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PAPER

Ruthenium(III)-catalysed phenylselenylation of allyl acetates by diphenyl diselenide and indium(I) bromide in neat: isolation and identification of intermediate†

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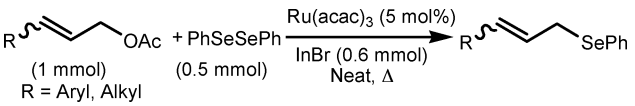
A fast and efficient phenylselenylation of allyl acetates by diphenyl diselenide and indium(I) bromide has been achieved in neat under the catalysis of $Ru(acac)_3$. The intermediate complex of diphenyl diselenide and indium has been isolated and identified as a polymeric pentacoordinated In(III) selenolate complex, $[In(SePh)_3]_n$.

Introduction

Allyl selenides have received considerable attention in recent times because of their importance as versatile synthetic intermediates.[1] Allyl selenides undergo [2,3] sigmatropic rearrangement under a variety of conditions to provide allylic amines,[2] halides[3] and alcohols.[4] The organic selenium compounds also display significant potential as anticancer and antioxidant agents.[5] Thus, development of efficient procedures for the synthesis of allyl selenides are of much importance. The traditional method for their synthesis involves a nucleophilic substitution of allyl halides with phenylseleno anion.[1,6] However, easily accessible, moderately active and configurationally stable[7] allyl acetates are more attractive. Surprisingly, only a limited number of methods using allyl acetates are available. Huang *et al.*[8] reported phenylselenylation of allyl acetates by phenyl selenium bromide using $Pd(PPh_3)_4$ and SmI_2 although the yields of products are not satisfactory (47–58%). A similar method using diphenyl diselenide in presence of $Pd(PPh_3)_4/SmI_2$ showed some improvement (47–84% yields).[9] However, a major drawback of this reaction is the loss of one equivalent of $PhSe^-$ as waste. The methods using diphenyl diselenide in presence of $La/Me_3SiCl/I_2/CuI$ in CH_3CN[10a] and $PhSeSiMe_3$ in the presence of ZnI_2[10b] had several disadvantages with regard to efficiency (low yield), environmental acceptability using toxic solvents like CH_3CN and benzene and generality (only 3 examples). Thus, a convenient and efficient procedure for the synthesis of allyl phenyl selenides is highly desirable. Recently Tunge[11] reported an elegant synthesis of chiral cyclohexenyl phenyl selenides through palladium catalyzed decarboxylative coupling. In this paper we report a coupling of allyl acetate and diphenyl diselenide in the presence of InBr and $Ru(acac)_3$ in neat (Scheme 1) to provide allyl phenyl selenide.



Scheme 1 Phenylselenylation of allyl acetates.

Results and discussion

To optimize the reaction conditions, a series of experiments were carried out for a representative reaction of cinnamyl acetate and diphenyl diselenide under varying reaction parameters such as catalyst, solvent, reaction temperature etc (Table 1). It was found that a combination of $Ru(acac)_3$ and InBr in neat provides a fast and efficient reaction (Table 1, entry 11). Other ruthenium catalysts such as $RuCl_3$ (Table 1, entry 1), $RuCl_2(PPh_3)_3$ (Table 1, entry 14), $[Ru(CO)_3Cl_2]_2$ (Table 1, entry 15), $[(C_6H_6)RuCl_2]_2$ (Table 1, entry 16), $Ru_3(CO)_{12}$ (Table 1, entry 17) and Ru(0) nanoparticles (Table 1, entry 2) are not very efficient. Although the Ru(II) catalysts (Table 1, entries 14, 15 and 16) are moderately active, the Ru(0) catalysts (Table 1, entries 2 and 17) are less active. The use of solvents has a retarding effect on this reaction. Only THF leads to a relatively good yield (36%). Other reducing agents to cleave diphenyl diselenide such as Zn dust and InI are also not as efficient as InBr. The amount of $Ru(acac)_3$ for an efficient reaction has also been optimized to 5 mol%.

Thus, in a typical experimental procedure a mixture of allyl acetate, diphenyl diselenide, InBr and $Ru(acac)_3$ was heated at 60–80 °C for a period of time as required to complete the reaction (TLC). Standard work-up followed by purification by column chromatography provided the pure product.

