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Photoredox-Catalyzed Intermolecular Radical Arylthiocyanation/Arylselenocyanation of Alkenes: Access to Aryl-Substituted Alkylthiocyanates/Alkylselenocyanates

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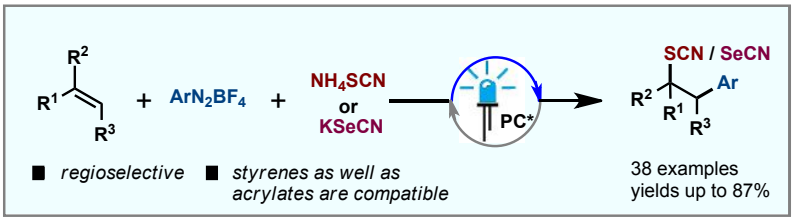


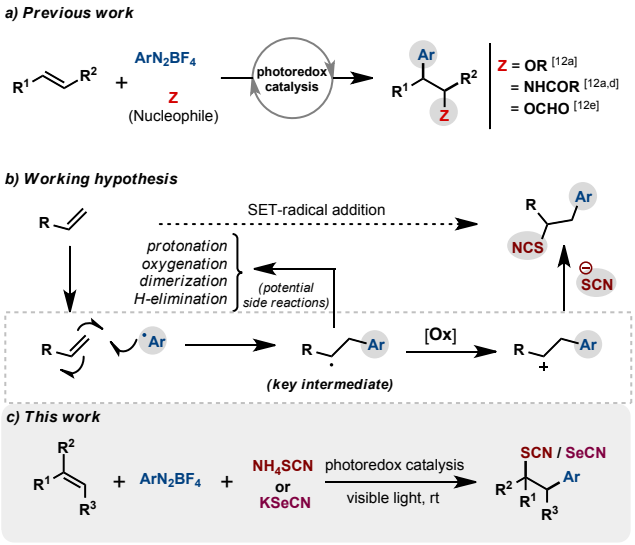
ABSTRACT: An efficient and highly selective approach for intermolecular arylthiocyanation/arylselenocyanation of alkenes has been reported in mild conditions. Using diazonium salts as the arylating agent and ammonium thiocyanate as the thiocyanate source, chemo-selective difunctionalisation of alkenes has been done under the irradiation of visible light. Both styrenes and acrylates work well to deliver various aryl-substituted alkylthiocyanates in good to excellent yields. In addition, hitherto unknown *β*-aryl alkylselenocyanates were also synthesized using the developed protocol with potassium selenocyanate.

INTRODUCTION

Organic thiocyanates are useful functional motifs present in various bioactive compounds and natural products.[1] Additionally, they have been widely used as intermediates in the synthesis of sulfur-containing heterocycles,[2] since thiocyano group could be easily transformed to other sulfur functional groups.[3] For instance, *β*-aryl substituted *β*-keto thiocyante are used as intermediates in the synthesis of many thiazoles.[4] Therefore, considerable effort has been made on the development of efficient methods for the incorporation of thiocyano group into small organic molecules. Traditional routes to this class of molecules include the nucleophilic substitution of thiocyanate to alkyl halides[5] or alcohols,[6] and electrophilic thiocyanation of thiocyanate salts[7] or isothiocyanate anion[8] in the presence of oxidant. However, the major drawback associated with most of them is use of large excess of strong oxidants, low region- and chemo-selectivity, as well as limited substrate scope. Thus, developing new and efficient thiocyanation reactions for the synthesis of SCN-containg small molecules is still highly desirable.

In the past decade, radical difunctionalization of olefins[9] has become a unique technique to transform simple alkenes to functionalised materials as value-added products. More recently, the visible light mediated single-electron transfer (SET) process has further matured this radical difunctionalization strategy in environmentally benign mild conditions.[10] In this context, photoredox-catalyzed Meerwein arylation using aryl diazonium salts have received considerable attention and significant progress have been made.[11] While several examples on the Meerwein arylation-addition reactions of alkenes,[12] such as oxyarylation,[12a-c] aminoarylation,[12d] formyloxyarylation,[12e] trifluoromethylthioarylation,[12f] haloarylation,[12g-h] and xanthatoarylation[12i-k] are known (Scheme 1a). But similar type of thiocyanoarylation with olefin is limited to some alkenes, [13] like *α*-halogenostyrene,[13a] *α,β,β*-trifluorostyrene,[13b] allylic compounds,[13c] and acrylate derivatives[13d-e] under

Scheme 1. a) Photoredox-catalyzed difunctionalization of alkens using aryl diazonium salts; b) Working hypothesis; c) Present protocol of photoredox-catalyzed arylthiocyanation/arylselenocyanation.

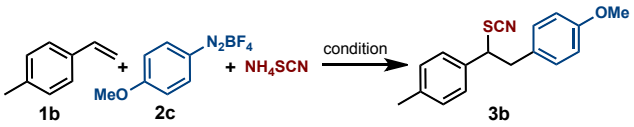


Cu-catalysis. Additionally, these reactions are not chemoselective and often furnished with by-products. We envisioned that visible light induced SET-aryl radical addition followed by oxidative trapping of the carbocation by thiocyanate nucleophile could render the desired *β*-aryl alkylthiocyanate (Scheme 1b). But the major challenges remain the chemo- and region-selective addition of aryl radical over thiocyanate radical onto the alkene double bond under the reaction conditions, as both thiocyanate anion[14] and diazonium salts[11] are known to generate radicals under visible light mediated photoredox catalysis. Secondly, the radical intermediate, which was generated after aryl radical addition was susceptible to generate undesired products by oxygenation to *α*-arylketone,[15] reduction followed by protonation to aryl alkane,[16] or H-elimination to *β*-aryl alkene.[17] So efficient single electron oxidation of the radical intermediate would selectively provide the targeted *β*-aryl alkylthiocyanate.

As part of our ongoing work on radical difunctionalization of olefin,[18] we report herein an efficient photoredox-catalyzed intermolecular arylthiocyanation of alkenes to deliver vicinal aryl-substituted alkyl thiocyanates using aryl diazonium salts as the arylating agent and ammonium thiocyanate as an inexpensive thiocyanation reagent (Scheme 1c). The method is mild (visible light, room temperature), operationally simple and display a broad substrate scope. In addition, *β*-aryl alkylselenocyanates were also synthesized first time using the developed protocol with potassium selenocyanate.

RESULTS AND DISSCUSION

Table 1. Optimization of the reaction condition[a]



entry	Photocatalyst	solvent	yield (%)[b]
1.[c]	$Ru(bpy)_3(PF_6)_2$	CH_3CN	31
2.	$Ru(bpy)_3(PF_6)_2$	CH_3CN	76
3.	$Ru(bpy)_3(PF_6)_2$	DCE	51
4.	$Ru(bpy)_3(PF_6)_2$	THF	32
5.	$Ru(bpy)_3(PF_6)_2$	Dioxane	17
6.	$Ru(bpy)_3(PF_6)_2$	Toluene	24
7.	$Ru(bpy)_3(PF_6)_2$	DMF	0
8.	$Ru(bpy)_3(PF_6)_2$	DMSO	0
9.	Eosin Y	CH_3CN	28
10.	Rose Bengal	CH_3CN	33
11.	Methylene Blue	CH_3CN	18
12.	Rhodamine B	CH_3CN	23
13.[d]	$Ru(bpy)_3(PF_6)_2$	CH_3CN	57
14.[e]	$Ru(bpy)_3(PF_6)_2$	CH_3CN	52
15.	-	CH_3CN	trace
16.[f]	$Ru(bpy)_3(PF_6)_2$	CH_3CN	trace

