Supporting Information

Pentamethylphenyl (Ph*) and Related Derivatives as Useful Acyl Protecting Groups for Organic Synthesis: A Preliminary Study

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I) General Experimental

Reaction Setup: Microwave vials and vial caps (containing a resealing Silicone/PTFE septum) were purchased from Kinesis (Cole-Palmer) and were used without flame-drying. Unless otherwise stated, all other reactions were performed in flame-dried glassware equipped with a stirrer bar using standard Schlenk techniques under an atmosphere of Ar. Fresh double-walled balloons of Ar or H₂ were used. Room temperature (RT) is defined to be 25 °C (298 K) unless otherwise stated.

Reagents and solvents: Unless detailed below or otherwise stated, all reagents and solvents were purchased and used as supplied from Sigma-Aldrich (now Merck KGaA), Thermo Fisher Scientific (including Alfa Aesar, Fisher Scientific and Acros Organics), Fluorochem, Honeywell, Tokyo Chemical Industry, Apollo Scientific, Manchester Organics (part of Navin Fluorine Int. Ltd.), Santa Cruz Biotechnology and Strem Chemicals.

TMSCl was freshly distilled (from CaH₂) under Ar at atmospheric pressure and used immediately. Anhydrous AlCl₃ (powder) was purchased from Alfa Aesar and used as supplied. Pearlman's catalyst (20 wt% Pd(OH)₂/C dry basis, contains 50 wt% H₂O) was purchased from Sigma-Aldrich and used as supplied. [Cp*IrCl₂]₂ and [(cod)IrCl]₂ were purchased from Sigma-Aldrich and/or Alfa Aesar and used as supplied. Anhydrous diisopropylamine and DMF, was purchased from Sigma-Aldrich in Sure/SealTM bottles. Anhydrous Et₂O, CH₂Cl₂, MeOH, THF and PhMe were obtained from a MBRAUN SPS-5 solvent purification system by passage through double filtration columns under N₂.

Chromatography: Thin layer chromatography (TLC) was performed on pre-coated aluminium- (200 µm) or glass-backed (250 µm) Merck Kieselgel 60 F₂₅₄ plates, or polyester-backed Macherey-Nagel Polygram® SIL G/UV254 plates (250 µm), visualised using UV irradiation (λ = 254 nm) and/or staining with potassium permanganate (KMnO₄), vanillin, 2,4-dinitrophenylhydrazine (2,4-DNPH) or cerium ammonium molybdate (CAM, or Hanessian's stain) solutions. Preparative TLC was performed using the abovementioned TLC plates for samples within 5–25 mg of crude mass, or Merck Kieselgel 60 F₂₅₄ preparative TLC plates (500 µm) for samples within 25–100 mg of crude mass.

Purification by flash column chromatography was performed with Merck Kieselgel 60 (40–63 μm) silica gel according to the method by W. C. Still et al.¹ All solvents used for chromatography were HPLC grade or equivalent and supplied by Honeywell, Sigma-Aldrich or Thermo Fisher Scientific.

Compound Naming and Numbering: Unless otherwise stated, systematic names were generated by the computer program ChemDraw according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC). In order to allow for the straightforward comparison of data, the NMR assignments given follow the numbering system shown on the relevant chemical structure.

Melting points: Melting points (m.p.) were obtained using a Leica VMTG heated-stage microscope equipped with a Testo 720 thermometer and are uncorrected.

Infrared spectroscopy: Fourier-transform infrared (FT-IR) spectra were recorded from evaporated films on a Bruker Tensor 27 spectrometer equipped with a Pike Miracle Attenuated Total Reflectance (ATR) sampling accessory. Absorption maxima are quoted in wavenumbers (ν_{max}) with units of cm^{-1} and for the range of 3600–600 cm^{-1} .

NMR spectroscopy: All spectra were acquired on a Bruker DPX 200 equipped with a 5 mm $^{13}\text{C}/^1\text{H}$ dual probe, a Bruker AVIII HD 400 equipped with a 5 mm z -gradient BBFO probe, Bruker AVIII HD 400 equipped with a 5 mm z -gradient BBFO “SMART” probe, Bruker AVII 500 equipped with a 5 mm BBFO “SMART” probe or 5 mm z -gradient TFI probe, or Bruker AVIII HD 500 equipped with a 5 mm triple resonance TBO probe. The deuterated solvent acted as internal deuterium lock.

^1H NMR experiments were recorded at 200, 400 or 500 MHz, and ^{13}C NMR at 101 or 126 MHz with broadband proton decoupling. NMR acquisition was performed using the software Bruker TopSpin®. NMR data processing and analyses were performed with the software MestReNova. Chemical shifts (δ) are quoted in parts per million (ppm) to the nearest 0.01 ppm for ^1H and 0.1 ppm for ^{13}C NMR; for cases where signals in ^{13}C NMR spectra are within 0.1 ppm, only the signals involved are reported to 0.01 ppm. Residual protic solvent signal acted as an internal reference for ^1H NMR, and deuterated solvent carbon signal acted as an internal reference for ^{13}C NMR (CDCl_3 : ^1H NMR = 7.26 ppm; ^{13}C NMR = 77.16 ppm. Every attempt was made to

obtain *J*-coupling information through multiplet analysis with the aid of line fitting and spectral deconvolution. The multiplicity of a signal is reported as such: s – singlet, d – doublet, t – triplet, q – quartet, quint. – quintet, m – multiplet, app. – apparent or approximate, br. – broad, v. – very, or combinations thereof. Coupling constants are quoted in Hz to the nearest 0.1 Hz. Structural assignments were made with the aid of DEPTQ, COSY, HSQC and HMBC experiments.

Mass spectrometry (MS): Low resolution MS were recorded on an Agilent 6120 Quadrupole mass spectrometer equipped with an Agilent 1260 Infinity LC pump, or a Waters LCT Premier XE mass spectrometer equipped with a Waters 1525 μ Binary HPLC pump, both with a flow rate of 0.2 mL min⁻¹ using H₂O:MeOH:HCOOH (10:89.9:0.1) as eluent. The mass reported is the mass-to-charge ratio (*m/z*) containing the most abundant isotopes under the conditions of electrospray ionisation (ESI), with each value to 1 decimal place.

HRMS under ESI conditions were recorded on a Thermo Exactive Orbitrap mass spectrometer equipped with a Waters Equity LC system, a Bruker MicroToF mass spectrometer equipped with an Agilent 1100 HPLC pump and autosampler, or on a Waters Xevo Quadrupole Time of Flight (Q-ToF) mass spectrometer. The Thermo Exactive system employs a flow rate of 0.2 mL min⁻¹ using H₂O:MeOH:HCOOH (10:89.9:0.1) as eluent, with a heated electrospray ionisation (HESI-II) probe and has a resolution of 50,000 FWHM. The Bruker system uses the built-in electrospray source, while the Waters system runs on a lock-mass mode with ESI performed by a secondary electrospray source, both using conditions identical to the Thermo Exactive system. Instrument control and data processing were performed using the softwares Thermo Xcalibur for the Thermo Exactive system, Compass DataAnalysis 4.0 for the Bruker system, and MassLynx for the Waters system.

All HRMS conditions were adjusted for maximum sensitivity, with an accuracy of better than 5 ppm for 24 h following external calibration on the day of analysis. Unless otherwise specified, the mass reported for HRMS is the mass-to-charge ratio containing the most abundant isotopes, with each value to 4 or 5 decimal places and within 5 ppm of the calculated mass.

Reporting of compounds: Compounds are reported in numerical order. Compounds that are not assigned a compound number in the main article are labelled S1, S2 etc.

II) Optimisation Studies

a) Preliminary Screening of different Brønsted and Lewis acids for the cleavage of Ph*

Typical Procedure: To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added ketone **9** (28.0 mg, 0.10 mmol), anisole (33 μ L, 0.30 mmol) and the appropriate acid (0.12 mmol, 1.2 equiv.) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a ResealTM septum) and heated to 100 °C in a preheated oil bath for 1 h 30 minutes. The reaction was cooled to RT and ice (250 mg) added. The mixture was extracted with CH₂Cl₂ (2 $\times$ 10 mL) and the combined organics washed with sat. aq. NaHCO₃ (10 mL), dried (MgSO₄) and concentrated *in vacuo*. The crude reaction mixture was then analysed using ¹H NMR.

Entry	Additive (1.2 equiv.)	Cleaved? ✓ or ✗
1	SnCl ₄	✓
2	InCl ₃	✓
3	AlCl ₃	✓
4	Al(Oi-Pr) ₃	✗
5	TfOH	✓
6	Montmorillonite K10 Clay	✓
7	AuCl ₃	✓
8	H ₂ SO ₄	✓
9	BF ₃ •OEt ₂	✓
10	HCl	✗
11	Pd(OAc) ₂	✗
12	AgOAc	✗
13	(Ph ₃ P)AuCl/AgSbF ₆	✓

b) Optimisation of AuCl₃ – Temperature and solvent

Entry	Conditions	Result (Isolated Yield)
1	AuCl ₃ , anisole, 100 °C	10 (38%)
2	AuCl ₃ , anisole, 80 °C	10 (38%)
3	AuCl ₃ , anisole, 60 °C	10 (45%)
4	AuCl ₃ , anisole, 40 °C	10 (52%)
5	AuCl ₃ , anisole, RT (18 °C)	10 (53%)
6	AuCl ₃ , anisole, RT (18 °C), CH₂Cl₂ (0.1 M)	10 (42%)
7	AuCl ₃ , anisole, RT (18 °C), CH₂Cl₂ (0.2 M)	10 (42%)
8	AuCl ₃ , anisole, RT (18 °C), CH₂Cl₂ (0.4 M)	10 (52%)
9	AuCl ₃ , <i>n</i>-BuOH , RT (18 °C), CH ₂ Cl ₂ (0.4 M)	No reaction
10	AuCl ₃ , <i>n</i>-BuOH , 50 °C , CH ₂ Cl ₂ (0.4 M)	No reaction

c) Optimisation of AuCl₃ – Solvent screen for one-pot *n*-BuOH process

Entry	Conditions	Ph* Cleaved? ✓ or ✗
1	AuCl ₃ , <i>n</i> -BuOH, RT, HFIP	✓ (1:1 mix of 9:11)
2	AuCl ₃ , <i>n</i> -BuOH, RT, THF	✗
3	AuCl ₃ , <i>n</i> -BuOH, RT, PhMe	✗
4	AuCl ₃ , <i>n</i> -BuOH, RT, MeCN	✗
5	AuCl ₃ , <i>n</i> -BuOH, RT, PhCF₃	✗
6	AuCl ₃ , <i>n</i> -BuOH, RT, MeNO₂	✗
7	AuCl ₃ , <i>n</i> -BuOH, RT, 1,4-dioxane	✗
8	AuCl ₃ , <i>n</i> -BuOH, RT, 1,2-DCE	✗
9	AuCl ₃ , <i>n</i> -BuOH, RT, DME	✗

d) Optimisation of AuCl₃ – Reaction time for one-pot *n*-BuOH process

Entry	Conditions	Result
1	AuCl ₃ , <i>n</i> -BuOH, RT, HFIP, 20 h	1:1 mix of 9:11 by ¹ H NMR
2	AuCl ₃ , <i>n</i> -BuOH, RT, HFIP, 48 h	2:1 mix of 11:9 by ¹ H NMR
3	AuCl ₃ , <i>n</i> -BuOH, RT, HFIP, 69 h	92% isolated yield (11)

e) Optimisation of AuCl₃ – Attempts to make the process catalytic

Entry	Conditions	Result (Isolated Yield)
1	AuCl ₃ (1.2 equiv.)	92%
2	AuCl ₃ (20 mol%), TFA (1.0 equiv.)	Trace conv.
3	AuCl ₃ (20 mol%), NH ₄ Cl (1.0 equiv.)	Trace conv.
4	AuCl ₃ (20 mol%), SiO ₂ (1.0 equiv.)	No reaction
5	AuCl ₃ (20 mol%), TMSCl (1.0 equiv.)	91%
6	AuCl ₃ (20 mol%), TMSCl (1.0 equiv.), 20 h	50% conv.
7	AuCl ₃ (10 mol%), TMSCl (1.0 equiv.), 20 h	50% conv.
8	AuCl ₃ (5 mol%), TMSCl (1.0 equiv.), 20 h	50% conv.
9	AuCl ₃ (5 mol%), TMSCl (1.0 equiv.), 69 h	85%
10	TMSCl (1.0 equiv.), 69 h	95%
11	AuCl ₃ (5 mol%), 69 h	Trace conv.

III) Additional Experiments for the cleavage of Ph*OH

a) Cleavage of Ph*OH with IBr

b) Cleavage of Ph*OH with aq. TFA (relative ratios by ¹H NMR reported)

c) Attempted cleavage of Ph*OH with HCl

IV) Experimental Procedures

4-Bromo-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one **S1**

To a solution of 4-bromobutyryl chloride (217 μL , 1.87 mmol) and pentamethylbenzene (222 mg, 1.50 mmol) in CH_2Cl_2 (15 mL) at 0 $^\circ\text{C}$ was added AlCl_3 (250 mg, 1.87 mmol) portion-wise over 5 minutes. The reaction was stirred at 0 $^\circ\text{C}$ for 3 h, and then carefully poured into cold H_2O (15 mL). The layers were separated and the organic layer washed with sat. aq. NaHCO_3 (20 mL). The aqueous layers were extracted with CH_2Cl_2 (3×20 mL) and the combined organics dried (MgSO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , eluent load, Pentane: Et_2O , 95:5) afforded ketone **S1** (0.38 g, 86%) as a colourless solid.

$R_f = 0.29$ (Pentane: Et_2O , 95:5), [UV, KMnO_4].

m.p. = 74–75 $^\circ\text{C}$.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 2925, 1697, 1575, 1438, 1403, 1315, 1243, 1110.

^1H NMR (CDCl_3 , 400 MHz) δ = 3.58 (2H, t, J = 6.4 Hz, C3H_2), 2.88 (2H, t, J = 6.9 Hz, C1H_2), 2.29 (2H, quint., J = 6.7 Hz, C2H_2), 2.24 (3H, s, Ar- CH_3), 2.19 (6H, s, $2 \times$ Ar- CH_3), 2.11 (6H, s, $2 \times$ CH_3).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 210.8 ($\text{C}=\text{O}$), 140.3 (Ar-C), 135.7 (Ar-C), 133.3 (2C, $2 \times$ Ar-C), 127.4 (2C, $2 \times$ Ar-C), 43.5 (C1H_2), 33.5 (C3H_2), 26.4 (C2H_2), 17.3 (2C, $2 \times$ Ar- CH_3), 16.8 (Ar- CH_3), 16.1 (2C, $2 \times$ Ar- CH_3).

