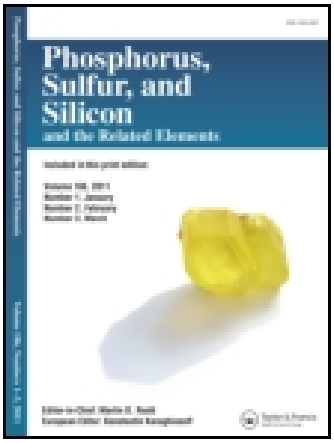

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INVESTIGATION ON THE Se-ACYLATION WITH *N*-ACYLBENZOTRIAZOLES

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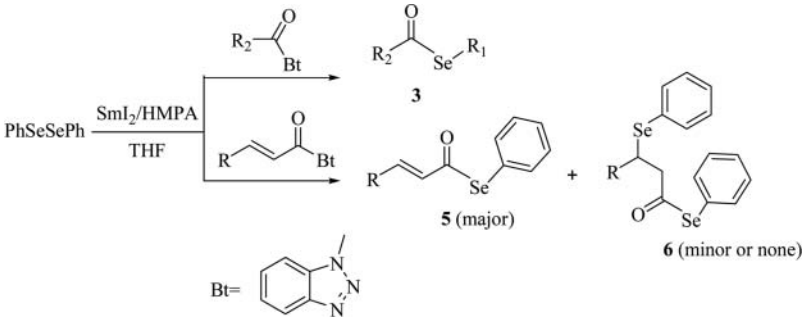
GRAPHICAL ABSTRACT



Abstract *The acylation of Se-nucleophiles with N-acylbenzotriazoles was investigated. Samarium phenylselenolate and benzylselenolate ($RSeSmI_2$) reacted with N-aroyl and N-alkanoylbenzotriazoles smoothly and afforded the corresponding selenol esters in good yields. Treatment of the $RSeSmI_2$ with α,β-unsaturated N-acylbenzotriazoles afforded the anticipated α,β-unsaturated selenol esters in moderate yields, due mainly to the side reaction of conjugate addition.*

Keywords *N*-Acylbenzotriazole; samarium(II) iodide; diselenides; Se-acylation; selenol esters

INTRODUCTION

N-Acylbenzotriazoles have found wide applications in organic synthesis. Being less sensitive toward moisture, milder in reactivity, and more readily to crystallize, *N*-acylbenzotriazoles often offer great advantages over the corresponding acid chlorides.

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They can acylate the N-, C-, O-, and S-nucleophiles smoothly under mild conditions with satisfactory yield.[1] Usually, racemization does not occur during the reaction[2–4] and good chemoselectivity could be obtained readily.[5,6] However, despite their general use and remarkable advantages in organic synthesis, the acylation of *N*-acylbenzotriazoles with Se-nucleophiles has not been reported.

Selenol esters are useful intermediates in organic synthesis[7,8] and a variety of methods have been developed for the preparation of them. These include: (a) acylation of acyl halides with selenols,[9] selenium anions generated in situ from diselenides,[10a–c,10f–i] or phenyl tributylstannyl selenide ($PhSeSnBu_3$);[10d,e] (b) reaction of carboxylic acids[11] or their triethylammonium salts[12] with phenylselenocyanate or benzeneselenenyl chloride in the presence of tributylphosphine; (c) ring opening of isopropylidene malonate derivatives by samarium aryl selenolate;[13] (d) reaction of acylzirconene chlorides with ArSeBr or diaryldiselenides;[14] (e) reaction of aldehydes and diisobutylaluminum selenoate (iBu_2AlSeR) under Tishchenko-type conditions;[15a] and (f) free-radical Se-acylation of the diselenides with In and acyl halides.[15b] However, although some of these synthetic approaches could afford good, even excellent, yields of the selenol esters, they either utilized acyl halides, which were moisture-sensitive and sometimes difficult to prepare and purify, or were limited to a narrow substrate scope. Sometimes, rarely available reagents, tedious procedures, and/or harsh conditions were employed. Therefore, alternative methods for the preparation of selenol esters were still required.