A series of substituted cinnamyl acetates underwent coupling with diphenyl diselenide by this procedure to produce the corresponding selenides. The results are summarized in Table 2. For

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† Electronic supplementary information (ESI) available: ^1H NMR and ^{13}C NMR spectra of all allyl selenides listed in Table 2. See DOI: 10.1039/c0ob00317d

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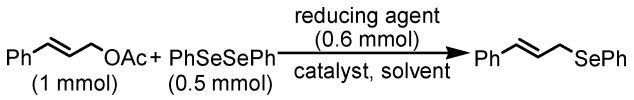
Table 1 Standardisation of reaction conditions



Entry	Reducing agent	Catalyst	Solvent	Temp. (°C)	Time	Yield[a] (%)
1	InBr	$RuCl_3$	THF	66	15 h	Trace
2	InBr	Ru NP[b]	THF	66	15 h	0
3	InBr	$Ru(acac)_3$	THF	66	15 h	36
4	InI	$Ru(acac)_3$	THF	66	15 h	22
5	Zn dust	$Ru(acac)_3$	THF	66	15 h	10
6	InBr	$Ru(acac)_3$	Dioxane	100	15 h	25
7	InBr	$Ru(acac)_3$	DMF	120	15 h	10
8	InBr	$Ru(acac)_3$	Toluene	100	15 h	13
9	InBr	$Ru(acac)_3$	Neat	100	5 h	62
10	InBr	$Ru(acac)_3$	Neat	80	10 min	77
11	**InBr**	**$Ru(acac)_3$**	**Neat**	**60**	**10 min**	**90**[c]
12	InBr	$Ru(acac)_3$	Neat	rt	48 h	55
13	InBr	—	Neat	60	5 h	35[d]
14	InBr	$RuCl_2(PPh_3)_3$	Neat	60	10 min	61
15	InBr	$[Ru(CO)_3Cl_2]_2$	Neat	60	10 min	58
16	InBr	$[(C_6H_6)RuCl_2]_2$	Neat	60	10 min	55
17	InBr	$Ru_3(CO)_{12}$	Neat	60	10 min	38

[a] Isolated yields of pure products. [b] Ru NP = Ru nanoparticles prepared by reducing $RuCl_3$ by $NaBH_4$ in MeOH. [c] 5 mol% of $Ru(acac)_3$ was optimised to give the best result. [d] Reaction was performed in absence of $Ru(acac)_3$.

1 equivalent of allyl acetate 0.5 equivalent of PhSeSePh was required for a complete reaction and thus two SePh moieties were consumed making this reaction more atom economic. Both electron-donating and electron-withdrawing substituents on the aromatic ring are compatible with this reaction although the electron-withdrawing substituted compounds took much longer time [Table 2, entries 3 (120 min) and 4 (90 min)].

The reactions of all aryl substituted allyl acetates were accomplished at 60–80 °C within 5–20 mins (except those in entries 3 and 4, Table 2) by conventional heating whereas the reactions of alkyl substituted allyl acetates remained incomplete by conventional heating even for a prolonged period. However, microwave heating produced much better results (Table 3). Thus reactions of all alkyl substituted allyl acetates were carried out under microwave irradiation. All linear and branched (Table 2, entries 9 and 15) allyl acetates provided exclusively linear allyl phenyl selenides through nucleophilic addition by organoselenium species from the less hindered side. The *trans*-allyl acetates except crotyl acetate (Table 2, entry 14) produced stereoselectively *trans*-selenides, while *cis*-allyl acetates led to a mixture of *cis* and *trans* with predominating *trans* isomer. Benzyl acetate having a partial allylic character was also phenylselenylated efficiently (Table 2, entry 10).

