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Iron salt, a cheap, highly efficient and environment-friendly metal catalyst for Se–Se bond cleavage and the further reaction with methylenecyclopropanes under mild conditions

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ABSTRACT

$FeCl_3$ was found to be a good catalyst in Se-Se bond cleavage. Further electrophilic additions to methylenecyclopropanes provide a convenient access to diphenylselenylcyclobutanes. Comparing with other Lewis acids, $FeCl_3$ is much cheaper and the reaction conditions are milde and more tolerance to air and moisture.

1. Introduction

Methylenecyclopropanes (MCPs) which are highly strained molecules are now readily accessible in laboratory [1,2]. The relief of MCPs' ring strain provides a potent thermodynamic driving force, which facilitates their novel reactions under mild conditions. Therefore, they are useful building blocks in organic synthesis. During the past decade, the applications of MCPs had been well investigated and a series of interesting organic skeletons could be easily constructed from MCPs, which include homoallylic compounds [3–8], allilic derivatives [9–11], dihydronaphthalenes [12–15], heterocyclic compounds [16–22], butadienes[23–25] and so on.

Four-membered carbon ring structures are widely present in natural products [26,27]. They are also valuable in organic synthesis [28]. However, they are not easy to be built due to the high ring strain. In the investigation field of MCPs, chemists have found that four-membered carbon ring could be directly constructed from MCPs and a series of interesting examples has been reported [29–33]. Transition metal catalyzed rearrangements of MCPs provided a facile access to cyclobutenes [29,30]. Reaction of MCPs with phenylsulfenyl chloride or phenylselenyl chloride gave the selenium or sulfur groups-substituted cyclobutene derivatives [31]. Oxidation of MCPs led to cyclobutanones [32]. Recently, Huang et al. have reported that Lewis acid mediated acylation of *E*-2-(arylmethylene) cyclopropylaldehyde generated bifunctional methylenecyclobutanes [33]. All of these analogs are potentially valuable in both organic synthesis and drug design.

Selenium containing compounds have extensive applications in organic synthesis [34–40]. Containing selenium element and a four-membered carbon ring, 1,1-diphenylselenylcyclobutanes are useful building blocks in organic synthesis and pharmacy [41]. Traditionally, 1,1-diphenylselenylcyclobutanes could be synthesized by the oxidation of MCPs [32] and the following reactions with benzeneselenol catalyzed by $ZnCl_2$ (Scheme 1, eq. (1)) [41]. This method is not convenient for the employment of benzeneselenol, which is effluvial, highly toxic and sensitive to air. Recently, we have developed a direct access to 1,1-diphenylselenylcyclobutanes from MCPs through the $TiCl_4$ catalyzed additions of diphenyldiselenide (Scheme 1, eq. (2)) [42]. Avoidance of benzeneselenol made this method more environment-friendly. However, low temperature, highly anhydrous conditions, and large amounts of catalyst made the reaction problematic. Therefore, searching a more advanced catalyst of Se–Se bond cleavage and developing a more convenient method for the synthesis of 1,1-diphenylselenylcyclobutanes under mild conditions is needful. Herein, we wish to report our recent improvements.

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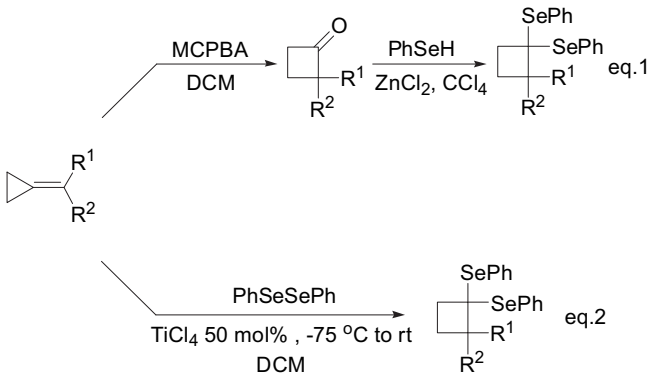


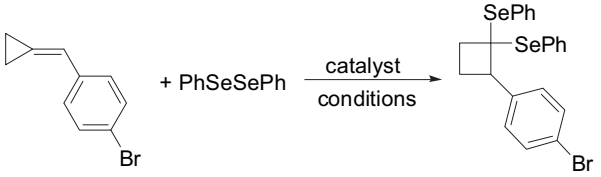
Scheme 1. Synthesis of 1,1-diphenylselenylcyclobutanes.

