Exploring Photoredox-Catalyzed (Re)functionalizations with Core-Modified Benziodoxolones

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Dedicated to Prof. Janine Cossy, President of the 55th Bürgenstock conference in 2022

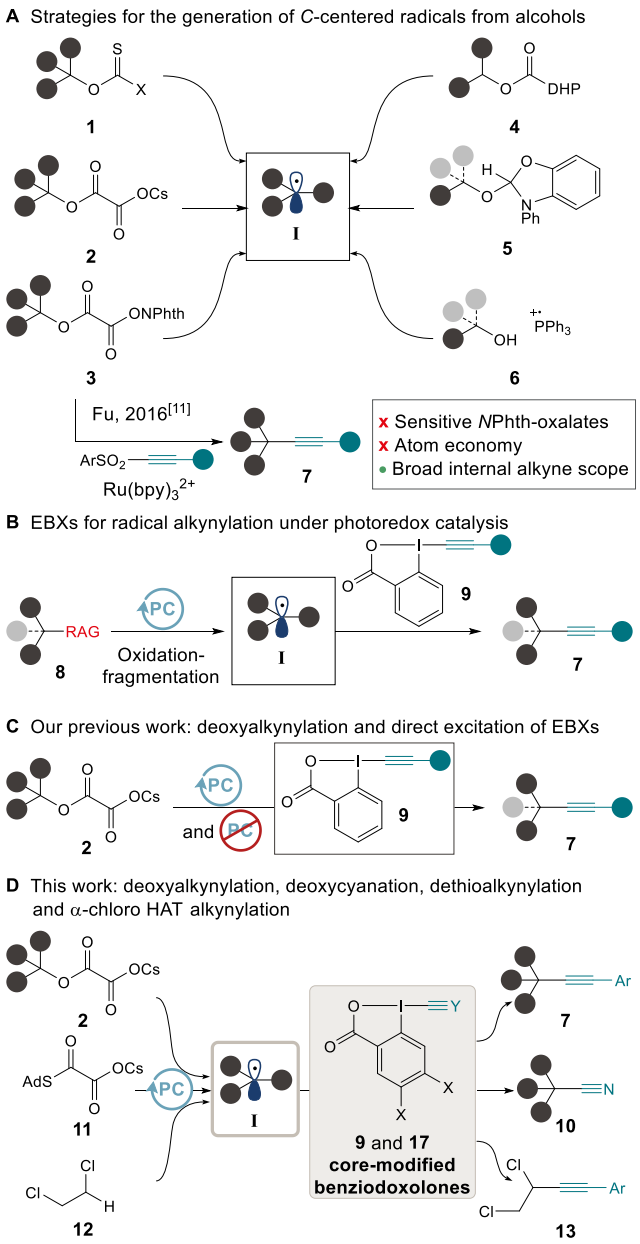
Alkynes and nitriles are valuable building blocks in organic synthesis and also have multiple applications in chemical biology and materials science. Due to the high availability of tertiary alcohols, developing methods for their conversion into alkynes and nitriles is particularly attractive. In a previous communication, our group has reported the conversion of alcohols into alkynes via cesium oxalates based on the powerful combination of photochemistry with Ethynyl BenziodoXolones (EBXs). Herein, we report further investigations into this transformation, including our findings on the effect that backbone modification of EBXs has on the deoxyalkynylation of cesium oxalates. In addition, we disclose preliminary data on the development of new deoxycyanation and dethioalkynylation processes. We also report the serendipitous discovery of the C-H alkynylation of 1,2-dichloroethane.

Keywords: alkyne, nitrile, alcohol, photoredox catalysis, hypervalent iodine.

Introduction

Over the past two decades photoredox catalysis has emerged as a valuable tool for the generation of reactive *C*-centered radical intermediates.[1–3] Consequently, the functionalization of such species has proven to be a highly valuable, versatile, and selective strategy for the synthesis of complex and sterically hindered substrates. To access *C*-centered radicals using photoredox catalysis, a variety of redox active groups (RAGs) can be used, including carboxylates, trifluoroborates, silicates, *N*-phthalimidoyl derivatives and pyridiniums.[4] More recently, due to the broad availability of alcohols, multiple alcohol-derived RAGs have been developed for the generation of *C*-centered radicals. At the time of our study, xanthates[5,6] **1** (Scheme 1, **A**) and oxalate derivatives **2** and **3** were the main precursors for photoredox-catalyzed deoxygenation reactions. Easily oxidizable cesium oxalates **2** (1.3 V vs SCE)[7] have been used for alkylation, arylation and halogenation.[7–9] In contrast, easily reducible *N*-phthalimidoyl oxalates **3** (-1.1 V vs SCE)[10] have been used in an alkylation and an alkynylation method.[10,11] During or after the completion of our studies, important contributions have enabled the activation of DHP esters **4**,[12,13] or NHC derivatives **5**,[14] and the *in situ* activation of alcohols **6** with triphenyl phosphine has also been developed.[15] Overall, these strategies covered a variety of C-C bond formation, but only the *N*-phthalimidoyl oxalates allowed the construction of C(sp^3)-C(sp) bonds delivering alkynes **7**.[11] Unfortunately, these substrates are quite sensitive to aqueous work-up and purification by column chromatography.[10] In this regard, using oxidizable cesium oxalates **2** would present a complementary strategy to access alkynylated quaternary centers. To this end, the use of alkynylated hypervalent iodine reagents **9** seemed an interesting option. Indeed, these reagents have been reported to react efficiently with *C*-centered radicals **I** for the synthesis of diverse alkynes (Scheme 1, **B**).[16–19] Under photoredox catalysis, they are highly compatible with oxidizable substrates **8** in redox neutral photocatalytic cycles.[16,20] In 2021, we reported a deoxyalkynylation strategy based on the use of cesium oxalates **2** that could be performed under photocatalytic conditions or through the direct excitation of ArEBXs **9** (Scheme 1, **C**) with a high intensity light source (2 x 40 W at 440 nm).[21] The same year, the Xie group also developed a photocatalyzed deoxyalkynylation with cesium oxalates and EBXs.[22]

In this work, we report further details on the influence of core-modified EBX reagents (**9**) on the deoxyalkynylation of cesium oxalates (**2**) under photoredox catalysis with lower intensity irradiation (460 nm ca. 10 W) (Scheme 1, **D**). In fact, the Chen group also observed that core modifications of EBXs can have a significant effect on various radical alkynylations using $Ru(bpy)_3^{2+}$ as a photocatalyst.[23] The core-modification of these reagents has helped improving the efficiency of alkynylations under biocompatible conditions.[24] Furthermore, we also report our preliminary results on the development of two new photocatalytic processes: the deoxycyanation of cesium oxalates **2** delivering nitriles **10** and the dethioalkynylation of thiols using thiooxoacetates **11**. Finally, we disclose a preliminary investigation of a C-H alkynylation of chloroalkane **12** providing propargyl chlorides **13**, discovered serendipitously during our studies.

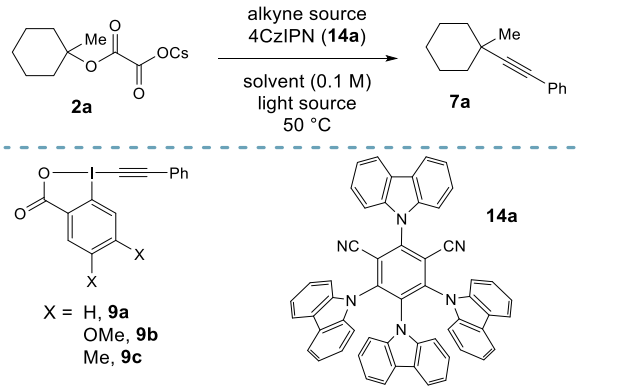


Scheme 1. State of the art: deoxygenation and photochemical alkynylations with EBXs (**A**- **C**) and this work: Influence of core-modified benziodoxolones and new transformations (**D**).

Results and Discussion

For the deoxyalkynylation strategy, we started our optimization studies using the same model substrate **2a** as previously reported by the Macmillan and Overman group[7,8] using PhEBX[25] (**9a**) as an alkyne source. Preliminary solvent and photocatalyst screening showed that DCE and 4CzIPN[26–29] (**14a**) afforded the desired compound in 55% yield (Table 1, entry 1). DMF performed as well as DCE (55% yield, entry 2), whereas THF and DME both performed poorly (<25%, entry 3). We attempted to help solubilize the cesium salt by adding 10 equivalents of H_2O, however this led to only 20% formation of **7a** (entry 4). Increasing the loading of PhEBX (**9a**) to 2.5 equiv led to a minor increase in yield (61% entry 5). At this stage we turned to modification of the backbone of PhEBX (**9a**). As described by the Chen group,[23] we tested dimethoxy-modified EBX **9b** and a dimethyl reagent **9c** that we speculated would be less electron rich, but may have improved solubility. Reagent **9b** gave the desired alkyne **7a** in 76% (entry 6) and **9c** afforded **7a** in 61% yield (entry 7) using only 1.5 equivalents. We decided to continue with **9b**. Interestingly, we found that lower intensity blue LED strips worked just as well as the Rayonnet photoreactor for this transformation (10 W vs 35 W, entry 8).

Table 1. Preliminary optimization study towards the deoxyalkynylation of **2a**

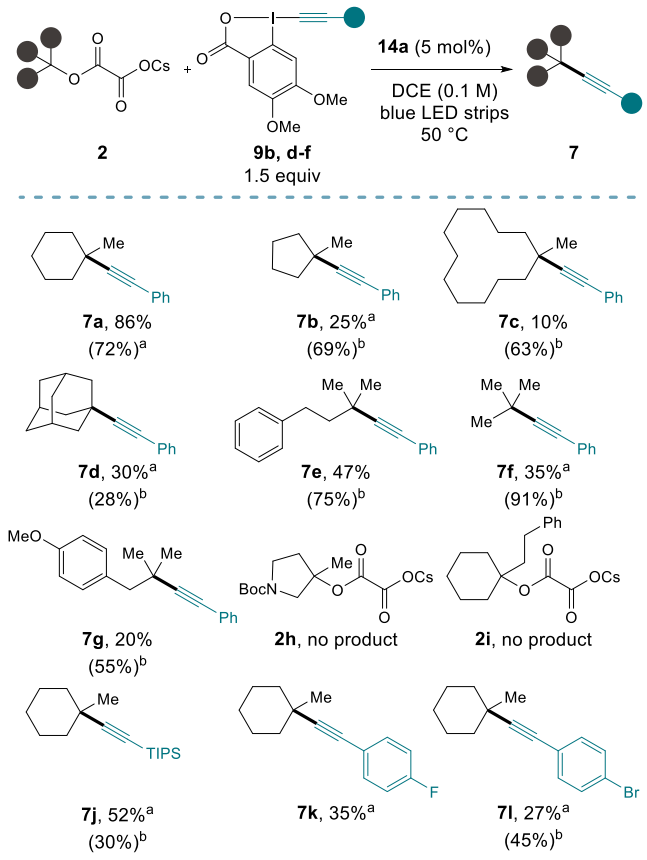


Entry	Reagent (equiv)	Solvent	Yield (%)[a]
1	**9a** (1.5)	DCE	55
2	**9a** (1.5)	DMF	55
3	**9a** (1.5)	THF or DME	<25
4[b]	**9a** (1.5)	DCE	20
5	**9a** (2.5)	DCE	61
6	**9b** (1.5)	DCE	76
7	**9c** (1.5)	DCE	61
8[c]	**9b** (1.5)	**DCE**	**70**

The reactions were performed with **2a** (0.10 mmol, 1.0 equiv), EBX (**9**), **14a** (5 mol%) in a degassed and anhydrous solvent. Irradiation for 18 hours at rt with a Rayonnet reactor (420 nm, 35 W). [a]Isolated yields. [b]Reaction was performed with 10 equiv of H_2O. [c]Reaction was performed under irradiation with 460 nm, 10 W blue LED strips.

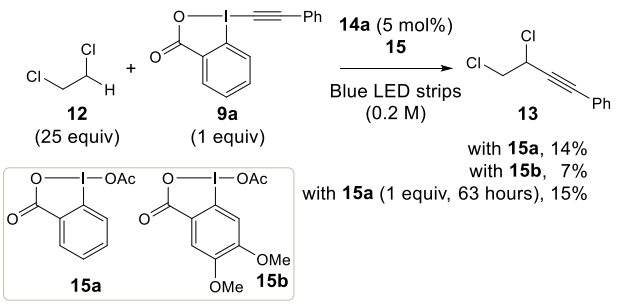
We then turned to the scope of our transformation. Surprisingly, we found that most substrates gave lower yields than the model substrate (Scheme 2). The latter performed slightly better on scope scale affording **7a** in 86% yield. 1-Methylcyclopentyl, 1-methylcyclododecyl and adamantyl alkynes **7b-d** could be accessed in 25%, 13% and 30% yield respectively. We also investigated non-cyclic substrates and found that **7e** and **7f** could be obtained in moderate 47% and 35% yield respectively, whereas the homobenzylic alkyne **7g** was formed in only 19% yield. Finally, two cesium salts **2h** and **2i** led to complex mixtures with no detectable formation of the desired alkynes. These results highlighted the lack of generality of our reaction conditions. We wondered if our conditions could tolerate modification on the side of the reagent: we synthesized three new dimethoxy core-modified EBXs (TIPS-alkyne **9d**, 4-FPhalkyne **9e** and 4-BrPhalkyne **9f**) and tested them with our model substrate **2a**. The

TIPS-alkyne could be transferred affording **7j** in 52% yield.[1] Halogen substituents on the aromatic ring delivered the desired alkynes **7k** and **7l** in 35% and 27% yield. Overall, the limitations in scope for both cesium salt and reagent showed that our optimized conditions were not broadly applicable. They worked well for the model system, but apparently minor modifications in substrate structure led to drastic drops in yield. Later, we found that the use of a higher intensity light source (2 x 40 W at 440 nm) allowed us to develop a more general process (yields are reported in parenthesis in Scheme 2).[21] It also led us to discover the direct excitation of ArEBXs, which may be occurring as a background process in our photochemical deoxyalkynylation. However, this approach was inefficient for the transfer of silyl alkynes. During our studies with this new light source, we found that for the reaction leading to alkyne **7e**, the dimethoxy reagent **9b** did not perform as well as the unmodified PhEBX reagent **9a**. Therefore, it appears that the use of core-modified reagents can lead to higher yields for specific substrates/conditions, but no generally superior reagent could be identified.



Scheme 2. Preliminary scope of the deoxyalkynylation of cesium oxalates with dimethoxy core-modified EBX reagents. The reactions were performed on 0.1 or 0.3 mmol scale with **9b** or **9d-f** (1.5 equiv) and **14a** under blue LED strip (10-15 W) irradiation for 18 hours. [a]Yields based on ^{1}H NMR analysis, the isolated yields can be found in the supporting information. [b]Yields in parentheses were obtained under the optimized conditions with a stronger light source and R-EBX as described in our previous work[21]

During our investigations with PhEBX (**9a**) for the deoxyalkynylation of cesium oxalates, we observed the alkynylation of DCE. Fuchs and co-workers had reported an example of DCE alkynylation using AIBN as an activator and an alkynyl sulfone as a radical trap.[30] However, the desired alkyne was only obtained in 29% yield. In addition to this single example, Liu and co-workers reported the HAT activation of DCM with a peroxide activator for the synthesis of 2-oxoindoles.[31] This precedence confirmed that the α-chloro hydrogen can indeed undergo abstraction and functionalization. In the deoxyalkynylation we suspected that the iodanyl radical was responsible for the HAT activation of DCE which would then be trapped by **9a**. We postulated that a combination of a photocatalyst (**14a**) and acetoxy-benziodoxolone (**15a** or **15b**) may help the generation of this radical and therefore improve the overall yield of the transformation.[32,33] To hamper the background reaction associated to the direct excitation of PhEBX (**9a**),[21] we decided to use blue LED strips (460 nm, 10 W). Irradiating PhEBX (**9a**), in presence of 4CzIPN (**14a**) with **15a** (0.3 equiv) in DCE (**12**) with this light source, we were able to obtain the alkynylated product **13** in 14% yield (Scheme 3). We then wondered if a core-modified BIOAc (**15b**) could help improve the yield of the transformation, unfortunately the desired alkyne was obtained in a lower 7% yield. Analysis of the crude mixture showed that the desired alkyne **13** seemed to be the only product of the transformation and the conversion of PhEBX (**9a**) was low. To improve the conversion, we increased the loading of **15a** and prolonged the reaction time (63 hours). Unfortunately, no improvement was observed (15%). Although the dimerization process of the EBX reagent was shut down with this light source, the increased loading of **15a** led to a highly heterogenous suspension, which may also have hampered the photocatalyzed transformation. Although the optimization of this reaction was not successful, its discovery led to a switch of solvent to DCM affording higher yield in the deoxyalkynylation using 2 x 440 nm 40 W blue LED lamps.[21]



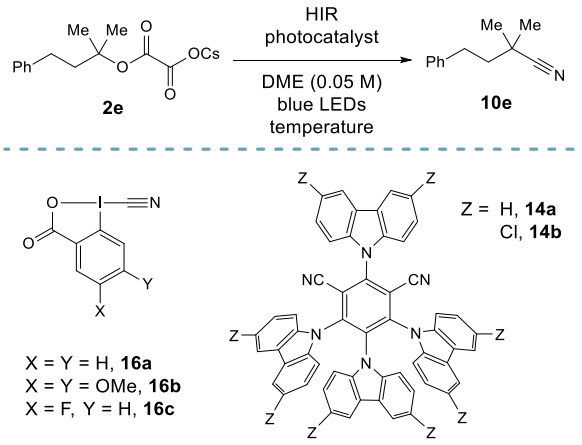
Scheme 3. Preliminary investigation of the HAT alkynylation of DCE with **9a** and **15**

While exploring the deoxyalkynylation of cesium oxalates, we were also interested in developing a deoxycyanation strategy. Indeed, decarboxylative cyanation had previously been achieved under

[1] In our previous report the desired alkyne could be obtained in only 30% with TIPS-EBX.

photoredox catalysis using CBX (Cyano BenziodoXolone, **16a**).[20] We started our optimization studies using **2e** as a model substrate to facilitate the study of this transformation both by TLC and ^{1}H NMR (Table 2). The reaction gave a cleaner reaction profile by ^{1}H NMR when cooling the reaction with an overhead ventilation (T = 28 °C). With 2 equiv of CBX (**16a**) and 4CzIPN (**14a**) as a photocatalyst the desired deoxycyanated product could be obtained in 23% yield (entry 1). Solvent screening then showed that DME gave promising results with a 39% yield of the desired product **10e** (entry 2).[2] We also found that the reaction time could be reduced to 3 hours with little change to the yield of the transformation (35% yield of **10e**, entry 3). We then wondered if core modification of CBX could help improve the yield of the transformation. We decided to test the dimethoxy-modified CBX (**16b**) and 3-fluoro-modified CBX (**16c**). In contrast to our improved results in the deoxyalkynylation strategy, the deoxycyanation with **16b** gave less than 5% yield of **10e** with the electron-rich reagent (entry 4). When turning to the electron poor reagent **16c**, we were able to obtain the desired deoxycyanated product in 21% yield (entry 5). Overall, the core modifications of CBX did not improve the yield of the transformation. We then investigated a more oxidizing photocatalyst (4ClCzIPN, **14b**) and the yield dropped slightly (30%, entry 6). Having identified early on the temperature sensitivity of the transformation, we screened further the temperature of the reaction. At higher temperatures 40 °C and 60 °C, we obtained the desired compound in 16% and 17% yield respectively (entries 7 and 8). By use of a cooled water bath, we could maintain the reaction temperature between 8 °C and 12 °C for 3 hours: this resulted in a 28% yield of the desired compound with incomplete conversion of the starting material (entry 9). As this set-up was not ideal[3] and could clearly result in reproducibility issues, we decided to attempt the transformation at 10 °C overnight using an immerged glass rod illuminated with an 8 W 420 nm LED. Unfortunately, the desired compound was obtained in only 5% yield (entry 10), we suspect this may be due to the intensity of the irradiation at the end of the glass rod which could be considerably lower than the LED itself. Finally, we tried to vary the equivalents of CBX (**16a**), both an increased (5 equiv) and decreased loading (1.5 equiv) led to poorer results (no product and 16%, entries 11 and 12). At this stage, it seemed that we were unable to improve the yield further than the 39% obtained with 2 equiv of CBX (**16a**), 4CzIPN (**14a**) at 28 °C. From a mechanistic standpoint, we suspect that the deoxycyanation may be going through a different mechanism to that of the deoxyalkynylation. Indeed, the photoredox catalyzed decarboxylative alkynylation with EBXs proceeds through the alkynylation of the radical resulting from the decarboxylation, whereas in presence of CBX this radical (α-amino or α-oxo exclusively) is oxidized to the cation, then trapped.[20] If this was also the case for the deoxycyanation, it may be that our tertiary radical generated from the deoxygenation may not be as easy to oxidize by the CBX reagent and the cyanation would be less efficient. Indeed, only very low yields were obtained for the decarboxylative cyanation of aliphatic carboxylic acids.[34]

Table 2. Optimization of the deoxycyanation of **2e** with cyanobenziodoxolones



Entry	Reagent (equiv)	Photocatalyst	Temp (°C)	Yield (%)[a]
1[b]	**16a** (2)	**14a**	28	23
2	**16a** (2)	**14a**	28	39
3[c]	**16a** (2)	**14a**	28	35
4[c]	**16b** (2)	**14a**	28	<5
5[c]	**16c** (2)	**14a**	28	21
6[c]	**16a** (2)	**14b**	28	30
7[c]	**16a** (2)	**14a**	40	16
8[c]	**16a** (2)	**14a**	60	17
9[c]	**16a** (2)	**14a**	8-14[d]	28
10[e]	**16a** (2)	**14a**	10	5
11[c]	**16a** (5)	**14a**	28	NR
12[c]	**16a** (1.5)	**14a**	28	16

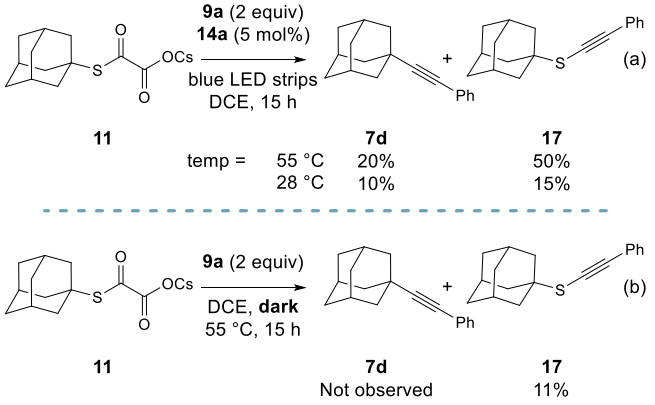
The reactions were performed with **2e** (0.10 mmol, 1.0 equiv), CBX (**16**), PC (**14**, 5 mol%) in a degassed and anhydrous solvent. Irradiation for 18 hours at rt with blue LED strips (460 nm, 10-12 W). [a]Determined by ^{1}H NMR using CH_2Br_2 as an internal standard. [b]The reaction was performed using DCE as a solvent. [c] The reaction was irradiated for 3 hours. [d]The reaction was maintained at this temperature with a cooled water bath that was renewed every 30 min. [e]The reaction was irradiated by an immerged glass rod illuminated by a 420 nm blue LED 8 W and maintained at 10 °C with a cryostat.

