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SUPPLEMENTARY MATERIAL TO
Synthesis of vinylidihydropyrene by cooperative catalysis

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ANALYTICAL AND SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS

(E)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2,2-diethoxyethyl)malonate (**7**). IR (ATR, cm⁻¹): 2979, 2936, 2902, 1735, 1230, 1065; ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 5.68–5.57 (2H, m), 4.57–4.48 (3H, m), 4.30–4.02 (4H, m), 3.71–3.56 (2H, m), 3.54–3.36 (2H, m), 2.71 (2H, d, J = 5.4 Hz), 2.24 (2H, d, J = 5.7), 2.0 (3H, s), 1.25 (6H, t, J = 7.1 Hz), 1.17 (6H, t, J = 7.1 Hz) (12H, m); ¹³C-NMR (50 MHz, CDCl₃, δ / ppm): 170.7 (C), 129.6 (CH), 128.4 (CH), 100.1 (CH), 64.5 (CH₂), 61.9 (CH₂), 61.2 (CH₂), 55.2 (C), 36.1 (CH₂), 35.7 (CH₂), 20.8 (CH₃), 15.0 (CH₃), 13.9 (CH₃); HRMS (ESI): Calcd. for C₁₉H₃₂O₈Na⁺ [M+Na]⁺: 411.1989. Found: 411.1984.

(E)-Diethyl 2-(2,2-diethoxyethyl)-2-{4-[(diethoxyphosphoryl)oxy]but-2-en-1-yl}malonate (**8**). Part 1: IR (ATR, cm⁻¹): 3462, 2979, 2934, 2903, 1732, 1127, 1065; ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 5.81–5.67 (1H, m), 5.62–5.47 (1H, m), 4.56 (1H, t, J = 5.7 Hz), 4.32–4.03 (6H, m), 3.71–3.60 (2H, m), 3.53–3.38 (2H, m), 2.71 (2H, d, J = 5.1 Hz), 2.24 (2H, d, J = 5.7 Hz), 1.75 (1H, bs), 1.29–1.14 (12H, m); ¹³C-NMR (50 MHz, CDCl₃, δ / ppm): 170.8 (C), 133.8 (CH), 126.0 (CH), 100.1 (CH), 63.2 (CH₂), 61.9 (CH₂), 61.2 (CH₂), 55.3 (C), 36.0 (CH₂), 35.5 (CH₂) 15.1 (CH₃), 13.9 (CH₃); HRMS (ESI): Calcd. for C₁₇H₃₀O₇Na⁺ [M+Na]⁺: 369.1884. Found: 369.1889.

Part 2: IR (ATR, cm⁻¹): 3474, 2980, 1732, 1274, 1033; ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 5.76–5.60 (1H, m), 4.54 (1H, t, J = 5.7 Hz), 4.49–4.43 (2H, m), 4.28–3.99 (8H, m), 3.72–3.54 (2H, m), 3.52–3.37 (2H, m), 2.72 (2H, d, J = 5.6 Hz), 2.23 (2H, d, J = 5.6 Hz), 1.41–1.11 (18H, m); ¹³C-NMR (50 MHz, CDCl₃, δ / ppm): 170.7 (C), 129.4 (CH), 129.1 (CH), 100.1 (CH), 67.4 (CH₂), 67.3

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(CH₂), 63.8 (CH₂), 63.7 (CH₂), 61.9 (CH₂), 61.2 (CH₂), 55.2 (C), 36.1 (CH₂), 35.6 (CH₂), 16.1 (CH₃), 15.1 (CH₃), 14.0 (CH₃); HRMS (ESI): Calcd. for C₂₁H₃₉O₁₀PNa⁺ [M+Na]⁺: 505.2173. Found: 505.2172.

(*Z*)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2,2-diethoxyethyl)malonate (**9**). IR (ATR, cm⁻¹): 2979, 2934, 2904, 1736, 1226, 1063; ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 5.77–5.45 (2H, *m*), 4.62 (2H, *d*, *J* = 6.4 Hz), 4.51 (2H, *t*, *J* = 5.7 Hz), 4.16 (4H, *q*, *J* = 7.1 Hz), 3.71–3.32 (4H, *m*), 2.76 (2H, *d*, *J* = 7.1 Hz), 2.24 (2H, *d*, *J* = 5.7 Hz), 2.05 (3H, *s*), 1.24 (6H, *t*, *J* = 7.1 Hz), 1.16 (6H, *t*, *J* = 7.1 Hz); ¹³C-NMR (50 MHz, CDCl₃, δ / ppm): 170.7 (C), 128.1 (CH), 127.2 (CH), 100.1 (CH), 61.9 (CH₂), 61.3 (CH₂), 60.1 (CH₂), 55.0 (C), 36.1 (CH₂), 30.1 (CH₂), 20.8 (CH₃), 15.1 (CH₃), 13.9 (CH₃); HRMS (ESI): Calcd. for C₁₉H₃₂O₈Na⁺ [M+Na]⁺: 411.1989. Found: 411.1995.

