Metal-Free Electrophilic Alkynylation of Sulfenate Anions with Ethynylbenziodoxolone Reagents

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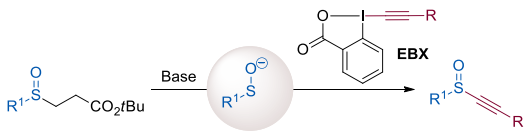


ABSTRACT: Alkynyl sulfoxides are important building blocks with unique reactivity in organic chemistry, but only few reliable methods have been reported to synthesize them. A novel route to access alkynyl sulfoxides is reported herein by using Ethynyl BenziodoXolone (EBX) reagents to trap sulfenate anions generated *in-situ*, *via* a retro-Michael reaction. The reaction takes place under metal-free and mild conditions. It is compatible with aryl, heteroaryl and alkyl sulfoxides with up to 90% yield. This practical access to alkynyl sulfoxides is expected to facilitate the application of these useful building blocks in organic synthesis.

Sulfoxides are well represented in natural products.[1] They constitute also important post-translational modifications of proteins and are biological precursors of flavours and aromas.[2] They have found applications in material science[3] and are preponderant in pharmaceutical and bioactive compounds. Remarkable examples include the top-selling proton pump inhibitor omeprazole (**1**),[4] the insecticide ethiprole (**2**), the anti-narcoleptic armodafinil (**3**) and the immunosuppressor oxisurane (**4**) (Figure 1).[5] Furthermore, chiral sulfoxides are often used as ligands or auxiliaries in asymmetric synthesis.[6]

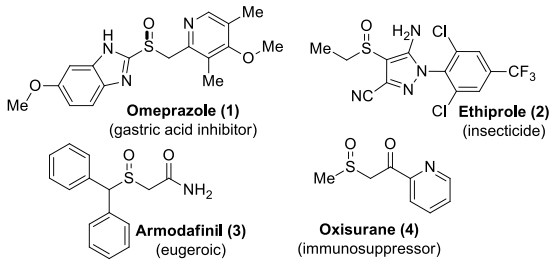
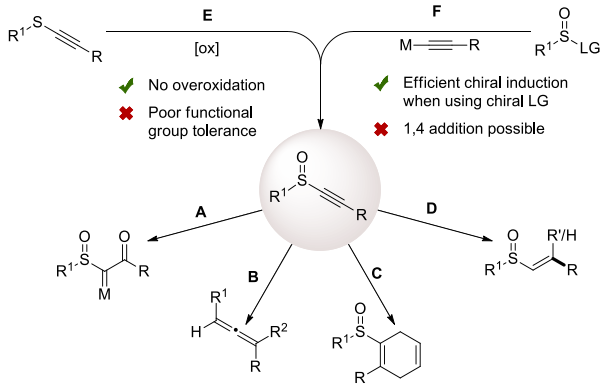


Figure 1 Examples of bioactive sulfoxide-containing compounds.

Alkynes play an essential role in numerous chemical transformations.[7] More specifically, alkynyl sulfoxides have found applications as α-sulfinyl carbene precursors (Scheme 1, **A**).[8] They also provide easy access to allenes (**B**)[9] and they can undergo cycloadditions (**C**).[10] They can also be converted to versatile vinyl sulfoxides *via* simple Michael-addition[11] or reduction to both *cis* and *trans* configuration (**D**).[12] The resulting α,β-unsaturated sulfoxides are common in pharmacological compounds[13] and can be used in vinylogous Pummerer rearrangements and other pericyclic reactions.[14]

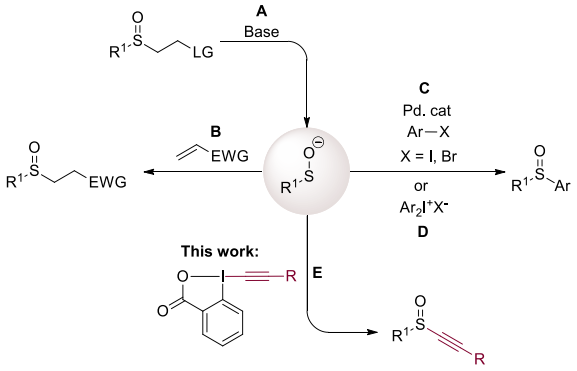
Scheme 1. Existing strategies to access alkynyl sulfoxides and their applications.



While the synthetic applications of these compounds look promising, further research and applications are limited by the lack of robust methods to access them. In fact, only two routes have been routinely used: oxidation of alkynyl sulfides and nucleophilic substitution on sulfoxide precursors (Scheme 1, **E** and **F**).[11,15] As alkynyl sulfides are strongly deactivated, the first approach relies on harsh oxidative conditions, which are not compatible with sensitive functional groups. Concerning the second approach, the use of acetylene nucleophiles like alkynyl Grignard reagents can lead to 1,4 addition after formation of the desired compound and side-reactions with other acidic or electrophilic functional groups.[11] In order

to overcome these limitations, we envisaged the use of an inversed polarity strategy for the synthesis of alkynyl sulfoxides. In this respect, Perrio and Metzner reported in 2005 the facile synthesis of alkylated sulfoxides by trapping an *in-situ* generated sulfenate anion with an electrophile (Scheme 2, **A** and **B**).[16] In this method the unstable sulfenate anion[17] is generated *via* a chemoselective retro-Michael reaction under mild conditions. This approach was later used for the synthesis of aryl and alkyl sulfoxides, in particular using palladium-catalysed cross-couplings (**C**).[18] During completion of our work, Bolm and Chen and co-workers independently reported similar procedures for the arylation of sulfenates by using diaryliodonium salts (**D**).[19] Nevertheless, the alkynylation of sulfenate anions has never been reported so far.

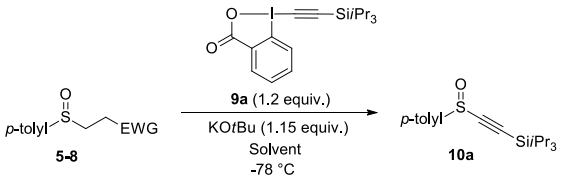
Scheme 2. Retro-Michael approach for sulfenate anion generation and applications in sulfoxide synthesis.



The exceptional reactivity of hypervalent iodine reagents[20] has opened the door to the development of electrophilic alkynylation reactions.[21] In particular, our group has shown the efficacy of cyclic Ethynyl BenziodoXolone (EBX) reagents as electrophilic alkynyl synthon transfer agents.[22] Over the past decade, they have been applied for the alkynylation of various carbon and heteroatom, more generally, soft nucleophiles.[22] In particular, our group has shown the convenient use of EBX reagents for the alkynylation of thiols and sulfinates.[23] These results demonstrated the high reactivity of EBX reagents towards sulfur nucleophiles. Herein, we present the first method for the synthesis of alkynyl sulfoxides by the reaction of *in-situ* generated sulfenates with EBX reagents (Scheme 2, **E**).

We started our investigations by examining various retro-Michael sulfenate precursors under Perrio's conditions[16] with TIPS-EBX (**9a**, TIPS = tri*iso*propylsilyl) in THF (Table 1).[24]

Table 1: Initial reaction condition for sulfenate precursor screening.



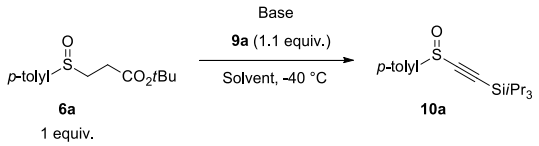
entry	EWG	solvent	yield (%)
1	CO_2Me (**5**)	THF	28
2	CO_2Me (**5**)	PhMe	48
3	CO_2tBu (**6a**)	PhMe	64
4	SO_2Ph (**7**)	PhMe	64
5	NO_2 (**8**)	PhMe	43

Reactions were performed with **5-8** (0.50 mmol, 1.0 equiv.), 9a (0.60 mmol, 1.2 equiv.) and KO*t*Bu (0.59 mmol, 1.15 equiv.) in the indicated solvent (0.16 M) at -78 °C for 3 h. [a]Reaction was left overnight to achieve full conversion.

Methyl (*p*-tolylsulfinyl)propanoate (**5**)[16] afforded the desired alkynyl sulfoxide **10a** in 28% yield (Entry 1). Changing the solvent to toluene increased the yield to 48% (Entry 2). The other precursors were then tested under the same conditions. Precursors **6a**[18b] and **7**[18c] gave both better results (64%. Entries 3 and 4), whereas precursor **8**[18c] yielded the desired compound **10a** in the same range of yield as **5** (Entry 5). More easily accessible *tert*-butyl ester **6**[25] was retained as the best candidate as its use led to a more convenient protocol (shorter reaction time, easily removed volatile *tert*-butyl acrylate generated as a side product).

Henceforth, we proceeded with the optimisation of the reaction conditions (Table 2). First, diluting the reaction (0.056 M instead of 0.16 M) and raising the temperature to -40 °C allowed us to attain 77% NMR yield (Entry 1) with a cleaner reaction profile. We then screened different bases, KOtBu proved to be the best base, even though the results with KHMDS were comparable (Entries 2-4). We tested reverse stoichiometry of **5** and **9a**, which resulted in a similar isolated yield (Entry 5). Other solvents were not more efficient than toluene (Entries 6-8). Meanwhile, *tert*-butyl *p*-tolylsulfinate was identified as an oxidation side product by MS and NMR analysis. Accordingly, oxygen was more carefully excluded from the reaction mixture by adding all of the dry reaction components under inert atmosphere (previously, KOtBu was added after the solvent). This modification improved the isolated yield to 81% (Entry 9). Further increasing the equivalents of KOtBu had a negative impact on the yield (Entry 10). Finally, when combining reversed stoichiometry and oxygen free conditions the desired alkynyl sulfoxide **10a** was isolated in 90% yield (Entry 11). When the reaction was performed at room temperature under the optimized conditions, a lower yield of 73% was obtained (Entry 12). Both *tert*-butyl *p*-tolylsulfinate and the alkynyl sulfone corresponding to **10a** were identified as side products in this case.

Table 2: Optimisation of the reaction conditions.



entry	base	solvent	yield (%)[a]
1	KO*t*Bu	PhMe	70 (77)
2	NaO*t*Bu	PhMe	(53)
3	KHDMS	PhMe	(70)
4	LDA[b]	PhMe	(52)

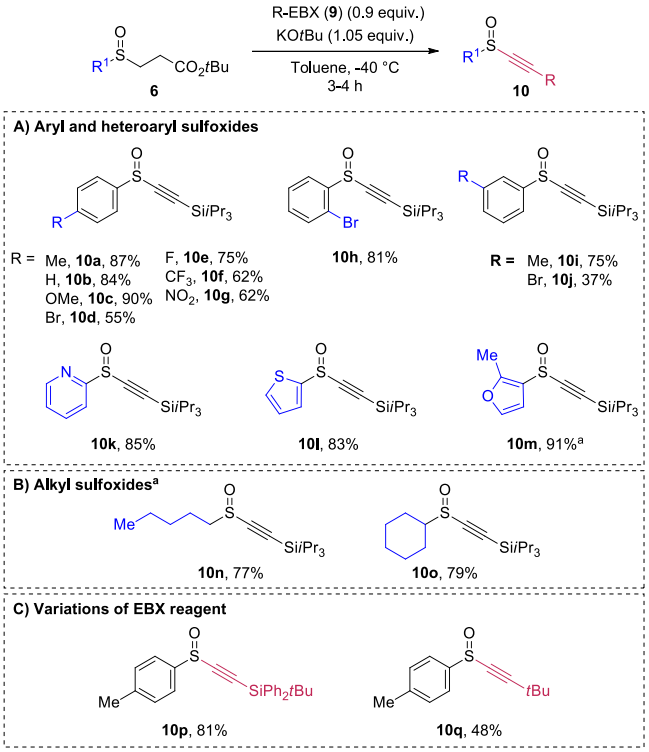
5[c]	KO*t*Bu	PhMe	75
6	KO*t*Bu	DMF	28(<40)
7	KO*t*Bu	PhMe/DCM (9:1)	(66)
8	KO*t*Bu	THF	(66)
9[d]	KO*t*Bu	PhMe	81
10[d]	KO*t*Bu[e]	PhMe	60
11[c,d]	KO*t*Bu	PhMe[f]	90
12[c,d]	KO*t*Bu	PhMe[g]	73

Reactions were performed with **6a** (0.10 mmol, 1.0 equiv.), (0.11 mmol, 1.1 equiv.) and the indicated base (0.105 mmol l.05 equiv.) in the indicated solvent (0.056 M) at -40 °C for 3h. [a]Isolated yield. [1]H-NMR yields using 1.0 equiv. of CH_2Br_2 as internal standard is given in parenthesis. [b]1.1 equiv. [c]0.9 equiv. of **9a**. [d]The dry reaction components were added under inert atmosphere. [e]1.25 equiv. [f]Degassed by bubbling Ar for 40 min at -40 °C prior to addition. [g]Degassing and reaction were performed at RT.

With the optimised reaction conditions in hand, we explored the scope of aryl sulfoxides (Scheme 3, **A**). The reaction tolerated both electron rich and electron poor *para* substitution affording compounds **10a**-**g** in good to excellent yields (55-90%). *Ortho* and *meta* substitution also provided the desired alkynyl sulfoxides **10h**-**j** in up to 81% yield. The method also allowed the synthesis of heteroaryl sulfoxides. Alkynyl pyridine sulfoxide **10k** and alkynyl thiophene sulfoxide **10l** were obtained in 85 and 83% yield respectively, and furanyl sulfoxide **10m** in 91% yield after warming the reaction to room temperature overnight. We then moved our attention onto the synthesis of alkyl alkynyl sulfoxides (Scheme 3, **B**). We discovered that the reaction needed to be warmed to room temperature and left overnight to ensure optimal yields. Primary and secondary alkyl groups were both well tolerated affording **10n** and **10o** in 77 and 79%

yield respectively. We then proceeded to test other EBX reagents (Scheme 3, **C**). TBDPS-EBX (**9b**) (TBDPS = *tert*-butyldiphenylsilyl) and *t*Bu-EBX (**9c**) (*t*Bu = *tert*-butyl) both served as efficient alkynyl transfer agents affording **10p** and **10q** in 81 and 48% yield respectively. However, attempts with $C_{14}H_{29}$-EBX and Ph-EBX reagents were unsuccessful.

Scheme 3. Scope of the alkynylation reaction.

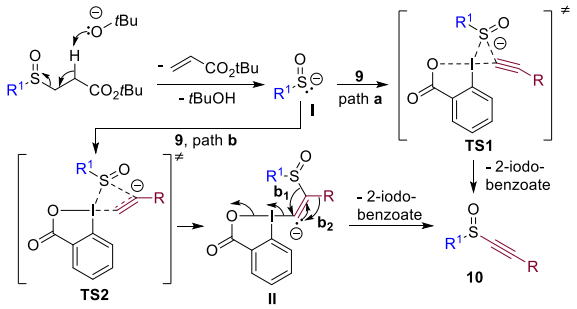


[a]The reaction was maintained at -40 °C for 2 h, then left to warm to rt over 18 h.

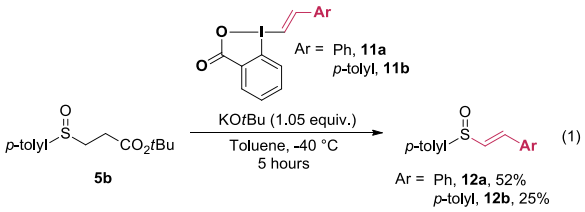
A speculative reaction mechanism can be proposed based on literature precedence (Scheme 4).[16,23b,d] A base-initiated retro-Michael reaction first generates the unstable sulfenate anion **I.**[16] Based on our previous studies on the addition of sulfur nucleophiles onto EBX reagents,[23b,d] two mechanism pathways can then be envisaged: 1) Direct concerted addition to give sulfoxide **10** via 3-atom transition state **TS1** (path **a**) or 2) Conjugate addition via 4-atom transition state **TS2** leading to vinyl benziodoxolone **II**. At this stage, a 1,2-shift of either the sulfoxide (path $\mathbf{b_1}$) or the R substituent (path $\mathbf{b_2}$) together with α-elimination of the iodine leads to sulfoxide **10**. This latter step can be either concerted, or via a carbene intermediate if

α-elimination precedes 1,2-shift. The exact reaction pathway is expected to be dependent on the nature of the R group on the alkyne.

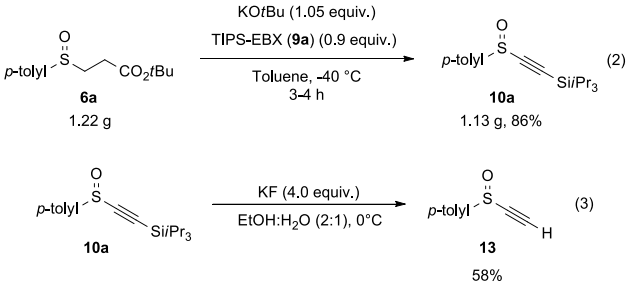
Scheme 4. Speculative reaction mechanism.



We then wondered if the functionalisation of sulfenate anions could be extended to vinylation using recently introduced Vinyl BenziodoXolone (VBX) reagents.[26] To our delight, we were able to access (E)-alkenyl sulfoxides **12a** and **12b** in yields of 52% and 25% respectively without changing the experimental procedure using the corresponding VBX reagents (eq. 1).



To confirm the synthetic utility of this procedure, we performed the reaction on gram-scale affording the desired alkynyl sulfoxide **10a** in 86% yield (eq. 2). Finally, the free alkyne **13** was obtained in 58% after deprotection of **10a** with potassium fluoride under mild conditions (eq. 3).



In conclusion, we have designed a new efficient route to access alkynyl sulfoxides. The use of an EBX reagent as a soft electrophilic acetylene transfer agent has allowed us to develop the first general synthetic method for alkynyl sulfoxides based on an inversed-polarity alkynylation under metal-free conditions. We

have been able to generate in-situ alkyl, heteroaryl and aryl sulfenate anions by using potassium *tert*-butoxide at low temperature to initiate a retro-Michael elimination. The trapping of the resulting sulfenate anions with EBX reagents afforded alkyl and aryl alkynyl sulfoxides in high yields. Additionally, two aryl vinyl sulfoxides were also isolated when using VBX reagents. When considering the availability of the starting materials and the straightforward reaction conditions, the developed method has the potential to facilitate the use of alkynyl sulfoxides in synthetic chemistry, chemical biology and material science.

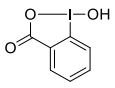
Experimental Section

General methods

HPLC grade or distilled solvents purchased from Sigma-Aldrich were used for flash chromatography. For non-air-sensitive reactions, analytical or reagent grade solvents purchased from Merck or Sigma-Aldrich were used unless specified. For all alkynylation reactions, toluene and THF dried by passage over activated alumina under nitrogen atmosphere (H2O content < 7 ppm, Karl-Fisher titration) or anhydrous solvents purchased from Sigma-Aldrich were used. Toluene was degassed by bubbling with a balloon of argon when mentioned. Reagents were purchased from Sigma-Aldrich, Acros, TCI, Fluorochem, Fluka, VWR or Merck, unless specified. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure or using Biotage Isolera Spektra One with pre-packaged silica cartridges purchased from Buchi, models: Sepacore or GraceResolve (4 g, 12 g, 25 g). TLC was performed on Merck silica gel 60 F254 TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain. Melting points were measured using a calibrated Buchi B-540 apparatus using open glass capillaries. 1H-NMR spectra were recorded on a Brucker DPX-400, 400 MHz, in $CDCl_3$, $(CD_3)_2SO$ or CD_3OD. All signals are reported in ppm using the residual solvent signal as internal reference ($CDCl_3$: 7.26 ppm, $(CD_3)_2SO$: 2.50 ppm or CD_3OD: 3.31 ppm). The data is reported as (multiplicity, coupling constants in Hz, integration, interpretation) using these abbreviations: s = singulet, d = doublet, t = triplet, m = multiplet, bs = broad signal.

13C{1H}-NMR spectra were carried out with 1H decoupling on a Brucker DPX-400, 101 MHz. All signals are reported in ppm using the residual solvent signal as internal reference ($CDCl_3$: 77.0 ppm, $(CD_3)_2SO$: 39.5 ppm or CD_3OD: 49.0). Infrared spectra were obtained on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported in cm^{-1} as (w = weak, m = medium, s = strong). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. Cooling baths were assured by using Huber TC100E and TC50E cryostats with an ethyl acetate bath.

Synthesis of 1-Hydroxy-1 λ3,2-benziodoxol-3(1H)-one (14)



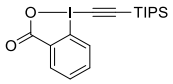
Following a reported procedure,[27] $NaIO_4$ (7.24 g, 33.8 mmol, 1.05 equiv.) and 2-iodobenzoic acid (8.00 g, 32.2 mmol, 1.00 equiv.) were suspended in 30% (v:v) aq. AcOH (48 mL). The mixture was stirred vigorously and refluxed for 4 hours. The reaction mixture was then diluted with cold water (180 mL) and allowed to cool to rt, protecting it from light. After 1 hour, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), then air-dried in the dark to give the pure product **14** (8.3 g, 31 mmol, 98%) as a colorless solid. **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$) δ = 8.02 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.97 (m, 1H), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.71 (td, *J* = 7.6, 1.2 Hz, 1H) ppm. **^{13}C{1H}-NMR** (101 MHz, $(CD_3)_2SO$) δ = 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4 ppm. The values of the NMR spectra are in accordance with reported literature data.[27]

Synthesis of triisopropylsilyl(trimethylsilyl)acetylene (15)

Following a reported procedure,[28] *n*-butyl lithium (2.5 M in hexanes, 12.0 mL, 29.9 mmol, 0.98 equiv.) was added dropwise to a solution of ethynyltrimethylsilane (3.0 g, 30 mmol, 1.0 equiv.) in THF (48 mL) at -78 °C in a two-neck 100 mL oven-dried flask under nitrogen. The mixture was warmed to 0 °C and stirred for 5 minutes. The mixture was cooled back to -78 °C and chlorotriisopropylsilane (6.4 mL, 30 mmol, 1 equiv.) was added dropwise. The mixture was then warmed to room temperature and stirred overnight. The reaction was then quenched with aq. sat. ammonium chloride (40 mL). The reaction mixture was extracted with diethyl ether (3 x 60 mL). The organic phases were combined, washed with

water and brine, dried with $MgSO_4$, filtered and concentrated under reduced pressure to obtain a colourless liquid which was further purified by Kugelrohr distillation (56-57 °C, 0.25 mmHg) affording **15** as a clear oil (4.57 g, 18 mmol, 85% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 1.08 (m, 21H), 0.18 (s, 9H) ppm. The values of the ^{1}H-NMR spectra are in accordance with reported literature data.[28]

Synthesis of 1-[(Tri*iso*propylsilyl)ethynyl]-1λ3,2-benziodoxol-3(1*H*)-one (TIPS-EBX, 9a)

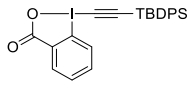


Following a reported procedure,[29] 2-iodosylbenzoic acid (**14**) (21.7 g, 82.0 mmol, 1.0 equiv.) was introduced into an oven-dried three-neck 1 L flask equipped with a magnetic stirrer. After 3 vacuum/nitrogen cycles, anhydrous acetonitrile (500 mL) was added via cannula and cooled to 0 °C. Trimethylsilyltriflate (16.4 mL, 90.0 mmol, 1.1 equiv.) was added dropwise via a dropping funnel over 30 minutes (no temperature increase was observed). After 15 minutes, tri*iso*propylsilyl(trimethylsilyl)acetylene (**15**) (23.0 g, 90.0 mmol, 1.1 equiv.) was added via cannula over 15 min (no temperature increase was observed). After 30 min, the suspension became an orange solution. After 10 minutes, pyridine (7.0 mL, 90 mmol, 1.1 equiv.) was added via syringe. After 15 min, the reaction mixture was transferred to a one-neck 1 L flask and concentrated under vacuum to provide an yellowish solid. The latter was dissolved in DCM (200 mL) and transferred to a 1 L separatory funnel. The organic layer was added and washed with aq. HCl (1.0 M; 200 mL) and the aqueous layer was extracted with dichloromethane (200 mL). The organic layers were combined, washed with a saturated aqueous solution of $NaHCO_3$ (2 x 200 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Recrystallization from acetonitrile (ca. 120 mL) afforded **9a** (30.1 g, 70.2 mmol, 86%) as a colorless crystalline solid. **mp:** 170-176 °C (decomposition); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.44 (m, 1H), 8.29 (m, 1H), 7.77 (m, 2H), 1.16 (m, 21H) ppm. **^{13}C{1H}-NMR** (101 MHz, $CDCl_3$) δ = 166.4, 134.6, 132.3, 131.4, 131.4, 126.1, 115.6, 114.1, 64.6, 18.4, 11.1 ppm. The values of the NMR spectra are in accordance with reported literature data.[29]

Synthesis of *tert*-butyldiphenylsilyl(trimethylsilyl)acetylene (16)

Following a reported procedure,[30] *n*-butyllithium (2.5 M in hexanes, 8.0 mL, 20 mmol, 0.98 equiv) was added dropwise to a stirred solution of ethynyltrimethylsilane (2.90 mL, 20.4 mmol, 1.0 equiv) in THF (30 mL) at –78 °C. The mixture was then warmed to 0 °C and stirred for 5 minutes. The mixture was then cooled back to –78 °C and *tert*butylchlorodiphenylsilane (6.4 mL, 30 mmol, 1.0 equiv.) was added dropwise. The mixture was then allowed to warm to room temperature and stirred overnight. A saturated aqueous solution of ammonium chloride (30 mL) was added, and the reaction mixture was extracted with diethyl ether (2 x 50 mL). The organic layer was washed with water and brine, then dried over $MgSO_4$, filtered and concentrated under reduced pressure to obtain a colorless liquid which was further purified by Kugelrohr distillation (150 °C, 0.25 mmHg) to yield **16** (2.95 g, 8.76 mmol, 44% yield) as a colorless liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.80 (m, 4H), 7.38 (m, 6H), 1.08 (s, 9H), 0.27 (s, 9H) ppm. **^{13}C{1H}-NMR** (101 MHz, $CDCl_3$) δ = 135.6, 133.2, 129.5, 127.7, 119.0, 108.7, 27.0, 18.5, -0.0 ppm. The values of the NMR spectra are in accordance with reported literature data.[30]

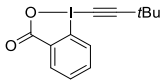
Synthesis of 1-[(*tert*-Butyldiphenylsilyl)ethynyl]-1λ3,2-benziodoxol-3(1*H*)-one (TBDPS-EBX, 9b)



Following a reported procedure,[31] trimethylsilyltriflate (freshly distilled; 1.6 mL, 8.7 mmol, 1.1 equiv.) was added dropwise to a stirred solution of 2-iodosylbenzoic acid (**14**) (2.07 g, 7.90 mmol, 1.0 equiv.) in acetonitrile (30 mL). *tert*-Butyldiphenyl((trimethylsilyl)ethynyl)silane (**16**) (2.95 g, 3.70 mmol, 1.1 equiv.) was then added dropwise, followed, after 15 min, by the addition of pyridine (710 µL, 3.70 mmol, 1.1 equiv.). The mixture was stirred 10 minutes. The solvent was then removed under reduced pressure and the resulting yellow crude oil was dissolved in dichloromethane. The organic layer was washed with aq. HCl (1.0 M, 15 mL), and the aqueous layer was extracted with dichloromethane. The organic layers were combined, washed with a sat. aq. $NaHCO_3$, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The resulting oil was stirred in hexane and ether and then concentrated under vacuum to afford a colorless solid. Recrystallization from acetonitrile (ca 20 mL) afforded **9b** (2.77 g, 5.42 mmol, 69% yield) as a colorless solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.43 (d, *J* = 6.5 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 6.6 Hz, 4H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.66 (m,

1H), 7.53-7.41 (m, 6H), 1.21 (s, 9H) ppm. **^{13}C{1H}-NMR** (101 MHz, $CDCl_3$) δ = 166.6, 135.5, 134.8, 132.4, 131.5, 131.3, 130.2, 128.1, 126.3, 116.0, 112.2, 68.5, 27.0, 18.7 ppm. The signal corresponding to one aromatic carbon was not resolved. The values of the NMR spectra are in accordance with reported literature data.[31]

Synthesis of 1-[(*tert*-Butylsilyl)ethynyl]-1λ3,2-benziodoxol-3(1*H*)-one (*t*Bu-EBX, 9c)



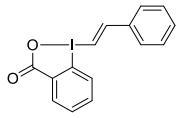
Following a reported procedure,[31] trimethylsilyltriflate (freshly distilled; 1.5 mL, 8.4 mmol, 1.0 equiv) was added dropwise to a stirred solution of 2-iodosylbenzoic acid (**14**) (2.69 g, 10.1 mmol, 1.2 equiv) in acetonitrile (30 mL). Commercially available 3,3-dimethylbut-1-yn-1-yl)trimethylsilane (1.30 g, 8.42 mmol, 1.0 equiv) was then added dropwise, followed, after 15 min, by the addition of pyridine (680 µL, 8.42 mmol, 1.0 equiv). The mixture was stirred 10 min. The solvent was then removed under reduced pressure. Dichloromethane and aq. NaOH (1.0 M) were added. The resulting suspension was filtered. The layers were separated and the aqueous layer was extracted with dichloromethane. The organic layers were combined, dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Two recrystallisations (with hot filtration) from acetonitrile were necessary to afford 1-[3,3- dimethylbutynyl]-1,2-benziodoxol-3(1*H*)-one (**9c**) (1.43g, 4.36 mmol, 57% yield) as a colorless solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.39 (m, 1H), 8.12 (m, 1H), 7.75 (m, 2H), 1.37 (s, 9H) ppm. The values of the NMR spectra are in accordance with reported literature data.[31]

General procedure A: Synthesis of VBX reagents (11a and **11b):**

Following a slightly modified reported proceedure,[32] to a suspension of 2-iodosylbenzoic acid (**14**) (0.343 g, 1.30 mmol, 1.00 equiv.) in dry dichloromethane (13 mL) was added TMSOTf (0.27 mL, 1.5 mmol, 1.15 equiv.) dropwise over 10 minutes and stirred for 30 minutes at room temperature. Afterwards, the corresponding vinyl boronic acid (**20a** or **20b**) (1.50 mmol, 1.15 equiv.) was added and the reaction mixture was stirred for 2 hours at room temperature. Pyridine (0.12 mL, 1.5 mmol, 1.15 equiv.) was added, after which the mixture was stirred for additional 10 minutes at room temperature. The solvent was then removed under reduced pressure. The resulting solid was dissolved in dihloromethane (20 mL) and

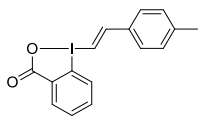
washed with aqueous HCl (1.0 M; 10 mL). The aqueous layer was extracted with dichloromethane (3 x 20 mL). The organic layers were combined, washed successively with a saturated aqueous solution of $NaHCO_3$ (40 mL) and water (3 x 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting solid was dissolved again in dichloromethane (minimum amount until dissolution) and precipitated in diethyl ether (ca. 100 mL). After precipitation at 4 °C for 2 hours, the solid was collected by filtration and washed with Et_2O to afford the corresponding VBX reagent.

(*E*)-1-Styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (11a)



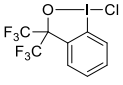
Following the **general procedure A**, **11a** was obtained as a colourless solid from *trans*-2-phenylvinylboronic acid (0.221 g, 1.50 mmol) and 2-iodosylbenzoic acid (**14**) (0.343 g, 1.30 mmol). Yield: 77% (0.351 g, 1.00 mmol). **^{1}H-NMR** (400 MHz, CD_3OD) δ = 8.32 - 8.25 (m, 1H), 7.97 (d, *J* = 15.5 Hz, 1H), 7.77 – 7.63 (m, 6H), 7.54 – 7.45 (m, 3H) ppm. **^{13}C{1H}-NMR** (101 MHz, CD_3OD) δ = 170.1, 155.8, 136.7, 135.3, 134.5, 133.3, 132.1, 131.8, 130.2, 129.0, 129.0, 115.5, 100.0 ppm. The values of the NMR spectra are in accordance with reported literature data.[32]

(*E*)-1-(4-Methylstyryl)-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (11b)



Following the **general procedure A**, **11b** was obtained as a colourless solid from *trans*-2-(4-methylphenyl)vinylboronic acid (0.242 g, 1.50 mmol) and 2-iodosylbenzoic acid (**14**) (0.343 g, 1.30 mmol). Yield: 71% (0.335 g, 0.920 mmol). **^{1}H-NMR** (400 MHz, CD_3OD) δ = 8.32 – 8.25 (m, 1H), 7.92 (d, *J* = 15.4 Hz, 1H), 7.76 – 7.64 (m, 3H), 7.62 – 7.54 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H) ppm. **^{13}C{1H}-NMR** (101 MHz, CD_3OD) δ = 169.9, 155.7, 142.8, 135.0, 134.3, 133.8, 133.1, 131.6, 130.6, 128.8, 115.3, 98.1, 21.3 ppm. The values of the NMR spectra are in accordance with reported literature data.[32]

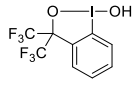
1-Chloro-1,3-dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole (17)



Following a reported procedure,[33] TMEDA (distilled over KOH) (0.63 mL, 4.1 mmol, 0.2 equiv) was added to a solution of *n*BuLi (2.5 M in hexanes, 18.3 mL, 45.8 mmol, 2.2 equiv).

After 15 min, the cloudy solution was cooled to 0 °C and α,α-bis(trifluoromethyl)benzyl alcohol (3.5 mL, 21 mmol, 1 equiv) in THF (3 mL) was added dropwise. The reaction was stirred 30 min at 0 °C and then 18 h at rt. I_2 (5.6 g, 22 mmol, 1.06 equiv.) was then added portion-wise at 0 °C and the mixture stirred at 0 °C for 30 min and 4 h at rt. The reaction was quenched with a saturated aqueous solution of NH_4Cl. Diethyl ether (50 mL) was added and the layers were separated. The aqueous layer was then extracted twice with diethyl ether (2 x 50 mL). The organic layers were combined, washed twice with a saturated aqueous solution of NaS_2O_3 (2 x 50 mL), dried over $MgSO_4$, filtered and reduced to afford 7.83 g of 2-iodo-α,α-bis(trifluoromethyl)-benzenemethanol as an orange oil which was used without further purification. The crude oil was dissolved in dichloromethane (20 mL) in the dark under air. *t*BuOCl (2.6 mL, 22 mmol, 1.05 equiv.) was then added dropwise at 0 °C. After 30 min, the resulting suspension was filtered to afford **17** (3.52 g, 8.70 mmol, 42%) as a yellow oil. The mother liquors were carefully reduced to one third and filtered to afford **17** (2.33 g, 5.76 mmol, 28%) as a yellow solid. Combined yield: 70%. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.09 (d, 1H, *J* = 8.4 Hz), 7.85 (m, 1H), 7.73 (m, 2H) ppm. **^{13}C{1H}-NMR** (101 MHz, $CDCl_3$) δ = 133.8, 132.1, 131.6, 129.7, 128.5,122.8 (q, 289 Hz), 113.4, 84.8 ppm. The values of the NMR spectra are in accordance with reported literature data.[34]

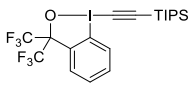
1-Hydroxy-3,3-bis(trifluoromethyl)-3-(1*H*)-1,2-benziodoxole (18)



Following a reported procedure,[35] Et_3BnNCl (0.083 g, 0.36 mmol, 0.05 equiv) was added to a stirring solution of **17** (3.00 g, 7.41 mmol, 1 equiv) in dichloromethane (50 mL) and KOH (0.415 g, 7.41 mmol, 1 equiv) in water (8 mL). The reaction was stirred for 3.5 hours under air. The organic layer was separated and dried over $MgSO_4$. The resulting solid was purified over a silica plug with ethyl acetate, then recrystallised in ethyl acetate and washed with pentane to afford **18** (1.24 g, 3.21 mmol, 43%) as a colourless solid. The mother liquors were reduced and recrystallised in ethyl acetate to afford a second batch of **18** (0.279 g, 0.723 mmol, 10 %) as a colourless solid. Combined yield: 53%. **^{1}H-NMR** (400 MHz, $(CD_3)_2SO$) δ = 7.96 (m, 2H), 7.73 (m, 2H) ppm. **^{13}C{1H}-NMR** (101 MHz, $(CD_3)_2SO$) δ = 133.3,

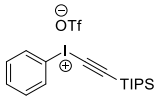
131.0, 130.8, 128.9, 127.9, 123.4 (q, *J* = 290 Hz), 117.2, 83.7 (m) ppm. The values of the NMR spectra are in accordance with literature data.[35]

1-[(Tri*iso*propylsilyl)ethynyl]-3,3-bis(trifluoromethyl)-3(1*H*)-1,2-benziodoxole (19)



TMSOTf (310 µL, 1.71 mmol, 1.1 equiv) was added to **18** (0.600 g, 1.55 mmol, 1.0 equiv) in dichloromethane (20 mL) at rt. After 20 min, the solution was reduced and the resulting oil was dissolved in acetonitrile (30 mL). (trimethylsilyl)(tri*iso*propylsilyl)acetylene (**16**) (0.514 g, 1.71 mmol, 1.1 equiv) was added and after 20 min pyridine (76 µL, 0.94 mmol, 0.6 equiv) was added. The reaction was then reduced under vacuum, dissolved in diethyl ether and filtered over a silica plug (eluant: diethyl ether). The resulting solid was purified by column chromatography (Petroleum ether:diethyl ether 95:5) to afford **19** (0.816 g, 1.48 mmol, 95%) as a colourless solid. **^{1}H-NMR** (400 MHz, Choroform-*d*) δ = 8.36 (dd, 1H, *J* = 7.9, 1.7 Hz), 7.84 (d, 1H, *J* = 6.7 Hz), 7.68 (m, 2H), 1.15 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 132.7, 131.1, 129.9, 129.9 (m), 128.2, 123.6 (q, 288 Hz), 112.1, 110.8, 81.4 (m), 69.7, 18.5, 11.2 ppm.

Phenyl(tri*iso*propylsilyl)iodonium triflate (20)



Following a reported procedure,[36] phenyliodonium diacetate (2.53 g, 7.85 mmol, 1.00 equiv) was diluted with dichloromethane (7 mL) and the mixture was stirred for 5 minutes. Triflic anhydride (0.60 mL, 3.9 mmol, 0.50 equiv.) was added dropwise at 0 °C and the resulting yellow mixture was stirred 30 min. (Trimethylsilyl)(tri*iso*propylsilyl)acetylene (**15**) (2.00 g, 7.86 mmol, 1.00 equiv) was added and the mixture was then stirred 2 h. Water was then added (30 mL) followed by extraction of the aqueous layer with dichloromethane (2 x 30 mL). The combined organic layers were dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The resulting solid was triturated in hexane (10 mL). Filtration and removal of solvent *in vacuo* afforded phenyl(tri*iso*propylsilyl)iodonium triflate (**20**) (2.90 g, 11.2 mmol, 70% yield) as a colorless solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.09 (m, 2H), 7.65 (m, 1H), 7.52 (m, 2H), 1.15-1.01 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (100 MHz, $CDCl_3$)

δ = 133.7, 132.5, 132.4, 119.7, 117.6, 117.6, 44.9, 18.3, 11.1 ppm. The values of the NMR spectra are in accordance with reported literature data.[36]

Preparation of Starting Materials

All thiols were commercially avaiable and purhased from Sigma-Aldrich, Alfa-Aesar, Fluorochem or TCI and used as purchased without any purification.

General procedure B: synthesis of *tert*-butyl β-sulfanyl esters (21a-21k)

Following a slightly modified version of a reported procedure,[37] the thiol (1 equiv.), *tert*-butyl acrylate (1.05 equiv.) and triethylamine (0.1 equiv.) were introduced into a microwave vial equipped with a magnetic stirrer. The vial was sealed and the reaction mixture was stirred at rt for 10 minutes then heated to 60 °C for 1-3 hours (until full conversion based on TLC analysis). The volatiles were then removed through evaporation under reduced pressure to afford β-sulfanyl esters (**21a**-**21k**) in sufficient purity to be used in next step without further purification.

In order to characterise the new compounds, preparative TLC (SiO_2, Heptane/EtOAc) was used to afford pure compounds.

General procedure C: synthesis of *tert*-butyl β-sulfanyl esters (21l, **21m)**

Following a reported procedure,[18e] the thiol (1.0 equiv.) and *tert*-butyl acrylate (1.0 equiv.) were dissolved in THF (5 M based on the thiol) in a round-bottomed flask equipped with a magnetic stirrer. Triethylamine (0.1 equiv.) was added and the reaction mixture was stirred at rt. overnight. It was then concentrated under reduced pressure to remove the volatiles. The crude was then submitted to column chromatography (SiO_2, pentane:Et_2O) affording β-sulfanyl esters (**21l**, **21m**).

General alkylation procedure D: synthesis of *tert*-butyl β-sulfanyl esters (21n, 21o)

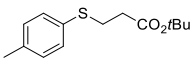
Following a slightly modified reported procedure,[38] the thiol (1.0 equiv.) was added to a suspension of KF/alumina 45wt% (4.2 equiv – 4.6 equiv) in acetonitrile (0.05 M based on the thiol). The reaction mixture was stirred for 5 minutes at rt. *tert*-Butyl acrylate (1.0 equiv.) was added and the reaction was heated

to 50-60 °C for 15 minutes. The reaction mixture was filtered on a Celite pad then concentrated under reduced pressure and filtered a second time on Celite and sand, washed with DCM. Solvents were evaporated under reduced pressure affording in sufficient purity the desired *tert*-butyl alkylthiopropanoate (**21n**, **21o)**.

Synthesis of alumina supported potassium fluoride 45wt%

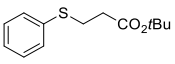
Following a reported procedure,[38] basic alumina (5.5 g) and potassium fluoride (4.5 g, 77 mmol) were charged in a 25 mL flask equipped with a magnetic stirrer. Water (10 mL) was added and the mixture was stirred at room temperature for 15 min. The water was evaporated under reduced pressure and the catalyst was left to dry in a vacuum oven at 110 °C overnight, yielding 10 g 45wt% KF/basic alumina support.

***Tert*-butyl 3-(4-methylphenylthio)propanoate (21a)**



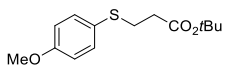
Following **general procedure B**, **21a** was obtained as a yellow oil from 4-methylbenzenethiol (1.24 g, 10.0 mmol) and *tert*-butyl acrylate (1.5 mL, 10 mmol). Yield: 99% (2.51 g, 9.95 mmol, 88% purity). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.11 (m, 2H), 3.07 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 1.45 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.2, 136.8, 131.8, 131.0, 129.9, 80.9, 35.8, 30.1, 28.2, 21.2 ppm. The values of the NMR spectra are in accordance with reported literature data.[39]

***Tert*-butyl 3-(phenylthio)propanoate (21b)**



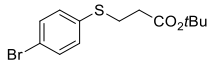
Following **general procedure B**, **21b** was obtained as a colourless oil from benzenethiol (0.73 mL, 7.1 mmol) and *tert*-butyl acrylate (1.1 mL, 7.5 mmol). Yield: 99% (1.68 g, 7.10 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.39 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 – 7.17 (m, 1H), 3.13 (dd, *J* = 7.9, 7.1 Hz, 2H), 2.54 (dd, *J* = 7.8, 7.1 Hz, 2H), 1.45 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.1, 135.6, 130.0, 129.0, 126.4, 81.0, 35.6, 29.2, 28.1 ppm. **HRMS** (APCI) calcd. For $C_{13}H_{18}O_2S^{+\circ}$ $[M]^{+\circ}$ 238.1028; found 238.1022. **IR** (film): $\tilde{\nu}$ = 2977 (m), 2935 (w), 1729 (s), 1480 (m), 1368 (m), 1249 (m), 1152 (s) cm^{-1}.

***Tert*-butyl 3-(4-methoxyphenylthio)propanoate (21c)**



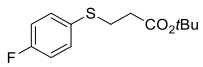
Following **general procedure B**, **21c** was obtained as a yellow oil from 4-methoxybenzenethiol (0.44 mL, 3.6 mmol) and *tert*-butyl acrylate (0.54 mL, 3.7 mmol). Yield: 99% (0.954 g, 3.55 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.37 (dt, *J* = 8.8, 2.1 Hz, 2H), 6.84 (dt, *J* = 8.8, 2.1 Hz, 2H), 3.80 (s, 3H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.44 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.3, 159.4, 134.2, 125.5, 114.7, 81.0, 55.5, 35.8, 31.4, 28.2 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{20}NaO_3S^+$ $[M+Na]^+$ 291.1025; found 291.1034. **IR** (film): $\tilde{\nu}$ = 2979 (w), 2934 (w), 2840 (w), 1727 (s), 1596 (m), 1579 (w), 1497 (m), 1368 (m), 1304 (w), 1250 (s), 1155 (s), 1089 (s), 1043 (s), 834 (m) cm^{-1}.

***Tert*-butyl 3-(4-bromophenylthio)propanoate (21d)**



Following **general procedure B**, **21d** was obtained as an off-white solid from 4-bromobenzenethiol (0.510 g, 2.70 mmol) and *tert*-butyl acrylate (0.4 mL, 3 mmol). Yield 96% (0.827 g, 2.61 mmol). **mp:** 46.8-47.9 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.41 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.22 (dt, *J* = 8.5, 2.0 Hz, 2H), 3.10 (t, *J* = 7.4 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.45 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.0, 134.9, 132.2, 131.6, 120.4, 81.3, 35.5, 29.4, 28.2 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{17}{}^{79}BrNaO_2S^+$ $[M+Na]^+$ 339.0030; found 339.0029. **IR** (film): $\tilde{\nu}$ = 2979 (w), 2938 (w), 1729 (s), 1476 (m), 1391 (w), 1367 (m), 1252 (m), 1156 (s), 1094 (w), 1009 (w), 814 (w) cm^{-1}.

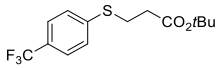
***Tert*-butyl 3-(4-fluorophenylthio)propanoate (21e)**



Following **general procedure B**, **21e** was obtained as a yellow oil from 4-fluorobenzenethiol (0.42 mL, 3.9 mmol) and *tert*-butyl acrylate (0.64 mL, 4.4 mmol). Yield: 92% (95% pure according to NMR analysis; 0.97 g, 3.6 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.38 (m, 2H), 7.12 – 6.72 (m, 2H), 3.06 (t, *J* = 7.4 Hz, 2H), 2.49 (t, *J* = 7.4 Hz, 2H), 1.44 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.0, 162.1 (d, *J* = 246.8 Hz), 133.2 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 3.4 Hz), 116.1 (d, *J* = 21.8 Hz), 81.0, 35.5, 30.6, 28.1 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -115.0 ppm. **HRMS** (ESI) calcd. for

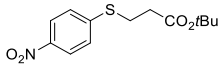
$C_{13}H_{17}FNaO_2S^+$ $[M+Na]^+$ 279.0825; found 279.0817. **IR** (film): $\tilde{\nu}$ = 2983 (m), 2923 (w), 1728 (s), 1591 (m), 1489 (s), 1368 (m), 1230 (s), 1153 (s), 828 (s) cm^{-1}.

***Tert*-butyl 3-(4-trifluoromethylphenylthio)propanoate (21f)**



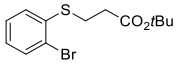
Following **general procedure B**, **21f** was obtained as a pale yellow oul from 4-trifluoromethylbenzenethiol (0.30 mL, 2.2 mmol) and *tert*-butyl acrylate (0.36 mL, 2.5 mmol). Yield: 99% (0.665 g, 2.17 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52 (m, 2H), 7.38 (m, 2H), 3.20 (t, *J* = 7.4 Hz, 2H), 2.58 (dd, *J* = 7.7, 7.1 Hz, 2H), 1.45 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.7, 141.4, 128.0, 127.8 (q, *J* = 32.8 Hz), 125.8 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 271.7 Hz), 81.3, 35.1, 28.1, 27.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.9 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{17}F_3O_2S^+$ $[M]^+$ 306.0896; found 306.0902. **IR** (film): $\tilde{\nu}$ = 2977 (w), 2935 (w), 1728 (m), 1608 (m), 1370 (m), 1327 (s), 1166 (s), 1127 (s), 1097 (s), 1065 (m), 1014 (m) cm^{-1}.

***Tert*-butyl 3-(4-nitrophenylthio)propanoate (21g)**



Following **general procedure B**, **21g** was obtained as a yellow crystalline solid from 4-nitrobenzenethiol (0.50 g, 3.2 mmol) and *tert*-butyl acrylate (0.56 mL, 3.9 mmol). Yield: 55% (0.50 g, 1.8 mmol). **mp:** 70.1 - 71.8 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.14 (m, 2H), 7.35 (m, 2H), 3.26 (t, *J* = 7.4 Hz, 2H), 2.62 (t, *J* = 7.3 Hz, 2H), 1.46 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.4, 146.7, 145.2, 126.5, 124.1, 81.6, 34.7, 28.1, 27.2 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{17}NNaO_4S^+$ $[M+Na]^+$ 306.0770; found 306.0761. **IR** (film): $\tilde{\nu}$ = 3094 (w), 3072 (w), 3002 (w), 2970 (w), 2932 (w), 1731 (s), 1591 (m), 1581 (m), 1503 (s), 1336 (s), 1225 (m), 1153 (s), 1089 (s), 855 (m), 836 (s), 744 (m) cm^{-1}.

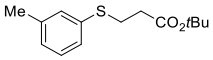
***Tert*-butyl 3-(2-bromophenylthio)propanoate (21h)**



Following **general procedure B**, **21h** was obtained as a yellow oil from 2-bromobenzenethiol (0.31 mL, 2.6 mmol) and *tert*-butyl acrylate (0.46 mL, 3.2 mmol). Yield: 99% (0.89 g, 2.6 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.51 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.01 (ddd,

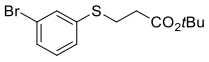
J = 7.9, 6.6, 2.3 Hz, 1H), 3.13 (t, J = 7.5 Hz, 2H), 2.55 (t, J = 7.5 Hz, 2H), 1.43 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.8, 137.2, 133.1, 128.7, 127.8, 127.0, 124.2, 81.2, 34.9, 28.2, 28.1 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{17}{}^{79}BrNaO_2S^+$ $[M+Na]^+$ 339.0025; found 339.0017. **IR** (film): $\tilde{\nu}$ = 3002 (w), 2976 (w), 2932 (w), 1725 (s), 1582 (w), 1449 (m), 1427 (m), 1367 (m), 1251 (m), 1147 (s), 1021 (m), 838 (m), 744 (s) cm^{-1}.

***Tert*-butyl 3-(3-methylphenylthio)propanoate (21i)**



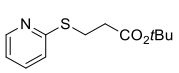
Following **general procedure B**, **21i** was obtained as a pale yellow oil from 3-methylbenzenethiol (1.00 mL, 8.4 mmol) and *tert*-butyl acrylate (1.3 mL, 9.0 mmol). Yield: 99% (2.1 g, 8.3 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.19 – 7.13 (m, 3H), 6.96 (m, 1H), 3.10 (t, J = 7.5 Hz, 2H), 2.52 (t, J = 7.5 Hz, 2H), 2.30 (s, 3H), 1.44 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.0, 138.6, 135.3, 130.5, 128.8, 127.2, 126.9, 80.8, 35.5, 29.1, 28.0, 21.3 ppm. **HRMS** (APPI) calcd. for $C_{14}H_{20}O_2S^{+\circ}$ $[M]^{+\circ}$ 252.1179; found 252.1174. **IR** (film): $\tilde{\nu}$ = 3008 (w), 2976 (w), 2932 (w), 1726 (s), 1595 (w), 1472 (w), 1364 (m), 1248 (m), 1149 (s), 844 (m), 771 (s) cm^{-1}.

***Tert*-butyl 3-(3-bromophenylthio)propanoate (21j)**



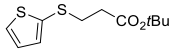
Following **general procedure B**, **21j** was obtained as a pale yellow oil from 3-bromobenzenethiol (0.30 mL, 2.6 mmol) and *tert*-butyl acrylate (0.4 mL, 3 mmol). Yield: 99% (0.82 g, 2.6 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.48 (t, J = 1.8 Hz, 1H), 7.32 (ddd, J = 7.9, 1.9, 1.0 Hz, 1H), 7.26 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.15 (t, J = 7.9 Hz, 1H), 3.13 (t, J = 7.4 Hz, 2H), 2.54 (t, J = 7.4 Hz, 2H), 1.45 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.8, 138.2, 131.8, 130.3, 129.3, 127.9, 122.9, 81.2, 35.3, 28.9, 28.1 ppm. **HRMS** (APPI) calcd. for $C_{13}H_{17}{}^{79}BrO_2S^{+\circ}$ $[M]^{+\circ}$ 316.0127; found 316.0132. **IR** (film): $\tilde{\nu}$ = 2977 (m), 2923 (w), 1728 (s), 1576 (m), 1557 (m), 1459 (m), 1391 (m), 1370 (m), 1247 (m), 1152 (s), 844 (m).

