**Synthesis of 3-Acyl-2-alkenylfurans based on Feist-Benary-Cyclization of
(2,4-Dioxobutylidene)phosphoranes with α -Haloketones and -aldehydes**

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Supporting Information

S2 General

S2 Experimental procedures

Experimental Section

General Comments. All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60-200 mesh) was used. Melting points are uncorrected.

General procedure for the synthesis of phosphonium halides **3**.

Procedure A. To a CH_2Cl_2 solution (20 mL) of chloroacetaldehyde (45%, aqueous solution) was added MgSO_4 . The solution was filtered and the MgSO_4 was washed with CH_2Cl_2 . The filtrate (50 mL) was added to phosphorane **1** and the solution was refluxed for 24 h. The solvent was removed *in vacuo*. For **3a,b**, the residue was washed with acetone. For **3c,e**, the residue was purified by column chromatography (silica gel; acetone, then MeOH, $\varnothing = 2.0$ cm).

Procedure B. To chloroacetaldehyde (55%, aqueous solution) was added MgSO_4 . The mixture was filtered to give neat chloroacetaldehyde. To neat chloroacetaldehyde or α -chloroacetone was added phosphorane **1** and the mixture was vigorously stirred at 80 °C for 1 h. After cooling to room temperature, the mixture was dissolved in CH_2Cl_2 (10 mL) and the solution was poured into hexane (500 mL). The oil layer was separated from hexane and was subsequently dissolved in CH_2Cl_2 (5 mL). The solution was filtered and the solvent of the filtrate was removed *in vacuo* to give the (furylmethyl)phosphonium chloride **3**.

Procedure C. The neat anhydrous haloketone **2** and phosphorane **1** were vigorously stirred at 80 °C for 1 h. The reaction vessel was repeatedly evacuated (10^{-2} bar). After cooling to room temperature, the mixture was dissolved in CH_2Cl_2 (10 mL) and the solution was poured into

hexane (500 mL). The oil layer was separated from hexane and was subsequently dissolved in CH_2Cl_2 (5 mL). The solution was filtered and the solvent of the filtrate was removed *in vacuo* to give the (furylmethyl)phosphonium halide **3**.

(3-Methoxycarbonylfuran-2-yl-methyl)triphenylphosphonium chloride (3a): Following procedure A, the starting materials 4-(triphenylphosphanylidene)acetic acid methyl ester (**1a**) (372 mg, 0.99 mmol) and chloracetaldehyde (**2a**) (85 mg, 1.1 mmol) yielded **3a** as a colourless solid (186 mg, 43%). ^1H NMR (250 MHz, CDCl_3): δ = 3.25 (s, 3H, OCH_3), 6.11 (d, $^2J_{\text{H-P}} = 15$ Hz, 2H, PCH_2), 6.48 (d, $^3J = 2$ Hz, 1H, H-4, Heta), 7.25 (d, $^3J = 2$ Hz, 1H, H-5, Heta), 7.45 – 7.60 (m, 6H, Ph), 7.65 – 7.85 (m, 9H, Ph). ^{13}C NMR (50.3 MHz, CDCl_3): δ = 24.4, 51.6, 110.7, 117.4, 118.4, 130.0, 133.9, 135.0, 143.4, 148.5, 162.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3005 (w), 2850 (w), 1702 (s), 1602 (m), 1439 (s), 1321 (s), 1207 (m), 1112 (s), 766 (s), 741 (s), 691 (m), 527 (m), 500 (m). MS (EI, 70 eV): m/z (%) 400 ($[\text{M} - \text{HCl}]^+$, 100), 262 (46), 183 (44). MS (CI, NH_3): m/z (%) = 401 ($[\text{M} - \text{Cl}]^+$, 5) 263 (100). Anal. calcd for $\text{C}_{25}\text{H}_{22}\text{ClO}_3\text{P}$ (436.87): C 69.26, H 5.36; found: C 69.00, H 5.25.

(3-Ethoxycarbonylfuran-2-yl-methyl)triphenylphosphonium chloride (3b): Following procedure A, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (410 mg, 1.05 mmol) and chloracetaldehyde (**2a**) (91 mg, 1.16 mmol) yielded **3b** as a colourless solid (186 mg, 41%). ^1H NMR (250 MHz, CDCl_3): δ = 1.10 (t, $^3J = 7$ Hz, 3H, CH_3), 3.94 (q, $^3J = 7$ Hz, 2H, OCH_2), 6.01 (d, $^2J_{\text{H-P}} = 15$ Hz, 2H, PCH_2), 6.46 (d, $^3J = 2$ Hz, 1H, H-4, Heta), 7.22 (d, $^3J = 2$ Hz, 1H, H-5, Heta), 7.50 – 7.65 (m, 6H, Ph), 7.65 – 7.80 (m, 9H, Ph). ^{13}C NMR (50.3 MHz, CDCl_3): δ = 14.0, 24.3, 60.6, 110.7, 117.5, 118.3, 130.0, 133.9, 135.0, 143.3, 148.4, 162.5. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3037 (w), 1704 (s), 1600 (m), 1439 (m), 1311 (s), 1197 (m), 1165 (m), 1111 (s), 1046 (m), 764 (m), 741 (m), 690 (m), 508 (m). MS (EI, 70

eV): m/z (%) = 414 $[(M - HCl)^+]$ (100), 262 (63), 183 (60), 108 (27). MS (ESI): 415 $[(M - Cl)^+]$, 100). Anal. calcd for $C_{26}H_{24}ClO_3P$ (436.87): C 68.73, H 5.08; found: C 68.47, H 4.80.

(3-Isopropoxycarbonylfuran-2-yl-methyl)triphenylphosphonium chloride (3c):

Following procedure A, the starting materials 4-(triphenylphosphanylidene)acetic acid isopropyl ester (**1c**) (434 mg, 1.07 mmol) and chloracetaldehyde (**2a**) (93 mg, 1.18 mmol) yielded **3c** as a colourless solid (359 mg, 72%). 1H NMR (250 MHz, $CDCl_3$): δ = 1.10 (d, 3J = 6 Hz, 6H, CH_3), 4.81 (sept, 3J = 6 Hz, 1H, $OCH(CH_3)_2$), 6.06 (d, $^2J_{H-P}$ = 15 Hz, 2H, PCH_2), 6.47 (d, 3J = 2 Hz, 1H, H-4, H_{etar}), 7.23 (d 3J = 2 Hz, 1H, H-5, H_{etar}), 7.35 – 7.55 (m, 3H, Ph), 7.55 – 7.70 (m, 6H, Ph), 7.70 – 7.85 (m, 6H, Ph). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6, 24.3, 68.3, 110.8, 117.6, 118.7, 130.0, 134.0, 135.0, 143.3, 148.4, 161.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2983 (w), 2916 (w), 2749 (w), 1718 (s), 1438 (m), 1307 (m), 1197 (m), 1181 (m), 1110 (s), 743 (m), 721 (m), 693 (m), 542 (m), 511 (m). MS (ESI): m/z (%) = 429 $[(M - Cl)^+]$, 100). HRMS (ESI): calcd for $C_{27}H_{26}O_3P$ $[(M - Cl)^+]$ 429.16141, found 429.16116.

(3-Carbamoylfuran-2-yl-methyl)triphenylphosphonium chloride (3d): Following procedure B, the starting materials 3-oxo-4-(triphenylphosphanylidene)butyramide (**1d**) (542 mg, 1.50 mmol) and chloracetaldehyde (**2a**) (234 mg, 3.00 mmol) yielded **3d** as a black hygroscopic solid (450 mg, 71%); mp = 246 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 2H, NH_2), 6.14 (d, $^2J_{H-P}$ = 15.0 Hz, 2H, CH_2P), 6.51 (d, 3J = 1.8 Hz, 1H, H_{etar}), 7.60–7.85 (m, 16H, Ph, H_{etar}). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.5, 110.9, 117.5, 118.2, 130.2, 134.0, 135.2, 143.7, 148.5, 162.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3055 (w), 2953 (w), 2852 (w), 1730 (s), 1604 (m), 1511 (w), 1440 (s). MS (EI, 70 eV): m/z (%) = 385 (M^+ , ^{35}Cl , 7), 384 (34), 276 (26), 261 (100), 260 (17), 183 (20), 182 (95), 107 (43).

[(3-(Pyrolidin-1-yl)carbonyl)furan-2-yl-methyl]triphenylphosphonium chloride (3e):

Following procedure A, the starting materials 4-(triphenylphosphanylidene)-1-pyrrolidin-1-yl-butane-1,3-dione (**1e**) (645 mg, 1.65 mmol) and chloracetaldehyde (**2a**) (135 mg, 1.72 mmol) yielded **3e** as a colourless solid (278 mg, 37%). 6-Chloro-1-pyrrolidin-1-yl-hex-4-ene-1,3-dione (107 mg, 32%) was isolated as a side-product. ^1H NMR (250 MHz, CDCl_3): δ = 1.80 – 1.95 (m, 4H, 2 x CH_2), 3.30 – 3.50 (m, 4H, 2 x NCH_2), 5.88 (d, $^2J_{\text{H-P}}$ = 15 Hz, 2H, PCH_2), 6.43 (d, 3J = 2 Hz, 1H, H-4, Hetar), 7.26 (d, 3J = 2 Hz, 1H, H-5, Hetar), 7.30 – 7.50 (m, 3H, Ph), 7.50 – 7.70 (m, 6H, Ph), 7.70 – 7.90 (m, 6H, Ph). ^{13}C NMR (50.3 MHz, CDCl_3): δ = 24.0, 26.4, 24.6, 46.4, 48.6, 110.1, 118.2, 121.0, 130.0, 134.1, 134.9, 142.5, 146.6, 162.2. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3056 (s), 3407 (s), 3055 (w), 2946 (w), 1612 (s), 1441 (s), 1187 (w), 1112 (m), 751 (m), 742 (m), 722 (m), 692 (m), 519 (w). MS (ESI): m/z (%) = 440 ($[\text{M} - \text{Cl}]^+$, 100). HRMS (ESI): calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{P}$ ($[\text{M} - \text{Cl}]^+$) 440.17739, found 440.17711.

[(3-(Piperidin-1-yl)carbonyl)furan-2-yl-methyl]triphenylphosphonium chloride (3f):

Following procedure B, the starting materials 4-(triphenylphosphanylidene)-1-piperidin-1-yl-butane-1,3-dione (**1f**) (644 mg, 1.50 mmol) and chloracetaldehyde (**2a**) (234 mg, 3.00 mmol) yielded **3f** as a slightly brown hygroscopic solid (164 mg, 22%); mp = 85 °C. ^1H NMR (300 MHz, CDCl_3): δ = 1.45–1.68 (m, 6H, 3 x CH_2 , Pip), 3.35–3.60 (m, 4H, 2 x CH_2 , Pip), 6.15 (d, $^2J_{\text{H-P}}$ = 14.8 Hz, 2H, CH_2P), 6.26 (d, 3J = 1.9 Hz, 1H, Hetar), 6.52 (d, $^3J_{\text{cis}}$ = 1.9 Hz, 1H, Hetar), 7.61–7.84 (m, 15H, Ph). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3427 (m), 2936 (m), 2856 (w), 1712 (w), 1617 (s), 1440 (s). MS (EI, 70 eV): m/z (%) = 454 (M^+ , ^{35}Cl , 2), 453 (8), 370 (14), 341 (14), 303 (25), 277 (82), 262 (96), 183 (100), 151 (20), 108 (24), 107 (65), 106 (19), 84 (25). HRMS (ESI): calcd for $\text{C}_{29}\text{H}_{29}\text{NO}_2\text{P}$ ($[\text{M} - \text{Cl}]^+$) 454.19304, found 454.19307.

(3-Benzoylfuran-2-yl-methyl)triphenylphosphonium chloride (3g): Following procedure B, the starting materials 1-phenyl-4-(triphenylphosphanylidene)butane-1,3-dione (**1g**) (624 mg, 1.48 mmol) and chloroacetaldehyde (**2a**) (231 mg, 2.96 mmol) yielded **3g** as a yellow to brown hygroscopic solid (358 mg, 50%); mp = 80 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.25 (d, ²J_{H-P} = 14.7 Hz, 2H, CH₂P), 6.47 (d, ³J = 1.8 Hz, 1H, Hetar), 7.35–7.91 (m, 21H, Ph, Hetar). ¹³C NMR (75 MHz, CDCl₃): δ = 25.1, 112.4, 117.8, 123.9, 128.5, 128.7, 130.2, 132.9, 134.1, 135.1, 137.7, 143.2, 149.4, 190.0. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3425 (s), 1646 (s), 1576 (m), 1440 (s). MS (EI, 70 eV): *m/z* (%) = 446 (M⁺, ³⁵Cl, 18), 277 (18), 262 (66), 185 (19), 184 (29), 183 (100), 152 (18). HRMS (EI, 70 eV): calcd for C₃₀H₂₄O₂P ([M-Cl]⁺) 447.15084, found 447.15125.

