HETEROCYCLES, Vol. 91, No. 8, 2015, pp. 1628 - 1636. © 2015 The Japan Institute of Heterocyclic Chemistry
Received, 21st April, 2015, Accepted, 11th June, 2015, Published online, 18th June, 2015
DOI: 10.3987/COM-15-13231

SYNTHESIS OF PHENYLSELANYLISOCHROMAN-1-ONES THROUGH HIGHLY SELECTIVE SELENOLACTONIZATION OF STYRENE-TYPED CARBOXYLIC ACIDS

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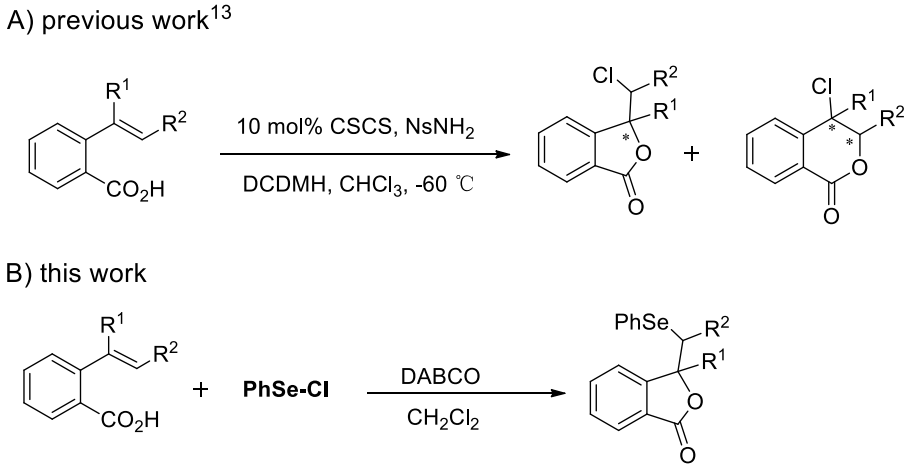
Abstract – The novel synthesis of phenylselanylisochroman-1-ones was achieved by selenolactonization of styrene-typed carboxylic acids and phenylselenenyl chloride in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO). The reactions give excellent yields with high *exo*-selectivity.

Selenocyclization of unsaturated acids is one of efficient methods for the synthesis of series of oxygenated heterocycles.[1] In particular, selenolactonization of alkenes attracts much attention in recent years since its widely application in total synthesis of bioactive compounds and natural products.[2-4] Since Nicolaou et al first reported the selenolactonization reaction with unsaturated carboxylic acids in 1978, a number of selenocyclofunctionalization reactions have been reported.[5-8] Although selenolactonization has been applied successfully to reactions involving allenoic acids,[9] phenylbutenoic acids[10] and other aliphatic acids,[11] aromatic acids were less involved. In 1991, Narasimhan and coworkers reported the selenolactonisation of 2-((6,6-dimethyl-2-oxodihydro-2*H*-pyran-3(4*H*)-ylidene)methyl)benzoic acid with benzeneselenenyl chloride in the presence of pyridine to form the selenide in only 50% yield.[12] However, there is still room for improvement regarding this type of selenolactonization reaction, for example, the existing reaction scope is still limited and the yield was poorer. Accordingly, the development of a practical, highly efficient reaction system for this type of selenolactonization is particularly attractive.

Recently, we have undertaken a program to investigate the halolactonization of styrene-typed carboxylic acids using C_3-symmetric cinchonine-squaramide as organocatalyst, affording the corresponding chiral lactones, which can act as efficient non-nucleoside reverse transcriptase inhibitors.[13] By analogy to previous work from this laboratory, selenolactonization of styrene-typed carboxylic acids has not been developed so far. Herein, we report the first examples of 1,4-diazabicyclo[2.2.2]octane (DABCO)

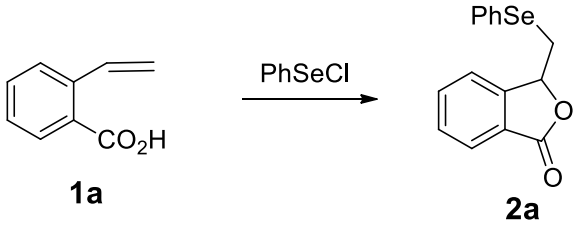
catalyzed selenolactonization of styrene-typed carboxylic acids in the presence of phenylselenenyl chloride to provide phenylselanylisochroman-1-ones derivatives in excellent yields (Scheme 1).



