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# Bis(chalcogenones) as pincer ligands: isolation and Heck activity of the selone-ligated unsymmetrical C,C,Se–Pd pincer complex†

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The reaction of *meta*-phenylene-bis(1-methyl-1*H*-imidazole-2(3*H*)-selone) with $[Pd_2(\mu\text{-}Cl)_2(2\text{-}C_6H_4CH_2NMe_2)_2]$ in dry benzene and glacial acetic acid resulted in the formation of an unsymmetrical 5,6-membered C,C,Se–Pd(II) pincer complex through C–H bond activation and extrusion of one selenium. This is the first example of a C,C,Se–Pd(II) complex wherein the central Pd(II) is simultaneously coordinated to a selone and an *N*-heterocyclic carbene. The chelated complex of the type $[PdL_2]^{2+}2[PF_6]^-$ (L = bis(selone)) was isolated from the reaction of the bis(selone) with $[PdCl_2(PhCN)_2]$ and $NH_4PF_6$. The unsymmetrical pincer complex was studied for Heck activity revealing its application as an acceptable catalyst in coupling of iodobenzene with acrylates and styrene.

## Introduction

Palladium complexes of pincer ligands of the type D,C,D (D = N, P, O, S) have attracted considerable current interest in various catalytic reactions.[1] However, the pincer ligands involving Se donors, usually selenoethers, are comparatively few due to difficulty in synthesis, handling and malodorous nature of the organoselenium ligands.[2] The first important result was demonstrated by Yao *et al.*[2c] wherein the symmetrical Se,C,Se–Pd(II) catalyst was synthesized through C–H activation of the bis(selenide). The palladium complex was shown to be an excellent Heck catalyst with its ability to couple relatively unreactive aryl bromides and *n*-butyl acrylate with extremely high TON (≈240 000) and high yield. The catalytic activity was not only comparable to the analogous P- and S-donor pincers but also outperforms them. Also, the catalytic efficiency of an air and moisture stable unsymmetrical C,N,Se pincer consisting of a Schiff-base ligand scaffold was studied in Suzuki–Miyaura C–C coupling.[3] A recent review highlights the synthesis and catalytic activity of organochalcogen based Pd(II) complexes including selenium-ligated Pd(II) pincer complexes in Heck catalysis.[4] More recently, Singh and coworkers have developed a related chelate complex with NHC and selenoether ligand and shown its catalytic activity for Suzuki–Miyaura coupling reactions.[5]

The pincer complexes discussed above have generally more common 5,5-membered ring systems; however, the examples of 6,6-membered Pd(II) pincers are relatively rare,[6] while there is no evidence of 7,7-membered pincer complexes. We intuited the use of selones as pincer donors instead of selenoethers. It was envisaged that a strong Pd–Se overlap due to the existence of considerable zwitterionic $C^+$–$Se^-$ character in C═Se may lead to the isolation of stable pincer complexes with higher than five-membered ring.[9] Recently, we reported a series of benzimidazolin-2-chalcogenones (chalcogen = S, Se, Te). Interestingly, the DFT calculation of the chalcogenones suggested the characteristic negative charge on the chalcogen atoms.[7] Even though the transition metal complexes of selones are reported in the literature,[8] the potential of these ligands as pincers has never been explored. Therefore, it was decided to explore the role of bis(chalcogenone) pincer ligands to access 6,6- and 7,7-membered Pd(II) pincer complexes. The present investigation reports the formation of an unprecedented C,C,Se unsymmetrical pincer complex, which was further explored for its catalytic ability in Heck C–C coupling of iodobenzene and alkenes.

## Results and discussion

### Synthesis of bis(chalcogenones)

Bis(selone) **7** was prepared from salt **1**[10] through a reported procedure with slight modification (route A, Scheme 1). The reactions of salts **2–6** with disodium dichalcogenides

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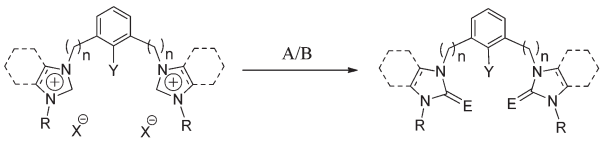
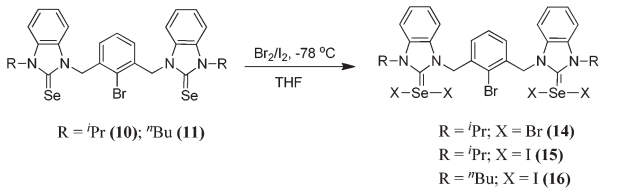
†Electronic supplementary information (ESI) available: NMR spectra, mass spectra and elemental analysis of the compounds. Crystal packing diagrams, bond lengths and bond angles for **8**, **9** and **13**. Cif files for **8**, **9**, **13**, **15** and **16**. CCDC 1061740–1061744. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01565k



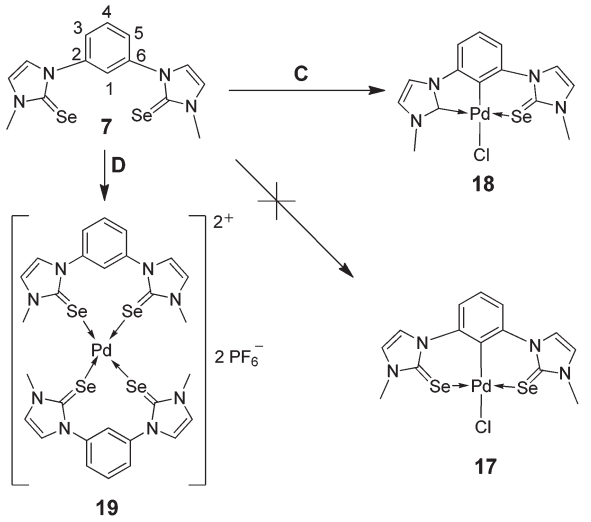

A = (i) 2.2 eq. $K_2CO_3$ (ii) 2.1 eq. Se; B = (i) $Na_2E_2$ (E = Se, Te); (ii) KO$^t$Bu

| Sr. No. | R | X | Y | n | NHC | Sr. No. | R | Y | n | NHC | E |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | Me | I | H | 0 | Im | **7** | Me | H | 0 | Im | Se |
| **2** | $^n$Bu | Br | H | 1 | BzIm | **8** | $^n$Bu | H | 1 | BzIm | Se |
| **3** | $^i$Pr | Br | Br | 1 | BzIm | **9** | $^n$Bu | H | 1 | BzIm | Te |
| **4** | $^n$Bu | Br | Br | 1 | BzIm | **10** | $^i$Pr | Br | 1 | BzIm | Se |
| **5** | $^t$Bu | Br | Br | 1 | BzIm | **11** | $^n$Bu | Br | 1 | BzIm | Se |
| **6** | Py | Br | Br | 1 | BzIm | **12** | $^t$Bu | Br | 1 | BzIm | Se |
| | | | | | | **13** | Py | Br | 1 | BzIm | Se |