(3-Methoxycarbonyl-4-methylfuran-2-yl-methyl)triphenylphosphonium chloride (3h): Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid methyl ester (**1a**) (564 mg, 1.50 mmol) and chloroacetone (**2b**) (276 mg, 3.00 mmol) yielded **3h** as a slightly brown hygroscopic solid (348 mg, 51%); mp = 83 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.99 (d, ⁴J = 1.2 Hz, 3H, CH₃), 3.56 (s, 3H, OCH₃), 6.06 (d, ²J_{H-P} = 14.7 Hz, 2H, CH₂P), 7.07 (q, ⁴J = 1.2 Hz, 1H, Hetar), 7.59–7.83 (m, 15H, Ph). ¹³C NMR (50 MHz, CDCl₃): δ = 9.6, 24.8, 51.3, 117.4, 118.3, 121.3, 130.0, 133.8, 135.0, 140.7, 148.8, 163.5. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3417 (w), 1715 (m), 1438 (m). MS (EI, 70 eV): *m/z* (%) = 516 (M⁺, ³⁵Cl, 100), 356 (22), 277 (17), 263 (17), 262 (91), 183 (72), 107 (28).

(3-Ethoxycarbonyl-4-methylfuran-2-yl-methyl)triphenylphosphonium chloride (3i): Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl

ester (**1b**) (880 mg, 2.25 mmol) and chloroacetone (**2b**) (414 mg, 4.50 mmol) yielded **3i** as a brown hygroscopic solid (509 mg, 48%); mp = 81 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.17 (t, ³J = 7.1 Hz, 3H, OCH₂CH₃), 1.99 (d, ⁴J = 1.2 Hz, 3H, CH₃), 4.00 (q, ³J = 7.1 Hz, 2H, OCH₂CH₃), 6.15 (d, ¹J_{H-P} = 14.7 Hz, 2H, CH₂P), 7.06 (q, ⁴J = 1.2 Hz, 1H, Hetar), 7.6–7.85 (m, 15H, Ph). ¹³C NMR (75 MHz, CDCl₃): δ = 9.8, 14.05, 24.9, 60.4, 117.7, 118.3, 130.0, 132.0, 134.0, 135.0, 140.7, 149.1, 163.3. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3376 (s), 3059 (m), 2976 (m), 2826 (m), 1710 (s), 1611 (m), 1552 (m), 1440 (s), 1409 (m). MS (EI, 70 eV): *m/z* (%) = 431 (M⁺, ³⁵Cl, 55), 277 (20), 263 (22), 262 (100). HRMS (EI, 70 eV): calcd for C₂₇H₂₆O₃P ([M-Cl]⁺) 429.16141, found 429.16170.

(3-Isopropoxycarbonyl-4-methylfuran-2-yl-methyl)triphenylphosphonium chloride (3j):

Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid isopropyl ester (**1c**) (562 mg, 1.39 mmol) and chloroacetone (**2b**) (276 mg, 3.00 mmol) yielded **3j** as a slightly brown hygroscopic solid (390 mg, 58%); mp = 86 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.18 (d, ³J = 6.2 Hz, 6H, CH(CH₃)₂), 1.98 (d, ⁴J = 1.2 Hz, 3H, CH₃), 4.85 (sep, ³J = 6.2 Hz, 1H, *i*Pr), 6.06 (d, ²J_{H-P} = 14.7 Hz, 2H, CH₂P), 7.07 (q, ⁴J = 1.2 Hz, 1H, Hetar), 7.28–7.80 (m, 15H, Ph). ¹³C NMR (75 MHz, CDCl₃): δ = 9.9, 21.6, 24.7, 68.1, 117.5, 118.6, 121.2, 130.0, 133.8, 135.1, 140.6, 148.9, 162.8. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3402 (w), 3036 (w), 2981 (w), 2818 (w), 1705 (m), 1610 (w), 1552 (w), 1438 (m), 1405 (w). UV-VIS (CH₃CN, nm): λ_{max} (log ε) = 4.20 (227.5). MS (EI, 70 eV): *m/z* (%) = 443 (M⁺, ³⁵Cl, 31), 442 (100), 400 (21), 327 (20), 303 (17), 262 (47), 183 (47), 107 (20). HRMS (EI, 70 eV): calcd for C₂₈H₂₇O₃P ([M-Cl]⁺) 442.1692, found 442.1698.

(3-Benzoyl-4-methylfuran-2-yl-methyl)triphenylphosphonium chloride (3k): Following procedure C, the starting materials 1-phenyl-4-(triphenylphosphanylidene)butane-1,3-dione (**1g**) (500 mg, 1.50 mmol) and chloroacetone (**2b**) (276 mg, 3.00 mmol) yielded **3k** as a yellow to brown hygroscopic solid (325 mg, 43%); mp = 83 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.68 (d, ⁴J = 1.2 Hz, 3H, CH₃), 5.76 (d, ²J_{H-P} = 14.5 Hz, 2H, CH₂P), 7.13 (q, ⁴J = 1.2 Hz, 1H, Hetar), 7.38–7.82 (m, 20H, Ph). ¹³C NMR (150 MHz, CDCl₃): δ = 9.9, 25.4, 117.9, 120.8, 126.5, 128.8, 129.1, 130.3, 133.3, 134.3, 135.1, 135.3, 141.1, 147.3, 191.8. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3427 (s), 3210 (m), 2890 (w), 1640 (s), 1598 (m), 1544 (m), 1440 (s). MS (EI, 70 eV): *m/z* (%) = 461 (M⁺, ³⁵Cl, 4), 460 (14), 263 (20), 262 (100), 261 (16), 184 (18), 183 (81), 107 (15). HRMS (ESI): calcd for C₃₁H₂₆O₂P ([M-Cl]⁺) 461.16649, found 461.16675.

(4-Chloromethyl-3-ethoxycarbonylfuran-2-yl-methyl)triphenylphosphonium chloride (3l): Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and 4-chlorobutan-2-one (**2c**) (381 mg, 3.00 mmol) yielded **3l** as a green hygroscopic solid (261 mg, 35%); mp = 83 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.19 (t, ³J = 7.2 Hz, 3H, CH₃), 4.03 (q, ³J = 7.2 Hz, 2H, OCH₂), 4.49 (d, ⁴J = 2.5 Hz, 2H, CH₂Cl), 6.22 (d, ²J_{H-P} = 14.8 Hz, 2H, CH₂P), 7.39 (d, ⁴J = 2.5 Hz, 1H, Hetar), 7.61–7.88 (m, 15H, Ph). ¹³C NMR (75 MHz, CDCl₃): δ = 13.9, 24.8, 35.9, 60.8, 116.8, 117.4, 123.1, 130.1, 133.9, 135.1, 142.7, 150.5, 162.1. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3428 (w), 1711 (m), 1555 (w), 1438 (m). MS (EI, 70 eV): *m/z* (%) = 462 (M⁺, ³⁵Cl, 3), 278 (16), 277 (40), 262 (59), 183 (39), 107 (30), 77 (18), 65 (82), 51 (19), 36 (31), 29 (55), 28 (100). HRMS (ESI): calcd for C₂₇H₂₅ClO₃P ([M-Cl]⁺) 463.12244, found 463.12265.

(4-*tert*-Butyl-3-ethoxycarbonylfuran-2-yl-methyl)triphenylphosphonium bromide (3m):

Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and 1-bromo-3,3-dimethylbutan-2-one (**2d**) (537 mg, 1.70 mmol) yielded **3m** as a colourless hygroscopic solid (626 mg, 75%); mp = 79 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.17 (t, ³J = 7.2 Hz, 3H, OCH₂CH₃), 1.20 (s, 9H, C(CH₃)₃), 4.01 (q, ³J = 7.2 Hz, 2H, OCH₂), 5.94 (d, ²J_{H-P} = 14.5 Hz, 2H, CH₂P), 7.04 (d, ⁵J = 2.6 Hz, 1H, H_{et}ar), 7.60–7.82 (m, 15H, Ph). ¹³C NMR (75 MHz, CDCl₃): δ = 13.9, 25.7, 29.6, 30.7, 60.8, 117.6, 118.2, 130.1, 133.9, 135.1, 135.6, 139.4, 149.9, 163.1. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3429 (s), 2961 (m), 2490 (w), 1721 (s), 1610 (w), 1439 (s). MS (EI, 70 eV): *m/z* (%) = 470 (M⁺, ⁷⁹Br, 4), 470 (15), 277 (18), 263 (22), 262 (100), 261 (21), 184 (17), 183 (71), 107 (26). HRMS (ESI): calcd for C₃₀H₃₂O₃P ([M-Br]⁺) 471.20836, found 471.20869.

(3-Ethoxycarbonyl-4-ethoxycarbonylmethylfuran-2-yl-

methyl)triphenylphosphonium chloride (3n): Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and 4-chloro-3-oxobutyric acid ethyl ester (**2e**) (445 mg, 2.70 mmol) yielded **3n** as a slightly yellow hygroscopic solid (509 mg, 63%); mp = 81 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.11 (t, ³J = 7.2 Hz, 3H, OCH₂CH₃), 1.24 (t, ³J = 7.2 Hz, 3H, OCH₂CH₃), 3.50 (d, ⁴J = 2.5 Hz, 2H, CH₂), 3.93 (q, ³J = 7.2 Hz, 2H, OCH₂), 4.13 (q, ³J = 7.2 Hz, 2H, OCH₂), 6.12 (d, ²J_{H-P} = 14.8 Hz, 2H, CH₂P), 7.26 (d, ⁴J = 2.5 Hz, 1H, H_{et}ar), 7.58–7.82 (m, 15H, Ph). ¹³C NMR (50 MHz, CDCl₃): δ = 14.0, 14.2, 25.1, 30.3, 60.6, 60.9, 117.6, 118.2, 118.8, 130.2, 134.0, 135.2, 142.5, 149.4, 162.7, 170.5. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3580 (w), 2984 (m), 1733 (s), 1715

(s) 1612 (w), 1556 (w), 1439 (s). MS (EI, 70 eV): m/z (%) = 500 (M^+ , ^{35}Cl , 3), 499 (12), 303 (18), 277 (34), 262 (63), 184 (21), 183 (100), 151 (19), 107 (45), 106 (17), 77 (22), 51 (18). HRMS (ESI): calcd for $\text{C}_{30}\text{H}_{30}\text{O}_5\text{P}$ ($[\text{M}-\text{Cl}]^+$) 501.18254, found 501.18283.

(3-Ethoxycarbonyl-4-phenylfuran-2-yl-methyl)triphenylphosphonium bromide (3o):

Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and phenacyl bromide (**2f**) (594 mg, 3.00 mmol) yielded **3o** as a slightly brown hygroscopic solid (453 mg, 53%); mp = 68 °C. ^1H NMR (300 MHz, CDCl_3): δ = 0.92 (t, 3J = 7.2 Hz, 3H, OCH_2CH_3), 3.85 (q, 3J = 7.2 Hz, 2H, OCH_2), 6.26 (d, $^2J_{\text{H-P}}$ = 14.6 Hz, 2H, CH_2P), 7.12-7.15 (m, 1H, H_{etar}), 7.26-7.32 (m, 5H, Ph), 7.63-7.90 (m, 15H, Ph). ^{13}C NMR (75 MHz, CDCl_3): δ = 13.5, 25.1, 60.5, 117.6, 117.6, 127.5, 127.5, 129.1, 130.1, 130.6, 133.8, 134.0, 135.1, 140.9, 149.7, 162.7. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3409 (w), 3054 (w), 2985(w), 1719 (m), 1701 (m), 1592 (w), 1439 (m), 1401 (w). MS (EI, 70 eV): m/z (%) = 491 (M^+ , ^{79}Br , 3), 277 (35), 263 (17), 262 (100), 261 (17), 183 (59), 107 (16), 28 (40). HRMS (ESI): calcd for $\text{C}_{32}\text{H}_{28}\text{O}_3\text{P}$ ($[\text{M}-\text{Br}]^+$) 491.17706, found 491.17724.