HRMS (ESI^+) Found $[\text{M}+\text{H}]^+ = 297.0850$; $\text{C}_{15}\text{H}_{22}\text{O}^{79}\text{Br}$ requires 297.0849, Δ 0.56 ppm. All spectroscopic data in agreement with that previously reported.²

Butyl 4-bromobutanoate **1**

To a 2–5 mL microwave vial equipped with a stirrer bar was added ketone **S1** (56.5 mg, 0.19 mmol) and CH₂Cl₂ (0.95 mL) sequentially in the open atmosphere. The vial was sealed with a microwave vial cap, cooled to –17 °C (ice/NaCl bath), then Br₂ (19 μL, 0.38 mmol) added. Once TLC analysis indicated complete consumption of the substrate (typically 15 minutes), *n*-BuOH (52 μL, 0.57 mmol) was added at –17 °C and the reaction allowed to warm up to RT over 16 h. To the reaction mixture was added Et₂O (1.2 mL), sat. aq. Na₂SO₃ (1.2 mL) and brine (1.2 mL) sequentially. The layers were separated and the aqueous layer extracted with Et₂O (3 × 10 mL). The combined organics were dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 98:2→95:5) afforded ester **1** (25.6 mg, 60%) as a colourless oil.

¹H NMR (CDCl₃, 200 MHz) δ = 4.08 (2H, t, *J* = 6.6 Hz, OCH₂), 3.47 (2H, t, *J* = 6.4 Hz, C3H₂), 2.50 (2H, app. t, *J* = 7.0 Hz, C1H₂), 2.27–2.09 (2H, m, C2H₂), 1.69–1.55 (2H, m, CH₂CH₂O), 1.48–1.26 (2H, m, CH₂CH₃), 0.93 (3H, t, *J* = 7.3 Hz, CH₂CH₃).

¹H NMR in agreement with that previously reported.³

4-Oxo-4-(2,3,4,5,6-pentamethylphenyl)butanoic acid **S2**

To a solution of succinic anhydride[†] (1.50 g, 15.0 mmol) and pentamethylbenzene (2.44 g, 16.5 mmol) in CH₂Cl₂ (50 mL) at RT was added AlCl₃ (4.40 g, 33.0 mmol) portion-wise over 5 minutes. The reaction was stirred for 5 minutes at RT, and then carefully poured into cold 1 N HCl (50 mL). The mixture was extracted with Et₂O (2 × 100 mL), and the combined organics washed with additional 1 N HCl (2 × 100 mL), dried (MgSO₄), and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, solid load, Pentane:Et₂O, 70:30→EtOAc) afforded carboxylic acid **S2** (3.26 g, 88%) as a colourless solid.

*R*_f = 0.31 (Pentane:EtOAc, 50:50), [UV, KnMO₄].

m.p. = 195 °C (decomposition).

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3025, 3016, 2999, 2962, 2935, 2917, 2874, 1696, 1430, 1401, 1392, 1385, 1342, 1302, 1291, 1251, 1222, 1170, 1118, 1069, 1051, 1027, 992.

¹H NMR (CDCl₃, 400 MHz) δ = 3.02 (2H, t, *J* = 6.4 Hz, C1H₂), 2.77 (2H, t, *J* = 6.4 Hz, C2H₂), 2.24 (3H, s, Ar-CH₃), 2.19 (6H, s, 2 × Ar-CH₃), 2.11 (6H, s, 2 × Ar-CH₃).[‡]

¹³C NMR (CDCl₃, 101 MHz) δ = 209.6 (C=O), 178.0 (C3=O), 139.8 (Ar-C), 135.8 (Ar-C), 133.3 (2C, 2 × Ar-C), 127.7 (2C, 2 × Ar-C), 40.1 (C1H₂), 27.6 (C2H₂), 17.2 (2C, 2 × Ar-CH₃), 16.8 (Ar-CH₃), 16.1 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 249.1487; C₁₅H₂₁O₃ requires 249.1485, Δ 0.83 ppm. All spectroscopic data in agreement with that previously reported.²

[†] Note: It is essential that the succinic anhydride is recrystallised prior to use.

[‡] The carboxylic acid proton was not observed.

Methyl 4-oxo-4-(2,3,4,5,6-pentamethylphenyl)butanoate **S3**

To a solution of carboxylic acid **S2** (200 mg, 0.81 mmol) in CH_2Cl_2 (2.1 mL) at 0 °C was added MeOH (72 μL , 1.78 mmol), DMAP (32.7 mg, 0.27 mmol) and DCC (216 mg, 1.05 mmol) sequentially. The mixture was allowed to warm to RT slowly over 17 h (ice bath kept in place), after which it was filtered through a pad of Celite[®], eluting with CH_2Cl_2 . The organics were washed with H_2O (10 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , solid load, Pentane: Et_2O , 90:10→80:20) afforded ester **S3** (201 mg, 95%) as a colourless solid.

R_f = 0.17 (Pentane: Et_2O , 90:10), [UV, KMnO_4].

m.p. = 64–65 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3005, 2986, 2947, 2916, 1744, 1705, 1668, 1460, 1438, 1398, 1382, 1351, 1299, 1244, 1207, 1174, 1115, 1068, 1029, 999.

^1H NMR (CDCl_3 , 400 MHz) δ = 3.73 (3H, s, OCH_3), 3.02 (2H, t, J = 6.5 Hz, C1H_2), 2.72 (2H, t, J = 6.5 Hz, C2H_2), 2.24 (3H, s, Ar- CH_3), 2.19 (6H, s, $2 \times$ Ar- CH_3), 2.12 (6H, s, $2 \times$ Ar- CH_3).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 209.7 (C=O), 173.3 (C3=O), 139.9 (Ar-C), 135.7 (Ar-C), 133.3 (2C, $2 \times$ Ar-C), 127.7 (2C, $2 \times$ Ar-C), 52.0 (OCH_3), 40.4 (C1H_2), 27.5 (C2H_2), 17.2 (2C, $2 \times$ Ar- CH_3), 16.8 (Ar- CH_3), 16.1 (2C, $2 \times$ Ar- CH_3).

HRMS (ESI⁺) Found $[\text{M}+\text{Na}]^+ = 285.1475$; $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Na}$ requires 285.1467, Δ 2.80 ppm.

Butyl methyl succinate **2**

To a 2–5 mL microwave vial equipped with a stirrer bar was added ester **S3** (51.0 mg, 0.19 mmol) and CH_2Cl_2 (0.95 mL) sequentially in the open atmosphere. The vial was sealed with a microwave vial cap, cooled to $-17\text{ }^\circ\text{C}$ (ice/ NaCl bath), then Br_2 (25 μL , 0.49 mmol) added. Once TLC analysis indicated complete consumption of the substrate (typically 15 minutes), *n*-BuOH (52 μL , 0.57 mmol) was added at $-17\text{ }^\circ\text{C}$ and the reaction allowed to warm up to RT over 16 h. To the reaction mixture was added Et_2O (1.2 mL), sat. aq. Na_2SO_3 (1.2 mL) and brine (1.2 mL) sequentially. The layers were separated and the aqueous layer extracted with Et_2O ($3 \times 10\text{ mL}$). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , eluent load, Pentane: Et_2O , 98:2→95:5) afforded ester **2** (20.5 mg, 57%) as a colourless oil.

^1H NMR (CDCl_3 , 400 MHz) δ = 4.09 (2H, t, J = 6.7 Hz, OCH_2), 3.69 (3H, s, OCH_3), 2.64–2.61 (4H, m, C1H_2 and C2H_2), 1.66–1.56 (2H, m, $\text{CH}_2\text{CH}_2\text{O}$), 1.41–1.30 (2H, m, CH_2CH_3), 0.92 (3H, t, J = 7.4 Hz, CH_2CH_3).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 172.9 ($\text{C}=\text{O}$ or $\text{C3}=\text{O}$), 172.5 ($\text{C}=\text{O}$ or $\text{C3}=\text{O}$), 64.8 (CH_2O), 52.0 (OCH_3), 30.7 ($\text{CH}_2\text{CH}_2\text{O}$), 29.3 (C1H_2 or C2H_2), 29.1 (C1H_2 or C2H_2), 19.2 (CH_2CH_3), 13.8 (CH_2CH_3).

^1H and ^{13}C NMR data in agreement with that previously reported.⁴

1-(2,3,4,5,6-Pentamethylphenyl)-3-(thiophen-2-yl)butan-1-one **3**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added 2',3',4',5',6'-pentamethylacetophenone (114.2 mg, 0.60 mmol), [Cp*IrCl₂]₂ (9.56 mg, 2.0 mol%), 1-(thiophen-2-yl)ethanol (153.8 mg, 1.20 mmol), PhMe (0.15 mL) and NaOt-Bu (173.0 mg, 1.80 mmol) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a ResealTM septum) and an Ar balloon fitted. The vial was heated to 85 °C in a preheated oil bath for 24 h. The mixture was cooled to RT, filtered through a SiO₂ plug (eluting with Et₂O) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 96:4) afforded ketone **3** (147.9 mg, 82%) as a colourless solid.

R_f = 0.40 (Pentane:Et₂O, 96:4), [UV, KMnO₄].

m.p. = 77–78 °C.

IR (film) $\nu_{\max}$ /cm⁻¹ 2926, 1701, 1653, 1559, 1541, 1521, 1507, 1457, 1399, 1343, 1304, 1276, 1119, 940.

¹H NMR (CDCl₃, 400 MHz) δ = 7.16 (1H, dd, J = 5.0, 1.2 Hz, SCH), 6.99–6.92 (2H, m, SCHCH and SCCH), 3.99–3.88 (1H, m, C2H), 3.14 (1H, dd, J = 19.0, 5.5 Hz, C1H_AH_B), 3.01 (1H, dd, J = 19.0, 7.7 Hz, C1H_AH_B), 2.27 (3H, s, Ar-CH₃), 2.22 (6H, s, 2 × Ar-CH₃), 2.09 (6H, br. s, 2 × Ar-CH₃), 1.53 (3H, d, J = 6.9 Hz, C3H₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 209.6 (C=O), 150.7 (SC), 140.2 (Ar-C), 135.5 (Ar-C), 133.1 (2C, 2 × Ar-C), 127.4 (2C, 2 × Ar-C), 126.6 (SCHCH), 123.2 (SCCH), 122.8 (SCH), 54.7 (C1H₂), 29.9 (C2H), 23.2 (C3H₃), 16.9 (2C, 2 × Ar-CH₃), 16.8 (Ar-CH₃), 16.0 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+Na]⁺ = 323.14398; C₁₉H₂₄OSNa requires 323.14401, Δ –0.08 ppm.

All spectroscopic data in agreement with that previously reported.⁵

(*E*)-1-(2,3,4,5,6-Pentamethylphenyl)-3-phenylprop-2-en-1-one S4

To a solution of 2',3',4',5',6'-pentamethylacetophenone (2.85 g, 15.0 mmol) and benzaldehyde (1.68 mL, 16.5 mmol) in EtOH (50 mL) was added a solution of NaOH (0.75 g, 18.75 mmol) in H₂O:EtOH (1:1, 50 mL) dropwise over 5 minutes in the open atmosphere. The reaction was stirred for 16 h, during which time the desired product precipitated out of solution. Filtration of the precipitated material, washing with H₂O (50 mL), afforded enone **S4** (4.07 g, 97%) as a pale yellow solid.

R_f = 0.23 (Pentane:Et₂O, 95:5), [UV, KMnO₄].

m.p. = 136–138 °C.

IR (film) $\nu_{\max}/\text{cm}^{-1}$ 3034, 2980, 2926, 2863, 1639, 1620, 1598, 1574, 1496, 1470, 1448, 1382, 1317, 1271, 1209, 1182, 1157, 1069, 1028, 1017, 998.

¹H NMR (CDCl₃, 400 MHz) δ = 7.53–7.49 (2H, m, Ph), 7.41–7.35 (3H, m, Ph), 7.19 (1H, d, J = 16.2 Hz, C2H), 6.96 (1H, d, J = 16.2 Hz, C1H), 2.29 (3H, s, Ar-CH₃), 2.22 (6H, s, 2 × Ar-CH₃), 2.12 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 203.0 (C=O), 146.8 (C2H), 138.1 (Ar-C), 135.6 (Ar-C), 134.7 (Ar-C), 133.0 (2C, 2 × Ar-C), 130.8 (Ar-CH), 129.2 (C1H), 129.1 (4C, 2 × Ar-C and 2 × Ar-CH), 128.6 (2C, 2 × Ar-CH), 17.6 (2C, 2 × Ar-CH₃), 16.9 (Ar-CH₃), 16.2 (2C, 2 × ArCH₃).

HRMS (ESI⁺) Found $[M+H]^+$ = 279.1744; C₂₀H₂₃O requires 279.1743, Δ 0.24 ppm. All spectroscopic data in agreement with that previously reported.²

1-(2,3,4,5,6-Pentamethylphenyl)-3-phenylpropan-1-one **9**

To a solution of enone **S4** (2.00 g, 7.18 mmol) in EtOAc (36 mL) was added Pd(OH)₂/C (200 mg, 10 wt%). The suspension was evacuated and back-filled with H₂ (× 4) and stirred under an atmosphere of H₂ for 45 minutes (TLC analysis indicated that the reaction was complete after this time). The mixture was filtered through a pad of Celite[®] under suction (eluting with EtOAc) and concentrated *in vacuo* to afford ketone **9** (1.99 g, 99%) as a colourless solid.

R_f = 0.39 (Pentane:Et₂O, 95:5), [UV, KMnO₄].

m.p. = 74–76 °C.

IR (film) $\nu_{\max}/\text{cm}^{-1}$ 3030, 2952, 2924, 2892, 2867, 1695, 1602, 1497, 1451, 1407, 1382, 1355, 1305, 1281, 1113, 1073, 1031, 1002, 984.

