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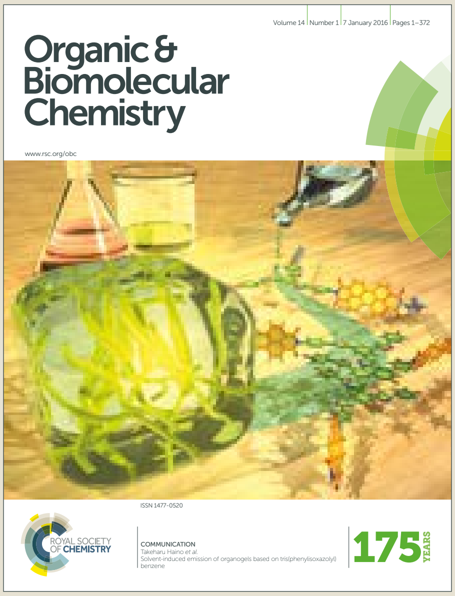

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ARTICLE

Visible-Light-Induced Phenylchalcogenyl-Oxygenation of Allenes Having Aryl- / or Electron Withdrawing Substituent with Ambient Air as Sole Oxidant

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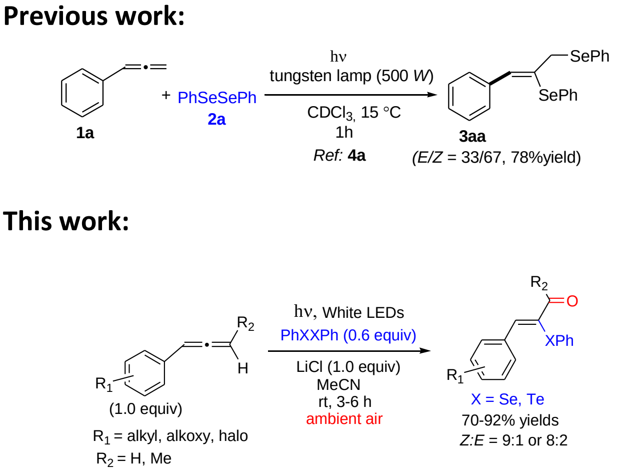
Abstract. Synthesis of regio- and stereoselective aryl substituted α,β-unsaturated aldehydes and ketones from activated allenes was achieved. This mild and non-metallic oxidation is exclusively driven by benign ambient air triggered by visible light. The same starting materials under ideal anaerobic conditions led to the 2, 3-diphenyselenation adduct with no trace of oxygenated product, demonstrating dissolved oxygen as chemical switch for two different reaction pathways. The salient feature of this protocol is the single electron transfer (SET) achieved by irradiation of one of two organic molecules thereby avoiding a sensitizer to form a radical ion pair and the side product PhSeOH generated during reaction is oxidized under the reaction conditions to starting material PhSeSePh.

Introduction

Research on visible-light-induced photo-redox catalysis has developed rapidly in recent years, such that this type of catalysis has become a reliable synthetic method in the area of carbon-carbon and carbon-heteroatom bond formation.[1] The activation of organic molecules by means of visible-light is considered as a sustainable, energetically favorable benign route that complies with the principles of green chemistry. Of late, the photo-induced single electron transfer (PET) activation mode has bestowed a manifold of practical procedures for the construction of organic molecules.[2] Recently, a diverse range of photocatalytic transformations with unconventional reactivity have emerged, and this scenario unlocks the opportunity to explore classical radical chemistry with reference to visible-light induced photo-redox catalysis.[3] Considering the organic transformations enabled by photo-redox catalysis, we initiated a program for the synthesis of functionalized organic compounds by means of the direct addition of two different heteroatom groups into carbon-carbon unsaturated bonds.

At the outset, we considered studying the effect of the single electron transfer (SET) phenomenon from diphenyl diselenide (PhSeSePh, **2a**) and 3-phenylpropa-1,2-diene **1a** under visible-light irradiation, anticipating the generation of an active radical ion pair. This radical ion pair is disproportionated and then undergoes element-element addition to an unsaturated carbon-carbon bond in analogy with an earlier report (Scheme 1, (c)).[4]



Scheme 1. Prior art synthesis of the diselenation adduct and arylchalcogenyl α,β-unsaturated aldehydes and ketones.

The reactivity of the photo-induced SET generated radical ions could be controlled by the solvent polarity.[5] Consequently, we hypothesized that solvent-separated ions in a polar aprotic solvent such as acetonitrile (dielectric constant ε at 25 °C = 36.64, oxygen solubility 8.1 mM / cm^3)[6] could be intercepted by dioxygen via selective radical coupling. Eventually, the peroxy intermediate would dismutate, then would likely deliver chalcogenyl-oxygenated compounds.

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† Electronic Supplementary Information (ESI) available: Copies of ^{1}H and ^{13}C NMR spectra's free of charge via Internet. See DOI: 10.1039/x0xx00000x

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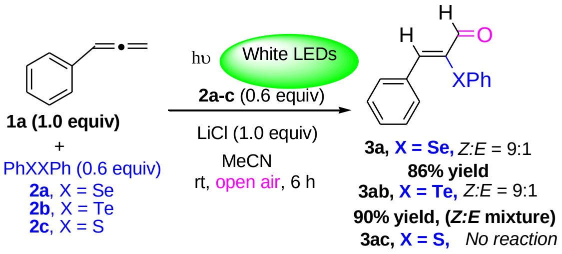
Results and Discussion

Initially, a reaction was carried out with 3-phenyl propa-1,2-diene **1a**[7] (1.0 mmol, 1.0 equiv) and PhSeSePh[8] **2a** (1.1 mmol, 1.1 equiv) in acetonitrile while stirring at ambient temperature and under irradiation with a household 7 W Day light-white LED lamp (λ_{max} = 430-730 nm) using an oxygen balloon. After 3 h, the sole product obtained in 45% yield was analyzed to be 2,3-adduct **3a** as a major isomer along with the minor *E* isomer. The *Z:E* mixture was separated by silica gel column chromatography, and the diastereoselectivity (9:1) was determined from the isolated individual weights of the *Z:E* isomers (Table 1, entry 1).[9] This was in contrast to previous reports wherein visible-light irradiation gave diselenation adduct **3aa** (Scheme 1 (c)) with an 8:2 ratio of the *Z:E* mixture as a sole product,[4] with no trace of formylated product **3a** observed.

Table 1. Optimization studies of the α-phenylselenyl-oxygenation of **1a** and **2a** with visible-light irradiation[a]

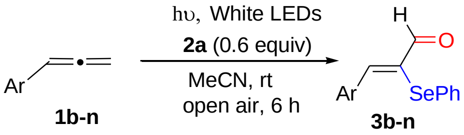


Entry	2 (equiv)	Solvent	Additive	% yield[b]
1	1.1	MeCN		**3a**, 45[c]
2	1.1	MeCN		**3aa**, 45[d]
3	1.1	MeCN		**3a**, 65
4	1.1	MeCN	LiCl (1.0 equiv)	**3a**, 85
5	1.1	MeCN	LiI (1.0 equiv)	**3a**, 40
6	1.1	MeCN	NaCl (1.0 equiv)	**3a**, 30
7	1.1	MeCN	LiCl (2.0 equiv)	**3a**, 86
8	1.1	1,4-dioxane	LiCl (1.0 equiv)	NR
9	1.1	DMF	LiCl (1.0 equiv)	NR
10	1.1	MeOH	LiCl (1.0 equiv)	**3a**, 80
11	1.1	$(CH_2Cl)_2$	LiCl (1.0 equiv)	25
12	0.6	MeCN	LiCl (1.0 equiv)	**3a, 86**[e]
13	0.6	MeCN	LiCl (1.0 equiv)	NR[f]
14	0.6	MeCN	LiCl (1.0 equiv)	NR[g]
15	(**2b**) 0.6	MeCN	LiCl (1.0 equiv)	**3ab**, 90
16	(**2c**) 0.6	MeCN	LiCl (1.0 equiv)	NR

[a] Unless otherwise stated, all reactions were carried out at the 0.5 mmol scale with **1a** (1.0 equiv) and **2a** (1.1 equiv) stirring at ambient temperature in MeCN irradiated for 6 h under open air. In entries 12-16, **2a** was used (0.6 equiv). [b] Yields refer to the major isomer after chromatographic purification. [c] Reaction carried out under oxygen balloon pressure. [d] Reaction carried out in deaerated anhydrous MeCN under an inert atmosphere. [e] CFL illumination also gave similar yield. [f] Reaction carried out under a dark condition. [g] Reaction carried out while heating at 45 °C under a dark condition. NR = No reaction.

