Supplementary Material (ESI) for Green Chemistry

Triflic Acid Adsorbed on Silica Gel as an Efficient and Recyclable Catalyst for the Addition of β-Dicarbonyl Compounds to Alcohols and Alkenes

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Supporting Information

1. General.

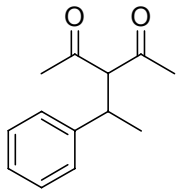
2. Analytical data of the α-alkyl-β-diketone compounds.

3. Crystal data and structure refinement of complex 3a.

1. General:

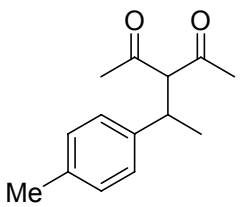
1-(4-Methylphenyl)ethanol **2b**, 1-(4-methoxyphenyl)ethanol **2c**, 1-(4-chlorophenyl)ethanol **2d**, 1-(2-naphthyl)ethanol **2e** and 1,3-diphenyl-2-propenol **2g** were prepared by reduction of the corresponding ketone precursors with $NaBH_4$ in methanol. Chromatography silica gel used as the support of TfOH was obtained from Qingdao Haiyang Chemical Co. Ltd. The other reagents were obtained from Aldrich and used without further purification. ^1H spectra were obtained from a Bruker DPX-400 spectrometer. Chemical shifts (δ, ppm) were reported using TMS as the internal standard. $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker DPX-400 spectrometer at 100.61 MHz; chemical shifts were internally referenced to $CHCl_3$ (δ = 77.0 ppm). Mass spectrometry was carried out with a Finnigan MAT 95S mass spectrometer and HRMS was carried out with Waters Micromass Q-Tof-2. Melting points were determined on a Barnstead Electrothermal 9100 apparatus and were uncorrected.

2. Analytical data of the α-alkyl-β-diketone compounds:



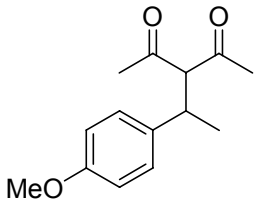
3-(1-Phenylethyl) pentane-2,4-dione (3a), CAS Registry Number: [5186-08-3].

Mp: 46-47 ^oC; 1H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, J = 6.9 Hz, 3H), 1.83 (s, 3H), 2.27 (s, 3H), 3.57-3.62 (m, 1H), 4.04 (d, J = 11.4 Hz, 1H), 7.18-7.22 (m, 3H), 7.27-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 29.6, 29.7, 40.3, 76.5, 126.8, 127.1, 128.7, 142.9, 203.2, 203.3; MS (ESI) *m/z* (%) 227.03 ($M+Na^+$, 100), 222.07, 205.02; HRMS calcd for $C_{13}H_{16}NaO_2^+$ ($M+Na^+$): 227.1043, found: 227.1059.



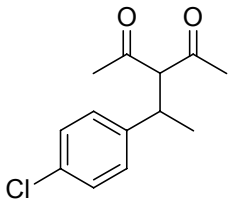
3-(1-p-Tolylethyl)pentane-2,4-dione (3b), CAS Registry Number: [727401-18-5].

Mp: 57-59 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, J = 6.8 Hz, 3H), 1.84 (s, 3H), 2.25 (s, 3H), 2.29 (s, 3H), 3.53-3.58 (m, 1H), 4.02 (d, J = 11.3 Hz, 1H), 7.06-7.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 29.6, 39.9, 76.6, 127.0, 129.3, 136.3, 139.8, 203.4; MS (ESI) *m/z* (%) 241.07 ($M+Na^+$, 100).



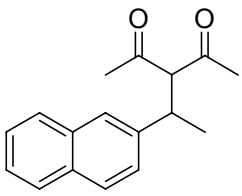
3-[1-(4-Methoxyphenyl)ethyl]pentane-2,4-dione (3c), CAS Registry Number: [727401-19-6]

Mp: 53-55 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, J = 6.9 Hz, 3H), 1.84 (s, 3H), 2.26 (s, 3H), 3.52-3.59 (m, 1H), 3.77 (s, 3H), 3.99 (d, J = 11.3 Hz, 1H), 6.82 (d, J = 8.7 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 29.5, 29.7, 39.5, 55.0, 114.0, 128.1, 134.8, 158.2, 203.3, 203.4; MS (ESI) *m/z* (%) 257.11 ($M+Na^+$, 100), 135.02.