**Scheme 1** Synthesis of pincer bis(chalcogenones).




**Scheme 2** Synthesis of bis(dihaloselones).




**Scheme 3** Synthesis of Pd(II) complexes of bis(selones) C = (i) $[Pd_2(\mu\text{-}Cl)_2(2\text{-}C_6H_4CH_2NMe_2)_2]$, benzene, 5 h; D = $[PdCl_2(PhCN)_2]$, $NH_4PF_6$ (2.2 eq.).

(prepared *in situ*) in the presence of potassium *t*-butoxide in dry THF afforded bis(chalcogenones) **8–13** (route B).[7] Bis(chalcogenones) **7–13** were characterized by $^1$H, $^{13}$C, $^{77}$Se and $^{125}$Te NMR spectroscopy. The $^{77}$Se NMR signals for bis(selones) **7**, **8** and **10–13** were observed at ~$\delta$ 32, 61, 59, 60, 198 and 102 ppm, respectively, while the $^{125}$Te NMR signal for bis(tellurone) **9** at $\delta$ −129 ppm. Compounds **8**, **9** and **13** were further characterized by single crystal X-ray diffraction studies (*vide infra*).

### Synthesis of bis(dihaloselones)

Bis(selones) **10** and **11** were further characterized by synthesizing their halogen derivatives (**14–16**) wherein the oxidative addition derivatives were obtained by the reaction of the corresponding halogens in THF at −78 °C (Scheme 2). The $^{13}$C NMR signals (~$\delta$ 150 ppm) and $^{77}$Se NMR signals (~$\delta$ 160 ppm) of the iodo-derivatives **15** and **16** suggested that the electron density has been shifted from selenium to carbene carbon with respect to the precursors **10** and **11** respectively.

### Synthesis of Pd(II) complexes of bis(chalcogenones)

In an attempt to prepare symmetrical 6,6-membered Pd(II) pincer complex **17**, bis(selone) **7** was refluxed with the Pd(II) precursor $[Pd_2(\mu\text{-}Cl)_2(2\text{-}C_6H_4CH_2NMe_2)_2]$[2c] in dry benzene and glacial acetic acid. This resulted in an unprecedented formation of 5,6-membered unsymmetrical C–H activated Pd(II) pincer complex **18** *via* extrusion of one selenium (route C, Scheme 3). The molecular structure was confirmed by single crystal X-ray crystallography (*vide infra*). The extrusion of selenium may take place *via* the formation of palladium selenide.[11a,b] The extrusion leads to an almost planar pincer complex accompanied with the formation of a 5-membered chelate ring where a NHC is strongly bonded to palladium. The formation of a planar, more rigid structure with one 5-membered chelate ring and NHC as a ligand may be the driving forces for the extrusion of selenium.

Also, cleavage of the C=Se bond has been reported in the literature.[11c] Attempts to prepare analogous symmetrical 6,6-membered PCP-Rh(I) pincer complexes by Chauvin and coworkers were unsuccessful, further demonstrating the difficulty in the synthesis of higher ring system pincer complexes.[12a] Significantly, **18** is the first example of a 5,6-membered selone ligated Pd(II) pincer complex reported to date. The synthesis of symmetrical 7,7-membered Pd(II) pincer complexes was attempted through extension of the same approach to bis(selones) **8** and **9** comprising a methylene spacer. This yielded an intractable mixture of compounds and the attempts to purify, isolate or characterize proved futile. The application of other synthetic strategies such as C–H activation of **8** and **9** through more electrophilic Pd(II) precursors like $Pd(OAc)_2$, $[Pd(CH_3CN)_4(BF_4)_2]$ or more facile oxidative addition of the C–Br bond (**10–13**) to the Pd(0) precursor $Pd_2(dba)_3$ also proved unsuccessful. Interestingly, Nicasio-Collazo and coworkers who synthesized an unsymmetrical 5,7-membered NNC-Pd(II) pincer emphasized the difficulty in the synthesis of palladacycles larger than six members due to the facile reductive elimination pathway.[12b]

The cationic Pd(II) complex (**19**) of the type $[PdL_2]^{2+}2[PF_6]^-$ (L = **7**) was isolated by the reaction of **7** with $[PdCl_2(PhCN)_2]$ (2 : 1 ratio) and $NH_4PF_6$ (route D, Scheme 3) and characterized by common NMR spectroscopy and single crystal X-ray crystallography (*vide infra*). The reaction of **7** with $[PdCl_2(PhCN)_2]$ in a 1 : 1 ratio and $NH_4PF_6$ also gives the same product **19** in low yield. However, attempts to isolate cationic Pd(II) complexes of **8–13** with $[PdCl_2(PhCN)_2]$ and $NH_4PF_6$ resulted in insoluble products, which could not be purified and characterized.