To confirm the source of aldehyde oxygen, we performed a photoreaction with deaerated, anhydrous acetonitrile in a completely inert atmosphere under conditions otherwise identical to those above. As expected, 1,2-diphenylselenation of the terminal double bond produced **3aa** as a *Z:E* mixture at a yield of 45%[4a] with a trace of **3a** (Table 1, entry 2). This result indicates that the aldehyde oxygen originates from molecular oxygen. Next, we became interested in performing the same reaction with anhydrous acetonitrile in open air. The desired product **3a** was obtained in 65% yield (Table 1, entry 3). Further, a significant increase in the yield of **3a** (85%) was found using 1 equivalent of LiCl (Table 1, entry 4).[10] Other salts such as LiI and NaCl gave inferior yields, whereas 2 equivalents of LiCl did not improve the yield of **3a** (Table 1, entries 5, 6 and 7). In the solvent screening step, halogenated, aprotic and protic solvents were assessed. Acetonitrile was found to be useful solvent for this transformation (Table 1, entries 8, 9, 10 and 11). Experimentation with the molar ratio of PhSeSePh indicated that 0.6 equivalent of **2a** is sufficient to complete the reaction. The 23W CFL illumination also promoted the reaction with equal efficiency (Table 1, entry 12). No reaction occurred in the absence of light, and heating at 45 °C also failed to give the **3a** (Table 1, entries 13 and 14). As expected, the visible-light promoted reaction between diphenyl ditelluride **2b** and **1a** under standard conditions proceeded effectively, and the expected product **3ab** was isolated as a 9:1 mixture in 90% yield (Table 1, entry 15).[4a] In sharp contrast, the reaction of diphenyldisulfide **2c** with **1a** under similar conditions did not occur, and only the starting materials were recovered (Table 1, entry 16).

Table 2. Scope of the reaction with respect to aryl allenes[a]



Entry	Ar (1b-n)	Product (3b-n) (*Z:E* ratio), % Yield of Major *Z* isomer
1	**1b**, Ar = (4-Me-C_6H_4)	**3b** (9:1), 86
2	**1c**, Ar = (4-*t*-Bu-C_6H_4)	**3c** (8:2), 75
3	**1d**, Ar = (2,4,5-Me-C_6H_2)	**3d** (9:1), 84
4	**1e**, Ar = (4-MeO-C_6H_4)	**3e** (9:1), 86
5	**1f**, Ar = (3,5-MeO-C_6H_3)	**3f** (9:1), 86
6	**1g**, Ar = (4-F-C_6H_4)	**3g** (9:1), 86
7	**1h**, Ar = (3,5-F-C_6H_3)	**3h** (9:1), 84
8	**1i**, Ar = (3,5-CF_3-C_6H_3)	**3i** (9:1), 84
9	**1j**, Ar = (3-Me, 4-F-C_6H_4)	**3j** (8:2), 75
10	**1k**, Ar = (4-NO_2-C_6H_4)	**3k** (9:1), 86
11	**1l**, Ar = (4-Ph-C_6H_4)	**3l** (9:1), 85
12	**1m**, Ar = (4-PhO-C_6H_4)	**3m** (8:2), 85[b]
13	**1n**, Ar = 2-(6-MeO-$C_{10}H_6$)	**3n** (8:2), 73

[a] Yields refer to the major isomer after chromatographic purification. [b] The yield refers to *Z:E* mixture.

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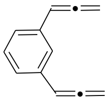
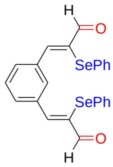
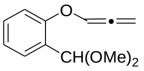
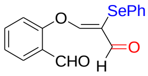
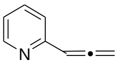
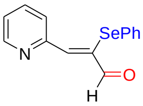
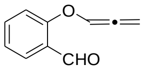
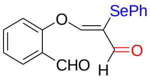
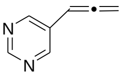
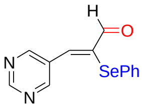
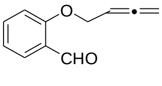
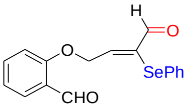
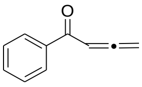
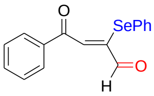
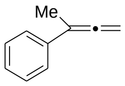
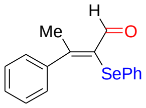
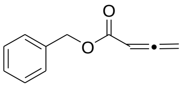
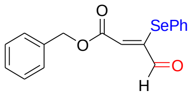
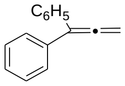
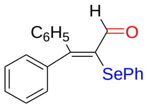
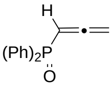
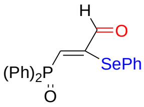
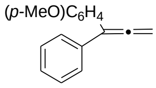
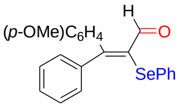
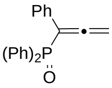
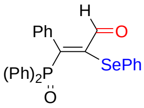
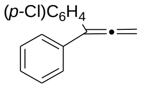
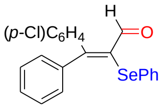
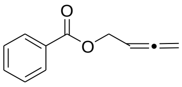
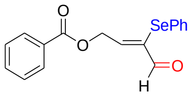
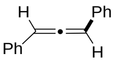
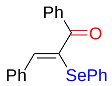
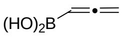
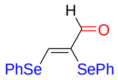
With the optimized conditions in hand, the scope of the reaction with respect to aromatic allenes was investigated. The corresponding results are summarized in Table 2.

According to the results, the reaction is tolerant of aromatic residues with electron-donating and electron-withdrawing substituents. The sterically hindered substrate 2,4,5-trimethylphenyl allene **1d** gave α,β-unsaturated aldehyde **3d** in 84% yield, analogous to the yield obtained with unsubstituted **1a** (Table 2). The substituted aryl terminal allenes **1e-n** underwent phenylseleno-oxygenation effectively irrespective of the inductive effect of the *meta* and *para* substitution pattern and gave the respective products **3e-n** in good to high yield (Table 2).

Under typical conditions, the irradiation of 1,3-diallenyl benzene **4a** provided the α,α'-diphenylselenyl product **5a** in high yield (Table 3). Likewise, the heteroaromatic allenes **4b-c** yielded the expected products **5b**[11] and **5c** in yields of 84 and 86%, respectively (Table 3).

Table 3. Scope of the reaction with respect to various allenes[a]

Substrate	Product	Substrate	Product
 **4a**	 **5a** (85% single isomer)	 **4j**	 **5j** (80% single isomer)
 **4b**	 **5b** (84% single isomer)	 **4k**	 **5j** (80% single isomer)
 **4c**	 **5c** (*Z:E* = 9:1, 86% major isomer yield)	 **4l**	 **5l** (*Z:E* = 9:1, 84% major *Z* isomer)
 **4d**	 **5d** (83% single isomer)	 **4m**	 **5m** (10:1, 80 % combined *Z:E* yield
 **4e**	 **5e** (82% single isomer)	 **4n**	 **5n** (90%)
 **4f**	 **5f** (90% single isomer)	 **4o**	 **5o** (~1:1, 92% isolated as *Z:E* mixture)
 **4g**	 **5g** (*Z:E* = 9:1) (90% major isomer)	 **4p**	 **5p** (1:1 separable, 95% combined *Z:E* yield)
 **4h**	 **5h** (82% single isomer)	 **4q**	 **5q** (90% isolated as 20:1, *Z:E* mixture)
 **4i**	 **5i** (84% single isomer)[b]		

[a] Yields refer to the major isomer after chromatographic purification. [b] The yield refers to 1.0 equiv of **4i** and 1.1 equiv of **2a** under otherwise identical conditions as above.

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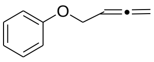
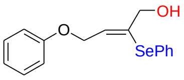
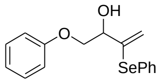
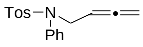
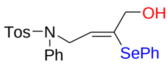
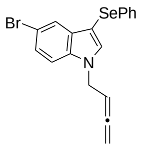
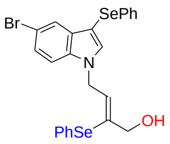
Further, α,β-unsaturated allenes **4d-g** were subjected to photo-induced phenylselenyl-oxygenation under the analogous conditions described above. It is noteworthy that in all cases the products **5d-g** were obtained as single regio- and stereoisomers in excellent yields with an exception of **5g** that was formed as *Z:E* mixture (9:1) (Table 3). These results imply that only terminal allenes could be functionalized under visible-light activation despite the presence of α,β-unsaturated double bond. Benzoate of buta-2,3-dien-1-ol **4h** showed good reactivity and led to product **5h** as a single isomer in 82% yield. Interestingly, allenylboronic acid **4i** as a substrate furnished the α,β-diselenyl unsaturated aldehyde **5i** in 84% yield (Table 3). Acetal **4j** was submitted to irradiation. The product identified was acetal-deprotected α,β-unsaturated aldehyde **5j** in a yield of 80%. Next, allene **4k** with an *ortho*-formyl functional group was submitted to the reaction, and the expected product **5j** was isolated in 80% yield (Table 3). Similarly, *ortho*-formyl allyloxy allene **4l** gave desired product **5l** in a yield of 84% (Table 3). We also evaluated the effect of geminal substituted substrates **4m-p** on the visible-light induced phenylseleno-oxygenation process. As expected, regardless of their substitution patterns, all of the substrates resulted in an excellent yield of the products **5m-p** as a *Z:E* (1:1) mixture with the exception of **5m**, which was obtained as *Z:E* (10:1) mixture in a yield of 80% (Table 3). We also tested 1,3-diphenyl-1,2-propadiene **4q** under the set standard conditions and found the expected product **5q** in 90% yield with highly selectivity (*Z:E* = 20:1) (Table 3). This observation indicates that the 1,3-substituted aryl allenes are also suitable substrates for this transformation.

