Supporting Information

Mercuric Chloride and Iodide Mediated Cyclization of Tethered Alkynedithioacetals As a General Route to Five- and Six-Membered Rings: Tuning of Regioselectivity by Alkyne Substitution

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Experimental

General Melting points are uncorrected. Assignment of CH₃, CH₂, CH and quaternary (q) carbon atoms in ¹³C NMR spectra was based on DEPT analysis. Organic extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure in a rotary evaporator. Unless otherwise mentioned 60–120 mesh silica gel was used for column chromatography. Solvents were distilled and dried immediately prior to use. Petroleum ether refers to a fraction having bp 60–80 °C. Room temperature refers to 25 °C.

General procedure for the preparation of **5**, **10**, **12**, **14** and **25**:

These compounds were prepared from the corresponding dialkylacetals or the aldehydes, and the general method is illustrated by the preparation of **14**.

A solution of *N*-*p*-toluenesulfonyl-*N*-propargyl-2,2-dimethoxyethylamine (0.500 g, 1.68 mmol) in conc.HCl (10 mL) was cooled to 0 °C with stirring for 15 min. EtSH (6 mL) was added dropwise and the resulting solution was stirred for 20 h at 0 °C. Then the reaction mixture was neutralized with solid NaHCO₃ and the solution was extracted with CH₂Cl₂. The combined organic layer was washed with water, dried and evaporated under reduced pressure yielding a light yellow syrup which was chromatographed over silica gel (EtOAc–petroleum ether, 1:16) to give **14** (0.48 g, 80%) as a light yellow liquid, IR (Neat): 3276, 2119, 1348, 1160 cm⁻¹; MS (positive ion ESI): *m/z* 380 (M + Na); ¹H NMR (300 MHz, CDCl₃): δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.37 (d, *J* = 2.4 Hz, 2H), 4.10 (t, *J* = 7.5 Hz, 1H), 3.45 (d, *J* = 7.5 Hz, 2H), 2.77–2.64 (m, 4H), 2.43 (s, 3H), 2.03 (t, *J* = 2.4 Hz, 1H), 1.29 (t, *J* = 7.4 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): 143.5 (q), 135.4 (q), 129.3 (2 x CH), 127.4 (2 x

CH), 76.4 (CH), 74.0 (q), 50.5 (CH₂), 50.4 (CH), 38.3 (CH₂), 24.7 (2 x CH₂), 21.3 (CH₃), 14.3 (2 x CH₃).

5

5: Prepared from the aldehyde; 74%; pale yellow liquid; IR (Neat): 3296, 2117 cm⁻¹; MS (EI): *m/z* 127 (M - SEt).

10

10: Prepared from the aldehyde; 72%; pale yellow liquid, IR (Neat): 3301, 2116 cm⁻¹; MS (EI): *m/z* 141 (M - SEt); ¹H NMR (300 MHz, CDCl₃): δ 3.10 (t, *J* = 12.0 Hz, 1H), 2.69-2.53 (m, 6H), 2.18 (t, *J* = 2.7 Hz, 1H), 2.06-1.84 (m, 2H), 1.77-1.60 (m, 2H), 1.26-1.21 (m, 6H);

12

12: Prepared from the diethylacetal; 76%; Colorless viscous liquid; IR (Neat): 3281, 1734 cm⁻¹; MS (positive ion EI): *m/z* 369 (M + Na). ¹H NMR (300 MHz, CDCl₃): δ 4.26-4.15 (m, 4H), 3.84 (t, *J* = 6.9 Hz, 1H), 2.96 (d, *J* = 2.6 Hz, 2H), 2.75-2.57 (m, 6H), 2.05 (t, *J* = 2.5 Hz, 1H), 1.31-1.22 (m, 12H).; ¹³C NMR (75 MHz, CDCl₃): δ 169.2 (2 x q), 78.4 (CH), 71.7 (q), 61.5 (2 x CH₂), 55.6 (q), 45.8 (CH), 37.7 (CH₂), 24.3 (2 x CH₂), 22.5 (CH₂), 13.9 (2 x CH₃), 13.6 (2 x CH₃).

