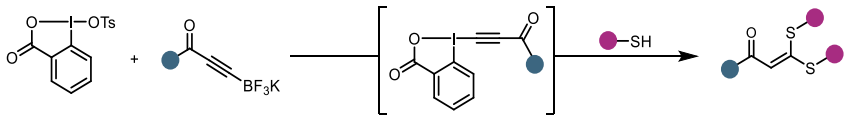
# Acyl-Ethynylbenziodoxolone (acyl-EBX): Access to Ketene Dithioarylacetals

Pierre Palamini,† Julien Borrel,† Maël Djaïd, Morgane Delattre and Jerome Waser*

Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, Switzerland.

*Supporting Information Placeholder*



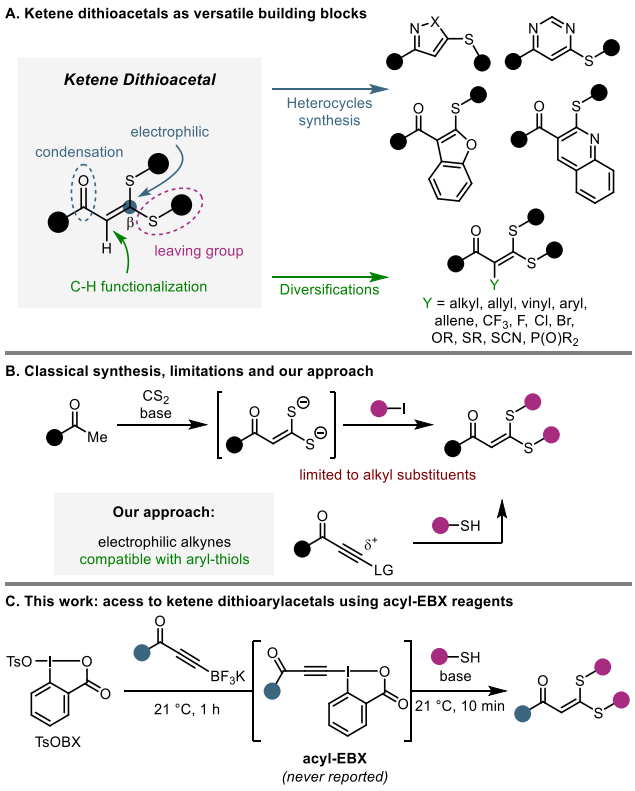

**ABSTRACT:** We report the synthesis of ketene dithioarylacetals in 41-97% yield using thiophenols and acyl-EBXs (ethynylbenziodoxolones) generated *in situ* from a common hypervalent iodine precursor and alkynyl trifluoroborate salts. The products could be further modified to afford functionalized ketene dithioacetals and various *S*-substituted heterocycles.

Ketene dithioacetals are an attractive motif in organic synthesis with a wide range of reactivity (Scheme 1A).[1] In particular ketene dithioacetals bearing an *α*-carbonyl group display biological activities, such as *Leishmania donovani* growth inhibition.[2] In addition, the push-pull polarization of the double bond produced by the sulfur atoms and the carbonyl group makes these compounds versatile building blocks for the preparation of bioactive molecules[3] or materials.[4] They are most often used as a 3-carbon synthon in the synthesis of heterocycles taking advantage of the electrophilicity of the *β*-carbon, the leaving group ability of the sulfur atom via an addition-elimination process, and the possibility of condensation on the carbonyl group. Accessible heterocycles include pyrazoles,[5] isoxazoles,[5] pyrimidines,[6] benzofurans[7] and quinolines.[8] Moreover, numerous C–H functionalization methods have been developed to transfer carbon substituents,[9] halides[10] and chalcogens[11] to the $\alpha$-carbon, allowing to access a large variety of building blocks.

Currently, this motif is most often synthesized starting from ketones, which upon deprotonation react with carbon disulfide (Scheme 1B). After further deprotonation, the resulting dithiolate dianion is quenched by addition of electrophilic alkyl halides to obtain the desired ketene dithioacetal.[9d,f] Based on this approach only alkyl groups on the sulfurs have been introduced as a challenging nucleophilic aromatic substitution would be required to access aryl substituents. Ketene dithioarylacetals have been only rarely reported and their access relies on the use of $\alpha$-*gem*-dihalovinyl intermediates.[12] Therefore, a straightforward synthesis of ketene dithioarylacetals would be of high interest to broaden the chemical space of accessible heterocycles.

To obtain ketene dithioarylacetals, a new approach involving the reaction of thiols with electrophilic alkynes bearing a leaving group appears as an attractive alternative strategy (Scheme 1B). In this context, ethynylbenziodoxolone (EBX) reagents appear as a perfect choice of electrophilic alkynes.[13] They are known to effectively react with thiols under mild reactions conditions to afford the corresponding thioalkynes.[14]

**Scheme 1. Ketene dithioacetals: state of the art and limitations.**



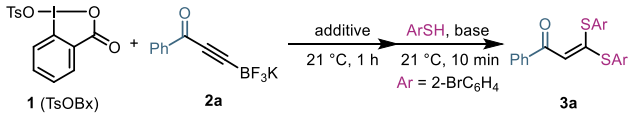
Furthermore, Miyake reported that aryl- and alkyl-substituted EBX reagents can be involved in double additions when using an excess of thiols.[15] However, 1,2-difunctionalization was observed due to an initial ionic *β*-addition on the alkyne followed by a radical *α*-addition-elimination on the vinylic intermediate. In the case of acyl-substituted EBXs, previous computational studies predicted a favored *α*-addition for the ionic pathway,[16] potentially leading to 1,1-difunctionalization instead. Nonetheless, to the best of our knowledge EBX reagents bearing an acyl or other strongly electron-withdrawing groups (EWG) on the alkyne have never been reported. These reagents may be unstable due to the extreme electrophilicity of the *α*-carbon induced by both the hypervalent iodine and the EWG. In fact, a very low activation energy had been predicted for the reaction of acyl-EBX with nucleophiles.[16]

Our group recently reported a novel method to synthesize EBXs starting from tosyloxybenziodoxolone (TsOBX) and alkynyl-trifluoroborate salts.[17] Using those mild conditions, EBX reagents could be formed and used in diverse transformations without isolation. We wondered if this method could allow access to elusive acyl-EBXs and enable their use for the synthesis of ketene dithioacetals. Herein, we report the implementation of this strategy (Scheme 1C). The mild reaction conditions allowed a high functional group tolerance on both thiols and ynones. The products could be further modified via C−H functionalization and applied to the synthesis of heterocycles.

We started our investigation using TsOBX (**1**), ynone trifluoroborate salt **2a**[18] and 2-bromothiophenol as model substrates. Preformation of acyl-EBX was carried out for 1 h using $NaHCO_3$ as additive in a mixture of acetonitrile/tetrahydrofuran. Afterwards, thiol addition using TMG as a base afforded ketene dithioarylacetal **3a** in a promising 74% isolated yield (Table 1, entry 1). Various solvents were evaluated with DME affording the best yield (entries 2-5). $NaHCO_3$ could be removed without any impact on the yield (entry 6).[19] Investigation of other bases such as DBU, TBD, $Cs_2CO_3$ and $K_3PO_4$ confirmed TMG as the most effective for this transformation (entries 7-10). Finally, decreasing the amount of alkyne salt to 1.1 equivalents showed a slight increase of isolated yield to 96% (entry 11).[20]

With the optimized conditions in hand, we explored the scope of thiophenols using ynone trifluoroborate **2a** (Scheme 2A). The model substrate **3a** was obtained in 96% yield on scope scale and in 92% yield on a 3 mmol scale. Using *p*-fluorothiophenol, **3b** was formed in 73% yield. A methyl ester substituent was tolerated and **3c** was isolated in 58% yield. A methoxy substituent afforded **3d** in 78% yield. The introduction of a *p*-acetamide substituted thiophenol afforded **3e** in 97% yield with complete selectivity for the sulfur atom. A more hindered 2,6-dimethylthiophenol gave ketene dithioacetal **3f** in 76% yield. Naphthalene thiol addition afforded **3g** in 73% yield. Heterocyclic thiols were also compatible: diimidazole **3h** and dibenzoxazole **3i** were obtained in 61% and 64% yield, respectively. Benzylic and aliphatic thiols were tolerated in the reaction and **3j** and **3k** were obtained in 84% and 92% yield, respectively. 1,3-Propanedithiol afforded cyclic **3l** in 84% yield. Finally, a Boc-protected cysteine methyl ester was introduced affording **3m** in 77% yield. Although ketene dithioacetals bearing alkyl substituents can be accessed by classical reported methods, the formation of **3m** would require the synthesis of an unnatural iodine-substituted amino acid.

**Table 1. Optimization of the ketene dithioarylacetals synthesis[a]**

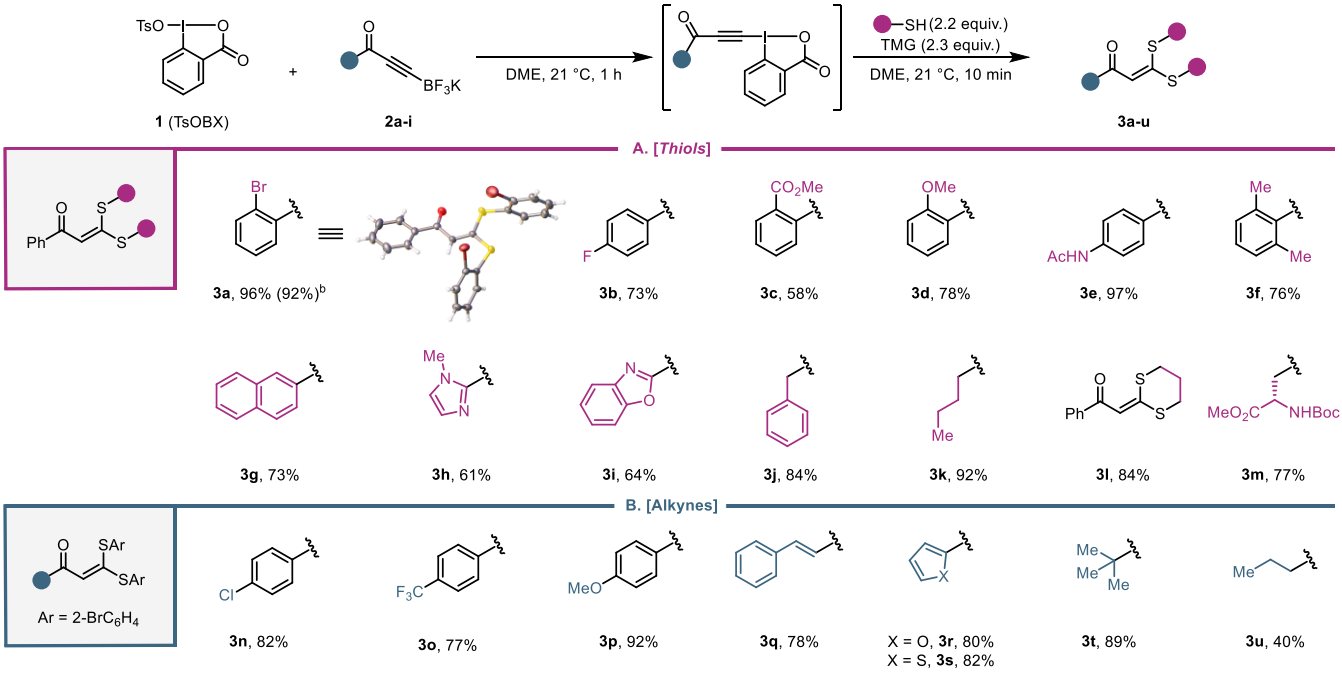



**1** (TsOBx) **2a** **3a**

| entry | solvent | additive | base | yield (%)[b] |
|---|---|---|---|---|
| 1 | $CH_3CN$/THF | $NaHCO_3$ | TMG | 79 (74)[c] |
| 2 | $CH_3CN$ | $NaHCO_3$ | TMG | 78 |
| 3 | THF | $NaHCO_3$ | TMG | 78 |
| 4 | DMF | $NaHCO_3$ | TMG | n.o |
| 5 | DME | $NaHCO_3$ | TMG | 89 |
| 6 | DME | - | TMG | 90 |
| 7 | DME | - | DBU | 88 |
| 8 | DME | - | TBD | 86 |
| 9 | DME | - | $Cs_2CO_3$ | 73 |
| 10 | DME | - | $K_3PO_4$ | 78 |
| **11[d]** | **DME** | **-** | **TMG** | **97 (96)[c]** |

[a]Reaction conditions: (1) TsOBX (**1**) (1.0 equiv.), **2a** (1.25 equiv.), additive (1.5 equiv.), solvent (3.0 mL), 21 °C; (2) 2-Bromothiophenol (2.2 equiv.), base (2.3 equiv.), solvent (1.4 mL), 21 °C, 10 min. Reactions were carried out on a 0.2 mmol scale. [b]NMR yield using dibromomethane as internal standard. [c]Isolated yield. [d]**2a** (1.1 equiv.).

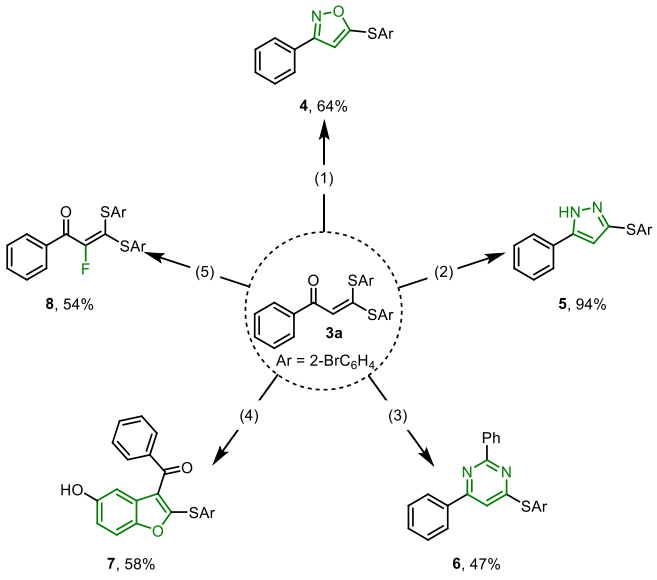
Having established the compatibility of the reaction with various thiols, we next explored functional group tolerance on the intermediate EBX (Scheme 2B). An ynone bearing a *p*-chlorophenyl afforded **3n** in 82% yield. Electron-poor ($CF_3$) and electron-rich (OMe) substituents on the aryl were well tolerated and **3o** and **3p** were obtained in 77% and 92% yields, respectively. Pleasingly, alkenoyl ketene dithioacetal **3q** could be synthetized in 78% yield. This class of substrates has found various applications as a 5-carbon synthon.[1c] Heterocycles were also compatible: furan **3r** and thiophene **3s** could be obtained in 80% and 82% yields, respectively. Alkyl-ynones could also be used, affording **3t** and **3u** bearing a *tert*-butyl or a propyl chain.




**Scheme 2**. Scope of the reaction. [a]Reaction conditions: (1) TsOBX (**1**) (1.0 equiv.), alkynyl-$BF_3K$ **2** (1.1 equiv.), DME (8 mL), 21 °C, 1 h; (2) thiol (2.2 equiv.), TMG (2.3 equiv.), DME (2.8 mL), 21 °C, 10 min. Reactions were carried on a 0.4 mmol scale. [b]3 mmol.

Having in hand diverse ketene dithioarylacetals, we explored the modification of **3a** (Scheme 3). Ketene dithioacetal **3a** could be transformed into various *S*-substituted heterocycles. Isoxazole **4** was obtained in 64% yield via condensation of hydroxylamine and loss of one of the thiophenol moiety (Eq. 1).[5]

**Scheme 3. Modifications of 3a**[a]




[a](1) $NH_2OH{\cdot}HCl$ (4.0 equiv.), KOH (4.0 equiv.), EtOH, 120 °C, 66 h; (2) $NH_2NH_2{\cdot}H_2O$ (4.0 equiv.), EtOH, 120 °C, 1.5 h; (3) Benzamidine hydrochloride (1.1 equiv.), NaH (2.3 equiv.), $CH_3CN$, 21 °C, 18 h; (4) 1,4-Benzoquinone (1.5 equiv.), $CuBr_2$ (2 mol%), $BF_3{\cdot}OEt_2$ (10 mol%), $CH_3CN$, 21 °C, 18 h; (5) Selectfluor (1.5 equiv.), $CH_3CN$, 21 °C, 8 h. See the Supporting Information for experimental details.

Following a similar pathway, pyrazole **5** could be accessed in 94% yield (Eq. 2). Pyrimidine **6** could also be synthesized from **3a** in 47% yield (Eq. 3).[6a] The copper/boron co-catalyzed cyclization of **3a** with *p*-quinone afforded benzofuran **7** in a 58% yield (Eq. 4).[7] Finally, ketene dithioarylacetal **3a** could be further modified by C−H fluorination of the conjugated double bond in 54 % yield (Eq. 5).[10a]

In conclusion, we have developed a method for the synthesis of complex ketene dithioacetals bearing aromatic rings on the sulfur atoms. This was possible via the *in situ* formation of acyl-EBX, a new class of EBX reagents, from TsOBX and alkynyl-trifluoroborate salts. The reaction tolerated a large variety of substituents on the aryl rings of the ynone and the thiols affording ketene dithioarylacetals in good yields. The transformation is also compatible with alkyl substituents at different positions. The obtained ketene dithioarylacetals could be further applied in the synthesis of polysubstituted heterocycles such as isoxazoles, pyrazoles and benzofurans.

## ASSOCIATED CONTENT

### Data Availability

The data underlying this study are available in the published article and its Supporting Information.

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental procedures and analytical data for all new compounds; copy of NMR spectra (PDF).

### Accession Codes

CCDC 2290050 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by

emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

## AUTHOR INFORMATION


### Corresponding Author

**Jerome Waser** - Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland. orcid.org/0000-0002-4570-914X; Email: jerome.waser@epfl.ch.

### Authors

**Pierre Palamini** - Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.
**Julien Borrel** - Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.
**Maël Djaïd** - Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.
**Morgane Delattre** - Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland.


### Author contributions

†P.P. and J.B. are shared first co-authors and contributed equally.
J.B. discovered the reaction and supervised M. Djaïd and M. Delattre for the optimization and a part of the scope. P.P. completed the scope, investigated the product modifications and prepared the experimental part. J.B. and P.P prepared the first draft of the manuscript. J.W. supervised the project, edited the manuscript and proofread the experimental part. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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(20) Attempts at lower temperature (-20 °C, -78 °C) using only one equivalent of thiol still lead to the exclusive formation of **3a**. No traces of thioalkyne formation via mono thiol addition was observed.

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# Acyl-Ethynylbenziodoxolone (acyl-EBX): Access to Ketene Dithioarylacetals

Pierre Palamini,[†] Julien Borrel,[†] Maël Djaïd, Morgane Delattre and Jerome Waser*

Laboratory of Catalysis and Organic Synthesis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, Switzerland.

jerome.waser@epfl.ch

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## 1. General information

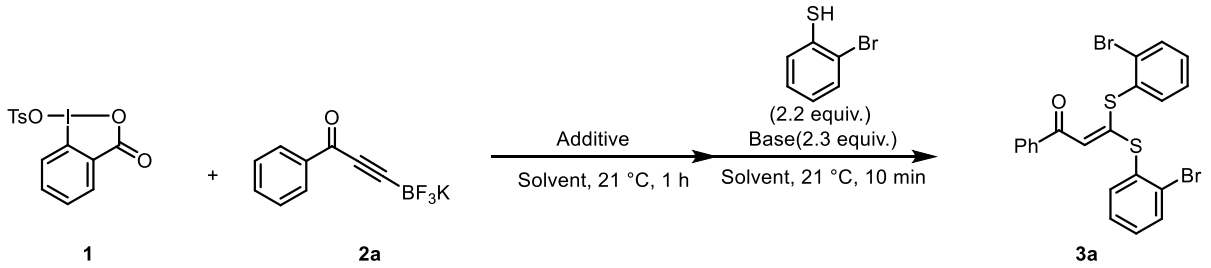
All reactions were carried out under nitrogen. Reactions requiring heating were carried out using DrySyn heating block. For flash chromatography, distilled technical grade solvents were used. THF, $CH_3CN$, $Et_2O$, $CH_2Cl_2$ and toluene were dried by passage over activated alumina under nitrogen atmosphere ($H_2O$ content <10 ppm, Karl-Fischer titration). All chemicals were purchased from Acros, Aldrich, Combi-blocks, Fluka, Fluorochem, Merck, TCI or VWR and used as such unless stated otherwise. 1,2-Dimethoxyethane (DME) was purchased from Acros Organics (99+%, extra pure, stabilized with BHT). Chromatographic purification was performed as flash chromatography using Silicycle silica 40-63 µm (230-400 mesh) or basic alumina (Acros, Brockmann activity I, 40-300 µm, 60Å), using the solvents indicated as eluent with 0.1-0.5 bar pressure unless stated otherwise. TLC was performed on Merck silica gel 60 F254 TLC glass plates and visualized with UV light and potassium permanganate, *p*-anisaldehyde or ceric ammonium molybdate. $^1$H-NMR spectra were recorded on a Bruker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-$d_6$ and acetone-$d_6$. All signals are reported in ppm using the residual solvent signal as internal reference (chloroform-d: 7.26 ppm, DMSO-$d_6$: 2.50 ppm, and acetone-$d_6$: 2.05 ppm). The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br s = broad signal, coupling constant(s) in Hz, integration, assignment). $^{13}$C-NMR spectra were recorded with {$^1$H} decoupling on a Bruker DPX-400 101 MHz spectrometer in chloroform-d, DMSO-$d_6$ and and acetone-$d_6$. All signals are reported in ppm using the residual solvent signal as internal reference (chloroform-d: 77.16 ppm, DMSO-$d_6$: 39.52 ppm, and acetone-$d_6$: 206.26 and 29.84 ppm). $^{19}$F-NMR spectra were recorded with {$^1$H} decoupling on a Bruker DPX-400 376 MHz spectrometer in chloroform-$d_3$, DMSO-$d_6$ and acetone-$d_6$. Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments. High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL. IR spectra were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters ($cm^{-1}$) with indicated relative intensities: s (strong, 0-33% T); m (medium, 34-66% T); w (weak, 67-100% T). Electrospray-ionisation HRMS data were acquired on a Q-Tof Ultima mass spectrometer (Waters) or a Q-Tof 6530 Accurate mass spectrometer (Agilent) operated in the positive ionization mode and fitted with a standard Z-spray ion source equipped with the Lock-Spray interface. Data from the Lock-Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. Atmospheric pressure photo-ionisation (APPI) HRMS measurements were done on a LTQ Orbitrap Elite instrument (Thermofisher) operated in the positive ionization mode. The raw data obtained from the Q-TOF Waters instrument does not take into account the mass of the electron for the ion, the obtained raw data has been corrected by removing (positive ionization) or adding (negative ionization) the mass of the electron (0.5 mDa). Melting points were measured on a Büchi B-540 and are uncorrected. X-ray analyses of compounds **3a** were performed by Dr. R. Scopelliti at the EPF Lausanne.

General note: It is known that carbons linked to the boron atom are difficult to be observed by $^{13}$C NMR due to a broadening of the signal caused by the quadrupole moment of $^{11}$B nuclei. This implies that the two carbons of the alkyne are too broad to be properly visible.[1] Therefore, they are not always listed in the characterization data.

[1] R. A. Oliveira, R. O. Silva, G. A. Molander, P. H. Menezes, *Magn. Reson. Chem.* **2009**, *47*, 873–878.

## 1. Optimization of the synthesis of ketene dithioaryloacetals

**Procedure**



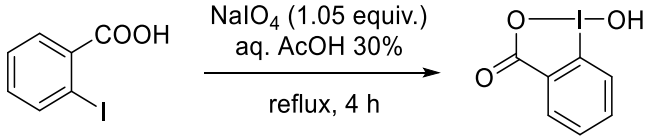

**1** **2a** **3a**

A capped oven dried microwave vial charged with TsOBX **1** (41.8 mg, 0.200 mmol, 1.00 equiv.) and potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (X equiv.) was evacuated and backfilled with $N_2$ (3x). Solvent (3.0 mL) was added under $N_2$. The reaction was stirred at 21 °C for 1 h. To a solution of 2-bromothiophenol (26.4 µL, 0.220 mmol, 2.20 equiv.) in solvent (1.4 mL) was added base (2.3 equiv.). The mixture was stirred for 5 minutes and then added to the previous solution. The reaction mixture was stirred at 21 °C for 10 minutes, quenched with $NaHCO_3$ (aq.) sat. (5 mL) and extracted with DCM (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and solvents were removed under reduced pressure. The yield was obtained by $^1H$ NMR using $CH_2Br_2$ as internal standard (using signal at 6.54 ppm).

## 2. Starting materials preparation

### 2.1 Synthesis of Hypervalent Iodine Reagents

**1-Hydroxy-1,2-benziodoxol-3-(1H)-one S2**

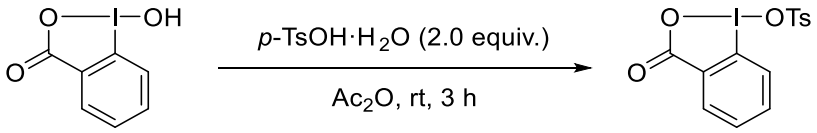



**S1** **S2**

Following a reported procedure, $NaIO_4$ (18.1 g, 84.7 mmol, 1.05 equiv.) and 2-iodobenzoic acid **S1** (20.0 g, 80.6 mmol, 1.00 equiv.) were suspended in a mixture of AcOH (36 mL) and water (84 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (100 mL) and allowed to cool to 21 °C protected from light. The crude product was collected by filtration, washed on the filter with ice water (3 x 50 mL) and acetone (3 x 50 mL), and air-dried in the dark to give the pure product **S2** (19.4 g, 73.6 mmol, 91%) as a white solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 8.02 (d, $J$ = 1.5 Hz, 1H, Ar*H*), 8.01 – 7.93 (m, 1H, Ar*H*), 7.84 (dd, $J$ = 8.2, 1.1 Hz, 1H, Ar*H*), 7.70 (td, $J$ = 7.4, 1.1 Hz, 1H, Ar*H*). **$^{13}$C NMR** (100 MHz, DMSO-$d_6$): δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. Spectroscopic data was consistent with the values reported in the literature.[2]

[2] L. Kraszkiewicz, L. Skulski, *Arkivoc* **2003**, *2003*, 120–125.

**1-(*p*-Methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(*1H*)-one (TsOBX) 1**



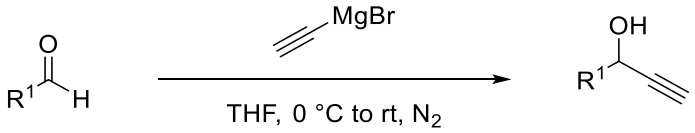

**S2** **1**

Following a reported procedure,[3] *p*-TsOH•$H_2O$ (5.71 g, 30.0 mmol, 2.0 equiv.) was added portionwise to an oven-dried flask containing a suspension of 1-hydroxy-1,2-benziodoxol-3-(1*H*)-one **S2** (3.96 g, 15.0 mmol, 1.0 equiv.) in acetic anhydride (15 mL). After 5 min, a slightly exothermic reaction began and the mixture turned into a clear slightly yellow solution. The reaction was stirred at 21 °C under $N_2$ for 3 h. During the course of the reaction precipitation of the product as a white solid might occur. Dry $Et_2O$ (40 mL) was added and the mixture was cooled to 0 °C for 10 min. At this point precipitation of the product should have occurred. The solid was filtered and washed with dry $Et_2O$ (4 x 40 mL) then dried *in vacuo* to afford 1-(*p*-methylbenzenesulfonyloxy)-1,2-benziodoxol-3-(1*H*)-one **1** (4.75 g, 11.4 mmol, 76%) as a white solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 8.01 (dd, *J* = 7.5, 1.5 Hz, 1H, Ar*H*), 7.98 – 7.93 (m, 1H, Ar*H*), 7.83 (dd, *J* = 8.1, 0.9 Hz, 1H, Ar*H*), 7.70 (td, *J* = 7.4, 1.0 Hz, 1H, Ar*H*), 7.51 – 7.46 (m, 2H, 2 x Ar*H*), 7.15 – 7.10 (m, 2H, Ar*H*), 2.28 (s, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 167.9, 145.2, 138.1, 134.6, 131.5, 131.2, 130.5, 128.3, 126.4, 125.6, 120.5, 20.9. Spectroscopic data was consistent with the values reported in the literature.[4]

## 2.2 Synthesis of Potassium Trifluoborate Salts

### 2.2.1 Synthesis of propargylic alcohols

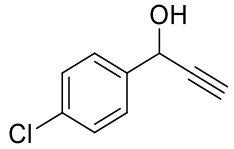
**General procedure A**




Following a reported procedure,[5] an oven-dried round-bottom flask, charged with aldehyde (1.0 equiv.) if solid, was evacuated and backfilled with $N_2$ (3x). Then, aldehyde (if liquid) and anhydrous THF (0.5 M) were added. The mixture was cooled to 0 °C and a solution of ethynylmagnesium bromide (0.50 M in THF, 1.2 equiv.) was added dropwise under $N_2$. The mixture was allowed to slowly warm to 21 °C and the reaction was followed by TLC until completion. Upon completion, the reaction was quenched with saturated $NH_4Cl$ (8 mL) and extracted with diethylether (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel to yield the desired propargylic alcohol.

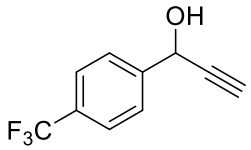
[3] M. Nappi, C. He, W. G. Whitehurst, B. G. N. Chappell, M. J. Gaunt, *Angew. Chem. Int. Ed.* **2018**, *57*, 3178–3182.
[4] Y. Yamamoto, H. Togo, *Synlett* **2005**, *2005*, 2486–2488.
[5] P. Fricero, L. Bialy, A. W. Brown, W. Czechtizky, M. Méndez, J. P. A. Harrity, *J. Org. Chem.* **2017**, *82*, 1688–1696.

**1-(4-Chlorophenyl)prop-2-yn-1-ol 9**



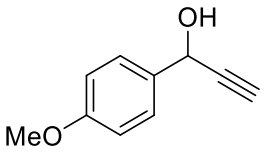

Synthesized following procedure A, starting from 4-chlorobenzaldehyde (1.05 mL, 7.50 mmol) for 3 h. Purification by column chromatography ($SiO_2$, pentane:EtOAc = 8:2) afforded 1-(chlorophenyl)prop-2-yn-1-ol **9** (1.01 g, 6.07 mmol, 81% yield) as an orange oil. **$R_f$** (pentane: EtOAc = 8:2) = 0.41. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.38 (m, 2H, 2 x Ar*H*), 7.37 – 7.28 (m, 2H, 2 x Ar*H*), 5.38 (d, *J* = 2.4 Hz, 1H, (OH)C*H*C≡C), 3.18 (s, 1H, C≡C*H*), 2.67 (d, *J* = 2.3 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.4, 134.3, 128.8, 128.1, 83.1, 75.3, 63.6. Spectroscopic data was consistent with the values reported in the literature.[6]

**1-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-ol 10**




Synthesized following procedure A, starting from 4-(trifluoromethyl)benzaldehyde (1.02 mL, 7.50 mmol) for 3 h. Purification by column chromatography ($SiO_2$, pentane:EtOAc = 8:2) afforded 1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol **10** (1.30 g, 6.50 mmol, 87% yield) as an orange oil. **$R_f$** (pentane: EtOAc = 8:2) = 0.52. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 4H, 4 x Ar*H*), 5.53 (dd, *J* = 5.9, 2.3 Hz, 1H, (OH)C*H*C≡C), 2.71 (d, *J* = 2.3 Hz, 1H, C≡C*H*), 2.45 (d, *J* = 5.9 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.8, 130.8 (q, *J* = 32.4 Hz), 127.0, 125.8 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 82.9, 75.7, 63.9. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -62.6. Spectroscopic data was consistent with the values reported in the literature.[7]

**1-(4-Methoxyphenyl)prop-2-yn-1-ol 11**

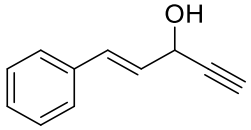



Synthesized following procedure A, starting from 4-methoxybenzaldehyde (0.913 mL, 7.50 mmol) for 3 h. Purification by column chromatography ($SiO_2$, pentane:EtOAc = 8:2) afforded 1-(4-methoxyphenyl)prop-2-yn-1-ol **11** (806 mg, 4.97 mmol, 66% yield) as an orange oil. **$R_f$** (pentane: EtOAc = 8:2) = 0.42. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H, Ar*H*), 6.96 – 6.86 (m, 2H, 2 x Ar*H*), 5.40 (dd, *J* = 6.0, 2.3 Hz, 1H, (OH)C*H*C≡C), 3.81 (s, 3H, C$H_3$), 3.10 – 3.00 (m, 1H, C≡C*H*), 2.68 (d, *J* = 2.3 Hz, 1H, O*H*).**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.6, 132.5, 128.1,

[6] C.-F. Xu, M. Xu, L.-Q. Yang, C.-Y. Li, *J. Org. Chem.* **2012**, *77*, 3010–3016.
[7] D. A. Petrone, M. Isomura, I. Franzoni, S. L. Rössler, E. M. Carreira, *J. Am. Chem. Soc.* **2018**, *140*, 4697–4704.

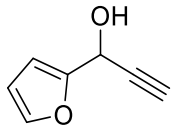
114.0, 83.9, 74.7, 63.8, 55.4. Spectroscopic data were consistent with the values reported in literature.[8]

***(E)*-1-Phenylpent-1-en-4-yn-3-ol 12**



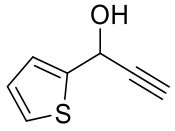

Synthesized following procedure A, starting from cinnamaldehyde (944 µL, 7.50 mmol) for 3 h. Purification by column chromatography ($SiO_2$, pentane:EtOAc = 9:1 to 8:2) afforded *(E)*-1-phenylpent-1-en-4-yn-3-ol **12** (1.03 g, 6.52 mmol, 87% yield) as a colorless oil. $\mathbf{R_f}$ (pentane: EtOAc = 8:2) = 0.47. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H, 2 x Ar*H*), 7.38 – 7.31 (m, 2H, 2 x Ar*H*), 7.31 – 7.27 (m, 1H, Ar*H*), 6.81 (dd, *J* = 15.8, 1.6 Hz, 1H, C$H_{alkene}$), 6.31 (dd, *J* = 15.8, 5.9 Hz, 1H, C$H_{alkene}$), 5.10 – 5.02 (m, 1H, (OH)C*H*C≡C), 2.65 (d, *J* = 2.3 Hz, 1H, C≡C*H*), 1.97 (d, *J* = 6.5 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 136.0, 132.5, 128.8, 128.4, 127.6, 127.0, 82.9, 74.8, 62.9. Spectroscopic data were consistent with the values reported in literature.[9]

**1-(Furan-2-yl)prop-2-yn-1-ol 13**




Synthesized following procedure A, starting from furfuraldehyde (621 µL, 7.50 mmol) for 3 h. Purification by column chromatography ($SiO_2$, pentane:EtOAc = 9:1 to 8:2) afforded 1-(furan-2-yl)prop-2-yn-1-ol **13** (915 mg, 7.49 mmol, 100% yield) as a colorless oil. $\mathbf{R_f}$ (pentane: EtOAc = 8:2) = 0.50. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 1.8, 0.9 Hz, 1H, Ar*H*), 6.48 (dt, *J* = 3.3, 0.8 Hz, 1H, Ar*H*), 6.37 (dd, *J* = 3.3, 1.9 Hz, 1H, Ar*H*), 5.47 (dd, *J* = 7.1, 2.3 Hz, 1H, C*H*OH), 2.63 (d, *J* = 2.3 Hz, 1H, C≡C*H*), 2.31 (d, *J* = 7.1 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.5, 143.3, 110.6, 108.2, 81.1, 74.3, 58.2. Spectroscopic data were consistent with the values reported in literature.[10]

**1-(Thiophen-2-yl)prop-2-yn-1-ol 14**

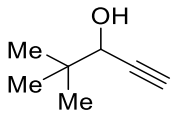



Synthesized following procedure A, starting from thiophene-2-carbaldehyde (380 µL, 4.07 mmol) for 3 h. Purification by column chromatography ($SiO_2$, pentane:EtOAc = 85:15) afforded 1-(thiophen-2-yl)prop-2-yn-1-ol **14** (493 mg, 3.57 mmol, 88% yield) as a yellow oil. $\mathbf{R_f}$ (pentane: EtOAc = 9:1) = 0.30. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 5.1, 1.3 Hz, 1H, Ar*H*), 7.21 (dt, *J* = 3.5, 1.1 Hz, 1H, Ar*H*), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H, Ar*H*), 5.67 (ddd, *J* = 7.1, 2.3, 1.0

[8] J. Park, J. Yun, J. Kim, D.-J. Jang, C. H. Park, K. Lee, *Synth. Commun.* **2014**, *44*, 1924–1929.
[9] H. J. Ghazvini, M. Armaghan, C. Janiak, S. Balalaie, T. J. J. Müller, *Eur. J. Org. Chem.* **2019**, *2019*, 7058–7062.
[10] D. Ahmadli, Y. Sahin, E. Calikyilmaz, O. Şahin, Y. E. Türkmen, *J. Org. Chem.* **2022**, *87*, 6336–6346.

Hz, 1H, (OH)C*H*C≡C), 2.69 (d, *J* = 2.3 Hz, 1H, C≡C*H*), 2.33 (d, *J* = 7.0 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 143.9, 126.8, 126.3, 125.9, 82.9, 74.4, 60.0. Spectroscopic data were consistent with the values reported in literature.[9]

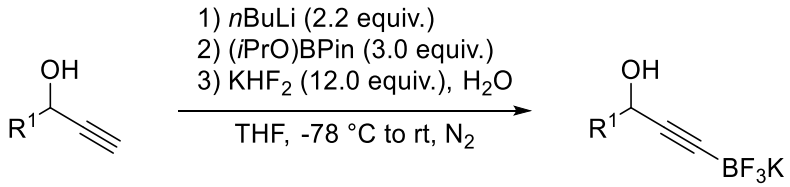
**4,4-Dimethylpent-1-yn-3-ol 15**




Synthesized following procedure A, starting from pivaldehyde (3.00 mL, 28.0 mmol) for 3 h. Purification by column chromatography ($SiO_2$, pentane:$Et_2O$ = 95:5 to 8:2) afforded 4,4-dimethylpent-1-yn-3-ol **15** (2.30 g, 20.5 mmol, 73% yield) as a colorless liquid. **$R_f$** (pentane: $Et_2O$ = 8:2) = 0.59. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.02 (dd, *J* = 6.1, 2.1 Hz, 1H, (OH)C*H*C≡C), 2.45 (d, *J* = 2.3 Hz, 1H, C≡C*H*), 1.79 (d, *J* = 6.1 Hz, 1H, O*H*), 1.00 (s, 9H, C($CH_3$)$_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 83.7, 73.9, 71.3, 35.7, 25.3. Spectroscopic data were consistent with the values reported in literature.[11]

## 2.2.2. Synthesis of potassium trifluoroborate propagylic alcohols saltss

### General procedure B

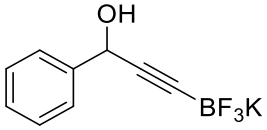



Following a reported procedure,[5] an oven-dried round bottom flask (PFA) was evacuated and backfilled with $N_2$ (3x), then propargylic alcohol (1.0 equiv.) and dry THF (0.25 M) were added. The solution was cooled to -78 °C and a solution of *n*BuLi (2.5 M in hexane, 2.2 equiv.) was added dropwise under $N_2$. The mixture was stirred at this temperature for 1 h. 4,4,5,5-Tetramethyl-2-propan-2-yloxy-1,3,2-dioxaborolane (3.0 equiv.) was added at once at -78 °C and the mixture was allowed to warm to -20 °C (ice/NaCl bath) and stirred for 1 h. A solution of $KHF_2$ (12.0 equiv.) in water (0.3 g/mL) was added. The reaction was stirred at 21 °C open to air for 1 h. The mixture was concentrated in vacuo, the wet solid obtained was further dried by co-evaporation with toluene (3 x 20 mL). The resulting solid was diluted with acetone (30 mL) and was put on the rotavap at $P_{atm}$ with the bath at 45 °C for 10 minutes. The solution was filtered with care to leave the insoluble material in the flask. This process was repeated 2 more times. Solvents were removed under reduced pressure. The obtained solid was dissolved in the minimum amount of hot acetone and precipitation of the desired product was performed by addition of diethyl ether. The mixture was cooled down to 0 °C, filtered off, washed with diethyl ether (3 x 20 mL) and dried under high vaccum to afford the desired potassium trifluoroborate propargylic alcohol.

[11] T. E. Nielsen, S. L. Quement, D. Tanner, *Synthesis* **2004**, *2004*, 1381–1390.

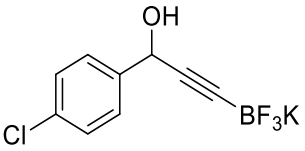
Note: This purification procedure usually affords the pure desired product. If it is not the case a more classical recrystallization from acetone/$Et_2O$ can be performed.

**Potassium trifluoro(3-hydroxy-3-phenylprop-1-yn-1-yl)borate 16**



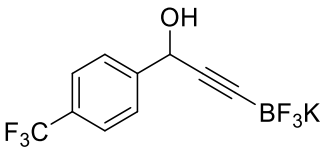

Synthesized following procedure B, starting from commercially available 1-phenylprop-2-yn-1-ol (1.98 mL, 15.0 mmol). Potassium trifluoro(3-hydroxy-3-phenylprop-1-yn-1-yl)borate **16** (2.91 g, 12.2 mmol, 81%) was obtained as a white solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 7.44 (dd, *J* = 8.2, 1.4 Hz, 2H, 2 x Ar*H*), 7.31 (dd, *J* = 8.0, 7.0 Hz, 2H, 2 x Ar*H*), 7.26 – 7.19 (m, 1H, Ar*H*), 5.58 (d, *J* = 5.8 Hz, 1H, C*H*OH), 5.16 (dd, *J* = 5.8, 1.8 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 143.7, 127.8, 126.9, 126.5, 90.3, 63.1. **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -135.0. **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -1.9 (dd, Jj = 63.4, 25.1 Hz). Spectroscopic data were consistent with the values reported in literature.[12]

**Potassium (3-(4-chlorophenyl)-3-hydroxyprop-1-yn-1-yl)trifluoroborate 17**




Synthesized following procedure B, starting from 1-(chlorophenyl)prop-2-yn-1-ol **9** (1.25 g, 7.50 mmol). Potassium (3-(4-chlorophenyl)-3-hydroxyprop-1-yn-1-yl)trifluoroborate **17** (1.64 g, 6.02 mmol, 80%) was obtained as a white solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 7.49 – 7.43 (m, 2H, 2 x Ar*H*), 7.37 (d, *J* = 8.7 Hz, 2H, 2 x Ar*H*), 5.70 (d, *J* = 6.0 Hz, 1H, C*H*OH), 5.16 (dd, *J* = 5.9, 1.7 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 142.7, 131.4, 128.3, 127.8, 62.4. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -131.6. **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -1.8. Spectroscopic data were consistent with the values reported in literature.[5]

**Potassium trifluoro(3-hydroxy-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate 18**

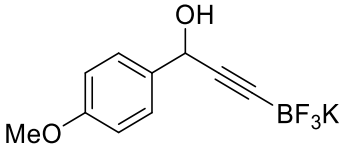



Synthesized following procedure B, starting from 1-(4-(trifluoromethyl)phenyl)prop-2-yn-1-ol **10** (1.00 g, 5.00 mmol). Potassium trifluoro(3-hydroxy-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate **18** (720 mg, 2.35 mmol, 47%) was obtained as a grey solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 7.75 – 7.62 (m, 4H, 4 x Ar*H*), 5.86 (d, *J* = 5.9 Hz, 1H, C*H*OH), 5.27 (d, *J* = 5.6 Hz, 1H, O*H*). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 148.3, 128.0 (q, *J* =31.2 Hz), 127.7, 125.9 (q, *J* = 3.7 Hz), 124.9 (q, *J* = 269 Hz), 90.3, 62.5. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -60.7, -131.7. **$^{11}$B NMR** (128

[12] J. D. Kirkham, S. J. Edeson, S. Stokes, J. P. A. Harrity, *Org. Lett.* **2012**, *14*, 5354–5357.