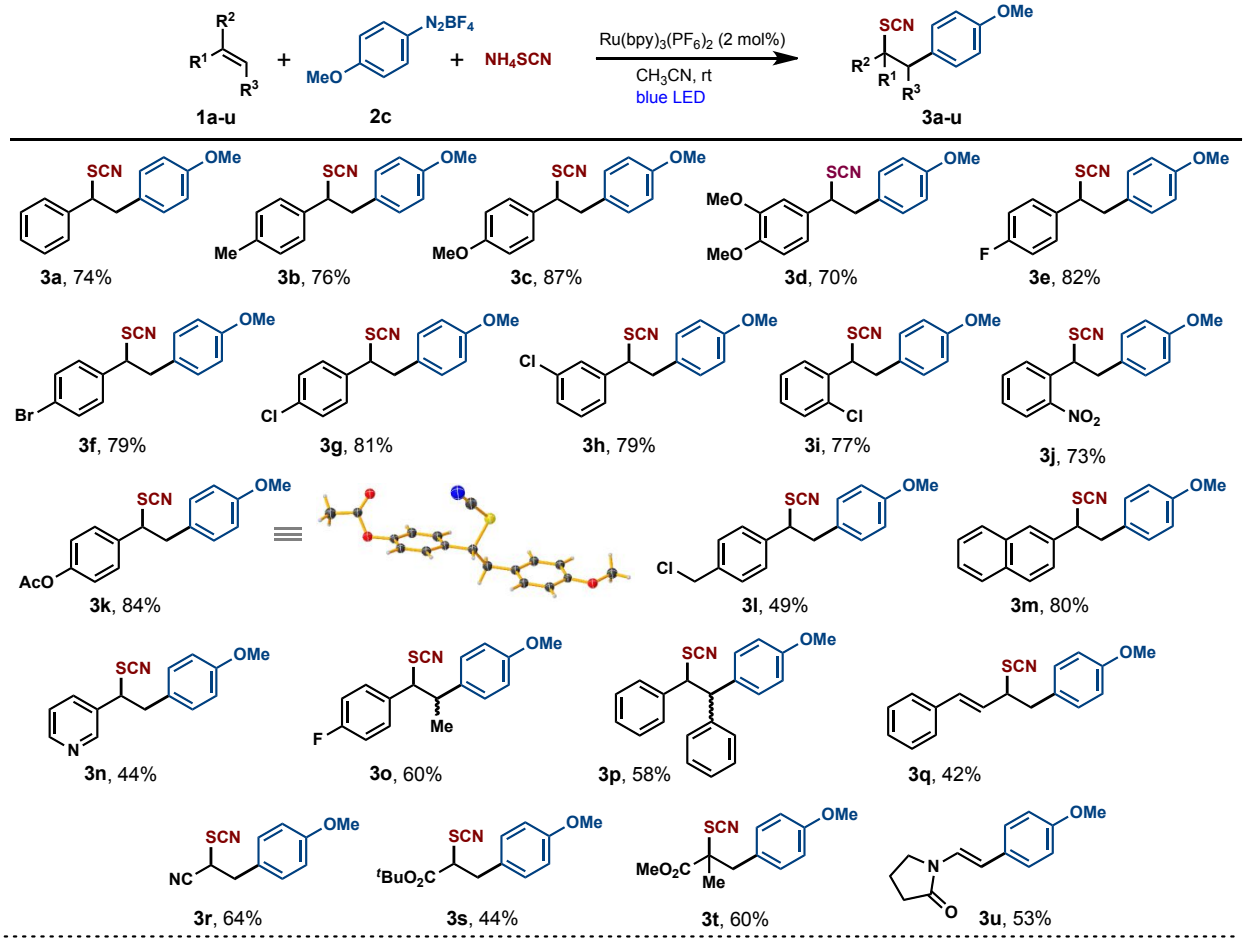
[a]Unless otherwise noted, all reactions were carried out with: **1b** (0.4 mmol), **2c** (0.2 mmol), NH_4SCN (0.6 mmol), photocatalyst (2 mol%), and degassed solvent (2 mL) in a culture tube under argon at rt irradiated with 12W blue LED for 6 h. [b] yield, [c]in air, [d]KSCN instead of NH_4SCN, [e]NaSCN instead of NH_4SCN, [f]in dark.

We commenced our investigation with 4-methyl styrene (**1b**), 4-methoxybenzenediazonium tetrafluoroborate (**2c**), and ammonium thiocyanate to evaluate the optimal conditions of the three-component reaction under visible light photoredox catalysis (Table 1).[19] Using a blue LED light, irradiation of a solution of **1b**, **2c**, and ammonium thiocyanate in acetonitrile with $[Ru(bpy)_3(PF_6)_2]$ in open air afforded the desired arylthiocyanation product **3b** in 31% yield (Table 1, entry 1). Degassing the reaction mixture by argon dramatically improved the yield of **3b** from 31% to 76% (entry 2). This is likely due to suppression of the competitive oxidative side reactions involving within two components of **2c** and thiocyanate with the styrene in the presence of oxygen from air. [14-15] It is also worth noting that complete regiocontrol was observed with respect to styrene in the difunctionalization event. Use of other common solvents such as DCE, THF, Dioxane, and Toluene led to lower yields of **3b** (entries 3-6) and no reaction took place in highly polar solvents DMF or DMSO (entries 7-8).[20] Other photocatalysts such as Eosin Y, Rose Bengal, Methylene Blue, and Rhodamine B were less effective in this transformation (entries 9-12). Further investigation revealed that commercially available other SCN sources such as KSCN and NaSCN could also afford the desired product **3b**, but in lower yields (entries 13 and 14). Finally, control experiments performed without catalyst or light produced only trace of the product (entries 15 and 16), thus indicating that both the catalyst and light were crucial for effective conversion into **3b**.

With the optimized reaction conditions in hand (Table 1, entry 2), the substrate scope of alkenes in three component reaction was explored. As shown in scheme 2, the developed method was found to easily accommodate a variety of styrenes and acrylates. Styrenes bearing various substituents on the aromatic ring, including electron-donating (**3b–d**) and electron-withdrawing (**3e–j**) groups, underwent the desired transformation, affording the corresponding products in good to excellent yields.

Interestingly, the position of substituents on the aromatic ring of styrene had little effect on the reaction outcome, as *para*-, *meta*- and *ortho*-chlorostyrenes gave similar yields of the corresponding products (**3g–i**). In addition, the survival of halogen handle in the products providing opportunities for further elaboration *via* traditional cross-coupling reaction. Orthogonal functionalities, including ester (**3k**), benzyl halide (**3l**) are also well tolerated under these mild, radical-mediated reaction conditions. The structure of **3k** was unambiguously confirmed by X-ray diffraction analysis (CCDC 1813182, Figure S4 in SI).[21] Pleasingly, vinylarene featuring fused aromatic ring **3m** and heteroatom **3n** was found to be well accommodated. Moreover, internal styrenes were also reacted smoothly to give the desired product **3o-p** with a mixture of diastereomers. Interestingly the conjugated diene, 1-phenyl-1,3-butadiene participated in the protocol, which occurred regioselectively at the terminal double bond to afford the desired product **3q**. Importantly, acrylates also participated in this reaction uneventfully, generating the desired products (**3r–t**) with excellent regioselectivity, but Meerwin arylation-elimination product **3u** was observed in case of 1-Vinyl-2-pyrrolidinone. Finally we have attempted photo-arylthiocyanation with aliphatic substrates such as 1-dodecene, norbornene, cyclohexene, and allylbenzene. These substrates did not react under the reaction

Scheme 2. Scope of Alkenes[a, b]

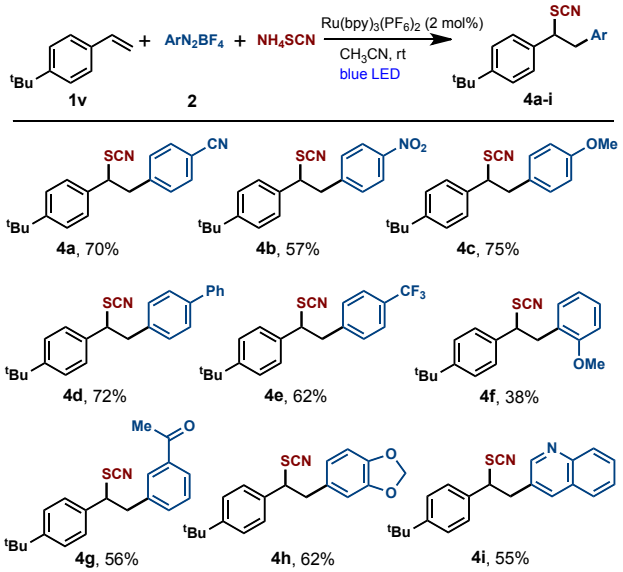


[a]Unless otherwise noted, all reactions were carried out with: **1** (0.4 mmol), **2c** (0.2 mmol), NH_4SCN (0.6 mmol), $Ru(bpy)_3(PF_6)_2$ (2 mol%), and degassed CH_3CN (2 mL) in a culture tube under argon at rt irradiated with 12W blue LED for 6 h. [b]yield.

conditions, presumably due to their intrinsic lower reactivity than aromatic alkenes or acrylates.[22]

We then explored the reactivity of different diazonium salts as aryl-group carrier. As shown in Scheme 3, aryldiazonium salts bearing electron-withdrawing and electrondonating substituents at the *para* position of phenyl ring **4a-e**, showed good reactivity. Both *ortho*-and *meta*-substituted aryldiazonium salts **4f–g** were suitable substrates, but the lower reactivity of *ortho*-substituent could be due to steric effect. Additionally, di-substituted aryldiazonium salts **4h** was compatible in the present study. Moreover, aryldiazonium salts containing quinoline heterocycle **4i** also participated in this event to produce desired product in good yield.

