From Photoredox Catalysis to the Direct Excitation of EthynylBenziodoXolones: Accessing Alkynylated Quaternary Carbons from Alcohols via Oxalates

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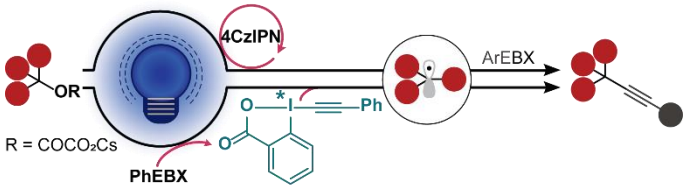
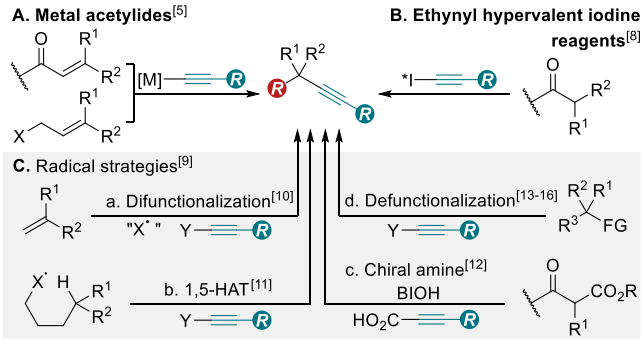


Abstract: EthynylBenziodoXolones (EBXs) are commonly used as radical traps in photocatalytic alkynylations. Herein, we report their application in two complementary deoxygenation strategies allowing the synthesis of valuable alkynylated all-carbon quaternary centers from tertiary alcohols via stable oxalate salts. Our first approach involves a photocatalytic process using 4CzIPN as an organic dye to promote oxidative degradation of the oxalate and EBXs to trap the formed radical. In our second approach, we demonstrate the direct photoexcitation of an EBX, which then acts as both oxidant and radical trap, alleviating the need for a photocatalyst in several EBX-mediated alkynylation processes.

Introduction

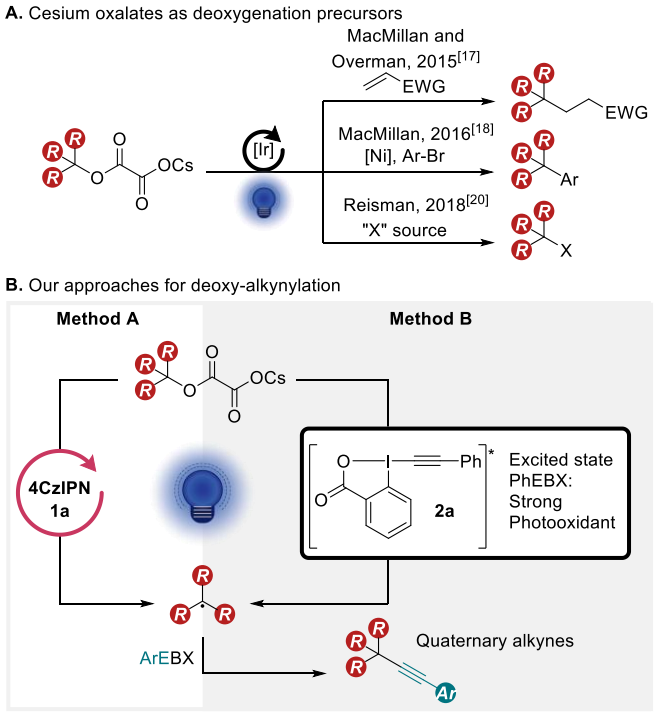
Alkynes have found broad applications in synthetic and medicinal chemistry, chemical biology, and materials science.[1] Triple C≡C bonds are stable yet offer a versatile panel of reactivity when activated either with transition metal or Lewis acid catalysts, allowing them to be easily converted to complex molecular structures. In medicinal chemistry and chemical biology, they can be used either as an inert and rigid connecting element or as a reactive unit.[2] Alkynes connected to all-carbon quaternary centers constitute an important subset, as they combine the versatility of transformations inherent to triple bonds with the challenge of constructing highly substituted compounds. They have therefore found numerous applications in total synthesis of complex natural products such as (+)-lactacystin, (-)-rhazinilam and (±)-grandisol.[3] They have also shown unique bioactivity in medicinal chemistry.[4] Unfortunately, accessing such scaffolds remains challenging. Alkyne-transfer reactions are attractive as usually more efficient than multi-step elaboration of the triple bond. The generation of alkynylated quaternary centers has been achieved by the addition of transition metal acetylides onto enones or activated allylic alcohols (Scheme 1A).[5] Metal acetylides have also enabled the alkynylation of diazo compounds, α-bromo esters and unactivated alkenes resulting in quaternary centers.[6] In addition to this approach, electrophilic alkynylation strategies with halogenides[7] and hypervalent iodine reagents (HIRs) have been used to functionalize activated carbonyl compounds (Scheme 1B).[8] These strategies rely on the specific reactivity of either electrophilic or nucleophilic functional groups, limiting the structural diversity of the products.



Scheme 1. State of the art: accessing alkynylated quaternary centers. A. Transition metal catalyzed approaches. B. Hypervalent iodine for electrophilic alkynylation. C. Generation of tertiary radicals for alkynylation.

Recently, the alkynylation of carbon radicals has emerged as an attractive complementary route for the formation of quaternary alkynylated centers.[9] Indeed, upon the generation of a highly reactive open-shell species, the limitations associated to steric hindrance that often hamper the formation of quaternary centers can be more easily overcome. Nowadays, a variety of mild methods can be used to generate radicals via thermal activation, transition metal catalysis or photomediated approaches (Scheme 1C). In this context, alkynylative alkene difunctionalization (a)[10] and 1,5-HAT (b)[11] strategies have been implemented successfully. Photoorganocatalysis has also enabled the formation of alkynylated quaternary centers from carbonyl compounds (c).[12] Another strategy for the alkynylation of tertiary radicals is to perform radical defunctionalization (d). Decarboxylation has been the most investigated,[13] but it still requires starting materials that themselves contain all-carbon quaternary centers. Alternatively, less abundant organoboron and organosulfur compounds can be used as precursors,[14] whereas C-N bond cleavage has been performed using azobis(isobutyronitrile) (AIBN) analogues.[15] In this context, starting from broadly available tertiary alcohols appears highly attractive, yet it has been only rarely reported. The only described photocatalytic deoxy-alkynylation exploited a reductive substrate activation strategy using unstable and non-isolable *N*-phthalimidoyl oxalates as precursors.[16]

Amidst the various activating groups used for photocatalytic deoxygenation, cesium oxalates appear as attractive starting materials. Not only are they bench stable, easily accessible, and easy to use, their side-products are gaseous CO_2 and a second cesium salt, as demonstrated by MacMillan and Overman in a deoxy-alkylation strategy (Scheme 2A).[17] They extended this approach to arylation,[18] and allylation,[19] whereas Reisman and co-workers developed deoxy-halogenation.[20] However, this approach has yet to be applied for alkynylation. In this context, we thought that EthynylBenziodoXolone reagents (EBXs) would be suitable radical traps using cesium oxalates as radical precursors. Indeed, EBX reagents have proven themselves to be efficient radical traps when combined with substrate oxidation.[9, 11a, 13c-d, 21]



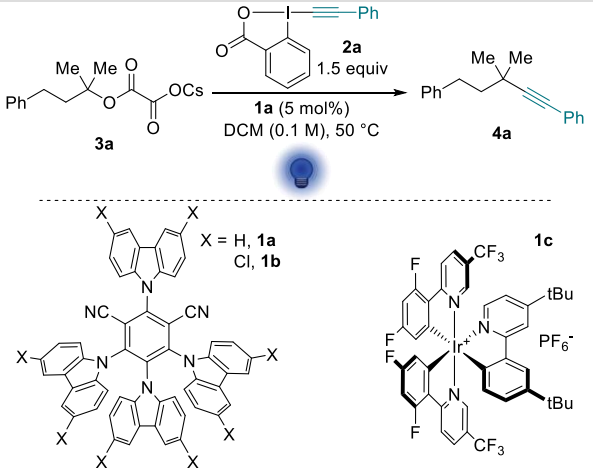
Scheme 2. A. Reported cesium oxalates-based transformations under photoredox catalysis. B. This work: Dual approach for photomediated deoxy-alkynylation: metal-free photocatalysis (Method A) vs excited state EBXs as photooxidants (Method B).

Herein, we report the use of the photoorganocatalyst 4CzIPN (2,4,5,6-tetrakis(9H-carbazol-9-yl) isophthalonitrile, **1a**) for the conversion of cesium oxalates to a variety of arylalkynes under visible light irradiation (Scheme 2B, Method A). During our studies, we discovered that the EBX reagent was undergoing photoactivation leading also to deoxy-alkynylation. A variety of HIRs have been reported to undergo excitation through spin forbidden transitions under visible light activation,[22] but, to the best of our knowledge, this activation mode has never been reported for EBXs. We now report that the excited state PhEBX* (**2a***) of PhEBX (**2a**) can be used as a photooxidant to perform a photocatalyst-free deoxy-alkynylation of cesium oxalates. Preliminary results indicate that the approach can be extended to other photomediated alkynylations (Scheme 2B, Method B).

Results and Discussion

Photocatalyst mediated deoxy-alkynylation. We started our investigation of the metal-free photocatalytic approach using the cesium oxalate **3a** as model substrate (Table 1). In presence of 5 mol% of 4CzIPN (**1a**) ($E_{1/2}$(**1a***/**1a**$^-$) = +1.35 V vs SCE),[21b] under light irradiation at 440 nm with 1.5 equivalent of PhEBX (**2a**) in DCM, the desired product (**4a**) was observed in 75% NMR yield (94% based on remaining starting material, entry 1). Even if the starting material and reagent were not fully soluble in DCM, using more polar solvents such as DMSO, MeCN, or a mixture of DME/DMF with 10 equivalents H_2O,[17] led to lower yields (entry 2, see Supporting Information for details).

Table 1. Optimization of the photocatalyzed method (method A).



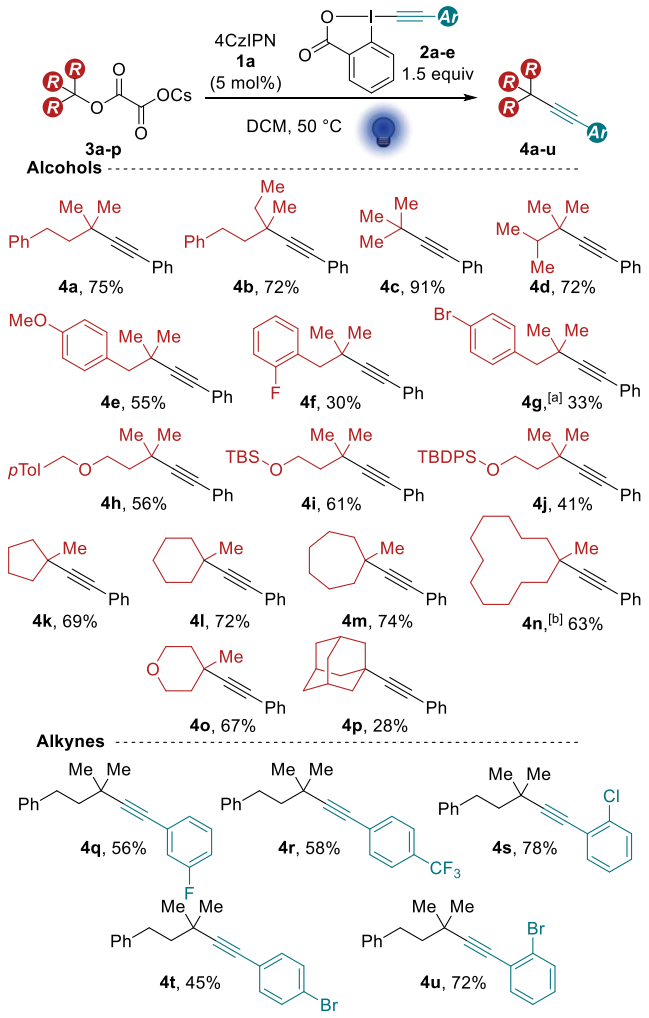
Entry[a]	Changes to the standard conditions	Yield[b]
1	None	75
2	other solvents[c]	<70
3	2.5 equiv **2a**	75
4	1.0 equiv **2a**	64
5	4ClCzIPN **1b**	75
6	**1c**	50
7	BIOAc **5a** (30 mol%)	60
8	no light[d]	0
9	no PC	50

[a] **3a** (0.1 mmol), **2a** (1.5 equiv) and **1a** (5 mol%) were dissolved in solvent [**3a**] = 0.1 M and irradiated with two lamps (40 W, 440 nm) for 18 h. [b] ^{1}H NMR Yield was determined using 1 equiv of CH_2Br_2 as internal standard. [c] DMSO, MeCN, DME/DMF + 10 equiv H_2O. [d] Reaction was performed with and without PC.

With a larger excess of PhEBX (**2a**) (2.5 equiv), the same yield was obtained, whereas **4a** was formed in only 64% yield when using one equivalent of **2a** (entries 3 and 4). When the reaction was carried out in presence of the more oxidizing photocatalyst 4ClCzIPN (**1b**, $E_{1/2}$(**1b***/**1b**$^-$) = +1.49 V vs SCE),[21b] we did not observe any improvement (entry 5). In turn, using the less oxidizing iridium photocatalyst [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ (**1c**, $E_{1/2}$(**1c***/**1c**$^-$) = +1.21 V vs SCE)[13d] led to less product formation

(entry 6). A range of other photocatalysts were examined but gave the product in lower yields (see Supporting Information). Furthermore, we investigated the use of benziodoxolone acetate (BIOAc, **5a**) as additive, as it was previously shown to improve the yield in photo-mediated alkynylation processes involving EBX reagents.[21d] In our case however, it led to a considerable drop in yield (entry 7). When the reaction was run with the exclusion of light, no product was formed, and NMR analysis showed no degradation of the starting material (entry 8). Surprisingly, when the reaction was performed under irradiation without the addition of 4CzIPN (**1a**), 50% yield of **4a** was still obtained (entry 9). Nevertheless, we decided to use the photocatalytic conditions to investigate the scope of the reaction, since they provided the desired product in higher yield.

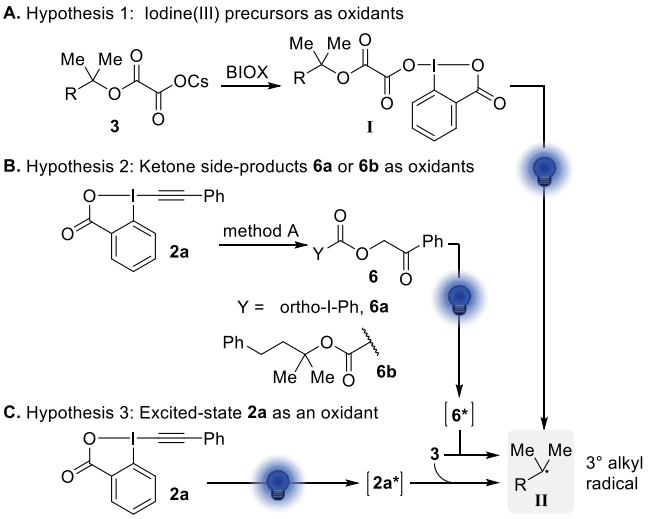
With the optimized reaction conditions established, we proceeded to explore the scope of cesium oxalates. The model substrate afforded the desired alkyne **4a** in 75% yield (Scheme 3).



Scheme 3. Scope Method A. Reactions were performed on 0.3 mmol scale using the corresponding cesium oxalate **3a-p** (1 equiv) and ArEBX **2a-e** (1.5 equiv) with 4CzIPN (**1a**, 5 mol%) in DCM (0.1 M). [a] Performed on 0.2 mmol scale. [b] Reaction was performed on 0.24 mmol scale with 1.9 equiv of **2a.**

When changing one of the methyl groups to an ethyl group the reaction afforded **4b** in 72% yield. The *tert*-butyl radical gave **4c** in 91% yield and bulkier **4d** was obtained in 72% yield. Homobenzylic scaffolds yielded compounds **4e-g** in 30 to 55% yield. A variety of benzyl and silyl protected alcohols afforded alkynes **4h-j** in up to 61% yield. Cyclic alcohols of variable ring sizes were investigated affording **4k-n** in 63-78% yield. A tetrahydropyran substrate was successfully converted to the corresponding alkyne **4o** in 67% yield. The adamantyl alkyne **4p** was obtained with an expectable drop in yield when considering the known complication with bridged carbon radicals.[23] Having established the scope of alcohols, we turned to explore different ArEBX reagents. Electron-poor fluorinated reagents afforded the corresponding alkynes **4q** and **4r** in 56% and 58% yield. Chlorinated and brominated aryl alkynes **4s**, **4t** and **4u** were obtained in 45 to 78% yield. Silyl- and alkyl- EBX reagents gave the product in only very low yield.

Investigation of the photoactive species in the photocatalyst-free transformation. With the photocatalyst promoted transformation established, we attempted to gain a better understanding of the photocatalyst-free alkynylation we had observed with PhEBX (**2a**) (Table 1, entry 9). We envisaged a variety of mechanistic hypotheses that could account for the oxidation of the starting material even in absence of a photocatalyst (Scheme 4). First, we considered that a residual HIR(III) species BIOX from the PhEBX synthesis could be the oxidant (Scheme 4A, hypothesis 1). Based on literature precedence, the formation of a covalent adduct **I** between the oxalate and the HIR would be expected.[12,24] Under visible light irradiation, homolytic cleavage of the hypervalent iodine I^{III}-O would form the O-centered radical, which then undergoes double decarboxylation to give the tertiary radical **II**.



Scheme 4. Alternative mechanisms for the oxidation of cesium oxalate **3** to give tertiary radical **II**. A. Hypothesis 1: Iodine(III) precursors as oxidants. B. Hypothesis 2: Ketone side products **6a** and **6b** as oxidants. C. Hypothesis 3: Excited state of **2a** as an oxidant.

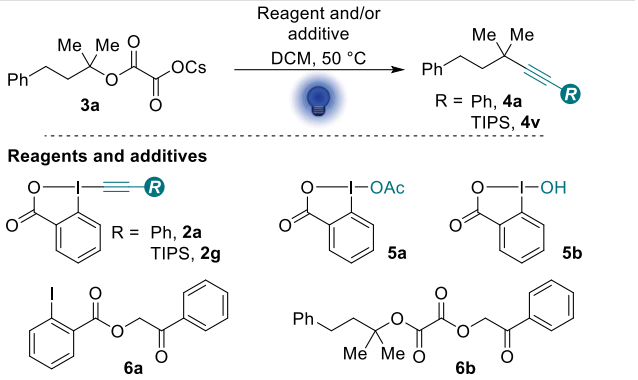
As a second hypothesis, side-products formed during the reaction could act as photooxidants (Scheme 4B, hypothesis 2). Indeed, two aromatic ketones **6a** and **6b** were observed as side products, resulting from degradation PhEBX (**2a**) with or without addition of the oxalate starting material **3a**.[25] Based on the broad use of aromatic ketones as photosensitizers,[26] we hypothesized that **6a**

or **6b** may be photoactive specie under our reaction conditions and potential oxidants in the excited state to generate **II**.

Finally, PhEBX (**2a**) may be undergoing direct photoexcitation (Scheme 4C, hypothesis 3). Surprisingly, we found no reference in the literature for such a process. However, previous studies were performed with less intensive irradiation and/or at different wavelengths,[10d-e, 11c, 13a,c-d, 14a, 15] which may explain why this activation process has yet to be reported. Here, we speculated that photoexcited **2a*** would be more oxidizing than the ground state **2a** and would generate the O-centered radical through a single electron transfer (SET), leading to **II** after fragmentation.

In order to gain support for one of the proposed alternatives, further experiments were performed (Table 2). Interestingly, when TIPS-EBX (TIPS = tri*iso*propylsilyl, **2g**) was used as an alkynylation reagent in absence of photocatalyst, no product was observed and both **2g** and the cesium oxalate **3a** remained untouched (Table 2, entry 1). **2g** has been reported to not undergo direct excitation at 400 nm,[27] but is known to work as a radical trap.[13c-d] When we performed the reaction with **1a** and **2g** based on the conditions for method A, we obtained 25% of alkynylation product **4v** confirming that it is able to react with the tertiary radical formed from cesium oxalates, even if the overall reaction is not very efficient (entry 2). This result confirmed that the aryl substituent on PhEBX (**2a**) was required for the reaction to proceed in absence of photocatalyst, but it still did not allow us to distinguish between our three hypotheses. Concerning hypothesis 1, BIOAc (**5a**) and BIOH (**5b**) have been shown as competent reagents to generate such covalent intermediates.[12, 24] Especially **5b** could be present in small amounts as impurity in PhEBX (**2a**), as it is used for its synthesis. However, when the reaction was performed with 0.2 equivalents of either additive, nearly no product formation was obtained (entries 3 and 4). Even with 1.5 equivalents of additive in absence of TIPS-EBX (**2g**), very little degradation of the starting material was observed upon irradiation (entries 5 and 6). This indicated that, under our reaction conditions, this pathway is not operative for generating the desired tertiary radical. We then turned to hypothesis 2: the side product ketones **6a** and **6b** as photooxidants. We observed the formation of **6a** and **6b** without the photocatalyst under light irradiation. In addition, when the reaction was performed in the dark at 50 °C, the conversion of **2a** to **6a** (0.45 equiv) and **6b** (0.2 equiv) could be observed by ^{1}H NMR. This suggests a thermal pathway for the formation of **6a** and **6b**. These ketones could result from the formal hydration of **2a** and the incorporation of a nucleophile (iodobenzoate or oxalate). We first explored the possibility of **6a** as a competent photocatalyst and performed the alkynylation with 0.2 equivalents of **6a** and TIPS-EBX **2g** as reagent (entry 7). Only traces of alkynylation product were observed. In presence of one equivalent of **6a**, no degradation of the cesium oxalate or **6a** was observed under irradiation (entry 8). These results showed that **6a** was not able to catalyze the alkynylation process. **6b** was subjected to the same control experiments with no notable alkynylation products detected (See Supporting Information).[28] Finally, we turned to hypothesis 3 and performed the alkynylation with 0.2 equivalents of PhEBX (**2a**) and 1.5 equivalents of TIPS-EBX (**2g**). In this case, 20% conversion of the cesium salt was observed with 8-13% deoxy-alkynylation with phenyl and TIPS alkyne products **4a** and **4v** formed in a 1:1 ratio based on ^{1}H NMR analysis (entry 9), giving strong support for **2a** acting as photooxidant.

Table 2. Optimization of the photocatalyzed method (method A).

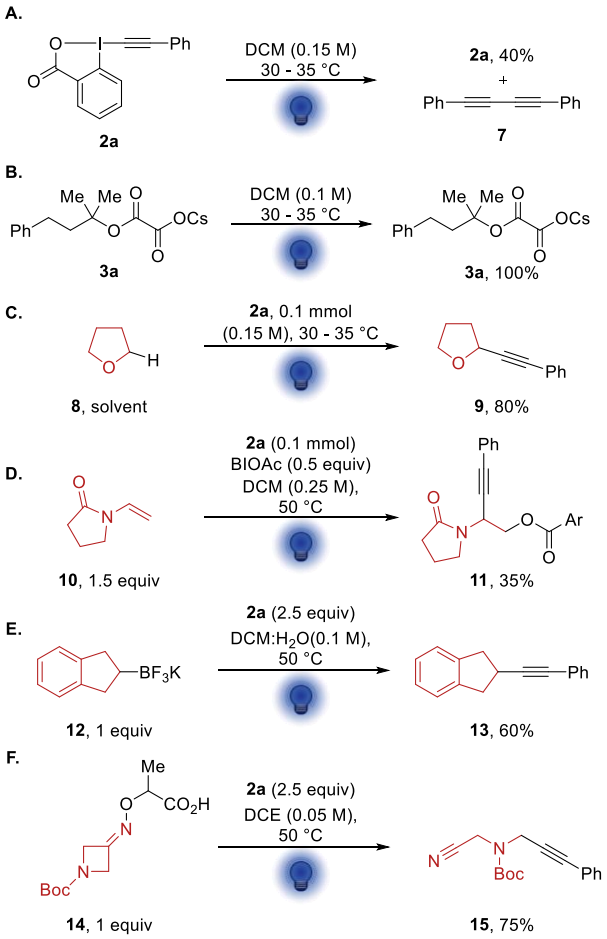


Entry[a]	Reagent	Additive (equiv)	Residual **3a** (%)	Yield[b] (%)
1	**2g**	-	100	nd
2	**2g**	**1a** (0.05)	30	25
3	**2g**	**5a** (0.2)	92	5
4	**2g**	**5b** (0.2)	92	5
5	**-**	**5a** (1.5)	90	-
6	**-**	**5b** (1.5)	100	-
7	**2g**	**6a** (0.2)	98	2
8	**-**	**6a** (1.0)	100	-
9	**2g**	**2a** (0.2)	80	8-13[c]

[a] **3a** (0.1 mmol), **2g** (1.5 equiv) and the additive were dissolved in DCM [**3a**] = 0.1 M and irradiated with two lamps (40 W, 440 nm) for 18 h. [b] ^{1}H NMR yield was determined using 1 equiv of CH_2Br_2 as internal standard. [c] Overall yield of deoxy-alkynylation, **4a**:**4v** = 1:1.

In addition to these results, the irradiation of PhEBX (**2a**) in the absence of cesium salt led also to non-negligible degradation of **2a** with significant formation of diyne **7** (Scheme 5A),[29] whereas the cesium salt **3a** did not show any degradation when irradiated separately (Scheme 5B). Interestingly, when we subjected **2a** to irradiation in THF (**8**) instead of DCM, we obtained 80% of C-H alkynylation product **9** demonstrating that the direct excitation of **2a** can lead to the well-established radical C-H functionalization of ethers (Scheme 5C).[27, 30] We suspect that **2a*** or one of its degradation products can perform a HAT to initiate the α-oxo alkynylation of THF (**8**).[31] In addition to this HAT transformation, we wondered if **2a*** could also act as a single electron oxidant in other types of EBX-mediated alkynylations beside deoxy-alkynylation. We were pleased to see that the enamide difunctionalization previously developed in our group[21d] gave 35% yield of the oxy-alkynylated product **11** (Scheme 5D). Furthermore, the deboronative alkynylation reported by Chen and co-workers[14a] could be also performed using 2.5 equiv of PhEBX (**2a**) in absence of photocatalyst and the additive BIOH (**5b**) (Scheme 5E). The alkyne **13** was obtained in 60% NMR yield. Finally, the decarboxylative fragmentation of oximes previously developed in our group[21b] also worked well with 75% NMR yield of fragmentation product **15** (Scheme 5F). It is important to note that the control experiments performed in absence of photocatalyst in the original reports of the reactions presented in Scheme 5D-F showed no product formation. This further

highlights that the light source used in our work (two 40 W Kessil lamps with irradiation centered around 440 nm) is essential for the observed direct activation of PhEBX (**2a**).



Scheme 5. Control experiments corroborating the photoactivation of PhEBX (**2a**) and its potential as a photooxidant. The reactions were performed on 0.1 mmol or 0.2 mmol scale and yields were determined by ^{1}H NMR by addition of 1 equiv of CH_2Br_2 as an internal standard. A. Photodegradation of **2a**. B. Photostability of **3a**. C. Photocatalyst-free THF (**8**) alkynylation. D. Photocatalyst-free oxyalkynylation of enamide **10**. E. Photocatalyst-free deboronative alkynylation of **12**. F. Photocatalyst-free decarboxylative fragmentation ring-opening alkynylation of oxime **14**.

With these results in hand, we turned to UV-Vis absorption and fluorescence spectroscopy to have further support for the photoactivity of PhEBX (**2a**) under our reaction conditions (Figure 1). We observed absorption until 460 nm (plain blue line) and fluorescence at 485 nm (dashed red line) (Figure 1A). Fluorescence excitation spectroscopy (dotted grey line) showed that irradiation of **2a** from 300 nm to 440 nm was responsible for the emission at 485 nm. Specifically, we observed two excitation bands ($\lambda_{max,1}$ = 380 nm, $\lambda_{max,2}$ = 430 nm) confirming the possibility of the photoexcitation of **2a** with a broad band light source with emission centered around 440 nm. To identify the molar extinction coefficient ε of **2a**, we performed a Beer-Lambert linear regression at 420 nm and 440 nm providing ε_{420nm} = 0.54 L.mol^{-1}.cm^{-1} and ε_{440nm} = 0.33 L.mol^{-1}.cm^{-1} (Figure 1B).[32] This is coherent with the weak absorption we observe in the 390 nm – 460 nm range, even at high concentrations. These low molar extinction coefficients suggest that the absorption at 420 nm and 440 nm could result from a spin forbidden electronic transition.[33]

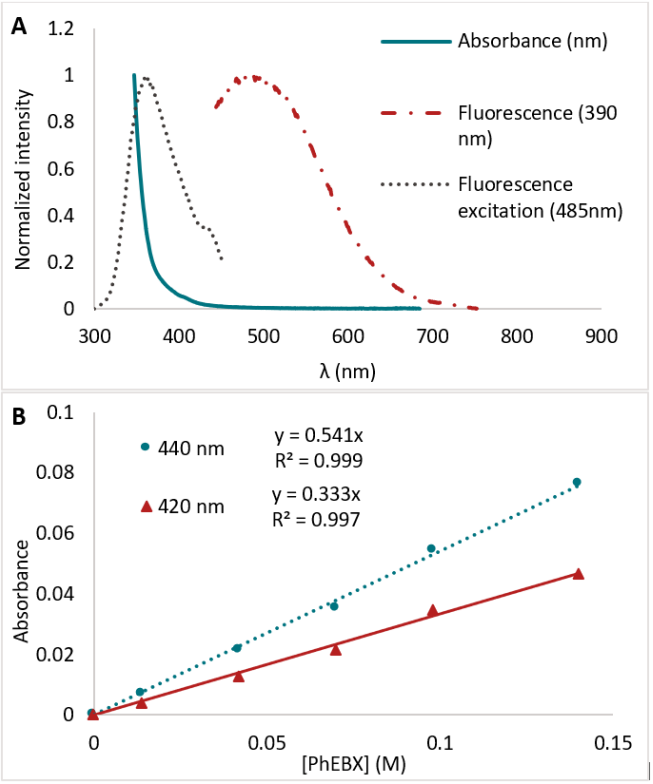


Figure 1. A. Normalized absorption of **2a** (blue plain line), emission (red dashed line, excitation at λ = 390 nm, λ_{max} = 485 nm) and fluorescence excitation (grey dotted line, for emission at 485 nm, λ_{max} = 362 nm). B. Beer Lambert linear regression for 420 nm (red plain line) and 440 nm (blue dotted line). A = εl[**2a**], l = 1 cm), ε_{420nm} = 0.54 L.mol^{-1}.cm^{-1} and $\varepsilon_{440\ nm}$ = 0.33 L.mol^{-1}.cm^{-1}.

Having identified that PhEBX (**2a**) was photoactive and absorbing under our reaction conditions, it was important to estimate the strength of **2a** as an oxidant in the excited state, in particular when considering the broad scope of substrates that could be oxidized with **2a***. First, cyclic voltammetry allowed us to determine the redox potential of the ground state $E_{1/2}$(**2a**/**2a**$^{\bullet-}$) = -0.87 V vs SCE (Figure 2). We could then calculate an estimate of the excited state $E_{1/2}$(**2a***/**2a**$^{\bullet-}$) = +1.8 V vs SCE,[34] thus confirming the thermodynamic feasibility of the SET oxidation of the substrate by the excited state **2a*** ($E_{1/2}$(oxalate$^{\bullet}$/oxalate^{-}) = 1.3 V vs SCE).[17] It is also strong enough to oxidize enamide **10**, boronate **12** and oxime **14** ($E_{1/2}$(**10**$^{\bullet+}$/**10**) ≈ +1.3 V vs SCE,[21d] $E_{1/2}$(**12**$^{\bullet+}$/**12**) ≈ +1.5 V vs SCE,[35] $E_{1/2}$(**14**$^{\bullet+}$/**14**) ≈ +1.5 V vs SCE for the corresponding potassium salt).[21b] In addition, the excited state **2a*** is a stronger oxidant than the excited state of 4CzIPN (**1a**) ($E_{1/2}$(**1a***/**1a**$^{\bullet-}$) = 1.35 V vs SCE).

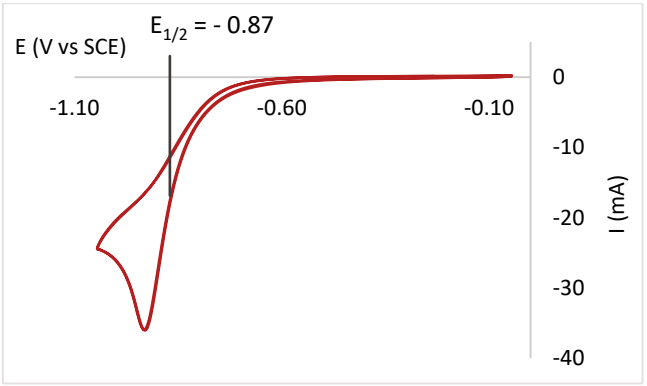


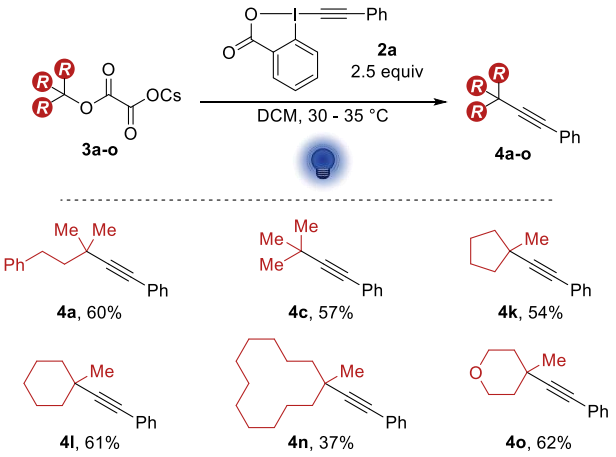
Figure 2. Cyclic voltammogram of **2a** (50 mV.s^{-1}, 1.0 µM in MeCN).

Excited-state EBX mediated deoxy-alkynylation. With PhEBX (**2a**) acting both as photooxidant and radical trap, a larger excess would be needed to promote the alkynylation. Furthermore, the formation of ketones **6a** and **6b** proceeds thermally suggesting that cooling the reaction media would be beneficial to avoid side reactions. Indeed, using 2.5 equivalents of PhEBX (**2a**), cooling the reaction media to 30 – 35 °C, and extending the reaction time to 24 h gave alkyne **4a** in 67% NMR yield on 0.1 mmol scale (79% based on remaining starting material, Scheme 6). In addition, the properties of the light source were important, as irradiation at lower wavelengths and intensities gave poorer results. Further fine-tuning of the reaction conditions (time, solvent, concentration, and additives) did not improve the yield (See Supporting Information).

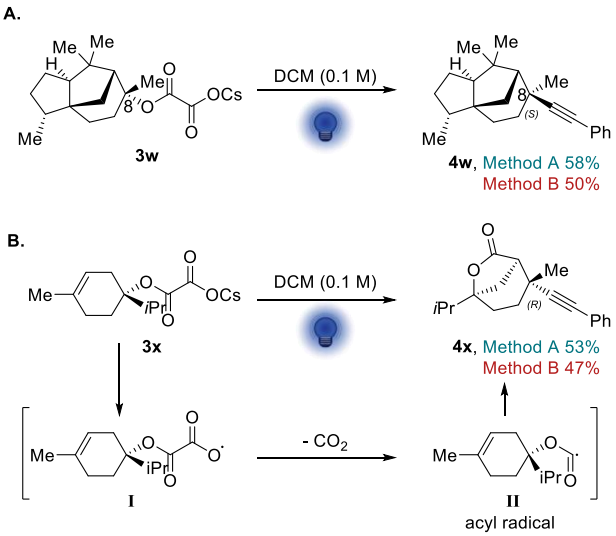
Scheme 6. Optimized reaction conditions for the direct excitation of PhEBX (**2a**) for deoxy-alkynylation of **3a** (Method B).

With these conditions in hand, we briefly examined the generality of the direct photoactivation approach with a few selected substrates on 0.3 mmol scale (Scheme 7). To our delight, we could obtain a variety of alkynylated products in only slightly lower yields when compared to the photocatalytic method A. Acyclic alkynes **4a** and **4c** could be obtained in 60 and 57% yield. Cyclic scaffolds **4k**, **4l** and **4n** were isolated in 37-61% yield. Finally, THP derivative **4o** was obtained in 62% yield.

Alkynylation of Natural Products. Finally, we were delighted to see that both methods A and B could be applied for the diastereoselective deoxy-alkynylation of (-)-cedrol oxalate **3w** (Scheme 8A). Method A afforded alkyne **4w** in 58% yield and method B in 50%. Both methods provided products in over 20:1 diastereoselectivity based on NMR analysis. NOESY analysis supported that the isomer obtained is of (*S*) configuration at C_8. Interestingly, when (-)-terpinen-4-ol-derived oxalate **3x** was used, a different outcome was observed: the 5-exo-trig cyclization of the intermediate acyl radical **II** onto the double bond was observed followed by alkynylation of the formed tertiary carbon radical (Scheme 8B). Both methods resulted in the formation of product **4x** in 53% and 47% yield, respectively. This indicates that the decarboxylations are stepwise and that the acyl radical **II** formed from the oxalate radical after the release of CO_2 is long-lived enough to undergo cyclization before the second decarboxylation. The remotely alkynylated product **4x** was also obtained in over 20:1 diastereoselectivity.



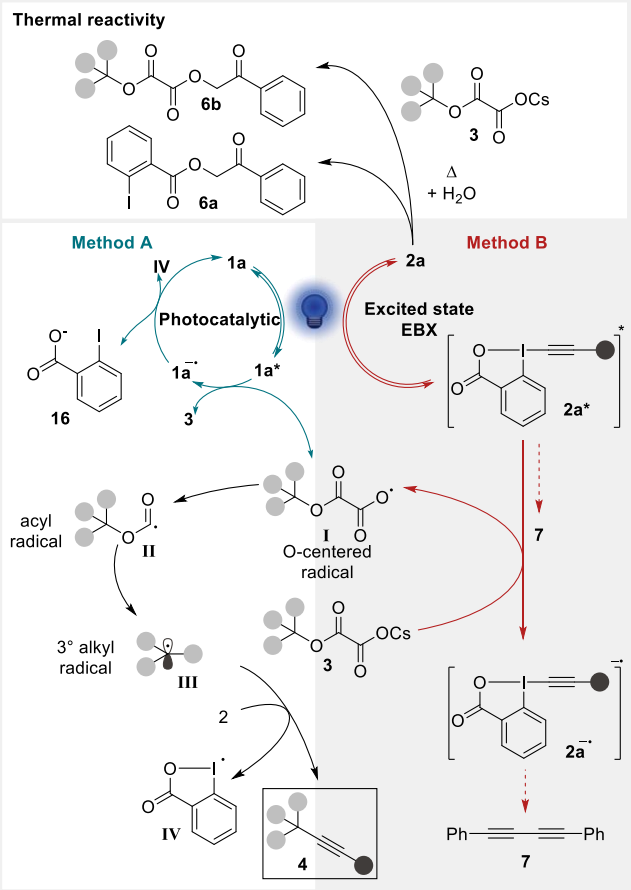
Scheme 7. Scope of Method B. Reactions were performed on 0.3 mmol scale using the corresponding cesium oxalate **3a-o** (1 equiv) and PhEBX **2a** (2.5 equiv) in DCM (0.1 M).



Scheme 8. Alkynylation of A. (-)-Cedrol oxalate **3w** and B. (-)-Terpinen-4-ol oxalate **3x**. Reactions were performed on 0.3 mmol scale under blue LED irradiation. Method A: **3w** or **3x** (1 equiv), **2a** (1.5 equiv), **1a** (5 mol%) in DCM (0.1 M), 50 °C. Method B: **3w** or **3x** (1 equiv), **2a** (2.5 equiv) in DCM (0.1 M).

Overall Mechanistic Proposal. With the results obtained in our work together with literature precedence,[17-20] we propose the following speculative mechanisms for our alkynylation methods (Scheme 9). First, in method A cesium oxalate **3** (for the *tert*-butyl oxalate +1.3 V vs SCE) would undergo oxidation by the excited state 4CzIPN, **1a*** (+1.35 V vs SCE). The resulting O-centered radical **I** fragments to the acyl radical **II** and finally the tertiary alkyl

radical **III** releasing two molecules of carbon dioxide. The latter can then add to the EBX reagent **2** affording the final product **4** and the iodanyl radical **IV**. **IV** (+0.25 V vs SCE)[21a] can then oxidize **1a**$^{\bullet-}$ (-1.2 V vs SCE) back down to the ground state ensuring photocatalytic turnover and affording iodobenzoate (**16**).[21b] Second, our experimental data associated to Method B (Figures 1 and 2) suggest that PhEBX (**2a**) undergoes direct photoexcitation to generate a highly oxidant excited state **2a*** (+1.8 V vs SCE), the latter can then perform a SET oxidation of the cesium salt **3** (+1.3 V vs SCE). In the same fashion as method A, the resulting O-centered radical **I** would then fragment twice to the desired radical **III** before being trapped by a second molecule of **2a** to give the desired alkyne **4**. Following the oxidation of oxalate **3**, we suspect that the reduced **2a**$^{\bullet-}$ would be highly unstable and degrade resulting in side products such as the observed 1,4-diphenylbutadiyne (**7**). Additionally, we cannot exclude the possibility of diyne formation from the excited state **2a***. The formation of ketones **6a** and **6b** seems to be a background process occurring under thermal conditions. These ketones impact the yield slightly in the case of the slower direct photoexcitation, due to the consumption of the starting materials. However, they do not seem to play a role in the reaction mechanism. In presence of the photocatalyst, both mechanisms are probably occurring in parallel leading to higher efficiency overall.



Scheme 9. Speculative mechanism.

Conclusion

In summary, we have developed two methods for the deoxy-alkynylation of tertiary alcohols. Both methods use bench stable cesium oxalates easily accessed from the corresponding alcohols and aryl EBX reagents as a somophilic alkyne source. Our first strategy involves a metal-free process using 4CzIPN (**1a**) as photocatalyst, demonstrating yet again its versatility as an organic dye, and affording a valuable scope of alkynes connected to all-carbon quaternary centers. Our second approach is based on the direct photoexcitation of EBX reagents and their use as strong photooxidants. The relevance of the direct excitation of aryl EBX reagents has been exemplified beyond deoxy-alkynylation by the successful C-H alkynylation of THF, the oxyalkynylation of enamides, a deboronative alkynylation and a cascade alkynylation from oximes. From the synthetic point of view, our methods constitute a practical access to alkynylated quaternary-centers and should contribute to further increase the use of these valuable building blocks. From the point of view of designing new photochemical processes, the direct excitation of aryl EBX reagents will open the door for new alkynylation processes without the need for sophisticated catalysts.

Acknowledgements

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Keywords: Alkynes; Hypervalent Iodine; Photochemistry; Quaternary centers; Synthetic methods.

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[25] In absence of the **3a**, we observed 60% degradation of **2a** and 3% of **6a**. In presence of **3a**, we observe 90% degradation of **2a**, 17% of **6a** and 12% **6b**.

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[28] Irradiation of **3a** (1 equiv) and **6b** (1 equiv) in DCM led to no observable degradation. Irradiation of **3a** (1 equiv), **6b** (0.7 equiv) with **2g** (1.5 equiv) led to less than 5% product formation. Irradiation of **6b** (1 equiv) and **2a** (1.5 equiv) in DCM led to no product formation confirming that **6b** is most likely not a reaction intermediate.

[29] Overlap of signals in the aromatic region of the NMR did not allow us to precisely determine the amount of 1,4-diphenylbutadiyne (**7**) formed.

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[31] This type of HAT-alkynylation with EBX reagents has been reported to proceed with thermal radical initiators such as TBHP[30a] and in presence of photocatalysts such as phenylglyoxilic acid[30b] or benzophenone,[27] but its promotion by direct irradiation of the reagent is, to the best of our knowledge, unprecedented.

[32] The reproducibility of the measurement was verified by 3 repetitions of the sample.

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[34] $E_{1/2}$(**2a***/**2a**$^{\bullet-}$) = $E_{0\text{-}0}$ + $E_{1/2}$(**2a**/**2a**$^{\bullet-}$). $E_{0\text{-}0}$ was determined experimentally from the position of the long wavelength tail of the absorption spectrum at 460 nm, as described in: L. Buzzetti, A. Prieto, S. R. Roy, P. Melchiorre, *Angew. Chem. Int. Ed.* **2017**, *56*, 15039–15043. *Angew. Chem.* **2017**, *129*, 15235–15239.

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Contents

1. General methods

All reactions that were carried out in oven dried glassware and under an atmosphere of nitrogen is stated at the start of the reaction conditions. For flash chromatography, distilled technical grade solvents were used. THF, CH_3CN, toluene, Et_2O and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, Karl-Fischer titration). The solvents were degassed by Freeze-Pump-Thaw method when mentioned. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, TCI, Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC glass plates and visualized with UV light and *p*-anisaldehyde stain (EtOH:H_2SO_4:AcOH:*p*-anisaldehyde 135:5:1.5:3.7 V:V:V:V).

^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in CDCl3, acetonitrile-d_3, DMSO-d_6 or acetone-d_6, all signals Are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal acetonitrile signal at 1.94 ppm, the internal methanol signal at 3.30 ppm, the internal DMSO signal at 2.50 ppm or the internal acetone signal at 2.05 ppm as standard. The data is reported as (s = singlet, d = doublet, t= triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation). ^{13}C-NMR spectra were recorded with ^{1}H-*d*ecoupling on a Brucker DPX-400 100 MHz spectrometer in CDCl3, acetonitrile-d_3 CD_3OD, DMSO-d_6 or acetone-d_6, all signals Are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal acetonitrile signal at 1.3 ppm the internal methanol signal at 49.0 ppm, the internal DMSO signal at 39.5 ppm or the internal acetone signals at 29.84 and 206.26 ppm as standard. Diastereoiomeric ratios has been determined after purification and stereochemistry has been assigned based on ^{1}H NMR analysis.

Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and is reported in cm^{-1} (w = weak, m = medium, s = strong).

High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API.

All photocatalyzed reactions were carried out in oven dried glassware and under inert atmosphere (freeze pump thaw solvent stored on molecular sieves and under argon for maximum one week) unless specified otherwise. They were performed in screw cap dram vials (0.5 – 7,5 mL) which were stuck to a glass plate that was placed on a stirring plate with 2 Kessil lamps (440 nm, 40 W) irradiating from both sides (the hood was free and coated with aluminum foil for personal protection). The distance between the Kessil lamps and the vials was approximatively 10 cm. Long irradiation resulted in temperature increasing up to 50 °C during overnight reactions unless a fan was used in which case the temperature raised to 30-35°C. Photos have been provided.

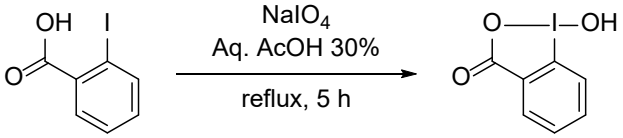
UV/Vis spectroscopy was performed on an Agilent Cary 60 UV-Vis and steady-state luminescence spectroscopy was recorded on a Varian Cary Eclipse spectrophotometer.

2. Synthesis of starting materials

2.1. Synthesis of hypervalent iodine reagents

The synthesis of reagents **6** and **2a-g** had already been described before.[1,2,3,4,5,6,7] Some of the procedures for accessing the ArEBX species have evolved slightly and have been updated with corresponding modifications, the modifications only apply to work-ups and purifications.

1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (5b)



16 **5b**

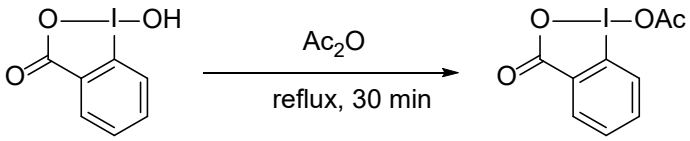
Following a reported procedure,[1] $NaIO_4$ (40.5 g, 189 mmol, 1.05 equiv) and 2-iodobenzoic acid (**16**, 44.8 g, 180 mmol, 1.0 equiv) were suspended in 30% (v:v) aq. AcOH (350 mL). The mixture was vigorously stirred and refluxed for 5 h. The reaction mixture was then diluted with cold water (250 mL) and allowed to cool to rt, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 150 mL) and acetone (3 x 150 mL), and air-dried in the dark overnight to afford 1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (**5b**, 44.3 g, 168 mmol, 93% yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (dd, *J* = 7.7, 1.4 Hz, 1H, Ar*H*), 7.97 (m, 1H, Ar*H*), 7.85 (dd, *J* = 8.2, 0.7 Hz, 1H, Ar*H*), 7.71 (td, *J* = 7.6, 1.2 Hz, 1H, Ar*H*).

^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4.

Consistent with reported data.[1]

1-Acetoxy-1,2-benziodoxol-3-(1H)-one (5a)



5b **5a**

Following a reported procedure,[8] compound **5b** (3.00 g, 11.3 mmol, 1.00 equiv) was heated in Ac_2O (10 mL) to reflux until the solution turned clear (without suspension, ca. 30 min). The mixture was then left to cool down and white crystals started to form. The crystallization was continued at -18 °C.

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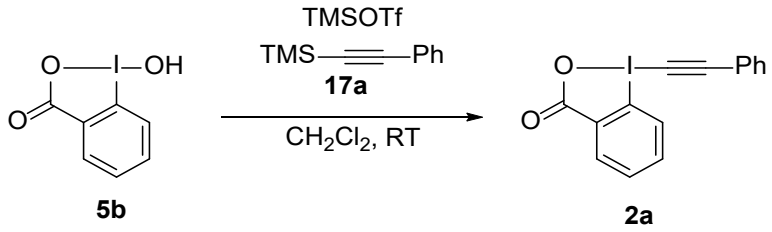
The crystals were then collected and dried overnight under high vacuum to give compound **5a** (3.06 g, 10.0 mmol, 86%).

^{1}H NMR (400 MHz, Chloroform-*d*$_3$) δ 8.25 (dd, 1 H, J = 7.6, 1.4 Hz, Ar*H*), 8.00 (dd, 1 H, J = 8.3, 0.5 Hz, Ar*H*), 7.92 (dt, 1 H, J = 7.0, 1.7 Hz, Ar*H*), 7.71 (td, 1 H, J = 7.6, 0.9 Hz, Ar*H*), 2.25 (s, 3 H, COC*H*$_3$). NMR data correspond to the reported values.[8]

1-[Phenylethynyl]-1,2-benziodoxol-3(1H)-one (PhEBX, 2a)



Following a reported procedure,[2] trimethylsilyltriflate (9.1 mL, 50 mmol, 1.1 equiv) was added dropwise to a suspension of 2-iodosylbenzoic acid (**5b**, 12.1 g, 45.8 mmol, 1.0 equiv) in CH_2Cl_2 (120 mL) at 0 °C. The mixture was stirred for 1 h, followed by the dropwise addition of trimethyl(phenylethynyl)silane (**17a**, 8.8 mL, 50 mmol, 1.1 equiv) (slightly exothermic). The resulting suspension was stirred for 6 h at RT, during this time a white solid was formed. A saturated solution of $NaHCO_3$ (120 mL) was added and the mixture was stirred vigorously for 30 min. The two layers of the mother liquors were separated and the organic layer was washed with sat. $NaHCO_3$ (2x50 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting solid was recrystalized in EtOAc:MeOH (7:3 v:v) (ca. 20 mL). The solution was left to cool to RT then in the freezer ovenight, filtered and dried under high vacuum to afford PhEBX (**2a**, 6.8 g, 25 mmol, 43% yield) as colorless crystals.

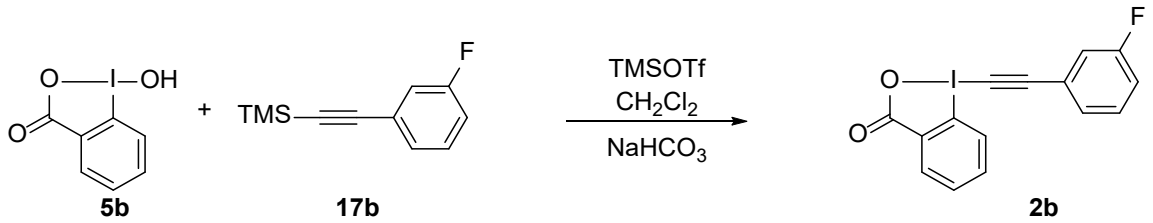
Mp (Dec.) 155 – 160 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (m, 1H, Ar*H*), 8.28 (m, 1H, Ar*H*), 7.80 (m, 2H, Ar*H*), 7.63 (m, 2H, Ar*H*), 7.48 (m, 3H, Ar*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 134.9, 132.9, 132.5, 131.6, 131.3. 130.8, 128.8, 126.2, 120.5, 116.2, 106.6, 50.2.

Consistent with reported data.[2]

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



Following a slightly modified reported procedure,[6] trimethylsilyl triflate (0.44 mL, 2.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (**5b**, 0.589 g, 2.23 mmol, 1.00 equiv) in CH_2Cl_2 (6.8 mL) at RT The resulting suspension was stirred for 1 h, followed by the dropwise addition of ((3-fluorophenyl)ethynyl)trimethylsilane (**17b**, 0.50 mL, 2.5 mmol, 1.1 equiv). The resulting suspension

was stirred for 6 h at RT. A saturated solution of $NaHCO_3$ (10 mL) was then added and the mixture was stirred vigorously for 30 minutes, resulting in a suspension. The mixture was diluted with chloroform (10 mL), water (5 mL) and MeOH (ca. 0.5 mL) resulting in two clear layers. The two layers were separated, and the organic layer was washed with sat. $NaHCO_3$ (7 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting solid was recrystallized in EtOAc:MeOH (7:3 v:v) (ca. 20 mL). The solution was left to cool to RT then was placed in the freezer (-20 °C) overnight. The crystals were filtered and washed with Et_2O to afford **2b** (787 mg, 2.15 mmol, 43% yield) as colorless crystals.

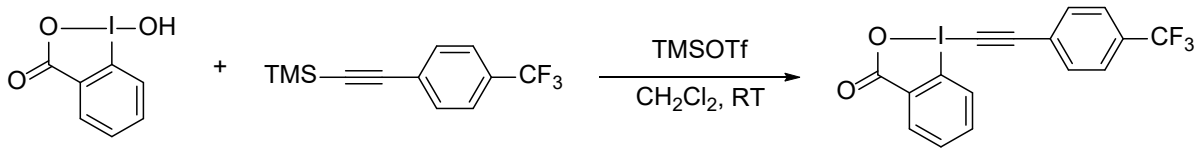
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (dd, *J* = 8.2, 0.8 Hz, 1H, Ar*H*), 8.13 (dd, *J* = 7.4, 1.7 Hz, 1H, Ar*H*), 7.91 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H, Ar*H*), 7.81 (td, *J* = 7.3, 0.9 Hz, 1H, Ar*H*), 7.64 – 7.59 (m, 1H, Ar*H*), 7.58 – 7.53 (m, 2H, Ar*H*), 7.47 – 7.37 (m, 1H, Ar*H*).

^{13}C NMR (101 MHz, DMSO-d_6)[9] 166.3, 161.8 (d, *J* = 245.6 Hz), 135.3, 131.9, 131.3, 131.2 (d, *J* = 8.7 Hz), 129.0 (d, *J* = 2.9 Hz), 127.7, 122.4 (d, *J* = 9.6 Hz), 119.2 (d, *J* = 23.4 Hz), 118.1 (d, *J* = 21.1 Hz), 116.4, 102.5 (d, *J* = 3.3 Hz), 53.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -111.7.

Consistent with reported data.[5]

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



5b **17c** **2c**

Following a reported procedure,[3] trimethylsilyl triflate (1.0 mL, 5.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (**5b**, 1.3 g, 5.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) at RT The resulting suspension was stirred for 1 h, followed by the dropwise addition of trimethyl((4-(trifluoromethyl)phenyl)ethynyl)silane (**17c**, 1.3 mL, 5.5 mmol, 1.1 equiv), which was dissolved in CH_2Cl_2 (1 mL). The resulting suspension was stirred for 6 h at RT A saturated solution of $NaHCO_3$ (20 mL) was then added and the mixture was stirred vigorously for 30 min, the two layers were separated and the organic layer was washed with sat. $NaHCO_3$ (20 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting solid was boiled in CH_3CN (20 mL). The mixture was cooled down, filtered and dried under high vacuum to afford **2c** (1.3 g, 3.2 mmol, 64% yield) as a pale yellow solid.

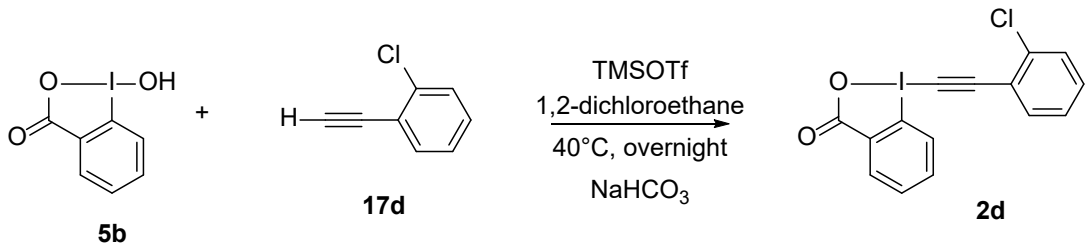
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.38 (m, 1H, Ar*H*), 8.28 – 8.19 (m, 1H, Ar*H*), 7.84 – 7.74 (m, 2H, Ar*H*), 7.74 – 7.65 (m, 4H, Ar*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 135.0, 133.0, 132.6, 132.2 (q, *J* = 33.0 Hz), 131.7, 131.2, 126.3, 125.7 (q, *J* = 3.6 Hz), 124.4, 123.4 (q, *J* = 272.6 Hz), 116.1, 104.2, 53.7.

Consistent with reported data.[3]

[9] One carbon is not resolved.

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



5b **17d** **2d**

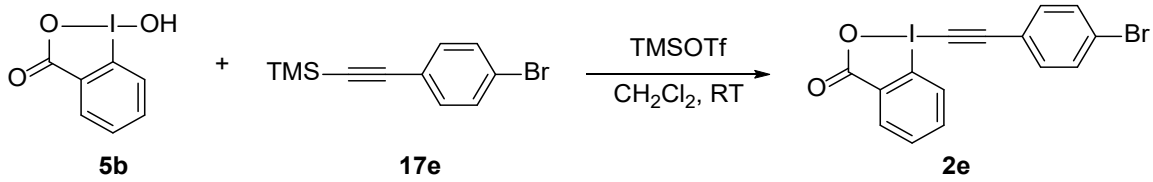
Following a slightly modified reported procedure,[6] trimethylsilyl triflate (0.40 mL, 2.2 mmol, 1.2 equiv) was added to a suspension of 2-iodosylbenzoic acid (**5b**, 0.548 g, 2.08 mmol, 1.1 equiv) in DCE (5.8 mL) at RT The resulting suspension was stirred for 1 h, followed by the drop wise addition of (2-chlorophenyl)acetylene (**17d**, 0.26 mL, 0.19 mmol, 1.0 equiv). The resulting suspension was stirred for 15 h at 40 °C A saturated solution of $NaHCO_3$ (20 mL) was then added and the mixture was stirred vigorously for 30 minutes resulting in a persistent emulsion/suspension. Water (5 mL) was added, followed by chloroform (15 mL) and MeOH (ca. 0.5 mL) resulting in 2 clear layers. The two layers were seperated and the organic layer was washed with sat. $NaHCO_3$ (5 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The resulting solid was recrystallized from EtOAc:MeOH (7:3 v:v, ca. 10 mL). The mixture was cooled down overnight in the freezer (-20 °C), filtered and washed with Et_2O to afford **2d** (0.217 g, 0.567 mmol, 30% yield) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 – 8.38 (m, 2H, Ar*H*), 7.84 – 7.73 (m, 2H, Ar*H*), 7.62 (dd, *J* = 7.6, 1.7 Hz, 1H, Ar*H*), 7.50 (dt, *J* = 8.2, 1.2 Hz, 1H, Ar*H*), 7.46 – 7.37 (m, 1H, Ar*H*), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H, Ar*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 137.2, 135.2, 134.5, 132.7, 131.8, 131.7, 131.3, 129.9, 127.0, 126.7, 121.0, 116.4, 102.7, 56.0.

Consistent with reported data[10]

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



5b **17e** **2e**

Following a reported procedure,[4] trimethylsilyl triflate (1.0 mL, 5.5 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (**5b**, 1.3 g, 5.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) at RT The resulting suspension was stirred for 1 h, followed by the dropwise addition of ((4-bromophenyl)ethynyl)trimethylsilane (**17e**, 1.2 g, 5.5 mmol, 1.1 equiv), which was dissolved in CH_2Cl_2 (1 mL). The resulting suspension was stirred for 6 h at RT A saturated solution of $NaHCO_3$ (20 mL) was then added and the mixture was stirred vigorously for 30 min, the two layers were separated and the organic layer was washed with sat. $NaHCO_3$ (20 mL), dried over $MgSO_4$, filtered and evaporated under

[10] Li, M.; Li, W.; Lin, C.-D.; Wang, J.-H.; Wen, L.-R. *J. Org. Chem.* **2019**, *84* (11), 6904–6915.

reduced pressure. The resulting solid was boiled in CH_3CN (20 mL). The mixture was cooled down, filtered and dried under high vacuum to afford **2e** (1.4 g, 3.3 mmol, 66% yield) as a pale yellow solid.

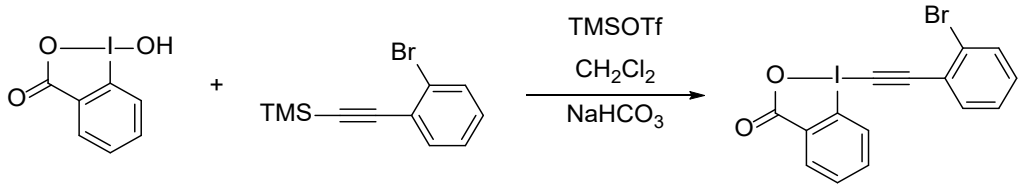
Mp 158-163 °C (decomposition).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.30 (m, 1H, Ar*H*), 8.30 – 8.13 (m, 1H, Ar*H*), 7.84 – 7.72 (m, 2H, Ar*H*), 7.58 (d, 2H, *J* = 8.5 Hz, Ar*H*), 7.46 (d, 2 H, *J* = 8.5 Hz, Ar*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 135.1, 134.3, 132.7, 132.3, 131.9, 131.4, 126.3, 125.7, 119.6, 116.3, 105.4, 52.1.

Consistent with reported data.[4]

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



5b **17f** **2f**

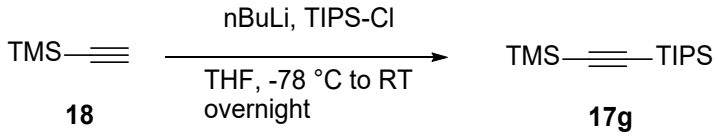
Following a slightly modified reported procedure,[5] trimethylsilyl triflate (0.42 mL, 2.4 mmol, 1.1 equiv) was added to a suspension of 2-iodosylbenzoic acid (**5b**, 0.562 g, 2.13 mmol, 1.00 equiv) in CH_2Cl_2 (6 mL) at RT The resulting suspension was stirred for 1 h, followed by the drop wise addition of ((2-bromophenyl)ethynyl)trimethylsilane (**17f**, 0.50 mL, 2.4 mmol, 1.1 equiv). The resulting suspension was stirred for 6 h at RT. A saturated solution of $NaHCO_3$ (10 mL) was then added and the mixture was stirred vigorously for 1 h resulting in a persistent emulsion/suspension. The mixture was diluted with $CHCl_3$ (10 mL), water (5 mL) and MeOH (ca. 2 mL) to afford 2 distinct layers. The two layers were separated, and the organic layer was washed with sat. $NaHCO_3$ (5 mL), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting solid was recrystallized in EtOAc:MeOH (7:3 v:v) (ca. 20 mL). The solution was left to cool to RT then was placed in the freezer (-20 °C) overnight. The crystals were filtered and washed with Et_2O afford **2f** (1.50 g, 3.51 mmol, 70% yield) as colorless crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (td, *J* = 7.3, 2.1 Hz, 2 H, Ar*H*), 7.84 – 7.74 (m, 2 H, Ar*H*), 7.68 (d, *J* = 1.1 Hz, 1 H, Ar*H*), 7.61 (dd, *J* = 7.6, 1.7 Hz, 1 H,*ArH*), 7.36 (m, 2 H, Ar*H*).

^{13}C NMR (101 MHz, $CDCl_3$)[7] δ 166.6, 135.2, 134.7, 133.0, 132.7 , 131.8, 131.3, 127.6, 126.8, 126.4, 123.2, 116.5, 104.3, 55.4.

Consistent with reported data.[5]

Tri*iso*propylsilyl trimethylsilylacetylene (17g)



18 **17g**

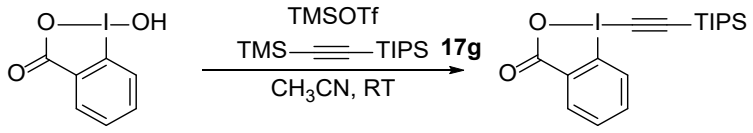
Following a reported procedure,[11] *n*-butyllithium (2.5 M in hexanes, 28 mL, 70 mmol, 0.98 equiv) was added dropwise to a stirred solution of ethynyltrimethylsilane (**18**, 7.0 g, 71 mmol, 1.0 equiv) in THF (100 mL) at -78 °C. The mixture was warmed to 0 °C and stirred for 5 min. The mixture was then cooled back to -78 °C and chlorotri*iso*propylsilane (15 mL, 71 mmol, 1.0 equiv) was added dropwise. The mixture was then allowed to warm to room temperature and stirred overnight. A saturated solution of ammonium chloride (100 mL) was added, and the reaction mixture was extracted with diethyl ether (2 x 100 mL). The combined organic layers were washed with water and brine, then dried over MgSO4, filtered and concentrated under reduced pressure to obtain a colorless liquid which was further purified by filtration on silica eluting with pentane (500 mL) to yield **17g** (16 g, 64 mmol, 90% yield) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.08 (m, 21H, TIPS), 0.18 (s, 9H, TMS).

Consistent with reported data.[11]

1-[(Tri*iso*-propylsilyl)ethynyl]-1,2-benziodoxol-3(1*H*)-one (TIPS-EBX, **2g**)

This compound can also be accessed in one pot from commercially available *o*-iodobenzoic acid and the free TIPS alkyne, however in the context of this study it was synthesized in the 2 step fashion.[12]



5b **2g**

Following a reported procedure,[7] 2-iodosylbenzoic acid (**5b**, 8.0 g, 30 mmol, 1.0 equiv) was charged in an oven-*d*ried round-bottomed 250 mL flask equipped with a magnetic stirrer. The solid was placed under a nitrogen atmosphere and anhydrous acetonitrile (100 mL) was added. The mixture was cooled to 0 °C. Trimethylsilyltriflate (6.0 mL, 33 mmol, 1.1 equiv) was added dropwise. After 15 min, (trimethylsilyl)(tri*iso*propylsilyl)acetylene (**17g**, 8.5 g, 33 mmol, 1.1 equiv) was added dropwise. After 30 min, the suspension became an orange solution. Pyridine (2.7 mL, 33 mmol, 1.1 equiv) was added dropwise. After 15 min, the reaction mixture was transferred in a one-neck 500 mL flask and concentrated under vacuum to afford a yellow solid. The solid was dissolved in CH_2Cl_2 (100 mL) and transferred in a 500 mL separatory funnel. The organic layer was washed with a 1 M HCl solution (50 mL) and the aqueous layer was extracted with CH_2Cl_2 (100 mL). The organic layers were combined, washed with a saturated solution of NaHCO3 (2 x 100 mL), dried over MgSO4, filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (40 mL) afforded TIPS-EBX (**2g**, 9.2 g, 21.5 mmol, 71% yield) as colorless crystals.

Mp (Dec.) 170-176 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (m, 1H, Ar*H*), 8.29 (m, 1H, Ar*H*), 7.77 (m, 2H, Ar*H*), 1.16 (m, 21H, TIPS).

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[11] Helal, C. J.; Magriotis, P. A.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 10938.

[12] Hari, D. P.; Caramenti, P.; Schouwey, L.; Chang, M.; Nicolai, S.; Bachert, D.; Wright, T.; Orella, C.; Waser, J. *Org. Process Res. Dev.* **2020**, *24*, 106–110.

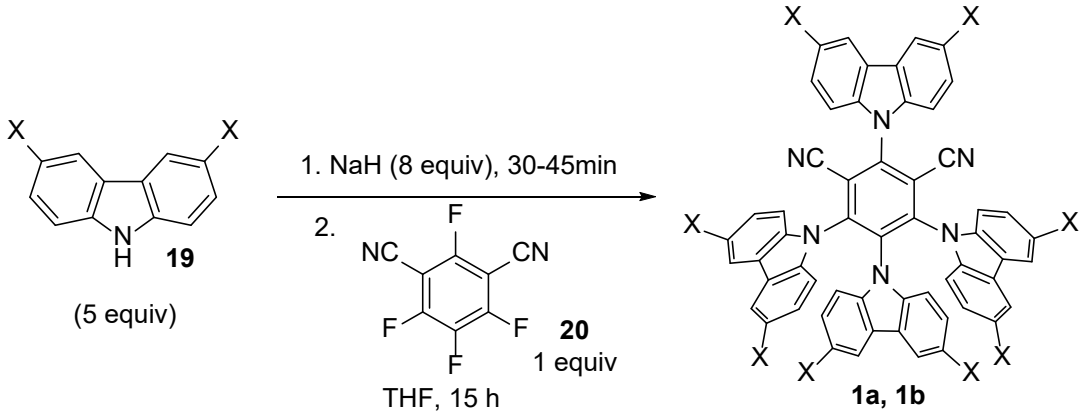
^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.4, 134.6, 132.3, 131.4, 131.4, 126.1, 115.6, 114.1, 64.6, 18.4, 11.1.

IR ν 2943 (m), 2865 (m), 1716 (m), 1618 (m), 1604 (s), 1584 (m), 1557 (m), 1465 (m), 1439 (w), 1349 (m), 1291 (m), 1270 (w), 1244 (m), 1140 (m), 1016 (m), 999 (m), 883 (m), 833 (m), 742 (m), 702 (s), 636 (m).

Consistent with reported data.[7]

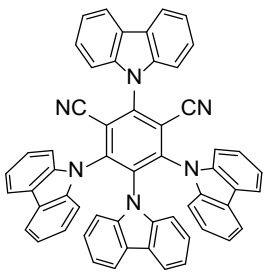
2.2.Synthesis of the photocatalysts

2.3.General procedure A: Synthesis of the photocatalysts



Sodium hydride (60% suspension in mineral oil, 8.0 equiv) was added slowly to a stirred solution of substituted-carbazole **19** (5.0 equiv) in dry THF (0.05 M) under a nitrogen atmosphere at RT After 30 min, 2,4,5,6-tetrafluoroisophthalonitrile **20** (1.0 mmol, 1.0 equiv) was added. After stirring at RT for 15 h, 2 mL water was added to the reaction mixture to quench the excess of NaH. The resulting mixture was then concentrated under reduced pressure. The crude product was purified by recrystallization from hexane:CH_2Cl_2 then filtered. The brown liquid filtrate was concentrated and recrystallized as before. The combined solids were then purified by column chromatography on silica gel with CH_2Cl_2:Hexane.

2,4,5,6-Tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN, **1a**)



Following *general procedure A* and starting from 9H-carbazole **19a** (X = H, 1.67 g, 10.0 mmol, 5.00 equiv), sodium hydride (0.60 g, 15 mmol, 7.5 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile **20** (0.40 g, 2.0 mmol) in 40 mL of THF. Recrystallization (Hexanes:CH_2Cl_2 (1:1, 90 mL)) afforded the crude product as a yellow powder. Column chromatography afforded 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (**1a**) as a bright yellow crystalline solid (1.14 g, 1.45 mmol, 73 % yield).

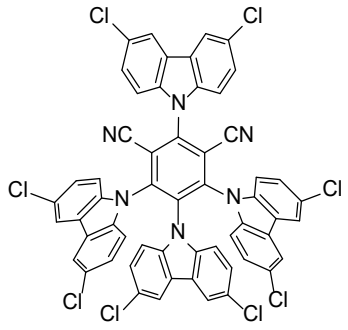
Rf (Hexane;CH_2Cl_2 1:1) = 0.29. (yellow spot on TLC).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.8 – 7.6 (m, 8H, Ar*H*), 7.5 (ddd, *J* = 8.0, 6.6, 1.6 Hz, 2H, Ar*H*), 7.3 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.2 (dd, *J* = 8.4, 1.5 Hz, 4H, Ar*H*), 7.2 – 7.0 (m, 8H, Ar*H*), 6.8 (t, *J* = 7.8 Hz, 4H, Ar*H*), 6.6 (td, *J* = 7.6, 1.2 Hz, 2H, Ar*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 144.6, 140.0, 138.2, 136.9, 134.7, 127.0, 125.8, 124.9, 124.7, 124.5, 123.8, 122.4, 121.9, 121.4, 121.0, 120.4, 119.6, 116.3, 111.6, 109.9, 109.5, 109.4.

^{1}H NMR shift in CDCl3 are consistent with reported data.[13]

(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-*d*ichloro-9*H*-carbazol-9-yl)isophthalonitrile (4ClCzIPN, 1b)



Following *general procedure A* and starting from 3,6-*d*ichloro-9H-carbazole **19b** (1.96 g, 6.00 mmol, 6.0 equiv), sodium hydride (0.320 g, 8.00 mmol, 8.0 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile **20** (200 mg, 1.00 mmol) in 20 mL of THF. Recrystallization (Hexanes:CH_2Cl_2 (1:2, 80 mL)) gave 900 mg of yellow powder, then second recrystallization gave 325 mg of brown powder. Column chromatography of the combined solid afforded (2r,4s,5r)-2,4,5,6-tetrakis(3,6-*d*ichloro-9H-carbazol-9-yl)isophthalonitrile (**1b**) as a bright yellow crystalline solid (830 mg, 0.780 mmol, 87 % yield).

Rf (Hexane:CH_2Cl_2 1:1): 0.25. (yellow spot on TLC).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.60 (d, *J* = 2.1 Hz, 2H, Ar*H*), 8.15 (d, *J* = 2.1 Hz, 4H, Ar*H*), 8.08 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.87 (dd, *J* = 8.8, 2.1 Hz, 2H, Ar*H*), 7.80 (d, *J* = 2.2 Hz, 2H, Ar*H*), 7.69 (d, *J* = 8.8 Hz, 4H, Ar*H*), 7.46 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.32 (dd, *J* = 8.8, 2.2 Hz, 4H, Ar*H*), 6.93 (dd, *J* = 8.8, 2.2 Hz, 2H, Ar*H*).

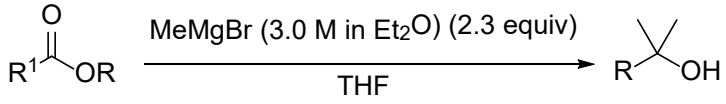
^{13}C NMR (101 MHz, DMSO-d_6) δ 145.0, 144.5, 138.5, 137.4, 136.5, 135.8, 134.5, 127.8, 127.0, 126.4, 125.7, 125.3, 124.2, 123.8, 123.3, 121.6, 120.9, 120.3, 116.8, 112.6, 112.5, 112.3, 111.7.

^{1}H NMR shift in CDCl3 are consistent with reported data.[6]

2.4.Synthesis of tertiary alcohols

Alcohols for substrates **3a**-**d**, **3k**-**m**, **3p**, **3w** and **3x** were purchased from commercial sources (Sigma-Aldrich, Acros, TCI, abcr) and used directly without prior purification.

General procedure B: Synthesis of tertiary alcohols from esters

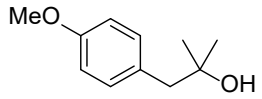


21e-g **22e-g**

An oven dried two necked flask, equipped with a magnetic stirrer, was charged with the ester **21e-g** (1.0 equiv) and dissolved in anhydrous THF (1.0 M). The reaction was cooled to 0 °C with an ice bath. The methyl magnesium bromide solution was diluted to 1 M with THF and added dropwise to the cooled solution *via* syringe. The reaction was left to stir at room temperature overnight (15 to 18 h) at this time the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted 3 times with EtOAc then the combined organic layers were washed with sat. aq. NaCl. The organic layers were then dried on $MgSO_4$, filtered and concentrated under reduced pressure. The compound was purified by column chromatography (SiO_2, pentane:EtOAc 9:1, 4:1, *p*-Anisaldehyde stain blue to purple and black spots) affording the desired alcohol.

[13] Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234.

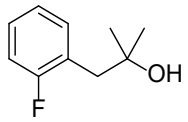
- 1-(4-Methoxyphenyl)-2-methylpropan-2-ol (**22e**)



22e was synthesized following the *general procedure B*: in THF (60 mL, 0.1 M) using methyl 2-(4-methoxyphenyl)acetate (**21e** ,1.0 mL, 6.3 mmol, 1.0 equiv) and methyl magnesium bromide (3 M in Et_2O) (4.8 mL, 14 mmol, 2.3 equiv) diluted with 10 mL of THF.
Column chromatography (SiO_2 ca. 40 g, pentane:EtOAc 9:1 to 8:2) afforded 1-(4-methoxyphenyl)-2-methylpropan-2-ol **22e** (0.898 g, 4.98 mmol, 79%).

Rf (pentane:EtOAc 9:1) = 0.3
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H, Ar*H*), 6.88 – 6.83 (m, 2H, Ar*H*), 3.80 (s, 3H, OMe), 2.71 (s, 2H, ArCH_2), 1.21 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 131.5, 129.9, 113.8, 70.9, 55.4, 48.9, 29.2.
The reported NMR data are consitant with the reported data.[14]

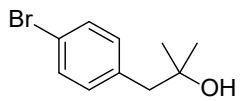
- 1-(2-Fluorophenyl)-2-methylpropan-2-ol (**22f**)



22f was synthesized following the *general procedure B*: in THF (60 mL, 0.1 M) using methyl 2-(2-fluorophenyl)acetate (**21f**, 1.0 mL, 6.8 mmol, 1.0 equiv) and methyl magnesium bromide (3 M in Et_2O) (5.2 mL, 16 mmol, 2.3 equiv) diluted with 10 mL of THF.
Column chromatography (SiO_2 ca. 40g, pentane:EtOAc 9:1 to 8:2) afforded 1-(2-fluorophenyl)-2-methylpropan-2-ol **22f** (0.723 g, 4.30 mmol, 63%).

Rf (pentane:EtOAc 9:1) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.18 (m, 2H, Ar*H*), 7.13 – 7.00 (m, 2H, Ar*H*), 2.83 (d, J = 1.5 Hz, 2H, CH_2), 1.48 (s, 1H, O*H*), 1.25 (d, J = 0.9 Hz, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244.7 Hz), 132.8 (d, *J* = 4.7 Hz), 128.3 (d, *J* = 8.2 Hz), 124.9 (d, *J* = 16.0 Hz), 123.8 (d, *J* = 3.5 Hz), 115.4 (d, *J* = 23.0 Hz), 71.3, 42.3, 29.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1.
IR (ν_{max}, cm^{-1}) 3420 (m), 3061 (m), 2975 (m), 2963 (m), 2936 (m), 1583 (m), 1493 (s), 1455 (s), 1228 (s), 1184 (s), 1134 (s), 753 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{10}H_{12}F^+$ 151.0918; Found 151.0921.

- 1-(4-Bromophenyl)-2-methylpropan-2-ol (**22g**)



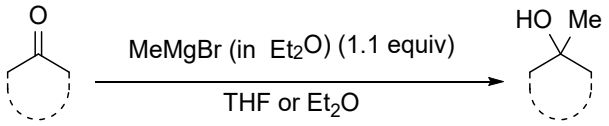
22g was synthesized following the *general procedure B*: in THF (40 mL, 0.1 M) using ethyl 2-(4-bromophenyl)acetate (**21g**, 1.00 g, 4.11 mmol, 1.0 equiv) and methyl magnesium bromide (3 M in Et_2O) (3.2 mL, 9.5 mmol, 2.3 equiv) diluted with 6 mL of THF.
Column chromatography (SiO_2 ca. 40 g, pentane:EtOAc 9:1 to 8:2) afforded 1-(4-bromophenyl)-2-methylpropan-2-ol **22g** (0.781 g, 3.41 mmol, 83%).

Rf (pentane:EtOAc 9:1) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H, Ar*H*), 7.13 – 7.06 (m, 2H, Ar*H*), 2.72 (s, 2H, CH_2), 1.38 (s, 1H, O*H*), 1.21 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 132.2, 131.2, 120.5, 70.7, 49.1, 29.2.

[14] Okamura, T.; Egoshi, S.; Dodo, K.; Sodeoka, M.; Iwabuchi, Y.; Kanoh, N. *Chem. – Eur. J.* **2019**, *25*, 16002–16006.

IR (ν_{max}, cm^{-1}) 3668 (m), 2972 (s), 2901 (s), 1488 (s), 1406 (s), 1377 (s), 1229 (s), 1075 (s), 1056 (s), 1012 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{10}H_{12}{}^{79}Br^+$ 211.0117; Found 211.0122.

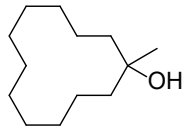
General procedure C: Synthesis of tertiary alcohols from ketones



21n-o **22n-o**

An oven dried two-necked flask, equipped with a magnetic stirrer, was charged with the ketone **21n-o** (1.0 equiv) and dissolved in anhydrous THF or Et_2O (0.2 M). The reaction was cooled to 0 °C with an ice bath. The methylmagnesium bromide solution (3.0 M in Et_2O) was diluted to 1 M and added dropwise to the cooled solution *via* a dropping funnel. The reaction was stirred at room temperature overnight (15 to 18 h) at this time the reaction was quenched with sat. aq. NH_4Cl, followed by the addition of water and EtOAc. The layers were separated, the aqueous layer was extracted 3 times with EtOAc then the combined organic layers were washed with sat. aq. NaCl. The organic layer was then dried on $MgSO_4$, filtered and concentrated under reduced pressure. The compound was purified by column chromatography (SiO_2, pentane:EtOAc, *p*-Anisaldehyde stain) affording the desired alcohol.

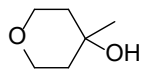
- Methylcyclododecan-1-ol (22n)



22n was synthesized following the *general procedure C* in Et_2O (25 mL, 0.2 M) from cyclododecanone (**21n**, 1.00 g, 5.49 mmol, 1.0 equiv) using methylmagnesium bromide (3.0 M in Et_2O, 2.0 mL, 6.00 mmol, 1.1 equiv) diluted with THF (4.0 mL).
Column chromatography (SiO_2, 10% EtOAC in Pentane) afforded methylcyclododecan-1-ol **22n** (609 mg, 3.07 mmol, 56 %) as a white amorphous solid. The NMR data was collected and the compound was used in the next step without further analysis.

Rf (pentane:EtOAc 9:1) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.59 – 1.52 (m, 2 H, CH_2), 1.45 – 1.25 (m, 20 H, CH_2), 1.17 (s, 3 H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 73.8, 36.3, 29.2, 26.6, 26.2, 22.7, 22.2, 20.1.

- 4-Methyltetrahydro-2*H*-pyran-4-ol (22o)

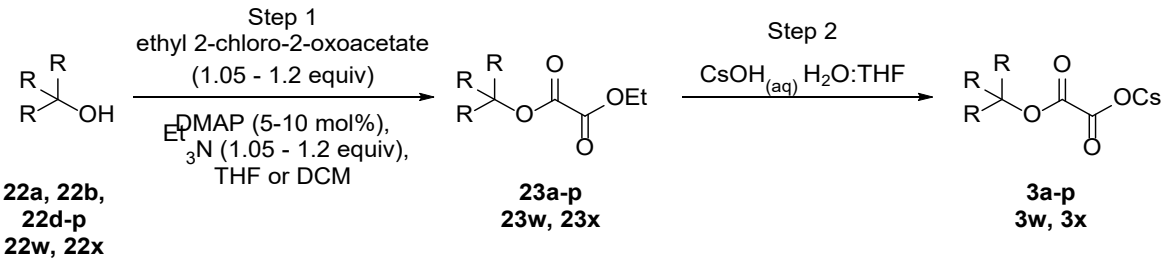


22o was synthesized following the *general procedure C* in THF (50 mL, 0.2 M) from tetrahydro-4*H*-pyran-4-one (**21o**, 0.94 mL, 10 mmol, 1.0 equiv) using methylmagnesium bromide (3.0 M in Et_2O, 3.7 mL, 11 mmol, 1.1 equiv) diluted with THF (7.3 mL). Column chromatography (SiO_2, 25% EtOAc in Pentane) afforded 4-methyltetrahydro-2*H*-pyran-4-ol **22o** (604 mg, 5.20 mmol, 52 %) as a colourless oil.

Rf (pentane:EtOAc 3:1) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.81 – 3.75 (m, 2H, OCH_2), 3.72 – 3.76 (m, 2H, OCH_2), 1.77 – 1.62 (m, 2H, CH_2), 1.58 – 1.48 (m, 2H, CH_2), 1.28 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 67.5, 64.4, 39.6, 30.3.

2.5. Synthesis of cesium salts

General procedure D: Synthesis of cesium salts from tertiary alcohols



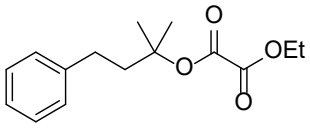
22a, 22b, 22d-p 22w, 22x | **23a-p 23w, 23x** | **3a-p 3w, 3x**

Step 1: Following a modified reported procedure,[15] a two necked round bottomed flask, equipped with a magnetic stirrer, was charged with THF or CH_2Cl_2 (0.1 or 0.2 M),[16] DMAP (0.15 mmol, 5 mol%), the tertiary alcohol **22a-x** (3.00 mmol, 1.00 equiv) and triethylamine (1.05 - 1.2 equiv) were then added. Ethyl 2-chloro-2-oxoacetate (1.05 - 1.2 equiv) was then added dropwise and giving a yellowish solution. The reaction was then stirred for 1 h – 2 h at room temperature. Upon full conversion of the alcohol, indicated by TLC analysis, the reactions were quenched with sat. aq. NH_4Cl. The layers were then separated and the organic layer was then washed twice with brine (ca. 10 mL). The organic layer was then dried over Na_2SO_4 and filtered. A solid deposit for flash chromatography was prepared: (ca. 5-7 g SiO_2) concentrated under reduced pressure. The compound was purified by flash chromatography (SiO_2, pentane:EtOAc 9:1, 4:1, *p*-Anisaldehyde stain blue, green or purple spots) affording the desired alkyl ethyl oxalate **23a-x**.

Step 2: Following a modified reported procedure,[13] a round-bottom flask was charged with ethyl oxoacetate **23a-x** (1.75 mmol, 1.00 equiv) followed by the addition of THF (1 M). To this solution, a 1 M stock solution of aq. CsOH (1.7 mmol, 1.00 equiv) was added dropwise (ca. 2 min). The mixture was stirred vigorously for 5 min at room temperature, then concentrated immediately under reduced pressure (T = 55°C - 60 °C: P = 300 mbar to 20 mbar).[17] The resulting solid was then dried under high vacuum for at least 4 hours affording a dry (rarely hygroscopic, some are soap-like) cesium salt **3a-x**.

Synthetic and characterization data for alkyl ethyl oxalate intermediates 23a-x and cesium salts 3a-x

*Ethyl 2-(2-methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**23a**)*



23a was synthesized following step 1 of general *procedure D* in THF (90 mL, 0.1 M) using 2-methyl-4-phenylbutan-2-ol (**22a**, 1.6 mL, 9.1 mmol, 1 equiv), DMAP (0.055 g, 0.46 mmol, 5 mol%), triethylamine (1.3 mL, 9.6 mmol, 1.05 equiv) and ethyl chloro-oxoacetate (1.1 mL, 9.6 mmol, 1.05 equiv).

Column chromatography (SiO_2, pentane:EtOAc 85:15) afforded ethyl (2-methyl-4-phenylbutan-2-yl) oxalate (**23a**, 2.00 g, 7.57 mmol, 83%) as a colorless oil.

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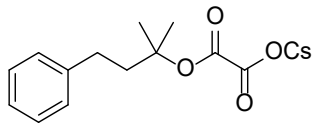
[15] Nawrat, C. C.; Jamison, C. R.; Slutskyy, Y.; MacMillan, D. W. C.; Overman, L. E. *J. Am. Chem. Soc.* **2015**, *137*, 11270–11273.

[16] We have not noticed particular changes of reactivity between THF and CH_2Cl_2 or between 0.1 M or 0.2 M, use of CH_2Cl_2 simplifies extraction.

[17] Other hydrolysis products have been observed when the reaction is left longer or triturated in diethyl ether to attempt purification.

Rf (pentane:EtOAc 9:1) = 0.5
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 2H, Ar*H*), 7.25 (d, *J* = 7.1 Hz, 3H, Ar*H*), 4.38 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$-CH$_3$), 2.79 – 2.71 (m, 2H, Ph-C*H*$_2$), 2.25 – 2.16 (m, 2H, C*H*$_2$), 1.66 (s, 6H, d*Me*), 1.43 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 157.1, 141.6, 128.5, 128.4, 126.0, 86.6, 62.8, 42.5, 30.2, 25.7, 14.0.
IR (vmax, cm-1) 3087 (w), 3062 (w), 3029 (m), 2983 (m), 2949 (m), 2872 (w), 1761 (s), 1737 (s), 1327 (m), 1188 (s), 1163 (s), 1118 (s), 912 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{20}NaO_4^+$ 287.1254; Found 287.1256.

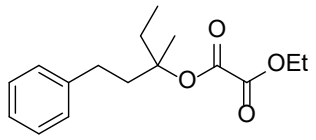
*Cesium 2-(2-methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**)*



3a was synthesized following step 2 of *general procedure D* in THF (6.5 mL, 0.1 M) using ethyl (2-methyl-4-phenylbutan-2-yl) oxalate (**23a**, 1.70 g, 6.43 mmol, 1.0 equiv) and 1 M aq. CsOH (6.4 mL, 6.4 mmol, 1.0 equiv), affording cesium 2-(2-methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 2.34 g, 6.36 mmol, 99%) as an off-white amorphous solid.

^{1}H NMR (400 MHz, D_2O) δ 7.31 (m, 5H, Ar*H*), 2.73 – 2.64 (m, 2H, ArC*H*$_2$), 2.20 – 2.11 (m, 2H, C*H*$_2$), 1.55 (s, 6H, C(C*H*$_3$)$_2$).
^{13}C NMR (101 MHz, D_2O) δ 165.2, 164.1, 142.5, 128.7, 128.5, 126.0, 86.0, 41.3, 29.7, 25.4.
HRMS (ESI/QTOF) m/z: $[M - Cs]^-$ Calcd for $C_{13}H_{15}O_4^-$ 235.0976; Found 235.0979.

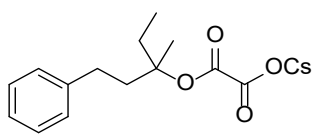
*Ethyl (3-methyl-1-phenylpentan-3-yl) oxalate (**23b**)*



23b was synthesized following step 1 of *general procedure D* in THF (60 mL, 0.1 M) using 3-methyl-1-phenylpentan-3-ol (**22b** 1.1 g, 6.0 mmol, 1.0 equiv), DMAP (73 mg, 0.60 mmol, 10 mol%), triethylamine (1.0 mL, 7.2 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.80 mL, 7.2 mmol, 1.2 equiv).
Column chromatography (SiO_2, 2% EtOAC in Pentane) afforded ethyl (3-methyl-1-phenylpentan-3-yl) oxalate (**23b**, 1.61 g, 5.78 mmol, 96 %) as a colourless oil.

