Electronic Supplementary Material (ESI) for RSC Advances

Microwave-Assisted Organocatalytic Cross-Aldol Condensation of Aldehydes

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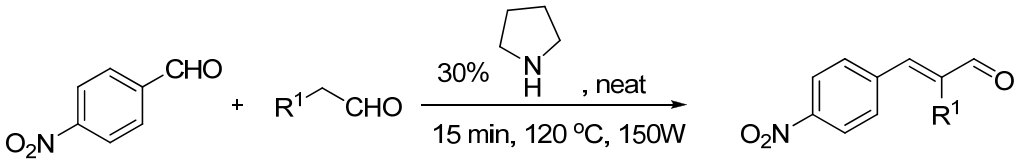
Supporting Information

Table of Contents	**Page**
General Remarks	**S2**
General Procedure 1: Microwave-Assisted Cross-Aldol Condensation of 4-Nitro Benzaldehyde with Aldehydes	**S3**
General Procedure 2: Microwave Assisted Cross-Aldol Condensation of Heptanal with Aldehydes	**S3**
Large Scale Synthesis of (*E*)-2-Benzylideneheptanal (jasminaldehyde)	**S15**
References	**S15**
NMR data	**S17**

General Remarks

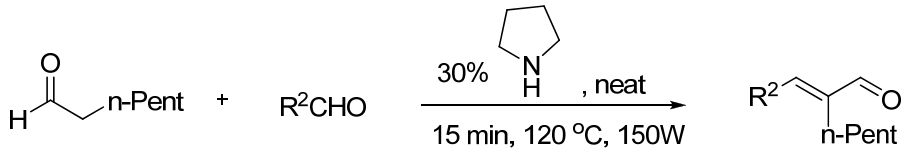
Chromatographic purification of products was accomplished using forced-flow chromatography on Merck Kieselgel 60 F_{254} 230-400 mesh. Thin-layer chromatography (TLC) was performed on aluminum backed silica plates (0.2 mm, 60 F_{254}). Visualization of the developed chromatogram was performed by fluorescence quenching using phosphomolybdic acid or ninhydrin stains. Melting points were determined on a Buchi 530 hot stage apparatus. Optical rotations were measured on a Perkin Elmer 343 polarimeter. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury (200 MHz or 50 MHz) and are internally referenced to residual solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad signal, bs m = broad signal multiplet), coupling constant and assignment. Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm). Mass spectra were recorded on a Finnigan Surveyor MSQ Plus, with only molecular ions and major peaks being reported with intensities quoted as percentages of the base peak. All microwave-assisted reactions were performed using CEM Discover® System. All aldehydes, except from the aromatic ones, were freshly distilled prior to use.

General Procedure 1: Microwave-Assisted Cross-Aldol Condensation of 4-Nitro Benzaldehyde with Aldehydes



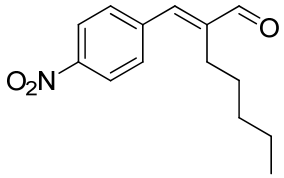
4-Nitro-benzaldehyde (76 mg, 0.50 mmol) was placed in a microwave vessel. The corresponding aldehyde (0.55 mmol) and pyrrolidine (11 mg, 12 μL, 0.15 mmol) were added consecutively. The reaction mixture was left stirring under microwave irradiation (initial setting at 150W) for 15 minutes at 120 °C. The crude product was purified using flash column chromatography (deactivated with Et_3N) to give the desired product.

General Procedure 2: Microwave Assisted Cross-Aldol Condensation of Heptanal with Aldehydes



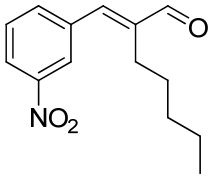
Aldehyde (0.50 mmol) was placed in a microwave vessel. Freshly distilled heptanal (63 mg, 0.55 mmol) and pyrrolidine (11 mg, 12 μL, 0.15 mmol) were added consecutively. The reaction mixture was left stirring under microwave irradiation (initial setting at 150W) for 15 minutes at 120 °C. The crude product was purified using flash column chromatography (deactivated with Et_3N) to give the desired product.