3-[1-(4-Chlorophenyl)ethyl]pentane-2,4-dione (3d), CAS Registry Number: [727401-20-9]

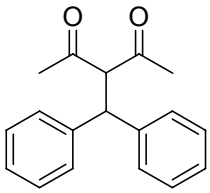
Mp: 77-79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, J = 6.9 Hz, 3H), 1.87 (s, 3H), 2.26 (s, 3H), 3.57-3.62 (m, 1H), 4.02 (d, J = 11.2 Hz, 1H), 7.14 (dd, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 2H), 7.26 (dd, J_1 = 6.8 Hz, J_2 = 1.9 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 29.5, 29.6, 39.5, 76.3, 128.5, 128.7, 132.4, 141.5, 202.7, 202.8; MS (ESI) *m/z* (%) 261.05 ($M+Na^+$, 100).



3-[1-(2-Naphthalenyl)ethyl]pentane-2,4-dione (3e), CAS Registry Number: [116140-57-9]

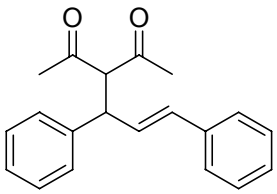
Mp: 86-88 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, J = 6.8 Hz, 3H), 1.81 (s, 3H), 2.28 (s, 3H), 3.74-3.79 (m, 1H), 4.16 (d, J = 11.3 Hz, 1H), 7.31-7.34 (m, 1H), 7.41-7.44 (m, 2H), 7.62 (d, J = 1.4 Hz,

1H), 7.76-7.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 29.6, 40.3, 76.3, 125.2, 125.6, 125.8, 126.1, 127.5, 127.6, 128.5, 132.3, 133.3, 140.4, 203.2; MS (ESI) *m/z* (%) 277.09 ($M+Na^+$, 100), 155.01.



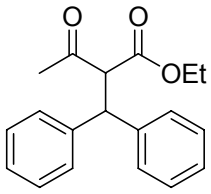
3-(Diphenylmethyl)pentane-2,4-dione (3f), CAS Registry Number: [19672-37-8]

Mp: 116-118 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (s, 6H), 4.75 (d, J = 12.4 Hz, 1H), 4.82 (d, J = 12.3 Hz, 1H), 7.11-7.16 (m, 2H), 7.21-7.28 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5, 51.0, 74.2, 126.8, 127.6, 128.7, 141.1, 202.7; HRMS calcd for $C_{18}H_{18}NaO_2^+$ ($M+Na^+$): 289.1199, found: 289.1215.



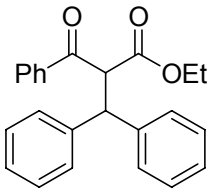
3-(1,3-Diphenyl-2-propenyl)pentane-2,4-dione (3g), CAS Registry Number: [171927-27-8]

Mp: 79-82 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90 (s, 3H), 2.23 (s, 3H), 4.33-4.35 (m, 2H), 6.17-6.23 (m, 1H), 6.42 (d, J = 15.8 Hz, 1H), 7.17-7.31 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.6, 29.8, 49.0, 74.2, 126.2, 127.1, 127.5, 127.8, 128.4, 128.8, 129.2, 131.5, 136.4, 140.0, 202.4, 202.6; HRMS calcd for $C_{20}H_{20}NaO_2^+$ ($M+Na^+$): 315.1356, found: 315.1446.



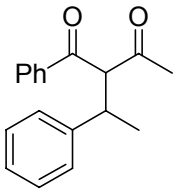
Ethyl-2-benzhydryl-3-oxobutanoate (3i), CAS Registry Number: [19289-28-2].

Mp: 88-90 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, J = 7.2 Hz, 3H), 2.09 (s, 3H), 3.97 (q, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 2H), 4.53 (d, J = 12.4 Hz, 1H), 4.76 (d, J = 12.4 Hz, 1H), 7.14-7.15 (m, 2H), 7.16-7.30 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 30.0, 50.8, 61.4, 65.1, 126.8, 126.9, 127.7, 127.8, 128.6, 128.8, 141.2, 141.5, 167.6, 201.7; HRMS (+ESI) calcd for $C_{19}H_{20}NaO_3^+$ ($M+Na^+$): 319.1305, found: 319.0761.



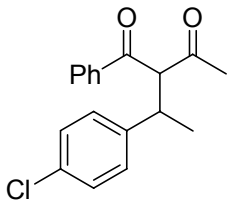
Ethyl-2-benzhydryl-3-oxo-3-phenylpropanoate (3j), CAS Registry Number:[60999-96-4].

