Supporting information: Direct Preparation of Monoarylidene Derivatives of Aldehydes and Enolizable Ketones with DIMCARB

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Synthesis of *E*-2-benzylidenecyclohexanone (Table 1, entry 1, method a).

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (10 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 50 °C and cyclohexanone (0.94 g, 9.4 mmol) was added in a single portion. Stirring at 50 °C was continued for 8 h. DIMCARB (6.45 g, 61 %) was recovered from the reaction mixture by distillation at 60 °C under an atmosphere of CO_2.

The undistilled residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with ether (3 × 25 mL). The combined ether fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a green oil (1.40 g). Si gel chromatography with hexane/ethyl acetate (1:1) yielded *E*-2-benzylidenecyclohexanone (1.00 g, 57 %), as a yellow solid m.p. 53-55 °C (lit.[i] 53-54 °C). ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.69 – 1.61 (m, 2H, -CH_2-), 1.85 – 1.77 (m, 2H, -CH_2-), 2.44 (t, *J* = 6.7 Hz, 2H, -CH_2-C=O), 2.73 (td, *J* = 6.4, 2.2 Hz, 2H, CH=CCH2), 7.36 - 7.19 (m, 5H, ArH), 7.43 (t, *J* = 2.2, 1H, Ar-CH=C). ^{13}C n.m.r.(75 MHz, $CDCl_3$): δ 23.25 (-<u>C</u>H_2-); 23.77 (-CH_2-); 28.80 (CH=C<u>C</u>H_2); 40.19 (<u>C</u>H_2-C=O); 128.25 (*o*-Ar); 128.42 (*p*-Ar); 130.19 (*m*-Ar); 135.37 (Ar-<u>C</u>H); 135.54 (<u>Ar</u>-CH=C); 136.57 (CH=<u>C</u>C=O); 201.29 (C=O).

Synthesis of 2-benzylidenecyclohexanone (Table 1, entry 1, method b).

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (3 mL) at ambient temperature with stirring. Gas was evolved. Cyclohexanone (0.925 g, 9.4 mmol) was added in a single portion. Stirring at ambient temperature was continued for 31.5 h. DIMCARB was recovered from the crude reaction mixture by distillation at 40 °C under high vacuum.

The undistilled residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with ether (3 × 25 mL). The combined ether fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a green oil (1.40 g). Si chromatography with 1:1 hexane/ethyl acetate yielded *E*-2-benzylidenecyclohexanone (0.99 g, 73 %) as a yellow solid, *E*,*E*-2,6-bisbenzylidenecyclohexanone as a yellow solid (0.21 g, 8.1 %) and a mixture of diastereoisomers of 2-(hydroxyphenylmethyl)cyclohexanone (0.14 g, 7.3 %) as a yellow solid. Physical data is consistent with prior experiments for this compound.

Synthesis of *E*-2-benzylidenecyclohexanone (Table 1, entry 1, method c).

Benzaldehyde (0.5 g, 4.7 mmol) was added to DIMCARB (2.5 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 50 °C and cyclohexanone (0.925 g, 9.4 mmol) was added in a single portion. Stirring at 50 °C was continued for 5.25 h during which the clear solution turned orange.

The reaction mixture was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to provide a green oil (0.80 g). Si chromatography with 1:1 hexane/ethyl acetate mixture yielded *E*-2-

benzylidenecyclohexanone (0.67 g, 76 %) as a yellow solid. Physical data is consistent with prior experiments for this compound.

Synthesis of *E*-2-benzylidenecyclopentanone (Table 1, entry 2, method a).

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (10 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 52 °C and cyclopentanone (0.79 g, 9.4 mmol) was added in a single portion. Stirring at 52 °C was continued for 3 h, after which the colorless reaction mixture had become dark brown. DIMCARB (8.71 g, 83 %) was recovered from the reaction mixture by distillation at 60 °C under high vacuum.