The dissymmetric electronic environment of **18** was evident from the $^1$H and $^{13}$C NMR spectra. As expected the four imidazole protons as well as the two protons ($C_3$–H and $C_5$–H) of the phenylene bridge are different from each other. The $C_1$–H proton peak (7.96 ppm) of the phenylene ring of ligand **7** is absent in the $^1$H NMR spectra of **18**. Interestingly, $^{13}$C NMR spectra for **18** exhibits two different methyl carbons at ~36 ppm and twelve aromatic carbons as compared to only one methyl peak and seven aromatic carbons in **7**. The observation of the $^{13}$C peak of C=Se in **18** at 171 ppm and the $^{77}$Se peak at 97 ppm much downfield with respect to **7** ($^{13}$C (156 ppm) and $^{77}$Se (32 ppm)) is the direct outcome of a deshielding effect due to coordinate bonding between Pd and Se, thereby reducing the electronic density on the selenium. A downfield shift of the $^{77}$Se NMR signal ($\delta$ 42 ppm) was observed for complex **19** compared to bis(selone) **7** ($\delta$ 32 ppm).

### X-ray crystallography

Compounds **8**, **9** and **13** crystallize in the $P2_1/c$ space group with a monoclinic crystal system. The molecular structure of compound **8** is shown in Fig. 1a. The significant bond distances and angles for **8**, **9** and **13** are mentioned in the ESI† (Table 1). In compound **8** the bond length Se1–C1 (1.833(4) Å) is slightly smaller than Se2–C20 (1.842(5) Å). Interestingly, the Se2–C20–N4A (131.0(4)°) bond angle is significantly higher than the related bond angles Se1–C1–N1 (126.6(3)°), Se1–C1–N2 (126.4(3)°) and Se2–C20–N3 (125.5(3)°). In the absence of the 1-bromo group on the central aryl ring, the two selenium atoms are *cis* to each other. In compound **9** (Fig. 1b) the bond lengths Te1–C1 (2.087(10) Å) and Te2–C20 (2.073(9) Å) are almost equal. Also all Te–C–N (126.00(1)°) bond angles are equal. The two tellurium atoms are *cis* to each other with respect to the middle benzene ring. In compound **13**, the bond length Se1–C2B (1.824(4) Å) is slightly smaller than Se2–C2A (1.836(4) Å) (Fig. 1c). However, these bond lengths are comparable to the Se–C bond lengths of related compounds.[7] The two benzimidazole ring planes are perpendicular to the middle benzene ring plane and also the two selenium atoms are *trans* to each other.

The molecular packing diagrams of compounds **8** and **9** show a 1-D network formed by π–π stacking interactions (3.777(1) Å for **8** (Fig. 78 in the ESI†) and 3.846(2) Å for **9** (Fig. 79 in the ESI†)). Due to these interactions, a supramolecular structure has been formed. The packing diagram of **13** showed a centrosymmetric pair due to intermolecular secondary Se1···Br* and Se1*···Br interactions (Fig. 80 in the ESI†). One of the selenium atoms interacts with the bromine atom of the other molecule. The Se1···Br* and Se1*–Br distance (3.668 Å) is significantly higher than the sum of the single bond covalent radii for Se (1.22 Å) and bromine (1.21 Å), but shorter than the sum of van der Waals radii (3.75 Å). Also the C2A–π interactions have been observed which are responsible for the formation of the 1-D network.

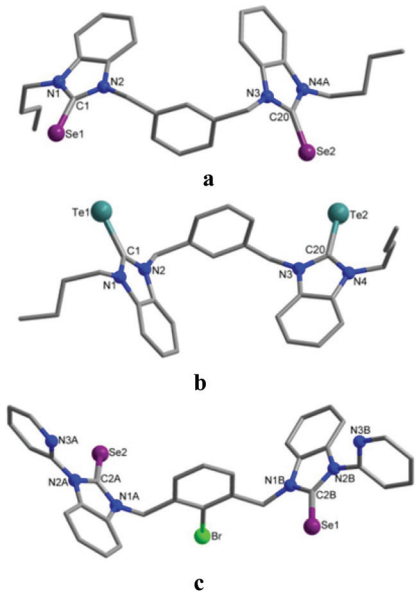



Fig. 1 Molecular structures of compounds **8** (a), **9** (b) and **13** (c). Hydrogen atoms are omitted for clarity.

The molecular structures of **18** and **19** with atomic numbering scheme are shown in Fig. 2.

The crystals of **18** were obtained by slow evaporation of an acetonitrile solution of the compound. The Pd(II) metal centre is bound in a tridentate way to the carbene^C^Se ligand, with the fourth site occupied by a chlorine atom. The geometry of this cyclometalated complex is distorted square planar as the C(4)–Pd–C(10) bond angle of 82.0° and the C(10)–Pd–Se bond angle of 95.9° deviate from ideal 90° due to the planar and rigid framework of the carbene^C^Se ligand (Fig. 2a). The Pd–Se bond length of 2.3773(5) Å is significantly shorter than that reported (~2.528 Å) for the selenium-ligated palladacycle reported by Singh and coworkers.[5] Moreover, it is also shorter than the Pd–Se bond distances of 2.4508(5) and 2.4553(5) Å observed for chelated complex **19**. The Pd–Cl bond length (2.3967(10) Å) is longer than the value of 2.325(16) Å for the selenium-ligated palladacycle reported by Singh and coworkers.[3] This may be due to the increase in s-character in $sp^2$ hybridised orbitals of selenium compared to $sp^3$ hybridization in selenoethers. This may facilitate a better overlap with d-orbitals of palladium, resulting in a very strong interaction and thus a shorter bond length.

Complex **19** crystallized as red crystals through slow evaporation of acetonitrile solution of the complex. Complex **19** is symmetrical where the Pd(II) metal centre is chelated to two bis(selone) ligands resulting in a square planar geometry with