Rf (pentane:EtOAc 98:2) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 – 7.24 (m, 2H, Ar*H*), 7.23 – 7.16 (m, 3H, Ar*H*), 4.32 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 2.72 – 2.59 (m, 2H, ArC*H*$_2$), 2.30 – 2.18 (m, 1H, C*H*$_2$), 2.17 – 1.99 (m, 2H, C*H*$_2$), 1.97 – 1.85 (m, 1H, C*H*$_2$), 1.57 (s, 3H, C*H*$_3$), 1.37 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 0.95 (t, *J* = 7.5 Hz, 3H, CH_2CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.7, 157.2, 141.8, 128.6, 128.5, 126.1, 89.6, 62.9, 39.7, 30.9, 30.1, 23.1, 14.1, 8.1.
IR (ν_{max}, cm^{-1}): 2979 (m), 2943 (w), 1739 (s), 1458 (m), 1323 (m), 1185 (s), 1115 (m), 1019 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{22}NaO_4^+$ 301.1410; Found 301.1412.

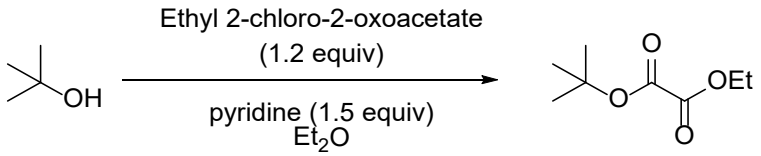
*Cesium 2-((3-methyl-1-phenylpentan-3-yl)oxy)-2-oxoacetate (**3b**)*



3b was synthesized following step 2 of *general procedure D* in THF (3.0 mL, 0.1 M) using ethyl (3-methyl-1-phenylpentan-3-yl) oxalate (**23b**, 835 mg, 3.00 mmol, 1.0 equiv) and 1 M aq. CsOH (3.0 mL, 3.00 mmol, 1.0 equiv). Cesium 2-((3-methyl-1-phenylpentan-3-yl)oxy)-2-oxoacetate (**3b**, 951 mg, 2.49 mmol, 83%) was obtained as an off-white amorphous solid.

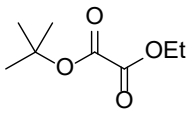
^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.29 – 7.24 (m, 2H, Ar*H*), 7.19 – 7.14 (m, 3H, Ar*H*), 2.59 – 2.54 (m, 2H, Ar-CH_2), 2.11 – 2.03 (m, 1H, CH_2), 1.97 – 1.84 (m, 2H, CH_2), 1.76 – 1.67 (m, 1H, CH_2), 1.36 (s, 3H, CH_3), 0.84 (t, *J* = 7.53 Hz, 3H, CH_2CH_3).
^{13}C NMR (101 MHz, DMSO-d_6) δ: 167.7, 163.5, 142.3, 128.3, 128.2, 125.6, 82.3, 64.8, 30.6, 29.3, 23.2, 7.8.
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{17}CsNaO_4^+$ 405.0074; Found 405.0075.

*Ethyl (tert-butyl)oxy-2-oxoacetate (**23c**)*



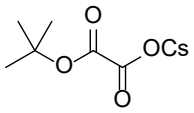
22c **23c**

Following a reported procedure,[18] ethyl 2-chloro-2-oxoacetate (3.6 mL, 32 mmol, 1.2 equiv) was added to a solution of *tert*-butanol (**22c**, 2.0 g, 27 mmol, 1.0 equiv) and pyridine (3.26 mL, 40.5 mmol) in Et_2O (100 mL) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic layer was washed with water (2 x 50 mL) and sat. aq. $NaHCO_3$ solution (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude material was purified by flash column chromatography on a short column of silica gel (1:20 Et_2O:pentane) to give *tert*-butyl ethyl oxalate (**23c**, 4.4 g, 25 mmol, 98%) as a colorless oil.



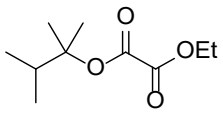
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (q, *J* = 7.1 Hz, 2H), 1.55 (s, 9H), 1.36 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 157.3, 85.0, 62.9, 27.9, 14.1. The NMR data obtained are consistent with the reported literature data.[16]

*Cesium (tert-butyl)oxy-2-oxoacetate (**3c**)*



3c was synthesized following step 2 of *general procedure D* in THF (2.1 mL, 0.1 M) using *tert*-butyl ethyl oxalate (**23c**, 0.366 g, 2.10 mmol, 1.0 equiv) and 1 M aq. CsOH (2.1 mL, 2.1 mmol, 1.0 equiv), affording cesium (*tert*-butyl)oxy-2-oxoacetate (**3c** 0.505 g, 1.82 mmol, 86%) as a colorless amorphous solid.
^{1}H NMR (400 MHz, DMSO-d_6) δ 1.37 (s, 9H, C(CH_3)$_3$).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.5, 163.5, 78.0, 27.9.
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_6H_9CsNaO_4^+$ 300.9448; Found 300.9451.

*Ethyl (2,3-dimethylbutan-2-yl)oxy-2-oxoacetate (**23d**)*

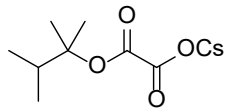


23d was synthesized following step 1 of *general procedure D* in DCM (24 mL, 0.1 M) using 2,3-dimethyl-2-butanol (**22d**, 0.30 mL, 2.4 mmol, 1.0 equiv), DMAP (30 mg, 0.24 mmol, 10 mol%), triethylamine (0.35 mL, 2.5 mmol, 1.05 equiv) and ethyl chloro-oxoacetate (0.3 mL, 2.5 mmol, 1.05 equiv).
Column chromatography (SiO_2, pentane:EtOAc 9:1) afforded ethyl (2,3-dimethylbutan-2-yl) oxalate (**23d**, 0.340 g, 1.68 mmol, 70%).

[18] Xu, Y.; McLaughlin, M.; Bolton, E. N.; Reamer, R. A. *J. Org. Chem.* **2010**, *75*, 8666–8669.

Rf (pentane:EtOAc 9:1) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (q, *J* = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 2.27 (hept, *J* = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 1.49 (s, 6H, OC(C*H*$_3$)$_2$), 1.35 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 0.94 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 157.3, 90.4, 62.8, 36.3, 22.5, 17.4, 14.1.
IR (ν_{max}, cm^{-1}) 2995 (m), 2983 (m), 2962 (w), 2946 (w), 2891 (w), 2878 (w), 2840 (w), 1763 (s), 1737 (s), 1467 (m), 1371 (m), 1324 (s), 1191 (s), 1130 (s), 1094 (s), 1017 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{18}NaO_4^+$ 225.1097; Found 225.1099.

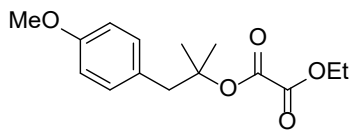
*Cesium (2,3-dimethylbutan-2-yl)oxy-2-oxoacetate (**3d**)*



3d was synthesized following step 2 of *general procedure D* in THF (1.0 mL, 0.1 M) using ethyl (2,3-dimethylbutan-2-yl) oxalate (**23d**, 0.200 g, 0.989 mmol, 1.0 equiv) and 1 M aq. CsOH (0.99 mL, 0.99 mmol, 1.0 equiv), affording cesium (2,3-dimethylbutan-2-yl)oxy-2-oxoacetate (**3d**, 137 mg, 0.447 mmol, 45%) as a colorless amorphous solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 2.22 (hept, *J* = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 1.30 (s, 6H, OC(C*H*$_3$)$_2$), 0.84 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.6, 163.6, 83.0, 35.3, 22.7, 17.1.
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_8H_{13}CsNaO_4^+$ 328.9761; Found 328.9768.

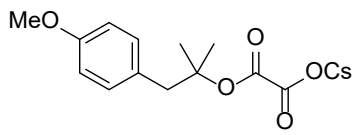
*Ethyl (1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**23e**)*



23e was synthesized following step 1 of *general procedure D* in DCM (30 mL, 0.1 M) using 1-(4-methoxyphenyl)-2-methylpropan-2-ol (**22e**, 500 mg, 2.77 mmol, 1.0 equiv), DMAP (33 mg, 0.28 mmol, 10 mol%), triethylamine (0.40 mL, 2.9 mmol, 1.05 equiv) and ethyl chloro-oxoacetate (0.30 mL, 2.9 mmol, 1.05 equiv).
Column chromatography (SiO_2, pentane:EtOAc 4:1) afforded ethyl (1-(4-methoxyphenyl)-2-methylpropan-2-yl) oxalate (**23e**, 270 mg, 0.963 mmol, 35%) as a pale-yellow oil.

Rf (pentane:EtOAc 4:1) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H, Ar*H*), 6.87 – 6.79 (m, 2H, Ar*H*), 4.32 (q, *J* = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 3.79 (s, 3H, OC*H*$_3$), 3.03 (s, 2H, ArC*H*$_2$), 1.53 (s, 6H (C*H*$_3$)$_2$), 1.38 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 158.6, 157.2, 131.8, 128.5, 113.6, 86.8, 62.9, 55.3, 46.1, 25.4, 14.1.
IR (ν_{max}, cm^{-1}) 2995 (m), 2985 (m), 2953 (m), 2937 (m), 2909 (m), 2837 (m), 1761 (s), 1738 (s), 1612 (m), 1513 (s), 1465 (m), 1370 (m), 1321 (s), 1247 (s), 1189 (s), 1177 (s), 1164 (s), 1034 (s), 1019 (s), 851 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{20}NaO_5^+$ 303.1203; Found 303.1206.

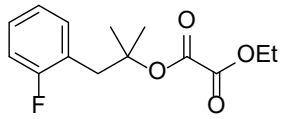
*Cesium (1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3e**)*



3e was synthesized following step 2 of *general procedure D* in THF (0.7 mL, 0.1 M) using ethyl (1-(4-methoxyphenyl)-2-methylpropan-2-yl) oxalate (**23e**, 0.20 g, 0.71 mmol, 1.0 equiv) and 1 M aq. CsOH (0.7 mL, 0.7 mmol, 1.0 equiv), affording cesium (1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3e**, 251 mg, 0.653 mmol, 92%) as a coloroless amorphous solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.18 – 7.11 (m, 2H, Ar*H*), 6.85 – 6.78 (m, 2H, Ar*H*), 3.72 (s, 3H, OCH_3), 2.95 (s, 2H, ArCH_2), 1.31 (s, 6H, (CH_3)$_2$).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.7, 163.3, 157.7, 131.5, 129.3, 113.2, 80.2, 54.9, 44.5, 25.8.
HRMS (ESI/QTOF) m/z: $[M - Cs]^-$ Calcd for $C_{13}H_{15}O_5^-$ 251.0925; Found 251.0936.

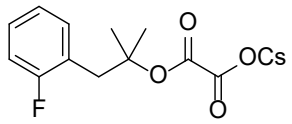
*Ethyl (1-(2-fluorophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**23f**)*



23f was synthesized following step 1 of *general procedure D* in DCM (30 mL, 0.1 M) using 1-(2-fluorophenyl)-2-methylpropan-2-ol (**22f**, 500 mg, 2.97 mmol, 1.0 equiv), DMAP (36 mg, 0.30 mmol, 10 mol%), triethylamine (0.44 mL, 3.1 mmol, 1.05 equiv) and ethyl chloro-oxoacetate (0.35 mL, 3.1 mmol, 1.05 equiv).
Column chromatography (SiO_2, pentane:EtOAc 9:1 to 8:2) afforded ethyl (1-(4-fluorophenyl)-2-methylpropan-2-yl) oxalate (**23f**, 467 mg, 1.74 mmol, 59%) as a colorless oil.

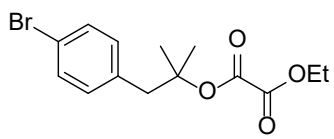
Rf (pentane:EtOAc 9:1) = 0.35.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (td, *J* = 7.6, 1.8 Hz, 1H, Ar*H*), 7.26 – 7.20 (m, 1H, Ar*H*), 7.12 – 6.99 (m, 2H, Ar*H*), 4.32 (q, *J* = 7.2 Hz, 2H, OCH_2CH$_3$), 3.16 (d, *J* = 1.4 Hz, 2H, ArCH_2), 1.57 (d, *J* = 1.0 Hz, 6H, (CH_3)$_2$), 1.38 (t, *J* = 7.2 Hz, 3H, OCH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 160.4, 157.8 (d, *J* = 141.6 Hz), 133.2 (d, *J* = 4.4 Hz), 128.8 (d, *J* = 8.2 Hz), 123.9 (d, *J* = 3.5 Hz), 123.5 (d, *J* = 15.7 Hz), 115.4 (d, *J* = 23.0 Hz), 86.6, 62.9, 39.3, 25.4, 14.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -115.9.
IR (ν_{max}, cm^{-1}) 3004 (m), 2989 (m), 2965 (w), 2938 (m), 2899 (w), 1764 (s), 1737 (s), 1495 (m), 1456 (m), 1372 (m), 1319 (m), 1233 (s), 1190 (s), 1172 (s), 1120 (s), 759 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{17}FNaO_4^+$ 291.1003; Found 291.1002.

*Cesium (1-(2-fluorophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3f**)*



3f was synthesized following step 2 of *general procedure D* in THF (1.5 mL, 0.1 M) using ethyl (1-(2-fluorophenyl)-2-methylpropan-2-yl) oxalate (**23f**, 0.40 g, 1.5 mmol, 1.0 equiv) and 1 M aq. CsOH (1.5 mL, 1.5 mmol, 1.0 equiv), affording cesium (1-(2-fluorophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3f**, 469 mg, 1.26 mmol, 84%) as a coloroless amorphous solid.
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 (td, *J* = 7.7, 1.9 Hz, 1H, Ar*H*), 7.33 – 7.23 (m, 1H, Ar*H*), 7.19 – 7.06 (m, 2H, Ar*H*), 3.08 (s, 2H, ArCH_2), 1.34 (d, *J* = 1.0 Hz, 6H, (CH_3)$_2$).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.6, 163.1, 160.9 (d, *J* = 243.4 Hz), 133.1 (d, *J* = 4.4 Hz), 128.5 (d, *J* = 8.2 Hz), 124.0 (d, *J* = 4.0 Hz), 124.0, 114.9 (d, *J* = 22.9 Hz), 80.0, 37.5, 25.7.
^{19}F NMR (376 MHz, DMSO-d_6) δ -116.6.
HRMS (ESI/QTOF) m/z: $[M - Cs]^-$ Calcd for $C_{12}H_{12}FO_4^-$ 239.0725; Found 239.0719.

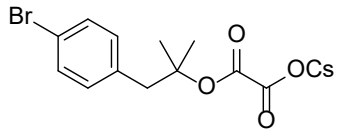
*Ethyl (1-(4-bromophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**23g**)*



23g was synthesized following step 1 of *general procedure D* in DCM (20 mL, 0.1 M) using 1-(4-bromophenyl)-2-methylpropan-2-ol (**22g**, 500 mg, 2.18 mmol, 1.0 equiv), DMAP (27 mg, 0.22 mmol, 10 mol%), triethylamine (0.30 mL, 2.4 mmol, 1.1 equiv) and ethyl chloro-oxoacetate (0.30 mL, 2.4 mmol, 1.1 equiv).
Column chromatography (SiO_2, pentane:EtOAc 9:1 to 8:2) afforded ethyl (1-(4-bromophenyl)-2-methylpropan-2-yl) oxalate (**3g** 461 mg, 1.40 mmol, 64%).

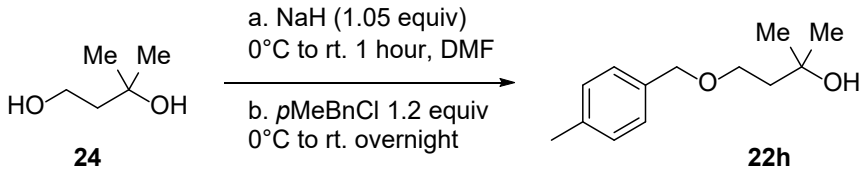
Rf (pentane:EtOAc 4:1) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 2H, Ar*H*), 7.16 – 7.09 (m, 2H, Ar*H*), 4.32 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 3.03 (s, 2H, ArCH_2), 1.53 (s, 6H, (CH_3)$_2$), 1.38 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 157.0, 135.4, 132.5, 131.3, 121.0, 86.1, 63.0, 46.5, 25.4, 14.1.
IR (ν_{max}, cm^{-1}) 3015 (w), 3002 (w), 2977 (w), 2934 (w), 2844 (w), 1760 (s), 1738 (s), 1490 (m), 1321 (m), 1188 (s), 1160 (s), 1115 (s), 1073 (m), 1012 (s), 796 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{17}{}^{79}BrNaO_4{}^+$ 351.0202; Found 351.0199.

*Cesium (1-(4-bromophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3g**)*

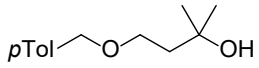


3g was synthesized following step 2 of *general procedure D* in THF (0.94 mL, 0.1 M) using ethyl (1-(4-bromophenyl)-2-methylpropan-2-yl) oxalate (**23g**, 310 mg, 0.941 mmol, 1.0 equiv) and 1 M aq. CsOH (0.94 mL, 0.94 mmol, 1.0 equiv), affording cesium (1-(4-bromophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3g**, 89 mg, 0.20 mmol, 22%) as a coloroless amorphous solid.
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.32 (m, 2H, Ar*H*), 7.32 – 7.10 (m, 2H, Ar*H*), 3.01 (s, 2H, ArCH_2), 1.32 (s, 6H, (CH_3)$_2$).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.7, 163.1, 136.9, 132.8, 130.6, 119.5, 79.7, 44.5, 25.9.
HRMS (ESI/QTOF) m/z: $[M - Cs]^-$ Calcd for $C_{12}H_{12}{}^{79}BrO_4{}^-$ 298.9924; Found 298.9914.

*4-Methylbenzylation of 3-methylbutane-1,3-diol (**22h**)*

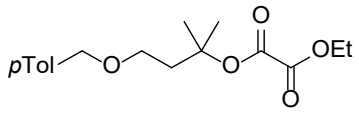


An oven dried 25 mL flask, equipped with a magnetic stirring bar, was flushed with nitrogen then charged with 3-methylbutane-1,3-diol (**24**, 0.26 mL, 2.4 mmol, 1.0 equiv) and anhydrous DMF (12.5 mL, 0.2 M). The solution was cooled to 0 °C and NaH (60% oil dispersion, 102 mg, 2.56 mmol, 1.05 equiv) was added portion-wise under nitrogen. The latter solution was stirred for 1 h at room temperature. The solution was cooled back down to 0 °C and 1-(chloromethyl)-4-methylbenzene (411 mg, 2.92 mmol, 1.2 equiv) was added under nitrogen. The reaction was left to warm up to RT slowly and was stirred overnight. The reaction was quenched with sat. aq. NH_4Cl (5 mL) then diluted with water (10 mL) and CH_2Cl_2 (15 mL). The layers were separated, and the aqueous layer was washed with CH_2Cl_2 (15 mL). The organic layers were combined and washed with a (sat. aq. NaCl):water (1:1) solution (15 mL) three times. The organic layers were then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude oil was purified by column chromatography (SiO_2, pentane:EtOAc 9:1 to 8:2) affording 2-methyl-4-((4-methylbenzyl)oxy)butan-2-ol (**22h**, 297 mg, 1.43 mmol, 59%) as a colorless oil with some trace impurities. After ^{1}H NMR and HRMS confirmation, the compound was used directly in next step with no further purification or analyses.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.15 (d, *J* = 7.8 Hz, 2H, Ar*H*), 4.48 (s, 2H, ArCH_2), 3.70 (t, *J* = 5.9 Hz, 2H, CH_2), 3.14 (bs, 1H, OH), 2.34 (s, 3H, ArCH_3), 1.79 (t, *J* = 5.9 Hz, 2H, CH_2), 1.23 (s, 6H, (CH_3)$_2$).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}NaO_2{}^+$ 231.1356; Found 231.1358.

*Ethyl (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl)oxy-2-oxoacetate (**23h**)*

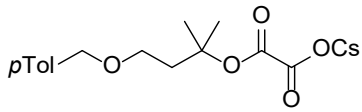


23h was synthesized following step 1 of *general procedure D* in THF (11 mL, 0.1 M) using 2-methyl-4-((4-methylbenzyl)oxy)butan-2-ol (**22h**, 220 mg, 1.06 mmol, 1.0 equiv), DMAP (13 mg, 0.11 mmol, 10 mol%), triethylamine (0.16 mL, 1.2 mmol, 1.1 equiv) and ethyl chloro-oxoacetate (0.16 mL, 1.2 mmol, 1.1 equiv).

Column chromatography (SiO_2, pentane:EtOAc 9:1 to 8:2) afforded ethyl (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl) oxalate (**23h**, 224 mg, 0.726 mmol, 69%).

Rf (pentane:EtOAc 9:1) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.18 – 7.11 (m, 2H, Ar*H*), 4.44 (s, 2H, ArCH_2), 4.28 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 3.59 (t, *J* = 6.6 Hz, 2H, CH_2), 2.34 (s, 3H, ArCH_3), 2.19 (t, *J* = 6.6 Hz, 2H, CH_2), 1.57 (s, 6H, (CH_3)$_2$), 1.34 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 157.2, 137.4, 135.3, 129.2, 127.8, 86.1, 73.0, 66.0, 62.9, 39.9, 26.3, 21.3, 14.1.
IR (ν_{max}, cm^{-1}) 3048 (m), 3016 (m), 2991 (m), 2929 (m), 2876 (m), 2860 (m), 1760 (m), 1737 (s), 1370 (m), 1325 (m), 1187 (s), 1134 (s), 1112 (s), 1096 (s), 1018 (m), 802 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{24}NaO_5^+$ 331.1516; Found 331.1518.

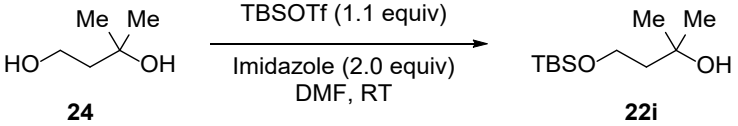
*Cesium (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl)oxy-2-oxoacetate (**3h**)*



3h was synthesized following step 2 of *general procedure D* in THF (0.6 mL, 0.1 M) using ethyl (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl) oxalate (**23h**, 0.19 g, 0.60 mmol, 1.0 equiv) and 1 M aq. CsOH (0.6 mL, 0.6 mmol, 1.0 equiv), affording cesium (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl)oxy-2-oxoacetate (**3h**, 233 mg, 0.565 mmol, 94%) as a coloroless amorphous solid.

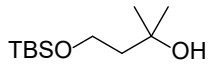
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.23 – 7.17 (m, 2H, Ar*H*), 7.14 (d, *J* = 7.9 Hz, 2H, Ar*H*), 4.38 (s, 2H, ArCH_2), 3.54 – 3.45 (m, 2H, CH_2), 2.28 (s, 3H, ArCH_3), 2.01 (t, *J* = 7.1 Hz, 2H, CH_2), 1.37 (s, 6H, (CH_3)$_2$).
^{13}C NMR (101 MHz, DMSO-d_6) δ 168.0, 163.7, 136.9, 136.0, 129.3, 128.0, 79.6, 72.3, 66.3, 30.2 26.9, 21.2.
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{19}CsNaO_5^+$ 435.0179; Found 435.0183.

*4-((tert-butyldimethylsilyl)oxy)-2-methylbutan-2-ol (**22i**)*



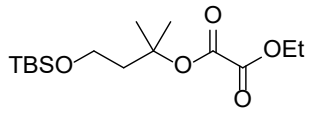
24 **22i**

To a solution of 3-methylbutane-1,3-diol (**24**, 500 mg, 4.80 mmol, 1.00 equiv) and 1H-imidazole (654 mg, 9.60 mmol, 2.00 equiv) in *N,N*-dimethylformamide (25 mL), TBSOTf (1.4 g, 1.2 mL, 5.3 mmol, 1.1 equiv) was added dropwise. The reaction mixture was stirred at room temperature until TLC showed full conversion of the starting material. DCM and a 1:1 solution of brine and water were added, the layers were separated and the organic layer was washed with half brine (2x), dried over MgSO4 and solvent removed *in vacuo*. The crude was purified by flash chromatography (SiO_2, 5% EtOAc in pentane) affording 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-ol (**22i**, 950 mg, 4.35 mmol, 91% yield) as a pale yellow oil. The NMR data was collected and the compound was used in the next step without further analyses.



Rf (pentane:EtOAc 95:5) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.91 (t, *J* = 5.8 Hz, 2H, OCH_2), 3.83 (bs, 1H, O*H*), 1.70 (t, *J* = 5.8 Hz , 2H, CH_2), 1.24 (s, 6H, C(CH_3)$_2$), 0.90 (s, 9H, C(CH_3)$_3$), 0.09 (s, 6H, Si(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 71.0, 61.1, 43.0, 29.4, 26.0, 18.2, -5.5.

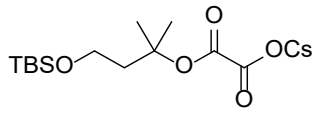
*4-((tert-Butyldimethylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**23i**)*



23i was synthesized following step 1 of *general procedure D* in THF (25 mL, 0.1 M) using 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-ol (**22i**, 500 mg, 2.30 mmol, 1.0 equiv), DMAP (28 mg, 0.23 mmol, 10 mol%), triethylamine (0.40 mL, 2.8 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.30 mL, 2.8 mmol, 1.2 equiv). Column chromatography (SiO_2, 2% EtOAc in Pentane) afforded 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**23i**, 517 mg, 1.62 mmol, 71 %) as a yellow oil.

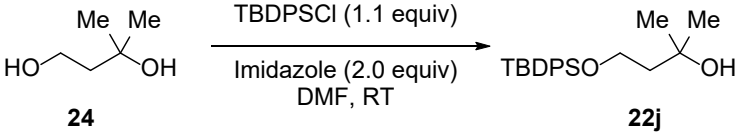
Rf (pentane:EtOAc 98:2) = 0.2.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (q, *J* = 7.2 Hz, 2H, COOCH_2), 3.75 (t, *J* = 6.7 Hz, 2H, OCH_2), 2.09 (t, *J* = 6.7 Hz, 2H, CH_2), 1.57 (s, 6H, C(CH_3)$_2$), 1.36 (t, *J* = 7.2 Hz, 3H, COOCH_3), 0.88 (s, 9H, C(CH_3)$_3$), 0.05 (s, 6H, Si(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 157.1, 86.4, 62.9, 59.0, 43.0, 26.3, 26.0, 18.4, 14.1, -5.3.
IR (ν_{max}, cm^{-1}): 2944 (m), 2891 (m), 2863 (m), 1744 (s), 1468 (m), 1323 (m), 1256 (m), 1190 (s), 1133 (s), 1098 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{30}NaO_5Si^+$ 341.1755; Found 341.1752.

*Cesium 2-((4-((tert-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**3i**)*



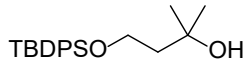
3i was synthesized following step 2 of *general procedure D* in THF (1.1 mL, 0.1 M) using 4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**23i**, 350 mg, 1.10 mmol, 1.0 equiv) and 1 M aq. CsOH (1.1 mL, 1.1 mmol, 1.0 equiv). Cesium 2-((4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**3i**, 450 mg, 1.07 mmol, 97 %) was obtained as an off-white amorphous solid.
^{1}H NMR (400 MHz, DMSO) δ 3.65 (t, *J* = 7.2 Hz, 2H, OCH_2), 1.94 (t, *J* = 7.2 Hz, 2H, CH_2), 1.37 (s, 6H, C(CH_3)$_2$), 0.85 (s, 9H, C(CH_3)$_3$), 0.03 (s, 6H, Si(CH_3)$_2$).
^{13}C NMR (101 MHz, DMSO) δ 167.5, 163.3, 79.1, 58.7, 42.7, 26.5, 25.8, 17.8, -5.3.
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{25}CsNaO_5Si^+$ 445.0418; Found 445.0418.

*4-((tert-butyldiphenylsilyl)oxy)-2-methylbutan-2-ol (**22j**)*



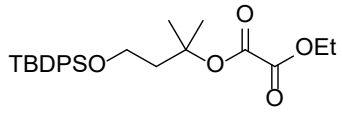
To a solution of 3-methylbutane-1,3-diol (**24**, 500 mg, 4.80 mmol, 1.00 equiv) and 1H-imidazole (654 mg, 9.60 mmol, 2.00 equiv) in *N,N*-dimethylformamide (25.0 mL), TBDPSCl (1.45 g, 1.37 mL, 5.28 mmol, 1.10 equiv) was added dropwise. The reaction mixture was stirred at room temperature until TLC showed full conversion of the starting material. DCM and half brine were added, the layers were separated and the organic layer was washed with half brine (2x), dried over MgSO4 and solvent

removed under vacuo. The crude product was purified by flash chromatography (SiO_2, 5% EtOAc in pentane) affording 4-((*tert*-butyldiphenylsilyl)oxy)-2-methylbutan-2-ol (**22j**, 1.64 g, 4.80 mmol, 100% yield) as a fain yellow oil. The NMR data was collected and the compound was used in the next step without further analyses.



Rf (pentane:EtOAc 95:5) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 – 7.65 (m, 4H, Ar*H*), 7.47 – 7.36 (m, 6H, Ar*H*), 3.90 (t, *J* = 5.8 Hz, 2H, OCH_2), 3.74 (bs, 1H, O*H*), 1.75 (t, *J* = 5.7 Hz, 2H, CH_2), 1.27 (s, 6H, C(CH_3)$_2$OH), 1.05 (s, 9H, C(CH_3)$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 132.9, 130.03, 128.0, 71.1, 62.2, 43.2, 29.5, 26.9, 19.1.

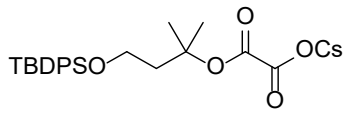
*4-((tert-Butyldiphenylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**23j**)*



23j was synthesized following step 1 of *general procedure D* in THF (30 mL, 0.1 M) using 4-((*tert*-butyldiphenylsilyl)oxy)-2-methylbutan-2-ol (**22j**, 1.00 g, 2.92 mmol, 1.0 equiv), DMAP (36 mg, 0.29 mmol, 10 mol%), triethylamine (0.50 mL, 3.5 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.40 mL, 3.5 mmol, 1.2 equiv).
Column chromatography (SiO_2, 2% EtOAc in Pentane) afforded 4-((*tert*-butyldiphenylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**23j**, 1.06g, 2.40 mmol, 82 %) as a pale yellow oil.

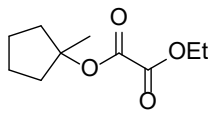
Rf (pentane:EtOAc 98:2) = 0.15.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 – 7.64 (m, 4H, Ar*H*), 7.43 – 7.35 (m, 6H, Ar*H*), 4.27 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.78 (t, *J* = 6.7 Hz, 2H, OCH_2), 2.16 (t, *J* = 6.7 Hz, 2H, CH_2), 1.55 (s, 6H, C(CH_3)$_2$), 1.32 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.04 (s, 9H, C(CH_3)$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.5, 157.0, 135.6, 133.6, 129.7, 127.7, 86.2, 62.8, 59.8, 42.6, 26.8, 26.2, 19.1, 13.9.
IR (ν_{max}, cm^{-1}): 3064 (w), 2939 (m), 2862 (m), 1743 (s), 1323 (m), 1190 (s), 1104 (s), 823 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{34}NaO_5Si^+$ 465.2068; Found 465.2076.

*Cesium 2-((4-((tert-butyldiphenylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**3j**)*



3j was synthesized following step 2 of *general procedure D* in THF (1.1 mL, 0.1 M) using 4-((*tert*-butyldiphenylsilyl)oxy)-2-methylbutan-2-yl ethyl oxalate (**23j**, 500 mg, 1.13 mmol, 1.0 equiv) and 1 M aq. CsOH (1.1 mL, 1.1 mmol, 1.0 equiv). Cesium 2-((4-((*tert*-butyldiphenylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**3j**, 600 mg, 1.10 mmol, 97 %) was obtained as an off-white amorphous solid.
^{1}H NMR (400 MHz, DMSO) δ 7.65 – 7.58 (m, 4H, Ar*H*), 7.48 – 7.41 (m, 6H, Ar*H*), 3.74 (t, *J* = 7.1 Hz, 2H, OCH_2), 2.03 (t, *J* = 7.1 Hz, 2H, CH_2), 1.34 (s, 6H, CH_3), 0.99 (s, 9H, C(CH_3)$_3$).
^{13}C NMR (101 MHz, DMSO) δ 167.5, 163.2, 135.0, 133.2, 129.8, 127.9, 79.1, 59.9, 42.7, 26.7, 26.4, 18.7.
HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{30}CsO_5Si^+$ 547.0912; Found 547.0908.

*Ethyl 2-(1-methylcyclopent-1-yl)oxy-2-oxoacetate (**23k**)*



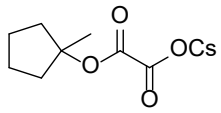
23k was synthesized following step 1 of *general procedure D* in THF (16 mL, 0.2 M) using 1-methylcyclopentan-1-ol (**22k**, 337 mg, 3.36 mmol, 1.0 equiv), DMAP (21 mg, 0.17 mmol, 5 mol%),

triethylamine (0.56 mL, 11 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.45 mL, 11 mmol, 1.2 equiv).

Column chromatography (SiO_2, pentane:EtOAc 9:1 to 8:2) afforded ethyl (1-methylcyclopentan-1-yl) oxalate (**23k**, 596 mg, 2.98 mmol, 89%).

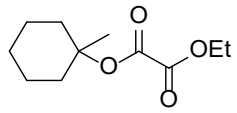
Rf (pentane:EtOAc 9:1) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (q, *J* = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 2.21 (ttd, *J* = 10.4, 4.8, 2.4 Hz, 2H, C*H*$_2$), 1.83 – 1.71 (m, 4H, C*H*$_2$), 1.71 – 1.58 (m, 5H, C*H*$_2$ + C*H*$_3$), 1.36 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 157.5, 94.2, 62.9, 39.0, 24.1, 23.8, 14.1.
IR (ν_{max}, cm^{-1}) 2984 (m), 2942 (m), 2910 (w), 1762 (s), 1737 (s), 1370 (m), 1324 (m), 1201 (s), 1139 (s), 1017 (m), 846 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{16}NaO_4^+$ 223.0941; Found 223.0935.

*Cesium 2-(1-methylcyclopent-1-yl)oxy-2-oxoacetate (**3k**)*



3k was synthesized following step 2 of *general procedure D* in THF (1.2 mL, 0.1 M) using ethyl (1-methylcyclopent-1-yl) oxalate (**23k**, 0.37 g, 1.8 mmol, 1.0 equiv) and 1 M aq. CsOH (1.8 mL, 1.8 mmol, 1.0 equiv), affording cesium 2-(1-methylcyclopent-1-yl)oxy-2-oxoacetate (**3k**, 0.541 g, 1.78 mmol, 97%).
^{1}H NMR (400 MHz, DMSO) δ 1.97 (dddt, *J* = 7.1, 5.3, 3.0, 1.8 Hz, 2H, C*H*$_2$), 1.72 – 1.49 (m, 6H, C*H*$_2$), 1.46 (s, 3H, C*H*$_3$).
^{13}C NMR (101 MHz, DMSO) δ 167.5, 163.5, 87.3, 24.3, 23.3, 14.2. Consistent with reported data.[15]

*Ethyl 2-(1-methylcyclohex-1-yl)oxy-2-oxoacetate (**23l**)*

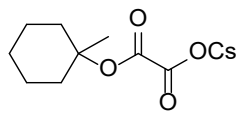


23l was synthesized following step 1 of *general procedure D* in THF (90 mL, 0.1 M) using 1-methylcyclohexan-1-ol (**22l**, 1.1 mL, 8.8 mmol, 1.0 equiv), DMAP (107 mg, 0.876 mmol, 0.1 equiv) triethylamine (1.50 mL, 10.5 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (1.20 mL, 10.5 mmol, 1.2 equiv).

Column chromatography (SiO_2, 2% EtOAc in Pentane) afforded ethyl (1-methylcyclohexyl) oxalate (**23l**, 1.18 g, 5.51 mmol, 63%) as a pale yellow oil.

Rf (pentane:EtOAc 98:2) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.30 (q, *J* = 7.12 Hz, 2H, CO_2C*H*$_2$), 2.21 – 2.18 (m, 2H, C*H*$_2$), 1.58 – 1.44 (m, 8 H, C*H*$_2$), 1.55 (s, 3H, C*H*$_3$), 1.35 (t, *J* = 7.12 Hz, 3 H, CO_2CH_2C*H*$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.8, 157.2, 86.7, 62.8, 36.4, 25.3, 25.1, 22.1, 14.1.
IR (ν_{max}, cm^{-1}): 2979 (w), 2938 (m), 2864 (w), 1743 (s), 1454 (w), 1326 (m), 1192 (s), 1146 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{18}NaO_4^+$ 237.1097; found 237.1094

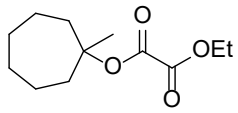
*Ethyl 2-(1-methylcyclohex-1-yl)oxy-2-oxoacetate (**3l**)*



3l was synthesized following step 2 of *general procedure D* in THF (5.0 mL, 0.1 M) using ethyl (1-methylcyclohexyl) oxalate (**23l**, 1.07 g, 5.00 mmol, 1.0 equiv) and 1 M aq. CsOH (5.0 mL, 5.0 mmol, 1.0 equiv). Affording cesium 2-((1-methylcyclohexyl)oxy)-2-oxoacetate (**3l**, 1.4 g, 4.4 mmol, 88%) as a coloroless amorphous solid.

^{1}H NMR (400 MHz, DMSO-d6) δ: 2.08 – 1.96 (m, 2H, CH_2), 1.56 – 1.43 (m, 3H, CH_2), 1.43 – 1.29 (m, 7H, CH_2 + CH_3), 1.27 – 1.18 (m, 1H, CH_2).
^{13}C NMR (101 MHz, DMSO) δ: 167.7, 163.6, 79.2, 36.2, 25.3, 25.0, 21.5.
HRMS (ESI/QTOF) m/z: [M - Cs]$^-$ Calcd for $C_9H_{13}O_4^-$ 185.0819; Found 185.0819.

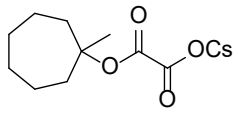
*Ethyl 2-(1-methylcycloheptan-1-yl)oxy-2-oxoacetate (**23m**)*



23m was synthesized following step 1 of *general procedure D* in DCM (35 mL, 0.1 M) using 1-methylcycloheptan-1-ol (**22m**, 0.30 mL, 3.4 mmol, 1 equiv), DMAP (42 mg, 0.34 mmol, 10 mol%), triethylamine (0.52 mL, 3.7 mmol, 1.1 equiv) and ethyl chloro-oxoacetate (0.42 mL, 3.8 mmol, 1.1 equiv).
Column chromatography (SiO_2, pentane:EtOAc 9:1) afforded ethyl (1-methylcycloheptan-1-yl) oxalate (**23m**, 0.373 g, 1.84 mmol, 54%).

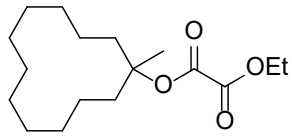
Rf (pentane:EtOAc 9:1) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 2.20 (ddd, *J* = 14.9, 8.6, 1.7 Hz, 2H, cyclic-CH_2), 1.82 (ddd, *J* = 14.7, 9.8, 1.8 Hz, 2H, cyclic-CH_2), 1.70 – 1.39 (m, 11H, cyclic-(CH_2))$_4$ + CH$_3$, 1.35 (t, *J* = 7.2 Hz, 3H, OCH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 157.3, 91.1, 62.8, 40.0, 29.5, 26.6, 22.6, 14.1.
IR (ν_{max}, cm^{-1}) 3005 (w), 2929 (m), 2858 (m), 1760 (s), 1736 (s), 1459 (m), 1446 (m), 1371 (m), 1323 (m), 1205 (s), 1186 (s), 1159 (s), 1128 (s), 861 (m).
HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{12}H_{20}NaO_4^+$ 251.1254; Found 251.1259.

*Cesium 2-(1-methylcycloheptan-1-yl)oxy-2-oxoacetate (**3m**)*



3m was synthesized following step 2 of *general procedure D* in THF (1.1 mL, 0.1 M) using ethyl (1-methylcycloheptan-1-yl) oxalate (**23m**, 0.250 g, 1.10 mmol, 1.0 equiv) and 1 M aq. CsOH (1.1 mL, 1.1 mmol, 1.0 equiv), affording cesium 2-(1-methylcycloheptan-1-yl)oxy-2-oxoacetate (**3m**, 0.332 g, 1.00 mmol, 91%). Amorphous solid.
^{1}H NMR (400 MHz, DMSO-d_6) δ 2.02 (ddd, *J* = 14.3, 8.6, 1.6 Hz, 2H, cyclic-CH_2), 1.67 (ddd, *J* = 14.4, 9.9, 1.9 Hz, 2H, cyclic-CH_2), 1.60 – 1.42 (m, 6H, cyclic-CH_2), 1.41 (s, 3H, CH_3), 1.40 – 1.28 (m, 2H, cyclic-CH_2).
^{13}C NMR (101 MHz, DMSO-d_6) δ 168.2, 164.1, 83.9, 29.3, 27.2, 22.5. 1 carbon is unresolved.

*Ethyl (1-methylcyclododecyl) oxalate **23n***

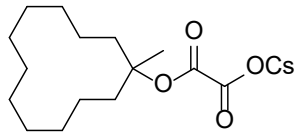


23n was synthesized following step 1 of *general procedure D* in THF (25 mL, 0.1 M) using 1-methylcyclododecan-1-ol (**22n**, 500 mg, 2.52 mmol, 1.0 equiv), DMAP (31 mg, 0.25 mmol, 10 mol%), triethylamine (0.42 mL, 3.0 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.34 mL, 3.0 mmol, 1.2 equiv).
Column chromatography (SiO_2, 20% EtOAc in Pentane) afforded ethyl (1-methylcyclododecyl) oxalate (**23n**, 1.08 g, 4.25 mmol, 71 %) as an off-white amorphous solid.

Rf (pentane:EtOAc 4:1) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (q, *J* = 7.2 Hz, 2H, CO$_2$CH_2), 2.10 – 1.98 (m, 2H, CH_2), 1.74 – 1.61 (m, 2H, CH_2), 1.55 (s, 3H, CH_3), 1.49 – 1.23 (m, 21H, CH_2 + CH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 157.1, 90.8, 62.9, 32.9, 26.2, 26.2, 24.0, 22.5, 22.0, 19.5, 14.1.

IR (ν_{max}, cm^{-1}): 2939 (s), 2861 (m), 1744 (s), 1467 (m), 1375 (m), 1325 (m), 1190 (s), 1152 (s)
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{30}NaO_4^+$ 321.2036; Found 321.2037.

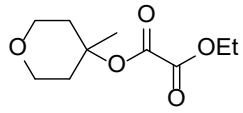
*Cesium 2-((1-methylcyclododecyl)oxy)-2-oxoacetate (**3n**)*



3n was synthesized following step 2 of *general procedure D* in THF (1.0 mL, 0.1 M) using ethyl (1-methylcyclododecyl) oxalate (**23n**, 300 mg, 1.00 mmol, 1.0 equiv) and 1 M aq. CsOH (1.0 mL, 1.00 mmol, 1.0 equiv). Cesium 2-((1-methylcyclododecyl)oxy)-2-oxoacetate (**3n**, 300 mg, 0.745 mmol, 74 %) was obtained as an off-white solid.

^{1}H NMR (400 MHz, DMSO) δ: 1.90 – 1.77 (m, 2H, CH_2), 1.56 – 1.42 (m, 2H, CH_2), 1.38 (s, 3H, CH_3), 1.34 – 1.18 (m, 18H, CH_2).
^{13}C NMR (101 MHz, DMSO) δ: 168.1, 164.0, 83.4, 33.21 26.3, 26.2, 24.4, 22.3, 22.0, 19.2.
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{25}CsNaO_4^+$ 425.0700; Found 425.0695.

*Ethyl (4-methyltetrahydro-2H-pyran-4-yl) oxalate (**23o**)*

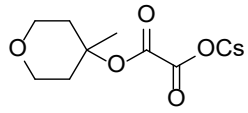


23o was synthesized following step 1 of *general procedure D* in THF (45 mL, 0.1 M) using 4-methyloxan-4-ol (**22o**, 500 mg, 4.30 mmol, 1.0 equiv), DMAP (53 mg, 0.43 mmol, 10 mol%), triethylamine (0.72 mL, 5.2 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.58 mL, 5.2 mmol, 1.2 equiv).

Column chromatography (SiO_2, 15% EtOAc in Pentane) afforded ethyl (4-methyltetrahydro-2*H*-pyran-4-yl) oxalate (**23o**, 785 mg, 3.63 mmol, 84 %) as a pale yellow oil.

Rf (pentane:EtOAc 85:15) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.33 (q, *J* = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.83 – 3.59 (m, 4H, OCH_2), 2.27 – 2.17 (m, 2H, CH_2), 1.78 (ddd, *J* = 14.6, 10.1, 5.0 Hz, 2H, CH_2), 1.62 (s, 3H, CH_3), 1.37 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.4, 157.1, 83.2, 63.7, 63.1, 36.6, 25.0, 14.1.
IR (ν_{max}, cm^{-1}): 2968 (w), 2864 (w), 1744 (s), 1462 (w), 1324 (m), 1192 (s), 1134 (s), 1023 (m).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{10}H_{16}NaO_5^+$ 239.0890; Found 239.0894.

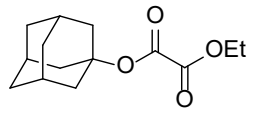
*cesium (4-methyltetrahydro-2H-pyran-4-yl) oxalate (**3o**)*



3o was synthesized following step 2 of *general procedure D* in THF (2.5 mL, 0.1 M) using ethyl (4-methyltetrahydro-2*H*-pyran-4-yl) oxalate (**23o**, 541 mg, 2.50 mmol, 1.0 equiv) and 1 M aq. CsOH (2.5 mL, 2.50 mmol, 1.0 equiv). Cesium 2-((3-methyl-1-phenylpentan-3-yl)oxy)-2-oxoacetate (**3o**, 725 mg, 2.27 mmol, 91%) was obtained as an off-white amorphous solid.

^{1}H NMR (400 MHz, DMSO) δ: 3.66 – 3.49 (m, 4H, OCH_2), 2.04 – 1.93 (m, 2H, CH_2), 1.67 – 1.53 (m, 2H, CH_2), 1.45 (s, 3H, CH_3).
^{13}C NMR (101 MHz, DMSO-d_6) δ: 167.6, 163.2, 76.5, 62.9, 36.6, 24.9.
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_8H_{11}CsNaO_5^+$ 342.9553; Found 342.9553.

*Ethyl 2-(((1S,3S)-adamantan-1-yl)oxy)-2-oxoacetate (**23p**)*

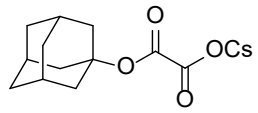


23p was synthesized following step 1 of *general procedure D* in DCM (25 mL, 0.1 M) using adamant-1-ol (**22p**, 378 mg, 2.48 mmol, 1.0 equiv), DMAP (30.4 mg, 248 mmol, 10 mol%), triethylamine (0.41 mL, 3.0 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.34 mL, 3.0 mmol, 1.2 equiv).

Column chromatography (SiO_2, 15% EtOAc in Pentane) afforded ethyl 2-(((1S,3S)-adamantan-1-yl)oxy)-2-oxoacetate (**2op**, 442 mg, 1.75 mmol, 71 %) as a pale yellow oil.

Rf (pentane:EtOac 9:1) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.31 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 2.19 (d, *J* = 2.7 Hz, 9H, ad-CH_x), 1.76 – 1.55 (m, 6H, ad-CH_x), 1.36 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 156.8, 85.1, 62.9, 41.0, 36.1, 31.1, 14.1.
IR (ν_{max}, cm^{-1}) 2911 (m), 2854 (w), 1760 (s), 1733 (s), 1176 (s), 1155 (s), 1044 (m).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{20}NaO_4^+$ 275.1254; Found 275.1256.

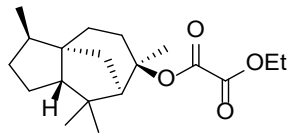
*Cesium 2-(((1S,3S)-adamantan-1-yl)oxy)-2-oxoacetate (**3p**)*



3p was synthesized following step 2 of *general procedure D* in THF (2.5 mL, 0.1 M) using ethyl 2-(((1*S*,3*S*)-adamantan-1-yl)oxy)-2-oxalate (**23p**, 252 mg, 1.00 mmol, 1.0 equiv) and 1 M aq. CsOH (2.5 mL, 2.5 mmol, 1.0 equiv). cesium 2-(((1*S*,3*S*)-adamantan-1-yl)oxy)-2-oxoacetate (**3p**, 0.32 g, 0.91 mmol, 91%) was obtained as an off-white amorphous solid.

^{1}H NMR (400 MHz, DMSO) δ: 2.12 – 2.07 (m, 3H, C*H*), 2.06 – 1.99 (m, 6H, CH_2), 1.64 – 1.59 (m, 6H, CH_2).
^{13}C NMR (101 MHz, DMSO) δ: 167.3, 163.4, 78.0, 41.0, 35.8, 30.2.
HRMS (ESI/QTOF) m/z: $[M - Cs]^-$ Calcd for $C_{12}H_{15}O_4^-$ 223.0976; Found 223.0974.

*Ethyl (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl) oxalate (**23w**)*

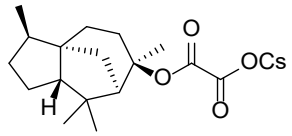


23w was synthesized following step 1 of *general procedure D* in DCM (50 mL, 0.1 M) using Cedrol (**22w**, 1.00 g, 4.46 mmol, 1.0 equiv), DMAP (0.054 g, 0.45 mmol, 10 mol%), triethylamine (0.68 mL, 4.9 mmol, 1.1 equiv) and ethyl chloro-oxoacetate (0.55 mL, 4.9 mmol, 1.1 equiv).

Column chromatography (SiO_2, pentane:EtOAc 9:1 to 8:2) afforded ethyl (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl) oxalate (**23w**, 0.343 g, 0.1.06 mmol, 24%).

Rf (pentane:EtOAc 9:1) = 0.45.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (q, *J* = 7.1 Hz, 2H, OCH_2CH$_3$), 2.46 – 2.40 (m, 1H, aliphatic-C*H* or CH_2), 2.17 (ddt, *J* = 13.6, 5.8, 1.7 Hz, 1H, aliphatic-C*H* or CH_2), 2.13 – 2.00 (m, 1H, aliphatic-C*H* or CH_2), 1.94 – 1.78 (m, 2H, aliphatic-C*H* or CH_2), 1.74 – 1.64 (m, 2H, aliphatic-C*H* or CH_2), 1.62 (d, *J* = 1.0 Hz, 3H, CH_3), 1.59 – 1.47 (m, 2H, aliphatic-C*H* or CH_2), 1.46 – 1.33 (m, 6H, aliphatic-C*H* or CH_2 + OCH$_2$CH_3), 1.32 – 1.23 (m, 1H, aliphatic-C*H* or CH_2), 1.18 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 0.84 (d, *J* = 7.1 Hz, 3H, CH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 157.1, 91.2, 62.8, 57.0, 56.8, 54.0, 43.7, 41.4, 41.2, 37.1, 33.0, 31.4, 28.5, 27.1, 25.5, 25.4, 15.6, 14.1.
IR (ν_{max}, cm^{-1}) 2990 (w), 2939 (w), 2876 (w), 1738 (s), 1373 (s), 1236 (s), 1186 (m), 1044 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{30}NaO_4^+$ 345.2036; Found 345.2029.

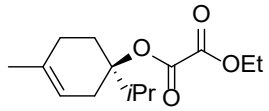
*(-)-Cedrol derived cesium oxalate: cesium (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl)oxy-2-oxoacetate (**3w**)*



3w was synthesized following step 2 of *general procedure D* in THF (0.78 mL, 0.1 M) using ethyl (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl) oxalate (**23w**, 0.250 g, 0.775 mmol, 1.0 equiv) and 1 M aq. CsOH (0.78 mL, 0.78 mmol, 1.0 equiv), affording cesium (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl)oxy-2-oxoacetate (**3w**, 0.330 g, 0.774 mmol, 100%). Amorphous white amorphous solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 2.34 (d, *J* = 5.1 Hz, 1H, aliphatic-C*H*), 1.90 – 1.71 (m, 4H, aliphatic-C*H*), 1.68 – 1.54 (m, 2H, aliphatic-CH or CH2), 1.45 (s, 4H, aliphatic-CH or CH2 + CH_3), 1.42 – 1.19 (m, 5H, aliphatic-CH or CH2), 1.16 (s, 3H, CH_3), 0.91 (s, 3H, CH_3), 0.81 (d, *J* = 7.1 Hz, 3H, CHCH_3).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.3, 163.5, 83.8, 56.4, 56.2, 53.6, 43.0, 40.7, 40.3, 36.4, 33.0, 30.6, 28.4, 27.3, 25.7, 24.9, 15.5.
HRMS (ESI/QTOF) m/z: [M - Cs]$^-$ Calcd for $C_{17}H_{25}O_4^-$ 293.1758; Found 293.1751.

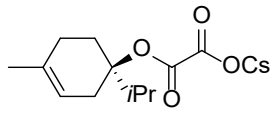
*(R)-Ethyl (1-isopropyl-4-methylcyclohex-3-en-1-yl) oxalate (**23x**)*



23x was synthesized following step 1 of *general procedure D* in THF (60 mL, 0.1 M) using (-)-terpinen-4-ol (**22x**, 1.00 mL, 6.00 mmol, 1.0 equiv), DMAP (73 mg, 0.60 mmol, 10 mol%), triethylamine (1.00 mL, 7.20 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.80 mL, 7.2 mmol, 1.2 equiv).
Column chromatography (SiO_2, 2% EtOAc in Pentane) afforded (*R*)-ethyl (1-isopropyl-4-methylcyclohex-3-en-1-yl) oxalate (**23x**, 1.08 g, 4.25 mmol, 71 %) as a pale yellow oil.

Rf (pentane:EtOAc 98:2) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.29 – 5.21 (m, 1H, C=C*H*), 4.29 (q, *J* = 7.1 Hz, 2H, CO_2CH_2), 2.71 (hept, *J* = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 2.54 – 2.43 (m, 2H, CH_2), 2.29 – 2.19 (m, 1H, CH_2), 2.11 – 1.98 (m, 1H, CH_2), 1.97 – 1.87 (m, 1H, CH_2), 1.78 – 1.68 (m, 1H, CH_2), 1.73 – 1.62 (m, 3H, CH_3), 1.34 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 0.95 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$), 0.94 (d, *J* = 6.9 Hz, 3H, CH(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.9, 157.6, 133.8, 117.2, 91.1, 62.7, 32.7, 29.9, 27.9, 27.3, 23.3, 17.7, 17.2, 14.1.
IR (ν_{max}, cm^{-1}): 2973 (m), 2933 (m), 1738 (s), 1444 (m), 1380 (m), 1324 (m), 1180 (s), 1014 (m).
HRMS (ESI/QTOF) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{22}NaO_4^+$ 277.1410; Found 277.1415.

*(-)Terpinen-4-ol derived cesium oxalate: cesium (R)-2-((1-isopropyl-4-methylcyclohex-3-en-1-yl)oxy)-2-oxoacetate (**3x**)*



3x was synthesized following step 2 of *general procedure D* in THF (2.0 mL, 0.1 M) using (*R*)-ethyl (1-isopropyl-4-methylcyclohex-3-en-1-yl) oxalate (**23x**, 509 mg, 2.00 mmol, 1.0 equiv) and 1 M aq. CsOH (2.0 mL, 2.0 mmol, 1.0 equiv). Cesium (*R*)-2-((1-isopropyl-4-methylcyclohex-3-en-1-yl)oxy)-2-oxoacetate (**3x**, 661 mg, 1.85 mmol, 92 %) was obtained as an off-white amorphous solid.
^{1}H NMR (400 MHz, DMSO) δ: 5.20 – 5.16 (m, 1H, C=C*H*), 2.66 (p, *J* = 7.0 Hz, 1H, C*H*(CH_3)$_2$), 2.40 – 2.31 (m, 1H, CH_2), 2.23 – 2.04 (m, 2H, CH_2), 2.04 – 1.90 (m, 1H, CH_2), 1.86 – 1.71 (m, 1H, CH_2), 1.60 (s, 3H, CH_3), 1.59 – 1.50 (m, 1H, CH_2), 0.86 (d, *J* = 7.0 Hz, 3H, CH(CH_3)$_2$), 0.84 (d, *J* = 7.0 Hz, 3H), CH(CH_3)$_2$).
^{13}C NMR (101 MHz, DMSO) δ: 168.1, 163.5, 132.8, 117.9, 83.3, 32.0, 29.5, 27.7, 26.7, 23.2, 17.4, 16.7.

HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{18}CsO_4^+$ 359.0254; Found 359.0260.

3. Photochemical experimental set-up

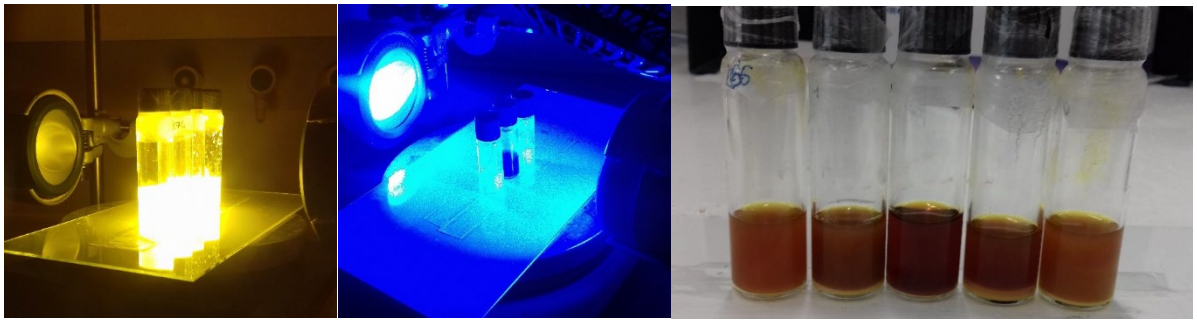
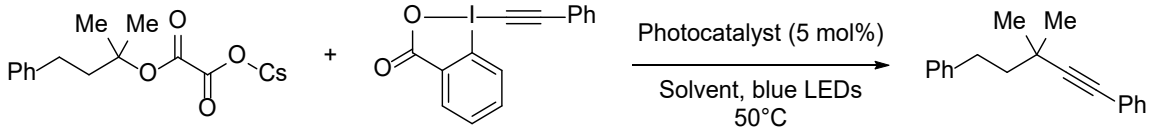


Figure S1. Left: Scope scale reactions (photo taken with a filter applied to it). Middle: optimization scale. Right: Scope scale reactions after irradiation (with PC, same appearance for PC-free reactions without)

4. Photomediated deoxygenation-alkynylation

4.1. Optimization studies method A (4CzIPN catalyzed)



3a **2a** **4a**

Experimental procedure: an oven dried dram vial (2 mL), equipped with a magnetic stirrer, was charged with the solid components following table S1: cesium oxalate **3a**, PhEBX (**2a**), photocatalyst, additive (as specified). The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), dry degassed (freeze pump thaw) solvent was added and the septum was replaced with a screw cap under a flux of Ar.[19] The reactions were placed between 2 x 440 nm Kessil lamps (at ca. 10 cm distance from both lamps (no ventilation, T = ca. 50 °C, with ventilation T = ca. 30-35°C as specified) and stirred under irradiation for 18 hours or 24 hours (as specified). The reaction was filtered through a small celite plug which was washed with CH_2Cl_2. The reaction crude was concentrated *in vacuo*, diluted with $CDCl_3$ and 1 equiv of CH_2Br_2 was added as internal standard for ^1H NMR analysis.

Table S1. Optimization pf method A

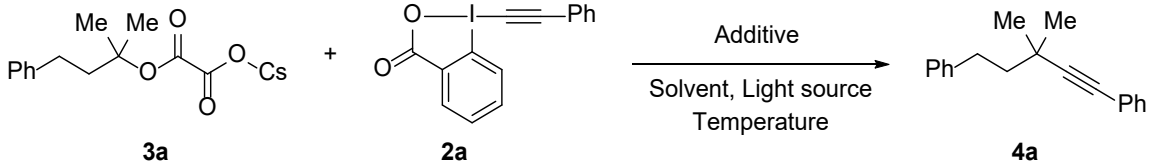
Entry	Solvent (M)	Photocatalyst	Stoichiometry (3a: 2a)	^1H NMR yield (%)
1	DMSO (0.1 M)	1a	1:1.5	52
2	MeCN (0.1 M)	1a	1:1.5	40
3	DME/DMF (0.1 M)	1a	1:1.5	70
4	DME/DMF + 10 eq H_2O (0.1 M)	1a	1:1.5	55

[19] Use of a screw cap or crimp cap is of great importance to prevent solvent evaporation as the irradiation causes an increase in temperature. When using a test-tube/septum set-up, the latter would fly off within an hour of irradiation. As shown in the optimization section DCE is not as good a solvent as CH_2Cl_2.

5	THF (0.1 M)	1a	1:1.5	22
6	DCE (0.1 M)	1a	1:1.5	67
7	DCM (0.1 M)	1a	1:1.5	75
8	DCM (0.1 M)	1b	1:1.5	75
9	DCM (0.1 M)	1c	1:1.5	50
10	DCM (0.1 M)	DCA	1:1.5	55
11	DCM (0.1 M)	MesAcr.BF_4	1:1.5	53
12	DCM (0.1 M)	$[Ru(bpy)_3]PF_6$	1:1.5	<10% decomp
13	DCM (0.1 M)	$[Ru(bpz)_3]PF_6$	1:1.5	20
14	DCM (0.1 M)	1a	1.2:1	45
15	DCM (0.1 M)	1a	1:1	64
16	DCM (0.1 M)	1a	1::1.2	56
17	DCM (0.1 M)	1a	1:1.8	70
18	DCM (0.1 M)	1a	1:2.5	75
19	DCM (0.5 M)	1a	1:1.5	75
20	DCM (0.05 M)	1a	1:1.5	73
21	DCM (0.02 M)	1a	1:1.5	55
22[a]	DCM (0.1 M)	1a	1:1.5	65

[a]Performed with 0.3 equiv BIOAc as an additive

4.1. Optimization studies method B (Excited state PhEBX 2a)



3a **2a** **4a**

Experimental procedure: an oven dried dram vial (2 mL), equipped with a magnetic stirrer, was charged with the solid components following table S2: cesium oxalate **3a**, PhEBX (**2a**), CsOBz, Cs_2CO_3. The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), dry degassed (freeze pump thaw) solvent was added, followed by the liquid additive THF or γ-terpinene (as specified) and the septum was replaced with a screw cap under a flux of Ar.[19] The reactions were placed between 2 x 440 nm Kessil lamps (unless specified otherwise) at ca. 10 cm distance from both lamps (no ventilation, T = ca. 50 °C, with ventilation T = ca. 30-35°C as specified) and stirred under irradiation for 18 hours or 24 hours (as specified). The reaction was filtered through a small celite plug which was washed with CH_2Cl_2. The reaction crude was concentrated *in vacuo*, diluted with $CDCl_3$ and 1 equiv of CH_2Br_2 was added as internal standard for ^1H NMR analysis.

Table S2. Optimization of method B

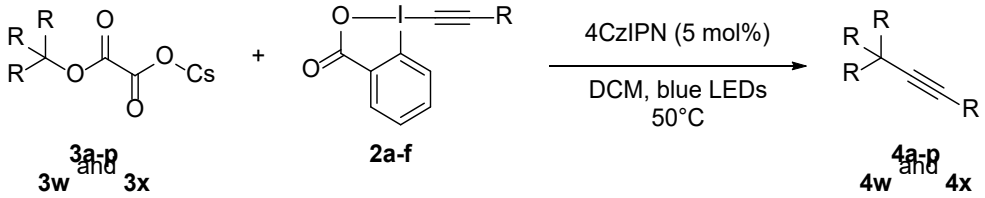
Entry	**2a (equiv)**	**Additive (equiv)**	**solvent (M)**	**T (°C)**	**λ (nm)**	**residual 3a (equiv)**	**^1H NMR yield (%)**
1	1.5	-	MeCN (0.1 M)	50	440	nd	4
2	1.5	-	MeCN:H2O (0.1 M)	50	440	nd	6
3	1.5	-	DMSO-d_6 (0.1 M)	50	440	nd	4
4	1.5	-	MeOH (0.1 M)	50	440	nd	17
5	1.5	-	DCM (0.1 M)	30-35	440	0.10	50
6[a]	1.5	-	DCM (0.1 M)	30-35	360[b]	0.10	50
7[b]	1.5	-	DCM (0.1 M)	30-35	460[c]	0.10	50

8	2.5	-	DCM (0.1 M)	30-35	440	0.40	57
9[c]	2.5	-	DCM (0.1 M)	30-35	440	0.20	67
10[c,d]	2.5	-	DCM (0.1 M)	30-35	440	0.34	41
11[c,d]	2.5	-	DCM (0.1 M)	30-35	427	0.36	43
12[c,d]	2.5	-	DCM (0.1 M)	30-35	390	0.48	34
13[c]	2.5	Cs_2CO_3 (0.5)	DCM (0.1 M)	30-35	440	nd	20
14[c]	2.5	CsOBz (1)	DCM (0.1 M)	30-35	440	nd	10
15[c]	2.5	THF (2)	DCM (0.1 M)	30-35	440	nd	nd
16[c]	2.5	γ-terpinene (2)	DCM (0.1 M)	30-35	440	nd	50

[a]Reaction was performed in Rayonet reactor, [b]Reaction was performed with blue LED strips, [c]Reaction was run for 24 hours, [d]Reaction was performed with 1 Kessil lamp of the corresponding wavelength

5. Deoxyalkynyation with methods A and B:

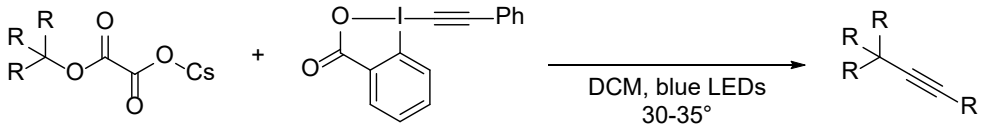
5.1. General procedure E: 4CzIPN catalyzed deoxy-alkynylation ("method A")



3a-p and **3w** **3x** **2a-f** **4a-p** and **4w** **4x**

An oven dried (7.5 mL) dram vial equipped with a magnetic stirrer was charged with the cesium salt **3a-x** (0.30 mmol, 1.00 equiv), the EBX reagent (1.5 mmol, 1.5 equiv) and 4CzIPN (**1a**, 0.015 mmol, 5 mol%). The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), dichloromethane (3.00 mL) was added and the septums were replaced with a screw cap under a flux of Ar then the seal was wrapped with parafilm.[19] The reactions were placed between 2 x 440 nm Kessil lamps at ca. 10 cm distance from both lamps (no ventilation, T = ca. 50 °C)[20] and stirred under irradiation for 15-18 hours. The reaction was filtered through a small celite plug which was washed with CH_2Cl_2. A solid deposit was prepared (ca. 2g SiO_2). The compound was purified by column chromatography (pentane:EtOAc).

5.2. General procedure F: Direct excitation of PhEBX for deoxy-alkynylation ("method B")



3a **2a** **4a-x**

An oven dried (7.5 mL) dram vial equipped with a magnetic stirrer was charged with the cesium salt **3a-x** (0.30 mmol, 1.00 equiv) and PhEBX (**2a,** 2.5 mmol, 2.5 equiv). The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), dichloromethane (3.00 mL) was added and the septums were replaced with a screw cap under a flux of Ar.[21] The reactions were

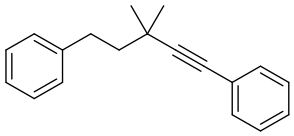
[20] The reaction temperature was measured with an internal thermometer on a model system using 5 mol% 4CzIPN in DCM.

[21] Use of a screw cap or crimp cap is of great importance, the irradiation causes an increase in temperature to ca. 50 °C causing the CH_2Cl_2 to evaporate and an overpressure inside the vessel. When using a septum, the latter

placed between 2 x 440 nm Kessil lamps at ca. 10 cm distance from both lamps (with ventilation, T = 30-35 °C) and stirred under irradiation for 24 hours. The reaction was filtered through a small celite plug which was washed with CH_2Cl_2. A solid deposit was prepared (ca. 2g SiO_2). The compound was purified by column chromatography (pentane:EtOAc).

5.3. Yields and characterization data of alkynes **4a-u 4w** and **4x**

- (3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (**4a**)

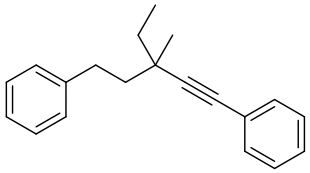


Method A: **4a** was synthesized following *general procedure E (Method A)* using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 0.110 g, 0.300 mmol, 1.0 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded (3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (**4a**, 0.056 g, 0.23 mmol, 75%) as a slightly yellow oil.

Method B: **4a** was synthesized following *general procedure F (Method B)* using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 0.110 g, 0.300 mmol, 1.00 equiv) and PhEBX (**2a**, 0.261 g, 0.750 mmol, 2.50 equiv) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded (3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (**4a**, 0.045 g, 0.18 mmol, 60%) as a slightly yellow oil.

Rf (pentane) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H, Ar*H*), 7.33 – 7.27 (m, 5H, Ar*H*), 7.26 – 7.16 (m, 3H, Ar*H*), 2.95 – 2.79 (m, 2H, ArCH_2), 1.86 – 1.75 (m, 2H, ArCH$_2$CH_2), 1.36 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 131.7, 128.6, 128.5, 128.3, 127.6, 125.8, 124.1, 97.0, 81.0, 45.7, 32.3, 32.0, 29.4.
IR (ν_{max}, cm^{-1}) 3084 (m), 3060 (m), 3027 (m), 2968 (m), 2945 (m), 2910 (m), 2866 (m), 2224 (m), 1946 (m), 1878 (m), 1804 (m), 1748 (m), 1491 (m), 1265 (m), 1070 (m), 755 (s), 740 (s), 690 (s).
HRMS (ESI/QTOF) m/z: $[M + Ag]^+$ Calcd for $C_{19}H_{20}Ag^+$ 355.0610; Found 355.0615.

- (3-Ethyl-3-methylpent-1-yne-1,5-diyl)dibenzene (**4b**)



4b was synthesized following the *general procedure E* using cesium 2-((3-methyl-1-phenylpentan-3-yl)oxy)-2-oxoacetate (**3b**, 115 mg, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.50 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 5 mol Column chromatography (SiO_2, Pentane) affording (3-ethyl-3-methylpent-1-yne-1,5-diyl)dibenzene (**4b**, 57 mg, 0.22 mmol, 72%) as a pale yellow oil.

Rf (pentane) = 0.3
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 – 7.41 (m, 2H, Ar*H*), 7.32 – 7.27 (m, 5H, Ar*H*), 7.25 – 7.22 (m, 2H, Ar*H*), 7.21 – 7.17 (m, 1H, Ar*H*), 2.90 – 2.77 (m, 2H, ArCH_2), 1.90 – 1.82 (m, 1H, CH_2), 1.76 – 1.63 (m, 2H, CH_2), 1.59 – 1.50 (m, 1H, CH_2), 1.30 (s, 3H, CH_3), 1.07 (t, *J* = 7.40 Hz, 3H, CH$_2$CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.1, 131.8, 128.6, 128.5, 128.3, 127.6, 125.8, 124.3, 96.1, 82.2, 43.7, 36.2, 34.5, 31.9, 26.0, 9.5.

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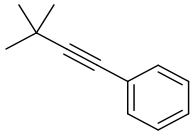
would fly off within an hour of irradiation. As shown in the optimization section DCE is not as good a solvent as CH_2Cl_2.

IR (ν_{max}, cm^{-1}): 3062 (w), 3031 (m), 2969 (m), 2929 (m), 2858 (w), 1599 (m), 1493 (m), 1454 (m).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{20}H_{22}^+$ 262.1716; Found 262.1716.

- (3,3-Dimethylbut-1-yn-1-yl)benzene (**4c**)

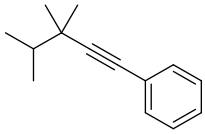


Method A: **4c** was synthesized following *general procedure E* using cesium *tert*-butoxyl-2-oxoacetate (**3c**, 0.083 g, 0.30 mmol, 1 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded (3,3-dimethylbut-1-yn-1-yl)benzene (**4c**, 0.051 g, 85% purity, 0.27 mmol, 91%) as a colorless oil. The compound could be partially purified from 1,4-diphenylbuta-1,4-diyne (major impurity) by preparative TLC (SiO_2, glass plate, Heptane) allowing full characterization of **4c**.

Method B: **4c** was synthesized following *general procedure F* using cesium (*tert*-butyl)oxy-2-oxoacetate (**3c**, 0.083 g, 0.30 mmol, 1 equiv) and PhEBX (**2a**, 0.261 g, 0.750 mmol, 2.50 equiv) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded (3,3-dimethylbut-1-yne-1-yl)benzene (**4c**, 0.067 g, 49% purity 0.17 mmol, 57%) as a slightly yellow oil.

Rf (pentane) = 0.8.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 2H, Ar*H*), 7.32 – 7.20 (m, 3H, Ar*H*), 1.32 (s, 9H, C(CH_3)$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.3, 127.5, 124.2, 98.7, 79.1, 31.2, 28.1.
IR (ν_{max}, cm^{-1}) 3084 (m), 3054 (m), 2971 (m), 2903 (m), 2871 (m), 1780 (m), 1723 (m), 909 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{12}H_{14}^+$ 158.1090; Found 158.1093.

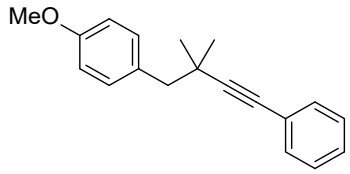
- (3,3,4-trimethylpent-1yn-1-yl)benzene (**4d**)



4d was synthesized following *general procedure E* using cesium (2,3-dimethylbutan-2-yl)oxy-2-oxoacetate (**3d**, 0.092 g, 0.30 mmol, 1.0 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded (3,3,4-trimethylpent-1-yn-1-yl)benzene (**4d**, 0.053 g, 85% purity, 0.21 mmol, 72%) as a colorless oil. The compound could be partially purified from 1,4-diphenylbuta-1,4-diyne (major impurity) by preparative TLC (SiO_2, glass plate, Heptane) allowing full characterisation of **4d**.

Rf (pentane) = 0.75.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 2H, Ar*H*), 7.32 – 7.22 (m, 3H, Ar*H*), 1.64 (hept, *J* = 6.8 Hz, 1H, C*H*(CH_3)$_2$), 1.25 (s, 6H, C(CH_3)$_2$), 1.03 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.3, 127.4, 124.4, 97.0, 81.0, 38.0, 35.6, 27.1, 18.5.
IR (ν_{max}, cm^{-1}) 3083 (m), 3055 (m), 2971 (s), 2939 (m), 2874 (m), 2228 (m), 1599 (m), 1489 (m), 1460 (m), 1369 (m), 1157 (m), 1061 (m), 911 (m), 755 (s), 691 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{14}H_{18}^+$ 186.1403; Found 186.1403.

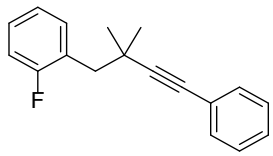
- 1-(2,2-Dimethyl-4-phenylbut-3-yn-1-yl)-4-methoxybenzene (**4e**)



4e was synthesized following *general procedure E* using cesium (1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3e**, 0.115 g, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).
Column chromatography (SiO_2, pentane:EtOAc 100:0 to 90:10) afforded 1-(2,2-dimethyl-4-phenylbut-3-yn-1-yl)-4-methoxybenzene (**4e**, 0.044 g, 0.17 mmol, 55%).

Rf (pentane:EtOAc 9:1) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H, Ar*H*), 7.31 – 7.21 (m, 5H, Ar*H*), 6.88 – 6.81 (m, 2H, Ar*H*), 3.80 (s, 3H, OCH_3), 2.74 (s, 2H, ArCH_2), 1.28 (s, 6H, (CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 131.7, 131.6, 130.7, 128.3, 127.6, 124.2, 113.2, 97.2, 81.7, 55.4, 48.4, 33.1, 29.1.
IR (ν_{max}, cm^{-1}) 3057 (m), 3034 (m), 2961 (m), 2933 (m), 2835 (m), 1786 (m), 1611 (m), 1512 (s), 1465 (m), 1302 (m), 1246 (s), 1177 (s), 1037 (s), 757 (s), 739 (s).
HRMS (ESI/QTOF) m/z: $[M + Ag]^+$ Calcd for $C_{19}H_{20}AgO^+$ 371.0560; Found 371.0552.

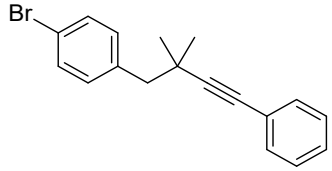
- 1-(2,2-Dimethyl-4-phenylbut-3-yn-1-yl)-2-fluorobenzene (**4f**)



4f was synthesized following *general procedure E* using cesium (1-(2-fluorophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3f**, 0.112 g, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).
Column chromatography (SiO_2, pentane) afforded 1-(2,2-dimethyl-4-phenylbut-3-yn-1-yl)-2-fluorobenzene (**4f**, 0.023 g, 0.091 mmol, 30%).

Rf (pentane) = 0.4.
^{1}H NMR (400 MHz, CDCl3) δ 7.43 (td, *J* = 7.6, 1.9 Hz, 1H, Ar*H*), 7.38 – 7.36 (m, 1H, Ar*H*), 7.35 (d, *J* = 2.0 Hz, 1H, Ar*H*), 7.30 – 7.25 (m, 3H, Ar*H*), 7.25 – 7.17 (m, 1H, Ar*H*), 7.13 – 6.99 (m, 2H, Ar*H*), 2.87 (d, *J* = 1.5 Hz, 2H, ArCH_2), 1.33 (d, *J* = 1.0 Hz, 6H, C(CH_3)$_2$).
^{1}H NMR {^{19}F} δ 7.42 (dd, *J* = 7.6, 1.8 Hz, 1H, Ar*H*), 7.39 – 7.32 (m, 2H, Ar*H*), 7.31 – 7.18 (m, 4H, Ar*H*), 7.13 – 7.01 (m, 2H, Ar*H*), 2.87 (s, 2H, ArCH_2), 1.33 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, *J* = 245 Hz), 133.1 (d, *J* = 5 Hz), 131.6, 128.3 (d, *J* = 8 Hz), 128.3, 127.7, 125.5 (d, *J* = 16 Hz), 124.1, 123.5 (d, *J* = 4 Hz), 115.2 (d, *J* = 23 Hz), 96.7, 81.5, 41.3, 33.3, 29.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.1.
IR (ν_{max}, cm^{-1}) 3061 (w), 2969 (w), 2925 (w), 1489 (m), 1488 (m), 1467 (m), 1280 (m), 1183 (m), 752 (s), 721 (m).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{18}H_{17}F^+$ 252.1309; Found 252.1308.

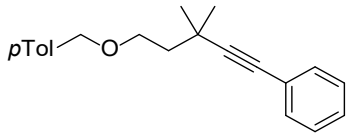
- 1-(2,2-Dimethyl-4-phenylbut-3-yn-1-yl)-4-bromobenzene (**4g**)



4g was synthesized following *general procedure E* using cesium (1-(4-bromophenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**3g**, 0.087 g, 0.20 mmol, 1.0 equiv), PhEBX (**2a**, 0.105 g, 0.300 mmol, 1.5 equiv), 4CzIPN (**1a**, 0.008 g, 1 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.067 M).
Column chromatography (SiO_2, pentane) afforded 1-(2,2-dimethyl-4-phenylbut-3-yn-1-yl)-4-bromobenzene (**4g**, 0.021 g, 0.067 mmol, 33%).

Rf (pentane) = 0.35.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H, Ar*H*), 7.38 – 7.31 (m, 2H, Ar*H*), 7.32 – 7.25 (m, 3H, Ar*H*), 7.23 – 7.17 (m, 2H, Ar*H*), 2.74 (s, 2H, ArCH_2), 1.29 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 132.4, 131.6, 130.9, 128.3, 127.8, 123.9, 120.6, 96.5, 82.1, 48.6, 32.9, 29.2.
IR (ν_{max}, cm^{-1}) 3080 (m), 3060 (m), 3033 (m), 2967 (m), 2921 (m), 2863 (m), 1763 (m), 1737 (m), 1598 (m), 1489 (s), 1443 (m), 1384 (m), 1277 (m), 1187 (m), 1072 (s), 1048 (m), 1013 (s), 912 (s), 841 (s), 756 (s), 741 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{18}H_{17}{}^{79}Br^+$ 312.0508; Found 312.0508.

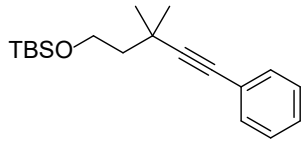
- 1-(((3,3-Dimethyl-5-phenylpent-4-yn-1-yl)oxy)methyl)-4-methylbenzene (**4h**)



4h was synthesized following *general procedure E* using cesium (2-methyl-4-((4-methylbenzyl)oxy)butan-2-yl)oxy-2-oxoacetate (**3h**, 0.124 g, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).
Column chromatography (SiO_2, pentane:EtOAc 100:0 to 80:20) afforded 1-(((3,3-dimethyl-5-phenylpent-4-yn-1-yl)oxy)methyl)-4-methylbenzene (**4h**, 0.049 g, 0.17 mmol, 56%).

Rf(pentane:EtOAc 8:2) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H, Ar*H*), 7.30 – 7.21 (m, 5H, Ar*H*), 7.17 – 7.11 (m, 2H, Ar*H*), 4.50 (s, 2H, ArCH_2), 3.74 (dd, *J* = 7.6, 6.9 Hz, 2H, CH_2), 2.34 (s, 3H, ArCH_3), 1.89 – 1.81 (m, 2H, CH_2), 1.32 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 135.6, 131.7, 129.2, 128.3, 127.9, 127.6, 124.0, 96.7, 80.8, 73.0, 68.2, 42.6, 30.6, 29.9, 21.3.
IR (ν_{max}, cm^{-1}) 3052 (m), 3033 (m), 2969 (m), 2907 (m), 2863 (m), 1960 (w), 1900 (w), 1715 (w), 1598 (m), 1490 (m), 1443 (m), 1361 (m), 1096 (s), 802 (s), 754 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{21}H_{24}O^+$ 292.1822; Found 292.1818.

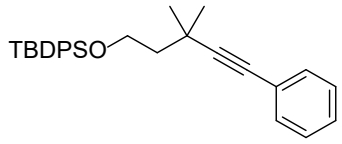
- *tert*-Butyl((3,3-dimethyl-5-phenylpent-4-yn-1-yl)oxy)dimethylsilane (**4i**)



4i was synthesized following the *general procedure E* using cesium 2-((4-((*tert*-butyldimethylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**3i**, 127 mg, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.50 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 5 mol%).
Column chromatography (SiO_2, 5% DCM in Pentane) afforded (3- *tert*-butyl((3,3-dimethyl-5-phenylpent-4-yn-1-yl)oxy)dimethylsilane (**4i**, 55 mg, 0.18 mmol, 61%) as a yellow oil.

Rf (pentane:DCM 95:5) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 – 7.34 (m, 2H, Ar*H*), 7.30 – 7.25 (m, 3H, Ar*H*), 3.90 (t, *J* = 7.5 Hz, 2H, OCH_2), 1.76 (t, *J* = 7.5 Hz, 2H, CH_2), 1.31 (s, 6H, C(CH_3)$_2$), 0.91 (s, 9H, C(CH_3)$_3$), 0.08 (s, 6H, Si(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 131.7, 128.3, 127.6, 124.1, 96.8, 80.7, 61.1, 45.8, 30.5, 29.9, 26.1, 18.5, -5.1.
IR (ν_{max}, cm^{-1}): 3668 (w), 2962 (s), 2901 (s), 1467 (m), 1393 (m), 1254 (m), 1092 (s), 1057 (s).
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{19}H_{31}OSi^+$ 303.2139; Found 303.2137.

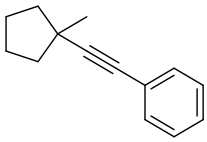
- *tert*-Butyl((3,3-dimethyl-5-phenylpent-4-yn-1-yl)oxy)diphenylsilane (**4j**)



4j was synthesized following the *general procedure E* using cesium 2-((4-((*tert*-butyldiphenylsilyl)oxy)-2-methylbutan-2-yl)oxy)-2-oxoacetate (**3j**, 164 mg, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.50 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 5 mol%).
Column chromatography (SiO_2, 5% DCM in Pentane) afforded *tert*-butyl((3,3-dimethyl-5-phenylpent-4-yn-1-yl)oxy)diphenylsilane (53 mg, 0.12 mmol, 41%) as a yellow oil.

Rf (pentane:DCM, 95:5) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 – 7.64 (m, 4H, Ar*H*), 7.44 – 7.31 (m, 6H, Ar*H*), 7.29 – 7.21 (m, 5H, Ar*H*), 3.96 (dd, *J* = 7.6, 6.8 Hz, 2H, OCH_2), 1.82 (dd, *J* = 7.6, 6.8 Hz, 2H, CH_2), 1.27 (s, 6H, C(CH_3)$_2$), 1.05 (s, 9H, C(CH_3)$_3$).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 135.7, 134.1, 131.7, 129.7, 128.2, 127.8, 127.6, 124.0, 96.7, 80.8, 62.0, 45.5, 30.5, 30.0, 27.0, 19.3.
IR (ν_{max}, cm^{-1}): 3668 (m), 3061 (m), 2966 (s), 2935 (s), 1478 (m), 1392 (m), 1258 (m), 1084 (s).
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{34}NaOSi^+$ 449.2271; Found 449.2269.

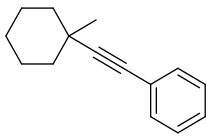
- ((1-Methylcyclopentyl)ethynyl)benzene (**4k**)



Method A: **4k** was synthesized following the *general procedure E* using cesium 2-((1-methylcyclopentyl)oxy)-2-oxoacetate (**3k**, 91 mg, 0.30 mmol, 1.0 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.50 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 5 mol%). Column chromatography (SiO_2, Pentane) afforded ((1-methylcyclopentyl)ethynyl)benzene (**4k**, 39 mg, 0.20 mmol, 69%) as a pale yellow oil.

Method B: **4k** was synthesized following *general procedure F* using cesium 2-((1-methylcyclopentyl)oxy)-2-oxoacetate (**3k**, 91 mg, 0.30 mmol, 1.0 equiv) and PhEBX (**2a**, 0.261 g, 0.75 mmol, 2.50 equiv) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded ((1-methylcyclopentyl)ethynyl)benzene (**4k**, 57 mg, 42% purity, 0.16 mmol, 54%) with major impurity 1,4-diphenylbutadiyne.
Rf (pentane) = 0.6.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 - 7.36 (m, 2H, Ar*H*), 7.29 - 7.23 (m, 3H, Ar*H*), 2.01 - 1.95 (m, 2H, CH_2), 1.90 - 1.80 (m, 2H, CH_2) 1.75 - 1.66 (m, 2H, CH_2), 1.62 - 1.51 (m, 2H, CH_2), 1.35 (s, 3H, CH_3)
^{13}C NMR (101 MHz, $CDCl_3$) δ: 131.7, 128.3, 127.4, 124.4, 98.6, 79.6, 41.8, 38.5, 27.6, 24.5.
IR (ν_{max}, cm^{-1}): 3060 (m), 2960 (s), 2869 (m), 1742 (m), 1488 (m), 1451 (m), 1322 (m), 1186 (m).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{14}H_{16}^+$ 184.1247; Found 184.1248.

- 2-(1-Methylcyclohexyl)ethynylbenzene (**4l**)

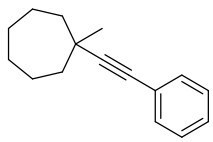


Method A: **4l** was synthesized following *general procedure E* using cesium 2-(1-methylcyclohexan-1-yl)oxy-2-oxoacetate (**3l**, 0.095 g, 0.30 mmol, 1 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography

(SiO_2, pentane) afforded (1-methylcyclohexyl)enthynylbenzene (**4l**, 0.053 g (80% purity), 0.22 mmol, 72%) as a colorless oil. The compound could be partially purified from 1,4-diphenylbuta-1,4-diyne (major impurity) by preparative TLC (SiO_2, glass plate, Heptane) allowing full characterisation of **4l**.

Method B: **4l** was synthesized following *general procedure F* using cesium 2-(1-methylcyclohexan-1-yl)oxy-2-oxoacetate (**3l**, 95 mg, 0.30 mmol, 1.0 equiv) and PhEBX (**2a**, 0.261 g, 0.750 mmol, 2.50 equiv) in degassed CH_2Cl_2 (3.0 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded ((1-methylcyclohexyl)ethynyl)benzene (**4l**, 0.063 mg (55% purity), 0.18 mmol, 61%) with major impurity 1,4-diphenylbutadiyne.
Rf (pentane) = 0.7.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H, Ar*H*), 7.32 – 7.22 (m, 3H, Ar*H*), 1.84 – 1.55 (m, 8H, CH_2), 1.28 (s, 3H, CH_3), 1.27 – 1.09 (m, 2H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.3, 127.5, 124.4, 96.9, 81.9, 39.7, 33.3, 30.4, 26.1, 23.6.
Consistent with the reported NMR data.[22]

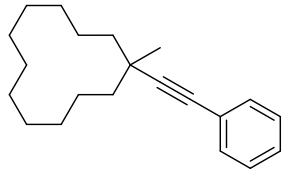
- 1-Methyl-1-(phenylethynyl)cycloheptane (4m)



4m was synthesized following *general procedure E* using cesium 2-(1-methylcycloheptan-1-yl)oxy-2-oxoacetate (**3m**, 0.110 g, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.5 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).
Column chromatography (SiO_2, pentane) afforded (3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (**4m**, 0.068 g, 75% purity 0.22 mmol, 74%) as a colorless oil. The compound could be partially purified from 1,4-diphenylbuta-1,4-diyne (major impurity) by preparative TLC (SiO_2, glass plate, Heptane) allowing full characterisation of **4m**.

Rf (pentane) = 0.7.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H, Ar*H*), 7.31 – 7.24 (m, 3H, Ar*H*), 1.95 – 1.84 (m, 2H, CH_2), 1.82 – 1.64 (m, 4H, CH_2), 1.64 – 1.56 (m, 2H, CH_2), 1.55 – 1.44 (m, 4H, CH_2), 1.29 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 128.3, 127.4, 124.5, 98.1, 81.1, 42.3, 36.1, 31.5, 28.4, 24.0.
IR (ν_{max}, cm^{-1}) 3081 (w), 3054 (w), 2961 (m), 2925 (s), 2855 (m), 1598 (m), 1491 (m), 1460 (m), 1231 (m), 912 (m), 755 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{16}H_{20}^+$ 212.1560; Found 212.1558.

