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Supporting Information

Supporting Information for the Paper

Pd(II)-Catalyzed Domino Heterocyclization/Cross-Coupling of α-Allenols and α-Allenic Esters. Efficient Preparation of Functionalized Buta-1,3-Dienyl Dihydrofurans

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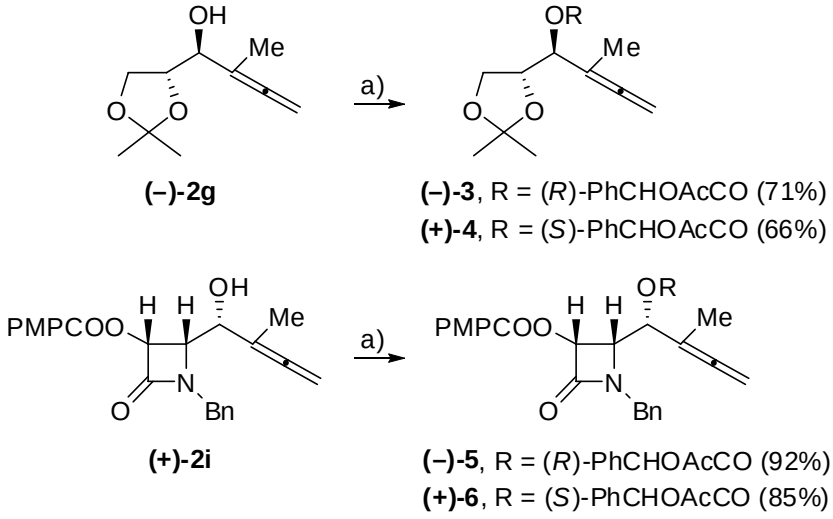


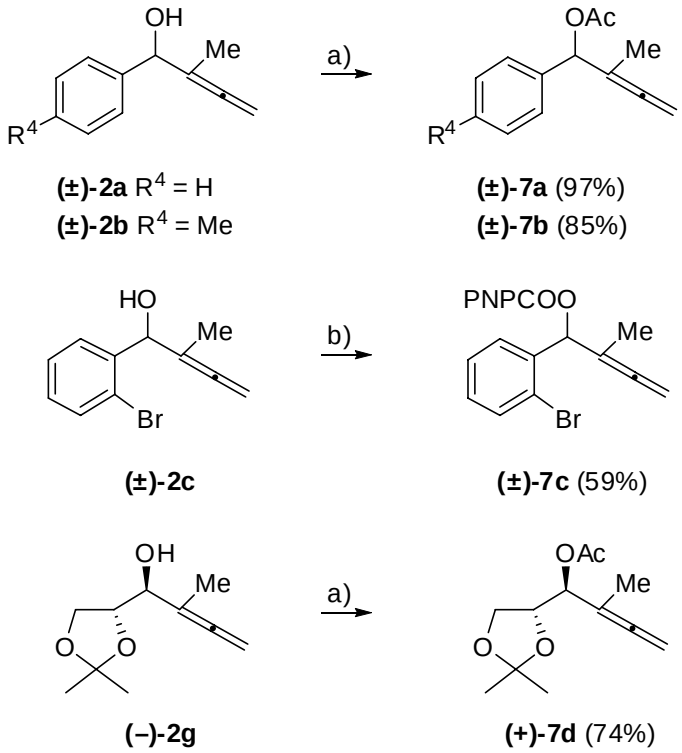
(–)-2g

(–)-3, R = (*R*)-PhCHOAcCO (71%)
(+)-4, R = (*S*)-PhCHOAcCO (66%)

(+)-2i

(–)-5, R = (*R*)-PhCHOAcCO (92%)
(+)-6, R = (*S*)-PhCHOAcCO (85%)

Scheme S1. Preparation of enantiopure acetylmandelates **3–6**. Reagents and conditions: a) (*R*)- or (*S*)-acetylmandelic acid, DCC, DMAP (cat.), CH_2Cl_2, RT, 16 h. DCC = Dicyclohexylcarbodiimide. DMAP = Dimethylaminopyridine.



Scheme S2. Preparation of esters **7a–d**. Reagents and conditions: a) Ac_2O, Et_3N, DMAP, CH_2Cl_2, RT. b) PNPCOCl, Et_3N, DMAP, CH_2Cl_2, RT. PNP = 4-$NO_2C_6H_4$.

Indium-promoted reaction between 3-substituted prop-2-ynyl bromides and aldehydes 1; general procedure for the synthesis of α-allenic alcohols 2a–j and 10e–g. 1-Bromo-2-butyne or 1-bromo-3-phenyl-2-propyne (3.0 mmol) was added to a well stirred suspension of the corresponding aldehyde **1** or ketone **9** (1.0 mmol) and indium powder (6.0 mmol) in THF/NH_4Cl (aq. sat.) (1:5, 5 mL) at 0 ^oC. After disappearance of the starting material (TLC) the mixture was extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for some representative pure forms of **2** and **10** follow.

α-Allenic alcohol (±)-2a. 200 mg (1.88 mmol) of aldehyde **1a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent affords compound (±)-**2a** (299 mg, 99%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.31 (m, 5H), 5.12 (t, *J* = 2.3 Hz, 1H), 4.88 (m, 2H), 3.18 (br s, 1H), 1.59 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 204.7, 141.7, 128.3, 127.8, 126.5, 102.5, 77.8, 74.6, 14.5; IR ($CHCl_3$): ν = 3419, 2980, 1935 cm^{-1}; MS (EI): *m/z* (%): 161 (7) $[M + H]^{+}$, 160 (100) $[M]^{+}$; elemental analysis calcd (%) for $C_{11}H_{12}O$ (160.2): C 82.46, H 7.55; found C 82.31, H 7.50.

α-Allenic alcohol (±)-2b. From 300 mg (2.50 mmol) of aldehyde **1b**, and after chromatography of the residue using hexanes/ethyl acetate (18:1) as eluent gave compound (±)-**2b** (287 mg, 66%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.29 and 7.18 (d, *J* = 8.0 Hz, each 2H), 5.08 (br s, 1H), 4.92 (m, 2H), 2.38 (s, 3H), 2.05 (br s, 1H), 1.60 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.1, 138.8, 130.2, 129.0, 126.5, 102.7, 77.8, 74.4, 21.1, 14.6; IR ($CHCl_3$): ν = 3415, 2982, 1937 cm^{-1}; MS (EI): *m/z* (%): 175 (5) $[M + H]^{+}$, 174 (100) $[M]^{+}$; elemental analysis calcd (%) for $C_{12}H_{14}O$ (174.2): C 82.72, H 8.10; found C 82.86, H 8.06.

α-Allenic alcohol (±)-2c. 100 mg (0.54 mmol) of aldehyde **1c**, and after chromatography of the residue using hexanes/ethyl acetate (10:1) as eluent affords compound (±)-**2c** (125 mg, 97%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.53 (m, 2H), 7.34 (dt, *J* = 7.3, 1.7 Hz,

1H), 7.15 (dt, *J* = 7.3, 2.0 Hz, 1H), 5.50 (m, 1H), 4.85 (m, 2H), 2.33 (br s, 1H), 1.65 (dt, *J* = 3.2, 0.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.7, 140.9, 132.9, 129.2, 128.5, 127.6, 123.2, 101.7, 78.0, 73.6, 15.1; IR ($CHCl_3$): ν = 3420, 2982, 1934 cm^{-1}; MS (EI): *m/z* (%): 240 (98) [*M* + 2]$^{+}$, 238 (100) [*M*]$^{+}$; elemental analysis calcd (%) for $C_{11}H_{11}BrO$ (239.1): C 55.25, H 4.64; found C 55.39, H 4.60.