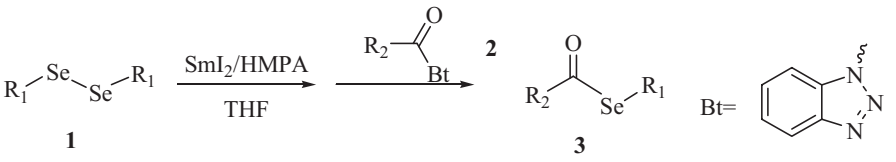
In continuation of our ongoing study on the nucleophilicity of heteroatom nucleophiles toward *N*-acylbenzotriazoles, herein we employed samarium selenolates ($RSeSmI_2$) as the Se-nucleophile and the potential of the Se-acylation for the preparation of selenol esters were explored.

RESULTS AND DISCUSSION

Samarium selenolates ($RSeSmI_2$) were generated by the reductive cleavage of RSeSeR with SmI_2.[16a] First, dibenzyldiselenide was subjected to the SmI_2–tetrahydrofuran (THF) solution. One hour later, the resulting mixture was treated by *N*-benzoylbenzotriazole. The usual work-up afforded the desired selenol esters, but the yield was rather unsatisfactory (Table 1, Entries 1 and 2).

Addition of hexamethylphosphoramide (HMPA), which was reported to enhance the reactivity of SmI_2 and facilitate the solubility of the selenolates,[16a,b] was attempted in the reductive cleavage process and improvement in the yields of the selenoesters was observed (Table 1, Entries 1 and 2). Especially the reaction of $BnSeSmI_2$ and *N*-acylbenzotriazole **2c** in the presence of HMPA afforded the expected product in 70% yield and thus made the reaction synthetically valuable (Table 1, Entry 3). Fortunately, the acylation with *N*-aroylbenzotriazoles of samarium phenylselenolate ($PhSeSmI_2$) generated from diphenyldiselenide afforded more satisfactory yields (Table 1, Entries 4–13), tolerating both electron-donating and electron-withdrawing substituents on the aryl. *N*-Alkanoyl benzotriazole worked equally well (Table 1, Entries 14–16). It should be noted that the acylation between the samarium selenolate and *N*-acylbenzotriazole was very fast and the reaction was quenched immediately after the addition of the *N*-acylbenzotriazole (in 3 min). In fact, prolonging the reaction time would lead to regeneration of the starting *N*-acylbenzotriazoles. It may suggest that the leaving benzotriazolyl could reattack the selenol ester carbonyl and make the reaction reversible (Table 1, Entry 4).

Table 1 Se-acylation with *N*-aroyl and *N*-alkanoylbenzotriazoles



1 **3**

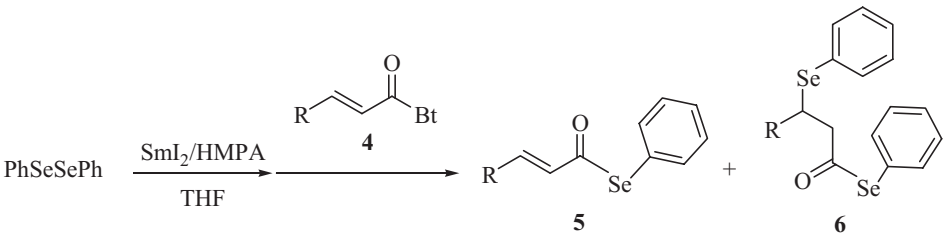
Entry	R_1	R_2	Product	Yield%[a]
1	Bn	Ph-**2a**	**3a**	33 (28[b])
2	Bn	*p*-MeO(C_6H_4)-**2b**	**3b**	42 (8[b])
3	Bn	*p*-Cl(C_6H_4)-**2c**	**3c**	70
4	Ph	Ph-**2a**	**3d**	78 (48[c])
5	Ph	*p*-Cl(C_6H_4)-**2c**	**3e**	83
6	Ph	*p*-MeO(C_6H_4)-**2b**	**3f**	71
7	Ph	*o*-Cl(C_6H_4)-**2d**	**3g**	80
8	Ph	*p*-NO_2(C_6H_4)-**2e**	**3h**	61
9	Ph	 **2f**	**3i**	68
10	Ph	*o*-CH_3(C_6H_4)-**2g**	**3j**	52
11	Ph	*p*-CH_3(C_6H_4)-**2h**	**3k**	78
12	Ph	*m*-CH_3(C_6H_4)-**2i**	**3l**	86
13	Ph	 **2j**	**3m**	83
14	Ph	CH_3CH_2-**2k**	**3n**	66
15	Ph	$CH_3(CH_2)_4CH_2$-**2l**	**3o**	60
16	Ph	$(CH_3)_2CH$-**2m**	**3p**	66