Mp: 138-140 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3H), 3.87-3.96 (m, 2H), 5.07(d, J = 11.6 Hz, 1H), 5.41(d, J = 11.6 Hz, 1H), 7.03-7.06 (m, 1H), 7.07-7.45 (m, 7H), 7.53-7.57 (m, 5H), 8.00-8.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 50.8, 59.4, 61.6, 126.5, 126.8, 127.7, 128.5, 128.6, 128.7, 133.6, 136.6, 141.7, 167.7, 192.8; HRMS calcd for $C_{24}H_{22}NaO_3$ $(M+Na)^+$: 381.1461, found: 381.1667.



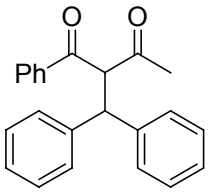
2-(1-Phenylethyl)-1-phenylbutane-1,3-dione (3k), CAS Registry Number: [5870-49-5]

Mp: 97-99 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, J = 6.9 Hz, 3H), 1.91 (s, 3H), 3.85-3.91 (m, 1H), 4.92 (d, J = 10.9 Hz, 1H), 7.20-7.22 (m, 1H), 7.28-7.32 (m, 4H), 7.47-7.52 (m, 2H), 7.60-7.61 (m, 1H), 8.08-8.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 27.9, 40.9, 70.8, 126.9, 127.4, 128.8, 133.8, 137.2, 143.2, 195.1, 203.1; MS (ESI) *m/z* (%) 289.20 ($M+Na^+$, 100), 163.10.



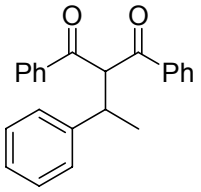
2-(1-(4-Chlorophenyl)ethyl)-1-phenylbutane-1,3-dione (3l), CAS Registry Number: [727401-25-4]

Mp: 89-92 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, J = 6.8 Hz, 3H), 1.91 (s, 3H), 3.81-3.88 (m, 1H), 4.85 (d, J = 11.2 Hz, 1H), 7.12-7.29 (m, 4H), 7.47-7.59 (m, 3H), 8.05-8.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 27.7, 39.8, 70.9, 128.4, 128.6, 128.7, 128.9, 132.4, 133.7, 136.9, 141.8, 194.8, 202.9; HRMS calcd for $C_{18}H_{17}ClNaO_2^+$ ($M+Na^+$): 323.0809, found: 323.0444 .



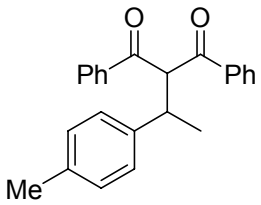
2-Benzhydryl-1-phenylbutane-1,3-dione (3m), CAS Registry Number: [33925-42-7]

Mp: 150-152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 3H), 5.10 (d, J = 12.0 Hz, 1H), 5.61 (d, J = 12.0 Hz, 1H), 7.02-7.11 (m, 3H), 7.13-7.18 (m, 3H), 7.28-7.37 (m, 6H), 7.44-7.56 (m, 1H), 7.93-7.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.7, 51.4, 68.8, 126.6, 127.1, 127.6, 128.1, 128.6, 128.7, 128.9, 133.6, 136.9, 141.2, 141.6, 194.2, 202.9; HRMS calcd for $C_{23}H_{20}NaO_2^+$ ($M+Na^+$): 351.1361, found: 351.1334.



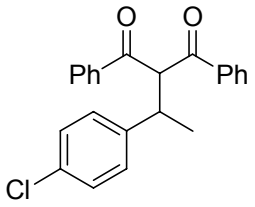
1,3-Diphenyl-2-(1-phenylethyl)propane-1,3-dione (3n), CAS Registry Number: [116140-58-0]

Mp: 128-129 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (d, J = 7.0 Hz, 3H), 4.06-4.11 (m, 1H), 5.65 (d, J = 10.0 Hz, 1H), 7.04-7.06 (m, 1H), 7.15-7.17 (m, 2H), 7.24-7.28 (m, 4H), 7.40-7.42 (m, 3H), 7.52-7.55 (m, 1H), 7.73-7.75 (m, 2H), 8.03-8.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 41.1, 64.6, 126.5, 127.6, 128.3, 128.4, 128.7, 128.8, 133.0, 133.5, 136.8, 137.1, 143.7, 194.5, 194.9; MS (ESI) *m/z* (%) 351.16 ($M+Na^+$, 100), 329.46, 289.37, 225.14, 162.99.