Scheme 1. Lactonization of styrene-typed carboxylic acids

This study was initiated with 2-vinylbenzoic acid **1a** and phenylselenenyl chloride (PhSeCl) at room temperature in DCM. The desired product **2a** was isolated in 55% yield (Table 1). Also, adjusting the DABCO loading demonstrated great influence on the activity of the reaction. The use of 5 mol% of DABCO gave the desired product **2a** in only 35% yield (entry 2). When 15 mol% of DABCO was used, **2a** was formed in 76% yield (entry 4). Screening of several solvents showed that DCM gave the best results. No reaction occurred when EtOAc and EtOH were used as solvent (entries 6, 7 and 8). Moreover, the amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) had significant effect on the reaction. When 20 mol% of DABCO was applied, the product was formed in 87% yield (entry 5).

Table 1. Optimized reaction condition for selenolactonization of carboxylic acid **1a**[a]



Entry	DABCO (mol%)	Solvent	Yield (%)[b]
1	0	DCM	0
2	5	DCM	35

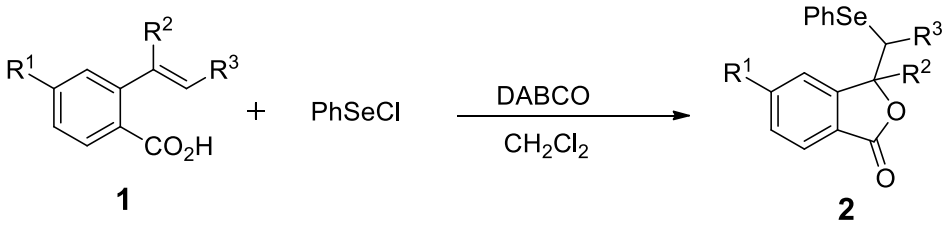
3	10	DCM	55
4	15	DCM	76
5	20	DCM	87
6	10	EtOAc	0
7	10	EtOH	0
8	10	MeCN	0

[a] All reactions were carried out with **1a** (1 equiv) and PhSeCl (1.1 equiv) in solvents at room temperature.

[b] Isolated yield.

Encouraged by the results obtained with styrene carboxylic acid **1a**, we investigated the selenolactonization of other unsaturated carboxylic acids with PhSeCl under these standard conditions. The results were summarized in Table 2. From Table 2, it was obvious that substituted benzoic acids can all be applied to afford series of phenylselanylisochroman-1-ones derivatives **2** in good to excellent yields (up to 94% yields) (entries 1-16). In all cases, a preference for the five-membered ring lactone **2** was observed, trace amount of six-membered ring lactone was detected. Interestingly, the substituted benzoic acids can all be tolerated in this reaction leading to the 5-*exo* selective products **2** in excellent yields. The substitutes at R^2 position had no significant effect on the cyclization. For example, when 2-(1-(4-bromophenyl)vinyl)benzoic acid **1d** was used in this reaction, the desired product **2d** was formed in 94% yield (entry 6). Surprisingly, when methyl and propyl groups were substituted at R^3 position, the yields were decreased. When the **1q** and **1r** were used, the corresponding products **2q** and **2r** were obtained in 75% and 60% yields, respectively (entries 17 and 18).

Table 2. Substrate scope of selenolactonization reaction[a]



Entry	**2**	R^1	R^2	R^3	Yield (%)[b]
1	**2a**	H	H	H	87
2	**2b**	H	Me	H	94

3	**2c**	H	Ph	H	93
4	**2d**	H	*p*-FC_6H_4	H	93
5	**2e**	H	*p*-ClC_6H_4	H	91
6	**2f**	H	*p*-BrC_6H_4	H	94
7	**2g**	H	*p*-IC_6H_4	H	91
8	**2h**	H	*p*-MeC_6H_4	H	90
9	**2i**	H	*p*-$MeOC_6H_4$	H	85
10	**2j**	Me	*p*-FC_6H_4	H	92
11	**2k**	Cl	*p*-FC_6H_4	H	91
12	**2l**	Cl	*p*-ClC_6H_4	H	89
13	**2m**	H	H	Me	78
14	**2n**	H	H	*m*-MeC_6H_4	94
15	**2o**	H	H	*p*-MeC_6H_4	92
16	**2p**	H	H	*p*-$MeOC_6H_4$	90
17	**2q**	H	Me	Me	75
18[c]	**2r**	H	*p*-BrC_6H_4	*n*-Pr	60

[a] All reactions were carried out with **1** (1 equiv) and PhSeCl (1.1 equiv) in the presence of 20% DABCO in DCM. [b] Isolated yield. [c] The six-membered ring lactone was isolated in 30% yield.