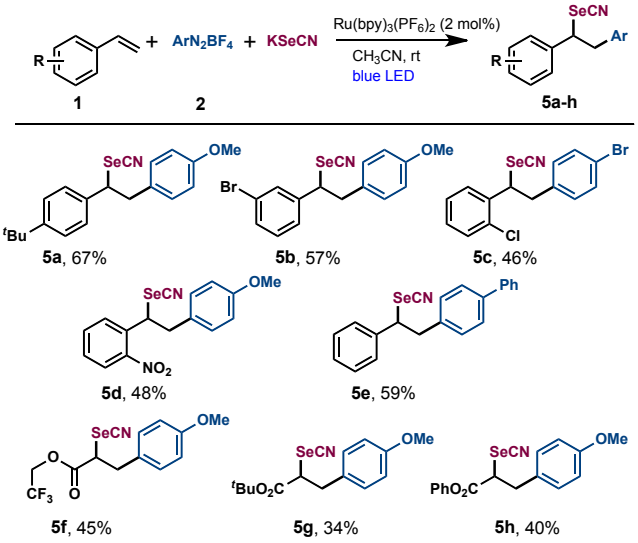
Scheme 3. Scope of aryldiazonium salts[a, b]



[a] Unless otherwise noted, all reactions were carried out with: **1v** (0.4 mmol), **2** (0.2 mmol), NH_4SCN (0.6 mmol), $Ru(bpy)_3(PF_6)_2$ (2 mol%), and degassed CH_3CN (2 mL) in a culture tube under argon at rt irradiated with 12W blue LED for 6 h. [b]yield.

Organoselenium compounds are ubiquitous in numbers of molecules including biological, pharmaceutical, and material interest.[23] They show a wide range of pharmaceutical activities like, antiviral, anti-inflammatory and antitumor properties.[24] Importantly, among organoselenium compounds, the selenocyanate derivatives displayed promising cancer chemopreventive agents[25a-b] and effective antioxidants.[25c] Furthermore, organoselenium compounds can usually be used in a wide varieties of organic transformations and have become a versatile tool in organic synthesis.[26] Keeping this in mind, we conducted a series of experiments to validate this intermolecular radical difunctionalization strategy to access arylsubstituted alkylselenocyanate using selenocyanate salt instead of thiocyanate in our newly developed transformation (scheme 4). Consequently, the arylselenocyanation of alkene under the optimized reaction conditions afforded the corresponding *β*-aryl alkylselenocyanates **5a-h** in moderate to good yields. To the best of our knowledge, this is the first reported synthesis of *β*-aryl alkylselenocyanates under visible light photoredox catalysis. Several functional groups including tert-butyl, methoxy, bromide, chloride, nitro, and phenyl were tolerated in this reaction. Styrenes with *para*, *meta* and *ortho* substituted groups (**5a-d**) were easily adaptable under these mild photo catalytic conditions. Acrylates with variable substituted ester handles were also well accommodated to provide the desired arylselenocyanation products (**5f-h**).

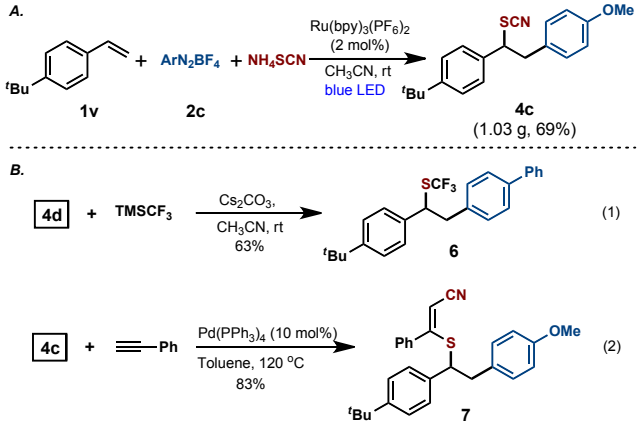
Scheme 4. Scope of photo-arylselenocyanation[a,b]



[a] Unless otherwise noted, all reactions were carried out with: **1** (0.4 mmol), **2** (0.2 mmol), KSeCN (0.6 mmol), $Ru(bpy)_3(PF_6)_2$ (2 mol%), and degassed CH_3CN (2 mL) in a culture tube under argon at rt irradiated with 12W blue LED for 6 h. [b]yield.

The practically synthetic potential of this new photo-arylthiocyanation reaction could be highlighted by its scalability and simplicity. The gram-scale reaction of **2c** under standard reaction conditions proceeded smoothly to provide the corresponding product **4c** in 69% yield (1.03 g) (Scheme 5A). To further illustrate the synthetic utility of the present method, few experiments were carried out (Scheme 5B). Upon treatment of **4d** with $TMSCF_3$ and Cs_2CO_3, the SCN group was converted to SCF_3 (**6**), a prevalent lipophilic group presents in various agrochemicals and pharmaceuticals (eq 1).[27] In addition, reaction of **4c** with phenyl acetylene under palladium catalysis, led cleanly to tri-substituted alkene **7** through a regioselective cyanothiolation of alkyne by cleaving the sulfur-cyano bond of SCN group (eq 2).[28]

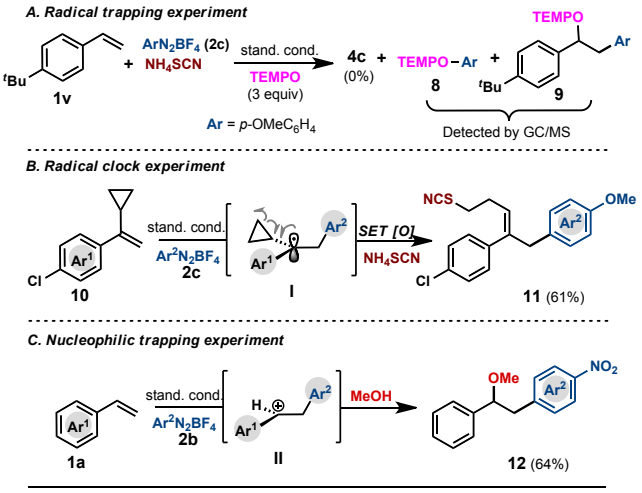
Scheme 5. A) Gram-scale photo-arylthiocyanation. B) Diversification of arylthiocyanates.



To gain insight into the mechanistic pathways of the raction, several control experiments were conducted. Firstly, TEMPO, a radical-trapping reagent, was introduced into the reaction mixture of **1v** (Scheme 6A). Under these conditions, no arylthiocyanation product **4c** was found, but

aryl-TEMPO **8** and benzyl-TEMPO **9** adducts were detected by GC/MS analysis of the crude reaction mixture.

Scheme 6. Mechanistic investigation.



These results indicate the photoredox process promotes the generation of aryl radical and that the generated aryl adduct (**15**, scheme 7) is one of the potential reactive species in the reaction. Furthermore, reaction of α-cyclopropyl styrene **10** with diazonium salt **2c** under our standard conditions produced homoallylic thiocyanate **11** resulting from ring-opening of the cyclopropropylmethyl radical (**I**), provides strong support for the participation of aryl radical in this transformation (Scheme 6B). Finally, a nucleophilic trapping experiment was conducted where methanol was added into the reaction mixture in place of ammonium thiocyanate (Scheme 6C). To our delight the methylether product **12** was isolated in 64% yield, providing direct evidence for the involvement of a carbocation intermediate (**II**) in the reaction pathway.

To probe the interaction of catalyst with substrates, a standard Stern-Volmer experiment[29] was conducted using the employed substrates (Figure 1). It was observed that the excited state of Ru(II)* showed a strongly enhanced quenching effect with diazonium salt. However, trace or very mild change of Ru(II)* luminescence in the presence of variable concentration of styrene or thiocyanate salt was observed. These results indicated that a oxidative quenching of Ru(II)* by diazonium salt was involved in the mechanism.