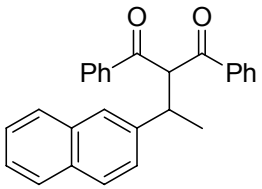
1.3-Diphenyl-2-(1-*p*-tolylethyl)propane-1,3-dione (3o), CAS Registry Number:[945548-16-3].

Mp: 103-105 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (d, J = 6.8 Hz, 3H), 2.22 (s, 3H), 4.01-4.08 (m, 1H), 5.57 (d, J = 10.4 Hz, 1H), 6.98-7.00 (m, 2H), 7.14-7.16 (m, 2H), 7.27-7.31 (m, 2H), 7.40-7.58 (m, 4H), 7.74-7.76 (m, 2H), 8.03-8.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 20.9, 40.8, 65.1, 127.6, 128.4, 128.6, 128.8, 128.9, 129.1, 133.0, 133.5, 136.1, 137.0, 137.2, 140.9, 194.6, 195.1; HRMS calcd for $C_{24}H_{21}O_2$ $(M-H)^-$: 341.1547, found: 341.1533.



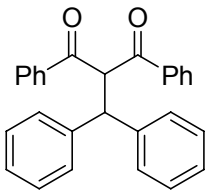
2-(1-(4-Chlorophenyl)ethyl)-1,3-diphenylpropane-1,3-dione (3p), CAS Registry Number: [727401-27-6]

Mp: 101-103 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (d, J = 7.0 Hz, 3H), 4.04-4.12 (m, 1H), 5.63 (d, J = 10.2 Hz, 1H), 7.11-7.13 (m, 2H), 7.20-7.29 (m, 4H), 7.39-7.42 (m, 3H), 7.53-7.56 (m, 1H), 7.76-7.78 (m, 2H), 8.04-8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 40.5, 64.4, 128.3, 128.4, 128.6, 128.8, 129.0, 132.1, 133.1, 133.6, 136.6, 136.9, 142.3, 194.3, 194.6; HRMS calcd for $C_{23}H_{19}ClNaO_2^+$ ($M+Na^+$): 385.0966, found: 385.1063.



2-(1-(Naphthalen-3-yl)ethyl)-1,3-diphenylpropane-1,3-dione (3q), CAS Registry Number: [1129424-70-9]

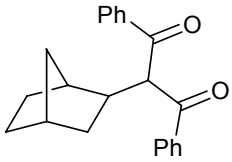
Mp: 130-132 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ1.41 (d, J = 7.2 Hz, 3H), 4.22-4.30 (m, 1H), 5.72 (d, J = 10.0 Hz, 1H), 7.20-7.24 (m, 2H), 7.25-7.55(m, 6H), 7.56-7.58 (m, 1H), 7.67-7.75 (m, 6H), 8.07-8.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 41.2, 64.9, 125.4, 125.9, 126.4, 127.4, 127.7, 128.1, 128.4, 128.9, 123.2, 133.3, 133.6, 136.7, 137.1, 141.3, 194.5, 195.0; HRMS calcd for $C_{27}H_{22}NaO_2^+$ ($M+Na^+$): 401.1512, found: 401.1788.



1,3-Diphenyl-2-(diphenylmethyl)propane-1,3-dione (3r), CAS Registry Number: [60999-93-1]

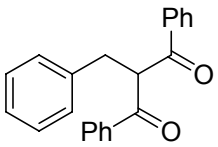
Mp: 227-229 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (d, J = 11.6 Hz, 1H), 6.35 (d, J = 11.6 Hz, 1H), 7.04-7.06 (m, 2H), 7.12-7.16 (m, 4H), 7.24-7.26 (m, 4H), 7.30-7.34 (m, 4H), 7.44-7.46 (m, 2H), 7.82-7.84

(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.4, 62.4, 126.6, 128.3, 128.4, 128.5, 128.6, 133.2, 137.0, 141.7, 194.0; HRMS calcd for $C_{28}H_{22}NaO_2^+$ ($M+Na^+$): 413.1512, found: 413.1609.



2-(Bicyclo[2.2.1]heptan-2-yl) -1,3-Diphenylpropane -1,3-dione (3s), CAS Registry Number: [727401-29-8].

