SUPPORTING INFORMATION

SYNTHESIS OF α-HALOBUTENOLIDES USING THE NUCLEOPHILICITY OF MAGNESIUM ALKYLIDENE CARBENOIDS

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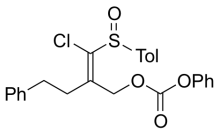
General methods

Melting points were measured using a Yanaco MP-S3 apparatus and are uncorrected. NMR spectra were measured in a $CDCl_3$ solution using JEOL JNM-LA 300, JEOL JNM-LA 500, Bruker AVANCE DPX 300, and Bruker AVANCE DPX 400 spectrometers. The assignments of the ^{13}C NMR spectra were made by DEPT 45, 90, and 135. Mass spectra were obtained at 70 eV by direct injection with a HITACHI M-80B mass spectrometer. IR spectra were recorded using a Perkin–Elmer Spectrum One FTIR instrument (KBr or neat) and a Perkin–Elmer Frontier FT-IR spectrometer in the ATR mode. Silica gel 60 N containing 0.5% fluorescence reagent 254 and a quartz column were used in the column chromatography, and the products that absorbed UV light were detected by UV irradiation. Anhydrous THF, α-bromoketones **2b–e**, BuLi in hexane, phenyl chloroformate, pyridine, and *i*-PrMgCl•LiCl in THF were commercially available and used as supplied. Halomethyl *p*-tolyl sulfoxides[1] and α-bromoketones **2a**, **2f**, and **2g**[2,3] were prepared according to the procedure described in the literature. Diisopropylamine was distilled from CaH_2. All of the reactions involving air- or water-sensitive compounds were routinely conducted in glassware that had been flame-dried under a positive pressure of argon. α-Halobutenolides **5b**, **5c**, **5d**, and **5f** are known compounds.[4,5]

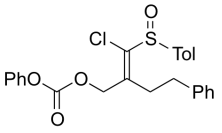
Characterization data for cyclization precursors 4 and α-halobutenolides 5

(*E*)-2-[Chloro(*p*-tolylsulfinyl)methylene]-4-phenylbutyl phenyl carbonate [(*E*)-4a]



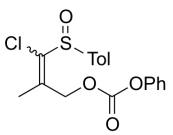
Colorless oil; IR (neat): 3062, 3028, 2926, 2867, 1770 (C=O), 1593, 1495, 1456, 1374, 1242, 1163, 1089, 1062, 1022, 811, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 2.73–2.91 (m, 4H), 5.18 (d, *J* = 12.6 Hz, 1H), 5.26 (d, *J* = 12.6 Hz, 1H), 7.16–7.23 (m, 5H), 7.25–7.33 (m, 5H), 7.39–7.44 (m, 2H), 7.51–7.54 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.4 (CH_3), 32.7 (CH_2), 34.5 (CH_2), 65.6 (CH_2), 120.8 (CH), 124.8 (CH), 126.3 (CH), 126.5 (CH), 128.3 (CH), 128.6 (CH), 129.6 (CH), 129.9 (CH), 137.5 (C), 139.9 (C), 142.0 (C), 142.2 (C), 142.3 (C), 150.9 (C), 153.2 (C); MS (FAB^+): *m*/*z* (%) = 455 ($[M+H]^+$, 29), 317 (100), 177 (18), 141 (19), 91 (32); HRMS (FAB^+): *m*/*z* [$(M+H)^+$] calcd for $C_{25}H_{24}ClO_4S$: 455.1084; found: 455.1088.

(*Z*)-2-[Chloro(*p*-tolylsulfinyl)methylene]-4-phenylbutyl phenyl carbonate [(*Z*)-4a]



Colorless crystals; mp 99.0–100.0 ℃ (hexane/EtOAc); IR (KBr): 3061, 3030, 2962, 2934, 1762 (C=O), 1592, 1495, 1457, 1425, 1369, 1286, 1251, 1210, 1086, 1054, 1018, 947, 802, 748, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 2.90–3.04 (m, 2H), 3.11–3.23 (m, 2H), 5.02 (d, *J* = 14.0 Hz, 1H), 5.08 (d, *J* = 14.0 Hz, 1H), 7.16–7.19 (m, 2H), 7.25–7.29 (m, 6H), 7.33–7.42 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.4 (CH_3), 32.9 (CH_2), 35.0 (CH_2), 66.9 (CH_2), 120.8 (CH), 124.7 (CH), 126.3 (CH), 126.7 (CH), 128.5 (CH), 128.8 (CH), 129.6 (CH), 129.9 (CH), 137.5 (C), 138.2 (C), 139.7 (C), 142.0 (C), 142.6 (C), 150.9 (C), 153.2 (C); MS (FAB^+): *m*/*z* (%) = 455 ($[M+H]^+$, 100), 317 (48), 154 (46), 136 (43), 93 (55); HRMS (FAB^+): *m*/*z* [$(M+H)^+$] calcd for $C_{25}H_{24}ClO_4S$: 455.1084; found: 455.1087.

