Optical resolution and racemization of areneseleninic acids

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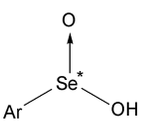
Various optically active areneseleninic acids ($ArSeO_2H$; Ar = 4-Me-C_6H_4; 4-MeO-C_6H_4; 2-MeO-C_6H_4; 2-MeOCO-C_6H_4; 2,4,6-Me_3-C_6H_2; 2,4,6-Et_3-C_6H_2; 2,4,6-$^i Pr_3$-C_6H_2; 2,4,6-$^t Bu_3$-C_6H_2; 2,4-$^t Bu_2$-6-MeO-C_6H_2) were obtained as solutions by optical resolution on a chiral column using medium-pressure liquid chromatography. Concentration of the eluate by evaporation under reduced pressure yielded completely racemized seleninic acids. Optically active seleninic acids with low-acidity were more stable against racemization than those with high-acidity. The bulky substituents at the *ortho* position on the benzene ring of the areneseleninic acids were also found to be effective for retarding the racemization. The mechanism for the racemization was clarified to proceed *via* seleninate anion with the extrusion of a proton under dilute conditions.

Introduction

Recently, our interest has been focused on the isolation and stereochemistry of optically active tricoordinated selenium and tellurium compounds.[1,2] Many chiral tricoordinated selenium and tellurium compounds, such as oxides,[3,4] onium salts,[5,6] ylides,[7,8] and imides[9,10] have been isolated, and their properties have been clarified.[1,2,11] Chalcogenic acids are also tricoordinated chalcogen compounds and are considered to be resolved into their enantiomers; however, optically active chalcogenic acids have not yet been isolated thus far, whereas chiral ^{16}O, ^{18}O-sulfinic acid salts {*p*-tol-S(^{16}O)$^{18}O^-M^+$; M^+ = Li^+, Na^+} have been studied.[12] One reason for the lack of studies on chiral chalcogenic acids may be their facile racemization. The second reason is that there has been no superior technique for resolving these compounds into their enantiomers until recently. The third reason is that sulfinic acids readily undergo disproportionation to give the corresponding thiol sulfonates and sulfonic acids.[13] However, areneseleninic acids do not disproportionate to the corresponding selenol selenonates and selenonic acids. Therefore, it would be possible to isolate optically active seleninic acids if the racemization were suppressed. We examined the optical resolution of various areneseleninic acids by means of liquid chromatography using an optically active column and found that seleninic acids could be optically resolved. However, they racemized in solution, particularly at high concentrations. Bulky alkyl and electron-donating groups on the benzene ring of areneseleninic acids were found to be effective for retarding the racemization.[14] In this paper, we describe the optical resolution of various areneseleninic acids and their stability against racemization.



1: Ar = 4-Me-C_6H_4
2: Ar = 4-MeO-C_6H_4
3: Ar = 2-MeO-C_6H_4
4: Ar = 2-MeOCO-C_6H_4
5: Ar = 2,4,6-Me_3-C_6H_2
6: Ar = 2,4,6-Et_3-C_6H_2
7: Ar = 2,4,6-$^i Pr_3$-C_6H_2
8: Ar = 2,4,6-$^t Bu_3$-C_6H_2
9: Ar = 2,4-$^t Bu_2$-6-MeO-C_6H_2

Results and discussion

Racemic areneseleninic acids **1**–**7** and **9** were prepared by oxidation of the corresponding diaryl diselenides with ozone followed by hydrolysis.[15] Seleninic acid **8** was prepared by hydrolysis of the corresponding methyl seleninate.[16]