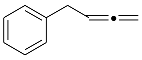
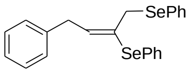
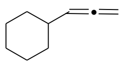
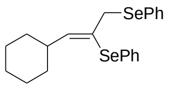
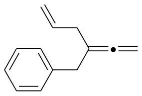
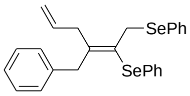
Table 4. Study of the α–phenylselenyl oxygenation of hetero-atom allenes[a]

Substrate	Product	%yield
 **6a**	 **7a**  **7aa**	**7a** (90%, 8:2 *Z* isomer and **7aa** mixture)
 **6b**	 **7b**	**7b** (82% single isomer)
 **6c**	 **7c**	**7c** (84% single isomer)

[a] Reactions were carried out with 1.0 equiv of **6a-c** and 0.6 equiv of **2a** stirring at ambient temperature in MeCN irradiated under open air

On the other hand, allene **6a** provided an 8:2 ratios of alcohol **7a** and **7aa**. The photo-reaction of *N*-homo allenylsulfonamide **6b** resulted in primary alcohol **7b** as the only detectable isomer. Further irradiation of **7b** failed to give aldehyde. Interestingly, under these reaction conditions, the bromo and phenylselenyl groups in **6c** were stable, but the isolated product was an alcohol **7c** in 84% yield, with no trace of the expected aldehyde (Table 4).

Table 5. Irradiation of benzyl allenes with **2a**[a]

Substrate	Product	Yield
 **8a**	 **9a**	**9a** (40% isolated as 3:1 *Z:E* mixture)[b] **9a** (90% isolated as 3:1 *Z:E* mixture)
 **8b**	 **9b**	**9b** (95% single isomer)
 **8c**	 **9c**	**9c** (93% isolated as 3:2 *Z:E* mixture)

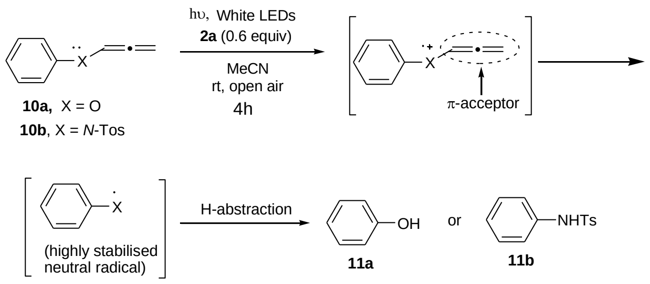
[a] Reactions were carried out with 1.0 equiv of **8a-c** and 1.1 equiv of **2a** stirring at ambient temperature in MeCN irradiated for 3 h under open air. [b] The yield refers to 1.0 equiv of **8a** and 0.6 equiv of **2a** under otherwise identical conditions as above.

To determine the necessity of the aryl group attached to the allenic bond, we prepared 3-cycloalkyl-, 3-benzyl-, 3-benzyl-3'-allyl attached terminal allenes **8a-c** and irradiated them under open air in a typical procedure.

Interestingly, in all cases the respective 3-cycloalkyl-, 3-benzyl-, 3-benzyl-3'-allyl 1-(phenylselenomethyl)vinyl selenides **9a-c** were isolated at good to high yields (Table 5). In other words, these results signify that the allenic bond conjugation with the aryl group or electron-withdrawing group is required to intercept the molecular oxygen in this transformation.

However, the unsubstituted phenoxy allene **10a** and *N*-(prop-1,2-dienyl)-*N*-tosylbenzeneamide **10b** gave phenol **11a** and aniline sulfonamide **11b** as the sole product in 75% yield each.

No trace of the desired phenylseleno-formyl product was observed. These reults can be rationalized on the basis of capto-dative stabilization,[12] wherein the radical cation is stabilized by an adjacent π-acceptor.



Scheme 2. SET initiated deprotection

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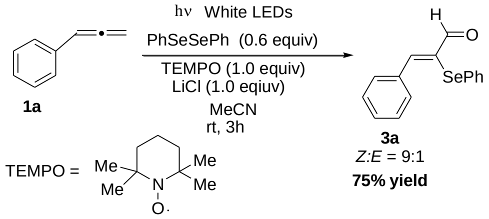
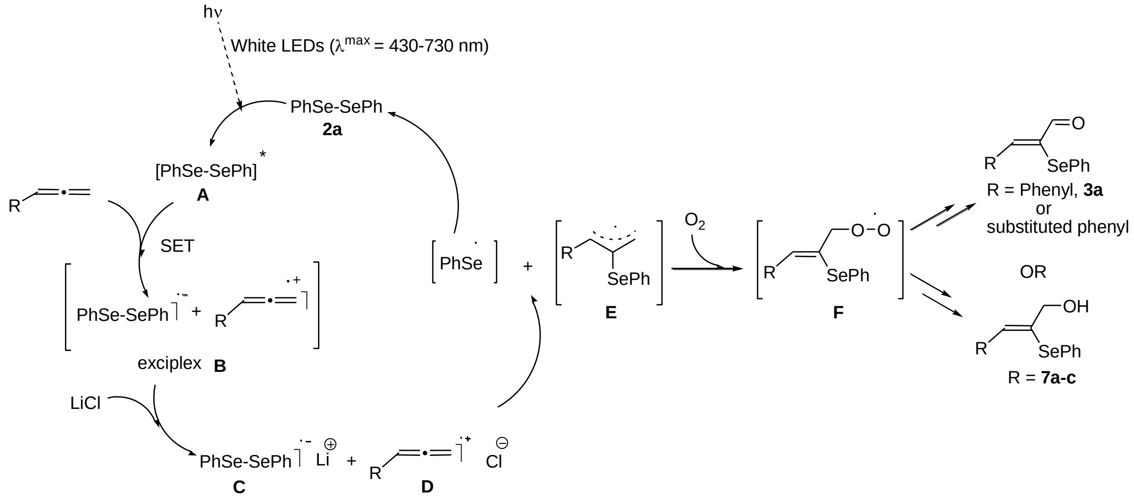
As a result, the highly stabilized neutral radical will result which in turn abstracts H-atom then, leading to observed product (Scheme 2).



Scheme 3. Radical trap experiment with **1a** and **2a**.

The monochromatic light (λ_{max} at 365 nm) promoted, chalcogen-centered radical additions to allenes are well-documented.[4a] Therefore, we have conducted a control experiment with **1a**, **2a** and TEMPO (1 equiv) under standard conditions. Only the regular product **3a** was observed, and no trace of the TEMPO terminated products was detected under these conditions, suggesting the SET pathway (Scheme 3).



Scheme 4. Proposed mechanism for the phenylseleno-oxygenation

A plausible mechanism can be envisaged based on the aforementioned observations together with available prior data[13] (Scheme 4). Upon visible-light irradiation **2a**[14] can attain a singlet excited-state which can be reduced (-1.25 eV vs SCE in MeCN)[15] via a single electron transfer from ground state **1a** (1.82 eV vs SCE in MeCN),[16] resulting in exciplex **B** formation. The exciplex **B** in the presence of LiCl generates solvent separated ions **C** and **D**.[10] A subsequent nucleophilic addition of phenylselenyl anion ($PhSe^-$) to electron deficient radical cation **D** can lead to allyl-stabilized radical intermediate **E** with simultaneous termination of phenylselenyl radical ($PhSe^{\cdot}$) to **2a**. The seleno-functionalized carbon radical **E** may be susceptible to oxidation in the presence of molecular oxygen. As a result, the oxygen is trapped by carbon radical **E** to form a peroxy-radical species **F**, which then disproportionate to either aldehyde (**3a**) or alcohol (**7a-c**), although it requires further experiments to elucidate the reaction pathways that lead to their production.[17]

Conclusions

In conclusion, we accomplished the chalcogenyl oxy-functionalization of allenes attached to either aryl group or electron withdrawing group with ambient air as a terminal oxidant. This rection proceeds with high regio- and stereoselectivity and produces the respective products in one-step in high yield. The by-product of this protocol is the benign water, hence considered eco-friendly reaction. Under the present reaction conditions, further oxidation of the aldehyde group did not take place, indicating its mildness when compared to metal-based oxidation. To the best of our knowledge, the one-step syntheses of the α-heteroatom-functionalized α,β-unsaturated aldehydes / ketones and diselenation adducts from the same starting material promoted by visible-light photo-reaction are described here for the first time. The synthetic utility of this strategy could well be conceived, and the results from this laboratory will be reported in due course.