Table 1 Catalytic activity of **18** in Heck C–C coupling of aryl halides and acrylates

| Entry | Aryl halide | Alkene | Product | Base | Solvent | Temp. | Time | Yield |
|---|---|---|---|---|---|---|---|---|
| 1 | Iodobenzene | Methyl acrylate | Methyl cinnamate | $Et_3N$ | DMA | 140 °C | 48 h | <5% |
| 2 | Iodobenzene | Methyl acrylate | Methyl cinnamate | NaOMe | DMA | 140 °C | 48 h | — |
| 3 | Iodobenzene | Methyl acrylate | Methyl cinnamate | KO$^t$Bu | DMA | 140 °C | 48 h | — |
| 4 | Iodobenzene | Methyl acrylate | Methyl cinnamate | $K_2CO_3$ | DMA | 140 °C | 7 h | 95% |
| 5 | Iodobenzene | Methyl acrylate | Methyl cinnamate | $Cs_2CO_3$ | DMA | 140 °C | 48 h | 75% |
| 6 | Iodobenzene | Methyl acrylate | Methyl cinnamate | $K_2CO_3$ | Xylene | 135 °C | 48 h | — |
| 7 | Iodobenzene | Methyl acrylate | Methyl cinnamate | $K_2CO_3$ | DMSO | 180 °C | 48 h | — |
| 8 | Iodobenzene | *n*-Butyl acrylate | *n*-Butyl cinnamate | $K_2CO_3$ | DMA | 140 °C | 8 h | 96% |
| 9 | Iodobenzene | *t*-Butyl acrylate | *t*-Butyl cinnamate | $K_2CO_3$ | DMA | 140 °C | 7 h | 95% |
| 10 | Iodobenzene | Styrene | Stilbene | $K_2CO_3$ | DMA | 140 °C | 20 h | 94% |
| 11 | Bromobenzene | Methyl acrylate | Methyl cinnamate | $K_2CO_3$ | DMA | 140 °C | 48 h | — |

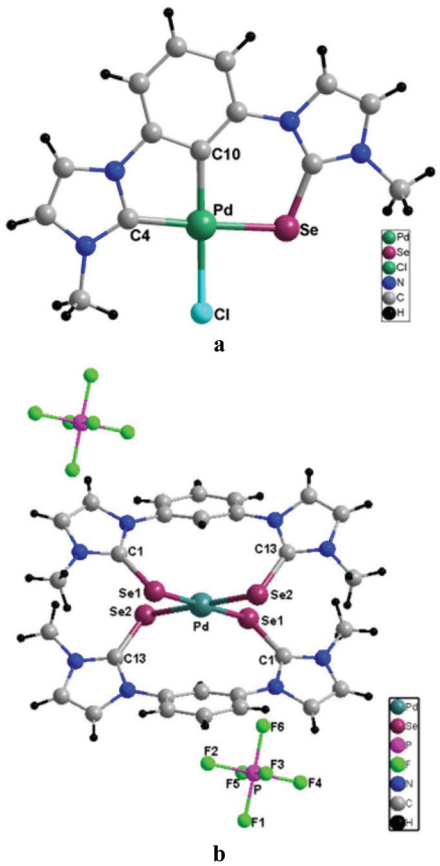



Fig. 2 Molecular structures of compounds **18** (a) and **19** (b). Significant bond lengths [Å] and angles [°] 15: Pd–C(10) 2.022(4); Pd–C(4) 2.014(4); Pd–Se 2.3773(5); Pd–Cl 2.3967(10); C(10)–Pd–Cl 178.75(12); C(4)–Pd–Se 176.36(13). 16: Pd–Se(1) 2.4508(5); Pd–Se(2) 2.4553(5) Se(1)–Pd–Se(1) #1180.000(1).

the Se–Pd–Se bond angle in the range of 88–91° (Fig. 2b). The two selone ligands are *anti* with respect to each other and are arranged in a zig-zag mode to the central metal. The Pd–Se bond distances 2.4508(5) and 2.4553(5) Å of **19** are comparable to those reported for Pd(II) coordination complexes of *N*,*N*-dimethylselenourea.[13] The two $PF_6^-$ anions are outside the coordination sphere and are involved in hydrogen bonding through fluorine with protons of the imidazole moiety.

### Catalytic activity of 18

The selone ligated Pd(II) pincer complex **18** was studied as a catalyst for the Heck C–C coupling reaction and the optimization and catalytic activity data are mentioned in Table 1.[14] The evaluation of various bases for coupling of iodobenzene with methyl acrylate in DMA (1 mol% catalyst loading) illustrated that $Et_3N$ is a relatively less active base (entry 1), and NaOMe and KO$^t$Bu are inactive bases (entries 2 and 3). It was observed that bases like $K_2CO_3$ and $Cs_2CO_3$ are more active resulting in 95% and 75% yields (entries 4 and 5) but eventually $K_2CO_3$ was preferred as a base over $Cs_2CO_3$ for further reactions with less reaction time as well as better yields. The unsuccessful assessment of other solvents like xylene and DMSO (entries 6 and 7) proved that DMA is a superior solvent for this reaction. The coupling of iodobenzene with *n*-butyl and *t*-butyl acrylates in DMA (1 mol% catalyst loading) resulted in high yields (~95%) in comparatively less reaction times (~7 h) (entries 8 and 9). Almost analogous high yields were obtained in coupling of iodobenzene with styrene under similar reaction conditions but moderately prolonged reaction time of 20 h (entry 10). Attempts to couple less reactive substrates like bromobenzene with acrylates proved futile (entry 11). The catalytic activity of **18** is observed to be high with respect to reactive substrates like iodobenzene, but has no activity as compared to other selenium-ligated Pd(II) pincer complexes studied which show better activity for less reactive and inexpensive substrates like ArBr and ArCl.[2c,3]

## Conclusions

In summary, we have demonstrated the application of bis(chalcogenone) ligands for synthesizing an unsymmetrical, rigid and selone ligated 5,6-membered C,C,Se–Pd(II) pincer complex through C–H bond activation. The synthesis of 7,7-membered pincer complexes was unsuccessful plausibly due to facile reductive elimination pathways. The pincer complex has Pd in a dissymmetric electronic environment with a very short Pd–Se and long Pd–Cl bond. The complex showed good Heck activity with respect to reactive substrates like iodobenzene.

