Copper-Catalyzed Insertion of Diazo Compounds into Vinyl Hypervalent Iodine Reagents to Generate Allylic Esters†

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ABSTRACT: An unprecedented copper(I)-catalyzed vinylation of (donor)-acceptor diazo compounds with VinylBenziodoxolone reagents (VBX) as partners is reported. The transformation tolerates variation of both donor- and acceptor substituents on the diazo compounds, delivering the corresponding benzoylated allylic alcohol products in good to excellent yields. Through the development of a protocol for the synthesis of functionalized alkanes, dienes and enynes substituted VBX reagents, a broad scope of substituents on the alkene could be accessed. The obtained products contain synthetically versatile functional groups, such as an aryl iodide, an ester and an allylic leaving group, enabling selective further modification.

Metal carbenes are highly versatile intermediates, easily generated from diazo compounds or N-tosylhydrazones, which have been extensively used in synthetic chemistry, in particular for the cyclopropanation of alkenes and insertion into carbon/heteroatom-hydrogen bonds. Recently, there is a growing interest in developing transformations introducing two groups different from hydrogen on the carbene center for the generation of more complex products (Figure 1A). The formation of at least one new C-C bond in this process is particularly attractive for building up molecular complexity and has been successful for alkylaation, arylation and alkynylation reactions using in particular palladium, copper and rhodium catalysis. The most successful approaches involve either cross-coupling through carbene migratory insertion (path a) or trapping of ylides with carbon electrophiles (path b). In contrast, the introduction of an olefin onto the carbene center has been much less investigated, and has been limited to formation of a C-alkenyl and a C-H bond by direct reaction of boronic acids or esters with diazo compounds or N-tosylhydrazones. This is a major drawback, as olefins are ubiquitous in chemical biology or material science and serve as a versatile platform for a plethora of chemical transformations.

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these transformations are based on the use of nucleophilic partners in the cross-coupling reaction and take advantage of the low acidity of alkynes or heterocycles. To the best of our knowledge, the addition of a simple olefin has therefore never been reported.

To overcome this current limitation of the field, we considered a reverse approach based on the use of an electrophilic partner for the coupling reaction. Indeed, our group recently developed an efficient copper-catalyzed 1,1-oxalkynylation of diazo compounds based on the use of electrophilic ethynylbenziodoxolone (EBX) hypervalent iodine reagents.\textsuperscript{10,11} To develop the first direct vinylation of diazo compounds, we therefore envisaged the use of the corresponding vinylbenziodoxolone (VBX) reagents. VBXs have been much less used than EBXs, and it is only recently that Olofsson and co-workers reported their synthesis and demonstrated their enhanced stability and distinct reactivity with carbon nucleophiles when compared with well-known alkenylidonium salts.\textsuperscript{12} This novel class of reagents has been already applied in metal-catalyzed C-H alkenylation\textsuperscript{13} and as SOMOphile in photoredox mediated transformations.\textsuperscript{14} These first applications are promising, but currently only aryl-substituted VBX reagents can be access in good yields, which limits the scope of the processes.

In this work, we would like to report the first copper-catalyzed insertion of diazo compounds into VBX reagents proceeding with broad scope and high yield at room temperature and leading to direct vinylation of the carbene center. By developing a new synthetic protocol, a broad range of alkyl VBX reagents were first accessed in high yield. A bisoxazolone ligand on the copper gave best results for the oxyvinylation of acceptor-substituted diazo compounds, whereas donor-acceptor substituted diazo compounds could be functionalized using a diimine ligand. The obtained allylic esters building blocks could be easily further modified.

**Synthesis of VBX reagents: new method for the synthesis of alkyl-substituted derivatives**

The synthesis of ary1-substituted VBX reagents was initially reported by Olofsson and co-workers, in a one-pot oxidation/boron-iodane exchange sequence, starting from 2-iodobenzoic acid and the corresponding boronic acid precursor.\textsuperscript{12} However, this protocol requires handling dry mCPBA as oxidant and strong trifluoromethanesulfonic acid as activator. We therefore preferred the use of the procedure reported by Nachtsheim and co-workers starting from the readily available hydroxybenziodoxolones 2 and boronic acids with trimethylsilyl triflate as activator (Figure 2 – Method A).\textsuperscript{13} These conditions reported for Ph- VBX (1a) were easily extended to obtain other aryl-substituted reagents 1b-e bearing alkyl, methoxy, fluoro or trifluoromethyl groups. The methodology was also applicable for accessing naphthyl VBX 1f, but could not be used to access thiophene VBX 1g. Modification of the aromatic core of the EBX reagents was also possible to give compounds 1h and 1i bearing a fluoro and a methoxy group in 58% and 85% yield respectively.

We were then interested to extend the scope of VBX reagents beyond aryl substituents. However, only the synthesis of cyclohexyl-substituted VBX reagent 1j has been reported in poor yield (27%) in the past by Olofsson and co-workers\textsuperscript{12} and no better results could be obtained using Nachtsheim procedure.\textsuperscript{13} Pleasingly, changing the iodane (III) precursor to acetoxybenziodoxolone (3), and employing BF\textsubscript{3}•OEt\textsubscript{2} as activator provided the VBX 1j in greatly improved 59% yield (Figure 2 – Method B). A range of alkyl-substituted VBX reagents were successfully synthesized applying this protocol. Reagents 1k-q bearing primary alkyl groups could be obtained in 28-74% yield, whereas a tert-butyl substituent was not tolerated (result not shown). Most importantly, this mild protocol allowed the synthesis of reagents bearing functionalized alkyl chains, including phenyl, chloro and ester substituents (reagents 1l-n). Substitution in allylic position is especially interesting to get useful building blocks for synthetic and medicinal chemistry, yet it makes reagent synthesis more challenging. Gratifyingly, VBX reagents 1o, 1p and 1q bearing an allylic chloro, oxygen and nitrogen substituent could be all accessed efficiently. Finally, the di-substituted cyclohexene substrate 1r could be obtained in 50% yield. In general, method B gave inferior results for the synthesis of alkyl-substituted VBX reagents, with the notable exception of thiophene-substituted reagent 1g, which could be accessed in 37% yield using this protocol. Conjugated dienes and enynes are other classes of sensitive compounds that can be found in natural products and serves as unique platforms for further synthetic transformations. However, they have never been introduced onto VBX reagents. We succeeded to prepare the diene-VBX reagents 1s and 1t in 55% and 40% respectively. The reagent 1u bearing a conjugated enyne motif was obtained in 79% yield.
Importantly, all the obtained reagents were stable and could be isolated in pure form via simple precipitation from the crude products. Currently, the synthesis of VBX reagents is limited to trans-olefin containing compounds. Indeed, (trans)-VBXs were obtained independently of the geometry of the alkenyl boronic acids.

**Optimization of the Cu(I)-catalyzed insertion into diazo compounds**

With a large variety of VBX reagents ready, we next turned our attention to their application as vinylation partners for insertion into diazo compounds (Table 1). No product could be obtained for reaction of ethyl diazoacetate 4a and Ph-VBX (1a) in the presence of Cu(CH$_3$CN)$_2$BF$_4$ (4 mol%) as catalyst. However, the desired allylic ester product 6a was formed in very good yield when diimine 5a was used as ligand (entry 2). No product was obtained in absence of the copper catalyst (entry 3). We were pleased to see that these conditions were also applicable to the phenyl-substituted diazoester 4b furnishing the corresponding product 7 in 80% yield (entry 4). Nevertheless, a reduction of the reaction efficiency was obtained with the more electron-rich VBX 1c (entry 5). Higher temperature, as well as a longer reaction time were needed for a complete conversion and an iodoalkene side product was obtained, indicating a loss of selectivity in alkenyl vs aryl transfer. Furthermore, no reaction occurred using the alkyl-substituted substrate 1j even after prolonged reaction time at higher temperature (entry 6). We therefore decided to investigate bisoxazoline (BOX) ligands, which had also been successful in our previous work.$^{10b}$ In fact, when using BOX ligand 5b, the reaction was accelerated and could be performed in four hours at room temperature to give 6a in 95% yield, albeit in nearly racemic form (entry 7). When cheaper non-chiral BOX ligand 5c lacking the tert-butyl groups was used, no product could be obtained (entry 8). Speculating that steric hindrance around the nitrogen atom could be important for reactivity, tetramethyl-substituted ligand 5d was therefore synthesized. Indeed, the reactivity was fully restored (entry 9). Using ligand 5d, a much better yield could be obtained with reagent 1c (entry 10), and the reaction was quantitative with alkyl-substituted VBX 1j (entry 11), whereas no product was obtained with diimine ligand 5a (entry 6). In contrast, the reaction was not successful for substituted diazo compounds with ligand 5d (entry 12). From the results obtained, we decided to use either ligand 5a or 5d depending on the presence or not of a second substituent (R$_1$) on the diazo compound. In all reactions, only the E-olefin was obtained, indicating no isomerization from the VBX reagents.
Table 1. Optimization of the insertion of (donor-) acceptor diazo compounds 4a and 4b into VBX (1).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Diazo</th>
<th>VBX</th>
<th>Product</th>
<th>Temp</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no ligand</td>
<td>H (4a)</td>
<td>Ph (1a)</td>
<td>6a</td>
<td>40 °C</td>
<td>24 h</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>2</td>
<td>5a</td>
<td>H (4a)</td>
<td>Ph (1a)</td>
<td>6a</td>
<td>40 °C</td>
<td>4 h</td>
<td>90%</td>
</tr>
<tr>
<td>3</td>
<td>5a</td>
<td>H (4a)</td>
<td>Ph (1a)</td>
<td>6a</td>
<td>40 °C</td>
<td>24 h</td>
<td>0%</td>
</tr>
<tr>
<td>4</td>
<td>5a</td>
<td>Ph (4b)</td>
<td>Ph (1a)</td>
<td>7</td>
<td>40 °C</td>
<td>4 h</td>
<td>80%</td>
</tr>
<tr>
<td>5</td>
<td>5a</td>
<td>H (4a)</td>
<td>PMP (1c)</td>
<td>6b</td>
<td>60 °C</td>
<td>24 h</td>
<td>50%</td>
</tr>
<tr>
<td>6</td>
<td>5a</td>
<td>H (4a)</td>
<td>Cy (1j)</td>
<td>8a</td>
<td>60 °C</td>
<td>24 h</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>7</td>
<td>5b</td>
<td>H (4a)</td>
<td>Ph (1a)</td>
<td>6a</td>
<td>25 °C</td>
<td>4 h</td>
<td>95%</td>
</tr>
<tr>
<td>8</td>
<td>5c</td>
<td>H (4a)</td>
<td>Ph (1a)</td>
<td>6a</td>
<td>60 °C</td>
<td>24 h</td>
<td>&lt; 5%</td>
</tr>
<tr>
<td>9</td>
<td>5d</td>
<td>H (4a)</td>
<td>Ph (1a)</td>
<td>6a</td>
<td>25 °C</td>
<td>4 h</td>
<td>95%</td>
</tr>
<tr>
<td>10</td>
<td>5d</td>
<td>H (4a)</td>
<td>PMP (1c)</td>
<td>6b</td>
<td>25 °C</td>
<td>4 h</td>
<td>81%</td>
</tr>
<tr>
<td>11</td>
<td>5d</td>
<td>H (4a)</td>
<td>Cy (1j)</td>
<td>8a</td>
<td>25 °C</td>
<td>4 h</td>
<td>99%</td>
</tr>
<tr>
<td>12</td>
<td>5d</td>
<td>Ph (4b)</td>
<td>Ph (1a)</td>
<td>7</td>
<td>40 °C</td>
<td>4 h</td>
<td>&lt; 5%</td>
</tr>
</tbody>
</table>

*Reactions were carried out on 0.10 mmol scale with 2.0 equiv. of diazo, 4 mol% of Cu(CH₂CN)BF₄, 5 mol% of ligand in DCE (0.04 M). *Isolated yields when > 5%. *Reaction was carried out without Cu(CH₂CN)BF₄. *Reaction was carried out on 0.20 mmol scale.

Scope of the vinylation reaction
With the optimized conditions in hand, we next investigated the scope of VBX reagents. Aryl-substituted VBX reagents were examined first using ethyl diazo acetate (EDA) 4a as carbene precursor (Figure 3A). Various electronically diverse substituents were well tolerated. Electron donating ether and alkyl groups afforded the desired products 6b-c in good yields. Fluorinated compounds 6d and 6e were obtained in 72% and 66% yield respectively. A naphthyl-substituted VBX was used successfully, leading to the formation of 6f in 81% yield. A similar result was obtained for 6g, bearing a thiophene heterocycle. Both electron-rich and -poor substituents on the benziodoxolone backbone were tolerated affording 6h and 6i in good yields. Next, we turned our attention to alkyl-substituted VBX reagents (Figure 3B). We were delighted to find that the vinylation reaction proceed well in most cases. Simple aliphatic chains (Cy, Bn, Ph) provided the desired alkyl esters 8a-c with excellent yields. The incorporation of electrophilic functions such as an ester (8d) or a chloride (8e) could also be achieved, providing access to compounds having useful handles for follow-up transformations.

The generation of the trisubstituted alkene product 8f was realized with an excellent yield (97%). VBX reagents possessing various functionalities in allylic position, including phthalimidoyl-protected amines, silyl ethers, and chlorides also delivered the corresponding products 8g-i. These results demonstrate the potential of this methodology to incorporate sensitive functional groups, which could be further exploited in synthetic transformations. Nevertheless, a lower yield was obtained for the formation of 8g and 8i. This may be due to the very low solubility of the corresponding VBX reagents in DCE. In addition to simple vinyl, π-conjugated systems could be readily incorporated (Figure 3C). The isoprene skeleton was introduced to...
give 9a in 82% yield. Conjugated diene 9b was also successfully synthesized. Furthermore, an enyne was transferred in 97% yield, providing compound 9v.

![figure 4](image-url)

**Figure 4.** Vinylation reaction: Scope of diazo compounds. Reactions were performed using Ph-VBX (1a) (0.2 mmol) in DCE (0.04 M). *5d* was used as ligand. *5a* was used as ligand.

We next investigate the scope of diazo compounds. Variation of the acceptor substituent was examined first (Figure 4A). Excellent yields were obtained in all cases. Bulky esters such as tBu or BHT were tolerated giving oxyvinylation products 10 and 11 in quantitative yield. The product 12 bearing a benzyl group was obtained in 92% yield and product 13 with an allyl group in 91% yield. Other electron-withdrawing groups than esters were then examined: 2-Diazo-N,N-diethylacetamide underwent the oxyvinylation to provide 14 in 94% yield. The Weinreb amide derivative 15 was isolated in 99% yield. Sulfonate- and phosphonate-diazoesters were efficient coupling partners, generating synthetically useful allyl-sulfonate and allyl-phosphonate products 16 and 17 in quantitative yields. Importantly, the molecule 18 incorporating a trifluoromethyl group was isolated in quantitative yield as well. Organofluorine compounds are of significant importance in the pharmaceutical, agrochemical and materials industry. Diazoketones were incompatible with this protocol. The desired product 19 was not observed, instead, degradations products from a Wolff rearrangement pathway were obtained. No conversion was obtained using trimethylsilyldiazomethane (20, 0% yield). This result highlights the necessity of an electron-withdrawing group in α position to the diazo functionality for the reaction to proceed. Finally, the reaction of disubstituted diazo compounds was investigated using diimine ligand 5a (Figure 4B). The products 7 and 21 with tertiary allylic centers were formed in very good yields. However, the presence of a second electron-withdrawing group completely suppressed the reactivity (22, 0% yield). A cyclic diazo compound also afforded the desired product 23 in 90% yield. Interestingly, diene product 24 could be obtained in good yield when starting from a vinyl diazo precursor. This indicated that attack of the nucleophile at the vinylogous center is favored.

**Product functionalization**

A series of modifications on the obtained building blocks was then realized (Scheme 1). First, product 6a was synthesized on 2.0 mmol scale using a lower catalyst loading at a higher concentration. The esters groups present in compound 6a were readily reduced with LiAlH4 to produce the alkenylated diol 25. Polysubstituted butenolide 26 resulting from formation of the α-keto ester followed by dimerization was formed under basic conditions. We then turned our attention to the activation of the iodobenzoate leaving group by a Lewis acid. Treatment of 6a with TiCl4 and allyl-TMS led to the formation of conjugated ester 27, functionalized with an allyl group at the γ-position in good yield. Propargyl-TMS can also be used as nucleophile in a similar transformation, giving the allene-containing product 28. The introduction of an azide was accomplished using TMSN3 to form 29 in very good yield. However, the allylic azide underwent a spontaneous isomerization at room temperature (Winstein rearrangement) resulting in a mixture of 29 and 29’ in a 70:30 ratio. Finally we examined modification of the iodine functionality originating from the reagent. The aryl iodide can be utilized in a Heck reaction between 21 and methyl acrylate to afford 30 in 66% yield. Chemoselective hydrogenolysis of the iodoarene was achieved with hydrogen and poisoned Pd/C to give product 31 in 77% yield. A complementary method, using visible light photoredox catalysis gave access to the deiodinated product 32 in 82% yield with E to Z isomerization of the olefin.
Scheme 1. Scale-up synthesis and product modifications.a

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) LiAlH₄ (3.00 equiv.), THF, 0 °C to rt, 1 h, 91%</td>
<td>6a</td>
<td>91%</td>
</tr>
<tr>
<td>b) DBU (10 equiv.), MeOH, 50 °C, 6 h, 93%</td>
<td>32</td>
<td>82%</td>
</tr>
<tr>
<td>c) Allyl-TMS (1.5 equiv.), TiCl₄ (1.05 equiv.), DCM, 0° C, 15 min, 83%</td>
<td>31</td>
<td>77%</td>
</tr>
<tr>
<td>d) Propargyl-TMS (2.0 equiv.), TiCl₄ (1.05 equiv.), DCM, -78 °C to 0 °C, 59%</td>
<td>27</td>
<td>83%</td>
</tr>
<tr>
<td>e) TMSN₃ (1.5 equiv.), TiCl₄ (1.05 equiv.), DCM, -20 °C to 0 °C, 70:30, 70%</td>
<td>20</td>
<td>66%</td>
</tr>
<tr>
<td>f) methyl acrylate (5.0 equiv.), PdCl₂ (PPh₃)₃ (5 mol%), PPh₃ (5 mol%), Et₃N, 80 °C, 24 h, 86%</td>
<td>29</td>
<td>86%</td>
</tr>
<tr>
<td>g) H₂, Pd/C (10 mol%, 10% w/w), DABCO (10 equiv.), MeOH, rt, 10 min, 77%</td>
<td>21</td>
<td>77%</td>
</tr>
<tr>
<td>h) fac-Ir(ppy)₃ (2.5 mol%), NBu₃ (10 equiv.), HCO₂H (10 equiv.), blue LED, MeCN, 40 °C, 18 h, 82%</td>
<td>28</td>
<td>59%</td>
</tr>
</tbody>
</table>

Speculative reaction mechanism

At this stage, only a highly speculative reaction mechanism can be proposed following two main pathways according to literature (Scheme 2). As hypervalent iodine are strong oxidants, path a would start with a fast oxidative addition of the VBX reagent 1 to the Cu(I) catalyst I to form a highly electrophilic vinyl-Cu(III) intermediate II. Then complex II would react with diazo compound 4 to form the copper carbene intermediate III after exclusion of nitrogen. The nucleophilic carboxylate group would then add/shift to the carbene center to form organocopper species IV. Finally, a reductive elimination, will deliver the desired product 6 and re-form the Cu(I) catalyst I. Alternatively, 1,2-shift of the vinyl group followed by C-O reductive elimination could be also considered. It is interesting to note that this mechanism would involve a Cu(III) intermediate, whereas all diazo reaction/cross-coupling sequence have been proposed to proceed via a Cu(I) intermediate so far. In a second alternative (path b), the first step would be the reaction of Cu(I) catalyst I with diazo compound 4 to give carbene complex V. Nucleophilic attack of the carboxylate group of VBX 1 would then give ylide VI. At this stage, oxidative transfer of the vinyl group would lead to intermediate IV. Alternatively, direct nucleophilic attack on the alkenyliodonium to give 6 without oxidation to Cu(III) could be also considered. As both diazo compound 4 and reagent 1 reacted fast with copper complex I, determining which pathway is occurring will require further studies.

Scheme 2. Plausible reaction mechanism.

Enantioselective transformation: preliminary results

Preliminary experiments were also done on an enantioselective variation of the vinylation reaction (Table 2). When the commercially available tBu-BOX ligand 5b has been used, 6a had been obtained in good yield but with poor enantioselectivity (entry 1). The use of the cyclopropyl derived BOX ligand 5e afforded 6a with a better enantioselectivity (entry 2). No further improvement was observed using a more sterically demanding alkyl VBX reagent as coupling partner (entry 3). However, a hindered diazo ester improved the enantioselectivity and gave the desired product 11 with 50% ee (entry 4). Unfortunately, further optimization of the ester structure and reaction conditions did not lead to further improvement, indicating that a better ligand will need to be found to achieve a highly enantioselective transformation.

Table 2. Preliminary results for the enantioselective vinylation reaction.a
In summary, we have developed a copper-catalyzed insertion of diazo compounds into vinyl hypervalent iodine reagents. Key for the first successful alkenylation of diazo compounds using a copper catalyst was the use of vinylbenziodoxolone (VBX) reagents, which can now be accessed with a broad range of functionalized substituents based on a new synthetic protocol. The use of inexpensive and earth-abundant copper associated to the high atom-efficiency of the reaction are notable advantages of the methodology. The transformation is tolerant to a wide range of functional groups and provides ready access to a broad scope of allylic esters in very high yields. The obtained products can be further modified to give important building blocks. Ongoing research is focused on the elucidation of the reaction mechanism and the development of the asymmetric version of the transformation based on our preliminary results.

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website.

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Notes
The authors declare no competing financial interest.

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REFERENCES


(15) The structure of 11 was confirmed by X-ray analysis. The data is available at the Cambridge Crystallographic Data Center (ccdc number 1897009).


Graphical abstract:
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Supporting Information

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1. General Methods

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless stated otherwise. For quantitative flash chromatography technical grade solvents were used. For flash chromatography for analysis, HPLC grade solvents from Sigma-Aldrich were used. THF, Et$_2$O, CH$_3$CN, toluene, hexane and CH$_2$Cl$_2$ were dried by passage over activated alumina under nitrogen atmosphere (H$_2$O 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, Aplichem or 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 aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain. Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. $^1$H NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in CDCl$_3$, DMSO-d$_6$ or CD$_3$OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being 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-decoupling on a Brucker DPX-400 100 MHz spectrometer in CDCl$_3$, DMSO-d$_6$ or CD$_3$OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are 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. HPLC measurements were done on a Agilent 1260 Infinity autosampler using a CHIRALPAK IA, IB, IC or ID column from DAICEL Chemical. Optical rotations were measured on a polarimeter using a 10 cm cell with a Na 589 nm filter. The blue LEDs were bought on www.conrad.ch/fr (Ruban LED avec câble à extrémités ouvertes Barthelme YS1516414 182405 24 V 502 cm bleu 1 pc(s)).
2. Synthesis of diazo-compounds

Ethyl 2-diazoacetate (4a), tert-butyl 2-diazoacetate (4c) and benzyl 2-diazoacetate (4e) were directly purchased from Sigma Aldrich. The synthesis of reagents 4d to 4m had already been described before by our group. The procedures are taken from the indicated publications to facilitate reproduction of the results by having all data in the same file.

**Ethyl 2-diazo-2-phenylacetate (4b)**

DBU (1.50 mL, 10.0 mmol, 2.00 equiv) was added slowly to a stirred solution of ethyl 2-phenylacetate (30) (0.80 mL, 5.0 mmol, 1.00 equiv) and p-ABSA (1.80 g, 7.50 mmol, 1.50 equiv) in dry MeCN (20 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 14 h, the reaction mixture was quenched with water (15 mL), and extracted with diethyl ether (3 x 15 mL). The organic layers were combined and washed with 10% NH₄Cl (20 mL), brine (20 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 3:97 as mobile phase affording the corresponding ethyl 2-diazo-2-phenylacetate (4b) as a red oil (0.80 g, 4.2 mmol, 84%).

$^1$H NMR (400 MHz, CDCl₃): δ 7.53 - 7.45 (m, 2H, ArH), 7.43 - 7.35 (m, 2H, ArH), 7.22 - 7.14 (m, 1H, ArH), 4.34 (q, $J$ = 7.1 Hz, 2H, OC₂H₅), 1.35 (t, $J$ = 7.1 Hz, 3H, OCH₂C₃H₇). $^{13}$C NMR (101 MHz, CDCl₃): δ: 165.2, 128.8, 125.6, 125.6, 124.0, 61.1, 14.6. The values of the NMR spectra are in accordance with reported literature data.\(^{1}\) One carbon was not resolved at 101 MHz.