- 1-Methyl-1-(phenylethynyl)cyclododecane (4n)

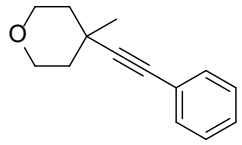


Method A: **4n** was synthesized following the *general procedure E* using cesium 2-((1-methylcyclododecyl)oxy)-2-oxoacetate (**3n**, 121 mg (purity 80%), 0.240 mmol, 1.00 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.9 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 6 mol%). Column chromatography (SiO_2, Pentane) afforded 1-methyl-1-(phenylethynyl)cyclododecane (**4n**, 43 mg, 0.15 mmol, 63%) as a pale yellow oil.

[22] Gao, C.; Li, J.; Yu, J.; Yang, H.; Fu, H. *Chem. Commun.* **2016**, *52*, 7292–7294.

Method B: **4n** was synthesized following *general procedure F* using cesium 2-(1-methylcyclododecan-1-yl)oxy-2-oxoacetate (**3n**, 151 mg (purity 80%), 0.300 mmol, 1.00 equiv) and PhEBX (**2a**, 0.261 g, 0.750 mmol, 2.50 equiv) in degassed CH_2Cl_2 (3.0 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded ((1-methylcyclododecyl)ethynyl)benzene (**4n**, 0.062 mg (47% purity), 0.11 mmol, 37%) with major impurity 1,4-diphenylbutadiyne.
Rf (pentane) = 0.6.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 – 7.36 (m, 3H, Ar*H*), 7.29 – 7.23 (m, 2H, Ar*H*), 1.46 – 1.29 (m, 22H, CH_2), 1.23 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 131.7, 128.2, 127.4, 124.4, 98.4, 80.6, 35.0, 34.4, 27.5, 26.6, 26.3, 22.7, 22.3, 19.9.
IR (ν_{max}, cm^{-1}): 3058 (w), 2936 (s), 2859 (m), 2226 (w), 1597 (w), 1479 (m), 1449 (m), 1273 (w).
HRMS (ESI/QTOF) m/z: $[M + Ag]^+$ Calcd for $C_{21}H_{30}Ag^+$ 389.1393; Found 389.1390.

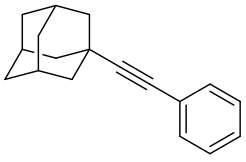
- 4-Methyl-4-(phenylethynyl)tetrahydro-2*H*-pyran (**4o**)



Method A: **4o** was synthesized following the *general procedure E* using ethyl (4-methyltetrahydro-2H-pyran-4-yl) oxalate (**3o**, 96 mg, 0.30 mmol, 1.0 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.50 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 5 mol%). Column chromatography (SiO_2, 1% to 5% EtOAc in Pentane) afforded, 4-methyl-4-(phenylethynyl)tetrahydro-2*H*-pyran (**4o**, 40 mg, purity: 94%, 0.19 mmol, 67%) as a colorless oil.

Method B: **4o** was synthesized following *general procedure F* using ethyl (4-methyltetrahydro-2H-pyran-4-yl) oxalate (**3o**, 0.096 g, 0.30 mmol, 1.0 equiv) and PhEBX (**2a**, 0.261 g, 0.750 mmol, 2.50 equiv) in degassed CH_2Cl_2 (3.0 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded 4-methyl-4-(phenylethynyl)tetrahydro-2*H*-pyran (**4o**, 0.040 g (93% purity), 0.19 mmol, 62%).
Rf (pentane:EtOAc 95:5) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 – 7.39 (m, 2H, Ar*H*), 7.32 – 7.27 (m, 3H, Ar*H*), 3.90 – 3.77 (m, 4H, OCH_2), 1.76 – 1.68 (m, 2H, CH_2), 1.61 (ddd, *J* = 13.2, 11.2, 5.0 Hz, 2H, CH_2), 1.35 (s, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 131.7, 128.4, 127.9, 123.8, 94.7, 83.0, 65.4, 39.4, 31.1, 30.2.
IR (ν_{max}, cm^{-1}): 3058 (m), 2959 (s), 2857 (m), 1746 (m), 1492 (m), 1448 (m), 1174 (s), 1107 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{14}H_{17}O^+$ 201.1274; Found 201.1273.

- 1-(Phenylethynyl)adamantane (**4p**)

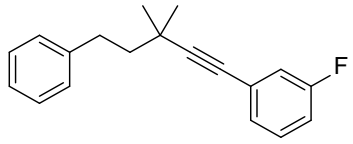


4p was synthesized following the *general procedure E* using cesium 2-(((1*S*,3*S*)-adamantan-1-yl)oxy)-2-oxoacetate (**3p**, 107 mg, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.50 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 5 mol%).

Column chromatography (SiO_2, Pentane) afforded 1-(phenylethynyl)adamantane (**4p**, 20 mg, 0.080 mmol, 28%) as a pale yellow oil.

Rf (pentane) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 – 7.32 (m, 2H, Ar*H*), 7.32 – 7.19 (m, 3H, Ar*H*), 2.07 – 1.97 (m, 3H, C*H*), 1.97 – 1.92 (m, 6H, CH_2), 1.75 – 1.69 (m, 6H, CH_2).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 131.8, 128.2, 127.5, 124.2, 98.6, 79.5, 43.0, 36.6, 30.2, 28.2.
IR (ν_{max}, cm^{-1}): 3060 (w), 2912 (s), 2853 (m), 1491 (m), 1450 (m).
HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{18}H_{20}^+$ 236.1560; Found 236.1561.

- 1-(3,3-Dimethyl-5-phenylpent-1-yn-1-yl)-3-fluorobenzene (**4q**)

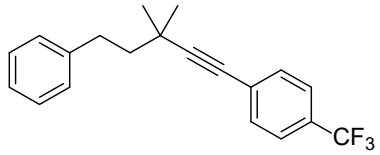


4q was synthesized following *general procedure E* using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 0.110 g, 0.300 mmol, 1 equiv), mFPhEBX (**2b**, 0.164 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).

Column chromatography (SiO_2, pentane) afforded 1-(3,3-dimethyl-5-phenylpent-1-yn-1-yl)-3-fluorobenzene (**4q**, 0.045 g, 0.17 mmol, 56%).

Rf (pentane) = 0.5.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 7H, Ar*H*), 7.10 (ddd, *J* = 9.6, 2.7, 1.4 Hz, 1H, Ar*H*), 6.98 (tdd, *J* = 8.3, 2.7, 1.2 Hz, 1H, Ar*H*), 2.87 – 2.79 (m, 2H, ArCH_2), 1.84 – 1.75 (m, 2H, CH_2), 1.35 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.8 Hz), 142.6, 129.7 (d, *J* = 8.7 Hz), 128.4, 127.5 (d, *J* = 2.9 Hz), 126.1 – 125.3 (m), 118.4 (d, *J* = 22.5 Hz), 114.8 (d, *J* = 21.1 Hz), 98.0, 79.8, 45.4, 32.1, 31.9, 29.1. 2 carbons are not resolved.
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5 (d, *J* = 4.5 Hz).
IR (ν_{max}, cm^{-1}) 3087 (m), 3062 (m), 2972 (s), 2937 (s), 2911 (s), 1608 (s), 1580 (s), 1075 (s), 1056 (s), 909 (s), 873 (s), 784 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{19}H_{19}F^+$ 266.1465; Found 266.1473.

- 1-(3,3-Dimethyl-5-phenylpent-1-yn-1-yl)-4-(trifluoromethyl)benzene (**4r**)

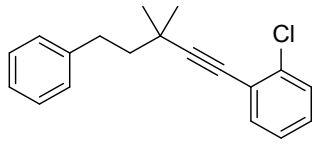


4r was synthesized following *general procedure E* using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 0.110 g, 0.300 mmol, 1 equiv), *p*CF_3PhEBX (**2c**, 0.187 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).

Column chromatography (SiO_2, pentane) afforded 1-(3,3-dimethyl-5-phenylpent-1-yn-1-yl)-4-(trifluoromethyl)benzene (**4r**, 0.055 g, 0.17 mmol, 58%).

Rf (pentane) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.46 (m, 4H, Ar*H*), 7.34 – 7.17 (m, 5H, Ar*H*), 2.88 – 2.79 (m, 2H, ArCH_2), 1.85 – 1.77 (m, 2H, CH_2), 1.36 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 132.0, 128.5 (m), 125.9, 125.2 (d, *J* = 3.9 Hz), 99.8, 80.0, 45.5, 32.3, 32.1, 29.2. 4 carbons not resolved.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7.
IR (ν_{max}, cm^{-1}) 3028 (w), 2975 (w), 2940 (m), 2859 (m), 2822 (w), 2239 (w), 1617 (m), 1505 (m), 1324 (s), 1168 (m), 1130 (s), 1066 (s), 910 (s), 766 (m), 743 (s).
HRMS (ESI/QTOF) m/z: $[M + Ag]^+$ Calcd for $C_{20}H_{19}AgF_3^+$ 423.0484; Found 423.0479.

- 1-(3,3-Dimethyl-5-phenylpent-1-yn-1-yl)-4-chlorobenzene (**4s**)

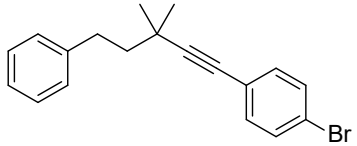


4s was synthesized following *general procedure E* using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 0.110 g, 0.300 mmol, 1.00 equiv), oClPhEBX (**2d**, 0.172 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).

Column chromatography (SiO_2, pentane) afforded 1-(3,3-dimethyl-5-phenylpent-1-yn-1-yl)-4-chlorobenzene (**4s**, 0.066 g, 0.23 mmol, 78%).

Rf (pentane) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.35 (m, 2H, Ar*H*), 7.33 – 7.14 (m, 7H, Ar*H*), 2.95 – 2.86 (m, 2H, ArCH_2), 1.86 – 1.77 (m, 2H, CH_2), 1.38 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 136.0, 133.3, 129.3, 128.7, 128.6, 128.5, 126.4, 125.8, 123.9, 102.7, 78.0, 45.7, 32.4, 32.3, 29.3.
IR (ν_{max}, cm^{-1}) 2972 (m), 2901 (m), 1495 (w), 1406 (m), 1229 (m), 1075 (s), 905 (s), 729 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{19}H_{19}{}^{35}Cl^+$ 282.1170; Found 282.1178.

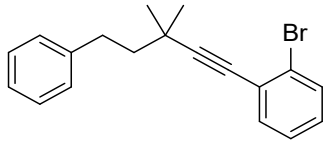
- 1-(3,3-Dimethyl-5-phenylpent-1-yn-1-yl)-4-bromobenzene (**4t**)



4t was synthesized following *general procedure E* using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 0.110 g, 0.300 mmol, 1.00 equiv), PhEBX (**2e**, 0.192 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).
Column chromatography (SiO_2, pentane) afforded 1-(3,3-dimethyl-5-phenylpent-1-yn-1-yl)-4-bromobenzene (**4t**, 0.044 g, 0.13 mmol, 45%).

Rf (pentane) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H, Ar*H*), 7.33 – 7.25 (m, 2H, Ar*H*), 7.29 – 7.21 (m, 3H, Ar*H*), 7.25 – 7.14 (m, 2H, Ar*H*), 2.87 – 2.78 (m, 2H, ArCH_2), 1.83 – 1.74 (m, 2H, CH_2), 1.34 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 133.2, 131.5, 128.5, 125.9, 123.1, 121.7, 98.3, 80.1, 45.5, 32.3, 32.1, 29.3. 1 carbon is not resolved.
IR (ν_{max}, cm^{-1}) 3086 (m), 3062 (m), 3026 (m), 2968 (m), 2920 (m), 2861 (m), 1485 (s), 1469 (m), 1312 (m), 1265 (m), 1070 (s), 1011 (s), 823 (s), 745 (s), 700 (s).
HRMS (ESI/QTOF) m/z: $[M + Ag]^+$ Calcd for $C_{19}H_{19}Ag^{79}Br^+$ 432.9716; Found 432.9707.

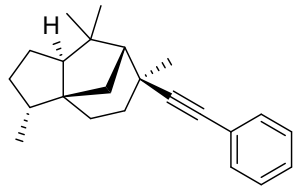
- 1-(3,3-dimethyl-5-phenylpent-1-yn-1-yl)-2-bromobenzene (**4u**)



4u was synthesized following *general procedure E* using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**3a**, 0.110 g, 0.300 mmol, 1.00 equiv), PhEBX (**2f**, 0.192 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M).
Column chromatography (SiO_2, pentane) afforded (3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (**4u**, 0.071 g, 0.22 mmol, 72%).

Rf (pentane) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 7.45 (dd, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 7.33 – 7.18 (m, 5H, Ar*H*), 7.22 – 7.14 (m, 1H, Ar*H*), 7.12 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 2.96 – 2.87 (m, 2H, ArCH_2), 1.87 – 1.78 (m, 2H, CH_2), 1.38 (s, 6H, C(CH_3)$_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 133.2, 132.3, 128.7, 128.5, 128.4, 126.9, 126.0, 125.7, 101.9, 79.7, 45.5, 32.3, 32.2, 29.1. 1 carbon is not resolved.
IR (ν_{max}, cm^{-1}) 3062 (m), 3026 (m), 2968 (s), 2925 (m), 2865 (m), 2226 (m), 1466 (s), 1058 (m), 1047 (s), 1027 (s), 753 (s), 700 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{19}H_{19}{}^{79}Br^+$ 326.0665; Found 326.0676.

- (3*R*,3a*S*,6*S*,7*R*,8a*S*)-3,6,8,8-tetramethyl-6-(phenylethynyl)octahydro-1H-3a,7-methanoazulene (**4w**)

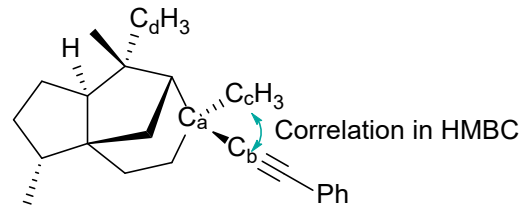


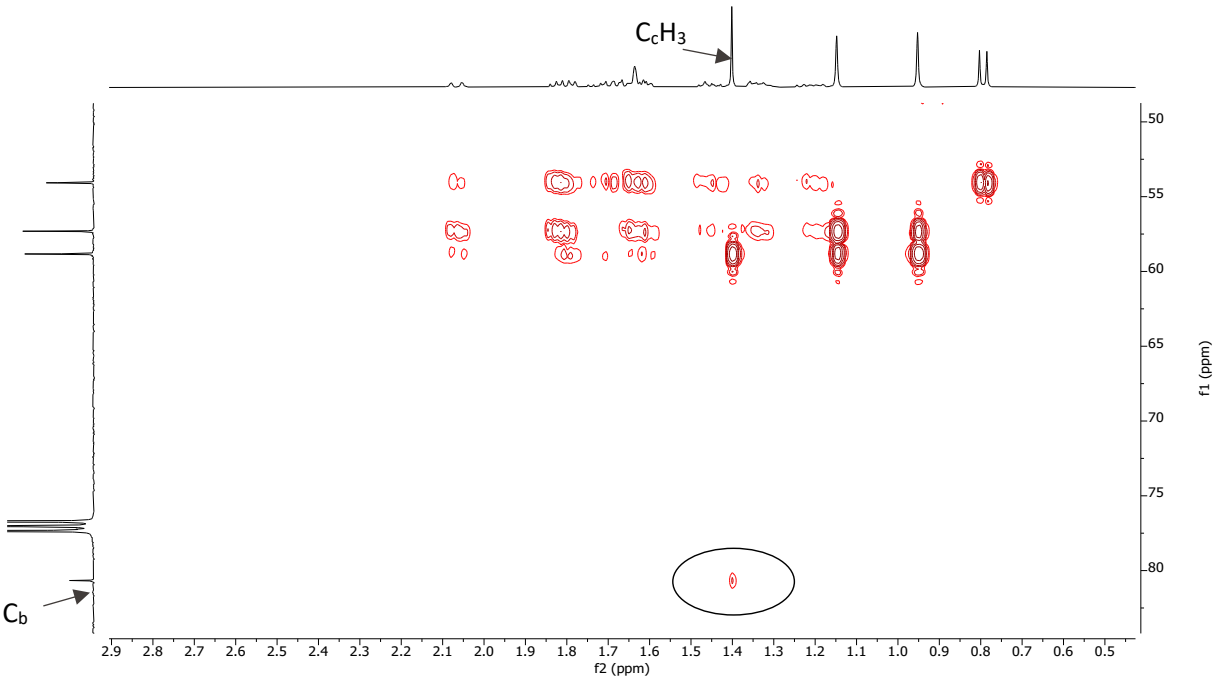
Method A: **4w** was synthesized following *general procedure E* using cedrol derived cesium oxalate **3w** (0.128 g, 0.300 mmol, 1 equiv), PhEBX (**2a**, 0.157 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**1a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded (3*R*,3a*S*,6*S*,7*R*,8a*S*)-3,6,8,8-tetramethyl-6-(phenylethynyl)octahydro-1H-3a,7-methanoazulene (**4w**) as a single diasteroisomer (0.075 g (70% purity), dr > 20:1, 0.17 mmol, 58%). The compound could be partially purified from 1,4-diphenylbuta-1,4-diyne (major impurity) by preparative TLC (SiO_2, glass plate, Heptane) allowing full characterisation of **4w**.

Method B: **4w** was synthesized following *general procedure F* using cedrol derived cesium oxalate **3w** (0.128 g, 0.300 mmol, 1 equiv) and PhEBX (**2a**, 0.261 g, 0.750 mmol, 2.50 equiv) in degassed CH_2Cl_2 (3 mL, 0.1 M). Column chromatography (SiO_2, pentane) afforded (3*R*,3a*S*,6*S*,7*R*,8a*S*)-3,6,8,8-tetramethyl-6-(phenylethynyl)octahydro-1H-3a,7-methanoazulene (**4w**) as a single diasteroisomer (0.077 g (48% purity), dr > 20:1, 0.15 mmol, 50%).

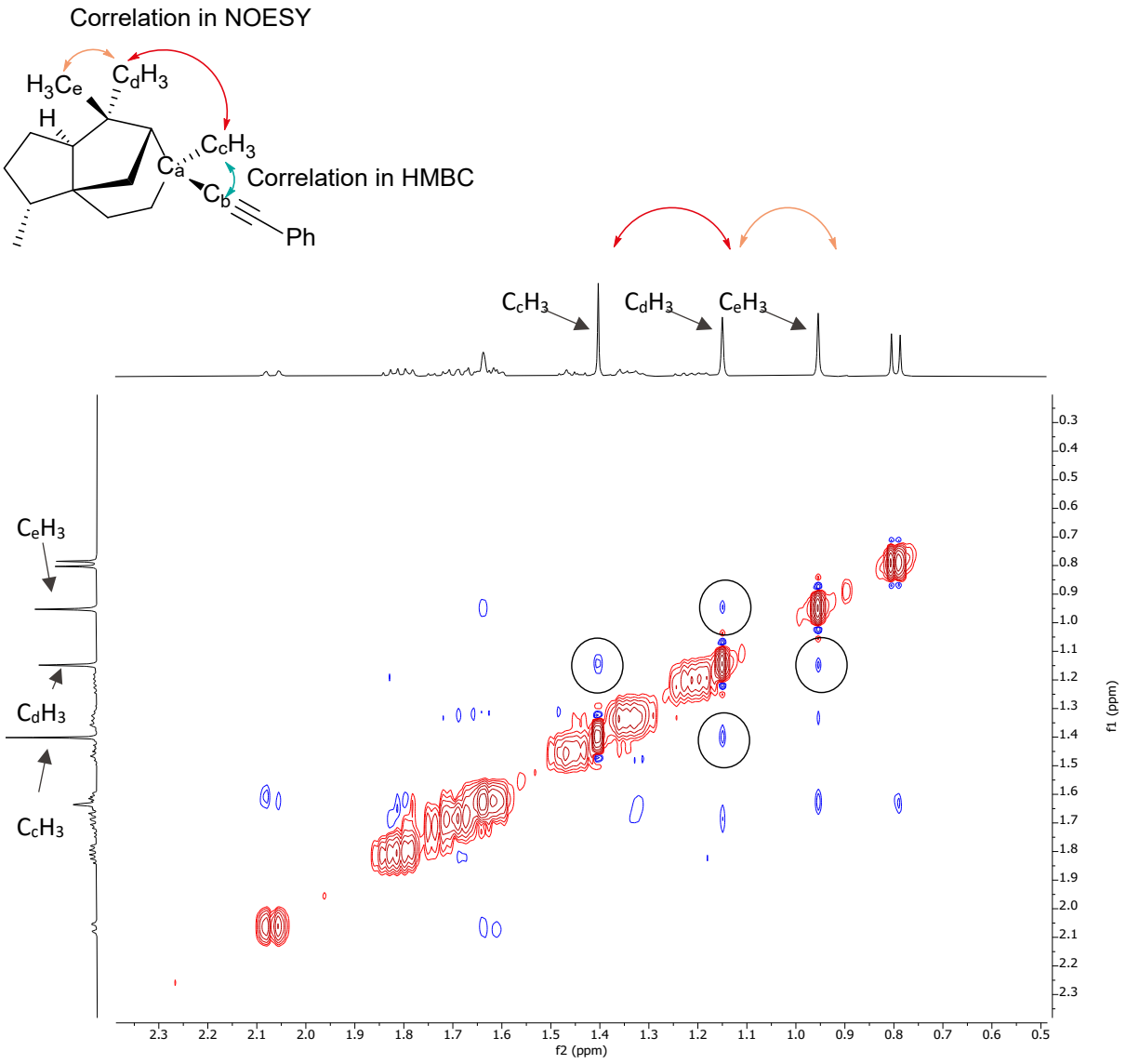
Rf (pentane) = 0.6.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2H, Ar*H*), 7.32 – 7.20 (m, 3H, Ar*H*), 2.18 – 2.10 (m, 1H, aliphatic-C*H* or CH_2), 1.95 – 1.83 (m, 2H, aliphatic-C*H* or CH_2), 1.85 – 1.76 (m, 1H, aliphatic-C*H* or CH_2), 1.79 – 1.65 (m, 5H, aliphatic-C*H* or CH_2), 1.60 – 1.50 (m, 1H, aliphatic-C*H* or CH_2), 1.48 (s, 3H, CH_3), 1.46 – 1.34 (m, 2H, aliphatic-C*H* or CH_2), 1.28 (dtd, *J* = 11.8, 7.7, 6.0 Hz, 1H, aliphatic-C*H* or CH_2), 1.22 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 0.87 (d, *J* = 7.1 Hz, 3H, CH_3).
^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 128.3, 127.3, 124.6, 100.0, 80.8, 59.0, 57.4, 54.2, 44.4, 44.0, 42.0, 39.1, 37.1, 34.9, 31.9, 29.8, 29.0, 28.5, 25.6, 15.7.
IR (ν_{max}, cm^{-1}) 3055 (m), 3010 (m), 2950 (m), 2870 (m), 2851 (m), 1648 (m), 1474 (m), 1442 (m), 1246 (m), 755 (s), 724 (m), 690 (s).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M]^+$ Calcd for $C_{23}H_{30}^+$ 306.2342; Found 306.2342.

HMBC

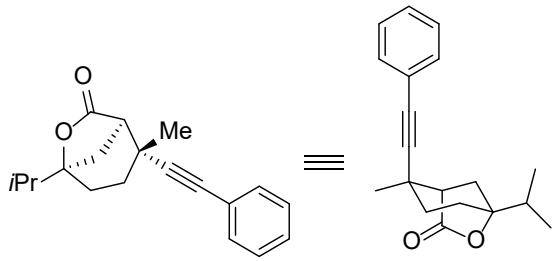




NOESY

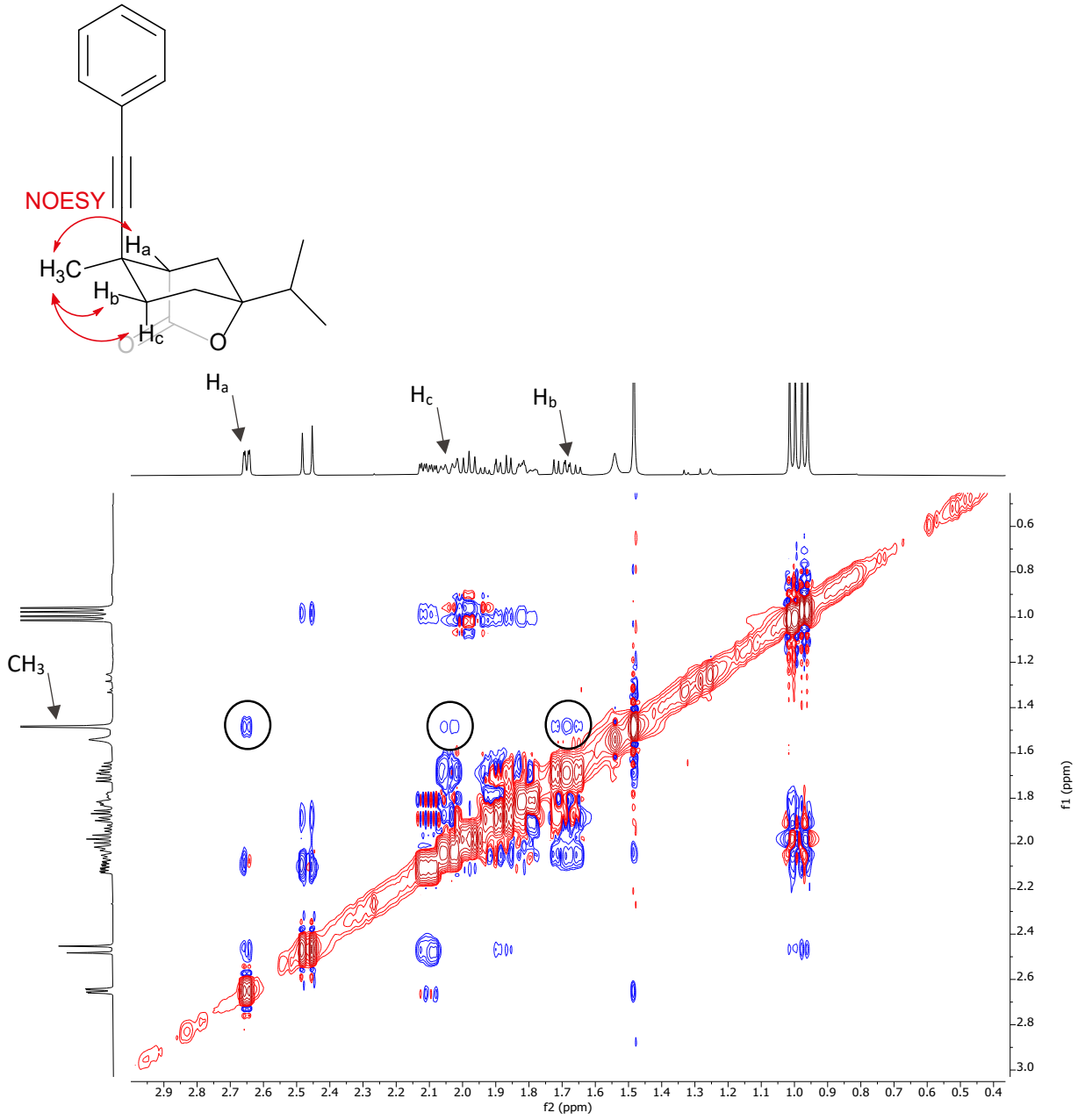

Correlation in NOESY
H3Ce
CdH3
H
CcH3
Ca
Cb
Correlation in HMBC
Ph
CcH3
CdH3
CeH3
CeH3
CdH3
CcH3
f2 (ppm)
f1 (ppm)

- (1R,2R,5R)-5-isopropyl-2-methyl-2-(phenylethynyl)-6-oxabicyclo[3.2.1]octan-7-one (**4x**)



Method A: **4x** was synthesized following the *general procedure E* using Cesium (*R*)-2-((1-isopropyl-4-methylcyclohex-3-en-1-yl)oxy)-2-oxoacetate (**3x**, 107 mg, 0.300 mmol, 1.00 equiv), PhEBX (**2a**, 157 mg, 0.450 mmol, 1.50 equiv) and 4CzIPN (**1a**, 12 mg, 0.015 mmol, 5 mol%). Column chromatography (SiO_2, 5% EtOAc in Pentane) afforded (1*R*,2*R*,5*R*)-5-isopropyl-2-methyl-2-(phenylethynyl)-6-oxabicyclo[3.2.1]octan-7-one (**4x**, 45 mg, dr > 20:1, 0.16 mmol, 53%) as a colorless oil.

Method B: **4x** was synthesized following the *general procedure F* using Cesium (*R*)-2-((1-isopropyl-4-methylcyclohex-3-en-1-yl)oxy)-2-oxoacetate (**3x**, 107 mg, 0.300 mmol, 1.00 equiv) and PhEBX (**2a**, 261 mg, 0.750 mmol, 2.5 equiv). Column chromatography (SiO_2, 5% EtOAc in Pentane) afforded (1*R*,2*R*,5*R*)-5-isopropyl-2-methyl-2-(phenylethynyl)-6-oxabicyclo[3.2.1]octan-7-one (**4x**, 40 mg, dr > 20:1, 0.16 mmol, 47%) as a colorless oil.
Rf (pentane:EtOAc 95:5) = 0.4.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 – 7.37 (m, 2H, Ar*H*), 7.35 – 7.28 (m, 3H, Ar*H*), 2.65 (dd, *J* = 5.6, 1.7 Hz, 1H, C*H*CO_2), 2.47 (d, *J* = 11.9 Hz, 1H, CO_2CHCH_{ax}), 2.15 – 2.08 (m, 1H, CO_2CHCH_{eq}), 2.07 – 2.00 (m, 1H, CCH_3CH_{ax}), 2.00 – 1.91 (m, 1H, $C(CH_3)_2H$), 1.91 – 1.85 (m, 1H, $COCH_{ax}$), 1.84 – 1.77 (m, 1H, $COCH_{eq}$), 1.74 – 1.63 (m, 1H, CCH_3CH_{eq}), 1.48 (s, 3H, CH_3), 1.01 (d, *J* = 6.8 Hz, 3H, $CH(CH_3)_2$), 0.97 (d, *J* = 6.9 Hz, 1H, $CH(CH_3)_2$).
^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.3, 131.8, 128.5, 128.3, 123.2, 93.1, 90.1, 82.6, 51.0, 37.4, 35.3, 34.7, 34.3, 27.3, 26.8, 17.2, 16.8.
IR (ν_{max}, cm^{-1}): 3059 (w), 2967 (m), 2881 (m), 1773 (s), 1593 (w), 1461 (m), 1171 (m), 930 (m).
HRMS (APPI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{22}NaO_2^+$ 305.1512; Found 305.1512.


NOESY
Ha
H3C
Hb
Hc
O
Ha
Hc
Hb
CH3
f2 (ppm)
f1 (ppm)

6. Mechanistic studies

6.1. NMR studies

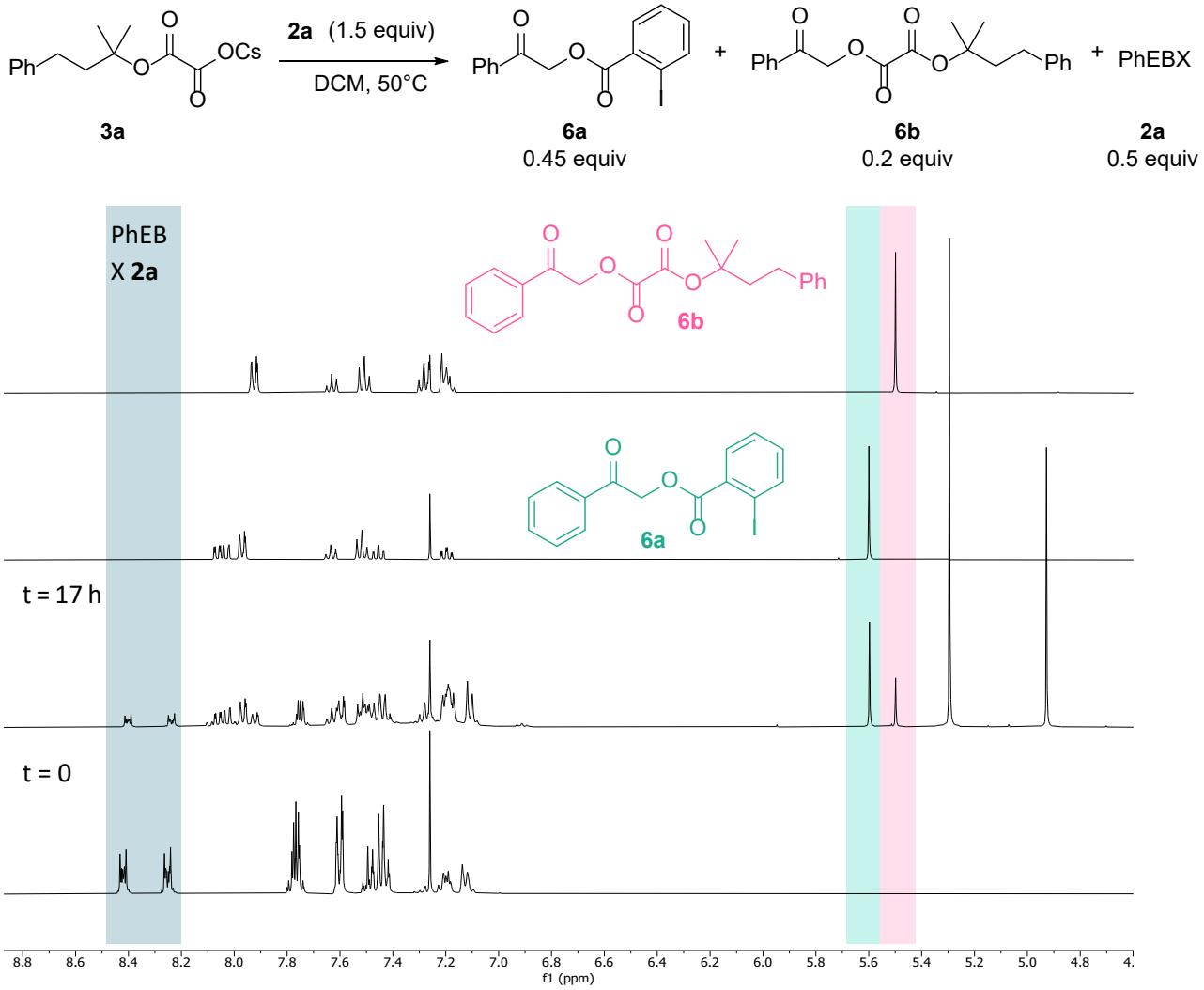


Figure S2. Thermal degradation of PhEBX in presence of **3a**

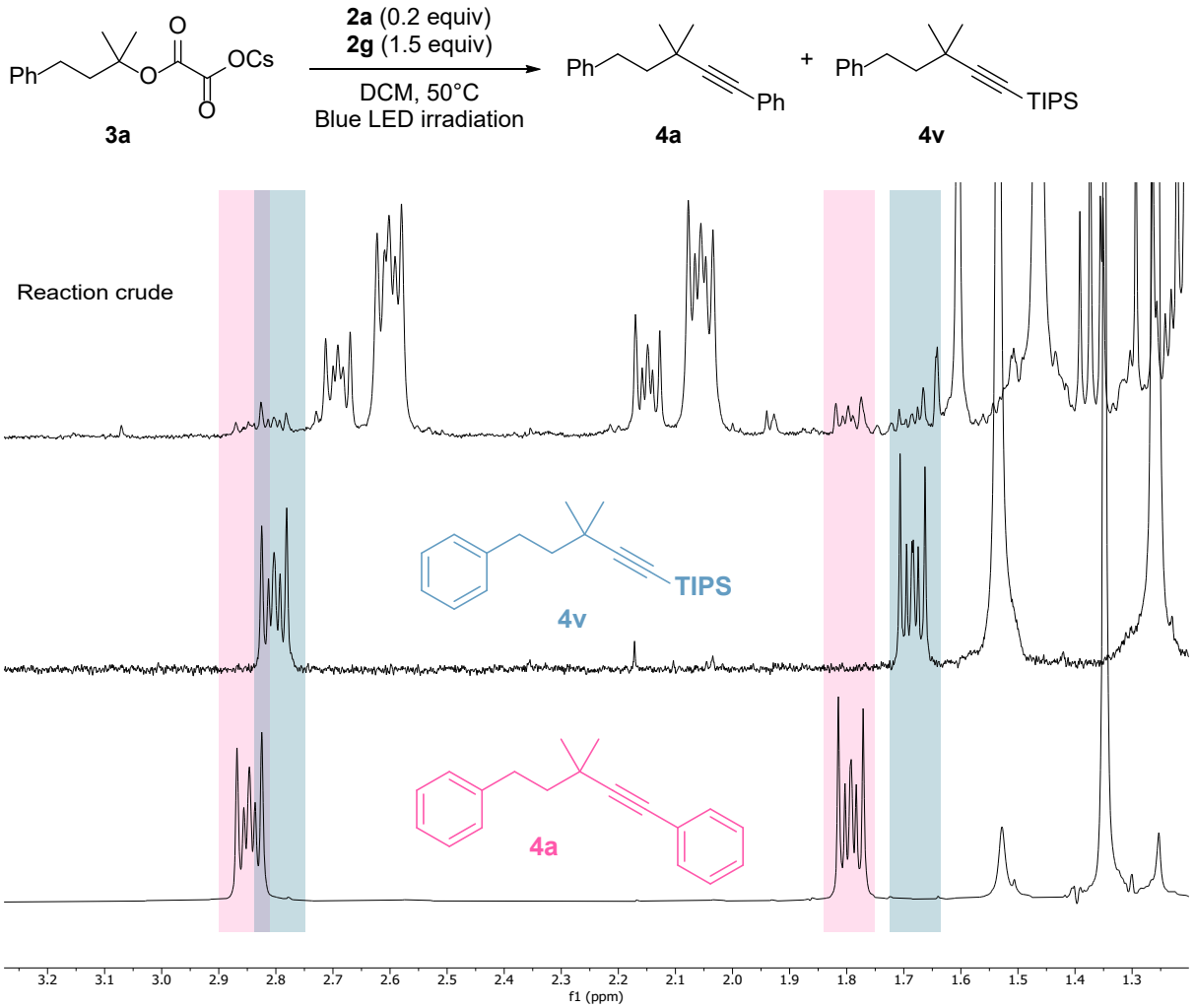
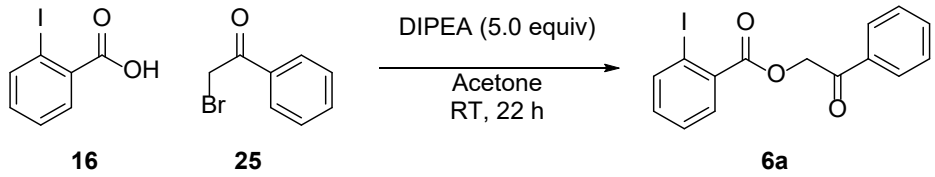


Figure S3. TIPS-alkynylation with PhEBX as a photooxidant

6.2. Synthesis and characterization of **6a**, **6b** and **4v**

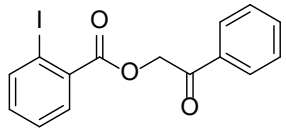
2-Oxo-2-phenylethyl 2-iodobenzoate (**6a**)



Following a reported procedure,[23] 2-iodobenzoic acid (**16**, 744 mg, 3.00 mmol, 1.00 equiv) and 2-bromo-1-phenylethanone (**25**, 657 mg, 3.30 mmol, 1.10 equiv) were dissolved in acetone (12.0 mL). DIPEA (2.6 mL, 15 mmol, 5.0 equiv) was then added and the reaction mixture was stirred overnight. The mixture was then diluted with EtOAc and washed with water. The organic layer was dried over

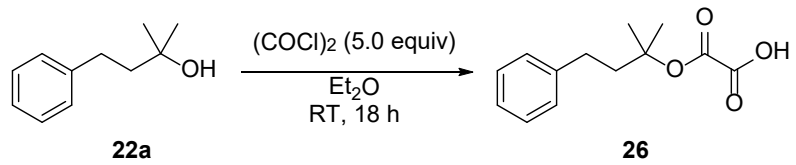
[23] Speckmeier, E.; Zeitler, K. *ACS Catal.* **2017**, *7*, 6821–6826.

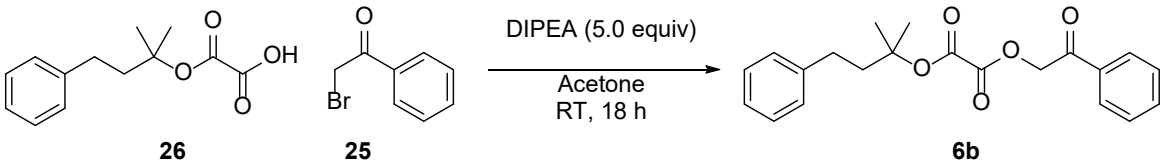
$MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2, 10% EtOAc in pentane, Rf = 0.4) obtaining 2-oxo-2-phenylethyl 2-iodobenzoate (**6a**, 660 mg, 1.80 mmol, 60% yield) as an off-white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 8.03 (dd, *J* = 8.0, 1.2 Hz, 1H, Ar*H*), 8.00 – 7.94 (m, 2H, Ar*H*), 7.68 – 7.59 (m, 1H, Ar*H*), 7.56 – 7.49 (m, 2H, Ar*H*), 7.45 (td, *J* = 7.7, 1.2 Hz, 1H, Ar*H*), 7.20 (td, *J* = 7.7, 1.7 Hz, 1H, Ar*H*), 5.60 (s, 2H, CH_2).
^{13}C NMR (101 MHz, CDCl3) δ: 191.8, 165.9, 141.6, 134.3, 134.2, 133.2, 131.8, 129.1, 128.2, 128.0, 94.6, 66.9. 1 Carbon atom is unresolved. Constitent with reported literature data.[23]

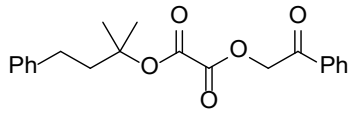
2-methyl-4-phenylbutan-2-yl (2-oxo-2-phenylethyl) oxalate (6b)





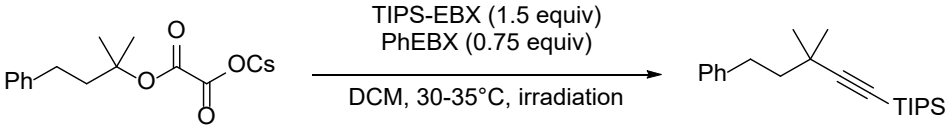
Following a modified reported procedure,[24] a solution of 2-methyl-4-phenylbutan-2-ol (**22a**, 0.85 mL, 5.0 mmol, 1.0 equiv) in Et_2O (40 mL) was cooled to 0 °C. Oxalyl dichloride (0.90 mL, 10 mmol, 2.0 equiv) was then added dropwise. The mixture was warmed to room temperature after 10 min, and after an additional 1.5 h, oxalyl dichloride (0.44 mL, 5.0 mmol, 1.0 equiv) were added. After an additional 1h oxalyl dichloride (0.90 mL, 10 mmol, 2.0 equiv) was added and the reaction was stirred for another hour. The reaction was carefully quenched at 0 °C by the dropwise addition of H2O (30 mL) after addition of a vent needle. The mixture was stirred vigorously and warmed to room temperature. The layers were separated, and the aqueous layer extracted with Et_2O (3 x 15 mL), and the combined organic layers dried with Na_2SO_4, filtered, and concentrated under reduced pressure affording 2-(2-methyl-4-phenylbutan-2-yl)oxy-2-oxoacetic acid as a clear oil (767 mg, 3.25 mmol, 65% yield), which was used directly in the next step. Following a modified reported procedure,[23] the crude oil of 2-(2-methyl-4-phenylbutan-2-yl)oxy-2-oxoacetic acid (**26**, 767 mg, 3.25 mmol, 1.0 equiv) was dissolved in acetone (12 mL). DIPEA (2.4 mL, 15 mmol, 5 equiv) and phenacyl bromide (**25**, 597 mg, 3.00 mmol, 0.9 equiv) were then added. The reaction was stirred overnight. The reaction was quenched with water (5 mL), diluted with EtOAc (20 mL). The organic layer was washed with sat. aq. NH4Cl (3 x 10 mL), then brine (10 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to afford 2-methyl-4-phenylbutan-2-yl (2-oxo-2-phenylethyl) oxalate as a crude yellow oil (**6b**, 930 mg, 2.62 mmol, 87% yield, 52% yield over both steps).

[24] Su, J. Y.; Grünenfelder, D. C.; Takeuchi, K.; Reisman, S. E. *Org. Lett.* **2018**, *20*, 4912–4916.



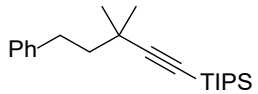
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.89 (m, 2H, Ar*H*), 7.67 – 7.58 (m, 1H, Ar*H*), 7.50 (t, *J* = 7.7 Hz, 2H, Ar*H*), 7.29 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.25 – 7.17 (m, 3H, Ar*H*), 5.50 (s, 2H, C(O)C*H*$_2$O), 2.77 – 2.69 (m, 2H, PhC*H*$_2$), 2.23 – 2.14 (m, 2H, C*H*$_2$), 1.65 (s, 6H, C(C*H*$_3$)$_2$.
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 157.7, 156.2, 141.6, 134.2, 133.9, 129.0, 128.5, 128.5, 127.9, 126.0, 87.2, 67.6, 42.6, 30.3, 25.8.
IR (ν_{max}, cm^{-1}) 2978 (s), 2904 (s), 1739 (m), 1705 (m), 1381 (m), 1242 (m), 1165 (s), 1111 (s), 1065 (s).
HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}NaO_5^+$ 377.1359; Found 377.1363.

(3,3-Dimethyl-5-phenylpent-1-yn-1-yl)triisopropylsilane (**4v**)



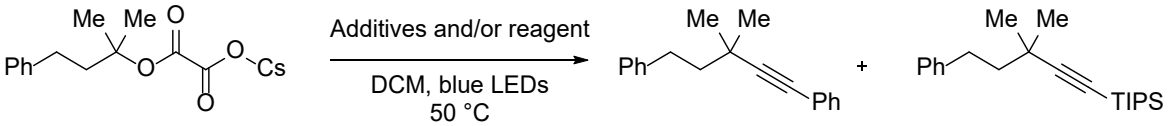
3a **4v**

An oven dried dram vial (2 mL), equipped with a magnetic stirrer, was charged with cesium oxalate (**3a**, 0.036 g, 0.10 mmol, 1 equiv), TIPS-EBX (**2g**, 0.064 g, 0.15 mmol, 1.5 equiv) and PhEBX (**2a**, 0.026 g, 0.075 mmol, 0.75 equiv). The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), dry degassed (freeze pump thaw) CH_2Cl_2 was added and the septum was replaced with a screw cap under a flux of Ar. The reactions were placed between 2 x 440 nm Kessil lamps at ca. 10 cm distance from both lamps (with ventilation T = ca. 30-35°C as specified) and stirred under irradiation for 18 hours. The reaction was filtered through a small celite plug which was washed with CH_2Cl_2. The reaction crude was concentrated *in vacuo*, and purified by preparative TLC (SiO2, heptane), affording (3,3-dimethyl-5-phenylpent-1-yn-1-yl)triisopropylsilane (**4v**, 2 mg, 0.006 mmol, 6% yield)



Rf (pentane) = 0.55
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.23 – 7.14 (m, 3H, Ar*H*), 2.85 – 2.75 (m, 2H, PhC*H*$_2$), 1.72 – 1.65 (m, 2H, C*H*$_2$), 1.26 (s, 6H, C(C*H*$_3$)$_2$), 1.13 – 0.98 (m, 22H, TIPS).
^{13}C NMR (101 MHz, CDCl3) δ 143.0, 128.4, 128.4, 125.6, 116.2, 79.4, 45.8, 32.2, 29.7, 29.4, 18.7, 11.3.
HRMS (APPI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{36}NaSi^+$ 351.2478; Found 351.2485.

6.3.Control experiments



3a **4a** **4v**

An oven dried dram vial (2 mL), equipped with a magnetic stirrer, was charged with the solid components following table S3: cesium oxalate **3a**, TIPSEBX (**2g**) , PhEBX (**2a**), 4CzIPN (**1a**), BIOAc (**5a**), BIOH (**5b**), **6a**, **6b**. The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), CH_2Cl_2 (3.0 mL) was added and the septum was replaced with a screw cap

under a flux of Ar.[25] The reactions were placed between 2 x 440 nm Kessil lamps (unless specified otherwise) at ca. 10 cm distance from both lamps (no ventilation, T = ca. 50 °C) and stirred under irradiation for 18 hours. The reaction was filtered through a small celite plug which was washed with CH_2Cl_2. The reaction crude was concentrated *in vacuo*, diluted with $CDCl_3$ and 1 equiv of CH_2Br_2 was added as internal standard for ^1H NMR analysis.

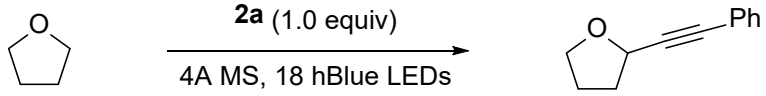
Table S3. Control reactions for the indetification of the photoactive species without photocatalyst

entry[a]	**Reagent** (**1.5 equiv**)	**additive** (**equiv**)	**residual 3a** (%)	**^1H NMR yield**[b] **(%)**
1	2g	-	100	nd
2	2g	**1a** (0.05)	30	25
3	2g	**5a** (0.2)	92	5
4	2g	**5b** (0.2)	92	5
5	-	**5a** (1.5)	90	-
6	-	**5b** (1.5)	100	-
7	2g	**6a** (0.2)	98	2
8	-	**6a** (1.0)	100	-
9[c]	Ph	**6b** (1.0)	-	nd[d]
10	2g	**6b** (0.7)	>90	<5
17	-	**6b** (1.0)	>95	-
18	2g	**2a** (0.2)	80	16

[c]No cesium salt was used. [d]No degradation of **6b** was observed, full decomposition of PhEBX. This suggests that **6b** is not a reaction intermediate.

6.4. Photocatalyst free alkynylations with EBXs:

HAT



8 **9**

Following a modified reported procedure,[26] an oven dried (7.5 mL) dram vial equipped with a magnetic stirrer was charged with MS 4Å (20 mg) and PhEBX (**2a**, 70 mg, 0.20 mmol, 1.0 equiv). The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), THF (4.00 mL) was added and the septum is replaced with a screw cap under a flux of Ar. The reactions were placed between 2 x 460 nm Kessil lamps at ca. 10 cm distance from both lamps (no ventilation, T = ca. 50 °C) and stirred under irradiation for 18 hours. The reaction was filtered through a small celite plug which was washed with CH_2Cl_2. The reaction crude was concentrated in vacuo. An NMR sample of the crude was prepared with 1 equiv of CH_2Br_2 (14.0 µL, 0.200 mmol, 1 equiv) in $CDCl_3$. The ^1H NMR yield was determined using the signal at 4.81 (dd, *J* = 7.2, 5.2 Hz, 1H, C*H*$_x$O): 80%.

[25] Use of a screw cap or crimp cap is of great importance, the irradiation causes an increase in temperature causing the CH_2Cl_2 to evaporate and an overpressure inside the vessel. When using a septum, the latter would fly off within an hour of irradiation. As shown in the optimization section DCE is not as good a solvent as CH_2Cl_2.
[26] Matsumoto, K.; Nakajima, M.; Nemoto, T. *J. Org. Chem.* **2020**, *85* (18), 11802–11811.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.41 (m, 2H, Ar*H*), 7.31−7.28 (m, 3H, Ar*H*), 4.81 (dd, *J* = 7.2, 5.2 Hz, 1H, CH_xO), 4.04−3.99 (m, 1H, CH_xO), 3.89−3.83 (m, 1H, CH_xO), 2.29−2.19 (m, 1H, CH_x), 2.15−2.04 (m, 2H, CH_x), 1.99−1.90 (m, 1H, CH_x). Corresponds to the reported literature data.[26]

Difunctionalisation

1.5 equiv
10

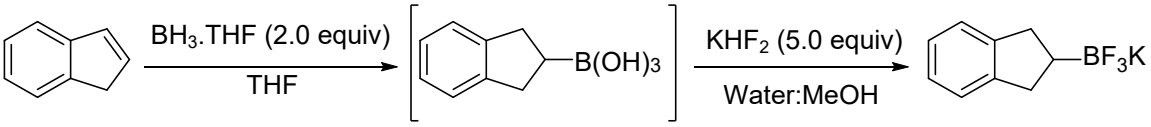
11

Following a modified reported procedure,[27] an oven dried dram vial, equipped with a magnetic stir bar was charged with **2a** (35 mg, 0.10 mmol, 1.0 equiv) and **5a** (15 mg, 0.050 mmol, 0.50 equiv). After 3 vacuum/nitrogen cycles refilling with Ar on the last cycle, degassed CH_2Cl_2 (0.40 mL) was added followed by *N*-vinylpyrolidinone (**10**) (16.7 mg, 16.0 µL, 150 µmol, 1.50 equiv). The reaction was irradiated for 19 hours with 2 x 440 nm Kessil lamps. The reaction was concentrated in vacuo. An NMR sample of the crude was prepared with 1 equiv of CH_2Br_2 (7.0 µL, 0.10 mmol, 1 equiv) in CD_3CN. The ^{1}H NMR yield was determined using the signal at 5.53 ppm (dd, *J* = 8.6, 4.8 Hz, 1H, NC*H*CH_2O): 35%

^{1}H NMR (400 MHz, Acetonitrile-d3) δ 8.06 (dd, *J* = 7.9, 1.2 Hz, 1H, Ar*H*), 7.81 (dd, *J* = 7.8, 1.7 Hz, 1H, Ar*H*), 7.58 – 7.47 (m, 3H, Ar*H* and Ph*H*), 7.47 – 7.33 (m, 3H, Ph*H*), 7.27 (td, *J* = 7.7, 1.8 Hz, 1H, Ar*H*), 5.53 (dd, *J* = 8.6, 4.8 Hz, 1H, NC*H*CH_2O), 4.64 (dd, *J* = 11.3, 8.6 Hz, 1H, NCHC*H*$_2$O), 4.50 (dd, *J* = 11.2, 4.8 Hz, 1H, NCHC*H*$_2$O), 3.75 – 3.52 (m, 2H, C*H*$_2$), 2.39 – 2.30 (m, 2H, C*H*$_2$), 2.12 – 2.02 (m, 2H, C*H*$_2$). Corresponds to the reported literature data.[27]

Deboronative alkynylation

*potassium 2,3-dihydro-1H-inden-2-yl-tris(fluoranyl)borate (**12**)*



1.0 equiv
27

28

12

Following a reported procedure,[28] a flame dried round bottom flask containing a solution of BH_3.THF (34.0 mL, 34.0 mmol, 1.00 M, 2.00 equiv) in THF was cooled to 0 °C. A solution of 1H-indene (**27**) (1.98 mL, 17.0 mmol, 1.00 equiv) in tetrahydrofuran (3.40 mL) was added and the mixture was warm to rt and stirred for 2 h. Water (3.40 mL) was added dropwise and the mixture was stirred for 3 h at rt. The mixture was concentrated in vacuo to remove the solvents except water. Ethyl acetate

[27] Amos, S. G. E.; Nicolai, S.; Waser, J. *Chem. Sci.* **2020**, *11*, 11274-11279
[28] Weng, W.-Z.; Liang, H.; Zhang, B. *Org. Lett.* **2018**, *20* (16), 4979–4983.

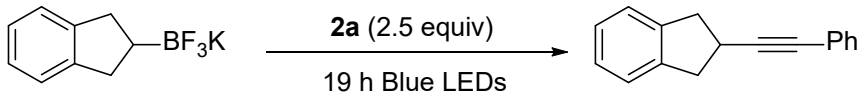
(50 mL) was added to the suspension and the mixture was washed with a sat. sol. of $NaHCO_3$ (50 mL) and brine (50 mL). The organic layers were combined, dried over $MgSO_4.(H_2O)_2$ and concentrated in vacuo. The crude oil was used directly in next step. To a round bottom flask (PFA) containing a solution of potassium hydrogen fluoride (6.64 g, 85.0 mmol, 5.00 equiv) in water (25.0 mL) were added the crude boronic acid (**28**) and methanol (34.0 mL). The mixture was stirred at rt open to air for 2 h. The mixture was concentrated in vacuo, the wet solid obtained was further dried by co-evaporation with acetone (3 times). The resulting solid was diluted with acetone (30 mL) and was put on the rotavap at P_{atm} with the bath at 45 °C for 10 minutes. The solution was filtered with care to leave the remaining insoluble solid in the flask. This process was repeated 2 more times, the solution of acetone was concentrated in vacuo to 1/3 of the initial volume. The solution was left to cool to rt then Et_2O was added to induce precipitation (~40 mL). The solution was cooled to 0 °C and left for 15 min standing at this temperature. The solid was filtered, washed with Et_2O and dried in vacuo to afford potassium 2,3-dihydro-1*H*-inden-2-yl-tris(fluoranyl)borate (**12**) (1.38 g, 6.14 mmol, 36% yield) as a white solid.

^{1}H NMR (400 MHz, Acetone) δ 7.07 (dd, *J* = 5.3, 3.3 Hz, 2H, Ar*H*), 6.95 (dd, *J* = 5.5, 3.1 Hz, 2H, Ar*H*), 2.75 (dd, *J* = 9.9, 3.6 Hz, 4H, CH_2), 1.29 (m, 1H, C*H*B).

^{13}C NMR (101 MHz, Acetone) δ 148.3, 125.6, 124.6, 36.8. One carbon is not resolved.

^{19}F NMR (376 MHz, Acetone) δ -146.34 (d, *J* = 95.0 Hz). Corresponds to the reported literature data.[29]

*Deboronative alkynylation: synthesis of **13***



1.0 equiv
12

13

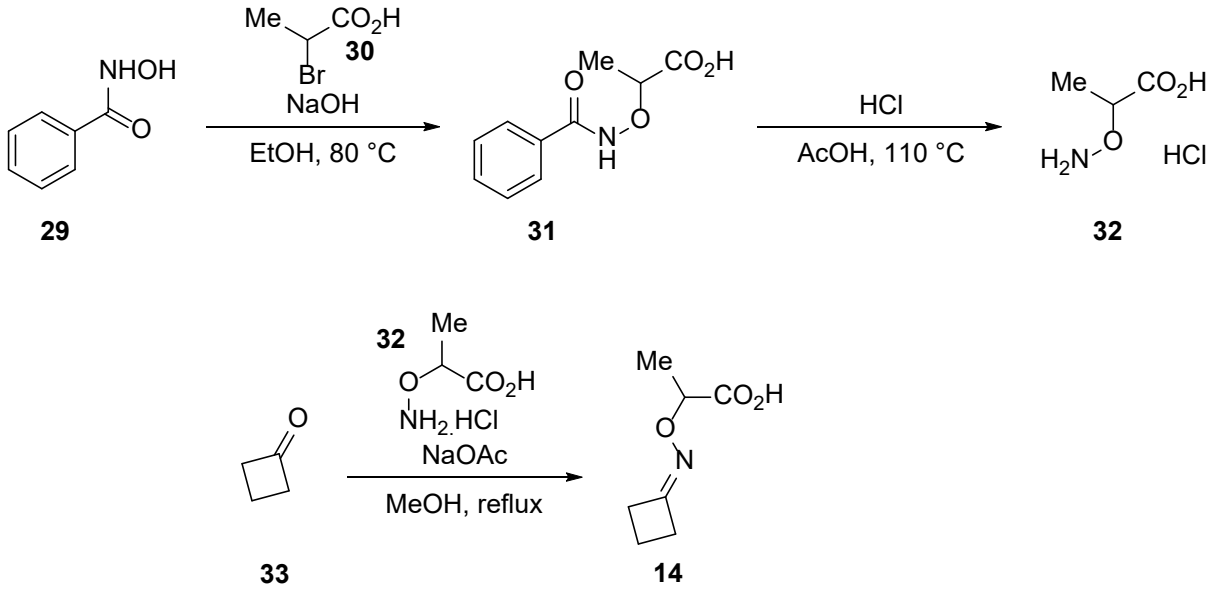
Following a modified reported procedure,[29] a dram vial, equipped with a magnetic stirring bar, was charged with potassium 2,3-dihydro-1H-inden-2-yl(trifluoro)borate (**12**, 22 mg, 0.10 mmol, 1.0 equiv), **2a** (87.0 mg, 250 µmol, 2.50 equiv) and sodium carbonate (21 mg, 0.20 mmol, 2.0 equiv). Degassed H_2O (0.5 mL) (water was bubbled with nitrogen gas for 30 minutes to remove oxygen before the experiment) and CH_2Cl_2 (0.5 mL) were added, the vial was sealed and the reaction was irradiated with 2 x 440 nm Kessil lamps under strong agitation for 19 hours. The reaction mixture was extracted with CH_2Cl_2 (3 x 7 mL). The organic layers were combined, washed with sat. aq. NaCl (10 mL) then dried over Na_2SO_4, filtered and concentrated in vacuo. An NMR sample of the crude was prepared with 1 equiv of CH_2Br_2 (7.0 µL, 0.10 mmol, 1 equiv) in CDCl3. The ^{1}H NMR yield was determined using the signal at 3.30 ppm (p, *J* = 8.5 Hz, 1H, CH-alkyne): 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.37 (m, 2H, Ar*H*), 7.31– 7.24 (m, 3H, Ar*H*), 7.24–7.19 (m, 2H, Ar*H*), 7.19–7.13 (m, 2H, Ar*H*), 3.43 (p, *J* = 8.5 Hz, 1H, C*H*-alkyne), 3.30 (dd, *J* = 15.4, 8.0 Hz, 2H, CH_2), 3.12 (dd, *J* = 15.4, 8.0 Hz, 2H, CH_2). Corresponds to reported literature data.[29]

[29] Huang, H.; Zhang, G.; Gong, L.; Zhang, S.; Chen, Y. *J. Am. Chem. Soc.* **2014**, *136* (6), 2280–2283.

Oxime fragmentation-alkynylation

*2-((Cyclobutylideneamino)oxy)propanoic acid (**14**)*



Compound **14** was taken directly from the batch synthesised for a previous project within our group.[30]

Following the reported procedure,[30] N-hydroxybenzamide (**29**) (6.08 g, 44.3 mmol, 1.0 equiv) and finely ground NaOH (5.32 g, 133 mmol, 3.0 equiv) were suspended in absolute EtOH (66 mL). To the resulting thick, off-white suspension, 2-bromopropanoic acid (**30**) (4.1 mL, 44 mmol, 1.0 equiv) was added slowly via syringe under stirring. This resulted in the conversion of the homogeneous suspension into a pale brown solution, which was then heated to 80 °C. Once this temperature was reached, the mixture looked again as a homogeneous, off-white suspension, which was stirred overnight. The mixture was then concentrated under reduced pressure to provide a solid residue, which was dissolved in water (90 mL). The resulting aqueous solution was washed once with diethyl ether (100 mL) and then acidified by careful addition of aq. HCl (37 % w/w) until pH = 1. It was then extracted with EtOAc (3 x 100 mL) and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum to provide an off-white solid. Recrystallization from hexane (50 mL) and EtOAc (100 mL) afforded 2-(benzamidooxy)propanoic acid (**31**) (7.08 g, 33.9 mmol, 76% yield) as a colorless solid. The compound was used directly in next step with no further analyses.

2-(Benzamidooxy)propanoic acid (**31**) (7.08 g, 33.8 mmol, 1.0 equiv) was suspended in acetic acid (20.5 mL). Aq. HCl (5.0 M; 68 mL, 34 mmol, 10 equiv) was then added and the mixture was heated to reflux (110 °C), which resulted in the formation of a pale yellow, clear solution. The latter was refluxed for 18 hours. It was then allowed to cool down to room temperature. This led to the precipitation of a crystalline solid (benzoic acid), which was filtered off. The resulting solution was stored at 4 °C overnight, which permitted the precipitation of a further amount of benzoic acid. Upon removal of the latter (4.13 g, 33.8 mmol, 100% yield) through filtration, the so-obtained clear solution was concentrated under vacuum. The resulting wet solid was further dried under vacuum at 60 °C for 3 hours. It was then refluxed in a mixture of EtOAc (30 mL) and EtOH (1.5 mL) for 20 minutes, filtered,

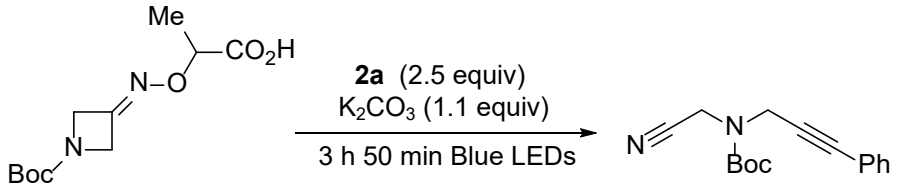
[30] H. Jiang, A. Studer, *Angew. Chem. Int. Ed.* **2017**, *56*, 12273–12276.

washed with pentane, and dried in the air. 2-(Aminooxy)propanoic acid hydrochloride (32) was obtained as a colorless solid (4.15 g, 29.3 mmol, 87% yield). The compound was used directly in next step with no further analyses.

Following a reported procedure,[31] a solution of cyclobutanone (**32**) (1.0 equiv) in MeOH (0.20 M) was treated with 2-(aminooxy)- propanoic acid hydrochloride (**31**) (226 mg, 1.60 mmol, 1.2 equiv), sodium acetate (2.4 equiv) and heated to reflux until complete by TLC analysis (4.5 – 6.0 hours). The mixture was then allowed to cool to room temperature and aq. Na_2CO_3 (2.0 M) was added. In some cases, the addition of a small volume of water was necessary to achieve the complete dissolution of the solids. The resulting aqueous solution was extracted once with Et_2O and the organic layer was washed with aq. Na_2CO_3 (2.0 M; 2 x). The combined aqueous extracts were then acidified by careful addition of aq. HCl solution (30% v/v) until pH < 2, and extracted with DCM (3 x). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum to provide the pure product 2-methyl-2-(((cyclobutylidene)amino)oxy)propanoic acid (**14**) was obtained as a pale yellow solid (0.150 g, 0.954 mmol, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 1H, CO_2H), 4.63 (q, *J* = 7.1 Hz, 1H, OC*H*), 3.09 – 2.77 (m, 4H, $CH_2CH_2CH_2C$=N), 2.00 (p, *J* = 8.4 Hz, 2H, $CH_2CH_2CH_2$), 1.47 (d, *J* = 7.1 Hz, 3H, *Me*). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.7, 161.4, 76.5, 31.6, 31.3, 16.8, 14.5.

*Oxime fragmentation-alkynylation: synthesis of **15***



1.0 equiv
14

15

Following a modified reported procedure,[32] a dram vial, equipped with a magnetic stirring bar, was charged with **2a** (87.0 mg, 250 µmol, 2.50 equiv), **14** (25.8 mg, 100 µmol, 1.00 equiv), potassium carbonate (15.2 mg, 110 µmol, 1.10 equiv). After 3 vacuum/nitrogen cycles, refilling with argon upon the last cycle, 1,2-dichloroethane (2.00 mL, degassed by bubbling Ar) was then added and the reaction was irradiated with 2 x 440 nm Kessil lamps for 3 h 50 min. An NMR sample of the crude was prepared with 1 equiv of CH_2Br_2 (7.0 µL, 0.10 mmol, 1 equiv) in $CDCl_3$. The ^{1}H NMR yield was determined using the signal at 4.34 ppm (s, 2H, CH_2): 75%.

^{1}H NMR H NMR (400 MHz, Acetonitrile-d_3) δ 7.46 (m, 2H, Ph*H*), 7.37 (m, 3H, Ph*H*), 4.34 (s, 2H, CH_2), 4.27 (s, 2H, CH_2), 1.49 (s, 9H, Boc). Corresponds to reported literature data.[32]

[31] E. M. Dauncey, S. P. Morcillo, J. J. Douglas, N. S. Sheikh, D. Leonori, *Angew. Chem. Int. Ed.* **2018**, *57*, 744–748.
[32] Le Vaillant, F.; Garreau, M.; Nicolai, S.; Gryn'ova, G.; Corminboeuf, C.; Waser, J. *Chem. Sci.* **2018**, *9*, 5883-5889.

6.5. UV-Vis absorption and fluorescence studies

Absorption and fluorescence studies of PhEBX **2a** and the cesium oxalate **3a**

A 5 mL 0.2 M stock solution of PhEBX (348 mg, 1.00 mmol) and a 2 mL 0.2 M stock solution of **3a** (147 mg, 0.4 mmol) were prepared in DMSO (from fresh ampoules, degassed and deuterated) were prepared in a 5 mL and 2 mL volumetric flask. The samples were prepared by dissolving 0.50 mL of stock solution with 0.5 mL of fresh DMSO, final concentration: 0.1 M. The samples were then submitted to UV-Vis, fluorescence and fluorescence excitation spectroscopy.

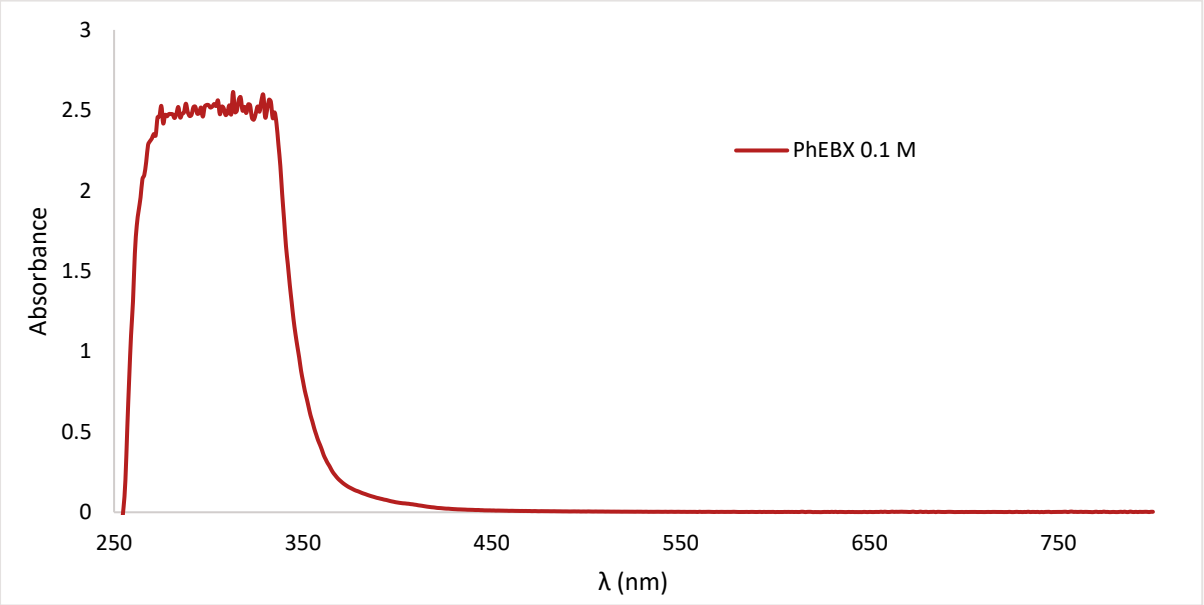


Figure S4. Absorption of PhEBX **2a**, 0.1 M in DMSO

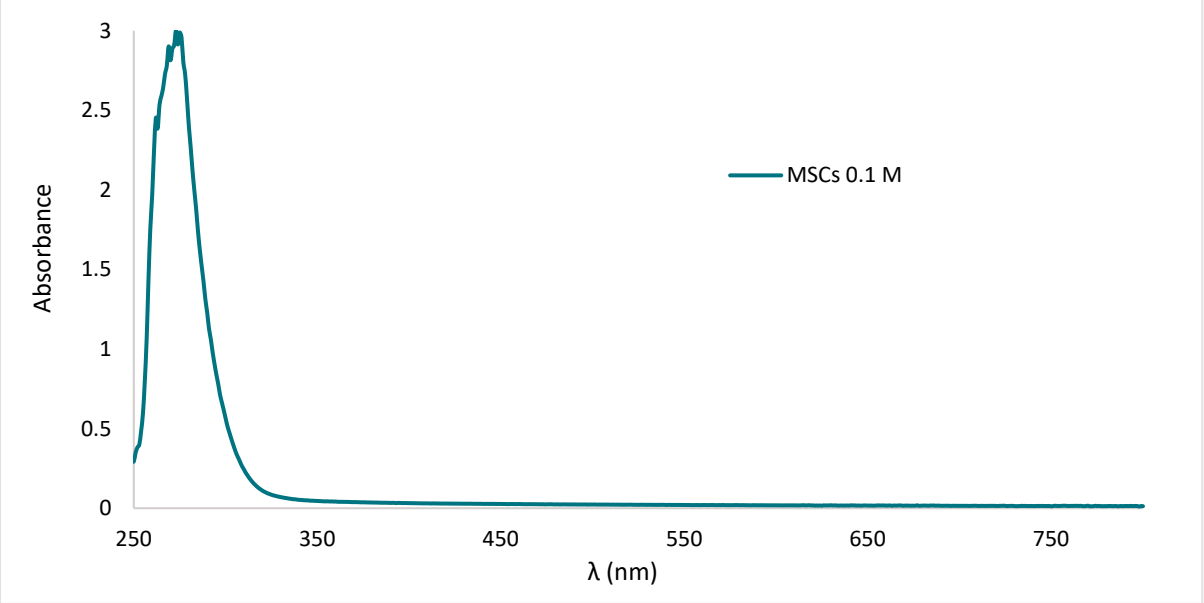


Figure S5. Absorption of **3a** 0.1 M in DMSO

We checked for the presence of an EDA complex by combining 0.50 mL of both stock solutions of **2a** and **3a** and measuring the UV-Vis spectrum, no new band can be observed (Figure S6)

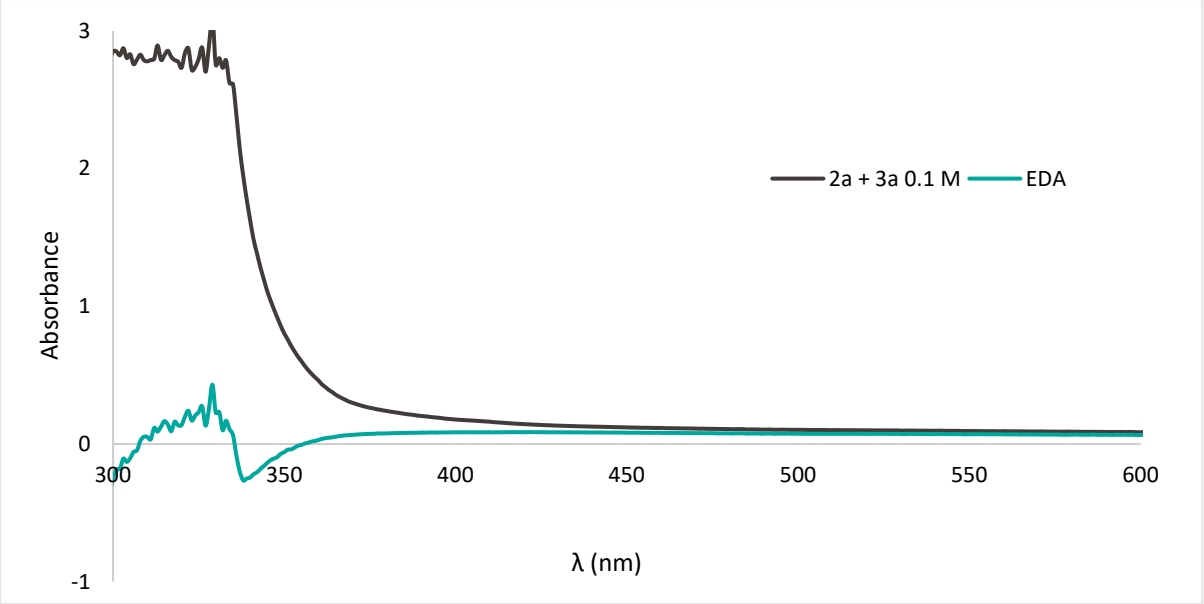


Figure S6. Absorption of a 1:1 mixture **2a**:**3a**.

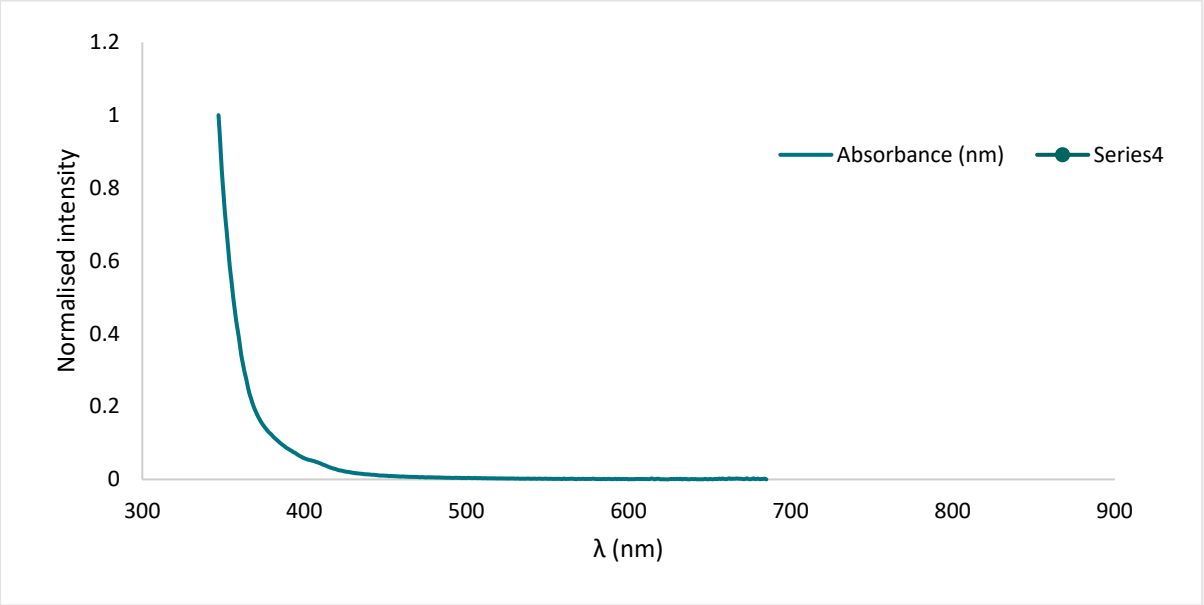


Figure S7. Normalized absorption, fluorescence (390 nm) and fluorescence excitation (485 nm) of **2a** (0.1 M) in DMSO

Absorption and Beer-Lambert linear regression at 420 nm and 440 nm of PhEBX (2a)

A 5 mL 0.14 M stock solution of PhEBX (**2a**, 243 mg, 0.700 mmol) in DMSO (from fresh ampoules, degassed and deuterated) was prepared in a 5 mL volumetric flask. Then 1 mL solutions were prepared following table S4, where C(**2a**) is the concentration of the stock solution, V(**2a**) is the volume of the stock solution used for the sample, V(DMSO) the volume of DMSO added for the dilution C_f(**2a**) the final concentration of the sample. UV-Vis spectra of each sample were then measured. Reproducibility of the measure was verified by repetition of the analyses.

Table S4. Sample preparation table for UV-Vis analyses for the Beer-Lambert linear regression

C(**2a**) (M)	V(**2a**) (mL)	V(DMSO) (mL)	C_f(**2a**) (M)
0.14	0	1.00	0
0.14	0.10	0.90	0.014
0.14	0.30	0.70	0.042
0.14	0.50	0.50	0.07
0.14	0.70	0.30	0.098
0.14	1.00	0	0.14

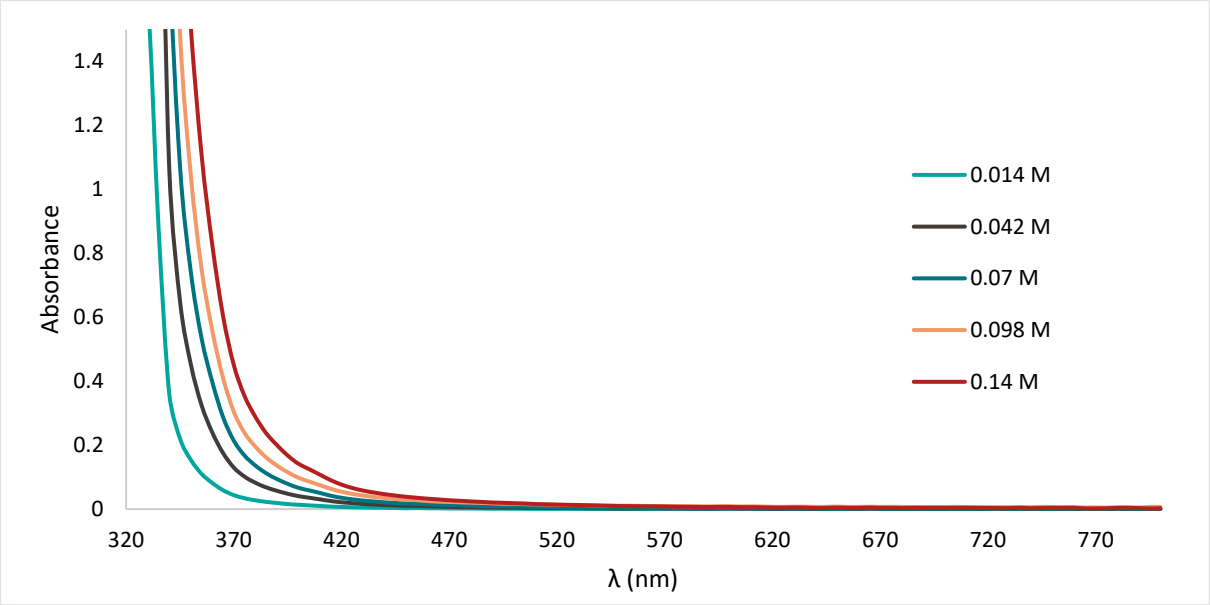


Figure S8. Absorption spectra of 2a at concentrations from 0.014 M to 0.14 M in DMSO

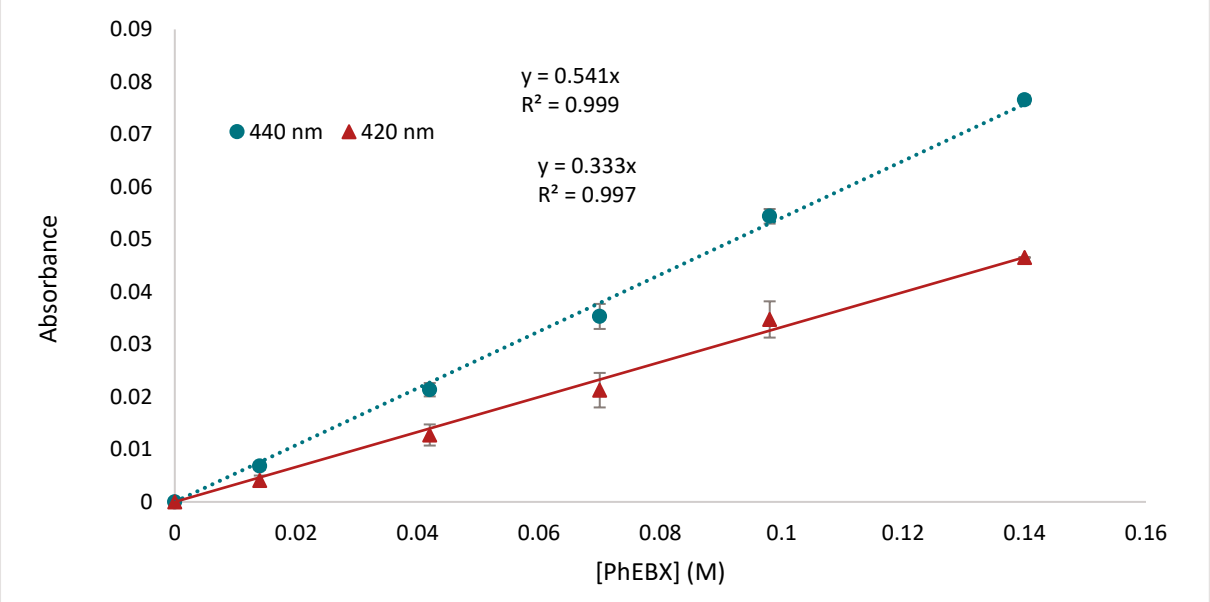


Figure S9. Beer-Lambert linear regression for 420 nm and 440 nm

6.6. Cyclic voltammetry of PhEBX (**2a**)

An Autolab potentiostat with a 3 electrode cell configuration: glassy carbon (working electrode), Pt wire as (control electrode), and Ag/AgCl (KCl, 3 M aq.) as (reference electrode) was used for the measures. Tetrabutyl ammonium hexafluorophosphhate (TBAP, 0.1 M in MeCN) was used as an electrolyte. PhEBX (**2a**, 3.5 mg, 0.01 mmol) was dissolved in a stock solution of TBAP (0.1 M, 10 mL in MeCN) and was degassed by bubbling Argon directly before measure. The redox couple E(**2a**/**2a**$^{\bullet-}$) is defined as the potential E measured for $\frac{I_{max}}{2}$.

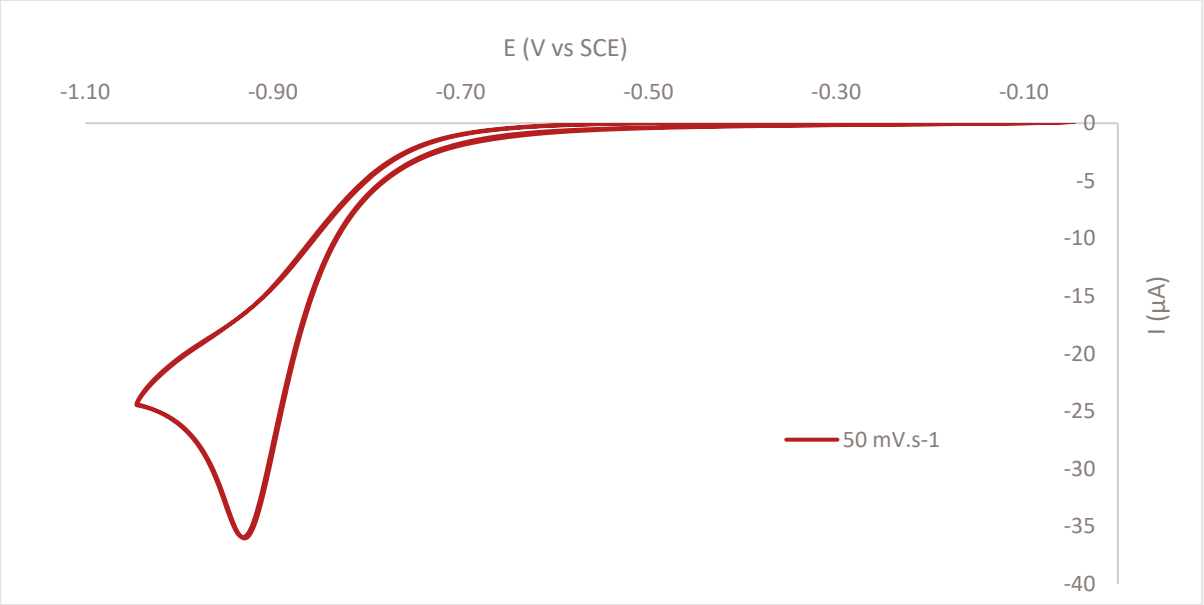


Figure S10. Cyclic voltammogram of **2a**

$$I_{max} = 36\ \mu A;\ \frac{I_{max}}{2} = 18\ \mu A\ E = -0.87\ V\ vs\ SCE\ for\ I = 18 \mu A$$

$$E_{1/2}(\mathbf{2a}/\mathbf{2a}^{\bullet-}) = -0.87\ V\ vs\ SCE$$

$E_{1/2}$(**2a***/**2a**$^{\bullet-}$) = $E_{0\text{-}0}$ + $E_{1/2}$(**2a**/**2a**$^{\bullet-}$). $E_{0\text{-}0}$ was determined experimentally by position of the long wavelength tail of the absorption spectrum at 460 nm (Figure S8).[33]

$$E = \frac{hc}{\lambda}$$

$$E_{0-0} = \frac{1240}{460} = 2.7\ eV$$

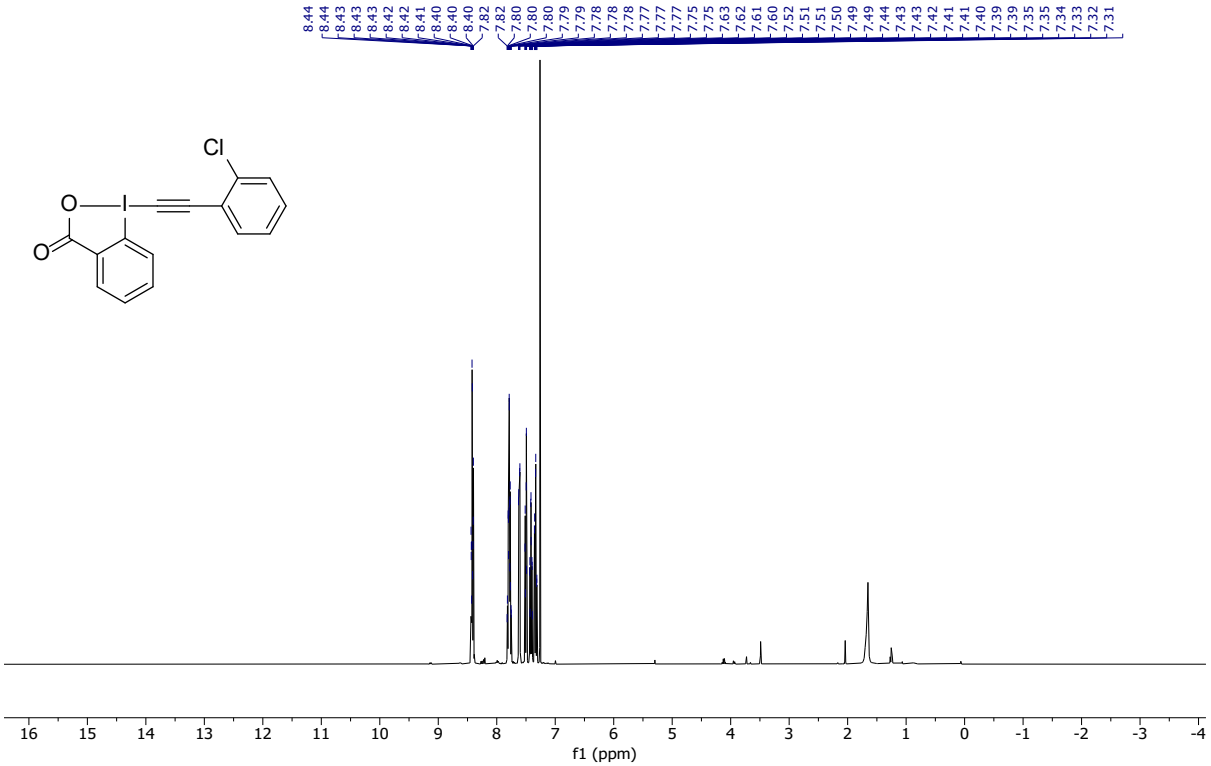
$$E_{1/2}(\mathbf{2a}^{*}/\mathbf{2a}^{\bullet-}) = E_{0-0} + E_{1/2}(\mathbf{2a}/\mathbf{2a}^{\bullet-}) = 2.7 - 0.87 = 1.83 = +1.8\ V\ vs\ SCE$$

7. NMR spectra of new compounds

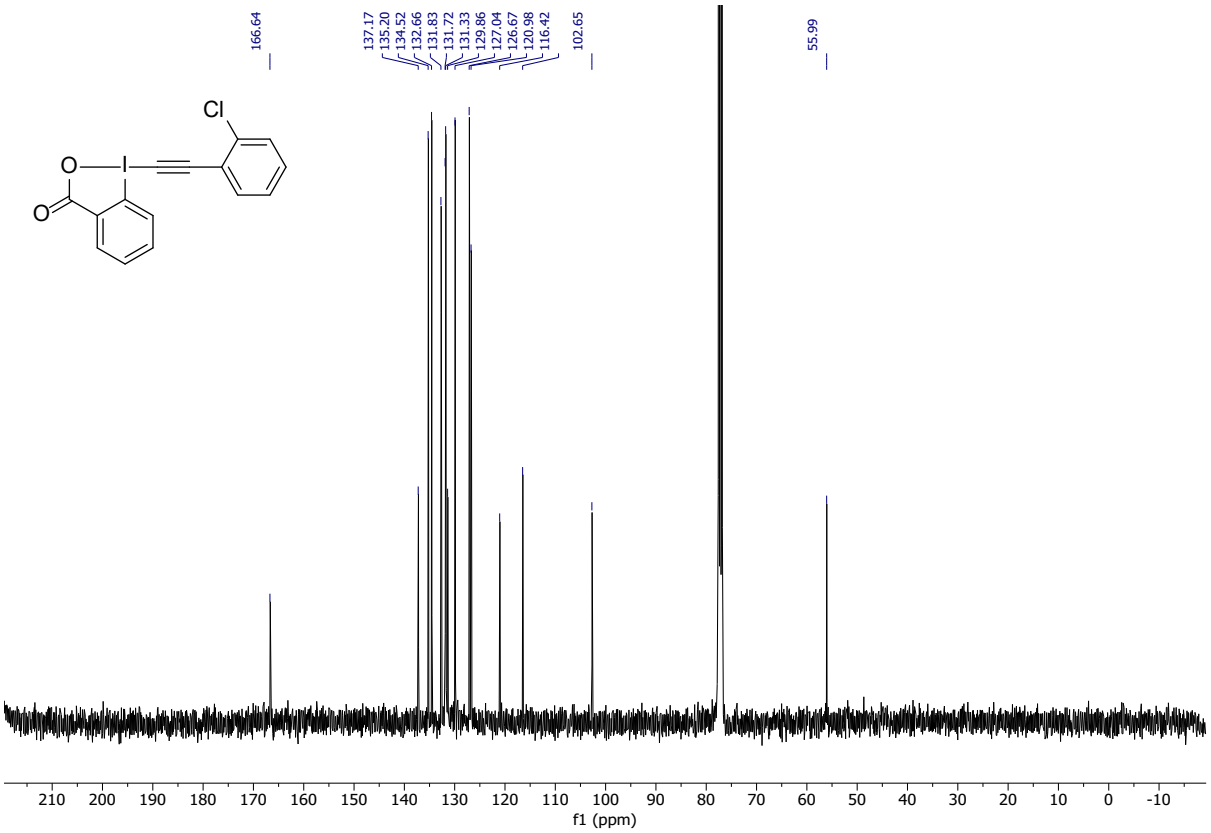
[33] Buzzetti, L.; Prieto, A.; Roy, S. R.; Melchiorre, P. *Angew. Chem. Int. Ed.* **2017**, *56* (47), 15039–15043.