The product **2d** was unambiguously confirmed by X-ray crystallography (Figure 1).

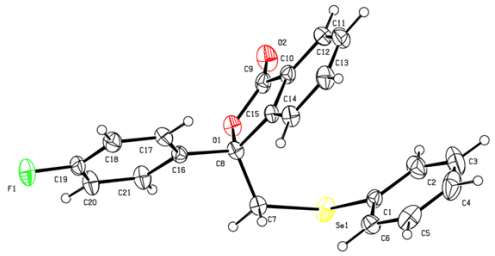


Figure 1. X-Ray crystallographic structure of **2d**

Table 3. X-Ray crystallographic data of **2d**

Empirical formula	C_{21} H_{15} F O_2 Se
Formula weight	397.29
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.1709(18) Å alpha = 64.078(3) deg.
	b = 10.707(2) Å beta = 66.282(3) deg.
	c = 10.708(2) Å gamma = 89.325(4) deg.
Volume	848.4(3) $Å^3$
Z, Calculated density	2, 1.555 Mg/m^3
Absorption coefficient	2.234 mm^{-1}
F(000)	400
Crystal size	0.30 × 0.29 × 0.28 mm
Theta range for data collection	2.16 to 26.50 deg.
Limiting indices	-6≤h≤11, -13≤k≤13, -13≤l≤13
Reflections collected / unique	5596 / 3522 [R(int) = 0.0332]
Completeness to theta = 26.50	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5735 and 0.5538
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3522 / 0 / 227
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.1092
R indices (all data)	R1 = 0.0553, wR2 = 0.1151
Extinction coefficient	0.025(3)
Largest diff. peak and hole	0.761 and -0.860 e. $Å^3$

In conclusion, we present the new selenolactonization of styrene-typed carboxylic acids using phenylselenenyl chloride in the presence of DABCO. The resulting phenylselanylisochroman-1-one derivatives were formed in excellent yields under mild conditions. This methodology will serve as a convenient access to interesting phenyl selenoheterocyles.

EXPERIMENTAL

Analytical-grade solvents were purchased, and used as received. NMR spectra were measured at 400 MHz for ^1H spectra and 100 MHz for ^{13}C spectra and calibrated from residual solvent signal. Analytical thin-layer chromatography (TLC) was performed on silica gel aluminum sheets with F-254 indicator. Visualization was accomplished by UV light. Purification by chromatography was performed using 230-400 mesh SiO_2 with compressed air as a source of positive pressure. Carboxylic acids **1** were prepared according to the literature procedure.[14]

Representative procedure for the selenolactonization of carboxylic acids

A solution of 2-vinylbenzoic acid **1a**, phenylselenenyl chloride (1.1 equiv.), and DABCO (20 mol%) in DCM was stirred for 2 h at room temperature. Upon completion, the solvent was removed and the residue was purified by SiO_2 column chromatography (petroleum ether/AcOEt = 6:1) to give **2a** as white solid.

2a: white solid; mp 73-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 1H), 7.58 – 7.50 (m, 3H), 7.47 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.23 (dt, *J* = 8.8, 4.8 Hz, 3H), 5.64 (t, *J* = 5.6 Hz, 1H), 3.45 (dd, *J* = 13.3, 5.0 Hz, 1H), 3.33 (dd, *J* = 13.3, 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.01, 148.57, 133.93, 133.64, 129.54, 129.29, 129.09, 127.77, 126.55, 125.66, 122.49, 79.11, 31.84. HRMS (ESI) calcd. for $C_{15}H_{13}O_2Se$ $[M+H]^+$ 299.0140, found 299.0131.

2b: white solid; mp 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 1H), 7.50 – 7.46 (m, 2H), 7.32 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 7.17 – 7.12 (m, 2H), 3.46 (d, *J* = 1.3 Hz, 2H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.50, 152.13, 133.80, 133.54, 130.10, 129.29, 129.00, 127.46, 126.63, 125.53, 121.22, 86.00, 38.98, 25.75. HRMS (ESI) calcd for $C_{16}H_{15}O_2Se$ $[M+H]^+$ 313.0296, found 313.0290.