***Tert*-butyl 3-(pyridin-2-ylthio)propanoate (21k)**



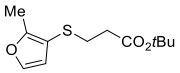
Following slightly modified **general procedure B**, **21k** was obtained as a dark brown oil from pyridine-2-thiol (0.82 g, 7.4 mmol) and *tert*-butyl acrylate (1.2 mL, 7.8 mmol) after heating to 80 °C over 16 hours. Yield: 90% (90% pure according to NMR analysis;1.75 g, 6.64 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.42 (ddd, *J* = 5.0, 1.9, 1.0 Hz, 1H), 7.46 (ddd, *J* = 8.0, 7.4, 1.9 Hz, 1H), 7.16 (dt, *J* = 8.1, 1.1 Hz, 1H), 6.96 (ddd, *J* = 7.4, 4.9, 1.1 Hz, 1H), 3.39 (t, *J* = 7.1 Hz, 2H), 2.68 (t, *J* = 7.1 Hz, 2H), 1.46 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.4, 158.5, 149.5, 135.9, 122.3, 119.4, 80.8, 35.8, 28.1, 25.1 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{18}NO_2S^+$ $[M+H]^+$ 240.1053; found 240.1047. **IR** (film): $\tilde{\nu}$ = 3049 (w), 2977 (w), 2935 (w), 1728 (s), 1580 (m), 1560 (w), 1534 (w), 1457 (m), 1418 (s), 1367 (s), 1285 (m), 1254 (s), 1151 (s), 1130 (s) cm^{-1}.

***Tert*-butyl 3-((thiophen-2-yl)thio)propanoate (21l)**



Following **general procedure C**, **21l** was obtained as a yellow oil from thiophenethiol (1.0 mL, 11 mmol, 1.0 equiv.) and *tert*-butyl acrylate (1.6 mL, 11 mmol, 1.0 equiv.). Yield: 70% (1.83 g, 7.48 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.36 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.14 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.98 (dd, *J* = 5.4, 3.6 Hz, 1H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.53 (t, *J* = 7.4 Hz, 2H), 1.45 (s, 9H) ppm. **^{13}C{1H}-NMR** (101 MHz, $CDCl_3$) δ = 170.1, 145.3, 131.2, 129.7, 127.5, 81.7, 53.0, 28.2, 28.0 ppm. **HRMS** (ESI) calcd. for $C_{11}H_{16}NaO_2S_2^+$ $[M+Na]^+$ 267.0484; found 267.0474. **IR** (film): $\tilde{\nu}$ = 2974 (m), 2928 (w), 1725 (s), 1407 (w), 1366 (m), 1247 (m), 1143 (s), 991 (w), 846 (s) cm^{-1}.

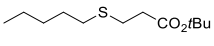
***Tert*-butyl 3-((2-methylfuran-3-yl)thio)propanoate (21m)**



Following **general procedure C**, **21m** was obtained as a colorless oil from 2-methylfuran-3-thiol (0.50 mL, 4.5 mmol) and *tert*-butyl acrylate (0.66 mL, 4.5 mmol). Yield: 76% (0.828 g, 3.42 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 2.0 Hz, 1H), 6.34 (d, *J* = 2.0 Hz, 1H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.43 (t, *J* = 7.3 Hz, 2H), 2.34 (s, 3H), 1.44 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.2, 155.4, 140.7, 115.1, 109.5, 80.8, 35.9, 31.1, 28.1, 11.8 ppm. **HRMS** (ESI) calcd. for

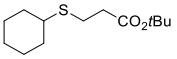
$C_{12}H_{18}NaO_3S^+$ $[M+Na]^+$ 265.0869; found 265.0858. **IR** (film): $\tilde{\nu}$ = 2979 (m), 2934 (w), 1730 (s), 1514 (w), 1370 (m), 1253 (m), 1142 (s), 1091 (m), 935 (m), 850 (m), 739 (m) cm^{-1}.

***Tert*-butyl 3-(pentylthio)propanoate (21n)**



Following **general procedure D**, **21n** was obtained as a yellow oil from 1-pentanethiol (1.24 g, 10.0 mmol, 1.0 equiv.), KF/alumina 45wt% (6.0 g, 42 mmol, 4.2 equiv.) and *tert*-butyl acrylate (1.5 mL, 10 mmol, 1 equiv.).Yield: 99% (2.51 g, 10.0 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.73 (t, *J* = 7.4 Hz, 2H), 2.59-2.43 (m, 4H), 1.65-1.49 (m, 2H), 1.45 (s, 9H), 1.40-1.26 (m, 4H), 0.95-0.82 (m, 3H,) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.5, 80.9, 36.3, 32.2, 31.2, 29.4, 28.2, 27.3, 22.5, 14.1 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{24}NaO_2S^+$ $[M+Na]^+$ 255.1389; found 255.1394. **IR** (film): $\tilde{\nu}$ = 2960 (m), 2929 (m), 2861 (w), 1731 (s), 1462 (w), 1392 (w), 1371 (w), 1251 (m), 1145 (s), 971 (w), 934 (w), 849 (w) cm^{-1}.

***Tert*-butyl 3-(cyclohexylthio)propanoate (21o)**



Following **general procedure D**, **21o** was obtained as a colorless oil from cyclohexylthiol (0.73 mL, 6.0 mmol, 1.0 equiv.), KF/alumina 45wt% (3.6 g, 25 mmol, 4.2 equiv.) and *tert*-butyl acrylate (0.90 mL, 6.2 mmol, 1.05 equiv.). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.75 (dd, *J* = 8.0, 7.1 Hz, 2H), 2.64 (tt, *J* = 10.4, 3.6 Hz, 1H), 2.49 (dd, *J* = 8.1, 7.1 Hz, 2H), 2.01 – 1.89 (m, 2H), 1.91 – 1.72 (m, 2H), 1.65 – 1.55 (m, 1H), 1.45 (s, 9H), 1.38 – 1.17 (m, 5H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.4, 80.7, 43.6, 36.5, 33.7, 28.1, 26.1, 25.8, 25.3 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{24}NaO_2S^+$$[M+Na]^+$ 267.1389; found 267.1390. **IR** (film): $\tilde{\nu}$ = 2981 (m), 2929 (s), 2857 (m), 1732 (s), 1447 (m), 1370 (s), 1250 (s), 1155 (s) cm^{-1}.

General oxidation procedure E (compounds 5, 6a-6j, 6n and **8)**

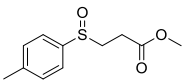
Following a slightly modified version of a reported procedure,[16] in a two-necked flask equipped with a magnetic stirrer, the sulfide **21** (1 equiv.) was dissolved in methanol (40 mL) and cooled to 0 °C. Sodium periodate (1.0 equiv. or 1.2 equiv.) dissolved in water (20 mL) was then added dropwise using a syringe

over a period of 30 minutes. The reaction mixture was then left to warm to room temperature under stirring overnight. The precipitated solids were then filtered off through a Celite pad and washed with methanol (20 mL). Methanol was evaporated under reduced pressure. The obtained aqueous layer was extracted three times with DCM (3 x 20 mL). The organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4 and filtered. Solvents were then evaporated under reduced pressure before submitting the crude to column chromatography (silica gel, DCM/EtOAc) affording the pure *tert*-butyl sulfinyl propanoates **5**, **6a-j**, **6n** and **8**.

General oxidation procedure F (compounds 6k-6l and **6o)**

Following a slightly modified reported procedure,[18e] in a 25 mL round-bottomed flask, *tert*-butyl 3-thiopropanoate **21** (1.0 equiv.) was dissolved in TFE (2 M based on thiopropanoate) and the resulting solution was cooled to 0 °C (ice-water bath). H_2O_2 (30% v/v in water; 1.8 equiv.) was added drop-wise at the same temperature. The mixture was then allowed to warm to room temperature and stirred for 5 hours. After this time, soldium sulfite (1.8 equiv.) was added and the the mixture was vigorously stirred for 30 minutes. It was then filtered through a plug of celite, which was then washed with several portions of DCM. The filtrate was dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting crude oil was submitted to column chromatography (SiO_2; DCM:MeOH) to afford desired *tert*-butyl 3-sulfinylpropanoates **6**.

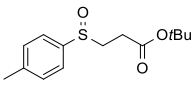
Synthesis of Methyl 3-((4-methylphenyl)sulfinyl)propanoate (5)



Following a slightly modified version of a reported procedure,[37] 4-methylbenzenethiol (2.8 g, 22 mmol, 1.0 equiv.), methyl acrylate (2.0 mL, 22 mmol, 1.0 equiv.) and triethylamine (0.30 mL, 2.2 mmol, 0.1 equiv.) were introduced into a microwave vial equipped with a magnetic stirrer. The vial was sealed and the reaction mixture was stirred at rt for 10 minutes then heated to 60 °C for 3 hours (until full conversion based on TLC analysis). The volatiles were then removed through evaporation under reduced pressure to afford methyl 3-((4-methylphenyl)thio)propanoate in 99% yield (4.6 g, 22 mmol) with

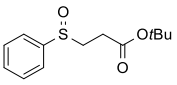
sufficient purity to be used in next step without further purification. Following **general oxidation procedure E**, **5** was obtained as a colorless oil from methyl 3-((4-methylphenyl)thio)propanoate (2.50 g, 21.4 mmol) and $NaIO_4$ (4.58 g, 21.4 mmol). Yield: 70% (3.41 g, 5.07 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.52-7.50 (m, 2H), 7.34 (d, 2H, *J* = 8.1 Hz), 3.67 (s, 3H), 3.25-3.18 (m, 1H), 3.00-2.92 (m, 1H), 2.87-2.79 (m, 1H), 2.59-2.51 (m, 1H), 2.43 (s, 3H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 171.7, 141.7, 139.7, 130.0, 124.1, 52.1, 51.2, 26.0, 21.4 ppm. The values of the NMR spectra are in accordance with reported literature data.[40]

***Tert*-butyl 3-[(4-methylphenyl)sulfinyl]propanoate (6a)**



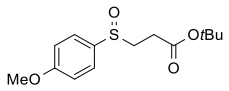
Following **general procedure E**, **6a** was obtained as a yellow solid from **21a** (1.49 g, 5.90 mmol, 1.0 equiv.) and sodium periodate (1.26 g, 5.90 mmol , 1.0 equiv.). Yield: 69% (1.09 g, 4.06 mmol). **mp:** 56.1 -57.7 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.14 (ddd, *J* = 13.5, 8.5, 6.7 Hz, 1H), 2.92 (ddd, *J* = 13.5, 8.4, 5.8 Hz, 1H) 2.73 (ddd, *J* = 17.2, 8.5, 6.8 Hz, 1H), 2.51-2.38 (m, 5H), 1.42 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.5, 141.6, 139.9, 130.1, 124.1, 81.5, 51.6, 28.1, 27.4, 21.5 ppm. The values of the NMR spectra are in accordance with reported literature data.[8]

***Tert*-butyl 3-[(phenyl)sulfinyl]propanoate (6b)**



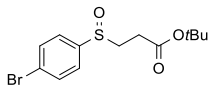
Following **general procedure E**, **6b** was obtained as a colorless oil from **21b** (1.0 g, 4.2 mmol, 1.0 equiv.) and sodium periodate (1.1 g, 5.0 mmol, 1.2 equiv.). Yield: 56% (0.59 g, 2.3 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.61 (dt, *J* = 7.6, 1.6 Hz, 2H), 7.58 – 7.47 (m, 3H), 3.16 (m, 1H), 2.92 (ddd, *J* = 13.8, 8.4, 5.7 Hz, 1H), 2.75 (ddd, *J* = 17.1, 8.5, 6.7 Hz, 1H), 2.43 (ddd, *J* = 17.1, 8.6, 5.8 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.4, 143.1, 131.1, 129.3, 124.0, 81.6, 51.5, 28.0, 27.3 ppm. The values of the NMR spectra are in accordance with reported literature data.[40]

***Tert*-butyl 3-[(4-methoxyphenyl)sulfinyl]propanoate (6c)**



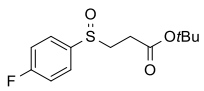
Following **general procedure E**, **6c** was obtained as a yellow solid from **21c** (0.950 g, 3.54 mmol, 1.0 equiv.) and sodium periodate (0.909 g, 4.25 mmol, 1.2 equiv.). Yield: 89% (0.900 g, 3.16 mmol). **mp:** 41.4-44.6 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.53 (dd, *J* = 8.9, 2.2 Hz, 2H), 7.00 (dd, *J* = 8.9, 2.2 Hz, 2H), 3.82 (s, 3H), 3.08 (ddd, *J* = 13.3, 8.5, 6.7 Hz, 1H), 2.98 - 2.84 (m, 1H), 2.77 - 2.61 (m, 1H), 2.48 - 2.35 (m, 1H), 1.39 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.5, 162.1, 133.9, 126.0, 114.9, 81.5, 55.6, 51.7, 28.1, 27.6 ppm. **HRMS** (ESI) calcd. for $C_{14}H_{20}NaO_4S^+$ $[M+Na]^+$ 307.0974; found 307.0971. **IR** (film): $\tilde{\nu}$ = 3068 (w), 2979 (w), 2934 (w), 2840 (w), 1727 (s), 1596 (m), 1579 (w), 1498 (m), 1461 (w), 1368 (m), 1304 (m), 1250 (s), 1155 (s), 1089 (s), 1043 (s), 834 (m) cm^{-1}.

***Tert*-butyl 3-[(4-bromophenyl)sulfinyl]propanoate (6d)**



Following **general procedure E**, **6d** was obtained as an off white solid from **21d** (0.428 g, 1.35 mmol, 1.0 equiv.) and sodium periodate (0.289 g, 1.35 mmol, 1.0 equiv.). Yield: 42% (0.190 g, 0.570 mmol). **mp:** 69.4-71.7 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.67 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.49 (dd, *J* = 8.5, 2.0 Hz, 2H), 3.17 (ddd, *J* = 13.5, 8.2, 6.9 Hz, 1H), 2.90 (ddd, *J* = 13.5, 8.1, 5.8 Hz, 1H), 2.75 (ddd, *J* = 17.3, 8.1, 6.9 Hz, 1H), 2.44 (ddd, *J* = 17.3, 8.2, 5.8 Hz, 1H), 1.42 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.4, 142.4, 132.6, 125.8, 125.7, 81.8, 51.6, 28.1, 27.3 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{17}{}^{79}BrNaO_3S^+$ $[M+Na]^+$ 354.9974; found 354.9985. **IR** (film): $\tilde{\nu}$ = 2978 (w), 2933 (w), 1730 (s), 1573 (w), 1474 (w), 1369 (m), 1250 (m), 1159 (s), 1086 (m), 1051 (s), 1009 (m), 844 (w), 822 (w) cm^{-1}.

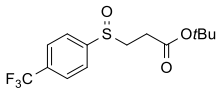
***Tert*-butyl 3-[(4-fluorophenyl)sulfinyl]propanoate (6e)**



Following **general procedure E**, **6e** was obtained as a colorless solid from **21e** (0.920 g, 3.59 mmol, 1.0 equiv.) and sodium periodate (0.921 g, 4.31 mmol, 1.2 equiv.). Yield: 83% (0.811 g, 2.98 mmol). **mp:** 82.4 - 83.5 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.61 (ddd, *J* = 9.8, 5.0, 2.5 Hz, 2H), 7.22 (m, 2H), 3.14 (ddd, *J* = 13.4, 8.3, 6.9 Hz, 1H), 2.91 (ddd, *J* = 13.5, 8.1, 5.8 Hz, 1H),

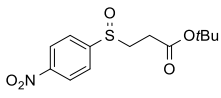
2.74 (ddd, *J* = 17.3, 8.1, 7.0 Hz, 1H), 2.45 (ddd, *J* = 17.3, 8.3, 5.8 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.3, 164.4 (d, *J* = 251.5 Hz), 138.6 (d, *J* = 3.1 Hz), 126.3 (d, *J* = 9.0 Hz), 116.7 (d, *J* = 22.7 Hz), 81.7, 51.7, 28.0, 27.3 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -108.5 ppm. **HRMS** calcd. for $C_{13}H_{17}FNaO_3S^+$[M+Na]$^+$ 295.0775; found 295.0777. **IR** (film): $\tilde{\nu}$ = 3062 (w), 2977 (w), 2931 (w), 1728 (s), 1591 (m), 1493 (s), 1369 (m), 1295 (w), 1233 (s), 1153 (s), 1086 (m), 838 (s), 815 (m) cm^{-1}.

***Tert*-butyl 3-[(4-trifluoromethylphenyl)sulfinyl]propanoate (6f)**



Following **general procedure E**, **6f** was obtained as an off-white solid from **21f** (0.645 g, 2.10 mmol, 1.0 equiv.) and sodium periodate (0.540 g, 2.53 mmol, 1.2 equiv.). Yield: 87% (0.592 g, 1.84 mmol). **mp:** 64.0-64.8 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.94 – 7.49 (m, 4H), 3.23 (ddd, *J* = 13.6, 8.0, 7.1 Hz, 1H), 2.93 (ddd, *J* = 13.6, 7.8, 5.8 Hz, 1H), 2.78 (ddd, *J* = 17.4, 7.8, 7.1 Hz, 1H), 2.46 (ddd, *J* = 17.4, 8.0, 5.8 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.1, 147.7, 133.1 (q, *J* = 32.8 Hz), 126.3 (q, *J* = 3.8 Hz), 124.6, 123.5 (q, *J* = 272.6 Hz), 81.8, 51.4, 28.0, 27.0 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.9 ppm. **HRMS** calcd. for $C_{14}H_{17}F_3NaO_3S^+$ [M+Na]$^+$ 345.0743; found 345.0737. **IR** (film): $\tilde{\nu}$ = 3053 (w), 2988 (w), 1728 (m), 1422 (w), 1403 (w), 1368 (w), 1325 (m), 1265 (s), 1169 (m), 1133 (m), 1060 (m), 1016 (w), 845 (w) cm^{-1}.

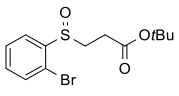
***Tert*-butyl 3-[(4-nitrophenyl)sulfinyl]propanoate (6g)**



Following **general procedure E**, **6g** was obtained as a yellow crystalline solid from **21g** (0.400 g, 1.41 mmol, 1.0 equiv.) and sodium periodate (0.362 g, 1.69 mmol, 1.2 equiv.). Yield: 29% (0.124 g, 0.414 mmol). **mp:** 90.4-91.2 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.38 (m, 2H), 7.82 (m, 2H), 3.26 (dt, *J* = 13.5, 7.6 Hz, 1H), 2.95 (ddd, *J* = 13.4, 7.6, 5.7 Hz, 1H), 2.81 (dt, *J* = 17.5, 7.5 Hz, 1H), 2.48 (ddd, *J* = 17.5, 7.8, 5.7 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.0, 150.9, 149.6, 125.2, 124.4, 82.0, 51.6, 28.0, 27.0 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{17}NNaO_5S^+$

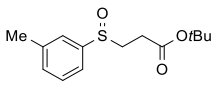
[M+Na]$^+$ 322.0720; found 322.0715. **IR** (film): $\tilde{\nu}$ = 3121 (w), 2966 (m), 2922 (m), 2854 (m), 1727 (s), 1522 (s), 1344 (s), 1258 (m), 1164 (s), 1083 (m), 1044 (s), 854 (s) cm^{-1}.

***Tert*-butyl 3-[(2-bromophenyl)sulfinyl]propanoate (6h)**



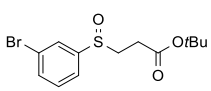
Following **general procedure E**, **6h** was obtained as a colorless crystalline solid from **21h** (0.734 g, 2.32 mmol, 1.0 equiv.) and sodium periodate (0.500 g, 2.33 mmol, 1.0 equiv.). Yield: 79% (0.609 g, 1.83 mmol). **mp:** 72.6-73.5 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7,83 (m, 1H), 7.66 – 7.49 (m, 2H), 7.37 (td, *J* = 7.6, 1.7 Hz, 1H), 3.39 (ddd, *J* = 13.7, 8.9, 6.5 Hz, 1H), 3.08 (ddd, *J* = 13.7, 8.9, 5.8 Hz, 1H), 2.79 (ddd, *J* = 17.1, 8.9, 6.5 Hz, 1H), 2.44 (ddd, *J* = 17.1, 8.9, 5.8 Hz, 1H), 1.40 (s, 9H) ppm. **^{13}C{1H}-NMR** (101 MHz, $CDCl_3$) δ = 170.3, 142.5, 133.1, 132.4, 128.4, 126.8, 118.9, 81.5, 47.8, 28.0, 26.8 ppm. **HRMS** calcd. for $C_{13}H_{17}{}^{79}BrNaO_3S^+$ [M+Na]$^+$ 354.9974; found 354.9976. **IR** (film): $\tilde{\nu}$ = 3062 (w), 2979 (w), 2930 (w), 2854 (w), 1730 (s), 1568 (w), 1449 (m), 1423 (w), 1393 (w), 1368 (m), 1245 (m), 1155 (s), 1095 (m), 1062 (s), 1016 (s), 954 (w), 843 (m) cm^{-1}.

***Tert*-butyl 3-[(3-methylphenyl)sulfinyl]propanoate (6i)**



Following **general procedure E**, **6i** was obtained as a pale yellow oil from **21i** (1.50 g, 5.94 mmol, 1.0 equiv.) and sodium periodate (1.27 g, 5.94 mmol, 1.0 equiv.). Yield: 66% (1.05 g, 3.91 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.42 (m, *J* = 1.8, 0.9 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.27 (m, 1H), 3.13 (ddd, *J* = 13.4, 8.6, 6.7 Hz, 1H), 2.90 (ddd, *J* = 13.4, 8.6, 5.7 Hz, 1H), 2.73 (ddd, *J* = 17.1, 8.6, 6.7 Hz, 1H), 2.57 – 2.35 (m, 4H), 1.40 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.4, 143.0, 139.5, 131.9, 129.1, 124.3, 121.1, 81.5, 51.5, 28.0, 27.4, 21.4 ppm. **HRMS** (APPI) calcd. for $C_{14}H_{20}O_2S^{+\circ}$ [M]$^{+\circ}$ 252.1179; found 252.1174. **IR** (film): $\tilde{\nu}$ = 2984 (w), 2928 (w), 1728 (s), 1362 (m), 1238 (m), 1153 (s), 1081 (m), 1045 (s), 974 (w), 948 (w), 842 (m), 785 (m), 693 (m) cm^{-1}.

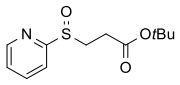
***Tert*-butyl 3-[(3-bromophenyl)sulfinyl]propanoate (6j)**



Following **general procedure E**, **6j** was obtained as a colorless oil from **21j** (0.815 g, 2.57 mmol, 1.0 equiv.) and sodium periodate (0.659 g, 3.08 mmol, 1.2 equiv.). Yield:

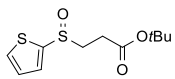
88% (0.754 g, 2.26 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.77 (t, *J* = 1.8 Hz, 1H), 7.61 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.51 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 3.18 (ddd, *J* = 13.5, 8.2, 7.0 Hz, 1H), 2.92 (ddd, *J* = 13.5, 8.2, 5.8 Hz, 1H), 2.76 (ddd, *J* = 17.3, 8.2, 7.0 Hz, 1H), 2.45 (ddd, *J* = 17.3, 8.2, 5.8 Hz, 1H), 1.42 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.2, 145.5, 134.2, 130.8, 126.9, 123.6, 122.6, 81.7, 51.6, 28.0 27.2 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{17}{}^{79}BrNaO_3S^+$ $[M+Na]^+$ 354.9974; found 354.9968. **IR** (film): $\tilde{\nu}$ = 3056 (w), 2980 (m), 1728 (s), 1569 (w), 1491 (w), 1459 (w), 1416 (w), 1395 (w), 1368 (m), 1248 (m), 1158 (s), 1079 (w), 1050 (m), 844 (w) cm^{-1}.

***Tert*-butyl 3-[(pyridin-2-yl)sulfinyl]propanoate (6k)**



Following **general procedure F**, **6k** was obtained as a yellow oil from **21k** (0.500 g, 2.09 mmol, 1.0 equiv.), H_2O_2 (30% v/v in water; 0.39 mL, 3.8 mmol, 1.8 equiv.) and sodium sulfite (0.474 g, 3.76 mmol, 1.8 equiv.). Yield: 35% (0.474 g, 1.29 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.63 (ddd, *J* = 4.7, 1.7, 1.0 Hz, 1H), 7.96 (m, 1H), 7.92 (m, 1), 7.37 (ddd, *J* = 7.1, 4.7, 1.6 Hz, 1H), 3.44 (ddd, *J* = 13.6, 9.6, 6.0 Hz, 1H), 3.13 (ddd, *J* = 13.6, 9.5, 5.8 Hz, 1H), 2.79 (ddd, *J* = 17.0, 9.4, 6.0 Hz, 1H), 2.34 (ddd, *J* = 17.0, 9.5, 5.7 Hz, 1H), 1.41 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.3, 163.9, 149.8, 137.9, 124.6, 120.1, 81.4, 48.3, 28.0, 26.8 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{17}NNaO_3S^+$ $[M+Na]^+$ 278.0821; found 278.0825. **IR** (film): $\tilde{\nu}$ = 2977 (m), 2941 (w), 3054 (w), 1730 (s), 1576 (m), 1458 (m), 1423 (m), 1368 (m), 1248 (s), 1154 (s), 1053 (s), 849 (w) cm^{-1}.

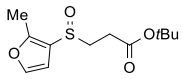
***Tert*-butyl 3-((thiophen-2-yl)sulfinyl)propanoate (6l)**



Following **general procedure F**, **6l** was obtained as a yellow oil from **21l** (0.900 g, 3.68 mmol, 1.0 equiv.), H_2O_2 (30% v/v in water; 0.68 mL, 6.6 mmol, 1.8 equiv.) and sodium sulfite (0.836 g, 6.63 mmol, 1.8 equiv.). Yield: 35% (0.335 g, 1.29 mmol). **mp:** 38.2-39.0 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.66 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.47 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H), 3.25 (dd, *J* = 7.6, 7.0 Hz, 2H), 2.74 (m, 1H), 2.58 (dt, *J* = 17.2, 7.2 Hz, 1H), 1.44 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.1, 145.3, 131.2, 129.7, 127.5, 81.7, 53.0, 28.2, 28.1 ppm.

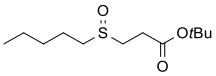
HRMS (ESI) calcd. for $C_{11}H_{16}NaO_3S_2^+$ $[M+Na]^+$ 283.0433; found 283.0440. **IR** (film): $\tilde{\nu}$ = 3084 (w), 2982 (w), 2906 (w), 2856 (w), 1726 (s), 1402 (w), 1364 (m), 1250 (m), 1161 (s), 1047 (s), 850 (m) cm^{-1}.

***Tert*-butyl 3-((2-methylfuran-3-yl)sulfinyl)propanoate (6m)**



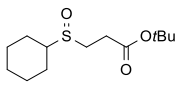
Following **general procedure F**, **6m** was obtained as a yellow oil from **21m** (0.828 g, 3.42 mmol, 1.0 equiv.) and H_2O_2 (30% v/v in water; 0.64 mL, 6.2 mmol, 1.8 equiv.), sodium sulfite (0.775 g, 6.15 mmol, 1.8 equiv.). Yield: 89% (0.784 g, 3.03 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 2.1 Hz, 1H), 6.66 (d, *J* = 2.1 Hz, 1H), 3.25 (ddd, *J* = 13.1, 7.8, 6.5 Hz, 1H), 3.08 (ddd, *J* = 13.1, 8.0, 6.9 Hz, 1H), 2.82 – 2.50 (m, 2H), 2.44 (s, 3H), 1.44 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.1, 154.8, 142.7, 121.8, 106.6, 81.6, 49.8, 28.8, 28.0, 12.4 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{18}NaO_4S^+$ $[M+Na]^+$ 281.0818; found 281.0820. **IR** (film): $\tilde{\nu}$ = 2942 (w), 2861 (w), 1592 (w), 1523 (w), 1466 (w), 1385 (w), 1227 (w), 1070 (s), 882 (m), 765 (s), 680 (m), 655 (m) cm^{-1}.

***Tert*-butyl 3-(pentylsulfinyl)propanoate (6n)**



Following **general procedure E**, **6c** was obtained as a yellow oil from **1d** (0.699 g, 3.01 mmol, 1.0 equiv.) and sodium periodate (0.643 g, 3.01 mmol, 1.0 equiv.). Yield: 65% (0.486 g, 1.96 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.99 (ddd, *J* = 12.5, 8.1, 7.3 Hz, 1H), 2.82 (m, 1H), 2.79-2.6 (m, 4H), 1.84-1.71 (m, 2H), 1.46 (s, 9H), 1.46-1.34 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.7, 81.7, 52.8, 47.2, 31.1, 28.3, 28.2, 22.5, 22.4, 14.0 ppm. **HRMS** (ESI) calcd. for $C_{12}H_{24}O_3NaS^+$ $[M+Na]^+$ 271.1344; found 271.1345. **IR** (film): $\tilde{\nu}$ = 2960 (w), 2930 (m), 2869 (w), 1727 (s), 1462 (w), 1419 (w), 1393 (w), 1366 (m), 1297 (w), 1247 (m), 1154 (s), 1035 (s), 977 (w), 951 (w), 845 (w) cm^{-1}.

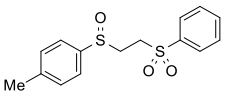
***Tert*-butyl 3-(cyclohexylsulfinyl)propanoate (6o)**



Following **general procedure** F, **6o** was obtained as a yellow oil from **21o** (0.800 g, 3.27 mmol, 1.0 equiv.) and H_2O_2 (30% v/v in water; 0.60 mL, 5.9 mmol, 1.8 equiv.), sodium sulfite (0.743 g, 5.89 mmol, 1.8 equiv.). Yield: 62% (0.530 g, 1.96 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$)

δ = 2.93 (m, 1H), 2.83 – 2.69 (m, 3H), 2.53 (tt, *J* = 11.5, 3.6 Hz, 1H), 2.09 (m, 1H), 1.95 – 1.78 (m, 3H), 1.68 (m, 1H), 1.53 – 1.20 (m, 14H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 170.7, 81.5, 59.3, 43.9, 28.4, 28.0, 26.2, 25.5, 25.4, 25.1, 25.0 ppm. **HRMS** (ESI) calcd. for $C_{13}H_{24}NaO_3S^+$ $[M+Na]^+$ 283.1338; found 283.1344. **IR** (film): $\tilde{\nu}$ = 2982 (m), 2932 (m), 2849 (m), 1726 (s), 1453 (m), 1364 (m), 1237 (m), 1155 (s), 1034 (s), 850 (m) cm^{-1}.

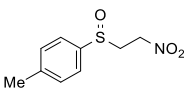
Synthesis of 1-Methyl-4-[(2-(phenylsulfonyl)ethyl)sulfinyl]benzene (7)



Following a reported procedure,[18c] 4-methylbenzenethiol (1.0 g, 8.1 mmol, 1 equiv.), potassium carbonate (0.111 g, 0.805 mmol, 0.1 equiv.) and dichloromethane (4.0 mL) were introduced into a 25 mL one-necked flask equipped with a magnetic stirrer. Vinylsulfonyl benzene (1.35 g, 8.05 mmol, 1.0 equiv.) was then added portion wise. The mixture was stirred at room temperature for 24 hours. It was then diluted with dichloromethane (5 mL), washed with aqueous NaOH (1.0 M; 5 mL), brine (2 x 5 mL), dried over $MgSO_4$ and filtered. The crude product was concentrated under reduced pressure affording (2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane as a colorless solid. The compound was used directly in next stage with no further purification. Following a slightly modified version of a reported procedure,[16] in a two-necked flask equipped with a magnetic stirrer, (2-(phenylsulfonyl)ethyl)(*p*-tolyl)sulfane (2.35 g, 8.04 mmol, 1.0 equiv.) was dissolved in methanol (62 mL) and cooled to 0 °C. Sodium periodate (1.72 g, 8.04 mmol, 1.0 equiv.) dissolved in water (20 mL) was then added dropwise using a syringe over a period of 30 minutes. The reaction mixture was then left to warm to room temperature under stirring overnight. The precipitated solids were then filtered off through a Celite pad and washed with methanol (20 mL). Methanol was evaporated under reduced pressure. The obtained aqueous phase was extracted three times with DCM (3 x 20 mL). The organic phases were combined washed with brine (10 mL), dried over Na_2SO_4 and filtered. Solvents were then evaporated under reduced pressure before submitting the crude to column chromatography (silica gel, DCM/EtOAc, 24/1 to 4/1) affording pure 7 as a yellow solid in 26% yield (0.635 g, 2.06 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.83-7.88 (m, 2H), 7.68 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.54-7.60 (m, 2H), 7.39-7.44 (m, 2H), 7.31-7.36 (m, 2H), 3.53 (ddd, *J* =

13.7, 12.1, 4.0 Hz, 1H), 3.30 (ddd, *J* = 13.0, 12.0, 4.0 Hz, 1H), 3.06 (ddd, *J* = 13.7, 12.0, 4.5 Hz, 1H), 2.95 (ddd, *J* = 13.0, 12.0, 4.5 Hz, 1H), 2.42 (s, 3H) ppm. **$^{13}C\{^{1}H\}$-NMR** (101 MHz, $CDCl_3$) δ = 142.2, 138.5, 134.3, 130.3, 128.1, 123.9, 48.2, 47.8, 21.5 ppm. Two carbons are not resolved. The values of the NMR spectra are in accordance with reported literature data.[18e]

1-Methyl-4-[(2-nitroethyl)sulfinyl]benzene (8)



Following a slightly modified reported procedure,[42] nitroethanol (0.75 mL, 10 mmol, 1 equiv.) was introduced in a two-necked 50 mL flask equipped with a magnetic stirrer and put in the dark. Anhydrous dichloromethane (16 mL), pyridine (0.85 mL, 10 mmol, 1 equiv.) and acetic anhydride (1.1 mL, 12 mmol, 1.1 equiv.) were then added. and the reaction mixture was stirred for 5 hours under inert atmosphere. The reaction mixture was then poured onto aqueous HCl (1.0 M; 10 mL). The aqueous layer was extracted with diethyl ether (2 x 15 mL). The organic layers were combined, washed with aqueous HCl (1.0 M; 10 mL), water (3 x 10 mL) and brine (10 mL), dried over $MgSO_4$ and filtered. The solvents were evaporated under reduced pressure yielding 2-nitroethylacetate (1.02 g, 7.69 mmol, 74% yield) as a crude yellow oil. The compound was used directly in next step with no further purification. In a two-necked 50 mL flask equipped with a magnetic stirrer, 2-nitroethyl acetate (1.02 g, 7.69 mmol, 1 equiv.) was stirred in acetonitrile (15 mL) and cooled to -10 °C with an ice-salt bath. 4-Methylbezenethiol (0.955 g, 7.69 mmol, 1 equiv.) was added in one portion and the reaction mixture was stirred at -10 °C for 5 minutes. A solution of triethylamine (1.3 mL, 9.3 mmol, 1.2 equiv.) in acetonitrile (6 mL) was added dropwise over a period of 20 minutes. The temperature was left to rise slowly to 0 °C over a period of 2 hours. The reaction mixture was poured onto aqueous HCl (1.0 M; 10 mL). Acetonitrile was then evaporated under reduced pressure. The obtained aqueous solution was extracted with pentane (3 x 15 mL). The organic layers were combined, washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford (2-nitroethyl)(*p*-tolyl)sulfane (1.4 g, 7.1 mmol, 92% yield) as a yellow oil, which was used in next step with no further purification. Following the **general procedure E**, **8** was obtained as a yellow oil from (2-nitroethyl)(*p*-tolyl)sulfane (1.38 g, 7.00 mmol) and

sodium periodate (1.50 g, 7.00 mmol). Yield: 51% (0.757 g, 3.55 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.83 (dt, *J* = 15.0, 7.2 Hz, 1H), 4.51 (ddd, *J* = 15.0, 7.2, 5.9 Hz, 1H), 3.57 (dt, *J* = 14.2, 7.2 Hz, 1H), 3.21 (ddd, *J* = 14.2, 7.2, 5.8 Hz, 1H), 2.42 (s, 3H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 142.6, 138.6, 130.5, 123.9, 67.3, 51.8, 21.6 ppm. The values of the NMR spectra are in accordance with reported literature data.[18c]

Alkynylation of sulfoxides

General procedure G: Synthesis of (hetero)aryl alkynyl sulfoxides (10a-10n, **10p** and **10q)**

The *tert*-butyl 3-(sulfinyl) propanoate (**6a-6n**) (0.56 mmol, 1.11 equiv.) and R^2-EBX (**9a-9c**) (0.5 mmol, 1 equiv.) were introduced into an oven-dried two-neck 25 mL flask equipped with a magnetic stirrer. The reaction vessel was evacuated and backfilled with nitrogen (3 times). The reaction vessel was transferred into a glove-box where potassium *tert*-butoxide (0.59 mmol, 1.17 equiv.) was added under inert atmosphere. The reaction vessel was removed from the glove-box and cooled to -40 °C. Toluene (degassed by bubbling a balloon of argon for 40 min prior to use; 10 mL) was then added at -40 °C, and the mixture was stirred at the same temperature for 3 hours. The mixture was then filtered on a SiO_2 pad and concentrated under reduced pressure. The crude was purified by column chromatography (pentane:EtOAc, 10:0 to 9:1 unless specified otherwise) affording alkynyl sulfoxides **10a-10n**, **10p** and **10q**.

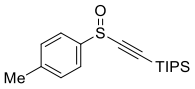
NB: Liquid substrates (**6b, 6i-6k**) were added simultaneously with toluene and not charged into the empty flask. Degradation of the substrate could be observed due to solvation of KO*t*Bu.

General procedure H: Synthesis of heteroaryl and alkyl alkynyl sulfoxides (10m-10o)

TIPS-EBX (**9a**) (0.5 mmol, 1 equiv.) was introduced into an oven-dried two-neck 25 mL flask equipped with a magnetic stirrer. The reaction vessel was evacuated and backfilled with nitrogen (3 times). The reaction vessel was transferred into a glove-box where potassium *tert*-butoxide (0.59 mmol, 1.2 equiv.) was added under inert atmosphere. The reaction vessel was removed from the glove-box and cooled to -40 °C. Toluene (degassed by bubbling a balloon of argon for 40 min prior to use; 10 mL) was then added

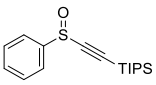
at -40 °C simultaneously with the *tert*-butyl 3-(sulfinyl) propanoate (**6m-6o**) (0.56 mmol, 1.11 equiv.). The mixture was stirred at the same temperature for 2 hours, the cryostat maintaining the cooling bath was turned off and the reaction mixture was left to warm to rt over a period of 18 hours. The mixture was then filtered on a SiO_2 pad and concentrated under reduced pressure. The crude was purified by column chromatography (pentane:EtOAc, 10:0 to 9:1 unless specified otherwise) affording alkynyl sulfoxides **10m-o**.

Tri*iso*propyl((4-methylphenylsulfinyl)ethynyl)silane (10a)



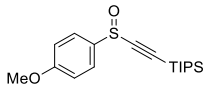
Following the **general procedure G, 10a** was obtained as a yellow oil from **6a** (0.150 g, 0.560 mmol), **9a** (0.216 g, 0.504 mmol) and potassium *tert*-butoxide (0.066 g, 0.59 mmol). Yield: 87% (0.141 g, 0.440 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.88 (dt, *J* = 8.0, 1.9 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.13 – 1.03 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 142.3, 141.0, 130.1, 125.3, 108.0, 102.3, 21.5, 18.4, 10.9 ppm. **HRMS** (ESI) calcd. for $C_{18}H_{29}OSSi^+$ $[M+H]^+$ 321.1703; found 321.1707. **IR** (film): $\tilde{\nu}$ = 2941 (s), 2867 (s), 1464 (s), 1384 (w), 1074 (s), 996 (m), 921 (w), 883 (s), 810 (w) cm^{-1}.

Tri*iso*propyl((phenylsulfinyl)ethynyl)silane (10b)



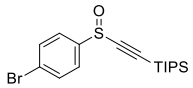
Following the **general procedure G, 10b** was obtained as a colorless oil from **6b** (0.141 g, 0.560 mmol), **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.59 mmol). Yield: 84% (0.129 g, 0.420 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.93 – 7.77 (m, 2H), 7.93 – 7.77 (m, 3H), 1.15 – 1.02 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 144.2, 131.7, 129.5, 125.1, 108.4, 102.3, 18.4, 11.0 ppm. **HRMS** (ESI) calcd. for $C_{17}H_{27}OSSi^+$ $[M+H]^+$ 307.1552; found 307.1546. **IR** (film): $\tilde{\nu}$ = 2947 (s), 2892 (m), 2866 (s), 1464 (m), 1445 (m), 1385 (w), 1092 (s), 1057 (s), 1021 (w), 997 (m), 884 (m) cm^{-1}.

Tri*iso*propyl((4-methoxyphenylsulfinyl)ethynyl)silane (10c)



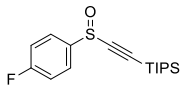
Following **general procedure G, 10c** was obtained as a yellow oil from **6c** (0.158 g, 0.556 mmol), **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.59 mmol). Yield: 90% (0.151 g, 0.450 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.88 (dt, *J* = 8, 1.9 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.13 – 1.03 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 162.6, 135.7, 127.8, 115.0, 108.0, 102.5, 55.7, 18.6, 11.1 ppm. **HRMS** (ESI) calcd. for $C_{18}H_{28}O_2NaSSi^+$ $[M+Na]^+$ 359.1477; found 359.1482. **IR** (film): $\tilde{\nu}$ = 3003 (w), 2978 (w), 2935 (w), 2837 (w), 1729 (s), 1594 (w), 1495 (s), 1463 (w), 1367 (w), 1286 (m), 1247 (s), 1172 (m), 1150 (s), 1034 (m), 830 (m) cm^{-1}.

Tri*iso*propyl((4-bromophenylsulfinyl)ethynyl)silane (10d)



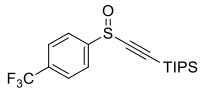
Following the **general procedure G, 10d** was Obtained as a colorless oil from **6d** (0.176 g, 0.528 mmol), **9a** (0.204 g, 0.475 mmol) and potassium *ter*t-butoxide (0.062 g, 0.56 mmol). Yield: 55% (0.101 g, 0.261 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.67 (s, 4H), 1.13 – 1.02 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 143.4, 132.8, 126.6, 126.4, 109.2, 101.8, 18.5, 11.1 ppm. **HRMS** (ESI) calcd. for $C_{17}H_{26}{}^{79}BrOSSi^+$ $[M+H]^+$ 385.0657; found 385.0654. **IR** (film): $\tilde{\nu}$ = 2946 (s), 2866 (s), 1568 (w), 1467 (m), 1386 (w), 1090 (s), 1063 (s), 1008 (m), 884 (m), 819 (w) cm^{-1}.

Tri*iso*propyl((4-fluorophenylsulfinyl)ethynyl)silane (10e)



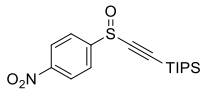
Following the **general procedure G, 10e** was obtained as a yellow oil from **6e** (0.151 g, 0.556 mmol), **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.59 mmol). Yield: 75% (0.122 g, 0.376 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.82 (m, 2H), 7.23 (m, 2H), 1.29 - 0.75 (m, 21H) **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 164.7 (d, *J* = 252.8 Hz), 139.9 (d, *J* = 3.2 Hz), 127.6 (d, *J* = 9.1 Hz), 116.8 (d, *J* = 22.7 Hz), 108.8, 102.1, 18.4, 11.0 ppm. **^{19}F NMR** (400 MHz, $CDCl_3$) δ = -107.2 (s, 1F) ppm. **HRMS** (ESI) calcd. for $C_{17}H_{26}FOSSi^+$ $[M+H]^+$ 325.1452; found 325.1451. **IR** (film): $\tilde{\nu}$ = 2946 (s), 2891 (m), 2866 (s), 1589 (m), 1491 (s), 1465 (m), 1233 (s), 1153 (m), 1087 (s), 1062 (s), 1014 (w), 998 (m), 882 (s), 835 (s) cm^{-1}.

Tri*iso*propyl((4-trifluorophenylsulfinyl)ethynyl)silane (10f)



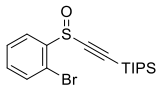
Following **general procedure G, 10f** was obtained as a yellow oil from **6f** (0.107 g, 0.333 mmol), **9a** (0.129 g, 0.300 mmol) and potassium *tert*-butoxide (0.039 g, 0.35 mmol). Purification: full pentane. Yield: 62% (0.070 g, 0.19 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.3 Hz, 2H), 1.24 – 0.88 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 148.3, 133.5 (q, *J* = 32.7 Hz), 126.5 (q, *J* = 3.9 Hz), 125.2, 123.4 (q, *J* = 272.8 Hz), 109.8, 101.6, 18.4, 11.0 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = -62.9 ppm. **HRMS** (ESI) calcd. for $C_{18}H_{25}F_3NaOSSi^+$ $[M+Na]^+$ 397.1240; found 397.1235. **IR** (film): $\tilde{\nu}$ = 2936 (w), 2869 (w), 2102 (w), 2065 (w), 1605 (w), 1464 (w), 1323 (s), 1170 (m), 1133 (m), 1095 (m), 1060 (s), 1012 (m), 884 (m), 841 (m), 765 (s) cm^{-1}.

Tri*iso*propyl((4-nitrosulfinyl)ethynyl)silane (10g)



Following the **general procedure G, 10g** was obtained as an off-white solid from **6g** (0.100 g, 0.333 mmol), **9a** (0.129 g, 0.300 mmol) and potassium *tert*-butoxide (0.039 g, 0.35 mmol). Yield: 62% (0.065 g, 0.19 mmol). **mp:** (°C) 51.3-52.0. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.41 (m, 2H), 7.97 (m, 2H), 1.25 – 0.92 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 151.1, 149.7, 125.6, 124.6, 110.7, 101.1, 18.4, 11.0 ppm. **HRMS** (ESI) calcd. for $C_{17}H_{26}NO_3SSi^+$ $[M+H]^+$ 352.1397; found 352.1380. **IR** (film): $\tilde{\nu}$ = 3095 (w), 2939 (m), 2864 (m), 1520 (s), 1460 (m), 1345 (s), 1088 (s), 1063 (s), 992 (w), 879 (m), 851 (m), 768 (s), 678 (s) cm^{-1}.

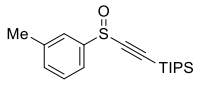
Tri*iso*propyl((2-bromophenylsulfinyl)ethynyl)silane (10h)



Following the **general procedure G, 10h** was obtained as a yellow oil from **6h** (0.185 g, 0.560 mmol), **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.58 mmol). Yield 81% (0.156 g, 0.405 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.02 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.69 – 7.50 (m, 2H), 7.39 (td, *J* = 7.7, 1.7 Hz, 1H), 1.11 – 0.97 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 143.4, 133.3, 132.5, 128.6, 126.0, 119.0, 107.2, 100.8, 18.4, 11.0 ppm. **HRMS** calcd. for

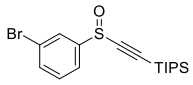
$C_{17}H_{26}{}^{79}BrOSSi^+$ $[M+H]^+$ 385.0652; found 385.0655. **IR** (film): $\tilde{\nu}$ = 2963 (m), 2887 (w), 2195 (w), 2164 (w), 1594 (m), 1495 (m), 1300 (m), 1086 (s), 1057 (s), 831 (m), 768 (m) cm^{-1}.

Tri*iso*propyl((3-methylphenylsulfinyl)ethynyl)silane (10i)



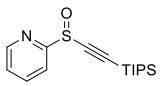
Following the **general procedure G, 10i** was obtained as a yellow oilfrom **6i** (0.149 g, 0.560 mmol), **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.58 mmol). Yield: 75% (0.120 g, 0.374 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.66 (m, 1H), 7.59 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.31 (m, 1H), 2.43 (s, 3H), 1.20 – 0.97 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 144.0, 139.7, 132.4, 129.2, 125.5, 122.3, 108.1, 102.4, 21.4, 18.4, 11.0 ppm. **HRMS** (ESI) calcd. for $C_{18}H_{28}NaOSSi^+$ $[M+Na]^+$ 343.1522; found 343.1506. **IR** (film): $\tilde{\nu}$ = 2938 (w), 2868 (w), 1466 (w), 1091 (m), 1066 (m), 882 (m), 761 (s), 685 (s) cm^{-1}.

Tri*iso*propyl((3-bromophenylsulfinyl)ethynyl)silane (10j)



Following the **general procedure G, 10j** was obtained as a yellow oil from **6j** (0.185 g, 0.560 mmol) **9b** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.59 mmol). Yield: 37% (0.071 g, 0.18 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.97 (q, *J* = 1.7 Hz, 1H), 7.71 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.65 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 1.17 – 0.98 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 146.2, 134.6, 130.9, 127.9, 123.5, 109.4, 101.8, 18.4, 11.0 ppm. One carbon is not resolved. **HRMS** calcd. for $C_{17}H_{26}{}^{79}BrOSSi^+$ $[M+H]^+$ 385.0657; found 385.0658. **IR** (film): $\tilde{\nu}$ = 2893 (m), 2866 (s), 1569 (m), 1461 (s), 1407 (m), 1238 (w), 1155 (w), 1091 (s), 1068 (s), 1018 (w), 996 (m), 921 (w), 883 (s), 2944 (s) cm^{-1}.

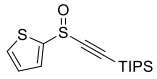
Tri*iso*propyl((pyridin-2-ylsulfinyl)ethynyl)silane (10k)



Following the **general procedure G, 10k** was obtained as an orange oil from **6k** (0.142 g, 0.560 mmol), **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.58 mmol). Yield: 85% (0.129 g, 0.419 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.65 (dt, *J* = 4.8, 1.3 Hz, 1H), 8.08 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.97 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (ddd, *J* = 7.5, 4.7, 1.2 Hz, 1H), 1.15 – 0.95

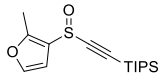
(m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 163.7, 149.9, 138.4, 125.4, 119.3, 07.9, 101.8, 18.4, 10.9 ppm. **IR** (film): $\tilde{\nu}$ = 2947 (m), 2868 (m), 1576 (w), 1456 (m), 1422 (m), 1119 (w), 1092 (s), 1060 (s), 990 (m), 920 (w), 882 (s) cm^{-1}. **HRMS** (ESI) calcd. for $C_{16}H_{25}NNaOSSi^+$ $[M+Na]^+$ 330.1318; found 330.1324.

Tri*iso*propyl((thiophen-2-ylsulfinyl)ethynyl)silane (10l)



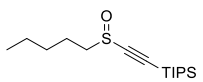
Following the **general procedure G, 10l** was obtained as a yellow oil from **6l** (0.087 g, 0.33 mmol), **9a** (0.129 g, 0.300 mmol) and potassium *tert*-butoxide (0.039 g, 0.35 mmol). Yield: 83% (0.078 g, 0.25 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.69 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.63 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.7 Hz, 1H), 1.32 – 0.98 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 145.8, 132.8, 132.2, 127.6, 108.6, 101.6, 18.5, 11.1 ppm. **HRMS** (ESI) calcd. for $C_{15}H_{25}OS_2Si^+$ $[M+H]^+$ 313.1111; found 313.1096. **IR** (film): $\tilde{\nu}$ = 3070 (w), 3039 (w), 2951 (w), 2857 (w), 1466 (w), 1322 (w), 1222 (w), 1091 (w), 1072 (m), 997 (m), 885 (w), 850 (w), 762 (s) cm^{-1}.

Tri*iso*propyl((2-methylfuran-3-ylsulfinyl)ethynyl)silane (10m)



Following the **general procedure H, 10m** was obtained as a yellow oil from **6m** (0.086 g, 0.33 mmol), **9a** (0.129 g, 0.300 mmol) and potassium *tert*-butoxide (0.039 g, 0.35 mmol). Yield: 91% (0.085 g, 0.27 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 2.1 Hz, 1H), 6.81 (d, *J* = 2.1 Hz, 1H), 2.51 (s, 3H), 1.23 – 1.04 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 155.7, 142.2, 124.4, 108.6, 107.0, 101.1, 18.5, 12.3, 11.0 ppm. **HRMS** (APPI) calcd. for $C_{16}H_{27}O_2SSi^{+\circ}$ $[M]^{+\circ}$ 311.1496; found 311.1490. **IR** (film): $\tilde{\nu}$ = 2942 (w), 2861 (w), 1592 (w), 1523 (w), 1466 (w), 1385 (w), 1227 (w), 1070 (s), 882 (m), 765 (s), 680 (m), 655 (m) cm^{-1}.