We were also interested in studying the conversion of thiols into alkynes. Radical desulfurization methods are of great interest with applications in native chemical ligation[35] and carbohydrate chemistry.[36,37] In addition, sulfones, sulfenates and sulfenamides have also been used to generate alkyl radicals[38–41] and dithiocarbamates have been used for the activation of alkyl chlorides for alkyl radical formation.[42,43] Finally, the direct

[2] Other solvents screened included DCE:DMF 1:1, MeOH, Acetone, THF, DCE:THF 3:1, see supporting information for more details.

[3] The temperature was maintained by changing every 20 min a cold-water bath, which was inside the LED equipped flask, considering the risk associated to having water close to electrical systems, this set-up was not further used.

dethiolation of α-thiol esters has also been reported using phosphines as a dethiolating agent.[44,45] Although these processes are highly relevant, there is, to the best of our knowledge, no photocatalytic method for the conversion of the C-S bond of thiols into a C-C bond. To this end, we synthesized the cesium thio-oxoacetate **11** and attempted the dethioalkynyation with PhEBX (**2a**, 2 equiv) and 4CzIPN (**14a**, 5 mol%) in DCE (Scheme 4, eq. a). At 50 °C, we observed the formation of two compounds: the desired dethioalkynylated product **7d** in 20% yield and the thioalkyne **17** in 50% yield. We decided to perform the reaction at 28 °C and we saw a decreased formation of both products (10% of **7d** and 15% of **17)**. However, the ratio between the two compounds had improved. We wondered if the formation of the thioalkyne resulted from a purely thermal process. Hence, we performed the reaction at 50 °C in absence of the photocatalyst in the dark. Although we did see formation of the thioalkyne **17**, it was only obtained in 11% yield (eq. b). This suggested that a thermal background process could indeed deliver the thioalkyne. However, the yield under irradiation with a photocatalyst was considerably higher (50% of **17**) at the same temperature suggesting that a photochemical pathway could potentially also deliver the thioalkyne. When turning back to the literature, we found a single study of thio-oxoacetates[46] suggesting that the first decarboxylation is an exothermic process. However, the second fragmentation, releasing carbonyl sulfide (SCO), is a thermodynamically uphill process resulting in an equilibrium between the desired alkyl radical and the thio(oxo)acyl radical. The authors concluded that the release of SCO from the thio(oxo)acyl radical may be difficult to implement experimentally. During our studies we were unable to identify other side products of the reaction. As the release of SCO may be uphill, we would expect to see formation of the alkynyl thioester resulting from trapping of the thio(oxo)acyl radical. However, this species was not detected by HRMS or ^{1}H and ^{13}C NMR analysis. This may indicate that a decarbonylation process may occur resulting in the sulfur radical, which would then be alkynylated. However, the incomplete mass balance showed that there may be an other not yet identified degradation processes. Overall, it seems difficult to optimize the dethioalkynylation by outcompeting the favored thioalkyne formation.



Scheme 4. Preliminary studies of the dethioalkynylation. The reactions were performed on 0.1 mmol scale under blue LED strip (10-15 W) irradiation for 18 hours.

Conclusions

Throughout our studies, we investigated the core-modification of EBXs and its effect on both deoxyalkynylation and deoxycyanation. Similar to the report of Chen and co-workers,[23] the trends associated to the core-modification are difficult to analyze. However, for some substrates the yield can indeed be improved with core-modification of the reagent. During our studies towards the deoxyalkynylation, we discovered the possibility to alkynylate the α-chloro position of DCE. Although our preliminary optimization studies were unfruitful, this did allow us to identify the main side reaction of the deoxyalkynylation process and hamper it to obtain optimal yields. An example of deoxycyanation in moderate yield could be also realized. In addition, we explored the oxidation-fragmentation of cesium thio-oxoacetates in the context of a dethioalkynylation. Interestingly, the desired product could be formed but was outcompeted by the formation of a thioalkyne which seems to be proceeding though a photomediated process. Further investigation on this pathway could potentially help uncover new reactivity of thiyl radicals. Overall, we believe that the findings we describe in our work will prove beneficial for further research on radical transformations with hypervalent iodine reagents. We could confirm the influence of the core structure of EBX reagents on their efficiency in photocatalytic transformations. The proof-of-concept results obtained for deoxycyanation and dethioalkynylation are promising, but also demonstrate the current limitations of the field and the need to develop more efficient transformations. New methods for the introduction of alkynes and nitriles are highly valuable for medicinal chemistry, chemical biology and materials science.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

S. G. E. A. performed experimental work and wrote the manuscript and supporting information. F le V. initiated the project, performed experimental work, and proofread and edited the manuscript and supporting information. J. W. supervised the project and proofread and edited the manuscript and supporting information. All authors have read and agreed to the published version of the manuscript.

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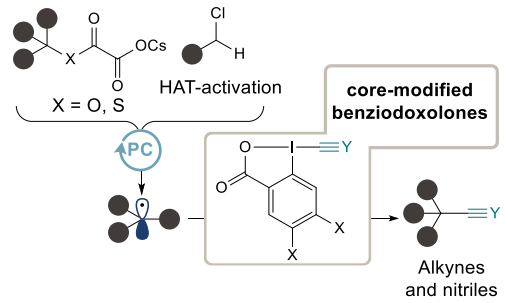

Twitter

@steph_ge_amos and @FranckF1476 at @LcsoLab @EPFL_CHEM_tweet give insights into the fine-tuning of hypervalent iodine reagents in photoredox-catalyzed reactions and preliminary results for new transformations.

Supporting Information

Exploring Photoredox-Catalyzed (Re)functionalizations with Core-Modified Benziodoxolones

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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:H2SO4: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 chloroform-*d*, acetonitrile-d^3 CD_3OD, 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 chloroform-*d*, 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.

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

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.

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.

Cyclic voltammetry experiments were performed on a Biologic SP-150 Potentiostat, with a three-electrode cell configuration: a glassy carbon electrode as the working electrode, Pt wire

as a counter electrode and an Ag/AgCl (KCl, 3M) electrode as the reference electrode. Bu_4NPF_6 was employed as the electrolyte (0.1 M).

All photochemical 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. All reactions were performed under the irradiation of blue LED strips (ca. 12 W, $\lambda_{max} \approx 460$ nm), Kessil lamps (40 W per lamp, 390, 427, 440, 467 nm) or a Rayonet reactor (for 360 nm).

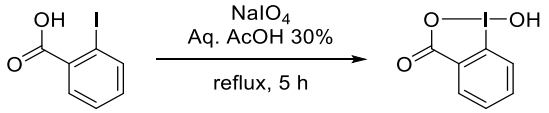
For the blue LED strips: the reactions were performed in 1.5 - 2.5 mL screw-cap vials which were stuck to the base of a crystallization dish. To the crystallization dish (a straight sided 15 cm diameter pyrex dish) were attached the blue LEDs (RUBAN LED 5MÈTRES - 60LED/M - 3528 BLEU - IP65 with Transformateur pour Ruban LED 24W/2A/12V, bought directly on RubanLED.com: 4.8 W/m: for 1 crystallisation dish: 2.5 meters were required total wattage: 12 W). The distance between the LEDs and the test tubes was approximatively 3 cm for all vials and test tubes. In order to keep the temperature as constant as possible all reactions were ventilated by use of an over-head ventilator (desk fan). Long irradiation resulted in temperature increasing up to 27°C during overnight reactions. Without cooling the temperature could rise to 60 °C by covering the dish with aluminium foil.

For the Kessil lamps: the reactions were performed in 2.5 -7.5 mL screw-cap vials, which were stuck to a glass plate, the two Kessil lamps were placed on each side of the vials. In the absence of cooling the reactions would heat up to 50 °C. With cooling by an over-head ventilator the reactions still warmed to 30 - 35 °C.

2. Synthesis of hypervalent iodine reagents

The synthesis of reagents **9a** and **16a**, **16b** and **16c** had already been described before by our group. The procedures are taken from the indicated publications.

1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (**19**)

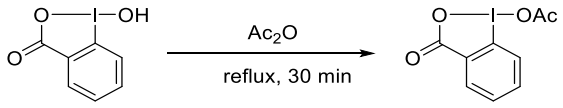


18 **19**

Following a reported procedure,[1] $NaIO_4$ (40.5 g, 189 mmol, 1.05 equiv) and 2-iodobenzoic acid (**18**) (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-*d*ried in the dark overnight to afford 1-Hydroxy-1,2-benziodoxol-3-(1*H*)-one (**19**) (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 (**15a**)



19 **15a**

Following a reported procedure,[2] compound **19** (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. The crystals were then collected and dried overnight under high vacuum to give compound **15a** (3.06 g, 10.0 mmol, 86% yield).

^{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.[2]

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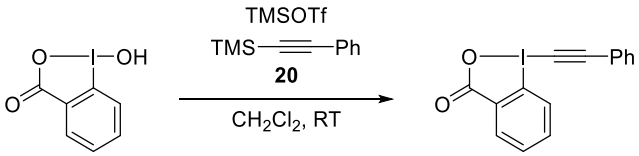
1-(Phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (**9a**)

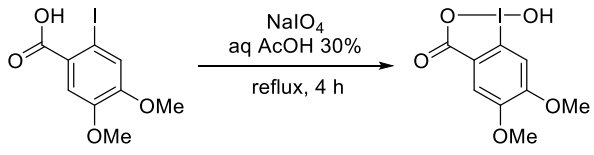


19 **9a**

Following a reported procedure,[1,3,4,5] trimethylsilyltriflate (9.1 mL, 50 mmol, 1.1 equiv) was added dropwise to a suspension of 2-iodosylbenzoic acid (**19**) (12.1 g, 45.8 mmol, 1.0 equiv) in CH_2Cl_2 (120 mL, 0.38 M) at 0 °C. The mixture was stirred for 1 h, followed by the dropwise addition of trimethyl(phenylethynyl)silane (**20**) (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 $NaHCO_3$ (50 mL) was added and the mixture was stirred vigorously for 30 min resulting in a biphasic suspension. The suspension was diluted with $CHCl_3$ and water, the solid aggregates could be further dissolved with MeOH (1-5%). The mixture was extracted twice with $CHCl_3$. The combined organic layers were washed 3 times with "water:aq. sat. $NaHCO_3$" (1:1 v:v), and brine. The organic layer was then dried over Na_2SO_4, filtered and evaporated under reduced pressure. The resulting mixture was combined with the solid obtained by recrystallisation in EtOAc:MeOH (2:1, ca. 28 mL/g). The mixture was cooled down, filtered, washed with Et_2O and dried under high vacuum to afford PhEBX (**9a**, 6.8 g, 20 mmol, 43% yield). Colourless to off-white needle like crystals.

Mp (Dec.) 155 – 160 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) 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, Chloroform-*d*) 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.[1]

4,5-Dimethoxy-1-hydroxy-1,2-benziodoxol-3-(1H)-one (**15b**)



21 **15b**

Following a reported procedure,[6] $NaIO_4$ (840 mg, 3.95 mmol, 1.05 equiv) and 4,5-dimethoxy-2-iodobenzoic acid (**21**) (1.16 g, 3.76 mmol, 1.00 equiv) were suspended in 30% (v:v) aq.

[3] Lu, B.; Wu, J.; Yoshikai, N. *J. Am. Chem. Soc.* **2014**, *136*, 11598.
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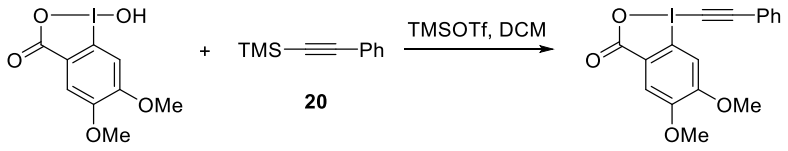
AcOH (1.8 mL in 4.5mL of H_2O). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (20 mL) and allowed to cool to rt, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 10 mL) and acetone (3 x 10 mL), and air-dried in the dark to give the pure product **15b** (1.22 g, 3.76 mmol, >99%) as a colorless solid.

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.99 (bs, 1 H, O*H*), 7.44 (s, 1 H, Ar*H*), 7.22 (s, 1 H, Ar*H*), 3.88 (bs, 6 H, OCH_3); **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 168.6, 154.1, 150.8, 124.3, 112.5, 110.9, 107.5, 56.2, 56.0. The compound was used directly in next steps with no further analysis.

4,5-Dimethoxy-1-[phenylethynyl]-1,2-benziodoxol-3(1H)-one (**9b**)



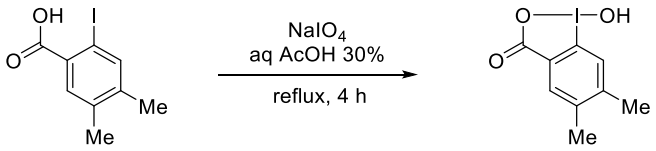
15b **9b**

Following a reported procedure,[7] trimethylsilyl triflate (1.47 mL, 8.15 mmol, 1.10 equiv) was added to a suspension of **15b** (2.40 g, 7.41 mmol, 1.00 equiv) in CH_2Cl_2 (37 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of trimethyl(phenylethynyl)silane (**20**) (1.60 mL, 8.15 mmol, 1.10 equiv). The resulting suspension was stirred for 6 h at RT, during this time a yellow suspension was formed. A saturated solution of $NaHCO_3$ (25 mL) was then added. The two layers were separated and the aqueous layer was extracted with DCM (25 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting solid was recrystallized in CH_3CN (50 mL) and a few EtOH to afford the reagent (2.41 mg, 5.90 mmol, 80%) as a colorless solid. The mother liquors was reflux in CH_3CN (4 mL), filtered and washed with cold CH_3CN and pentane and dried under high vacuum to afford the reagent **9b** (100 mg, 0.245 mmol, 3.3%) as a colorless solid. Combined yield: 81%.

Mp (Dec.) 176-179 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) (*ca* 0.08 mmol/mL) 7.89 (s, 1 H; Ar*H*), 7.70 (s, 1 H; Ar*H*), 7.60 (m, 2 H; Ar*H*), 7.50 (m, 3 H; Ar*H*), 4.05 (s, 3 H; CH_3), 3.98 (s, 3 H; CH_3). **^{13}C NMR** (101 MHz, $CDCl_3$) 166.8, 154.9, 152.2, 132.6, 130.8, 128.9, 124.4, 120.5, 113.3, 107.6, 106.3, 105.3, 56.7, 56.4, 51.2. **IR** 3079 (w), 2935 (w), 2854 (w), 2147 (w), 1742 (w), 1623 (s), 1569 (m), 1497 (s), 1442 (m), 1396 (s), 1300 (m), 1272 (s), 1215 (s), 1167 (m), 1128 (w), 1023 (m), 906 (w), 781 (m), 735 (s), 656 (w), 635 (s). **HRMS** (ESI) calcd for $C_{17}H_{14}O_4I^+$ (M+H) 408.9937, found 408.9949.

[7] Pan, Y.; Jia, K.; Chen, Y.; Chen, Y. *Beilstein J. Org. Chem.* **2018**, *14*, 1215–1221.

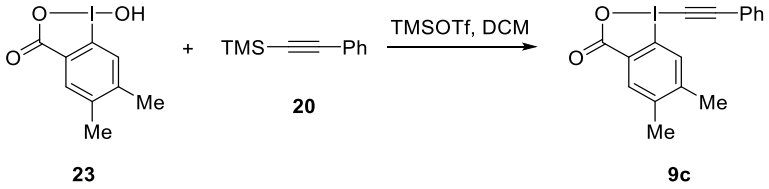
4,5-Dimethyl-1-hydroxy-1,2-benziodoxol-3-(1H)-one (**23**)



Following a reported procedure,[1] $NaIO_4$ (0.81 g, 3.8 mmol, 1.05 equiv) and 2-iodo-4,5-dimethylbenzoic acid (**22**) (1.00 g, 3.62 mmol, 1.00 equiv) were suspended in 30% (v:v) aq. AcOH (4.8 mL). The mixture was vigorously stirred and refluxed for 3 h30. The reaction mixture was then diluted with cold water (8 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 5 mL) and acetone:water (1:1) (5 mL), and N_2-dried in the dark to give the pure product **23** (1.00 g, 3.25 mmol, 90%) as a colorless solid (95% purity by ^{1}H NMR).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (s, 1H, O*H*), 7.78 (s, 1H, Ar*H*), 7.54 (s, 1H, Ar*H*), 2.38 (s, 3H, *Me*), 2.37 (s, 3H, *Me*).**^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.9, 144.2, 139.4, 131.8, 129.2, 126.3, 117.0, 20.1, 18.9. **HRMS (ESI)** calcd for $C_9H_{10}IO_3^+$ $[M+H]^+$ 292.9669; found 292.9667

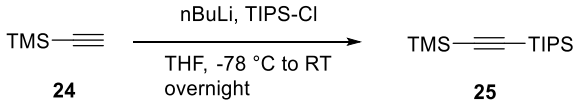
4,5-Dimethyl-1-[phenylethynyl]-1,2-benziodoxol-3(1H)-one (**9c**)



Following a modified reported procedure,[1] trimethylsilyltriflate (0.64 mL, 3.5 mmol, 1.1 eq.) was added dropwise to a stirred solution of 4,5-dimethyl-2-iodosylbenzoic **23** (0.94 g, 3.2 mmol, 1 equiv) in CH_2Cl_2 (16 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of trimethyl(phenylethynyl)silane (**20**) (0.69 mL, 3.5 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 $NaHCO_3$ (10 mL) was then added and the mixture was stirred vigorously. The two layers were separated and the aqueous layer was extracted with DCM (10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting solid was recrystallized in CH_3CN (40 mL) to afford the expected reagent (758 mg, 2.02 mmol, 63%) as a colorless solid. The mother liquors was condensed then reflux in CH_3CN (4 mL), filtered and washed with cold CH_3CN and pentane and dried under high vacuum to afford the reagent **9c** (100 mg, 0.266 mmol, 8.3%, not pure) as a colorless solid. Combined yield: 71%.

Mp (Dec.) 159.9 – 160.8 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H, Ar*H*), 7.90 (s, 1H, Ar*H*), 7.72 – 7.57 (m, 2H, Ar*H*), 7.57 – 7.40 (m, 3H, Ar*H*), 2.41 (d, *J* = 7.3 Hz, 6H, 2 x C*H*$_3$). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.1, 145.2, 141.2, 133.2, 132.8, 130.7, 128.9, 128.8, 126.5, 120.7, 112.6, 106.2, 20.7, 19.4. (1C not resolved) **IR** (ν_{max}, cm^{-1}) 3052 (m), 2900 (m), 2130 (s), 1648 (s), 1469 (s), 1382 (s), 1277 (s), 1073 (s). **HRMS** (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{17}H_{14}IO_2^+$ 377.0033; Found 377.0031.

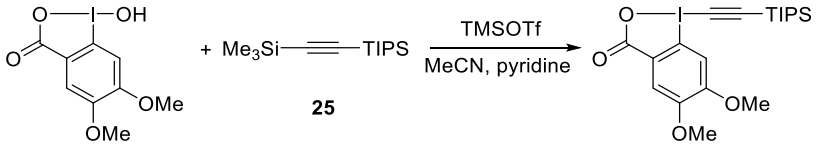
4,5-Dimethoxy-1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(1H)-one (**9d**)



24 **25**

Following a reported procedure,[8] *n*-butyllithium (2.5 M in hexanes, 28 mL, 70 mmol, 0.98 equiv) was added dropwise to a stirred solution of ethynyltrimethylsilane (**24**) (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 **25** (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.[8]



15b **9d**

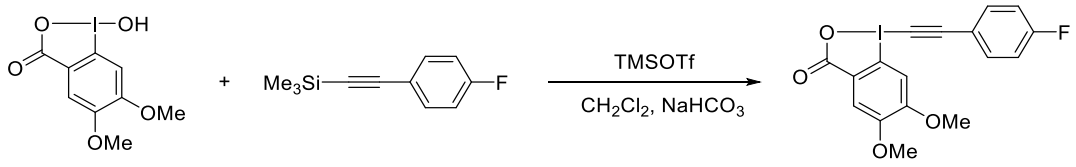
Following a modified procedure,[7] trimethylsilyltriflate (400 µL, 2.20 mmol, 1.1 equiv, freshly distilled) was added dropwise to a stirred solution of **15b** (648 mg, 2.00 mmol, 1.0 equiv) in acetonitrile (10 mL). After 2 min, (trimethylsilyl)(tri*iso*-propylsilyl)acetylene (**25**) (560 mg, 2.20 mmol, 1.1 equiv) was added dropwise, followed, after 20 min, by the addition of pyridine (180 µL, 2.20 mmol, 1.1 equiv). The mixture was stirred 20 min. The solvent was then removed under reduced pressure and the yellow crude oil was dissolved in dichloromethane (20 mL).

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

The organic layer was washed with 1 M HCl (20 mL) and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (40 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Recrystallization from acetonitrile (*ca* 8 mL) and wash with hexanes afforded **9d** (575 mg, 1.18 mmol, 59%) as colorless cristals.

Mp (Dec.) 180-183°C. **^{1}H NMR** (400 MHz, $CDCl_3$) (*ca* 0.09 mmol/mL) 7.83 (s, 1 H, Ar*H*), 7.61 (s, 1 H, Ar*H*), 3.99 (s, 3 H, OMe), 3.97 (s, 3 H, OMe), 1.14 (m, 21 H, TIPS). **^{13}C NMR** (101 MHz, $CDCl_3$) 166.7, 154.9, 152.2, 124.5, 113.8, 113.2, 107.8, 104.7, 66.0, 56.7, 56.5, 18.5, 11.2. **IR** 2945 (w), 1616 (m), 1569 (w), 1497 (m), 1464 (w), 1396 (m), 1317 (w), 1269 (m), 1215 (m), 1181 (w), 1129 (w), 1026 (w), 921 (w), 884 (w), 778 (w), 734 (m), 708 (m), 639 (s). **HRMS** (ESI) calcd for $C_{20}H_{30}O_4ISi^+$ (M+H) 489.0958, found 489.0950.

4,5-Dimethoxy-1-[(4-fluorophenyl)ethynyl]-1,2-benziodoxol-3(1H)-one (**9e**)

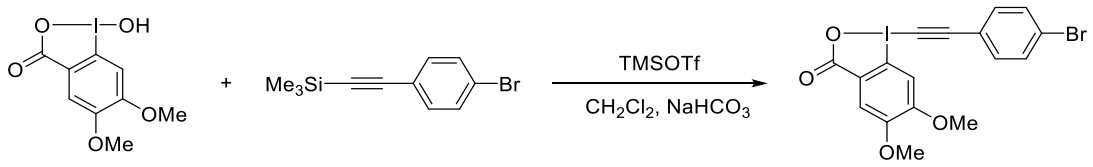


15b **26** **9e**

Following a modified procedure,[7] trimethylsilyl trifluoromethanesulfonate (0.398 mL, 2.20 mmol) was added to a suspension of **15b** (0.648 g, 2.000 mmol) in CH_2Cl_2 (10 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of ((4-fluorophenyl)ethynyl)trimethylsilane **26** (0.446 mL, 2.20 mmol). The resulting suspension was stirred for 6 h at RT, during this time a yellow suspension was formed. A saturated solution of $NaHCO_3$ (5 mL) was then added. The two layers were separated and the aqueous layer was extracted with DCM (5 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting solid was recrystallized in CH_3CN (10 mL) and to afford **9e** (570 mg, 1.33 mmol, 67%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H, ArH), 7.62 (s, 1H, ArH), 7.62 – 7.48 (m, 2H, ArH), 7.24 – 7.05 (m, 2H, ArH), 4.29 – 3.69 (m, 6H, dMeO). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.9, 163.9 (d, *J* = 254.0 Hz), 155.0, 152.3, 134.9 (d, *J* = 8.8 Hz), 124.4, 116.6 (d, *J* = 3.9 Hz), 116.4 (d, *J* = 22.4 Hz), 113.3, 107.6, 105.2 (d, *J* = 13.5 Hz), 56.7, 56.4, 51.4 (d, *J* = 1.2 Hz). 1 carbon is not resolved. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}FIO_4^+$ 426.9837; Found 426.9841.