2c: white solid; mp 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 1H), 7.54 – 7.45 (m, 4H), 7.37 – 7.31 (m, 4H), 7.28 – 7.25 (m, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 2H), 3.88 – 3.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.53, 150.79, 139.49, 133.84, 130.12, 129.47, 128.96, 128.83, 128.65, 128.12, 127.54, 126.74, 125.68, 125.29, 122.56, 88.43, 39.87. HRMS (ESI) calcd for $C_{21}H_{17}O_2Se$ $[M+H]^+$ 375.0453, found 375.0444.

2d: white solid; mp 103-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 1H), 7.51 – 7.45 (m, 4H), 7.34 (dd, *J* = 6.0, 1.8 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.19 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.12 (dd, *J* = 10.1, 4.5 Hz, 2H), 7.04 – 6.98 (m, 2H), 3.80 (d, *J* = 1.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.32, 162.67 (d, $^1J_{C\text{-}F}$ = 247.00 Hz), 150.56, 135.34, 135.30, 134.01, 133.84, 129.97, 129.65, 129.01, 127.63, 127.39 (d, $^2J_{C\text{-}F}$ = 8.00 Hz), 126.64, 125.75, 122.58, 115.72 (d, $^3J_{C\text{-}F}$ = 21.00 Hz), 88.05, 39.87. HRMS (ESI) calcd for $C_{21}H_{16}FO_2Se$ $[M+H]^+$ 393.0358, found 393.0360.

2e: white solid; mp 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 6.2, 1.8 Hz, 1H), 7.52 – 7.42 (m, 4H), 7.34 – 7.20 (m, 6H), 7.13 (t, *J* = 7.3 Hz, 2H), 3.80 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.21, 150.40, 137.99, 134.69, 134.00, 133.89, 129.90, 129.69, 129.01, 128.95, 127.65, 126.81, 126.58, 125.84, 122.45, 87.92, 39.71.

2f: white solid; mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 6.2, 1.9 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.48 – 7.44 (m, 2H), 7.36 – 7.30 (m, 3H), 7.26 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.23 – 7.18 (m, 1H), 7.14 (dd, *J* = 10.1, 4.5 Hz, 2H), 3.80 (d, *J* = 1.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.56, 150.75, 138.33, 135.04, 134.35, 134.25, 130.25, 130.04, 129.36, 129.30, 128.01, 127.16, 126.93, 126.19, 122.80, 88.27, 40.06. HRMS (ESI) calcd for $C_{21}H_{16}BrO_2Se$ $[M+H]^+$ 452.9558, found 452.9562.

2g: white solid; mp 100-102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.53 (m, 4H), 7.37 (dd, *J* = 8.9, 6.5 Hz, 5H), 7.30 – 7.22 (m, 3H), 6.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.19, 146.29, 137.79, 135.94, 134.66, 133.87, 130.46, 129.99, 129.90, 129.08, 129.02, 128.85, 128.67, 128.62, 128.40, 126.45, 125.80, 123.81, 84.18, 82.56, 46.14. HRMS (ESI) calcd for $C_{21}H_{16}IO_2Se$ $[M+H]^+$ 500.9419, found 500.9414.

2h: white solid; mp 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.8, 1.6 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.22 (m, 4H), 7.15 (dd, *J* = 11.0, 4.3 Hz, 4H), 3.87 – 3.79 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.62, 150.98, 138.59, 136.52, 133.83, 133.79, 130.18, 129.49, 129.41, 128.95, 127.50, 126.72, 125.84, 125.60, 125.25, 125.11, 122.58, 88.48, 39.82, 21.09. HRMS (ESI) calcd for $C_{22}H_{19}O_2Se$ $[M+H]^+$ 389.0609, found 389.0604.

2i: white solid; mp 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 6.1, 1.9 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.33 (dd, *J* = 6.1, 1.7 Hz, 1H), 7.26 (dd, *J* = 5.3, 3.0 Hz, 3H), 7.22 – 7.18 (m, 1H), 7.13 (t, *J* = 7.3 Hz, 2H), 6.88 – 6.84 (m, 2H), 3.82 (d, *J* = 3.8 Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.52, 159.75, 150.95, 133.77, 133.73, 131.36, 130.18, 129.38, 128.93, 127.48, 126.84, 125.65, 122.61, 114.07, 113.98, 88.41, 55.34, 39.81. HRMS (ESI) calcd for $C_{22}H_{19}O_3Se$ $[M+H]^+$ 405.0558, found 405.0553.