α-Allenic alcohol (±)-2d. From 250 mg (0.97 mmol) of aldehyde **1d**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (±)-**2d** (233 mg, 77%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.16 and 7.00 (d, *J* = 9.0 Hz, each 2H), 7.58 (dt, *J* = 7.2, 2.3 Hz, 1H), 7.33 (m, 2H), 7.16 (dd, *J* = 7.6, 1.7 Hz, 1H), 5.33 (t, *J* = 2.6 Hz, 1H), 4.58 (m, 2H), 3.90 (s, 3H), 2.60 (br s, 1H), 1.56 (dt, *J* = 2.7, 0.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.1, 164.8, 163.9, 148.5, 133.6, 132.3, 128.7, 128.1, 126.0, 122.8, 121.5, 113.9, 113.8, 101.4, 77.6, 69.9, 55.5, 14.6; IR ($CHCl_3$): ν = 3424, 2980, 1938, 1735 cm^{-1}; MS (EI): *m/z* (%):311 (4) [*M* + H]$^{+}$, 310 (100) [*M*]$^{+}$; elemental analysis calcd (%) for $C_{19}H_{18}O_4$ (310.3): C 73.53, H 5.85; found C 73.66, H 5.80.

α-Allenic alcohol (±)-2e. 50 mg (0.41 mmol) of aldehyde **1e**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent affords compound (±)-**2e** (69 mg, 96%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.89 (s, 1H), 7.20 (ddd, *J* = 8.3, 7.1, 1.8 Hz, 1H), 7.02 (m, 1H), 6.89 (d, *J* = 0.5 Hz, 1H), 6.83 (dd, *J* = 7.1, 1.2 Hz, 1H), 5.29 (dd, *J* = 5.1, 2.7 Hz, 1H), 4.90 (dt,

J = 3.2, 5.9 Hz, 2H), 3.22 (d, *J* = 2.9 Hz, 1H), 1.66 (dt, *J* = 3.2, 0.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 204.6, 155.7, 129.2, 128.1, 124.2, 119.7, 117.1, 101.3, 77.8, 75.8, 14.6; IR ($CHCl_3$): ν = 3432, 2990, 1942 cm^{-1}; MS (EI): *m/z* (%):177 (8) $[M + H]^+$, 176 (100) $[M]^+$; elemental analysis calcd (%) for $C_{11}H_{12}O_2$ (176.2): C 74.98, H 6.86; found C 75.12, H 6.81.

α-Allenic alcohol (±)-2f. From 220 mg (0.96 mmol) of aldehyde **1f**, and after chromatography of the residue using dichloromethane/ethyl acetate (40:1) as eluent gave compound (±)-**2f** (143 mg, 58%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.76 and 6.99 (d, *J* = 9.0 Hz, each 2H), 6.88 (q, *J* = 1.6 Hz, 1H), 6.40 (qd, *J* = 1.7, 0.5 Hz, 1H), 6.17 (t, *J* = 3.3 Hz, 1H), 5.26 (m, 1H), 4.63 (m, 2H), 3.90 (s, 3H), 2.81 (br s, 1H), 1.79 (td, *J* = 3.2, 0.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 209.5, 167.2, 163.5, 133.6, 132.6, 127.0, 125.2, 118.9, 113.8, 110.5, 107.8, 76.9, 68.5, 55.6, 16.4; IR ($CHCl_3$): ν = 3428, 2988, 1938, 1732 cm^{-1}; MS (ES): *m/z* (%):284 (100) $[M + H]^+$, 283 (8) $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{17}NO_3$ (283.3): C 72.07, H 6.05, N 4.94; found C 71.92, H 6.09, N 4.98.

α-Allenic alcohol (–)-2g. 248 mg (1.91 mmol) of aldehyde (–)-**1g**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent affords compound (–)-**2g** (165 mg, 67%) as a colorless oil; $[\alpha]_D$ = –2.1 (*c* = 2.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 4.76 (m, 2H), 4.14 (m, 2H), 3.96 (m, 2H), 2.46 (br s, 1H), 1.74 (t, *J* = 3.2 Hz, 3H), 1.41 and 1.32 (s, each 3H); ^{13}C

NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 205.7, 109.2, 99.1, 77.5, 76.9, 72.0, 65.2, 26.5, 25.1, 15.4; IR ($CHCl_3$): ν = 3431, 2991, 1942 cm^{-1}; MS (ES): *m/z* (%):185 (100) $[M + H]^+$, 184 (5) $[M]^+$; elemental analysis calcd (%) for $C_{10}H_{16}O_3$ (184.2): C 65.19, H 8.75; found C 65.32, H 8.70.

Preparation of α-allenic alcohols (+)-2h and *anti*-(+)-2h. From 55 mg (0.234 mmol) of aldehyde (+)-**1h**, and after chromatography of the residue using dichloromethane/ethyl acetate (9:1) as eluent, 47 mg (70%) of the less polar compound (+)-**2h** and 5 mg (7%) of the more polar compound *anti*-(+)-**2h** were obtained.

α-Allenic alcohol (+)-2h. Colorless solid; m. p. 117–119 ^oC; $[\alpha]_D$ = +213.8 (*c* = 0.7 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.33 and 6.87 (d, *J* = 9.0 Hz, each 2H), 4.48 (d, *J* = 4.9 Hz, 1H), 4.65 (m, 3H), 4.40 (dd, *J*= 4.9, 3.4 Hz, 1H), 3.79 and 3.67 (s, each 3H), 3.07 (d, *J* = 4.0 Hz, 1H), 1.83 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 205.5, 164.2, 156.7, 129.9, 119.6, 114.4, 99.1, 84.1, 81.2, 76.3, 69.3, 59.9, 59.1, 55.5, 15.7; IR ($CHCl_3$): ν = 3422, 2990, 1940, 1748 cm^{-1}; MS (ES): *m/z* (%): 290 (100) $[M + H]^+$, 289 (16) $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{19}NO_4$ (289.3): C 66.42, H 6.62, N 4.84; found C 66.50, H 6.60, N 4.83.

α-Allenic alcohol *anti*-(+)-2h. Colorless oil; $[\alpha]_D^{25}$ = +753.5 (*c* = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.31 and 6.88 (d, *J* = 9.0 Hz, each 2H), 4.68 (m, 2H), 4.59 (d, *J* = 5.0 Hz, 1H), 4.48 (t, *J* = 5.0 Hz, 1H), 4.39

(s, 1H), 3.79 and 3.64 (s, each 3H), 2.42 (d, *J* = 4.6 Hz, 1H), 1.78 (t, *J* = 3.0 Hz, 3H); IR ($CHCl_3$): ν = 3420, 2993, 1940, 1747 cm^{-1}; MS (ES): *m/z* (%): 290 (100) $[M + H]^+$, 289 (21) $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{19}NO_4$ (289.3): C 66.42, H 6.62, N 4.84; found C 66.35, H 6.64, N 4.83.