25

25: Prepared from the dimethylacetal; 82%; Yellow sticky liquid; IR (Neat): 2224, 1347, 1159 cm⁻¹; MS (EI): *m/z* 372 (M + H), 310 (M-SEt); ¹H NMR (300 MHz,

CDCl₃): δ 7.75 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 4.27 (br s, 2H), 4.09 (t, J = 7.5 Hz, 1H), 3.42 (d, J = 7.5 Hz, 2H), 2.73-2.69 (m, 4H), 2.43 (s, 3H), 1.56 (br s, 3H), 1.29 (t, J = 7.3 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): 143.3 (q), 135.7 (q), 129.1 (2 x CH), 127.6 (2 x CH), 81.7 (q), 71.7 (q), 50.7 (CH₂), 50.5 (CH), 39.0 (CH₂), 24.8 (2 x CH₂), 21.3 (CH₃), 14.4 (2 x CH₃), 3.1 (CH₃).

General procedure for the preparation of **29, **21** and **32**:**

These compounds were prepared by the Sonogashira reaction from the corresponding alkynes and iodobenzene as illustrated by the preparation of **29**.

To a mixture of CuI (0.051 g, 0.27 mmol) and triphenylphosphine (0.071 g, 0.27 mmol) in argon atmosphere was added triethylamine (8 mL), PdCl₂ (0.024 g, 0.14 mmol), iodobenzene (0.55 g, 2.7 mmol) and **14** (1.15 g, 3.22 mmol) and the mixture was heated at 70-80 °C for 8 h. After cooling, the reaction mixture was quenched with saturated aqueous NH₄Cl solution and was then extracted with ether. The combined ether layers were dried and evaporated to dryness. The crude material was chromatographed (EtOAc–petroleum ether, 1:16) to give **29** (1.12 g, 80%) as a light yellow liquid, IR (Neat): 1349, 1160 cm⁻¹; MS (positive ion ESI): m/z 456 (M + Na); ¹H NMR (300 MHz, CDCl₃): δ 7.78 (d, J = 8.1 Hz, 2H), 7.27-7.20 (m, 5H), 7.06 (d, J = 8.1 Hz, 2H), 4.56 (s, 2H), 4.09 (t, J = 7.5 Hz, 1H), 3.56 (d, J = 7.5 Hz, 2H), 2.79–2.67 (m, 4H), 2.34 (s, 3H), 1.30 (t, J = 7.4 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): 143.5 (q), 135.6 (q), 131.3 (2 x CH), 129.4 (2 x CH), 128.3 (CH), 128.0 (2 x CH), 127.6 (2 x CH), 121.8 (q), 85.6 (q), 81.7 (q), 51.0 (CH₂), 50.7 (CH), 39.4 (CH₂), 24.9 (2 x CH₂), 21.2 (CH₃), 14.4 (2 x CH₃).

21

21: 82%; Colorless viscous liquid; IR (Neat): 2237 cm^{-1} ; MS (positive ion ESI): m/z 343 ($M + \text{Na}$); ^1H NMR (300 MHz, CDCl_3): δ 7.43 (m, 2H), 7.29 (m, 3H), 4.68 (d, $J = 15.3$ Hz, 1H), 4.55 (d, $J = 15.3$ Hz, 1H), 4.36 (s, 1H), 2.90–2.81 (m, 4H), 2.33–2.25 (m, 1H), 2.13–2.08 (m, 1H), 1.76 (m, 1H), 1.38 (s, 3H), 1.03 (d, $J = 6.9$ Hz, 3H), 1.01 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 131.6 (2 x CH), 128.1 (2 x CH), 128.0 (CH), 123.1 (q), 86.7 (q), 84.9 (q), 82.2 (q), 58.8 (CH), 53.3 (CH_2), 32.7 (CH), 31.9 (CH_2), 31.7 (CH_2), 26.3 (CH_2), 18.1 (CH_3), 17.8 (CH_3), 16.8 (CH_3).