When toluene-4-seleninic acid (**1**) was subjected to high-performance liquid chromatography on an analytical scale at room temperature (propan-2-ol) using a chiral column (4.6 × 250 mm) packed with amylose carbamate derivative–silica gel, two peaks corresponding to the two enantiomers were observed on the chromatogram, although their separation was not complete. This result indicates that the hydrogen atom in seleninic acid is fixed to a certain extent to one oxygen atom. In the cases of seleninic acids **2**–**5**, unusual elution profiles, indicating that enantiomerization is occurring in the column, were observed in their respective chromatograms, although partial resolution was achieved, as shown in Fig. 1. When the chromatographic resolution of these seleninic acids was carried out at 0 °C, the elution profile of **5** was improved, and the two enantiomers could be optically resolved whereas no such improvement was observed for **2**–**4**. In the cases of **6**, **7**, and **9** that have bulkier substituents, satisfactory separation was observed on an analytical scale. These results indicate that bulky alkyl substituents at the *ortho* position of the benzene ring are useful for retarding the enantiomerization in the column. However, the fact that the resolution of seleninic acid **8** was not complete may be due to insufficient recognition of the chirality because the two bulky alkyl substituents at the *ortho* position mask the chiral selenium center.

Optical resolution of the racemic areneseleninic acids **1**–**9** into their optical isomers on a preparative scale was examined on a larger column of the same type (10 × 250 mm) using medium-pressure liquid chromatography. In all cases, the first- and second-fractions containing the isomers were collected. However, concentration of the solutions by evaporation under reduced pressure yielded completely racemized seleninic acids. Therefore, specific rotation and circular dichroism spectrum of each enantiomer were measured in the eluate; concentrations were calculated based on the comparison of UV spectra with those of authentic racemic samples. In the cases of seleninic acids **5**–**9**, their enantiomeric purities were determined by HPLC analysis. In these cases, enantiomerically pure seleninic

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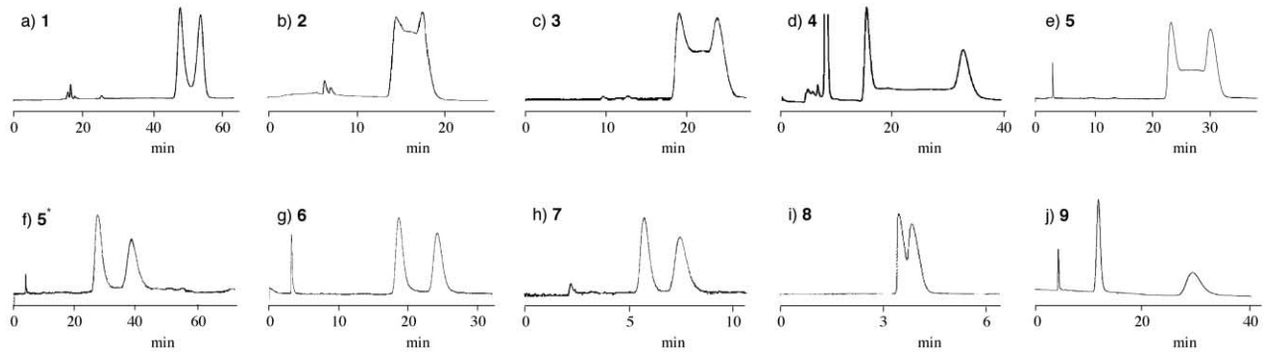


Fig. 1 Chromatographic resolution of racemic areneseleninic acids **1**–**9** on an optically active column packed with amylose carbamate derivative–silica gel by means of HPLC at an analytical scale at 25 °C. Eluent: (a) propan-2-ol; (b) hexane–propan-2-ol = 50 : 50; (c) propan-2-ol; (d) propan-2-ol; (e) hexane–propan-2-ol = 95 : 5; (f) hexane–propan-2-ol = 90 : 10 (at 0 °C); (g) hexane–propan-2-ol = 98 : 2; (h) hexane–propan-2-ol = 99 : 1; (i) hexane–propan-2-ol = 99.5 : 0.5; (j) hexane–propan-2-ol = 95 : 5.

