SUPPORTING INFORMATION

SYNTHESIS OF 2-AMINO-1,3-BENZOSELENAZOLE VIA METAL-FREE CYCLIZATION FROM ISOTHIOCYANATE AND BIS(*o*-AMINOPHENYL) DISELENIDE

Hayato Ichikawa,* Naoka Miyashi, Yui Ishigaki and Minako Mitsuhashi

College of Industrial Technology, Nihon University, 1-2-1 Izumicho Narashino, Chiba 275-8575, Japan. e-mail:ichikawa.hayato64@nihon-u.ac.jp

EXPERIMENTAL

^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured using TMS as the internal standard with a Bruker Avance III 500 (500 MHz) spectrometer. For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by preparative column chromatography on silica gel (Kanto, silica gel 60). In experiments requiring dry tetrahydrofuran (THF), THF was purchased from Kanto Chemicals Co., Ltd. in the "Dehydrated" form. Dichloromethane and chloroform were stored over molecular sieves 4A.

Preparation of bis(*o*-aminophenyl) diselenides 1

Method A (**1a** and **1c**): To dehydrated THF (45 mL) in a 300 mL three-neck flask that was dried and flushed with argon, lithium (69.7 mmol, 2.2 equiv.) and diphenylacetylene (0.30 g,

1.80 mmol, 0.058 equiv.) were added, and the reaction mixture was stirred vigorously at 0 °C for 1 h. After the solution changed to blue, elemental selenium powder (69.7 mmol, 2.2 equiv.) was added and the reaction mixture was stirred for 24 h to produce dilithium diselenide. To the solution was dropped HMPA (10 mL, 57.5 mmol, 1.8 equiv). The reaction mixture was stirred for 30 min and then dehydrated THF solution of corresponding 2-chloronitrobenzene (31.3 mmol) was added by means of a cannula. After stirring for 20 h at room temperature, the solution was quenched with water, selenium was filtered off using Celite, and chloroform extraction was carried out. The organic extracts were washed with brine and dried over $MgSO_4$. After filtration, solvent evaporation and purification of the oily residue by column chromatography on silica gel (hexane/$CHCl_3$ = 2:1 as eluent) were carried out. Recrystallization from $CHCl_3$ gave bis(*o*-nitrophenyl) diselenides (31–53%). To a methanol solution (15 mL) of bis(*o*-nitrophenyl) diselenides in a two-neck flask were added activated carbon (5 mmol, 1.3 equiv.) and $FeCl_3$•$6H_2O$ (51 μmol, 0.014 equiv.). After refluxing for 10 min, hydrazine monohydrate (22.6 mmol, 6.0 equiv.) was dropped and the reaction mixture was refluxed for an additional 2 h. The reaction mixture was filtered through Celite to remove activated carbon and the solvent was removed under reduced pressure. The residue was extracted with chloroform and the organic layer was washed with brine and dried over $MgSO_4$. Solvent evaporation and recrystallization from EtOH gave corresponding diselenide (90–97%).

Bis(*o*-aminophenyl) diselenide (**1a**): yield 92%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.12 (t, *J* = 7.75 Hz, 1H, Ar-*H*), 6.68 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 6.54 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 4.24 (br, 2H, N*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.87, 138.33,

131.54, 118.43, 115.03, 114,79; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 405.62.

Bis(2-amino-4-methylphenyl) diselenide (**1c**): yield 97%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.24 (m, 1H, Ar-*H*), 6.26–6.25 (m, 1H, Ar-*H*), 6.17–6.15 (m, 1H, Ar-*H*), 4.31 (s, 2H, N*H*$_2$), 3.77 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.73, 150.30, 139.81, 106.81, 104.89, 99.66, 55.20; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 413.35.