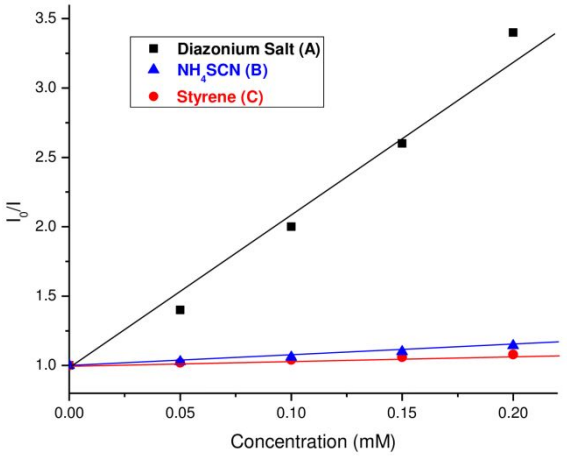
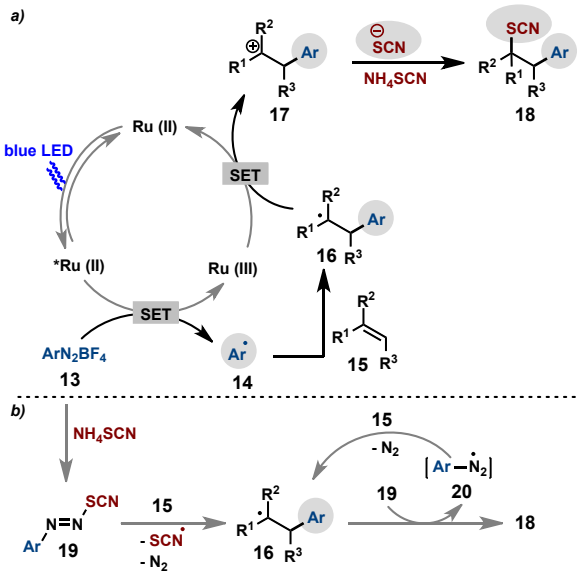


Fig 1. Stern-Volmer plots of $Ru(bpy)_3(PF_6)_2$ quenching with (A) 4-Methoxybenzene diazonium tetrafluoroborate, (B) Ammonium thiocyanate and (C) 4-Methyl Styrene. (see the supporting information for details).

Based on the above results and previous reports,[12d-e] a plausible reaction mechanism for the present photocatalyzed arylthiocyanation is proposed in Scheme 7a. Irradiation of Ru(II) with visible light yields a photoexited *Ru(II), which reduces aryldiazonium salt **13** to aryl radical **14** via single electron transfer (SET) process and itself oxidises to Ru(III). Addition of the aryl radical to olefin generates a new radical intermediate **16**, which is further oxidized by Ru(III) to give a carbenium ion intermediate[30] **17** and regenerating the photocatalyst. Finally, **17** in presence of NH_4SCN furnishes the arylated alkylthiocyanate product **18**. The key to the success of this reaction is rely on efficient single electron oxidation of the radical intermediate **16** to the corresponding cation **17**, which is relatively easy for aryl radical added styrenes, but not for acrylates (bezylic radical *vs* acrylate radical). However an alternative mechanism can be envisioned (Scheme 7b), where this oxidation scenario can be avoided.[12i-k, 31] In this path the SCN group is transferred to the adduct radical **16** from aryldiazo thiocyanate **19** present in the reaction mixture. Meanwhile the aryldiazenyl radical **20**, which is subsequently generated during thiocyanate transfer step, then further propagates the radical chain.

Scheme 7. Plausible reaction mechanism



CONCLUSIONS

In summary, we have developed a photoredox-catalyzed intermolecular radical arylthiocyanation of alkenes with arenediazonium salts and NH_4SCN to construct both C-C and C-S bonds simultaneously. The method is mild (visible light, room temperature), operationally simple and exhibits broad substrate scope with excellent functional group compatibility. Furthermore, β-aryl alkylselenocyanates were also synthesized using the developed protocol with potassium selenocyanate.

EXPERIMENTAL SECTION

General Information.

All commercially available chemicals and reagents were used without any further purification unless otherwise stated. All reactions were carried out in oven-dried glassware under argon or nitrogen atmosphere with freshly distilled anhydrous solvents.[32] Photoreactions were carried out in borosilicate made reaction tube using blue light source (PAR38 12W blue LED bulb). The progress of the reaction was monitored by thin layer chromatography (TLC) using silica gel Alumini-um Sheet (Merck, TLC Silica gel 60 F254). All compounds were purified through column chromatography using silica gel (230 – 400 mesh). Nuclear magnetic resonance spectra were recorded on, Bruker Avance II 400, Bruker Avance III 400, Bruker Avance III 500 and Jeol 400YH instruments. Chemical shifts (δ) are quoted in ppm relative to residual solvent signals, $CDCl_3$ referenced at δ 7.26 ppm for ^1H and 77.16 ppm for $^{13}C\{^1H\}$. TMS are used as internal standard and Coupling constants (*J*) are quoted in hertz (Hz). Multiplicity is reported with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets. HRMS were recorded using a QTOF micro MS system by ESI technique. Elemental (CHN) analyses were carried out in PerkinElmer CHNS/O analyzer (Model no-2400, series II). GC-MS analysis was done by Thermo Scientific ISQ QD single quadrupole GC-MS system using a TG-5MS column (30 m x 0.25 mm x 0.25 μm). Fluorescence quenching experiments were performed using a PerkinElmer LS 55 Fluorescence Spectrometer. Melting points (°C) are uncorrected.

General Procedure for Preparation of Aryl Diazonium Tetrafluoroborates.[33] **Method A:** In a 50 ml round bottom flask, the aniline (5.0 mmol) was dissolved in a mixture of distilled water (1 ml) and an aqueous solution of fluoroboric acid (50% in water, 1.9 ml) in rt. The mixture was cooled to 0°C with an ice bath and a solution of sodium nitrite (0.68 g in 1 ml water) was added dropwise. After addition the reaction mixture was stirred at 0°C for 1h. A thick precipitate was formed, collected by filtration and dissolved in minimum amount of acetone. Then diazonium salt was reprecipitated by the addition of diethyl ether. The aryl diazonium salt was filtered, washed three times with diethyl ether and dried in vacuo and used directly without further purification.

Method B: In a 50 ml round bottom flask, the aniline (5 mmol) was dissolved in a mixture of absolute ethanol (2 mL) and an aqueous solution of fluoroboric acid (50%, 1.9 ml). The mixture was cooled to 0°C with an ice bath and tert-butyl nitrite (1.4 ml) was added dropwise. After addition the reaction mixture was stirred at 0°C for 30 min and another 1h at rt. Then diethyl ether (20 ml) was added to precipitate the diazonium salt. The thick precipitate was filtered off and washed three times with diethyl ether. Then diazonium salt was dried in vacuo and used directly without further purification.

General Procedure of Photoredox-Catalysed Arylthiocyanation of Alkene: A culture tube equipped with magnetic stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (3.5 mg, 0.004 mmol, 2 mol%), aryldiazonium tetrafluoroborate (0.2 mmol) and degassed acetonitrile (2 ml). The tube was sealed with a Teflon screw cap, before styrene (0.4 mmol) and ammonium thiocyanate (0.6 mmol) were added to it. Then the orange reaction mixture was degassed with argon and irradiated at rt with a 12W blue LED bulb at a distance of app. 8 cm for 6h. A high-speed fan was used to maintain the temperature. After the reaction was complete, the mixture was filtered through a short pad of silica gel and eluted with Et_2O (10 mL). The solution was concentrated and the residue was purified by column chromatography on silica gel (EtOAc in petroleum ether) to afford the corresponding product.

Characterization Data of Products: *1–Methoxy–4-(2–phenyl–2-thiocyanatoethyl) benzene (**3a**).* Pale yellow gummy solid; 74% yield (39 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.39 – 7.30 (m, 5H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.51 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.37 (d, *J* = 7.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* (ppm): 158.9, 138.1, 130.3, 129.2, 129.1, 128.8, 127.8, 114.1, 111.8, 55.5, 55.3, 41.4; Anal. Calcd for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20%; Found: C, 71.17; H, 5.58; N, 5.36%.

*1-Methoxy-4- (2-thiocyanato-2- (p-tolyl)ethyl) benzene (**3b**).* Pale yellow viscous liquid; 76% yield (43 mg); R_f value = 0.6 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.21 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.50 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.36 (d, *J* = 7.7 Hz, 2H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* (ppm): 158.8, 139.0, 135.0, 130.3, 129.8, 129.0, 127.7, 114.1, 112.0, 55.4, 55.3, 41.3, 21.3; HRMS (ESI) *m/z* Calcd for $C_{17}H_{17}NOSNa$ $[M+Na]^+$: 306.0929; Found: 306.0926.

*4,4'-(1-Thiocyanatoethane-1,2-diyl)bis (methoxybenzene) (**3c**).* Pale yellow viscous liquid; 87% yield (52 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.15 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.85 – 4.81(m, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.14 – 3.04 (m, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* (ppm): 159.6, 158.9, 130.7, 128.3, 127.5, 114.2, 114.0, 63.1, 55.4, 55.3, 44.9; HRMS (ESI) *m/z* Calcd for $C_{17}H_{21}N_2O_2S$ $[M+NH_4]^+$: 317.1324; Found: 317.1326.