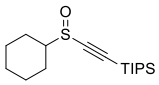
Tri*iso*propyl((pentylsulfinyl)ethynyl)silane (10n)



Following the **general procedure H, 10n** was obtained as a pale yellow oil from **6n** (0.138 g, 0.556 mmol) **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.59 mmol, 1.1 equiv.). Yield: 77% (0.115 g, 0.383 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.07 (dt, *J* = 8.2, 6.8 Hz,

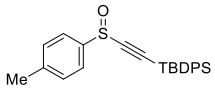
2H), 1.98-1.81 (m, 2H), 1.53-1.30 (m, 4H), 1.20-1.02 (m, 21H), 0.92 (t, J = 7.2 Hz, 3H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 107.3, 101.6, 56.5, 30.6, 22.3, 22.1, 18.5, 13.8, 11.0 ppm. **HRMS** (ESI) calcd. for $C_{16}H_{32}OSSi^+$ $[M+H]^+$ 301.2021; found 301.2021. **IR** (film): $\tilde{\nu}$ = 2941 (s), 2866 (s), 1464 (m), 1384 (w), 1075 (s), 997 (w), 922 (w), 883 (s) cm^{-1}.

Tri*iso*propyl((cyclohexylsulfinyl)ethynyl)silane (10o)



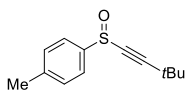
Following the **general procedure H, 10o** was obtained as a pale yellow oil from **6o** (0.145 g, 0.556 mmol) **9a** (0.214 g, 0.500 mmol) and potassium *tert*-butoxide (0.065 g, 0.59 mmol, 1.1 equiv.). Yield: 79% (0.123 g, 0.393 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 2.95 (tt, J = 11.7, 3.6 Hz, 1H), 2.22 (dqd, J = 12.8, 3.6, 1.8 Hz, 1H), 2.13 (dtq, J = 10.4, 3.4, 1.9 Hz, 1H), 1.93 (dddd, J = 14.6, 7.8, 4.1, 1.4 Hz, 2H), 1.84 – 1.69 (m, 1H), 1.64 – 1.01 (m, 26H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 107.8, 100.4, 63.6, 25.7, 25.5, 25.5, 25.5, 25.4, 18.5, 11.0 ppm. **HRMS** (ESI) $[M+Na]^+$ calcd. for $C_{17}H_{32}NaOSSi^+$ $[M+Na]^+$ 335.1835; found 335.1820. **IR** (film): $\tilde{\nu}$ = 2945 (m), 2863 (m), 1456 (w), 1065 (m), 996 (w), 883 (m), 763 (s), 674 (m) cm^{-1}.

***Tert*butyldiphenyl((4-methylphenylsulfinyl)ethynyl)silane (10p)**



Following the **general procedure G, 10p** was obtained as a yellow oil from **6p** (0.087 g, 0.32 mmol), **9b** (0.149 g, 0.292 mmol) and potassium *tert*-butoxide (0.038 g, 0.34 mmol). Yield: 81% (0.095 g, 0.24 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.81 – 7.74 (m, 2H), 7.68 (ddd, J = 6.8, 3.8, 1.9 Hz, 4H), 7.46 – 7.38 (m, 2H), 7.40 – 7.31 (m, 6H), 2.45 (s, 3H), 1.07 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 142.7, 140.8, 135.5, 131.3, 130.3, 130.1, 128.0, 125.4, 106.1, 104.5, 26.9, 21.6, 18.8 ppm. **HRMS** (APPI) calcd. for $C_{25}H_{27}OSSi^+$ $[M+H]^+$ 403.1546; found 403.1541. **IR** (film): $\tilde{\nu}$ = 3076 (w), 2939 (w), 2927 (w), 2858 (w), 1589 (w), 1464 (w), 1427 (w), 1389 (w), 1196 (w), 1109 (m), 1091 (m), 1060 (m), 1010 (w), 811 (m), 761 (s), 699 (s) cm^{-1}.

***Tert*butyl((4-methylphenylsulfinyl)ethynyl)silane (10q)**

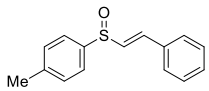


Following the **general procedure G, 10q** was obtained as a yellow oil from **6q** (0.070 g, 0.26 mmol), **9c** (0.077 g, 0.24 mmol) and potassium *tert*-butoxide (0.031 g, 0.27 mmol). Yield 58% (0.030 g, 0.14 mmol). **^{1}H-NMR** (400 MHz, CD_3OD) δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.46 – 7.41 (m, 2H), 2.44 (s, 3H), 1.29 (s, 9H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, CD_3OD) δ = 143.1, 140.6, 130.1, 125.1, 113.4, 75.9, 28.7, 28.3, 20.1 ppm. **HRMS** (APPI) calcd. for $C_{13}H_{17}OS^+$ $[M+H]^+$ 221.0995; found 221.0993. **IR** (film): $\tilde{\nu}$ = 2971 (m), 2929 (w), 2863 (w), 1597 (w), 1489 (w), 1453 (w), 1364 (w), 1252 (m), 1202 (w), 1087 (s), 1059 (s), 1017 (w), 934 (w), 809 (s) cm^{-1}.

General procedure I: Synthesis of aryl alkenyl sulfoxides (12a-b)

The *tert*-butyl 3-((4-methyl)sulfinyl)propanoate (**6a**) (0.33 mmol, 1.1 equiv.) and Ar-VBX (**11a** or **11b**) (0.30 mmol, 1.0 equiv.) were introduced into an oven-dried two-neck 25 mL flask equipped with a magnetic stirrer. The reaction vessel was evacuated and backfilled with nitrogen (3 times). The reaction vessel was transferred into a glove-box where potassium *tert*-butoxide (0.35 mmol, 1.2 equiv.) was added under inert atmosphere. The reaction vessel was removed from the glove-box and cooled to -40 °C. Toluene (degassed by bubbling a balloon of argon for 40 min prior to use; 10 mL) was then added at -40 °C, and the mixture was stirred at the same temperature for 5 hours. The mixture was then filtered on a SiO_2 pad and concentrated under reduced pressure. The crude was purified by column chromatography (pentane:EtOAc, 10:0 to 9:1 unless specified otherwise) affording alkynyl sulfoxides **12a** and **12b**.

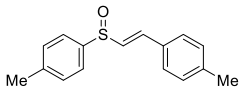
Phenyl((4-methylphenylsulfinyl)ethenyl)silane (12a)



Following **general procedure I**, **12a** was obtained as a colorless solid from **6a** (0.089 g, 0.33 mmol), **11a** (0.105 g, 0.300 mmol) and potassium *tert*-butoxide (0.039 g, 0.35 mmol). Yield: 52% (0.038 g, 0.16 mmol). **mp:** 62.1 - 62.4 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 - 7.42 (m, 2H), 7.40 - 7.29 (m, 6H), 6.81 (d, *J* = 15.5 Hz, 1H), 2.41 (s, 3H). **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 141.9, 140.8, 136.2, 134.0, 133.2, 130.3, 129.9, 129.0, 127.9, 125.1, 21.6 ppm. H**RMS** (APCI) calcd. for $C_{15}H_{15}OS^+$ $[M+H]^+$ 243.0838; found 243.0841. **IR** (film): $\tilde{\nu}$ = 3040 (w),

2959 (w), 2928 (w), 2854 (w), 1492 (w), 1443 (w), 1080 (m), 1043 (s), 1015 (m), 952 (m), 814 (s), 734 (s) cm^{-1}.

4-Methylphenyl((4-methylphenylsulfinyl)ethenyl)silane (12b)

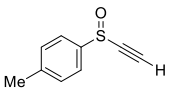


Following **general procedure I, 12b** was obtained as a colorless solid from **6a** (0.089 g, 0.33 mmol), **11b** (0.109 g, 0.300 mmol) and potassium *tert*-butoxide (0.039 g, 0.35 mmol). Yield: 25% (0.020 g, 0.080 mmol). **mp:** 95.0 - 96.4 °C. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.60 – 7.53 (m, 2H), 7.37 – 7.28 (m, 5H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 15.5 Hz, 1H), 2.41 (s, 3H), 2.35 (s, 3H). **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 141.7, 140.9, 140.2, 136.5, 132.0, 131.1, 130.1, 129.6, 127.8, 124.9, 21.5, 21.4 ppm. H**RMS** (ESI) calcd. for $C_{16}H_{17}OS^+$ $[M+H]^+$ 257.0995; found 257.0999. **IR** (film): $\tilde{\nu}$ = 3013 (w), 2920 (w), 2846 (w), 1513 (w), 1486 (w), 1440 (w), 1173 (w), 1082 (m), 1047 (s), 980 (m), 791 (s) cm^{-1}.

5. Gram-scale synthesis of 10a

The *tert*-butyl 3-((4-methylphenyl)sulfinyl) propanoate (**6a**) (1.22 g, 4.54 mmol, 1.11 equiv.) and TIPS-EBX (**9a**) (1.74 g, 4.09 mmol, 1.0 equiv.) were introduced into an oven-dried two-neck 250 mL flask equipped with a magnetic stirrer. The reaction vessel was evacuated and backfilled with nitrogen (3 times). The reaction vessel was transferred into a glove-box where potassium *tert*-butoxide (0.535 g, 4.77 mmol, 1.17 equiv.) was added under inert atmosphere. The reaction vessel was removed from the glove-box and cooled to -40 °C. Toluene (degassed by bubbling a balloon of argon for 40 min prior to use; 80 mL) was then added at -40 °C, and the mixture was stirred at the same temperature for 4 hours. The mixture was then filtered on a SiO_2 pad and concentrated under reduced pressure. The crude was purified by column chromatography (pentane:EtOAc, 10:0 to 9:1) affording pure **10a** in 86% yield (1.13 g, 3.52 mmol). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.88 (dt, *J* = 8.0, 1.9 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 1.13 – 1.03 (m, 21H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 142.3, 141.0, 130.1, 125.3, 108.0, 102.3, 21.5, 18.4, 10.9.

6. Desilylation of 10a



Following a modified reported procedure,[43] in a 10 mL round-bottomed, single-necked flask, tri*iso*propyl((4-methylphenylsulfinyl)ethynyl)silane (**10a**) (0.127 g, 0.396 mmol, 1.0 equiv.) was dissolved in ethanol (2.7 mL). The resulting solution was cooled to 0 °C (ice-water bath) under stirring. An ice-cold solution of KF (0.092 g, 1.6 mmol, 4.0 equiv.) in water (1.3 mL) was then added drop-wise. The initially pale yellow solution slowly darkened to orange. The mixture was stirred at 0 °C for 2 hours. The reaction was quenched by addition of water (10 mL) and the aqueous layer was then extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting yellow crude oil was submitted to column chromatography (SiO_2; DCM:MeOH 1:0 to 9:1) to afford pure 1-(ethynylsulfinyl)-4-methylbenzene **13** in 58% yield (0.037 g, 0.23 mmol) as a colorless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.71 (d, J = 8.3 Hz, 2H), 7.36 (m, 2H), 3.71 (s, 1H), 2.43 (s, 3H) ppm. **^{13}C{^{1}H}-NMR** (101 MHz, $CDCl_3$) δ = 142.9, 140.0, 130.3, 125.2, 90.1, 81.8, 21.5 ppm. H**RMS** (APCI) calcd. for $C_9H_9OS^+$ $[M+H]^+$ 165.0369; found 165.0371. **IR** (film): $\tilde{\nu}$ = 3275 (w), 3186 (m), 3054 (w), 2039 (m), 1089 (s), 1053 (s), 808 (s), 910 (m), 1017 (m), 1406 (w), 1453 (w), 1489 (w), 1597 (w) cm^{-1}.

Acknowledgment

We thank ERC (European Research Council, Starting Grant iTools4MC, number 334840) and EPFL for financial support. S. G. E. A. thanks the Institute of Chemical Sciences and Engineering (ISIC) at EPFL for an ISIC master grant.

Supporting Information.

Reactions schemes for the synthesis of starting materials and reagents, reaction optimization details, accident report, and chromatogram and NMR spectra of new compounds or reported compounds synthesized using modified methods. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) St-Gelais, A.; Legault, J.; Mshvildadze, V.; Pichette, A. Dirchromones: Cytotoxic Organic Sulfur Compounds Isolated from Dirca Palustris. *J. Nat. Prod.* **2015**, *78*, 1904–1909.

(2) a) Jacob, C.; Giles, G. I.; Giles, N. M.; Sies, H. Sulfur and Selenium: The Role of Oxidation State in Protein Structure and Function. *Angew. Chem. Int. Ed.* **2003**, *42*, 4742–4758. b) Kubota, K.; Hirayama, H.; Sato, Y.; Kobayashi, A.; Sugawara, F. Amino Acid Precursors of the Garlic-Like Odour in Scorodocarpus Borneensis. *Phytochemistry* **1998**, *49*, 99–102.

(3) Numata, M.; Aoyagi, Y.; Tsuda, Y.; Yarita, T.; Takatsu, A. Preparation of Sulfoxide Residue Bonded Silica Stationary Phase for Separation of Polychlorinated Biphenyls from Mineral Oils. *Anal. Chem.* **2008**, *80*, 509–509.

(4) McTavish, D.; Buckley, M. M.-T.; Heel, R. C. Omeprazole. *Drugs* **1991**, *42*, 138–170.

(5) a) Ramos, E. T.; Hungenberg, H.; Balabhadrapathruni, S. Patent EP 2422620 A1, 2012. b) Adler, M.; Braude, V.; Chen, K.; Moshkovits-Kaptsan, R. Patent EP 2159219 A2, **2010**.

(6) a) Carreno, M. C., Applications of Sulfoxides to Asymmetric-Synthesis of Biologically-Active Compounds. *Chem. Rev.* **1995**, *95* , 1717-1760. b) Fernandez, I.; Khiar, N., Recent developments in the synthesis and utilization of chiral sulfoxides. *Chem. Rev.* **2003**, *103*, 3651-3705. c) Otocka, S.; Kwiatkowska, M.; Madalińska, L.; Kiełbasiński, P. Chiral Organosulfur Ligands/Catalysts with a Stereogenic Sulfur Atom: Applications in Asymmetric Synthesis. *Chem. Rev.* **2017**, *117*, 4147–4181.

(7) *Modern Alkyne Chemistry: Catalytic and Atom-Economic Transformations*; Trost, B. M., Li, C.-J., Eds.; Wiley-VCH: Weinheim, 2015.

(8) Barrett, M. J.; Khan, G. F.; Davies, P. W.; Grainger, R. S. Alkynyl Sulfoxides as α-Sulfinyl Carbene Equivalents: Gold-Catalysed Oxidative Cyclopropanation. *Chem. Commun.* **2017**, *53*, 5733–5736.

(9) a) Varghese, J. P.; Knochel, P.; Marek, I. New Allene Synthesis via Carbocupration−Zinc Carbenoid Homologation and β-Elimination Sequence. *Org. Lett.* **2000**, *2*, 2849–2852. b) Marek, I. A Shift in Retrosynthetic Paradigm. *Chem. Eur. J.* **2008**, *14*, 7460–7468.

(10) Bouillon, J.-P.; Musyanovich, R.; Portella, C.; Shermolovich, Y. 1-(Alkylsulfinyl- and -Alkylsulfonyl)-2-(F-Alkyl)Ethynes − Applications in Cycloaddition Reactions and Synthesis of Aromatic Derivatives. *Eur. J. Org. Chem.* **2001**, *2001* , 3625–3629.

(11) Souza, F. B.; Shamim, A.; Argomedo, L. M. Z.; Pimenta, D. C.; Stefani, H. A. Synthesis of Enyne and Aryl Vinyl Sulfoxides: Functionalization via Pummerer Rearrangement. *Mol. Divers.* **2015**, *19*, 773–785.

(12) a) Zhong, P.; Huang, X.; Ping-Guo, M. Hydrozirconation of Alkynyl Sulfoxides: The Reactions of Zirconated Vinyl Sulfoxide Intermediates. *Tetrahedron* **2000**, *56*, 8921–8925. b) Huang, X.; Duan, D.; Zheng, W. Studies on Hydrozirconation of 1-Alkynyl Sulfoxides or Sulfones and the Application for the Synthesis of Stereodefined Vinyl Sulfoxides or Sulfones. *J. Org. Chem.* **2003**, *68*, 1958–1963.

(13) a) Pfizer, Inc., Patent US5716965 A1, **1998**. b) P. E. Reddy, R. M. V. Reddy, S. C. Bell, Patent WO 2005046599 A2, **2005.** c) Millennium Pharmaceuticals, Inc., M. O. Duffey, D. B. England, Z. Hu, M. Ito, S. P. Langston, C. Mcintyre, H. Mizutani, H. Xu, Patent WO2015/2994 A2, **2015**.

(14) a) Marino, J. P.; Neisser, M. Stereospecific Reactions of Dichloroketene with Vinyl Sulfoxides: A New Type of Polar Cycloaddition. *J. Am. Chem. Soc.* **1981**, *103*, 7687–7689. b) Westwell, A. D.; Rayner, C. M. Chapter 5: The Chemistry of α,β-Unsaturated Sulfoxides. In *Organosulfur Chemistry*; Page, P., Ed.; Academic Press, 1998; Vol. 2, pp 157–228. c) Bur, S. K.; Padwa, A. The Pummerer Reaction: Methodology and Strategy for the Synthesis of Heterocyclic Compounds. *Chem. Rev.* **2004**, *104*, 2401–2432. d) Nishimura, T.; Unni, A. K.; Yokoshima, S.; Fukuyama, T. Concise Total Synthesis of (+)-Lyconadin A. *J. Am. Chem. Soc.* **2011**, *133*, 418–419.

(15) a) Kabanyane, S. T.; MaGee, D. I. An Efficient and General Synthesis of Alkyl Alkynyl Sulfoxides. *Can. J. Chem.* **1992**, *70*, 2758–2763. b) Davis, F. A.; Reddy, R. T.; Han, W.; Carroll, P. J. Chemistry of Oxaziridines. 17. N-(Phenylsulfonyl)(3,3-Dichlorocamphoryl)Oxaziridine: A Highly Efficient Reagent for the Asymmetric Oxidation of Sulfides to Sulfoxides. *J. Am. Chem. Soc.* **1992**, *114*, 1428–1437. c) Zhong, P.; Guo, M.-P.; Huang, N.-P., A Selective and Convenient Oxidation of Acetylenic Sulfides to Acetylenic Sulfoxides Using Trichloroisocyanuric Acid. *Synth. Commun.* **2002**, *32*, 175-179. d) Zhang,

G.; Zhang, L. Au-Containing All-Carbon 1,3-Dipoles: Generation and [3+2] Cycloaddition Reactions. *J. Am. Chem. Soc.* **2008**, *130*, 12598–12599.

(16) Caupène, C.; Boudou, C.; Perrio, S.; Metzner, P. Remarkably Mild and Simple Preparation of Sulfenate Anions from β-Sulfinylesters: A New Route to Enantioenriched Sulfoxides. *J. Org. Chem.* **2005**, *70*, 2812–2815.

(17) O'donnell, J. S.; Schwan, A. L. Generation, Structure and Reactions of Sulfenic Acid Anions. *J. Sulfur Chem.* **2004**, *25*, 183–211.

(18) Selected examples: a) Maitro, G.; Vogel, S.; Prestat, G.; Madec, D.; Poli, G. Aryl Sulfoxides via Palladium-Catalyzed Arylation of Sulfenate Anions. *Org. Lett.* **2006**, *8*, 5951–5954. b) Maitro, G.; Vogel, S.; Sadaoui, M.; Prestat, G.; Madec, D.; Poli, G. Enantioselective Synthesis of Aryl Sulfoxides via Palladium-Catalyzed Arylation of Sulfenate Anions. *Org. Lett.* **2007**, *9*, 5493–5496. c) Gelat, F.; Jayashankaran, J.; Lohier, J.-F.; Gaumont, A.-C.; Perrio, S. Organocatalytic Asymmetric Synthesis of Sulfoxides from Sulfenic Acid Anions Mediated by a Cinchona-Derived Phase-Transfer Reagent. *Org. Lett.* **2011**, *13*, 3170–3173. d) Söderman, S. C.; Schwan, A. L., The Diastereoselective Alkylation of Arenesulfenate Anions Using Homochiral Electrophiles. *Org. Lett.* **2011**, *13*, 4192-4195. e) Zong, L.; Ban, X.; Kee, C. W.; Tan, C.-H. Catalytic Enantioselective Alkylation of Sulfenate Anions to Chiral Heterocyclic Sulfoxides Using Halogenated Pentanidium Salts. *Angew. Chem. Int. Ed.* **2014**, *53*, 11849–11853. f) Jia, T.; Zhang, M.; Jiang, H.; Wang, C. Y.; Walsh, P. J. Palladium-Catalyzed Arylation of Alkyl Sulfenate Anions. *J. Am. Chem. Soc.* **2015**, *137*, 13887–13893. g) Jia, T. Z.; Zhang, M. N.; McCollom, S. P.; Bellomo, A.; Montel, S.; Mao, J. Y.; Dreher, S. D.; Welch, C. J.; Regalado, E. L.; Williamson, R. T.; Manor, B. C.; Tomson, N. C.; Walsh, P. J., Palladium-Catalyzed Enantioselective Arylation of Aryl Sulfenate Anions: A Combined Experimental and Computational Study. *J. Am. Chem. Soc.* **2017**, *139*, 8337-8345. h) Wang, L.; Chen, M.; Zhang, P.; Li, W.; Zhang, J. Palladium/PC-Phos-Catalyzed Enantioselective Arylation of General Sulfenate Anions: Scope and Synthetic Applications. *J. Am. Chem. Soc.* **2018**, *140*, 3467–3473.

(19) a) Yu, H.; Li, Z.; Bolm, C. Transition-Metal-Free Arylations of In-Situ Generated Sulfenates with Diaryliodonium Salts. *Org. Lett.* **2018**, *20*, 7104-7106. b) Zhang, J.; Wang, L.; Chen, M. Transition Metal-

Free Base-Promoted Arylation of General Sulfenate Anions with Diaryliodonium Salts. *Org. Chem. Front*. **2018**, *6*, 32-35.

(20) Yoshimura, A.; Zhdankin, V. V., Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chem. Rev.* **2016**, *116*, 3328-3435.

(21) Hari, D. P.; Nicolai, S.; Waser, J. Alkynylations and Vinylations. In *PATAI'S Chemistry of Functional Groups*; Z. Rappoport (Ed.), 2018; pp 1–58.

(22) Li, Y.; Hari, D. P.; Vita, M. V.; Waser, J., Cyclic Hypervalent Iodine Reagents for Atom-Transfer Reactions: Beyond Trifluoromethylation. *Angew. Chem., Int. Ed.* **2016**, *55*, 4436-4454.

(23) a) Frei, R.; Waser, J. A Highly Chemoselective and Practical Alkynylation of Thiols. *J. Am. Chem. Soc.* **2013**, *135*, 9620–9623. b) Frei, R.; Wodrich, M. D.; Hari, D. P.; Borin, P.-A.; Chauvier, C.; Waser, J. Fast and Highly Chemoselective Alkynylation of Thiols with Hypervalent Iodine Reagents Enabled through a Low Energy Barrier Concerted Mechanism. *J. Am. Chem. Soc.* **2014**, *136*, 16563–16573. c) Chen, C. C.; Waser, J. One-Pot, Three-Component Arylalkynyl Sulfone Synthesis. *Org. Lett.* **2015**, *17*, 736–739. d) Wodrich, M. D.; Caramenti, P.; Waser, J., Alkynylation of Thiols with Ethynylbenziodoxolone (EBX) Reagents: α- or β- π-Addition? *Org. Lett.* **2016,** *18*, 60-63.

(24) Similar results were obtained with other ethynylbenziodoxole reagents and alkynyliodonium salts gave much lower yields. See Supporting Information.

(25) See experimental part for details. Precursors **5-7** were synthesized using reported procedures (ref. 18b-c) by sequential Michael-addition then oxidation in respectively, 66%, 79% and 26% yield over two steps. **8** was synthesised *via* a three-step procedure: a) acetylation of nitroethanol, b) substitution of the acetylated position with the thiol, c) oxidation, in 62% overall yield.

(26) Stridfeldt, E.; Seemann, A.; Bouma, M. J.; Dey, C.; Ertan, A.; Olofsson, B., Synthesis, Characterization and Unusual Reactivity of Vinylbenziodoxolones-Novel Hypervalent Iodine Reagents. *Chem. Eur. J.* **2016**, *22*, 16066-16070.

(27) Kraszkiewicz, L.; Skulski, L. Optimized Syntheses of Iodylarenes from Iodoarenes, with Sodium Periodate as the Oxidant. Part II. *Arkivoc* **2003**, *2003*, 120.

(28) Helal, C. J.; Magriotis, P. A.; Corey, E. J. Direct Catalytic Enantioselective Reduction of Achiral α,β-Ynones. Strong Remote Steric Effects Across the C−C Triple Bond. *J. Am. Chem. Soc.* **1996**, *118*, 10938–10939.

(29) Brand, J. P.; Waser, J. Direct Alkynylation of Thiophenes: Cooperative Activation of TIPS–EBX with Gold and Brønsted Acids. *Angew. Chem. Int. Ed.* **2010**, *49* (40), 7304–7307.

(30) Cuadrado, P.; González-Nogal, A. M.; Valero, R. Regiospecific Synthesis of 5-Silyl Azoles. *Tetrahedron* **2002**, *58* (24), 4975–4980.

(31) Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. Ethynyl Benziodoxolones for the Direct Alkynylation of Heterocycles: Structural Requirement, Improved Procedure for Pyrroles, and Insights into the Mechanism. *Chem. Eur. J.* **2012**, *18* (18), 5655–5666.

(32) Boelke, A.; Caspers, L. D.; Nachtsheim, B. J. NH2-Directed C–H Alkenylation of 2-Vinylanilines with Vinylbenziodoxolones. *Org. Lett.* **2017**, *19* (19), 5344–5347.

(33) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H.; Dess, D.; Ross, M. R.; Martin, J. C. Directed Dilithiation of Hexafluorocumyl Alcohol - Formation of a Reagent for the Facile Introduction of a Stabilizing Bidentate Ligand in Compounds of Hypervalent Sulfur (10-S-4), Phosphorus (10-P-5), Silicon (10-Si-5), and Iodine (10-I-3). *J. Org. Chem.* **1981**, *46* (6), 1049–1053.

(34) Cvengroš, J.; Stolz, D.; Togni, A. A Concise Synthesis of *Ortho* -Iodobenzyl Alcohols via Addition of *Ortho* -Iodophenyl Grignard Reagent to Aldehydes and Ketones. *Synthesis* **2009**, *2009* (16), 2818–2824.

(35) Blake, A. J.; Novak, A.; Davies, M.; Robinson, R. I.; Woodward, S. Preparation of 1,1′-Oxy-Bis(3,3-Bis(Trifluoromethyl)-3(1H)-1,2-Benziodoxole) and 2-(N-(p-Toluenesulfonyl)Imino)Iodobenzyl-methyl Ether. *Synthetic Communications* **2009**, *39* (6), 1065–1075.

(36) Kitamura, T. An Alternative Synthesis of Alkynyl(Phenyl)Iodonium Triflates Using (Diacetoxy-iodo)Benzene and Alkynylsilanes. *Synthesis* **1998**, *1998* (10), 1416–1418.

(37) Kita, Y.; Shibata, N.; Tamura, O.; Miki, T. Chemistry of *O*-Silylated Ketene Acetals : A Mild and Convenient Synthesis of β-Lactam Antibiotics. Chem. Pharm. Bull. **1991**, *39*, 2225–2232.

(38) Moghaddam, F. M.; Bardajee, G. R.; Chadorneshine Veranlou, R. O. KF/Al2O3-Mediated Michael Addition of Thiols to Electron-Deficient Olefins. Synthetic Communications **2005**, *35*, 2427–2433.

(39) Maitro, G.; Prestat, G.; Madec, D.; Poli, G. Preparation of Allyl Sulfoxides by Palladium-Catalyzed Allylic Alkylation of Sulfenate Anions. *J. Org. Chem.* **2006**, *71*, 7449–7454.

(40) Yue, H.-L.; Klussmann, M. Acid-Catalyzed Oxidative Addition of Thiols to Olefins and Alkynes for a One-Pot Entry to Sulfoxides. *Synlett* **2016**, *27*, 2505–2509.

(41) Cui, H.; Wei, W.; Yang, D.; Zhang, Y.; Zhao, H.; Wang, L.; Wang, H. Visible-Light-Induced Selective Synthesis of Sulfoxides from Alkenes and Thiols Using Air as the Oxidant. *Green Chem.* **2017**, *19*, 3520–3524.

(42) López, R.; Zalacain, M.; Palomo, C. Catalytic Asymmetric Synthesis of γ-Substituted Vinyl Sulfones. *Chem. Eur. J.* **2011**, *17* (8), 2450–2457.

(43) Shinde, P. S.; Patil, N. T. Gold-Catalyzed Dehydrazinative C(Sp)–S Coupling Reactions of Arylsulfonyl Hydrazides with Ethynylbenziodoxolones for Accessing Alkynyl Sulfones. *Eur. J. Org. Chem.* **2017**, *2017*, 3512–3515.

Supporting Information for

Metal-Free Electrophilic Alkynylation of Sulfenate Anions with Ethynylbenziodoxolone Reagents

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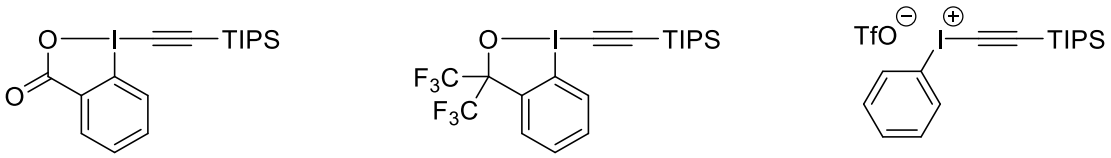
(65 pages)

Table of Contents

1. Optimisation of sulfoxide alkynylation reactions conditions

General method for the optimisation of the synthesis of 10a

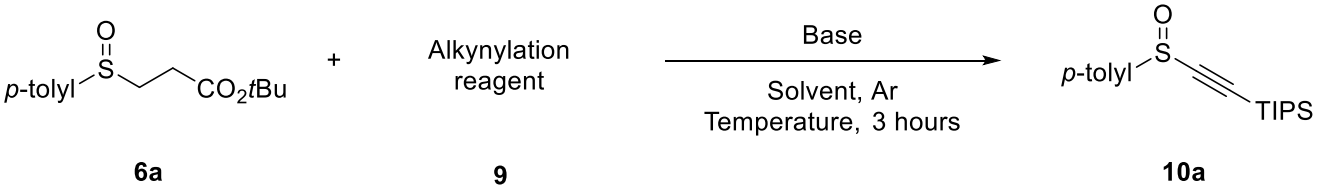
Into an oven-dried test-tube equipped with a magnetic stirrer, *tert*-Butyl 3-(4-methylphenylsulfinyl)propanoate (**6a**, X mmol) and the hypervalent iodine reagent (**9**, Y mmol) anhydrous toluene (2 mL, 0.05 M,unless specified otherwise) and the base (Z equiv.) were then added and the reaction mixture was stirred at -40 °C, unless specified otherwise. The crude mixture was then filtered over SiO_2. The resulting solution was concentrated under reduced pressure. ^1H NMR yield was determined using CH_2Br_2 as internal standard: CH_2Br_2 (7 µL, 0.1 mmol) was added to the crude and the crude was homogenised with Chloroform-*d*. The crude product was then purified by preparative TLC (SiO_2 glass plate, Heptane/EtOAc: 8/2). Compound was then retrieved using EtOAc.



9a **25** **26**

Figure S1: Reagents tested during optimisation

Table S1: Optimisation of the alkynylation reaction

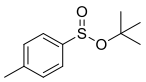


6a **9** **10a**

Entry	T. (°C)	X (mmol)	Reagent	Y(mmol)	Base (Z equiv.)	Solvent	Yield (%)
1	-78	0.1	**9a**	0.11	KO*t*Bu (1.05)	PhMe (0.16 M)	64
2	-40	0.1	**9a**	0.11	KO*t*Bu (1.05)	PhMe (0.16 M)	70 (77)
3	-25	0.1	**9a**	0.11	KO*t*Bu (1.05)	PhMe (0.16 M)	68
4	-40	0.1	**9a**	0.11	NaO*t*Bu (1.05)	PhMe	(53)
5	-40	0.1	**9a**	0.11	KHDMS (1.05)	PhMe	(70)
6	-40	0.1	**9a**	0.11	LDA (1.1)	PhMe	(52)
7	-40	0.1	**25**	0.11	KO*t*Bu (1.05)	PhMe	(84)
8	-40	0.1	**26**	0.11	KO*t*Bu (1.05)	PhMe	(44)
9	-40	0.11	**9a**	0.1	KO*t*Bu (1.05)	PhMe	75
10	-40	0.1	**9a**	0.11	KO*t*Bu (1.05)	DMF	28
11	-40	0.1	**9a**	0.11	KO*t*Bu (1.05)	PhMe:DCM (7:3)	(58)
12	-40	0.1	**9a**	0.11	KO*t*Bu (1.05)	PhMe:DCM (9:1)	(66)
13	-40	0.1	**9a**	0.11	KO*t*Bu (1.05)	THF	(66)
14[a]	-40	0.1	**9a**	0.11	KO*t*Bu (1.05)	PhMe	81
15[a]	-40	0.1	**9a**	0.11	KO*t*Bu (1.25)	PhMe	60
16[a]	-40	0.11	**9a**	0.1	KO*t*Bu (1.05)	PhMe[b]	90
17[a,c]	RT	0.11	**9a**	0.1	KO*t*Bu (1.05)	PhMe[d]	73

[a]Oxygen free procedure: **6a** and **9a** were introduced into an oven-dried flask equipped with a magnetic stirrer. After three vaccum/N_2 cycles potassium *tert*-butoxide was added under the inert atmosphere of a glove-box. [b]Degassed with a ballon of argon while cooling down to -40 °C. [c]Two impurities were identified as *tert*-butyl sulfinate (**S1**) and alkynyl sulfone (**S2**) Degassed with a ballon of argon at RT.

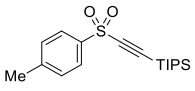
Tert-butyl 4-methylbenzenesulfinate (**S1**):



This compound was isolated under the reaction conditions (Optimisation table, entry 17) as a colourless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.56 (m, 2H), 7.31 (m, 2H), 2.41 (s, 3H), 1.55 (s, 11H) ppm. **HRMS** (APCI/QTOF) calcd. for

$C_{11}H_{16}NaO_2S^+$ $[M + Na]^+$ 235.0763; found 235.0759. The values of the NMR spectra are in accordance with reported literature data.[1]

Tri*iso*propyl(tosylethynyl)silane (**S2**):



This compound was isolated under the reaction conditions (Optimisation table, entry 17) as a colourless oil. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.89 (m, 2H), 7.36 (m, 2H), 2.46 (s, 3H), 1.16 – 0.92 (m, 21H) ppm. HRMS (ESI/QTOF) m/z: calcd. for $C_{18}H_{29}O_2SSi^+$ $[M + H]^+$ 337.1652; found 337.1657. The values of the NMR spectra are in accordance with reported literature data.[2]

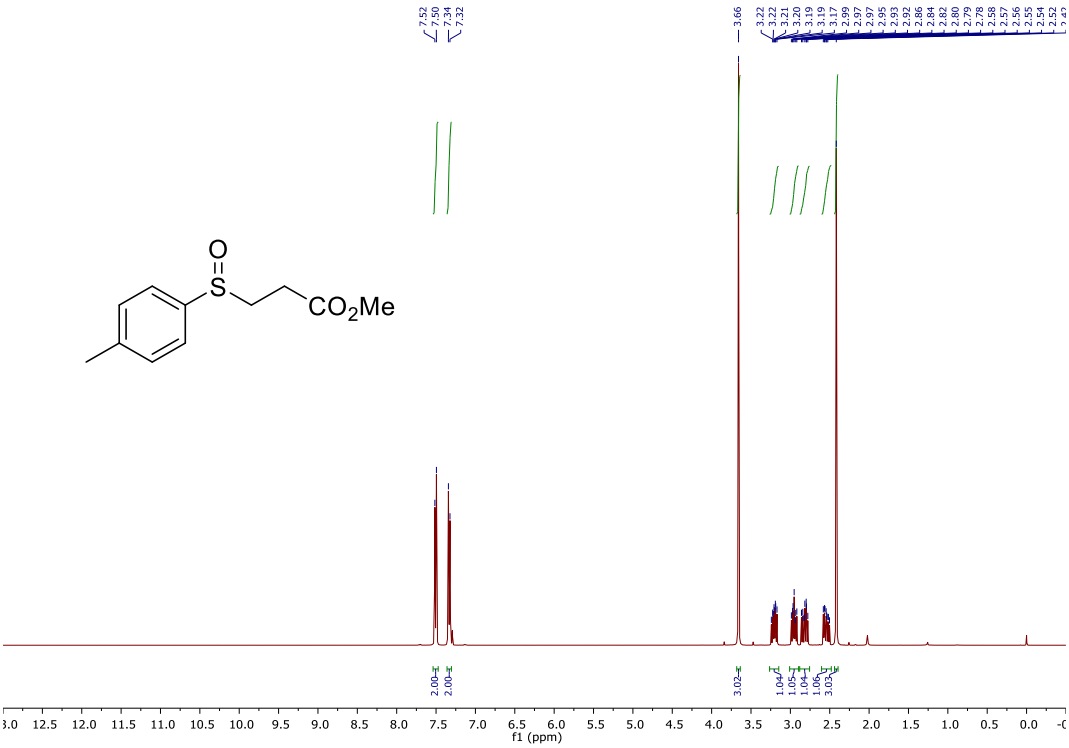
2. ^{1}H and ^{13}C NMRspectra of new compounds

[1] Kadari, L.; Radha Krishna, P.; Lakshmi Prapurna, Y. Sulfination of Alcohols with P-Toluenesulfonylmethyl Isocyanide under Metal-Free Conditions: A Mitsunobu Approach. *Adv. Syn. Catal.* **2016**, *358*, 3863–3868.

[2] Shinde, P. S.; Patil, N. T. Gold-Catalyzed Dehydrazinative C(Sp)–S Coupling Reactions of Arylsulfonyl Hydrazides with Ethynylbenziodoxolones for Accessing Alkynyl Sulfones. *Eur. J. Org. Chem.* **2017**, *2017*, 3512–3515.

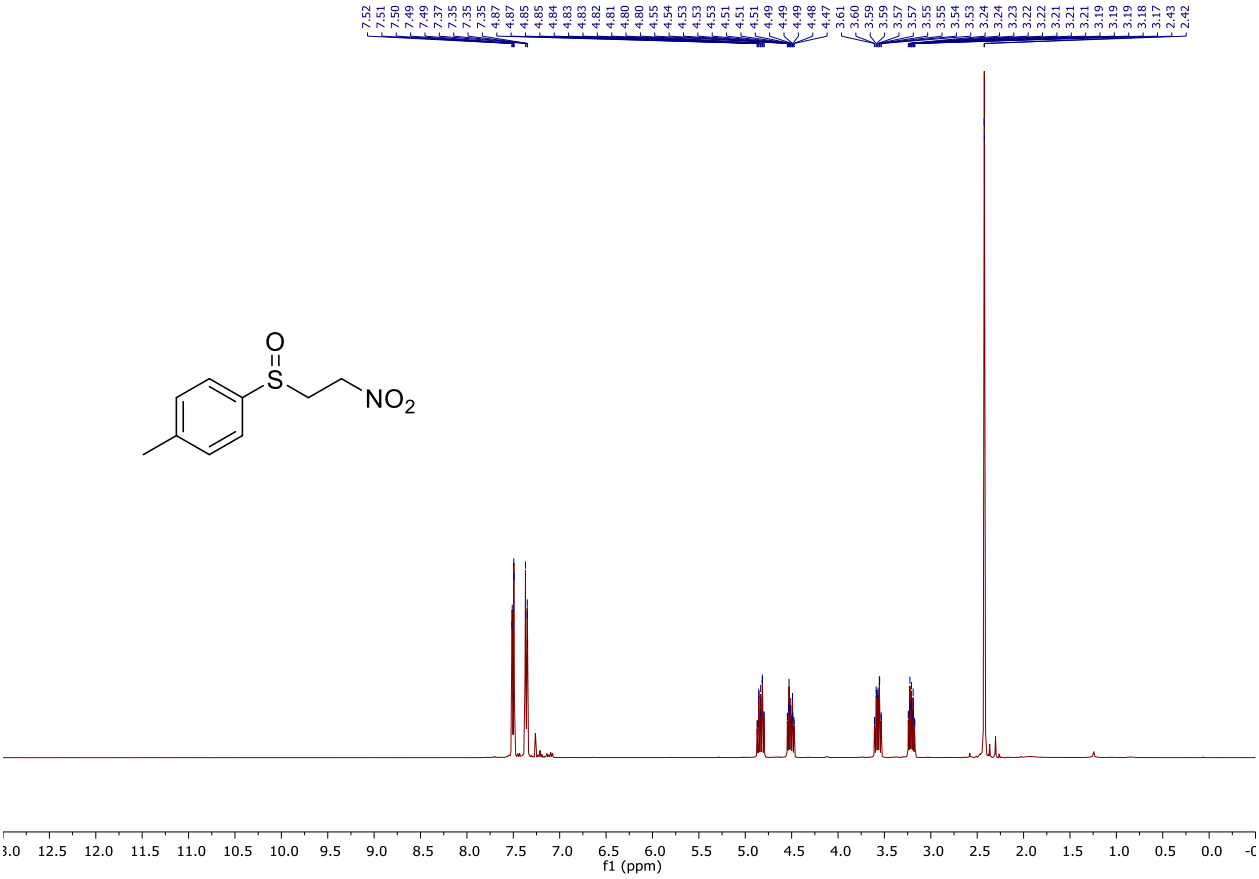
Methyl 3-((4-methylphenyl)sulfinyl)propanoate (5)

^{1}H NMR (400 MHz, Chloroform-*d*)



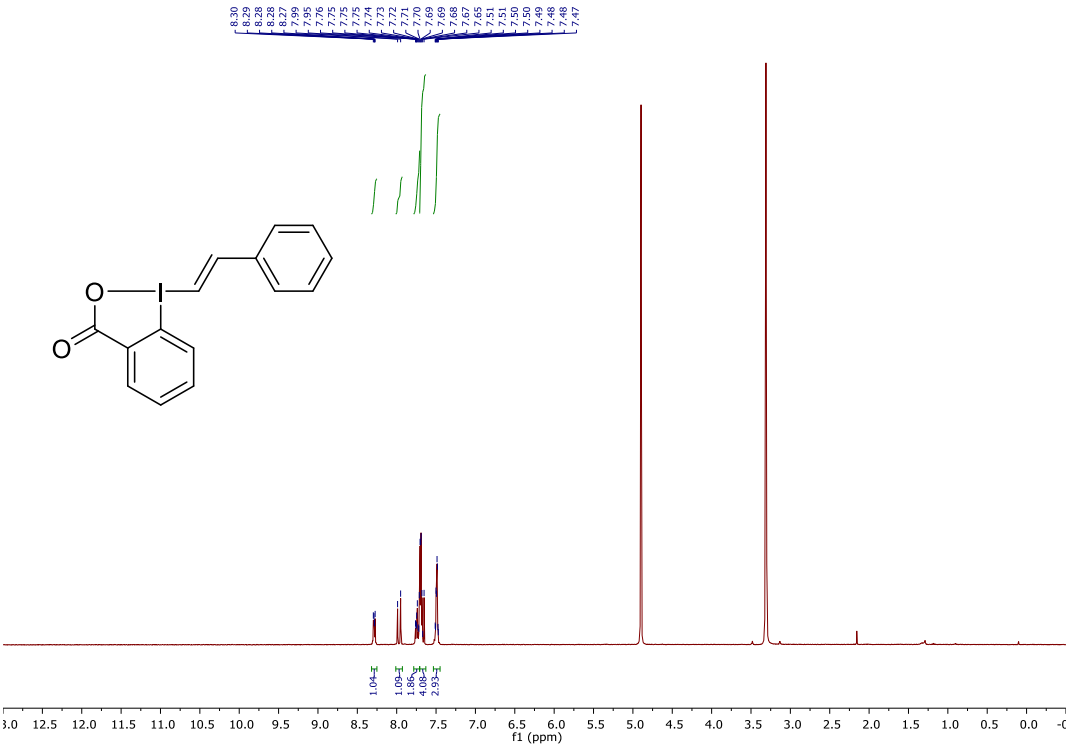
1-Methyl-4-[(2-nitroethyl)sulfinyl]benzene (8)

^{1}H NMR (400 MHz, Chloroform-*d*)



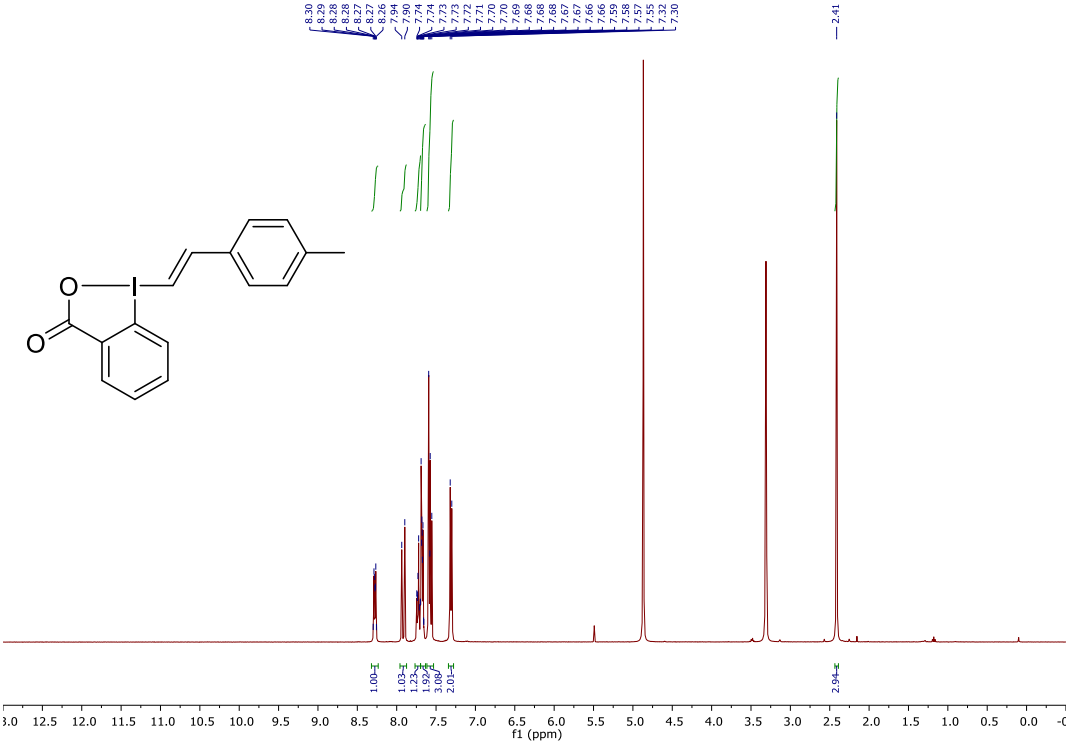
(*E*)-1-Styryl-1λ^3-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (11a)

^{1}H NMR (400 MHz, Chloroform-*d*)



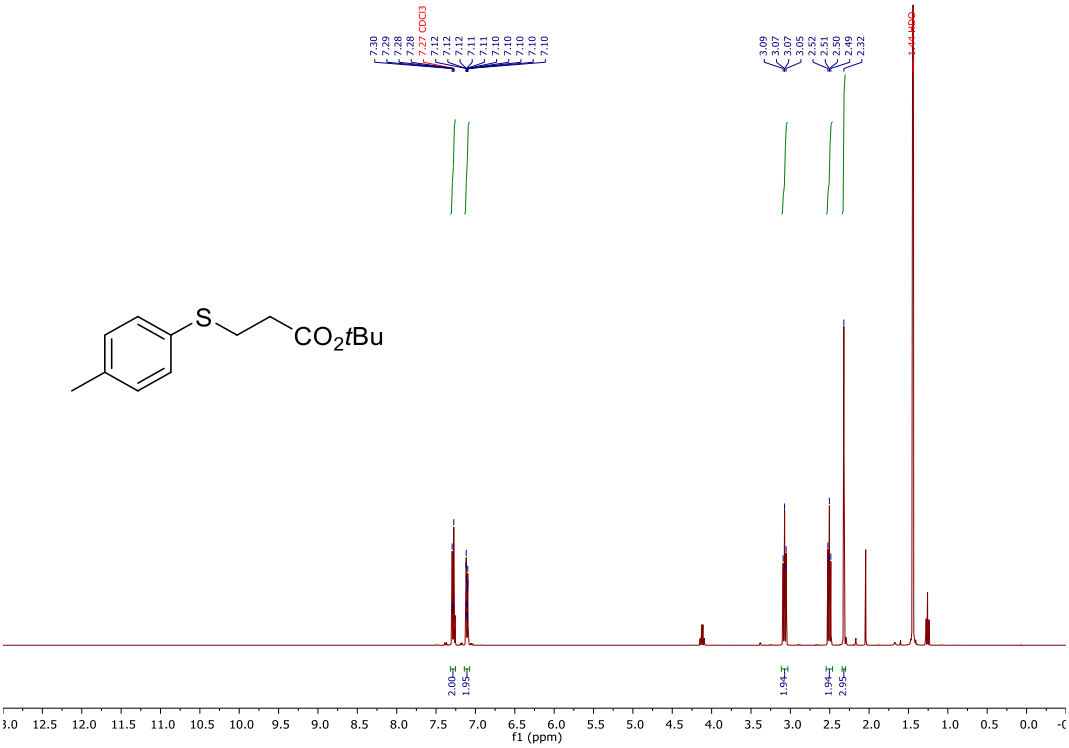
(*E*)-1-(4-Methylstyryl)-1λ^3-benzo[d][1,2]iodaoxol-3(1H)-one (11b)

^{1}H NMR (400 MHz, Chloroform-*d*)



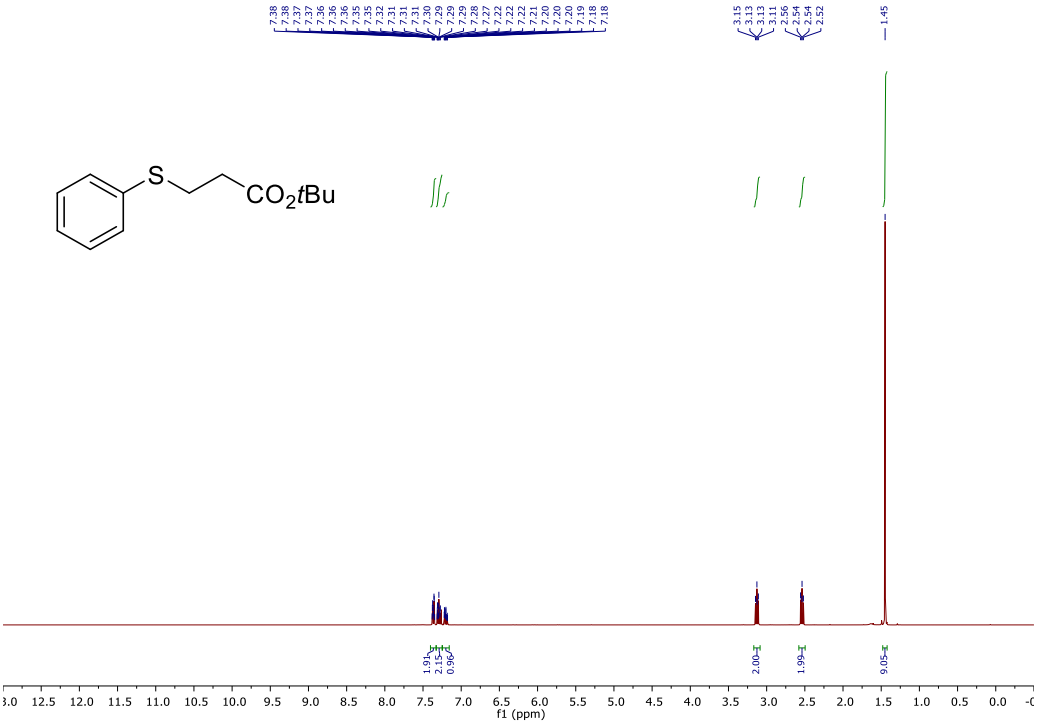
Tert-butyl 3-(4-methylphenylthio)propanoate (21a)

^{1}H NMR (400 MHz, Chloroform-*d*)