Method B (**1b**, **1d**–**f**): To an ethereal solution of BF_3 etherate (14.0 mmol, 1.4 equiv.) in a 300 mL three-neck flask at -15 °C was added a dichloromethane solution of the corresponding anilines (10.0 mmol) by means of a cannula, and the reaction mixture was stirred for 15 min at the same temperature. After dropping *t*-butyl nitrite (12.0 mmol, 1.2 equiv.), the reaction mixture was stirred for 1 h at 0 °C. Cold pentane was added to the solution and this was followed by vacuum filtration. The crude diazonium salts were used in further reactions. To cold water (50 mL) were slowly added the crude diazonium salts and a solution of potassium selenocyanate (10.2 mmol, 1.0 equiv.) in water (20 mL) at 0 °C. After stirring for 15 min, the reaction mixture was filtered and solvent was evaporated under vacuum. The crude products were extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, and filtered, and the solvent was evaporated. Purification of the residue by column chromatography on silica gel (hexane/CH_2Cl_2 = 2:1 as eluent) gave the corresponding selenocyanates. To a solution of the selenocyanates (1.0 mmol) in dehydrated THF (10 mL) in a 100 mL two-neck flask was added $LiAlH_4$ (0.114 g, 3.0 mmol, 3.0 equiv.) at 0 °C. The resulting mixture was stirred at room temperature for 20 min. The solution was quenched with water (1 mL), 1M NaOH (0.3 mL), and then water (3 mL). After filtration through Celite, THF was evaporated under reduced pressure and the residue was

acidified with 1M HCl. Extraction was carried out with ethyl acetate. The organic layer was dried over $MgSO_4$ and solvent evaporation gave the crude products. Purification of the residue by column chromatography on silica gel (hexane/$CHCl_3$ = 1:1 as eluent) gave the corresponding diselenides.

Bis(2-amino-4-methoxyphenyl) diselenide (**1b**): yield 48%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 6.55 (m, 1H, Ar-*H*), 6.41–6.39 (m, 1H, Ar-*H*), 4.21 (br, 2H, N*H*$_2$), 2.26 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.80, 141.96, 138.24, 119.64, 115.42, 112.13, 21.48; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 406.48.

Bis(2-amino-4-ethoxyphenyl)diselenide (**1d**): yield 78%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 6.23–6.22 (m, 1H, Ar-*H*), 6.15–6.12 (m, 1H, Ar-*H*), 4.29 (br, 2H, N*H*$_2$), 3.97 (q, *J* = 7.0 Hz, 2H, C*H*$_2$CH$_3$), 1.38 (t, *J* = 7.0 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.10, 150.34, 139.80, 106.65, 105.42, 100.19, 63.37, 14.82; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 414.41.

Bis(2-amino-4-chlorophenyl) diselenide (**4e**)**:** yield 47%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.21 (m, 1H, Ar-*H*), 6.71–6.70 (m, 1H, Ar-*H*), 6.55–6.53 (m, 1H, Ar-*H*), 4.36 (s, 2H. N*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.68, 138.25, 136.45, 117.41, 113.16, 111.72; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 405.92.

Bis(2-amino-5-chlorophenyl) diselenide (**1f**): yield 48%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 1H, Ar-*H*), 7.10–7.08 (m, 1H, Ar-*H*), 6.64 (d, *J* = 9.0 Hz, 1H, Ar-*H*), 4.26 (s, 2H, N*H*$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.36, 137.17, 131.51, 122.21, 115.59, 115.28; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 419.98.

Preparation of 1,3-benzoselenazoles 3

To a chloroform solution (3 mL) of diselenide **1** (0.167 mmol) in a 50 mL two-neck flask was dropped isothiocyanate **2** (0.5 mmol, 3.3 eq.) under argon, and the resulting mixture was refluxed for 24 h.[1] The mixture was extracted with ethyl acetate and the organic layer was dried over $MgSO_4$. Solvent evaporation and recrystallization from toluene gave 1,3-benzoselenazoles **3** in each yields.

