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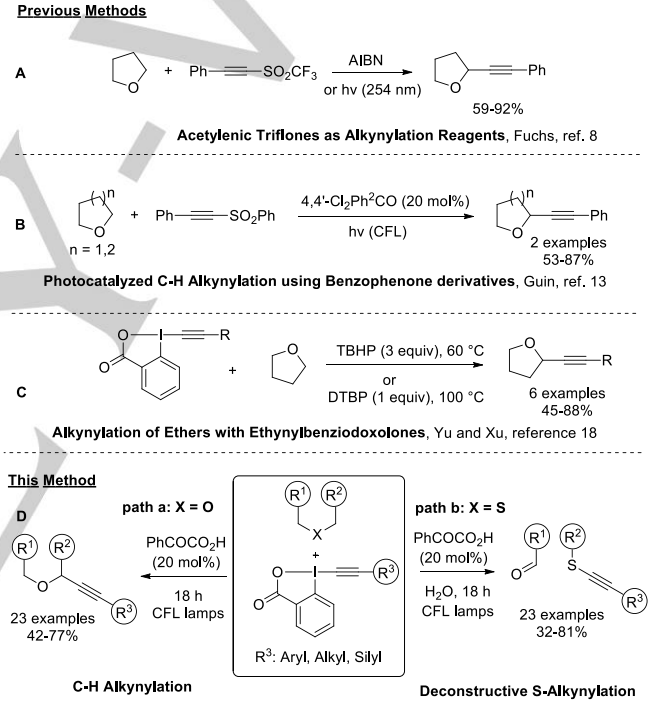
Photochemical Functionalization of Heterocycles with EBX Reagents; C-H Alkynylation *versus* Deconstructive Ring Cleavage

Errika Voutyritsa,[a,b] Marion Garreau,[b] Maroula G. Kokotou,[a] Ierasia Triandafillidi,[a] Jérôme Waser[b]* and Christoforos G. Kokotos[a]*

Abstract: The development of novel methodologies for the functionalization of heterocycles is highly desirable. Herein, we report a green, cheap and efficient photochemical method for the C-H functionalization of saturated *O*-heterocycles, as well as the deconstructive ring-cleavage of *S*-heterocycles, employing hypervalent iodine alkynylation reagents (Ethynylbenziodoxolones, EBX). This photochemical alkynylation is performed utilizing phenylglyoxylic acid as the photoinitiator, leading to the corresponding products in good to high yields, under household fluorescent light bulb irradiation. When *O*-heterocycles were employed, the expected α-C-H alkynylation took place. In contrast, oxidative ring-opening to form a thioalkyne and an aldehyde was observed with *S*-heterocycles. Preliminary mechanistic experiments are presented to give first insights into this puzzling divergent reactivity.

In recent years, C-H bond functionalization has attracted increasing interest in organic chemistry. Synthetic strategies based on C-H functionalization have been applied in multiple fields, including natural product synthesis and medicinal chemistry.[1] Saturated heterocycles are important building blocks in organic synthesis.[2] Therefore, the development of strategies for C-H functionalization at the *α* position of the heteroatom has been intensively investigated. The main focus of research has been on *N*-heterocycles based on transition-metal catalysis,[3] whereas the functionalization of *O*- or *S*-heterocycles has been less investigated and involve usually radical pathways.[4] In addition to direct C-H functionalization, more complex "deconstructive" processes involving cleavage of the C-X bond of the heterocycles have attracted strong interest recently, as they give access selectively to multi-substituted acyclic building blocks. Most successes have been met with *N*-heterocycles[5] and *S*-heterocycles,[6] but for the latter product mixtures were obtained due to oxidation of the sulfur atom under the required strong oxidative/light irradiation conditions.

Among possible transformations, the *α*-alkynylation of saturated cyclic ethers is a particularly useful reaction, since this motif is present in natural products and the obtained building blocks widely serve as key intermediates for the synthesis of bioactive compounds.[7] In 1996, Fuchs introduced alkynyl triflone reagents for the thermally-induced or photochemical (UV-light) radical alkynylation of tetrahydrofuranyl derivatives, under high temperature using AIBN as the initiator (Scheme 1, **A**).[8] This seminal work inspired other researchers to develop alkynylation methods based on radical or carbocation intermediates, but most protocols require relatively harsh conditions to generate the reactive intermediate.[9]



Scheme 1. Approaches for the α-alkynylation of heterocycles.

In recent years, photoredox catalysis has become a powerful synthetic methodology to perform challenging transformations using visible light irradiation by accessing reactive intermediates under mild conditions.[10] Most examples rely on the use of metal-based catalysts, mainly ruthenium or iridium, thanks to the advantage of rational tuning of their electronic properties via ligand manipulation. Unfortunately, these types of complexes can be toxic, expensive, and some are not commercially-available. In order to solve this problem, a number of organic molecules have been employed as photocatalysts, which in many cases provide similar reactivities as the metal catalysts making photo-organocatalysis a low-cost and environmentally friendly alternative.[11] In 2013, Inoue presented a stoichiometric photocatalytic method for the alkynylation of 2-pyrrilidinone derivatives with tosyl alkynes, employing benzophenone in stoichiometric quantities.[12] Guin

[a] E. Voutyritsa, Dr. M. G. Kokotou, Dr. I. Triandafillidi, Prof. Dr. C. G. Kokotos
Laboratory of Organic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis 15771, Athens, Greece. E-mail: ckokotos@chem.uoa.gr

[b] E. Voutyritsa, Marion Garreau, Prof. Dr. Jérôme Waser
Laboratory of Catalysis and Organic Synthesis, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland. E-mail: jerome.waser@epfl.ch

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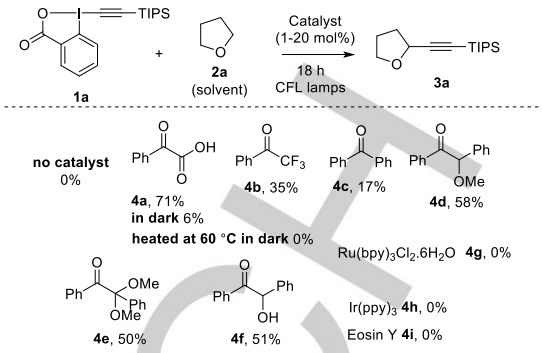
later showed that the reaction also worked with a catalytic amount of a benzophenone derivative, but only two examples of cyclic ethers were reported in this work (Scheme 1, **B**).[13]

In order to further expand the scope of alkynylation reactions, the development of new reagents able to react rapidly with radical intermediates is crucial. In this context, hypervalent iodine compounds are attractive reagents, due to their high reactivity towards both nucleophiles and radicals.[14] In particular, ethynylbenziodoxolones (EBX) reagents have been increasingly investigated for alkynylation reactions over the last decades.[15] They were used for the alkynylation of radicals generated by traditional or photoredox-based methods,[16] and of heteroatom nucleophiles such as thiols.[17] Yu and co-workers, as well as Xu and co-workers, reported a method for the alkynylation of saturated heterocycles using EBX reagents.[18] This method is metal-free, but requires heating and peroxides as oxidants (Scheme 1, **C**). There is currently no mild photoredox-based methods for the α-alkynylation of cyclic ethers using EBX reagents.

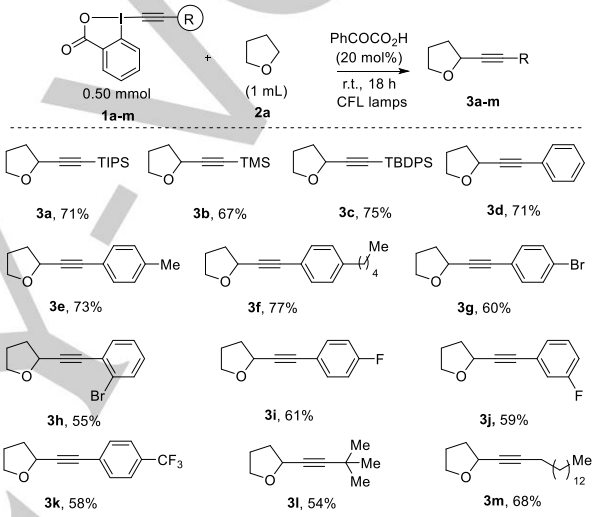
We have recently developed a photochemical methodology, employing a small organic molecule, phenylglyoxylic acid, as the photoinitiator which is cheap and commercially available.[19] This protocol works with cheap household lamps as the irradiation source. Herein, we report a simple and efficient method for the mild and green alkynylation of ethers, using phenylglyoxylic acid as the photochemical promoter and EBX reagents, as the alkynylation source, under photochemical conditions (Scheme 1, **D**, path a). We further demonstrate that a different, unprecedented pathway is followed in the case of thioethers: deconstructive oxidative ring cleavage to form acyclic bifunctionalized building blocks bearing an aldehyde and a thioalkyne (Scheme 1, **D**, path b). In contrast to previously C-S bond cleavage based on light irradiation, a clean reaction was observed without side products resulting from sulfur oxidation. The reaction was successful both for cyclic and benzylic thioethers.

We first established the optimum reaction conditions for the photochemical alkynylation of THF, starting from the identification of the appropriate photocatalyst for the reaction between THF (**2a**) and TIPS-EBX (**1a**) (Scheme 2). A variety of known photocatalysts or photoinitiators (**4a-j**) led to moderate yields. Phenylglyoxylic acid (**4a**) proved to be an ideal promoter, providing **3a** in high yield. Interestingly, benzophenone, which has been successful with sulfone reagents, gave only a very low yield with TIPS-EBX (**1a**). Attempts to decrease the amount of THF and use other solvents led to decreased yields.[20]

The optimized reaction conditions were subsequently applied to a variety of hypervalent iodine reagents (Scheme 3). Silyl-substituted EBX reagents (**1a**-**c**) reacted well, leading to the desired products in good to high yields (**3a**-**c**). Aryl-substituted EBX reagents, containing either electron-donating groups or electron-withdrawing groups (**1d**-**k**) reacted smoothly leading to **3d**-**k** in high yields. In addition, alkyl-substituted EBX reagents (**1l** and **1m**) were tested, leading to the formation of **3l** and **3m** in moderate to good yields.

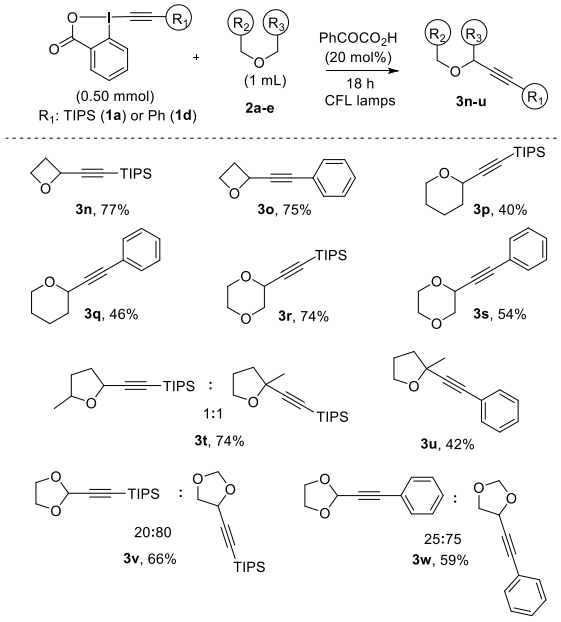


Scheme 2. Catalyst screening for the photochemical synthesis of **3a.**



Scheme 3. Substrate scope for the photochemical alkynylation of THF with different EBX reagents.

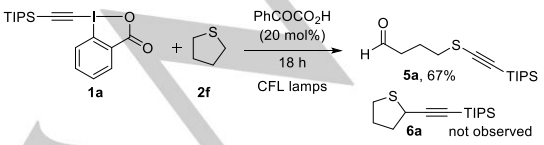
Next, we turned our attention to the ether partner (Scheme 4). First, oxetane (**2b**) was tested in the reaction, leading to the formation of the desired products in high yields (**3n** and **3o**). Moving from five-membered to six-membered cyclic ethers, like tetrahydropyran and dioxane (**2c** and **2d**), led to **3p-s** in moderate to good yields. Other tetrahydrofuranyl adducts, like 2-methyl-THF (**2e**), reacted well leading to the desired products in good yields (**3t** and **3u**). When 2-methyl tetrahydrofuran reacted with **1a**, two regioisomers were observed (**3t**). In the case of **3u**, a single regioisomer was formed. The reaction between 1,3-dioxolone and Ph-EBX (**1d**) under thermal radical conditions provides mainly the regioisomer where the alkynyl moiety is placed between the two oxygens.[18a] Interestingly, in our case, this reaction led to an inversed regioselectivity (**3w**). A similar outcome was also observed in the case of **3v**. Unfortunately, when non-cyclic ethers were employed, they did not afford the desired products.



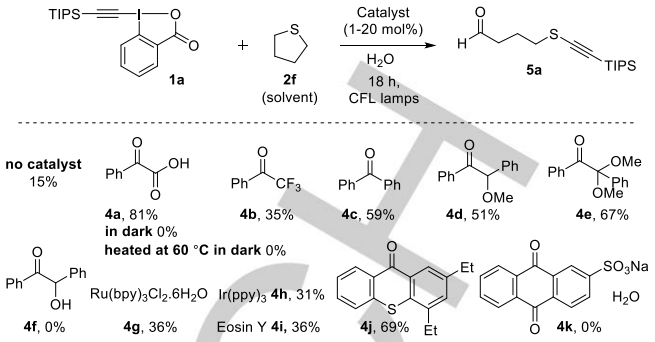
Scheme 4. Substrate scope of ethers in the photochemical reaction with EBX reagents.

In order to extend our methodology, we envisaged the application of other heterocycles. The alkynylation of *N*-heterocycles was not successful. In contrast, when the reaction was run with tetrahydrothiophene (THT, **2f**), an alkynylation product was obtained in 67% (Scheme 5). However, to our surprise this was not the expected product **6a**, but the oxidative deconstructive thio-alkynylated aldehyde **5a**. To the best of our knowledge, such a product has never been observed, as only α-alkynylation in moderate yield has been reported so far with other methods.[8,9b,18b] Except from small amounts of disulfide, no side products from sulfur oxidation were obtained, in contrast to previously reported methods.[6] When considering that the reaction gave two highly useful functionalities (an aldehyde and a thioalkyne, which is easily converted into thioesters or participate to a broad range of cycloadditions),[17,21] we decided to optimize this process.

We first established the optimum reaction conditions for the photochemical alkynylation of tetrahydrothiophene (THT, **2f**) (Scheme 6). Attempts to optimize the reaction conditions and decrease the amount of THT, using other organic solvents, led to decreased yields.[20] However, when H_2O was employed as a co-solvent, **5a** was formed in higher yield.[20] It should be highlighted that, when the reaction was tested in the presence of molecular sieves, no product was formed.



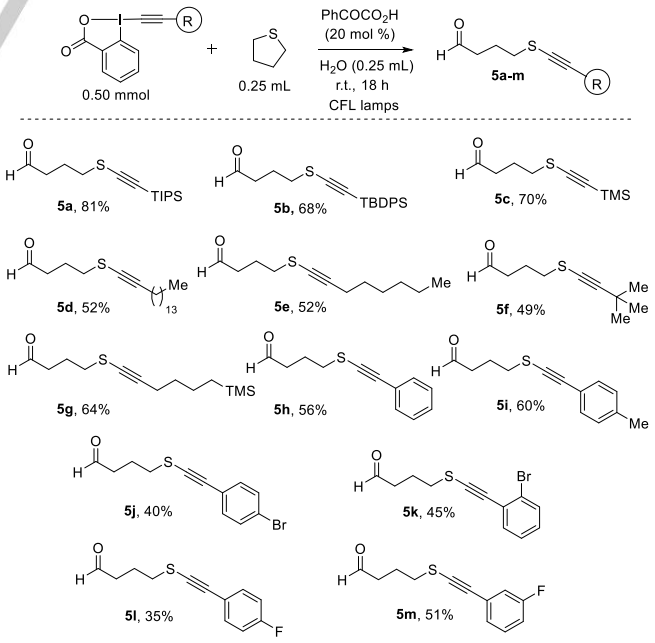
Scheme 5. Unexpected formation of aldehyde **5a** obtained when attempting α-alkynylation of tetrahydrothiophene (**2f**).



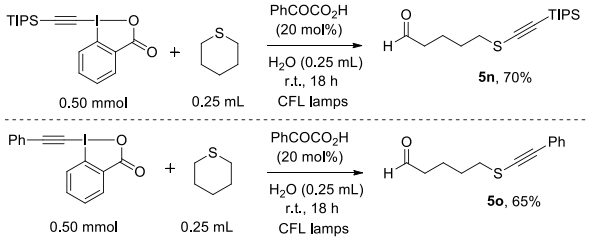
Scheme 6. Catalyst screening for the photochemical synthesis of **5a**.

In consequence, H_2O is necessary for the reaction to proceed. The next step was the identification of the appropriate photocatalyst for the reaction between THT (**2f**) and TIPS-EBX (**1a**) (Scheme 6). A variety of known photocatalysts or photoinitiators (**4a-k**) led to moderate yields. Phenylglyoxylic acid (**4a**) proved to be an ideal promoter, providing **5a** in high yield. Attempts to further lower the amount of **2f** led to diminished yields.

The optimized reaction conditions were subsequently applied to a variety of hypervalent iodine reagents (Scheme 7). Silyl-substituted EBX reagents reacted well, leading to the desired products in good to high yields (**5a**-**c**). Alkyl-substituted EBX reagents were tested, leading to the formation of **5d**-**g** in moderate to high yields. In addition, aryl-substituted EBX reagents, containing either electron-donating groups, or electron-withdrawing groups reacted smoothly leading to **5h**-**m** in moderate to good yields. Moving from five-membered to six-membered, tetrahydrothiopyran (**2g**), led to **5n** and **5o** in good yields (Scheme 8).

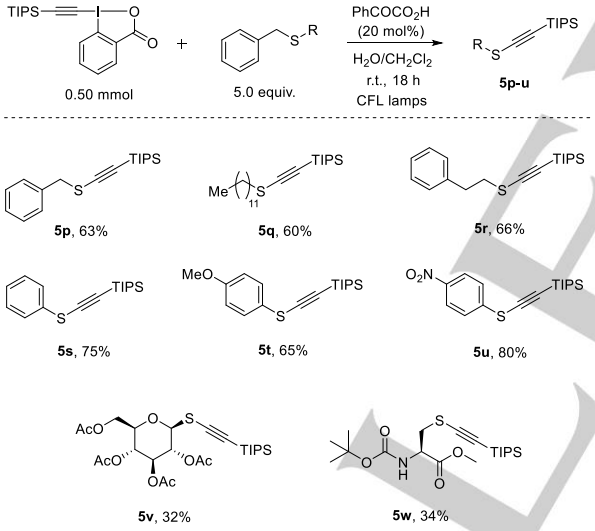


Scheme 7. Substrate scope for the photochemical alkynylation of THT with different EBX reagents.



Scheme 8. Photochemical alkynylation of tetrahydrothiopyran with different EBX reagents.

Next, we turned our attention to non-cyclic thioethers (Scheme 9). A range of benzyl sulfides was synthesized and tested in the reaction conditions, as the benzylic position was expected to be easier to oxidize as recently reported by Masson and co-workers.[22] In this case, the amount of sulfide could be reduced to 5 equiv. with no loss in reactivity, while using CH_2Cl_2 as the solvent.[20] Unfortunately, further reduction of the amount of the thioether led to diminished yields. Both aromatic and aliphatic sulfides reacted well, leading to the alkynylated products (**5g**-**5u**) in good to high yields. Protected carbohydrates and amino acids also reacted smoothly, albeit in lower yields (**5v**, **5w**).



Scheme 9. Substrate scope of benzylic thioethers in the photochemical reaction with TIPS-EBX reagent.

In order to understand the reaction mechanism, experiments were performed, starting with fluorescence quenching studies (Figure 1).[20] After irradiation of phenylglyoxylic acid (1 mM in MeCN) at 360 nm, its fluorescence was measured at 402 nm. Increasing the added amount of THF, a slight decrease in the fluorescence was observed (Figure 1, **A**). Increasing the added amount of **1a**, a constant decrease in the fluorescence was also observed (Figure 1, **B**). Increasing the added amount of THT, no decrease in the fluorescence was observed (Figure 1, **C**). In all cases, quenching is minimal, thus excited $PhCOCO_2H$ is most probably not directly responsible for the initiation of the process.

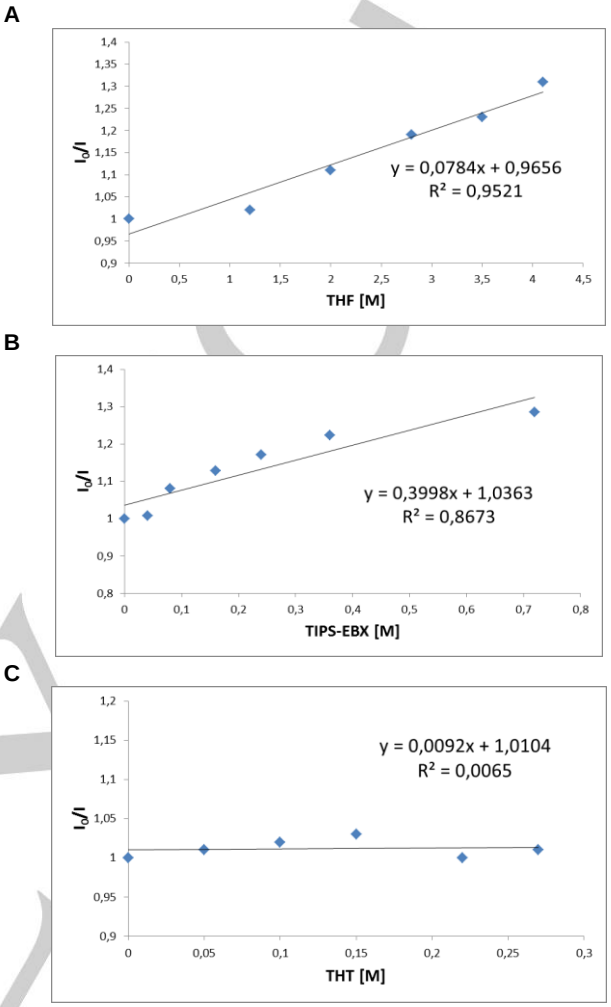
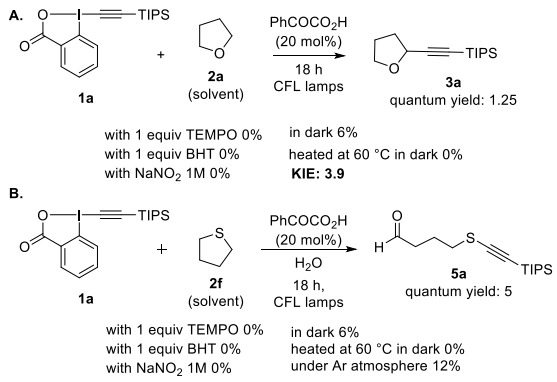


Figure 1. A. Stern-Volmer plot of the fluorescence quenching of PhCOCOOH (1 mM in MeCN) with THF. **B.** Stern-Volmer plot of the fluorescence quenching of PhCOCOOH (1 mM in MeCN) with **1a. C.** Stern-Volmer plot of the fluorescence quenching of PhCOCOOH (1 mM in MeCN) with THT.

Next UV-Vis experiments were performed. The association of an electron-rich molecule with an electron-acceptor can lead to the formation of an aggregate, called electron donor-acceptor (EDA) complex. EDA complexes are known in literature since the 1950s,[23,24] and recently Melchiorre and others have identified them as active species in photochemical reactions.[25] Upon mixing phenylglyoxylic acid and **1a** in THF or THT, no significant increase in the UV absorbance was observed.[20]

The photodecomposition of $PhCOCO_2H$ in THF and the reaction mixture in THF were monitored by ^1H- and ^{13}C-NMR.[20] As in previous studies,[19g] the photodecomposition of $PhCOCO_2H$ seems to be crucial for the initiation of the reaction. In THF, $PhCOCO_2H$ photodecomposes to benzaldehyde (via benzoyl radical, see Scheme 11, **III**) and diphenyltartaric acid (via dimerization of radical **I**, Scheme 11).[20] In THT, similar

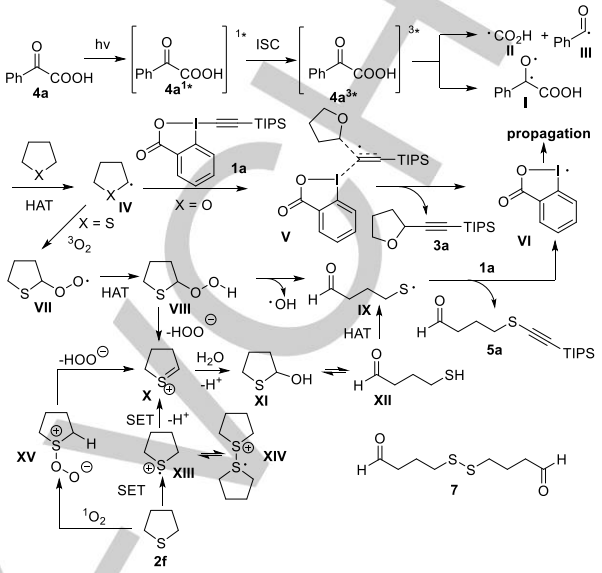
photodecomposition is taking place.[20] Similar decompositions are also observed in both reaction mixtures.[20]



Scheme 10. Control experiments and quantum yield determination.

Further mechanistic studies supported the radical nature of the reaction, since the addition of TEMPO, BHT or sodium nitrite prevents the reaction from occurring for both THF (**2a**) and THT (**2f**) (Scheme 10, **A** and **B**). When **1a** reacted with TEMPO in the presence of phenylglyoxylic acid in THF (**2a**) or THT (**2f**), an adduct was formed and was identified by GC-MS.[20] In the case of THF (**2a**), this strongly supports the existence of a carbon radical α to the oxygen, whereas for THT (**2f**), the same radical is plausible, but formation of an adduct on sulfur by reaction of a radical cation can also be considered. In the absence of light, the reactions did not proceed, even upon heating the reaction mixture at 60 °C. In the presence of a cut-off filter (below 400 nm), the products were also not formed (0%). Without catalyst, no **3a** was formed and **5a** was obtained in very low yield (<15%). As oxygen has been reported as an efficient oxidant for the cleavage of C-S bonds under light irradiation conditions,[6a] we then performed the reaction with **2f** under an argon atmosphere. **5a** was obtained in low yield (12%), suggesting that oxygen plays a role in the reaction mechanism. Using potassium ferrioxalate as the actinometer,[26,27] we calculated the quantum yield of the reactions. Values of Φ of 1.25 and 5 were obtained respectively for the two reactions, indicating a chain propagation mechanism.[20]

Based on the above experiments, a speculative reaction mechanism is proposed in Scheme 11. Upon irradiation, $PhCOCO_2H$ (**4a**) is excited to the singlet state **4a^{1}***, followed by intersystem crossing, leading to triplet phenylglyoxylic acid (**4a^{3}***)[19g,28] In THF, $PhCOCO_2H$ photodecomposes to benzaldehyde or to diphenyltartaric acid via the homolytic cleavage of triplet excited $PhCOCO_2H$ from benzoyl radical **III** and radical **I**, respectively.[20] In other solvents (*i*PrOH), the homolytic cleavage leads only to radical **I**,[25] or only to benzoyl radical **III**.[19g,28] With THF present, one of the radicals formed by the irradiation of $PhCOCO_2H$ (**I** or **III**) abstracts a H (Hydrogen Atom Transfer, HAT), leading to the first α-radical of THF (**IV**) (trapped by TEMPO, observed by GC-MS[20]), which initiates the process. Addition of radical **IV** to **1a** leads to the desired product **3a** and radical intermediate **VI**.[18a] Although this step has been proposed to occur stepwise in the past, a concerted mechanism via transition state **V** has been recently demonstrated to be feasible based on computation.[16d] Intermediate **VI** is responsible for the propagation of the reaction with THF via HAT.



Scheme 11. Proposed reaction mechanism.

The divergent reactivity observed for THT (**2f**) is puzzling. In principle, radical **IV** could react with small amounts of oxygen present in the reaction mixture (see experiment under argon, Scheme 10 and mechanistic studies with HRMS[20]) to give peroxide **VIII** (observed by HRMS) after HAT. Peroxide **VIII** would then fragment to thiol radical **IX** (trapped with Tempo, observed by HRMS) and a hydroxy radical.[6a] Fast reaction of thiol **IX** with **1a** would then lead to **VI**. The presence of radical **IX** is supported by the isolation of disulfide **7** as side product from the reaction mixture (also observed by HRMS). However, this mechanism does not rationalize the essential role of water in the reaction. An explanation could be that fragmentation of **VIII** is not productive, and elimination of peroxide proceeds instead to give sulfonium **X** (observed by HRMS), which could be trapped by water to give thio half acetal **XI**, in equilibrium with free thiol **XII** (observed by HRMS). In presence of numerous radical intermediates, HAT from **XII** to give **IX** is expected to be fast.

Although this mechanism hypothesis is plausible, the complete divergence of reactivity of α-heteroatom radical **IV** observed for oxygen and sulfur cannot be easily rationalized. Indeed, at least small amounts of α-alkynylation of **2f** would have been expected based on literature precedence.[8,9b,18b] Therefore, other pathways to generate intermediate **X** should be considered. In fact, oxidation of the sulfur atom of thiophene by single electron transfer (SET) to give radical cation **XIII** is known to be easy, as it has been observed for example in the presence of copper(II) as oxidant.[29] This oxidation is also facilitated by the stabilization of **XIII** as its dimer **XIV**.[30] Reaction of **XIII** with TEMPO may also lead to the adduct observed by mass spectrometry. Radical **VI** is expected to be competent oxidant for this step. **XIII** would then be further oxidized to **X** via a second

oxidation step coupled with a loss of proton. This could occur for example by recombination with triplet oxygen, followed by HAT and loss of hydrogen peroxide. Alternatively, sensitization of triplet oxygen by **4a**^{3*} could generate singlet oxygen, which reacts very fast with thiophene to give intermediate **XV**.[6a] Elimination of peroxide would then lead to **X**. However, **4a** is known to be a mediocre sensitizer for singlet oxygen generation,[19l] and side-products resulting from sulfur overoxidation would have been expected in presence of singlet oxygen.[6a] Finally, a mechanism involving alkynylation of sulfur, followed by attack of water and oxidation appears less probable, as side product **7** would not have been observed in this case, and the alkynylation process is known to require a copper catalyst and high temperature to proceed.[17c]

In conclusion, we have developed a green and efficient method for the direct C-H alkynylation of ethers and the deconstructive alkynylation of thioethers using hypervalent iodine-alkynes. The first efficient photocatalytic alkynylation of thioethers using EBX reagents was developed. The deconstructive alkynylation observed for thioethers is unprecedented and proceeded in high yield with only very few sulfur oxidation side products. Mechanistic studies shed first light in this puzzling divergence of reactivity, although further investigations will be needed to fully understand the deconstructive alkynylation process of thioethers.

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Keywords: Photochemistry • Green chemistry • HAT • C-H activation • EBX-reagents • Heterocycles

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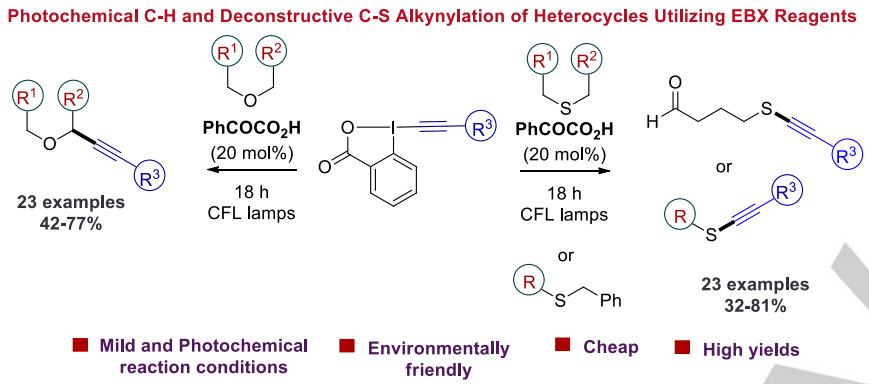
Entry for the Table of Contents

COMMUNICATION



Errika Voutyritsa, Marion Garreau, Maroula G. Kokotou, Ierasia Triandafillidi, Jérôme Waser and Christoforos G. Kokotos**

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Photochemical Functionalization of Heterocycles with EBX Reagents; C-H Alkynylation versus Deconstructive Ring Cleavage

Photochemistry: A mild, metal-free and easy-to-execute protocol for the direct photochemical C-H alkynylation of cyclic ethers and the deconstructive alkynylation of thioethers utilizing EBX reagents was developed with phenylglyoxylic acid as the photoinitiator.

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Supporting Information

Photochemical Functionalization of Heterocycles with EBX Reagents: C–H Alkynylation versus Deconstructive Ring Cleavage**

Errika Voutyritsa,[a, b] Marion Garreau,[b] Maroula G. Kokotou,[a] Ierasia Triandafillidi,[a] Jérôme Waser,*[b] and Christoforos G. Kokotos*[a]

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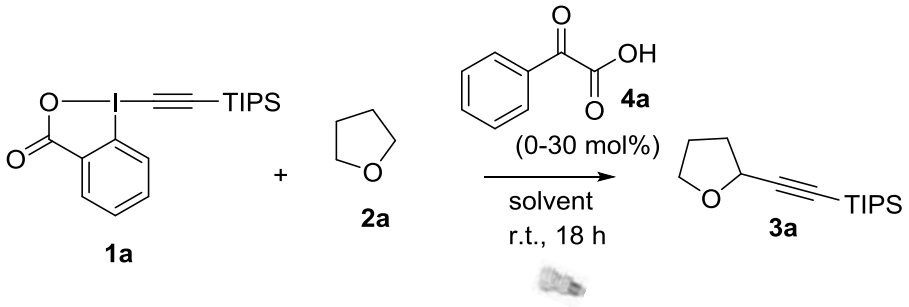
General Remarks

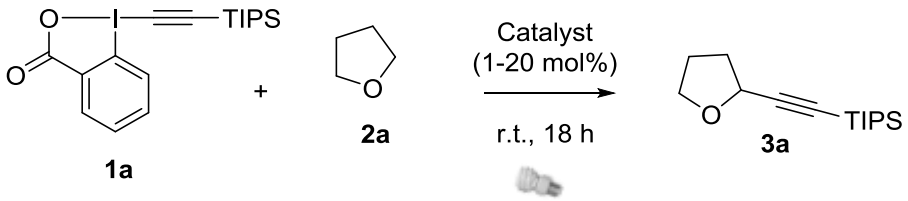
Chromatographic purification of products was accomplished using forced-flow chromatography on Merck® Kieselgel 60 F_{254} 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid, anisaldehyde or potassium permanganate stains. Mass spectra (ESI) were recorded on a Finningan® Surveyor MSQ LC-MS spectrometer. HRMS spectra were recorded on Bruker® Maxis Impact QTOF spectrometer. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Varian® Mercury (200 MHz, 188 MHz and 50 MHz) and on a Brucker DPX-400 (400 MHz, 376 MHz and 100 MHz) spectrometer in $CDCl_3$ and are internally referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad signal), coupling constant and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm). ^{19}F NMR spectra are internally referenced to fluoroform (376 MHz) or trifluoroacetic acid (188 MHz). Mass spectra and conversions of the reactions were recorded on a Shimadzu® GCMS-QP2010 Plus Gas Chromatograph Mass Spectrometer utilizing a MEGA® column (MEGA-5, F.T.: 0.25μm, I.D.: 0.25mm, L: 30m, T_{max}: 350 ^{o}C, Column ID# 11475). A Varian® Cary 50 UV-Vis spectrophotometer was used as the light source for the quantum yield measurements and the UV-Vis data. A Scinco® FS-2 fluorescence spectrometer was used for the fluorescence studies. All reactions were performed with commercially available solvents or compounds, without any previous manipulation or purification (e.g. distillation) and under no special conditions, unless otherwise stated. No precaution for oxygen or moisture was taken. <u>*CAUTION:*</u> *Although we did not observe any problems in our reactions, extra caution should be given, since ether peroxides may arise either from the starting material or the reaction mixtures, which could be explosive.*

Optimization of the Reaction Conditions for the Photochemical Reaction of 1-[(Tri*iso*-propylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) with Tetrahydrofuran

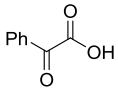
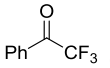
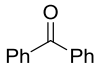
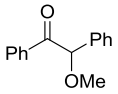
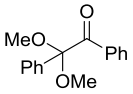
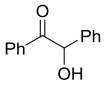


Entry	Solvent	Catalyst Loading (mol%)	Yield (%)[a]
1	THF	30	68
2	**THF**	**20**	**71**
3	THF/Pet. Eth. (1:1)	20	13
4	THF/AcOEt (1:1)	20	8
5	THF/CH_2Cl_2 (1:1)	20	5
6	THF/MeCN (1:1)	20	9
7	THF/toluene (1:1)	20	6
8	THF/$CHCl_3$ (1:1)	20	7
9	THF/H_2O (1:1)	20	12
10	THF	10	traces
11	THF	0	0
12[b]	THF	20	6
13[c]	THF	20	0
14[d]	THF	20	0
15[e]	THF	20	0

[a] Isolated yield. The reaction was performed with TIPS-EBX **1a** (214 mg, 0.50 mmol), phenylglyoxylic acid **4a** (0-30 mol%, 0-0.15 mol) and THF (0.5-1 mL), under household bulb irradiation for 18 h. [b] The reaction was performed in the dark. [c] The reaction mixture was heated at 60 °C for 18 h, under dark conditions. [d] 1 equiv. BHT was added. [e] 1 equiv. TEMPO was added.

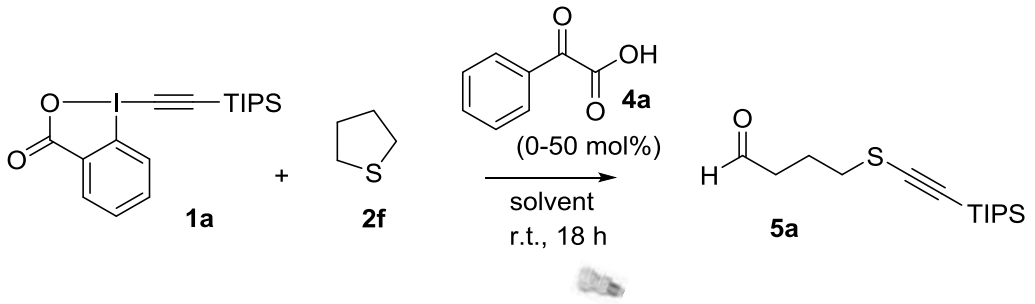


1a + **2a** → **3a**

Entry	Catalyst	Catalyst loading (%)	Yield (%)[a]
1	 **4a** **Phenylglyoxylic acid**	**20**	**71**
2	 **4b** Trifluoromethylacetophenone	20	35
3	 **4c** Benzophenone	20	17
4	 **4d** Methoxy benzoin	20	58
5	 **4e** 2,2-Dimethoxy-2-phenyl-acetophenone	20	50
6	 **4f** Benzoin	20	51
7	$Ru(bpy)_3Cl_2 \cdot 6H_2O$ **4g**	1	0
8	$Ir(ppy)_3$ **4h**	1	0
9	Eosin Y **4i**	20	0

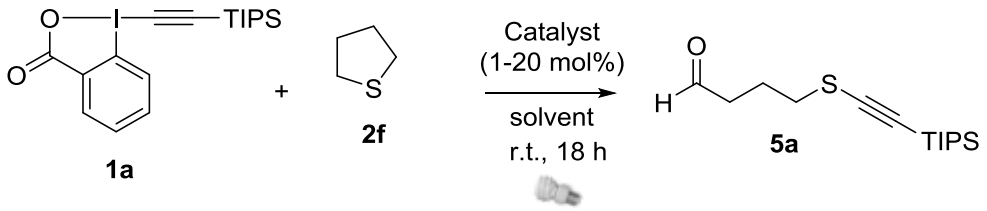
[a] Isolated yield. The reaction was performed with TIPS-EBX **1a** (214 mg, 0.50 mmol), catalyst (1-20 mol%, 0.005-0.1 mol) and THF (1 mL), under household bulb irradiation for 18 h.

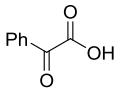
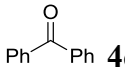
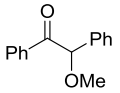
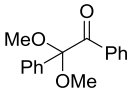
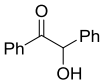
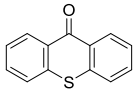
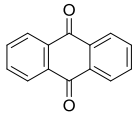
Optimization of the Reaction Conditions for the Photochemical Reaction of 1-[(Tri*iso*-propylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX) with Tetrahydrothiophene



Entry	Solvent	Catalyst Loading (mol%)	Yield (%)[a]
1	THT	20	67
2	THT	50	81
3	THT/Pet. Eth. (1:1)	20	10
4	THT/AcOEt (1:1)	20	5
5	THT/CH_2Cl_2 (1:1)	20	6
6	THT/MeCN (1:1)	20	11
7	THT/toluene (1:1)	20	8
8	THT/$CHCl_3$ (1:1)	20	5
9	**THT/H_2O (1:1)**	**20**	**81**
10	THT	0	15
11[b]	THT/H_2O (1:1)	20	0
12[c]	THT/H_2O (1:1)	20	0
13[d]	THT/H_2O (1:1)	20	0
14[e]	THT/H_2O (1:1)	20	0
15[f]	THT/H_2O (1:1)	20	12
16[g]	THT	20	0

[a] Isolated yield. The reaction was performed with EBX **1a** (214 mg, 0.50 mmol), phenylglyoxylic acid **4a** (0-30 mol%, 0-0.15 mol) and THT **2f** (0.5-1 mL), under household bulb irradiation for 18 h. [b] The reaction was performed in the dark. [c] The reaction mixture was heated at 60 °C for 18 h, under dark conditions. [d] 1 equiv. BHT was added. [e] 1 equiv. TEMPO was added. [f] The reaction was performed under Argon atmosphere. [g] Molecular sieves were added.

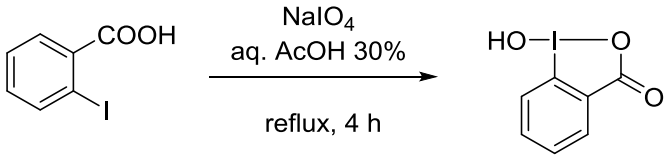


Entry	Catalyst	Catalyst loading (%)	Yield (%)[a]
1	 **4a** **Phenylglyoxylic acid**	**20**	**81**
2	 **4c** Benzophenone	20	59
3	 **4d** Methoxy benzoin	20	51
4	 **4e** 2,2-Dimethoxy-2-phenyl-acetophenone	20	67
5	 **4f** Benzoin	20	0
6	Eosin Y **4i**	20	36
7	 Thioxanthone **4j**	20	69
8	 Anthraquinone **4k**	20	0
9	$Ru(bpy)_3Cl_2 \cdot 6H_2O$ **4g**	1	0
10	$Ir(ppy)_3$ **4h**	1	0

[a] Isolated yield. The reaction was performed with EBX **1a** (214 mg, 0.50 mmol), catalyst (1-20 mol%, 0.005-0.1 mol) and THT/H_2O (1 mL, 1:1), under household bulb irradiation for 18 h.

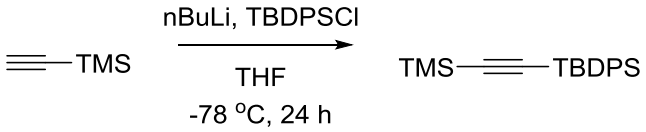
Synthesis of Starting Materials

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



$NaIO_4$ (17.68 g, 83.00 mmol, 1.00 equiv.) and 2-iodobenzoic acid (20.50 g, 83.00 mmol, 1.00 equiv.) were suspended in 30% (v:v) aq. AcOH (48 mL). The reaction mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (109 mL) and allowed to cool to room temperature, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 20 mL) and acetone (3 x 20 mL), and air-dried in the dark to give the pure product (19.30 g, 73.00 mmol, 88%) as a colorless solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.02 (1H, dd, J = 7.5 and 1.4 Hz, ArH), 7.99-7.94 (1H, m, ArH), 7.85 (1H, d, J = 7.5 Hz, ArH), 7.71 (1H, t, J = 7.5, Hz, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 168.3, 135.4, 131.3, 131.0, 129.8, 126.0, 120.2; **MS (ESI) m/z (%)** 265 $[M+H, 75\%]^+$.

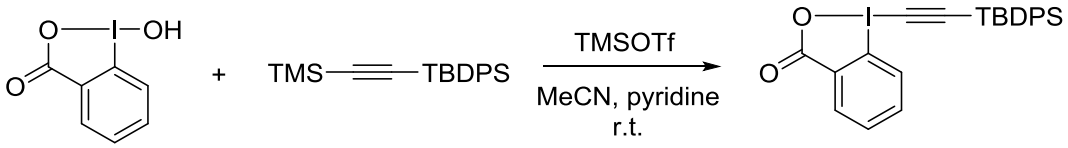
tert-Butyldiphenylsilyl trimethylsilylacetylene[1]



n-Butyllithium (2.5 M in hexanes, 0.5 mL, 5.35 mmol, 0.98 equiv.) was added dropwise to a stirred solution of ethynyltrimethylsilane (0.76 mL, 5.46 mmol, 1.00 equiv.) in THF (7 mL) at -78 °C. The reaction mixture was warmed to 0 °C and stirred for 5 min. The reaction mixture was cooled back to -78 °C and *tert*-butylchlorodiphenylsilane (1.4 mL, 5.46 mmol, 1.00 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. A saturated aqueous solution of ammonium

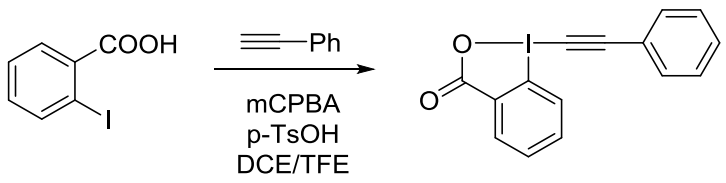
chloride (7 mL) was added, and the reaction mixture was extracted with diethyl ether (2 x 12 mL). The organic layer was washed with water (3 x 20 mL) and brine (3 x 20 mL), then dried over $MgSO_4$, filtered and concentrated under reduced pressure to obtain a colorless liquid, which was further purified by column chromatography (pentane) to yield a colorless liquid (268 mg, 4.37 mmol, 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.86-7.74 (4H, m, ArH), 7.43-7.31 (6H, m, ArH), 1.07 (9H, s, *t*Bu), 0.26 (9H, s, TMS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 135.6, 133.2, 129.4, 127.8, 119.0, 108.6, 27.0, 18.4, 0.1; **MS (ESI) m/z (%)** 337 $[M+H, 70\%]^+$.

1-[(*tert*-Butyldiphenylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (1b)[1]



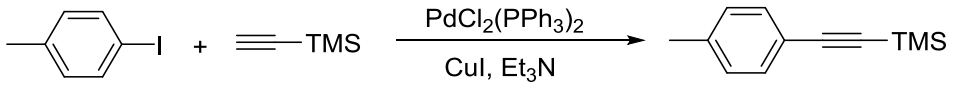
Trimethylsilyltriflate (1.58 mL, 8.70 mmol, 1.10 equiv.) was added dropwise to a stirred solution of 2-iodosylbenzoic acid (2.07 g, 7.90 mmol, 1.00 equiv.) in acetonitrile (30 mL). *tert*-Butyldiphenyl((trimethylsilyl)ethynyl)silane (2.95 g, 3.70 mmol, 1.10 equiv.) was added dropwise, followed, after 15 min, by the addition of pyridine (710 µL, 3.70 mmol, 1.10 equiv.). The reaction mixture was stirred 10 min. The solvent was removed under reduced pressure and the yellow crude oil was dissolved in dichloromethane (20 mL). The organic layer was washed with HCl (1 M, 15 mL) and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (15 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The resulting oil was stirred in hexane (20 mL) and ether (20 mL) and then reduced under vacuum to afford a colorless solid. Recrystallization from acetonitrile (20 mL) afforded a colorless solid (484 mg, 8.26 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.41 (1H, d, J = 7.4 Hz, ArH), 8.25 (1H, d, J = 8.2 Hz, ArH), 7.88 (4H, d, J = 6.6 Hz, ArH), 7.65 (1H, t, J = 7.8 Hz, ArH), 7.55-7.40 (7H, m, ArH), 1.17 (9H, s, *t*Bu); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.5, 135.6, 134.9, 132.6, 131.7, 131.3, 130.3, 128.2, 126.2, 116.0, 112.6, 68.9, 27.0, 18.8; **MS (ESI) m/z (%)** 511 $[M+H, 74\%]^+$.

1-[Phenylethynyl]-1,2-benziodoxol-3(1*H*)-one (Ph-EBX) (1c)[1]



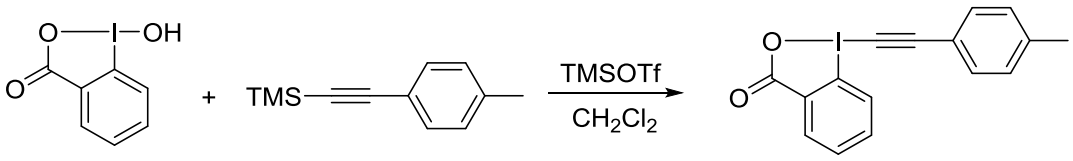
A three-necked flask was charged with 2-iodobenzoic acid (10.00 g, 40.30 mmol), 4-toluenesulfonic acid monohydrate (7.65 g, 40.30 mmol), dichloroethane (60 mL) and trifluoroethanol (60 mL) and stirring was started. 3-Chloroperbenzoic acid (9.88 g, 44.00 mmol, 1.10 equiv.) was added in portions over 10 min, through a funnel. After the addition of *m*CPBA, the flask was placed in an oil bath at 55 ^{o}C and stirred. The reaction mixture turned from a white suspension to a clear yellow color solution during 20 min. After 1.5 h, ethynylbenzene (10.20 g, 12.56 mL, 56.00 mmol) was added via a syringe and stirring was continued for the next 24 hours. After cooling at room temperature, the yellow color solution was transferred to a flask and the reaction flask was rinsed with dichloromethane (20 mL). The reaction mixture was concentrated via rotary evaporation to afford a palle yellow solid. Dichloromethane (200 mL) was added to the pale yellow solid, followed by a saturated aq. solution of $NaHCO_3$ (200 mL), which was added in a 10 min-period. The biphasic mixture was stirred for 1 h. The reaction mixture was transferred to a separatory funnel and was rinsed with dichloromethane (20 mL). The two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (2 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered into a flask and concetrated via rotary evaporation to afford a pale yellow solid. The crude product was purified by recrystallization using acetonitrile (24 mL) to afford a white solid (4.91 g, 14.11 mmol, 35%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.44-8.39 (1H, m, ArH), 8.27-8.22 (1H, m, ArH), 7.79-7.74 (2H, m, ArH), 7.63-7.56 (2H, m, ArH), 7.51-7.41 (3H, m, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.6, 134.9, 132.9, 132.5, 131.6, 131.3, 130.8, 128.8, 126.2, 120.5, 116.1, 106.7, 50.3; **MS (ESI) m/z (%)** 349 $[M+H, 75\%]^{+}$.

(4-Methylphenylethynyl)trimethylsilane[2]



1-Iodo-4-methylbenzene (2.18 g, 10.00 mmol 1.00 equiv.) was dissolved in Et_3N (15 mL). After three freeze-thraw-pump cycles, $PdCl_2(PPh_3)_2$ (0.07 g, 0.10 mmol, 0.01 equiv.) and CuI (0.04 g, 0.20 mmol, 0.02 equiv.) were added under N_2. After the addition of trimethylsilylacetylene (2.2 mL, 15.00 mmol, 1.50 equiv.), the green suspension was stirred at room temperature for 1 h. The reaction solvent was evaporated under vacuum, the mixture was dissolved in dichloroethane (60 mL), washed with 5% aq. EDTA solution (60 mL) and water (60 mL). The organic layers were dried over $MgSO_4$, filtered and evaporated under vacuum. The resulting oil was purified by column chromatography to afford the product (1.78 g, 9.50 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.35 (2H, d, J = 8.1 Hz, ArH), 7.09 (2H, d, J = 8.1 Hz, ArH), 2.33 (3H, s, CH_3), 0.23 (9H, s, TMS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.6, 131.9, 128.9, 120.0, 105.3, 93.2, 21.9, 0.0; **MS (ESI) m/z (%)** 189 $[M+H, 85\%]^+$.

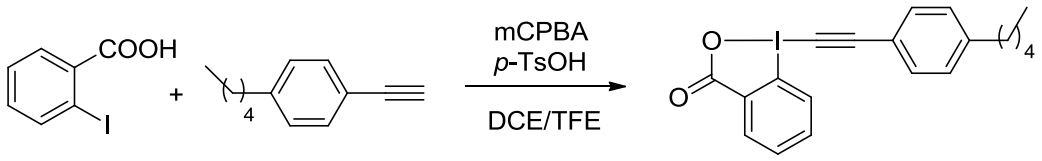
1-[4-Methylphenylethynyl]-1,2-benziodoxol-3(1*H*)-one (1d)[3]



In a 100 mL round-bottomed flask, 2-iodosylbenzoic acid (1.50 g, 5.68 mmol) was placed in dichloromethane (19 mL), giving a white suspension under a nitrogen atmosphere. The flask was cooled with an ice bath and TMSOTf (1.12 mL, 6.25 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 1 h to afford a yellow suspension. Trimethyl(p-tolylethynyl)silane (1.18 g, 6.25 mmol, 1.10 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 6 h. A saturated aq. solution of $NaHCO_3$ (19 mL) was added and the

reaction mixture was stirred for 30 min. The resulting suspension was filtered. The two layers of the filtrate were separated and the aqueous phase was backextracted with dichloromethane (19 mL). The combined organic phases were washed with a saturated aq. solution of $NaHCO_3$ (19 mL), dried over $MgSO_4$, filtered and concentrated under vacuum to afford a yellow solid. The solid obtained by filtration was added and the crude product was recrystallized in acetonitrile (28 mL) to afford a pale yellow solid (1.42 g, 3.92 mmol, 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.45-8.38 (1H, m, ArH), 8.26-8.21 (1H, m, ArH), 7.79-7.73 (2H, m, ArH), 7.49 (2H, d, J = 8.1 Hz, ArH), 7.23 (2H, d, J = 8.1 Hz, ArH), 2.42 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.5, 141.5, 134.8, 132.8, 132.4, 131.5, 129.5, 126.2, 117.4, 116.2, 49.2, 21.7; **MS (ESI) m/z (%)** 363 $[M+H, 77\%]^+$.

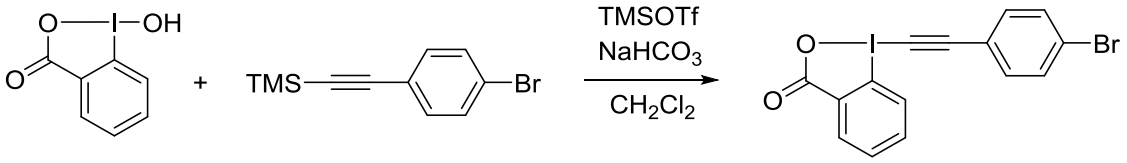
1-((4-Ethylphenyl)ethynyl)-benzo[1,2]iodaoxol-3(1*H*)-one (1e)



In a sealed tube, 2-iodobenzoic acid (1.00 g, 4.00 mmol, 1.00 equiv.), 4-methylbenzenesulfonic acid (0.78 g, 4.00 mmol, 1.00 equiv.) and *m*CPBA (0.99 g, 4.40 mmol, 1.10 equiv.) were suspended in DCE:TFE 1:1 (12 mL) and stirred for 1 h at 55 °C. 1-Ethynyl-4-pentylbenzene (1.08 ml, 5.64 mmol) was added and the reaction mixture was stirred at 55 °C for 24 h. The solvent was evaporated and the residue was redissolved in dichloromethane (20 mL) and stirred vigorously with a saturated aq. solution of $NaHCO_3$ (30 mL). After 1 h, the reaction mixture was transferred into a separating funnel and the layers were separated. The aqueous layer was extracted with dichloromethane (2 x 50 mL). The combined organic layers were washed with a saturated aq. solution of $NaHCO_3$ (50 mL), dried over $MgSO_4$, filtered and concentrated under vacuum. The resulting solid was boiled in MeCN (20 mL), then purified by column chromatography using pure ethyl acetate to afford a pale yellow solid (189 mg, 0.45 mmol, 10 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.45-8.37 (1H, m, ArH), 8.26-8.20 (1H, m, ArH), 7.78-7.70 (2H, m,

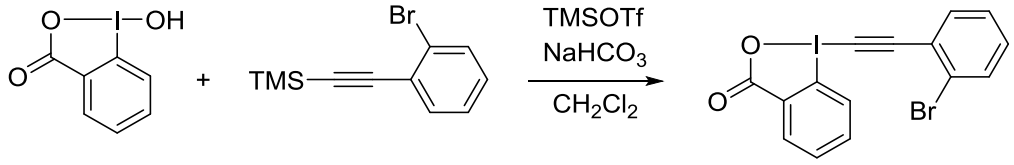
ArH), 7.50 (2H, d, *J* = 8.2 Hz, ArH), 7.23 (2H, d, *J* = 8.2 Hz, ArH), 2.65 (2H, t, *J* = 7.9 Hz, 2 x CH*H*), 1.68-1.56 (2H, m, 2 x CH*H*), 1.38-1.24 (4H, m, 4 x CH*H*), 0.89 (3H, t, *J* = 6.9 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ*: 166.5, 146.5, 134.8, 132.9, 132.5, 131.6, 131.4, 128.9, 126.2, 117.6, 116.2, 107.2, 49.3, 36.0, 31.4, 30.8, 22.4, 14.0; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{20}H_{20}IO_2^+$) requires *m/z* 419.0430, found *m/z* 419.0425.

1-[4-Bromophenylethynyl]-1,2-benziodoxol-3(1*H*)-one (1f)[1]



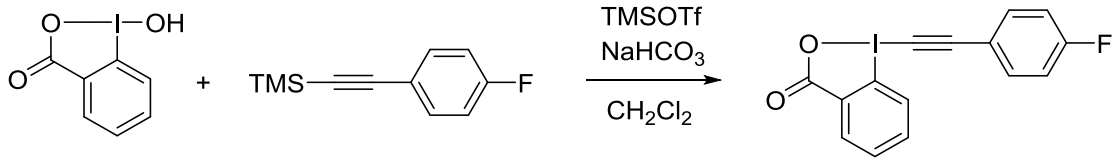
In a 100 mL round-bottomed flask, 2-iodosylbenzoic acid (1.00 g, 3.79 mmol, 1.00 equiv.) was placed in dichloromethane (12 mL), giving a white suspension under a nitrogen atmosphere. The flask was cooled with an ice bath and TMSOTf (0.75 mL, 4.17 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 1 h to afford a yellow suspension. ((4-Bromophenyl)ethynyl)trimethylsilane (1.05 g, 4.17 mmol, 1.10 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 6 h. A saturated aq. solution of $NaHCO_3$ (12 mL) was added and the reaction mixture was stirred for 30 min. The resulting suspension was filtered. The two layers of the filtrate were separated and the aqueous phase was backextracted with dichloromethane (12 mL). The combined organic phases were washed with a saturated aq. solution of $NaHCO_3$ (12 mL), dried over $MgSO_4$, filtered and concentrated under vacuum to afford a yellow solid. The solid obtained by filtration was added and the crude product was recrystallized in acetonitrile (19 mL) to afford a pale yellow solid (1.60 g, 3.75 mmol, 99%). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*: 8.44-8.40 (1H, m, ArH), 8.23-8.19 (1H, m, ArH), 7.80-7.74 (2H, m, ArH), 7.58 (2H, d, *J* = 8.5 Hz, ArH), 7.45 (2H, d, *J* = 8.5 Hz, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ*: 166.5, 135.0, 134.1, 132.5, 132.1, 131.8, 131.3, 126.2, 125.5, 119.4, 116.4, 105.2, 52.0; **MS (ESI) m/z (%)** 427 $[M+H, 79\%]^+$.

1-[2-Bromophenylethynyl]-1,2-benziodoxol-3(1*H*)-one (1g)[1]



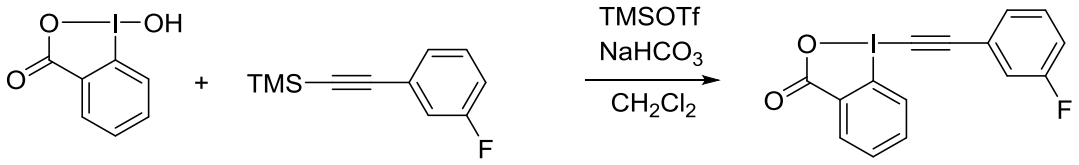
In a 100 mL round-bottomed flask, 2-iodosylbenzoic acid (1.00 g, 3.79 mmol, 1.00 equiv.) was placed in dichloromethane (12 mL), giving a white suspension under a nitrogen atmosphere. The flask was cooled with an ice bath and TMSOTf (0.75 mL, 4.17 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 1 h to afford a yellow suspension. ((4-Bromophenyl)ethynyl)trimethylsilane (1.05 g, 4.17 mmol, 1.10 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 6 h. A saturated aq. solution of $NaHCO_3$ (12 mL) was added and the reaction mixture stirred for 30 min. The resulting suspension was filtered. The two layers of the filtrate were separated and the aqueous phase was backextracted with dichloromethane (12 mL). The combined organic phases were washed with a saturated aq. solution of $NaHCO_3$ (12 mL), dried over $MgSO_4$, filtered and concentrated under vacuum to afford a yellow solid. The solid obtained by filtration was added and the crude product was recrystallized in acetonitrile (19 mL) to afford a pale yellow solid (1.25 g, 2.92 mmol, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.46-8.40 (2H, m, ArH), 7.82-7.75 (2H, m, ArH), 7.70-7.65 (1H, m, ArH), 7.63-7.53 (1H, m, ArH), 7.42-7.28 (2H, m, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.5, 135.0, 134.6, 132.8, 132.5, 131.7, 131.2, 127.4, 126.6, 126.3, 123.1, 116.3, 104.1, 55.3; **MS (ESI) m/z (%)** 427 $[M+H, 78\%]^+$.

1-[4-Fluorophenylethynyl]-1,2-benziodoxol-3(1*H*)-one (1h)[4]



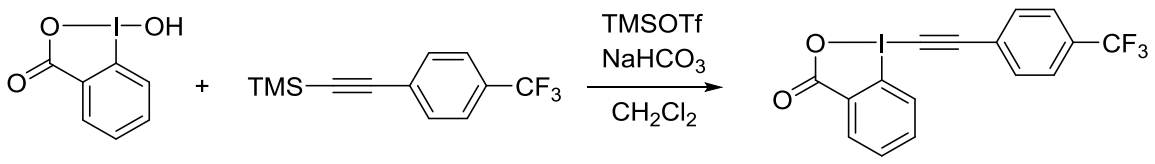
In a 100 mL round-bottomed flask, 2-iodosylbenzoic acid (1.00 g, 3.79 mmol, 1.00 equiv.) was placed in dichloromethane (12 mL), giving a white suspension under a nitrogen atmosphere. The flask was cooled with an ice bath and TMSOTf (0.75 mL, 4.17 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 1 h to afford a yellow suspension. ((4-Fluorophenyl)ethynyl)trimethylsilane (0.80 g, 0.85 mL, 4.17 mmol, 1.10 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 6 h. A saturated aq. solution of $NaHCO_3$ (12 mL) was added and the mixture stirred for 30 min. The resulting suspension was filtered. The two layers of the filtrate were separated and the aqueous phase was backextracted with dichloromethane (12 mL). The combined organic phases were washed with a saturated aq. solution of $NaHCO_3$ (12 mL), dried over $MgSO_4$, filtered and concentrated under vacuum to afford a yellow solid. The solid obtained by filtration was added and the crude product was recrystallized in acetonitrile (19 mL) to afford a white solid (1.18 g, 3.22 mmol, 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.45-8.40 (1H, m, ArH), 8.24-8.20 (1H, m, ArH), 7.80-7.74 (2H, m, ArH), 7.63-7.56 (2H, m, ArH), 7.17-7.08 (2H, m, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.6, 163.8 (d, J = 253.8 Hz), 135.1 (d, J = 8.8 Hz), 134.9, 132.4, 131.6, 131.4, 126.3, 116.7 (d, J = 3.5 Hz), 116.3, 116.2 (d, J = 22.3 Hz), 105.3, 50.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -105.8; **MS (ESI) m/z (%)** 367 $[M+H, 67\%]^+$.

1-[3-Fluorophenylethynyl]-1,2-benziodoxol-3(1*H*)-one (1i)



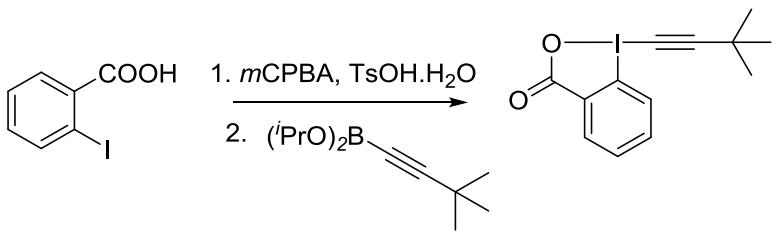
In a 100 mL round-bottomed flask, 2-iodosylbenzoic acid (1.00 g, 3.79 mmol, 1.00 equiv.) was placed in dichloromethane (12 mL), giving a white suspension under a nitrogen atmosphere. The flask was cooled with an ice bath and TMSOTf (0.75 mL, 4.17 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 1 h to afford a yellow suspension. ((4-Fluorophenyl)ethynyl)trimethylsilane (0.80 g, 0.85 mL, 4.17 mmol, 1.10 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 6 h. A saturated aq. solution of $NaHCO_3$ (12 mL) was added and the reaction mixture stirred for 30 min. The resulting suspension was filtered. The two layers of the filtrate were separated and the aqueous phase was backextracted with dichloromethane (12 mL). The combined organic phases were washed with a saturated aq. solution of $NaHCO_3$ (12 mL), dried over $MgSO_4$, filtered and concentrated under vacuum to afford a yellow solid. The solid obtained by filtration was added and the crude product was recrystallized in acetonitrile (19 mL) to afford a pale yellow solid (963 mg, 2.65 mmol, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.46-8.39 (1H, m, ArH), 8.25-8.19 (1H, m, ArH), 7.81-7.75 (2H, m, ArH), 7.43-7.37 (2H, m, ArH), 7.31-7.27 (1H, m, ArH), 7.22-7.17 (1H, m, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.4, 162.3 (d, J = 247.4 Hz), 135.0, 132.6, 131.7, 131.1, 130.5 (d, J = 8.5 Hz), 128.8, 126.2, 122.3 (d, J = 9.2 Hz), 119.6 (d, J = 23.2 Hz), 118.3 (d, J = 21.2 Hz), 116.1, 104.7, 52.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -111.2; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{15}H_9FIO_2^+$) requires *m/z* 366.9553, found *m/z* 366.9557.