**2,6-Di-tert-butyl-4-methylphenyl 2-diazoacetate (4d)**

Following a slightly modified procedure,\(^{2}\) a mixture of 2,6-di-tert-butyl-4-methylphenol (31) (5.51 g, 25.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4H-1,3-dioxin-4-one (32) (3.32 mL, 25.0 mmol, 1.00 equiv), and xylene (5 mL) was stirred at 140 °C for 1.5 h. After cooling to room temperature, the reaction mixture was directly loaded on silica and was purified by column chromatography using EtOAc:pentane 2:98 as mobile phase to afford 2,6-di-tert-butyl-4-methylphenyl 3-oxobutanoate (33) as a white solid (5.77 g, 19.0 mmol, 76%), colorless thick oil (5.00 g, 19.1 mmol, 76%). $^1$H NMR (400 MHz, CDCl₃): δ 12.08 (s, 0.22H, OH of enol form), 7.31 - 7.24 (m, 1H, ArH of enol and keto form), 7.24 - 7.18 (m, 2H, ArH of enol and keto form), 5.38 (s, 0.2H, vinyl H of enol form), 3.81 (s, 1.56H, CH₂COCH₂ of keto form), 3.03 (m, 3.96H, vinyl group).\(^{2}\)

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2H, 2 x CH(CH₃)₂ of enol and keto form), 2.41 (s, 2.32H, CH₂COCH₂ of keto form), 2.08 (s, 0.6H, CH₃ of enol form), 1.28 - 1.21 (m, 12H, 2 x CH(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃), Enol form: δ 177.7, 171.5, 144.5, 140.5, 126.5, 123.9, 88.7, 23.7, 22.7, 21.4; ¹³C NMR (101 MHz, CDCl₃), Keto form: δ 199.9, 165.7, 145.1, 140.2, 126.8, 124.0, 49.6, 30.4, 27.4, 27.3. The values of the NMR spectra are in accordance with reported literature data.³

Following a slightly modified procedure,² to a solution of 2,6-di-tert-butyl-4-methylphenyl 3-oxobutanoate (33) (5.48 g, 18.00 mmol, 1.00 equiv) in MeCN (22 mL) was added triethylamine (3.26 mL, 23.40 mmol, 1.30 equiv). The reaction mixture was cooled in an ice bath and a solution of tosyl azide (3.9 g, 19.8 mmol, 1.1 equiv) in MeCN (22 mL) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. 8% aqueous KOH solution (90 mL) was added and stirred vigorously for 4 h. The reaction mixture was diluted with water (50 mL), extracted with diethyl ether (3 x 100 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography using Et₂O:pentane 2:98 as mobile phase to afford 2,6-di-tert-butyl-4-methylphenyl 2-diazoacetate (4d) as a yellow solid (4.80 g, 16.59 mmol, 92%). ¹H NMR (400 MHz, CDCl₃): δ 7.12 (s, 2H, ArH), 5.00 (s, 1H, CHN₂), 2.32 (s, 3H, ArCH₃), 1.36 (s, 18H, 2 x C(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃): δ 166.3, 145.1, 142.4, 134.8, 127.0, 47.3, 35.3, 31.5, 21.5. The values of the NMR spectra are in accordance with reported literature data.⁴

Allyl 2-diazoacetate (4f)

Following a reported procedure,⁵ to a solution of allyl acetoacetate (34) (1.10 mL, 8.00 mmol, 1.00 equiv) and 4-acetamidobenzenesulfonyl azide (2.11 g, 7.34 mmol, 92%). ¹H NMR (400 MHz, CDCl₃): δ 5.94 (ddt, J = 17.2, 10.4, 5.8 Hz, 1H, CHCH₃), 5.40 - 5.26 (m, 2H, CHCH₂), 4.73 (dt, J = 5.8, 1.3 Hz, 2H, CH₂O), 2.48 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃): δ 190.2, 161.2, 131.6, 119.3, 66.0, 28.4. One carbon was not resolved at 101 MHz. The values of the NMR spectra are in accordance with reported literature data.⁵

To a solution of allyl 2-diazo-3-oxobutanoate (35) (0.840 g, 5.00 mmol, 1.00 equiv) in MeCN (15 mL) was added 8% aqueous KOH solution (25 mL) and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with water (15 mL), extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 10:90 as mobile phase to afford allyl 2-diazoacetate (4f) as a yellow oil (154 mg, 1.22 mmol, 24%). ¹H NMR (400 MHz, CDCl₃): δ 5.92 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H, CHCH₃), 5.38 - 5.20 (m, 2H, CHCH₂), 4.77 (s, 1H, CH₂O).

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$^{13}$C NMR (101 MHz, CDCl$_3$): δ 166.6, 132.4, 118.5, 65.2, 46.4. The values of the NMR spectra are in accordance with reported literature data.\(^6\)

**2-Diazo-$N,N$-diethylacetamide (4g)**

\[
\begin{align*}
\text{NH} & \quad \text{O} & \quad \text{Br} & \quad \text{NaHCO}_3 & \quad \text{MeCN} & \quad \text{TsNHNNHTs} & \quad \text{THF} \\
\text{36} & \quad \text{37} & \quad \text{38} & \quad & \text{4g}
\end{align*}
\]

Following a reported procedure,\(^7\) diethyl amine (36) (0.73 g, 10 mmol, 1.0 equiv) and NaHCO$_3$ (2.52 g, 30.0 mmol, 3.00 equiv) were dissolved in dry CH$_2$Cl$_2$ (20 mL) and bromoacetyl bromide (37) (1.75 mL, 20.0 mmol, 2.00 equiv) was added slowly at 0 °C and the reaction was stirred for 6 h at room temperature, quenched with 100 mL of H$_2$O and the solution was extracted with CH$_2$Cl$_2$ (3 x 50 mL). The combined organic layers were washed with water (100 mL) and dried over MgSO$_4$, the solvent was evaporated and the residue was used in the next step without purification. The resulting diethyl amine (36) and $N,N'$-ditosylhydrazine (2.10 g, 6.08 mmol, 0.60 equiv) were dissolved in dry THF (20 mL) and cooled down to 0 °C, then DBU (2.30 mL, 15.2 mmol, 1.52 equiv) was added dropwise and stirred at room temperature for 1 h and then quenched with saturated solution of NaHCO$_3$ (50 mL) and extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure and purified by column chromatography using EtOAc:pentane 30:70 as mobile phase affording the corresponding 2-diazo-$N,N'$-diethylacetamide (4g) as a yellow oil (0.725 g, 5.14 mmol, 52%). \(^6\)

$^1$H NMR (400 MHz, CDCl$_3$): δ 4.92 (s, 1H, C$_2$H$_2$N$_2$), 3.26 (br s, 4H, 2 x C$_2$H$_5$CH$_3$), 1.14 (t, $J = 7.2$ Hz, 6H, 2 x CH$_2$CH$_3$); \(^13\)C NMR (101 MHz, CDCl$_3$): δ 165.8, 46.4, 41.4, 13.9. The values of the NMR spectra are in accordance with reported literature data.\(^8\)

**2-Diazo-$N$-methoxy-$N$-methylacetamide (4h)**

\[
\begin{align*}
\text{NH} & \quad \text{O} & \quad \text{OH} & \quad \text{Et$_3$N} & \quad \text{PhMe, 110 °C} & \quad \text{TsNHNNHTs} & \quad \text{MeCN} & \quad \text{8% KOH} \\
\text{39} & \quad \text{32} & \quad \text{40} & \quad & & \text{4h}
\end{align*}
\]

Following a reported procedure,\(^9\) a mixture of $N,O$-dimethylhydroxylamine hydrochloride (39) (2.44 g, 25.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4H-1,3-dioxin-4-one (32) (5.00 mL, 37.5 mmol, 1.50 equiv) and triethylamine (3.85 mL, 27.5 mmol, 1.10 equiv) was dissolved in toluene (75 mL) and refluxed for 2 h. The reaction mixture was cooled to room temperature and washed with aqueous hydrochloric acid (90 mL, 1.0 M) and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried over MgSO$_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase to afford $N$-methoxy-$N$-methyl-3-oxobutanamide (40) as a yellow oil (2.40 g, 16.5 mmol, 66%). \(^1\)H NMR (400 MHz, CDCl$_3$): δ 13.65 (s, 0.13H, O$_2$H of enol form), 5.32 (s, 0.13H, vinyl $H$ of enol form) 3.60 (s, 3H, OCH$_3$), 3.50 (s, 1.74H, CH$_3$COCH$_2$ of keto form), 3.13 (s, 2.6H, $N$-CH$_3$ of keto form), 3.11 (s, 0.4H, enol form of N-CH$_3$), 2.17 (s, 2.6H, CH$_3$COCH$_2$ of keto form), 1.89 (s, 0.4H, enol form of $CH_3$); \(^13\)C NMR (101 MHz, CDCl$_3$): δ 201.7, 167.8, 61.1, 48.3, 31.8, 30.0; Enol form, \(^13\)C NMR (101 MHz, CDCl$_3$): δ 175.0, 172.2,


86.5, 21.6. Two carbons were not resolved at 101 MHz. The characterization data corresponded to the reported values.9

Following a slightly modified procedure,2 to a solution of N-methoxy-N-methyl-3-oxobutanamide (40) (0.73 g, 5.0 mmol, 1.0 equiv) in MeCN (6 mL) was added triethylamine (660 mg, 6.50 mmol, 1.30 equiv). The reaction mixture was cooled in an ice bath and a solution of tosyl azide (1.1 g, 5.5 mmol, 1.1 equiv) in MeCN (6 mL) was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 20 h. 8% aqueous KOH solution (25 mL) was added and stirred vigorously for 4 h. The reaction mixture was diluted with water (15 mL), extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over MgSO4 and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase to afford 2-diazo-N-methoxy-N-methylacetamide (4h) as a yellow oil (350 mg, 2.71 mmol, 54%). 1H NMR (400 MHz, CDCl3): δ 5.30 (s, 1H, CHN2), 3.60 (s, 3H, OCH3), 3.12 (s, 3H, CH3); 13C NMR (101 MHz, CDCl3): δ 168.1, 61.3, 46.1, 33.0. The values of the NMR spectra are in accordance with reported literature data.10

Ethyl diazomethanesulfonate (4i)

Following a reported procedure,11 to a solution of ethyl methanesulfonate (41) (1.86 g, 15.0 mmol, 1.00 equiv) in dry THF (50 mL) was added a 1 M LiHMDS solution in hexane (18 mL, 18 mmol, 1.2 equiv) at -78 ºC. After stirring the reaction mixture for 30 min at this temperature, 2,2,2-trifluoroethyl trifluoroacetate (2.4 mL, 18 mmol, 1.2 equiv) was added rapidly in one portion via syringe. After 10 min, the reaction mixture was poured into a solution of diethyl ether (20 mL) and 5% HCl (50 mL). The mixture was extracted with diethyl ether (3 x 50 mL), washed with brine (50 mL), dried over MgSO4, filtered and concentrated under reduced pressure to give a yellow oil. The resulting ethyl 3,3,3-trifluoro-2-oxopropane-1-sulfonate (42) was immediately dissolved in dry MeCN (30 mL). To this solution was added p-ABSA (4.32 g, 18.0 mmol, 1.20 equiv), Et3N (2.5 mL, 18 mmol, 1.2 equiv), and water (0.27 mL, 15 mmol, 1.0 equiv). After stirring the reaction mixture overnight at room temperature, the solvent was removed under reduced pressure and the residue was filtered on short plug of silica gel and washed with a mixture of ethyl acetate (100 mL) and hexane (100 mL). The filtrate was concentrated under vacuum and the residue was purified by column chromatography using EtOAc:pentane 10:90 as mobile phase affording the corresponding ethyl diazomethanesulfonate (4i) as a yellow oil (0.9 g, 6 mmol, 40%). 1H NMR (400 MHz, CDCl3): δ 5.25 (s, 1H, CHN2), 4.26 (q, J = 7.1 Hz, 2H, CH2CH3), 1.41 (t, J = 7.1 Hz, 3H, CH2CH3); 13C NMR (101 MHz, CDCl3): δ 67.4, 52.4, 14.6. The values of the NMR spectra are in accordance with reported literature data.11

Diethyl (diazomethyl)phosphonate (4j)

Following a reported procedure, a mixture of diethyl (2-oxopropyl)phosphonate (43) (1.15 mL, 6.00 mmol, 1.00 equiv), tosyl azide (1.3 g, 6.6 mmol, 1.10 equiv) and triethylamine (6 mL) was stirred at room temperature for 18 h. After evaporation of the triethylamine under reduced pressure, the residue was dissolved in diethyl ether (50 mL). The precipitate was filtered off, the filtrate was evaporated and the residue was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase affording the corresponding diethyl (1-diazo-2-oxopropyl)phosphonate (44) as a yellow oil (0.810 g, 3.68 mmol, 61%).

\[ \text{Me} \underbrace{\begin{array}{c} \text{O} \\ \text{O} \end{array}}_{\text{43}} \xrightarrow{\text{TsN}_3 \text{ Et}_3 \text{N}} \underbrace{\begin{array}{c} \text{O} \\ \text{O} \end{array}}_{\text{44}} \xrightarrow{\text{Na}_2\text{CO}_3 \text{ MeOH}} \underbrace{\begin{array}{c} \text{H} \\ \text{O} \end{array}}_{\text{4j}} \]

\[ \text{H} NMR (400 MHz, CDCl}_3\]: δ 4.04 - 4.19 (m, 4H, 2 × CH\textsubscript{2}CH\textsubscript{3}) 2.19 (s, 3H, CH\textsubscript{3}), 1.30 (t, J = 7.0 Hz, 6H, 2 × CH\textsubscript{2}CH\textsubscript{3}); 13\text{C NMR (101 MHz, CDCl}_3\): δ 190.1 (d, J = 13.2 Hz), 63.4 (d, J = 5.6 Hz), 27.1, 16.0 (d, J = 6.8 Hz). The values of the NMR spectra are in accordance with reported literature data.

To a solution of diethyl (1-diazo-2-oxopropyl)phosphonate (44) (694 mg, 3.15 mmol, 1.00 equiv) in MeOH (9.0 mL) was added Na\textsubscript{2}CO\textsubscript{3} (401 mg, 3.78 mmol, 1.20 equiv). The mixture was stirred at room temperature for 15 min. The precipitate was filtered off, the filtrate was evaporated and the residue was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase affording the corresponding diethyl (diazomethyl)phosphonate (4j) as a yellow oil (533 mg, 2.99 mmol, 95%).

\[ \text{H} NMR (400 MHz, CDCl}_3\): δ 4.17 - 4.08 (m, 4H, 2 × CH\textsubscript{2}CH\textsubscript{3}), 3.75 (d, J = 11.1 Hz, 1H, CH\textsubscript{N}2), 1.34 (td, J = 7.1, 0.7 Hz, 6H, 2 × CH\textsubscript{2}CH\textsubscript{3}); 13\text{C NMR (101 MHz, CDCl}_3\): δ 62.6 (d, J = 5.3 Hz), 16.1 (d, J = 6.9 Hz). The values of the NMR spectra are in accordance with reported literature data. One carbon was not resolved at 101 MHz.

2,2,2-Trifluorodiazoethane (4k)

\[ \text{H}_2\text{N} \underbrace{\text{CF}_3}_{\text{45}} \xrightarrow{\text{NaNO}_2 \text{ H}_2\text{O}} \underbrace{\text{H} \underbrace{\text{CF}_3}_{\text{4k}}}_{\text{CH}_2\text{Cl}_2} \]

Following a reported procedure, under argon, 2,2,2-trifluoroethanamine hydrochloride (45) (0.678 g, 5.00 mmol, 1.00 equiv) and sodium nitrite (0.379 g, 5.50 mmol, 1.10 equiv) were dissolved in degassed CH\textsubscript{2}Cl\textsubscript{2} (10 mL). Degassed water (1.00 mL, 55.5 mmol, 11.1 equiv) was added slowly at 0 °C. The solution was stirred for 2 h at 0 °C and 1 h at room temperature. The aqueous layer was frozen in the freezer overnight (-18 °C) and the organic layer was dried over a plug of potassium carbonate, transferred into a vial, sealed and stored at -18 °C. The concentration of the obtained solution was determined to be 0.37 M by 19\text{F NMR analysis (according to an internal reference, PhCF\textsubscript{3}). 19\text{F NMR (377 MHz, CH}_2\text{Cl}_2\): δ -55.56. The values of the NMR spectra are in accordance with reported literature data.}

Ethyl 2-diazopropanoate (4l)

Following a modified reported procedure, DBU (1.8 mL, 12 mmol, 3.0 equiv) was added slowly to a stirred solution of ethyl 2-methylacetoacetate (46) (0.60 mL, 4.0 mmol, 1.0 equiv) and p-ABSA (1.4 g, 6.0 mmol, 1.5 equiv) in MeCN (80 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 12 h, the reaction mixture was quenched with 1 M HCl (8 mL), and extracted with hexane (3 x 40 mL). The organic layers were combined, washed with a saturated solution of NaHCO$_3$ (40 mL), brine (40 mL), dried over MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using Et$_2$O:pentane 2:98 as mobile phase affording the corresponding ethyl 2-diazopropanoate (4I) as a yellow oil (241 mg, 1.88 mmol, 47%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 4.20 (q, $J = 7.1$ Hz, 2H, CH$_2$CH$_3$), 1.94 (s, 3H, N$_2$CCCH$_3$), 1.25 (t, $J = 7.1$ Hz, 3H, CH$_2$CH$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$): δ 167.9, 60.7, 14.5, 8.4. The values of the NMR spectra are in accordance with reported literature data.

3-Diazodihydrofuran-2(3H)-one (4m)

Following a reported procedure, sodium azide (2.42 g, 37.2 mmol, 4.00 equiv), sodium hydroxide (78 mL, 2 M in water), tetrabutylammonium bromide (30 mg, 0.090 mmol, 0.01 equiv), and pentane (40 mL) were mixed in a 250 mL round-bottom flask with magnetic stir bar open to the air and allowed to cool to 0 °C. With vigorous stirring, Tf$_2$O (3.10 mL, 18.6 mmol, 2.00 equiv) was added dropwise. After 10 min, a solution of 2-acetyl-butyrolactone (47) (1.00 mL, 9.30 mmol, 1.00 equiv) in MeCN (35 mL) was poured into the round-bottom flask through a funnel, followed by an additional MeCN (10 mL) to complete the transfer. The initially colorless reaction mixture immediately turned yellow. After allowing to stir for 30 min at 0 °C, the mixture was diluted with ice water (25 mL) and chilled EtOAc (25 mL) and transferred to a separatory funnel. After phase separation and removal of the organic layer, the aqueous layer was washed with cold EtOAc (2 x 50 mL). The combined organic layers were dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc:pentane 50:50 as mobile phase affording the corresponding 3-diazodihydrofuran-2(3H)-one (4m) as a bright yellow crystalline solid (0.32 g, 2.8 mmol, 30%). $^1$H NMR (400 MHz, CDCl$_3$): δ 4.38 (t, $J = 8.0$ Hz, 2H, CH$_2$), 3.36 (t, $J = 8.0$ Hz, 2H, CH$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$): 170.6, 65.3, 49.4, 23.1. The values of the NMR spectra are in accordance with reported literature data.

Methyl (E)-2-diazopent-3-enoate (4n)

Following a reported procedure,\textsuperscript{17} to a stirring solution of methyl trans-pent-3-enoate (48) (1.00 g, 8.76 mmol, 1.00 equiv) and p-ABSA (3.16 g, 13.1 mmol, 1.50 equiv) in dry MeCN (20 mL) at 0 °C, was added DBU (2.65 mL, 17.5 mmol, 2.00 equiv) slowly in 5 min. The reaction mixture was stirred at 0 °C for 1 h and then 12 h at room temperature. The reaction mixture was quenched with NH\textsubscript{4}Cl (saturated solution, 20 mL). The aqueous layer was extracted with Et\textsubscript{2}O (3 x 40 mL) and the combined organic layers were washed with brine (40 mL), dried over MgSO\textsubscript{4}, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using pentane as mobile phase affording the corresponding methyl (E)-2-diazo-pent-3-enoate (4n) as an orange oil (950 mg, 6.78 mmol, 77%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 5.73 (dd, \textit{J} = 15.8, 1.7 Hz, 1H, CH\textsubscript{3}CHC\textsubscript{H}), 5.38 - 5.29 (m, 1H, CH\textsubscript{3}C\textsubscript{H}CH), 3.79 (s, 3H, OCH\textsubscript{3}), 1.84 (dd, \textit{J} = 6.7, 1.7 Hz, 3H, CH\textsubscript{2}CHCH); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): δ 166.1, 120.4, 112.6, 52.0, 18.2. The values of the NMR spectra are in accordance with reported literature data.\textsuperscript{17} One carbon was not resolved at 101 MHz.

3. Synthesis of ligands

Ligand 5a was synthesized using a simple reported procedure. The ligand 5b was purchased directly from TCI.

\[ \text{Cl} \quad \text{Cl} \quad \text{N} \quad \text{N} \quad \text{Cl} \quad \text{Cl} \]

2,2'-{Propane-2,2-diyl}bis(4,5-dihydrooxazole) (5c)

Following a reported procedure, \( K_2CO_3 \) (2.76 g, 20.0 mmol, 4.0 equiv) was suspended in DCM (50 mL) at 0 °C under argon and then ethanolamine (49) (0.63 mL, 10.5 mmol, 2.1 equiv) was added. A solution of dimethylmalonyl dichloride (50) (0.660 mL, 5.00 mmol, 1.0 equiv) in DCM (10 mL) was added dropwise to the cold mixture. The mixture was allowed to warm to room temperature and stirred for 16 h. MeOH (50 mL) was added and the mixture was stirred for 2 h. The whole reaction mixture was filtered through Celite (5 g) and rinsed twice with MeOH (2 × 10 mL). The solvent was removed under reduce pressure. The crude \( N^1,N^3\)-bis(2-hydroxyethyl)-2,2-dimethylmalonamide (51) was obtained as a white residue (1.12 g) and was used directly into the next step without further purification.

The crude bisamide (51) was dissolved in toluene (30 mL) and heated to 70 °C under argon. Thionyl chloride (1.46 mL, 20.0 mmol, 4.0 equiv) was added in one portion and the resulting mixture was stirred at 70 °C for 5 h. The reaction was cooled to 0 °C and quenched with a saturated NaHCO\(_3\) solution (15 mL). The mixture was extracted with DCM (5 × 30 mL) and the combined organic layers were dried over MgSO\(_4\), filtered, and the solvent was removed under reduced pressure to furnish a pale yellow oil. The residue was dissolved in 17.0 mL of a 5% methanolic NaOH solution (0.830 g of NaOH was completely dissolved in 0.850 mL H\(_2\)O and then diluted with 16.1 mL MeOH) and heated to reflux for 2 h under argon. The solvent was removed under reduced pressure and the resulting residue was partitioned between DCM (10 mL) and H\(_2\)O (10 mL). The aqueous phase was extracted with DCM (5 × 10 mL). The combined organic layers were dried over MgSO\(_4\), filtered, and the solvent was removed under reduced pressure to furnish afford 2,2'-{propane-2,2-diyl}bis(4,5-dihydrooxazole) (5c) as a pale yellow wax (412 mg, 2.26 mmol, 45%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.28 (t, \( J = 9.5 \) Hz, 4H, 2 x CH\(_2\)O), 3.87 (t, \( J = 9.5 \) Hz, 4H, 2 x CH\(_2\)N), 1.51 (s, 6H, 2 x CH\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 170.0, 68.2, 54.5, 38.8, 24.4. The values of the NMR spectra are in accordance with reported literature data.

2,2'-{propane-2,2-diyl}bis(4,4-dimethyl-4,5-dihydrooxazole) (5d)

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2-Amino-2-methylpropan-1-ol (52) (0.952 mL, 10.5 mmol, 2.1 equiv) was added to a suspension of K₂CO₃ (2.76 g, 20.0 mmol, 4.0 equiv) DCM (50 mL) at 0 °C under argon. A solution of dimethylmalonyl dichloride (50) (0.660 mL, 5.00 mmol, 1.0 equiv) in DCM (10 mL) was added dropwise to the cold mixture. The mixture was allowed to warm to room temperature and stirred for 16 h. MeOH (50 mL) was added and the mixture was stirred for 2 h. The whole reaction mixture was filtered through Celite (5 g) and rinsed twice with MeOH (2 × 10 mL). The solvent was removed under reduced pressure to furnish a white residue (1.42 g) and was used directly into the next step without further purification.

The crude bisamide (53) was dissolved in toluene (30 mL) and heated to 70 °C under argon. Thionyl chloride (1.50 mL, 20.0 mmol, 4.0 equiv) was added in one portion and the resulting mixture was stirred at 70 °C for 5 h. The reaction was cooled to 0 °C and quenched with a saturated NaHCO₃ solution (15 mL). The mixture was extracted with DCM (5 × 30 mL) and the combined organic layers were dried over MgSO₄, filtered and the solvent was removed under reduced pressure to furnish a pale yellow oil. The residue was dissolved in 17.0 mL of a 5% methanolic NaOH solution (0.830 g of NaOH was completely dissolved in 0.850 mL H₂O and then diluted with 16.1 mL MeOH) and heated to reflux for 2 h under argon. The reaction was removed under reduced pressure and the resulting residue was partitioned between DCM (10 mL) and H₂O (10 mL). The aqueous layer was extracted with DCM (5 × 10 mL). The combined organic layers were dried over MgSO₄, filtered and the solvent was removed under reduced pressure to furnish afford 2,2'-((propane-2,2-diyl)bis(4,4-dimethyl-5,5-dihydrooxazole) (5d) as a pale yellow wax (471 mg, 2.00 mmol, 40%). ¹H NMR (400 MHz, CDCl₃) δ 3.92 (s, 3H, NCH₂), 1.49 (s, 6H, 2 x CH₃), 1.27 (s, 12H, 4 x CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 167.6, 79.4, 67.0, 38.2, 28.0, 25.4. The values of the NMR spectra are in accordance with reported literature data.

(4S,5S)-2,2'-((Cyclopropane-1,1-diyl)bis(4-(tert-butyl)-4,5-dihydrooxazole) (5e)

Following a reported procedure,²¹ to a solution of (S)-tert-leucinol (55) (0.94 g, 8.0 mmol, 2.0 equiv) in DCM (40 mL) was added diethyl malonimidate dihydrochloride (54) (0.93 g, 4.0 mmol, 1.0 equiv). The resulting cloudy solution was stirred at room temperature for 36 h. The reaction mixture was diluted with water (8 mL) and extracted with DCM (3 × 20 mL). The combined organic layers were washed with brine (40 mL), dried over MgSO₄, and concentrated. The resulting oily residue was distilled bulb-to-bulb (Kugelrohr distillation, 150 °C at 0.2 mbar) to afford bis((S)-4-(tert-butyl)-4,5-dihydrooxazol-2-yl)methane (56) as a white solid (0.600 g, 2.84 mmol, 71%). ¹H NMR (400 MHz, CDCl₃) δ 4.13 (dd, J = 10.1, 8.7 Hz, 2H, 2 x OCH₃), 4.02 (dd, J = 8.7, 7.7 Hz, 2H, 2 x C(CH₃)₂CH), 3.81 (ddt, J = 10.1, 7.8, 1.1 Hz, 2H, 2 x OCH₃), 3.27 (t, J = 1.2 Hz, 2H, O(C=NC(CH₃)₂), 0.82 (s, 18H, 2 x C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃):

δ 161.5, 76.0, 69.1, 34.0, 28.4, 26.0. The values of the NMR spectra are in accordance with reported literature data.²¹

Following a reported procedure,²¹ to a solution of bis((S)-4-(tert-butyl)-4,5-dihydrooxazol-2-yl)methane (56) (75 mg, 0.28 mmol, 1.0 equiv) in THF (5 mL) in a 20 mL microwave vial, was added TMEDA (85 μL, 0.56 mmol, 2.0 equiv) and i-Pr₂NH (40 mL, 0.28 mmol, 1.0 equiv). The solution was cooled to -78 °C and n-BuLi (0.38 mL, 1.5 M in hexane, 0.56 mmol, 2.0 equiv) was added. The reaction mixture was warmed to -20 °C and stirred at that temperature for 30 minutes. The solution was cooled back to -78 °C and 1,2-dibromoethane (57) (25 μL, 0.28 mmol, 2.0 equiv) was added. After the addition, the cold bath was removed and the reaction mixture was allowed to stir at room temperature for an additional 16 h. The reaction mixture was quenched by the addition of sat. aq. NH₄Cl (2.5 mL) and diluted with water (2 mL) to dissolve the resulting salts. The mixture was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, and concentrated. The resulting oily residue was purified by column chromatography using EtOAc/pentane 1:2 to 1:1 as mobile phase to afford (4S,4'S)-2,2'-((cyclopropane-1,1-diyl)bis(4-(tert-butyl)-4,5-dihydrooxazole) (5e) as a white solid (42 mg, 0.14 mmol, 51%). ¹H NMR (400 MHz, CDCl₃): δ 4.18 (dd, J = 10.0, 8.6 Hz, 2H, 2 x OC₃H₇), 4.10 (dd, J = 8.7, 7.3 Hz, 2H, 2 x C(CH₃)₃CH), 3.82 (dd, J = 10.0, 7.2 Hz, 2H, 2 x OCH₃), 1.52 - 1.47 (m, 2H, 2 x CH₃ of CyP), 1.30 - 1.24 (m, 2H, 2 x CH₃ of CyP), 0.86 (s, 18H, 2 x C(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 75.2, 69.1, 33.8, 25.7, 18.2, 15.1. The values of the NMR spectra are in accordance with reported literature data.²¹
4. Preparation of the alkenyl boronic acids precursors

trans-2-Phenylvinylboronic acid (58a), trans-2-(4-Methylphenyl)vinylboronic acid (58b), trans-2-(4-Methoxyphenyl)vinylboronic acid (58c), trans-2-(4-Fluorophenyl)vinylboronic acid (58d), trans-2-(4-(Trifluoromethyl)phenyl)vinylboronic acid (58e), trans-3-Phenyl-1-propen-1-ylboronic acid (58i), 2-Cyclohexyvinylboronic acid (58j), 1-Penten-1-ylboronic acid (58k), trans-2-Chloromethylvinylboronic acid (58o), and 1-Cyclohexenylboronic acid (58r) were directly purchased from Sigma Aldrich and washed in pentane/Et₂O 3:1 prior to use.