# Experimental section

All reactions were carried out under a nitrogen or an argon atmosphere using standard Schlenk techniques. Solvents were purified and dried by standard procedures and were distilled prior to use. Melting points were recorded on a Veego VMP-I melting point apparatus in capillary tubes and were uncorrected. The $^{1}$H (400 MHz) and $^{13}$C (100.56 MHz) NMR spectra were recorded on Varian VXR 400S and Bruker AV 400 spectrometers at 25 °C. The $^{77}$Se (57.22 MHz and 76.3 MHz) and $^{125}$Te (94.79 MHz and 157.97 MHz) NMR spectra were recorded on Varian VXR 300S and Bruker AV 400 spectrometers. Chemical shifts are cited with respect to $Me_4Si$ as the internal standard ($^{1}$H, $^{13}$C) and $Me_2Se$ ($^{77}$Se) and $Me_2Te$ ($^{125}$Te) as external standards. Elemental analyses were performed on a Carlo Erba Model 1106 elemental analyzer. The ESI mass spectra were recorded on a Q-Tof micro (YA-105) mass spectrometer.

### Synthesis of salts 1

Salt **1** was obtained by stirring a mixture of acetonitrile solution of 1,3-di(1*H*-imidazol-1-yl)benzene (1.35 g, 6.42 mmol) with methyl iodide (5 eq.) (4.55 g, 2 mL, 32.1 mmol) at room temperature for 8 h by slightly modifying a reported procedure.[10] The white precipitate formed was washed with diethyl ether and dried. Yield: 2.95 g (93%). $^{1}$H NMR (400 MHz, DMSO): $\delta$ (ppm) 9.80 (s, 2H), 8.36 (m, 2H), 8.25 (m, 1H), 8.00–7.90 (m, 4H), 3.95 (s, 6H). $^{13}$C NMR (100 MHz, DMSO): $\delta$ (ppm) 136.3, 135.6, 132.2, 124.7, 122.8, 121.0, 115.9.

### General procedure for the synthesis of salts 2–6

Salts **2–6** were synthesized by dissolving 2,6-bis(bromomethyl)-1-bromophenylene (1 eq.) in 1,4-dioxane and the corresponding *N*-alkyl or *N*-aryl benzimidazole (2.2 eq.). The reaction mixtures were refluxed for 14 h under a nitrogen atmosphere. The white solids formed were filtered and washed with THF and diethyl ether to afford salts **2–6**.

**2**: The reagents used are 2,6-bis(bromomethyl)benzene (2.01 g, 7.59 mmol) and *N*-butyl benzimidazole (2.91 g, 16.71 mmol). Yield: 4.6 g (99%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 11.13 (s, 2H), 8.30 (s, 1H), 8.04 (d, $J$ = 8.1 Hz, 2H), 7.75 (d, $J$ = 8.0 Hz, 2H), 7.63 (d, $J$ = 7.7 Hz, 2H), 7.59–7.51 (m, 4H), 7.29 (t, $J$ = 7.7 Hz, 1H), 5.92 (s, 4H), 4.63 (t, $J$ = 7.3 Hz, 4H), 2.06–1.99 (m, 4H), 1.48–1.39 (m, 4H), 0.95 (t, $J$ = 7.7 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 141.8 (NCN), 134.0, 131.1, 130.8, 129.8, 129.7, 129.4, 127.1, 126.9, 114.3, 112.8, 66.8, 50.2, 47.5 (1,4-dioxane), 30.9, 19.6, 13.3. Anal. calcd for $C_{30}H_{36}Br_2N_4 + 1H_2O$ (%): C, 57.15; H, 6.08; N, 8.89. Found: C, 57.35; H, 6.04; N, 8.24.

**3**: The reagents used were 2,6-bis(bromomethyl)-1-bromophenylene (4.59 g, 13.38 mmol) and *N*-iso-propyl benzimidazole (4.71 g, 29.43 mmol). Yield: 7.8 g (88%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 9.88 (s, 2H), 9.82 (d, $J$ = 6.4 Hz, 2H), 8.10 (d, $J$ = 8.2 Hz, 2H), 7.78–7.70 (m, 2H), 7.66–7.61 (m, 2H), 7.50–7.42 (m, 3H), 5.97 (s, 4H), 5.21–5.10 (m, 2H), 1.76 (d, $J$ = 6.7 Hz, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 142.4 (NCN), 135.6, 133.1, 132.6, 132.5, 130.3, 128.6, 128.4, 126.1, 115.4, 115.1, 68.2, 53.2, 52.8, 22.4. Anal. calcd for $C_{28}H_{31}Br_3N_4$ (%): C, 50.70; H, 4.71; N, 8.45. Found: C, 49.70; H, 4.20; N, 8.99.

**4**: The reagents used are 2,6-bis(bromomethyl)-1-bromophenylene (0.50 g, 1.45 mmol) and *N*-butyl benzimidazole (0.51 g, 2.91 mmol). Yield: 0.84 g (87%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 11.12 (s, 2H), 8.04 (d, 2H), 7.75 (d, 2H), 7.69–7.50 (m, 4H), 7.29 (s, br, 3H), 5.92 (s, 4H), 4.62 (t, $J$ = 7.2 Hz, 4H), 2.02 (quint, $J$ = 7.2 Hz, 4H), 1.44 (sext, $J$ = 7.2 Hz, 4H), 0.91 (t, $J$ = 7.2 Hz, 6H). $^{13}$C NMR ($CDCl_3$): $\delta$ 141.8, 133.9, 131.1, 130.8, 129.8, 129.6, 129.3, 127.1, 126.9, 114.3, 112.8, 50.2, 47.5, 30.9, 19.6, 13.3.

**5**: The reagents used are 2,6-bis(bromomethyl)-1-bromophenylene (1.55 g, 4.52 mmol) and *N*-*tert*-butyl benzimidazole (1.73 g, 9.94 mmol). Yield: 2.6 g (83%). Mp. 227–229 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 9.84 (s, 2H), 8.30 (d, $J$ = 8.7 Hz, 2H), 7.72–7.68 (m, 4H), 7.60 (t, $J$ = 7.1 Hz, 2H), 7.43 (t, $J$ = 8.6 Hz, 1H), 7.35 (d, $J$ = 7.5 Hz, 2H), 6.02 (s, 4H), 1.95 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 142.9 (NCN), 135.6, 133.9, 132.0, 131.7, 130.1, 128.2, 128.1, 125.3, 118.0, 117.9, 115.3, 63.3, 52.7, 29.4, 29.3, 29.2. Anal. calcd for $C_{30}H_{35}Br_3N_4 + 1H_2O$ (%): C, 50.80; H, 5.26; N, 7.90. Found: C, 50.78; H, 4.46; N, 8.54.