*1,2-Dimethoxy-4- (2-(4-methoxyphenyl)-1- thiocyanato ethyl) benzene (**3d**).* Pale yellow viscous liquid; 70% yield (46 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:4 (v/v)]; ^1H NMR (500 MHz, $CDCl_3$) *δ* (ppm): 7.01 (d, *J* = 8.6 Hz, 2H), 6.82 (dd, *J* = 8.5, 2.2 Hz, 3H), 6.77 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 4.82 (dd, *J* = 7.6, 6.0 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 3.10 (dd, *J* = 9.7, 6.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* (ppm): 158.9, 149.1, 149.0, 131.1, 130.8, 128.3, 118.6, 114.0, 111.1, 109.3, 63.4, 56.1, 55.4, 44.9; Anal. Calcd for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25%; Found: C, 66.02; H, 5.57; N, 4.12%.

*1-Fluoro-4- (2-(4-methoxyphenyl)-1- thiocyanatoethyl) benzene (**3e**).* Pale yellow gummy solid; 82% yield (47 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.31 – 7.28 (m, 2H), 7.07 – 6.99 (m, 4H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.51 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.33 (dd, *J* = 7.7, 5.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* (ppm): 162.9 (d, *J* = 248.8 Hz), 158.9, 134.0 (d, *J* = 3.3 Hz), 130.3, 129.6(d, *J* = 8.6 Hz), 128.5, 116.2 (d, *J* = 21.8 Hz), 114.2, 111.6, 55.3, 54.7, 41.4; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -111.9 (s, 1F); Anal. Calcd for $C_{16}H_{14}FNOS$: C, 66.88; H, 4.91; N, 4.87%; Found: C, 66.79; H, 4.62; N, 4.92%.

*1-Bromo-4- (2-(4-methoxyphenyl)-1- thiocyanatoethyl) benzene (**3f**).* Pale yellow viscous liquid; 79% yield (55 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.49 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.47 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.32 (dd, *J* = 7.7, 4.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) *δ* (ppm): 159.0, 137.2, 132.3, 130.3, 129.4, 128.3, 123.1, 114.2, 111.4, 55.3, 54.7, 41.1; Anal. Calcd for $C_{16}H_{14}BrNOS$: C, 55.18; H, 4.05; N, 4.02%; Found: C, 55.39; H, 3.63; N, 3.92%.

*1-Chloro-4- (2-(4-methoxyphenyl)-1- thiocyanatoethyl) benzene (**3g**).* Pale yellow solid; mp: 75 – 77 °C; 81% yield (49 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.25 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 4.40 (t, *J* = 7.7 Hz, 1H), 3.69 (s, 3H), 3.24 (dd, *J* = 7.7, 4.6 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.0, 136.7, 134.9, 130.3, 129.4, 129.2, 128.4, 114.2, 111.4, 55.3, 54.6, 41.2; Anal. Calcd for $C_{16}H_{14}ClNOS$: C, 63.25; H, 4.64; N, 4.61%; Found: C, 62.96; H, 4.42; N, 4.51%.

*1-Chloro-3- (2-(4-methoxyphenyl)-1- thiocyanatoethyl) benzene (**3h**).* Pale yellow viscous liquid; 79% yield (48 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 – 7.30 (m, 3H), 7.22 – 7.19 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.46 (t, *J* = 7.7 Hz, 1H), 3.78 (s, 3H), 3.32 (d, *J* = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.0, 140.2, 135.0, 130.4, 130.3, 129.3, 128.3, 127.9, 126.0, 114.3, 111.3, 55.4, 54.7, 41.1; HRMS (ESI) *m/z* Calcd for $C_{16}H_{18}ClN_2OS$ $[M+NH_4]^+$: 321.0828; Found: 321.0827.

*1-Chloro-2- (2-(4-methoxyphenyl)-1- thiocyanatoethyl) benzene (**3i**).* Pale yellow viscous liquid; 77% yield (47 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.35 (td, *J* = 7.6, 1.4 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.98 (t, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 3.39 (d, *J* = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.0, 135.9, 133.8, 130.3, 130.2, 130.0, 128.5, 128.3, 127.7, 114.2, 111.2, 55.4, 50.8, 40.0; Anal. Calcd for $C_{16}H_{14}ClNOS$: C, 63.25; H, 4.64; N, 4.61%; Found: C, 63.05; H, 4.29; N, 4.24%.

*1-(2-(4-Methoxyphenyl)-1- thiocyanatoethyl)-2-nitro benzene (**3j**).* Pale yellow viscous liquid; 73% yield (46 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.99 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.79 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.72 (td, *J* = 7.8, 1.2 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.13 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.24 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.79 (s, 3H), 3.41 (dd, *J* = 15.3, 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.2, 148.1, 134.1, 130.3, 129.7, 128.9, 128.0, 125.6, 114.4, 111.0, 55.4, 48.6, 40.3; HRMS (ESI) *m/z* Calcd for $C_{16}H_{14}N_2O_3SNa$ $[M+Na]^+$: 337.0623; Found: 337.0621.

*4-(2-(4-Methoxyphenyl)-1-thiocyanatoethyl) phenyl acetate (**3k**).* Pale yellow solid; mp: 97 – 99 °C; 84% yield (55 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 4.49 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.34 (d, *J* = 7.7 Hz, 2H), 2.30 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 169.2, 158.9, 151.0, 135.6, 130.3, 128.9, 128.6, 122.3, 114.2, 111.6, 55.3, 54.8, 41.3, 21.2; HRMS (ESI) *m/z* Calcd for $C_{18}H_{17}NO_3SNa$ $[M+Na]^+$: 350.0827; Found: 350.0825.

*1-(Chloromethyl)-4- (2-(4-methoxyphenyl)-1- thiocyana toethyl) benzene (**3l**).* Pale yellow viscous liquid; 49% yield (31 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.58 (s, 2H), 4.51 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.35 (d, *J* = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 158.9, 138.4, 138.3, 130.3, 129.3, 128.6, 128.2, 114.2, 111.6, 55.3, 55.0, 45.7, 41.2; HRMS (ESI) *m/z* Calcd for $C_{17}H_{16}ClNOSNa$ $[M+Na]^+$: 340.0539; Found: 340.0541.

*2-(2-(4-Methoxyphenyl)-1- thiocyanatoethyl) naphthalene (**3m**).* Pale yellow solid; mp: 104 – 106 °C; 80% yield (51 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.89 – 7.81 (m, 3H), 7.75 (d, *J* = 1.3 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 4.70 (t, *J* = 7.7 Hz, 1H), 3.76 (s, 3H), 3.47 (dd, *J* = 7.7, 2.0 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 158.9, 135.3, 133.5, 133.2, 130.3, 129.3, 128.8, 128.3, 127.9, 127.4, 126.9, 126.8, 124.8, 114.9, 111.8, 55.8, 55.3, 41.2; HRMS (ESI) *m/z* Calcd for $C_{20}H_{21}N_2OS$ $[M+NH_4]^+$: 337.1375; Found: 337.1374.

*3-(2-(4-Methoxyphenyl)-1- thiocyanatoethyl) pyridine (**3n**).* Pale yellow viscous liquid; 44% yield (24 mg); R_f value = 0.3 [EtOAc:petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.59 (d, *J* = 4.7 Hz, 1H), 8.53 (d, *J* = 1.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 7.8, 4.9 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.51 (t, *J* = 7.7 Hz, 1H), 3.77 (s, 3H), 3.35 (dd, *J* = 9.7, 8.1 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.1, 150.2, 149.1, 135.2, 134.3, 130.3, 127.9, 124.0, 114.3, 111.0, 55.4, 52.5, 40.9; HRMS (ESI) *m/z* Calcd for $C_{15}H_{15}N_2OS$ $[M+H]^+$: 271.0900; Found: 271.0902.

*1-Fluoro-4- (2-(4-methoxyphenyl)- 1-thiocyanatopropyl) benzene (**3o**).* Pale yellow viscous liquid; 60% yield (36 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (for the mixture) 7.37 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.13 – 7.06 (m, 4H), 6.94 – 6.88 (m, 6H), 6.71 (d, *J* = 8.6 Hz, 2H), 4.47 – 4.44 (m, 2H), 3.82 (s, 3H), 3.73 (s, 3H), 3.38 (dd, *J* = 9.0, 7.1 Hz, 1H), 3.26 (dd, *J* = 10.4, 6.9 Hz, 1H), 1.51 (d, *J* = 6.9 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): (for major isomer) 162.4 (d, *J* = 249.5 Hz), 159.3, 134.2 (d, *J* = 3.5 Hz), 133.4, 130.0, 128.8, 115.7 (d, *J* = 21.6 Hz), 113.9, 111.9, 60.2, 55.3, 44.4, 20.7; (for minor isomer) 161.9 (d, *J* = 249.5 Hz), 158.6, 134.0 (d, *J* = 3.5 Hz), 133.9, 129.9, 128.5, 115.7 (d, *J* = 21.6 Hz), 114.4, 112.0, 60.7, 55.4, 44.9, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.2 (s, 1F); HRMS (ESI) *m/z* Calcd for $C_{17}H_{16}FNOSNa$ $[M+Na]^+$: 324.0834; Found: 324.0835.