The $^{13}$C NMR signal for carbons attached to boron was broad or did not appear in the collected spectra due to the quadrupolar splitting of $^{11}$B.\(^{22}\)

\((E)-(2-(Naphthalen-1-yl)vinyl)boronic acid (58f)\)

Following a modified reported procedure,\(^{23}\) catecholborane (60) (640 µl, 6.00 mmol, 1.20 equiv) was added dropwise to stirring neat 1-ethynynaphthalene (59) (711 µl, 5.00 mmol, 1.00 equiv) at 0 °C under inert atmosphere. The reaction mixture was stirred at room temperature until the gas evolution had ceased and, then was heated to 70 °C and stirred for 3 h. The resulting thick oil was dissolved in THF (8 mL) and then slowly added to an ice-cold mixture of 1:1 Et₂O/water (25 mL) and stirred for an additional 30 minutes. The two layers were separated and the aqueous layer was extracted with Et₂O (2 x 15 mL). The combined organic layers were washed with water (5 x 15 mL), dried over MgSO₄, filtered and the solvent was evaporated under reduced pressure. The resulting crude residue was dissolved in boiling water (70 mL). The insoluble materials were discarded by hot filtration and the aqueous filtrate was allowed to cool to room temperature. The precipitate was collected by filtration to give (E)-(2-(naphthalen-1-yl)vinyl)boronic acid (58f) as a white solid (324 mg, 1.60 mmol, 33%). $^1$H NMR (400 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 8.21 (d, $J = 8.3$ Hz, 1H, ArH), 8.09 (d, $J = 18.2$ Hz, 1H, BCHCH), 7.93 - 7.82 (m, 2H, ArH), 7.73 (d, $J = 7.2$ Hz, 1H, ArH), 7.62 - 7.44 (m, 3H, ArH), 6.20 (d, $J = 18.2$ Hz, 1H, BCHCH); $^{13}$C NMR (101 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 143.5, 135.6, 134.0, 131.3, 129.4, 129.3, 127.3, 126.9, 126.6, 124.2, 124.0; $^{11}$B NMR (128 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 29.0. The $^{13}$C NMR signal for the carbon attached to boron did not appear due to the quadrupolar splitting of $^{11}$B. The values of the NMR spectra are in accordance with reported literature data.\(^{23}\)


(E)-(2-(Thiophen-2-yl)vinyl)boronic acid (58g)

Following a reported procedure,24 CuCl (15.0 mg, 0.150 mmol, 0.03 equiv), NaOtBu (29.0 mg, 0.300 mmol, 0.06 equiv) and DPEPhos (81.0 mg, 0.150 mmol, 0.03 equiv) were dissolved in THF (5 mL) under argon. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (61) (1.40 g, 5.50 mmol, 1.10 equiv) and THF (2.5 mL) were added and the reaction mixture was stirred for another 10 min and then 2-ethynylthiophene (62) (0.475 mL, 5.00 mmol, 1.00 equiv) was added, followed by MeOH (0.405 mL, 10.0 mmol, 2.00 equiv). The reactor wall was washed with THF (1.5 mL), sealed, and stirred for 4 h. The reaction mixture was filtered through a pad of Celite, washed with EtOAc and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography using EtOAc/pentane 5:95 as mobile phase affording (E)-4,4,5,5-tetramethyl-2-(2-thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (63) as a clear yellow oil (1.07 g, 4.53 mmol, 91%). 

1H NMR (400 MHz, CDCl3) δ 7.47 (d, J = 18.1 Hz, 1H, CHCB), 7.24 (d, J = 5.1, 1H, ArH), 6.99 (dd, J = 5.1, 3.6 Hz, 1H, ArH), 5.91 (d, J = 18.1 Hz, 1H, CHCB), 1.30 (s, 12H, 4 x CH3); 13C NMR (101 MHz, CDCl3) δ 144.1, 141.9, 127.8, 126.4, 83.5, 24.9. The 11B NMR signal for the carbon attached to boron did not appear due to the quadrupolar splitting of 11B. The values of the NMR spectra are in accordance with reported literature data.24

(E)-4,4,5,5-tetramethyl-2-(2-thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (63) (1.00 g, 4.23 mmol, 1.00 equiv), NH2OAc (1.63 g, 21.2 mmol, 5.00 equiv), NaIO4 (4.53 g, 21.2 mmol, 5.00 equiv) were suspended in a mixture: 1:1 acetone/water (42 mL). The resulting slurry was stirred at room temperature for 16 h. It was then diluted with EtOAc (30 mL), washed successively with water (2 x 20 mL) and brine (20 mL), dried over MgSO4, filtered and the solvent was removed under reduced pressure affording (E)-2-(2-thiophen-2-yl)vinyl)boronic acid (58g) as a clear yellow solid (0.416 g, 2.70 mmol, 64%). M.p. 118-120 °C; 1H NMR (400 MHz, DMSO-d6/D2O 9:1) δ 7.47 (d, J = 5.1 Hz, 1H, ArH), 7.36 (d, J = 18.1 Hz, 1H, CHCB), 7.14 (m, 1H, ArH), 7.04 (dd, J = 5.1, 3.5 Hz, 1H, ArH), 5.80 (d, J = 18.1 Hz, 1H, CHCB); 13C NMR (101 MHz, DMSO-d6/D2O 9:1) δ 144.0, 138.8, 128.2, 127.6, 126.4, 122.6 (br); 11B NMR (128 MHz, DMSO-d6/D2O 9:1) δ 28.5. The 13C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of 11B. The values of the NMR spectra are in accordance with reported literature data.25

(E)-(5-Chloropent-1-en-1-yl)boronic acid (58m)

A solution of 1 M dibromoborane dimethyl sulfide complex in DCM (6.00 mL, 6.00 mmol, 1.2 equiv) was added dropwise to neat 5-chloropent-1-ynne (64) (0.523 mL, 5.00 mmol, 1.0 equiv) at 0 °C. The resulting solution was allowed to warm to room temperature. After stirring for 4 h, the solution was

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transferred slowly to an ice-cooled mixture of 2:1 diethyl ether/water (18 mL) and stirred vigorously for 15 min. The mixture was diluted with diethyl ether (20 mL) and extracted with water (2 x 10 mL). The organic layer was then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na₂CO₃), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over MgSO₄, filtered and the solvent was removed under reduced pressure affording (E)-(6-chloropent-1-en-1-yl)boronic acid (58m) as a light yellow oil (461 mg, 3.11 mmol, 62 %). ¹H NMR (400 MHz, DMSO-d₆/D₂O 9:1) δ 6.40 (dt, J = 17.9, 6.5 Hz, 1H, CHCH₂CH), 5.35 (dt, J = 17.9, 1.5 Hz, 1H, BCHCH), 3.60 (t, J = 6.5 Hz, 2H, CH₂Cl), 2.19 (ddt, J = 7.8, 6.6, 1.6 Hz, 2H, CH₂CH₂CH₂Cl), 1.79 (dq, J = 8.4, 6.6 Hz, 2H, CH₂CH₂Cl); ¹³C NMR (101 MHz, DMSO-d₆/D₂O 9:1) δ 149.0, 125.8 (br), 45.3, 32.4, 31.3; ¹B NMR (128 MHz, DMSO-d₆/D₂O 9:1) δ 27.3; IR (νmax, cm⁻¹) 2961 (m), 2922 (w), 1634 (m), 1347 (s), 1305 (m), 1225 (m), 1051 (w), 998 (m), 691 (m), 652 (m); HRMS (ESI) calcd for C₇H₉BClO₃ [M⁺] 147.0390; found 147.0394. The ¹³C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ¹¹B.

(E)-(6-Methoxy-6-oxohex-1-en-1-yl)boronic acid (58n)

Following a modified reported procedure,²⁶ a solution of 1 M dibromoborane dimethyl sulfide complex in DCM (6.00 mL, 6.00 mmol, 1.2 equiv) was added dropwise to neat methyl hex-5-ynoate (65) (631 mg, 5.00 mmol, 1.00 equiv) at 0 °C. The resulting solution was allowed to warm to room temperature. After stirring for 4 h, the solution was transferred slowly to an ice-cooled mixture of 2:1 diethyl ether/water (18 mL) and stirred vigorously for 15 min. The mixture was diluted with diethyl ether (20 mL) and extracted with water (2 x 10 mL). The organic layer was then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na₂CO₃), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over MgSO₄, filtered and the solvent was removed under reduced pressure affording (E)-(6-methoxy-6-oxohex-1-en-1-yl)boronic acid (58n) as a light brown oil (517 mg, 3.01 mmol, 60 %). ¹H NMR (400 MHz, DMSO-d₆/D₂O 9:1) δ 6.38 (dt, J = 17.9, 6.4 Hz, 1H, CHCH₂CH), 5.30 (dt, J = 17.9, 1.6 Hz, 1H, BCHCH), 3.55 (s, 3H, OCH₃), 2.26 (t, J = 7.4 Hz, 2H, CH₂CH₂O), 2.10 - 2.00 (m, 2H, CH₂BCC), 1.59 (p, J = 7.4 Hz, 2H, CH₂CH₂CH₂); ¹³C NMR (101 MHz, DMSO-d₆/D₂O 9:1) δ 174.4, 150.1, 125.2 (br), 51.8, 34.5, 33.0, 23.6. The ¹³C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ¹¹B. The values of the NMR spectra are in accordance with reported literature data.²⁶

(E)-(3-((Triisopropylsilyl)oxy)prop-1-en-1-yl)boronic acid (58p)

Following a reported procedure,²⁷ a solution of propargyl alcohol (66) (1.04 mL, 17.8 mmol, 1.00 equiv), imidazole (3.04 g, 44.7 mmol, 2.50 equiv), and triisopropylchlorosilane (5.73 mL, 26.8 mmol, 1.50 equiv) in DCM (30 mL) was stirred at room temperature for 16 h. The reaction mixture was diluted with DCM (30 mL) and quenched with water (10 mL). The aqueous layer was separated and extracted with DCM (2 x 15 mL). The combined organic layers were washed successively with water (2 x 15 mL) and brine (15 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude

product was purified by column chromatography using pentane as mobile phase providing trisopropyl(prop-2-yn-1-yl)oxy)silane (67) as a colorless oil (3.23 g, 15.2 mmol, 85%). 1H NMR (400 MHz, CDCl3) δ 4.38 (d, J = 2.4 Hz, 2H, CH2O), 2.39 (t, J = 2.4 Hz, 1H, CH), 1.26 - 0.99 (m, 21H, TIPS); 13C NMR (101 MHz, CDCl3) δ 82.5, 72.7, 51.7, 17.8, 12.0. The values of the NMR spectra are in accordance with reported literature data.27

Catecholborane (60) (1.71 mL, 16.0 mmol, 1.05 equiv) was added dropwise to stirring neat trisopropyl(prop-2-yn-1-yl)oxy)silane (67) (3.23 g, 15.2 mmol, 1.00 equiv) at 0 °C under inert atmosphere. The reaction mixture was stirred at room temperature until the gas evolution had ceased and, then was heated to 70 °C and stirred for 4 h. After cooling to room temperature, the reaction mixture was stirred for another 10 min, the mixture was transferred to a separatory funnel and the layers were separated. The organic layer was washed with 1 N NaOH (60 mL), water (3 x 60 mL) and 1:1 water/brine (60 mL). The organic layer was dried over MgSO4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using Et2O/pentane 50:50 as mobile phase affording (E)-(3-(trisopropylsilyl)oxy)prop-1-en-1-y1)boronic acid (58p) as a colorless oil (2.12 g, 8.21 mmol, 54%). TLC (Et2O/pentane, 50:50): Rf = 0.37. KMnO4; 1H NMR (400 MHz, CDCl3) δ 6.46 (dt, J = 17.9, 3.7 Hz, 1H, CHCHB), 5.59 (dt, J = 17.9, 2.0 Hz, 1H, CHCHB), 4.22 (dd, J = 3.7, 2.0 Hz, 2H, CH2O), 1.05 - 0.94 (m, 21H, TIPS); 13C NMR (101 MHz, CDCl3) δ 6.46 (dt, J = 17.9, 3.7 Hz, 1H, CHCHB), 5.59 (dt, J = 17.9, 2.0 Hz, 1H, CHCHB), 4.22 (dd, J = 3.7, 2.0 Hz, 2H, CH2O), 1.05 - 0.94 (m, 21H, TIPS); 13C NMR (101 MHz, CDCl3) δ 149.6, 122.0 (br), 65.1, 18.5, 12.1; 11B (128 MHz, DMSO-d6/D2O 9:1) δ 26.1; IR (νmax, cm−1) 2942 (m), 2895 (m), 2867 (m), 1638 (m), 1462 (m), 1372 (s), 1344 (s), 1291 (s), 1258 (m), 1131 (s), 1107 (s), 1055 (m), 1017 (m), 994 (m), 953 (m), 882 (s), 771 (m), 681 (s), 663 (s), 653 (s); HRMS (ESI) calc for C12H26BO3Si [M+ ] 257.1750; found 257.1749. The 13C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of 11B.

(E)-(3-(1,3-Dioxoisindolin-2-yl)prop-1-en-1-yl)boronic acid (58q)

![Chemical Diagram]

Following a reported procedure,24 CuCl (15.0 mg, 0.150 mmol, 0.03 equiv), NaOtBu (29.0 mg, 0.300 mmol, 0.06 equiv) and DPEPhos (81.0 mg, 0.150 mmol, 0.03 equiv) were dissolved in THF (5 mL) under argon. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (61) (1.40 g, 5.50 mmol, 1.10 equiv) and THF (2.5 mL) were added and the reaction mixture was stirred for another 10 min and then N-propargylphthalimide (68) (0.926 g, 5.00 mmol, 1.00 equiv) was added, followed by MeOH (0.405 mL, 10.0 mmol, 2.00 equiv). The reactor wall was washed with THF (1.5 mL), sealed, and stirred for 4 h. The reaction mixture was filtered through a pad of Celite, washed with EtOAc and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography using EtOAc/pentane 15:85 as mobile phase affording (E)-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)isoindoline-1,3-dione (69) as a white solid (1.49 g, 4.75 mmol, 95%). 1H NMR (400 MHz, CDCl3) δ 7.85 (dd, J = 5.4, 3.1 Hz, 2H, ArH), 7.72 (dd, J = 5.5, 3.1 Hz, 2H, ArH), 6.59 (dt, J = 18.0, 4.5 Hz, 1H, CHCHB), 5.48 (dt, J = 18.0, 1.9 Hz, 1H, CHCHB), 4.38 (dd, J =
4.6, 1.8 Hz, 2H, CH₃), 1.22 (s, 12H, 4 x CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 145.4, 134.2, 132.2, 123.5, 83.5, 41.1, 24.9. The ¹³C NMR signal for the carbon attached to boron did not appear due to the quadrupolar splitting of ¹¹B. The values of the NMR spectra are in accordance with reported literature data.²⁴

(−)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allylisooindoline-1,3-dione (69) (1.49 g, 4.75 mmol), NH₂OAc (1.83 g, 23.7 mmol, 5.00 equiv), NaIO₄ (5.08 g, 23.7 mmol, 5.00 equiv) were suspended in a mixture 1:1 acetone/water (46 mL). The resulting slurry was stirred at room temperature for 16 h. It was then diluted with EtOAc (30 mL), washed successively with water (2 x 20 mL) and brine (20 mL), dried over MgSO₄, filtered, and concentrated under reduced pressure affording (−)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allylisooindoline-1,3-dione (58a) as a white solid (0.805 g, 3.48 mmol, 73%). M.p. 145-147 °C; ¹H NMR (400 MHz, DMSO-d₆/D₂O 9:1) δ 7.95 - 7.77 (m, 4H, ArH), 6.41 (dt, J = 18.0, 4.3 Hz, 1H, CHCHB), 5.24 (dt, J = 18.0, 1.9 Hz, 1H, CHCHB), 4.22 (dd, J = 4.3, 1.9 Hz, 2H, CH₂N); ¹³C NMR (101 MHz, DMSO-d₆/D₂O 9:1) δ 168.2, 143.2, 135.2, 131.9, 124.4 (br), 123.7, 41.0; ¹¹B NMR (128 MHz, DMSO-d₆/D₂O 9:1) δ 26.8; IR (νmax, cm⁻¹) 2985 (m), 2904 (m), 1773 (m), 1716 (s), 1427 (m), 1395 (s), 1343 (m), 1071 (s), 1055 (s), 726 (m); HRMS (ESI) calcd for C₃₃H₃₁BNO₄ + [M+H]+ 232.0776; found 232.0775. The ¹³C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ¹¹B.

(E)-(3-Methylbuta-1,3-dien-1-yl)boronic acid (58s)

![Diagram of the reaction]

Following a reported procedure,²⁸ to a flask containing Cp₂ZrHCl (64.0 mg, 0.250 mmol, 0.05 equiv) at 0 °C under argon atmosphere was added pinacolborane (71) (0.798 mL, 5.50 mmol, 1.10 equiv) then dropwise 2-methylbut-1-en-3-yne (70) (0.485 mL, 5.00 mmol, 1.00 equiv). The resulting mixture was stirred at 0 °C for 30 min then at room temperature for 24 h. The crude reaction was directly purified by column chromatography using EtOAc/pentane 2:98 as mobile phase affording 4,4,5,5-tetramethyl-2-[(1E)-3-methylbuta-1,3-dien-1-yl]-1,3,2-dioxaborolane (72) as a colorless oil (789 mg, 4.05 mmol, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.10 (d, J = 18.2 Hz, 1H, CHCHB), 5.56 (d, J = 18.2 Hz, 1H, CHCHB), 5.21 - 5.13 (m, 2H, CHCH₃), 1.85 (t, J = 1.1 Hz, 3H, CH₃), 1.28 (s, 12H, 4 x CH₃). ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 143.2, 120.3, 116.7 (br), 83.4, 24.9, 17.9. The ¹³C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of ¹¹B. The values of the NMR spectra are in accordance with reported literature data.²⁸

Following a reported procedure,²⁸ to a stirred solution of 4,4,5,5-tetramethyl-2-[(1E)-3-methylbuta-1,3-dien-1-yl]-1,3,2-dioxaborolane (72) (772 mg, 3.98 mmol, 1.00 equiv) in acetone (125 mL) were added an aqueous solution of NH₂OAc (79 mL, 0.1 M, 1.50 equiv) and NaIO₄ (2.55 g, 11.9 mmol, 3.0 equiv). The cloudy mixture was stirred at room temperature for 24 h. After cautious acidification with aqueous 2 M HCl (pH = 3), the aqueous layer was extracted with AcOEt (2 x 80 mL). The combined organic layers were dried over MgSO₄, filtered and the solvent was removed under reduced pressure affording (E)-(3-methylbuta-1,3-dien-1-yl)boronic acid (58s) as a light yellow solid (200 mg, 1.79 mmol, 36%). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 17.8 Hz, 1H, CHCHB), 5.68 (d, J = 17.9 Hz, 1H, CHCHB), 5.29 (s, 1H, CHCH₃), 5.27 (s, 1H, CHCH₂), 1.92 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 154.9, 143.2, 121.6, 120.0 (br), 18.1; ¹¹B NMR (128 MHz, DMSO-d₆/D₂O 9:1) δ 19.38. The ¹³C NMR signal for the


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carbon attached to boron was broad due to the quadrupolar splitting of $^{11}$B. The values of the NMR spectra are in accordance with reported data.  

$((1E,3E)-4$-Phenylbuta-1,3-dien-1-yl)boronic acid (58t)  

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\begin{align*}
\text{73} \quad & \quad + \quad \text{60} \quad \text{neat, } 70 ^\circ \text{C} \quad \rightarrow \quad \text{58t}
\end{align*}
\]

Catecholborane (60) (533 µl, 5.00 mmol, 1.00 equiv) was added dropwise to stirring neat (E)-but-1-en-3-yn-1-ylbenzene (73) (641 mg, 5.00 mmol, 1.00 equiv) at 0 °C under inert atmosphere. The reaction mixture was stirred at room temperature until the gas evolution had ceased and, then was heated to 70 °C and stirred for 1 h. The reaction was cooled to 0 °C and quenched by dropwise addition of water (3 mL). The solid was suspended in water (20 mL) and vigorously stirred at room temperature for 18 h. The mixture was extracted with diethyl ether (2 x 20 mL) and washed with water (5 x 20 mL). The organic layer was then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na$_2$CO$_3$), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure affording $((1E,3E)-4$-phenylbuta-1,3-dien-1-yl)boronic acid (58t) as a off-white solid (461 mg, 3.11 mmol, 62 %). M.p. 110 - 112 °C; $^1$H NMR (400 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 7.54 - 7.48 (m, 2H), 7.38 - 7.30 (m, 2H), 7.30 - 7.22 (m, 1H), 7.08 - 6.87 (m, 2H), 6.69 (d, J = 15.4 Hz, 1H), 5.65 (d, J = 17.3 Hz, 1H); $^{13}$C NMR (101 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 146.9, 137.0, 134.7, 131.4, 129.1, 128.6 (br), 128.4, 127.0; $^{11}$B NMR (128 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 29.2; IR (ν$_\text{max}$, cm$^{-1}$) 2967 (m), 2912 (m), 1622 (m), 1427 (m), 1456 (s), 1082 (s), 1021 (s); HRMS (ESI) calcd for C$_{10}$H$_{11}$BO$_2$ [M$^+$] 174.0847; found 174.0847. The $^{13}$C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of $^{11}$B.

(E)-Non-1-en-3-yn-1-ylboronic acid (58u)  

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\begin{align*}
\text{74} \quad & \quad + \quad \text{75} \quad \text{THF, } -78 ^\circ \text{C} \quad \rightarrow \quad \text{76} \quad \text{NaIO}_4, \text{NH}_2\text{OAc, acetone/H}_2\text{O} \quad \rightarrow \quad \text{58u}
\end{align*}
\]

Following a reported procedure, a 100 mL flask was charged with LiTMP (883 mg, 6.00 mmol, 1.20 equiv), sealed with a septum cap, and removed from the glovebox. The reaction flask was cooled to 0 °C, and dry THF (6 mL), followed by a solution of bis[(pinacolato)boryl)methane (75) (1.60 g, 6.00 mmol, 1.20 equiv) in THF (12 mL) were added. The reaction was stirred for 5 minutes at 0 °C and then was cooled to -78 °C, and a solution of oct-2-ynal (74) (0.735 mL, 5.00 mmol, 1.00 equiv) in THF (6.00 mL) was added slowly. The reaction was stirred at -78 °C for 4 h and the solvent was removed under reduced pressure. The crude reaction mixture was purified by column chromatography using EtOAc/pentane 2:98 as mobile phase affording (E)-4,4,5,5-tetramethyl-2-(non-1-en-3-yn-1-yl)-1,3,2-dioxaborolane (76) as a clear yellow oil (805 mg, 3.24 mmol, 65 %); $^1$H NMR (400 MHz, CDCl$_3$) δ 6.42

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(dt, $J = 18.3, 2.1$ Hz, 1H, CHCHB), 5.92 (dd, $J = 18.3, 2.1$ Hz, 1H, CHCHB), 2.32 (tdd, $J = 7.2, 2.2, 0.6$ Hz, 2H, CH$_2$), 1.56 - 1.48 (m, 2H, CHCH$_2$), 1.42 - 1.27 (m, 4H, 2 x CH$_2$), 1.26 (s, 12H, 4 x CH$_3$ pinacol), 0.89 (t, $J = 7.1$ Hz, 3H, CH$_2$C$_3$H$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 130.5, 95.4, 83.6, 81.0, 31.2, 28.4, 24.9, 22.3, 19.7, 14.1. The $^{13}$C NMR signal for the carbon attached to boron did not appear due to the quadrupolar splitting of $^{11}$B. The values of the NMR spectra are in accordance with reported literature data.