(*E*)-2-(4-Nitrobenzylidene)heptanal (Table 2, Entry 1)[1]



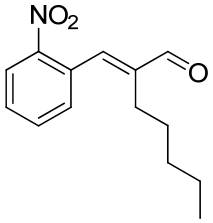
Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether:Et_2O (80:20). Yellow solid, mp 160-162 ^oC; 98% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 9.57 (1H, s, CHO), 8.27 (2H, d, J = 8.7 Hz, ArH), 7.62 (2H, d, J = 8.7 Hz, ArH), 7.29 (1H, s, =CH), 2.52-2.39 (2H, m, =C-CH_2), 1.51-1.36 (1H, m, C*H*H), 1.34-1.16 (5H, m, 5 x C*H*H), 0.83 (3H, t, J = 6.9 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 194.8, 147.0, 146.0, 145.9, 141.1, 129.9, 123.8, 31.8, 27.9, 24.7, 22.2, 13.8; MS 248 ($M+H^+$, 58).

(*E*)-2-(3-Nitrobenzylidene)heptanal (Table 2 Entry 2)



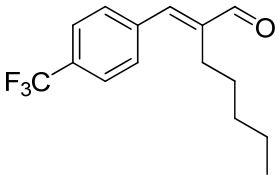
Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. ether:Et_2O (85:15). Oil; 96% yield; IR (film) 2956, 2929, 2860, 1685, 1627, 1530, 1351, 912, 735 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.60 (1H, s, CHO), 8.36 (1H, t, J = 1.9 Hz, ArH), 8.25 (1H, ddd, J = 8.1, 1.9 and 1.2 Hz, ArH), 7.79 (1H, ddd, J = 8.1, 1.9 and 1.2 Hz, ArH), 7.65 (1H, t, J = 8.1 Hz, ArH), 7.26 (1H, s, =CH), 2.57-2.45 (2H, m, =C-CH_2), 1.52-1.16 (6H, m, 6 x C*H*H), 0.86 (3H, t, J = 6.9 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 194.9, 148.4, 146.0, 145.5, 136.4, 134.1, 129.8, 123.9, 123.8, 31.9, 27.0, 24.8, 22.3, 14.0; MS 248 ($M+H^+$, 85); HRMS exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}NO_3$) requires *m/z* 248.1281, found *m/z* 248.1271.

(*E*)-2-(2-nitrobenzylidene)heptanal (Table 2, Entry 3)



Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. ether:Et_2O (70:30). Oil; 95% yield; IR (film) 2955, 2928, 2859, 1689, 1606, 1524, 1343, 856 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.62 (0.85H, s, CHO), 9.61 (0.15H, s, CHO), 8.18 (1H, dd, J = 8.1 and 1.3 Hz, ArH), 7.82-7.51 (3H, m, ArH and =CH), 7.38 (1H, d, J = 8.1 Hz, ArH), 2.37 (0.3H, t, J = 7.3 Hz, =C-CH_2), 2.24 (1.7H, t, J = 7.3 Hz, =C-CH_2), 1.53-1.07 (6H, m, 6 x C*H*H), 0.87 (0.45H, t, J = 6.6 Hz, CH_3); 0.74 (2.55H, t, J = 6.6 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 194.7, 146.0, 144.0, 142.3, 133.6, 131.0, 130.4, 129.6, 125.0, 31.5, 28.0, 24.6, 22.1, 13.7; MS 248 ($M+H^+$, 91); HRMS exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}NO_3$) requires *m/z* 248.1281, found *m/z* 248.1274.

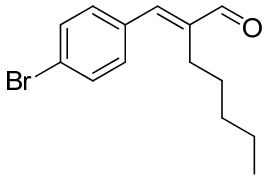
(*E*)-2-(4-(Trifluoromethyl)benzylidene)heptanal (Table 2, Entry 4)



Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. ether:Et_2O (85:15). Oil; 98% yield; IR (film) 2957, 2931, 2861, 1687, 1615, 1325, 1167, 1127, 1086 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.58 (1H, s, CHO), 7.70 (2H, d, J = 8.1 Hz, ArH), 7.58 (2H, d, J = 8.1 Hz, ArH), 7.24 (1H, s, =CH), 2.54-2.38 (2H, m, =C-CH_2), 1.57-1.20 (6H, m, 6 x C*H*H), 0.88 (3H, t, J = 6.4 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.5, 147.7, 145.3, 138.6, 131.2 (q, J = 32.7 Hz), 129.8, 125.9 (q, J = 3.7 Hz), 124.0 (q, J = 272.2 Hz), 32.2, 28.3, 25.0, 22.6, 14.2; ^{19}F NMR (188 MHz,

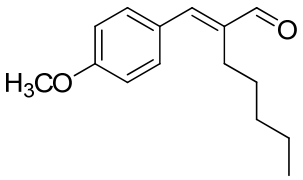
$CDCl_3$) δ 3.58 (s); MS 271 ($M+H^+$, 100); HRMS exact mass calculated for $[M+H]^+$ ($C_{15}H_{18}F_3O$) requires *m/z* 271.1304, found *m/z* 271.1300.