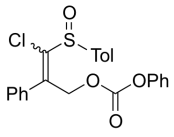
3-Chloro-2-metyl-3-(*p*-tolylsulfinyl)allyl phenyl carbonate (4b)



Colorless solid; mp 68.2–69.2 °C; IR (ATR): 3012, 2954, 2922, 1762 (C=O), 1613, 1593, 1487, 1457, 1444, 1380, 1364, 1305, 1244, 1228, 1200, 1115, 1083, 1053, 1021, 1013, 972, 925, 894, 858, 809, 776, 708, 690, 620 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, M: major isomer, m: minor isomer): δ = 2.13 (s, $3H_m$), 2.412 (s, $3H_M$), 2.417 (s, $3H_m$), 2.422 (s, $3H_M$), 4.95 (d, *J* = 14.0 Hz, $1H_M$), 5.02 (d, *J* = 14.0 Hz, $1H_M$), 5.22 (d, *J* = 12.4 Hz, $1H_m$), 5.43 (d, *J* = 12.4 Hz, $1H_m$), 7.16–7.22 (m, $2H_M$, $2H_m$), 7.25–7.34 (m, $3H_M$, $3H_m$), 7.38–7.44 (m, $2H_M$, $2H_m$), 7.50–7.52 (m, $2H_M$) 7.56–7.58 (m, $2H_m$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.1, 19.2, 21.4 (two signals overlapping), 66.8, 68.2, 120.79, 120.82, 124.5, 124.8, 126.28, 126.33, 129.5, 129.6, 129.85, 129.94, 136.7, 137.5, 137.9, 139.2, 139.5, 141.0, 142.0, 142.1, 150.92, 150.95, 153.25, 153.27;

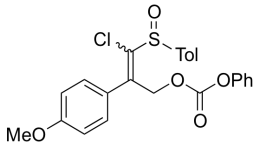
MS (FAB$^+$): *m*/*z* (%) = 365 ([M+H]$^+$, 100), 227 (52), 191 (39), 179 (28), 154 (31); HRMS (FAB$^+$): *m*/*z* [(M+H)$^+$] calcd for $C_{18}H_{18}ClO_4S$: 365.0614; found: 365.0612.

3-Chloro-2-phenyl-3-(*p*-tolylsulfinyl)allyl phenyl carbonate (4c)



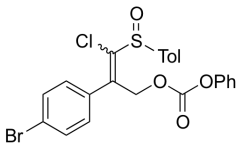
Colorless solid; mp 120.1–121.1 °C; IR (KBr): 3060, 1767 (C=O), 1593, 1493, 1444, 1366, 1231, 1208, 1086, 1051, 1024, 1006, 950, 887, 806, 762, 715, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, M: major isomer, m: minor isomer): δ = 2.41 (s, $3H_M$), 2.43 (s, $3H_m$), 5.24 (s, $2H_M$), 5.45 (d, *J* = 12.6 Hz, $1H_m$), 5.70 (d, *J* = 12.6 Hz, $1H_m$), 6.90–6.93 (m, $2H_M$), 7.04–7.08 (m, $2H_m$), 7.19–7.53 (m, $12H_M$, $10H_m$), 7.66–7.69 (m, $2H_m$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.5 (two signals overlapping), 66.7, 67.7, 120.76, 120.80, 124.9, 125.0, 126.2, 126.3, 128.0, 128.6, 128.8, 129.2, 129.3, 129.4, 129.5, 129.8, 130.0, 133.8, 135.6, 137.91, 137.94, 140.68, 140.71, 141.6, 142.2, 142.8, 143.3, 150.8, 150.9, 152.9, 153.1; MS (FAB$^+$): *m*/*z* (%) = 427 ([M+H]$^+$, 100), 289 (31), 154 (34), 137 (30), 93 (37); HRMS (FAB$^+$): *m*/*z* [(M+H)$^+$] calcd for $C_{23}H_{20}ClO_4S$: 427.0771; found: 427.0771.