The undistilled residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a brown oil (1.21 g). Si chromatography with ethyl acetate yielded *E*-2-benzylidenecyclopentanone (1.06 g, 74 %) as a yellow solid m.p. 54-57 °C. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 2.06 (app p, *J* = 7.6 Hz, 2H, -CH_2-), 2.44 (t, *J* = 8.0 Hz, 2H, -CH_2-C=O), 3.00 (td, *J* = 7.2, 2.7 Hz, 2H, C=CCH_2), 7.48 – 7.30 (m, 4H, 3 × ArCH, 1 × Ar-CH=C), 7.59 – 7.56 (m, 2H, ArCH). ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 20.20 (-$\underline{C}H_2$-); 29.36 (-$\underline{C}H_2$-C=C); 37.79 (-$\underline{C}H_2$-C=O); 128.73 (*o*-Ar); 128.36 (*p*-Ar); 130.55 (*m*-Ar); 132.42 (Ar-$\underline{C}$H); 135.57 ($\underline{Ar}$-CH=C); 136.12 (CH=$\underline{C}$C=O); 208.24 (C=O).

Synthesis of *E*-2-benzylidenecyclopentanone (Table 1, entry 2, method b).

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (3 mL) at ambient temperature with stirring. Gas was evolved. Cyclopentanone (0.79 g, 9.4 mmol) was added in a single portion. Stirring at ambient temperature was continued for 3 h, during which time the colorless reaction mixture became orange.

The reaction mixture was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a brown oil (1.35 g). Si chromatography with 1:1 hexane/ethyl acetate mixture yielded *E*-2-benzylidenecyclopentanone (1.03 g, 64 %) as a yellow solid. Physical data is consistent with prior experiments for this compound.

Synthesis of *E*-phenylbut-1-en-3-one (Table 1, entry 3, method a).

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (10 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 54 °C and acetone (0.547 g, 9.4 mmol) was added in a single portion. Stirring at 54 °C was continued for 3 h during which the clear, colorless solution turned red. DIMCARB (5.84 g, 56 %) was recovered from the reaction mixture by distillation at 45 °C under an atmosphere of CO_2.

The undistilled residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with ethyl acetate (2 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$. An aliquot (60%) of the solution was worked up by filtration of $MgSO_4$ and solvent removal *in vacuo* to afford a red oil (0.66 g). Purification of this fraction was

performed by Si chromatography using a 1:1 hexane/ethyl acetate mixture to afford *E*-phenylbut-1-en-3-one (0.36g, 43 %) as an oil. Crystallisation yielded white crystals m.p. 37-39 °C(lit. 39-42 °C). ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 2.35 (s, 3H, -CH_3), 6.70 (d, *J* = 16.9 Hz, 1H, =CH-C=O), 7.39 - 7.35 (m, 3H, ArH), 7.54 - 7.47 (m, 3H, 2 × ArH, Ar-CH=).

Synthesis of *E*-phenylbut-1-en-3-one (Table 1, entry 3, method b).

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (3 mL) at ambient temperature with stirring. Gas was evolved. Acetone (0.547 g, 9.4 mmol) was added in a single portion. Stirring at ambient temperature was continued for 3 h during which the colorless solution became orange.

The reaction mixture was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a brown oil (1.23 g). ^{1}H n.m.r. spectra showed a 5 : 1 ratio of mono to bis adducts. Although these compounds were not separated, the ^{1}H n.m.r. spectrum indicated a 75 % yield of the mono adduct.

Synthesis of a mixture of *E*-phenylpent-1-en-3-one and *E*-2-methyl-1-phenylbut-1-en-3-one (Table 1, entry 4).

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (10 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 50 °C and butanone (0.546 g, 9.4 mmol) was added in a single portion. Stirring at ambient

temperature was continued for 24h. DIMCARB was removed from the reaction mixture by distillation.

The undistilled residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford an orange oil. The oil was washed with hexane (5 mL) and the resulting precipitate was filtered. The solvent of the filtrate was removed *in vacuo* to yield a mixture of the benzylidenebutanone isomers (1.04 g). The GC showed a ratio of 3.3 **:** 1 of the methyl substituted isomer (54 % yield) and the methylene substituted isomer (16 % yield), respectively. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.17 (t, *J* = 7.3 Hz, 3H, -CH_3 {1}); 2.06 (s, 3H, =C-CH_3 {2}); 2.45 (s, 3H, O=C-CH_3 {2}); 2.69 (q, *J* = 7.3 Hz, 2H, -CH_2- {1}); 6.76 (d, *J* = 16.2 Hz, 1H, C=C*H*-C=O {1}); 7.45 – 7.34 (m, 4H, 3 × ArCH, 1 × Ar-CH=C {1,2}); 7.59 – 7.52 (m, 2H, 2 × ArCH, {1,2}). Individual isomers not separated.