Table 1 Optical purities and chiroptical properties of optically active areneseleninic acids

Compd	Order of elution	Optical purity[a]	$[\alpha]_{435}$ (conc)	CD λ_{max}/nm ($[\theta]$)
1	First	–[b]	—	255 (+)[c]
				224 (−)
2	First	—	—	263 (+)[d]
				239 (−)
	Second	—	—	263 (−)[d]
				239 (+)
3	First	—	—	291 (−)[c]
	Second	—	—	291 (+)[c]
4	First	—	—	290 (+)[c]
	Second	—	—	290 (−)[c]
5	First	100%	+710 (*c* 0.01)[e]	283 (+2.12 × 10^4)[e]
				229 (−2.16 × 10^4)
	Second	58%	−337 (*c* 0.01)[e]	282 (−1.54 × 10^4)[e]
				231 (+1.78 × 10^4)
6	First	100%	+471 (*c* 0.01)[f]	283 (+1.81 × 10^4)[f]
				239 (−2.92 × 10^4)
	Second	30%	−132 (*c* 0.01)[f]	284 (−5.84 × 10^3)[f]
				238 (+9.06 × 10^3)
7	First	100%	−493 (*c* 0.01)[g]	282 (−2.53 × 10^4)[g]
				240 (+5.11 × 10^4)
	Second	68%	+395 (*c* 0.01)[g]	281 (+1.89 × 10^4)[g]
				240 (−3.88 × 10^4)
8	First	36%	−120 (*c* 0.02)[h]	286 (−5.10 × 10^3)[h i]
				248 (+7.00 × 10^3)
	Second	19%	+80 (*c* 0.02)[h]	285 (+4.68 × 10^3)[h]
				247 (−5.22 × 10^3)
9	First	100%	+320 (*c* 0.02)[j]	296 (+1.38 × 10^4)[j]
				274 (+1.18 × 10^4)
				243 (−2.01 × 10^4)
				217 (−3.17 × 10^4)
	Second	98%	−310 (*c* 0.01)[j]	296 (−1.20 × 10^4)[j]
				274 (−1.04 × 10^4)
				243 (+1.78 × 10^4)
				217 (+2.67 × 10^4)

[a] Optical purity was determined by HPLC analysis. [b] Optical purity was not determined due to rapid racemization and/or incomplete separation in HPLC analysis. [c] In propan-2-ol. [d] In hexane–propan-2-ol (50 : 50). [e] In hexane–propan-2-ol (90 : 10). [f] In hexane–propan-2-ol (98 : 2). [g] In hexane–propan-2-ol (99 : 1). [h] In hexane–propan-2-ol (99.5 : 0.5). [i] At 17% ee. [j] In hexane–propan-2-ol (95 : 5).

acids (+)-**5**, (+)-**6**, (−)-**7**, and (+)-**9** were obtained in their respective first-fractions, as shown in Table 1. The failure of collection of enantiomerically pure seleninic acids from the later fractions is due to tailing off of the enantiomers that were eluted first on a preparative scale. Enantiomeric purities and specific rotations of optically active seleninic acids **1**–**4** could not be determined due to incomplete separation on the column and/or rapid racemization in the solution. All (+)-isomers of areneseleninic acids **5**–**9** show positive first Cotton effects in the range 281 to 296 nm in their circular dichroism spectra, and the (−)-isomers show negative first Cotton effects in the corresponding regions. The circular dichroism spectra are shown in Fig. 2.

The kinetics for racemization of the optically active seleninic acids were examined. The rates of racemization of the optically active seleninic acids, obtained from the first-fractions, showed good linear relationship with first-order rate plots under dilute conditions at 24 °C. The rate constants and half-lives for racemization are summarized in Table 2. The rate constant of **1** is 5.50 × 10^{-4} s^{-1} in propan-2-ol, and is larger than that of the less-acidic seleninic acid[17] **2** (3.38 × 10^{-4} s^{-1}). Comparing the *ortho* substituted areneseleninic acids **3** and **4**, the rate constant of **4** (2.15 × 10^{-3} s^{-1}) is also larger than that of the less-acidic seleninic acid **3** (3.64 × 10^{-4} s^{-1}). In the case of **9**, the addition of water accelerated the racemization, proving that water participates in the racemization. Vertex (pyramidal) inversion is also a possible pathway for the racemization of seleninic acid. In tricoordinated sulfur compounds, vertex inversion occurs frequently.[18] However, the barriers for vertex inversion of the corresponding selenium analogues are too high to allow such