Compound **2d**

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

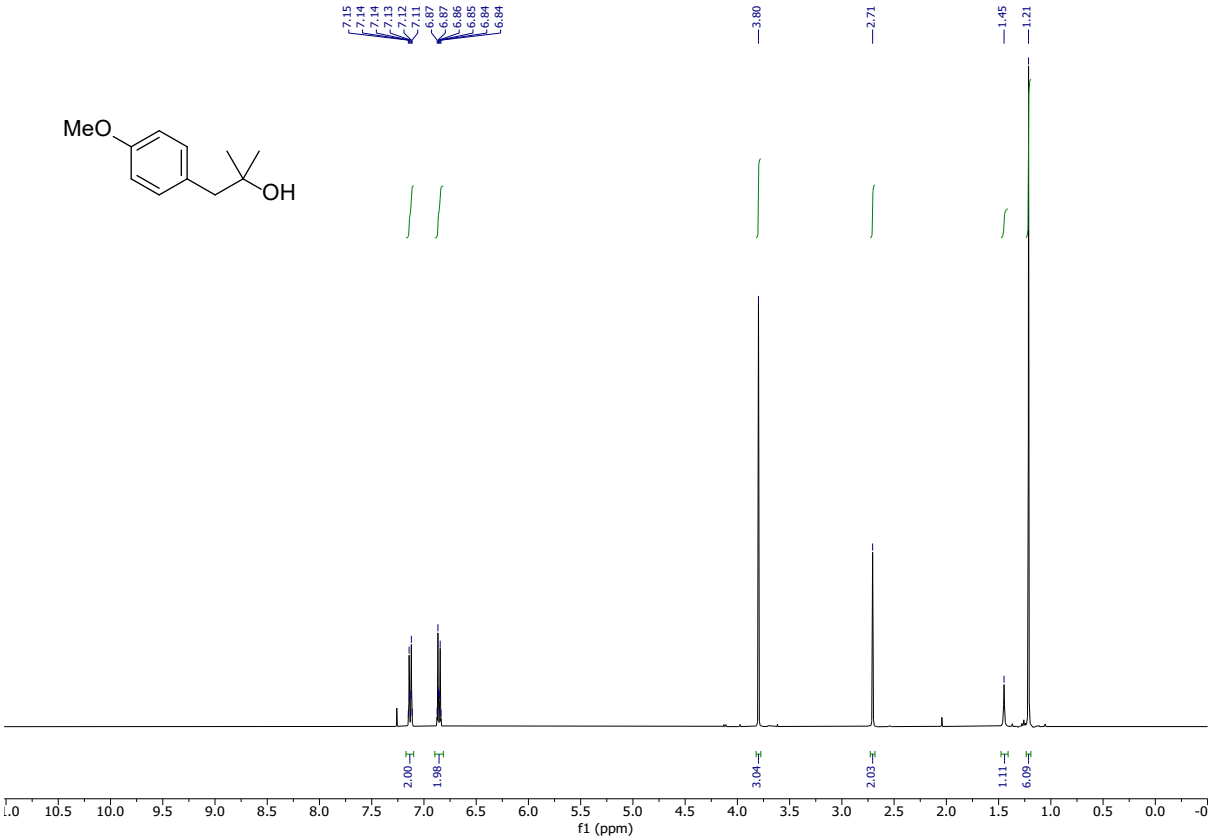


^{13}C NMR, $CDCl_3$, 101 MHz

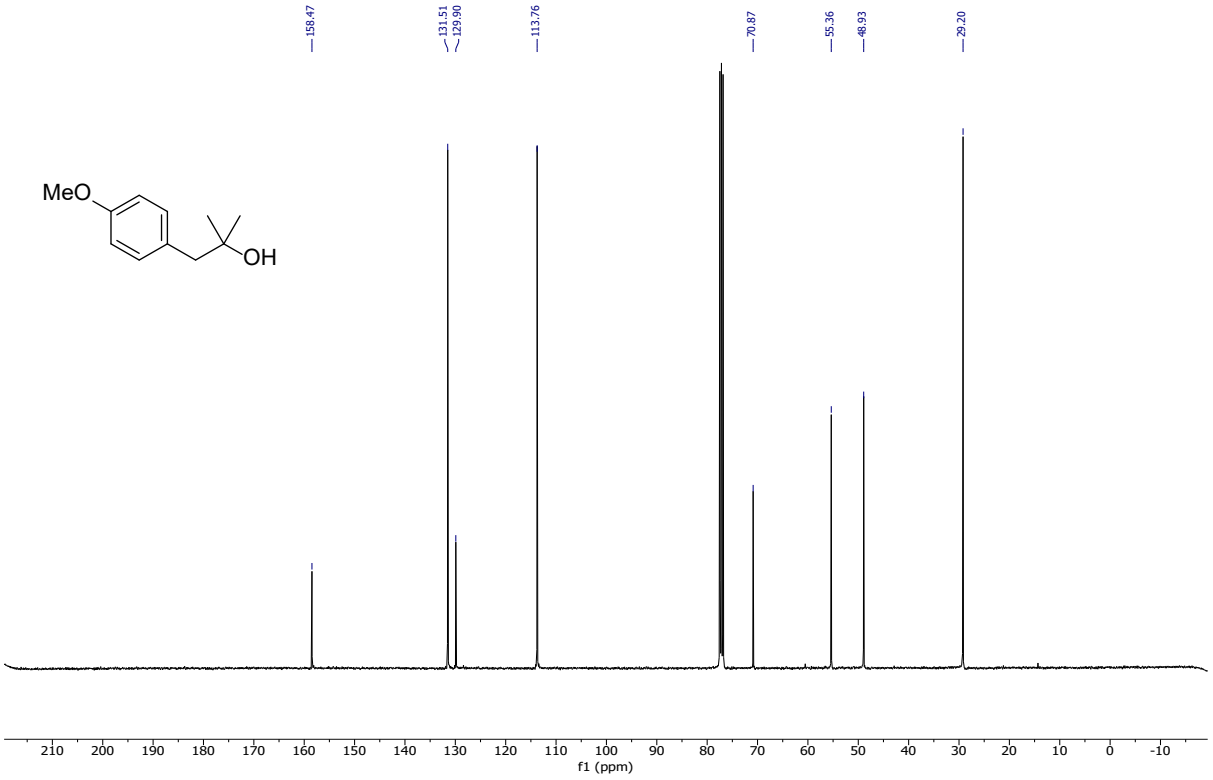


Compound **22e**

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

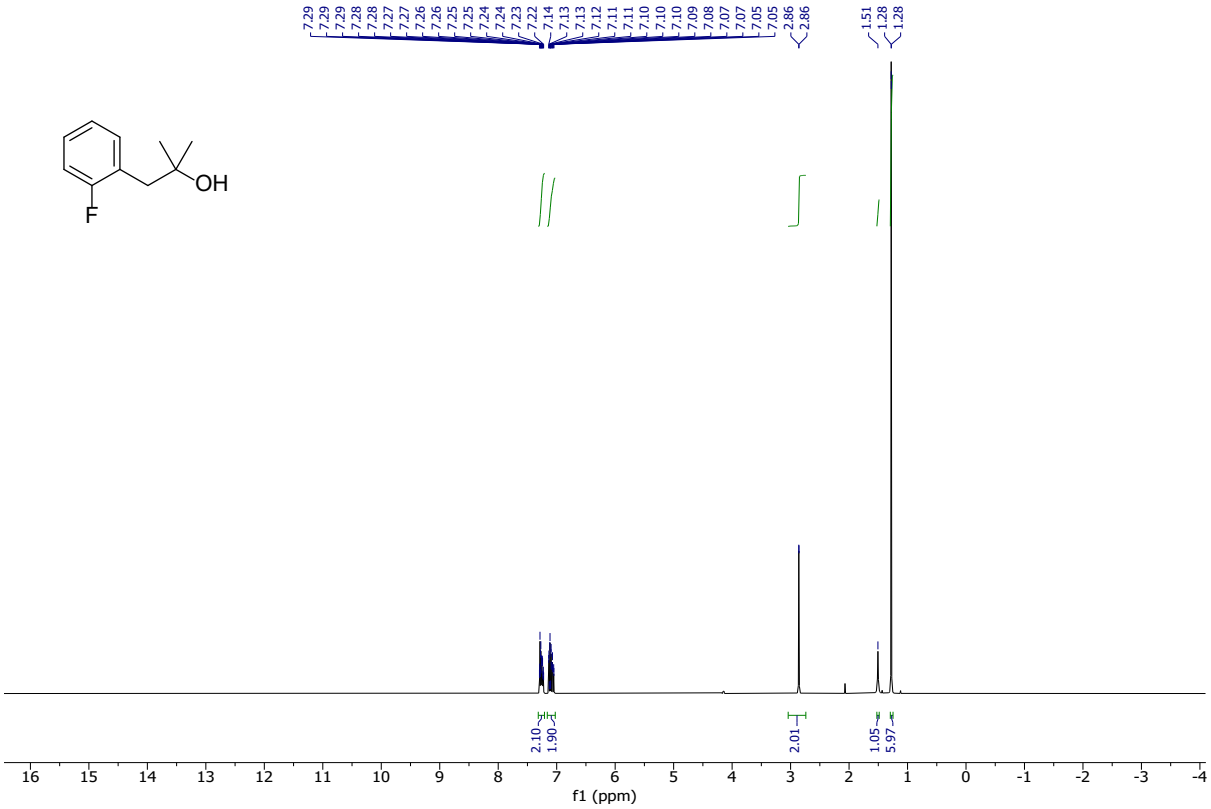


^{13}C NMR, $CDCl_3$, 101 MHz

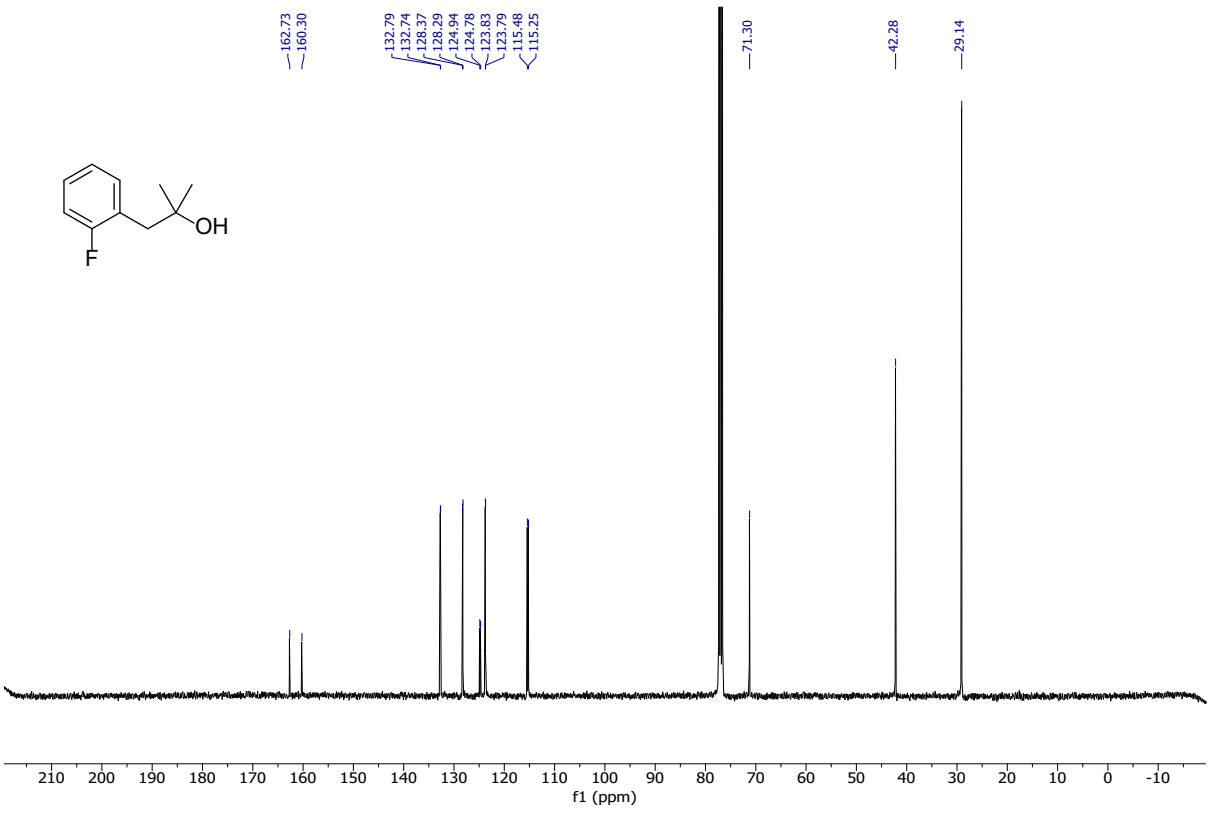


Compound **22f**

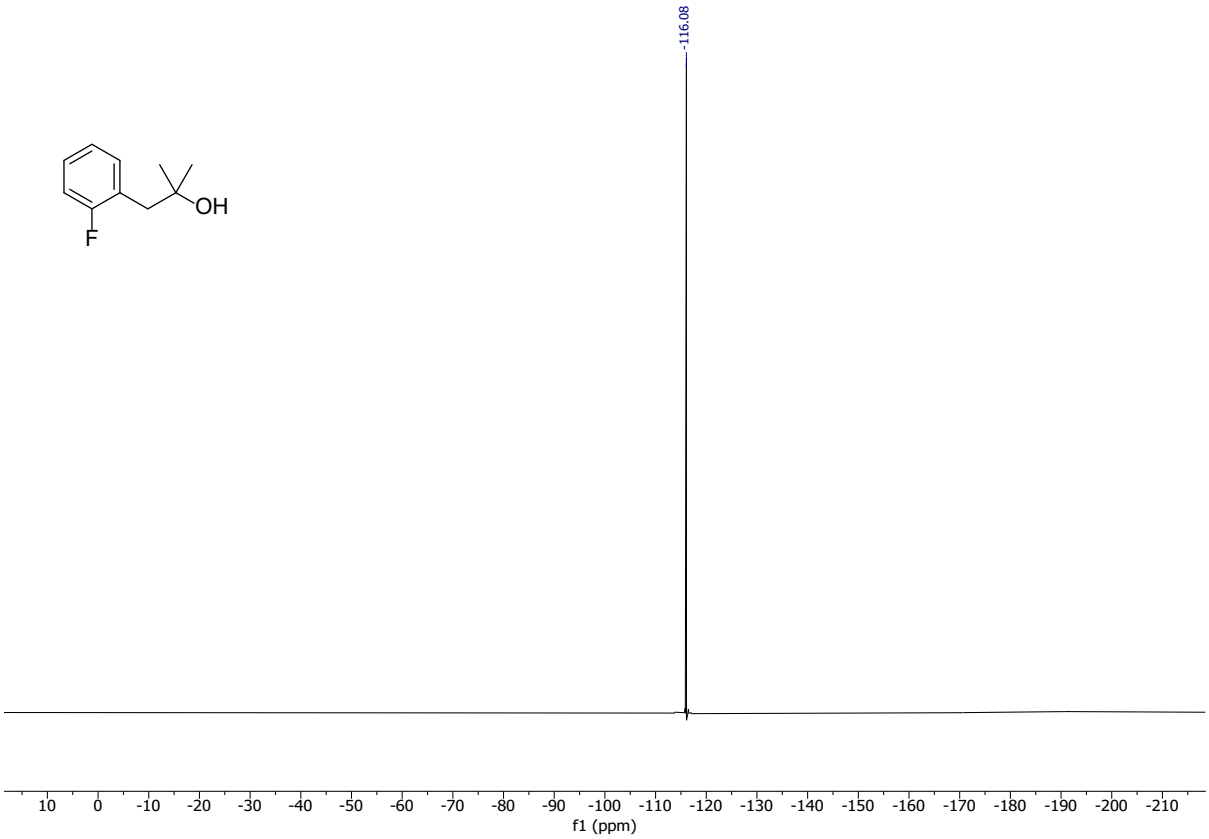
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