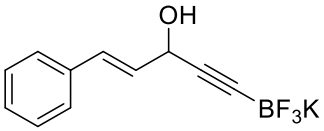
MHz, DMSO-$d_6$) δ -2.0. Spectroscopic data were consistent with values reported in literature.[12]

**Potassium trifluoro(3-hydroxy-3-(4-methoxyphenyl)prop-1-yn-1-yl)borate 19**



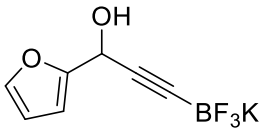

Synthesized following procedure B, starting from 1-(4-methoxyphenyl)prop-2-yn-1-ol **11** (973 mg, 6.00 mmol). Potassium trifluoro(3-hydroxy-3-(4-methoxyphenyl)prop-1-yn-1-yl)borate **19** (518 mg, 1.93 mmol, 32%) was obtained as a white solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 7.35 (d, *J* = 8.7 Hz, 2H, 2 x Ar*H*), 6.87 (d, *J* = 8.8 Hz, 2H, 2 x Ar*H*), 5.45 (d, *J* = 5.8 Hz, 1H, C*H*OH), 5.10 (dd, *J* = 5.8, 1.5 Hz, 1H, O*H*), 3.73 (s, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 158.3, 135.9, 127.8, 113.2, 62.7, 55.1. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -131.5. **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -1.7. Spectroscopic data were consistent with values reported in literature.[12]

**Potassium *(E)*-trifluoro(3-hydroxy-5-phenylpent-4-en-1-yn-1-yl)borate 20**



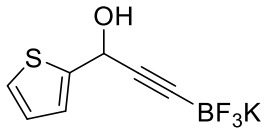

Synthesized following procedure B, starting from *(E)*-1-phenylpent-1-en-4-yn-3-ol **12** (902 mg, 5.70 mmol). Potassium *(E)*-trifluoro(3-hydroxy-5-phenylpent-4-en-1-yn-1-yl)borate **20** (1.05 g, 3.96 mmol, 69%) was obtained as a white solid. **m. p.** (dec.) 207 °C. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 7.47 – 7.39 (m, 2H, 2 x Ar*H*), 7.33 (t, *J* = 7.6 Hz, 2H, 2 x Ar*H*), 7.23 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.57 (d, *J* = 15.7 Hz, 1H, C$H_{alkene}$), 6.24 (dd, *J* = 15.9, 6.0 Hz, 1H, C$H_{alkene}$), 5.31 (d, *J* = 5.8 Hz, 1H, C*H*OH), 4.79 – 4.72 (m, 1H, O*H*). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 136.6, 131.8, 128.6, 128.3, 127.4, 126.3, 61.7. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -131.6. **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.6 (q, *J* = 35.0 Hz). **IR** ($\nu_{max}$, cm$^{-1}$) 3400 (br), 1713 (w), 1121 (m), 979 (s), 750 (s). **HRMS** (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_{11}H_9BF_3O^-$ 225.0704; Found 225.0708.

**Potassium trifluoro(3-(furan-2-yl)-3-hydroxyprop-1-yn-1-yl)borate 21**



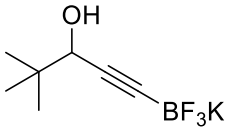

Synthesized following procedure B, starting from 1-(furan-2-yl)prop-2-yn-1-ol **13** (855 mg, 7.00 mmol). Potassium trifluoro(3-(furan-2-yl)-3-hydroxyprop-1-yn-1-yl)borate **21** (864 mg, 3.79 mmol, 54%) was obtained as a white solid. **m. p.** (dec.) 113 °C. **$^1$H NMR** (400 MHz, acetone-$d_6$) δ 7.42 (dt, *J* = 2.0, 1.0 Hz, 1H, Ar*H*), 6.37 (d, *J* = 3.3 Hz, 1H, Ar*H*), 6.32 (dd, *J* = 3.3, 1.9 Hz, 1H, Ar*H*), 5.27 – 5.21 (m, 1H, C*H*OH), 4.53 (s, 1H, O*H*). **$^{13}$C NMR** (101 MHz, acetone-$d_6$) δ 157.1, 142.7, 110.8, 107.1, 58.7. **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -134.8 – -135.4 (m). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.7 (q, *J* = 34.8 Hz). **IR** ($\nu_{max}$, cm$^{-1}$) 3522 (br), 1707 (w), 1094 (s), 1010 (s). **HRMS** (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_7H_5BF_3O_2^-$ 189.0340; Found 189.0345.

**Potassium trifluoro(3-hydroxy-3-(thiophen-2-yl)prop-1-yn-1-yl)borate 22**



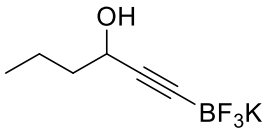

Synthesized following procedure B, starting from 1-(4-methoxyphenyl)prop-2-yn-1-ol **14** (973 mg, 6.00 mmol). Potassium trifluoro(3-hydroxy-3-(thiophen-2-yl)prop-1-yn-1-yl)borate **22** (955 mg, 3.91 mmol, 81%) was obtained as a brown solid. **m. p.** (dec.) 139 °C. **$^{1}$H NMR** (400 MHz, acetone-$d_6$) δ 7.29 (dd, *J* = 5.1, 1.3 Hz, 1H, Ar*H*), 7.11 (dt, *J* = 2.3, 1.2 Hz, 1H, Ar*H*), 6.91 (dd, *J* = 5.1, 3.5 Hz, 1H, Ar*H*), 5.51 – 5.46 (m, 1H, C*H*OH), 4.72 – 4.63 (m, 1H, O*H*). **$^{13}$C NMR** (101 MHz, acetone-$d_6$) δ 149.2, 126.8, 125.5, 125.2, 60.9. **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -136.2 (dd, *J* = 65.2, 32.6 Hz). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.7 (q, *J* = 32.4 Hz). **IR** ($\nu_{max}$, $cm^{-1}$) 3488 (w), 1710 (w), 1274 (m), 1105 (s), 1011 (s), 748 (s). **HRMS** (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_7H_5BF_3OS^-$ 205.0112; Found 205.0113.

**Potassium trifluoro(3-hydroxy-4,4-dimethylpent-1-yn-1-yl)borate 23**




Synthesized following procedure B, starting from 4,4-dimethylpent-1-yn-3-ol **15** (1.68 g, 15.0 mmol). Potassium trifluoro(3-hydroxy-4,4-dimethylpent-1-yn-1-yl)borate **23** (2.63 g, 10.0 mmol, 67%) was obtained as a white solid. **$^{1}$H NMR** (400 MHz, acetone-$d_6$) δ 3.83 (s, 1H, C*H*OH), 3.62 (d, *J* = 4.9 Hz, 1H, O*H*), 0.93 (s, 9H, C(C$H_3$)$_3$). **$^{13}$C NMR** (101 MHz, acetone-$d_6$) δ 90.0, 71.8, 36.2, 25.9. **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -133.6 – -136.3 (m). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.6 (q, *J* = 37.2 Hz). Spectroscopic data were consistent with values reported in literature.[12]

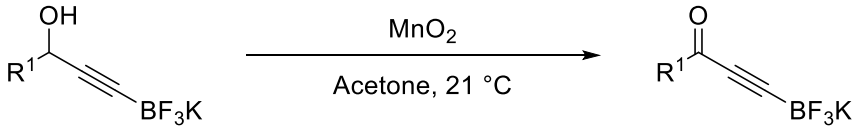
**Potassium trifluoro(3-hydroxyhex-1-yn-1-yl)borate 24**




Synthesized following procedure B, starting from commercially available hex-1-yn-3-ol (840 mL, 7.50 mmol). Potassium trifluoro(3-hydroxyhex-1-yn-1-yl)borate **24** (1.11 g, 5.46 mmol, 73%) was obtained as a white solid. **$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ 4.79 (d, *J* = 5.4 Hz, 1H, O*H*), 4.01 (tdd, *J* = 6.7, 5.0, 1.6 Hz, 1H, C*H*OH), 1.50 – 1.27 (m, 4H, 2 x C$H_2$), 0.85 (t, *J* = 7.3 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 91.8, 60.7, 40.5, 18.3, 13.8. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -131.2 – -131.7 (m). **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -1.7. Spectroscopic data were consistent with values reported in literature.[12]

## 2.2.3. Synthesis of alkynyl trifluoroborate salts

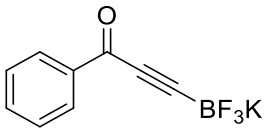
### General procedure C




Following a reported procedure,[12] to a suspension of $MnO_2$ (5.00 equiv.) in acetone (0.3 M) was added the corresponding potassium trifluoroborate propargylic alcohol (1.00 equiv.) portionwise at 21 °C. The reaction was followed by $^{19}F$ NMR spectroscopy. Upon completion, the mixture was filtered through a pad of celite and eluted with $Et_2O$ (20 mL). All volatiles were removed under reduced pressure. The obtained solid was dissolved in the minimum amount of hot acetone (10 mL) and precipitation of the desired product was performed by addition of diethyl ether (150 mL). The mixture was cooled down to 0 °C, filtered off, washed with diethyl ether (3 x 20 mL) and dried under high vaccum to afford the desired product.

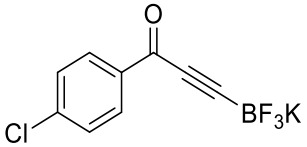
Note: This purification procedure usually affords the pure desired product. If it is not the case a more classical recrystallization from acetone/$Et_2O$ can be performed.

**Potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate 2a**



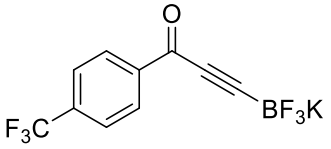

Synthesized following procedure C, starting from potassium trifluoro(3-hydroxy-3-phenylprop-1-yn-1-yl)borate **16** (960 mg, 4.00 mmol) for 3 h. Potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (840 mg, 3.50 mmol, 88%) was obtained as a white solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 8.11 – 8.03 (m, 2H, 2 x Ar*H*), 7.72 – 7.64 (m, 1H, Ar*H*), 7.56 (ddd, *J* = 8.1, 6.5, 1.2 Hz, 2H, 2 x Ar*H*). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 178.2, 136.8, 133.8, 128.9, 128.7. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -131.6 – -135.2 (m). **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -2.0 (q, *J* = 33.0 Hz). Spectroscopic data were consistent with values reported in literature.[12]

**Potassium (3-(4-chlorophenyl)-3-oxoprop-1-yn-1-yl)trifluoroborate 2b**



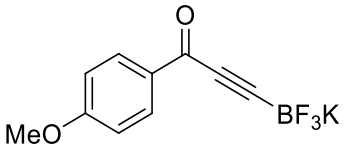

Synthesized following procedure C, starting from potassium (3-(4-chlorophenyl)-3-hydroxyprop-1-yn-1-yl)trifluoroborate **17** (1.36 g, 5.00 mmol). Potassium (3-(4-chlorophenyl)-3-oxoprop-1-yn-1-yl)trifluoroborate **2b** (599 mg, 2.21 mmol, 44%) was obtained as a white solid. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 8.07 – 8.00 (m, 2H, 2 x Ar*H*), 7.68 – 7.60 (m, 2H, 2 x Ar*H*). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 176.9, 138.83, 135.5, 130.7, 129.0. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -133.2 (dd, *J* = 63.5, 28.4 Hz). **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -2.0 (q, *J* = 32.0 Hz). Spectroscopic data were consistent with values reported in literature.[5]

**Potassium trifluoro(3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate 2c**



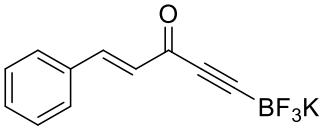
Synthesized following procedure C, starting from potassium trifluoro(3-hydroxy-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate **18** (500 mg, 1.63 mmol). Potassium trifluoro(3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate **2c** (212 mg, 0.699 mmol, 43%) was obtained as a white solid. **$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ 8.23 (d, *J* = 8.1 Hz, 2H, 2 x Ar*H*), 7.96 (d, *J* = 8.2 Hz, 2H, 2 x Ar*H*). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 177.0, 139.7, 133.0 (q, *J* = 31.9 Hz), 127.8, 125.9 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.9 Hz). **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -61.6, -133.2 (dd, *J* = 64.0, 29.3 Hz). **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -2.0 (q, *J* = 32.8 Hz). Spectroscopic data were consistent with values reported in literature.[12]

**Potassium trifluoro(3-(4-methoxyphenyl)-3-oxoprop-1-yn-1-yl)borate 2d**



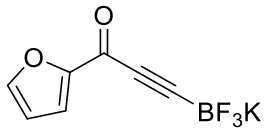
Synthesized following procedure C, starting from potassium potassium trifluoro(3-hydroxy-3-(4-methoxyphenyl)prop-1-yn-1-yl)borate **19** (670 mg, 2.50 mmol). Potassium trifluoro(3-(4-methoxyphenyl)-3-oxoprop-1-yn-1-yl)borate **2d** (518 mg, 1.95 mmol, 78%) was obtained as a white solid. **$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ 8.02 (d, *J* = 8.9 Hz, 2H, 2 x Ar*H*), 7.08 (d, *J* = 8.9 Hz, 2H, 2 x Ar*H*), 3.85 (s, 3H, C*H*$_3$). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 176.9, 163.7, 131.26, 130.1, 114.0, 55.6. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -128.9 – -135.7 (m). **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -1.9 (q, *J* = 32.2 Hz). Spectroscopic data were consistent with values reported in literature.[12]

**Potassium *(E)*-trifluoro(3-oxo-5-phenylpent-4-en-1-yn-1-yl)borate 2e**



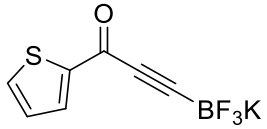
Synthesized following procedure C, starting from potassium *(E)*-trifluoro(3-hydroxy-5-phenylpent-4-en-1-yn-1-yl)borate **20** (1.00 g, 3.80 mmol). Potassium *(E)*-trifluoro(3-oxo-5-phenylpent-4-en-1-yn-1-yl)borate **2e** (564 mg, 2.15 mmol, 57%) was obtained as a white solid. **m. p.** (dec.) 157 °C **. $^{1}$H NMR** (400 MHz, acetone-$d_6$) δ 7.90 (d, *J* = 16.1 Hz, 1H, C$H_{alkene}$), 7.72 (dd, *J* = 7.3, 2.1 Hz, 2H, 2 x Ar*H*), 7.52 – 7.41 (m, 3H, 3 x Ar*H*), 6.76 (d, *J* = 16.1 Hz, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, acetone-$d_6$) δ 179.8, 147.1, 135.6, 131.3, 130.1, 129.9, 129.3, 127.3. **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -136.1 (dd, *J* = 65.9, 32.6 Hz). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.7 (q, *J* = 33.2 Hz). **IR** (vmax, cm$^{-1}$) 3400 (br), 1713 (w), 1121 (m), 979 (s), 750 (s). **HRMS** (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_{11}H_7BF_3O^-$ 223.0548; Found 223.0548.

**Potassium trifluoro(3-(furan-2-yl)-3-oxoprop-1-yn-1-yl)borate 2f**



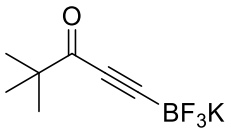
Synthesized following procedure C, starting from potassium trifluoro(3-hydroxy-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate **21** (456 mg, 2.00 mmol). Potassium trifluoro(3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate **2f** (198 mg, 0.876 mmol, 44%) was obtained as a white solid. **m. p.** (dec.) 185 °C. **$^{1}$H NMR** (400 MHz, acetone-$d_6$) δ 7.78 (m, 1H, Ar*H*), 7.32 (dd, *J* = 3.5, 0.8 Hz, 1H, Ar*H*), 6.64 (dd, *J* = 3.6, 1.7 Hz, 1H, Ar*H*). **$^{13}$C NMR** (101 MHz, acetone-$d_6$) δ 165.6, 147.3, 119.6, 112.1. (1C not resolved). **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -136.4 – -136.7 (m). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.8 (q, J = 32.4 Hz). **IR** ($\nu_{max}$, $cm^{-1}$) 1713 (w), 1620 (s), 1464 (s), 1397 (m), 1076 (s), 1020 (s). **HRMS** (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_7H_3BF_3O_2^-$ 187.0184; Found 187.0191.

**Potassium trifluoro(3-oxo-3-(thiophen-2-yl)prop-1-yn-1-yl)borate 2g**



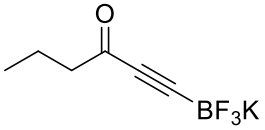
Synthesized following procedure C, starting from potassium potassium trifluoro(3-hydroxy-3-(thiophen-2-yl)prop-1-yn-1-yl)borate **22** (610 mg, 2.50 mmol). Potassium trifluoro(3-oxo-3-(thiophen-2-yl)prop-1-yn-1-yl)borate **2g** (217 mg, 0.897 mmol, 36%) was obtained as a brown solid. **m. p.** (dec.) 166 °C. **$^{1}$H NMR** (400 MHz, acetone-$d_6$) δ 7.94 (dd, *J* = 3.8, 1.4 Hz, 1H, Ar*H*), 7.85 – 7.83 (m, 1H, Ar*H*), 7.21 (dd, *J* = 5.0, 3.8 Hz, 1H, Ar*H*). **$^{13}$C NMR** (101 MHz, acetone- $d_6$) δ 171.6, 146.9, 135.5, 134.9, 129.0, 88.4. **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -136.4 (dd, *J* = 65.2, 32.6 Hz). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.7 (q, *J* = 32.4 Hz). **IR** ($\nu_{max}$, $cm^{-1}$) 2924 (w), 1609 (m), 1411 (s), 1281 (s), 1033 (s), 751 (s). **HRMS** (ESI/QTOF) m/z: $[M]^+$ Calcd for $C_7H_3BF_3OS^-$ 202.9955; Found 202.9951.

**Potassium (4,4-dimethyl-3-oxopent-1-yn-1-yl)trifluoroborate 2h**



Synthesized following procedure C, starting from potassium trifluoro(3-hydroxy-4,4-dimethylpent-1-yn-1-yl)borate **23** (556 mg, 2.55 mmol). Potassium trifluoro(3-oxohex-1-yn-1-yl)borate **2h** (325 mg, 1.51 mmol, 59%) was obtained as a white solid. **$^{1}$H NMR** (400 MHz, DMSO-$d_6$) δ 1.09 (s, 9H, C(C$H_3$)$_3$). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 194.3, 89.8, 25.6. **$^{19}$F NMR** (376 MHz, DMSO-$d_6$) δ -134.6. **$^{11}$B NMR** (128 MHz, DMSO-$d_6$) δ -2.0 (q, *J* = 33.0 Hz). Spectroscopic data were consistent with values reported in literature.[12]

**Potassium trifluoro(3-oxohex-1-yn-1-yl)borate 2i**



Synthesized following procedure C, starting from potassium trifluoro(3-hydroxyhex-1-yn-1-yl)borate **24** (1.02 g, 5.00 mmol). Potassium trifluoro(3-oxohex-1-yn-1-yl)borate **2i** (740 mg, 3.67 mmol, 73%) was obtained as a white solid. **$^1$H NMR** (400 MHz, acetone-$d_6$) δ 2.40 (t, *J* = 7.3 Hz, 2H, C$H_2$), 1.62 (h, *J* = 7.3 Hz, 2H, C$H_2$), 0.89 (t, *J* = 7.4 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, acetone-$d_6$) δ 189.0, 47.9, 18.4, 13.8. **$^{19}$F NMR** (376 MHz, acetone-$d_6$) δ -136.4 (dd, *J* = 66.1, 32.9 Hz). **$^{11}$B NMR** (128 MHz, acetone-$d_6$) δ -1.8 (q, *J* = 32.8 Hz). Spectroscopic data were consistent with values reported in literature.[12]

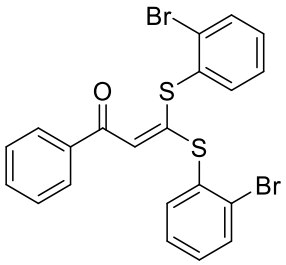
## 3. Scope of the reaction

**General procedure D**


TsOBX (1.0 equiv) **1** | (1.1 equiv) **2a-i** | **3a-u**

A capped oven dried microwave vial charged with TsOBX **1** (167 mg, 0.400 mmol, 1.00 equiv.) and potassium trifluoroborate ynone (1.1 equiv.) was evacuated and backfilled with $N_2$ (3x). DME (6.0 mL) was added under $N_2$. The reaction was stirred at 21 °C for 1 h. To a solution of thiol (2.20 equiv.) in DME (2.8 mL) was added 1,1,3,3-tetramethylguanidine (115 µL, 0.920 mmol, 2.30 equiv.). The mixture was stirred for 5 minutes and then added to the previous solution. The reaction mixture was stirred at 21 °C for 10 minutes, quenched with $NaHCO_3$ (aq.) sat. (5 mL) and extracted with DCM (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and solvents were removed under reduced pressure. Flash chromatography afforded the desired ketene dithioarylacetal.

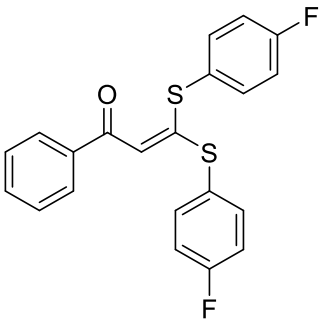
**3,3-Bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one 3a**



Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 95:5 to 7:3) afforded 3,3-bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one **3a** (194 mg, 0.383 mmol, 96% yield) as a yellow solid. **$R_f$** ($SiO_2$,

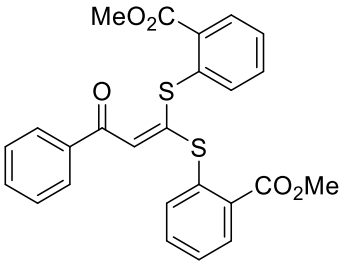
pentane: EtOAc = 95:5) = 0.26. **m. p.** 130-132 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H, Ar*H*), 7.74 – 7.68 (m, 4H, 4 x Ar*H*), 7.60 (dd, *J* = 7.6, 1.8 Hz, 1H, Ar*H*), 7.52 – 7.43 (m, 1H, Ar*H*), 7.41 – 7.28 (m, 6H, 6 x Ar*H*), 6.54 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.5, 161.2, 138.6, 138.5, 137.1, 134.2, 133.6, 132.34, 132.26, 132.0, 131.7, 131.5, 130.0, 128.8, 128.6, 128.1, 127.9, 114.2. (1C not resolved). **IR** (vmax, cm$^{-1}$) 3065 (w), 1620 (m), 1496 (s), 1476 (s), 1227 (s), 1025 (m), 755 (s). **HRMS** (ESI/QTOF) m/z: [M+H]+ Calcd for $C_{21}H_{15}Br_2OS_2^+$ 504.8926; Found 504.8923.

**3,3-Bis((4-fluorophenyl)thio)-1-phenylprop-2-en-1-one 3b**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 4-fluorothiophenol (103 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 9:1) afforded 3,3-bis((4-fluorophenyl)thio)-1-phenylprop-2-en-1-one **3b** (113 mg, 0.293 mmol, 73% yield) as a yellow solid. **$R_f$** ($SiO_2$, pentane: EtOAc = 95:5) = 0.32. **m. p.** 122-124 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H, 2 x Ar*H*), 7.66 – 7.61 (m, 2H, 2 x Ar*H*), 7.49 – 7.41 (m, 3H, 3 x Ar*H*), 7.41 – 7.33 (m, 2H, 2 x Ar*H*), 7.20 – 7.09 (m, 4H, 4 x Ar*H*), 6.45 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.4, 165.9, 164.3 (d, *J* = 251.8 Hz), 164.1 (d, *J* = 252.5 Hz), 139.0 (d, *J* = 8.7 Hz), 138.7, 137.7 (d, *J* = 8.7 Hz), 132.3, 128.7, 127.9, 126.0 (d, *J* = 3.3 Hz), 125.1 (d, *J* = 3.6 Hz), 117.5 (d, *J* = 22.2 Hz), 116.3 (d, *J* = 22.2 Hz), 112.75. **$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -109.0, -109.4. **IR** (vmax, cm$^{-1}$) 3061 (w), 1625 (m), 1588 (s), 1499 (s), 1480 (s), 1224 (s), 1159 (m), 832 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{15}F_2OS_2^+$ 385.0527; Found 385.0531.

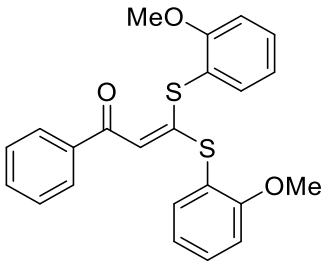
**Dimethyl 2,2'-((3-oxo-3-phenylprop-1-ene-1,1-diyl)bis(sulfanediyl))dibenzoate 3c**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and methyl thiosalicylate (163 mg, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 7:3) afforded dimethyl 2,2'-((3-oxo-3-

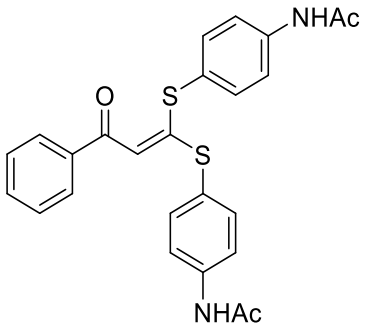
phenylprop-1-ene-1,1-diyl)bis(sulfanediyl))dibenzoate **3c** (108 mg, 0.232 mmol, 58% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 1:1) = 0.74. **m. p.** 114-115 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H, 2 x Ar*H*), 7.68 (dd, *J* = 8.0, 1.5 Hz, 1H, Ar*H*), 7.60 (dd, *J* = 7.8, 1.5 Hz, 1H, Ar*H*), 7.46 – 7.39 (m, 2H, 2 x Ar*H*), 7.39 – 7.28 (m, 3H, 2 x Ar*H* and C$H_{alkene}$), 7.27 – 7.10 (m, 5H, 5 x Ar*H*), 3.72 (s, 3H, OC$H_3$), 3.70 (s, 3H, OC$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 187.3, 166.4, 166.1, 159.4, 138.2, 137.4, 135.2, 134.7, 133.2, 132.6, 132.2, 132.0, 131.4, 131.0, 130.6, 129.2, 128.7, 128.3, 127.6, 122.4, 52.34, 52.31. (1C not resolved). **IR** (νmax, $cm^{-1}$) 3072 (w), 2953 (w), 2845 (w), 1713 (s), 1631 (m), 1508 (s), 1436 (s), 1292 (s), 1256 (s), 1227 (s), 1056 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{21}O_5S_2^+$ 465.0825; Found 465.0823.

**3,3-Bis((2-methoxyphenyl)thio)-1-phenylprop-2-en-1-one 3d**



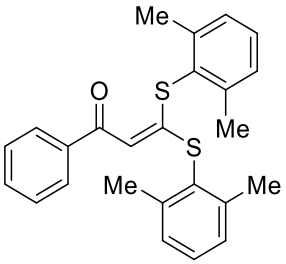

Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 2-methoxythiophenol (115 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 7:3) afforded 3,3-bis((2-methoxyphenyl)thio)-1-phenylprop-2-en-1-one **3d** (128 mg, 0.313 mmol, 78% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 1:1) = 0.74. **m. p.** 132-133 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.5, 1.8 Hz, 1H, Ar*H*), 7.66 – 7.62 (m, 2H, 2 x Ar*H*), 7.50 – 7.39 (m, 4H, 4 x Ar*H*), 7.37 – 7.29 (m, 2H, 2 x Ar*H*), 7.03 – 6.93 (m, 4H, 4 x Ar*H*), 6.47 (s, 1H, C$H_{alkene}$), 3.94 (s, 3H, OC$H_3$), 3.81 (s, 3H, OC$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.0, 165.6, 161.0, 159.8, 139.2, 138.5, 137.4, 132.52, 132.46, 131.7, 128.4, 127.9, 121.7, 121.0, 118.8, 118.1, 111.8, 111.7, 111.5, 56.1. (1 O*C*$H_3$ not resolved). **IR** (νmax, $cm^{-1}$) 3058 (w), 2932 (w), 2838 (w), 1627 (m), 1584 (m), 1496 (s), 1474 (s), 1278 (s), 1227 (s), 1022 (s), 753 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}O_3S_2^+$ 409.0927; Found 409.0929.

***N,N'*-(((3-oxo-3-phenylprop-1-ene-1,1-diyl)is(sulfanediyl))bis(4,1-phenylene))diacetamide 3e**



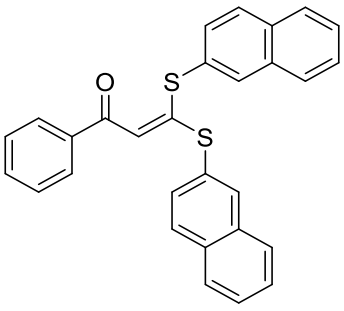
Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 4-acetamidothiophenol (147 mg, 0.880 mmol, 2.20 equiv.). Precipitation in DCM afforded N,N'-(((3-oxo-3-phenylprop-1-ene-1,1-diyl)is(sulfanediyl))bis(4,1-phenylene)) diacetamide **3e** (179 mg, 0.388 mmol, 97% yield) as a yellow solid. **m. p.** (dec.) 251 °C. **$^1$H NMR** (400 MHz, DMSO-$d_6$) δ 10.23 (s, 1H, N*H*), 10.22 (s, 1H, N*H*), 7.78 – 7.68 (m, 4H, 4 x Ar*H*), 7.68 – 7.61 (m, 2H, 2 x Ar*H*), 7.53 – 7.40 (m, 7H, 7 x Ar*H*), 6.35 (s, 1H, C$H_{alkene}$), 2.08 (s, 3H, C$H_3$), 2.08 (s, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, DMSO-$d_6$) δ 184.8, 168.9, 168.8, 167.4, 141.52, 141.48, 138.4, 137.3, 136.2, 132.2, 128.8, 127.1, 122.2, 121.6, 120.2, 119.2, 110.8, 24.2, 24.1. **IR** ($\nu_{max}$, cm$^{-1}$) 3277 (br), 1698 (m), 1590 (s), 1530 (s), 1495 (s), 1479 (s), 1371 (m), 1313 (s), 1231 (s), 1025 (s). **HRMS** (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{22}N_2NaO_3S_2^+$ 485.0964; Found 485.0971.

**3,3-Bis((2,6-dimethylphenyl)thio)-1-phenylprop-2-en-1-one 3f**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 2,6-dimethylbenzenethiol (117 µL, 880 µmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 95:5) afforded 3,3-bis((2,6-dimethylphenyl)thio)-1-phenylprop-2-en-1-one **3f** (124 mg, 306 µmol, 76% yield) as a yellow solid. **$R_f$** ($SiO_2$, pentane: EtOAc = 95:5) = 0.45. **m. p.** 154-156 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H, 2 x Ar*H*), 7.45 – 7.38 (m, 1H, Ar*H*), 7.37 – 7.27 (m, 4H, 4 x Ar*H*), 7.25 – 7.16 (m, 4H, 4 x Ar*H*), 6.24 (s, 1H, C$H_{alkene}$), 2.63 (s, 6H, 2 x C$H_3$), 2.38 (s, 6H, 2 x C$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.9, 164.9, 145.1, 143.8, 139.1, 131.8, 130.8, 130.7, 129.2, 129.10, 129.05, 128.5, 128.3, 127.9, 108.8, 22.2, 21.2. **IR** (vmax, cm$^{-1}$) 2985 (w), 1621 (m), 1497 (s), 1480 (s), 1229 (s), 1054 (m), 769 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{25}OS_2^+$ 405.1341; Found 405.1344.

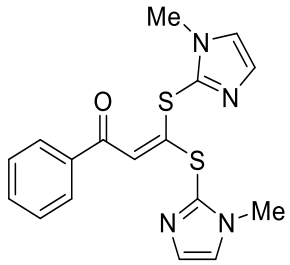
**3,3-Bis(naphthalen-2-ylthio)-1-phenylprop-2-en-1-one 3g**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 2-

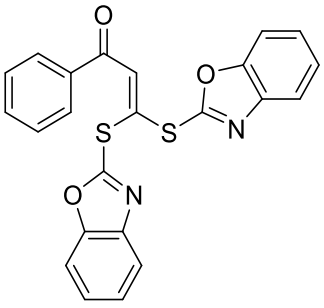
naphthalenethiol (162 mg, 880 µmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 8:2) afforded 3,3-bis(naphthalen-2-ylthio)-1-phenylprop-2-en-1-one **3g** (132 mg, 293 µmol, 73% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.21. **m. p.** 155-157 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.27 – 8.20 (m, 1H, Ar*H*), 7.93 – 7.83 (m, 6H, 6 x Ar*H*), 7.77 (dd, *J* = 12.5, 8.4 Hz, 2H, 2 x Ar*H*), 7.65 – 7.60 (m, 2H, 2 x Ar*H*), 7.60 – 7.46 (m, 5H, 5 x Ar*H*), 7.43 – 7.36 (m, 1H, Ar*H*), 7.29 (dd, *J* = 8.0, 6.5 Hz, 2H, 2 x Ar*H*), 6.67 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.5, 165.8, 138.8, 137.0, 135.3, 133.9, 133.8, 133.6, 133.4, 132.9, 132.1, 131.0, 129.7, 128.6, 128.5, 128.4, 128.1, 128.1, 128.01, 127.97, 127.9, 127.8, 127.7, 127.2, 127.1, 126.8, 113.5. **IR** (νmax, $cm^{-1}$) 3058 (m), 2986 (w), 1627 (m), 1494 (s), 1479 (s), 1227 (s), 1051 (m). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{21}OS_2^+$ 449.1028; Found 449.1029.

**3,3-Bis((1-methyl-1H-imidazol-2-yl)thio)-1-phenylprop-2-en-1-one 3h**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 1-methyl-2-imidazolethiol (100 mg, 880 µmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 8:2) afforded 3,3-bis((1-methyl-1H-imidazol-2-yl)thio)-1-phenylprop-2-en-1-one **3h** (86.8 mg, 244 µmol, 61% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, EtOAc) = 0.17 . **m. p.** (dec.) 185 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 2H, 2 x Ar*H*), 7.53 – 7.44 (m, 1H, Ar*H*), 7.41 – 7.34 (m, 2H, 2 x Ar*H*), 7.31 (d, *J* = 1.3 Hz, 1H, Ar*H*), 7.27 (d, *J* = 1.3 Hz, 1H, Ar*H*), 7.20 (d, *J* = 1.3 Hz, 1H, Ar*H*), 7.18 (d, *J* = 1.4 Hz, 1H, Ar*H*), 6.27 (s, 1H, C$H_{alkene}$), 3.84 (s, 3H, C$H_3$), 3.69 (s, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.4, 161.8, 137.8, 136.0, 134.6, 132.7, 131.8, 130.9, 128.7, 128.1, 125.4, 124.9, 113.5, 34.6, 34.2. **IR** ($\nu_{max}$, $cm^{-1}$) 2950 (w), 1631 (m), 1504 (s), 1456 (m), 1281 (s), 1227 (s), 766 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_4OS_2^+$ 357.0838; Found 357.0843.

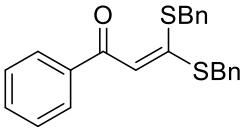
**3,3-Bis(benzo[d]oxazol-2-ylthio)-1-phenylprop-2-en-1-one 3i**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 1,3-

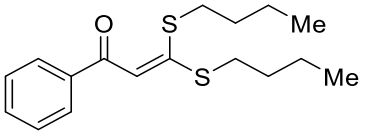
benzoxazole-2-thiol (133 mg, 880 µmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 7:3) afforded 3,3-bis(benzo[d]oxazol-2-ylthio)-1-phenylprop-2-en-1-one **3i** (110 mg, 255 µmol, 64% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 8:2) = 0.38. **m. p.** 146-148 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H, C$H_{alkene}$), 8.04 – 8.01 (m, 2H, 2 x Ar*H*), 7.69 – 7.58 (m, 3H, 3 x Ar*H*), 7.54 – 7.46 (m, 3H, 3 x Ar*H*), 7.42 – 7.32 (m, 5H, 5 x Ar*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 187.7, 158.7, 158.3, 152.4, 152.0, 142.8, 141.72, 141.67, 136.8, 133.8, 130.1, 129.1, 128.8, 126.4, 125.8, 125.1, 125.1, 120.6, 120.0, 110.9, 110.7. **IR** (vmax, $cm^{-1}$) 3062 (w), 2917 (w), 1641 (m), 1523 (m), 1497 (s), 1447 (s), 1231 (s), 1090 (s), 744 (s). **HRMS** (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{14}N_2NaO_3S_2^+$ 453.0338; Found 453.0335.

**3,3-Bis(benzylthio)-1-phenylprop-2-en-1-one 3j**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and benzyl mercaptan (103 µL, 880 µmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 98:2 to 9:1) afforded 3,3-bis(benzylthio)-1-phenylprop-2-en-1-one **3j** (126 mg, 334 µmol, 84% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.21. **m. p.** 110-112 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 2H, 2 x Ar*H*), 7.53 – 7.26 (m, 13H, 13 x Ar*H*), 6.88 (s, 1H, C$H_{alkene}$), 4.31 (s, 2H, C$H_{2Bn}$), 4.27 (s, 2H, C$H_{2Bn}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.0, 163.0, 139.1, 135.8, 134.2, 132.0, 129.6, 129.2, 128.8, 128.6, 128.3, 128.0, 127.7, 112.1, 39.5, 36.7. (1C not resolved). **IR** (vmax, $cm^{-1}$) 3061 (w), 3025 (w), 2924 (w), 1627 (m), 1597 (m), 1494 (s), 1473 (s), 1227 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}OS_2^+$ 377.1028; Found 377.1028. Spectroscopic data were consistent with values reported in literature.[13]

**3,3-Bis(butylthio)-1-phenylprop-2-en-1-one 3k**

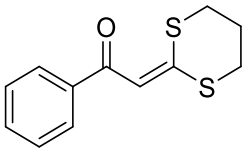



Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 1-butanethiol (107 µL, 880 µmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 97:3 to 9:1) afforded 3,3-bis(butylthio)-1-phenylprop-2-en-1-one **3k** (113 mg, 368 µmol, 92% yield) as a yellow oil. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.39. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H, 2 x Ar*H*), 7.52 – 7.40 (m, 3H, 3 x Ar*H*), 6.82 (s, 1H, C$H_{alkene}$), 3.04 (dt, *J* = 14.9, 7.3 Hz, 4H, 2 x C$H_2$), 1.82 – 1.66 (m, 4H, 2 x C$H_2$), 1.57 – 1.44 (m, 4H, 2 x C$H_2$), 0.98 (t, *J* = 7.3 Hz, 3H, C$H_3$), 0.94 (t, *J* = 7.3 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.7, 165.4, 139.6, 131.8, 128.6, 127.9, 110.4, 34.1, 31.4, 31.1, 29.6, 22.3, 22.2, 13.8. (1C

[13] F. Qi, H.-F. Yu, Y.-N. Wang, Y. Lv, Y.-X. Li, L. Han, R. Wang, X.-N. Feng, *Synth. Commun.* **2017**, *47*, 2220–2224.

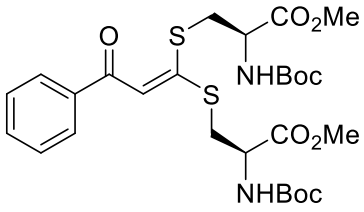
not resolved). **IR** ($\nu_{max}$, $cm^{-1}$) 2964 (m), 2921 (m), 2871 (m), 1628 (m), 1496 (s), 1475 (s), 1230 (s), 1058 (m), 762 (m). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}OS_2^+$ 309.1341; Found 309.1353.

**2-(1,3-Dithian-2-ylidene)-1-phenylethan-1-one 3l**



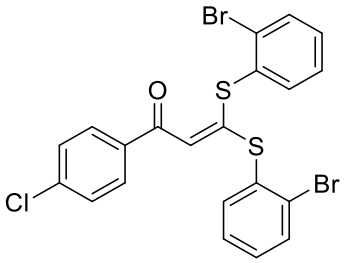
Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and 1,3-dithiol (44.2 µL, 440 µmol, 1.10 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 7:3) afforded 2-(1,3-dithian-2-ylidene)-1-phenylethan-1-one **3l** (79.5 mg, 336 µmol, 84% yield) as a yellow oil. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 8:2) = 0.34. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H, 2 x Ar*H*), 7.52 – 7.45 (m, 1H, Ar*H*), 7.45 – 7.38 (m, 2H, 2 x Ar*H*), 7.32 (s, 1H, C$H_{alkene}$), 3.03 (t, *J* = 7.1 Hz, 2H, C$H_2$), 2.97(t, *J* = 6.5 Hz, 2H, C$H_2$), 2.26 (p, 2H, *J* = 6.8 Hz, C$H_2$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.4, 164.4, 138.6, 132.1, 128.6, 128.0, 117.6, 29.1, 28.3, 24.0. **IR** (vmax, $cm^{-1}$) 3065 (w), 2921 (w), 2849 (w), 1623 (m), 1497 (s), 1486 (s), 1227 (s), 1043 (m), 1024 (m), 769 (m). **HRMS** (APCI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{12}NaOS_2^+$ 259.0222; Found 259.0230.

**Methyl (6R,12R)-12-((tert-butoxycarbonyl)amino)-6-(methoxycarbonyl)-2,2-dimethyl-4-oxo-9-(2-oxo-2-phenylethylidene)-3-oxa-8,10-dithia-5-azatridecan-13-oate 3m**



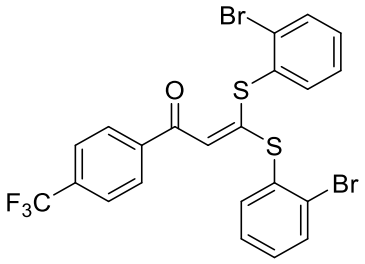
Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (104 mg, 0.440 mmol, 1.10 equiv.) and Boc-Cys-OMe (181 µL, 880 µmol, 2.20 equiv.). Purification by column chromatography ($SiO_2$, pentane:EtOAc = 7:3 to 6:4) afforded methyl (6R,12R)-12-((tert-butoxycarbonyl)amino)-6-(methoxycarbonyl)-2,2-dimethyl-4-oxo-9-(2-oxo-2-phenylethylidene)-3-oxa-8,10-dithia-5-azatridecan-13-oate **3m** (183 mg, 306 µmol, 77% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 1:1) = 0.71. **m. p.** 67-68 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H, 2 x Ar*H*), 7.55 – 7.49 (m, 1H, Ar*H*), 7.48 – 7.41 (m, 2H, 2 x Ar*H*), 7.19 (s, 1H, C$H_{alkene}$), 5.50 (d, *J* = 7.5 Hz, 1H, N*H*), 5.36 (d, *J* = 8.6 Hz, 1H, N*H*), 4.74 – 4.61 (m, 2H, 2 x C*H*), 3.77 (s, 3H, OC$H_3$), 3.75 (s, 3H, OC$H_3$), 3.66 – 3.30 (m, 4H, 2 x $CH_2$), 1.42 (s, 9H, C(C$H_3$)$_3$), 1.41 (d, 9H, C(C$H_3$)$_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.4, 171.0, 170.7, 158.3, 155.2, 138.5, 132.5, 128.7, 128.3, 117.1, 80.8, 80.4, 53.1, 52.9, 52.8, 36.7, 35.0, 28.4. (3C not resolved). **IR** (vmax, $cm^{-1}$) 3382 (w), 2979 (m), 1753 (m), 1721 (s), 1509 (m), 1483 (s), 1367 (m), 1220 (s), 1162 (s), 1054 (m). **HRMS** (ESI/QTOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{38}N_2NaO_9S_2^+$ 621.1911; Found 621.1912.

**3,3-Bis((2-bromophenyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one 3n**



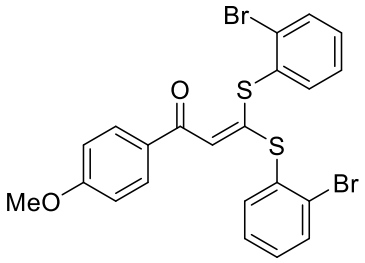

Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium (3-(4-chlorophenyl)-3-oxoprop-1-yn-1-yl)trifluoroborate **2b** (134 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 95:5) afforded 3,3-bis((2-bromophenyl)thio)-1-(4-chlorophenyl)prop-2-en-1-one **3n** (177 mg, 0.328 mmol, 82% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.27. **m. p.** 136-137 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 1H, Ar*H*), 7.75 – 7.69 (m, 2H, 2 x Ar*H*), 7.64 – 7.58 (m, 3H, 3 x Ar*H*), 7.42 – 7.29 (m, 6H, 6 x Ar*H*), 6.43 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.2, 162.5, 138.7, 138.6, 137.3, 137.0, 134.2, 133.7, 132.3, 132.2, 132.1, 131.9, 131.3, 130.1, 129.4, 128.91, 128.86, 128.0, 113.3. **IR** (vmax, cm$^{-1}$) 3061 (w), 1625 (m), 1588 (s), 1496 (s), 1476 (s), 1447 (s), 1224 (s), 1090 (s), 1012 (s), 755 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{14}Br_2F_3OS_2^+$ 572.8799; Found 572.8805.