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Experimental Section

General Information: All reactions were conducted under open air atmosphere. Apparatus used for reactions were oven dried. THF was distilled over sodium benzophenone ketyl before use and CH_2Cl_2 distilled over calcium hydride. MeCN purchased directly from the commercial suppliers and used without further purification. All other chemicals used were commercially available. Progress of the reactions was monitored by TLC on pre-coated silica gel 60 F-254 plates. Evaporation of solvents was performed at reduced pressure on a rotary evaporator. Column chromatography was carried out with silica gel grade 60-120 and 100-200 mesh. ^1H NMR spectra were recorded at 300, 400 & 500 MHz and ^{13}C NMR 75, 100 &125 MHz in $CDCl_3$. Chemical shifts (δ) are reported in ppm. Tetramethylsilane (δ = 0.00 ppm for ^1H) and $CDCl_3$ (δ = 77.00 ppm for ^{13}C) were used as the internal standard. Scalar coupling constants (*J*) are reported in hertz (Hz). Mass spectral data were compiled using MS (ESI), and High resolution mass spectra (HRMS) were recorded by ESI probe in positive mode using ORBITRAP analyzer. Electrochemical measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. The experiments were performed in a 1 *mM* phenyl allene solution in CAN at scan rate of 100 mV s^{-1}using 0.1 *M* tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. The working electrode was glassy carbon, a standard calomel electrode (SCE) was the reference electrode and platinum wire was an auxiliary electrode. After a cyclic voltammogram (CV) had been recorded, ferrocene was added, and a second voltammogram was measured. The UV spectrum was recorded on a HITACHI U-2910 double beam UV/VIS spectrophotometer. The 7W 6500K, 42mA (220-240Vac 50Hz) PHILIPS (Made in India) LED bulbs were used for irradiation.

Typical procedure for the synthesis (*Z*)-3-Phenyl-2-(phenylselenyl)acrylaldehyde (3a): Diphenyldiselenide **2a**, (187.3 mg, 0.6 mmol), 3-phenyl propa-1, 2-diene **1a** (116.2 mg, 1.0 mmol) and LiCl (41mg, 1.0 mmol) were charged into a test tube. While stirring, acetonitrile (4 mL, 0.01 *M*) was added and the resulting homogeneous reaction mixture containing test tube was placed into a beaker and irradiated with two 7*W* white LED lamps under open air. After completion of reaction (6 h), the reaction mixture was evaporated under vacuum to give a residue which was purified over silica gel column chromatography using *n*-hexane:EtOAc (95:5) as eluant to afford the phenylseleno-oxygenation product **3a** (247 mg, 86%) as yellow liquid along with minor isomer (23 mg, 8%).
R_f = 0.20;^1H NMR (500 MHz, $CDCl_3$): δ = 9.50 (s, 1H), 8.00 (s, 1H), 7.84-7.86 (m, 2H), 7.42-7.44 (m, 3H), 7.38-7.40 (m, 2H), 7.19-7.20 (m, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.4, 152.3, 134.2, 132.3, 131.9, 131.0 130.8, 129.2, 128.5, 127.3. IR (neat): 1684, 1586, 1565, 1475, 1441, 1391, 1287, 1211, 1180, 1110, 1068, 1022, 998, 924, 879, 736, 688 cm^{-1}. HRMS (*ESI*) calcd for $C_{15}H_{13}O$ Se [M+H] 289.0126, found 289.0126.

(*E*)-3-Phenyl-2-(phenylselenyl)acrylaldehyde(3a): yellow liquid; R_f = 0.40 (*n*-hexane:EtOAc = 98:2), 23 mg, (8% yield). ^1H NMR (500MHz, $CDCl_3$): δ = 9.79 (s, 1H), 7.65-7.67 (m, 2H), 7.37-7.39 (m, 5H), 7.32 (s, 1H), 7.22-7.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.0, 145.5, 138.4, 136.4, 134.7, 132.0, 129.8, 129.00, 128.6, 127.3, 126.6.

All reactions were carried out with **2a**, (0.6 mmol), allene (1.0 mmol) employing above typical procedure and the yields reported based on the disappearance of respective allene.
3-Phenyl-2-(phenyltellenyl)acrylaldehyde (3ab): Irradiated for 6 h; Obtained as an inseparable mixture (*Z*:*E* = 9:1 by ^1H NMR); yellow oil; R_f = 0.5 (*n*-hexane:EtOAc = 97:3); 304 mg (90% yield). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.29 (s, 1H), 8.14 (s, 1H), 7.59-7.61 (m, 4H), 7.33-7.38 (m, 3H), 7.17-7.20 (m, 1H), 7.07-7.10 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 157.0, 141.4, 138.2, 135.2, 130.4, 130.0, 129.4, 129.2, 128.5, 128.2, 127.9, 124.3, 112.7, 29.7. IR (neat): 3056, 2920, 2849, 1682, 1564, 1435, 1106, 997, 734, 691 cm^{-1}. HRMS (*EI*) calcd for $C_{15}H_{12}OTe$ [M^+] 337.9950, found 337.9950.
(*Z*)-2-(Phenylselenyl)-3-(*p*-tolyl)acrylaldehyde (3b): Irradiated for 6 h; yellow liquid; R_f = 0.20 (*n*-hexane:EtOAc = 95:5); 258 mg, (86% yield , *Z* isomer). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.48 (s, 1H), 7.98 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.37-7.39 (m, 2H),7.24 (d, *J* = 8.1 Hz, 2H), 7.18-7.20 (m, 3H), 2.39(s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 153.3, 141.8, 131.6, 131.4,131.3, 130.9, 129.5, 129.2, 129.1, 127.1, 21.6. IR (neat): 1688, 1583, 1507, 1476, 1438, 1286, 1218, 1184, 1104, 1068, 1021, 810, 772, 737, 689 cm^{-1}. HRMS (*ESI*) calcd for $C_{16}H_{15}OSe$ [M+H] 303.0283, found 303.0275.
(*Z*)-3-(4-(*tert*-Butyl)phenyl)-2-(phenylselenyl)acrylaldehyde (3c): Irradiated for 6 h; yellow liquid; R_f = 0.25(*n*-hexane:EtOAc = 95:5); 258 mg, (75% yield, *Z* isomer). ^1H NMR (500MHz, $CDCl_3$): δ = 9.48 (s, 1H), 7.99 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.5Hz, 2H), 7.37-7.39 (m, 2H), 7.18-7.20 (m, 3H), 1.33 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 154.8, 153.0, 131.6, 131.4, 131.2, 131.0, 129.5, 129.2, 127.1, 125.5, 35.0, 31.0. IR (neat): 1690, 1583, 1503, 1475, 1438, 1413, 1364, 1269, 1219, 1105, 1020, 829, 772, 737, 690 cm^{-1}. HRMS (*ESI*) calcd for $C_{19}H_{21}OSe$ [M+H] 345.0752, found 345.0755.
(*E*)-3-(4-(*tert*-Butyl)phenyl)-2-(phenylselenyl)acrylaldehyde (3c): yellow liquid; R_f = 0.35(*n*-hexane:EtOAc = 98:2); 40 mg, (12% yield). ^1H NMR (500MHz, $CDCl_3$): δ = 9.82 (S, 1H), 7.82-7.85 (m,2H), 7.63-7.67(m, 2H), 7.44-7.46 (m, 1H), 7.36-7.39 (m, 4H), 7.34(s,1H), 7.17-7.19(m,2H), 1.31(s,9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.0, 158.7, 156.4, 153.0, 146.1, 143.9, 137.5, 136.1, 133.5, 132.0, 131.4, 131.2, 131.2, 130.3, 129.5, 129.2, 128.8, 127.1, 125.5, 125.3, 35.0, 31.1.
(*Z*)-2-(Phenylselenyl)-3-(2,4,5-trimethylphenyl)acrylaldehyde (3d): Irradiated for 6 h; yellow liquid; R_f = 0.20 (*n*-hexane:EtOAc = 95:5); 277 mg, (84% yield , *Z* isomer). ^1H NMR (500 MHz, $CDCl_3$): δ = 9.52 (s, 1H), 8.13 (s, 1H), 7.38 (s, 1H), 7.34-7.36 (m, 2H), 7.15-7.17 (m, 3H), 6.98 (s, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.3, 151.1, 145.9, 139.4, 136.3, 135.1, 133.6, 132.3, 131.6, 130.7, 129.7, 129.0, 127.1, 19.7, 19.4, 19.3. IR (neat): 1692, 1578, 1496, 1475, 1442, 1385, 1271, 1193, 1113, 1022, 874, 739, 691cm^{-1}.

HRMS (ESI) calcd for $C_{18}H_{18}ONaSe$ [M+Na] 353.0415, found 353.0410.

(*Z*)-3-(4-Methoxyphenyl)-2-(phenylselenyl)acrylaldehyde (3e): Irradiated for 6 h; yellow liquid; R_f = 0.25 (*n*-hexane:EtOAc = 95:5); 273 mg, (86% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.48 (s, 1H), 7.95-7.97 (m, 3H), 7.36-7.38 (m, 2H), 7.18-7.20 (m, 3H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 162.0, 153.6, 133.6, 131.2, 129.7, 129.2, 128.8, 126.9, 126.8, 114.0, 55.4. IR (neat): 1685, 1601, 1582, 1562, 1507, 1475, 1438, 1297, 1257, 1177, 1123, 1103, 1026, 901, 829, 772, 738, 690 cm^{-1}. HRMS (*ESI*) calcd for $C_{16}H_{15}O_2Se$ [M+H] 319.0232, found 319.0231.