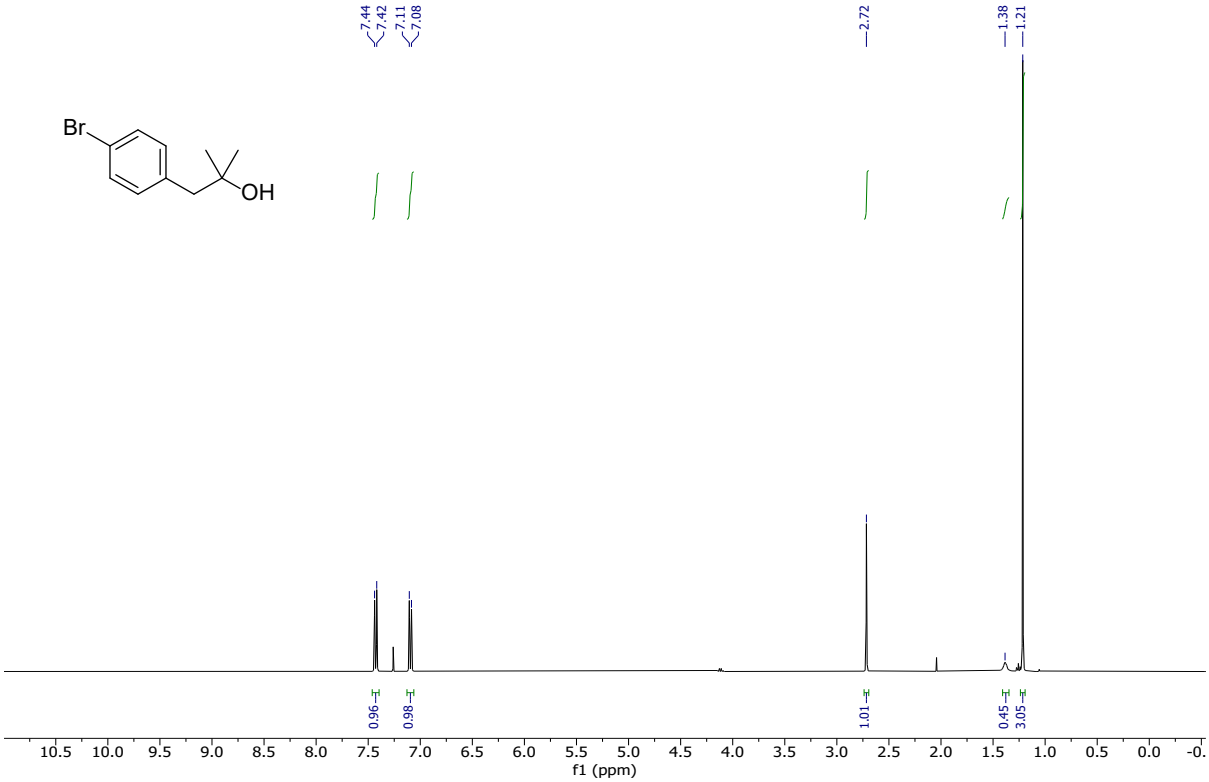


^{19}F NMR, $CDCl_3$, 376 MHz

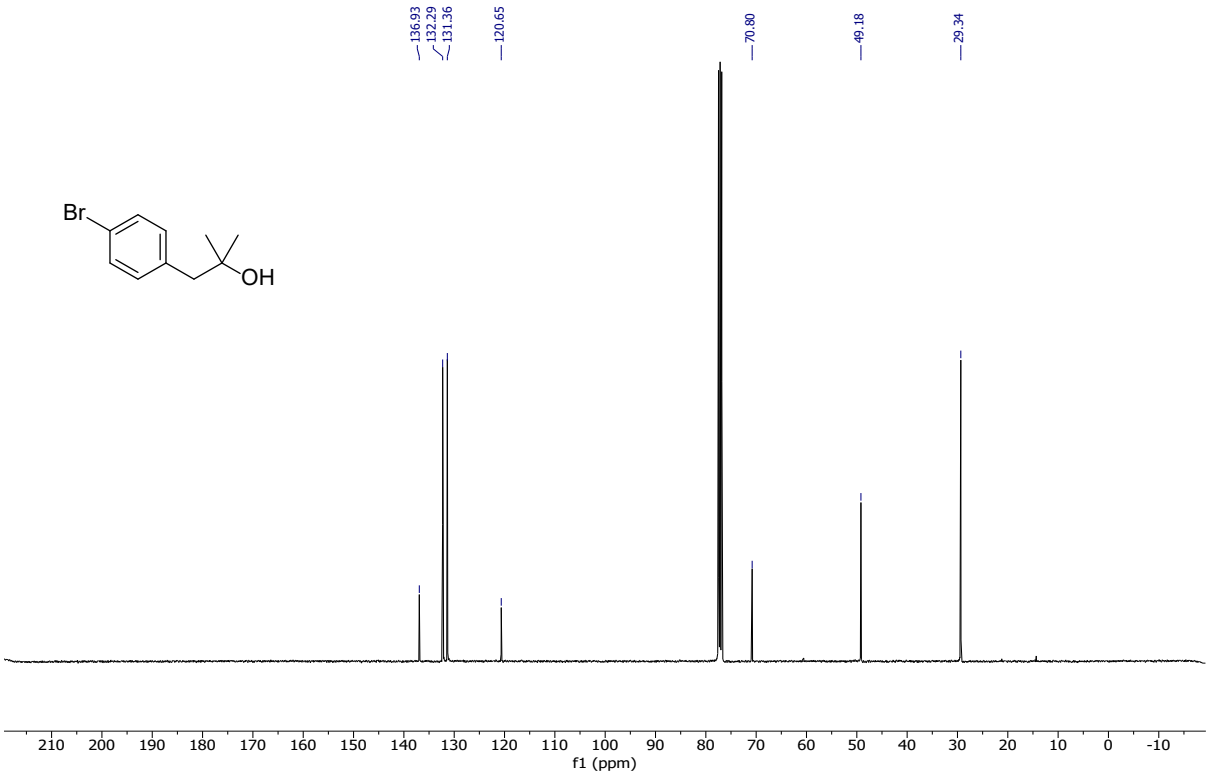


Compound **22g**

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

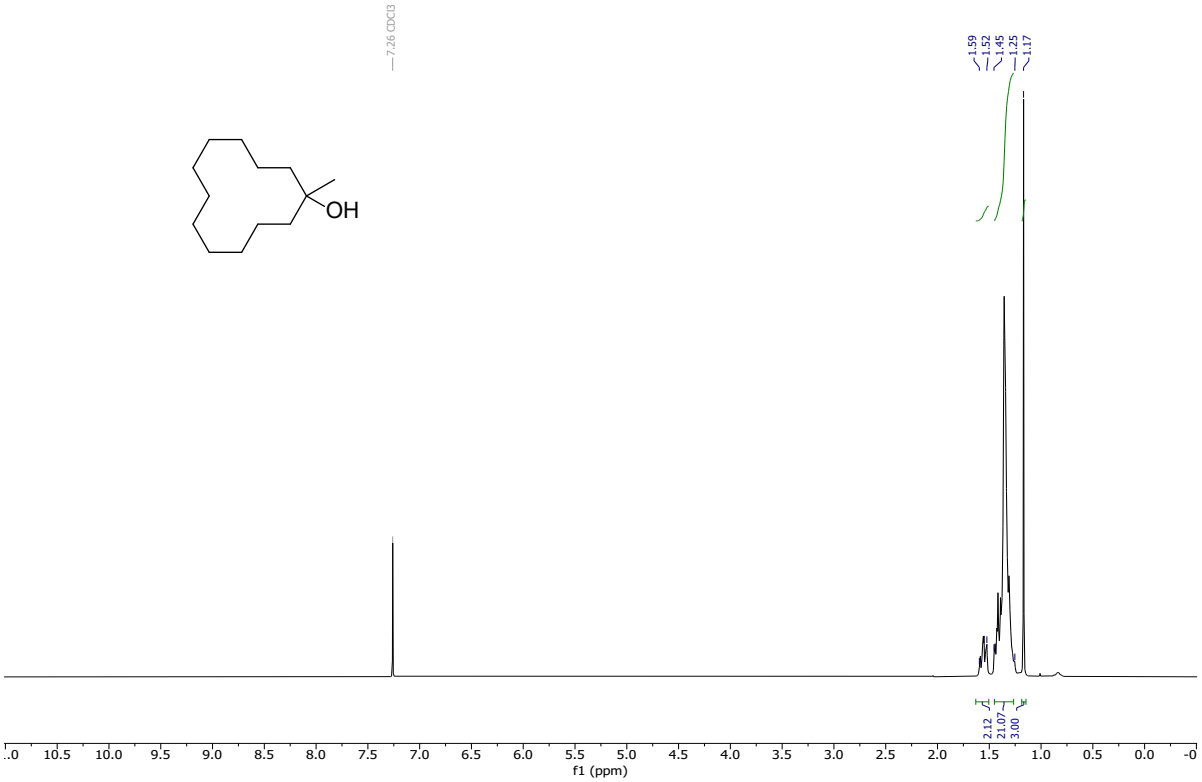


^{13}C NMR, $CDCl_3$, 101 MHz

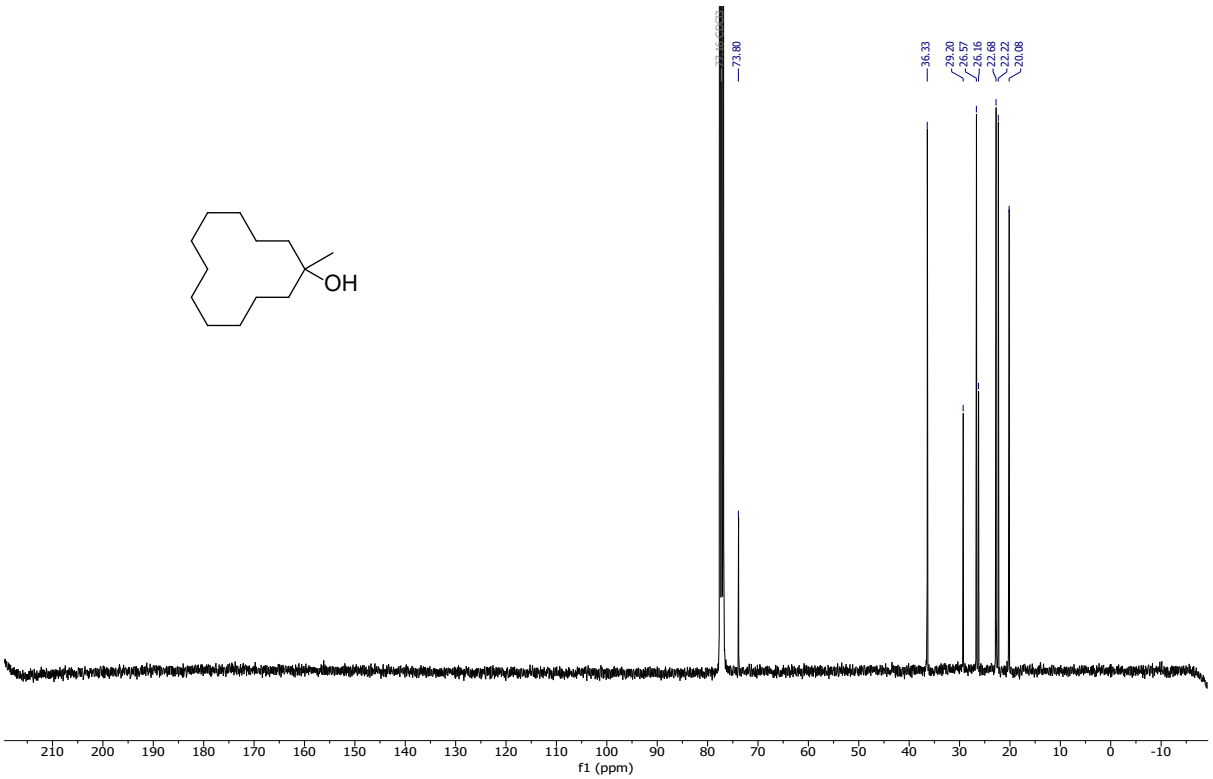


Compound **22n**

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

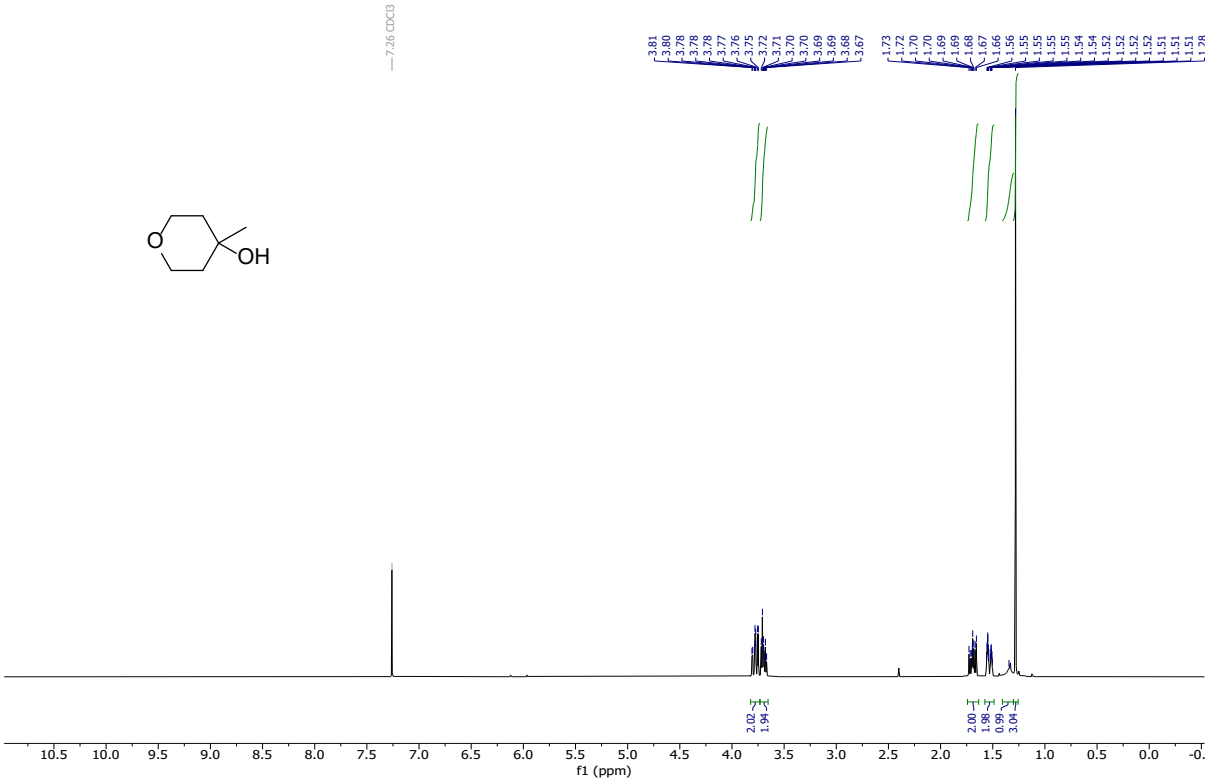


^{13}C NMR, $CDCl_3$, 101 MHz

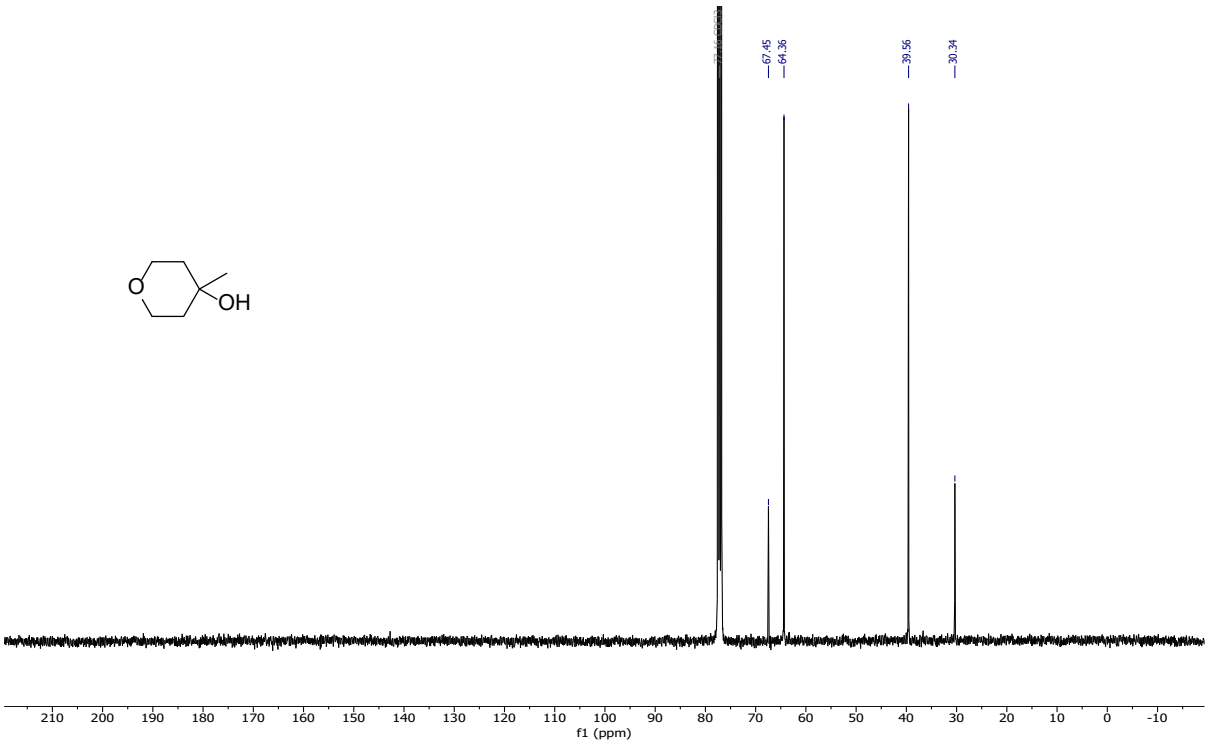


Compound **22o**

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

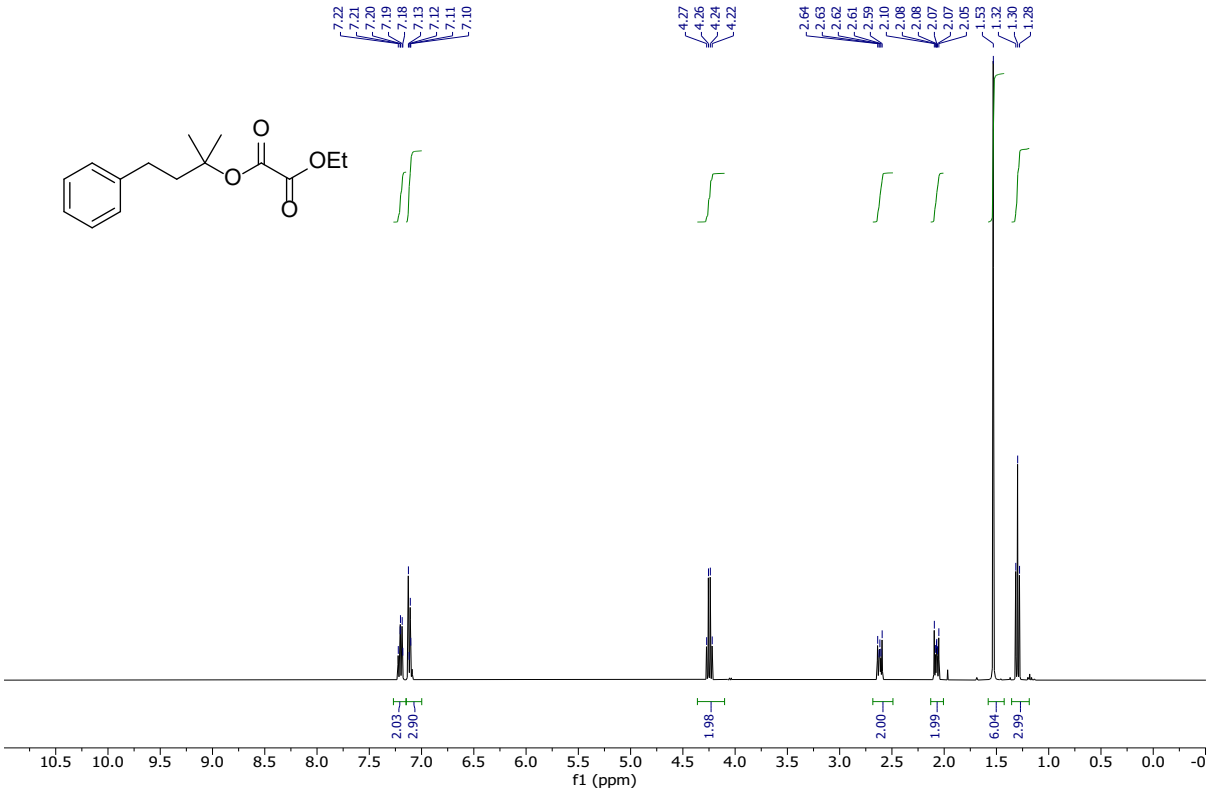


^{13}C NMR, $CDCl_3$, 101 MHz

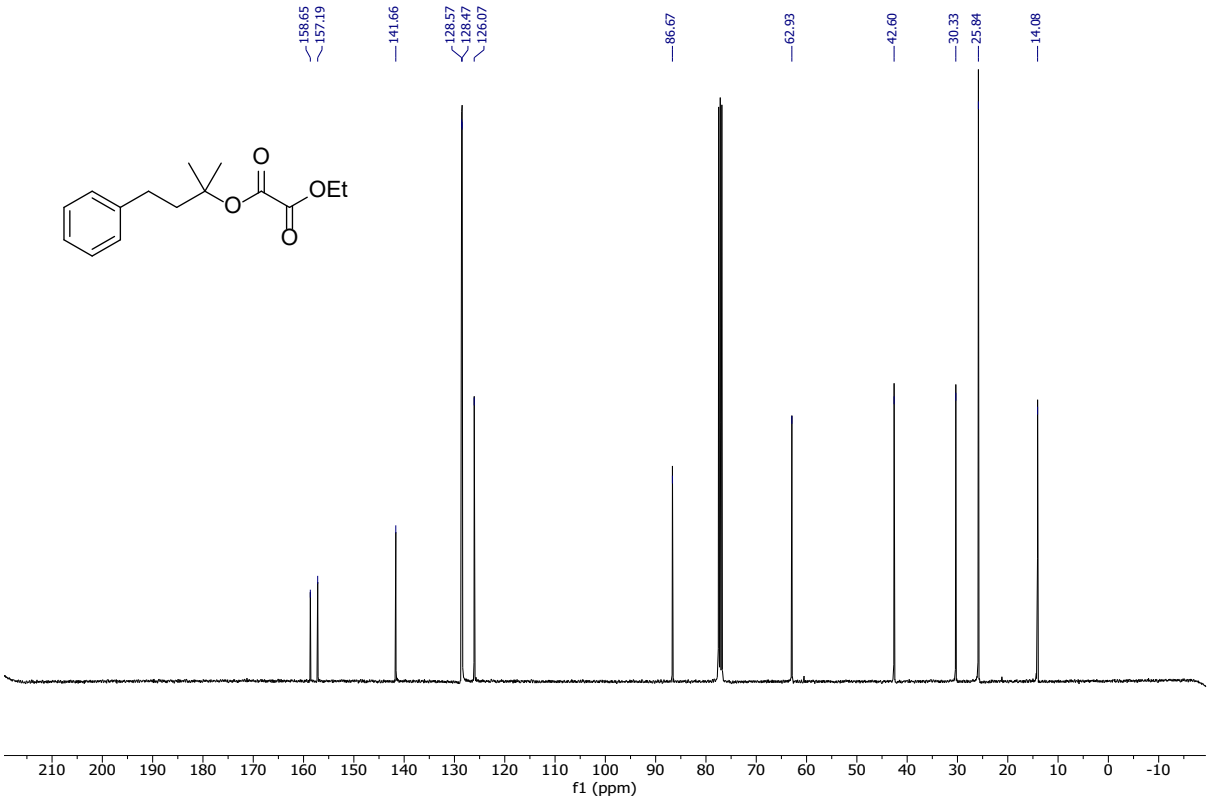


Compound **23a**

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

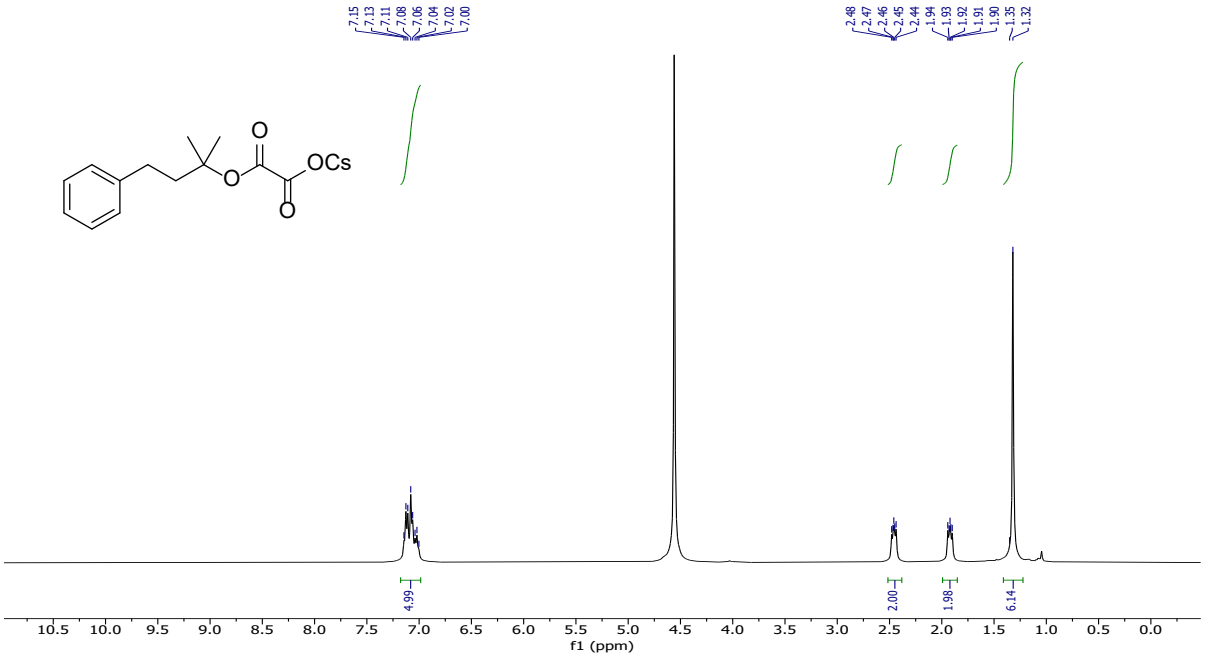


^{13}C NMR, $CDCl_3$, 400 MHz

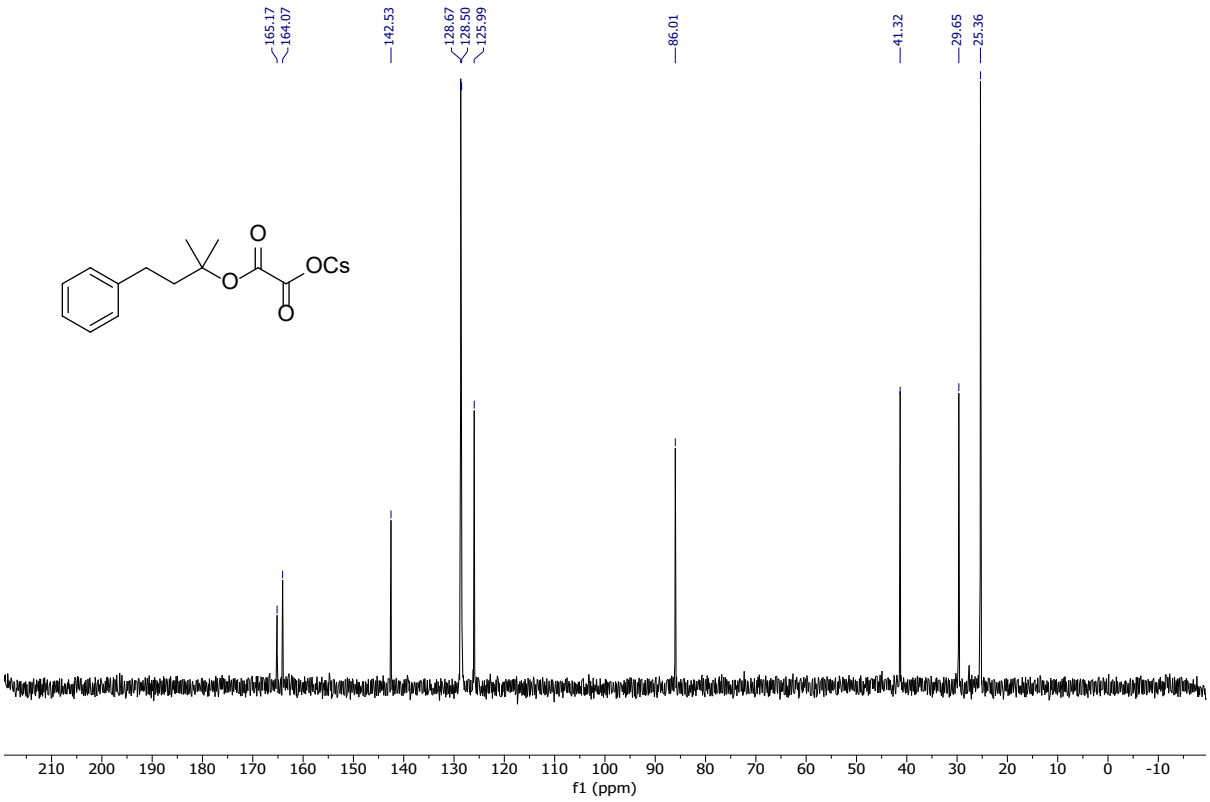


Compound **3a**

^{1}H NMR, D_2O, 400 MHz

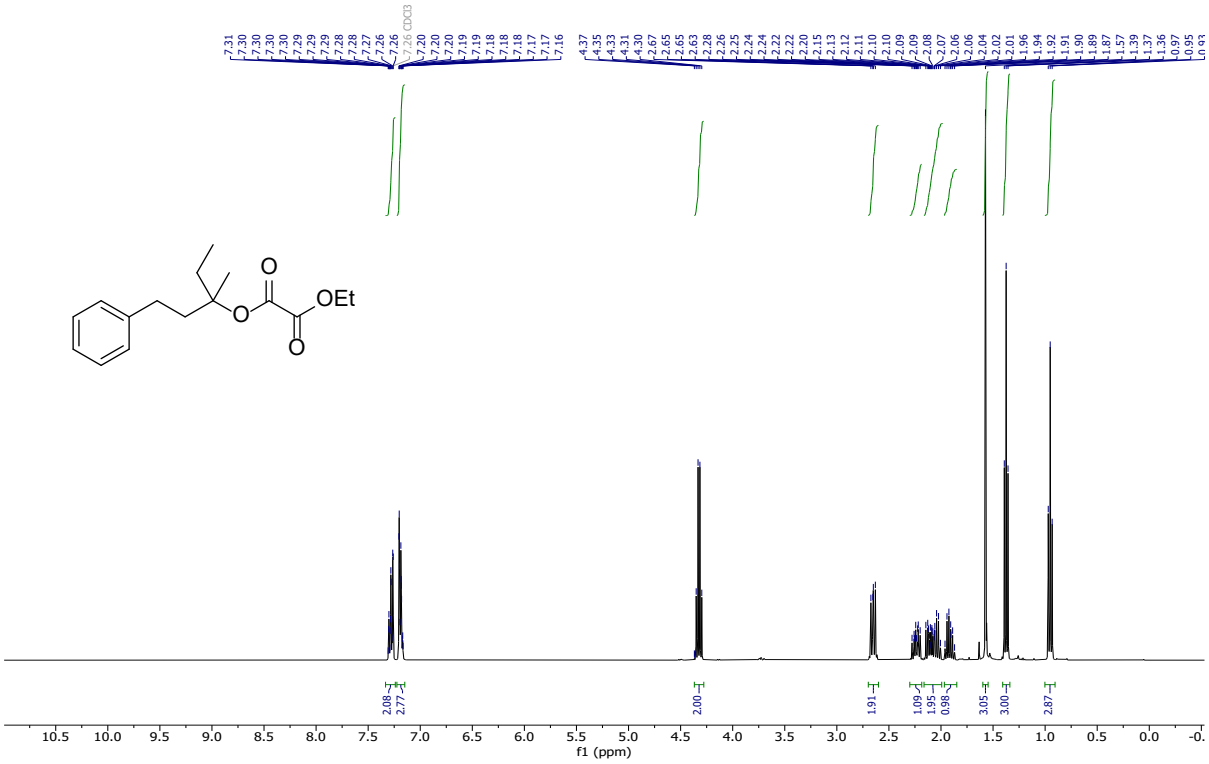


^{13}C NMR, D_2O, 101 MHz

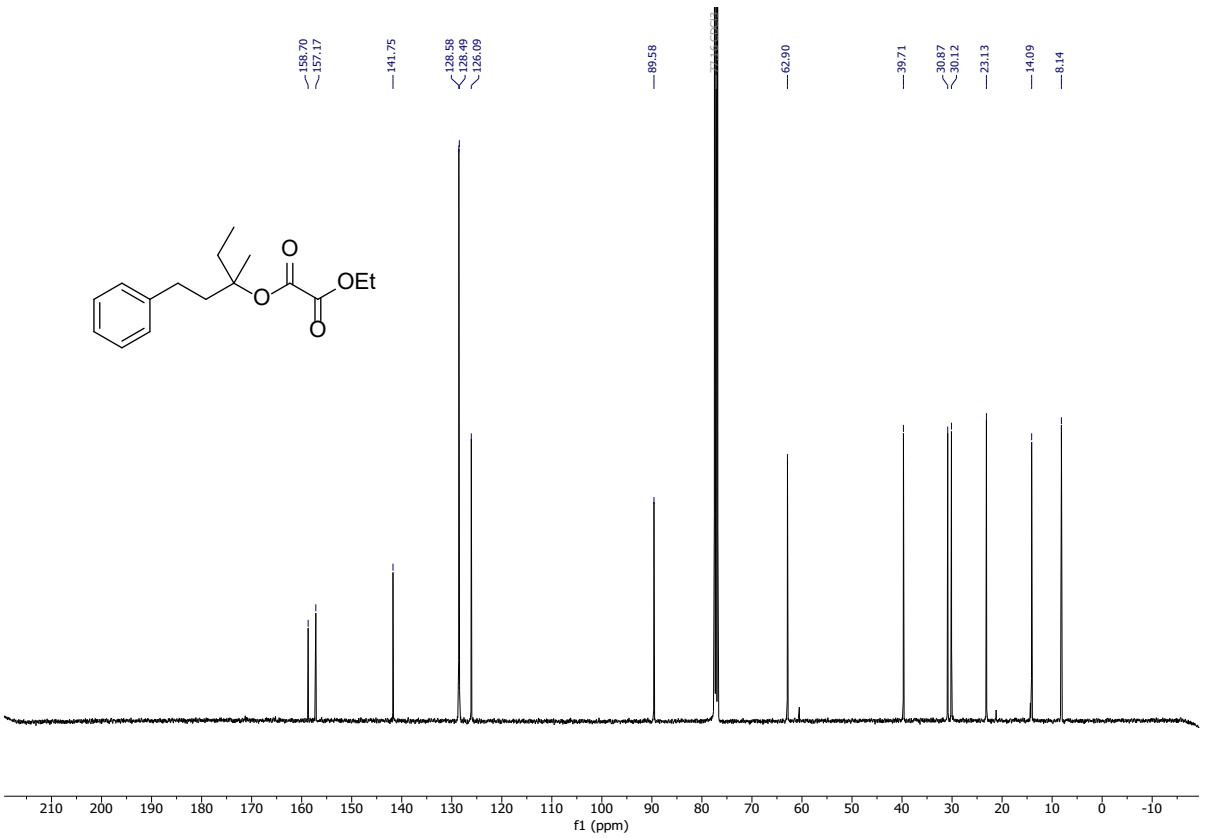


Compound **23b**

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

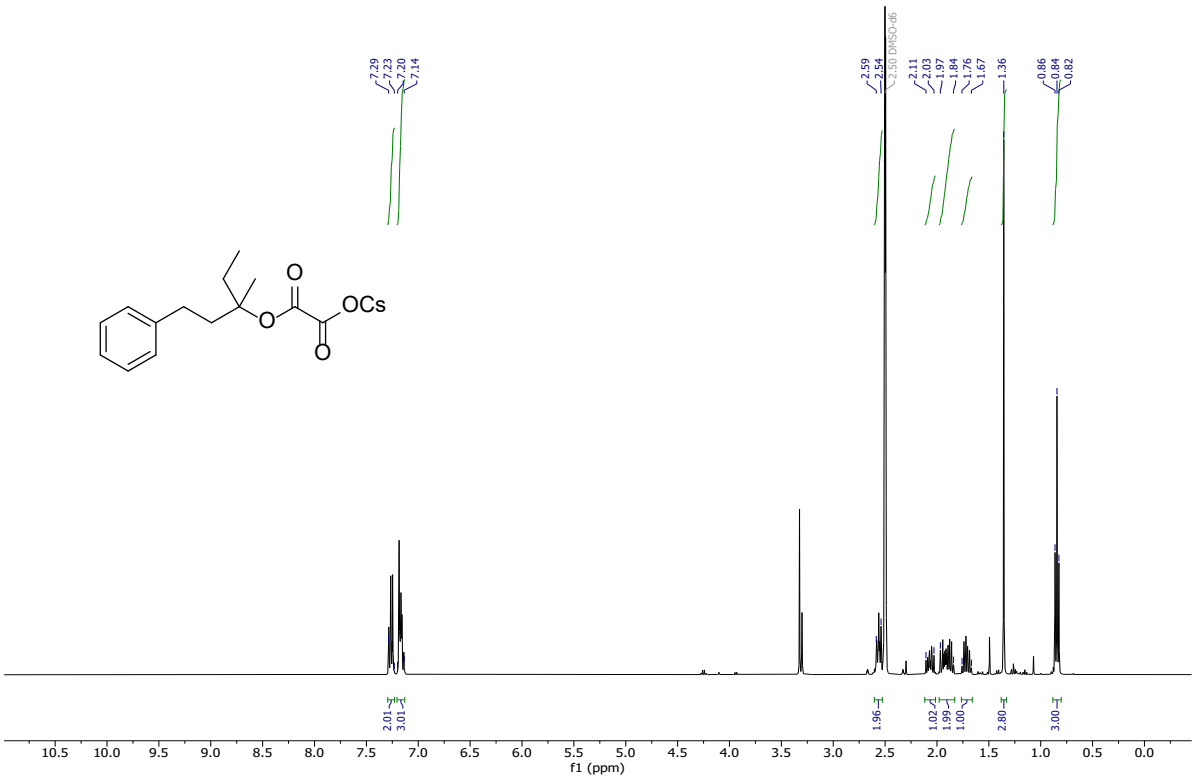


^{13}C NMR, $CDCl_3$, 101 MHz

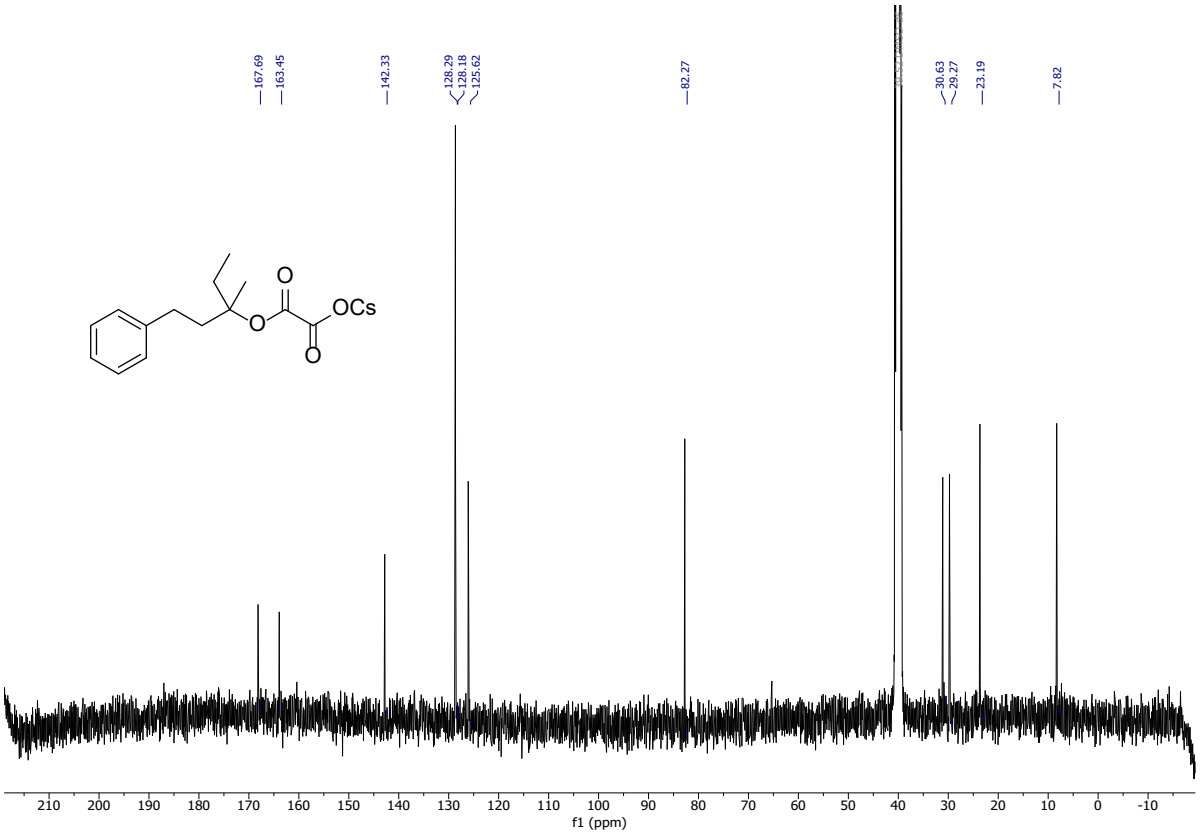


Compound **3b**

^{1}H NMR, DMSO, 400 MHz

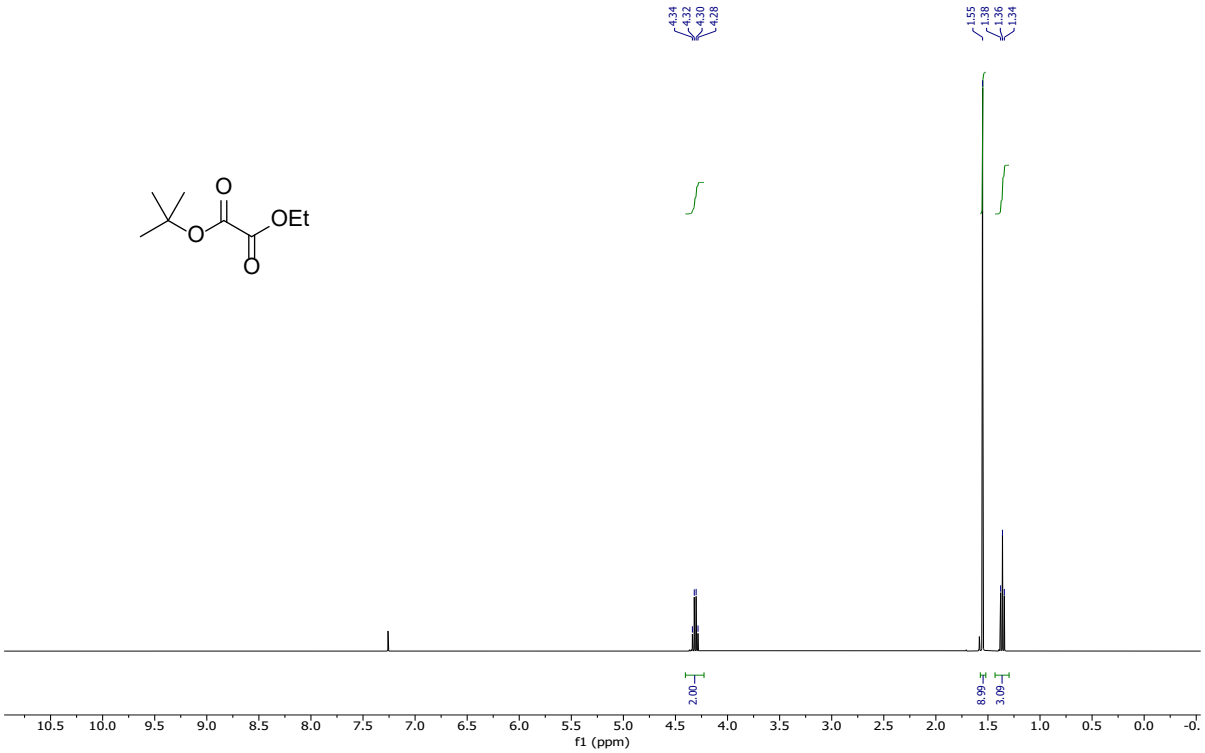


^{13}C NMR, DMSO, 101 MHz

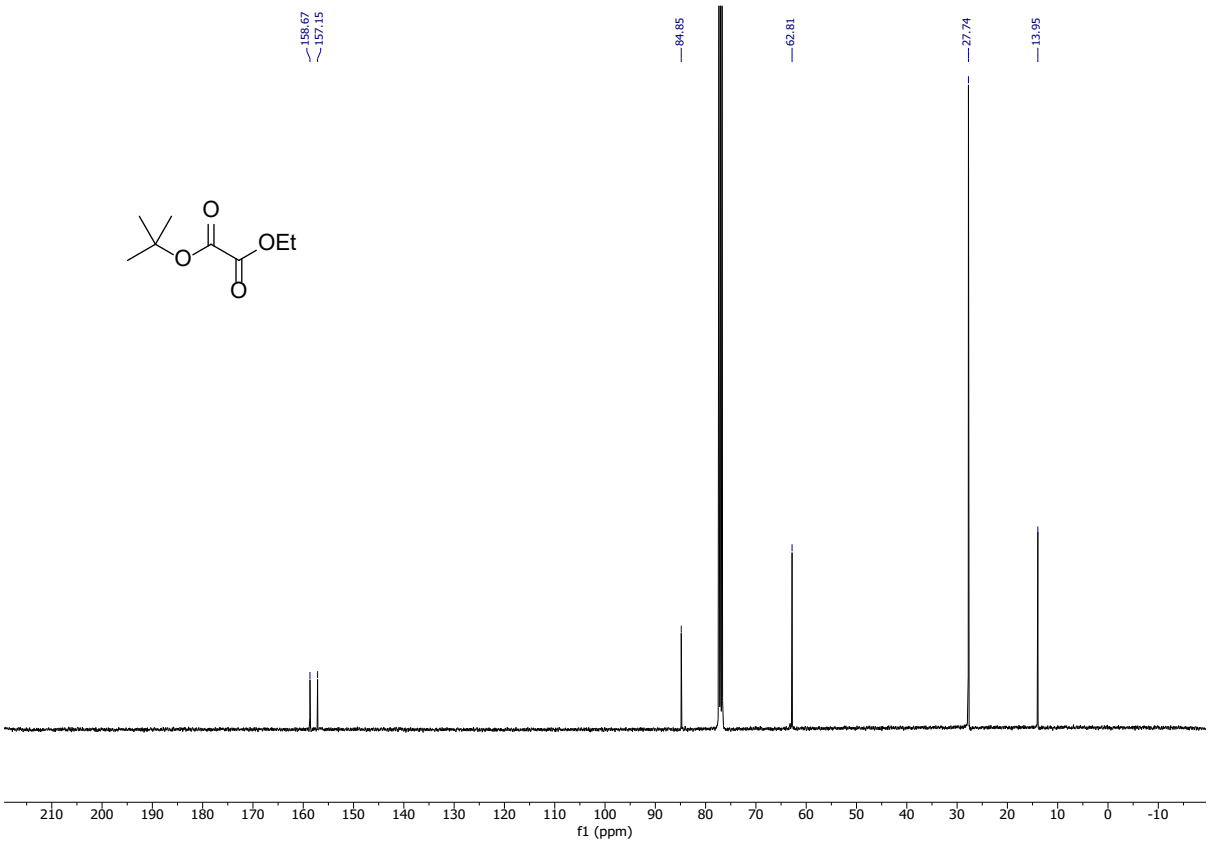


Compound **23c**

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

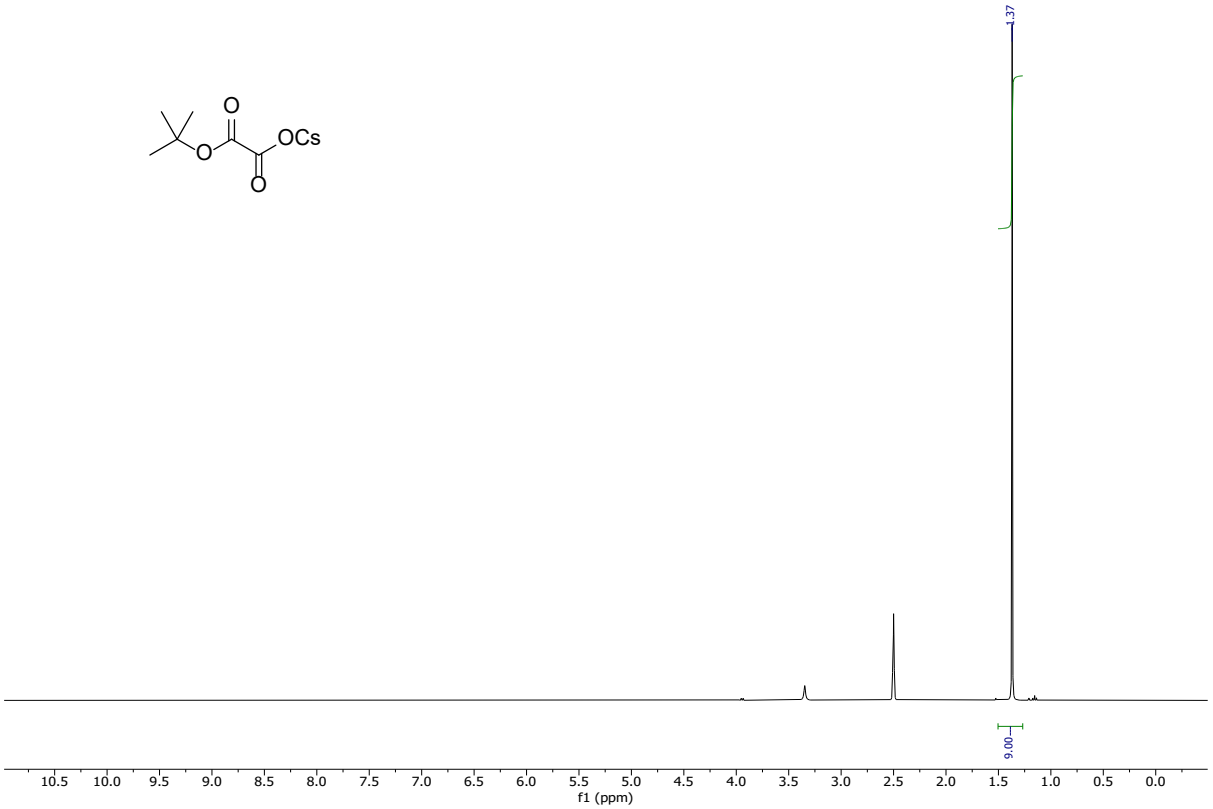


^{13}C NMR, $CDCl_3$, 101 MHz

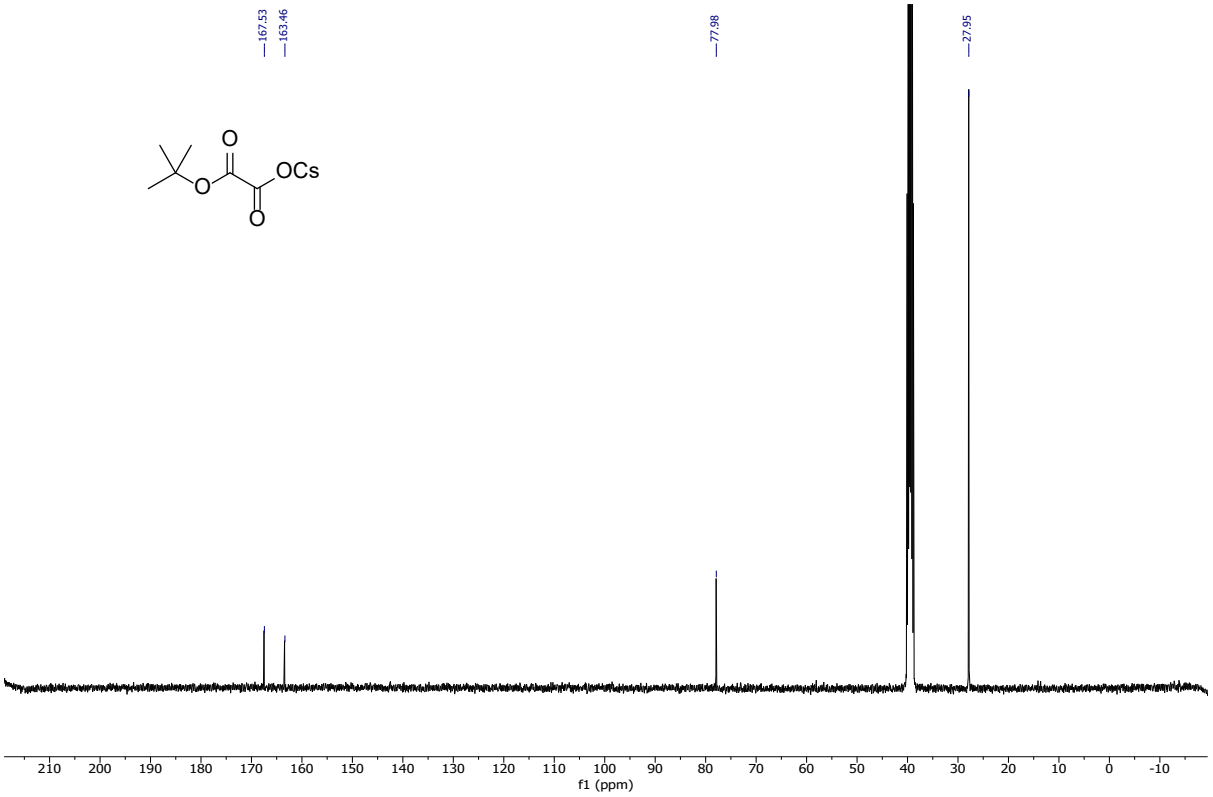


Compound **3c**

^{1}H NMR, DMSO, 400 MHz

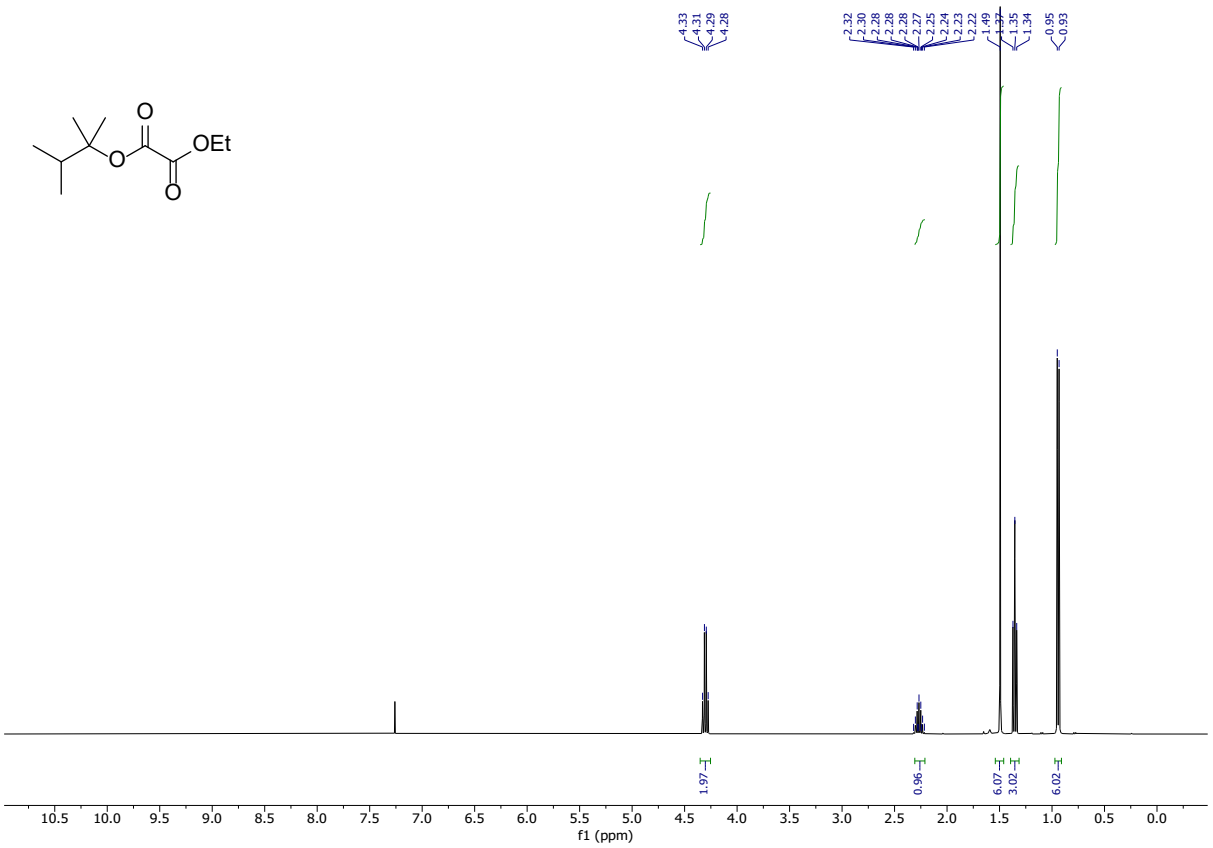


^{13}C NMR, DMSO, 101 MHz

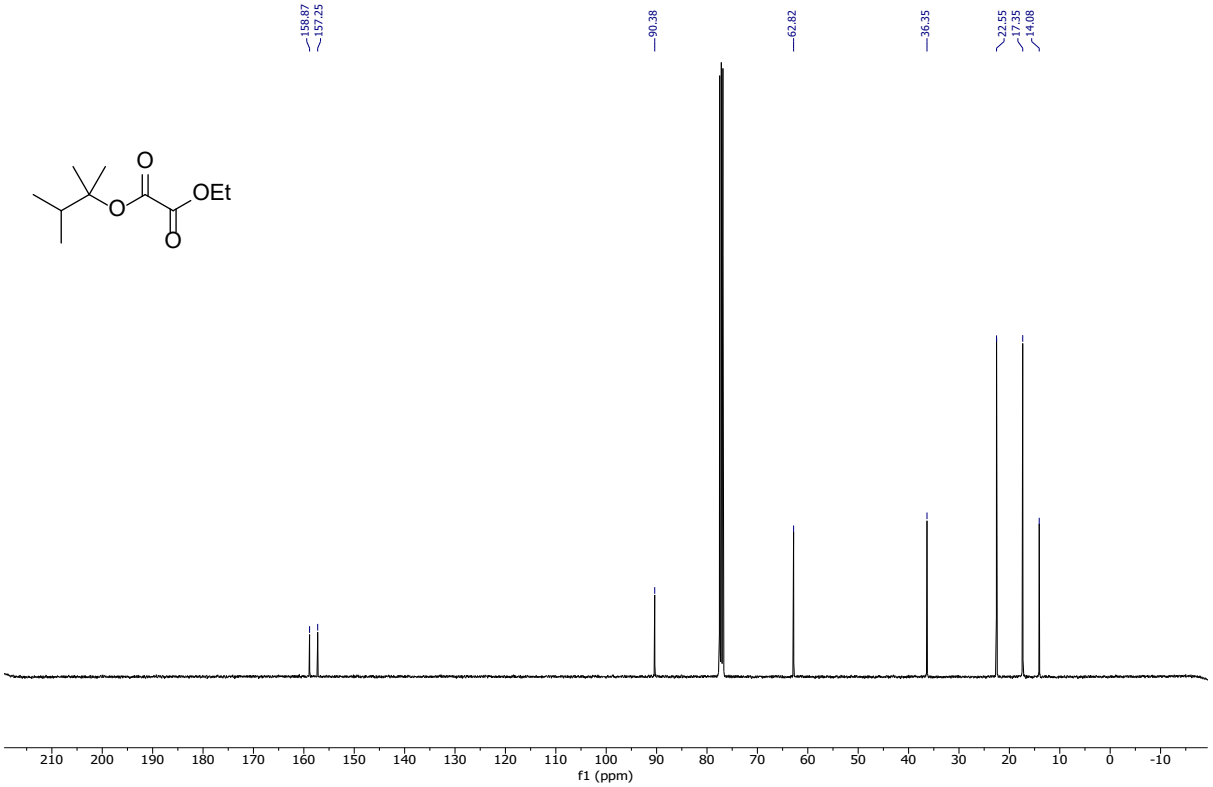


Compound **23d**

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

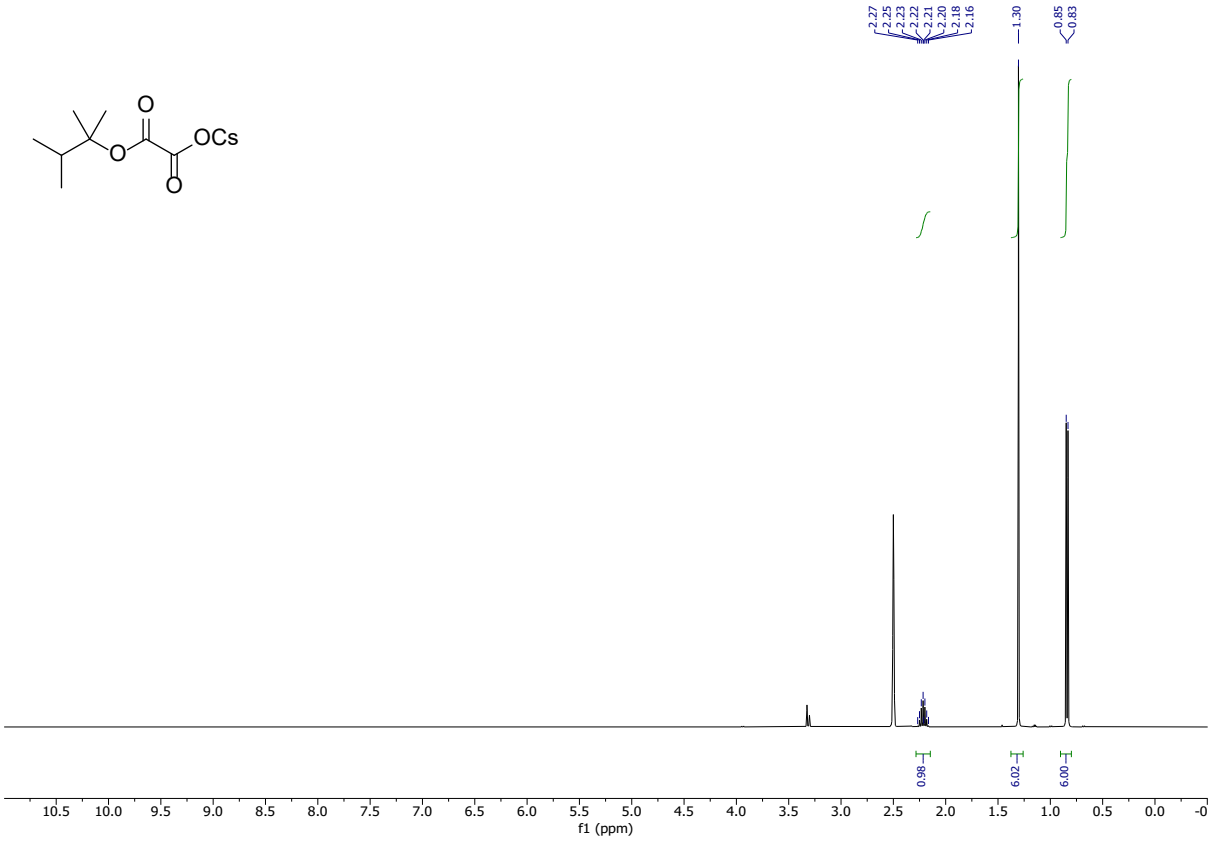


^{13}C NMR, $CDCl_3$, 101 MHz

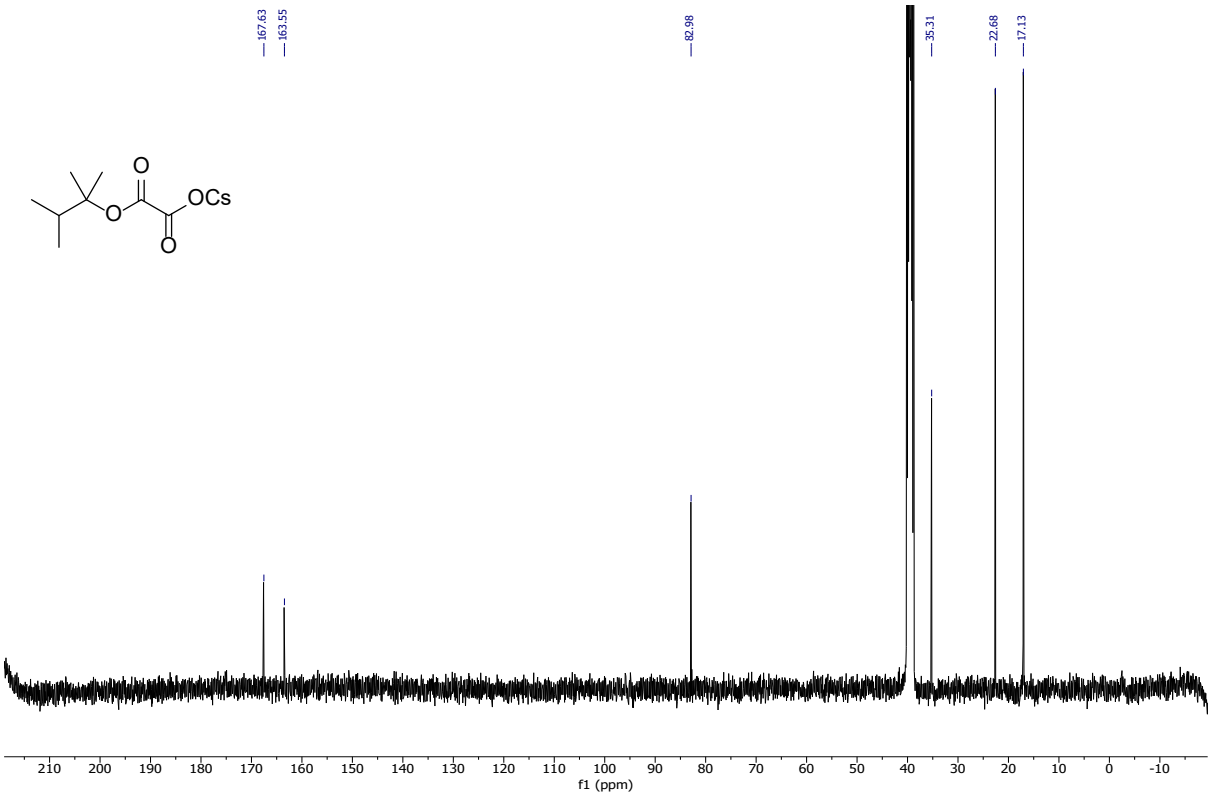


Compound **3d**

^{1}H NMR, DMSO, 400 MHz

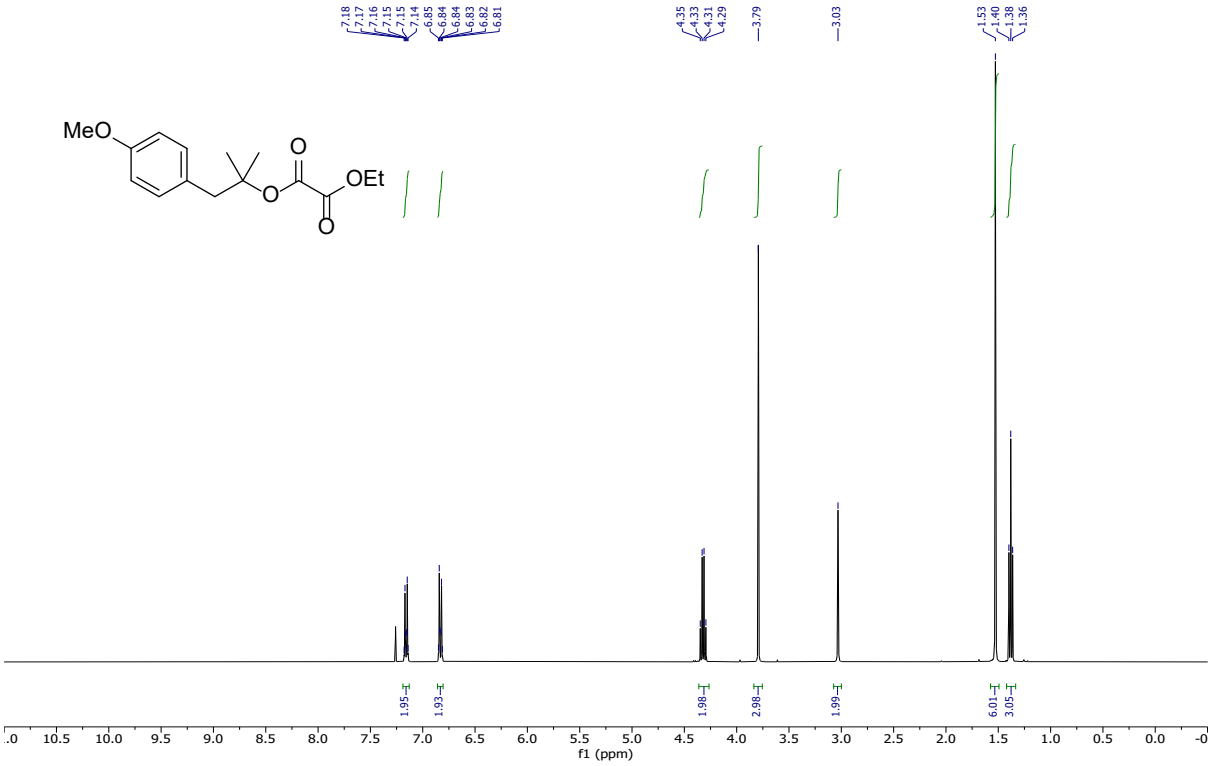


^{13}C NMR, DMSO, 101 MHz

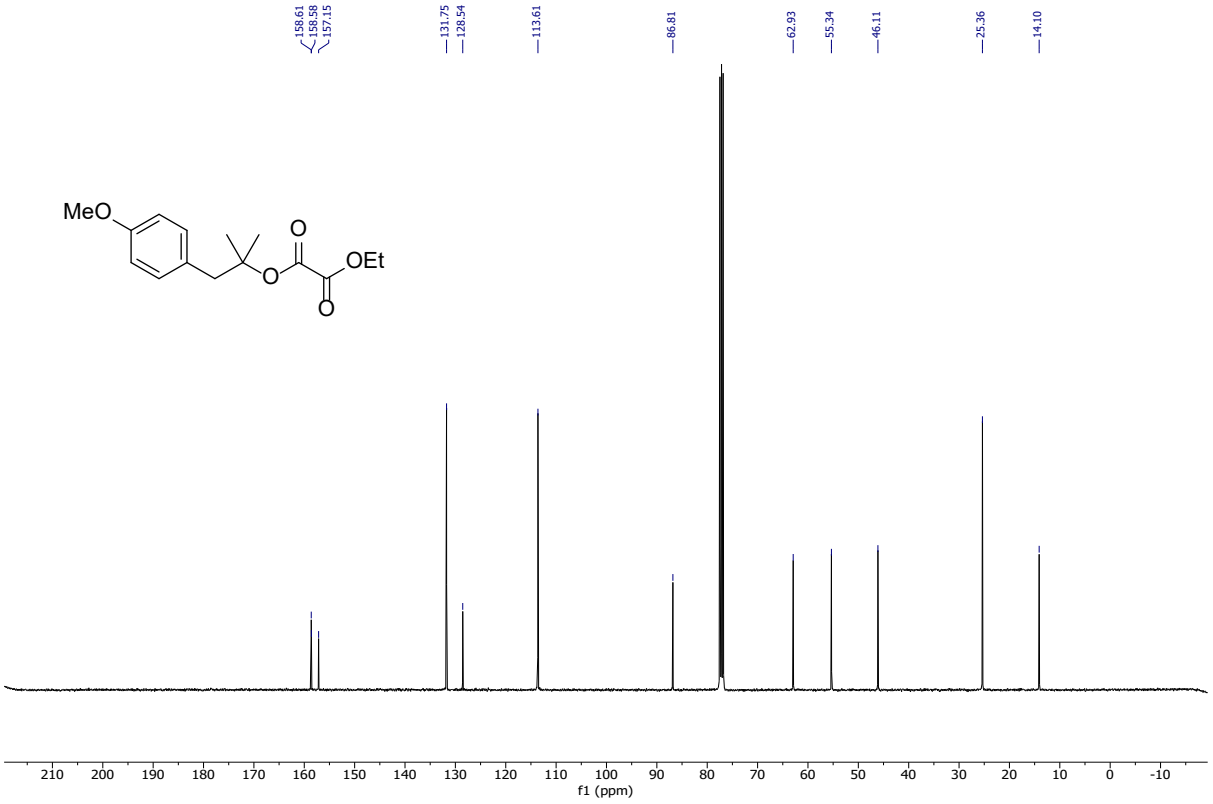


Compound **23e**

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

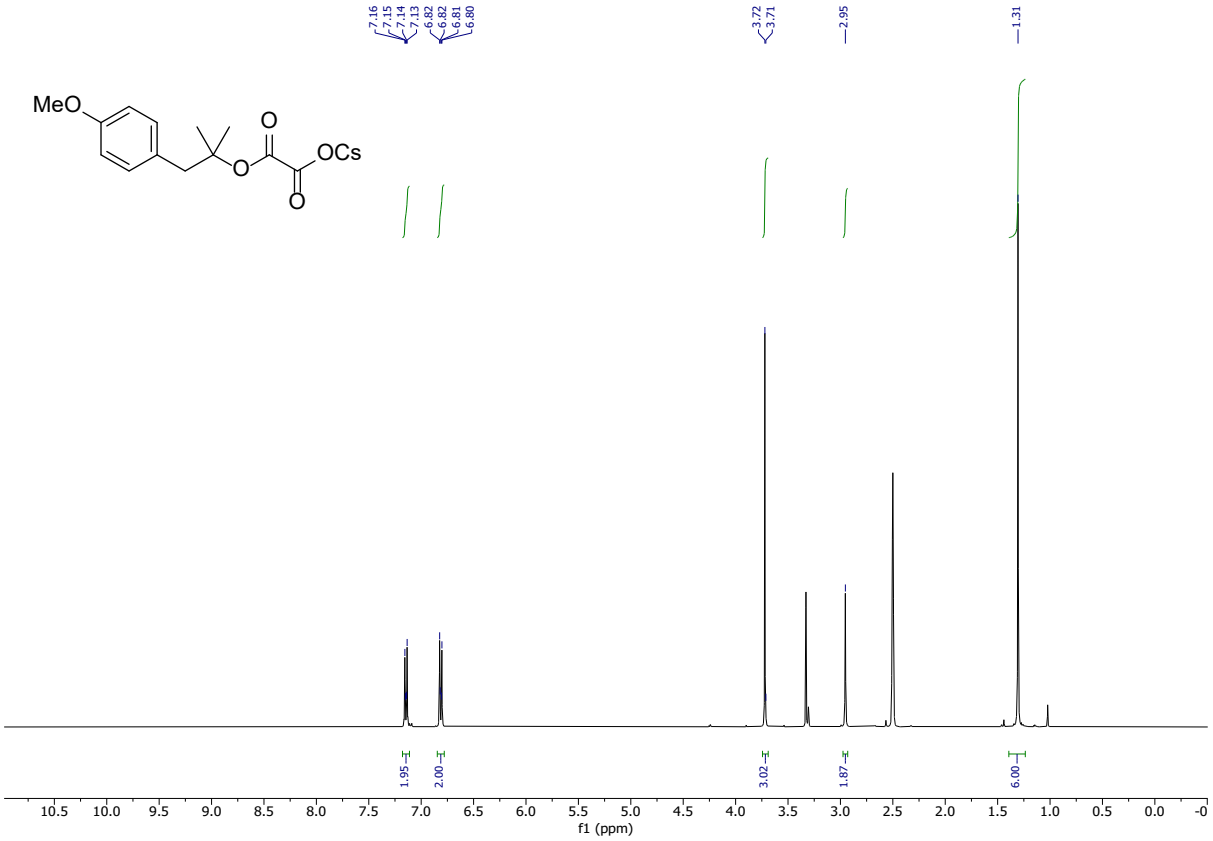


^{13}C NMR, $CDCl_3$, 101 MHz

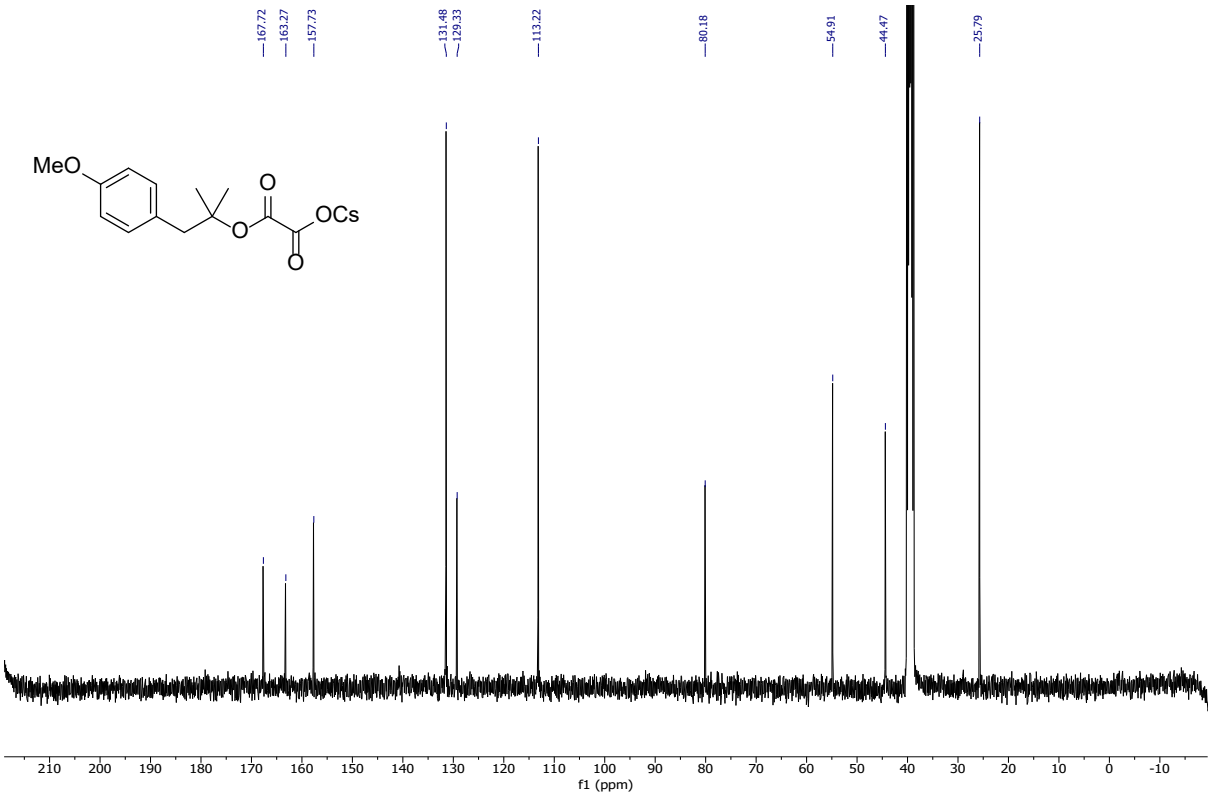


Compound **3e**

^{1}H NMR, DMSO, 400 MHz

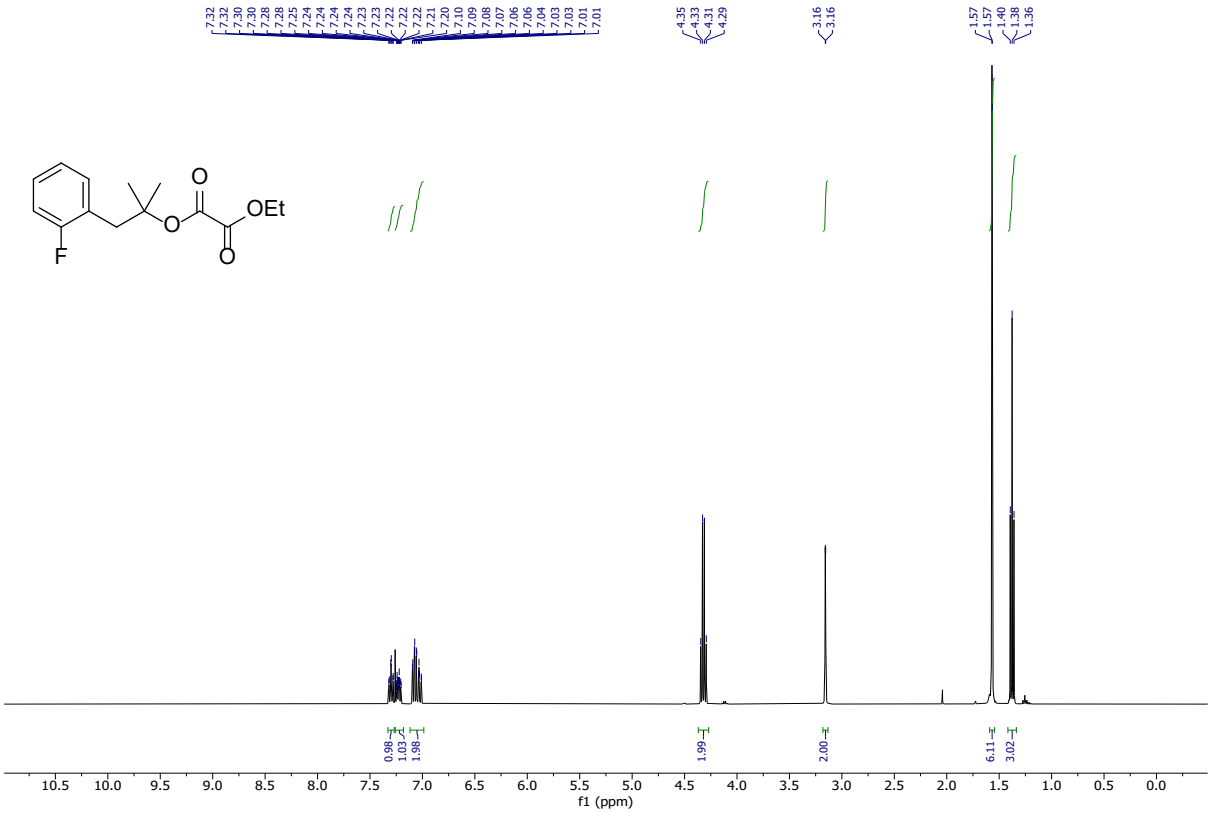


^{13}C NMR, DMSO, 101 MHz

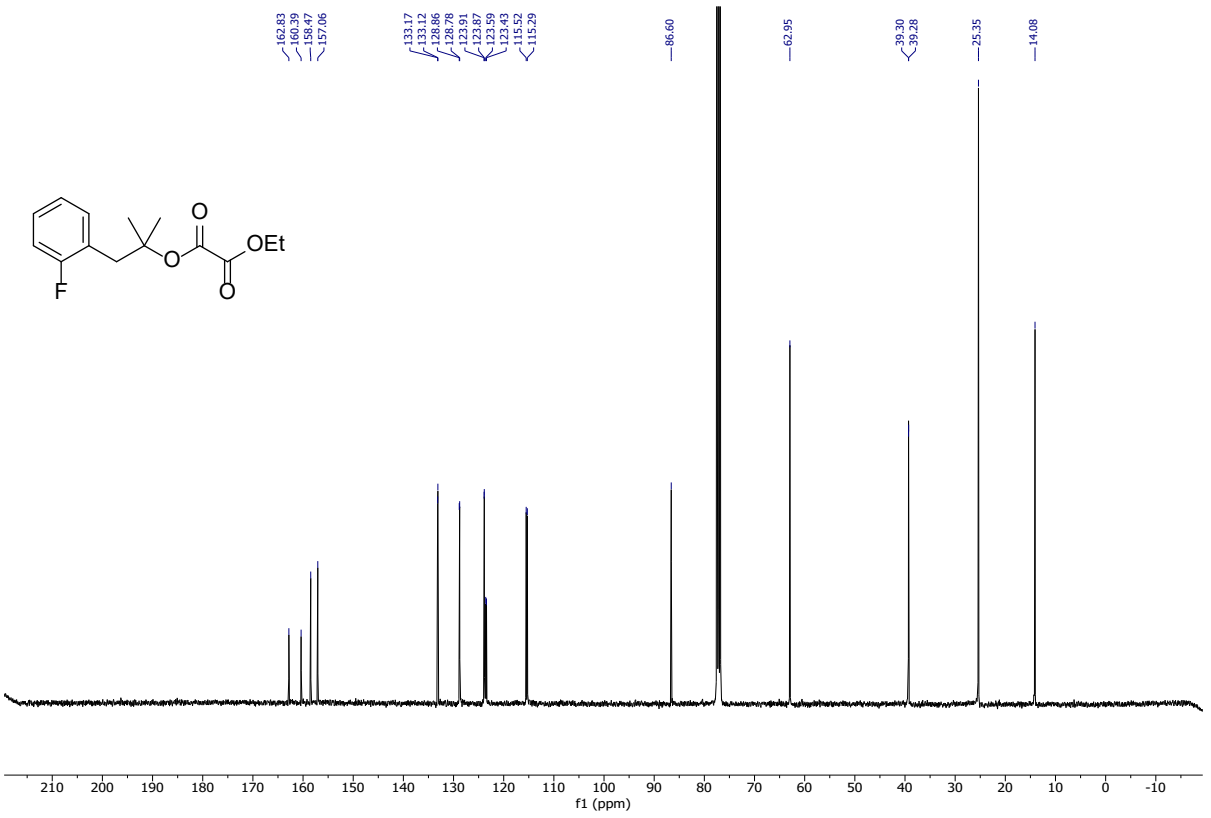


Compound **23f**

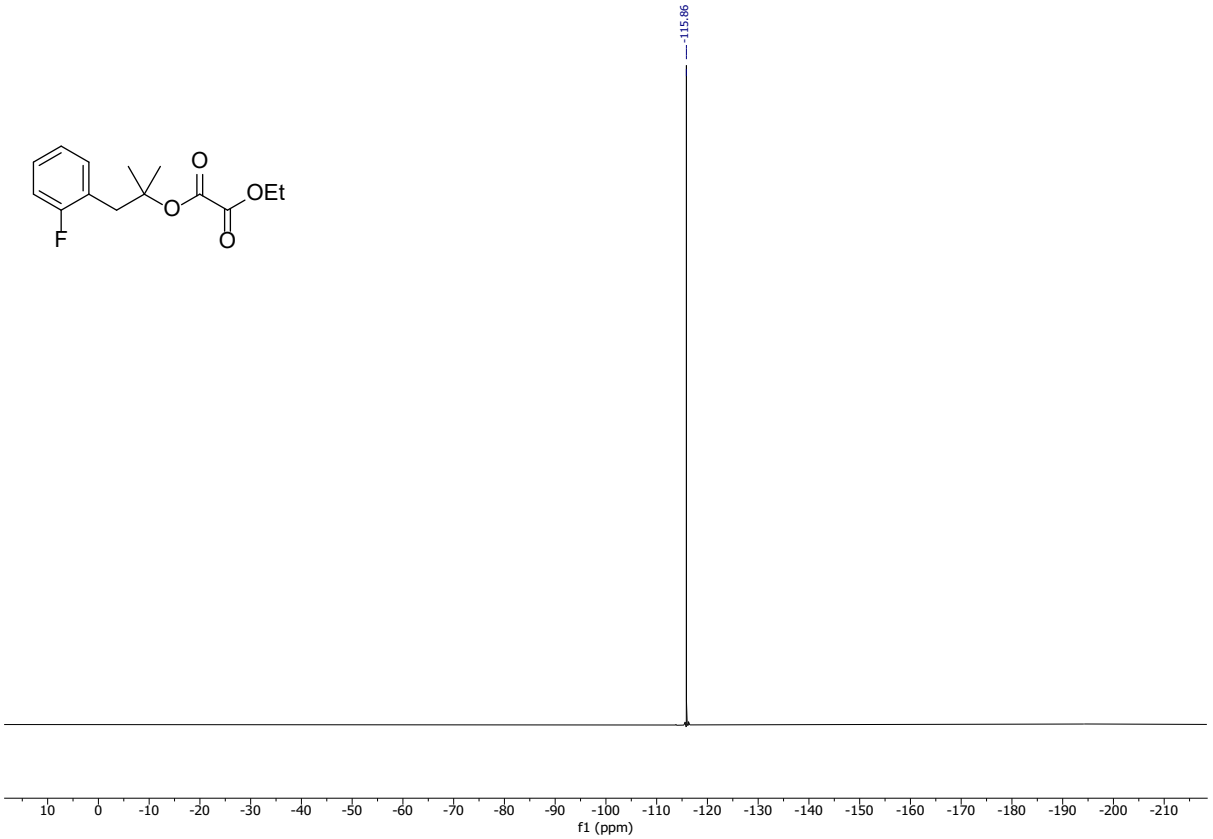
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

