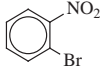

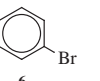

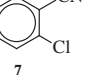

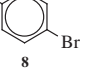

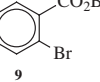

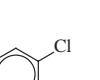






**Table 1** Nucleophilic aromatic substitution with **1** in DMSO–MeOH

Substrate	Product	t/h	T/°C	Yield (%)
		1	20	76 <sup>a</sup>
		1	20	79 <sup>a</sup>
		1	125	72 <sup>a</sup>
		20	125	68 <sup>a</sup>
		20	125	48 <sup>a</sup>
		24	125	54 <sup>b</sup>
		24	125	6 <sup>b</sup>

<sup>a</sup> Of isolated, pure compound. <sup>b</sup> Inseparable product mixture, composition analyzed by GC-MS.

to clean solutions of **1** containing a precisely defined amount of a reagent with a sufficiently high nucleophilic reactivity for most synthetic purposes.

## Experimental

### Preparation of 1 M sodium benzeneselenolate solutions

DMSO (Lab-Scan), 25% sodium methanolate in methanol (Aldrich) and hydrazine hydrate (Fluka) were used directly. NMP (Aldrich) was distilled from sodium methanolate prior to use in order to remove an unknown impurity causing a red coloring of the reagent solution. Diphenyl diselenide (**2**) was purified by oxidation to dihydroxy phenylselenonium toluene-*p*-sulfonate followed by reduction of the recrystallized salt according to ref 8. To a stirred solution containing **2** (5 mmol) and hydrazine hydrate (2.75 mmol) in DMSO or NMP (8 ml) was added 25% methanolic sodium methanolate (approximately 2 g, the last 0.2 g added dropwise with intervals of 5 s until the yellow color of **2** disappeared). A reagent with increased reactivity can be obtained by removing the methanol,

e.g. at 60 °C, 1–2 kPa (membrane pump) or at ~90 °C in a stream of nitrogen.

### Conjugate addition of benzeneselenol

To a solution of **1** (10 mmol) prepared in NMP was added a mixture of acetic acid (10 mmol) and the appropriate acrylic acid derivative (10 mmol). After 10 min the mixture was poured into water and the product isolated by extraction (hexane–ethyl acetate, 4 : 1), flash chromatography (silica gel 60) and bulb-to-bulb distillation (10 Pa, air bath 200 °C). Yields: **3**, 93%, purity (GC-MS), 98% ; **4**, 84%, purity (GC-MS), 96%.

### (Phenylseleno)arenes (11–17)

The haloarene (10 mmol) was added to a solution of **1** (10 mmol) and the mixture was stirred in a nitrogen atmosphere as specified in Table 1. The reaction mixture was poured into water and extracted with ether. The ether phase was filtered through alumina (neutral, 6 g) and solid residues from evaporation were recrystallized: 2-nitrophenyl phenyl selenide (**11**), mp 90 °C (from ethanol) (lit.,<sup>12</sup> 91 °C); 4-nitrophenyl phenyl selenide (**12**), mp 60 °C (from ethanol) (lit.,<sup>12</sup> 54 °C); 2-(phenylseleno)benzonitrile (**13**), mp 73 °C (from methanol) (lit.,<sup>10a</sup> 70 °C); 4-(phenylseleno)benzonitrile (**14**), mp 52 °C (from hexane) (lit.,<sup>13</sup> 52 °C). A 50% excess of **1** was applied in the preparation of *tert*-butyl 2-(phenylseleno)benzoate (**15**). The product was purified by column chromatography (silica gel 60, pentane). Colorless oil [Found: C, 61.2%; H 5.5%; M<sup>+</sup> (<sup>80</sup>Se) 334; C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>Se requires C, 61.2%; H 5.4%; M(<sup>80</sup>Se), 334]; δ(<sup>77</sup>Se) (57.3 MHz; CDCl<sub>3</sub>; Me<sub>2</sub>Se), 469 ppm.

## Notes and references

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