Supporting Information.

A Novel Reactivity Pattern of Alkynoate Lead by Nucleophiles: A Source of Reactive Alkynilides

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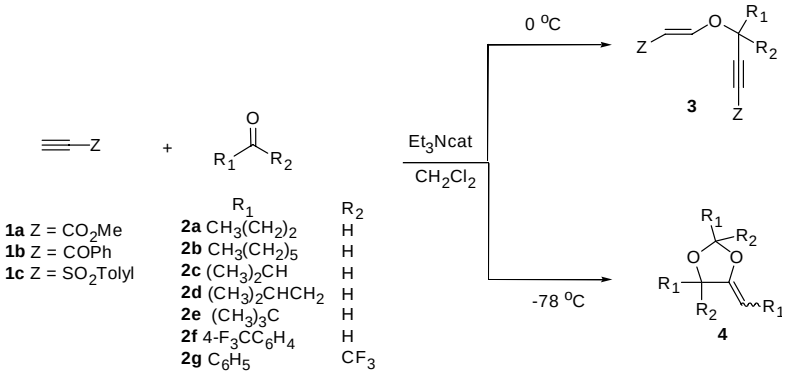

Experimental Procedure.

All reactions were carried out under nitrogen atmosphere. Dichloromethane was distilled from CaH_2. Triehylamine was fractionally distilled from KOH. All other materials were obtained from commercial suppliers and used as received.

Method A (representative example): To a solution of methyl propiolate (3.90 mmol) and butyraldehyde (2.34 mmol) in dry CH_2Cl_2 (10 ml) cooled to 0 ºC triethylamine (1.95 mmol) was added. The reaction mixture was stirred for 2 h and then quenched with 1M HCl (5 ml). After extraction with CH_2Cl_2 (3 x 10 ml) the organic layers were dried over anhydrous sodium sulfate. After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 90/10) to yield **3a** 397 mg (85%).

Method B (representative example): To a solution of methyl propiolate (2.58 mmol) and butyraldehyde (5.17 mmol in dry CH_2Cl_2 (10 ml) cooled to -78 ºC triethylamine (1.29 mmol) was added. The reaction mixture was stirred for 2 h and then quenched with 1M HCl (5 ml). After extarction with CH_2Cl_2 (3 x 10 ml) the organic layers were dried over anhydrous sodium sulfate. After removing the solvent at reduced pressure the products were purified by flash column chromatography (silica gel, n-hexane/EtOAc 90/10) to yield **4a** in 94% yield as a mixture of diasteroisomers: **4a*E*** 29% (4.6:1, *syn:anti*) as an inseparable mixture of isomers and **4a*Z*** 65% (5.3:1, *syn:anti*) which can be partially separated.

Spectroscopic data. ^{13}C NMR data given for the **Z***syn* diasteroisomer (major product), which can always be partially separated from the Z*syn/anti* mixture.

Methyl 4-{[(1*E*)-3-methoxy-3-oxo-1-propenyl]oxy}-2-heptynoate 3a: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.93 (t, 3H, *J* = 7.4 Hz), 1.44–1.52 (m, 2H), 1.81-1.88 (m, 2H), 3.67 (s, 3H), 3.75 (s, 3H), 4.61 (t, 1H, *J* = 6.6 Hz), 5.34 (d, 1H, *J* = 12.5 Hz), 7.51 (d, 1H, *J* = 12.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.30, 159.74, 152.89, 98.89, 82.85, 78.35, 70.08, 52.67, 50.95, 36.27, 17.90, 13.24. IR ($CHCl_3$, cm^{-1}) 2242.3, 1716.0, 1646.1, 1625.8. Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.11; H, 6.57. MS, *m/z* (relative intensities) 240 (M+, 5.2), 181 (22), 139 (100), 107 (24), 79(22).