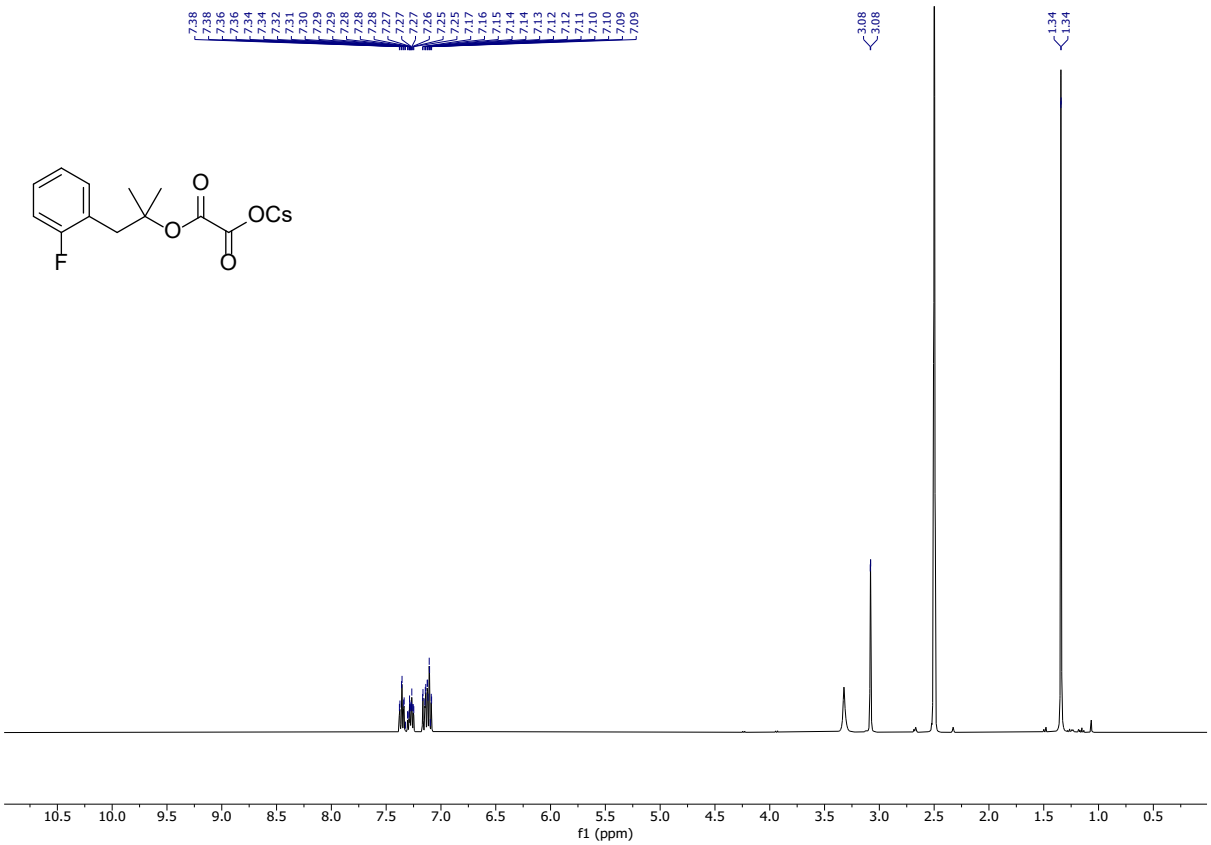


^{19}F NMR, $CDCl_3$, 376 MHz

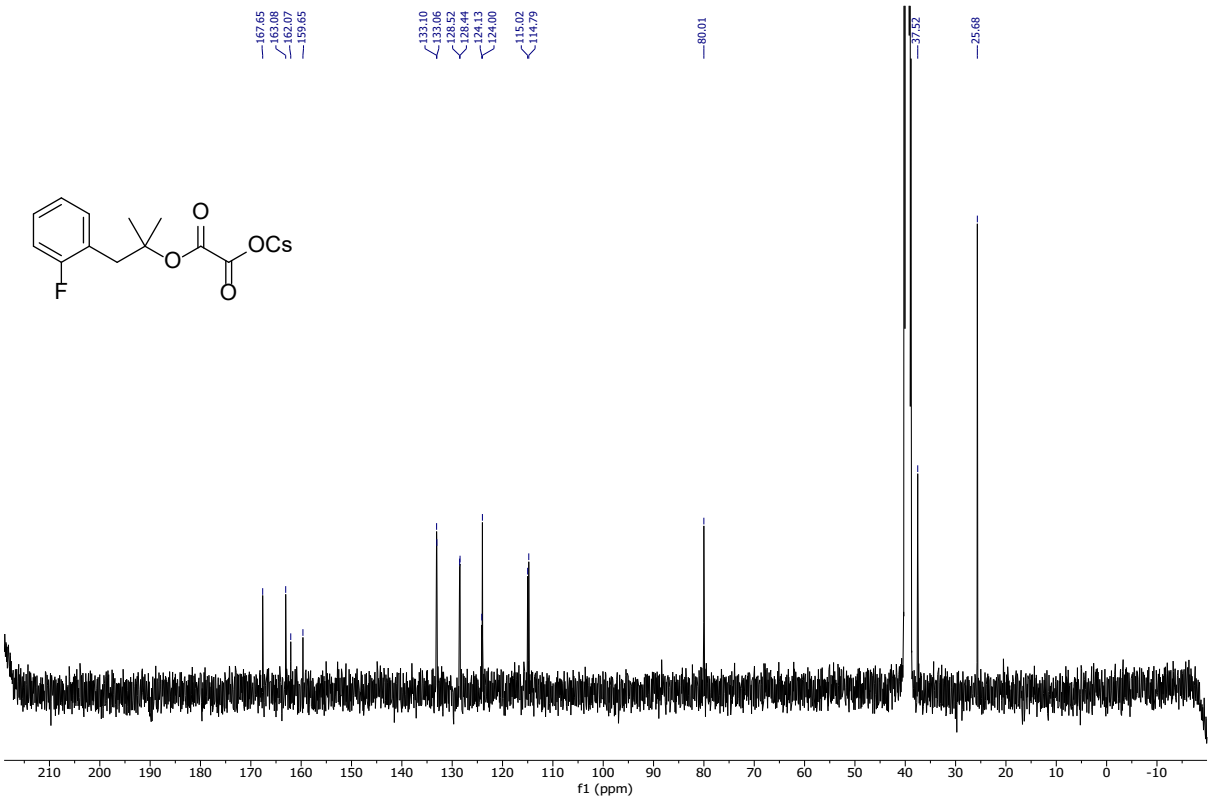


Compound **3f**

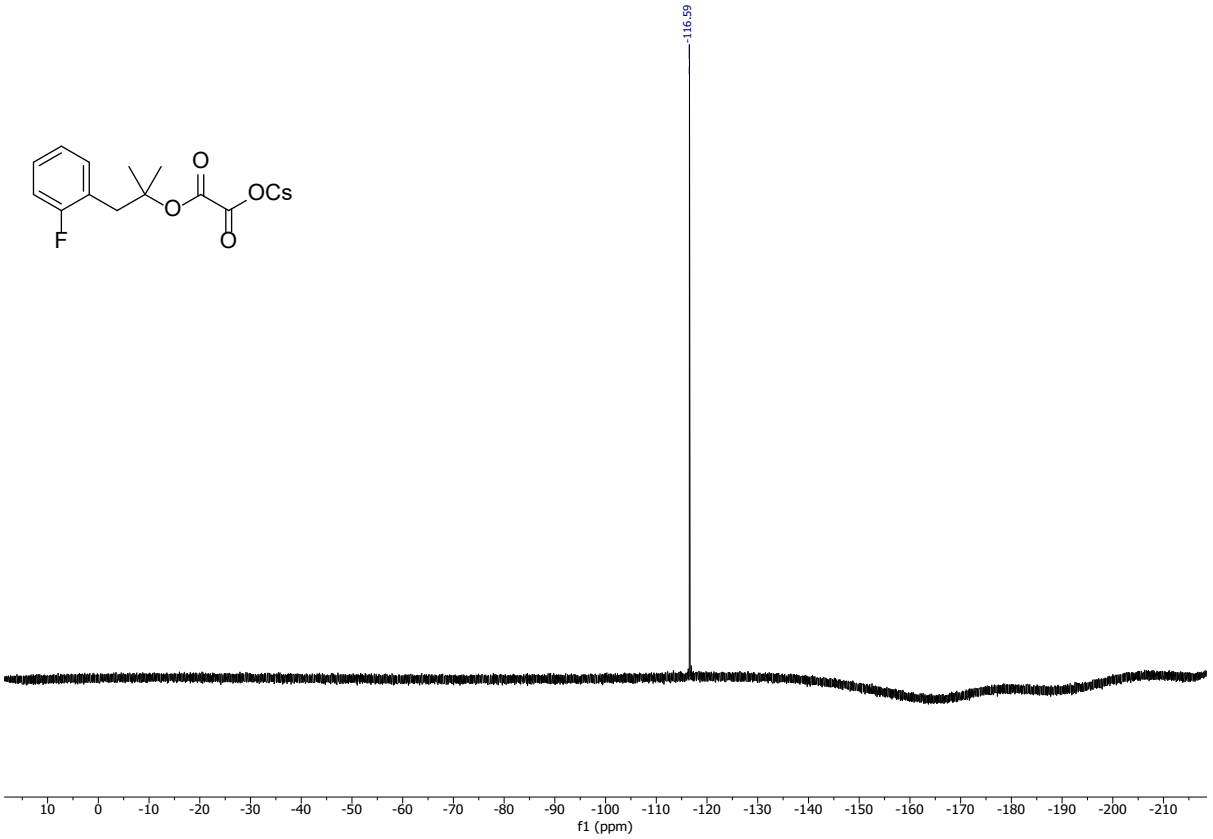
^{1}H NMR, DMSO, 400 MHz



^{13}C NMR, DMSO, 101 MHz

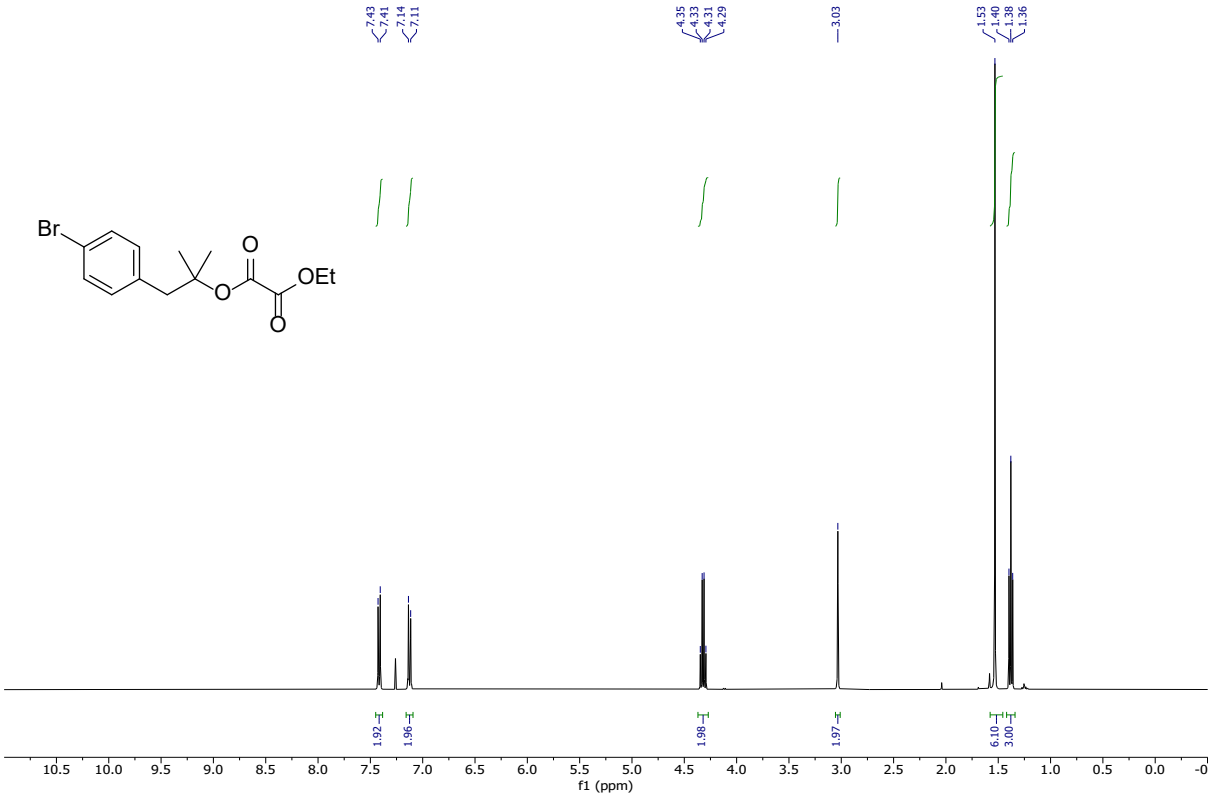


^{19}F NMR, DMSO, 376 MHz

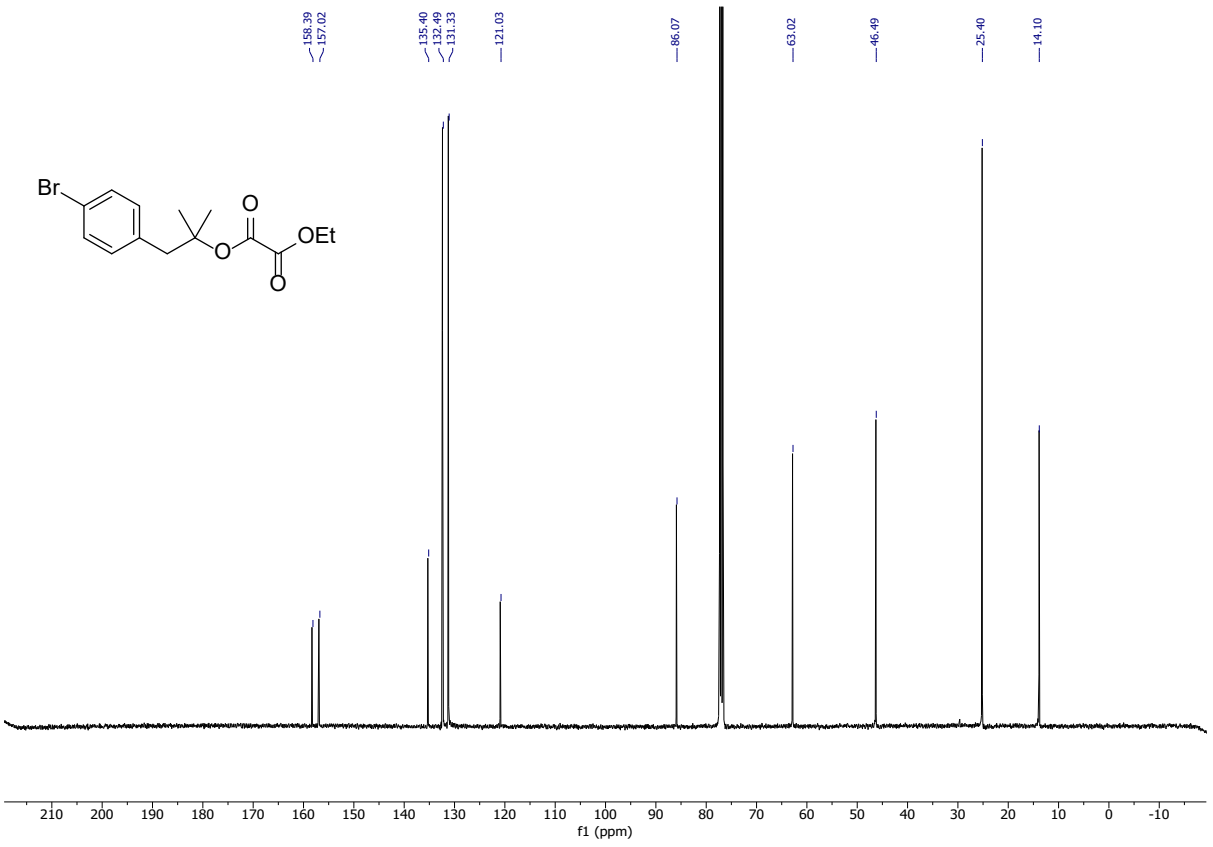


Compound **23g**

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

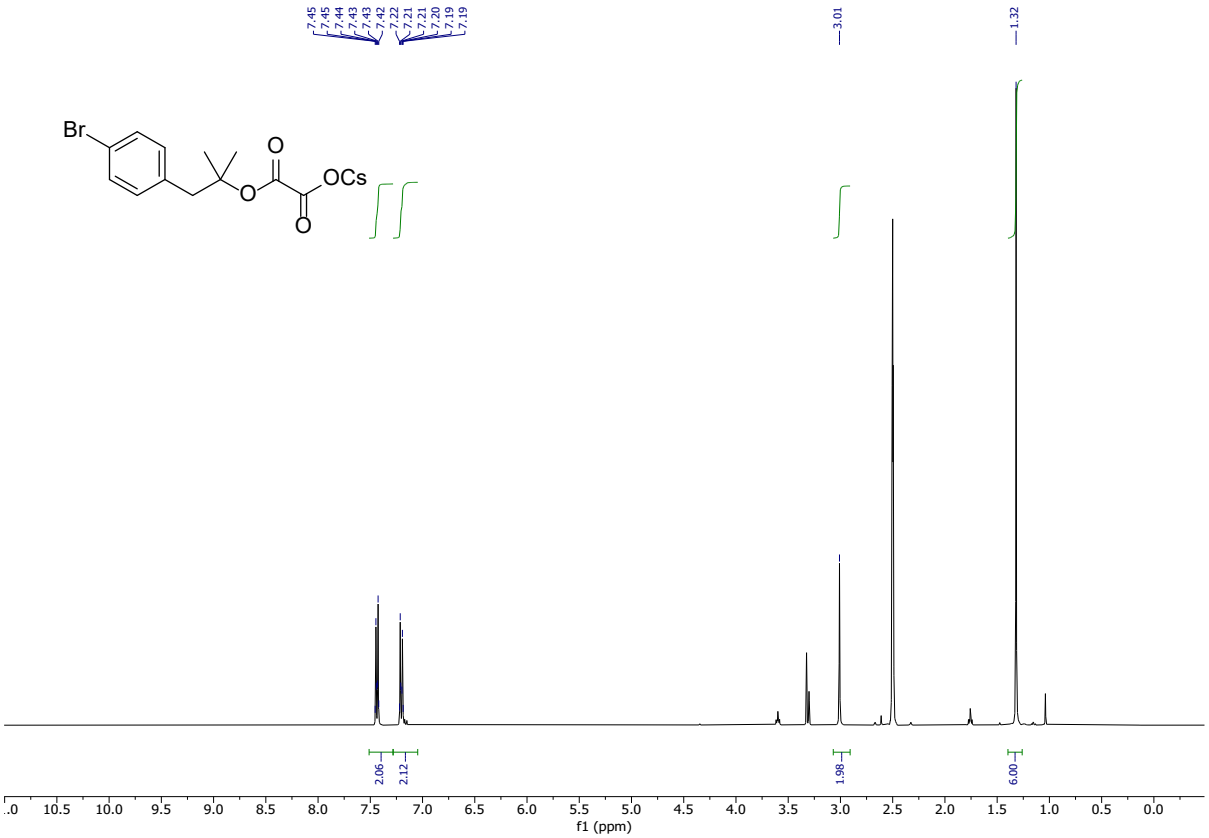


^{13}C NMR, $CDCl_3$, 101 MHz

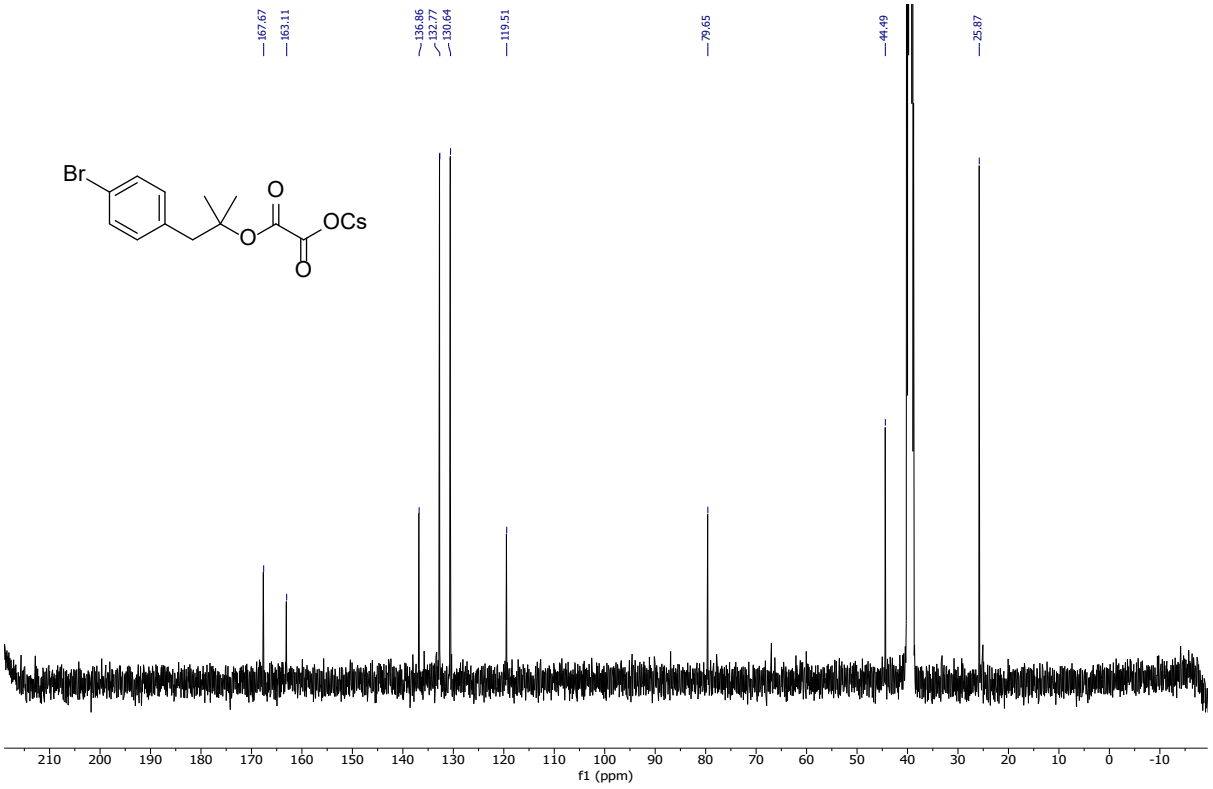


Compound **3g**

^{1}H NMR, DMSO, 400 MHz

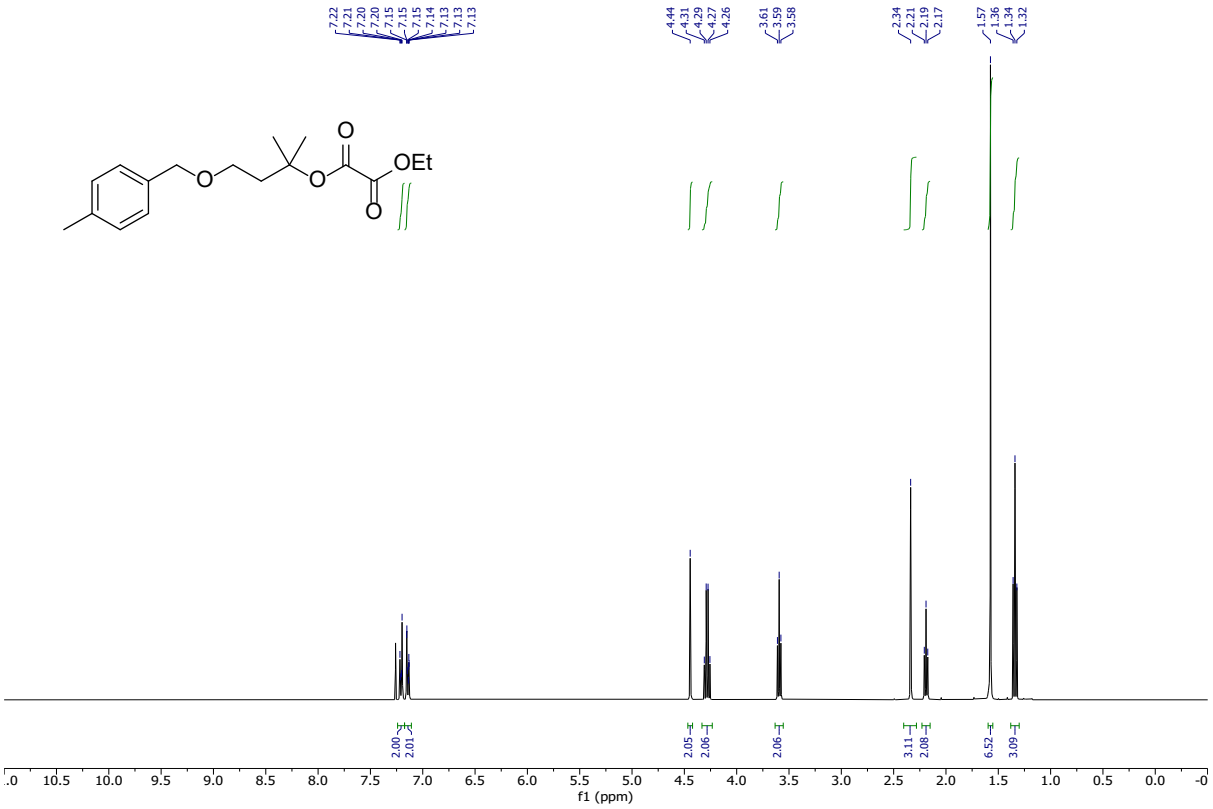


^{13}C NMR, DMSO, 101 MHz

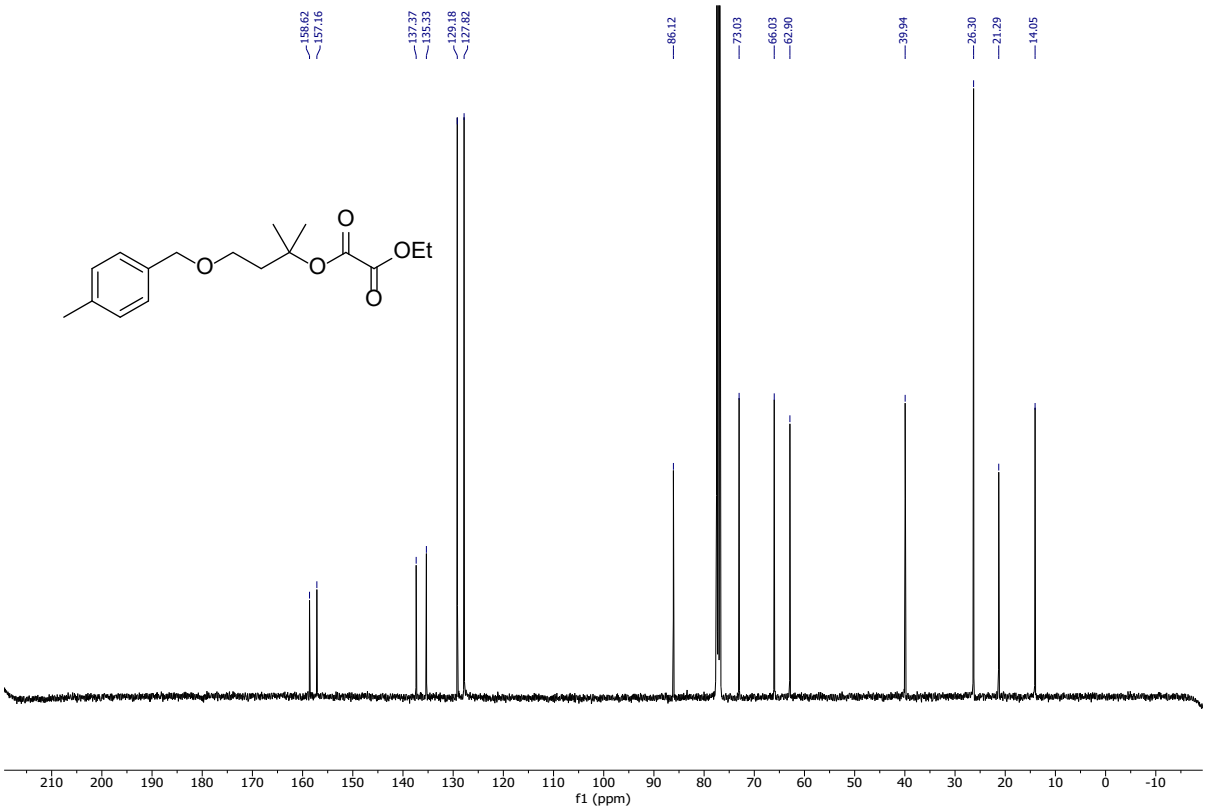


Compound **23h**

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

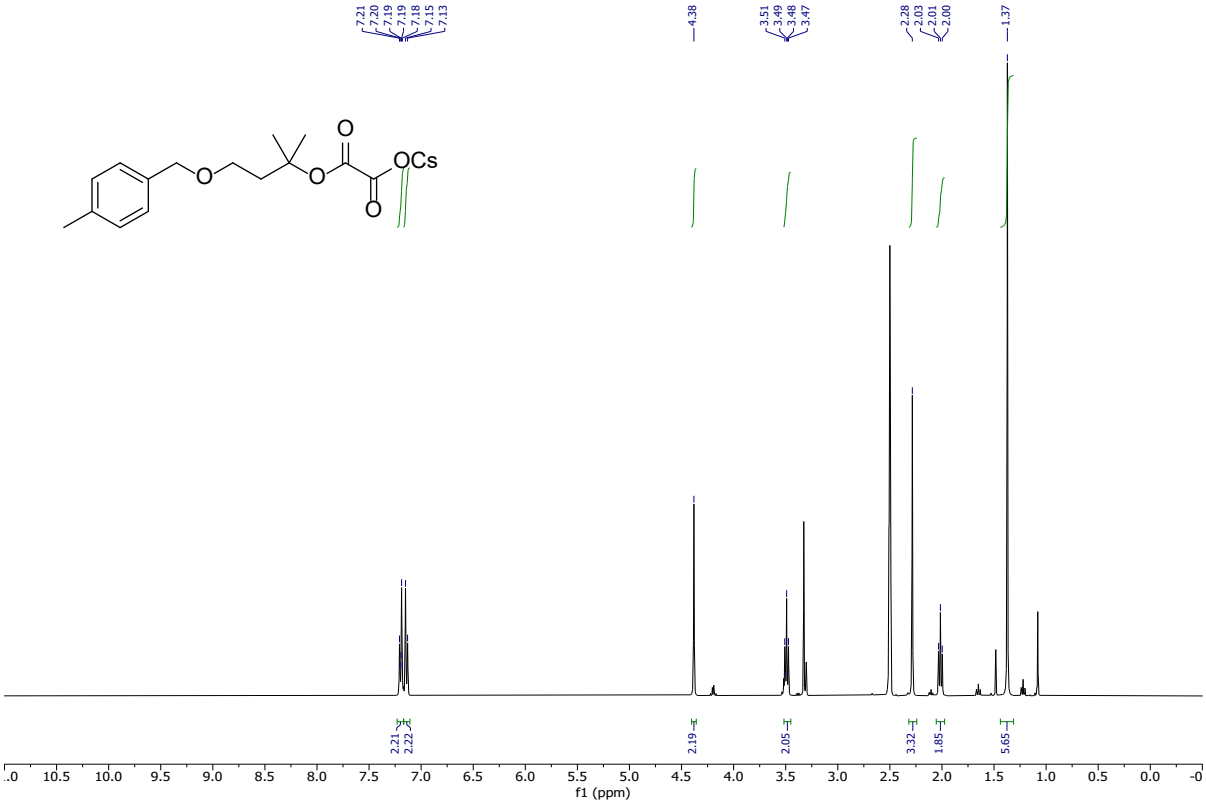


^{13}C NMR, $CDCl_3$, 101 MHz

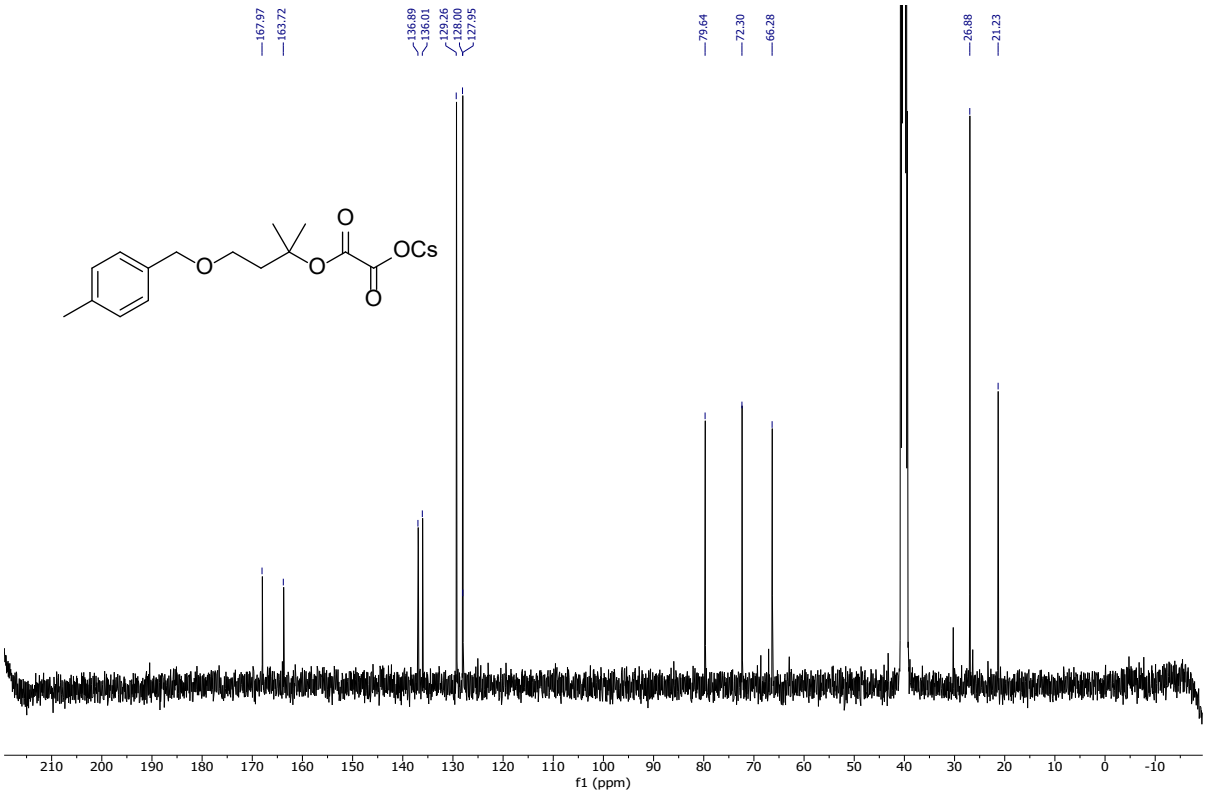


Compound **3h**

^{1}H NMR, DMSO, 400 MHz

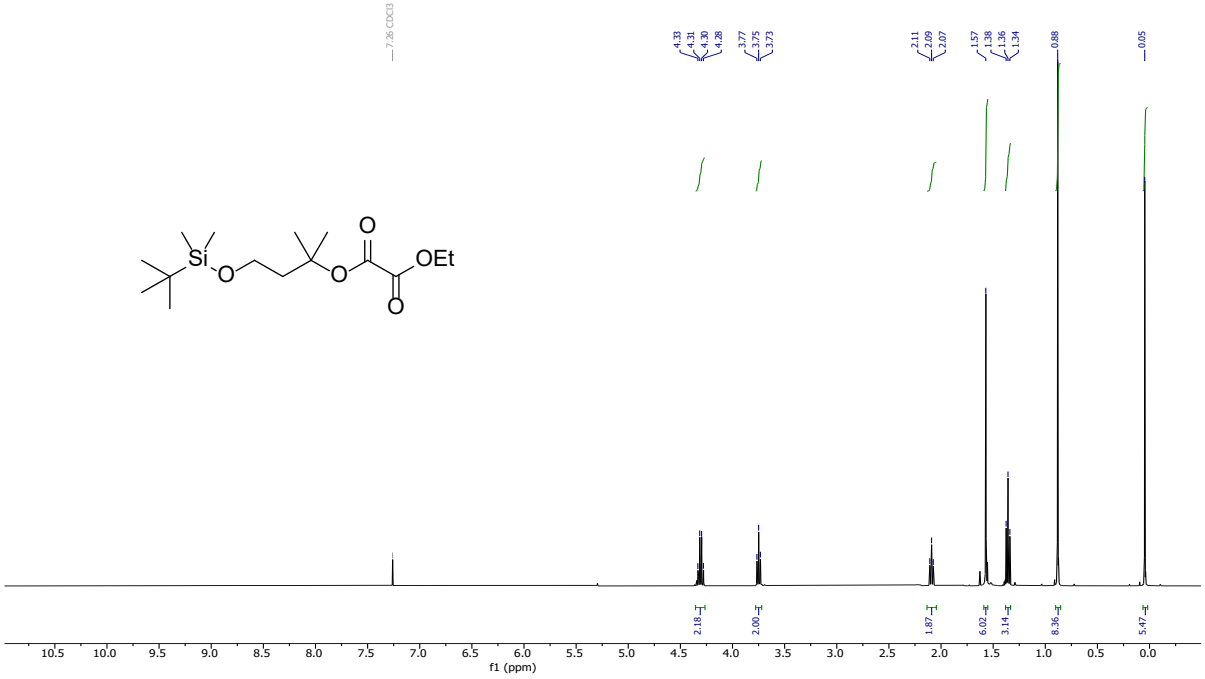


^{13}C NMR, DMSO, 101 MHz

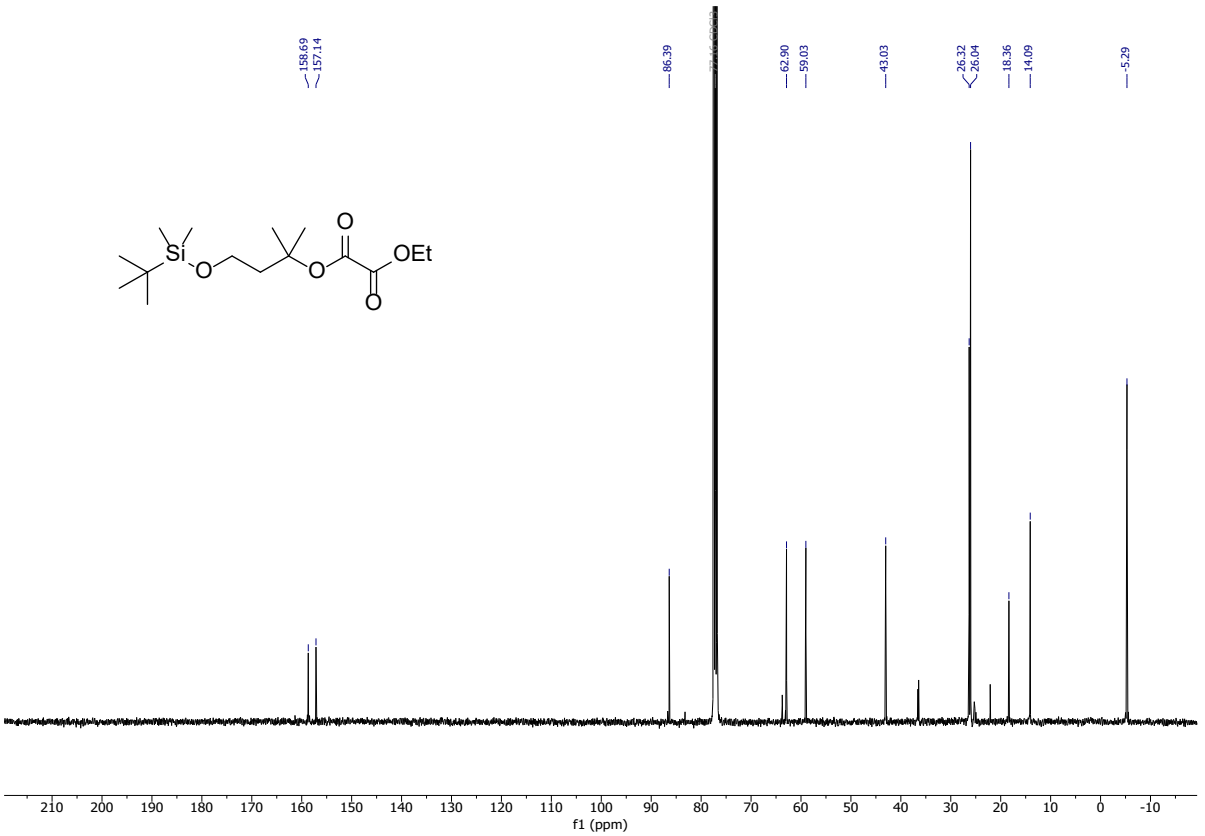


Compound **23i**

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

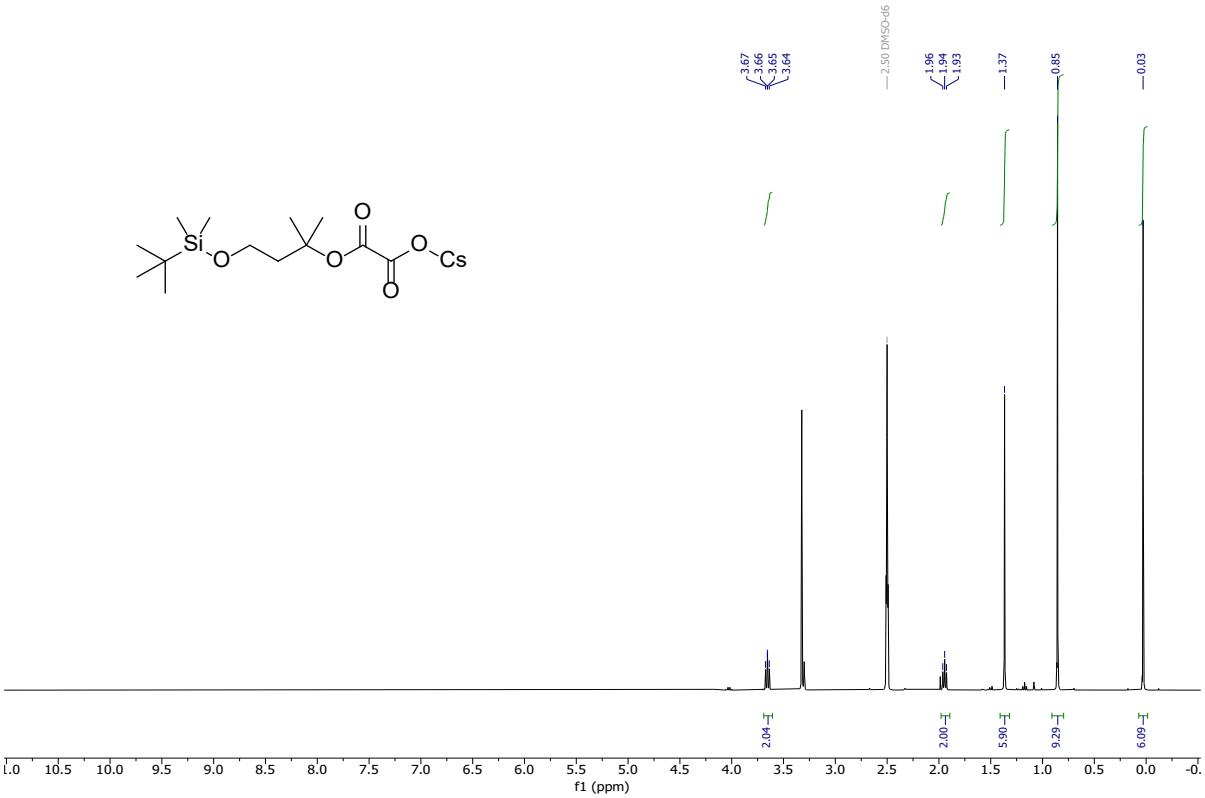


^{13}C NMR, $CDCl_3$, 101 MHz

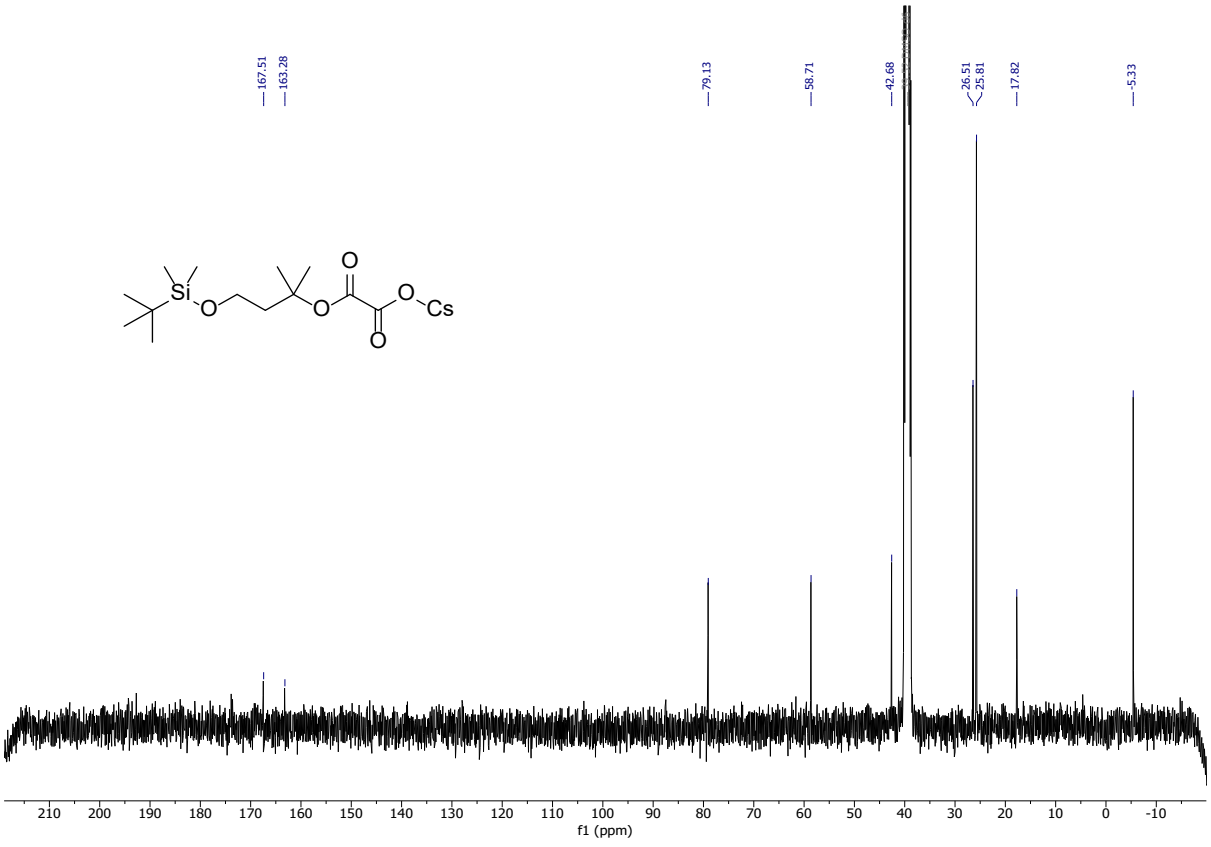


Compound **3i**

^{1}H NMR, DMSO, 400 MHz

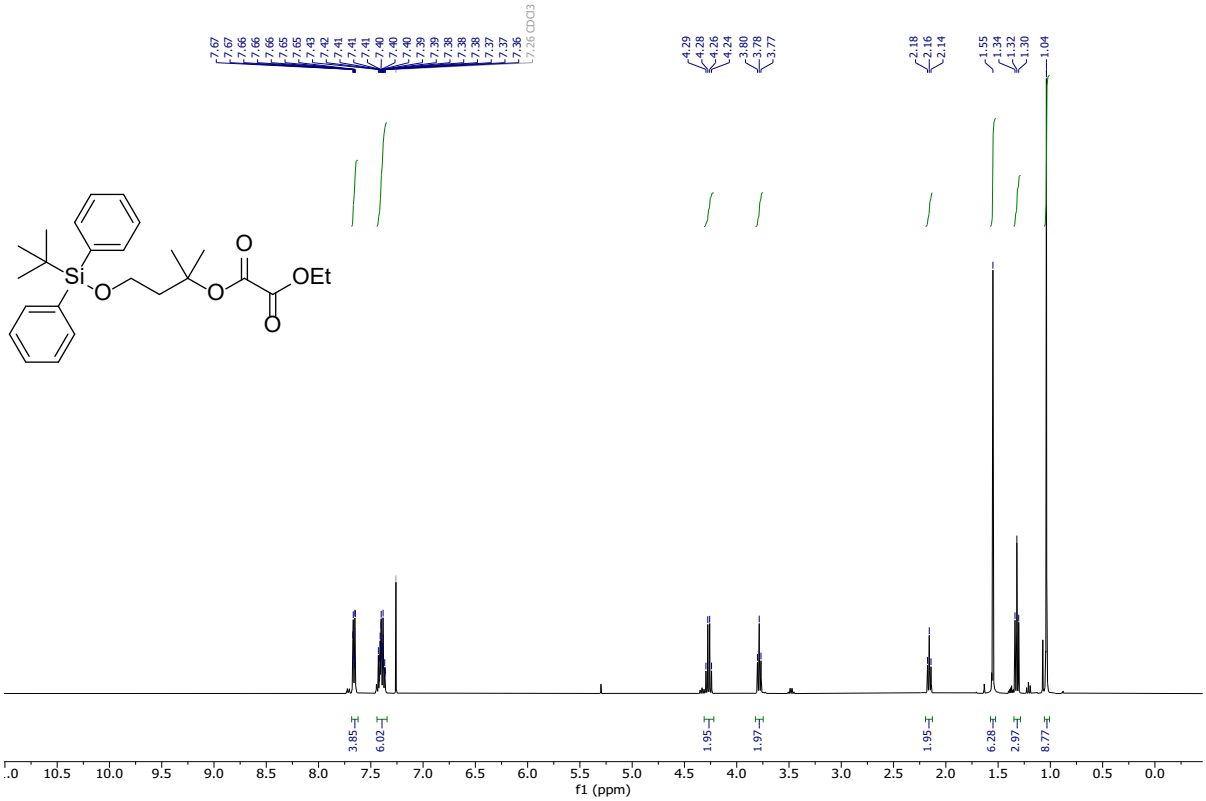


^{13}C NMR, DMSO, 101 MHz

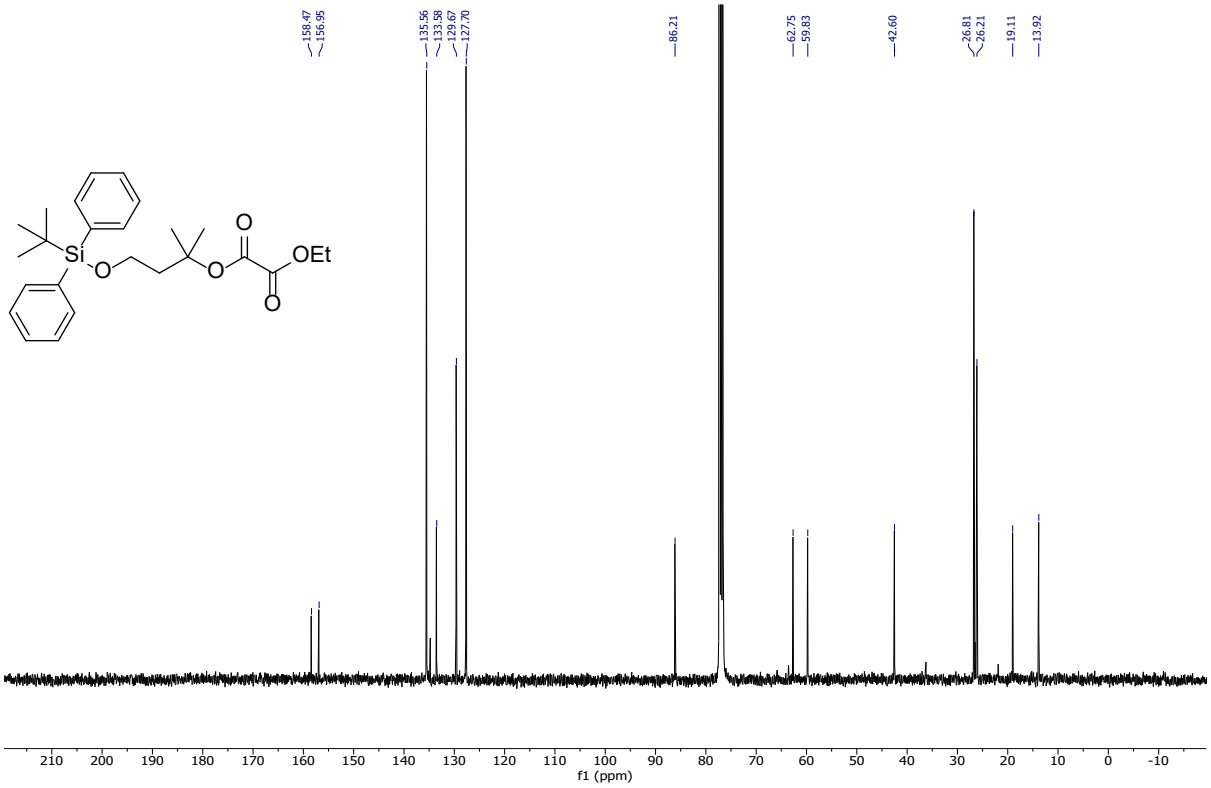


Compound **23j**

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

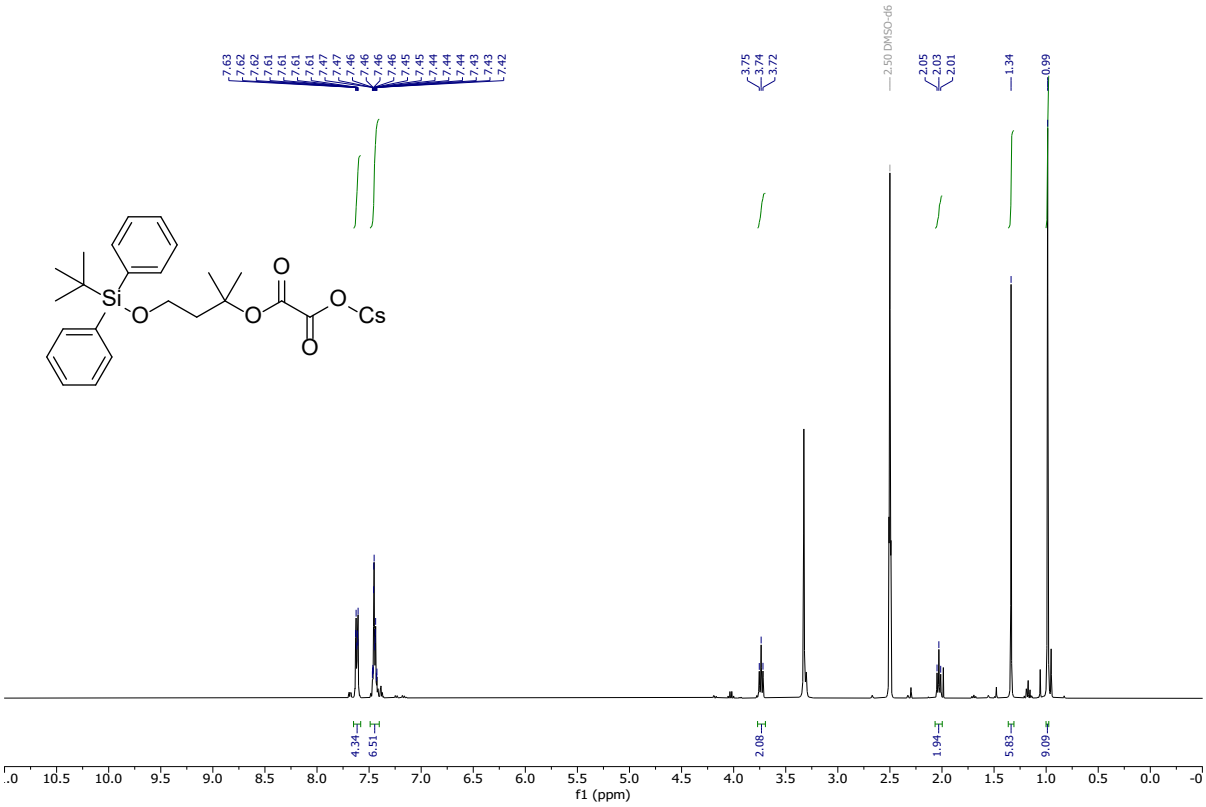


^{13}C NMR, $CDCl_3$, 101 MHz

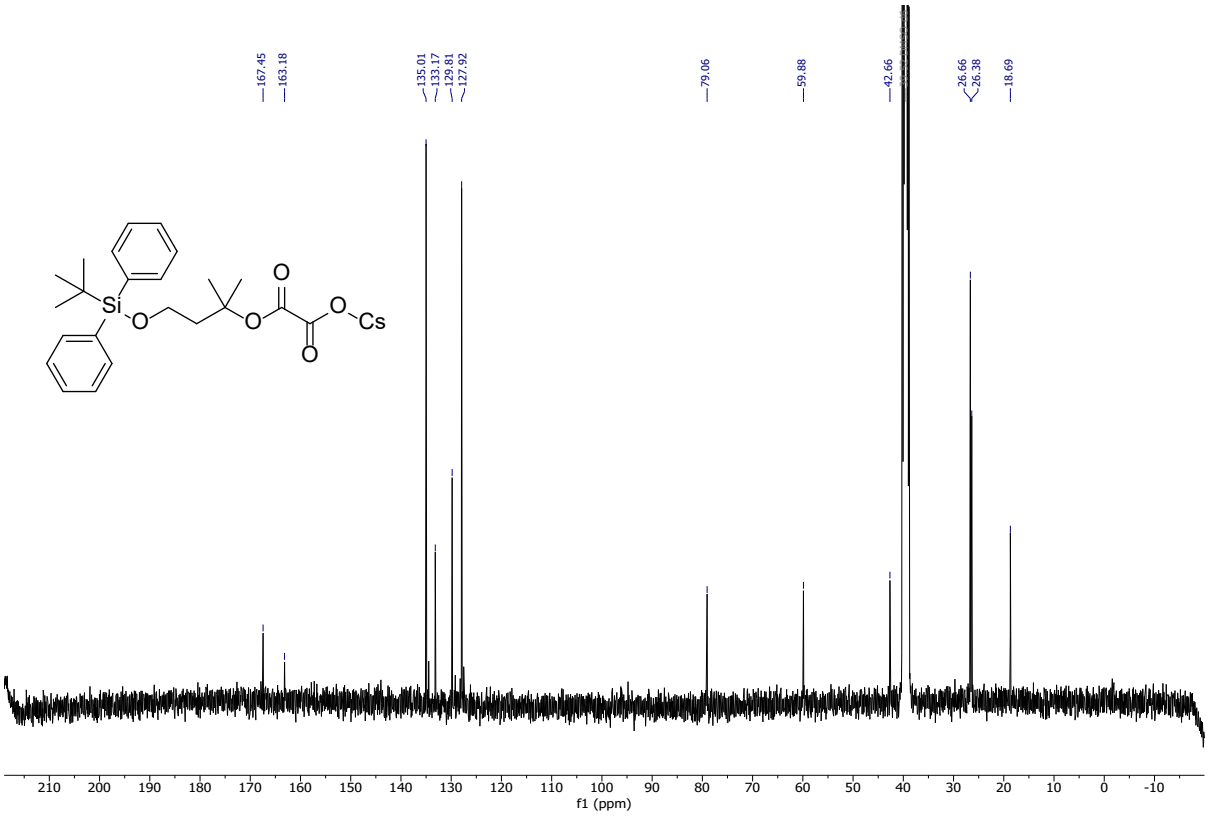


Compound **3j**

^{1}H NMR, DMSO, 400 MHz

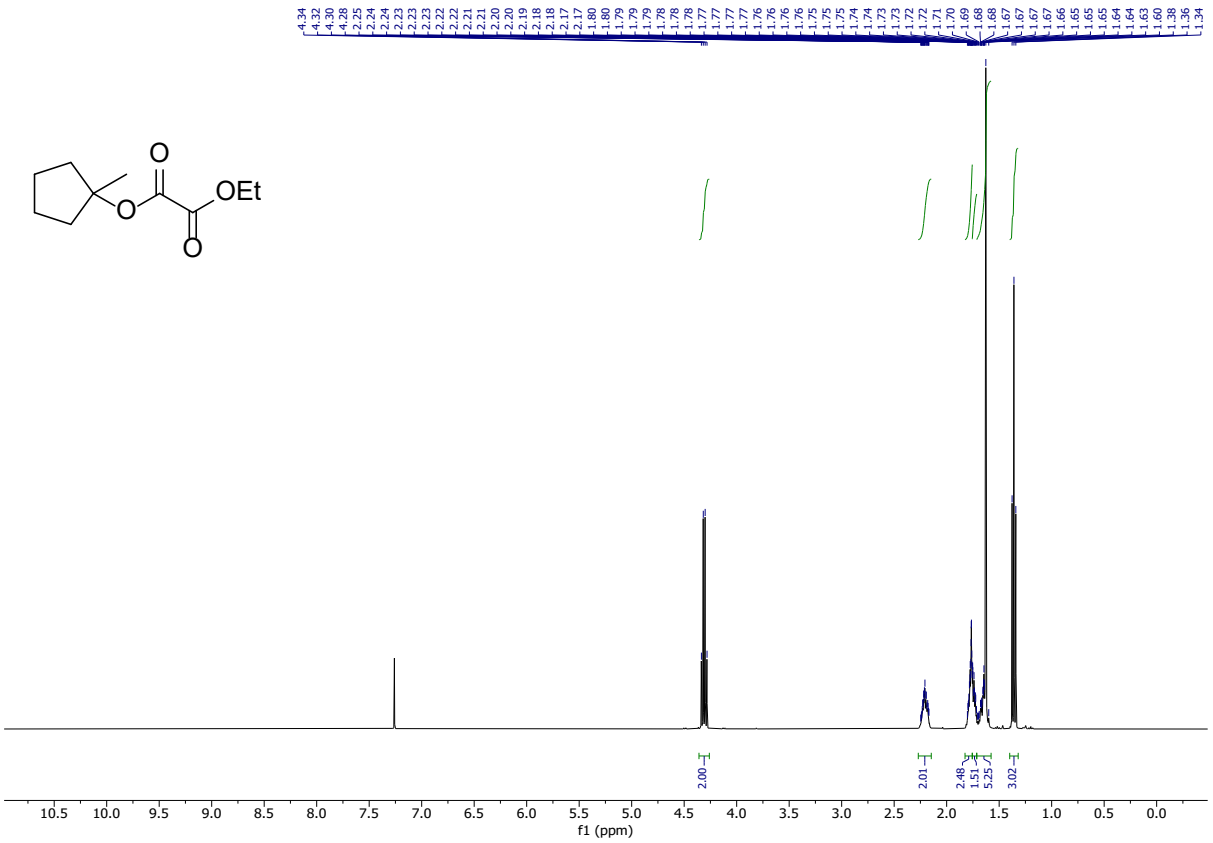


^{13}C NMR, DMSO, 101 MHz

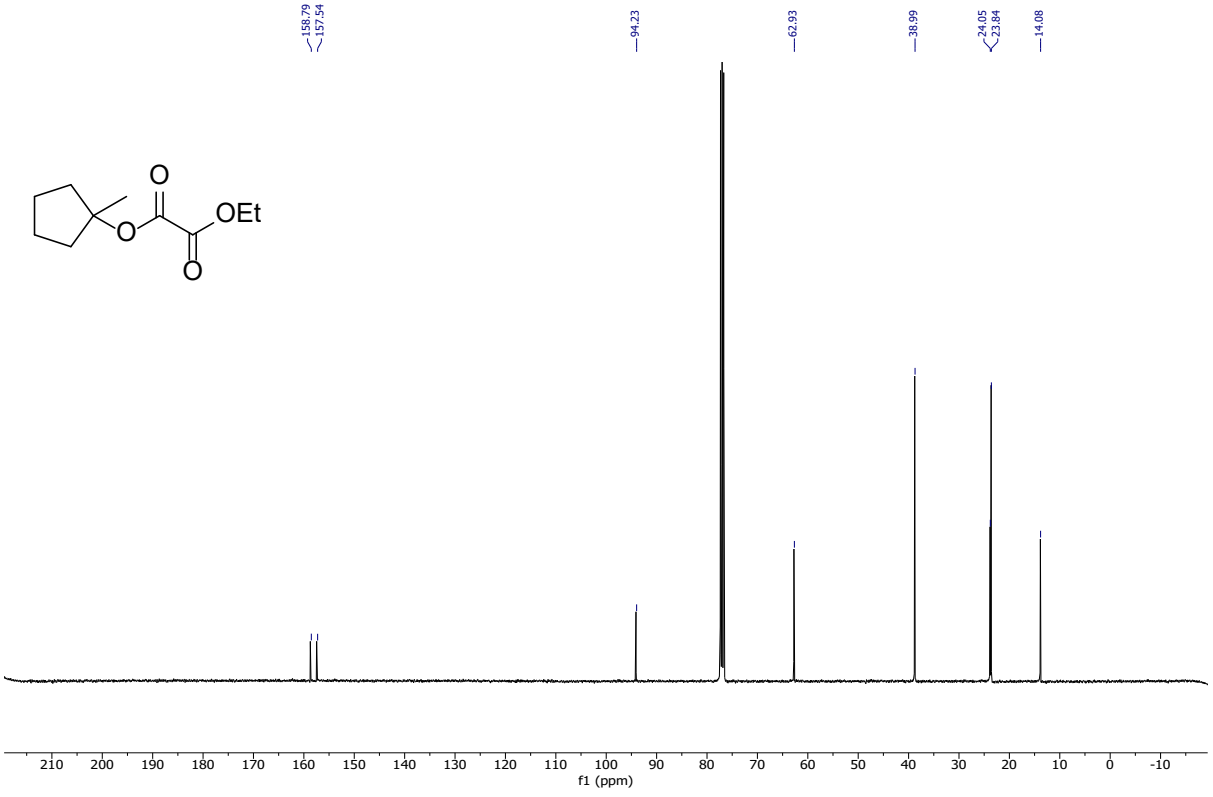


Compound **23k**

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

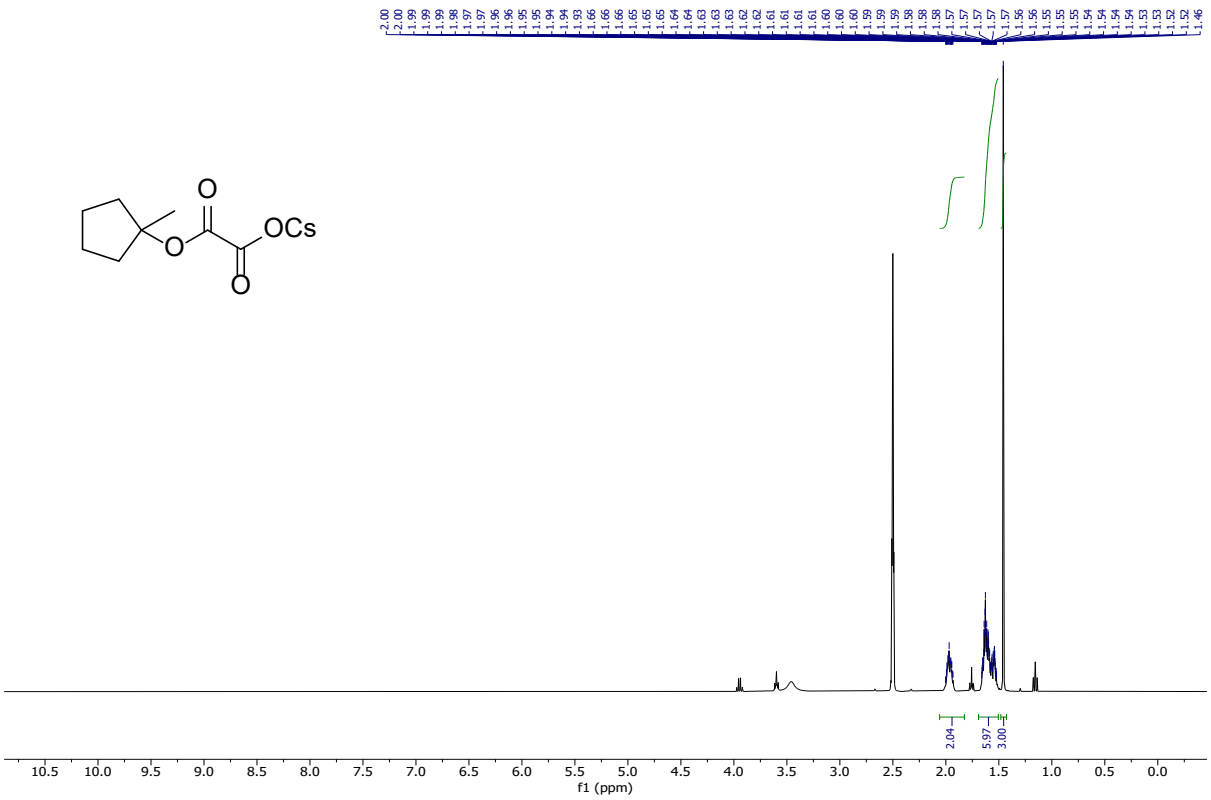


^{13}C NMR, $CDCl_3$, 101 MHz

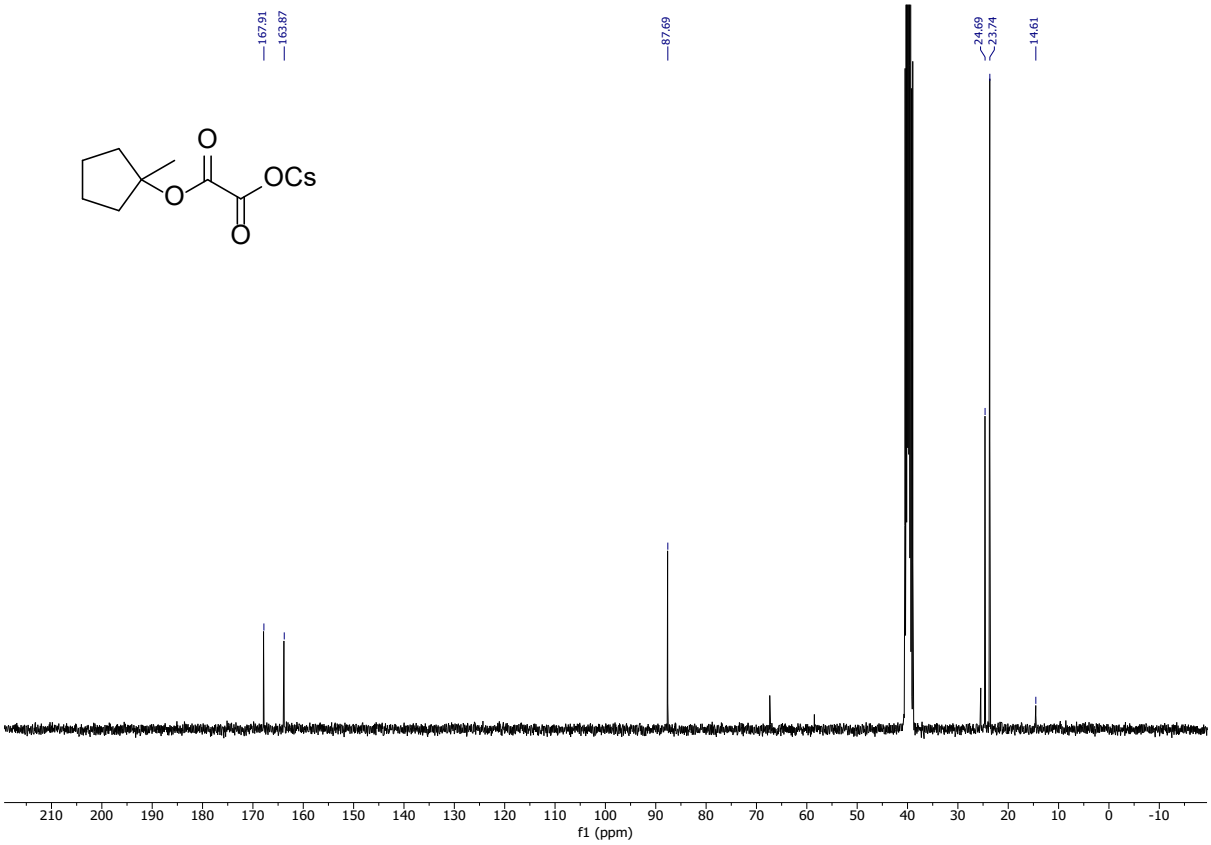


Compound **3k**

^{1}H NMR, DMSO, 400 MHz

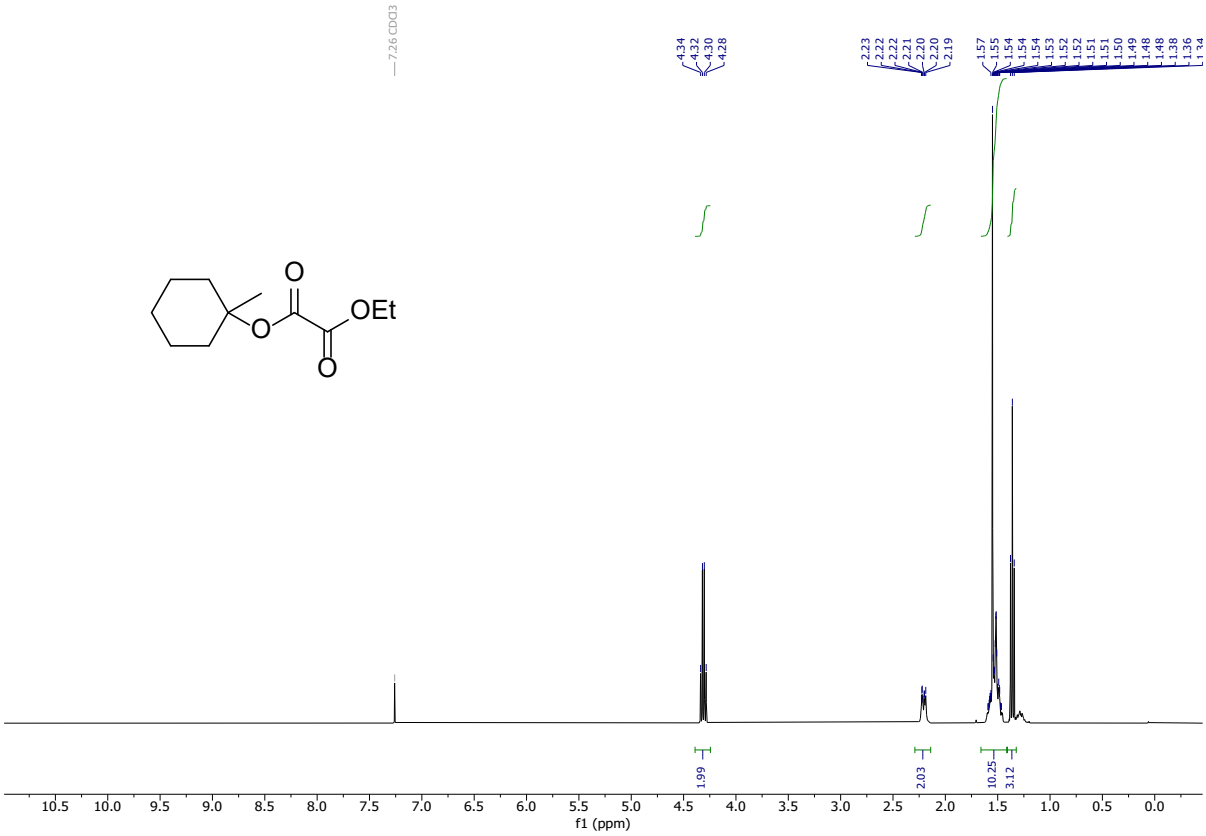


^{13}C NMR, DMSO, 101 MHz

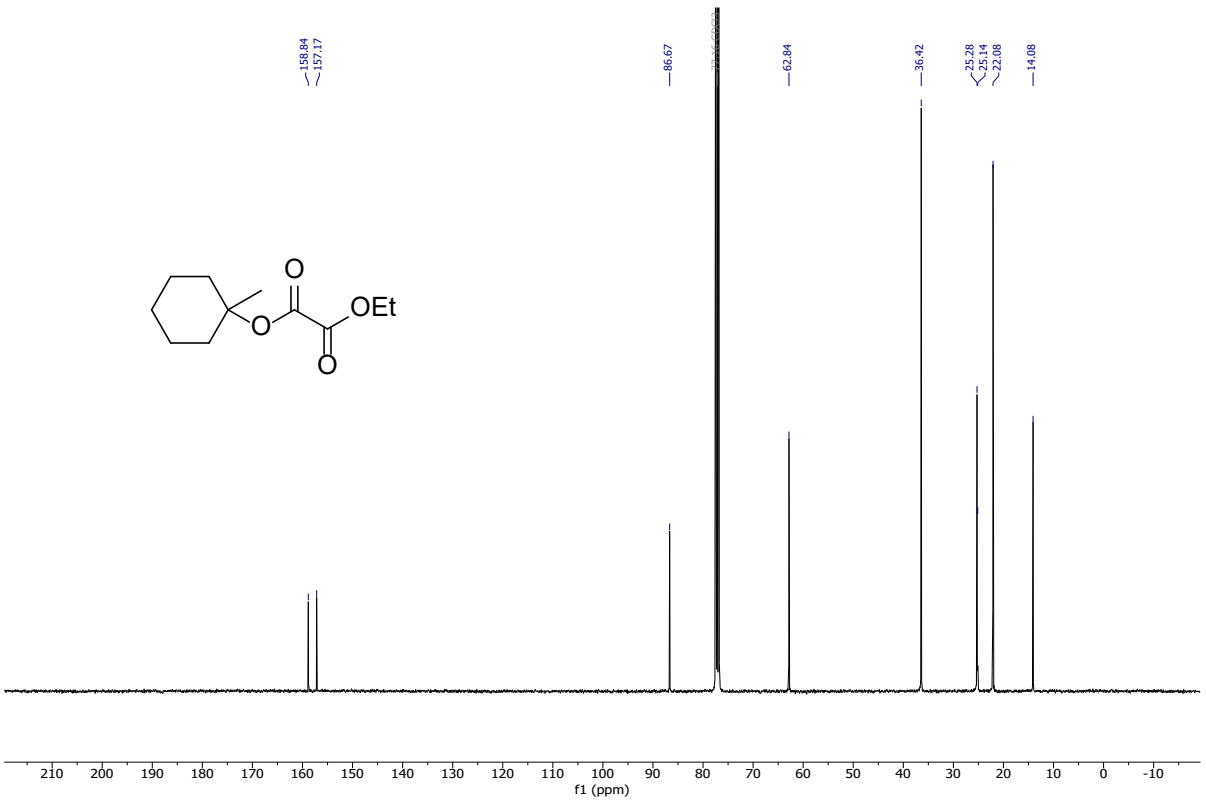


Compound **23l**

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

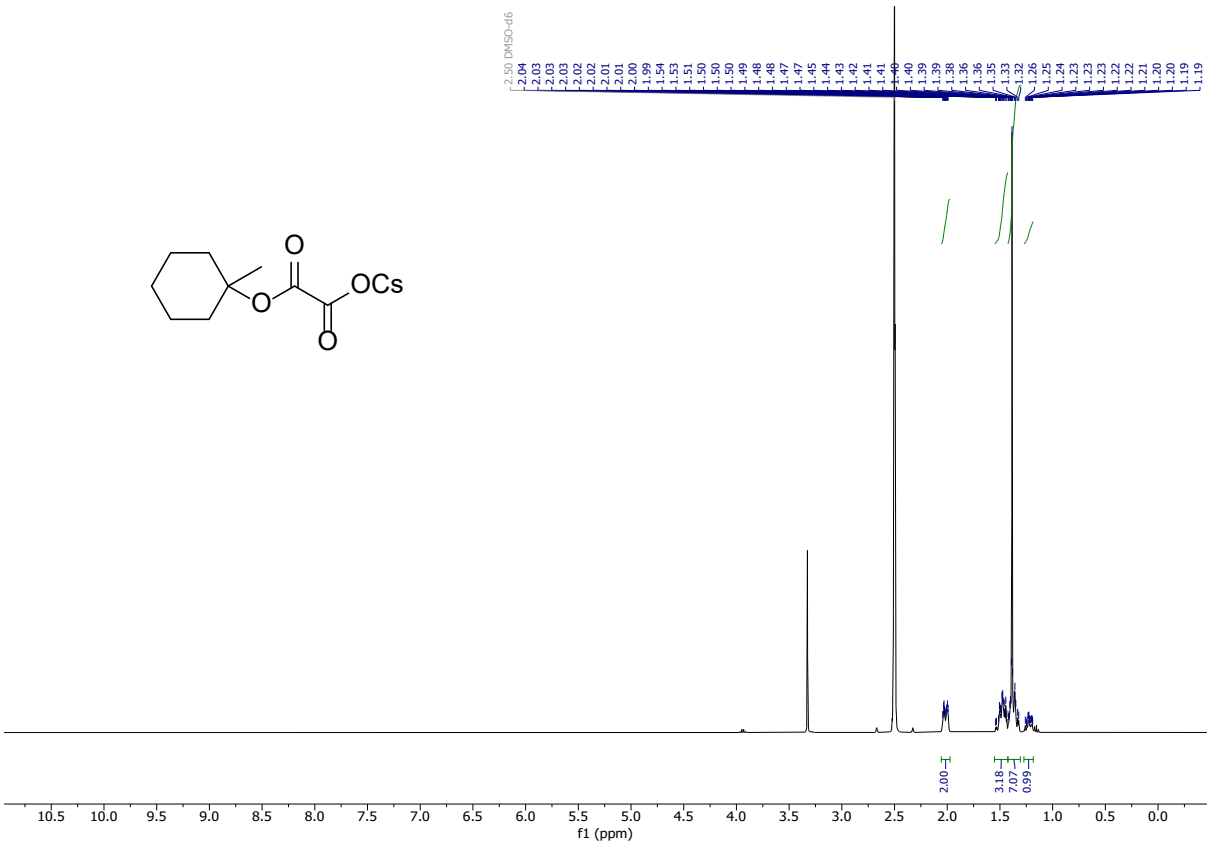


^{13}C NMR, $CDCl_3$, 101 MHz

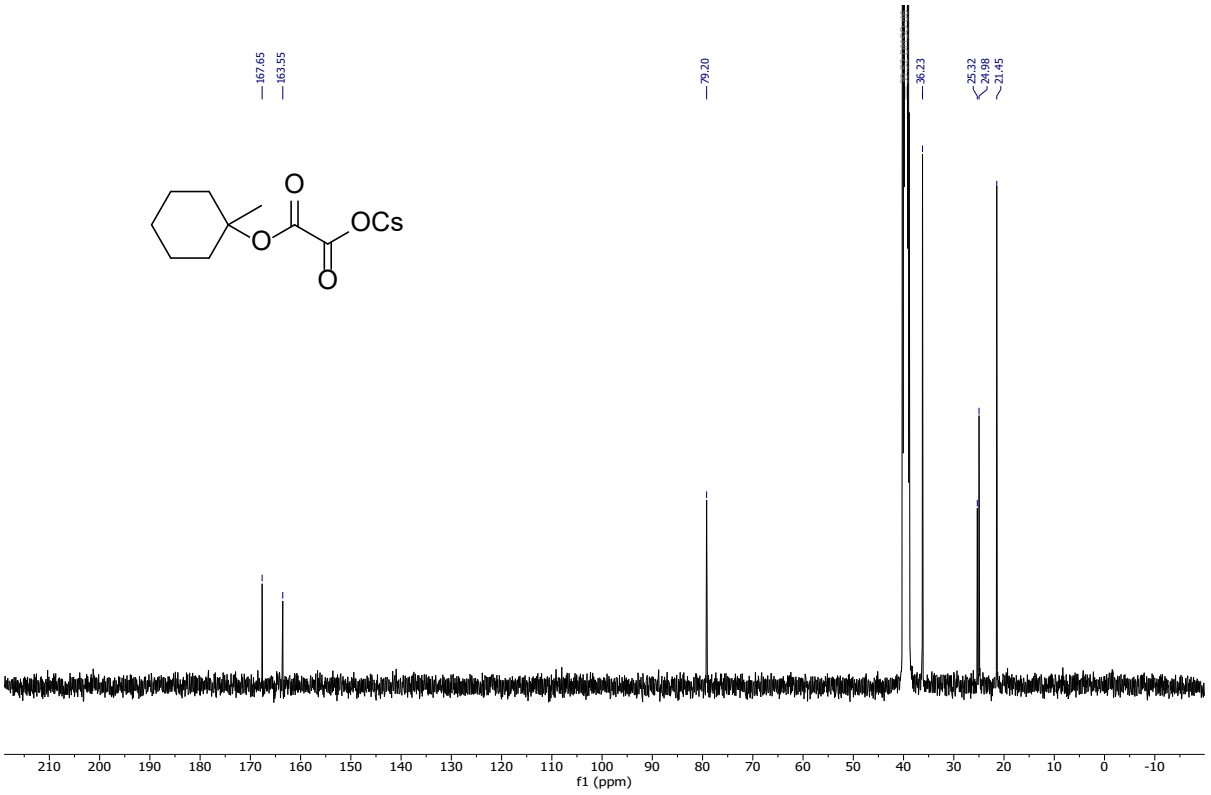


Compound **3l**

^{1}H NMR, DMSO, 400 MHz

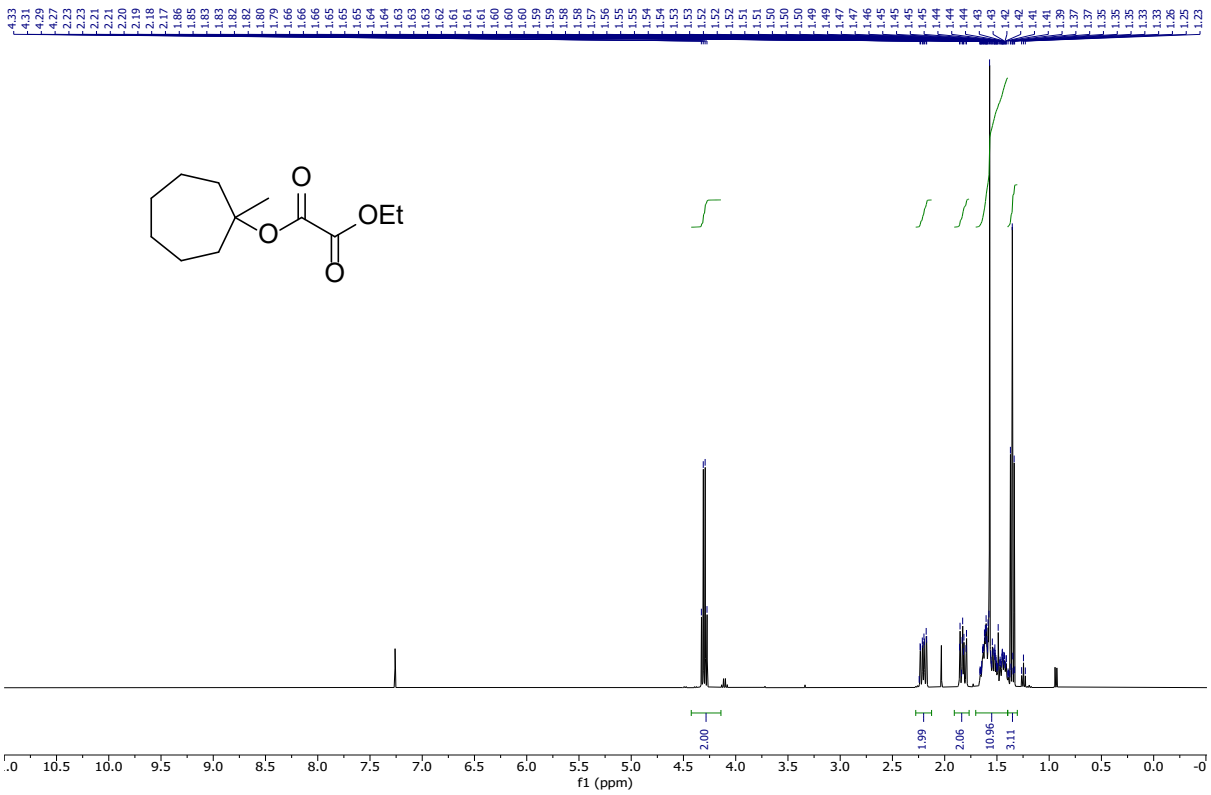


^{13}C NMR, DMSO, 101 MHz

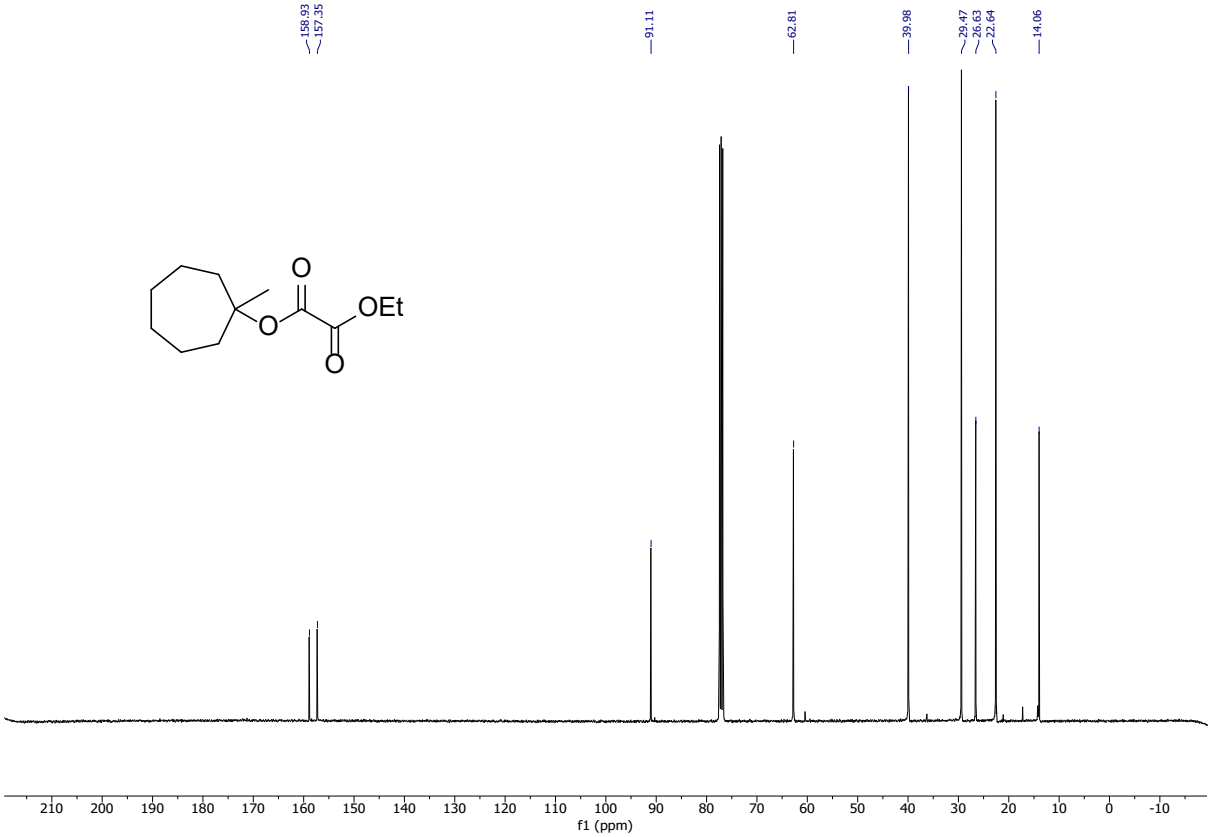


Compound **23m**

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

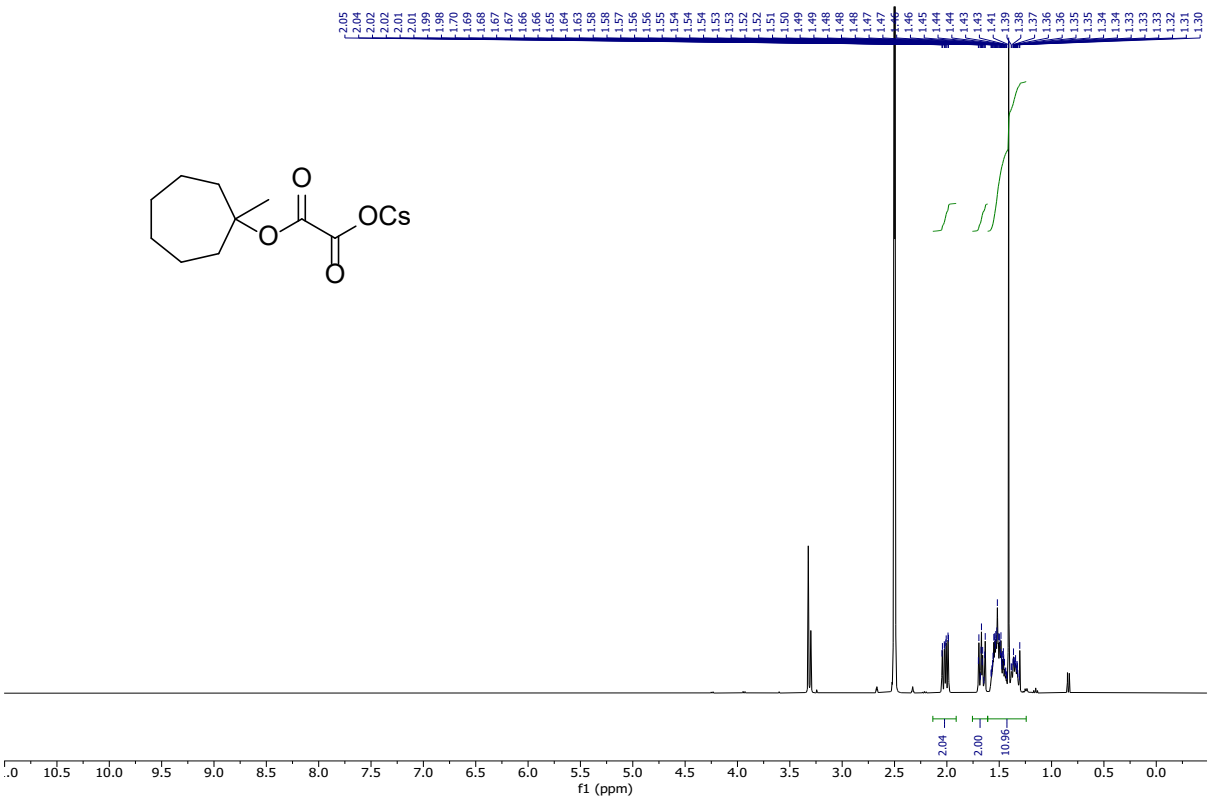


^{13}C NMR, $CDCl_3$, 101 MHz

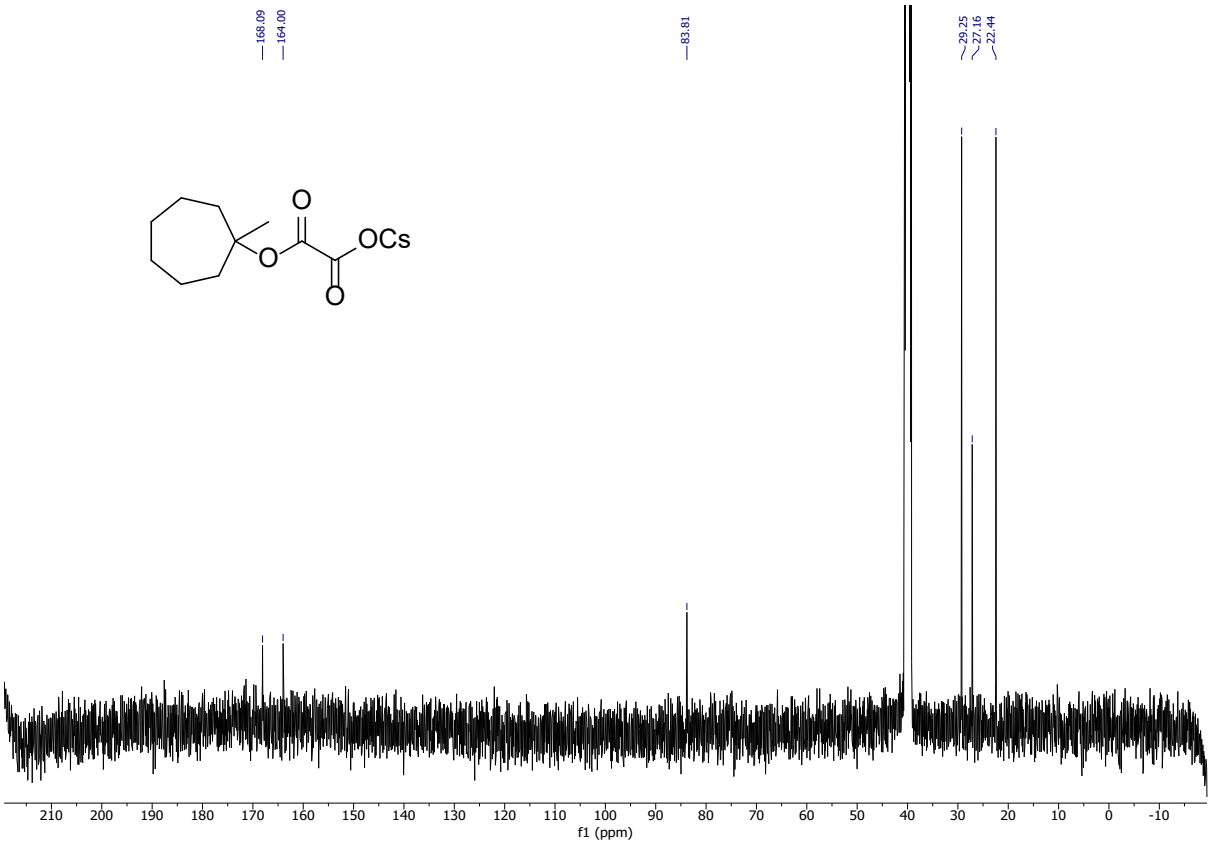


Compound **3m**

^{1}H NMR, DMSO, 400 MHz

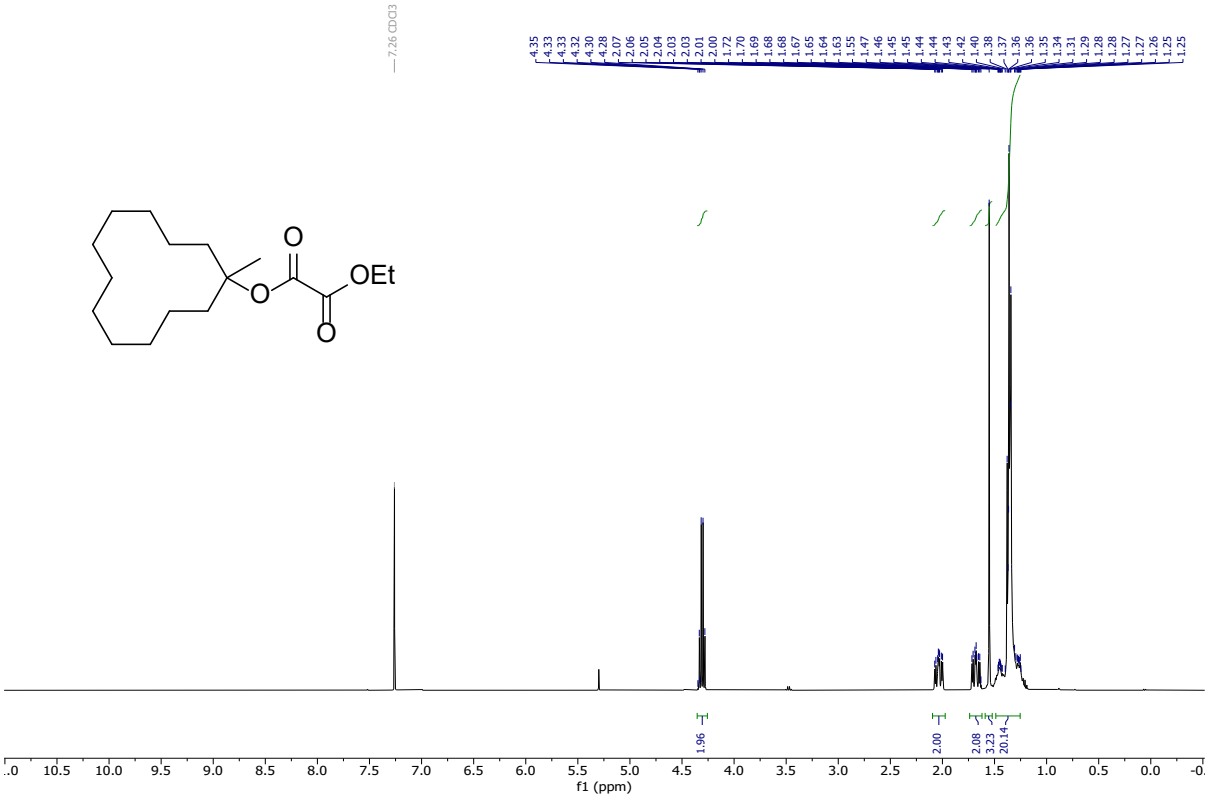


^{13}C NMR, DMSO, 101 MHz

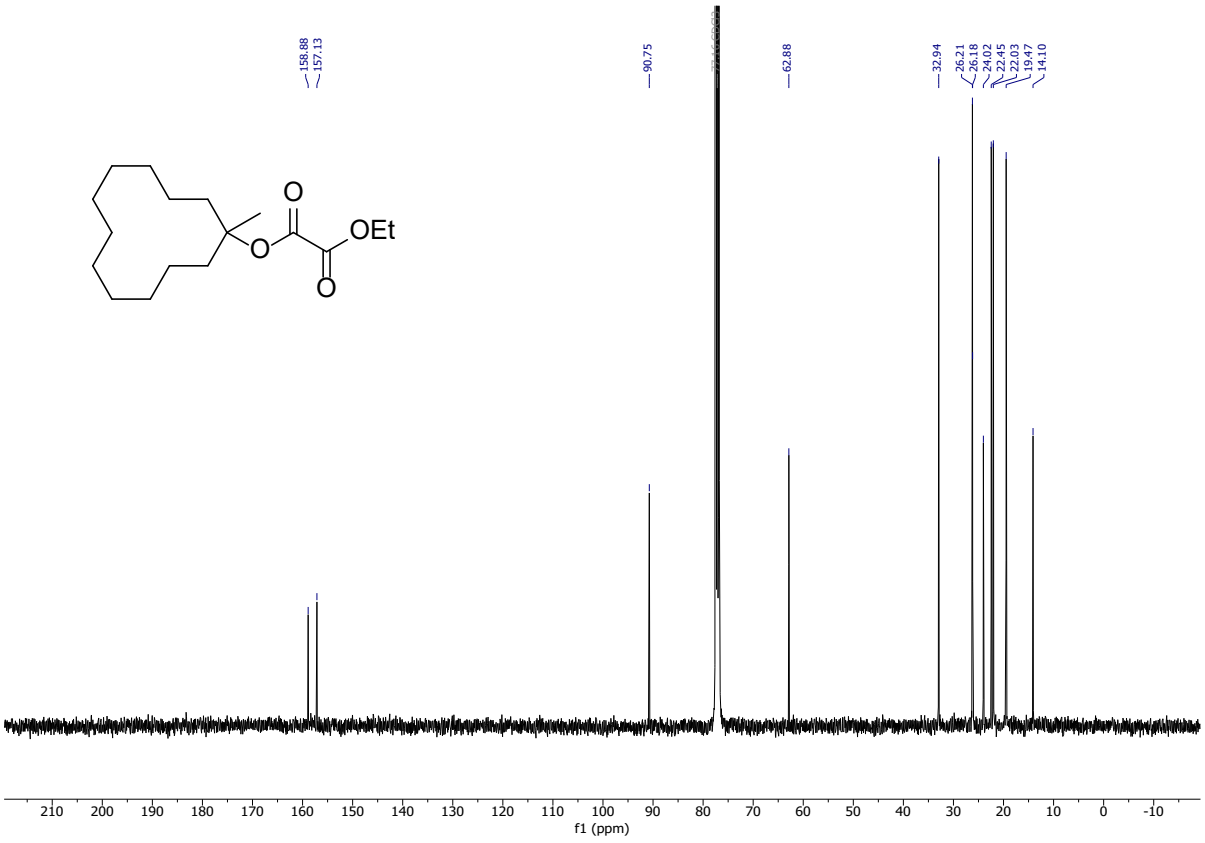


Compound **23n**

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

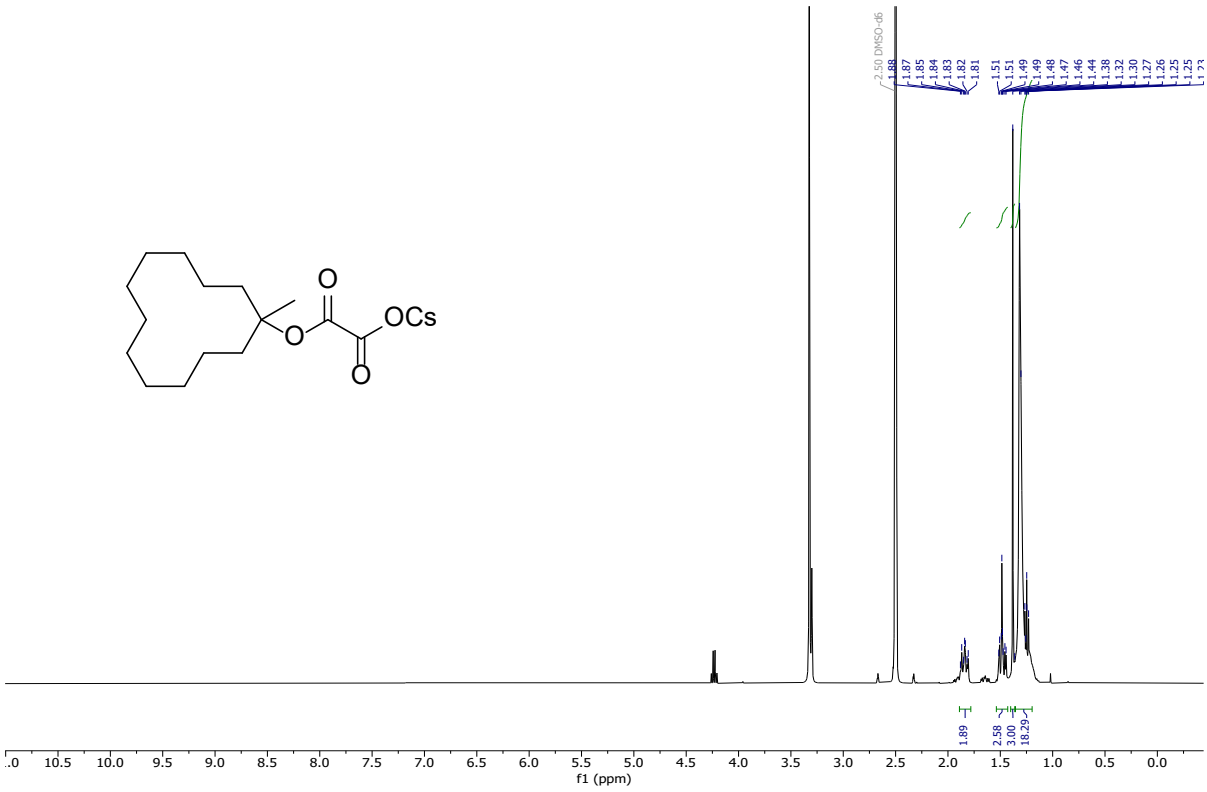


^{13}C NMR, $CDCl_3$, 101 MHz

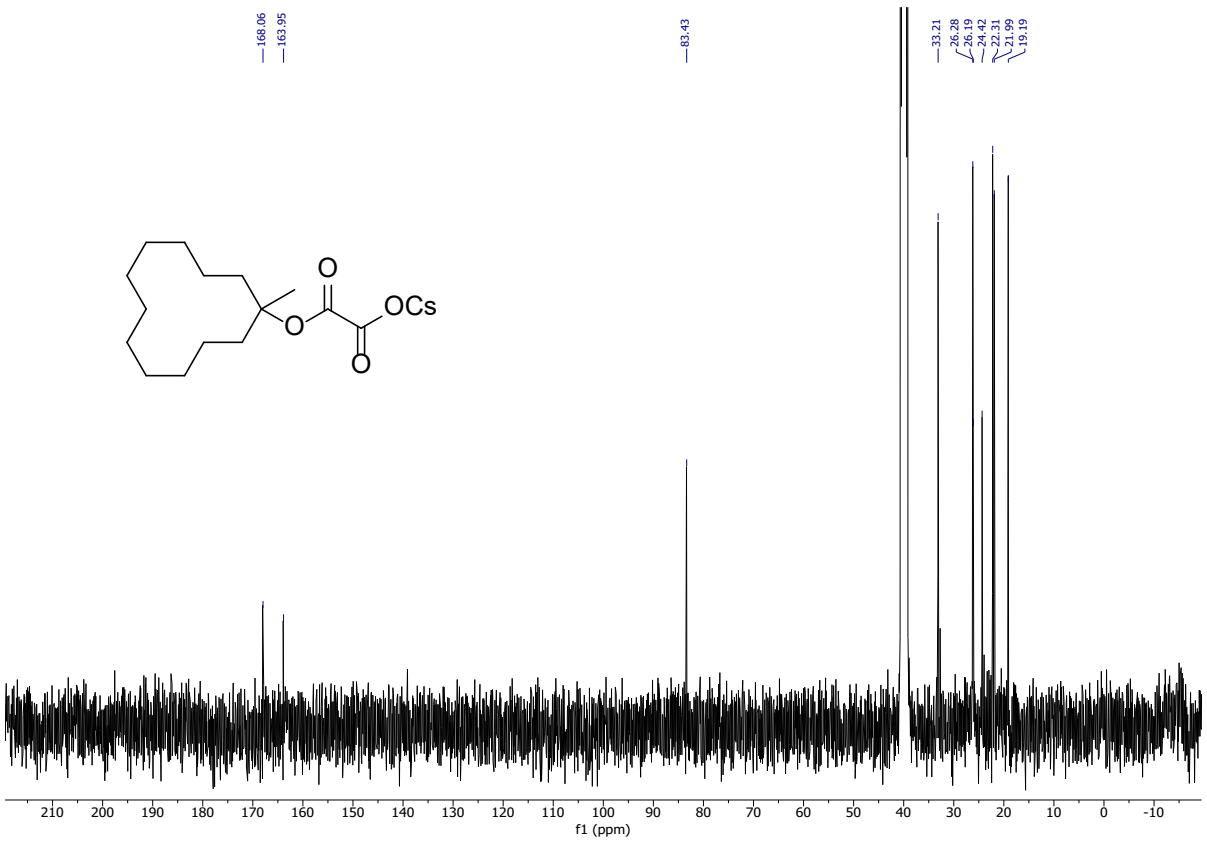


Compound **3n**

^{1}H NMR, DMSO, 400 MHz

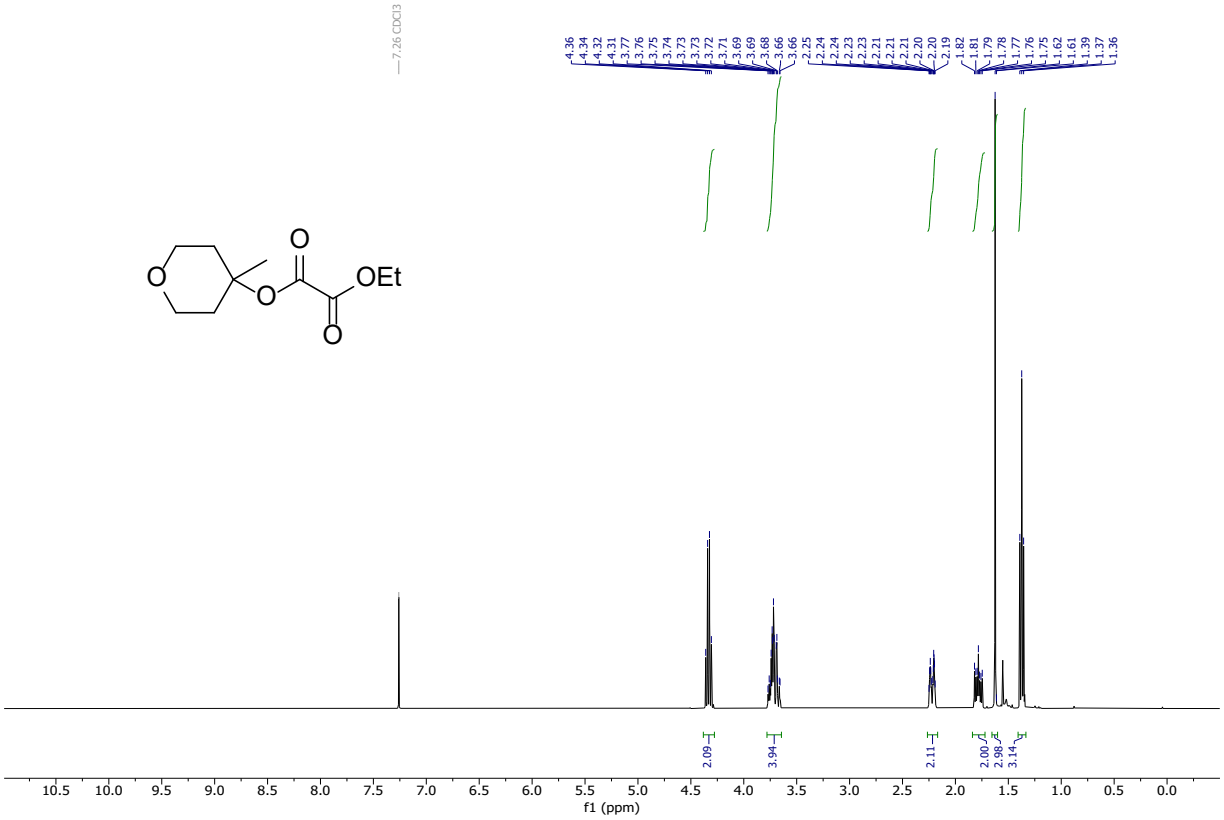


^{13}C NMR, DMSO, 101 MHz

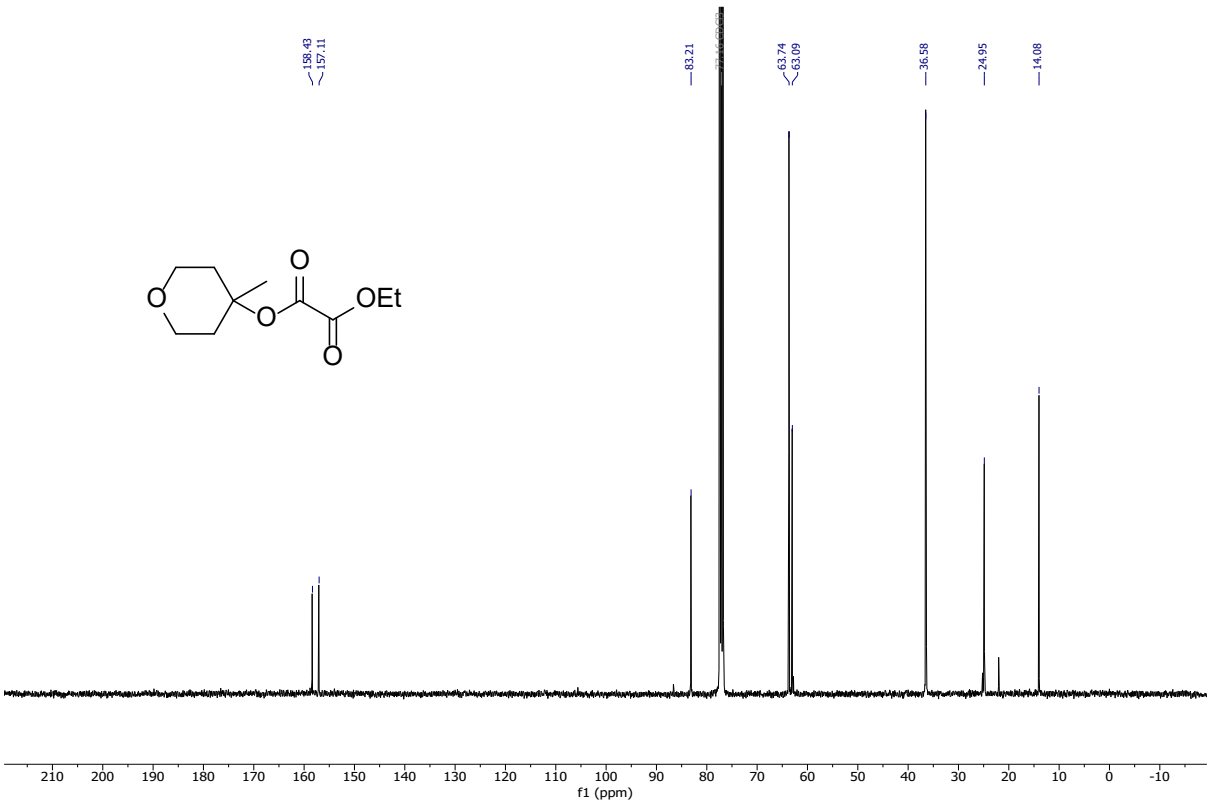


Compound **23o**

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

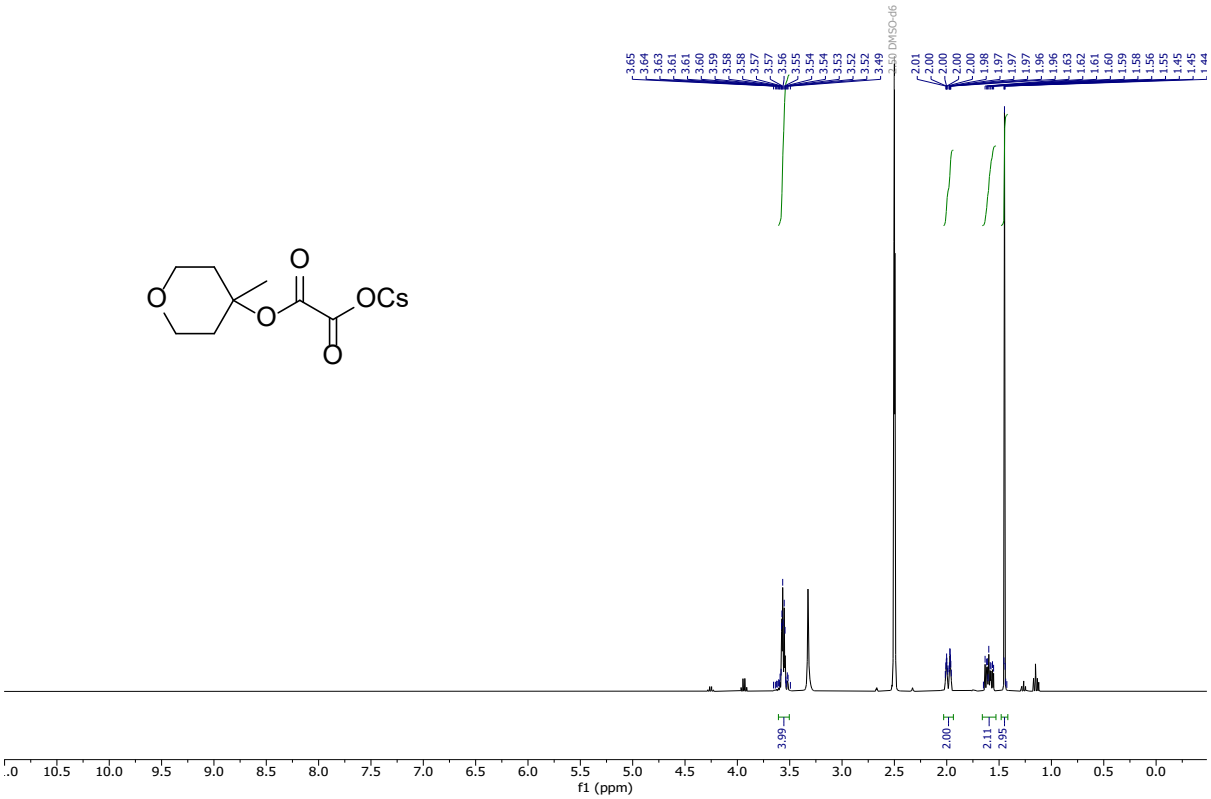


^{13}C NMR, $CDCl_3$, 101 MHz

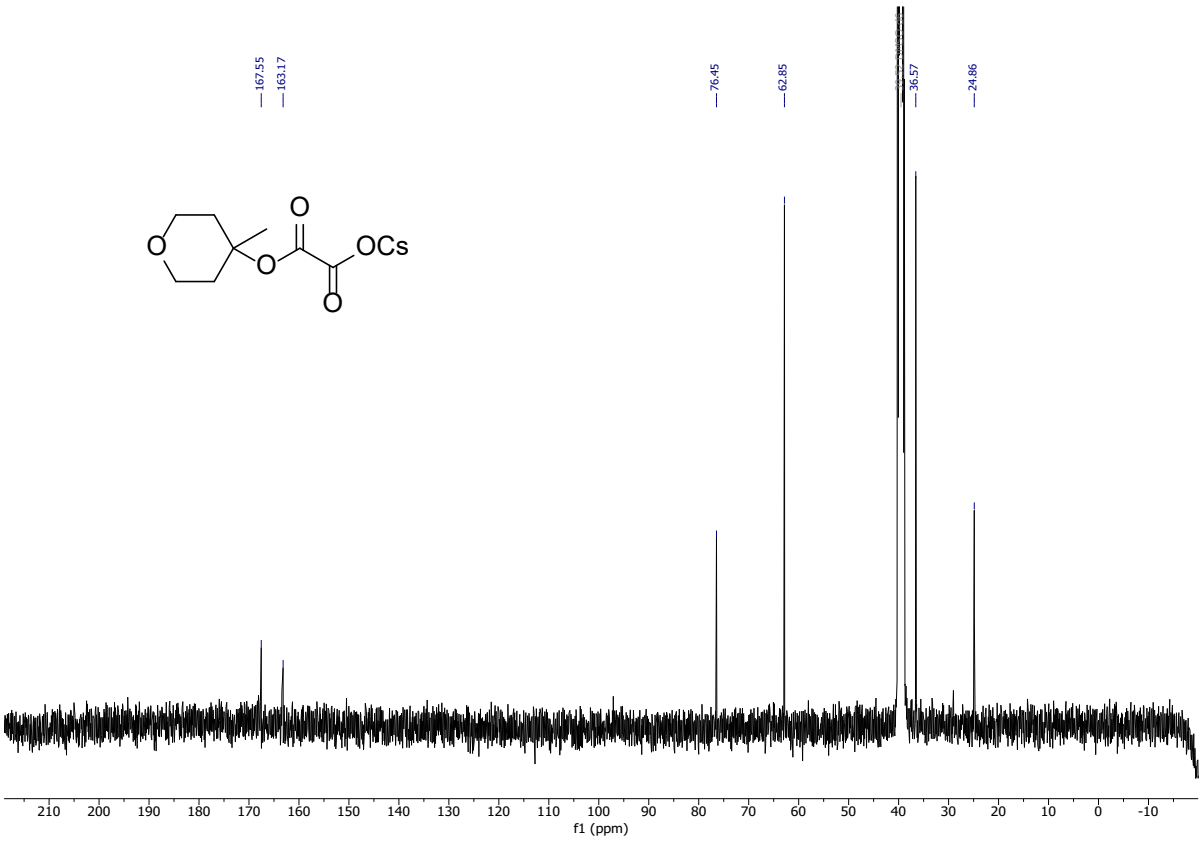


Compound **3o**

^{1}H NMR, DMSO, 400 MHz

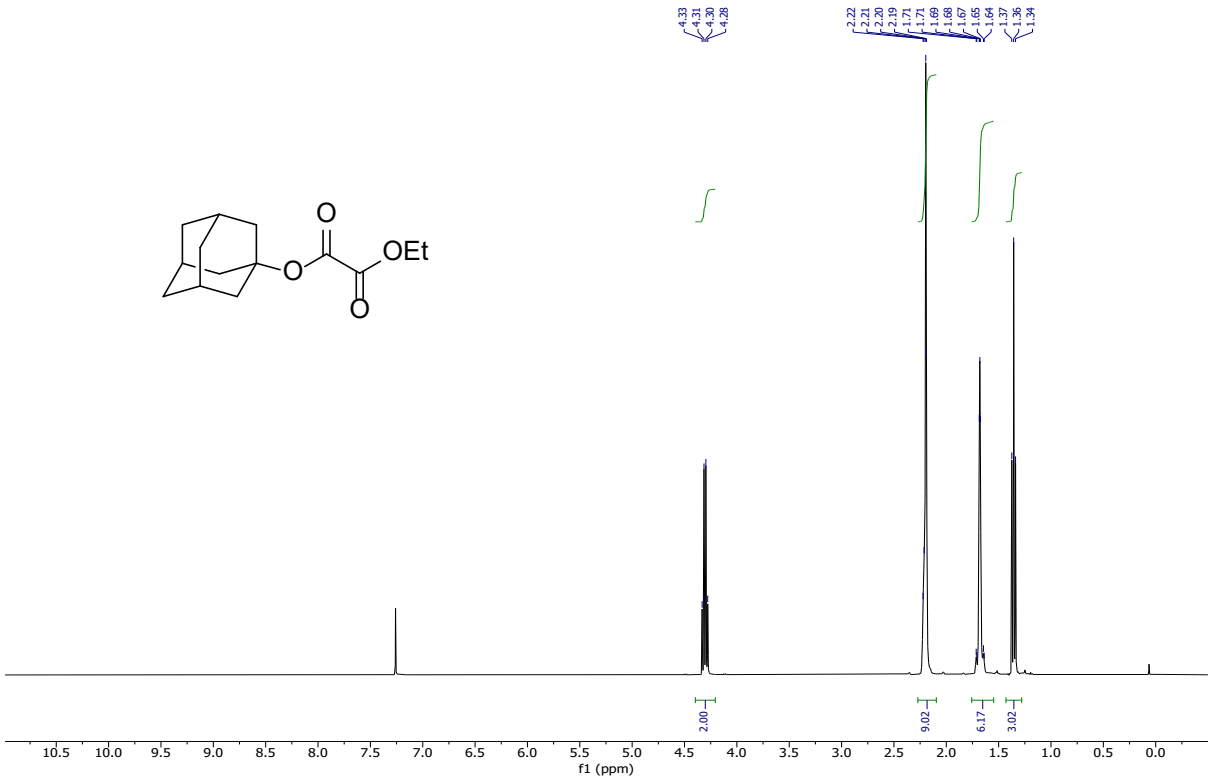


^{13}C NMR, DMSO, 101 MHz

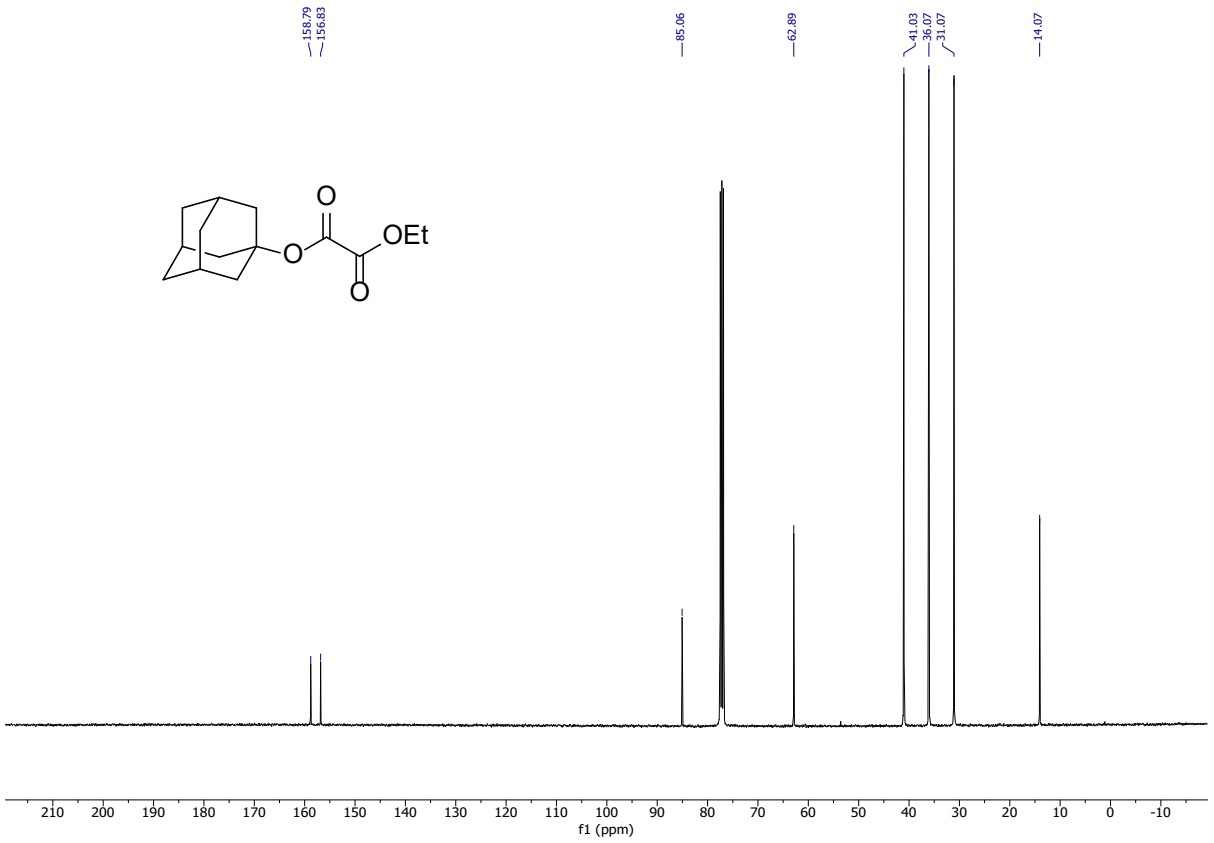


Compound **23p**

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

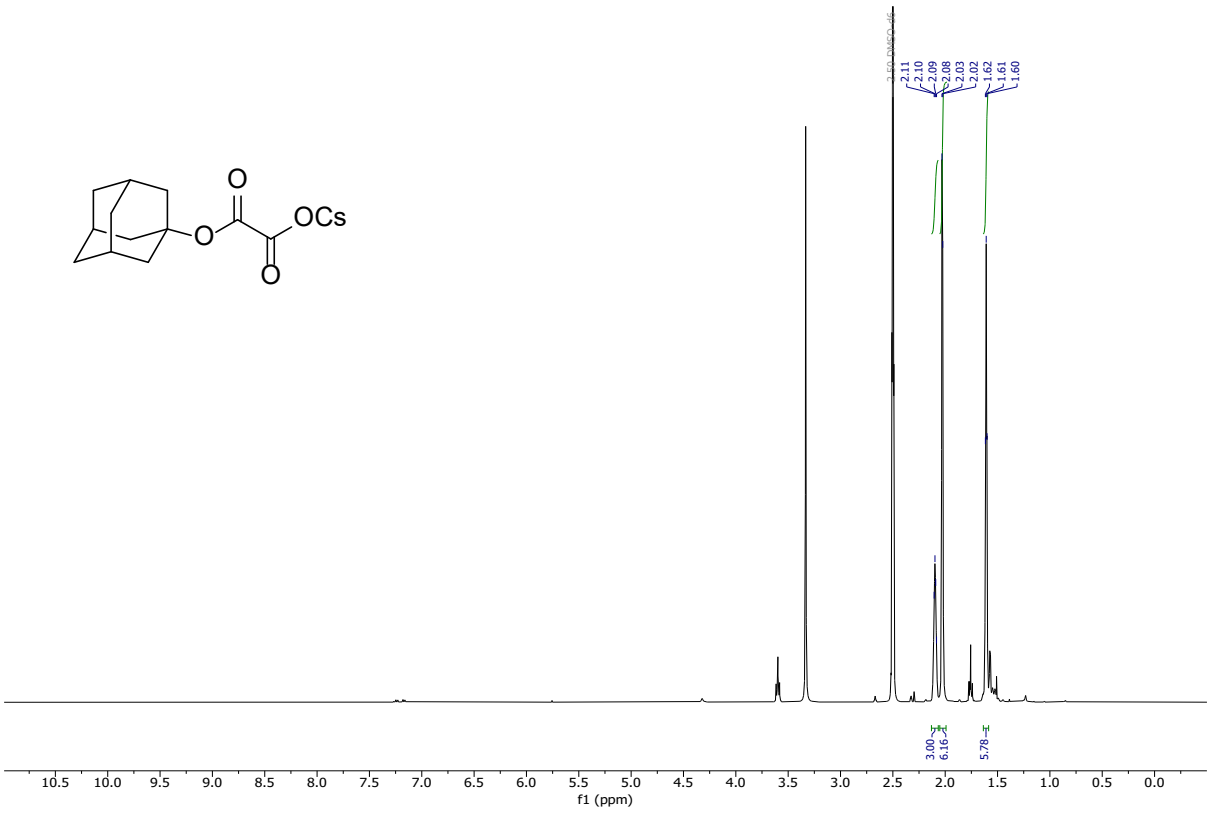


^{13}C NMR, $CDCl_3$, 101 MHz

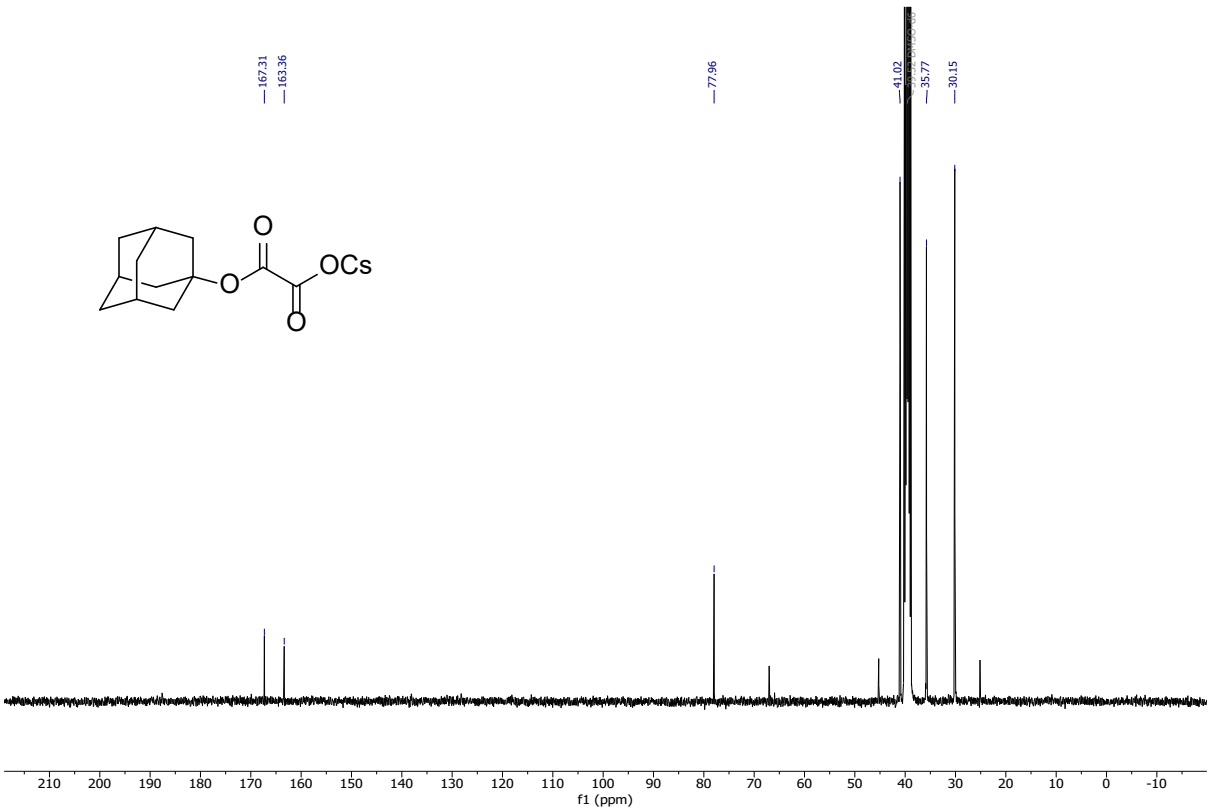


Compound **3p** (with 25% **23p**)

