Supporting Information for

Ruthenium(III) Chloride Catalyzed Efficient Synthesis of Unsymmetrical Diorganyl Selenides via Cleavage of Dibenzyl and Diphenyl Diselenides in the Presence of Zinc

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Experimental Section (Supporting Information)

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1. General experimental procedure

All operations were performed under argon. Dried solvents were used in all experiments. Melting points are not corrected. Instrumentation: ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained with Bruker DRX-400 spectrometer (chemical shifts refer to $\delta_{\text{TMS}} = 0.00$ ppm); IR Bruker Tensor 27. Elemental analysis was achieved by the Analysis Center, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

2. NMR spectral data

Heptyl benzyl selenide (4a): colorless liquid; ^1H NMR (400Hz, CDCl_3 , 23 °C) δ 7.30 and 7.22 (m each, 4:1 H, aromatic CH), 3.79 (s, 2H, CH_2Se), 2.50 (t, 2H, SeCH_2), 1.62 (m, 2H, CH_2), 1.32 (m, 8H, $4\times\text{CH}_2$), 0.91 (t, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 Hz, CDCl_3 , 23 °C) δ 139.76 (*i*-C of phenyl), 128.90, 128.54, 126.67, 31.83 (CH_2Se), 30.39 (SeCH_2), 30.02, 28.92, 27.02, 24.21, and 22.72 (s each, CH_2), 14.20 (s, CH_3). Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{Se}$: C, 62.44; H, 8.23. Found: C, 61.84; H, 8.21.

Pentyl benzyl selenide (4b): colorless liquid; ^1H NMR (400Hz, CDCl_3 , 23 °C) δ 7.30 and 7.23 (m each, 4:1 H, aromatic CH), 3.78 (s, 2H, CH_2Se), 2.51 (t, 2H, SeCH_2), 1.65 (m, 2H, CH_2), 1.34 (m, 4H), 0.90 (t, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 Hz, CDCl_3 , 23 °C) δ 139.75 (s, Cq, *i*-C of phenyl), 128.90, 128.54, 126.67, 32.25 (s, CH_2Se), 30.09 (s, SeCH_2), 27.03, 24.18, 22.32, 14.10 (s, CH_3).

Butyl benzyl selenide (4c): colorless liquid; ^1H NMR (400Hz, CDCl_3 , 23 °C) δ 7.34 (d) and 7.27-7.23 (m) (4 : 1 H, aromatic CH), 3.81 (s, 2H, CH_2Se), 2.54 (t, 2H, SeCH_2), 1.68 ~ 1.62 (m, 2H, CH_2), 1.45-1.39 (m, 2H, CH_2), 0.94 (t, 3H, CH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (400 Hz, CDCl_3 , 23 °C) δ 139.67 (*i*-C of phenyl), 128.83 (2-C), 128.45 (3-C),

126.58 (4-C), 32.41 (CH₂Se), 26.91 (SeCH₂), 23.75 and 23.07 (s each, CH₂), 13.66 (s, CH₃).

Dodecyl benzyl selenide (4d): colorless liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.31 and 7.23 (m each, 4:1 H, aromatic CH), 3.80 (s, 2H, CH₂Se), 2.52 (t, 2H, SeCH₂), 1.66 (m, 2H, CH₂), 1.33 (m, 18H, 9×CH₂), 0.93 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 139.73 (s, Cq, *i*-C of phenyl), 128.87 and 128.49 (s, each, aromatic CH), 126.62 (s, aromatic CH), 32.03 (s, CH₂Se), 30.37 (SeCH₂), 30.05, 29.75, 29.62, 29.47, 29.25, 26.98, 24.16, 22.80, 14.23 (s, CH₃).

Dibenzyl selenide (4e): M.p. 45 - 46 °C; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.32 and 7.28 (m each, 8:2 H, aromatic CH), 3.78 (s, 2H, CH₂Se); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 139.26 (s, Cq, *i*-C of phenyl), 129.06, 128.56, 126.78, 27.62 (CH₂Se).