In general, the reactions are clean and fast. The products are obtained in high yields with good purity. Several functional groups such as OMe, NO_2, COMe, Cl, I are compatible with this reaction. The reaction is uniform with *o*-, *m*-, and *p*- substituted aryl allyl acetates. The palladium catalysts frequently used for the phenylselenylation are prone to selenium poisoning. However, the ruthenium catalyst used here is free from this drawback. To the best of our knowledge this is the first report of use of Ru-catalyst in phenylselenylation of allyl acetate, although Yu *et al.*[18] reported phenylselenylation of alkyl halides including allyl bromide (one example) by diphenyl diselenide using Zn dust and $RuCl_3$. Interestingly, there are several reports of phenylselenylation of alkyl halides including allyl bromides with diphenyl diselenide using Zn dust only (for the cleavage of PhSeSePh) and without the use of any transition metal catalyst including Ru.[19] Being curious we repeated the phenylselenylation of allyl bromide by diphenyl diselenide under Yu's condition using Zn dust only and without $RuCl_3$. The reaction goes remarkably well giving 91% conversion. On the other hand, the reactions of allyl acetates and diphenyl diselenide did not go efficiently in absence of Ru-catalyst.

To understand the reaction pathway we considered isolation of the intermediate. As the reaction proceeds very fast in neat we have not been able to isolate any intermediate. However, as the reaction proceeds in THF giving 36% yield (Table 1, entry 3) we decided to check the reaction of cinnamyl acetate and diphenyl diselenide in presence of InBr/$Ru(acac)_3$ in THF. We are successful to isolate a highly polar pale yellow solid from the reaction mixture. The NMR spectrum revealed the presence of aromatic protons. The X-Ray crystallographic analysis showed a polymeric pentacoordinated indium-selenolate complex, $[In(SePh)_3]_n$, where each indium center remains in a trigonal bipyramidal environment with one terminal SePh and two bridging SePh groups (Fig. 1).[20] This complex on reaction with cinnamyl acetate in presence of $Ru(acac)_3$/InBr under identical reaction conditions produced the cinnamyl phenyl selenide in comparably high yield. Thus, this observation unequivocally established the intermediacy of $[In(SePh)_3]_n$ in this reaction. Nevertheless, this intermediate transfers SePh anion to allyl acetates in this reaction and this complex was formed by the interaction of PhSeSePh and InBr under the reaction conditions. In all reports[14,21] of In(I)-mediated cleavage of PhSeSePh, $In(SePh)_2I$ has been suggested as possible intermediate and our results vacated this prediction and settled this issue once for all.

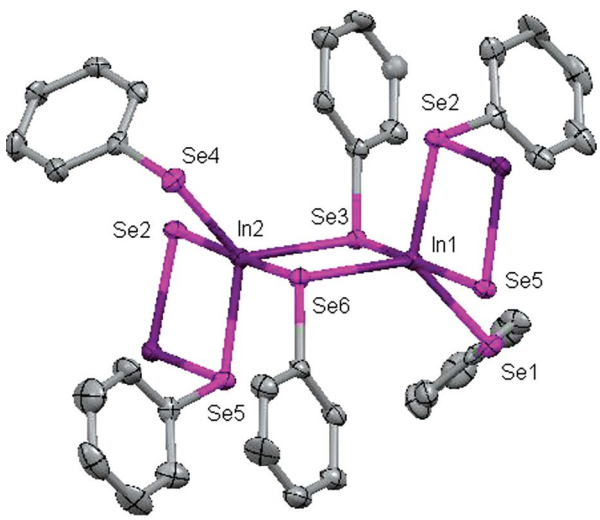


Fig. 1 Molecular view of intermediate $[In(SePh)_3]_n$.

To investigate the mechanism we carried out this reaction in presence of TEMPO (Tetramethyl piperidine *N*-oxide) keeping other reaction parameters unaltered. A marginal effect on rate of conversion and yield was observed. Thus, it is unlikely that the reaction is going through a radical pathway.