(*E*)-2-(4-Bromobenzylidene)heptanal (Table 2 Entry 5)



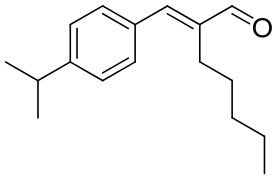
Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. Ether:Et_2O (85:15). Oil; 94% yield; IR (film) 2952, 2924, 2863, 1681, 1612, 1584, 1455, 1085 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.54 (1H, s, CHO), 7.58 (2H, d, *J* = 8.7 Hz, ArH), 7.36 (2H, d, *J* = 8.7 Hz, ArH), 7.14 (1H, s, =CH), 2.54-2.43 (2H, m, =C-CH_2), 1.54-1.25 (6H, m, 6 x C*H*H), 0.89 (3H, t, *J* = 6.9 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.4, 148.2, 143.7, 133.8, 132.0, 131.0, 123.8, 32.0, 27.9, 24.7, 22.4, 14.0; MS 281 ($M+H^+$, 32); HRMS exact mass calculated for $[M+H]^+$ ($C_{14}H_{18}BrO$) requires *m/z* 281.0536, found *m/z* 281.0529.

(*E*)-2-(4-Methoxybenzylidene)heptanal (Table 2, Entry 6)[2]



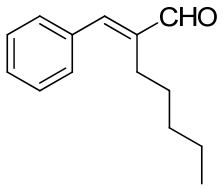
Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. Ether:Et_2O (85:15). Oil; 65% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 9.49 (1H, s, CHO), 7.49 (2H, d, *J* = 8.9 Hz, ArH), 7.13 (1H, s, C=CH), 6.97 (2H, d, *J* = 8.9 Hz, ArH), 3.84 (3H, s, OCH_3), 2.57-2.41 (2H, m, =C-CH_2), 1.54-1.16 (6H, m, 6 x C*H*H), 0.89 (3H, t, *J* = 7.3 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.6, 160.8, 149.6, 141.9, 131.4, 127.6, 113.9, 55.2, 32.4, 27.9, 24.6, 22.3, 14.1; MS 233 ($M+H^+$, 62).

(*E*)-2-(4-Isopropylbenzylidene)heptanal (Table 2, Entry 7)



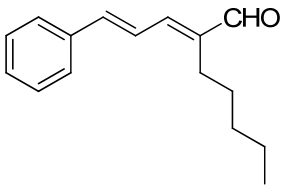
Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. Ether:Et_2O (85:15). Oil; 63% yield; IR (film) 2958, 2927, 2868, 1681, 1622, 1456, 1086 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.53 (1H, s, CHO), 7.47 (2H, d, J = 8.3 Hz, ArH), 7.32 (2H, d, J = 8.3 Hz, ArH), 7.18 (1H, s, =CH), 2.97 [1H, hept, J = 6.9 Hz, C*H*$(CH_3)_2$], 2.60-2.46 (2H, m, =C-CH_2), 1.55-1.22 (12H, m, 6 x C*H*H and 2 x CH_3), 0.95-0.84 (3H, m, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.9, 150.9, 150.0, 142.5, 132.5, 130.0, 126.9, 34.0, 32.1, 27.9, 24.8, 23.8, 22.4, 14.1; MS 245 ($M+H^+$, 58); HRMS exact mass calculated for $[M+H]^+$ ($C_{17}H_{25}O$) requires *m/z* 245.1900, found *m/z* 245.1895.

(*E*)-2-Benzylideneheptanal (jasminaldehyde 1, Table 2 Entry 8)[2]



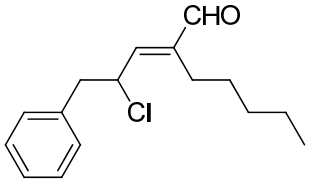
Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. ether:Et_2O (80:20). Oil; 93% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 9.56 (1H, s, CHO), 7.55-7.38 (5H, m, ArH), 7.22 (1H, s, =CH), 2.60-2.48 (2H, m, =C-CH_2), 1.65-1.27 (6H, m, 6 x C*H*H), 0.96-0.85 (3H, m, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.8, 149.8, 143.3, 134.9, 129.6, 129.5, 128.8, 32.1, 28.0, 24.7, 22.4, 14.0; MS 202 ($M+H^+$, 35).