1-[4-Trifluoromethylphenylethynyl]-1,2-benziodoxol-3(1*H*)-one (1j)[1]



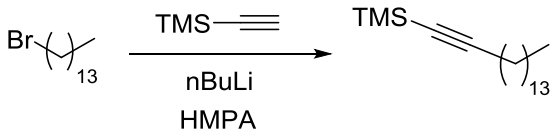
In a 100 mL round-bottomed flask, 2-iodosylbenzoic acid (1.00 g, 3.79 mmol, 1.00 equiv.) was placed in dichloromethane (12 mL), giving a white suspension under a nitrogen atmosphere. The flask was cooled with an ice bath and TMSOTf (0.75 mL, 4.17 mmol, 1.10 equiv.) was added dropwise. The reaction mixture was warmed up to room temperature and stirred for 1 h to afford a yellow suspension. Trimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane (0.98 mL, 4.17 mmol, 1.10 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 6 h. A saturated aq. solution of $NaHCO_3$ (12 mL) was added and the reaction mixture stirred for 30 min. The resulting suspension was filtered. The two layers of the filtrate were separated and the aqueous phase was backextracted with dichloromethane (12 mL). The combined organic phases were washed with a saturated aq. solution of $NaHCO_3$ (12 mL), dried over $MgSO_4$, filtered and concentrated under vacuum to afford a yellow solid. The solid obtained by filtration was added and the crude product was recrystallized in acetonitrile (19 mL) to afford a white solid (725 mg, 1.74 mmol, 46%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.44-8.40 (1H, m, ArH), 8.25-8.20 (1H, m, ArH), 7.80-7.75 (2H, m, ArH), 7.72-7.67 (4H, m, ArH); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.6, 135.1, 133.1, 132.6, 132.3 (q, J = 33.0 Hz), 131.8, 131.2, 126.2, 125.7 (q, J = 3.5 Hz), 124.3, 123.5 (q, J = 272.4 Hz), 116.1, 104.3, 53.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -63.1; **MS (ESI) m/z (%)** 417 [M+H, 67%]$^+$.

3,3-Dimethylbutynyl-1,2-benziodoxol-3(1*H*)-one (1k)[1]



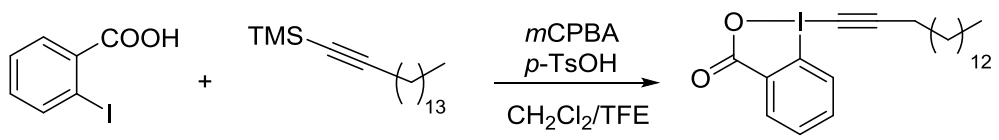
2-Iodobenzoic acid (0.50 g, 2.02 mmol, 1.00 equiv.), *para*-toluenesulfonic acid monohydrate (0.38 g, 2.02 mmol, 1.00 equiv.) and *meta*-chloroperoxybenzoic acid (0.38 g, 2.22 mmol, 1.10 equiv.) were dissolved in dichloromethane (4 mL) and 2,2,2-trifluoroethanol (4 mL). The reaction mixture was stirred at room temperature under nitrogen for 1 hour, after which diisopropyl (3,3-dimethylbut-1-yn-1-yl)boronate (0.59 g, 2.82 mmol, 1.40 equiv.) was added in one portion. The reaction mixture was stirred for 1 hour at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (40 mL) and under vigorous stirring a saturated aq. $NaHCO_3$ (40 mL) was added. The reaction mixture was stirred for 1 h, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford a white solid (530 mg, 1.66 mmol, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.42-8.37 (1H, m, ArH), 8.14-8.09 (1H, m, ArH), 7.77-7.71 (2H, m, ArH), 1.37 (9H, s, 3 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.5, 134.6, 132.4, 131.4, 131.4, 125.8, 117.5, 115.6, 38.2, 30.6, 29.6; **MS (ESI) m/z (%)** 329 [M+H, 77%]$^+$

Hexadec-1-yn-1-yltrimethylsilane[1]



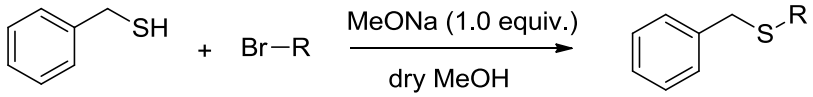
To a solution of trimethylsilylacetylene (1.19 g, 12.07 mmol, 1.20 equiv.) in dry THF (6.5 mL) at -78 °C under nitrogen, nBuLi 2.5 M in hexanes (1.12 mL, 12.07 mmol, 1.20 equiv.) was added over a 10 minute-time period. The resulting light yellow solution was stirred at -78 °C for 1 h, after which a solution of 1-bromotetradecane (3 mL, 2.80 g, 10.06 mmol, 1.00 equiv.), hexamethylphosphoramide (HMPA, 1.9 mL, 11.07 mmol, 1.10 equiv.) in dry THF (3.2 mL) was slowly added via cannula over a 20 minute-time period. The reaction mixture was stirred for 1 h at -78 °C, followed by stirring at room temperature for 24 h. The reaction mixture was quenched at 0 °C with saturated aq. NH_4Cl (7 mL) and diluted with water (2 mL) and EtOAc (7 mL). The two layers were separated and the aqueous layer was extracted with additional portions of EtOAc (3 x 10 mL). The combined organic layers were washed with water (2 x 20 mL), brine (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The light brown crude liquid was finally pushed through a small plug of silica gel with pentane as eluent to afford pure hexadec-1-yn-1-yltrimethylsilane (3.32 g, 11.35 mmol, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.19 (2H, t, J = 7.2 Hz, 2 x CH*H*), 1.53-1.44 (2H, m, 2 x CH*H*), 1.38-1.23 (22H, m, 22 x CH*H*), 0.86 (3H, t, J = 6.8 Hz, CH_3), 0.13 (9H, s, TMS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 107.8, 84.2, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 28.8, 28.6, 22.7, 29.9, 14.1, 0.2; **MS (ESI) m/z (%)** 295 $[M+H, 87\%]^+$.

Hexadecynyl-1,2-benziodoxol-3(1*H*)-one (1l)[1]



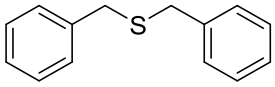
2-Iodobenzoic acid (1.80 g, 7.30 mmol, 1.00 equiv.), *para*-toluenesulfonic acid monohydrate (1.38 g, 7.30 mmol, 1.00 equiv.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 1.38 g, 8.00 mmol, 1.10 equiv.) were dissolved in dichloromethane (15 mL) and 2,2,2-trifluoroethanol (15 mL). The reaction mixture was stirred at room temperature under nitrogen for 1 hour, after which hexadec-1-yn-1-yltrimethylsilane (3 g, 10.20 mmol, 1.40 equiv.) was added in one portion. The reaction mixture was stirred for 14 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (100 mL) and was stirred for 1 h, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford a white solid (1.26 g, 2.70 mmol, 37%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.43-8.35 (1H, m, ArH), 8.22-8.12 (1H, m, ArH), 7.79-7.69 (2H, m, ArH), 2.59 (2H, t, J = 7.1 Hz, 2 x CH*H*), 1.69-1.59 (2H, m, 2 x CH*H*), 1.50-1.17 (22H, m, 22 x CH*H*), 0.87 (3H, t, J = 6.8 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 166.5, 134.6, 132.4, 131.5, 131.4, 126.1, 115.5, 109.8, 39.2, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 29.9, 14.1; **MS (ESI) m/z (%)** 469 $[M+H, 88\%]^+$.

General Procedure for the Synthesis of Benzyl Sulfides[5]



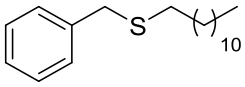
Benzyl mercaptan (1.07 g, 5.00 mmol, 1.00 equiv.) or thiol (for naturally-occurring compounds, 5.00 mmol, 1.00 equiv.) was dissolved in dry methanol (10 mL). Sodium methoxide (270 mg, 5.00 mmol, 1.00 equiv.) was added and the reaction mixture was left stirring at -10 ^{o}C for 10 min. Alkyl or benzyl bromide (5.50 mmol, 1.10 equiv.) was added dropwise and the reaction mixture was left stirring at room temperature for 2-24 h. The reaction mixture was concentrated *in vacuo*. The resulting oil was dissolved in ethyl acetate (20 mL) and washed with water (3 x 25 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (petr. ether) to afford the desired benzyl sulfide.

Dibenzylsulfide[6]



Colorless viscous oil (96%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.26-7.14 (10H, m, ArH), 3.55 (4H, s, 2 x SCH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.3, 129.5, 128.6, 126.8, 35.7; **MS (ESI) m/z (%)** 215 $[M+H, 75\%]^{+}$.

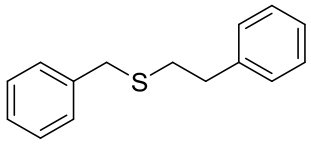
Benzyldodecylsulfide[7]



Colorless viscous oil (92%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36-7.24 (5H, m, ArH), 3.70 (2H, s, SCH_2), 2.40 (2H, t, J = 7.0 Hz, SCH_2), 1.61-1.55 (2H, m, 2 x CH*H*), 1.38-1.25 (18H, m, 18 x CH*H*), 0.90-0.81 (3H, m, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:

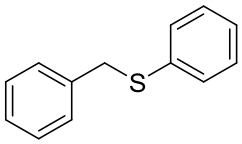
138.5, 128.6, 128.4, 126.9, 36.4, 31.9, 31.4, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7, 22.8, 14.1; **MS (ESI) m/z (%)** 293 $[M+H, 73\%]^+$.

Benzyl(phenethyl)sulfide[8]



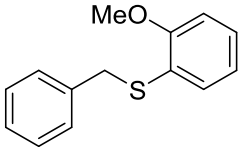
Colorless viscous oil (89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31-7.14 (10H, m, ArH), 3.71 (2H, s, SCH_2), 2.80 (2H, t, J = 7.0 Hz, $PhCH_2$), 2.65 (2H, t, J = 7.0 Hz, SCH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 139.5, 138.1, 128.9, 128.7, 128.4, 128.1, 126.9, 126.3, 36.4, 35.9, 31.4; **MS (ESI) m/z (%)** 293 $[M+H, 58\%]^+$.

Benzyl(phenyl)sulfide[9]



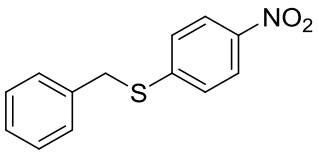
Colorless solid (81%); m.p.: 50-52 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.11-7.04 (10H, m, ArH), 4.01 (2H, s, SCH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 137.2, 136.7, 129.6, 128.8, 128.5, 128.2, 127.1, 126.2, 39.1; **MS (ESI) m/z (%)** 201 $[M+H, 63\%]^+$.

Benzyl(2-methoxyphenyl)sulfide[10]



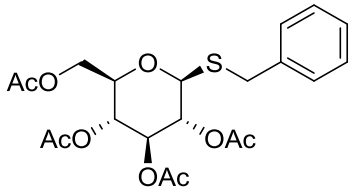
Colorless solid (75%); m.p.: 88-90 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.31-7.24 (7H, m, ArH), 7.01-6-85 (2H, m, ArH), 4.00 (2H, s, SCH_2), 3.75 (3H, s, OCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 158.9, 138.2, 134.1, 128.8, 128.1, 126.9, 126.2, 114.5, 55.5, 41.0; **MS (ESI) m/z (%)** 231 $[M+H, 83\%]^+$.

Benzyl(4-nitrophenyl)sulfide[11]



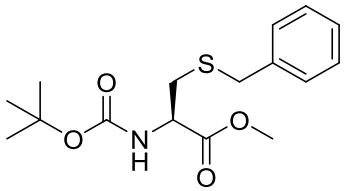
Pale yellow solid 68%); m.p.: 97-99 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.21-8.04 (2H, m, ArH), 7.41-6-25 (7H, m, ArH), 4.20 (2H, s, SCH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.1, 145.5, 135.2, 128.9, 128.8, 127.8, 126.5, 124.1, 37.1; **MS (ESI) m/z (%)** 246 $[M+H, 76\%]^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(Acetoxymethyl)-6-(benzylthio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate[12]



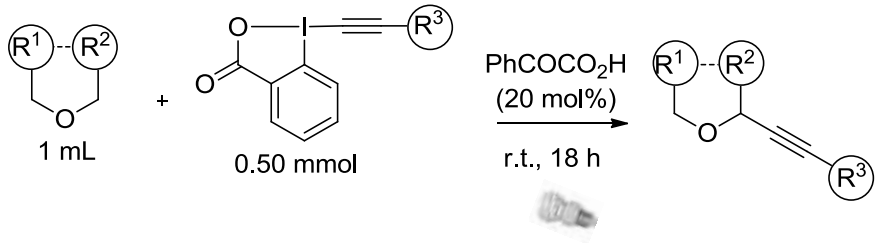
White solid (73%); m.p.: 97-99 ^{o}C; $[\alpha]^{26}_{D}$ -110.0 (c 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.28-7.25 (5H, m, ArH), 5.17-5.00 (3H, m, 3 x OCH), 4.27 (1H, d, J = 8.7 Hz, OCH), 4.23 (1H, dd, J = 12.5 and 5.0 Hz, OC*H*H), 4.10 (1H, dd, J = 12.5 and 2.4 Hz, OCH*H*), 3.92 (1H, d, J = 12.9 Hz, SC*H*H), 3.80 (1H, d, J = 12.9 Hz, SCH*H*), 3.60-3.52 (1H, m, OCH), 2.09 (3H, s, CH_3), 1.99 (6H, s, 2 x CH_3), 1.97 (3H, s, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.5, 170.1, 169.4, 169.3, 136.7, 129.0, 128.6, 127.4, 81.9, 75.6, 73.8, 69.7, 68.3, 62.1, 33.7, 20.7, 20.6, 20.5, 20.4; **MS (ESI) m/z (%)** 455 $[M+H, 81\%]^+$.

Methyl (*S*)-benzyl-*N*-(*tert*-butoxycarbonyl)-*L*-cysteinate[13]



Viscous colorless oil (82%); $[\alpha]^{26}_{D}$ -2.0 (c 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.28-7.22 (5H, m, ArH), 5.35 (1H, br s, NH), 4.49 (1H, d, J = 6.4 Hz, NCH), 3.68 (2H, s, $PhCH_2$), 3.67 (3H, s, OCH_3), 2.88-2.69 (2H, m, SCH_2), 1.42 (9H, s, 3 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 171.4, 154.9, 137.4, 128.7, 128.3, 127.0, 79.8, 52.8, 52.3, 36.3, 33.2, 28.0; **MS (ESI) m/z (%)** 326 $[M+H, 72\%]^+$.

General Procedure for the Photochemical Reaction of Substituted Tetrahydrofurans with EthynylBenziodoXolone (EBX) Reagents



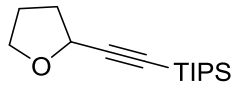
In a glass vial with a screw cap containing ethynylbenziodoxolone (EBX) reagent (0.50 mmol) in heterocycle (1 mL), phenylglyoxylic acid (15 mg, 0.10 mmol) was added. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 85W household lamps, see photos below) for 18 h. The solvent was removed *in vacuo* and the desired product was isolated after purification by column chromatography. *CAUTION: Although we did not observe any problems in our reactions, extra caution should be given since ether peroxides may arise in the reaction mixtures, which could be explosive.*

A

B

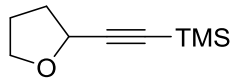
Scheme. **A**: 2 x 85W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

Triisopropyl((tetrahydrofuran-2-yl)ethynyl)silane (3a)[1]



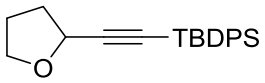
Pale yellow oil (71%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 4.65-4.55 (1H, m, OCH), 4.01-3.73 (2H, m, 2 x OCH*H*), 2.20-1.77 (4H, m, 4 x CH*H*), 1.04 (21H, s, TIPS); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 107.7, 85.0, 68.5, 67.5, 33.6, 25.1, 18.5, 11.1; **MS (ESI) m/z (%)** 253 $[M+H, 34\%]^+$.

Trimethyl((tetrahydrofuran-2-yl)ethynyl)silane (3b)[14]



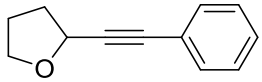
Colorless oil (67%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.44-4.36 (1H, m, OCH), 3.83-3.74 (1H, m, OCH*H*), 3.66-3.60 (1H, m, OCH*H*), 2.01-1.67 (4H, m, 4 x CH*H*), 0.00 (9H, s, TMS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 105.5, 89.0, 68.4, 67.9, 33.3, 25.4, 0.1; **MS (ESI) m/z (%)** 169 $[M+H, 54\%]^+$.

***tert*-Butyldiphenyl((tetrahydrofuran-2-yl)ethynyl)silane (3c)**



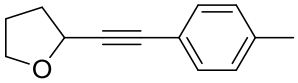
Pale yellow oil (75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.74-7.68 (4H, m, ArH), 7.35-7.27 (6H, m, ArH), 4.72-4.66 (1H, m, OCH), 4.00-3.92 (1H, m, OCH*H*), 3.86-3.78 (1H, m, OCH*H*), 2.20-2.12 (1H, m, CH*H*), 2.09-2.01 (2H, m, 2 x CH*H*), 1.94-1.83 (1H, m, CH*H*), 1.01 (9H, s, 3 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 135.6, 133.2, 129.5, 127.7, 110.1, 84.2, 68.7, 67.8, 33.9, 27.0, 25.3, 18.5; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{22}H_{27}OSi^+$) requires *m/z* 335.1826, found *m/z* 335.1829.

2-(Phenylethynyl)tetrahydrofuran (3d)[15]



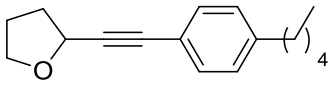
Yellow oil (71%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.47-7.37 (2H, m, ArH), 7.33-7.23 (3H, m, ArH), 4.86-4.75 (1H, m, OCH), 4.08-3.95 (1H, m, OCH*H*), 3.90-3.78 (1H, m, OCH*H*), 2.26-1.88 (4H, m, 2 x CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 131.7, 128.2, 128.1, 122.8, 89.0, 84.4, 68.6, 67.9, 33.4, 25.5; **MS (ESI) m/z (%)** 173 $[M+H, 71\%]^+$.

2-(4-Tolylethynyl)tetrahydrofuran (3e)[15]



Yellow oil (73%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.25 (2H, d, J = 8.1 Hz, ArH), 7.02 (2H, d, J = 8.1 Hz, ArH), 4.78-4.69 (1H, m, OCH), 3.99-3.89 (1H, m, OCH*H*), 3.82-3.73 (1H, m, OCH*H*), 2.26 (3H, s, CH_3), 2.19-2.09 (1H, m, CH*H*), 2.05-1.95 (2H, m, 2 x CH*H*), 1.91-1.82 (1H, m, CH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 138.3, 131.6, 128.9, 119.7, 88.3, 84.6, 68.6, 67.9, 33.4, 25.5, 21.4; **MS (ESI) m/z (%)** 187 $[M+H, 73\%]^+$.

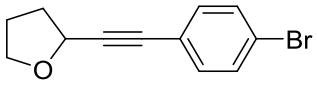
2-((4-Pentylphenyl)ethynyl)tetrahydrofuran (3f)[16]



Colorless oil (77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.27 (2H, d, J = 8.1 Hz, ArH), 7.03 (2H, d, J = 8.1 Hz, ArH), 4.78-4.70 (1H, m, OCH), 3.99-3.90 (1H, m, OCH*H*), 3.84-3.76 (1H, m, OCH*H*), 2.51 (2H, t, J = 7.6 Hz, $PhCH_2$), 2.21-2.10 (1H, m, CH*H*), 2.07-1.95 (2H, m, 2 x CH*H*), 1.92-1.82 (1H, m, CH*H*), 1.59-1.46 (2H, m, 2 x CH*H*), 1.30-1.16 (4H, m, 4 x CH*H*), 0.81 (3H, t, J = 6.9 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 143.4,

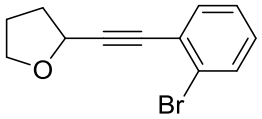
131.6, 128.3, 119.9, 88.3, 84.6, 68.7, 67.9, 35.8, 33.4, 31.4, 30.9, 25.5, 22.9, 14.0; **MS (ESI) m/z (%)** 243 $[M+H, 63\%]^+$.

2-((4-Bromophenyl)ethynyl)tetrahydrofuran (3g)[17]



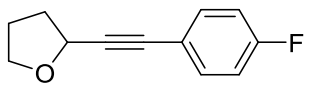
Yellow oil (60%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.36 (2H, d, J = 8.4 Hz, ArH), 7.22 (2H, d, J = 8.4 Hz, ArH), 4.76-4.68 (1H, m, OCH), 3.98-3.89 (1H, m, OCH*H*), 3.83-3.76 (1H, m, OCH*H*), 2.23-2.11 (1H, m, CH*H*), 2.05-1.98 (2H, m, 2 x CH*H*), 1.93-1.82 (1H, m, CH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 133.1, 131.5, 122.5, 121.7, 90.3, 83.4, 68.5, 68.0, 33.3, 25.5; **MS (ESI) m/z (%)** 251 $[M+H, 70\%]^+$.

2-((2-Bromophenyl)ethynyl)tetrahydrofuran (3h)[16]



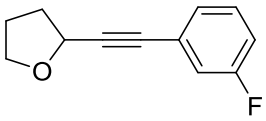
Yellow oil (55%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.55-7.45 (1H, m, ArH), 7.43-7.37 (1H, m, ArH), 7.18-7.15 (1H, m, ArH), 7.13-7.06 (1H, m, ArH), 4.85-4.78 (1H, m, OCH), 4.02-3.93 (1H, m, OCH*H*), 3.86-3.78 (1H, m, OCH*H*), 2.23-2.14 (1H, m, CH*H*), 2.11-2.04 (2H, m, 2 x CH*H*), 1.95-1.85 (1H, m, CH*H*); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 133.4, 132.3, 129.4, 126.9, 125.7, 124.9, 93.9, 83.0, 68.6, 67.9, 33.3, 25.3; **MS (ESI) m/z (%)** 251 $[M+H, 71\%]^+$.

2-((4-Fluorophenyl)ethynyl)tetrahydrofuran (3i)[18]



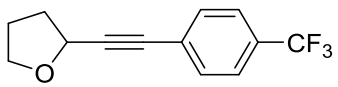
Pale yellow oil (61%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.38-7.30 (2H, m, ArH), 6.92 (2H, t, J = 8.7 Hz, ArH), 4.75-4.68 (1H, m, OCH), 3.96-3.91 (1H, m, OCH*H*), 3.84-3.74 (1H, m, OCH*H*), 2.21-2.11 (1H, m, CH*H*), 2.06-1.96 (2H, m, 2 x CH*H*), 1.91-1.84 (1H, m, CH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 162.5 (d, J = 249.3 Hz), 133.6 (d, J = 8.4 Hz), 118.9 (d, J = 3.4 Hz), 115.5 (d, J = 22.0 Hz), 88.7, 83.4, 68.5, 68.0, 33.4, 25.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -111.1; **MS (ESI) m/z (%)** 191 $[M+H, 80\%]^+$.

2-((3-Fluorophenyl)ethynyl)tetrahydrofuran (3j)[19]



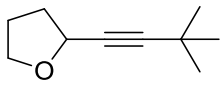
Pale yellow oil (55%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.18-7.11 (2H, m, ArH), 7.08-7.02 (1H, m, ArH), 6.97-6.90 (1H, m, ArH), 4.77-4.70 (1H, m, OCH), 3.98-3.90 (1H, m, OCH*H*), 3.84-3.76 (1H, m, OCH*H*), 2.22-2.12 (1H, m, CH*H*), 2.08-1.97 (2H, m, 2 x CH*H*), 1.93-1.84 (1H, m, CH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 162.3 (d, J = 246.3 Hz), 129.8 (d, J = 8.6 Hz), 127.6 (d, J = 3.0 Hz), 124.6 (d, J = 9.5 Hz), 118.5 (d, J = 22.8 Hz), 115.6 (d, J = 21.2 Hz), 90.1, 83.3, 68.5, 68.0, 33.3, 25.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -113.1; **MS (ESI) m/z (%)** 191 $[M+H, 72\%]^+$.

2-((4-(Trifluoromethyl)phenyl)ethynyl)tetrahydrofuran (3k)[17]



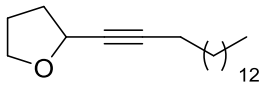
Yellow oil (58%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.62-7.52 (4H, m, ArH), 4.87-4.79 (1H, m, OCH), 4.08-3.99 (1H, m, OCH*H*), 3.95-3.84 (1H, m, OCH*H*), 2.33-2.21 (1H, m, CH*H*), 2.16-2.07 (2H, m, 2 x CH*H*), 2.04-1.93 (1H, m, CH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 131.9, 130.0 (q, J = 32.6 Hz), 126.6, 125.1 (q, J = 3.7 Hz), 123.9 (q, J = 272.1 Hz), 91.6, 83.1, 68.4, 68.1, 33.3, 25.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ: -63.0; **MS (ESI) m/z (%)** 241 $[M+H, 62\%]^+$.

2-(3,3-Dimethylbut-1-yn-1-yl)tetrahydrofuran (3l)



Yellow oil (54%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 4.50-4.43 (1H, m, OCH), 3.92-3.83 (1H, m, OCH*H*), 3.74-3.66 (1H, m, OCH*H*), 2.10-1.99 (1H, m, CH*H*), 1.98-1.89 (1H, m, CH*H*), 1.86-1.76 (2H, m, 2 x CH*H*), 1.14 (9H, s, 3 x CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 93.4, 78.2, 68.4, 67.6, 33.6, 31.0, 27.3, 25.3; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{10}H_{17}O^+$) requires *m/z* 153.1274, found *m/z* 153.1278.

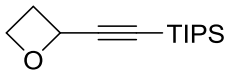
2-(Hexadec-1-yn-1-yl)tetrahydrofuran (3m)



Colorless oil (68%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.53-4.46 (1H, m, OCH), 3.92-3.85 (1H, m, OCH*H*), 3.74-3.69 (1H, m, OCH*H*), 2.12 (2H, t, J = 7.1 Hz, 2 x CH*H*), 2.09-2.01 (1H, m, CH*H*), 1.99-1.91 (1H, m, CH*H*), 1.88-1.77 (2H, m, 2 x CH*H*), 1.46-1.37 (2H, m,

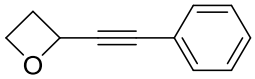
2 x CH*H*), 1.25-1.12 (22H, m, 22 x CH*H*), 0.81 (3H, t, *J* = 6.8 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ*: 85.3, 79.9, 68.4, 67.6, 33.5, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.1, 28.9, 28.6, 25.4, 22.7, 18.8, 14.1; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{20}H_{37}O^+$) requires *m/z* 293.2839, found *m/z* 293.2835.

Triisopropyl(oxetan-2-ylethynyl)silane (3n)



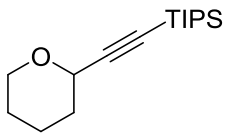
Colorless oil (77%); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*: 5.41-5.32 (1H, m, OCH), 4.72-4.61 (2H, m, 2 x OCH*H*), 3.03-2.92 (1H, m, CH*H*), 2.83-2.71 (1H, m, CH*H*), 1.10 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ*: 107.2, 89.7, 70.3, 68.9, 30.1, 18.6, 11.1; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{14}H_{27}OSi^+$) requires *m/z* 239.1826, found *m/z* 239.1829.

2-(Phenylethynyl)oxetane (3o)[20]



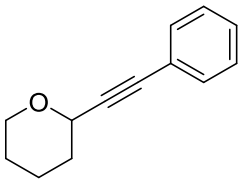
Colorless oil (75%); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ*: 7.53-7.44 (2H, m, ArH), 7.40-7.32 (3H, m, ArH), 5.64-5.56 (1H, m, OCH), 4.77-4.68 (2H, m, 2 x OCH*H*), 3.09-3.00 (1H, m, CH*H*), 2.97-2.89 (1H, m, CH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ*: 131.7, 128.6, 128.3, 122.4, 88.7, 88.5, 70.4, 69.0, 29.8; **MS (ESI) m/z (%)** 159 $[M+H, 55\%]^+$.

Triisopropyl((tetrahydro-2*H*-pyran-2-yl)ethynyl)silane (3p)[1]



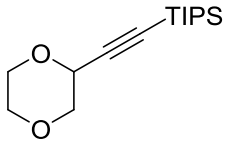
Pale yellow oil (40%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.44-4.35 (1H, m, OCH), 4.05-3.91 (1H, m, OCH*H*), 3.60-3.48 (1H, m, OCH*H*), 1.94-1.77 (2H, m, 2 x CH*H*), 1.65-1.45 (4H, m, 4 x CH*H*), 1.05 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 106.3, 86.2, 66.9, 65.6, 32.1, 25.7, 21.1, 19.0, 11.1; **MS (ESI) m/z (%)** 267 $[M+H, 78\%]^+$.

2-(Phenylethynyl)tetrahydro-2*H*-pyran (3q)[16]



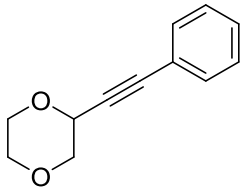
Yellow oil (46%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.51-7.38 (2H, m, ArH), 7.34-7.21 (3H, m, ArH), 4.57-4.44 (1H, m, OCH), 4.13-3.96 (1H, m, OCH*H*), 3.66-3.49 (1H, m, OCH*H*), 2.04-1.48 (6H, m, 6 x CH*H*); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 131.7, 128.3, 128.2, 122.7, 88.1, 85.2, 67.4, 66.7, 32.2, 25.7, 21.8; **MS (ESI) m/z (%)** 287 $[M+H, 88\%]^+$.

((1,4-Dioxan-2-yl)ethynyl)triisopropylsilane (3r)



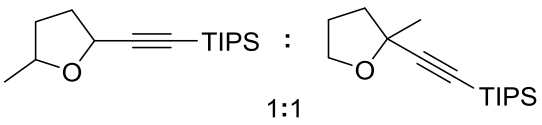
Colorless oil (74%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 4.42-4.29 (1H, m, OCH), 3.92-3.74 (2H, m, 2 x OCH*H*), 3.70-3.55 (4H, m, 4 x OCH*H*), 1.05 (21H, s, TIPS); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 102.5, 87.9, 70.5, 66.5, 66.3, 65.6, 18.5, 11.0; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{15}H_{29}O_2Si^+$) requires *m/z* 269.1931, found *m/z* 269.1935.

2-(Phenylethynyl)-1,4-dioxane (3s)[17]



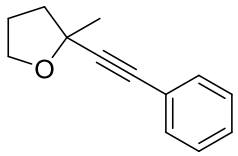
Yellow oil (54%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.50-7.39 (2H, m, ArH), 7.35-7.22 (3H, m, ArH), 4.61-4.50 (1H, m, OCH), 3.99-3.85 (2H, m, 2 x OCH*H*), 3.78-3.63 (4H, m, 4 x OCH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 131.9, 128.7, 128.3, 122.0, 86.6, 84.2, 70.4, 66.5, 66.4, 65.8; **MS (ESI) m/z (%)** 189 $[M+H, 86\%]^+$.

Triisopropyl((5-methyltetrahydrofuran-2-yl)ethynyl)silane, Triisopropyl((2-methyltetrahydrofuran-2-yl)ethynyl)silane (3t)[15]



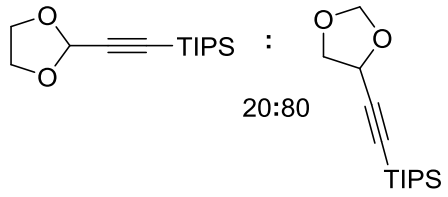
Colorless oil (75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 4.78-4.65 (0.5H, m, OCH), 4.29-4.14 (0.5H, m, OCH), 4.00-3.82 (1H, m, OCH_2), 2.26-1.85 (4H, m, 4 x CH*H*), 1.54 (3H, m, CH_3), 1.04 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 111.0, 108.3, 84.8, 82.7, 77.2, 74.7, 68.4, 67.3, 34.4, 34.0, 33.0, 32.6, 27.3, 25.4, 21.8, 20.9, 18.6, 11.1; **MS (ESI) m/z (%)** 267 $[M+H, 69\%]^+$.

2-Methyl-2-(phenylethynyl)tetrahydrofuran (3u)[15]



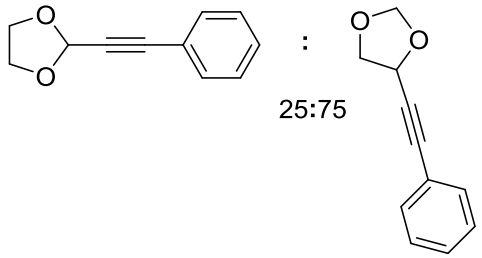
Yellow oil (42%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.48-7.36 (2H, m, ArH), 7.33-7.16 (3H, m, ArH), 4.09-3.88 (2H, m, OCH_2), 2.35-1.78 (4H, m, 4 x CH*H*), 1.63 (3H, s, CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 131.7, 128.2, 128.1, 123.0, 92.3, 82.7, 68.3, 67.6, 40.1, 27.7, 25.7; **MS (ESI) m/z (%)** 187 $[M+H, 51\%]^+$.

((1,3-Dioxolan-2-yl)ethynyl)triisopropylsilane, ((1,3-Dioxolan-4-yl)ethynyl)triisopropylsilane (3v)



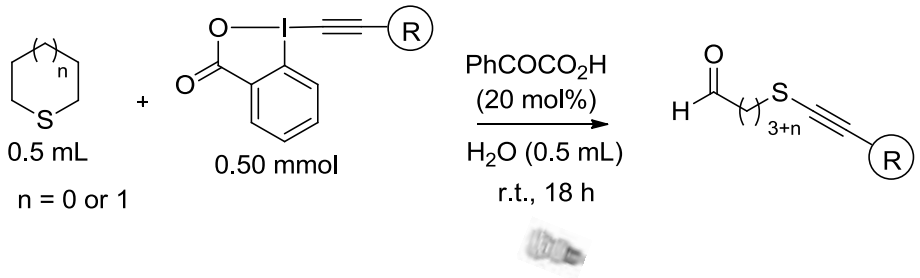
Colorless oil (66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.60 (0.2H, s, OCH), 4.96 (1.6H, d, J = 11.2 Hz, OCH_2), 4.65 (0.8H, t, J = 5.7 Hz, OCH), 4.09-4.03 (0.8H, m, OCH*H*), 4.03-3.98 (0.4H, m, 2 x OCH*H*), 3.90-3.85 (0.4H, m, 2 x OCH*H*), 3.74 (0.8H, dd, J = 7.6 and 5.7 Hz, OCH*H*), 1.00 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 104.1, 102.4, 94.9, 92.7, 87.8, 86.8, 70.8, 70.8, 65.7, 64.2, 18.5, 11.0; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{14}H_{27}O_2Si^+$) requires *m/z* 255.1702, found *m/z* 255.1706.

2-(Phenylethynyl)-1,3-dioxolane, 4-(Phenylethynyl)-1,3-dioxolane, (3w)[15]



Colorless oil (59%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.49-7.43 (2H, m, ArH), 7.41-7.34 (3H, m, ArH), 5.82 (0.25H, s, OCH), 5.01 (1.5H, d, J = 7.9 Hz, OCH_2), 4.86 (0.75H, t, J = 6.1 Hz, OCH), 4.16-4.09 (0.75H, m, OCH*H*), 4.08-4.04 (0.5H, m, 2 x OCH*H*), 3.95-3.91 (0.5H, m, 2 x OCH*H*), 3.86 (0.75H, dd, J = 7.8 and 5.9 Hz, OCH*H*); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 134.1, 133.1, 131.8, 130.8, 129.6, 128.3, 122.0, 95.2, 93.5, 86.9, 86.2, 85.6, 77.2, 70.6, 68.6, 65.8, 64.6; **MS (ESI) m/z (%)** 175 $[M+H, 69\%]^+$.

General Procedure for the Photochemical Reaction of Tetrahydroythiophene and Tetrahydro-2*H*-thiopyran with EthynylBenziodoXolone (EBX) Reagents



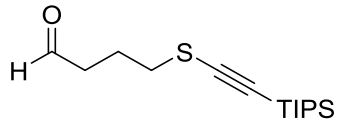
In a glass vial with a screw cap containing ethynylbenziodoxolone (EBX) reagent (0.50 mmol) in heterocycle (0.5 mL) and water (0.5 mL), phenylglyoxylic acid (15 mg, 0.10 mmol) was added. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 85W household lamps, see photos below) for 18 h. The solvent was removed *in vacuo* and the desired product was isolated after purification by column chromatography.

A

B

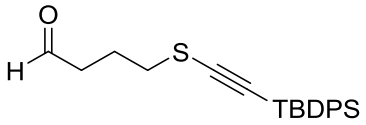
Scheme. **A**: 2 x 85W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

4-(((Triisopropylsilyl)ethynyl)thio)butanal (5a)



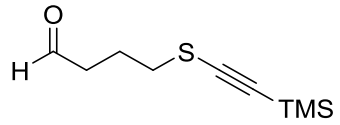
Colorless oil (81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.78 (1H, s, CHO), 2.75 (2H, t, J = 6.8 Hz, SCH_2), 2.65 (2H, t, J = 7.0 Hz, $COCH_2$), 2.05-2.25 (2H, m, CH_2), 1.04 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.3, 97.7, 94.7, 41.8, 34.7, 21.2, 18.6, 11.3; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{15}H_{29}OSSi^+$) requires *m/z* 285.1703, found *m/z* 285.1697.

4-(((*tert*-Butyldiphenylsilyl)ethynyl)thio)butanal (5b)



Colorless oil (69%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.76 (1H, s, CHO), 7.84-7.71 (4H, m, ArH), 7.45-7.30 (6H, m, ArH), 2.86 (2H, t, J = 6.8 Hz, SCH_2), 2.67 (2H, t, J = 7.0 Hz, $COCH_2$), 2.07-2.21 (2H, m, CH_2), 1.09 (9H, s, 3 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.0, 135.5, 133.1, 129.5, 127.7, 98.0, 96.5, 41.7, 34.8, 27.0, 26.9, 21.5; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{22}H_{27}OSSi^+$) requires *m/z* 367.1546, found *m/z* 367.1540.

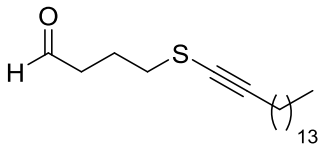
4-(((Trimethylsilyl)ethynyl)thio)butanal (5c)



Colorless oil (70%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.81 (1H, s, CHO), 2.77 (2H, t, J = 6.8 Hz, SCH_2), 2.66 (2H, t, J = 7.0 Hz, $COCH_2$), 2.17-1.99 (2H, m, CH_2), 0.17 (9H, s, 3 x

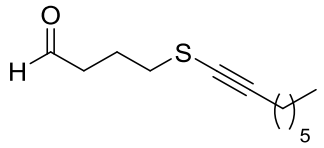
CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.2, 101.1, 94.0, 41.8, 34.6, 21.3, -0.1; **HRMS** exact mass calculated for $[M+H]^+$ ($C_9H_{17}OSSi^+$) requires *m/z* 201.0764, found *m/z* 201.0756.

4-(Hexadec-1-yn-1-ylthio)butanal (5d)



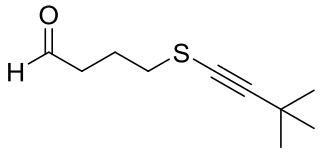
Pale yellow oil (52%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.80 (1H, s, CHO), 2.75-2.56 (2H, m, SCH_2), 2.27 (2H, t, *J* = 7.0 Hz, $COCH_2$), 2.01-2.16 (2H, m, CH_2), 1.52-1.18 (26H, m 26 x CH*H*), 0.87 (3H, t, *J* = 5.4 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.4, 95.0, 67.2, 41.9, 34.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.1, 28.9, 28.4, 22.7, 21.4, 20.1, 14.1; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{29}H_{37}OS^+$) requires *m/z* 325.2560, found *m/z* 325.2567.

4-(Oct-1-yn-1-ylthio)butanal (5e)



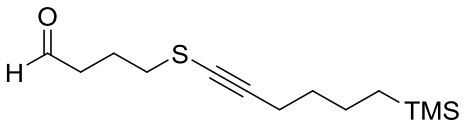
Colorless oil (52%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 9.80 (1H, s, CHO), 2.75-2.53 (4H, m, SCH_2 και $COCH_2$), 2.33-2.22 (2H, m, CH_2), 2.06 (2H, t, *J* = 6.7 Hz, CH_2), 1.39-1.17 (8H, m 8 x CH*H*), 0.87 (3H, t, *J* = 6.2 Hz, CH_3); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 201.3, 90.0, 68.4, 42.0, 39.0, 34.5, 31.3, 28.7, 22.5, 21.5, 20.1, 14.0; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{12}H_{21}OS^+$) requires *m/z* 213.1308, found *m/z* 213.1311.

4-((3,3-Dimethylbut-1-yn-1-yl)thio)butanal (5f)



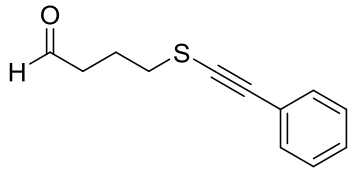
Colorless oil (49%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.80 (1H, s, CHO), 2.74-2.58 (4H, m, SCH_2 και $COCH_2$), 2.00-2.18 (2H, m, CH_2), 1.21 (9H, s, 3 x CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.5, 102.8, 77.2, 41.9, 34.5, 30.9, 29.9, 21.2; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{10}H_{16}OSNa^+$) requires *m/z* 207.0814, found *m/z* 207.0818.

4-((6-(Trimethylsilyl)hex-1-yn-1-yl)thio)butanal (5g)



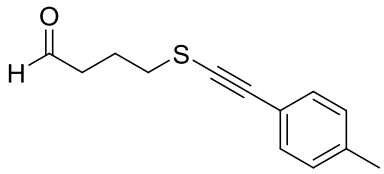
Colorless oil (64%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 9.81 (1H, s, CHO), 2.77-58 (4H, m, SCH_2 και $COCH_2$), 2.50-2.39 (2H, m, 2 x CH*H*), 2.35-2.28 (2H, m, 2 x CH*H*), 2.27-2.18 (2H, m, 2 x CH*H*), 2.11-2.01 (2H, m, 2 x CH*H*), 1.67-1.57 (2H, m, 2 x CH*H*), 0.14 (9H, s, TMS); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 201.3, 107.0, 94.3, 41.9, 34.5, 29.8, 28.0, 27.7, 21.5, 19.4, -0.1; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{13}H_{25}OSSi^+$) requires *m/z* 257.1390, found *m/z* 257.1398.

4-((Phenylethynyl)thio)butanal (5h)



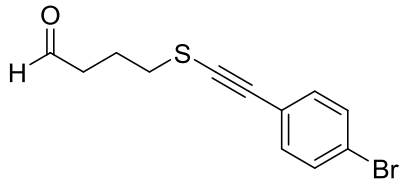
Pale yellow oil (56%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.82 (1H, s, CHO), 7.44-7.34 (2H, m, ArH), 7.33-7.22 (3H, m, ArH), 2.84 (2H, t, J = 6.8 Hz, SCH_2), 2.69 (2H, t, J = 7.1 Hz, $COCH_2$), 2.60-2.73 (2H, m, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.3, 131.4, 128.3, 128.2, 123.2, 93.4, 78.5, 41.9, 34.8, 21.5; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{12}H_{13}OS^+$) requires *m/z* 205.0682, found *m/z* 205.0679.

4-((*p*-Tolylethynyl)thio)butanal (5i)



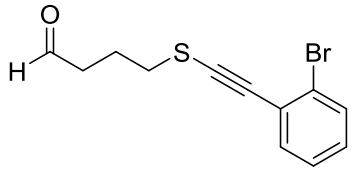
Yellow oil (60%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 9.82 (1H, s, CHO), 7.35-7.22 (2H, d, J = 7.2 Hz, ArH), 7.14-7.02 (2H, d, J = 7.2 Hz, ArH), 2.82 (2H, t, J = 6.9 Hz, SCH_2), 2.69 (2H, t, J = 7.1 Hz, $COCH_2$), 2.33 (3H, s, CH_3), 2.04-2.23 (2H, m, CH_2); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 201.3, 138.4, 131.5, 129.1, 120.1, 93.4, 77.2, 41.9, 34.8, 21.6, 21.5; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}OS^+$) requires *m/z* 219.0838, found *m/z* 219.0847.

4-(((4-Bromophenyl)ethynyl)thio)butanal (5j)



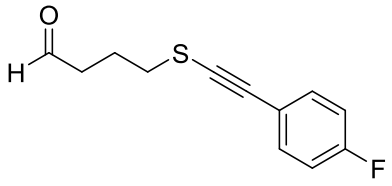
Colorless oil (40%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.82 (1H, s, CHO), 7.42 (2H, d, J = 8.2 Hz, ArH), 7.24 (2H, d, J = 8.2 Hz, ArH), 2.84 (2H, t, J = 6.5 Hz, SCH_2), 2.69 (2H, t, J = 7.0 Hz, $COCH_2$), 2.06-2.23 (2H, m, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.1, 132.8, 132.0, 127.2, 122.3, 92.3, 80.1, 41.9, 34.8, 21.6; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{12}H_{12}BrOS^+$) requires *m/z* 282.9787, found *m/z* 282.9781.

4-(((2-Bromophenyl)ethynyl)thio)butanal (5k)



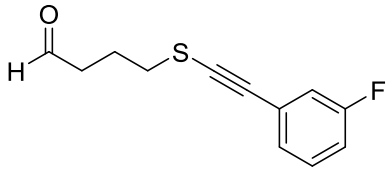
Colorless oil (45%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.83 (1H, s, CHO), 7.61-7.51 (1H, m, ArH), 7.46-7.35 (1H, m, ArH), 7.22-7.06 (2H, m, ArH), 2.88 (2H, t, J = 6.7 Hz, SCH_2), 2.71 (2H, t, J = 7.1 Hz, $COCH_2$), 2.33-2.12 (2H, m, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.3, 133.5, 132.8, 132.3, 129.0, 127.0, 124.9, 92.1, 84.0, 41.9, 34.8, 21.6; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{12}H_{12}BrOS^+$) requires *m/z* 282.9787, found *m/z* 282.9780.

4-(((4-Fluorophenyl)ethynyl)thio)butanal (5l)



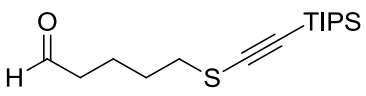
Colorless oil (35%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 9.82 (1H, s, CHO), 7.44-7.32 (2H, m, ArH), 7.04-6.91 (2H, m, ArH), 2.83 (2H, t, J = 7.0 Hz, SCH_2), 2.69 (2H, t, J = 7.3 Hz, $COCH_2$), 2.02-2.24 (2H, m, CH_2); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 201.1, 157.3 (d, J = 266.1 Hz), 133.5 (d, J = 8.8 Hz), 129.4 (d, J = 13.9 Hz), 115.6 (d, J = 22.6 Hz), 92.2, 78.2, 41.9, 34.8, 21.6; **^{19}F NMR** (188 MHz, $CDCl_3$) δ: -68.7; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{12}H_{12}FOS^+$) requires *m/z* 223.0587, found *m/z* 223.0586.

4-(((3-Fluorophenyl)ethynyl)thio)butanal (5m)



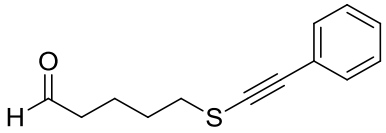
Pale yellow oil (51%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 9.83 (1H, s, CHO), 7.27-6.92 (4H, m, ArH), 2.85 (2H, t, J = 6.8 Hz, SCH_2), 2.70 (2H, t, J = 7.0 Hz, $COCH_2$), 2.04-2.25 (2H, m, CH_2); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 201.1, 162.3 (d, J = 246.5 Hz), 133.3 (d, J = 15.5 Hz), 129.9 (d, J = 8.9 Hz), 127.2 (d, J = 3.0 Hz), 118.0 (d, J = 22.9 Hz), 115.4 (d, J = 21.1 Hz), 99.4, 92.3, 41.8, 34.8, 21.6; **^{19}F NMR** (188 MHz, $CDCl_3$) δ: -70.9; **HRMS** exact mass calculated for $[M+Na]^+$ ($C_{12}H_{11}FOSNa^+$) requires *m/z* 244.0407, found *m/z* 244.0418.

5-(((Triisopropylsilyl)ethynyl)thio)pentanal (5n)



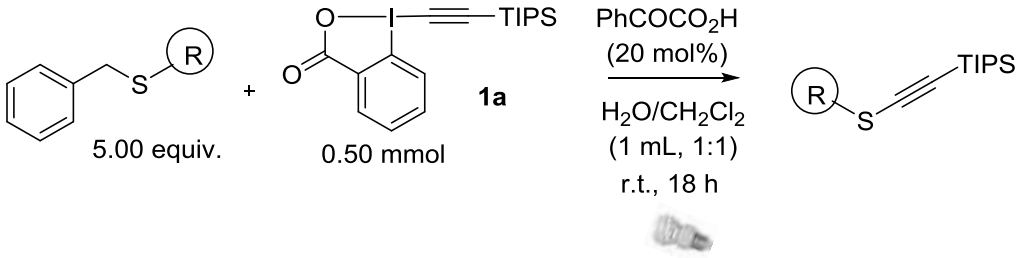
Colorless oil (70%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.77 (1H, s, CHO), 2.72 (2H, t, J = 6.7 Hz, SCH_2), 2.46 (2H, t, J = 6.2 Hz, $COCH_2$), 1.85-1.13 (4H, m, 2 x CH_2), 1.05 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 201.9, 97.4, 95.3, 43.3, 35.3, 28.3, 20.5, 18.6, 11.3; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{16}H_{31}OSSi^+$) requires *m/z* 299.1859, found *m/z* 299.1863.

5-((Phenylethynyl)thio)pentanal (5o)



Colorless oil (65%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 9.78 (1H, s, CHO), 7.45-7.34 (2H, m, ArH), 7.33-7.19 (3H, m, ArH), 2.87-2.71 (2H, m, SCH_2), 2.56-2.42 (2H, m, $COCH_2$), 1.93-1.74 (4H, m, 2 x CH_2); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 201.9, 137.6, 131.4, 128.3, 128.1, 89.9, 77.2, 43.3, 35.3, 29.7, 28.7; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{13}H_{15}OS^+$) requires *m/z* 219.0838, found *m/z* 219.0832.

General Procedure for the Photochemical Reaction of Benzyl Sulfides with TIPS-EBX



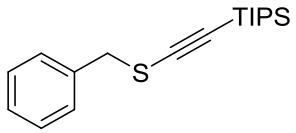
In a glass vial with a screw cap containing TIPS-EBX (214 mg, 0.50 mmol) in dichloromethane (0.5 mL) and water (0.5 mL), phenylglyoxylic acid (15 mg, 0.10 mmol) and benzyl sulfide (5.00 equiv.) were added. The vial was sealed with a screw cap and left stirring under household bulb irradiation (2 x 85W household lamps, see photos below) for 18 h. The solvent was removed *in vacuo* and the desired product was isolated after purification by column chromatography.

A

B

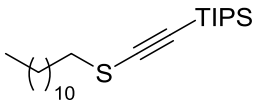
Scheme. **A**: 2 x 85W fluorescent household lamps utilized for the photocatalytic reaction. Bulbs are placed symmetrically 3 cm away from the reaction tube. **B**: Beginning of the reaction.

((Benzylthio)ethynyl)triisopropylsilane (5p)[21]



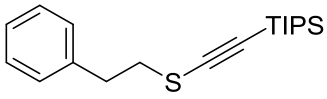
Colorless oil (63%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.42-7.17 (5H, m, ArH), 3.93 (2H, s, SCH_2), 1.02 (21H, s, TIPS); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 136.7, 129.0, 128.5, 127.6, 98.7, 96.2, 43.5, 18.6, 11.3; **MS (ESI) m/z (%)** 305 $[M+H, 86\%]^+$.

Triisopropyl((dodecylthio)ethynyl)silane (5q)



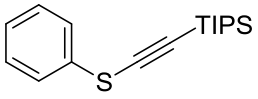
Colorless oil (60%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 2.74 (2H, t, J = 7.2 Hz, SCH_2), 1.83-1.73 (2H, m, 2 x CH*H*), 1.48-1.39 (2H, m, 2 x CH*H*), 1.37-1.22 (16H, m, 16 x CH*H*), 1.09 (21H, s, TIPS), 0.91 (3H, t, J = 6.9 Hz, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 96.8, 77.2, 35.9, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.2, 22.7, 18.6, 14.1, 11.4; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{23}H_{47}SSi^+$) requires *m/z* 383.3162, found *m/z* 383.3169.

Triisopropyl((phenethylthio)ethynyl)silane (5r)



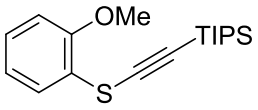
Colorless oil (66%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.39-7.13 (5H, m, ArH), 3.17-3.04 (2H, m, SCH_2), 2.96-2.82 (2H, m, $PhCH_2$), 1.09 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 139.7, 128.7, 128.6, 126.6, 97.8, 95.5, 37.0, 35.5, 18.7, 11.4; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{19}H_{31}SSi^+$) requires *m/z* 319.1910, found *m/z* 319.1915.

Triisopropyl((phenylthio)ethynyl)silane (5s)



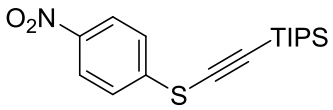
Colorless oil (75%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.48-7.15 (5H, m, ArH), 1.11 (21H, s, TIPS); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 133.0, 129.4, 126.5, 126.2, 103.5, 91.3, 18.9, 11.6; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{17}H_{27}SSi^+$) requires *m/z* 291.1597, found *m/z* 291.1592.

Triisopropyl(((2-methoxyphenyl)thio)ethynyl)silane, (5t)



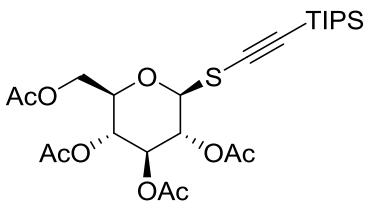
Colorless oil (65%); **^{1}H NMR** (200 MHz, $CDCl_3$) δ: 7.70-7.60 (1H, m, ArH), 7.23-7.11 (1H, m, ArH), 7.06-6.94 (1H, m, ArH), 6.88-6.77 (1H, m, ArH), 3.87 (3H, s, OCH_3), 1.12 (21H, s, TIPS); **^{13}C NMR** (50 MHz, $CDCl_3$) δ: 155.1, 127.2, 126.6, 121.6, 103.4, 91.1, 55.9, 18.6, 11.4; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{18}H_{29}OSSi^+$) requires *m/z* 321.1630, found *m/z* 321.1633.

Triisopropyl(((4-nitrophenyl)thio)ethynyl)silane, (5u)[22]



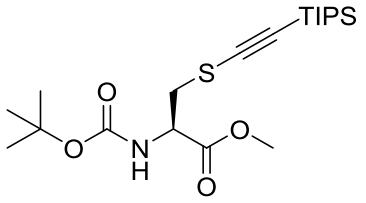
Yellow oil (80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 8.23 (2H, d, J = 9.0 Hz, ArH), 7.60 (2H, d, J = 9.0 Hz, ArH), 1.17 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 146.3, 142.9, 125.8, 124.3, 106.8, 88.0, 18.7, 11.4; **MS (ESI) m/z (%)** 336 $[M+H, 82\%]^+$.

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(Acetoxymethyl)-6-(((triisopropylsilyl)ethynyl)thio)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (5v)



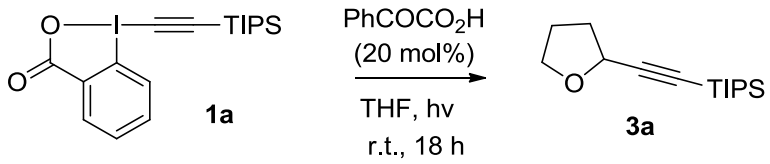
Viscous colorless oil (32%); $[\alpha]^{26}_{D}$ -85.0 (c 0.2, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.29-5.22 (2H, m, 2 x OCH), 5.14-5.07 (1H, m, OCH), 4.61-4.56 (1H, m, OCH), 4.28 (1H, dd, *J* = 12.5 and 4.8 Hz, OC*H*H), 4.14 (1H, dd, *J* = 12.5 and 2.2 Hz, OCH*H*), 3.77 (1H, ddd, *J* = 10.1, 4.7 and 2.2 Hz, OCH), 2.09 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.04 (3H, s, CH_3), 2.02 (3H, s, CH_3), 1.11 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.6, 170.2, 169.2, 168.9, 102.2, 88.8, 84.8, 76.4, 73.7, 69.8, 67.7, 61.9, 20.7, 20.6, 20.5, 20.4, 18.6, 18.5, 11.2; **HRMS** exact mass calculated for $[M+H]^+$ ($C_{25}H_{41}O_9SSi^+$) requires *m/z* 545.2235, found *m/z* 545.2230.

Methyl *N*-(*tert*-butoxycarbonyl)-(*S*)-((triisopropylsilyl)ethynyl)-*L*-cysteinate (5w)[22]



Yellow oil (34%); $[\alpha]^{26}_{D}$ -24.0 (c 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 5.47 (1H, d, *J* = 7.4 Hz, NH), 4.75-4.66 (1H, m, NCH), 3.80 (3H, s, OCH_3), 3.27 (1H, dd, *J* = 13.6 and 4.1 Hz, SC*H*H), 3.15 (1H, dd, *J* = 13.6 and 5.6 Hz, SCH*H*), 1.47 (9H, s, 3 x CH_3), 1.09 (21H, s, TIPS); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.7, 155.1, 98.1, 94.5, 80.3, 53.9, 52.7, 38.4, 28.2, 18.6, 11.2; **MS (ESI) m/z (%)** 416 $[M+H, 78\%]^+$.

Gram Scale Photochemical Reaction of Tetrahydrofuran with EthynylBenziodoXolone (EBX) Reagent



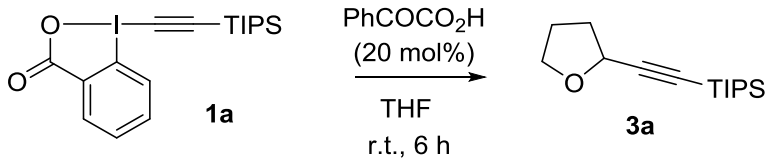
A round-bottomed flask was charged with 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (1.00 g, 2.33 mmol), tetrahydrofuran (15.6 mL) and phenylglyoxylic acid **4a** (70 mg, 0.47 mmol). The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 18 h. After irradiation, the temperature was measured between the lamps (thermometer reading: 44 ^{o}C) and inside of the flask (thermometer reading: 45 ^{o}C). The solvent was removed *in vacuo* and the desired product was isolated in 68% yield after purification by column chromatography (Pet. Ether:Ethyl acetate 90:10).

Determination of the Quantum Yield

Determination of the photon flux

The photon flux of the lamps was determined following the work of Yoon and coworkers,[23] utilizing standard ferrioxalate actinometry,[24,25] and was calculated to be 6.66 $\times 10^{-10}$ einstein s^{-1}.

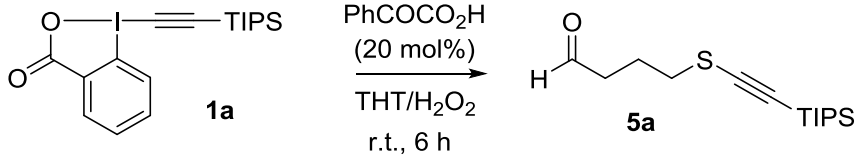
Determination of the quantum yield for the photochemical reaction of tetrahydrofuran with TIPS-EBX



A cuvette was charged with 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol), tetrahydrofuran (0.5 mL) and phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol). The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 21600 s (6 h). After irradiation, the solvent was removed and the yield of the product was determined by ^{1}H NMR (37%). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{27.8 \times 10^{-6}\ \text{mol}}{6.66 \times 10^{-10}\ \text{einstein}\ s^{-1} \times 21600\ s \times 0.99999} = 1.93$$

Determination of the quantum yield for the photochemical reaction of tetrahydrothiophene with TIPS-EBX



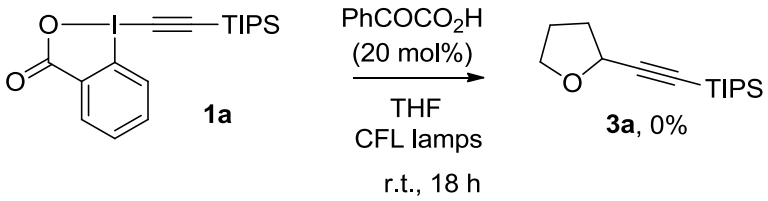
A cuvette was charged with 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol), tetrahydrothiophene (0.25 mL), water (0.25 mL) and phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol). The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 21600 s (6 h). After irradiation, the solvent was removed and the yield of the product was determined by ^{1}H NMR (66%). The quantum yield was determined with the following equation:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f} = \frac{49 \times 10^{-6}\ \text{mol}}{6.66 \times 10^{-10}\ \text{einstein s}^{-1} \times 21600\ \text{s} \times 0.99999} = 3.41$$

Photochemical reaction of tetrahydrofuran with TIPS-EBX

(Cut-off Filter below 400 nm)

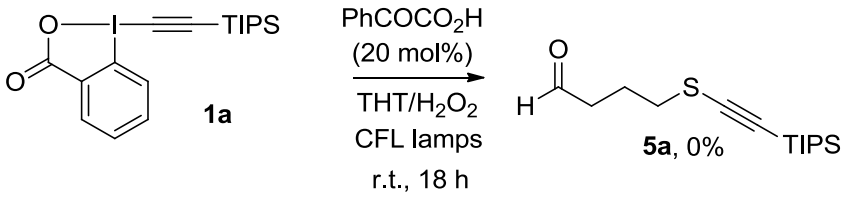
In a glass vial with a screw cap containing phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol), 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol), tetrahydrofuran (0.5 mL). The vial was sealed with a screw cap and was placed in a solution of $NaNO_2$ (1M) in a tube-in-tube arrangement. The vial was sealed with a screw cap and left stirring under household bulb irradiation for 18 h. After irradiation, the yield of the product was determined by ^{1}H-NMR.



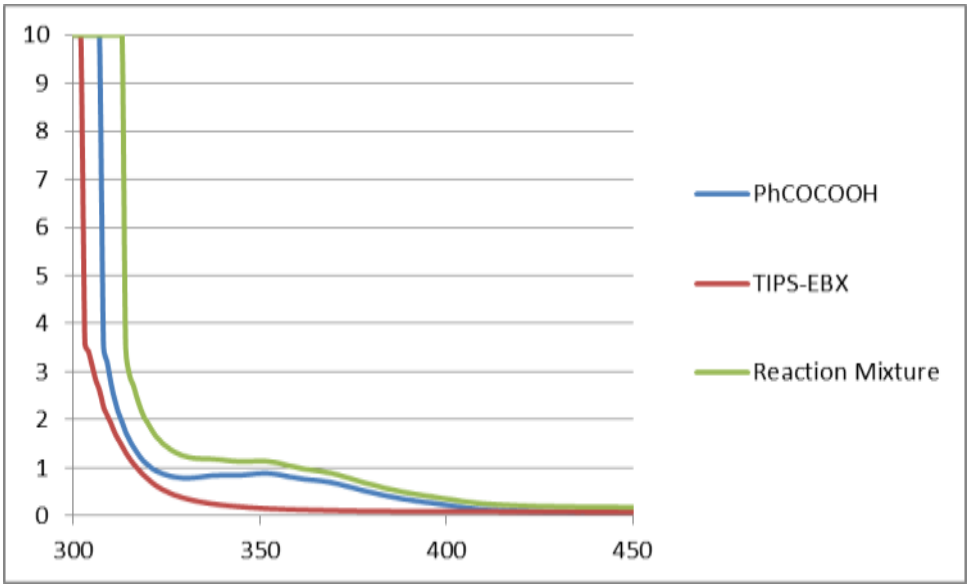
Photochemical reaction of tetrahydrothiophene with TIPS-EBX

(Cut-off Filter below 400 nm)

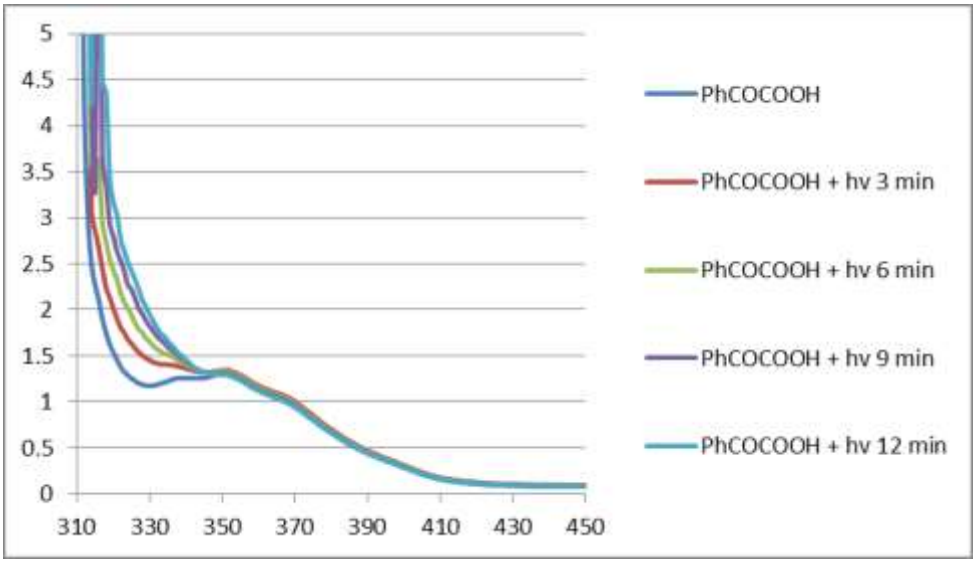
In a glass vial with a screw cap containing phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol), 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol), tetrahydrothiophene (0.25 mL) and water (0.25). The vial was sealed with a screw cap and was placed in a solution of $NaNO_2$ (1M) in a tube-in-tube arrangement. The reaction was left stirring under household bulb irradiation for 18 h. After irradiation, the yield of the product was determined by ^{1}H-NMR.