¹H NMR (CDCl₃, 400 MHz) δ = 7.30–7.21 (4H, m, Ph), 7.20–7.15 (1H, m, Ph), 3.08–3.02 (2H, m, C2H₂), 3.01–2.95 (2H, m, C1H₂), 2.21 (3H, s, Ar-CH₃), 2.15 (6H, s, 2 × Ar-CH₃), 2.03 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 211.1 (C=O), 141.1 (Ar-C), 140.6 (Ar-C), 135.6 (Ar-C), 133.2 (2C, 2 × Ar-C), 128.6 (4C, 4 × Ar-CH), 127.5 (2C, 2 × Ar-C), 126.2 (Ar-CH), 47.2 (C1H₂), 29.5 (C2H₂), 17.2 (2C, 2 × Ar-CH₃), 16.8 (Ar-CH₃), 16.1 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 281.1901; C₂₀H₂₅O requires 281.1900, Δ 0.36 ppm. All spectroscopic data in agreement with that previously reported.²

2-Bromo-1-(2,3,4,5,6-pentamethylphenyl)-3-phenylpropan-1-one **4**

To a solution of ketone **9** (500 mg, 1.78 mmol) in AcOH (2.7 mL) at RT was added Br₂ (100 μ L, 1.96 mmol) dropwise. The mixture was stirred at RT for 10 minutes after which AcOH was removed *in vacuo*. The residue was re-dissolved in CH₂Cl₂ (10 mL) and washed with sat. aq. NaHCO₃ (2 $\times$ 10 mL). The aqueous layers were further extracted with CH₂Cl₂ (2 $\times$ 20 mL) and the combined organics dried (MgSO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, solid load, Pentane:Et₂O, 98:2) afforded α -bromoketone **4** (340 mg, 53%) as a colourless solid.

R_f = 0.36 (Pentane:Et₂O, 98:2), [UV, KMnO₄].

m.p. = 68–69 °C.

IR (film) $\nu_{\max}$ /cm⁻¹ 3059, 3023, 2921, 2874, 1699, 1601, 1573, 1494, 1454, 1435, 1379, 1350, 1332, 1311, 1259, 1189, 1161, 1153, 1109, 1075, 1047, 1020, 999.

¹H NMR (CDCl₃, 400 MHz) δ = 7.36–7.24 (5H, m, Ph), 4.85 (1H, dd, J = 8.7, 5.9 Hz, C1HBr), 3.68 (1H, dd, J = 14.5, 5.9 Hz, C2H_AH_B), 3.26 (1H, dd, J = 14.5, 8.6 Hz, C2H_AH_B), 2.23 (3H, s, Ar-CH₃), 2.17 (6H, s, 2 $\times$ Ar-CH₃), 2.16–1.96 (6H, v. br. s, 2 $\times$ Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 201.9 (C=O), 137.6 (Ar-C), 137.2 (Ar-C), 136.9 (Ar-C), 133.4 (2C, 2 $\times$ Ar-C), 129.8 (4C, 2 $\times$ Ar-C and 2 $\times$ Ar-CH), 128.7 (2C, 2 $\times$ Ar-CH), 127.2 (Ar-CH), 56.1 (C1HBr), 39.3 (C2H₂), 18.4 (2C, 2 $\times$ Ar-CH₃), 17.0 (Ar-CH₃), 16.2 (2C, 2 $\times$ Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 359.10056; C₂₀H₂₄O⁷⁹Br requires 359.10050, Δ 0.14 ppm.

2-Benzyl-1-(2,3,4,5,6-pentamethylphenyl)prop-2-en-1-one **5**

To a round bottom flask equipped with a water condenser was added ketone **9** (981 mg, 3.50 mmol), morpholine (152 mg, 1.75 mmol), paraformaldehyde (315 mg, 10.5 mmol) and AcOH (7.0 mL). The mixture was heated to reflux for 1.5 h, during which time two additional portions of paraformaldehyde (105 mg, 3.50 mmol) were added in 30 minute intervals. The reaction was cooled to RT, diluted with CH₂Cl₂ (40 mL) and ice/H₂O (20 mL), then neutralised with 10% aq. NaOH. The layers were separated, the aqueous layer extracted with CH₂Cl₂ (4 × 40 mL), and the combined organics washed with 1 M aq. HCl (20 mL), dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 98.5:1.5) afforded enone **5** (824 mg, 81%) as a colourless solid.

m.p. = 62–64 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3111, 3021, 2979, 2903, 1662, 1599, 1578, 1492, 1450, 1428, 1407, 1342, 1321, 1291, 1255, 1193, 1095, 1073, 1029, 992, 966, 944, 903, 858.

¹H NMR (CDCl₃, 400 MHz) δ = 7.36–7.30 (2H, m, Ph), 7.30–7.27 (2H, m, Ph), 7.27–7.20 (1H, m, Ph), 5.75 (1H, td, J = 1.5, 1.0 Hz, C3H_{syn}H_{anti}), 5.72 (1H, q, J = 0.9 Hz, C3H_{syn}H_{anti}), 3.80 (2H, s, C2H₂), 2.24 (3H, s, Ar-CH₃), 2.18 (6H, s, 2 × Ar-CH₃), 1.98 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 203.4 (C=O), 149.5 (C1), 139.1 (Ar-C), 137.6 (Ar-C), 135.4 (Ar-C), 132.8 (2C, 2 × Ar-C), 130.6 (C3H₂), 129.5 (2C, 2 × Ar-CH), 129.2 (2C, 2 × Ar-C), 128.5 (2C, 2 × Ar-CH), 126.4 (Ar-CH), 36.1 (C2H₂), 17.4 (2C, 2 × Ar-CH₃), 16.8 (Ar-CH₃), 16.0 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 293.19016; C₂₁H₂₅O requires 293.18999, Δ 0.56 ppm.

3-Hydroxy-1-(2,3,4,5,6-pentamethylphenyl)-3-phenylpropan-1-one **6**

To EtMgBr (3.0 M in Et₂O, 1.26 mL, 3.78 mmol) at RT was added a solution of 2',3',4',5',6'-pentamethylacetophenone (600 mg, 3.15 mmol) in Et₂O (7 mL + 2 × 2 mL rinse) dropwise over 20 minutes (a gentle reflux was observed). The solution was heated to 40 °C and stirred for 30 minutes, during which time a white precipitate formed. To this mixture was added benzaldehyde (370 µL, 3.59 mmol) in Et₂O (2 mL + 2 × 1 mL rinse) dropwise over 1 h *via* syringe pump. The reaction was maintained at 40 °C for 18 h and then cooled to RT and poured onto a mixture of ice/conc. HCl (4.7 g/0.95 mL). The mixture was extracted with CH₂Cl₂ (3 × 20 mL) and the combined organics washed with brine (50 mL), dried (MgSO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, solid load, Pentane:EtOAc, 95:5→92:8→90:10) afforded alcohol **6** (780 mg, 83%) as a white solid.

*R*_f = 0.26 (Pentane:Et₂O, 80:20), [UV, KMnO₄].

m.p. = 84–86 °C.

IR (film) ν_{max} /cm⁻¹ 2981, 2889, 1696, 1454, 1383, 1253, 1154, 1115, 1059, 941.

¹H NMR (CDCl₃, 400 MHz) δ = 7.43–7.40 (2H, m, Ph), 7.39–7.33 (2H, m, Ph), 7.31–7.26 (1H, m, Ph), 5.39 (1H, dt, *J* = 8.5, 3.3 Hz, C2H), 3.61 (1H, d, *J* = 3.2 Hz, OH), 3.15 (1H, dd, *J* = 18.6, 8.6 Hz, C1H_AH_B), 3.08 (1H, dd, *J* = 18.7, 3.6 Hz, C1H_AH_B), 2.24 (3H, s, Ar-CH₃), 2.19 (6H, s, 2 × Ar-CH₃), 2.14 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 212.5 (C=O), 142.8 (Ar-C), 139.8 (Ar-C), 136.0 (Ar-C), 133.3 (2C, 2 × Ar-C), 128.6 (2C, 2 × Ar-CH), 127.8 (Ar-CH), 127.4 (2C, 2 × Ar-C), 125.9 (2C, 2 × Ar-CH), 69.8 (C2H), 54.0 (C1H₂), 17.2 (2C, 2 × Ar-CH₃), 16.8 (Ar-CH₃), 16.0 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 319.1670; C₂₀H₂₄O₂Na requires 319.1669, Δ 0.54 ppm.

1-(2,3,4,5,6-Pentamethylphenyl)-2-(1,4-dioxaspiro[4.5]decan-8-yl)ethan-1-one **7**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added 2',3',4',5',6'-pentamethylacetophenone (114.2 mg, 0.60 mmol), [Cp*IrCl₂]₂ (2.39 mg, 0.50 mol%), 1,4-dioxaspiro[4.5]decan-8-ol (142.4 mg, 0.90 mmol), PhMe (0.15 mL) and NaOt-Bu (115.3 mg, 1.20 mmol) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a ResealTM septum) and an Ar balloon fitted. The vial was heated to 85 °C in a preheated oil bath for 24 h. The mixture was cooled to RT, filtered through a SiO₂ plug (eluting with Et₂O) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 70:30) afforded ketone **7** (196.3 mg, 99%) as a colourless solid.

R_f = 0.30 (Pentane:Et₂O, 70:30), [UV, KMnO₄].

m.p. = 145–146 °C.

IR (film) $\nu_{\max}$ /cm⁻¹ 2942, 2873, 1696, 1444, 1402, 1378, 1336, 1310, 1285, 1194, 1172, 1141, 1104, 1078, 1030, 1005, 974.

¹H NMR (CDCl₃, 400 MHz) δ = 4.04–3.85 (4H, m, 2 × C6H₂), 2.62 (2H, d, J = 6.5 Hz, C1H₂), 2.23 (3H, s, Ar-CH₃), 2.18 (6H, s, 2 × Ar-CH₃), 2.16–2.03 (1H, m, C2H), 2.09 (6H, s, 2 × Ar-CH₃), 1.96–1.85 (2H, m, 2 × C3H_AH_B), 1.80–1.73 (2H, m, 2 × C4H_AH_B), 1.65 (2H, td, J = 13.2, 4.2 Hz, 2 × C4H_AH_B), 1.32 (2H, qd, J = 11.5, 3.9 Hz, 2 × C3H_AH_B).

¹³C NMR (CDCl₃, 101 MHz) δ = 210.9 (C=O), 140.6 (Ar-C), 135.4 (Ar-C), 133.2 (2C, 2 × Ar-C), 127.3 (2C, 2 × Ar-C), 108.9 (C5), 64.3 (2C, 2 × C6H₂), 52.0 (C1H₂), 34.5 (2C, 2 × C4H₂), 31.1 (C2H), 30.2 (2C, 2 × C3H₂), 17.1 (2C, 2 × Ar-CH₃), 16.8 (Ar-CH₃), 16.0 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 331.22647; C₂₁H₃₁O₃ requires 331.22677, Δ –0.91 ppm.

All spectroscopic data in agreement with that previously reported.⁵

2-Benzyl-2,3-dibromo-1-(2,3,4,5,6-pentamethylphenyl)propan-1-one **8**

To a 2–5 mL microwave vial equipped with a stirrer bar was added enone **5** (35.0 mg, 0.12 mmol) and CH_2Cl_2 (0.60 mL) sequentially in the open atmosphere. The vial was sealed with a microwave vial cap, cooled to $-17\text{ }^\circ\text{C}$ (ice/ NaCl bath), then Br_2 (12 μL , 0.24 mmol) added. Once TLC analysis indicated complete consumption of the substrate (typically 15 minutes), *n*-BuOH (83 μL , 0.42 mmol) was added at $-17\text{ }^\circ\text{C}$ and the reaction allowed to warm up to RT over 16 h. To the reaction mixture was added Et_2O (1.2 mL), sat. aq. Na_2SO_3 (1.2 mL) and brine (1.2 mL) sequentially. The layers were separated and the aqueous layer extracted with Et_2O ($3 \times 10\text{ mL}$). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , eluent load, Pentane: Et_2O , 99:1) afforded α -bromoketone **8** (42.4 mg, 76%) as a colourless solid.

m.p. = $129\text{--}131\text{ }^\circ\text{C}$.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3086, 3062, 3031, 3006, 2927, 1698, 1603, 1571, 1495, 1454, 1433, 1412, 1384, 1299, 1259, 1224, 1148, 1089, 1074, 1011, 938, 910, 885.

^1H NMR (CDCl_3 , 400 MHz) δ = 7.49–7.43 (2H, m, Ph), 7.35–7.29 (3H, m, Ph), 4.25 (1H, dd, J = 10.6, 1.2 Hz, $\text{C}2\text{H}_\text{A}\text{H}_\text{B}$), 3.88 (1H, d, J = 14.2 Hz, $\text{C}3\text{H}_\text{A}\text{H}_\text{B}$), 3.65 (1H, d, J = 10.6 Hz, $\text{C}2\text{H}_\text{A}\text{H}_\text{B}$), 3.28 (1H, dd, J = 14.1, 1.1 Hz, $\text{C}3\text{H}_\text{A}\text{H}_\text{B}$), 2.27 (3H, s, Ar- CH_3), 2.26 (3H, s, Ar- CH_3), 2.19 (3H, s, Ar- CH_3), 2.18 (3H, s, Ar- CH_3), 2.08 (3H, s, Ar- CH_3).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 202.0 (C=O), 136.4 (Ar-C), 135.5 (Ar-C), 135.0 (Ar-C), 133.6 (Ar- C_A), 133.2 (Ar- C_B), 131.6 (2C, $2 \times$ Ar-CH), 129.65 (Ar- C_A), 129.56 (Ar- C_B), 128.3 (2C, $2 \times$ Ar-CH), 127.7 (Ar-CH), 71.0 (C_1), 40.6 ($\text{C}2\text{H}_2$), 34.9 ($\text{C}3\text{H}_2$), 20.1 (Ar- $\text{C}_\text{A}\text{H}_3$), 19.8 (Ar- $\text{C}_\text{B}\text{H}_3$), 16.9 (Ar- CH_3), 16.4 (Ar- $\text{C}_\text{A}\text{H}_3$), 16.2 (Ar- $\text{C}_\text{B}\text{H}_3$).

HRMS (ESI^+) Found $[\text{M}+\text{Na}]^+ = 473.00867$; $\text{C}_{21}\text{H}_{24}^{79}\text{Br}_2\text{ONa}$ requires 473.00861, Δ 0.12 ppm.

1-(4-Methoxyphenyl)-3-phenylpropan-1-one **10**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added ketone **9** (28.0 mg, 0.10 mmol), anisole (33 μ L, 0.30 mmol), CH₂Cl₂ (0.25 mL) and AuCl₃ (36.4 mg, 0.12 mmol) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a ResealTM septum) and stirred at RT (18 °C) for 20 h. The reaction mixture was concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 95:5) afforded ketone **10** (12.8 mg, 53%) as a colourless oil.

R_f = 0.20 (Pentane:Et₂O, 90:10), [UV, KMnO₄].

m.p. = 98 – 99 °C.

IR (film) $\nu_{\max}/\text{cm}^{-1}$ 3062, 3027, 3011, 2934, 2842, 1669, 1601, 1548, 1506, 1493, 1452, 1422, 1365, 1295, 1253, 1209, 1176, 1108, 1078, 1026, 1002, 977.