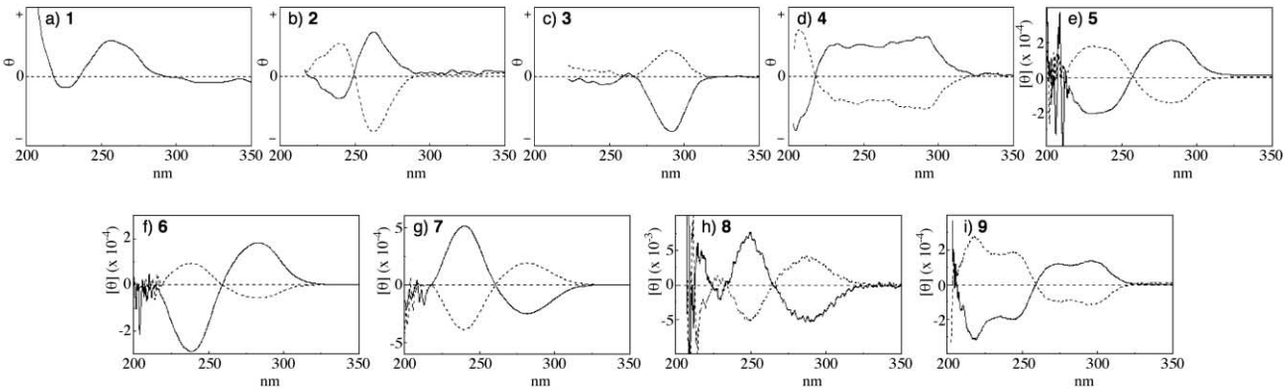


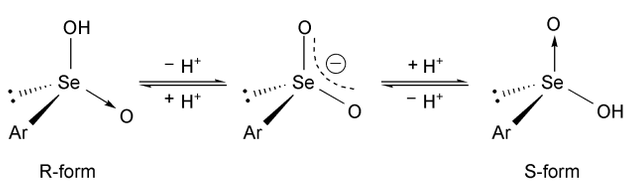
Fig. 2 Circular dichroism spectra of optically active areneseleninic acids **1**–**9**. —: first-eluted enantiomer. - - -: second-eluted enantiomer. Solvent: (a) propan-2-ol; (b) hexane–propan-2-ol = 50 : 50; (c) propan-2-ol; (d) propan-2-ol; (e) hexane–propan-2-ol = 90 : 10; (f) hexane–propan-2-ol = 98 : 2; (g) hexane–propan-2-ol = 99 : 1; (h) hexane–propan-2-ol = 99.5 : 0.5; (i) hexane–propan-2-ol = 95 : 5.

Table 2 First-order rate constants and half-lives for racemization of optically active areneseleninic acids[a]

Compd	Solvent	k/s^{-1} ($t_{1/2}$)
1	Propan-2-ol[b]	5.50×10^{-4} (21.0 min)
2	Propan-2-ol[c]	3.38×10^{-4} (35.2 min)
3	Propan-2-ol[d]	3.64×10^{-4} (31.7 min)
4	Propan-2-ol[e]	2.15×10^{-3} (5.37 min)
5	Propan-2-ol[f]	1.13×10^{-4} (1.70 h)
5	Hexane–propan-2-ol = 90 : 10[g]	6.97×10^{-5} (2.76 h)
6	Hexane–propan-2-ol = 98 : 2[h]	3.81×10^{-5} (5.05 h)
7	Hexane–propan-2-ol = 99 : 1[i]	1.11×10^{-5} (17.3 h)
8	Hexane–propan-2-ol = 99.5 : 0.5[j]	2.85×10^{-5} (6.76 h)
9	Propan-2-ol[k]	1.55×10^{-5} (12.4 h)
9	Propan-2-ol–H_2O = 80 : 20[l]	2.88×10^{-5} (6.70 h)

[a] Each first-eluted enantiomer was used. Racemization was measured by circular dichroism spectra at 24 °C. [b] At 4.13×10^{-5} mol L^{-1}. [c] At 7.40×10^{-6} mol L^{-1}. [d] At 4.19×10^{-5} mol L^{-1}. [e] At 1.25×10^{-4} mol L^{-1}. [f] At 3.95×10^{-5} mol L^{-1}. [g] At 1.52×10^{-4} mol L^{-1}. [h] At 1.08×10^{-4} mol L^{-1}. [i] At 1.09×10^{-4} mol L^{-1}. [j] At 2.55×10^{-5} mol L^{-1}. [k] At 3.04×10^{-5} mol L^{-1}. [l] At 4.33×10^{-5} mol L^{-1}.

