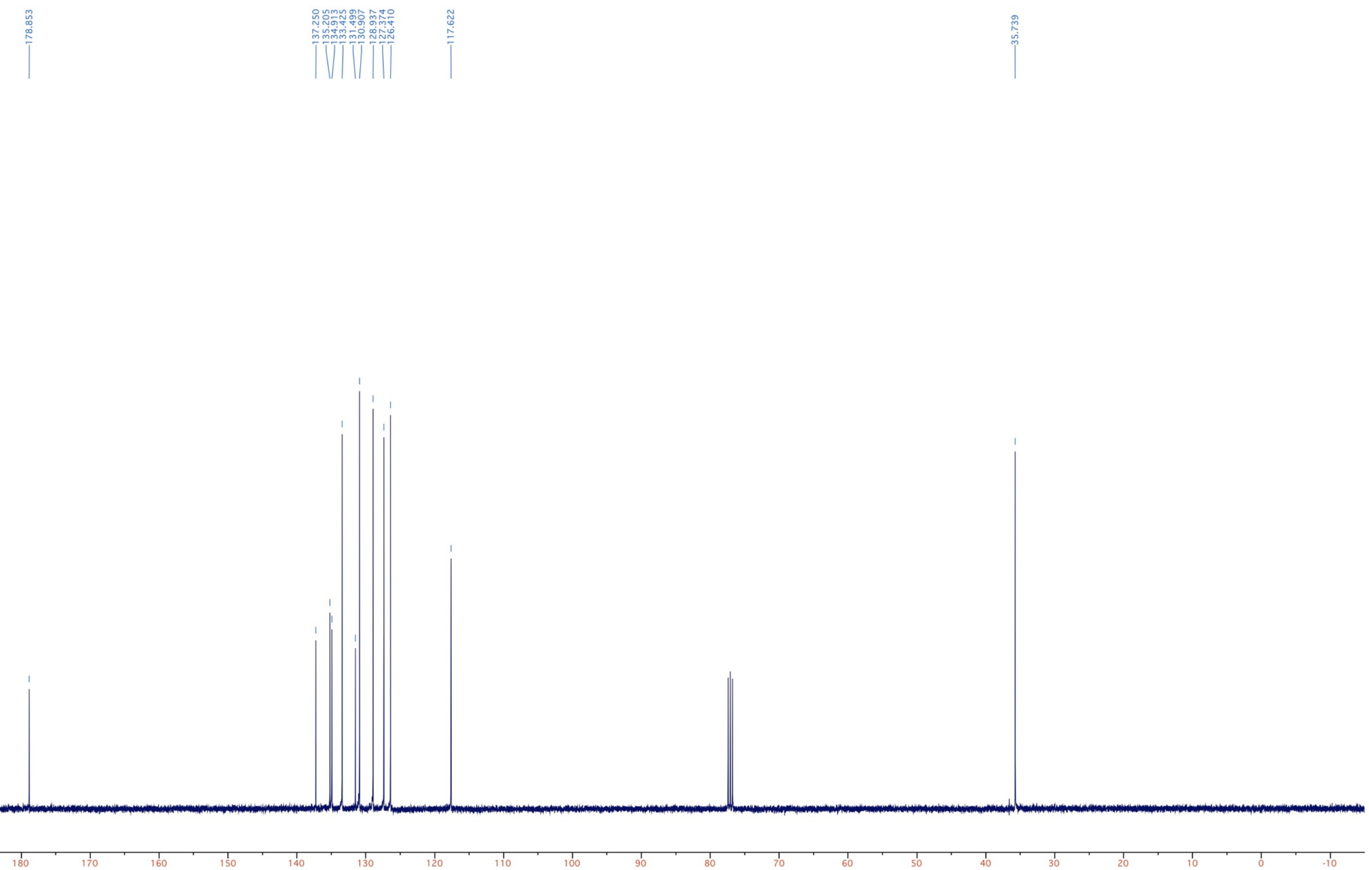
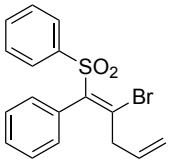
0.867
0.976
1.78
0.848
1.9
2
ppm 10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