32

32: 74%; Colorless sticky liquid; IR (Neat): 1735 cm^{-1} ; MS (positive ion ESI): m/z 445 ($M + \text{Na}$); ^1H NMR (300 MHz, CDCl_3): δ 7.37–7.26 (m, 5H), 4.28–4.16 (m, 4H), 3.90 (t, $J = 6.9$ Hz, 1H), 3.18 (s, 2H), 2.74 – 2.58 (m, 6H), 1.30–1.17 (m, 12H); ^{13}C NMR (75 MHz, CDCl_3): δ 169.7 (2 x q), 131.5 (2 x CH), 128.1 (2 x CH), 128.0 (CH), 123.0 (q), 84.1 (q), 84.0 (q), 61.7 (2 x CH_2), 56.3 (q), 46.1 (CH), 38.1 (CH_2), 24.6 (2 x CH_2), 23.6 (CH_2), 14.1 (2 x CH_3), 13.9 (2 x CH_3).

General procedure for the preparation of 36, 34, 7, 19, 23 and 17:

36

These compounds were prepared by the alkylation of the corresponding hydroxy compounds by propargyl bromide or 1-bromo-2-butyne as illustrated by the preparation of **36**.

The alcohol (0.924 gm, 4.2 mmol) was added in portions to a stirred suspension of NaH (60% suspension in mineral oil, 0.26 g, 6.5 mmol) in THF (20 mL) at 0 °C. After the addition was over, the mixture was stirred at 25 °C for 1 h. To this mixture was added dropwise with stirring a solution of propargyl bromide (80% w/v, 0.95 mL, 6.36 mmol) in THF (10 mL) at 0 °C and stirring was continued for 30 min. The mixture was heated at 25 °C for 12 h. It was then cooled to 0 °C and few drops of water were added to destroy excess NaH. After concentration of the mixture, the residue was extracted with CH₂Cl₂. The combined organic layers were washed with water, dried, concentrated and the residue was chromatographed over silica gel (EtOAc-petroleum ether, 1: 20) to give **36** (0.87 g, 80%) as a light yellow liquid.

IR (Neat): 3293, 2117 cm⁻¹; MS (FAB): *m/z* 281 (M + Na); ¹H NMR (300 MHz, CDCl₃): δ 4.57 (dd, *J* = 15.0, 2.3 Hz, 1H), 4.34 (dd, *J* = 15.0, 2.3 Hz, 1H), 3.04–2.95 (m, 2H), 2.85–2.77 (m, 2H), 2.48 (septet, *J* = 6.8 Hz, 1H), 2.39 (t, *J* = 2.3 Hz, 1H), 2.08–1.98 (m, 1H), 1.95–1.80 (m, 1H), 1.86 (s, 3H), 1.39 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 86.2 (q), 81.0 (CH), 73.0 (q), 60.2 (q), 52.9 (CH₂), 33.0 (CH), 27.1 (CH₂), 26.7 (CH₂), 25.1 (CH₂), 25.0 (CH₃), 20.1 (CH₃), 19.1 (CH₃), 14.8 (CH₃).

34

34: 89%; Yellow viscous liquid; IR (Neat): 3291, 2117 cm⁻¹; MS (positive ion ESI): *m/z* 293 (M + Na); ¹H NMR (300 MHz, CDCl₃): δ 4.52 (d, *J* = 2.3 Hz, 2H), 3.10–3.02 (m, 2H), 2.76–2.68 (m, 2H), 2.41 (t, *J* = 2.3 Hz, 1H), 2.09–2.02 (m, 2H), 1.88 (s, 3H), 1.85–1.58 (m, 9H), 1.23–1.18 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ 82.5 (CH), 81.1 (q), 72.9 (q), 60.4 (q), 53.0 (CH₂), 29.4 (2 x CH₂), 26.7 (2 x CH₂), 25.5 (CH₂), 25.2 (CH₂), 24.2 (CH₃), 22.0 (2 x CH₂).