Methyl 4-{[(1*E*)-3-methoxy-3-oxo-1-propenyl]oxy}-2-decynoate 3b: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.84 (t, 3H, *J* = 6.8 Hz), 1.20–1.50 (m, 8H), 1.80-1.90 (m, 2H), 3.67 (s, 3H), 3.75 (s, 3H), 4.59 (t, 1H, *J* = 6.9 Hz), 5.33 (d, 1H, *J* = 11.7 Hz), 7.51 (d, 1H, *J* = 12.5 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 167.3, 159.8, 152.9, 98.9, 82.9, 78.4, 70.4, 52.7, 51.0, 34.4, 31.3, 28.5, 24.5, 22.3, 13.8. IR ($CHCl_3$, cm^{-1}) 2242.6, 1715.7, 1645.7, 1625.7. Anal. Calcd. for $C_{17}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.92; H, 7.60. MS, *m/z* (relative intensities) 282 (M^+, 0.6), 251 (14), 223 (22), 181 (100), 149 (17), 121 (30), 93 (17), 79 (15).

Methyl 4-{[(1*E*)-3-methoxy-3-oxo-1-propenyl]oxy}-5-methyl-2-hexynoate 3c: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.01 (d, 3H, *J* = 6.8 Hz), 1.03 (d, 3H, *J* = 6.8 Hz), 2.09 (m, 1H), 3.67 (s, 3H), 3.75 (s, 3H), 4.39 (d, 1H, *J* = 5.8 Hz), 5.33 (d, 1H, *J* = 12.6 Hz), 7.51 (d, 1H, *J* = 12.6 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 167.4, 160.1, 152.9, 98.8, 81.9, 79.0, 75.6, 52.7, 51.0, 32.7, 17.7, 17.3. IR ($CHCl_3$, cm^{-1}) 2242.5, 1705.4, 1636.0, 1625.5. Anal. Calcd. for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.98; H, 6.77. MS, *m/z* (relative intensities) 240 (M^+, 2.5), 139 (100), 138 (39), 111 (30), 107 (58), 80 (36), 79(73), 59 (42).

Methyl 4-{[(1*E*)-3-methoxy-3-oxo-1-propenyl]oxy}-6-methyl-2-heptynoate 3d: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.91 (d, 3H, *J* = 6.4 Hz), 0.92 (d, 3H, *J* = 6.3 Hz), 1.67–1.71 (m, 1H), 1.80-1.85 (m, 2H), 3.68 (s, 3H), 3.75 (s, 3H), 4.64 (t, 1H, *J* = 6.9 Hz), 5.34 (d, 1H, *J* = 12.5 Hz), 7.51 (d, 1H, *J* = 12.5 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.48, 159.72, 153.04, 99.08, 83.07, 78.44, 69.04, 52.80, 51.12, 43.08, 24.36, 22.82, 21.92. IR ($CHCl_3$, cm^{-1}) 2243.1, 1715.3, 1645.6, 1625.7. Anal. Calcd. for $C_{13}H_{18}O_5$: C, 61.41; H, 7.13. Found: C, 61.69; H, 7.43. MS, *m/z* (relative intensities) 254 (M^+, 2.1), 197 (16), 153 (100), 121 (68), 111(97), 93 (77), 91 (26), 79 (74), 77 (31), 59 (28).

Methyl 4-{[(1*E*)-3-methoxy-3-oxo-1-propenyl]oxy}-5,5-dimethyl-2-hexynoate 3e: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.02 (s, 9H), 3.68 (s, 3H), 3.76 (s, 3H), 4.22 (s, 1H), 5.35 (d, 1H, *J* = 12.5 Hz), 7.53 (d, 1H, *J* = 12.5 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 167.3, 160.5, 152.8, 98.6, 81.9, 79.1, 79.0, 52.5, 50.8, 35.8, 25.1. IR ($CHCl_3$, cm^{-1}) 2241.8, 1715.8, 1645.5, 1625.8. Anal. Calcd. for $C_{13}H_{18}O_5$: C, 61.41; H, 7.13. Found: C, 61.11; H, 7.11. MS, *m/z* (relative intensities) 254 (M^+, 2.6), 166 (52), 153 (95), 152 (86), 125 (46), 121 (60), 93 (100), 77 (41), 57 (63).