**6**: The reagents used are 2,6-bis(bromomethyl)-1-bromophenylene (5.00 g, 14.57 mmol) and *N*-pyridyl benzimidazole (6.15 g, 31.5 mmol). Yield: 9.58 g (84%). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 10.69 (s, 2H), 8.80 (d, $J$ = 2.7 Hz, 2H), 8.51 (d, $J$ = 8.3 Hz, 2H), 8.30 (t, $J$ = 7.3 Hz, 1H), 8.12 (d, $J$ = 8.2 Hz, 2H), 7.95 (d, $J$ = 8.3 Hz, 2H), 7.81–7.72 (m, 6H), 7.49–7.42 (m, 4H), 6.07 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 149.3 (NCN), 147.1, 143.2, 140.5, 133.6, 131.3, 130.5, 129.6, 128.5, 127.8, 127.4, 125.2, 123.9, 117.3, 116.1, 114.0, 51.2. Anal. calcd for $C_{32}H_{25}Br_3N_6$ (%): C, 52.41; H, 3.44; N, 11.46. Found: C, 51.76; H, 2.92; N, 12.54.

### Synthesis of bis(selone) 7

A mixture of **1** (1.43 g, 2.89 mmol), Se powder (0.48 g, 6.0 mmol) and $K_2CO_3$ (0.88 g, 6.36 mmol) was refluxed in dry methanol (50 mL) for 6 h after which the solvent was evaporated and the residual solid was extracted with chloroform. The chloroform extract was concentrated to 4 mL and 1 mL of methanol was added to yield a white crystalline solid of **7** (0.644 g, 56%) Mp. 247 °C (dec.). $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 156.9 (NCN), 139.1, 129.7, 126.3, 124.6, 120.9, 120.3, 37.6. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 32.2. Anal. calcd for $C_{14}H_{14}N_4Se_2$ (%): C, 42.44; H, 3.56; N, 14.14. Found: C, 42.64; H, 3.66; N, 14.67. HRMS: ($m/z$) 398.9647 $[M + 1]^+$.

### General procedure for the synthesis of bis(chalcogenones) 8–13

Bis(chalcogenones) **8–13** were synthesized by addition of respective salts **2–6** (1 eq.) into a brownish red solution of $Na_2E_2$ (3 eq.; E = Se, Te) (prepared *in situ*) under a nitrogen atmosphere and the reaction mixture was stirred for 8–10 h at room temperature. Potassium *tert*-butoxide was added to the

reaction mixture and the reaction was further stirred for 5–7 h at room temperature. The reaction mixture was quenched by adding water (50 mL) and extracted with diethyl ether/chloroform, dried over sodium sulfate. Combined organic layer was evaporated under reduced pressure to obtain bis(chalcogenones) **8–13**.

**8**: Yield: 0.47 g (58%). Mp. 120–122 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.44 (s, 1H), 7.24 (m, 6H), 7.11 (m, 5H), 5.67 (s, 4H), 4.47 (t, $J$ = 7.7 Hz, 4H), 1.87 (m, 4H), 1.49 (m, 4H), 1.00 (t, $J$ = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 167.2 (NCN), 136.2, 133.3, 132.9, 129.5, 127.3, 127.2, 123.5, 110.5, 109.7, 50.1, 47.0, 30.3, 20.3, 13.9. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 60.7. Anal. calcd for $C_{30}H_{34}N_4Se_2$ (%): C, 59.21; H, 5.63; N, 9.21. Found: C, 59.61; H, 5.49; N, 9.95.

**9**: Yield: 0.61 g (34%). Mp. 160–162 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.43 (s, 1H), 7.37 (d, $J$ = 8.2 Hz, 2H), 7.29–7.10 (m, 9H), 5.75 (s, 4H), 4.55 (t, $J$ = 7.7 Hz, 4H), 1.94–1.86 (m, 4H), 1.56–1.46 (m, 4H), 1.02 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 146.2 (NCN), 135.6, 134.2, 133.8, 129.4, 127.3, 123.8, 123.7, 111.2, 110.4, 53.2, 50.2, 30.6, 20.2, 13.9. $^{125}$Te NMR (126.2 MHz, $CDCl_3$): $\delta$ (ppm) −129.1. HRMS: ($m/z$) 711.0993 $[M]^+$.

**10**: Yield: 0.35 g (54%). Mp. 114–116 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.55 (d, $J$ = 8 Hz, 2H), 7.22 (m, 4H), 7.10 (d, $J$ = 8 Hz, 2H), 6.98 (t, $J$ = 7.8 Hz, 1H), 6.60 (d, $J$ = 8.0 Hz, 2H), 5.92 (m, 2H), 5.90 (s, 4H), 1.67 (d, $J$ = 7.1 Hz, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 167.2 (NCN), 135.1, 133.5, 131.5, 128.1, 126.9, 123.5, 123.3, 122.3, 111.5, 110.7, 52.3, 50.9, 20.3, 20.2, 15.4. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 59.3. Anal. calcd for $C_{28}H_{29}BrN_4Se_2$ (%): C, 51.00; H, 4.43; N, 8.50. Found: C, 50.67; H, 4.50; N, 8.06.

**11**: Yield: 0.85 g (57%). Mp. 193–195 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.96 (d, $J$ = 7.6 Hz, 1H), 7.35–7.17 (m, 4H), 7.04 (d, $J$ = 8 Hz, 1H), 6.66 (dd, $J$ = 0.8 Hz, 7.2 Hz, 1H), 5.79 (s, 2H), 4.50 (t, $J$ = 7.6 Hz, 2H), 1.91 (m, 2H), 1.50 (m, 2H), 1.02 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 167.5 (NCN), 135.1, 133.2, 132.9, 128.0, 127.0, 123.8, 123.7, 122.3, 110.4, 109.8, 50.5, 47.0, 30.3, 20.3, 13.9. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 60.2. Anal. calcd for $C_{30}H_{33}BrN_4Se_2$ (%): C, 52.42; H, 4.84; N, 8.15. Found: C, 52.56; H, 4.58; N, 8.94.