[a]Isolated yields based on *N*-acylbenzotriazoles. [b]In the absence of HMPA. [c]The acylation proceeded for more than 15 min.

Compared with the acyl halides method,[16a] the acylation of the samarium selenolates with *N*-acylbenzotriazoles was more efficient and the use of excess acylating reagent was unnecessary. The reason may be that acyl halides could also induce the ring opening of THF in the presence of the resulting Sm(III) salt,[17] while *N*-acylbenzotriazoles would not.

We then extended the substrates to a,b-unsaturated *N*-acylbenzotriazoles. Thus, cinnamoyl benzotriazole **4a** was added to the samarium selenolate. After usual work-up, the residue was purified by flash column chromatography on silica gel to give a solid, but ^{1}H NMR spectrum showed that the solid was crude **5a** contaminated with a byproduct resulting from Michael addition as indicated by the three characteristic *dd* peaks: δ 3.32 (dd, J = 6.4 Hz, J = 16.0 Hz, 1H), 3.51 (dd, J = 9.2 Hz, J = 16.0 Hz, 1H), and 4.77 (dd, J = 6.4 Hz, J = 9.2 Hz, 1H) (see supporting information). The byproduct could not be isolated because of its similar polarity to **5a**, but pure **5a** could be obtained by further recrystallization. Both the ^{1}H-NMR spectra of pure **5a** and crude **5a** (containing the byproduct) indicated the absence of benzotriazolyl group. The liquid chromatography-mass spectrometry (LC-MS) spectra of crude **5a** showed two characteristic peaks: 311 and 467 (m/z). The LC-MS combined with the 1H NMR spectra suggested that the byproduct should be compound **6a** (467 was ascribed to the molecular ion peak of **6a** [M (444)+Na] and 311 was ascribed to that of **5a** [M (287)+Na+H]; see supporting information). The ratio of **5a** and **6a** was 1:0.4 as determined by ^{1}H NMR analysis (Table 2, Entry 1).

Table 2 The reaction between samarium phenylselenolate and unsaturated *N*-acylbenzotriazoles 4



Entry	R	Product	Temperature (°C)	Time (h)	Ratio[a]	Yield%[b]
1	Ph-**4a**	**5a**:**6a**	20	0.5	1:0.42	–
2	Ph-**4a**	**5a**:**6a**	60	0.5	1:0.07	43
3	Ph-**4a**	**5a**:**6a**	70	0.5	1:0.19	55
4	*p*-Cl(C_6H_4)- **4b**	**5b**:**6b**	60	0.5	1:0.27	39
5	*p*-Cl(C_6H_4)- **4b**	**5b**:**6b**	60	5	1:0.07	39
6	*p*-MeO(C_6H_4)- **4c**	**5c**	60	0.5	1:0	72
7	 **4d**	**5d**	60	0.5	1:0	49
8	*p*-CH_3 (C_6H_4)-**4e**	**5e**:**6e**	60	5	1:0.14	64
9	Ph-**4a**	**5a**:**6a**	60	1	1:0.6[c]	40 (24[d])

[a]Determined by ^{1}H-NMR. [b]Isolated yields of product **5**. [c]Four equivalents of $PhSeSmI_2$ were used. [d]PMR yield of **6a**.