2. Results and discussion

2.1. Optimize of the reaction conditions

Metal triflate is a kind of Lewis acid, which is more tolerant to moisture. In many cases, their dosages are low [43]. We have recently investigated the metal triflates catalyzed Se–Se bond cleavage and the selective additions to allenes [44]. On the basis of our previous investigations, we initially examined the $Cu(OTf)_2$ catalyzed reactions. Unfortunately, only a series of unidentified complexes was obtained (Table 1, entry 1). When the reaction was catalyzed by $Yb(OTf)_3$, a cyclopropyl ring intact adduct **2a** was obtained in 20% yield (Table 1, entry 2). We then employed Fe $(OTf)_3$ as catalyst and still no desired product was observed (Table 1, entry 3). Accidentally, we found that catalyzed by anhydrous $FeCl_3$, the desired product **3a** could be synthesized in 77% yield (Table 1, entry 4). Further screening demonstrated that the dosage of $FeCl_3$ could be cut to 20 mol% equivalent (Table 1, entry 5). This reaction went on smoothly at room temperature and heat was not required (Table 1, entry 7). We also examined other solvents and the experimental results showed that DCM was a better one (Table 1, entries 8–10). The reaction should be carried out in chloro-substituted alkanes. When it was taken in simple alkane (e.g. cyclohexane), only traces of the desired product was observed. This was probably due to the complexing effect of chloro-atom with ion, which facilitated the dissolution of $FeCl_3$ and broke the polymeric $FeCl_3$ to single molecular. Compared with $TiCl_4$, $FeCl_3$ was much more tolerant to moisture and the solvents were dried just by anhydrous $MgSO_4$ instead of strict operations. When the reaction was carried out without nitrogen protection, the yield of **3a** did not decrease much (Table 1, entry 11).

Table 1
Reaction of MCP **1a** with PhSeSePh under different conditions. [a]



1a **3a**

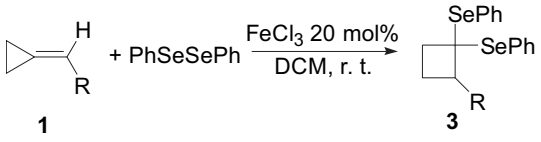
Entry	Catalyst (amount)	Solvent[b]	Temp.	Time (h)[c]	Yield of **3a** (%)[d]
1	$Cu(OTf)_2$ (5%)	DCM	r. t.	12	0[e]
2	$Yb(OTf)_3$ (5%)	DCM	r. t.	12	0[f]
3	Fe $(OTf)_3$ (5%)	DCM	r. t.	12	0[e]
4	$FeCl_3$ (50%)	DCM	r. t.	6	77
5	*$FeCl_3$ (20%)*	*DCM*	*r. t.*	*8*	*82*
6	$FeCl_3$ (10%)	DCM	r. t.	12	63
7	$FeCl_3$ (20%)	DCM	40 °C	6	75
8	$FeCl_3$ (20%)	$CHCl_3$	r. t.	9	66
9	$FeCl_3$ (20%)	CCl_4	r. t.	10	53
10	$FeCl_3$ (20%)	DCE	r. t.	8	67
11	$FeCl_3$ (20%)	DCM	r. t.	8	70[g]

[a] 0.24 mmol of **1a**, 0.2 mmol of PhSeSePh and 1 mL of solvent were employed.
[b] The solvent was dried by $MgSO_4$.
[c] The reaction was monitored by TLC (eluent: petroleum ether).
[d] Isolated yields.
[e] A series of unidentified complexes was observed.
[f] Compound **2a** was obtained in 20% yield (Fig. 1).
[g] In entries 1–10, the reactions were carried out under nitrogen atmosphere; In entry 11, the reaction was carried out without nitrogen atmosphere protection.