4,5-Dimethoxy-1-[(4-bromophenyl)ethynyl]-1,2-benziodoxol-3(1H)-one (**9f**)

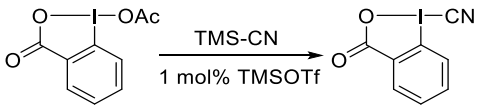


15b **27** **9f**

Following a modified procedure,[7] trimethylsilyl trifluoromethanesulfonate (0.398 mL, 2.20 mmol) was added to a suspension of **15b** (0.648 g, 2.000 mmol) in CH_2Cl_2 (37 mL) at RT. The resulting yellow mixture was stirred for 1 h, followed by the dropwise addition of ((4-bromophenyl)ethynyl)trimethylsilane **27** (0.557 g, 2.20 mmol) (solution in 1 mL DCM, rinced with 0.5 mL). The resulting suspension was stirred for 6 h at RT, during this time a yellow suspension was formed. A saturated solution of $NaHCO_3$ (25 mL) was then added. The two layers were separated and the aqueous layer was extracted with DCM (25 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting solid was recrystallized in CH_3CN (50 mL) and a few drops EtOH to afford the reagent **9f** (800 mg, 1.64 mmol, 82%) as a colorless solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 (s, 1H, Ar*H*), 7.70 – 7.52 (m, 3H, ArH), 7.52 – 7.37 (m, 2H, Ar*H*), 4.16 – 3.67 (m, 6H, dMeO). **^{13}C NMR** (101 MHz, Chloroform-d) δ 166.8, 155.0, 152.3, 133.9, 132.3, 125.6, 124.4, 113.3, 107.6, 105.2, 104.9, 56.7, 56.5. 2 carbons are not resolved. **HRMS** (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{13}{}^{79}BrIO_4{}^+$ 486.9036; Found 486.9040.

1-Cyano-1,2-benziodoxol-3-(1H)-one (**16a**)

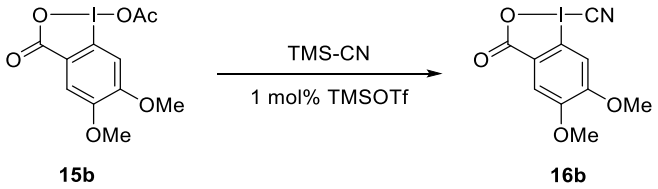


15a **16a**

Following a reported procedure,[6] **15a** (3.50 g, 11.4 mmol, 1.00 equiv.) was dissolved under nitrogen in dry DCM (60 mL, 0.19 M). To the clear colourless solution was added via syringe trimethylsilyl cyanide (TMSCN, 3.0 mL, 23 mmol, 2.00 equiv.) over a five minute time period, then trimethylsilyl trifluoromethanesulfonate (TMSOTf, 21 µL, 0.11 mmol, 0.01 equiv.). Precipitation occurred within 5 min and the reaction mixture was stirred at room temperature and under nitrogen for 30 min to ensure the completion of the reaction. The resulting thick white suspension was diluted with hexane (5 mL) before being filtered and the solid was washed with hexane (3 x 20 mL) and dried *in vacuo* affording **16a** (96%, 2.99 g, 11.0 mmol).

^{1}H NMR (400 MHz, DMSO-d6) δ 8.29 (d, J = 8.3 Hz, 1 H, Ar*H*), 8.13 (dd, *J* = 7.4, 1.7 Hz, 1 H, Ar*H*), 8.06-7.97 (m, 1 H, Ar*H*), 7.88 (t, *J* = 7.3 Hz, 1 H, Ar*H*). **^{13}C NMR** (101 MHz, DMSO-d6) δ 166.7, 136.5, 132.0, 131.9, 130.2, 127.8, 117.5, 87.9. The data correspond to those reported in literature.[6]

4,5-Dimethoxy-1-Cyano-1,2-benziodoxol-3-(1H)-one (**16b**)

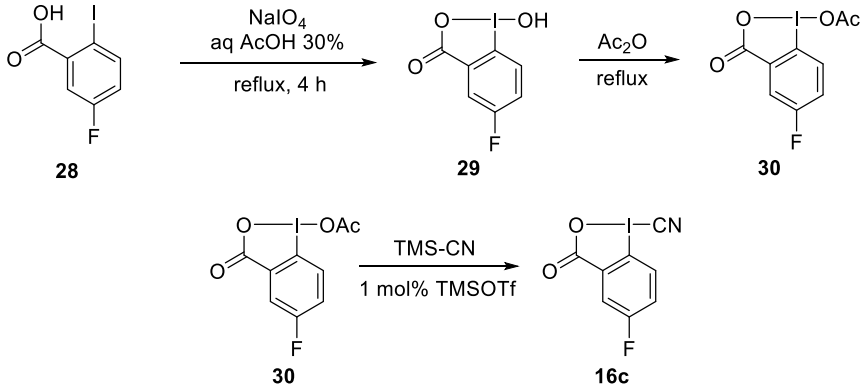


15b **16b**

Following a reported procedure,[6] 4,5-dimethoxy-1-acetoxy-1,2-benziodoxol-3-(1*H*)-one (**15b**, 92 mg, 0.251 mmol, 1.00 equiv.) was dissolved under nitrogen in dry dichloromethane (2 mL). To the clear colorless solution was added *via* syringe trimethylsilyl cyanide (TMS-CN, 67 µL, 0.50 mmol, 2.00 equiv.) over a five minute time period, then trimethylsilyl trifluoromethanesulfonate (TMS-OTf, 0.90 µL, 5.03 µmol, 0.02 equiv.). Precipitation occurred within 5 min and the reaction mixture was stirred at room temperature and under nitrogen for 30 min to ensure the completion of the reaction. The resulting thick white suspension was diluted with hexane (5 mL) before being filtered and the solid was washed with hexane (3 x 20 mL) and dried *in vacuo* affording **16b** (75 mg, 0.225 mmol, 90 %) as a white solid.

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 7.63 (s, 1H, Ar*H*), 7.53 (s, 1H, Ar*H*), 3.93 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 166.6, 155.2, 151.9, 123.1, 112.7, 109.2, 107.0, 88.7, 56.2, 55.0. The characterization data is in accordance with reported literature values.[6]

5-Fluoro-1-Cyano-1,2-benziodoxol-3-(1H)-one (**16c**)



28 **29** **30** **30** **16c**

Following a reported procedure, [2] $NaIO_4$ (760 mg, 3.55 mmol, 1.05 equiv) and 5-fluoro-2-iodobenzoic acid (**28**) (900 mg, 3.38 mmol, 1.00 equiv) were suspended in 30% (v:v) aq. AcOH (1.8 mL) / H_2O (4.5 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (180 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 10 mL) and acetone (3 x 10 mL), and air-dried in the dark to give the pure product **29** (908 mg, 3.22 mmol, 95%) as a colorless solid.

^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 8.25 (bs, 1 H, O*H*), 7.90 – 7.78 (m, 2 H, Ar*H*), 7.75 (dd, *J* = 8.4, 2.5 Hz, 1 H, Ar*H*). **^{13}C NMR** (100 MHz, $(CD_3)_2SO$) δ 166.7 (d, *J* = 2.6 Hz), 164.0 (d, *J* = 248.3 Hz), 134.2 (d, *J* = 7.5 Hz), 128.5 (d, *J* = 8.7 Hz), 121.98 (d, *J* = 23.9 Hz), 117.4 (d, *J* = 23.6 Hz), 114.4. The compound was used in the next step with no further analysis.

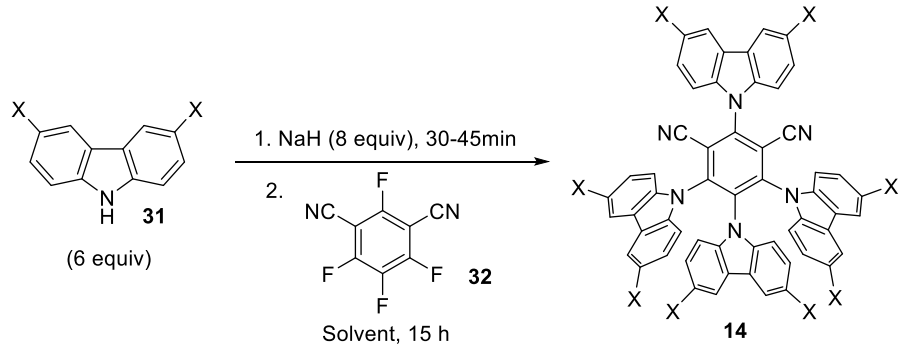
Following a reported procedure,[2] hypervalent iodine precursor **29** (800 mg, 2.84 mmol, 1.00 equiv.) was suspended in acetic anhydride (2.80 mL, 29.7 mmol, 10.5 equiv) and heated to reflux for 30 minutes. The resulting clear, slightly yellow solution was slowly let to cool down to room temperature and then cooled to 0 °C for 30 minutes. The white suspension was filtered and the filtrate was again cooled to 0 °C for 30 minutes. The suspension was once again filtered and the combined two batches of solid product were washed with hexane (2 x 20 mL) and dried in vacuo affording **30** (825 mg, 2.55 mmol, 90%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H, Ar*H*), 7.64 (ddd, *J* = 9.1, 7.7, 2.9 Hz, 1H, Ar*H*), 2.26 (s, 3H, OC(O)*Me*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 166.7 (d, *J* = 2.9 Hz), 165.0 (d, *J* = 254.5 Hz), 131.7 (d, *J* = 8.0 Hz), 131.0 (d, *J* = 8.1 Hz), 123.7 (d, *J* = 24.0 Hz), 120.0 (d, *J* = 24.3 Hz), 111.2 (d, *J* = 2.3 Hz), 20.2. The compound was used in the next step with no further analysis.

Following a reported procedure,[6] **30** (750 g, 2.31 mmol, 1.00 equiv.) was dissolved under nitrogen in dry dichloromethane (15 mL). To the clear colorless solution was added *via* syringe trimethylsilyl cyanide (TMS-CN, 0.62 mL, 4.6 mmol, 2.0 equiv.), over a five minute time period, then trimethylsilyl trifluoromethanesulfonate (TMS-OTf, 4.2 µL, 23 µmol, 0.010 equiv.). Precipitation occurred within 5 min and the reaction mixture was stirred at room temperature and under nitrogen for 30 min to ensure the completion of the reaction. The resulting thick white suspension was diluted with hexane (5 mL) before being filtered and the solid was washed with hexane (3 x 20 mL) and dried *in vacuo* affording **16c** (610 mg, 2.10 mmol, 91 %) as a white solid.

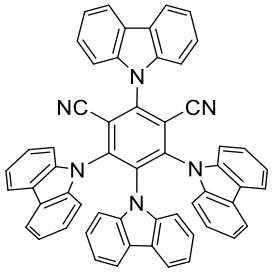
Mp. 181.1 – 184.1°C (decomp). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.25 (dd, *J* = 8.9, 4.2 Hz, 1H, Ar*H*), 7.99 – 7.75 (m, 2H, Ar*H*). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 165.3 (d, *J* = 2.4 Hz), 164.6 (d, *J* = 251.5 Hz), 133.1 (d, *J* = 7.7 Hz), 130.1 (d, *J* = 8.9 Hz), 123.8 (d, *J* = 24.5 Hz), 118.4 (d, *J* = 24.1 Hz), 111.4, 87.4. **IR** (solid) 3870 (s), 3740 (s), 3686 (s), 3620 (m), 3435 (w), 3335 (w), 3227 (w), 3109 (w), 2988 (w), 2914 (w), 2360 (m), 2162 (w), 2005 (w), 1926 (w), 1865 (w), 1739 (m), 1702 (m), 1647 (m), 1518 (s), 1457 (m), 1419 (m), 1306 (m), 1141 (w), 1025 (s), 823 (w). **HRMS** (ESI) calcd for $C_8H_4FINO_2^+$ $[M+H]^+$ 291.9265; found 291.9270.

3. GP1: Synthesis of the photocatalysts



Following a reported procedure,[9] Sodium hydride (60% suspension in mineral oil, 8.0 equiv) was added slowly to a stirred solution of substituted-carbazole **31** (5.0 equiv) in dry THF (0.05 M) under a nitrogen atmosphere at RT After 30 min, 2,4,5,6-tetrafluoroisophthalonitrile **32** (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, **14a**)

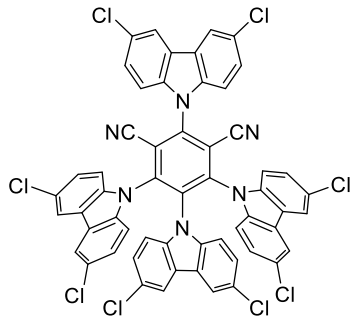


Following **GP1** and starting from 9*H*-carbazole **31a** (X = H, 1.67 g, 10.0 mmol, 5.00 equiv), sodium hydride (0.60 g, 15 mmol, 7.5 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile **32** (0.40 g, 2.0 mmol) in 40 mL of THF. Recrystallisation (Hexanes:CH_2Cl_2 (1:1, 90 mL)) afforded the crude product as a yellow powder. Column chromatography afforded 2,4,5,6-tetra(9H-carbazol-9-yl)isophthalonitrile (**14a**) 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, Chloroform-*d*) 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, Chloroform-*d*) 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 Chloroform-*d* are consistent with reported data.[10]

[9] Le Vaillant, F.; Garreau, M.; Nicolai, S.; Gryn'ova, G.; Corminboeuf, C.; Waser, J. *Chem. Sci.* **2018**, *9*, 5883–5889.
[10] Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234.

(2r,4s,5r)-2,4,5,6-Tetrakis(3,6-dichloro-9*H*-carbazol-9-yl)isophthalonitrile (4ClCzIPN, **14b**)



Following **GP1** and starting from 3,6-*d*ichloro-9*H*-carbazole **31b** (X = Cl, 1.96 g, 6.00 mmol, 6.0 equiv), sodium hydride (320 mg, 8.00 mmol, 8.0 equiv) and 2,4,5,6-tetrafluoroisophthalonitrile **32** (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 (**14b**) as a bright yellow crystalline solid (830 mg, 0.780 mmol, 87 % yield).

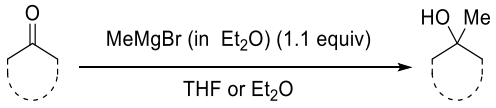
Rf (Hexane:CH_2Cl_2 1:1) 0.25. (yellow spot on TLC). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.60 (d, *J* = 2.1 Hz, 2H, Ar*H*), 8.15 (d, *J* = 2.1 Hz, 4H, Ar*H*), 8.08 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.87 (dd, *J* = 8.8, 2.1 Hz, 2H, Ar*H*), 7.80 (d, *J* = 2.2 Hz, 2H, Ar*H*), 7.69 (d, *J* = 8.8 Hz, 4H, Ar*H*), 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. **HRMS** (ESI) calcd for $C_{56}H_{24}Cl_8N_6$ [M+] 1059.9565; found 1059.9573.

4. Deoxyalkynylation

Synthesis of tertiary alcohols

Alcohols for substrates **2a, 2b, 2d**-**f** were purchased from commercial sources (Sigma-Aldrich, Acros, TCI, abcr) and used directly without prior purification.

GP2: Synthesis of tertiary alcohols from ketones

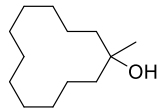


33 **34**

An oven dried two-necked flask, equipped with a magnetic stirrer, was charged with the ketone **33** (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 **34**.

Methylcyclododecan-1-ol (**34c**)



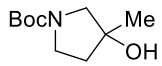
Following **GP2**: from cyclododecanone (**33c**, 1.00 g, 5.49 mmol, 1.0 equiv) in Et_2O (25 mL, 0.2 M) using methylmagnesium bromide (3.0 M in Et_2O, 2.0 mL, 6.00 mmol, 1.1 equiv) diluted with THF (4.0 mL).

Column chromatography (SiO_2, 10% EtOAC in Pentane) afforded methylcyclododecan-1-ol **34c** (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, C*H*$_2$), 1.45 – 1.25 (m, 20 H, C*H*$_2$), 1.17 (s, 3 H, C*H*$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 73.8, 36.3, 29.2, 26.6, 26.2, 22.7, 22.2, 20.1.

N-Boc-3-hydroxy-3-methyl pyrrolidine (**34h**)



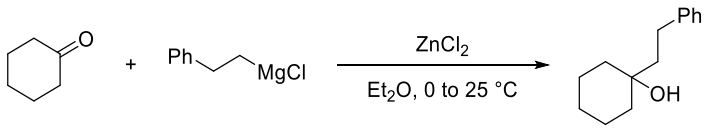
Following **GP2**: *N*-Boc pyrrolidin-3-one (**33h**, 2.04 g, 11.01 mmol, 1.0 equiv.) in anhydrous Et_2O (20 ml, 0.55 M) using methylmagnesium bromide (3.0 M in Et_2O, 3.7 mL, 11 mmol, 1.1 equiv).

Column chromatography (SiO_2, hexanes:EtOAc 1:1 ratio) afforded *N*-Boc-3-hydroxy-3-methyl pyrrolidine (**34h**, 604 mg, 5.20 mmol, 52 %) as a colourless oil. The NMR data was collected and the compound was used in the next step without further analysis.

Rf (hexanes:EtOAc 1:1) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.53 – 3.43 (m, 2H), 3.37 (dd, *J* = 11.4, 1.6 Hz, 1H), 3.22 (d, *J* = 11.5 Hz, 1H), 1.93 – 1.73 (m, 2H), 1.45 (s, 9H), 1.40 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.7, 79.3, 58.8, 44.8, 39.2, 28.5, 28.4, 25.4.

1-Phenethylcyclohexanol (**34i**)

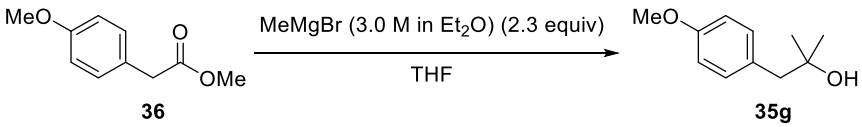


33i **35** **34i**

Following a modified reported procedure,[11] a 20 mL round-bottomed test tube was charged with zinc(II) chloride (0.263 g, 1.93 mmol, 25 mol%), sealed, and evacuated. Diethyl ether (dry; 10 mL) was then added via syringe, followed by cyclohexanone **33i** (0.80 mL, 7.7 mmol, 1.0 equiv). The solution was cooled to 0 °C (ice-water bath) and phenethylmagnesium chloride **35** (1.0 M in THF; 9.3 mL, 9.3 mmol, 1.2 equiv) was then added dropwise. Stirring was continued at 0 °C for 2 hours. The mixture was then warmed to room temperature and stirred overnight. After 20 hours, the initially grey solution converted into a pale grey suspension. At this point, the reaction was quenched by cautious addition of sat. aq. NH_4Cl (20 mL). The aqueous layer was extracted with ether (3 x 20 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The resulting crude oil was submitted to column chromatography (Biotage, 40 g SiO_2; EtOAc in pentane, 5 to 20%) to furnish 1-phenethylcyclohexanol **34i** (0.423 g, 2.07 mmol, 27% yield) as a colorless solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 - 7.23 (m, 2H), 7.24 - 7.14 (m, 3H), 2.77 - 2.63 (m, 2H), 1.84 - 1.70 (m, 2H), 1.67 - 1.55 (m, 5H), 1.55 - 1.42 (m, 2H), 1.39 - 1.17 (m, 1H), 1.24 (br s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.9, 128.4, 128.4, 125.7, 71.4, 44.3, 37.5, 29.4, 25.8, 22.3. The values of the NMR spectrum are in accordance with reported literature data.[12]

1-(4-Methoxyphenyl)-2-methylpropan-2-ol (**34g**)



36 **35g**

An oven dried two necked flask, equipped with a magnetic stirrer, was charged with **36** (1.0 mL, 6.3 mmol, 1.0 equiv) and dissolved in anhydrous THF (60 mL, ca. 1.0 M). The reaction was cooled to 0 °C with an ice bath. The methyl magnesium bromide solution (3 M in Et_2O) (4.8 mL, 14 mmol, 2.3 equiv) was diluted to 1 M with THF (10 mL) and added dropwise to the cooled solution *via* syringe. The reaction was left to stir at room temperature overnight (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 crude was purified by column chromatography (SiO_2, pentane:EtOAc 9:1, 4:1, *p*-

[11] Hatano, M.; Suzuki, S.; Ishihara, K. *J. Am. Chem. Soc.* **2006**, *128*, 9998.
[12] Yus, M.; Martínez, P.; Guijarro, D. *Tetrahedron* **2001**, *57*, 10119.

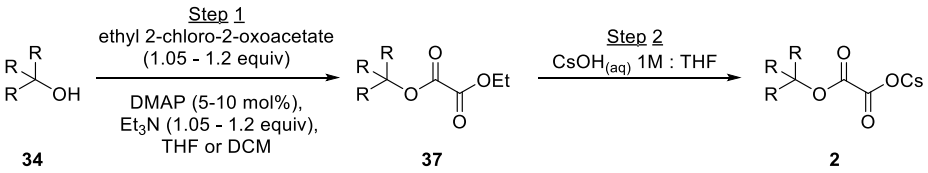
Anisaldehyde stain blue to purple and black spots) affording the desired alcohol (**34g**, 0.898 g, 4.98 mmol, 79 %).

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 consistent with the reported data.[13]

Synthesis of cesium salts

GP3: Synthesis of cesium salts from tertiary alcohols



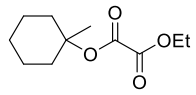
Step 1: Following a modified reported procedure,[14] a two necked round bottomed flask, equipped with a magnetic stirrer, was charged with THF or CH_2Cl_2 (0.1 or 0.2 M),[15] DMAP (0.15 mmol, 5 mol%), the tertiary alcohol **34** (3.00 mmol, 1.00 equiv) and triethylamine (1.05 - 1.2 equiv) were then added. 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 **37**.

Step 2: Following a modified reported procedure,[14] a round-bottom flask was charged with ethyl oxoacetate **37** (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

[13] Okamura, T.; Egoshi, S.; Dodo, K.; Sodeoka, M.; Iwabuchi, Y.; Kanoh, N. *Chem. – Eur. J.* **2019**, *25*, 16002–16006.
[14] Nawrat, C. C.; Jamison, C. R.; Slutskyy, Y.; MacMillan, D. W. C.; Overman, L. E. *J. Am. Chem. Soc.* **2015**, *137*, 11270–11273.
[15] 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.

immediately under reduced pressure (T = 55°C - 60 °C: P = 300 mbar to 20 mbar).[16] 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 **2**.

Ethyl 2-(1-methylcyclohex-1-yl)oxy-2-oxoacetate (**37a**)



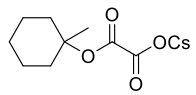
37a was synthesized following step 1 of **GP3** in THF (90 mL, 0.1 M) using 1-methylcyclohexan-1-ol (**34a**, 1.1 mL, 8.8 mmol, 1.0 equiv), DMAP (107 mg, 0.876 mmol, 0.1 equiv) triethylamine (1.50 mL, 10.5 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (1.20 mL, 10.5 mmol, 1.2 equiv).