3-Chloro-2-(4-methoxyphenyl)-3-(*p*-tolylsulfinyl)allyl phenyl carbonate (4d)



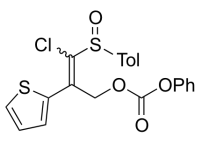
Colorless solid; mp 133.3–134.2 °C; IR (ATR): 2964, 2839, 1768 (C=O), 1757, 1610, 1575, 1509, 1494, 1457, 1445, 1378, 1365, 1294, 1246, 1226, 1203, 1176, 1112, 1084, 1048, 1030, 1004, 964, 951, 903, 889, 835, 807, 783, 763, 746, 712, 687, 662, 620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, M: major isomer, m: minor isomer): δ = 2.41 (s, $3H_M$), 2.43 (s, $3H_m$), 3.83 (s, $3H_m$), 3.88 (s, $3H_M$), 5.22 (s, $2H_M$), 5.45 (d, *J* = 12.6 Hz, $1H_m$), 5.70 (d, *J* = 12.6 Hz, $1H_m$), 6.91–7.39 (m, $11H_M$, $11H_m$), 7.43–7.46 (m, $2H_M$) 7.65–7.68 (m, $2H_m$); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.5 (two signals overlapping), 55.3, 55.4, 66.8, 67.9, 114.0, 114.3, 120.83, 120.85, 124.99, 125.02, 125.9, 126.2, 126.3, 127.6, 129.46, 129.55, 129.76, 129.87, 130.0, 130.7, 137.7, 138.2, 140.3, 141.4, 142.0, 142.2, 143.3, 150.92, 150.97, 153.0, 153.1, 160.3, 160.5; MS (FAB$^+$): *m*/*z* (%) = 457 ([M+H]$^+$, 100), 319 (39), 271 (36), 154 (34), 136 (29); HRMS (FAB$^+$): *m*/*z* [(M+H)$^+$] calcd for $C_{24}H_{22}ClO_5S$: 457.0876; found: 457.0874.

2-(4-Bromophenyl)-3-chloro-3-(*p*-tolylsulfinyl)allyl phenyl carbonate (4e)



Colorless solid; mp 156.0–157.0 °C; IR (KBr): 3062, 3037, 1769 (C=O), 1591, 1486, 1446, 1394, 1380, 1367, 1252, 1233, 1085, 1051, 1024, 1011, 953, 891, 841, 807, 771, 737, 709, 688 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, M: major isomer, m: minor isomer): δ = 2.42 (s, $3H_M$), 2.44 (s, $3H_m$), 5.21 (s, $2H_M$), 5.44 (d, *J* = 12.6 Hz, $1H_m$), 5.67 (d, *J* = 12.6 Hz, $1H_m$), 6.92–6.96 (m, $2H_M$), 7.06–7.09 (m, $2H_m$), 7.17–7.43 (m, $9H_M$, $7H_m$), 7.54–7.57 (m, $2H_m$), 7.62–7.67 (m, $2H_M$, $2H_m$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.5 (two signals overlapping), 66.4, 67.5, 120.7, 120.8, 123.5, 123.9, 124.9, 126.27, 126.34, 129.5, 129.6, 129.7, 129.9, 130.1, 130.9, 131.9, 132.1, 132.7, 134.4, 137.3, 137.7, 140.39, 140.41, 141.3, 142.0, 142.4, 142.5, 150.76, 150.83, 152.9, 153.0; MS (FAB$^+$): *m*/*z* (%) = 507 (79), 505 ([M+H]$^+$, 57), 185 (54), 154 (99), 137 (83), 93 (100); HRMS (FAB$^+$): *m*/*z* [(M+H)$^+$] calcd for $C_{23}H_{19}BrClO_4S$: 504.9876; found: 504.9874.

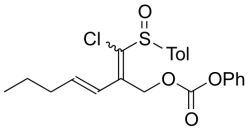
3-Chloro-2-(thiophen-2-yl)-3-(*p*-tolylsulfinyl)allyl phenyl carbonate (4f)



Colorless solid; mp 106.2–107.2 °C; IR (ATR): 3069, 1764 (C=O), 1591, 1564, 1493, 1457, 1431, 1419, 1375, 1364, 1293, 1274, 1254, 1230, 1198, 1085, 1053, 1021, 1009, 965, 928, 897, 880, 847, 812, 776, 767, 727, 690, 620 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, M: major isomer, m: minor isomer): δ = 2.42 (s, $3H_M$, $3H_m$), 5.20 (d, *J* = 13.3 Hz, $1H_M$), 5.26 (d, *J* = 13.3 Hz, $1H_M$), 5.71 (d, *J* = 12.5 Hz, $1H_m$), 5.85 (d, *J* = 12.5 Hz, $1H_m$), 7.01–7.06 (m, $1H_M$, $2H_m$), 7.13–7.43 (m, $7H_M$, $8H_m$),