**3,3-Bis((2-bromophenyl)thio)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one 3o**



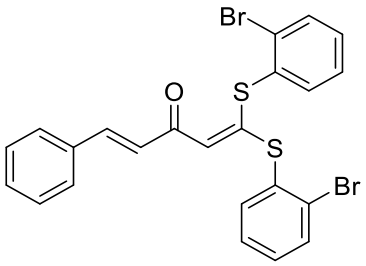

Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-(4-(trifluoromethyl)phenyl)prop-1-yn-1-yl)borate **2c** (119 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 9:1) afforded 3,3-bis((2-bromophenyl)thio)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one **3o** (176 mg, 0.307 mmol, 77% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.32. **m. p.** 121-122 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 1H, Ar*H*), 7.79 – 7.71 (m, 4H, 4 x Ar*H*), 7.67 – 7.58 (m, 3H, 3 x Ar*H*), 7.45 – 7.30 (m, 4H, 4 x Ar*H*), 6.41 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.1, 164,2, 141.5, 138.8, 137.5, 134.3, 133.4 (q, *J* = 32.5 Hz), 133.8, 132.31, 132.28, 132.2, 131.9, 131.0, 130.4, 129.0, 128.3, 128.1, 125.7 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 112.6. **$^{19}$F NMR** (377 MHz, $CDCl_3$) δ -63.0. **IR** (vmax, cm$^{-1}$) 2992 (w), 1627 (w), 1490 (m), 1321 (m), 1065 (m), 741 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}Br_2ClOS_2^+$ 538.8536; Found 538.8551.

**3,3-Bis((2-bromophenyl)thio)-1-(4-methoxyphenyl)prop-2-en-1-one 3p**



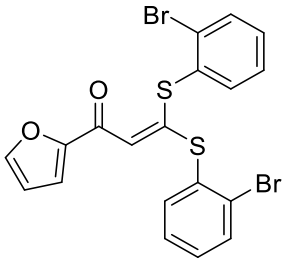

Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-(4-methoxyphenyl)-3-oxoprop-1-yn-1-yl)borate **2d** (117 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 95:5 to 8:2) afforded 3,3-bis((2-bromophenyl)thio)-1-(4-methoxyphenyl)prop-2-en-1-one **3p** (197 mg, 0.328 mmol, 92% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 9:1) = 0.44. **m. p.** 129-131 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 5H, 5 x Ar*H*), 7.59 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.37 (td, *J* = 7.6, 1.4 Hz, 1H, Ar*H*), 7.33 – 7.26 (m, 3H, 3 x Ar*H*), 6.90 – 6.84 (m, 2H, 2 x Ar*H*), 6.58 (s, 1H, C$H_{alkene}$), 3.83 (s, 3H, OC$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.5, 163.0, 159.3, 138.5, 136.8, 134.1, 133.6, 132.7, 132.2, 131.84, 131.81, 131.5, 131.4, 130.3, 129.7, 128.7, 127.8, 115.1, 113.9, 55.6. **IR** (vmax, cm$^{-1}$) 3050 (w), 2838 (w), 1598 (s), 1497 (s), 1446 (m), 1238 (s), 1170 (s), 1022 (s), 754 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{17}Br_2O_2S_2^+$ 534.9031; Found 534.9043.

**(*E*)-1,1-Bis((2-bromophenyl)thio)-5-phenylpenta-1,4-dien-3-one 3q**



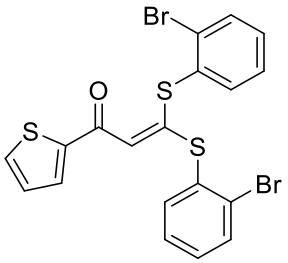

Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium (E)-trifluoro(3-oxo-5-phenylpent-4-en-1-yn-1-yl)borate **2e** (115 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 95:5 to 8:2) afforded (*E*)-1,1-bis((2-bromophenyl)thio)-5-phenylpenta-1,4-dien-3-one **3q** (166 mg, 0.311 mmol, 78% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 8:2) = 0.33. **m. p.** 139-141 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 1H, Ar*H*), 7.73 – 7.67 (m, 2H, 2 x Ar*H*), 7.58 (dd, *J* = 7.7, 1.7 Hz, 1H, C$H_{styrene}$), 7.55 – 7.47 (m, 3H, 3 x Ar*H*), 7.41 – 7.28 (m, 7H, 7 x Ar*H*), 6.64 (d, *J* = 15.9 Hz, 1H, C$H_{styrene}$), 6.05 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 185.3, 160.2, 142.4, 138.6, 137.0, 135.2, 134.2, 133.6, 132.4, 132.3, 131.9, 131.7, 131.6, 130.3, 129.9, 129.0, 128.8, 128.4, 127.9, 127.0, 117.8. **IR** (vmax, cm$^{-1}$) 3050 (w), 2956 (w), 1648 (m), 1602 (m), 1490 (s), 1443 (m), 1123 (s), 755 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}Br_2OS_2^+$ 530.9082; Found 530.9095.

**3,3-Bis((2-bromophenyl)thio)-1-(furan-2-yl)prop-2-en-1-one 3r**



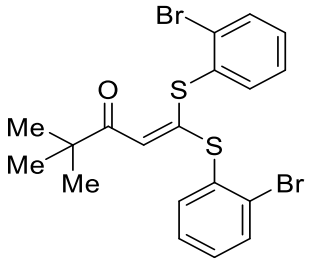

Synthesized following procedure D, starting from TsOBX **1** (126 mg, 0.300 mmol), potassium trifluoro(3-(furan-2-yl)-3-oxoprop-1-yn-1-yl)borate **2f** (74.6 mg, 0.330 mmol, 1.10 equiv.) and 2-bromothiophenol (79.3 µL, 0.660 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, toluene:EtOAc = 95:5 to 8:2) afforded 3,3-bis((2-bromophenyl)thio)-1-(furan-2-yl)prop-2-en-1-one **3r** (120 mg, 0.241 mmol, 80% yield) as a yellow visquous oil. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 8:2) = 0.45. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H, Ar*H*), 7.72 – 7.66 (m, 2H, 2 x Ar*H*), 7.59 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar*H*), 7.45 (dd, *J* = 1.8, 0.8 Hz, 1H, Ar*H*), 7.38 (td, *J* = 7.6, 1.4 Hz, 1H, Ar*H*), 7.35 – 7.28 (m, 3H, 3 x Ar*H*), 6.95 (dd, *J* = 3.5, 0.9 Hz, 1H, Ar*H*), 6.45 (dd, *J* = 3.5, 1.7 Hz, 1H, Ar*H*), 6.42 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 175.4, 161.0, 153.7, 145.8, 138.7, 137.0, 134.1, 133.6, 132.3, 132.3, 132.0, 131.6, 131.5, 129.9, 128.7, 127.9, 116.1, 113.8, 112.4. **IR** (vmax, cm$^{-1}$) 3058 (w), 1631 (m), 1571 (s), 1496 (s), 1465 (s), 1252 (m), 1021 (m), 912 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}Br_2O_2S_2^+$ 494.8718; Found 494.8716.

**3,3-Bis((2-bromophenyl)thio)-1-(thiophen-2-yl)prop-2-en-1-one 3s**



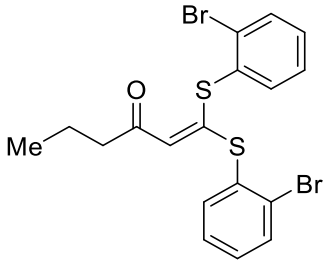

Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium trifluoro(3-oxo-3-(thiophen-2-yl)prop-1-yn-1-yl)borate **2g** (107 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, toluene:EtOAc = 98:2 to 95:5) afforded 3,3-bis((2-bromophenyl)thio)-1-(thiophen-2-yl)prop-2-en-1-one **3s** (168 mg, 0.327 mmol, 82% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 8:2) = 0.57. **m. p.** 99-101 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 1H, Ar*H*), 7.74 – 7.67 (m, 2H, 2 x Ar*H*), 7.61 (dd, *J* = 7.6, 1.8 Hz, 1H, Ar*H*), 7.53 (dd, *J* = 5.0, 1.2 Hz, 1H, Ar*H*), 7.39 (td, *J* = 7.6, 1.5 Hz, 1H, Ar*H*), 7.36 – 7.29 (m, 3H, 3 x Ar*H*), 7.28 (dd, *J* = 3.8, 1.2 Hz, 1H, Ar*H*), 7.02 (dd, *J* = 4.9, 3.8 Hz, 1H, Ar*H*), 6.34 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 179.1, 160.8, 145.8, 138.7, 137.2, 134.2, 133.7, 133.0, 132.4, 132.3, 132.0, 131.8, 131.4, 130.4, 130.1, 128.8, 128.1, 127.9, 113.9. **IR** (vmax, cm$^{-1}$) 3058 (w), 1616 (m), 1515 (s), 1497 (s), 1447 (m), 1414 (s), 1238 (s), 1022 (m), 760 (s), 755 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{13}Br_2OS_3^+$ 510.8490; Found 510.8490.

**1,1-Bis((2-bromophenyl)thio)-4,4-dimethylpent-1-en-3-one 3t**



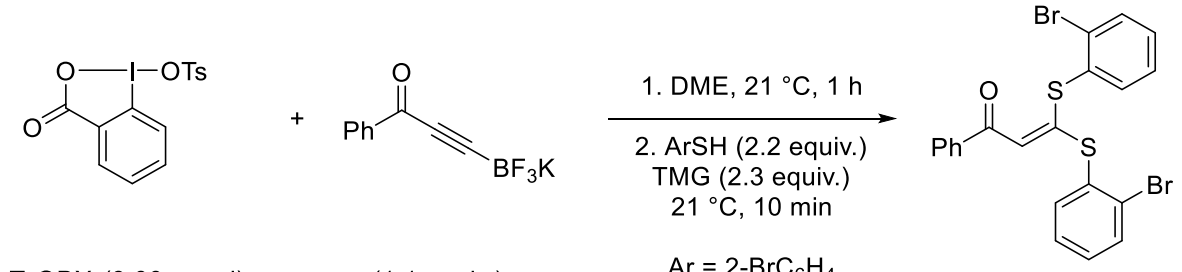

Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium (4,4-dimethyl-3-oxopent-1-yn-1-yl)trifluoroborate **2h** (95.1 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 97.5:2.5 to 95:5) afforded 1,1-bis((2-bromophenyl)thio)-4,4-dimethylpent-1-en-3-one **3t** (172 mg, 0.355 mmol, 89% yield) as a white solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.46. **m. p.** 84-86 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 3H, 3 x Ar*H*), 7.50 (dd, *J* = 7.7, 1.8 Hz, 1H, Ar*H*), 7.32 – 7.19 (m, 4H, 4 x Ar*H*), 6.00 (s, 1H, C$H_{alkene}$), 0.98 (s, 9H, C(C$H_3$)$_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 201.9, 158.4, 138.6, 136.9, 134.0, 133.5, 132.7, 132.4, 131.8, 131.7, 131.4, 129.8, 128.6, 127.7, 114.3, 43.1, 26.7. **IR** (νmax, cm$^{-1}$) 3058 (w), 2964 (m), 1648 (m), 1497 (s), 1446 (s), 1105 (s), 1022 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}Br_2OS_2^+$ 484.9239; Found 484.9244.

**1,1-Bis((2-bromophenyl)thio)hex-1-en-3-one 3u**




Synthesized following procedure D, starting from TsOBX **1** (167 mg, 0.400 mmol), potassium potassium trifluoro(3-oxohex-1-yn-1-yl)borate **2i** (88.9 mg, 0.440 mmol, 1.10 equiv.) and 2-bromothiophenol (106 µL, 0.880 mmol, 2.20 equiv.). Purification by column chromatography ($SiO_2$, pentane:EtOAc = 98:2 to 95:5) afforded 1,1-bis((2-bromophenyl)thio)hex-1-en-3-one **3u** (75.5 mg, 0.160 mmol, 40% yield) as a yellow sticky oil. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.33. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.56 (m, 3H, 3 x Ar*H*), 7.48 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.30 (td, *J* = 7.5, 1.4 Hz, 1H, Ar*H*), 7.26 – 7.20 (m, 3H, 3 x Ar*H*), 5.78 (s, 1H, C$H_{alkene}$), 2.27 (t, *J* = 7.4 Hz, 2H, C$H_2$), 1.53 (h, *J* = 7.4 Hz, 2H, C$H_2$), 0.85 (t, *J* = 7.4 Hz, 3H, C$H_3$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.0, 157.5, 138.6, 136.9, 134.1, 133.6, 132.4, 132.3, 131.8, 131.6, 131.4, 129.7, 128.6, 127.8, 117.7, 45.3, 18.1, 14.0. **IR** ($\nu_{max}$, cm$^{-1}$) 2956 (m), 2929 (m), 2870 (w), 1625 (m), 1496 (s), 1473 (s), 1228 (m). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}Br_2OS_2^+$ 470.9082; Found 470.9081.

## 4. Scale-up

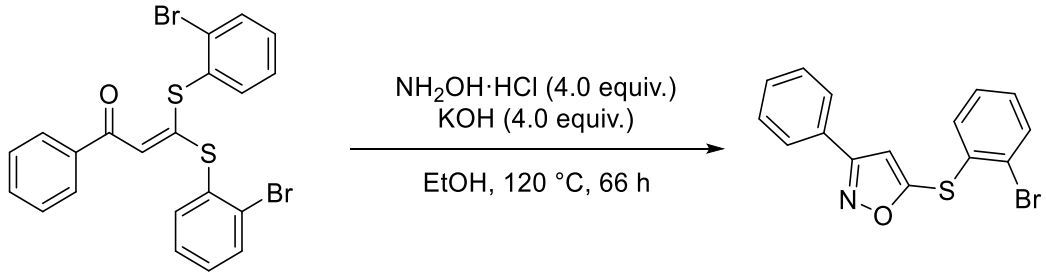



TsOBX (3.00 mmol) **1** (1.1 equiv.) **2a** **3a**

A capped oven dried microwave vial charged with TsOBX **1** (1.26 g, 3.00 mmol, 1.00 equiv.) and potassium trifluoro(3-oxo-3-phenylprop-1-yn-1-yl)borate **2a** (779 mg, 3.30 mmol, 1.10 equiv.) was evacuated and backfilled with $N_2$ (3x). DME (45 mL) was added under $N_2$. The reaction was stirred at 21 °C for 1 h. To a solution of 2-bromothiophenol (793 µL, 6.60 mmol, 2.20 equiv.) in DME (20 mL) was added 1,1,3,3-tetramethylguanidine (866 µL, 6.90 mmol, 2.30 equiv.). The mixture was stirred for 5 minutes and then added to the previous solution. The reaction mixture was stirred at 21 °C for 10 minutes, quenched with $NaHCO_3$ (aq.) sat. (50 mL) and extracted with DCM (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and solvents were removed under reduced pressure. Purification by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 95:5 to 7:3) afforded 3,3-bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one **3a** (1.39 g, 2.75 mmol, 92% yield) as a yellow solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.26. **m. p.** 130-132 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H, Ar*H*), 7.74 – 7.68 (m, 4H, 4 x Ar*H*), 7.60 (dd, *J* = 7.6, 1.8 Hz, 1H, Ar*H*), 7.52 – 7.43 (m, 1H, Ar*H*), 7.41 – 7.28 (m, 6H, 6 x Ar*H*), 6.54 (s, 1H, C$H_{alkene}$). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.5, 161.2, 138.6, 138.5, 137.1, 134.2, 133.6, 132.34, 132.26, 132.0, 131.7, 131.5, 130.0, 128.8, 128.6, 128.1, 127.9, 114.2. (1C not resolved). **IR** (vmax, $cm^{-1}$) 3065 (w), 1620 (m), 1496 (s), 1476 (s), 1227 (s), 1025 (m), 755 (s). **HRMS** (ESI/QTOF) m/z: [M+H]+ Calcd for $C_{21}H_{15}Br_2OS_2^+$ 504.8926; Found 504.8923.

## 5. Product modification of 3a

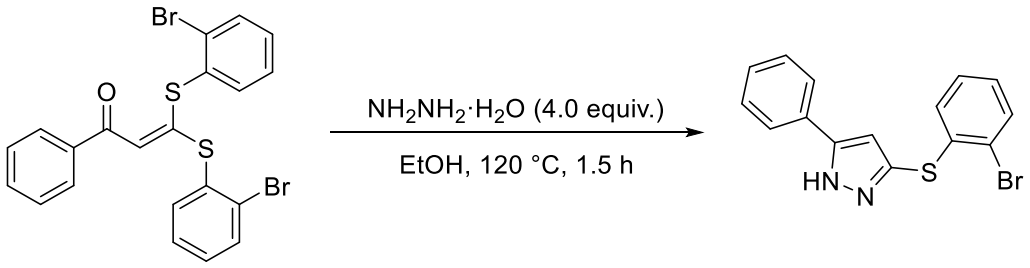
**5-((2-Bromophenyl)thio)-3-phenylisoxazole 4**




**3a** **4**, 64%

Following a reported procedure,[14] a solution of 3,3-bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one **3a** (50.6 mg, 0.100 mmol, 1.00 equiv.), $NH_2OH{\cdot}HCl$ (27.8 mg, 0.400 mmol, 4.00 equiv.) and KOH (22.4 mg, 0.400 mmol, 4.00 equiv.) in EtOH (1 mL) was stirred at 120 °C for 66 h. After cooling down to 21 °C, the solvents were removed under reduced pressure. The residue was dissolved in $CHCl_3$ (10 mL) and washed three times with water (3 x 10 mL). The orgnic layers were gathered, washed with brine, dried over $MgSO_4$, filtered off and solvents were removed under reduced pressure. The crude was purified by column chromatography ($SiO_2$, pentane:EtOAc = 97.5:2.5 to 95:5) to afford 5-((2-bromophenyl)thio)-3-phenylisoxazole **4** (21.3 mg, 64.1 µmol, 64%) as a colorless oil. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95:5) = 0.53. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H, 2 x Ar*H*), 7.63 (dd, *J* = 7.9, 1.6 Hz, 1H, Ar*H*), 7.50 – 7.44 (m, 3H, 3 x Ar*H*), 7.32 – 7.27 (m, 2H, 2 x Ar*H*), 7.17 (ddd, *J* = 8.0, 6.7, 2.3 Hz, 1H, Ar*H*), 6.71 (s, 1H, Ar*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.57, 163.55, 133.7, 133.4, 131.9, 130.5, 129.5, 129.2, 128.6, 128.5, 126.9, 124.6, 107.3. **IR** ($\nu_{max}$, $cm^{-1}$) 3061 (w), 2921 (w), 1555 (m), 1458 (s), 1449 (s), 1393 (s), 1022 (m), 762 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{11}BrNOS^+$ 331.9739; Found 331.9740.

**5-((2-Bromophenyl)thio)-3-phenyl-1H-pyrazole 5**

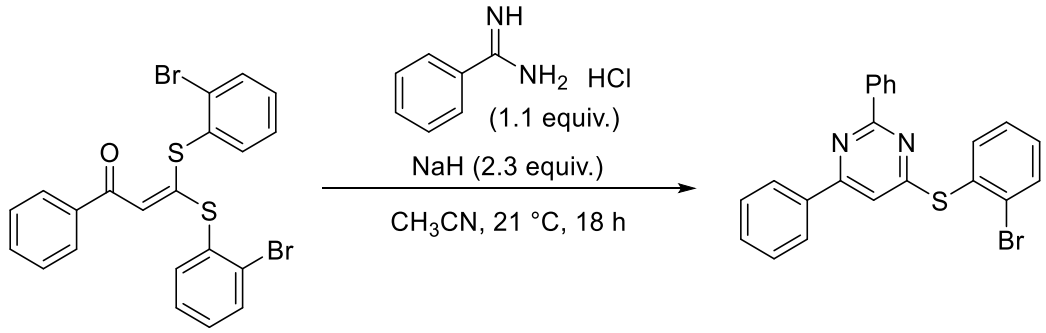



**3a** **5**, 94%

Following a reported procedure,[14] a solution of 3,3-bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one **3a** (50.6 mg, 0.100 mmol, 1.00 equiv.), $NH_2NH_2{\cdot}H_2O$ (20.0 mg, 0.400 mmol, 4.00 equiv.) in EtOH (1 mL) was stirred at 120 °C for 1.5 h. After cooling down to 21 °C, solvents were removed under reduced pressure. The residue was dissolved in $CHCl_3$ (10 mL) and washed three times with water (3 x 10 mL). The organic layers were gathered, washed with brine, dried over $MgSO_4$, filtered off and solvents were removed under reduced pressure. The crude was purified by column chromatography ($SiO_2$, pentane:EtOAc = 85:15) to afford 5-((2-bromophenyl)thio)-3-phenyl-1H-pyrazole **5** (31.1 mg, 938 µmol, 94%) as a white solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 85:15) = 0.40. **m. p.** 132-133 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.55 (s, 1H, N*H*), 7.75 – 7.67 (m, 2H, 2 x Ar*H*), 7.54 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar*H*), 7.44 (ddd, *J* = 7.5, 6.1, 1.4 Hz, 2H, 2 x Ar*H*), 7.41 – 7.35 (m, 1H, Ar*H*), 7.15 (ddd, *J* = 7.9, 7.3, 1.4 Hz, 1H, Ar*H*), 7.07 – 6.99 (m, 1H, Ar*H*), 6.92 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 6.83 (s, 1H, Ar*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.8, 133.1, 129.2, 128.9, 128.19, 128.16, 127.4, 125.7, 121.5, 110.0. (3C not resolved). **IR** (vmax, $cm^{-1}$) 3097 (br), 1574 (w), 1450 (m), 1446 (s), 1019 (s), 744 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}BrN_2S^+$ 330.9899; Found 330.9892.

[14] P. K. Mahata, U. K. Syam Kumar, V. Sriram, H. Ila, H. Junjappa, *Tetrahedron* **2003**, *59*, 2631–2639.

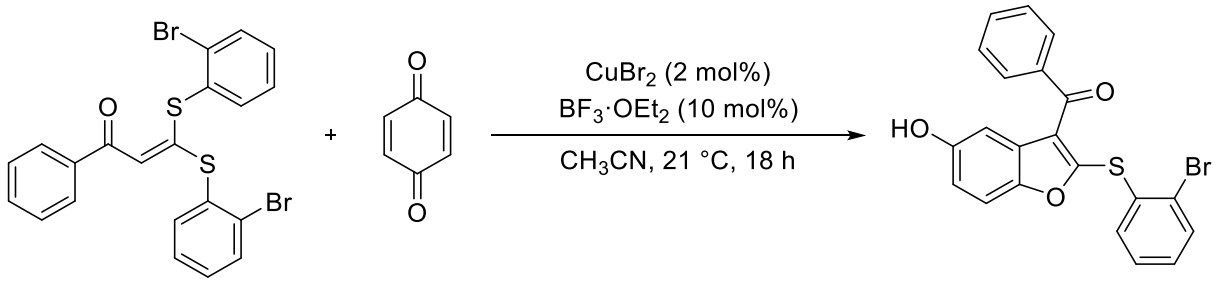
**4-((2-Bromophenyl)thio)-2,6-diphenylpyrimidine 6**




**3a** **6**, 47%

Following a reported procedure,[15] NaH (60% dipersion in oil, 18.4 mg, 0.460 mmol, 2.30 equiv.) was added to a solution of benzamidine hydrochloride (34.5 mg, 0.220 mmol, 1.10 equiv.) in toluene (1.5 mL) and DMF (0.050 mL). 3,3-Bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one **3a** (101 mg, 0.200 mmol, 1.00 equiv.) was added and the mixture was stirred at 110 °C for 1 h. The reaction was pourred into ice cold water (10 mL) and extracted three times with DCM (3 x 10 mL). The organic layers were gathered, washed with brine, dried over $MgSO_4$, filtered off and the solvents were removed under reduced pressure. The crude was purified by column chromatography ($SiO_2$, pentane:EtOAc = 99 :1) to afford 4-((2-bromophenyl)thio)-2,6-diphenylpyrimidine **6** (39.1 mg, 0.0932 mmol, 47%) as a white solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 98:2) = 0.48. **m.p.** 123-125 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H, Ar*H*), 8.54 – 8.50 (m, 2H, 2 x Ar*H*), 7.93 – 7.87 (m, 2H, 2 x Ar*H*), 7.60 (dd, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 7.50 (m, 6H, 6 x Ar*H*), 7.25 – 7.17 (m, 2H, 2 x Ar*H*), 7.13 (ddd, *J* = 8.0, 6.8, 2.4 Hz, 1H, Ar*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.9, 163.0, 160.7, 137.5, 137.1, 135.3, 133.9, 132.8, 131.1, 130.3, 129.4, 129.3, 128.8, 128.5, 128.4, 126.1, 126.0. (1C not resolved). **IR** ($\nu_{max}$, $cm^{-1}$) 3059 (w), 1540 (s), 1512 (m), 1490 (m), 1445 (m), 1404 (s), 1374 (m), 1019 (m), 747 (s). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{16}BrN_2S^+$ 419.0212; Found 419.0205.

**(2-((2-Bromophenyl)thio)-5-hydroxybenzofuran-3-yl)(phenyl)methanone 7**



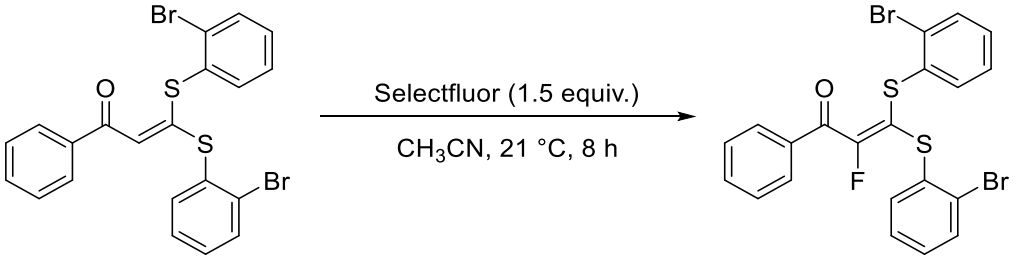

**3a** **7**, 58%

Following a reported procedure,[16] to a solution of 3,3-bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one **3a** (50.6 mg, 0.100 mmol, 1.00 equiv.) and *p*-benzoquinone (16.2 mg, 0.150 mmol, 1.50 equiv.) in $CH_3CN$ (0.4 mL) was added $BF_3{\cdot}OEt_2$ (1M in $CH_3CN$, 10.0 µL, 10.0

[15] K. T. Potts, M. J. Cipullo, P. Ralli, G. Theodoridis, *J. Org. Chem.* **1983**, *48*, 4841–4843.
[16] Y. Liu, M. Wang, H. Yuan, Q. Liu, *Adv. Synth. Catal.* **2010**, *352*, 884–892.

µmol, 10.0 mol%) followed by $CuBr_2$ (0.447 mg, 2.00 µmol, 2.00 mol%). The reaction mixture was stirred at 21 °C for 18 h. The resulting mixture was poured into brine (5 mL), neutralized with aqueous $NaHCO_3$, and extracted with $CH_2Cl_2$ (3 x 20 mL). The organic layers were gathered, washed with brine, dried over $MgSO_4$, filtered off and solvents were removed under reduced pressure. The crude was purified by column chromatography ($SiO_2$, pentane:EtOAc = 7:3 to 6:4) to afford (2-((2-bromophenyl)thio)-5-hydroxybenzofuran-3-yl)(phenyl)methanone **7** (24.7 mg, 0.0580 mmol, 58%) as a white solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 6:4) = 0.55. **m. p.** 160-162 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H, 2 x Ar*H*), 7.63 – 7.56 (m, 2H, 2 x Ar*H*), 7.50 – 7.45 (m, 2H, 2 x Ar*H*), 7.42 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.30 – 7.25 (m, 2H, 2 x Ar*H*), 7.20 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.08 (d, *J* = 2.5 Hz, 1H, Ar*H*), 6.83 (dd, *J* = 8.8, 2.6 Hz, 1H, Ar*H*), 5.59 (s, 1H, O*H*). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 191.4, 156.9, 153.1, 150.8, 138.8, 133.9, 133.7, 133.1, 132.4, 130.1, 129.2, 128.7, 128.3, 127.6, 126.7, 121.5, 114.1, 111.9, 106.4. **IR** ($\nu_{max}$, $cm^{-1}$) 3367 (br), 2952 (m), 1610 (m), 1473 (s), 1234 (m). **HRMS** (ESI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}BrO_3S^+$ 424.9842; Found 424.9845.

**3,3-Bis((2-bromophenyl)thio)-2-fluoro-1-phenylprop-2-en-1-one 8**




**3a** **8**, 54%

Following a reported procedure,[17] to a well stirred solution of selectfluor (106 mg, 0.300 mmol, 1.50 equiv.) in $CH_3CN$ (1 ml) at 0 °C was added a solution of 3,3-bis((2-bromophenyl)thio)-1-phenylprop-2-en-1-one **3a** (101 mg, 0.200 mmol, 1.00 equiv.) in $CH_3CN$ (1 ml) drop wise. The reaction mixture was stirred at 21 °C for 8 h. The reaction was pourred into ice cold water (10 mL) and extracted three times with EtOAc (3 x 10 mL). The organic layers were gathered, washed with brine, dried over $MgSO_4$, filtered off and the solvents were removed under reduced pressure. The crude was purified by column chromatography (basic $Al_2O_3$, pentane:EtOAc = 97.5 :2.5 to 9 :1) to afford 3,3-bis((2-bromophenyl)thio)-2-fluoro-1-phenylprop-2-en-1-one **8** (56.6 mg, 0.108 mmol, 54%) as yellow amorphous solid. $\mathbf{R_f}$ ($SiO_2$, pentane: EtOAc = 95 :5) = 0.5. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H, 2 x Ar*H*), 7.62 (m, 1H, Ar*H*), 7.53 – 7.49 (m, 3H, 3 x Ar*H*), 7.45 (dd, *J* = 7.9, 1.4 Hz, 1H, Ar), 7.29 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.25 – 7.16 (m, 3H, 3 x Ar*H*), 7.16 – 7.09 (m, 2H, 2 x Ar*H*). **$^{13}$C{$^1$H, $^{19}$F} NMR** (101 MHz, $CDCl_3$) δ 185.2, 155.3, 135.5, 134.3, 134.1, 133.8, 133.3, 133.2, 133.1, 132.5, 129.8, 129.7, 129.6, 128.84, 127.8, 127.7, 127.4, 127.1, 125.7. **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -89.4. **IR** ($\nu_{max}$, $cm^{-1}$) 2923 (m), 2849 (w), 1677 (m), 1447 (s), 1278 (s), 1022 (m), 751 (s). **HRMS** (APCI/QTOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{14}Br_2FOS_2^+$ 522.8831; Found 522.8832.

[17] T. P. Charanraj, P. Ramachandra, N. Ramesh, H. Junjappa, *Tetrahedron Lett.* **2016**, *57*, 3264–3267.

## 6. Crystal structures

**Crystal structure of 3a**

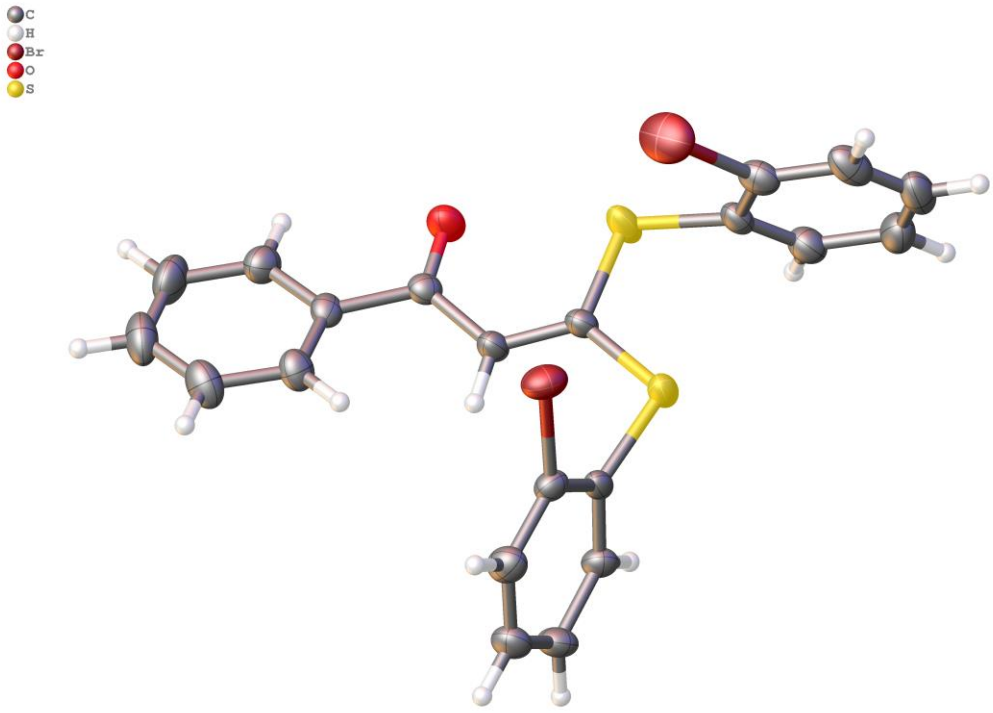



Figure S1: Ellipsoid plot (probability level 50%) of **3a**

| **Compound** | **3a** |
|---|---|
| Formula | $C_{21}H_{14}Br_2OS_2$ |
| $D_{calc.}$/ g cm$^{-3}$ | 1.708 |
| $\mu$/mm$^{-1}$ | 4.337 |
| Formula Weight | 506.26 |
| Colour | clear pale yellow |
| Shape | irregular-shaped |
| Size/mm$^3$ | 0.43×0.23×0.16 |
| $T$/K | 200.00(10) |
| Crystal System | monoclinic |
| Space Group | $P2_1/n$ |
| $a$/Å | 10.8765(5) |
| $b$/Å | 14.0744(6) |
| $c$/Å | 13.5229(6) |
| $\alpha$/° | 90 |
| $\beta$/° | 108.006(5) |
| $\gamma$/° | 90 |
| V/Å$^3$ | 1968.72(16) |
| $Z$ | 4 |
| $Z'$ | 1 |
| Wavelength/Å | 0.71073 |
| Radiation type | Mo K$_\alpha$ |
| $\Theta_{min}$/° | 2.560 |
| $\Theta_{max}$/° | 32.684 |
| Measured Refl's. | 21335 |
| Indep't Refl's | 6670 |
| Refl's I≥2 $\sigma$(I) | 4481 |
| $R_{int}$ | 0.0357 |
| Parameters | 339 |
| Restraints | 420 |
| Largest Peak | 0.676 |
| Deepest Hole | -0.712 |
| GooF | 1.070 |
| $wR_2$ (all data) | 0.0859 |
| $wR_2$ | 0.0735 |
| $R_1$ (all data) | 0.0819 |

Crystals were grown by preparing a solution of **3a** in EtOH, leaving the solution slowly evaporate over 2-3 days.

Analysis of the crystal: A suitable crystal with dimensions 0.43 × 0.23 × 0.16 mm$^3$ was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady T = 200.00(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2019/3 (Sheldrick, 2015) using full matrix least squares minimisation on **F$^2$.**

Supplementary crystallographic data for this compound have been deposited at Cambridge Crystallographic Data Centre (CCDC **2290050**) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

## 7. References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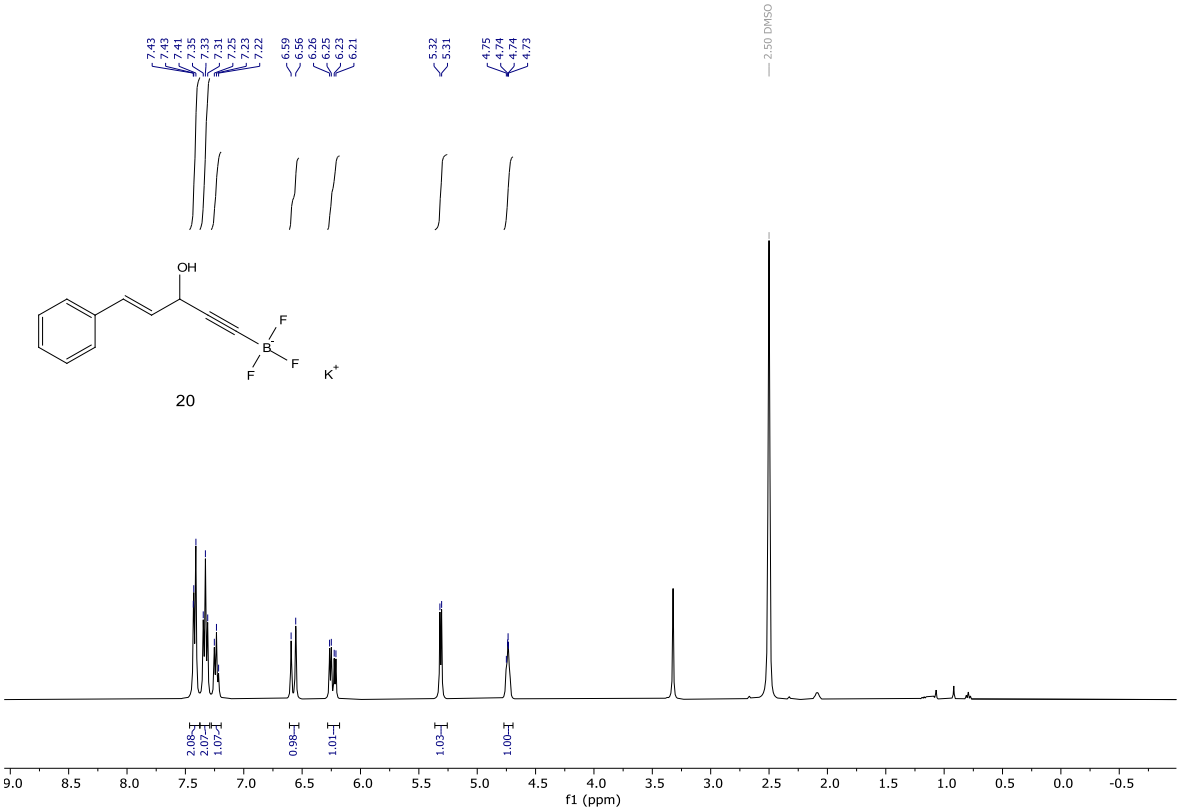
[16] Y. Liu, M. Wang, H. Yuan, Q. Liu, *Adv. Synth. Catal.* **2010**, *352*, 884–892.

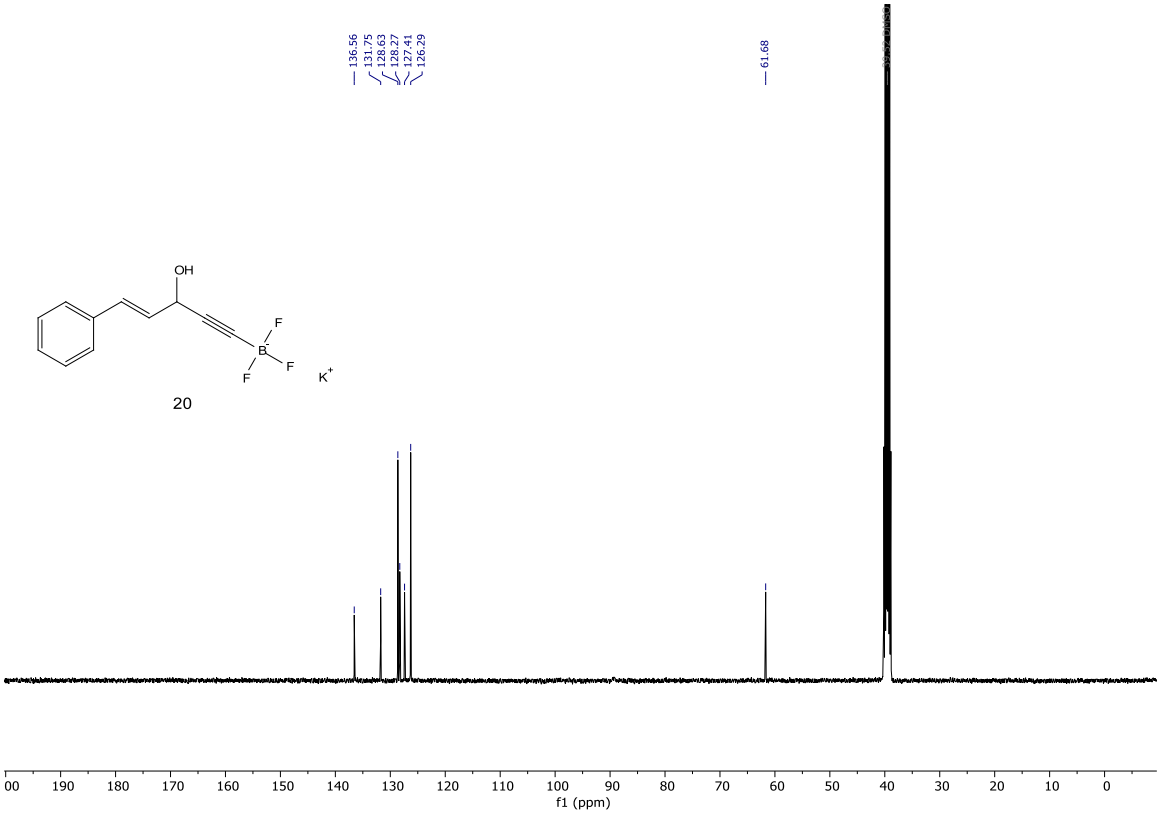
[17] K. T. Potts, M. J. Cipullo, P. Ralli, G. Theodoridis, *J. Org. Chem.* **1983**, *48*, 4841–4843.