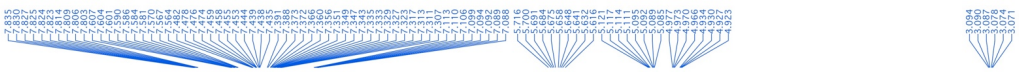

O
S

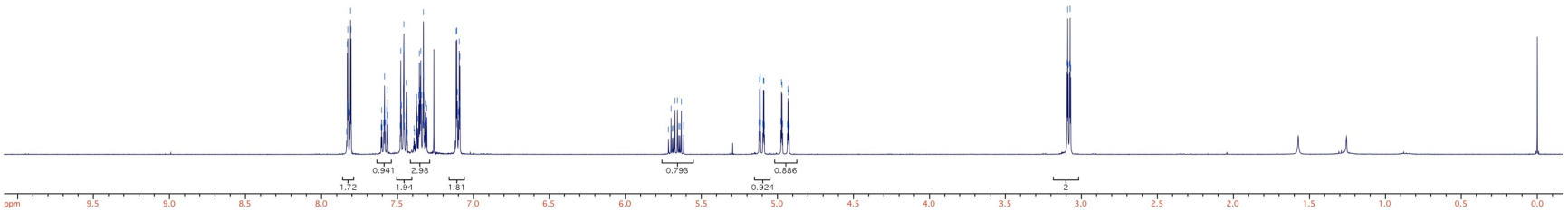
8

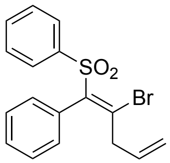

178.853
137.250
135.205
134.913
133.425
131.499
130.907
128.937
127.374
126.410
117.622
35.739
ppm 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