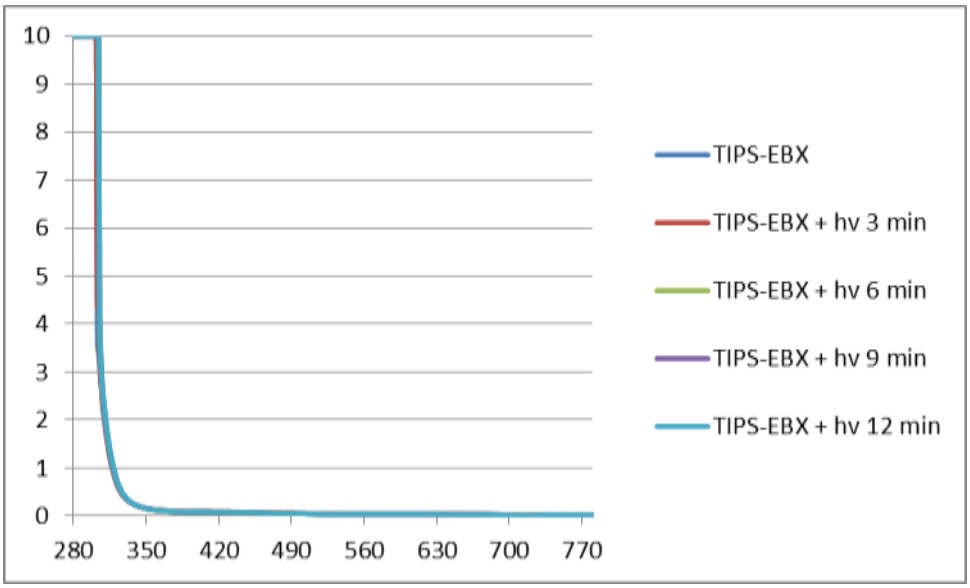
Mechanistic Investigations with UV-Vis Absorption Spectra



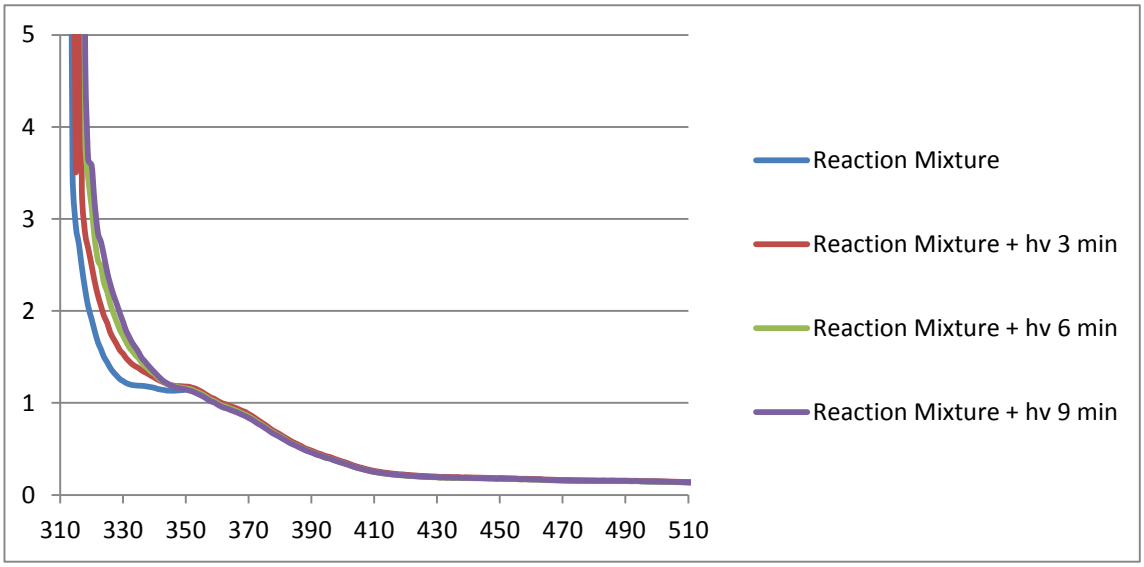
UV-Vis absorption of phenylglyoxylic acid (10^{-2} M), TIPS-EBX (0.05 M) and phenylglyoxylic acid (10^{-2} M) with TIPS-EBX (0.05 M) in THF



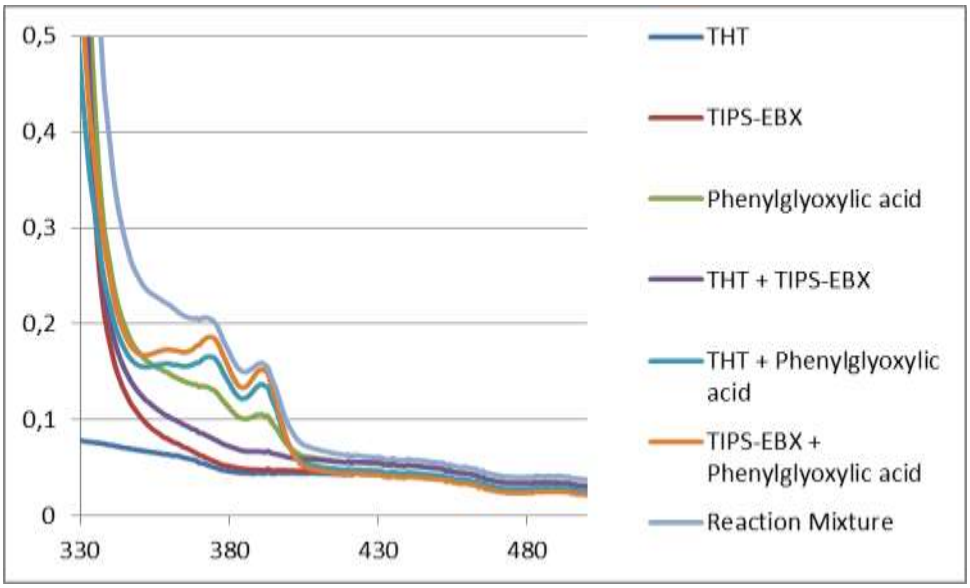
Phenylglyoxylic acid (10^{-2} M) in THF



TIPS-EBX (0.05 M) in THF



Phenylglyoxylic acid (10^{-2} M) and TIPS-EBX (0.05 M) in THF

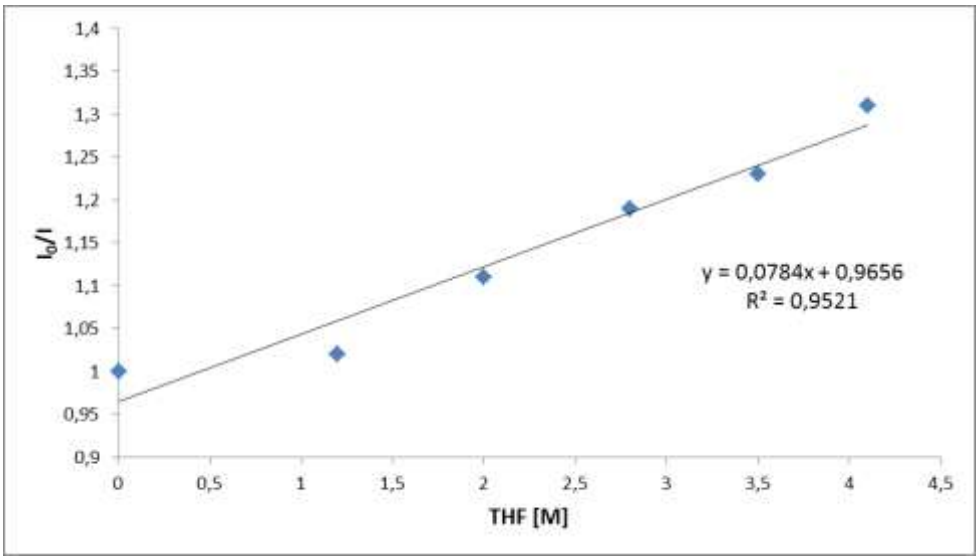


THT (3×10^{-2} M), phenylglyoxylic acid (7×10^{-4} M), TIPS-EBX (4×10^{-3} M) their mixtures in CH_2Cl_2

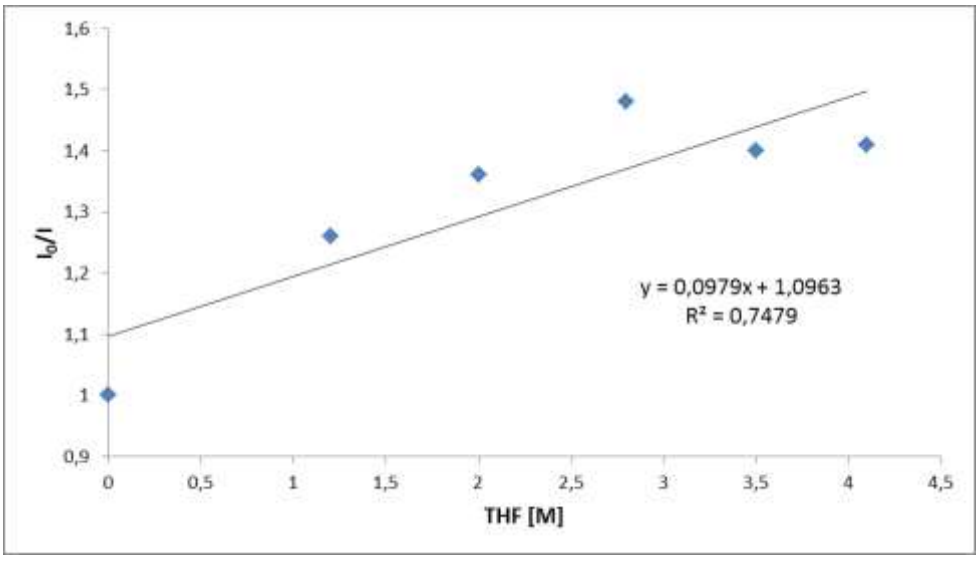
Fluorescence Quenching Studies

After irradiation of phenylglyoxylic acid (1 mM in solvent) at 360 nm, its fluorescence was measured at 402 nm. Increasing the added amount of THF, a low decrease in the fluoroscence was observed. The corresponding Stern-Volmer plots in acetonitrile (diagram **A**) or in CH_2Cl_2 (diagram **B**) are presented below.

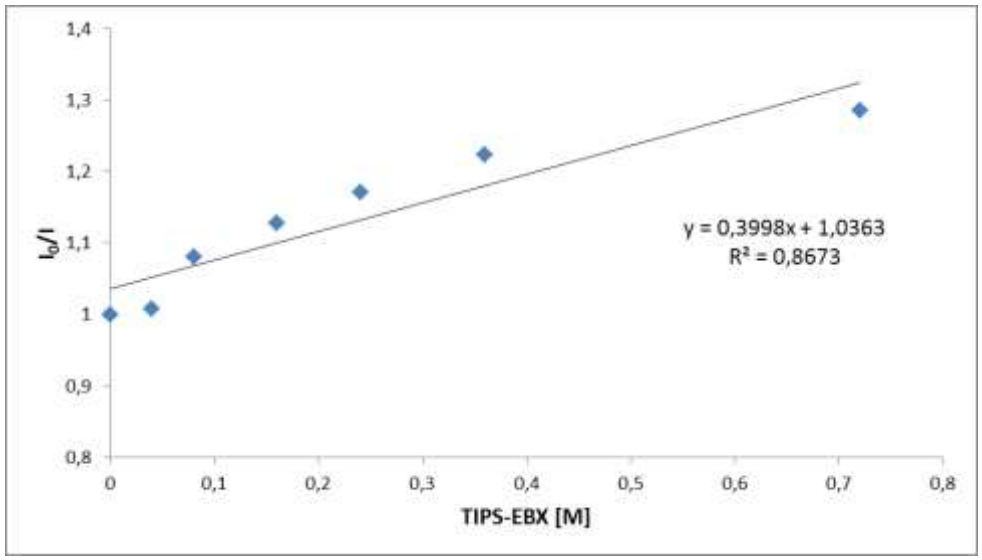
A



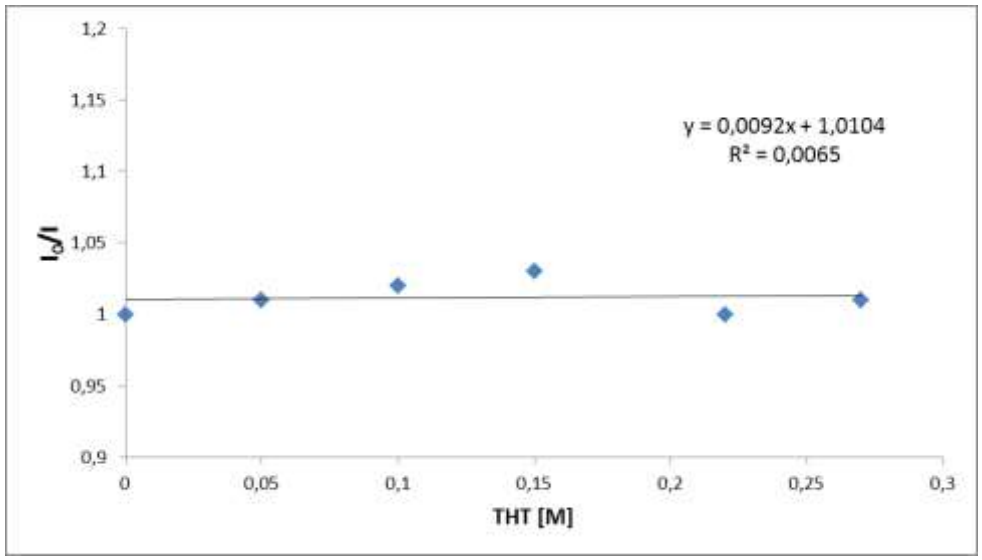
B



After irradiation of phenylglyoxylic acid (1 mM in MeCN) at 360 nm, its fluorescence was measured at 402 nm. Increasing the added amount of TIPS-EBX, a constant decrease in the fluoroscence was observed. The corresponding Stern-Volmer plot is presented below.

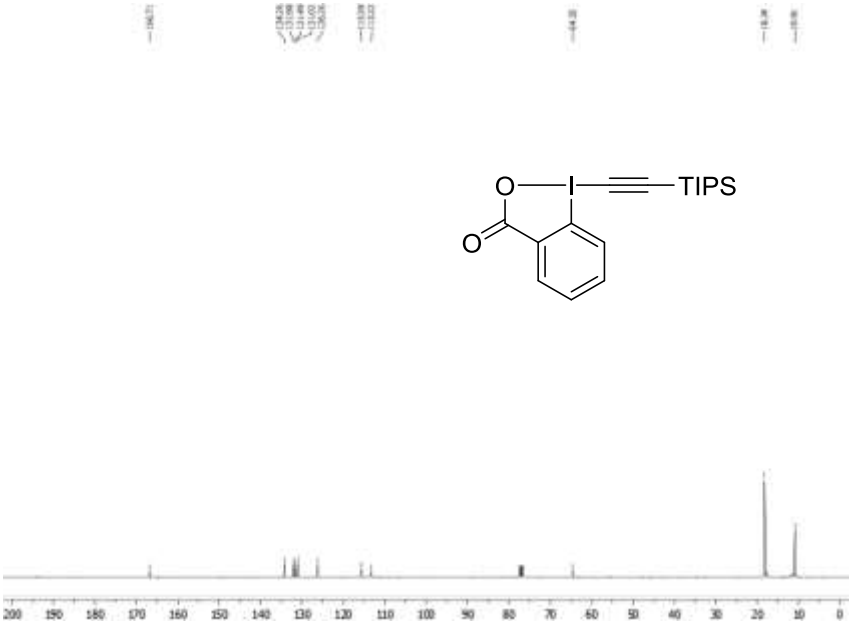


After irradiation of phenylglyoxylic acid (1 mM in MeCN) at 360 nm, its fluorescence was measured at 402 nm. Increasing the added amount of THT, no decrease in the fluoroscence was observed. The corresponding Stern-Volmer plot is presented below.

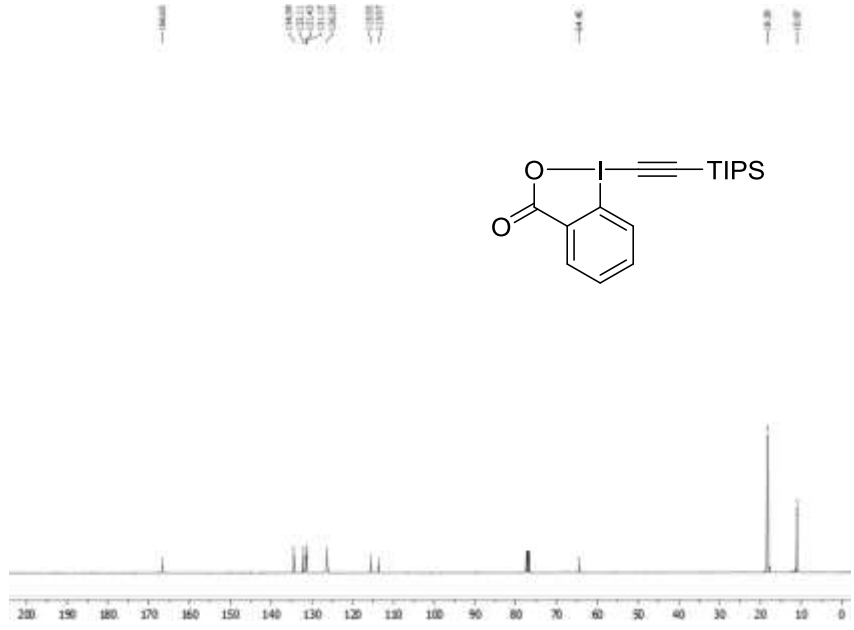


^{13}C-NMR Mechanistic Experiments

Initially, the ^{13}C-NMR spectra of TIPS-EBX in $CDCl_3$ were recorded before and after irradiation for 4 h (in THF, then evaporation). The two spectra are the same. No photodecomposition is observed.

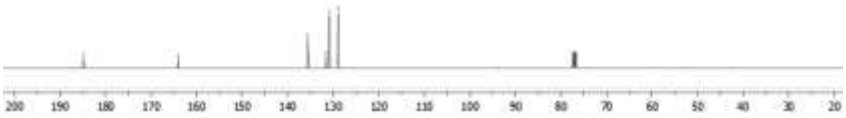


^{13}C NMR spectrum of TIPS-EBX in $CDCl_3$

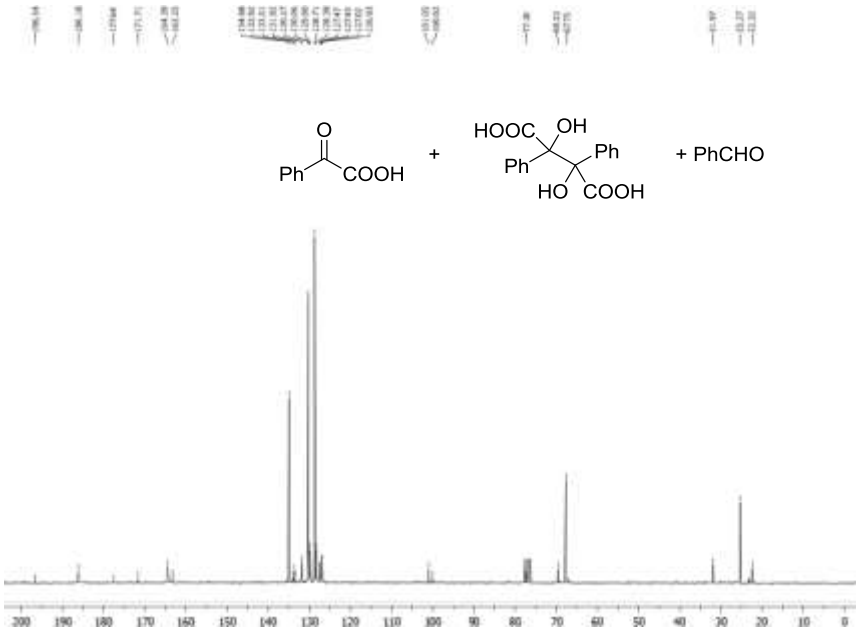


^{13}C NMR spectrum of TIPS-EBX $CDCl_3$, after irradiation for 4 h (in THF)

^{13}C-NMR spectra (in $CDCl_3$) of $PhCOCO_2H$, before and after irradiation for 4 h (in THF) were recorded. After irradiation, additional peaks were observed, that can be attributed mainly to the dimerization product[26] (product from photodecomposition, **101 and 100 ppm**) and partly to decomposition to benzaldehyde (**196 ppm**).[27]

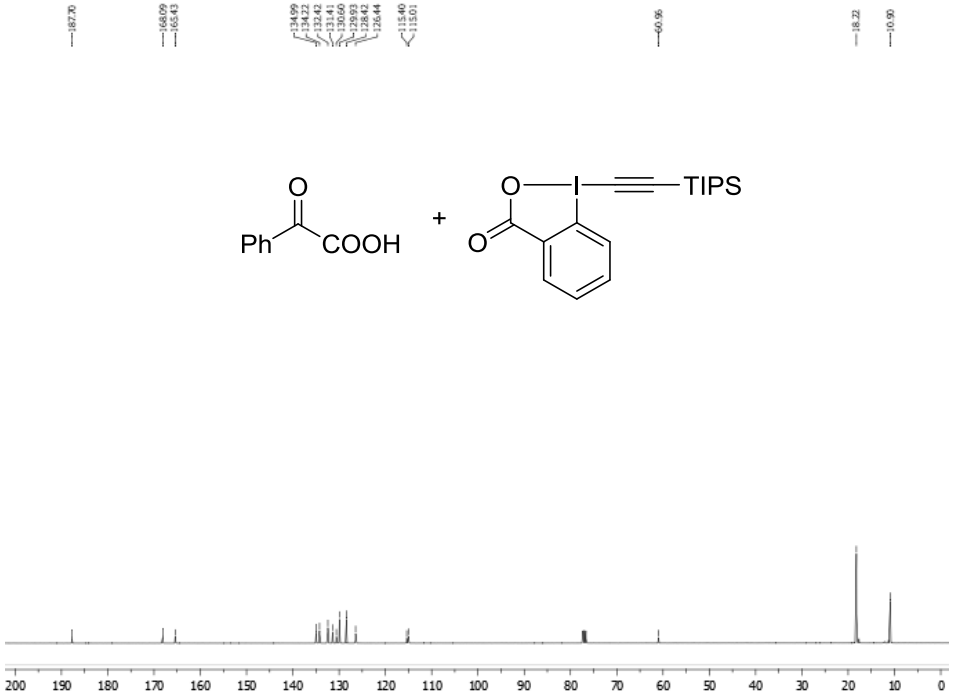


^{13}C NMR spectrum of PhCOCOOH in $CDCl_3$

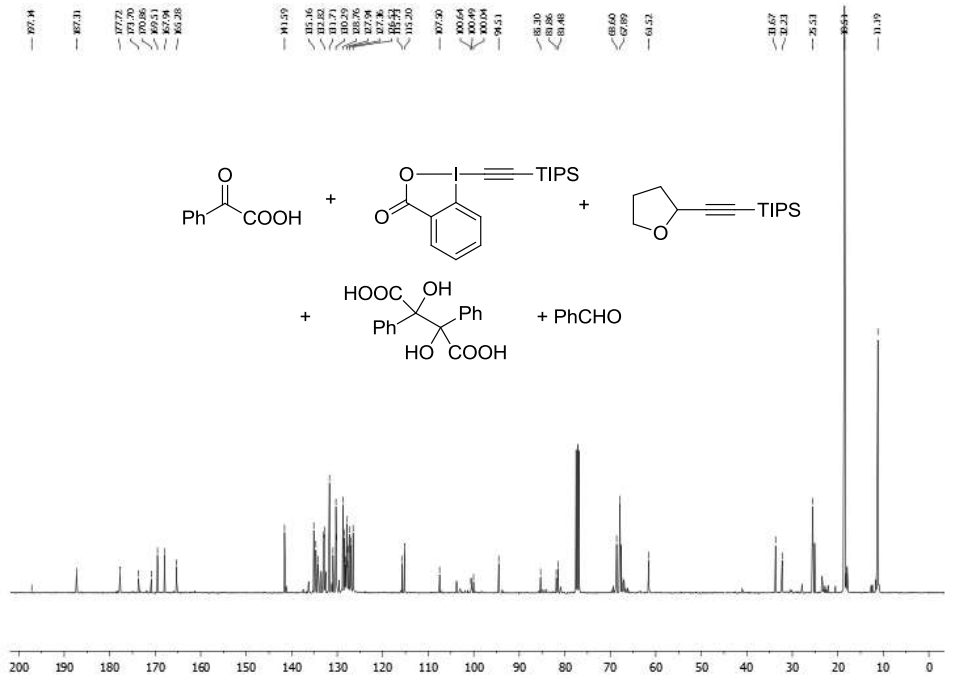


^{13}C NMR spectrum of PhCOCOOH in $CDCl_3$, after irradiation for 4 h (in THF)

Finally, the reaction mixture (PhCOCOOH and TIPS-EBX) (in $CDCl_3$) presented all expected signals. Similar photodecomposition of PhCOCOOH is observed (dimerization product, **100 ppm** and benzaldehyde, **197 ppm**).

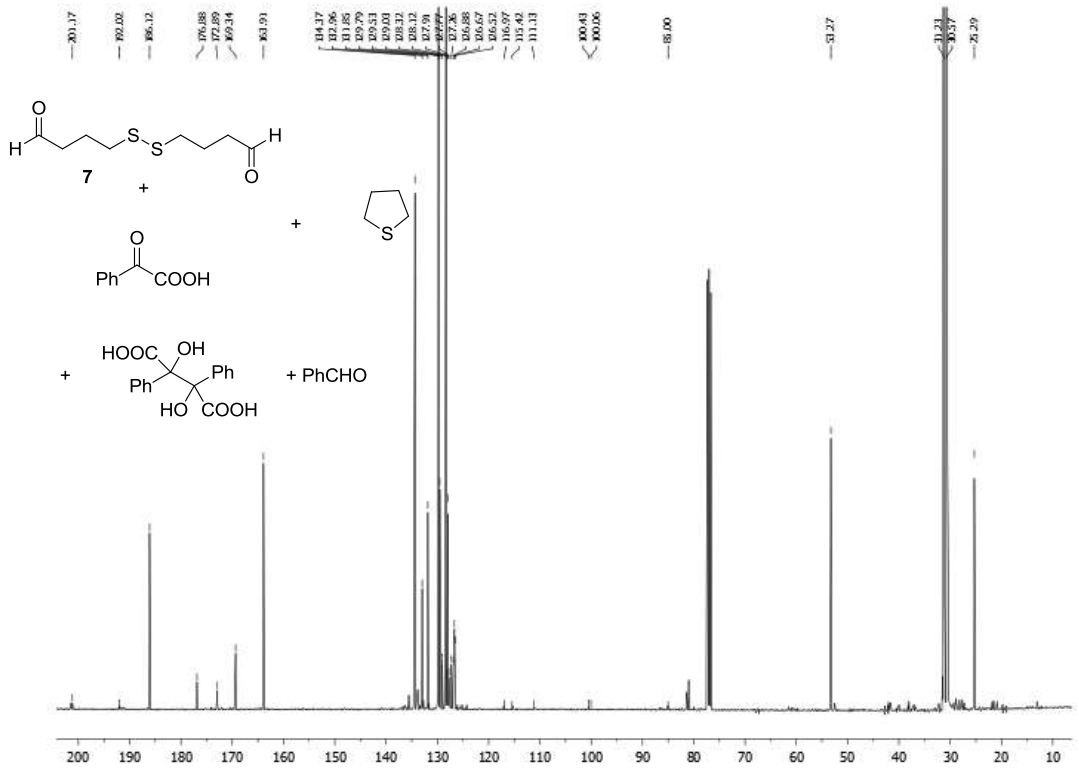


^{13}C NMR spectrum of the reaction mixture in $CDCl_3$



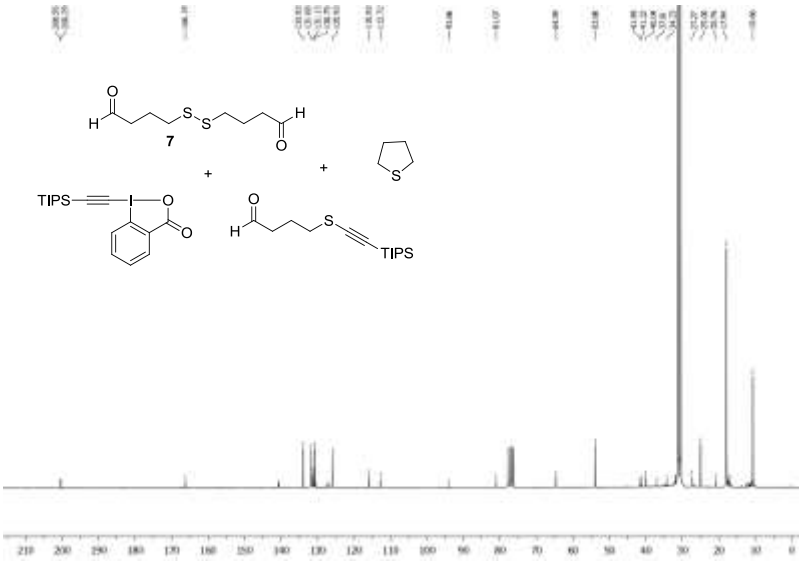
^{13}C NMR spectrum of the reaction mixture in $CDCl_3$, after irradiation for 4 h (in THF)

^{13}C-NMR spectra (in $CDCl_3$) of $PhCOCO_2H$, before (See S58, top) and after irradiation for 4 h (in THT and water) were recorded. After irradiation, additional peaks were observed, that can be attributed mainly to the disulfide **7** bearing an aldehyde, **201 ppm** and photodecomposition of PhCOCOOH (dimerization product, **100 ppm** and benzaldehyde, **197 ppm**).



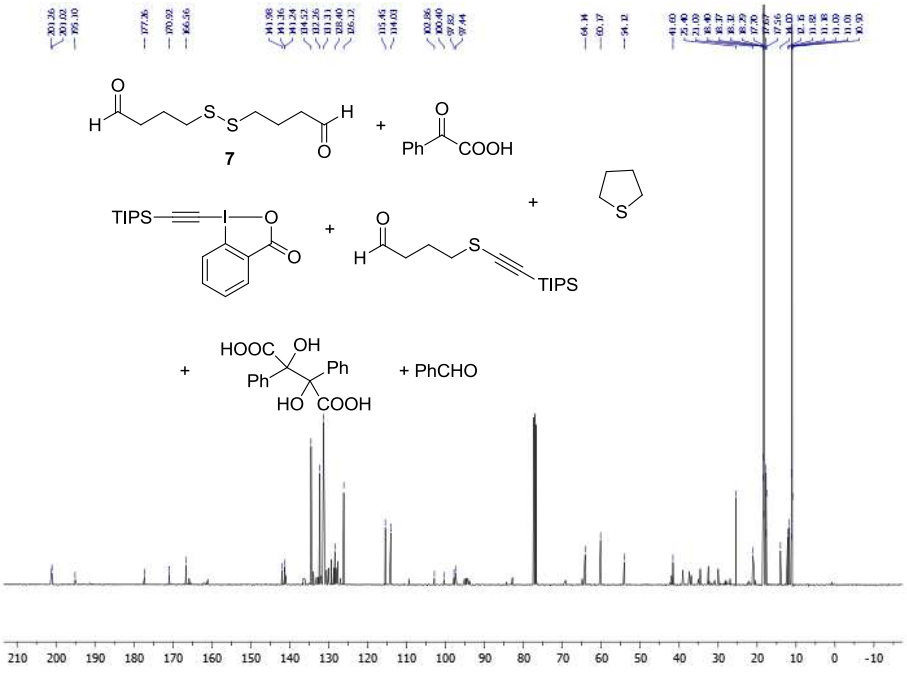
^{13}C NMR spectrum of PhCOCOOH in $CDCl_3$, after irradiation for 4 h (in THT/H_2O)

^{13}C-NMR spectra of TIPS-EBX in $CDCl_3$ were recorded before (See S57, top) and after irradiation for 4 h (in THT and water). Additional peaks were observed, that can be attributed mainly to **7** and product **5a**.



^{13}C NMR spectrum of TIPS-EBX in $CDCl_3$, after irradiation for 4 h (in THT/H_2O)

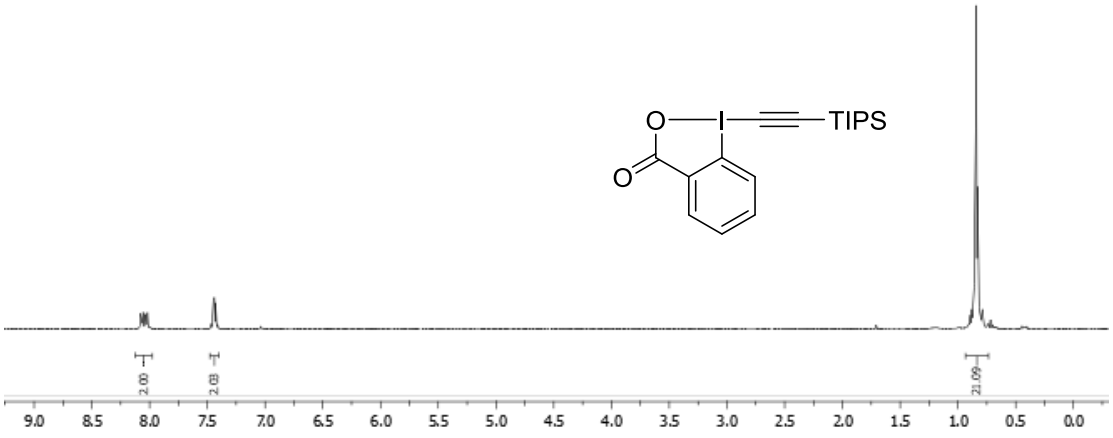
Finally, the reaction mixture (PhCOCOOH and TIPS-EBX) (in $CDCl_3$), before (See S59, top) and after irradiation for 4 h (in THT and water), presented all expected signals (and photodecomposition of PhCOCOOH, dimerization product, **100 ppm** and benzaldehyde, **197 ppm**.



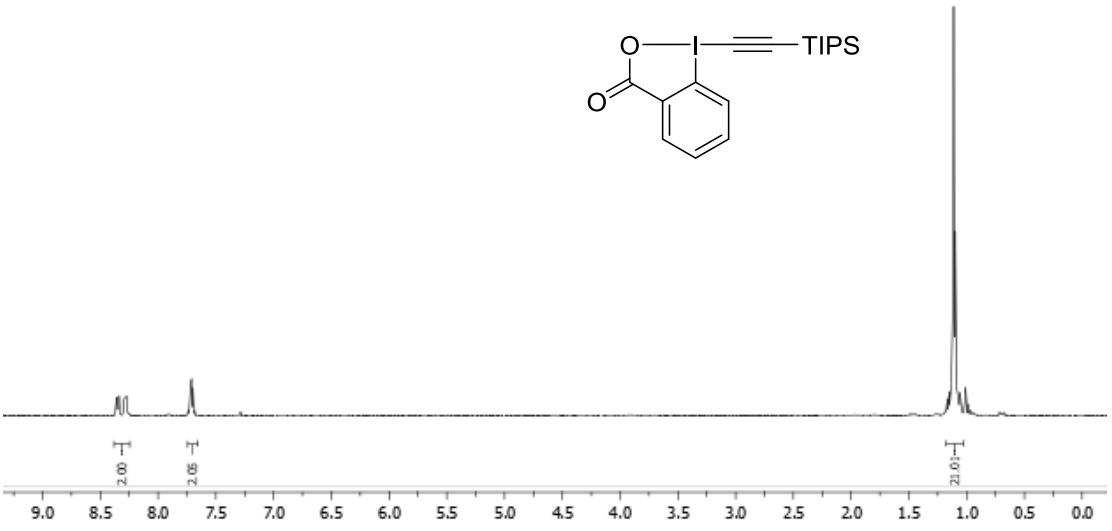
^{13}C NMR spectrum of the reaction mixture in $CDCl_3$, after irradiation for 4 h (in THT/H_2O)

^{1}H-NMR Mechanistic Experiments

Initially, the ^{1}H-NMR spectra of TIPS-EBX in $CDCl_3$ were recorded before and after irradiation for 4 h (in THF, then evaporation). The two spectra are the same.

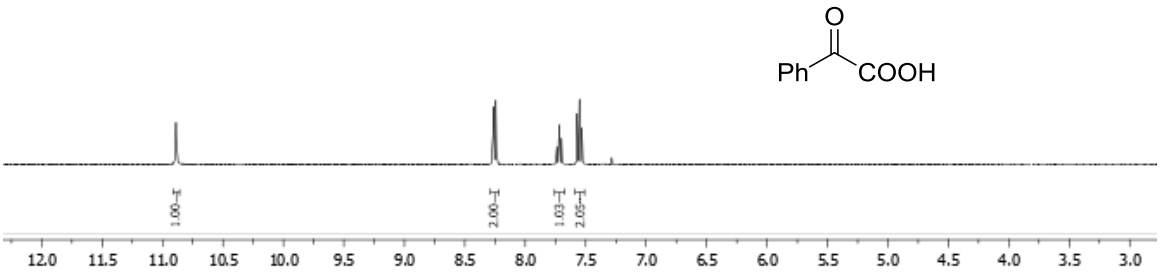


^{1}H NMR spectrum of TIPS-EBX in (in THF)

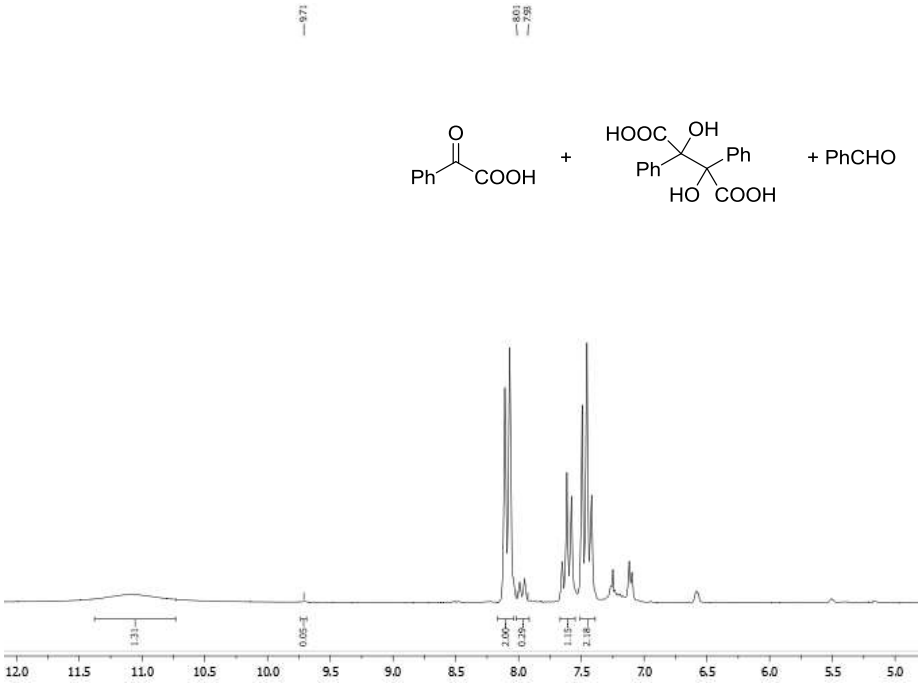


^{1}H NMR spectrum of TIPS-EBX in $CDCl_3$, after irradiation for 4 h (in THF)

^{1}H-NMR spectra (in $CDCl_3$) of $PhCOCO_2H$, before and after irradiation for 60 min (in THF) were recorded. After irradiation, additional peaks were observed, that can be attributed mainly to the dimerization product[26] (product from photodecomposition, **8.01-7.93 ppm**) and benzaldehyde (**9.71 ppm**).[27]

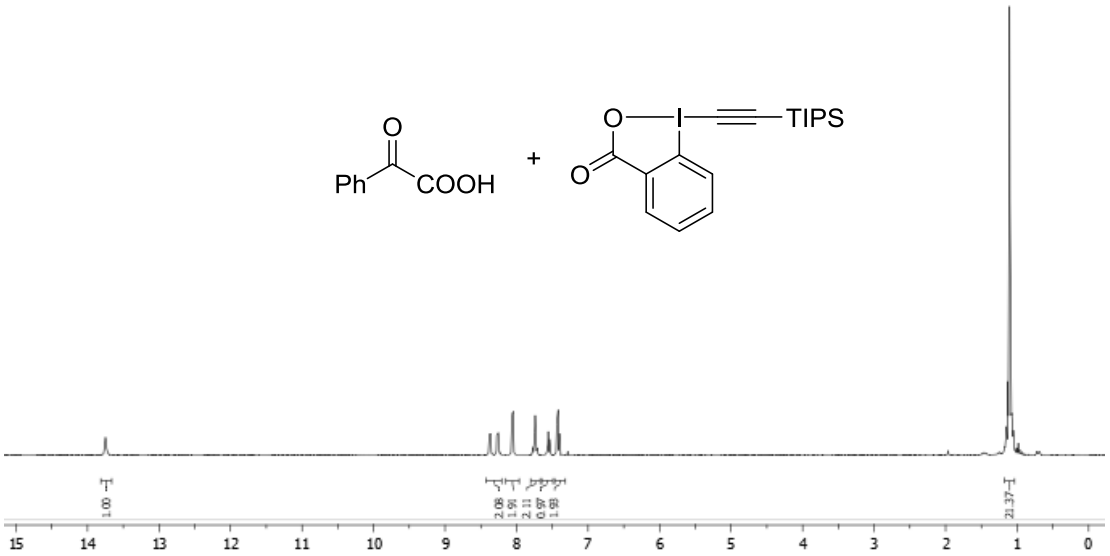


^{1}H NMR spectrum of PhCOCOOH in $CDCl_3$ (in THF)

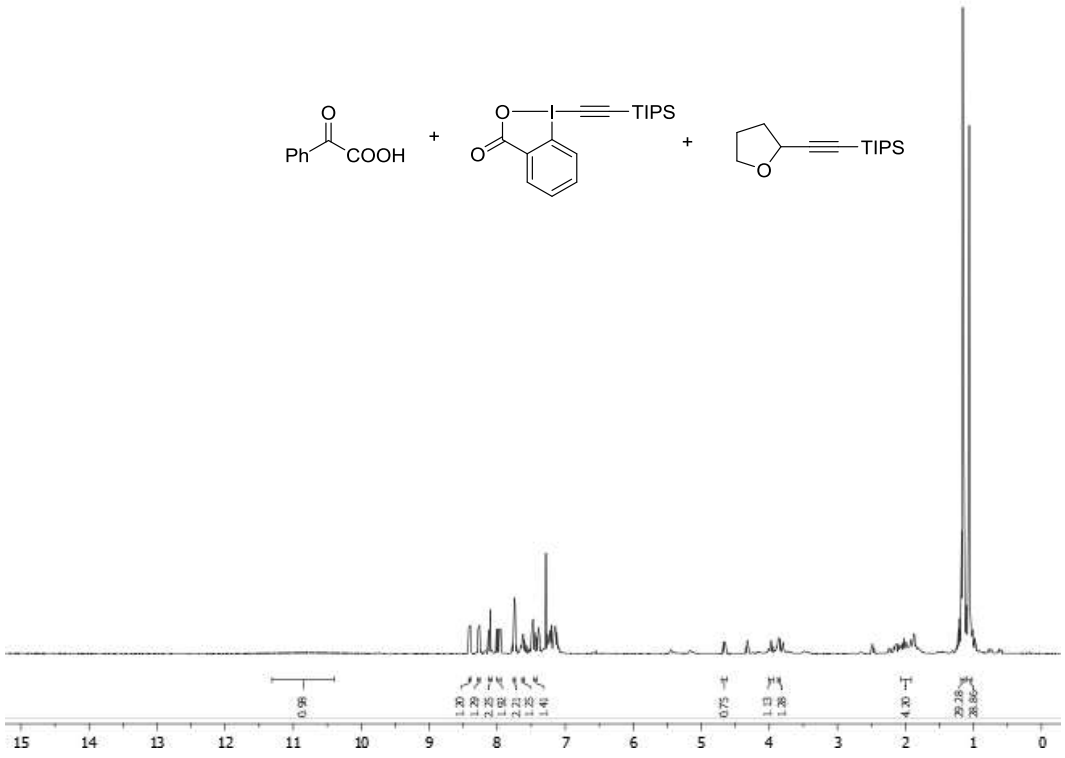


^{1}H NMR spectrum of PhCOCOOH in $CDCl_3$, after irradiation for 4 h (in THF)

Finally, the reaction mixture (PhCOCOOH and TIPS-EBX) (in $CDCl_3$) presented all expected signals.

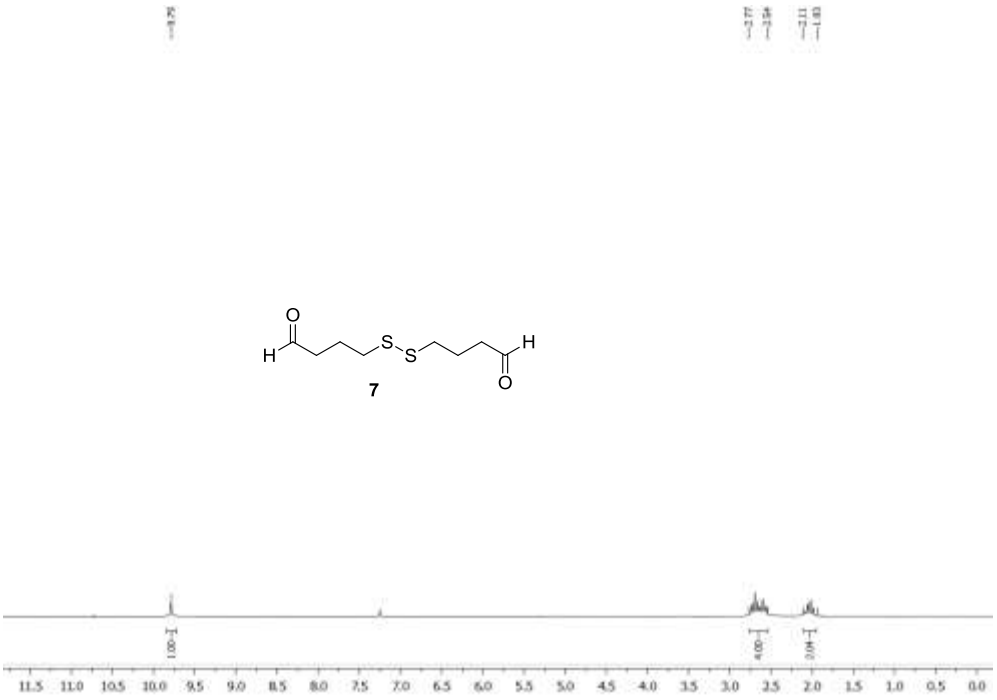


^{1}H NMR spectrum of the reaction mixture in $CDCl_3$ (in THF)

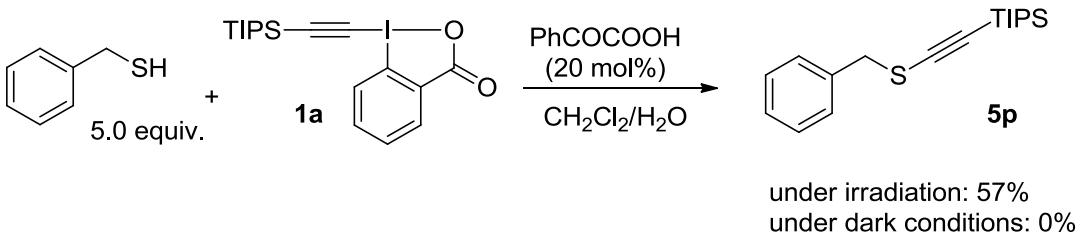


^{1}H NMR spectrum of the reaction mixture in $CDCl_3$, after irradiation for 4 h (in THF)

Compound **7** (deriving from water addition to THT radical) was isolated by column chromatography. The ^{1}H-NMR spectrum is presented below.

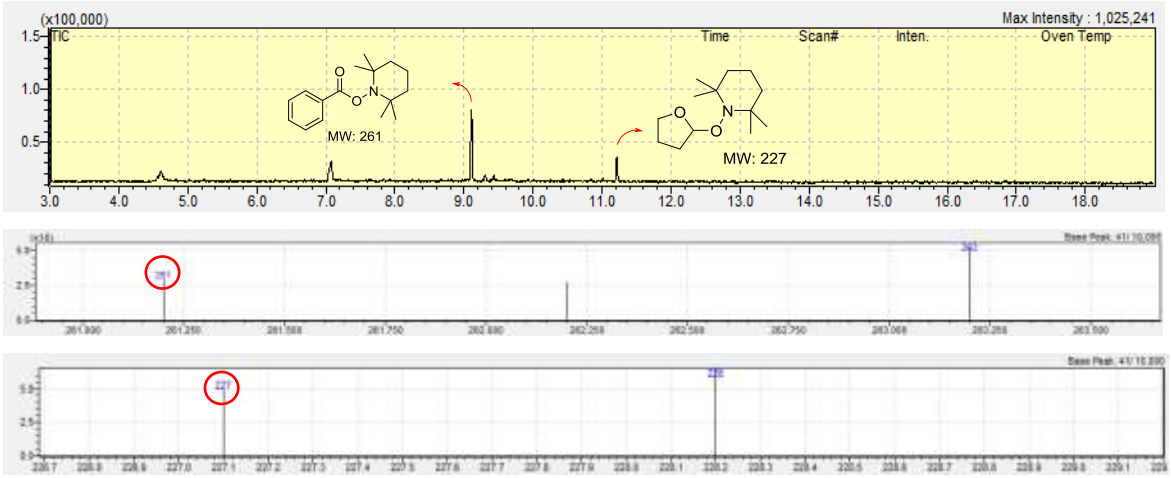


Furthermore, when TIPS-EBX (**1a**) (21.4 mg, 0.05 mmol), phenylglyoxylic acid (**4a**) (1.5 mg, 0.010 mmol) and benzyl mercaptan (31.0 mg, 0.25 mmol) in CH_2Cl_2/H_2O (1 mL), were added in a glass vial with a screw cap and left stirring for 18 h, **5p** was isolated in 57% yield. When the reaction was kept in dark, **5p** was not formed.



Photochemical Reaction between TIPS-EBX, THF and TEMPO

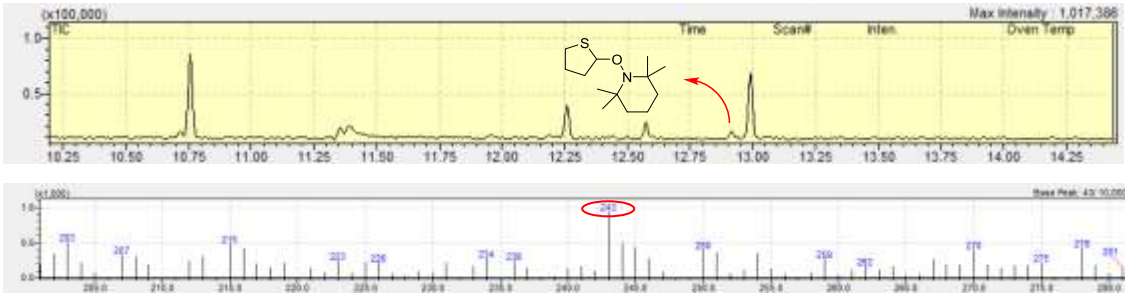
In a glass vial with a screw cap containing TIPS-EBX (**1a**) (214 mg, 0.50 mmol), TEMPO (78 mg, 0.50 mmol), phenylglyoxylic acid (**4a**) (15 mg, 0.10 mmol) in THF (1 mL), was added. The vial was sealed with a screw cap and left stirring under household bulb irradiation for 18 h. The reaction mixture was analyzed by Gas Chromatograph Mass Spectrometer (GC-MS). The spectra recorded are presented below. 2,2,6,6-tetramethyl-1-((tetrahydrofuran-2-yl)oxy)piperidine and THF-TEMPO were observed, hinting the formation of a benzoyl radical and α-THF radical.



The adducts formed from the reaction between TIPS-EBX and TEMPO in THF, in the presence of phenylglyoxylic acid, identified by GC-MS.

Photochemical Reaction between TIPS-EBX, THT and TEMPO

In a glass vial with a screw cap containing TIPS-EBX (**1a**) (214 mg, 0.50 mmol), TEMPO (78 mg, 0.50 mmol), phenylglyoxylic acid (**4a**) (15 mg, 0.10 mmol) in THT/H_2O (1 mL, 1:1), was added. The vial was sealed with a screw cap and left stirring under household bulb irradiation for 18 h. The reaction mixture was analyzed by Gas Chromatograph Mass Spectrometer (GC-MS). The spectra recorded are presented below. 2,2,6,6-tetramethyl-1-((tetrahydrothiofuran-2-yl)oxy)piperidine was observed, hinting the formation of α-THT radical.



The adduct formed from the reaction between TIPS-EBX and TEMPO in THT, in the presence of phenylglyoxylic acid, identified by GC-MS.

High Resolution Mass Spectrometry Studies

Instrumentation

The High Resolution Mass Spectra were recorded with a Q-TOF (Time of Flight Mass Spectrometry) Bruker Maxis Impact with ESI source and U-HPLC Thermo Dionex Ultimate 3000 pump and autosampler. N_2 was used as collision gas and electrospray ionization (ESI) – positive and negative mode - was used for the MS experiments. The data acquisition was carried out with Data Analysis from Bruker Daltonics (version 4.1). For the MS experiments, a solution approximately of 10 mg/L in acetonitrile for each analyte was used. Acetonitrile LC-MS gradient was obtained from Carlo Erba Reagents (Chaussée du Vexin, France). (Source conditions: End plate offset 500V, Capillary 4500V, Nebulizer 0.4 Bar, Dry gas 4.0 l/min, Dry temperature 180 ^{o}C and Quadrupole conditions: Ion energy 5 eV, Collision energy 10 eV, Transfer time 143 μs, Collision ion RF 3500 vpp, Pre pulse storage 1μs). The photochemical setup was placed next to the Q-TOF instrument and a direct infusion, directly from the irradiated reaction mixture, was performed, in order to minimize time without irradiation. Since the crude reaction mixture was analyzed by this method, there are a lot of peaks with different intensities. Most peaks assigned to intermediates are not visible in the full-scan spectra and thus zoomed-in insets are provided.

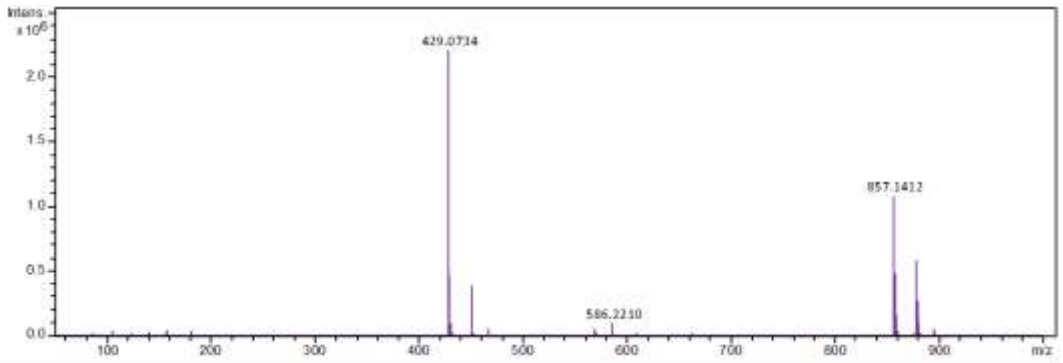
Reaction between THF and **1a** in the presence of **4a** under irradiation

In a glass vial with a screw cap containing 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol) in tetrahydrofuran (0.5 mL), phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol) was added. The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 4 h. The photochemical setup was placed next to the Q-TOF instrument and a direct infusion, directly from the irradiated reaction mixture, was performed, in order to minimize time without irradiation. Since the crude reaction mixture was analyzed by this method, there

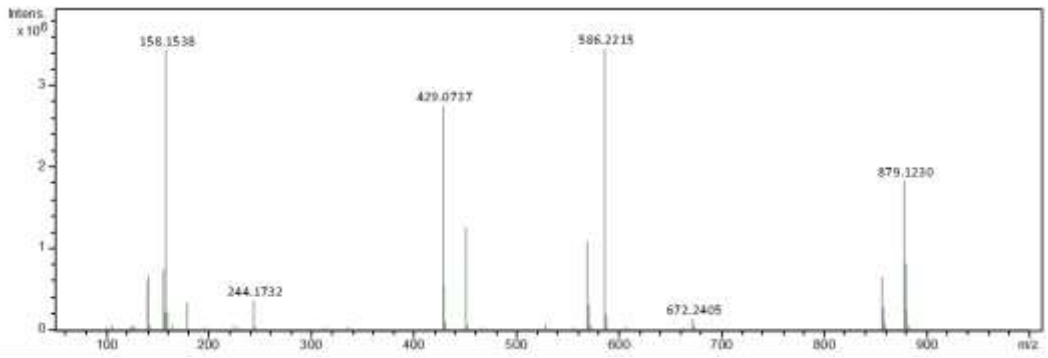
are a lot of peaks with different intensities. Most peaks assigned to intermediates are not visible in the full-scan spectra and thus zoomed-in insets are provided.

High Resolution Mass Spectrometry in Positive ESI mode

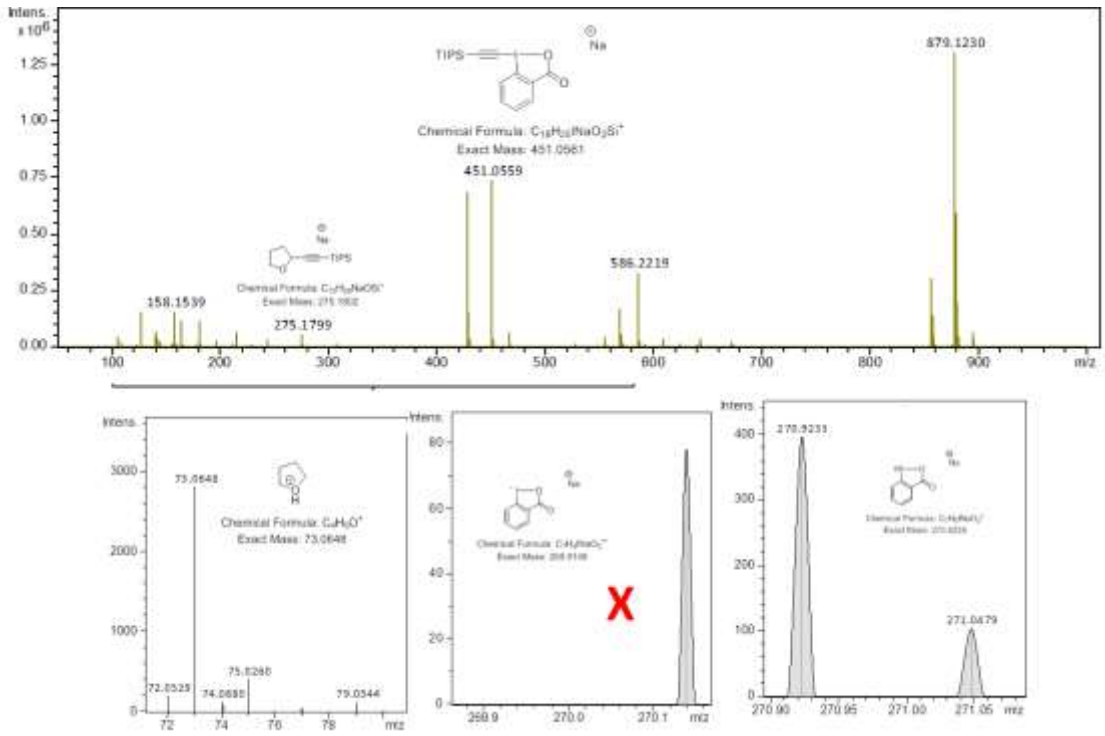
1 h



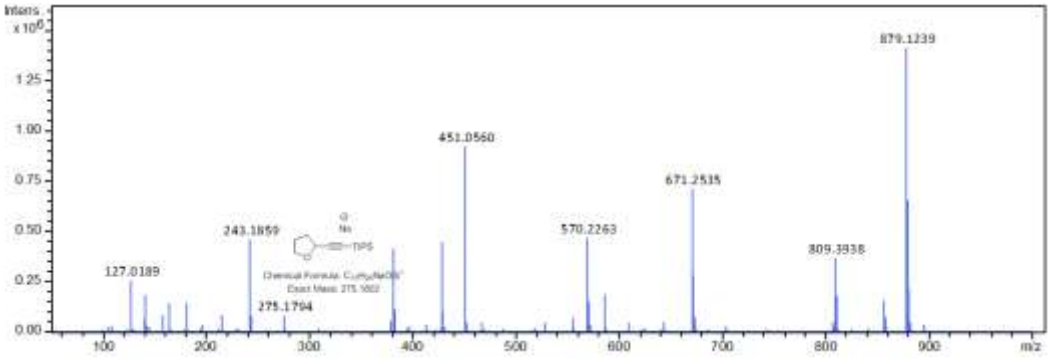
2 h



3 h

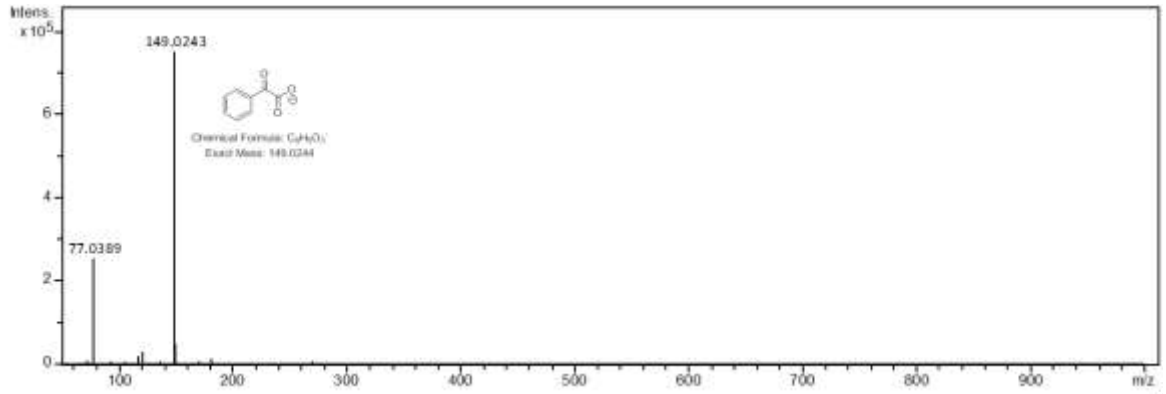

Intens.
x 10^6
1.25
1.00
0.75
0.50
0.25
0.00
TIPS
O
O
Na
Chemical Formula: C19H32NaO3Si+
Exact Mass: 451.0561
451.0559
879.1230
586.2218
158.1539
275.1799
100
200
300
400
500
600
700
800
900
m/z
Intens.
3000
2000
1000
0
73.0648
Chemical Formula: C4H9O+
Exact Mass: 73.0648
72.0573
74.0680
75.0280
79.0544
72
74
76
78
m/z
Intens.
80
60
40
20
0
X
268.9
270.0
270.1
m/z
Intens.
400
300
200
100
0
270.9233
271.0479
270.90
270.95
271.00
271.05
m/z

4 h

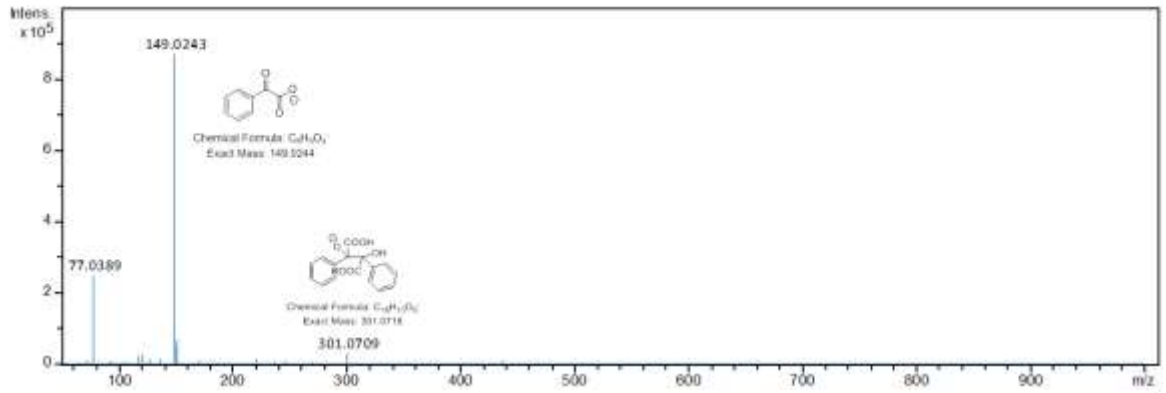

Intens.
x 10^6
1.25
1.00
0.75
0.50
0.25
0.00
879.1239
451.0560
671.2515
243.1859
570.2263
809.3938
127.0189
275.1794
Na
TIPS
100
200
300
400
500
600
700
800
900
m/z

High Resolution Mass Spectrometry in Negative ESI mode

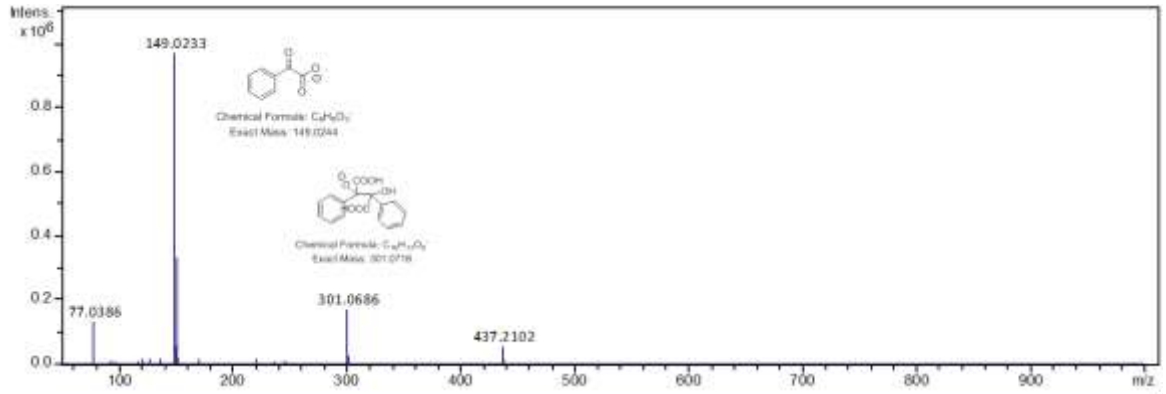
1 h



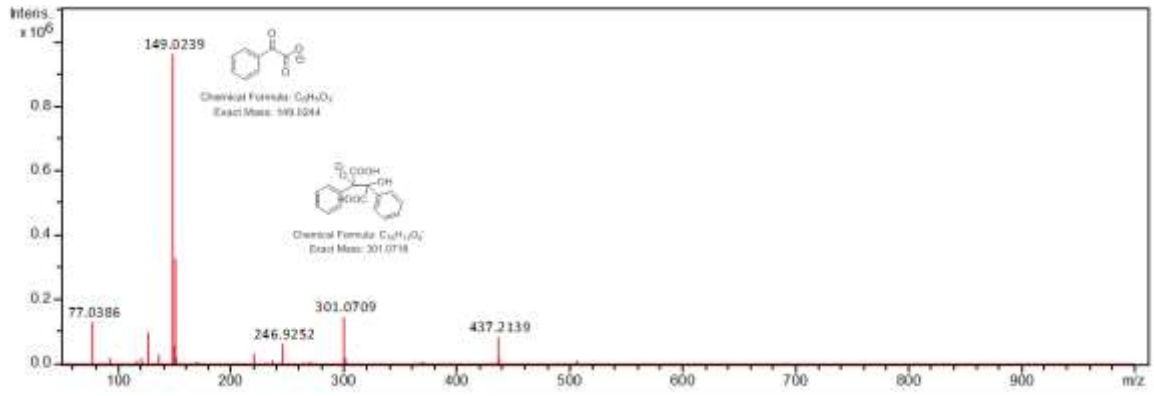
2 h



3 h



4 h

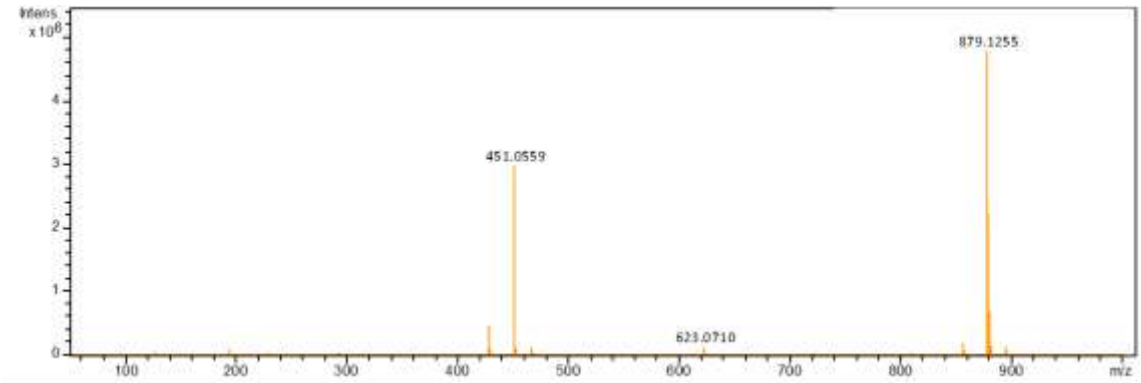


Reaction between THT and **1a** in the presence of **4a** under irradiation

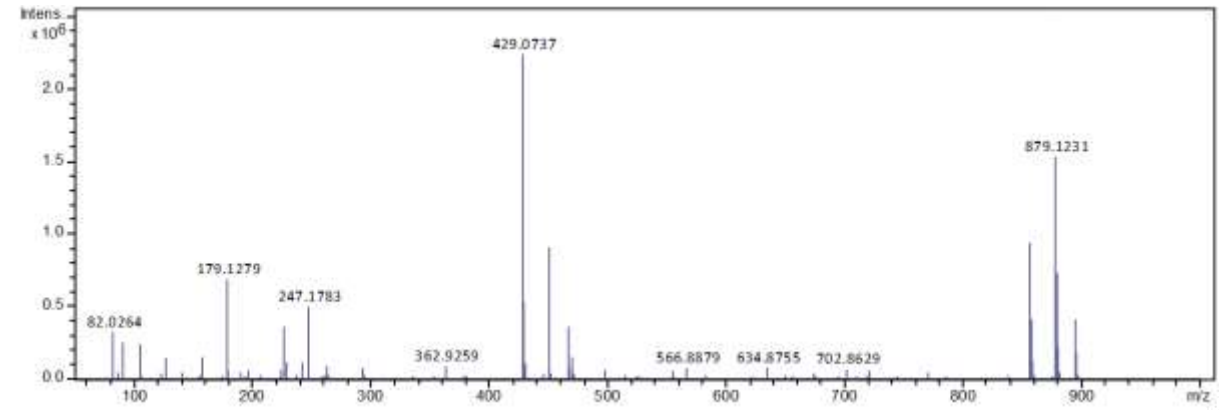
In a glass vial with a screw cap containing 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol) in tetrahydrothiophene (0.25 mL) and water (0.25 mL), phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol) was added. The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 4 h. The photochemical setup was placed next to the Q-TOF instrument and a direct infusion, directly from the irradiated reaction mixture, was performed, in order to minimize time without irradiation. Since the crude reaction mixture was analyzed by this method, there are a lot of peaks with different intensities. Most peaks assigned to intermediates are not visible in the full-scan spectra and thus zoomed-in insets are provided.