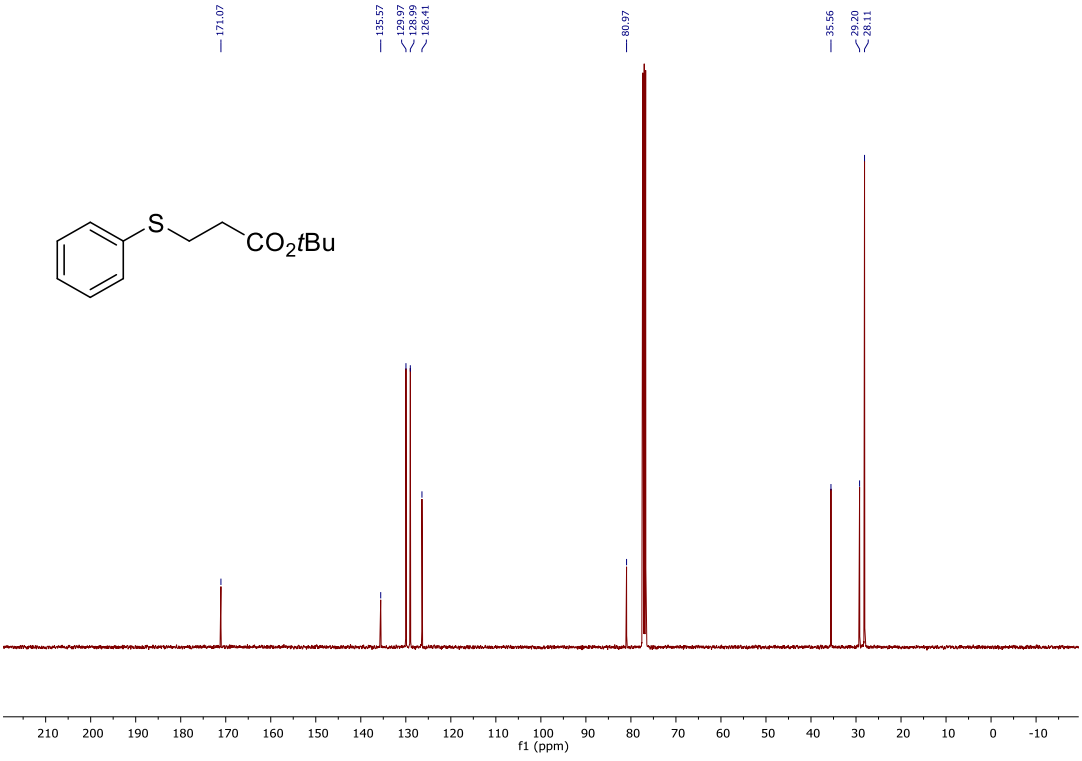


Tert-butyl 3-(phenylthio)propanoate (21b)

^{1}H NMR (400 MHz, Chloroform-*d*)

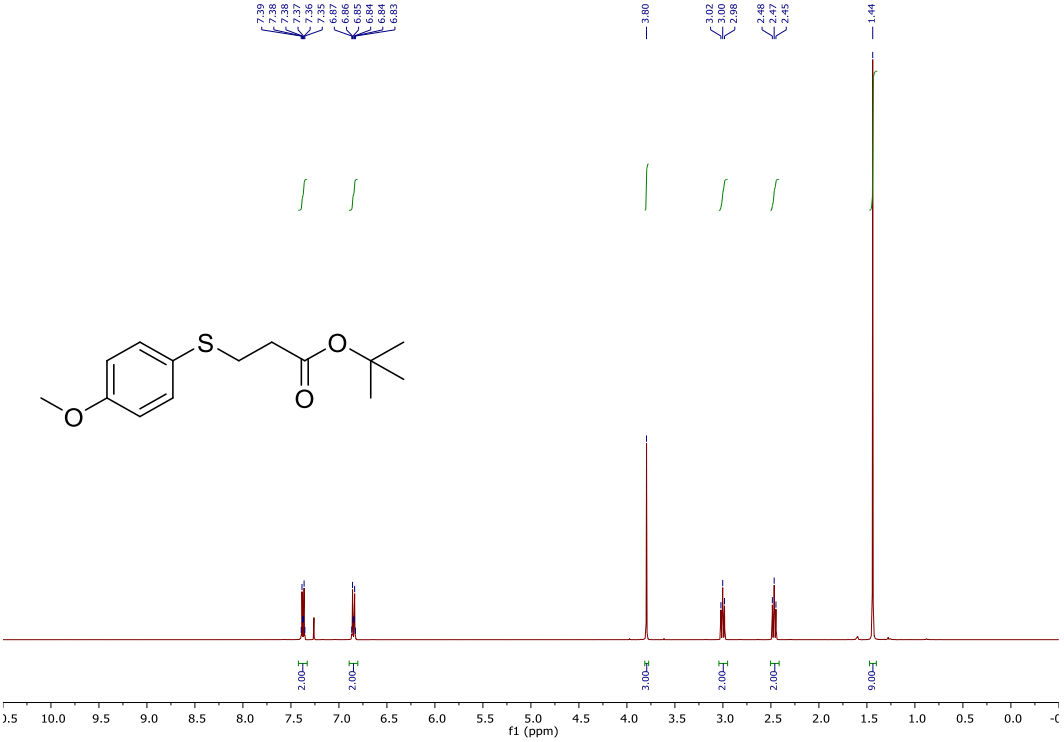


^{13}C NMR (101 MHz, Chloroform-*d*)

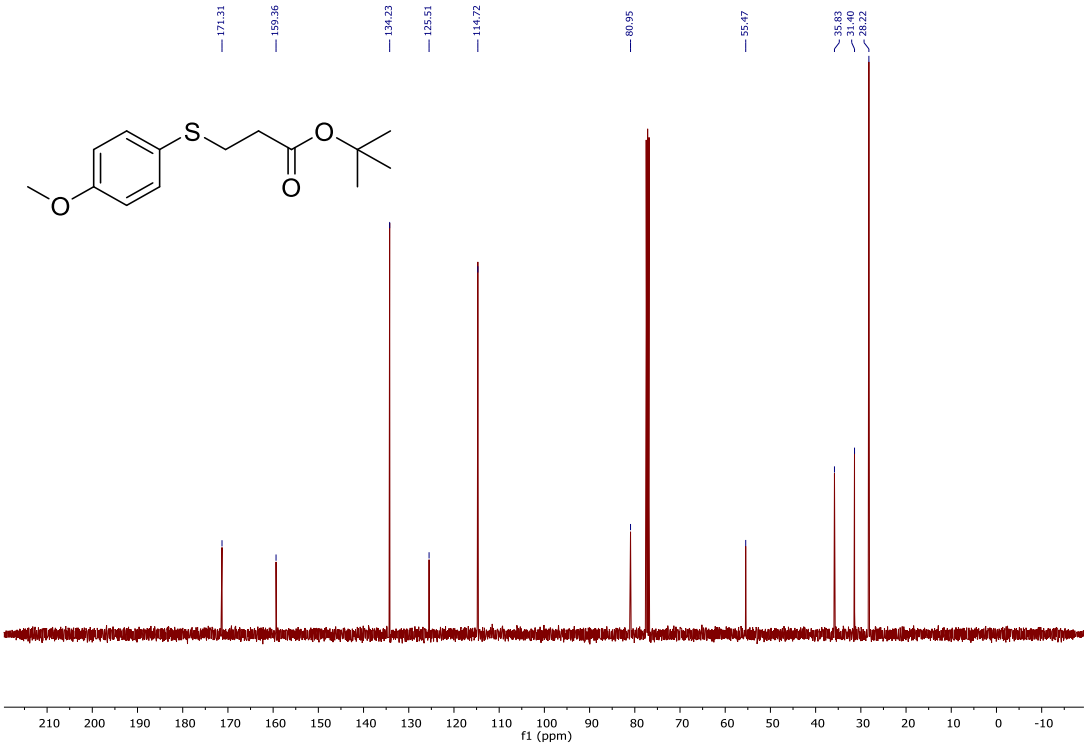


Tert-butyl 3-(4-methoxyphenylthio)propanoate (21c)

^{1}H NMR (400 MHz, Chloroform-*d*)

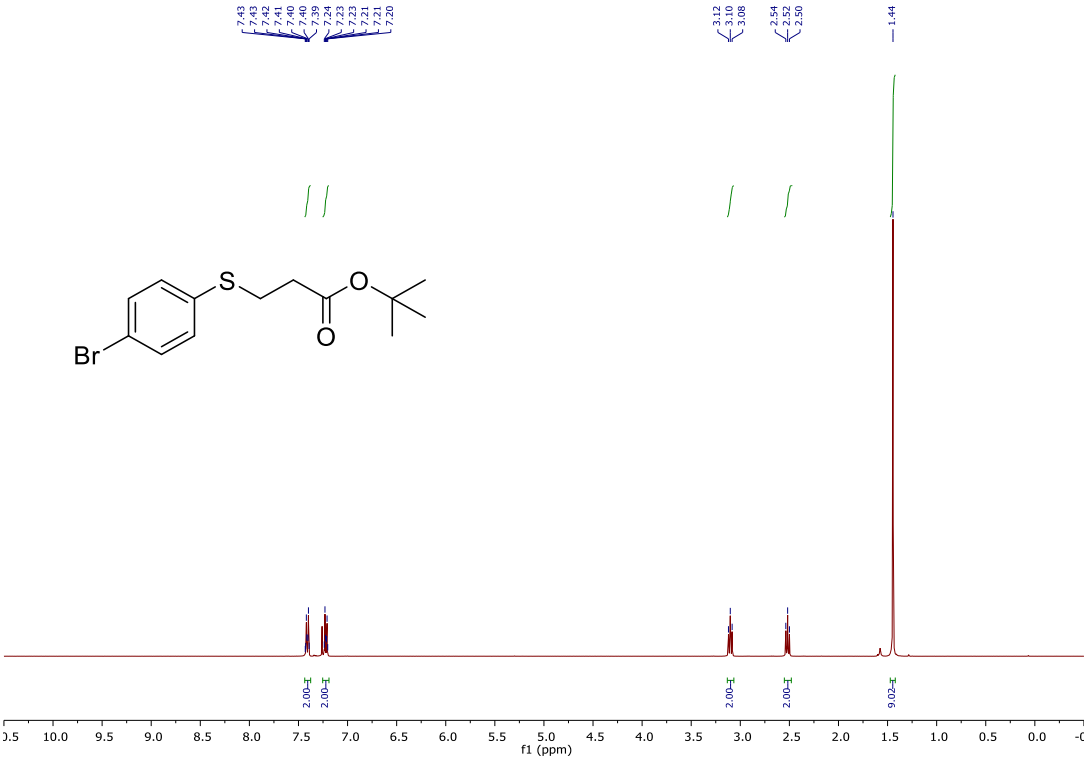


^{13}C NMR (101 MHz, Chloroform-*d*)



Tert-butyl 3-(4-bromophenylthio)propanoate (21d)

^{1}H NMR (400 MHz, Chloroform-*d*)



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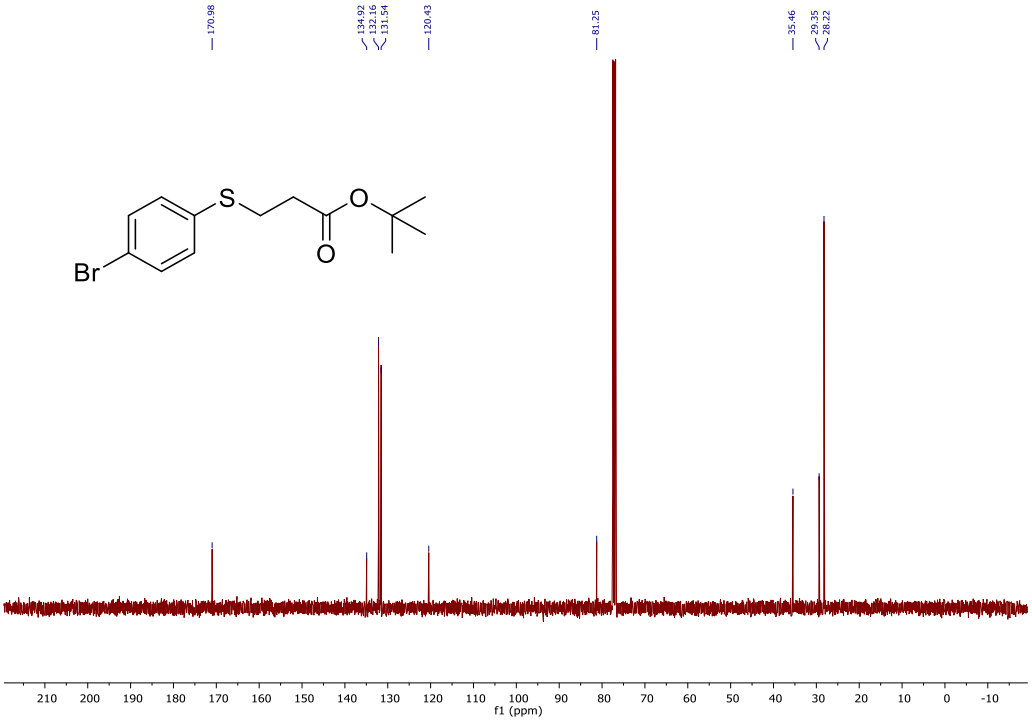
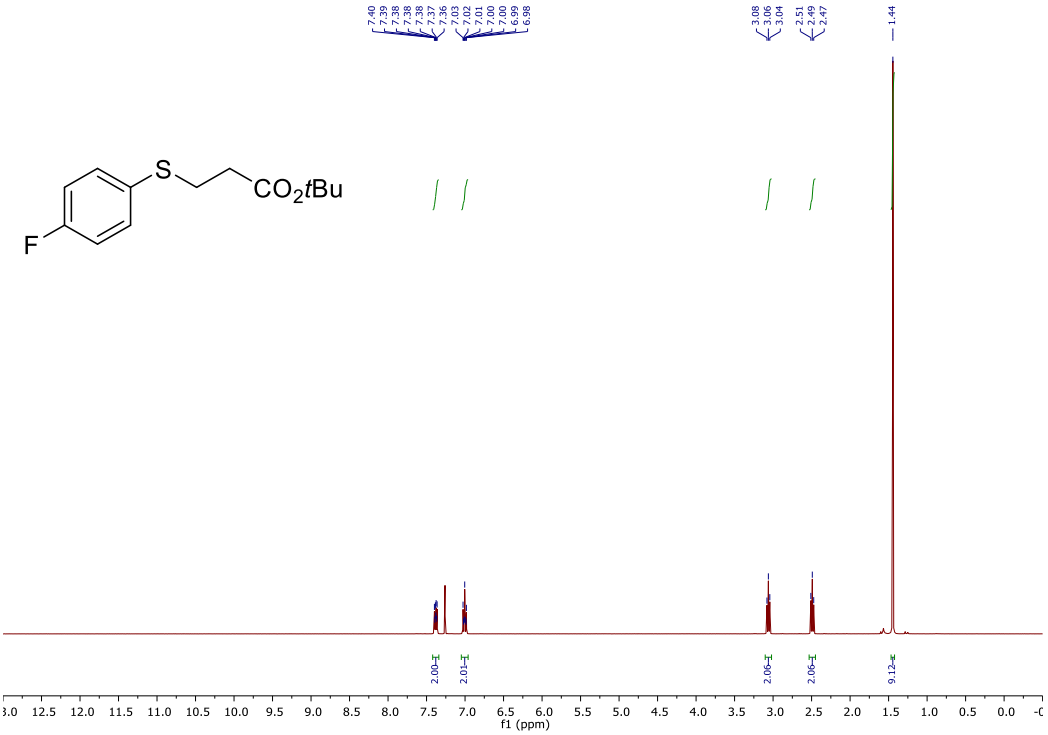


Tert-butyl 3-(4-fluorophenylthio)propanoate (21e)

^{1}H NMR (400 MHz, Chloroform-*d*)



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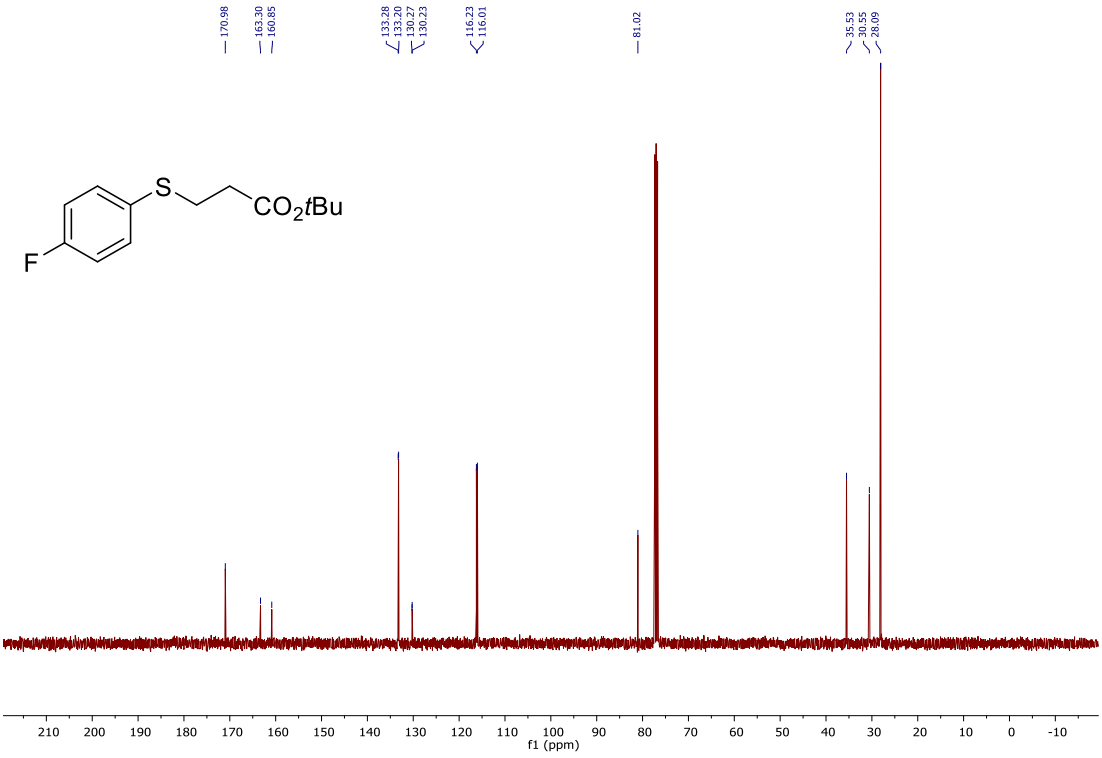
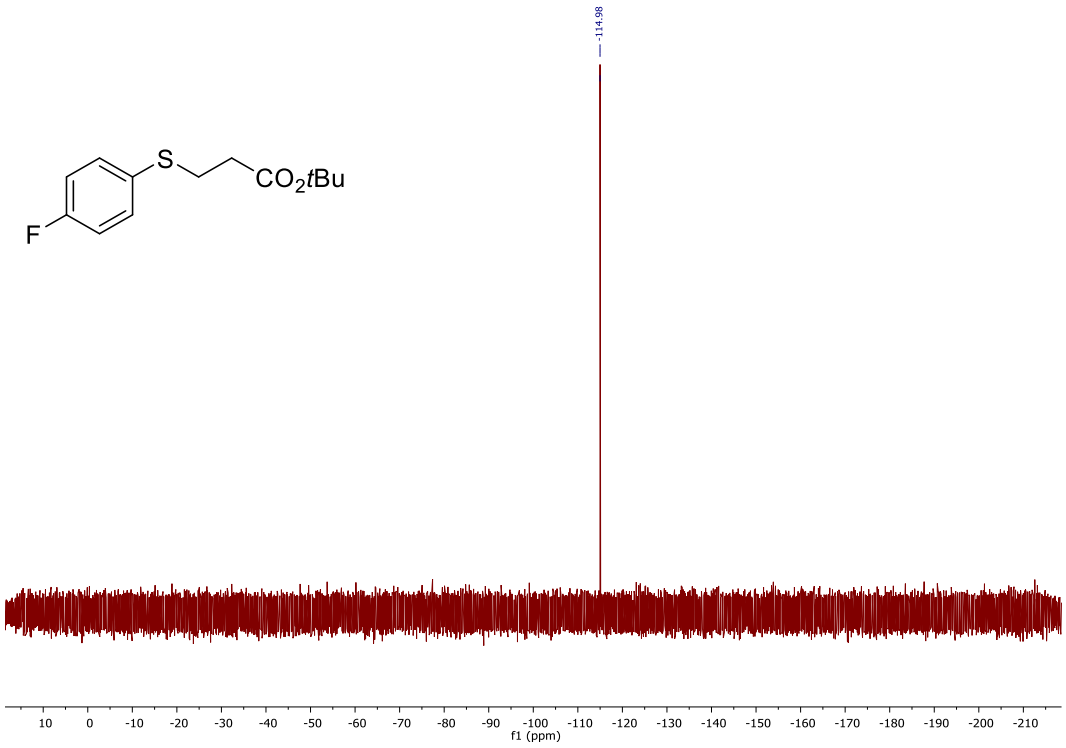
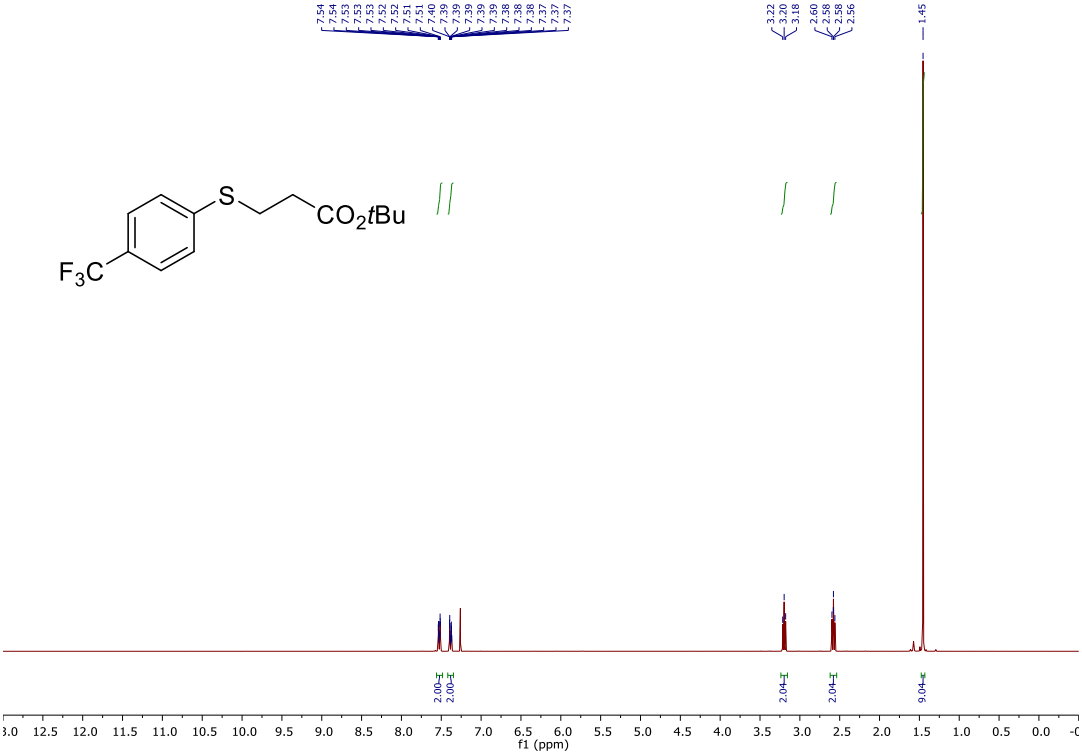


^{19}F NMR (376 MHz, Chloroform-d)



Tert-butyl 3-(4-trifluoromethylphenylthio)propanoate (21f)

^{1}H NMR (400 MHz, Chloroform-*d*)



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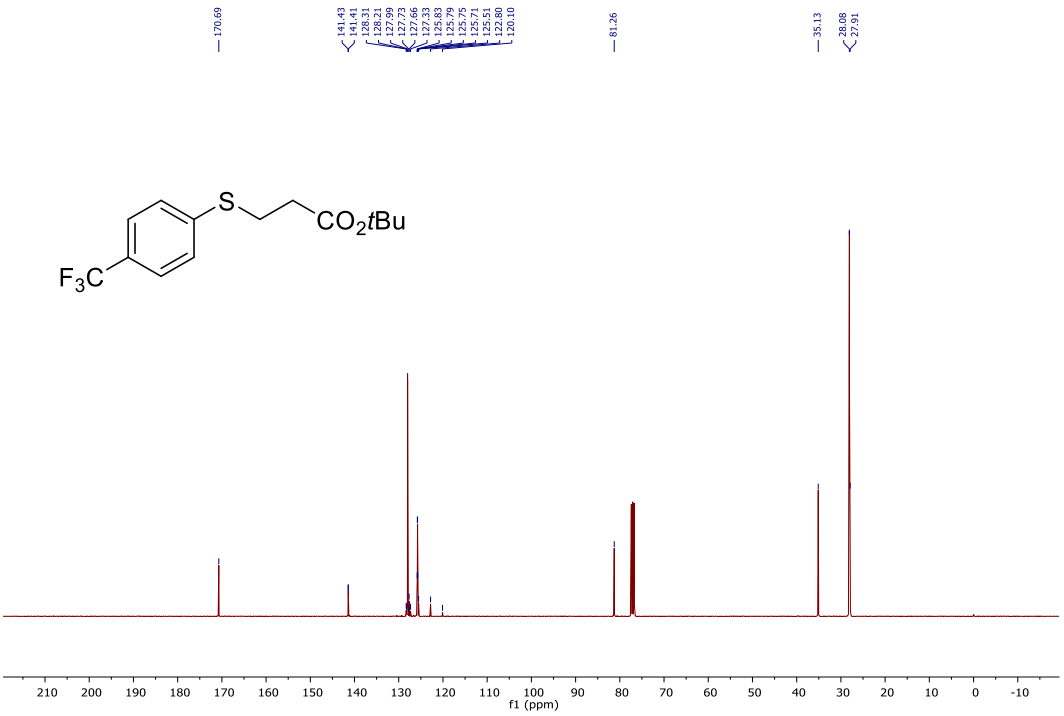
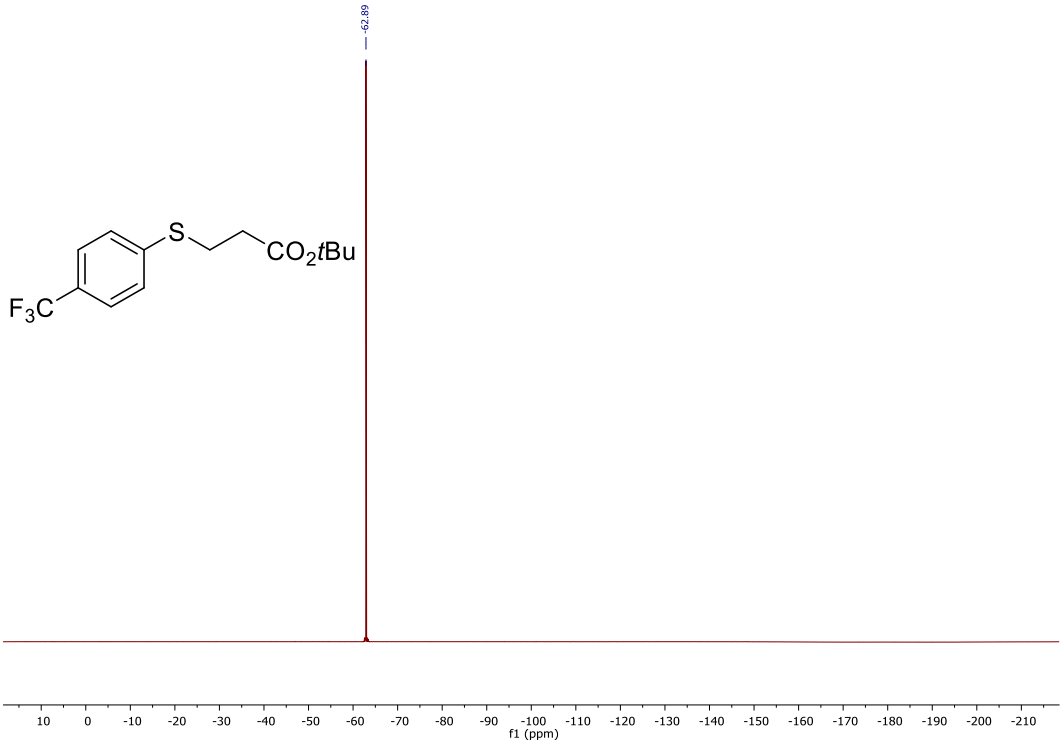
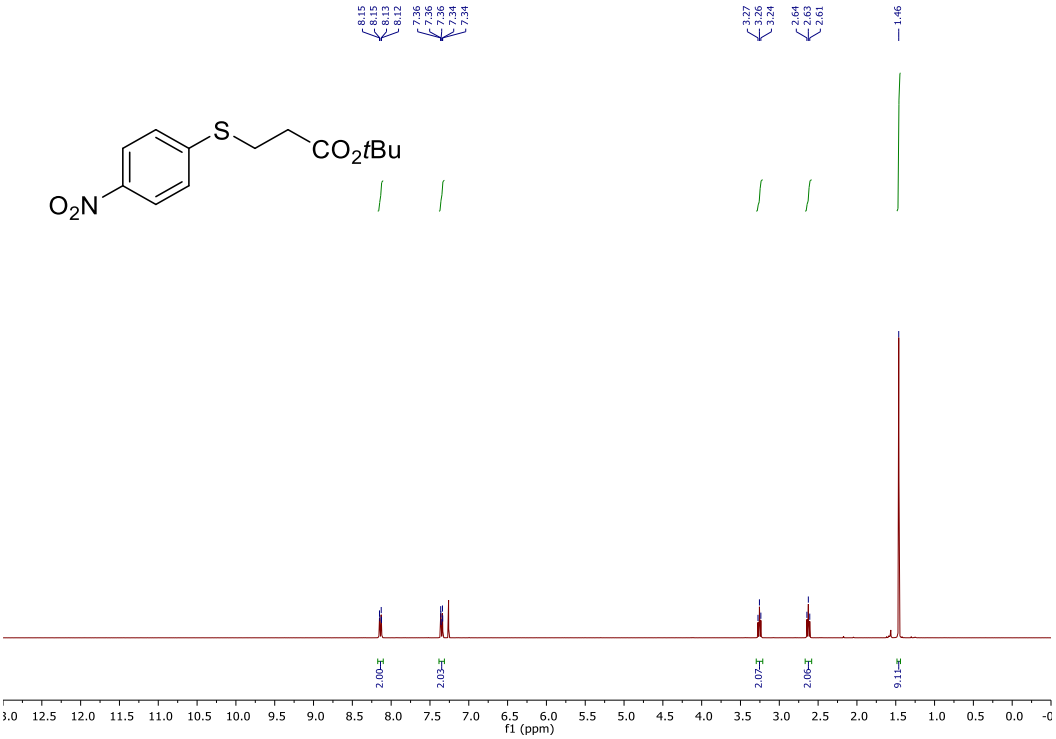


^{19}F NMR (376 MHz, Chloroform-d)

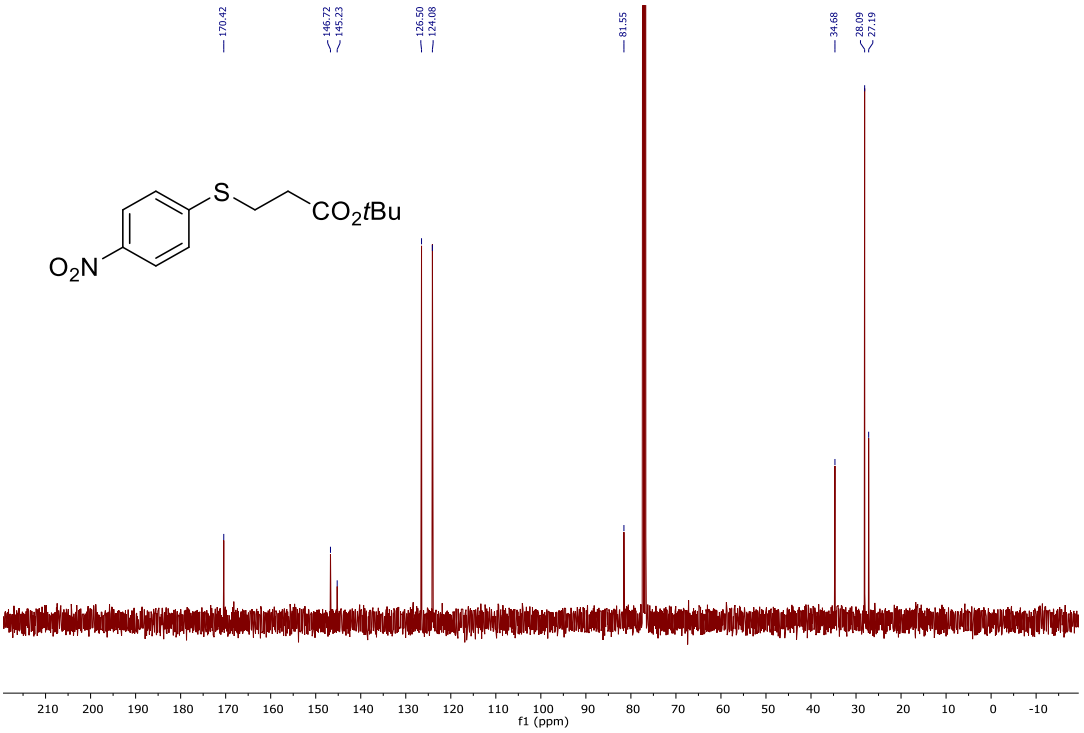


Tert-butyl 3-(4-nitrophenylthio)propanoate (21g)

^{1}H NMR (400 MHz, Chloroform-*d*)

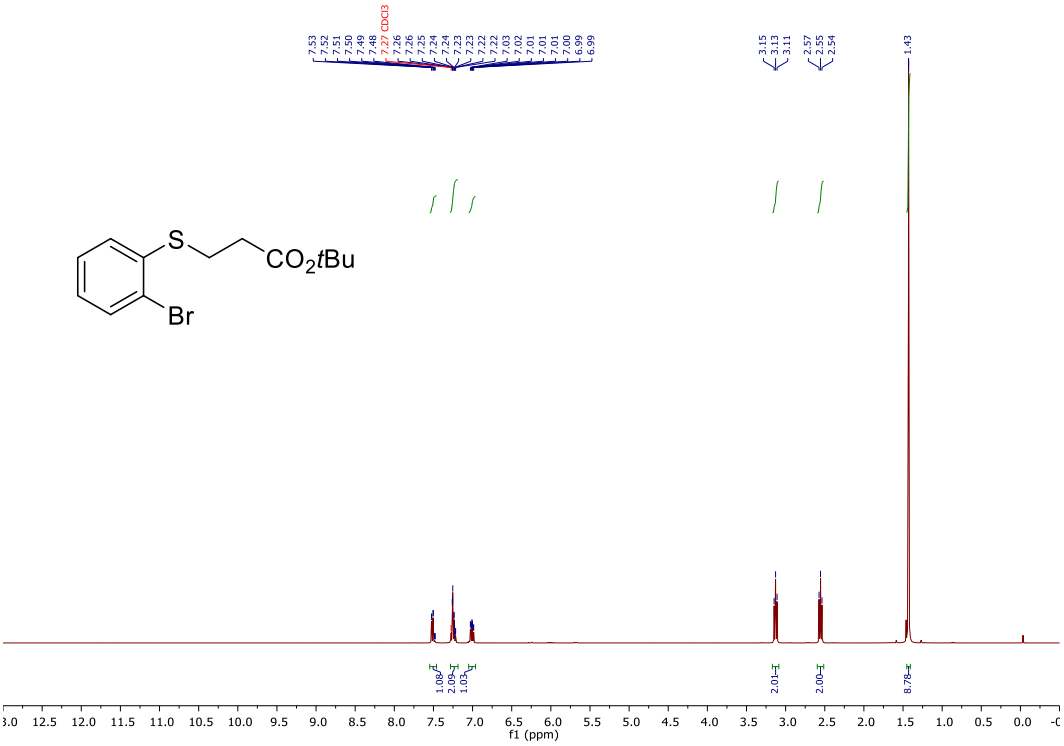


^{13}C NMR (101 MHz, Chloroform-*d*)

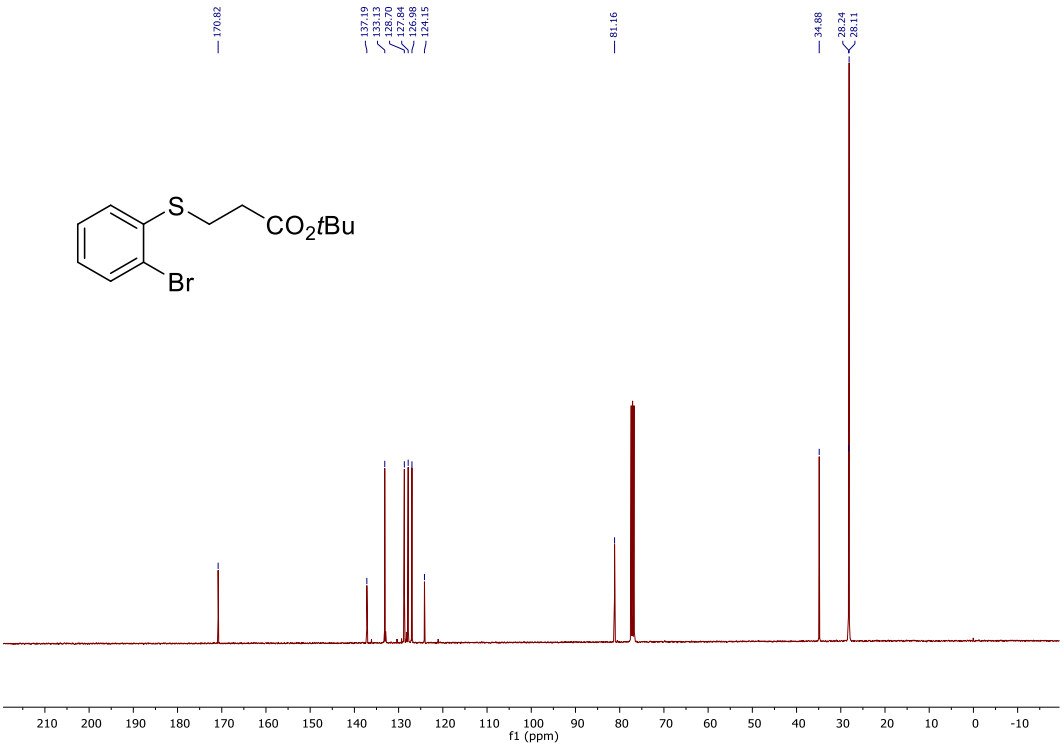


Tert-butyl 3-(2-bromophenylthio)propanoate (21h)

^{1}H NMR (400 MHz, Chloroform-*d*)

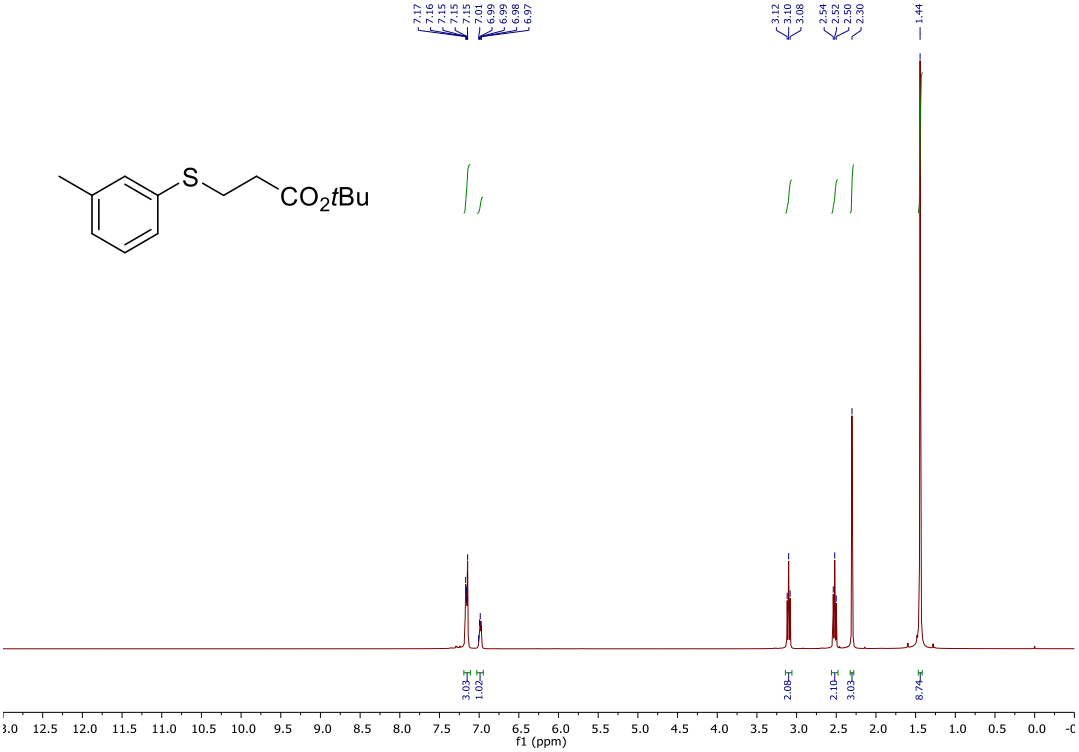


^{13}C NMR (101 MHz, Chloroform-*d*)

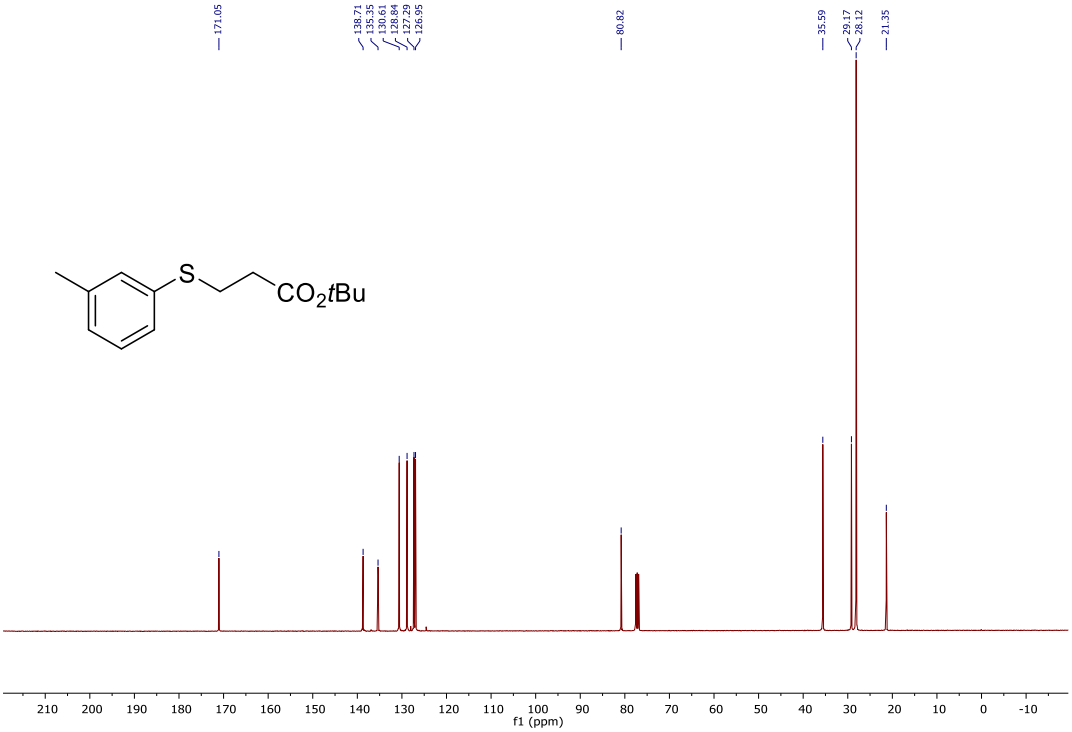


Tert-butyl 3-(3-methylphenylthio)propanoate (21i)

^{1}H NMR (400 MHz, Chloroform-*d*)

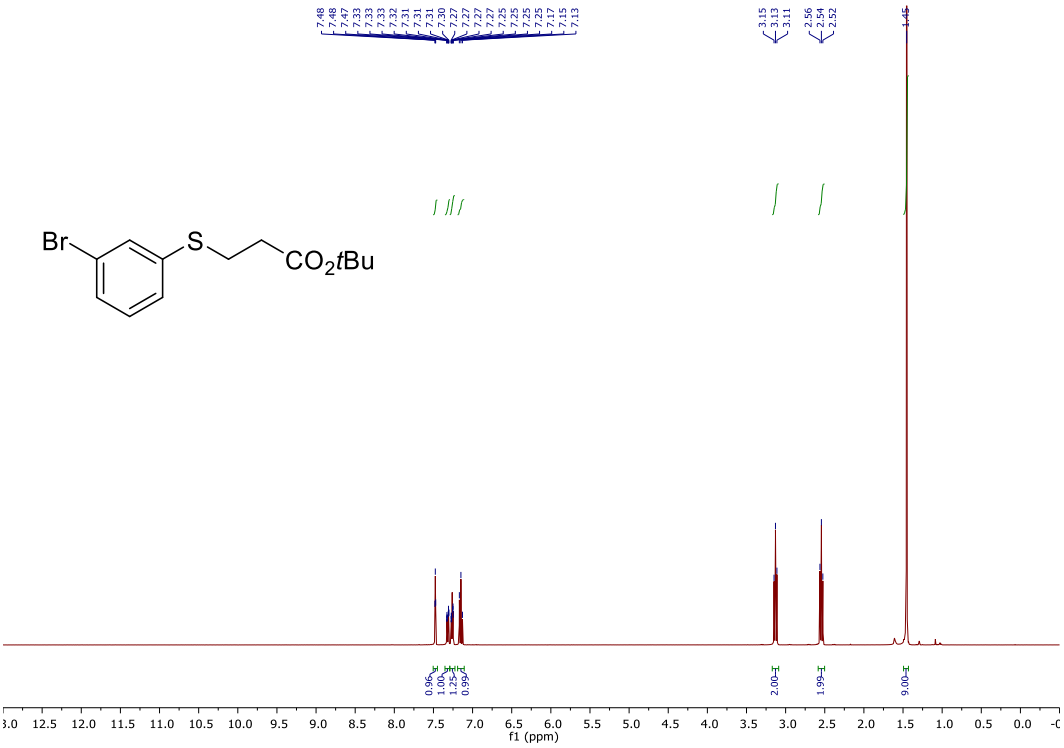


^{13}C NMR (101 MHz, Chloroform-*d*)

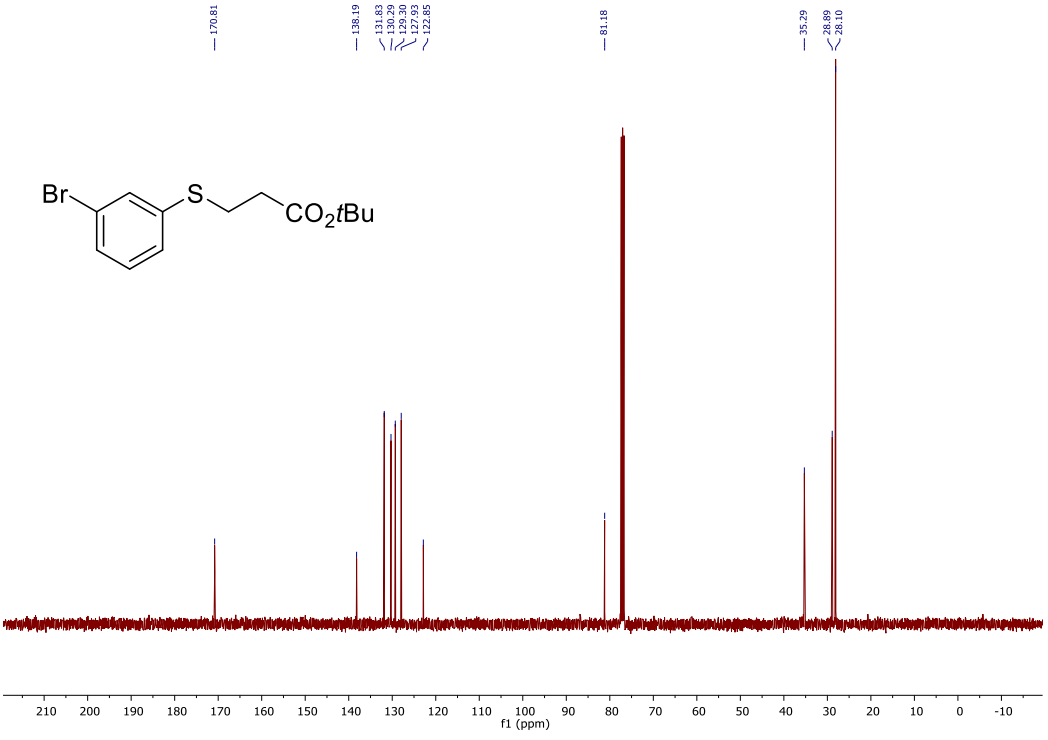


Tert-butyl 3-(3-bromophenylthio)propanoate (21j)

^{1}H NMR (400 MHz, Chloroform-*d*)

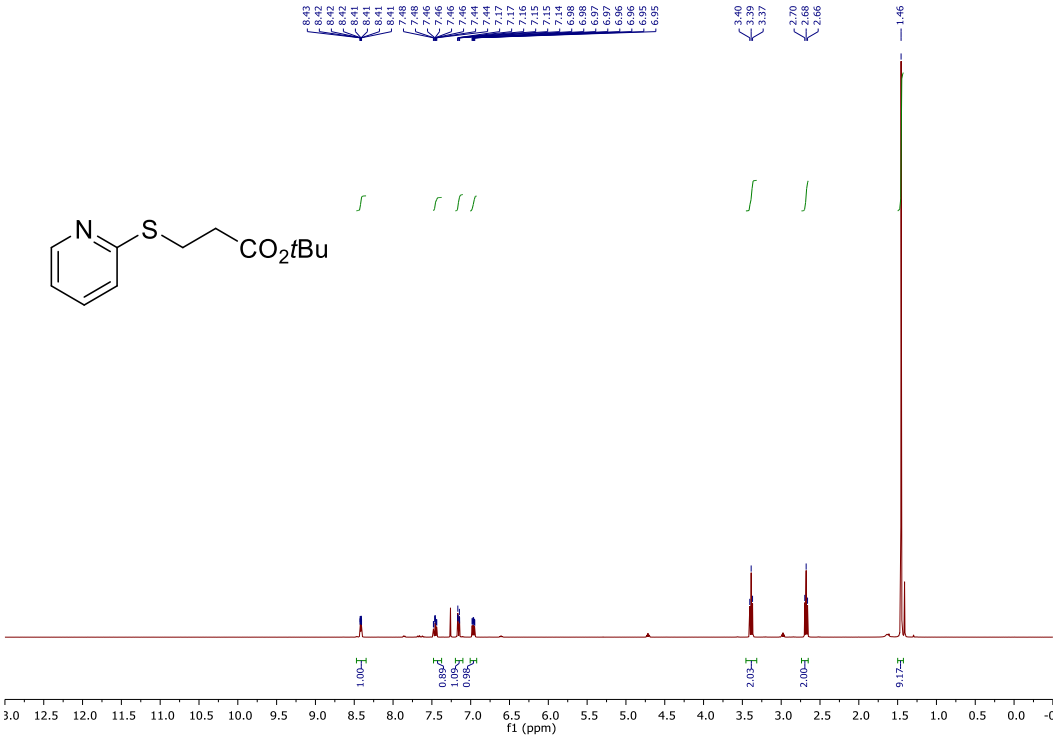


^{13}C NMR (101 MHz, Chloroform-*d*)