2j: white solid; mp 100-102 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.82 – 7.62 (m, 6H), 7.77 – 7.65 (m, 5H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.28 (m, 7H), 7.46 – 7.25 (m, 7H), 7.25 – 7.09 (m, 9H), 7.25 – 7.11 (m, 9H), 4.11 (d, *J* = 13.4 Hz, 2H), 4.11 (d, *J* = 13.4 Hz, 2H), 4.02 – 3.90 (m, 2H), 3.99 – 3.91 (m, 2H), 2.43 (s, 2H), 2.36 (d, *J* = 55.9 Hz, 5H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, Acetone-d_6) δ 169.50, 163.42 (d, $^1J_{C\text{-}F}$ = 245.00 Hz), 152.28, 149.40, 146.42, 140.99, 137.50, 136.09, 134.07, 133.93, 131.65, 131.04, 130.88, 129.78, 129.77, 128.52 (d, $^2J_{C\text{-}F}$ = 8.00 Hz), 128.19, 128.08, 127.41, 125.83, 125.66, 124.80, 124.34, 123.59, 116.34 (d, $^3J_{C\text{-}F}$ = 22.00 Hz), 88.43, 88.26, 39.68, 39.49, 22.05, 21.16. HRMS (ESI) calcd for $C_{22}H_{18}FO_2Se$ $[M+H]^+$ 407.0515, found 407.0505.

2k: white solid; mp 140-141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 11.7, 4.9 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.28 – 7.20 (m, 4H), 7.19 – 7.12 (m, 2H), 7.04 (ddd, *J* = 8.5, 5.3, 2.1 Hz, 2H), 3.83 – 3.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.17, 163.91 (d, $^1J_{C\text{-}F}$ = 235.00 Hz), 152.02, 140.70, 133.85, 133.78, 130.36, 129.08, 129.00, 128.03, 127.25 (d, $^2J_{C\text{-}F}$ = 8.00 Hz), 126.83, 123.15, 115.91 (d, $^3J_{C\text{-}F}$ = 22.00 Hz), 87.60, 39.55. HRMS (ESI) calcd for $C_{21}H_{15}ClFO_2Se$ $[M+H]^+$ 426.9969, found 426.9961.

2l: white solid; mp 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 11.6, 4.9 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.26 – 7.19 (m, 4H), 7.15 (dt, *J* = 12.2, 5.5 Hz, 3H), 3.81 – 3.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.76, 148.41, 137.41, 136.05, 134.96, 133.93, 133.88, 133.81, 130.42, 129.13, 129.08, 129.02, 128.06, 127.78, 126.87, 126.73, 126.66, 125.57, 123.67, 123.08, 87.85, 39.67. HRMS (ESI) calcd for $C_{21}H_{15}Cl_2O_2Se$ $[M+H]^+$ 442.9673, found 442.9667.

2m: white solid; mp 92-94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.51 – 7.47 (m, 2H), 7.30 (ddd, *J* = 5.9, 3.4, 1.3 Hz, 2H), 7.25 – 7.22 (m, 1H), 5.59 (d, *J* = 2.9 Hz, 1H), 3.88 (tt, *J* = 7.2, 3.6 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.31, 147.20, 135.61, 134.79, 133.66, 129.50, 129.30, 129.23, 128.33, 128.16, 127.21, 125.66, 123.13, 82.76, 41.42, 16.43. HRMS (ESI) calcd for $C_{16}H_{15}O_2Se$ $[M+H]^+$ 313.0296, found 313.0290.

2n: white solid; mp 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.3 Hz, 1H), 6.90 (s, 1H), 6.86 (d, *J* = 7.9 Hz, 1H), 5.80 (d, *J* = 1.8 Hz, 1H), 4.86 (d, *J* = 2.2 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.69, 138.40, 138.13, 138.02, 136.62, 133.93, 130.06, 129.36, 129.11, 129.03, 128.47, 128.40, 128.24, 127.62, 126.62, 124.84, 122.89, 82.29, 43.78, 21.44. HRMS (ESI) calcd for $C_{22}H_{19}O_2Se$ $[M+H]^+$ 389.0609, found 389.0608.