(*Z*)-3-(3, 5-Dimethoxyphenyl)-2-(phenylselenyl)acrylaldehyde (3f): Irradiated for 6 h; yellow liquid; R_f = 0.20 (*n*-hexane:EtOAc = 95:5); 298 mg, (86% yield , *Z* isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (s, 1H), 7.92(s, 1H), 7.38-7.40 (m, 2H), 7.19-7.21 (m, 3H), 7.04(d, *J* = 2.2 Hz, 2H), 6.53-6.54 (m,1H), 3.79 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 191.3, 160.5, 152.2, 135.8, 132.4, 131.8, 131.4, 129.2, 127.2, 108.8, 103.4, 55.4. IR (neat): 1685, 1573, 1455, 1424, 1345, 1301, 1258, 1202, 1152, 1105, 1059, 996, 837, 737, 686 cm^{-1}. HRMS (*ESI*) calcd for $C_{17}H_{17}O_3$ Se [M+H] 349.0337, found 349.0332.

(*Z*)-3-(4-Fluorophenyl)-2-(phenylselenyl)acrylaldehyde (3g): Irradiated for 6 h; yellow liquid; R_f = 0.25 (*n*-hexane:EtOAc = 95:5); 263 mg, (86% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.49 (s, 1H), 7.95 (s, 1H), 7.87-7.90 (m, 2H), 7.36-7.38 (m, 2H), 7.18-7.20 (m, 3H), 7.08-7.12 (m,2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 165.2, 162.7, 151.1, 133.3,131.8, 130.4, 129.3, 129.0 127.3, 115.8,115.6. IR (neat): 1690, 1596, 1575, 1504, 1476, 1438, 1289, 1232, 1160, 1114, 1094, 1020, 887, 831, 773, 738, 690 cm^{-1}. HRMS (*ESI*) calcd for $C_{15}H_{11}OFNaSe$ [M+Na] 328.9851, found 328.9853.

(*Z*)-3-(3, 5-Difluorophenyl)-2-(phenylselenyl)acrylaldehyde (3h): Irradiated for 6 h; yellow liquid; R_f = 0.20 (*n*-hexane:EtOAc = 95:5); 272 mg, (84% yield , *Z* isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (s, 1H), 7.83 (s, 1H), 7.38-7.40 (m, 2H), 7.32-7.34 (m, 2H), 7.20-7.23 (m, 3H), 6.84 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ = 190.8, 163.6, 163.5, 161.6, 161.5, 147.3, 137.1, 137.0, 136.8, 135.4, 132.6, 129.4, 128.1, 127.8, 113.4, 113.2, 105.8, 105.6, 105.4. IR (neat): 1692, 1615, 1578, 1473, 1435, 1319, 1226, 1120, 1045, 990, 851,738, 668 cm^{-1}. HRMS (*ESI*) calcd for$C_{15}H_{11}OF_2Se$ [M+H] 324.9938, found 324.9935.

(*Z*)-3-(3, 5-Bis(trifluoromethyl)phenyl)-2-(phenylselenyl)acrylaldehyde (3i): Irradiated for 6 h; yellow liquid; R_f = 0.20 (*n*-hexane:EtOAc = 95:5); 355 mg, (84% yield , *Z* isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.55 (s, 1H), 8.11 (s, 2H), 7.95 (s, 1H), 7.82 (s, 1H), 7.33-7.35 (m, 2H), 7.14-7.19 (m, 3H).^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.7, 145.7, 137.6, 136.1, 132.9, 132.1, 131.9, 131.6, 131.3, 129.9, 129.5, 128.0, 127.5, 124.0, 123.2, 121.8, 119.7. IR (neat): 1692, 1581, 1477, 1440, 1372, 1278, 1175, 1134, 940, 903, 739, 697 cm^{-1}. HRMS (*ESI*) calcd for $C_{17}H_{11}OF_6Se$ [M+H] 424.9874, found 424.9876.

(*Z*)-3-(4-Fluoro-3-methylphenyl)-2-(phenylselenyl)acrylaldehyde (3j): Irradiated for 6 h; yellow liquid; R_f = 0.20 (*n*-hexane:EtOAc = 90:10); 240 mg, (75% yield , *Z* isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48 (s, 1H), 7.92 (s, 1H), 7.69-7.73 (m, 2H), 7.36-7.38 (m, 2H), 7.17-7.21 (m, 3H), 7.01-7.06 (m, 1H), 2.29 (d, *J* = 2.0Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 191.3, 163.9, 161.3, 161.3, 151.6, 134.7, 131.7, 131.5, 130.8, 130.7, 130.1, 130.0, 129.2, 129.1, 127.2, 125.3, 125.1, 115.4, 115.1, 14.5. IR (neat): 1689, 1580, 1497, 1438, 1384, 1292, 1251, 1218, 1069, 1107, 1069, 999, 906, 819, 738, 690 cm^{-1}. HRMS (*ESI*) calcd for $C_{16}H_{14}OFSe$ [M+H] 321.0188, found 321.0183.

(*E*)-3-(4-Fluoro-3-methylphenyl)-2-(phenylselenyl)acrylaldehyde (3j): yellow liquid; R_f = 0.35 (*n*-hexane:EtOAc = 95:5); 32 mg, (10% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.76 (s, 1H), 7.63-7.66 (m, 3H), 7.38-7.41 (m, 3H), 7.24 (S, 1H), 7.00-7.01 (m, 2H), 2.26(S, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 188.7, 144.6, 138.0, 136.5,136.3,132.7, 130.6, 129.8, 129.7, 129.0,128.8,126.6, 125.7, 115.2, 14.5.

(*Z*)-3-(4-Nitrophenyl)-2-(phenylselenyl)acrylaldehyde (3k): Irradiated for 6 h; yellow solid; R_f = 0.20 (*n*-hexane:EtOAc = 95:5); 286 mg, (86% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.52 (s, 1H), 8.23 (d, *J* = 8.9 Hz, 2H), 7.99 (s, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.37-7.39 (m, 2H), 7.19-7.23 (m, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ = 190.6, 148.0, 146.3, 140.3, 136.9, 132.7, 131.1, 129.5, 128.0, 127.8, 123.5. IR (neat): 1693, 1578, 1517, 1476, 1438, 1344, 1289, 1100, 1069, 1020, 999, 887, 740, 690 cm^{-1}. HRMS (*EI*) calcd for $C_{15}H_{11}NO_3Se$ [M$^+$] 332.9904, found 332.9914.

(*Z*)-3-([1, 1'-Biphenyl]-4-yl)-2-(phenylselenyl)acrylaldehyde (3l): Irradiated for 6 h; yellow solid. R_f = 0.25 (*n*-hexane:EtOAc = 90:10); 309 mg, (85% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.50 (s, 1H), 8.02 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.61-7.66 (m, 4H), 7.44-7.47(m, 2H), 7.37-7.42 (m, 3H), 7.19-7.21(m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 152.0, 143.5, 139.8, 133.0, 131.9, 131.8, 131.7, 129.3, 129.2, 128.9, 128.0, 127.2, 127.0. IR (neat): 1689, 1579,1552,1482,1284, 1219, 1102, 1002, 900, 834, 771, 692 cm^{-1}. HRMS (*ESI*) calcd for $C_{21}H_{17}OSe$ [M+H] 365.0439, found 365.0436.

(*Z*)-3-(4-Phenoxyphenyl)-2-(phenylselenyl)acrylaldehyde (3m): Irradiated for 6 h; obtained as an inseparable mixture (*Z:E* = 80:20); yellow liquid; R_f = 0.25 (*n*-hexane:EtOAc = 95:5); 325 mg, (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.48-9.49 (d, *J* = 4.4 Hz, 1H), 7.95-7.97 (m, 1H), 7.89-7.93 (m 1H), 7.35-7.43 (m, 4H), 7.17-7.21 (m, 3H), 7.04-7.10 (m, 3H), 6.95-7.01 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 191.5, 186.5, 160.6, 160.3, 155.6, 155.4, 152.5, 144.7, 136.1, 133.4, 133.3, 131.5, 131.3, 130.2, 130.1, 130.0, 129.8, 129.5, 129.2, 128.6, 127.1, 126.8, 124.7, 12.5, 120.2, 120.1, 119.7, 118.1, 117.8, 117.6. IR (neat): 1690, 1584, 1502, 1487, 1244, 1169, 1102, 1069, 872, 745, 692, cm^{-1}. HRMS (*ESI*) calcd for $C_{21}H_{16}$ O_2NaSe [M+Na] 403.0208, found 403.0200.