α-Allenic alcohol (+)-2i. 175 mg (0.52 mmol) of aldehyde (–)-**1i**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent affords compound (+)-**2i** (140 mg, 68%) as a colorless oil; $[\alpha]_D$ = +22.5 (*c* = 1.7 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.99 and 6.92 (d, *J* = 9.0 Hz, each 2H), 7.34 (m, 5H), 6.11 (d, *J* = 4.9 Hz, 1H), 4.82 and 4.42 (d, *J* = 14.9 Hz, each 1H), 4.66 and 4.61 (dd, *J*= 3.2, 1.8 Hz, each 1H), 4.32 (m, 1H), 4.25 (dt, *J*= 7.8, 1.8 Hz, 1H), 3.92 (dd, *J*= 7.6, 4.9 Hz, 1H), 3.87 (s, 3H), 1.56 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 205.6, 165.6, 164.4, 163.9, 135.7, 132.3, 128.4, 128.0, 127.8, 121.0, 113.7, 98.5, 77.3, 73.8, 72.8, 59.3, 55.4, 45.8, 14.9; IR ($CHCl_3$): ν = 3420, 2992, 1941, 1745, 1732 cm^{-1}; MS (ES): *m/z* (%): 394 (100) $[M + H]^+$, 393 (9) $[M]^+$; elemental analysis calcd (%) for $C_{23}H_{23}NO_5$ (393.4): C 70.21, H 5.89, N 3.56; found C 70.34, H 5.93, N 3.52.

α-Allenic alcohol (+)-2j. From 175 mg (0.30 mmol) of aldehyde (–)-**1i**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (+)-**2j** (102 mg, 74%) as a colorless oil; $[\alpha]_D$ = +20.1 (*c* = 2.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.74 and

6.69 (d, *J* = 9.0 Hz, each 2H), 7.25 (m, 10H), 6.16 (d, *J* = 4.9 Hz, 1H), 5.17 and 5.06 (dd, *J*= 12.5, 1.8 Hz, each 1H), 4.91 (br s, 1H), 4.90 and 4.49 (d, *J* = 14.9 Hz, each 1H), 4.08 (dd, *J*= 8.3, 4.9 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.3, 165.7, 164.0, 163.6, 135.7, 133.4, 131.9, 128.9, 128.5, 128.4, 127.9, 127.2, 126.3, 120.7, 113.4, 105.9, 81.5, 73.8, 71.1, 60.0, 55.4, 45. 9; IR ($CHCl_3$): ν = 3424, 2987, 1943, 1747, 1730 cm^{-1}; MS (ES): *m/z* (%): 456 (100) $[M + H]^+$, 455 (11) $[M]^+$; elemental analysis calcd (%) for $C_{28}H_{25}NO_5$ (455.5): C 73.83, H 5.53, N 3.08; found C 73.69, H 5.49, N 3.11.

α-Allenic alcohol (–)-10e. From 210 mg (0.766 mmol) of azetidine-2,3-dione (–)-**9c**, 236 mg (94%) of compound (–)-**10e** was obtained as a colorless oil; $[\alpha]_D$ = –16.9 (*c* = 0.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.30 (m, 5H), 4.87 (d, *J* = 14.6 Hz, 1H), 4.79 (m, 2H), 4.64 (br s, 1H), 4.41 (m, 1H), 4.18 (d, *J* = 14.4 Hz, 1H), 4.16 (m, 1H), 3.71 (dd, *J* = 9.0, 5.4 Hz, 1H), 3.52 (d, *J* = 8.0 Hz, 1H), 1.73 (t, *J* = 3.2 Hz, 3H), 1.36 and 1.35 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.1, 169.5, 135.4, 128.8, 128.5, 127.8, 109.8, 98.0, 84.3, 76.4, 64.7, 64.6, 45.6, 26.6, 25.1, 14.0; IR ($CHCl_3$): ν = 3342, 2990, 1941, 1744 cm^{-1}; MS (ES): *m/z* (%): 330 (100) $[M + H]^+$, 329 (9) $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{23}NO_4$ (329.4): C 69.28, H 7.04, N 4.25; found C 69.40, H 7.00, N 4.23.

α-Allenic alcohol (–)-10f. From 200 mg (0.727 mmol) of azetidine-2,3-dione (–)-**9c**, 280 mg (98%) of compound (–)-**10f** was obtained as a colorless oil; $[\alpha]_D$ = –28.5 (*c* = 0.8

in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.58 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.31 (m, 6H), 7.14 (m, 2H), 5.18 (d, *J* = 12.4 Hz, 1H), 5.09 (d, *J* = 12.4 Hz, 1H), 4.92 (d, *J* = 14.9 Hz, 1H), 4.48 (dd, 1H, *J* = 6.6, 5.4 Hz), 4.16 (d, 1H, *J* = 14.9 Hz), 4.14 (dd, *J* = 8.9, 6.9 Hz, 1H), 3.89 (br s, 1H), 3.68 (d, *J* = 6.3 Hz, 1H), 3.64 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.38 and 1.35 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 207.2, 168.6, 135.2, 132.6, 128.7, 128.6, 128.5, 128.4, 127.7, 127.6, 110.0, 85.0, 80.5, 75.7, 66.6, 64.2, 44.9, 26.4, 25.0; IR ($CHCl_3$): ν = 3344, 2992, 1940, 1743 cm^{-1}; MS (ES): *m/z* (%): 392 (100) $[M + H]^+$, 391 (16) $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{25}NO_4$ (391.5): C 73.64, H 6.44, N 3.58; found C 73.51, H 6.48, N 3.60.

α-Allenic alcohol (+)-10g. From 50.5 mg (0.173 mmol) of azetidine-2,3-dione (+)-**10g**, 44 mg (74%) of compound (+)-**9d** was obtained as a colorless oil; $[\alpha]_D$ = +75.4 (*c* = 0.7 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.63 and 6.86 (dd, *J* = 7.0, 2.5 Hz, each 2H), 4.98 (dd, *J* = 6.4, 3.0 Hz, 2H), 4.49 (q, *J* = 7.0 Hz, 1H), 4.32 (dd, *J* = 8.8, 6.8 Hz, 1H), 4.24 (d, *J* = 7.7 Hz, 1H), 4.14 (brs, 1H), 3.80 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.79 (s, 3H), 1.85 (t, *J* = 3.0 Hz, 3H), 1.51 and 1.36 (s, each 3H),; ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 205.2, 166.6, 156.7, 130.7, 120.0, 114.0, 109.7, 98.6, 83.5, 79.4, 76.8, 66.8, 66.5, 55.4, 26.6, 25.0, 13.9; IR ($CHCl_3$): ν = 3340, 2991, 1940, 1742 cm^{-1}; MS (ES): *m/z* (%): 346 (100) $[M + H]^+$, 345 (20) $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{23}NO_5$ (345.4): C 66.07, H 6.71, N 4.06; found C 66.13, H 6.65, N 4.00.

Indium-promoted reaction between 3-substituted prop-2-ynyl bromides and isatins 9; general procedure for the synthesis of α-allenic alcohols 10a–d. The appropriate propargyl bromide (1.5 mmol) was added to a well stirred suspension of the corresponding 2,3-indolinedione **9** (0.5 mmol) and indium powder (344 mg, 3.0 mmol) in THF/H_2O (1:1, 5 mL) at 5 °C. After disappearance (typically 2 h) of the starting material (TLC), saturated aqueous sodium hydrogen carbonate (2.5 mL) was added at 0 °C, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 3 mL). The organic extract was washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate or ethyl acetate/dichloromethane mixtures gave analytically pure compounds **10**. Spectroscopic and analytical data for some representative forms of **10** follow.