¹H NMR (CDCl₃, 400 MHz) δ = 7.95 (2H, d, J = 9.0 Hz, Ph), 7.35–7.28 (2H, m, Ph), 7.28–7.24 (2H, m, Ph), 7.24–7.18 (1H, m, Ph), 6.93 (2H, d, J = 9.0 Hz, Ph), 3.87 (3H, s, OCH₃), 3.29–3.22 (2H, m, C1H₂), 3.09–3.02 (2H, m, C2H₂).

¹³C NMR (CDCl₃, 101 MHz) δ = 198.0 (C=O), 163.6 (Ar-C(OCH₃)), 141.6 (Ar-C), 130.4 (2C, 2 $\times$ Ar-CH), 130.1 (Ar-C), 128.63 (2C, 2 $\times$ Ar-CH), 128.55 (2C, 2 $\times$ Ar-CH), 126.2 (Ar-CH), 113.8 (2C, 2 $\times$ Ar-CH), 55.6 (OCH₃), 40.3 (C1H₂), 30.4 (C2H₂).

HRMS (ESI⁺) Found $[M+H]^+$ = 241.12234; C₁₆H₁₇O₂ requires 241.12231, Δ 0.16 ppm.

The analytical data matches that obtained from a commercial sample (Alfa Aesar).

Butyl 3-phenylpropanoate **11**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added ketone **9** (28.0 mg, 0.10 mmol), HFIP (0.25 mL), *n*-BuOH (27.0 μ L, 0.30 mmol) and freshly distilled TMSCl (13.0 μ L, 0.10 mmol) sequentially. The reaction vessel was immediately sealed with a microwave vial cap (containing a Reseal[™] septum) and stirred at RT for 69 h. Following this, Et₂O (2 mL) and H₂O (2 mL) were added and the layers separated. The organic layer was washed with sat. aq. NaHCO₃ (2 mL), brine (2 mL), dried (MgSO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 98:2) afforded ester **11** (19.6 mg, 95%) as a colourless oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.23–7.19 (2H, m, Ph), 7.15–7.11 (3H, m, Ph), 4.00 (2H, t, J = 6.7 Hz, OCH₂), 2.88 (2H, app. t, J = 7.8 Hz, C1H₂), 2.56 (2H, app. t, J = 8.0, 7.4 Hz, C2H₂), 1.51 (2H, ddt, J = 8.9, 8.0, 6.6 Hz, CH₂CH₂O), 1.34–1.21 (2H, m, CH₂CH₃), 0.84 (3H, t, J = 7.4 Hz, CH₂CH₃).

¹H NMR data in agreement with that previously reported.⁶

Butyl 3-(thiophen-2-yl)butanoate **12**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added ketone **3** (90.1 mg, 0.30 mmol), HFIP (0.75 mL), *n*-BuOH (82.0 μ L, 0.90 mmol) and freshly distilled TMSCl (38.0 μ L, 0.30 mmol) sequentially. The reaction vessel was immediately sealed with a microwave vial cap (containing a Reseal[™] septum) and heated to 40 °C in a preheated oil bath for 24 h. The mixture was cooled to RT and concentrated in vacuo. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 98:2) afforded ester **12** (40.5 mg, 60%) as a colourless oil.

R_f = 0.40 (Pentane:Et₂O, 95:5), [UV, KMnO₄].

IR (film) $\nu_{\max}/\text{cm}^{-1}$ 2960, 2932, 2873, 1732, 1457, 1439, 1417, 1380, 1348, 1313, 1281, 1246, 1215, 1165, 1069, 1023, 965.

¹H NMR (CDCl₃, 400 MHz) δ = 7.13 (1H, dd, J = 5.1, 1.2 Hz, SCH), 6.91 (1H, dd, J = 5.1, 3.4 Hz, SCHCH), 6.83 (1H, dt, J = 3.5, 1.0 Hz, SCCH), 4.06 (2H, t, J = 6.7 Hz, CH₂O), 3.65–3.54 (1H, m, C2H), 2.69 (1H, dd, J = 15.2, 6.8 Hz, C1H_AH_B), 2.56 (1H, dd, J = 15.2, 8.0 Hz, C1H_AH_B), 1.62–1.53 (2H, m, CH₂CH₂O), 1.38 (3H, d, J = 6.9 Hz, C3H₃), 1.39–1.29 (2H, m, CH₂CH₃), 0.91 (3H, t, J = 7.3 Hz, CH₂CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 172.2 (C=O), 149.8 (SC), 126.7 (SCHCH), 123.1 (SCCH), 123.0 (SCH), 64.5 (CH₂O), 44.1 (C1H₂), 32.2 (C2H), 30.8 (CH₂CH₂O), 22.9 (C3H₃), 19.2 (CH₂CH₃), 13.8 (CH₂CH₃).

HRMS (ESI⁺) Found $[M+\text{Na}]^+ = 249.09200$; C₁₂H₁₈O₂SNa requires 249.09197, Δ 0.09 ppm.

All spectroscopic data in agreement with that previously reported.⁵

(E)-3-Phenyl-1-(2,3,5,6-tetramethylphenyl)prop-2-en-1-one S5

To a solution of durene (6.71 g, 50.0 mmol) in anhydrous CH_2Cl_2 (100 mL) was added cinnamoyl chloride (9.16 g, 55.0 mmol) RT. The reaction mixture was cooled to 0 °C, then AlCl_3 (8.33 g, 62.5 mmol) was carefully added and the reaction stirred at 0 °C for 1.5 h. The reaction mixture was then poured onto ice/ H_2O (250 mL), allowed to warm up to RT, then diluted with CH_2Cl_2 (250 mL) and saturated with NaCl. The layers were separated, the aqueous layer extracted with CH_2Cl_2 (3×100 mL), and the combined organics dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , eluent load, Pentane: Et_2O , 99:1) afforded enone **S5** (13.2 g, 100%) as a pale yellow solid.

m.p. = 86–89 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3060, 3028, 3003, 2970, 2939, 2921, 2866, 1701, 1673, 1646, 1621, 1600, 1575, 1494, 1469, 1449, 1376, 1316, 1243, 1173, 1119, 1011, 980, 881.

^1H NMR (CDCl_3 , 400 MHz) δ = 7.56–7.48 (2H, m, Ph), 7.44–7.35 (3H, m, Ph), 7.18 (1H, d, J = 16.2 Hz, C2H), 7.02 (1H, s, Ar-CH), 6.96 (1H, d, J = 16.3 Hz, C1H), 2.25 (6H, s, $2 \times$ Ar- CH_3), 2.09 (6H, s, $2 \times$ Ar- CH_3).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 202.6 (C=O), 146.9 (C2H), 140.3 (Ar-C), 134.6 (Ar-C), 134.3 (2C, $2 \times$ Ar-C), 131.9 (Ar-CH), 130.9 (Ar-CH), 129.8 (2C, $2 \times$ Ar-C), 129.1 (2C, $2 \times$ Ar-CH), 128.8 (C1H), 128.6 (2C, $2 \times$ Ar-CH), 19.7 (2C, $2 \times$ Ar- CH_3), 16.4 (2C, $2 \times$ Ar- CH_3).

HRMS (ESI⁺) Found $[\text{M}+\text{Na}]^+ = 287.14063$; $\text{C}_{19}\text{H}_{20}\text{ONa}$ requires 287.14064, Δ –0.04 ppm.

3-Phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one **13**

To a solution of enone **S5** (1.53 g, 5.79 mmol) in EtOAc (30 mL) was added Pd(OH)₂/C (15.3 mg, 1.0 wt%). The suspension was evacuated and back-filled with H₂ (× 4) and stirred under an atmosphere of H₂ for 16 h. The mixture was filtered through a pad of Celite® under suction (eluting with EtOAc) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 99:1) afforded ketone **13** (1.38 g, 90%) as a colourless solid.

m.p. = 68–70 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3085, 3062, 3027, 3003, 2923, 2866, 1700, 1604, 1496, 1470, 1454, 1400, 1354, 1306, 1232, 1112, 1075, 1017, 973.

¹H NMR (CDCl₃, 400 MHz) δ = 7.32–7.27 (2H, m, Ph), 7.26–7.23 (2H, m, Ph), 7.23–7.17 (1H, m, Ph), 6.95 (1H, s, Ar-CH), 3.11–3.04 (2H, m, C2H₂), 3.04–2.98 (2H, m, C1H₂), 2.20 (6H, s, 2 × Ar-CH₃), 2.01 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 210.8 (C=O), 142.7 (Ar-C), 141.1 (Ar-C), 134.5 (2C, 2 × Ar-C), 131.7 (Ar-CH), 128.64 (2C, 2 × Ar-CH), 128.58 (2C, 2 × Ar-CH), 128.1 (2C, 2 × Ar-C), 126.2 (Ar-CH), 46.9 (C1H₂), 29.5 (C2H₂), 19.6 (2C, 2 × Ar-CH₃), 16.0 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 267.17441; C₁₉H₂₃O requires 267.17434, Δ 0.25 ppm.

Phthaloyl peroxide **S6**⁷

To a vigorously stirred suspension of $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$ (2.36 g, 15.0 mmol) and Na_2CO_3 (530 mg, 5.00 mmol) in water-saturated CH_2Cl_2 (50 mL)* was added phthaloyl chloride (1.45 mL, 2.03 mmol) at RT and stirred for 3 h. The reaction mixture was filtered under suction through a pad of Celite[®], eluting with CH_2Cl_2 (100 mL), and the eluent concentrated *in vacuo*, ensuring that the water bath temperature does not exceed 30 °C. The residue was re-dissolved in a minimum amount of warm benzene without any additional source of direct heat, then poured into ice-cold pentane (100–150 mL). The suspension was filtered, eluting with cold pentane (50 mL), and the filtrate similarly concentrated *in vacuo* to afford phthaloyl peroxide **S6** (555 mg, 34 %) as a colourless solid.

m.p. = >79 °C (slow decomposition).

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 1740, 1720, 1596, 1461, 1326, 1283, 1226, 1107, 1094, 1039, 1021.

^1H NMR (CDCl_3 , 400 MHz) δ = 8.29 (2H, app. dd, J = 5.8, 3.3 Hz, $2 \times \text{Ar-CH}$), 8.03 (2H, dd, J = 5.8, 3.3 Hz, $2 \times \text{Ar-CH}$).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 162.1 (2C, $2 \times \text{C=O}$), 136.6 (2C, $2 \times \text{Ar-CH}$), 130.3 (2C, $2 \times \text{Ar-CH}$), 123.8 (2C, $2 \times \text{Ar-C}$).

*Water-saturated CH_2Cl_2 can be prepared by simply putting CH_2Cl_2 and DI H_2O in a separating funnel and shaking it vigorously, then removing only the organic phase and avoiding any obvious water droplets.

Note: The material should be stored in the freezer immediately to extend its longevity.

All spectroscopic data in agreement with that previously reported.⁷

1-(4-Hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one **14**

To a flame-dried flask containing a solution of ketone **13** (266 mg, 1.00 mmol) in HFIP (10 mL) over Ar was added phthaloyl peroxide **S6** (213 mg, 1.30 mmol) at RT. The reaction mixture was then warmed to 40 °C and stirred for 12 h. The reaction mixture was directly concentrated *in vacuo*, followed by the addition of aq. sat. NaHCO₃:MeOH (1:9, 0.05 M) over Ar. The ensuing suspension was heated to 40 °C and stirred for a further 12 h. The reaction mixture was cooled to RT, then diluted with brine (30 mL) and CH₂Cl₂ (20 mL). The layers were separated, the aqueous layer extracted with CH₂Cl₂ (5 × 15 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 80:20→60:40) afforded phenol **14** (194 mg, 69%) as a colourless solid that gradually turns pale yellow solid on exposure to air.

m.p. = 96–99 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3464, 3086, 3062, 3027, 2925, 1685, 1603, 1576, 1496, 1454, 1400, 1385, 1359, 1295, 1260, 1216, 1122, 1090, 1029, 944, 917.

¹H NMR (CDCl₃, 500 MHz) δ = 7.31–7.27 (2H, m, Ph), 7.26–7.22 (2H, m, Ph), 7.22–7.18 (1H, m, Ph), 4.82 (1H, s, OH), 3.06 (2H, m, C2H₂), 2.99 (2H, m, C1H₂), 2.12 (6H, s, 2 × Ar-CH₃), 2.02 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 126 MHz) δ = 210.9 (C=O), 151.9 (Ar-COH), 141.1 (Ar-C), 135.7 (Ar-C), 129.1 (2C, 2 × Ar-C), 128.62 (2C, 2 × Ar-CH), 128.58 (2C, 2 × Ar-CH), 126.2 (Ar-CH), 120.0 (2C, 2 × Ar-C), 47.4 (C1H₂), 29.6 (C2H₂), 16.7 (2C, 2 × Ar-CH₃), 11.8 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+Na]⁺ = 305.15090; C₁₉H₂₂O₂Na requires 305.15120, Δ –0.98 ppm.

Note: The compound gradually turns yellow on exposure to air, owing to oxidation of the phenolic group to duroquinone.

6-Methoxy-2,3,5,6-tetramethyl-4-(3-phenylpropanoyl)cyclohexa-2,4-dien-1-one **15**

To a solution of phenol **14** (56.5 mg, 0.20 mmol) in HFIP:MeOH (1:1, 2.0 mL) was added PIDA (83.8 mg, 0.26 mmol), then stirred at RT for 2 h. To the reaction mixture was added water (2 mL), sat. aq. Na₂SO₃ (2 mL) and CH₂Cl₂ (4 mL) sequentially, then saturated with NaCl. The layers were separated, the aqueous layer extracted with CH₂Cl₂ (3 × 3 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 80:20) afforded cyclohexadienone **15** (48.7 mg, 78%) as a yellow oil.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3063, 3028, 2954, 2924, 2854, 1737, 1704, 1658, 1604, 1577, 1496, 1454, 1401, 1376, 1360, 1326, 1299, 1260, 1227, 1180, 1157, 1100, 1030, 972.

¹H NMR (CDCl₃, 500 MHz) δ = 7.32–7.27 (2H, m, Ph), 7.25–7.19 (3H, m, Ph), 3.05–2.99 (2H, m, C₂H₂), 3.00 (3H, s, OCH₃), 2.99–2.87 (2H, m, C₁H₂), 1.88 (3H, s, CH₃), 1.81 (3H, s, CH₃), 1.78 (3H, s, CH₃), 1.30 (3H, s, CH₃).