7

7: 86%; Yellow viscous liquid; $[\alpha]_D^{25} -43.9$ (*c* 1.75, CHCl₃); IR (Neat): 3283, 2121, 1377 cm⁻¹; MS (FAB): *m/z* 437 (*M* + *H*), 421 (*M* – CH₃); ¹H NMR (300 MHz, CDCl₃): δ 7.36–7.28 (m, 5H), 5.90 (d, *J* = 3.6 Hz, 1H), 4.65 (s, 2H), 4.59 (d, *J* = 3.6 Hz, 1H), 4.54 (dd, *J* = 15.2 Hz, 2.4 Hz, 1H), 4.53–4.51 (m, 1H), 4.43 (dd, *J* = 15.2 Hz, 2.4 Hz, 1H), 4.34 (dd, *J* = 15.4 Hz, 2.1 Hz, 1H), 4.10–4.08 (m, 2H), 2.92–2.87 (m, 4H), 2.38 (t, *J* = 2.4 Hz, 1H), 2.09 (m, 1H), 1.92 (m, 1H), 1.50 (s, 3H), 1.31 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 137.4 (q), 128.3 (2 xCH), 127.7 (CH), 127.6 (2 x CH), 112.0 (q), 104.9 (CH), 81.9 (CH), 81.4 (CH), 79.4 (CH), 79.0 (CH), 78.7 (CH), 75.0 (q), 72.0 (CH₂), 59.3 (CH₂), 49.9 (CH), 31.4 (CH₂), 29.8 (CH₂), 26.9 (CH₃), 26.4 (CH₃), 26.2 (CH₂).

19

19: 83%; yellow viscous liquid; IR (Neat): 2237 cm⁻¹; MS (EI): *m/z* 258 (*M*), 215 (*M* – isopropyl); ¹H NMR (300 MHz, CDCl₃): δ 4.42 (dd, *J* = 14.1, 1.6 Hz, 1H), 4.32 (s, 1H), 4.25 (dd, *J* = 14.1, 1.6 Hz, 1H), 2.89–2.79 (m, 4H), 2.28–2.19 (m, 1H), 2.11–2.06 (m, 1H), 1.84 (s, 3H), 1.76 (m, 1H), 1.30 (s, 3H), 0.99 (d, *J* = 5.2 Hz, 3H), 0.97 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 81.3 (q), 80.6 (q), 75.7 (q), 58.3 (CH), 52.4 (CH₂), 31.8 (CH), 31.7 (CH₂), 31.4 (CH₂), 26.0 (CH₂), 17.7 (CH₃), 17.6 (CH₃), 16.4 (CH₃), 3.4 (CH₃).

23

23: 81%; light yellow viscous liquid; IR (Neat): 2239 cm^{-1} ; MS (EI): m/z 270 (M); ^1H NMR (300 MHz, CDCl_3): δ 4.30 (s, 1H), 4.15 (d, $J = 2.3$ Hz, 2H), 2.92–2.79 (m, 4H), 2.11–2.06 (m, 1H), 1.90–1.76 (m, 1H), 1.86 (t, $J = 2.3$ Hz, 3H), 1.70–1.50 (m, 9H), 1.23–1.21 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 80.9 (q), 77.9 (q), 75.5 (q), 57.2 (CH), 50.1 (CH_2), 31.9 (2 $\times$ CH_2), 31.2 (2 $\times$ CH_2), 26.0 (CH_2), 25.3 (CH_2), 21.3 (2 $\times$ CH_2), 3.6 (CH_3).

17

17: 85%; pale yellow sticky liquid; IR (KBr): 2292 cm^{-1} ; MS (positive ion ESI): m/z 331 (M + Na); ^1H NMR (300 MHz, CDCl_3): δ 7.30 (dd, $J = 6.9$ Hz, 1.7 Hz, 2H), 6.90 (d, $J = 6.9$ Hz, 2H), 4.68 (d, $J = 7.3$ Hz, 1H), 4.37 (d, $J = 7.3$ Hz, 1H), 4.16 (dq, $J = 15.3$ Hz, 2.4 Hz, 1H), 3.88–3.81 (m, 1H), 3.81 (s, 3H), 2.87–2.78 (m, 4H), 2.10–2.04 (m, 1H), 1.89–1.83 (m, 1H), 1.84 (t, $J = 2.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 159.8 (q), 129.3 (q), 128.8 (2 $\times$ CH), 113.6 (2 $\times$ CH), 82.8 (q), 81.3 (CH), 74.5 (q), 56.5 (CH_2), 55.1 (CH_3), 52.9 (CH), 30.2 (CH_2), 29.9 (CH_2), 25.8 (CH_2), 3.6 (CH_3).