***N*-(benzo[*d*][1,3]selenazol-2-yl)benzamide** (**3a**): ^{1}H NMR (500 MHz, acetone-d_6) δ 11.59 (brs, 1H, N*H*), 8.28–8.26 (m, 2H, Ar-*H*), 8.04–8.02 (m, 1H, Ar-*H*), 7.78–7.76 (m, 1H, Ar-*H*), 7.69–7.68 (m, 1H, Ar-*H*), 7.62–7.59 (m, 2H, Ar-*H*), 7.46–7.43 (m, 1H, Ar-*H*), 7.28–7.25 (m, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.78, 161.13, 148.65, 144.04, 134.38, 132.16, 128.92, 127.95, 126.14, 124.44, 124.02, 121.84; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 593.32.

***N*-(benzo[*d*][1,3]selenazol-2-yl)-3-methylbenzamide** (**3b**): yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.78 (brs, 1H, N*H*), 7.87 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.77 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.24–7.13 (m, 6H, Ar-H), 1.97 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.67, 161.64, 148.71, 138.84, 134.38, 133.67, 132.01, 128.78, 128.51, 126.06, 125.39, 124.35, 123.95, 121.97, 20.82; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 593.05.

***N*-(benzo[*d*][1,3]selenazol-2-yl)acetamide** (**3c**): yield 75%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.48 (brs, 1H, N*H*), 7.91–7.89 (m, 1H, Ar-*H*), 7.81–7.79 (m, 1H, Ar-*H*), 7.47–7.44 (m, 1H, Ar-*H*), 7.29–7.26 (m, 1H, Ar-*H*), 2.28 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.03, 160.43, 149.18, 134.72, 126.42, 124.68, 124.10, 121.97, 23.62; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 593.25.

***N*-(benzo[*d*][1,3]selenazol-2-yl)butyramide** (**3d**): yield 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.62 (brs, 1H, N*H*), 7.91–7.89 (m, 1H, Ar-*H*), 7.78 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.46–7.43

(m, 1H, Ar-*H*), 7.29–7.25 (m, 1H, Ar-*H*), 2.42 (t, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_2$CH$_3$), 1.72 (sext, *J* = 7.5 Hz, 2H, CH$_2$C*H*$_2$CH$_3$), 0.89 (t, *J* = 7.0 Hz, 3H, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.19, 160.48, 149.19, 134.64, 126.35, 124.69, 124.03, 121.83, 38.43, 18.52, 13.57; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 592.80.

***N*-(benzo[*d*][1,3]selenazol-2-yl)heptanamide** (**3e**): yield quant.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.98 (brs, 1H, N*H*), 7.89 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.80 (d, *J* = 8.0 Hz ,1H, Ar-*H*), 7.44 (t, *J* = 7.75 Hz, 1H, Ar-*H*), 7.27 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 2.44 (t, *J* = 7.75 Hz, 2H, C*H*$_2$), 1.69 (*J* = 7.0 Hz, 2H, C*H*$_2$), 1.26–1.23 (m, 4H, 2C*H*$_2$), 0.85 (t, *J* = 6.25 Hz, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.10, 159.83, 149.37, 134.80, 126.33, 124.62, 124.05, 122.03, 36.67, 31.17, 24.68, 22.25, 13.80; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 592.44.

***N*-(benzo[*d*][1,3]selenazol-2-yl)isobutyramide** (**3f**): yield 76%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.43 (brs, 1H, N*H*), 8.01 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.73 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.42–7.39 (m, 1H, Ar-*H*), 7.21 (t, J = 8.0 Hz, 1H, Ar-*H*), 2.80 (sep, *J* = 7.0 Hz, 1H, C*H*(CH$_3$)$_2$), 1.16 (d, *J* = 7.0 Hz, 6H, CH(C*H*$_3$)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.45, 159.30, 145.48, 134.74, 126.19, 124.54, 123.86, 121.86, 35.46,19.13; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 590.72.