2.2. Synthesis of 1,1-diphenylselenylcyclobutanes

Iron is abundant on earth and a low-cost metal. Therefore, this $FeCl_3$-catalyzed reaction is much more economic. The reactions are easy to operate due to the milder conditions, which may facilitate its further applications in organic synthesis. Hence, with the optimized conditions in hand, we examined the application scope of these $FeCl_3$-catalyzed reactions. A series of MCPs **1** was prepared and employed to synthesize the corresponding 1,1-diphenylselenylcyclobutanes **3**. It is obvious that from mono-substituted MCPs, 1,1-deiphenylselenyl cyclobutanes could be smoothly prepared under mild conditions and the yields were generally good (Table 2).

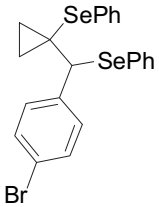
Table 2
Synthesis of 1,1-diphenylselenylcyclobutanes. [a]



1 **3**

Entry	R	Yield of **3** (%)[b]
1	*p*-BrC_6H_4 (**1a**)	82 (**3a**)
2	C_6H_5 (**1b**)	78 (**3b**)
3	*p*-ClC_6H_4 (**1c**)	57 (**3c**)
4	*m*-ClC_6H_4 (**1d**)	54 (**3d**)
5	*p*-$CH_3C_6H_4$ (**1e**)	85 (**3e**)
6	*p*-$Bu^tC_6H_4$ (**1f**)	81 (**3f**)
7	C_7H_{15} (**1g**)	77 (**3g**)
8	C_9H_{19} (**1h**)	80 (**3h**)

[a] 0.24 mmol of **1**, 0.2 mmol of PhSeSePh and 1 mL of DCM were employed.
[b] Isolated yields.

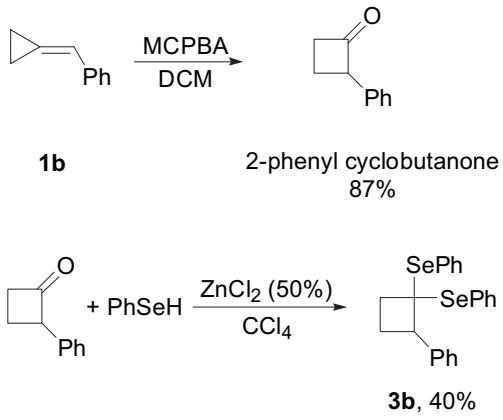


2a, 20%

Fig. 1. Structure of **2a**.

2.3. Further structure confirmation

To confirm the existence of the four-membered ring in products, we synthesized compound **3b** through the traditional way (Scheme 2) and the ^{1}H NMR spectra were in agreement. Fortunately, we succeeded to preparing the single crystal of compound **3b**. The X-ray diffraction finally confirmed the structure (Fig. 2).



Scheme 2. Synthesis of **3b** through traditional method.

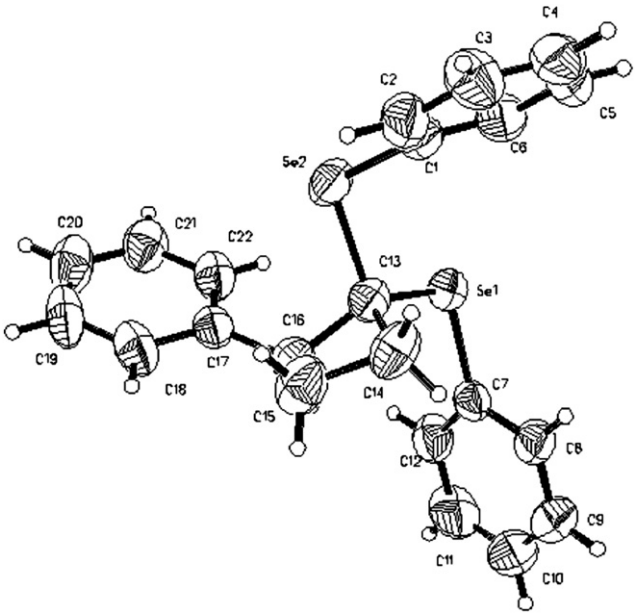
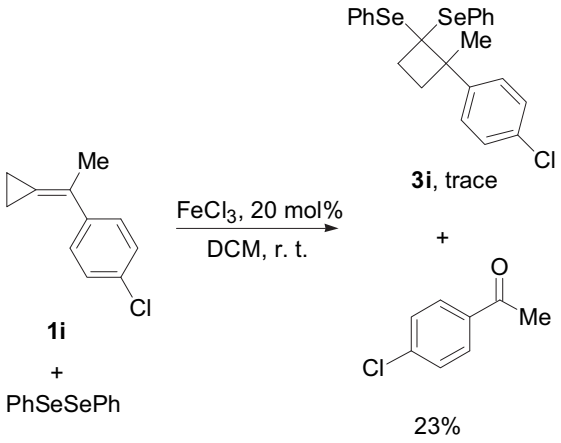