(*E*)-2-((*E*)-3-Phenylallylidene)heptanal (Table 2, Entry 9)[3]



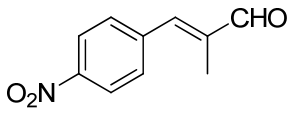
Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. Ether:Et_2O (90:10). Oil; 72% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.49 (1H, s, CHO), 7.58-7.52 (2H, m, ArH), 7.46-7.28 (3H, m, ArH), 7.23 (1H, d, J = 14.6 and 11.8 Hz, =CH), 7.01 (1H, d, J = 14.6 Hz, =CH), 6.99 (1H, d, J = 11.8 Hz, =CH), 2.52-2.38 (2H, m, =C-CH_2), 1.52-1.37 (6H, m, 6 x C*H*H), 0.90 (3H, t, J = 6.4 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.8, 149.8, 123.3, 134.9, 131.7, 130.1, 129.6, 129.5, 128.8, 32.1, 28.0, 24.7, 22.4, 14.0; MS 229 ($M+H^+$, 100).

(*E*)-2-(2-Chloro-3-phenylpropylidene)heptanal (Table 2, Entry 10)



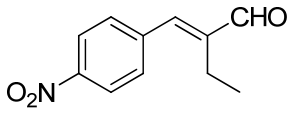
Following Procedure 2, the product was purified using flash column chromatography eluting with Pet. ether:Et_2O (90:10). Oil; 52% yield; IR (film) 2957, 2924, 2862, 1684, 1589, 1453, 1121 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.40 (1H, s, CHO), 7.37-7.15 (5H, m, ArH), 6.37 (1H, d, J = 10.3 Hz, =CH), 4.93 (1H, ddd, J = 10.3, 7.7 and 6.5 Hz CHCl), 3.29 (1H, dd, J = 13.7 and 6.5 Hz, ArCH*H*), 3.12 (1H, dd, J = 13.7 and 7.7 Hz, ArCH*H*), 2.12-2.02 (2H, m, =C-CH_2), 1.38-1.09 (6H, m, 6 x C*H*H), 0.83 (3H, t, J = 6.7 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 194.5, 149.5, 143.8, 135.9, 129.6, 128.6, 127.7, 56.1, 44.5, 31.7, 28.2, 24.1, 22.3, 13.9; MS 265 ($M+H^+$, 73); HRMS exact mass calculated for $[M+H]^+$ ($C_{16}H_{22}ClO$) requires *m/z* 265.1354, found *m/z* 265.1345.

(*E*)-2-Methyl-3-(4-nitrophenyl)acrylaldehyde (Table 3 Entry 1)[4]



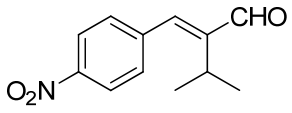
Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (70:30). white solid, mp 113-115 ^oC; 94% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 9.65 (0.8H, d, J = 1.8 Hz, CHO), 9.50 (0.2H, d, J = 1.8 Hz, CHO), 8.30 (1.6H, d, J = 8.9 Hz, ArH), 8.25 (0.4H, d, J = 8.9 Hz, ArH), 7.67 (1.6H, d, J = 8.9 Hz, ArH), 7.50 (0.4H, d, J = 8.9 Hz, ArH), 7.33 (0.8H, s, =CH), 7.26 (0.2H, s, =CH), 2.09 (2.4H, t, J = 1.8 Hz, CH_3), 2.05 (0.6H, t, J = 1.8 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.6, 194.7, 153.2, 146.1, 141.2, 134.5, 130.4, 129.9, 123.8, 123.6, 18.3, 11.1; MS 192 ($M+H^+$, 100).

(*E*)-2-(4-Nitrobenzylidene)butanal (Table 3, Entry 2)[3]



Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (80:20). Oil; 95% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 9.60 (1H, s, CHO), 8.27 (2H, d, J = 8.9 Hz, ArH), 7.63 (2H, d, J = 8.9 Hz, ArH), 7.28 (1H, s, =CH), 2.52 (2H, q, J = 7.5 Hz, CH_2), 1.14 (3H, t, J = 7.5 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 194.7, 147.7, 147.1, 145.8, 141.1, 130.0, 123.9, 18.2, 12.9; MS 206 ($M+H^+$, 82).