Synthesis of chalcone (Table 1, entry 5).

Acetophenone (1.0 g, 8.3 mmol) was added to DIMCARB (5 mL) at ambient temperature with stirring. The solution was heated to 50 °C and benzaldehyde (0.88 g, 8.3 mmol) was added in a single portion. Gas was evolved. Stirring at 50 °C was continued for 48 h. DIMCARB was removed from the reaction mixture by distillation.

The undistilled reaction mixture was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to provide a yellow oil (1.75 g). The ^{1}H n.m.r. spectrum showed 66 % conversion of the aldehyde and a 65 %

yield of chalcone. ^{13}C n.m.r.(75 MHz, $CDCl_3$): δ 122.26, 125.42, 128.58, 128.63, 128.68, 128.75, 129.09, 130.67 (Ar<u>C</u>H), 132.90 (O=C<u>C</u>H); 144.96 (ArCH=C); 135.03, 138.35 (ArC); 190.66 (C=O).

<u>Synthesis of *E*-2-methyl-3-phenylpropenal (Table 1, entry 6).</u>

Benzaldehyde (1.0 g, 9.4 mmol) was added to DIMCARB (3 mL) at ambient temperature with stirring. Gas was evolved. Propionaldehyde (0.547 g, 9.4 mmol) was added in a single portion. Stirring at ambient temperature was continued for 48 h, during which the colorless mixture became a dark maroon. DIMCARB was removed from the reaction mixture by distillation leaving a yellow solid.

The residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a red oil (1.20 g). Si chromatography with 95:5 hexane/ether yielded (0.84 g, 61 %) as a clear liquid. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 2.07 (d, *J* = 1.3, 3H, -CH_3); 7.25 (app s, ArCH=C); 7.53 – 7.36 (m, 5H, ArH); 9.58 (s, 1H, O=CH). ^{13}C n.m.r.(75 MHz, $CDCl_3$): δ 11.06 (-<u>C</u>H_3); 128.85 (*o*-Ar<u>C</u>H); 129.69 (*p*-Ar<u>C</u>H); 130.16 (*m*-Ar<u>C</u>H); 135.32 (Ar<u>C</u>-CH=C); 138.54 (Ar-CH=<u>C</u>); 149.85 (ArC-<u>C</u>H=C); 195.58 (C=O).

Synthesis of *E*-2-(4-methoxybenzylidene)cyclohexanone (Table 1, entry 7).

p-Anisaldehyde (1.0 g, 7.4 mmol) was added to DIMCARB (10 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 50 °C and cyclohexanone (0.73 g, 7.4 mmol) was added in a single portion. Stirring at 50 °C was continued for 24 h. DIMCARB was removed by distillation.

The undistilled residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a brown oil (1.51 g) shown by spectral analysis to contain mono and bis products.

E-2-(4-Methoxybenzylidene)cyclohexanone (1.17 g, 73 %) m.p. 64-66 °C; ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.73 – 1.65 (m, 2H, -CH_2-); 1.87 – 1.79 (m, 2H, -CH_2-); 2.44 (t, *J* = 6.7 Hz, 2H, -CH_2-C=O); 2.76 (td, *J* = 6.4, 2.2 Hz, 2H, C=CCH_2); 3.75 (s, 3H, -OCH_3); 6.83 (d, *J* = 8.8 Hz, 2H, *o*-ArH); 7.31 (d, *J* = 8.8 Hz, 2H, *m*-ArH); 7.41 (t, *J* = 2.1 Hz, 1H, Ar-CH=C); and *E*,*E*-2,6-bis(4-methoxybenzylidene)cyclohexanone (0.29 g, 12 %) ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 23.20 (-CH_2-); 28.68 (-C=CCH_2); 55.46 (-OCH_3); 114.09 (*o*-ArCH); 128.9 (ArC); 132.40 (*m*-ArCH); 134.51 (ArCH=C); 136.64 (ArCH=C); 160.11 (ArC-OCH_3) were recrystallized from hexane.