α-Allenic alcohol (±)-10a. From 81 mg (0.50 mmol) of 2,3-indolinedione **9a**, 97 mg (90%) of compound (±)-**10a** was obtained as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.37 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.35 and 7.10 (td, *J* = 7.5, 1.0 Hz, each 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 5.04 (q, *J* = 3.1 Hz, 2H), 3.21 (s, 3H), 1.55 (t, *J* = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 204.8, 176.7, 143.8, 129.9, 129.1, 124.5, 123.2, 108.4, 100.7, 80.3, 26.3, 13.7; IR ($CHCl_3$): ν = 3298, 1954, 1715 cm^{-1}; MS (EI): *m/z* (%): 216 (9) $[M + H]^+$, 215 (100) $[M]^+$; elemental analysis calcd (%)

for $C_{13}H_{13}NO_2$ (215.3): C 72.54, H 6.09, N 6.51; found C 72.66, H 6.05, N 6.45.

α-Allenic alcohol (±)-10b. From 73 mg (0.5 mmol) of 2,3-indolinedione **9b**, 90 mg (90%) of compound (±)-**10b** was obtained as a colorless solid; m. p. 179–180 °C (hexanes/ethyl acetate); ^{1}H NMR (300 MHz, d_6-acetone, 25 °C): δ = 9.24 (br s, 1H), 7.18 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.10 (td, *J* = 7.7, 1.3 Hz, 1H), 6.87 and 6.77 (td, *J* = 7.5, 1.0 Hz, each 1H), 4.98 (s, 1H), 4.69 (qd, *J* = 3.1, 1.3 Hz, 2H), 1.59 (t, *J* = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, d_6-acetone, 25 °C): δ = 207.1, 178.7, 143.1, 132.6, 130.5, 126.0, 123.1, 110.9, 102.0, 78.5, 77.6, 14.3; IR ($CHCl_3$): ν = 3423, 3296, 1955, 1714 cm^{-1}; MS (EI): *m/z* (%): 202 (7) [*M* + H]$^+$, 201 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{12}H_{11}NO_2$ (201.2): C 71.63, H 5.51, N 6.96; found C 71.52, H 5.54, N 7.00.

α-Allenic alcohol (±)-10c. From 112 mg (0.70 mmol) of 2,3-indolinedione **9a**, 158 mg (82%) of compound (±)-**10c** was obtained as a colorless solid; m. p. 106–108 °C (hexanes/ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30 (m, 2H), 7.15 (m, 5H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H), 5.28 (s, 2H), 3.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.9, 176.3, 143.7, 133.1, 130.1, 129.2, 128.4 (2C), 128.2 (2C), 127.6, 124.9, 123.2, 108.5, 108.0, 77.1, 81.3, 26.3; IR ($CHCl_3$): ν = 3295, 1953, 1712 cm^{-1}; MS (EI): *m/z* (%): 278 (15) [*M* + H]$^+$, 277 (100) [*M*]$^+$; elemental analysis calcd (%) for $C_{18}H_{15}NO_2$ (277.3): C 77.96, H 5.45, N 5.05; found C 78.07, H 5.41, N 5.10.

α-Allenic alcohol (±)-10d. From 100 mg (0.68 mmol) of 2,3-indolinedione **9b**, 109 mg (61%) of compound (±)-**10d** was obtained as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.87 (br s, 1H), 7.25 (m, 6H), 7.04 (td, *J* = 7.6, 1.0 Hz, 1H), 6.91 (m, 1H), 6.84 (dt, *J* = 7.8, 1.0 Hz, 1H), 5.32 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 209.2, 175.1, 154.2, 142.9, 135.1, 132.3, 130.4, 129.3, 128.7, 127.9, 125.8, 122.8, 110.7, 110.6, 80.2; IR ($CHCl_3$): ν = 3425, 3295, 1951, 1714 cm^{-1}; MS (EI): *m/z* (%): 264 (9) $[M + H]^+$, 263 (100) $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{13}NO_2$ (263.3): C 77.55, H 4.98, N 5.32; found C 77.68, H 5.03, N 5.28.

General procedure for the preparation of the *O*-acetylmandelates 3-6. The appropriate (*R*)- or (*S*)-*O*-acetylmandelic acid (0.10 mmol), 4-dimethylaminopyridine (DMAP) (cat.), and a solution of dicyclohexylcarbodiimide (DCC) (0.18 mmol) in dichloromethane (5 mL) were sequentially added at 0 °C to a solution of the corresponding α-allenic alcohol **2** (0.09 mmol) in dichloromethane (1.0 mL). The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under reduced pressure and diethyl ether was added. The mixture was then filtered and the filtrate was concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate mixtures gave analytically pure *O*-acetylmandelates.

(*R*)-*O*-Acetylmandelate (-)-3. 85 mg (0.46 mmol) of α-allenic alcohol (–)-**2g**, and after chromatography of the

residue using hexanes/ethyl acetate (7:1) as eluent affords the (*R*)-*O*-acetylmandelate (139 mg, 71%) as a colorless oil; $[\alpha]_D$ = –17.8 (*c* = 2.5 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.48 (m, 2H), 7.39 (m, 3H), 5.93 (s, 1H), 5.27 (dt, *J* = 6.1, 1.7 Hz, 1H), 4.64 and 4.44 (ddd, *J* = 10.7, 3.2, 1.7 Hz, each 1H), 4.27 (q, *J* = 6.1 Hz, 1H), 4.04 and 3.88 (dd, *J* = 8.7, 5.5 Hz, each 1H), 2.20 (s, 3H), 1.45 (t, *J* = 3.7 Hz, 3H), 1.44 and 1.35 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 206.8, 170.1, 167.9, 133.6, 129.2, 128.7, 127.7, 109.7, 95.9, 76.7, 75.4, 75.0, 74.3, 65.7, 26.4, 25.2, 20.6, 15.1; IR ($CHCl_3$): ν = 2990, 1942, 1750, 1742 cm^{-1}; MS (ES): *m/z* (%):361 (100) $[M + H]^+$, 360 (9) $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{24}O_6$ (360.4): C 66.65, H 6.71; found C 66.78, H 6.67.

(*S*)-*O*-Acetylmandelate (+)-4. From 85 mg (0.46 mmol) of α-allenic alcohol (–)-**2g**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent gave the (*S*)-*O*-acetylmandelate (129 mg, 66%) as a colorless oil; $[\alpha]_D$ = +90.8 (*c* = 2.5 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.47 (m, 2H), 7.38 (m, 3H), 5.91 (s, 1H), 5.23 (dt, *J* = 6.1, 1.8 Hz, 1H), 4.81 (dq, *J* = 3.2, 1.0 Hz, 2H), 4.18 (q, *J* = 6.1 Hz, 1H), 3.74 and 3.49 (dd, *J* = 8.5, 6.5 Hz, each 1H), 2.19 (s, 3H), 1.75 (t, *J* = 3.2 Hz, 3H), 1.24 and 1.07 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 206.9, 170.0, 167.8, 133.5, 128.7, 128.6, 127.6, 109.2, 96.1, 76.9, 75.2, 75.0, 74.4, 65.3, 25.9, 25.0, 20.5, 15.3; IR ($CHCl_3$): ν = 2992, 1942, 1748, 1746 cm^{-1}; MS (ES): *m/z* (%):361 (100) $[M + H]^+$, 360 (11) $[M]^+$; elemental analysis

calcd (%) for $C_{20}H_{24}O_6$ (360.4): C 66.65, H 6.71; found C 66.50, H 6.66.