(3-Ethoxycarbonyl-4,5-diphenylfuran-2-yl-methyl)triphenylphosphonium bromide (3p):

Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and 2-bromo-1,2-diphenylethanone (**2g**) (585 mg, 1.50 mmol) yielded **3p** as a yellowish hygroscopic solid (448 mg, 46%); mp = 90 °C. ^1H NMR (300 MHz, CDCl_3): δ = 0.79 (t, 3J = 7.2 Hz, 3H, OCH_2CH_3), 3.76 (q, 3J = 7.2 Hz, 2H, OCH_2), 6.29 (d, $^2J_{\text{H-P}}$ = 14.7 Hz, 2H, CH_2P), 6.95–7.96 (m, 25H, Ph). ^{13}C NMR (75 MHz, CDCl_3): δ = 13.3, 25.1, 60.3, 117.7,

120.4, 122.1, 125.4, 128.2, 129.7, 130.1, 131.9, 134.1, 135.1, 147.0, 150.2, 162.6. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3396 (w), 3054 (w), 2985(w), 1724 (m), 1705 (m), 1595 (w), 1483 (w), 1439(m). MS (EI, 70 eV): m/z (%) = 566 (M^+ , ^{79}Br , 53), 303 (45), 277 (28), 263 (16), 262 (79), 261 (24), 183 (54), 151 (25), 114 (16), 107 (100), 107 (37), 105 (65). HRMS (ESI): calcd for $\text{C}_{38}\text{H}_{32}\text{O}_3\text{P}$ ($[\text{M}-\text{Br}]^+$) 567.20836, found 567.20873.

(3-Ethoxycarbonyl-4-*p*-tolylfuran-2-yl-methyl)triphenylphosphonium bromide (3q):

Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and *p*-methylphenacyl bromide (**2h**) (636 mg, 3.00 mmol) yielded **3q** as a slightly brown hygroscopic solid (702 mg, 80%); mp = 75 °C. ^1H NMR (300 MHz, CDCl_3): δ = 0.95 (t, 3J = 7.2 Hz, 3H, OCH_2CH_3), 2.35 (d, 4J = 6.3 Hz, 3H, CH_3), 3.87 (q, 3J = 7.2 Hz, 2H, OCH_2), 6.25 (d, $^2J_{\text{H-P}}$ = 14.7 Hz, 2H, CH_2P), 7.03 (d, 3J = 8.1 Hz, 1H, Ar), 7.11 (d, 3J = 7.9 Hz, 1H, Ar), 7.24 (d, 5J = 2.6 Hz, 1H, Hetar), 7.46–7.86 (m, 17H, Ph, Ar). ^{13}C NMR (50 MHz, CDCl_3): δ = 13.8, 21.2, 25.2, 60.6, 117.4, 119.3, 128.6, 129.1, 130.0, 130.6, 133.0, 133.9, 135.0, 137.4, 140.7, 149.4, 162.6. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3423 (w), 2985(w), 1714 (m), 1603 (w), 1591 (w), 1440 (s). MS (EI, 70 eV): m/z (%) = 504 (M^+ , ^{79}Br , 80), 277 (19), 260 (100), 183 (98), 107 (35). Anal. calcd for $\text{C}_{33}\text{H}_{30}\text{BrO}_3\text{P}$: C 67.70, H 5.16; found C 67.70, H 5.19.

[4-(*p*-Bromophenyl)-3-ethoxycarbonylfuran-2-yl-methyl]triphenylphosphonium

chloride (3r): Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and *p*-bromophenacyl chloride (**2i**) (696 mg, 3.00 mmol) yielded **3r** as a yellow hygroscopic solid (589 mg, 65%); mp = 78 °C. ^1H NMR (300 MHz, CDCl_3): δ =

0.95 (t, $^3J = 7.2$ Hz, 3H, OCH_2CH_3), 3.87 (q, $^3J = 7.2$ Hz, 2H, OCH_2), 6.31 (d, $^2J_{\text{H-P}} = 14.7$ Hz, 2H, CH_2P), 7.01 (d, $^4J = 1.8$ Hz, 1H, Ar), 7.03 (d, $^4J = 1.8$ Hz, 1H, Ar), 7.28 (s, 1H, Hetar), 7.42 (d, $^3J = 1.9$ Hz, 1H, Ar), 7.45 (d, $^3J = 1.9$ Hz, 1H, Ar), 7.63–7.89 (m, 15H, Ph). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 13.6, 25.4, 60.5, 117.2, 117.6, 121.8, 126.4, 129.5, 130.0, 130.2, 130.8, 133.9, 135.0, 140.9, 150.1, 162.6$. IR (KBr, cm^{-1}): $\tilde{\nu} = 3420$ (w), 3052(w), 2984(w), 1716 (m), 1588 (w), 1548 (w), 1482 (w), 1438 (s), 1411 (w). MS (EI, 70 eV): m/z (%) = 569 (M^+ , ^{35}Cl , 100), 303 (15), 262 (18). HRMS (EI, 70 eV): calcd for $\text{C}_{32}\text{H}_{26}\text{O}_3\text{BrP}^+$ ($[\text{M-Cl}]^+$) 568.0800, found 568.0803.

[3-Ethoxycarbonyl-4-(*p*-nitrophenyl)furan-2-yl-methyl]triphenylphosphonium

chloride (3s): Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and *p*-nitrophenacyl bromide (**2j**) (729 mg, 3.00 mmol) yielded **3s** as a red to brown hygroscopic solid (686 mg, 80%); mp = 80 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 0.95$ (t, $^3J = 7.2$ Hz, 3H, OCH_2CH_3), 3.88 (q, $^3J = 7.2$ Hz, 2H, OCH_2), 6.40 (d, $^2J_{\text{H-P}} = 14.8$ Hz, 2H, CH_2P), 7.32 (d, $^3J = 1.9$ Hz, 1H, Ar), 7.34 (d, $^3J = 1.9$ Hz, 1H, Ar), 7.40 (s, 1H, Hetar), 7.64–7.92 (m, 15H, Ph), 8.17 (d, $^3J = 1.9$ Hz, 1H, Ar), 8.19 (d, $^3J = 1.9$ Hz, 1H, Ar). ^{13}C NMR (50 MHz, CDCl_3): $\delta = 13.6, 25.0, 60.8, 116.9, 117.6, 122.9, 125.6, 130.0, 130.3, 133.9, 135.9, 137.5, 141.5, 147.6, 150.5, 162.3$. IR (KBr, cm^{-1}): $\tilde{\nu} = 3420$ (m), 2985(w), 1714 (m), 1595 (m), 1515 (s), 1438 (s). MS (EI, 70 eV): m/z (%) = 535 (M^+ , ^{35}Cl , 6), 303 (20), 278 (24), 277 (41), 262 (51), 183 (19), 160 (28), 70 (15), 57 (17), 45 (100), 43 (66.3), 41 (39). HRMS (EI, 70 eV): calcd for $\text{C}_{32}\text{H}_{26}\text{NO}_5\text{P}$ ($[\text{M-Cl}]^+$) 535.1543, found 535.1549.

[4-(*p*-Chlorophenyl)-3-ethoxycarbonylfuran-2-yl-methyl]triphenylphosphonium

bromide (3t): Following procedure C, the starting materials 4-(triphenylphosphanylidene)acetic acid ethyl ester (**1b**) (585 mg, 1.50 mmol) and *p*-chlorophenacyl bromide (**2k**) (695 mg, 3.00 mmol) yielded **3t** as a brown hygroscopic solid (473 mg, 52%); mp = 77 °C. ¹H NMR (300 MHz, CDCl₃): δ = 0.96 (t, ³*J* = 7.2 Hz, 3H, OCH₂CH₃), 3.88 (q, ³*J* = 7.2 Hz, 2H, OCH₂), 6.21 (d, ²*J*_{H-P} = 14.7 Hz, 2H, CH₂P), 7.07 (d, ⁴*J* = 1.9 Hz, 1H, Ar, Hetar), 7.09 (d, ⁴*J* = 1.9 Hz, 1H, Ar, Hetar), 7.26–7.30 (m, 3H, Ar, Hetar), 7.64–7.88 (m, 15H, Ph). ¹³C NMR (50 MHz, CDCl₃): δ = 13.8, 25.0, 60.8, 117.3, 117.4, 127.8, 129.0, 130.1, 130.4, 133.6, 133.8, 134.7, 135.2, 141.1, 157.3, 161.6. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3431 (m), 1746 (m), 1484 (w), 1438 (m). MS (EI, 70 eV): *m/z* (%) = 528 (M⁺, ⁷⁹Br, 1), 277 (27), 263 (33), 262 (100), 261 (28), 183 (46), 107 (31). HRMS (ESI): calcd for C₃₂H₂₇O₃BrClP ([M-Br]⁺) 525.13809, found 525.13809.

General procedure for the synthesis of 2-alkenylfurans 5.

Procedure A. To a THF solution (5 mL, in case solid aldehydes: 2.5 mL) of the phosphonium halide **3** was added *n*BuLi (1.0 equiv) at 0 °C. After stirring for 0.5 h at 0 °C, aldehyde **4** (1.0 equiv.) was added; solid aldehydes were added as a THF solution or suspension (2.5 mL). The solution was stirred for 0.5 h at 0 °C and at 20 °C until the reaction was completed (tlc control). The mixture was poured into ice water (40 mL) and ether (100 mL) was added. The organic and the aqueous layer were separated and the latter was extracted with ether (50 mL). The combined organic layers were dried (MgSO₄), filtered and the solvent of the filtrate was removed *in vacuo*. The residue was purified by column chromatography (silica gel, column Ø = 2.0 cm). The starting materials were separated by elution with acetone and the product was subsequently isolated by elution with methanol.

Procedure B. To a THF solution (10 mL) of the phosphonium halide **3** was added *n*BuLi (1.1 equiv) at 0 °C. After stirring for 0.5 h at 0 °C, aldehyde **4** (1.1–2.0 equiv.) was added and the solution was stirred for 72 h at 20 °C. The mixture was poured into ice water (40 mL) and ether (25 mL) was added. The organic and the aqueous layer were separated and the latter was extracted with ether (5 x 25 mL). The combined organic layers were dried (MgSO₄), filtered and the solvent of the filtrate was removed *in vacuo*. The residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 40:1, column: Ø = 8.0 cm, height = 10 cm) and, subsequently, by HPLC (Lichrosorb 60, 7 µm, Ø = 3.0 cm, l = 20 cm; eluent CH₂Cl₂).

Isopropyl 2-(prop-1-enyl)furan-3-carboxylate (5a): The reaction of **3c** (503 mg, 1.12 mmol) with *n*BuLi (1.12 mmol) and acetaldehyde (**4a**) (49 mg, 1.12 mmol) was carried out as described in procedure A (reaction time 23 h). After purification by column chromatography (*n*-pentane/diethyl ether = 50:1), **5a** was isolated as a yellow oil (130 mg, 62%, *E/Z* = 4:1); *R*_f = 0.35. ¹H NMR (250 MHz, CDCl₃, isomeric mixture): δ = 1.33 (d, ³*J* = 6 Hz, 6H, 2 x CH₃), 1.92 (dd, ³*J* = 7 Hz, ⁴*J* = 2 Hz, 3H, CH₃, *E*-isomer), 2.10 (dd, ³*J* = 7 Hz, ⁴*J* = 2 Hz, 3H, CH₃, *Z*-isomer), 5.17 (sept, ³*J* = 6 Hz, 1H, OCH(CH₃)₂), 5.92 (dq, ³*J* = 12 Hz, ³*J* = 7 Hz, 1H, CH=CH, *Z*-isomer), 6.49 (dq, ³*J* = 16 Hz, ³*J* = 7 Hz, 1H, CH=CH, *E*-isomer), 6.65 (d, ³*J* = 2 Hz, 1H, H-4, Heter, *E*-isomer), 6.71 (d, ³*J* = 2 Hz, 1H, H-4, Heter, *Z*-isomer), 6.91 (dd, ³*J* = 12 Hz, ⁴*J* = 2 Hz, 1 H, CH=CH, *Z*-Isomer), 6.97 (dd, ³*J* = 16 Hz, ⁴*J* = 2 Hz, 1H, CH=CH, *E*-isomer), 7.21 (d, ³*J* = 2 Hz, 1H, H-5, Heter, *E*-isomer), 7.33 (d, ³*J* = 2 Hz, 1H, H-5, Heter, *Z*-isomer). ¹³C (50.3 MHz, CDCl₃, *E*-isomer) δ = 18.6, 21.9, 67.6, 111.3, 112.5, 119.1 130.7, 140.4, 156.7, 163.2. IR (neat, cm⁻¹): $\tilde{\nu}$ = 2983 (m), 2936 (w), 1716 (s), 1453 (m), 1412 (m), 1378 (m), 1302 (m), 1183 (m), 1107 (s), 1025 (m), 840 (w), 756 (m), 605 (w). MS (EI, 70 eV): *m/z* (%) = 194 (M⁺, 35), 152 (100), 137 (60), 135 (42). Anal. calcd for C₁₁H₁₄O₃ (194.23): C 68.02, H 7.27; found: C 67.85, H, 6.94.