We propose an oxidative addition of Ru(II), generated *in situ* by the reduction of Ru(III) by InBr,[22] to allyl acetate resulting to a

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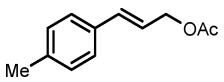
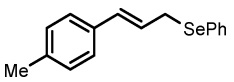
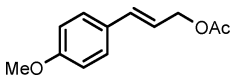
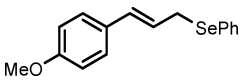
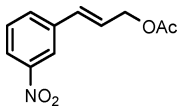
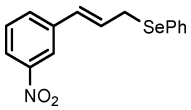
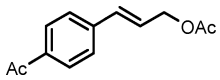
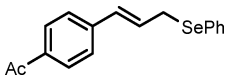
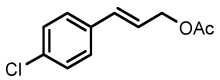
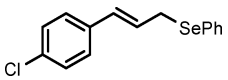
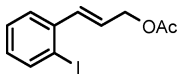
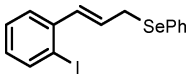
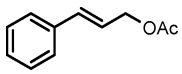
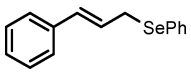
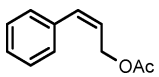
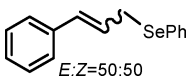
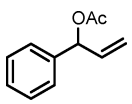
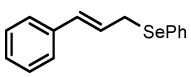
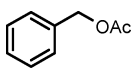
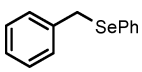
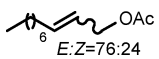
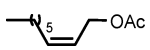
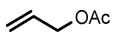
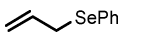
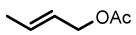
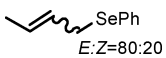
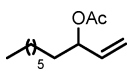
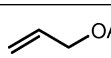
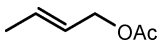
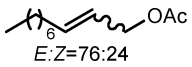
Table 2 Synthesis of allyl phenyl selenides

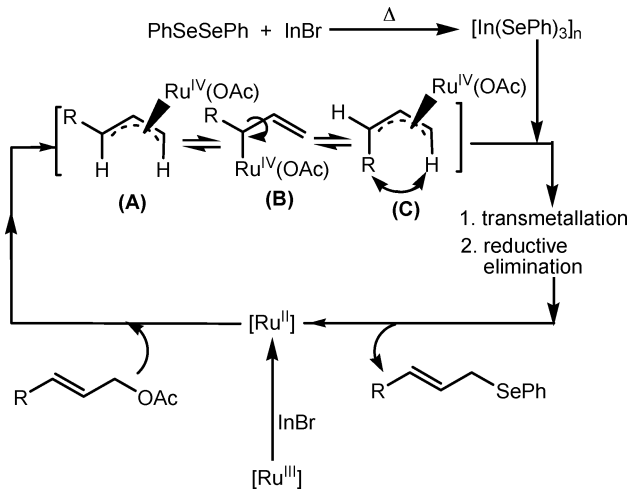
Entry	Allyl acetates	Product	Time (min)	Temp. (°C)	Yield[a] (%)	Ref.
1			5	60	70	
2			5	60	71	12
3			120	80	80	
4			90	80	81	
5			20	60	75	13
6			20	60	78	
7			10	60	90	14
8			10	60	85	15
9			20	70	70	14
10[b]			10	80	92	14
11[b]			20	100	75	16
12[b]			20	100	72	17
13[b,c]			20	95	93	14
14[b]			20	100	94	14
15[b]			25	100	63	16

[a] Isolated yields of pure products. [b] Microwave irradiation at 200 watt. [c] Allyl acetate was used in 2 equivalents.

η^3-π-allyl complex, **A** or **C** which undergoes very fast transmetallation with $[In(SePh)_3]_n$ followed by reductive elimination to give the product (Scheme 2). The catalytic cycle involving Ru(II) to Ru(IV) is very common in Ru catalyzed allylation reactions.[23] Our hypothesis of involvement of *in situ* generated Ru(II) in the reaction gains support from the observation that three commercially available Ru(II) catalysts also catalyse this reaction producing the corresponding products (55–61%, Table 1, entries 14, 15 and 16) under identical reaction conditions. In case of *trans*-allyl acetate we predict direct interaction of π-allyl complex **A** with $[In(SePh)_3]_n$ followed by reductive elimination to give the *trans* product. However in case of *cis*-allyl acetate the complex **C**, formed after the oxidative addition, having steric interaction between α-H and γ-R group is likely to equilibrate with **A** *via* a η^1-σ-alkyl complex **B**. Thus both the intermediates **A** and **C** participate in the catalytic cycle to give the product as a mixture of

Table 3 Comparison of results of reactions in conventional heating and microwave heating