(*R*)-*O*-Acetylmandelate (-)-5. 70 mg (0.18 mmol) of α-allenic alcohol (+)-**2i**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent affords the (*R*)-*O*-acetylmandelate (94 mg, 92%) as a colorless oil; $[\alpha]_D$ = –74.5 (*c* = 2.7 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.88 and 6.90 (d, *J* = 9.0 Hz, each 2H), 7.54 (m, 2H), 7.34 (m, 7H), 6.97 (m, 1H), 6.03 (d, *J* = 4.9 Hz, 1H), 5.96 (s, 1H), 5.57 (dt, *J*= 7.8, 1.9 Hz, 1H), 4.72 (ddd, *J*= 11.0, 3.1, 2.0 Hz, 1H), 4.46 and 3.15 (d, *J* = 15.1 Hz, each 1H), 4.45 (m, 1H), 4.04 (dt, *J*= 7.8, 5.1 Hz, 1H), 3.87 (s, 3H), 2.21 (s, 3H), 1.55 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 206.9, 170.2, 167.9, 165.3, 164.3, 163.9, 135.1, 132.9, 132.1, 129.8, 129.1, 128.7, 128.1, 128.0, 120.6, 113.7, 95.8, 78.0, 75.0, 74.5, 73.7, 56.6, 55.4, 44.9, 20.6, 15.5; IR ($CHCl_3$): ν = 2990, 1942, 1752, 1746, 1734 cm^{-1}; MS (ES): *m/z* (%): 570 (100) $[M + H]^+$, 569 (11) $[M]^+$; elemental analysis calcd (%) for $C_{33}H_{31}NO_8$ (569.6): C 69.58, H 5.49, N 2.46; found C 69.72, H 5.45, N 2.43.

(*S*)-*O*-Acetylmandelate (+)-6. From 70 mg (0.18 mmol) of α-allenic alcohol (+)-**2i**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the (*S*)-*O*-acetylmandelate (87 mg, 85%) as a colorless oil; $[\alpha]_D$ = +15.7 (*c* = 2.1 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.96 and 6.90 (d, *J* = 9.0 Hz, each 2H), 7.38 (m, 10H), 6.16 (d, *J* = 4.9 Hz, 1H), 5.91 (s, 1H), 5.59 (dt, *J*=

8.8, 2.0 Hz, 1H), 5.01 and 4.17 (d, *J* = 15.4 Hz, each 1H), 4.53 (ddd, *J*= 11.2, 3.2, 1.6 Hz, 1H), 4.10 (m, 1H), 4.04 (dd, *J*= 8.8, 5.1 Hz, 1H), 3.85 (s, 3H), 2.25 (s, 3H), 1.11 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.2, 170.3, 167.9, 167.8, 165.3, 164.2, 135.1, 132.9, 132.1, 129.4, 128.9, 128.7, 128.1, 127.6, 120.6, 113.7, 94.7, 77.3, 74.5, 74.4, 73.7, 56.5, 55.4, 45.0, 20.6, 14.5; IR ($CHCl_3$): ν = 2994, 1944, 1750, 1744, 1732 cm^{-1}; MS (ES): *m/z* (%): 570 (100) $[M + H]^+$, 569 (5) $[M]^+$; elemental analysis calcd (%) for $C_{33}H_{31}NO_8$ (569.6): C 69.58, H 5.49, N 2.46; found C 69.45, H 5.44, N 2.49.

General procedure for the synthesis of α-allenic acetates or *p*-nitrobenzoates 7a–d. Acetic anhydride (48 mg, 0.468 mmol) or *p*-nitrobenzoyl chloride (87 mg, 0.468 mmol), DMAP (cat.), and triethylamine (95 mg, 0.936 mmol) were sequentially added dropwise to a stirred solution of the appropriate α-allenic alcohol **2** (0.39 mmol) in dichloromethane (4 mL) at 0 ^{o}C, and the mixture was stirred at room temperature until disappearance of the starting material (TLC). Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds **3**. Spectroscopic and analytical data for some representative pure forms of **3** follow.

α-Allenic acetate (±)-3a. 300 mg (1.87 mmol) of α-allenic alcohol (±)-**2a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent affords compound (±)-**3a** (370 mg, 97%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.37 (m, 5H), 6.21 (t, *J* = 2.3

Hz, 1H), 4.82 (m, 2H), 2.14 (s, 3H), 1.64 (t, *J* = 3.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 206.3, 169.8, 138.3, 128.2, 128.0, 126.9, 98.9, 76.6, 75.9, 21.0, 14.8; IR ($CHCl_3$): ν = 2983, 1937, 1742 cm^{-1}; MS (EI): *m/z* (%): 203 (5) [*M* + H]$^{+}$, 202 (100) [*M*]$^{+}$; elemental analysis calcd (%) for $C_{13}H_{14}O_2$ (202.2): C 77.20, H 6.98; found C 77.32, H 6.93.

α-Allenic acetate (±)-3b. From 280 mg (1.60 mmol) of α-allenic alcohol (±)-**2b**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (±)-**3b** (297 mg, 85%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.28 and 7.17 (d, *J* = 8.0 Hz, each 2H), 6.14 (t, *J* = 2.3 Hz, 1H), 4.81 (q, *J* = 2.9 Hz, 2H), 2.36 (s, 3H), 2.12 (s, 3H), 1.62 1.60 (t, *J* = 3.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 206.2, 169.9, 137.9, 135.3, 128.9, 127.0, 99.1, 76.6, 75.8, 21.1, 21.0, 14.9; IR ($CHCl_3$): ν = 2984, 1934, 1740 cm^{-1}; MS (EI): *m/z* (%): 217 (7) [*M* + H]$^{+}$, 216 (100) [*M*]$^{+}$; elemental analysis calcd (%) for $C_{14}H_{16}O_2$ (216.3): C 77.75, H 7.46; found C 77.89, H 7.41.

α-Allenic *p*-nitrobenzoate (±)-3c. From 387 mg (1.62 mmol) of α-allenic alcohol (±)-**2c**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent affords compound (±)-**3c** (373 mg, 59%) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.29 (m, 4H), 7.60 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.54 and 7.20 (dd, *J* = 7.7, 1.8 Hz, each 1H), 7.35 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.77 (t, *J* = 2.6 Hz, 1H), 4.78 (m, 2H), 1.78 (t, *J* = 3.2

Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.0, 163.4, 150.6, 137.2, 135.4, 132.9, 130.8, 129.8, 128.4, 127.5, 123.5, 123.3, 98.7, 78.0, 77.5, 76.4, 15.4; IR ($CHCl_3$): ν = 2982, 1936, 1738 cm^{-1}; MS (EI): *m/z* (%): 389 (98) $[M + 2]^+$, 387 (100) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{14}BrNO_4$ (388.21): C 55.69, H 3.63, N 3.61; found C 55.82, H 3.60, N 3.65.