^{1}H NMR, DMSO, 400 MHz

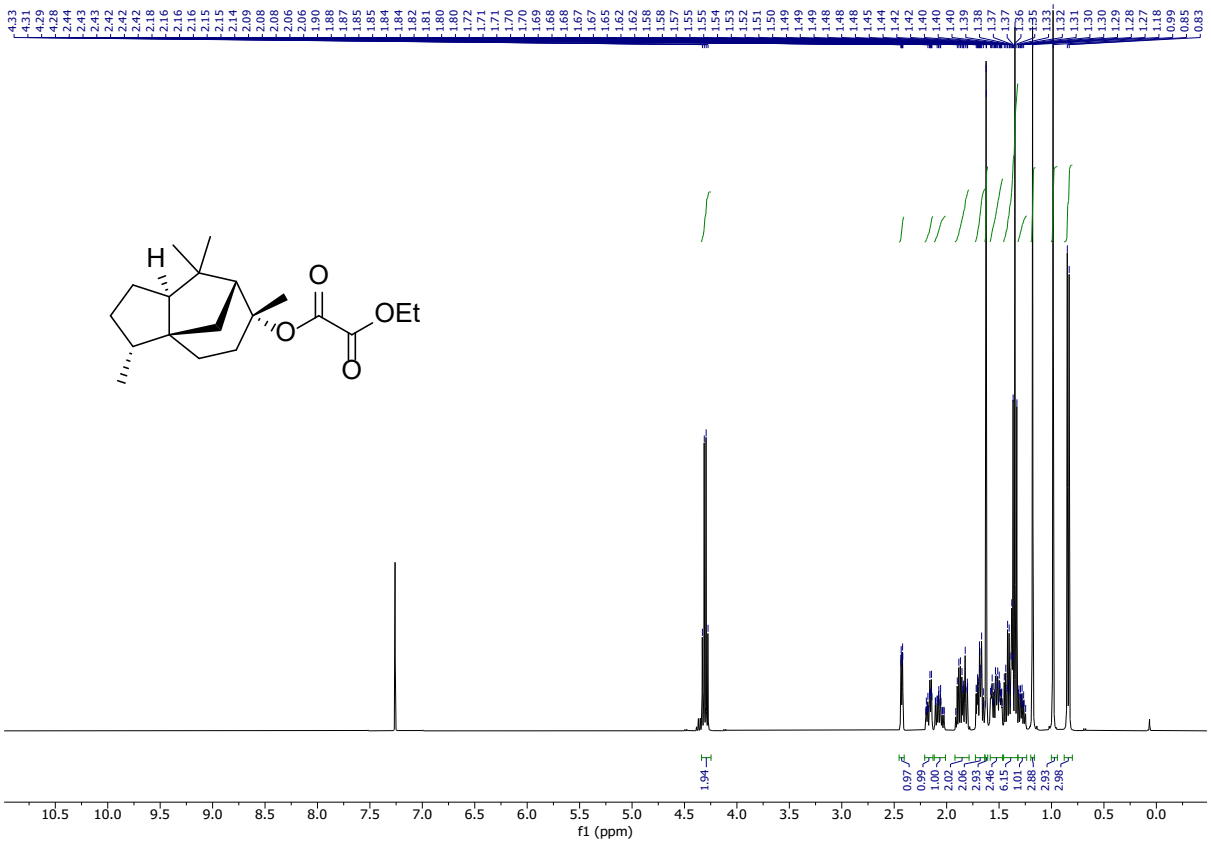


^{13}C NMR, DMSO, 101 MHz

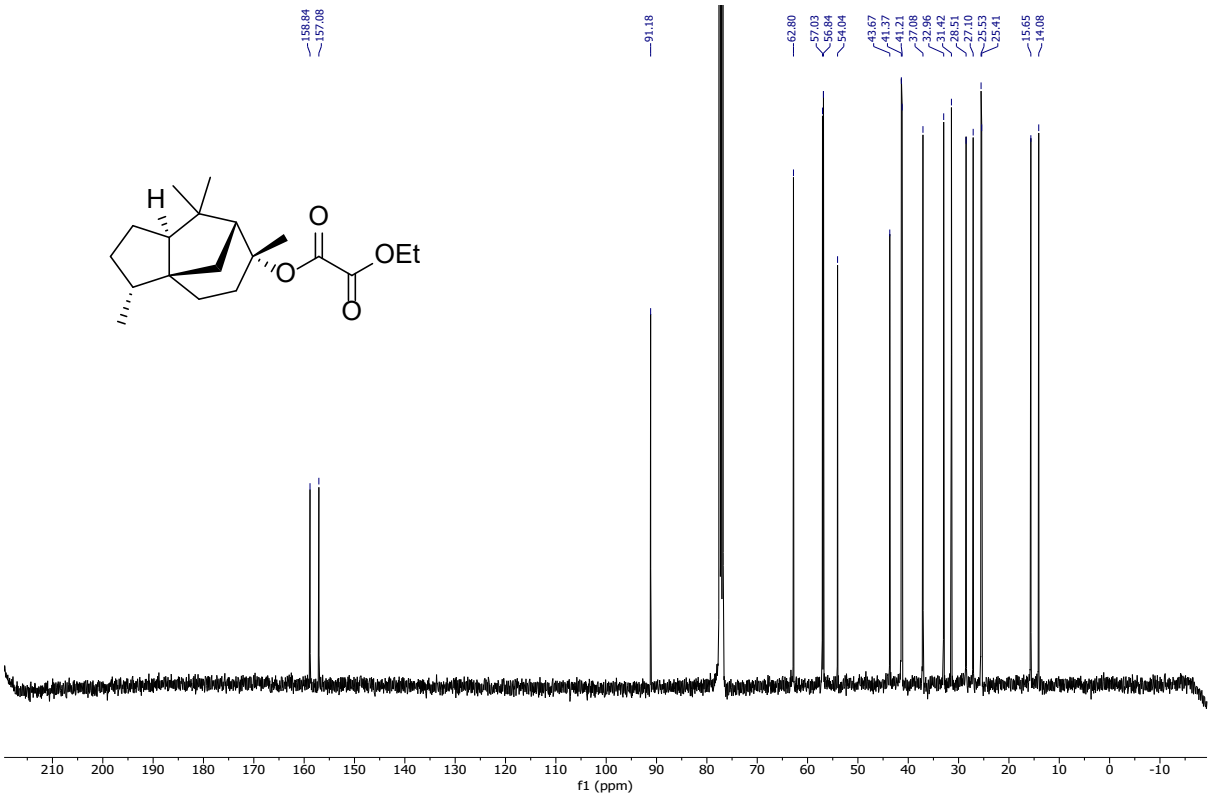


Compound **23w**

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

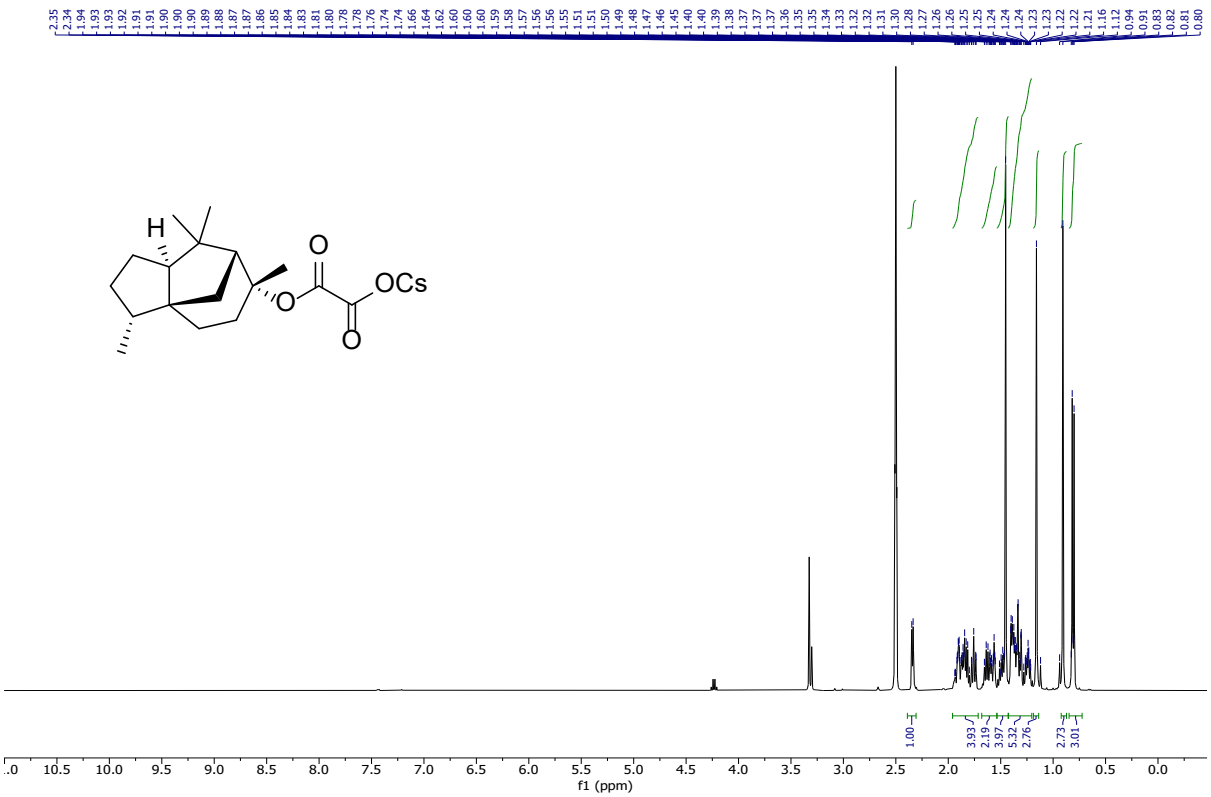


^{13}C NMR, $CDCl_3$, 101 MHz

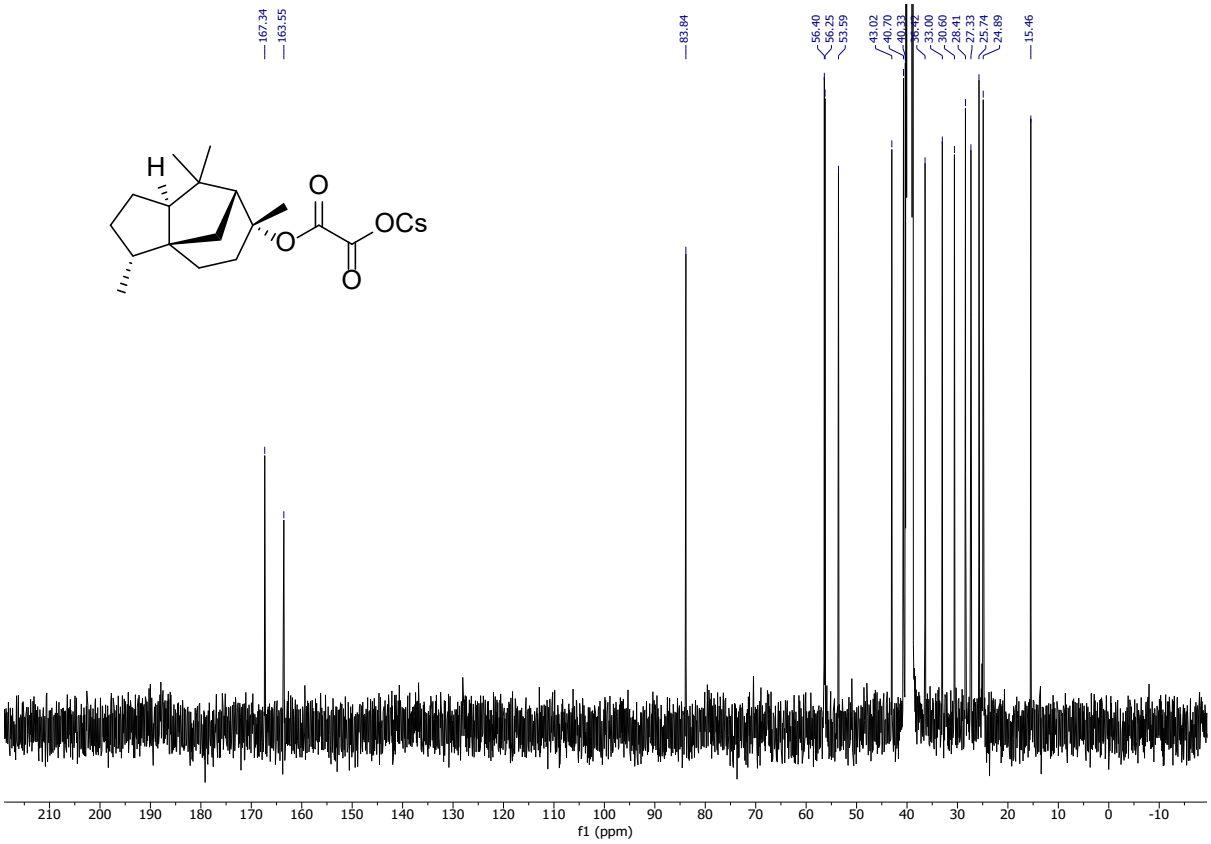


Compound **3w**

^{1}H NMR, DMSO, 400 MHz

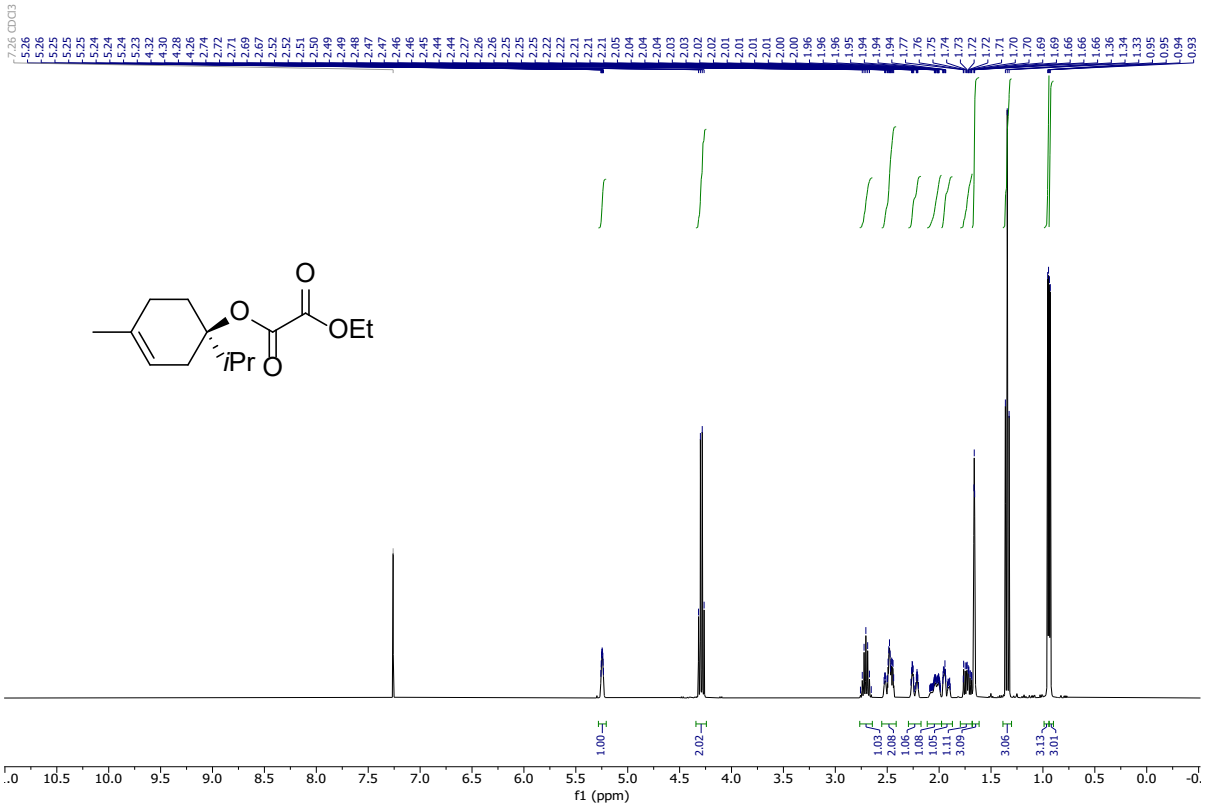


^{13}C NMR, DMSO, 101 MHz

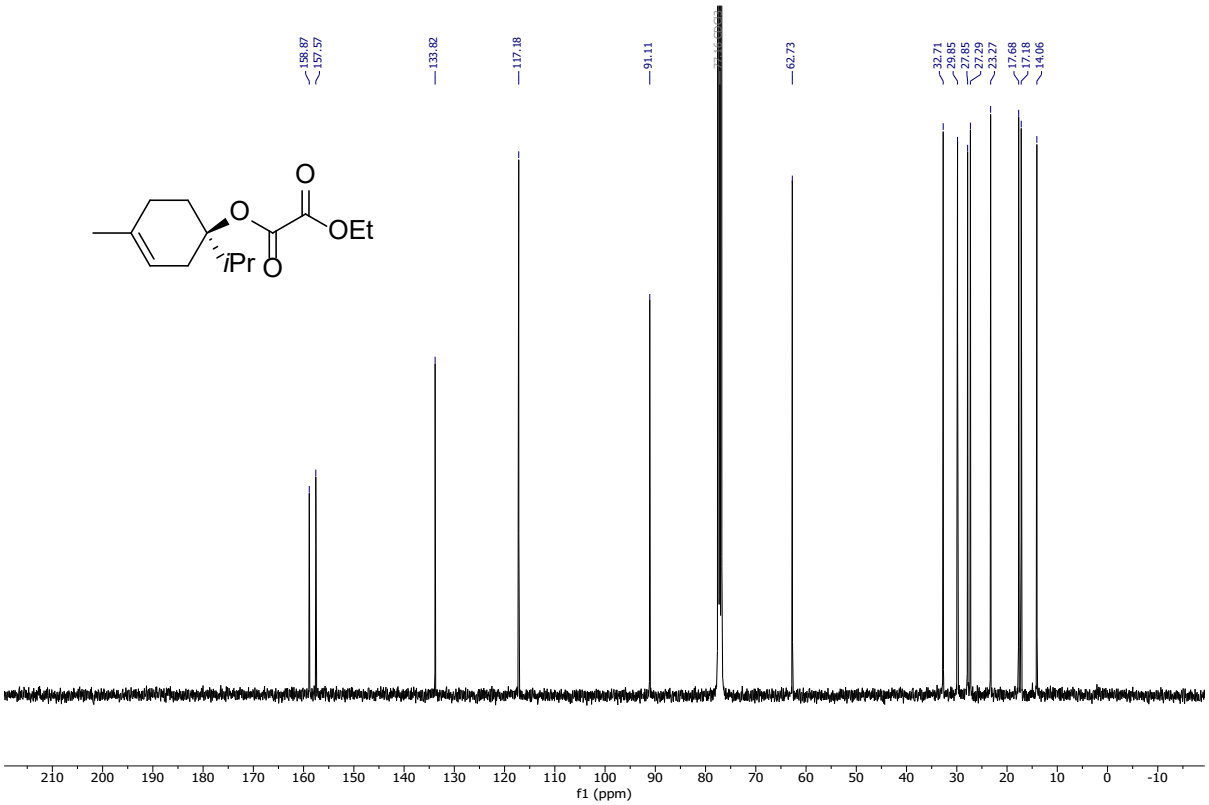


Compound **23x**

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

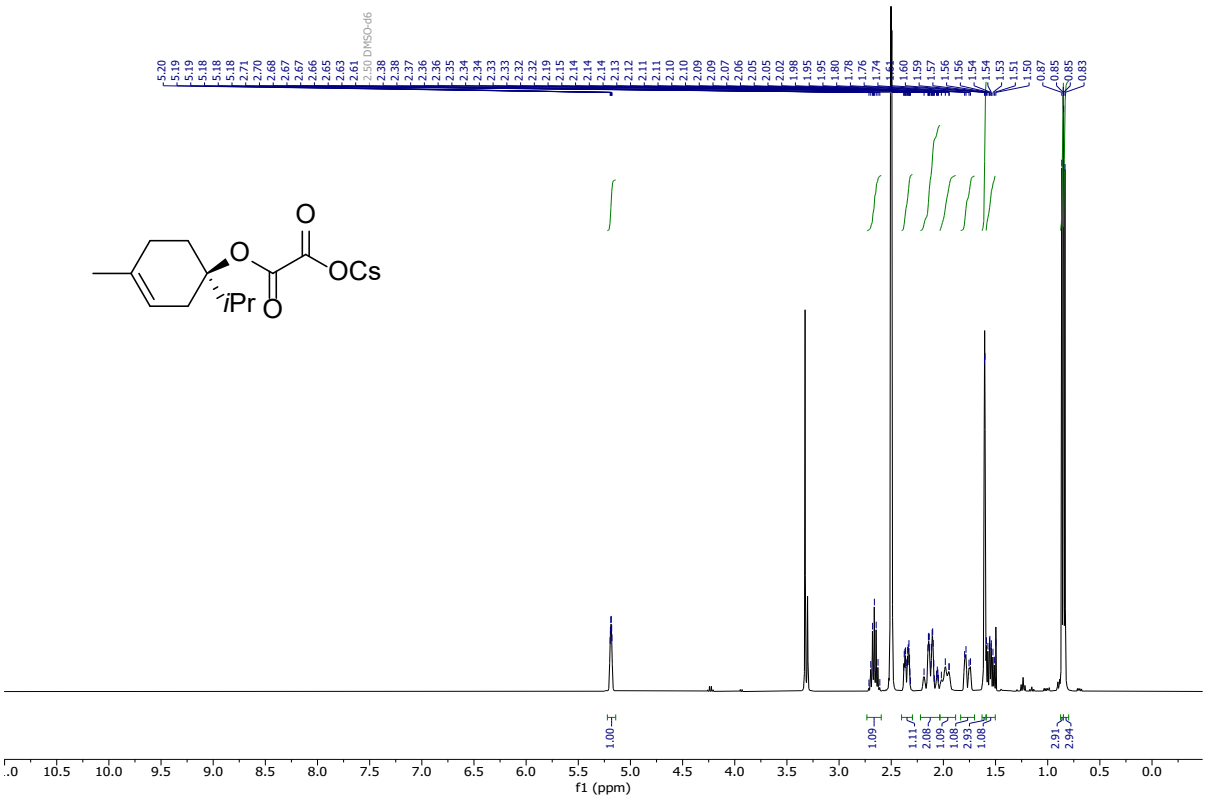


^{13}C NMR, $CDCl_3$, 101 MHz

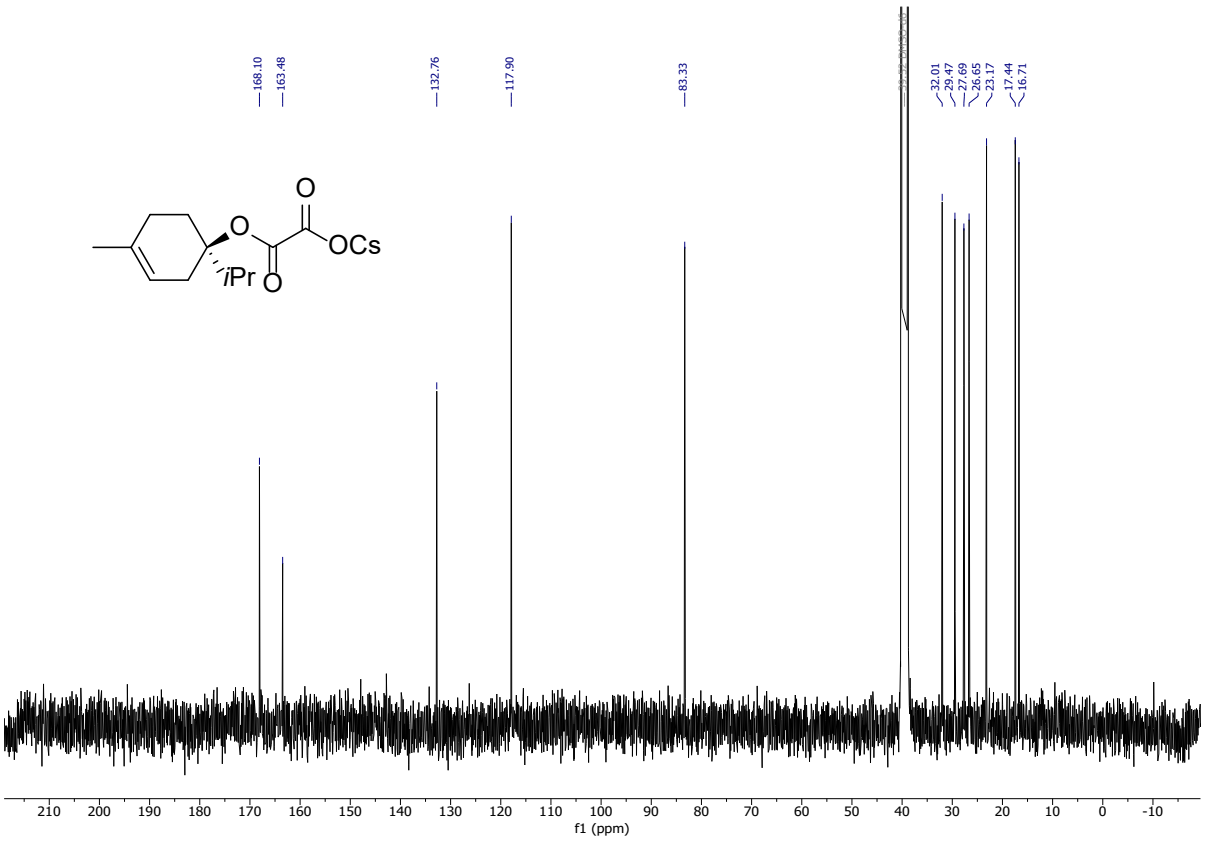


Compound **3x**

^{1}H NMR, DMSO, 400 MHz

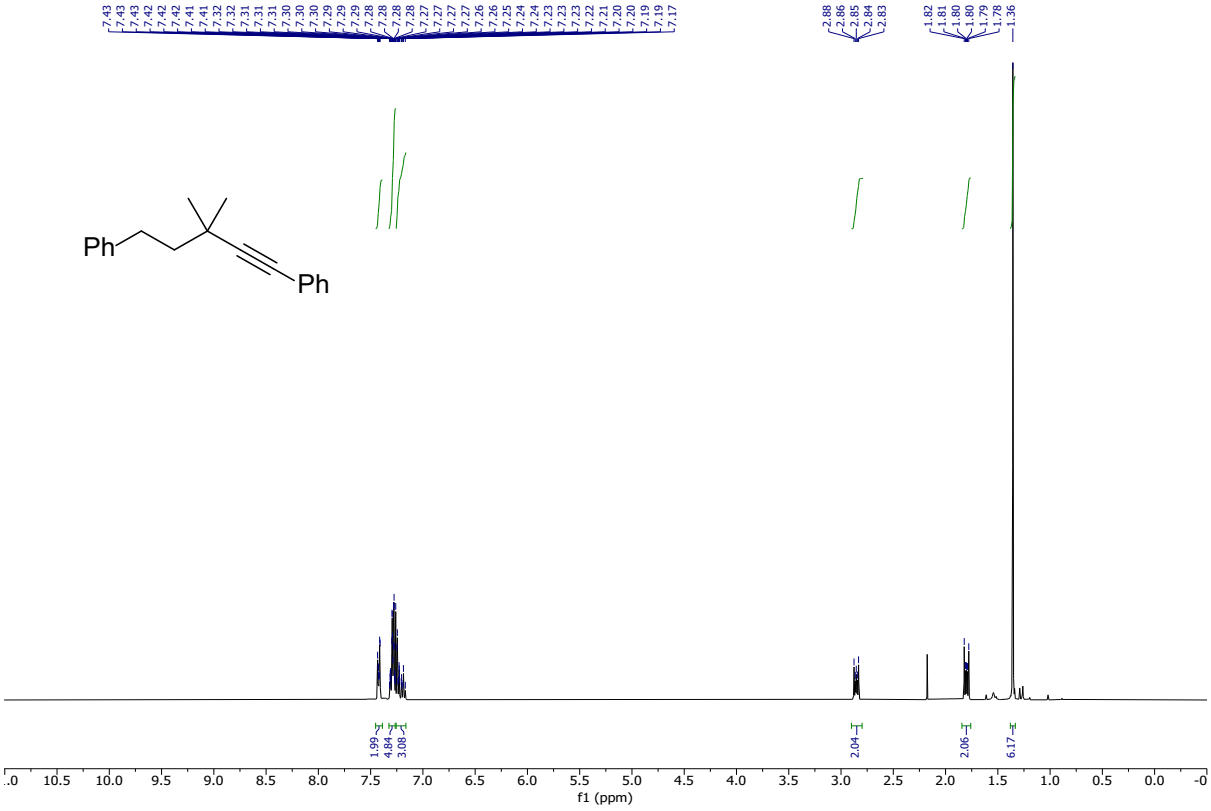


^{13}C NMR, DMSO, 101 MHz

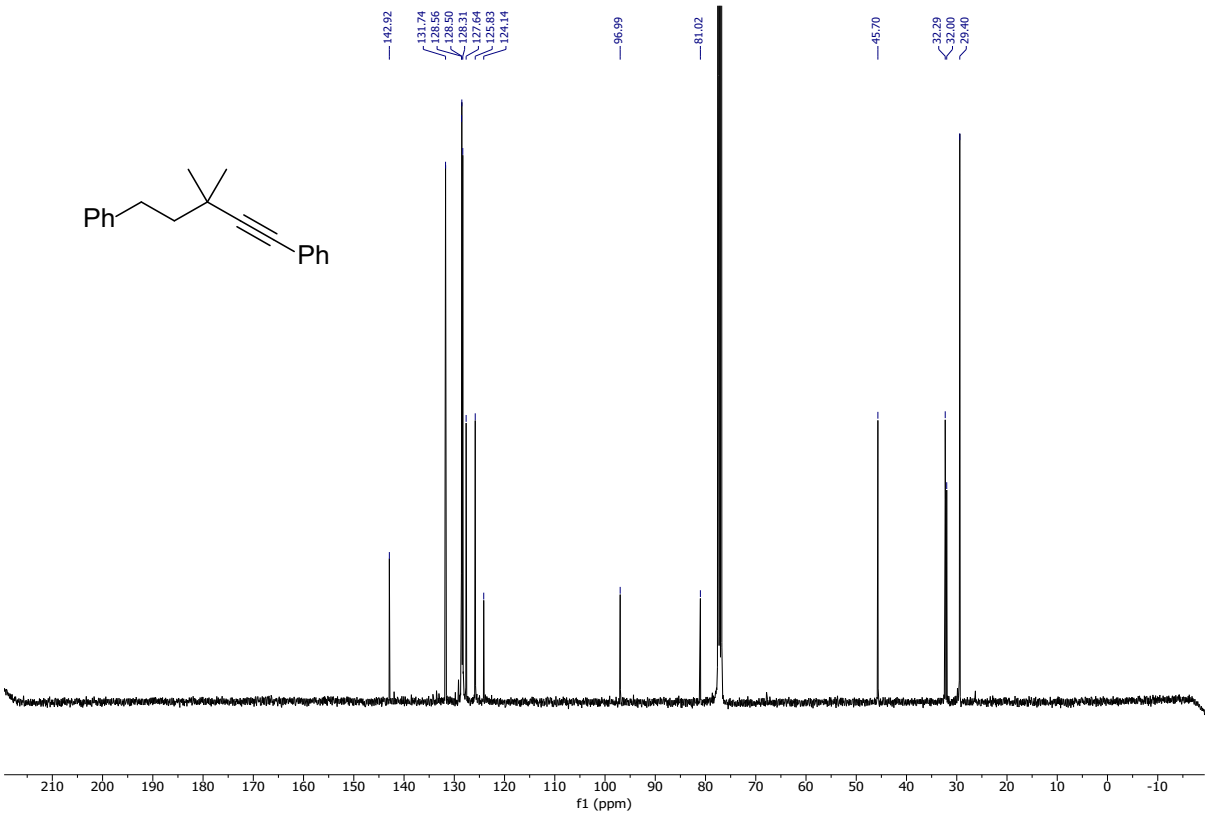


Compound **4a**

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

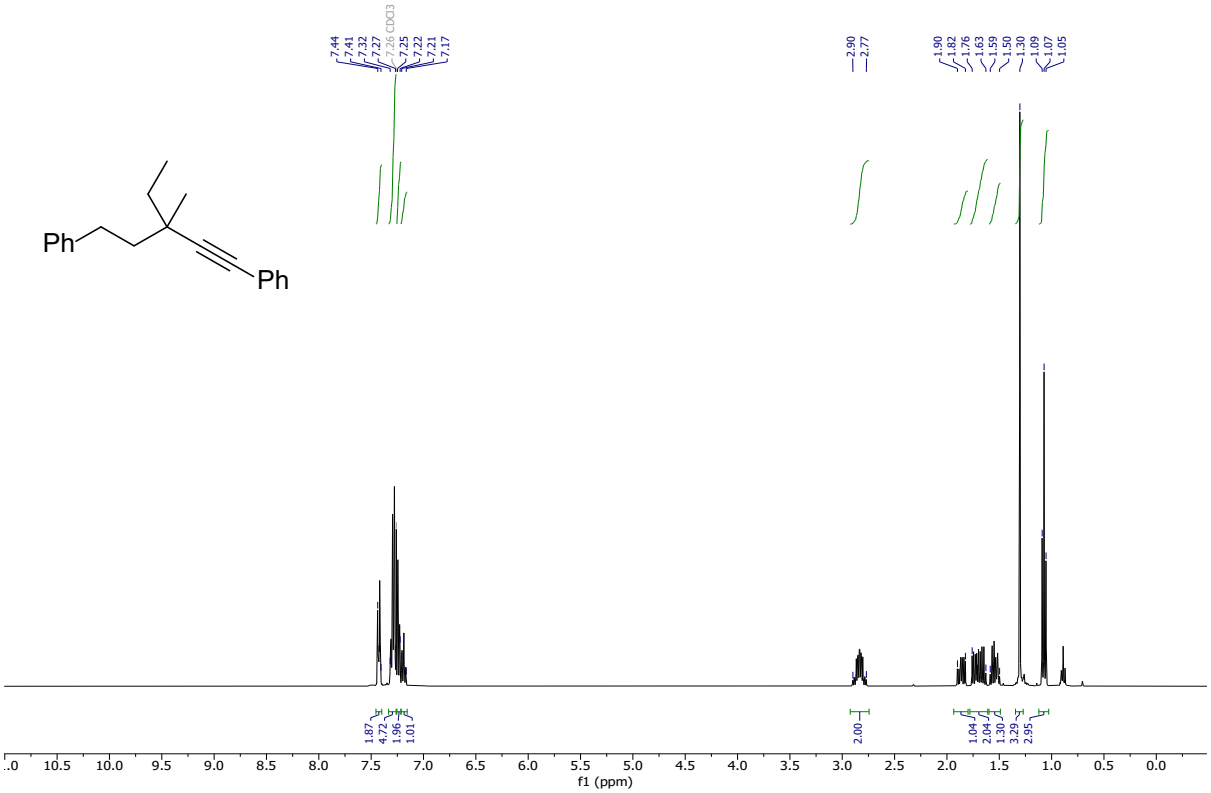


^{13}C NMR, $CDCl_3$, 101 MHz

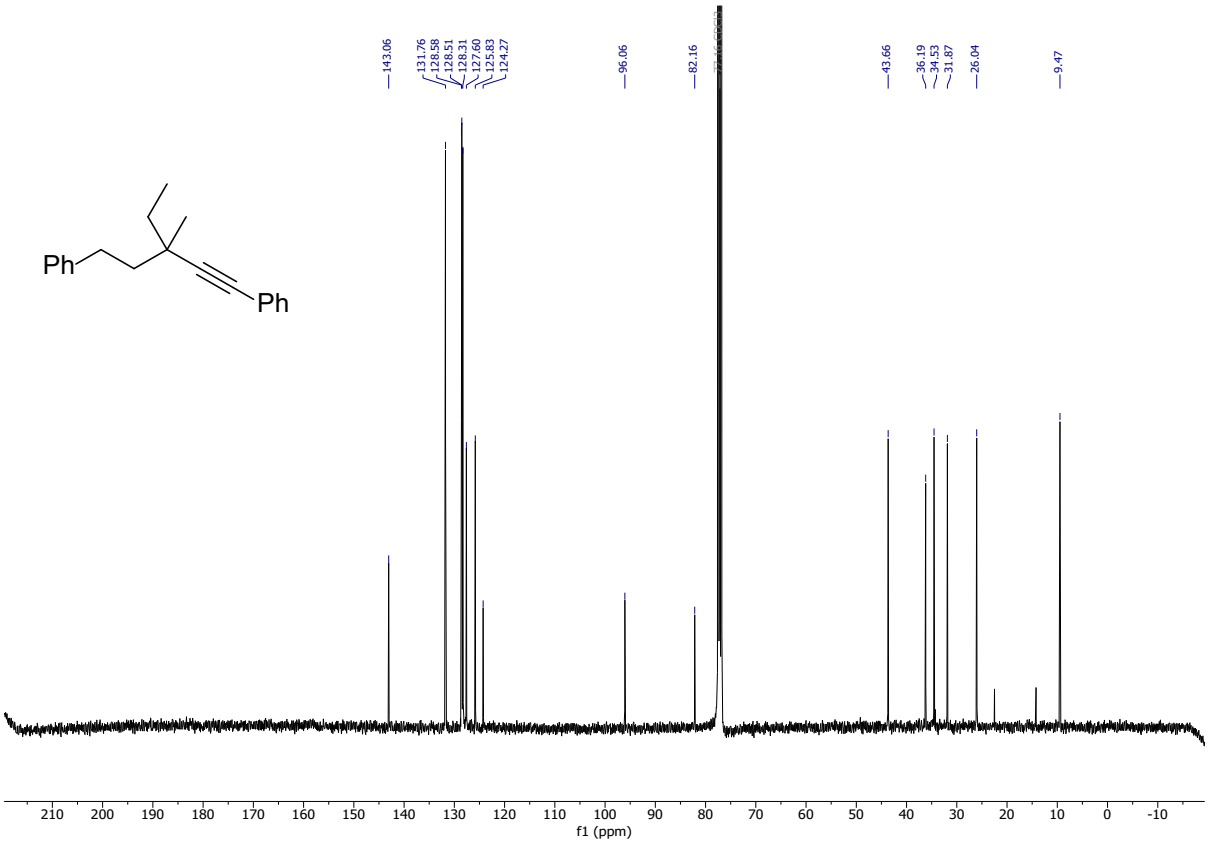


Compound **4b**

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

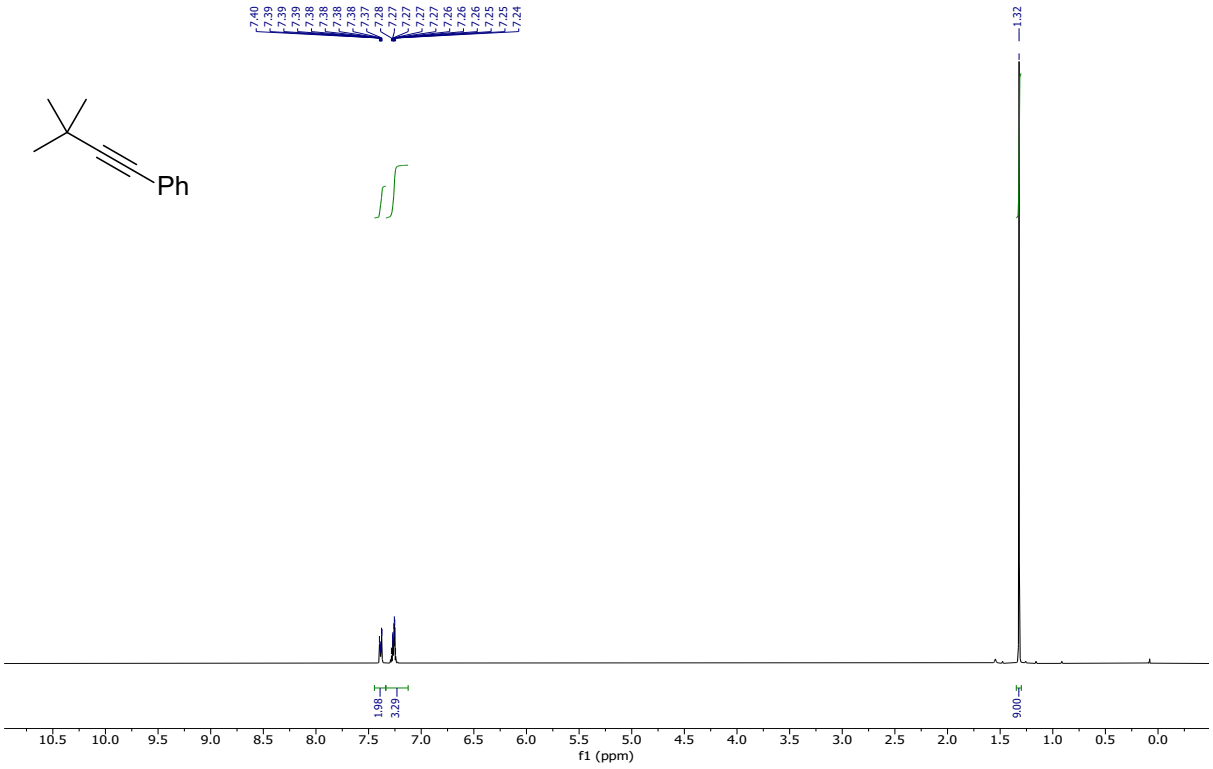


^{13}C NMR, $CDCl_3$, 101 MHz

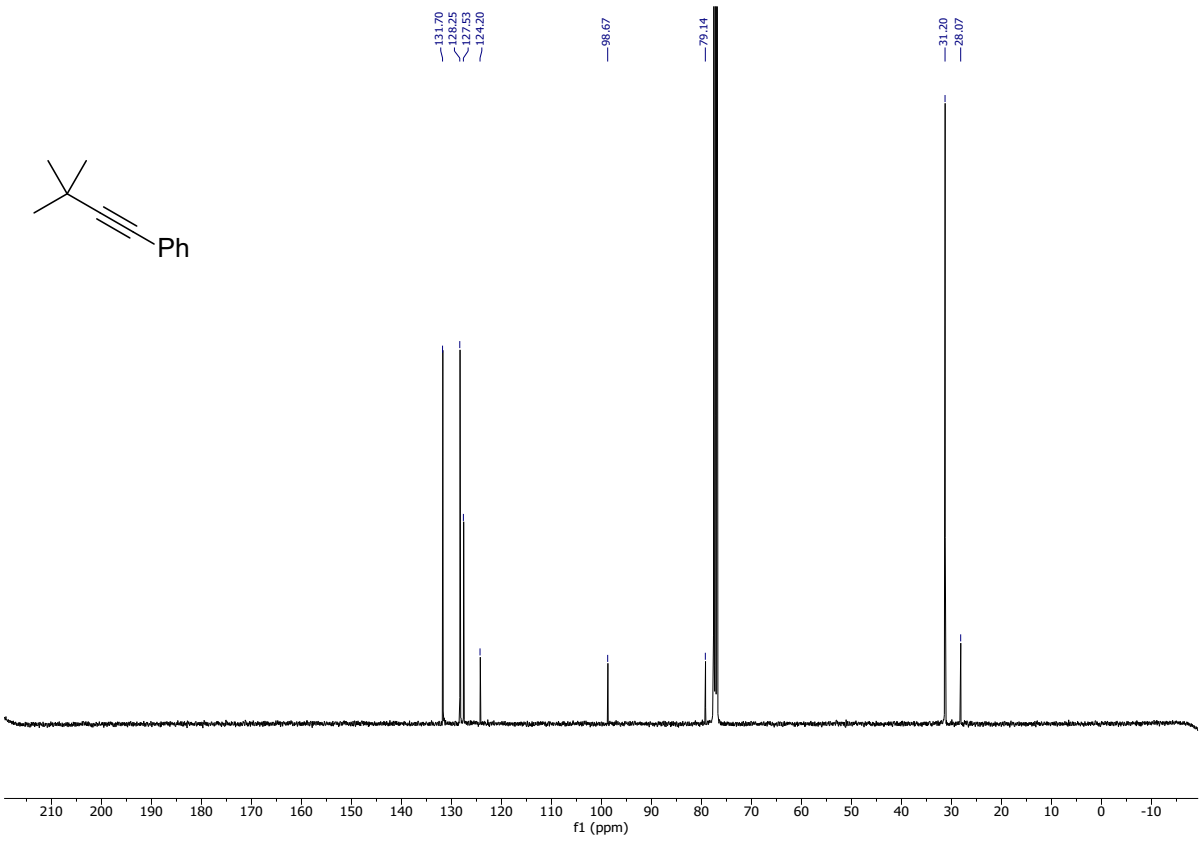


Compound **4c**

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

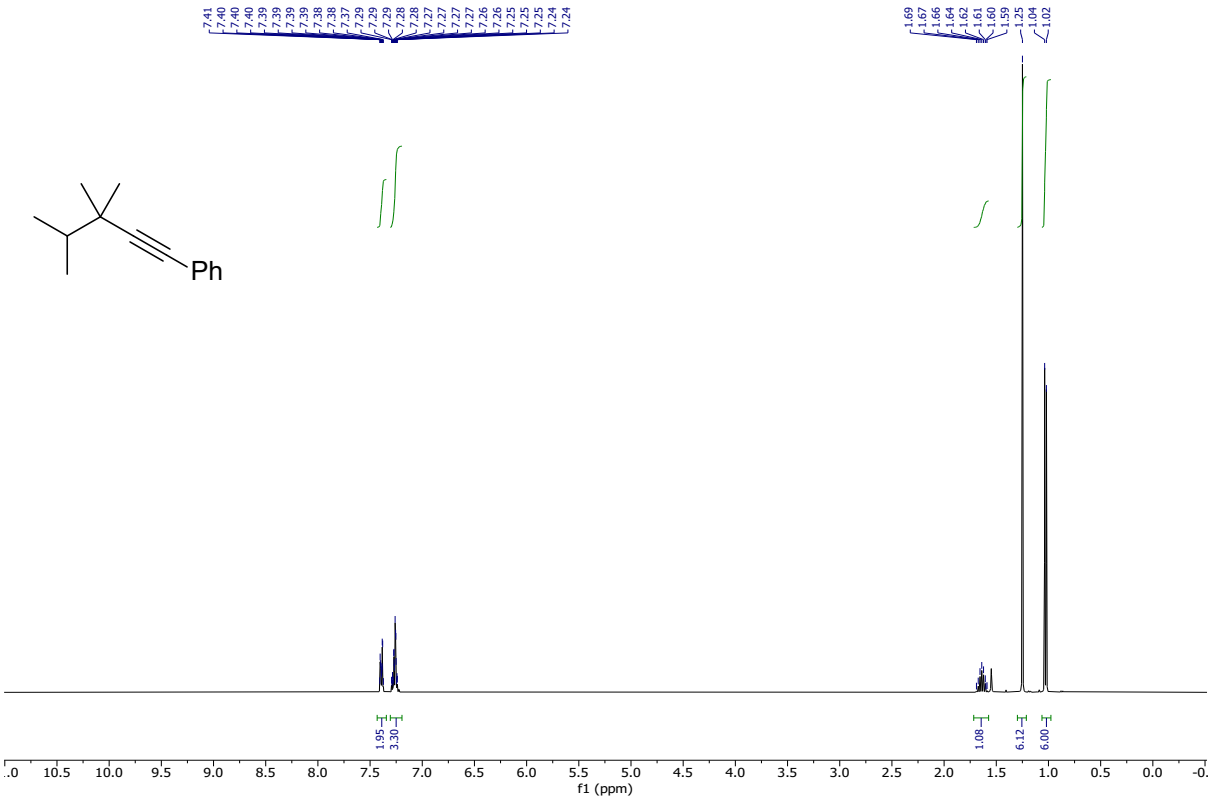


^{13}C NMR, $CDCl_3$, 101 MHz

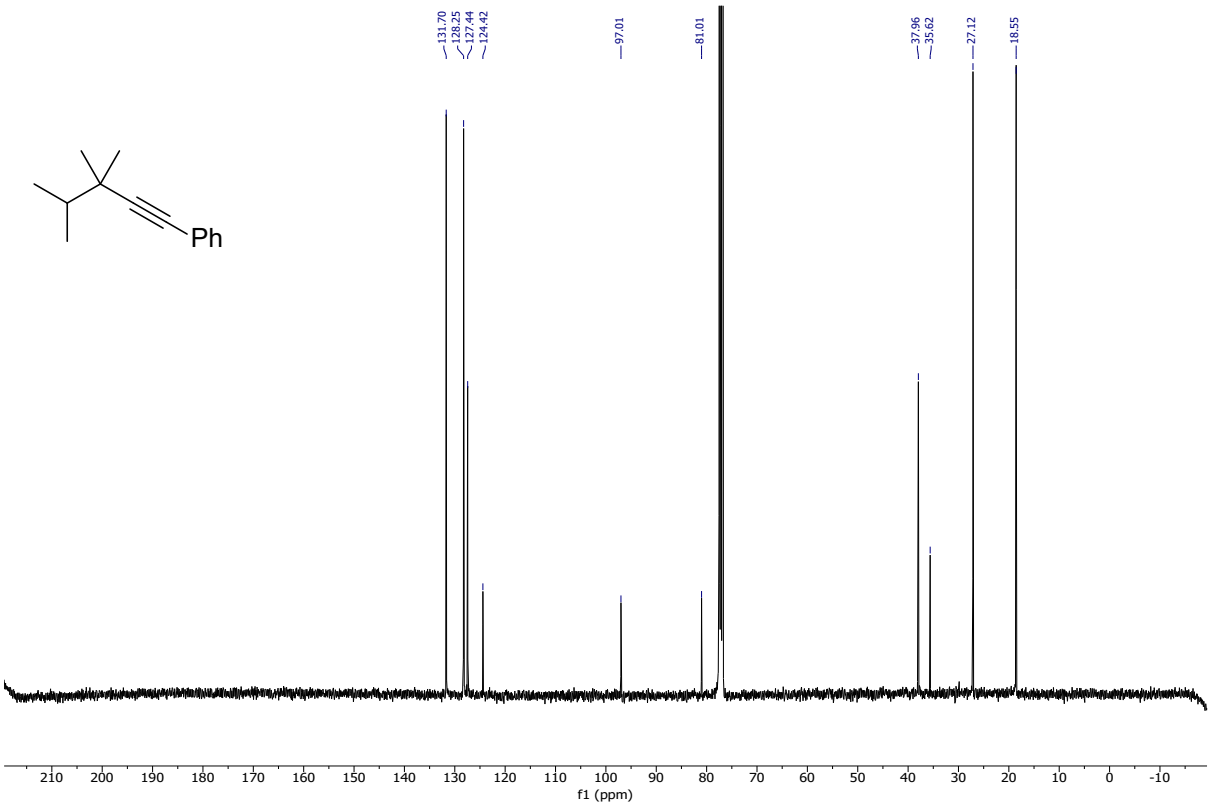


Compound **4d**

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

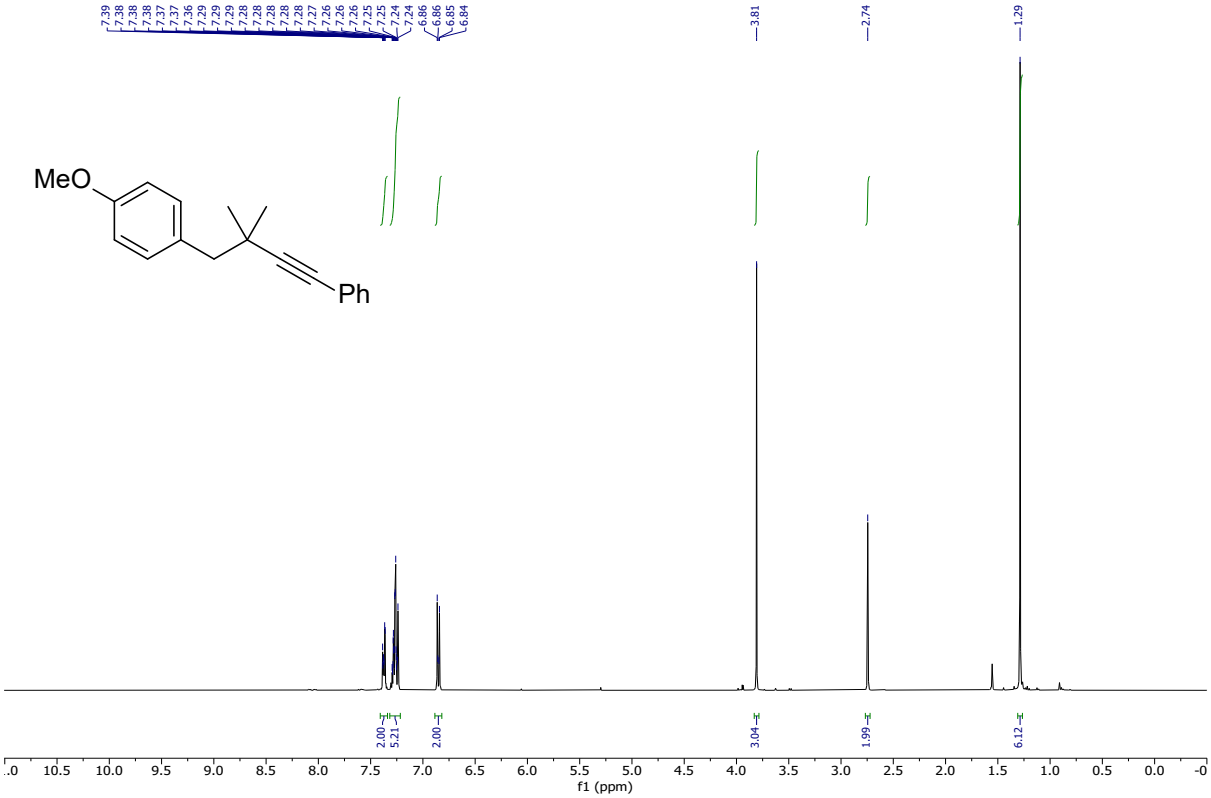


^{13}C NMR, $CDCl_3$, 101 MHz

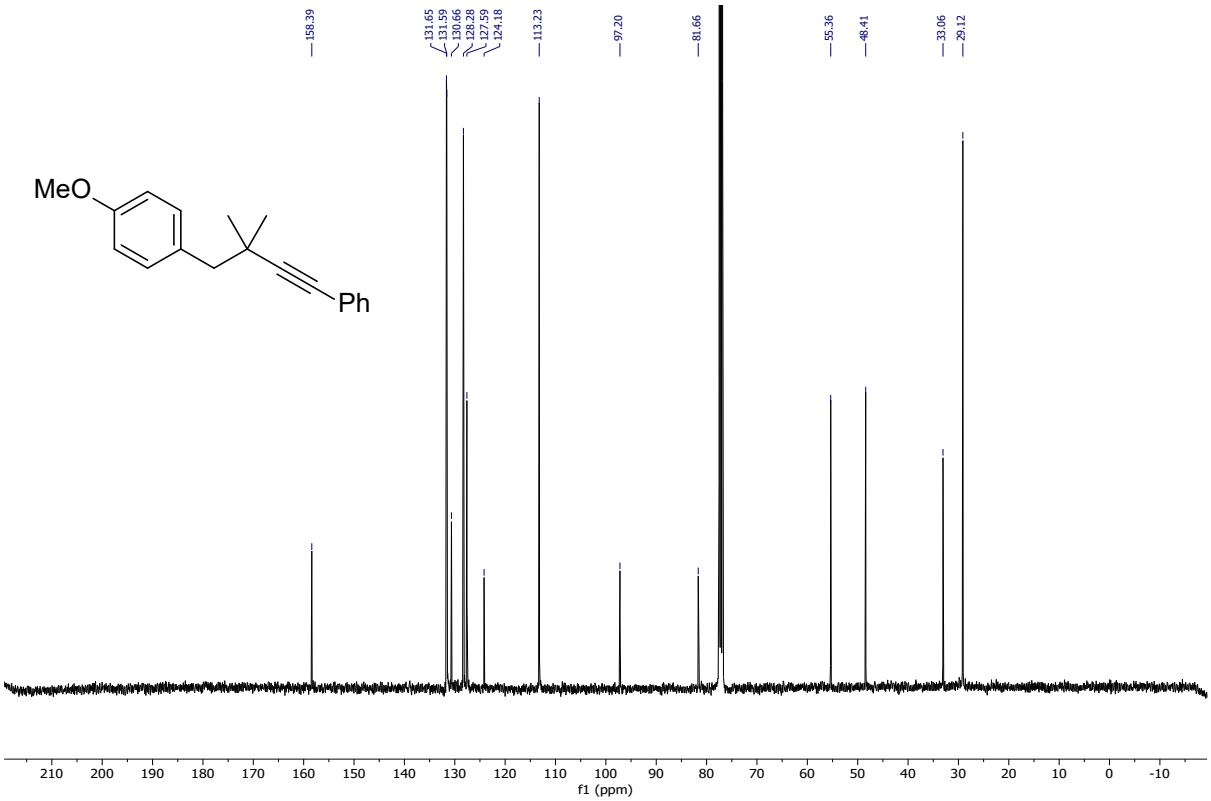


Compound **4e**

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

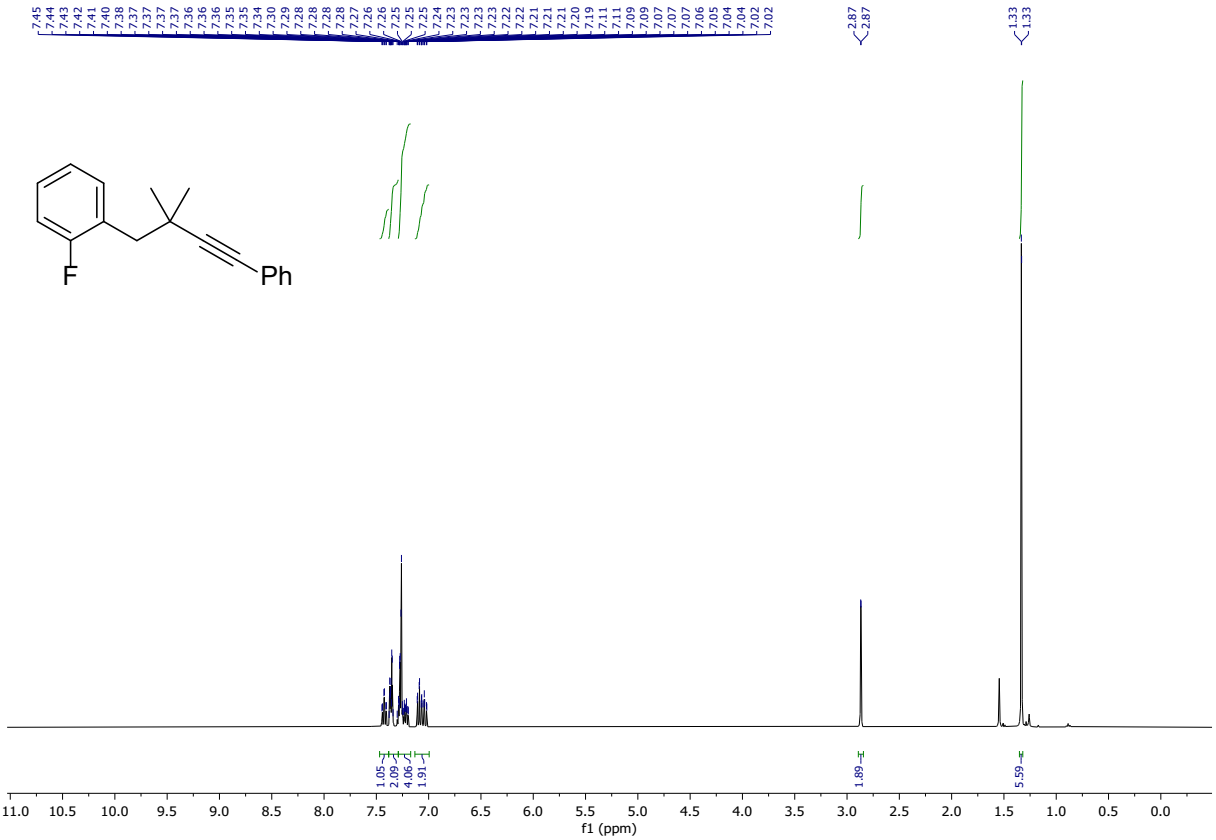


^{13}C NMR, $CDCl_3$, 101 MHz

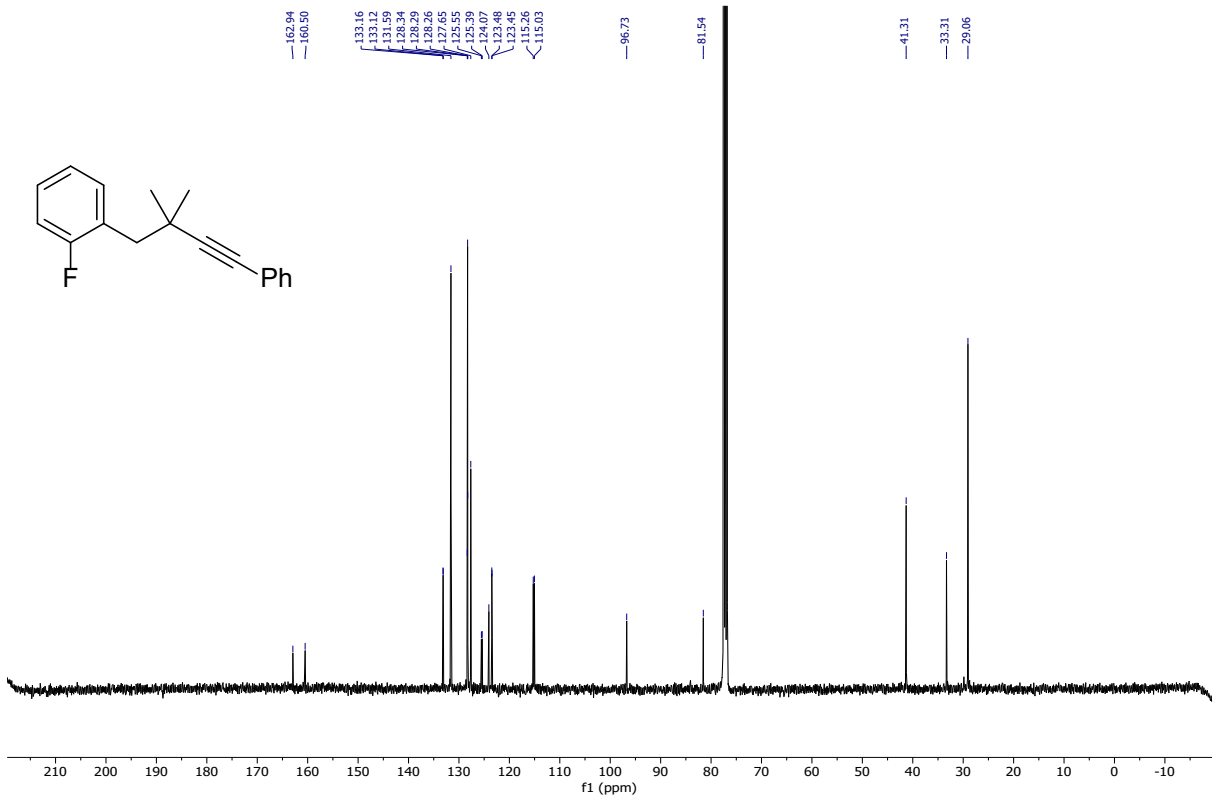


Compound **4f**

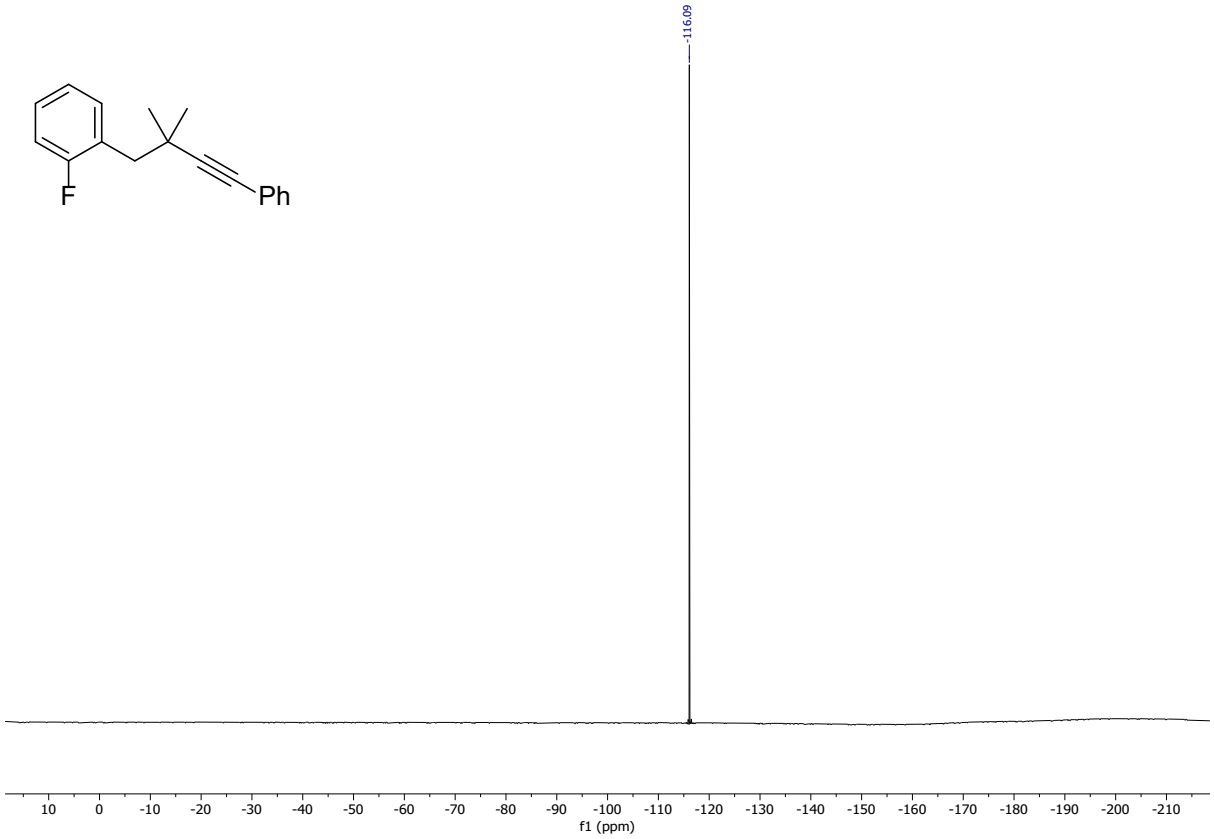
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