Subsequent optimization of the conditions found that performing the acylation step at 60 °C could improve the yield of **5a** (Table 2, Entry 2). Increasing the temperature could give better yield of **5a**, but at the same time resulted in poorer selectivity (Table 2, Entry 3). It was also found that prolonging the time could improve the selectivity for the unsaturated selenol esters; thus, **5b/6b** and **5e/6e** were obtained in a ratio of 1:0.07 and 1:0.14 (Table 2, Entries 5 and 8). Again, the isolation of pure **6b** and **6e** failed, and only pure **5b** and **5e** were obtained by further recrystallization. Under the optimized conditions, it was gratifying to find that substrates **4c** and **4d** underwent clean Se-acylation, providing the corresponding selenol esters **5c** and **5d** in 72% and 49% yield, respectively (Table 2, Entries 6 and 7). In addition, we tried to use excess $PhSeSmI_2$ in hope of getting byproduct **6** as the main or sole product. Thus, four equivalents of $PhSeSmI_2$ and one equivalent of cinnamoyl benzotriazole **4a** were used as the substrates. However, the reaction resulted in a mixture of **5a** and **6a** in a molar ratio of 1:0.6 (Table 2, Entry 9).

It may be interesting to compare the reactivity of samarium selenolate and samarium thiolate. Samarium thiolate attacked preferably on the carbonyl of a,b-unsaturated *N*-acylbenzotriazoles and afforded a,b-unsaturated thioesters exclusively,18 while the softer samarium selenolate could also attack the electron-deficient olefin carbon, which combined with the Se-acylation and finally afforded the b-phenylselanyl selenol ester **6**.

CONCLUSION

The Se-acylation ability of *N*-acylbenzotriazoles has been demonstrated. With samarium selenolate as the Se-nucleophile, *N*-aroyl and *N*-alkanoylbenzotriazoles underwent the acylation smoothly and afforded the selenol esters in moderate to good yields. The

Se-acylation with α,β-unsaturated *N*-acylbenzotriazoles could also be achieved with high regioselectivity.

EXPERIMENTAL

THF was distilled from sodium benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points are uncorrected. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AV400 NMR instrument in $CDCl_3$ [with tetramethylsilane (TMS) as internal standard]. Chemical shifts (δ) are reported in ppm and coupling constant *J* is given in Hz. IR spectra were recorded using KBr disks with a NEXUS 670 FTIR spectrometer. Elemental analyses were performed on a Vario-ELIII instrument. MS spectrum was analyzed on a Varian 500-MS equipped with an electrospray ionization source and ion trap analyzer in the positive ionization mode, with data acquisition using the Varian MS Workstation (Varian, America). LC-MS was carried on Agilent 1100 LC/MSD SL.

General Procedure for the Preparation of Selenol Esters 3a–n and 5a–e

General Procedure for the Preparation of Selenol Esters 3a–n. To a solution of SmI_2 (1.3 mmol) in dry THF (10 mL) under a nitrogen atmosphere was added HMPA (0.6 mL) and diselenide (0.6 mmol) in anhydrous THF (2 mL) by syringe. After the mixture was stirred at room temperature for 1 h, *N*-acylbenzotriazole **2** (1.0 mmol) in anhydrous THF (2 mL) was added at room temperature. When the purple color of the mixture faded (after 3 min), hydrochloric acid (0.1 N, 3 mL) was added immediately to quench the reaction followed by extraction with EtOAc (20 mL × 3). The organic layer was washed successively with $Na_2S_2O_3$ (aq), Na_2CO_3 (aq), and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give a residue, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 80:1–50:1) to give the corresponding selenol ester.

General Procedure for the Preparation of Selenol Esters 5a–e. To the solution of SmI_2 (1.3 mmol) in dry THF (10 mL) under nitrogen atmosphere was added HMPA (0.6 mL) and diselenide (0.6 mmol) in anhydrous THF (2 mL) by syringe. After the mixture was stirred at room temperature for 1 h, the temperature was raised to 60 °C. *N*-Acylbenzotriazole **4** (1.0 mmol) in anhydrous THF (4 mL) was then added and stirring was continued for the time indicated in Table 2. Hydrochloric acid (0.1 N, 3 mL) was added followed by extraction with EtOAc (20 mL × 3). The organic layer was washed successively with $Na_2S_2O_3$ (aq), Na_2CO_3 (aq), and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give a residue, which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 80:1–50:1) to give a mixture of **5** and **6** as solid. Crystallization in THF afforded pure **5**.