(E)-4,4,5,5-Tetramethyl-2-(non-1-en-3-yn-1-yl)-1,3,2-dioxaborolane (76) (0.805 g, 3.24 mmol, 1.00 equiv), NH$_4$OAc (1.250 g, 16.22 mmol, 5.00 equiv) and NaIO$_4$ (3.470 g, 16.22 mmol, 5.00 equiv) were suspended in a mixture 1:1 acetone/water (30 mL). The resulting slurry was stirred at room temperature for 16 h. It was then diluted with EtOAc (30 mL), washed successively with water (2 x 20 mL) and brine (20 mL), dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The resulting yellow oil was dissolved in diethyl ether (20 mL) then shaken 5 min with a basic aqueous solution of sorbitol (25 mL, 1 M sorbitol, 1 M Na$_2$CO$_3$), the aqueous layer was re-acidified with 4 M HCl (25 mL, pH = 2) and extracted with diethyl ether (35 mL). The organic layer was dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure affording (E)-non-1-en-3-yn-1-ylboronic acid (58u) as a yellow oil (0.365 g, 2.20 mmol, 68%). $^1$H NMR (400 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 6.27 (dt, $J = 18.3, 2.1$ Hz, 1H, CHCHB), 5.83 (d, $J = 18.4$ Hz, 1H, CHCHB), 2.32 (td, $J = 7.0, 2.2$ Hz, 2H, CH$_2$), 1.46 (m, 2H, CH$_2$), 1.38 - 1.23 (m, 4H, 2 x CH$_2$), 0.86 (t, $J = 7.0$ Hz, 3H, CH$_3$CH$_2$); $^{13}$C NMR (101 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 136.6 (br), 126.6, 93.7, 81.2, 30.6, 27.9, 21.7, 18.7, 14.0; $^{11}$B NMR (128 MHz, DMSO-d$_6$/D$_2$O 9:1) δ 27.2; IR ($\nu_{\text{max}}$, cm$^{-1}$) 2985 (m), 2904 (m), 2881 (m), 1773 (m), 1716 (s), 1427 (m), 1395 (s), 1343 (m), 1071 (s), 1055 (s), 726 (m); HRMS (APPI/LTQ-Orbitrap) m/z: [M]$^+$ Calcd for C$_9$H$_{15}$BO$_2$ 166.1160; found 166.1161. The $^{13}$C NMR signal for the carbon attached to boron was broad due to the quadrupolar splitting of $^{11}$B.
5. Preparation of VBX reagents

2-Iodosylbenzoic acid (2a)

Following a reported procedure,\textsuperscript{30} NaIO\textsubscript{4} (18.1 g, 85.0 mmol, 1.05 equiv) and 2-iodobenzoic acid (76) (20.0 g, 81.0 mmol, 1.00 equiv) were suspended in 30\% (v/v) aq. AcOH (160 mL). The mixture was vigorously stirred under reflux for 4 h and allowed to cool to room temperature. The precipitate was collected by filtration, washed on the filter with ice water (3 x 40 mL) and acetone (45 mL), and air-dried in the dark to give 2-Iodosylbenzoic acid (2a) as a white solid (20.8 g, 79.0 mmol, 98\%). \textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}): δ 8.02 (dd, \(J = 7.7, 1.4\) Hz, 1H, ArH), 7.97 (m, 1H, ArH), 7.85 (dd, \(J = 8.2, 0.7\) Hz, 1H, ArH); \textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}): δ 167.7, 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. The values of the NMR spectra are in accordance with reported literature data.\textsuperscript{30}

1-Hydroxy-5-methoxy-1λ\textsuperscript{3}-benzo[d][1,2]iodaoxol-3(1H)-one (2b)

Following a reported procedure,\textsuperscript{31} NaIO\textsubscript{4} (2.25 g, 10.5 mmol, 1.05 equiv) and 2-iodo-5-methoxybenzoic acid (77) (2.78 g, 10.0 mmol, 1.00 equiv) were suspended in 30\% (v/v) aq. AcOH (27 mL). The mixture was vigorously stirred under reflux for 4 h and allowed to cool to room temperature. The precipitate was collected by filtration, washed on the filter with ice water (3 x 8 mL) and acetone (3 x 6 mL), and air-dried in the dark to give 1-Hydroxy-5-methoxy-1λ\textsuperscript{3}-benzo[d][1,2]iodaoxol-3(1H)-one (2b) as a white solid (2.31 g, 7.90 mmol, 79\%). \textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}) δ 8.00 (s, 1H, ArH), 7.72 - 7.61 (m, 1H, ArH), 7.59 - 7.47 (m, 1H, ArH), 3.88 (s, 3H, OCH\textsubscript{3}); \textsuperscript{13}C NMR (101 MHz, DMSO-d\textsubscript{6}) δ 167.9, 162.0, 133.5, 127.6, 122.0, 115.4, 109.5, 56.4. The values of the NMR spectra are in accordance with reported literature data.\textsuperscript{31}

5-Fluoro-1-hydroxy-1λ\textsuperscript{3}-benzo[d][1,2]iodaoxol-3(1H)-one (2c)

Following a reported procedure,\textsuperscript{31} NaIO\textsubscript{4} (2.25 g, 10.5 mmol, 1.05 equiv) and 5-fluoro-2-iodobenzoic acid (78) (2.70 g, 10.0 mmol, 1.00 equiv) were suspended in 30\% (v/v) aq. AcOH (27 mL). The mixture was vigorously stirred under reflux for 4 h and allowed to cool to room temperature. The precipitate was collected by filtration, washed on the filter with ice water (3 x 8 mL) and acetone (3 x 6 mL), and

\textsuperscript{30} L. Kraszkiewicz and L. Skulski, \textit{Arkivoc}. \textbf{2003}, 6, 120.

air-dried in the dark to give 5-fluoro-1-hydroxy-1λ^3-benzo[d][1,2]iodaoxol-3(1H)-one (2c) as a white solid (2.62 g, 9.30 mmol, 93%). ¹H NMR (400 MHz, DMSO-d₆) δ 8.21 (s, 1H, ArH), 7.89 - 7.78 (m, 2H, ArH), 7.78 - 7.72 (m, 1H, ArH); ¹³C NMR (101 MHz, DMSO-d₆) δ 166.5, 164.0 (d, J = 248.3 Hz), 134.2 (d, J = 7.3 Hz), 128.4 (d, J = 8.6 Hz), 121.8 (d, J = 24.0 Hz), 117.5 (d, J = 23.5 Hz), 114.3; ¹⁹F NMR (376 MHz, DMSO-d₆) δ -112.7. The values of the NMR spectra are in accordance with reported literature data.

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

Following a reported procedure, 2-iodosylbenzoic acid (2a) (20.8 g, 79.0 mmol, 1.00 equiv) was suspended in acetic anhydride (75.0 mL, 788 mmol, 10.0 equiv) and heated to reflux (140 °C) until complete dissolution (about 15 min). The resulting clear solution was allowed to cool to room temperature and then cooled to 5 °C overnight. The white crystals were filtered, washed with pentane (3 x 30 mL) and dried under reduced pressure to afford 1-acetoxy-1,2-benziodoxol-3-(1H)-one (3) as a white solid (22.3 g, 73.0 mmol, 92%). ¹H NMR (CDCl₃, 400 MHz) δ 8.24 (dd, J = 7.6, 1.6 Hz, 1H, ArH), 8.00 (dd, J = 8.3, 1.0 Hz, 1H, ArH), 7.92 (ddd, J = 8.4, 7.2, 1.6 Hz, 1H, ArH), 7.71 (td, J = 7.3, 1.1 Hz, 1H, ArH), 2.25 (s, 3 H, COCH₃); ¹³C NMR (CDCl₃, 100 MHz) δ 176.5, 168.2, 136.2, 133.3, 131.4, 129.4, 129.1, 118.4, 20.4. The values of the NMR spectra are in accordance with reported literature data.

General procedure A: Synthesis of VBX reagents:

To a suspension of 2-iodosylbenzoic acid (2a - 2c) (1.30 mmol, 1.00 equiv) in dry DCM (13 mL) was added TMSOTf (0.270 mL, 1.50 mmol, 1.15 equiv) dropwise over 10 min and stirred for 30 min at room temperature. Afterwards, the corresponding vinyl boronic acid (58a - 58i) (1.50 mmol, 1.15 equiv) was added and the reaction mixture was stirred until the reaction was completed (1 to 8 h, monitored by TLC, MeOH/DCM 5:95). Pyridine (0.121 mL, 1.50 mmol, 1.15 equiv) was added and after further stirring for 10 min at room temperature, the solvent was removed under reduced pressure. The resulting solid was dissolved in DCM (20 mL) and washed with 1 M HCl (10 mL). The aqueous layer was extracted with DCM (3 x 20 mL). The organic layers were combined, washed successively with a saturated solution of NaHCO₃ (40 mL) and water (3 x 20 mL), dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The resulting solid was dissolved again in DCM (minimum amount until dissolution) and precipitated in Et₂O (ca. 150 mL). After precipitation at 4 °C for 2 h, the solid was filtered and washed with Et₂O to afford the corresponding VBX reagent.

General procedure B: Synthesis of VBX reagents:

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To a solution of the corresponding vinyl boronic acid (58j - 58u) (1.30 mmol, 1.00 equiv) in dry DCM (13 mL) was added BF$_3$:OEt$_2$ (0.198 mL, 1.56 mmol, 1.20 equiv) dropwise at 0 °C. After 15 minutes, 1-acetoxy-1,2-benziodoxol-3-(1H)-one (3) (477 mg, 1.56 mmol, 1.20 equiv) was added in one portion at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred until the reaction was completed (4 to 24 h, monitored by TLC using MeOH/DCM 5:95). The reaction was then quenched with a saturated solution of NaHCO$_3$ (13 mL) and stirred vigorously for 1 h. The resulting suspension was filtered and the filtrate was extracted with DCM (3 x 20 mL). The combined organic layers were washed with water (3 x 20 mL), dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure. The resulting solid was dissolved in DCM (minimum amount until dissolution) and precipitated in Et$_2$O (ca. 150 mL). After precipitation at 4 °C for 2 h, the solid was filtered and washed with Et$_2$O to afford the corresponding VBX reagent.

(E)-1-Styryl-$\lambda^1$-benzo[d][1,2]iodaoxol-3(1H)-one (1a)

Following general procedure A, starting from trans-2-phenylvinylboronic acid (58a) (221 mg, 1.50 mmol) and 2-iodosylbenzoic acid (2a) (343 mg, 1.30 mmol), afforded (E)-1-styryl-$\lambda^1$-benzo[d][1,2]iodaoxol-3(1H)-one (1a) as a white solid (351 mg, 1.00 mmol, 77%). $^1$H NMR (400 MHz, MeOD) δ 8.32 - 8.25 (m, 1H, ArH), 7.97 (d, $J = 15.5$ Hz, 1H, ICHCHPh), 7.77 - 7.63 (m, 6H, ArH and ICHCHPh), 7.54 - 7.45 (m, 3H, ArH and ICHCHPh). $^{13}$C NMR (101 MHz, MeOD) δ 170.1, 155.8, 136.7, 135.3, 134.5, 133.3, 132.1, 131.8, 130.2, 129.0, 115.5, 100.0. The values of the NMR spectra are in accordance with reported literature data.\(^{34}\)

The reaction was scaled up to trans-2-phenylvinylboronic acid (58a) (1.48 g, 10.0 mmol) and 2-iodosylbenzoic acid (2a) (2.30 g, 8.70 mmol) affording (E)-1-styryl-$\lambda^1$-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (2.20 g, 6.30 mmol, 72%).

(E)-1-(4-Methylstyryl)-$\lambda^1$-benzo[d][1,2]iodaoxol-3(1H)-one (1b)

Following general procedure A, starting from trans-2-(4-methylphenyl)vinylboronic acid (58b) (242 mg, 1.50 mmol) and 2-iodosylbenzoic acid (2a) (343 mg, 1.30 mmol), afforded (E)-1-(4-methylstyryl)-$\lambda^1$-benzo[d][1,2]iodaoxol-3(1H)-one (1b) as a white solid (335 mg, 0.920 mmol, 71%). $^1$H NMR (400 MHz, MeOD) δ 8.32 - 8.25 (m, 1H, ArH), 7.92 (d, $J = 15.4$ Hz, 1H, ICHCHPh), 7.79 - 7.64 (m, 3H, ArH), 7.62 - 7.54 (m, 3H, ArH and ICHCHPh), 7.31 (d, $J = 7.9$ Hz, 2H, ArH), 2.42 (s, 3H, CH$_3$); $^{13}$C NMR (101 MHz, MeOD) δ 167.3, 155.0, 136.6, 135.3, 134.5, 133.3, 132.1, 131.8, 131.2, 130.2, 129.0, 115.5, 100.0. The values of the NMR spectra are in accordance with reported literature data.\(^{34}\)

MeOD) δ 169.9, 155.7, 142.8, 135.0, 134.3, 133.8, 133.1, 131.6, 130.6, 128.8, 128.7, 115.3, 98.1, 21.3. The values of the NMR spectra are in accordance with reported literature data.\(^{34}\)

\((E)-1-(4-Methoxystyril)-1\lambda^3\text{-benzo}[d][1,2]\text{iodaoxol-3(1H)-one (1c)}\)

Following general procedure A, starting from trans-2-(4-methoxyphenyl)vinylboronic acid (58c) (266 mg, 1.50 mmol) and 2-iodosylbenzoic acid (2a) (343 mg, 1.30 mmol), afforded \((E)-1-(4-methoxystyril)-1\lambda^3\text{-benzo}[d][1,2]\text{iodaoxol-3(1H)-one (1c)}\) as a white solid (306 mg, 0.805 mmol, 62%). \(^1\)H NMR (400 MHz, MeOD) δ 8.29 (dt, \(J = 5.8, 3.5\) Hz, 1H, ArH), 7.89 (d, \(J = 15.3\) Hz, 1H, ICHCPh), 7.78-7.60 (m, 5H, ArH), 7.45 (d, \(J = 15.4\) Hz, 1H, ICHCPh), 7.12-6.95 (m, 2H, ArH), 3.87 (s, 3H, OC\(_3\)H\(_3\)); \(^{13}\)C NMR (101 MHz, MeOD) δ 170.1, 163.7, 155.8, 135.2, 134.5, 133.3, 131.8, 130.8, 129.4, 115.6, 115.5, 95.9, 56.0. The values of the NMR spectra are in accordance with reported literature data.\(^{34}\)

\((E)-1-(4-Fluorostyril)-1\lambda^3\text{-benzo}[d][1,2]\text{iodaoxol-3(1H)-one (1d)}\)

Following general procedure A, starting from trans-2-(4-fluorophenyl)vinylboronic acid (58d) (248 mg, 1.50 mmol) and 2-iodosylbenzoic acid (2a) (343 mg, 1.30 mmol), afforded \((E)-1-(4-fluorostyril)-1\lambda^3\text{-benzo}[d][1,2]\text{iodaoxol-3(1H)-one (1d)}\) as a white solid (424 mg, 1.152 mmol, 89%). M.p. 146-148 °C; \(R_f = 0.11\) (MeOH/DCM 5:95); \(^1\)H NMR (400 MHz, MeOD) δ 8.38-8.31 (m, 1H, ArH), 8.02 (d, \(J = 15.2\) Hz, 1H, ICHCPh), 7.85-7.71 (m, 5H, ArH), 7.66 (d, \(J = 15.3, 1H, ICHCPh\)), 7.50-7.22 (m, 2H, ArH); \(^{13}\)C NMR (101 MHz, MeOD) δ 170.9, 166.4 (d, \(J = 25.1\) Hz), 155.9, 137.0, 134.2, 133.3 (d, \(J = 3.0\) Hz), 132.6, 132.2, 131.9 (d, \(J = 8.7\) Hz), 130.4, 117.7 (d, \(J = 22.3\) Hz), 115.7, 98.2; \(^{19}\)F NMR (376 MHz, MeOD) δ -110.9; IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 3018 (s), 2946 (s), 2858 (m), 1750 (s), 1731 (s), 1542 (s), 1512 (s), 1319 (s), 1271 (s), 1243 (s), 1200 (s), 1165 (s), 1124 (s), 968 (s), 838 (m); HRMS (ESI) calcd for C\(_{15}\)H\(_{11}\)F\(_2\)O\(_2\)+ [M+H]\(^+\) 368.9782; found 368.9785.

\((E)-1-(4-(Trifluoromethyl)-1\lambda^3\text{-benzo}[d][1,2]\text{iodaoxol-3(1H)-one (1e)}\)

Following general procedure A, starting from trans-2-[4-(trifluoromethyl)phenylvinyl]boronic acid (58e) (323 mg, 1.50 mmol) and 2-iodosylbenzoic acid (2a) (343 mg, 1.30 mmol), afforded \((E)-1-(4-(trifluoromethyl)-1\lambda^3\text{-benzo}[d][1,2]\text{iodaoxol-3(1H)-one (1e)}\) as a white solid (275 mg, 0.658 mmol, 51%). \(^1\)H NMR (400 MHz, MeOD) δ 8.30 (m, 1H, ArH), 7.95 (d, \(J = 15.3\) Hz, 1H, ICHCPh), 7.93-7.84 (m, 3H, ArH and ICHCPh), 7.81 (m, 2H, ArH), 7.74 (m, 3H, ArH); \(^{13}\)C NMR (101 MHz, MeOD) δ 170.6, 154.1,
Following general procedure A, starting from (E)-(2-(naphthalen-1-yl)vinyl)boronic acid (58f) (296 mg, 1.50 mmol) and 2-iodosylenoic acid (2a) (343 mg, 1.30 mmol), afforded (E)-1-(2-(naphthalen-1-yl)-1λ³-benzo[d][1,2]iodoxol-3(1H)-one (1f) as a white solid (316 mg, 0.790 mmol, 61%). M.p. 164-166°C; Rf = 0.20 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.79 (d, J = 15.1 Hz, 1H, ICHC\textsubscript{H}Ph), 8.33-8.28 (m, 1H, ArH), 8.27-8.23 (m, 1H, ArH), 8.05-7.89 (m, 3H, ArH), 7.85-7.79 (m, 1H, ArH), 7.74-7.66 (m, 3H, ArH and ICHPh), 7.65-7.55 (m, 3H, ArH); 13C NMR (101 MHz, MeOD) δ 168.7, 151.7, 133.9, 133.8, 133.1, 132.6, 131.9, 131.0, 130.8, 130.4, 128.5, 127.7, 127.0, 126.2, 125.2, 122.8, 114.3, 101.2, 78.1; IR (\nu\textsubscript{max}, cm\textsuperscript{-1}) 2985 (s), 2906 (s), 1390 (m), 1247 (m), 1227 (m), 1065 (s), 1051 (s), 896 (m), 867 (m); HRMS (ESI) calcd for C\textsubscript{19}H\textsubscript{13}INaO\textsubscript{2}\textsuperscript{+} [M+Na]\textsuperscript{+} 422.9852; found 422.9851.

Following general procedure B, with a final purification by column chromatography using MeOH/DCM 5:95 as mobile phase to obtain the titled compound in pure form. Starting from (E)-(2-(thiophen-2-yl)vinyl)boronic acid (58g) (169 mg, 1.10 mmol) and 1-acetoxy-1,2-benziodoxol-3(1H)-one (3) (477 mg, 1.56 mmol), afforded (E)-1-(non-1-en-3-yn-1-yl)-1λ³-benzo[d][1,2]iodoxol-3(1H)-one (1g) as a beige solid (145 mg, 0.407 mmol, 37%). M.p. (dec.) 201-205°C; Rf = 0.13 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD/CD\textsubscript{2}Cl\textsubscript{2} 9:1) δ 8.32-8.25 (m, 1H, ArH), 8.04 (d, J = 15.3 Hz, 1H, ICHCH), 7.74-7.65 (m, 3H, ArH), 7.62 (dt, J = 5.0, 0.9 Hz, 1H, ArH), 7.43 (dd, J = 3.7, 1.1 Hz, 1H, ArH), 7.29 (d, J = 15.3 Hz, 1H, ICHCH), 7.18 (dd, J = 5.1, 3.7 Hz, 1H, ArH); 13C NMR (101 MHz, MeOD/CD\textsubscript{2}Cl\textsubscript{2} 9:1) δ 169.8, 148.0, 140.9, 135.1, 134.2, 133.2, 132.3, 131.7, 130.7, 129.1, 128.5, 115.7, 96.3; IR (\nu\textsubscript{max}, cm\textsuperscript{-1}) 2987 (s), 2967 (s), 2907 (m), 1750 (m), 1735 (m), 1649 (m), 1573 (m), 1557 (m), 1540 (m), 1512 (m), 1452 (w), 1393 (m), 1251 (m), 1101 (w), 1068 (s), 1054 (s), 869 (m), 765 (m), 734 (m), 687 (m); HRMS (ESI/QTOF) m/z: [M+H]\textsuperscript{+} calcd for C\textsubscript{13}H\textsubscript{10}IO\textsubscript{2}S\textsuperscript{+} 356.9441; found 356.9442.

(E)-5-Fluoro-1-styryl-1λ³-benzo[d][1,2]iodoxol-3(1H)-one (1h)
Following general procedure A, starting from (E)-styrylboronic acid (58h) (221 mg, 1.50 mmol) and 1-hydroxy-5-fluoro-1,2-benziodoxol-3-(1H)-one (2c) (367 mg, 1.30 mmol), afforded (E)-5-fluoro-1-styrly-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1h) as a white solid (367 mg, 1.30 mmol, 58%). M.p. 174-176 °C; Rf = 0.15 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.03 - 7.94 (m, 2H, ArH and ICHCHPh), 7.77 - 7.64 (m, 4H, ArH and ICHCHPh), 7.55 - 7.44 (m, 3H, ArH); 13C NMR (101 MHz, MeOD) δ 168.7, 166.1 (d, J = 250.5 Hz), 156.1, 137.3, 136.6, 132.2, 131.0 (d, J = 8.4 Hz), 130.2, 129.0, 122.3 (d, J = 24.0 Hz), 119.8 (d, J = 23.9 Hz), 108.5, 99.7; 19F NMR (376 MHz, MeOD) δ -113.5; IR (νmax, cm⁻¹) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI/QTOF) m/z: [M + Na]⁺ calcd for C16H16F1NaO₂⁺ 380.9982; Found 380.9980.

(E)-5-Methoxy-1-styrly-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1i)

Following general procedure A, starting from (E)-styrylboronic acid (58i) (221 mg, 1.50 mmol) and 5-methoxy-1-hydroxy-1,2-benziodoxol-3-(1H)-one (2b) (382 mg, 1.30 mmol), afforded (E)-5-methoxy-1-styrly-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1i) as a white solid (422 mg, 1.11 mmol, 85%). M.p. 167-168 °C; Rf = 0.13 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 7.95 (d, J = 15.4 Hz, 1H, ICHCHPh), 7.82 (d, J = 3.0 Hz, 1H, ArH), 7.74 - 7.61 (m, 3H, ArH and ICHCHPh), 7.55 (d, J = 9.0 Hz, 1H, ArH), 7.52 - 7.44 (m, 3H, ArH), 7.25 (dd, J = 9.0, 3.1 Hz, 1H, ArH), 3.88 (s, 3H, OCH₃); 13C NMR (101 MHz, MeOD) δ 169.9, 163.7, 155.6, 136.7, 135.9, 132.1, 130.2, 129.7, 129.0, 121.7, 117.8, 103.6, 99.6, 56.4; IR (νmax, cm⁻¹) 2977 (s), 2903 (m), 1617 (w), 1580 (w), 1411 (s), 1379 (s), 1259 (m), 1052 (s), 811 (m), 881 (m); HRMS (ESI/QTOF) m/z: [M+H]⁺ calcd for C16H16F1O₂⁺ 380.9982; Found 380.9980.

(E)-1-(2-Cyclohexylvinyl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1j)

Following general procedure B, starting from trans-2-cyclohexylvinyl)boronic acid (58j) (200 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (3) (477 mg, 1.56 mmol), afforded (E)-1-(2-cyclohexylvinyl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1j) as a white solid (274 mg, 0.769 mmol, 59%). M.p. 136-138 °C; Rf = 0.19 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.31 - 8.24 (m, 1H, ArH), 7.75 - 7.65 (m, 3H, ArH), 7.13 (dd, J = 15.1, 7.0 Hz, 1H, ICHCHcy), 6.84 (dd, J = 15.1, 1.2 Hz, 1H, ICHCHcy), 2.54 - 2.41 (m, 1H, cy-H), 1.99 - 1.90 (m, 2H, cy-H), 1.89 - 1.79 (m, 2H, cy-H), 1.78 - 1.69 (m, 1H, cy-H), 1.50 - 1.21 (m, 5H, cy-H); 13C NMR (101 MHz, MeOD) δ 170.4, 166.0, 135.6, 134.9, 133.8, 132.2, 129.2, 115.2, 99.4, 46.2, 33.2, 27.3, 27.2. The values of the NMR spectra are in accordance with reported literature data.  

(E)-1-(Pent-1-en-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1k)
Following general procedure B, starting from *trans*-1-penten-1-ylboronic acid (58k) (148 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (2) (477 mg, 1.56 mmol), afforded (E)-1-(pent-1-en-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1k) as a white solid (115 mg, 0.364 mmol, 28%). M.p. (dec.) 154-160 °C; Rf = 0.15 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.34 - 8.22 (m, 1H, ArH), 7.80 - 7.63 (m, 3H, ArH), 7.16 (dt, J = 14.9, 7.0 Hz, 1H, ICHCHCH₂), 6.87 (dt, J = 15.0, 1.4 Hz, 1H, ICHCHCH₂), 2.49 (qd, J = 7.2, 1.5 Hz, 2H, CH₂CH₂CH₂), 1.65 (h, J = 7.4 Hz, 2H, CH₂CH₂CH₃), 1.05 (t, J = 7.4 Hz, 3H, CH₃CH₃); 13C NMR (101 MHz, MeOD) δ 169.7, 160.4, 134.9, 133.1, 131.6, 128.7, 114.7, 100.1, 38.6, 22.2, 13.7; IR (νmax, cm⁻¹) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1599 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (s); HRMS (ESI) calcd for C₁₂H₁₄O₄⁺ [M+H]+ 317.0033; found 317.0033.

(E)-1-(3-Phenylprop-1-en-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1l)

Following general procedure B, starting from *trans*-3-phenyl-1-propen-1-ylboronic acid (58l) (211 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (3) (477 mg, 1.56 mmol), afforded (E)-1-(3-phenylprop-1-en-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1l) as a white solid (332 mg, 0.912 mmol, 70%). M.p. 144-145 °C; Rf = 0.18 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.30 - 8.23 (m, 1H, ArH), 7.72 - 7.64 (m, 3H, ArH), 7.41 - 7.23 (m, 6H, ArH and ICHCHPh), 6.88 (dt, J = 14.9, 1.5 Hz, 1H, ICHCHCH₂), 3.83 (dd, J = 6.9, 1.4 Hz, 2H, CH₂Ph); 13C NMR (101 MHz, MeOD) δ 170.0, 159.0, 138.4, 135.2, 134.2, 133.4, 131.8, 130.0, 130.0, 129.0, 128.1, 115.0, 101.2, 42.7; IR (νmax, cm⁻¹) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1599 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI) calcd for C₁₃H₁₅O₄⁺ [M+H]+ 365.0033; found 365.0033.

(E)-1-(5-Chloropent-1-en-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1m)

Following general procedure B, starting from (E)-[5-chloropent-1-en-1-yl]boronic acid (58m) (193 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (2) (477 mg, 1.56 mmol), afforded (E)-1-(5-chloropent-1-en-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1m) as a white solid (201 mg, 0.573 mmol, 44%). M.p. 133-135 °C; Rf = 0.19 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.34 - 8.24 (m, 1H, ArH), 7.83 - 7.66 (m, 3H, ArH), 7.19 (dt, J = 15.0, 6.9 Hz, 1H, ICHCHCH₂), 6.97 (dt, J = 15.0, 1.5 Hz, 1H, ICHCHCH₂), 3.70 (t, J = 6.4 Hz, 2H, CH₂Cl), 2.76 - 2.62 (m, 2H, CH₂CH₂CH₂), 2.09 (p, J = 6.7 Hz, 2H, CH₂CH₂Cl); 13C NMR (101 MHz, MeOD) δ 168.6, 157.4, 133.8, 133.1, 131.9, 130.4, 127.6, 113.5, 100.1, 43.4, 32.5, 30.4; IR (νmax, cm⁻¹) 2968 (m), 2897 (m), 1719 (w), 1596 (m), 1557 (m), 1346 (m), 1276 (m), 780 (m), 757 (m), 692 (m), 688 (m), 605 (m), 567 (m), 529 (m), 457 (s), 433 (s), 402 (m), 369 (m).
Methyl (E)-6-(3-oxo-1λ³-benzo[1,2]iodaoxol-1(3H))-yl)hex-5-enoate (1n)

Following general procedure B, starting from (E)-(6-methoxy-6-oxohex-1-en-1-yl)boronic acid (58n) (224 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (3) (477 mg, 1.56 mmol), afforded methyl (E)-6-(3-oxo-1λ³-benzo[1,2]iodaoxol-1(3H))-yl)hex-5-enoate (1n) (210 mg, 0.561 mmol, 43%) as an off-white solid. M.p. 147-149 °C; Rf = 0.07 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.31 - 8.23 (m, 1H, ArH), 7.78 - 7.64 (m, 3H, ArH), 7.15 (dt, J = 15.0, 6.9 Hz, 1H, ICHCH), 6.90 (dt, J = 14.9, 1.4 Hz, 1H, ICHCH), 3.68 (s, 3H, OCH3), 2.61 - 2.50 (m, 2H, CH2CC), 2.46 (t, J = 7.3 Hz, 2H, CH2CO2Me), 1.91 (p, J = 7.4 Hz, 2H, CH2CH2CH2); 13C NMR (101 MHz, MeOD) δ 175.2, 170.0, 159.4, 135.2, 134.6, 133.3, 131.8, 129.0, 114.9, 101.1, 52.1, 35.9, 33.8, 24.3; IR (νmax, cm⁻¹) 3443 (w), 3047 (w), 2958 (w), 2922 (w), 1748 (m), 1737 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1261 (m), 1056 (m), 830 (m), 751 (s); HRMS (ESI) calcd for C12H33ClIO5 [M+H]+ 375.0088; found 375.0091.