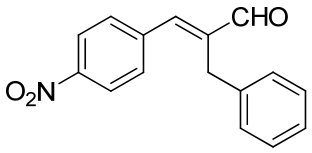
(*E*)-3-Methyl-2-(4-nitrobenzylidene)butanal (Table 3, Entry 3)[5]



Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (90:10). Oil; 92% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 9.59 (1H, s, CHO), 8.29 (2H, d, J = 8.9 Hz, ArH), 7.51 (2H, d, J = 8.9 Hz, ArH), 7.24 (1H, s, =CH), 3.02 (1H, hept, J = 6.9 Hz, CH), 1.27 (6H, d, J = 6.9 Hz, 2 x CH_3); ^{13}C (50 MHz,

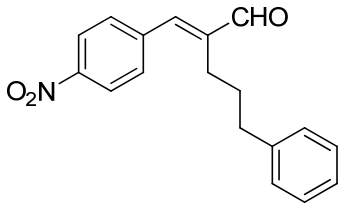
$CDCl_3$) δ 194.8, 150.3, 147.6, 145.9, 141.6, 129.6, 123.8, 27.2, 20.3; MS 220 ($M+H^+$, 75).

(*E*)-2-Benzyl-3-(4-nitrophenyl)acrylaldehyde (Table 3, Entry 4)[6]



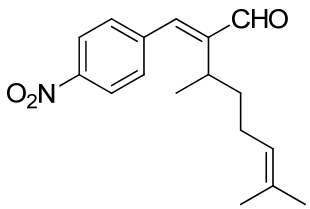
Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether:EtOAc (80:20). Oil; 97% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.74 (1H, s, CHO), 8.21 (2H, d, J = 8.9 Hz, ArH), 7.61-7.54 (3H, m, ArH and =CH), 7.31-7.06 (5H, m, ArH), 3.90 (2H, s, CH_2Ph); ^{13}C (50 MHz, $CDCl_3$) δ 194.3, 152.4, 147.8, 143.2, 141.0, 137.4, 130.1, 128.7, 127.7, 126.5, 123.8, 30.3; MS 268 ($M+H^+$, 85).

(*E*)-2-(4-Nitrobenzylidene)-5-phenylpentanal (Table 3, Entry 5)



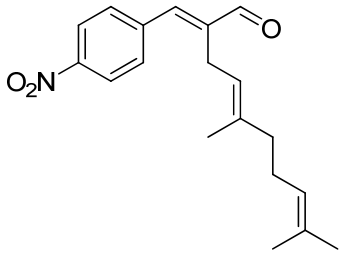
Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether:etOAc (80:20). Oil; 95% yield; IR (film) 2933, 2857, 1684, 1625, 1519, 1345, 1126 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.59 (1H, s, CHO), 8.11 (2H, d, J = 8.9 Hz, ArH), 7.38 (2H, d, J = 8.9 Hz, ArH), 7.32-7.13 (6H, m, ArH and =CH), 2.69 (2H, t, J = 7.1 Hz, CH_2), 2.56-2.44 (2H, m, CH_2), 1.90-1.70 (2H, m, CH_2); ^{13}C (50 MHz, $CDCl_3$) δ 194.7, 147.5, 146.1, 145.5, 141.2, 140.8, 130.0, 128.6, 128.3, 126.1, 123.7, 35.6, 29.6, 23.9; MS 318 ($M+Na^+$, 100); HRMS exact mass calculated for $[M+Na]^+$ ($C_{18}H_{17}NO_3Na$) requires *m/z* 318.1101, found *m/z* 318.1089.

(*E*)-3,7-dimethyl-2-(4-Nitrobenzylidene)oct-6-enal (Table 3, Entry 6)



Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (90:10). Oil; 94% yield; IR (film) 2965, 2919, 2855, 1691, 1624, 1594, 1519, 1453, 1345 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.60 (1H, s, CHO), 8.28 (2H, d, J = 8.8 Hz, ArH), 7.51 (2H, d, J = 8.8 Hz, ArH), 7.29 (1H, s, =CH), 4.92 (1H, t, J = 6.0 Hz, =CH), 2.94-2.77 (1H, m, CH), 1.89-1.72 (3H, m, 3 x C*H*H), 1.71-1.58 (1H, m, C*H*H), 1.56 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.27 (3H, d, J = 7.0 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 194.8, 149.3, 147.6, 146.7, 141.7, 132.0, 129.6, 123.8, 123.7, 33.8, 31.9, 26.2, 25.6, 18.6, 17.6; MS 310 ($M+Na^+$, 42); HRMS exact mass calculated for $[M+Na]^+$ ($C_{17}H_{21}NO_3Na$) requires *m/z* 310.1414, found *m/z* 310.1399.