Benzenecarboselenoic acid Se-benzyl ester 3a.[15b] Yellow oil; IR (neat): υ (cm-1) 1670; 1H NMR δ 4.36 (s, 2H), 7.23–7.32 (m, 3H), 7.38 (d, J = 7.6 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.48–7.52 (m, 1H); 7.90 (d, J = 8.0 Hz, 2H).

Benzenecarboselenoic acid, 4-methoxy-Se-benzyl ester 3b. Light brown solid; mp 40 °C–41 °C; IR (KBr): υ (cm^{-1}) 1659; ^{1}H NMR δ 3.87 (s, 3H), 4.33 (s, 2H), 6.92 (d, J = 8.0 Hz, 2H), 7.20–7.38 (m, 5H), 7.88 (d, J = 7.6 Hz, 2H); ^{13}C NMR δ 28.9, 55.6, 114.0, 126.9, 128.6, 129.0, 129.6, 132.3, 139.6, 164.1, 193.2; MS *m/z* (J_{rel}.,%): 307 (100) $[M+H]^+$. Anal. Calcd. for $C_{15}H_{14}O_2Se$: C, 59.02; H, 4.62. Found: C, 59.53; H, 4.61.

Benzenecarboselenoic acid, 4-chloro-Se-benzyl ester 3c.[19] Colorless solid; mp 68 °C–69 °C (lit. mp 70–71 °C); IR (KBr): υ (cm^{-1}) 1671; ^1H NMR δ 4.36 (s, 2H), 7.21–7.36 (m, 5H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.84 (d, $J = 8.4$ Hz, 2H).

Benzenecarboselenoic acid Se-phenyl ester 3d.[15b] Yellow solid; mp 37 °C–38 °C (lit. mp 37 °C–38 °C); IR (neat): υ (cm^{-1}) 1678; ^1H NMR δ 7.31–7.39 (m, 5H), 7.49–7.51 (m, 3H), 7.83 (d, $J = 7.6$ Hz, 2H).

Benzenecarboselenoic acid, 4-chloro-Se-phenyl ester 3e. Beige solid; mp 84 °C–85 °C (lit.[11] mp 83.5 °C–84.5 °C); IR (KBr): υ (cm^{-1}) 1690; ^1H NMR δ 7.42–7.52 (m, 5H), 7.58 (d, $J = 6.4$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 2H).

Benzenecarboselenoic acid, 4-methoxy-Se-phenyl ester 3f.[11] White solid; mp 76 °C–78 °C (lit. mp 62–63 °C); IR (KBr): υ (cm^{-1}) 1683; ^1H NMR δ 3.88 (s, 3H), 6.96 (d, $J = 8.0$ Hz, 2H), 7.41–7.42 (m, 3H), 7.58–7.60 (m, 2H), 7.91 (d, $J = 7.6$ Hz, 2H); 13C NMR δ 55.6, 114.1, 126.0, 128.9, 129.3, 129.7, 131.3, 136.4, 164.2, 191.4.

Benzenecarboselenoic acid, 2-chloro-Se-phenyl ester 3g.[15b] Light brown solid; mp 57 °C–58 °C (lit. mp 59 °C); IR (KBr): υ (cm^{-1}) 1701; ^1H NMR δ 7.37–7.45 (m, 6H), 7.60–7.62 (m, 2H), 7.73 (d, $J = 1.2$ Hz, 1H).

Benzenecarboselenoic acid, 4-nitro-Se-phenyl ester 3h.[15b] Yellow solid; mp 127 °C–128 °C (lit. mp 136 °C–138 °C); IR (KBr): υ (cm^{-1}) 1676; ^1H NMR δ 7.45–7.48 (m, 3H), 7.64 (d, $J = 6.4$ Hz, 2H), 8.09 (d, $J = 8.8$ Hz, 2H), 8.35 (d, $J = 8.8$ Hz, 2H).

Furan-2-carboselenoic acid Se-phenyl ester 3i.[10c] Pale yellow solid; mp 60 °C–61 °C; IR (KBr): υ (cm^{-1}) 1679; ^1H NMR δ 6.59–6.61 (m, 1H), 7.22–7.23 (m, 1H), 7.42–7.43 (m, 3H), 7.58–7.60 (m, 2H), 7.65–7.66 (m, 1H).