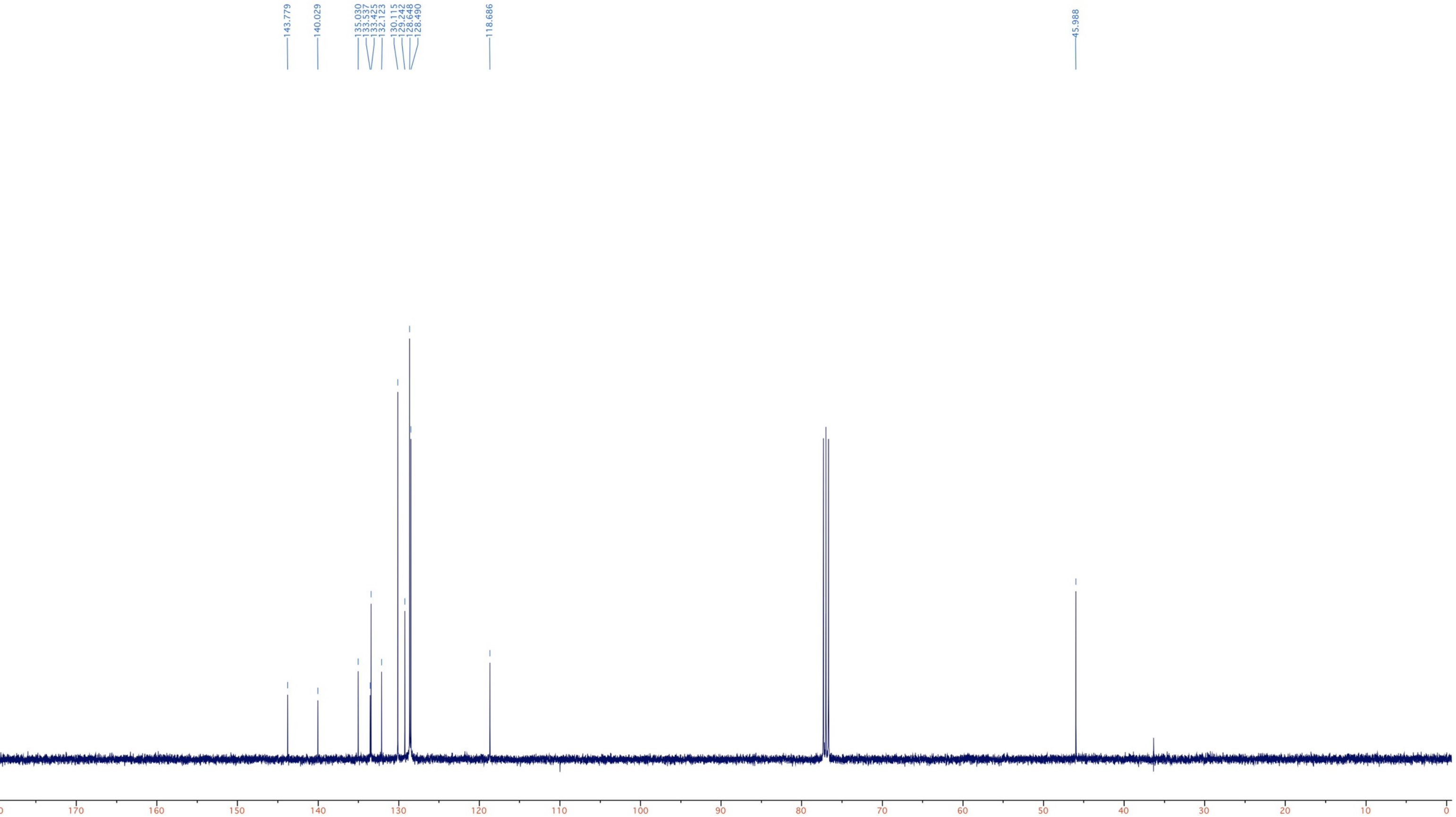
9






SO2
Br

9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132.123
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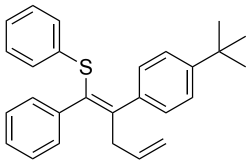
129.242
128.648
128.490
118.686
45.988
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



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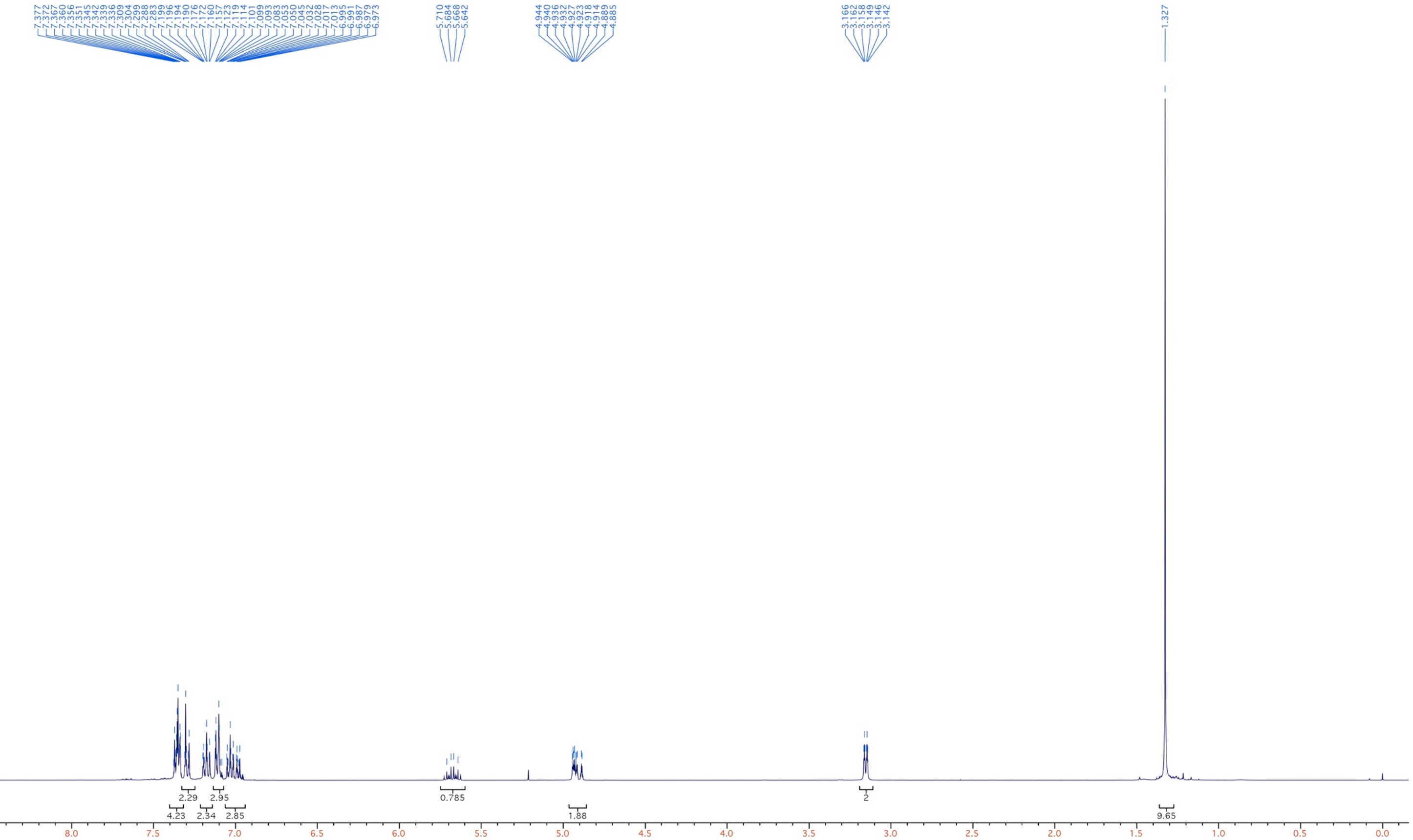