General procedure for the HgCl_2 mediated cyclization of alkynedithioacetals.

The general procedure is illustrated by the cyclization of **12** to **13**.

13

A mixture of **12** (0.250 g, 0.72 mmol) in 80% aq. CH_3CN (30 mL), HgCl_2 (0.590 g, 2.17 mmol) and CaCO_3 (0.290 g, 2.90 mmol) was stirred at 25 $^\circ\text{C}$ for 4 h. After completion of the reaction as revealed by TLC, the resulting precipitate was filtered and washed with CH_3CN . The combined filtrate and washings were evaporated under

reduced pressure. The residue was extracted with CH_2Cl_2 and the combined organic extracts were washed with water and dried. Removal of solvent yielded a yellow liquid, which on chromatography over silica gel (EtOAc-petroleum ether, b.p. 60-80 °C, 1:19) afforded **13** (0.078 g, 45%) as a colorless sticky liquid.

IR (Neat): 1732, 1685 cm^{-1} ; MS (positive ion ESI): m/z 263 ($M + \text{Na}$); ^1H NMR (300 MHz, CDCl_3): δ 6.90 (dt, $J = 10.1$ Hz, 4.1 Hz, 1H), 6.04 (dt, $J = 10.1$ Hz, 1.9 Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 4H), 2.98 (dd, $J = 3.9$ Hz, 1.8 Hz, 2H), 2.92 (s, 2H), 1.25 (t, $J = 7.1$ Hz, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.6 (q), 169.6 (2 x q), 145.8 (CH), 129.6 (CH), 62.1 (2 x CH_2), 55.4 (q), 42.6 (CH_2) 31.2 (CH_2) 13.9 (2 x CH_3).

8

8: 28%; light yellow viscous liquid; $[\alpha]_D^{25} -10.5$ (c 0.21, CHCl_3); IR (Neat): 1694, 1379 cm^{-1} ; MS (positive ion ESI): m/z 369 ($M + \text{Na}$); ^1H NMR (300 MHz, CDCl_3): δ 7.33 (m, 6H), 6.19 (d, $J = 10.5$ Hz, 1H), 5.95 (d, $J = 3.3$ Hz, 1H), 4.72 (d, $J = 11.7$ Hz, 1H), 4.63 (d, $J = 3.6$ Hz, 1H), 4.59 (d, $J = 11.7$ Hz, 1H), 4.24 (d, $J = 13.2$ Hz, 1H), 4.18-4.04 (m, 4H), 1.48 (s, 3H), 1.33 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.2 (q), 150.2 (CH), 137.3 (q), 128.5 (2 x CH), 128.1 (CH), 127.8 (2 x CH), 127.0 (CH), 112.1 (q), 105.2 (CH), 82.4 (CH), 81.2 (CH), 80.5 (CH), 72.7 (CH_2), 71.2 (CH_2), 70.8 (CH), 26.8 (CH_3), 26.2 (CH_3).

9

9: 14%; pale yellow viscous liquid; $[\alpha]_D^{25} +6.4$ (c 0.30, CHCl_3); IR (Neat): 1684, 1379 cm^{-1} ; MS (positive ion ESI): m/z 369 ($M + \text{Na}$); ^1H NMR (300 MHz, CDCl_3): δ 9.84 (s, 1H), 7.36-7.31 (m, 5H), 7.06 (d, $J = 1.9$ Hz, 1H), 5.92 (d, $J = 3.6$ Hz, 1H), 4.92-4.82 (m, 1H), 4.71-4.61 (m, 4H), 4.17-4.10 (m, 3H), 1.48 (s, 3H), 1.33 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 186.9 (q), 147.1 (CH), 143.2 (q), 137.4 (q), 128.5 (2 x CH), 128.0 (CH), 127.7 (2 x CH), 112.0 (q), 105.3 (CH), 83.6 (CH), 82.5 (CH), 82.1 (CH), 81.7 (CH), 72.8 (CH_2), 72.6 (CH_2), 26.8 (CH_3), 26.2 (CH_3).