High Resolution Mass Spectrometry in Positive ESI mode

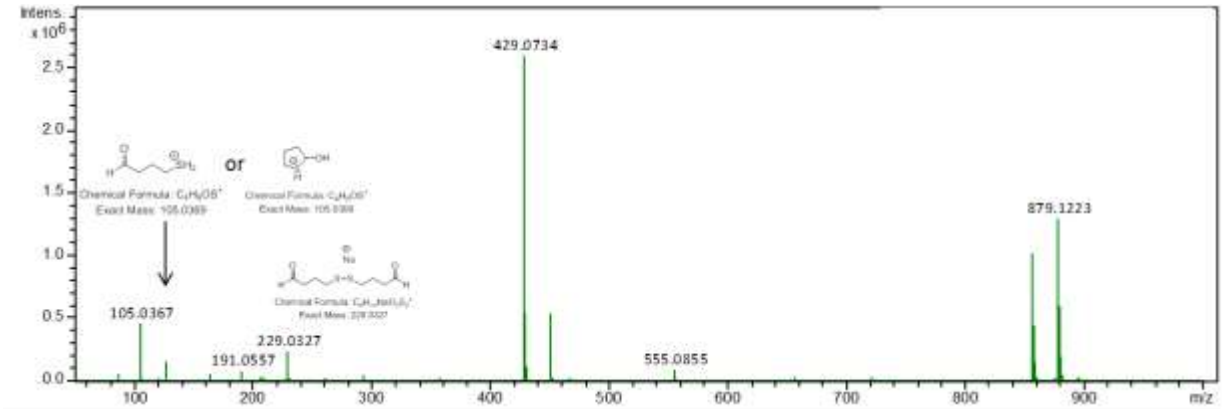
0 min



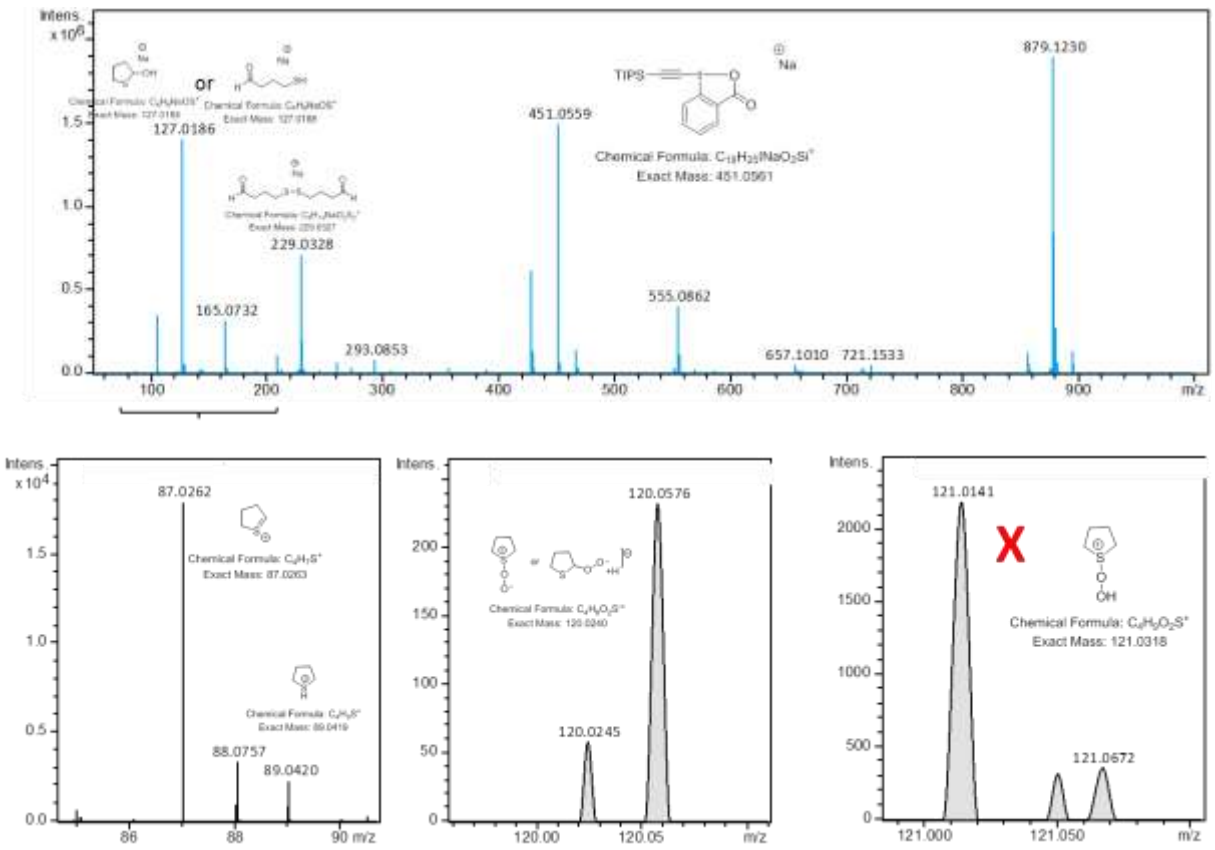
1 h

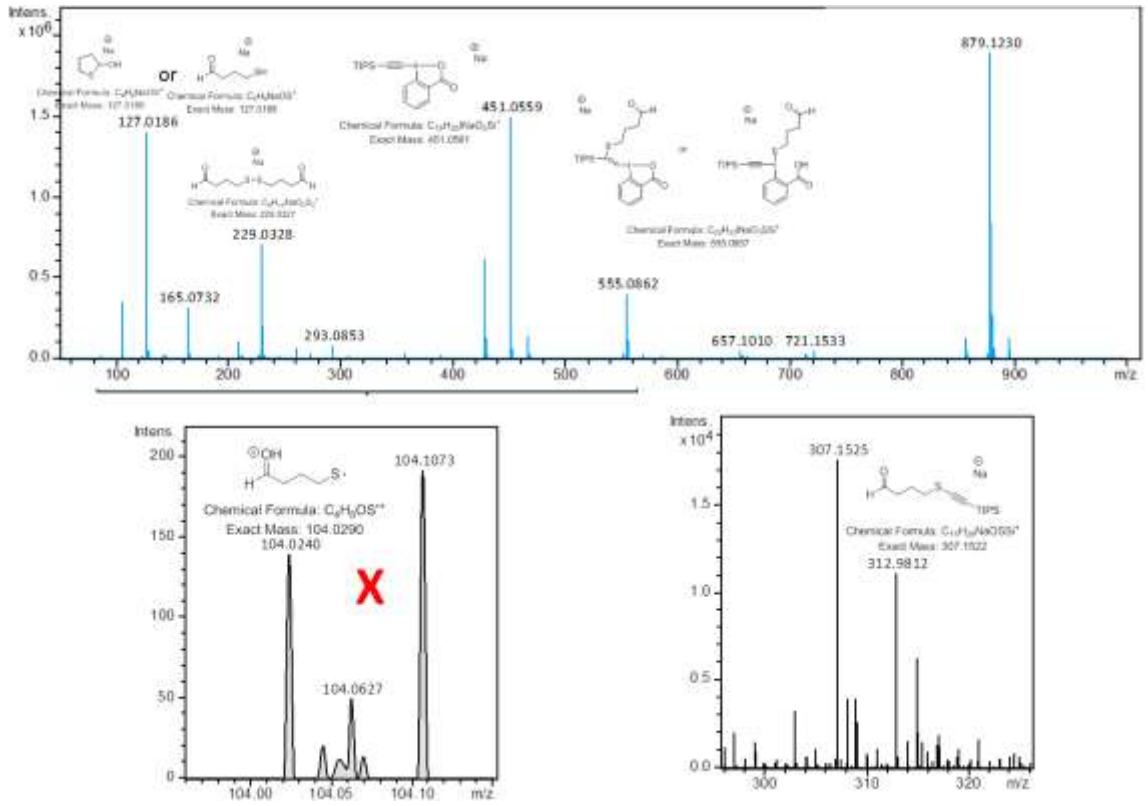


2 h

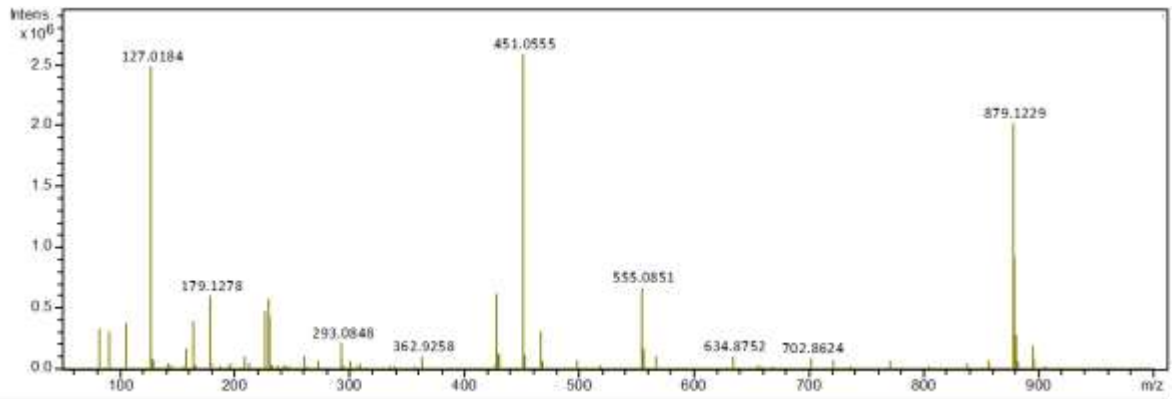


3 h


Intens.
x 10^6
or
127.0186
229.0328
165.0732
293.0853
451.0559
555.0862
657.1010
721.1533
879.1230
TIPS
Na
Chemical Formula: C18H25INaO2Si+
Exact Mass: 451.0561
m/z
Intens.
x 10^4
87.0262
Chemical Formula: C4H3S+
Exact Mass: 87.0263
88.0757
89.0420
m/z
Intens.
120.0576
120.0245
Chemical Formula: C4H5O2S+
Exact Mass: 121.0318
m/z
Intens.
121.0141
X
121.0672
Chemical Formula: C4H5O2S+
Exact Mass: 121.0318
m/z


Intens.
x10^6
or
127.0186
229.0328
165.0732
293.0853
451.0559
555.0862
657.1010
721.1533
879.1230
m/z
Intens.
104.1073
Chemical Formula: C4H9OS+
Exact Mass: 104.0290
104.0240
X
104.0627
104.00
104.05
104.10
m/z
Intens.
x10^4
307.1525
312.9812
300
310
320
m/z

4 h


Intens.
x10^6
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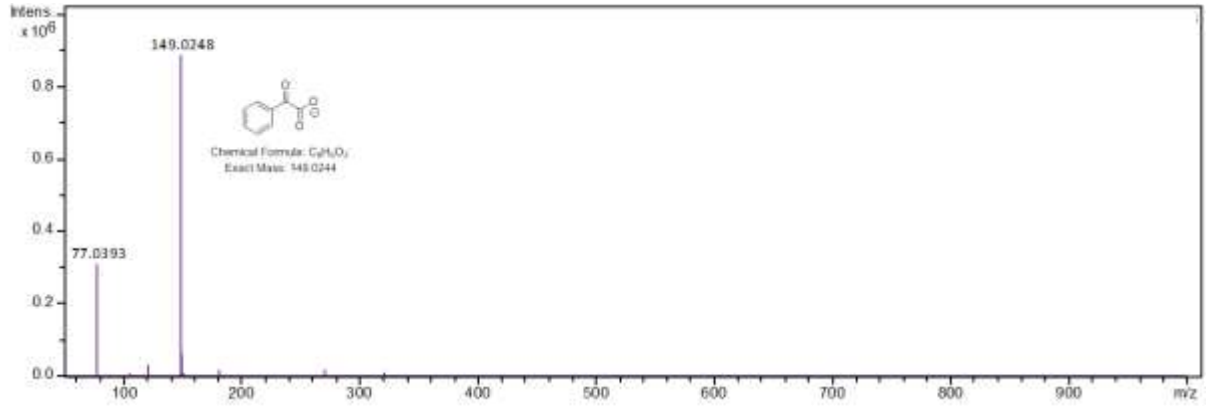
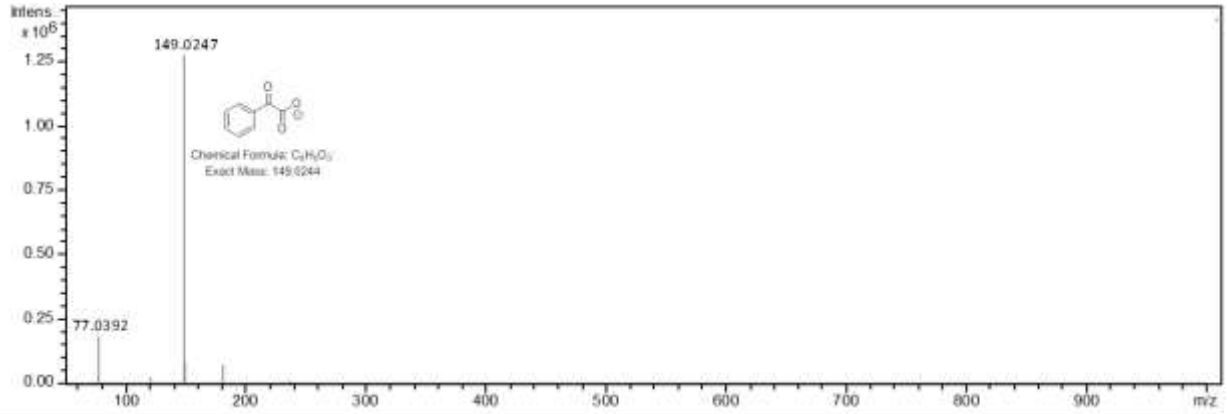
879.1229
179.1278
555.0851
293.0848
362.9258
634.8752
702.8624
m/z

High Resolution Mass Spectrometry in Negative ESI mode

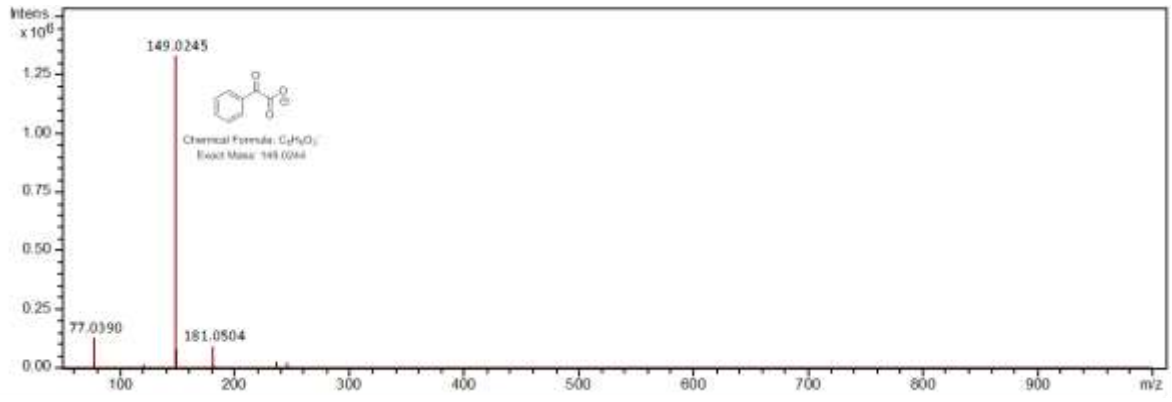
0 min



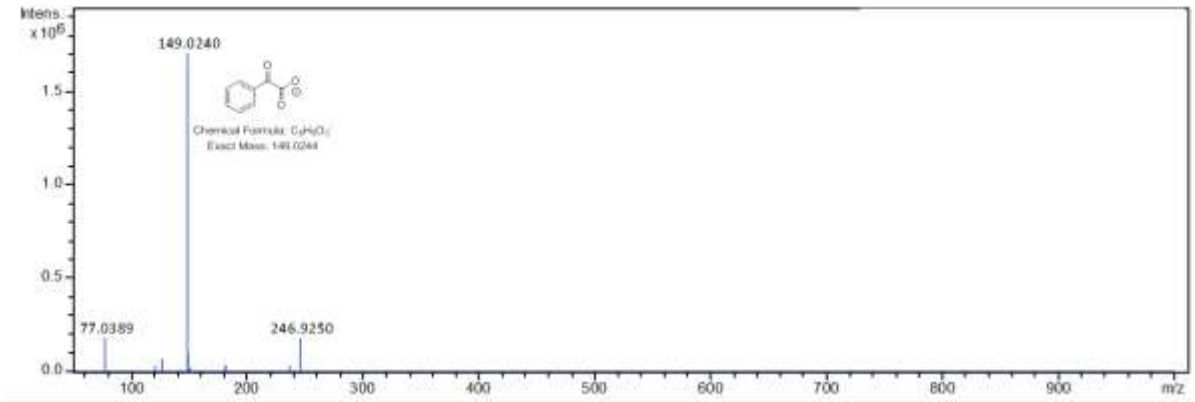
1 h



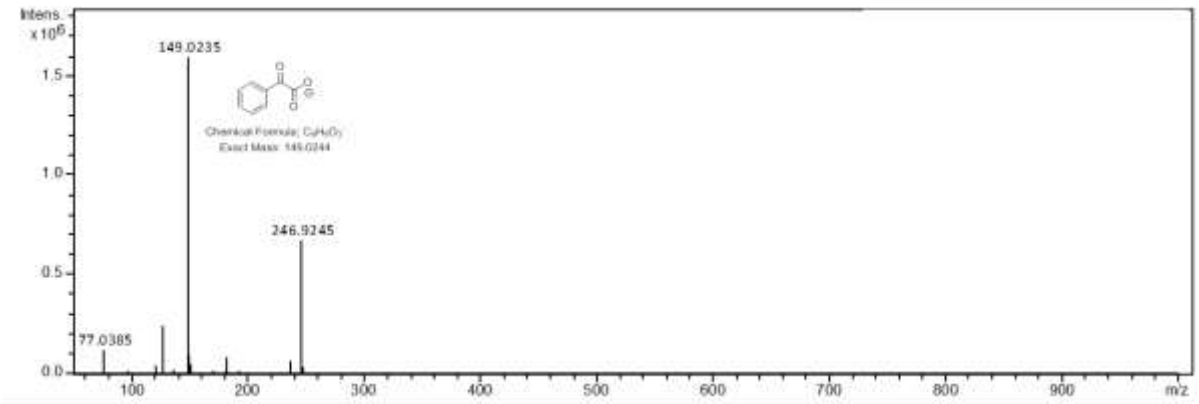
2 h



3 h



4 h

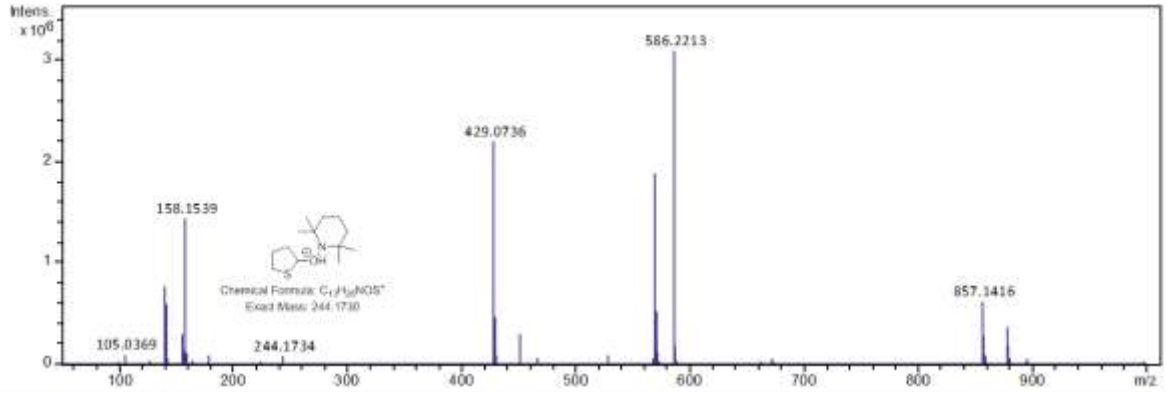


Reaction between THT and **1a** in the presence of **4a** and Tempo under irradiation

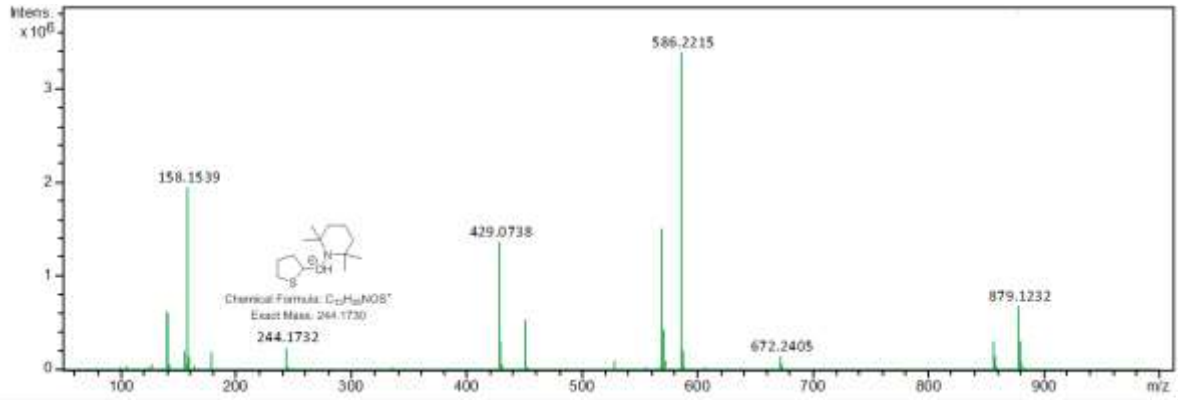
In a glass vial with a screw cap containing 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol) in tetrahydrothiophene (0.25 mL) and water (0.25 mL), phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol) and Tempo (12 mg, 0.075 mmol) were added. The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 4 h. The photochemical setup was placed next to the Q-TOF instrument and a direct infusion, directly from the irradiated reaction mixture, was performed, in order to minimize time without irradiation. Since the crude reaction mixture was analyzed by this method, there are a lot of peaks with different intensities. Most peaks assigned to intermediates are not visible in the full-scan spectra and thus zoomed-in insets are provided.

High Resolution Mass Spectrometry in Positive ESI mode

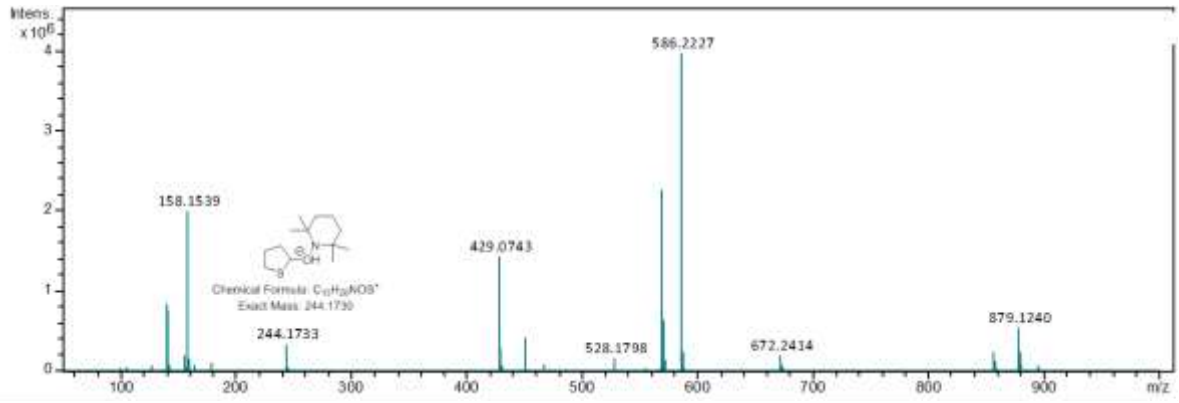
1 h

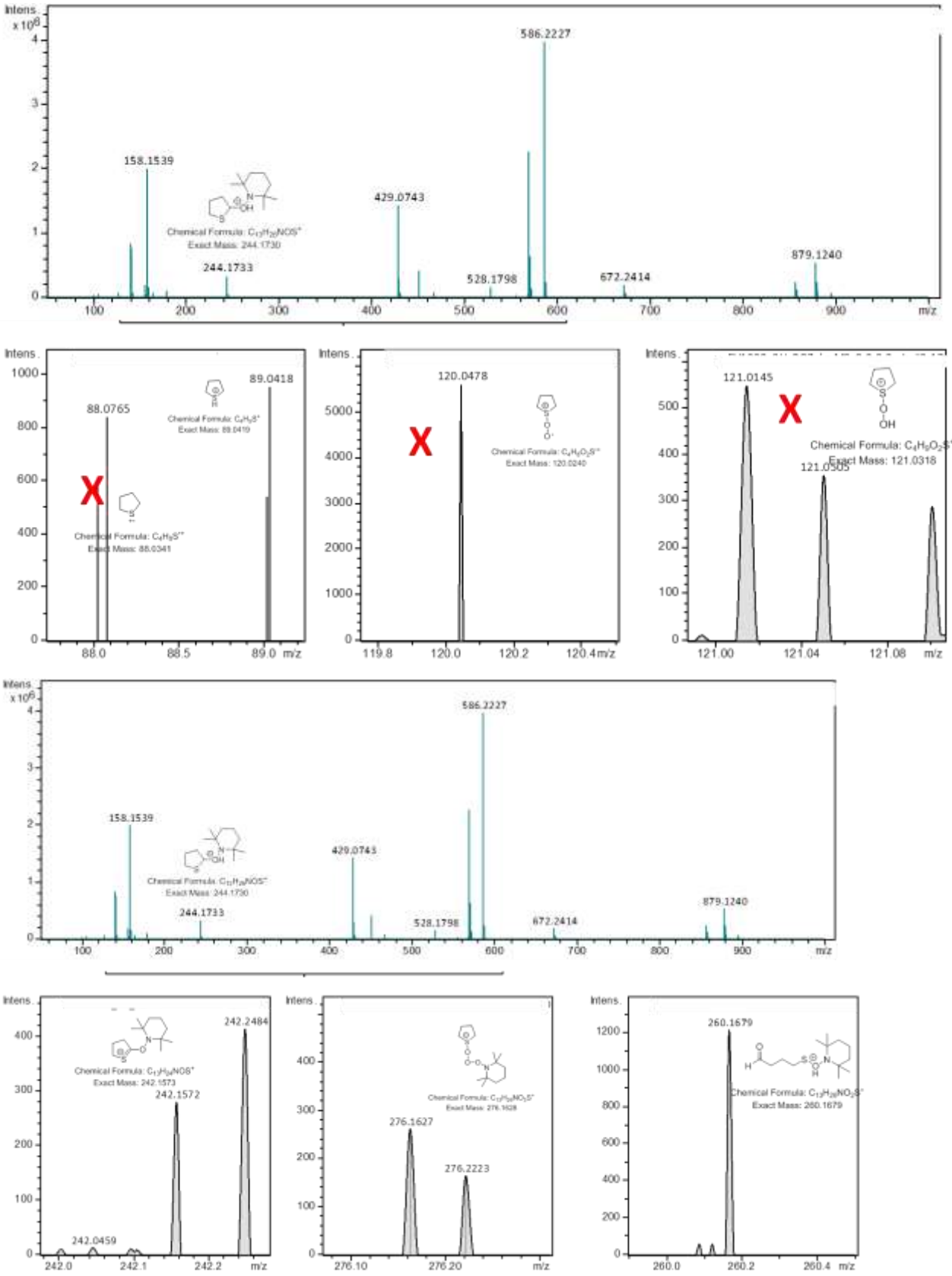


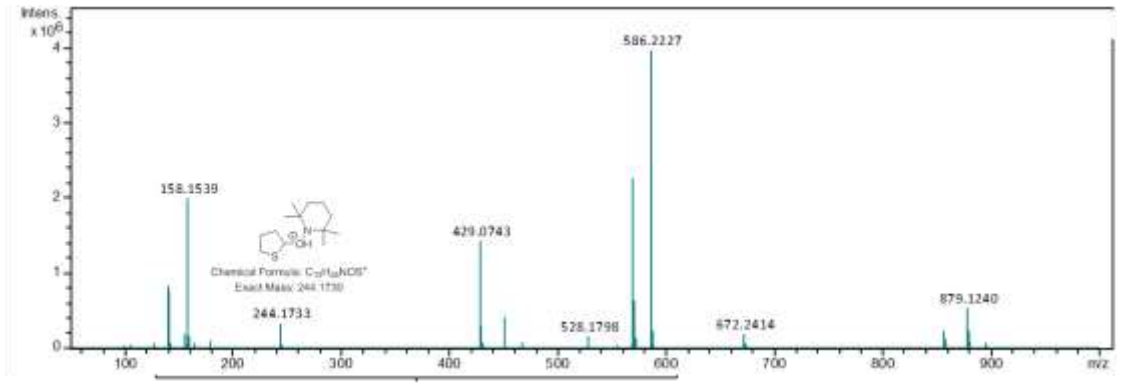
2 h

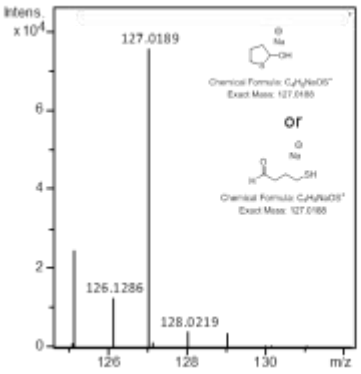


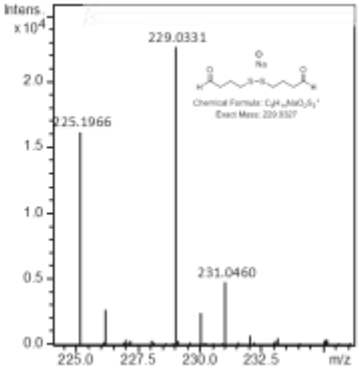
3 h

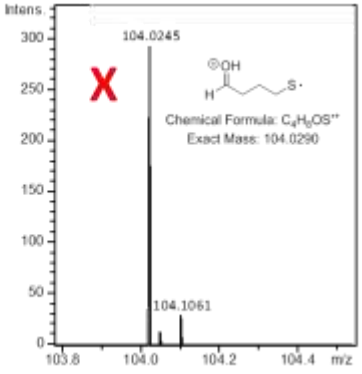


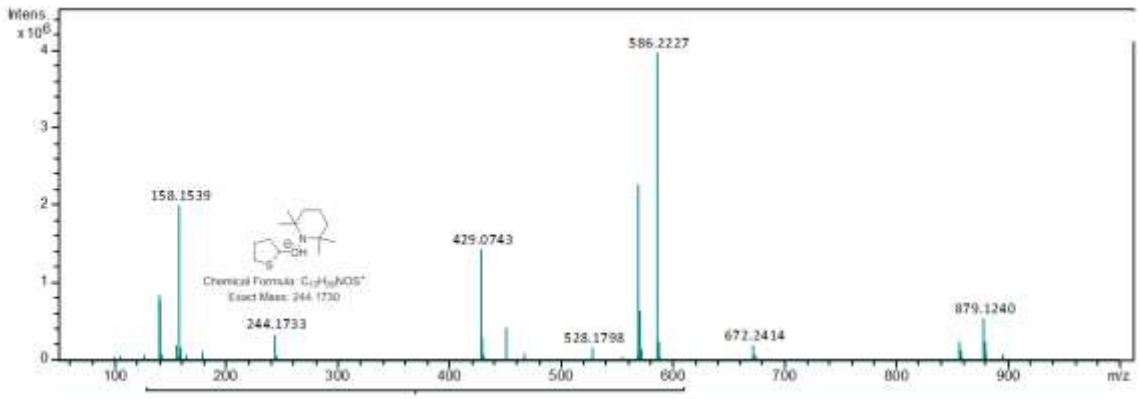

Intens.
x10^6
586.2227
158.1539
429.0743
244.1733
528.1798
672.2414
879.1240
m/z
Intens.
88.0765
89.0418
X
Intens.
120.0478
X
Intens.
121.0145
X
121.0505
Chemical Formula: C4H9O2S+
Exact Mass: 121.0318
Intens.
x10^6
586.2227
158.1539
429.0743
244.1733
528.1798
672.2414
879.1240
m/z
Intens.
242.2484
242.1572
242.0459
Intens.
276.1627
276.2223
Intens.
260.1679
Chemical Formula: C13H26NO3S+
Exact Mass: 260.1679

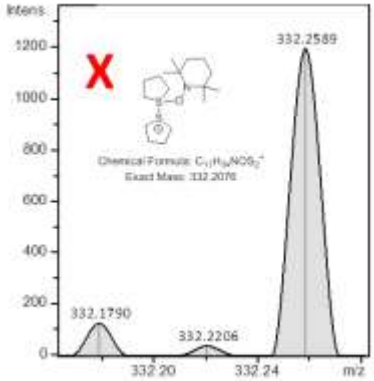

Intens.
x 10^6
586.2227
158.1539
429.0743
244.1733
528.1798
672.2414
879.1240
m/z

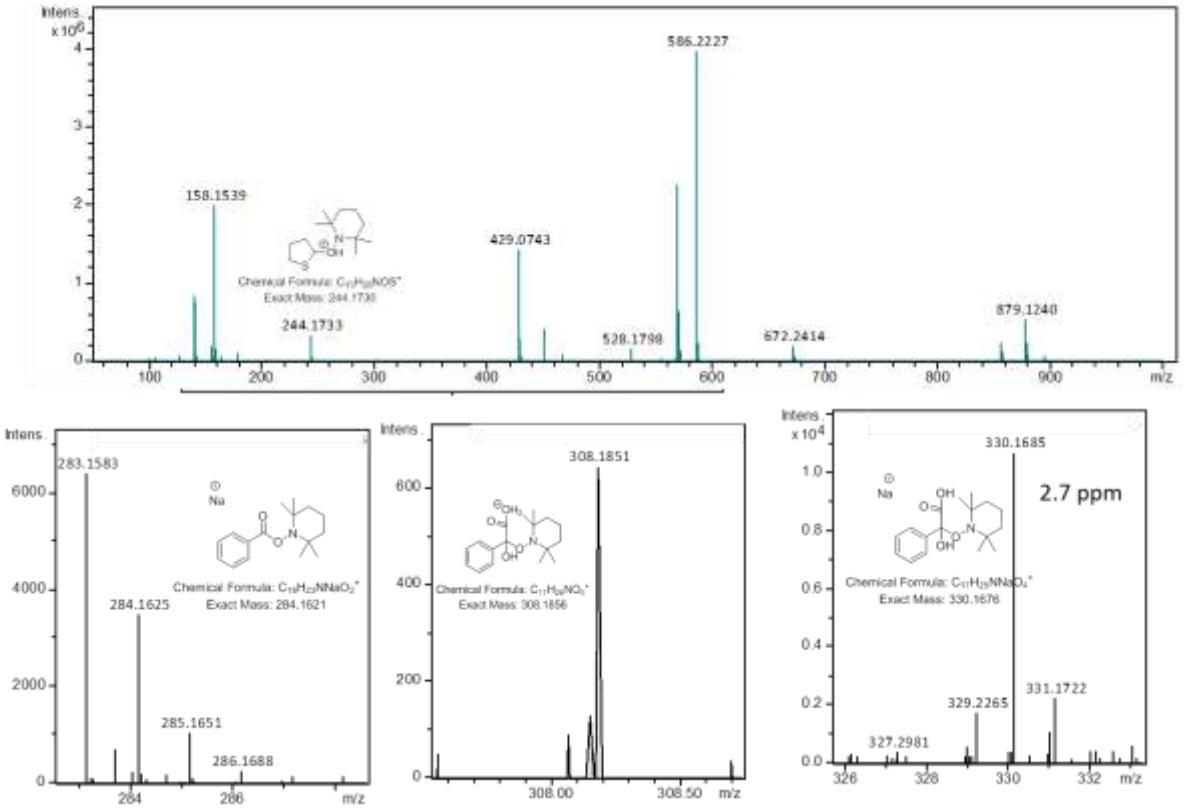

Intens.
x 10^4
127.0189
or
126.1286
128.0219
m/z


Intens.
x 10^4
229.0331
225.1966
231.0460
m/z

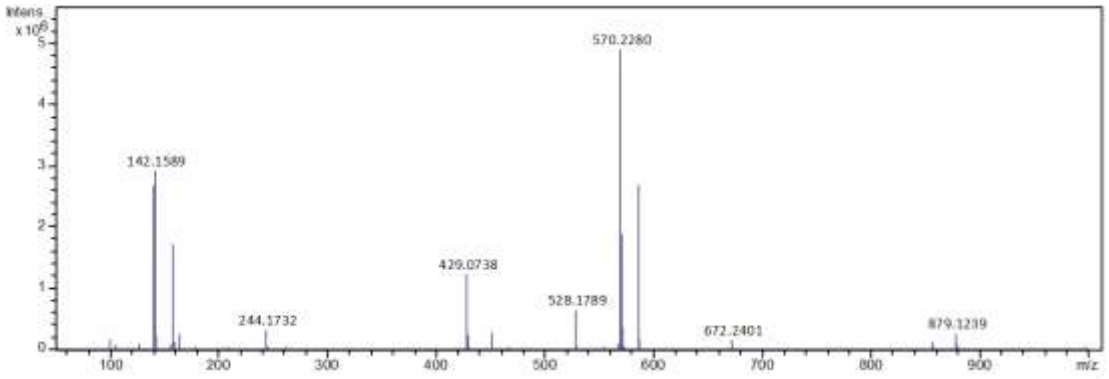

Intens.
104.0245
Chemical Formula: C4H5OS+
Exact Mass: 104.0290
104.1061
m/z


Intens.
x 10^6
586.2227
158.1539
429.0743
244.1733
528.1798
672.2414
879.1240
m/z


Intens.
332.2589
332.1790
332.2206
m/z

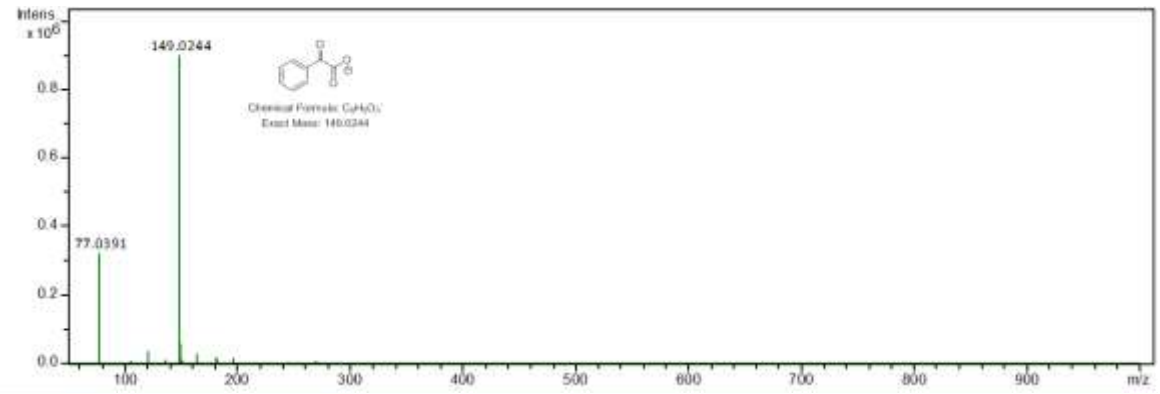

Intens
x 10^6
586.2227
158.1539
429.0743
244.1733
528.1798
672.2414
879.1240
m/z
Intens
283.1583
284.1625
285.1651
286.1688
Chemical Formula: C15H23NNaO2+
Exact Mass: 284.1621
Intens
308.1851
Chemical Formula: C17H26NO3+
Exact Mass: 308.1856
Intens
x 10^4
330.1685
2.7 ppm
Chemical Formula: C17H25NNaO4+
Exact Mass: 330.1676
329.2265
331.1722
327.2981

4 h

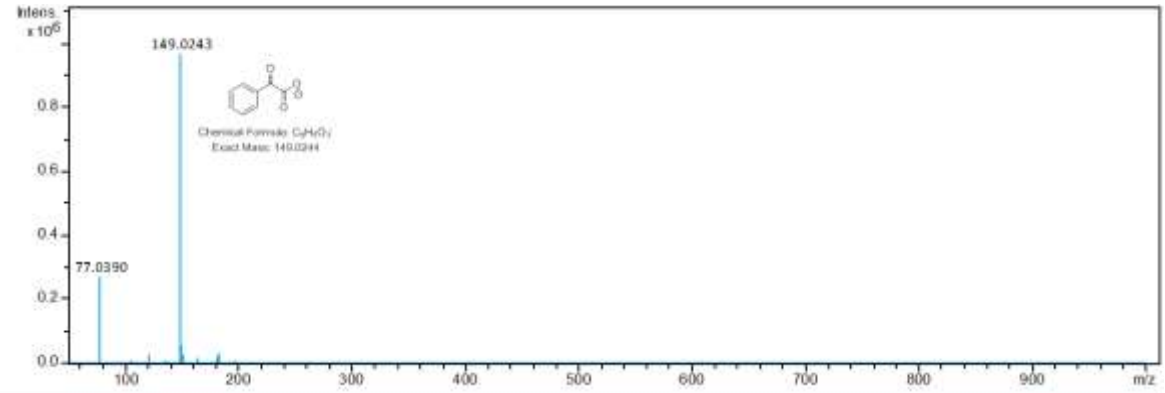

Intens
x 10^6
570.2280
142.1589
429.0738
244.1732
528.1789
672.2401
879.1239
m/z

High Resolution Mass Spectrometry in Negative ESI mode

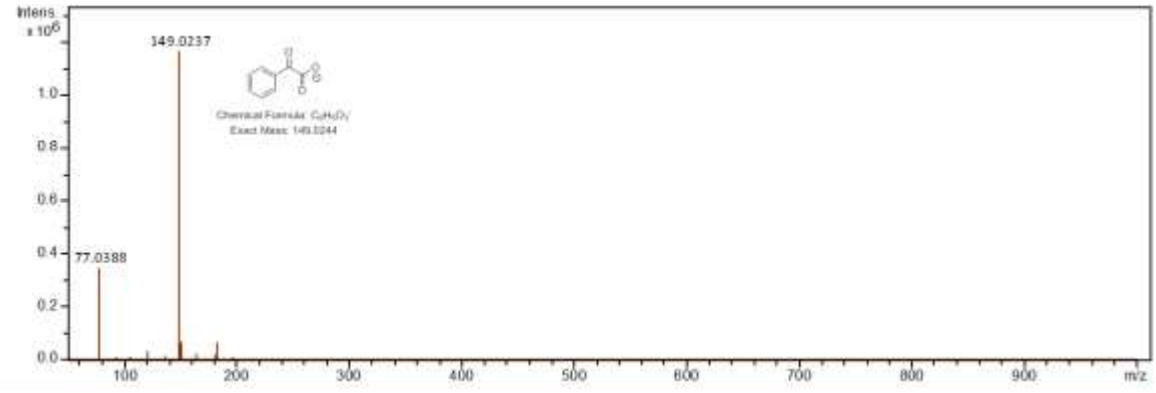
1 h



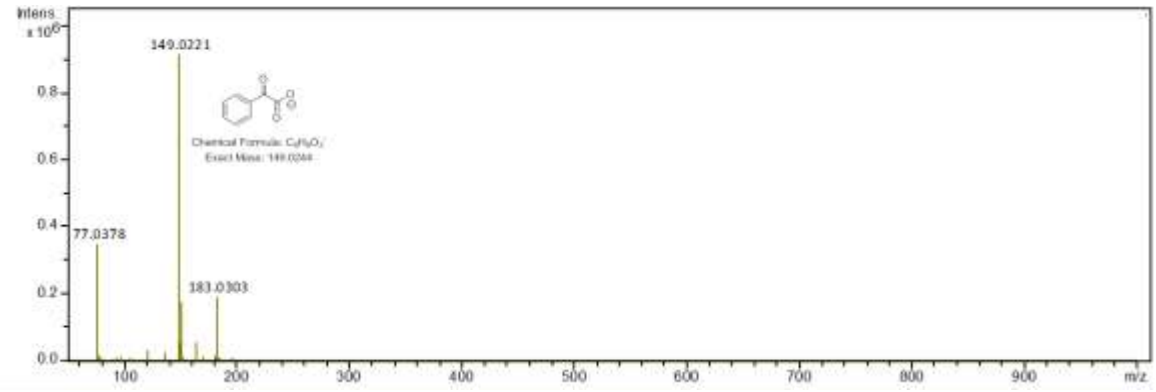
2 h



3 h



4 h

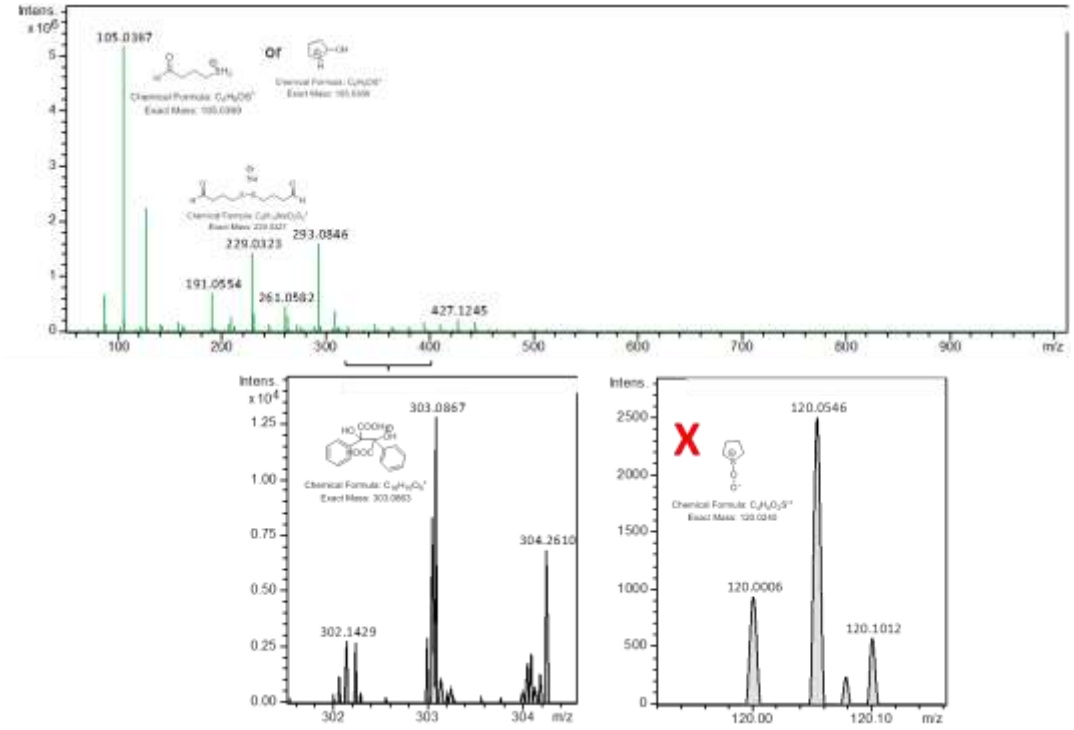


Reaction between THT and **1a** in the presence of **4a** under argon and irradiation

In a glass vial with a screw cap containing 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol) in tetrahydrothiophene (0.25 mL) and water (0.25 mL), phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol) was added. The reaction mixture was freeze-pumped-thawed and stirred under argon. The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 3 h. The photochemical setup was placed next to the Q-TOF instrument and a direct infusion, directly from the irradiated reaction mixture, was performed, in order to minimize time without irradiation. Since the crude reaction mixture was analyzed by this method, there are a lot of peaks with different intensities. Most peaks assigned to intermediates are not visible in the full-scan spectra and thus zoomed-in insets are provided.

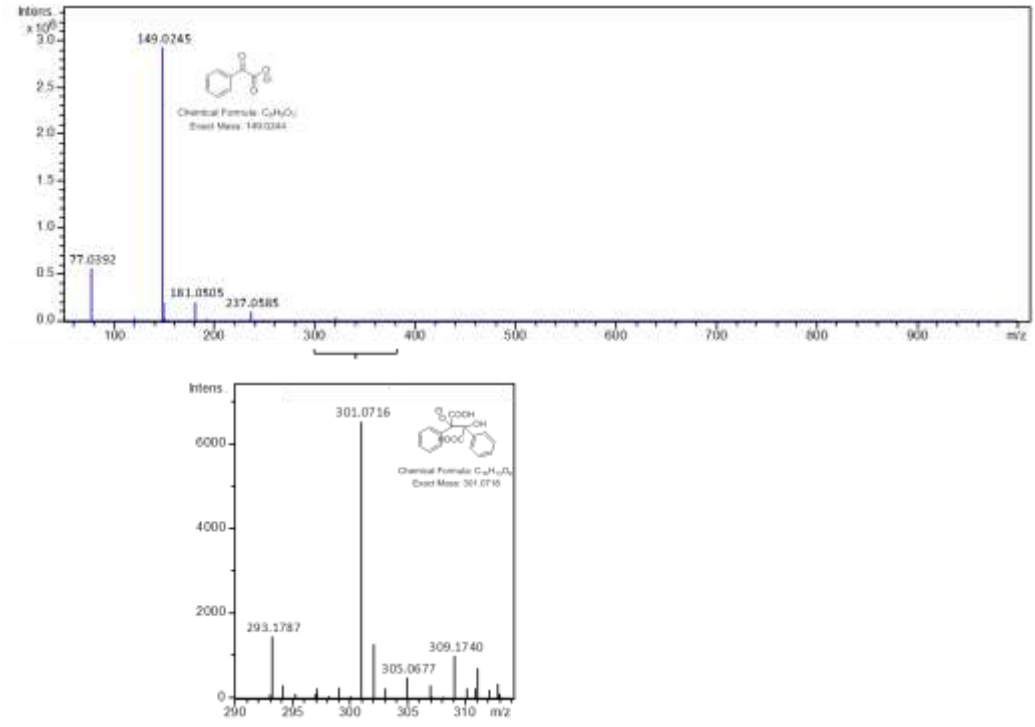
High Resolution Mass Spectrometry in Positive ESI mode

3 h



High Resolution Mass Spectrometry in Negative ESI mode

3 h



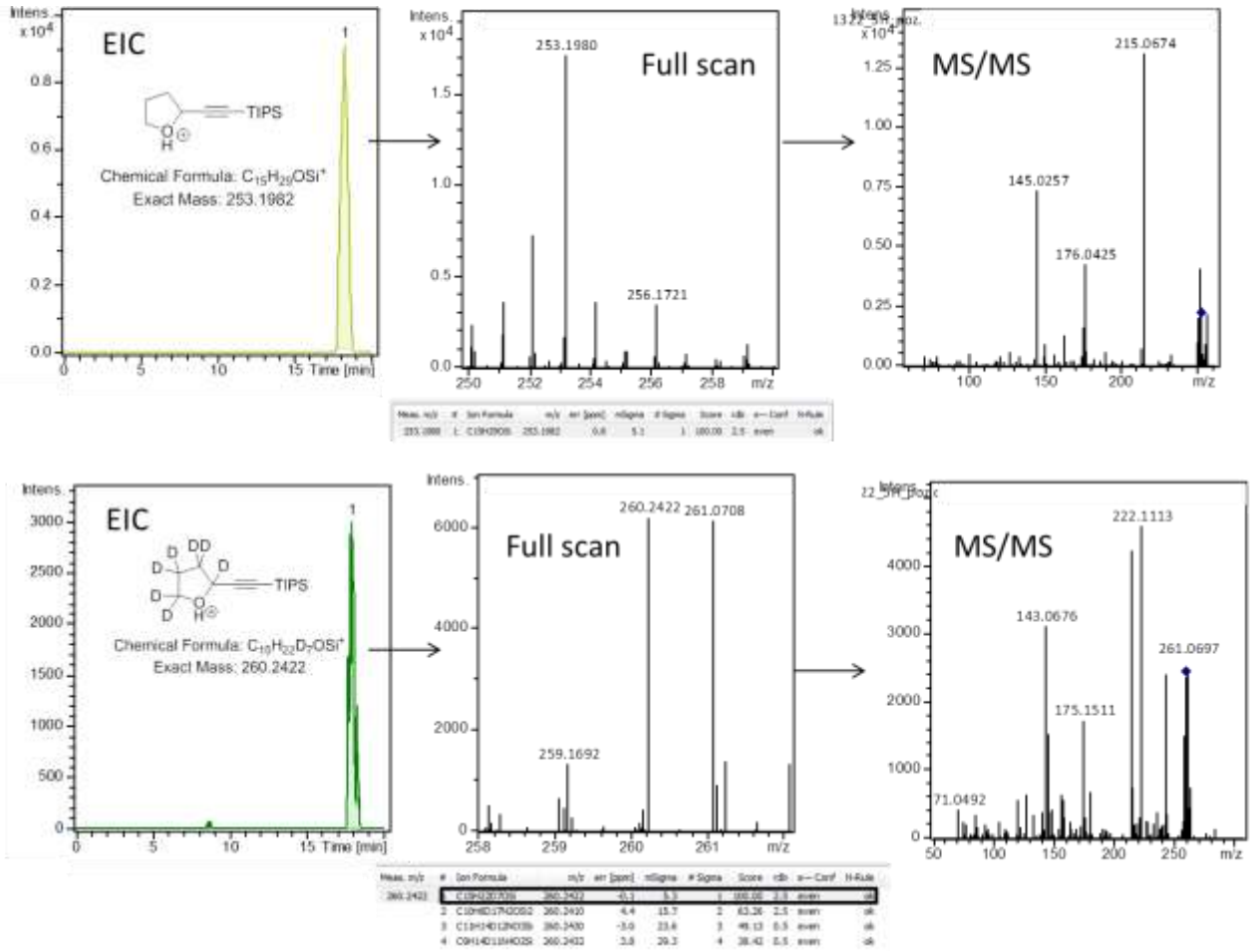
Determination of the KIE with High Resolution Mass Spectrometry (HRMS)

Instrumentation

The High Resolution Mass Spectrometry spectra were recorded on a Q-TOF (Time of Flight Mass Spectrometry) Bruker Maxis Impact with ESI source and U-HPLC Thermo Dionex Ultimate 3000 pump and autosampler. N_2 was used as the collision gas and electrospray ionization (ESI) –positive mode- was used for the Auto MS experiments. Chromolith (RP) (100 x 4.6 mm, Merck) was used as a column and the mobile phase was consisted of MeCN/H_2O (80/20, v/v):0.5% formic acid at 0.3 mL/min as flow rate. The data acquisition was carried out with Data analysis from Bruker Daltonics (version 4.1). The same reaction procedure was performed as above.

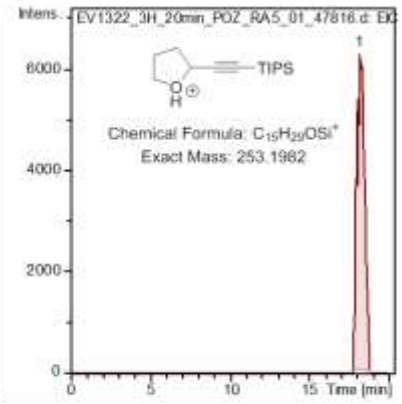
Reaction between THF/THF-*d8* and **1a** in the presence of **4a** under irradiation

In a glass vial with a screw cap containing 1-((triisopropylsilyl)ethynyl)benzo[1,2]iodaoxol-3(1*H*)-one **1a** (32 mg, 0.075 mmol) in tetrahydrofuran (0.25 mL): tetrahydrofuran-*d8* (0.25 mL), phenylglyoxylic acid **4a** (2.3 mg, 0.015 mmol) was added. The reaction mixture was stirred and irradiated using 2 x 85W household lamps for 3-5 h. The reaction conversion after 5 h was 20%. The photochemical setup was placed next to the Q-TOF instrument and a direct infusion, directly from the irradiated reaction mixture, was performed. Since the crude reaction mixture was analyzed by this method, there are a lot of peaks with different intensities. Most peaks assigned to intermediates are not visible in the full-scan spectra and thus zoomed-in insets are provided.

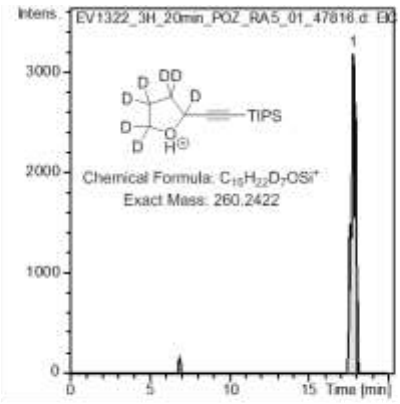


EICs (Extracted Ion Chromatograms) in Positive ESI mode

3 h



RT [min]	Area	Chromatogram
18.1	220193	EIC 253.1982

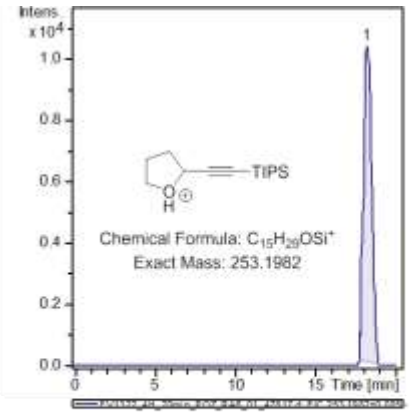


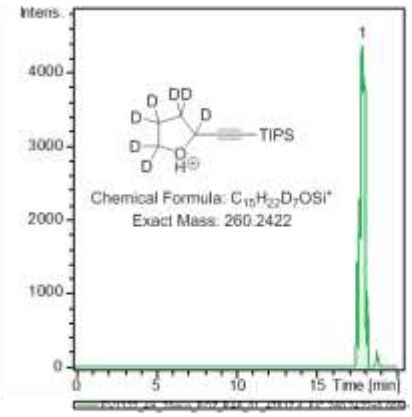
RT [min]	Area	Chromatogram
17.8	57901	EIC 260.2422

Kinetic Isotope Effect

d-0 / d-7 = 220193 / 57901 = 3.8

4 h





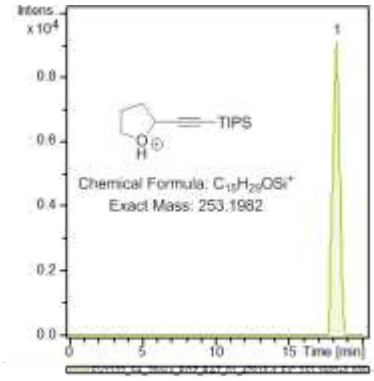
RT [min]	Area	Chromatogram
18.2	374735	EIC 253.1982

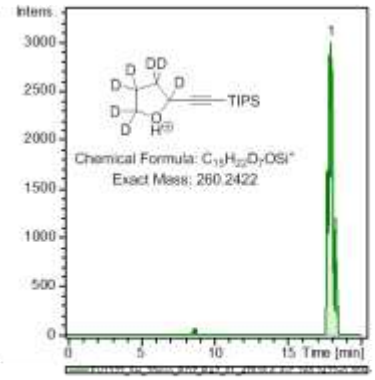
RT [min]	Area	Chromatogram
17.8	96720	EIC 260.2422

Kinetic Isotope Effect

d-0 / d-7 = 374735 / 96720 = 3.9

5 h





RT [min]	Area	Chromatogram
18.2	280087	EIC 253.1982

RT [min]	Area	Chromatogram
17.9	70570	EIC 260.2422

Kinetic Isotope Effect

d-0 / d-7 = 280087 / 70570 = 4.0

The results showed high mass accuracy (less than 5 ppm) and acceptable isotopic fit values (less than 50 mSigma).

Sigma: is a rate for the agreement of the theoretical and measured isotopic pattern of the mass peak of interest. It combines the standard deviation of the masses and intensities for all isotopic peaks. The values are given in [milliSigma] and lower numbers indicate a better fit.

Score: Score of the formula (a value between 0 and 100%). rdb: Number of rings and double bonds in the formula.

e^-Conf: Indicates whether the electron configuration is even or odd.

N-Rule: Indicates whether the nitrogen rule is fulfilled.