(*Z*)-3-(6-Methoxynaphthalen-2-yl)-2-(phenylselenyl)acrylaldehyde (3n): Irradiated for 6 h; yellow solid; R_f = 0.20 (*n*-hexane:EtOAc = 90:10); 268 mg, (73% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54 (s, 1H), 8.27 (s, 1H), 8.12 (s, 1H), 8.06-8.09 (m,1H), 7.78 (d, *J* = 8.9Hz, 1H), 7.73 (d, *J* = 8.7Hz, 1H), 7.40-7.43 (m, 2H), 7.17-7.20 (m, 4H), 7.12 (d, *J* = 2.5 Hz, 1H), 3.94 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 159.4, 153.5, 135.9, 132.7, 131.6, 130.7, 130.6, 129.6, 129.5, 129.2, 128.1, 127.8, 127.1, 126.8, 119.6, 105.7, 55.4. IR (neat): 1684, 1624, 1565, 1478, 1438, 1416, 1390, 1345, 1269, 1224, 1175,

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1107, 1026, 998, 910, 854, 810, 737, 689 cm^{-1}. HRMS (*ESI*) calcd for $C_{20}H_{17}O_2Se$ [M+H] 369.0388, found 369.0380.

(*E*)-3-(6-Methoxynaphthalen-2-yl)-2-(phenylselenyl)acrylaldehyde (3n): yellow solid; R$_f$ = 0.35 (*n*-hexane:EtOAc = 95:5); 44 mg, (12% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.00 (s, 1H), 8.26 (s, 1H), 7.89-7.94 (m, 3H), 7.80-7.82 (m, 2H), 7.23-7.26 (m, 2H), 7.16-7.19 (m, 2H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0,160.2, 138.3, 134.2, 133.5, 132.3, 131.7, 131.1, 127.7, 125.1, 123.7, 120.0, 106.1, 105.9, 55.5.

(2*Z*, 2*Z'*)-3, 3'-(1, 3-Phenylene)-bis(2-(phenylselenyl)acrylaldehyde) (5a): Irradiated for 6 h; yellow solid; R$_f$ = 0.15 (*n*-hexane:EtOAc = 85:15); 422 mg, (85% yield , *Z* isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.51 (s, 2H), 8.30 (s, 1H), 8.0 (s, 2H), 7.82 (dd, *J* = 1.7,7.8 Hz, 2H), 7.5 (t, *J* = 7.8Hz, 1H), 7.36-7.38 (m, 4H), 7.18-7.21 (m, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 191.1, 150.2, 134.5, 133.6, 132.8, 132.6, 132.1, 129.3, 128.8, 128.6, 127.5. IR (neat): 1689, 1576, 1475, 1437, 1388, 1281, 1175, 1108 1068, 1021, 998, 914, 772, 738, 689 cm^{-1}. HRMS (*ESI*) calcd for $C_{24}H_{18}O_2NaSe_2$ [M+Na] 520.9529, found 520.9535.

(*Z*)-2-(Phenylselenyl)-3-(pyridin-2-yl)prop-2-en-1-ol (5bc): Irradiated for 6 h and the solvent was evoporated under reduced pressure. The resulting residue was dissolved in methanol (20 mL) and cooled to 0 °C. To this, cerium(III) chloride heptahydrate (410 mg, 1.1 mmol) was added by portionwise. To the resulting reaction mixture, sodium borohydride (42 mg, 1.1 mmol) was added and the combined contents were stirred 0.5 h at 0 °C. Then, saturated aqueous NH_4Cl (20 mL) and allowed to ambient temperature. The aqueous layer was extracted with CH_2Cl_2 (2x20 mL). The organic contents were dried over anhydrous Na_2SO_4, filtered and evoporated. The resulting residue was purified by silica gel flash column chromatography eluting with ethyl acetate/*n*-hexane (1:9) (R$_f$ = 0.20) to give a brown oil 252 mg (86%yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (d, *J* = 4.4 Hz, 1H), 7.74-7.77 (m, 2H), 7.65-7.69 (m, 1H), 7.37-7.42 (m, 1H), 7.30-7.35 (m, 3H), 7.11-7.15 (m, 2H), 4.16 (d, *J* = 1.2 Hz, 2H), 1.82 (br.s, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 147.7, 141.9, 137.0, 136.4, 129.1, 128.8, 128.2, 124.2, 122.8, 120.9. IR (neat): 3393, 3053, 3009, 1609, 1585, 1553, 1470, 1428, 1369, 1306, 1217, 1150, 1104, 1076, 999, 887, 843, 741, 694 cm^{-1}. HRMS (*ESI*) calcd for $C_{14}H_{14}ONSe$ [M+H] 292.0235, found 292.0228.

(*Z*)-2-(Phenylselenyl)-3-(pyrimidin-5-yl)acrylaldehyde (5c): Irradiated for 6 h; yellow liquid; R$_f$ = 0.20 (*n*-hexane:EtOAc = 90:10); 249 mg, (86% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.54 (s, 1H), 9.16 (s, 1H), 9.07 (s, 2H), 7.87 (s, 1H), 7.38-7.40 (m, 2H), 7.20-7.25 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.2, 158.7, 157.3, 141.9, 137.6, 132.8, 130.2, 129.6, 128.7, 128.2, 127.6. IR (neat): 1693, 1573, 1548, 1476, 1411, 1315, 1217, 1190, 1103, 1068, 998, 919, 772, 744, 691 cm^{-1}. HRMS (*ESI*) calcd for $C_{13}H_{11}ON_2Se$ [M+H] 291.0031, found 291.0029.

(*Z*)-4-Oxo-4-phenyl-2-(phenylselenyl)but-2-enal (5d): Irradiated for 6 h; pink liquid; R$_f$ = 0.75(*n*-hexane:toluene = 5:95); 262 mg, (83% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.31 (s, 1H), 8.13 (s, 1H), 8.06-8.08 (m, 2H), 7.66-7.68 (m, 2H), 7.60-7.63 (m, 1H), 7.51-7.54 (m, 2H), 7.41-7.43 (m, 1H), 7.36-7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.8, 152.7, 137.3, 135.8, 133.4, 131.5, 129.7, 129.5, 128.9, 128.4, 126.6, 123.2; IR (neat) 1692, 1629, 1577, 1527, 1475, 1440, 1376, 1330, 1295, 1215, 1157, 1084, 1059, 860, 742, 668 cm^{-1}. HRMS (*ESI*) calcd for $C_{16}H_{13}O_2Se$ [M+H] 317.0075, found 317.0071.

(*Z*)-Benzyl 4-oxo-3-(phenylselenyl)but-2-enoate (5e): Irradiated for 6 h; colored liquid; R$_f$ = 0.45 (*n*-hexane:EtOAc = 90:10); 283 mg, (82% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.18 (s, 1H), 7.62-7.64 (m, 2H), 7.34-7.41 (m, 7H), 7.0 (s, 1H), 5.27 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.9, 166.0, 150.9, 135.9, 135.3, 130.3, 129.7, 129.4, 128.6, 128.4, 125.4, 122.0, 67.1. IR (neat): 1788, 1735, 1712, 1689, 1576, 1498, 1476, 1456, 1378, 1302, 1177, 1020, 966, 907, 850, 741, 694 cm^{-1}. HRMS (*ESI*) calcd for $C_{17}H_{14}O_3NaSe$ [M+Na] 369.0000, found 369.0007.

(*Z*)-3-(Diphenylphosphoryl)-2-(phenylselenyl)acrylaldehyde (5f): Irradiated for 6 h; yellow solid; R$_f$ = 0.50 (*n*-hexane:EtOAc = 50:50); 370 mg, (90% yield , *Z* isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.9 (s, 1H), 7.56-7.58 (m, 2H), 7.50-7.54 (m, 4H), 7.38-7.48 (m, 9H), 6.49 (d, *J* = 18.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.6, 189.5, 158.4, 137.2, 133.0, 132.2, 131.3, 130.8, 130.7, 130.6, 130.2, 129.9, 128.9, 128.7, 125.5. IR (neat): 1967, 1894, 1676, 1548, 1478, 1436, 1370, 1278, 1193, 1118, 1049, 998, 774, 743, 694 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{18}O_2PSe$ [M+H] 413.0204, found 413.0206.

(*Z*)-3-(Diphenylphosphoryl)-3-phenyl-2-(phenylselenyl)acrylaldehyde (5g): Irradiated for 6 h; yellow solid; R$_f$ = 0.50 (*n*-hexane:EtOAc = 50:50); 438 mg, (90% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.1 (s, 1H), 7.49-7.57 (m, 9H), 7.37-7.41 (m, 5H), 7.27-7.32 (m, 2H), 7.21-7.25 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 2H), 6.77-6.79 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 190.8, 152.9, 152.8, 136.3, 136.2, 132.3, 132.2, 132.0,131.1, 130.3, 129.4, 129.0, 128.6, 128.4, 128.3, 125.7. IR (neat): 1694, 1571, 1481, 1438, 1374, 1220, 1185, 1116, 1070, 1025, 999, 962, 922, 747, 696 cm^{-1}. HRMS (*ESI*) calcd for $C_{27}H_{22}O_2PSe$ [M+H] 489.0517, found 489.0514.