Column chromatography (SiO_2, 2% EtOAc in Pentane) afforded ethyl (1-methylcyclohexyl) oxalate (**37a**, 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_2CH_2), 2.21 – 2.18 (m, 2H, CH_2), 1.58 – 1.44 (m, 8 H, CH_2), 1.55 (s, 3H, CH_3), 1.35 (t, *J* = 7.12 Hz, 3 H, $CO_2CH_2CH_3$). **^{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

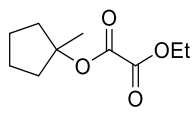
Cesium 2-(1-methylcyclohex-1-yl)oxy-2-oxoacetate (**2a**)



2a was synthesized following step 2 of **GP3** in THF (5.0 mL, 0.1 M) using ethyl (1-methylcyclohexyl) oxalate (**37a**, 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 (**2a**, 1.4 g, 4.4 mmol, 88%) as a colorless 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-methylcyclopent-1-yl)oxy-2-oxoacetate (**37b**)



37b was synthesized following step 1 of **GP3** in THF (16 mL, 0.2 M) using 1-methylcyclopentan-1-ol (**34b**, 337 mg, 3.36 mmol, 1.0 equiv), DMAP (21 mg, 0.17 mmol, 5 mol%), triethylamine (0.56 mL,

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

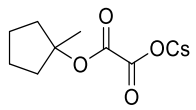
11 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.45 mL, 11 mmol, 1.2 equiv).

Column chromatography (SiO_2, pentane:EtOAc 9:1 to 8:2) afforded ethyl (1-methylcyclopentan-1-yl) oxalate (**37b**, 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.

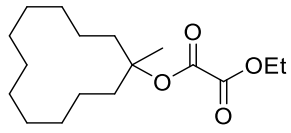
Cesium 2-(1-methylcyclopent-1-yl)oxy-2-oxoacetate (**2b**)



2b was synthesized following step 2 of **GP3** in THF (1.2 mL, 0.1 M) using ethyl (1-methylcyclopent-1-yl) oxalate (**37b**, 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 (**2b** 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.[14]

Ethyl (1-methylcyclododecyl) oxalate (**37c**)



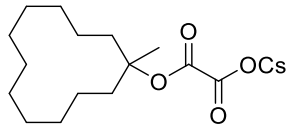
37c was synthesized following step 1 of **GP3** in THF (25 mL, 0.1 M) using 1-methylcyclododecan-1-ol (**34c**, 500 mg, 2.52 mmol, 1.0 equiv), DMAP (31 mg, 0.25 mmol, 10 mol%), triethylamine (0.42 mL, 3.0 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.34 mL, 3.0 mmol, 1.2 equiv).

Column chromatography (SiO_2, 20% EtOAc in Pentane) afforded ethyl (1-methylcyclododecyl) oxalate (**37c**, 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$_2$C*H*$_2$), 2.10 – 1.98 (m, 2H, C*H*$_2$), 1.74 – 1.61 (m, 2H, C*H*$_2$), 1.55 (s, 3H, C*H*$_3$), 1.49 – 1.23 (m, 21H, C*H*$_2$ + CH$_2$C*H*$_3$). **^{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.

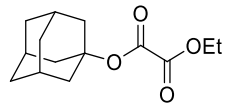
Cesium 2-((1-methylcyclododecyl)oxy)-2-oxoacetate (**2c**)



2c was synthesized following step 2 of **GP3** in THF (1.0 mL, 0.1 M) using ethyl (1-methylcyclododecyl) oxalate (**37c**, 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 (**2c**, 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, C*H*$_2$), 1.56 – 1.42 (m, 2H, C*H*$_2$), 1.38 (s, 3H, C*H*$_3$), 1.34 – 1.18 (m, 18H, C*H*$_2$). **^{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 2-(((1S,3S)-adamantan-1-yl)oxy)-2-oxoacetate (**37d**)



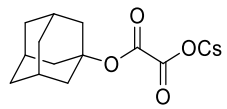
37d was synthesized following step 1 of **GP3** in DCM (25 mL, 0.1 M) using adamant-1-ol (**34d**, 378 mg, 2.48 mmol, 1.0 equiv), DMAP (30.4 mg, 248 mmol, 10 mol%), triethylamine (0.41 mL, 3.0 mmol, 1.2 equiv) and ethyl chloro-oxoacetate (0.34 mL, 3.0 mmol, 1.2 equiv).

Column chromatography (SiO_2, 15% EtOAc in Pentane) afforded ethyl 2-(((1S,3S)-adamantan-1-yl)oxy)-2-oxoacetate (**37d**, 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, OC*H*$_2$CH$_3$), 2.19 (d, *J* = 2.7 Hz, 9H, ad-C*H*$_x$), 1.76 – 1.55 (m, 6H, ad-C*H*$_x$), 1.36 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$). **^{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.

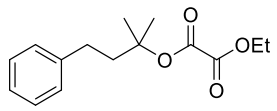
Cesium 2-(((1S,3S)-adamantan-1-yl)oxy)-2-oxoacetate (**2d**)



2d was synthesized following step 2 of **GP3** in THF (2.5 mL, 0.1 M) using ethyl 2-(((1*S*,3*S*)-adamantan-1-yl)oxy)-2-oxalate (**37d**, 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 (**2d**, 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, C*H*$_2$), 1.64 – 1.59 (m, 6H, C*H*$_2$). **^{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-(2-methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**37e**)



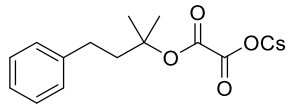
37e was synthesized following step 1 of **GP6** in THF (90 mL, 0.1 M) using 2-methyl-4-phenylbutan-2-ol (**34e**, 1.6 mL, 9.1 mmol, 1 equiv), DMAP (0.055 g, 0.46 mmol, 5 mol%), triethylamine (1.3 mL, 9.6 mmol, 1.05 equiv) and ethyl chloro-oxoacetate (1.1 mL, 9.6 mmol, 1.05 equiv).

Column chromatography (SiO_2, pentane:EtOAc 85:15) afforded ethyl (2-methyl-4-phenylbutan-2-yl) oxalate (**37e**, 2.00 g, 7.57 mmol, 83%) as a colorless oil.

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.

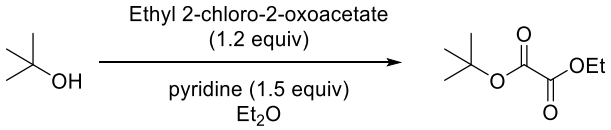
Cesium 2-(2-methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**2e**)



2e was synthesized following step 2 of **GP6** in THF (6.5 mL, 0.1 M) using ethyl (2-methyl-4-phenylbutan-2-yl) oxalate (**37e**, 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 (**2e**, 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 (tert-butyl)oxy-2-oxoacetate (**37f**)

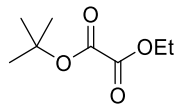


5.8c **5.10c**

Following a reported procedure,[17] ethyl 2-chloro-2-oxoacetate (3.6 mL, 32 mmol, 1.2 equiv) was added to a solution of *tert*-butanol (**34f**, 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. $NaHCO_3$

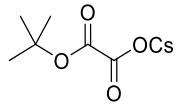
[17] Xu, Y.; McLaughlin, M.; Bolton, E. N.; Reamer, R. A. *J. Org. Chem.* **2010**, *75*, 8666–8669.

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 (**37f**, 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, OC*H*$_2$), 1.55 (s, 9H, *t*Bu), 1.36 (t, *J* = 7.1 Hz, 3H, CH_2CH_3). **^{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]

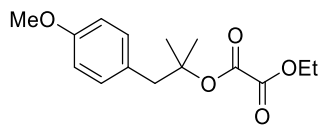
Cesium (tert-butyl)oxy-2-oxoacetate (**2f**)



2f was synthesized following step 2 of **GP3** in THF (2.1 mL, 0.1 M) using *tert*-butyl ethyl oxalate (**37f**, 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 (**2f,** 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(C*H*$_3$)$_3$). **^{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 (1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**37g**)



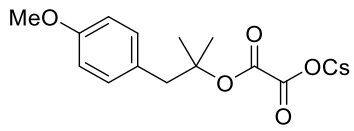
37g was synthesized following step 1 of **GP3** in DCM (30 mL, 0.1 M) using 1-(4-methoxyphenyl)-2-methylpropan-2-ol (**34g**, 500 mg, 2.77 mmol, 1.0 equiv), DMAP (33 mg, 0.28 mmol, 10 mol%), triethylamine (0.40 mL, 2.9 mmol, 1.05 equiv) and ethyl chloro-oxoacetate (0.30 mL, 2.9 mmol, 1.05 equiv).

Column chromatography (SiO_2, pentane:EtOAc 4:1) afforded ethyl (1-(4-methoxyphenyl)-2-methylpropan-2-yl) oxalate (**37g**, 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.

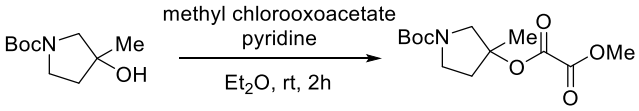
Cesium (1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**2g**)



2g was synthesized following step 2 of **GP3** in THF (0.7 mL, 0.1 M) using ethyl (1-(4-methoxyphenyl)-2-methylpropan-2-yl) oxalate (**37g**, 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 (**2g**, 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.

1-(*Tert*-butoxycarbonyl)-3-methylpyrrolidin-3-yl methyl oxalate (**37h**)

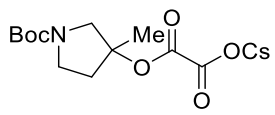


34h **37h**

Following a modified reported procedure,[17] methyl chlorooxoacetate (1.00 ml, 10.9 mmol, 2.0 equiv.) was added to a solution of **34h** (1.1 g, 5.47 mmol, 1.0 equiv.) and pyridine (0.88 ml, 11 mmol, 2.0 equiv.) in Et_2O (100 mL, 0.25 M) and the resulting yellow solution was stirred at room temperature for 4 hours. The organic phase was washed with water (2 x 25 mL) and an aqueous saturated solution of $NaHCO_3$ (25 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 (1:19 - 1:9 Et_2O:hexanes) to give the product **37h** as a colorless oil (1.5 g, 5.2 mmol, 96%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.87 (s, 4H, NCH_2 + MeO), 3.52 – 3.36 (m, 3H, NCH_2), 2.47 (m, 1H, CH_2), 2.01 (m, 1H, CH_2), 1.69 (s, 3H, Me), 1.44 (s, 9H, *t*Bu). **^{13}C NMR** (101 MHz, Chloroform-*d*) mixture of rotamers δ 158.3, 156.8, 154.3, 89.5, 88.8, 79.8, 60.4, 56.0, 53.5, 44.2, 43.8, 36.6, 28.5, 21.3, 21.1, 14.2. The values of the NMR spectra are in accordance with reported literature data.[14]

Cesium 2-((1-(*tert*-butoxycarbonyl)-3-methylpyrrolidin-3-yl)oxy)-2-oxoacetate (**2h**)

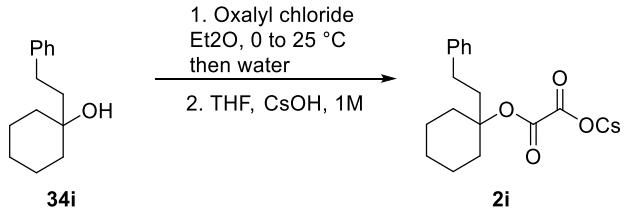


2h was synthesized following step 2 of **GP3** in THF (51 mL, 0.1 M) using ethyl (1-(tert-butoxycarbonyl)-3-methylpyrrolidin-3-yl) oxalate (**37h**, 1.5 g, 5.1 mmol, 1.0 equiv) and 1 M aq. CsOH (1.0 mL, 1.0 mmol, 1.0 equiv). Cesium 2-((1-(tert-butoxycarbonyl)-3-

methylpyrrolidin-3-yl)oxy)-2-oxoacetate (**2h**, 1.9 g, 4.7 mmol, 92%) was obtained as an off-white solid.

^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.95 – 3.84 (m, 1H, NC*H*$_2$), 3.54 – 3.45 (m, 3H, NC*H*$_2$), 2.49 (m, 1H, C*H*$_2$), 2.10 (m, 1H, C*H*$_2$), 1.67 (s, 3H, Me), 1.46 (s, 9H, *t*Bu).
The values of the ^{1}H NMR spectrum are in accordance with reported literature data.[14]

Cesium (1-phenyleth-2-yl)cyclohexan-1-yl)oxy)-2-oxoacetate (**2i**)



34i **2i**

Following a modified reported procedure,[18] 1-phenethylcyclohexanol **34i** (0.200 g, 0.979 mmol, 1.0 equiv.) was dissolved in diethyl ether (dry; 4.9 mL), and the resulting colourless solution was cooled to 0 °C (ice-water bath). A solution of oxalyl chloride (0.14 mL, 1.7 mmol, 1.7 equiv.) in diethyl ether (dry; 3.0 mL) was then added by syringe drop-wise at the same temperature. Stirring was continued at 0 °C for 2 hours. The pale yellow mixture was then warmed to room temperature and, after 1 hour, an additional amount of oxalyl chloride (0.90 mL, 1.1 equiv.) was added. Stirring was further continued at room temperature for 2 days, checking the consumption of the starting material by TLC analysis (pentane/EtOAc 9/1). After this time, the volatiles were removed under reduced pressure to furnish a greyish oil. The latter was dissolved in diethyl ether (10 mL) and treated by drop-wise addition of water (10 mL). After stirring for 5 minutes, the aqueous layer was separated and extracted with diethyl ether (3 x 10 mL). The combined ethereal extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure, to afford a pale yellow oil (0.263 g). The latter was dissolved in THF (5.0 mL) and water (0.5 mL), and aq. CsOH (1.0 M; 0.90 mL, 0.90 mmol, 0.92 equiv.) was added slowly under vigorous stirring. After stirring for 5 minutes, the solution was submitted to low pressure distillation in order to remove the THF. The resulting pale yellow aqueous solution was then washed with a 1:1 mixture of pentane/diethyl ether (3 x 15 mL). It was then concentrated under reduced pressure and co-evaporated with toluene. The resulting off-white solid was then dried under high vacuum overnight. Caesium 2-oxo-2-((1-phenethylcyclohexyl)oxy)acetate **2i** (0.346 g, 0.848 mmol) was obtained in 87% yield.

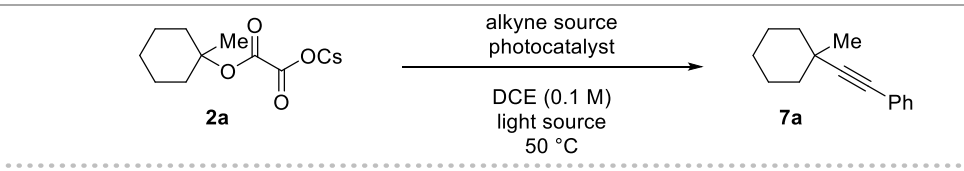
^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 7.23 (dd, *J* = 7.9, 6.9 Hz, 2H, Ph), 7.20 - 7.16 (m, 2H, Ph), 7.15 - 7.10 (m, 1H, Ph), 2.68 - 2.61 (m, 2H, PhC*H*$_2$), 2.33 (dt, *J* = 15.3, 3.7 Hz, 2H, PhCH$_2$-C*H*$_2$), 2.24 - 2.18 (m, 2H, cyclic-C*H*$_2$), 1.73 - 1.58 (m, 4H, cyclic-C*H*$_2$), 1.58 - 1.47 (m, 4H, cyclic-C*H*$_2$). **^{13}C NMR** (101

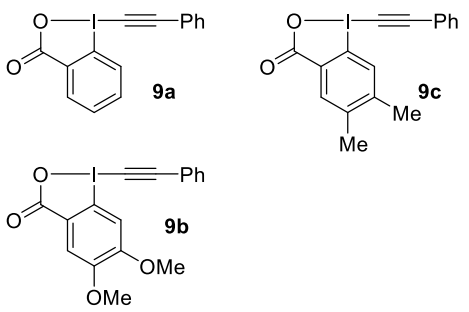
[18] Su, J. Y.; Grünenfelder, D. C.; Takeuchi, K.; Reisman, S. E. *Org. Lett.* **2018**, *20*, 4912–4916.

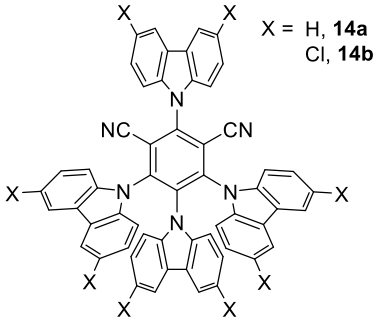
MHz, Methanol-d_4) δ 166.7, 166.4, 143.8, 129.4, 126.7, 86.4, 41.1, 35.6, 30.5, 26.7, 22.9. One carbon was not resolved. **HRMS** (ESI/QTOF) m/z: $[M]^-$ Calcd for $C_{16}H_{19}O_4^-$ 275.1289; Found 275.1289.

Optimization studies toward the deoxyalkynylation of **2a**

An oven dried test tube (5 mL) equipped with a magnetic stirrer was charged with the cesium salt **2a** (0.1 mmol, 1.00 equiv), the alkyne source and the photocatalyst (5 mol%). The reaction vial was sealed with a septum. After 3 vacuum/N_2 cycles (backfilling with Ar on the last cycle), degassed solvent was added. The upper part of the test tube and septum were wrapped in parafilm. The reactions were placed in the Rayonet reactor or a crystallization bath coated on the outside by blue LED strips (460 nm, ca. 10 W, at ca. 5 cm distance (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 crude was purified by preparative TLC (SiO_2, pentane 100%).



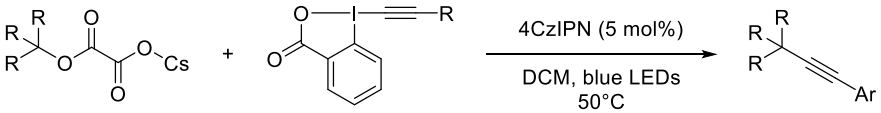




Entry	Reagent (equiv)	Photocatalyst	Solvent	Light source	Yield (%)
1	**9a** (1.5)	**14a**	DCE	Rayonet	55
2	**9a** (1.5)	**14a**	THF	Rayonet	25
3	**9a** (1.5)	**14a**	DME	Rayonet	10
4	**9a** (1.5)	**14a**	DMF	Rayonet	55
5[a]	**9a** (1.5)	**14a**	DCE	Rayonet	20
6	**9a** (2.5)	**14a**	DCE	Rayonet	61
7	**9c** (1.5)	**14a**	DCE	Rayonet	61
8	**9b** (1.5)	**14a**	DCE	Rayonet	76
9	**9b** (2.0)	**14a**	DCE	Rayonet	76
10	**9b** (1.5)	**14b**	DCE	Rayonet	70
11	**9b (1.5)**	**14a**	**DCE**	**Blue LED strips**	**70**

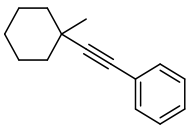
[a]Reaction was performed with 10 equiv H_2O

GP4: 4CzIPN catalysed deoxyalkynylation with dimethoxy core-modified EBXs:



An oven dried test tube (5 mL) equipped with a magnetic stirrer was charged with the cesium salt **2** (0.1 mmol or 0.3 mmol scale, 1.00 equiv), the EBX reagent (**9b**, **9d**, **9e** or **9f**, 1.5 equiv) and 4CzIPN (**14a**, 5 mol%). The reaction vial was sealed with a septum. After 3 vacuum/N2 cycles (backfilling with Ar on the last cycle), 1,2-dichloroethane (DCE, 1 M based on cesium salt) was added. The upper part of the test tube and septum were wrapped in parafilm. The reactions were placed in a crystalization bath coated on the outside by blue LED strips (460 nm, ca. 10 W, at ca. 5 cm distance (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. ^{1}H NMR yields were determined at this point by dissolving the crude in $CDCl_3$ followed by the addition of CH_2Br_2 (1 equiv), the peak used for calculation is specified for each compound. Most compounds were purified column chromatography: solid deposit (ca. 2 g SiO_2), column (Si_2O, pentane:EtOAc).

2-(1-Methylcyclohexyl)ethynylbenzene (**7a**)



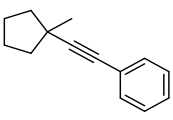
7a was synthesized following **GP4** using cesium 2-(1-methylcyclohexan-1-yl)oxy-2-oxoacetate (**2a**, 0.095 g, 0.30 mmol, 1 equiv), **9b** (0.184 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**14a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed DCE (3 mL, 0.1 M).

Column chromatography (SiO_2, pentane) followed by preparative TLC (SiO_2, glass plate, Heptane) afforded (1-methylcyclohexyl)enthynylbenzene (**7a**, 0.051 g, 0.26 mmol, 86 %) as a colorless oil.

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. [19,2020]

((1-Methylcyclopentyl)ethynyl)benzene (**7b**)



7b was synthesized following the **GP4** using cesium 2-((1-methylcyclopentyl)oxy)-2-oxoacetate (**2b**, 0.030 g, 0.10 mmol, 1.0 equiv), **9b**, 0.061 g, 0.150 mmol, 1.50 equiv) and 4CzIPN (**14a**, 0.004 mg, 0.5 µmol, 5 mol%) in degassed DCE (1 mL, 0.1 M).

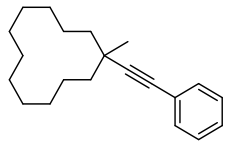
[19] Amos, S. G. E.; Cavalli, D.; Le Vaillant, F.; Waser, J. *Angew. Chem. Int. Ed.* **2021**, *60*, 23827–23834.
[20] Gao, C.; Li, J.; Yu, J.; Yang, H.; Fu, H. *Chem. Commun.* **2016**, *52*, 7292–7294.

NMR yield: 25 % based on singlet at 1.35 (s, 3H, C*H*$_3$) ppm.

Column chromatography (SiO_2, pentane) afforded 1-Methyl-1-(phenylethynyl)cyclopentane (**7b**, 0.005 g, 0.02 mmol, 20 %) as a slightly yellow oil.

^{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, C*H*$_2$), 1.90 - 1.80 (m, 2H, C*H*$_2$) 1.75 - 1.66 (m, 2H, C*H*$_2$), 1.62 - 1.51 (m, 2H, C*H*$_2$), 1.35 (s, 3H, C*H*$_3$). Consistent with reported data.[19]

1-Methyl-1-(phenylethynyl)cyclododecane (**7c**)

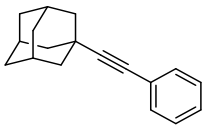


7c was synthesized following the **GP4** using cesium 2-((1-methylcyclododecyl)oxy)-2-oxoacetate (**2c**, 0.040 mg, 0.10 mmol, 1.00 equiv), **9b** (0.061 g, 0.15 mmol, 1.5 equiv) and 4CzIPN (**14a**, 0.004 g, 0.005 mmol, 5 mol%) in degassed DCE (1 mL, 0.1 M).

Column chromatography (SiO_2, pentane) afforded 1-Methyl-1-(phenylethynyl)cyclododecane (**7c**, 0.004 g, 0.01 mmol, 10 %) as a slightly yellow oil.

^{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, C*H*$_2$), 1.23 (s, 3H, C*H*$_3$). Consistent with reported NMR data.[19]

1-(Phenylethynyl)adamantane (**7d**)



7d was synthesized following the **GP4** using cesium 2-(((1*S*,3*S*)-adamantan-1-yl)oxy)-2-oxoacetate (**2d**, 0.036 g, 0.10 mmol, 1.00 equiv), **9b** (0.061 g, 0.15 mmol, 1.5 equiv) and 4CzIPN (**14a**, 0.004 g, 0.005 mmol, 5 mol%) in degassed DCE (1 mL, 0.1 M).

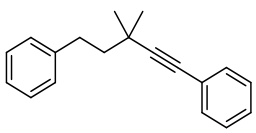
NMR yield: 30 % based on massif at 1.64 – 1.59 (m, 6H, C*H*$_2$) ppm.