(E)-1-(3-Chloroprop-1-en-1-yl)-1λ³-benzo[1,2]iodaoxol-3(1H)-one (1o)

Following general procedure B, with the addition of 2,2,2-trifluoroethanol (1.3 mL) after 3 h of reaction to dissolve the insoluble material. Starting from trans-2-chloromethylvinylboronic acid (58o) (156 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (2) (477 mg, 1.56 mmol), afforded (E)-1-(3-chloroprop-1-en-1-yl)-1λ³-benzo[1,2]iodaoxol-3(1H)-one (1o) as a white solid (137 mg, 0.425 mmol, 46%). M.p. (dec.) 166-170 °C; Rf = 0.10 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.37 - 8.27 (m, 1H, ArH), 7.84 - 7.70 (m, 3H, ArH and ICHCHCH2), 7.33 - 7.28 (m, 2H, ArH), 4.53 - 4.46 (m, 2H, CH2Cl); 13C NMR (101 MHz, MeOD) δ 170.3, 153.6, 136.0, 133.6, 132.9, 132.1, 129.6, 115.0, 104.3, 45.2; IR (νmax, cm⁻¹) 2987 (s), 2973 (s), 2905 (s), 1748 (m), 1737 (m), 1649 (m), 1559 (m), 1540 (m), 1512 (m), 1395 (m), 1255 (m), 1079 (s), 1054 (s), 863 (m); HRMS (ESI) calcd for C10H2ClClO5 [M+H]+ 322.9330; found 322.9332.

(E)-1-(3-((Triisopropylsilyloxy)prop-1-en-1-yl)-1λ³-benzo[1,2]iodaoxol-3(1H)-one (1p)

Following general procedure B, starting from (E)-(3-((triisopropylsilyloxy)prop-1-en-1-yl)boronic acid (58p) (336 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (3) (477 mg, 1.56 mmol), afforded (E)-1-(3-((triisopropylsilyloxy)prop-1-en-1-yl)-1λ³-benzo[1,2]iodaoxol-3(1H)-one (1p) (370
mg, 0.804 mmol, 62%) as a white solid. M.p. 157-159 °C; Rf = 0.20 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.36 - 8.26 (m, 1H, ArH), 7.73 (m, 3H, ArH), 7.34 (dt, J = 14.7, 3.2 Hz, 1H, CH=CH), 7.08 (dt, J = 14.7, 2.2 Hz, 1H, CH=CH), 4.71 (dd, J = 3.2, 2.1 Hz, 2H, CH₂O), 1.31 - 1.10 (m, 21H, TIPS); 13C NMR (101 MHz, MeOD) δ 170.3, 159.7, 135.7, 133.6, 132.9, 129.3, 114.9, 98.7, 66.2, 18.5, 13.2; IR (vmax, cm⁻¹) 3057 (w), 2944 (w), 2863 (w), 1644 (w), 1607 (w), 1264 (m), 1129 (w), 1014 (w), 943 (w), 170.0, 152.3, 135.8, 133.8, 129.0, 118.6, 113.5, 35.2, 30.1, 25.7, 21.5; HRMS (ESI) calcd for C₅₂H₄₅NO₄+ [M+H]+ 461.1003; found 461.1015.

(E)-2-[(3-Oxo-1λ³-benzo[d][1,2]iodaoxol-1(3H)-yl)allyl]isoindoline-1,3-dione (1q)

Following general procedure B, with the addition of 2,2,2-trifluoroethanol (1.3 mL) after 3 h of reaction to dissolve the insoluble material. Starting from (E)-3(1,3-dioxoisoidol-2-yl)prop-1-en-1-yl)boronic acid (58q) (300 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3(1H)-one (3) (477 mg, 1.56 mmol), afforded (E)-2-[(3-oxo-1λ³-benzo[d][1,2]iodaoxol-1(3H)-yl)allyl]isoindoline-1,3-dione (1q) as a white solid (417 mg, 0.963 mmol, 74%). M.p. (dec.) 163-167 °C; Rf = 0.12 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.40 - 8.34 (m, 1H, ArH), 7.98 - 7.77 (m, 7H, ArH). 7.34 (dt, J = 14.8, 4.8 Hz, 1H, CH=CH), 7.21 (dt, J = 14.8, 1.6 Hz, 1H, CH=CH), 4.75 (dd, J = 4.8, 1.6 Hz, 2H, CH₂N); 13C NMR (101 MHz, MeOD) δ 171.0, 169.2, 154.8, 137.6, 135.7, 134.1, 133.4, 132.5, 131.1, 129.1, 124.5, 114.8, 100.4, 42.0; IR (vmax, cm⁻¹) 2977 (s), 2917 (s), 1722 (m), 1483 (m), 1407 (s), 1374 (m), 1261 (m), 1329 (m), 1056 (s), 875 (w); HRMS (ESI) calcd for C₂₈H₂₁NNaO₄⁺ [M+Na]+ 455.9703; found 455.9702.

(E)-1-(Cyclohex-1-en-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1r)

Following general procedure B, starting from 1-cyclohexenylboronic acid (58r) (164 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3(1H)-one (2) (477 mg, 1.56 mmol), afforded (E)-1-(cyclohex-1-en-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1r) as a white solid (213 mg, 0.649 mmol, 50%). M.p. 116-118 °C; Rf = 0.15 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.28 (dt, J = 7.2, 1.3 Hz, 1H, ArH), 7.78 - 7.66 (m, 3H, ArH), 7.07 (tt, J = 3.9, 1.8 Hz, 1H, ICCH), 2.73-2.68 (m, 2H, cy-H), 2.53 (tq, J = 6.0, 3.0 Hz, 2H, cy-H), 1.94 (pd, J = 6.0, 3.6 Hz, 2H, cy-H), 1.88 - 1.80 (m, 2H, cy-H); 13C NMR (101 MHz, MeOD) δ 170.0, 152.3, 135.8, 133.8, 129.0, 118.6, 113.5, 35.2, 30.1, 25.7, 21.5; IR (vmax, cm⁻¹) 2976 (w), 2934 (w), 2906 (w), 1651 (m), 1600 (s), 1558 (m), 1435 (m), 1377 (m), 1346 (m), 1332 (m), 1107 (s), 905 (s), 853 (m), 826 (m), 748 (s); HRMS (ESI) calcd for C₁₉H₁₄IO₄⁺ [M+H]+ 329.0033; found 329.0031. One carbene was not resolved at 101 MHz.

(E)-1-(3-Methylbuta-1,3-dien-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1s)

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Following general procedure B, starting from (E)-(3-methylbuta-1,3-dien-1-yl)boronic acid (58s) (146 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (2) (477 mg, 1.56 mmol), afforded (E)-1-(3-methylbuta-1,3-dien-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1s) as a beige solid (225 mg, 0.716 mmol, 55%). M.p. (dec.) 70-72 °C; Rf = 0.11 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.31 - 8.26 (m, 1H, ArH), 7.78 - 7.61 (m, 4H, ArH and ICHCH), 7.09 (d, J = 15.2 Hz, 1H, ICHCH), 5.53 - 5.42 (m, 2H, CCH2), 2.05 (t, J = 1.1 Hz, 3H, CH3); 13C NMR (101 MHz, MeOD) δ 170.6, 158.7, 143.6, 135.9, 134.3, 133.8, 132.3, 129.5, 126.2, 115.5, 100.5, 18.3; IR (νmax, cm⁻¹) 2987 (s), 2896 (m), 1632 (w), 1584 (m), 1570 (m), 1407 (m), 1381 (m), 1261 (m), 1230 (m), 1054 (s), 873 (m), 813 (m); HRMS (ESI) calcd for C13H11NaO3⁺ [M+Na]⁺ 336.9696; found 336.9695.

(E)-1-((1E,3E)-4-Phenylbuta-1,3-dien-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1t)

Following general procedure B, starting from ((1E,3E)-4-phenylbuta-1,3-dien-1-yl)boronic acid (58t) (226 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (2) (477 mg, 1.56 mmol), afforded (E)-1-((1E,3E)-4-phenylbuta-1,3-dien-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1t) as a beige solid (196 mg, 0.520 mmol, 40%). M.p. (dec.) 169-173 °C; Rf = 0.17 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.35 - 8.27 (m, 1H, ArH), 7.82 - 7.68 (m, 4H, ArH and ICHCH), 7.62 - 7.56 (m, 2H, ArH), 7.45 - 7.32 (m, 3H, ArH), 7.22 (dd, J = 15.6, 10.6 Hz, 1H, CHCHPh), 7.13 (d, J = 14.7 Hz, 1H, ICHCH), 7.05 (d, J = 15.6 Hz, 1H, CHCHPh); 13C NMR (101 MHz, MeOD) δ 170.4, 156.9, 143.1, 137.2, 136.0, 133.7, 133.5, 132.2, 131.0, 130.2, 129.5, 128.9, 127.8, 115.7, 100.0; IR (νmax, cm⁻¹) 2975 (s), 2911 (m), 1720 (m), 1448 (m), 1409 (s), 1381 (m), 1259 (m), 1056 (s), 873 (m), 809 (m), 782 (m); HRMS (ESI) calcd for C17H13NaO3⁺ [M+Na]⁺ 398.9852; found 398.9852.

(E)-1-(Non-1-en-3-yn-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1u)

Following general procedure B, starting from (E)-non-1-en-3-yn-1-ylboronic acid (58u) (216 mg, 1.30 mmol) and 1-acetoxy-1,2-benziodoxol-3-(1H)-one (2) (477 mg, 1.56 mmol), afforded (E)-1-(non-1-en-3-yn-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1u) as a white solid (376 mg, 1.02 mmol, 79%). M.p. 139-141 °C; Rf = 0.26 (MeOH/DCM 5:95); 1H NMR (400 MHz, MeOD) δ 8.30 - 8.22 (m, 1H, ArH), 7.77 - 7.62 (m, 3H, ArH), 7.33 (d, J = 15.5 Hz, 1H, ICHCH), 7.06 (dt, J = 15.5, 2.3 Hz, 1H, ICHCH), 2.47 (td, J = 7.0, 2.2 Hz, 2H, CCH2CH2), 1.66 - 1.56 (m, 2H, CCH2CH2), 1.51 - 1.31 (m, 4H, 2 x CH2), 0.94 (t, J = 7.1 Hz, 3H, CH3); 13C NMR (101 MHz, MeOD) δ 170.0, 136.3, 135.4, 134.3, 133.3, 131.9, 129.1, 115.5, 111.8, 101.4, 79.2, 32.2, 29.1, 23.2, 20.2, 14.3; IR (νmax, cm⁻¹) 2975 (s), 2911 (m), 1720 (m), 1448 (m), 1409 (s), 1381 (m), 1259 (m), 1056 (s), 873 (m), 809 (m), 782 (m); HRMS (ESI) calcd for C16H18O³⁺ [M+H]⁺ 369.0346; found 369.0340.
6. Ligand optimization for the Cu(I)-catalyzed oxy-vinylation of diazo compounds

A solution of catalyst was prepared by mixing Cu(CH_{3}CN)_{2}BF_{4} (12.6 mg, 40.0 µmol) and ligand (xx - xx) (50.0 µmol) in DCE (5.0 mL) at room temperature for 1 h. 0.5 mL of the catalytic solution was then added to a stirring suspension of VBX (0.10 mmol, 1.00 equiv) and diazo compound (0.200 mmol, 1.00 equiv) in DCE (2.0 mL). The reaction mixture was stirred at the indicated temperature and time. After completion of the reaction, the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography (EtOAc/pentane) directly without further work-up to afford the corresponding product.

![Reaction scheme](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>Ligand</th>
<th>diazo R¹ =</th>
<th>VBX R² =</th>
<th>temp.</th>
<th>time</th>
<th>yield</th>
<th>by-product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no ligand</td>
<td>H</td>
<td>Ph</td>
<td>40 °C</td>
<td>24 h</td>
<td>&lt; 5%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5a</td>
<td>H</td>
<td>Ph</td>
<td>40 °C</td>
<td>4 h</td>
<td>90%</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5a (no Cu)</td>
<td>H</td>
<td>Ph</td>
<td>40 °C</td>
<td>24 h</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5a</td>
<td>Ph</td>
<td>Ph</td>
<td>40 °C</td>
<td>4 h</td>
<td>80%</td>
<td>Ph (&lt; 10%)</td>
</tr>
<tr>
<td>5</td>
<td>5a</td>
<td>H</td>
<td>PMP</td>
<td>60 °C</td>
<td>24 h</td>
<td>50%</td>
<td>Ph (27%)</td>
</tr>
<tr>
<td>6</td>
<td>5a</td>
<td>H</td>
<td>Cy</td>
<td>60 °C</td>
<td>24 h</td>
<td>&lt; 5%</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5b</td>
<td>H</td>
<td>Ph</td>
<td>RT</td>
<td>&lt; 1 h</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5c</td>
<td>H</td>
<td>Ph</td>
<td>60 °C</td>
<td>&lt; 1 h</td>
<td>&lt; 5%</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>5d</td>
<td>H</td>
<td>Ph</td>
<td>RT</td>
<td>24 h</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>5d</td>
<td>H</td>
<td>PMP</td>
<td>RT</td>
<td>&lt; 1 h</td>
<td>81%</td>
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</tr>
<tr>
<td>11</td>
<td>5d</td>
<td>Ph</td>
<td>Cy</td>
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<td>24 h</td>
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<tr>
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<td>&lt; 1 h</td>
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</tr>
<tr>
<td>13</td>
<td>5e</td>
<td>H</td>
<td>Ph</td>
<td>RT</td>
<td>24 h</td>
<td>&lt; 5%</td>
<td></td>
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</tbody>
</table>
This study points out the dramatic effect of the bisoxazoline ligands (5b or 5d) when the reaction is performed with unsubstituted α-diazoesters (R₁ = H). The reactions were completed in less than 1 hour and at room temperature with ethyl diazoacetate for both Aryl-VBX and Alkyl-VBX (entry 7 and entries 9 to 11). Unfortunately, the presence of a substitution (R₁ ≠ H) was not tolerated using the BOX ligand (5d) (entry 12). Nevertheless, using the diimine ligand (5a) allowed substituted and unsubstituted diazo partners (entries 2 and 4) but the reaction was less efficient with electron-rich VBX (entry 5) and did not proceed with Alkyl-VBX (entry 6). The ligands 5c and 5e where inefficient (entries 8 and 13). Finally, the reaction did not proceed in absence of copper or ligand (entry 1 and 3).
7. Oxy-vinylation reaction with VBX reagents

General procedure C: Copper catalyzed oxy-vinylation of acceptor diazo compound:

\[
\begin{align*}
R_2 - & - \text{I} + \text{N}_2 - \\
A & - \text{ phenylacetate} \\
\rightarrow & - \text{R} - \\
\end{align*}
\]

A catalytic solution was prepared by mixing Cu(CH₃CN)₄BF₄ (12.6 mg, 40.0 µmol) and 2,2'-(propane-2,2-diyl)bis(4,4-dimethyl-4,5-dihydrooxazole) (5d) (11.9 mg, 50.0 µmol) in DCE (5.0 mL) at room temperature for 1 h. 1.0 mL of the catalytic solution was then added to a stirring suspension of VBX (1a - 1u) (0.200 mmol, 1.00 equiv) and acceptor diazo compound (4a - 4q) (0.400 mmol, 2.00 equiv) in DCE (4.0 mL). The reaction mixture was stirred at 25 °C. After the reaction was completed (4 h or less, monitored by TLC, EtOAc/pentane 5:95 and MeOH/DCM 5:95), the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography (EtOAc/pentane, the solvent ratio indicated in the Rf measurement was used) directly without further work-up to afford the corresponding product (6 - 24).

General procedure D: Copper catalyzed oxy-vinylation of substituted diazo compound:

\[
\begin{align*}
R' - & - \text{I} + \text{N}_2 - \\
A & - \text{ phenylacetate} \\
\rightarrow & - \text{R} - \\
\end{align*}
\]

A catalytic solution was prepared by mixing Cu(CH₃CN)₄BF₄ (12.6 mg, 40.0 µmol) and (1E,1'E)-N,N'-(ethane-1,2-diyl)bis(1-(2,6-dichlorophenyl)methanimine) (5a) (18.7 mg, 50.0 µmol) in DCE (5.0 mL) at room temperature for 1 h. 1.0 mL of the catalytic solution was then added to a stirring suspension of VBX (1a - 1u) (0.200 mmol, 1.00 equiv) and substituted diazo compound (4a - 4q) (0.400 mmol, 2.00 equiv) in DCE (4.0 mL). The reaction mixture was stirred at 40 °C. After the reaction was completed (4 h or less, monitored by TLC, EtOAc/pentane 5:95 and MeOH/DCM 5:95), the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography (EtOAc/pentane, the solvent ratio indicated in the Rf measurement was used) directly without further work-up to afford the corresponding product (6 - 24).

(E)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a)

Following general procedure C, starting from (E)-1-styryl-1λ₃-benzo[d][1,2]iодаоксол-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 µL, 87% wt in DCM, 0.400 mmol), afforded
(E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) as a colorless oil (83 mg, 0.19 mmol, 95%). Rf = 0.24 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.01 (ddd, J = 10.8, 7.9, 1.4 Hz, 2H, ArH), 7.49 - 7.41 (m, 3H, ArH), 7.38 - 7.27 (m, 3H, ArH), 7.19 (ddd, J = 7.9, 7.4, 1.7 Hz, 1H, ArH), 6.93 (dd, J = 15.9, 1.2 Hz, 2H, CHCPh), 6.38 (dd, J = 15.9, 7.1 Hz, 1H, CHCPh), 5.87 (dd, J = 7.1, 1.3 Hz, 1H, OCHCC), 4.29 (qd, J = 7.1, 2.4 Hz, 2H, OCH3CH2), 3.12 (t, J = 7.1 Hz, 3H, OCH3CH2); 13C NMR (101 MHz, CDCl3) δ 168.5, 165.6, 141.6, 135.8, 135.7, 134.2, 133.2, 131.7, 128.8, 128.8, 128.1, 127.0, 94.6, 74.3, 62.2, 14.3; IR (νmax, cm⁻¹) 2978 (m), 2902 (m), 1735 (s), 1582 (w), 1451 (m), 1395 (m), 1369 (m), 1278 (s), 1258 (s), 1199 (m), 1129 (m), 1098 (s), 1044 (s), 1016 (s), 966 (m), 863 (m), 764 (s), 750 (s); HRMS (ESI) calcd for C16H13INaO2⁺ [M+Na]⁺ 459.0664; found 459.0070.

(E)-1-Ethoxy-4-(4-methoxyphenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (6b)

Following general procedure C, starting from (E)-1-(4-methoxystyril)-1λ3-benzo[d][1,2]iodaoxo-3(1H)-one (1e) (76.0 mg, 0.200 mmol) and ethyl 2-diazaacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-4-(4-methoxyphenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (6b) as a colorless oil (76 mg, 0.16 mmol, 81%). Rf = 0.12 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.05 - 7.95 (m, 2H, ArH), 7.44 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.40 - 7.34 (m, 2H, ArH), 7.18 (ddd, J = 7.9, 7.4, 1.7 Hz, 1H, ArH), 6.90 - 6.82 (m, 3H, ArH and CHCPh), 6.23 (ddd, J = 15.9, 7.4 Hz, 1H, CHCPh), 5.83 (dd, J = 7.4, 1.2 Hz, 1H, OCHCC), 4.28 (qd, J = 7.1, 3.0 Hz, 2H, OCH3CH2), 3.81 (s, 3H, ArOCH3), 1.31 (t, J = 7.1 Hz, 3H, OCH2CH3); 13C NMR (101 MHz, CDCl3) δ 168.7, 165.7, 160.1, 141.6, 135.6, 134.2, 133.2, 131.7, 128.4, 128.3, 128.1, 118.3, 114.2, 94.5, 74.6, 62.1, 55.5, 14.3; IR (νmax, cm⁻¹) 2933 (m), 2862 (w), 2091 (w), 1731 (s), 1607 (m), 1582 (w), 1511 (s), 1465 (m), 1288 (m), 1248 (s), 1194 (m), 1175 (s), 1128 (m), 1096 (s), 1015 (s), 969 (m), 824 (m); HRMS (ESI) calcd for C20H19INaO2⁺ [M+Na]⁺ 489.0169; found 489.0169.

(E)-1-Ethoxy-1-oxo-4-(p-tolyl)but-3-en-2-yl 2-iodobenzoate (6c)

Following general procedure C, starting from (E)-1-(4-methylstyril)-1λ3-benzo[d][1,2]iodaoxo-3(1H)-one (1b) (72.8 mg, 0.200 mmol) and ethyl 2-diazaacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-4-(p-tolyl)but-3-en-2-yl 2-iodobenzoate (6c) as a colorless oil (83 mg, 0.18 mmol, 92%). Rf = 0.26 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.01 (ddd, J = 9.7, 7.9, 1.4 Hz, 2H, ArH), 7.44 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.37 - 7.29 (m, 2H, ArH), 7.23 - 7.12 (m, 3H, ArH), 6.93 - 6.85 (m, 1H, CHCPh), 6.32 (ddd, J = 15.9, 7.2 Hz, 1H, CHCPh), 5.85 (dd, J = 7.2, 1.3 Hz, 1H, OCHCC), 4.28 (qd, J = 7.1, 2.2 Hz, 2H, OCH3CH2), 2.35 (s, 3H, ArCH3), 1.31 (t, J = 7.1 Hz, 3H, OCH2CH3); 13C NMR (101 MHz, CDCl3) δ 168.6, 165.6, 141.6, 138.8, 135.8, 134.2, 133.2, 132.9, 129.5, 128.1, 126.9, 119.6, 94.5, 74.5, 62.1, 21.4, 14.3; IR (νmax, cm⁻¹) 2979 (m), 2906 (m), 1732 (s), 1462 (m), 1429 (m), 1372 (m), 1294 (s), 1239 (s), 1198 (s), 1127 (s), 1098 (s), 1041 (s), 1014 (s), 965 (s), 855 (m), 810 (m), 740 (s); HRMS (ESI) calcd for C20H19INaO2⁺ [M+Na]⁺ 473.0220; found 473.0220.
Following general procedure C, starting from (E)-1-(4-(trifluoromethyl)-1λ3-benzo[d][1,2]iodoxol-3(1H)-one (1e) (84.0 mg, 0.200 mmol) and ethyl 2-diazacacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl 2-iodobenzoate (6d) as a colorless oil (73 mg, 0.15 mmol, 72%). Rf = 0.22 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.02 (dd, J = 15.1, 7.9, 1.4 Hz, 2H, ArH), 7.60 (d, J = 8.2 Hz, 2H, ArH), 7.53 (d, J = 8.2 Hz, 2H, ArH), 7.46 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.24 - 7.17 (m, 1H, ArH), 6.96 (dd, J = 16.0, 1.4 Hz, 1H, CHCHPh), 6.48 (dd, J = 16.0, 6.6 Hz, 1H, CHCHPh), 5.91 (dd, J = 6.7, 1.4 Hz, 1H, OCHCC), 4.30 (qd, J = 7.1, 2.3 Hz, 2H, OCH2CH3), 1.33 (t, J = 7.1 Hz, 3H, OCH2CH3); 13C NMR (101 MHz, CDCl3) δ 168.1, 165.5, 141.7, 139.2, 134.0, 133.9, 133.4, 131.7, 130.5 (q, J = 32.6 Hz), 128.2, 127.2, 125.8 (q, J = 3.9 Hz), 124.1 (q, J = 272.0 Hz), 123.5, 94.6, 73.8, 62.4, 14.3; 19F NMR (376 MHz, CDCl3) δ -62.7; IR (νmax, cm⁻¹) 2979 (m), 2914 (m), 1732 (m), 1466 (w), 1415 (m), 1374 (w), 1325 (s), 1243 (s), 1196 (m), 1166 (m), 1108 (s), 1076 (s), 1047 (s), 1014 (s), 969 (m), 857 (m), 822 (m), 742 (s); HRMS (ESI) calcd for C20H16F3NaO4+ [M+Na]+ 526.9938; found 526.9951.

(E)-1-Ethoxy-4-(4-fluorophenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (6e)

Following general procedure C, starting from (E)-1-(4-fluoroostyryl)-1λ3-benzo[d][1,2]iodoxol-3(1H)-one (1d) (73.6 mg, 0.200 mmol) and ethyl 2-diazacacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-4-(4-fluorophenyl)-1-oxobut-3-en-2-yl 2-iodobenzoate (6e) as a colorless oil (60 mg, 0.13 mmol, 66%). Rf = 0.22 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.02 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.99 (dd, J = 7.8, 1.8 Hz, 1H, ArH), 7.50 - 7.36 (m, 3H, ArH), 7.19 (td, J = 7.7, 1.7 Hz, 1H, ArH), 7.08 - 6.99 (m, 2H, ArH), 6.93 - 6.84 (m, 1H, CHCHPh), 6.30 (dd, J = 15.9, 7.1 Hz, 1H, CHCHPh), 5.85 (dd, J = 7.1, 1.3 Hz, 1H, OCHCC), 4.28 (qd, J = 7.1, 3.2 Hz, 2H, OCH2CH3), 1.32 (t, J = 7.1 Hz, 3H, OCH2CH3); 13C NMR (101 MHz, CDCl3) δ 168.5, 165.6, 163.0 (d, J = 248.5 Hz), 141.6, 134.6, 134.1, 133.3, 131.9 (d, J = 3.3 Hz), 131.7, 128.7 (d, J = 8.2 Hz), 128.2, 120.5 (d, J = 2.2 Hz), 115.8 (d, J = 21.7 Hz), 94.5, 74.2, 62.2, 14.3; 19F NMR (376 MHz, CDCl3) δ -112.7; IR (νmax, cm⁻¹) 2981 (m), 2932 (w), 1734 (s), 1601 (m), 1585 (m), 1509 (s), 1466 (m), 1423 (m), 1376 (m), 1290 (s), 1211 (s), 1131 (s), 1104 (s), 1016 (s), 967 (m), 859 (m), 826 (m), 740 (s), 716 (m); HRMS (ESI) calcd for C19H16F3NaO4+[M+Na]+ 476.9970; found 476.9971.