References

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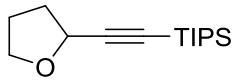
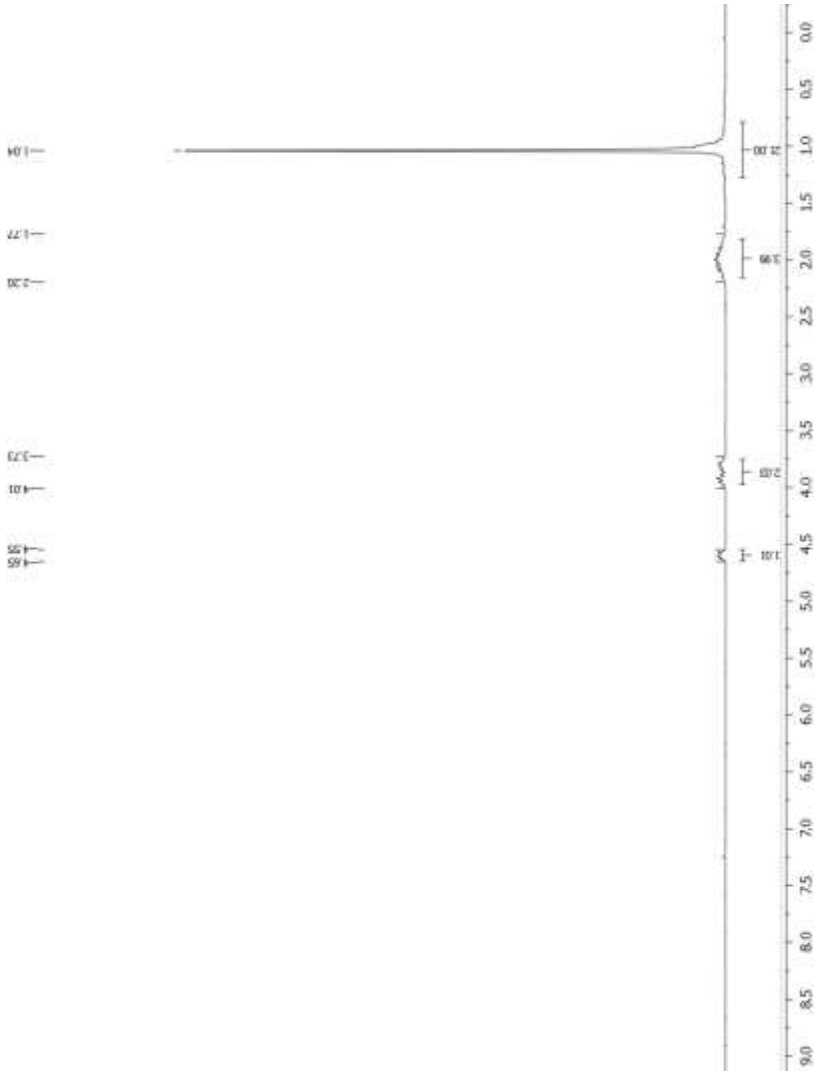
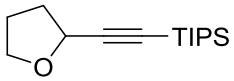
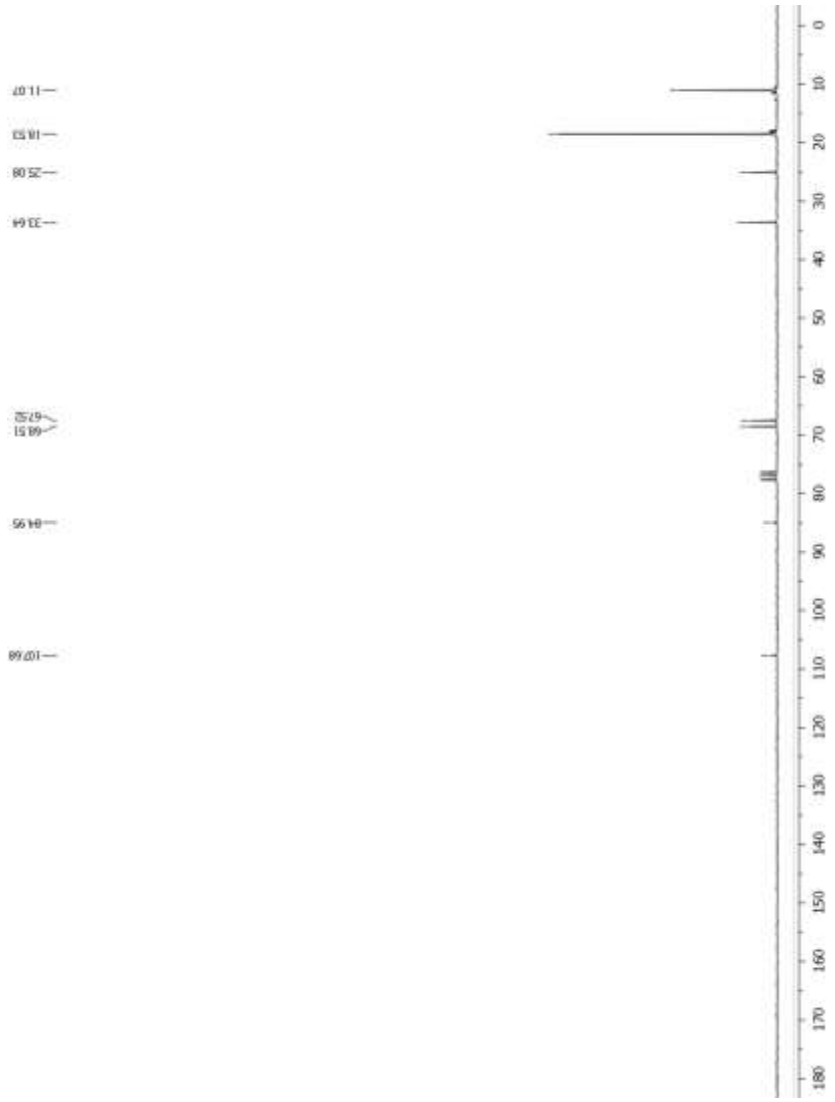


3a




TIPS
O

3a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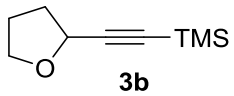

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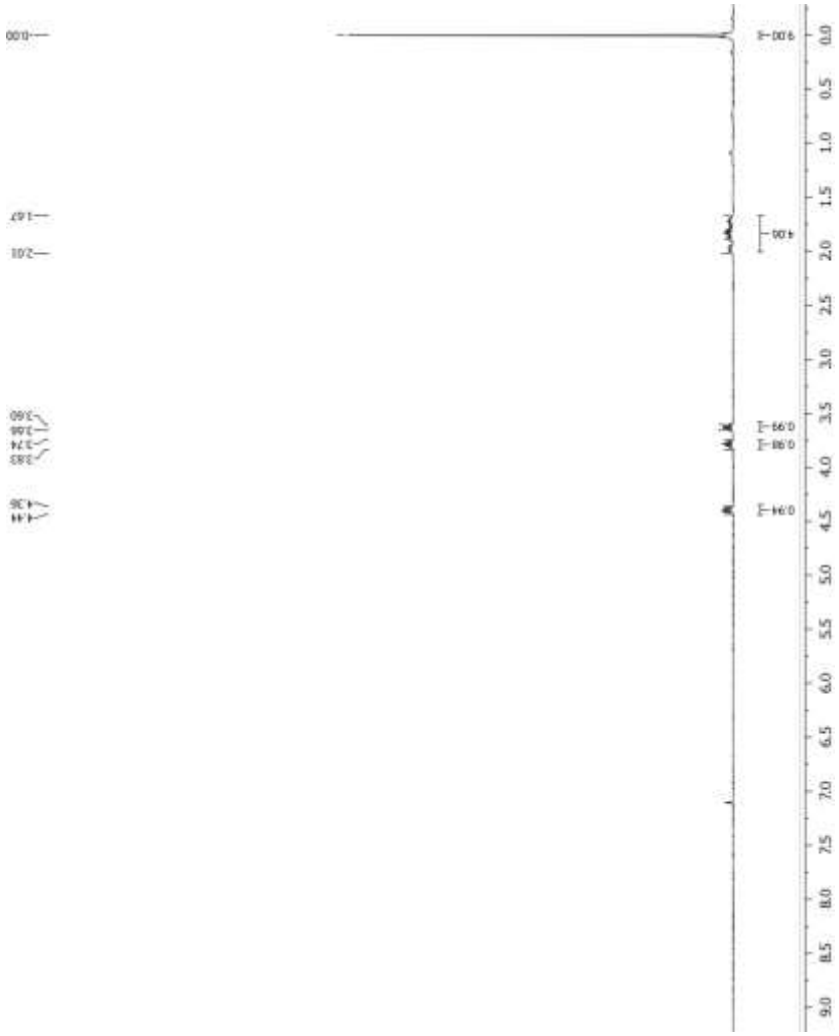

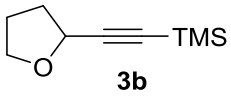

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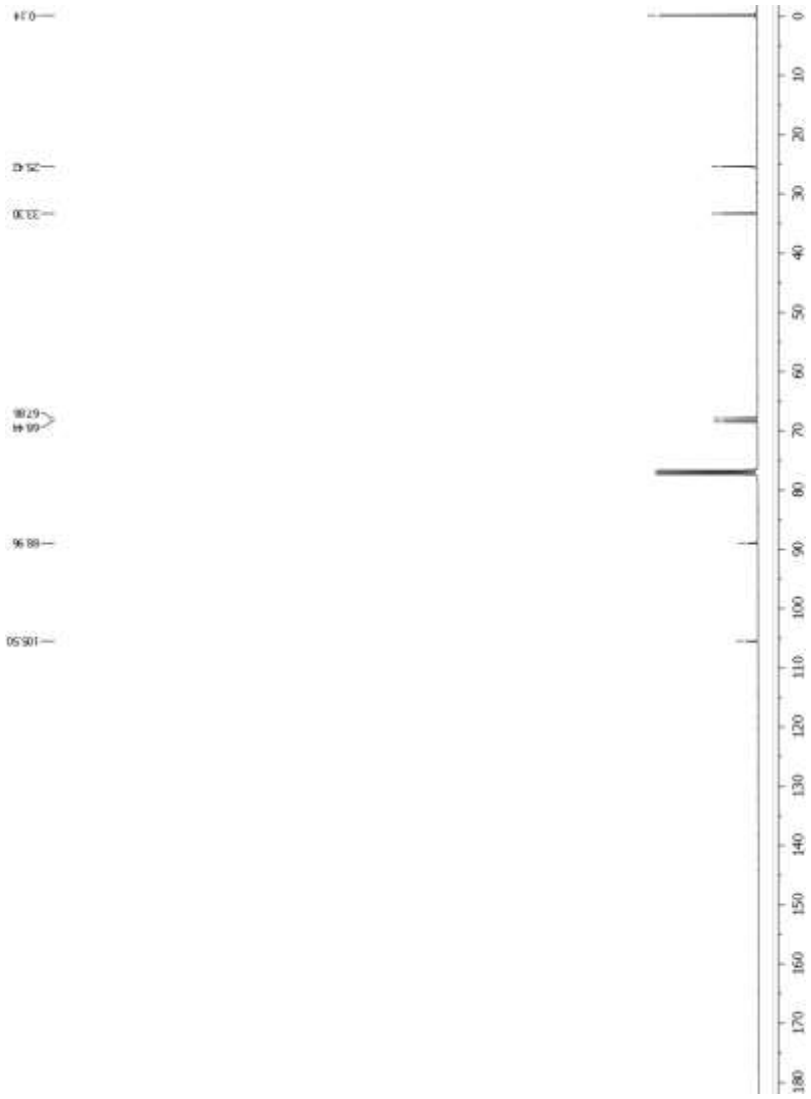

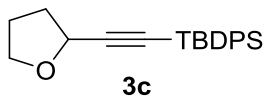

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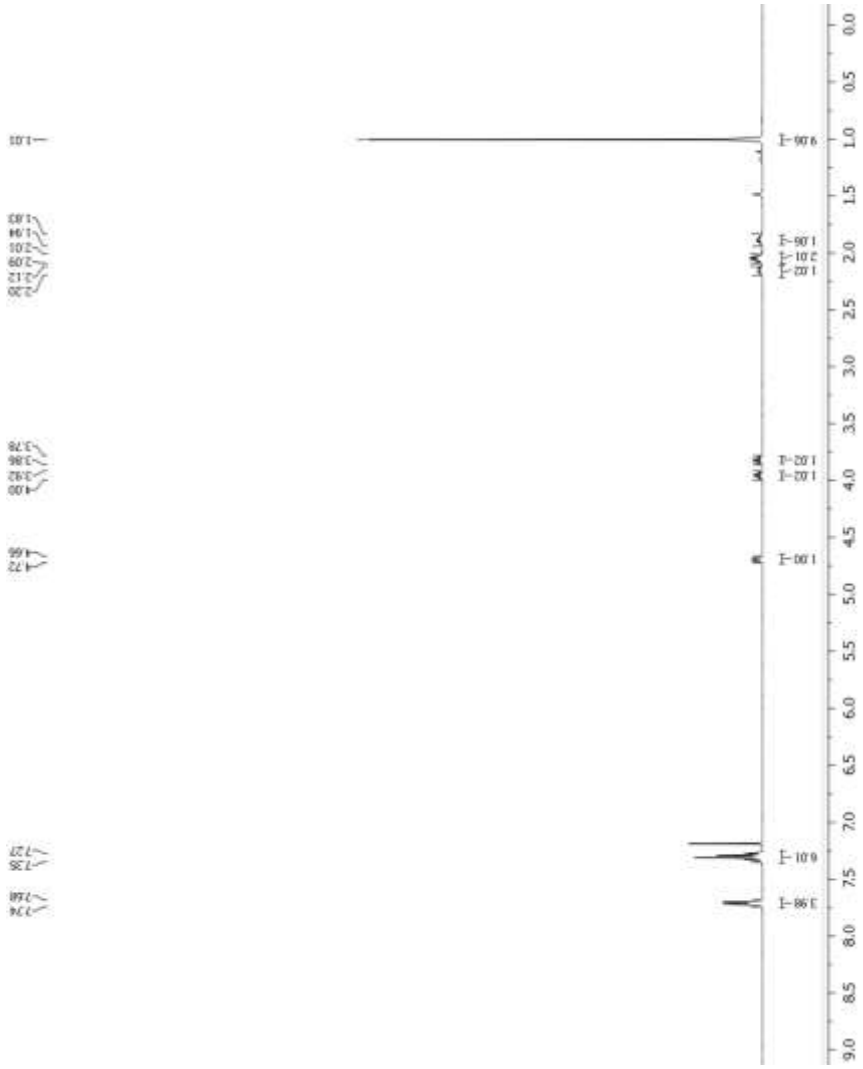

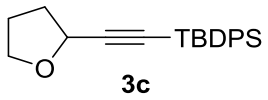

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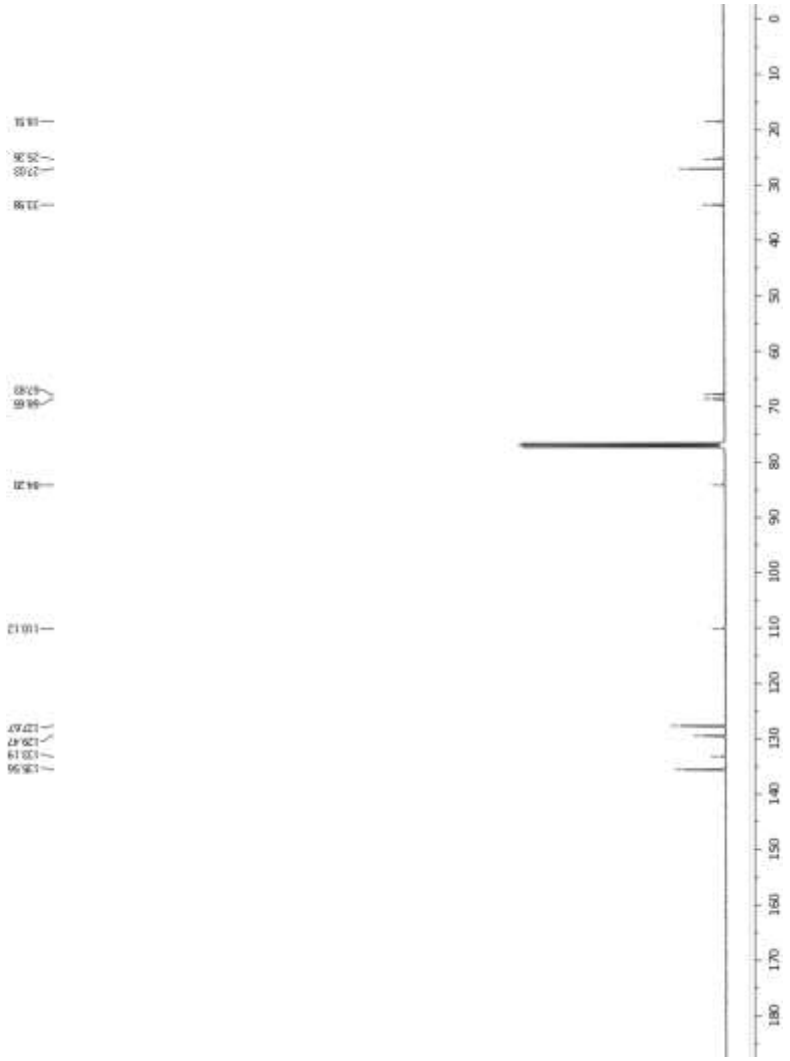

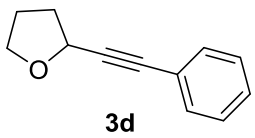

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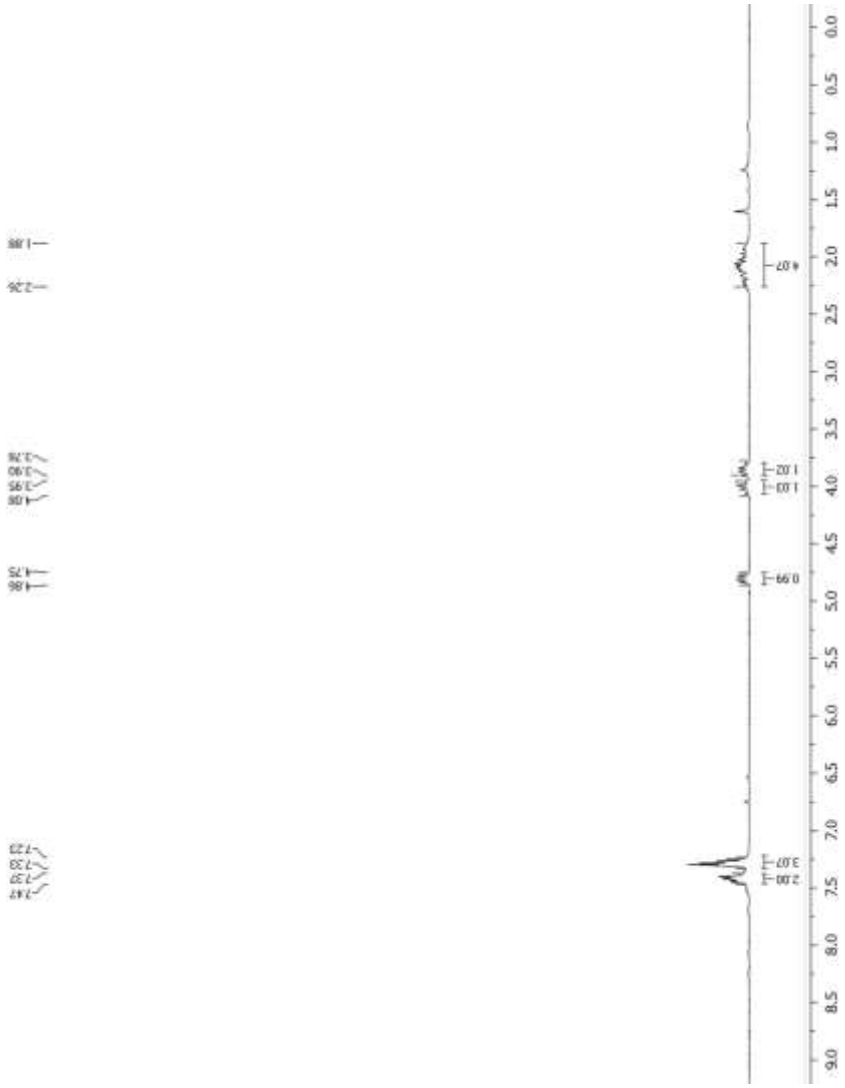

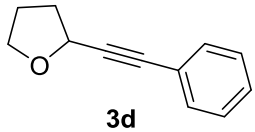

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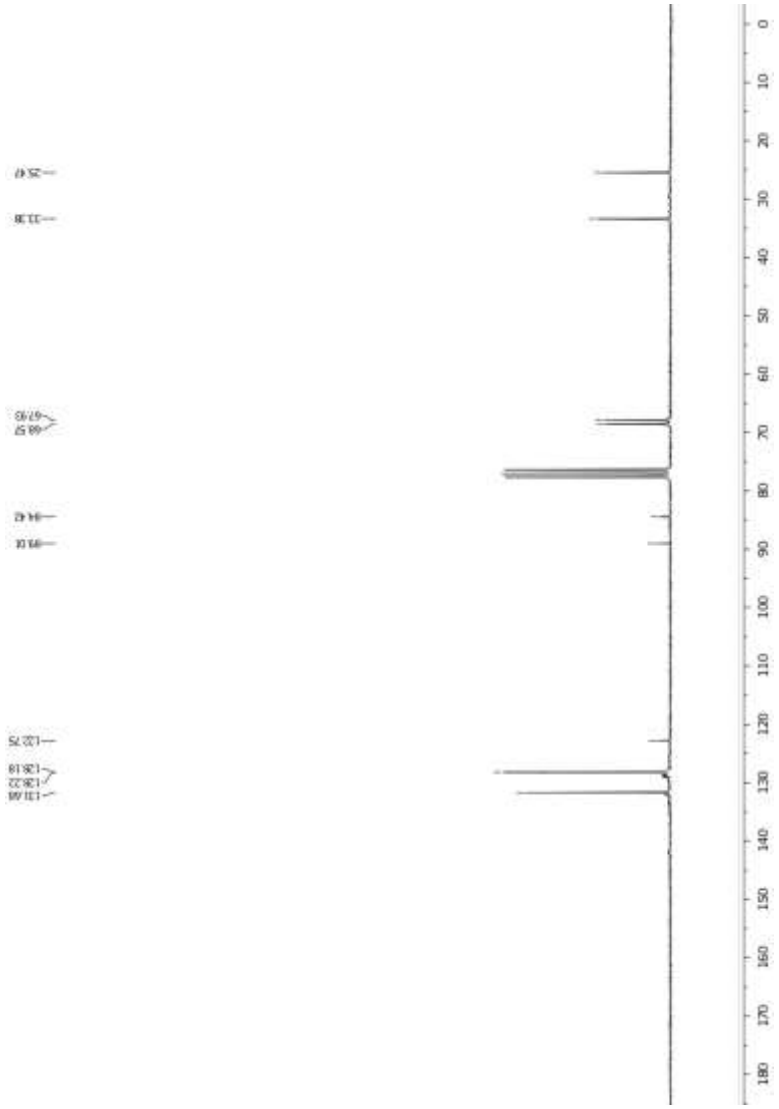

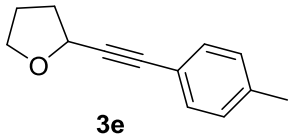

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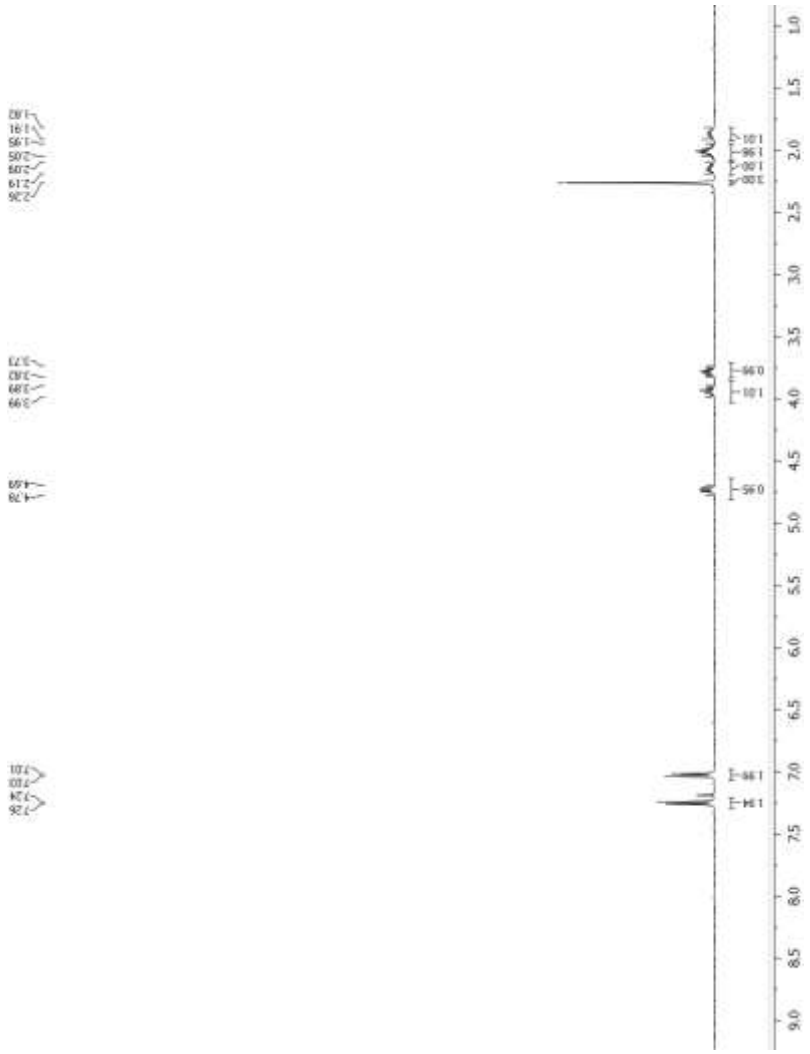

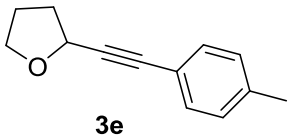

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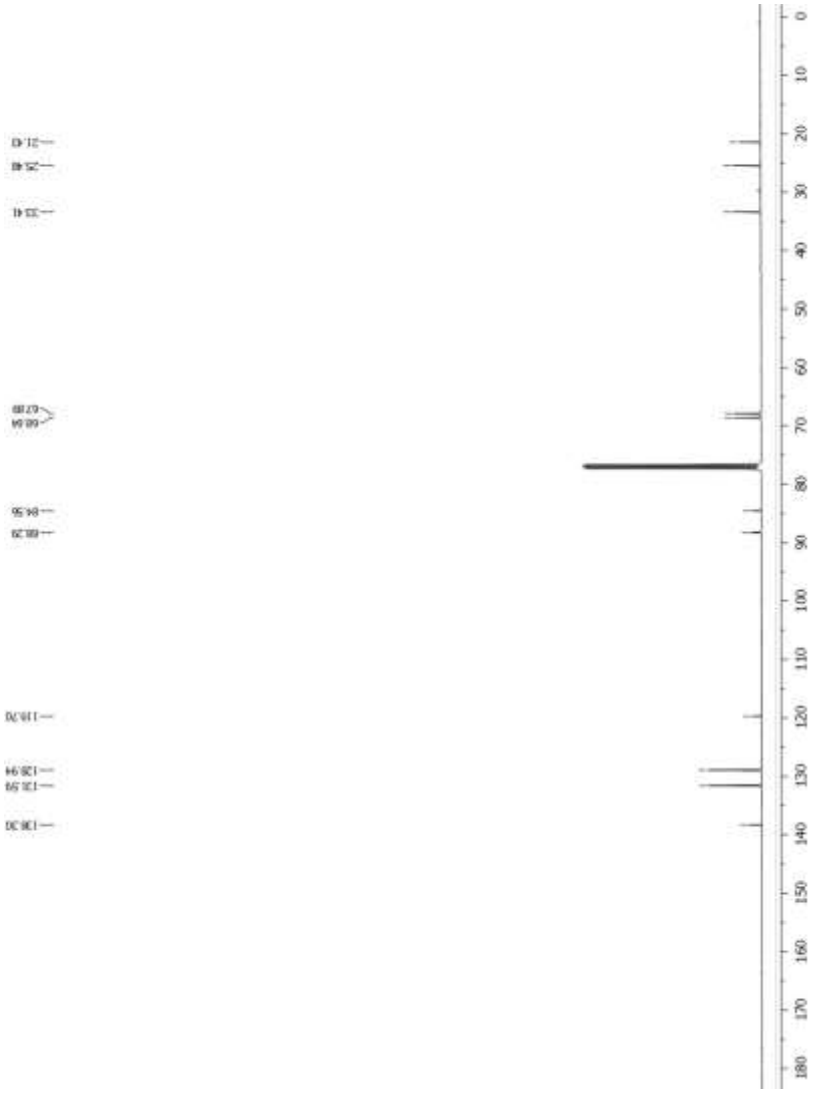

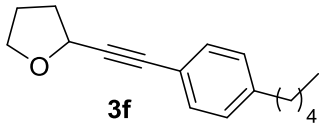

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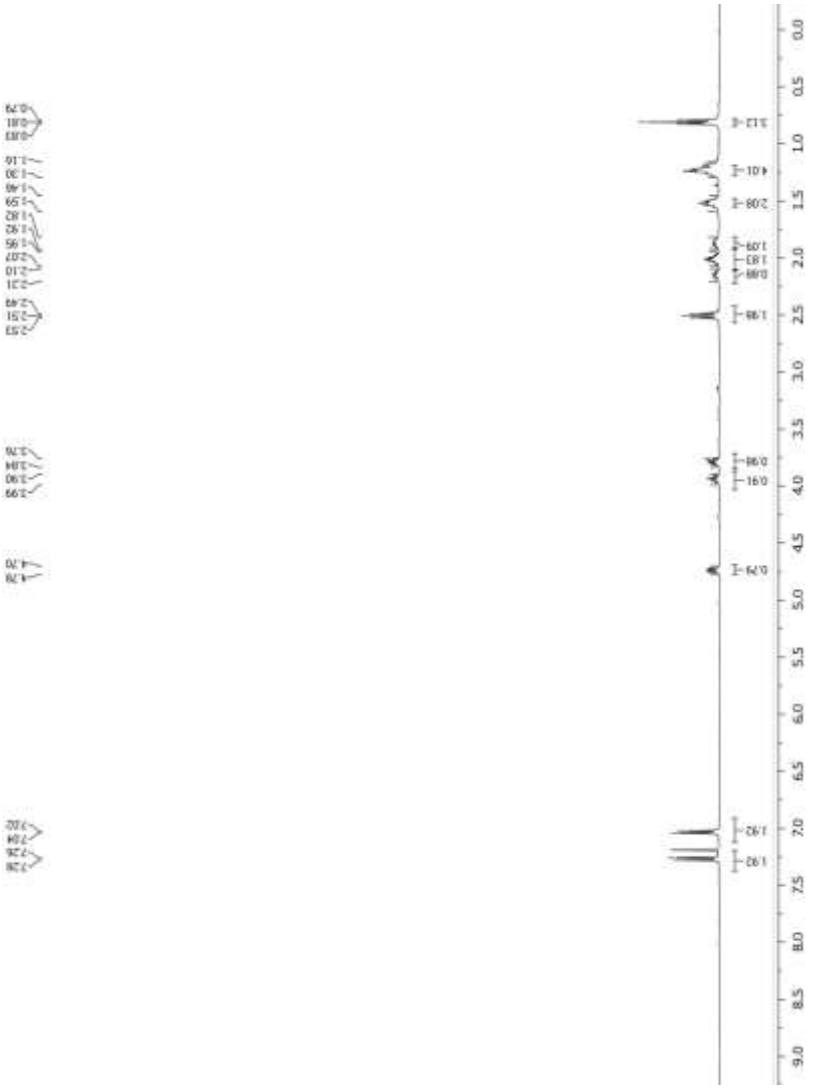

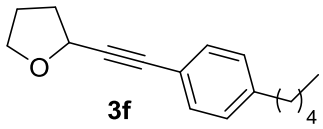

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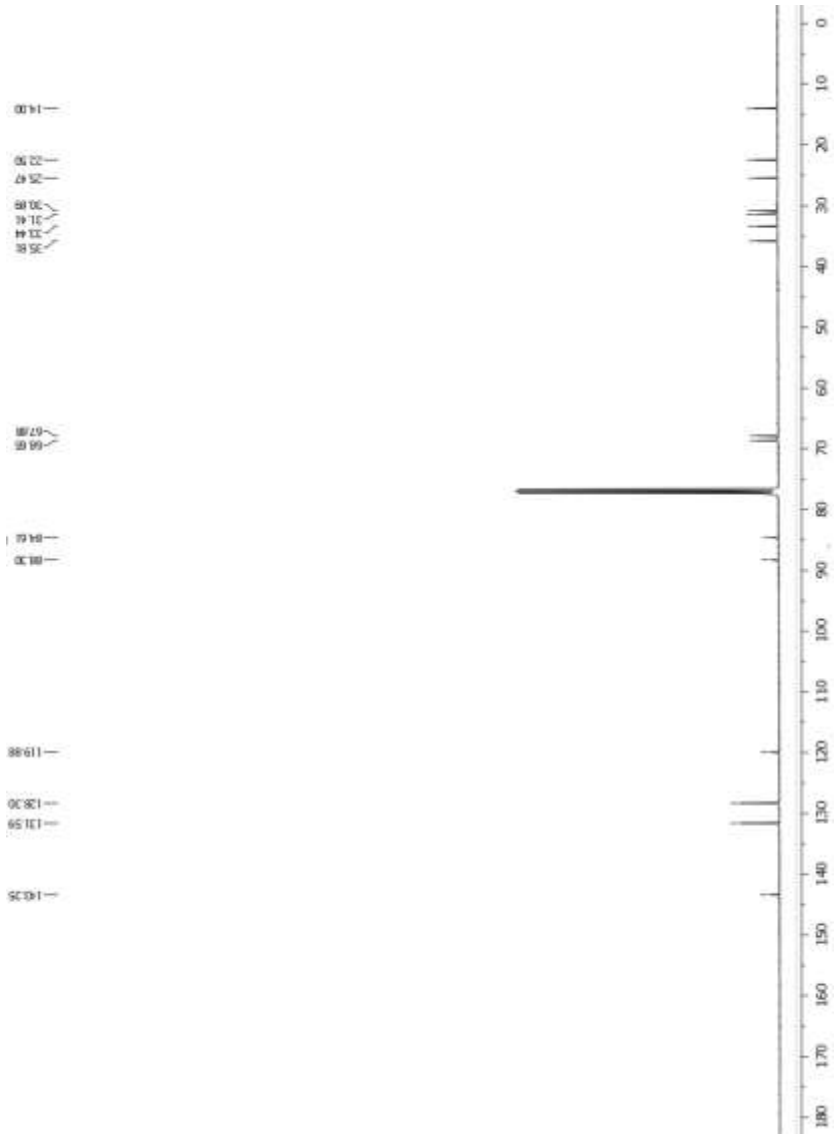

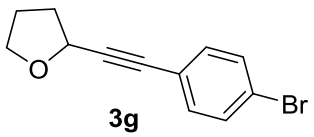

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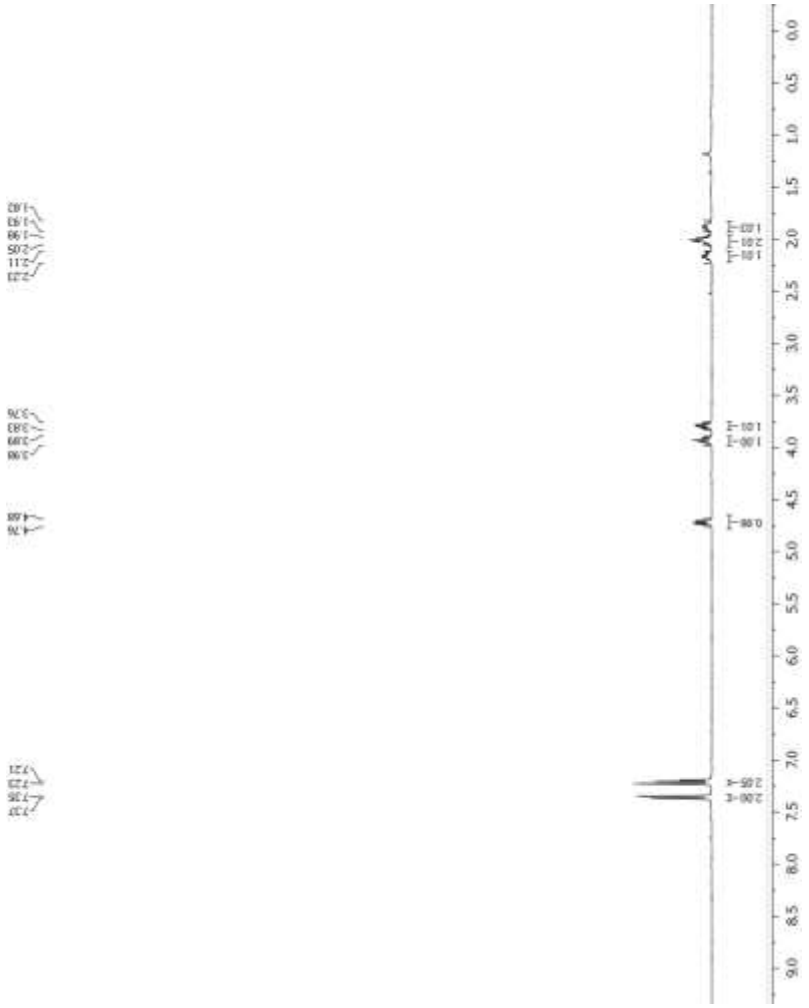

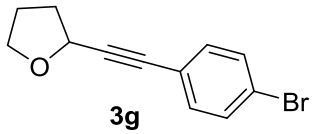

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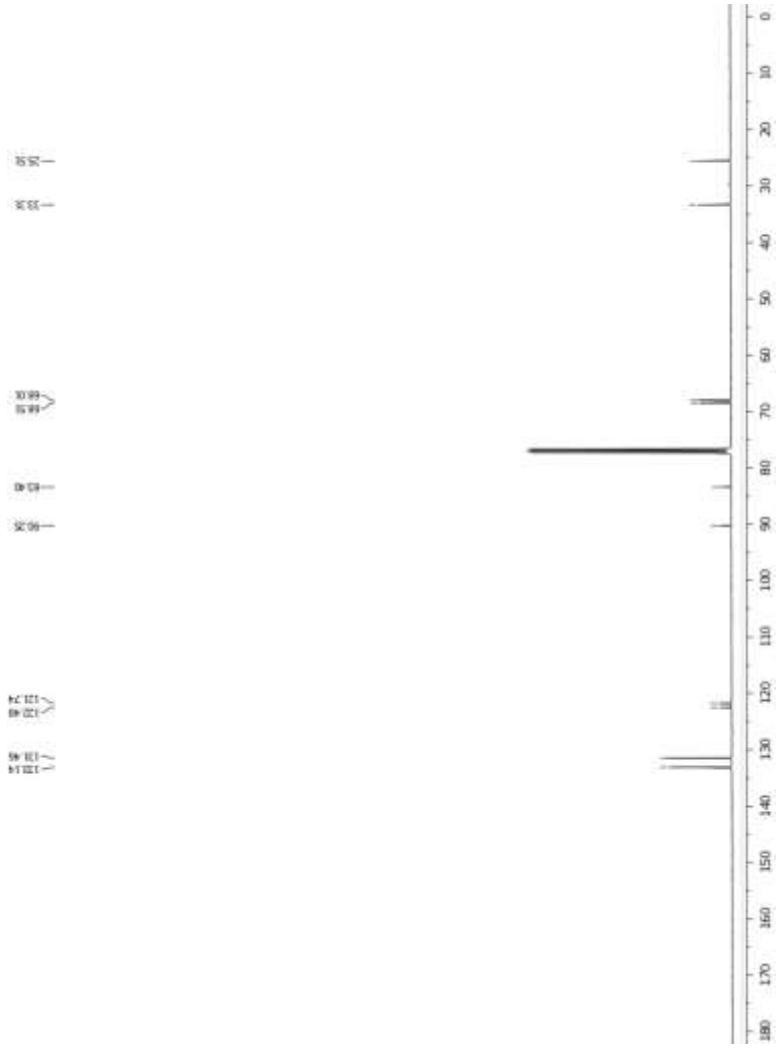

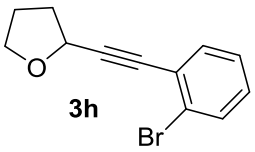

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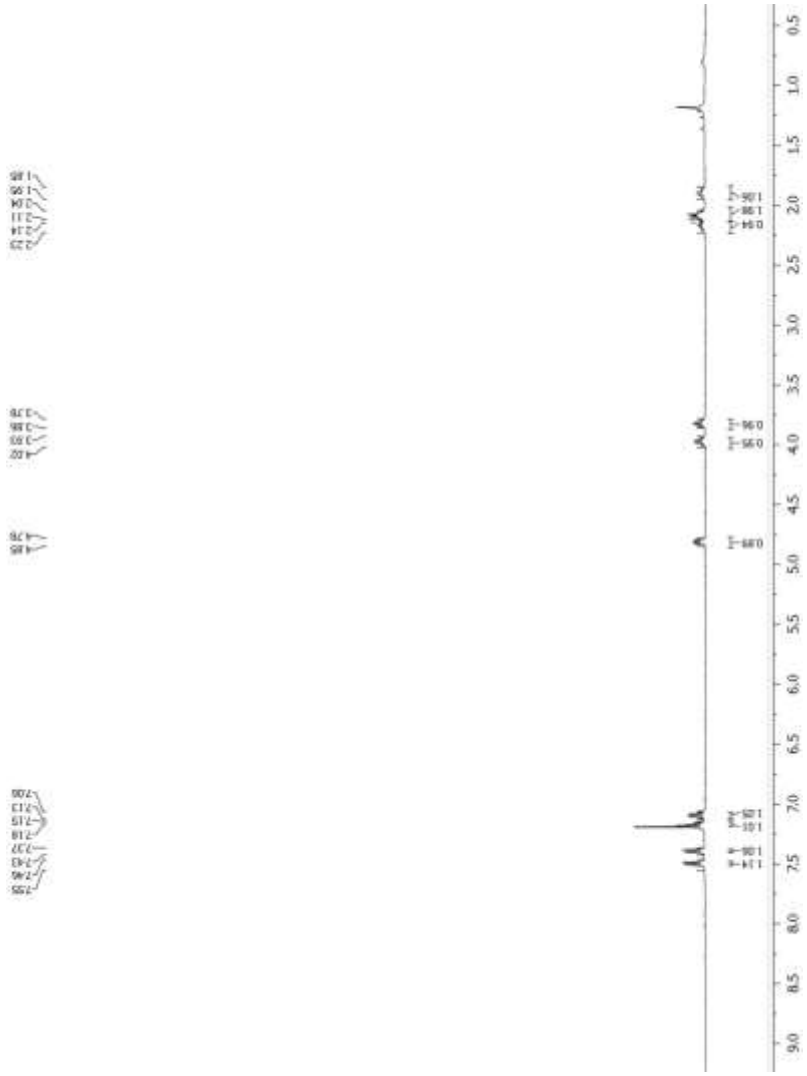

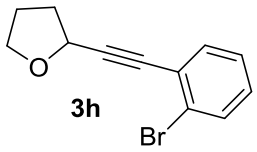

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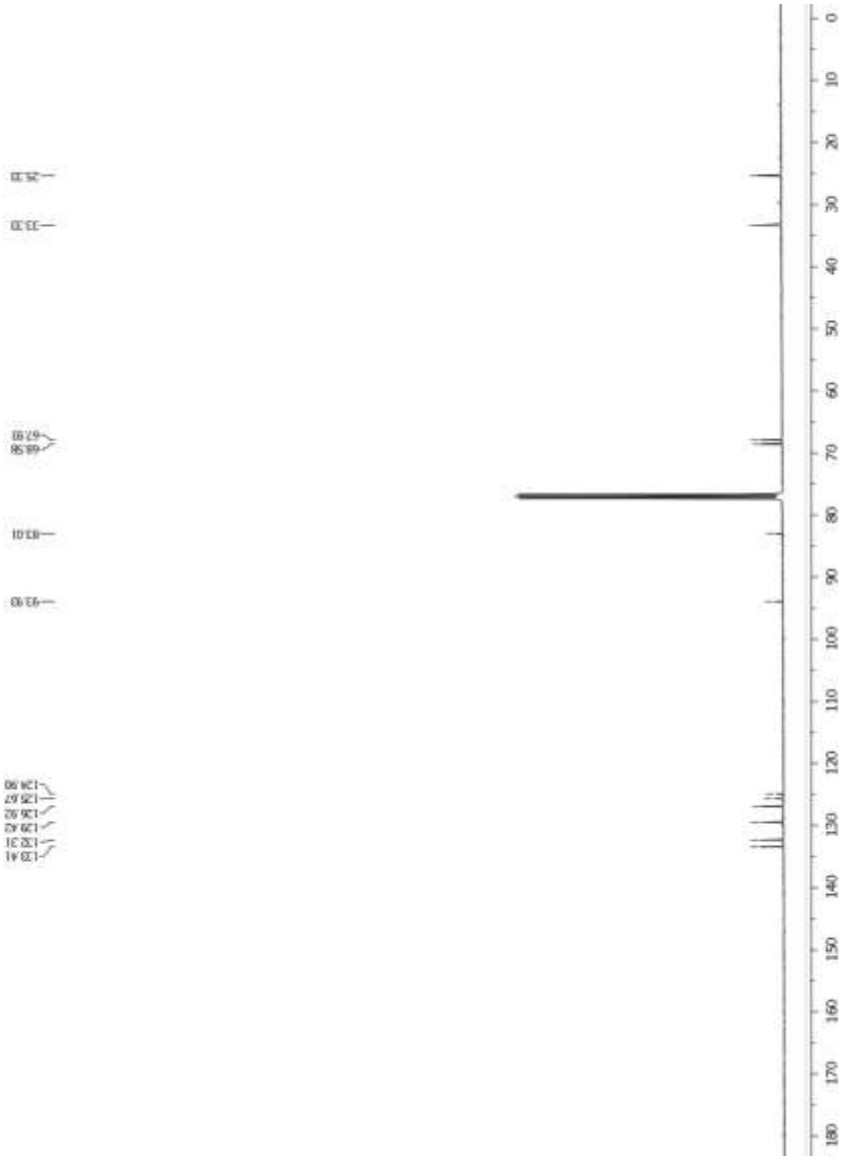

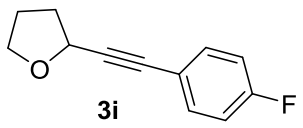

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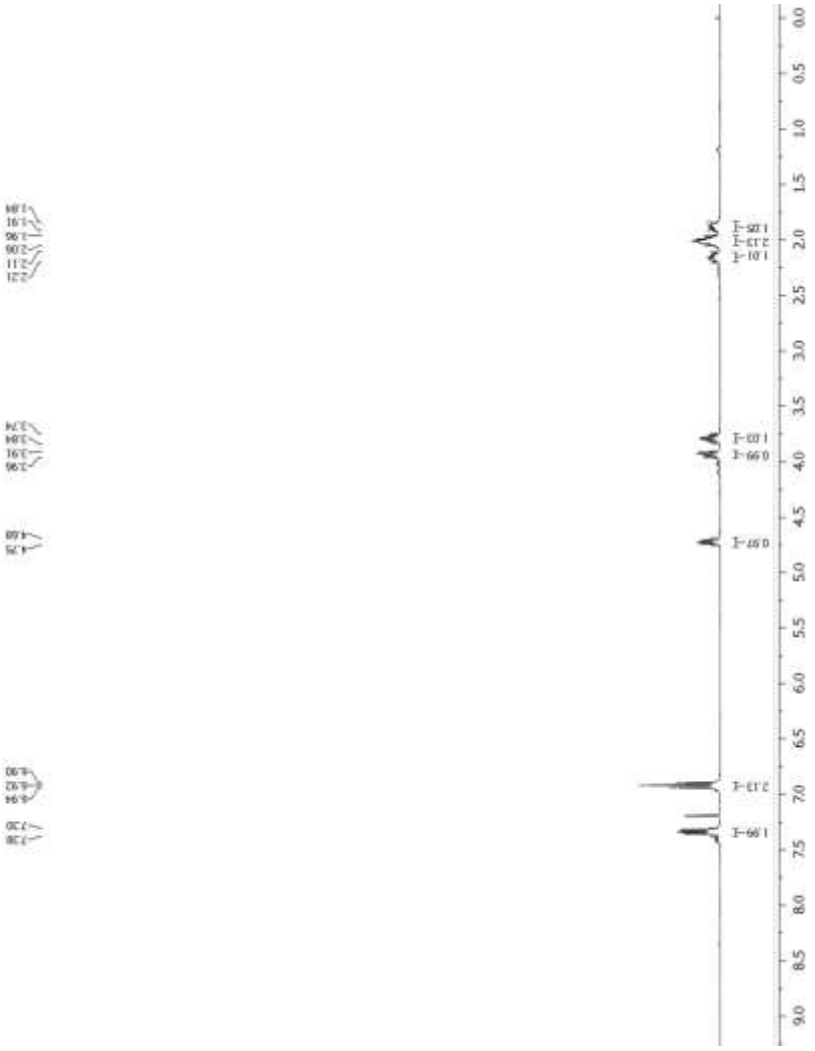

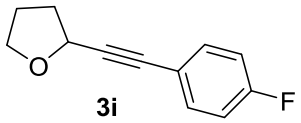

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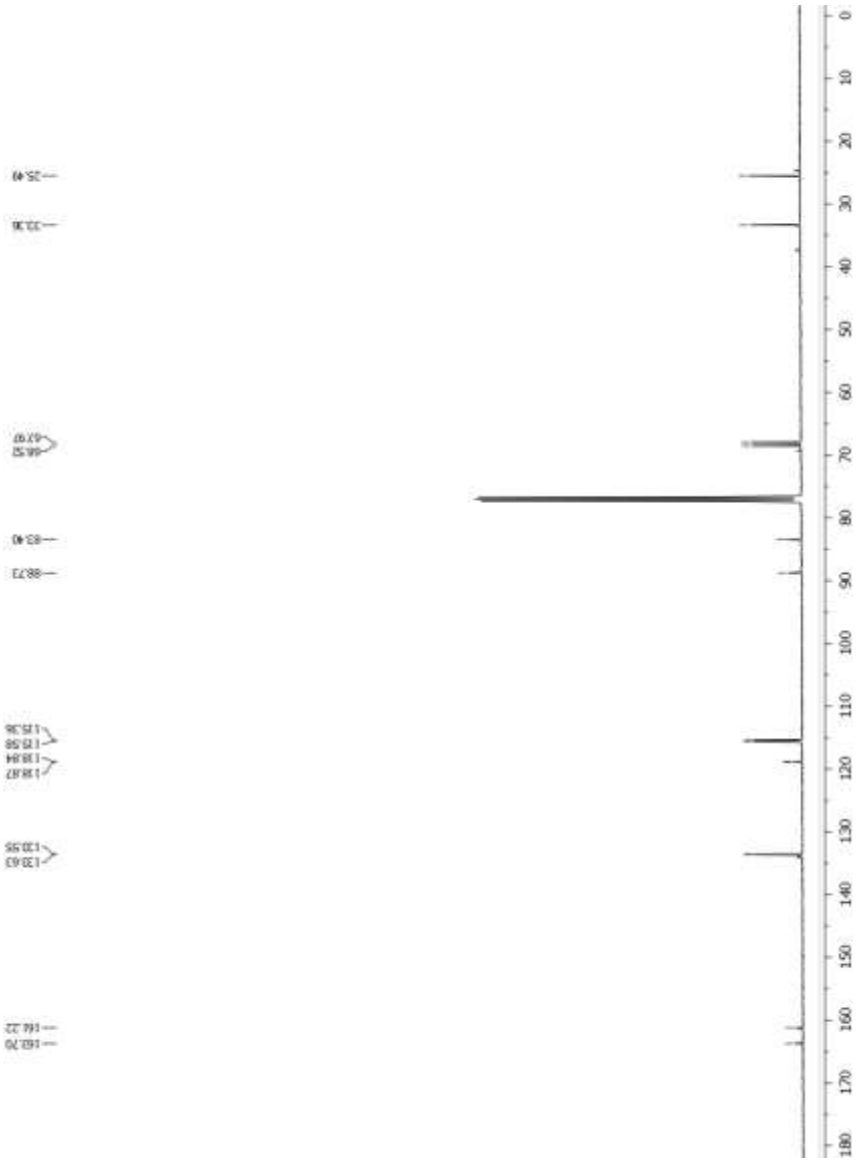

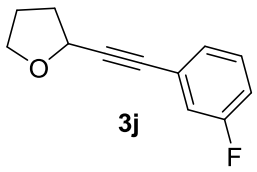

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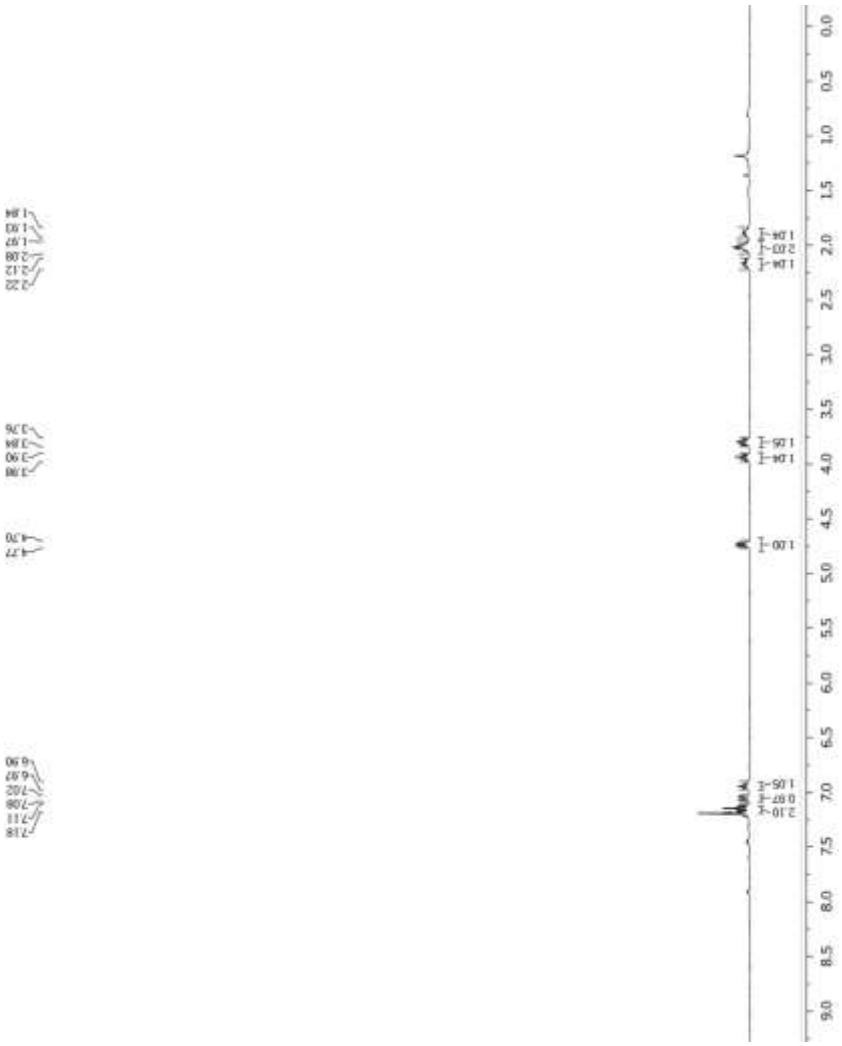

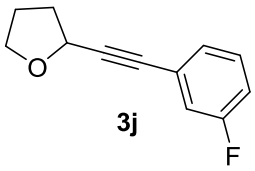

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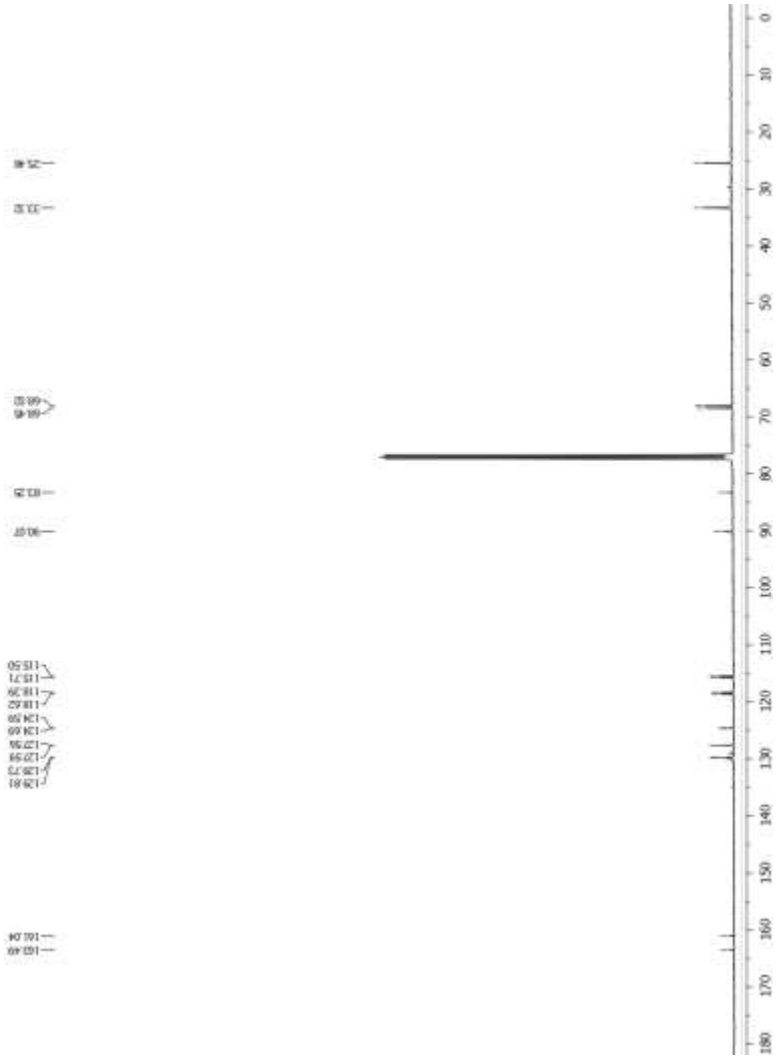

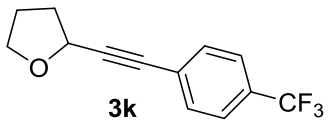

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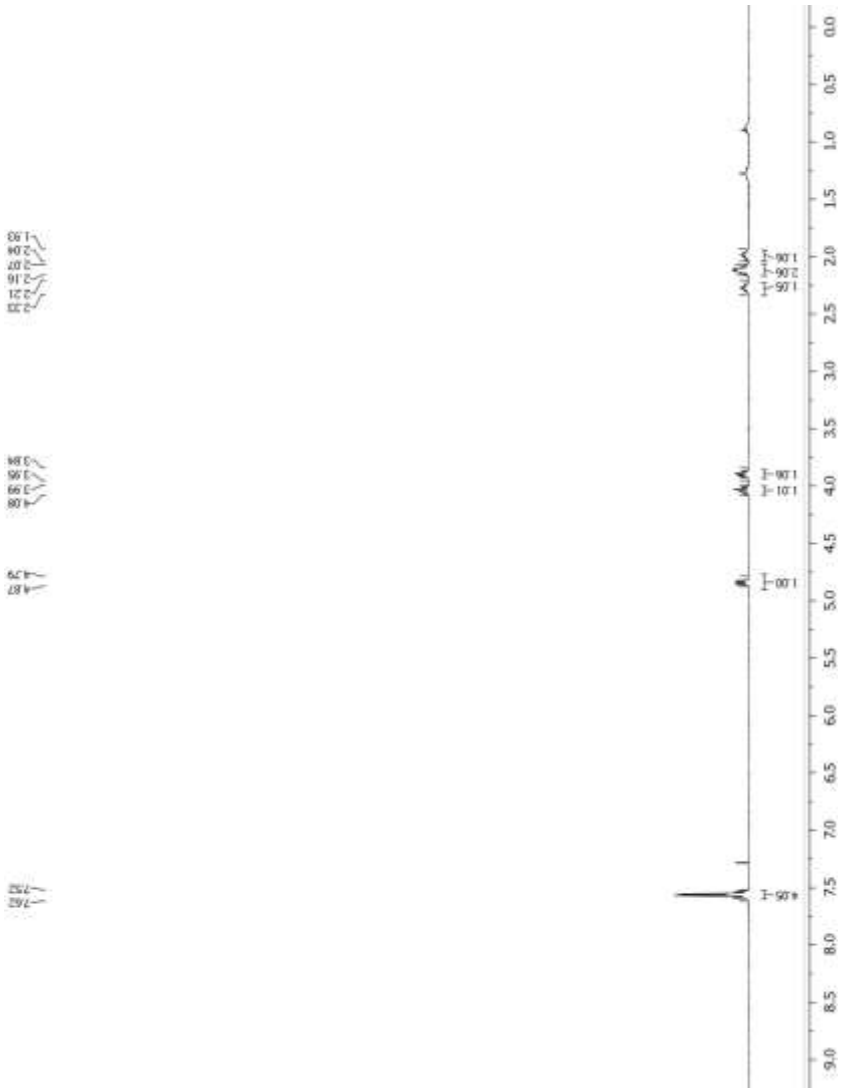

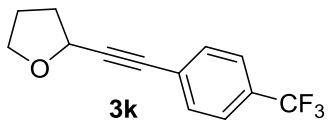

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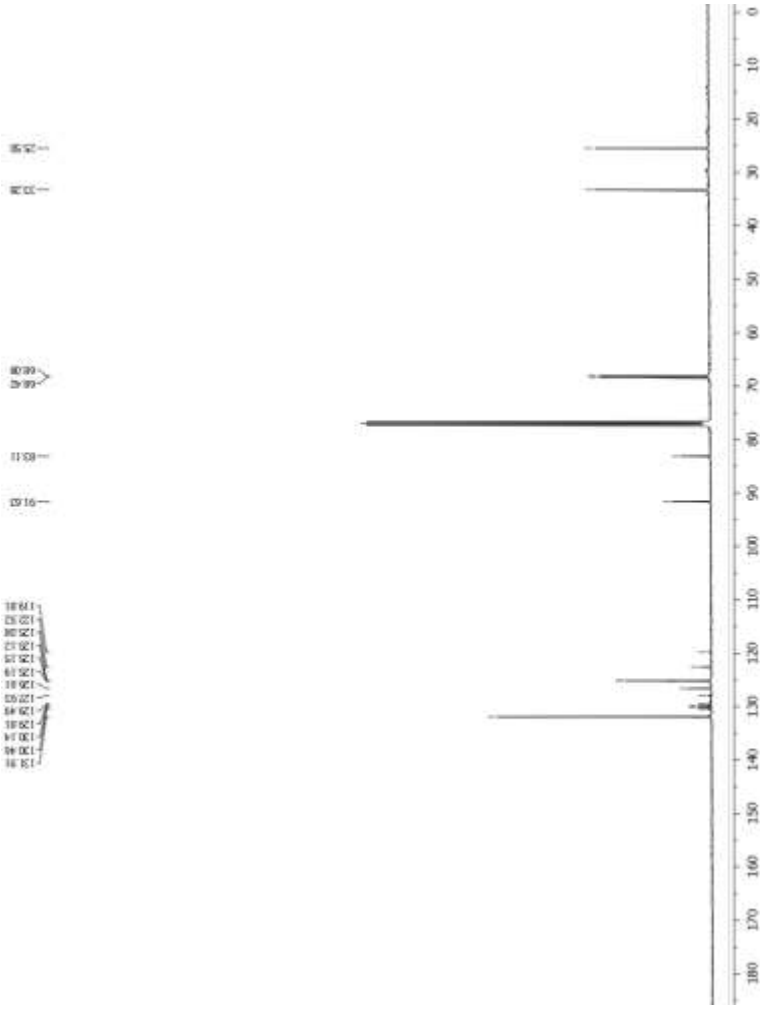

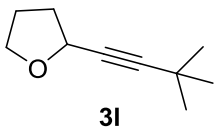

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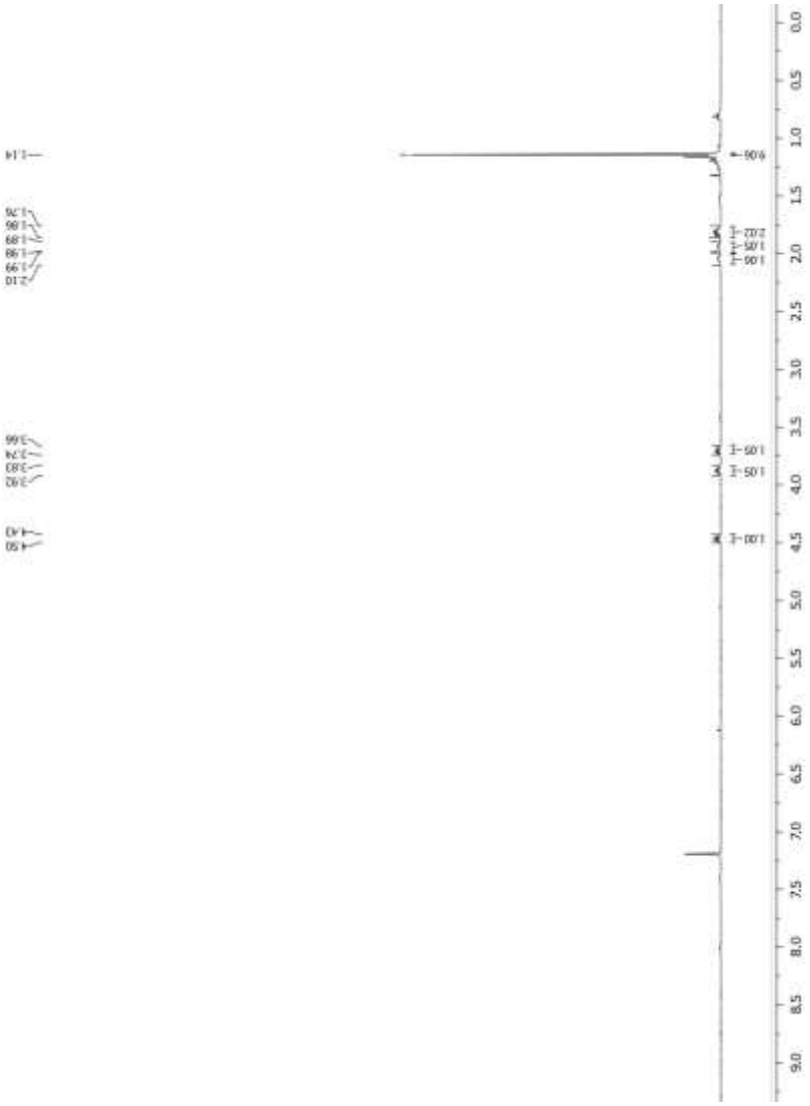

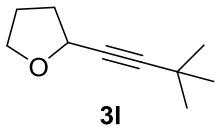

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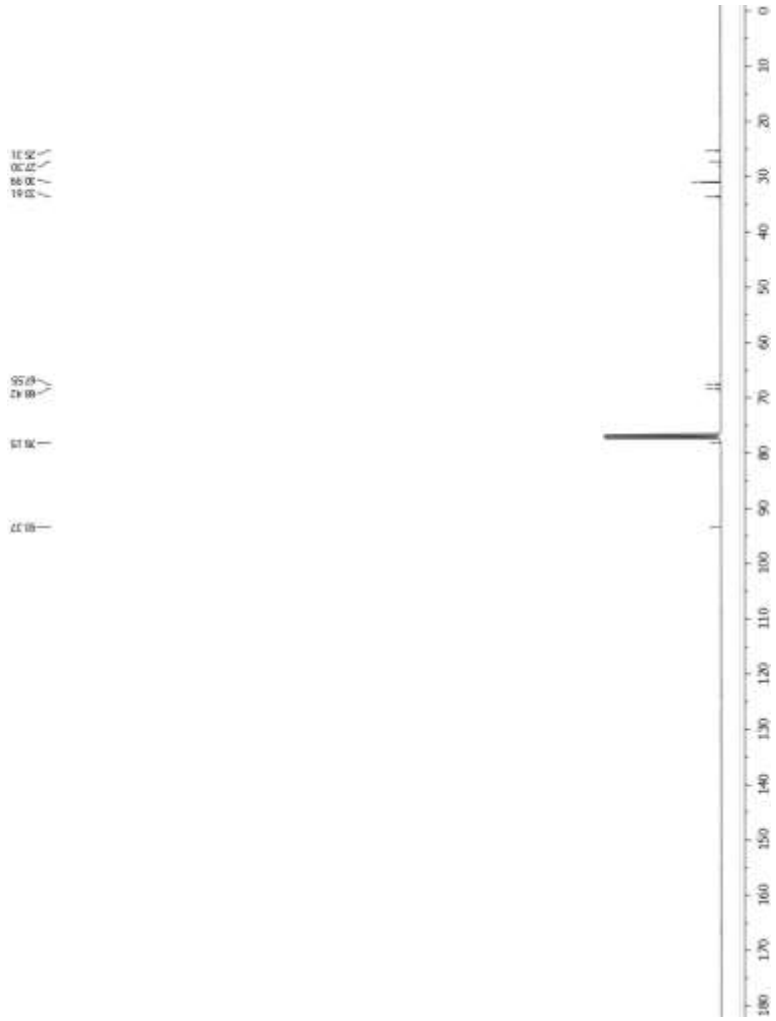