¹³C NMR (CDCl₃, 126 MHz) δ = 207.0 (C=O), 201.3 (C=O), 143.48 (C), 143.43 (C), 140.5 (Ar-C), 139.1 (C), 130.0 (C), 128.74 (2C, 2 × Ar-CH), 128.65 (2C, 2 × Ar-CH), 126.5 (Ar-CH), 81.8 (C(OCH₃)CH₃), 54.1 (C(OCH₃)CH₃), 46.6 (C₁H₂), 29.3 (C₂H₂), 26.4 (C(OCH₃)CH₃), 17.9 (CH₃), 13.9 (CH₃), 11.0 (CH₃).

HRMS (ESI⁺) Found [M+Na]⁺ = 335.16170; C₂₀H₂₄O₃Na requires 335.16170, Δ –0.19 ppm.

Methyl 3-phenylpropanoate **16**

To a solution of phenol **14** (28.2 mg, 0.10 mmol) in MeOH (1.0 mL) was titrated a solution of CAN (272 mg, 0.50 mmol) in MeOH (0.5 mL) at RT in the open atmosphere until the colour of the CAN solution persisted (orange, typically 4–5 equiv.). The reaction mixture was diluted with H₂O (3 mL) and stirred for 5–10 minutes,* then further diluted with CH₂Cl₂ (2 mL) and saturated with NaCl. The layers were separated, and the aqueous layer extracted with CH₂Cl₂ (5 × 1.5 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 99:1) afforded ester **16** (10.1 mg, 61%) as a volatile colourless oil.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3087, 3064, 3028, 3002, 2952, 1735, 1604, 1497, 1454, 1436, 1365, 1293, 1255, 1195, 1161, 1079, 1029, 986, 950, 896, 837, 771, 750, 699.

¹H NMR (CDCl₃, 500 MHz) δ = 7.38–7.26 (2H, m, Ph), 7.25–7.17 (3H, m, Ph), 3.68 (3H, s, OCH₃), 3.05–2.90 (2H, m, C₂H₂), 2.68–2.58 (2H, m, C₁H₂).

¹³C NMR (CDCl₃, 126 MHz) δ = 173.5 (C=O), 140.6 (Ar-C), 128.6 (2C, 2 × Ar-CH), 128.4 (2C, 2 × Ar-CH), 126.4 (Ar-CH), 51.8 (OCH₃), 35.8 (C₁H₂), 31.1 (C₂H₂).

The spectroscopic data matches that obtained from a commercial sample (Sigma-Aldrich).

*If the step involving stirring with water is omitted, then duroquinone dimethyl acetal will be present in varying amounts which may interfere with chromatographic purification.

3-Phenylpropanoic acid **17**

To a solution of phenol **14** (28.2 mg, 0.10 mmol) in H₂O (1 mL) was titrated a solution of CAN (272 mg, 0.50 mmol) in H₂O (0.5 mL) at RT in the open atmosphere until the colour of the CAN solution persisted (yellow typically 4–5 equiv.). The reaction mixture was diluted with H₂O (3 mL) and stirred for 5–10 minutes,* then further diluted with CH₂Cl₂ (2 mL) and saturated with NaCl. The layers were separated, and the aqueous layer extracted with CH₂Cl₂ (5 × 1.5 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 99:1) afforded carboxylic acid **17** (15.0 mg, 100%) as a colourless oil.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3063, 3029, 2931, 2656, 1705, 1605, 1497, 1454, 1412, 1297, 1248, 1215, 1162, 1078, 928, 834, 750, 699.

¹H NMR (CDCl₃, 500 MHz) δ = 11.08 (1H, v. br. s, OH), 7.34–7.27 (2H, m, Ph), 7.26–7.19 (3H, m, Ph), 3.01–2.94 (2H, m, C₂H₂), 2.73–2.67 (2H, m, C₁H₂).

¹³C NMR (CDCl₃, 126 MHz) δ = 179.1 (C=O), 140.3 (Ar-C), 128.7 (2C, 2 × Ar-CH), 128.4 (2C, 2 × Ar-CH), 126.5 (Ar-CH), 35.7 (C₁H₂), 30.7 (C₂H₂).

The spectroscopic data were identical to those from a commercial sample (Sigma-Aldrich).

*If the step involving stirring with water is omitted, then duroquinone dimethyl acetal will be present in varying amounts which may interfere with chromatographic purification.

2-Benzyl-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)prop-2-en-1-one **S7**

To a well-stirred flask containing a solution of phenol **13** (282 mg, 1.00 mmol) in EtOH:H₂O (1:1, 5 mL) was added K₂CO₃ (276 mg, 2.00 mmol) and paraformaldehyde (901 mg, 30.0 mmol), and the solution stirred at 50 °C for 24 h. The reaction mixture was cooled down to RT and filtered. The residue was washed with H₂O (10 mL) and cold EtOH:H₂O (1:1, 5 mL), then dried *in vacuo* to give enone **S7** (190 mg) as a yellow solid.

The filtrate was extracted with EtOAc (3 × 20 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 85:15) afforded enone **S7** (67 mg, total 257 mg, 87%) as a yellow solid.

m.p. = 96–98 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3385, 3086, 3062, 3028, 2924, 1644, 1602, 1576, 1494, 1454, 1397, 1345, 1293, 1215, 1174, 1104, 1030, 1015, 992, 950, 914.

¹H NMR (CDCl₃, 500 MHz) δ = 7.35–7.29 (2H, m, Ph), 7.29–7.25 (2H, m, Ph), 7.25–7.18 (1H, m, Ph), 5.74 (1H, q, J = 1.3 Hz, C3H_{syn}H_{anti}), 5.70 (1H, s, C3H_{syn}H_{anti}), 4.81 (1H, s, OH), 3.77 (2H, s, C2H₂), 2.11 (6H, s, 2 × Ar-CH₃), 1.93 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 126 MHz) δ = 203.2 (C=O), 151.9 (Ar-COH), 149.8 (C1), 139.2 (Ar-C), 132.7 (Ar-C), 130.8 (2C, 2 × Ar-C), 130.6 (C3H₂), 129.5 (2C, 2 × Ar-CH), 128.6 (2C, 2 × Ar-CH), 126.4 (Ar-CH), 119.6 (2C, 2 × Ar-C), 36.2 (C2H₂), 16.9 (2C, 2 × Ar-CH₃), 11.8 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 295.16925; C₂₀H₂₃O₂ requires 295.16926, Δ –0.02 ppm.

Note: *syn* and *anti* with respect to C=O.

Methyl 2-benzylacrylate **18**

To a solution of phenol **S7** (29.4 mg, 0.10 mmol) in MeOH (3.5 mL) was titrated a solution of CAN (274 mg, 0.50 mmol) in MeOH (1.2 mL) at RT in the open atmosphere until the colour of the CAN solution persisted (orange typically 4–5 equiv.). The reaction mixture was diluted with H₂O (3 mL) and stirred for 5–10 minutes,* then further diluted with CH₂Cl₂ (4 mL) and saturated with NaCl. The layers were separated, and the aqueous layer extracted with CH₂Cl₂ (5 × 3 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 99:1) afforded a pale yellow solid (26.8 mg) that contained an inseparable 1:1.33 mixture of ester **18** (67.8 μmol, 68%) and duroquinone (90.4 μmol, 90%).

¹H NMR (CDCl₃, 500 MHz) δ = 7.25–7.32 (2H, m, Ph), 7.24–7.16 (3H, m, Ph), 6.24–6.21 (1H, m, C3H_{syn}H_{anti}), 5.46 (1H, q, J = 1.5 Hz, C3H_{syn}H_{anti}), 3.73 (3H, s, OCH₃). 3.63 (2H, s, C2H₂).
¹H NMR in agreement with that previously reported.⁸

*If the step involving stirring with water is omitted, then duroquinone dimethyl acetal will be present in varying amounts which may interfere with chromatographic purification.

3-Hydroxy-3-phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one S8

To a solution of $i\text{-Pr}_2\text{NH}^\dagger$ (0.14 mL, 1.00 mmol) in THF (3 mL) at -78°C was added $n\text{-BuLi}^\ddagger$ (2.22 M, 0.45 mL, 1.00 mmol) dropwise over 5 minutes. The mixture was stirred for 1 minute after which a solution of 1-(2,3,5,6-tetramethylphenyl)ethan-1-one[¶] (176 mg, 1.00 mmol) in THF (2 mL + 2 $\times$ 1 mL rinse) was added dropwise over 5 minutes at -78°C . The cloudy mixture was stirred at -78°C for 1 h before $\text{CeCl}_3^\ddagger$ (447 mg, 1.2 mmol) was added in one portion. The reaction was maintained at -78°C for 30 minutes after which benzaldehyde (0.093 mL, 0.92 mmol) was added dropwise over 5 minutes. The mixture was stirred at -78°C for a further 1 h and then quenched by the addition of sat. aq. NH_4Cl (2 mL), H_2O (2 mL) and warmed to RT. The mixture was extracted with Et_2O (3 $\times$ 15 mL) and the combined organics washed with brine (30 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , eluent load, Pentane: Et_2O , 85:15) afforded β -hydroxyketone **S8** (244 mg, 94%) as a colourless solid.

$R_f = 0.12$ (Pentane: Et_2O , 80:20), [UV, KMnO_4].

m.p. = $83\text{--}85^\circ\text{C}$.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3479, 3086, 3065, 2973, 2948, 2916, 2887, 1686, 1602, 1491, 1464, 1452, 1406, 1386, 1376, 1355, 1330, 1299, 1261, 1228, 1200, 1177, 1112, 1082, 1057, 1020, 1003, 974.

^1H NMR (CDCl_3 , 400 MHz) δ = 7.43–7.38 (2H, m, Ph), 7.38–7.32 (2H, m, Ph), 7.31–7.25 (1H, m, Ph), 6.96 (1H, s, Ar-CH), 5.38 (1H, dt, J = 8.7, 3.1 Hz, C2H), 3.54 (1H, d, J = 3.1 Hz, OH), 3.14 (1H, dd, J = 18.6, 8.8 Hz, $\text{C1H}_\text{A}\text{H}_\text{B}$), 3.07 (1H, dd, J = 18.6, 3.4 Hz, $\text{C1H}_\text{A}\text{H}_\text{B}$), 2.20 (6H, s, 2 $\times$ Ar- CH_3), 2.08 (6H, s, 2 $\times$ Ar- CH_3).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 212.3 (C=O), 142.7 (Ar-C), 141.9 (Ar-C), 134.7 (2C, 2 $\times$ Ar-C), 132.0 (Ar-CH), 128.7 (2C, 2 $\times$ Ar-CH), 128.0 (2C, 2 $\times$ Ar-C), 127.8 (Ar-CH), 125.9 (2C, 2 $\times$ Ar-CH), 69.8 (C2H), 53.8 (C1H_2), 19.6 (2C, 2 $\times$ Ar- CH_3), 16.1 (2C, 2 $\times$ Ar- CH_3).

[†] $i\text{-Pr}_2\text{NH}$ freshly distilled from CaH_2 at $86^\circ\text{C}/760$ mmHg prior to use.

[‡] $n\text{-BuLi}$ titrated prior to use.

[¶] Azeotroped with PhH ($\times 3$) and dried under vacuum prior to use.

[‡] $\text{CeCl}_3 \cdot \text{H}_2\text{O}$ was dried *in vacuo* at 150°C for 2 h prior to use.

HRMS (ESI⁺) Found [M+Na]⁺ = 305.15125; C₁₉H₂₂O₂Na requires 305.15120, Δ 0.14 ppm.

3-Hydroxy-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one **S9**

To a flame-dried flask containing a solution of ketone **S8** (141 mg, 0.50 mmol) in HFIP (5 mL) over Ar was added phthaloyl peroxide **S6** (123 mg, 0.75 mmol) at RT. The reaction mixture was then warmed to 40 °C and stirred for 12 h. The reaction mixture was directly concentrated *in vacuo*, followed by the addition of aq. sat. NaHCO₃:MeOH (1:9, 0.05 M) over Ar. The ensuing suspension was heated to 40 °C and stirred for a further 12 h. The reaction mixture was cooled to RT, then diluted with brine (15 mL) and CH₂Cl₂ (10 mL). The layers were separated, the aqueous layer extracted with CH₂Cl₂ (5 × 10 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 85:15→70:30) afforded phenol **S9** (89.0 mg, 62%) as a yellow solid.

m.p. = 142–144 °C.

IR (film) ν_{max} /cm⁻¹ 3422, 3087, 3063, 3031, 2924, 1685, 1623, 1575, 1494, 1454, 1385, 1353, 1332, 1296, 1215, 1122, 1090, 1055, 1029, 1015, 946, 911.

¹H NMR (CDCl₃, 400 MHz) δ = 7.45–7.38 (2H, m, Ph), 7.37–7.32 (2H, m, Ph), 7.31–7.24 (1H, m, Ph), 5.35 (1H, dd, *J* = 8.5, 3.6 Hz, C2H), 4.81 (1H, br. s, OH), 3.53 (1H, v. br. s, C2HOH), 3.12 (1H, dd, *J* = 18.5, 8.5 Hz, C1H_AH_B), 3.05 (1H, dd, *J* = 18.5, 3.6 Hz, C1H_AH_B), 2.13 (6H, s, 2 × Ar-CH₃), 2.11 (6H, s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 212.2 (C=O), 152.2 (COH), 142.8 (Ar-C), 135.1 (Ar-C), 129.2 (2C, 2 × Ar-C), 128.7 (2C, 2 × Ar-CH), 127.8 (Ar-CH), 125.9 (2C, 2 × Ar-CH), 120.0 (2C, 2 × Ar-C), 69.9 (C2H), 54.2 (C1H₂), 16.8 (2C, 2 × Ar-CH₃), 11.8 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+Na]⁺ = 321.14615; C₁₉H₂₂O₃Na requires 321.13612, Δ 0.10 ppm.

Methyl 3-hydroxy-3-phenylpropanoate **19**

To a solution of phenol **S9** (44.8 mg, 0.15 mmol) in MeOH (3.5 mL) was titrated a solution of CAN (411 mg, 0.75 mmol) in MeOH (1.8 mL) at RT in the open atmosphere until the colour of the CAN solution persisted (orange typically 4–5 equiv.). The reaction mixture was diluted with H₂O (6 mL) and stirred for 5–10 minutes,* then further diluted with CH₂Cl₂ (4 mL) and saturated with NaCl. The layers were separated, and the aqueous layer extracted with CH₂Cl₂ (5 × 3 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 90:10→80:20) afforded β-hydroxyester **19** (20.2 mg, 75%) as a colourless oil.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3459, 3087, 3064, 3031, 3005, 2953, 2924, 2852, 1728, 1495, 1453, 1438, 1402, 1360, 1294, 1268, 1199, 1161, 1083, 1060, 1025, 987.