Isopropyl 2-(but-1-enyl)furan-3-carboxylate (5b): The reaction of **3c** (425 mg, 0.91 mmol) with *n*BuLi (0.91 mmol) and propionaldehyde (**4b**) (53 mg, 0.91 mmol) was carried out as described in procedure A (reaction time 25 h). After purification by column chromatography (*n*-pentane/diethyl ether = 50:1), **5b** was isolated as a yellow oil (118 mg, 62%, *E/Z* = 6:1); *R*_f = 0.36. ¹H NMR (250 MHz, CDCl₃, isomeric mixture): δ = 1.10 (t, ³*J* = 7 Hz, 3H, CH₃), 1.32 (d, ³*J* = 6 Hz, 6H, 2 x CH₃), 2.27 (dq, ³*J* = 7 Hz, ³*J* = 6 Hz, 1H, CH, *E*-isomer), 2.58 (dq, ³*J* = 6 Hz, ³*J* = 7 Hz, 1H, CH, *Z*-isomer), 5.16 (sept, ³*J* = 6 Hz, 1H, OCH(CH₃)₂), 5.80 (dt, ³*J* = 12 Hz, ³*J* = 7 Hz, 1H, H_{etar}-CH=CH, *Z*-isomer), 6.53 (dt, ³*J* = 16 Hz, ³*J* = 7 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 6.67 (d, ³*J* = 1 Hz, 1H, H-4, H_{etar}, *E*-isomer), 6.70 (d, ³*J* = 2 Hz, 1H, H-4, H_{etar}, *Z*-isomer), 6.86 (d, ³*J* = 12 Hz, 1H, H_{etar}-CH=CH, *Z*-isomer), 6.95 (d, ³*J* = 16 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 7.21 (d, ³*J* = 1 Hz, 1H, H-5, H_{etar}, *E*-isomer), 7.31 (d, ³*J* = 2 Hz, 1H, H-5, H_{etar}, *Z*-isomer). ¹³C NMR (50.3 MHz, CDCl₃, *E*-isomer): δ = 12.9, 21.9, 26.02, 67.6, 111.4, 112.8, 116.9, 137.3, 140.5, 156.9, 163.2. IR (neat, cm⁻¹): $\tilde{\nu}$ = 2978 (m), 2868 (m), 1713 (m), 1654 (m), 1569 (m), 1381 (m), 1298 (m), 1183 (m), 1119 (s), 1049 (m), 1021 (m), 974 (w), 841 (w), 743 (w). MS (EI, 70 eV): *m/z* (%) = 208 (M⁺, 6), 91 (33), 77 (31), 51 (35), 43 (100). Anal. calcd for C₁₂H₁₆O₃ (208.26): C 69.21, H 7.74; found: C 68.91, H 7.78.

Isopropyl 2-(penta-1,3-dienyl)furan-3-carboxylate (5c): The reaction of **3c** (421 mg, 0.90 mmol) with *n*BuLi (0.90 mmol) and crotonaldehyde (**4c**) (63 mg, 0.90 mmol) was carried out as described in procedure A (reaction time 4 h). After purification by column chromatography (*n*-pentane/diethyl ether = 50:1), **5c** was isolated as a yellow oil (58 mg, 29%, *E/Z* = 10:1); *R*_f = 0.35. The products are not stable on exposure to the air. ¹H NMR (250 MHz, CDCl₃, *E*-isomer): δ = 1.33 (d, ³*J* = 6 Hz, 6H, CH₃), 1.84 (d, ³*J* = 7 Hz, 6H, CH₃), 5.17 (sept, ³*J* = 6 Hz, 1H, OCH(CH₃)₂), 5.96 (dq, ³*J* = 15 Hz, ³*J* = 7 Hz, 1H, CH=CH),

6.15 – 6.39 (m, 1H, CH=CH), 6.68 (d, $^3J = 2$ Hz, 1H, H-4, Hetar), 6.80 – 7.00 (m, 2H, CH=CH), 7.24 (d, $^3J = 2$ Hz, 1H, H-5, Hetar). ^{13}C -NMR (50.3 MHz, CDCl_3 , *E*-isomer): $\delta = 18.5, 22.0, 67.7, 111.8, 113.9, 116.7, 131.6, 132.9, 133.7, 140.8, 157.0, 163.2$. IR (neat, cm^{-1}): $\tilde{\nu} = 2980$ (s), 2935 (s), 2872 (s), 1714 (s), 1452 (m), 1380 (s), 1301 (s), 1183 (s), 1108 (s), 1026 (s), 839 (m), 758 (m), 739 (m), 602 (w). MS (EI, 70 eV): m/z (%) = 220 (M^+ , 100), 133 (85), 105 (54). Anal. calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$ (220.27): C 70.89, H 7.32; found: C 70.67, H 7.08.

Isopropyl 2-(2-cyclohex-3-enylvinyl)furan-3-carboxylate (5d): The reaction of **3c** (460 mg, 0.99 mmol) with *n*BuLi (0.99 mmol) and (cyclohex-3-ene)carbaldehyde (**4d**) (110 mg, 0.99 mmol) was carried out as described in procedure A (reaction time 4 h). After purification by column chromatography (*n*-pentane/diethyl ether = 50:1), **5d** was isolated as a yellow oil (158 mg, 61%, *E/Z* = 10:1); $R_f = 0.35$. ^1H NMR (250 MHz, CDCl_3 , *E*-isomer): $\delta = 1.33$ (d, $^3J = 6$ Hz, 6H, 2 x CH_3), 1.40 – 1.60 (m, 1H, CH_2), 1.80 – 2.05 (m, 2H, CH_2), 2.05 – 2.25 (m, 3H, CH_2), 2.40 – 2.55 (m, 1H, CH), 5.17 (sept, $^3J = 6$ Hz, 1H, $\text{OCH}(\text{CH}_3)_2$), 5.60 – 5.80 (m, 2H, CH=CH), 6.51 (dd, $^3J = 16$ Hz, $^3J = 7$ Hz, 1H, CH=CH), 6.67 (d, $^3J = 2$ Hz, 1H, H-4, Hetar), 6.98 (d, $^3J = 16$ Hz, 1H, CH=CH), 7.23 (d, $^3J = 2$ Hz, 1H, H-5, Hetar). ^{13}C NMR (50.3 MHz, CDCl_3 , *E*-isomer): $\delta = 22.0, 24.6, 28.2, 30.8, 37.0, 67.7, 111.5, 113.2, 116.1, 125.7, 127.0, 140.2, 140.6, 156.8, 163.24$. IR (neat, cm^{-1}): $\tilde{\nu} = 2980$ (m), 2918 (m), 1709 (s), 1651 (m), 1568 (m), 1508 (m), 1431 (m), 1299 (m), 1177 (s), 1109 (s), 1050 (m), 1021 (m), 974 (m), 740 (m), 655 (w). MS (EI, 70 eV): m/z (%) = 260 (M^+ , 27), 138 (66), 119 (85), 91 (81), 80 (100), 41 (42). HRMS (EI, 70 eV): calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ (M^+) 260.1412, found 260.1412 ± 2 ppm.

Isopropyl 2-(2-phenylvinyl)furan-3-carboxylate (5e): The reaction of **3c** (496 mg, 1.07 mmol) with *n*BuLi (1.07 mmol) and benzaldehyde (**4e**) (113 mg, 1.07 mmol) was carried

out as described in procedure A (reaction time 4 h). After purification by column chromatography (*n*-pentane/diethyl ether = 50:1), **5e** was isolated as an orange oil (197 mg, 67%, *E/Z* > 98:2, contains 6% of benzaldehyde); R_f = 0.35. ^1H NMR (250 MHz, CDCl_3 , *E*-isomer): δ = 1.38 (d, 3J = 6 Hz, 6H, 2 x CH_3), 5.22 (sept, 3J = 6 Hz, 1H, $\text{OCH}(\text{CH}_3)_2$), 6.74 (d, 3J = 2 Hz, 1H, H-4, H_{et}ar), 7.25 – 7.45 (m, 5H, $\text{CH}=\text{CH}$, Ph, H-5, H_{et}ar), 7.50 – 7.60 (m, 2H, Ph), 7.69 (d, 3J = 15 Hz, 1H, $\text{CH}=\text{CH}$). ^{13}C NMR (75.5 MHz, CDCl_3 , *E*-isomer): δ = 22.0, 67.9, 112.0, 114.8, 115.5, 128.5, 131.9, 127.0, 128.7, 136.4, 141.2, 157.0, 163.1. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2980 (m), 2927 (m), 1708 (s), 1634 (m), 1562 (m), 1450 (m), 1296 (s), 1182 (s), 1108 (s), 1054 (s), 1024 (s), 743 (s), 694 (m), 599 (w). MS (EI, 70 eV): m/z (%) = 256 (M^+ , 100), 214 (44). HRMS (EI): calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3$ (M^+) 256.1099, found 256.1099 ± 2 ppm.

6-Chloro-3-hydroxyhexa-2,4-dienoic acid pyrrolidide (3e'). From the acetone fraction was isolated **3e'** (107 mg, 32%) as a greenish liquid. ^1H NMR (250 MHz, CDCl_3): δ = 1.80 – 2.05 (m, 4 H, CH_2), 3.30 – 3.55 (m, 4 H, N- CH_2), 4.17 (d, 3J = 7 Hz, 2 H, Cl- CH_2), 5.09 (s, 1 H, CH, Enol), 6.06 (d, $^3J(E)$ = 15 Hz, 1 H, CH, $\text{CH}=\text{CH}$), 6.63 (dt, $^3J(E)$ = 15 Hz, 3J_t = 7 Hz, 1 H, CH, $\text{CH}=\text{CH}$). ^{13}C NMR (50.3 MHz, CDCl_3): δ = 24.4, 25.7 (CH_2), 43.7 (Cl- CH_2), 45.2, 46.2 (N- CH_2), 92.0 (CH, enol), 128.5, 132.0 (CH, $\text{CH}=\text{CH}$), 166.6, 170.0 (C, =C-O, CO, amide). IR (neat, cm^{-1}): $\tilde{\nu}$ = 3442 (m), 2978 (m), 2869 (s), 1631 (m), 1606 (m), 1448 (m), 1297 (m), 1123 (s), 1076 (m), 843 (w), 790 (w). MS (EI, 70 eV): 215 [M^+] (22), 180 (52), 166 (26), 70 (100). MS (CI, NH_3 , 70 eV): 233 [$(\text{M}+\text{NH}_4)^+$] (22), 216 [$(\text{M}+\text{H})^+$] (100), 182 (60).

Isopropyl 2-[2-(3-methylphenyl)vinyl]furan-3-carboxylate (5f): The reaction of **3c** (422 mg, 0.91 mmol) with *n*BuLi (0.91 mmol) and 3-methylbenzaldehyde (**4f**) (120 mg, 0.91 mmol) was carried out as described in procedure A (reaction time 24 h). After purification by column chromatography (*n*-pentane/diethyl ether = 50:1), **5f** was isolated as a yellow oil (192 mg, 53%, *E/Z* > 98:2); R_f = 0.28. ^1H NMR (250 MHz, CDCl_3 , *E*-isomer): δ =

1.38 (d, $^3J = 6$ Hz, 6H, 2 x CH₃), 2.38 (s, 3H, CH₃), 5.22 (sept, $^3J = 6$ Hz, 1H, OCH(CH₃)₂), 6.74 (d, $^3J = 2$ Hz, 1H, H-4, Hetar), 7.11 (d, $^3J = 2$ Hz, 1H, Ar), 7.20 – 7.40 (m, 5H, CH=CH, H-5, Hetar, Ar), 7.68 (d, $^3J = 16$ Hz, 1 H, CH=CH). ¹³C NMR (50.3 MHz, CDCl₃, *E*-isomer): $\delta = 21.4, 22.0, 67.8, 111.9, 114.6, 115.3, 124.3, 127.5, 128.6, 129.3, 132.1, 136.4, 138.3, 141.2, 156.9, 163.2$. IR (neat, cm⁻¹): $\tilde{\nu} = 2981$ (m), 2931 (w), 1708 (s), 1635 (m), 1563 (m), 1298 (s), 1266 (m), 1181 (s), 1055 (s), 1025 (s), 970 (m), 786 (m), 741 (m). MS (EI, 70 eV): m/z (%) = 270 (M⁺, 100), 228 (27), 183 (29), 182 (24), 155 (30), 153 (22). HRMS (EI): calcd for C₁₇H₁₈O₃ (M⁺) 270.1256, found 270.1256 $\pm$ 2 ppm.