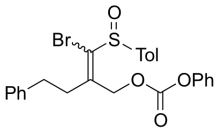
7.52–7.57 (m, $3H_M$, $1H_m$), 7.63-7.67 (m, $1H_M$, $1H_m$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.41, 21.43, 66.2, 68.0, 120.78, 120.81, 124.99, 125.01, 126.2, 126.3, 127.1, 127.5, 128.8, 129.4, 129.6, 129.8, 129.91, 129.94, 130.3, 131.1, 132.9, 133.9, 136.0, 136.9, 137.6, 137.9, 141.2, 142.1, 142.2, 143.2, 150.88, 150.93, 153.03, 153.07; MS (FAB^+): *m/z* (%) = 433 ($[M+H]^+$, 100), 295 (38), 259 (24), 247 (28), 154 (22); HRMS (FAB^+): *m/z* [$(M+H)^+$] calcd for $C_{21}H_{18}ClO_4S_2$: 433.0335; found: 433.0336.

(3*E*)-2-[Chloro(*p*-tolylsulfinyl)methylene]hept-3-en-1-yl pheny carbonate (4g)



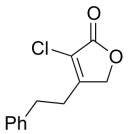
Colorless oil; IR (neat): 2960, 2930, 2872, 1764 (C=O), 1593, 1494, 1457, 1379, 1247, 1212, 1089, 1062, 1017, 970, 809, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, M: major isomer, m: minor isomer): δ = 0.94 (t, *J* = 7.4 Hz, $3H_m$), 0.98 (t, *J* = 7.2 Hz, $3H_M$), 1.44–1.61 (m, $2H_M$, $2H_m$), 2.20–2.31 (m, $2H_M$, $2H_m$), 2.42 (s, $3H_M$, $3H_m$), 5.13 (d, *J* = 12.2 Hz, $1H_M$), 5.19 (d, *J* = 12.2 Hz, $1H_M$), 5.45 (d, *J* = 12.3 Hz, $1H_m$), 5.59 (d, *J* = 12.3 Hz, $1H_m$), 6.22–6.31 (dt, *J* = 7.0, 15.7 Hz, $1H_M$), 6.40 (dt, *J* = 6.7, 16.0 Hz, $1H_m$), 6.54 (d, *J* = 16.0 Hz, $1H_m$), 6.98 (d, *J* = 15.7 Hz, $1H_M$) 7.13–7.44 (m, $7H_M$, $7H_m$), 7.51 (d, *J* = 8.3 Hz, $2H_M$), 7.61 (d, *J* = 8.3 Hz, $2H_m$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.6 (two signals overlapping), 21.4 (two signals overlapping), 21.9, 22.0, 35.5, 35.6, 62.7, 64.8, 120.79, 120.82, 122.8, 124.5, 124.9, 125.0, 126,1, 126.3, 129.4, 129.5, 129.8, 129.9, 136.8, 137.6, 138.0, 138.3, 139.6, 141.0, 141.5, 141.9, 141.99, 142.01, 150.956, 150.964, 153.08, 153.14; MS (FAB^+): *m/z* (%) = 419 ($[M+H]^+$, 100), 281 (47), 123 (21), 105 (23), 77 (16); HRMS (FAB^+): *m/z* [$(M+H)^+$] calcd for $C_{22}H_{24}ClO_4S$: 419.1084; found: 419.1083.

2-[Bromo(*p*-tolylsulfinyl)methylene]-4-phenylbutyl phenyl carbonate (4h)



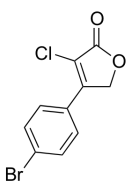
Colorless solid; mp 58.2–59.5 °C; IR (ATR): 3061, 3029, 2961, 2932, 2870, 1761 (C=O), 1591, 1494, 1456, 1424, 1393, 1368, 1283, 1246, 1208, 1177, 1165, 1084, 1070, 1054, 1017, 979, 945, 911, 879, 853, 832, 801, 768, 747, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, M: major isomer, m: minor isomer): δ = 2.40 (s, $3H_m$), 2.42 (s, $3H_M$), 2.79–3.25 (m, $4H_M$, $4H_m$), 5.01 (d, *J* = 14.2 Hz, $1H_m$), 5.08 (d, *J* = 14.2 Hz, $1H_m$), 5.20 (d, *J* = 12.4 Hz, $1H_M$), 5.27 (d, *J* = 12.4 Hz, $1H_M$), 7.17–7.44 (m, $13H_M$, $13H_m$), 7.50–7.52 (m, $1H_M$, $1H_m$); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 21.48, 21.49, 32.8, 34.2, 35.0, 37.5, 66.2, 69.6, 120.9 (two signals overlapping), 124.7, 124.9, 126.37, 126.40, 126.6, 126.8, 128.4, 128.5, 128.7, 128.9, 129.62, 129.64, 129.88, 129.89, 132.9, 138.0, 138.2, 138.3, 139.7, 139.9, 141.9, 142.0, 145.2, 145.8, 150.95, 150.96, 153.20, 153.23; MS (FAB^+): *m/z* (%) = 501 (100), 499 ($[M+H]^+$, 96), 363 (99), 361 (96), 91 (39); HRMS (FAB^+): *m/z* [$(M+H)^+$] calcd for $C_{25}H_{24}BrO_4S$: 499.0579; found: 499.0578.