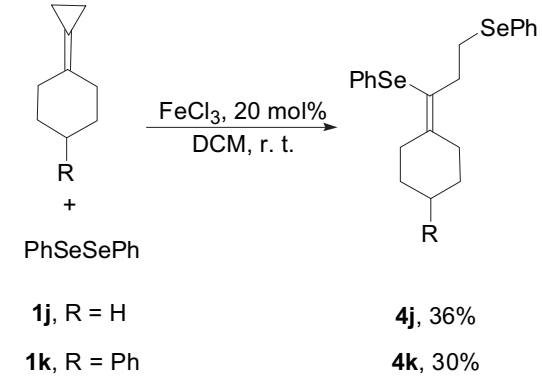
Fig. 2. Molecular structure of compound **3b** in crystal.

2.4. Efferts on the synthesis of 1,1-diphenyldiselenylcyclobutanes from disubstituted MCPs

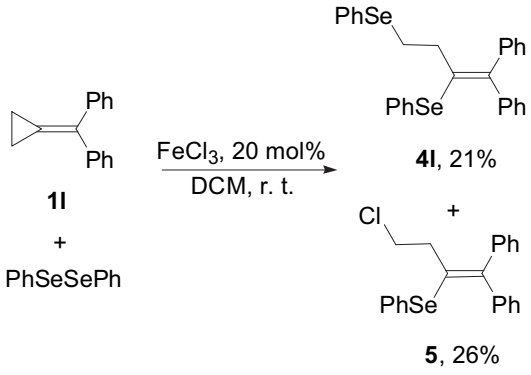
We then tried to synthesize 1,1-phenylselenylcyclobutanes from disubstituted MCPs. When MCP **1i** was employed, only trace of the desired product was observed in ^{1}H NMR spectrum. *p*-Chloroacetophenone, which was the decomposed product of **1i**, was also obtained in 23% yield (Scheme 3). Only ring-opened adduct **4j** and **4k** were obtained in 36% and 30% yield respectively when cyclopropylidenecyclohexane **1j** and **1k** were employed (Scheme 4). When diphenyl substituted MCP **1l** was employed, both ring-opened adduct **4l** and **5** were obtained in 21% and 26% yields, respectively (Scheme 5). These failed results were probably attributed to the higher steric hindrance in substrates.



Scheme 3. Reaction of **1i**.



Scheme 4. Reaction of **1j** and **1k**.

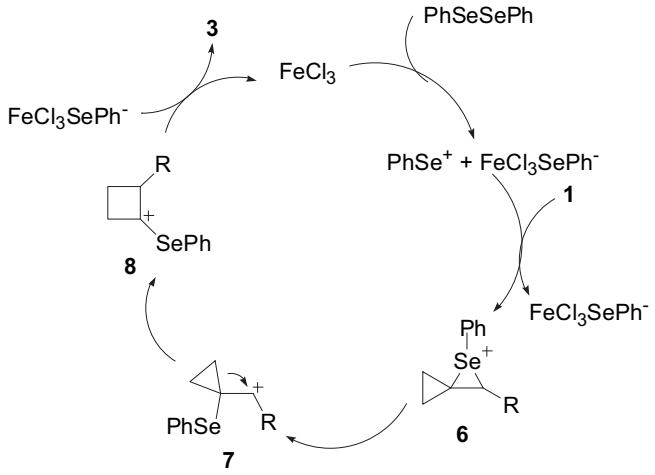


Scheme 5. Reaction of **1l**.