Isopropyl 2-[2-(4-methoxyphenyl)vinyl]furan-3-carboxylate (5g): The reaction of **3c** (419 mg, 0.90 mmol) with *n*BuLi (0.90 mmol) and 4-methoxybenzaldehyde (**4g**) (123 mg, 0.90 mmol) was carried out as described in procedure A (reaction time 22.5 h). After purification by column chromatography (*n*-pentane/diethyl ether = 25:1), **5g** could be isolated as an orange oil (171 mg, 66%, *E/Z* > 98:2); $R_f = 0.24$. ¹H NMR (250 MHz, CDCl₃, *E*-isomer): $\delta = 1.37$ (d, $^3J = 6$ Hz, 6H, 2 x CH₃), 3.84 (s, 3H, OCH₃), 5.21 (sept, $^3J = 6$ Hz, 1H, OCH(CH₃)₂), 6.73 (d, $^3J = 2$ Hz, 1H, H-4, Hetar), 6.90 (d, $^3J = 9$ Hz, 2H, Ar), 7.25 (d, $^3J = 16$ Hz, 1H, CH=CH), 7.30 (d, $^3J = 2$ Hz, 1H, H-5, Hetar), 7.49 (d, $^3J = 9$ Hz, 2H, Ar), 7.55 (d, $^3J = 16$ Hz, 1H, CH=CH). ¹³C NMR (75.5 MHz, CDCl₃, *E*-isomer): $\delta = 22.0, 55.3, 67.74, 111.8, 113.5, 131.6, 113.9, 114.2, 128.3, 129.2, 140.8, 157.1, 156.0, 163.2$. IR (neat, cm⁻¹): $\tilde{\nu} = 2981$ (m), 2936 (m), 2838 (w), 1705 (s), 1604 (s), 1561 (s), 1513 (s), 1297 (s), 1252 (s), 1177 (s), 1108 (s), 1053 (s), 1026 (s), 970 (m), 823 (m), 741 (m), 524 (w). MS (EI, 70 eV): m/z (%) = 286 (M⁺, 100), 244 (74). Anal. calcd for C₁₇H₁₈O₄ (286.33): C 71.31, H 6.34; found: C 71.05, H, 6.02.

Isopropyl 2-[2-(3,4-dimethoxyphenyl)vinyl]furan-3-carboxylate (5h): The reaction of **3c** (411 mg, 0.88 mmol) with *n*BuLi (0.88 mmol) and 3,4-dimethoxybenzaldehyde (**4h**) (150 mg,

0.88 mmol) was carried out as described in procedure A (reaction time 25 h). After purification by column chromatography (*n*-pentane/diethyl ether = 5:1), **5h** was isolated as a yellow oil (204 mg, 73%, *E/Z* > 98:2; *R*_f = 0.25. ¹H NMR (250 MHz, CDCl₃, *E*-isomer): δ = 1.37 (d, ³*J* = 6 Hz, 6H, 2 x CH₃), 3.90 (s, 3H, OCH₃), 3.93 (s, 3H, OCH₃), 5.20 (sept, ³*J* = 6 Hz, 1H, OCH(CH₃)₂), 6.73 (d, ³*J* = 2 Hz, 1H, H-4, Hetar), 6.85 (d, ³*J* = 9 Hz, 1H, Ar), 7.10 – 7.20 (m, 2H, Ar), 7.24 (d, ³*J* = 16 Hz, 1H, CH=CH), 7.29 (d, ³*J* = 2 Hz, 1H, H-5, Hetar) 7.55 (d, ³*J* = 16 Hz, 1H, CH=CH). ¹³C NMR (75.5 MHz, CDCl₃, *E*-isomer): δ = 22.0, 55.8, 55.9, 67.7, 108.6, 111.1, 113.7, 121.0, 131.9, 111.9, 114.0, 129.5, 140.9, 149.1, 149.6, 157.0, 163.2. IR (neat, cm⁻¹): $\tilde{\nu}$ = 2979 (m), 2936 (w), 1705 (s), 1590 (m), 1515 (s), 1463 (m), 1420 (m), 1301 (s), 1267 (s), 1181 (m), 1140 (m), 1109 (m), 1025 (s), 967 (w), 805 (w), 744 (w), 599 (w). MS (EI, 70 eV): *m/z* (%) = 316 (M⁺, 100), 274 (28). Anal. calcd for C₁₈H₂₀O₅ (316.35): C 68.34, H 6.37; found: C 68.04, H 6.01.

Isopropyl 2-[2-(4-dimethylaminophenyl)vinyl]furan-3-carboxylate (5i): The reaction of **3c** (429 mg, 0.92 mmol) with *n*BuLi (0.92 mmol) and 4-dimethylaminobenzaldehyde (**4i**) (145 mg, 0.99 mmol, 1.1 equiv) was carried out as described in procedure A (reaction time 24 h). After purification by column chromatography (*n*-pentane/diethyl ether = 10:1), **5i** was isolated as a yellow solid (204 mg, 54%, *E/Z* > 98:2; *R*_f = 0.25. ¹H NMR (250 MHz, CDCl₃, *E*-isomer): δ = 1.37 (d, ³*J* = 6 Hz, 6H, 2 x CH₃), 3.00 (s, 6H, N(CH₃)₂), 5.21 (sept, ³*J* = 6 Hz, 1H, OCH(CH₃)₂), 6.70 (d, ³*J* = 9 Hz, 2H, Ar), 6.71 (d, ³*J* = 2 Hz, 1H, H-4, Hetar), 7.25 (d, ³*J* = 16 Hz, 1H, CH=CH), 7.27 (d, ³*J* = 2 Hz, 1H, H-5, Hetar), 7.45 (d, ³*J* = 9 Hz, 2H, Ar), 7.48 (d, ³*J* = 16 Hz, 1H, CH=CH). ¹³C NMR (75.5 MHz, CDCl₃, *E*-isomer): δ = 22.0, 40.2, 67.5, 111.2, 132.5, 111.7, 112.1, 128.3, 112.8, 124.5, 140.4, 150.6, 157.9, 163.4. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 2978 (w), 2936 (w), 2895 (w), 1700 (s), 1600 (s), 1566 (s), 1524 (s), 1356 (s), 1296 (s), 1179 (s), 1106 (s), 1053 (m), 1023 (m), 815 (m), 742 (m), 525 (w). MS (EI, 70 eV): *m/z* (%)

= 299 (M^+ , 100), 257 (90). Anal. calcd for $C_{18}H_{21}NO_3$ (299.36): C 72.22, H 7.07, N 4.68; found: C 71.98, H 6.88, N 4.47.

Isopropyl 2-[2-(3-chlorophenyl)vinyl]furan-3-carboxylate (5j): The reaction of **3c** (437 mg, 0.94 mmol) with *n*BuLi (0.94 mmol) and 3-chlorobenzaldehyde (**4j**) (132 mg, 0.94 mmol) was carried out as described in procedure A (reaction time 18 h). After purification by column chromatography (*n*-pentane/diethyl ether = 50:1), **5j** was isolated as a red oil (147 mg, 54%, *E/Z* = 10:1); R_f = 0.40. 1H NMR (250 MHz, $CDCl_3$, *E*-isomer): δ = 1.38 (d, 3J = 6 Hz, 6H, 2 x CH_3), 5.12 (sept, 3J = 6 Hz, 1H, $OCH(CH_3)_2$), 6.75 (d, 3J = 2 Hz, 1H, H-4, H_{et}ar), 7.15 – 7.40 (m, 5H, $CH=CH$, Ar, H-5, H_{et}ar), 7.52 (s, 1H, Ar), 7.68 (d, 3J = 16 Hz, 1H, $CH=CH$). ^{13}C NMR (75.5 MHz, $CDCl_3$, *E*-isomer): δ = 22.0, 68.0, 112.0, 115.4, 116.7, 130.2, 125.1, 126.7, 128.3, 129.9, 134.7, 138.3, 141.6, 156.1, 163.0. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3069 (w), 2981 (s), 2936 (m), 1714 (s), 1591 (s), 1570 (s), 1472 (s), 1427 (s), 1300 (s), 1184 (s), 1108 (s), 1056 (s), 1024 (s), 967 (s), 743 (s), 690 (s), 602 (m), 435 (w). MS (EI, 70 eV): m/z (%) = 290 (M^+ , 100), 248 (44), 139 (38). Anal. calcd for $C_{16}H_{15}ClO_3$ (290.75): C 66.10, H 5.20; found: C 66.01, H 4.99.

Isopropyl 2-[2-(3-nitrophenyl)vinyl]furan-3-carboxylate (5k): The reaction of **3c** (440 mg, 0.95 mmol) with *n*BuLi (0.95 mmol) and 3-nitrobenzaldehyde (**4k**) (151 mg, 1.00 mmol, 1.05 equiv) was carried out as described in procedure A (reaction time 18 h). After purification by column chromatography (*n*-pentane/diethyl ether = 20:1), **5k** was isolated as a yellow solid (171 mg, 60%, *E/Z* = 12:1); R_f = 0.23. 1H NMR (250 MHz, $CDCl_3$, *E*-Isomer): δ = 1.39 (d, 3J = 6 Hz, 6H, 2 x CH_3), 5.23 (sept, 3J = 6 Hz, 1H, $OCH(CH_3)_2$), 6.77 (d, 3J = 2 Hz, 1H, H-4, H_{et}ar), 7.31 (d, 3J = 16 Hz, 1H, $CH=CH$), 7.38 (d, 3J = 2 Hz, 1H, H-5, H_{et}ar), 7.54 (dd, 3J = 3J = 8 Hz, 1H, Ar), 7.80 (d, 3J = 16 Hz, 1H, $CH=CH$), 7.85 (dd, 3J = 8 Hz, 4J = 2 Hz, 1H, Ar), 8.13 (dd, 3J = 8 Hz, 4J = 2 Hz, 1H, Ar), 8.36 (dd, 3J = 3J = 2 Hz, 1H, Ar). ^{13}C NMR

(75.5 MHz, CDCl_3 , *E*-Isomer): δ = 21.96, 68.2, 112.1, 116.2, 138.2, 118.1, 128.9, 121.5, 122.7, 129.6, 132.3, 142.0, 148.7, 155.5, 162.8. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2979 (m), 2922 (w), 2854 (w), 1709 (s), 1638 (m), 1532 (s), 1352 (s), 1301 (m), 1185 (m), 1110 (m), 1055 (m), 1025 (m), 967 (w), 736 (m). MS (EI, 70 eV): m/z (%) = 301 (M^+), 259 (100), 242 (21), 139 (22). Anal. calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_5$ (301.30): C 63.78, H 5.02, N 4.65; found: C 63.96, H 4.79, N, 4.52.

Isopropyl (2-(2-pyrid-3-yl)vinyl)furan-3-carboxylate (5l): The reaction of **3c** (450 mg, 0.97 mmol) with *n*BuLi (0.97 mmol) and pyridine-3-carbaldehyde (**4l**) (103 mg, 0.97 mmol) was carried out as described in procedure A (reaction time 4 h). After purification by column chromatography (*n*-pentane/diethyl ether = 1.5:1), **5l** was isolated as a red oil (184 mg, 74%, *E/Z* = 10:1); R_f = 0.26. ^1H (250 MHz, CDCl_3 , isomeric mixture) δ = 1.35 (d, 3J = 6 Hz, 6H, 2 x CH_3), 5.20 (sept, 3J = 6 Hz, 1H, $\text{OCH}(\text{CH}_3)_2$), 6.64 (d, 3J = 12 Hz, 1H, $\text{CH}=\text{CH}$, *Z*-isomer), 6.71 (d, 3J = 2 Hz, 1H, H-4, Hetar, *Z*-isomer), 5.74 (d, 3J = 2 Hz, 1H, H-4, Hetar, *E*-isomer), 7.20 – 7.40 (m, 3H, Py, Hetar), 7.72 (d, 3J = 16 Hz, 1H, $\text{CH}=\text{CH}$, *E*-isomer), 7.85 (d, 3J = 8 Hz, 1H, Py), 8.49 (d, 3J = 8 Hz, 1H, Py), 8.62 (s, 1H, Py, *Z*-isomer), 8.71 (d, 4J = 2 Hz, 1H, Py, *E*-isomer). ^{13}C (50.3 MHz, CDCl_3 , *E*-Isomer) δ = 22.0, 68.1, 112.1, 115.6, 117.4, 123.6, 127.9, 128.4, 149.0, 149.2, 132.2, 141.7, 155.8, 162.9. IR (neat, cm^{-1}): $\tilde{\nu}$ = 2981 (m), 1708 (s), 1637 (m), 1561 (m), 1504 (w), 1424 (m), 1304 (m), 1265 (m), 1184 (s), 1108 (s), 1056 (m), 1024 (m), 970 (m), 747 (m), 707 (w). MS (EI, 70 eV): m/z (%) = 257 (M^+ , 71), 170 (100), 142 (44), 141 (52). HRMS (EI): calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$ (M^+) 257.1052, found 257.1052 $\pm$ 2 ppm.