**12**: Yield: 0.58 g (87%). Mp. 203 °C (decomposed). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.86 (m, 2H), 7.16 (m, 4H), 7.03 (m, 2H), 6.95 (t, $J$ = 7.7 Hz, 1H), 6.49 (d, $J$ = 8.0 Hz, 2H), 5.99 (s, 4H), 2.23 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 165.9 (NCN), 134.9, 133.9, 133.4, 127.9, 126.6, 123.4, 123.1, 122.2, 114.5, 110.6, 64.6, 50.2, 30.8. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 197.6. Anal. calcd for $C_{30}H_{33}BrN_4Se_2$ (%): C, 52.42; H, 4.84; N, 8.15. Found: C, 52.22; H, 4.77; N, 6.73.

**13**: Yield: 0.7 g (74%). Mp. 240–242 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.73 (dd, $J$ = 4.9 Hz, $J$ = 1.9 Hz, 2H), 8.16 (d, $J$ = 8.3 Hz, 2H), 8.01 (dt, $J$ = 7.6 Hz, $J$ = 1.8 Hz, 2H), 7.48 (m, 2H), 7.42 (m, 2H), 7.25 (m, 4H), 7.12 (m, 2H), 7.05 (t, $J$ = 7.7 Hz, 1H), 6.80 (d, $J$ = 7.6 Hz, 2H), 5.98 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 168.2 (NCN), 150.3, 149.4, 138.4, 134.8, 133.5, 133.0, 128.2, 127.2, 124.6, 124.4, 124.2, 123.9, 111.9, 110.4, 50.7. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 102.1. Anal. calcd for $C_{32}H_{23}BrN_6Se_2$ (%): C, 52.69; H, 3.18; N, 11.52. Found: C, 52.21; H, 4.76; N, 6.73.

### General procedure for the synthesis of bis(dihaloselones) 14–16

The bis(selenones) **10** or **11** (1 eq.) was taken in dry THF (15 mL) and iodine/bromine (2 eq.) in THF was added at −78 °C under a nitrogen atmosphere. The reaction mixtures were stirred for 16–20 h at room temperature. The reaction mixtures were concentrated in a vacuum and $n$-pentane (15–20 mL) was added. Crystalline compounds were obtained at −30 °C.

**14**: Yield: 0.65 g (87%). Mp. 208 °C (decomposed). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.92 (d, $J$ = 7.7 Hz, 2H), 7.58 (m, 4H), 7.45 (d, $J$ = 7.7 Hz, 2H), 7.22 (d, $J$ = 7.0 Hz, 2H), 7.16 (t, $J$ = 6.2 Hz, 1H), 6.19 (s, 4H), 5.95 (m, 2H), 1.92 (d, $J$ = 7.0 Hz, 12H). $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 290.4. ESI-MS: $m/z$ 738.9 $[M - Br_3]^+$, 685.9 $[M - C_4H_{10}Br_3]^+$, 581.1 $[M - Br_5]^+$; Anal. calcd for $C_{28}H_{29}Br_5N_4Se_2$ (%): C, 34.35; H, 2.99; N, 5.72. Found: C, 34.17; H, 2.84; N, 6.00.

**15**: Yield: 0.12 g (68%). Mp. 119–129 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.86 (d, $J$ = 6.7 Hz, 2H), 7.53 (m, 4H), 7.45 (d, $J$ = 7 Hz, 2H), 7.17 (t, $J$ = 7.8 Hz, 1H), 6.95 (d, $J$ = 7.6 Hz, 2H), 6.00 (s, 4H), 5.79 (t, $J$ = 7.1 Hz, 2H), 1.87 (d, $J$ = 7.1 Hz, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 150.0 (NCN), 133.6, 133.5, 131.1, 129.4, 128.7, 127.1, 126.6, 122.8, 114.2, 113.6, 55.8, 53.2, 20.7. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 154.6.

**16**: Yield: 0.42 g (81%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.80 (d, $J$ = 8 Hz, 1H), 7.48–7.34 (m, 4H), 7.05 (t, $J$ = 8 Hz, 1H), 6.38 (d, $J$ = 8 Hz, 1H), 5.85 (s, 2H), 4.51 (t, $J$ = 7.2 Hz, 2H), 1.79 (m, 2H), 1.40 (m, 2H), 0.93 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 156.4 (NCHN), 134.7, 132.5, 127.9, 126.6, 125.3, 121.9, 112.1, 111.9, 50.8, 47.1, 30.0, 19.4, 13.6. $^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 166.09. Anal. calcd for $C_{30}H_{33}BrI_4N_4Se_2$ (%): C, 30.15; H, 2.78; N, 4.69. Found: C, 30.07; H, 2.46; N, 5.21.

### Synthesis of 18

The reaction mixture of **7** (0.215 g, 0.54 mmol) and $[Pd_2(\mu\text{-}Cl)_2(2\text{-}C_6H_4CH_2NMe_2)_2]$ (0.179 g, 0.32 mmol) in benzene (30 mL) and glacial acetic acid was refluxed for 5 h. The reaction mixture was evaporated to dryness and washed with diethyl ether to isolate the crude product. The solid was extracted with chloroform and filtered through celite pad. The solvent was evaporated and the residue was treated with diethyl ether to yield a reddish brown solid. Yield: 0.105 g (42%). Mp. 205 °C (dec.). $^1$H NMR (400 MHz, DMSO): $\delta$ (ppm). 8.21 (d, $J$ = 2.4 Hz, 1H), 8.09 (d, $J$ = 1.9 Hz, 1H), 7.77 (d, $J$ = 2.3 Hz, 1H), 7.53 (d, $J$ = 7.2 Hz, 1H), 7.47 (d, $J$ = 7.9 Hz, 1H), 7.37 (d, $J$ = 1.9 Hz, 1H), 7.32 (t, $J$ = 7.8 Hz, 1H), 4.10 (s, 3H), 3.74 (s, 3H). $^{13}$C NMR (100 MHz, DMSO): $\delta$ (ppm) 171.6, 148.4, 143.1, 139.2, 132.7, 125.9, 123.4, 122.6, 119.4, 117.1, 115.1, 111.2, 37.1, 36.6. $^{77}$Se NMR (57 MHz, DMSO): $\delta$ (ppm) 97.8. ESI-MS: $m/z$ 422.9 $[M - Cl]^+$, 343.0 $[M - (Se + Cl)]^+$, 317.0 $[M - (Pd + Se + Cl)]^+$. Anal. calcd for $C_{14}H_{13}ClN_4PdSe$ (%): C, 36.70; H, 2.86; N, 12.23. Found: C, 36.82; H, 2.95; N, 12.60.