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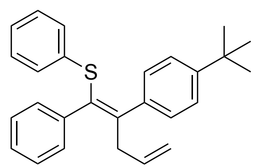
5.668
5.642
4.944
4.940
4.936
4.932
4.927
4.923
4.918
4.914
4.889
4.885
3.166
3.162
3.158
3.149
3.146
3.142
1.327
2.29
2.95
4.23
2.34
2.85
0.785
1.88
2
9.65
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



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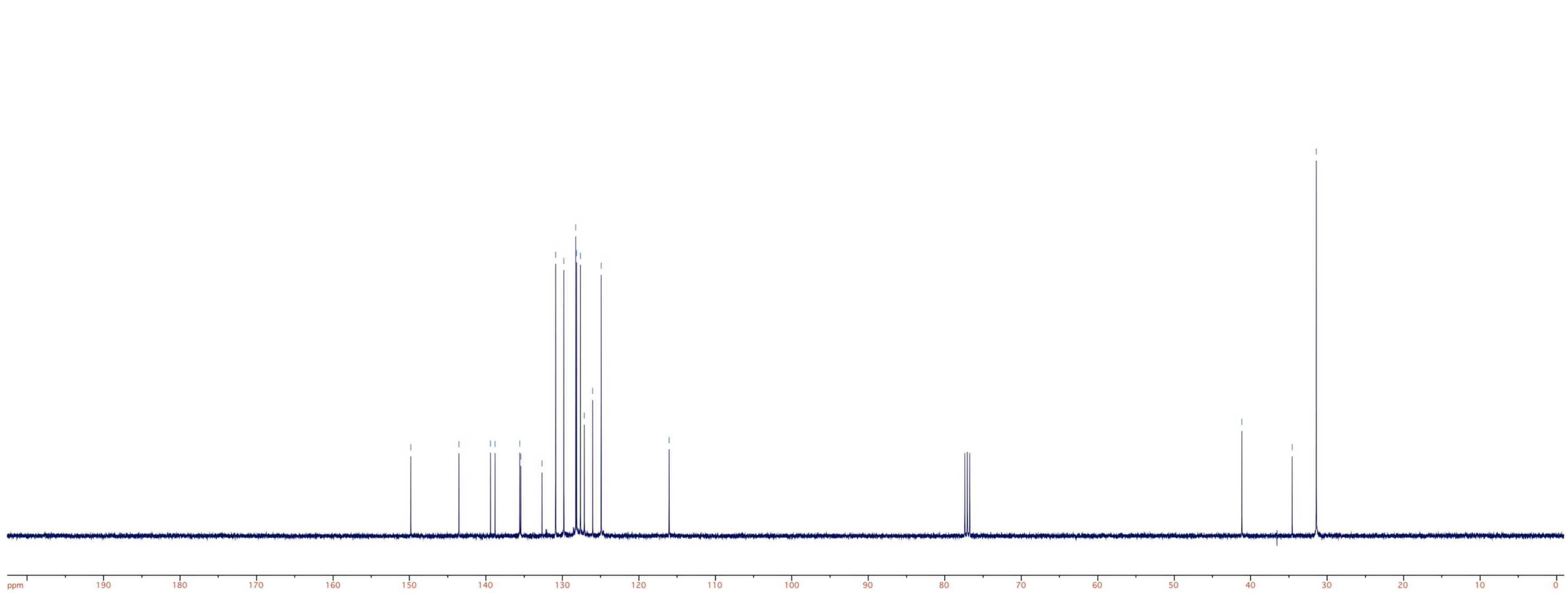

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139.400
138.806
135.574
135.438
132.669
130.884
129.813
128.262
128.146
127.644
127.135
126.044
124.931
116.047
41.154
34.569
31.417
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0