Reaction of 1c and 2a at 0 ºC to form 1-Methyl-4-{[(*E*)-2-({3-[(4-methylphenyl)sulfonyl]-1-propyl-2-propynyl}oxy)ethenyl]sulfonyl}benzene: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.87 (t, 3H, *J* = 6.8 Hz), 1.30–1.46 (m, 2H), 1.72-1.85 (m, 2H), 2.40 (s, 3H), 2.44 (s, 3H), 4.62 (t, 1H, *J* = 5.9 Hz), 5.79 (d, 1H, *J* = 11.9 Hz), 7.32 (t, 4H, *J* = 7.9 Hz), 7.41 (d, 1H, *J* = 11.7 Hz), 7.75 (dd, 4H, *J* = 13.7, 7.8 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 157.84, 146.04, 143.93, 138.95, 137.84, 130.17, 129.83, 127.48, 126.95, 111.18, 88.36, 84.74, 70.97, 35.93, 21.74, 21.53, 17.87, 13.31. IR ($CHCl_3$, cm^{-1}) 2201.3, 1721.8, 1610.8. Anal. Calcd. for $C_{22}H_{24}O_5S_2$: C, 61.09; H, 5.59. Found: C, 61.41; H, 5.86. MS, *m/z* (relative intensities) 432 (M^+, 4.6), 235 (67), 199 (25), 181 (25), 155(35), 139 (87), 92 (33), 91 (100), 77 (25), 65 (27).

Methyl (2,5-dipropyl-1,3-dioxolan-4-ylidene)ethanoate 4a: : ^{1}H NMR ($CDCl_3$, 500 MHz): **E*syn*** δ 0.93 (t, 3H, *J* = 7.6 Hz), 0.95 (t, 3H, *J* = 7.5 Hz), 1.39–1.51 (m, 4H), 1.59-1.68 (m, 1H), 1.68-1.74 (m, 2H), 2.02-2.09 (m, 1H), 3.64 (s, 3H), 5.10 (dt, 1H, *J* = 8.3, 2.1 Hz), 5.29 (t, 1H, *J* = 7.8 Hz), 5.32 (d, 1H, *J* = 1.8 Hz). Charasteristic of **E*anti*** δ 5.23 (d, 1H, *J* = 1.2 Hz), 5.35 (dm, 1H, *J* = 9.6 Hz), 5.42 (t, 1H, *J* = 4.7 Hz). **Z*syn*** δ 0.93 (t, 3H, *J* = 7.6 Hz), 0.94 (t, 3H, *J* = 7.6 Hz), 1.41–1.55 (m, 4H), 1.56-1.63 (m, 1H), 1.64-1.74 (m, 1H), 1.74-1.88 (m, 2 H), 3.66 (s, 3H), 4.51 (dd, 1H, *J* = 7.7, 3.4 Hz), 4.75 (d, 1H, *J* = 1.4 Hz), 5.36 (t, 1H, *J* = 4.7 Hz). Charasteristic of **Z*anti*** δ 4.69 (dd, 1H, *J* = 8.5, 4.0 Hz), 4.77 (s, 1H), 5.60 (t, 1H, *J* = 4.9 Hz). **Z*syn*** δ 167.24, 165.97, 108.31, 85.60, 79.99, 50.82, 35.15, 34.16, 18.11, 16.51, 13.70. IR ($CHCl_3$, cm^{-1}) 1709.8, 1667.9. Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.17; H, 8.86. MS, *m/z* (relative intensities) 228 (M^+, 30), 186 (55), 185 (30), 157 (27), 127(37), 114 (100), 101 (65), 84 (25), 69 (68), 55 (24).