Benzenecarboselenoic acid, 2-methyl-Se-phenyl ester 3j. Light brown solid; mp 46 °C–47 °C; IR (KBr): υ (cm^{-1}) 1699; ^1H NMR δ 2.48 (s, 3H), 7.26–7.35 (m, 2H), 7.43–7.46 (m, 4H), 7.60–7.62 (m, 2H), 7.91 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR δ 20.9, 126.1, 127.0, 128.9, 129.0, 129.4, 131.9, 132.3, 136.1, 136.6, 138.3, 195.5; MS *m/z* (J_{rel}.,%): 277 (100) [M+H]+. Anal. Calcd. for $C_{14}H_{12}OSe$: C, 61.10; H, 4.40. Found: C, 60.97; H, 4.36.

Benzenecarboselenoic acid, 4-methyl-Se-phenyl ester 3k.[10d] White solid; mp 97 °C–98 °C; IR (KBr): υ (cm^{-1}) 1689; ^1H NMR δ 2.43 (s, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.42–7.44 (m, 3H), 7.59–7.61 (m, 2H), 7.84 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR δ 21.8, 126.0, 127.5, 129.0, 129.4, 129.6, 136.0, 136.4, 144.9, 192.8.

Benzenecarboselenoic acid, 3-methyl-Se-phenyl ester 3l. Light brown solid; mp 47 °C–48 °C; IR (KBr): υ (cm^{-1}) 1680; ^1H NMR δ 2.44 (s, 3H), 7.38–7.44 (m, 5H), 7.59–7.61 (m, 2H), 7.73–7.75 (m, 2H); ^{13}C NMR δ 21.4, 124.6, 125.9, 127.8, 128.8, 129.1, 129.4, 134.7, 136.4, 138.6, 138.9, 193.5; MS *m/z* (J_{rel}.,%): 277 (100) $[M+H]^+$. Anal. Calcd. for $C_{14}H_{12}OSe$: C, 61.10; H, 4.40. Found: C, 61.17; H, 4.43.

Naphthalene-1-carboselenoic acid Se-phenyl ester 3m.[10d] Light brown solid; mp 68–69 °C; IR (KBr): υ (cm^{-1}) 1696; ^1H NMR δ 7.47–7.60 (m, 6H), 7.67–7.69 (m, 2H), 7.90 (d, $J = 7.6$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 8.20 (d, $J = 7.2$ Hz, 1H), 8.56 (d, $J =$ 8.4 Hz, 1H); 13C NMR δ 124.6, 125.3, 126.9, 127.3, 127.3, 128.4, 128. 4, 128.4, 129.1, 129.5, 133.6, 133.9, 136.2, 136.3, 195.4.

Propaneselenoic acid Se-phenyl ester 3n.[20] Yellow oil; IR (neat): υ (cm^{-1}) 1721; ^1H NMR δ 1.22 (t, $J = 7.6$ Hz, 3H), 2.74 (q, $J = 7.6$ Hz, 2H), 7.38–7.40 (m, 3H), 7.52–7.54 (m, 2H).

Heptaneselenoic acid Se-phenyl ester 3o.[8a] Yellow oil; IR (neat): υ (cm^{-1}) 1724; ^1H NMR δ 0.88 (t, $J = 6.8$ Hz, 3H), 1.24–1.37 (m, 6H), 1.67–1.70 (m, 2H), 2.69 (t, $J =$ 7.6 Hz, 2H), 7.36–7.38 (m, 3H), 7.49–7.51 (m, 2H).

2-methylpropaneselenoic acid Se-phenyl ester 3p.[10d] Yellow oil; IR (neat): υ (cm^{-1}) 1720; ^1H NMR δ 1.25 (t, J = 7.2 Hz, 6H), 2.86–2.93 (m, 1H), 7.36–7.37 (m, 3H), 7.48–7.51 (m, 2H).

(E)-2-propeneselenoic acid, 3-phenyl-Se-phenyl ester 5a.[14b] Yellow solid; mp 82 °C–83 °C (lit. mp 80 °C–81 °C); IR (KBr): υ (cm^{-1}) 1685, 1607; ^1H NMR δ 6.78 (d, J = 16.0 Hz, 1H), 7.41–7.43 (m, 6H), 7.56–7.60 (m, 5H).