3-Chloro-4-phenetylfuran-2(5*H*)-one (5a)



Colorless crystals; mp 71.0–72.0 ℃ (hexane/EtOAc); IR (KBr): 2932, 1756 (C=O), 1651, 1602, 1496, 1455, 1353, 1136, 1037, 996, 758, 708 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.81–2.95 (m, 4H), 4.55 (s, 2H), 7.16–7.19 (m, 2H), 7.22–7.35 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 28.7, 32.6, 71.3, 119.8, 126.9, 128.1, 128.9, 139.2, 159.0, 168.5; MS (EI): *m/z* (%) = 222 (M^+, 6), 187 (7), 91 (100); HRMS (EI): *m/z* [M^+] calcd for $C_{12}H_{11}ClO_2$: 222.0448; found: 222.0446.

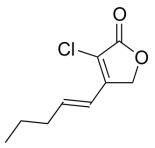
4-(4-Bromophenyl)-3-chlorofuran-2(5*H*)-one (5e)



Colorless crystals; mp 184.5–185.5 ℃ (hexane/EtOAc); IR (ATR): 2987, 2933, 2872, 1741 (C=O), 1709, 1612, 1587, 1559, 1508, 1485, 1447, 1404, 1359, 1320, 1300, 1276, 1262, 1217, 1196, 1189, 1122, 1080, 1065, 1040, 1009, 983, 945, 880, 820, 813, 754, 737, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 5.20 (s, 2H), 7.66–7.69 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 69.9, 118.1, 126.5, 127.6, 128.6, 132.6, 150.6, 168.8; MS (EI): *m/z* (%) = 274 (100), 272 (M^+, 77), 245 (66), 243 (52), 164

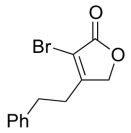
(66), 136 (36); HRMS (EI): *m*/*z* [M^+] calcd for $C_{10}H_6BrClO_2$: 271.9240; found: 271.9246.

(*E*)-3-Chloro-4-(pent-1-en-1-yl)furan-2(5*H*)-one (5g)



Colorless oil; IR (ATR): 2961, 2932, 2873, 1784, 1758 (C=O), 1650, 1603, 1509, 1448, 1381, 1356, 1324, 1172, 1129, 1032, 1009, 966, 754, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.3 Hz, 3H), 1.52 (sextet, *J* = 7.3 Hz, 2H), 2.26 (dq, *J* = 1.4, 7.3 Hz, 2H), 4.96 (s, 2H), 6.21 (dt, *J* = 7.3, 16.1 Hz, 1H), 6.47 (br d, *J* = 16.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 22.1, 36.0, 69.6, 117.0, 119.9, 143.2, 152.9, 169.5; MS (EI): *m*/*z* (%) = 186 (M^+, 46), 145 (100), 115 (59), 77 (19), 65 (17); HRMS (EI): *m*/*z* [M^+] calcd for $C_9H_{11}ClO_2$: 186.0448; found: 186.0448.

3-Bromo-4-phenethylfuran-2(5*H*)-one (5h)



Colorless crystals; mp 81.5–82.5 ℃ (hexane/EtOAc); IR (ATR): 3052, 3026, 2966, 2929, 2868, 1750 (C=O), 1644, 1602, 1581, 1495, 1453, 1435, 1341, 1305, 1255, 1173, 1154, 1135, 1077, 1034, 1010, 984, 939, 914, 853, 829, 754, 721, 707, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.80–2.95 (m, 4H), 4.52 (s, 2H), 7.16–7.35 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 30.1, 32.6, 72.8, 109.3, 127.0, 128.2, 128.9, 139.2, 163.3, 169.1; MS (EI): *m*/*z* (%) = 268 (0.2), 266 (M^+, 0.2), 187 (48), 91 (100); HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{11}BrO_2$: 265.9942; found: 265.9941.

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