Column chromatography (SiO_2, pentane) afforded 1-(phenylethynyl)adamantane (**7d**, 0.007 g, 0.03 mmol, 30 %) as a slightly 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, C*H*$_2$), 1.75 – 1.69 (m, 6H, C*H*$_2$). Consistent with reported NMR data.[19]

(3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (**7e**)



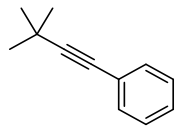
7e was synthesized following **GP4** using cesium 2-(methyl-4-phenylbutan-2-yl)oxy-2-oxoacetate (**2e**, 0.110 g, 0.300 mmol, 1.0 equiv), **9b** (0.184 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**14a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed DCE (3 mL, 0.1 M).

Column chromatography (SiO_2, pentane) afforded (3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (**7e**, 0.035 g, 0.14 mmol, 47 %) 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.

(3,3-Dimethylbut-1-yn-1-yl)benzene (**7f**)

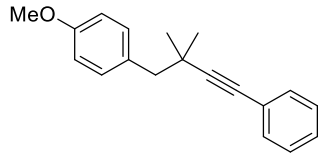


7d was synthesized following **GP4** using cesium *tert*-butoxyl-2-oxoacetate (**2d**, 0.028 g, 0.10 mmol, 1 equiv), **9b** (0.061 g, 0.150 mmol, 1.50 equiv), 4CzIPN (**14a**, 0.004 g, 0.5 µmol, 5 mol%) in degassed DCE (1 mL, 0.1 M).

NMR yield: 35 % based on singlet at 1.32 (s, 9H, C(CH_3)$_3$) ppm.

^{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)$_3$). Consistent with reported NMR data.[19]

1-(2,2-Dimethyl-4-phenylbut-3-yn-1-yl)-4-methoxybenzene (**7g**)

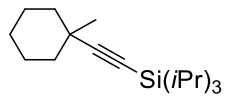


7g was synthesized following **GP4** using cesium (1-(4-methoxyphenyl)-2-methylpropan-2-yl)oxy-2-oxoacetate (**2g**, 0.038 g, 0.100 mmol, 1.00 equiv), **9b** (0.061 g, 0.150 mmol, 1.50 equiv), 4CzIPN (**14a**, 0.004 g, 0.5 µmol, 5 mol%) in degassed DCE (1 mL, 0.1 M).

Column chromatography (SiO_2, pentane) afforded 1-(2,2-Dimethyl-4-phenylbut-3-yn-1-yl)-4-methoxybenzene (**7g**, 0.005 g, 0.02 mmol, 20 %) as a slightly yellow oil.

^{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)$_2$). Consistent with reported NMR data.[19]

2-(1-Methylcyclohexyl)ethynylbenzene (**7j**)

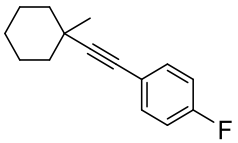


7j was synthesized following **GP4** using cesium 2-(1-methylcyclohexan-1-yl)oxy-2-oxoacetate (**2a**, 0.032 g, 0.10 mmol, 1 equiv), **9d** (0.082 g, 0.15 mmol, 1.50 equiv), 4CzIPN (**14a**, 0.004 g, 0.5 µmol, 5 mol%) in degassed DCE (3 mL, 0.1 M).

NMR yield: 52 % based on massif at 1.75 - 1.60 (m, 5H, CH_2) ppm.

^{1}H NMR (400 MHz, Chloroform-d) δ 1.75 - 1.60 (m, 5H, CH_2), 1.55 (m, 3H, CH_2), 1.19 (s, 3H, *Me*), 1.17 - 1.08 (m, 2H, CH_2), 1.08 - 1.05 (m, 18H, *TIPS*), 1.05 - 0.96 (m, 3H, *TIPS*). **^{13}C NMR** (101 MHz, Chloroform-d) δ 115.9, 80.1, 39.5, 33.5, 30.6, 25.9, 23.4, 18.7, 11.3. Consistent with the reported NMR data.[21]

1-Fluoro-4-((1-methylcyclohexyl)ethynyl)benzene (**7k**)

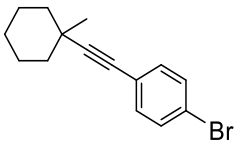


7k was synthesized following **GP4** using cesium 2-(1-methylcyclohexan-1-yl)oxy-2-oxoacetate (**2a**, 0.095 g, 0.30 mmol, 1 equiv), **9e** (0.192 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**14a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed DCE (3 mL, 0.1 M).

NMR yield: 35% based on massif at 1.86 – 1.75 (m, 2H, cyclic-CH_2) ppm.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (m, 2H, Ar*H*), 7.06 – 6.75 (m, 2H, Ar*H*), 1.86 – 1.75 (m, 2H, cyclic-CH_2), 1.74 – 1.56 (m, 6H, cyclic-CH_2), 1.26 (s, 3H, Me), 1.25 – 1.10 (m, 2H, cyclic-CH_2). Consistent with the reported NMR data.[20]

1-Bromo-4-((1-methylcyclohexyl)ethynyl)benzene (**7l**)



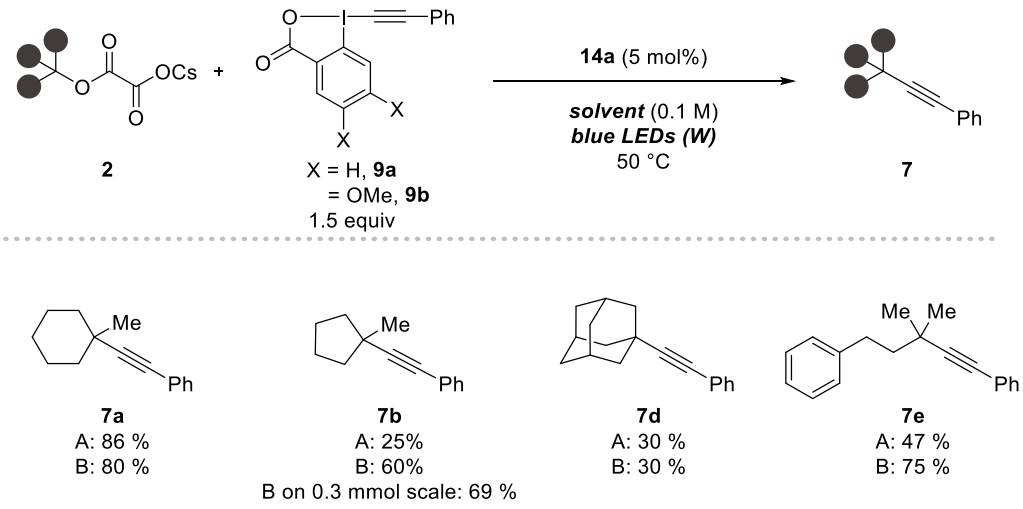
7l was synthesized following **GP4** using cesium 2-(1-methylcyclohexan-1-yl)oxy-2-oxoacetate (**2a**, 0.095 g, 0.30 mmol, 1 equiv), **9f** (0.219 g, 0.450 mmol, 1.50 equiv), 4CzIPN (**14a**, 0.012 g, 1.5 µmol, 5 mol%) in degassed DCE (3 mL, 0.1 M).

NMR yield: 27% based on massif at 1.85 – 1.74 (m, 2H, cyclic-CH_2) ppm.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.36 (m, 2H, Ar*H*), 7.29 – 7.22 (m, 2H, Ar*H*), 1.85 – 1.74 (m, 2H, cyclic-CH_2), 1.71 – 1.56 (m, 6H, cyclic-CH_2), 1.26 (s, 3H, cyclic-CH_2), 1.30 – 1.08 (m, 2H, cyclic-CH_2). Consistent with the reported NMR data.[20]

[21] Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 14330–14333.

Comparative study between optimized conditions with core modified reagent **9b** and the optimized conditions previously published[19]



7a
A: 86 %
B: 80 %

7b
A: 25%
B: 60%
B on 0.3 mmol scale: 69 %

7d
A: 30 %
B: 30 %

7e
A: 47 %
B: 75 %

Conditions A (GP 4): **9b** (1.5 equiv), blue LED strips (10-15 W), DCE (0.1 M).
Conditions B (previously reported): **9a** (1.5 equiv), 2 blue LED lamps (ca. 80 W), CH_2Cl_2 (0.1 M) (^{1}H NMR yields)

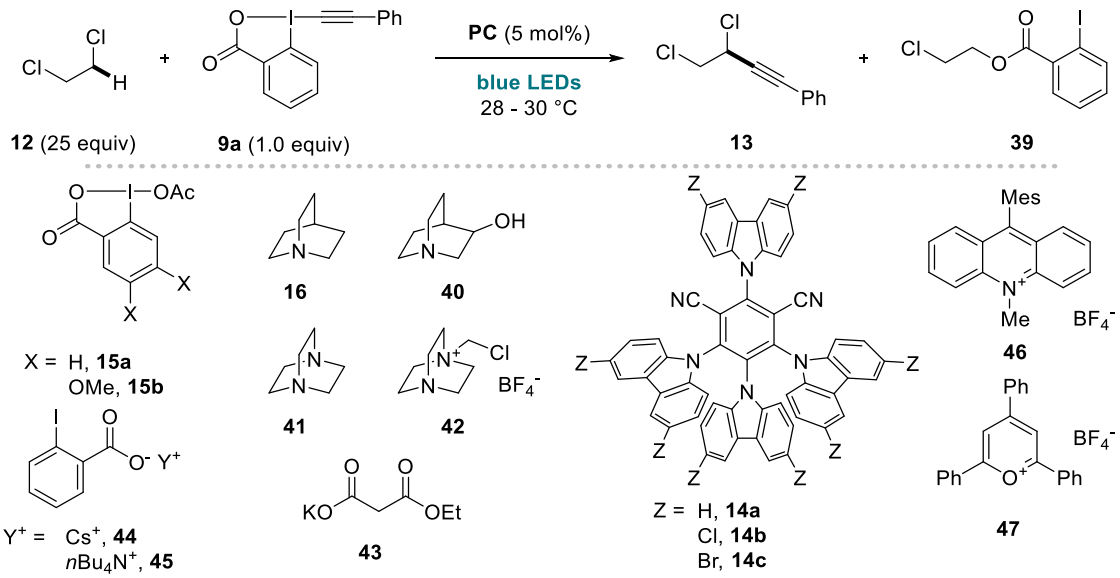
Scheme SI-1. Comparative study between GP3 (conditions A) and the optimized conditions previously published (conditions B).[19]

5. α-chloro alkynylation of DCE

Optimisation studies towards the α-chloro alkynylation of DCE

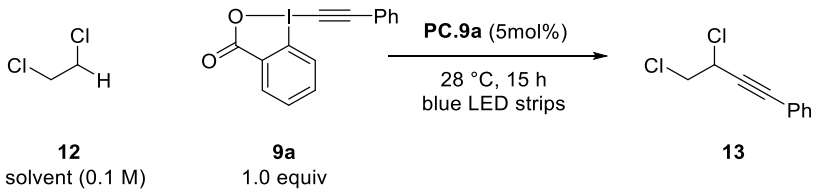
According to Table SI-2, a flame dried screw-cap vial, equipped with a magnetic stir bar was charged with **9a** (0.25 mmol, 1.00 equiv), the photocatalyst (2 mol%) and HAT agent. The reaction was evacuated then backfilled with Ar. 1,2-dichloroethane (0.50 mL, 6.3 mmol, 25 equiv) was then added and the reaction was irradiated with blue LED strips under stirring for the corresponding amount of time. The reactions were then concentrated in vacuo and resolubilized in $CDCl_3$ before adding the internal standard: CH_2Br_2 (1 equiv) and preparing the NMR sample and submitted to analysis.

Table SI-2. Preliminary optimization studies towards the α-chloro alkynylation of DCE with EBXs.



Entry	HAT agent (equiv)	PC	λ (nm)	I (W)	^{1}H NMR yield of 13 (%)
1	-	**14a**	440	80	11
2	**15a** (0.3)	**14a**	440	80	9
3	**15a** (0.3)	**14b**	440	80	8
4	**15a** (0.3)	**14a**	460	10 - 12	14
5	**15a** (0.3)	**14b**	460	10 - 12	15
6[a]	**15a** (1.0)	**14a**	460	10 - 12	15
7	**15b** (0.3)	**14a**	460	10 - 12	7
8	**39** (0.3)	**14a**	460	10 - 12	nd
9	**40** (0.3)	**14a**	460	10 - 12	nd
10	**41** (0.3)	**14a**	460	10 - 12	nd
11	**42** (0.3)	**14a**	460	10 - 12	nd
12	**42** (0.3)	**14c**[b]	460	10 - 12	nd
13	**42** (0.3)	**46**	460	10 - 12	nd
14	**42** (0.3)	**47**	460	10 - 12	nd
15	**43** (0.3)	**14a**	460	10 - 12	traces
16	**43** (0.3)	**14c**	460	10 - 12	Traces
16	**44** (0.3)	**14a**	460	10 - 12	traces + 6% of **39**
18	**45** (0.3)	**14a**	460	10 - 12	8% of **39**
19[c]	**45** (1.0)	**-**	460	10 - 12	nd; 100% of **39**

[a]The reaction was run for 2.7 days. [b]This compound was synthesized following the reported procedure form our previous studies[9] [c]The reaction was performed without **9a**.



A flame dried screw-cap vial, equipped with a magnetic stir bar was charged with **9a** (87.0 mg, 250 µmol, 1.00 equiv), 4CzIPN (1 mg. 1 µmol, 2 mol%) and **15a** (21 mg, 68 µmol, 0.28 equiv). The reaction was evacuated then backfilled with Ar. 1,2-dichloroethane (0.50 mL, 6.3 mmol, 25 equiv) was then added and the reaction was irradiated with blue LED strips under stirring for 2 days 14 hours 51 minutes. The crude was concentrated then purified by preparative TLC (SiO_2, heptane) affording **13** (8 mg, 0.04 mmol, 10%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.14 (m, 5H, Ph), 4.90 (t, *J* = 6.7 Hz, 1H, ClC*H*), 3.99 – 3.78 (m, 2H, $ClCH_2$). Consistent with the reported data.[22]

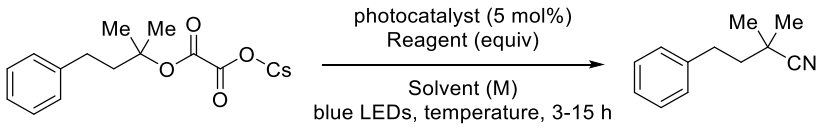
6. Deoxygenation-cyanation: synthesis of **10e**

Optimization studies toward the deoxycyanation of **2e**

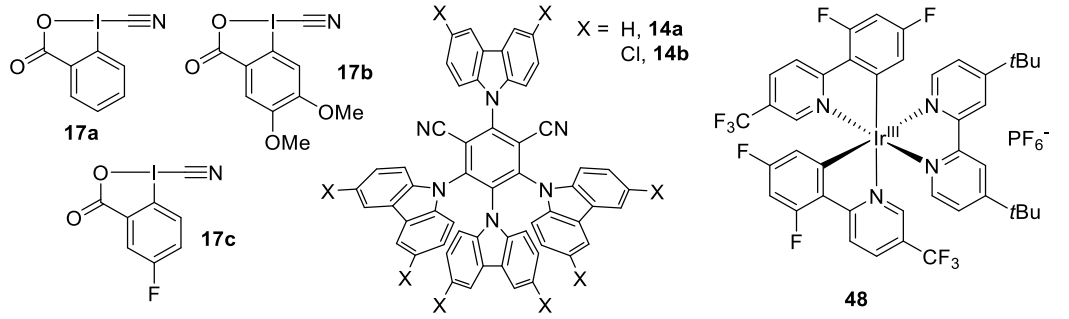
According to table SI-3, an oven-dried 5 mL test-tube was charged with **2e** (0.1 mmol, 1 equiv), the nitrile source **16** and the photocatalyst (5 mol%). After three vacuum/N_2 cycles, solvent was added the reaction was degassed for 5 min by a balloon of Ar. The reaction was irradiated under ventilation with blue LEDs at 28 °C for 4 hours. The reaction was filtered over a celite pad and washed with acetone and concentrated under reduced pressure. ^{1}H NMR yields were determined at this point by dissolving the crude in $CDCl_3$ followed by the addition of CH_2Br_2 (1 equiv).

[22] Xiang, J.; Jiang, W.; Fuchs, P. L. *Tetrahedron Lett.* **1997**, *38*, 6635–6638.

Table SI-3. Optimization studies towards the deoxycyanation of 2e with CBXs.



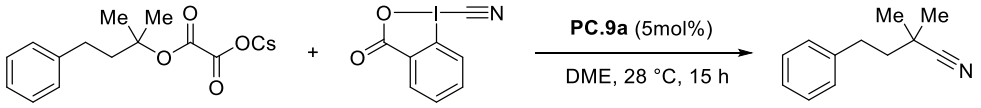
2e **10e**



48

Entry	Solvent (M)	Photocatalyst	Reagent (equiv)	T (°C)	NMR yield (%)[b]
1	DCE (0.05)	**14a**	**16a** (2)	28	23
2	9:1 DCE:DMF (0.05)	**14a**	**16a** (2)	28	25
3	MeOH (0.05)	**14a**	**16a** (2)	28	<5
4	Acetone (0.05)	**14a**	**16a** (2)	28	15
5	THF (0.05)	**14a**	**16a** (2)	28	30
6	DME (0.05)	**14a**	**16a** (2)	28	39
7	1:3 DCE:THF (0.05)	**14a**	**16a** (2)	28	40
8[a]	DME (0.05)	**14a**	**16a** (2)	28	35
9[a]	DME (0.05)	**14b**	**16a** (2)	28	30
10[a]	DME (0.05)	**48**	**16a** (2)	28	29
11[a]	DME (0.05)	**14a**	**16b (2)**	28	<5
12[a]	DME (0.05)	**14a**	**16c** (2)	28	21
13[a]	DME (0.05)	**14a**	**16a** (2)	40	16
14[a]	DME (0.05)	**14a**	**16a** (2)	60	17
15[a]	DME (0.05)	**14a**	**16a** (2)	8-14[b]	28
16	DME (0.05)	**14a**	**16a** (2)	10[c,d]	5
16	DME (0.05)	**14a**	**16a** (2)	28[c]	10
18[a]	DME (0.2)	**14a**	**16a** (2)	28	<5
19[a]	DME (0.01)	**14a**	**16a** (2)	28	15
20[a]	DME (0.05)	**14a**	**16a** (5)	28	NR
21[a]	DME (0.05)	**14a**	**16a** (1.5)	28	23
22[e]	DME (0.05)	**14a**	**16a** (1.5)	28	16

[a]Reaction was run for 3 hours. [b]The reaction was maintained at this temperature with a cooled water bath that was renewed every 30 min [c]The reaction was irradiated by an immerged glass rod illuminated by a 420 nm blue LED 8 W. [d]The reaction was cooled down by use of a cryostat. [e]Reaction was irradiated using 2 blue LED lamps (2 x 40 W, λ_{max} = 440 nm)



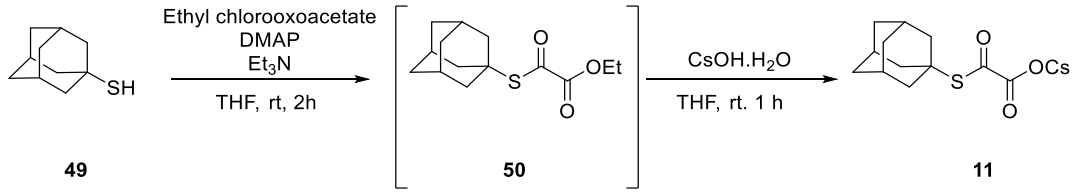
2e **16a** 2.0 equiv. **10e**

An oven-dried 5 mL test-tube was charged with **2e** (0.037 g, 0.10 mmol, 1.0 equiv.), **16a** (0.055 g, 0.20 mmol, 2.0 equiv.) and 4CzIPN (**14a**, 3.9 mg, 5.0 µmol, 5 mol%). After three vacuum/N_2 cycles, DME (2 mL, 0.05 M) was added the reaction was degassed for 5 min by a balloon of Ar. The reaction was irradiated under ventilation with blue LEDs at 28 °C for 4 hours. The reaction was filtered over a celite pad and washed with acetone and concentrated under reduced pressure. Crude was purified by prep TLC (9:1 Hept:EtOAc) affording **10e** (7 mg, 0.04 mmol, 40%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H, Ar*H*), 7.24 – 7.19 (m, 3H, Ar*H*), 2.86 – 2.76 (m, 2H, Ar-CH_2), 1.86 – 1.80 (m, 2H, Ar-CH_2-CH_2), 1.41 (s, 6H, (CH_3)$_2$). The results reported correspond to those in literature.[23]

7. Dethioalkynylation of **11**

Synthesis of cesium 2-((3S,5S,7S)-adamant-1-ylthio)oxo-2-acetate (**11**)



49 **50** **11**

(3S,5S,7S)-adamantane-1-thiol (**49**, 1.2 g, 7.1 mmol, 1.00 equiv.) was charged into a two necked round-bottomed flask with THF (35.7 mL, 0.2 M) equipped with a magnetic stirrer. Triethylamine (1.1 mL, 7.5 mmol, 1.1 equiv.) and DMAP (0.044 g, 0.36 mmol, 10 mol%) were then added. Ethyl 2-chloro-2-oxoacetate (0.84 mL, 7.5 mmol, 1.1 equiv.) was then added dropwise. The reaction was then stirred for 1 hour at room temperature. The reaction was quenched with sat. aq. NaCl (15 mL), then washed with 50%vv sat. aq. NaCl (2 x 6 mL). Caesium hydroxide hydrate (1.19 g, 7.06 mmol) with water (7 mL) was added to organic

[23] Zhang, L.; Ang, G. Y.; Chiba, S. *Org. Lett.* **2011**, *13*, 1622.

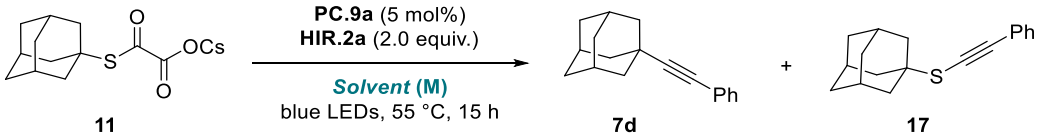
phase. The latter was agitated for 5 min. Hexane (25 mL) was added. The aqueous layer was separated. The organic layer was back extracted with water (2 x 10 mL). The aqueous layers were combined and concentrated under reduced pressure. The resulting salt was dried overnight under reduced pressure by means of a desiccator (drying agent: SiO_2). The crude product was suspended in Et_2O for 1 h, washed and dried in desiccator (drying agent: SiO_2) affording **11** (1.6 g, 4.3 mmol, 60 % yield) as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) 2.00 (bs, 6H, adamantyl-CH_2), 1.97 (bs, 3H, adamantyl-CH), 1.71-1.64 (m, 6H, adamantyl-CH_2). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 197.2, 162.5, 47.6, 41.9, 36.5, 29.5. **IR** (ν_{max}, cm^{-1}) 2908 (m), 2855 (w), 1667 (s), 1642 (s), 1580 (s), 1354 (m), 1300 (m), 984 (m), 778 (s), 758 (m). **HRMS** (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}CsNaO_3S^+$ 394.9689; Found 394.9686.