Synthesis of *E*-2-(4-methoxybenzylidene)cyclopentanone (Table 1, entry 8, method a).

p-Anisaldehyde (1.0 g, 7.4 mmol) was added to DIMCARB (3 mL) at ambient temperature with stirring. Gas was evolved. Cyclopentanone (0.62 g, 7.4 mmol) was added in a single portion. Stirring at ambient temperature was continued for 3 h, during which the colorless reaction mixture became orange.

The reaction mixture was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with dichloromethane (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford 2-(4-methoxybenzylidene)cyclopentanone (1.16 g, 78 %) as an orange solid m.p. 64-66 °C (lit.[ii] 66-68 °C). ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.90 (app p, *J* = 7.6, 2H, -CH_2-); 2.27 (t, *J* = 7.9 Hz, 2H, -CH_2-C=O); 2.82 (td, *J* = 7.2 Hz, 2H, C=CCH_2); 3.72 (s, 3H, -OCH_3); 6.83 (d, *J* = 8.8 Hz, 2H, *o*-ArH); 7.24 (t, *J* = 2.7 Hz, 1H, ArCH=C); 7.38 (d, *J* = 8.8 Hz, 2H, *m*-ArH). ^{13}C n.m.r.(75 MHz, $CDCl_3$): δ 20.11 (-$\underline{C}H_2$-); 29.24 (-$\underline{C}H_2$-C=C); 37.71 (-$\underline{C}H_2$-C=O); 55.33 (-OCH_3); 114.25 (*o*-Ar); 128.23 (Ar-$\underline{C}$H); 132.11 ($\underline{Ar}$-CH=C); 132.29 (*m*-Ar); 133.71 (CH=$\underline{C}$C=O); 160.57 (Ar$\underline{C}OCH_3$); 207.95 (C=O).

Synthesis of *E*-2-(4-methoxybenzylidene)cyclopentanone (Table 1, entry 8, method b).

p-Anisaldehyde (0.5 g, 3.7 mmol) was added to DIMCARB (1.5 mL) at ambient temperature with stirring. Gas was evolved. Cyclopentanone (0.62 g, 3.7 mmol) was added in a single portion. Stirring at ambient temperature was continued for 2 h.

The reaction was quenched by passing through silica gel with 1:1 ethyl acetate/hexane. The eluent was collected and removal *in vacuo* afforded *E*-2-(4-methoxy-benzylidene)cyclopentanone (1.15 g, 77 %) as an orange oil, which solidified on standing. Physical data is consistent with prior experiments for this compound.

Synthesis of *E*-2-(4-chlorobenzylidene)cyclohexanone (Table 1, entry 9).

4-Chlorobenzaldehyde (1.0 g, 7.1 mmol) was added to DIMCARB (10 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 50 °C and cyclohexanone (0.684 g, 7.1 mmol) was added in a single portion. Stirring at 50 °C continued for 28 h.

The crude mixture was distilled under high vacuum where the temperature was decreased to 40 °C. DIMCARB (4.98 g, 47 %) was recovered from the reaction mixture by distillation at 60 °C under an atmosphere of CO_2.

The undistilled residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic fractions was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a yellow oil (1.47 g). Si chromatography with 1:1 hexane/ethyl acetate mixture yielded *E*-2-(4-chlorobenzylidene)cyclohexanone (0.72 g, 48 %) as a beige solid m.p. 44-46 °C. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.69 – 1.61 (m, 2H, -CH_2-); 1.85 – 1.77 (m, 2H, -CH_2-); 2.42 (t, *J* = 6.8 Hz, 2H, -CH_2-C=O); 2.68 (td, *J* = 6.4, 2.3 Hz, 2H, C=CCH_2); 7.25 – 7.19 (m, 4H, ArH); 7.32 (t, *J* = 2.2 Hz, 1H, Ar-CH=C). ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 23.23 (-$\underline{C}H_2$-); 23.74 (-$\underline{C}H_2$-); 28.85 (-$\underline{C}H_2$-C=C); 40.20 (-$\underline{C}H_2$-C=O); 128.53 (*o*-Ar); 131.47 (*m*-Ar); 134.02 (Ar-CH); 134.34 (Ar-CH=C); 137.07 (CH=CC=O); 201.08 (C=O).

Synthesis of *E*-2-(1-naphthylidene)cyclohexanone (Table 1, entry 10).

1-Naphthaldehyde (1.0 g, 6.4 mmol) was added to DIMCARB (3 mL) at ambient temperature with stirring. Gas was evolved. The solution was heated to 50 °C and cyclohexanone (0.627 g, 6.4 mmol) was added in a single portion. Stirring was continued for 18 h.