(*Z*)-3-Formyl-3-(phenylselenyl)allyl benzoate (5h): Irradiated for 6 h; colored liquid; R$_f$ = 0.20 (*n*-hexane:EtOAc = 90:10); 284 mg, (82% yield , *Z* isomer). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (s, 1H), 8.00-8.07 (m, 2H), 7.58-7.62 (m, 1H), 7.45-7.52 (m, 4H), 7.33 (t, *J* = 5.4 Hz, 1H), 7.25-7.29 (m, 3H), 5.19 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 188.7, 166.1, 152.1, 136.5, 133.4, 132.9, 131.5, 129.7, 129.5, 128.5, 128.2, 63.9. IR (neat): 1721, 1602, 1579, 1451, 1315, 1270, 1111, 1069, 1025, 973, 772, 712, 690 cm^{-1}. HRMS (*ESI*) calcd for $C_{17}H_{14}O_3NaSe$ [M+Na] 369.0000, found 368.9993.

In case of **5i**, the reaction was carried out **2a** (1.1mmol), allene (1.0 mmol) employing above typical procedure and the yields reported based on the disappearance of respective allene.

(*Z*)-2, 3-Bis(phenylselenyl)acrylaldehyde (5i): Irradiated for 6 h; yellow liquid; R$_f$ = 0.20 (*n*-hexane:EtOAc = 95:5); 308 mg, (84% yield , *Z* isomer). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.28 (s, 1H), 8.83 (s, 1H), 7.61-7.63 (m, 2H), 7.49-7.51 (m, 2H), 7.37-7.41 (m, 3H), 7.25-7.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =

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186.3, 165.9, 133.6, 133.3, 133.1, 132.3, 131.9, 129.8, 129.3, 129.1, 127.5; IR (neat): 1675, 1576, 1535, 1476, 1438, 1377, 1233, 1157, 1101, 1021, 835, 770, 737, 690 cm^{-1}. HRMS (*ESI*) calcd for $C_{15}H_{12}ONaSe_2$ [M+Na] 390.9111, found 390.9107.

(*Z*)-2-((3-Oxo-2-(phenylselenyl)prop-1-en-1-yl)oxy)benzaldehyde (5j): Irradiated for 6 h; pale brown liquid; R_f = 0.70 (*n*-hexane:EtOAc = 95:5); 265 mg, (80% yield , *Z* isomer). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 11.05 (s, 1H), 9.85 (s, 1H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.99 (s, 1H), 7.70 (dd, *J* = 2.2, 8.7 Hz, 1H), 7.37-7.39 (m, 2H), 7.27-7.28 (m, 2H), 7.23-7.25 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 196.0, 161.5, 143.3, 139.8, 135.3, 131.8, 131.6, 129.4, 129.2, 127.7, 127.2, 121.4, 119.8, 119.1. IR (neat): 1672, 1653, 1610, 1574, 1469, 1437, 1364, 1277, 1225, 1180, 1069, 1021, 897, 833, 737, 691 cm^{-1}. HRMS (*EI*) calcd for $C_{16}H_{11}O_3Se$ [M-H$^+$]: 330.9873, found 330.9873.

(*Z*)-2-((4-oxo-3-(phenylselenyl)but-2-en-1-yl)oxy)benzaldehyde (5l): Irradiated for 6 h; yellow liquid; R_f = 0.45 (*n*-hexane:EtOAc = 80:20); 290 mg, (84% yield , *Z* isomer). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 10.49 (s, 1H), 9.46 (s, 1H), 7.86 (dd, *J* = 1.8, 7.6Hz, 1H), 7.49-7.62 (m, 4H), 7.40 (t, *J* = 5.2 Hz, 1H), 7.29-7.31 (m, 2H), 7.08 (t, *J* = 7.5Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 4.95 (d, *J* = 8.2 Hz, 2H).^{13}C NMR (100 MHz, CDCl$_3$): δ = 189.4, 189.2, 159.9, 152.0, 136.9, 135.9, 135.3, 133.0, 129.6, 129.0, 128.1, 125.1, 121.6, 112.3, 67.5. IR (neat): 1689, 1600, 1578, 1479, 1459, 1395, 1287, 1240, 1160, 1067, 1020, 841, 740, 690cm^{-1}. HRMS (*ESI*) calcd for $C_{17}H_{14}O_3NaSe$ [M+Na] 369.0000, found 368.9999.

***Z:E* mixture of 3-Phenyl-2-(phenylselenyl)but-2-enal (5m):** Irradiated for 6 h; Obtained as an inseparable mixture (*Z:E* = 10:1); yellow oil; R_f = 0.5 (*n*-hexane:EtOAc = 98:2) 242 mg, (80% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.33 (s, 1H), 7.41-7.44 (m, 5H), 7.18-7.30 (m, 5H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 189.5, 167.6, 139.7, 134.7, 133.6, 131.3, 129.3, 129.2, 128.5, 128.5, 126.8, 28.6. IR (neat): 3055, 1760, 1675, 1438, 1219, 1135, 770, 736, 691 cm^{-1}. HRMS (*EI*) calcd for $C_{16}H_{14}OSe$ [M+] 302.0209, found 302.0210.

3, 3-Diphenyl-2-(phenylselenyl)acrylaldehyde (5n): Irradiated for 6 h; Obtained as a yellow oil; R_f = 0.25 (*n*-hexane:EtOAc= 98:2); 328 mg, (90% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.43 (s, 1H), 7.42-7.46 (m, 1H), 7.36-7.40 (m, 2H), 7.28-7.33 (m, 3H), 7.24-7.27 (m, 2H), 7.18-7.21 (m, 4H), 7.12-7.14 (m, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 190.0, 166.1, 141.9, 139.4, 134.7, 132.2, 131.1, 130.9, 130.0, 129.6, 129.2, 128.9, 128.3, 127.9, 126.8. IR (neat): 1729, 1674, 1441, 1294, 1117, 771, 698 cm^{-1}. HRMS (*EI*) calcd for $C_{21}H_{16}OSe$ [M$^+$] 364.0366, found 364.0356.

***Z:E* mixture of 3-(4-Methoxyphenyl)-3-phenyl-2-(phenylselenyl)acrylaldehyde (5o):** Irradiated for 6 h; Obtained as an inseparable mixture (*Z:E* = 50:50); yellow oil; R_f = 0.5 (*n*-hexane:EtOAc); 362 mg, (92% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.43 (s, 1H), 9.36 (s, 1H), 7.11-7.46 (m, 24H), 6.88 (m, 2H), 6.78 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 190.0, 189.8, 166.6, 166.3, 161.5, 160.7, 142.1, 139.8, 134.2, 133.4, 133.2, 133.1, 132.0, 131.8, 131, 3, 130.1, 129.8, 129.3, 128.9, 128.3, 127.9, 126.7, 113.8, 113.3, 55.4, 55.3. IR (neat): 3054, 2925, 2839, 1713, 1669, 1600, 1504, 1252, 1176, 116, 1027, 773, 736, 697 cm^{-1}; HRMS (*EI*): calcd for $C_{22}H_{18}O_2Se$ [M$^+$] 394.0472, found 394.0469.

(*Z*)-3-(4-Chlorophenyl)-3-phenyl-2-(phenylselenyl)acrylaldehyde (5p): Irradiated for 6 h; Obtained as a separable mixture (*Z:E* = 50:50); yellow solid; R_f = 0.5 (*n*-hexane:EtOAc= 98:2); 189 mg, (47% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.42 (s, 1H), 7.35-7.37 (m, 2H), 7.25-7.32 (m, 4H), 7.12-7.18 (m, 8H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 189.4, 163.9, 141.5, 137.8, 136.4, 135.5, 132.5, 132.3, 130.5, 129.5, 128.7, 128.1, 127.0. IR (neat): 3056, 1900, 1672, 1438, 1117, 1089, 769, 736, 693 cm^{-1}. HRMS (*EI*): calcd for $C_{21}H_{15}ClOSeM$+] 397.9976, found 397.9966.

(*E*)-3-(4-Chlorophenyl)-3-phenyl-2-(phenylselenyl)acrylaldehyde (5p): yellow solid; R_f = 0.6 (*n*-hexane:EtOAc= 98:2); 189 mg, (48% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.41 (s, 1H), 7.30-7.47 (m, 1H), 7.36-7.40 (m, 2H), 7.26-7.28 (m, 3H), 7.10-7.22 (m, 8H).^{13}C NMR (125 MHz, CDCl$_3$): δ = 127.04, 128.17, 128.46, 128.91, 130.24, 130.96, 131.09, 132.50, 135.19, 135.72, 139.04, 140.14, 164.08, 189.70. IR (neat): 3056, 2922, 2851, 1666, 1483, 1440, 1117, 1089, 767, 736, 693 cm^{-1}. HRMS (*EI*) calcd for $C_{21}H_{15}ClOSe$ [M+] 397.9976, found 397.9965.

1, 3-Diphenyl-2-(phenylselenyl)prop-2-en-1-one (5q): Irradiated for 6 h; Obtained as an inseparable mixture (*Z:E* = 20:1); yellow oil; R_f = 0.5 (*n*-hexane:EtOAc = 98:2) 327 mg, (90% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.08-7.17 (m, 3H), 7.32-7.40 (m, 5H), 7.42-7.45 (m, 3H), 7.48-7.51 (m, 1H), 7.63-7.65 (m, 2H), 7.72-7.74 (m, 2H).^{13}C NMR (125 MHz, CDCl$_3$): δ = 194.6, 138.8, 137.2, 136.9, 135.4, 134.6, 134.3,134.1, 133.4, 132.5, 129.7, 129.5, 129.0, 128.5, 128.1, 127.9, 127.7. IR (neat): 3057, 2923, 2198, 1726, 1657, 1577, 1444, 1222, 738, 688 cm^{-1}. HRMS (*EI*) calcd for $C_{21}H_{16}OSe$ [M$^+$] 364.0366, found 364.0356.