15

15: 41%; white crystalline solid; mp 102-104 °C (EtOAc: pet ether); IR (KBr): 1684 cm^{-1} ; MS (EI): m/z 251(M); ^1H NMR (300 MHz, CDCl_3): δ 7.67 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 6.93 (td, J = 10.3, 3.6 Hz, 1H), 6.06 (td, J = 10.3, 2.1 Hz, 1H), 3.97 (t, J = 2.4 Hz, 2H), 3.80 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 191.0 (q), 144.9 (CH), 144.4 (q), 132.8 (q), 130.0 (2 x CH), 127.9 (CH), 127.6 (2 x CH), 52.8 (CH_2), 44.4 (CH_2), 21.5 (CH_3).

16

16: 7 %; white solid; mp 73-75 °C (EtOAc: pet ether); IR (Neat): 1684 cm^{-1} ; MS (FAB): m/z 274 (M + Na); ^1H NMR (300 MHz, CDCl_3): δ 9.64 (s, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.68 (t, J = 1.8 Hz, 1H), 4.41-4.38 (m, 2H), 4.28-4.27 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 186.5 (CH), 144.0 (q), 142.3 (CH), 141.6 (q), 133.8 (q), 130.0 (2 x CH), 127.5 (2 x CH), 55.5 (CH_2), 51.8 (CH_2), 21.4 (CH_3).

18

18: 34%; pale yellow viscous liquid; IR (Neat): 1670 cm^{-1} ; MS (FAB): m/z 241 (M + Na), 219 (M + H); ^1H NMR (300 MHz, CDCl_3): δ 7.23 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.64 (m, 1H), 5.94 (m, 1H), 5.02 (m, 1H), 4.92 (m, 1H), 3.81 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.5 (q), 159.8 (q), 141.2 (q), 140.4 (CH), 132.1 (q), 127.8 (2 x CH), 114.2 (2 x CH), 88.4 (CH), 74.3 (CH_2), 55.3 (CH_3), 27.2 (CH_3).

20

20: 32%; colorless viscous liquid; IR (Neat): 1672 cm^{-1} ; MS (positive ion ESI): m/z 191 ($M + \text{Na}$); ^1H NMR (300 MHz, CDCl_3): δ 6.57 (br.s, 1H), 4.82 (dd, $J = 12.9, 2.0$ Hz, 1H), 4.75 (dd, $J = 12.9, 2.0$ Hz, 1H), 2.35 (s, 3H), 1.87 (m, 1H), 1.31 (s, 3H), 0.94 (d, $J = 6.8$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.4 (q), 143.5 (CH), 140.2 (q), 94.1 (q), 72.9 (CH_2), 36.9 (CH), 26.6 (CH_3), 22.7 (CH_3), 17.6 (CH_3), 17.2 (CH_3).

22

22: 37%; pale yellow viscous liquid; IR (Neat): 1645 cm^{-1} ; MS (positive ion ESI): m/z 253 ($M + \text{Na}$); ^1H NMR (300 MHz, CDCl_3): δ 7.78 (d, $J = 7.2$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 2H), 6.48 (br.s, 1H), 5.03 (dd, $J = 12.9, 2.0$ Hz, 1H), 4.95 (dd, $J = 12.9, 2.0$ Hz, 1H), 1.92 (m, 1H), 1.36 (s, 3H), 0.99 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 191.2 (q), 145.4 (CH), 138.7 (q), 138.0 (q), 132.4 (CH), 128.6 (2 x CH), 128.4 (2 x CH), 94.8 (q), 74.2 (CH_2), 37.2 (CH), 23.0 (CH_3), 18.0 (CH_3), 17.5 (CH_3).