(E)-2-propeneselenoic acid, 3-(4-chlorophenyl)-Se-phenyl ester 5b.[14b] Yellow solid; mp 103 °C–104 °C (lit. mp 99–100 °C); IR (KBr): υ (cm^{-1}) 1674, 1602; ^1H NMR δ 6.74 (d, J = 15.6 Hz, 1H), 7.37–7.59 (m, 10H).

(E)-2-propeneselenoic acid, 3-(4-methoxyphenyl)-Se-phenyl ester 5c. Yellow solid; mp 83 °C–84 °C; IR (KBr): υ (cm^{-1}) 1690, 1592; ^1H NMR δ 3.86 (s, 3H), 6.65 (d, J = 16.0 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 7.40–7.43 (m, 3H), 7.51–7.60 (m, 5H); ^{13}C NMR δ 55.5, 114.6, 123.9, 126.5, 128.9, 129.4, 130.5, 136.0, 141.1, 162.0, 190.5; MS *m/z* (J_{rel}.,%): 307 (100) $[M+H]^+$. Anal. Calcd. for $C_{16}H_{14}O_2Se$: C, 60.58; H, 4.45. Found: C, 60.41; H, 4.41.

(E)-2-propeneselenoic acid, 3-(furan-2-yl)-Se-phenyl ester 5d. Brown solid; mp 56 °C–57 °C; IR (KBr): υ (cm^{-1}) 1666, 1607; ^1H NMR δ 6.51 (d, J = 2.0 Hz, 1H), 6.67 (d, J = 15.2 Hz, 1H), 6.74 (d, J = 3.2Hz, 1H); 7.34 (d, J = 15.2 Hz, 1H), 7.40–7.42 (m, 3H), 7.54–7.59 (m, 3H); ^{13}C NMR δ 112.9, 117.2, 123.6, 126.4, 126.7, 129.0, 129.4, 135.9, 145.5, 150.5, 190.7; MS *m/z* (J_{rel}.,%): 279 (100) $[M+H]^+$. Anal. Calcd. for $C_{13}H_{10}O_2Se$: C, 56.33; H, 3.64. Found: C, 56.18; H, 3.64.

(E)-2-propeneselenoic acid, 3-(4-methylphenyl)-Se-phenyl ester 5e. Yellow solid; mp 86 °C–87 °C; IR (KBr): υ (cm^{-1}) 1697, 1608; ^1H NMR δ 2.39 (s, 3H), 6.74 (d, J = 16.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.41–7.47 (m, 5H), 7.58–7.62 (m, 3H); ^{13}C NMR δ 21.7, 125.3, 126.4, 128.7, 129.0, 129.4, 129.9, 131.2, 136.0, 141.3, 141.6, 191.1; MS *m/z* (J_{rel}.,%): 303 (100) $[M+H]^+$. Anal. Calcd. for $C_{16}H_{14}OSe$: C, 63.79; H, 4.68. Found: C, 63.87; H, 4.67.