Allyl benzyl selenide (4f): pale yellow liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.31 and 7.24 (m each, 4:1 H, aromatic CH), 5.92 (m, 1H, CH=), 5.08 (m, 2H, =CH₂), 3.76 (s, 2H, CH₂Se) and 3.15 (d, 2H, SeCH₂); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 139.42 (s, Cq, *i*-C of phenyl), 135.06, 129.08, 128.56, 126.74, 116.56, 26.73, 26.36.

Heptyl 4-methylbenzyl selenide (4h): pale yellow liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.21 and 7.12 (d, each, 2 : 2 H, aromatic CH), 3.78 (s, 2H, CH₂Se), 2.52 (t, 2H, SeCH₂), 2.36 (s, 3H, CH₃), 1.65 (m, 2H), 1.33 (m, 8H), 0.92 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 136.60 and 136.18 (s each, Cq, *i*-C of phenyl), 129.19, 128.75, 31.81, 30.39, 30.12, 28.91, 26.72, 24.10, 22.70, 21.15, 14.17 (s, CH₃). Anal. Calcd for C₁₅H₂₄Se: C, 63.59; H, 8.54. Found: C, 62.91; H, 8.52.

Butyl 4-methylbenzyl selenide (4i): pale yellow liquid; ¹H NMR (400Hz, CDCl₃,

23 °C) δ 7.22 and 7.14 (d each, 2 : 2 H, aromatic CH), 3.79 (s, 2H, CH₂Se), 2.54 (t, 2H, SeCH₂), 2.37 (s, 3H, CH₃), 1.66 (m, 2H), 1.43 (m, 2H), 0.95 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 136.54 and 136.14 (s each, Cq each, *i*-C of phenyl), 129.16, 128.71, 32.45, 26.66, 23.72, 23.13, 21.13, 13.68 (s, CH₃). Anal. Calcd for C₁₂H₁₈Se: C, 59.75; H, 7.52. Found: C, 59.52; H, 7.31.

Benzyl 4-methylbenzyl selenide (4j): pale yellow oil; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.33-7.16 (m, 9H, aromatic CH), 3.76 and 3.74 (s each, 2:2 H, 2×CH₂), 2.38 (s, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 139.38 and 136.12 (s each, Cq each, *i*-C of phenyl), 129.27, 129.06, 128.95, 128.56, 126.74, 27.57, 27.37, 21.22.

Heptyl 2-methylbenzyl selenide (4k): pale yellow liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.17 (m, 4H), 3.80 (s, 2H, CH₂Se), 2.55 (m, 2H), 2.42 (s, 3H, CH₂), 1.67 (m, 2H), 1.34 (m, 8H), 0.93 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 137.70 and 136.35 (s each, Cq, *i*-C of phenyl), 130.70, 129.49, 127.01, 125.87, 31.82, 30.53, 30.04, 28.93, 25.11, 24.38, 22.71, 19.29, 14.19 (s, CH₃). Anal. Calcd for C₁₅H₂₄Se: C, 63.59; H, 8.54. Found: C, 62.66; H, 8.49.

Butyl 2-methylbenzyl selenide (4l): pale yellow liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.30 (m, 4H, aromatic CH), 3.93 (s, 2H, CH₂Se), 2.69 (t, 2H, SeCH₂), 2.55 (s, 3H, CH₃), 1.80 (m, 2H), 1.55 (m, 2H), 1.07 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 137.31 and 136.36 (s each, Cq each, *i*-C of phenyl), 130.70, 129.50, 127.02, 125.88, 32.62, 25.10, 24.05, 23.19, 19.29, 13.73 (s, CH₃). Anal. Calcd for C₁₂H₁₈Se: C, 59.75; H, 7.52. Found: C, 59.58; H, 7.42.

Benzyl 2-methylbenzyl selenide (4m): colorless oil; ¹H NMR (400Hz, CDCl₃, 23

°C) δ 7.36 (m, 4H), 7.30 (m, 1H), 7.22 (m, 4H), 3.84 and 3.80 (s each, 2:2 H, 2 $\times$ CH₂), 2.37 (s, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 139.26, 136.80, 136.52, 130.69, 129.62, 129.05, 128.55, 127.55, 127.12, 125.95, 27.75 (d), 25.86 (d), 19.17.