## 8. NMR spectra

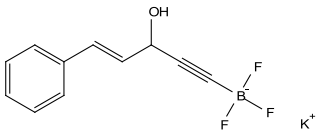
**$^{1}$H NMR** (400 MHz, DMSO-$d_6$) of compound **20**




**$^{13}$C NMR** (400 MHz, DMSO-$d_6$) of compound **20**



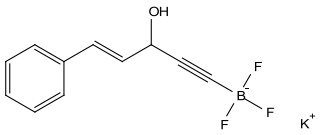
**$^{19}$F NMR** (376 MHz, DMSO-$d_6$) of compound **20**




20

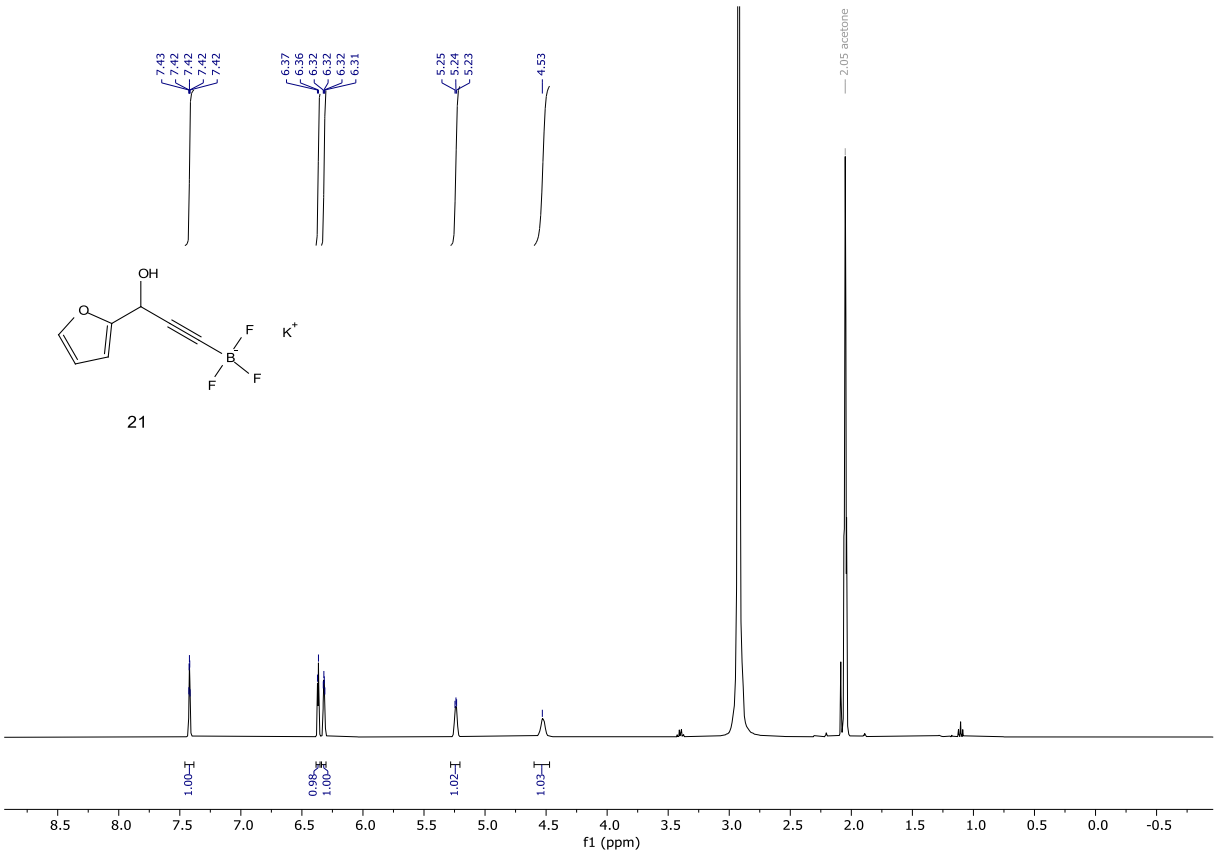



**$^{11}$B NMR** (128 MHz, DMSO-$d_6$) of compound **20**

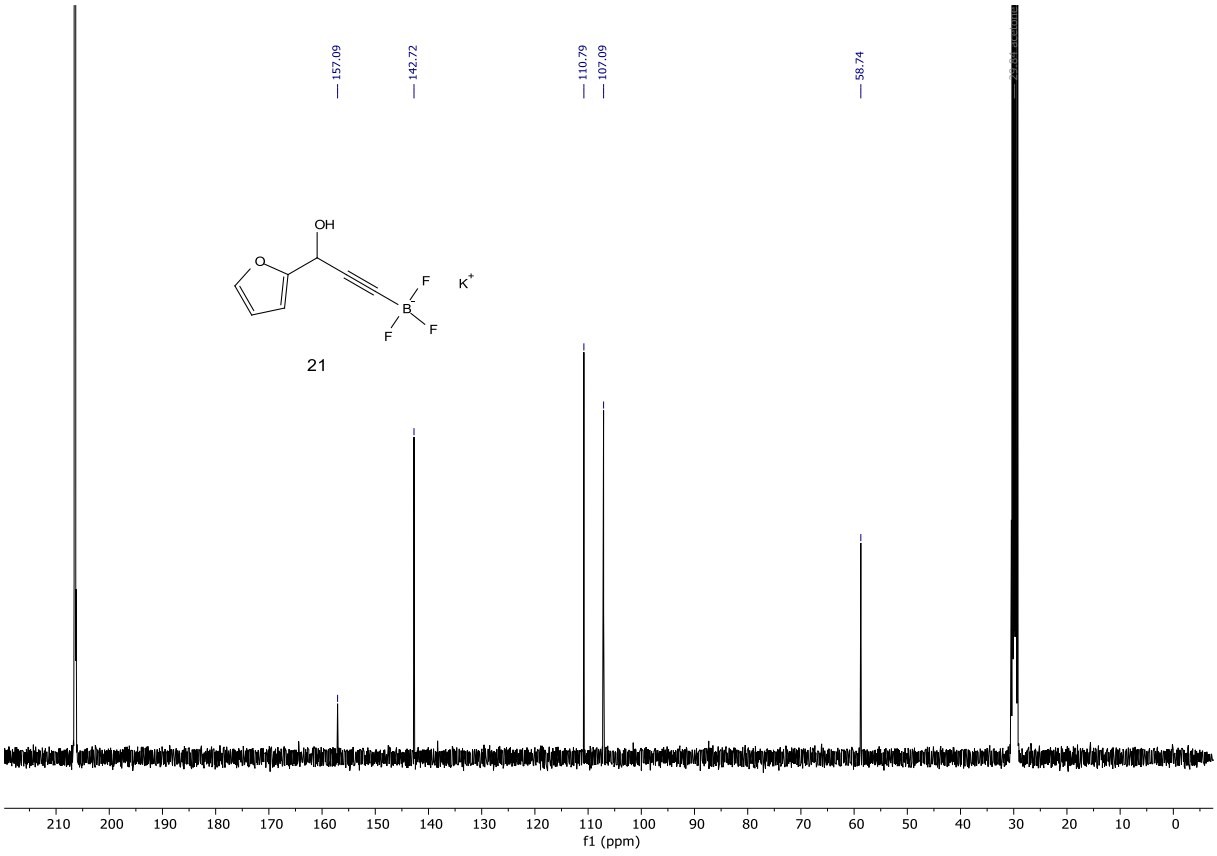



20

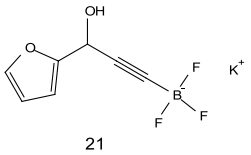
**$^{1}$H NMR** (400 MHz, acetone-$d_6$) of compound **21**




**$^{13}$C NMR** (400 MHz, acetone-$d_6$) of compound **2**



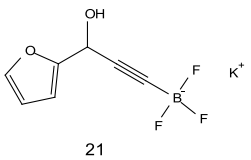
**$^{19}$F NMR** (376 MHz, acetone-$d_6$) of compound **21**




21

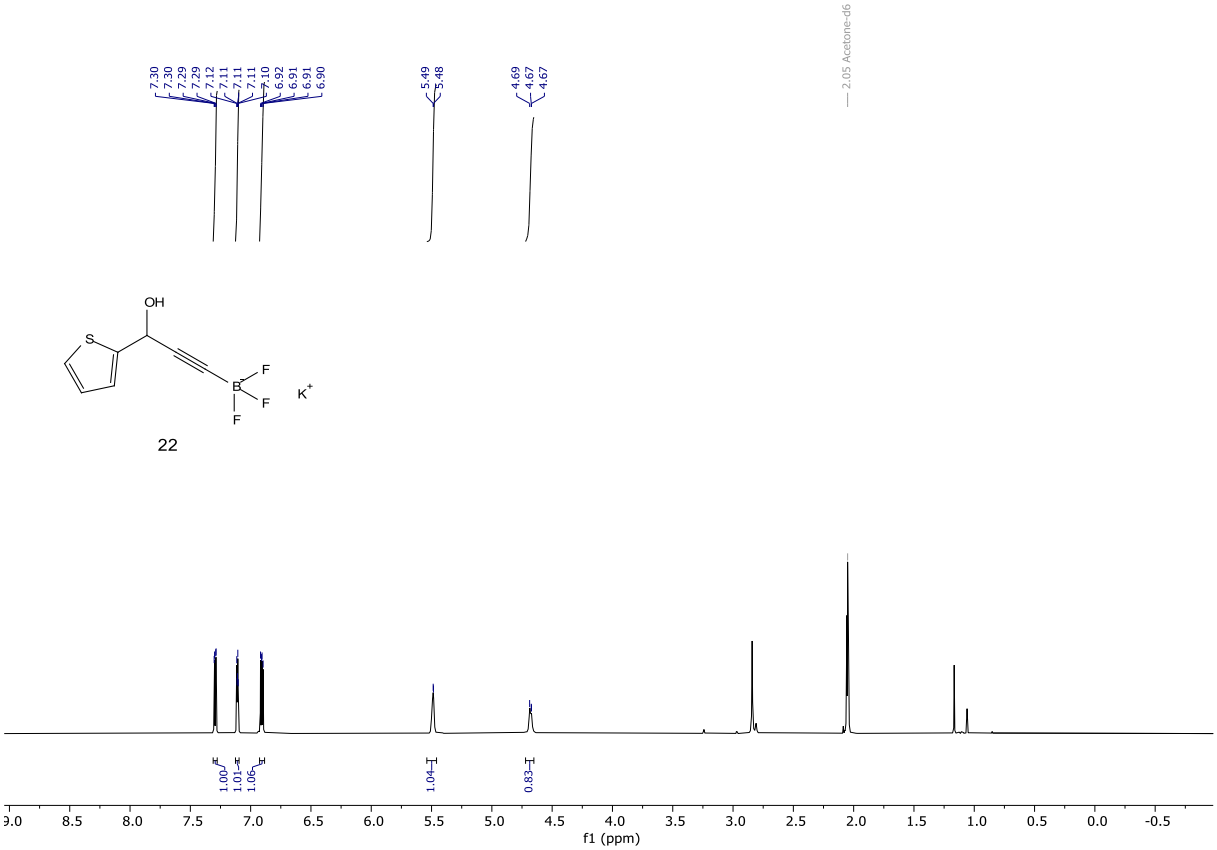



**$^{11}$B NMR** (128 MHz, acetone-$d_6$) of compound **21**

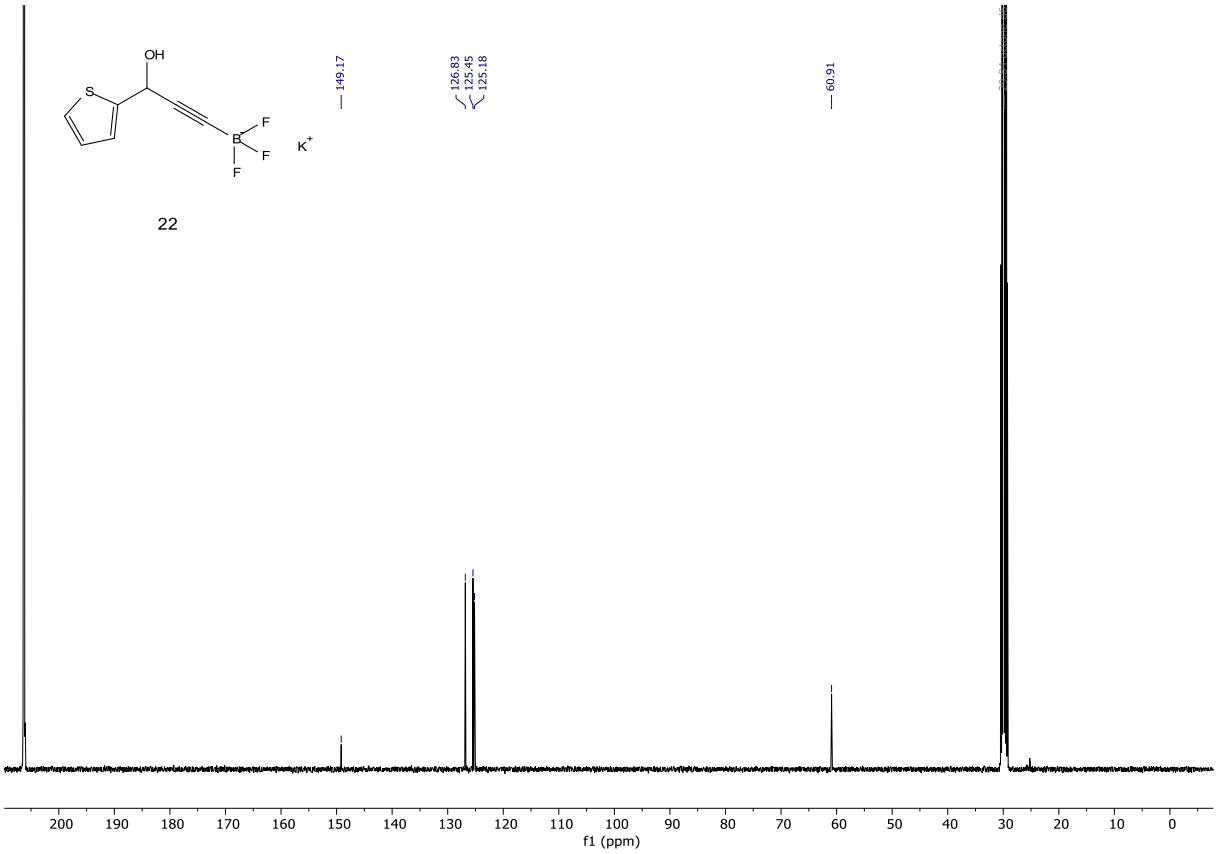



21

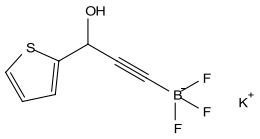
**$^{1}$H NMR** (400 MHz, acetone-$d_6$) of compound **22**




**$^{13}$C NMR** (400 MHz, acetone-$d_6$) of compound **22**



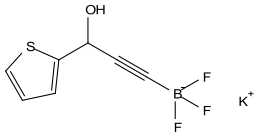
**$^{19}$F NMR** (376 MHz, acetone-$d_6$) of compound **22**




22

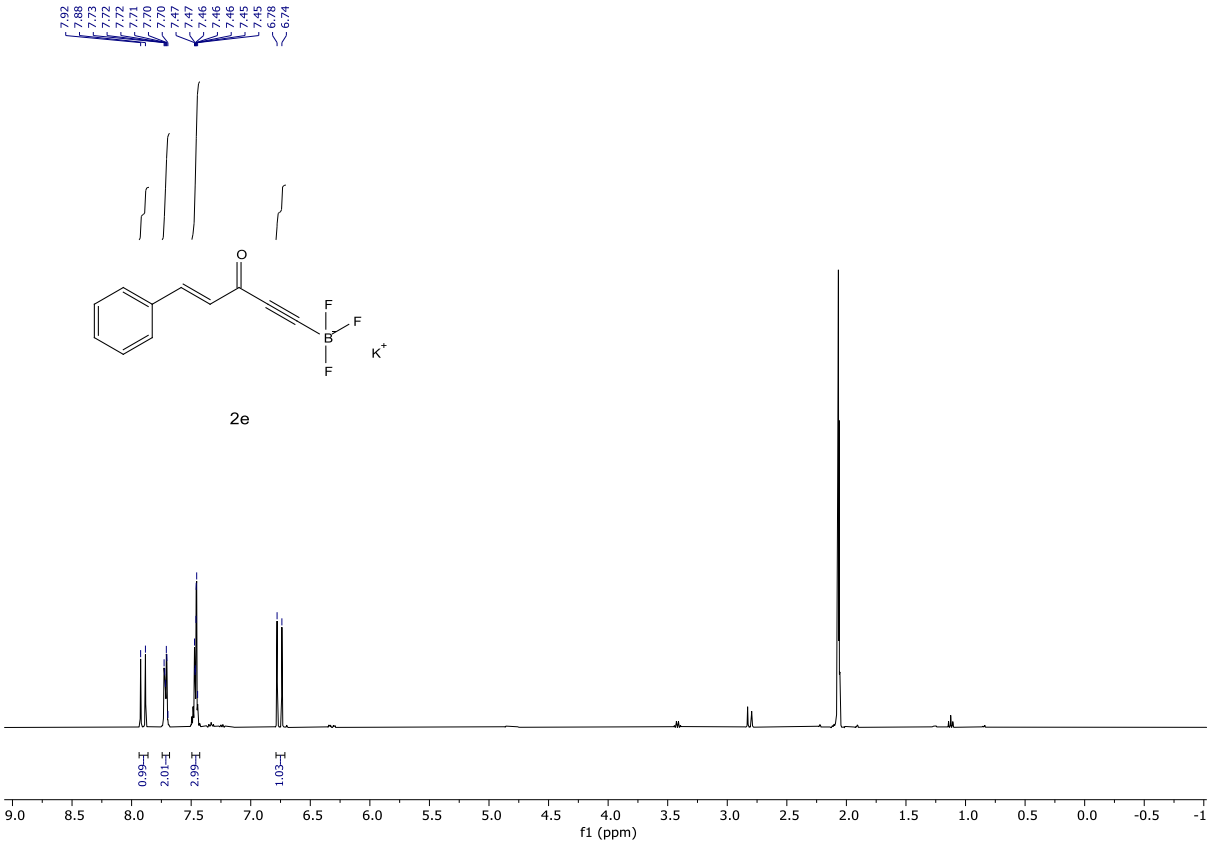



**$^{11}$B NMR** (128 MHz, acetone-$d_6$) of compound **22**

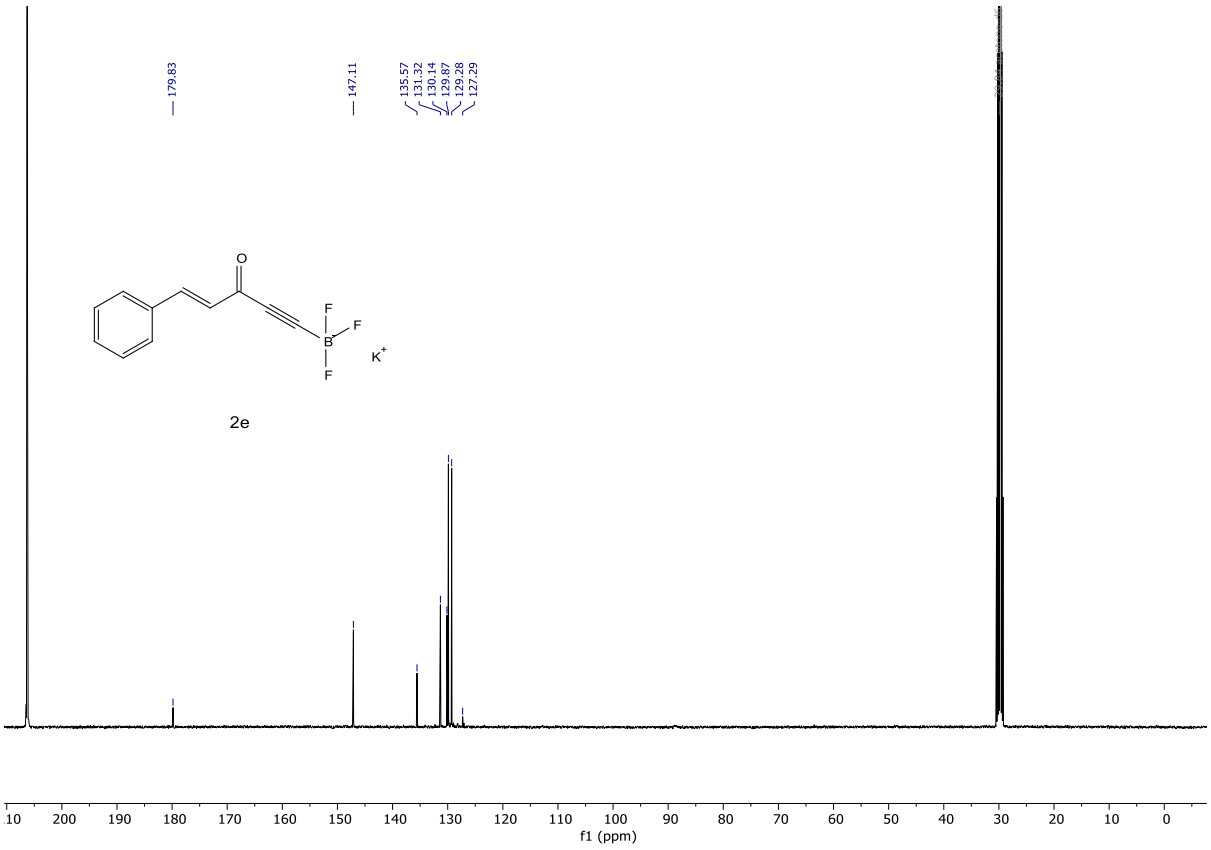



22

**$^{1}$H NMR** (400 MHz, acetone-$d_6$) of compound **2e**

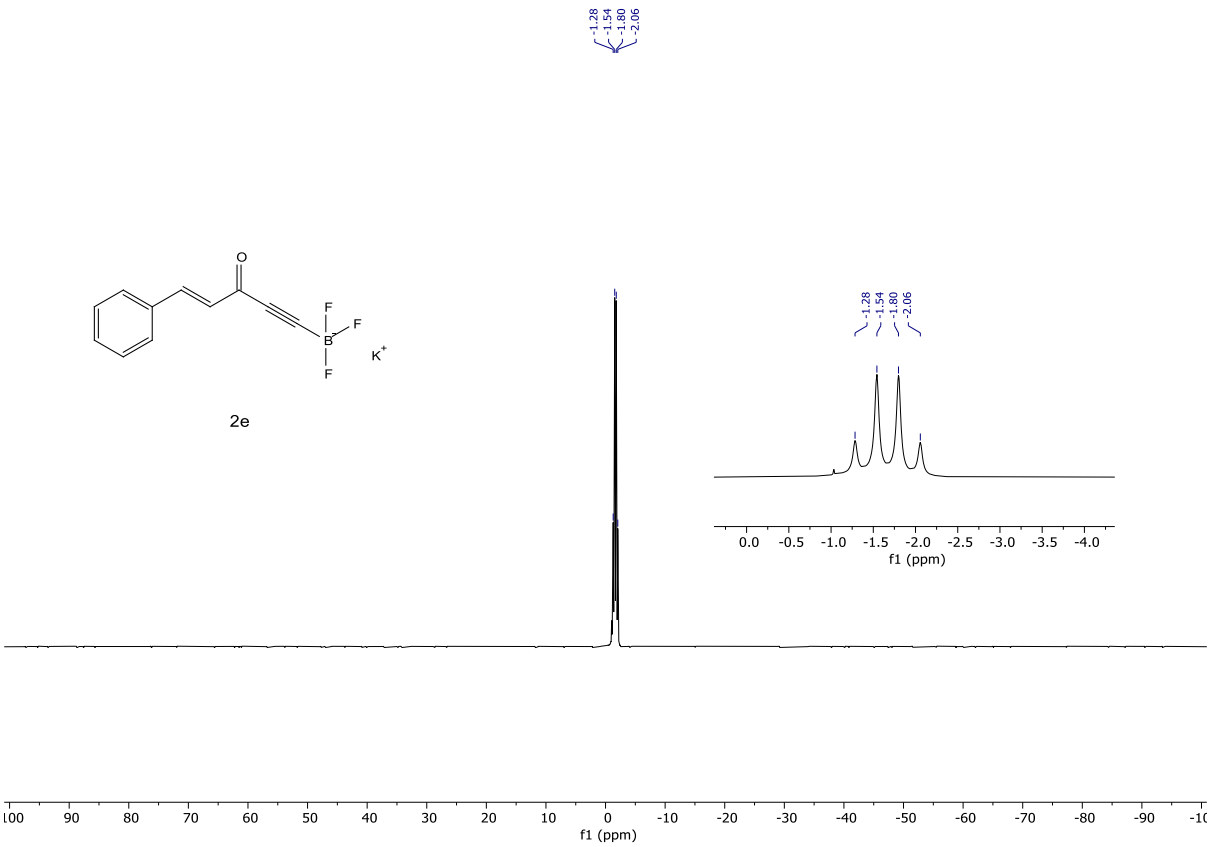



**$^{13}$C NMR** (400 MHz, acetone-$d_6$) of compound **2e**

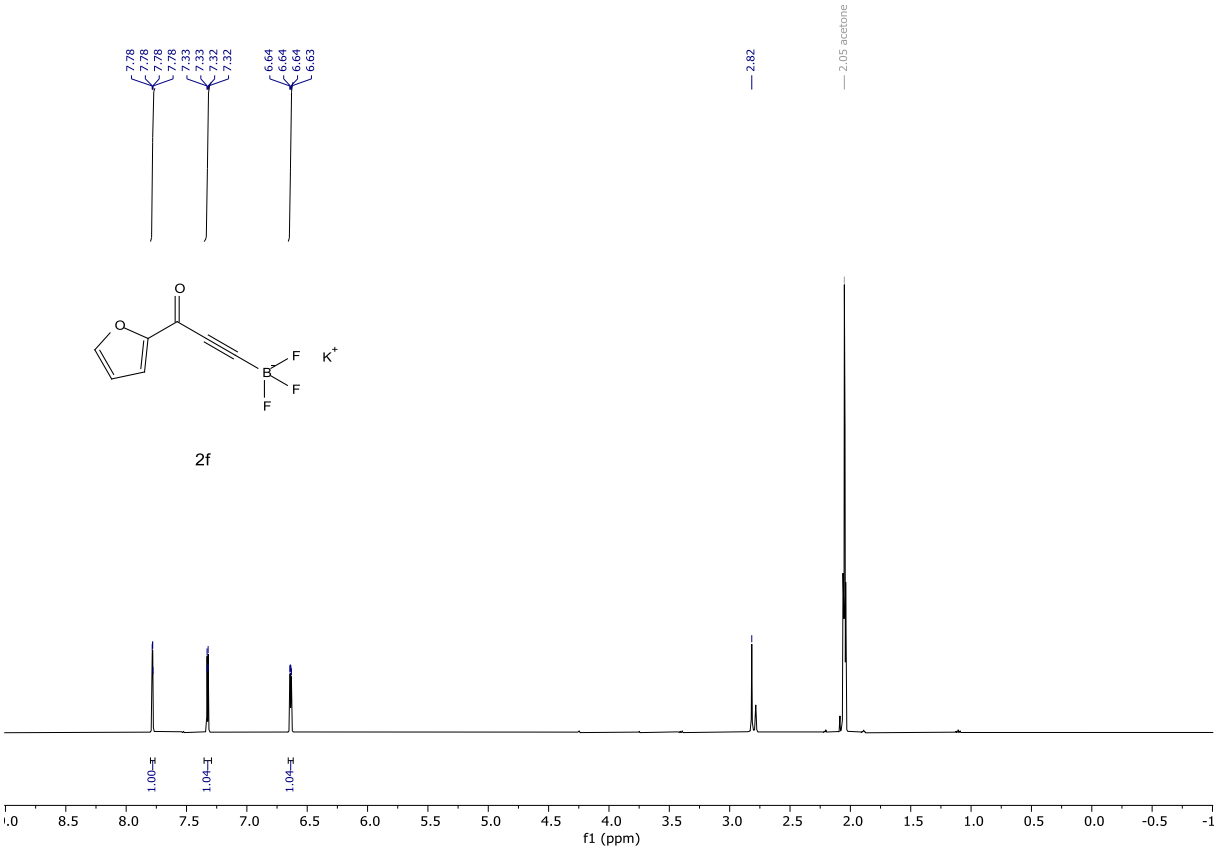


**$^{19}$F NMR** (376 MHz, acetone-$d_6$) of compound **2e**


**$^{11}$B NMR** (128 MHz, acetone-$d_6$) of compound **2e**



**$^{1}$H NMR** (400 MHz, acetone-$d_6$) of compound **2f**

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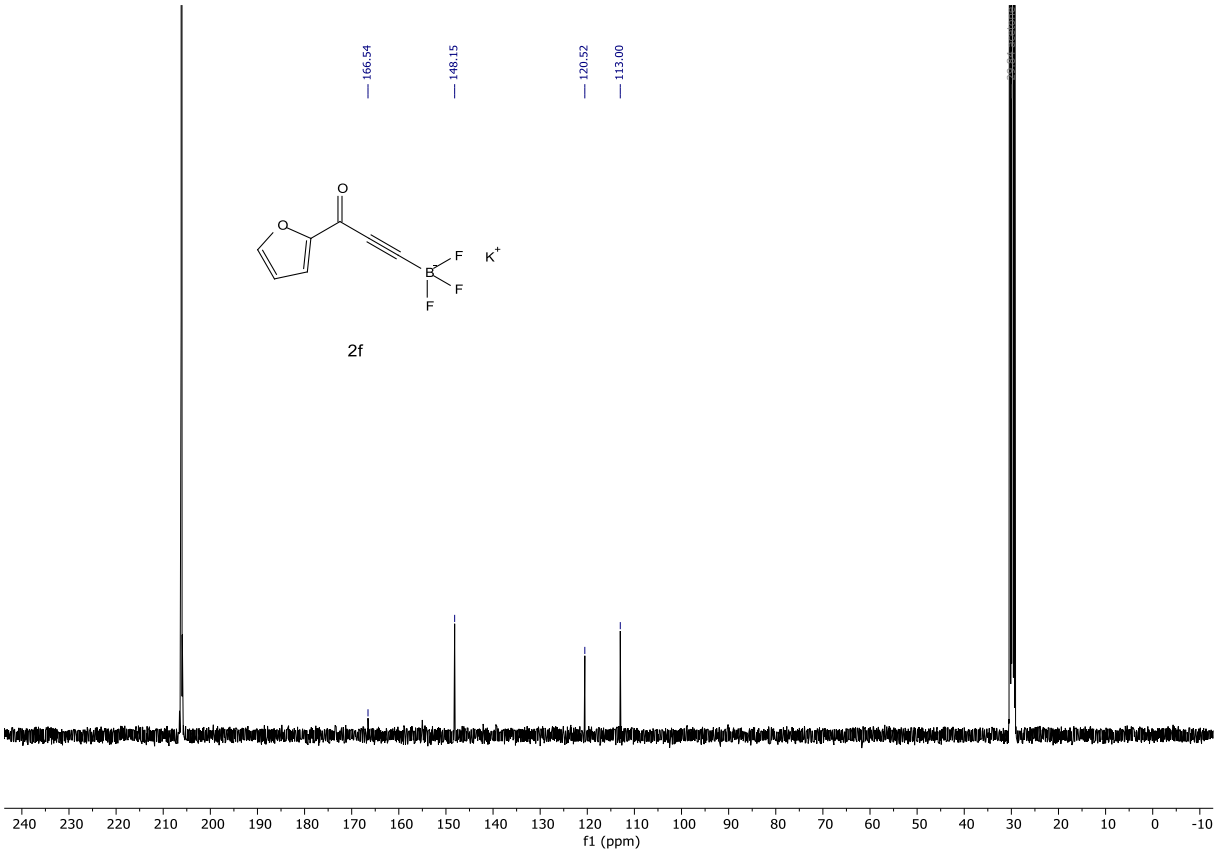
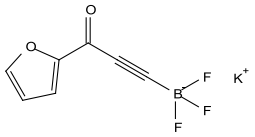


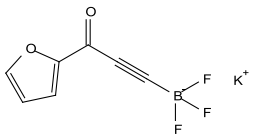
**$^{19}$F NMR** (376 MHz, acetone-$d_6$) of compound **2f**



2f

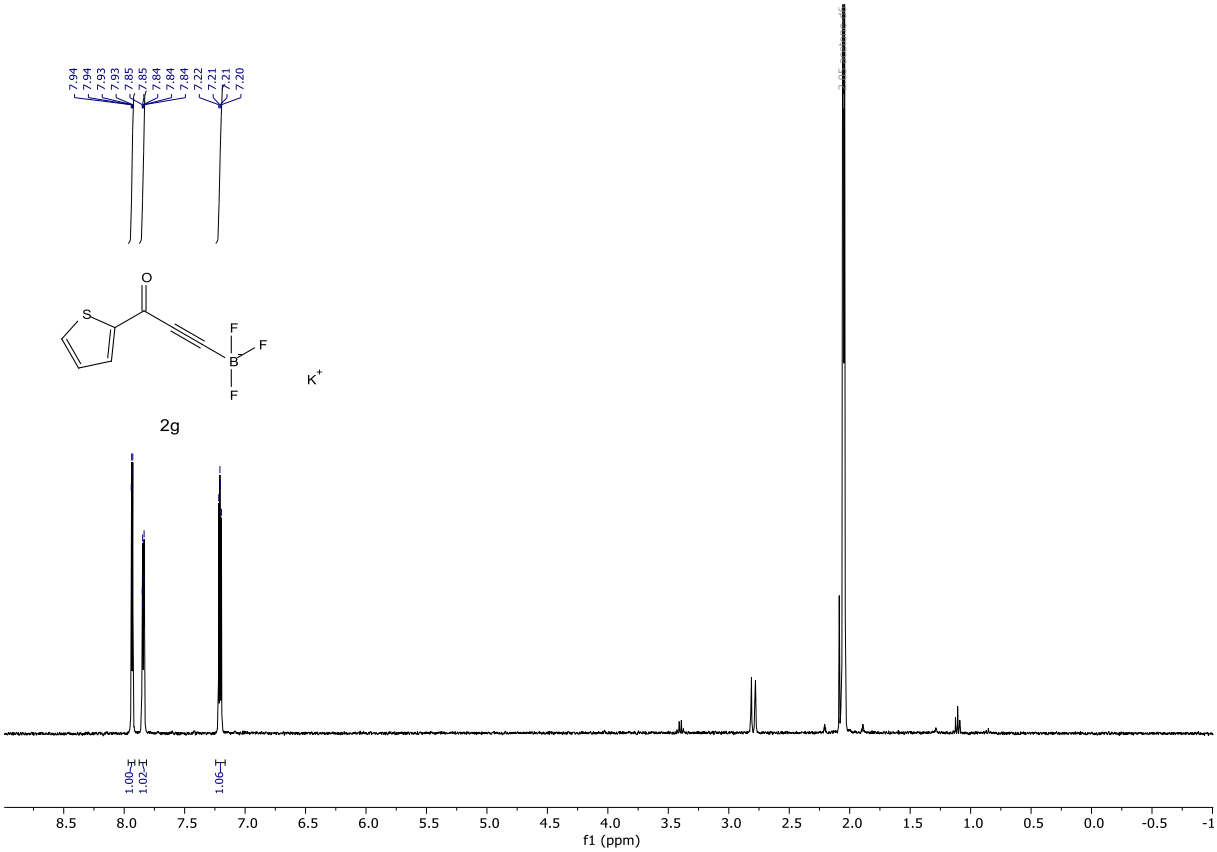



**$^{11}$B NMR** (128 MHz, acetone-$d_6$) of compound **2f**

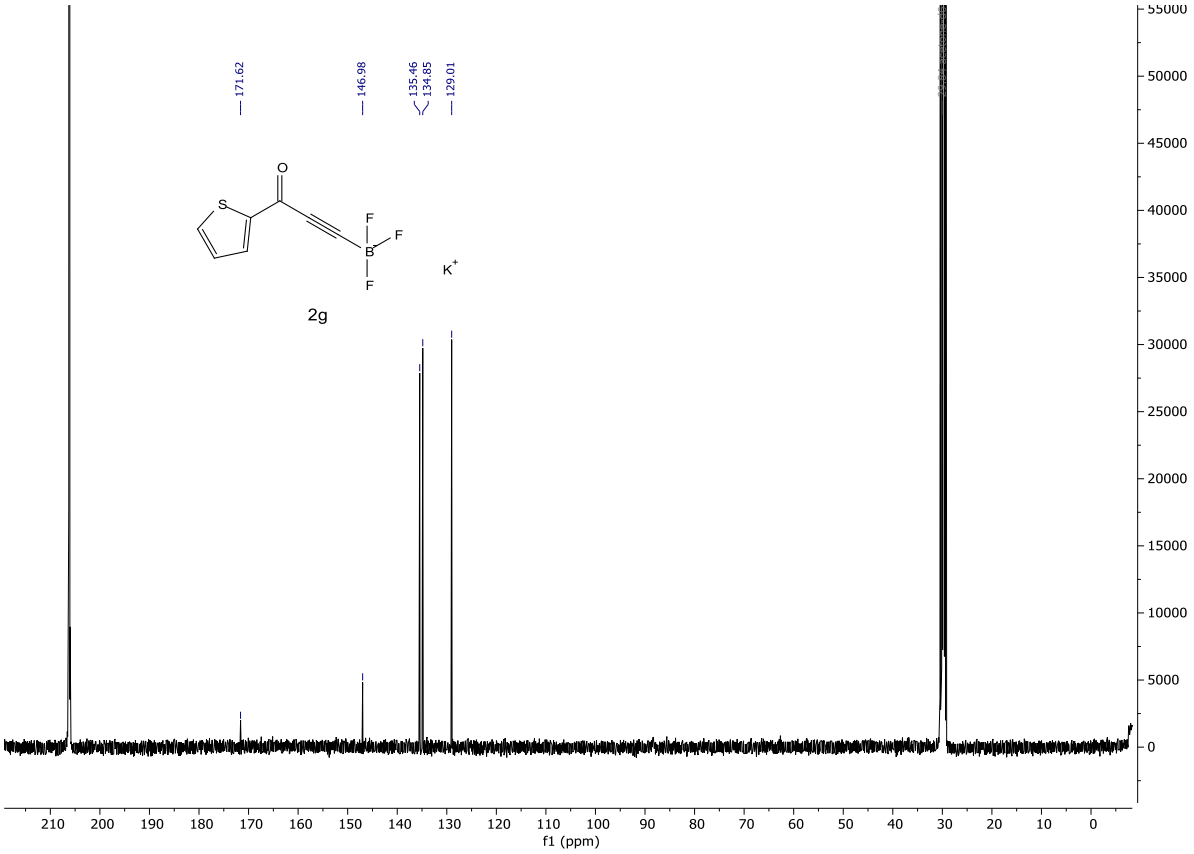


2f

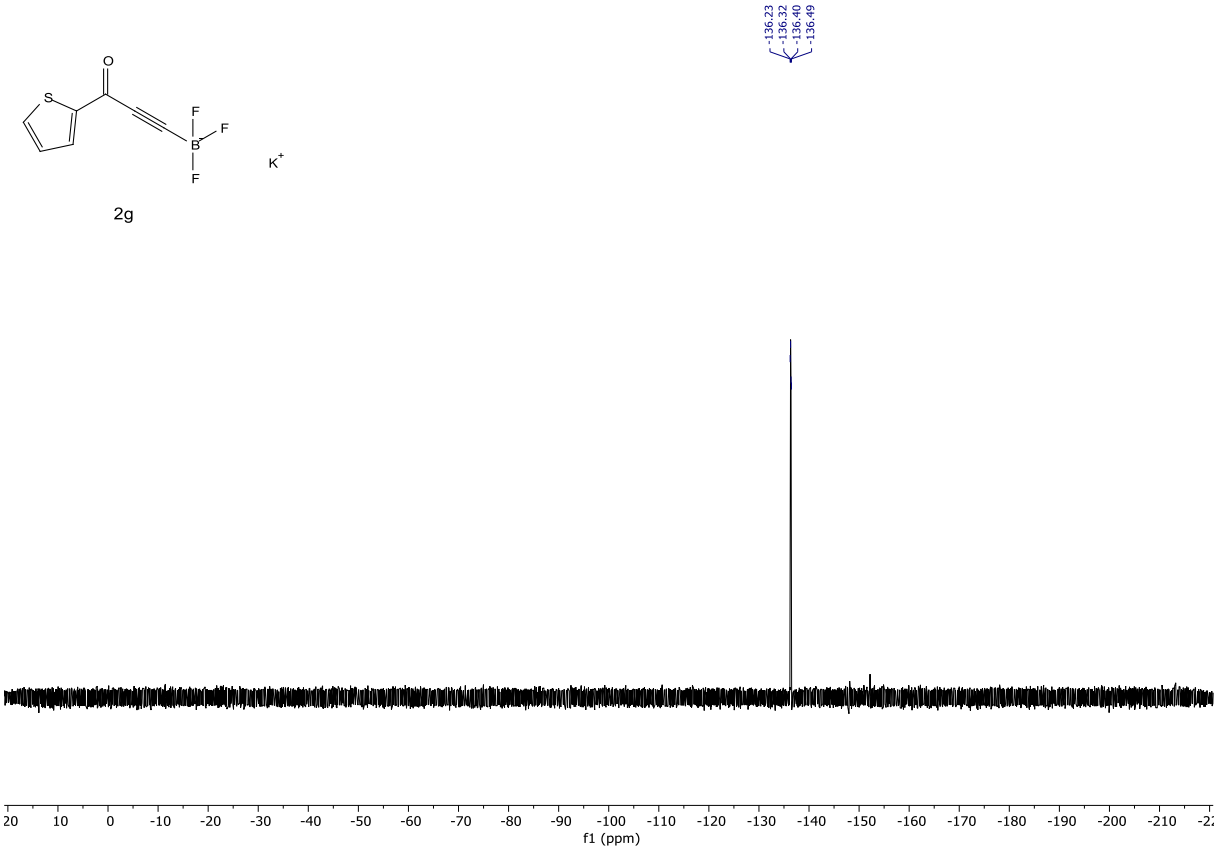
**$^{1}$H NMR** (400 MHz, acetone-$d_6$) of compound **2g**



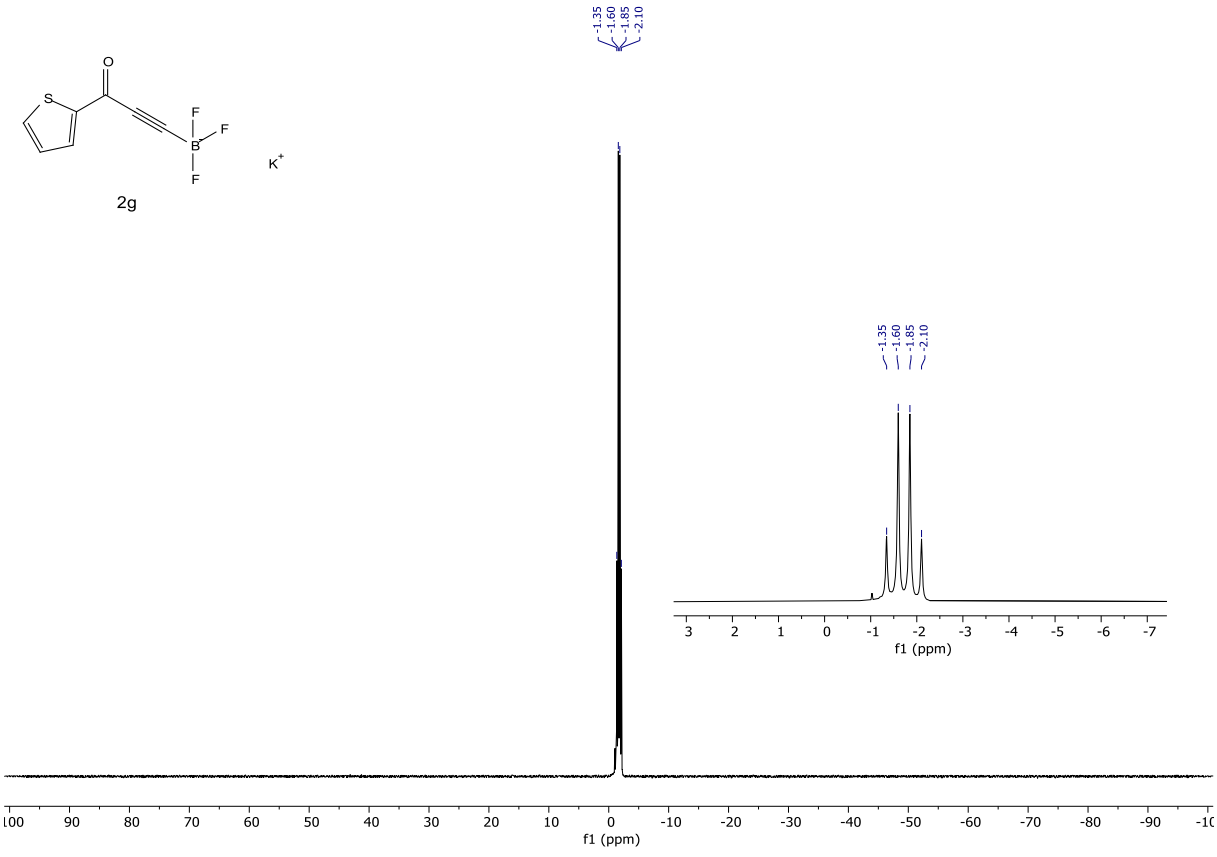

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **2g**



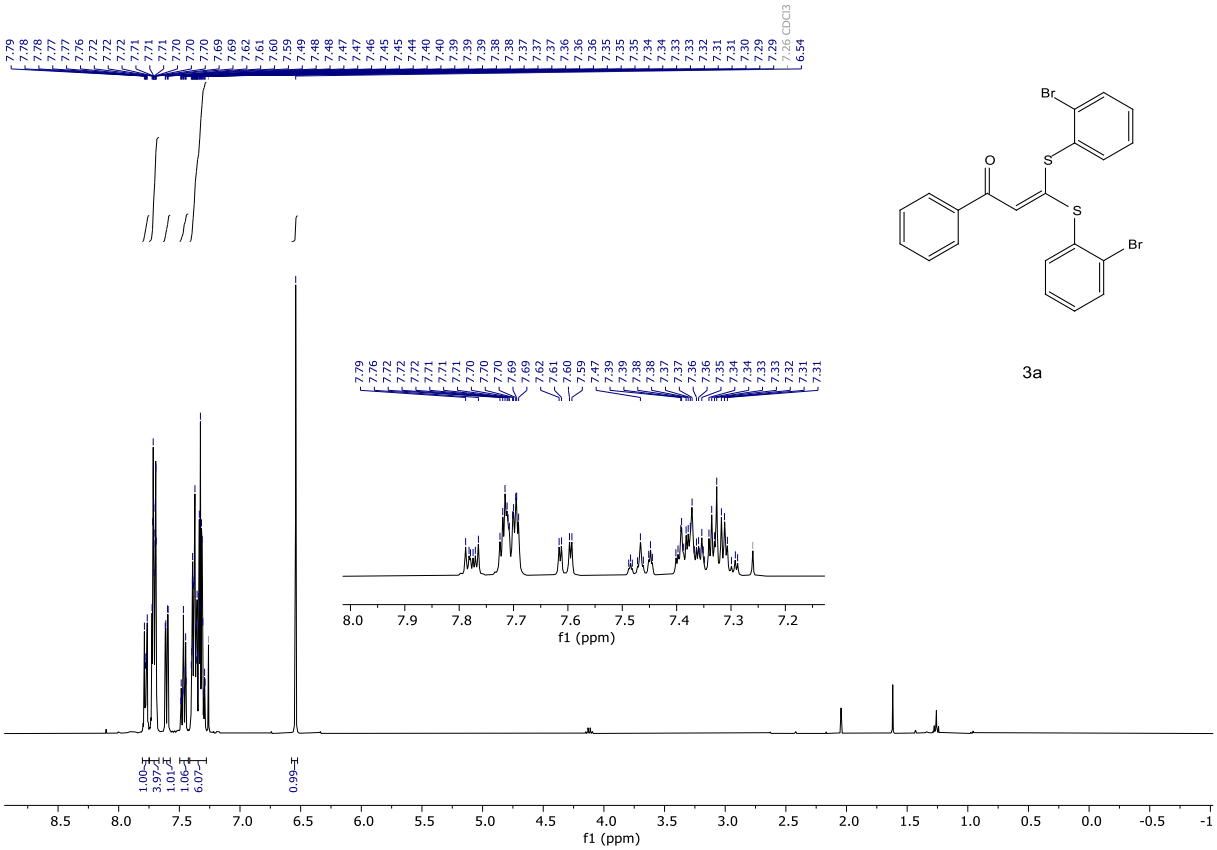
**$^{19}$F NMR** (376 MHz, acetone-$d_6$) of compound **2g**