(*Z*)-Diethyl 2-(2,2-diethoxyethyl)-2-{4-[(diethoxyphosphoryl)oxy]but-2-en-1-yl}malonate (**10**). Part 1: IR (ATR, cm⁻¹): 3456, 2979, 2935, 2902, 1731, 1190, 1062; ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 5.89–5.67 (1H, *m*), 5.46–5.33 (1H, *m*), 4.54 (1H, *t*, *J* = 5.6 Hz), 4.28–4.09 (6H, *m*), 3.75–3.55 (2H, *m*), 3.55–3.37 (2H, *m*), 2.77 (2H, *d*, *J* = 7.9 Hz), 2.26 (2H, *d*, *J* = 5.6 Hz), 1.94 (1H, *bs*), 1.29–1.14 (12H, *m*); ¹³C NMR (50 MHz, CDCl₃, δ / ppm): 170.9 (C), 132.5 (CH), 125.9 (CH), 100.1 (CH), 61.8 (CH₂), 61.3 (CH₂), 58.0 (CH₂), 55.2 (C), 36.1 (CH₂), 30.6 (CH₂), 15.1 (CH₃), 13.9 (CH₃); HRMS (ESI): Calcd. for C₁₇H₃₀O₇Na⁺ [M+Na]⁺: 369.1884. Found: 369.1892.

Part 2: IR (ATR, cm⁻¹): 3480, 2980, 1733, 1276, 1031; ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 5.81–5.64 (1H, *m*), 5.64–5.45 (1H, *m*), 4.64–4.58 (2H, *m*), 4.53 (1H, *t*, *J* = 5.7 Hz), 4.24–4.04 (8H, *m*), 3.74–3.54 (2H, *m*), 3.54–3.36 (2H, *m*), 2.75 (2H, *d*, *J* = 7.5 Hz), 2.24 (2H, *d*, *J* = 5.7 Hz), 1.40–1.12 (18H, *m*); ¹³C-NMR (50 MHz, CDCl₃, δ / ppm): 170.7 (C), 128.0 (CH), 127.9 (CH), 100.1 (CH), 63.8 (CH₂), 63.7 (CH₂), 62.8 (CH₂), 62.7 (CH₂), 61.9 (CH₂), 61.3 (CH₂), 55.0 (C), 36.1 (CH₂), 30.8 (CH₂), 16.1 (CH₃), 15.1 (CH₃), 13.9 (CH₃); HRMS (ESI): Calcd. for C₂₁H₃₉O₁₀PNa⁺ [M+Na]⁺: 505.2173. Found: 505.2177.

(*E*)-Diethyl 2-(4-bromobut-2-enyl)-2-(2-oxoethyl)malonate (**11**). ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 9.70 (1H, *s*), 5.92–5.47 (2H, *m*), 4.21 (4H, *q*, *J* = 7.1 Hz), 3.87 (2H, *d*, *J* = 6.8 Hz), 2.95 (2H, *s*), 2.75 (2H, *d*, *J* = 6.7 Hz), 1.25 (6H, *t*, *J* = 7.1 Hz).

(*E*)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2-oxoethyl)malonate (**12**). ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 9.69 (*s*, 1H), 5.70–5.55 (*m*, 2H), 4.47 (*d*, *J* = 4.2 Hz, 2H), 4.20 (*q*, *J* = 7.1 Hz, 4H), 2.92 (*s*, 2H), 2.74 (*d*, *J* = 2.6 Hz, 2H), 2.03 (*s*, 3H), 1.24 (*t*, *J* = 7.1 Hz, 6H).

(*E*)-Diethyl 2-{4-[(diethoxyphosphoryl)oxy]but-2-en-1-yl}-2-(2-oxoethyl)malonate (**13**). IR (ATR, cm⁻¹): 3467, 2964, 1729, 1265, 1030, 980; ¹H-NMR (200 MHz, CDCl₃, δ / ppm): 9.71 (1H, *s*), 5.69–5.64 (2H, *m*), 4.47 (2H, *dd*, *J*₁ = 3.9 Hz, *J*₂ = 8.2 Hz), 4.27–4.04 (8H, *m*), 2.96 (2H, *d*, *J* = 1.12 Hz), 2.78 (2H, *d*,

$J = 5.4$ Hz), 1.37–1.21 (12H, *m*); HRMS (ESI): Calcd. for $C_{17}H_{29}O_9PNa^+$ $[M+Na]^+$: 431.1441. Found: 431.1443.