(*Z*)-4-Phenoxy-2-(phenylselenyl)but-2-en-1-ol (7a): Irradiated for 6 h; Obtained as a *Z* isomer **7a** and internal double bond attacked isomer **7aa** in 8:2; yellow liquid; R_f = 0.75 (*n*-hexane:EtOAc = 98:2); 287 mg, (90% yield , *Z* isomer). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.50- 7.57 (m, 2H), 7.24-7.32 (m, 6H), 6.87-6.98 (m, 3H), 6.57-6.59 (m, 1H), 4.81 (d, *J* = 5.6 Hz, 2H), 4.15 (d, *J* = 1.1Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.2, 158.0, 138.8, 134.6, 134.0, 133.2, 131.5, 129.5, 128.1, 128.0, 127.86, 123.7, 121.4, 121.1, 114.9, 114.7, 70.9, 67.1, 64.5, 62.2, 48.5, 42.8. IR (neat): 3059, 1596, 1492, 1437, 1373, 1300, 1212, 1171, 1073, 1014, 883, 734, 686 cm^{-1}. HRMS (*EI*) calcd for $C_{10}H_{10}O_2Se$ [M-C_6H_6] 241.9846, found 241.9845.

(*Z*)-*N*-(4-Hydroxy-3-(phenylselenyl)but-2-en-1-yl)-4-methyl-*N*-Phenylbenzenesulfonamide (7b): Irradiated for 6 h; yellow liquid; R_f = 0.25 (*n*-hexanes:EtOAc = 90:10); 387 mg, (82% yield, *Z* isomer). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.48 (d, *J* = 8.2 Hz, 2H), 7.27-7.31 (m, 6H), 7.18-7.25 (m, 4H), 6.99-7.01 (m, 2H), 5.88 (t, *J* = 7.2 Hz, 1H), 4.29 (d, *J* = 7.2 Hz, 2H), 4.01 (s, 2H), 2.44 (s, 3H), 2.43(s, 1H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 143.7, 138.8, 135.2, 134.0, 133.4, 133.0, 129.5, 129.4, 129.1, 128.8, 128.6, 128.2, 128.0, 127.7, 48.8, 42.5, 21.6. IR (neat): 3058, 1595, 1491, 1438, 1348, 1258, 1162, 1090, 1067, 996, 928, 814, 770, 694, 658. HRMS (*EI*) calcd for $C_{23}H_{22}NO_2SSe$ [M-OH] 456.0537, found 456.0552.

(*Z*)-4-(5-Bromo-3-(phenylselenyl)-1H-indol-1-yl)-2-(phenylselanyl)but-2-en-1-ol (7c): Irradiated for 6 h; brown liquid; R$_f$ = 0.35 (*n*-hexane:EtOAc = 95:5); 485 mg, (84% yield , *Z* isomer). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.76 (s, 1H), 7.54-7.56 (m, 2H), 7.28-7.37 (m, 5H),7.20-7.23 (m, 3H), 7.12-7.17 (m, 3H), 6.06 (t, *J* = 6.7 Hz, 1H), 4.89 (d, *J* = 6.7 Hz, 2H), 4.28 (s, 2H), 1.26 (br.s, 1H).^{13}C NMR (125 MHz, CDCl$_3$): δ = 135.4, 135.1, 134.8, 133.6, 133.4, 132.7, 132.0, 131.5, 129.6, 129.1, 128.7, 127.7, 125.8, 125.7, 123.3, 114.5, 111.2, 96.95, 45.02, 42.21. HRMS (*EI*) calcd for $C_{24}H_{20}BrNOSe_2$ [M$^+$] 576.9059, found 576.9052.

In case of **9a-c**, the reactions were carried out **2a** (1.1mmol), allene (1.0 mmol) employing above typical procedure and the yields reported based on the disappearance of respective allene.

3, 4-Bis(phenylselenyl)but-2-enyl)benzene (9a): Irradiated for 3 h; Obtained as an inseparable mixture (*Z:E* = 3:1); yellow liquid; R$_f$ = 0.25 (*n*-hexane:EtOAc= 99:1); 400 mg, (90% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.41-7.57 (m, 4H), 7.15-7.26 (m, 10H), 6.99-7.04 (m, 2H), 6.06-6.10 (t, *J* = 7.6 Hz, 1H), 5.91-5.94 (t, *J* = 7.2 Hz, 1H), 3.86 (s, 2H), 3.73 (s, 2H), 3.57 (d, *J* = 7.2 Hz, 2H), 3.15 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 134.7, 134.2, 133.3, 132.7, 131.5, 130.2, 129.7, 129.5, 129.4, 129.2, 129.0, 128.4, 127.7, 127.4, 127.1, 126.2, 126.1, 38.3, 37.8, 35.5, 31.2. IR (neat): 3057, 2997, 1575, 1474, 1435, 1020, 730, 686 cm^{-1}. HRMS (*EI*) calcd for$C_{22}H_{20}Se_2$ [M$^+$] 443.9895, found 443.9890.

(*Z*)-4-Cyclohexyl-2-(phenylselenyl)but-2-enylselanyl)benzene (9b): Irradiated for 3 h; yellow oil; R$_f$ = 0.25 (*n*-hexane:EtOAc = 98:2); 414 mg, (95% yield , *Z* isomer). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.44-7.46 (m, 4H), 7.20-7.25 (m, 6H), 5.55 (d, *J* = 9.1 Hz, 1H), 3.63 (s, 2H), 2.44-2.52 (m, 1H),1.58-1.63 (m, 2H), 1.49 (d, *J* = 15.7 Hz, 2H), 1.18-1.27 (m, 2H), 1.05-1.14 (m,1H), 0.91-0.98 (m, 2H).^{13}C NMR (100 MHz, CDCl$_3$): δ = 144.1, 134.5, 132.6, 131.5, 129.1, 128.8, 127.7, 127.4, 126.5, 41.0, 37.9, 32.5, 25.8, 25.5. IR (neat): 3057, 2922, 2849, 1577, 1474, 1438, 1215, 1021, 753, 687 cm^{-1}. HRMS (*EI*) calcd for $C_{21}H_{24}Se_2$ [M+] 436.0208, found 436.0201.

2-(1, 2-Bis(phenylselenyl)ethylidene)pent-4-enyl)benzene (9c): Irradiated for 3 h; Obtained as an inseparable mixture (*Z:E* = 3:2); yellow oil; R$_f$ = 0.25 (*n*-hexane:EtOAc = 99:1); 450 mg, (93% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.09- 7.49 (m, 15H), 5.61-5.71 (m, 2H), 5.02-5.04 (m, 2H), 4.97-4.98 (m, 1H), 3.92 (s, 2H), 3.87 (s, 2H),3.82 (s, 2H), 3.33 (s, 2H), 3.10 (d, *J* = 6.4 Hz, 2H), 2.65 (d, *J* = 6.3 Hz, 2H).^{13}C NMR (125 MHz, CDCl$_3$): δ = 144.3, 143.9, 139.1, 138.7, 134.4, 132.8, 132.5, 129.2, 128.4, 127.5, 127.4, 127.1, 126.3, 126.2, 116.3, 42.3, 41.0, 37.2, 35.8, 33.7, 33.4. IR (neat): 3057, 2999, 2922, 2851, 1729, 1576, 1436, 1176, 1021, 772, 735, 690 cm^{-1}. HRMS (*EI*) calcd for $C_{25}H_{24}Se_2$ [M$^+$] 484.0208, found 484.0202.

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Visible-Light-Induced Phenylchalcogenyl-Oxygenation of Allenes Having Aryl- / or Electron Withdrawing Substituent with Ambient Air as Sole Oxidant

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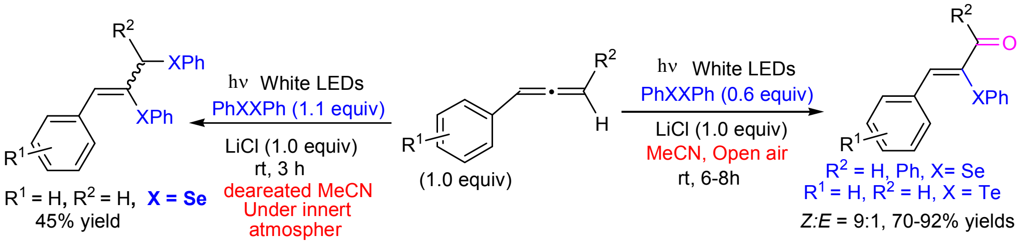

The stereoselective synthesis of α-phenylselenyl- or Telluryl β-aryl acryladehydes / ketones from aryl allenes / 1,3-diarylallene by an oxidative photo-induced single electron transfer process using benign ambient air as sole oxidant was achieved.