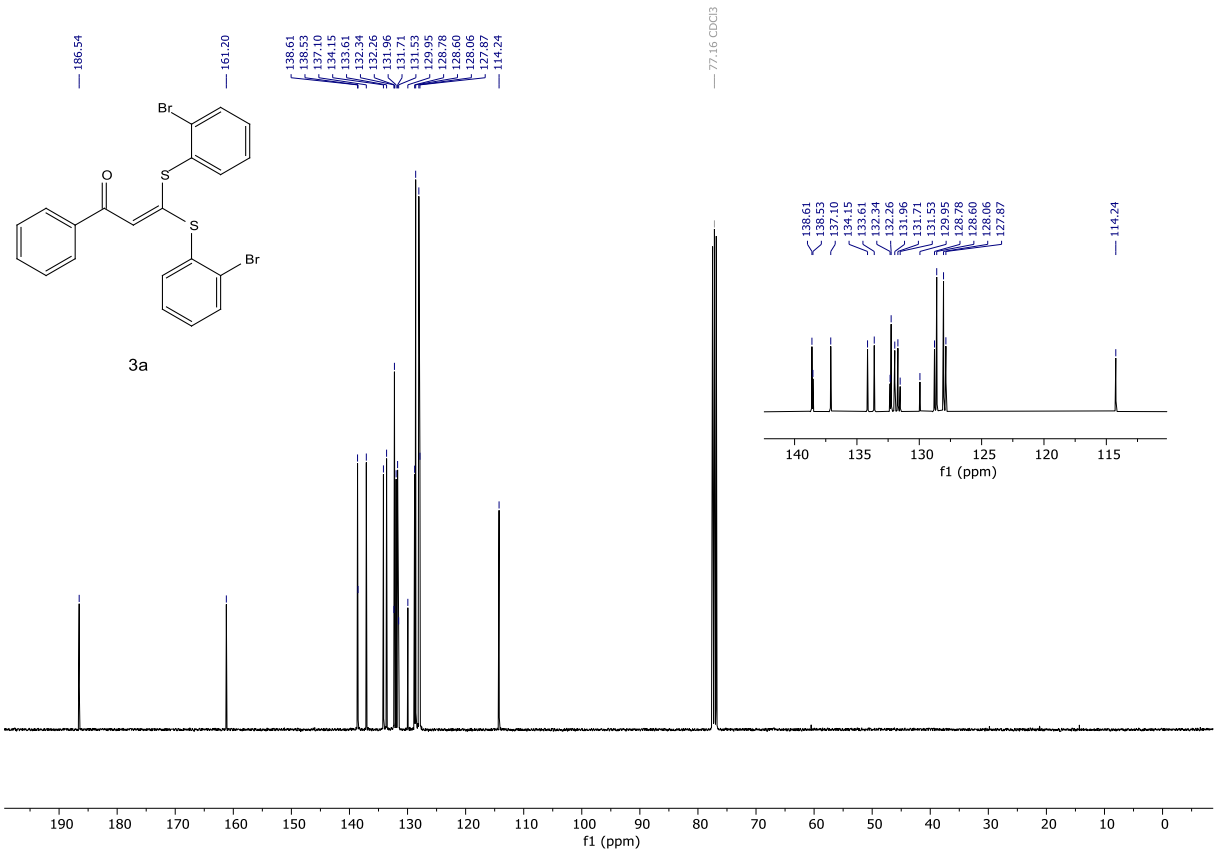

**$^{11}$B NMR** (128 MHz, acetone-$d_6$) of compound **2g**



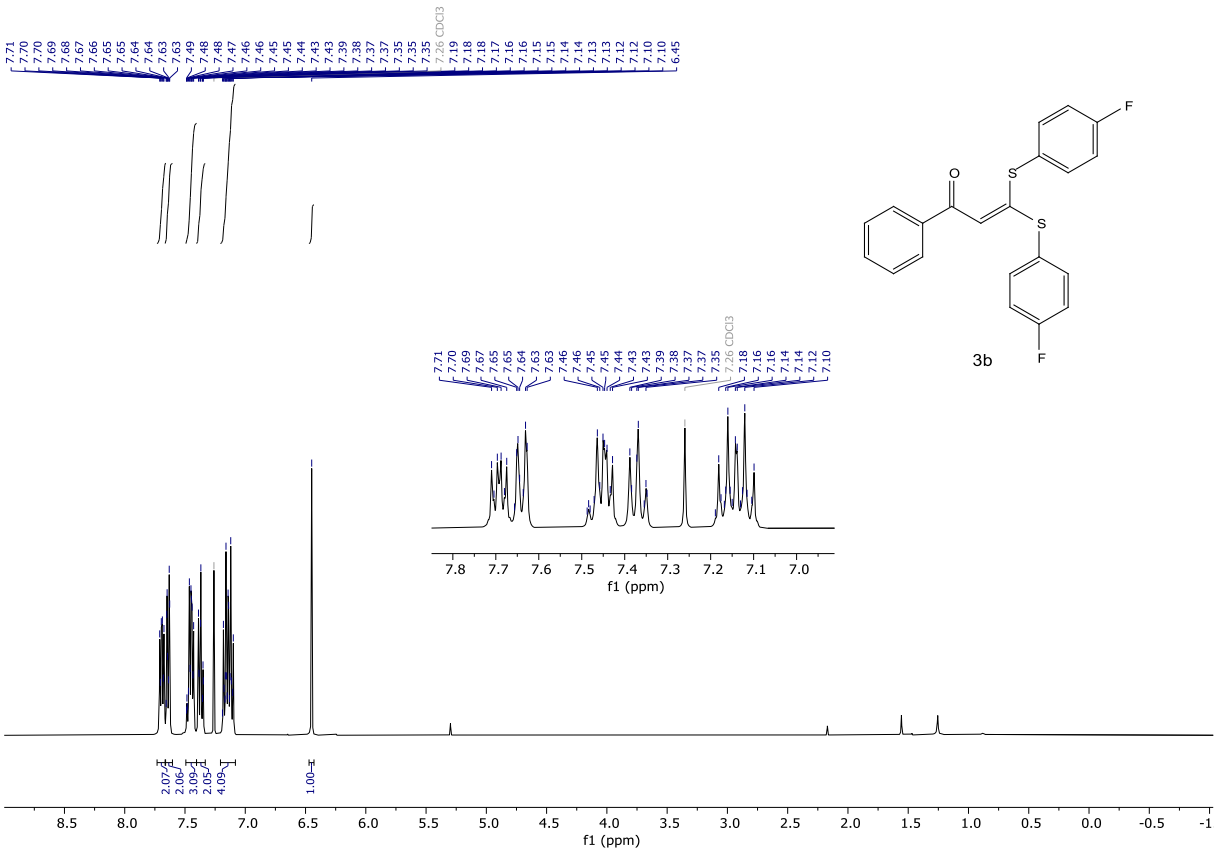
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3a**



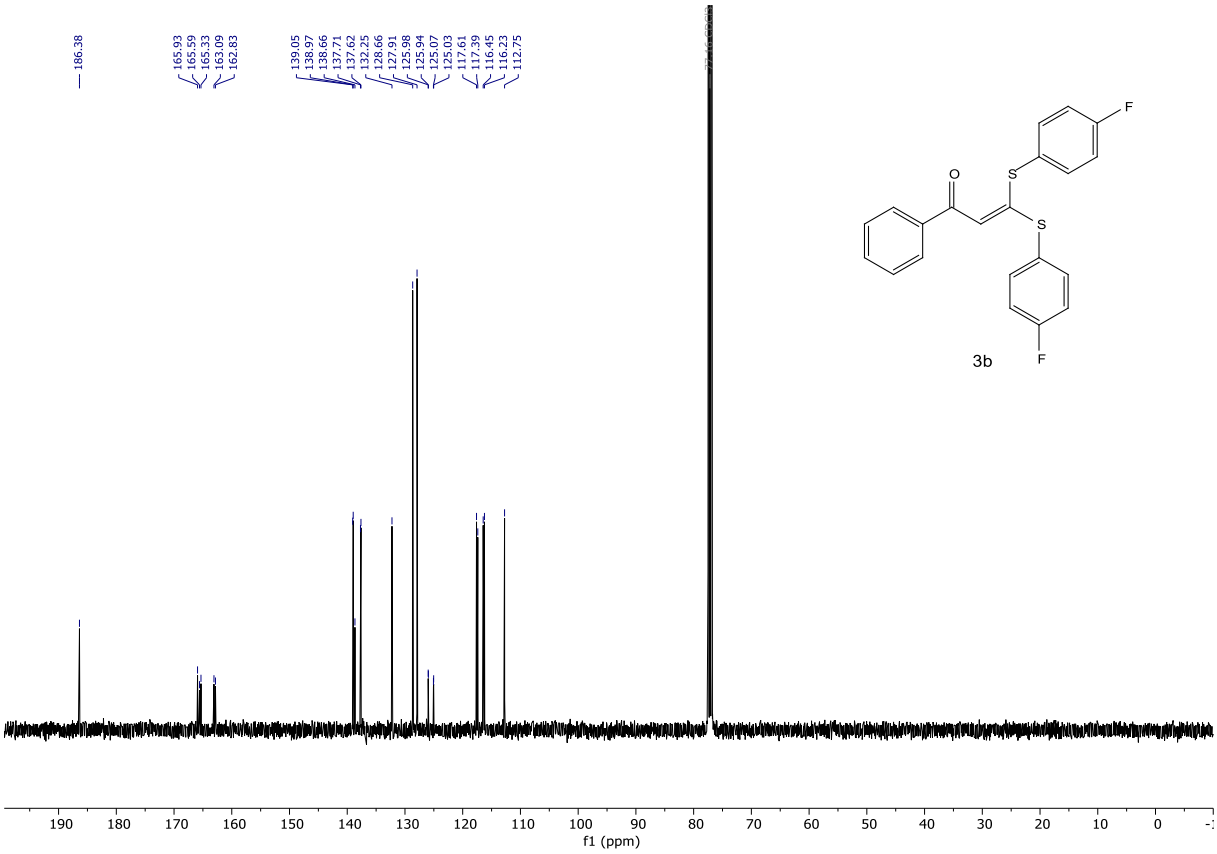

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3a**



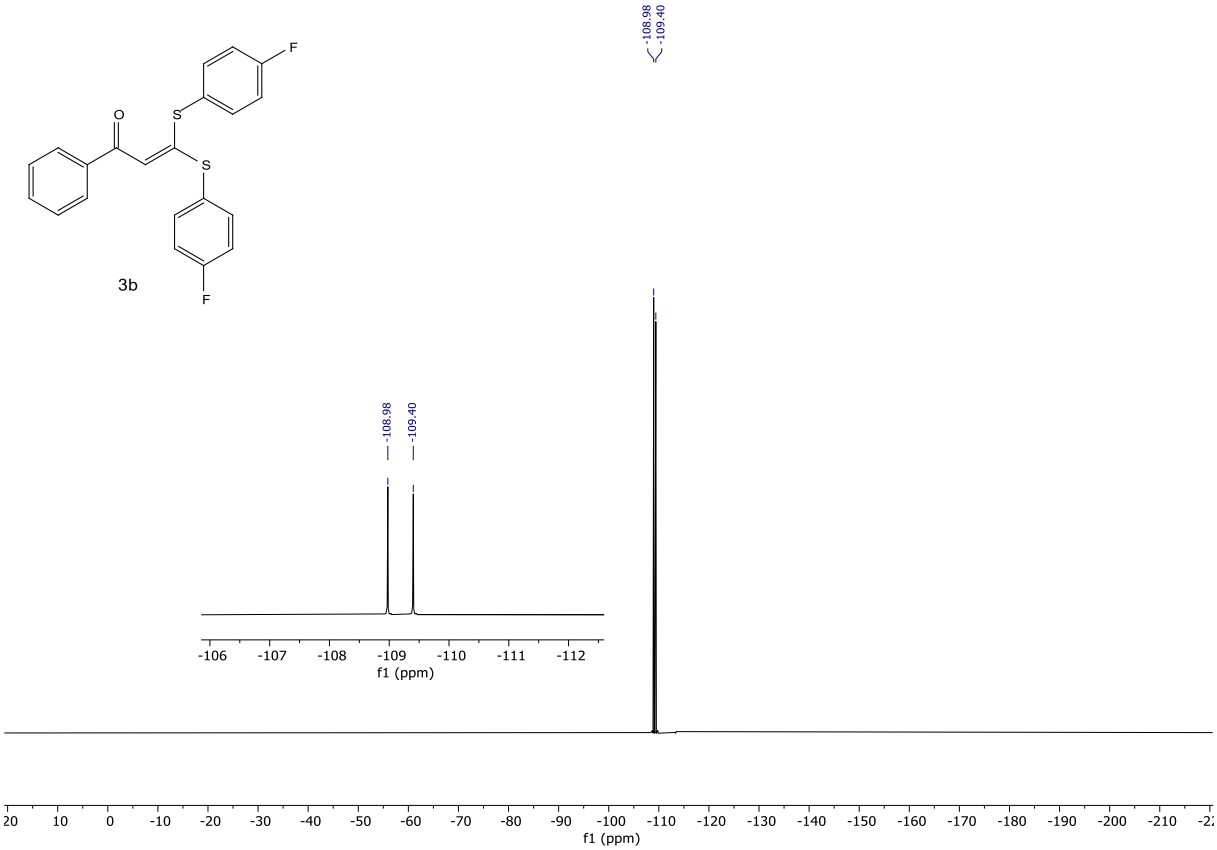
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3b**



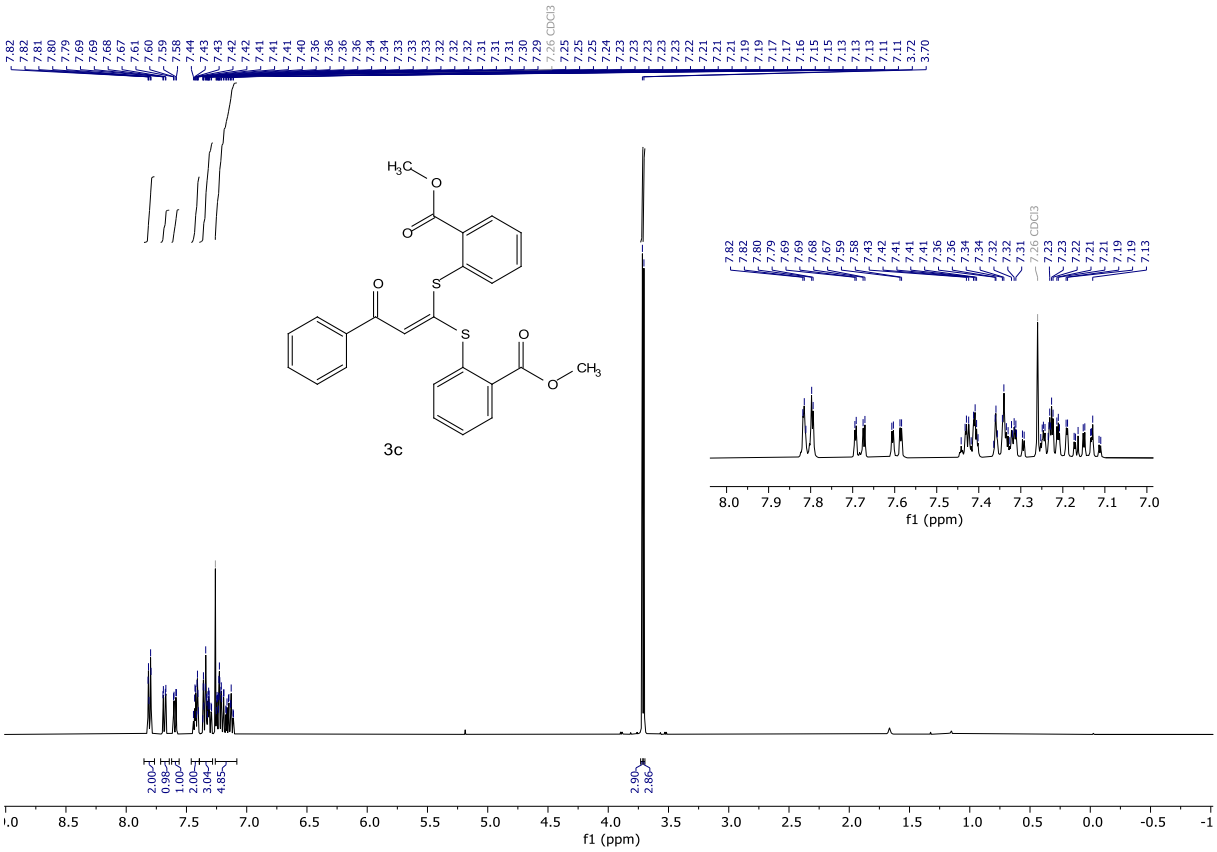

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3b**



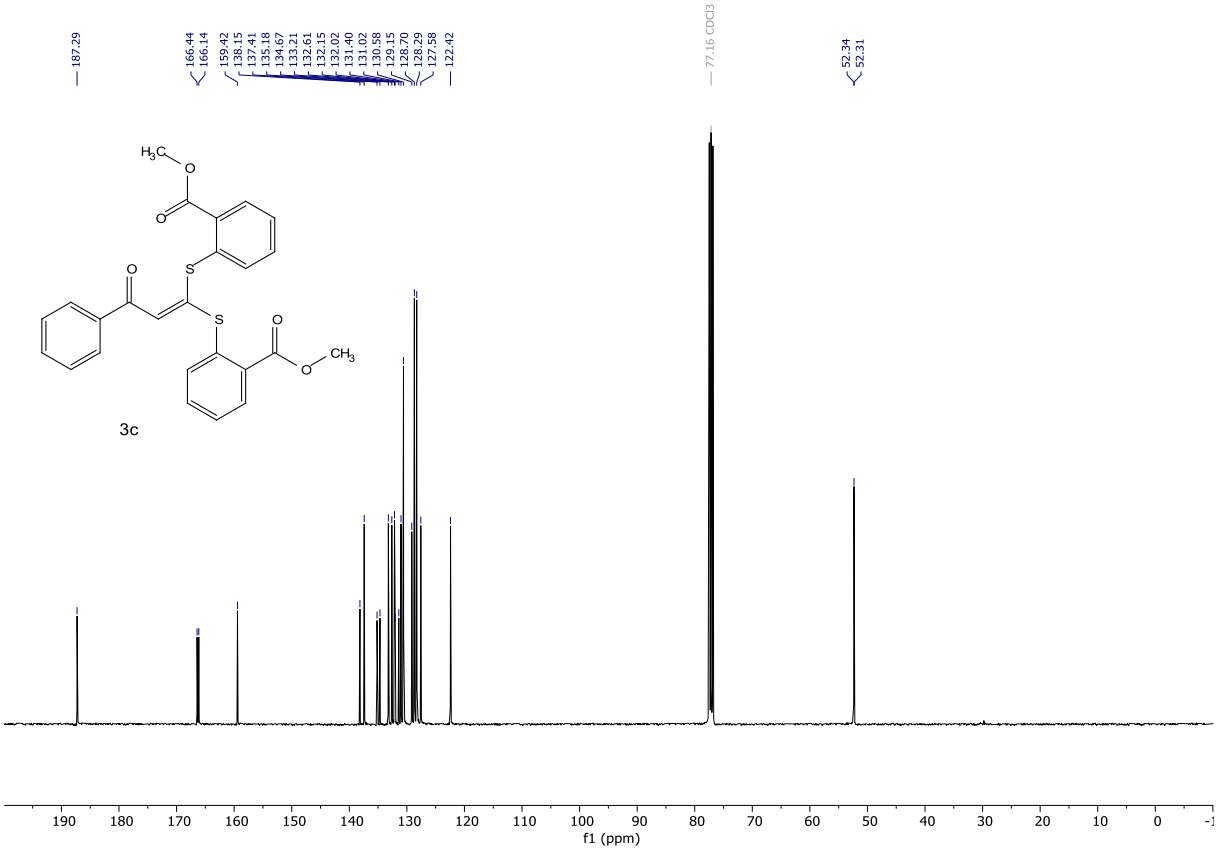
**$^{19}$F NMR** (376 MHz, $CDCl_3$) of compound **3b**



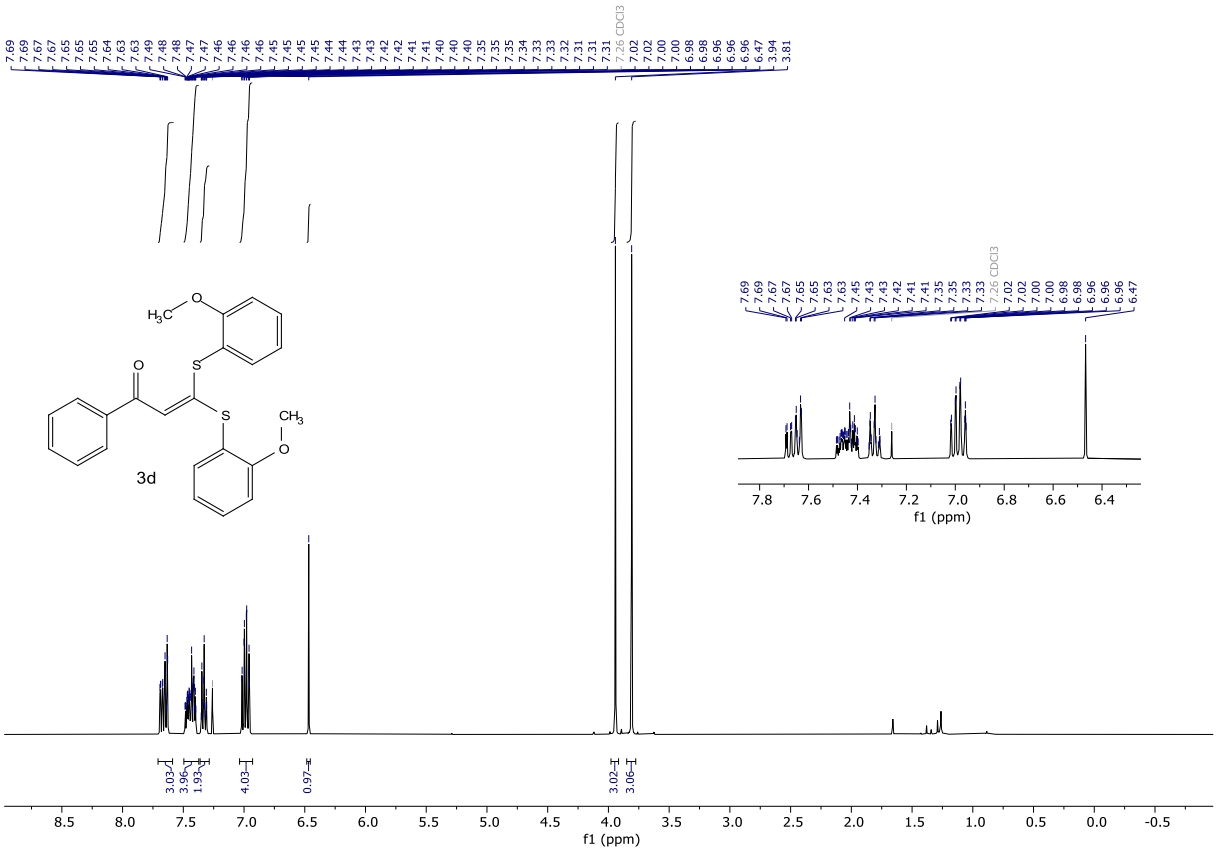

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3c**



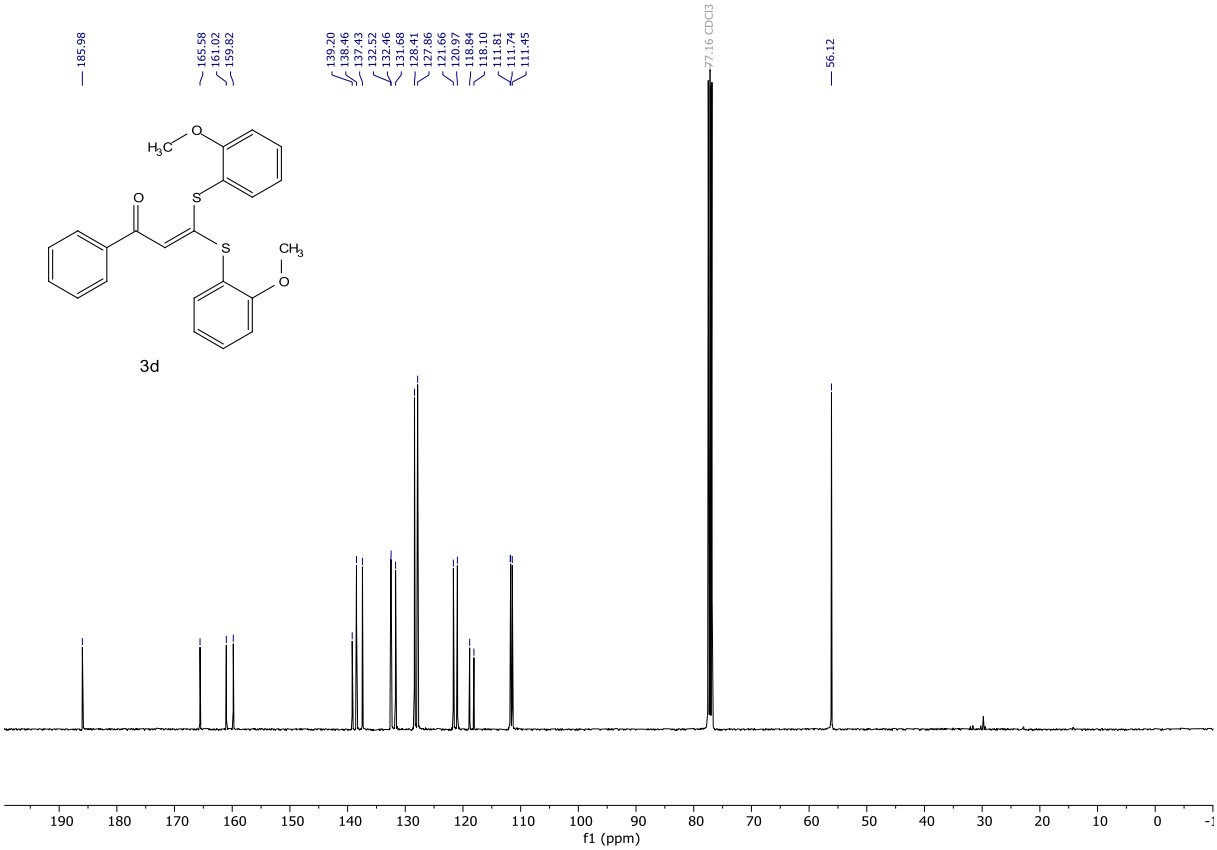
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3c**



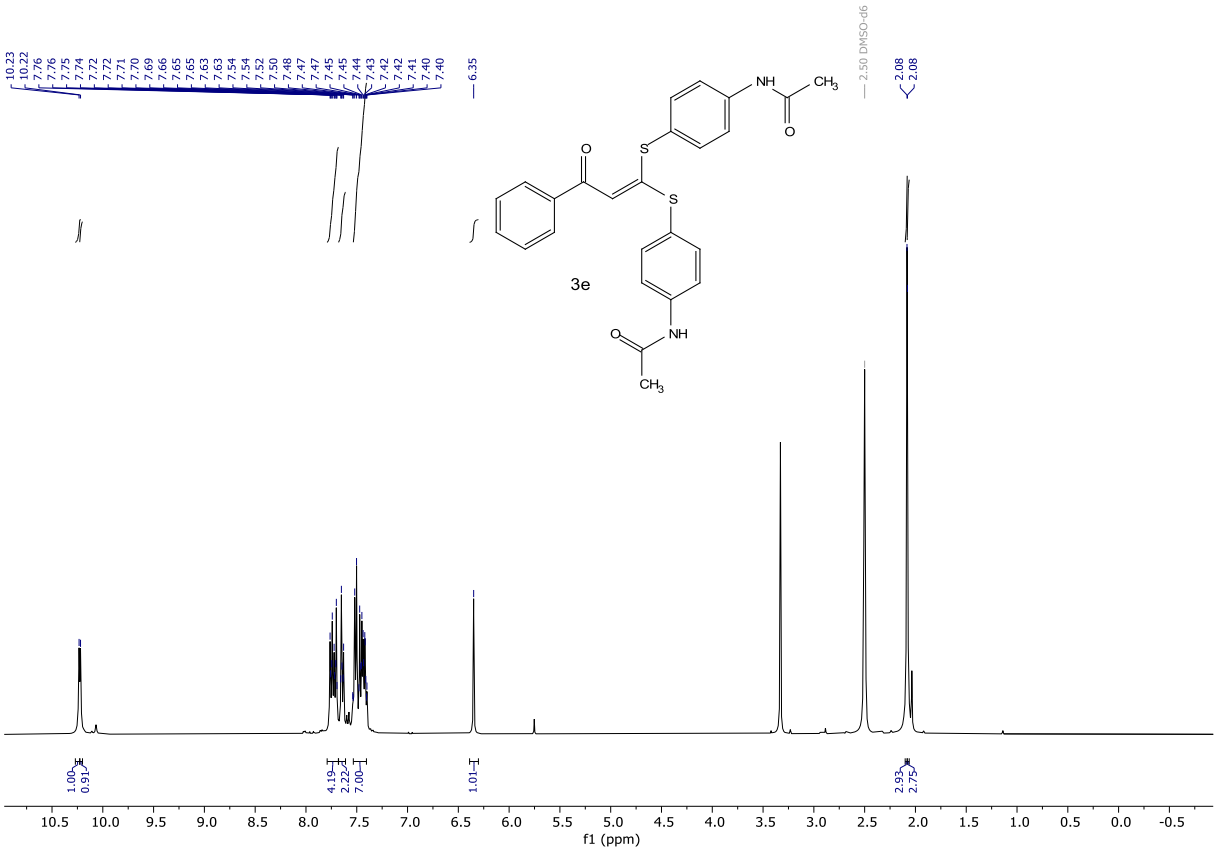

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3d**



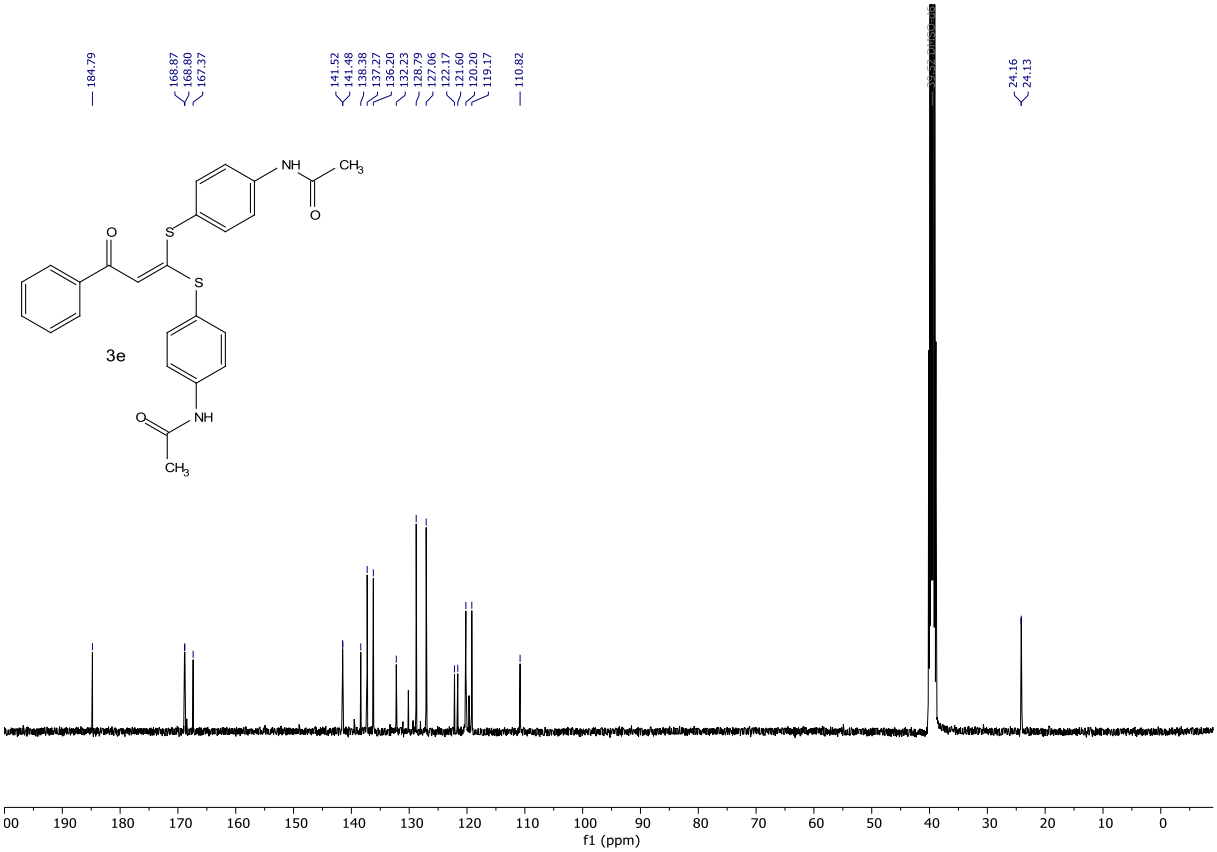
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3d**



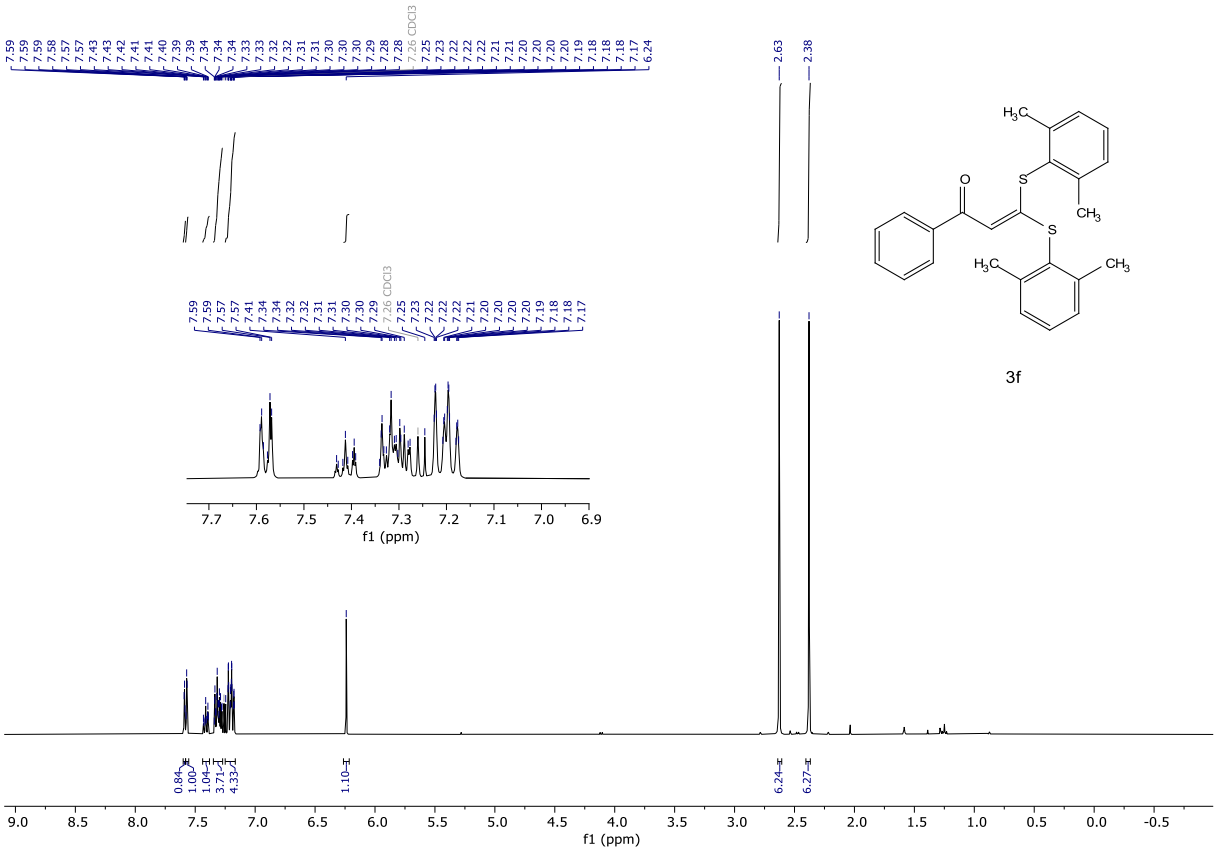

**$^{1}$H NMR** (400 MHz, DMSO-$d_6$) of compound **3e**



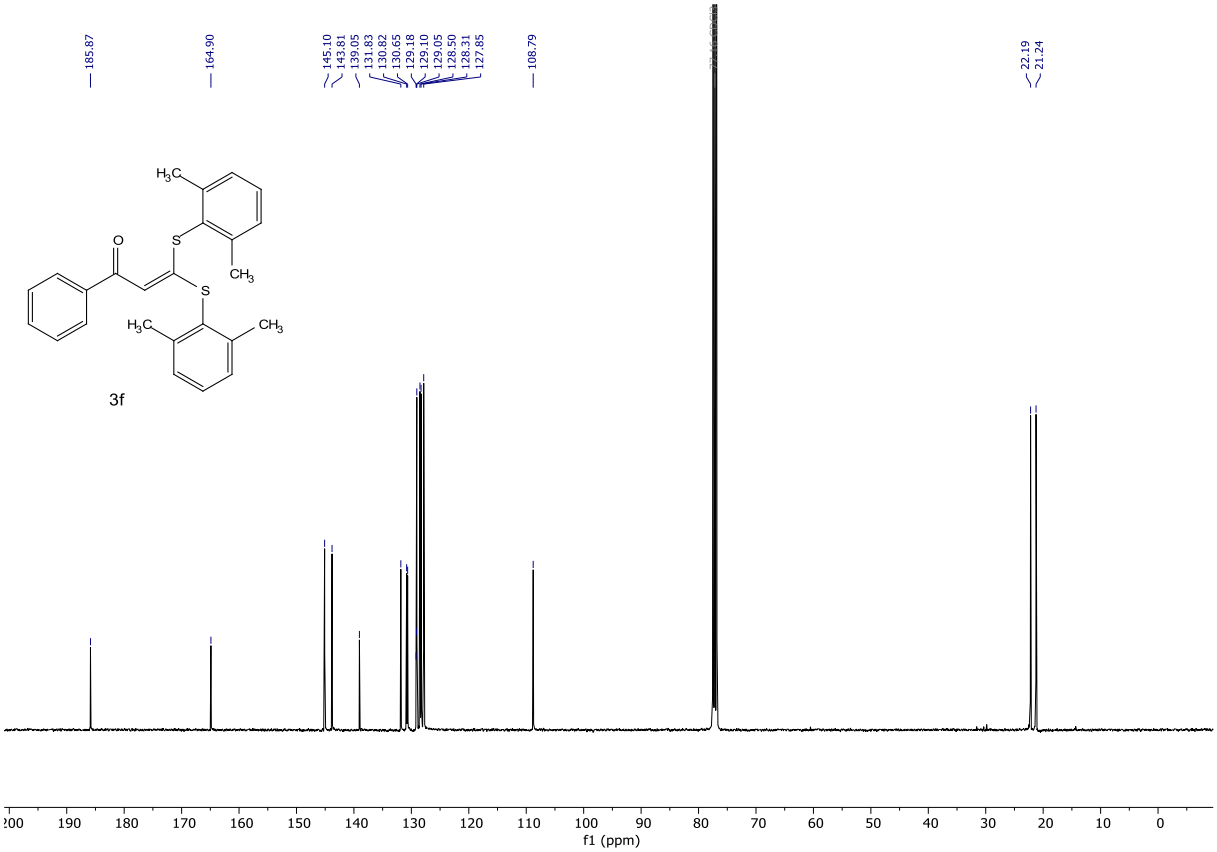
**$^{13}$C NMR** (400 MHz, DMSO-$d_6$) of compound **3e**