¹H NMR (CDCl₃, 400 MHz) δ = 7.41–7.33 (4H, m, Ph), 7.32–7.27 (1H, m, Ph), 5.14 (1H, dd, J = 8.9, 4.0 Hz, C2H), 3.73 (3H, s, OCH₃), 2.92 (1H, v. br. s, OH), 2.78 (1H, dd, J = 16.4, 8.9 Hz, C1H_AH_B), 2.72 (1H, dd, J = 16.4, 4.0 Hz, C1H_AH_B).

¹³C NMR (CDCl₃, 101 MHz) δ = 172.9 (C=O), 142.6 (Ar-C), 128.7 (2C, 2 × Ar-CH), 128.0 (Ar-CH), 125.8 (2C, 2 × Ar-CH), 70.4 (C2H), 52.0 (OCH₃), 43.3 (C1H₂).

HRMS (ESI⁺) Found $[\text{M}+\text{Na}]^+ = 203.06798$; C₁₀H₁₂O₃Na requires 203.06787, Δ 0.55 ppm.

*If the step involving stirring with water is omitted, then duroquinone dimethyl acetal will be present in varying amounts which may interfere with chromatographic purification.

2-(1,4-Dioxaspiro[4.5]decan-8-yl)-1-(2,3,5,6-tetramethylphenyl)ethan-1-one **S10**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added acetyldurene (264 mg, 1.50 mmol), [Cp*IrCl₂]₂ (23.9 mg, 2 mol%), 4-hydroxycyclohexanone glycol acetal (261 mg, 1.65 mmol), PhMe (375 μ L) and KOH (337 mg, 6.00 mmol) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a Reseal[™] septum) and an Ar balloon fitted. The vial was heated to 85 °C in a preheated oil bath for 24 h. The mixture was cooled to RT, filtered through a SiO₂ plug (eluting with Et₂O) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 96:4) afforded ketone **S10** (392 mg, 79%) as a colourless solid.

m.p. = 148–150 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 2939, 2867, 1698, 1470, 1442, 1396, 1379, 1357, 1337, 1313, 1301, 1281, 1260, 1231, 1196, 1172, 1144, 1112, 1102, 1077, 1031, 1007, 977, 947, 930.

¹H NMR (CDCl₃, 500 MHz) δ = 6.94 (1H, s, Ar-CH), 4.00–3.91 (4H, m, 2 $\times$ C₆H₂), 2.62 (2H, d, J = 6.5 Hz, C₁H₂), 2.19 (6H, s, 2 $\times$ Ar-CH₃), 2.12 (1H, ddq, J = 11.5, 6.5, 3.6 Hz, C₂H), 2.05 (6H, s, 2 $\times$ Ar-CH₃), 1.90 (2H, dq, J = 12.7, 4.1 Hz, 2 $\times$ C₃H_{ax}H_{eq}), 1.77 (2H, ddt, J = 13.9, 3.4, 3.2 Hz, 2 $\times$ C₄H_{ax}H_{eq}), 1.65 (2H, td, J = 13.2, 4.2 Hz, 2 $\times$ C₄H_{ax}H_{eq}), 1.32 (2H, qd, J = 13.1, 3.7 Hz, 2 $\times$ C₃H_{ax}H_{eq}).

¹³C NMR (CDCl₃, 126 MHz) δ = 210.8 (C=O), 142.9 (Ar-C), 134.5 (2C, 2 $\times$ Ar-C), 131.6 (Ar-CH), 128.0 (2C, 2 $\times$ Ar-C), 108.9 (C₅), 64.4 (2C, 2 $\times$ C₆H₂), 51.8 (C₁H₂), 34.6 (2C, 2 $\times$ C₄H₂), 31.1 (C₂H), 30.3 (2C, 2 $\times$ C₃H₂), 19.6 (2C, 2 $\times$ Ar-CH₃), 15.9 (2C, 2 $\times$ Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 317.21118; C₂₀H₂₉O₃ requires 317.21112, Δ 0.19 ppm.

1-(4-Hydroxy-2,3,5,6-tetramethylphenyl)-2-(1,4-dioxaspiro[4.5]decan-8-yl)ethan-1-one
S11

To a flame-dried flask containing a solution of ketone **S10** (316 mg, 1.00 mmol) in HFIP (10 mL) over Ar was added phthaloyl peroxide **S6** (246 mg, 1.50 mmol) at RT. The reaction mixture was then warmed to 40 °C and stirred for 12 h. The reaction mixture was directly concentrated *in vacuo*, followed by the addition of aq. sat. NaHCO₃:MeOH (1:9, 0.05 M) over Ar. The ensuing suspension was heated to 40 °C and stirred for a further 12 h. The reaction mixture was cooled to RT, then diluted with brine (30 mL) and CH₂Cl₂ (20 mL). The layers were separated, the aqueous layer extracted with CH₂Cl₂ (5 × 20 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 85:15→80:20→75:25) afforded phenol **S11** (91.3 mg, 28%) as a pale yellow solid.

m.p. = 173–175 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3473, 2928, 2883, 1694, 1576, 1446, 1399, 1379, 1355, 1337, 1292, 1216, 1173, 1146, 1105, 1033, 1009, 974, 928.

¹H NMR (CDCl₃, 400 MHz) δ = 4.76 (1H, s, OH), 3.99–3.90 (4H, m, 2 × C6H₂), 2.61 (2H, d, J = 6.5 Hz, C1H₂), 2.13 (6H, s, 2 × Ar-CH₃), 2.16–2.00 (1H, m, C2H), 1.89 (2H, dq, J = 12.9, 4.4 Hz, 2 × C3H_{ax}H_{eq}), 1.76 (2H, dq, J = 14.0, 3.0 Hz, 2 × C4H_{ax}H_{eq}), 1.64 (2H, td, J = 13.3, 4.3 Hz, 2 × C4H_{ax}H_{eq}), 1.31 (2H, qd, J = 13.1, 3.9 Hz, 2 × C3H_{ax}H_{eq}).

¹³C NMR (CDCl₃, 101 MHz) δ = 210.8 (C=O), 151.9 (COH), 136.0 (Ar-C), 129.0 (2C, 2 × Ar-C), 119.9 (2C, 2 × Ar-C), 108.9 (C5), 64.4 (2C, 2 × C6H₂), 52.3 (C1H₂), 34.5 (2C, 2 × C4H₂), 31.3 (C2H), 30.3 (2C, 2 × C3H₂), 16.6 (2C, 2 × Ar-CH₃), 11.8 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found $[M+H]^+$ = 333.20627; C₂₀H₂₉O₄ requires 333.20604, Δ 0.70 ppm.

Methyl 2-(1,4-dioxaspiro[4.5]decan-8-yl)acetate **20**

To a solution of phenol **S11** (28.8 mg, 0.10 mmol) in MeOH (2.4 mL) was titrated a solution of CAN (274 mg, 0.50 mmol) in MeOH (1.2 mL) at RT in the open atmosphere until the colour of the CAN solution persisted (orange typically 4–5 equiv.). The reaction mixture was diluted with H₂O (3 mL) and stirred for 5–10 minutes,* then further diluted with CH₂Cl₂ (4 mL) and saturated with NaCl. The layers were separated, and the aqueous layer extracted with CH₂Cl₂ (5 × 3 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 90:10) afforded ester **20** (9.7 mg, 45%) as a colourless oil.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 2930, 2883, 1737, 1640, 1438, 1380, 1359, 1338, 1314, 1292, 1240, 1167, 1135, 1106, 1086, 1035, 1016, 979, 949, 931.

¹H NMR (CDCl₃, 400 MHz) δ = 3.98–3.88 (4H, m, 2 × C6H₂), 3.66 (3H, s, OCH₃), 2.24 (2H, d, J = 7.1 Hz, C1H₂), 1.84 (1H, dddd, J = 18.2, 14.2, 7.0, 3.1 Hz, C2H), 1.78–1.69 (4H, m, 2 × C4H_{ax}H_{eq} and 2 × C3H_{ax}H_{eq}), 1.56 (2H, ddd, J = 13.7, 12.9, 4.5 Hz, 2 × C4H_{ax}H_{eq}), 1.32 (2H, td, J = 12.3, 2.5 Hz, 2 × C3H_{ax}H_{eq}).

¹³C NMR (CDCl₃, 101 MHz) δ = 173.5 (C=O), 108.7 (C5), 64.4 (2C, 2 × C6H₂), 51.6 (OCH₃), 40.9 (C1H₂), 34.4 (2C, 2 × C4H₂), 33.6 (C2H), 30.1 (2C, 2 × C3H₂).

HRMS (ESI⁺) Found [M+H]⁺ = 215.12789; C₁₁H₁₉O₄ requires 215.12779, Δ 0.49 ppm.

*If the step involving stirring with water is omitted, then duroquinone dimethyl acetal will be present in varying amounts which may interfere with chromatographic purification.

2-Bromo-3-phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one **S12**

To a solution of ketone **13** (200 mg, 0.75 mmol) in AcOH (1.1 mL) at RT was added Br₂ (42.0 μL, 0.825 mmol) dropwise. The mixture was stirred at RT for 30 minutes after which AcOH was removed *in vacuo*. The residue was re-dissolved in CH₂Cl₂ (10 mL) and washed with sat. aq. NaHCO₃ (2 × 10 mL). The aqueous layers were further extracted with CH₂Cl₂ (2 × 20 mL) and the combined organics dried (MgSO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 98:2) afforded α-bromoketone **S12** (213 mg, 82%) as a colourless solid.

R_f = 0.50 (Pentane:Et₂O, 95:5), [UV, KMnO₄].

m.p. = 74–75 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3067, 3038, 3007, 2967, 2939, 2919, 2882, 2859, 1688, 1602, 1497, 1464, 1453, 1427, 1392, 1375, 1353, 1323, 1305, 1287, 1232, 1188, 1155, 1113, 1077, 1046, 1040, 1031, 1016, 1005, 968.

¹H NMR (CDCl₃, 400 MHz) δ = 7.36–7.24 (5H, m, Ph), 7.00 (1H, s, Ar-CH), 4.87 (1H, dd, J = 8.4, 6.0 Hz, C1HBr), 3.70 (1H, dd, J = 14.5, 6.0 Hz, C2H_AH_B), 3.28 (1H, dd, J = 14.5, 8.4 Hz, C2H_AH_B), 2.20 (6H, s, 2 × Ar-CH₃), 2.11–1.96 (6H, v. br. s, 2 × Ar-CH₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 201.6 (C=O), 139.3 (Ar-C), 137.5 (Ar-C), 134.7 (2C, 2 × Ar-C), 132.9 (Ar-CH), 129.8 (4C, 2 × Ar-C and 2 × Ar-CH), 128.7 (2C, 2 × Ar-CH), 127.3 (Ar-CH), 55.5 (C1HBr), 39.3 (C2H₂), 19.8 (2C, 2 × Ar-CH₃), 17.1 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 345.08487; C₁₉H₂₂O⁷⁹Br requires 345.08485, Δ 0.04 ppm.

2-Bromo-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one **21**

To a flame-dried flask containing a solution of ketone **S12** (425 mg, 1.23 mmol) in HFIP (12 mL) over Ar was added phthaloyl peroxide **S6** (303 mg, 1.85 mmol) at RT. The reaction mixture was then warmed to 40 °C and stirred for 12 h. The reaction mixture was directly concentrated *in vacuo*, followed by the addition of aq. sat. NaHCO₃:MeOH (1:9, 0.05 M) over Ar. The ensuing suspension was heated to 40 °C and stirred for a further 12 h. The reaction mixture was cooled to RT, then diluted with brine (30 mL) and CH₂Cl₂ (20 mL). The layers were separated, the aqueous layer extracted with CH₂Cl₂ (5 × 20 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 90:10) afforded phenol **21** (146 mg, 33%) as a colourless solid.

m.p. = 92–94 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3511, 3087, 3063, 3029, 3003, 2927, 1691, 1603, 1571, 1496, 1454, 1384, 1349, 1322, 1296, 1217, 1118, 1095, 1030, 1013, 948, 908.

¹H NMR (CDCl₃, 500 MHz) δ = 7.34–7.24 (5H, m, Ph), 4.86 (1H, dd, J = 8.3, 6.2 Hz, C1H), 4.82 (1H, br. s, OH), 3.67 (1H, dd, J = 14.4, 6.2 Hz, C2H_AH_B), 3.27 (1H, dd, J = 14.4, 8.3 Hz, C2H_AH_B), 2.13 (6H, s, 2 × Ar-CH₃), 2.06 (6H, s, 2 × ArCH₃).

¹³C NMR (CDCl₃, 126 MHz) δ = 201.2 (C=O), 152.8 (COH), 137.6 (Ar-C), 132.3 (Ar-C), 131.4 (2C, br. s, 2 × Ar-C), 129.8 (2C, 2 × Ar-CH), 128.7 (2C, 2 × Ar-CH), 127.2 (Ar-CH), 120.0 (2C, 2 × Ar-C), 56.0 (C1H), 39.4 (C2H₂), 17.8 (2C, 2 × Ar-CH₃), 11.9 (2C, 2 × Ar-CH₃).

HRMS (ESI⁺) Found $[M+\text{Na}]^+ = 383.06180$; C₁₉H₂₁⁷⁹BrO₂Na requires 383.06171, Δ 0.22 ppm.

1-(4-Hydroxyphenyl)-3-phenylpropan-1-one **22**

To a solution of 4'-hydroxychalcone (224 mg, 1.00 mmol) in EtOAc:EtOH (10 mL) was added Pd(OH)₂/C (11.2 mg, 5 wt%). The suspension was evacuated and back-filled with H₂ (× 4) and stirred under an atmosphere of H₂ for 15 minutes (TLC analysis indicated that the reaction was complete after this time).^{*} The mixture was filtered through a pad of Celite[®] under suction (eluting with EtOAc) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 80:20) afforded phenol **22** (119 mg, 53%) as a colourless solid.

m.p. = 93–95 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3282, 3084, 3063, 3026, 2955, 2930, 1656, 1602, 1582, 1514, 1495, 1452, 1408, 1366, 1283, 1235, 1209, 1168, 1108, 1078, 1030, 980, 840, 783, 749, 700, 637, 614.

¹H NMR (CDCl₃, 400 MHz) δ = 7.98–7.84 (2H, m, Ph), 7.33–7.27 (2H, m, Ph), 7.26–7.23 (2H, m, Ph), 7.23–7.18 (1H, m, Ph), 6.94–6.84 (2H, m, Ph), 6.36 (1H, s, OH), 3.31–3.22 (2H, m, C1H₂), 3.11–3.02 (2H, m, C2H₂).

