



prepared by the reaction of ytterbium with iodine and can be stored for a few hours.

The experimental conditions given in Scheme 1 have been optimized from the reaction of ytterbium metal with iodine or 1,2-diiodoethane at 0 °C, 20 °C and 25

°C. The reaction of ytterbium metal with 1,2-diiodoethane at 0 °C completed after 50 h whereas that with iodine finished within 3.5 h at 0 °C. As already observed in Table 1, the increase of temperature speeds up the reaction.

Table 1 Preparation of YbI<sub>2</sub>

Entry	Reactants	Reaction conditions		Conversion (%) <sup>a</sup>	Product <sup>b</sup>
		Temp. (°C)	Time (h)		
1	Yb, ICH <sub>2</sub> CH <sub>2</sub> I	0	50	98	YbI <sub>2</sub>
2	Yb, I <sub>2</sub>	0	3.5	100	YbI <sub>2</sub>
3	Yb, ICH <sub>2</sub> CH <sub>2</sub> I	20	48	100	YbI <sub>2</sub>
4	Yb, I <sub>2</sub>	20	2.5	100	YbI <sub>2</sub>
5	Yb, ICH <sub>2</sub> CH <sub>2</sub> I	25	45	100	YbI <sub>2</sub>
6	Yb, I <sub>2</sub>	25	2	100	YbI <sub>2</sub>

<sup>a</sup>Present conversion of ytterbium metal was calculated by gravimetry; <sup>b</sup>yellow-green solution of ytterbium diiodide.

For practical and financial reasons, iodine is preferable to 1,2-diiodoethane in the above preparation of ytterbium diiodide.

Scheme 2 summarizes the cleavage of Se—Se bond in diselenides with ytterbium diiodide and the subsequent synthesis of allylselenides. It was found that under

mild conditions, ytterbium arylselenolates could be easily prepared *in situ* by the treatment of diselenides with ytterbium diiodide in THF-HMPA system, and then reacted smoothly with allylic bromide in a one-pot manner to afford the desired allylselenides in moderate to good yields (see Table 2).

Table 2 Reaction conditions and yields of products

Entry	R	Time (h)	Temp. (°C)	Isolated yield (%) <sup>a</sup>	Product
1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	4	50	55	5a
2	2-ClC <sub>6</sub> H <sub>4</sub>	2.5	20–25	85	5b
3	3-ClC <sub>6</sub> H <sub>4</sub>	2.5	20–25	82	5c
4	4-ClC <sub>6</sub> H <sub>4</sub>	2.5	20–25	84	5d
5	2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	20–25	77	5e
6	3-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	3	20–25	80	5f
7	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2.5	20–25	78	5g
8	C <sub>6</sub> H <sub>5</sub>	2.5	20–25	81	5h

<sup>a</sup>Isolated yield based on diselenide.

In order to confirm the formation of the ytterbium selenolates as an intermediate, according to Fukuzawa,<sup>8</sup> a transmetalation reaction of the intermediate with trimethylchlorosilane was performed [Eq. (1)]. Phenylselenonotrimethylsilane was isolated quantitatively by this reaction, indicating the formation of the ytterbium selenolates species as an intermediate.



The yield of aryl allylselenide was better than that of alkyl allylselenide and the reason maybe that the free anion of arylselenolate is more stable than that of

alkylselenolate.

## Experimental

Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl. Commercial HMPA was dried over calcium hydride, distilled *in vacua* and stored over 4 Å molecular sieves. Allylic bromide was distilled prior to use. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-80 spectrometer using TMS as internal standard. Infrared spectra were obtained on an IR-408 spectrometer in film. Mass spectra were recorded on an HP 5989B MS spectrometer. Microanalysis was carried on a Carlo-

Erba 1106 instrument.

*General procedure for the preparation of YbI<sub>2</sub>*

Ytterbium powder (0.086 g, 0.5 mmol), THF (12 mL) and iodine (0.125 g, 0.5 mmol) were added to a 50 mL of three-necked flask under nitrogen atmosphere. The mixture was magnetically stirred for about 2–3 h at 20–25 °C to obtain a yellow-green solution of YbI<sub>2</sub>.

*General procedure for the synthesis of allylselenides*

The yellow-green solution of YbI<sub>2</sub> (0.5 mmol) in 12 mL of THF was treated with 0.5 mL of HMPA. Then 0.25 mmol of diselenides were added in one portion at 20–25 °C under nitrogen atmosphere. The mixture was stirred for 0.5 h. To the mixture was added 0.061 g (0.5 mmol) of freshly distilled allyl bromide at 20–25 °C, then stirred for 1.5–2.5 h (see Table 2) at the same temperature. The reaction mixture was extracted with ether (10 mL × 3) and dried over MgSO<sub>4</sub>. The solvent was removed by evaporation. The crude products were purified by preparative TLC on silica gel [cyclohexane and ethylacetate (20:1) as eluent]. All products were identified by IR, <sup>1</sup>H NMR and MS spectra.