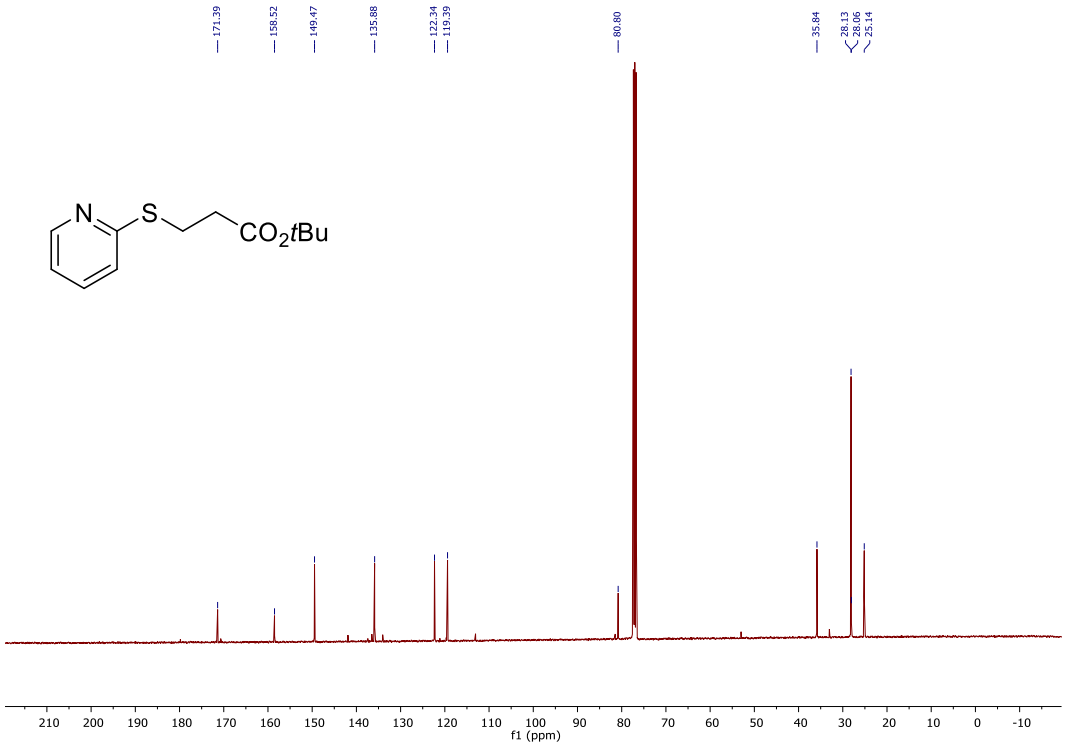


Tert-butyl 3-((pyridin-2-yl)thio)propanoate (21k)

^{1}H NMR (400 MHz, Chloroform-*d*)

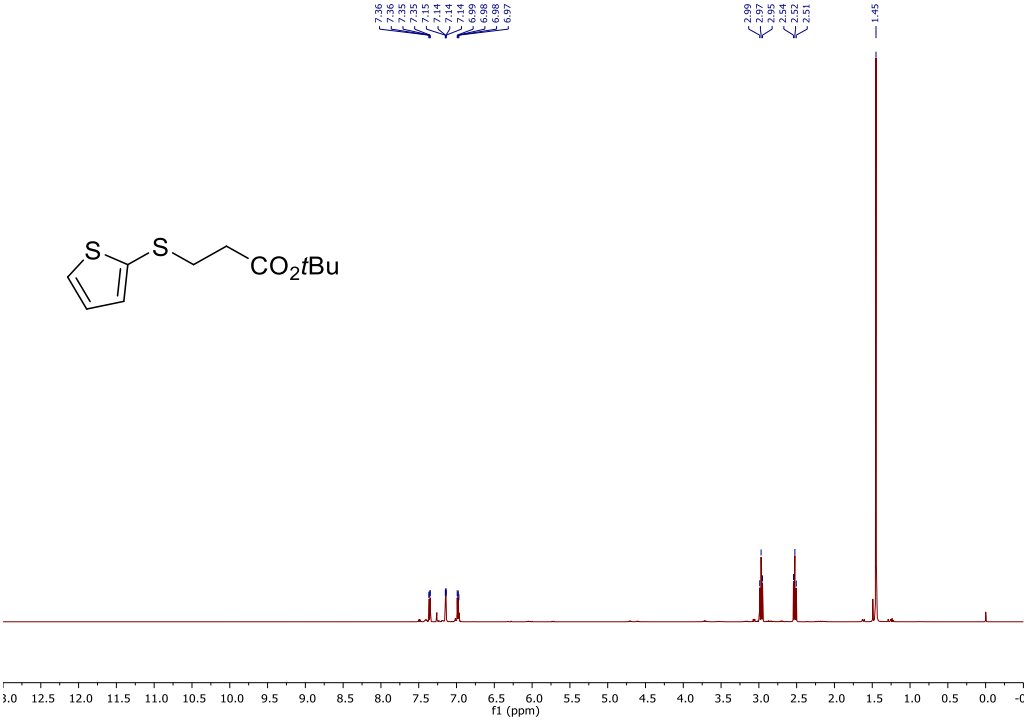


^{13}C NMR (101 MHz, Chloroform-*d*)

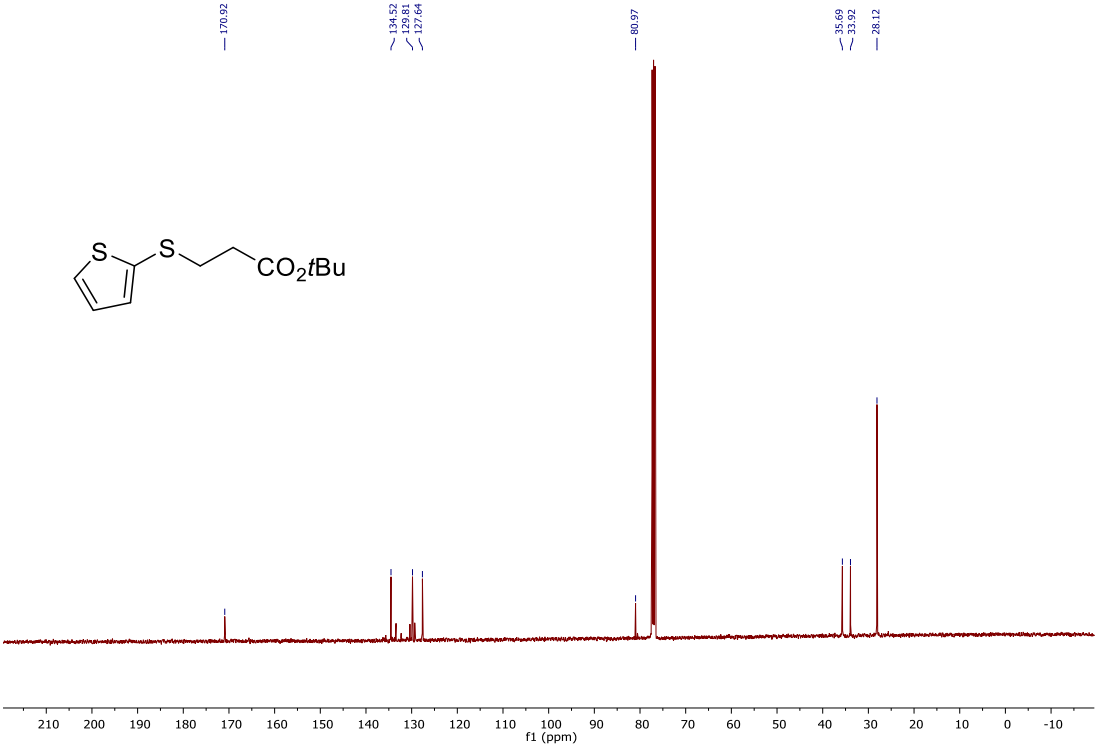


Tert-butyl 3-((thiophen-2-yl)thio)propanoate (21l)

^{1}H NMR (400 MHz, Chloroform-*d*)

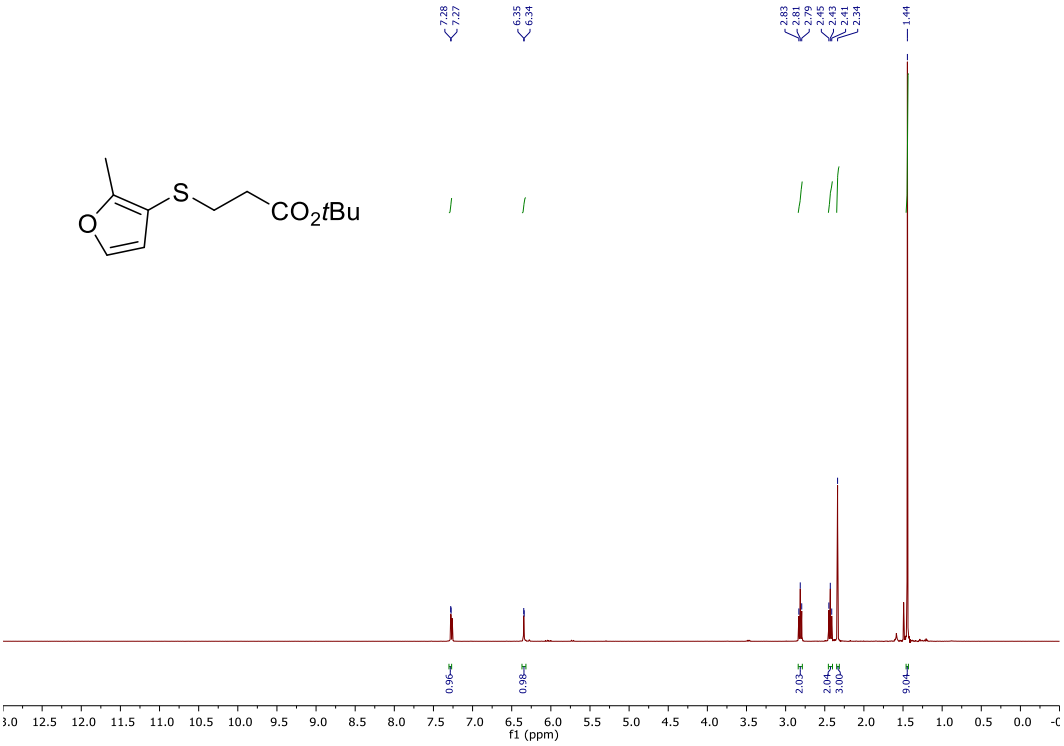


^{13}C NMR (101 MHz, Chloroform-*d*)

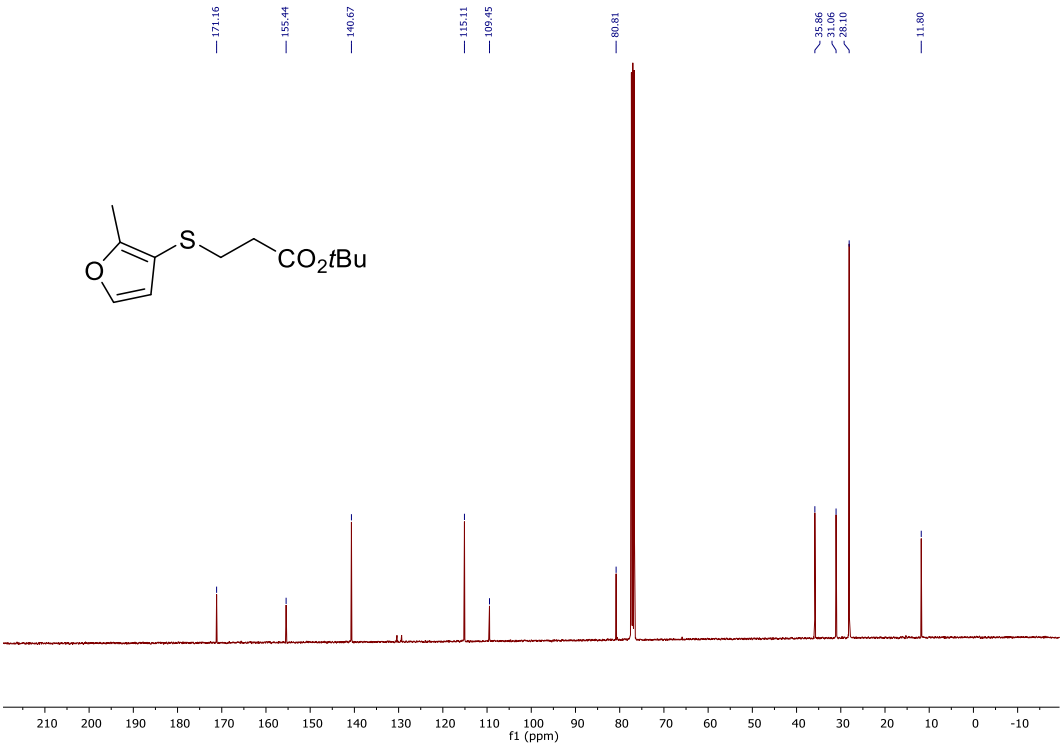


Tert-butyl 3-((2-methylfuran-3-yl)thio)propanoate (21m)

^{1}H NMR (400 MHz, Chloroform-*d*)

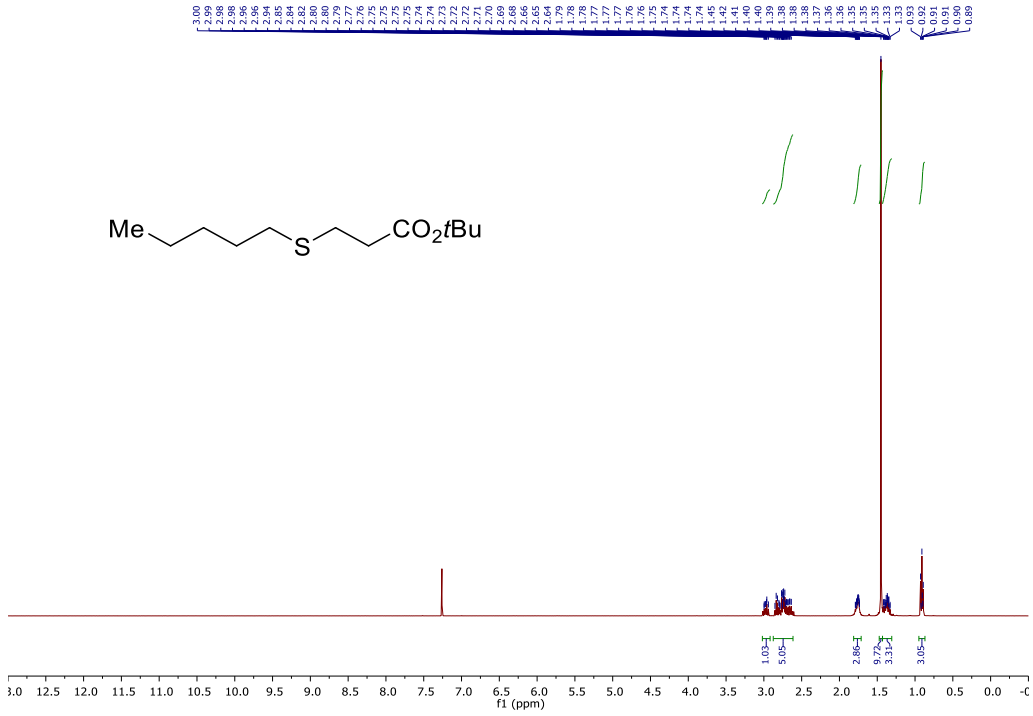


^{13}C NMR (101 MHz, Chloroform-*d*)

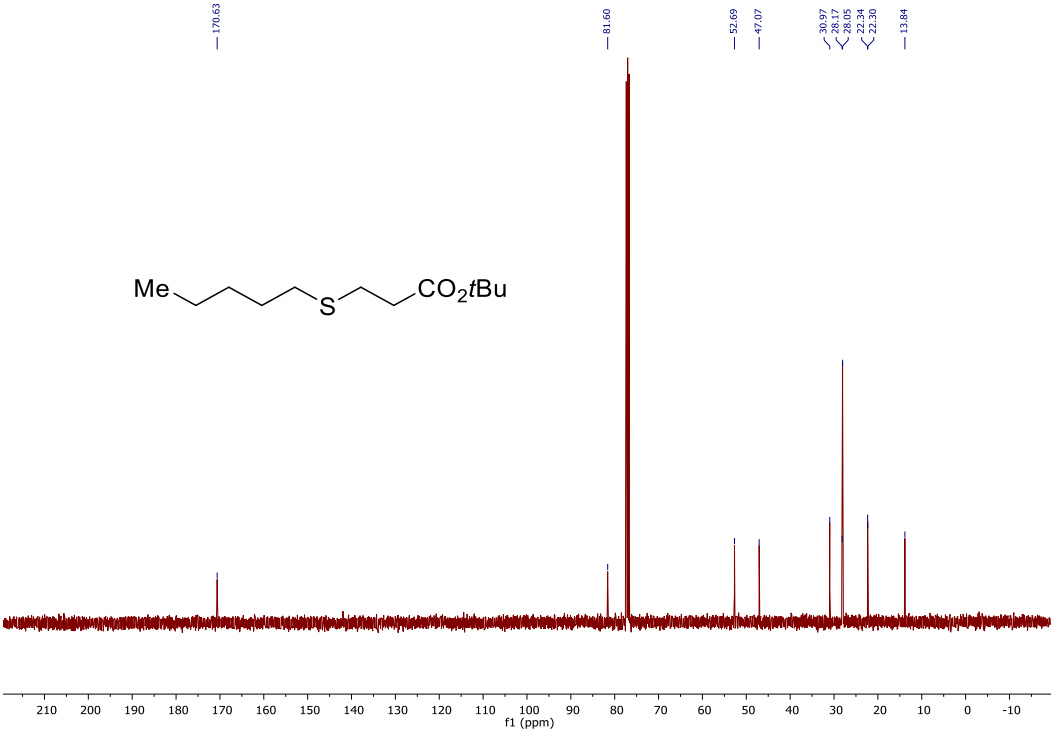


Tert-butyl 3-(pentylthio)propanoate (21n)

^{1}H NMR (400 MHz, Chloroform-d)

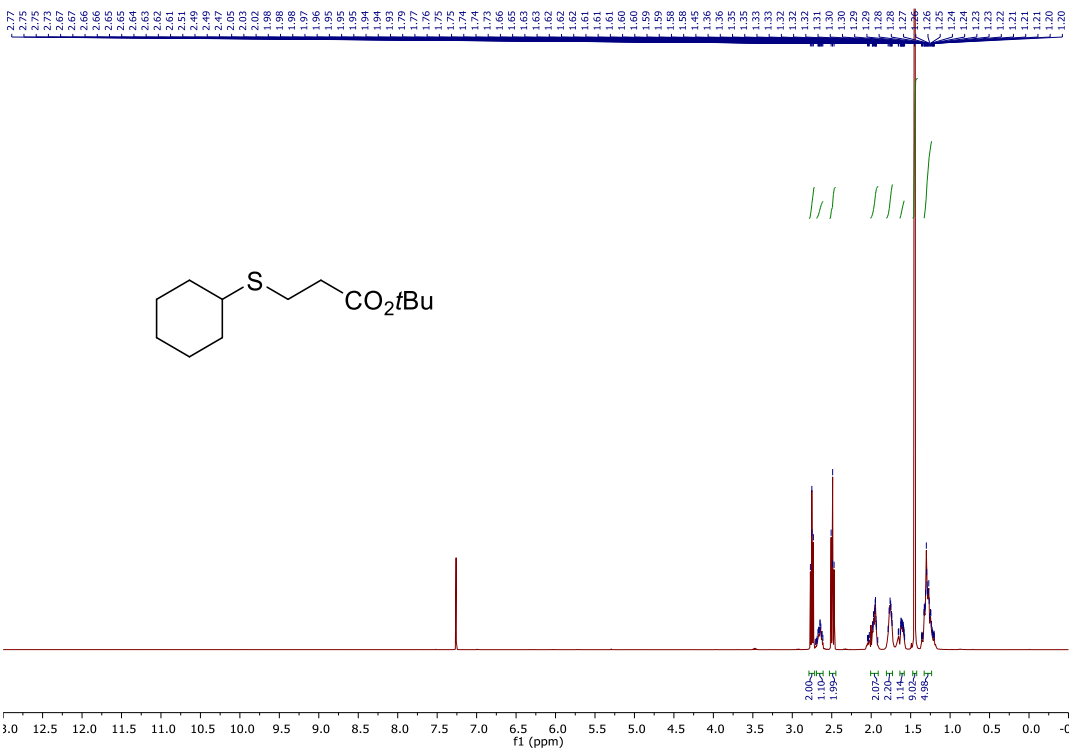


^{13}C NMR (101 MHz, Chloroform-d)

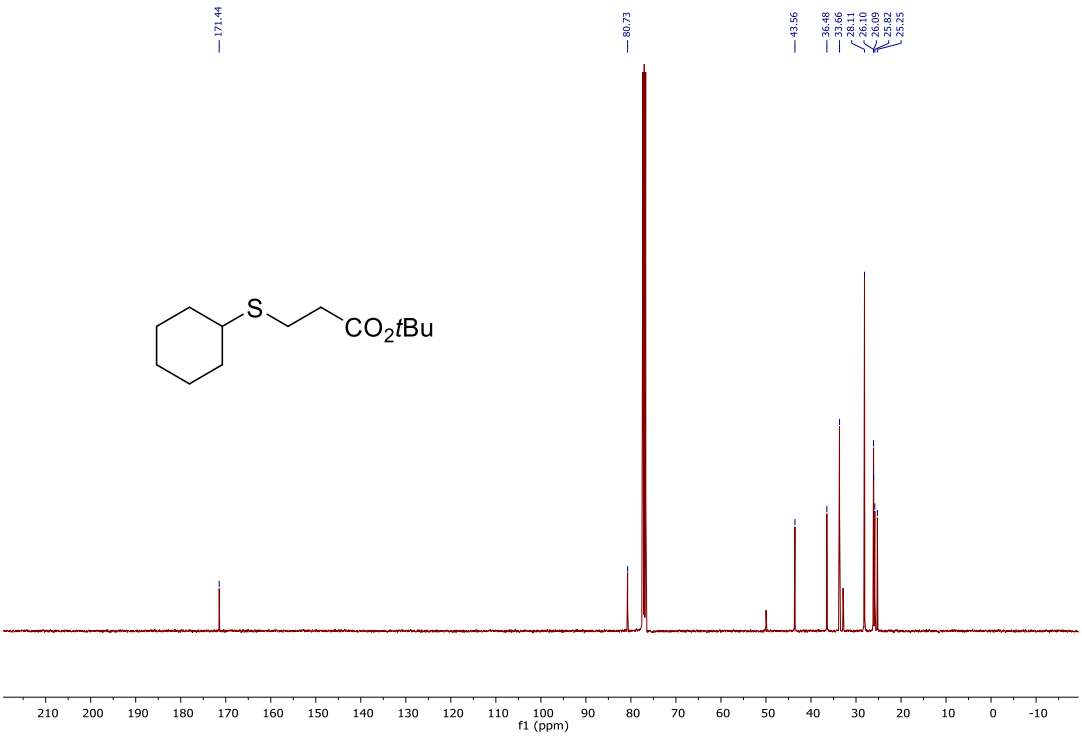


Tert-butyl 3-(cyclohexylthio)propanoate (21o)

^{1}H NMR (400 MHz, Chloroform-*d*)

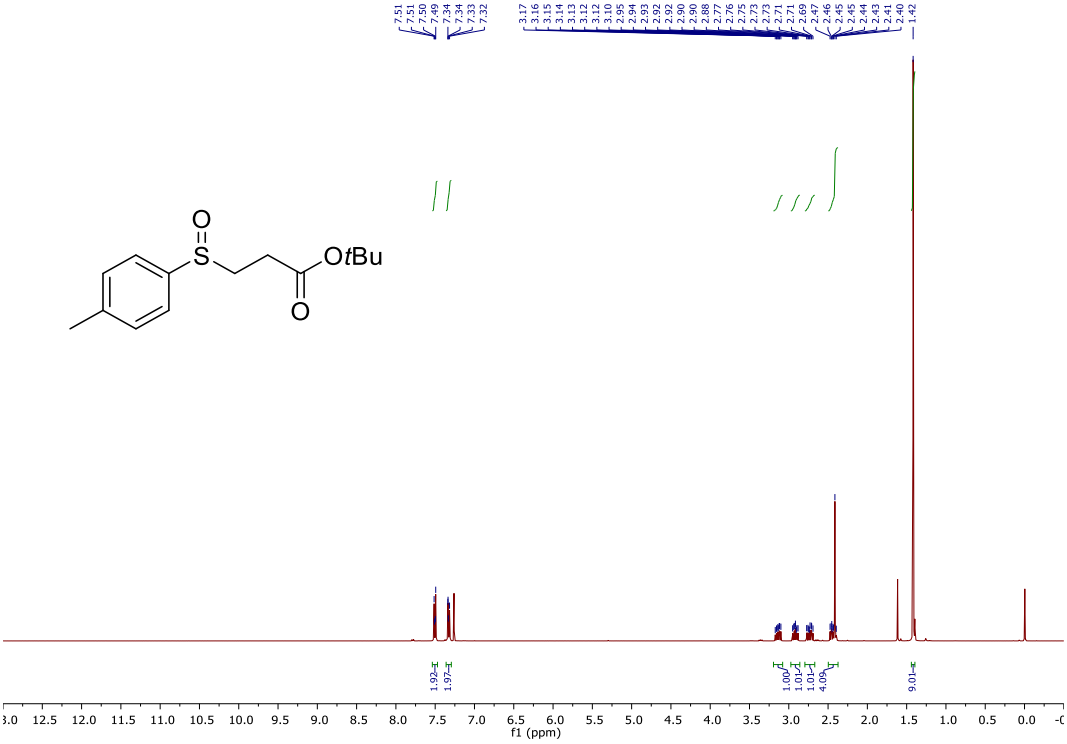


^{13}C NMR (101 MHz, Chloroform-*d*)

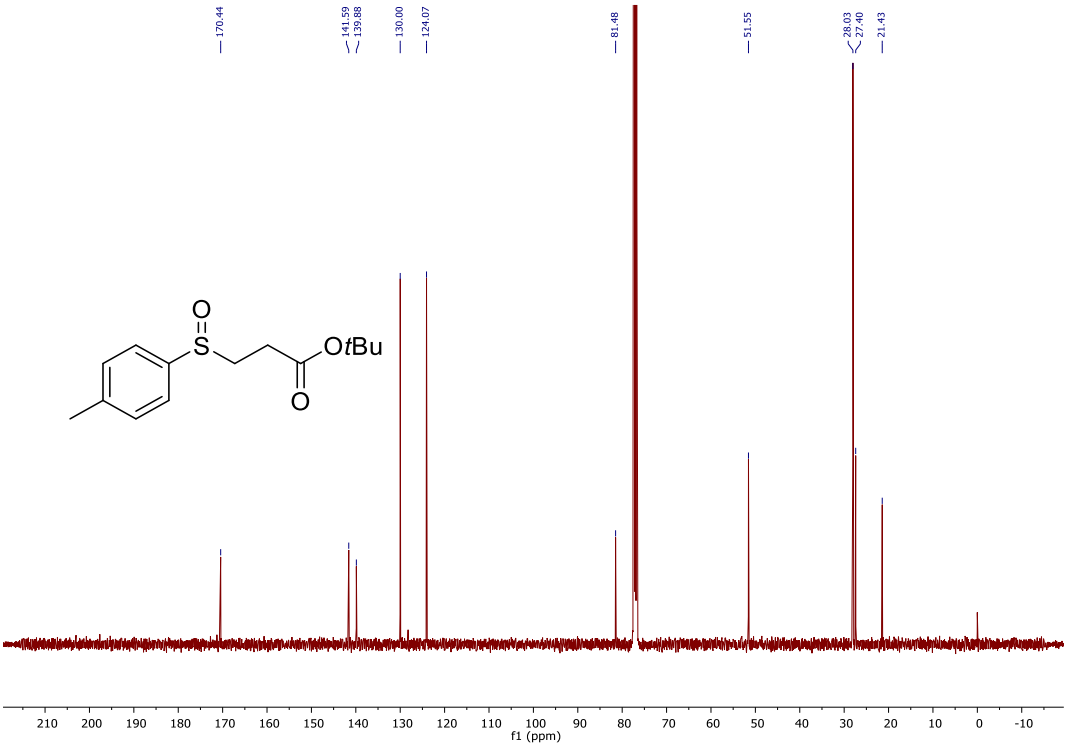


Tert-butyl 3-((4-methylphenyl)sulfinyl)propanoate (6a)

^{1}H NMR (400 MHz, Chloroform-*d*)

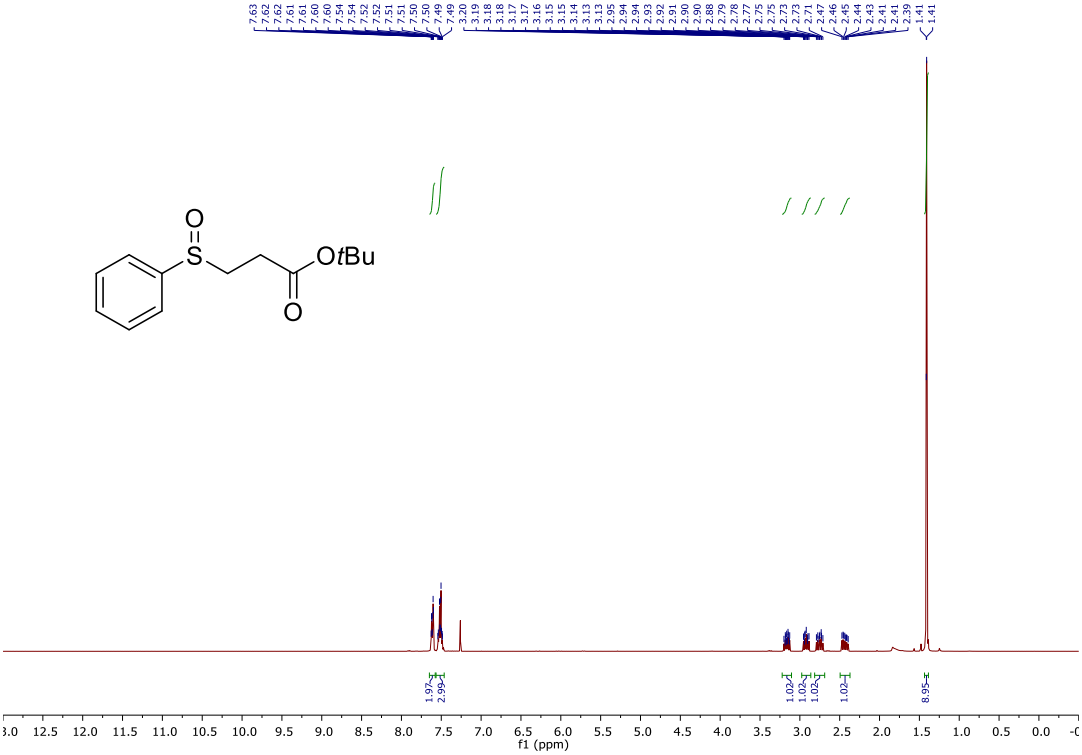


^{13}C NMR (101 MHz, Chloroform-*d*)

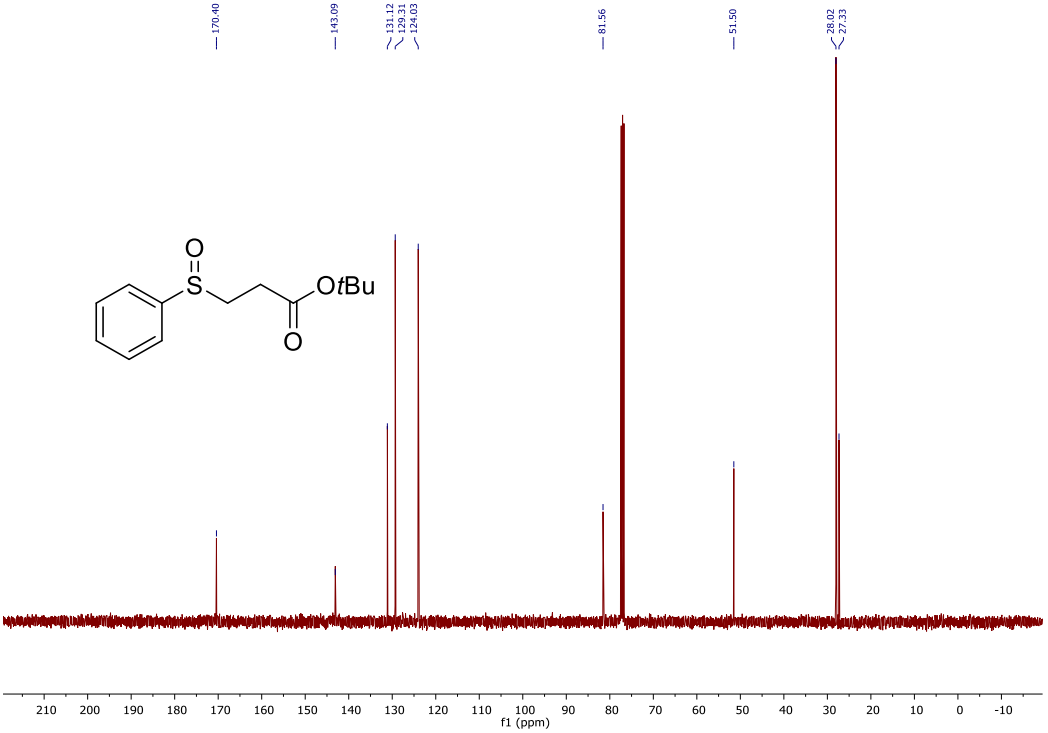


Tert-butyl 3-[(phenyl)sulfinyl]propanoate (6b)

^{1}H NMR (400 MHz, Chloroform-*d*)

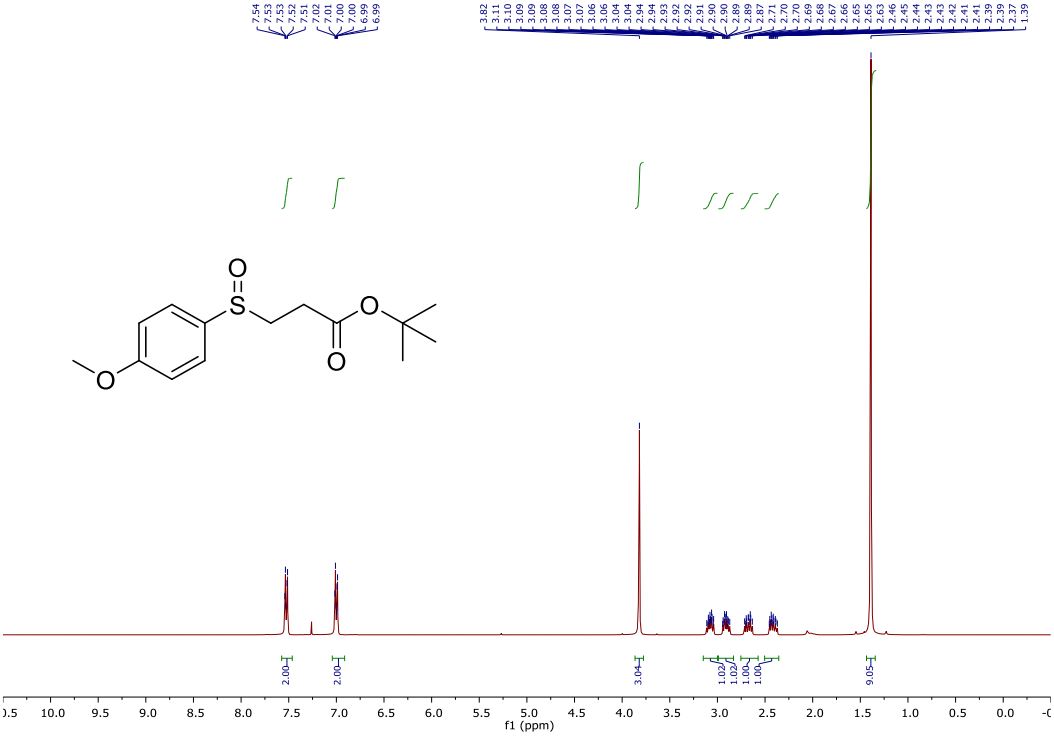


^{13}C NMR (101 MHz, Chloroform-*d*)

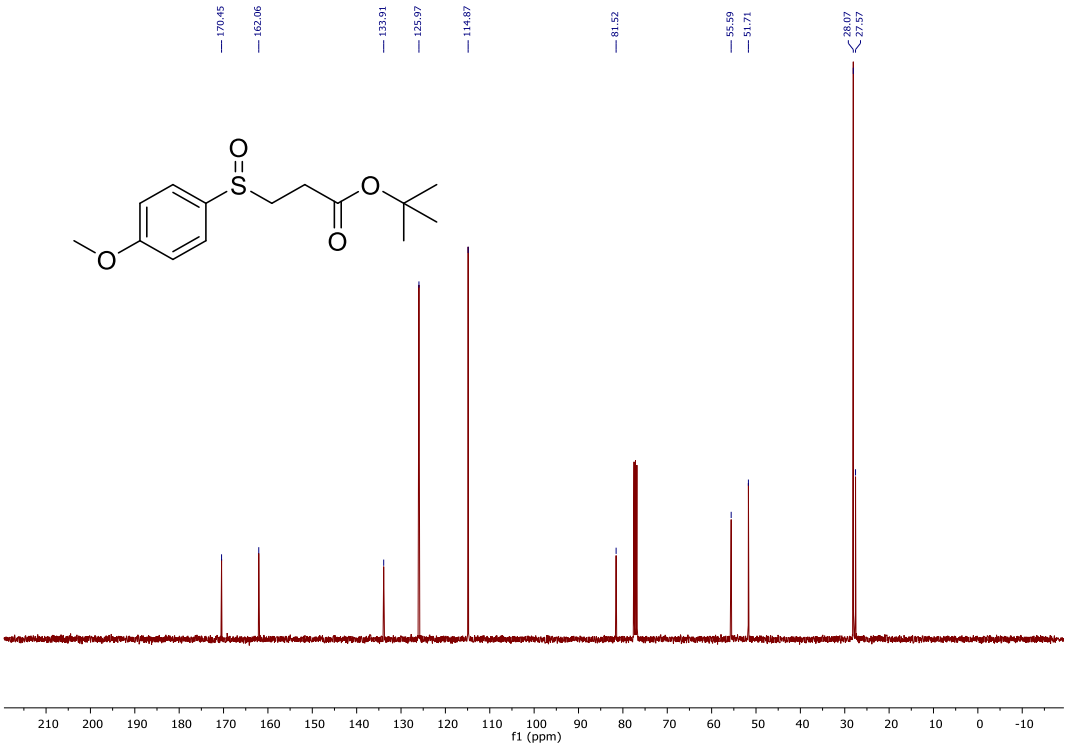


Tert-butyl 3-[(4-methoxyphenyl)sulfinyl]propanoate (6c)

^{1}H NMR (400 MHz, Chloroform-*d*)

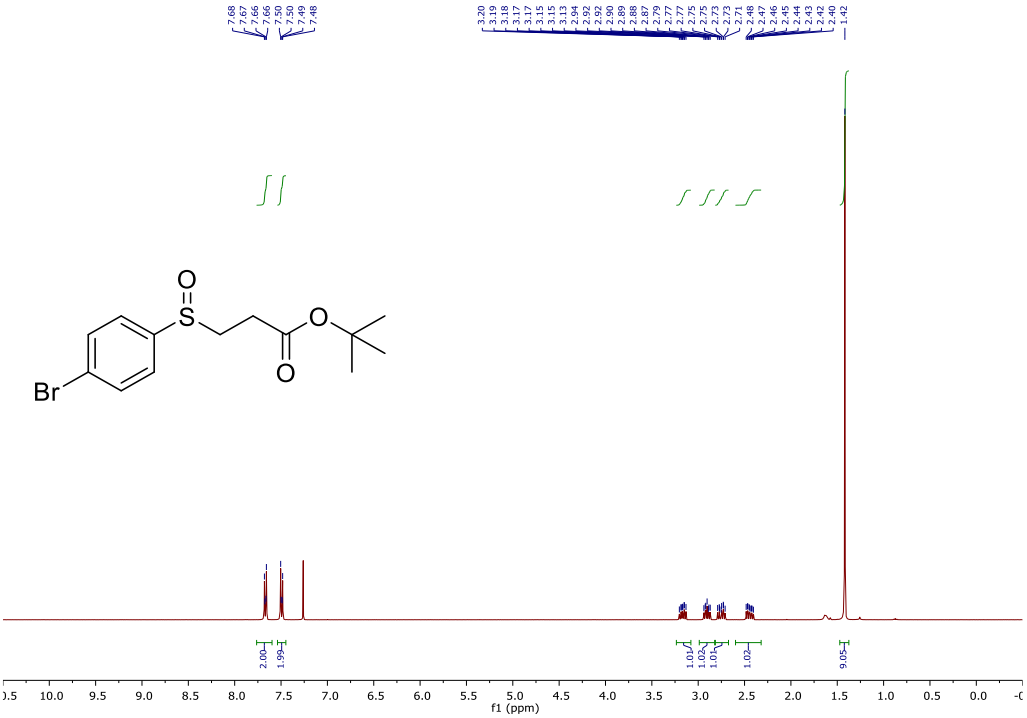


^{13}C NMR (101 MHz, Chloroform-*d*)

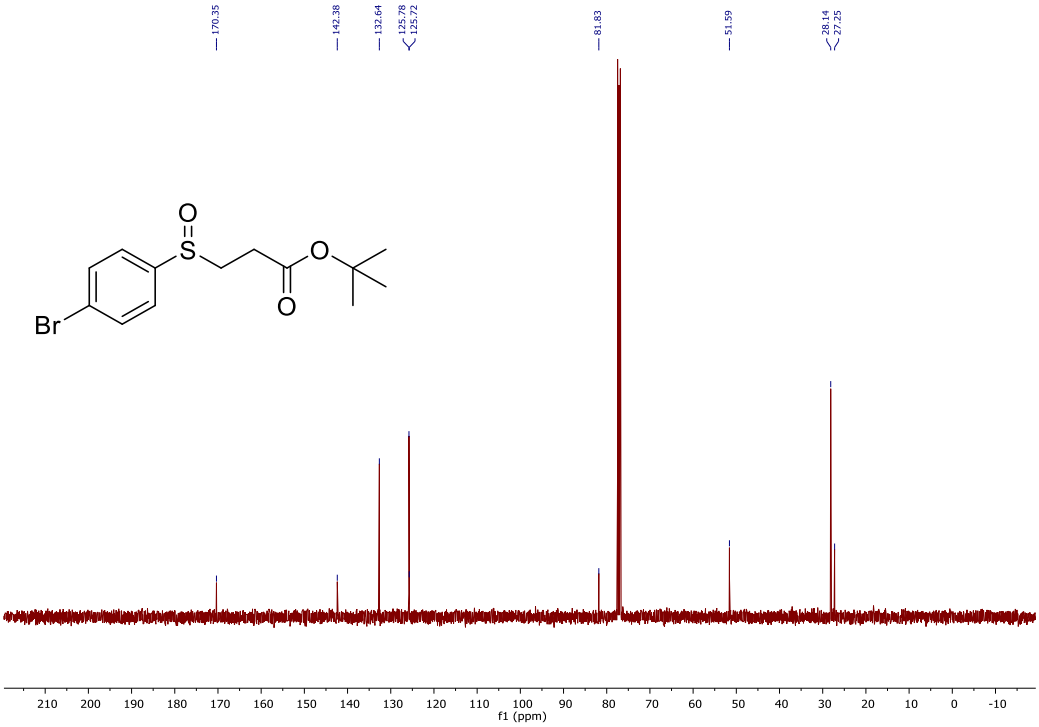


Tert-butyl 3-[(4-bromophenyl)sulfinyl]propanoate (6d)

^{1}H NMR (400 MHz, Chloroform-*d*)

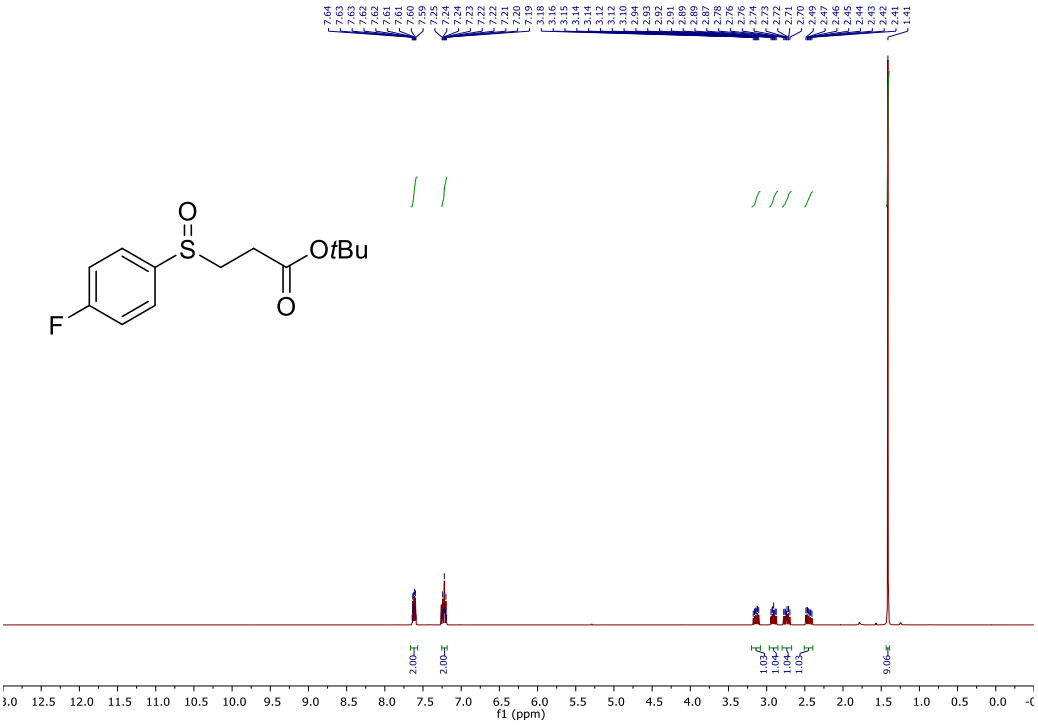


^{13}C NMR (101 MHz, Chloroform-*d*)

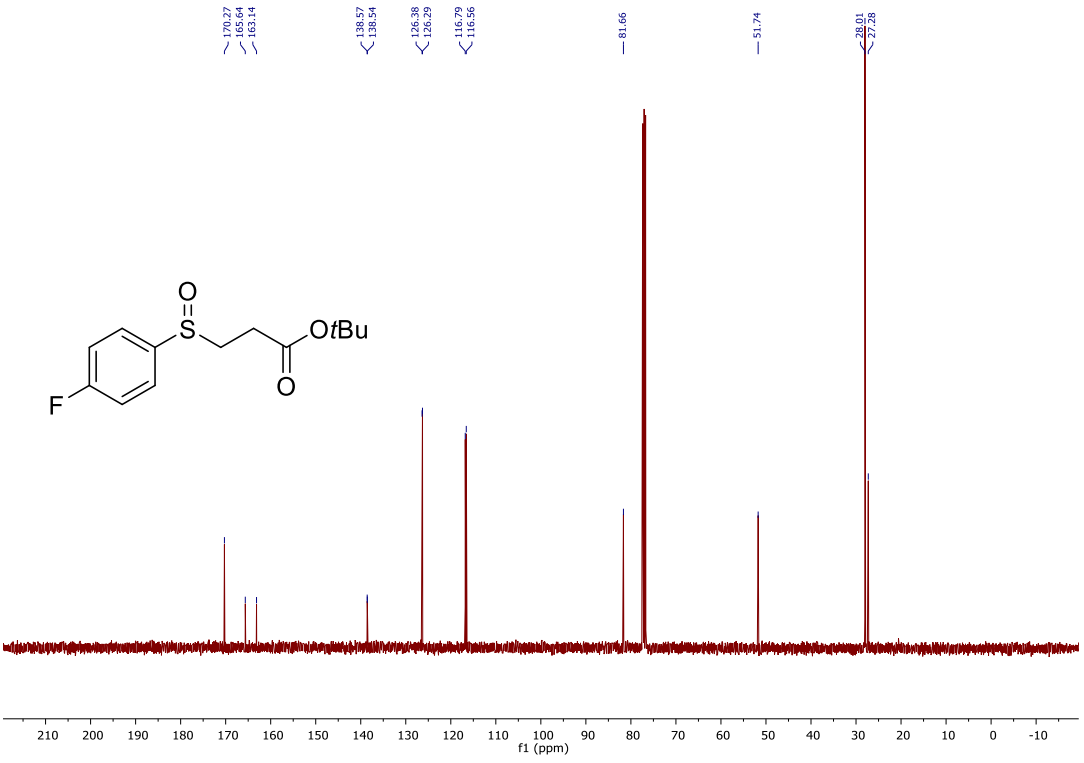


Tert-butyl 3-[(4-fluorophenyl)sulfinyl]propanoate (6e)

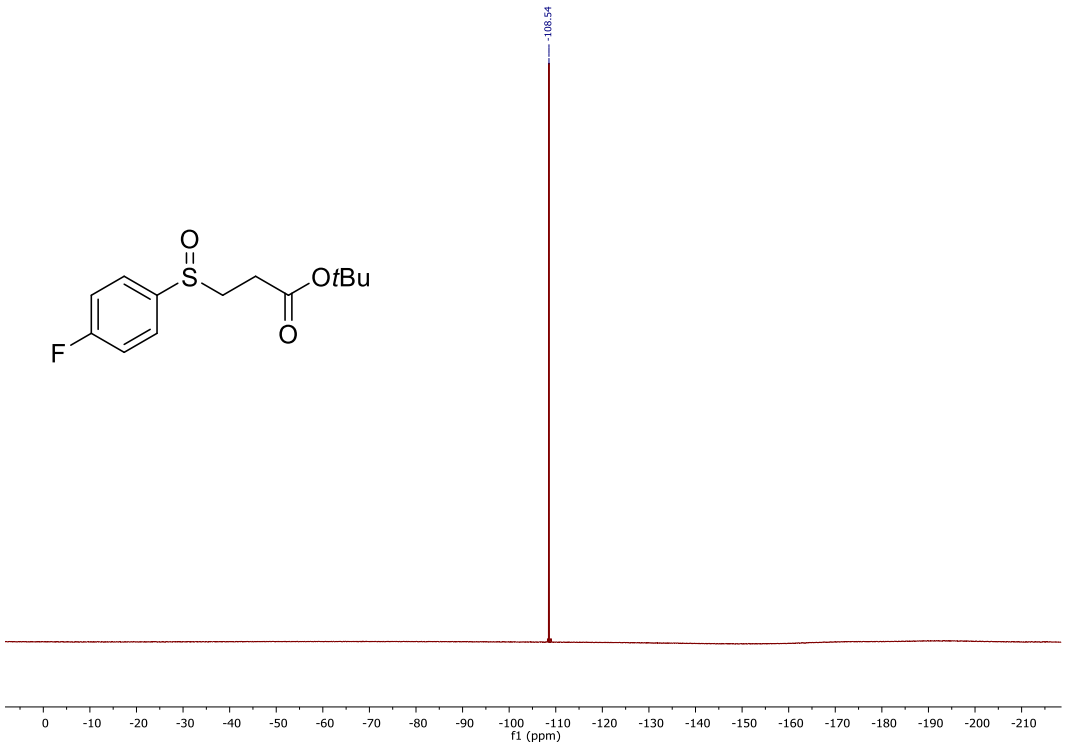
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)

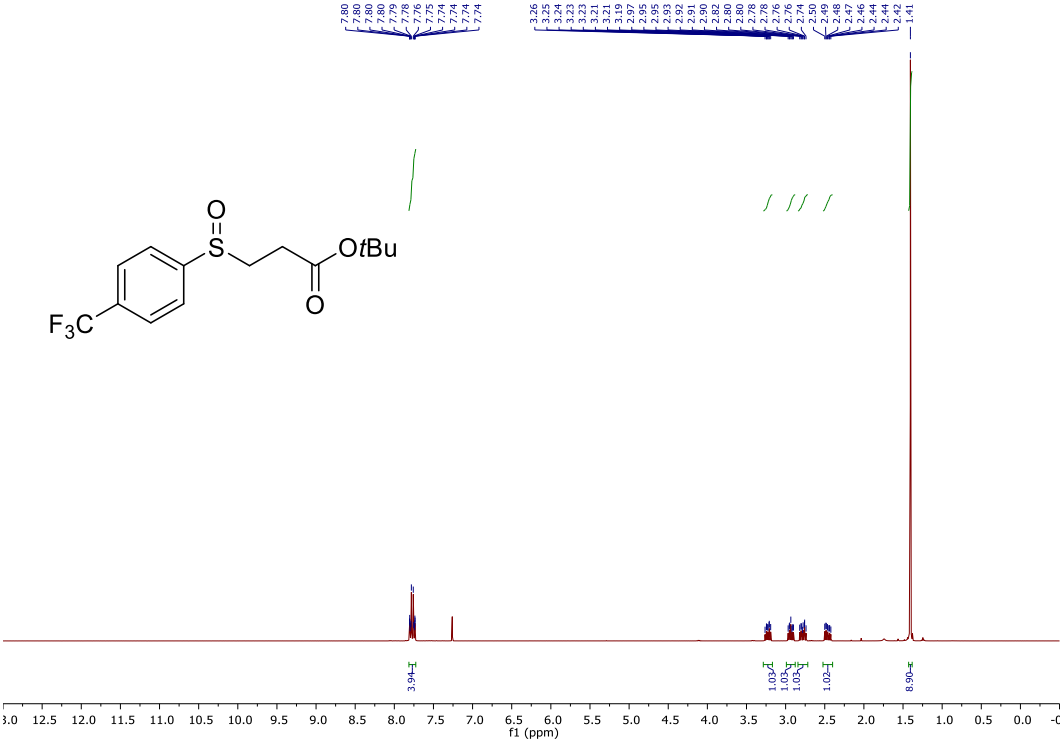


^{19}F NMR (376 MHz, Chloroform-d)