		Conventional heating			Microwave heating		
Entry	Substrate	Time (h)	T/°C	Yield (%) (E : Z)	Time (h)	Temp. (°C)	Yield (%) (E : Z)
1		14	85	80	0.3	95	93
2		16	100	37 (74 : 26)	0.3	100	94 (80 : 20)
3	 *E*:*Z*=76:24	16	100	16 (90 : 10)	0.3	100	75 (80 : 20)



Scheme 2 Proposed mechanistic pathway.

cis- and *trans*-allyl selenides. The transition state for the formation of Ru-π-allyl complex is likely to become more stable by the π-electron of the aromatic nucleus of aryl substituted allyl acetates due to stabilization of the electron deficient Ru centre. Thus, the reaction becomes faster in presence of electron donating group (Me, OMe) on the aromatic ring of cinnamyl acetate, while rate of the reaction becomes slow in presence of electron withdrawing group (COMe, NO_2). In case of branched aromatic allyl acetate exclusively the linear allyl selenide was obtained as the product indicating the formation of a η^3-π-allyl complex followed by the reductive elimination from the less hindered side of the allyl complex. In case of R = alkyl group, the Ru-π-allyl complex does not get enough stabilization due to absence of the aromatic ring and the reaction becomes extremely slow. Thus, the reactions of alkyl substituted allyl acetates proceeded faster under microwave irradiation.[24] From all these observations it may be concluded that the formation of η^3-π-allyl complex is the rate determining step. In case of *trans*-crotyl acetate (R = Me) the product was obtained as a mixture of *cis* and *trans*-allyl selenide. This may be due to presence of a less bulky Me group which makes complex **A** to equilibrate with **C** producing a mixture of *cis* and *trans*-allyl selenide.

Conclusion

In conclusion, a simple and efficient Ru-catalyzed one pot procedure for the phenylselenylation of allyl acetate involving diphenyl diselenide and indium(I) bromide has been developed. Significantly, the selenium-indium intermediate complex, $[In(SePh)_3]_n$ formed during the cleavage of PhSeSePh by In(I) has been isolated and characterized for the first time. This vacates the earlier prediction of $In(SePh)_2I$ as possible intermediate in In(I)-mediated cleavage of PhSeSePh. The other attractive features of this reaction are novel use of Ru catalyst for the selenylation reaction, involvement of air stable, commercially available diphenyl diselenide and allyl acetate, high regioselectivity giving exclusively linear selenides, excellent streoselectivity for *trans* allyl acetates, reaction in neat in open atmosphere without requirement of any inert gas and organic solvent, involvement of two SePh moieties of diphenyl deselenide enhancing atom economy, very fast reaction and high yields. Certainly this protocol shows greater promise towards further useful applications.

Experimental section

IR spectra were taken as thin films for liquid compounds and as KBr pellets for solids on a FT-8300 Shimadzu spectrometer. NMR spectra were recorded on a Bruker AVANCE^{III} 500 instrument at 500 MHz for ^{1}H NMR and at 125 MHz for ^{13}C NMR in $CDCl_3$ solutions.

Representative experimental procedure for the phenylselenylation of cinnamyl acetate (entry 7, Table 2)

A mixture of cinnamyl acetate (1 mmol, 176 mg), diphenyl diselenide (0.5 mmol, 156 mg), InBr (0.6 mmol, 117 mg) and $Ru(acac)_3$ (0.05 mmol, 5 mol%, 20 mg) was heated at 60 °C for 10 min (TLC). After completion of the reaction the reaction mixture was cooled, diluted with EtOAc (5 mL) and was filtered to remove the metal residue. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography over silica gel (hexane–Et_2O, 98 : 2) to furnish the pure product as a white solid (245 mg, 90%). The compound was identified as *trans*-cinnamyl(phenyl)selenide by comparison of its mp and spectra (^{1}H NMR and ^{13}C NMR) with those reported earlier.[14]

This procedure was followed for the reactions of all aryl-substituted allyl acetates listed in Table 2 (entries 1 to 9). However, for reactions of alkyl-substituted allyl acetates the reaction mixture was heated under microwave irradiation (CEM, Discover model, 200 W) in place of conventional heating. All of these products except four (Table 2, entries 1, 3, 4 and 6) are known and have been identified by comparison of their spectroscopic data (IR, ^{1}H NMR and ^{13}C NMR) with those reported (references in Table 2).