((2-Pent-1-enyl)furan-3-yl)phenylmethanone (5m): The reaction of **3g** (159 mg, 0.33 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (29 mg, 0.40 mmol) was carried out as described in procedure B yielding **5m** as a colourless oil (11 mg, 12%, *E/Z* =

3:1). ^1H NMR (300 MHz, CDCl_3 , isomeric mixture): δ = 0.94 (t, 3J = 7.4 Hz, 3H, CH_3), 1.49 (tq, 3J = 7.4 Hz, 2H, CH_2), 2.21 (dt, 3J = 7.4 Hz, 2H, CH_2), 6.57 (dt, 3J = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 6.60 (d, 3J = 1.9 Hz, 1H, H_{etar}), 6.77 (d, 3J = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 7.29 (d, 3J = 1.9 Hz, 1H, Ph), 7.38–7.58 (m, 3H, Ph), 7.80 (d, 3J = 6.9 Hz, 2H, Ph). IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2961 (m), 2929 (m), 1725 (w), 1650 (s), 1600 (m), 1574 (w), 1549 (m), 1503 (m), 1449 (m), 1406 (m). UV-VIS (CH_3CN , nm): λ_{max} (log ϵ) = 251.15 (4.01). MS (EI, 70 eV): m/z (%) = 240.0 (M^+ , 18), 198 (15), 197 (100), 105 (31), 77 (35). HRMS (EI, 70 eV): calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$ ($[\text{M}+1]^+$) 240.1150, found 240.1150 ± 2 ppm.

Phenyl-[2-(2-phenylvinyl)furan-3-yl]methanone (5n): The reaction of **3g** (358 mg, 0.74 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (106 mg, 1.00 mmol) was carried out as described in procedure B yielding **5n** as a colourless oil (122 mg, 60%, *E/Z* > 98:2). ^1H NMR (300 MHz, CDCl_3 , *E*-isomer): δ = 6.61 (d, $^3J_{\text{cis}}$ = 1.9 Hz, 1H, H-3, H_{etar}), 7.18–7.83 (m, 13H, H_{etar}, Ph, CH=CH). ^{13}C NMR (75 MHz, CDCl_3 , *E*-isomer): δ = 113.3, 115.9, 121.3, 127.3, 128.6, 128.8, 128.9, 129.2, 129.3, 133.0, 136.5, 139.3, 141.3, 157.4, 191.0. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3062 (w), 3027 (w), 1701 (m), 1650 (s), 1600 (m), 1578 (m), 1544 (m), 1502 (m), 1478 (m), 1407 (m). UV-VIS (CH_3CN , nm): λ_{max} (log ϵ) = 248.32 (4.16), 255.81 (4.16), 354.71 (4.24). MS (EI, 70 eV): m/z (%) = 274 (M^+ , 100), 273 (23), 197 (36), 114 (18), 105 (60), 77 (67), 51 (15). HRMS (EI, 70 eV): calcd for $\text{C}_{19}\text{H}_{14}\text{O}_2$ ($[\text{M}+1]^+$) 274.0994, found 274.0994 ± 2 ppm.

2-(2-Phenylvinyl)furan-3-carboxamide (5o): The reaction of **3d** (430 mg, 1.02 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (127 mg, 1.20 mmol) was

carried out as described in procedure B yielding **5o** as a colourless oil (52 mg, 24%, *E/Z* = > 98:2). ^1H NMR (600 MHz, CDCl_3 , *E*-isomer): δ = 3.86 (s, 2H, NH_2), 6.73 (d, $^3J_{\text{cis}}$ = 1.8 Hz, 1H, H-4, Hetar), 7.28–7.37 (m, 5H, Hetar, Ph, $\text{CH}=\text{CH}$), 7.54 (d, 3J = 7.8 Hz, 2H, Ph), 7.65 (d, $^3J_{\text{trans}}$ = 16.8 Hz, 1H, $\text{CH}=\text{CH}$). ^{13}C NMR (75 MHz, CDCl_3 , *E*-isomer): δ = 112.0, 114.2, 115.5, 127.2, 128.8, 128.9, 132.5, 136.5, 141.6, 157.2, 164.2. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3151 (w), 3131 (w), 3064 (m), 3024 (m), 2951 (m), 1710 (s), 1633 (s), 1565 (s), 1502 (m), 1430 (s), 1411 (m). UV-VIS (CH_3CN , nm): λ_{max} (log ϵ) = 228.41 (4.01), 328.64 (4.31), 336.96 (4.31). MS (EI, 70 eV): m/z (%) = 213 (M^+ , 1), 197 (16), 169 (26), 168 (46), 141 (80), 140 (69), 139 (69), 114 (46).

Methyl 4-methyl-2-(pent-1-enyl)furan-3-carboxylate (5p): The reaction of **3h** (260 mg, 0.58 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (86 mg, 1.20 mmol) was carried out as described in procedure B yielding **5p** as a colourless oil (74 mg, 60%, *E/Z* = 4:1). ^1H NMR (300 MHz, CDCl_3 , isomeric mixture): δ = 0.95 (t, 3J = 7.1 Hz, 3H, CH_3), 1.50 (tq, 3J = 7.1 Hz, 2H, CH_2), 2.13 (s, 3H, CH_3), 2.21 (dt, 3J = 7.1 Hz, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.47 (dt, $^3J_{\text{trans}}$ = 16.0 Hz, 3J = 7.1 Hz, 1H, Hetar- $\text{CH}=\text{CH}$, *E*-isomer), 6.92 (d, $^3J_{\text{trans}}$ = 16.0 Hz, 1H, Hetar- $\text{CH}=\text{CH}$, *E*-isomer), 7.09 (s, 1H, Hetar). ^{13}C NMR (75 MHz, CDCl_3 , isomeric mixture): 10.1, 13.9, 22.3, 35.2, 51.1, 112.3, 118.5, 121.8, 135.8, 138.3, 157.8, 164.9. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2960 (m), 2931 (m), 2871 (w), 1715 (s), 1649 (w), 1594 (w), 1530 (m), 1438 (m), 1403 (w). UV-VIS (CH_3CN , nm): λ_{max} (log ϵ) = 297.19 (4.11). MS (EI, 70 eV): m/z (%) = 208 (M^+ , 14), 148 (16), 43 (18), 28 (100). HRMS (EI, 70 eV): calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ ($[\text{M}+1]^+$) 208.1099, found 208.1099 ± 2 ppm.

Ethyl 4-methyl-2-(2-phenylvinyl)furan-3-carboxylate (5q): The reaction of **3i** (664 mg, 1.43 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (155 mg, 1.46 mmol) was carried out as described in procedure B yielding **5q** as a colourless oil (225 mg, 61%, *E/Z* = > 98:2). ¹H NMR (300 MHz, CDCl₃, *E*-isomer): δ = 1.41 (t, ³*J* = 7.1 Hz, 3H, OCH₂CH₃), 2.18 (s, 3H, CH₃), 4.35 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 7.14 (d, ⁴*J* = 1.2 Hz, 1H, H_{et}ar), 7.23–7.38 (m, 5H, CH=CH, Ph, H_{et}ar), 7.52–7.54 (m, 1H, CH=CH, Ph, H_{et}ar), 7.66 (d, ³*J* = 16.4 Hz, 1H, CH=CH, Ph, H_{et}ar). ¹³C NMR (75 MHz, CDCl₃, *E*-isomer): δ = 10.2, 14.5, 60.3, 114.5, 116.2, 122.5, 127.1, 128.5, 128.9, 131.8, 136.7, 139.1, 157.7, 164.4. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3064 (w), 3026 (w), 2980 (m), 2931 (w), 2904 (w), 1710 (s), 1671 (w), 1632 (m), 1592 (m), 1529 (m), 1493 (w), 1471 (w), 1448 (m), 1408 (m). UV-VIS (CH₃CN, nm): λ_{max} (log ε) = 333.29 (4.32), 228.80 (4.12). MS (EI, 70 eV): *m/z* (%) = 256 (M⁺, 100), 183 (15), 155 (22), 154 (30), 152 (30), 44 (57). Anal. calcd for C₁₆H₁₆O₃ (256.30): C 74.98, H 6.29; found: C 75.04, H 6.26.

Ethyl 4-methyl-2-(pent-1-enyl)furan-3-carboxylate (5r): The reaction of **3i** (300 mg, 0.65 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (58 mg, 0.80 mmol) was carried out as described in procedure B yielding **5r** as a colourless oil (101 mg, 70%, *E/Z* = 4:1). ¹H NMR (300 MHz, CDCl₃, isomeric mixture): δ = 0.88 (t, ³*J* = 7.3 Hz, 3H, CH₃), 1.29 (t, ³*J* = 7.1 Hz, 3H, OCH₂CH₃), 1.43 (tq, ³*J* = 7.3 Hz, 2H, CH₂), 2.07 (d, ⁴*J* = 1.2 Hz, 3H, CH₃), 2.14 (dt, ³*J* = 7.1 Hz, 2H, CH₂), 4.23 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 6.38 (dt, ³*J*_{trans} = 16.0 Hz, ³*J* = 7.3 Hz, 1H, H_{et}ar-CH=CH, *E*-isomer), 6.86 (d, ³*J*_{trans} = 16.0 Hz, 1H, H_{et}ar-CH=CH, *E*-isomer), 6.96 (d, ⁴*J* = 1.2 Hz, 1H, H_{et}ar). ¹³C NMR (150 MHz, CDCl₃, isomeric mixture): δ = 10.3, 13.9, 14.5, 22.4, 35.3, 60.2, 112.7, 116.7, 122.0, 135.7, 138.4, 158.0, 164.7. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 2963 (m), 2931 (m), 2871 (w), 1710

(s), 1650 (w), 1594 (w), 1530 (m), 1457 (w), 1412 (m). UV-VIS (CH₃CN, nm): $\lambda_{\max}$ (log ϵ) = 296.94 (4.09). MS (EI, 70 eV): m/z (%) = 222 (M⁺, 100), 193 (64), 180 (16), 177 (16), 175 (31), 148 (19), 147 (18), 147 (52), 120 (15), 119 (25), 93 (17), 91 (60), 77 (32), 66 (20). HRMS (EI, 70 eV): calcd for C₁₃H₁₈O₃ ([M+1]⁺) 222.1256, found 222.1256 $\pm$ 2 ppm.

Isopropyl 4-methyl-2-(pent-1-enyl)furan-3-carboxylate (5s): The reaction of **3j** (330 mg, 0.69 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (162 mg, 0.69 mmol) was carried out as described in procedure B yielding **5s** as a colourless oil (56 mg, 33%, *E/Z* = 4:1). ¹H NMR (300 MHz, CDCl₃, isomeric mixture): δ = 0.95 (t, ³*J* = 7.3 Hz, 3H, CH₃), 1.33 (d, ⁴*J* = 2.2 Hz, 6H, CH(CH₃)₂), 1.50 (tq, ³*J* = 7.3 Hz, 2H, CH₂), 2.14 (d, ⁴*J* = 1.1 Hz, 3H, CH₃), 2.21 (dt, ³*J* = 7.3 Hz, 2H, CH₂), 5.18 (sep, ³*J* = 6.1 Hz, 1H, CH(CH₃)₂), 6.45 (dt, ³*J*_{trans} = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 6.94 (d, ³*J*_{trans} = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 7.03 (d, ⁴*J* = 1.1 Hz, 1H, H_{etar}). ¹³C NMR (50 MHz, CDCl₃, isomeric mixture): δ = 10.2, 13.9, 22.1, 31.7, 35.2, 67.4, 112.8, 118.5, 121.8, 135.4, 138.2, 157.7, 164.0. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 2963 (m), 2931 (m), 2872 (m), 1707 (s), 1650 (m), 1593 (w), 1530 (m), 1460 (m), 1409 (m). UV-VIS (CH₃CN, nm): $\lambda_{\max}$ (log ϵ) = 269.41 (4.12). MS (EI, 70 eV): m/z (%) = 236 (M⁺, 36), 194 (32), 193 (52), 177 (16), 165 (39), 147 (42), 139 (21), 119 (19), 91 (57), 77 (30), 66 (20), 43 (29), 41 (23), 39 (16), 32 (20), 28 (100). HRMS (EI, 70 eV): calcd for C₁₄H₂₀O₃ ([M+1]⁺) 236.1412, found 236.1412 $\pm$ 2 ppm. Anal. calcd for C₁₄H₂₀O₃ (236.31): C 71.16, H 8.53; found: C 71.05, H 8.85.