(*Z*)-Diethyl 2-(4-acetoxybut-2-en-1-yl)-2-(2-oxoethyl)malonate (**14**). 1H -NMR (200 MHz, $CDCl_3$, δ / ppm): 9.71 (1H, *s*), 5.78–5.60 (1H, *m*), 5.58–5.39 (1H, *m*), 4.56 (2H, *d*, $J = 6.6$ Hz), 4.21 (4H, *q*, $J = 7.1$ Hz), 2.97 (2H, *s*), 2.84 (2H, *d*, $J = 7.6$ Hz), 2.04 (3H, *s*), 1.25 (6H, *t*, $J = 7.1$ Hz).

(*Z*)-Diethyl 2-{4-[(diethoxyphosphoryl)oxy]but-2-enyl}-2-(2-oxoethyl)malonate (**15**). 1H -NMR (200 MHz, $CDCl_3$, δ / ppm): 9.69 (1H, *s*), 5.84–5.63 (2H, *m*), 4.60–4.48 (2H, *m*), 4.28–3.96 (8H, *m*), 2.96 (2H, *d*, $J = 1.2$ Hz), 2.80 (2H, *d*, $J = 7.9$ Hz), 1.43–0.81 (12H, *m*).

Diethyl 2-vinyl-2,3-dihydro-4H-pyran-4,4-dicarboxylate (**1**). IR (film, cm^{-1}): 2981, 2925, 2853, 1732, 1644, 1465, 1442, 1367, 1277, 1246, 1182, 1055, 1026, 926, 740; 1H -NMR (200 MHz, $CDCl_3$, δ / ppm): 6.57 (1H, *d*, $J = 6.2$ Hz), 5.99–5.82 (1H, *m*), 5.41–5.82 (2H, *m*), 5.02 (1H, *dd*, $J_1 = 2.2$ Hz, $J_2 = 6.2$ Hz), 4.46–4.38 (1H, *m*), 4.30–4.12 (4H, *m*), 2.75 (1H, *dt*, $J_1 = 2.2$ Hz, $J_2 = 13.4$ Hz), 1.83 (1H, *dd*, $J_3 = 11.2$ Hz, $J_2 = 13.4$ Hz), 1.30–1.22 (6H, *m*); ^{13}C -NMR (50 MHz, $CDCl_3$, δ / ppm): 170.5 (C), 145.9 (CH), 136.4 (CH), 116.9 (CH₂), 98.0 (CH), 73.5 (CH), 61.8 (CH₂), 33.6 (CH₂), 14.0 (CH₃); HRMS (ESI): Calcd. for $C_{13}H_{18}O_5Na^+$ $[M+Na]^+$: 277.1052. Found: 277.1032.

(*E*)-Ethyl 6-acetoxy-2-(2-oxoethyl)hex-4-enoate (**16**). 1H -NMR (500 MHz, $CDCl_3$, δ / ppm): 9.76 (1H, *s*), 5.78–5.33 (2H, *m*), 4.51 (2H, *d*, $J = 5.1$ Hz), 4.19–4.16 (2H, *m*), 3.03–2.93 (1H, *m*), 2.92–2.82 (1H, *m*), 2.61–2.51 (1H, *m*), 2.47–2.42 (1H, *m*), 2.34–2.29 (1H, *m*), 2.06 (3H, *s*), 1.26 (3H, *t*, $J = 7.1$ Hz); ^{13}C -NMR (125 MHz, $CDCl_3$, δ / ppm): 199.9 (C), 173.8 (C), 170.7 (C), 131.2 (CH), 127.4 (CH), 64.5 (CH₂), 60.9 (CH₂), 44.5 (CH₂), 38.0 (CH), 34.3 (CH₂), 20.9 (CH₃), 14.0 (CH₃).