REFERENCES

1. Katritzky, A. R.; Suzuki, K.; Wang, Z. Q. *Synlett* **2005,** 1656-1665.
2. Katritzky, A. R.; Suzuki, K.; Singh, S. K. *Synthesis* **2004,** 2645-2652.
3. Katritzky, A. R.; Angrish, P.; Hür, D.; Suzuki, K. *Synthesis* **2005,** 397-402.
4. Katritzky, A. R.; Angrish, P.; Suzuki, K. *Synthesis* **2006,** 411-424.
5. Katritzky, A. R.; Tala, S. R.; Abo-Dya, N. E.; Gyanda, K.; El-Gendy, B.; El-Dien, M.; Abdel-Samii, Z. K.; Steel, P. J. *J. Org. Chem.* **2009,** 74, 7165-7167.
6. Katritzky, A. R.; Singh, S. K.; Cai, C.; Bobrov, S. *J. Org. Chem.* **2006,** 71, 3364-3374.
7. Ogawa, A.; Sonoda, N., In *Comprehensive Organic Functional Group Transformations*, A. R. Katrizky, O. Meth-Cohn, and C. W. Ress, Eds. (Pergamon, Oxford, 1995), Vol 5, pp. 231-255.
8. (a) Toyofuku, M.; Murase, E.; Fujiwara, S.-i.; Shin-ike, T.; Kuniyasu, H.; Kambe, N. *Org. Lett.* **2008,** 10, 3957-3960; (b) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992,** 57, 1429-1443; (c) Schwartz, C. E.; Curran, D. P. *J. Am. Chem. Soc.* **1990,** 112, 9272-9284.
9. Renson, M.; Draguet, C. *Bull. Soc. Chim. Belg.* **1962,** 71, 260-262.
10. (a) Ranu, C. B.; Mandal, T.; Samanta, S. *Org. Lett.* **2003,** 5, 1439-1441; (b) Ranu, C. B.; Mandal, T. *J. Org. Chem.* **2004,** 69, 5793-5795; (c) Munbunjong, W.; Lee, E. H.; Ngernmaneerat, P.; Sung, J. K.; Singh, G.; Warinthorn, C.; Jang, D. O. *Tetrahedron* **2009,** 65, 2467-2471; (d) Nishiyama, Y.; Kawamatsu, H.; Funato, S.; Tokunaga, K.; Sonoda, N. *J. Org.*

Chem. **2003,** 68, 3599-3602; (e) Beletskaya, I. P.; Sigeev, A. S.; Peregudov, A. S.; Petrovskii, P. V. *Russian J. Org. Chem.* **2001,** 37, 1703-1709; (f) Ajiki, K.; Hirano, M., and Tenaka, K. *Org. Lett.* **2005,** 7, 4193-4195; (g) Fukuzawa, S. I.; Niimoto, Y.; Fujinami, T.; Sakai, S. *Heteroatom Chem.* **1990,** 1, 491-495; (h) Graciane, M.; Antonio, L. B.; Anderson, S. R.; Fabio, Z. G.; Robert, A. B.; Hugo, G.; Marcio, W. P. *Tetrahedron* **2009,** 65, 4614-4618; (i) Peppe, C.; Borges de Castro, L. *Can. J. Chem.* **2009,** 87, 678-683.

11. Grieco, P. A.; Yokoyama, Y.; Williams, E. *J. Org. Chem.* **1978,** 43, 1283-1285.
12. Batty, D.; Crich, D. *Synthesis* **1990,** 273-275.
13. Bao, W. L.; Zhang, Y. M. *Synth. Commun.* **1995,** 25, 143-148.
14. (a) Huang, X.; Liang, C. *J. Chem. Res.*, 634-635 (**1999**); (b) Zhong, P.; Xiong, Z. X.; Huan, X. *Synth. Commun.* **2000,** 30, 887-893.
15. (a) Inoue, T.; Takeda, T.; Kambe, N.; Ogawa, A.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1994,** 59, 5824-5827; (b) Graciane, M.; Antonio, L. B.; Anderson, S. R.; Fabio, Z. G.; Robert, A. B.; Hugo, G.; Marcio, W. P. *Tetrahedron* **2009,** 65, 4614-4618.
16. (a) Zhang, Y. M.; Yu, Y. P.; Lin, R. H. *Synth. Commun.* **1993,** 23, 189-193; (b) Edmonds, D. J.; Johnston, D.; Procter, D. J. *Chem. Rev.* **2004,** 104, 3371-3403; (c) Liotta, D.; Sunay, U.; Santiesteban, H.; Markiewicz, W. *J. Org. Chem.* **1981,** 46, 2605-2610.
17. Yu, Y.; Zhang, Y.; Ling, R. *Synth. Commun.* **1993,** 23, 1973-1977.
18. Wang, X. X.; Zou, X. F.; Du, J. X. *J. Chem. Res.* **2006,** 64-66.
19. Movassagh, B.; Mirshojaei, F. *Monatsh. Chem.* **2003,** 134, 831-835.
20. Chen, R. E.; Su, W. K. *J. Indian Chem. Soc.* **2004,** 81, 492-494.