Heptyl 4-chlorobenzyl selenide (4n): pale yellow liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.26-7.20 (m, 4H, aromatic CH), 3.72 (s, 2H, CH₂Se), 2.48 (t, 2H, SeCH₂), 1.62 (m, 2H), 1.27 (m, 8H), 0.89 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 138.32 and 132.32 (s each, Cq each, *i*-C of phenyl), 130.18, 128.62, 31.79 (s, CH₂Se), 30.30 (s, SeCH₂), 29.97, 28.89, 26.15, 24.25, 22.70, 14.18 (s, CH₃). Anal. Calcd for C₁₂H₁₈Se: C, 55.36; H, 6.97. Found: C, 55.21; H, 6.98.

Heptyl 4-methoxybenzyl selenide (4o): pale yellow liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.21 and 6.83 (d each, 2:2 H, aromatic CH), 3.79 (s, 3H, OCH₃), 3.75 (s, 2H, CH₂Se), 2.48 (t, 2H, SeCH₂), 1.63 (m, 2H), 1.28 (m, 8H), 0.90 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 158.32 and 131.61 (s each, Cq each, *i*-C of phenyl), 129.85, 113.86, 55.24, 31.76, 30.37, 29.98, 28.87, 26.38, 24.00, 22.66, 14.13 (s, CH₃). Anal. Calcd for C₁₅H₂₄OSe: C, 60.19; H, 8.08. Found: C, 60.18; H, 8.07.

Heptyl 2-methoxybenzyl selenide (4p): pale yellow liquid; ¹H NMR (400Hz, CDCl₃, 23 °C) δ 7.20 and 6.88 (m each, 2 : 2 H, aromatic CH), 3.87 (s, 3H, OCH₃), 3.81 (s, 2H, CH₂Se), 2.56 (t, 2H, SeCH₂), 1.67 (m, 2H), 1.33 (m, 8H), 0.91 (t, 3H, CH₃); ¹³C {¹H} NMR (400 Hz, CDCl₃, 23 °C) δ 157.10 and 128.50 (s each, Cq each, *i*-C of phenyl), 130.11, 127.96, 120.41, 110.68, 55.43, 31.82, 30.60, 30.09, 28.94, 24.41, 22.70, 21.22, 14.16 (s, CH₃). Anal. Calcd for C₁₅H₂₄OSe: C, 60.19; H, 8.08. Found: C, 60.18; H, 8.10.

(4a)

¹³C NMR (zxd-157 in CDCl₃)

(4a)

(4b)

¹³C NMR (zxd-200 in CDCl₃)

(4b)

(4f)

¹³C NMR (expd 224 in CDCl₃)

26.734
26.355

77.464
77.145
76.828

139.416
135.058
129.077
128.559
127.160
126.735
116.555

ppm

(4f)

(4h)

¹³C NMR (2x4-194 in CDCl₃)

(4h)

¹H NMR (zxd-201 in CDCl₃)

(4i)

¹³C NMR (zxd-201 in CDCl₃)

(4i)

(4k)

¹³C NMR (zxd-215 in CDCl₃)

(4k)

(4l)

(41)

¹H NMR (zxd-193 in CDCl₃)

(4n)

(4n)

¹H NMR (zxd-195 in CDCl₃)

(4o)

¹³C NMR (zxd-195 in CDCl₃)

(4o)

(4p)

¹³C NMR (zxd-197 in CDCl₃)

(4p)

(4c)

¹³C NMR (zxd-190 in CDCl₃)

(4c)

(4d)

¹³C NMR (zxd-192 in CDCl₃)

(4d)

(4e)

¹³C NMR (zxd-187 in CDCl₃)

(4e)

¹H NMR (zxd-206 in CDCl₃)

7.3300
7.2829
7.2050
7.1629

3.7597
3.7434
3.6965

2.9823
2.9356

(4j)

¹³C NMR (zxd-206 in CDCl₃)

(4j)

(4m)

¹³C NMR (zxd-216 in CDCl₃)

(4m)