(E)-1-Ethoxy-4-(naphthalen-1-yl)-1-oxobut-3-en-2-yl 2-iodobenzoate (6f)

Following general procedure C, starting from (E)-1-(2-(naphthalen-1-yl)-1λ3-benzo[d][1,2]iodoxol-3(1H)-one (1f) (80.0 mg, 0.200 mmol) and ethyl 2-diazacacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-4-(naphthalen-1-yl)-1-oxobut-3-en-2-yl 2-iodobenzoate (6f) as a white solid (79 mg, 0.16 mmol, 81%). M.p. 59-61 °C; Rf = 0.18 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.15 - 8.09 (m, 1H, ArH), 8.04 (dt, J = 7.8, 1.4 Hz, 2H, ArH), 7.91 - 7.78 (m, 2H, ArH), 7.71 (d, J
= 15.7 Hz, 1H, CHCPh), 7.64 (dt, J = 7.2, 1.0 Hz, 1H, ArH), 7.58 - 7.42 (m, 4H, ArH), 7.20 (ddd, J = 7.9, 7.4, 1.7 Hz, 1H, ArH), 6.44 (dd, J = 15.7, 6.9 Hz, 1H, CHCPh), 6.01 (dd, J = 6.9, 1.4 Hz, 1H, OCHCC), 4.33 (q, J = 7.1 Hz, 2H, OCH₂CH₃), 1.35 (t, J = 7.1 Hz, 3H, OCH₃CH₂CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 165.7, 141.6, 134.2, 133.7, 133.5, 133.1, 131.7, 131.2, 129.0, 128.7, 128.2, 126.5, 126.1, 125.7, 124.5, 123.9, 123.8, 94.5, 74.4, 62.2, 14.3; IR (νₘₙₓ, cm⁻¹) 3057 (w), 2985 (m), 2904 (m), 1732 (s), 1583 (m), 1464 (m), 1429 (m), 1395 (m), 1370 (m), 1335 (m), 1284 (s), 1241 (s), 1192 (s), 1131 (s), 1094 (s), 1016 (s), 967 (s), 859 (m), 775 (s), 736 (s); HRMS (ESI) calcd for C₃₂H₃₉N₃O₅⁺ [M+Na]⁺ 509.0220; found 509.0233.

(E)-1-Ethoxy-1-oxo-4-(thiophen-2-yl)but-3-en-2-yl 2-iodobenzoate (6g)

Following general procedure C, starting from (E)-1-(2-(thiophen-2-yl)viny1)-1λ³-benzo[d][1,2]iodoxaol-3(1H)-one (1g) (71.2 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 mL, 87% wt in DCM, 0.400 mmol), afforded (E]-1-ethoxy-1-oxo-4-(thiophen-2-yl)but-3-en-2-yl 2-iodobenzoate (6g) as a clear yellow oil (67 mg, 0.15 mmol, 76%). Rᵣ = 0.24 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.06 - 7.95 (m, 2H, ArH), 7.45 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.24 (dt, J = 5.0, 0.9 Hz, 1H, ArH), 7.19 (ddd, J = 7.9, 7.4, 1.7 Hz, 1H, ArH), 7.08 - 7.00 (m, 2H, ArH and CHCPh), 6.99 (dd, J = 5.1, 3.6 Hz, 1H, ArH), 6.20 (dd, J = 15.7, 7.2 Hz, 1H, CHCPh), 5.82 (dd, J = 7.2, 1.3 Hz, 1H, OCHCC), 4.28 (qq, J = 7.1, 3.6 Hz, 2H, OCH₂CH₃), 1.32 (t, J = 7.1 Hz, 3H, OCH₃CH₂CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 165.6, 141.6, 140.6, 134.1, 133.3, 131.7, 128.9, 128.2, 127.7, 127.6, 125.8, 119.9, 94.6, 74.1, 62.2, 14.3; IR (νₘₙₓ, cm⁻¹) 3057 (w), 2985 (m), 2904 (m), 1732 (s), 1583 (m), 1464 (m), 1429 (m), 1395 (m), 1370 (m), 1335 (m), 1284 (s), 1241 (s), 1192 (s), 1131 (s), 1094 (s), 1016 (s), 967 (s), 859 (m), 775 (s), 736 (s); HRMS (ESI) calcd for C₃₁H₃₉O₅ [M⁺] 441.9730; found 441.9733.

(E)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodo-5-methoxybenzoate (6h)

Following general procedure C, starting from (E)-5-methoxy-1-styryl-1λ³-benzo[d][1,2]iodoxaol-3(1H)-one (1i) (76.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodo-5-methoxybenzoate (6h) as a colorless oil (78 mg, 0.17 mmol, 84%). Rᵣ = 0.14 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.7 Hz, 1H, ArH), 7.52 (d, J = 3.1 Hz, 1H, ArH), 7.48 - 7.41 (m, 2H, ArH), 7.39 - 7.27 (m, 3H, ArH), 6.93 (dd, J = 16.0, 1.2 Hz, 1H, CHCPh), 6.79 (dd, J = 8.7, 3.1 Hz, 1H, ArH), 6.38 (dd, J = 15.9, 7.1 Hz, 1H, CHCPh), 5.85 (dd, J = 7.1, 1.3 Hz, 1H, OCHCC), 4.29 (qd, J = 7.1, 2.8 Hz, 2H, OCH₂CH₃), 3.84 (s, 3H, ArOCH₃), 1.32 (t, J = 7.1 Hz, 3H, OCH₃CH₂CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 168.5, 165.5, 159.7, 142.1, 135.8, 135.7, 135.0, 128.8, 128.8, 127.0, 120.7, 119.8, 117.2, 82.8, 74.4, 62.1, 55.7, 14.3; IR (νₘₙₓ, cm⁻¹) 2986 (w), 2937 (w), 1736 (s), 1590 (m), 1565 (m), 1469 (m), 1449 (m), 1394 (m), 1368 (m), 1313 (m), 1284 (s), 1241 (s), 1213 (s), 1184 (s), 1092 (s), 1046 (s), 1029 (s), 1009 (s), 966 (s), 911 (m), 811 (m), 777 (m), 732 (s), 693 (s); HRMS (ESI) calcd for C₃₀H₃₇O₅ [M⁺] 466.0272; found 466.0276.

(E)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl 5-fluoro-2-iodobenzoate (6i)
Following general procedure C, starting from (E)-5-fluoro-1-styryl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1h) (73.6 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 5-fluoro-2-iodobenzoate (6i) as a colorless oil (77 mg, 0.17 mmol, 85%). Rf = 0.34 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.7, 5.3 Hz, 1H, ArH), 7.73 (dd, J = 8.9, 3.1 Hz, 1H, ArH), 7.48 - 7.41 (m, 2H, ArH), 7.39 - 7.28 (m, 3H, ArH), 7.01 - 6.88 (m, 2H, ArH and CHCHPh), 6.37 (dd, J = 15.9, 7.2 Hz, 1H, CHCHPh), 5.85 (dd, J = 7.2, 1.3 Hz, 1H, OCHCC), 4.29 (qd, J = 7.1, 3.3 Hz, 2H, OCH₂CH₃), 1.32 (t, J = 7.1 Hz, 3H, OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 168.3, 164.5 (d, J = 2.6 Hz), 162.5 (d, J = 249.7 Hz), 143.0 (d, J = 7.3 Hz), 136.1, 135.6 (d, J = 7.3 Hz), 135.6, 128.9, 127.0, 120.9 (d, J = 21.4 Hz), 120.4, 119.2 (d, J = 24.2 Hz), 87.6 (d, J = 3.6 Hz), 74.6, 62.3, 14.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.0; IR (νmax, cm⁻¹) 1736 (s), 1575 (m), 1465 (m), 1449 (m), 1394 (m), 1370 (m), 1296 (m), 1264 (s), 1241 (s), 1188 (s), 1127 (m), 1084 (m), 1017 (s), 964 (m), 819 (m), 777 (m), 734 (s), 691 (m); HRMS (ESI) calcd for C₁₉H₁₅FIO₄ [M⁺] 545.0072; found 545.0074. One carbon was not resolved at 101 MHz.

(E)-1-Ethoxy-1-oxo-2,4-diphenylbut-3-en-2-yl 2-iodobenzoate (7)

Following general procedure D, starting from (E)-1-styryl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and ethyl 2-diazo-2-phenylacetate (4b) (76.0 mg, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-2,4-diphenylbut-3-en-2-yl 2-iodobenzoate (7) as a colorless oil (73 mg, 0.14 mmol, 71%). Rf = 0.40 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.0 Hz, 1H, ArH), 7.95 (dd, J = 7.7, 1.7 Hz, 1H, ArH), 7.76 - 7.64 (m, 2H, ArH), 7.52 - 7.14 (m, 11H, ArH and CHCHPh), 6.53 (d, J = 16.3 Hz, 1H, CHCHPh), 4.41 - 4.15 (m, 2H, OCH₂CH₃), 1.26 (t, J = 7.2 Hz, 3H, OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 169.8, 165.2, 141.5, 138.2, 136.2, 135.2, 133.9, 133.0, 131.2, 128.7, 128.6, 128.4, 128.2, 127.1, 126.6, 94.1, 84.2, 62.4, 14.2; IR (νmax, cm⁻¹) 2974 (m), 2900 (m), 1735 (s), 1495 (m), 1449 (m), 1431 (m), 1276 (s), 1256 (s), 1092 (s), 1042 (s), 1016 (s), 974 (m), 764 (s), 750 (s); HRMS (ESI) calcd for C₂₉H₂₆I₃NaO₉⁺ [M+Na⁺] 521.0220; found 521.0222. One carbon was not resolved at 101 MHz.

(E)-4-Cyclohexyl-1-ethoxy-1-oxobut-3-en-2-yl 2-iodobenzoate (8a)

Following general procedure C, starting from (E)-1-(2-cyclohexylvinyl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1j) (71.2 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-5-phenylpent-3-en-2-yl 2-iodobenzoate (8a) as a colorless oil (88 mg, 0.20 mmol, 99%). Rf = 0.37 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.94 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.42 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.17 (dd, J = 7.9, 7.4, 1.7 Hz, 1H, ArH), 6.04 - 5.94 (m, 1H, CHCHCy), 5.66 - 5.57 (m, 2H, CHCH₃ and OCHCC), 4.24 (qd, J = 7.1, 2.7 Hz, 2H, OCH₂CH₃), 2.98 (m, 1H, cy-H), 1.80 - 1.69 (m, 4H, cy-H), 1.69 - 1.61 (m, 1H, cy-H), 1.34 - 1.03 (m, 8H, cy-H and OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 165.7, 143.9, 141.5, 134.3, 133.1, 131.7,
128.1, 119.4, 94.5, 74.6, 61.8, 40.6, 32.5 - 32.3 (2 s, rotamer), 32.5, 32.4, 26.2, 26.0, 14.3; IR (ν\textsubscript{max}, cm\textsuperscript{-1}) 2977 (m), 2920 (m), 2848 (m), 1736 (s), 1579 (m), 1450 (m), 1286 (s), 1239 (s), 1190 (s), 1133 (s), 1100 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for C\textsubscript{39}H\textsubscript{29}NaO\textsubscript{4}\textsuperscript{+} [M+Na]\textsuperscript{+} 465.0533; found 465.0542.

(E)-1-Ethoxy-1-oxo-5-phenylpent-3-en-2-yl 2-iodobenzoate (8b)

Following general procedure C, starting from (E)-1-(3-phenylprop-1-en-1-yl)-1λ\textsuperscript{3}-benzo[d][1,2]iodaoxol-3(1H)-one (1I) (72.8 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-5-phenylpent-3-en-2-yl 2-iodobenzoate (8b) as a colorless oil (81 mg, 0.18 mmol, 90%). R\textsubscript{t} = 0.26 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.00 (dd, J = 8.0, 1.1 Hz, 1H, ArH), 7.94 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.42 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.35 - 7.27 (m, 2H, ArH), 7.25 - 7.13 (m, 4H, ArH), 6.22 (dd, J = 14.7, 6.8, 0.8 Hz, 1H, CHCH\textsubscript{3}Bn), 5.80 - 5.66 (m, 2H, CHCH\textsubscript{3}Bn and OCH\textsubscript{3}), 4.26 (qd, J = 7.1, 2.4 Hz, 2H, OCH\textsubscript{2}CH\textsubscript{3}), 3.50 - 3.43 (m, 2H, CH\textsubscript{2}CH\textsubscript{2}Ph), 1.29 (t, J = 7.1 Hz, 3H, OCH\textsubscript{2}CH\textsubscript{2}Ph); 13C NMR (101 MHz, CDCl\textsubscript{3}) δ 168.6, 165.5, 141.4, 138.9, 136.3, 134.1, 133.0, 131.5, 126.8, 126.8, 128.0, 126.4, 123.1, 94.4, 74.0, 61.8, 38.6, 14.2; IR (ν\textsubscript{max}, cm\textsuperscript{-1}) 2981 (w), 2918 (m), 1733 (s), 1456 (m), 1429 (m), 1288 (s), 1129 (s), 1098 (s), 1016 (s), 973 (s), 742 (s), 699 (s); HRMS (ESI) calcd for C\textsubscript{39}H\textsubscript{29}NaO\textsubscript{4}\textsuperscript{+} [M+Na]\textsuperscript{+} 473.0220; found 473.0223.

(E)-1-Ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (8c)

Following general procedure C, starting from (E)-1-(1-((pent-1-en-1-yl)-1λ\textsuperscript{3}-benzo[d][1,2]iodaoxol-3(1H)-one (1k) (63.2 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (8c) as a colorless oil (76 mg, 0.19 mmol, 94%). R\textsubscript{t} = 0.37 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.00 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 7.95 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.42 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.21 - 7.12 (m, 1H, ArH), 6.10 - 5.99 (m, 1H, CHCH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{3}), 5.72 - 5.60 (m, 2H, CHCH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{3} and OCH\textsubscript{3}), 4.25 (td, J = 7.2, 6.7 Hz, 2H, OCH\textsubscript{2}CH\textsubscript{3}), 2.15 - 2.05 (m, 2H, CHCH\textsubscript{2}CH\textsubscript{3}), 1.45 (h, J = 7.3 Hz, 2H, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.29 (t, J = 7.1 Hz, 3H, OCH\textsubscript{2}CH\textsubscript{3})), 0.91 (t, J = 7.4 Hz, 3H, CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{3}); 13C NMR (101 MHz, CDCl\textsubscript{3}) δ 169.0, 165.7, 141.6, 138.4, 134.3, 133.1, 131.7, 128.1, 121.9, 94.5, 74.5, 61.8, 34.5, 21.9, 14.3, 13.7; IR (ν\textsubscript{max}, cm\textsuperscript{-1}) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for C\textsubscript{39}H\textsubscript{29}NaO\textsubscript{4}\textsuperscript{+} [M+Na]\textsuperscript{+} 425.0223; found 425.0232.

(E)-1-Ethyl 8-methyl 2-((2-iodobenzoyl)oxy)oct-3-enedioate (8d)

Following general procedure C, starting from methyl (E)-6-(3-oxo-1λ\textsuperscript{3}-benzo[d][1,2]iodaoxol-1(3H)-one (1n) (74.8 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol),
afforded (E)-1-ethyl 8-methyl 2-(2-iodobenzoyl)oxy)cot-3-enedioate (8d) as a colorless oil (77 mg, 0.17 mmol, 84%). \( R_t = 0.13 \) (EtOAc/pentane 5:95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.00 (dd, \( J = 8.0, 1.1 \) Hz, 1H, Ar\( H \)), 7.94 (dd, \( J = 7.8, 1.7 \) Hz, 1H, Ar\( H \)), 7.42 (td, \( J = 7.6, 1.2 \) Hz, 1H, Ar\( H \)), 7.21 - 7.14 (m, 1H, Ar\( H \)), 6.01 (ddt, \( J = 14.8, 6.8, 0.8 \) Hz, 1H, CH\( \text{CHCH}_2\)), 5.75 - 5.60 (m, 2H, OCH\( \text{CC} \) and CH\( \text{CHCH}_2\)), 4.24 (q, \( J = 7.1 \) Hz, 2H, O\( \text{CHCH}_2\)), 3.66 (s, 3H, O\( \text{CH}_3\)), 2.32 (t, \( J = 7.5 \) Hz, 2H, CH\( \text{COCH}_3\)), 2.21 - 2.12 (m, 2H, CH\( \text{CHCH}_2\)), 1.76 (p, \( J = 7.3 \) Hz, 2H, CH\( \text{CHCH}_2\)), 1.29 (t, \( J = 7.1 \) Hz, 3H, O\( \text{CHCH}_2\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 173.9, 168.7, 165.6, 141.5, 136.9, 134.2, 133.1, 131.6, 128.1, 122.8, 94.5, 74.2, 61.9, 51.7, 33.3, 31.7, 23.9, 14.3; IR (\( \nu_{\text{max}} \), cm\(^{-1}\)) 2956 (w), 1735 (s), 1606 (s), 1436 (m), 1367 (w), 1344 (m), 1292 (m), 1238 (m), 1209 (m), 1157 (m), 1096 (m), 1017 (s), 965 (m), 834 (m); HRMS (ESI) calcd for \( \text{C}_{18}\text{H}_{18}\text{INaO}_4^\text{+} \) [M+Na]\(^+\) 483.0275; found 483.0280.

(E)-7-Chloro-1-ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (8e)

Following general procedure C, starting from (E)-1-(5-chloropent-1-en-1-yl)-1\(^3\)-benzod[d][1,2]iodaoxol-3(1H)-one (1m) (70.1 mg, 0.200 mmol) and ethyl 2-diazoacetate (\( \text{4a} \)) (48.0 \( \mu\)L, 87% wt in DCM, 0.400 mmol), afforded (E)-7-chloro-1-ethoxy-1-oxohept-3-en-2-yl 2-iodobenzoate (8e) as a colorless oil (82 mg, 0.19 mmol, 94%). \( R_t = 0.20 \) (EtOAc/pentane 5:95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.01 (dd, \( J = 7.9, 1.1 \) Hz, 1H, Ar\( H \)), 7.94 (dd, \( J = 7.8, 1.7 \) Hz, 1H, Ar\( H \)), 7.43 (td, \( J = 7.6, 1.2 \) Hz, 1H, Ar\( H \)), 7.18 (td, \( J = 7.7, 1.7 \) Hz, 1H, Ar\( H \)), 6.02 (ddt, \( J = 15.1, 6.9, 1.1 \) Hz, 1H, CH\( \text{CHCH}_2\)), 5.75 (ddt, \( J = 15.3, 7.1, 1.4 \) Hz, 1H, CH\( \text{CHCH}_2\)), 5.66 (dd, \( J = 7.1, 1.0 \) Hz, 1H, OCH\( \text{CC}\)), 4.25 (q, \( J = 7.1 \) Hz, 2H, O\( \text{CHCH}_2\)), 3.54 (t, \( J = 6.5 \) Hz, 2H, CH\( \text{CHCH}_2\)), 2.35 - 2.24 (m, 2H, CH\( \text{CHCH}_2\)), 1.96 - 1.85 (m, 2H, CH\( \text{CHCH}_2\)), 1.30 (t, \( J = 7.1 \) Hz, 3H, O\( \text{CHCH}_2\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 168.7, 165.6, 141.6, 136.1, 134.2, 133.2, 131.6, 128.1, 123.3, 94.5, 74.1, 62.0, 44.2, 31.4, 29.5, 14.3; IR (\( \nu_{\text{max}} \), cm\(^{-1}\)) 2977 (m), 2920 (m), 2848 (m), 1736 (s), 1579 (m), 1450 (m), 1286 (s), 1239 (s), 1190 (s), 1133 (s), 1100 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for \( \text{C}_{18}\text{H}_{18}\text{ClNaO}_4^\text{+} \) [M+Na]\(^+\) 458.9831; found 458.9835.

1-(Cyclohex-1-en-1-yl)-2-ethoxy-2-oxoethyl 2-iodobenzoate (8f)

Following general procedure C, starting from (E)-1-(cyclohex-1-en-1-yl)-1\(^3\)-benzod[d][1,2]iodaoxol-3(1H)-one (1r) (65.6 mg, 0.200 mmol) and ethyl 2-diazoacetate (\( \text{4a} \)) (48.0 \( \mu\)L, 87% wt in DCM, 0.400 mmol), afforded 1-(cyclohex-1-en-1-yl)-2-ethoxy-2-oxoethyl 2-iodobenzoate (8f) as a colorless oil (80 mg, 0.19 mmol, 97%). \( R_t = 0.36 \) (EtOAc/pentane 5:95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.00 (dd, \( J = 8.0, 1.1 \) Hz, 1H, Ar\( H \)), 7.94 (dd, \( J = 7.8, 1.7 \) Hz, 1H, Ar\( H \)), 7.42 (td, \( J = 7.6, 1.2 \) Hz, 1H, Ar\( H \)), 7.20 - 7.14 (m, 1H, Ar\( H \)), 6.04 - 5.99 (m, 1H, CH\( \text{CHCH}_2\)), 5.55 (d, \( J = 1.0 \) Hz, 1H, OCH\( \text{CC}\)), 4.25 (q, \( J = 7.1 \) Hz, 2H, O\( \text{CHCH}_2\)), 2.30 - 1.18 (m, 1H, cy-\( H \)), 2.16 - 1.96 (m, 3H, cy-\( H \)), 1.74 - 1.58 (m, 4H, cy-\( H \)), 1.29 (t, \( J = 7.1 \) Hz, 3H, O\( \text{CHCH}_2\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 168.7, 165.9, 141.6, 134.4, 133.1, 131.7, 131.1, 130.5, 128.1, 94.5, 78.1, 61.7, 25.4, 24.9, 22.4, 22.0, 14.3; IR (\( \nu_{\text{max}} \), cm\(^{-1}\)) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for \( \text{C}_{17}\text{H}_{17}\text{INaO}_4^\text{+} \) [M+Na]\(^+\) 437.0220; found 437.0225.

(E)-5-(1,3-Dioisoindoindol-2-yl)-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (8g)
Following general procedure C, starting from (E)-2-(3-oxo-1λ3-benzo[d][1,2]iodaoxol-1(3H)-yl)-allylisoindoline-1,3-dione (1q) (87.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-5-(1,3-dioxoisindolin-2-yl)-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (8g) as a white sticky solid (31.0 mg, 0.06 mmol, 30%). M.p. 77-78 °C; Rf = 0.31 (EtOAc/pentane 25:75); 1H NMR (400 MHz, CDCl3) δ 7.99 (dd, J = 8.0, 1.1 Hz, 1H, ArH), 7.93 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.89 - 7.81 (m, 2H, ArH), 7.77 - 7.69 (m, 2H, ArH), 7.42 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.17 (td, J = 7.7, 1.7 Hz, 1H, ArH), 6.12 (dt, J = 15.5, 5.9, 1.4 Hz, 1H, CHCH2N), 5.96 (ddt, J = 15.5, 6.0, 1.4 Hz, 1H, CHCH2N), 5.71 (dd, J = 6.0, 1.3 Hz, 1H, OCHCC), 4.36 (dt, J = 5.9, 1.2 Hz, 2H, CH2NPhth), 4.24 (qd, J = 7.1, 0.9 Hz, 2H, OCH2CH3), 1.28 (t, J = 7.1 Hz, 3H, OCH2CH3); 13C NMR (101 MHz, CDCl3) δ 168.0, 167.9, 165.4, 141.6, 134.3, 133.9, 133.2, 132.2, 131.7, 129.1, 128.1, 123.6, 94.5, 73.1, 62.2, 38.9, 14.2; IR (vmax, cm⁻¹): 3463 (w), 3053 (w), 2985 (w), 2922 (m), 2854 (w), 1733 (m), 1709 (s), 1582 (w), 1467 (m), 1430 (m), 1392 (s), 1288 (m), 1244 (m), 1200 (m), 1130 (m), 1101 (m), 1046 (m), 1017 (s), 944 (m); HRMS (ESI) calcd for C23H21N4O6⁺ [M+Na]⁺ 542.0071; found 542.0082.

(E)-1-Ethoxy-1-oxo-5-((triisopropylsilyl)oxy)pent-3-en-2-yl 2-iodobenzoate (8h)

Following general procedure C, starting from (E)-1-((triisopropylsilyl)oxy)prop-1-en-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1p) (92.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-5-((triisopropylsilyl)oxy)pent-3-en-2-yl 2-iodobenzoate (8h) as a colorless oil (94 mg, 0.17 mmol, 86%). Rf = 0.54 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.01 (dd, J = 8.0, 1.1 Hz, 1H, ArH), 7.96 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.42 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.17 (td, J = 7.7, 1.7 Hz, 1H, ArH), 6.14 (dt, J = 15.4, 3.7, 1.2 Hz, 1H, CHCH2O), 6.02 (dt, J = 15.4, 6.5, 2.0 Hz, 1H, CHCH2O), 5.74 (dq, J = 6.5, 1.3 Hz, 1H, OCHCC), 4.33 (dt, J = 3.6, 1.7 Hz, 2H, CH2OTIPS), 4.25 (qd, J = 7.1, 1.2 Hz, 2H, OCH2CH3), 1.29 (t, J = 7.1 Hz, 3H, OCH2CH3); 13C NMR (101 MHz, CDCl3) δ 168.0, 167.9, 165.6, 141.6, 136.0, 134.2, 133.2, 131.7, 128.1, 120.8, 94.5, 73.8, 62.8, 61.9, 18.1, 14.3, 12.1; IR (vmax, cm⁻¹): 2960 (m), 2941 (s), 2866 (s), 2727 (w), 1736 (s), 1463 (m), 1378 (w), 1284 (m), 1248 (s), 1200 (m), 1124 (s), 1044 (s), 1017 (s), 967 (m), 880 (s); HRMS (ESI) calcd for C23H21N4O6Si⁺ [M+Na]⁺ 569.1191; found 569.1197.

(E)-5-Chloro-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (8i)

Following general procedure C, starting from (E)-1-(3-chloroprop-1-en-1-yl)-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1q) (64.5 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-5-chloro-1-ethoxy-1-oxopent-3-en-2-yl 2-iodobenzoate (8i) as a colorless oil (26.0 mg, 0.06 mmol, 32%). Rf = 0.19 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl3) δ 8.02 (dd, J = 8.0, 1.1 Hz, 1H, ArH), 7.96 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.44 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.20 (ddd, J = 8.0, 7.4, 1.7 Hz, 1H, ArH), 6.20 (dt, J = 15.3, 6.4, 1.4 Hz, 1H, CHCH2CI), 6.04 (ddt, J =
15.3, 6.0, 1.3 Hz, 1H, CHCHCH\textsubscript{2}Cl), 5.76 (dq, J = 5.9, 1.1 Hz, 1H, OCH\textsubscript{CC}), 4.27 (q, J = 7.1 Hz, 2H, OCH\textsubscript{2}CH\textsubscript{3}), 4.11 (dt, J = 6.4, 1.1 Hz, 2H, CH\textsubscript{2}Cl), 1.31 (t, J = 7.2 Hz, 3H, OCH\textsubscript{3}CH\textsubscript{3})); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 167.9, 165.4, 141.7, 133.9, 133.3, 131.7, 131.3, 128.2, 126.0, 94.6, 72.9, 62.3, 43.6, 14.3; IR (\textit{v}\textsubscript{max}, cm\textsuperscript{-1}) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for C\textsubscript{14}H\textsubscript{14}ClNaO\textsubscript{4}\textsuperscript{+} [M+Na]\textsuperscript{+} 430.9518; found 430.9521.