¹³C NMR (CDCl₃, 101 MHz) δ = 198.9 (C=O), 160.6 (COH), 141.4 (Ar-C), 130.9 (2C, 2 × Ar-CH), 130.0 (2C, 2 × Ar-CH), 128.7 (2C, 2 × Ar-CH), 128.5 (Ar-C), 126.3 (2C, 2 × Ar-CH), 115.6 (2C, 2 × Ar-CH), 40.3 (C1H₂), 30.6 (C2H₂).

HRMS (ESI⁺) Found [M+H]⁺ = 227.10675; C₁₅H₁₅O₂ requires 227.10666, Δ 0.41 ppm.

All spectroscopic data in agreement with that previously reported.⁹

^{*}The reaction should be closely monitored as extended reaction times will lead to complete loss of the ketone group to the corresponding alkane.

1-(4-Methoxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one **23**

To a flame-dried flask containing NaH (60% dispersion in mineral oil, 24.0 mg, 0.60 mmol) at 0 °C was added a solution of phenol **14** (169 mg, 0.60 mmol) in anhydrous DMF (3.0 mL) over 10 minutes (caution: exotherm and effervescence). The flask was then warmed up to RT and stirred for a further 20 minutes, during which time small amounts of DMF were used to rinse the sides of the flask periodically, followed by the addition of iodomethane (37 μ L, 142 mg, 0.60 mmol). The reaction mixture was stirred at RT for the 1 h, then diluted with Et₂O (12 mL), sat. aq. NH₄Cl (6 mL) and brine (15 mL) sequentially. The layers were separated, the aqueous layer extracted with Et₂O (3 $\times$ 10 mL) and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 98:2) afforded ketone **23** (129 mg, 72%) as a colourless solid.

m.p. = 132–134 °C.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3085, 3062, 3027, 2987, 2936, 2828, 1700, 1604, 1573, 1496, 1454, 1402, 1384, 1355, 1310, 1263, 1249, 1189, 1154, 1117, 1094, 1004, 986, 932, 910.

¹H NMR (CDCl₃, 500 MHz) δ = 7.32–7.26 (2H, m, Ph), 7.26–7.22 (2H, m, Ph), 7.22–7.17 (1H, m, Ph), 3.64 (3H, s, OCH₃), 3.10–3.03 (2H, m, C₂H₂), 3.03–2.97 (2H, m, C₁H₂), 2.16 (6H, s, 2 $\times$ Ar-CH₃), 2.02 (6H, s, 2 $\times$ Ar-CH₃).

¹³C NMR (CDCl₃, 126 MHz) δ = 210.7 (C=O), 156.8 (COCH₃), 141.1 (Ar-C), 138.8 (Ar-C), 129.6 (2C, 2 $\times$ Ar-C), 128.63 (2C, 2 $\times$ Ar-CH), 128.59 (2C, 2 $\times$ Ar-CH), 127.7 (2C, 2 $\times$ Ar-C), 126.2 (Ar-CH), 60.2 (OCH₃), 47.1 (C₁H₂), 29.5 (C₂H₂), 16.6 (2C, 2 $\times$ Ar-CH₃), 12.4 (2C, 2 $\times$ Ar-CH₃).

HRMS (ESI⁺) Found [M+Na]⁺ = 319.16675; C₂₀H₂₄O₂Na requires 319.16685, Δ –0.32 ppm.

3-Phenyl-1-(2,3,4,5-tetramethylphenyl)propan-1-one **S13**

To a solution of prehnitene (1.34 g, 10.0 mmol) in anhydrous CH_2Cl_2 (50 mL) was added hydrocinnamoyl chloride (1.63 mL, 1.86 g, 11.0 mmol) RT. The reaction mixture was cooled to 0 °C, then AlCl_3 (1.67 g, 12.5 mmol) was carefully added and the reaction stirred at 0 °C for 1 h. The reaction mixture was then poured onto ice/ H_2O (200 mL), allowed to warm up to RT, then diluted with CH_2Cl_2 (150 mL) and saturated with NaCl. The layers were separated, the aqueous layer extracted with CH_2Cl_2 (3×100 mL), and the combined organics dried (Na_2SO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , eluent load, Pentane: Et_2O , 100:0→99:1) afforded ketone **S13** (1.69 g, 63%) as a colourless oil.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3085, 3062, 3026, 2924, 2868, 1682, 1602, 1562, 1496, 1453, 1407, 1382, 1355, 1302, 1244, 1119, 1074, 1030, 1003, 947, 863.

^1H NMR (CDCl_3 , 500 MHz) δ = 7.33–7.27 (2H, m, $2 \times \text{Ph}$), 7.26–7.23 (2H, m, $2 \times \text{Ph}$), 7.23–7.18 (1H, m, Ph), 7.09 (1H, s, Ar-CH), 3.22–3.12 (2H, m, C1H₂), 3.09–2.99 (2H, m, C2H₂), 2.28 (3H, s, Ar-CH₃), 2.28 (3H, s, Ar-CH₃), 2.23 (6H, s, $2 \times \text{Ar-CH}_3$).

^{13}C NMR (CDCl_3 , 126 MHz) δ = 205.7 (C=O), 141.4 (Ar-C), 138.3 (Ar-C), 137.8 (Ar-C), 136.8 (Ar-C), 133.4 (Ar-C), 132.4 (Ar-C), 128.59 (2C, $2 \times \text{Ar-CH}$), 128.56 (2C, $2 \times \text{Ar-CH}$), 126.25 (Ar-CH), 126.19 (Ar-CH), 44.4 (C1H₂), 30.6 (C2H₂), 20.9 (Ar-CH₃), 17.2 (Ar-CH₃), 16.6 (Ar-CH₃), 16.2 (Ar-CH₃).

HRMS (ESI⁺) Found $[\text{M}+\text{H}]^+ = 267.17428$; $\text{C}_{19}\text{H}_{23}\text{O}$ requires 267.17434, Δ –0.22 ppm.

1-(2-Hydroxy-3,4,5,6-tetramethylphenyl)-3-phenylpropan-1-one **24**

To a flame-dried flask containing a solution of ketone **S13** (986 mg, 3.70 mmol) in HFIP (37 mL) over

Ar was added phthaloyl peroxide **S6** (789 mg, 4.81 mmol) at RT. The reaction mixture was then warmed to 40 °C and stirred for 12 h. The reaction mixture was directly concentrated *in vacuo*, followed by the addition of aq. sat. NaHCO₃:MeOH (1:9, 0.05 M) over Ar. The ensuing suspension was heated to 40 °C and stirred for a further 12 h. The reaction mixture as cooled to RT, then diluted with brine (100 mL) and CH₂Cl₂ (70 mL). The layers were separated, the aqueous layer extracted with CH₂Cl₂ (5 × 50 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 99:1→98:2→95:5) afforded phenol **24** (278 mg, 27%, 49% BRSM) as a pale yellow oil. Ketone **S13** (440 mg, 45%) was also recovered from the reaction.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3294, 3086, 3062, 3027, 3001, 2925, 2871, 1687, 1618, 1496, 1454, 1404, 1381, 1344, 1308, 1262, 1154, 1126, 1086, 1031, 1002, 943, 919.

¹H NMR (CDCl₃, 500 MHz) δ = 10.34 (1H, s, OH), 7.33–7.26 (2H, m, 2 × Ph), 7.24–7.15 (3H, m, Ph), 3.24–3.12 (2H, m, C1H₂), 3.09–2.95 (2H, m, C2H₂), 2.33 (3H, s, Ar-CH₃), 2.24 (3H, s, Ar-CH₃), 2.20 (3H, s, Ar-CH₃), 2.15 (3H, s, Ar-CH₃).

¹³C NMR (CDCl₃, 126 MHz) δ = 209.2 (C=O), 154.7 (COH), 142.1 (Ar-C), 141.0 (Ar-C), 132.4 (Ar-C), 128.7 (2C, 2 × Ar-CH), 128.5 (2C, 2 × Ar-CH), 127.2 (Ar-C), 126.3 (Ar-CH), 122.5 (Ar-C), 122.3 (Ar-C), 46.4 (C1H₂), 31.7 (C2H₂), 20.5 (Ar-CH₃), 17.3 (Ar-CH₃), 15.8 (Ar-CH₃), 12.2 (Ar-CH₃).

HRMS (ESI⁺) Found [M+H]⁺ = 283.16934; C₁₉H₂₃O₂ requires 283.16926, Δ 0.30 ppm.

4-Methoxy-2,3,4,5-tetramethyl-6-(3-phenylpropanoyl)cyclohexa-2,5-dien-1-one **25**

To a solution of phenol **24** (56.5 mg, 0.20 mmol) in MeOH (5.0 mL) was titrated a solution of CAN (548 mg, 1.00 mmol) in MeOH (2.0 mL) at RT in the open atmosphere until the colour of the CAN solution persisted (orange typically 4–5 equiv.). The reaction mixture was diluted with H₂O (3 mL) and stirred for 5–10 minutes,* then further diluted with CH₂Cl₂ (4 mL) and saturated with NaCl. The layers were separated, and the aqueous layer extracted with CH₂Cl₂ (5 × 3 mL), and the combined organics dried (Na₂SO₄) and concentrated *in vacuo*. Purification by preparative TLC (Pentane:Et₂O, 75:25) afforded cyclohexadienone **25** (14.1 mg, 23%) as a yellow solid.

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3086, 3062, 3027, 2990, 2931, 2825, 1704, 1660, 1628, 1497, 1453, 1380, 1351, 1270, 1219, 1173, 1088, 1048.

¹H NMR (CDCl₃, 500 MHz) δ = 7.26 (2H, m, Ph), 7.24–7.18 (2H, m, Ph), 7.21–7.13 (1H, m, Ph), 3.05–2.89 (4H, m, C1H₂ and C2H₂), 2.90 (3H, s, OCH₃), 1.98 (3H, q, J = 1.0 Hz, Ar-CH₃), 1.89 (3H, q, J = 1.0 Hz, Ar-CH₃), 1.80 (3H, s, Ar-CH₃), 1.34 (3H, s, Ar-CH₃).

¹³C NMR (CDCl₃, 126 MHz) δ = 205.4 (C=O), 182.6 (C=O), 156.6 (Ar-C), 155.1 (Ar-C), 141.1 (Ar-C), 140.7 (Ar-C), 133.6 (Ar-C), 128.54 (2C, 2 × Ar-CH), 128.51 (2C, 2 × Ar-CH), 126.2 (Ar-CH), 77.1 (C(OCH₃)CH₃), 52.6 (OCH₃), 45.7 (C1H₂), 29.6 (C2H₂), 25.5 (CH₃), 14.6 (Ar-CH₃), 14.2 (Ar-CH₃), 11.1 (Ar-CH₃).

HRMS (ESI⁺) Found $[M+H]^+ = 313.17981$; C₂₀H₂₅O₃ requires 313.17982, Δ –0.04 ppm.

*If the step involving stirring with water is omitted, then duroquinone dimethyl acetal will be present in varying amounts which may interfere with chromatographic purification.

2-Bromo-1-(4-methoxyphenyl)-3-phenylpropan-1-one **26**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added ketone **4** (36.5 mg, 0.10 mmol), anisole (39 μ L, 0.36 mmol) and AlCl_3 (19.2 mg, 0.14 mmol) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a ResealTM septum) and heated to 100 °C in a preheated oil bath for 1 h 30 minutes. The reaction was cooled to RT and ice (250 mg) added. The mixture was extracted with CH_2Cl_2 (2×10 mL) and the combined organics washed with sat. aq. NaHCO_3 (10 mL), dried (MgSO_4) and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 , eluent load, Pentane: Et_2O , 95:5) afforded α -bromoketone **26** (15.4 mg, 48%) as a colourless oil.

R_f = 0.27 (Pentane: Et_2O , 95:5), [UV, KMnO_4].

IR (film) $\nu_{\text{max}}/\text{cm}^{-1}$ 3063, 3029, 2926, 2841, 1674, 1598, 1574, 1511, 1496, 1455, 1440, 1421, 1360, 1315, 1289, 1263, 1244, 1170, 1120, 1080, 1028, 975.

^1H NMR (CDCl_3 , 400 MHz) δ = 7.98–7.94 (2H, m, $2 \times \text{Ar-CH}$), 7.32–7.19 (5H, m, Ph), 6.96–6.90 (2H, m, $2 \times \text{Ar-CH}$), 5.29 (1H, t, J = 7.3 Hz, C1HBr), 3.86 (3H, s, OCH_3), 3.66 (1H, dd, J = 14.3, 7.5 Hz, $\text{C2H}_\text{A}\text{H}_\text{B}$), 3.34 (1H, dd, J = 14.3, 7.1 Hz, $\text{C2H}_\text{A}\text{H}_\text{B}$).

^{13}C NMR (CDCl_3 , 101 MHz) δ = 191.5 (C=O), 164.1 (Ar-C), 137.8 (Ar-C), 131.4 (2C, $2 \times \text{Ar-CH}$), 129.6 (2C, $2 \times \text{Ar-CH}$), 128.7 (2C, $2 \times \text{Ar-CH}$), 127.4 (Ar-C), 127.1 (Ar-CH), 114.1 (2C, $2 \times \text{Ar-CH}$), 55.7 (OCH_3), 46.8 (C1HBr), 39.7 (C2H_2).

HRMS (ESI^+) Found $[\text{M}+\text{H}]^+ = 319.03296$; $\text{C}_{16}\text{H}_{16}\text{O}_2^{79}\text{Br}$ requires 319.03282, Δ 0.44 ppm. All spectroscopic data in agreement with that previously reported.⁹

2-Benzyl-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one **S14**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added ketone **9** (84.1 mg, 0.30 mmol), [(cod)IrCl]₂ (2.0 mg, 1 mol%), 1,2-bis(diphenylphosphino)benzene (dppBz) (2.7 mg, 2 mol%), *n*-BuOH (0.27 mL, 3.00 mmol) and KOH (33.7 mg, 0.60 mmol) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a Reseal[™] septum) and purged with Ar for 5 minutes using a balloon. Following this, the vial (complete with an Ar balloon) was heated to 85 °C in a preheated oil bath for 24 h. The mixture was cooled to RT, filtered through a SiO₂ plug (eluting with Et₂O) and concentrated *in vacuo*. Purification by column chromatography (SiO₂, eluent load, Pentane:Et₂O, 99:1→98:2) afforded ketone **S14** (98.8 mg, 98%) as a colourless solid.

*R*_f = 0.70 (Pentane:Et₂O, 95:5), [UV, vanillin].

m.p. = 93–95 °C.

IR (film) ν_{max} /cm⁻¹ 2955, 2930, 2860, 1688, 1498, 1468, 1453, 1431, 1374, 1308, 1259, 1211, 1137, 1104, 1072, 1030, 1018, 995.