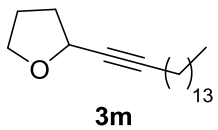

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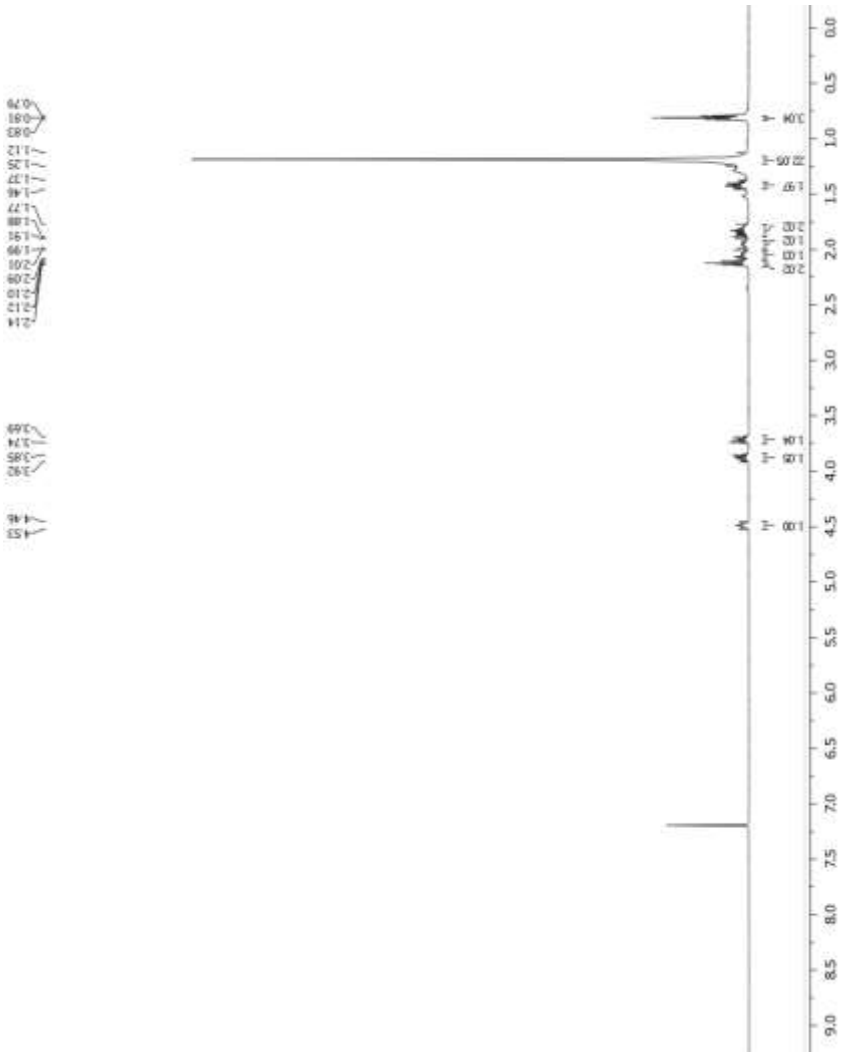

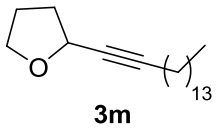

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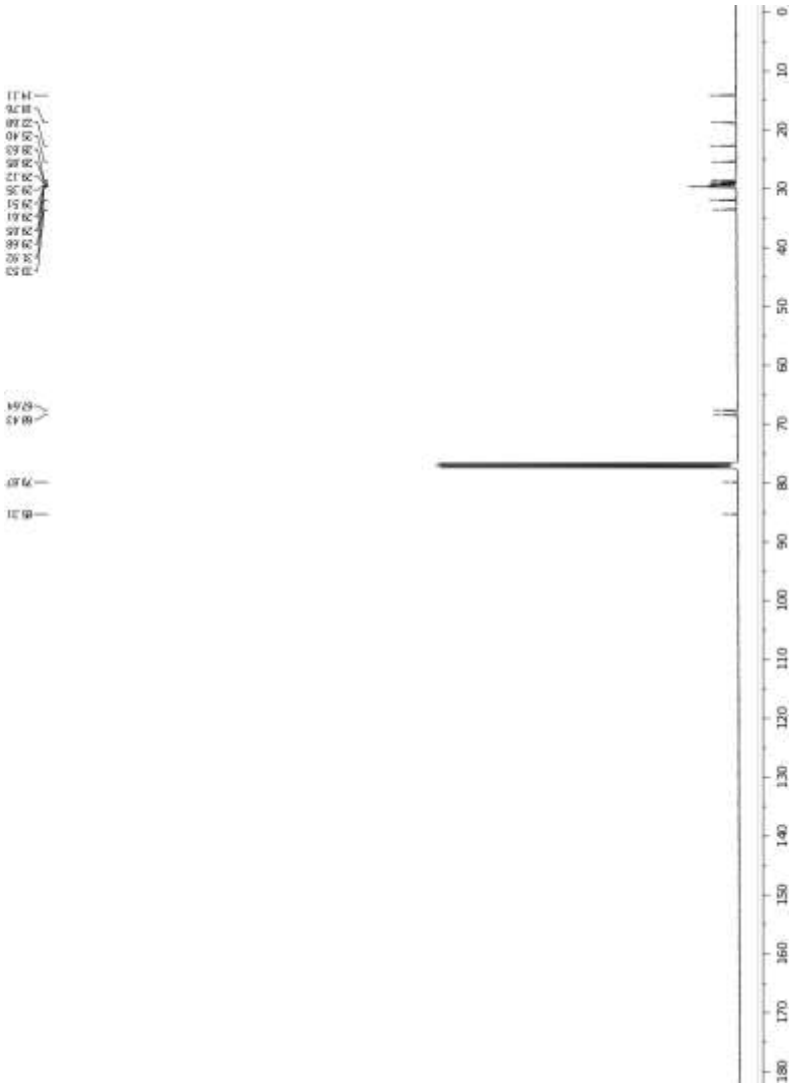

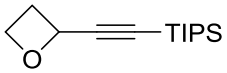

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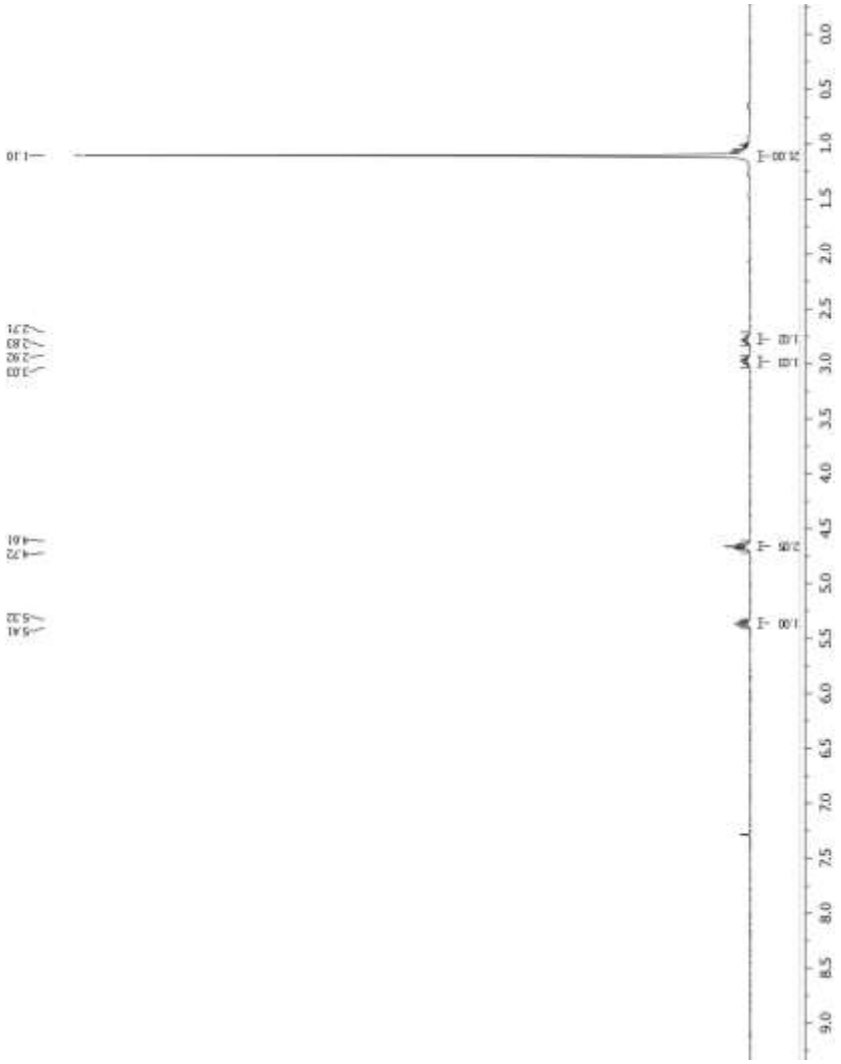

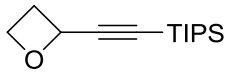

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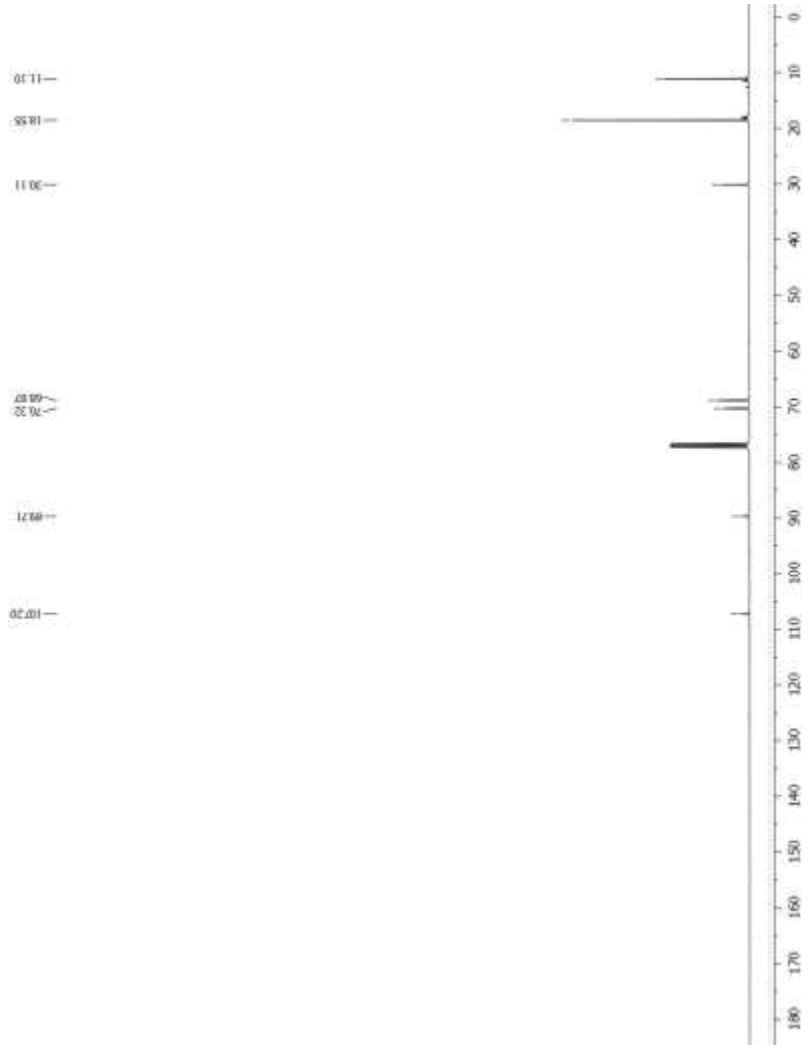

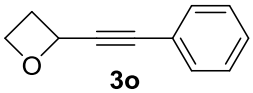

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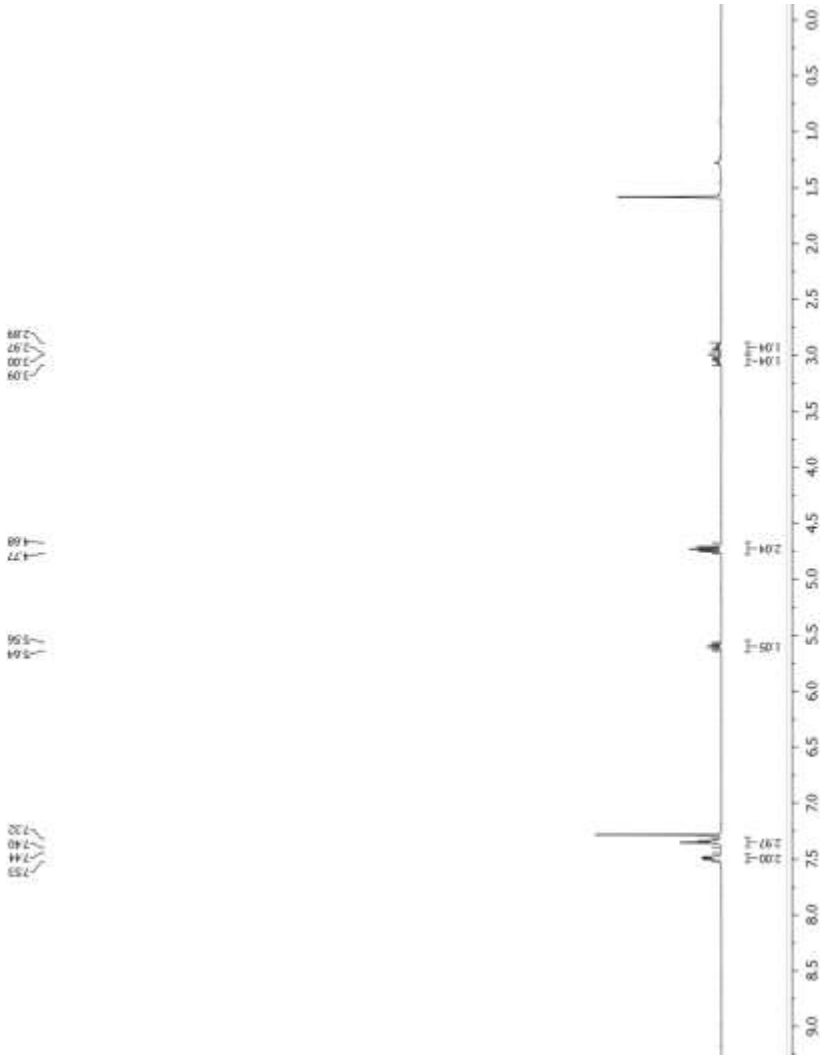

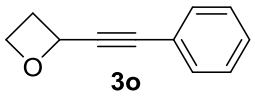

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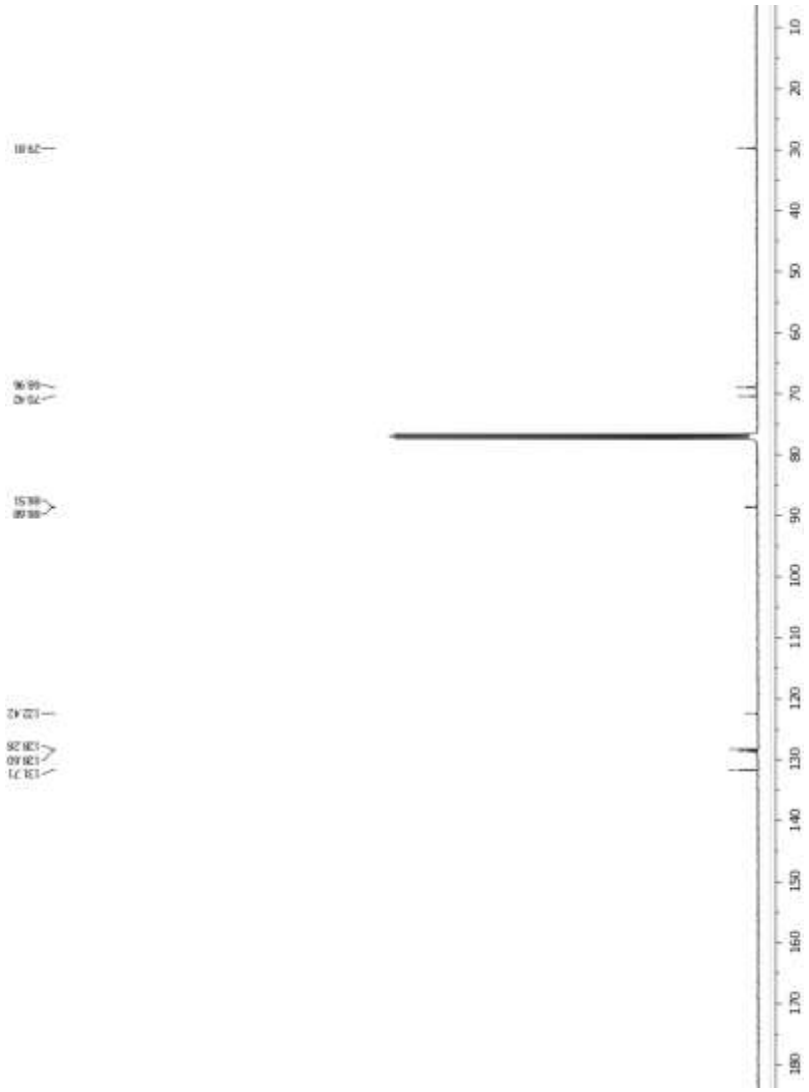

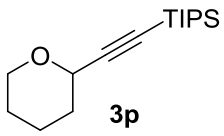

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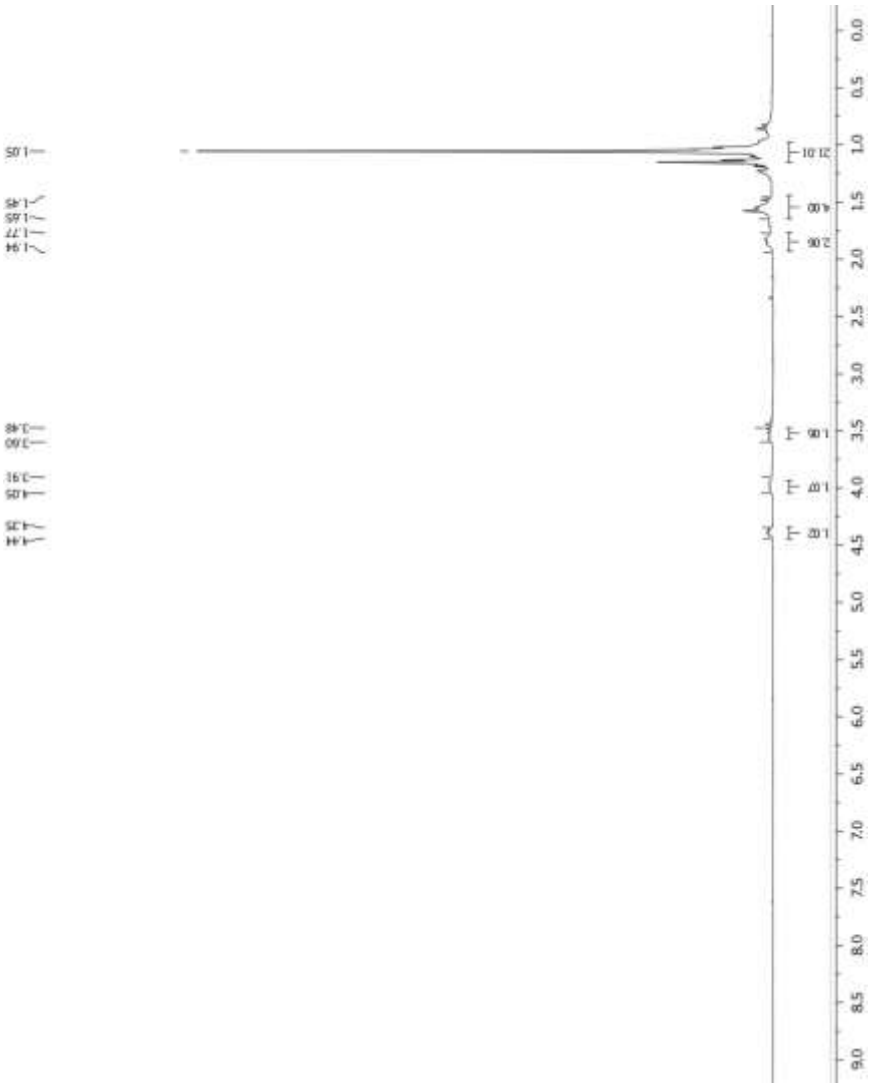

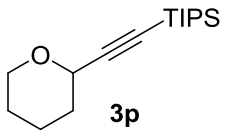

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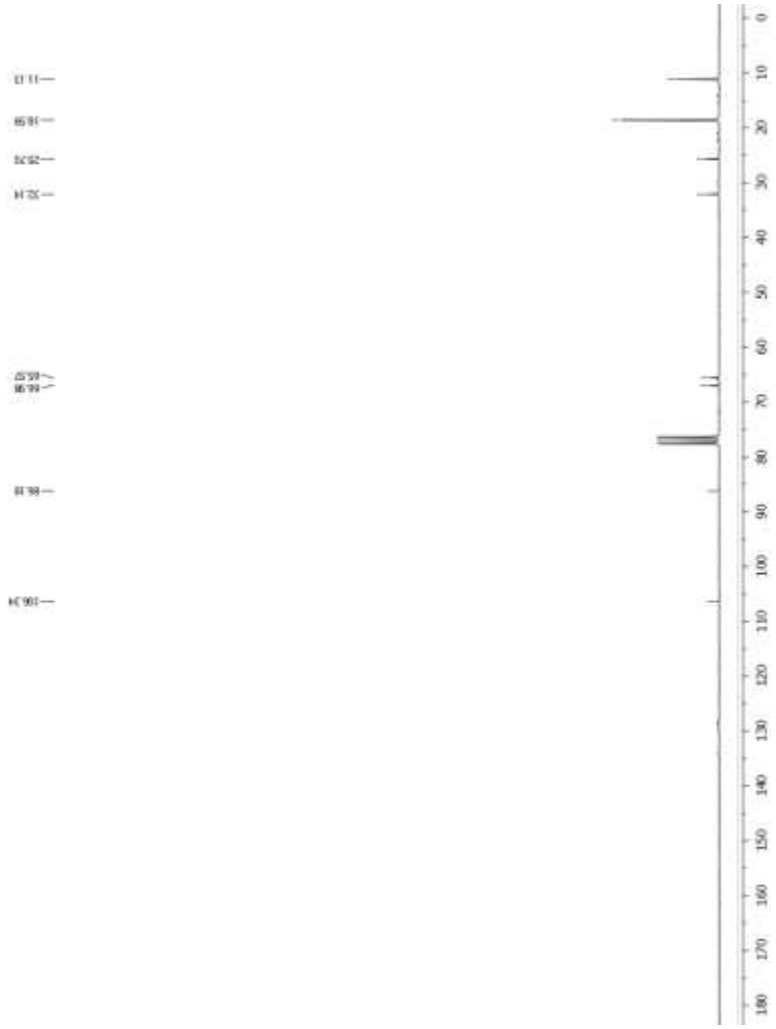

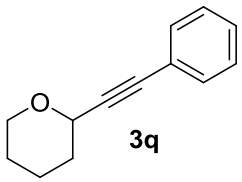
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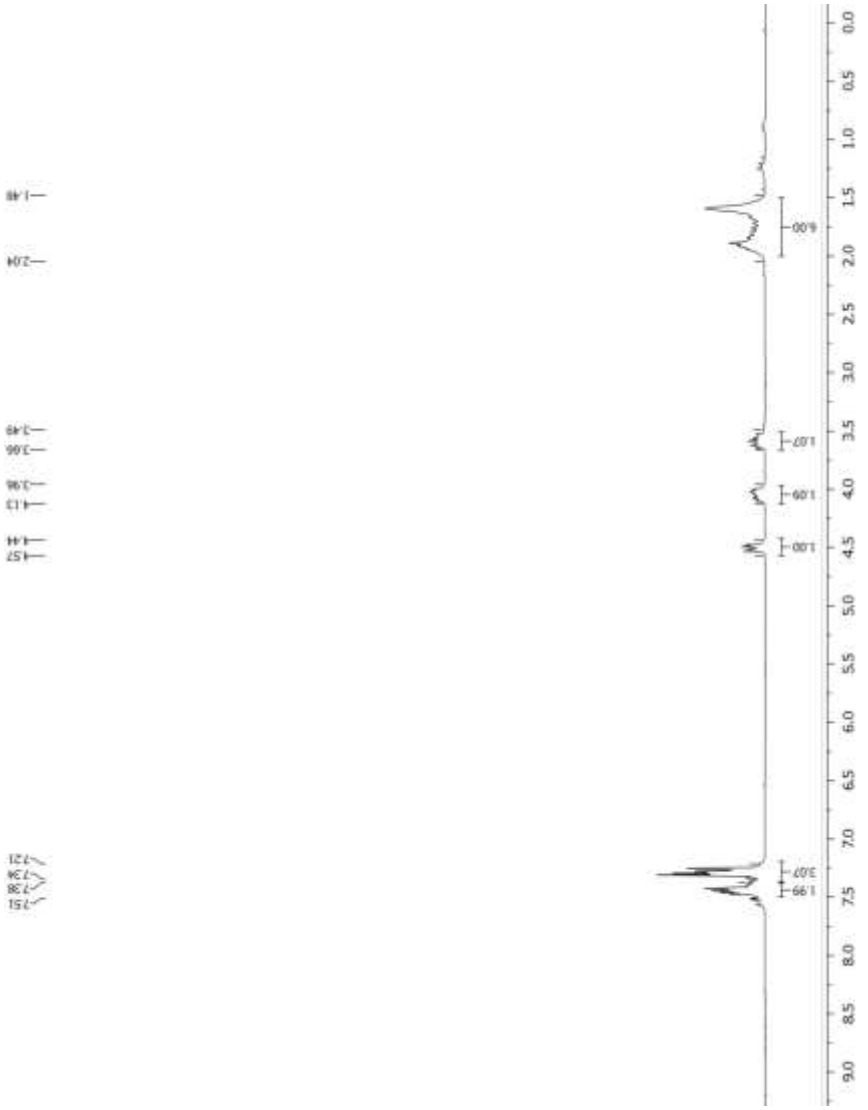
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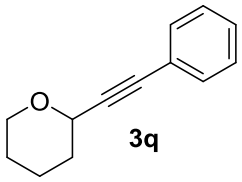

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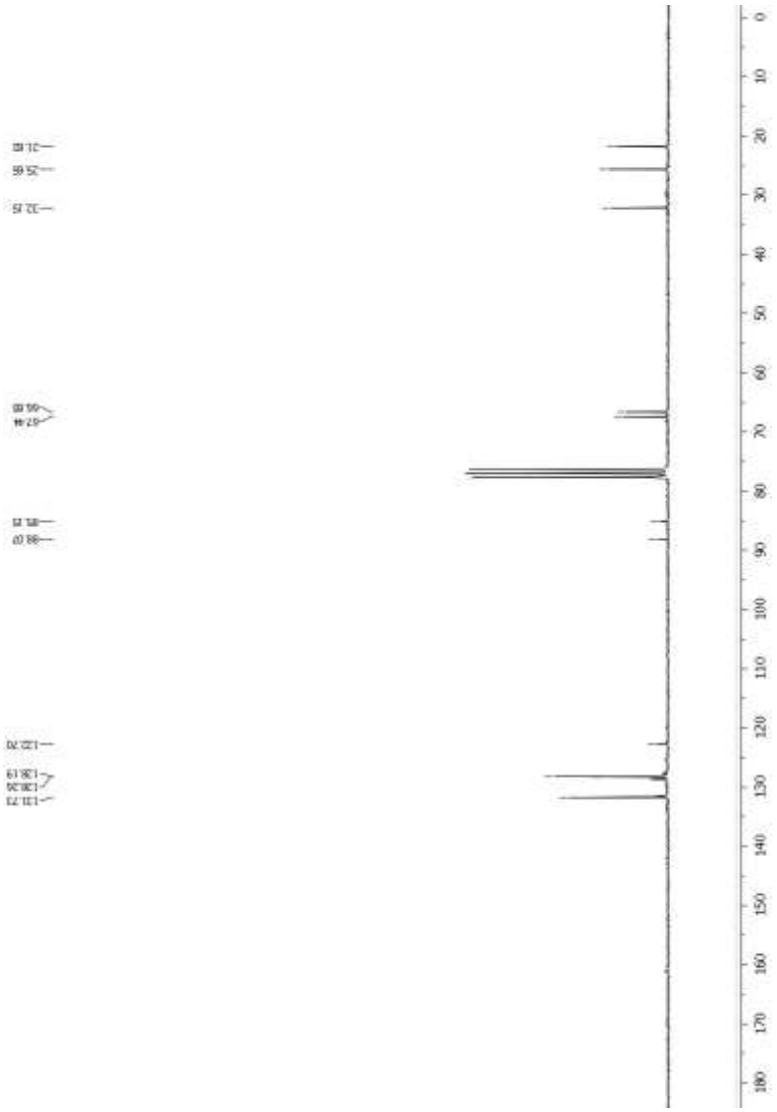

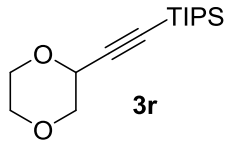

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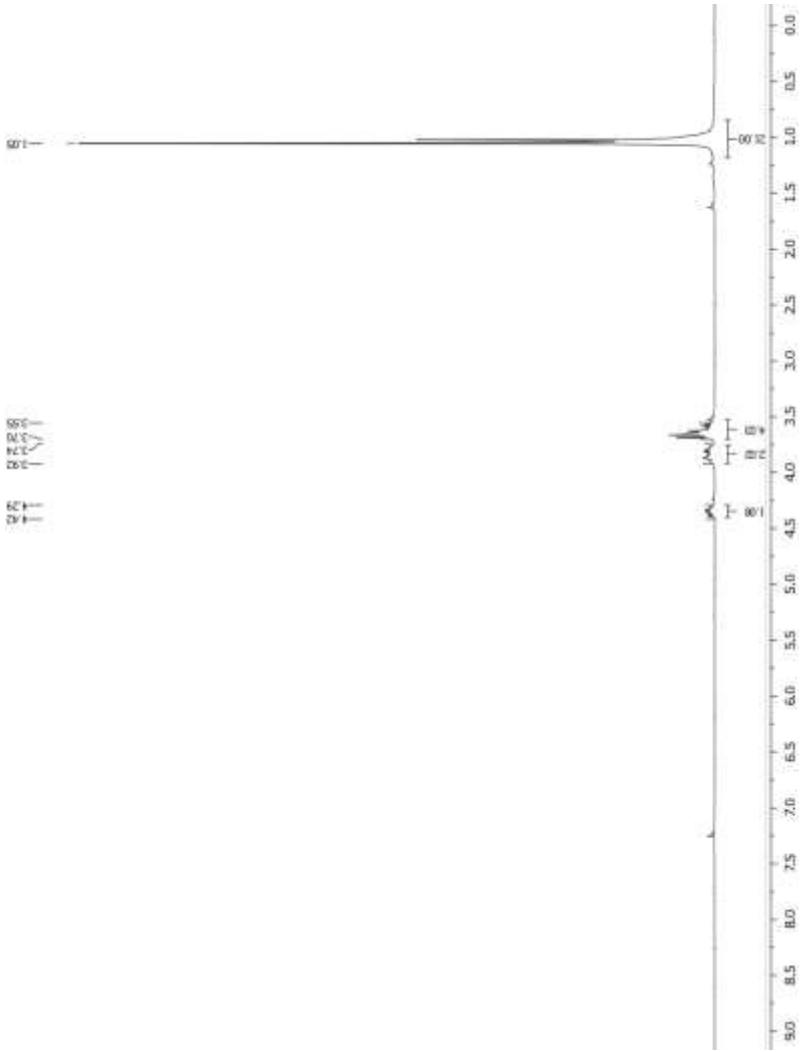

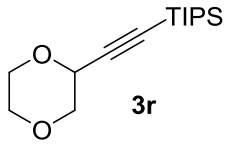

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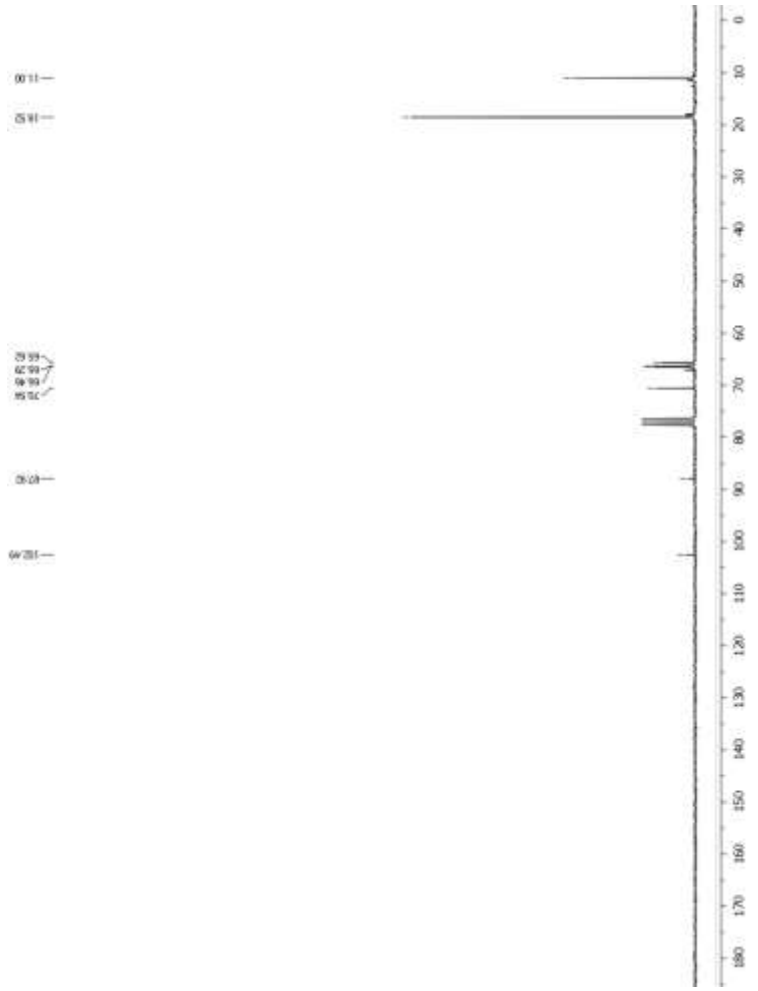

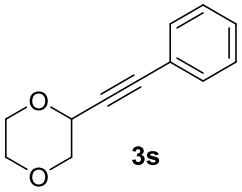

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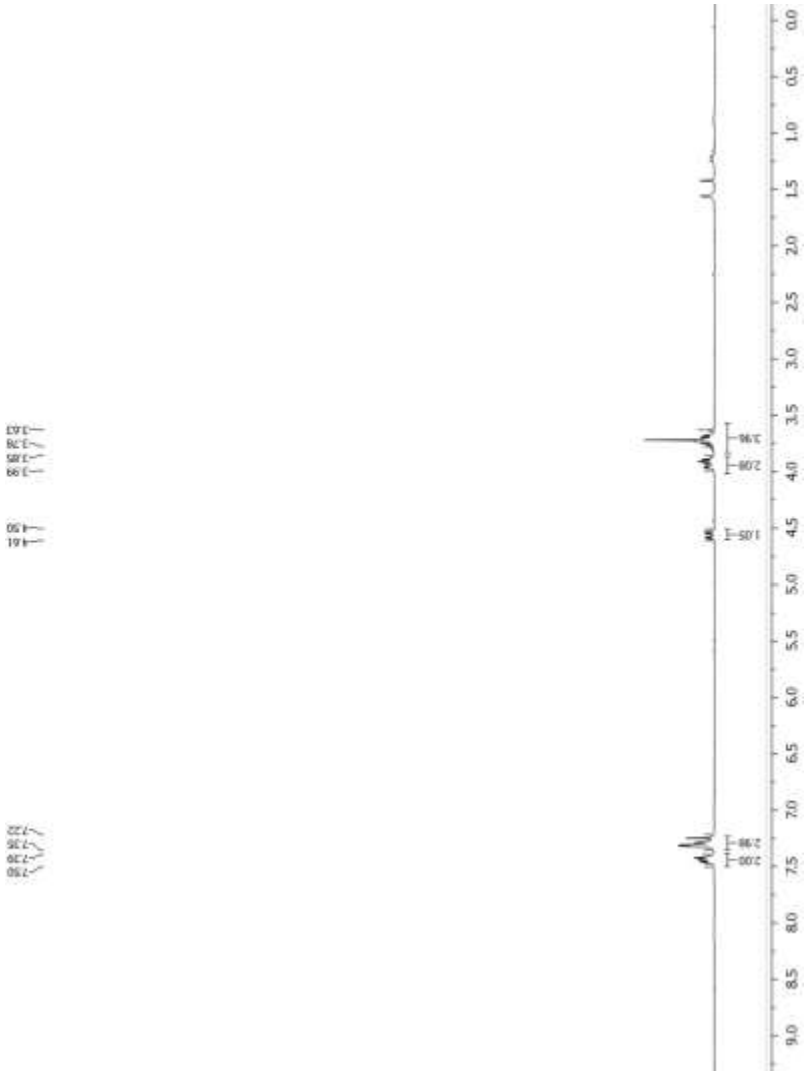

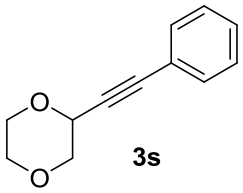

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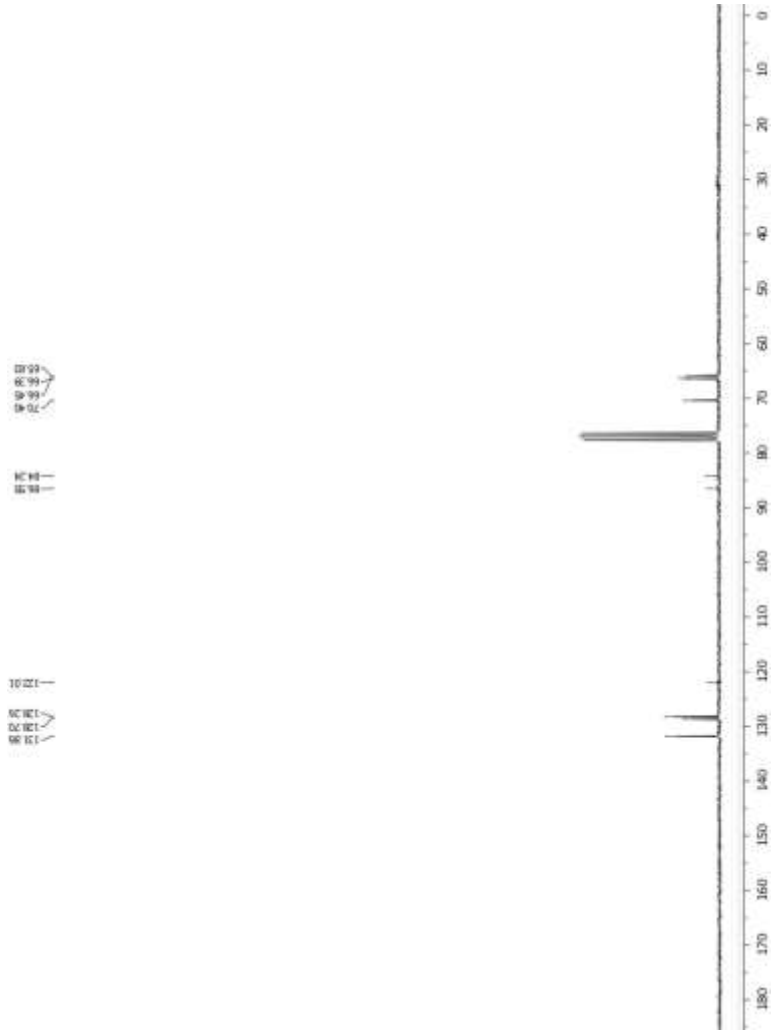

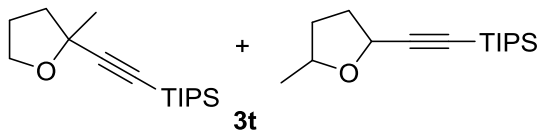

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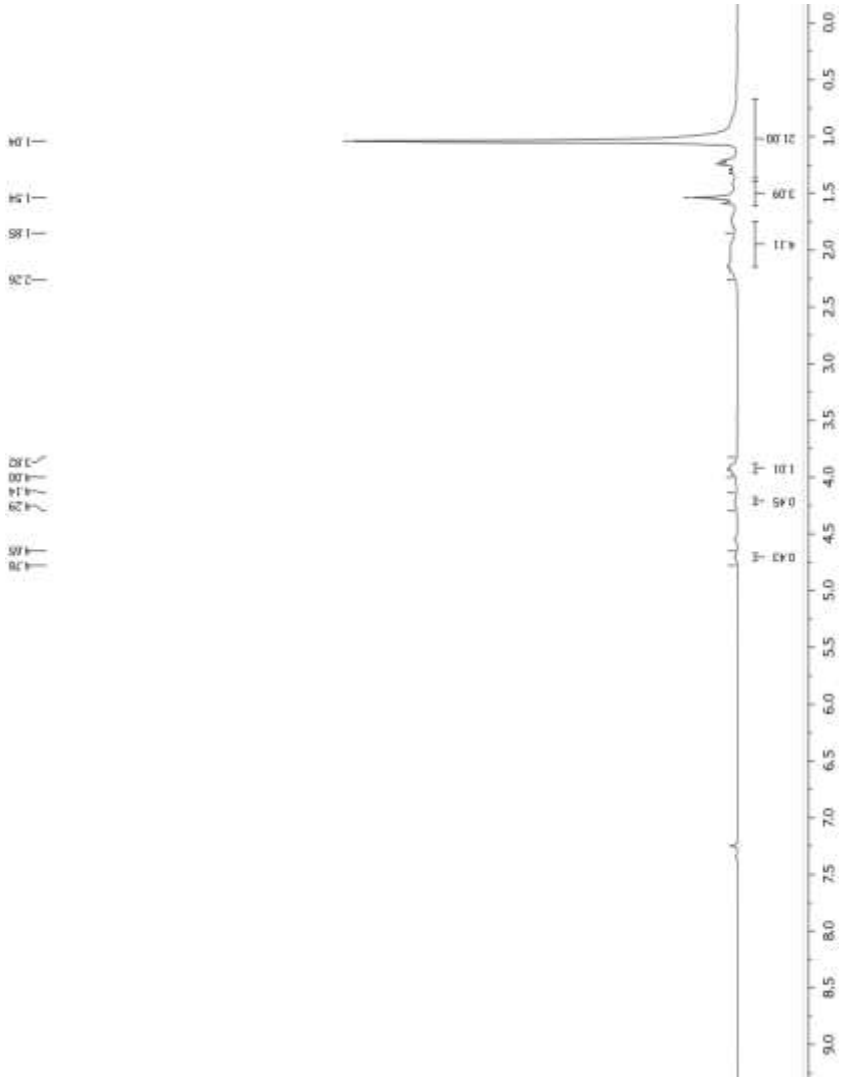

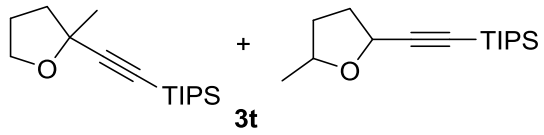

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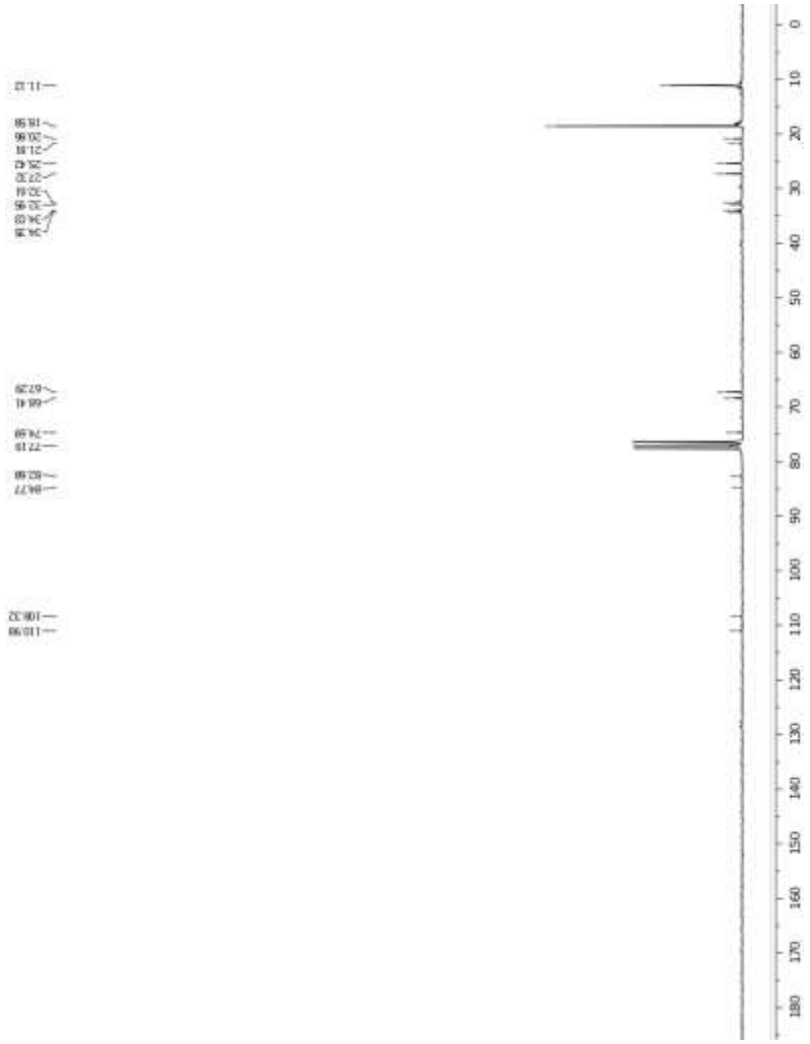

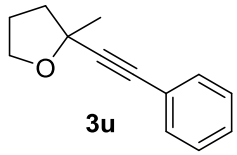

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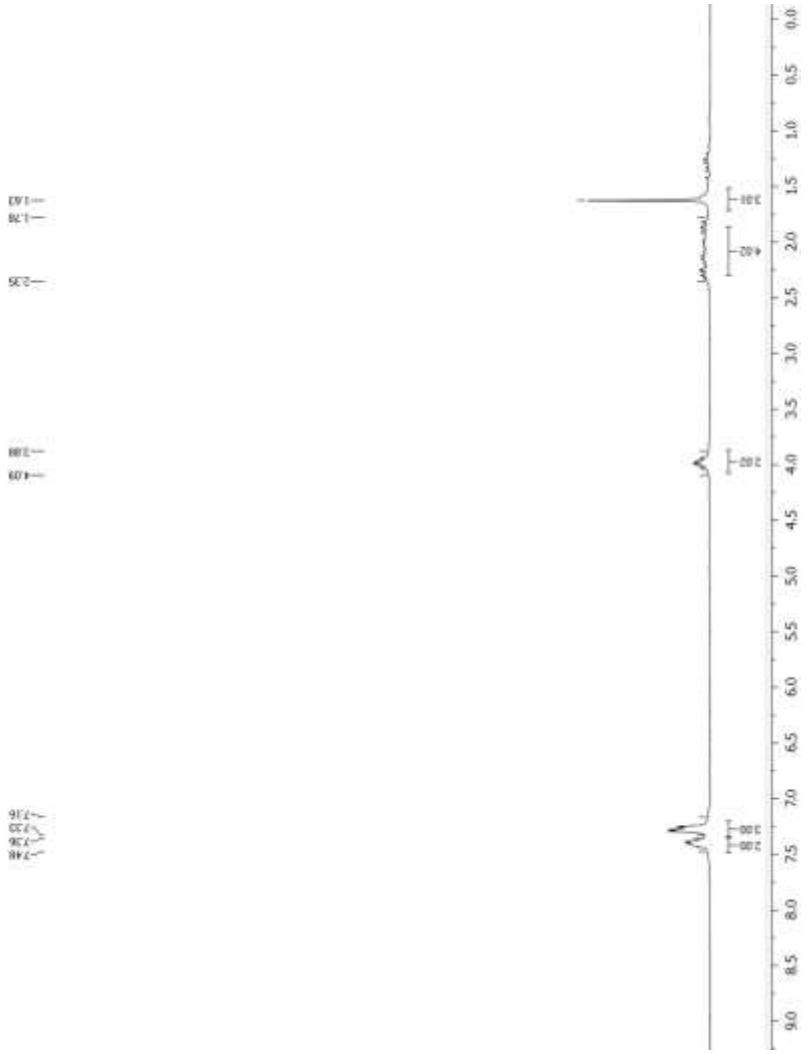

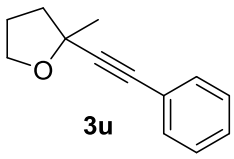

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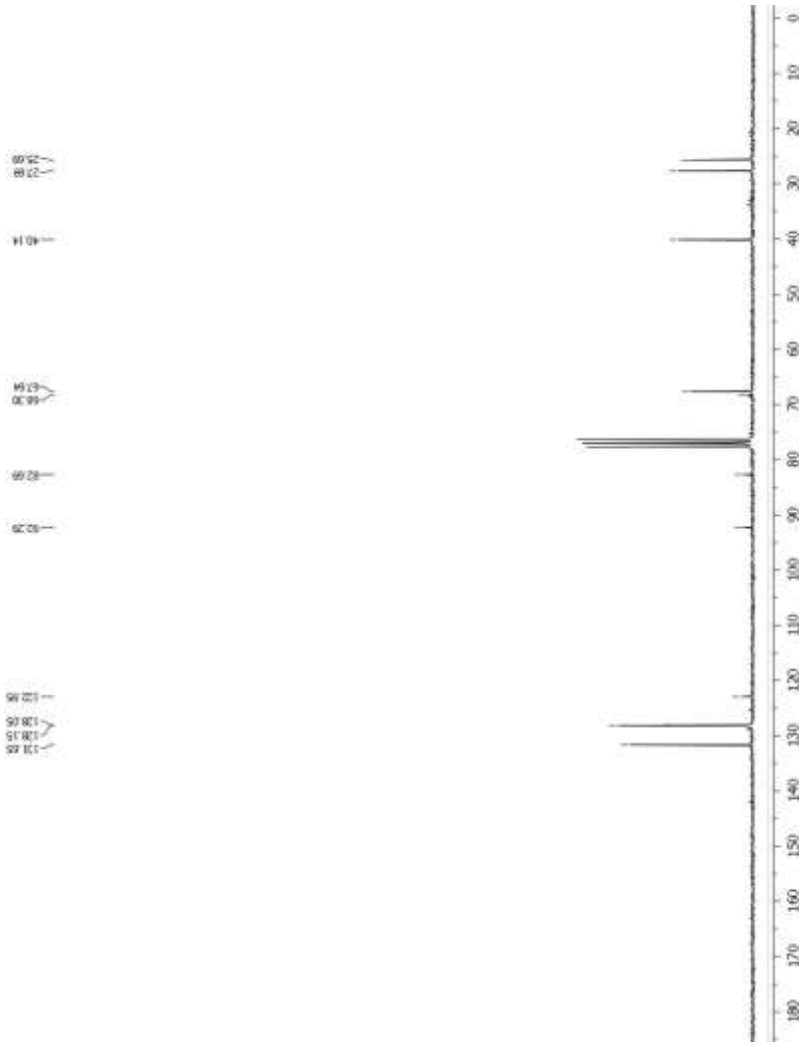

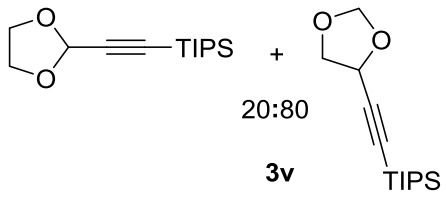
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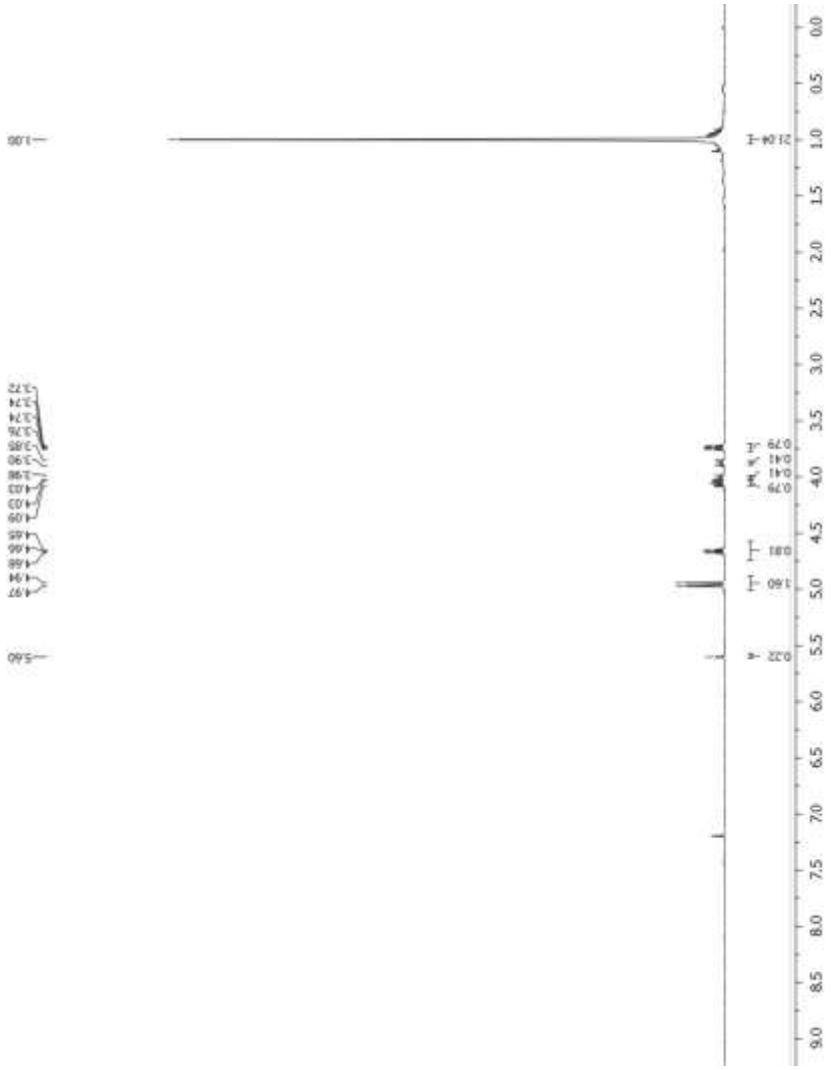

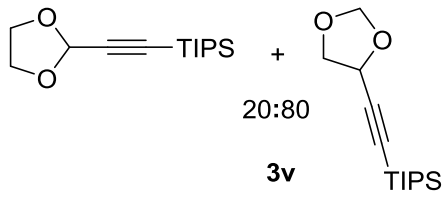
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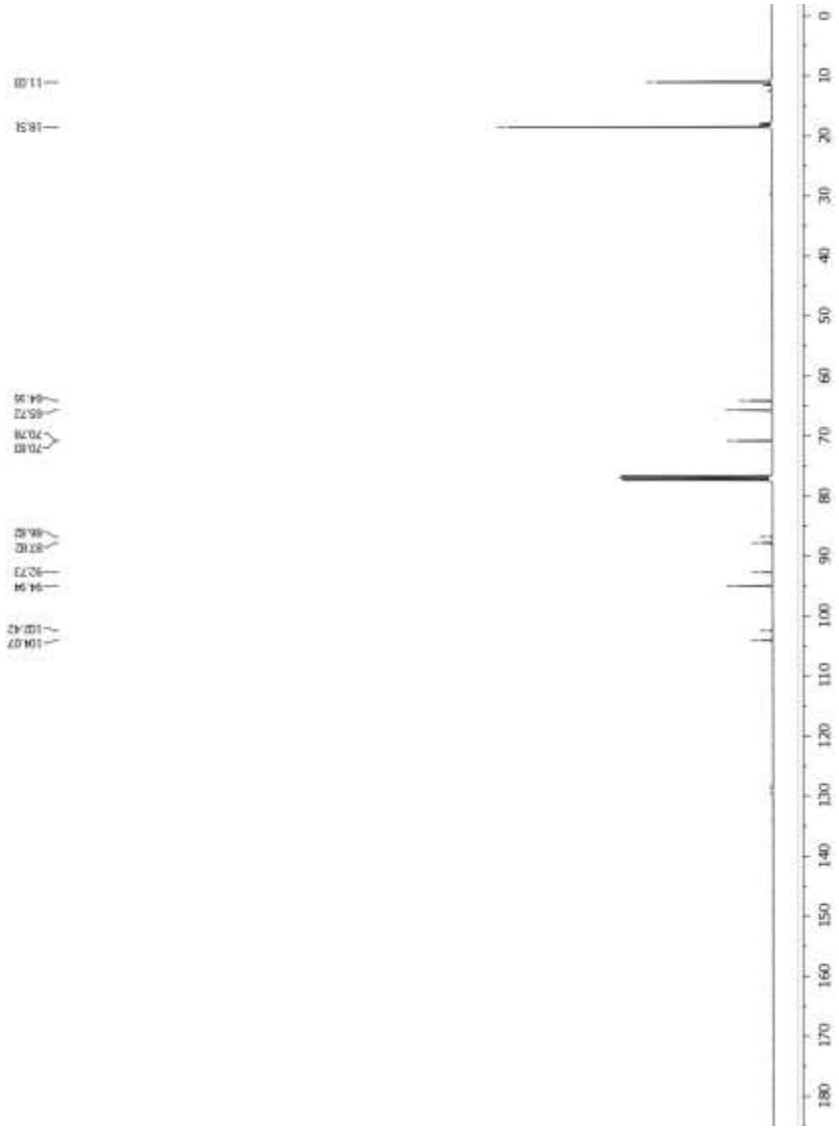

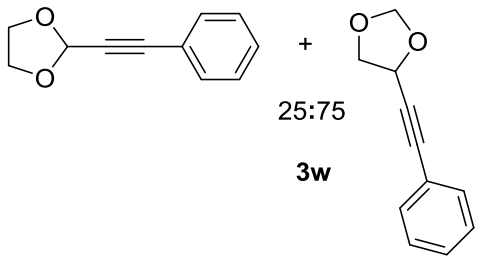

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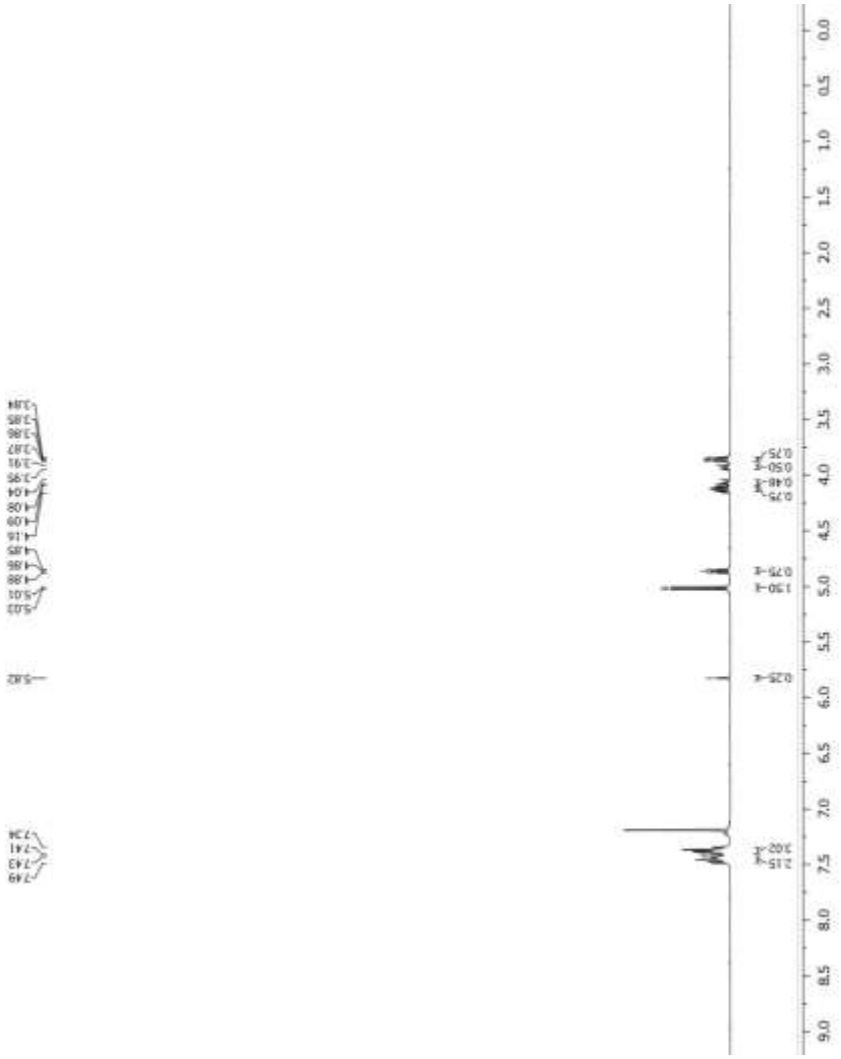

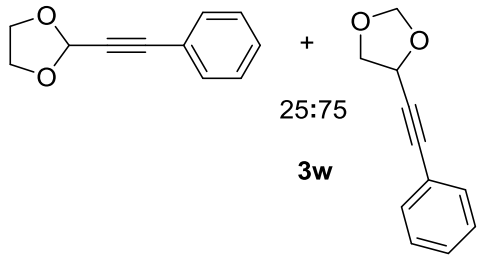
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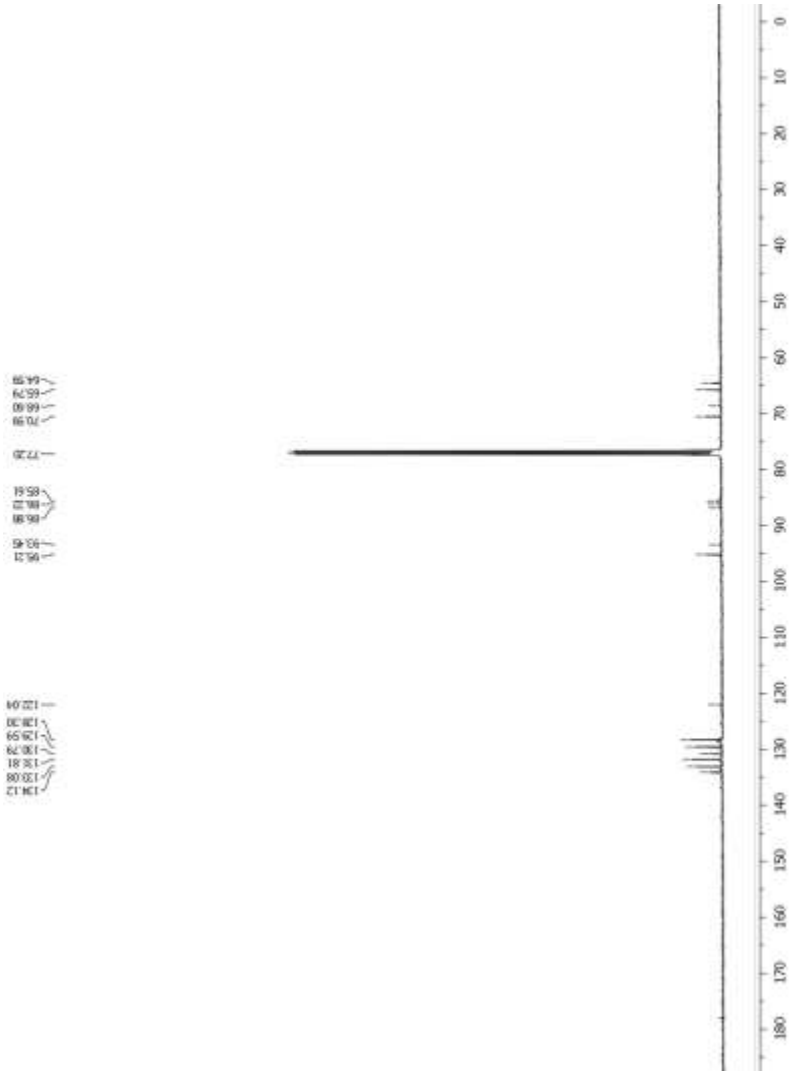

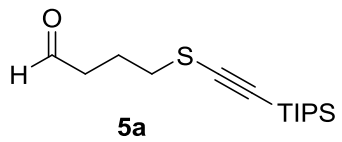

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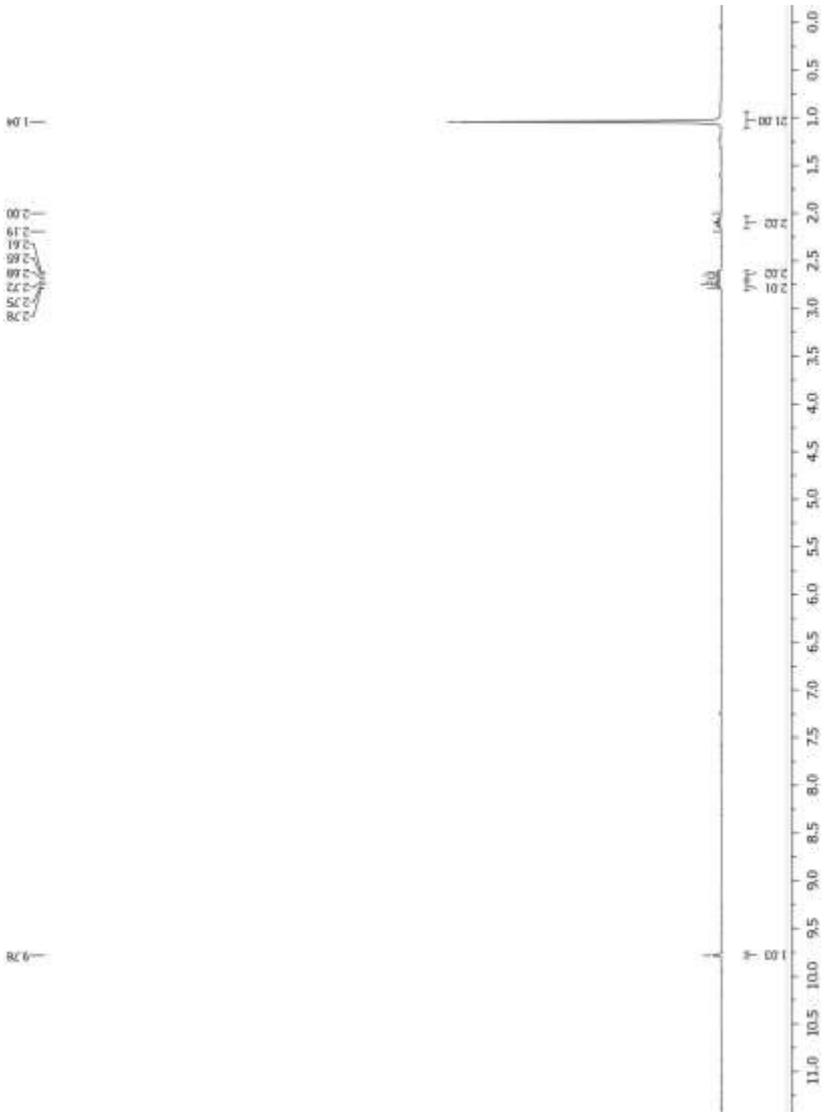