(E)-1-Ethoxy-5-methyl-1-oxohexa-3,5-dien-2-yl 2-iodobenzoate (9a)

Following general procedure C, starting from (E)-1-(3-methylbuta-1,3-dien-1-yl)-1\textsuperscript{3}-benzo[d][1,2]iodaaxol-3(1H)-one (1s) (62.8 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 \textmu L, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-5-methyl-1-oxohexa-3,5-dien-2-yl 2-iodobenzoate (9a) as a colorless oil (66 mg, 0.17 mmol, 82%). R\textsubscript{t} = 0.33 (EtOAc/pentane 5:95); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.01 (dd, J = 7.9, 1.2 Hz, 1H, ArH), 7.97 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.43 (td, J = 7.6, 1.2 Hz, 1H, ArH), 7.18 (ddd, J = 8.0, 7.5, 1.7 Hz, 1H, ArH), 6.63 (d, J = 15.3 Hz, 1H, CHCH), 5.85 - 5.73 (m, 2H, CHCH and OCHCH), 5.14 - 5.09 (m, 2H, CH\textsubscript{2}CH\textsubscript{3}), 4.27 (qd, J = 7.1, 1.7 Hz, 2H, OCH\textsubscript{2}CH\textsubscript{3}), 1.88 (t, J = 1.0 Hz, 3H, CCH\textsubscript{3}), 1.31 (t, J = 7.1 Hz, 3H, OCH\textsubscript{2}CH\textsubscript{3}); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 168.5, 165.6, 141.6, 140.8, 138.5, 134.2, 133.2, 131.7, 128.1, 120.7, 119.6, 94.5, 74.3, 62.1, 18.5, 14.3; IR (\textit{v}\textsubscript{max}, cm\textsuperscript{-1}) 2959 (m), 2928 (m), 2867 (m), 1732 (s), 1591 (m), 1464 (m), 1431 (m), 1368 (m), 1284 (s), 1239 (s), 1192 (s), 1131 (s), 1096 (s), 1014 (s), 965 (s), 740 (s); HRMS (ESI) calcd for C\textsubscript{21}H\textsubscript{17}ClNaO\textsubscript{4}\textsuperscript{+} [M+Na]\textsuperscript{+} 423.0064; found 423.0065.

(3E,5E)-1-Ethoxy-1-oxo-6-phenylhexa-3,5-dien-2-yl 2-iodobenzoate (9b)

Following general procedure C, starting from (E)-1-[(1E,3E)-4-phenylbuta-1,3-dien-1-yl]-1\textsuperscript{3}-benzo[d][1,2]iodaaxol-3(1H)-one (1t) (75.0 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 \textmu L, 87% wt in DCM, 0.400 mmol), afforded (3E,5E)-1-ethoxy-1-oxo-6-phenylhexa-3,5-dien-2-yl 2-iodobenzoate (9b) as a colorless oil (84 mg, 0.18 mmol, 91%). R\textsubscript{t} = 0.23 (EtOAc/pentane 5:95); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.02 (dd, J = 7.9, 1.1 Hz, 1H, ArH), 7.98 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 0.200 (S, 3H, ClINaO); 13C NMR (101 MHz, CDCl\textsubscript{3}) δ 168.5, 165.6, 141.6, 136.8, 136.0, 135.5, 134.1, 133.2, 131.7, 128.8, 128.3, 128.1, 127.2, 126.8, 124.0, 94.6, 74.1, 62.1, 14.3; IR (\textit{v}\textsubscript{max}, cm\textsuperscript{-1}) 2985 (m), 2918 (w), 1732 (s), 1583 (w), 1466 (w), 1284 (m), 1243 (s), 1129 (m), 1100 (m), 1014 (s), 988 (m), 738 (s), 689 (s); HRMS (ESI) calcd for C\textsubscript{21}H\textsubscript{17}ClNaO\textsubscript{4}\textsuperscript{+} [M+Na]\textsuperscript{+} 485.0220; found 485.0216.

(E)-1-Ethoxy-1-oxoundec-3-en-5-yn-2-yl 2-iodobenzoate (9c)
Following general procedure C, starting from (E)-1-(non-1-en-3-yn-1-yl)-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1u) (73.6 mg, 0.200 mmol) and ethyl 2-diazoacetate (4a) (48.0 μL, 87% wt in DCM, 0.400 mmol), afforded (E)-1-ethoxy-1-oxo-undec-3-en-5-yn-2-yl 2-iodobenzoate (9c) as a colorless oil (88 mg, 0.19 mmol, 97%). Rf = 0.40 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.04 (dd, J = 7.9, 1.1 Hz, 1H, ArH), 7.95 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.40 (m, 3H, Ar), 7.32 (m, 2H, Ar), 7.18 (dd, J = 7.9, 7.4, 1.7 Hz, 1H, ArH), 6.17 (ddt, J = 15.8, 2.1, 1.4 Hz, 1H, CHCH₂), 5.72 (dd, J = 6.6, 1.4 Hz, 1H, OCH₂), 4.25 (qd, J = 7.1, 2.2 Hz, 2H, OCH₂CH₃), 2.31 (td, J = 7.1, 2.2 Hz, 2H, CCH₂CH₃), 1.57 - 1.48 (m, 2H, CCH₂CH₃), 1.42 - 1.21 (m, 7H, penty-H and OCH₂CH₃), 0.90 (t, J = 7.1 Hz, 3H, CH₃CH₂), ³¹C NMR (101 MHz, CDCl₃) δ 167.7, 165.2, 141.5, 133.7, 133.2, 131.8, 131.6, 128.0, 116.1, 94.5, 94.2, 77.5, 73.4, 62.1, 31.1, 28.2, 22.2, 19.4, 14.1, 14.0; IR (νmax, cm⁻¹) 2957 (m), 2935 (m), 2859 (w), 2219 (w), 1738 (s), 1584 (m), 1465 (m), 1429 (m), 1370 (m), 1284 (m), 1241 (s), 1196 (s), 1131 (s), 1096 (s), 1043 (m), 1027 (s), 1017 (s), 954 (s), 738 (s); HRMS (ESI) calcd for C₂₀H₂₄IO₂⁺ [M+H]⁺ 455.0714; found 455.0720.

(E)-1-(tert-Butoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (10)

Following general procedure C, starting from (E)-1-styryl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and tert-butyl 2-diazoacetate (4c) (65.0 μL, 85% wt in DCM, 0.400 mmol), afforded (E)-1-(tert-butoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (10) as a white solid (90 mg, 0.19 mmol, 97%). M.p. 62-64 °C; Rf = 0.36 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.01 (td, J = 7.9, 1.4 Hz, 2H, ArH), 7.47 - 7.40 (m, 3H, ArH), 7.38 - 7.32 (m, 2H, ArH), 7.32 - 7.27 (m, 1H, ArH), 7.19 (ddd, J = 7.9, 7.4, 1.8 Hz, 1H, ArH), 6.90 (dd, J = 15.9, 1.4 Hz, 1H, CHCH₂Ph), 6.37 (dd, J = 16.0, 6.9 Hz, 1H, CHCH₂Ph), 5.75 (dd, J = 6.9, 1.4 Hz, 1H, OCHCC), 1.51 (s, 9H, C(CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 167.5, 165.7, 141.6, 135.9, 135.2, 134.4, 133.1, 131.7, 128.8, 128.6, 128.1, 127.0, 121.2, 94.5, 83.1, 74.8, 28.2; IR (νmax, cm⁻¹) 2978 (m), 2902 (m), 1735 (s), 1582 (w), 1451 (m), 1395 (m), 1369 (m), 1278 (s), 1258 (s), 1199 (m), 1129 (m), 1098 (s), 1044 (s), 1016 (s), 966 (m), 863 (m), 764 (s), 750 (s); HRMS (ESI) calcd for C₂₁H₂₁NaO₄⁺ [M+Na]⁺ 487.0377; found 487.0382.

(E)-1-(2,6-di-tert-Butyl-4-methylphenoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (11)

Following general procedure C, starting from (E)-1-styryl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and 2,6-di-tert-butyl-4-methylphenyl 2-diazoacetate (4d) (115 mg, 0.400 mmol), afforded (E)-1-(2,6-di-tert-butyl-4-methylphenoxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (11) as a white solid (123 mg, 0.200 mmol, 100%). Rf = 0.45 (EtOAc/pentane 5:95); M.p.
Following general procedure C, starting from (E)-1-styryl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and benzyl 2-diazoacetate (4e) (88.0 μL, 90% wt in DCM, 0.400 mmol), afforded (E)-1-(Benzzyloxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (12) as a colorless oil (92.0 mg, 0.19 mmol, 92%). Rₖ = 0.26 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, J = 8.0, 1.1 Hz, 1H, ArH), 7.96 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.46 - 7.27 (m, 11H, ArH), 7.19 (td, J = 7.7, 1.7 Hz, 1H, ArH), 6.90 (dd, J = 16.0, 1.3 Hz, 1H, CHCHPh), 6.37 (dd, J = 15.9, 7.1 Hz, 1H, CHCHPh), 5.93 (dd, J = 7.1, 1.3 Hz, 1H, OCHCC), 5.26 (s, 2H, OCH₂Ph); ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 165.6, 141.6, 136.0, 135.7, 135.3, 134.1, 133.3, 131.7, 128.8, 128.8, 128.6, 128.4, 128.1, 127.0, 120.5, 94.5, 74.3, 67.7; IR (νmax, cm⁻¹) 2978 (m), 2902 (m), 1735 (s), 1582 (w), 1451 (m), 1395 (m), 1278 (s), 1258 (s), 1199 (m), 1129 (m), 1098 (s), 1044 (s), 1016 (s), 966 (m), 863 (m), 764 (s), 750 (s); HRMS (ESI) calcd for C₁₃H₁₁NaO₄⁺ [M+Na⁺] 521.0220; found 521.0231.

(E)-1-(Allyloxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (13)

Following general procedure C, starting from (E)-1-styryl-1λ³-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and allyl 2-diazoacetate (4f) (50.4 mg, 0.400 mmol), afforded (E)-1-(allyloxy)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (13) as a colorless oil (82 mg, 0.18 mmol, 91%). Rₖ = 0.24 (EtOAc/pentane 5:95); ¹H NMR (400 MHz, CDCl₃) δ 8.01 (ddd, J = 10.7, 7.9, 1.4 Hz, 2H, ArH), 7.45 (td, J = 7.6, 1.2 Hz, 3H, ArH), 7.39 - 7.27 (m, 3H, ArH), 7.19 (td, J = 7.7, 1.7 Hz, 1H, ArH), 6.94 (dd, J = 16.0, 1.2 Hz, 1H, CHCHPh), 6.39 (dd, J = 15.9, 7.1 Hz, 1H, CHCHPh), 6.00 - 5.87 (m, 2H, OCHCC and OCH₂CH₂), 5.36 (dq, J = 17.2, 1.5 Hz, 1H, CHCH₂), 5.26 (dq, J = 10.5, 1.3 Hz, 1H, CHCH₂), 4.72 (dt, J = 5.8, 1.4 Hz, 2H, OCH₂CH₂); ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 165.6, 141.6, 136.0, 135.7, 134.1, 133.3, 131.7, 131.5, 128.9, 128.8, 128.1, 127.0, 120.6, 119.1, 94.6, 74.3, 66.5; IR (νmax, cm⁻¹) 3063 (w), 3026 (w), 2946 (w), 1736 (s), 1585 (m), 1427 (w), 1290 (m), 1239 (s), 1188 (s), 1133 (s), 1096 (s), 1043 (m), 1014 (s), 963 (s), 937 (m), 742 (s), 689 (s); HRMS (ESI) calcd for C₂₀H₁₇NaO₄⁺ [M+Na⁺] 471.0064; found 471.0063.
(E)-1-(Diethylamino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (14)

Following general procedure C, starting from (E)-1-styryl-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and 2-diazo-N,N-diethylacetamide (4g) (56.5 mg, 0.400 mmol), afforded (E)-1-(diethylamino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (14) as a white solid (87 mg, 0.19 mmol, 94%). R_f = 0.24 (EtOAc/pentane 20:80); M.p. 113-115 °C; 1H NMR (400 MHz, CDCl_3) δ 8.06 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.98 (dd, J = 7.9, 1.1 Hz, 1H, ArH), 7.46 - 7.38 (m, 3H, ArH), 7.38 - 7.27 (m, 3H, ArH), 7.15 (td, J = 7.7, 1.7 Hz, 1H, ArH), 6.88 (d, J = 16.0 Hz, 1H, CHCPh), 6.43 (dd, J = 16.0, 7.9 Hz, 1H, CHCPh), 6.12 (dd, J = 7.9, 0.9 Hz, 1H, OCHCC), 3.59 - 3.30 (m, 4H, N(CH_3)CH_3), 1.31 (t, J = 7.2 Hz, 3H, N(CH_3)CH_3), 1.17 (t, J = 7.3 Hz, 3H, N(CH_3)CH_3); 13C NMR (101 MHz, CDCl_3) δ 166.9, 166.1, 141.3, 136.9, 135.7, 134.5, 133.0, 128.9 (2 C), 128.1, 127.1, 122.0, 94.4, 72.9, 41.9, 41.0, 14.5, 13.0; IR (ν_{max}, cm^{-1}) 3063 (w), 3026 (w), 2946 (w), 1736 (s), 1585 (m), 1427 (w), 1290 (m), 1239 (s), 1188 (s), 1133 (s), 1096 (s), 1043 (m), 1014 (s), 963 (s), 937 (m), 742 (s), 689 (s); HRMS (ESI) calc'd for C_{21}H_{22}INaO_3^+ [M+Na]^+ 486.0537; found 486.0535.

(E)-1-(Methoxy(methyl)amino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (15)

Following general procedure C, starting from (E)-1-styryl-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and 2-diazo-N-methoxy-N-methylacetamide (4h) (51.6 mg, 0.400 mmol), afforded (E)-1-(methoxy(methyl)amino)-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (15) as a white solid (89 mg, 0.20 mmol, 99%). R_f = 0.27 (EtOAc/pentane 20:80); M.p. 90-92 °C; 1H NMR (400 MHz, CDCl_3) δ 8.05 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 8.00 (dd, J = 7.9, 1.1 Hz, 1H, ArH), 7.45 - 7.40 (m, 3H, ArH), 7.37 - 7.26 (m, 3H, ArH), 7.17 (td, J = 7.7, 1.7 Hz, 1H, ArH), 6.93 (d, J = 15.9 Hz, 1H, CHCPh), 6.41 (dd, J = 15.9, 7.5 Hz, 1H, CHCPh), 6.27 (d, J = 7.5 Hz, 1H, OCHCC), 3.87 (s, 3H, OCH_3), 3.27 (s, 3H, NCH_3); 13C NMR (101 MHz, CDCl_3) δ 168.4, 166.0, 141.4, 136.0, 136.0, 134.4, 134.3, 132.1, 132.0, 128.8, 128.7, 128.1, 127.0, 121.0, 94.4, 72.9, 61.7, 32.5; IR (ν_{max}, cm^{-1}) 3055 (w), 3020 (w), 2973 (w), 2942 (w), 1728 (s), 1681 (s), 1466 (m), 1431 (m), 1284 (m), 1251 (s), 1133 (s), 1102 (s), 1016 (m), 969 (s), 738 (s); HRMS (ESI) calc'd for C_{19}H_{18}O_3N_3NaO_3^+ [M+Na]^+ 474.0173; found 474.0175.

(E)-1-(Ethoxysulfonfonyl)-3-phenyllallyl 2-iodobenzoate (16)

Following general procedure C, starting from (E)-1-styryl-1λ3-benzo[d][1,2]iodaoxol-3(1H)-one (1a) (70.0 mg, 0.200 mmol) and ethyl diazomethanesulfonate (4i) (60.1 mg, 0.400 mmol), afforded (E)-1-(ethoxysulfonfonyl)-3-phenyllallyl 2-iodobenzoate (16) as a colorless oil (96 mg, 0.20 mmol, 100%). R_f = 0.12 (EtOAc/pentane 5:95); 1H NMR (400 MHz, CDCl_3) δ 8.07 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 8.01 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.51 - 7.44 (m, 3H, ArH), 7.40 - 7.30 (m, 3H, ArH), 7.27 - 7.21 (m, 1H, ArH), 7.12 -
Following general procedure C, starting from \((\mathbf{E})-1\)-styr1-\(\lambda^3\)-benzo[\(d\)]1,2]iodaooxol-3(1\(H\))one (1\(a\)) (70.0 mg, 0.200 mmol) and diethyl (diazomethyl) phosphonate (4\(j\)) (71.3 mg, 0.400 mmol), afforded \((\mathbf{E})-1\)-(dithiooxophosphoryl)-3-phenylallyl 2-iodobenzoate (17) as a colorless oil (97 mg, 0.19 mmol, 97%). \(R_t = 0.28\) (EtOAc/pentane 50:50); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.03\) (dd, \(J = 7.9, 1.2\) Hz, 1H, Ar\(H\)), 7.93 (dd, \(J = 7.8, 1.7\) Hz, 1H, Ar\(H\)), 7.47 - 7.40 (m, 3H, Ar\(H\)), 7.36 - 7.27 (m, 3H, Ar\(H\)), 7.22 - 7.16 (m, 1H, Ar\(H\)), 6.91 - 6.83 (m, 1H, ChCPh\(H\)), 6.37 (dd, \(J = 15.9, 7.6\) Hz, 1H, CHCPh\(H\)), 6.09 (dd, \(J = 13.5, 7.6, 1.3\) Hz, 1H, OCHCC), 4.27 - 4.16 (m, 4H, (O)P(O)CH\(_2\)CH\(_3\)), 1.33 (t, \(J = 7.1\) Hz, 6H, (O)P(O)CH\(_2\)CH\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 164.9\) (d, \(J = 7.9\) Hz), 141.7, 136.0, 135.9 (d, \(J = 3.1\) Hz), 134.1, 133.3, 131.5, 128.8, 128.6, 128.2, 127.0, 120.0 (d, \(J = 4.5\) Hz), 94.7, 70.6 (d, \(J = 170.7\) Hz), 63.6 (dd, \(J = 9.0, 6.8\) Hz), 16.7 (t, \(J = 5.8\) Hz); \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta 17.4\); IR (v\(_{max}\), cm\(^{-1}\)) 3057 (w), 2981 (w), 2930 (w), 2901 (w), 1734 (m), 1288 (m), 1241 (s), 1131 (m), 1096 (m), 1014 (s), 967 (s), 793 (m), 738 (s), 691 (m); HRMS (ESI) calcd for C\(_{20}\)H\(_{21}\)InO\(_5\)P\(^\cdot\)M\(^{+}\)Na\(^{+}\) 523.0142; found 523.0154.

\((\mathbf{E})-1,1,1\)-Trifluoro-4-phenylbut-3-en-2-yl 2-iodobenzoate (18)

Following general procedure C, starting from \((\mathbf{E})-1\)-styr1-\(\lambda^3\)-benzo[\(d\)]1,2]iodaooxol-3(1\(H\))one (1\(a\)) (70.0 mg, 0.200 mmol) and 2-diazo-1,1,1-trifluoroethene (4\(k\)) (1.08 mL, 0.37 M in DCM, 0.400 mmol), afforded \((\mathbf{E})\)-1,1,1-trifluoro-4-phenylbut-3-en-2-yl 2-iodobenzoate (18) as a colorless oil (88 mg, 0.20 mmol, 100%). \(R_t = 0.52\) (EtOAc/pentane 5:95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.05\) (dd, \(J = 8.0, 1.2\) Hz, 1H, Ar\(H\)), 7.93 (dd, \(J = 7.8, 1.7\) Hz, 1H, Ar\(H\)), 7.45 (ddt, \(J = 7.7, 4.1, 1.9\) Hz, 3H, Ar\(H\)), 7.40 - 7.29 (m, 3H, Ar\(H\)), 7.21 (td, \(J = 7.7, 1.7\) Hz, 1H, Ar\(H\)), 7.00 (d, \(J = 15.9\) Hz, 1H, CHCPh\(H\)), 6.24 (dd, \(J = 15.9, 7.9\) Hz, 1H, CHCPh\(H\)), 6.12 - 6.02 (m, 1H, OCHCC); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 164.2, 141.9, 139.6, 135.1, 133.6, 133.3, 131.6, 129.3, 128.9, 128.2, 127.2, 123.3 (q, \(J = 280.6\) Hz), 117.0 (d, \(J = 1.7\) Hz), 94.8, 72.4 (q, \(J = 33.8\) Hz); \(^31\)P NMR (376 MHz, CDCl\(_3\)) \(\delta -75.9\); HRMS (ESI) calcd for C\(_{17}\)H\(_{12}\)F\(_2\)O\(_2\) [M\(^+\)Na\(^{+}\)] 431.9829; found 431.9846.

\((\mathbf{E})\)-1-Ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (21)

\((\mathbf{E})\)-1-(Diethoxyphosphoryl)-3-phenylallyl 2-iodobenzoate (17)
Following general procedure D, starting from (E)-1-styryl-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaaxol-3(1\(H\))-one (1a) (70.0 mg, 0.200 mmol) and ethyl 2-diazopropanoate (4l) (51.3 mg, 0.400 mmol), afforded (E)-1-ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (21) as a colorless oil (80 mg, 0.18 mmol, 89%). \(R_f = 0.26\) (EtOAc/pentane 5:95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99 (dd, \(J = 8.0, 1.2\) Hz, 1H, ArH), 7.85 (dd, \(J = 7.8, 1.7\) Hz, 1H, ArH), 7.45 - 7.39 (m, 3H, ArH), 7.35 - 7.29 (m, 2H, ArH), 7.28 - 7.23 (m, 1H, ArH), 7.16 (dd, \(J = 8.0, 7.4, 1.7\) Hz, 1H, ArH), 6.80 (d, \(J = 16.3\) Hz, 1H, CHCPhH), 6.62 (d, \(J = 16.2\) Hz, 1H, CHCPhH), 4.27 (qd, \(J = 7.1, 2.6\) Hz, 2H, OCH\(_2\)CH\(_3\)), 1.92 (s, 3H, CCH\(_3\)), 1.29 (t, \(J = 7.1\) Hz, 3H, OCH\(_2\)CH\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 170.7, 165.4, 141.4, 136.1, 135.3, 132.9, 131.4, 128.8, 128.4, 128.1, 127.8, 126.9, 94.0, 81.4, 62.1, 23.2, 14.2; IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 2963 (w), 2920 (m), 2856 (w), 1744 (m), 1345 (w), 1274 (m), 1241 (s), 1180 (s), 1131 (s), 1092 (s), 1043 (m), 1016 (s), 965 (m), 914 (m), 736 (s), 691 (s); HRMS (ESI) calc for C\(_{20}\)H\(_{13}\)NaO\(_2\) \([M+Na]^+\) 473.0220; found 473.0213.

(E)-2-Oxo-3-styryltetrahydrofuran-3-yl 2-iodobenzoate (23)

Following general procedure D, starting from (E)-1-styryl-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaaxol-3(1\(H\))-one (1a) (70.0 mg, 0.200 mmol) and 3-diazohydrofuran-2(3\(H\))-one (4m) (44.8 mg, 0.400 mmol), afforded (E)-2-oxo-3-styryltetrahydrofuran-3-yl 2-iodobenzoate (23) as a thick colorless oil (78 mg, 0.18 mmol, 90%). \(R_f = 0.31\) (EtOAc/pentane 20:80); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.00 (dd, \(J = 7.9, 1.1\) Hz, 1H, ArH), 7.91 (dd, \(J = 7.8, 1.7\) Hz, 1H, ArH), 7.50 - 7.39 (m, 3H, ArH), 7.39 - 7.28 (m, 3H, ArH), 7.18 (td, \(J = 7.7, 1.7\) Hz, 1H, ArH), 6.95 (d, \(J = 16.2\) Hz, 1H, CHCPhH), 6.48 (d, \(J = 16.2\) Hz, 1H, CHCPhH), 4.65 (td, \(J = 9.2, 2.4\) Hz, 1H, OCH\(_2\)i), 4.36 (td, \(J = 9.4, 7.0\) Hz, 1H, OCH\(_2\)i), 3.10 (dt, \(J = 13.4, 9.4\) Hz, 1H, CHCH\(_2\)i), 2.90 (ddd, \(J = 13.4, 7.0, 2.5\) Hz, 1H, CHCH\(_2\)i); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.5, 165.2, 141.6, 135.1, 134.6, 133.9, 133.4, 131.6, 129.1, 128.9, 128.2, 127.2, 123.1, 94.3, 80.4, 65.0, 33.4; IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 2974 (w), 2900 (m), 1735 (s), 1495 (m), 1449 (m), 1431 (m), 1276 (s), 1256 (s), 1127 (m), 1042 (s), 1016 (s), 974 (m), 764 (s), 750 (s); HRMS (ESI) calc for C\(_{15}\)H\(_{13}\)NaO\(_2\) \([M+Na]^+\) 456.9907; found 456.9906.