α-Allenic acetate (+)-3d. From 90 mg (0.49 mmol) of α-allenic alcohol (–)-**2g**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (+)-**3d** (68 mg, 74%) as a colorless oil; $[\alpha]_D$ = +34.0 (*c* = 2.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 5.31 (m, 1H), 4.79 (m, 2H), 4.31 (dd, *J* = 11.7, 6.1 Hz, 1H), 4.05 and 3.89 (dd, *J* = 8.4, 6.5 Hz, each 1H), 2.09 (s, 3H), 1.73 (t, *J* = 3.1 Hz, 3H), 1.41 and 1.35 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 206.9, 170.3, 109.5, 96.4, 76.7, 75.8, 73.5, 65.6, 26.4, 25.2, 20.9, 15.6; IR ($CHCl_3$): ν = 2990, 1940, 1740 cm^{-1}; MS (ES): *m/z* (%):185 (100) $[M + H]^+$, 184 (5) $[M]^+$; elemental analysis calcd (%) for $C_{12}H_{18}O_4$ (226.3): C 63.70, H 8.02; found C 63.56, H 8.07.

Spectroscopic and analytical data for some representative pure forms of 2,3,4-trisubstituted 2,5-dihydrofurans **8** follow.

2,3,4-Trifunctionalized 2,5-dihydrofuran (±)-8b. From 50 mg (0.28 mmol) of α-allenol (±)-**2e**, and after chromatography of the residue using hexanes/ethyl acetate

(9:1) as eluent gave compound (±)-**8b** (71 mg, 75%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.61 (br s, 1H), 7.22 (m, 5H), 7.08 (m, 1H), 6.89 (m, 2H), 6.57 (br s, 1H), 5.93 (m, 1H), 5.43 and 5.09 (d, *J* = 1.0 Hz, each 1H), 4.88 (m, 2H), 2.37 (s, 3H), 2.07 (d, *J* = 1.2 Hz, 3H), 1.53 (dd, *J* = 1.8, 3.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 171.2, 155.8, 144.4, 136.5, 134.8, 133.6, 132.7, 129.4, 129.2, 128.9, 128.8, 128.2, 123.6, 119.7, 117.0, 114.6, 91.8, 77.4, 21.1, 15.6, 11.0; IR ($CHCl_3$): ν = 3450 cm^{-1}; MS (ES): *m/z* (%): 333 (100) $[M + H]^+$, 332 (8) $[M]^+$; elemental analysis calcd (%) for $C_{23}H_{24}O_2$ (332.4): C 83.10, H 7.28; found C 82.04, H 7.34.

2,3,4-Trifunctionalized 2,5-dihydrofuran (±)-8c. 50 mg (0.18 mmol) of α-allenol (±)-**2f**, and after chromatography of the residue using hexanes/ethyl acetate (18:1) as eluent affords compound (±)-**8c** (43 mg, 54%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.80 and 6.99 (d, *J* = 9.0 Hz, each 2H), 7.18 (m, 4H), 6.93 and 6.35 (q, *J* = 1.7 Hz, each 1H), 6.65 (br s, 1H), 6.40 (m, 1H), 6.21 (t, *J* = 3.3 Hz, 1H), 5.42 and 5.10 (d, *J* = 1.5 Hz, each 1H), 4.79 (m, 2H), 3.90 (s, 3H), 2.37 (s, 3H), 2.08 (d, *J* = 1.2 Hz, 3H), 1.72 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 162.7, 151.2, 134.1, 133.3, 133.1, 132.6, 131.9, 130.9, 130.5, 130.0, 129.9, 129.7, 129.4, 129.3, 127.7, 126.3, 124.6, 113.9, 113.7, 110.5, 82.5, 77.2, 55.0, 29.8, 21.4, 15.9; IR ($CHCl_3$): ν = 1728 cm^{-1}; MS (ES): *m/z* (%): 440 (100) $[M + H]^+$, 439 (11) $[M]^+$; elemental analysis calcd (%) for

$C_{29}H_{29}NO_3$ (439.5): C 79.24, H 6.65, N 3.19; found C 79.38, H 6.60, N 3.15.

2,3,4-Trifunctionalized 2,5-dihydrofuran (+)-8d. From 110 mg (0.60 mmol) of α-allenol (–)-**2g**, and after chromatography of the residue using hexanes/ethyl acetate (12:1) as eluent gave compound (+)-**8d** (167 mg, 58%) as a colorless oil; $[\alpha]_D$ = +13.9 (*c* = 4.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.59 (dd, *J* = 7.8, 1.2 Hz, 3H), 7.29 (m, 2H), 7.12 (m, 1H), 6.55 (br s, 1H), 5.46 and 5.10 (d, *J* = 0.5 Hz, each 1H), 4.78 (m, 3H), 4.21 (dd, *J* = 11.7, 6.1 Hz, 3H), 4.09 and 3.98 (dd, *J* = 8.0, 6.3 Hz, each 1H), 1.94 (d, *J* = 1.2 Hz, 3H), 1.77 (br s, 3H), 1.46 and 1.38 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 143.7, 134.0, 133.4, 132.5, 130.8, 128.9, 128.4, 128.3, 127.9, 126.8, 123.7, 115.3, 109.5, 89.2, 78.5, 78.3, 66.3, 26.6, 25.5, 15.2, 11.4; IR ($CHCl_3$): ν = 3450 cm^{-1}; MS (ES): *m/z* (%): 407 (98) $[M + 2 + H]^+$, 405 (100) $[M + H]^+$; elemental analysis calcd (%) for $C_{21}H_{25}BrO_3$ (405.3): C 62.23, H 6.22; found C 62.36, H 6.16.

2,3,4-Trifunctionalized 2,5-dihydrofuran (+)-8f. 50 mg (0.13 mmol) of α-allenol (+)-**2i**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent affords compound (+)-**8f** (47 mg, 67%) as a colorless oil; $[\alpha]_D$ = +28.6 (*c* = 2.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.09 and 6.94 (d, *J* = 9.0 Hz, each 2H), 7.30 (m, 10H), 6.46 (br s, 1H), 6.12 (d, *J* = 4.9 Hz, 1H), 5.41 and 5.00 (d, *J* = 1.2 Hz, each 1H), 5.08 and 4.12 (d, *J* = 14.6 Hz, each 1H), 4.97 (m, 1H), 4.80 (m, 2H), 3.92 (dd, *J* =

4.8, 4.2 Hz, 1H), 3.87 (s, 3H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.43 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.4, 165.0, 163.9, 144.3, 137.5, 135.7, 135.2, 134.7, 132.3, 131.2, 129.3, 129.1, 128.8, 128.2, 128.1, 127.9, 126.8, 121.3, 114.7, 113.8, 87.1, 78.5, 74.4, 58.0, 55.5, 45.3, 15.8, 10.9; IR ($CHCl_3$): ν = 1747, 1734 cm^{-1}; MS (ES): *m/z* (%): 536 (100) $[M + H]^+$, 535 (12) $[M]^+$; elemental analysis calcd (%) for $C_{34}H_{33}NO_5$ (535.6): C 76.24, H 6.21, N 2.62; found C 76.11, H 6.25, N 2.60.