(4-Methyl-2-pent-1-enylfuran-3-yl)phenylmethanone (5t): The reaction of **3k** (300 mg, 0.60 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (58 mg, 0.80 mmol) was carried out as described in procedure B yielding **5t** as a yellow oil (25 mg, 15%, *E/Z* = 3:1). ¹H NMR (300 MHz, CDCl₃, isomeric mixture): δ = 0.96 (t, ³*J* = 7.2 Hz, 3H, CH₃), 1.35 (tq, ³*J* = 7.2 Hz, 2H, CH₂), 1.95 (d, ⁴*J* = 1.2 Hz, 3H, CH₃), 2.02 (dt, ³*J* = 7.2 Hz, 2H, CH₂), 6.57 (dt, ³*J*_{trans} = 16.0 Hz, ³*J* = 7.2 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 7.23 (d, ⁴*J* = 1.2 Hz, 1H, H_{etar}), 7.38–7.65 (m, 5H, Ph), 7.80 (d, ³*J*_{trans} = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer). ¹³C NMR (150 MHz, CDCl₃, isomeric mixture): δ = 3.6, 13.9, 22.3, 35.3, 119.6, 128.5, 128.6, 129.7, 129.8, 132.4, 132.2, 139.4, 140.6, 157.6, 191.2. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3444 (w), 3152 (w), 3062 (w), 2950 (s), 2871 (m), 1809 (w), 1650 (s), 1599 (m), 1547 (m), 1502 (m), 1406 (m). UV-VIS (CH₃CN, nm): λ_{max} (log ε) = 251.95 (4.08). MS (EI, 70 eV): *m/z* (%) = 254 (M⁺, 3), 240 (20), 211 (16), 196 (100), 104 (49), 77 (53), 43 (41).

Ethyl 4-*tert*-butyl-2-(pent-1-enyl)furan-3-carboxylate (5u): The reaction of **3m** (388 mg, 0.77 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (61 mg, 0.85 mmol) was carried out as described in procedure B yielding **5u** as a colourless oil (12 mg, 5%, *E/Z* = 6:1). ¹H NMR (300 MHz, CDCl₃, isomeric mixture): δ = 0.95 (t, ³*J* = 7.3 Hz, 3H, CH₃) 1.33 (s, 9H, C(CH₃)₃), 1.37 (t, ³*J* = 7.1 Hz, 3H, CH₃), 1.48 (tq, ³*J* = 7.3 Hz, 2H, CH₂), 2.20 (dt, ³*J* = 7.3 Hz, 2H, CH₂), 4.32 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 6.42 (dt, ³*J*_{trans} = 16 Hz, ³*J* = 7.3 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 6.79 (d, ³*J*_{trans} = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 7.02 (s, 1H, H_{etar}). MS (EI, 70 eV): *m/z* (%) = 264 (M⁺, 100), 235 (41), 203 (50), 163 (23), 161 (34), 91 (17), 57 (28). HRMS (EI, 70 eV): calcd for C₁₆H₂₄O₃ ([M+1]⁺) 264.1725, found 264.1725 ± 2 ppm.

Ethyl 4-*tert*-butyl-2-(2-phenylvinyl)furan-3-carboxylate (5v): The reaction of **3m** (300 mg, 0.60 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (106 mg, 1.35 mmol) was carried out as described in procedure B yielding **5v** as a colourless oil (115 mg, 64%, *E/Z* = >98:2). ¹H NMR (300 MHz, CDCl₃, *E*-isomer): δ = 1.36 (s, 9H, C(CH₃)₃), 1.44 (t, ³*J* = 7.1 Hz, 3H, OCH₂CH₃), 4.38 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 7.12 (s, 1H, CH, Hetar), 7.20–7.56 (m, 7H, CH=CH, Ph). ¹³C NMR (150 MHz, CDCl₃, *E*-isomer): δ = 14.5, 30.1, 31.1, 60.7, 114.5, 116.5, 127.0, 128.4, 128.9, 131.6, 136.4, 136.9, 137.8, 158.0, 164.7. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3079 (w), 3025 (m), 2950 (s), 2910 (s), 2872 (m), 1710 (s), 1630 (m), 1577 (w), 1517 (m), 1482 (m), 1450 (m). UV-VIS (CH₃CN, nm): λ_{max} (log ε) = 228.62 (4.09), 333.64 (4.36). MS (EI, 70 eV): *m/z* (%) = 298 (M⁺, 100), 237 (40), 181 (13), 165 (10). HRMS (EI, 70 eV): calcd for C₁₉H₂₂O₃ ([M+1]⁺) 298.1569, found 298.1569 ± 2 ppm.

Ethyl 4-chloromethyl-2-(pent-1-enyl)furan-3-carboxylate (5w): The reaction of **3l** (242 mg, 0.49 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (36 mg, 0.50 mmol) was carried out as described in procedure B yielding **5w** as a colourless oil (62 mg, 49%, *E/Z* = 3:1). ¹H NMR (300 MHz, CDCl₃, isomeric mixture): δ = 0.88 (t, ³*J* = 7.3 Hz, 3H, CH₃), 1.31 (t, ³*J* = 7.1 Hz, 3H, OCH₂CH₃), 1.43 (tq, ³*J* = 7.3 Hz, 2H, CH₂), 2.16 (dt, ³*J* = 7.3 Hz, 2H, CH₂), 4.26 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 4.59 (s, 2 H, CH₂Cl), 6.45 (dt, ³*J*_{trans} = 16.0 Hz, 1H, Hetar-CH=CH, *E*-isomer), 6.85 (d, ³*J*_{trans} = 16.0 Hz, 1H, Hetar-CH=CH *E*-isomer), 7.26 (s, 1H, Hetar). ¹³C NMR (75 MHz, CDCl₃, isomeric mixture): δ = 13.9, 14.0, 22.2, 35.3, 37.2, 60.7, 110.8, 118.2, 123.8, 137.2, 140.4, 158.8, 163.7. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 2962 (m), 2931 (m), 2871 (w), 1710 (s), 1650 (m), 1593

(w), 1535 (m), 1458 (m), 1420 (m). UV-VIS (CH₃CN, nm): $\lambda_{\max}$ (log ϵ) = 291.82 (4.19). MS (EI, 70 eV): m/z (%) = 256 (M⁺, 47), 221 (17), 220 (100), 192 (63), 163 (16), 147 (73), 119 (59), 117 (16), 91 (66), 77 (32). Anal. calcd for C₁₃H₁₇ClO₃ (256.73): C 60.82, H 6.67; found: C 61.15, H 6.31.

Ethyl 4-chloromethyl-2-[2-(4-methoxyphenyl)vinyl]furan-3-carboxylate (5x):

The reaction of **3l** (189 mg, 0.38 mmol) with *n*BuLi (1.1 equiv) and 4-methoxybenzaldehyde (**4g**) (53 mg, 0.39 mmol) was carried out as described in procedure B yielding **5x** as a colourless oil (75 mg, 62%, *E/Z* = > 98:2). ¹H NMR (300 MHz, CDCl₃, *E*-isomer): δ = 1.42 (t, ³*J* = 7.1 Hz, 3H, CH₃), 3.83 (s, 3H, OCH₃), 4.37 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 4.69 (s, 2H, CH₂Cl), 6.89 (d, ³*J* = 8.8 Hz, 2H, CH, Ar), 7.25 (s, 1H, H-4, Heter), 7.27 (d, ³*J*_{trans} = 16.4 Hz, 1H, CH=CH, *E*-isomer), 7.48 (d, ³*J* = 8.8 Hz, 2H, CH, Ar), 7.51 (d, ³*J*_{trans} = 16.4 Hz, 1H, CH=CH, *E*-isomer). ¹³C NMR (75 MHz, CDCl₃, *E*-isomer): δ = 14.4, 37.2, 55.5, 60.7, 111.7, 113.5, 114.4, 124.1, 128.7, 129.1, 132.8, 140.6, 159.1, 160.4, 163.6. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 2976 (w), 1690 (s), 1629 (m), 1600 (s), 1576 (w), 1534 (s), 1507 (m), 1481 (w), 1407 (m). UV-VIS (CH₃CN, nm): $\lambda_{\max}$ (log ϵ) = 227.92 (4.12), 345.14 (4.38). MS (EI, 70 eV): m/z (%) = 320 (M⁺, 100), 166 (17), 135 (68), 77 (16), 57 (16), 44 (66). HRMS (EI, 70 eV): calcd for C₁₇H₁₇O₄Cl ([M+1]⁺) 320.0815, found 320.0815 ± 2 ppm. Anal. calcd for C₁₇H₁₇ClO₄ (320.77): C 63.65, H 5.34; found: C 63.35, H 4.92.

Ethyl 4-(ethoxycarbonylmethyl)-2-(pent-1-enyl)furan-3-carboxylate (5y):

The reaction of **3n** (493 mg, 0.92 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (72 mg, 1.00 mmol) was carried out as described in procedure B yielding **5y** as a yellow oil (122 mg, 45%, *E/Z* = 4:1). ¹H NMR (300 MHz, CDCl₃, isomeric mixture): δ =

0.95 (t, $^3J = 7.3$ Hz, 3H, CH₃), 1.25 (t, $^3J = 7.2$ Hz, 3H, CH₃), 1.32 (t, $^3J = 7.1$ Hz, 3H, CH₃), 1.51 (tq, $^3J = 7.3$ Hz, 2H, CH₂), 2.23 (dt, $^3J = 7.3$ Hz, 2H, CH₂), 3.63 (s, 2H, CH₂), 4.16 (q, $^3J = 7.1$ Hz, 2H, OCH₂), 4.27 (q, $^3J = 7.2$ Hz, 2H, OCH₂), 6.49 (dt, $^3J_{\text{trans}} = 16.0$ Hz, 1H, Hetar-CH=CH, *E*-isomer), 6.93 (d, $^3J_{\text{trans}} = 16.0$ Hz, 1H, Hetar-CH=CH, *E*-isomer), 7.26 (s, 1H, Hetar). ¹³C NMR (50 MHz, CDCl₃, isomeric mixture): $\delta = 13.9, 14.3, 22.2, 30.8, 35.2, 60.6, 60.9, 111.8, 118.7, 119.1, 136.3, 139.8, 158.1, 164.0, 171.2$. IR (KBr, cm⁻¹): $\tilde{\nu} = 2953$ (s), 2933 (s), 2873 (m), 1740 (s), 1690 (s), 1651 (m), 1596 (w), 1534 (m), 1460 (m), 1413 (m). UV-VIS (CH₃CN, nm): λ_{max} (log ϵ) = 292.98 (4.03). MS (EI, 70 eV): m/z (%) = 294 (M⁺, 35), 249 (31), 248 (59), 221 (28), 220 (100), 202 (24), 191 (24), 180 (17), 174 (22), 153 (26), 147 (46), 119 (33), 91 (35), 77 (23), 55 (24). HRMS (EI, 70 eV): calcd for C₁₆H₂₂O₅ ([M+1]⁺) 294.1467, found 294.1467 $\pm$ 2 ppm.

Ethyl 4-(ethoxycarbonyl)methyl-2-(2-phenylvinyl)furan-3-carboxylate (5z**):**

The reaction of **3n** (288 mg, 0.54 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (58 mg, 0.55 mmol) was carried out as described in procedure B yielding **5z** as a colourless oil (75 mg, 41%, *E/Z* = > 98:2). ¹H NMR (300 MHz, CDCl₃, *E*-isomer): $\delta = 1.27$ (t, $^3J = 7.1$ Hz, 3H, OCH₂CH₃), 1.38 (t, $^3J = 7.1$ Hz, 3H, OCH₂CH₃), 3.67 (d, $^4J = 1.2$ Hz, 2H, CH₂), 4.17 (q, $^3J = 7.1$ Hz, 2H, OCH₂), 4.32 (q, $^3J = 7.1$ Hz, 2H, OCH₂), 7.25–7.38 (m, 6H, CH=CH, Ph), 7.53 (d, $^4J = 1.2$ Hz, 1H, Hetar), 7.66 (d, $^3J = 16.5$ Hz, 1H, CH=CH, *E*-isomer). ¹³C NMR (50 MHz, CDCl₃, *E*-isomer): $\delta = 14.3, 14.4, 30.8, 60.5, 60.9, 113.7, 116.0, 119.6, 127.2, 128.7, 128.9, 132.4, 136.6, 140.5, 157.9, 163.8, 171.1$. IR (KBr, cm⁻¹): $\tilde{\nu} = 2982$ (w), 1732 (s), 1680 (s), 1633 (w), 1586 (w), 1529 (w), 1446 (w). UV-VIS (CH₃CN, nm): λ_{max} (log ϵ) = 227.94 (4.12), 328.8 (4.31). MS (EI, 70 eV):

m/z (%) = 328 (M^+ , 100), 254 (22), 152 (38), 151 (29), 86 (24), 84 (40), 51 (20), 49 (58). HRMS (EI, 70 eV): calcd for $C_{19}H_{20}O_5$ ($[M+1]^+$) 328.1311, found 328.1311 ± 2 ppm.