*Transmetalation reaction of diphenyl diselenide with trimethylchlorosilane mediated by YbI<sub>2</sub>*

To the yellow-green THF-HMPA (10–0.5 mL) solution prepared from YbI<sub>2</sub> (0.5 mmol) and diphenyl diselenide (0.085 g, 0.25 mmol) as described above, trimethylchlorosilane was added by injection through a rubber septum with a syringe at room temperature. After being stirred at ambient temperature for 1 h, the solution was diluted with dry hexane (25 mL) and the precipitate was removed by filtration. The precipitate was further washed with dry hexane (20 mL) and the filtrates were combined. The solvent was removed by a rotary evaporator under vacuum. <sup>1</sup>H NMR spectral measurement of the residue indicates the formation of almost pure phenylselenotrimethylsilane.<sup>8</sup> Yield 0.113 g, 99%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ: 0.32 (s, 9H), 6.70–7.60 (m, 5H).

*Allyl butylselenide (5a)* Oil;<sup>9</sup> <sup>1</sup>H NMR

(CDCl<sub>3</sub>, 80 MHz) δ: 5.90–5.53 (m, 1H), 4.79 (d, *J* = 6.2 Hz, 2H), 3.00–2.70 (m, 2H), 0.98–1.68 (m, 7H); IR (film) ν: 2962, 2930, 2884, 1642, 1468, 1318, 992, 910 cm<sup>-1</sup>.

*Allyl 2-chlorophenylselenide (5b)* Light yellow oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ: 3.46 (d, *J* = 6.0 Hz, 2H), 5.0 (d, *J* = 6.2 Hz, 2H), 5.6–5.95 (m, 1H), 6.9–7.4 (m, 4H); IR (film) ν: 3050, 2930, 1630, 1575, 1450, 1430, 1250, 1190, 1130, 915, 740 cm<sup>-1</sup>; MS *m/z* (%): 234 (M<sup>+</sup> + 2, 21), 233 (M<sup>+</sup> + 1, 11), 230 (M<sup>+</sup> - 2, 26); Anal. calcd for C<sub>9</sub>H<sub>9</sub>ClSe: C 46.68, H 3.92; found C 46.56, H 3.80.

*Allyl 3-chlorophenylselenide (5c)* Red oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ: 3.54 (d, *J* = 6.2 Hz, 2H), 5.91–5.98 (m, 1H), 7.18–7.49 (m, 4H); IR (film) ν: 3100, 2950, 2400, 1590, 1470, 1100, 920, 775, 750, 680 cm<sup>-1</sup>; MS *m/z* (%): 234 (M<sup>+</sup> + 2, 15), 232 (M<sup>+</sup>, 33), 191 (19), 112 (8), 111 (12), 41 (100); Anal. calcd for C<sub>9</sub>H<sub>9</sub>ClSe: C 46.68, H 3.92; found C 46.58, H 3.86.

*Allyl 4-chlorophenylselenide (5d)* Oil;<sup>9,10</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ: 2.33 (s, 3H), 3.3 (d, *J* = 6.0 Hz, 2H), 4.82 (d, *J* = 6.2 Hz, 2H), 5.60–6.00 (m, 1H), 6.70–7.60 (m, 4H); IR (film) ν: 3110, 2950, 1650, 1480, 1180, 1100, 1000, 820, 690 cm<sup>-1</sup>.

*Allyl 2-methylphenylselenide (5e)* Oil;<sup>9</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ: 2.33 (s, 3H), 3.31 (d, *J* = 6.0 Hz, 2H), 4.60–5.05 (d, *J* = 6.2 Hz, 2H), 5.60–6.00 (m, 1H), 6.70–7.60 (m, 4H); IR (film) ν: 3080, 2960, 1645, 1510, 1380, 990, 900, 830 cm<sup>-1</sup>.

*Allyl 3-methylphenylselenide (5f)* Red oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ: 2.40 (s, 3H), 3.33 (d, *J* = 6.0 Hz, 2H), 4.82 (d, *J* = 6.2 Hz, 2H), 5.50–6.05 (m, 1H), 6.9–7.20 (m, 4H); IR (film) ν: 3370, 3030, 2920, 2360, 1580, 1470, 1280, 1210, 1160, 1060, 980, 910, 820, 770, 670 cm<sup>-1</sup>; MS *m/z* (%): 212 (M<sup>+</sup>, 21), 211 (3), 171 (13), 91 (100), 77 (6), 41 (20); Anal. calcd for C<sub>10</sub>H<sub>12</sub>Se: C 56.88, H 5.73; found C 56.78, H 5.70.

*Allyl 4-methylphenylselenide (5g)* Oil;<sup>9,11</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 80 MHz) δ: 2.30 (s, 3H), 3.33 (d, *J* = 6.0 Hz, 2H), 4.75 (d, *J* = 6.2 Hz, 2H), 5.50–5.90 (m, 1H), 6.70–7.50 (m, 4H); IR (film) ν: 3100, 2970, 2880, 1640, 1510, 1380,

990, 840  $\text{cm}^{-1}$ .

*Allyl phenyl selenide (5h)* Oil;<sup>9,11</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 80 MHz)  $\delta$ : 3.30 (d,  $J = 6.0$  Hz, 2H), 4.75 (d,  $J = 6.2$  Hz, 2H), 5.50—5.90 (m, 1H), 7.00—7.60 (m, 5H); IR (film)  $\nu$ : 3080, 2940, 1640, 1480, 1180, 990, 910, 730, 680  $\text{cm}^{-1}$ .

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