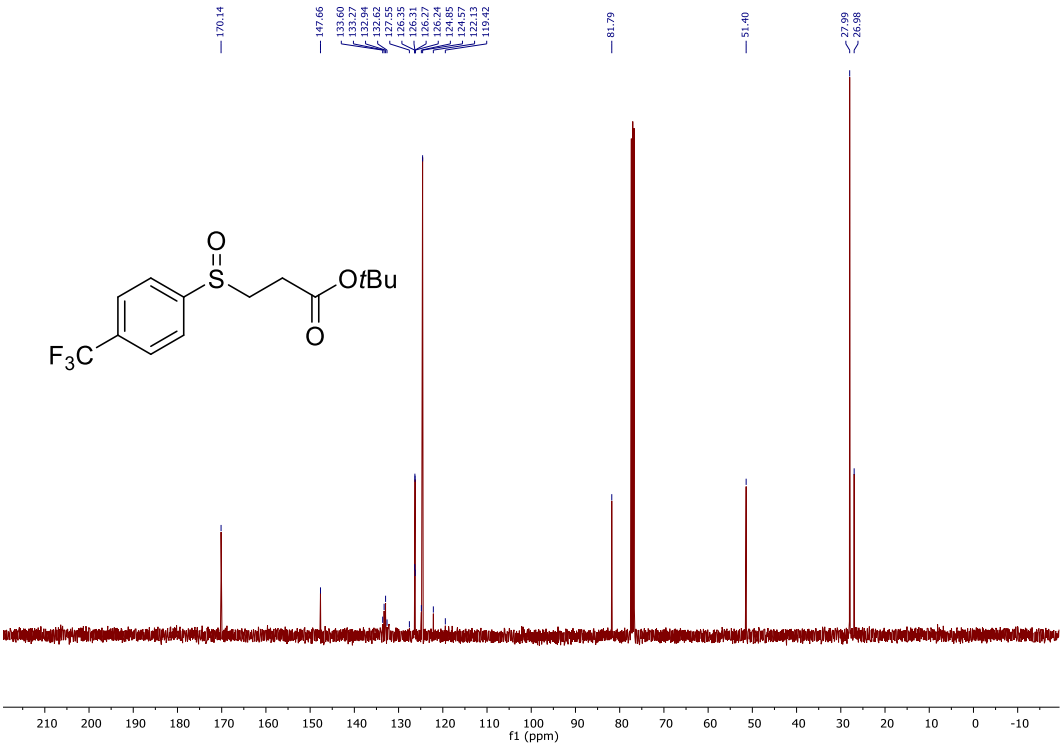


Tert-butyl 3-[(4-trifluoromethylphenyl)sulfinyl]propanoate (6f)

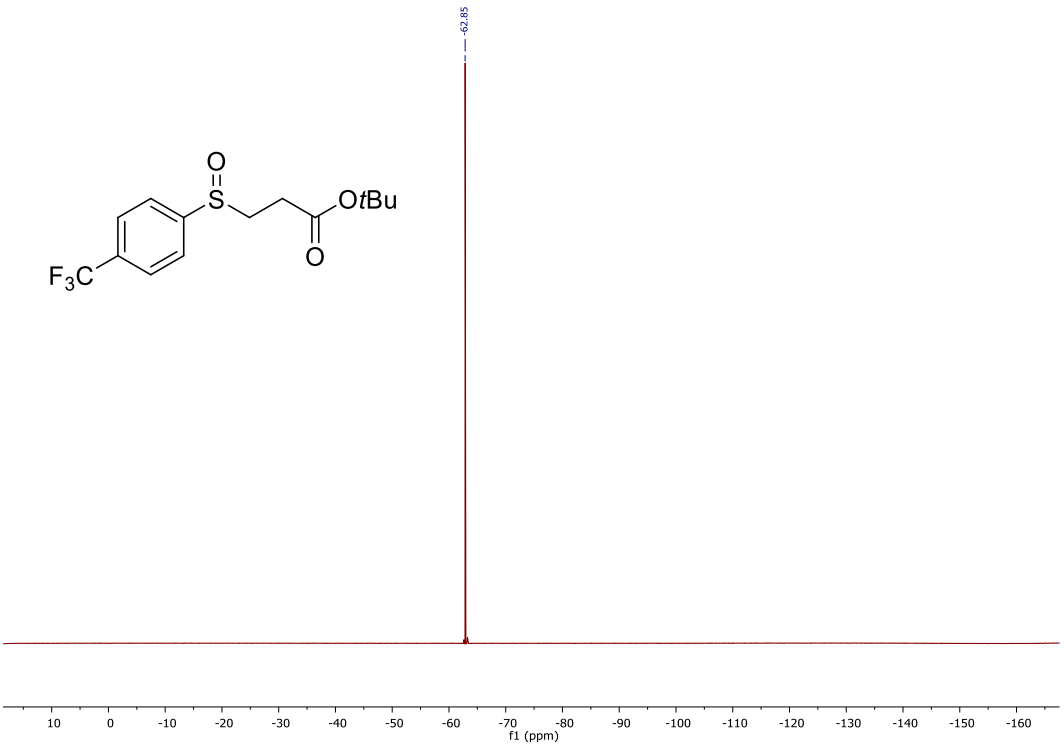
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)

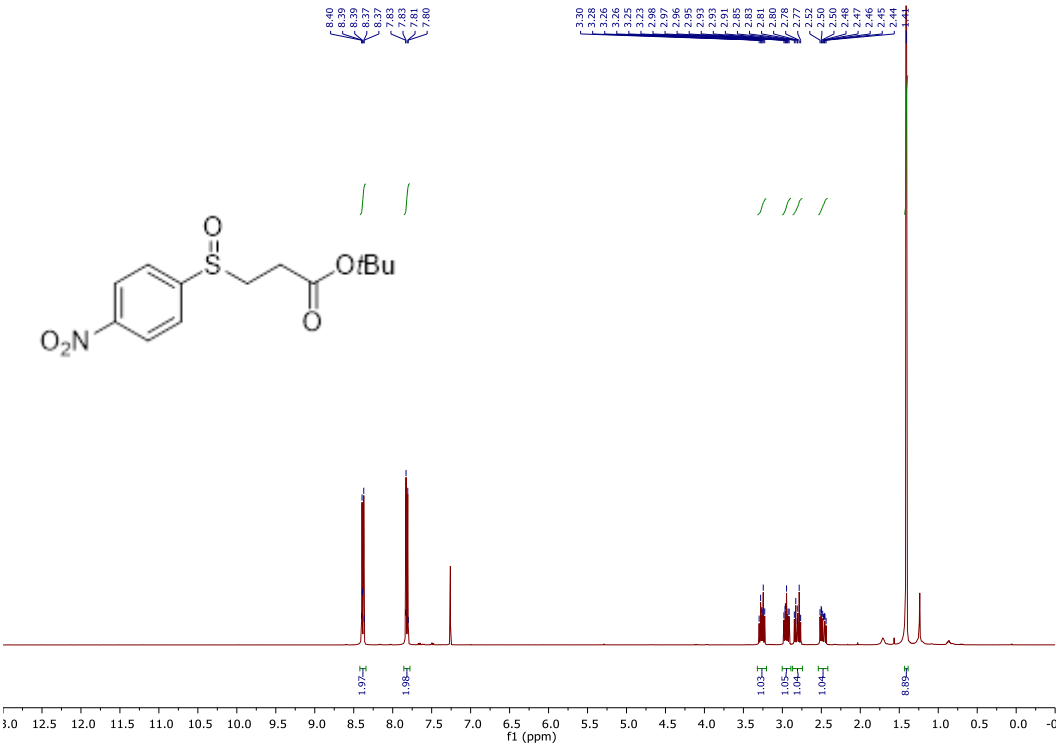


^{19}F NMR (376 MHz, Chloroform-d)

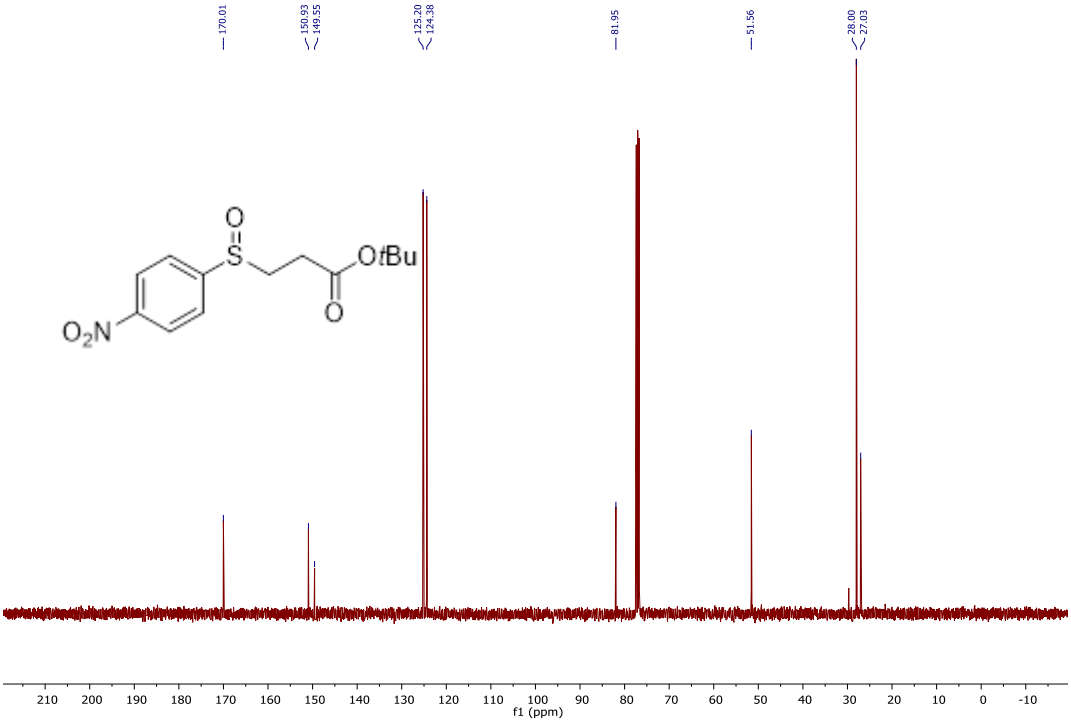


Tert-butyl 3-[(4-nitrophenyl)sulfinyl]propanoate (6g)

^{1}H NMR (400 MHz, Chloroform-*d*)

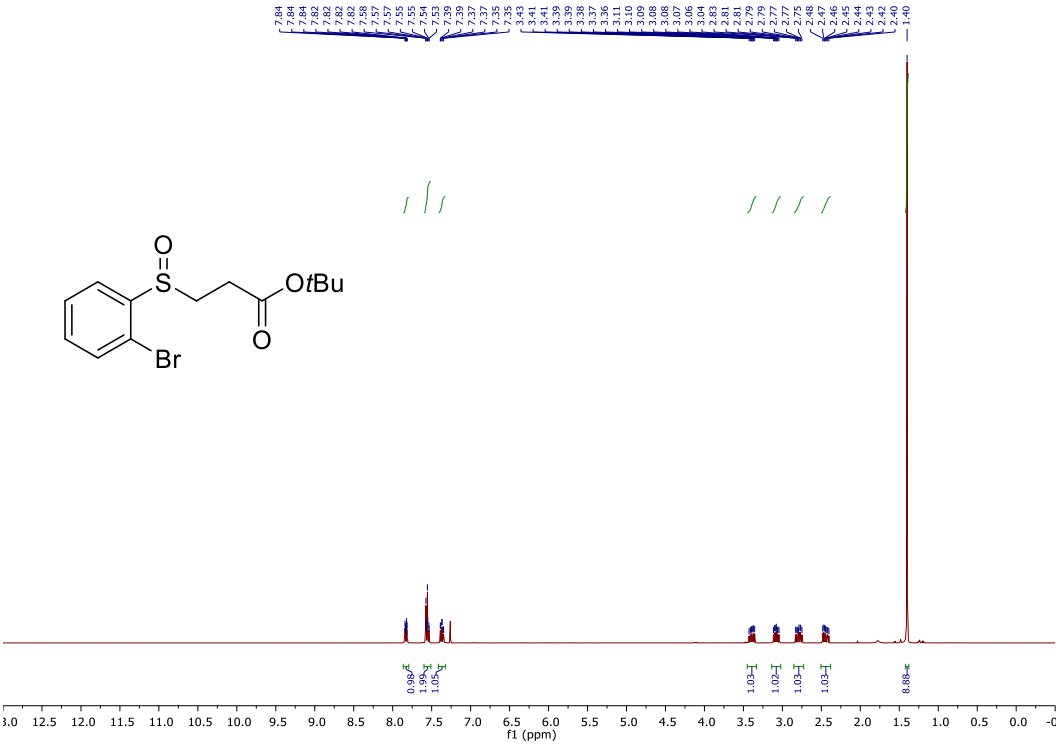


^{13}C NMR (101 MHz, Chloroform-*d*)

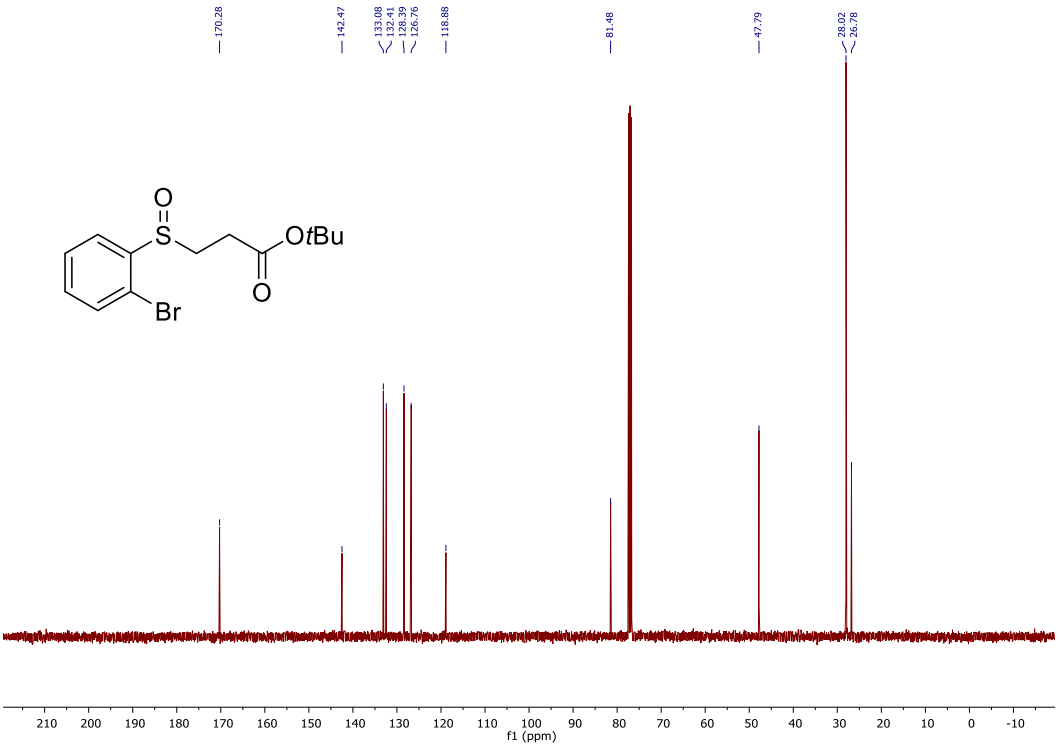


Tert-butyl 3-[(2-bromophenyl)sulfinyl]propanoate (6h)

^{1}H NMR (400 MHz, Chloroform-*d*)

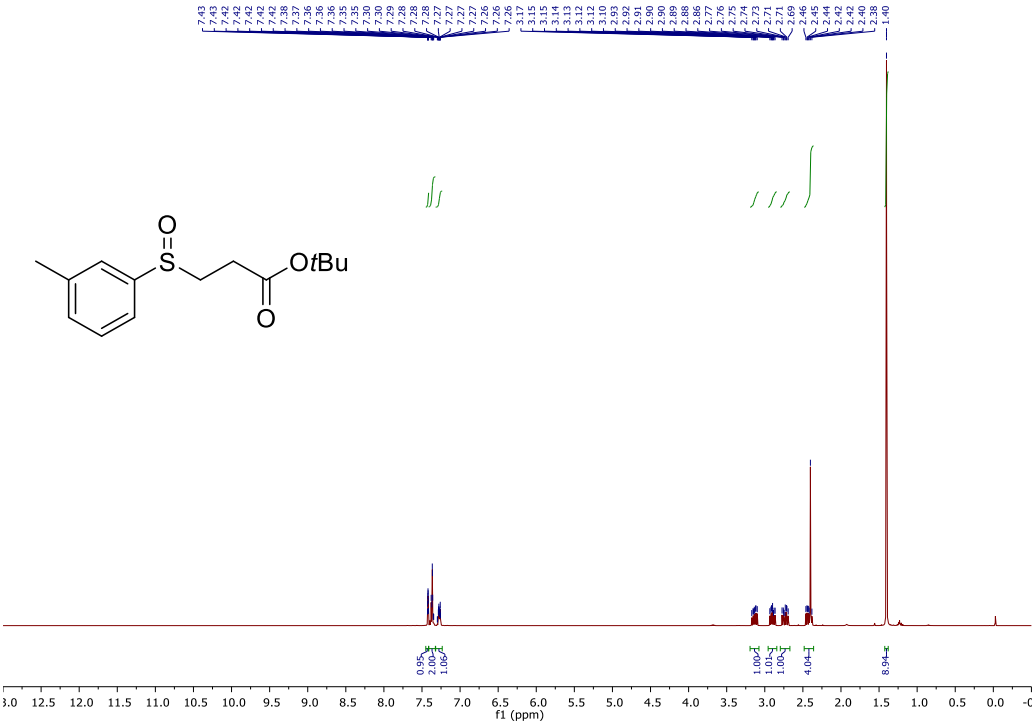


^{13}C NMR (101 MHz, Chloroform-*d*)

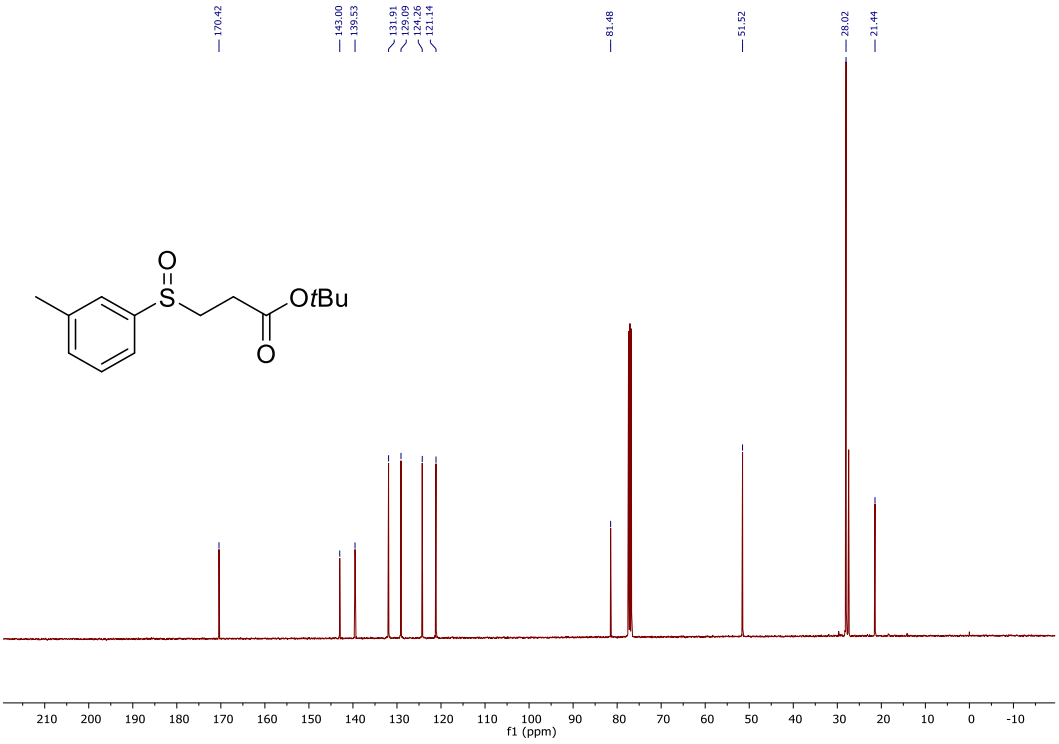


Tert-butyl 3-[(3-methylphenyl)sulfinyl]propanoate (6i)

^{1}H NMR (400 MHz, Chloroform-*d*)

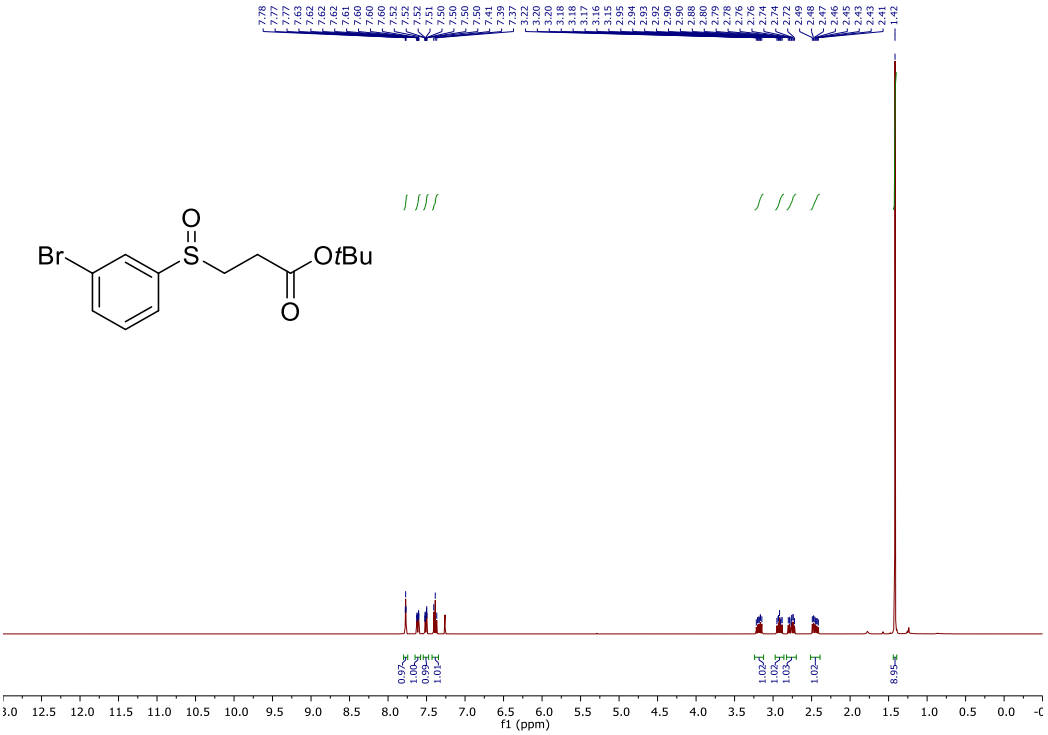


^{13}C NMR (101 MHz, Chloroform-*d*)

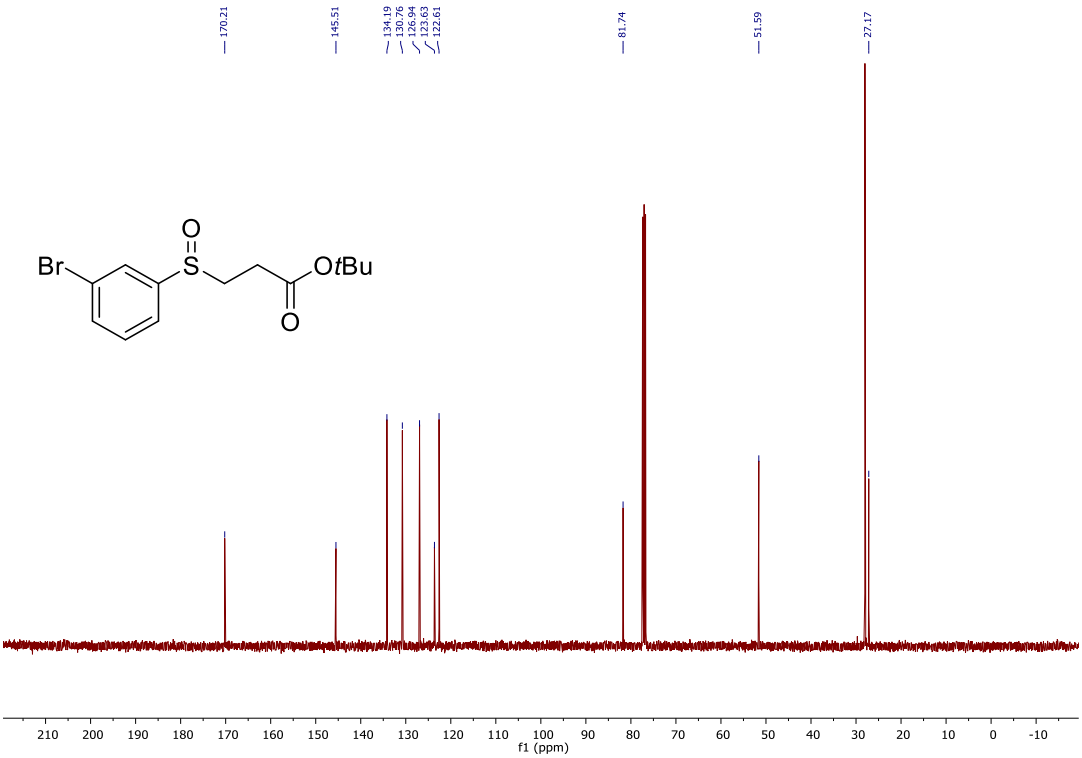


Tert-butyl 3-[(3-bromophenyl)sulfinyl]propanoate (6j)

^{1}H NMR (400 MHz, Chloroform-*d*)

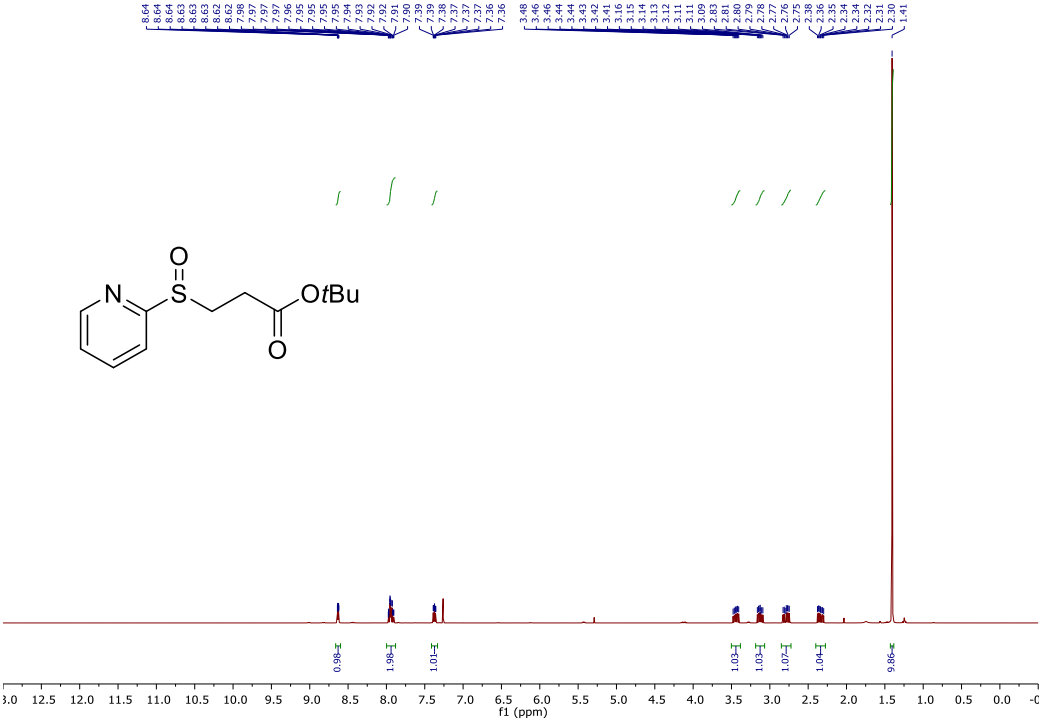


^{13}C NMR (101 MHz, Chloroform-*d*)

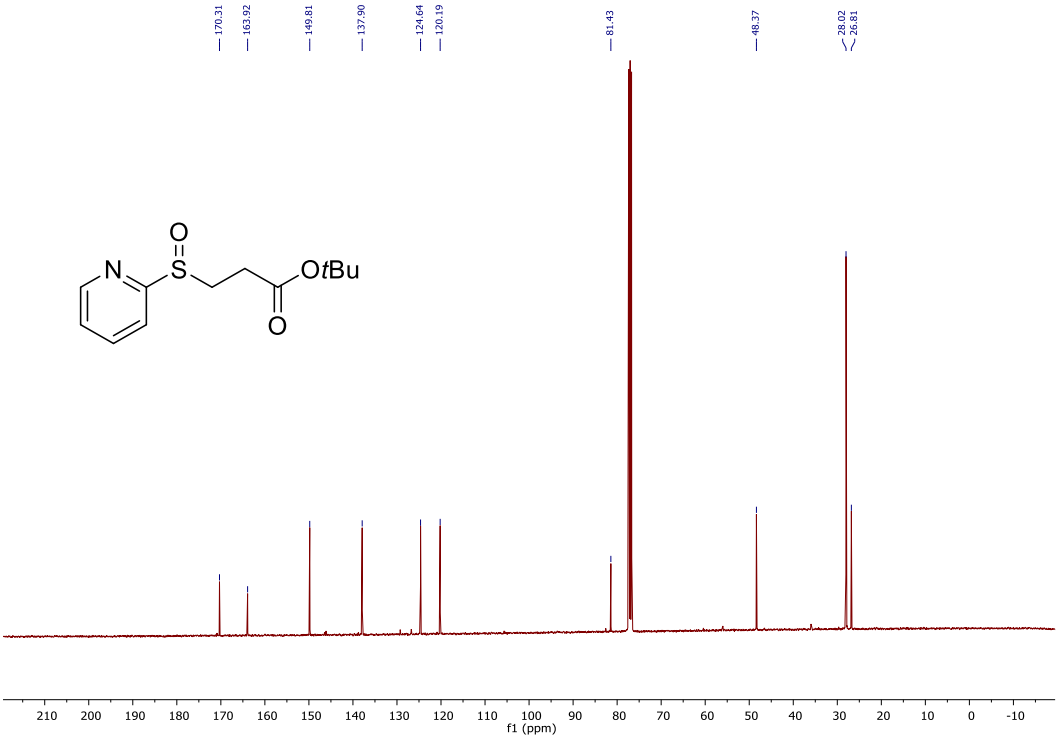


Tert-butyl 3-((pyridin-2-yl)sulfinyl)propanoate (6k)

^{1}H NMR (400 MHz, Chloroform-*d*)

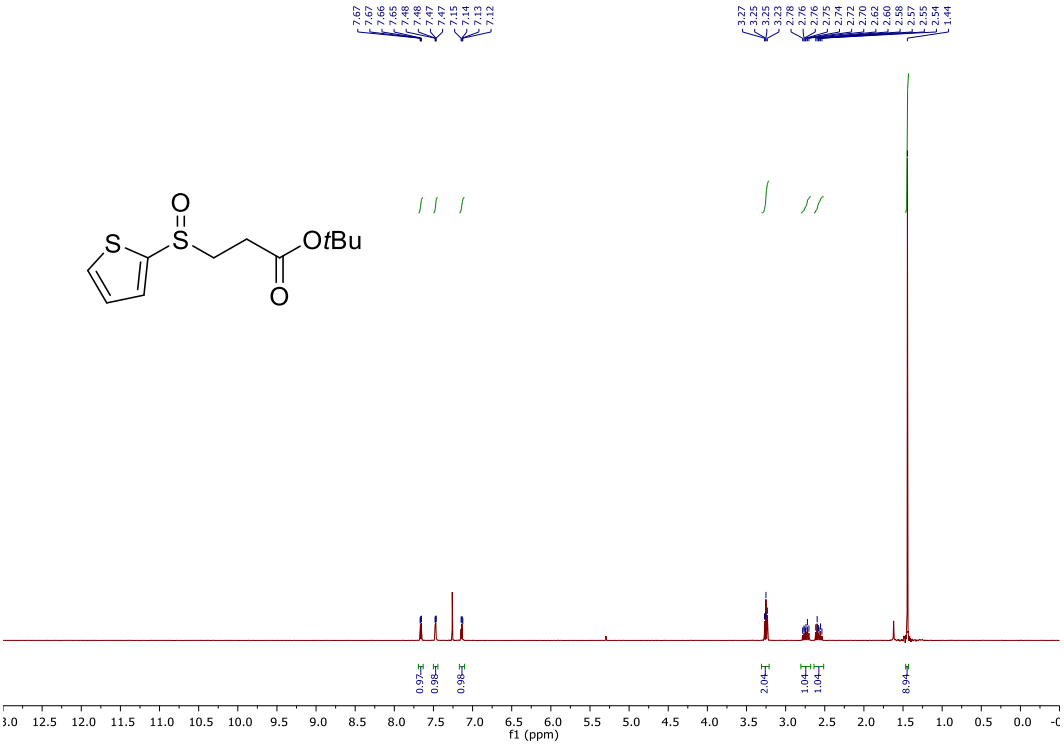


^{13}C NMR (101 MHz, Chloroform-*d*)

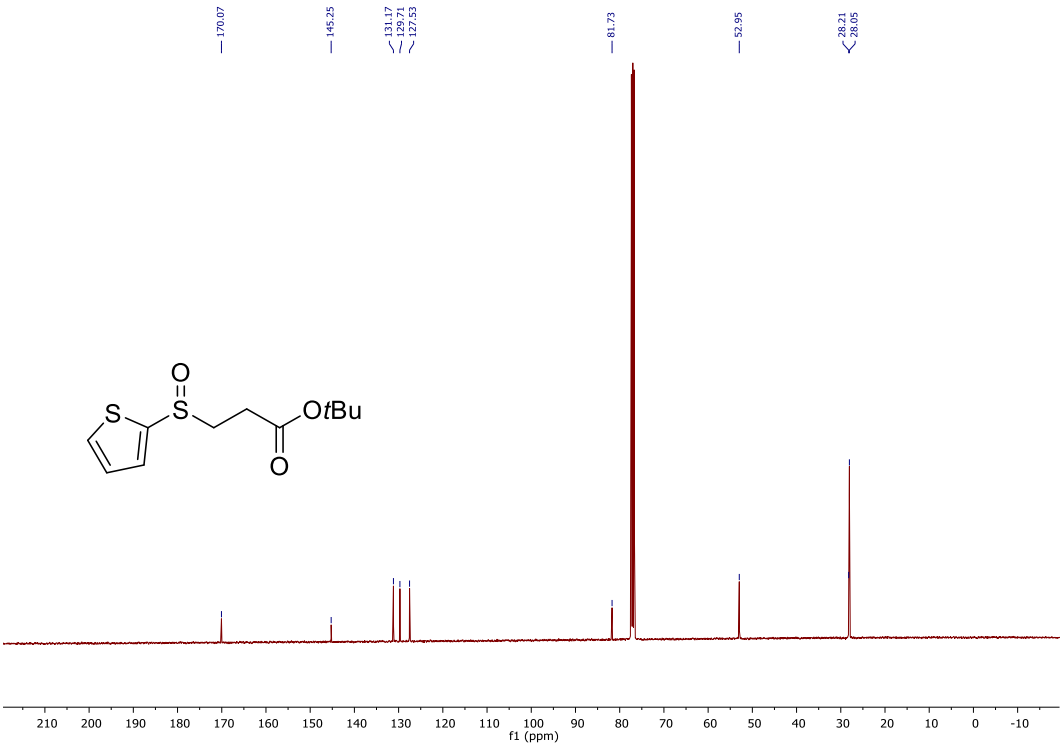


Tert-butyl 3-((thiophen-2-yl)sulfinyl)propanoate (6l)

^{1}H NMR (400 MHz, Chloroform-*d*)

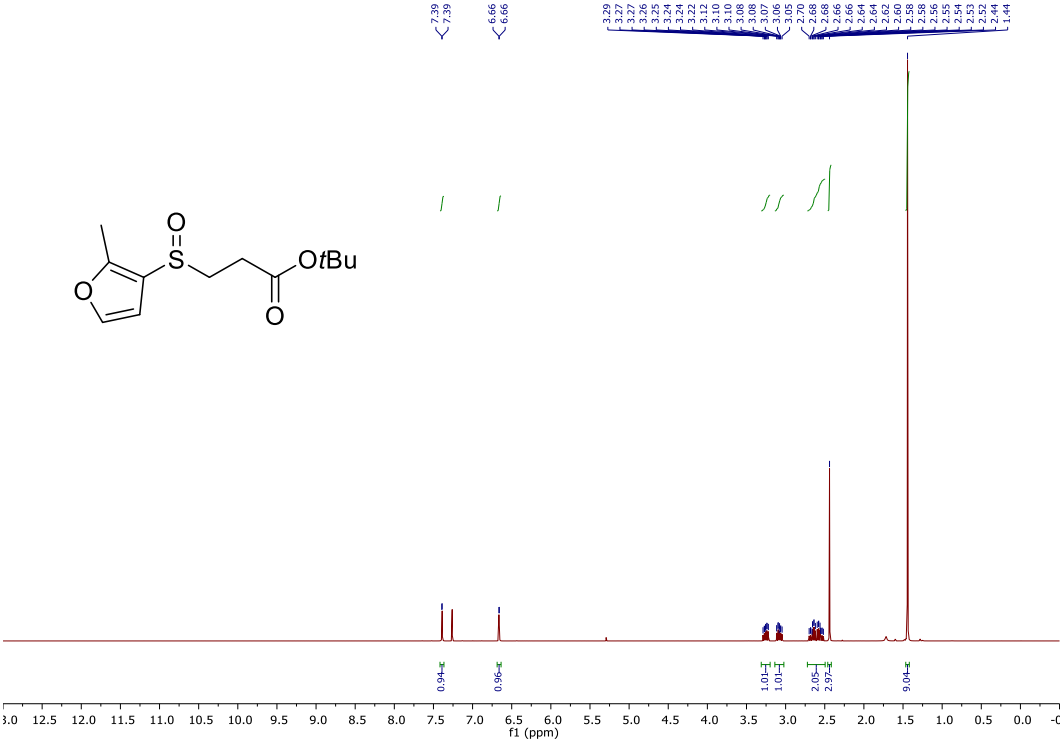


^{13}C NMR (101 MHz, Chloroform-*d*)

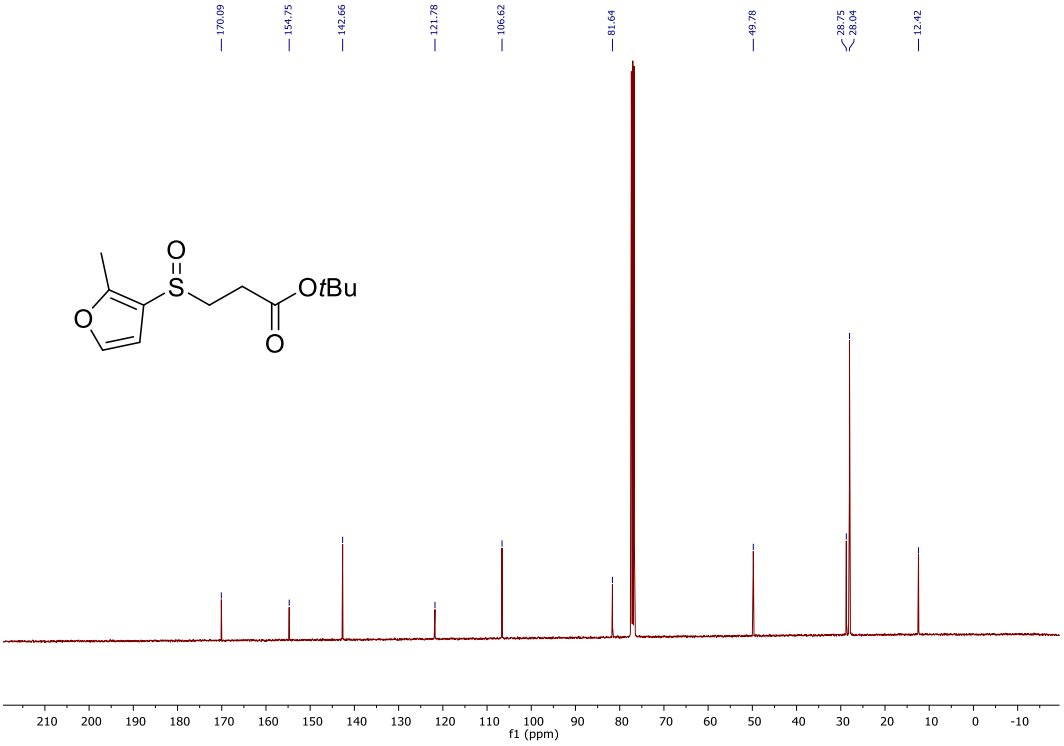


Tert-butyl 3-((2-methylfruna-3-yl)sulfinyl)propanoate (6m)

^{1}H NMR (400 MHz, Chloroform-*d*)

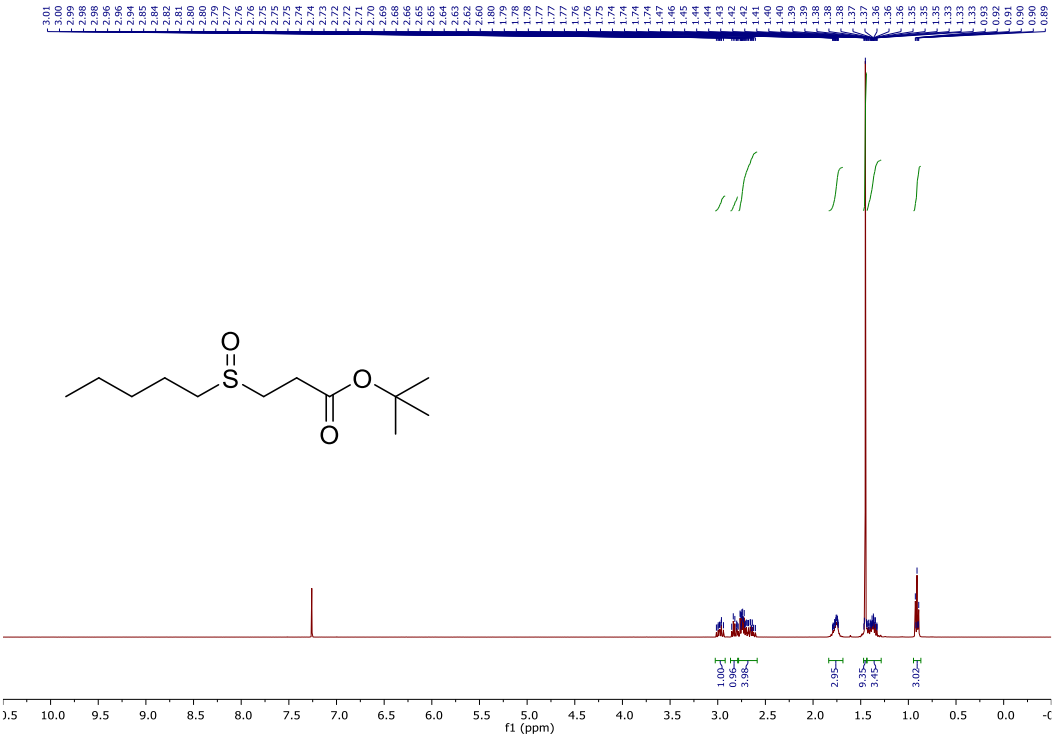


^{13}C NMR (101 MHz, Chloroform-*d*)

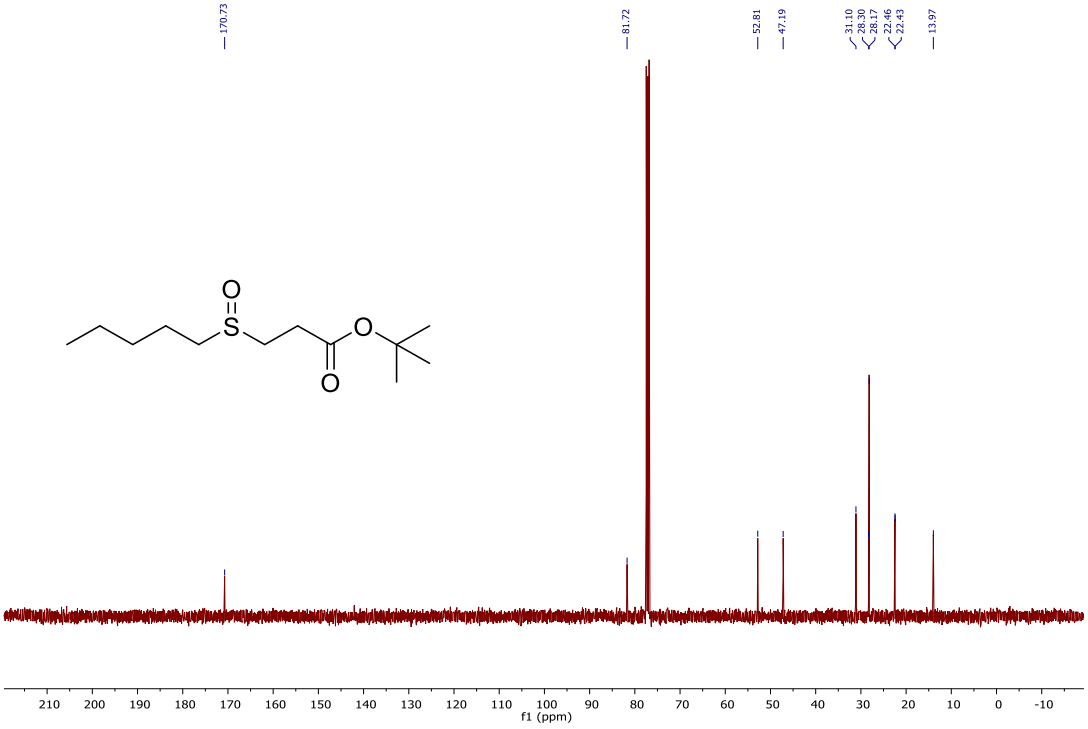


Tert-butyl 3-(pentylsulfinyl)propanoate (6n)

^{1}H NMR (400 MHz, Chloroform-*d*)

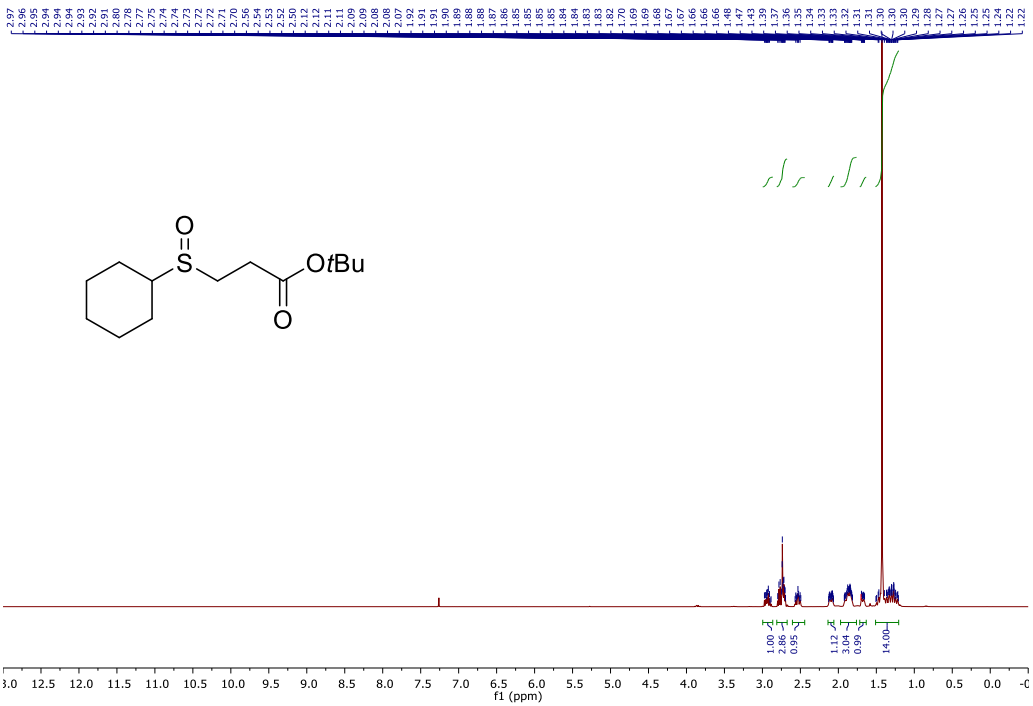


^{13}C NMR (101 MHz, Chloroform-*d*)

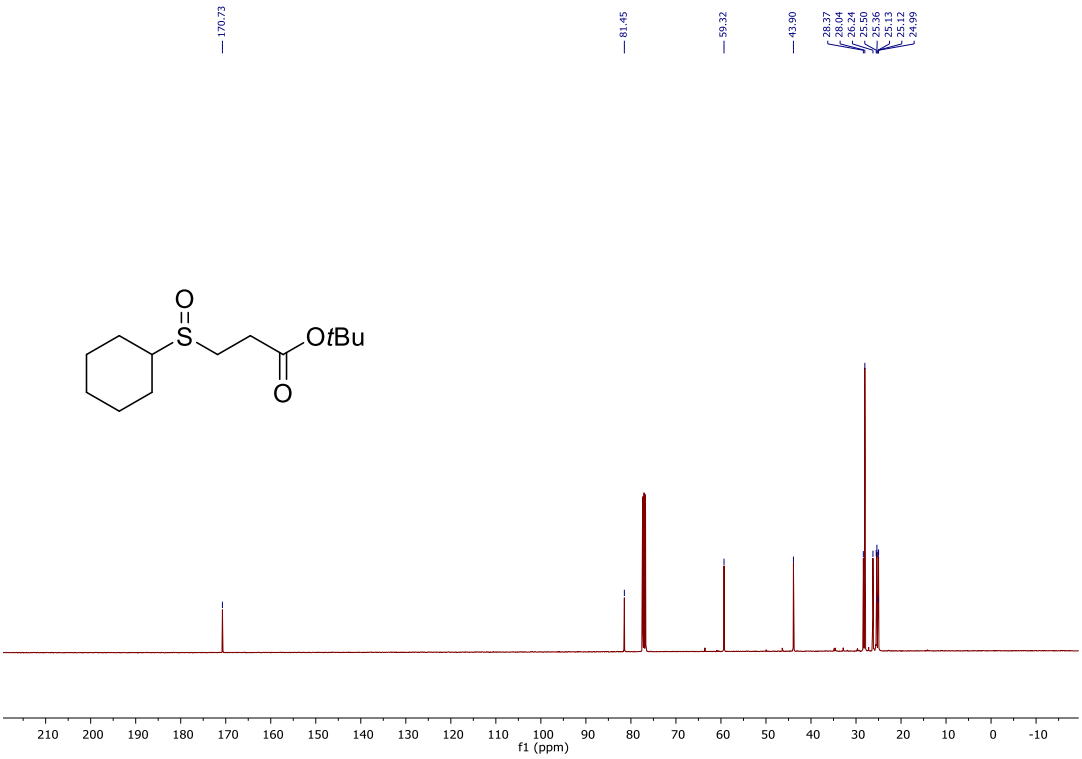


Tert-butyl 3-(cyclohexylsulfinyl)propanoate (6o)

^{1}H NMR (400 MHz, Chloroform-*d*)