<u>Solvent and concentration screening studies towards the dethioalkynylation of **11**</u>

According to table SI-4, an oven-dried 5 mL test-tube was charged **11** (0.037 g, 0.10 mmol, 1.0 equiv), PhEBX (**9a**, 0.070 g, 0.20 mmol, 2.0 equiv.) and 4CzIPN (**14a**, 3.9 mg, 5.0 µmol, 5 mol%). After three vacuum/N_2 cycles, DCE (1 mL, 0.1 M) was added the reaction was degassed for 5 min by a balloon of Ar. The reaction was irradiated with blue LEDs at 55 °C for 15 hours. The reaction was filtered over a celite pad and washed with acetone and concentrated under reduced pressure. Crude was purified by prep TLC (Heptane) affording **7d** and **17** as impure fractions.

Table SI-4. Preliminary optimisation studies towards a dethioalkynylation of **11** with **9a** and **14a**.



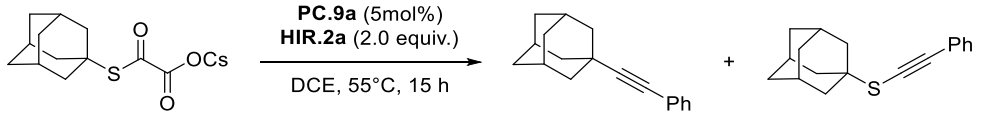
11 7d 17

Entry	Solvent	(M)	NMR yield 7d (%)	NMR yield 17 (%)
1	DCE	0.05	20	50
2	DME	0.05	10	71
3	THF	0.05	15	73
4	PhMe	0.05	<5	<10
5	DCE	0.03	15	67

6	DCE	0.07	23	54
7	DCE	0.1	25	55
8	DCE	0.2	20	40
9[a]	DCE	0.05	10	15

[a]Performed at 28°C

Photocatalysed dethioalkynylation and thioalkynylation with **11** and **9a**



11 **7d** **17**

To an oven-dried 5 mL test-tube was charged **11** (0.037 g, 0.10 mmol, 1.0 equiv.), PhEBX (**9a**, 0.070 g, 0.20 mmol, 2.0 equiv.) and 4CzIPN (**14a**, 3.9 mg, 5.0 µmol, 5 mol%). After three vacuum/N_2 cycles, DCE (1 mL, 0.1 M) was added the reaction was degassed for 5 min by a balloon of Ar. The reaction was irradiated with blue LEDs at 55 °C for 15 hours. The reaction was filtered over a celite pad and washed with acetone and concentrated under reduced pressure. Crude was purified by prep TLC (Heptane) affording **7d** and **17** as impure fractions.

For ^{1}H NMR yield calculations: CH_2Br_2 (6.0 µL, 0.086 mmol, 0.85 equiv.) was added as internal standard after work-up and concentration. The crude was immediately solubilised in $CDCl_3$ after addition. The 6H massif at 1.94-1.96 ppm for **7d** and the 3H broad singlet at 2.11-2.13 ppm for **18b** were used for the calculation.

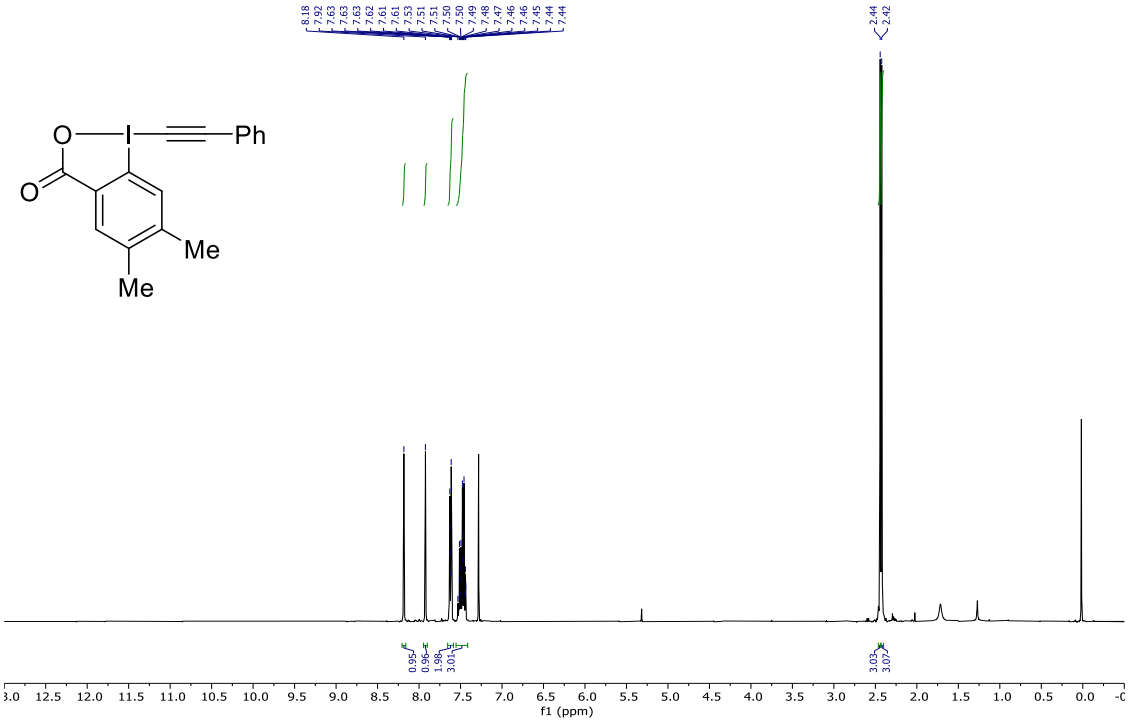
7d: **^{1}H NMR** (400 MHz, chloroform-*d*) δ 2.00-1.98 (bs, 3H, adamantyl-C*H*), 1.96-1.94 (m, 6H, adamantyl-CH_2), 1.73-1.71 (m, 6H, adamantyl-CH_2). ^{13}C NMR (100 MHz, chloroform-*d*) δ 131.6, 128.0, 127.3, 124.0, 98.3, 79.3, 42.8, 36.3, 30.0, 28.0. Consistent with the reported data.[19]

17: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.44 – 7.37 (m, 2H, Ar*H*), 7.32 – 7.24 (m, 3H, Ar*H*), 2.12 – 2.06 (m, 3H, adamantyl-C*H*), 2.00 (d, *J* = 2.9 Hz, 6H, adamantyl-CH_2), 1.69 (m, *J* = 3.1 Hz, 6H, adamantyl-CH_2). HRMS (ESI$^+$) calcd. for $[M+H]^+$ 269.1364. Found 269.1358.

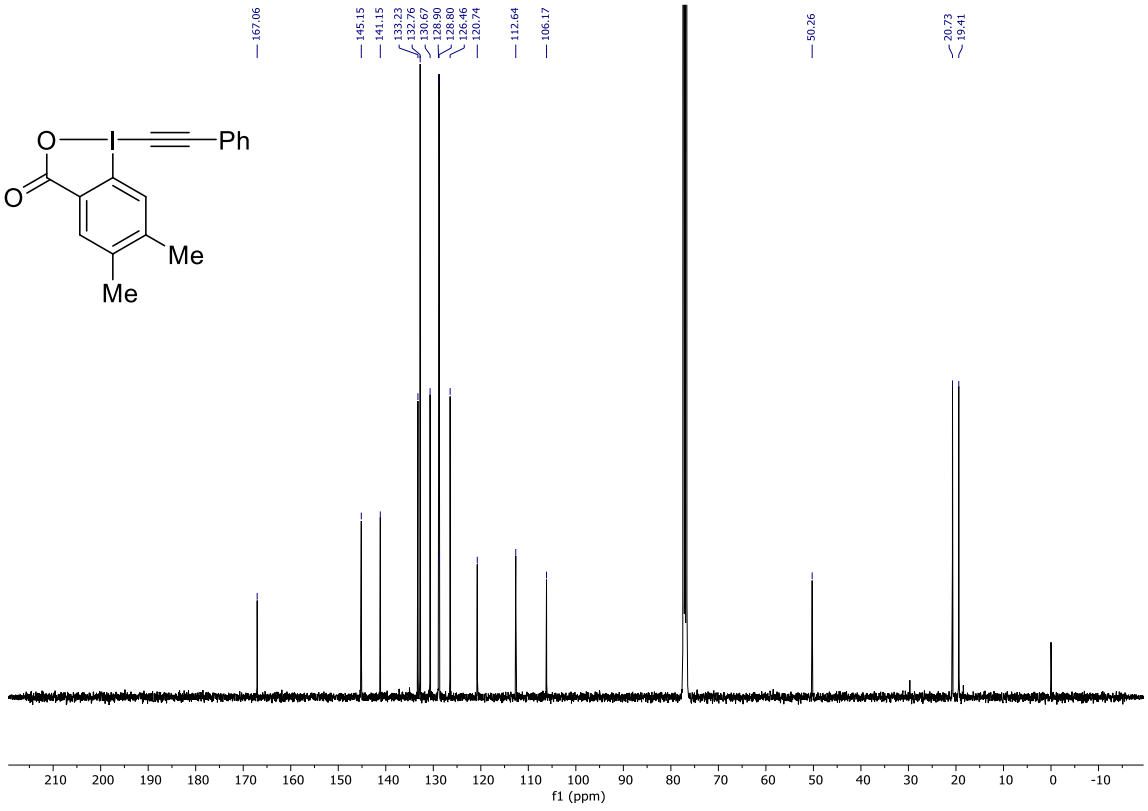
8. Spectra of new and synthesized compounds

4,5-Dimethyl-1-[phenylethynyl]-1,2-benziodoxol-3(1H)-one (9c)

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

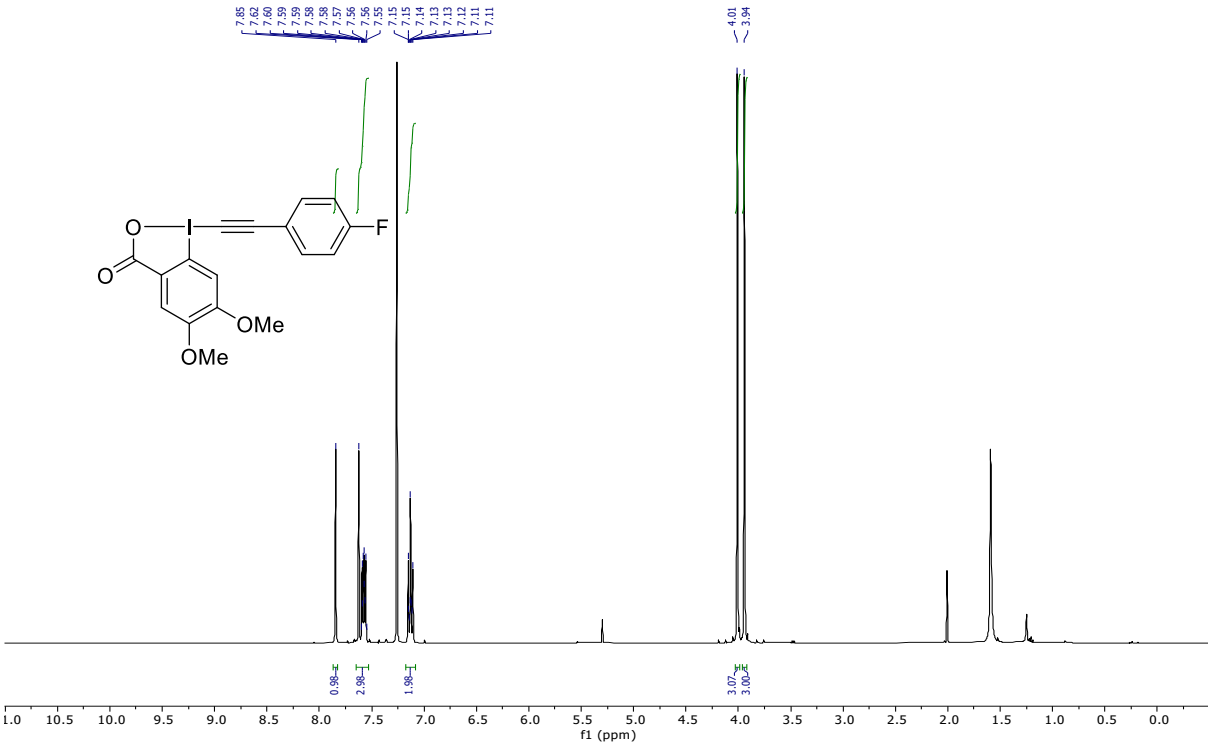


^{13}C NMR (101 MHz, Chloroform-*d*)

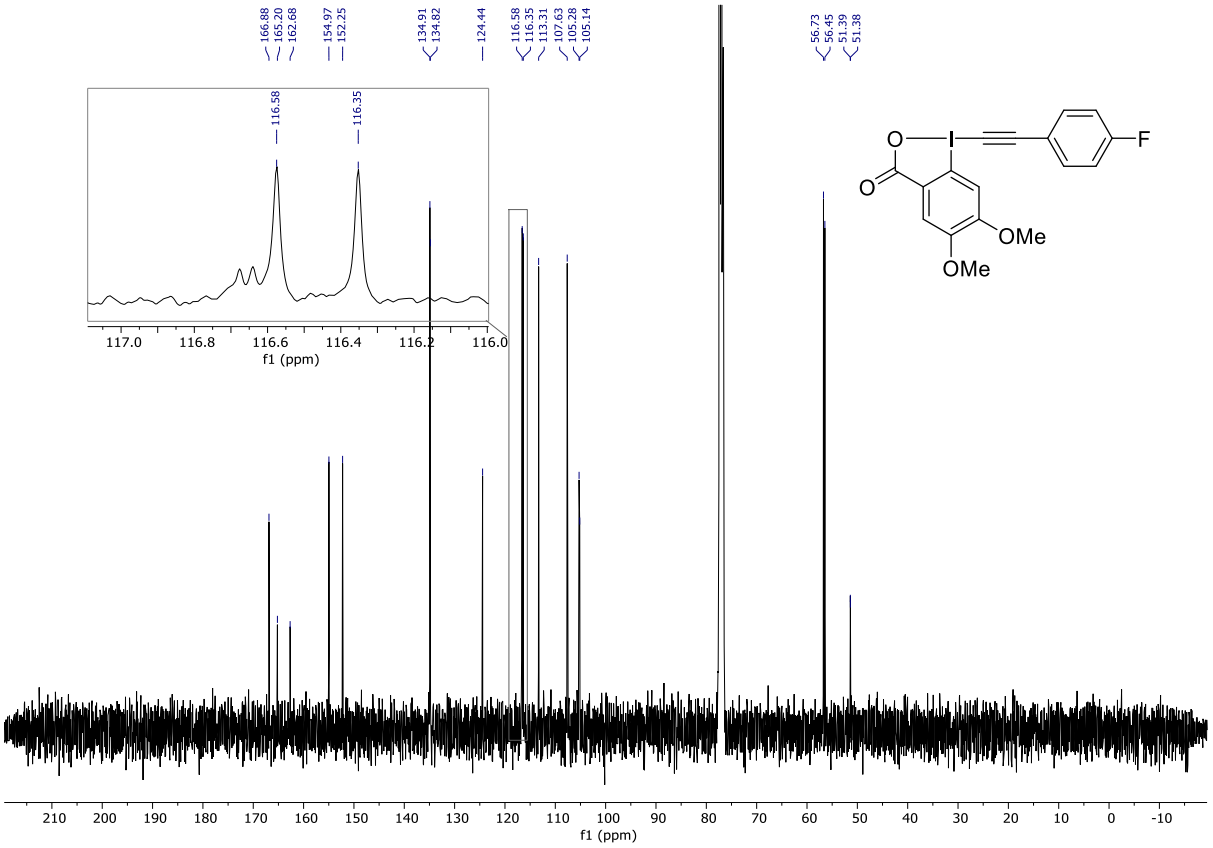


4,5-Dimethoxy-1-[(4-fluorophenyl)ethynyl]-1,2-benziodoxol-3(1H)-one (9e)

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

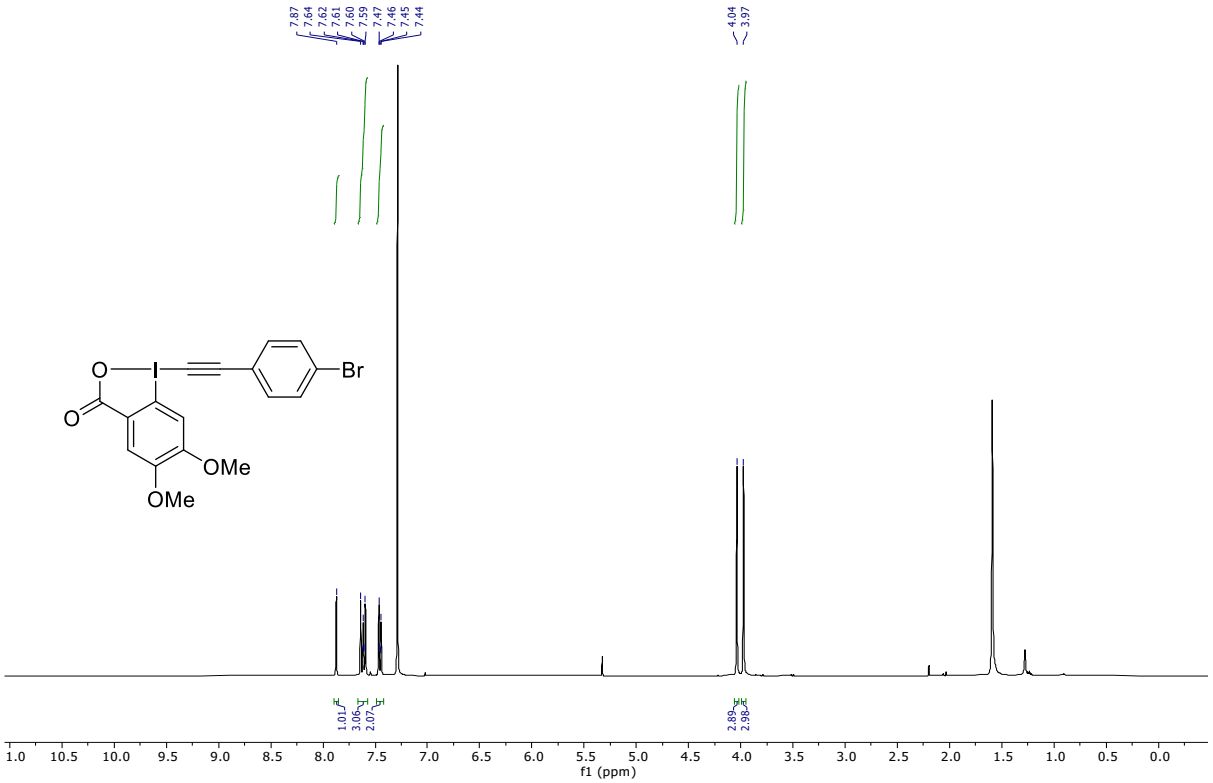


^{13}C NMR (101 MHz, Chlorofrom-*d)*

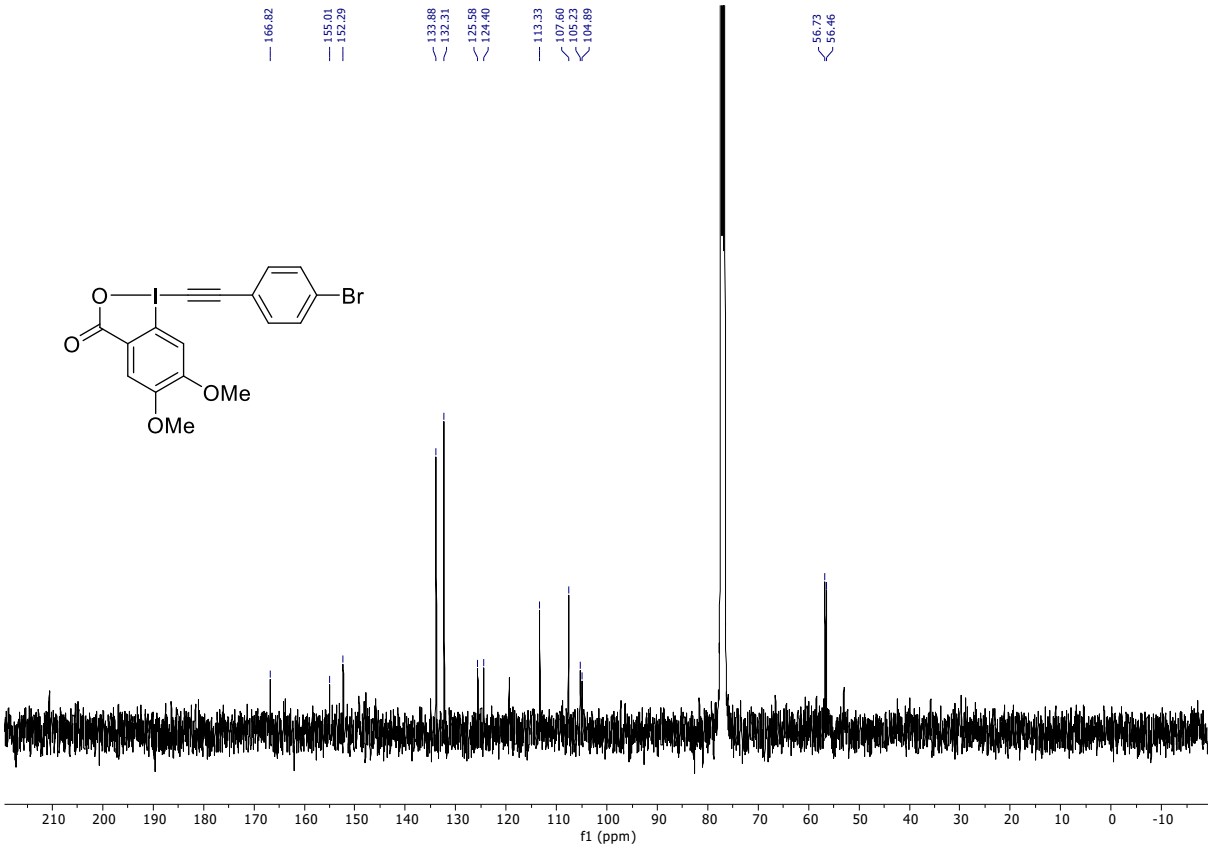


4,5-Dimethoxy-1-[(4-bromophenyl)ethynyl]-1,2-benziodoxol-3(1H)-one (9f)

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

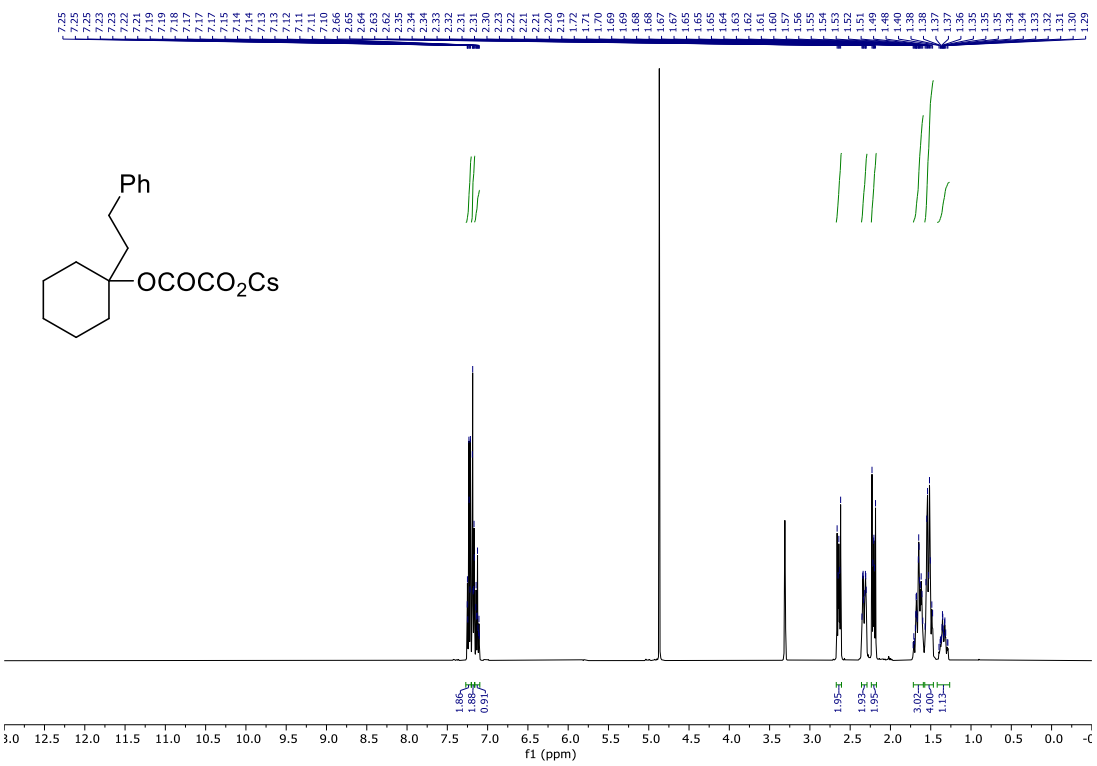


^{13}C NMR (101 MHz, Chlorofrom-*d*)