inversion to occur at room temperature.[1,19] Thus, the vertex inversion mechanism is unlikely for the racemization of the seleninic acids. Therefore, the racemization of the seleninic acids is considered to proceed *via* the corresponding seleninate anions with the extrusion of a proton, at least under dilute conditions. In the racemization, propan-2-ol and/or water remaining in the solvent may play the role of a proton acceptor.



In the cases of **5**–**7**, the rate constants decreased with an increase in bulkiness of the substituents. This means that the bulky alkyl substituents on the benzene ring of areneseleninic acids are effective for retarding the racemization whereas the rate constant of seleninic acid **8** with the bulkiest substituent was larger than that of **7**.

It was also found that the rate of racemization increased with an increase in concentration in the case of **7** (at 1.46×10^{-3} mol L^{-1} in propan-2-ol; initial $t_{1/2}$ = 2.06 h), and the rate at high concentrations deviated from the first-order rate plot. These results may show that racemization by intermolecular proton exchange reaction *via* intermolecular associated structures also takes place at high concentrations. This can explain why the concentration of the eluate by evaporation of the solvent led to complete racemization of the seleninic acids.

Conclusion

Optically active areneseleninic acids were obtained as solutions by optical resolution on a chiral column using liquid chromatography. Their isolation as crystals was difficult due to the rapid racemization that occurred during concentration of the solutions. The mechanism for the racemization of optically active seleninic acids was clarified to proceed *via* the seleninate anion with the extrusion of a proton under dilute conditions. The electron-donating groups and the bulky substituents at the *ortho* position on the benzene ring of the areneseleninic acids were found to be effective for retarding the racemization.

Experimental

General

Hexane, dichloromethane, and propan-2-ol were distilled from calcium hydride before use. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were measured with Me_4Si for ^{1}H and ^{13}C and Me_2Se for ^{77}Se as internal standard. Optical rotations are given in 10^{-1} deg cm^2 g^{-1}.

Typical procedure for preparation of racemic areneseleninic acids

Ozone was bubbled into a dichloromethane solution (100 mL) of diaryl diselenide (2.0 mmol) at temperatures ranging from −30 to −40 °C. After disappearance of color for diselenide, water (50 mL) was added to the solution, and the solution was stirred vigorously for 1 h at room temperature. The organic layer was separated. The organic component remaining in the aqueous layer was extracted with dichloromethane (30 mL × 2), and the combined organic layer was dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and resulting colorless solid was washed with hexane to give areneseleninic acid as colorless solid.[15] **1**: 46%; **2**: 38%; **3**: 60%; **4**: 42%; **5**: 64%; **6**: 28%; **7**: 72%; **9**: 79%. Seleninic acid **8** was prepared by hydrolysis of the corresponding methyl ester according to the literature.[16]

Toluene-4-seleninic acid (1)[17,20]

Mp 154 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.91 (br, 1H), 2.44 (s, 3H), 7.37 (d, 2H, J = 8.0 Hz), 7.72 (d, 2H, J = 8.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 21.6, 127.5, 131.1, 142.7, 145.0; ^{77}Se NMR (95 MHz, CD_3OD) δ 1229; UV (propan-2-ol): λ_{max} 231 (ε 1.02×10^4), 200 (ε 2.02×10^4) nm; MS (EI) m/z 203 (^{80}Se, $M^+ - 1$), 201 (^{78}Se, $M^+ - 1$), 187, 185.