***N*-(benzo[*d*][1,3]selenazol-2-yl)pivalamide** (**3g**): yield 90%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (brs, 1H, N*H*), 7.86–7.85 (m, 1H, Ar-*H*), 7.79–7.77 (m. 1H, Ar-*H*), 7.43–7.40 (m, 1H, Ar-*H*), 7.24–7.21 (m, 1H, Ar-*H*), 1.31 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.01, 158.60, 149.77, 135.07, 126.27, 124.46, 123.95, 122.38, 39.36, 27.10; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 591.57.

Ethyl benzo[*d*][1,3]selenazol-2-ylcarbamate (**3h**): yield 74%; ^{1}H NMR (500 MHz, $CDCl_3$)

δ 11.82 (brs, 1H, N*H*), 7.96 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.84 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.41–7.38 (m, 1H, Ar-*H*), 7.23 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 4.42 (q, *J* = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 1.40 (t, *J* = 7.0 Hz, 3H, CH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.89, 154.61, 150.06, 134.16, 125.83, 124.16, 123.62, 122.18, 62.91, 14.43; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 578.31.

***N*-(5-methylbenzo[*d*][1,3]selenazol-2-yl)benzamide** (**3i**): yield 83%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.08 (brs, 1H, N*H*), 8.00–7.98 (m, 1H, Ar-*H*), 7.74 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.56–7.52 (m, 1H, Ar-*H*), 7.42–7.39 (m, 2H, Ar-*H*), 7.05–7.04 (m, 2H, Ar-*H*), 2.62 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.47, 162.14, 148.57, 135.86, 132.76, 132.66, 130.74, 128.64, 128.29, 125.38, 123.85, 122.12, 21.22; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 589.43.

***N*-(5-methoxybenzo[*d*][1,3]selenazol-2-yl)benzamide** (**3j**): yield 91%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.42 (brs, 1H, N*H*), 8.00–7.99 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.74–7.72 (m, 1H, Ar-*H*), 7.59–758 (m, 1H, Ar-*H*), 7.44 (t, *J* = 7.0 Hz, 2H, Ar-*H*), 7.00 (m, 1H, Ar-*H*), 6.89–6.87 (m, 1H, Ar-*H*), 3.67 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.84, 162.93, 158.88, 149.71, 133.02, 132.14, 128.89, 128.25, 125.39, 124.63, 113.59, 105.14, 55.18; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 588.75.

***N*-(5-ethoxybenzo[*d*][1,3]selenazol-2-yl)benzamide** (**3k**): yield quant.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.25 (brs, 1H, N*H*), 7.99–7.97 (m, 2H, Ar-*H*), 7.70–7.68 (m,1H, Ar-*H*), 7.51–7.47 (m, 1H, Ar-*H*), 7.33–7.30 (m, 2H, Ar-*H*), 6.84–6.82 (m, 1H, Ar-*H*), 6.70–6.69 (m, 1H, Ar-*H*), 3.61 (q, *J* = 7.0 Hz, 2H, OC*H*$_2$CH$_3$), 1.29 (t, *J* = 7.0 Hz, 3H, OCH$_2$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.86, 162.88, 158.25, 149.58, 133.01, 132.18, 128.88, 128.23, 125.21, 124.60, 114.07, 105.86, 63.44, 14.67; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 588.46.

***N*-(5-chlorobenzo[*d*][1,3]selenazol-2-yl)benzamide** (**3l**): yield 84%; ^{1}H NMR (500 MHz,

$CDCl_3$) δ 11.35 (brs, 1H, N*H*), 7.98–7.97 (m, 2H, Ar-*H*), 7.79–7.77 (m, 1H, Ar-*H*), 7.63–7.59 (m, 1H, Ar-*H*), 7.47 (t, *J* = 7.75 Hz, 2H, Ar-*H*), 7.31 (m, 1H, Ar-*H*), 7.21–7.19 (m, 1H, Ar-*H*); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.29, 161.63, 150.36, 133.41, 132.78, 132.12, 131.81, 129.17, 127.80, 125.11, 124.31, 122.06; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 598.00.