Methyl (2,5-dihexyl-1,3-dioxolan-4-ylidene)ethanoate 4b: ^{1}H NMR ($CDCl_3$, 200 MHz): **E*syn*** δ 0.86 (t, 6H, *J* = 6.1 Hz), 1.27–1.57 (m, 14H), 1.57-1.77 (m, 5H), 2.00-2.10 (m, 1H), 3.64 (s, 3H), 5.10 (dt, 1H, *J* = 8.3, 2.0 Hz), 5.29 (t, 1H, *J* = 5.4 Hz), 5.31 (d, 1H, *J* = 1.5 Hz). Charasteristic of **E*anti*** δ 5.24 (d, 1H, *J* = 1.0 Hz), 5.33 (dm, 1H), 5.41 (t, 1H, *J* = 4.4 Hz). **Z*syn*** δ 0.81 (t, 6H, *J* = 6.4 Hz), 1.22–1.82 (m, 20H), 3.62 (s, 3H), 4.47 (dd, 1H, *J* = 6.4, 3.1 Hz), 4.72 (s, 1H), 5.32 (t, 1H, *J* = 4.6 Hz). Charasteristic of **Z*anti*** δ 4.68 (dd, 1H, *J* = 7.3, 4.9 Hz), 4.78 (s, 1H), 5.60 (t, 1H, *J* = 4.8 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): **Z*syn*** δ 167.21, 165.89, 108.43, 85.65, 80.16, 50.71, 33.23, 32.15, 31.46, 28.85, 24.69, 23.02, 22.39, 13.85. IR ($CHCl_3$, cm^{-1}) 1709.8, 1668.5. Anal. Calcd. for $C_{18}H_{32}O_4$: C, 69.09; H, 10.32. Found: C, 69.16; H, 10.19. MS, *m/z* (relative intensities) 312 (M^+, 24), 227 (34), 181 (44), 127 (32), 114(45), 113 (34), 101 (74), 97 (38), 69 (55), 55 (100).

Methyl (2,5-diisopropyl-1,3-dioxolan-4-ylidene)ethanoate 4c: ^{1}H NMR ($CDCl_3$, 200 MHz): **E*syn*** δ 0.74-1.08 (4d, J = 6.8 Hz, 12H), 1.75–2.00 (m, 1H), 2.66 (md, 1H, *J* = 2.0 Hz), 3.62 (s, 3H), 4.87 (d, 1H, *J* = 6.3 Hz), 4.98 (s, 1H), 5.37 (d, 1H, *J* = 1.9 Hz). Charasteristic of **E*anti*** δ 2.32 (md, 1H, *J* = 2.9 Hz), 5.21 (s, 1H), 5.30 (d, 1H, *J* = 4.8 Hz), 5.32 (d, 1H, *J* = 2.9 Hz). **Z*syn*** δ 0.85 (d, 3H, *J* = 6.3 Hz), 1.00 (d, 3H, *J* = 6.9 Hz), 1.02 (d, 3H, *J* = 5.8 Hz), 1.06 (d, 3H, *J* = 7.3 Hz), 2.10–2.70 (m, 2H), 3.63 (s, 3H), 4.41 (s, 1H), 4.71 (s, 1H), 5.09 (d, 1H, *J* = 4.4 Hz). Charasteristic of **Z*anti*** δ 4.48 (s, 1H), 4.75 (s, 1H), 5.39 (d, 1H, *J* = 4.4 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): **Z*syn*** δ 166.47, 165.97, 111.44, 85.91, 84.49, 50.71, 31.51, 30.28, 19.57, 16.38, 15.98, 15.01. IR ($CHCl_3$, cm^{-1}) 1708.9, 1664.3. Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.06; H, 9.09. MS, *m/z* (relative intensities) 228 (M^+, 38), 185 (80), 139(40), 101 (100), 69 (46), 56 (59).