4-Methoxybenzeneseleninic acid (2)[17]

Mp 110–111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.15 (s, 1H), 7.04 (d, 2H, J = 8.6 Hz), 7.75 (d, 2H, J = 8.6 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 56.2, 115.9, 129.4, 136.8,

164.8; ^{77}Se NMR (95 MHz, CD_3OD) δ 1230; UV (propan-2-ol): λ_{max} 253 (ε 1.28 × 10^4), 200 (ε 2.14 × 10^4) nm; MS (EI) *m*/*z* 221 (^{80}Se, M$^+$ + 1), 219 (^{78}Se, M$^+$ + 1), 186, 184.

2-Methoxybenzeneseleninic acid (3)[21]

Mp 132–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 3H), 6.20 (br, 1H), 6.97 (d, 1H, *J* = 8.2 Hz), 7.17 (dd, 1H, *J* = 7.5, 7.5 Hz), 7.52 (dd, 1H, *J* = 7.5, 8.2 Hz), 8.01 (d, 1H, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.2, 111.4, 121.7, 126.5, 134.2 (duplicate), 158.2; ^{77}Se NMR (95 MHz, CD_3OD) δ 1210; UV (propan-2-ol): λ_{max} 290 (ε 4.03 × 10^3), 233 (ε 6.01 × 10^3), 206 (ε 2.48 × 10^4) nm; MS (EI) *m*/*z* 219 (^{80}Se, M$^+$ − 1), 217 (^{78}Se, M$^+$ − 1), 202, 200, 185, 183, 107, 77.

2-Methoxycarbonylbenzeneseleninic acid (4)[21,22]

Mp 147–148 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 3H), 4.74 (s, 1H), 7.65 (d, 1H, *J* = 8.0 Hz), 7.81 (dd, 1H, *J* = 8.0, 8.0 Hz), 8.07 (dd, 1H, *J* = 8.0, 8.0 Hz), 8.21 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 53.6, 126.4, 129.8, 132.0, 133.4, 134.7, 148.2, 168.3; ^{77}Se NMR (95 MHz, CD_3OD) δ 1220; UV (propan-2-ol): λ_{max} 280 (ε 2.30 × 10^3), 235 (ε 7.92 × 10^3), 206 (ε 2.98 × 10^4) nm; MS (EI) *m*/*z* 246 (^{80}Se, M$^+$ − 2), 230, 228, 215, 213, 156, 77.

2,4,6-Trimethylbenzeneseleninic acid (5)

Mp 130–132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.29 (s, 3H), 2.70 (s, 6H), 6.88 (s, 2H), 7.10 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.3, 21.2, 130.9, 139.2, 139.4, 142.7; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 1245; IR (KBr) ν_{max} 3200–2600, 2600–2000, 833, 804, 677 cm^{-1}; UV (hexane–propan-2-ol = 90 : 10): λ_{max} 274 (ε 2.53 × 10^3), 241 (ε 9.23 × 10^3), 213 (ε 2.02 × 10^4) nm; MS (EI) *m*/*z* 231 (^{80}Se, M$^+$ − 1), 229 (^{78}Se, M$^+$ − 1), 199, 197, 119, 91. Anal. Calcd for $C_9H_{12}O_2Se$: C, 46.76; H, 5.23. Found: C, 46.67; H, 5.17%.

2,4,6-Triethylbenzeneseleninic acid (6)

Mp 111–112 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, 3H, *J* = 7.6 Hz), 1.32 (t, 6H, *J* = 7.6 Hz), 2.62 (q, 2H, *J* = 7.6 Hz), 3.15 (q, 4H, *J* = 7.6 Hz), 6.97 (s, 2H), 9.18 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.2, 17.0, 25.8, 28.7, 128.1, 139.1, 146.1, 149.0; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 1276; IR (KBr) ν_{max} 3100–2600, 2600–2200, 871, 826, 796, 682 cm^{-1}; UV (hexane–propan-2-ol = 98 : 2): λ_{max} 274 (ε 3.17 × 10^3), 238 (ε 6.59 × 10^3), 211 (ε 1.74 × 10^4) nm; MS (EI) *m*/*z* 273 (^{80}Se, M$^+$ − 1), 271 (^{78}Se, M$^+$ − 1), 195, 161, 119, 91. Anal. Calcd for $C_{12}H_{18}O_2Se$: C, 52.75; H, 6.64. Found: C, 52.81; H, 6.48%.