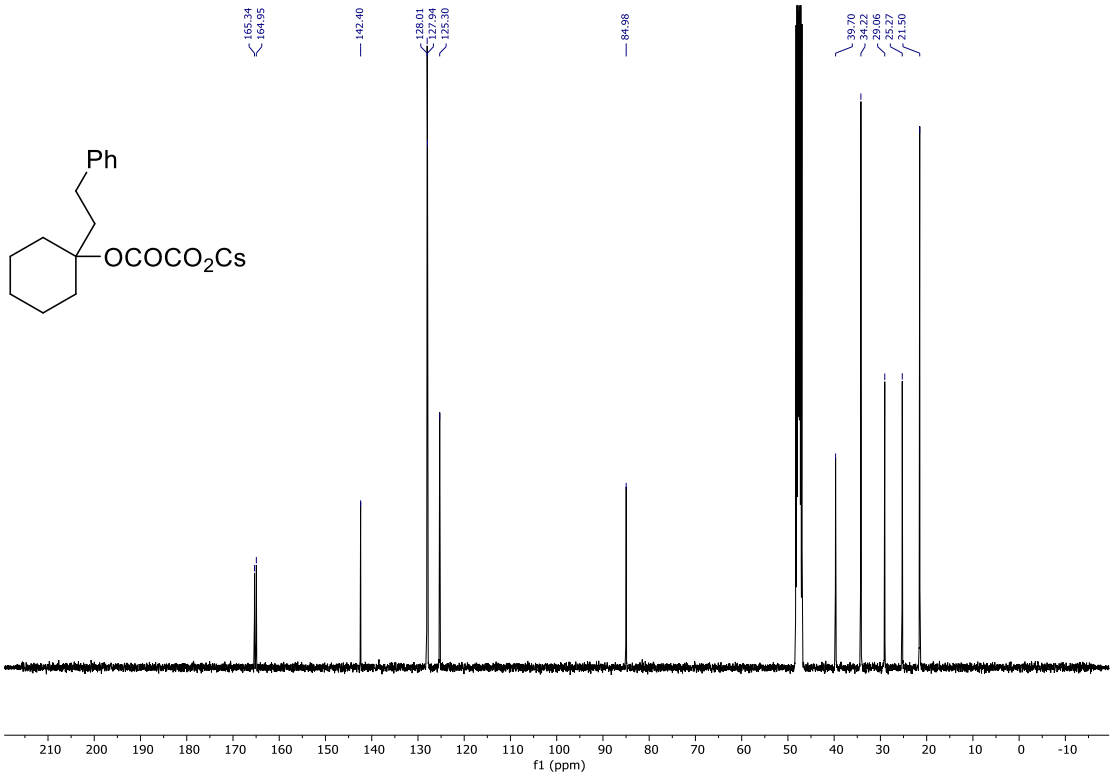


Cesium (1-phenyleth-2-yl)cyclohexan-1-yl)oxy)-2-oxoacetate (2i)

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

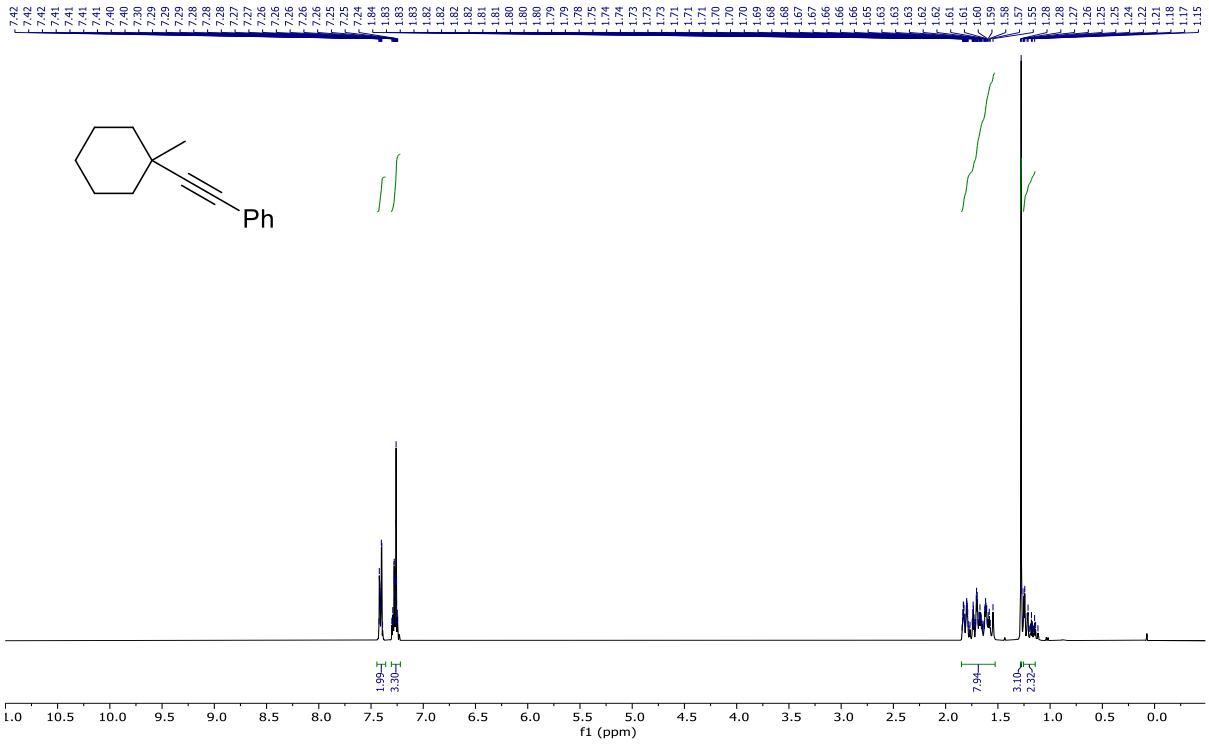


^{13}C NMR (101 MHz, Chloroform-*d*)

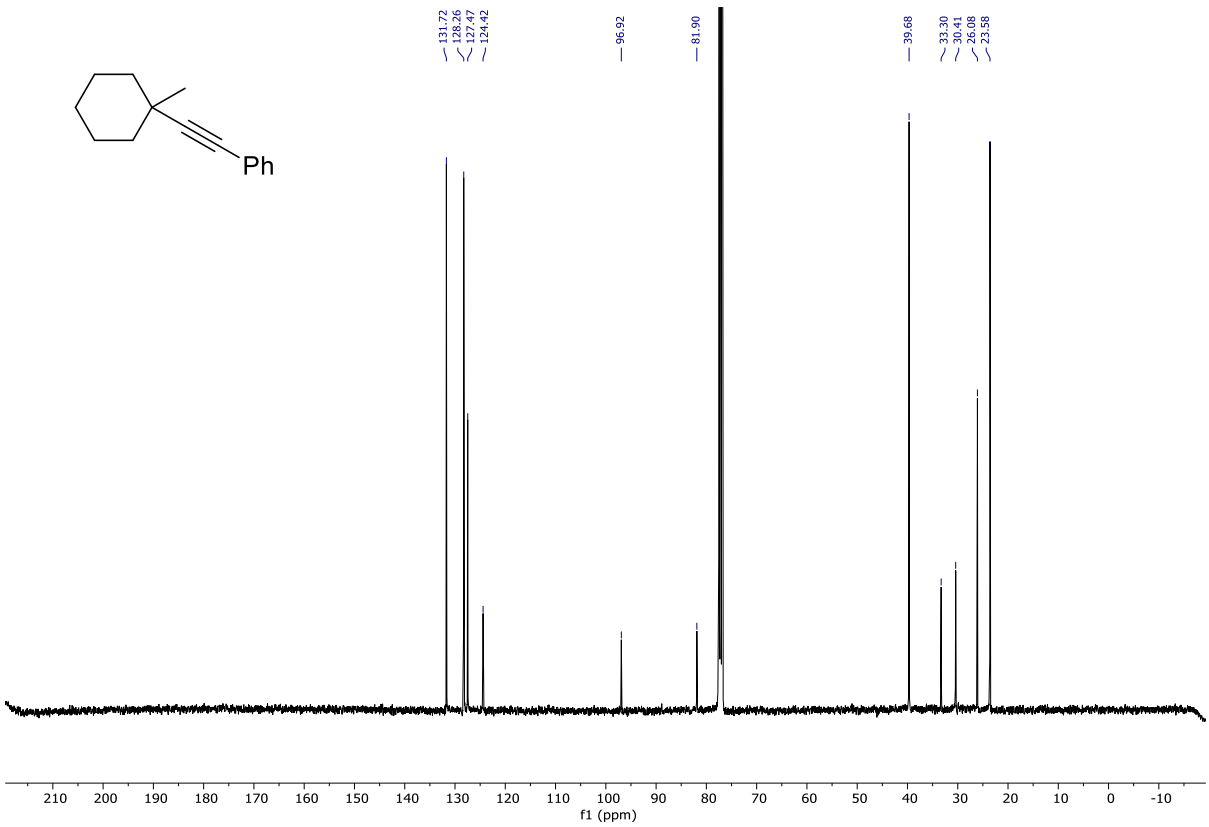


2-(1-Methylcyclohexyl)ethynylbenzene (7a)

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

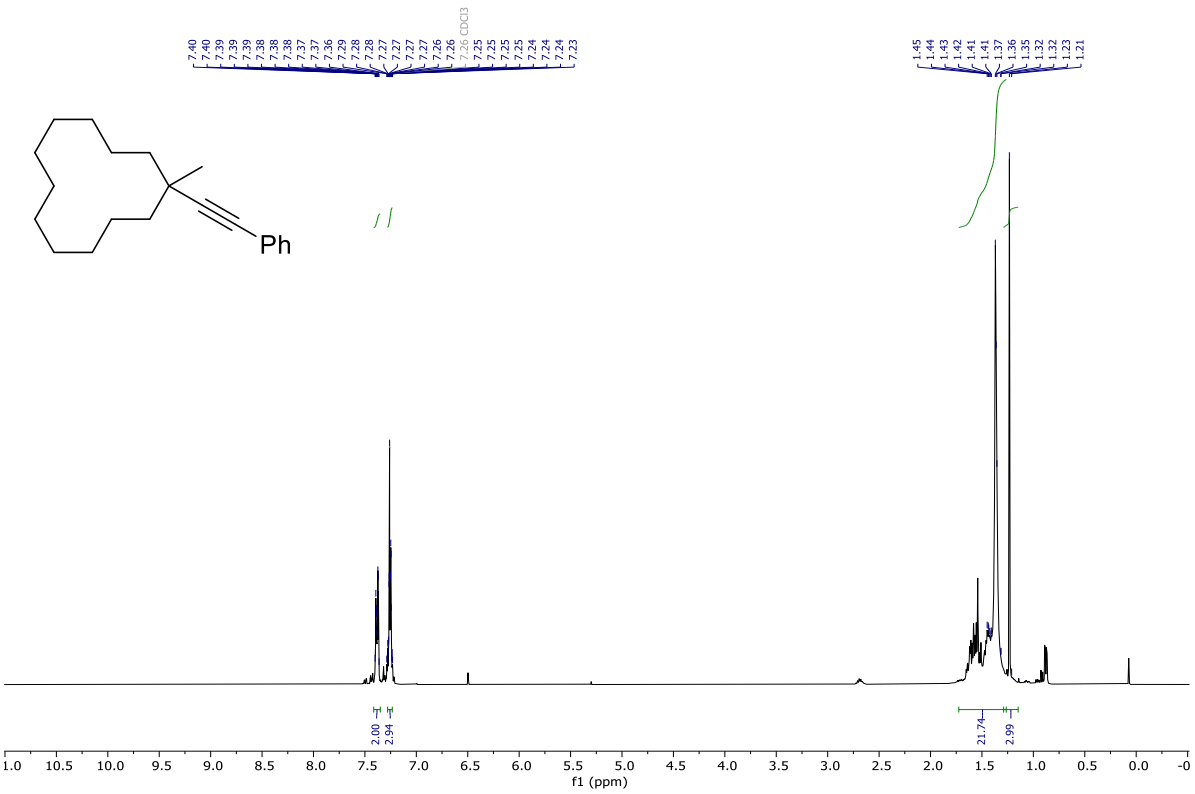


^{13}C NMR, $CDCl_3$, 400 MHz

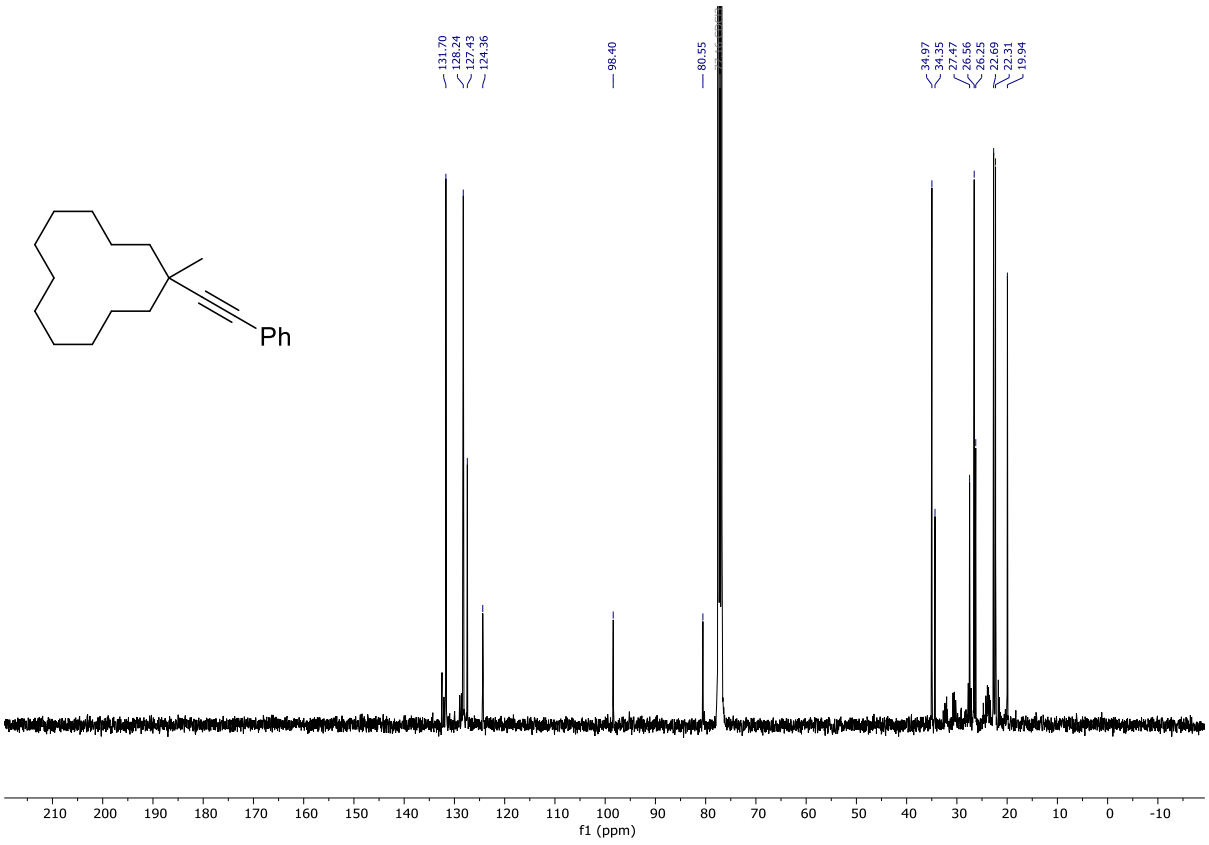


1-Methyl-1-(phenylethynyl)cyclododecane (7c)

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

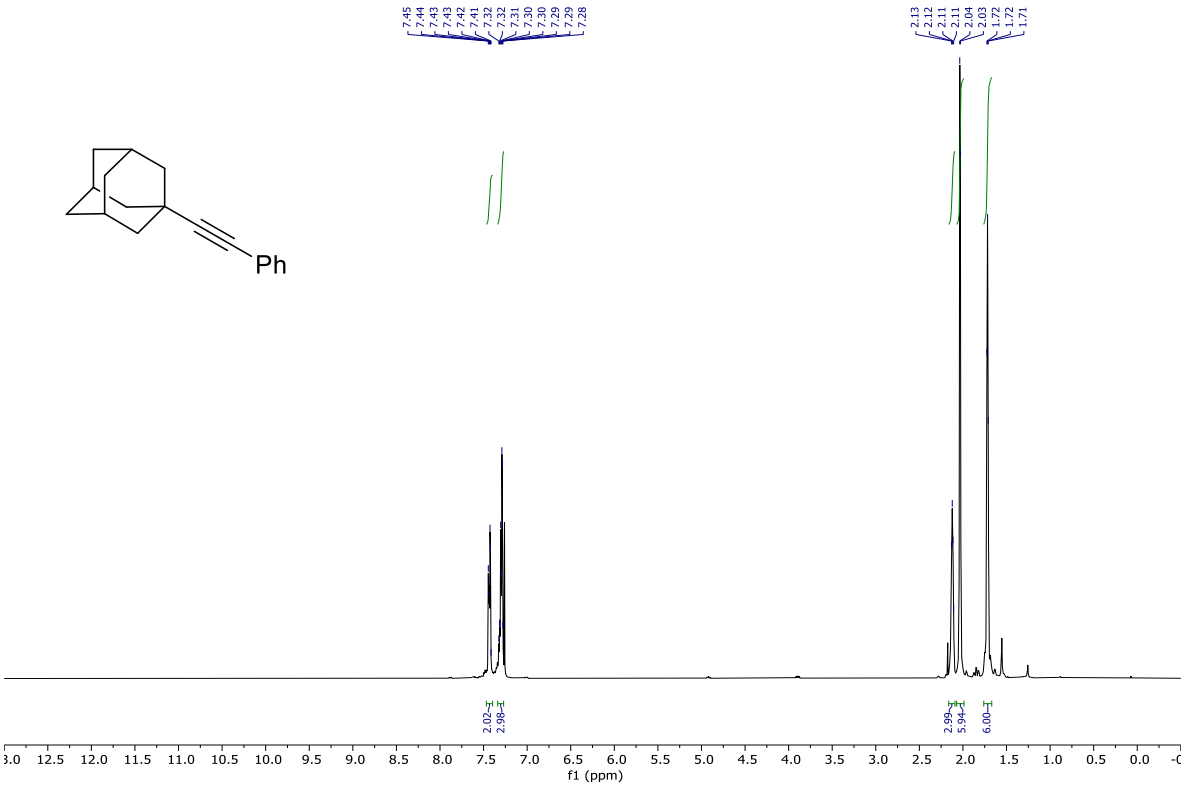


^{13}C NMR, $CDCl_3$, 101 MHz

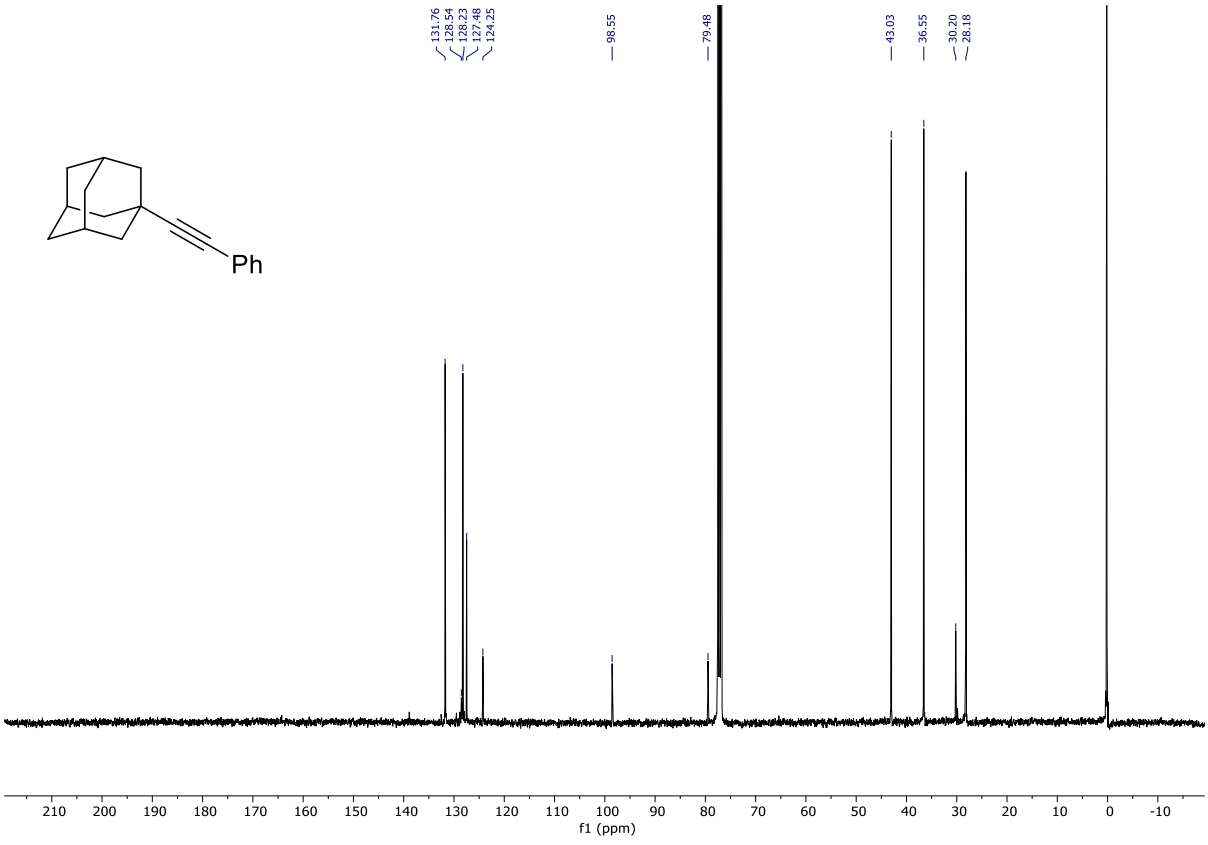


1-(Phenylethynyl)adamantane (7d)