2.5. Mechanism discussion

Based on the above experimental results as well as literatures, a plausible mechanism was supposed. Reaction of the Lewis acid $FeCl_3$ with PhSeSePh affords the phenylselenyl cation and the phenylselenyltrichloroiron anion [45]. Electrophilic addition of

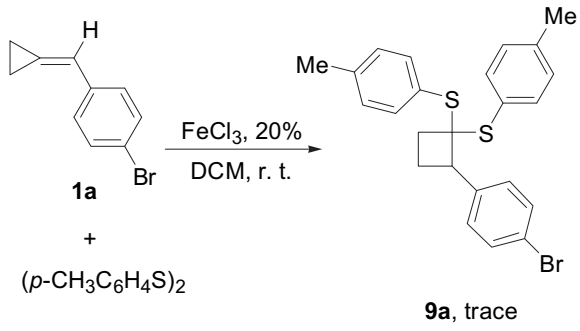
phenylselenyl cation to MCPs **1** leads to intermediate **6** as the episelenium cation, which could be transformed to the intermediate α-phenylselenyl cyclopropylcarbinyl cation **7**. The rearrangement of **7** constructs the four-membered carbon ring structure unit and gives the ring-enlarged cyclobutyl cation **8** [31]. Future reaction of **8** with the phenylselenyltrichloroion anion leads to the final product **3** and regenerates the catalyst $FeCl_3$ (Scheme 6).



Scheme 6. Proposed mechanisms.

2.6. Efferts on the reaction with diaryl disulfide

Sulfur-contained compounds have the similar properties to selenium compounds and are also useful in organic synthesis. Therefore, we tried to examined the similar $FeCl_3$ catalyzed S–S bond cleavage and the subsequent addition to MCPs. However, the experimental results are not satisfying, probably because of the stronger combine force of ion with sulfur element. Only trace of the desired product was obtained (Scheme 7).



Scheme 7. Reaction with diaryl disulfide.

3. Conclusions

Thus, $FeCl_3$ is a good Lewis acid catalyst in Se–Se bond heterogeneous cleavage. Comparing with the previous $TiCl_4$ system, it is more tolerant to air and moisture. Catalyzed by $FeCl_3$, the reactions now could be carried out at room temperature. Meanwhile, the low price and dosage of the catalyst make this system more economic. All of these advantages provide a more operable preparation of 1,1-diphenylselenylcyclobutanes, which are useful intermediates in organic synthesis.

4. Experimental

4.1. General procedure for the preparation of *3*

In an Schlenk tube, 62.4 mg of PhSeSePh (0.2 mmol) and 6.4 mg of $FeCl_3$ (20%) were added. Under nitrogen atmosphere, a solution of 0.24 mmol of MCPs **1** in 1 mL of DCM was injected. The mixture was stirred at room temperature and the reaction was monitored by TLC (eluent: petroleum ether). When the reaction terminated, the mixture was separated by preparative TLC (eluent: petroleum ether: EtOAc 10: 1) to give the corresponding product **3a**–**h**.

4.2. Preparation of *3b* through traditional method

1 mmol of **1b** (130 mg) and 1.75 mmol of MCPBA (356 mg, 85% weight purity) were stirred in 4 mL of CH_2Cl_2 at 0 °C for 1 h. The solution was then successively washed with solutions of $NaHCO_3$, $NaHSO_3$ and $NaHCO_3$ and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the residue was purified by preparation TLC (eluent: petroleum ether/EtOAc 8/1) to give 2-phenyl cyclobutanone in 87% yield (127 mg). Then, 2-phenyl cyclobutanone (127 mg, 0.87 mmol) was dissolved in 1 mL of anhydrous CCl_4. The solution was then added to a mixture of anhydrous $ZnCl_2$ (0.45 mmol), newly distilled PhSeH (0.9 mmol, prepared by the reduction of PhSeSePh) and anhydrous CCl_4 (1 mL, dried by P_2O_5) under nitrogen atmosphere and stirred at room temperature for 12 h. Then, 5 mL of water was added. The mixture was extracted with ether (3 × 5 mL) and the combined organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the residue was isolated by preparation TLC (eluent: petroleum ether/EtOAc 10/1) to give the product **3b** in 40% yield (154 mg). The ^1H NMR spectrum showed that the product prepared through traditional method and the compound synthesized by the $FeCl_3$ catalyzed addition are same.