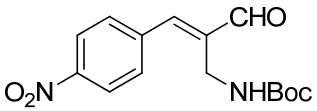
(2*E*,4*E*)-5,9-Dimethyl-2-(4-nitrobenzylidene)deca-4,8-dienal (Table 3, Entry 7)



Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (90:10). Oil; 95% yield; IR (film) 2965, 2916, 2854, 1686, 1624, 1596, 1520, 1492, 1345 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.64 (0.92H, d, J = 2.1 Hz CHO), 9.51 (0.08H, d, J = 2.1 Hz CHO), 8.28 (1.84H, d, J = 8.9 Hz, ArH), 8.10 (0.16H, d, J = 8.9 Hz, ArH), 7.64 (2H, d, J = 8.9 Hz, ArH), 7.32 (1H, s, =CH), 5.18- 4.89 (2H, m, 2 x =CH), 3.20 (2H, m, CH_2), 2.13-1.94 (4H, m, 4 x C*H*H), 1.73-1.53 (9H, m, 3 x CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 194.4, 146.2, 146.1, 144.9, 141.1, 138.5, 138.0, 130.3,

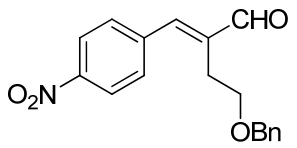
123.8, 120.0, 119.6, 39.5, 32.2, 25.7, 24.1, 17.7, 16.4; MS 314 ($M+H^+$, 95); HRMS exact mass calculated for $[M+H]^+$ ($C_{19}H_{24}NO_3$) requires *m/z* 314.1751, found *m/z* 314.1739.

(*E*)-Tert-butyl (2-formyl-3-(4-nitrophenyl)allyl)carbamate (Table 3, Entry 8)



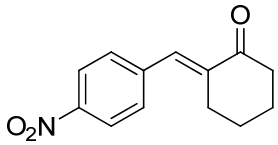
Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (60:40). Oil; 88% yield; IR (film) 3417, 2974, 2930, 1685, 1596, 1520, 1454, 1346, 1248, 1165 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 9.85 (0.2H, s, CHO), 9.64 (0.8H, s, CHO), 8.34 (1.6H, d, *J* = 8.9 Hz, ArH), 8.29 (0.4H, d, *J* = 8.9 Hz, ArH), 7.87 (1.6H, d, *J* = 8.9 Hz, ArH), 7.73 (0.2H, s, =CH), 7.49 (0.4H, d, *J* = 8.9 Hz, ArH), 7.42 (0.8H, s, =CH), 5.29 (0.8H, t, *J* = 6.3 Hz, NH), 5.07 (0.2H, t, *J* = 6.3 Hz, NH), 4.19 (1.6H, d, *J* = 6.3 Hz, NHCH_2), 4.07 (0.4H, d, *J* = 6.3 Hz, NHCH_2), 1.44 [1.8H, s, $C(CH_3)_3$], 1.42 [7.2H, s, $C(CH_3)_3$]; ^{13}C (50 MHz, $CDCl_3$) δ 195.2, 191.5, 155.5, 148.0, 143.6, 140.7, 139.7, 130.6, 124.0, 79.8, 40.7, 35.5, 28.3; MS 329 ($M+Na^+$, 100); HRMS exact mass calculated for $[M+Na]^+$ ($C_{15}H_{18}N_2O_5Na$) requires *m/z* 329.1108, found *m/z* 329.1092.