2o: white solid; mp 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.47 – 7.43 (m, 1H), 7.37 – 7.32 (m, 2H), 7.29 (s, 1H), 7.16 (ddd, *J* = 13.9, 7.3, 4.9 Hz, 2H), 6.99 (q, *J* = 8.3 Hz, 4H), 5.81 (d, *J* = 1.9 Hz, 1H), 4.84 (d, *J* = 2.2 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.69, 138.09, 138.04, 136.59, 135.26, 133.90, 133.78, 130.04, 129.46, 129.36, 129.28, 129.08, 128.93, 128.38, 128.23, 127.62, 125.80, 125.23, 124.88, 82.22, 43.77, 21.03. HRMS (ESI) calcd for $C_{22}H_{19}O_2Se$ $[M+H]^+$ 389.0609, found 389.0603.

2p: white solid; mp 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.38 – 7.33 (m, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.79 (d, *J* = 2.4 Hz, 1H), 4.83 (d, *J* = 2.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.70, 159.41, 138.21, 136.54, 133.95, 130.26, 130.09, 129.35, 129.06, 128.39, 128.28, 127.62, 127.38, 124.89, 113.93, 82.20, 55.23, 43.83. HRMS (ESI) calcd for $C_{22}H_{19}O_3Se$ $[M+H]^+$ 405.0558, found 405.0550.

2q: white solid; mp 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 6.0, 2.0 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.43 (dd, *J* = 6.0, 1.9 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.27 – 7.24 (m, 1H), 7.23 – 7.16 (m, 2H), 3.71 (q, *J* = 7.2 Hz, 1H), 1.76 (s, 3H), 1.44 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.85, 152.30, 134.79, 133.72, 129.64, 129.30, 129.06, 127.88, 126.66, 125.55, 121.73, 89.17, 48.12, 25.04, 17.88. HRMS (ESI) calcd for $C_{17}H_{17}O_2Se$ $[M+H]^+$ 327.0453, found 327.0451.

2r: white solid; mp 112-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.32 (dd, *J* = 15.6, 8.5 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 2H), 7.02 – 6.95 (m, 2H), 3.83 (dd, *J* = 10.9, 2.1 Hz, 1H), 1.94 – 1.84 (m, 1H), 1.57 – 1.38 (m, 3H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.79, 151.09, 138.27, 134.54, 133.50, 129.32, 128.82, 128.75, 127.57, 126.51, 125.73, 122.57, 91.59, 57.34, 33.27, 21.51, 13.64. HRMS (ESI) calcd for $C_{24}H_{22}BrO_2Se$ $[M+H]^+$ 495.0027, found 495.0014.

ACKNOWLEDGEMENTS

We are grateful to the Fundamental Research Funds for the Central Universities (2042014kf0248) for support of this research.

REFERENCES

1. C. Paulmier, 'Selenium Reagents and Intermediates in Organic Synthesis', Chapter VIII, Pergamon, Oxford, 1986.
2. N. Petragnani, H. A. Stefani, and C. J. Valduga, *Tetrahedron,* 2001, **57**, 1411.
3. P. Wipf and S. R. Spencer, *J. Am. Chem. Soc*., 2005, **127**, 225.
4. A. Endo and S. J. Danishefsky, *J. Am. Chem. Soc*., 2005, **127**, 8289.
5. K. C. Nicolaou, S. P. Seitz, W. J. Sipio, and J. F. Blount, *J. Am. Chem. Soc*., 1979, **101**, 3884.
6. S. E. Denmark, D. Kalyani, and W. R. Collins, *J. Am. Chem. Soc*., 2010, **132**, 15752.
7. R. Deziel and E. Malenfant, *J. Org. Chem*., 1995, **60**, 4660.
8. S. S. Khokhar and T. Wirth, *Angew. Chem. Int. Ed*., 2004, **43**, 631.
9. S. Ma, F. Pan, X. Hao, and X. Huang, *Synlett*, 2004, 85.
10. S. E. Denmark and W. R. Collins, *Org. Lett*., 2007, **9**, 3801.
11. M. Gruttadauria, C. Aprile, and R. Noto, *Tetrahedron Lett*., 2002, **43**, 1669.
12. M. D. Chordia and N. S. Narasimhan, *J. Chem. Soc., Perkin Trans. 1*, 1991, 371.
13. X. Han, C. Dong, and H. B. Zhou, *Adv. Synth. Catal*., 2014, **356**, 1275.
14. S. A. Shahzad, C. Vivant, and T. Wirth, *Org. Lett*., 2010, **12**, 1364.