***N*-(6-chlorobenzo[*d*][1,3]selenazol-2-yl)benzamide** (**3m**): yield 89%; ^{1}H NMR (500 MHz, acetone-d_6) δ 11.61 (brs, 1H, N*H*), 8.11 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.96 (d, *J* = 2.2 Hz, 1H, Ar-*H*), 7.61 (d, *J* =8.5 Hz, 1H, Ar-*H*), 7.57 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.48 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 7.30 (m, 1H, Ar-H); ^{13}C NMR (125 MHz, acetone-d_6) δ 166.58, 160.10, 148.79, 136.31, 133.03, 132.28, 128.77, 128.48, 128.17, 126.44, 124.32, 122.77; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 604.81.

***N*-(5-methylbenzo[*d*][1,3]selenazol-2-yl)acetamide** (**3n**): yield 29%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.51 (brs, 1H, N*H*), 7.75 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 7.26 (m, 1H, Ar-*H*), 7.10 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 2.47 (s, 3H, C*H*$_3$), 2.27 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.27, 161.14, 148.50, 136.60, 130.74, 125.70, 124.22, 121.86, 23.58, 21.42; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 587.68.

***N*-(5-methoxybenzo[*d*][1,3]selenazol-2-yl)acetamide** (**3o**): yield 42%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.61 (brs, 1H, N*H*), 7.71 (d, *J* = 8.5 Hz, 1H, Ar-*H*), 7.32 (s, 1H, Ar-*H*), 6.92–6.89 (m, 1H, Ar-*H*), 3.87 (s, 3H, OC*H*$_3$), 2.30 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.18, 159.22, 150.86, 126.16, 124.70, 106.20, 55.58, 23.63; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 586.01.

***N*-(5-chlorobenzo[*d*][1,3]selenazol-2-yl)acetamide** (**3p**): yield 31%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.32 (brs, 1H, N*H*), 7.77–7.75 (m, 2H, Ar-*H*), 7.24–7.22 (m, 1H, Ar-*H*), 2.33 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.85, 160.17, 149.50, 131.87, 131.34, 124.36,

123.35, 120.91, 22.57; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 597.25.

***N*-(6-chlorobenzo[*d*][1,3]selenazol-2-yl)acetamide** (**3q**): yield 31%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (brs, 1H, N*H*), 7.84 (m, 1H, Ar-*H*), 7.69 (d, *J* = 8.6 Hz, 1H, Ar-*H*), 7.41–7.39 (m, 1H, Ar-*H*), 2.30 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.46, 158.90, 148.19, 136.22, 129.63, 126.95, 124.16, 122.96, 23.56; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 604.54.

Hydrolysis of 3c

To a 100 mL two-neck flask were added **3c** (3.6 mmol) and 20% H_2SO_4 (15 mL), and reflux was carried out for 16 h. The resulting mixture was extracted with ethyl acetate and the organic layer was dried over $MgSO_4$. Solvent evaporation and purification of the residue by column chromatography on silica gel ($CHCl_3$/EtOAc = 1:1 as eluent) gave 2-amino-1,3-benzoselenazole (**4**) (2.9 mmol, 80%).^{1}H NMR (500 MHz, acetone-d_6) δ 7.69–7.67 (m, 1H, Ar-*H*), 7.41–7.39 (m, 1H, Ar-*H*), 7.24–7.20 (m, 1H, Ar-*H*), 7.10 (brs, 2H, NH_2), 7.00–6.95 (m, 1H, Ar-*H*); ^{13}C NMR (125 MHz, acetone-d_6) δ 166.39, 154.78, 134.47, 125.68, 124.21, 121.37, 119.54; ^{77}Se NMR (95 MHz, acetone-d_6) δ 509.87.

REFERENCES AND NOTES

1. Preparation of acyl isothiocyanates **2**: K. G. Bedane, and G. S. Singh, *ARKIVOC*, 2015, **vi**, 206 and reference cited therein.