The reaction mixture was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford a yellow solid. Si chromatography with 1:1 hexane/ethyl acetate yielded *E*-2-(1-naphthylidene)cyclohexanone (1.21 g, 80 %) as a beige solid m.p. 54-56 °C. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.76 – 1.68 (m, 2H, -CH_2-); 2.06 – 1.92 (m, 2H, -CH_2-); 2.62 (t, *J* = 6.7 Hz, 2H, -CH_2-C=O); 2.69 (td, *J* = 6.4, 2.0 Hz, 2H, C=CCH_2); 7.38 (d, *J* = 7.1 Hz, 1H, ArH); 7.55 – 7.46 (m, 3H, ArH); 7.90 – 7.83 (m, 2H, ArH); 8.00 – 7.94 (m, 2H, ArH); 8.02 (app s, 1H, Ar-CH=C). ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 23.92 (-CH_2-); 24.25 (-CH_2-); 29.27 (-CH_2-C=C); 40.80 (-CH_2-C=O); 124.86, 125.13, 126.26, 126.53, 127.02, 128.71, 128.93 (ArCH); 132.14, 132.27, 133.67, 139.16 (ArC); 133.27 (ArCH=C); 201.96 (C=O).

Synthesis of *E*-2-benzylidenecyclopentanone (Table 2, entry 1).

DIMCARB (3.275 mL, 27.5 mmol) was added to a solution of benzaldehyde (0.508 mL, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved. Cyclopentanone (0.445 mL, 5.0 mmol) was added in a single portion. Stirring at ambient temperature was continued for 18 h during which the colorless reaction mixture became orange.

The solvent mixture was removed *in vacuo* and the residue was acidified with 0.5 M H_2SO_4 (10 mL) and extracted with ether (3 × 20 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to yield pure 2-benzylidenecyclopentanone (0.73 g, 85 %) as a brown solid. Physical data is consistent with prior experiments for this compound.

Synthesis of 2-(4-methoxybenzylidene)cyclopentanone (Table 2, entry 2).

DIMCARB (3.275 mL, 27.5 mmol) was added to a solution of *p*-anisaldehyde (0.608 mL, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved. Cyclopentanone (0.445 mL, 5.0 mmol) was added in a single portion. Stirring at ambient temperature was continued for 17 h during which the colorless reaction mixture became orange.

The solvent mixture was removed *in vacuo*, the residue was acidified with 0.5 M H_2SO_4 (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to yield *E*-2-(4-methoxy benzylidene)cyclopentanone (0.92 g, 91 %) in high purity as an orange solid. Physical data is consistent with prior experiments for this compound.

Synthesis of *E*-2-(2-methoxybenzylidene)cyclopentanone (Table 2, entry 3).

DIMCARB (3.275 mL, 27.5 mmol) was added to a solution of *o*-anisaldehyde (0.681 g, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved. Cyclopentanone (0.445 mL, 5.0 mmol) was added in a single portion. Stirring at ambient temperature was continued for 17 h during which the colorless reaction mixture became orange.

The solvent was removed *in vacuo,* the residue was acidified with 0.5 M H_2SO_4 (10 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to yield *E*- 2-(2-methoxybenzylidene)cyclopentanone (0.88 g, 87 %) as a brown solid in high purity. ^{1}H n.m.r. (300 MHz, $CDCl_3$): δ 1.99 (app p, *J* = 7.5 Hz, 2H, -CH_2-); 2.39 (t, *J* = 7.9 Hz, 2H, -CH_2-C=O); 2.91 (dt, *J* = 7.1, 2.7 Hz, 2H, C=CCH_2); 3.86 (s, 3H, O-CH_3); 6.91 (d, *J* = 8.3 Hz, 1H, ArH); 6.99 (dt, *J* = 8.1, 0.5 Hz, 1H, ArH); 7.33 (dt, *J* = 7.9, 1.7 Hz, 1H, ArH); 7.46 (dd, *J* = 7.7, 1.3 Hz, 1H, ArH); 7.80 (t, *J* = 2.7 Hz, 1H, Ar-CH=C). ^{13}C n.m.r. (75 MHz, $CDCl_3$): δ 20.60 (-$\underline{C}H_2$-); 29.69 (-$\underline{C}H_2$-C=C); 38.13 (-$\underline{C}H_2$-C=O); 55.71 (O-$\underline{C}H_3$); 111.00, 120.44, 127.18, 129.88, 130.94 (Ar$\underline{C}$H, Ar-$\underline{C}$H=C); 124.89, 136.27 (Ar-CH=C, CH=$\underline{C}$C=O); 159.14 (Ar$\underline{C}$-OCH_3); 208.08 (C=O).