Methyl (2,5-diisobutyl-1,3-dioxolan-4-ylidene)ethanoate 4d: ^{1}H NMR ($CDCl_3$, 200 MHz): **E*syn*** δ 0.91-1.02 (m, 12H), 1.43–1.48 (m, 1H), 1.55-1.69 (m, 2H), 1.80–1.93 (m, 2H), 1.94-2.00 (m, 1H), 3.66 (s, 3H), 5.17 (d, 1H, *J* = 10.1 Hz), 5.31 (d, 1H, *J* = 1.4 Hz), 5.39 (t, 1H, *J* = 5.4 Hz). Charasteristic of **E*anti*** δ 5.23 (s, 1H), 5.43 (d, 1H, *J* = 3.4 Hz), 5.46 (t, 1H, *J* = 7.6 Hz). **Z*syn*** δ 0.91 (m, 12H), 1.35-1.92 (m, 6H), 3.61 (s, 3H), 4.48 (dd, 1H, *J* = 9.7, 2.0 Hz), 4.70 (s, 1H), 5.34 (t, 1H, *J* = 4.9 Hz). Charasteristic of **Z*anti*** δ 4.65-4.72 (m, 2H), 5.58 (t, 1H, *J* = 5.4 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): **Z*syn*** δ 167.71, 165.89, 107.77, 85.65, 78.69, 50.71, 42.01, 41.38, 25.00, 24.00, 23.24, 22.79, 22.60, 21.44. IR ($CHCl_3$, cm^{-1}) 1702.8, 1651.7. Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.64; H, 9.46. MS, *m/z* (relative intensities) 256 (M^+, 2.0), 200 (100), 143(22), 127 (28), 114 (61), 101 (45), 96 (27), 69 (32), 55 (18).

Methyl (2,5-di*tert*-butyl-1,3-dioxolan-4-ylidene)ethanoate 4e: ^{1}H NMR ($CDCl_3$, 500 MHz): **E*syn*** δ 0.93 (s, 9H), 0.98 (s, 9H), 3.63 (s, 3H), 4.58 (s, 1H), 4.96 (d, 1H, *J* = 1.9 Hz), 5.55 (d, 1H, *J* = 1.9 Hz). Charasteristic of **E*anti*** δ 5.14 (s, 1H), 5.21 (s, 1H), 5.38 (s, 1H). **Z*syn*** δ 0.99 (s, 9H), 1.03 (s, 9H), 3.67 (s, 3H), 4.23 (s, 1H), 4.90 (s, 1H), 5.01 (s, 1H). Charasteristic of **Z*anti*** δ 4.35 (s, 1H), 4.85 (s, 1H), 5.33 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): **Z*syn*** δ 165.87, 165.87, 111.88, 88.12, 87.57, 50.73, 34.24, 34.13, 26.02, 23.99. IR ($CHCl_3$, cm^{-1}) 1713.8, 1664.0. Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.73; H, 9.51. MS, *m/z* (relative intensities) 256 (M^+, 6.9), 225 (7.3), 200(88), 143 (51), 111 (30), 101 (61), 70 (100), 55 (58).

Methyl (2,5-dimethyl-2,5-diphenyl-1,3-dioxolan-4-ylidene)ethanoate 4g: ^{1}H NMR ($CDCl_3$, 200 MHz): ***Zsyn*** δ 3.83 (s, 3H), 5.59 (s, 1H), 7.18-7.27 (m, 6H), 7.43-7.55 (m, 4H). ***Zanti*** δ 3.80 (s, 3H), 5.59 (s, 1H), 7.47 (m, 6H), 7.72 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): **Zsyn** δ 163.79, 157.43, 131.28, 130.72, 130.51, 130.04, 128.24, 128.06, 127.00, 126.69, 124.92, 123.60, 119.28, 117.91, 95.23, 51.62. IR ($CHCl_3$, cm^{-1}) 1727.7, 1682.6. Anal. Calcd. for $C_{20}H_{14}O_4F_6$: C, 55.56; H, 3.26. Found: C, 55.73; H, 3.15. MS, *m/z* (relative intensities) 432 (M^+, 7.8), 364 (22), 363(100), 258 (16), 229 (15), 199 (12), 198 (12), 189 (15), 105 (24).