(*Z*)-Ethyl 6-acetoxy-2-(2-oxoethyl)hex-4-enoate (**17**). 1H -NMR (500 MHz, $CDCl_3$, δ / ppm): 9.77 (1H, *s*), 5.71–5.62 (1H, *m*), 5.61–5.53 (1H, *m*), 4.65–4.54 (2H, *m*), 4.15 (2H, *q*, $J = 7.1$ Hz), 3.04–2.95 (1H, *m*), 2.95–2.84 (1H, *m*), 2.57 (1H, *ddd*, $J_1 = 0.7$ Hz, $J_2 = 4.9$ Hz, $J_3 = 18.1$ Hz), 2.53–2.44 (1H, *m*), 2.44–2.36 (1H, *m*), 2.06 (3H, *s*), 1.26 (3H, *t*, $J = 7.1$ Hz); ^{13}C -NMR (125 MHz, $CDCl_3$, δ / ppm): 199.8 (C), 173.7 (C), 170.8 (C), 130.4 (CH), 126.6 (CH), 61.0 (CH₂), 59.9 (CH₂), 44.5 (CH₂), 38.7 (CH), 29.4 (CH₂), 20.9 (CH₃), 14.2 (CH₃).

Diethyl 2-(2-oxo-2-phenylethyl)malonate (**21**). IR (ATR, cm^{-1}): 3062, 2984, 2938, 1734, 1689, 1598, 1449, 1332, 1275, 1178, 1155, 1034, 861, 760; 1H -NMR (500 MHz, $CDCl_3$, δ / ppm): 8.00–7.96 (2H, *m*), 7.62–7.55 (1H, *m*), 7.49–7.44 (2H, *m*), 4.27–4.18 (4H, *m*), 4.06 (1H, *t*, $J = 7.1$ Hz), 3.63 (2H, *d*, $J = 7.1$ Hz), 1.32–1.25 (6H, *m*); ^{13}C -NMR (125 MHz, $CDCl_3$, δ / ppm): 196.5 (C), 169.0 (C), 167.0 (C), 136.1 (CH), 133.5 (CH), 128.6 (CH), 128.1 (CH), 62.0 (CH₂), 61.7 (CH), 51.8 (CH), 47.2 (CH₂), 14.0 (CH₃), 13.9 (CH₃); GC/MS (m/z): 278.1 (M^+), 278.1, 233.0, 105.0 (100 %), 77.1, 45.0.

Diethyl (E)-2-(4-bromobut-2-en-1-yl)-2-(2-oxo-2-phenylethyl)malonate (22). IR (ATR, cm^{-1}): 3060, 2981, 2935, 1731, 1688, 1597, 1446, 1361, 1277, 1203, 1056, 1027, 971, 862, 691; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ / ppm): 8.00–7.92 (2H, *m*), 7.62–7.40 (3H, *m*), 5.71–5.62 (2H, *m*), 4.21 (4H, *q*, $J = 7.2$ Hz), 3.84–3.78 (2H, *m*), 3.66 (2H, *s*), 2.93–2.85 (2H, *m*), 1.24 (6H, *t*, $J = 7.2$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 196.6 (C), 170.2 (C), 136.5 (C), 133.4 (CH), 131.0 (CH), 131.1 (CH), 128.6 (CH), 128.0 (CH), 61.7 (CH_2), 55.3 (C), 41.2 (CH_2), 35.7 (CH_2), 32.0 (CH_2), 14.0 (CH_3); GC/MS (m/z): 410.1 (M^+), 331.0, 226.1, 105.0 (100 %), 77.0, 45.0.

Diethyl 6-phenyl-2-vinyl-2,3-dihydro-4H-pyran-4,4-dicarboxylate (23). IR (ATR, cm^{-1}): 3059, 2982, 2932, 1734, 1647, 1446, 1295, 1239, 1182, 1094, 1059, 754, 695; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ / ppm): 7.69–7.63 (2H, *m*), 7.37–7.29 (4H, *m*), 6.07–6.00 (1H, *m*), 5.61 (1H, *s*), 5.49 (1H, *dt*, $J = 17.3$ Hz, $J = 1.4$ Hz), 5.29 (1H, *dt*, $J_1 = 10.6$ Hz, $J_2 = 1.4$ Hz), 4.64–4.58 (1H, *m*), 4.31–4.16 (4H, *m*), 2.66 (1H, *dt*, $J_1 = 13.8$ Hz, $J_2 = 1.9$ Hz), 1.90 (1H, *dd*, $J_1 = 13.8$ Hz, $J_2 = 11.6$ Hz), 1.28 (6H, *dt*, $J_1 = 7.1$, $J_2 = 2.1$ Hz); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 170.6 (C), 153.4 (C), 136.6 (CH), 135.0 (C), 128.8 (CH_2), 128.1 (CH_2), 125.3 (CH_2), 116.6 (CH_2), 94.1 (CH), 74.2 (CH), 61.8 (CH_2), 52.1 (C), 33.5 (CH_2), 14.0 (CH_3); GC/MS (m/z): 330.1 (M^+), 284.1, 257.1, 211.0, 183.1, 167.1, 105.0 (100 %), 77.0, 51.0.