*(1-(4-Methoxyphenyl)-2- thiocyanatoethane-1,2-diyl) di benzene (**3p**).* Pale yellow viscous liquid; 58% yield (40 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): (for the mixture) 7.45 (d, *J* = 7.2 Hz, 2H), 7.39 – 7.34 (m, 8H), 7.31 – 7.27 (m, 6H), 7.25 – 7.21 (m, 2H), 7.11 (d, *J* = 4.3 Hz, 4H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 5.11 (dd, *J* = 12.0, 9.7 Hz, 2H), 4.53 (dd, *J* = 12.0, 3.4 Hz, 2H), 3.80 (s, 3H), 3.66 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): (for major isomer) 159.2, 140.9, 138.1, 132.7, 129.3, 129.0, 128.9, 128.7, 128.3, 127.8, 126.9, 114.0, 111.6, 58.2, 55.9, 55.2; (for minor isomer) 158.3, 140.9, 138.1, 132.6, 129.1, 128.9, 128.8, 128.7, 128.1, 127.8, 126.9, 114.5, 111.7, 58.6, 55.9, 55.4; HRMS (ESI) *m/z* Calcd for $C_{22}H_{19}NOSNa$ $[M+Na]^+$: 368.1085; Found: 368.1087.

*(E)-1-Methoxy-4-(4-phenyl- 2-thiocyanatobut-3-en-1-yl) benzene (**3q**).* Pale yellow viscous liquid; 42% yield (25 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:19 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 – 7.28 (m, 5H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.60 (dd, *J* = 15.7, 1.2 Hz, 1H), 6.12 (dd, *J* = 15.8, 6.3 Hz, 1H), 4.53 (qd, *J* = 6.6, 1.3 Hz, 1H), 3.81 (s, 3H), 3.01 (d, *J* = 6.7 Hz, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.0, 135.8, 132.3, 130.8, 128.8, 128.4, 128.1, 126.8, 126.0, 114.2, 61.5, 55.4, 42.8; HRMS (ESI) *m/z* Calcd for $C_{18}H_{17}NOSNa$ $[M+Na]^+$: 318.0929; Found: 318.0927.

*3-(4-Methoxyphenyl)-2- thiocyanato propanenitrile (**3r**).* Pale yellow viscous liquid; 64% yield (28 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.04 – 4.01 (m, 1H), 3.82 (s, 3H), 3.37 – 3.23 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 160.0, 130.6, 125.3, 115.8, 114.8, 107.9, 55.5, 38.6, 37.1; HRMS (ESI) *m/z* Calcd for $C_{11}H_{10}N_2OSNa$ $[M+Na]^+$: 241.0412; Found: 241.0462.

*tert-Butyl 3-(4-methoxyphenyl)-2-thiocyanatopropanoate (**3s**).* Pale yellow viscous liquid; 44% yield (26 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:19 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.15 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.84 (d, J = 7.4 Hz, 1H), 3.80 (s, 3H), 3.21 (ddd, J = 60.6, 14.3, 7.4 Hz, 2H), 1.45 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 167.4, 159.1, 130.4, 127.5, 114.1, 110.2, 84.0, 55.3, 51.6, 37.1, 27.8; HRMS (ESI) *m/z* Calcd for $C_{15}H_{23}N_2O_3S$ $[M+NH_4]^+$: 311.1429; Found: 311.1427.

*Methyl 3-(4-methoxyphenyl)-2-methyl-2-thiocyanato propanoate (**3t**).* Pale yellow viscous liquid; 60% yield (32 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.10 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 3.79 (s, 3H), 3.79 (s, 3H), 3.25 (q, J = 14.2 Hz, 2H), 1.76 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 170.8, 159.2, 131.1, 126.5, 113.9, 111.0, 61.0, 55.2, 53.4, 44.1, 24.9; HRMS (ESI) *m/z* Calcd for $C_{13}H_{15}NO_3SNa$ $[M+Na]^+$: 288.0670; Found: 288.0668.

*(E)-1-(4-Methoxystyryl) pyrrolidin-2-one (**3u**).*[34] White solid; mp: 104 – 106 °C; 53% yield (23 mg); R_f value = 0.3 [EtOAc:petroleum ether = 3:7 (v/v)]; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J = 14.9 Hz, 1H), 7.28 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.85 (d, J = 14.8 Hz, 1H), 3.80 (s, 3H), 3.64 (t, J = 7.2 Hz, 2H), 2.53 (t, J = 8.2 Hz, 2H), 2.18 – 2.12 (m,2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 173.2, 158.5, 129.0, 126.8, 122.1, 114.2, 111.5, 55.3, 45.3, 31.3, 17.5; HRMS (ESI) *m/z* Calcd for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 240.1000; Found: 240.0989.

*4-(2-(4-(Tert-butyl) phenyl)-2- thiocyanatoethyl) benzonitrile (**4a**).* Pale yellow viscous liquid; 70% yield (45 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.1 Hz, 4H), 4.52 (t, J = 7.7 Hz, 1H), 3.57 – 3.46 (m, 2H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 152.7, 142.3, 133.9, 132.5, 130.1, 127.3, 126.8, 126.3, 118.7, 111.4, 54.0, 42.1, 34.8, 31.3; HRMS (ESI) *m/z* Calcd for $C_{20}H_{20}N_2SNa$ $[M+Na]^+$: 343.1245; Found: 343.1246.

*1-(Tert-butyl)-4-(2-(4-nitrophenyl)-1- thiocyanato ethyl) benzene (**4b**).* Pale yellow viscous liquid; 57% yield (39 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.55 (t, J = 7.7 Hz, 1H), 3.63 – 3.51 (m, 2H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 152.8, 147.3, 144.4, 133.7, 130.2, 127.3, 126.4, 124.0, 111.4, 54.0, 41.9, 34.9, 31.3; HRMS (ESI) *m/z* Calcd for $C_{19}H_{20}N_2O_2SNa$ $[M+Na]^+$: 363.1143; Found: 363.1148.

*1-(Tert-butyl)-4- (2-(4-methoxyphenyl)-1- thiocyanato ethyl) benzene (**4c**).* Pale yellow viscous liquid; 75% yield (49 mg); R_f value = 0.6 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 5.8 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.48 (t, J = 7.6 Hz, 1H), 3.77 (s, 3H), 3.36 (d, J = 8.0 Hz, 2H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 158.9, 152.2, 135.2, 130.4, 129.1, 127.4, 126.1, 114.1, 112.0, 55.5, 55.4, 41.3, 34.8, 31.4; Anal. Calcd for $C_{20}H_{23}NOS$: C, 73.81; H, 7.12; N, 4.30%; Found: C, 74.19; H, 7.06; N, 4.37%.

*4-(2-(4-(Tert-butyl) phenyl)-2- thiocyanatoethyl)-1,1'-biphenyl (**4d**).* Pale yellow gummy solid; 72% yield (54 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (d, J = 7.1 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.45 – 7.39 (m, 4H), 7.35 (d, J = 7.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.57 (t, J = 7.7 Hz, 1H), 3.48 (d, J = 7.7 Hz, 2H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 152.2, 140.6, 140.2, 136.1, 135.0, 129.7, 128.9, 127.5, 127.4, 127.1, 126.1, 111.9, 55.0, 41.6, 34.8, 31.4; HRMS (ESI) *m/z* Calcd for $C_{25}H_{25}NSNa$ $[M+Na]^+$: 394.1606; Found: 394.1603.

*1-(Tert-butyl)-4- (1-thiocyanato-2- (4-(trifluoromethyl) phenyl) ethyl) benzene (**4e**).* Pale yellow solid; mp: 78 – 80 °C; 62% yield (45 mg); R_f value = 0.6 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 7.24 (dd, J = 8.2, 3.9 Hz, 4H), 4.52 (t, J = 7.6 Hz, 1H), 3.51 (dd, J = 7.6, 2.3 Hz, 2H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 152.6, 141.0, 134.3, 129.9 (q, J = 34.0 Hz), 129.7, 127.3, 127.2 (q, J = 276.0 Hz), 126.3, 125.7(q, J = 4.0 Hz), 111.6, 54.4, 41.8, 34.9, 31.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4(s, 3F); HRMS (ESI) *m/z* Calcd for $C_{20}H_{20}F_3NSNa$ $[M+Na]^+$: 386.1166; Found: 386.1164.