Mp: 110-112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11-1.20 (m, 3H), 1.24-1.27 (m, 1H), 1.44-1.52 (m, 3H), 1.59-1.62 (m, 1H), 1.95 (s, 1H), 2.21 (s, 1H), 2.72-2.75 (m, 1H), 5.09 (d, J = 11.1 Hz, 1H), 7.33-7.37 (m, 2H), 7.42-7.47 (m, 3H), 7.51-7.54 (m, 1H), 7.95 (d, J = 7.6 Hz, 2H), 8.06 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 29.9, 35.8, 36.5, 37.1, 39.4, 43.5, 63.9, 128.5, 128.7, 133.1, 133.3, 136.9, 137.0, 195.0, 195.7; HRMS calcd for $C_{22}H_{22}NaO_2^+$ ($M+Na^+$): 341.1512, found: 341.1612. calcd for $C_{22}H_{23}O_2^+$ ($M+H^+$): 319.1693, found: 319.1792.



2-Benzyl-1,3-diphenylpropane-1,3-dione (3t), CAS Registry Number:[28918-09-4].

Mp: 82-85 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.45 (d, J = 6.4 Hz, 2H), 5.51 (t, J = 6.8 Hz, 1H), 7.22-7.26 (m, 5H), 7.38-7.42 (m, 4H), 7.51-7.55 (m, 2H), 7.88-7.90 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.3, 59.1, 126.6, 128.6, 128.7, 128.8, 129.0, 133.5, 136.0, 139.1, 195.4; HRMS calcd for $C_{22}H_{18}KO_2$ $(M+K)^+$: 353.0938, found: 353.0928.

3. Crystal data and structure refinement of complex 3a.

Crystallographic structure analysis of 3-(1-phenylethyl)pentane-2,4-dione (3a): Oily 3-(1-phenylethyl)pentane-2,4-dione (**3a**) was placed in a sealed flask for several weeks and the compound sublimated from the bottom to upper part of the flask to form colorless single crystals. A suitable crystal with dimensions of 0.32 x 0.22 x 0.12 mm^3 was mounted on a Bruker CCD area detector diffractometer

using Mo Kα radiation (λ = 0.71073Å) from a generator operating at 50kV, 30mA condition. The intensity data were collected with SMART program and corrected by SAINT (Ver. 6.45, 2003) and SADABS (Bruker) program. The structure was solved by direct methods, expended by difference Fourier syntheses and refined by full-matrix least squares on F^2 using Bruker SHELXT1 program packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in ideal positions and refined as riding atoms. The final cycle of the full-matrix least-squares refinement based on 2715 observed reflections (I>2sigma(I)) and 139 parameters converged to the R and R_w values of 0.0734 and 0.2234 for 3-(1-phenylethyl)pentane-2,4-dione. CCDC 651081 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

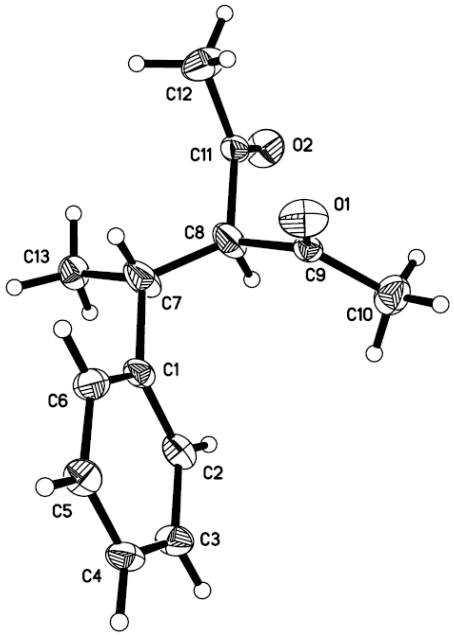


Figure 1. ORTEP diagram of compound **3a**.

Table 1. Crystal data and structure refinement for compound **3a**.

Identification code	**3a**	
Empirical formula	$C_{13}H_{16}O_2$	
Formula weight	204.26	
Temperature	294(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.286(3) Å	α= 90°.
	b = 5.6083(12) Å	β= 95.142(4)°.
	c = 15.808(3) Å	γ = 90°.
Volume	1173.2(4) $Å^3$	
Z	4	

Density (calculated)	1.156 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	440
Crystal size	0.32 x 0.22 x 0.12 mm^3
Theta range for data collection	1.92 to 27.58°.
Index ranges	-17<=h<=17, -7<=k<=7, -20<=l<=20
Reflections collected	10563
Independent reflections	2715 [R(int) = 0.0982]
Completeness to theta = 27.58°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.610
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2715 / 0 / 139
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0734, wR2 = 0.2234
R indices (all data)	R1 = 0.1829, wR2 = 0.2822
Largest diff. peak and hole	0.435 and -0.373 $e.Å^{-3}$