Table 2 Details of the X-ray data collection parameters

| Compound | 8 | 9 | 13 | 18 | 19 |
|---|---|---|---|---|---|
| Formula | $C_{30}H_{33}N_4Se_2$ | $C_{30}H_{34}N_4Te_2$ | $C_{32}H_{23}BrN_6Se_2$ | $C_{14}H_{13}ClN_4PdSe$ | $C_{28}H_{28}F_{12}N_8P_2PdSe_4$ |
| $M_r$ | 607.52 | 705.81 | 729.39 | 458.09 | 1188.76 |
| System | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P*21/*c* | *P*21/*c* | *P*121/*c*1 | *P*21/*c* | *P*21/*c* |
| *a* [Å] | 9.74100(10) | 9.7586(3) | 13.4416(4) | 8.0559(2) | 6.82075(19) |
| *b* [Å] | 21.5258(5) | 21.6201(13) | 20.7586(7) | 13.1124(3) | 10.9648(3) |
| *c* [Å] | 13.7748(2) | 14.0678(5) | 12.6712(4) | 13.8977(3) | 25.1631(6) |
| *α* [°] | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| *β* [°] | 94.4040(10) | 93.418(3) | 107.462(4) | 96.673(2) | 95.769(2) |
| *γ* [°] | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| *V* [Å$^3$] | 2879.81(8) | 2962.8(2) | 3372.69(19) | 1458.10(6) | 1872.38(9) |
| *Z* | 4 | 4 | 4 | 4 | 2 |
| Size [mm$^3$] | 0.48 × 0.41 × 0.24 | 0.44 × 0.39 × 0.22 | 0.49 × 0.32 × 0.15 | 0.4159 × 0.1574 × 0.1395 | 0.3662 × 0.1823 × 0.0907 |
| $\rho_{calcd}$ [Mg m$^{-3}$] | 1.401 | 1.582 | 1.436 | 2.087 | 2.109 |
| $\mu$ [mm$^{-1}$] | 3.391 | 1.993 | 3.406 | 14.786 | 10.132 |
| Reflections collected | 1 1694 | 12 138 | 36 999 | 8995 | 6718 |
| Observed reflns [*R*(int) = 0.0615] | 5827 | 5995 | 11 354 | 2978 | 3731 |
| $R_1$ observed reflns | 0.0636 | 0.0896 | 0.0493 | 0.0402 | 0.0450 |
| w$R_2$, all | 0.1959 | 0.2995 | 0.1285 | 0.1107 | 0.1226 |

### Synthesis of 19

To a solution of selone **7** (0.133 g, 0.33 mmol) in acetonitrile, $PdCl_2(PhCN)_2$ (0.064 g, 0.16 mmol) and $NH_4PF_6$ (0.061 g, 0.36 mmol) were added and the mixture was refluxed with stirring for 3 h. The reaction mixture was then evaporated to dryness and the residual solid was washed with methanol followed by diethyl ether. The solid was extracted with acetonitrile and filtered. The filtrate was evaporated to dryness to yield a reddish brown solid. Yield: 0.165 g (83%). Mp. 217 °C (dec.). $^1$H NMR (400 MHz, $CD_3CN$): $\delta$ (ppm). 7.95 (t, $J$ = 1.2 Hz, 2H), 7.75 (t, $J$ = 8.7 Hz, 2H), 7.66 (d, $J$ = 1.5 Hz, 4H), 7.56 (d, $J$ = 8.1 Hz, 4H), 7.41 (d, $J$ = 1.9 Hz, 4H), 3.53 (s, 12H).$^{77}$Se NMR (57 MHz, $CDCl_3$): $\delta$ (ppm) 42.8. Anal. calcd for $C_{28}H_{28}F_{12}N_8P_2PdSe_4$ (%): C, 28.29; H, 2.37; N, 9.43. Found: C, 28.41; H, 2.11; N, 8.71.

### X-Ray crystallographic study

The single crystal X-ray diffraction measurements were performed on an Oxford Diffraction Gemini diffractometer. The data were corrected for Lorentz, polarization, and absorption effects. The structures were determined by routine heavy-atom methods using SHELXS 97[15] and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogen with fixed isotropic thermal parameters of 0.07 Å$^2$ using the SHELXL 97[16] program. The hydrogens were partially located from difference electron density maps, and the rest were fixed at predetermined positions. Scattering factors were from common sources.[17] Details of the X-ray data collection parameters are given in Table 2.

### General method for optimization of the catalytic reaction conditions using gas chromatography

A two-necked round-bottomed flask was charged with aryl halide (1 mmol), alkene (1.5 mmol), catalyst **18** (1 mol%), base (2 mmol) and solvent (5 mL) and the reaction mixture was heated in a preheated oil bath for a specified time at the given temperature. After completion of the reaction, it was cooled to room temperature. The reaction mixture was filtered through a celite pad and washed with water and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and filtered. The sample was injected in the gas chromatographic column using a microsyringe and run for 30 min under the preset temperature program. Yields were calculated from the conversion of the aryl halides.

### General method for Heck coupling of iodobenzene and bromobenzene

A round-bottom flask was charged with aryl halide (1 mmol), alkene (1.5 mmol), catalyst **18** (1 mol%), base (2 mmol), and solvent (5 mL). The reaction mixture was heated in a preheated oil bath for a given time at a specified temperature. After the completion of the reaction, it was worked up as described above and purified by column chromatography (silica: 60–120, hexane–ethyl acetate).

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