4.3. Spectrum data

4.3.1. Compound *3a*

Oil. IR (film): 2950, 1435, 1232, 1071, 1009, 911, 822, 741, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.21–7.63 (m, 14H), 3.68–3.71 (m, 1H), 2.51–2.54 (m, 1H), 2.13–2.17 (m, 1H), 1.97–2.08 (m, 1H), 1.84–1.87 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 22.3, 31.7, 49.0, 55.7, 121.0, 128.1, 128.5, 128.7, 128.8, 129.2, 129.3, 130.3, 131.1, 136.7, 138.0, 138.6; MS (EI, 70 eV): *m*/*z* (%) 522 (1) [M^+], 365 (14) [M^+ − PhSe], 340 (76) [M^+ − *p*-$BrC_6H_4CHCH_2$], 183 (88), 128 (100); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{19}BrNaSe_2$ $(M + Na)^+$ 544.8898, Found 544.8889.

4.3.2. Compound *3b*

Solid. m.p. = 70–72 °C; IR (KBr): 2982, 1577, 1494, 1475, 1435, 1234, 1066, 1021, 875, 761, 739, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.28–7.74 (m, 15H), 3.85–3.88 (m, 1H), 2.65–2.68 (m, 1H), 2.22–2.25 (m, 1H), 2.06–2.10 (m, 1H), 1.93–1.96 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.8, 31.2, 48.9, 55.6, 126.5 (d), 127.6, 127.8, 127.9, 128.2, 128.6, 128.7, 129.9, 136.2, 137.5, 139.2; MS (EI, 70 eV): *m*/*z* (%) 444 (2) [M^+], 340 (64) [M^+ − $C_6H_5CHCH_2$], 287 (30) [M^+ − PhSe], 128 (100); *Anal.* Calcd for $C_{22}H_{20}Se_2$: C, 59.74; H, 4.56. Found: C, 59.52; H, 4.31.

4.3.3. Compound *3c*

Oil. IR (film): 2984, 1738, 1577, 1492, 1436, 1236, 1091, 1016, 826, 740, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.25–7.72 (m, 14H), 3.78–3.81 (m, 1H), 2.60–2.63 (m, 1H), 2.22–2.25 (m, 1H), 2.06–2.09 (m, 1H), 1.92–1.94 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 22.3, 31.8, 49.1, 55.8, 128.2, 128.4 (d), 128.7, 129.2 (d), 136.7, 137.9; MS (EI, 70 eV): *m*/*z* (%) 478 (1) [M^+], 340 (72) [M^+ − *p*-$ClC_6H_4CHCH_2$],

321 (22) [M^+ − PhSe], 183 (100), 128 (95); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{19}ClNaSe_2$ $(M + Na)^+$ 500.9403, Found 500.9415.

4.3.4. Compound **3d**

Oil IR (film): 2941, 1575, 1475, 1436, 1301, 1022, 784, 738, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.30–7.40 (m, 14H), 3.84–3.85 (m, 1H), 2.63–2.64 (m, 1H), 2.25–2.27 (m, 1H), 2.09–2.11 (m, 1H), 1.94–1.96 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 22.3, 31.7, 49.2, 55.5, 125.2, 127.2, 127.6, 128.5, 128.8, 129.0, 129.1, 129.2, 129.3, 133.2, 134.0, 136.8, 138.0, 141.8; ^{1} MS (EI, 70 eV): *m*/*z* (%) 478 (1) [M^+], 340 (70) [M^+ − *p*-$ClC_6H_4CHCH_2$], 321 (24) [M^+ − PhSe], 183 (100); HRMS (ESI): *m*/*z* calcd for $C_{22}H_{19}ClNaSe_2$ $(M + Na)^+$ 500.9403, Found 500.9423.