24

24: 53%; light yellow sticky liquid; IR (Neat): 1667 cm^{-1} ; MS (EI): m/z 180 (M); ^1H NMR (300 MHz, CDCl_3): δ 6.67 (m, 1H), 4.78 (d, $J = 2.1$ Hz, 2H), 2.35 (s, 3H), 1.70-1.40 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3): δ 195.0 (q), 144.4 (CH), 140.1 (q), 90.5 (q), 72.1 (CH_2), 36.1 (2 x CH_2), 27.0 (CH_3), 25.2 (CH_2), 22.9 (2 x CH_2).

26

26: 27%; white crystalline solid; mp 157-158 °C; IR (KBr): 1679 cm⁻¹; MS (positive ion ESI): m/z 288 (M + Na), 266 (M + H); ¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.63 (m 1H), 3.92 (m, 2H), 3.79 (s, 2H), 2.43 (s, 3H), 1.72 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 191.7 (q), 144.3 (q), 139.5 (CH), 134.8 (q), 132.8 (q), 130.0 (2 x CH), 127.8 (2 x CH), 52.9 (CH₂), 44.8 (CH₂), 21.5 (CH₃), 14.8 (CH₃).

27

27: 31 %; Pale yellow solid; mp 156-158 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.73 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.50 (br.s, 1H), 4.36 (m, 2H), 4.27-4.26 (m, 2H), 2.43 (s, 3H), 2.27 (s, 3H). (lit. Rhee, J. U.; Krische, M. J.; *Org. Lett.* **2005**, 7, 2493-2495)

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28: 13 %; Yellow viscous liquid; ¹H NMR (300 MHz, CDCl₃): δ 9.67 (s, 1H), 7.70 (dt, J = 8.4, 1.8 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H), 4.08 (q, J = 2.4 Hz, 2H), 3.90 (d, J = 1.5 Hz, 2H), 2.42 (s, 3H), 1.59 (t, J = 2.1 Hz, 3H). (lit. Rhee, J. U.; Krische, M. J.; *Org. Lett.* **2005**, 7, 2493-2495)

30

30: 16 %; white solid; mp 134-136 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.76 (d, J = 7.8 Hz, 2H), 7.66 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.42 (t, J = 7.3 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 6.35 (s, 1H), 4.45-4.42 (m, 4H), 2.44 (s, 3H). (lit. Rhee, J. U.; Krische, M. J.; *Org. Lett.* **2005**, 7, 2493-2495)

31

31: 38 %; light yellow solid; mp 80-82 °C; ^1H NMR (300 MHz, CDCl_3): δ 9.72 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.35-7.25 (m, 6H), 7.13 (d, J = 6.6 Hz, 2H), 4.39 (s, 2H), 3.99 (s, 2H), 2.38 (s, 3H). (lit. Rhee, J. U.; Krische, M. J.; *Org. Lett.* **2005**, 7, 2493-2495)

33

33: 52 %; Yellow viscous liquid; ^1H NMR (300 MHz, CDCl_3): δ 7.73-7.71 (d, J = 6.6 Hz, 2H), 7.53-7.51 (m, 1H), 7.43 (t, J = 6.6 Hz, 2H), 6.38 (br.s, 1H), 4.24 (q, J = 6.9 Hz, 4H), 3.44 (br.s, 2H), 3.30 (br.s, 2H), 1.28 (t, J = 6.9 Hz, 6H). (lit. Rhee, J. U.; Krische, M. J.; *Org. Lett.* **2005**, 7, 2493-2495)

35

35: 46 %; pale yellow viscous liquid; IR (Neat): 1675 cm^{-1} ; MS (EI): m/z 180 (M), 165 (M- CH_3). ^1H NMR (300 MHz, CDCl_3): δ 5.86 (d, J = 0.9 Hz, 1H), 4.16 (s, 2H), 1.94 (d, J = 0.9 Hz, 3H), 1.87-1.53 (m, 9H), 1.25-1.18 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 195.6 (q), 168.1 (q), 123.4 (CH), 75.6 (q), 66.0 (CH_2), 31.2 (2 x CH_2), 24.9 (CH_2), 20.9 (2 x CH_2), 20.3 (CH_3).