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The unknown compounds (Table 2, entries 1, 3, 4 and 6) were characterised properly by their spectroscopic data as follows:

4-Methyl cinnamyl(phenyl)selenide (Table 2, entry 1)

Pale yellow viscous liquid; IR (neat) ν_{max}/cm^{-1} 3435, 3051, 3022, 2920, 2860, 1724, 1678, 1662, 1606, 1575, 1514, 1475, 1437, 1020, 736, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.38 (s, 3H), 3.74 (d, J = 7 Hz, 2H), 6.27-6.37 (m, 2H), 7.15 (d, J = 7.5 Hz, 2H), 7.24 (d, J = 8 Hz, 2H), 7.31–7.34 (m, 3H), 7.58–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.2, 30.8, 124.8, 126.2 (2C), 127.3, 128.9 (2C), 129.2 (2C), 130.0, 132.0, 133.9 (2C), 134.1, 137.3. Anal. Calcd for $C_{16}H_{16}Se$: C, 66.90; H, 5.61. Found: C, 66.92; H, 5.60.

3-Nitro cinnamyl(phenyl)selenide (Table 2, entry 3)

Pale yellow liquid; IR (neat) ν_{max}/cm^{-1} 3057, 2926, 1577, 1527, 1477, 1437, 1350, 1072, 1020, 960, 898, 802, 732, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.67 (d, J = 7.5 Hz, 2H), 6.19 (d, J = 15.5 Hz, 1H), 6.41–6.48 (m, 1H), 7.23–7.28 (m, 3H), 7.42 (t, J = 7.5 Hz, 1H), 7.51–7.54 (m, 3H), 8.03 (dd, J_1 = 2.5 Hz, J_2 = 8 Hz, 1H), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 30.3, 120.9, 122.0, 127.8, 129.1 (2C), 129.4, 129.5, 129.6, 132.0, 134.4 (3C), 138.7, 148.7. Anal. Calcd for $C_{15}H_{13}NO_2Se$: C, 56.61; H, 4.12; N, 4.40. Found: C, 56.59; H, 4.10; N, 4.41.

4-Acetyl cinnamyl(phenyl)selenide (Table 2, entry 4)

Pale yellow viscous liquid; IR (neat) ν_{max}/cm^{-1} 3028, 2924, 2852, 1741, 1676, 1602, 1479, 1438, 1406, 1359, 1269, 1224, 1182, 1070, 1020, 966, 827, 804, 732, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.49 (s, 3H), 3.60 (d, J = 7.5 Hz, 2H), 6.13 (d, J = 15.5 Hz, 1H), 6.33–6.38 (m, 1H), 7.16–7.19 ((m, 3H), 7.25 (d, J = 8.5 Hz, 2H), 7.43–7.45 (m, 2H), 7.78 (d, J = 8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.6, 30.6, 126.4 (3C), 127.7, 128.8 (2C), 129.1 (2C), 129.5, 131.0, 134.3 (2C), 136.0, 141.6, 197.5. Anal. Calcd for $C_{17}H_{16}OSe$: C, 64.76; H, 5.12. Found: C, 64.78; H, 5.11.

2-Iodo cinnamyl(phenyl)selenide (Table 2, entry 6)

Pale yellow liquid; IR (neat) ν_{max}/cm^{-1} 3053, 2924, 1579, 1475, 1460, 1433, 1178, 1070, 1008, 956, 734, 688, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.70 (d, J = 7.5 Hz, 2H), 6.15–6.22 (m, 1H), 6.47 (d, J = 15.5 Hz, 1H), 6.85–6.88 (m, 1H), 7.21–7.27 (m, 4H), 7.36–7.38 (m, 1H), 7.53–7.55 (m, 2H), 7.77 (d, J = 8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 30.2, 99.7, 126.6, 127.4, 128.3, 128.9, 129.1 (2C), 129.2, 129.6, 133.8 (2C), 135.5, 139.4, 139.9. Anal. Calcd for $C_{15}H_{13}ISe$: C, 45.14; H, 3.28. Found: C, 45.16; H, 3.29.

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