2,3,4-Trifunctionalized 2,5-dihydrofuran (+)-8g. From 50 mg (0.11 mmol) of α-allenol (+)-**2j**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (+)-**8g** (37 mg, 54%) as a colorless oil; $[\alpha]_D$ = +27.1 (*c* = 2.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.12 and 6.96 (d, *J* = 9.0 Hz, each 2H), 7.13 (m, 12H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.50 (br s, 1H), 5.87 (d, *J* = 4.9 Hz, 1H), 5.56 (m, 1H), 5.40 and 5.02 (br s, each 1H), 4.99 (m, 2H), 4.94 and 4.13 (d, *J* = 15.0 Hz, each 1H), 4.11 (dd, *J* = 4.9, 1.7 Hz, 1H), 3.89 (s, 3H), 2.31 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.9, 165.3, 163.9, 136.5, 136.4, 135.5, 134.6, 133.8, 133.7, 132.5, 132.4, 129.9, 128.9, 128.8, 128.7, 128.4, 128.0, 127.9, 127.7, 127.6, 121.3, 113.7, 85.3, 80.5, 78.5, 74.8, 58.3, 55.5, 46.6, 21.1, 15.4; IR ($CHCl_3$): ν = 1745, 1735 cm^{-1}; MS (ES): *m/z* (%): 598 (100) $[M + H]^+$, 597 (17) $[M]^+$; elemental analysis calcd (%) for $C_{39}H_{35}NO_5$ (597.7): C 78.37, H 5.90, N 2.34; found C 78.52, H 5.85, N 2.31.

2,3,4-Trifunctionalized 2,5-dihydrofuran (+)-8h. 50 mg (0.13 mmol) of α-allenol (+)-**2i**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent affords compound (+)-**8h** (43 mg, 59%) as a colorless oil; $[\alpha]_D$ = +14.0 (*c* = 3.5 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 8.09 and 6.94 (d, *J* = 9.0 Hz, each 2H), 6.09 (d, *J* = 5.1 Hz, 1H), 5.45 (d, *J* = 8.5 Hz, 1H), 5.33 (br s, 1H), 5.05 and 4.07 (d, *J* = 14.9 Hz, each 1H), 4.94 (m, 2H), 4.85 (dd, *J* = 14.1, 7.9 Hz, 1H), 4.74 and 4.67 (m, each 1H), 4.09 (dd, *J* = 7.9, 6.1 Hz, 1H), 3.89 (m, 1H), 3.88 (s, 3H), 3.49 (t, *J* = 7.9 Hz, 1H), 1.85 (d, *J* = 1.2 Hz, 3H), 1.39 (s, 3H), 1.38 and 1.26 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 165.4, 165.1, 163.9, 143.3, 137.7, 135.3, 134.1, 132.4, 131.4, 128.8, 128.2, 127.9, 127.3, 121.1, 115.2, 113.8, 109.2, 87.1, 78.4, 74.5, 73.1, 69.2, 57.9, 55.5, 45.3, 26.8, 25.9, 14.9, 10.9; IR ($CHCl_3$): ν = 1748, 1735 cm^{-1}; MS (ES): *m/z* (%): 560 (100) $[M + H]^+$, 559 (7) $[M]^+$; elemental analysis calcd (%) for $C_{33}H_{37}NO_7$ (559.6): C 70.82, H 6.66, N 2.50; found C 70.96, H 6.60, N 2.47.

Spectroscopic and analytical data for some representative pure forms of spiranic 2,3,4-trisubstituted 2,5-dihydrofurans **11** follow.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (±)-11b. From 50 mg (0.25 mmol) of α-allenol (±)-**10b**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (±)-**11b** (49 mg, 54%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 8.60 (br s, 1H), 7.23 (m, 6H), 7.08 (td, *J* = 7.4, 1.0 Hz, 1H), 6.89

(m, 1H), 6.79 (br s, 1H), 5.48 and 5.21 (br s, each 1H), 5.17 (m, 1H), 5.05 (ddd, *J* = 11.7, 3.7, 1.7 Hz, 1H), 2.37 (s, 3H), 2.10 (d, *J* = 1.2 Hz, 3H), 1.41 (t, *J* = 1.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 178.2, 143.8, 141.1, 137.2, 136.5, 134.9, 134.5, 131.2, 130.1, 129.6, 129.3, 128.9, 128.8, 124.8, 123.2, 115.0, 110.4, 94.5, 79.8, 21.2, 15.5, 9.6; IR ($CHCl_3$): ν = 3420, 1715 cm^{-1}; MS (ES): *m/z* (%): 358 (100) $[M + H]^+$, 357 (9) $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{23}NO_2$ (357.4): C 80.64, H 6.49, N 3.92; found C 80.78, H 6.56, N 2.50.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (±)-11c. 30 mg (0.11 mmol) of α-allenol (±)-**10c**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent affords compound (±)-**11c** (24 mg, 50%) as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.38 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.28 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.02 (m, 10H), 6.85 (br s, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.41 and 5.25 (br s, each 1H), 5.33 and 5.16 (d, *J* = 12.5 Hz, each 1H), 3.13 (s, 3H), 2.35 (s, 3H), 1.94 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C): δ = 175.8, 145.7, 144.1, 143.9, 137.2, 136.5, 135.8, 134.9, 134.5, 132.6, 131.2, 129.6, 129.2, 129.3, 128.9, 128.5, 124.5, 123.2, 114.9, 108.3, 94.1, 79.5, 30.1, 26.7, 21.6; IR ($CHCl_3$): ν = 1716 cm^{-1}; MS (ES): *m/z* (%): 434 (100) $[M + H]^+$, 433 (11) $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{27}NO_2$ (433.5): C 83.11, H 6.28, N 3.23; found C 82.08, H 6.32, N 3.20.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (±)-11d. From 50 mg (0.19 mmol) of α-allenol (±)-**10d**, and after

chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave compound (±)-**11d** (52 mg, 65%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.59 (br s, 1H), 7.38 (m, 1H), 7.22 (td, *J* = 7.7, 1.5 Hz, 1H), 7.07 (m, 10H), 6.88 (br s, 1H), 6.78 (m, 1H), 5.44 and 5.27 (br s, each 1H), 5.34 and 5.18 (d, *J* = 12.5 Hz, each 1H), 2.35 (s, 3H), 1.96 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 177.7, 143.9, 141.1, 140.6, 136.4, 134.9, 134.6, 134.2, 132.1, 130.3, 130.2, 130.1, 129.1, 128.7, 128.0, 127.9, 127.7, 125.3, 123.2, 115.8, 110.5, 94.0, 79.7, 21.2, 15.5; IR ($CHCl_3$): ν = 3422, 1714 cm^{-1}; MS (ES): *m/z* (%): 420 (100) $[M + H]^+$, 419 (9) $[M]^+$; elemental analysis calcd (%) for $C_{29}H_{25}NO_2$ (419.5): C 83.03, H 6.01, N 3.34; found C 83.17, H 6.06, N 3.30.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (±)-11e. 25 mg (0.12 mmol) of α-allenol (±)-**10a**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent affords compound (±)-**11e** (24 mg, 47%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.61 (td, *J* = 7.8, 1.0 Hz, 1H), 7.33 (m, 4H), 7.12 (m, 1H), 7.07 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.84 (m, 1H), 6.78 (br s, 1H), 5.54 (dd, *J* = 1.2, 0.5 Hz, 1H), 5.29 (br s, 1H), 5.14 (m, 2H), 3.22 (s, 3H), 1.98 (d, *J* = 1.5 Hz, 3H), 1.38 (t, *J* = 2.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 174.3, 148.8, 144.1, 143.1, 138.0, 137.0, 136.2, 132.5, 131.7, 130.1, 129.2, 128.5, 128.4, 126.8, 124.7, 124.6, 123.1, 116.1, 108.3, 94.0, 26.3, 15.2, 9.6; IR ($CHCl_3$): ν = 1712 cm^{-1}; MS (ES): *m/z* (%): 438 (100) $[M + H + 2]^+$, 437 (22) $[M + 2]^+$,

435 (25) $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{22}BrNO_2$ (436.3): C 66.06, H 5.08, N 3.21; found C 66.19, H 5.04, N 3.24.