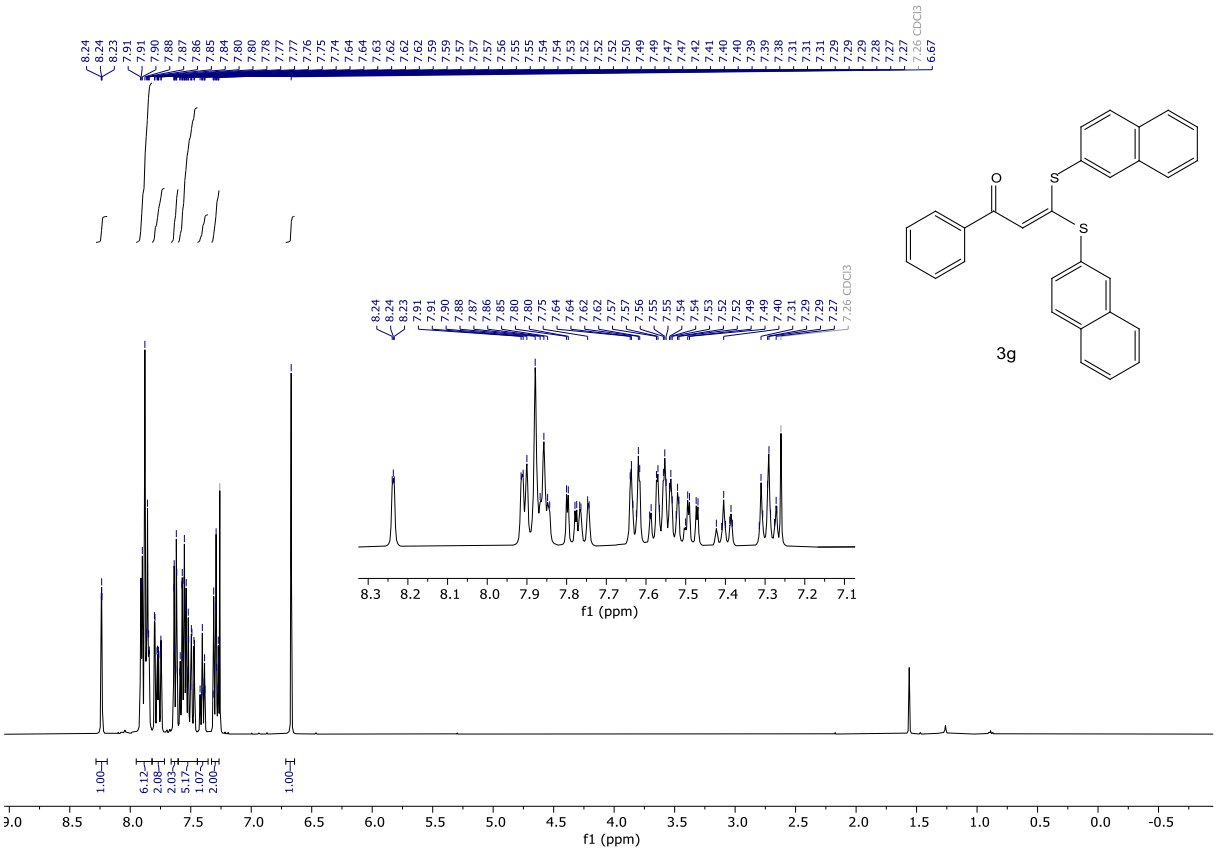

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3f**



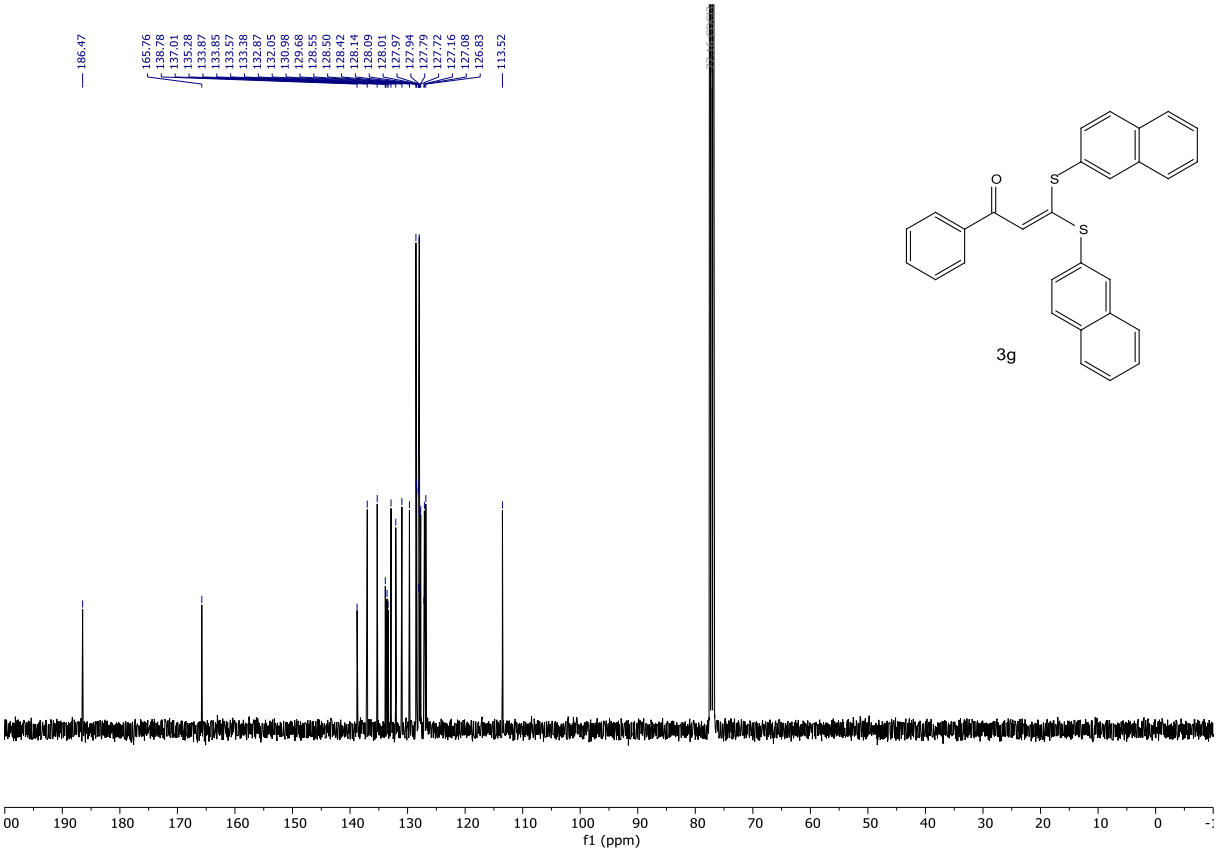
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3f**



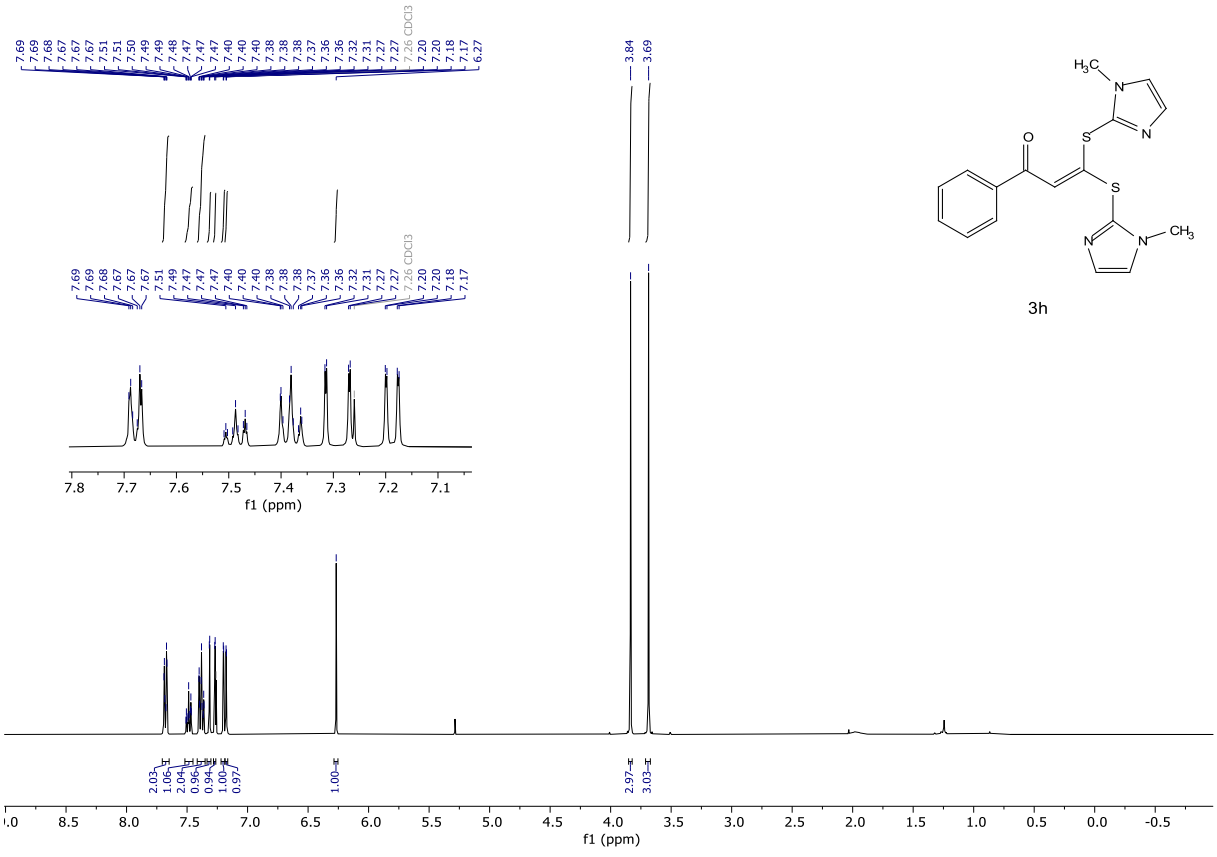

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3g**



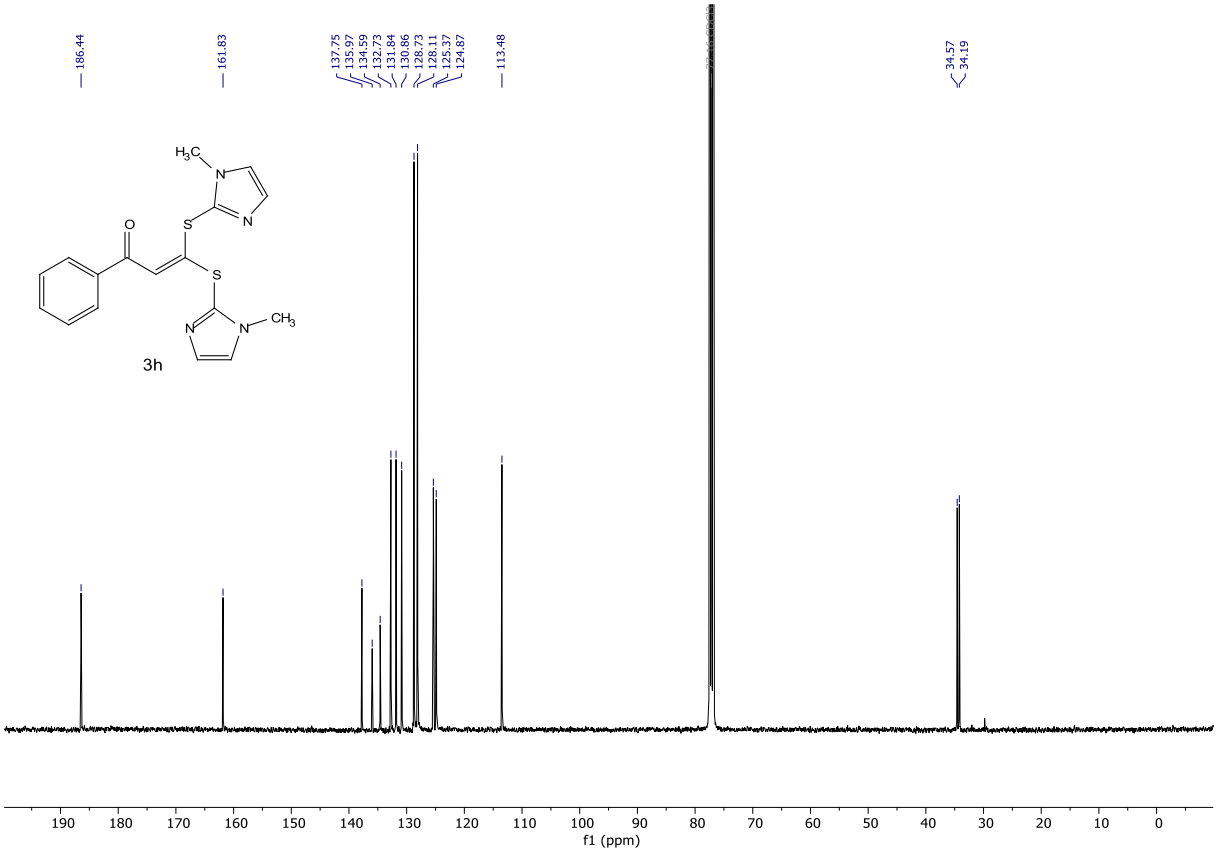
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3g**



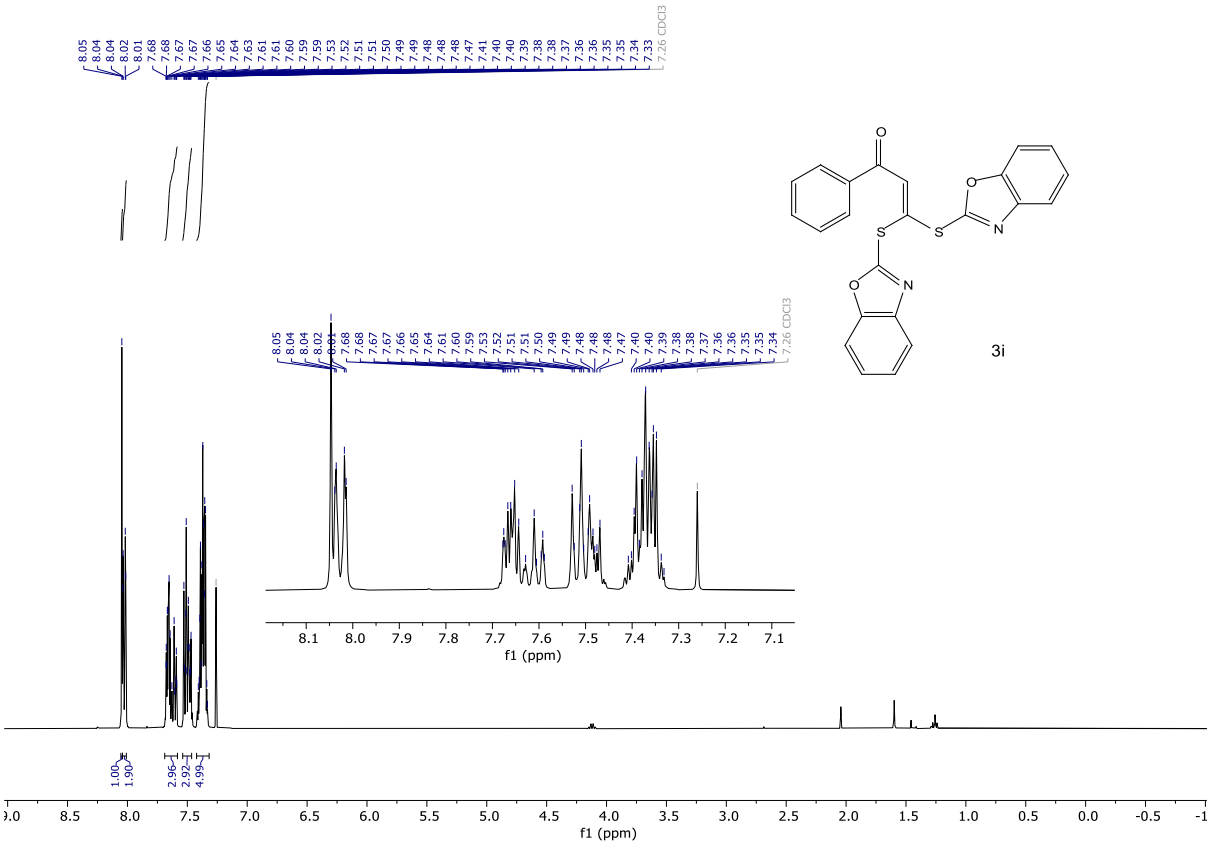

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3h**



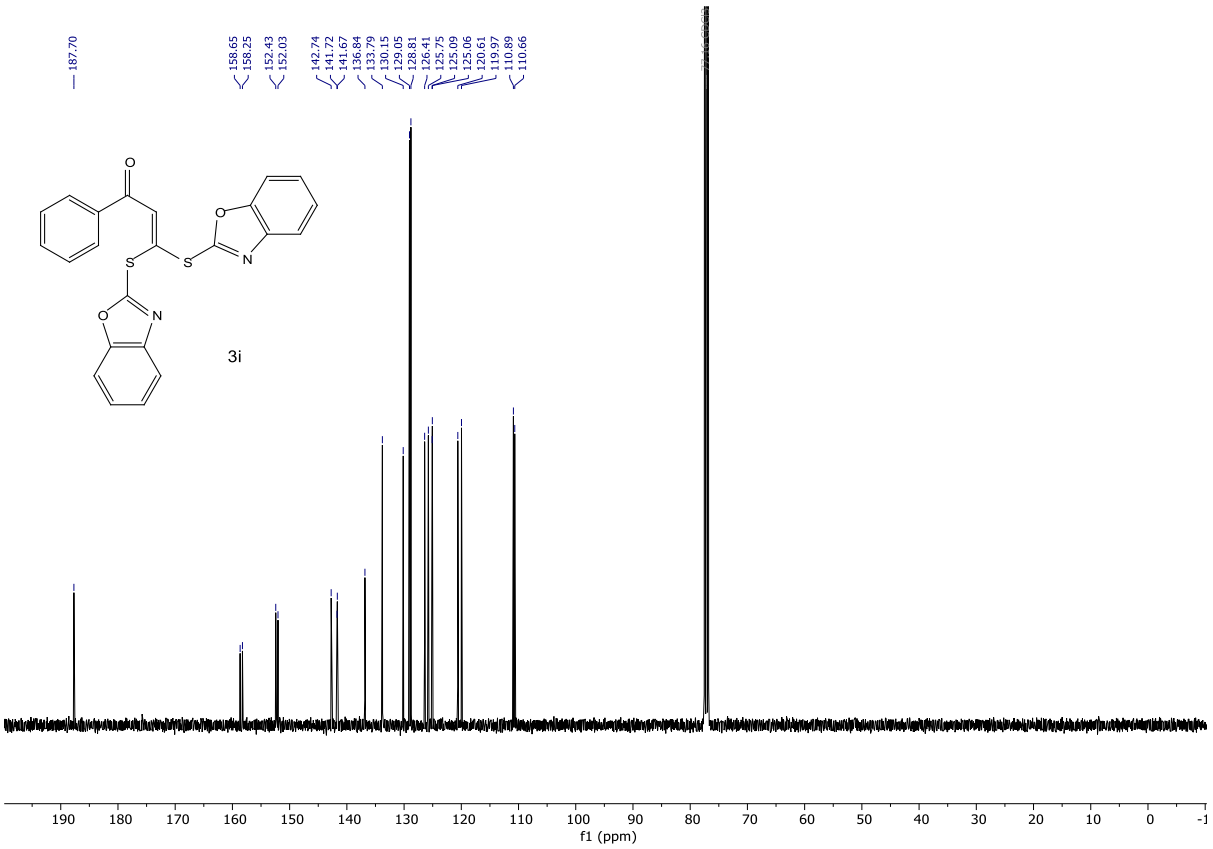
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3h**



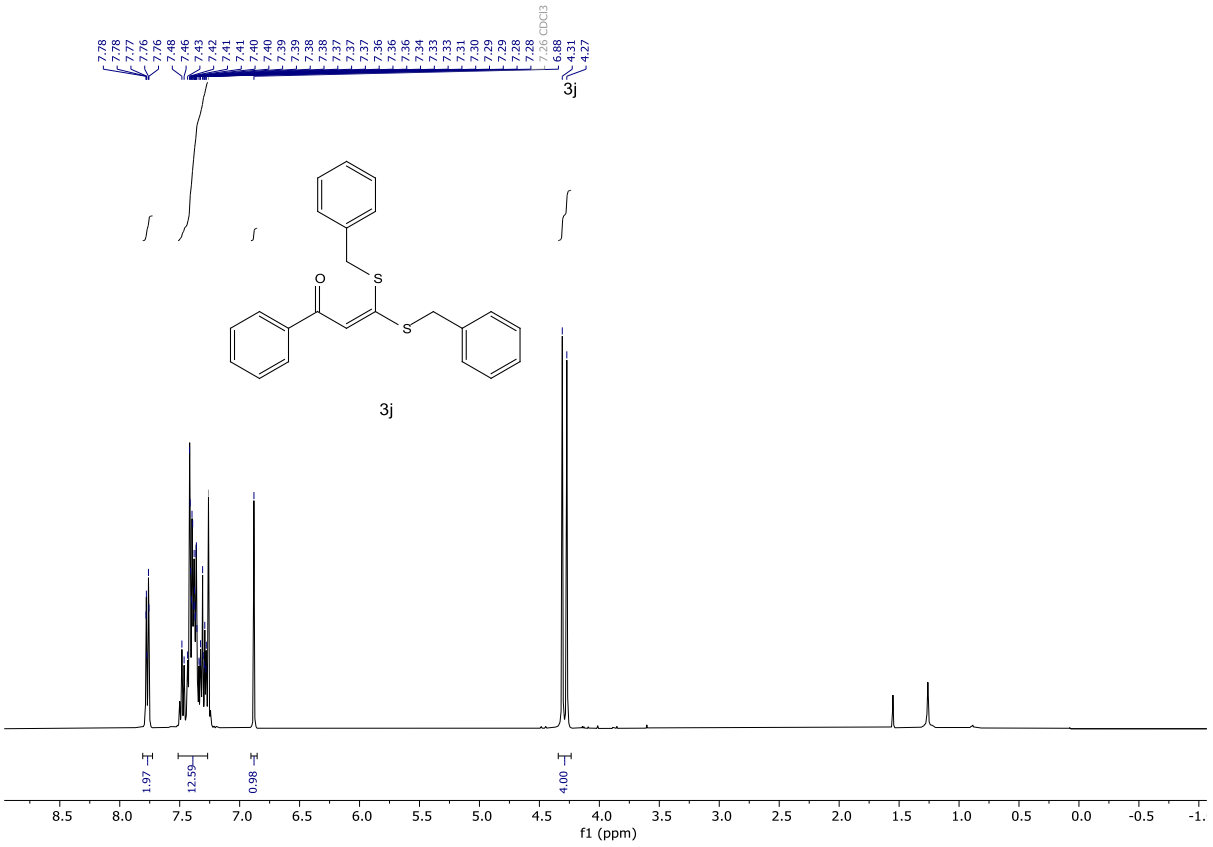

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3i**



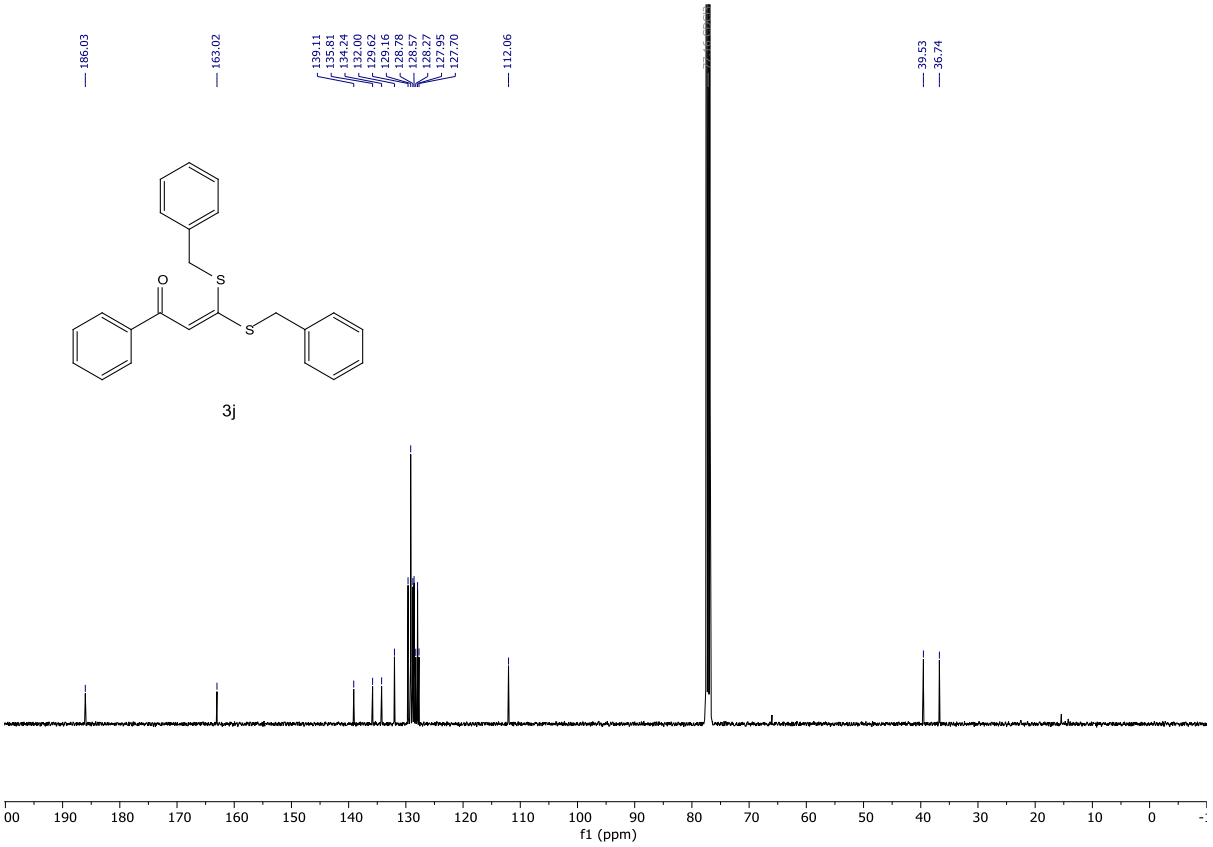
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3i**



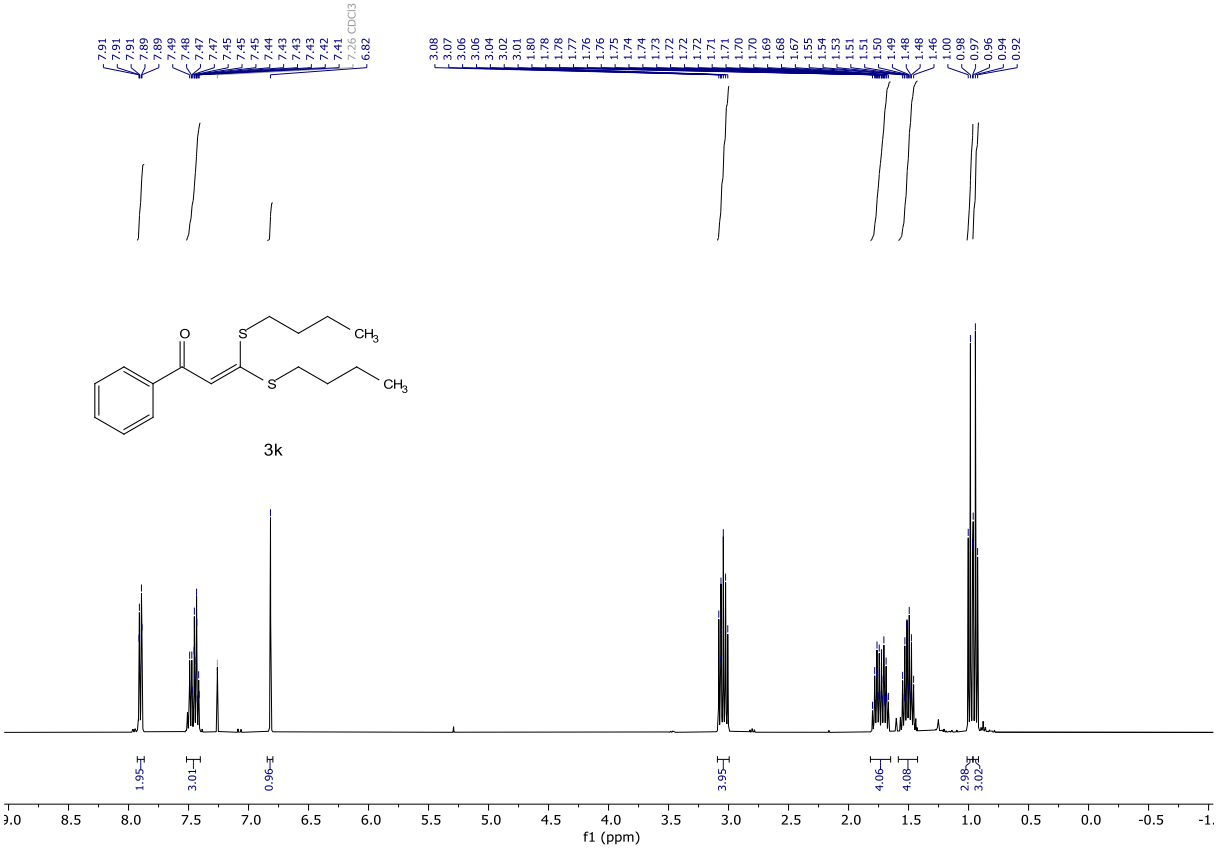

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3j**



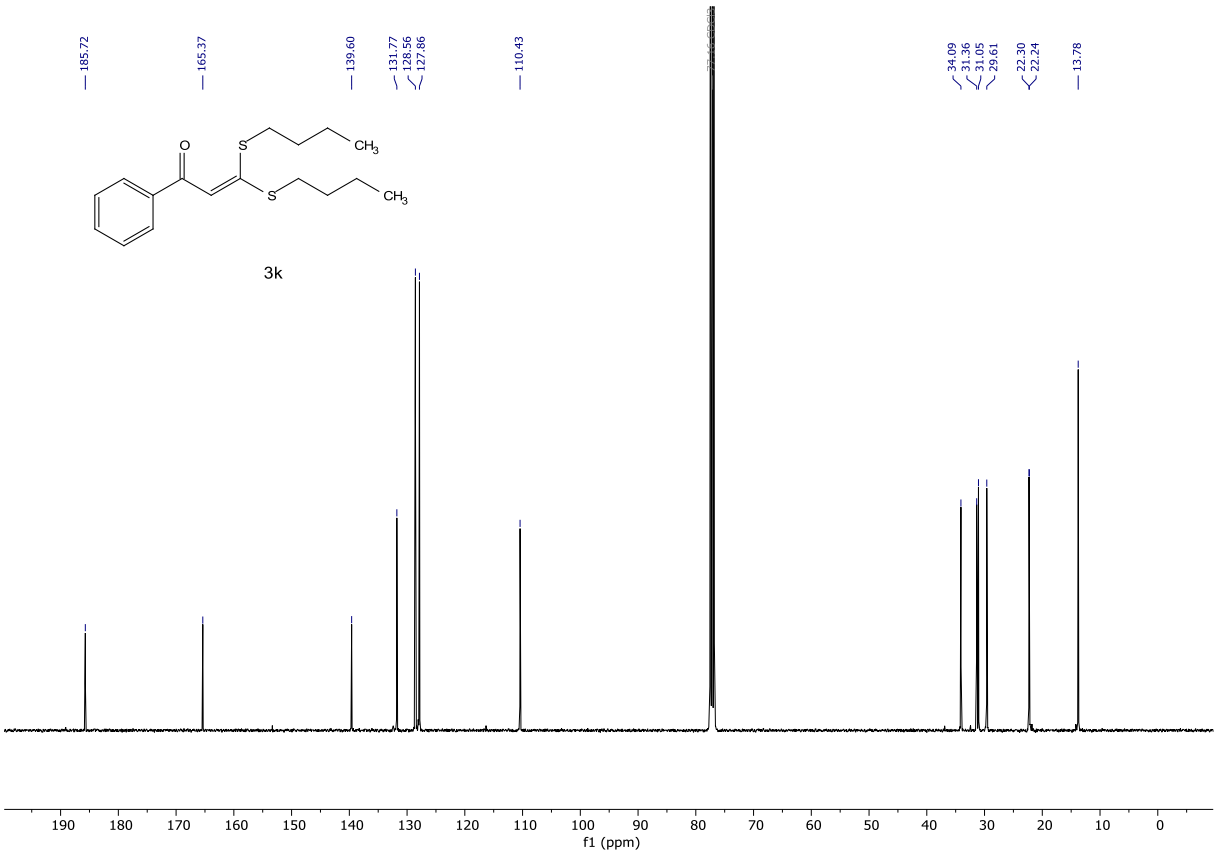
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3j**



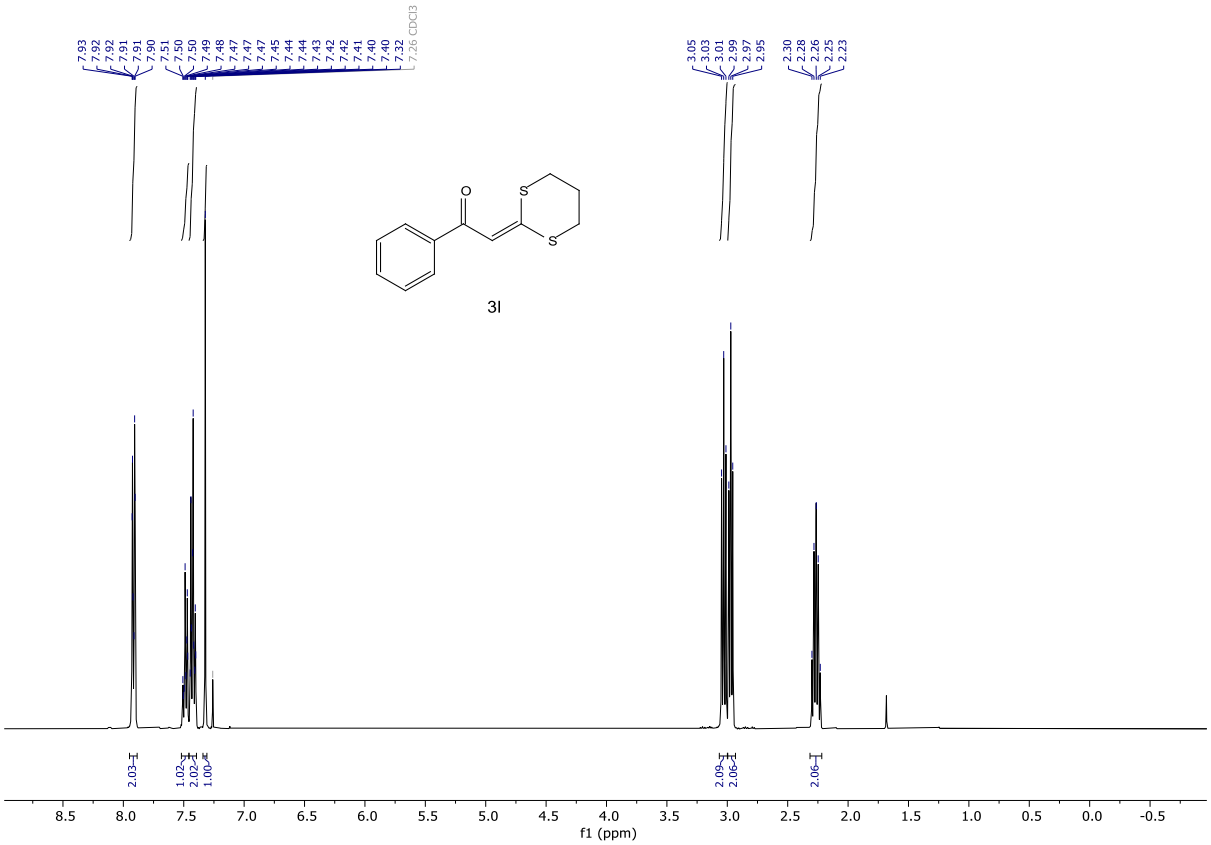

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3k**



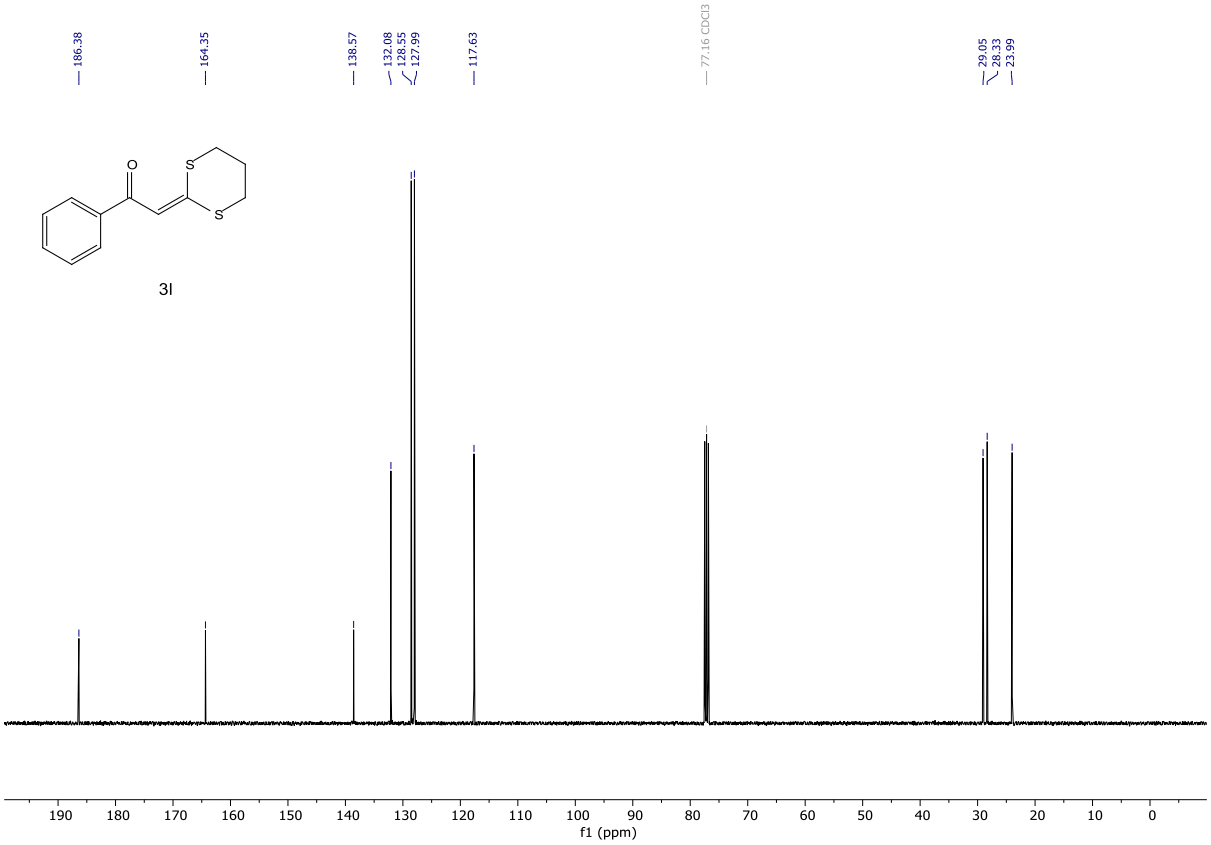
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3k**



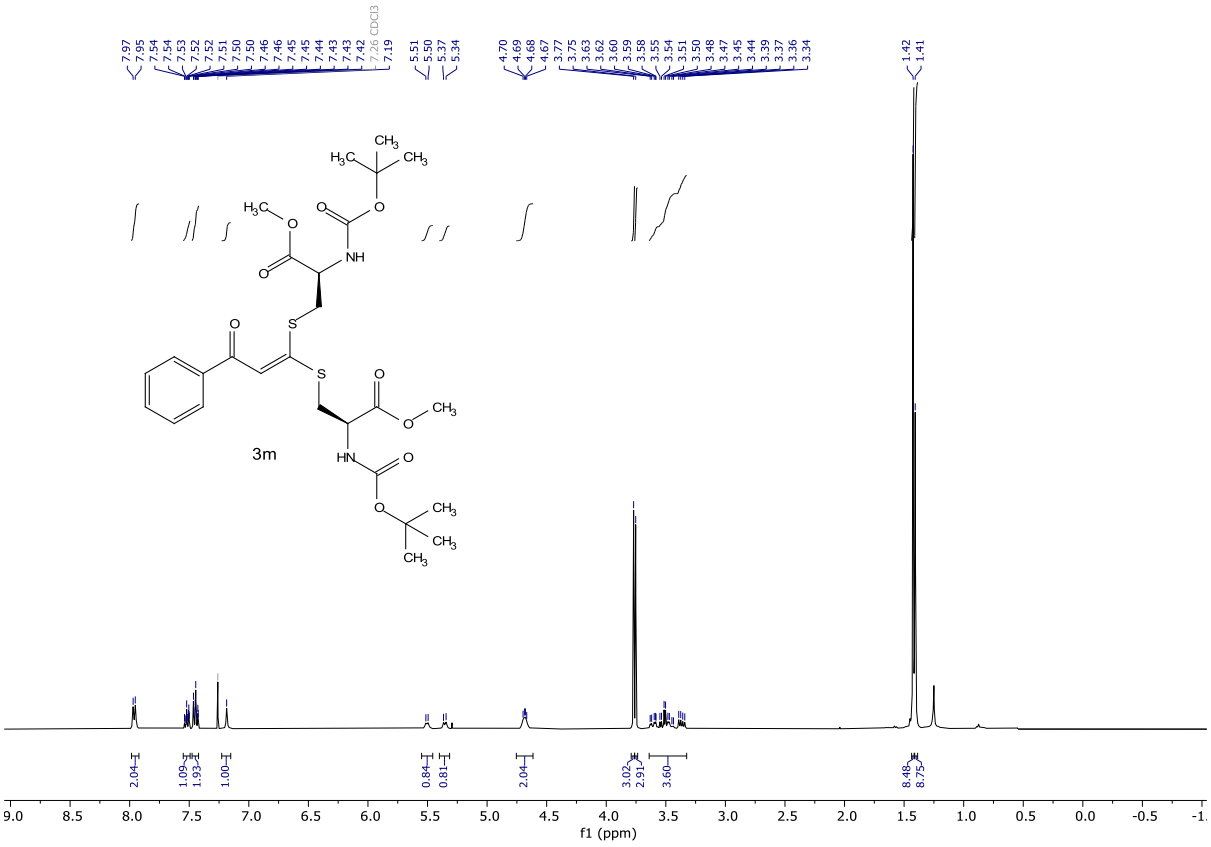

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3l**



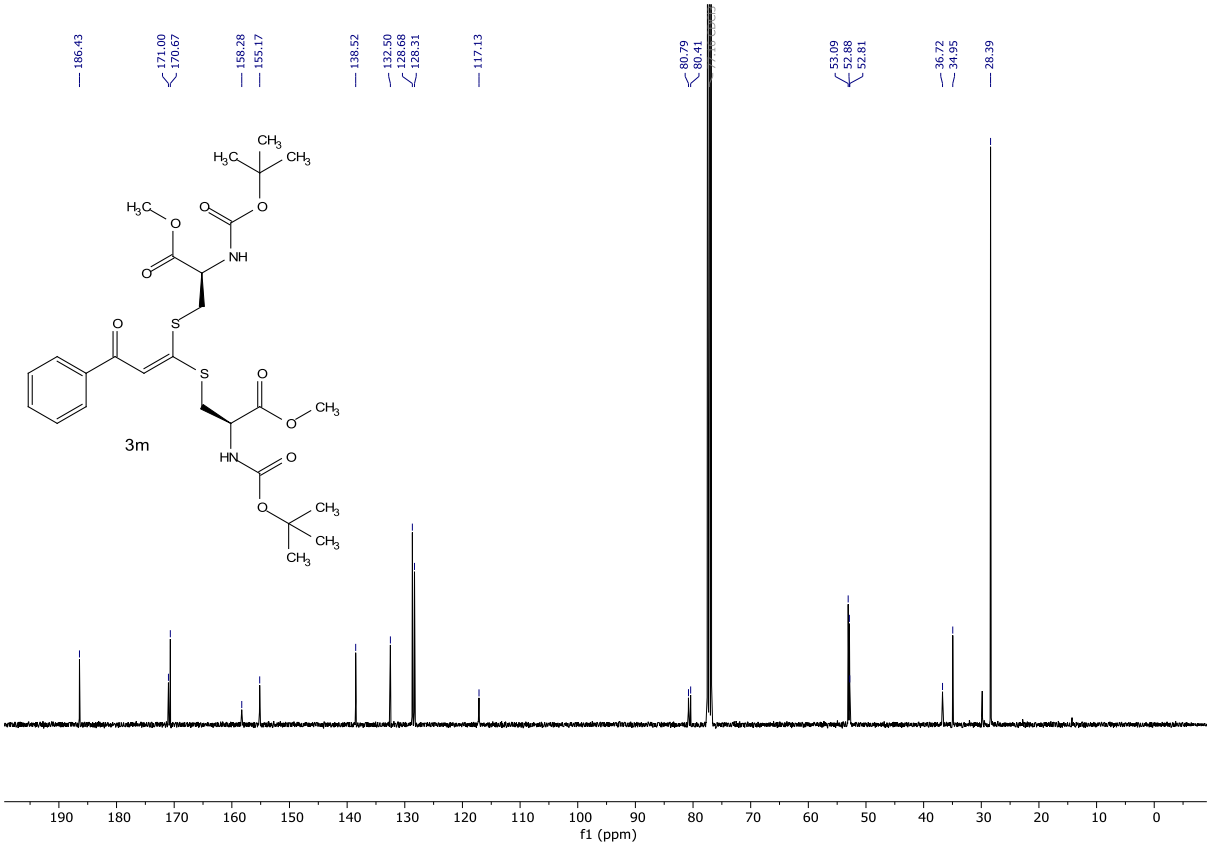
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3l**



