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Chiral building blocks from *R*-(–)-carvone: *N*-bromosuccinimide-mediated addition–sceletal rearrangement of (–)-*cis*-carveol

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*(1*R*,5*R*)-5-Isopropenyl-2-methylcyclohex-2-en-1-ol* **2**: colorless oil, yield 90%; $[\alpha]_D^{20}$–23.6 (*c* 0.85, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.47–1.52 (m, 1H), 1.72 (s, 3H), 1.74 (d, 3H, *J* 2 Hz), 1.85–2.30 (m, 5H), 4.17 (br, 1H), 4.71 (s, 2H), 5.44 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 18.7, 20.4, 30.7, 37.6, 40.1, 70.6, 108.9, 123.6, 135.8, 148.7. IR (KBr, *ν*/cm^{-1}): 3331, 3082, 1645, 1450, 1437, 1375. Found (%): C, 78.76; H, 10.81. Calc. for $C_{10}H_{16}O$ (%): C, 78.95; H, 10.53.

*(1*R*,5*R*,6*S*)-6-Iodomethyl-2,6-dimethyl-7-oxabicyclo[3.2.1]oct-2-ene* **3***:* colorless oil, yield 73%; $[\alpha]_D^{20}$–17.5 (*c* 5.0, EtOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.45 (s, 3H), 1.70–1.72 (m, 3H), 1.91–1.95 (m, 1H), 2.28–2.38 (m, 3H), 2.50 (m, 1H), 3.30 (d, 1H, *J* 9 Hz), 3.37 (d, 1H, *J* 9 Hz), 4.13–4.15 (m, 1H), 5.26 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.2, 21.4, 27.9, 29.8, 35.1, 40.8, 77.5, 84.0, 120.7, 139.8. IR (KBr, *ν*/cm^{-1}): 1449, 1373, 1088. Found (%): C, 43.06; H, 5.49; I, 45.30. Calc. for $C_{10}H_{15}IO$ (%): C, 43.17; H, 5.40; I, 45.68.

*(1*R*,5*R*,6*S*)-6-Iodomethyl-2,6-dimethyl-7-oxabicyclo[3.2.1]oct-2-en-4-one* **4**: yellow oil, yield 65%; $[\alpha]_D^{20}$+350.3 (*c* 4.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.55 (s, 3H), 2.08 (s, 3H), 2.36 (d, 1H, *J* 12 Hz), 2.46–2.50 (m, 1H), 3.10 (m, 1H), 3.12 (d, 1H, *J* 9 Hz), 3.22 (d, 1H, *J* 9 Hz), 4.47–4.49 (m, 1H), 5.78–5.79 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.7, 22.2, 28.2, 40.0, 58.4, 78.3, 81.4, 125.7, 165.4, 199.0. IR (KBr, *ν*/cm^{-1}): 1676, 1435, 1375. MS (APCI), *m/z* (%): 293 [$(M+H)^+$, ^{127}I] (100), 165 [$((M-HI)+H)^+$, ^{127}I] (42.4). Found (%): C, 40.96; H, 4.24; I, 43.12. Calc. for $C_{10}H_{13}IO_2$ (%): C, 41.10; H, 4.45; I, 43.49.

*(2*S*,5*R*)-5-Acetyl-2-iodomethyl-2-methyldihydrofuran-3-ylidenehydroxyacetaldehyde* **7***:* yellow oil, yield 72%; $[\alpha]_D^{20}$ +57.3°, (*c* 2.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.64 (s, 3H), 2.43 (s, 3H), 2.99-3.08 (m, 1H), 3.27-3.35 (m, 1H), 3.56 (d, 1H, *J* 9 Hz), 3.93 д (d, 1H, *J* 9 Hz), 4.45-4.51 (m, 1H), 6.04 (br, 1H), 9.60 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.40, 21.49, 26.58, 30.96, 81.71, 85.46, 136.44, 140.84, 185.20, 208.39. IR (KBr, *ν*/cm^{-1}): 3412, 1716, 1658. MS

(APCI), *m/z* (%): 197 [((M-HI)+H)$^+$, ^{127}I] (100), 325 [(M+H)$^+$, ^{127}I] (1.25). Found (%): C, 36.88; H, 3.76; I, 38.79. Calc. for $C_{10}H_{13}IO_4$ (%): C, 37.06; H, 4.04; I, 39.15.