Spectroscopic and analytical data for some representative pure forms of spiro 2,3,4-trisubstituted 2,5-dihydrofurans **12** follow.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (–)-12a. From 50 mg (0.16 mmol) of α-allenol (–)-**10e**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave compound (–)-**12a** (31 mg, 51%) as a colorless oil; $[\alpha]_D$ = –19.4 (*c* = 1.8 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.30 (m, 10H), 6.45 (br s, 1H), 5.41 (d, *J* = 0.7 Hz, 1H), 5.05 (br s, 1H), 4.93 and 4.21 (d, *J* = 14.4 Hz, each 1H), 4.85 and 4.66 (ddd, *J* = 12.5, 2.2, 2.0 Hz, each 1H), 4.44 (m, 1H), 4.17 (d, *J* = 15.4 Hz, 1H), 3.49 (d, *J* = 8.3 Hz, 1H), 3.46 (d, *J* = 8.8 Hz, 1H), 2.01 (d, *J* = 1.2 Hz, 3H), 1.48 (t, *J* = 2.1 Hz, 3H), 1.41 and 1.36 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ =169.8, 143.5, 137.5, 136.3, 135.8, 135.4, 129.4, 129.2, 129.1, 128.6, 128.5, 128.2, 127.8, 126.8, 115.6, 109.8, 102.0, 79.1, 77.6, 66.5, 64.0, 45.3, 26.7, 24.8, 15.7, 9.4; IR ($CHCl_3$): ν = 1744 cm^{-1}; MS (ES): *m/z* (%): 472 (100) $[M + H]^+$, 471 (11) $[M]^+$; elemental analysis calcd (%) for $C_{30}H_{33}NO_4$ (471.6): C 76.41, H 7.05, N 2.97; found C 76.28, H 7.09, N 2.94.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (–)-12b. 50 mg (0.16 mmol) of α-allenol (–)-**10e**, and after

chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent affords compound (–)-**12b** (58 mg, 75%) as a colorless oil; $[\alpha]_D$ = –12.5 (*c* = 1.4 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.33 (m, 5H), 7.15 (br s, 4H), 6.41 (br s, 1H), 5.39 (d, *J* = 1.0 Hz, 1H), 5.04 (br s, 1H), 4.94 and 4.21 (d, *J* = 14.4 Hz, each 1H), 4.84 and 4.66 (dq, *J* = 12.2, 2.0 Hz, each 1H), 4.44 (m, 1H), 4.18 (dd, *J* = 8.0, 7.1 Hz, 1H), 3.48 (m, 1H), 3.47 (d, *J* = 8.3 Hz, 1H), 2.35 (s, 3H), 2.01 (d, *J* = 1.2 Hz, 3H), 1.48 (t, *J* = 1.9 Hz, 3H), 1.41 and 1.37 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ =168.1, 143.6, 136.6, 136.4, 135.8, 134.6, 134.5, 129.3, 129.2, 129.1, 128.9, 128.5, 128.4, 127.7, 115.3, 109.8, 102.0, 79.1, 77.6, 66.5, 64.0, 45.2, 26.6, 24.8, 21.1, 15.7, 9.3; IR ($CHCl_3$): ν = 1742 cm^{-1}; MS (ES): *m/z* (%): 486 (100) $[M + H]^+$, 485 (15) $[M]^+$; elemental analysis calcd (%) for $C_{31}H_{35}NO_4$ (485.6): C 76.67, H 7.26, N 2.88; found C 76.80, H 7.05, N 2.91.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (+)-12c. From 44 mg (0.12 mmol) of α-allenol (–)-**10f**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave compound (+)-**12c** (31 mg, 47%) as a colorless oil; $[\alpha]_D$ = +9.5 (*c* = 1.2 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 8.09 (m, 1H), 7.11 (m, 13H), 6.48 (br s, 1H), 5.34 and 5.05 (br s, each 1H), 5.01 and 4.90 (d, *J* = 12.9 Hz, each 1H), 4.81 and 4.14 (d, *J* = 14.6 Hz, each 1H), 4.45 (m, 1H), 4.21 and 3.55 (dd, *J* = 8.3, 5.9 Hz, each 1H), 3.33 (d, *J* = 9.0 Hz, 1H), 2.34 (s, 3H), 1.86 (d, *J* = 1.2 Hz, 3H), 1.31 and 1.20 (s, each 3H); ^{13}C NMR (75

MHz, $CDCl_3$, 25 ^oC): δ =168.2, 143.5, 139.1, 136.5, 134.8, 134.5, 133.2, 132.0, 131.5, 129.9, 129.3, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.9, 127.2, 113.7, 109.8, 102.4, 78.9, 77.6, 66.5, 64.1, 45.6, 26.4, 24.9, 21.2, 15.7; IR ($CHCl_3$): ν = 1743 cm^{-1}; MS (ES): *m/z* (%): 548 (100) $[M + H]^+$, 547 (11) $[M]^+$; elemental analysis calcd (%) for $C_{36}H_{37}NO_4$ (547.7): C 78.95, H 6.81, N 2.56; found C 78.80, H 6.85, N 2.54.

Spiro 2,3,4-trifunctionalized 2,5-dihydrofuran (+)-12d. 50 mg (0.14 mmol) of α-allenol (+)-**10g**, and after chromatography of the residue using hexanes/ethyl acetate (12:1) as eluent affords compound (+)-**12d** (40 mg, 57%) as a colorless oil; $[\alpha]_D$ = +4.2 (*c* = 1.1 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.76 and 6.90 (d, *J* = 9.3 Hz, each 2H), 7.19 (m, 4H), 6.51 (br s, 1H), 5.45 (d, *J* = 0.7 Hz, 1H), 5.11 (br s, 1H), 4.93 and 4.73 (dq, *J* = 12.5, 2.0 Hz, each 1H), 4.52 (m, 1H), 4.34 (dd, *J* = 8.4, 7.0 Hz, 1H), 4.15 (d, *J* = 8.5 Hz, 1H), 3.82 (s, 3H), 3.63 (dd, *J* = 8.4, 6.2 Hz, 1H), 2.37 (s, 3H), 2.06 (d, *J* = 1.2 Hz, 3H), 1.69 (t, *J* = 2.0 Hz, 3H), 1.57 and 1.37 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ =165.9, 156.6, 143.5, 136.9, 136.7, 134.5, 131.0, 129.5, 129.2, 128.9, 128.2, 128.1, 119.7, 115.5, 114.0, 110.0, 101.5, 79.3, 77.4, 77.1, 66.7, 55.5, 26.6, 24.6, 21.2, 15.7, 9.4; IR ($CHCl_3$): ν = 1741 cm^{-1}; MS (ES): *m/z* (%): 502 (100) $[M + H]^+$, 501 (15) $[M]^+$; elemental analysis calcd (%) for $C_{31}H_{35}NO_5$ (501.6): C 74.23, H 7.03, N 2.79; found C 74.10, H 7.07, N 2.82.