Synthesis of *E*-2-(4-hydroxybenzylidene)cyclopentanone (Table 2, entry 4).

DIMCARB (3.275 mL, 27.5 mmol) was added to a suspension of 4-hydroxybenzaldehyde (0.611 g, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved and the solid dissolved. Cyclopentanone (0.445 mL, 5.0 mmol) was added in a single portion. Stirring at ambient temperature was continued for 18 h during which the colorless reaction mixture became deep red.

The solvent mixture was removed *in vacuo*, the residue was acidified with 0.5 M H_2SO_4 (10 mL) and extracted with CH_2Cl_2 (2 × 80 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to yield *E*-2-(4-hydroxybenzylidene)cyclopentanone (0.81 g, 86 %), as yellow solid m.p. 188-192 °C. ^{1}H n.m.r. (200 MHz, CD_3OD): δ 2.02 (app p, *J* = 7.5 Hz, 2H, -CH_2-); 2.39 (t, *J* = 7.6 Hz,

2H, -CH_2-C=O); 2.91 (dt, *J* = 7.2, 2.7 Hz, 2H, C=CCH_2); 6.85 (d, *J* = 8.8 Hz, 2H, *o*-ArH); 7.28 (t, *J* = 2.7 Hz, 1H, Ar-CH=C); 7.45 (d, *J* = 8.8 Hz, 2H, *m*-ArH). ^{13}C n.m.r. (50 MHz, CD_3OD): δ 21.21 (-CH_2-); 30.35 (-CH_2-C=C); 38.73 (-CH_2-C=O); 116.93 (*o*-Ar); 133.93 (*m*-Ar); 134.38 (Ar-CH=C); 128.20, 134.18 (Ar-CH=C, CH=CC=O); 160.65 (Ar-OH); 210.88 (C=O).

Synthesis of *E*-2-(4-chlorobenzylidene)cyclopentanone (Table 2, entry 5).

DIMCARB (3.275 mL, 27.5 mmol) was added to a solution of *p*-chlorobenzaldehyde (0.703 g, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved. Cyclopentanone (0.445 mL, 5.0 mmol) was added in a single portion. Stirring at ambient temperature was continued for 60 h during which the colorless reaction mixture became yellow-green.

The solvent was removed *in vacuo*, the residue was acidified with 0.5 M H_2SO_4 (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to provide a brown solid (0.94 g, 91 %) m.p. 57-59 °C. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2.04 (app p, *J* = 7.6 Hz, 2H, -CH_2-); 2.41 (t, *J* = 7.9 Hz, 2H, -CH_2-C=O); 2.93 (dt, *J* = 7.3, 2.6 Hz, 2H, C=CCH_2); 7.30 (t, *J* = 2.8 Hz, 1H, Ar-CH=C); 7.38 (d, *J* = 8.4 Hz, 2H, *o*-ArH); 7.53 (d, *J* = 8.4 Hz, 2H, *m*-ArH). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 20.29 (-CH_2-); 29.46 (-CH_2-C=C); 37.88 (-CH_2-C=O); 123.76, 134.65, 136.88 (ArC); 131.75 (Ar-CH=C); 131.98, 132.11 (ArCH); 207.88 (C=O).

Synthesis of *E*-2-(4-bromobenzylidene)cyclopentanone (Table 2, entry 6).

DIMCARB (3.275 mL, 27.5 mmol) was added to a solution of *p*-bromobenzaldehyde (0.925 g, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved. Cyclopentanone (0.445 mL, 5.0 mmol) was added in a single portion. Stirring at ambient temperature was continued for 60 h during which time the colorless reaction mixture became beige.