*(3*S*,6*S*,7*R*)-6,7-Dibromo-3-iodomethyl-1,3-dimethyl-2-oxabicyclo[2.2.2]octane* **12**: white crystalline solid, yield 68%, mp 92–93°C; $[\alpha]_D^{20}$–17.5 (*c* 3.15, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.42 (s, 3H), 1.51 (s, 3H), 2.20–2.22 (m, 1H), 2.27–2.30 (m, 2H), 2.80–2.89 (m, 2H), 3.15 (d, 1H, *J* 9 Hz), 3.20 (d, 1H, *J* 9 Hz), 4.17–4.23 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6) δ: 14.4, 24.5, 24.7, 34.2, 35.6, 36.5, 46.7, 46.8, 75.1, 75.8. IR (KBr, *ν*/cm^{-1}): 1460, 1445, 1377, 1082. Found (%): C, 27.28; H, 3.31; Br, I, 65.17. Calc. for $C_{10}H_{15}Br_2IO$ (%): C, 27.40; H, 3.42; Br, 36.53; I, 29.0.

*(1*R*,2*S*,3*R*,5*S*)-5-Isopropenyl-2,3-epoxy-2-methylcyclohex-2-en-1-ol* **13***:* colorless oil, yield 91%; $[\alpha]_D^{20}$–48.5 (*c* 1.64, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.25 (m, 1H), 1.44 (s, 3H), 1.75 (s, 3H), 1.87 (d, 1H, *J* 6 Hz), 1.98–2.22 (m, 3H), 3.17 (br, 1H), 3.80–4.00 (m, 1H), 4.76–4.78 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.1, 20.4, 30.6, 34.4, 36.5, 60.9, 61.9, 68.9, 109.3, 148.1. IR (KBr, *ν*/cm^{-1}): 3368, 2976, 2854, 1643, 1036, 891. Found (%): C, 71.18; H, 9.43. Calc. for $C_{10}H_{16}O_2$ (%): C, 71.39; H, 9.59.

*(1*R*,2*S*,3*R*,5*S*,6*S*)-6-Iodomethyl-2,6-dimethyl-2,3-epoxy-7-oxabicyclo[4.2.1.0]octane* **14***:* yellow oil, yield 71%; $[\alpha]_D^{20}$–36.4 (*c* 3.3, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.38 (s, 3H), 1.43 (s, 3H), 1.94–1.98 (m, 2H), 2.04–2.09 (m, 2H), 2.19–2.26 (m, 1H), 2.93–2.95 (m, 1H), 3.08 (d, 1H, *J* 9 Hz), 3.40 (d, 1H, *J* 9 Hz), 4.32–4.33 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.1, 18.7, 26.7, 27.5, 30.9, 39.9, 57.1, 59.3, 80.0, 82.8. IR (KBr, *ν*/cm^{-1}): 2976, 2940, 1445, 1375, 1084, 1031. Found (%): C, 40.79; H, 5.22; I, 42.76. Calc. for $C_{10}H_{15}IO_2$ (%): C, 40.83; H, 5.14; I, 43.15.

*(1*R*,2*S*,3*R*,5*S*,6*S*)-2-Fluoro-3-acetoxy-6-iodomethyl-2,6-dimethyl-7-oxabicyclo[3.2.1]octane* **15**: colorless oil, yield 64%; $[\alpha]_D^{20}$–47.2 (*c* 1.65, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.36 (d, 3H, *J* 22.5 Hz), 1.48 (s, 3H), 1.55–1.65 (m, 2H), 2.10 (s, 3H), 2.25–2.35 (m, 4H), 3.43 (d, 1H, *J* 9 Hz), 3.48 (d, 1H, *J* 9 Hz), 4.23 (br, 1H), 5.10 (dddd, 1H, *J* 6.4, 10.9, 24.1 Hz,). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 10.5 (CH_2I), 20.9, 21.1 (CH_3, $^2J_{C,F}$=17.36 Hz), 21.5 (CH_3), 27.5 (CH_3), 29.6 (CH_2), 31.8 (CH_2), 40.4 (C^5), 70.8, 71.1 (C^3, $^2J_{C,F}$=17.4 Hz), 81.7, 82.0 (C^1, $^2J_{C,F}$=17.4 Hz), 84.3 (C^6), 92.0, 94.5 (C^2, $^1J_{C,F}$=182.6 Hz). IR (KBr, *ν*/cm^{-1}): 2980, 2938, 1736, 1375, 1238, 1051, 908. MS (APCI), *m/z* (%): 229 [M–^{127}I]$^+$ (100), 169 [M–^{127}I–CH_3COOH]$^+$ (77), 296 [M-CH_3COOH]$^+$ (45), 356 [M]$^+$ (11). Found (%): C, 40.30; H, 4.98; I, F, 40.61. Calc. for $C_{12}H_{18}O_3IF$ (%): C, 40.47; H, 5.09; I, 35.63; F, 5.33.