Reaction of 1b and 2a at –78 ºC to form (2*Z*)-2-(2,5-dihexyl-1,3-dioxolan-4-ylidene)-1-phenylethanone: ^{1}H NMR ($CDCl_3$, 200 MHz): ***Esyn*** δ 0.90-1.02 (m, 6H), 1.40–1.91 (m, 7H), 2.06-2.22 (m, 1H), 5.29 (d, 1H, *J* = 8.3 Hz), 5.37 (t, 1H, *J* = 4.9 Hz), 6.50 (d, 1H, *J* = 2.0 Hz), 7.35-7.47 (m, 3H), 7.87 (d, 2H, *J* = 8.3 Hz). Charasteristic of **E*anti*** δ 5.48 (t, 1H, *J* = 4.6 Hz), 5.53 (d, 1H, *J* = 8.3 Hz), 6.46 (s, 1H). ***Zsyn*** δ 0.92-1.05 (m, 6H), 1.50–2.00 (m, 8H), 4.64 (dd, 1H, *J* = 7.3,3.4 Hz), 5.43 (t, 1H, *J* = 4.4 Hz), 5.84 (s, 1H), 7.33-7.49 (m, 3H), 7.89 (d, 2H, *J* = 7.8 Hz). Charasteristic of ***Zanti*** δ 4.79 (dd, 1H, *J* = 7.8,4.4 Hz), 5.67 (t, 1H, *J* = 4.9 Hz), 5.88 (s, 1H). ^{13}C NMR ($CDCl_3$, 50.3 MHz): ***Zsyn*** δ 188.26, 167.82, 139.29, 131.80, 128.22, 127.69, 108.76, 91.25, 80.49, 35.24, 34.48, 18.32, 16.50, 13.65. IR ($CHCl_3$, cm^{-1}) 1669.5, 1608.2. Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08. Found: C, 74.36; H, 8.45. MS, *m/z* (relative intensities) 274 (M^+, 70), 173 (71), 160 (100), 105 (88), 102(45), 77 (46), 69 (33).

Reaction of 1b and 2g at –78 ºC to form (2*Z*)-2-(2,5-dimethyl-2,5-diphenyl-1,3-dioxolan-4-ylidene)-1-phenylethanone: ^{1}H NMR ($CDCl_3$, 200 MHz): ***Zsyn*** δ 6.53 (s, 1H), 7.20-7.27 (m, 6H), 7.47-7.60 (m, 7H), 7.99 (d, 2H, *J* = 6.8 Hz). Charasteristic of ***Zanti*** δ 6.52 (s, 1H, anti). ^{13}C NMR ($CDCl_3$, 50.3 MHz): ***Zsyn*** δ 187.56, 156.42, 138.04, 133.08, 131.34, 130.95, 130.50, 130.11, 128.71, 128.29, 128.34, 128.08, 127.15, 128.78, 125.17, 123.62, 119.53, 117.92, 99.76. IR ($CHCl_3$, cm^{-1}) 1686.7, 1629.7. Anal. Calcd. for $C_{25}H_{16}F_6O_3$: C, 62.77; H, 3.74. Found: C, 62.52; H, 3.37. MS, *m/z* (relative intensities) 479 (14), 478 (M^+, 54), 409 (6.2), 304 (8.9), 275 (6.8), 235 (6.7), 163 (8.0), 129 (9.5), 106 (16), 105 (100), 102 (70), 77 (48).