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

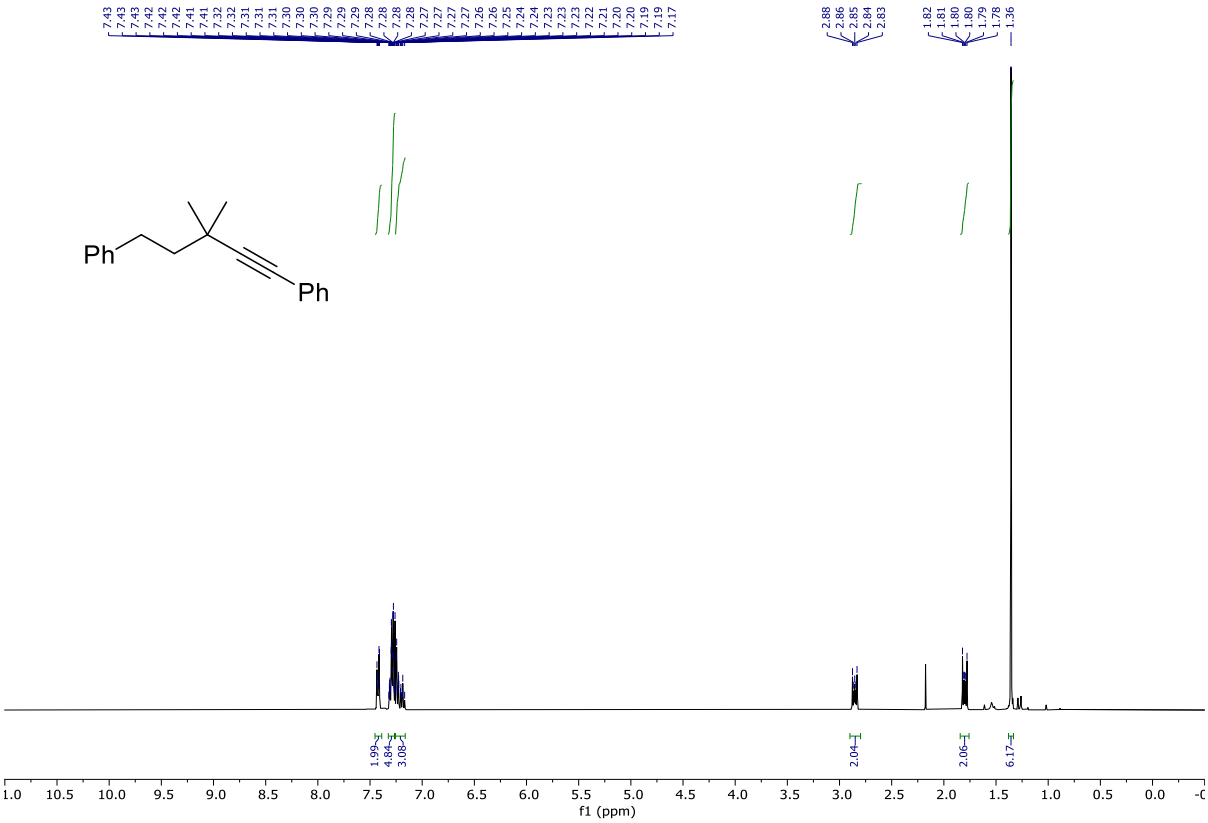


^{13}C NMR, $CDCl_3$ (with 1V% TMS), 101 MHz

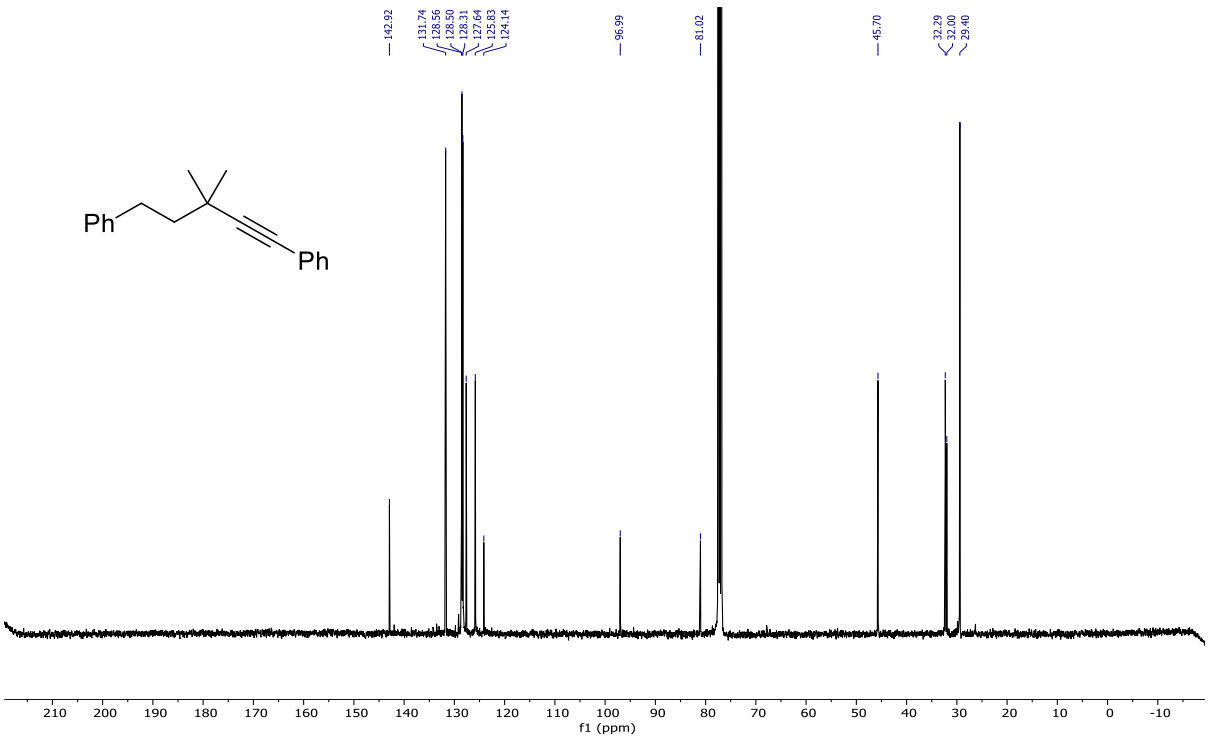


(3,3-dimethylpent-1-yne-1,5-diyl)dibenzene (7e)

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

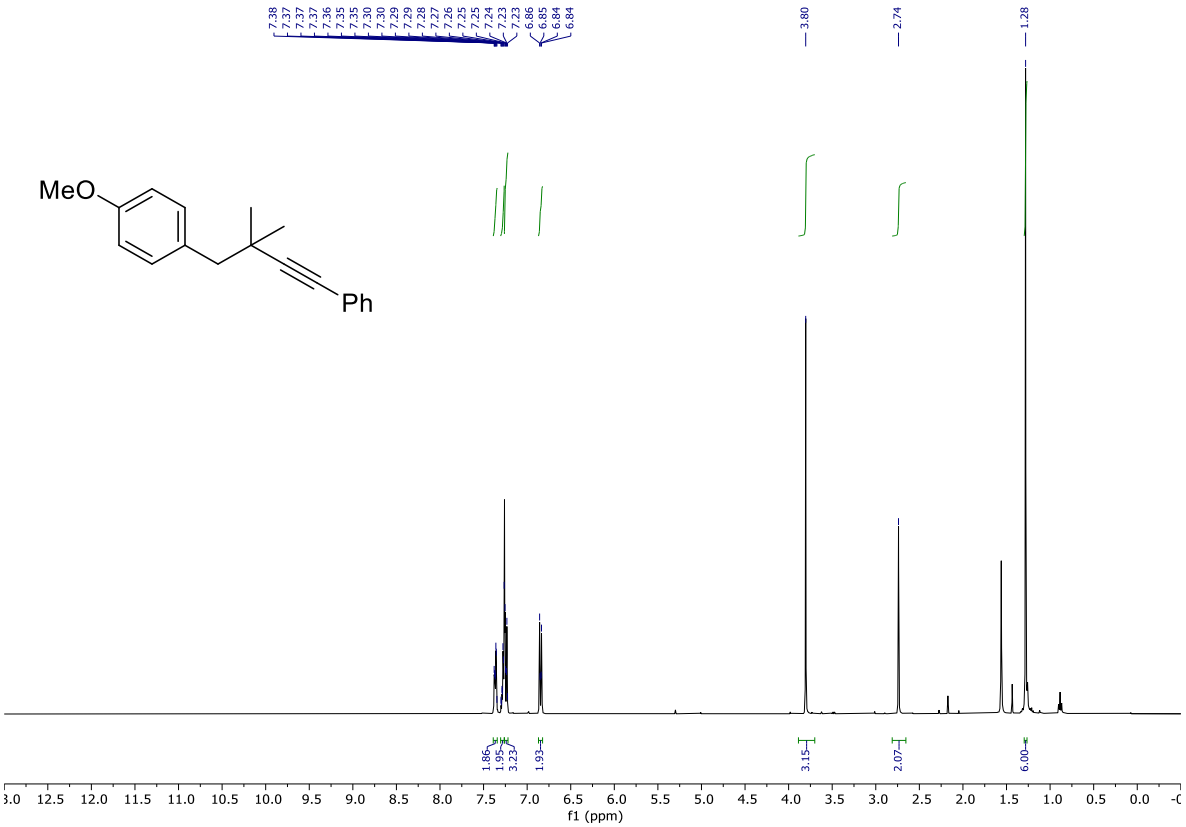


^{13}C NMR, $CDCl_3$, 101 MHz

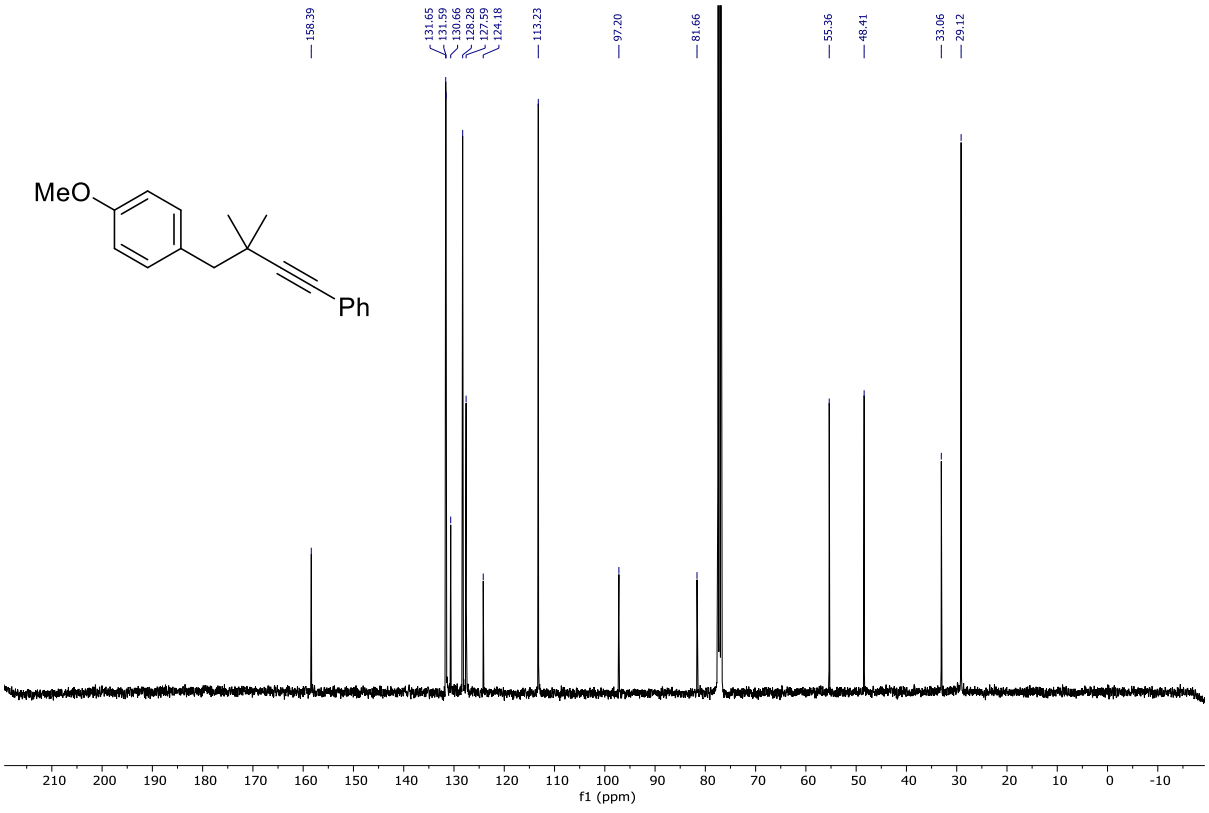


1-(2,2-Dimethyl-4-phenylbut-3-yn-1-yl)-4-methoxybenzene (7g)

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

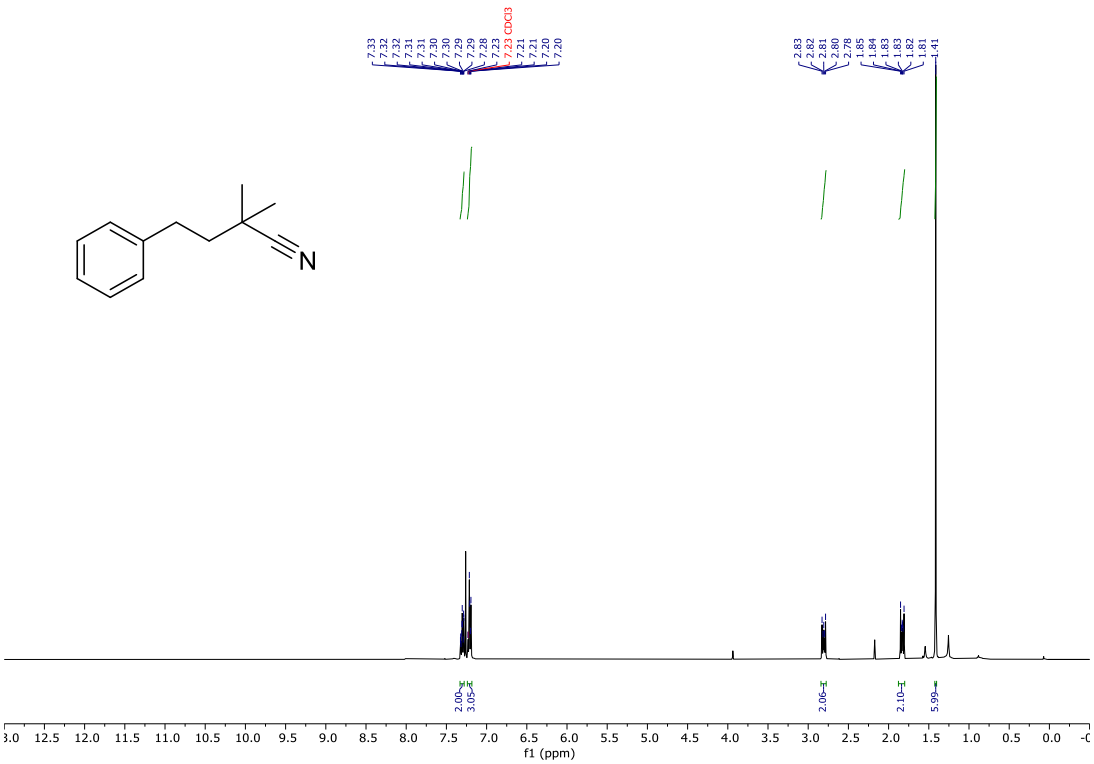


^{13}C NMR, $CDCl_3$, 101 MHz

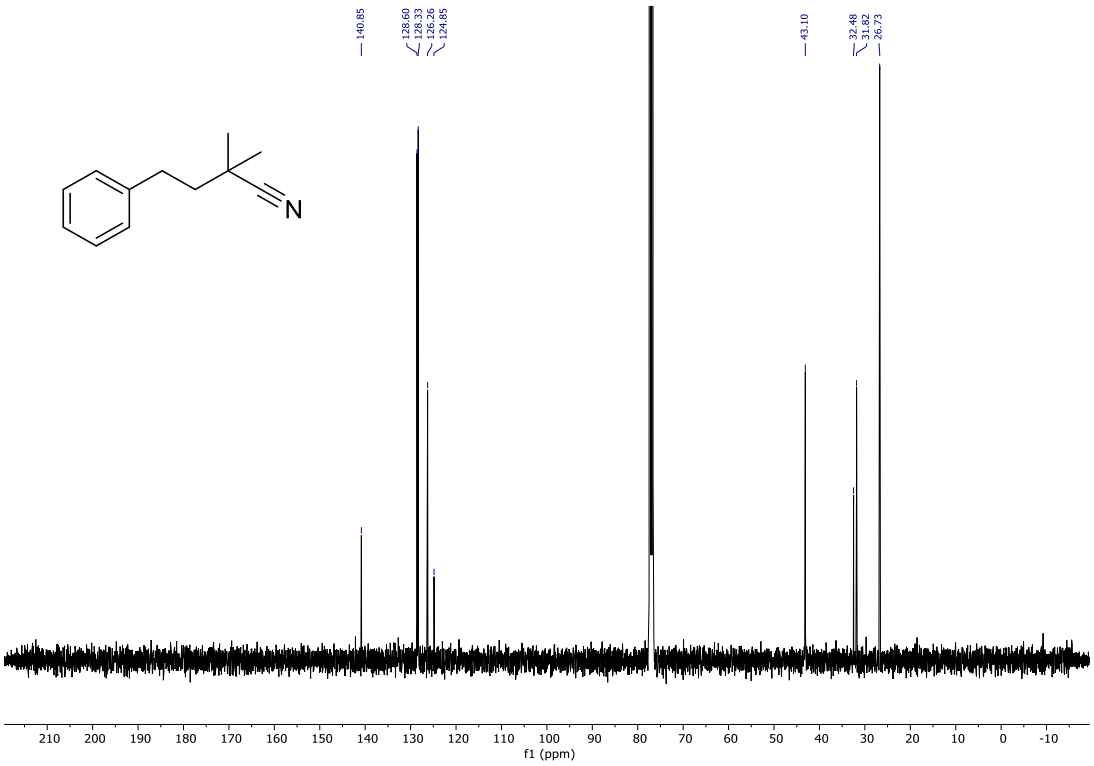


4-Phenyl-2-methyl-2-cyano-butane (10e)

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

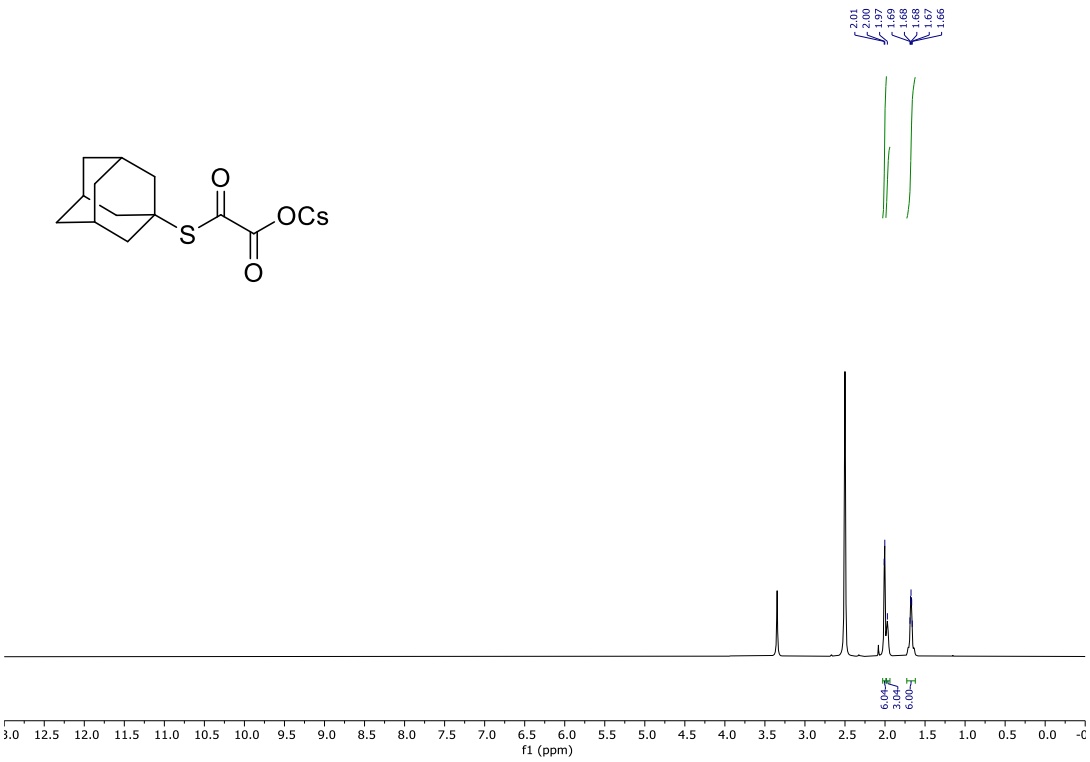


^{13}C NMR (101 MHz, Chloroform-*d*)

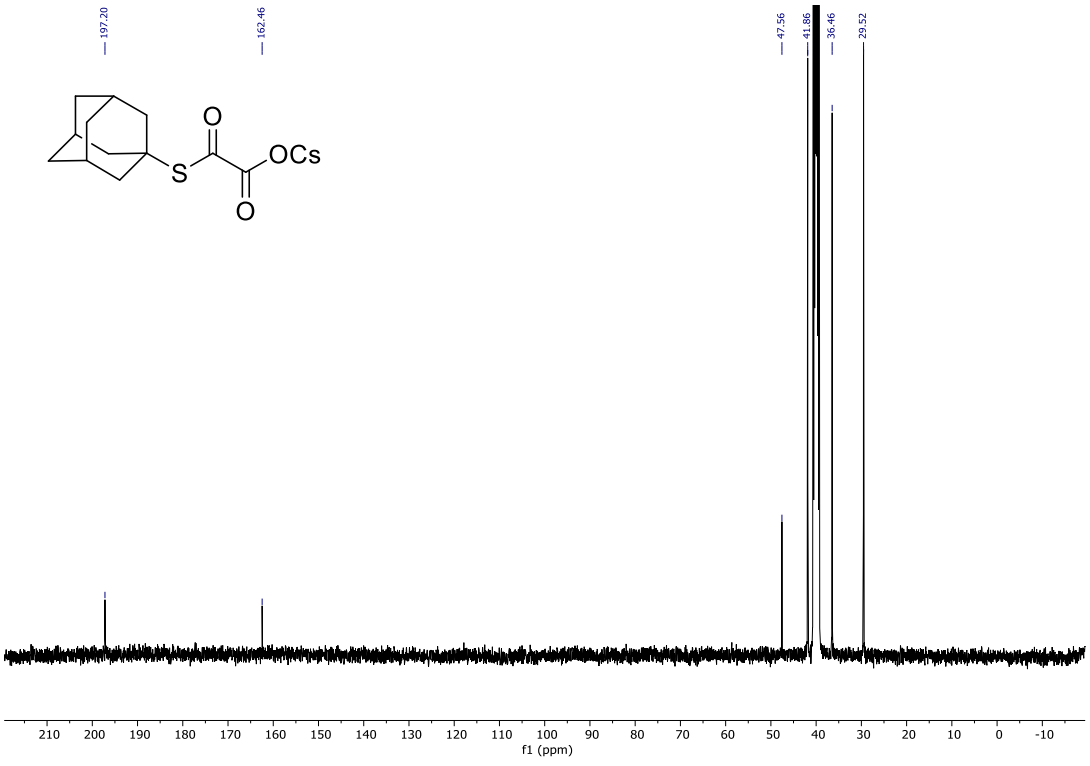


Cesium 2-((3S,5S,7S)-adamant-1-ylthio)oxo-2-acetate (11)

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



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



((3s,5s,7s)-adamantan-1-yl)(phenylethynyl)sulfane (17)

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