4.3.5. Compound **3e**

Oil. IR (film): 3054, 2982, 2942, 1514, 1475, 1436, 1021, 913, 816, 742, 693 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.16–7.72 (m, 14H), 3.81–3.84 (m, 1H), 2.63–2.66 (m, 1H), 2.35 (s, 3H), 2.20–2.25 (m, 1H), 2.06–2.09 (m, 1H), 1.89–1.93 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.3, 22.4, 31.8, 49.3, 56.5, 126.9, 127.8, 128.3, 128.5, 128.7, 128.8, 129.1, 129.2, 130.5, 131.6, 136.7, 138.1; MS (EI, 70 eV): *m*/*z* (%) 458 (1) [M^+], 340 (25), 183 (100), 128 (60); *Anal*. Calcd for $C_{23}H_{22}Se_2$: C, 60.54; H, 4.86. Found: C, 60.23; H, 4.71.

4.3.6. Compound **3f**

Oil. IR (film): 3055, 2962, 2904, 2866, 1475, 1436, 1021, 913, 831, 742, 693 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.27–7.73 (m, 14H), 3.81–3.84 (m, 1H), 2.64–2.68 (m, 1H), 2.21–2.26 (m, 1H), 2.06–2.09 (m, 1H), 1.89–1.94 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 22.4, 31.5, 31.8, 34.6, 49.3, 56.5, 125.0, 126.8, 128.3, 128.4, 128.7, 129.1, 129.2, 130.5, 136.6, 136.8, 138.1, 149.9; MS (EI, 70 eV): *m*/*z* (%) 500 (1) [M^+], 340 (12), 183 (100); *Anal*. Calcd for $C_{26}H_{28}Se_2$: C, 62.65; H, 5.66. Found: C, 62.28; H, 5.43.

4.3.7. Compound **3g**

Oil. IR (film): 2925, 2862, 1578, 1476, 1436, 1022, 910, 739, 692 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.31–7.76 (m, 10H), 2.51–2.57 (m, 1H), 2.08–2.18 (m, 2H), 1.86–1.93 (m, 1H), 1.73–1.78 (m, 1H), 1.62–1.66 (m, 1H), 1.45–1.49 (m, 1H), 1.20–1.32 (m, 10H), 0.90 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.2, 22.7, 24.9, 27.0, 29.2, 29.6, 31.9, 32.1, 33.5, 48.7, 56.3, 128.3, 128.5, 128.7 (d), 128.8, 130.3, 136.6, 137.8; MS (EI, 70 eV): *m*/*z* (%) 465 (1) [M^+ − 1], 309 (100) [M^+ − PhSe]; *Anal*. Calcd for $C_{23}H_{30}Se_2$: C, 59.48; H, 6.51. Found: C, 59.26; H, 6.20.

4.3.8. Compound **3h**

Oil. IR (film): 2924, 2854, 1576, 1467, 1443, 1236, 1012, 734, 686 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.30–7.75 (m, 10H), 2.53–2.55 (m, 1H), 2.08–2.16 (m, 2H), 1.88–1.91 (m, 1H), 1.74–1.77 (m, 1H), 1.63–1.65 (m, 1H), 1.45–1.49 (m, 1H), 1.22–1.32 (m, 14H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.3, 21.8, 24.0, 26.1, 28.5, 28.6, 28.7, 31.0, 31.2, 32.6, 47.8, 55.4, 127.4, 127.6, 127.8 (d), 127.9, 129.4, 135.7, 136.8; MS (EI, 70 eV): *m*/*z* (%) 493 (1) [M^+ − 1], 337 (100) [M^+ − PhSe]; *Anal*. Calcd for $C_{25}H_{34}Se_2$: C, 60.97; H, 6.96. Found: C, 60.65; H, 6.61.