Reaction of 1c and 2a at –78 ºC to form (5*Z*)-2,4-dihexyl-5-{[(4-methylphenyl)sulfonyl]methylene}-1,3-dioxolane: ^{1}H NMR ($CDCl_3$, 200 MHz): ***Zsyn*** δ 0.91 (t, 6H, *J* = 6.8 Hz), 1.16–1.74 (m, 8H), 2.37 (s, 3H), 4.47 (s, 1H), 5.28 (t, 1H, *J* = 4.9 Hz), 5.39 (s, 1H), 7.24 (d, 2H, *J* = 7.8 Hz), 7.80 (d, 2H, *J* = 8.8 Hz). Charasteristic of ***Zanti*** δ 4.61 (s, 1H), 5.54 (t, 1H, *J* = 4.9 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): ***Zsyn*** δ 164.13, 143.46, 140.00, 129.19, 127.29, 109.00, 97.89, 79.99, 34.93, 33.71, 21.48, 18.10, 16.10, 13.62. IR ($CHCl_3$, cm^{-1}) 1728.3, 1651.1. Anal. Calcd. for $C_{17}H_{24}O_4S$: C, 62.94; H, 7.46. Found: C, 62.89; H, 7.53. MS, *m/z* (relative intensities) 324 (M^+, 6.5), 282 (42), 225 (28), 197 (39), 169 (41), 155 (45), 139 (72), 132 (68), 127 (61), 97 (60), 91 (100).

Reaction of 1c and 2g at –78 ºC to form (5*Z*)-2,4-dimethyl-5-{[(4-methylphenyl)sulfonyl]methylene}-2,4-diphenyl-1,3-dioxolane:^{1}H NMR ($CDCl_3$, 200 MHz): ***Zsyn*** δ 2.45 (s, 3H), 6.28 (s, 1H), 7.10-7.98 (m, 14H). Charasteristic of ***Zanti*** δ 2.42 (s, 3H), 6.24 (s, 1H), ^{13}C NMR ($CDCl_3$, 50.3 MHz): ***Zsyn*** δ 154.43, 144.86, 138.24, 130.75, 130.35, 129.69, 128.40, 128.19, 127.77, 126.87, 126.53, 124.53, 123.13, 118.88, 117.43, 107.99, 21.56. IR ($CHCl_3$, cm^{-1}) 1665.4. Anal. Calcd. for $C_{25}H_{18}F_6O_4S$: C, 56.82; H, 3.43. Found: C, 56.60; H, 3.55. MS, *m/z* (relative intensities) 528 (M^+, 9.3), 459 (44), 199 (26), 151 (18), 139 (39), 132 (80), 105 (100), 91 (28), 77 (26).

Experimetal procedure for the hydrolisis of 4b to form the acid derivative To a solution of **4b** (2.0 mmol) in THF/H_2O 2/1 (10 ml) lithium hydroxide monohydrate (8.0 mmol) was added and the resulting mixture was refluxed for 3 days. After quenching with 1M HCl and extracting the organic layer into dichloromethane, the product was purified by flash chromatography (98/2 to 95/5 CH_2Cl_2/MeOH) giving the acid in 89% yield. The acid was further purified by crystalization from n-hexane.

(2*Z*)-(2,5-dihexyl-1,3-dioxolan-4-ylidene)ethanoic acid. ^{1}H NMR ($CDCl_3$, 200 MHz): **Zsyn** δ 0.87 (t, 6H, *J* = 6.8 Hz), 1.15–1.55 (m, 16H), 1.60-1.93 (m, 4H), 4.55 (dd, 1H, *J* = 7.4, 2.9 Hz), 4.79 (s, 1H), 5.40 (t, 1H, *J* = 4.9 Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): **Zsyn** δ 169.87, 168.56, 109.07, 86.07, 80.53, 33.25, 32.12, 31.57, 28.95, 24.81, 23.06, 22.51, 14.01. IR ($CHCl_3$, cm^{-1}) 1695.5, 1649.6. Anal. Calcd. for $C_{17}H_{30}O_4$: C, 68.43; H, 10.13. Found: C, 68.29; H, 9.91. MS, *m/z* (relative intensities) 298 (M^+, 29), 213 (39), 167 (51), 97 (43), 87(27), 69 (31), 55 (100).