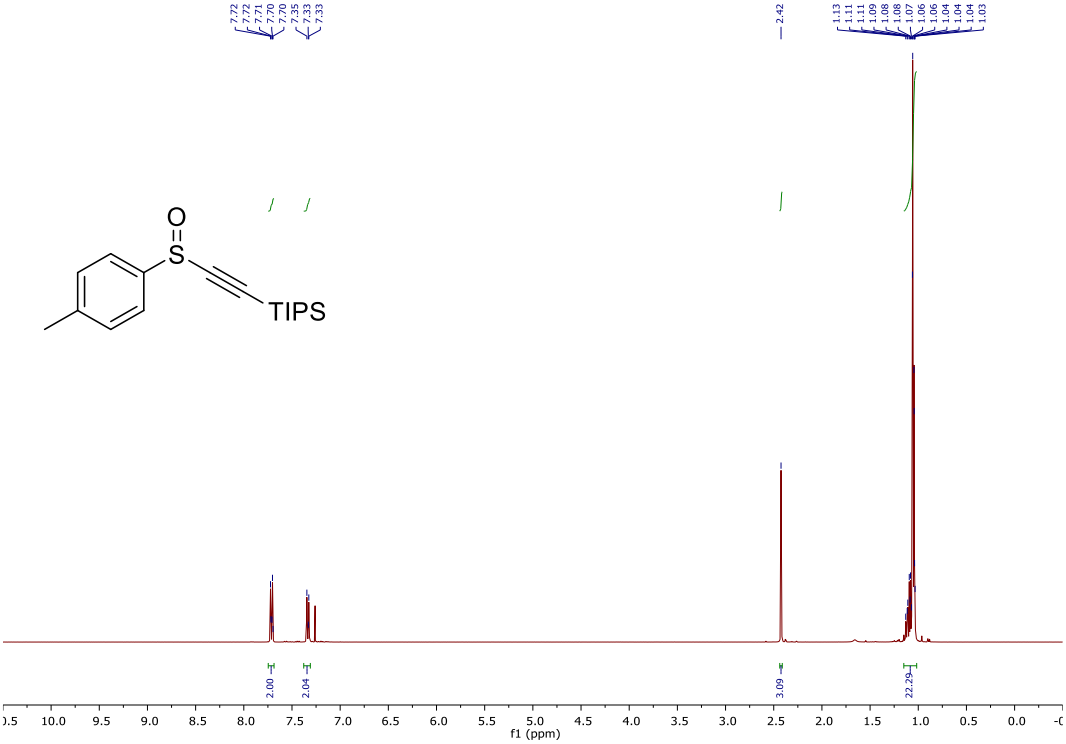


^{13}C NMR (101 MHz, Chloroform-*d*)

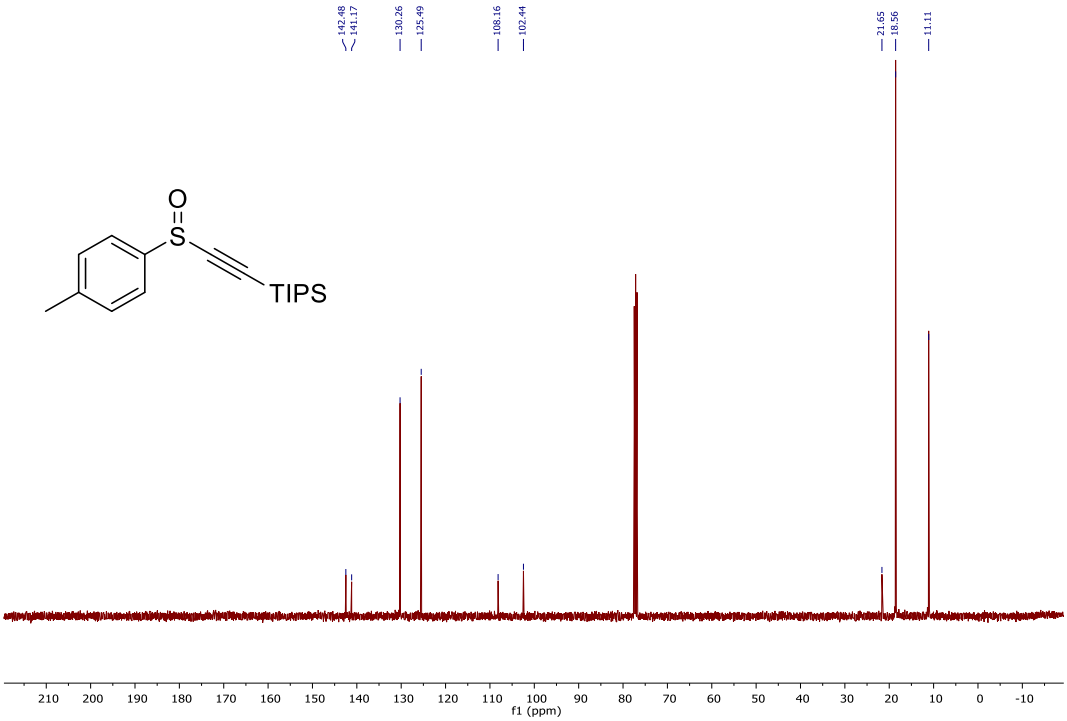


Tri*iso*propyl((4-methylphenylsulfinyl)ethynyl)silane (10a)

^{1}H NMR (400 MHz, Chloroform-*d*)

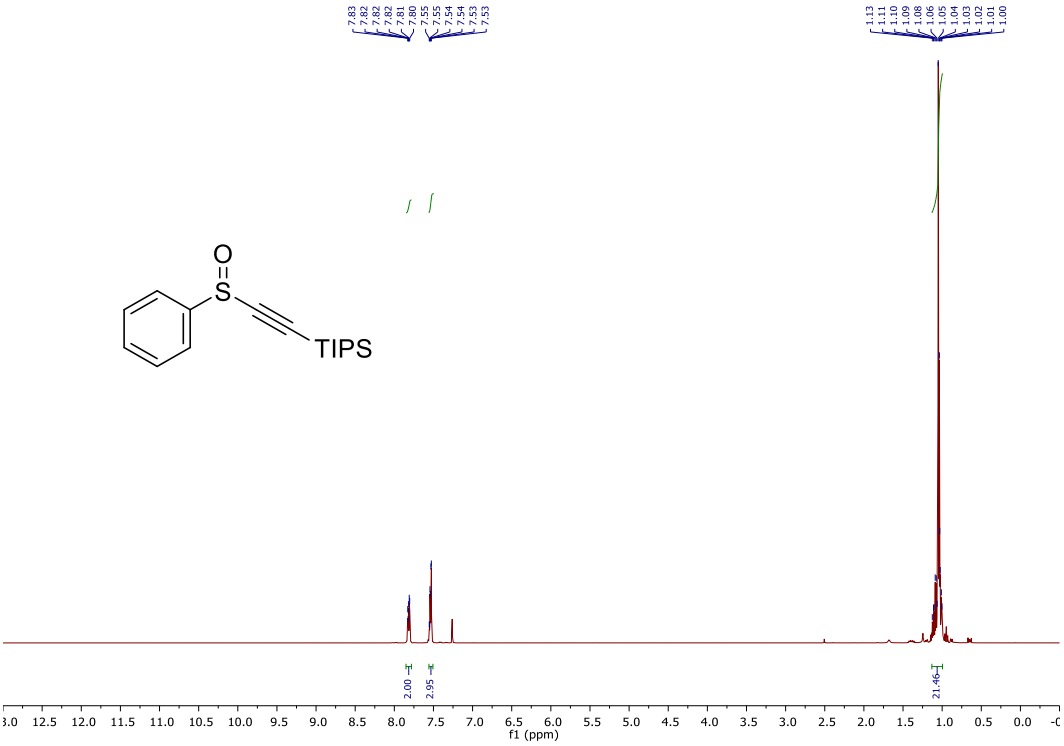


^{13}C NMR (101 MHz, Chloroform-*d*)

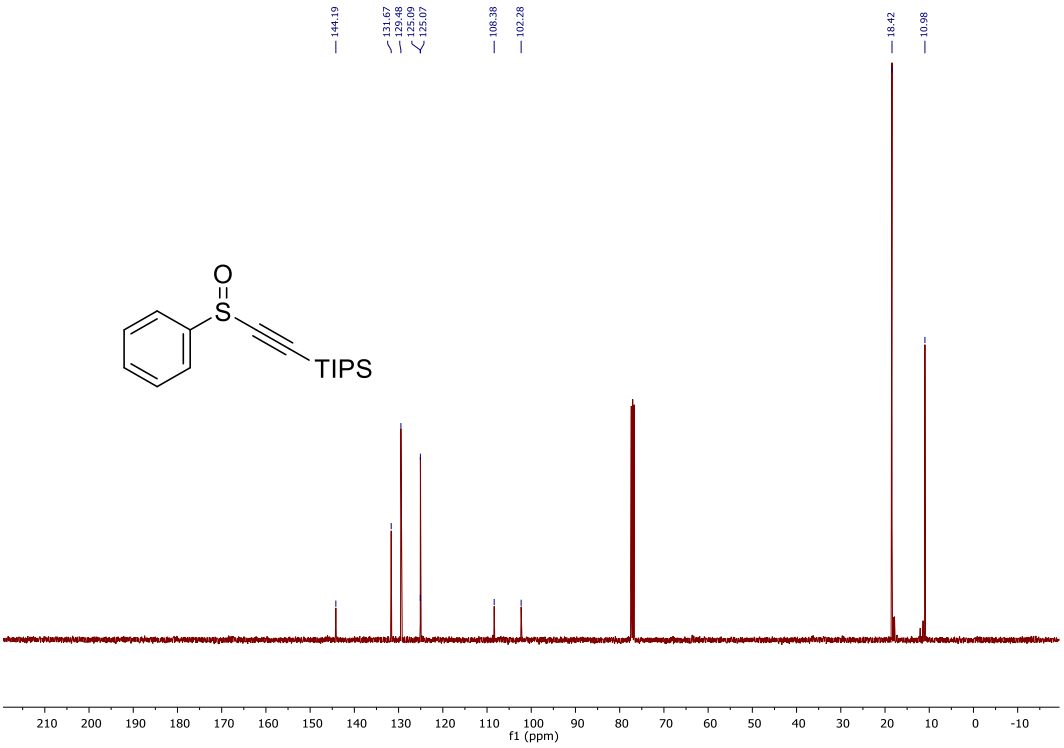


Tri*iso*propyl((phenylsulfinyl)ethynyl)silane (10b)

^{1}H NMR (400 MHz, Chloroform-*d*)

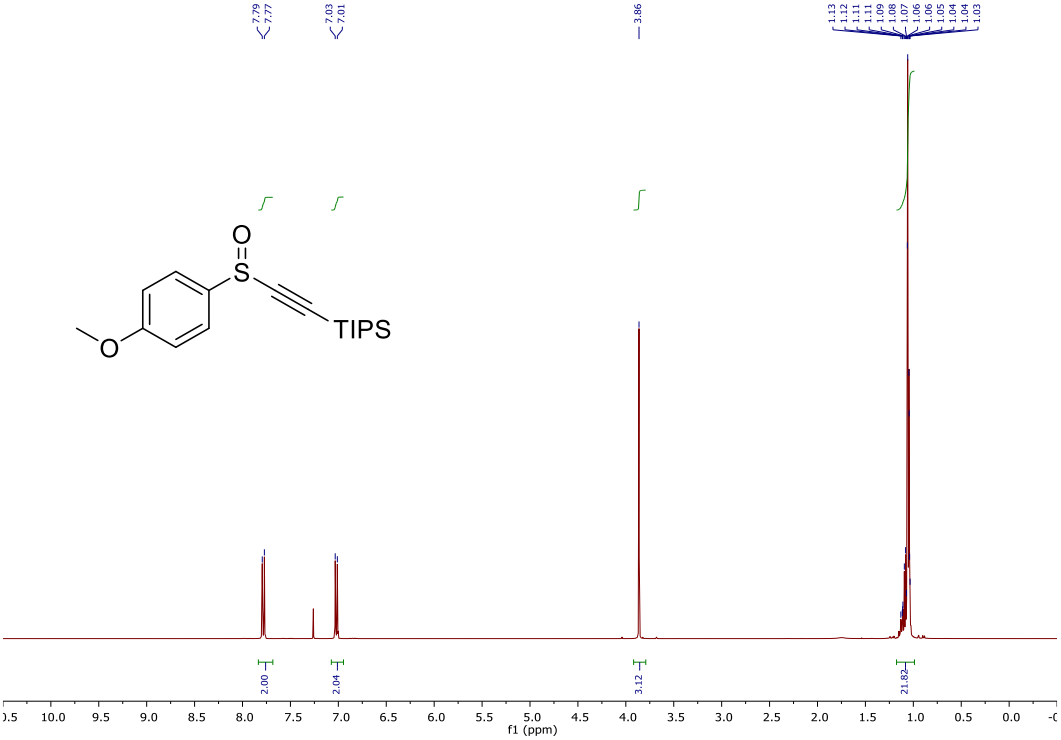


^{1} ^{3}C NMR (101 MHz, Chloroform-*d*)

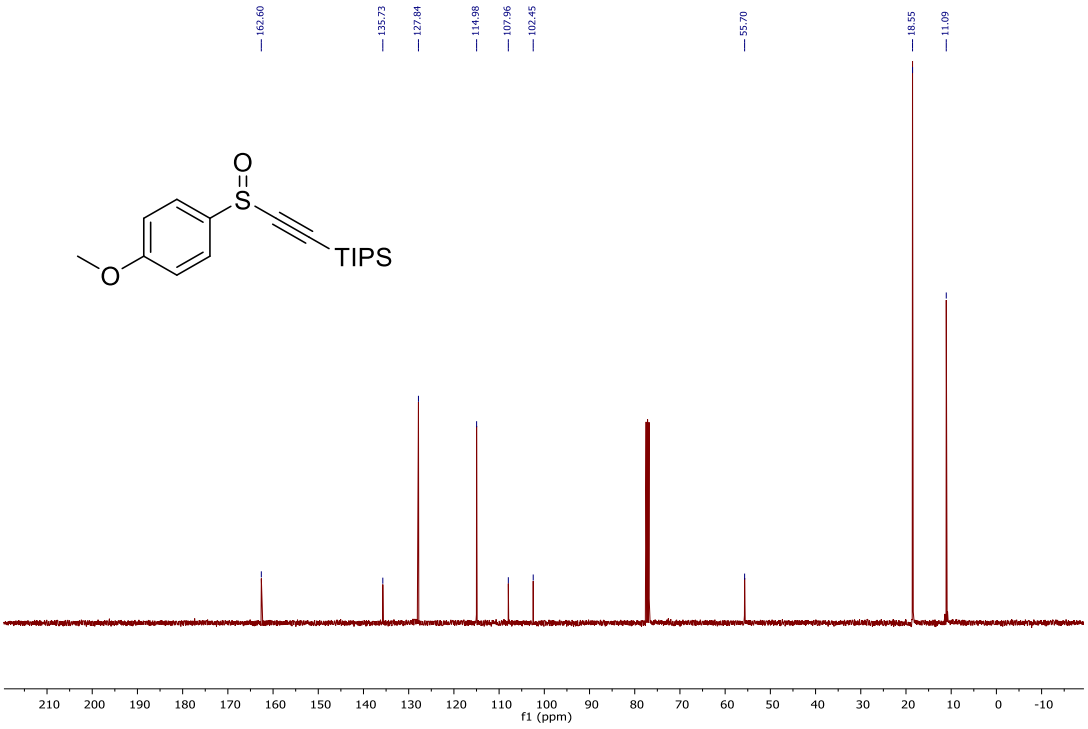


Tri*iso*propyl((4-methoxyphenylsulfinyl)ethynyl)silane (10c)

^{1}H NMR (400 MHz, Chloroform-*d*)

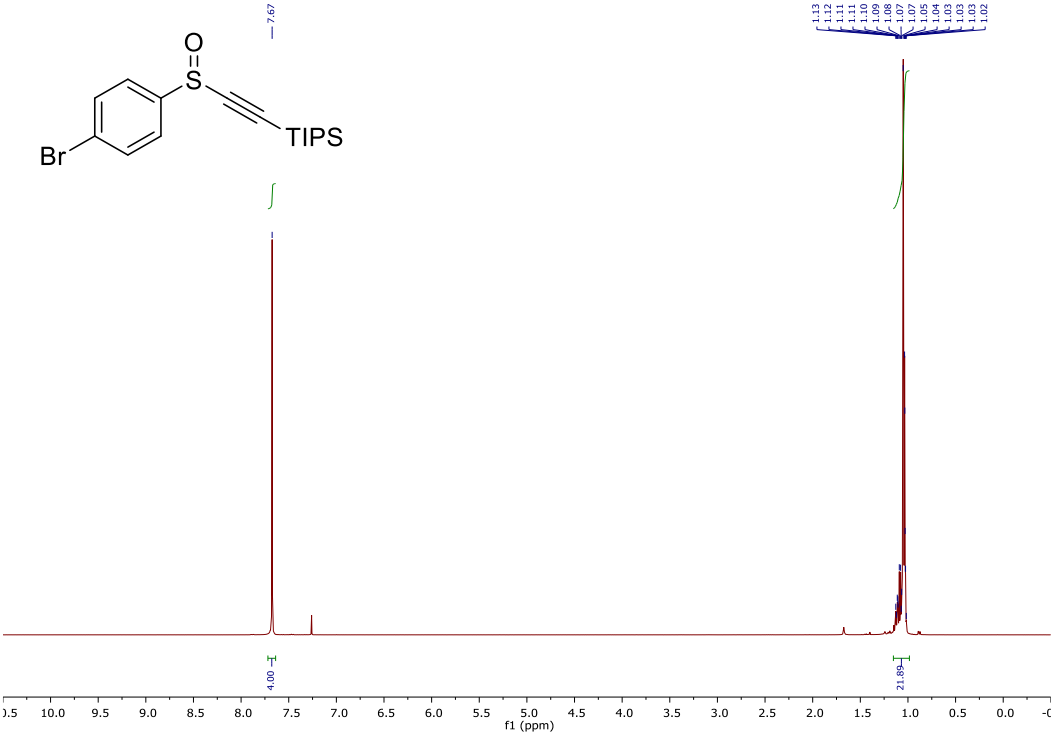


^{13}C NMR (101 MHz, Chloroform-*d*)

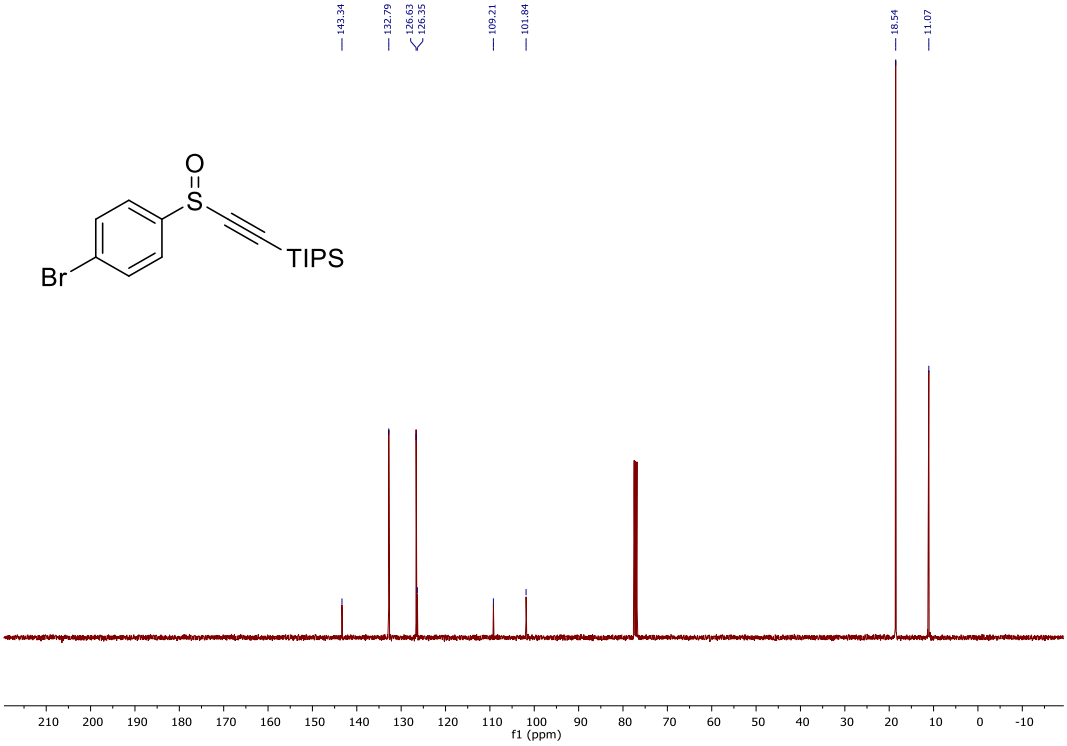


Tri*iso*propyl((4-bromophenylsulfinyl)ethynyl)silane (10d)

^{1}H NMR (400 MHz, Chloroform-*d*)

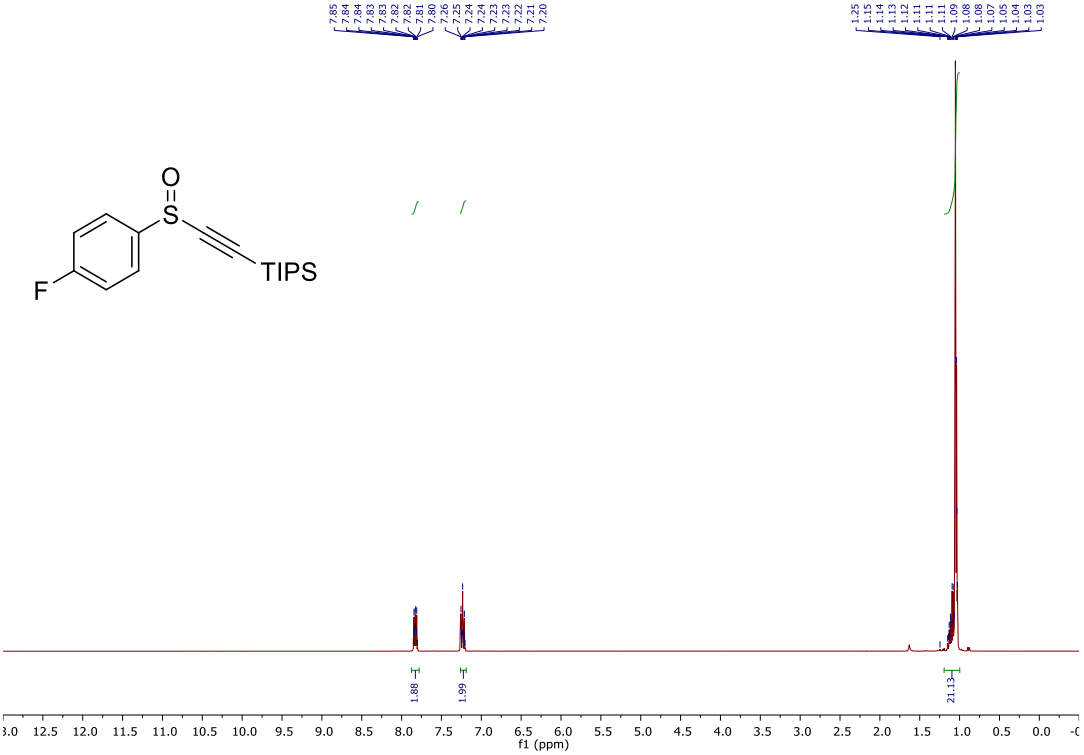


^{13}C NMR (101 MHz, Chloroform-*d*)

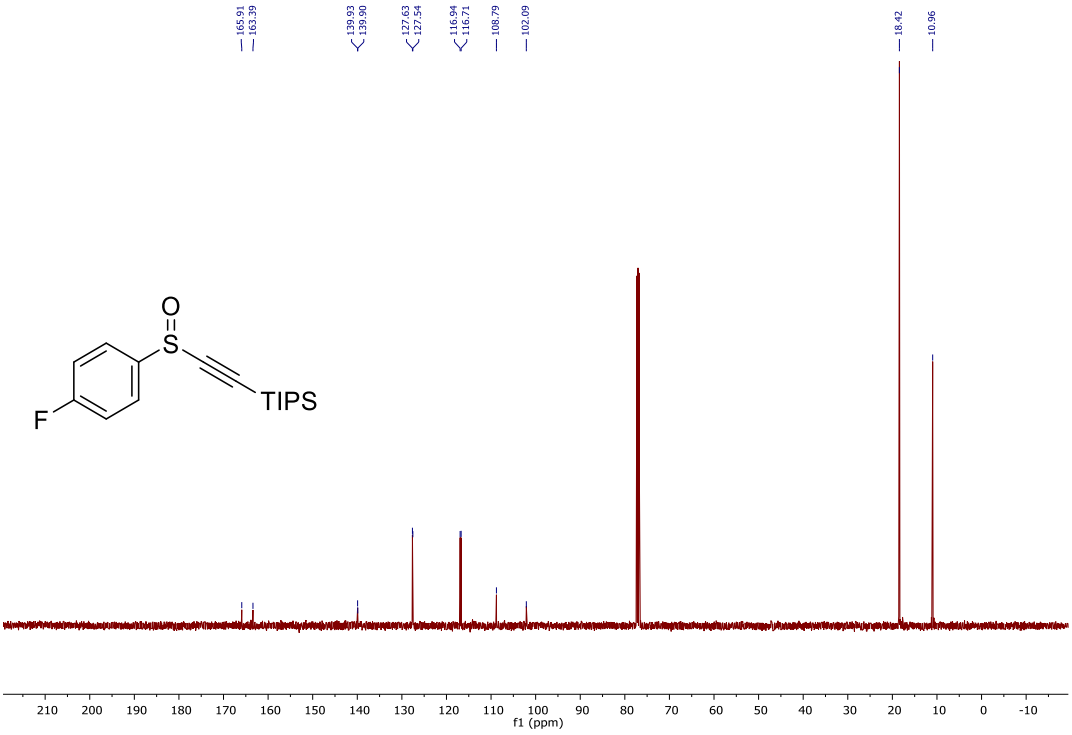


Tri*iso*propyl((4-fluorophenylsulfinyl)ethynyl)silane (10e)

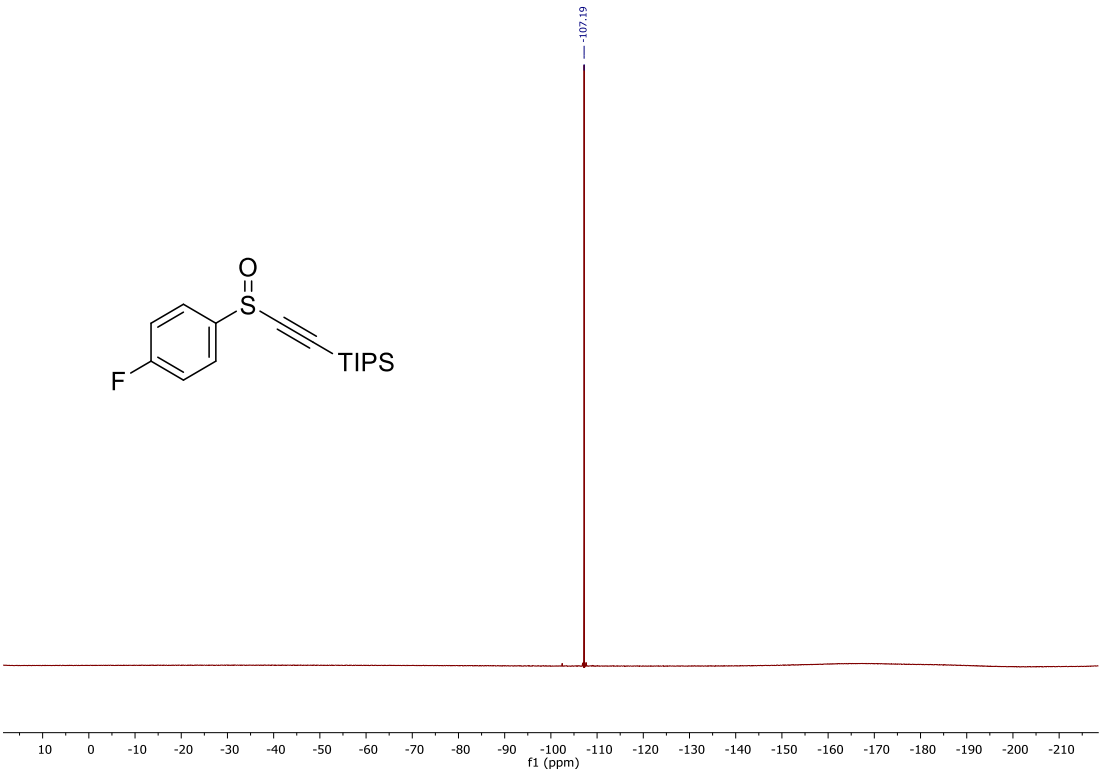
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)

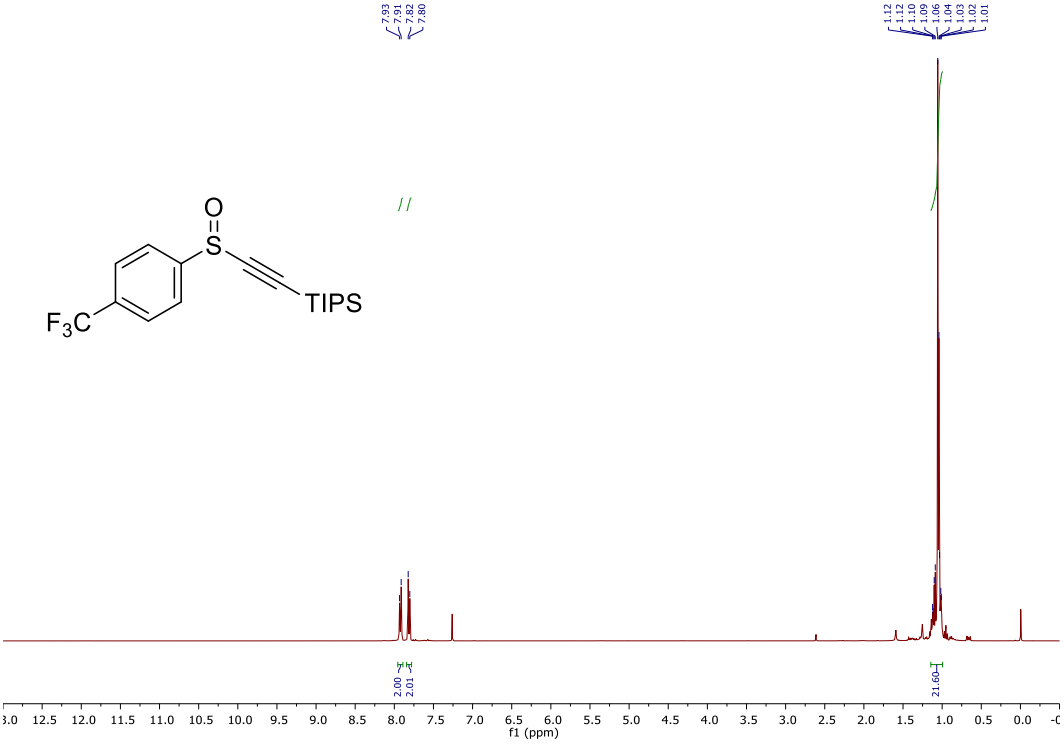


^{19}F NMR (376 MHz, Chloroform-d)

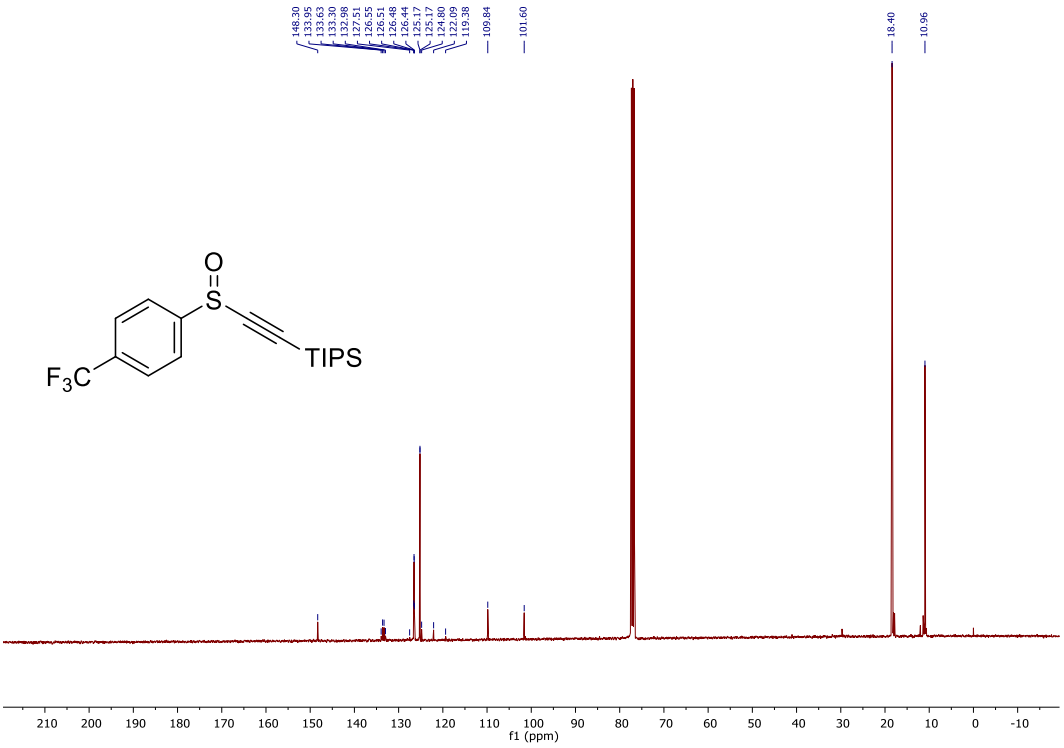


Tri*iso*propyl((4-trifluoromethylphenylsulfinyl)ethynyl)silane (10f)

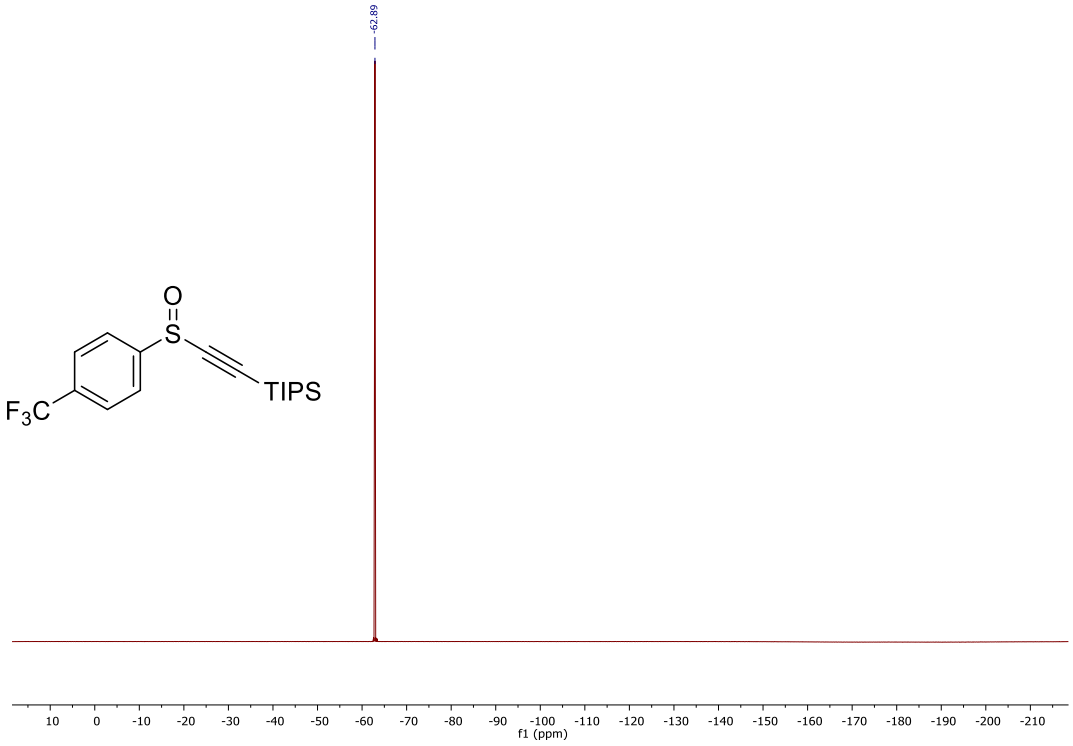
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)

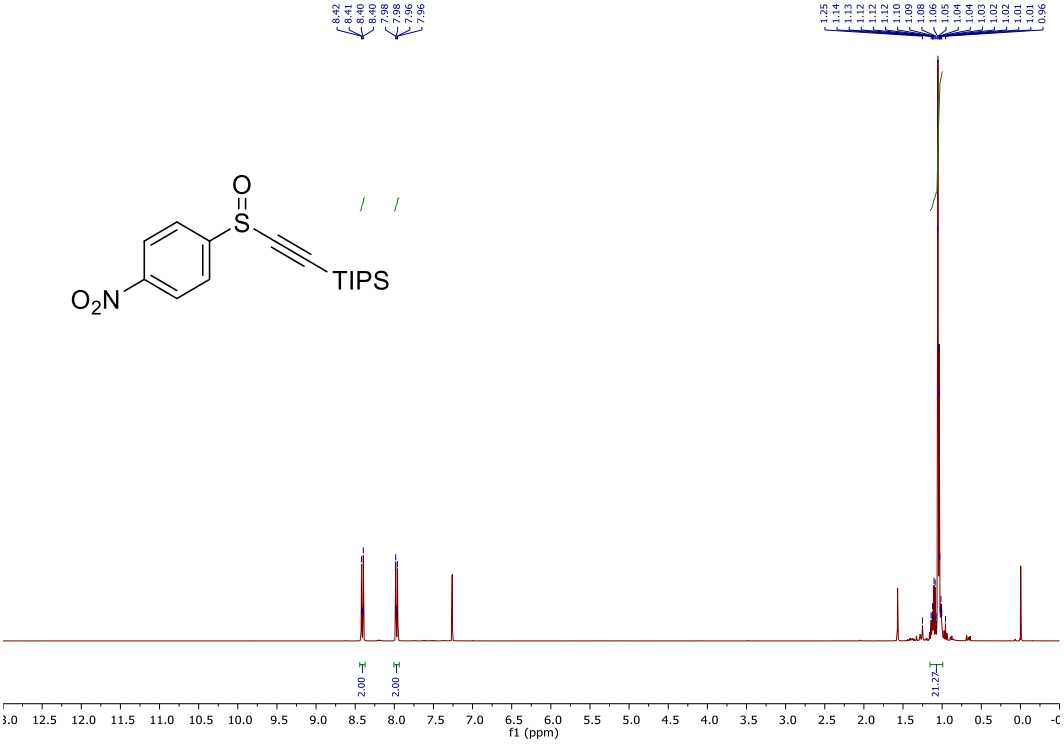


^{19}F NMR (376 MHz, Chloroform-d)

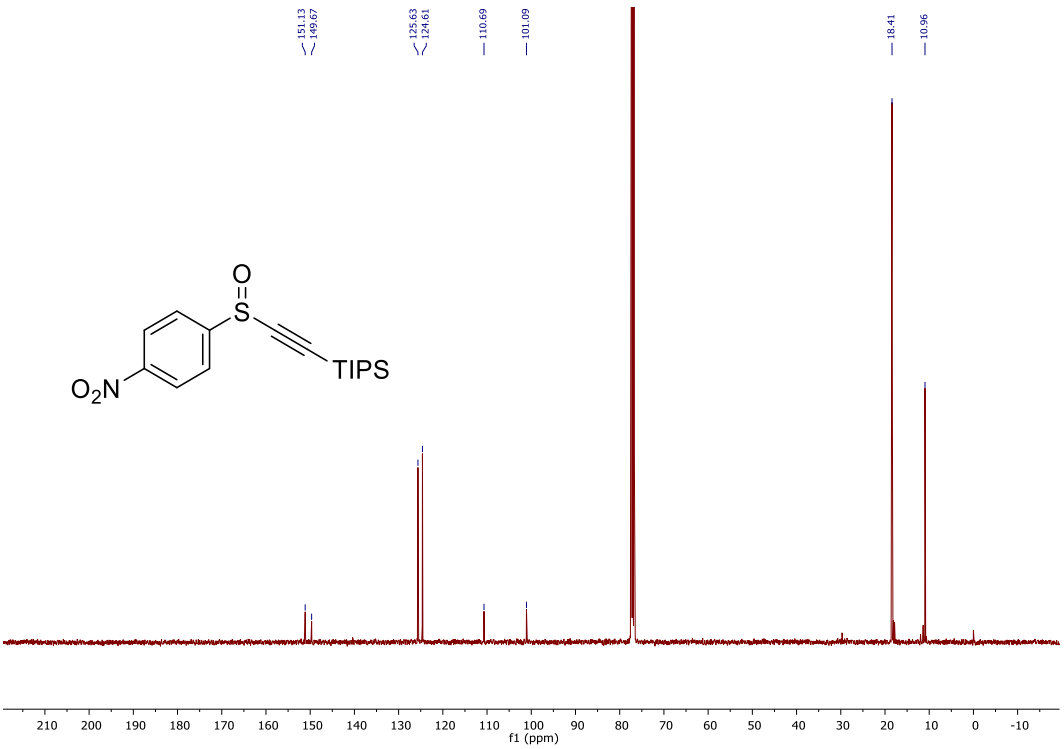


Tri*iso*propyl((4-nitrophenylsulfinyl)ethynyl)silane (10g)

^{1}H NMR (400 MHz, Chloroform-*d*)

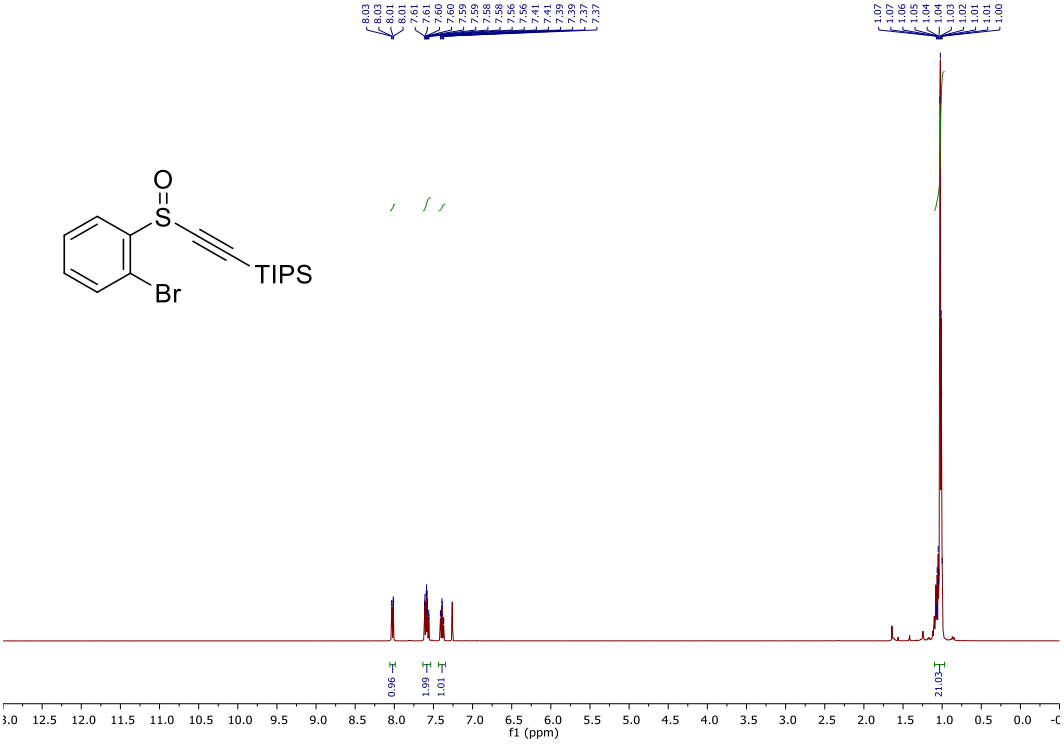


^{13}C NMR (101 MHz, Chloroform-*d*)

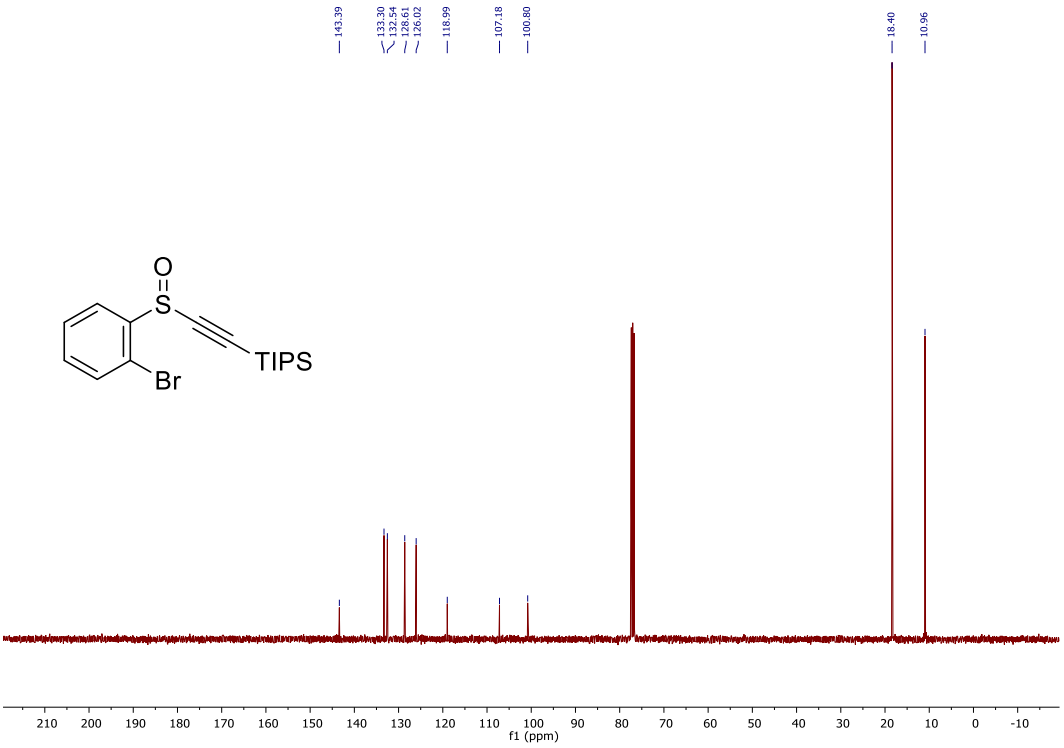


Tri*iso*propyl((2-bromophenylsulfinyl)ethynyl)silane (10h)

^{1}H NMR (400 MHz, Chloroform-*d*)

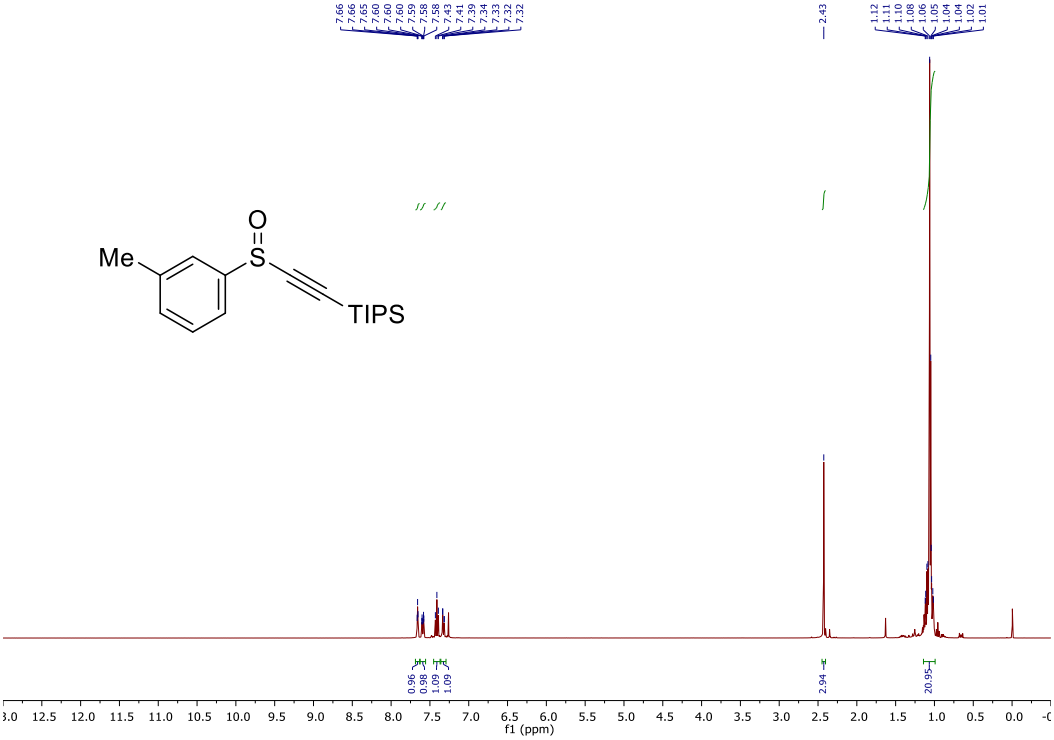


^{13}C NMR (101 MHz, Chloroform-*d*)

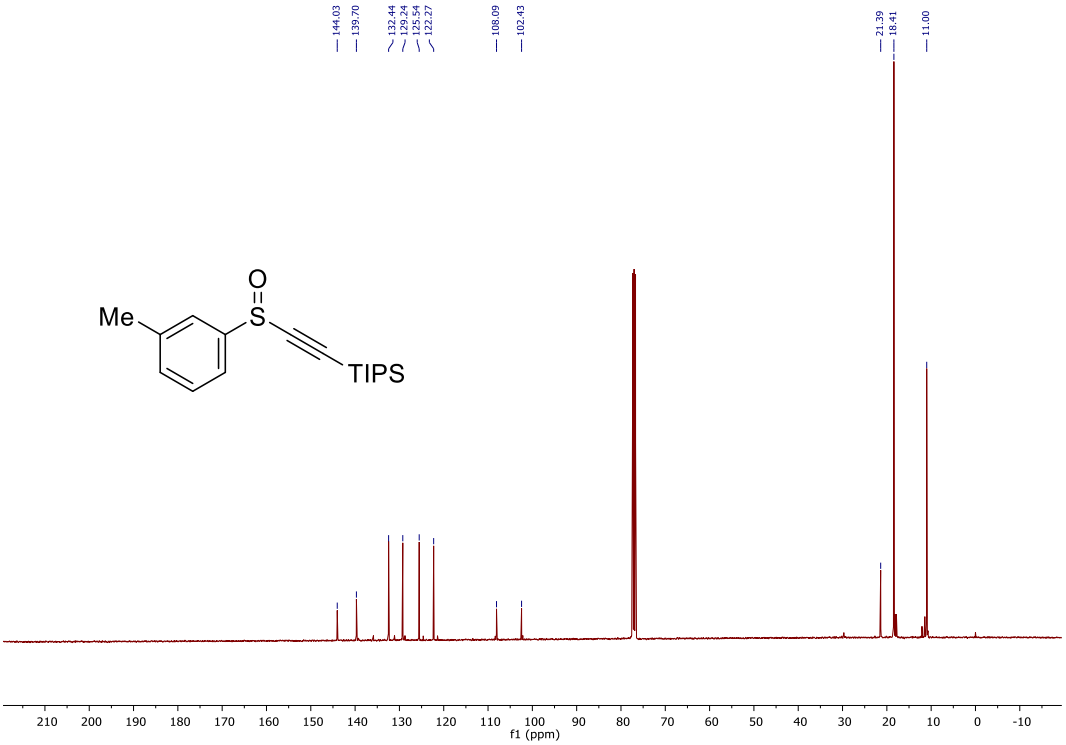


Tri*iso*propyl((3-methylphenylsulfinyl)ethynyl)silane (10i)

^{1}H NMR (400 MHz, Chloroform-*d*)

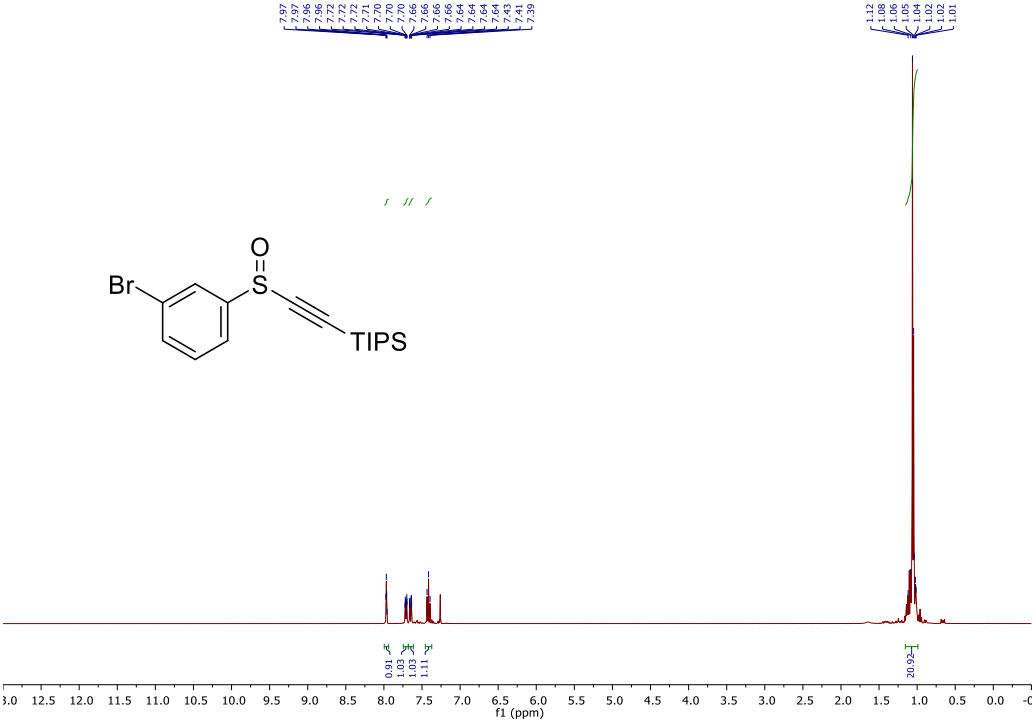


^{13}C NMR (101 MHz, Chloroform-*d*)