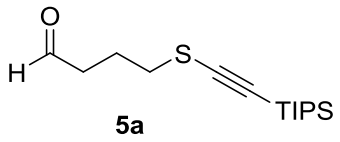

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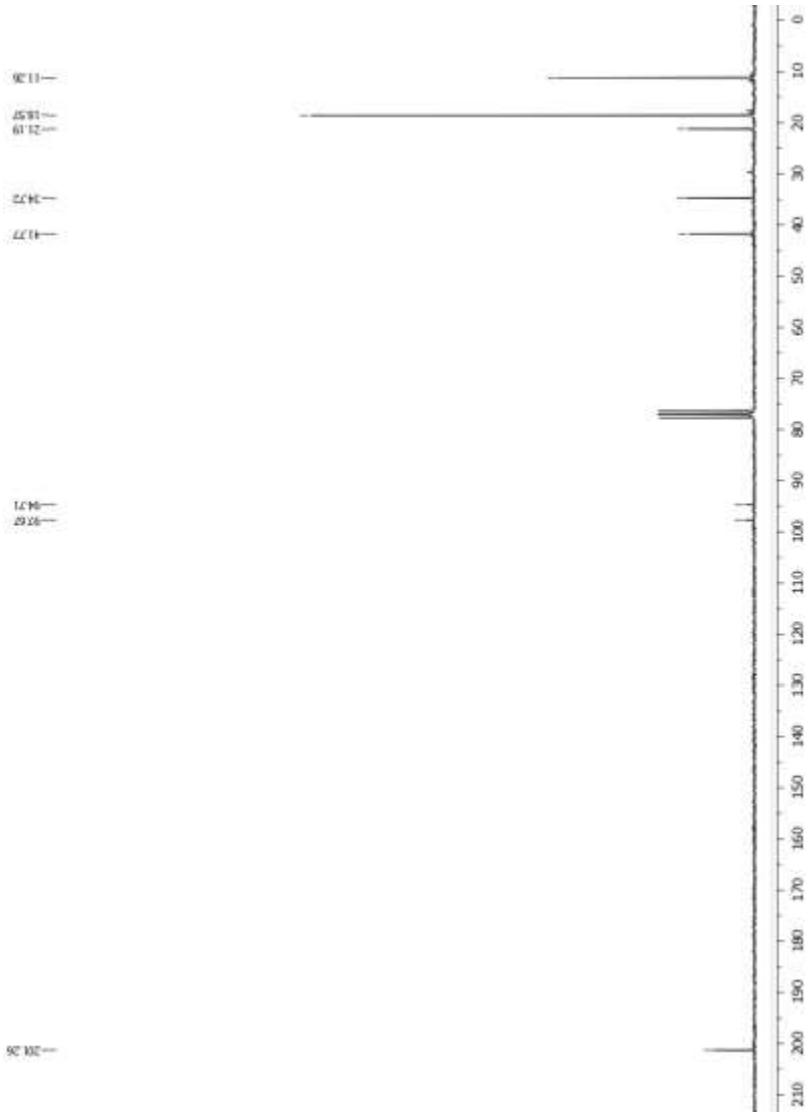

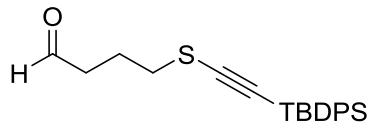

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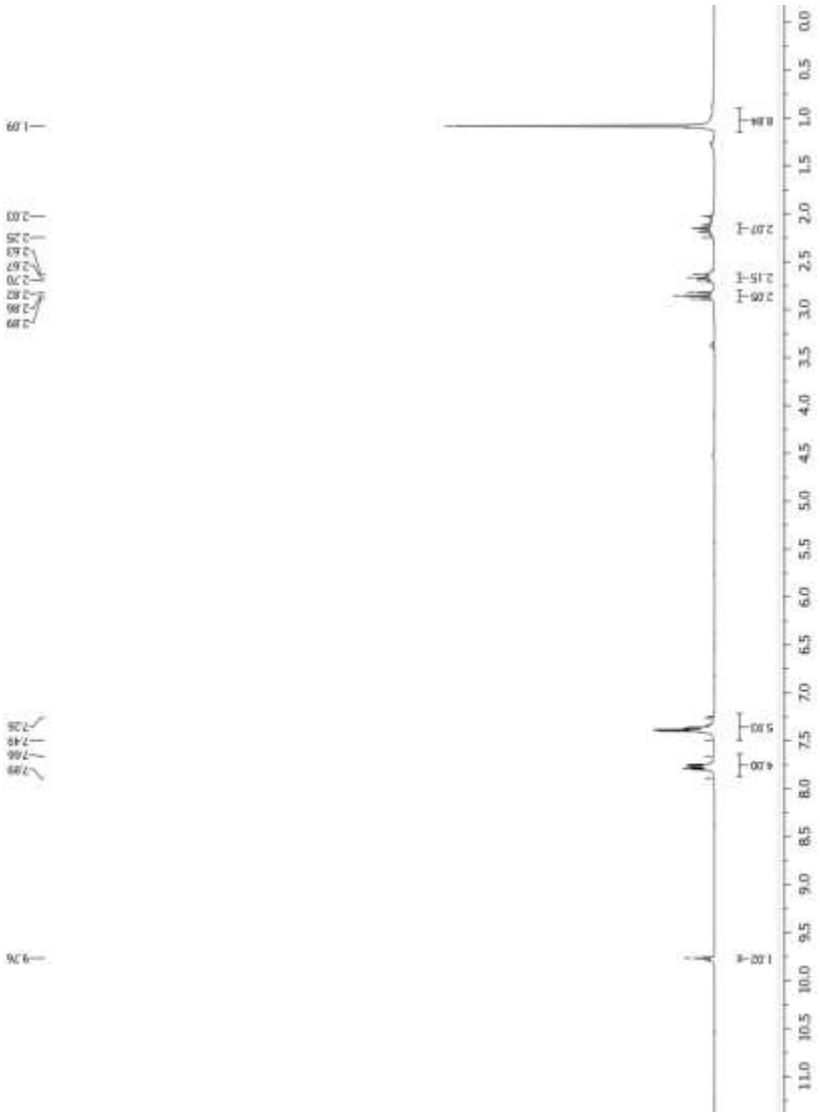

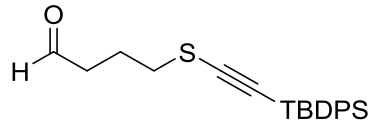

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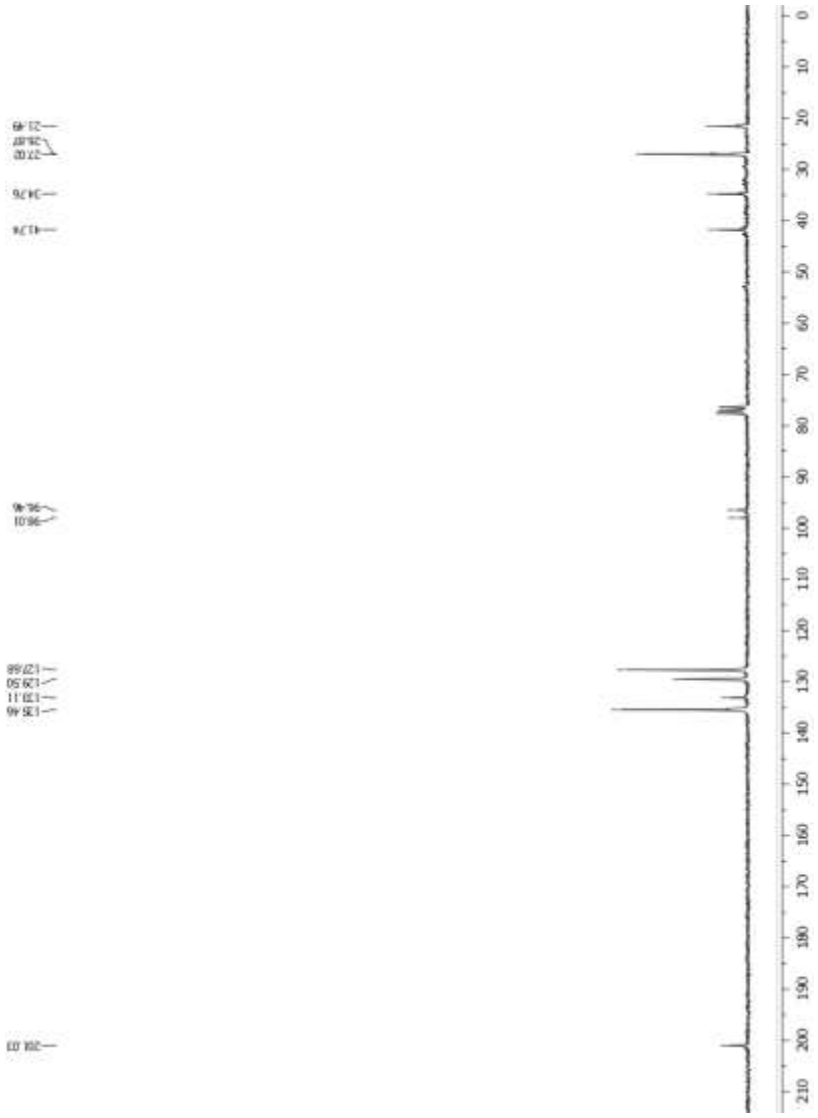

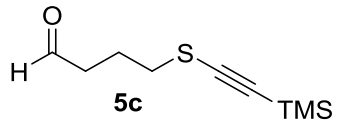

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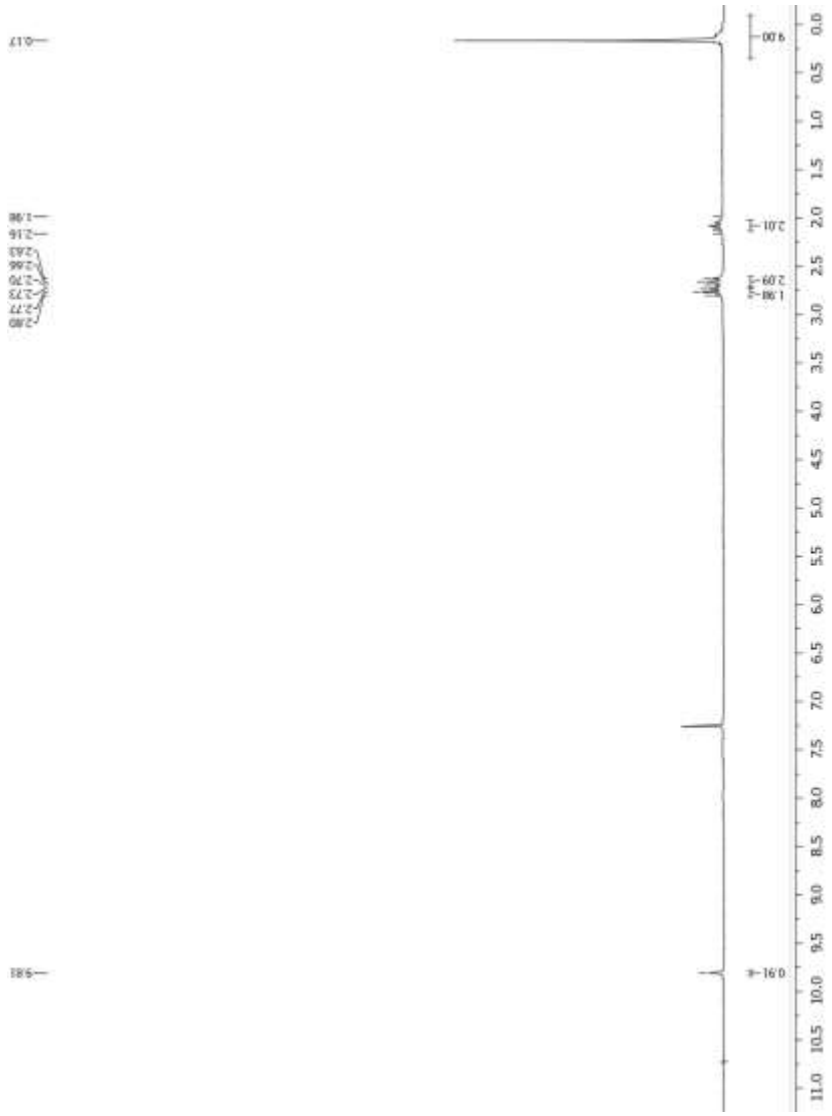

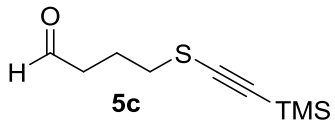

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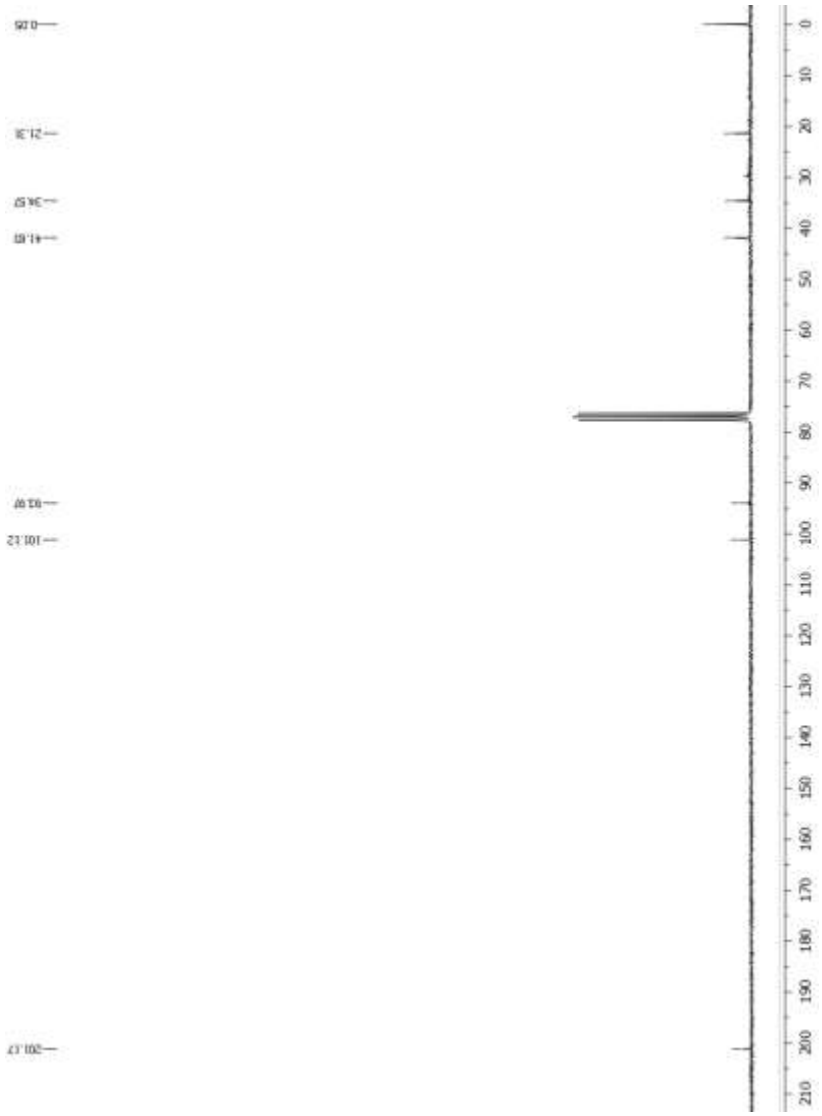

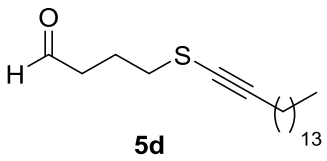

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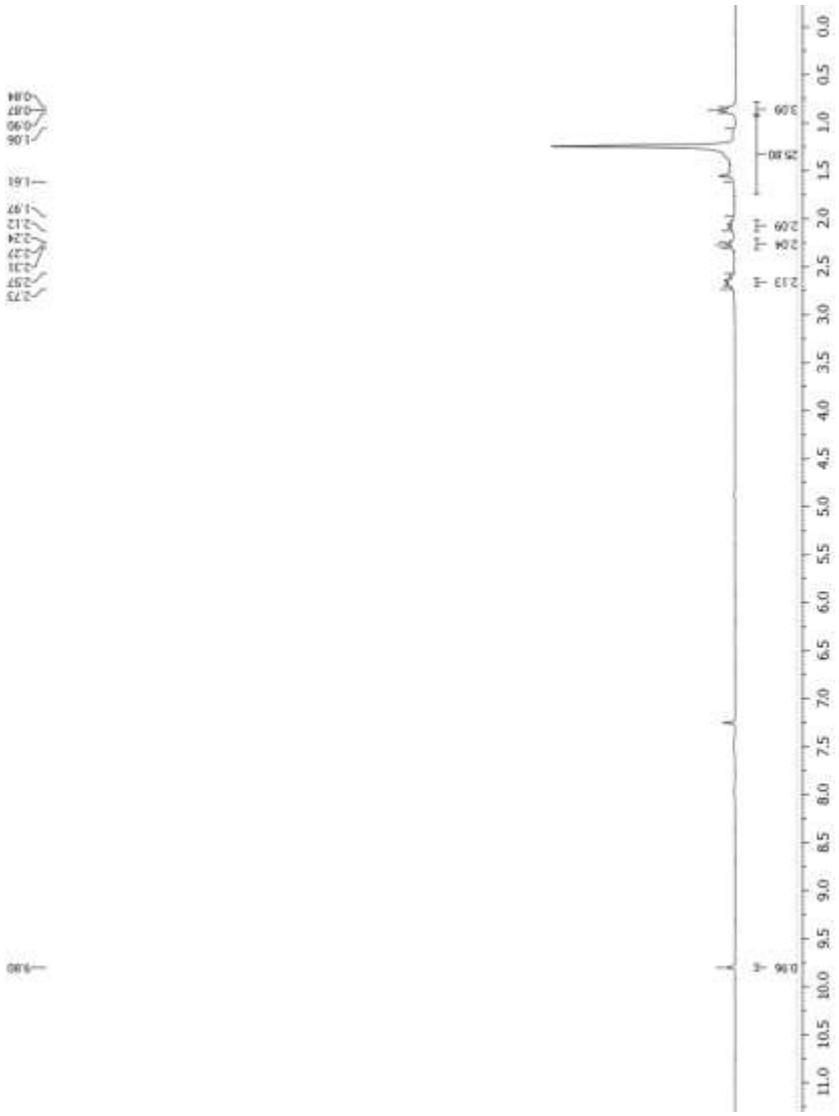

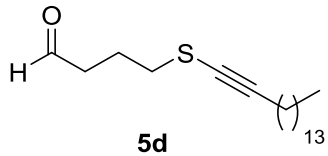

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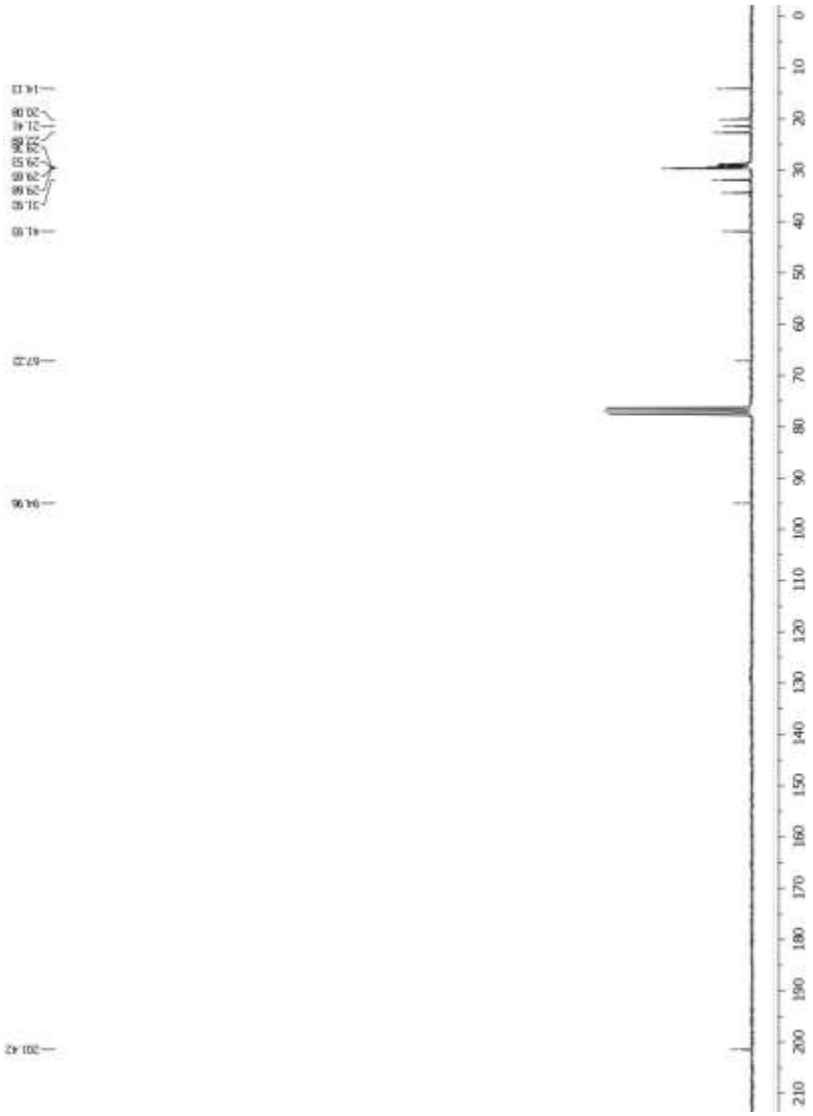

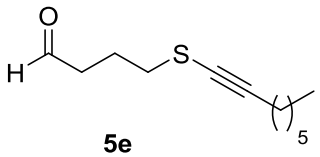

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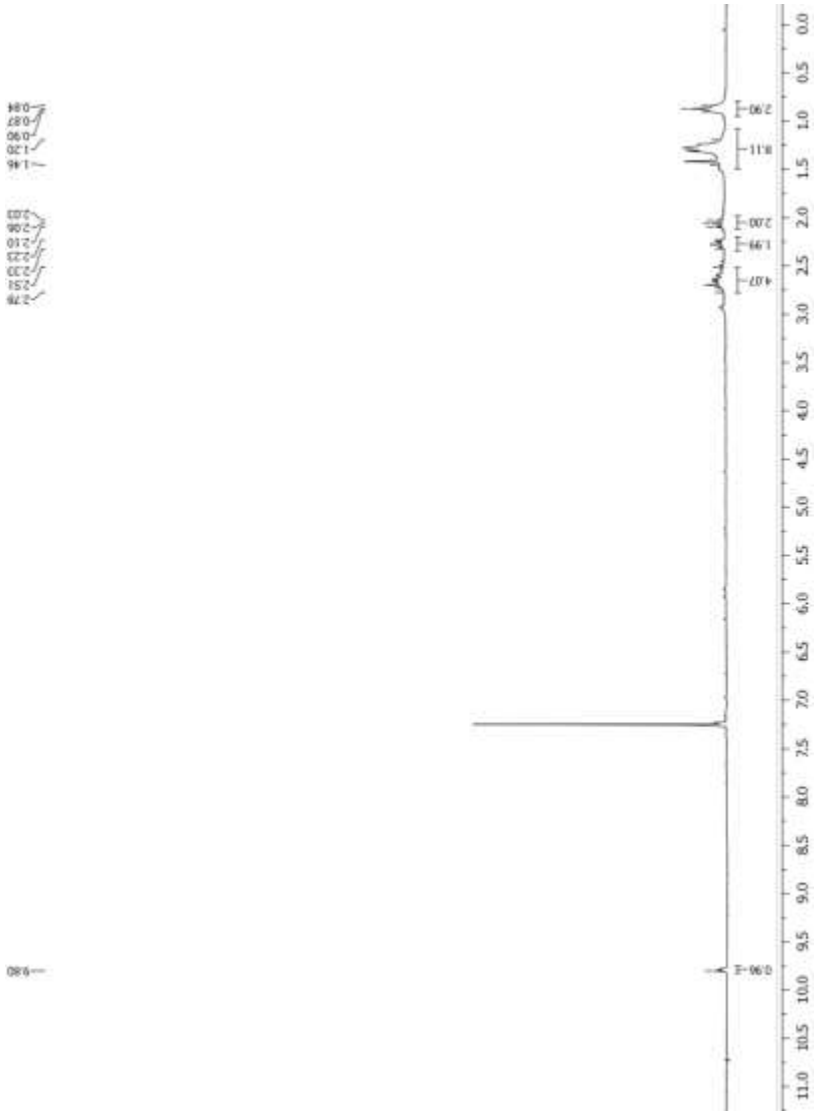

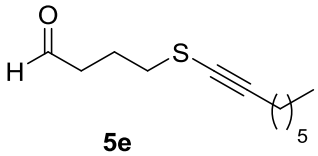

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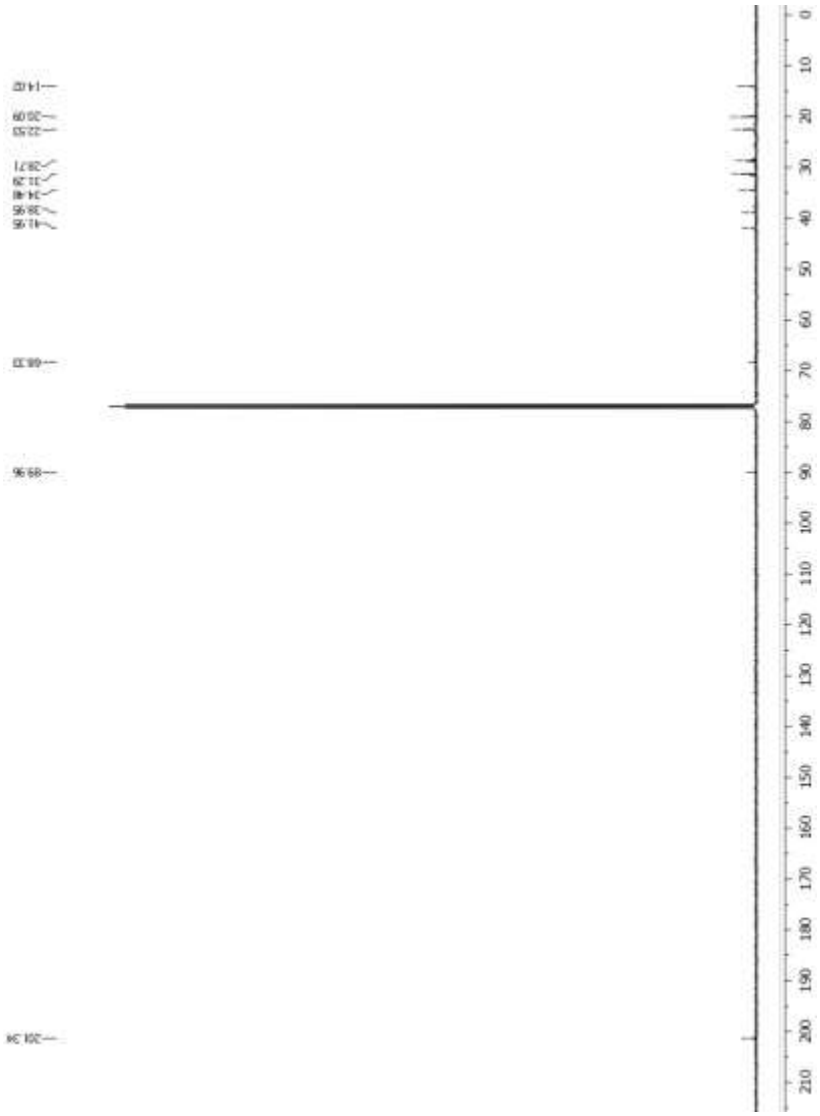

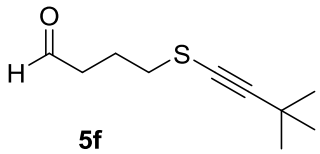

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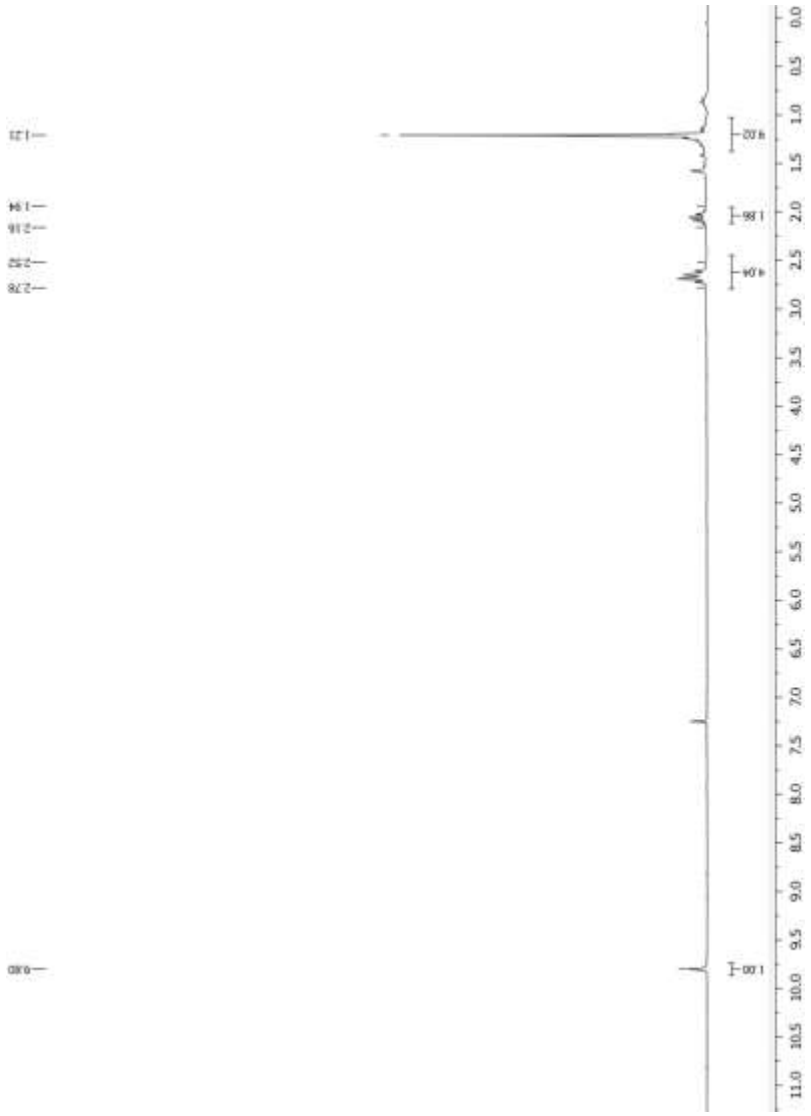

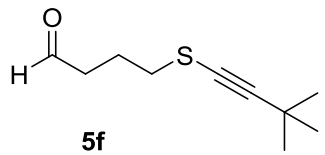

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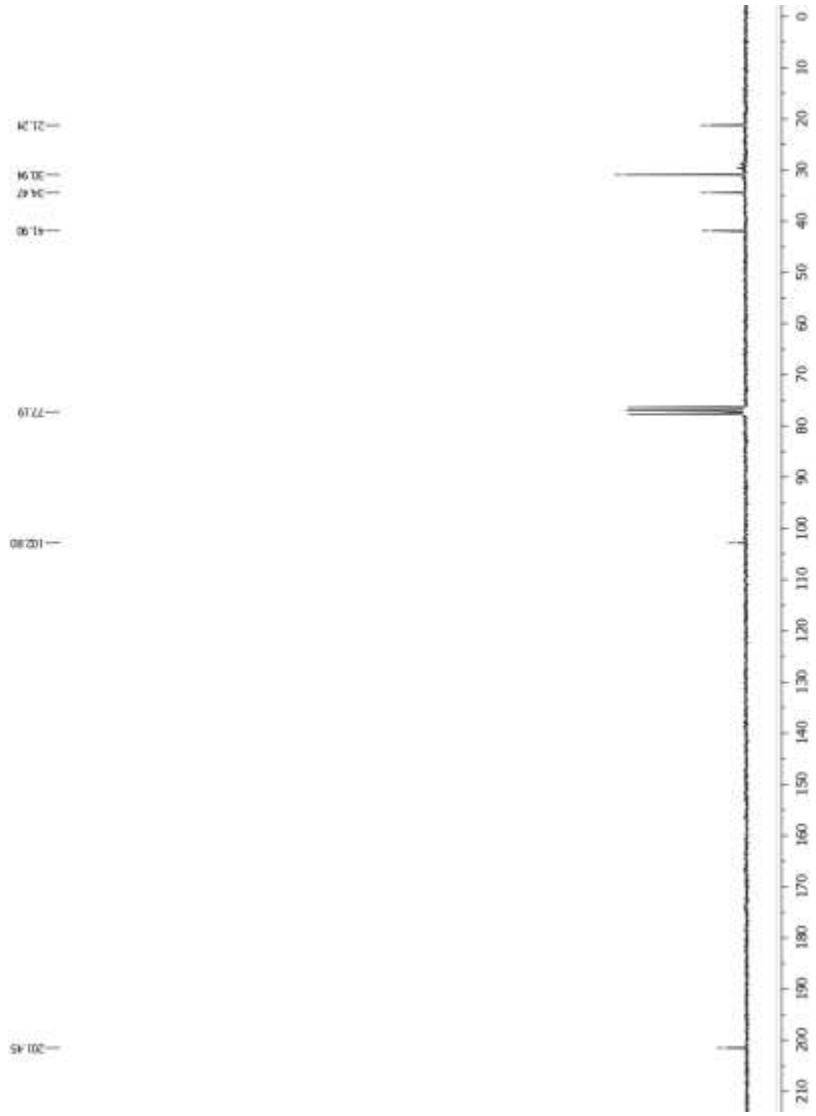

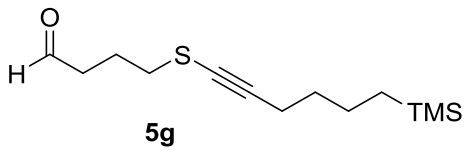

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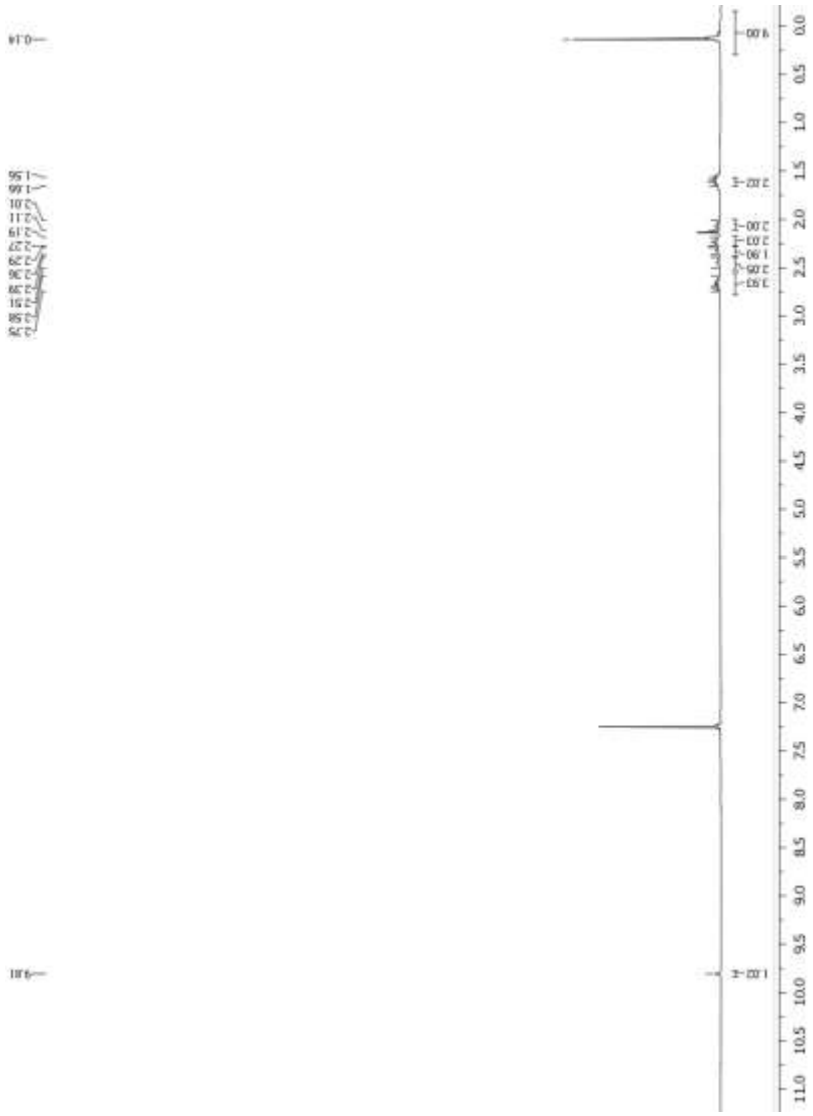

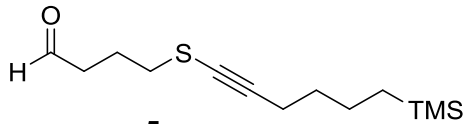

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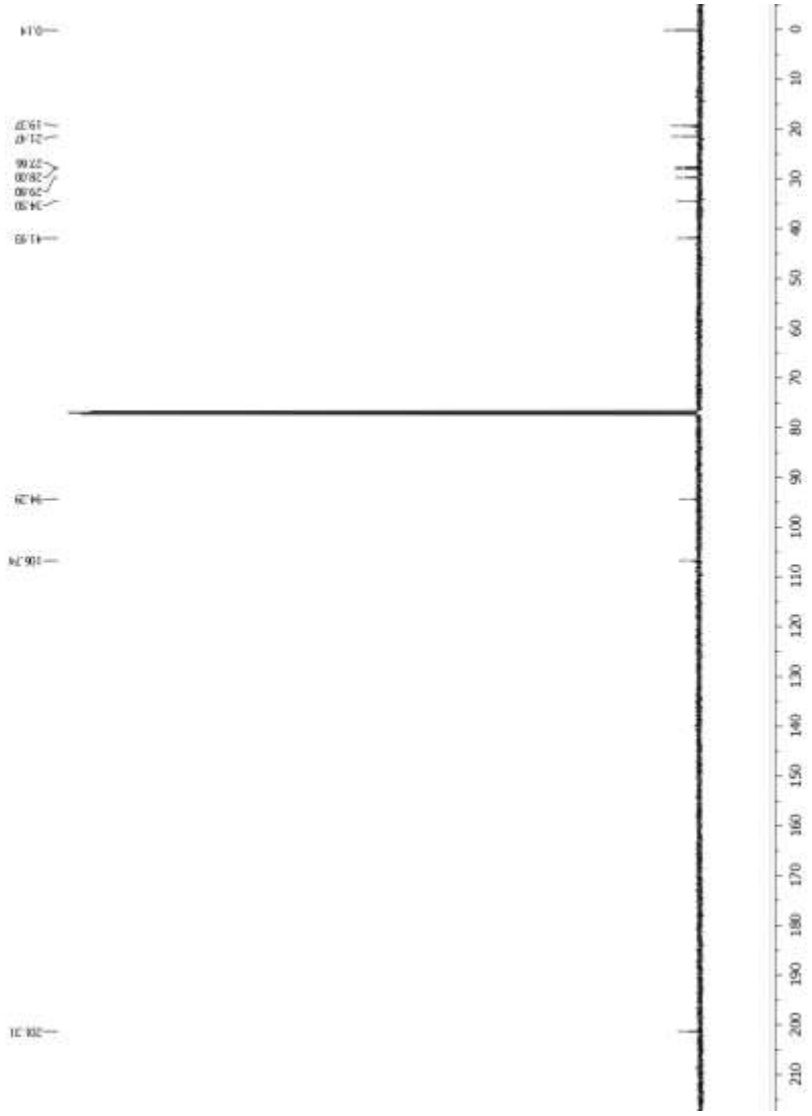

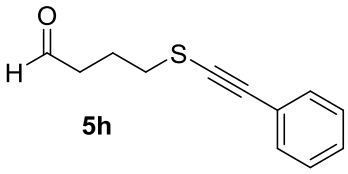

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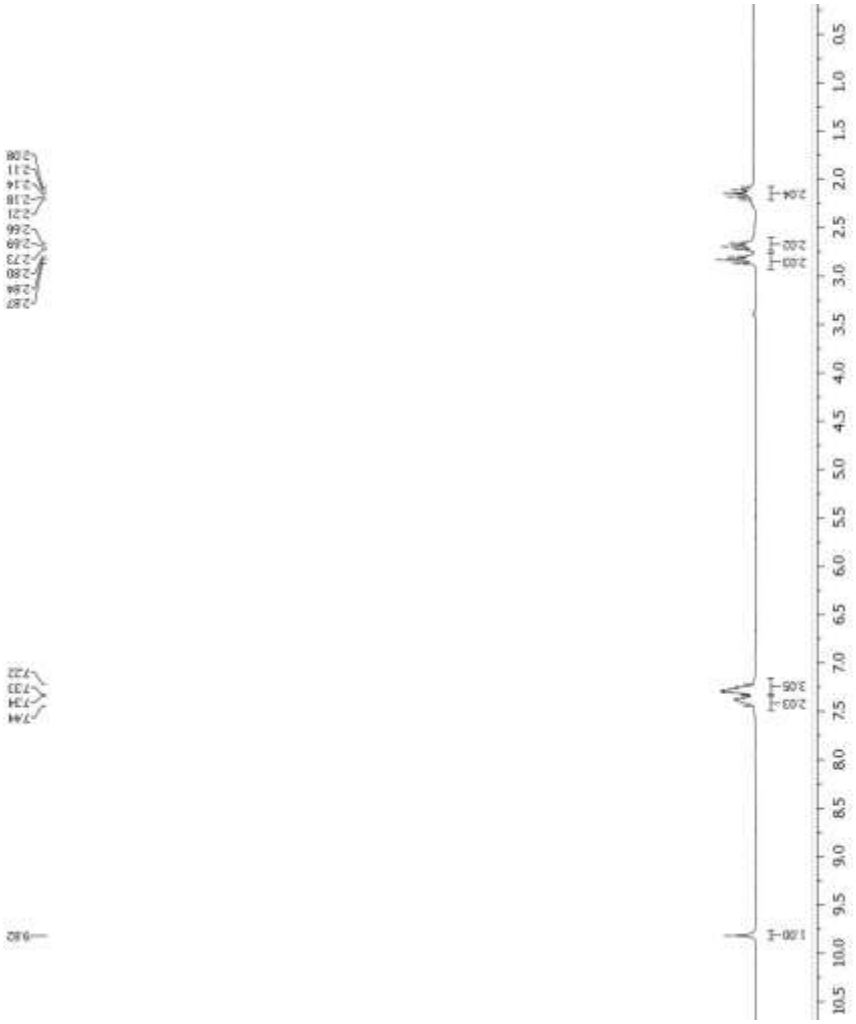

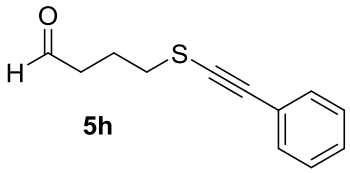

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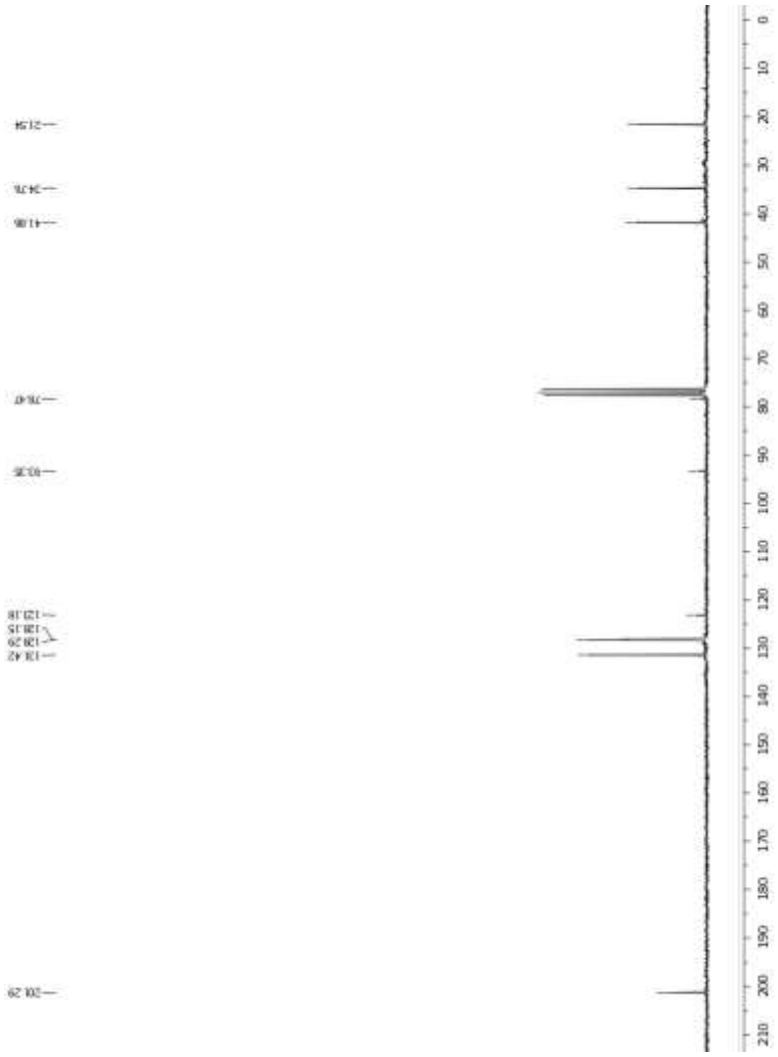

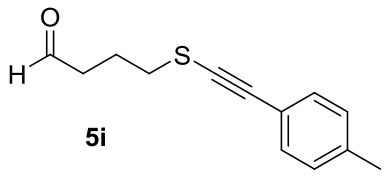

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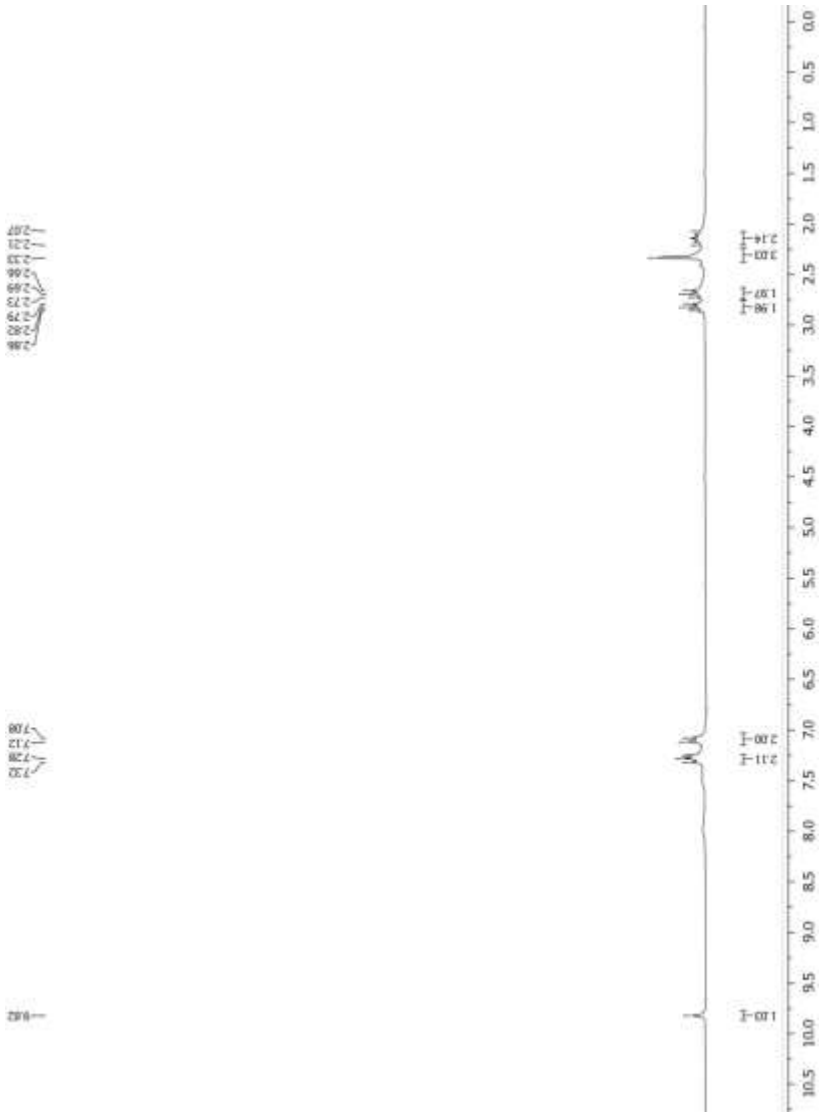

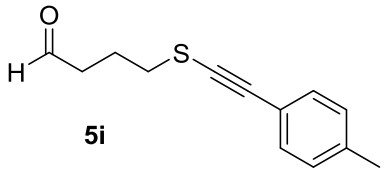

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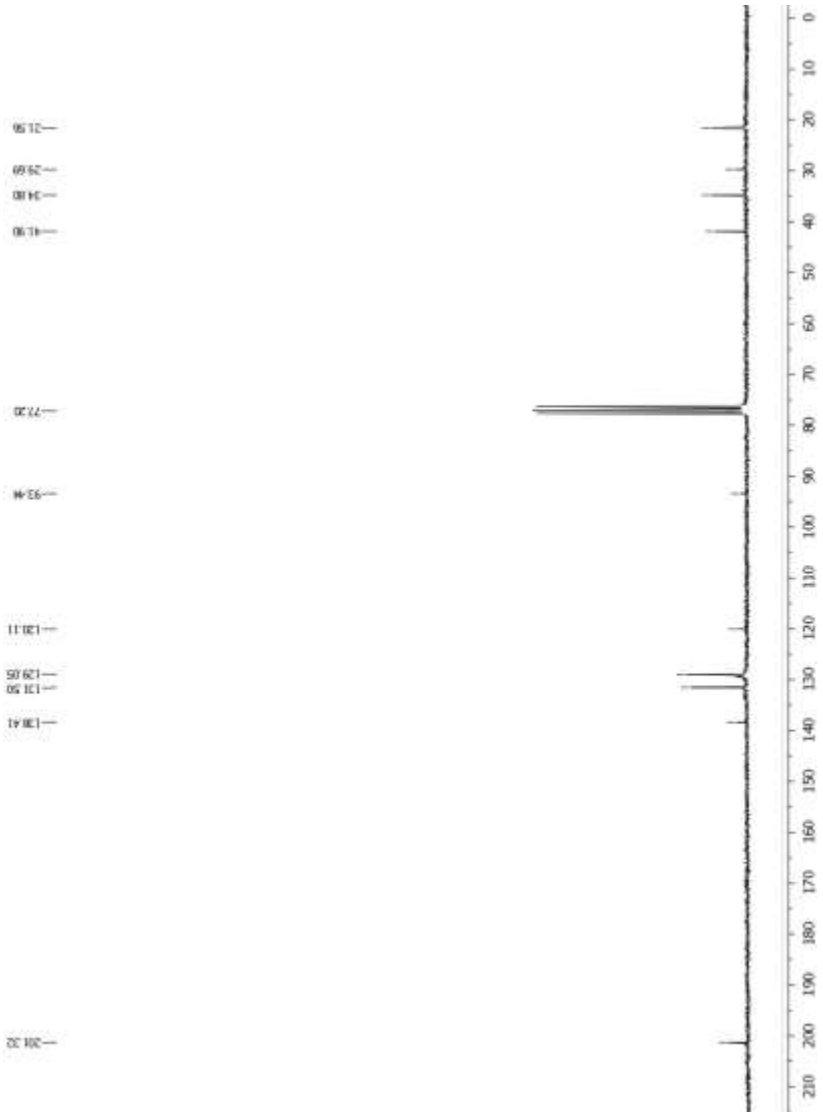

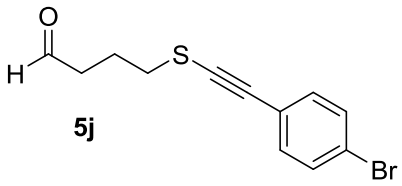

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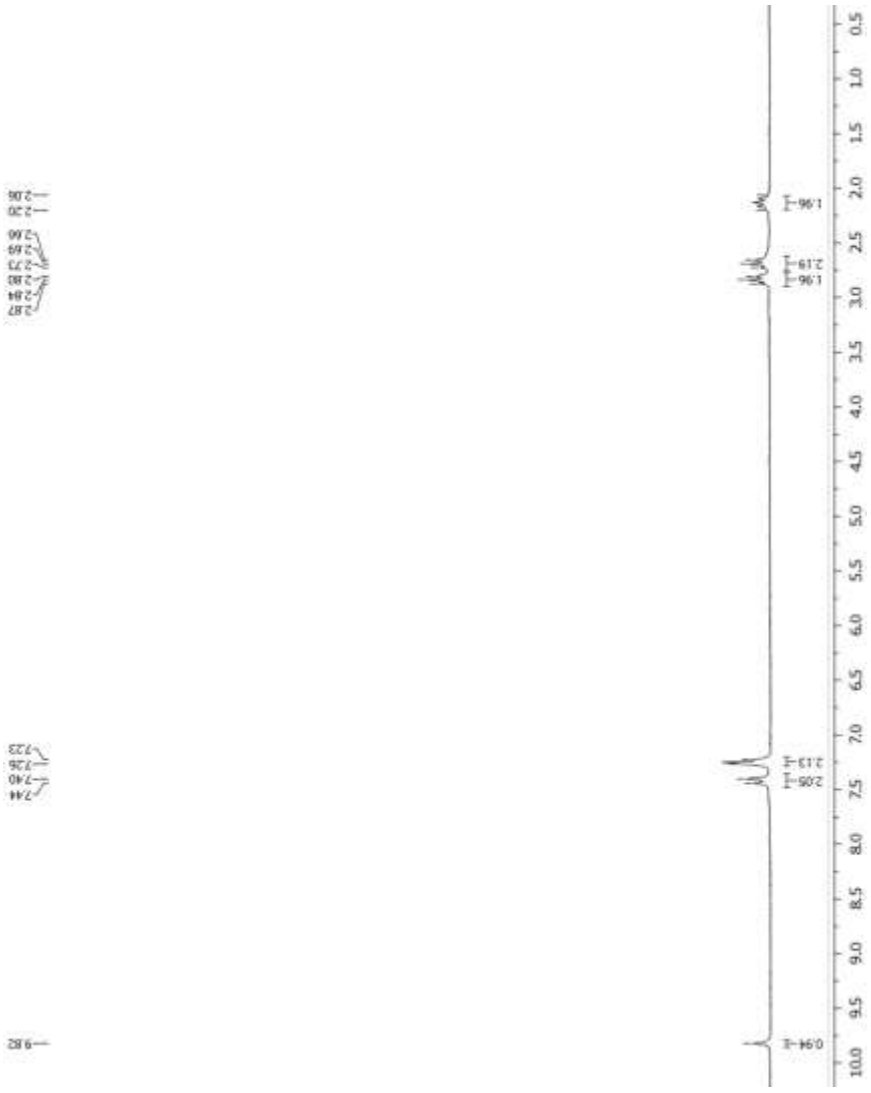

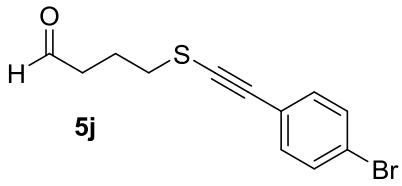

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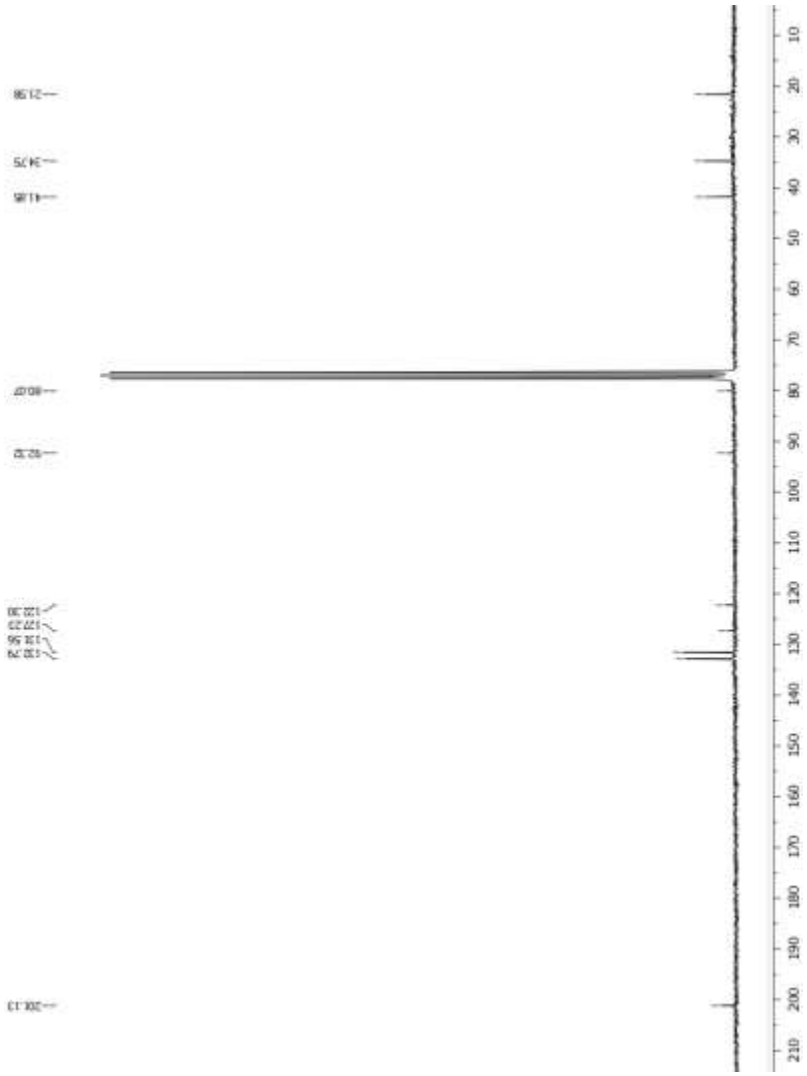

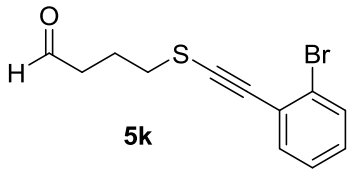

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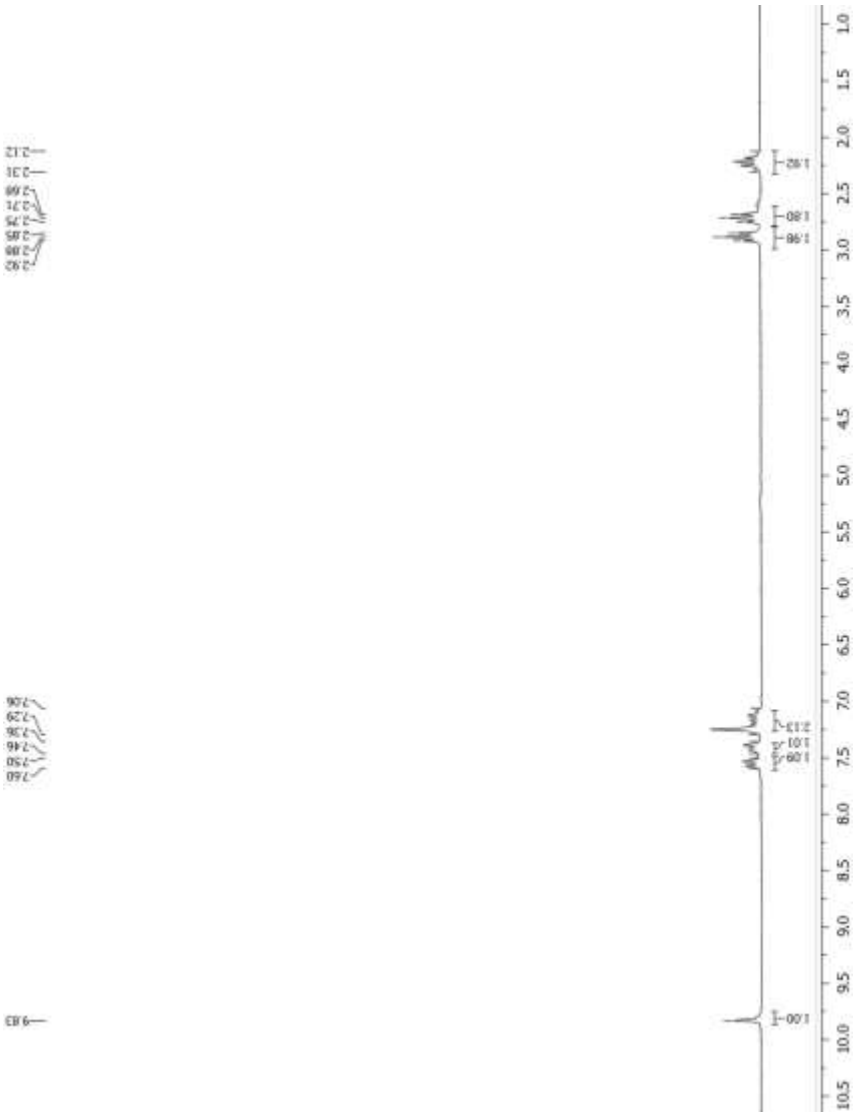

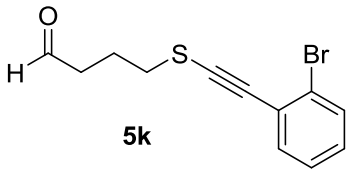

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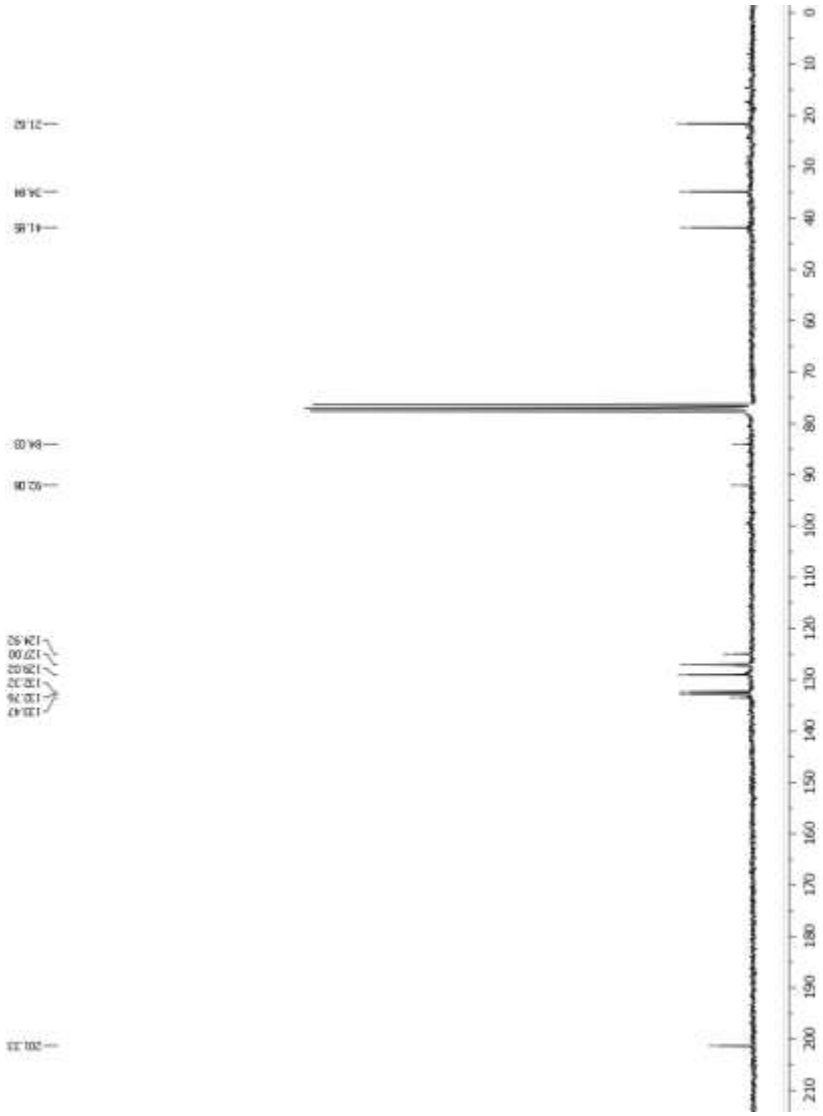

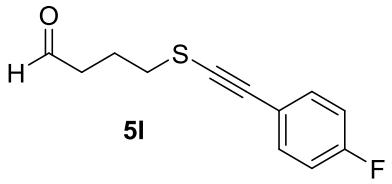

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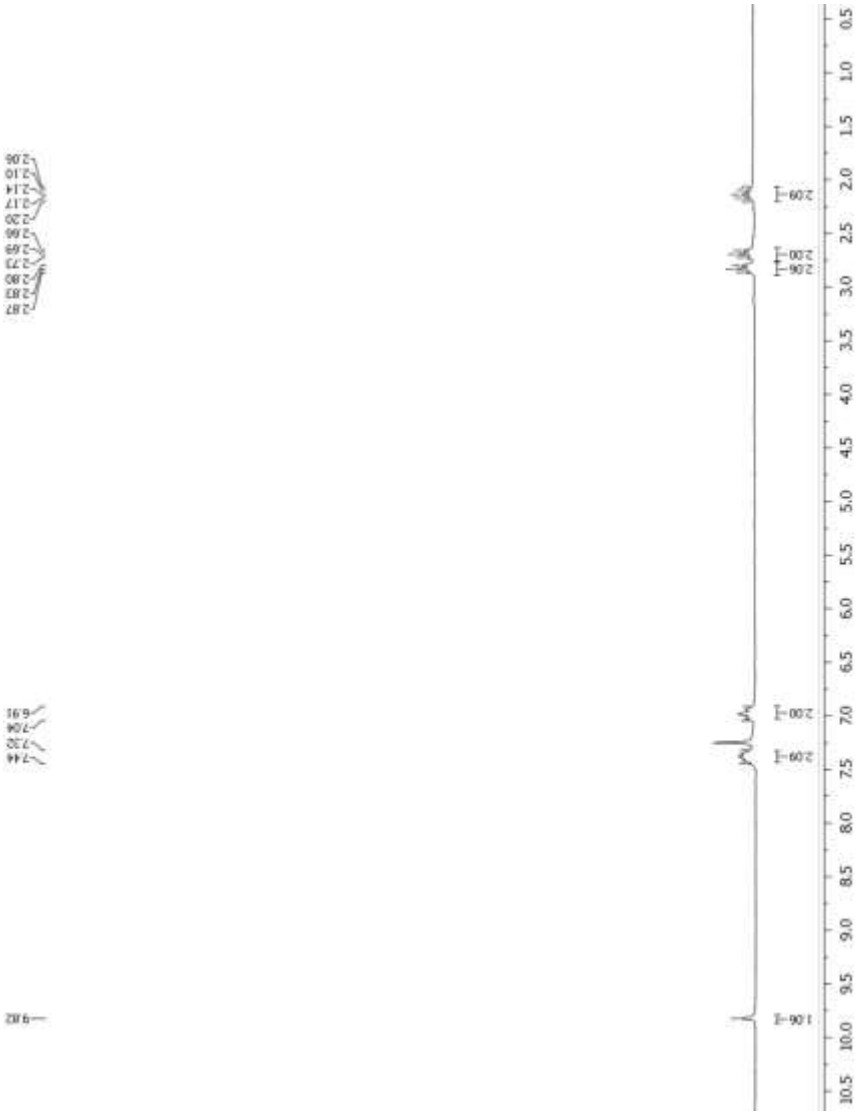