Ethyl 4-phenyl-2-(pent-1-enyl)furan-3-carboxylate (5aa): The reaction of **3o** (423 mg, 0.80 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (61 mg, 0.85 mmol) was carried out as described in procedure B yielding **5aa** as a colourless oil (69 mg, 30%, *E/Z* = 3:1). 1H NMR (300 MHz, $CDCl_3$, isomeric mixture): δ = 0.97 (t, 3J = 7.3 Hz, 3H, CH_3), 1.15 (t, 3J = 7.1 Hz, 3H, OCH_2CH_3), 1.53 (tq, 3J = 7.3 Hz, 2H, CH_2), 2.20 (dt, 3J = 7.3 Hz, 2H, CH_2), 4.18 (q, 3J = 7.1 Hz, 2H, OCH_2), 6.54 (dt, $^3J_{trans}$ = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 6.95 (d, $^3J_{trans}$ = 16.0 Hz, 1H, H_{etar}-CH=CH, *E*-isomer), 7.25–7.37 (m, 6H, Ph, H_{etar}). ^{13}C NMR (150 MHz, $CDCl_3$, isomeric mixture): δ = 13.9, 14.1, 22.3, 35.4, 60.4, 111.8, 118.4, 127.5, 128.0, 128.2, 129.5, 132.1, 136.1, 139.1, 158.1, 164.1. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2961 (m), 2931 (m), 2871 (w), 1775 (w), 1710 (s), 1649 (w), 1531 (w), 1449 (w), 1406 (w). UV-VIS (CH_3CN , nm): λ_{max} (log ϵ) = 294.98 (4.09). MS (EI, 70 eV): m/z (%) = 284 (M^+ , 100), 257 (23), 255 (25), 244 (52), 201 (22), 199 (33), 171 (40), 129 (68), 114 (78), 105 (40), 102 (74), 77 (45), 55 (90).

Ethyl 4,5-diphenyl-2-(pent-1-enyl)furan-3-carboxylate (5ab): The reaction of **3p** (350 mg, 0.54 mmol) with *n*BuLi (1.1 equiv) and butyraldehyde (**4m**) (51 mg, 0.70 mmol) was carried out as described in procedure B yielding **5ab** as a colourless oil (77 mg, 39%, *E/Z* = 3:1). 1H NMR (300 MHz, $CDCl_3$, isomeric mixture): δ = 0.99 (t, 3J = 7.3 Hz, 3H, CH_3), 1.00 (t, 3J = 7.1 Hz, 3H, OCH_2CH_3), 1.57 (tq, 3J = 7.3 Hz, 2H, CH_2), 2.29 (dt, 3J = 7.3 Hz, 2H, CH_2), 4.07 (q, 3J = 7.1 Hz,

2H, OCH₂), 6.68 (dt, $^3J_{\text{trans}} = 15.9$ Hz, 1H, Hetar-CH=CH, *E*-isomer), 7.01 (d, $^3J_{\text{trans}} = 15.9$ Hz, 1H, Hetar-CH=CH, *E*-isomer), 7.15–7.41 (m, 10H, CH, Ph). ¹³C NMR (75 MHz, CDCl₃, isomeric mixture): $\delta = 13.9, 14.0, 22.4, 35.5, 60.1, 114.9, 116.3, 118.3, 123.3, 125.9, 127.6, 128.4, 130.3, 130.4, 133.9, 136.5, 137.4, 147.9, 155.9, 164.0$. IR (KBr, cm⁻¹): $\tilde{\nu} = 2961$ (m), 2930 (m), 2870 (w), 1765 (m), 1705 (s), 1646 (m), 1604 (w), 1539 (m), 1501 (w), 1445 (m), 1410 (m). UV-VIS (CH₃CN, nm): λ_{max} (log ϵ) = 234.13 (4.32), 313.9 (4.21). MS (EI, 70 eV): m/z (%) = 360 (M⁺, 100), 331 (40), 306 (31), 105 (52), 77 (23). HRMS (EI, 70 eV): calcd for C₂₄H₂₄O₃ ([M+1]⁺) 360.1725, found 360.1725 $\pm$ 2 ppm.

Ethyl 4,5-diphenyl-2-(2-phenylvinyl)furan-3-carboxylate (5ac): The reaction of **3p** (117 mg, 0.18 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (21 mg, 0.20 mmol) was carried out as described in procedure B yielding **5ac** as a colourless oil (20 mg, 28%, *E/Z* = > 98:2). ¹H NMR (300 MHz, CDCl₃, *E*-isomer): $\delta = 1.05$ (t, $^3J = 7.1$ Hz, 3H, OCH₂CH₃), 4.12 (q, $^3J = 7.1$ Hz, 2H, OCH₂), 7.20–7.43 (m, 16H, CH=CH, Ph), 7.74 (d, $^3J_{\text{trans}} = 16.4$ Hz, 1H, CH=CH, *E*-isomer). ¹³C NMR (75 MHz, CDCl₃, *E*-isomer): $\delta = 14.0, 60.3, 115.9, 116.8, 123.9, 126.1, 127.3, 127.8, 128.0, 128.3, 128.5, 128.7, 129.0, 130.3, 130.4, 132.4, 133.7, 136.4, 148.7, 155.8, 163.9$. IR (KBr, cm⁻¹): $\tilde{\nu} = 3443$ (m), 3061 (w), 2978 (m), 2928 (w), 2864 (w), 1710 (s), 1628 (m), 1603 (w), 1539 (m), 1480 (w), 1446 (m), 1405 (m). MS (EI, 70 eV): m/z (%) = 394 (M⁺, 79), 215 (70), 202 (95), 201 (23), 200 (18), 104 (24), 32 (26), 28 (100). HRMS (EI, 70 eV): calcd for C₂₇H₂₂O₃ ([M+1]⁺) 394.1569, found 394.1569 $\pm$ 2 ppm.

Ethyl 2-(2-phenylvinyl)-4-(*p*-tolyl)furan-3-carboxylate (5ad): The reaction of **3q** (773 mg, 1.30 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (636 mg, 2.60 mmol) was carried out as described in procedure B yielding **5ad** as a colourless oil (180 mg, 42%, *E/Z* = > 98:2). ¹H NMR (300 MHz, CDCl₃, *E*-isomer): δ = 1.19 (t, ³*J* = 7.1 Hz, 3H, OCH₂CH₃), 1.43 (s, 3H, CH₃), 4.23 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 7.25–7.40 (m, 11H, CH=CH, Ph, Hetar), 7.68 (d, ³*J*_{trans} = 16.4 Hz, 1H, CH=CH, *E*-isomer). ¹³C NMR (50 MHz, CDCl₃, *E*-isomer): δ = 14.0, 30.3, 60.3, 113.4, 115.8, 127.1, 127.5, 127.8, 127.9, 129.1, 129.2, 129.3, 131.7, 132.4, 136.5, 139.4, 157.8, 163.7. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3077 (w), 2979 (w), 2908 (w), 1711 (s), 1631 (w), 1581 (w), 1530 (m), 1485 (w), 1447 (m), 1402 (m). UV-VIS (CH₃CN, nm): λ_{max} (log ε) = 330.13 (4.23), 229.76 (4.19). Anal. calcd for C₂₂H₂₀O₃ (332.40): C 79.50, H 6.06; found: C 79.04, H 6.30.

Ethyl 4-(4-bromophenyl)-2-(2-phenylvinyl)furan-3-carboxylate (5ae): The reaction of **3r** (647 mg, 1.00 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (212 mg, 2.00 mmol) was carried out as described in procedure B yielding **5ae** as a yellow oil (172 mg, 43%, *E/Z* = > 98:2). ¹H NMR (300 MHz, CDCl₃, *E*-isomer): δ = 1.23 (t, ³*J* = 7.1 Hz, 3H, OCH₂CH₃), 4.24 (q, ³*J* = 7.1 Hz, 2H, OCH₂), 7.25–7.57 (m, 11H, CH=CH, Ph, Hetar), 7.67 (d, ³*J*_{trans} = 16.4 Hz, 1H, CH=CH, *E*-isomer). ¹³C NMR (50 MHz, CDCl₃, *E*-isomer): δ = 14.0, 60.4, 113.0, 115.6, 121.6, 127.1, 127.4, 128.6, 128.8, 130.6, 130.9, 130.9, 132.7, 136.3, 139.4, 158.0, 163.5. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 2981 (w), 1699 (s), 1628 (w), 1579 (w), 1528 (m), 1482 (m), 1448 (w), 1410 (w). UV-VIS (CH₃CN, nm): λ_{max} (log ε) = 230.94 (4.39), 330.13 (4.36). MS (EI, 70 eV): *m/z* (%) = 396 (M⁺, 98), 318 (20), 295 (18), 271 (15), 225 (19), 216 (39), 215 (88), 213 (24), 114 (19).

HRMS (EI, 70 eV): calcd for $C_{21}H_{17}O_3Br$ ($[M+1]^+$) 396.0361, found 396.0361 ± 2 ppm.

Ethyl 4-(4-nitrophenyl)-2-(2-phenylvinyl)furan-3-carboxylate (5af): The reaction of **3s** (725 mg, 1.20 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (254 mg, 2.40 mmol) was carried out as described in procedure B yielding **5af** as a colourless oil (54 mg, 12%, *E/Z* = > 98:2). 1H NMR (300 MHz, $CDCl_3$, *E*-isomer): δ = 1.24 (t, 3J = 7.1 Hz, 3H, OCH_2CH_3), 4.26 (q, 3J = 7.1 Hz, 2H, OCH_2), 7.33–7.44 (m, 7H, $CH=CH$, Ph, Hetar), 7.57 (d, 3J = 6.8 Hz, 2H, $CH=CH$, Ph, Hetar), 7.68 (d, $^3J_{trans}$ = 16.4 Hz, 1H, $CH=CH$, *E*-isomer), 8.24 (d, 3J = 6.8 Hz, 2H, $CH=CH$, Ph, Hetar). ^{13}C NMR (50 MHz, $CDCl_3$, *E*-isomer): δ = 14.1, 60.7, 112.6, 115.3, 123.1, 126.8, 127.2, 128.9, 128.9, 130.1, 133.5, 136.1, 138.7, 140.1, 147.2, 158.5, 163.2. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2984 (w), 1695 (s), 1630 (w), 1600 (m), 1576 (w), 1530 (m), 1512 (s), 1487 (w), 1445 (w), 1416 (w). UV-VIS (CH_3CN , nm): λ_{max} (log ϵ) = 341.31 (4.48), 232.02 (4.21), 279.86 (4.08). MS (EI, 70 eV): m/z (%) = 363 (M^+ , 100), 310 (17), 225 (47), 215 (28). HRMS (ESI): calcd for $C_{21}H_{17}NO_5$ ($[M+1]^+$) 364.11795, found 364.11796.

Ethyl 4-(4-chlorophenyl)-2-(2-phenylvinyl)furan-3-carboxylate (5ag): The reaction of **3t** (473 mg, 0.78 mmol) with *n*BuLi (1.1 equiv) and benzaldehyde (**4e**) (159 mg, 1.50 mmol) was carried out as described in procedure B yielding **5ag** as a yellow oil (102 mg, 36%, *E/Z* = > 98:2). 1H NMR (300 MHz, $CDCl_3$, *E*-isomer): δ = 1.23 (t, 3J = 7.1 Hz, 3H, OCH_2CH_3), 4.25 (q, 3J = 7.1 Hz, 2H, OCH_2), 7.25–7.41 (m, 9H, $CH=CH$, Ph, Hetar), 7.56 (d, 3J = 8.3 Hz, 2H, $CH=CH$, Ph, Hetar), 7.68 (d, $^3J_{trans}$ = 16.4 Hz, 1H, $CH=CH$, *E*-isomer). ^{13}C NMR (50 MHz,

CDCl_3 , *E*-isomer): $\delta = 14.1, 60.4, 113.1, 115.6, 127.1, 127.4, 128.0, 128.7, 128.8, 130.2, 130.6, 132.7, 133.5, 136.3, 139.5, 158.0, 163.5$. IR (KBr, cm^{-1}): $\tilde{\nu} = 3436$ (w), 2983 (w), 1694 (s), 1628 (w), 1580 (w), 1529 (m), 1485 (m), 1447 (w), 1413 (w). UV-VIS (CH_3CN , nm): $\lambda_{\text{max}} (\log \varepsilon) = 333.40 (4.32), 230.34 (4.30)$. MS (EI, 70 eV): m/z (%) = 352 (M^+ , 100), 250 (16), 249 (16), 216 (17), 215 (45).