(*E*)-4-(Benzyloxy)-2-(4-nitrobenzylidene)butanal (Table 3, Entry 9)



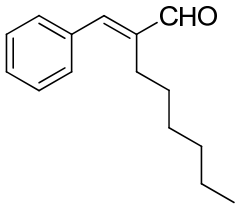
Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (80:20). Oil; 95% yield; IR (film) 2967, 2858, 1682, 1588, 1517, 1345, 1275, 1260, 763, 749 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.60 (1H, s, CHO), 8.21 (2H, d, *J* = 8.9 Hz, ArH), 7.81 (2H, d, *J* = 8.9 Hz, ArH), 7.40 (1H, s, =CH), 7.37-7.19 (5H, m, ArH), 4.47 (2H, s, OCH_2), 3.68 (2H, t, *J* = 6.3 Hz, OCH_2), 2.78 (2H, t, *J* = 6.3 Hz, CH_2); ^{13}C (50 MHz, $CDCl_3$) δ 194.8, 148.5, 144.2, 142.3, 140.8, 138.0, 130.3, 128.3, 127.7, 127.5, 123.7, 73.1, 67.4, 25.9; MS 312 ($M+H^+$, 100); HRMS exact mass calculated for $[M+H]^+$ ($C_{18}H_{18}F_6NO_4$) requires *m/z* 312.1230, found *m/z* 312.1216.

(*E*)-2-(4-Nitrobenzylidene)cyclohexanone (Table 3, Entry 10)[7]



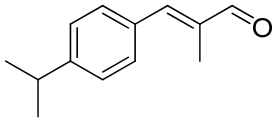
Following Procedure 1, the product was purified using flash column chromatography eluting with Pet. ether: Et_2O (90:10). Yellow solid, mp 117-119 ^oC; 88% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 8.24 (2H, d, J = 8.9 Hz, ArH), 7.52 (2H, d, J = 8.9 Hz, ArH), 7.46 (1H, s, =CH), 2.87-2.74 (2H, m, 2 x C*H*H), 2.64-2.53 (2H, m, 2 x C*H*H), 2.05-1.88 (2H, m, 2 x C*H*H), 1.87-1.72 (2H, m, 2 x C*H*H); ^{13}C (50 MHz, $CDCl_3$) δ 201.4, 147.0, 142.1, 139.9, 132.5, 130.7, 123.5, 40.4, 23.0, 23.7, 23.3; MS 232 ($M+H^+$, 100).

(*E*)-2-Benzylideneoctanal (hexyl cinnamaldehyde 2, Scheme 2)[8]



Following Procedure 1 (Scale: benzaldehyde 0.53 g, 5.00 mmol), the product was purified using flash column chromatography eluting with Pet. ether:Et_2O (80:20). Oil; 90% yield; ^1H NMR (200 MHz, $CDCl_3$) δ 9.58 (1H, s, CHO), 7.53-7.39 (5H, m, ArH), 7.21 (1H, s, =CH), 2.54 (2H, t, J = 6.7 Hz, =C-CH_2), 1.53-1.19 (8H, m, 8 x C*H*H), 0.89 (3H, t, J = 6.1 Hz, CH_3); ^{13}C (50 MHz, $CDCl_3$) δ 195.7, 149.7, 143.3, 135.0, 129.6, 129.5, 128.8, 31.5, 29.5, 28.2, 24.8, 22.6, 14.0.

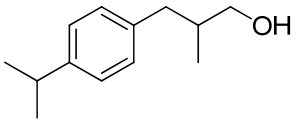
(*E*)-3-(4-isopropylphenyl)-2-methylacrylaldehyde (Scheme 3)[9]



4-Isopropyl-Benzaldehyde (0.74 g, 5.00 mmol) was placed in a microwave vessel. Freshly distilled propanal (0.32 g, 5.50 mmol) and pyrrolidine (0.12 mL, 1.50 mmol)

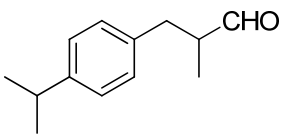
were added consecutively. The reaction mixture was left stirring under microwave irradiation (initial setting at 150W) for 15 minutes at 120 °C. The crude product was purified using flash column chromatography [Pet. ether: Et_2O (5:5)] (deactivated with Et_3N) to give the desired product. Oil; 63% yield; IR (film) 2960, 2868, 1679, 1606, 1359, 1187 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 9.56 (0.9H, s, CHO), 9.47 (0.1H, s, CHO), 7.49 (2H, d, *J* = 8.3 Hz, ArH), 7.31 (2H, d, *J* = 8.3 Hz, ArH), 7.23 (1H, s, =C*H*), 3.03-2.87 [1H, m, C*H*$(CH_3)_2$], 2.09 (2.7H, s, =C-CH_3), 2.04 (0.3H, s, =C-CH_3), 1.28 [6H, d, *J* = 6.9 Hz, CH(C$H_3)_2$]; ^{13}C (50 MHz, $CDCl_3$) δ 195.8, 195.4, 155.3, 150.7, 149.9, 148.6, 138.2, 137.3, 132.7, 130.2, 129.4, 126.3, 33.9, 33.8, 23.7, 23.6, 17.9, 10.8.