The solvent was removed *in vacuo*, the residue was acidified with 0.5 M H_2SO_4 (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to afford *E*-2-(4-bromobenzylidene)cyclopentanone (1.26 g, 82 %) as a brown solid in high purity 89-91 °C. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2.03 (app p, *J* = 7.6 Hz, 2H, -CH_2-); 2.40 (t, *J* = 7.9 Hz, 2H, -CH_2-C=O); 2.92 (dt, *J* = 7.2, 2.8 Hz, 2H, C=CCH_2); 7.30 (t, *J* = 2.7 Hz, 1H, Ar-CH=C); 7.36 (d, *J* = 8.5 Hz, 2H, *o*-ArH); 7.44 (d, *J* = 8.5 Hz, 2H, *m*-ArH). ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 20.15 (-$\underline{C}H_2$-); 29.30 (-$\underline{C}H_2$-C=C); 37.73 (-$\underline{C}H_2$-C=O); 129.00, 131.66 (Ar$\underline{C}$H); 130.91 (Ar-$\underline{C}$H=C); 134.09, 135.26, 136.61 (ArC, Ar-CH=$\underline{C}$); 207.84 (C=O).

Synthesis of *E*-2-(1-naphthylidene)cyclopentanone (Table 2, entry 7).

DIMCARB (3.275 mL, 27.5 mmol) was added to a solution of 1-naphthaldehyde (0.679 mL, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved. Cyclopentanone (0.485 mL, 5.5 mmol) was added in a single portion. Stirring at ambient temperature was continued for 24 h during which the colorless reaction mixture became yellow.

The solvent mixture was removed *in vacuo* and the residue was acidified with 0.5 M H_2SO_4 (10 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to yield *E*-2-(1-naphthylidene)cyclopentanone (0.92 g, 83 %) as a brown oil. ^{1}H n.m.r. (200 MHz, $CDCl_3$): δ 1.93 (app p, *J* = 7.3 Hz, 2H, -CH_2-); 2.42 (t, *J* = 7.9 Hz, 2H, -CH_2-C=O); 2.84 (dt, *J* = 7.1, 2.7 Hz, 2H, C=CCH_2); 7.59-7.41 (m, 4H, ArC*H*=C, Ar*H*); 7.85-7.80 (m, 2H, Ar*H*); 8.14-8.09 (m, 2H, Ar*H*).

Synthesis of *E*-2-(4-carboxybenzylidene)cyclopentanone (Table 2, entry 8).

DIMCARB (3.275 mL, 27.5 mmol) was added to a suspension of 4-carboxybenzaldehyde (0.751 g, 5.0 mmol) in CH_2Cl_2 (5.5 mL) at ambient temperature. Gas was evolved and the solid dissolved. Cyclopentanone (0.445 mL, 5.0 mmol) was added in a single portion. Stirring at ambient temperature was continued for 13 h during which the colorless reaction mixture became a deep yellow.

The solvent was removed *in vacuo*, the residue was acidified with 0.5 M H_2SO_4 (25 mL) and extracted with CH_2Cl_2 (2 × 80 mL). The combined organic fraction was dried with anhydrous $MgSO_4$, filtered and the solvent removed *in vacuo* to yield *E*-2-(4-carboxybenzylidene)cyclopentanone (0.93 g, 74 %) as an orange solid m.p. 208-209 °C. ^{1}H n.m.r. (400 MHz, CD_3OD): δ 2.05 (app p, *J* = 7.6 Hz, 2H, -CH_2-); 2.41 (t, *J* = 7.9 Hz, 2H, -CH_2-C=O); 3.01 (dt, *J* = 7.2, 2.8 Hz, 2H, C=CCH_2); 7.34 (t, *J* = 2.8 Hz, 1H, Ar-C*H*=C); 7.64 (d, *J* = 8.3 Hz, 2H, *o*-Ar*H*); 8.06 (d, *J* = 8.3 Hz, 2H, *m*-Ar*H*). ^{13}C n.m.r. (100 MHz, CD_3OD): δ 21.23 (-$\underline{C}H_2$-); 30.48 (-$\underline{C}H_2$-C=C); 38.71(-$\underline{C}H_2$-C=O); 131.14 (*o*-

Ar); 131.53 (*m*-Ar); 131.89 (Ar-CH=C); 132.46, 140.01, 141.29 (Ar-CH=C, Ar-CO_2H, CH=CC=O); 169.40 (Ar-CO_2H); 210.22 (C=O).

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