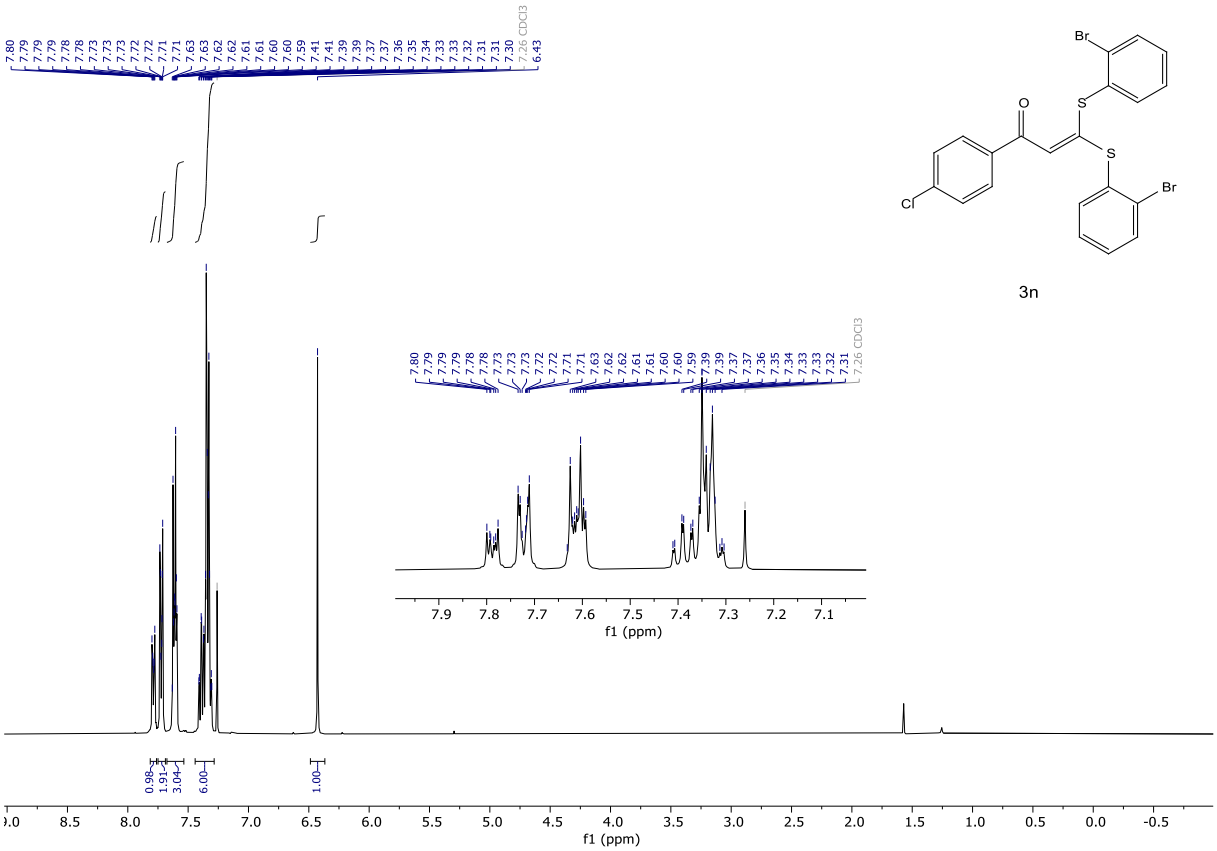

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3m**



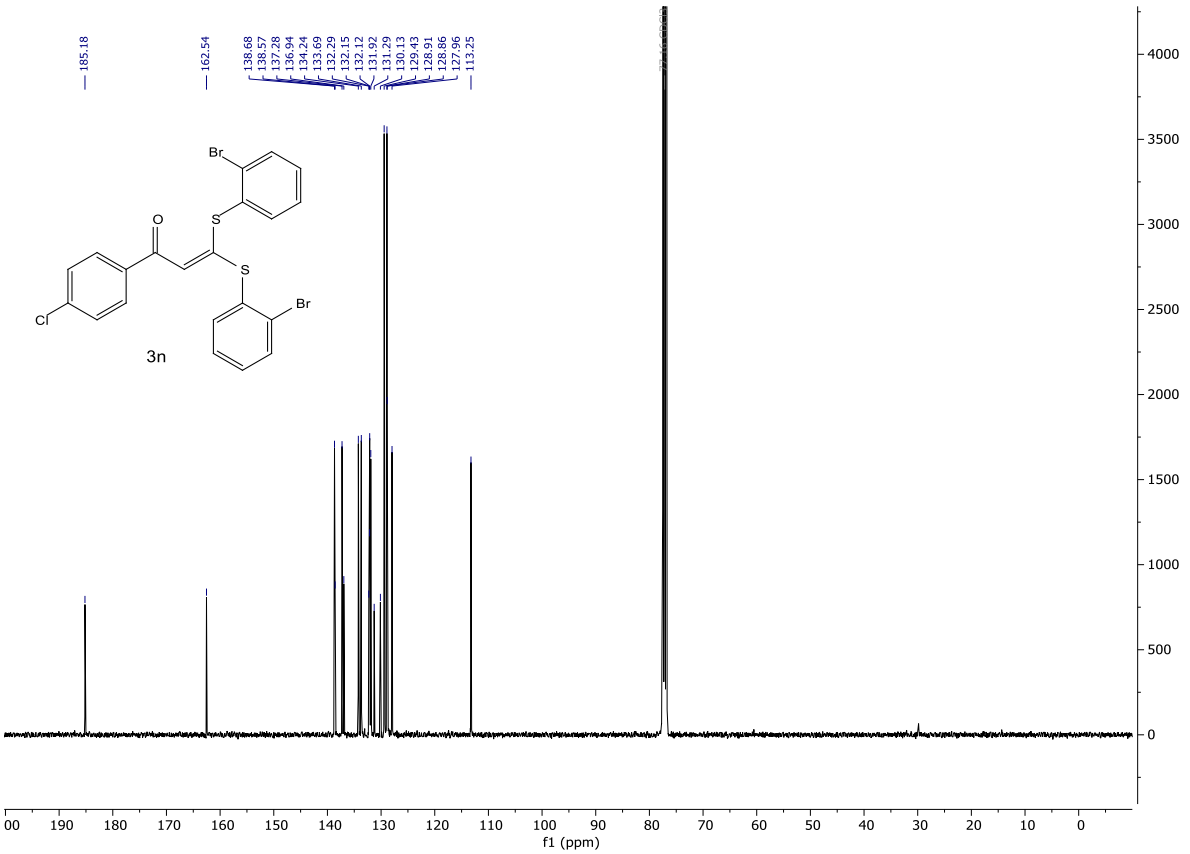
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3m**



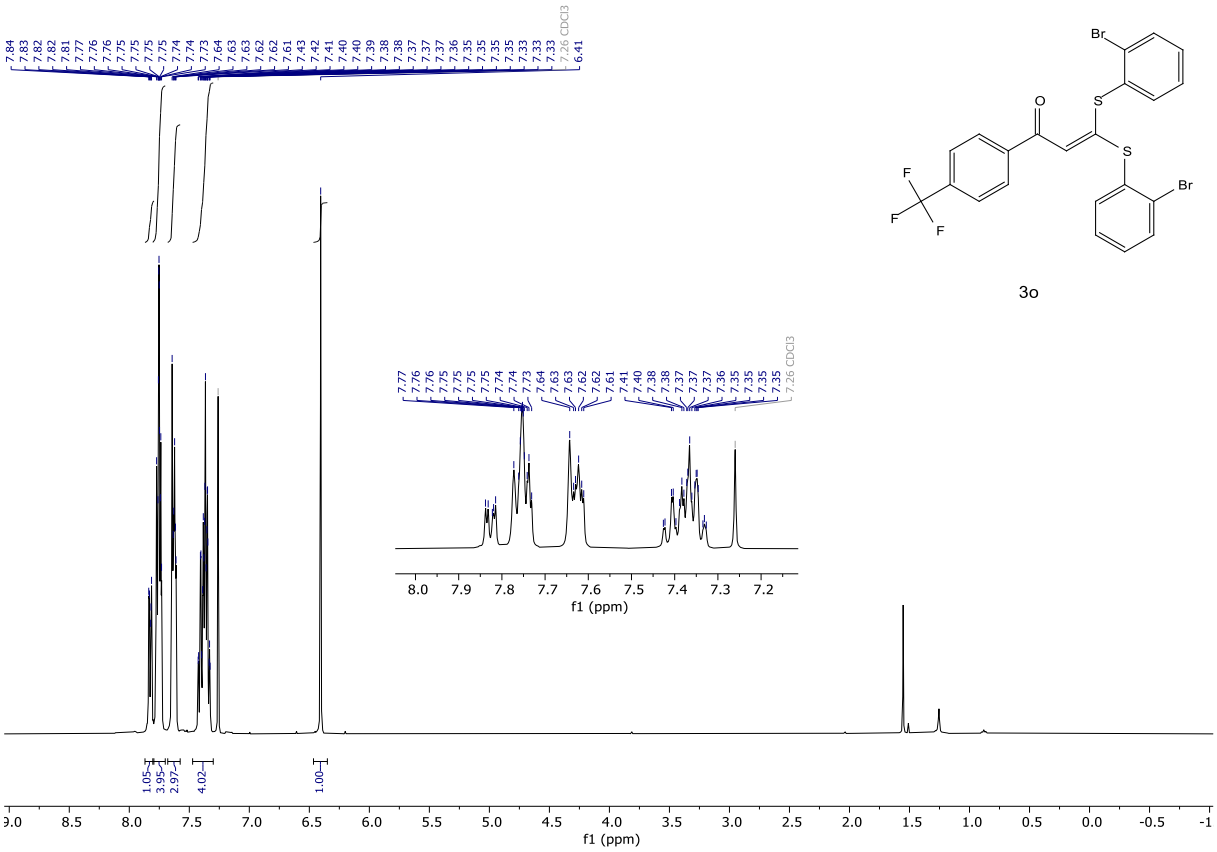

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3n**



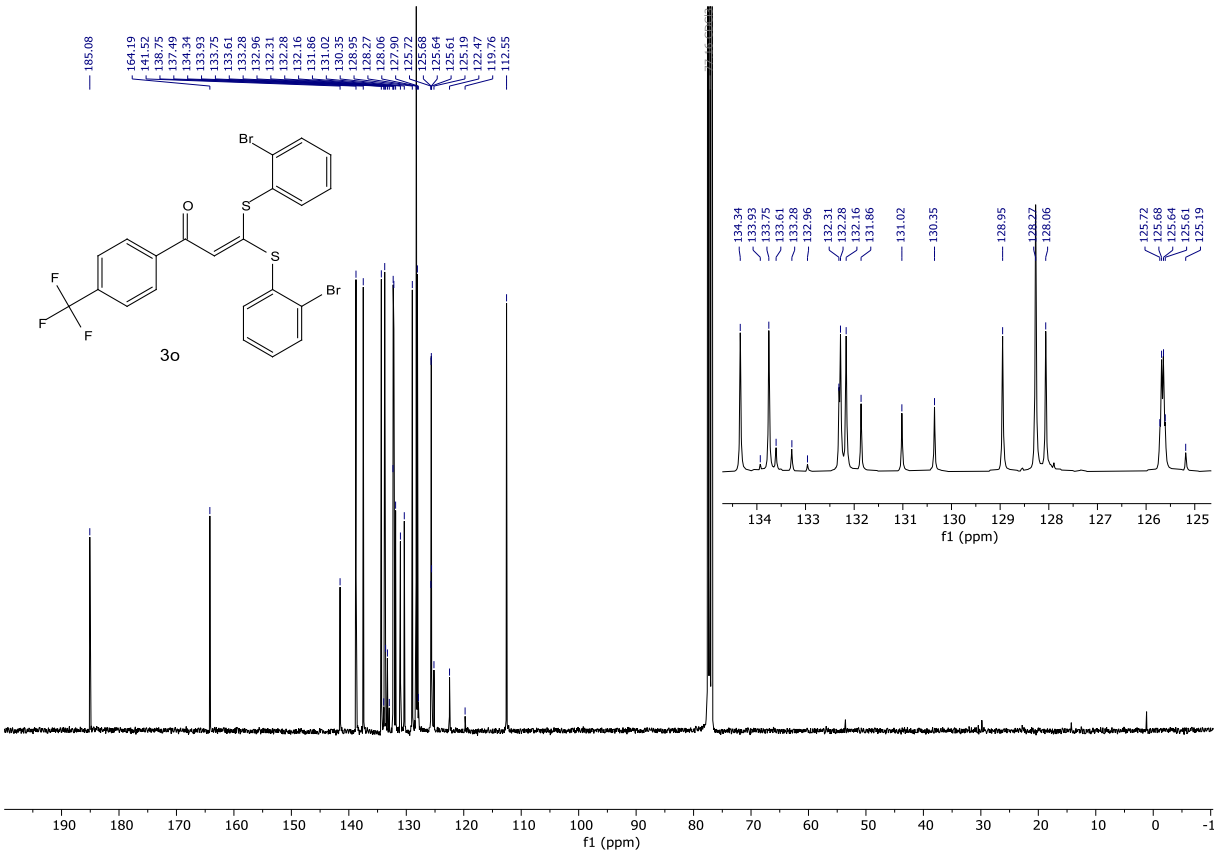
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3n**



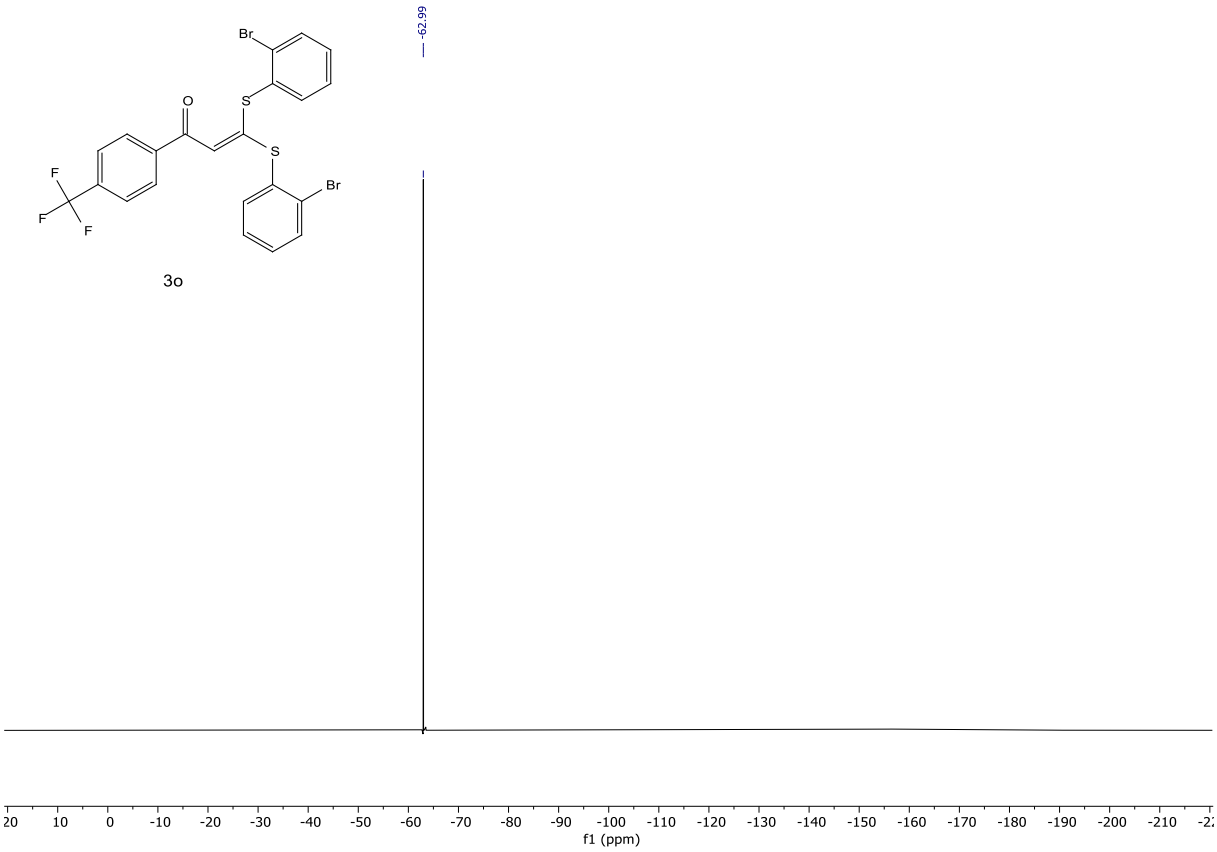

**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3o**



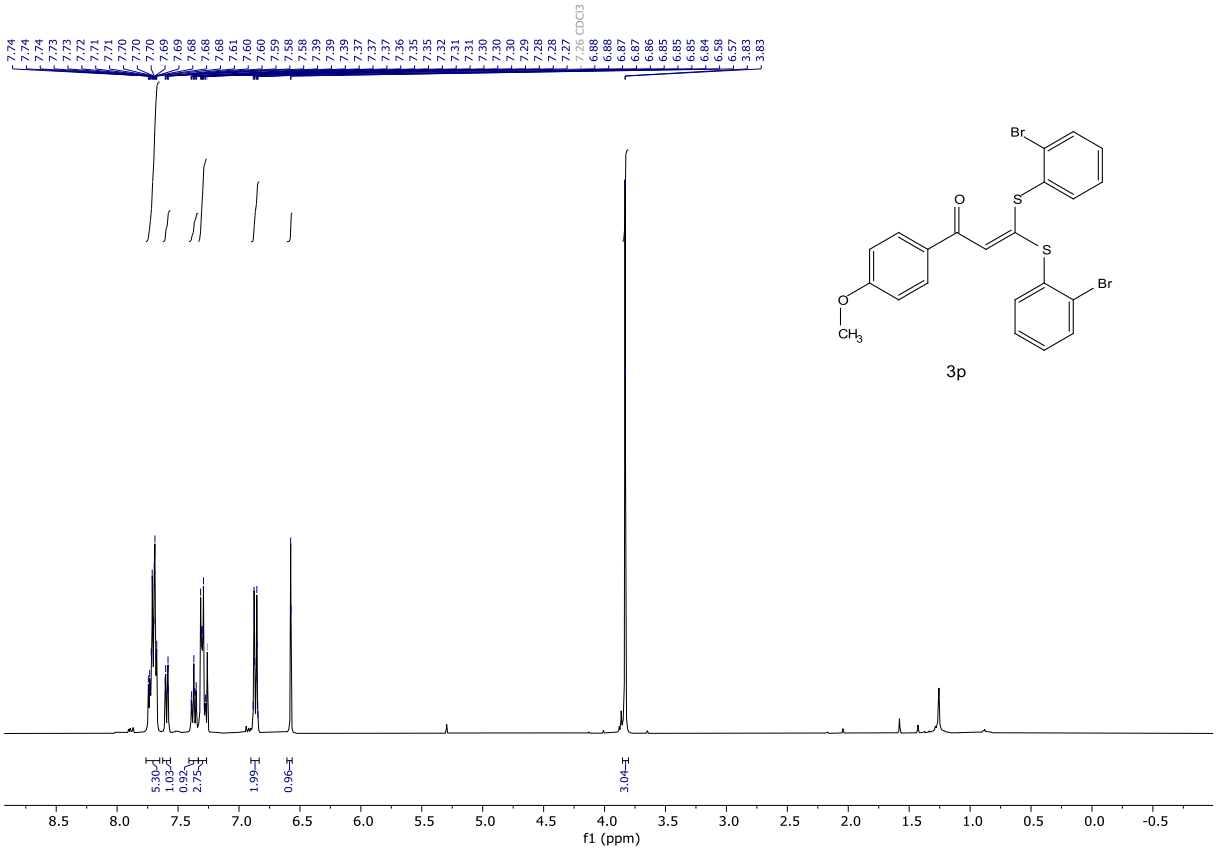
**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3o**



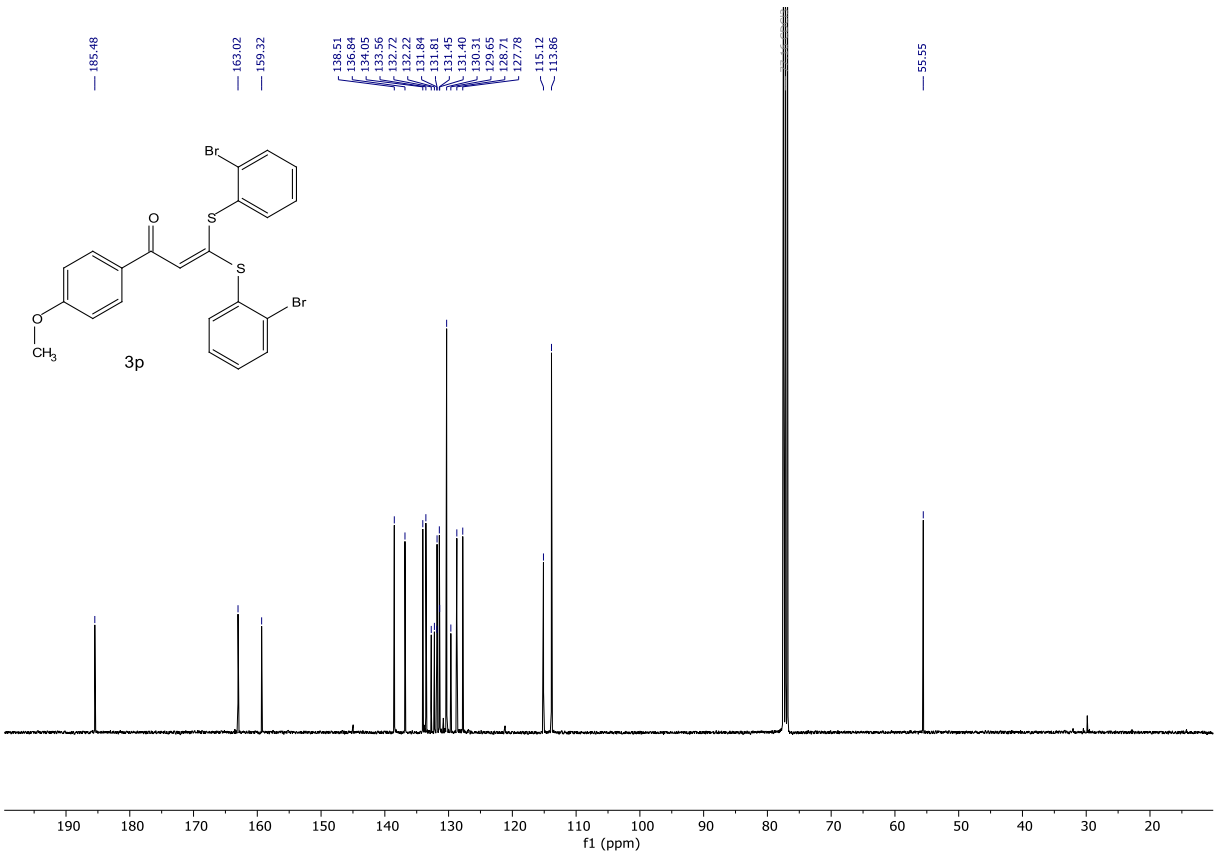

**$^{19}$F NMR** (376 MHz, $CDCl_3$) of compound **3o**



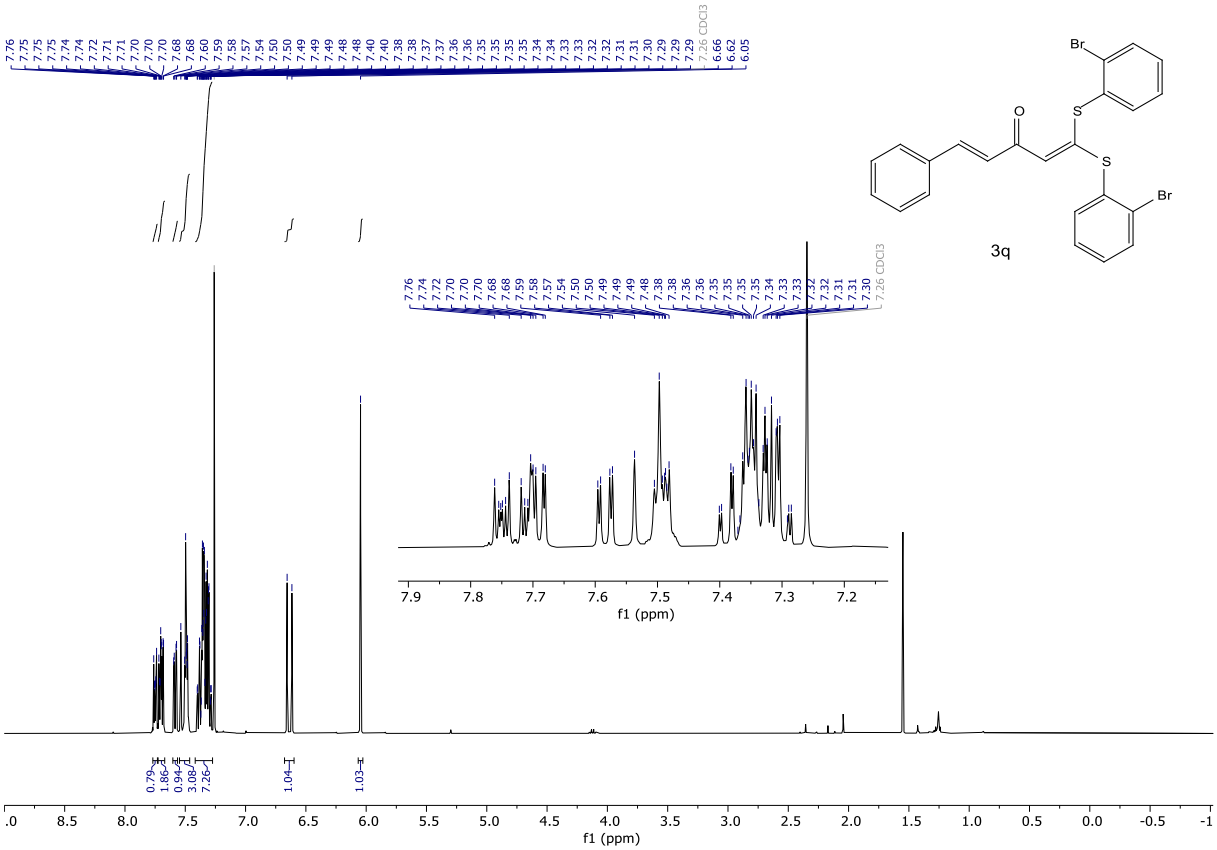
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3p**



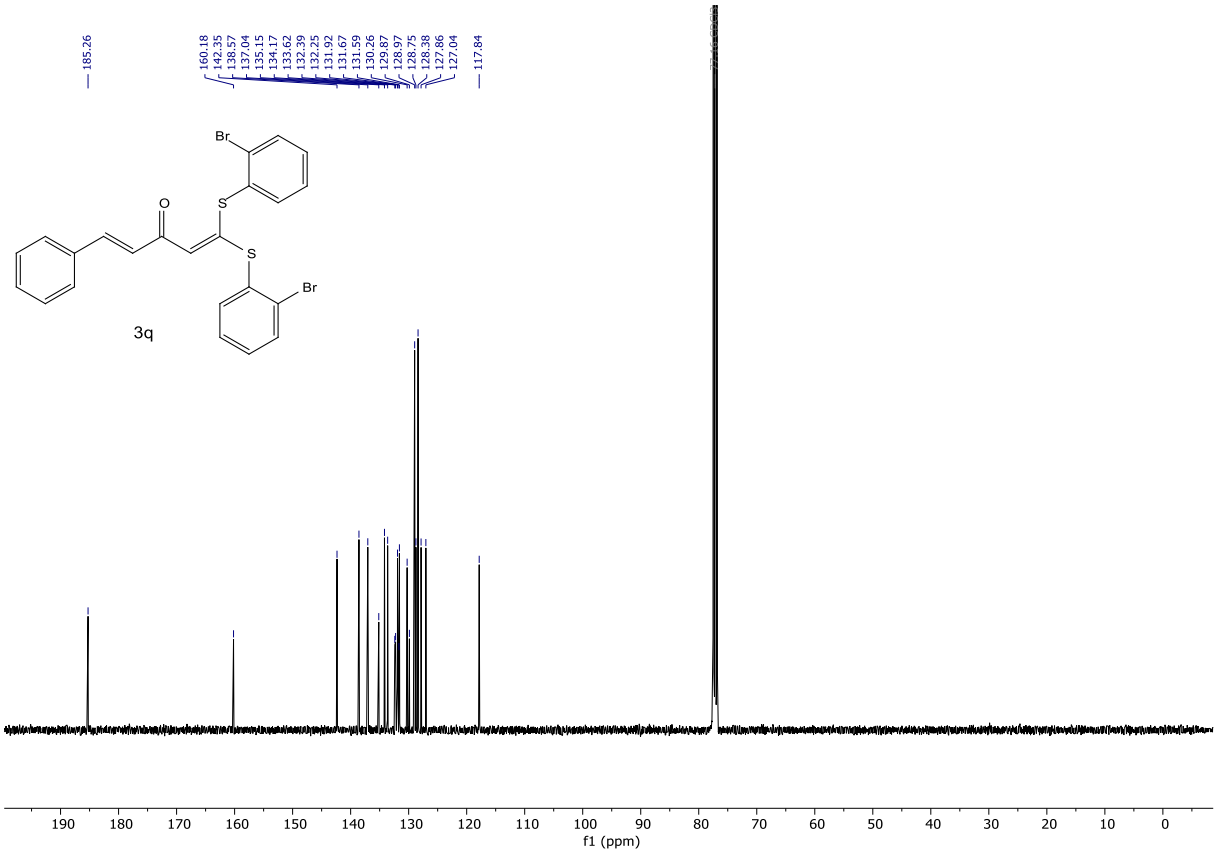

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3p**



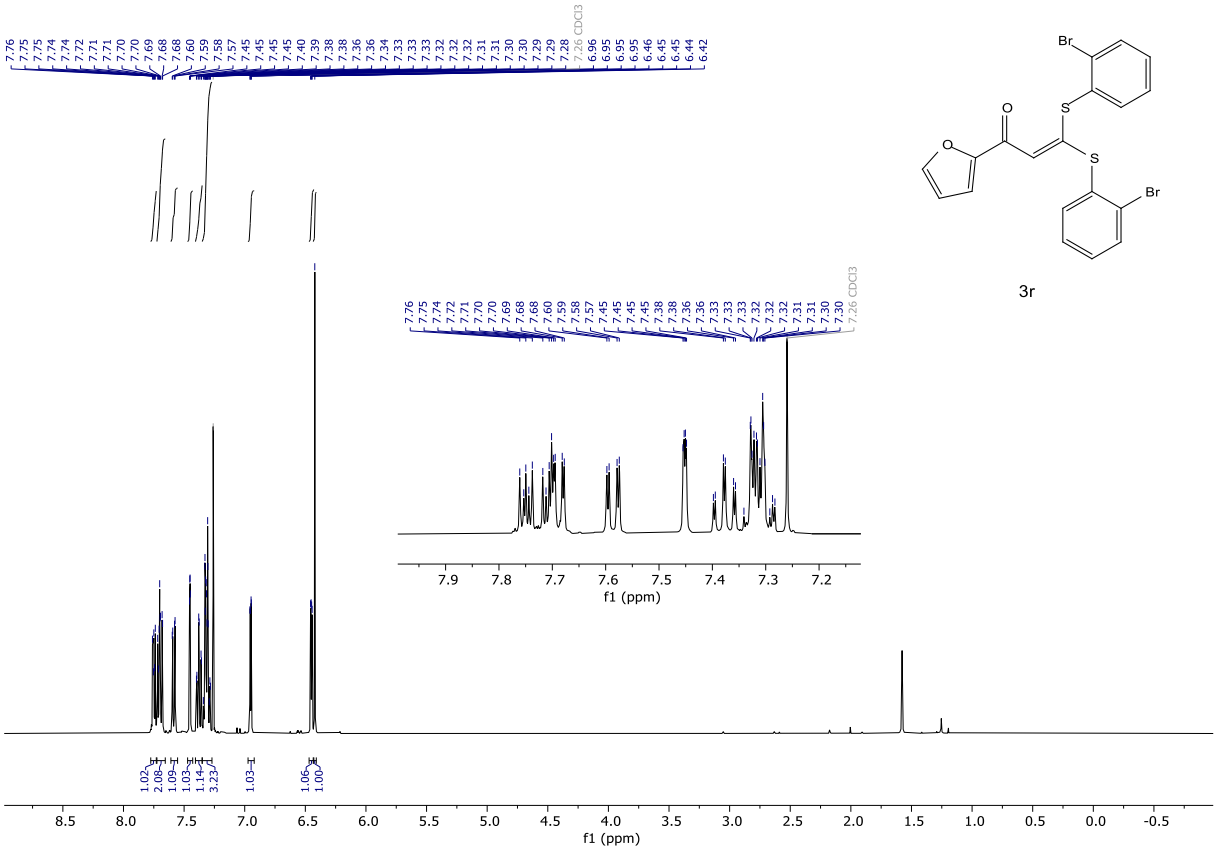
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3q**



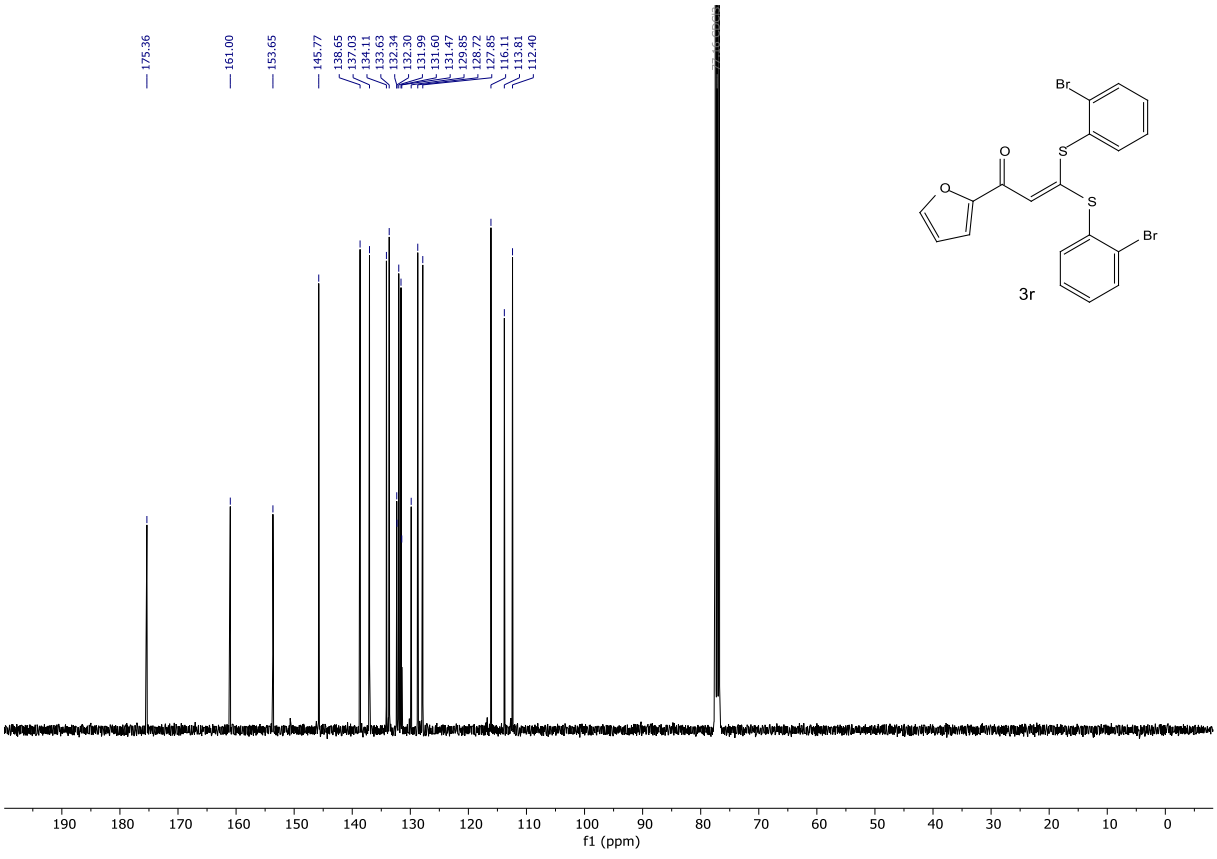

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3q**



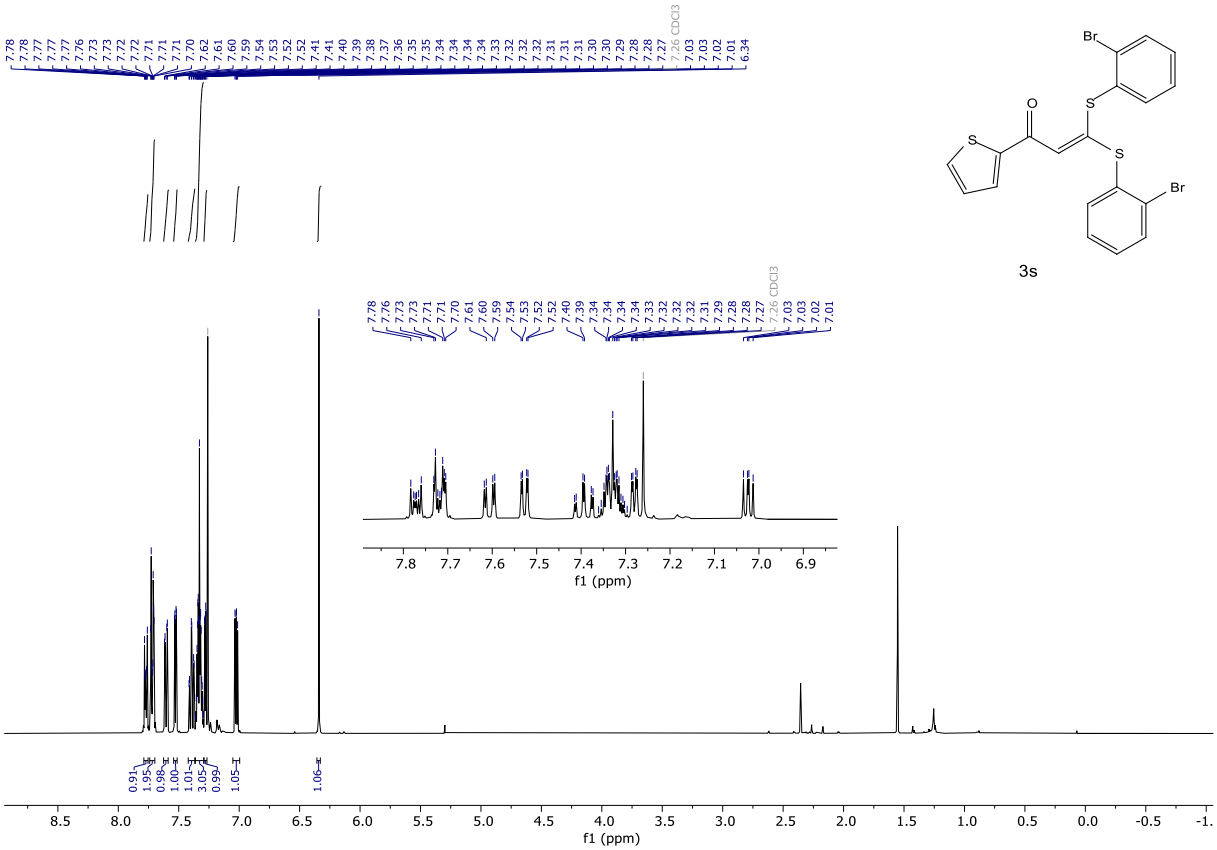
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3r**



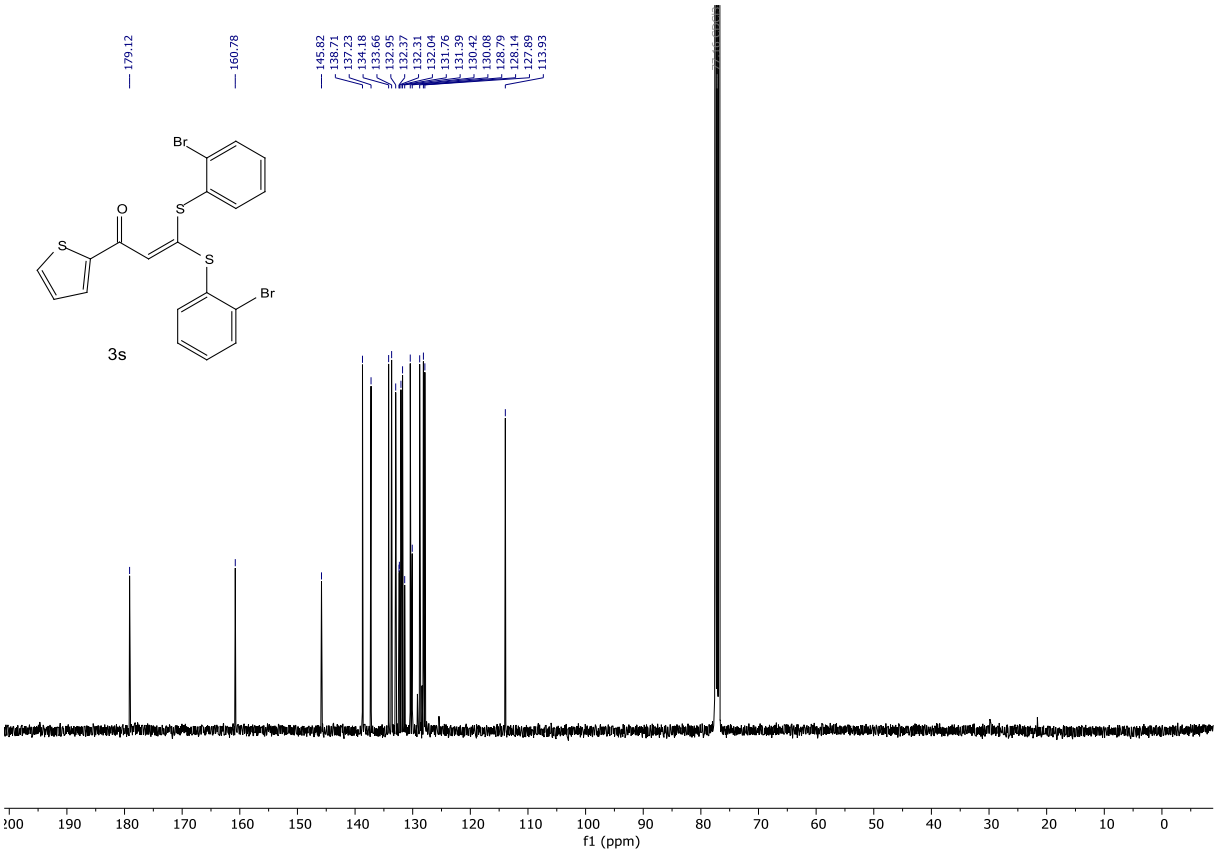

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3r**



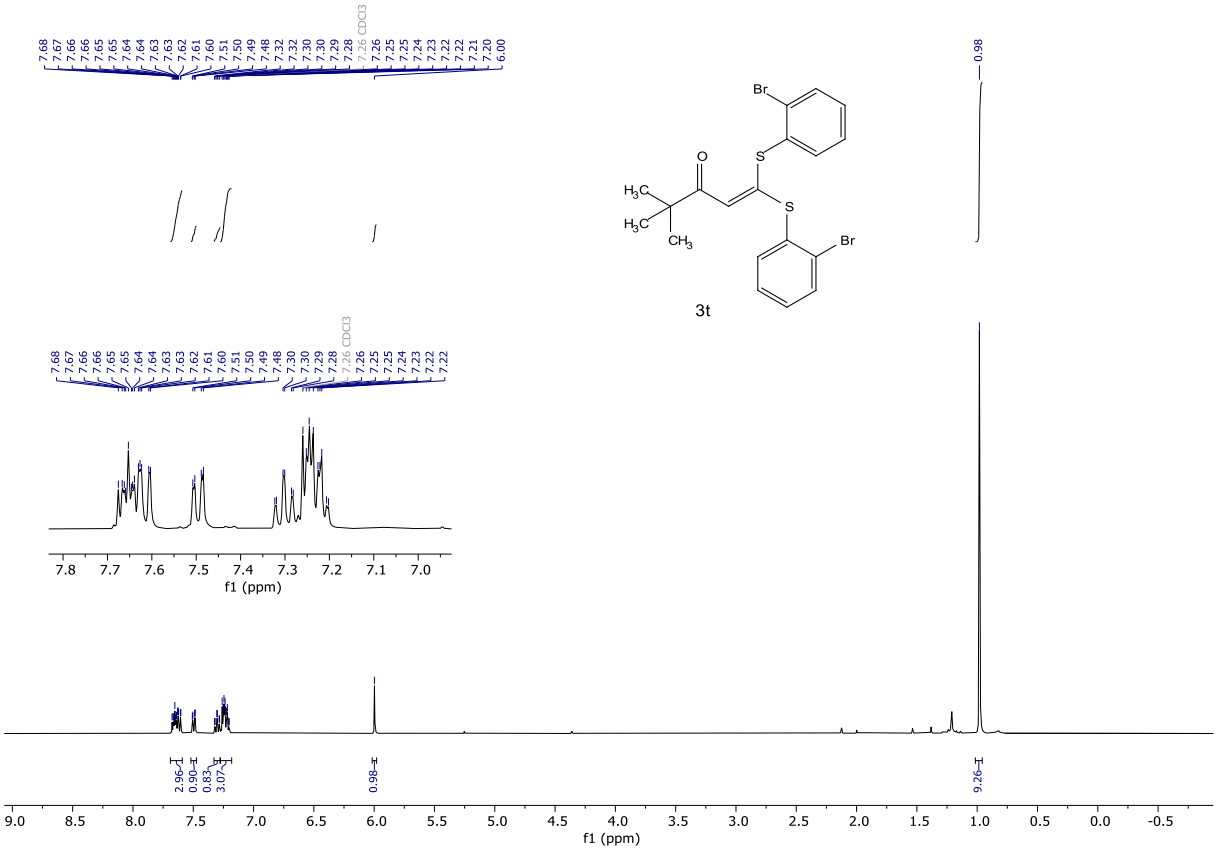
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3s**