37

37: 51%; colorless sticky liquid; IR (Neat): 1672 cm^{-1} ; MS (positive ion ESI): m/z 191 (M + Na); ^1H NMR (300 MHz, CDCl_3): δ 5.92 (d, J = 0.9 Hz, 1H), 4.21 (d, J = 16.8 Hz, 1H), 4.13 (d, J = 16.8 Hz, 1H), 2.02-1.93 (m, 1H), 1.93 (s, 3H), 1.38 (s, 3H), 1.01 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 195.0 (q),

167.3 (q), 124.7 (CH), 78.6 (q), 66.9 (CH₂), 34.3 (CH), 20.5 (CH₃), 19.6 (CH₃), 17.3 (CH₃), 15.7 (CH₃).

38

38: This compound was obtained from the cyclization reaction described above by using 1.0 equiv. of HgCl₂ and 1.1 equiv. CaCO₃; yellow viscous liquid; 64%;

IR (Neat): 1450, 1346 cm⁻¹; MS (positive ion ESI): *m/z* 396 (M + K), 380 (M + Na);

¹H NMR (300 MHz, CDCl₃): δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.65–5.63 (m, 1H), 3.74–3.62 (m, 2H), 3.54–3.43 (m, 2H), 2.96 (dd, *J* = 11.8 Hz, 7.2 Hz, 1H), 2.75–2.66 (m, 2H), 2.65–2.55 (m, 2H), 2.44 (s, 3H), 1.25 (t, *J* = 7.4 Hz, 3H), 1.24 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 143.7 (q), 133.0 (q), 131.1 (q), 129.6 (2 x CH), 127.3 (2 x CH), 123.0 (CH), 48.4 (CH₂), 47.2 (CH₂), 40.2 (CH), 25.3 (CH₂), 24.3 (CH₂), 21.3 (CH₃), 14.8 (CH₃), 13.8 (CH₃).

Cyclization of dithioacetals by HgI₂. The general procedure is illustrated by the cyclization of **42** and **43**.

44

A mixture of **42** (0.030 g, 0.123 mmol) in 80% aq. CH₃CN (8 mL), HgI₂ (0.222 g, 0.490 mmol) and CaCO₃ (0.037 g, 0.370 mmol) was stirred at 25 °C for 4 h. After completion of reaction as revealed by TLC, the resulting precipitate was filtered and washed with CH₃CN. The combined filtrate and washings were evaporated under reduced pressure. The residue was extracted with CH₂Cl₂ and the combined organic extracts were washed with water and dried. Removal of solvent yielded a yellow liquid, which on chromatography over silica gel (EtOAc-petroleum ether, 1:19) afforded **44** (0.016 g, 58%) as a colorless sticky liquid. The spectral data of this

compound were identical with those reported (Ghorai, S.; Bhattacharjya, A. *Org. Lett.* **2005**, 7, 207-210).

45 and 46: The cyclization of **43** afforded an inseparable 2:1 mixture (62%) of **45** and **46**. The spectral data refer to this mixture. ^1H NMR (300 MHz, CDCl_3): δ 7.45-7.26 (m, 10H), 6.24 (d, $J = 10.2$ Hz, 1H, **45**), 6.11 (br.s, 1H, **46**), 5.89 (d, $J = 10.1$ Hz, 1H, **45**), 4.82 (dd, $J = 23.8, 12.3$ Hz, 2H, **46**), 4.72 (s, 1H), 4.21 (d, $J = 11.9$ Hz, 1H, **45**), 3.78 (d, $J = 11.8$ Hz, 1H, **45**), 3.04-2.70 (m, 8H), 2.12-2.07 (m, 2H), 1.94-1.83 (m, 2H), 1.66 (s, 3H, **46**), 1.62 (s, 3H, **45**).