(3\(E,5E\))-4-(Methoxycarbonyl)-6-phenyhexa-3,5-dien-2-yl 2-iodobenzoate (24)

Following general procedure D, starting from (E)-1-styryl-1\(\lambda^3\)-benzo[\(d\)][1,2]iodaaxol-3(1\(H\))-one (1a) (70.0 mg, 0.200 mmol) and (E)-methyl 2-diazopent-3-enoate (4n) (0.400 mL, 1.0 M in pentane, 0.400 mmol), afforded (3\(E,5E\))-4-(methoxycarbonyl)-6-phenyhexa-3,5-dien-2-yl 2-iodobenzoate (24) as a colorless oil (58 mg, 0.13 mmol, 63%). \(R_f = 0.22\) (EtOAc/pentane 5:95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99 (dd, \(J = 8.0, 1.2\) Hz, 1H, ArH), 7.79 (dd, \(J = 7.8, 1.7\) Hz, 1H, ArH), 7.53 - 7.46 (m, 2H, ArH), 7.43 - 7.31 (m, 3H, ArH), 7.31 - 7.27 (m, 1H, ArH), 7.15 (td, \(J = 7.7, 1.7\) Hz, 1H, ArH), 7.09 (d, \(J = 16.3\) Hz, 1H, CHCPhH), 6.97 (d, \(J = 16.0\) Hz, 1H, CHCPhH), 6.71 (d, \(J = 8.7\) Hz, 1H, CHCPhH), 6.15 (dq, \(J = 8.3, 6.5\) Hz, 1H, OCH\(_3\)h), 3.83 (s, 3H, OCH\(_3\)h), 1.59 (d, \(J = 6.5\) Hz, 3H, OCH\(_3\)h); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 167.3, 165.9, 141.5, 139.3, 136.9, 135.7, 135.2, 132.8, 131.7, 131.1, 128.8, 128.5, 128.1, 127.1, 120.2, 94.2, 68.9, 52.4, 20.5; IR (\(\nu_{\text{max}}, \text{cm}^{-1}\)) 2948 (w), 2995 (w), 2844 (w), 1789 (w), 1718 (s), 1583 (m), 1436 (m), 1282 (m), 1241 (s), 1156 (m), 1129 (s), 1098 (s), 1039 (s), 1015 (s), 968 (m), 739 (s), 694 (s); HRMS (ESI) calc
for C_{21}H_{19}NaO_{4}^{+} [M+Na]^{+} 485.0220; found 485.0219. We assumed the $E$ geometry of the tri-substituted olefin based on crystal structure obtained in our previous oxy-alkynylation work.³

**Scale-up synthesis of 6a using DCM as solvent and using a lower catalyst loading**

![Chemical reaction diagram]

A catalytic solution was prepared by mixing Cu(CH$_3$CN)$_4$BF$_4$ (12.6 mg, 40.0 µmol) and 2,2’-(propane-2,2-diyl)bis(4,4-dimethyl-4,5-dihydrooxazole) (5d) (11.9 mg, 50.0 µmol) in DCM (5.0 mL) at room temperature for 1 h.

The catalyst solution was then added to a stirring suspension of Ph-VBX (1a) (700 mg, 2.00 mmol, 1.00 equiv) and ethyl 2-diazoacetate (4a) (0.484 mL, 4.00 mmol, 2.00 equiv) in DCM (20.0 mL).

The reaction mixture was stirred at 25 °C for 2 h, then the solvent was removed under reduced pressure and the resulting crude oil was purified by column chromatography using EtOAc/pentane 5:95 as mobile phase to afford (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) as a colorless oil (562 mg, 1.29 mmol, 64%).
8. Product modifications

(E)-4-Phenylbut-3-ene-1,2-diol (25)

Following a reported procedure, \(^3\) (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) (87.2 mg, 0.200 mmol, 1.00 equiv) was dissolved in anhydrous THF (2.00 mL) under \(\text{N}_2\) in a 5 mL microwave vial. Then LiAlH\(_4\) (2.4 M in THF, 0.300 mL, 0.600 mmol, 3.00 equiv) was added at 0 °C and stirred for 1 h. The resulting solution was quenched by the addition of saturated aqueous potassium sodium tartrate (2.00 mL) and the biphasic mixture was stirred for 1 h at room temperature. Then the reaction mixture was diluted with water (2.0 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over MgSO\(_4\), filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 50:50 as mobile phase affording (E)-4-phenylbut-3-ene-1,2-diol (25) as a white solid (30.0 mg, 0.183 mmol, 91 %).

1H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 - 7.18 (m, 5H, ArH), 6.70 (dd, \(J = 16.0, 1.3\) Hz, 1H, CHC\(_3\)H\(_2\)Ph), 6.21 (dd, \(J = 16.0, 6.3\) Hz, 1H, CHC\(_3\)Ph), 4.44 (m, 1H, HOC\(_3\)H\(_2\)CC), 3.76 (dd, \(J = 11.2, 3.6\) Hz, 1H, C\(_2\)H\(_2\)OH), 3.61 (dd, \(J = 11.2, 7.3\) Hz, 1H, C\(_2\)H\(_2\)OH), 2.09 (br s, 2H, 2 x O\(_2\)H);

13C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 136.4, 132.4, 128.8, 128.1, 127.8, 126.7, 73.3, 66.6. The values of the NMR spectra are in accordance with reported literature data.

Ethyl 3-benzyl-4-hydroxy-5-oxo-2-phenethyl-2,5-dihydrofuran-2-carboxylate (26)

DBU (0.151 mL, 1.00 mmol, 10.0 equiv) was added to a solution of (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) (43.6 mg, 0.100 mmol, 1.00 equiv) in ethanol (1 mL). The resulting solution was stirred 6 h at 50 °C. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography using MeOH/DCM 2:98 as mobile phase affording ethyl 3-benzyl-4-hydroxy-5-oxo-2-phenethyl-2,5-dihydrofuran-2-carboxylate (26) as a white solid (17 mg, 0.046 mmol, 93%). M.p. 111 - 113 °C; \(R_f = 0.55\) (MeOH/DCM 3:97); 1H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33 - 7.27 (m, 2H, ArH), 7.27 - 7.21 (m, 5H, ArH), 7.20 - 7.14 (m, 1H, ArH), 7.01 - 6.94 (m, 2H, ArH), 5.78 (br s, 1H, O\(_2\)H), 3.95 (q, \(J = 7.1\) Hz, 2H, OCH\(_2\)CH\(_3\)), 3.67 (s, 2H, CCH\(_2\)Ph), 2.55 - 2.32 (m, 3H, CH\(_2\)), 2.19 - 2.05 (m, 1H, CH\(_2\)), 1.15 (t, \(J = 7.1\) Hz, 3H, OCH\(_2\)CH\(_3\)); 13C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 169.1, 168.0, 140.4, 139.1, 136.2, 130.9, 129.1, 128.9, 128.5, 127.2, 126.4, 87.2, 62.6, 36.0, 30.2, 29.3, 14.0; IR (\(\nu_{\text{max}}\), cm\(^{-1}\)) 2919 (w), 1739 (s), 1292 (m), 1249 (m), 1136 (m), 1105 (m), 1017 (m), 748 (s), 691 (m), 668 (s); HRMS (ESI) calcd for C\(_{22}\)H\(_{23}\)O\(_5\)^+ [M+H]^+ 367.1540; found [M+H]^+ 367.1549.

(E)-ethyl 4-phenylhepta-2,6-dienoate (27)

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To a solution of (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) (87.2 mg, 0.200 mmol, 1.00 equiv) and allyltrimethylsilane (80) (48.0 μL, 0.300 mmol, 1.50 equiv) in dry DCM (2.0 mL) was added TiCl₄ (23.0 μL, 0.210 mmol, 1.05 equiv) dropwise at 0 °C under N₂. The reaction was allowed to warm slowly to 0 °C and then quenched with a saturated solution of NaHCO₃ (2.0 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using DCM/pentane 10:90 as mobile phase affording (E)-ethyl 4-phenylhepta-2,5,6-dienoate (27) as a colorless oil (38.0 mg, 0.165 mmol, 83 %). Rₜ = 0.50 (DCM/pentane 50:50); ¹H NMR (400 MHz, CDCl₃) δ 7.36 - 7.28 (m, 2H, ArH), 7.27 - 7.15 (m, 3H, ArH), 7.09 (dd, J = 15.7, 7.5 Hz, 1H, CHCH₂CO₂Et), 5.78 (dd, J = 15.7, 1.4 Hz, 1H, CHCH₂CO₂Et), 5.69 (ddt, J = 17.1, 10.1, 6.9 Hz, 1H, CHC₃H₃), 5.10 - 4.96 (m, 2H, CHC₃H₃), 4.17 (q, J = 7.2 Hz, 2H, OCH₂CH₃), 3.50 (qd, J = 7.5, 1.3 Hz, 1H, PhCH₂CH₂), 2.56 (tt, J = 7.1, 1.3 Hz, 2H, PhCHCH₂), 1.27 (t, J = 7.1 Hz, 3H, OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 151.0, 141.7, 135.7, 128.8, 128.0, 127.2, 121.3, 117.2, 60.5, 48.4, 39.3, 14.4; IR (ν₃max, cm⁻¹) 2975 (m), 2924 (m), 1718 (s), 1650 (m), 1456 (w), 1368 (m), 1311 (m), 1270 (m), 1233 (m), 1168 (s), 1045 (m), 981 (m), 916 (m), 759 (m), 699 (s); HRMS (ESI) calcd for C₁₃H₁₉O₂⁺ [M+H]⁺ 231.1380; found 231.1377.

(E)-Ethyl 4-phenylhepta-2,5,6-trienoate (28)

To a solution of (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) (87.2 mg, 0.200 mmol, 1.00 equiv) and propargyltrimethylsilane (81) (60.0 μL, 0.400 mmol, 2.00 equiv) in dry DCM (2.0 mL) was added TiCl₄ (23.0 μL, 0.210 mmol, 1.05 equiv) dropwise at -78 °C under N₂. The reaction was allowed to warm slowly to 0 °C and then quenched with a saturated solution of NaHCO₃ (2.0 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 2:98 as mobile phase affording (E)-ethyl 4-phenylhepta-2,5,6-trienoate (28) as a colorless oil (27.0 mg, 0.118 mmol, 59 %). Rₜ = 0.54 (DCM/pentane 50:50); ¹H NMR (400 MHz, CDCl₃) δ 7.38 - 7.31 (m, 2H, ArH), 7.29 - 7.20 (m, 3H, ArH), 7.13 (dd, J = 15.6, 7.0 Hz, 1H, CHCH₂CO₂Et), 5.84 (dd, J = 15.6, 1.5 Hz, 1H, CHCH₂CO₂Et), 5.37 (q, J = 6.8 Hz, 1H, CHC₃H₃), 4.82 (dd, J = 6.6, 2.7 Hz, 2H, CHC₃H₃), 4.18 (q, J = 7.1 Hz, 3H, PhCH and OCH₂CH₃), 1.28 (t, J = 7.1 Hz, 3H, OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 208.6, 166.6, 149.4, 140.9, 128.9, 128.1, 127.3, 121.9, 91.9, 77.2, 60.5, 47.4, 14.4; IR (ν₃max, cm⁻¹) 2982 (m), 2924 (m), 2853 (w), 1958 (w), 1715 (s), 1650 (m), 1454 (m), 1367 (m), 1307 (m), 1269 (m), 1232 (m), 1169 (s), 1071 (m), 1040 (s), 982 (m), 853 (m); HRMS (ESI) calcd for C₁₅H₁₉O₂⁺ [M+H]⁺ 229.1223; found 229.1220.

(E)-Ethyl 4-azido-4-phenylbut-2-enoate (29) and (E)-Ethyl 2-azido-4-phenylbut-3-enoate (29')
To a solution of (E)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) (87.2 mg, 0.200 mmol, 1.00 equiv) and azidotrimethylsilane (40.0 µL, 0.300 mmol, 1.50 equiv) in dry DCM (2.0 mL) was added TiCl₄ (23.0 µL, 0.210 mmol, 1.05 equiv) dropwise at -20 °C under N₂. The reaction was allowed to warm to room temperature and then quenched with a saturated solution of NaHCO₃ (2.0 mL). The layers were separated and the aqueous layer was extracted with DCM (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using DCM/pentane 10:90 as mobile phase affording an isomeric mixture of (E)-ethyl 4-azido-4-phenylbut-2-enoate (29) and (E)-ethyl 2-azido-4-phenylbut-3-enoate (29') as a colorless oil, 70:30 mixture of 29 and 29' (40 mg, 0.17 mmol, 86%). ¹H NMR (400 MHz, CDCl₃) δ 7.45 - 7.28 (m, 5H, ArH), 6.94 (dd, J = 15.5, 5.7 Hz, 1H, CHCHCO₂Et), 6.14 (dd, J = 15.5, 1.6 Hz, 1H, CHCHCO₂Et), 5.18 (dd, J = 5.7, 1.6 Hz, 1H, N(CH₃)CC), 4.33 - 4.18 (m, 2H, OCH₂CH₃), 1.34 - 1.28 (m, 3H, OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 165.9, 144.0, 129.3, 129.1, 127.6, 127.0, 123.0, 65.6, 60.9, 14.4 for γ-azidated ester (29); ¹H NMR (400 MHz, CDCl₃) δ 7.45 - 7.28 (m, 5H, ArH), 6.77 (dd, J = 15.8 Hz, 1.2 Hz, 1H, PhCHH), 6.27 (dd, J = 15.8, 7.5 Hz, 1H, PhCHH), 4.54 (dd, J = 7.5, 1.3 Hz, 1H, N(CH₃)CO₂Et), 4.33 - 4.18 (m, 2H, OCH₂CH₃), 1.34 - 1.28 (m, 3H, OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 169.1, 136.6, 136.0, 135.5, 128.9, 128.9, 120.8, 63.9, 62.4, 14.3 for α-azidated ester (29'). The values of the NMR spectra are in accordance with reported literature data.³⁶

(⁰)-1-Ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-((⁰)-3-methoxy-3-oxoprop-1-en-1-yl)benzoate (30)

A flame dried 8 mL microwave vial was charged with (E)-1-ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (21) (45.0 mg, 0.100 mmol, 1.00 equiv), bis(triphenylphosphine)palladium (II) chloride (3.51 mg, 5.00 µmol, 0.05 equiv), triphenylphosphine (1.31 mg, 5.00 µmol, 0.05 equiv) and trimethylamine (0.5 mL). The resulting reaction mixture was degassed by “pump-freeze-thaw” cycles (3 times) via a syringe needle and then methyl acrylate (79) (45.0 µL, 0.500 mmol, 5.00 equiv) was added by syringe and the reaction mixture was stirred at 80 °C for 24 h. The solvent was removed under reduced pressure and the product was purified by column chromatography using EtOAc/pentane 15:85 as mobile phase affording (E)-1-ethoxy-2-methyl-1-oxo-4-phenylbut-3-en-2-yl 2-((E)-3-methoxy-3-oxoprop-1-en-1-yl)benzoate (30) as a thick colorless oil (27.0 mg, 66.1 µmol, 66%). Rₜ = 0.32 (EtOAc/pentane 15:85); ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, J = 15.9 Hz, 1H, ArCHCH₂CO₂Me), 7.99 (dd, J = 7.8, 1.4 Hz, 1H, ArH), 7.66 - 7.59 (m, 1H, ArH), 7.59 - 7.54 (m, 1H, ArH), 7.47 (td, J = 7.5, 1.5 Hz, 1H, ArH), 7.44 - 7.39 (m, 2H, ArH), 7.37 - 7.30 (m, 2H, ArH), 7.29 - 7.22 (m, 1H, ArH), 6.77 (d, J = 16.2 Hz, 1H, CHCH₂Ph), 6.65 (d, J = 16.2 Hz, 1H, CHCH₂Ph), 6.34 (d, J = 15.9 Hz, 1H, ArCHCH₃CO₂Me), 4.28 (qd, J = 7.1, 1.9 Hz, 2H, OCH₂CH₃), 3.74 (s, 3H, OCH₃), 1.93 (s, 3H, CH₃), 1.29 (t, J = 7.1 Hz, 3H, OCH₂CH₃); ¹³C NMR (101 MHz, CDCl₃) δ 170.8, 167.0, 165.8, 144.0, 136.3, 136.1, 132.7, 131.4, 131.0, 130.3, 129.6, 128.8, 128.4, 128.0, 127.9, 127.0, 120.8, 81.3, 62.1, 51.9, 23.2, 14.2; IR (νmax, cm⁻¹) 2991 (m), 2956 (m).

2926 (m), 1715 (s), 1636 (w), 1479 (m), 1448 (m), 1377 (w), 1269 (s), 1196 (m), 1173 (m), 1121 (m), 1071 (s), 1044 (m), 1021 (m), 972 (m), 865 (m); HRMS (ESI) calcd for C_{23}H_{23}NaO_6\[^{+}\] [M+Na\(^{+}\)] 431.1465; found 431.1472.

\((\text{E})\)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (31)

Following a slightly modified procedure,\(^{37}\) in a 20 mL Schlenk flask, \((\text{E})\)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) (43.6 mg, 0.100 mmol, 1.00 equiv), DABCO (112 mg, 1.00 mmol, 10.0 equiv) and Pd/C (5.0 mg) were suspended in MeOH (10 mL). The reaction flask was evacuated and backfilled with argon (3 times) before being evacuated and backfilled with \(\text{H}_2\) (1 atm). The reaction was stirred 10 min at room temperature, then the hydrogen was evacuated and replaced with argon. The reaction mixture was filtered through a pad of celite and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography using EtOAc/pentane 5:95 as mobile phase affording \((\text{E})\)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (31) as a colorless oil (24.0 mg, 77.0 μmol, 77%). \(R_f = 0.29\) (EtOAc/pentane 5:95); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.19 (d, \(J = 7.1\) Hz, 3H, OCH\(_2\)Ph), 6.92 (dd, \(J = 16.0, 1.0\) Hz, 1H, CHPh), 5.85 (dd, \(J = 7.0, 1.3\) Hz, 1H, OCH(CH\(_3\))\(_2\)), 4.27 (qd, \(J = 7.1, 5.1\) Hz, 2H, OCH\(_2\)CH\(_3\)), 1.30 (t, \(J = 7.1\) Hz, 3H, OCH\(_2\)CH\(_3\)); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 168.8, 165.9, 135.8, 135.4, 133.6, 130.1, 129.5, 128.8, 128.7, 128.6, 127.0, 121.2, 73.8, 62.0, 14.3; IR (\(v_{\text{max}}, \text{cm}^{-1}\)) 3057 (w), 3030 (w), 1748 (m), 1724 (s), 1452 (m), 1315 (w), 1272 (s), 1272 (s), 1251 (m), 1196 (m), 1106 (s), 1069 (m), 1024 (m), 965 (m), 738 (m), 712 (s), 689 (s); HRMS (ESI) calcd for C\(_{33}\)H\(_{31}\)NaO\(_4\)\[^{+}\] [M+Na\(^{+}\)] 333.1097; found 333.1099.

\((\text{Z})\)-1-Ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (32)

Following a reported procedure,\(^{38}\) a flame dried 8 mL microwave vial with a rubber septum and magnetic stirring bar was charged with \((\text{E})\)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl 2-iodobenzoate (6a) (43.6 mg, 0.100 mmol, 1.00 equiv), MeCN (1.0 mL), tributylamine (240 μL, 1.00 mmol, 10.0 equiv), formic acid (38 μL, 1.00 mmol, 10.0 equiv) and \(\text{fac-Ir(ppy)_3} \) (1.64 mg, 2.50 μmol, 0.025 equiv). The resulting reaction mixture was degassed by “pump-freeze-thaw” cycles (3 times) via a syringe needle and placed in a 250 mL beaker with blue LEDs wrapped inside. The reaction mixture was stirred at 40 °C for 18 h. The solvent was removed under reduced pressure and the product was purified by column chromatography using DCM/pentane 50:50 as mobile phase affording \((\text{Z})\)-1-ethoxy-1-oxo-4-phenylbut-3-en-2-yl benzoate (32) as a white solid (25.2 mg, 82.0 μmol, 82%). M.p. 76-78 °C; \(R_f\) = (DCM/pentane 50:50); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.11 - 8.03 (m, 2H, ArH), 8.60 - 7.54 (m, 1H, ArH), 7.51 - 7.28 (m, 7H, ArH), 6.94 (d, \(J = 11.4\) Hz, 1H, CHCHPh), 6.05 (dd, \(J = 9.8, 0.9\) Hz, 1H, OCHCC), 5.91 (dd, \(J = 11.4, 9.9\) Hz, 1H, CHCHPh), 4.28 (q, \(J = 7.1\) Hz, 2H, OCH\(_2\)CH\(_3\)), 1.30 (t, \(J = 7.1\) Hz, 3H, OCH\(_2\)CH\(_3\)).

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$^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.2, 165.8, 136.8, 135.4, 133.5, 130.1, 129.0, 128.7, 128.5, 128.3, 123.0, 70.3, 62.0, 14.2; IR (ν$_{max}$, cm$^{-1}$) 3065 (w), 3024 (w), 2981 (w), 1750 (s), 1722 (s), 1452 (m), 1370 (w), 1333 (w), 1315 (m), 1278 (s), 1258 (s), 1194 (m), 1100 (s), 1069 (s), 1026 (s), 814 (m), 773 (m), 710 (s); HRMS (ESI) calcd for C$_{19}$H$_{18}$NaO$_4$ $^{\star}$ [M+Na]$^+$ 333.1097; found 333.1106.
9. Enantioselective transformation: preliminary results

A catalytic solution was prepared by mixing Cu(I) catalyst (4.00 μmol, 0.08 equiv), and BOX ligand (5.00 μmol, 0.10 equiv) in DCE (0.500 mL) at room temperature for 1 h. 0.250 mL of the catalytic solution was then added to a stirring suspension of VBX (0.05 mmol, 1.00 equiv) and acceptor diazo compound (0.10 mmol, 2.00 equiv) in DCE (1.0 mL). The reaction mixture was stirred at the indicated temperature and time (monitored by TLC (EtOAc/pentane 5:95 and MeOH/DCM 5:95)) and the solvent was removed under reduced pressure. The resulting crude oil was purified by preparative TLC (EtOAc/pentane) directly without further work-up to afford the corresponding allylic ester product.

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<th>temp. 25 °C</th>
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<td>2 h</td>
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* NMR yield using CH₂Br₂ as internal standard. ⁰ Obtained by chiral HPLC. ⁴ Using DCE/acetone 4:1 as solvent. ⁵ Dropwise addition of diazo.
HPLC of compound 6a (entry 3)

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SS3
HPLC of compound 11 (entry 9)
10. X-ray diffraction parameters and data for 11

```
Empirical formula C_{32}H_{35}IO_4
Formula weight 610.50
Temperature 101(1) K
Wavelength 1.54184 Å
Crystal system Triclinic
Space group P-1
Unit cell dimensions a = 10.8114(6) Å, α = 81.599(4)°.
b = 10.9975(5) Å, β = 82.906(5)°.
c = 12.6115(7) Å, γ = 78.119(4)°.
Volume 1444.84(13) Å^3
Z 2
Density (calculated) 1.403 Mg/m^3
Absorption coefficient 8.972 mm^-1
F(000) 624
Crystal size 0.635 x 0.181 x 0.049 mm^3
Theta range for data collection 3.559 to 75.162°.
Index ranges -13 ≤ h ≤ 13, -13 ≤ k ≤ 10, -15 ≤ l ≤ 15
Reflections collected 10366
Independent reflections 5771 [R_int = 0.0382]
Completeness to theta = 67.684° 99.9 %
Absorption correction Analytical
Max. and min. transmission 0.675 and 0.116
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 5771 / 0 / 341
Goodness-of-fit on F^2 1.039
Final R indices [I > 2sigma(I)]
R1 = 0.0400, wR2 = 0.1027
R indices (all data)
R1 = 0.0464, wR2 = 0.1072
Largest diff. peak and hole 0.919 and -1.211 e.Å^-3
```
11. Spectra of new compounds

$^1$H-NMR (400 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58m

![NMR Spectra](image-url)
$^{13}$C-NMR (101 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58m

$^{11}$B-NMR (128 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58m
$^1$H-NMR (400 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58p

$^{13}$C-NMR (101 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58p
\[ {^{11}B}\text{-NMR} \ (128 \text{ MHz, DMSO-}d_6/\text{D}_2\text{O 9:1}) \text{ of compound 58p} \]
$^1$H-NMR (400 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58q

$^{13}$C-NMR (101 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58q
$^{11}\text{B-NMR}$ (128 MHz, DMSO-\textit{d}$_6$/D$_2$O 9:1) of compound 58q
$^1$H-NMR (400 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58t

$^{13}$C-NMR (101 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58t
$^{11}$B-NMR (128 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58t
$^1$H-NMR (400 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58u

$^{13}$C-NMR (101 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58u
$^{11}$B-NMR (128 MHz, DMSO-$d_6$/D$_2$O 9:1) of compound 58u
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1d

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1d
$^{19}$F-NMR (376 MHz, CD$_3$OD) of compound 1d
$^1\text{H}-\text{NMR}$ (400 MHz, CD$_3$OD) of compound 1f

$^{13}\text{C}-\text{NMR}$ (101 MHz, CD$_3$OD) of compound 1f
$^1$H-NMR (400 MHz, CD$_3$OD/CD$_2$Cl$_2$ 9:1) of compound 1g

$^{13}$C-NMR (101 MHz, CD$_3$OD/CD$_2$Cl$_2$ 9:1) of compound 1g
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1h

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1h
$^{19}$F-NMR (376 MHz, CD$_3$OD) of compound 1h
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1i

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1i
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1j

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1j
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1k

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1k
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1l

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1l
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1m

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1m
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1n

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1n
$^{1}$$H$-NMR (400 MHz, CD$_{3}$OD) of compound 1o

$^{13}$C-NMR (101 MHz, CD$_{3}$OD) of compound 1o
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1p

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1p
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1q

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1q
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1r

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1r
\(^1\text{H-NMR}\) (400 MHz, CD\(_3\text{OD}\)) of compound 1s

\(^{13}\text{C-NMR}\) (101 MHz, CD\(_3\text{OD}\)) of compound 1s
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1t

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1t
$^1$H-NMR (400 MHz, CD$_3$OD) of compound 1u

$^{13}$C-NMR (101 MHz, CD$_3$OD) of compound 1u
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6a

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6a
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6b

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6b
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6c

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6c
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6d

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6d
$^{19}$F-NMR (376 MHz, CDCl$_3$) of compound 6d
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6e

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6e
$^{19}$F-NMR (376 MHz, CDCl$_3$) of compound 6e
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6f

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6f
$^{1}$H-NMR (400 MHz, CDCl$_3$) of compound 6g

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6g
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6h

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6h
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 6i

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 6i
$^{19}$F-NMR (376 MHz, CDCl$_3$) of compound 6i
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 7

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 7
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 8a

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 8a
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 8b

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 8b
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 8c

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 8c
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 8d

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 8d
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 8e

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 8e
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 8f

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 8f
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 8g

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 8g
\(^1\text{H-NMR} (400 \text{ MHz, CDCl}_3)\) of compound 8h

\[^{13}\text{C-NMR} (101 \text{ MHz, CDCl}_3)\) of compound 8h
\(^1\text{H-NMR}\) (400 MHz, CDCl\(_3\)) of compound 8i

\(^{13}\text{C-NMR}\) (101 MHz, CDCl\(_3\)) of compound 8i
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 9a

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 9a
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 9b

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 9b
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 9c

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 9c
\[ ^1H-NMR \ (400\ MHz,\ CDCl_3) \ of\ compound\ 10 \]

\[ ^{13}C-NMR \ (101\ MHz,\ CDCl_3) \ of\ compound\ 10 \]
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 11

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 11
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 12

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 12
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 13

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 13
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 14

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 14
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 15

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 15
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 16

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 16
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 17

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 17
$^{31}\text{P-NMR}$ (126 MHz, CDCl$_3$) of compound 17
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 18

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 18
$^{19}$F-NMR (376 MHz, CDCl$_3$) of compound 18
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 21

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 21
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 23

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 23
$^{1}H$-NMR (400 MHz, CDCl$_3$) of compound 24

$^{13}C$-NMR (101 MHz, CDCl$_3$) of compound 24
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 26

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 26
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 27

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 27
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 28

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 28
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 30

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 30
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 31

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 31
$^1$H-NMR (400 MHz, CDCl$_3$) of compound 32

$^{13}$C-NMR (101 MHz, CDCl$_3$) of compound 32