*1-(2-(4-(tert-Butyl) phenyl)- 2-thiocyanatoethyl)-2-methoxybenzene (**4f**).* Pale yellow viscous liquid; 38% yield (25 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:19 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.10 (dd, J = 7.6, 1.6 Hz, 1H), 6.89 – 6.86 (m, 2H), 4.72 (t, J = 7.6 Hz, 1H), 3.83 (s, 3H), 3.43 – 3.31 (m, 2H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 157.7, 151.8, 136.1, 131.3, 128.8, 127.3, 125.9, 125.4, 120.6, 112.3, 110.5, 55.4, 53.5, 37.3, 34.8, 31.4; HRMS (ESI) *m/z* Calcd for $C_{20}H_{23}NOSNa$ $[M+Na]^+$: 348.1398; Found: 348.1394.

*1-(3-(2-(4-(Tert-butyl)phenyl)-2- thiocyanatoethyl) phenyl) ethan-1-one (**4g**).* Pale yellow solid; mp: 57 – 59 °C; 56% yield (38 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.82 (d, J = 7.3 Hz, 1H), 7.64 (s, 1H), 7.39 – 7.34 (m, 4H), 7.25 (d, J = 8.6 Hz, 2H), 4.54 (t, J = 7.7 Hz, 1H), 3.50 (dd, J = 7.6, 2.1 Hz, 2H), 2.52 (s, 3H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 197.8, 152.4, 137.4, 137.3, 134.4, 133.9, 129.0, 128.9, 127.3, 126.1, 111.5, 54.5, 41.9, 34.7, 31.2, 26.6; HRMS (ESI) *m/z* Calcd for $C_{21}H_{23}NOSNa$ $[M+Na]^+$: 360.1398; Found: 360.1396.

*5-(2-(4-(Tert-butyl) phenyl)-2- thiocyanatoethyl) benzo [d][1,3]dioxole (**4h**).* Pale yellow viscous liquid; 62% yield (42 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 6.7 Hz, 2H), 6.70 (d, J = 8.5 Hz, 1H), 6.59 (d, J = 6.7 Hz, 2H), 5.92 (s, 2H), 4.47 (t, J = 7.6 Hz, 1H), 3.33 (d, J = 7.4 Hz, 2H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 152.3, 147.9, 146.9, 135.0, 130.7, 127.4, 126.1, 122.6, 111.9, 109.5, 108.5, 101.2, 55.4, 41.8, 34.8, 31.4; HRMS (ESI) *m/z* Calcd for $C_{20}H_{21}NO_2SNa$ $[M+Na]^+$: 362.1191; Found: 362.1194.

*3-(2-(4-(Tert-butyl) phenyl)-2-thiocyanatoethyl) quinoline (**4i**).* Pale yellow gummy solid; 55% yield (38 mg); R_f value = 0.4 [EtOAc:petroleum ether = 3:7 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.64 (d, J = 2.2 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 1.9 Hz, 1H), 7.75 – 7.67 (m, 2H), 7.54 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.62 (t, J = 7.6 Hz, 1H), 3.65 (dd, J = 7.6, 3.8 Hz, 2H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm): 152.7, 151.4, 147.4, 136.2, 133.9, 129.8, 129.7, 129.3, 127.9, 127.7, 127.4, 127.2, 126.4, 111.6, 54.4, 39.5, 34.8, 31.3; HRMS (ESI) *m/z* Calcd for $C_{22}H_{23}N_2S$ $[M+H]^+$: 347.1577; Found: 347.1575.

*1-(Tert-butyl)-4-(2- (4-methoxyphenyl)-1- selenocyanatoethyl) benzene (**5a**).* Pale yellow viscous liquid; 67% yield (50 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.80 (t, J = 7.8 Hz, 1H), 3.77 (s, 3H), 3.48 (t, J = 7.3 Hz, 2H), 1.31 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ (ppm): 158.8, 152.0, 136.0, 130.1, 127.4, 126.0, 116.0, 114.0, 102.6,

55.5, 52.9, 41.8, 34.7, 31.2; HRMS (ESI) *m/z* Calcd for $C_{20}H_{23}NOSeNa$ $[M+Na]^+$: 396.0844; Found: 396.0842.

*1-Bromo-3-(2-(4-methoxyphenyl)-1- selenocyanato ethyl) benzene (**5b**).* Pale yellow viscous liquid; 57% yield (45 mg); R_f value = 0.4 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.49 (t, *J* = 1.7 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.29 – 7.26 (m, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.72 (t, *J* = 7.9 Hz, 1H), 3.78 (s, 3H), 3.43 (dd, *J* = 7.9, 5.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 158.9, 141.0, 132.0, 130.8, 130.6, 130.0, 128.9, 126.5, 123.0, 114.2, 101.8, 55.3, 51.6, 41.5; HRMS (ESI) *m/z* Calcd for $C_{16}H_{14}BrNOSeNa$ $[M+Na]^+$: 417.9322; Found: 417.9317.

*1-(2-(4-Bromophenyl)-1-selenocyanatoethyl)-2-chloro benzene (**5c**).* Pale yellow solid; mp: 129 – 131 °C; 46% yield (37 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.51 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.39 (m, 3H), 7.33 (td, *J* = 7.6, 1.0 Hz, 1H), 7.27 (ddd, *J* = 7.6, 5.7, 1.6 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 5.11 (t, *J* = 7.9 Hz, 1H), 3.56 (dd, *J* = 7.9, 2.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 136.2, 136.2, 133.5, 131.9, 130.7, 130.2, 129.9, 128.1, 127.6, 121.4, 101.3, 47.3, 40.9; HRMS (ESI) *m/z* Calcd for $C_{15}H_{15}BrClN_2Se$ $[M+NH_4]^+$: 416.9262; Found: 416.9260.

*1-(2-(4-Methoxyphenyl)- 1-selenocyanatoethyl)- 2-nitro benzene (**5d**).* Pale yellow viscous liquid; 48% yield (35 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.01 (d, *J* = 8.1 Hz, 1H), 7.72 (dt, *J* = 15.0, 7.4 Hz, 2H), 7.52 – 7.47 (m, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.21 (t, *J* = 7.8 Hz, 1H), 3.78 (s, 3H), 3.53 (dd, *J* = 7.8, 3.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 159.1, 147.5, 135.7, 134.3, 130.2, 129.5, 129.1, 128.9, 125.8, 114.4, 102.0, 55.4, 46.0, 40.7; HRMS (ESI) *m/z* Calcd for $C_{16}H_{15}N_2O_3Se$ $[M+H]^+$: 363.0249; Found: 363.0246.

*4-(2-Phenyl-2- selenocyanatoethyl)-1,1'-biphenyl (**5e**).* White solid; mp: 94 – 96 °C; 59% yield (43 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.56 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 3.8, 1.6 Hz, 3H), 7.36 – 7.32 (m, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.88 (t, *J* = 7.9 Hz, 1H), 3.60 (dd, *J* = 7.8, 3.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 140.5, 140.2, 138.4, 136.5, 129.5, 129.2, 129.0, 128.8, 127.8, 127.4, 127.0, 102.3, 52.2, 42.3; HRMS (ESI) *m/z* Calcd for $C_{21}H_{17}NSeNa$ $[M+Na]^+$: 386.0424; Found: 386.0416.

*2,2,2-Trifluoroethyl-3-(4-methoxyphenyl)-2- selenocyanato propanoate (**5f**).* Pale yellow viscous liquid: 45% yield (33 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.14 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.53 (qd, *J* = 8.2, 2.3 Hz, 2H), 4.14 (dd, *J* = 8.1, 7.1 Hz, 1H), 3.79 (s, 3H), 3.35 (ddd, *J* = 21.5, 14.5, 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 168.3, 159.3, 130.2, 127.6, 122.5 (q, *J* = 276 Hz), 114.4, 99.2, 61.5 (q, *J* = 37 Hz), 55.3, 45.0, 37.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.4 (s, 3F); HRMS (ESI) *m/z* Calcd for $C_{13}H_{12}F_3NO_3SeNa$ $[M+Na]^+$: 389.9833; Found: 389.9836.

*Tert-butyl-3-(4-methoxyphenyl)-2-selenocyanato propanoate (**5g**).* Pale yellow viscous liquid: 34% yield (23 mg); R_f value = 0.6 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.16 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.09 (dd, *J* = 7.9, 6.6 Hz, 1H), 3.79 (s, 3H), 3.37 – 3.24 (m, 2H), 1.44 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 168.4, 159.0, 130.4, 128.3, 114.1, 100.8, 83.8, 55.3, 48.3, 37.6, 27.8; HRMS (ESI) *m/z* Calcd for $C_{15}H_{19}NO_3SeNa$ $[M+Na]^+$: 364.0428; Found: 364.0426.