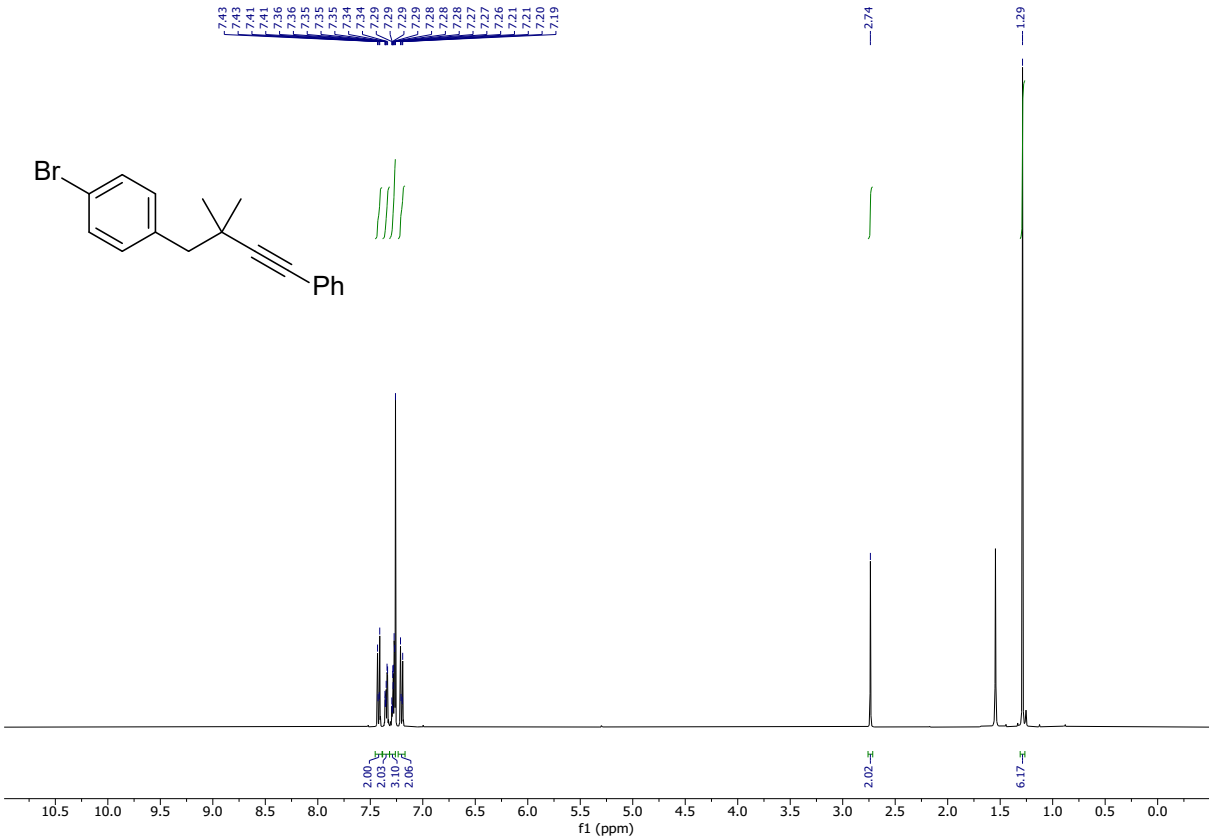


^{19}F NMR, $CDCl_3$, 376 MHz

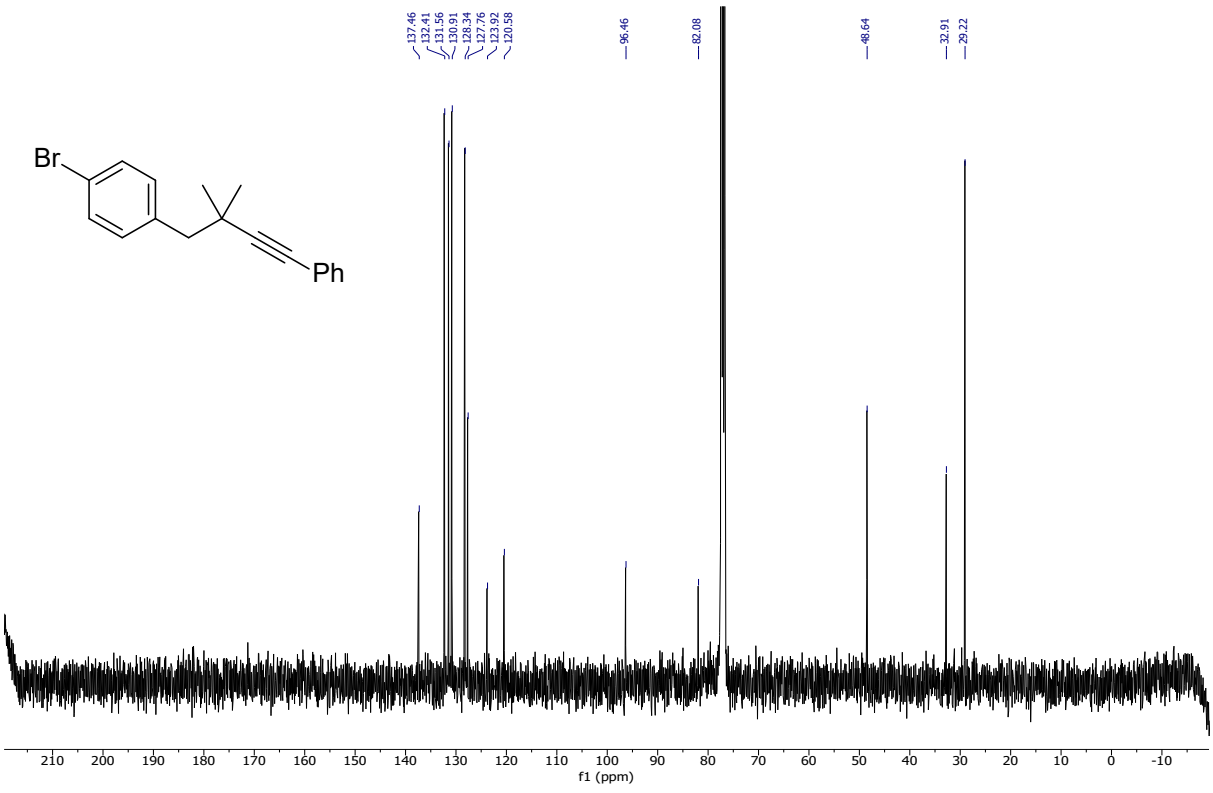


Compound **4g**

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

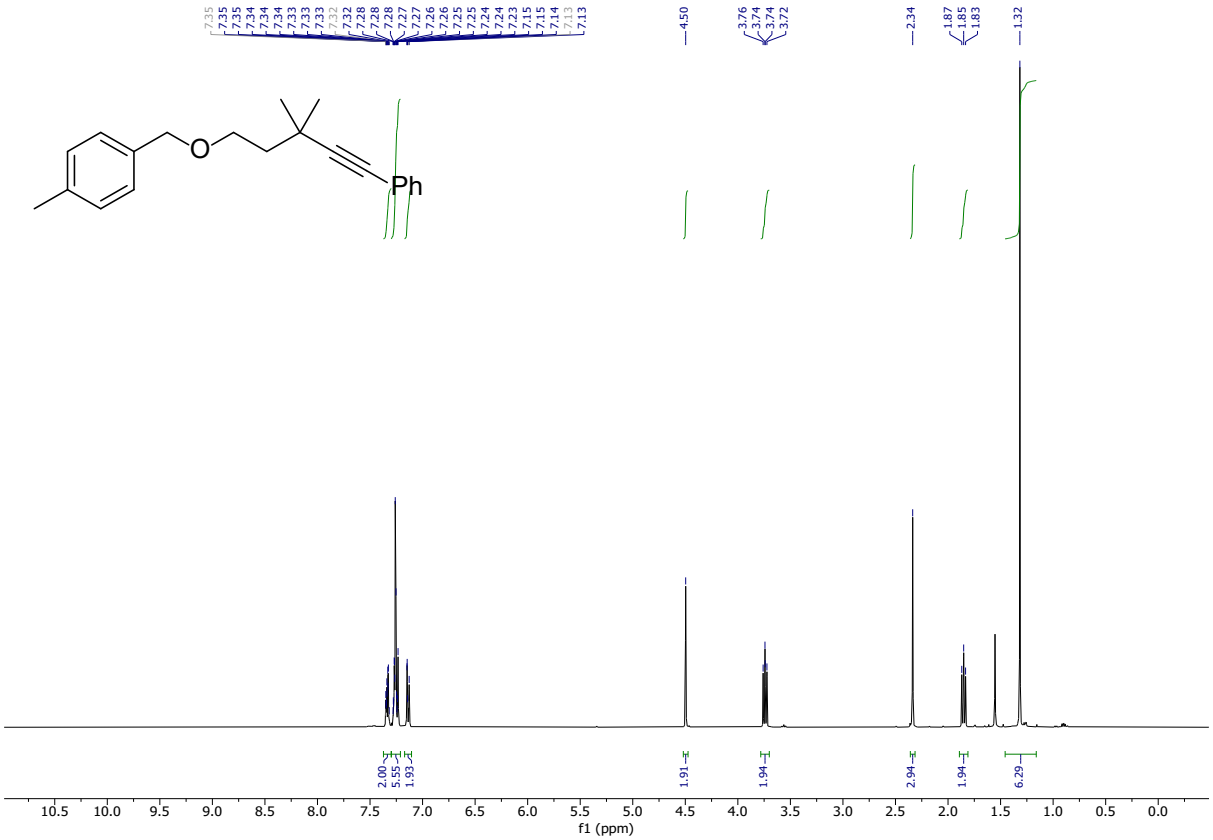


^{13}C NMR, $CDCl_3$, 101 MHz

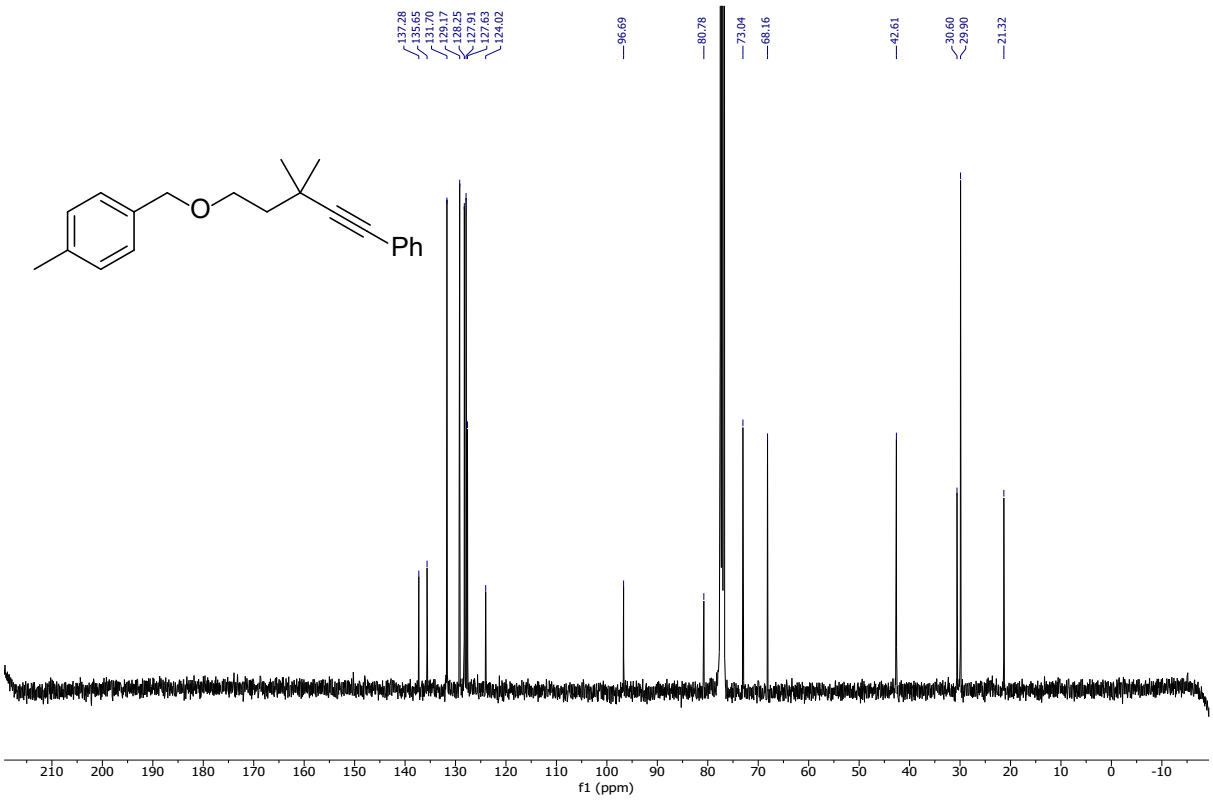


Compound **4h**

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

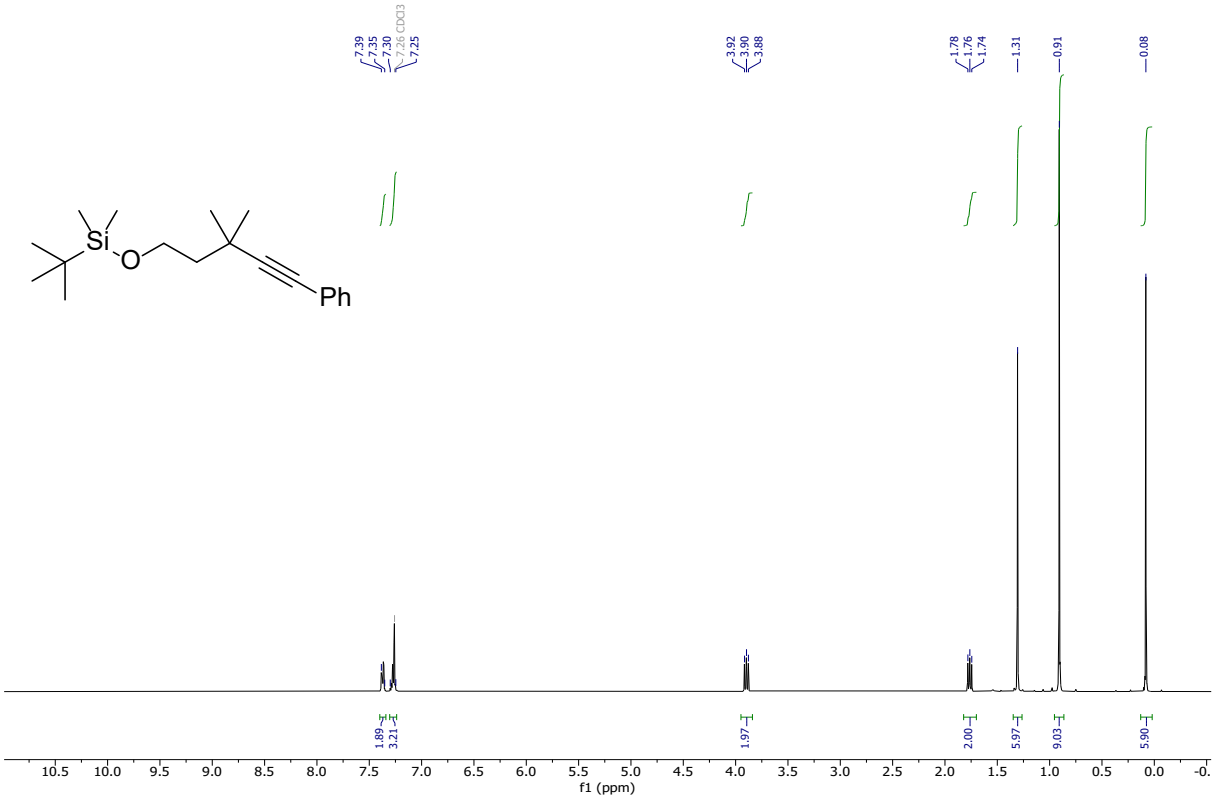


^{13}C NMR, $CDCl_3$, 101 MHz

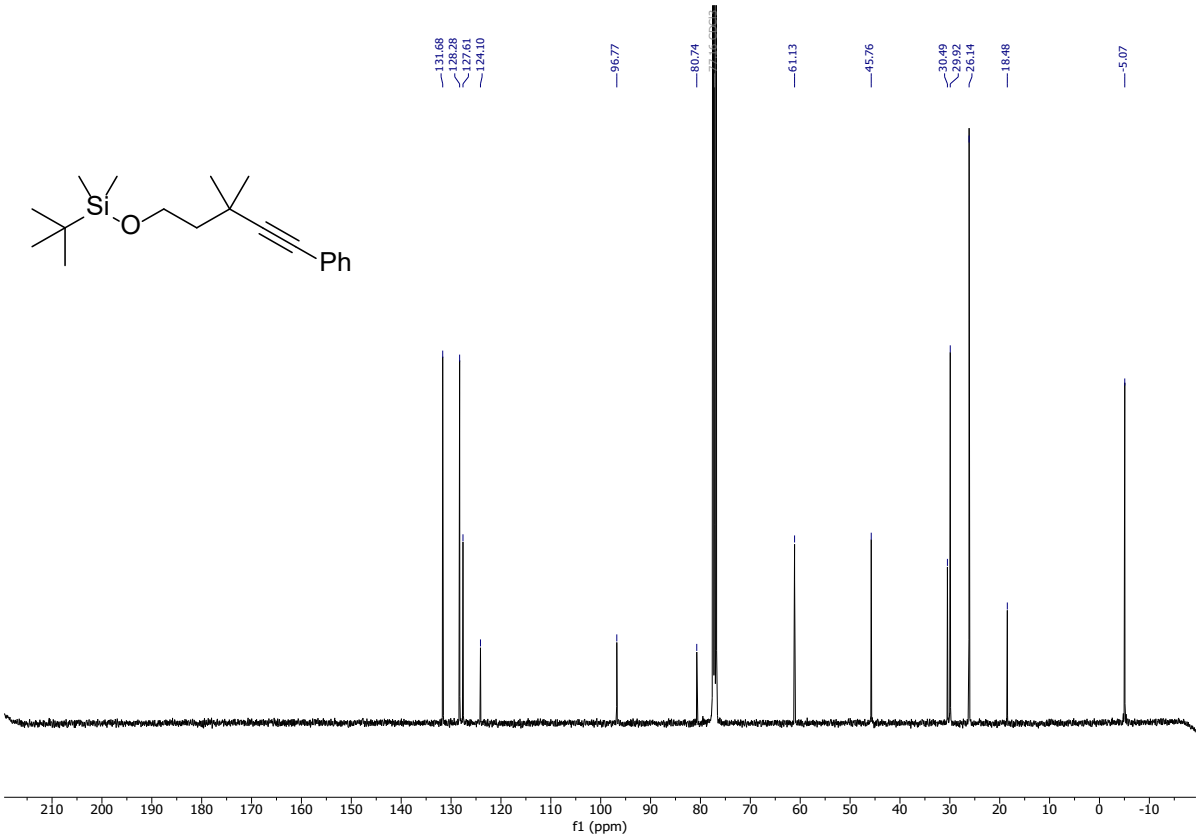


Compound **4i**

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

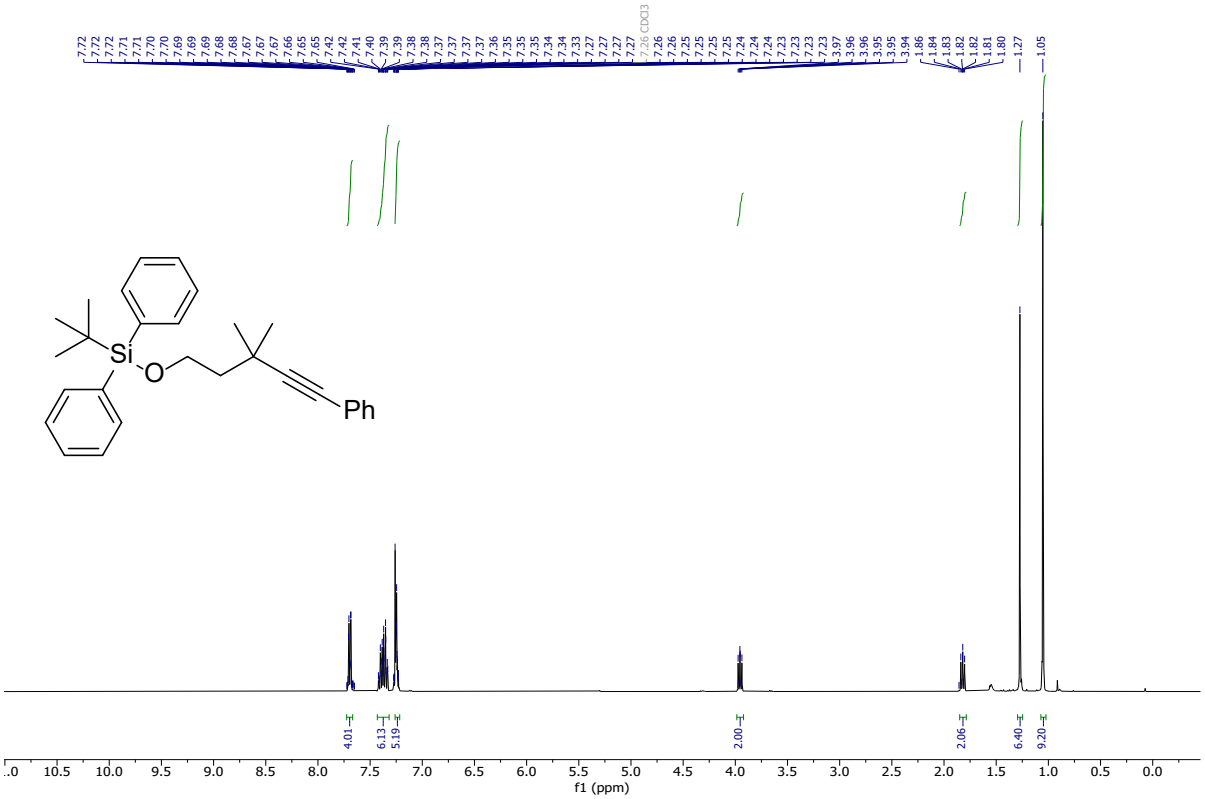


^{13}C NMR, $CDCl_3$, 101 MHz

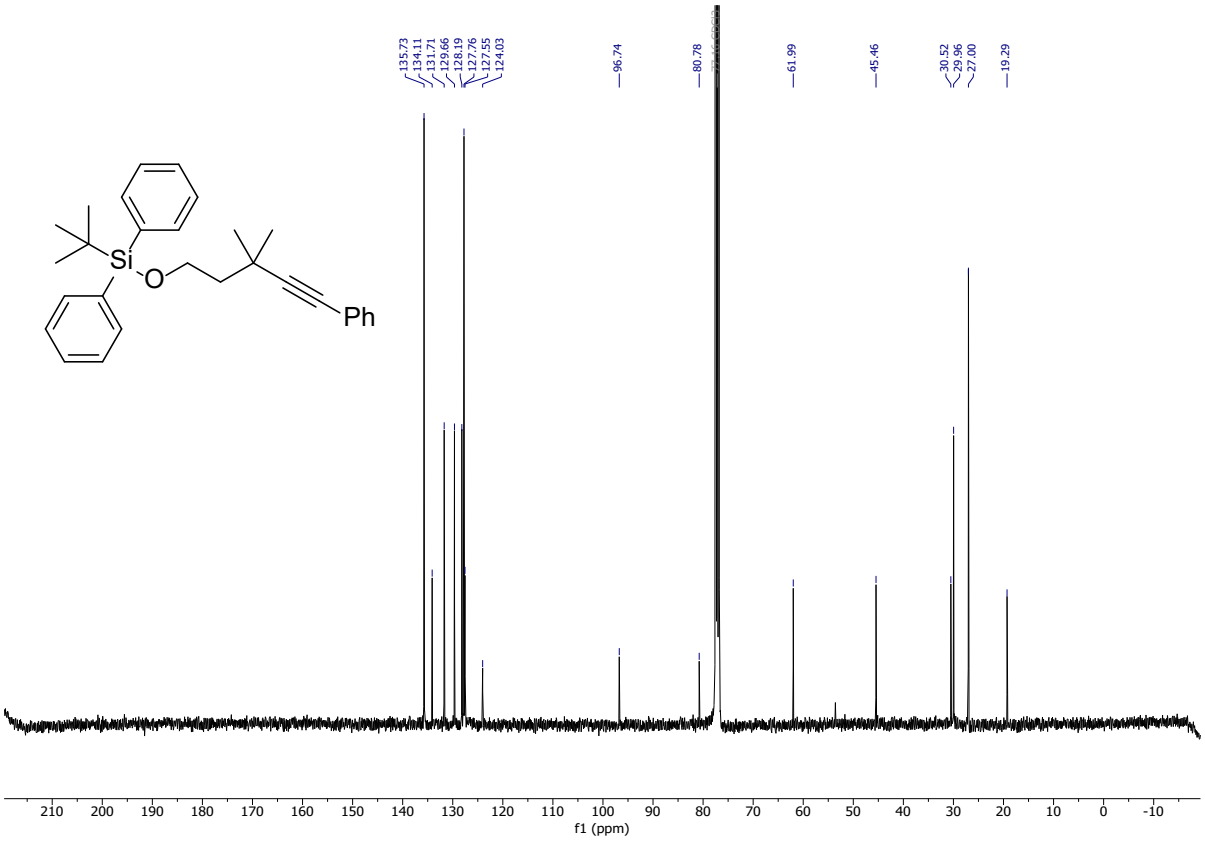


Compound **4j**

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

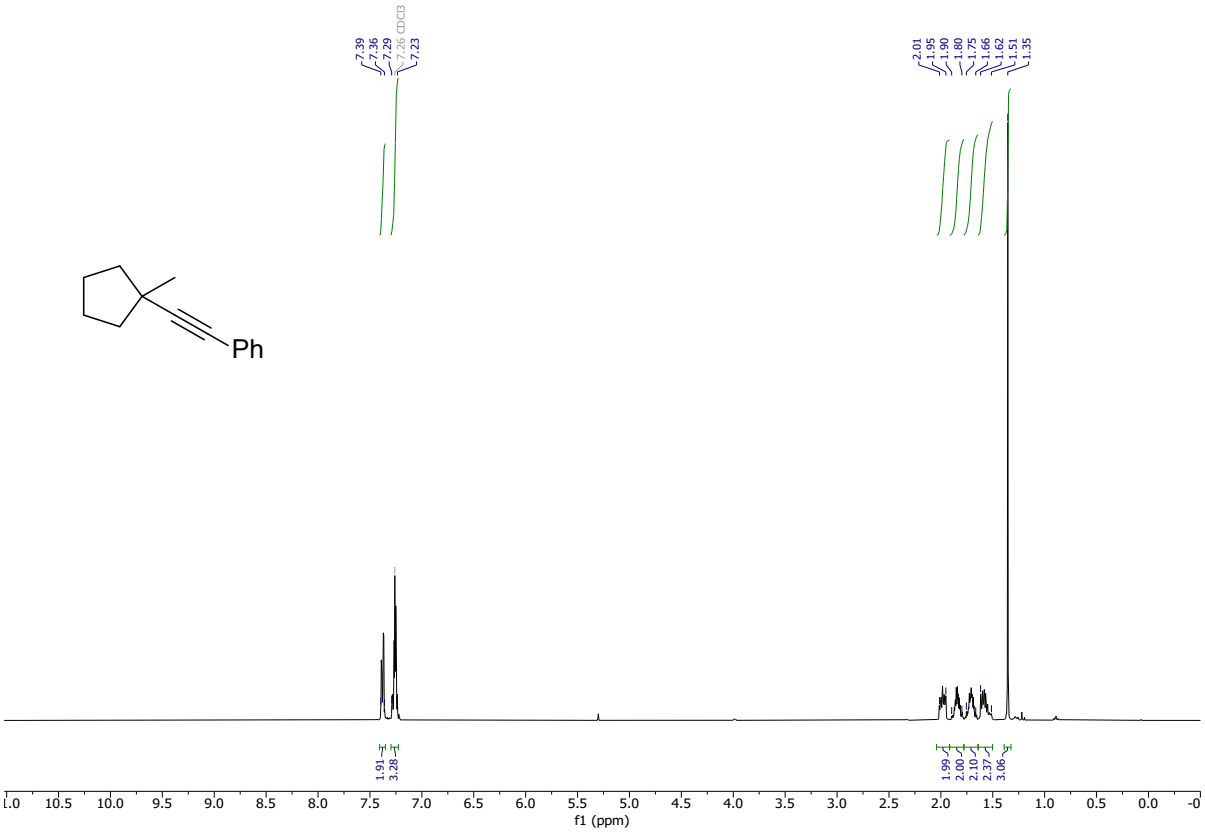


^{13}C NMR, $CDCl_3$, 101 MHz

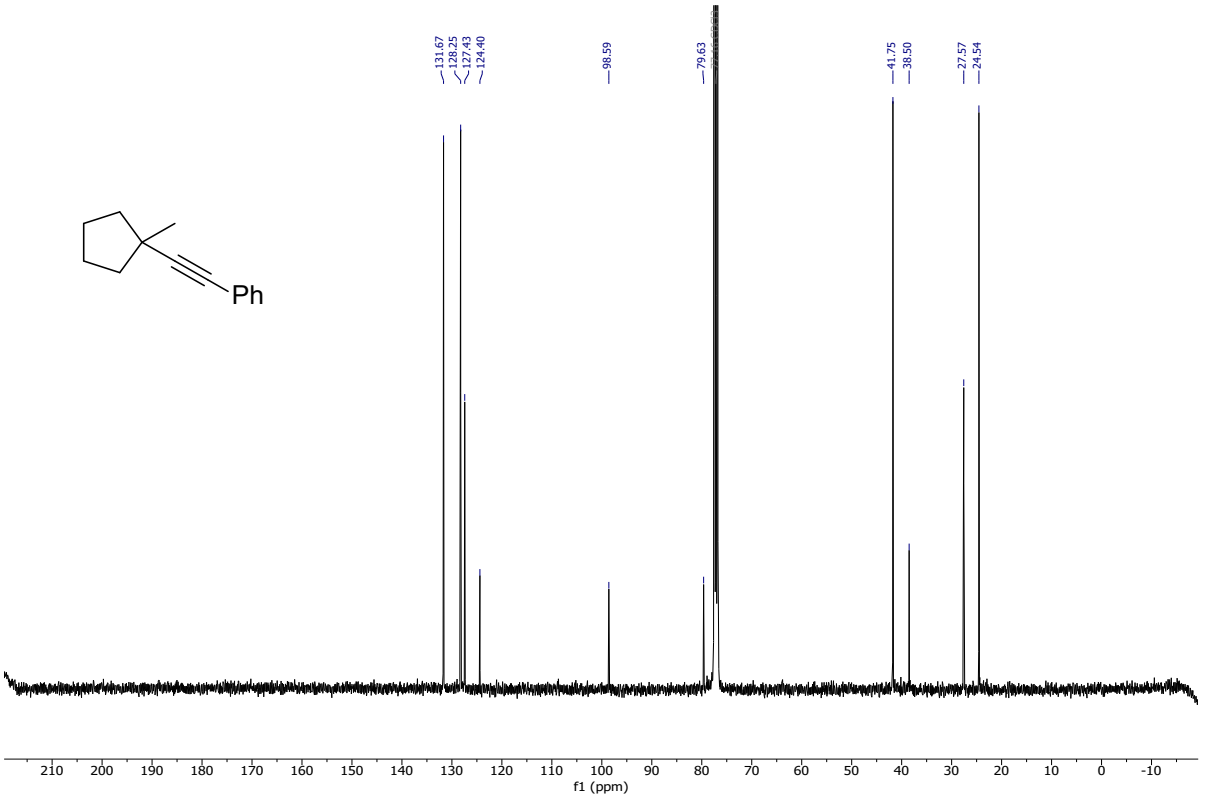


Compound **4k**

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

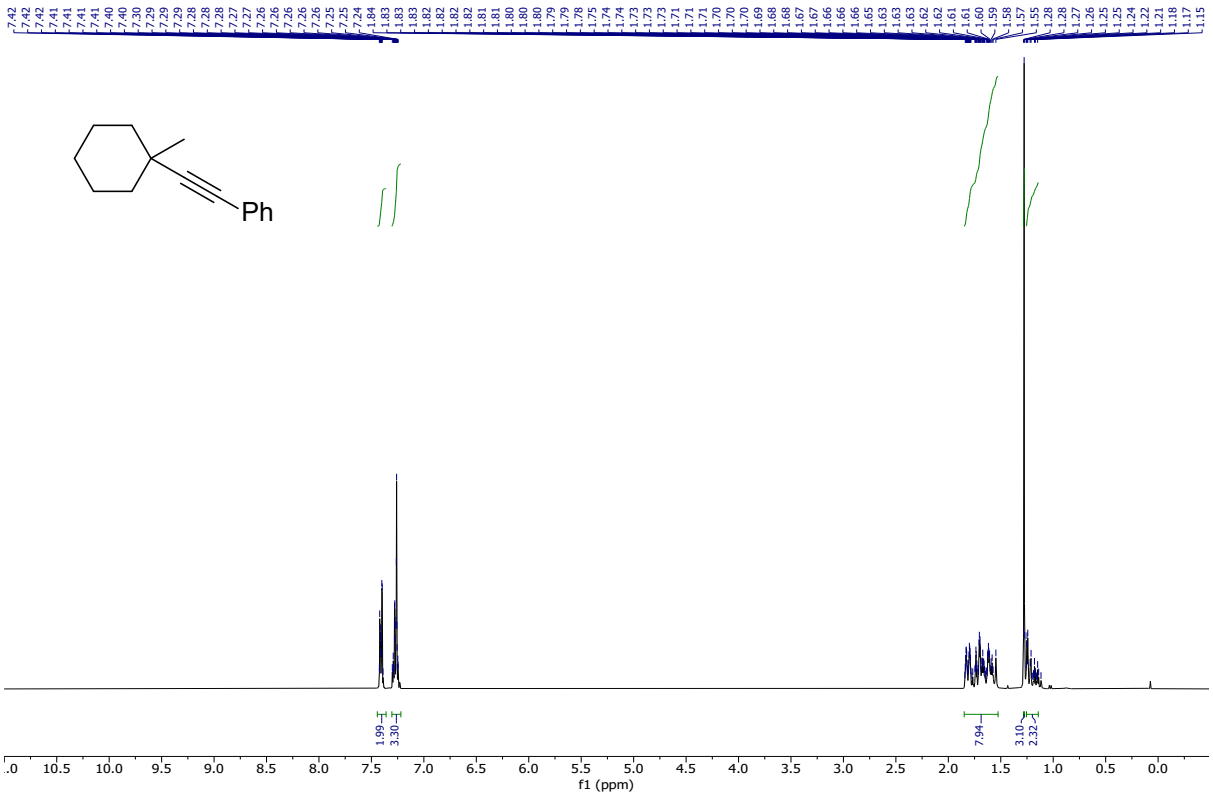


^{13}C NMR, $CDCl_3$, 101 MHz

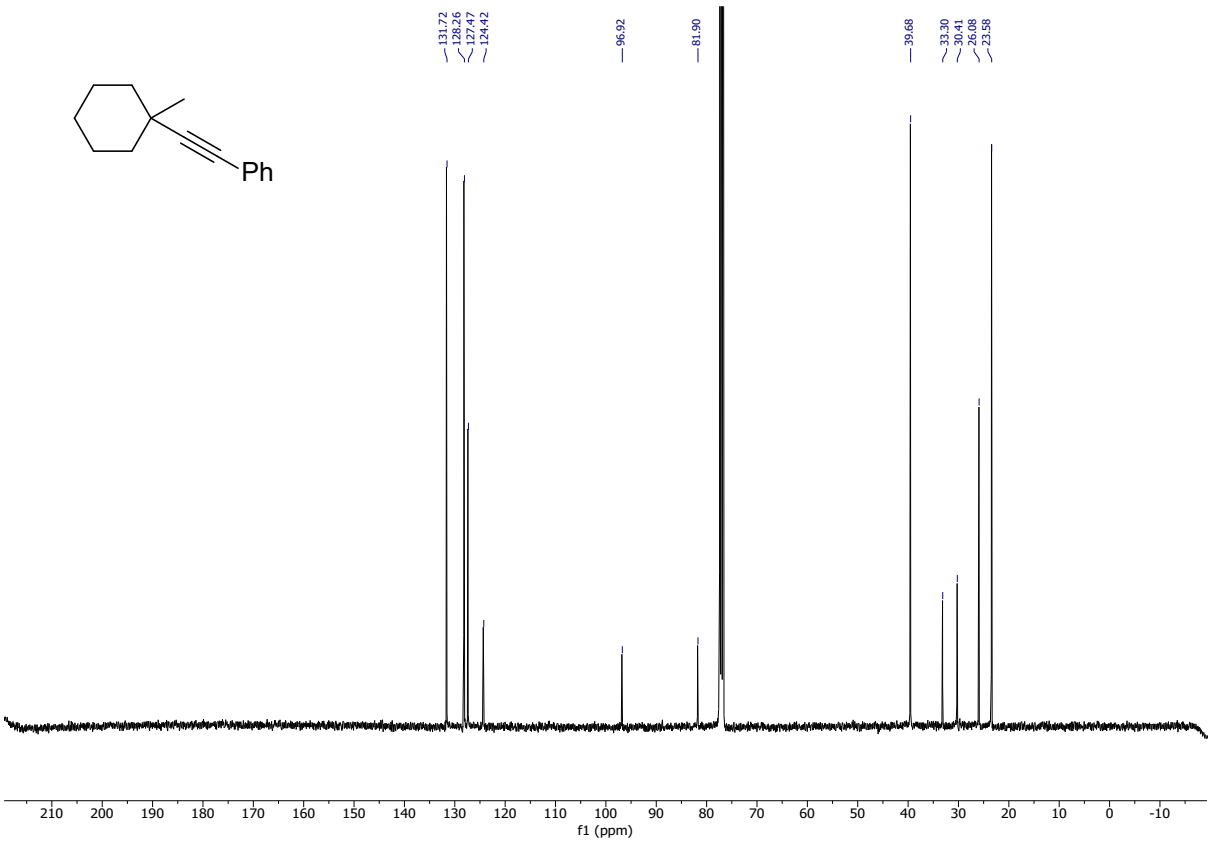


Compound **4l**

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

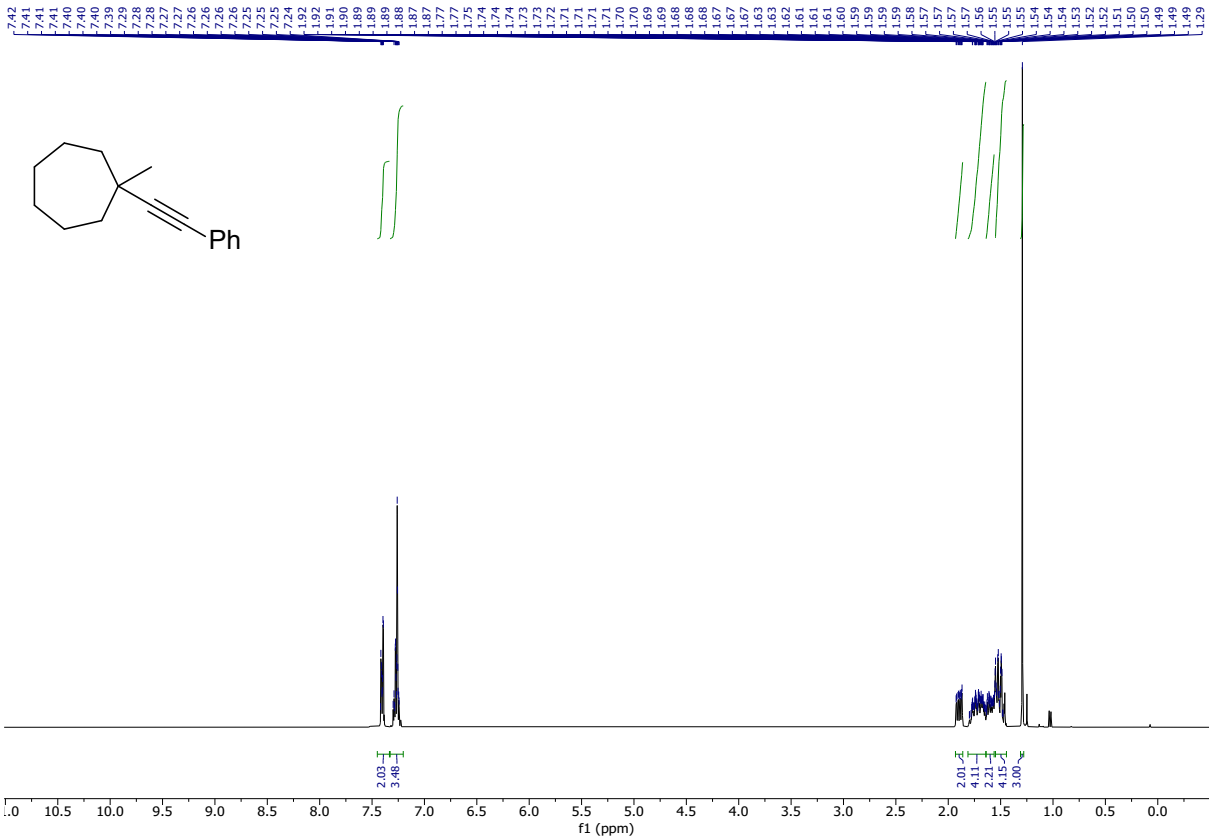


^{13}C NMR, $CDCl_3$, 400 MHz

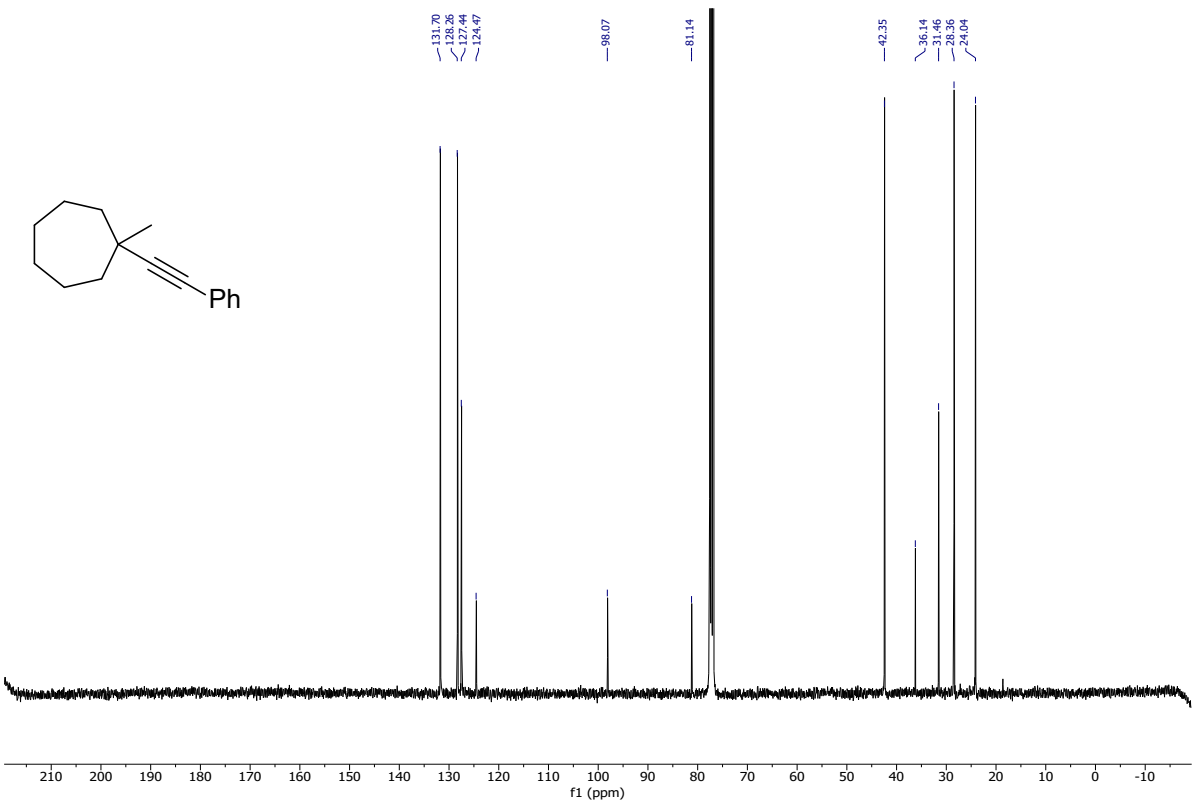


Compound **4m**

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

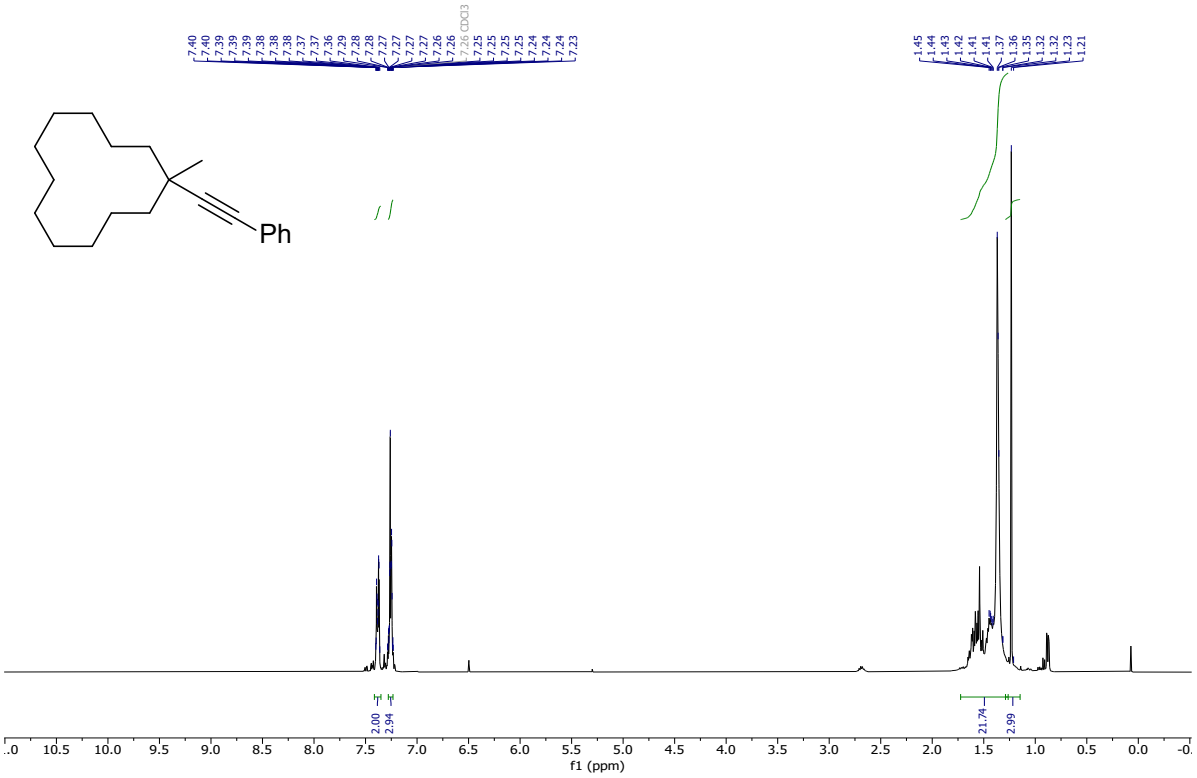


^{13}C NMR, $CDCl_3$, 400 MHz

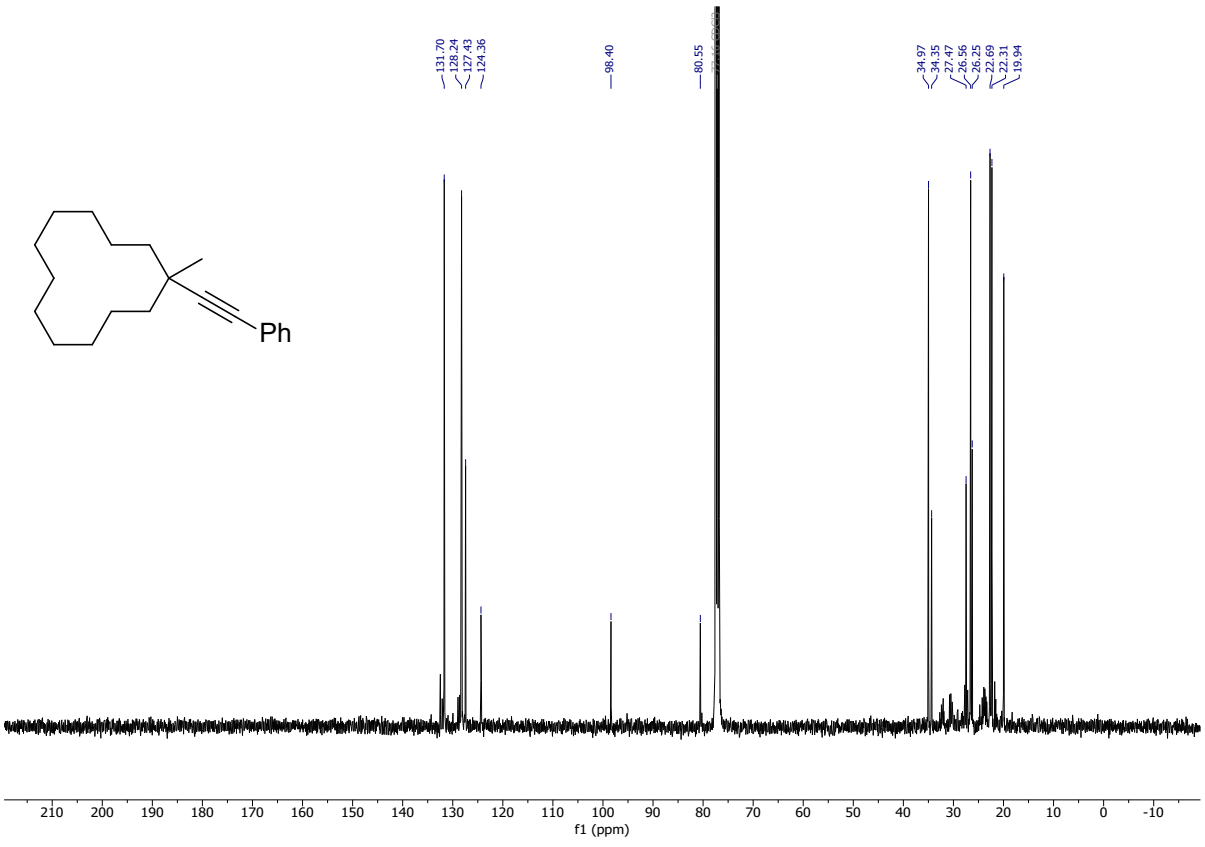


Compound **4n**

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

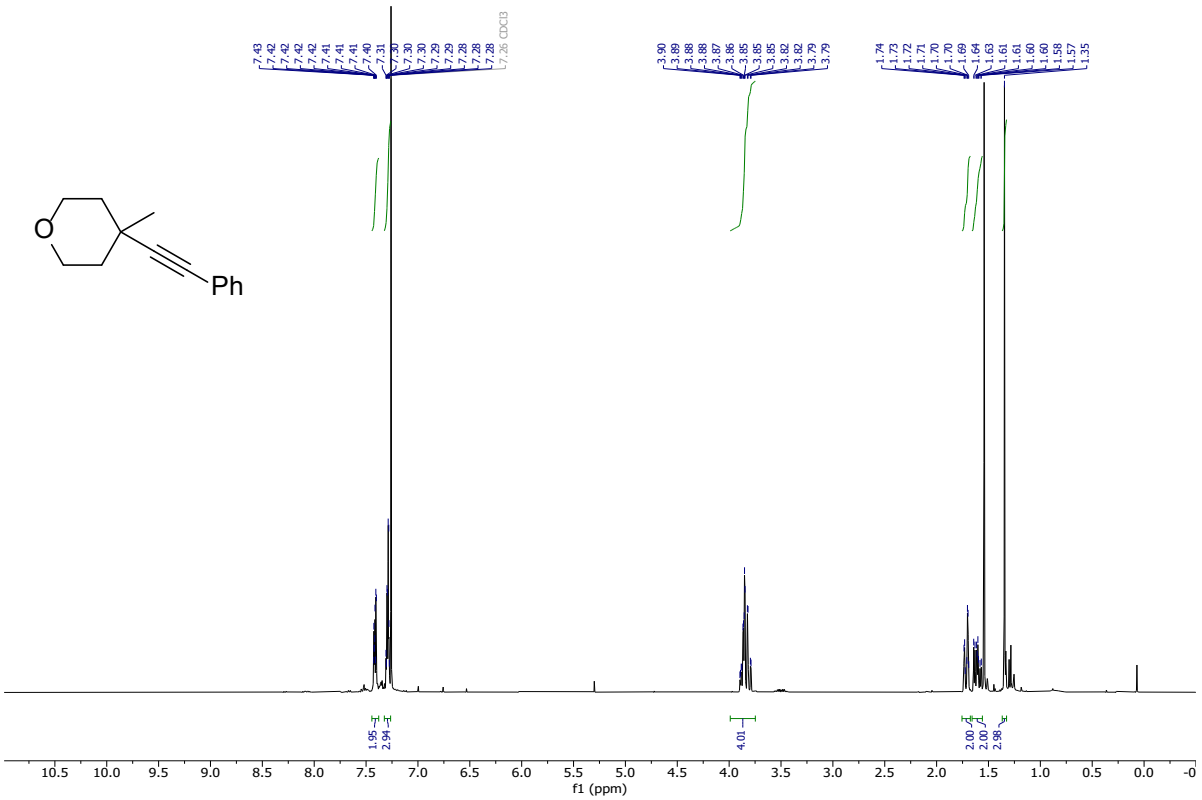


^{13}C NMR, $CDCl_3$, 101 MHz

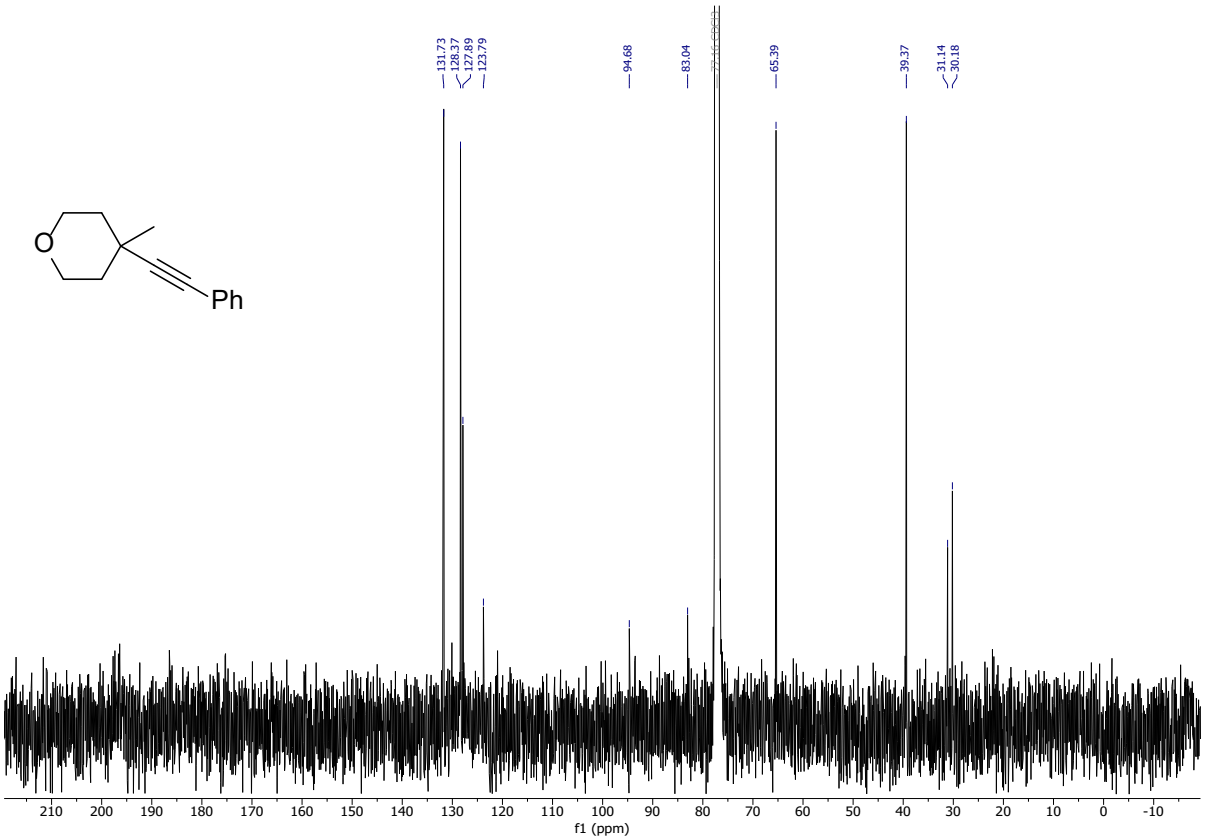


Compound **4o**

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

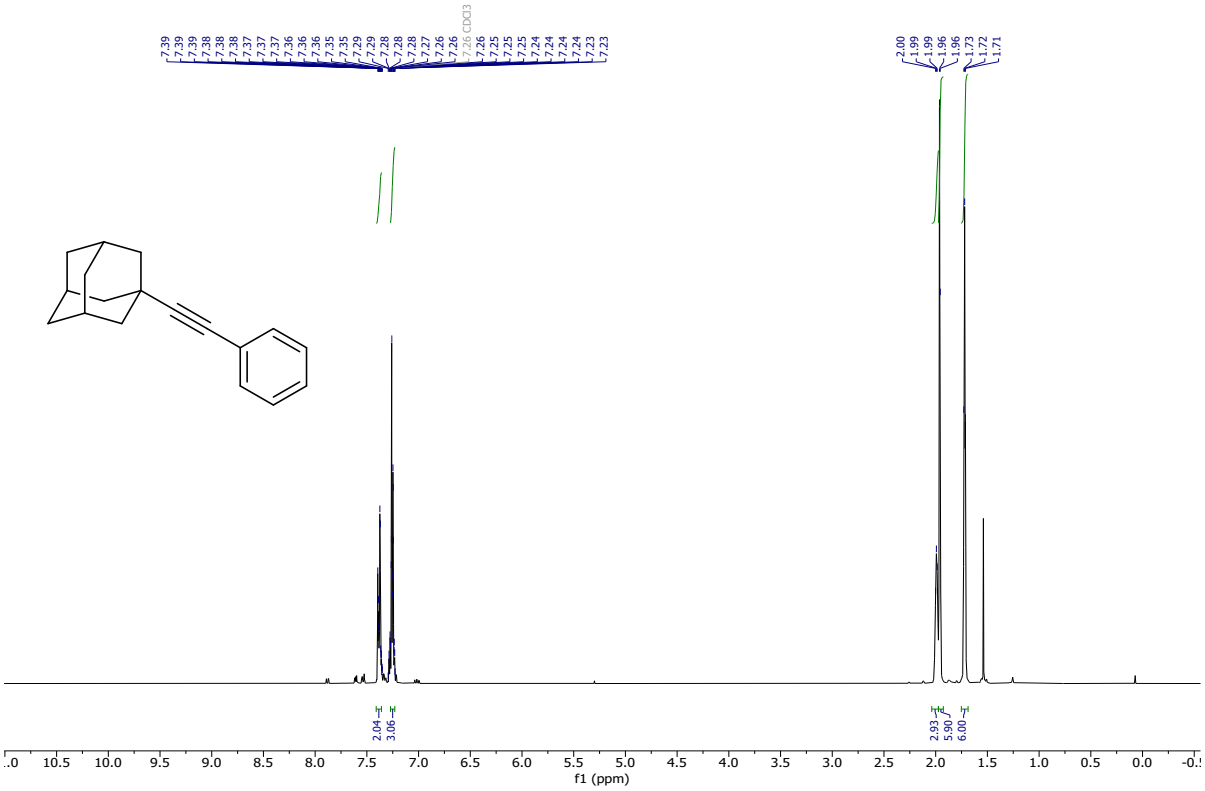


^{13}C NMR, $CDCl_3$, 101 MHz

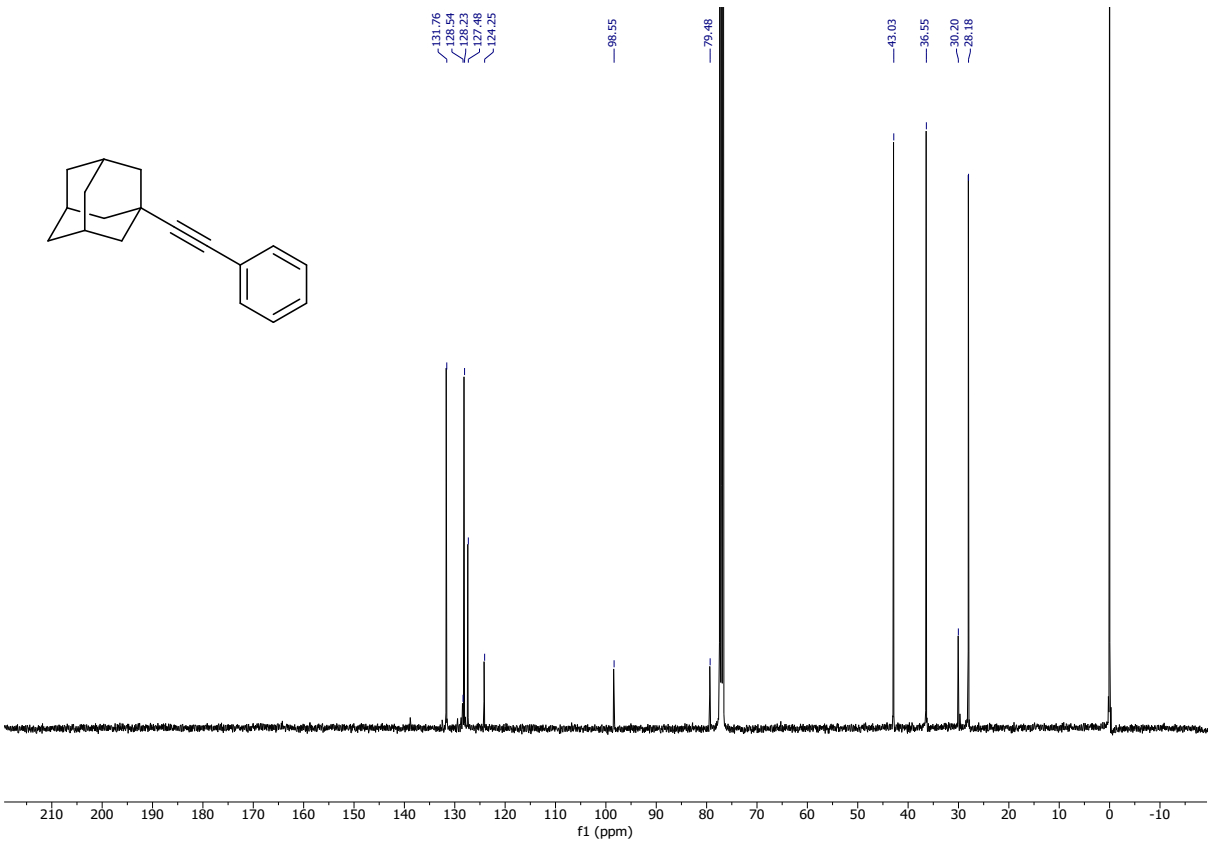


Compound **4p**

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

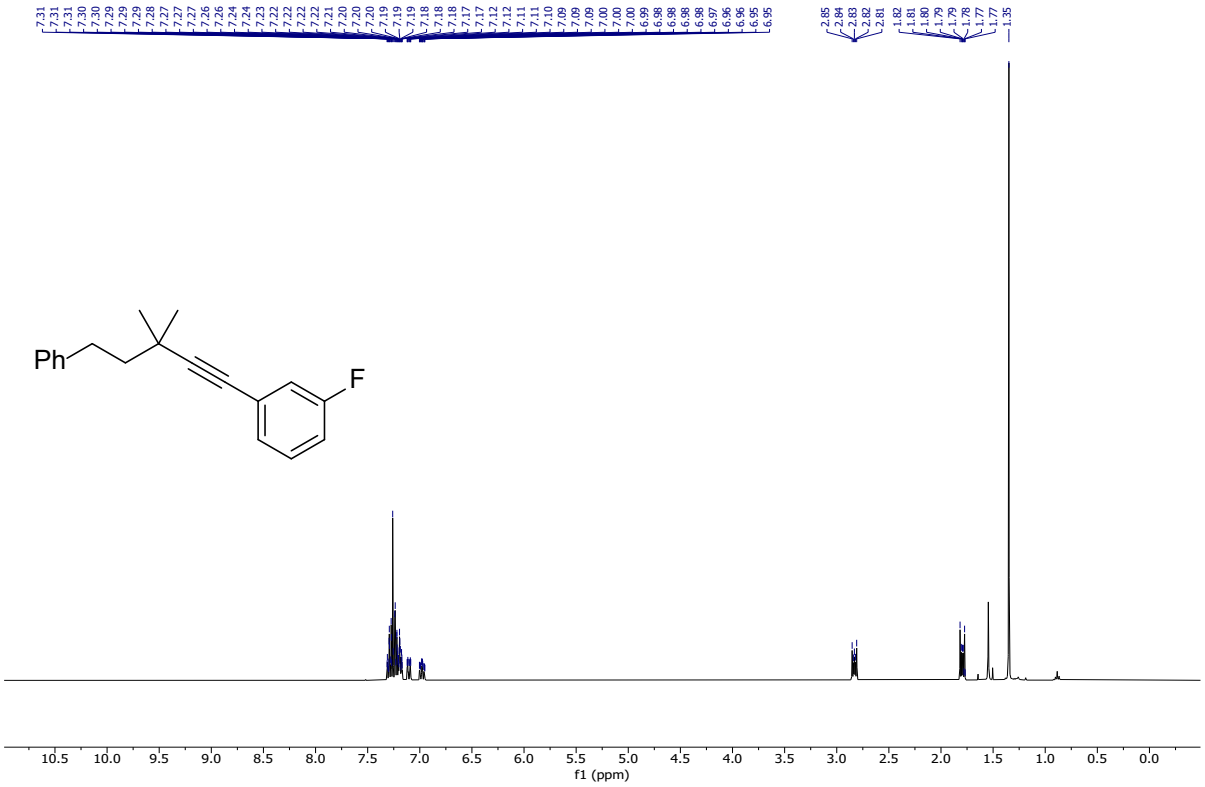


^{13}C NMR, $CDCl_3$ (with 1V% TMS), 101 MHz

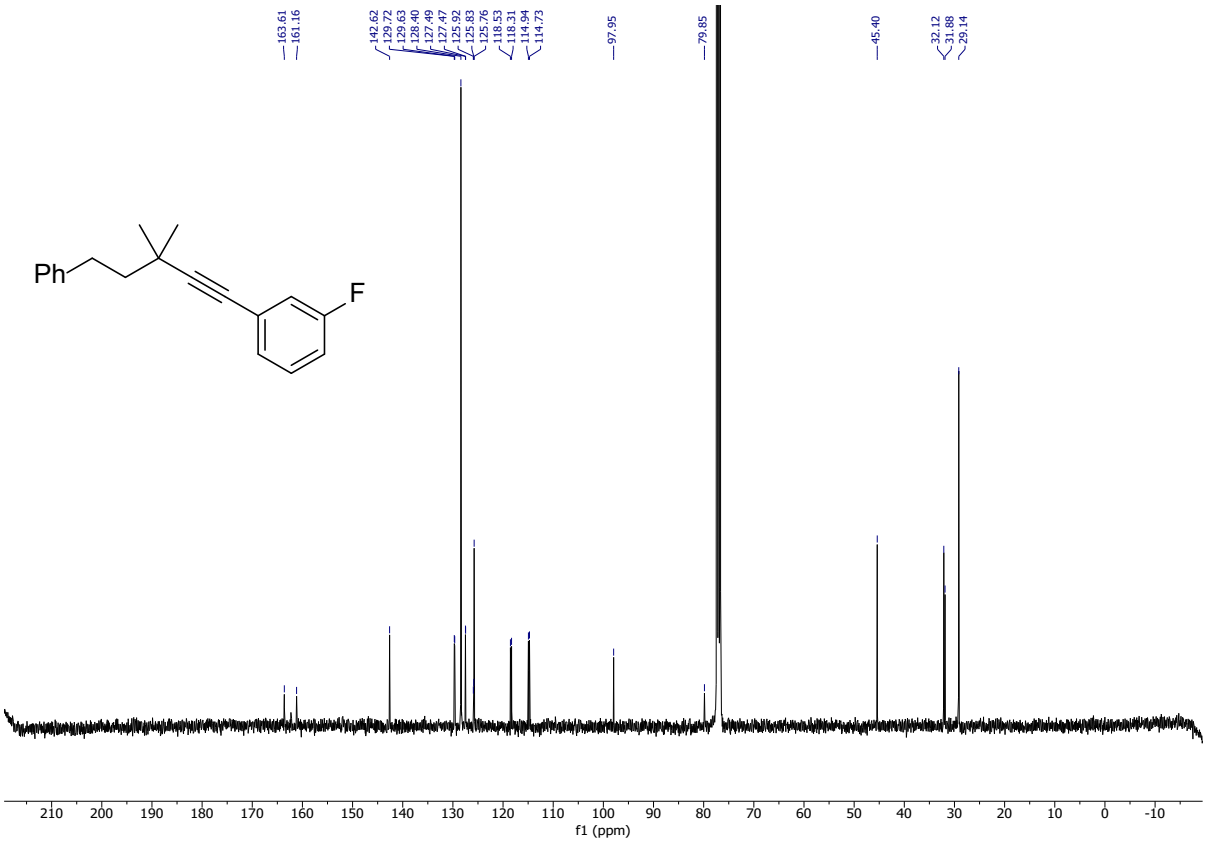


Compound **4q**

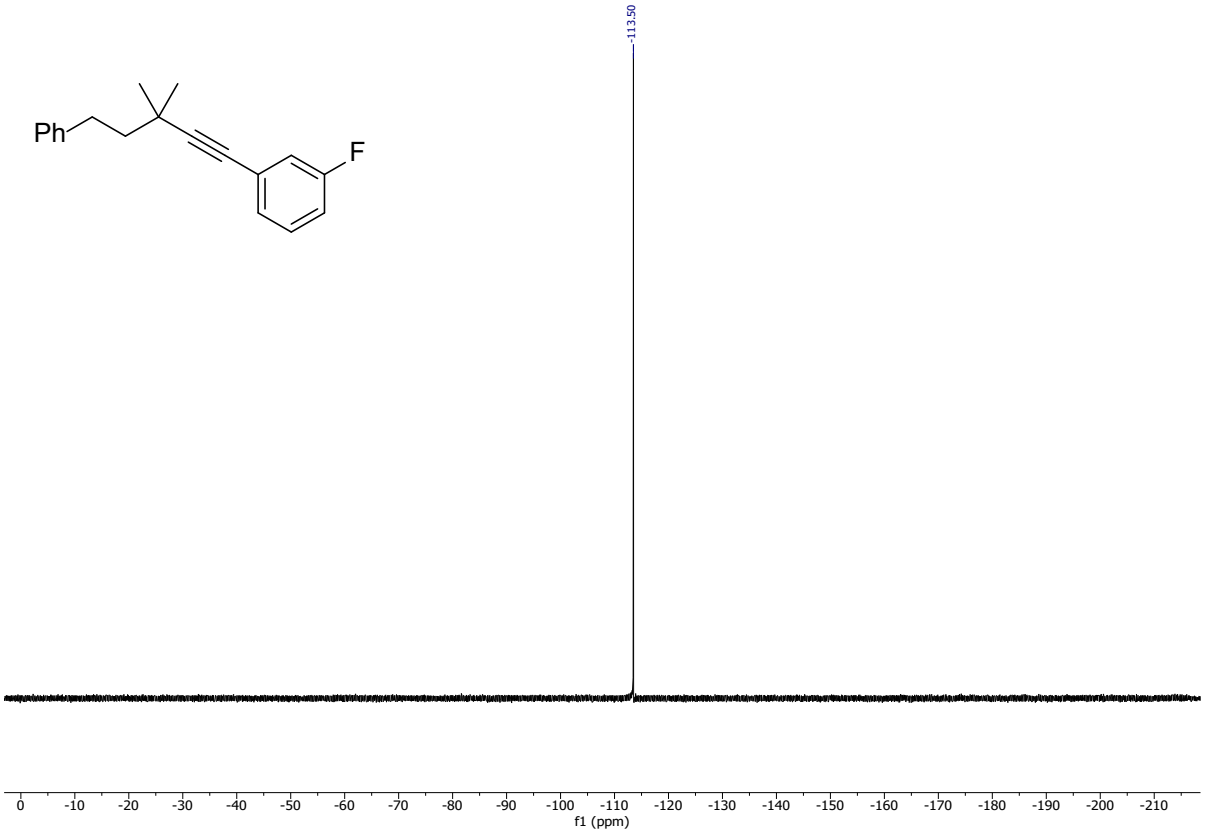
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

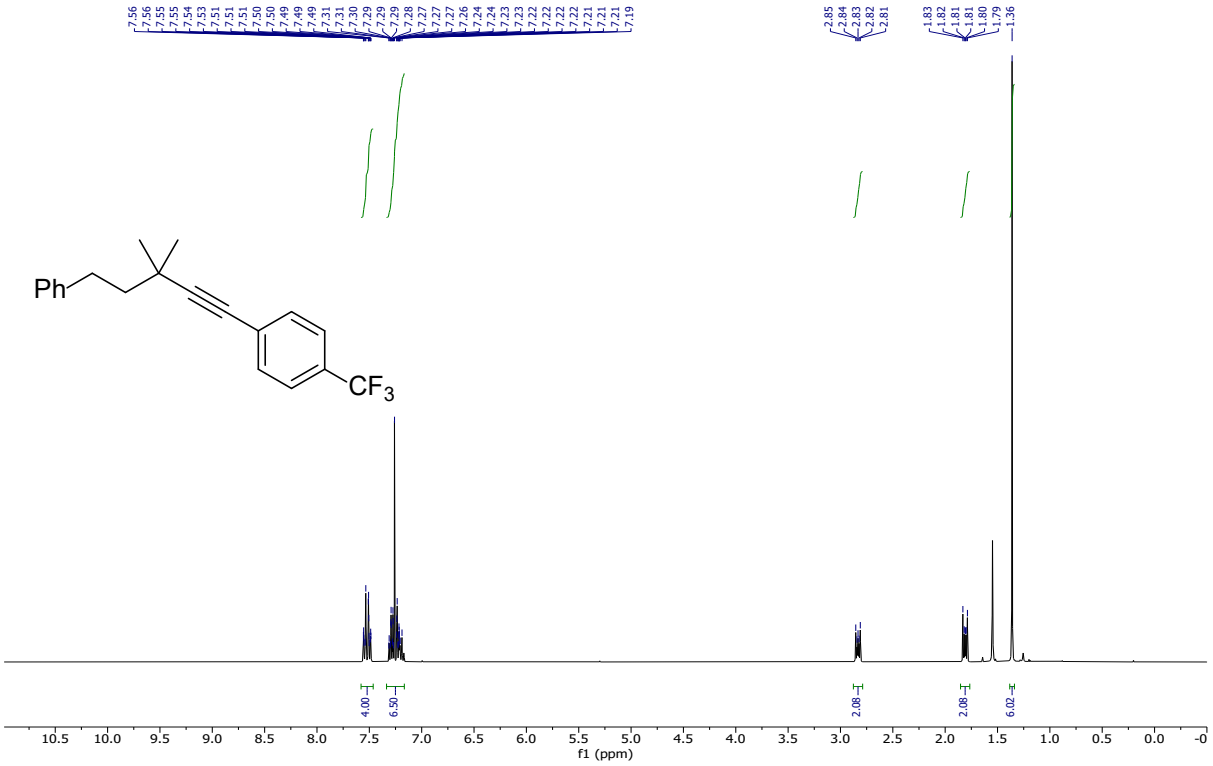


^{19}F NMR, $CDCl_3$, 376 MHz

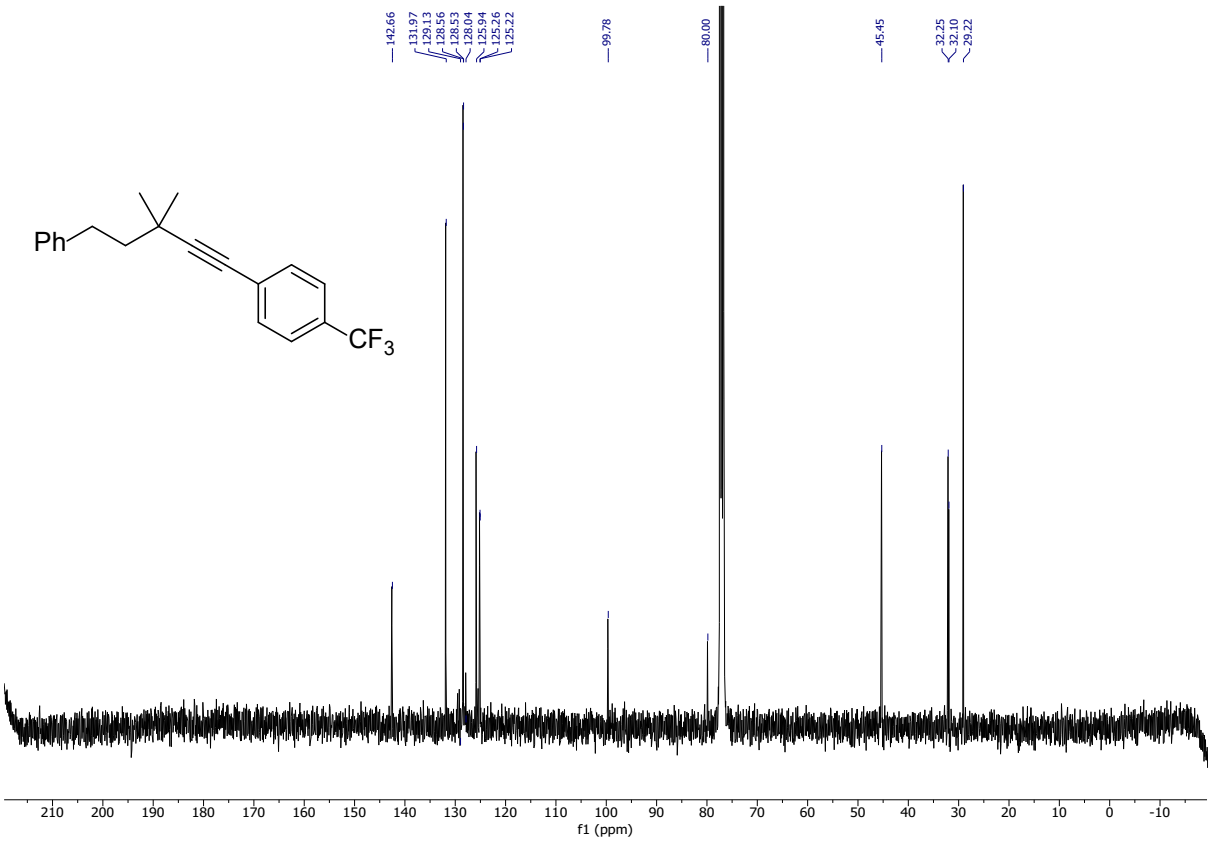


Compound **4r**

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



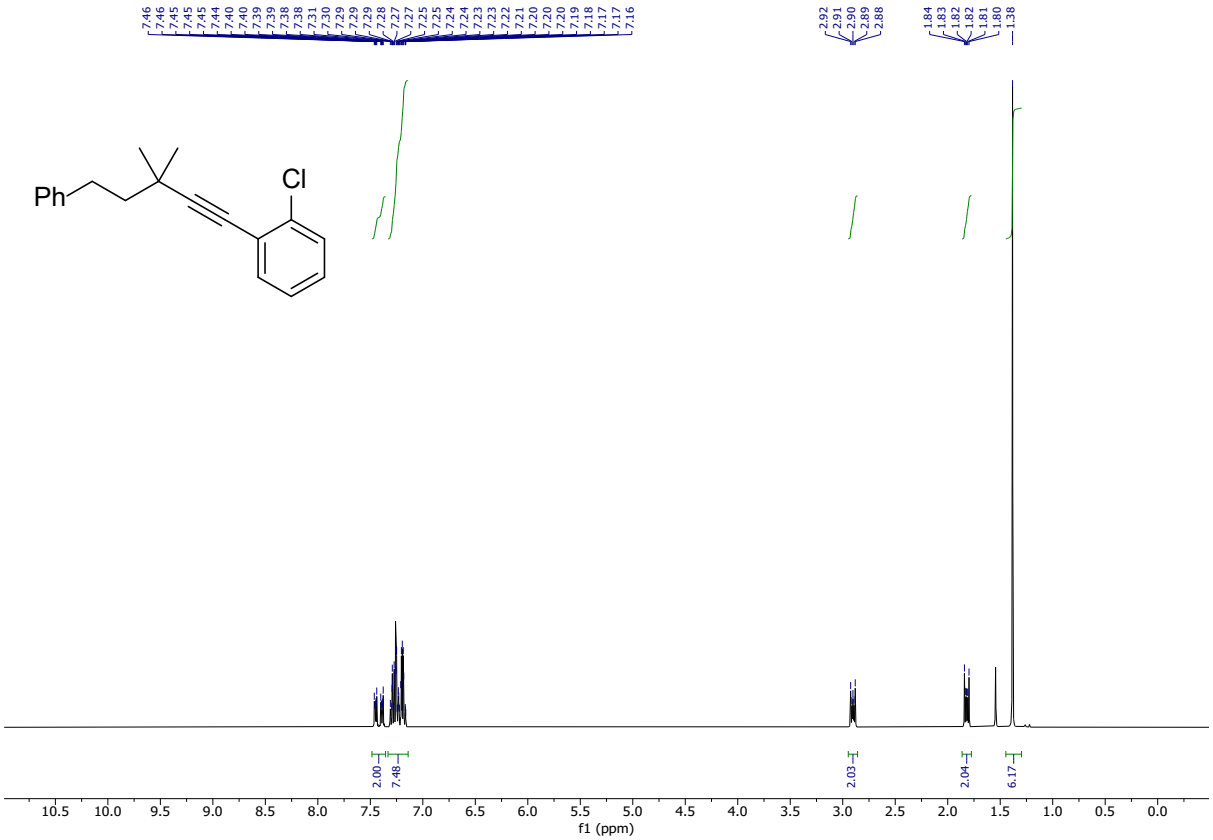
^{13}C NMR, $CDCl_3$, 101 MHz



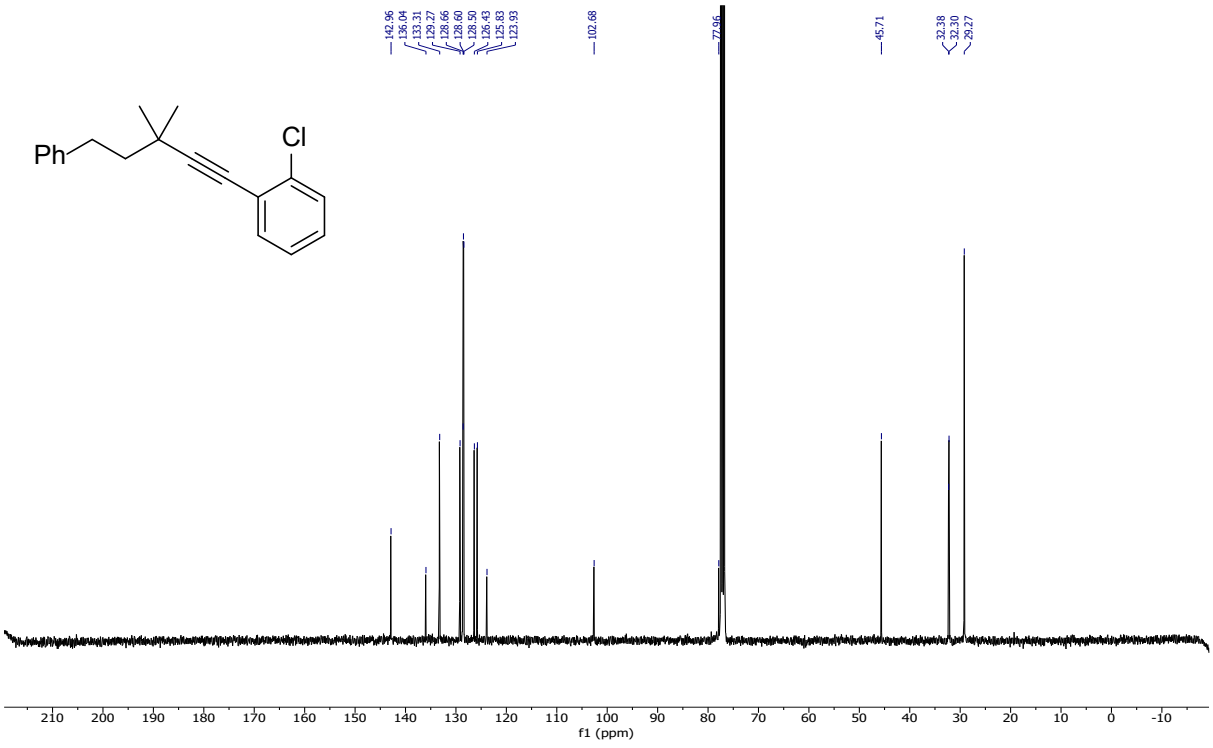
^{19}F NMR, $CDCl_3$, 376 MHz,

Compound **4s**

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

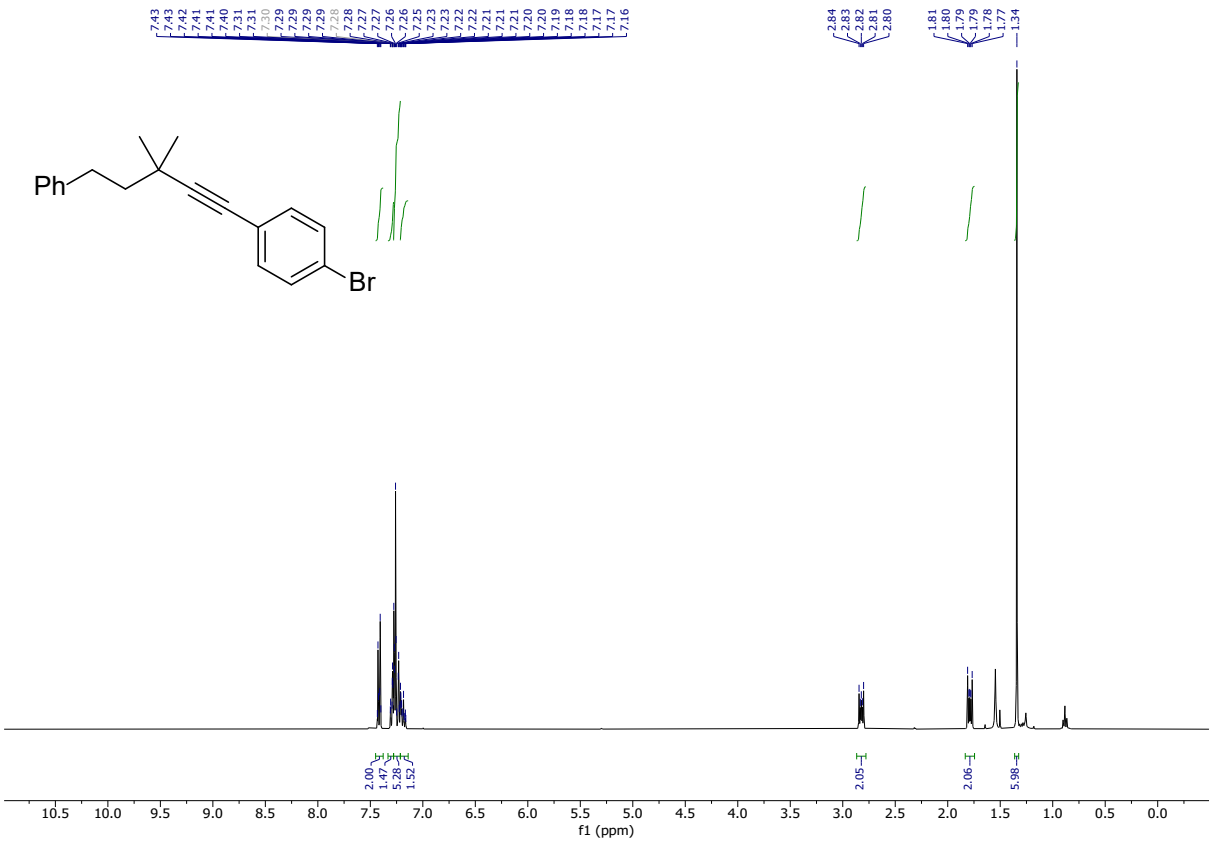


^{13}C NMR, $CDCl_3$, 400 MHz

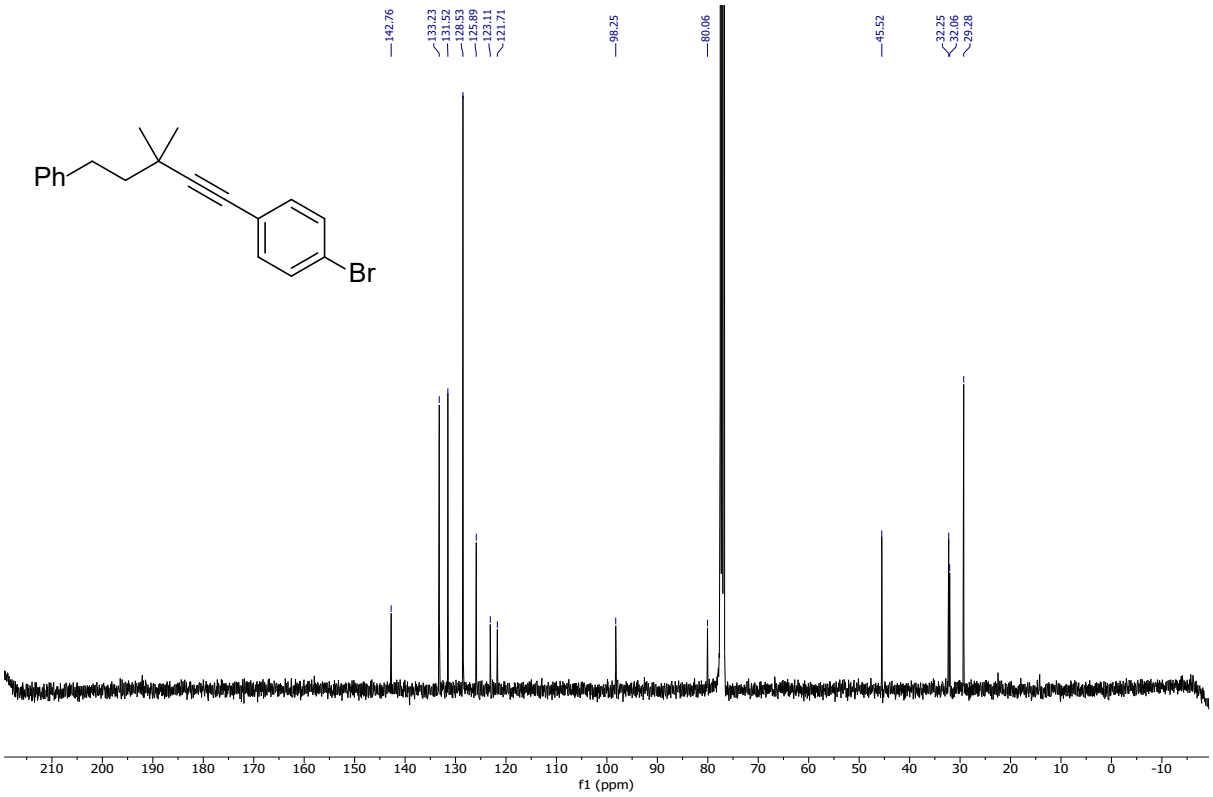


Compound **4t**

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

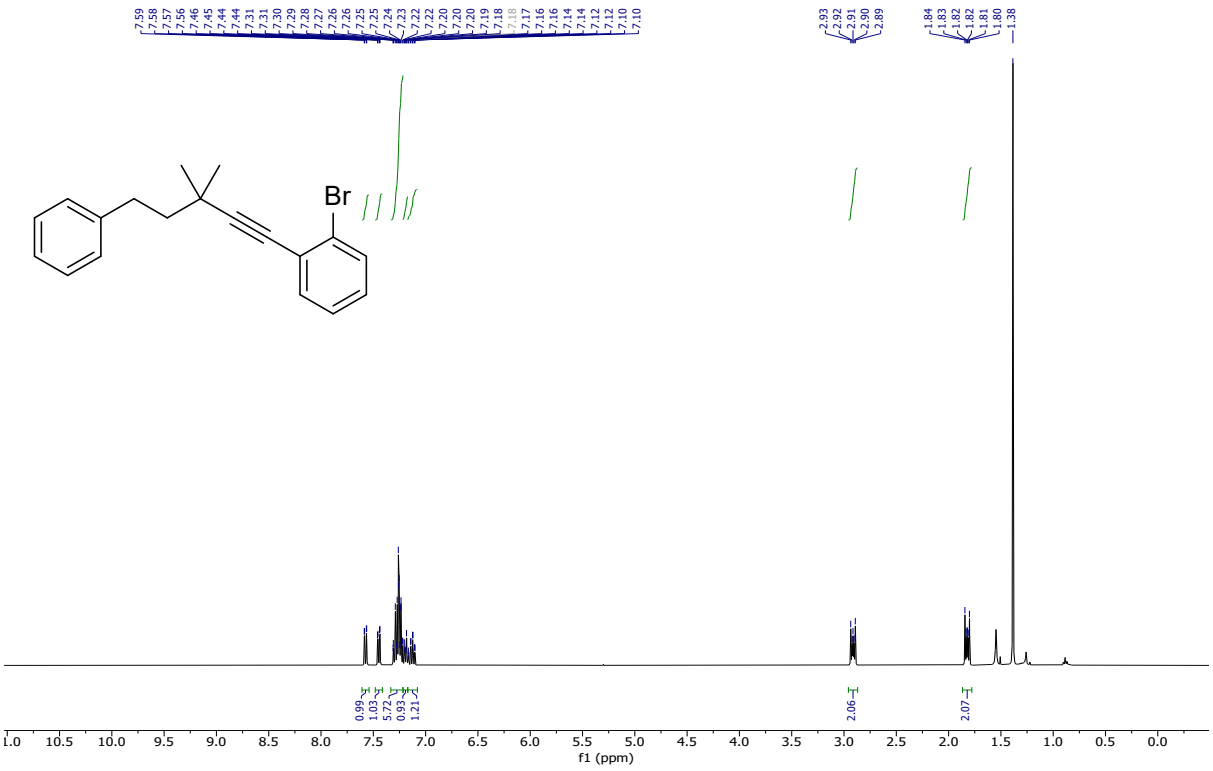


^{13}C NMR, $CDCl_3$, 101 MHz

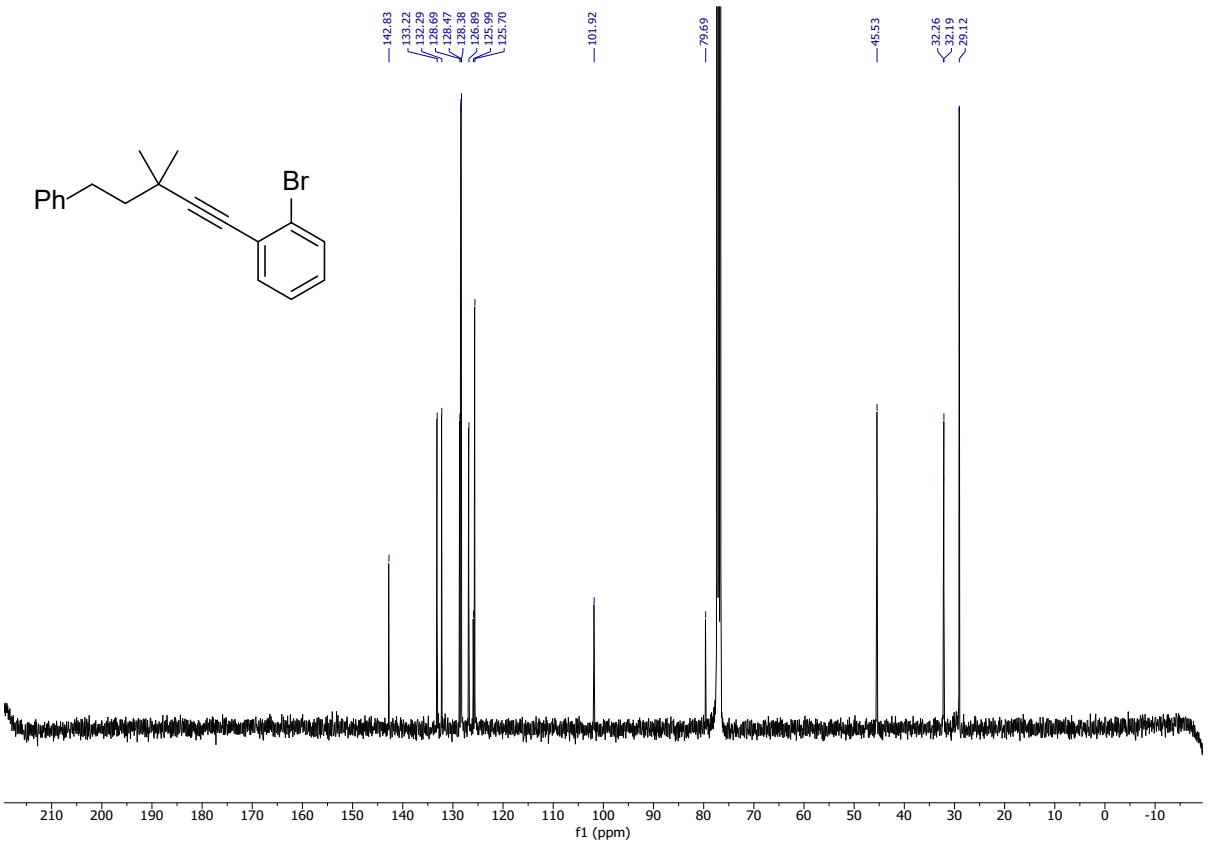


Compound **4u**

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

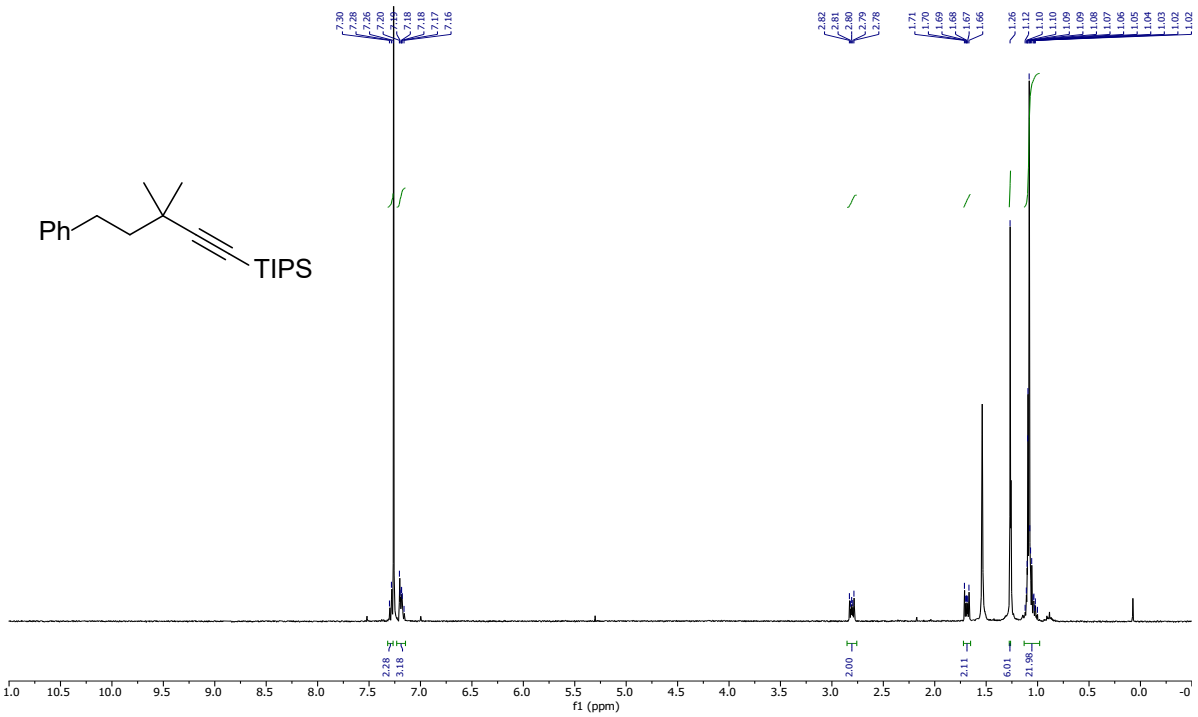


^{13}C NMR, $CDCl_3$, 101 MHz

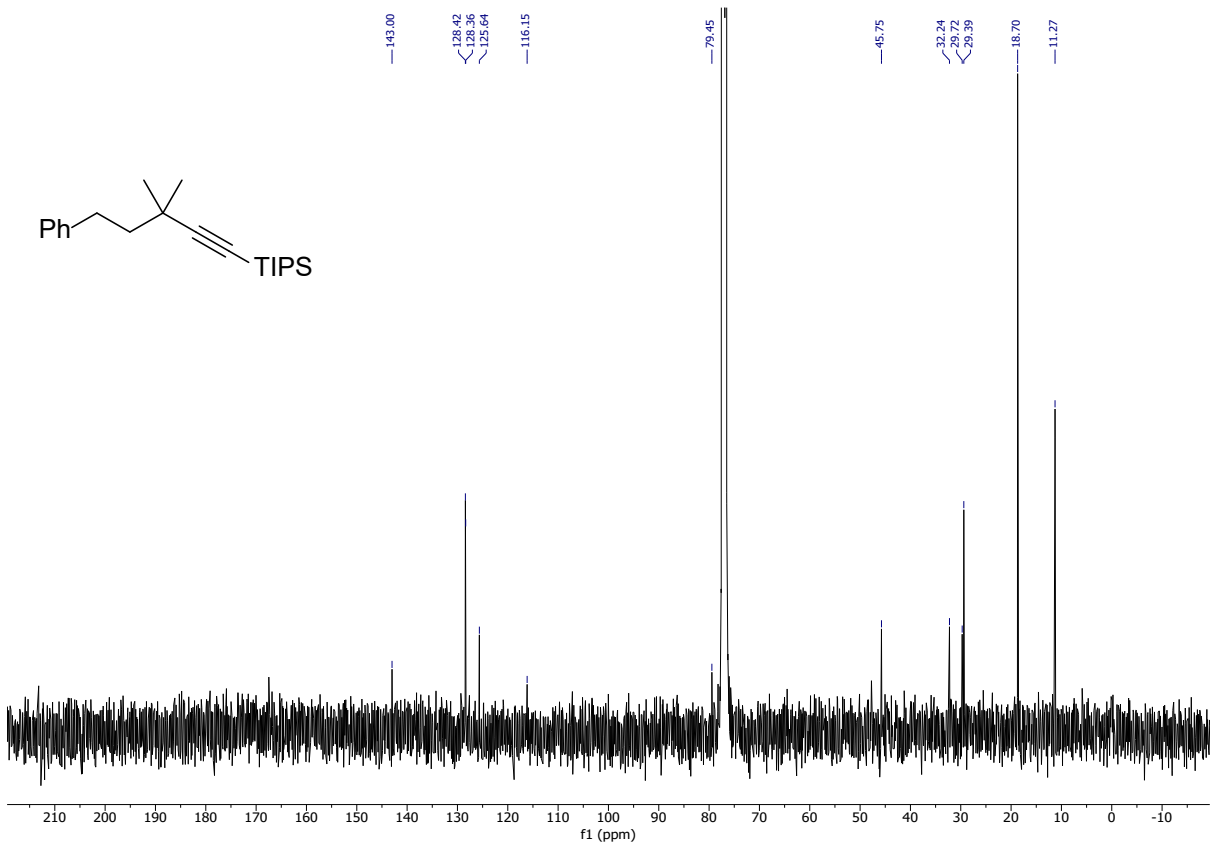


Compound **4v**

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

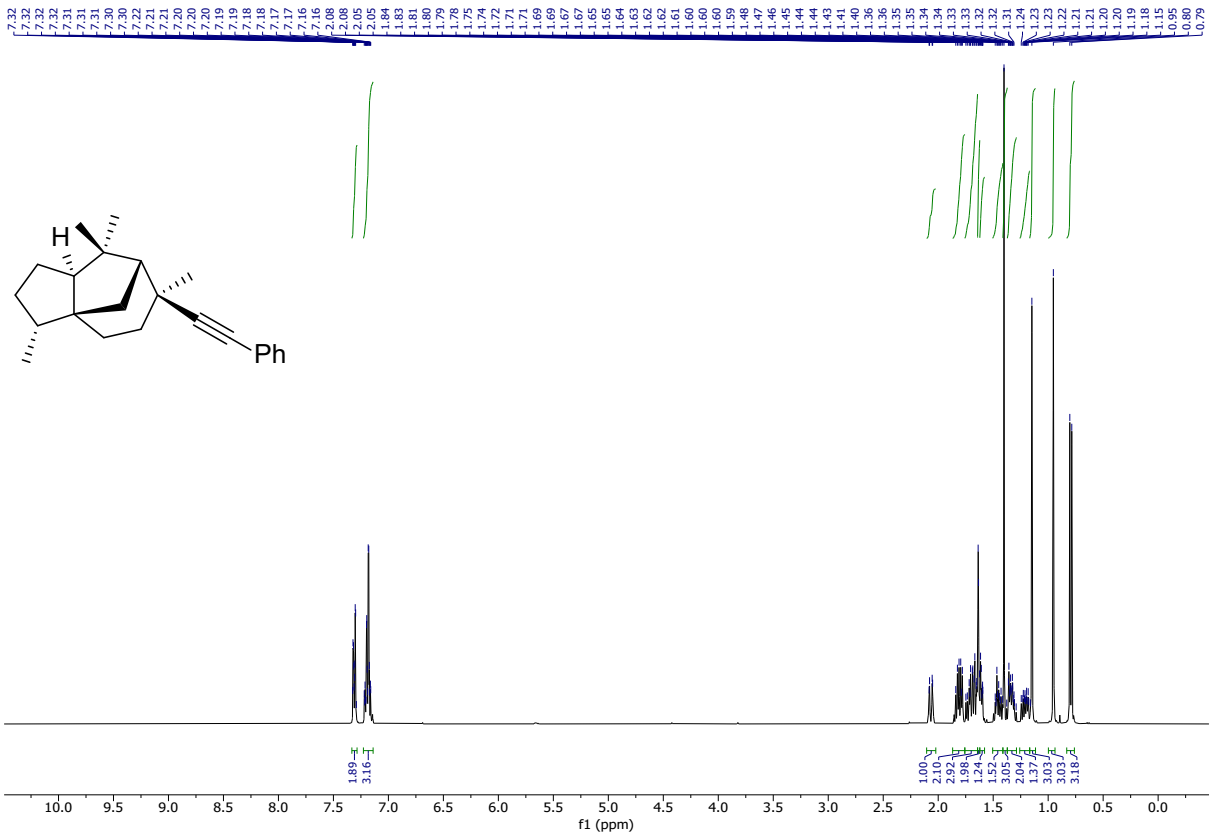


^{13}C NMR, $CDCl_3$, 101 MHz

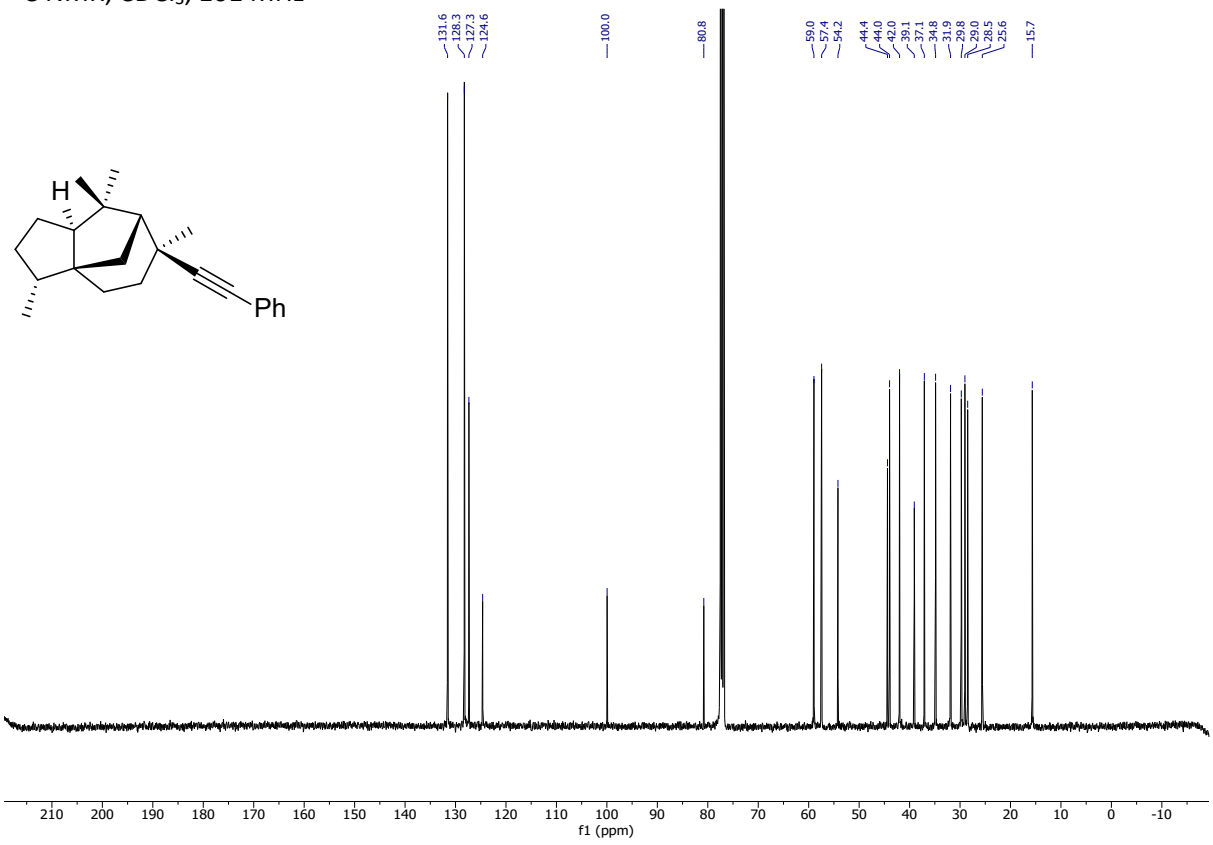


Compound **4w**

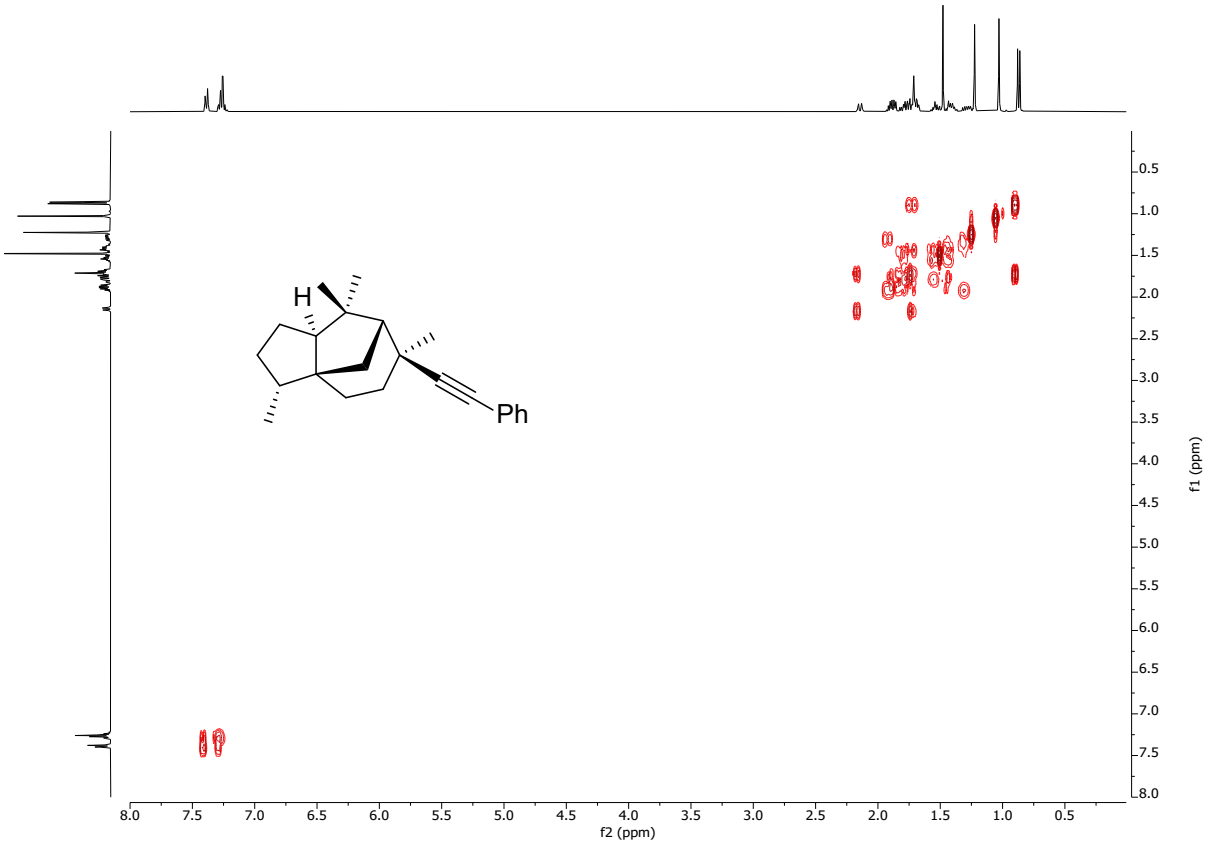
^{1}H NMR, $CDCl_3$,400 MHz



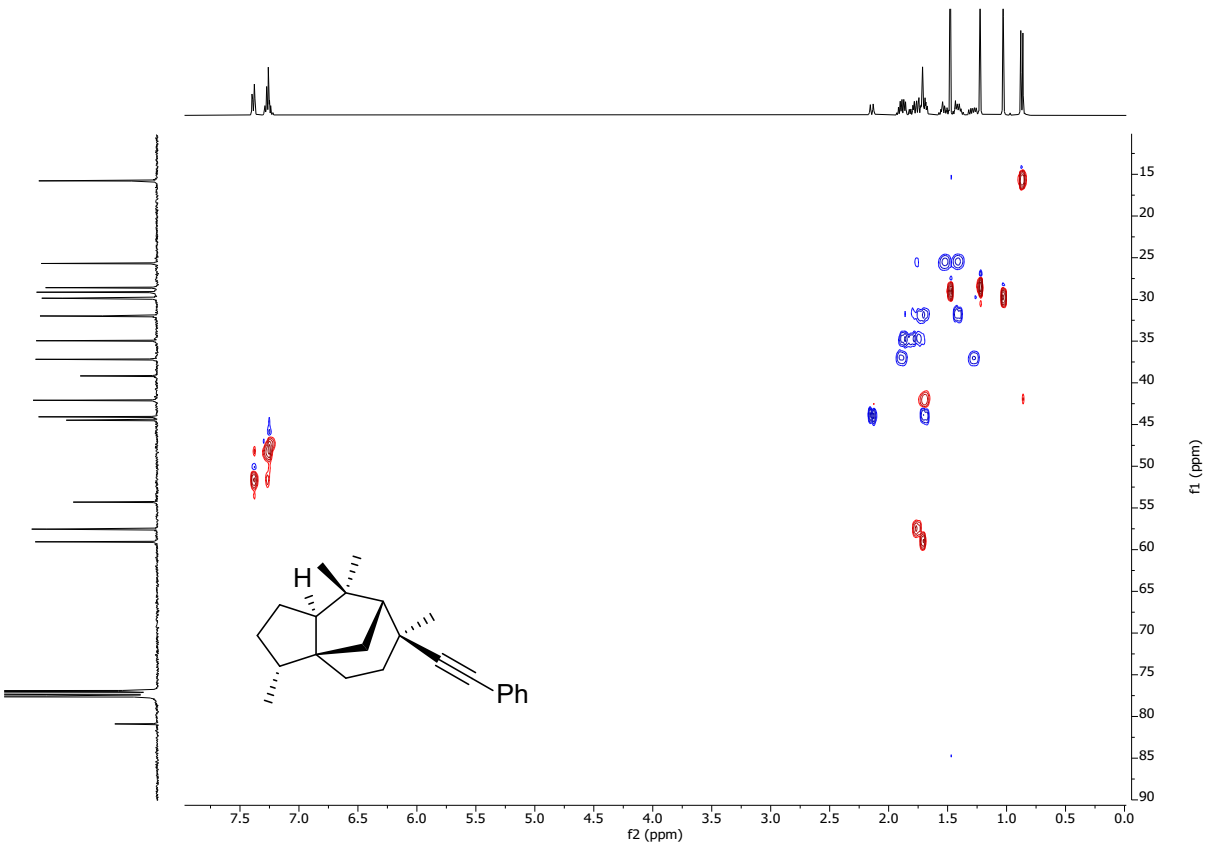
^{13}C NMR, $CDCl_3$, 101 MHz



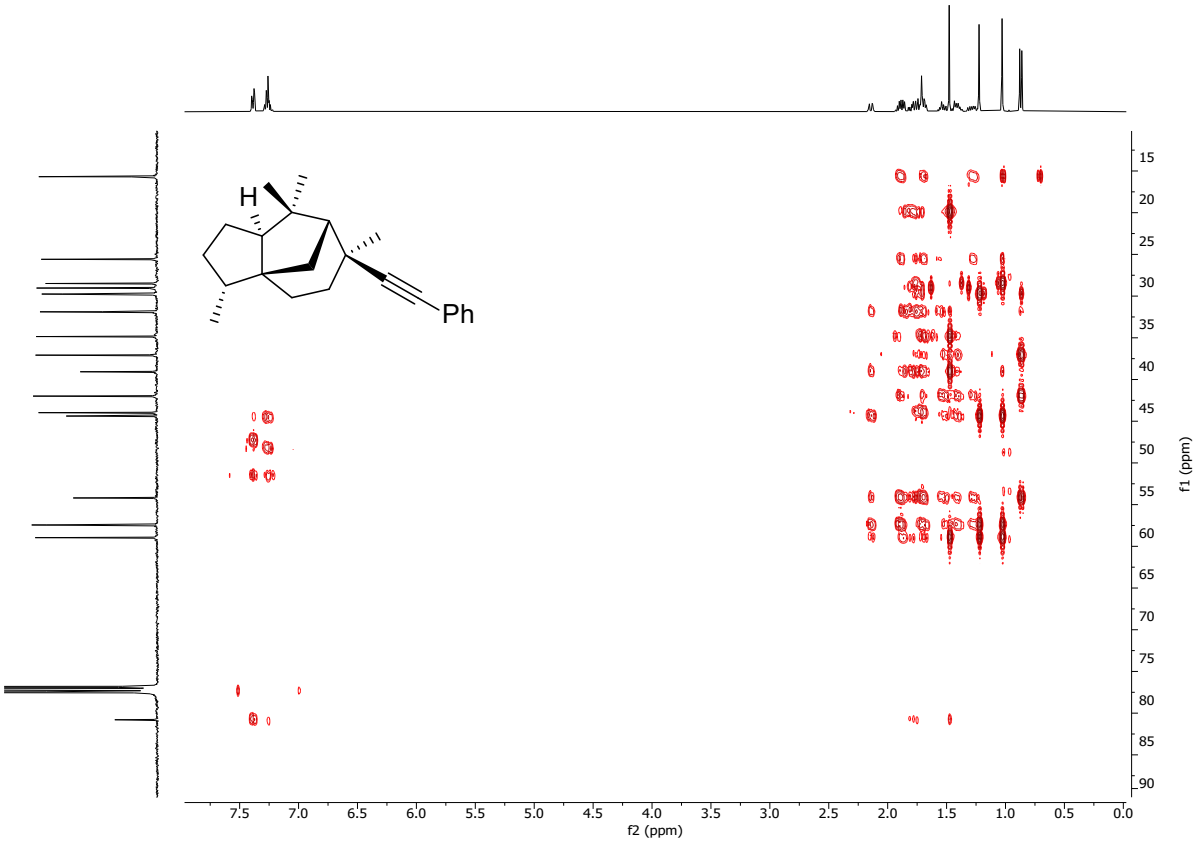
COSY



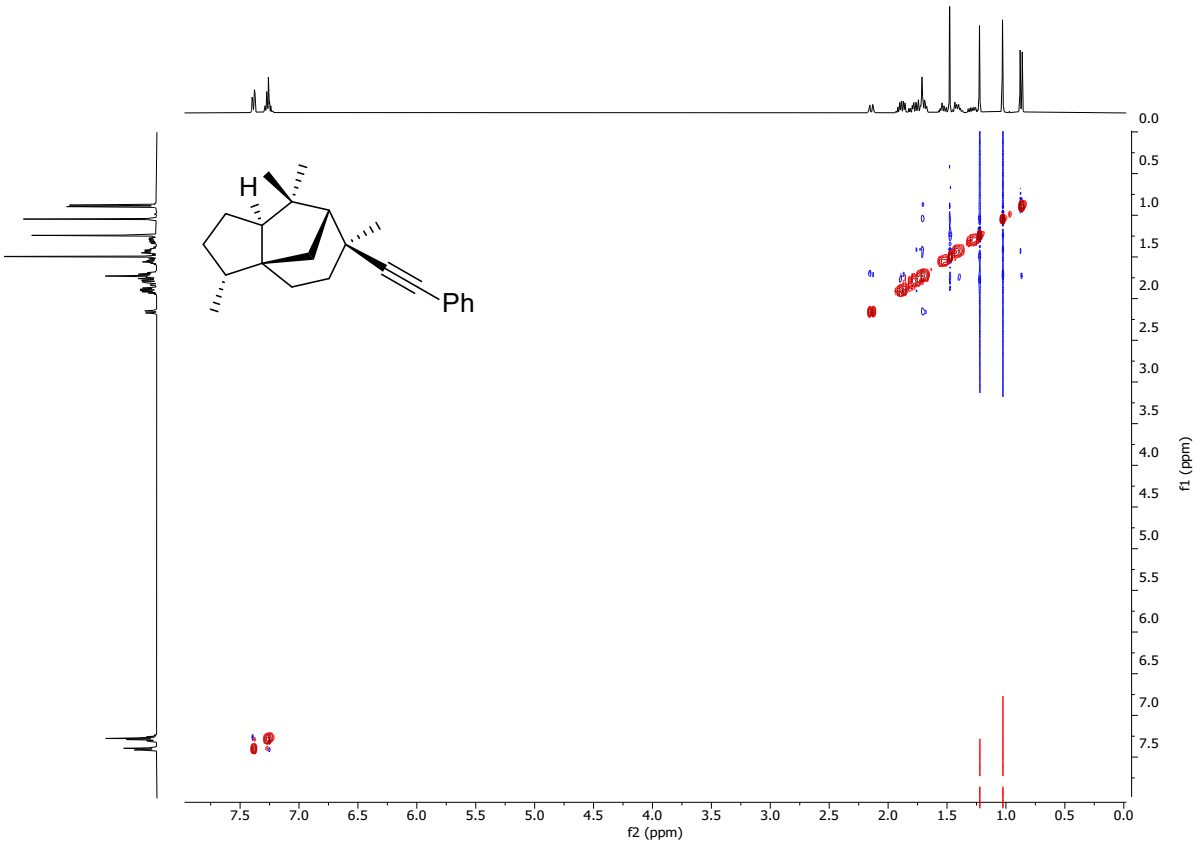
HSQC (O1P = 55 ppm, SW =80 ppm)



HMBC (O1P = 55 ppm; SW = 80 ppm)

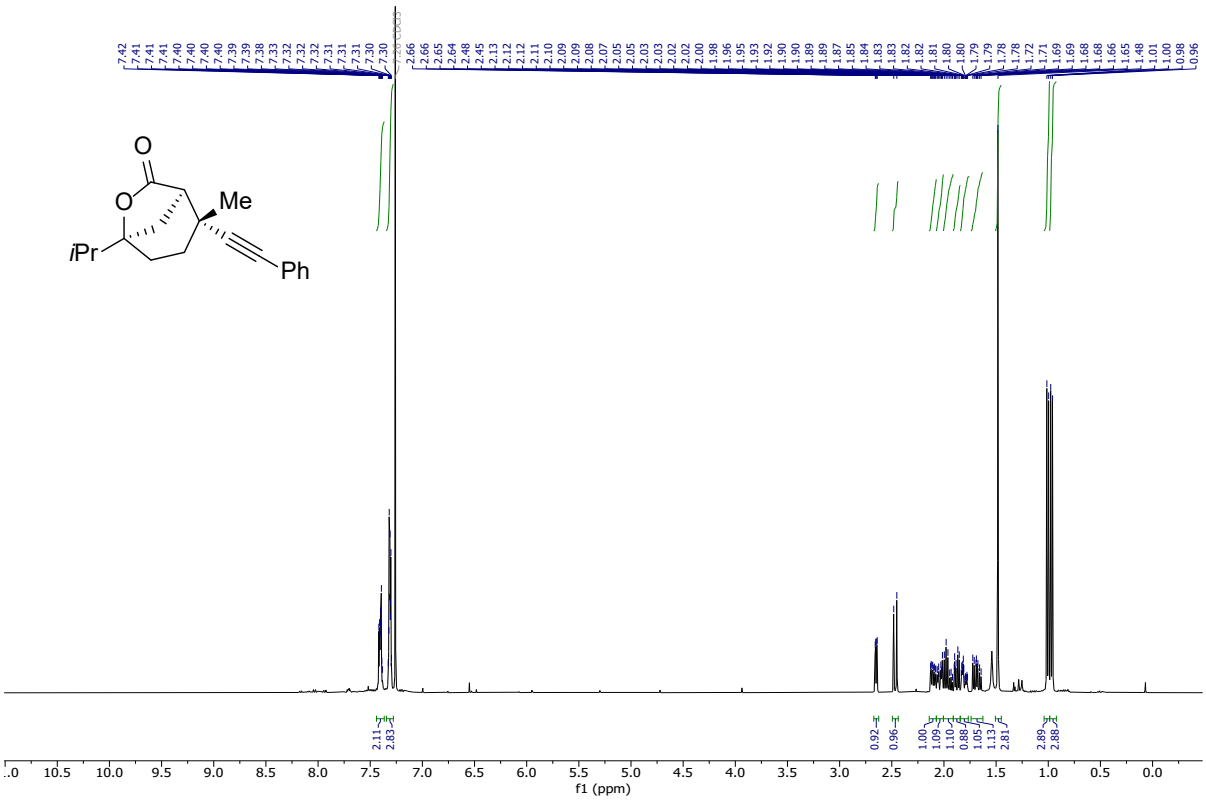


NOESY (O1P = 4 ppm, SW = 8 ppm)

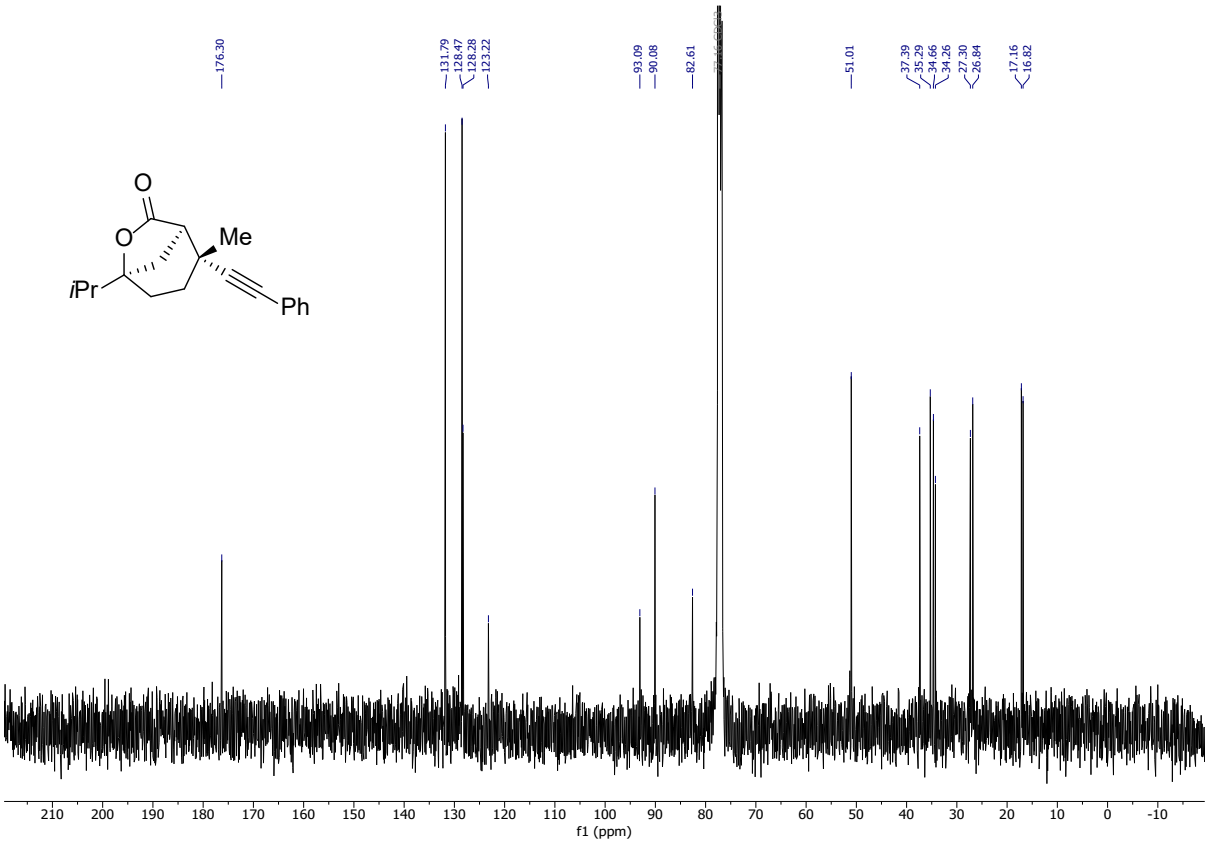


Compound **4x**

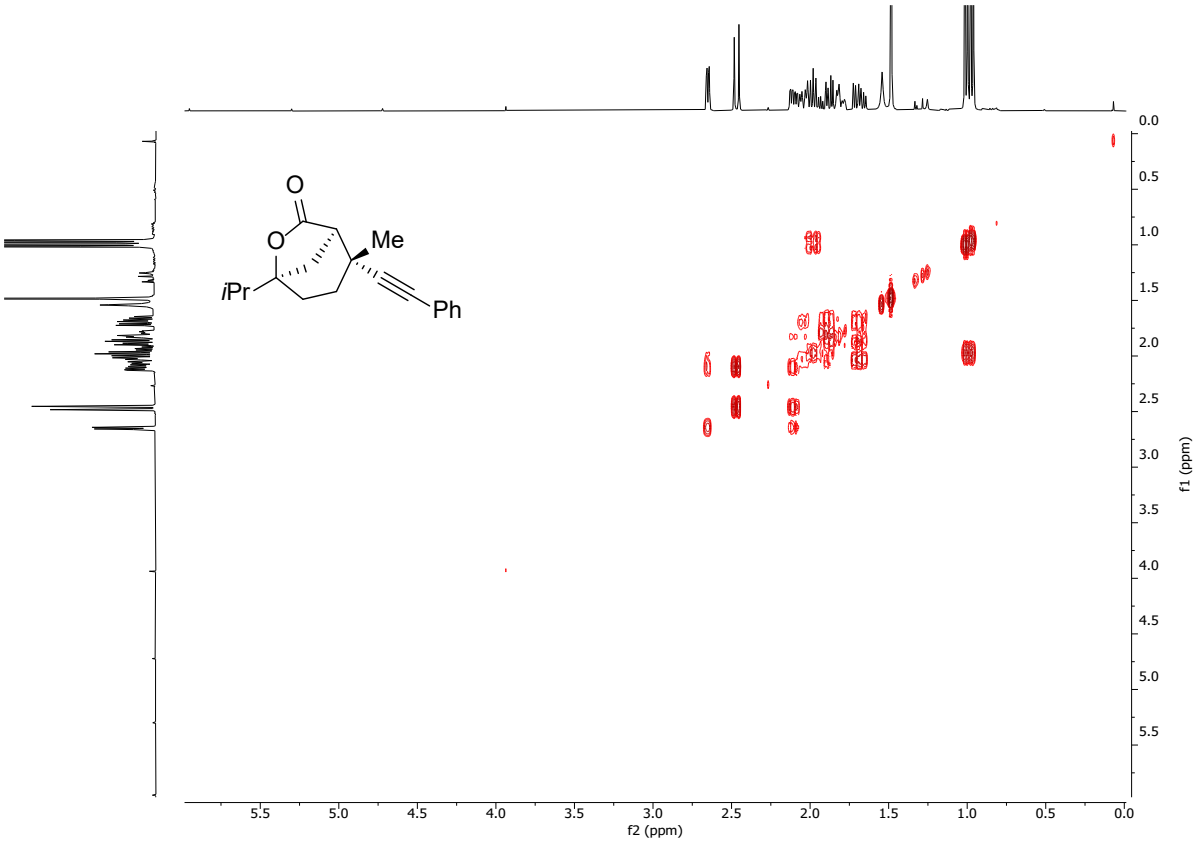
^{1}H NMR, $CDCl_3$, 400 MHz



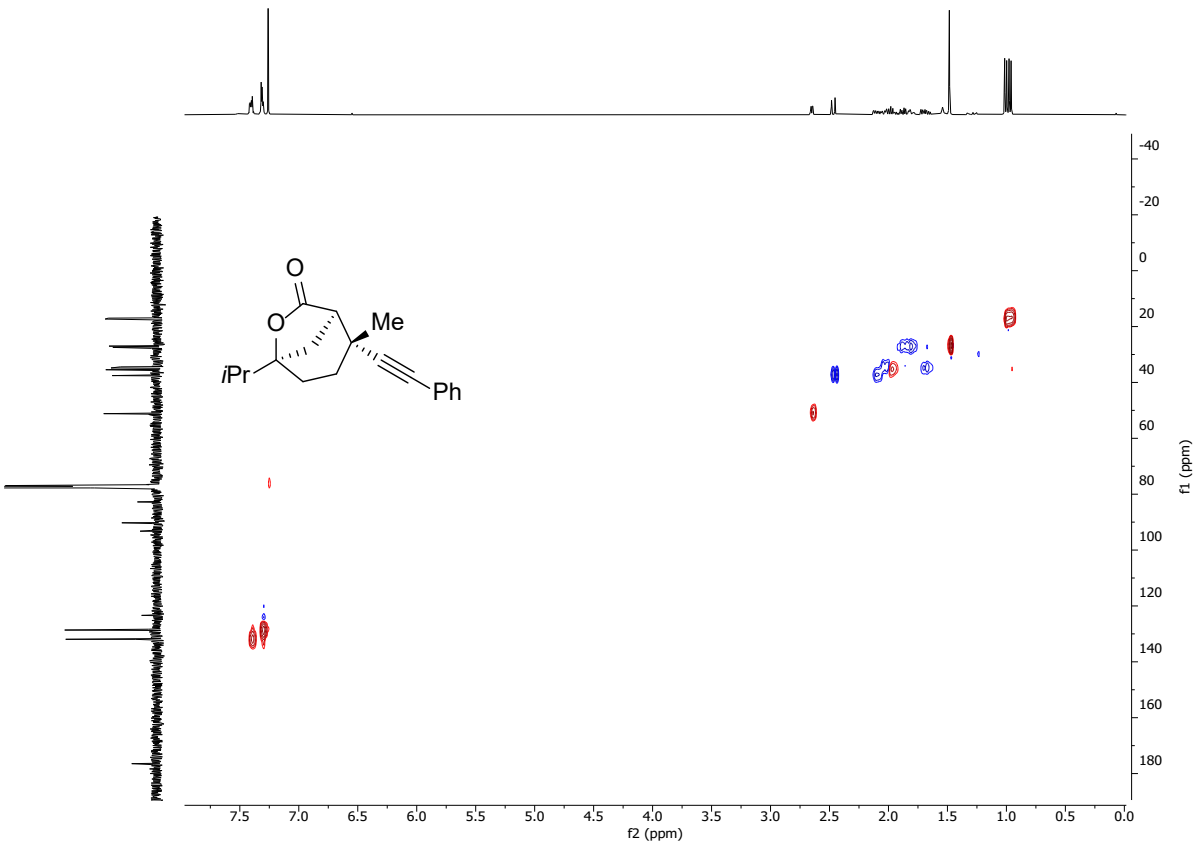
^{13}C NMR, $CDCl_3$, 101 MHz



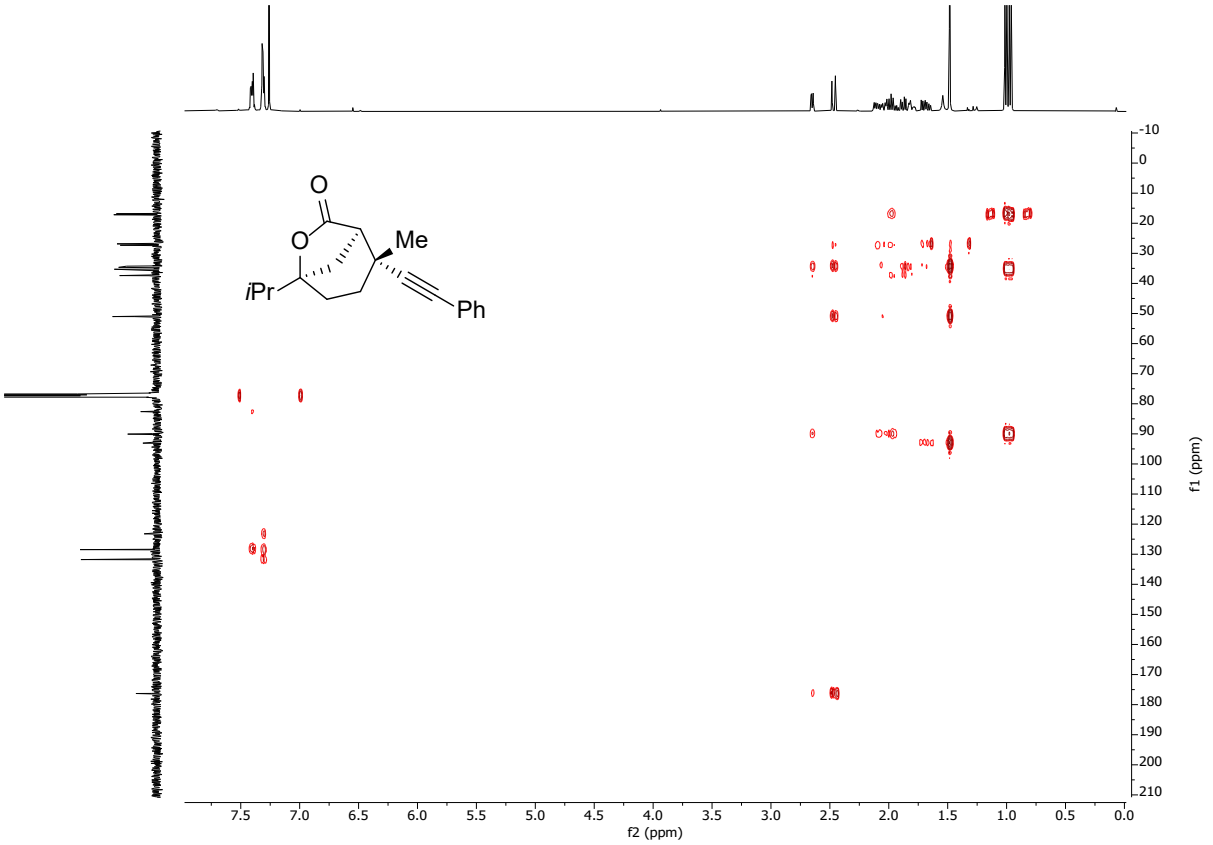
COSY (O1P = 3 ppm; SW = 6 ppm)



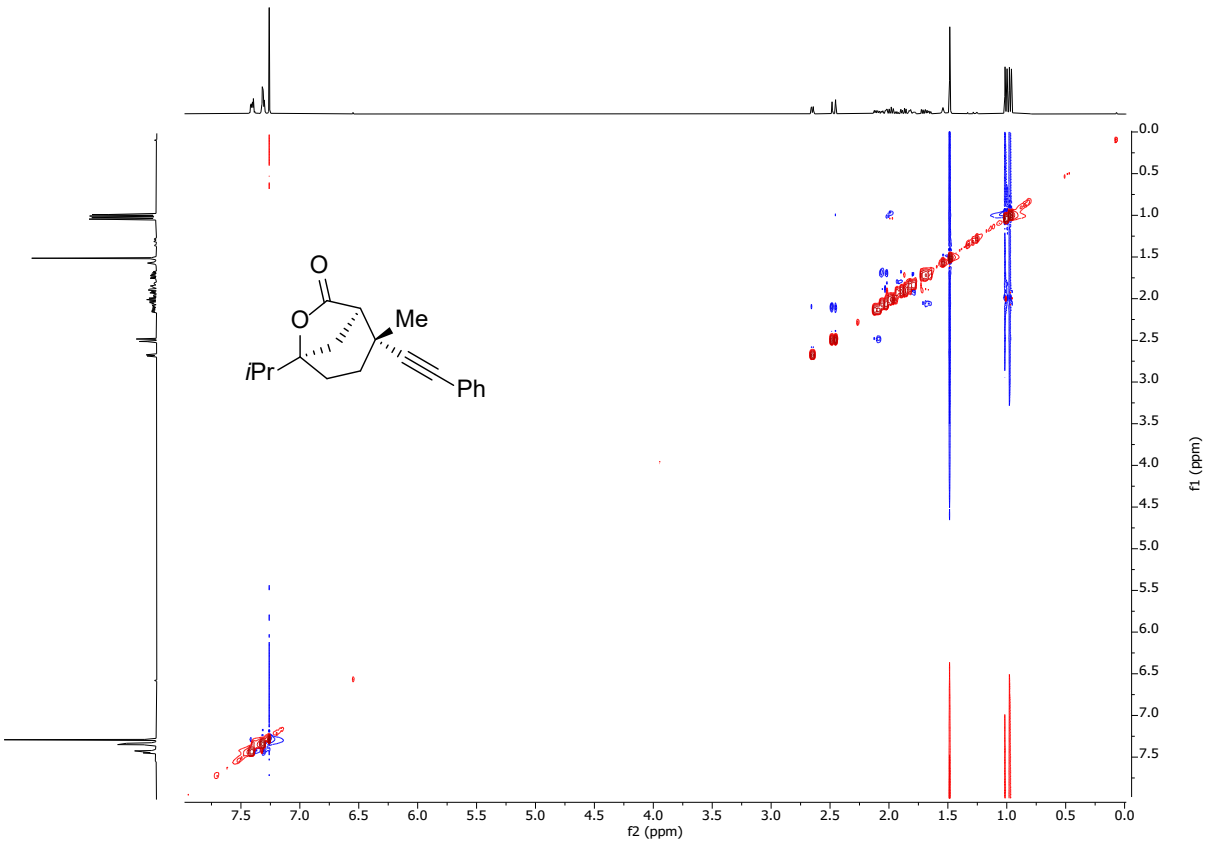
HSQC



HMBC

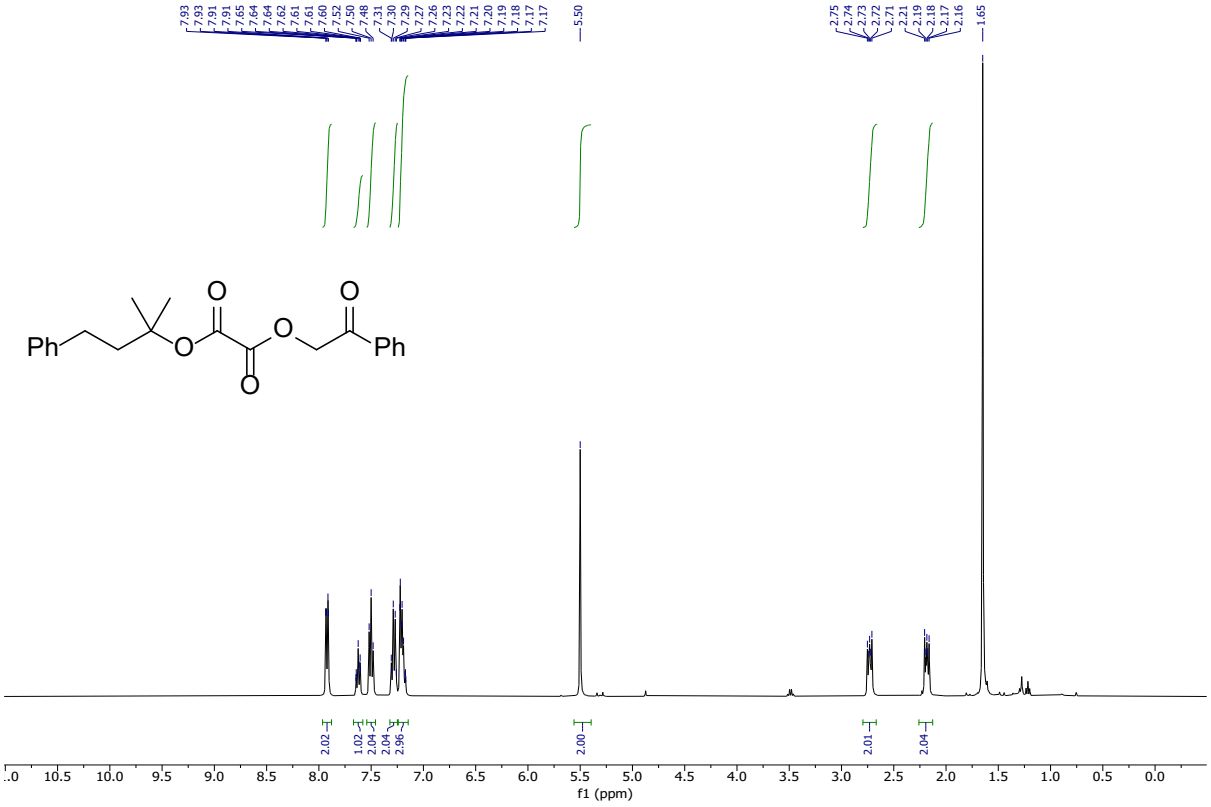


NOESY



Compound **6b**

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



^{13}C NMR, $CDCl_3$, 101 MHz