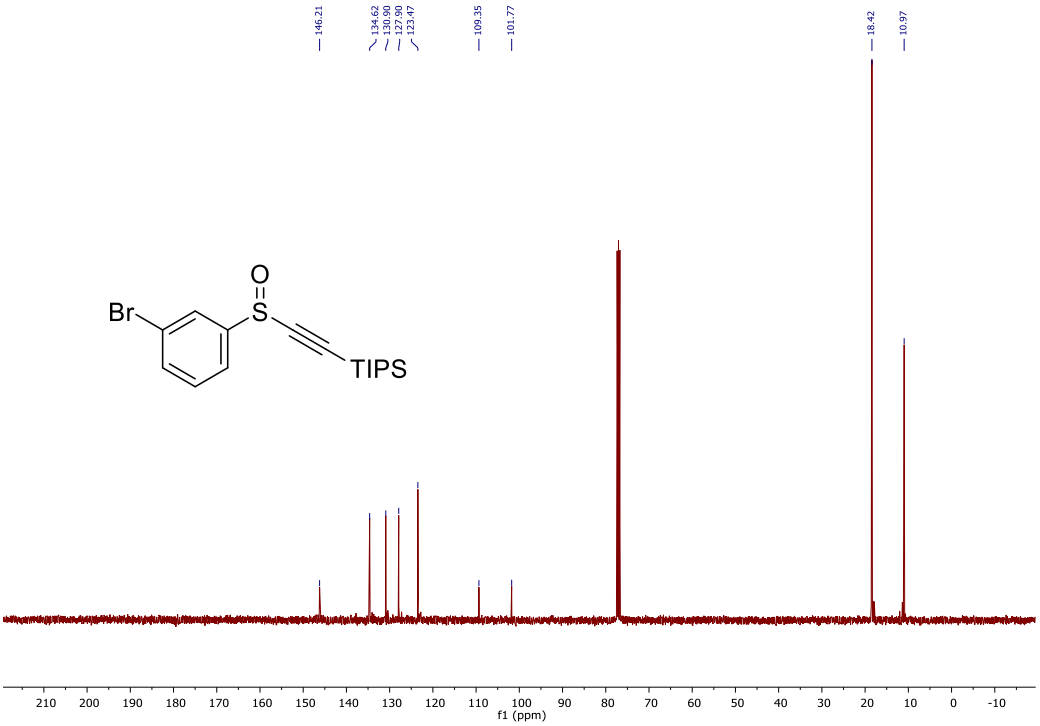


Tri*iso*propyl((3-bromophenylsulfinyl)ethynyl)silane (10j)

^{1}H NMR (400 MHz, Chloroform-*d*)

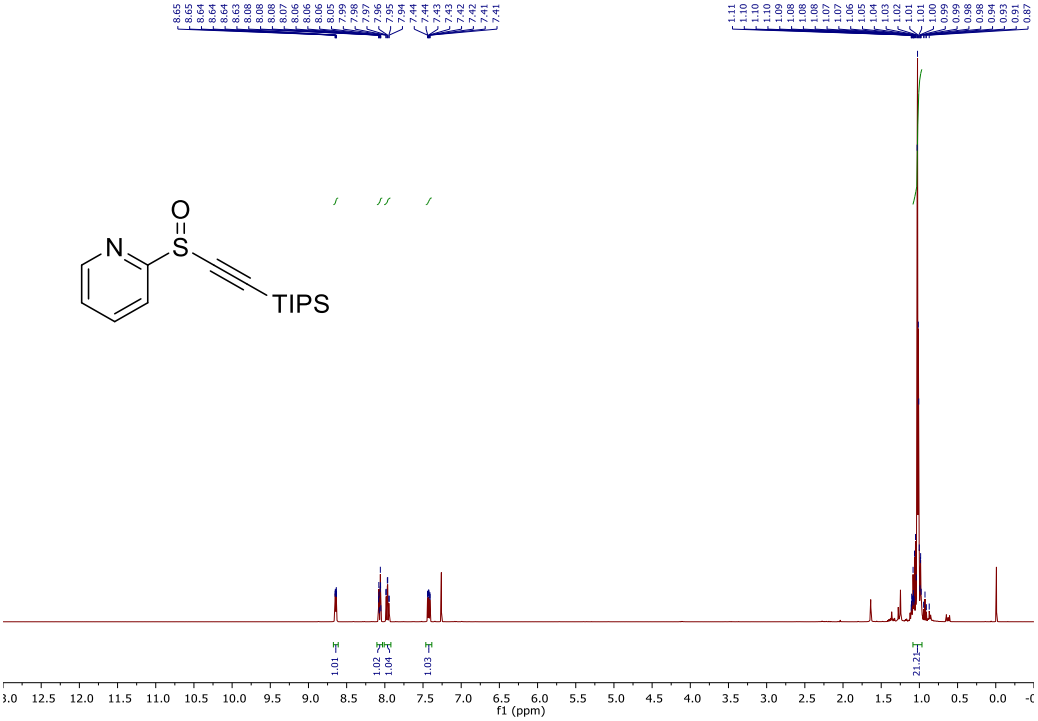


^{13}C NMR (101 MHz, Chloroform-*d*)

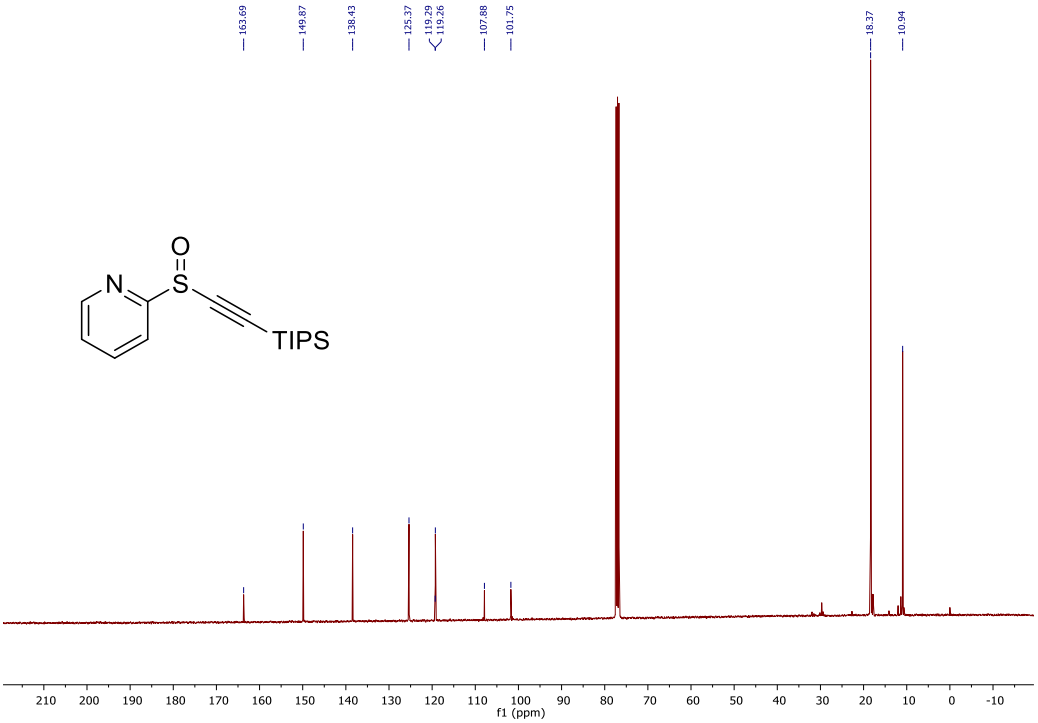


Tri*iso*propyl((pyridin-2-ylsulfinyl)ethynyl)silane (10k)

^{1}H NMR (400 MHz, Chloroform-*d*)

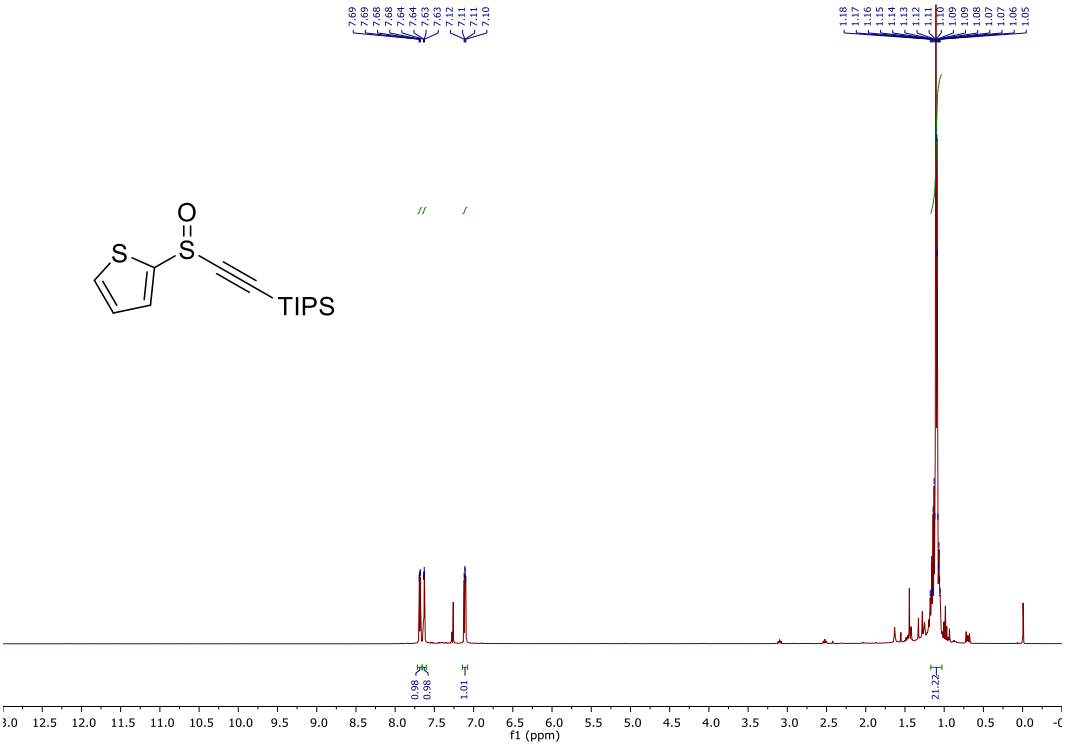


^{13}C NMR (101 MHz, Chloroform-*d*)

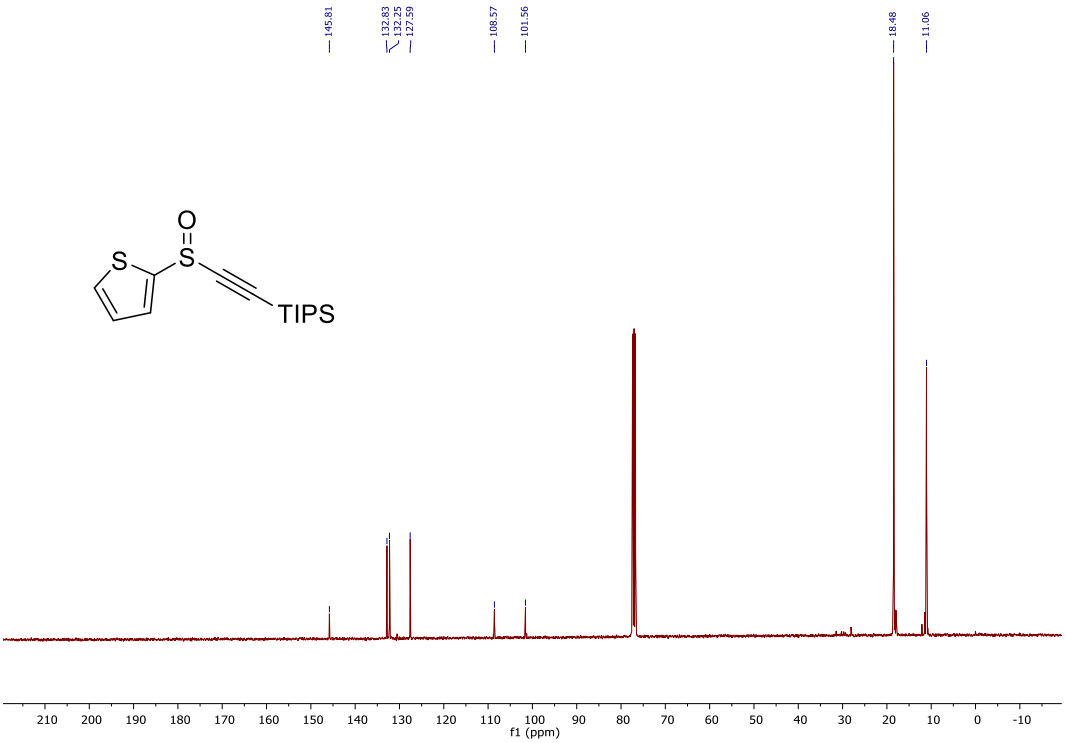


Tri*iso*propyl((thiophen-2-ylsulfinyl)ethynyl)silane (10l)

^{1}H NMR (400 MHz, Chloroform-*d*)

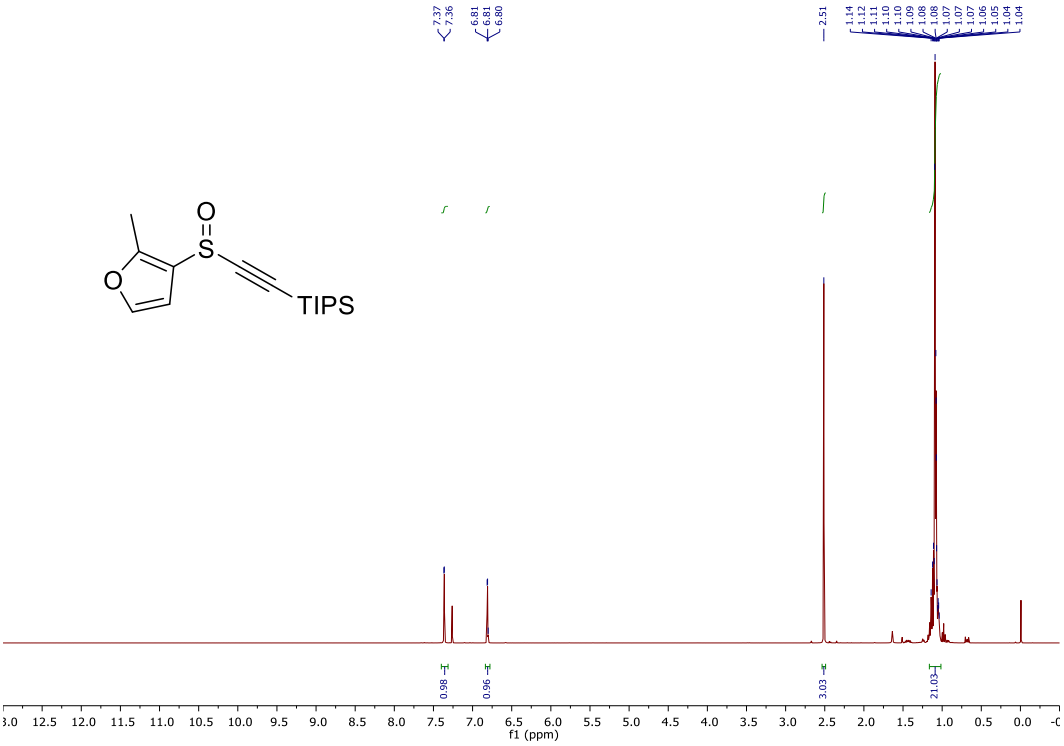


^{13}C NMR (101 MHz, Chloroform-*d*)

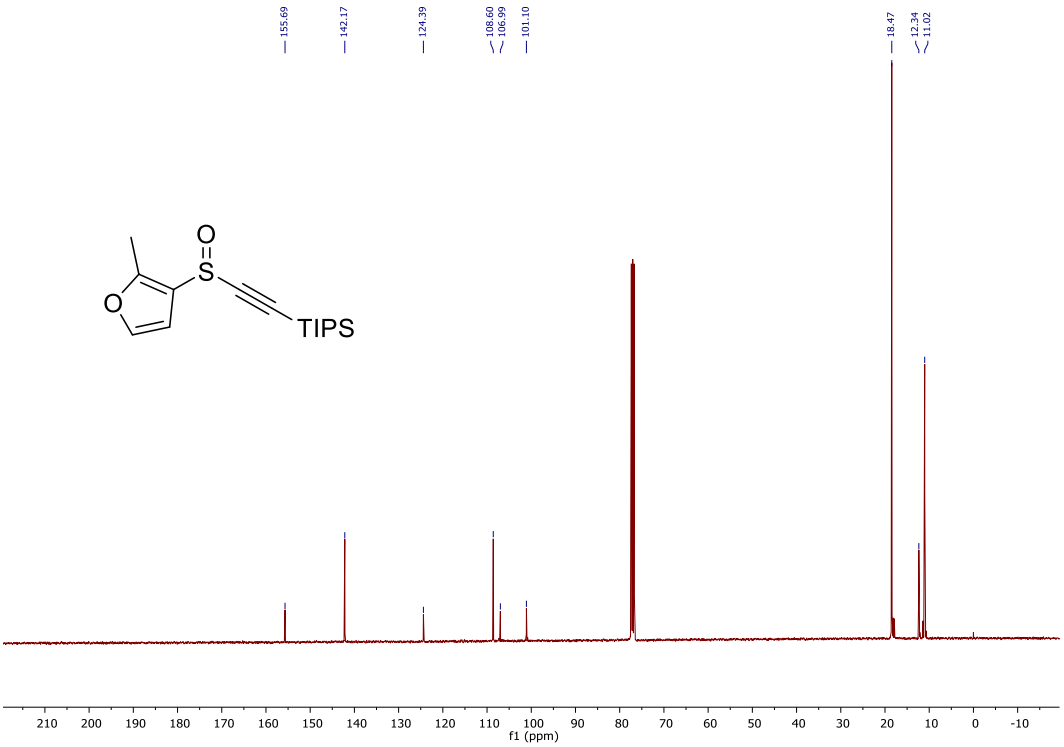


Tri*iso*propyl((2-methylfuran-3-ylsulfinyl)ethynyl)silane (10m)

^{1}H NMR (400 MHz, Chloroform-*d*)

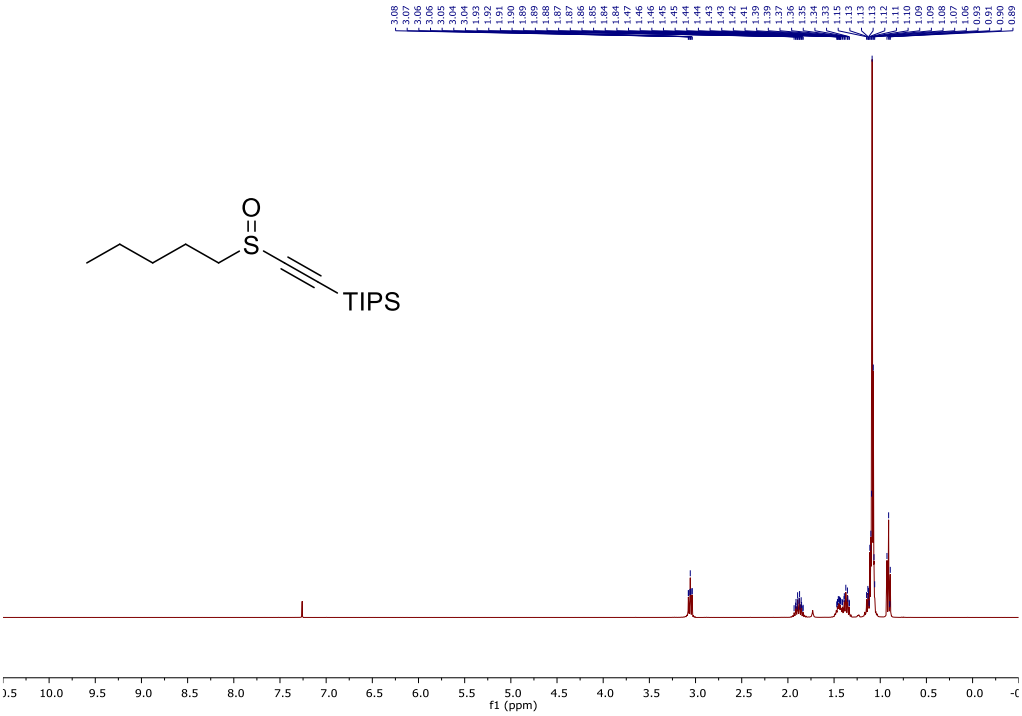


^{13}C NMR (101 MHz, Chloroform-*d*)

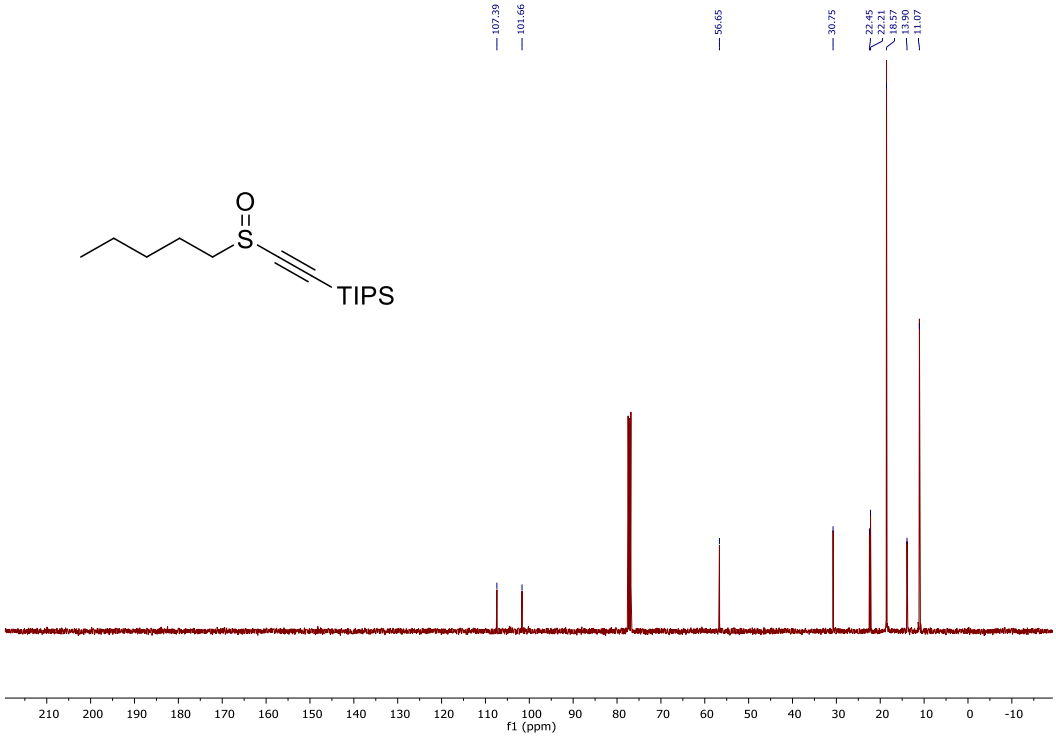


Tri*iso*propyl((pentylsulfinyl)ethynyl)silane (10n)

^{1}H NMR (400 MHz, Chloroform-*d*)

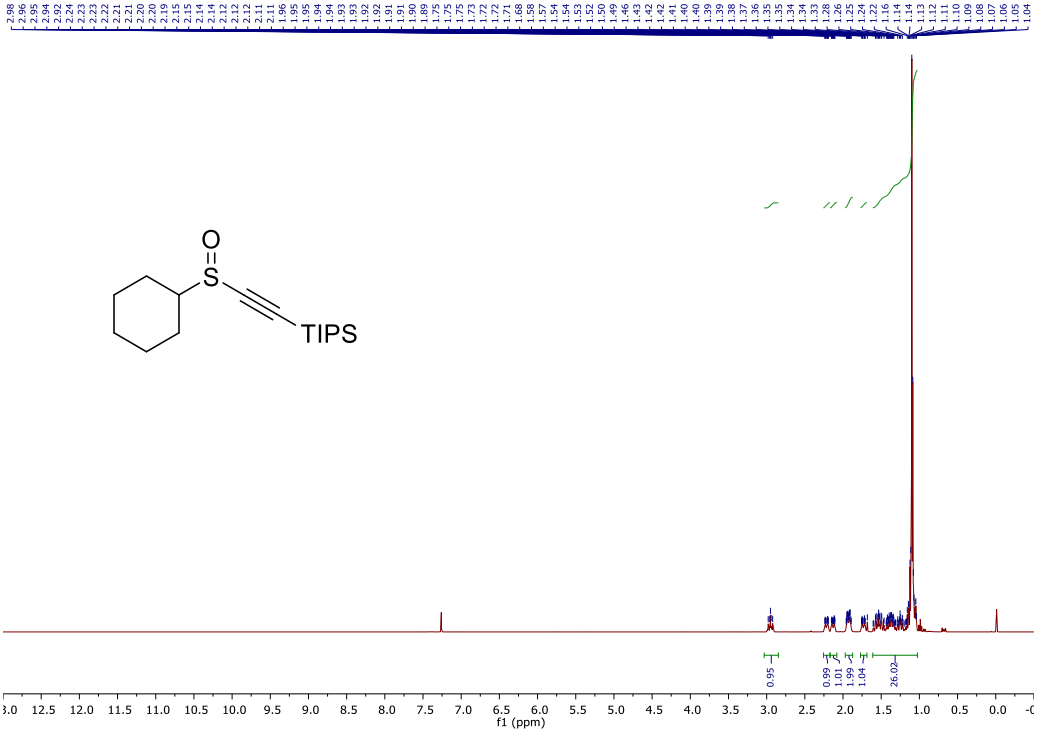


^{13}C NMR (101 MHz, Chloroform-*d*)

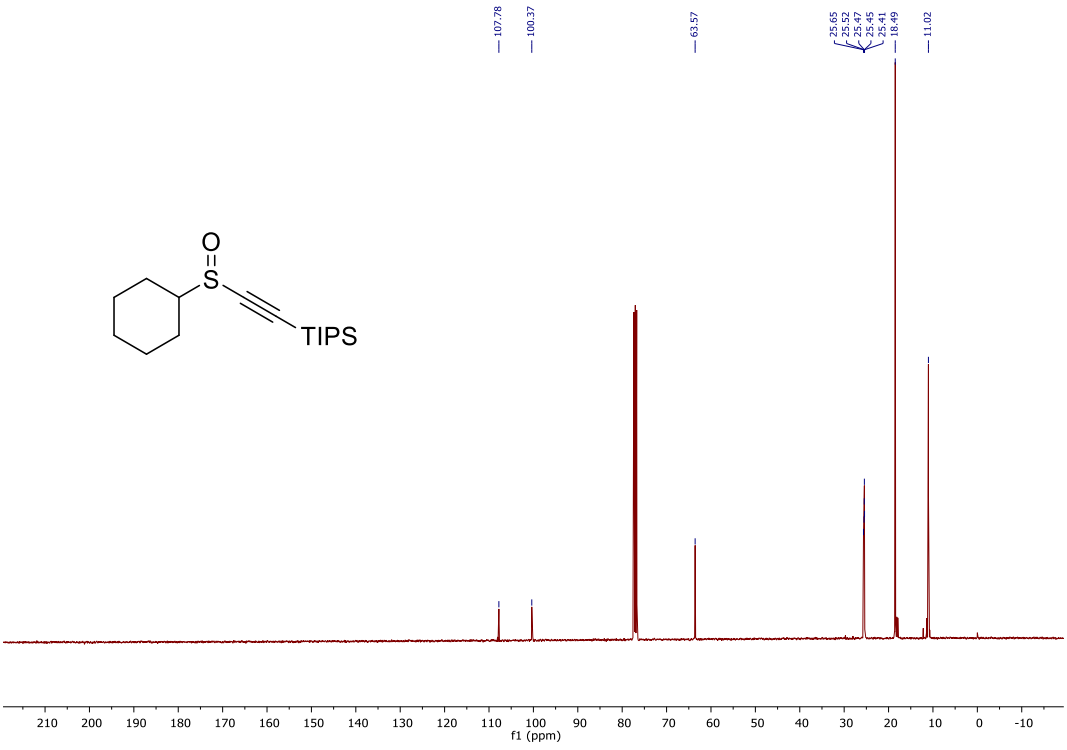


Tri*iso*propyl((cyclohexylsulfinyl)ethynyl)silane (10o)

^{1}H NMR (400 MHz, Chloroform-*d*)

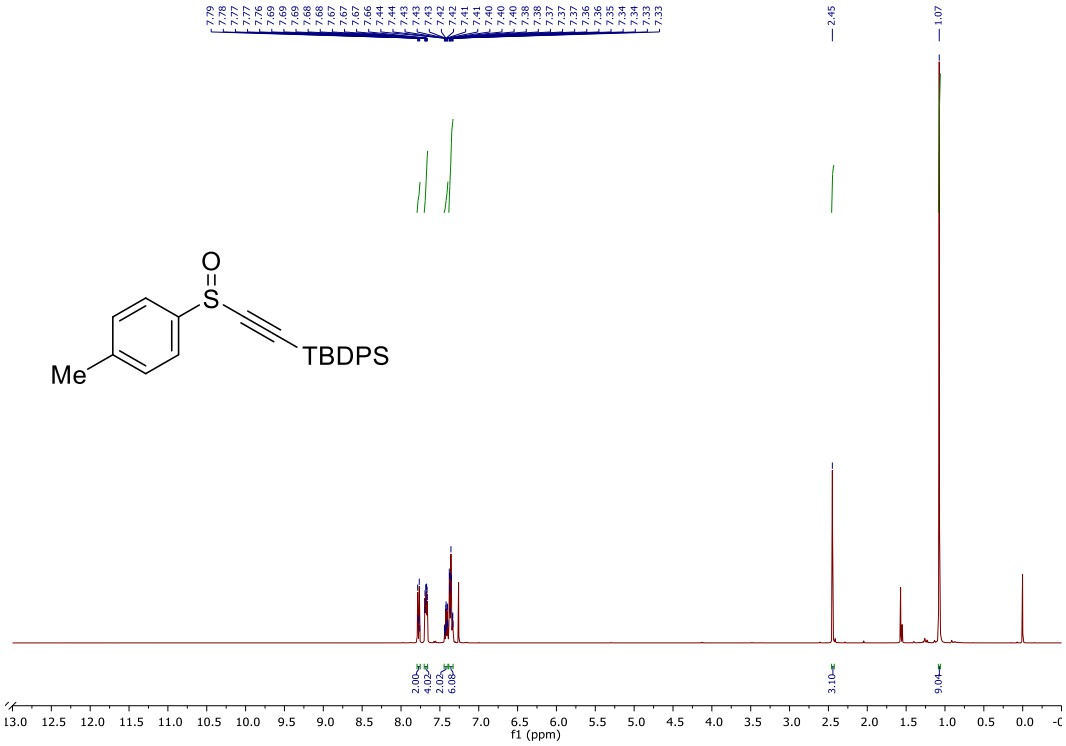


^{13}C NMR (101 MHz, Chloroform-*d*)

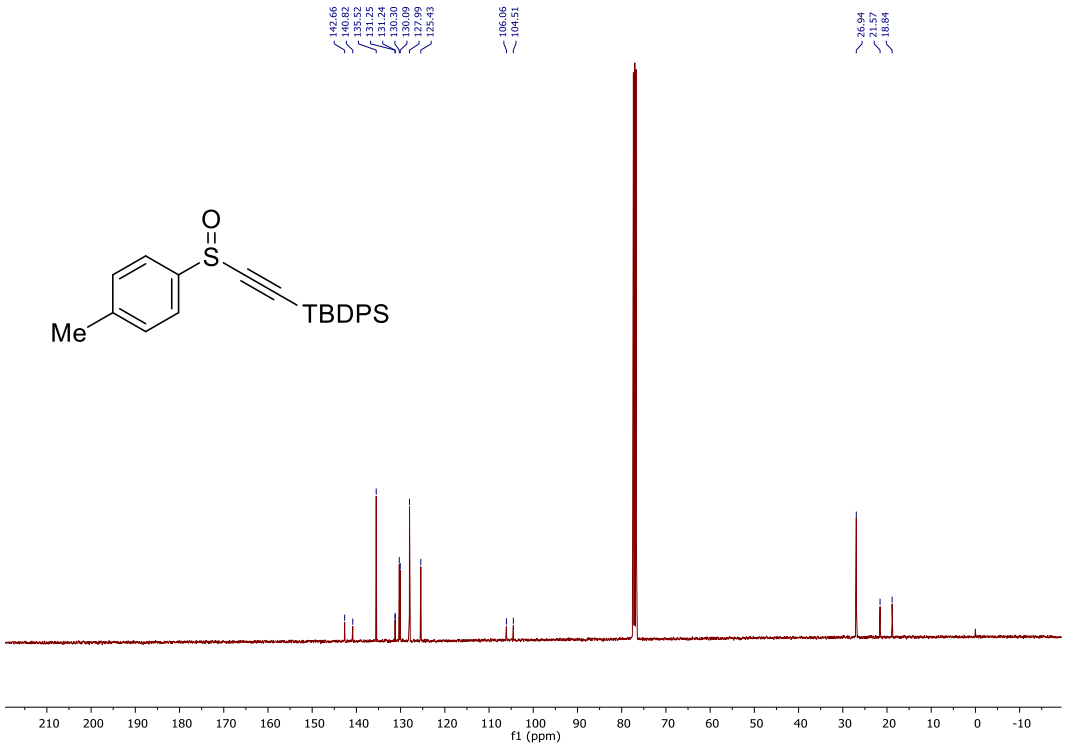


Tert-butyldiphenyl((4-methylphenylsulfinyl)ethynyl)silane (10p)

^{1}H NMR (400 MHz, Chloroform-*d*)

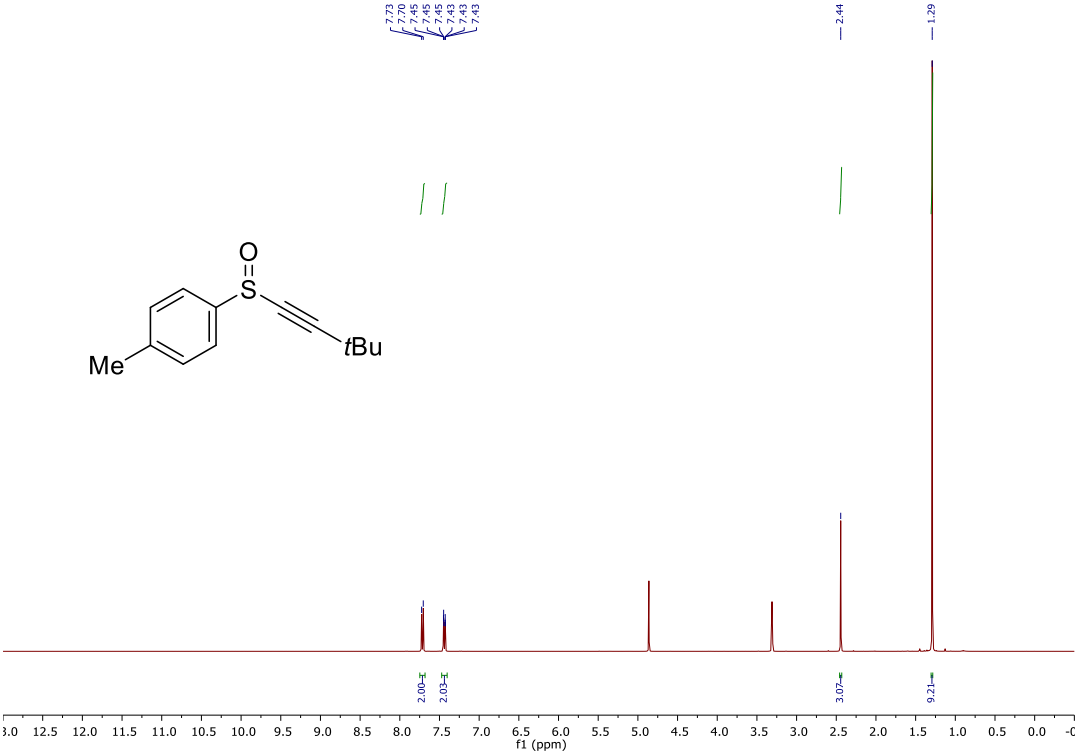


^{13}C NMR (101 MHz, Chloroform-*d*)

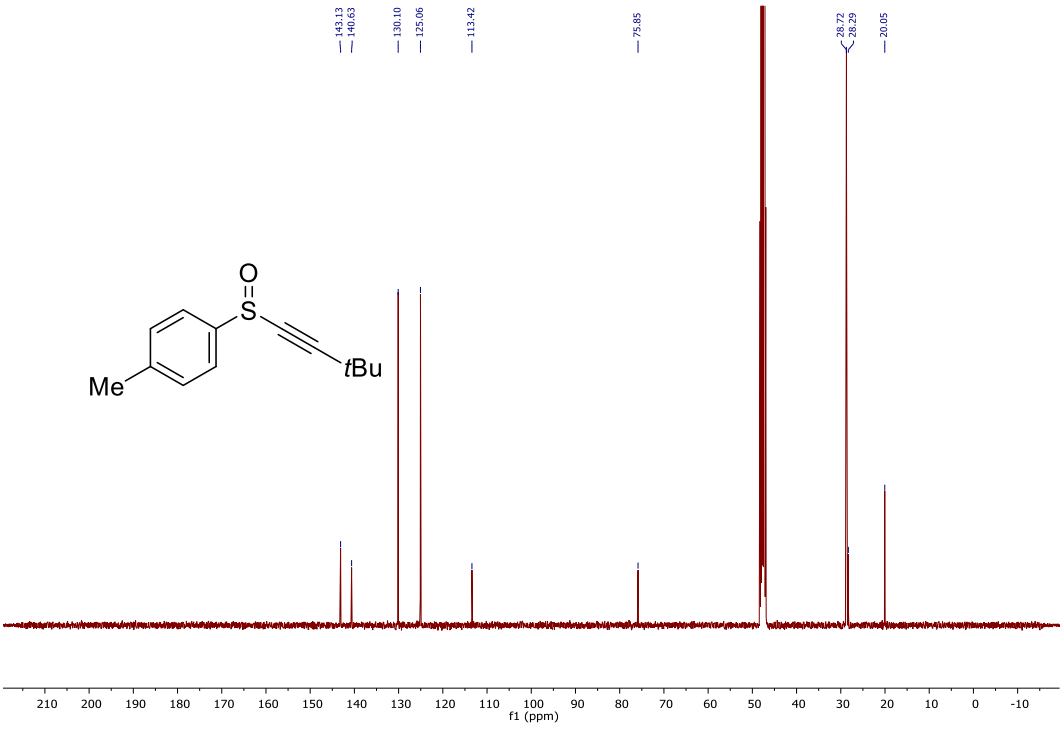


Tert-butyl((4-methylphenylsulfinyl)ethynyl)silane (XX)

^{1}H NMR (400 MHz, Methanol-d_4)

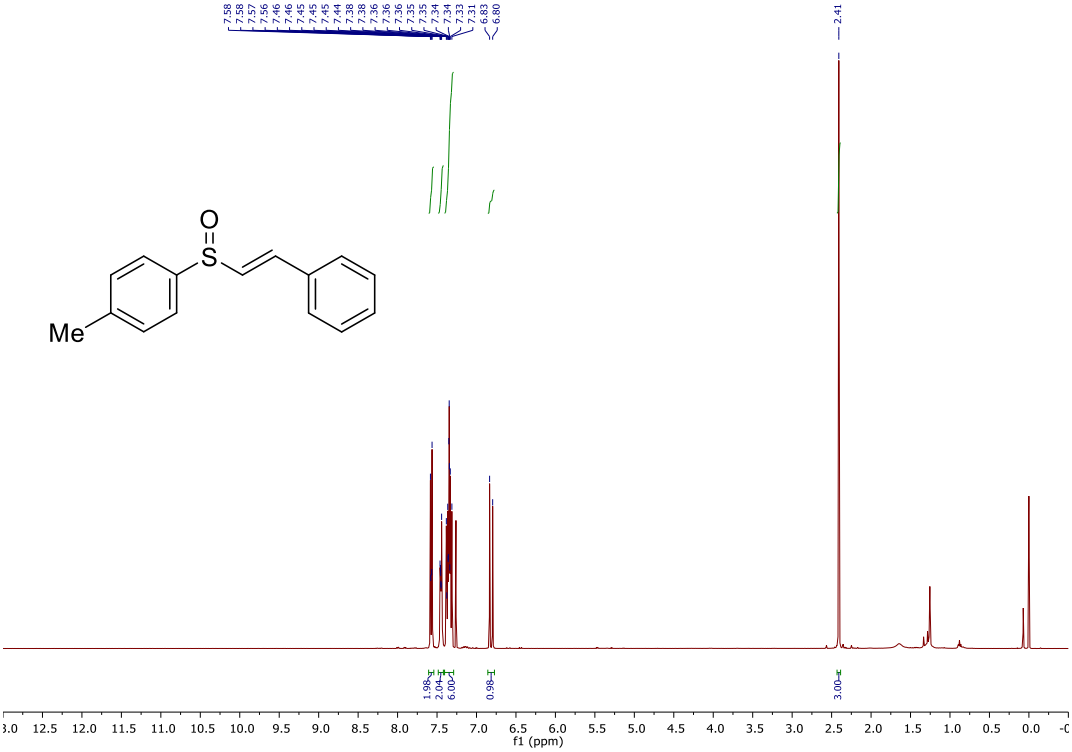


^{13}C NMR (101 MHz, Methanol-d_4)

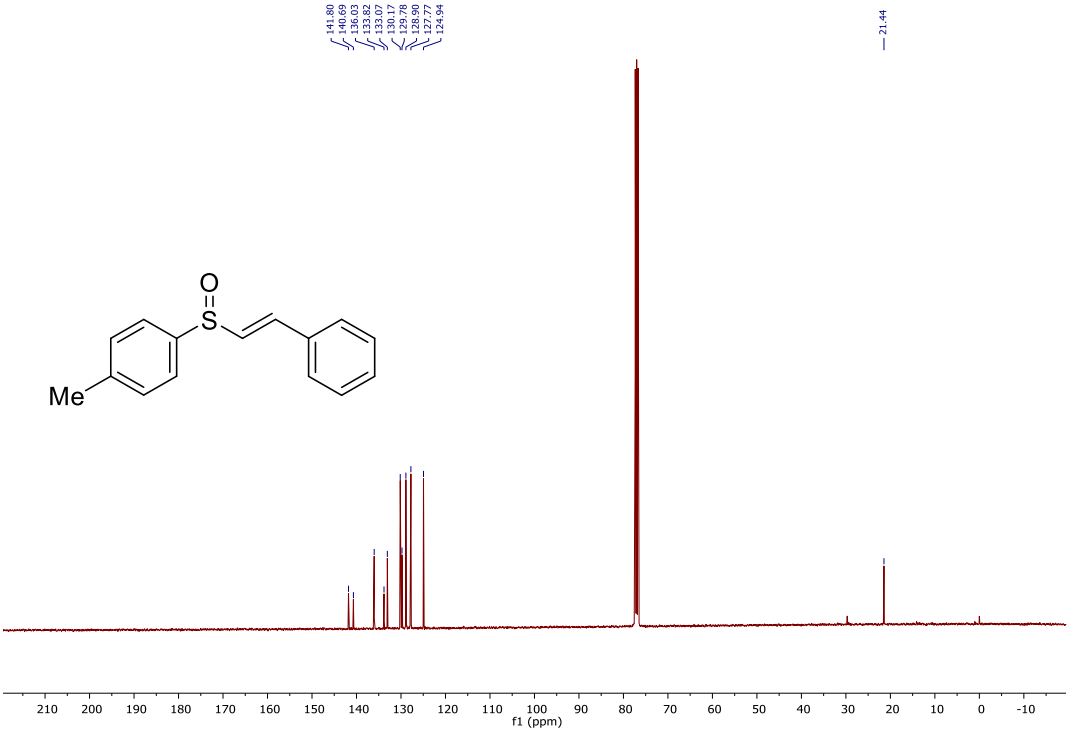


Phenyl((4-methylphenylsulfinyl)ethenyl)silane (12a)

^{1}H NMR (400 MHz, Chloroform-*d*)

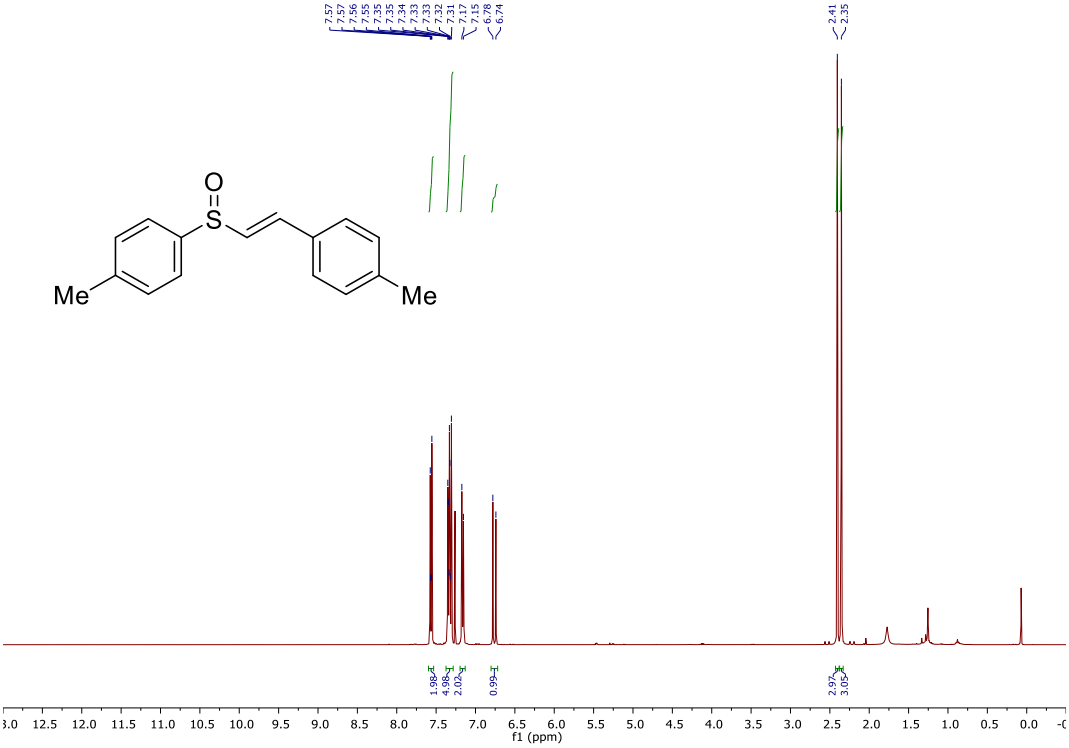


^{13}C NMR (101 MHz, Chloroform-*d*)

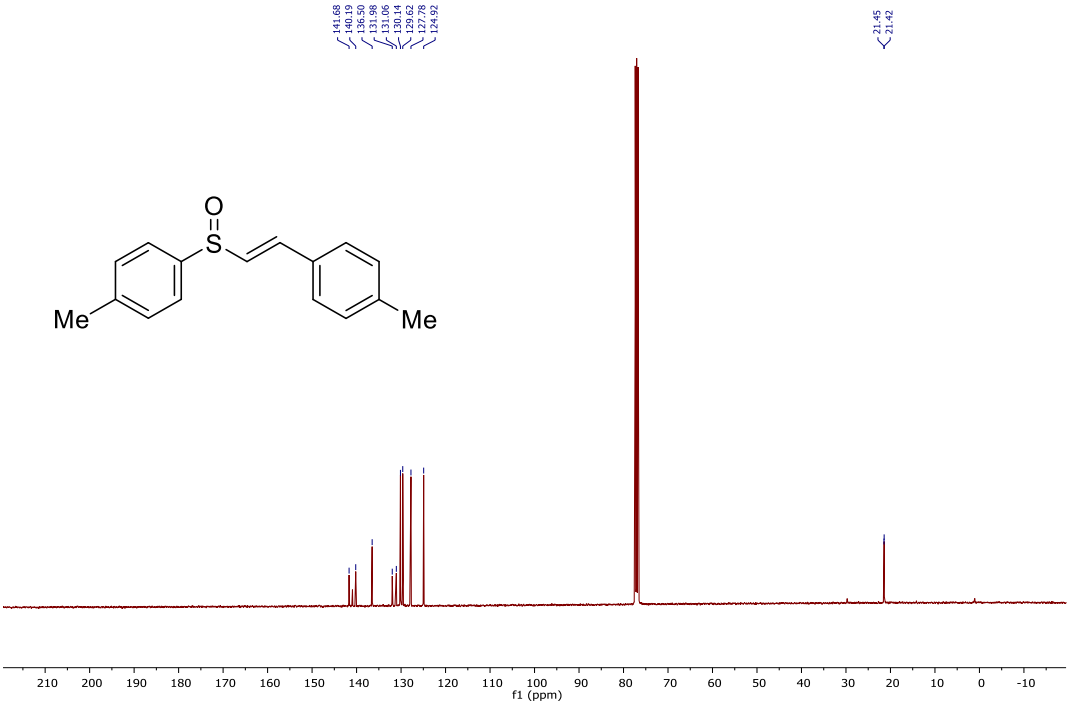


4-methylphenyl((4-methylphenylsulfinyl)ethenyl)silane (12b)

^{1}H NMR (400 MHz, Chloroform-*d*)

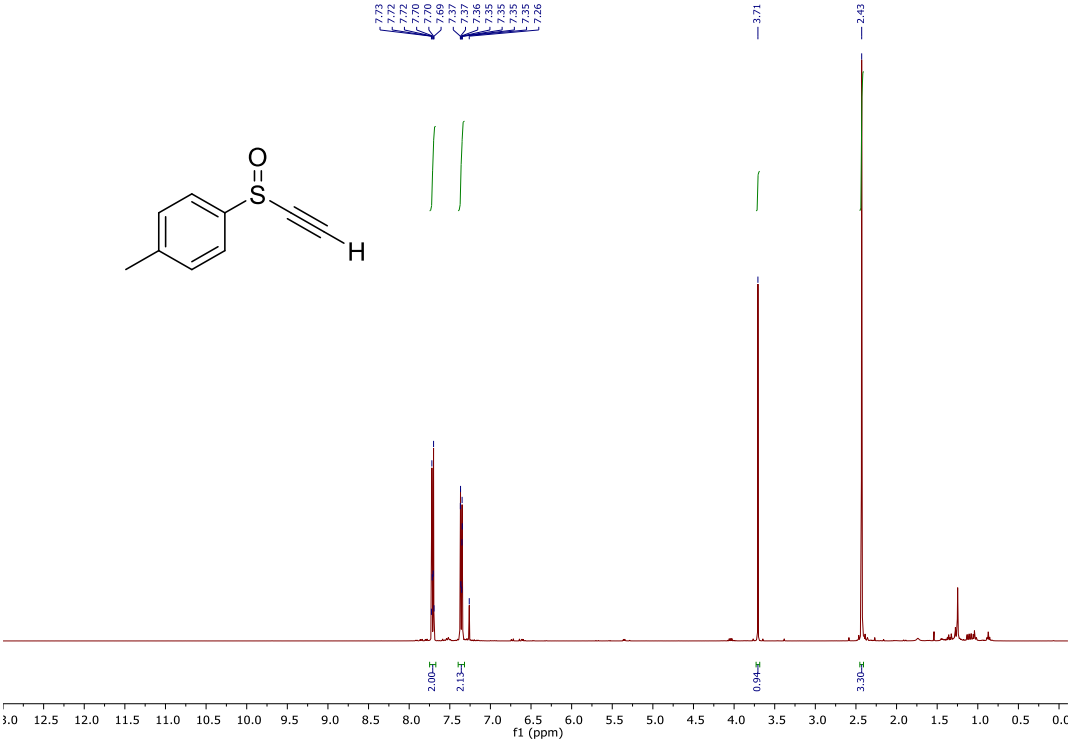


^{13}C NMR (101 MHz, Chloroform-*d*)



1-(ethynylsulfinyl)-4-methylbenzene (13)

^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)