*Phenyl-3-(4-methoxyphenyl)-2- selenocyanato propanoate (**5h**).* Pale yellow viscous liquid: 40% yield (29 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 – 7.35 (m, 2H), 7.27 – 7.21 (m, 3H), 7.04 (dd, *J* = 8.6, 1.1 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.32 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.80 (s, 3H), 3.44 (ddd, *J* = 21.1, 14.4, 7.5 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 168.2, 159.3, 150.2, 130.9, 129.6, 127.9, 126.5, 121.1, 114.4, 99.8, 55.3, 46.1, 37.5; HRMS (ESI) *m/z* Calcd for $C_{17}H_{15}NO_3SeNa$ $[M+Na]^+$: 384.0116; Found: 384.0115.

Procedure of gram scale synthesis of compound 4c: A RB flask equipped with magnetic stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (79 mg, 2 mol%), 4-methoxybenzene diazonium tetrafluoroborate 2c (1.02 g, 4.6 mmol) and degassed acetonitrile (46 mL). The flask was sealed with a septum, before 4-tert butyl styrene **1v** (1.68 mL, 9.2 mmol) and ammonium thiocyanate (1.05 g, 13.8 mmol) were added to it. Then the orange reaction mixture was degassed with argon and irradiated at rt with a 12W blue LED bulb at a distance of app. 8 cm for 6h. A high-speed fan was used to maintain the temperature. After the reaction was complete, the mixture was filtered through a short pad of silica gel and eluted with Et_2O (200 mL). The solution was concentrated and the residue was purified by column chromatography on silica gel (EtOAc in petroleum ether) to afford the corresponding product 4c (1.03g, 69%).

*Synthesis of (2-([1,1'-Biphenyl]-4-yl)-1-(4- (tert-butyl) phenyl) ethyl) (trifluoromethyl) sulfane (**6**).* In a 25 ml RB flask with a magnetic stir bar were charged **4d** (74 mg, 0.2 mmol), CH_3CN (3 ml) and Cs_2CO_3 (130 mg, 0.4 mmol). Then $TMSCF_3$ (59 µL, 0.4 mmol) was added at once to the ice-cold reaction mixture and the resulting mixture was stirred at ambient temperature for 2 h. The crude mixture was filtered through a short pad of celite and extracted with DCM (3 × 5.0 mL). The resulting organic phage was washed with water (10 mL) and brine (10 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (230-400 mesh) using EtOAc/petroleum ether as eluent to afforded the corresponding products **6** (52 mg, 63%) as pale-yellow liquid. R_f value = 0.5 [EtOAc:petroleum ether = 1:19 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.41 (m, 5H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.56 (t, *J* = 7.6 Hz, 1H), 3.37 – 3.28 (m, 2H), 1.32 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.0, 140.7, 139.6, 135.1, 131.5 (q, *J* = 308 Hz), 129.6, 128.7, 127.3, 127.2 126.9, 126.3, 125.1, 50.7, 42.9, 34.5, 31.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -39.69 (s, 3F); HRMS (ESI) calcd for $C_{25}H_{25}F_3S$ $[M]^+$: 414.1629; found 414.1625.

*Synthesis of (Z)-3-((1-(4-(Tert-butyl) phenyl)-2-(4-methoxyphenyl) ethyl)thio)-3-phenylacrylonitrile (**7**).* In a 15 ml reaction tube with magnetic stir bar under argon atmosphere were charged $Pd(PPh_3)_4$ (24 mg, 10 mol%), toluene (2 ml), phenyl acetylene (44 µl, 0.4 mmol) and **4c** (65 mg, 0.2 mmol). The reaction mixture was degassed with argon for 10 min. The pressure tube was sealed and heated at 120 °C for 48 h. After completion of reaction, the crude mixture was filtered through Celite bed and concentrated in vacuo. Then the resulting mixture was purified by silica gel column chromatography (230-400 mesh) using EtOAc/petroleum ether as eluent to afforded the corresponding product **7** (71 mg, 83%) as pale-yellow liquid. R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.32 (s,

1H), 4.10 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.06 (ddd, *J* = 22.2, 14.0, 7.6 Hz, 2H), 1.29 (s, 9H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 162.5, 158.4, 150.5, 137.2, 136.7, 130.5, 130.3, 130.2, 128.8, 128.2, 127.4, 125.4, 116.8, 113.7, 97.5, 55.3, 53.9, 42.7, 34.5, 31.3; HRMS (ESI) *m/z* Calcd for $C_{28}H_{29}NOSNa$ $[M+Na]^+$: 450.1868; Found: 450.1866.

Procedure of radical trapping experiment: A culture tube equipped with magnetic stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (3.5 mg, 2 mol%), 4-methoxybenzene diazonium tetrafluoroborate **2c** (45 mg, 0.2 mmol) and degassed acetonitrile (2 mL). The tube was sealed with a Teflon screw cap, before 4-tert butyl styrene **1v** (73 μL, 0.4 mmol), ammonium thiocyanate (46 mg, 0.6 mmol) and TEMPO (94 mg, 0.6 mmol) were added to it. Then the orange reaction mixture was degassed with argon and irradiated at rt with a 12W blue LED bulb at a distance of app. 8 cm for 6h. A high-speed fan was used to maintain the room temperature. After 6h, the reaction mixture was analysed by GC/MS.

Procedure of radical clock experiment: A culture tube equipped with magnetic stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (3.5 mg, 2 mol%), 4-methoxybenzene diazonium tetrafluoroborate **2c** (45 mg, 0.2 mmol) and degassed acetonitrile (2 mL). The tube was sealed with a Teflon screw cap, before α-cyclopropyl-4-chlorostyrene **10** (62 μL, 0.4 mmol), and ammonium thiocyanate (46 mg, 0.6 mmol) were added to it. Then the orange reaction mixture was degassed with argon and irradiated at rt with a 12W blue LED bulb at a distance of app. 8 cm for 6h. A high-speed fan was used to maintain the room temperature. After the reaction was complete, the mixture was filtered through a short pad of silica gel and eluted with Et_2O (10 mL). The solution was concentrated and the residue was purified by column chromatography on silica gel (EtOAc in petroleum ether) to afford the corresponding product **11**.

*1-Chloro-4-(1-(4-methoxyphenyl)-5- thiocyanatopent-2-en-2-yl) benzene (**11**).* Pale yellow viscous liquid; 61% yield (42 mg); R_f value = 0.3 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.25 – 7.22 (m, 4H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 5.85 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 2H), 3.74 (s, 3H), 3.02 (t, *J* = 7.1 Hz, 2H), 2.76 (q, *J* = 7.2 Hz, 2H).; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 158.2, 141.2, 140.7, 133.2, 130.7, 129.1, 128.6, 127.8, 125.5, 114.1, 112.2, 55.3, 35.2, 33.8, 29.4; HRMS (ESI) *m/z* Calcd for $C_{19}H_{18}ClNOSNa$ $[M+Na]^+$: 366.0695; Found: 366.0692.

Procedure of nucleophilic trapping experiment: A culture tube equipped with magnetic stir bar was charged with $Ru(bpy)_3(PF_6)_2$ (3.5 mg, 2 mol%), 4-nitrobenzene diazonium tetrafluoroborate **2b** (47 mg, 0.2 mmol) and degassed acetonitrile (2 mL). The tube was sealed with a Teflon screw cap, before styrene **1a** (46 μL, 0.4 mmol), and MeOH (0.5 mL) were added to it. Then the orange reaction mixture was degassed with argon and irradiated at rt with a 12W blue LED bulb at a distance of app. 8 cm for 6h. A high-speed fan was used to maintain the room temperature. After the reaction was complete, the mixture was filtered through a short pad of silica gel and eluted with Et_2O (10 mL). The solution was concentrated and the residue was purified by column chromatography on silica gel (EtOAc in petroleum ether) to afford the corresponding product **12**.

*1-(2-Methoxy-2-phenylethyl)-4-nitrobenzene (**12**).*[12a] Pale yellow viscous liquid; 64% yield (33 mg); R_f value = 0.5 [EtOAc:petroleum ether = 1:9 (v/v)]; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, *J* = 8.7 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.23 – 7.21 (m, 2H), 4.35 (dd, *J* = 7.7, 5.4 Hz, 1H), 3.19 (s, 3H), 3.20 – 3.16 (m, 1H), 3.03 – 2.99 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm): 146.6, 146.3, 140.7, 130.4, 128.5, 128.0, 126.6, 123.3, 84.1, 56.8, 44.5.

ASSOCIATED CONTENT

Supporting Information

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

Additional screening data, mechanistic experimental details, X-ray crystallographic data for product **3k**, and copies of ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra of all new products.

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Notes

Any additional relevant notes should be placed here.

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