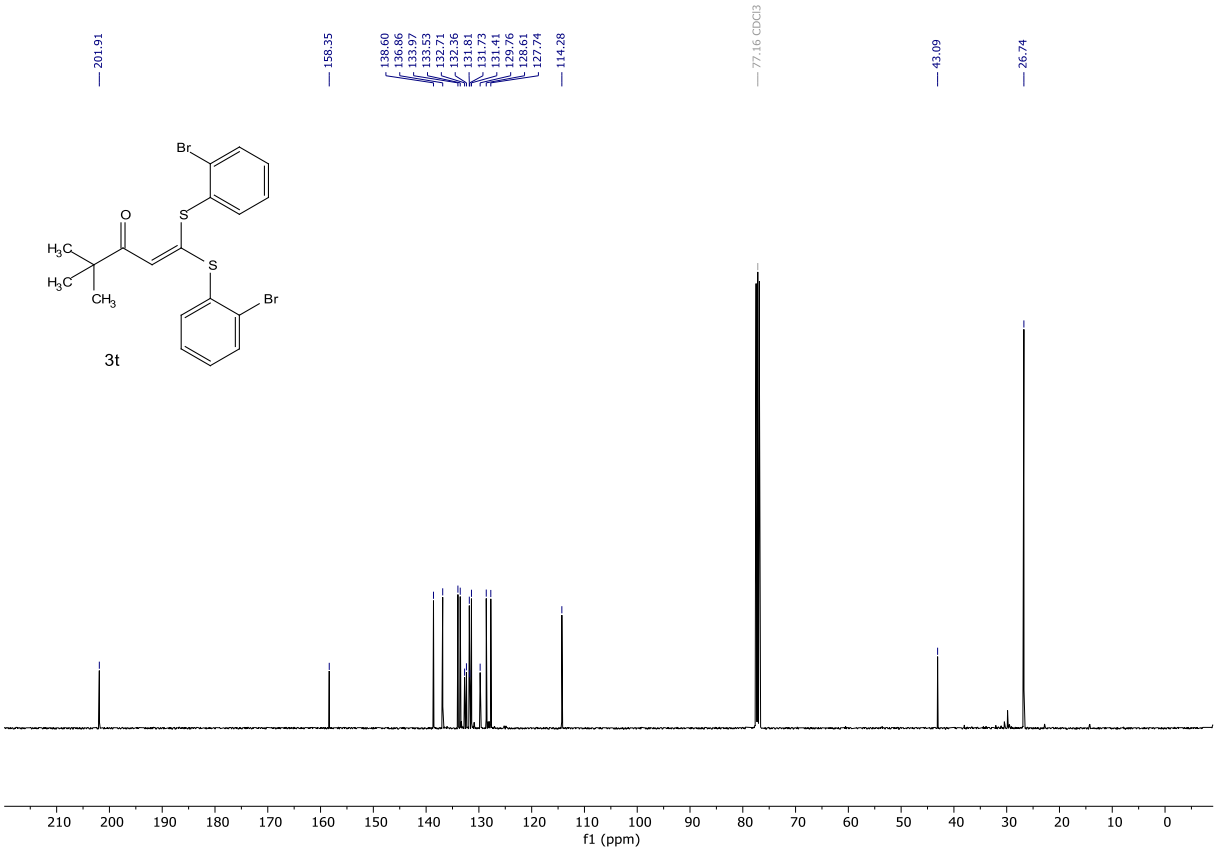

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3s**



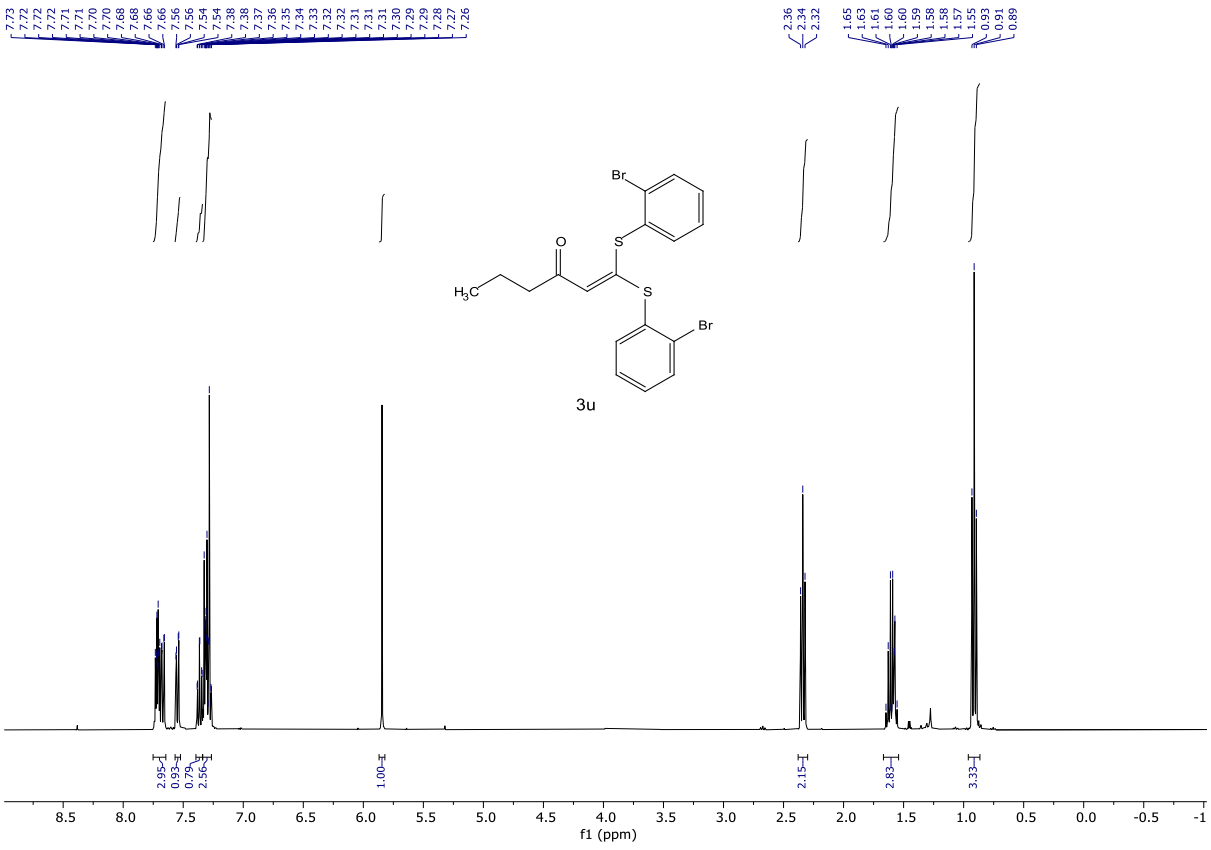
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3t**



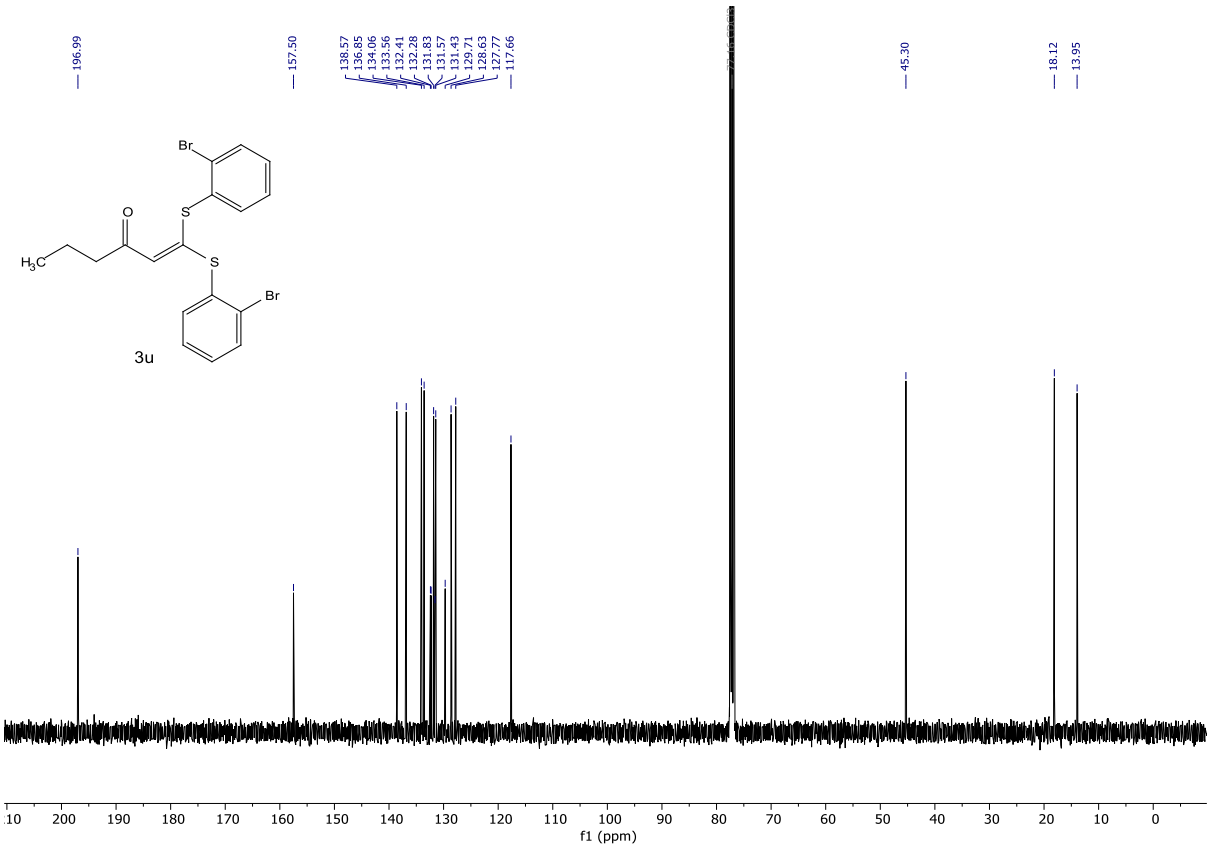

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3t**



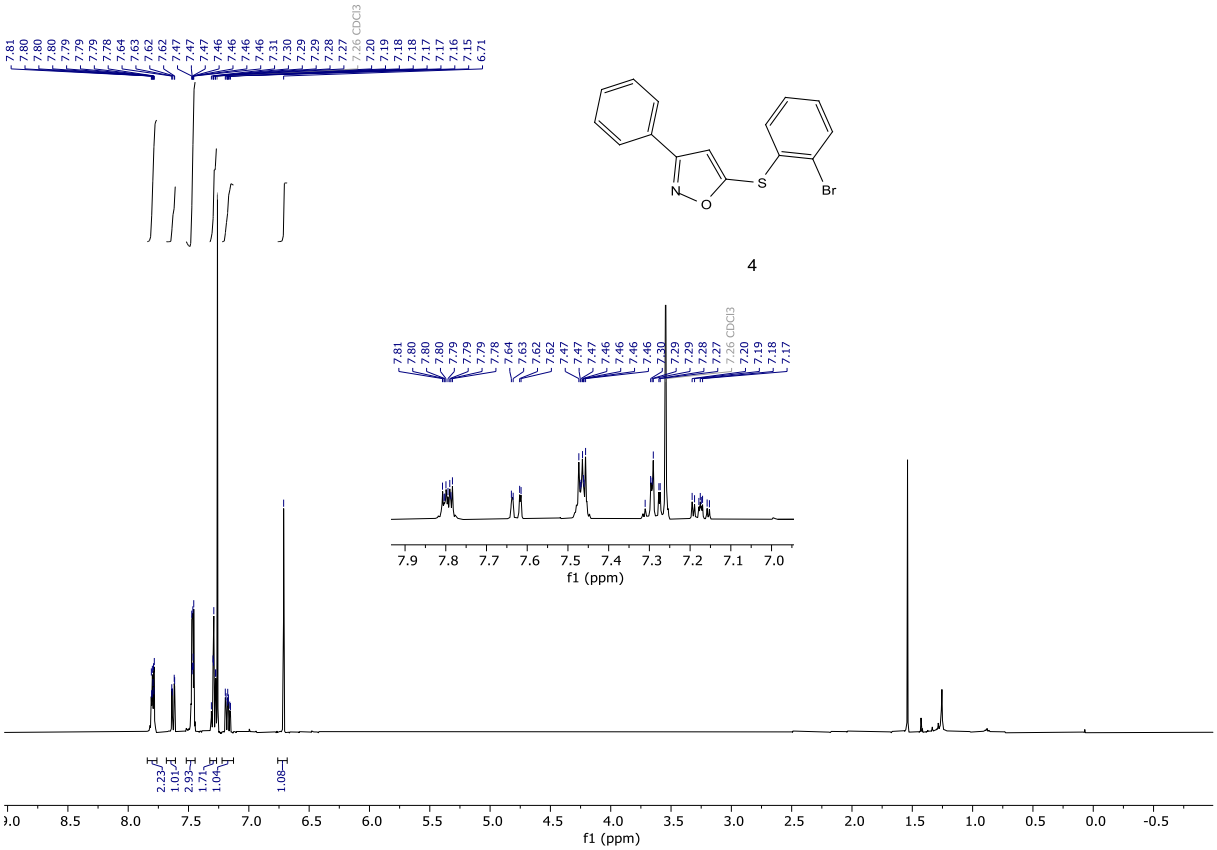
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **3u**



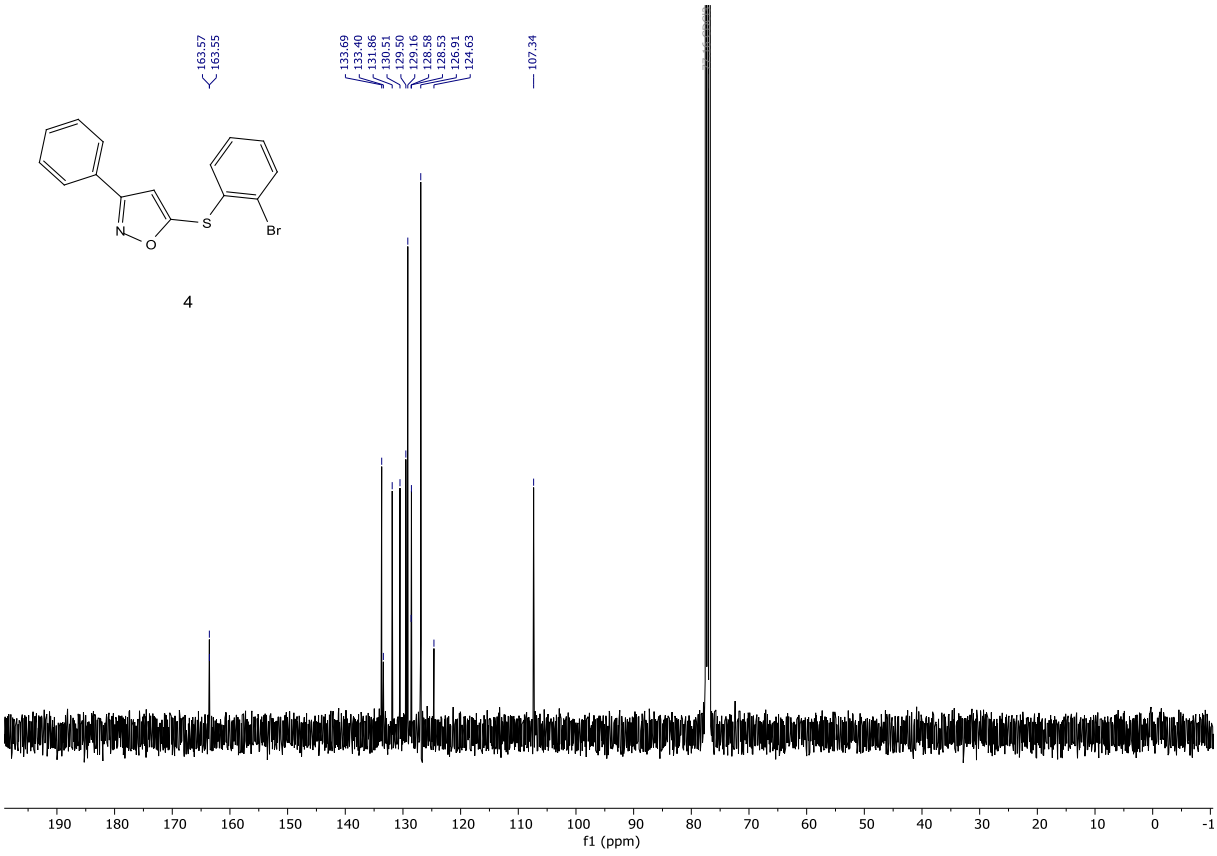

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **3u**



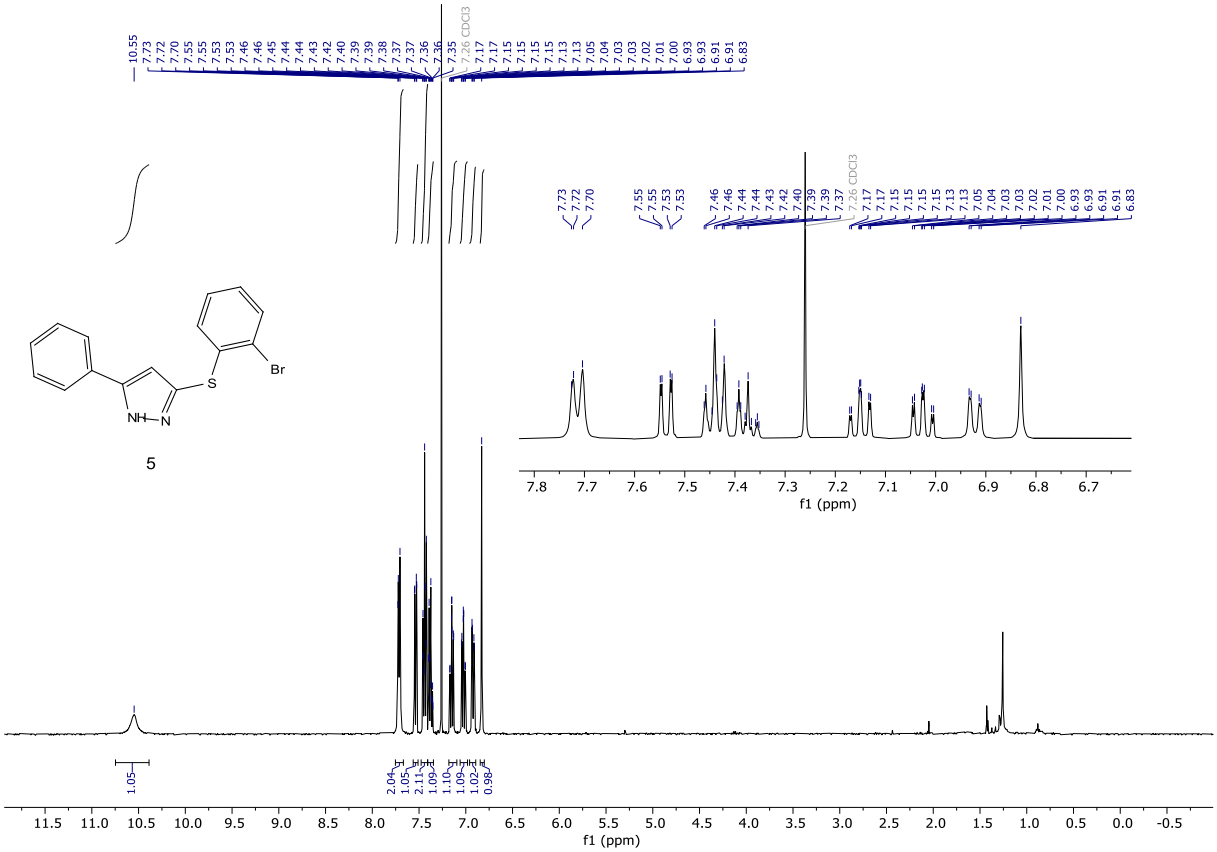
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **4**



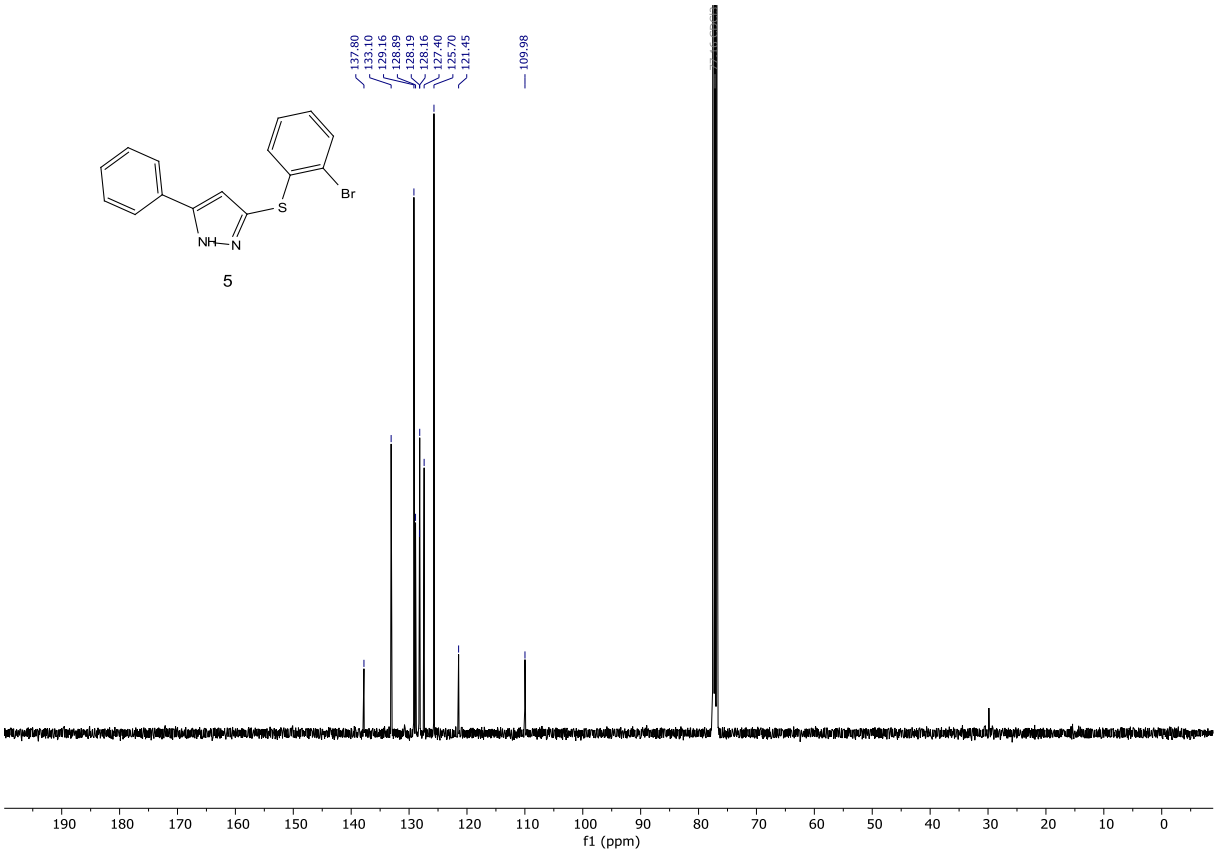

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **4**



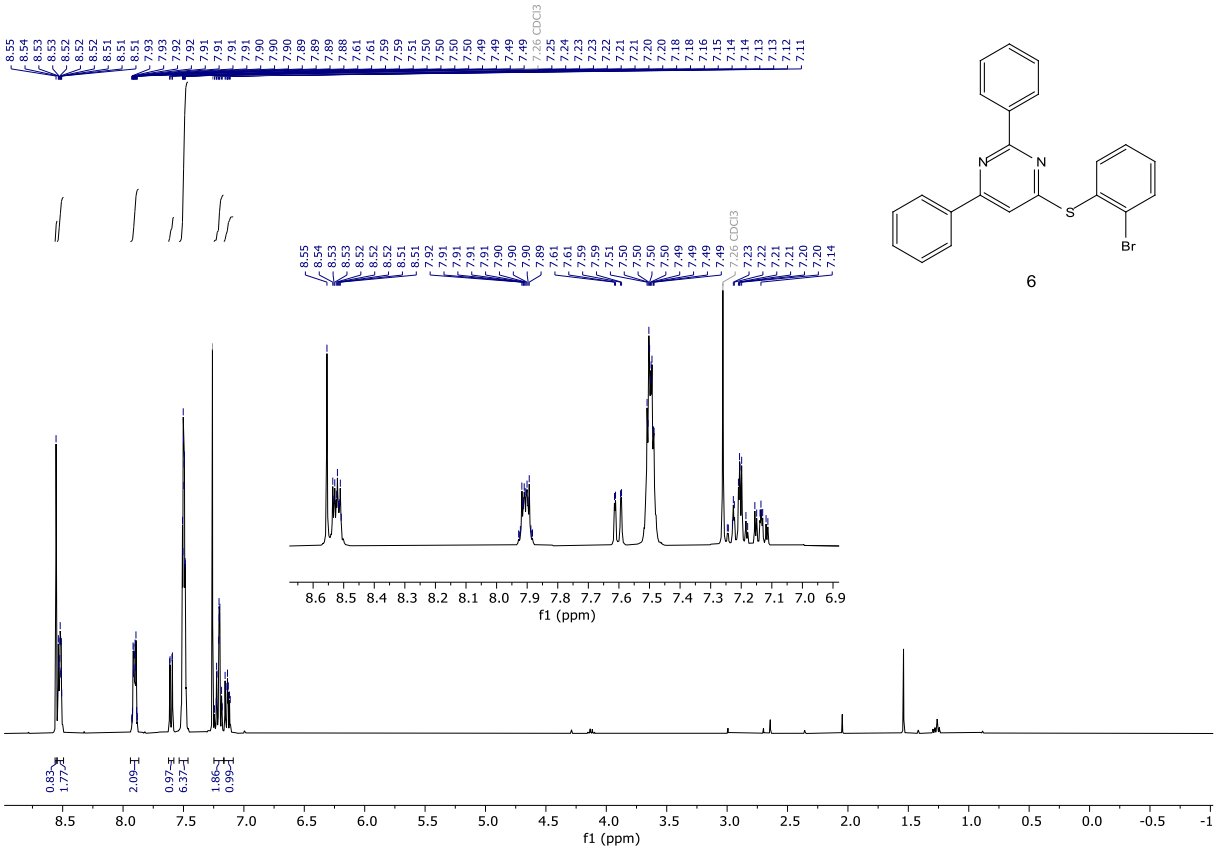
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **5**



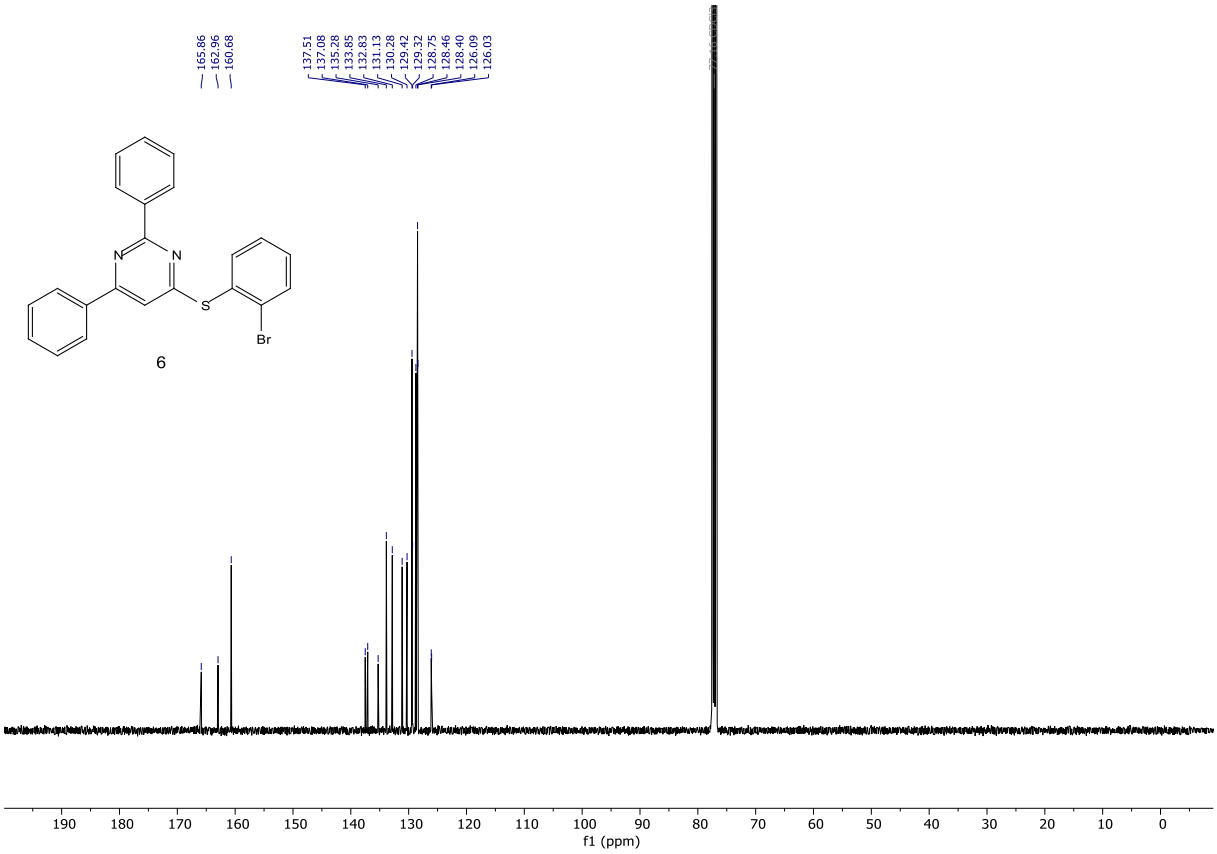

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **5**



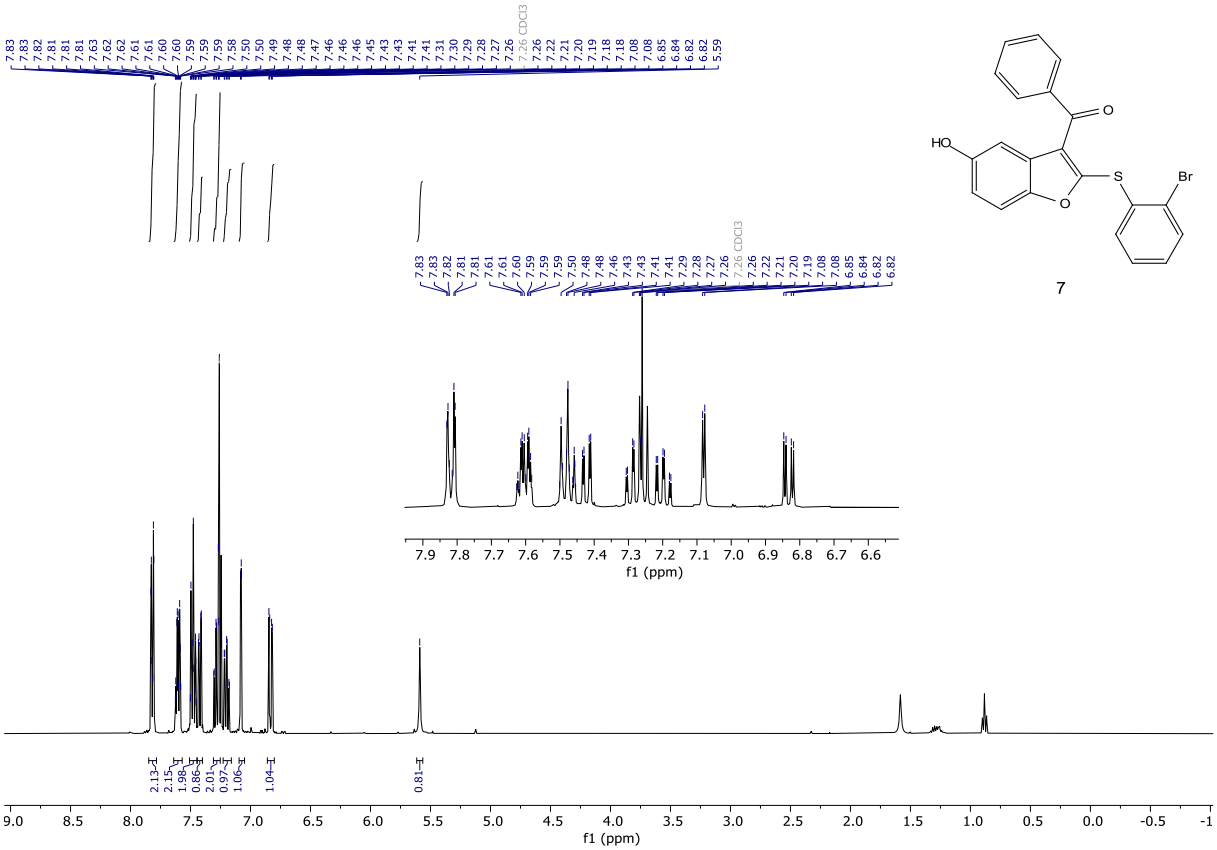
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **6**



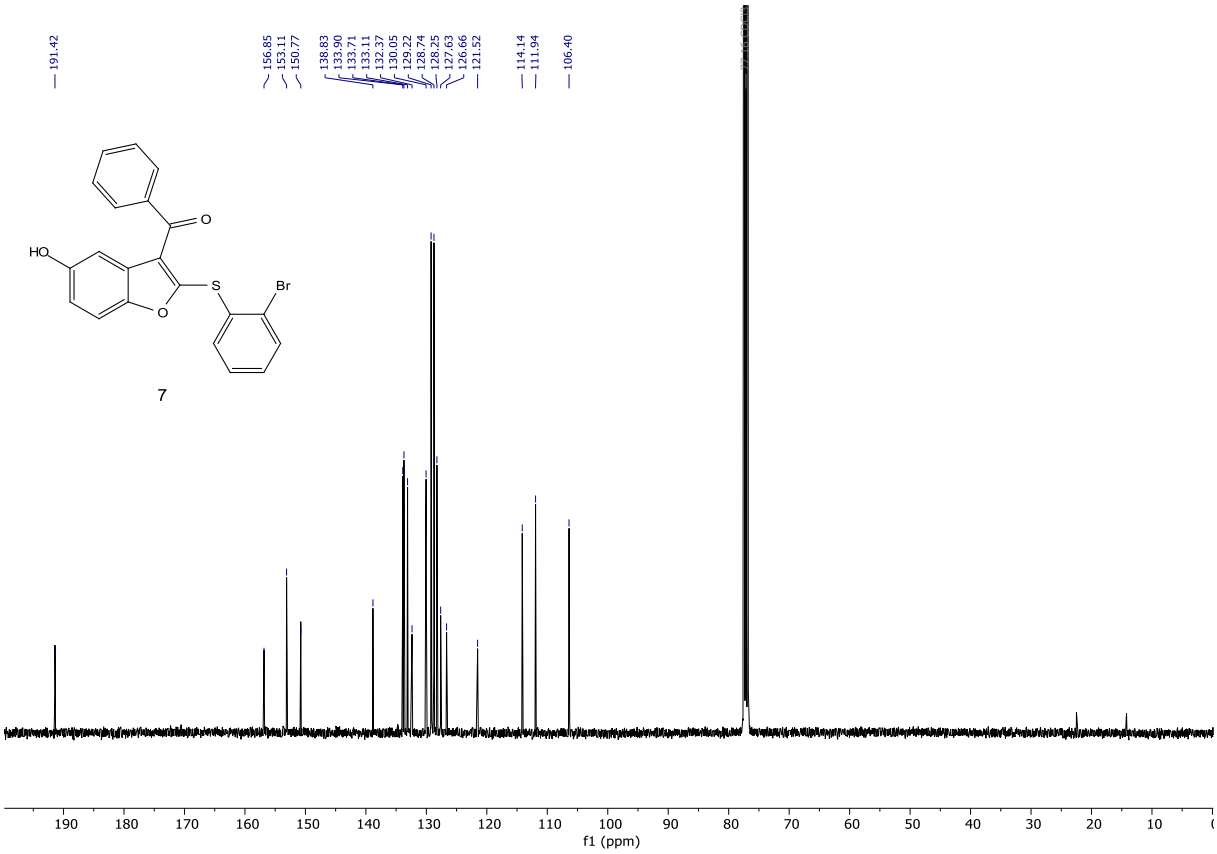

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **6**



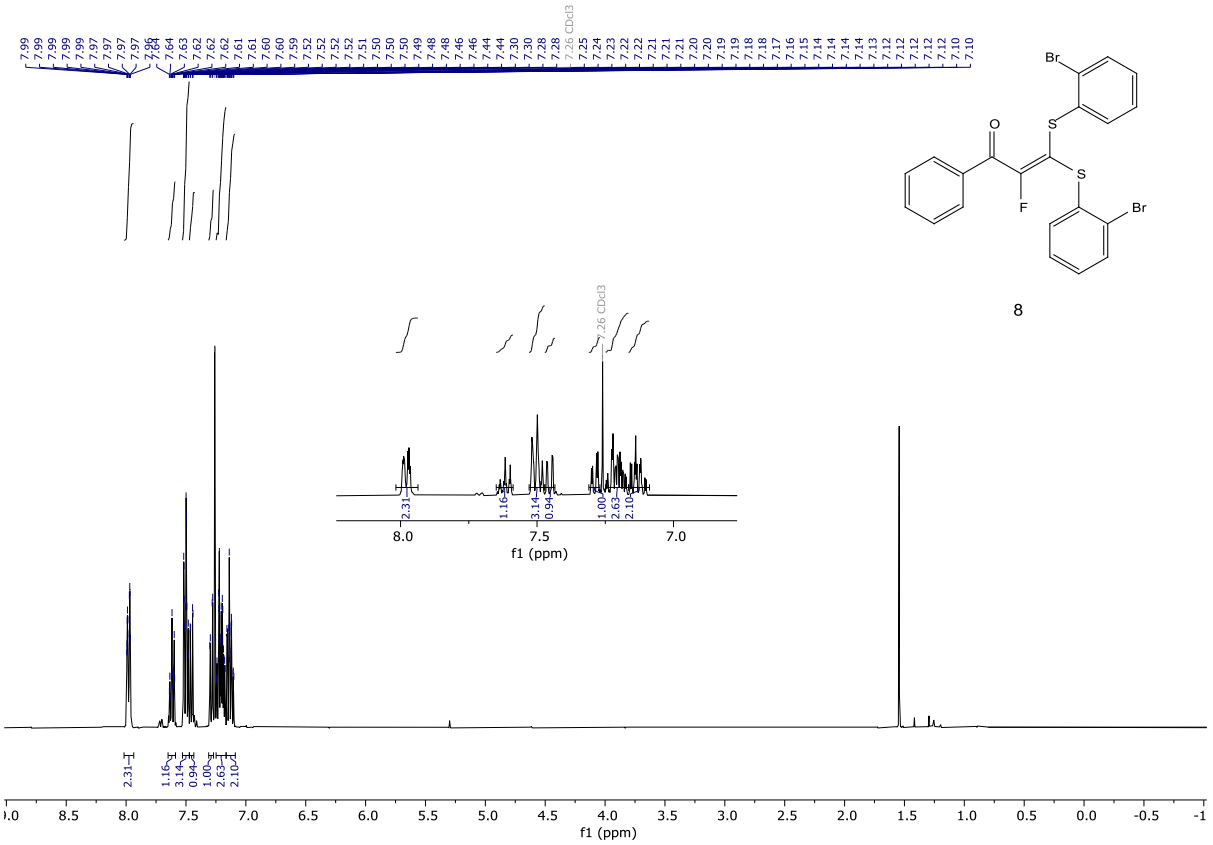
**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **7**



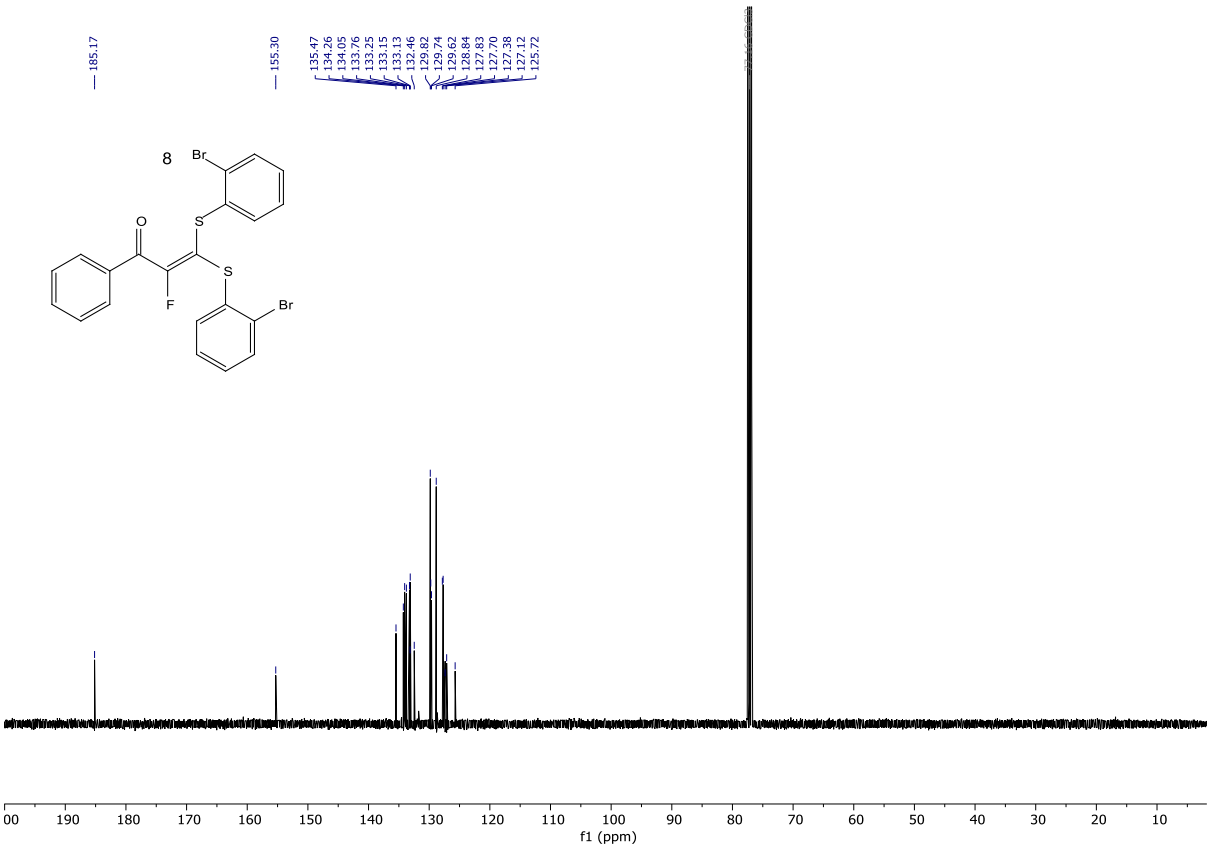

**$^{13}$C NMR** (400 MHz, $CDCl_3$) of compound **7**



**$^{1}$H NMR** (400 MHz, $CDCl_3$) of compound **8**




**$^{13}$C{$^{1}$H, $^{19}$F} NMR** (400 MHz, $CDCl_3$) of compound **8**



**$^{19}$F NMR** (376 MHz, $CDCl_3$) of compound **8**