3-(4-isopropylphenyl)-2-methylpropan-1-ol (Scheme 3)[10]



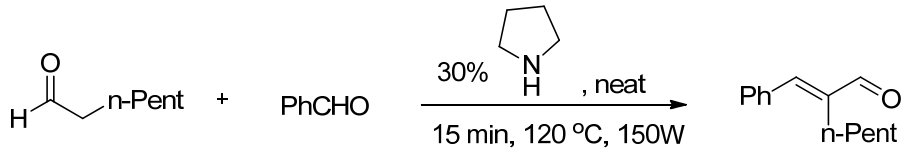
To a stirring solution of (*E*)-3-(4-isopropylphenyl)-2-methylacrylaldehyde (0.5 g, 2.65 mmol) in methanol (20 mL), 10% Palladium on activated charcoal was added. The reaction was left stirring under hydrogen atmosphere for 18 h. The mixture was then filtered through a thin layer of celite followed by removal of the solvent under reduced pressure. The resulting residue was purified by flash column chromatography [Pet. ether: Et_2O (5:5)] to give the product. Oil; 71% yield; IR (film) 3337, 2958, 2925, 2870, 1511, 1461, 1381, 1034 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 7.21-7.06 (4H, m, ArH), 3.62-3.41 (2H, m, CH_2OH), 2.98-2.80 [1H, m, C*H*$(CH_3)_2$], 2.72 (1H, dd, *J* = 13.5 and 7.8 Hz, ArC*H*H), 2.41 (1H, dd, *J* = 13.5 and 7.8 Hz, ArC*H*H), 2.07-1.82 (1H, m, C*H*CH_3), 1.26 [6H, d, *J* = 6.9 Hz, CH(C$H_3)_2$], 0.94 (3H, d, *J* = 6.7 Hz, CHCH_3), ^{13}C (50 MHz, $CDCl_3$) δ 146.4, 137.8, 129.0, 126.3, 67.7, 39.3, 37.8, 33.7, 24.0, 16.6.

3-(4-isopropylphenyl)-2-methylpropanal (Cyclamen aldehyde 3, Scheme 3)[11]



To a stirring solution of 3-(4-isopropylphenyl)-2-methylpropan-1-ol (0.25 g, 1.30 mmol) in dry DCM (5 mL), Dess-Martin periodinane (0.66 g, 1.55 mmol) was added. The reaction was left stirring for 1 hour. After adding 10 % aqueous $Na_2S_2O_3$ (5 mL), the aqueous phase was extracted with DCM (3 x 5 mL), dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified using flash column chromatography [Pet. ether: Et_2O (6:4)] to afford the desired product. Oil; 77% yield; IR (film) 2960, 2926, 1728, 1514, 1455, 1260 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) 9.74 (1H, d, J = 1.5 Hz, CHO), 7.21-7.07 (4H, m , ArH), 3.07 (1H, dd, J = 12.0 and 4.5 Hz, ArC*H*H), 2.98-2.80 [1H, m, C*H*$(CH_3)_2$], 2.76-2.52 (2H, m, 1xArCH*H* and C*H*CH_3), 1.25 [6H, d, J = 6.9 Hz, CH$(CH_3)_2$], 1.11 (3H, d, J = 6.9 Hz, CHCH_3) ^{13}C (50 MHz, $CDCl_3$) δ 204.8, 147.0, 136.1, 129.0, 126.6, 48.1, 36.2, 33.7, 24.0, 13.3.

Large Scale Synthesis of (*E*)-2-Benzylideneheptanal (jasminaldehyde)



Benzaldehyde (6.0 g, 56.6 mmol) was placed in a microwave vessel. Freshly distilled heptanal (7.1 g, 62.3 mmol) and pyrrolidine (1.2 g, 1.4 mL, 17.0 mmol) were added consecutively. The reaction mixture was left stirring under microwave irradiation (initial setting at 150W) for 15 minutes at 120 °C. The crude product was purified using either flash column chromatography (deactivated with Et_3N) (90% yield) or by fraction distillation (66% yield).

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