¹H NMR (CDCl₃, 400 MHz) δ = 7.27–7.23 (2H, m, Ph), 7.21–7.15 (3H, m, Ph), 3.16 (1H, dd, *J* = 13.4, 6.3 Hz, C2H_AH_B), 3.08–3.03 (1H, m, C1H), 2.67 (1H, dd, *J* = 13.5, 7.4 Hz, C2H_AH_B), 2.21 (3H, s, Ar-CH₃), 2.15 (6H, s, 2 × Ar-CH₃), 2.20–1.70 (6H, v. br., 2 × Ar-CH₃), 1.73–1.61 (1H, m, C1'H_AH_B), 1.45–1.16 (5H, m, C1'H_AH_B, C2'H₂ and C3'H₂), 0.80 (3H, t, *J* = 7.2 Hz, C4'H₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 213.1 (C=O), 140.5 (Ar-C), 139.7 (Ar-C), 135.7 (Ar-C), 133.2 (2C, 2 × Ar-C), 129.5 (2C, 2 × Ar-CH), 128.8 (2C, 2 × Ar-C), 128.4 (2C, 2 × Ar-CH), 126.1 (Ar-CH), 56.1 (C1H), 35.6 (C2H₂), 29.5 (C1'H₂), 29.4 (C2'H₂), 23.0 (C3'H₂), 17.8 (2C, 2 × Ar-CH₃), 16.9 (Ar-CH₃), 16.2 (2C, 2 × Ar-CH₃), 14.0 (C4'H₃).

HRMS (ESI⁺) Found [M+H]⁺ = 337.2526; C₂₄H₃₃O requires 337.2526, Δ 0.01 ppm. All spectroscopic data in agreement with that previously reported.²

2-Benzyl-2-bromo-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one **27**

To a solution of ketone **S14** (127 mg, 0.38 mmol) in AcOH (0.57 mL) at RT was added Br₂ (21.2 μ L, 0.42 mmol) dropwise. The mixture was stirred at RT for 10 minutes after which the acetic acid was removed *in vacuo*. The residue was re-dissolved in CH₂Cl₂ (10 mL) and washed with sat. aq. NaHCO₃ (2 $\times$ 10 mL). The aqueous layers were further extracted with CH₂Cl₂ (2 $\times$ 20 mL) and the combined organics dried (MgSO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, solid load, Pentane:Et₂O, 98:2) afforded α -bromoketone **27** (79.4 mg, 50%) as a colourless solid.

R_f = 0.60 (Pentane:Et₂O, 95:5), [UV, KMnO₄].

m.p. = 104–106 °C.

IR (film) $\nu_{\max}$ /cm⁻¹ 3026, 2960, 2927, 2874, 2856, 1688, 1494, 1454, 1440, 1382, 1302, 1258, 1225, 1169, 1119, 1094, 1076, 1072, 1058, 1029, 1020, 1002, 982.

¹H NMR (CDCl₃, 400 MHz) δ = 7.35–7.25 (5H, m, Ph), 3.55 (1H, d, J = 14.0 Hz, C2H_AH_B), 3.49 (1H, d, J = 14.0 Hz, C2H_AH_B), 2.23 (3H, s, Ar-CH₃), 2.16 (3H, s, Ar-CH₃), 2.15 (3H, s, Ar-CH₃), 2.04–1.99 (2H, obscured m, C1'H_AH_B), 2.02 (3H, s, Ar-CH₃), 1.96 (3H, s, Ar-CH₃), 1.72–1.52 (2H, m, C2'H₂), 1.36–1.23 (2H, m, C3'H₂), 0.91 (3H, t, J = 7.3 Hz, C4'H₃).

¹³C NMR (CDCl₃, 101 MHz) δ = 207.6 (C=O), 137.7 (Ar-C), 136.2 (Ar-C), 135.8 (Ar-C), 133.1 (Ar-C), 133.0 (Ar-C), 131.9 (2C, 2 $\times$ Ar-CH), 129.4 (Ar-C), 128.6 (Ar-C), 128.0 (2C, 2 $\times$ Ar-CH), 127.2 (Ar-CH), 76.6 (C1Br), 44.5 (C2H₂), 38.9 (C1'H₂), 28.4 (C2'H₂), 22.8 (C3'H₂), 19.5 (Ar-CH₃), 19.1 (Ar-CH₃), 16.9 (Ar-CH₃), 16.3 (Ar-CH₃), 16.2 (Ar-CH₃), 14.1 (C4'H₃).

HRMS (ESI⁺) Found [M+Na]⁺ = 437.14499; C₂₄H₃₁O⁷⁹BrNa requires 437.14505, Δ –0.14 ppm.

2-Butyl-2,3-dihydro-1H-inden-1-one **28**

To a 2–5 mL Biotage[®] microwave vial equipped with a stirrer bar was added ketone **27** (66.5 mg, 0.16 mmol), anisole (53 μ L, 0.49 mmol) and TfOH (17.0 μ L, 0.19 mmol) sequentially in the open atmosphere. The reaction vessel was sealed with a microwave vial cap (containing a Reseal[™] septum) and heated to 100 °C in a preheated oil bath for 1 h 30 minutes. The reaction was cooled to RT and ice (250 mg) added. The mixture was extracted with CH₂Cl₂ (2 $\times$ 10 mL) and the combined organics washed with sat. aq. NaHCO₃ (10 mL), dried (MgSO₄) and concentrated *in vacuo*. Purification by flash column chromatography (SiO₂, eluent load, Pentane:Et₂O, 95:5) afforded ketone **28** (7.2 mg, 24%) as a colourless oil.

R_f = 0.20 (Pentane:Et₂O, 95:5), [UV, KMnO₄].

¹H NMR (CDCl₃, 200 MHz) δ = 7.75 (1H, d, J = 7.6 Hz, Ph), 7.58 (1H, td, J = 7.5, 1.2 Hz, Ph), 7.46 (1H, d, J = 7.7 Hz, Ph), 7.36 (1H, t, J = 7.4 Hz, Ph), 3.33 (1H, dd, J = 17.3, 7.9 Hz, C2H_AH_B), 2.82 (1H, dd, J = 17.2, 3.9 Hz, C2H_AH_B), 2.70–2.61 (1H, m, C1'H_AH_B), 2.02–1.91 (1H, m, C1'H_AH_B), 1.52–1.27 (5H, m, C1H, C2'H₂ and C3'H₂), 0.91 (3H, t, J = 7.3 Hz, C4'H₃).
¹H NMR in agreement with that previously reported.¹⁰

V) NMR Spectra

¹H NMR: 4-Bromo-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one S1

¹³C NMR: 4-Bromo-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one S1

¹H NMR: Butyl 4-bromobutanoate 1

¹H NMR: 4-Oxo-4-(2,3,4,5,6-pentamethylphenyl)butanoic acid S2

¹³C NMR: 4-Oxo-4-(2,3,4,5,6-pentamethylphenyl)butanoic acid S2

¹H NMR: Methyl 4-oxo-4-(2,3,4,5,6-pentamethylphenyl)butanoate S3

¹³C NMR: Methyl 4-oxo-4-(2,3,4,5,6-pentamethylphenyl)butanoate S3

¹H NMR: Butyl methyl succinate 2

¹³C NMR: Butyl methyl succinate 2

^1H NMR: 1-(2,3,4,5,6-Pentamethylphenyl)-3-(thiophen-2-yl)butan-1-one 3

^{13}C NMR: 1-(2,3,4,5,6-Pentamethylphenyl)-3-(thiophen-2-yl)butan-1-one 3

¹H NMR: (*E*)-1-(2,3,4,5,6-Pentamethylphenyl)-3-phenylprop-2-en-1-one S4

¹³C NMR: (*E*)-1-(2,3,4,5,6-Pentamethylphenyl)-3-phenylprop-2-en-1-one S4

¹H NMR: 1-(2,3,4,5,6-Pentamethylphenyl)-3-phenylpropan-1-one 9

¹³C NMR: 1-(2,3,4,5,6-Pentamethylphenyl)-3-phenylpropan-1-one 9

¹H NMR: 2-Bromo-1-(2,3,4,5,6-pentamethylphenyl)-3-phenylpropan-1-one 4

¹³C NMR: 2-Bromo-1-(2,3,4,5,6-pentamethylphenyl)-3-phenylpropan-1-one 4

¹H NMR: 2-Benzyl-1-(2,3,4,5,6-pentamethylphenyl)prop-2-en-1-one 5

¹³C NMR: 2-Benzyl-1-(2,3,4,5,6-pentamethylphenyl)prop-2-en-1-one 5

¹H NMR: 3-Hydroxy-1-(2,3,4,5,6-pentamethylphenyl)-3-phenylpropan-1-one 6

¹³C NMR: 3-Hydroxy-1-(2,3,4,5,6-pentamethylphenyl)-3-phenylpropan-1-one 6

¹H NMR: 1-(2,3,4,5,6-Pentamethylphenyl)-2-(1,4-dioxaspiro[4.5]decan-8-yl)ethan-1-one

7

¹³C NMR: 1-(2,3,4,5,6-Pentamethylphenyl)-2-(1,4-dioxaspiro[4.5]decan-8-yl)ethan-1-one

7

¹H NMR: 2-Benzyl-2,3-dibromo-1-(2,3,4,5,6-pentamethylphenyl)propan-1-one 8

¹³C NMR: 2-Benzyl-2,3-dibromo-1-(2,3,4,5,6-pentamethylphenyl)propan-1-one 8

¹H NMR: 1-(4-Methoxyphenyl)-3-phenylpropan -1-one 10

¹³C NMR: 1-(4-Methoxyphenyl)-3-phenylpropan-1-one 10

¹H NMR: Butyl 3-phenylpropanoate 11

¹H NMR: Butyl 3-(thiophen-2-yl)butanoate 12

¹³C NMR: Butyl 3-(thiophen-2-yl)butanoate 12

¹H NMR: (*E*)-3-Phenyl-1-(2,3,5,6-tetramethylphenyl)prop-2-en-1-one S5

¹³C NMR: (*E*)-3-Phenyl-1-(2,3,5,6-tetramethylphenyl)prop-2-en-1-one S5

¹H NMR: 3-Phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one 13

¹³C NMR: 3-Phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one 13

¹H NMR: Phthaloyl peroxide S6

¹³C NMR: Phthaloyl peroxide S6

¹H NMR: 1-(4-Hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one 14

¹³C NMR: 1-(4-Hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one 14

¹H NMR: 6-Methoxy-2,3,5,6-tetramethyl-4-(3-phenylpropanoyl)cyclohexa-2,4-dien-1-one 15

¹³C NMR: 6-Methoxy-2,3,5,6-tetramethyl-4-(3-phenylpropanoyl)cyclohexa-2,4-dien-1-one 15

¹H NMR: Methyl 3-phenylpropanoate 16

¹³C NMR spectrum of Methyl 3-phenylpropanoate 16

¹H NMR: 3-Phenylpropanoic acid 17

¹³C NMR: 3-Phenylpropanoic acid 17

¹H NMR: 2-Benzyl-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)prop-2-en-1-one S7

¹³C NMR: 2-Benzyl-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)prop-2-en-1-one S7

¹H NMR: Methyl 2-benzylacrylate 18

*Signal corresponds to inseparable duroquinone (12H).

^1H NMR: 3-Hydroxy-3-phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one S8

^{13}C NMR: 3-Hydroxy-3-phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one S8

^1H NMR: 3-Hydroxy-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one S9

^{13}C NMR: 3-Hydroxy-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one S9

¹H NMR: Methyl 3-hydroxy-3-phenylpropanoate 19

¹³C NMR: Methyl 3-hydroxy-3-phenylpropanoate 19

¹H NMR: 2-(1,4-Dioxaspiro[4.5]decan-8-yl)-1-(2,3,5,6-tetramethylphenyl)ethan-1-one
S10

¹³C NMR: 2-(1,4-Dioxaspiro[4.5]decan-8-yl)-1-(2,3,5,6-tetramethylphenyl)ethan-1-one
S10

¹H NMR: 1-(4-Hydroxy-2,3,5,6-tetramethylphenyl)-2-(1,4-dioxaspiro[4.5]decan-8-yl)ethan-1-one S11

¹³C NMR: 1-(4-Hydroxy-2,3,5,6-tetramethylphenyl)-2-(1,4-dioxaspiro[4.5]decan-8-yl)ethan-1-one S11

¹H NMR: Methyl 2-(1,4-dioxaspiro[4.5]decan-8-yl)acetate 20

¹³C NMR: Methyl 2-(1,4-dioxaspiro[4.5]decan-8-yl)acetate 20

¹H NMR: 2-Bromo-3-phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one S12

¹³C NMR: 2-Bromo-3-phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one S12

¹H NMR: 2-Bromo-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one 21

¹³C NMR: 2-Bromo-1-(4-hydroxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one 21

¹H NMR: 1-(4-Hydroxyphenyl)-3-phenylpropan-1-one 22

¹³C NMR: 1-(4-Hydroxyphenyl)-3-phenylpropan-1-one 22

¹H NMR: 1-(4-Methoxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one 23

¹³C NMR: 1-(4-Methoxy-2,3,5,6-tetramethylphenyl)-3-phenylpropan-1-one 23

¹H NMR: 3-Phenyl-1-(2,3,4,5-tetramethylphenyl)propan-1-one S13

¹³C NMR: 3-Phenyl-1-(2,3,4,5-tetramethylphenyl)propan-1-one S13

¹H NMR: 1-(2-Hydroxy-3,4,5,6-tetramethylphenyl)-3-phenylpropan-1-one 24

¹³C NMR: 1-(2-Hydroxy-3,4,5,6-tetramethylphenyl)-3-phenylpropan-1-one 24

¹H NMR: 4-Methoxy-2,3,4,5-tetramethyl-6-(3-phenylpropanoyl)cyclohexa-2,5-dien-1-one 25

¹³C NMR: 4-Methoxy-2,3,4,5-tetramethyl-6-(3-phenylpropanoyl)cyclohexa-2,5-dien-1-one 25

¹H NMR: 2-Bromo-1-(4-methoxyphenyl)-3-phenylpropan-1-one 26

¹³C NMR: 2-Bromo-1-(4-methoxyphenyl)-3-phenylpropan-1-one 26

¹H NMR: 2-Benzyl-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one S14

¹³C NMR: 2-Benzyl-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one S14

¹H NMR: 2-Benzyl-2-bromo-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one 27

¹³C NMR: 2-Benzyl-2-bromo-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one 27

2-Butyl-2,3-dihydro-1H-inden-1-one 28

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