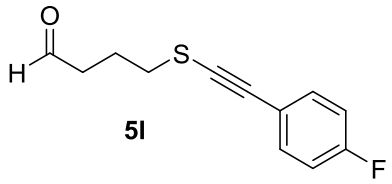

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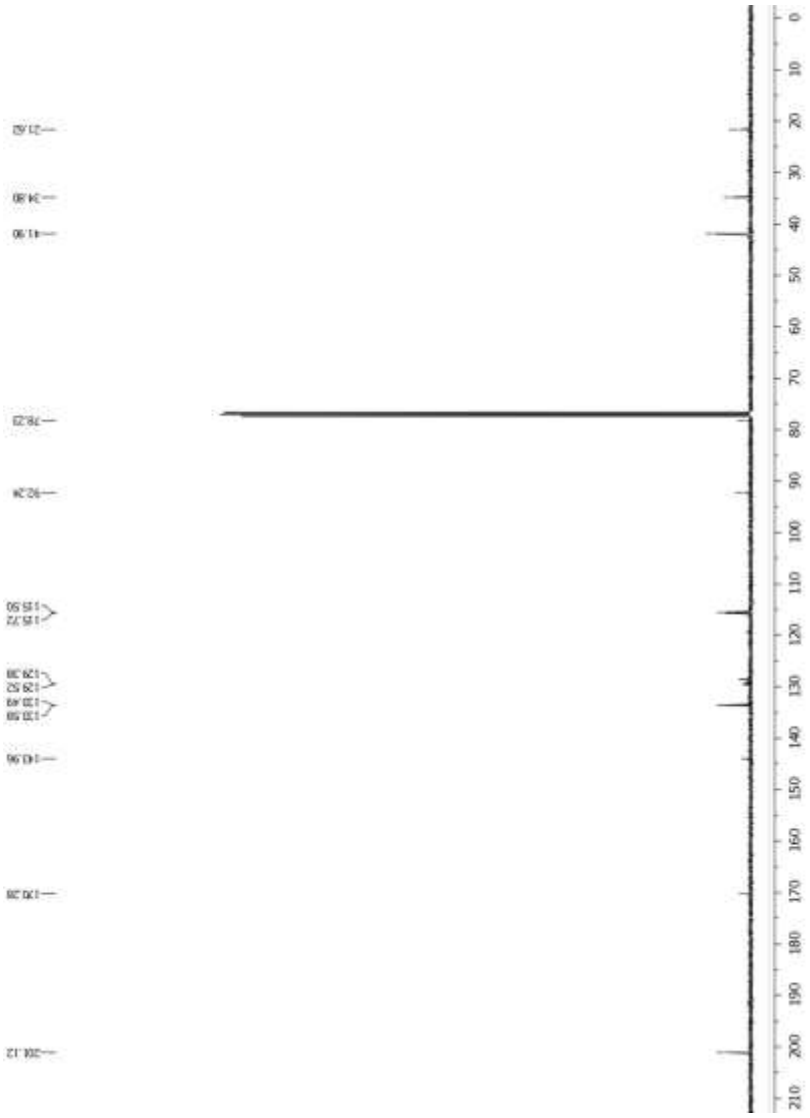

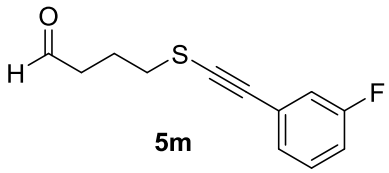

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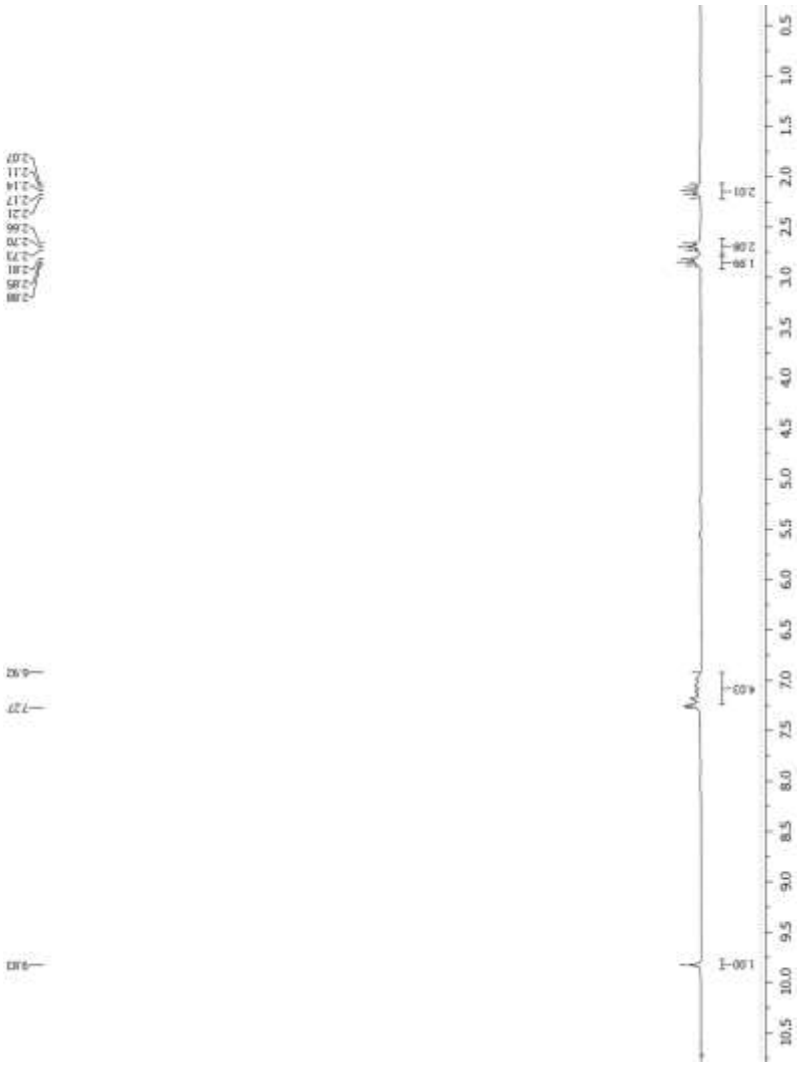

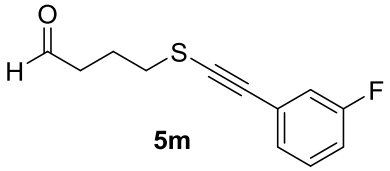

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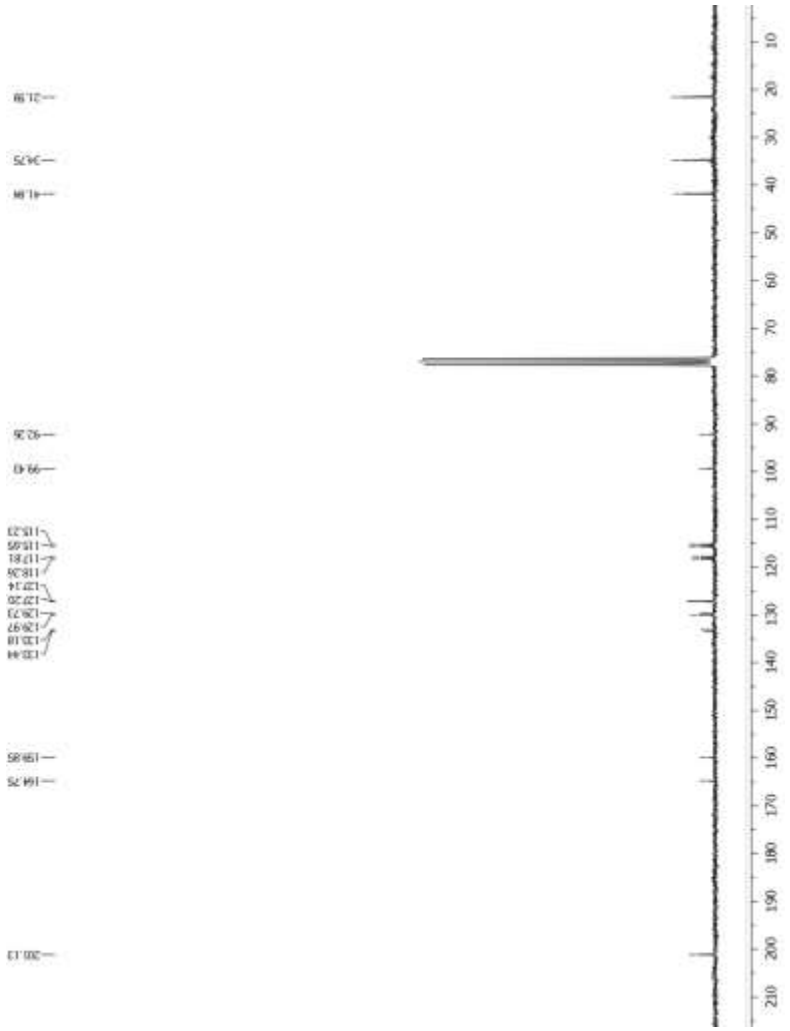

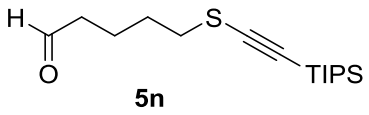

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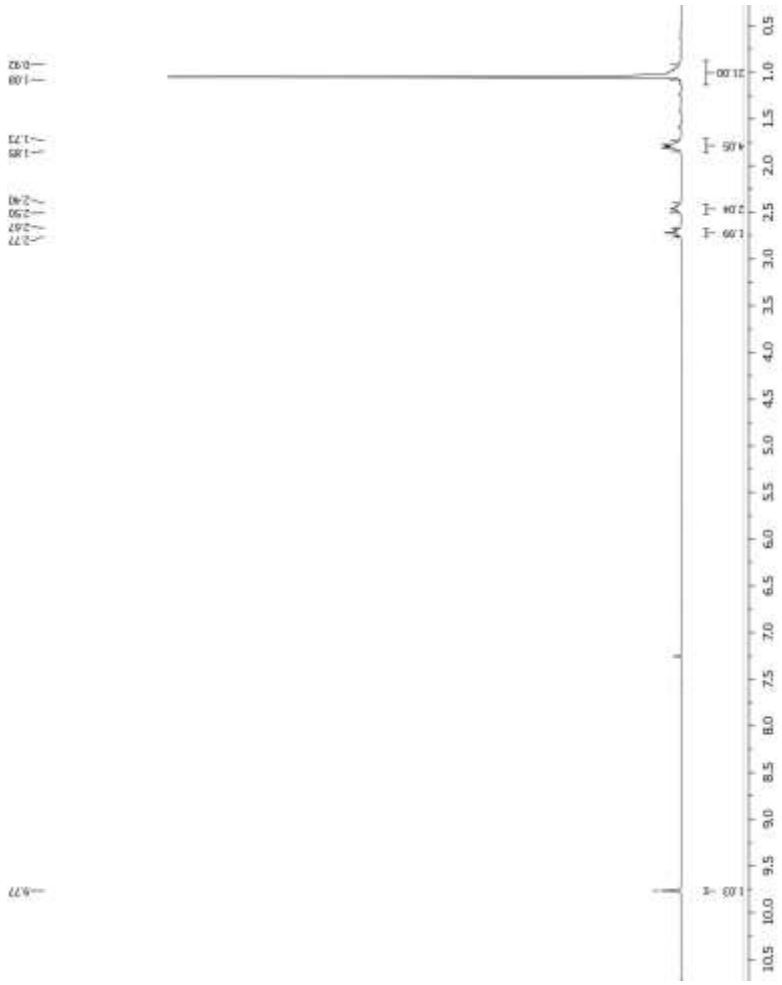

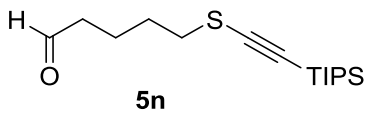

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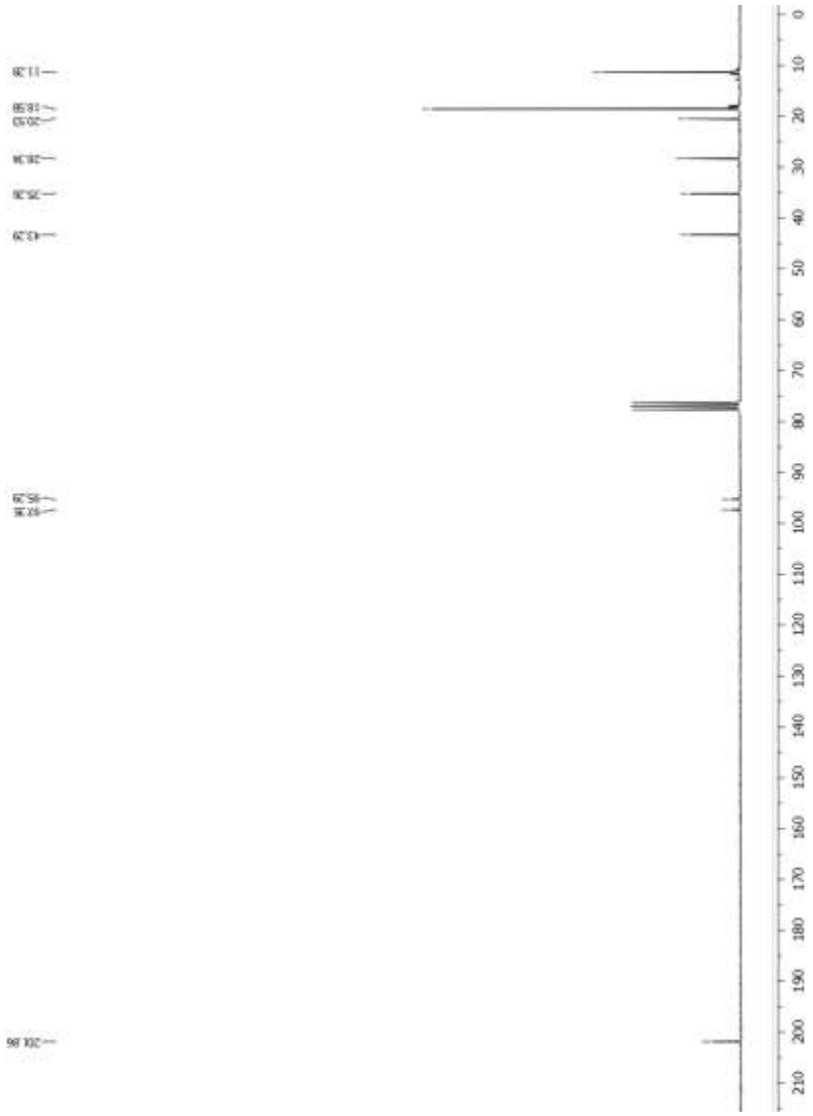

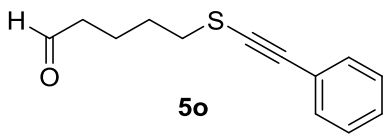

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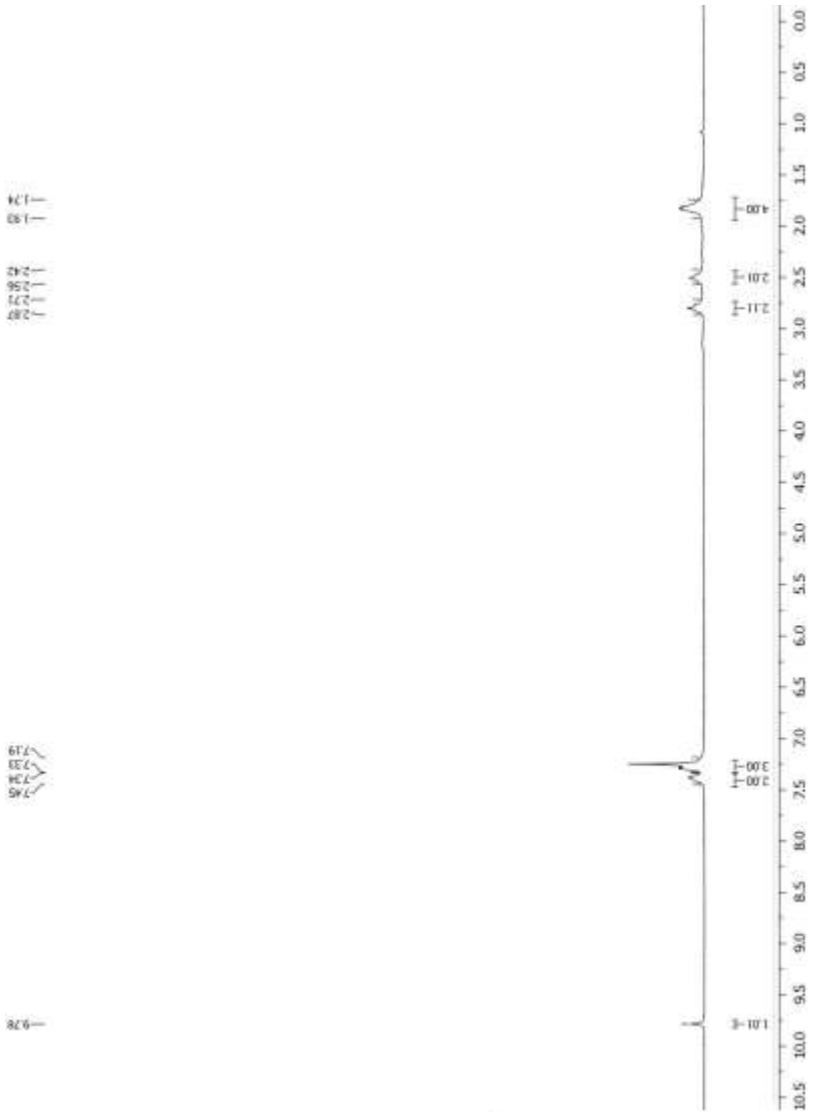

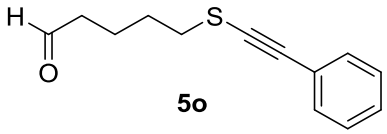

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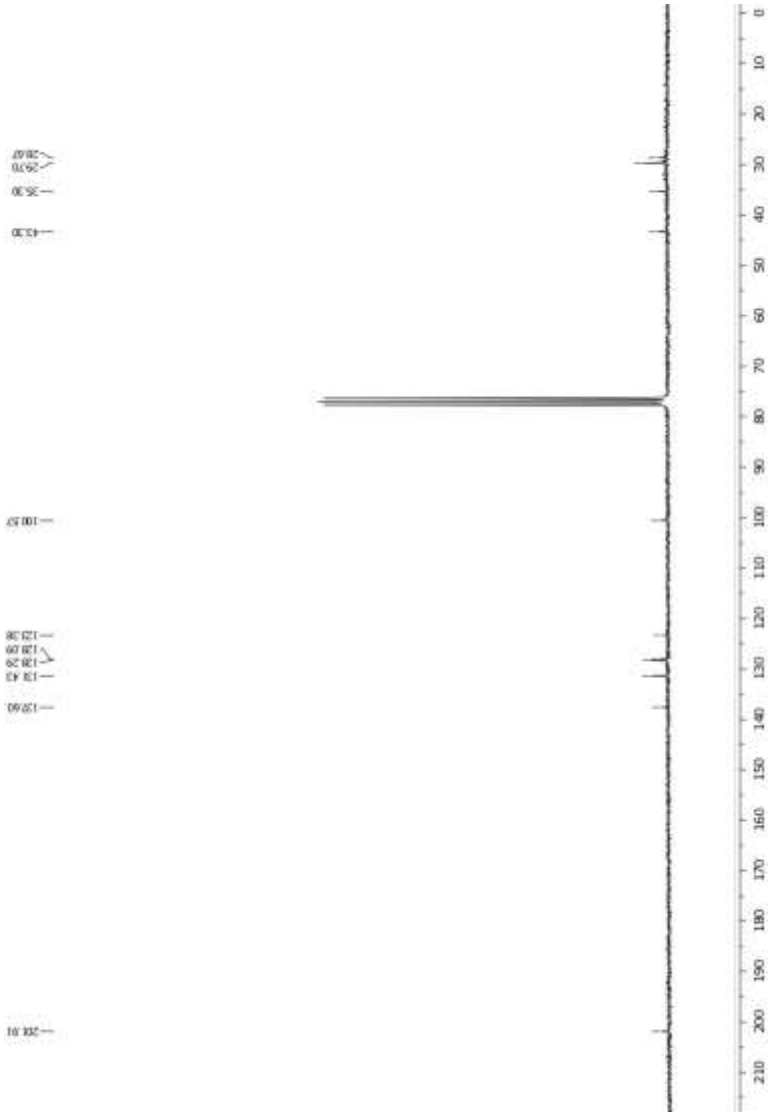

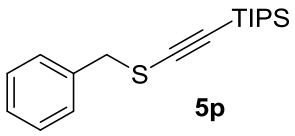

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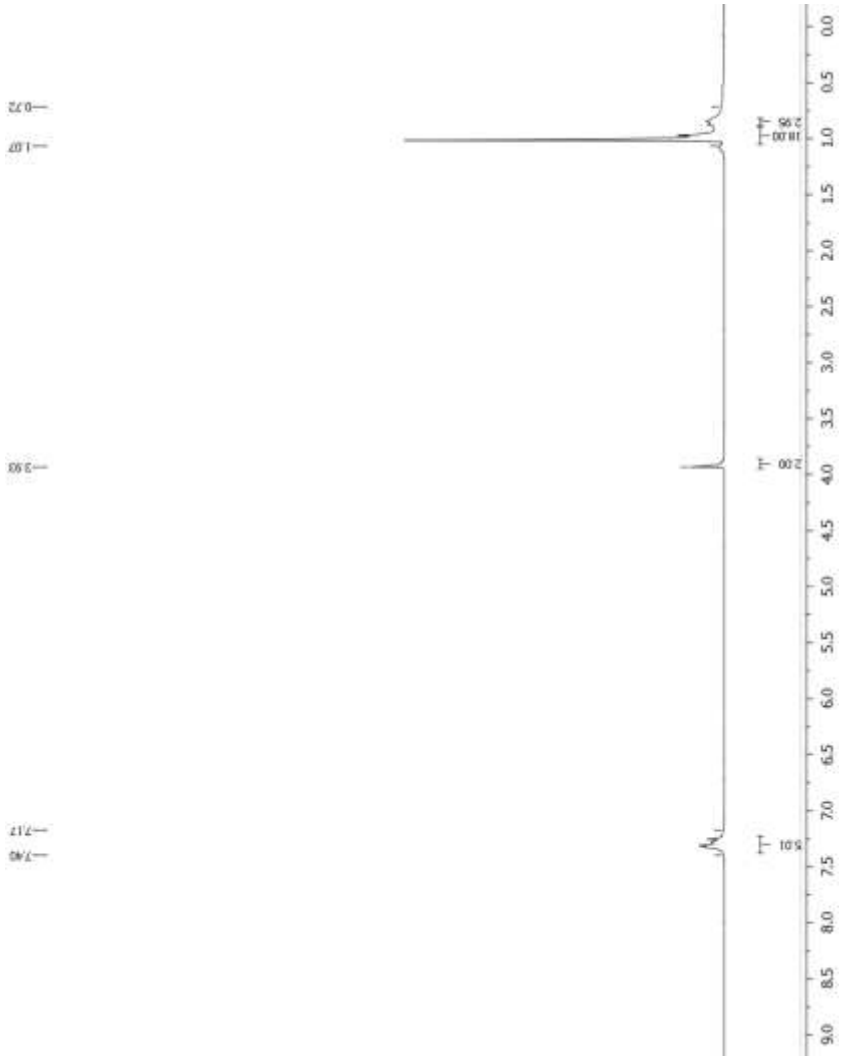

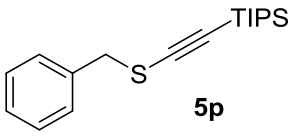

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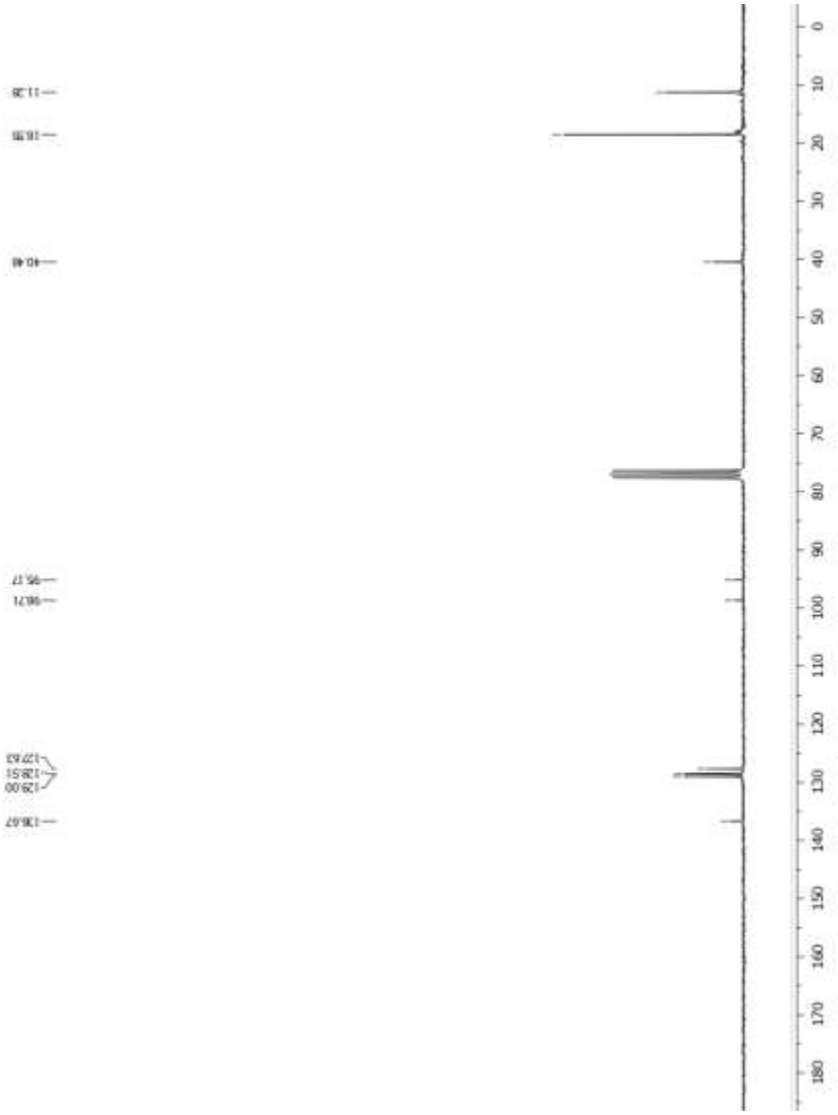

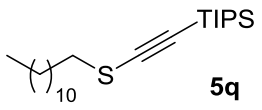

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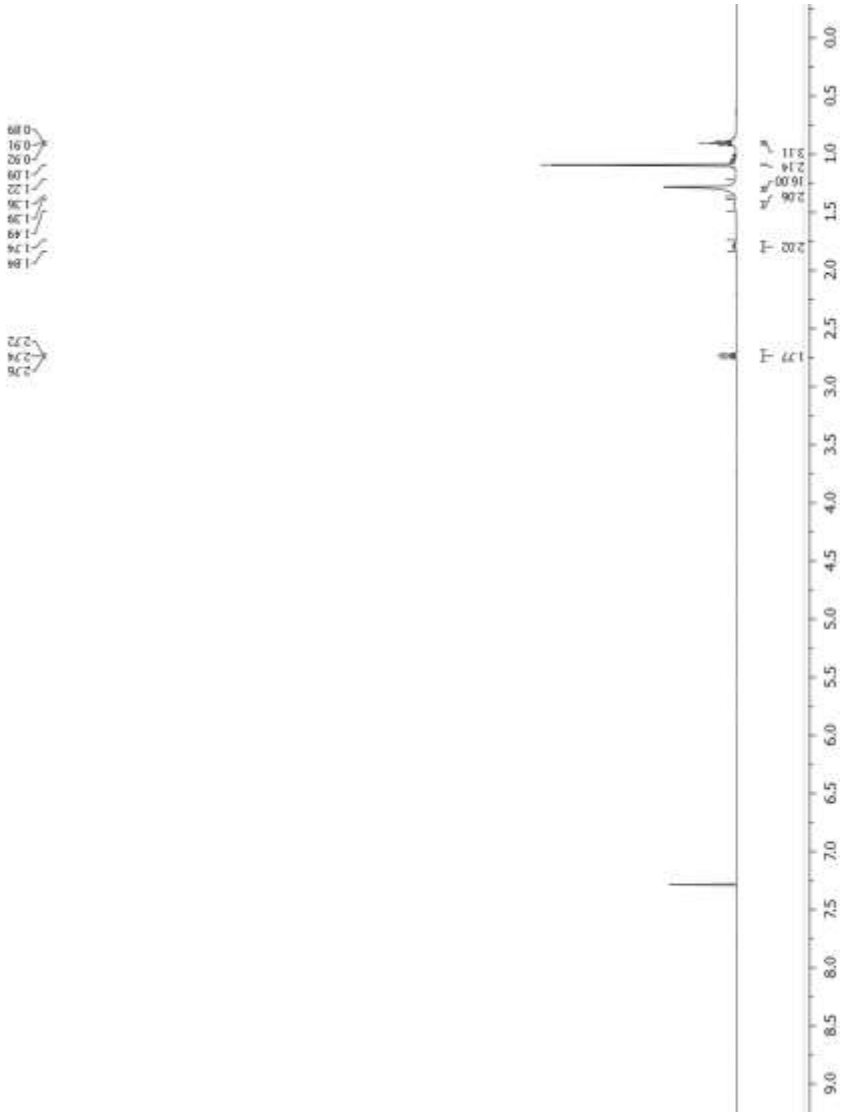

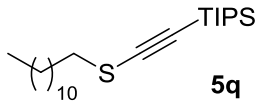

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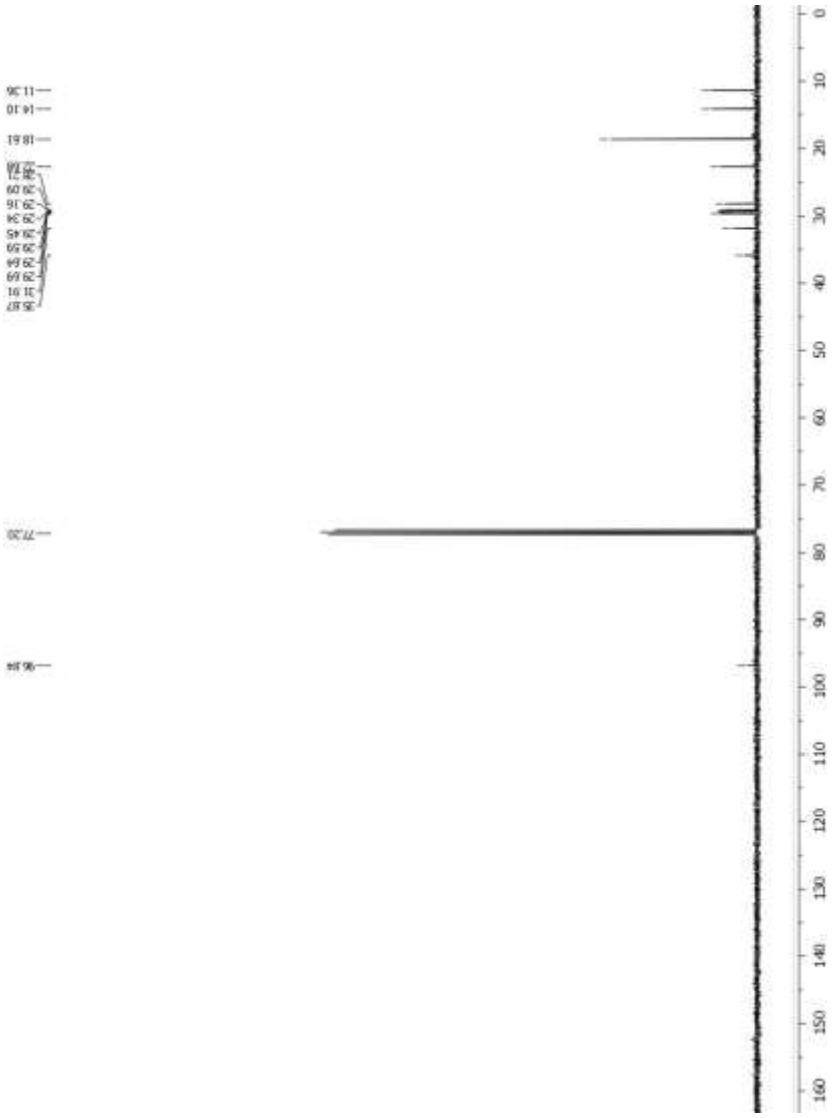

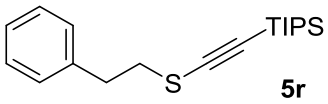

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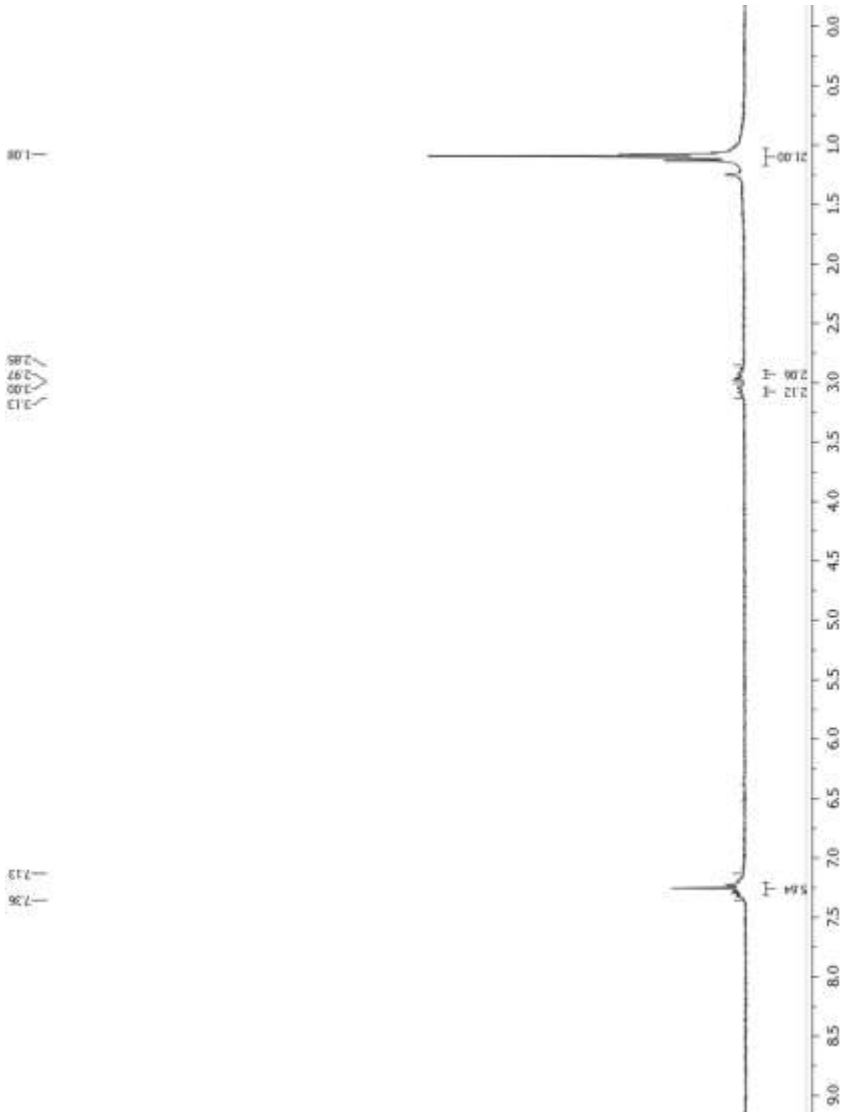

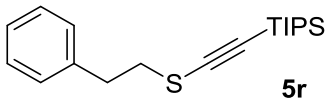

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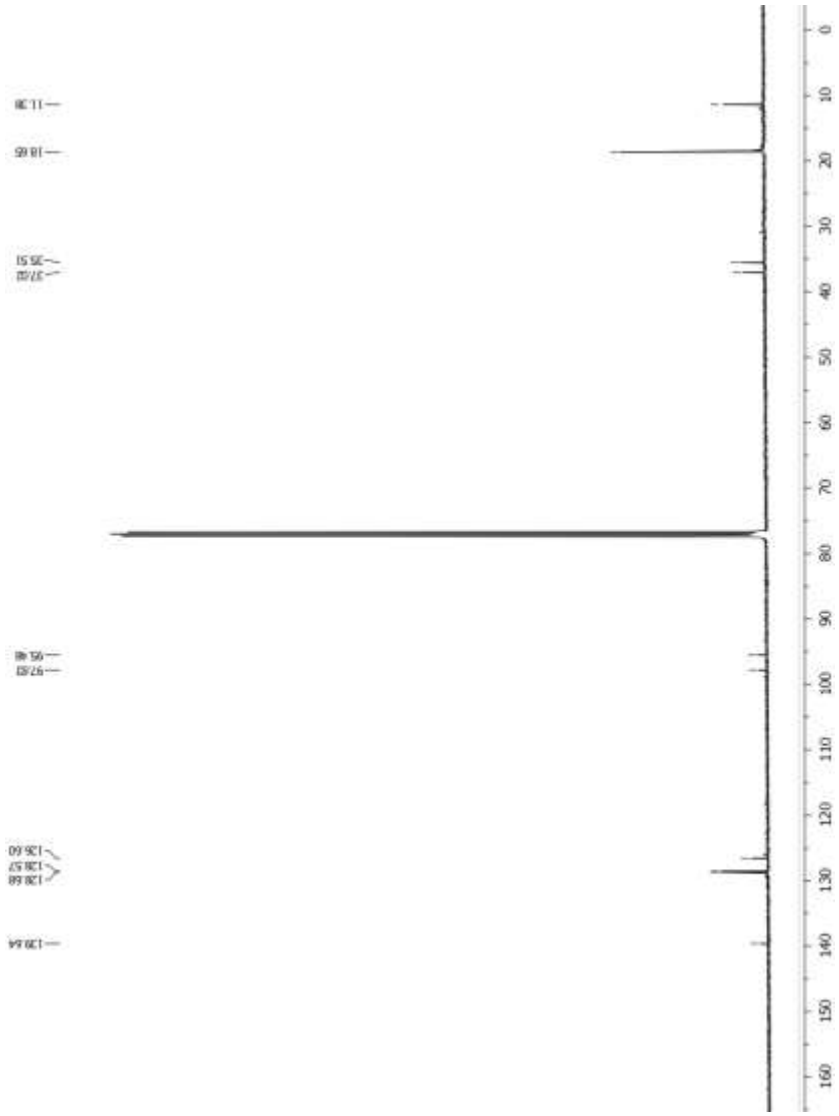

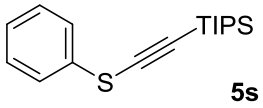

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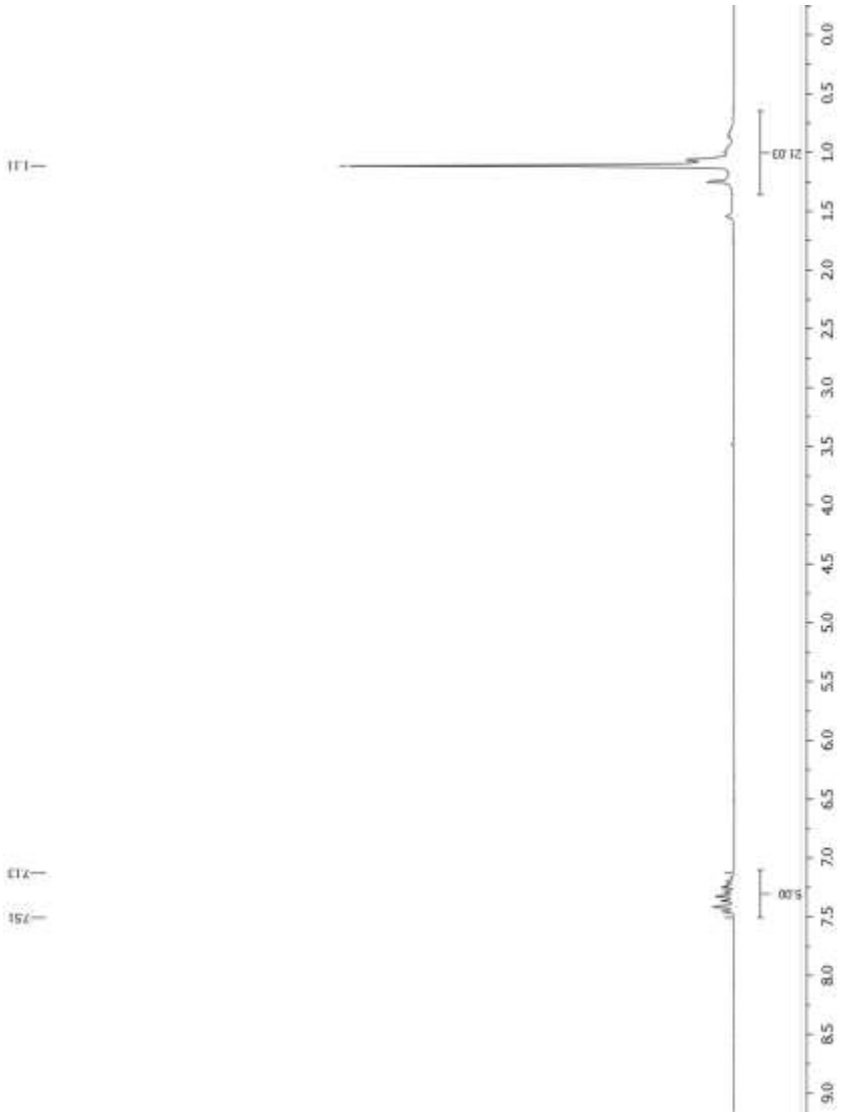

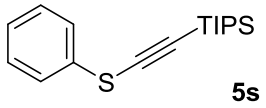

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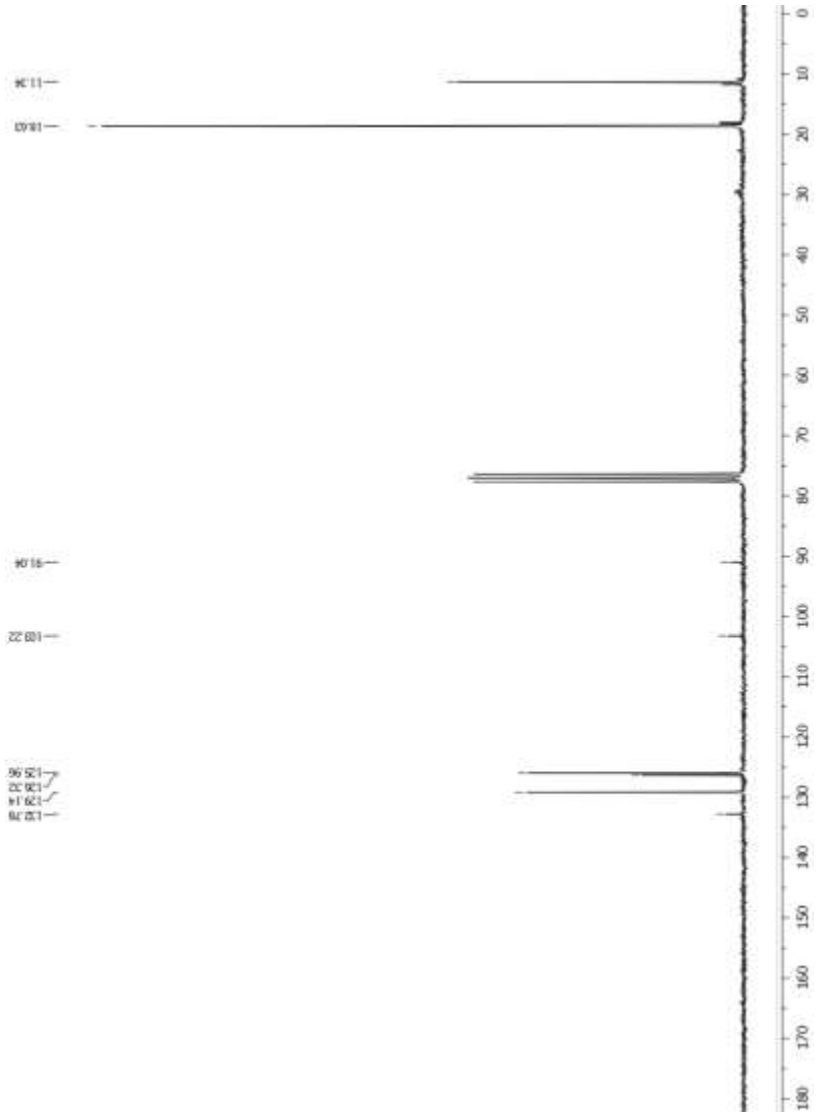

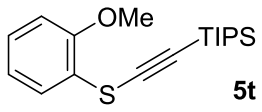

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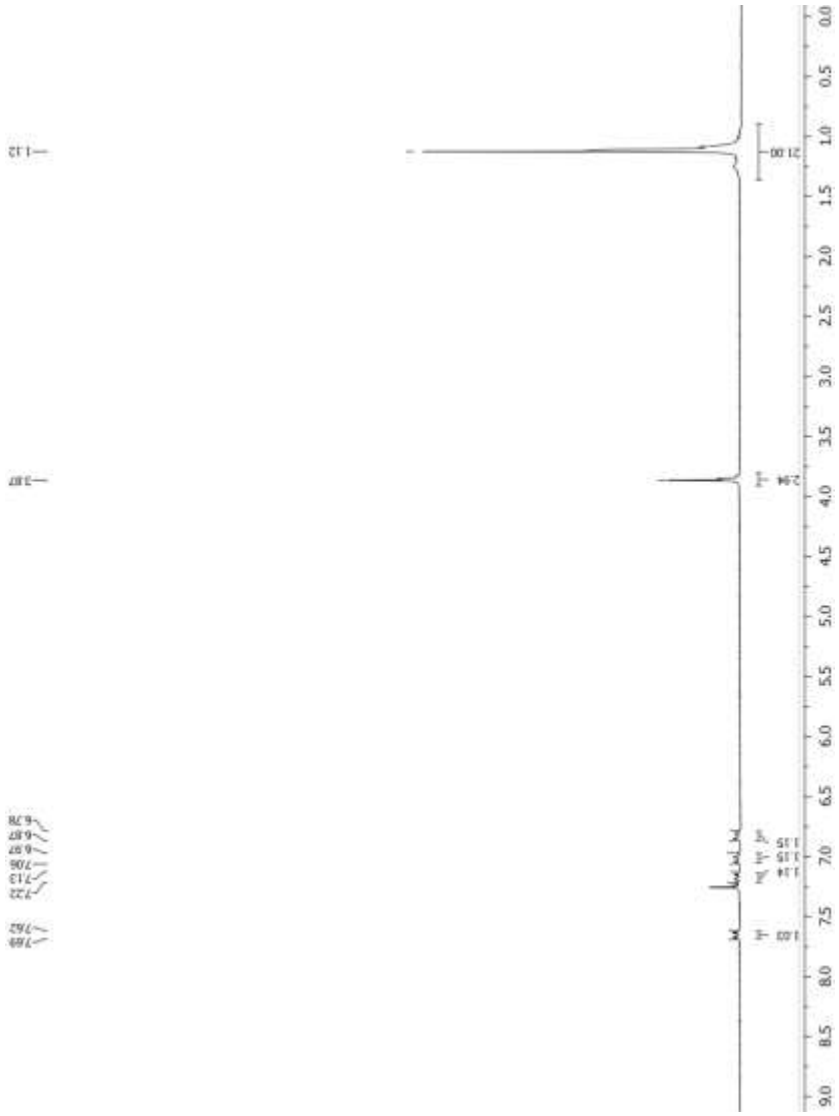

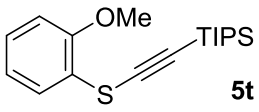

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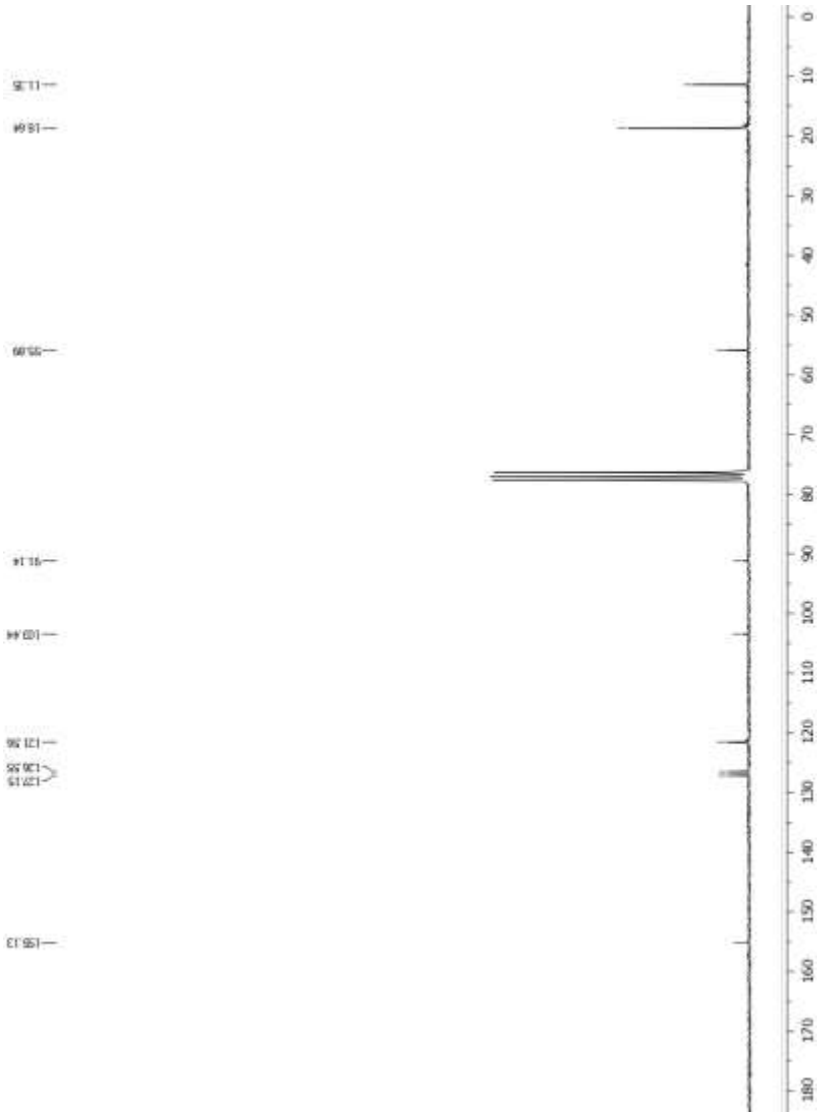

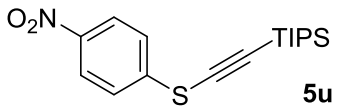

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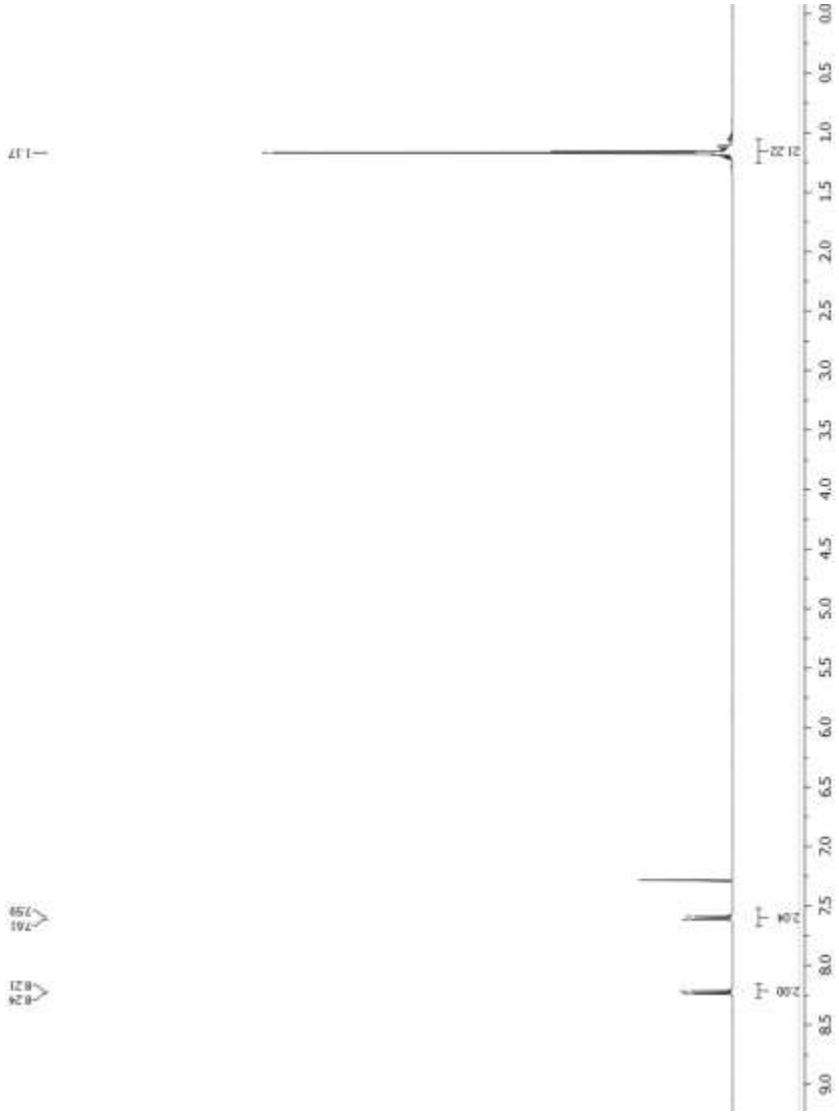

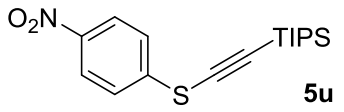

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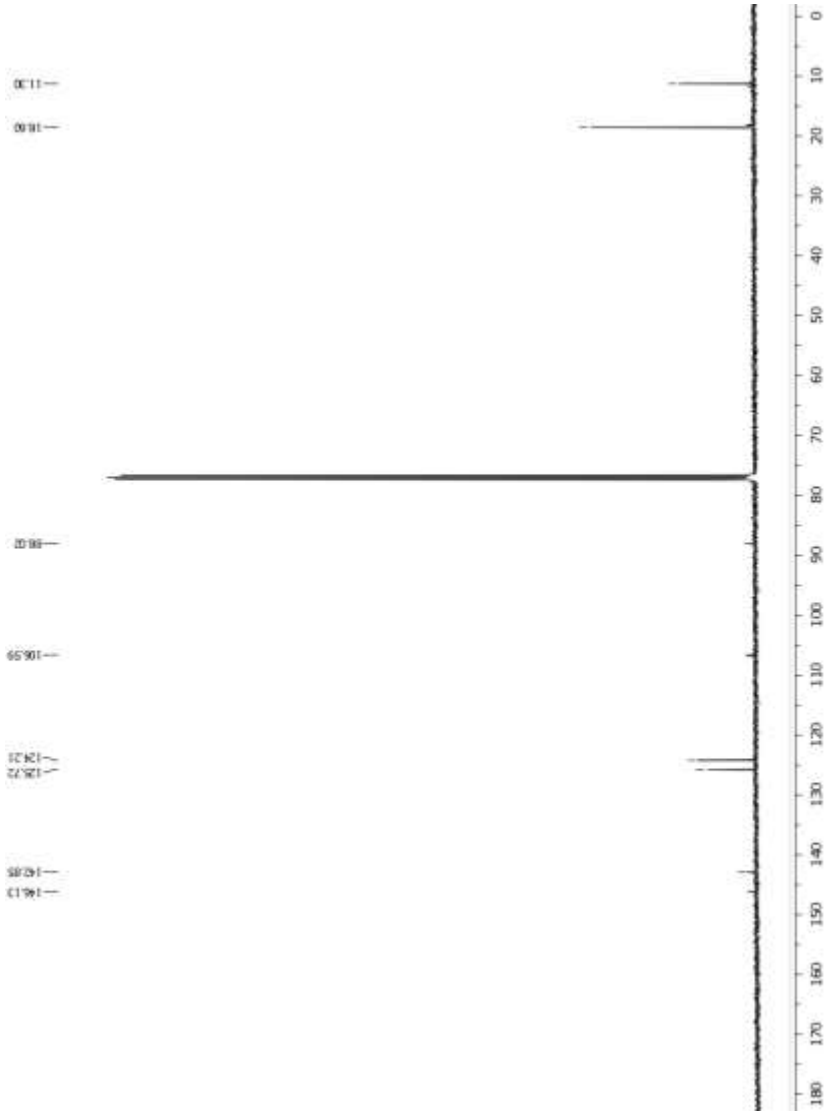

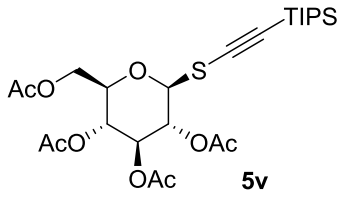

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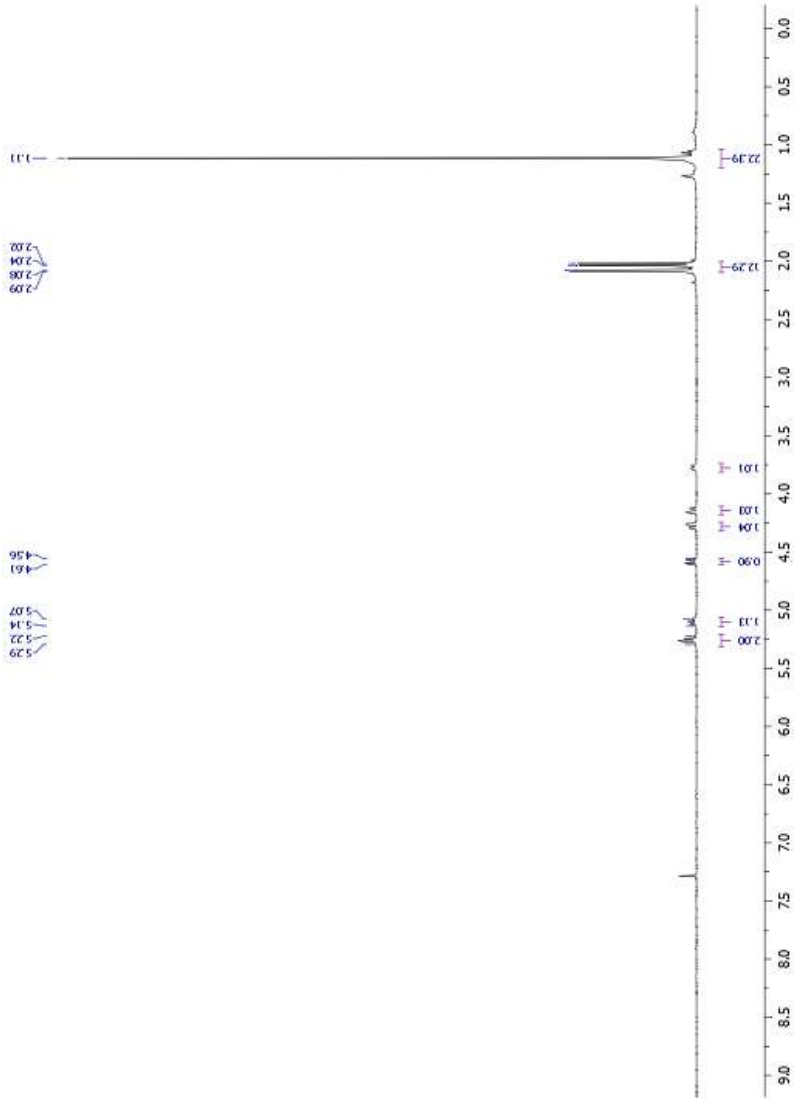

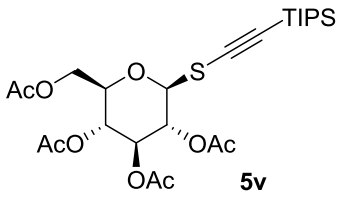

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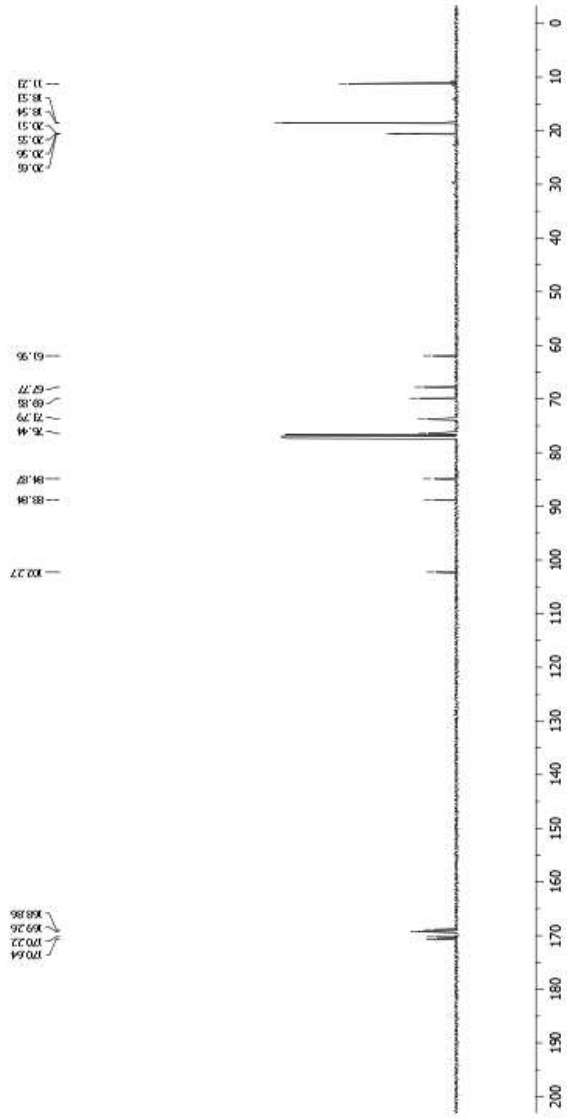

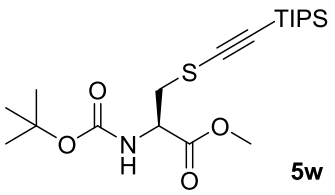

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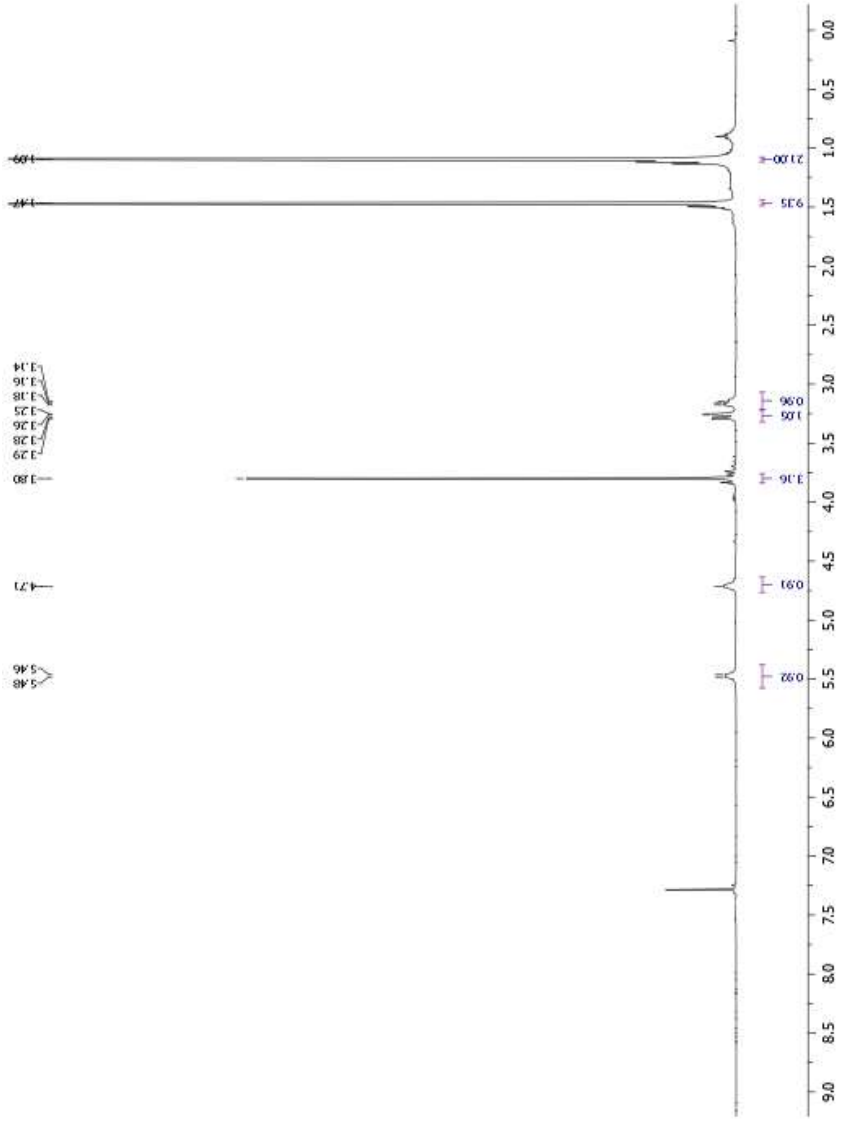

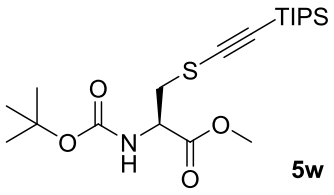
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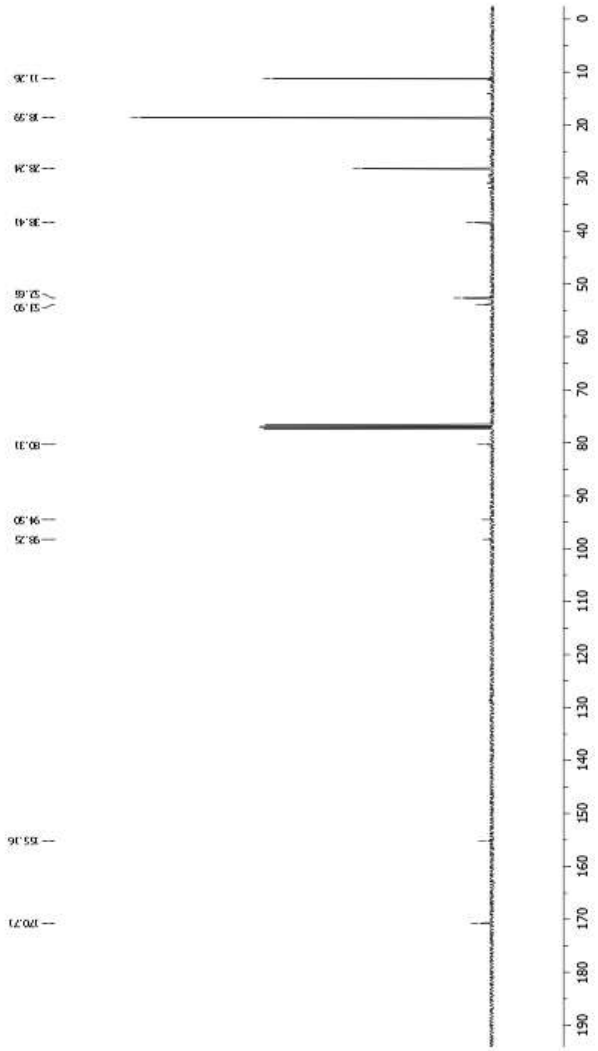
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