2,4,6-Triisopropylbenzeneseleninic acid (7)

Mp 114–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (d, 6H, *J* = 7.0 Hz), 1.33 (d, 12H, *J* = 6.7 Hz), 2.89 (septet, 1H, *J* = 7.0 Hz), 4.07 (septet, 2H, *J* = 6.7 Hz), 6.56 (br, 1H), 7.11 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.7, 24.7, 29.3, 34.5, 123.1, 139.3, 150.6, 153.4; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 1200; IR (KBr) ν_{max} 3300–2500, 833, 816 cm^{-1}; UV (hexane–propan-2-ol = 99 : 1): λ_{max} 275 (ε 3.18 × 10^3), 238 (ε 1.09 × 10^4), 211 (ε 2.66 × 10^4) nm; MS (EI) *m*/*z* 315 (^{80}Se, M$^+$ − 1), 313 (^{78}Se, M$^+$ − 1), 284, 203, 117, 91. Anal. Calcd for $C_{15}H_{24}O_2Se$: C, 57.14; H, 7.67. Found: C, 57.02; H, 7.54%.

2,4,6-Tri-*tert*-butylbenzeneseleninic acid (8)[16]

Mp 173 °C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.60 (br, 1H), 1.62 (br, 18H), 7.50 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 34.1, 35.2, 38.9, 124.5, 144.6, 153.0, 153.7; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 1211; MS (EI) *m*/*z* 357 (^{80}Se, M$^+$ − 1), 355 (^{78}Se, M$^+$ − 1), 342, 340, 244, 229, 81.

2,4-Di-*tert*-butyl-6-methoxybenzeneseleninic acid (9)

Mp 101–103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 9H), 1.52 (s, 9H), 2.42 (br, 1H), 4.08 (s, 3H), 7.00 (d, 1H, *J* = 1.6 Hz), 7.14 (d, 1H, *J* = 1.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 33.3, 35.6, 36.9, 57.8, 110.3, 117.1, 133.6, 150.8, 156.4, 160.4; ^{77}Se NMR (95 MHz, $CDCl_3$) δ 1213; IR (KBr) ν_{max} 3220 (br), 2961, 2362, 1591, 1559, 1405, 1302, 1240, 1057, 847, 661 cm^{-1}; UV (hexane–propan-2-ol = 95 : 5): λ_{max} 294 (ε 4.65 × 10^3), 242 (sh, ε 7.06 × 10^3), 212 (ε 2.26 × 10^4) nm; MS (EI) *m*/*z* 316 (^{80}Se, M$^+$ − 16), 314 (^{78}Se, M$^+$ − 16), 298, 296, 187, 71. Anal. Calcd for $C_{15}H_{24}O_3Se$: C, 54.38; H, 7.30. Found: C, 54.73; H, 7.35%.

Typical procedure for optical resolution of areneseleninic acids

Racemic areneseleninic acid (50 mg) in eluent (0.3 mL) was charged to a chiral column packed with amylose carbamate derivative–silica gel (Daicel Chiralpak AS; 10 × 250 mm) and eluted with propan-2-ol (for **1**, **3**, and **4**) or hexane containing 50 (for **2**), 10 (for **5**), 5 (for **9**), 2 (for **6**), 1 (for **7**), and 0.5 (for **8**) vol% propan-2-ol at a flow rate of 1.0 mL min^{-1}. About each 15 mg of optically active areneseleninic acid was collected as eluates from the fastest eluted portion and next portion, and the specific rotations and the circular dichroism spectra were measured in the eluates, and the concentrations of which were determined based on a comparison of the UV spectra with those of authentic racemic samples. Chiroptical properties of the optically active seleninic acids are summarized in Table 1, and the chemical structures were confirmed by the Mass spectra and ^{1}H NMR spectra after concentration, although racemization was occurring during the concentration.

Kinetic study for racemization of optically active areneseleninic acids

Kinetic studies on the racemization of optically active seleninic acids were examined in solutions (10^{-3}–10^{-6} mol L^{-1}) at 24 °C. The rates of racemization were calculated based on their circular dichroism spectra and were plotted to the first-order rate equation.

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