4.3.9. Compound **3i**

(Trace, only observed from ^1H NMR of *p*-Chloro acetophenone). ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.27–7.90 (m, 14H), 3.18–3.23 (m, 1H), 3.02–3.06 (m, 1H), 2.46–2.48 (m, 1H), 2.15–2.18 (m, 1H), 1.93 (s, 1H), 1.53 (s, 3H).

4.3.10. *p*-Chloro acetophenone

^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.44–7.91 (m, 4H), 2.60 (s, 3H). Known compound and the spectrums were accordance to SDBS Information (SDBS No.: 2376) http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi

4.3.11. Compound **2a**

Oil. IR (film): 1638, 1479, 1436, 1385, 1134, 1070, 1015, 913, 740, 691. ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.15–7.34 (m, 14H), 4.55 (s, 1H), 1.13–1.39 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): (*E* and *Z* mixture) δ 14.5, 15.6, 27.1, 56.3, 121.0, 127.3, 127.4, 128.7, 128.9, 129.0, 130.1, 130.3, 131.3, 133.3, 133.5, 140.8. MS (EI, 70 eV): *m*/*z* (%) 522 (2) [M^+], 365 (29) [M^+ − PhSe], 128 (100). HRMS (ESI): *m*/*z* calcd for $C_{22}H_{19}BrNaSe_2$ $(M + Na)^+$ 544.8898, Found 544.8885.

4.3.12. Compound **4j**

Oil. IR (film): 3069, 2926, 2851, 1578, 1476, 1438, 1384, 1022, 998, 734, 690, 669 cm^{-1} ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.20–7.42 (m, 10H), 3.03 (t, $J = 7.8$ Hz, 2H), 2.74 (t, $J = 7.8$ Hz, 2H), 2.56 (t, $J = 5.7$ Hz, 2H), 2.27 (t, $J = 5.7$ Hz, 2H), 1.56–1.57 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.6, 26.7, 28.3, 28.4, 31.3, 35.8, 36.2, 121.8, 126.2, 126.5, 129.0, 129.1, 130.5, 131.0, 132.0, 132.1, 148.9. MS (EI, 70 eV): *m*/*z* (%) 436 (11) [M^+], 279 (45) [M^+ − PhSe], 79 (100). (Known compound) [8].

4.3.13. Compound **4k**

Oil. IR (film): 3058, 2924, 2853, 1631, 1579, 1476, 1437, 1384, 1119, 1068, 1022, 1000, 735, 693, 668 cm^{-1} ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.20–7.44 (m, 15H), 3.36–3.38 (m, 1H), 3.06 (t, $J = 7.2$ Hz, 2H), 2.72–2.82 (m, 4H), 1.99–2.12 (m, 4H), 1.51–1.55 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.8, 30.9, 35.3, 35.5, 35.8, 35.9, 44.4, 122.8, 126.2, 126.3, 126.6, 126.8, 128.4, 129.0, 129.1, 130.4, 131.3, 131.8, 132.2, 146.3, 147.2. MS (EI, 70 eV): *m*/*z* (%) 512 (7) [M^+], 355 (27) [M^+ − PhSe], 91 (100). (Known compound) [8].

4.3.14. Compound **4l**

Solid. m.p. 78–80 °C; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.06–7.45 (m, 20H), 3.02 (t, $J = 7.2$ Hz, 2H), 2.71 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 26.8, 35.3, 126.3, 127.2, 127.4(d), 128.0, 128.3, 128.4, 128.9, 129.1 (d), 129.2, 130.3, 131.6, 132.9, 133.7, 141.5, 143.3, 147.1. (Known compound) [7,8].

4.3.15. Compound **5**

Solid. m.p. 105–107 °C; ^1H NMR (600 MHz, $CDCl_3$, TMS): δ 7.21–7.50 (m, 15H), 3.61 (t, $J = 6.6$ Hz, 2H), 2.73 (t, $J = 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 36.9, 43.7, 127.3, 127.6 (d), 128.1, 128.4, 129.0, 129.3, 129.5, 130.0, 133.7, 141.4, 143.2, 148.9. (Known compound) [31].

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Appendix A. Supplementary materials

CCDC 780201 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif

Appendix A. Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2010.11.047.

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