Supporting Information

Base-free two-step synthesis of 1,3-diketones and β-ketoesters from α-diazocarbonyl compounds, trialkylboranes, and aromatic aldehydes

Miguel A. Sanchez-Carmona, David A. Contreras-Cruz and Luis D. Miranda

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán México D. F. 04510, México.

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Experimental Methods

General. All reagents and solvents were obtained from Aldrich and Fluka. Tetrahydrofuran was freshly distilled from sodium/benzophenone, Melting points were determined on a Fisher apparatus and are uncorrected. All reactions were performed under a dry Ar atmosphere unless otherwise specified. Reaction progress was monitored by analytical thinlayer chromatography using GF silica plates purchased from Merck. Visualization was achieved by short-wave UV light (254 nm). $^1$H and $^{13}$C NMR spectra were recorded on both a Varian Gemini-200 and JEOL Eclipse-300 model spectrometers using CDCl$_3$ as solvent. Chemical shifts are reported as parts per million downfield from an internal tetramethylsilane standard ($\delta = 0.0$ for $^1$H) or from solvent references. NMR coupling constants are reported in hertz (Hz). IR spectra were obtained with a Nicolet Magna 750 FT-IR spectrometer. Low- and high-resolution electron impact mass spectra were obtained on JEOL JMS-AX505HA spectrometer.

General procedure for the synthesis of aldols. (5a-k) To a stirred solution of aldehyde (1 eq), and trialkylborane or triphenylborane 1 M (3 eq.), in THF under argon, a solution of diazoketone(1 eq.) in THF was added dropwise. Then, the reaction mixture was stirred at room temperature until disappearance of diketone as evident by TLC analysis (~1h). The solvent was removed under reduced pressure and the crude oil obtained was purified by flash chromatography eluting with a hexane/ethyl acetate (9:1) solvent system.

General procedure for the oxidation of aldols to 1,3 diketones. To a stirred solution of the corresponding aldol 5a-f (1 eq) in CH$_2$Cl$_2$ (20 ml) and 1g of molecular sieves 4 Å, PCC (5 eq.) was added at 0 °C. The reaction mixture was stirred for 4 h, and then diluted with Et$_2$O and pass through a short celite plug. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography eluting with a hexane/ethyl acetate (9:1) solvent system.

2-Ethyl-1,3-Bisphenylpropane-1,3-dione (6a). 2-Diazo-1-phenyletanone 1a (0.15g, 1 mmol) was reacted with triethylborane 1M in THF 2a (3 mmol) and benzaldehyde 4a (0.11 g, 1 mmol) according to the general procedure to provide 5a (0.1 g, 41%). Then, 5a was oxidized with PCC to afford 6a as a white solid (0.06 g, 58%) Mp: 81-85 °C.
Spectral data were identical with those reported previously: \(^1\) \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 1.05\) (t, 3H, \(J = 7.4\)), 2.17 (q, 2H, \(J = 7.4\)), 5.12 (t, 1H, \(J = 6.5\)) 7.42-7.58 (m, 6H), 7.94-7.98 (m, 4H); \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta = 12.8, 22.9, 58.7, 128.5, 128.8, 133.4, 136.1, 196.1\).

2-Ethyl-1(4-methylphenyl), 3-Phenyl-propane-1,3-dione (6b). 2-Diazo-1-(4-methylphenyl)-etanone 1b (0.1 g, 0.625 mmol) was reacted with triethylborane 1M in THF 2a (1.9 mmol) and benzaldehyde 4a (0.07 g, 0.625 mmol) according to the general procedure to afford 5b (0.095 g, 56%). Then, 5b was oxidized with PCC to afford 6b as a white oil (73%). \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 1.04\) (t, 3H, \(J = 7.4\)), 2.15 (q, 2H, \(J = 7.1\)), 2.39 (s, 3H), 5.08 (t, 1H, \(J = 7.1\)), 7.25-7.23 (d, 2H, \(J = 8\)), 7.45-7.41 (t, 2H, \(J = 7.4, 7.1\)), 7.56-7.52 (t, 1H, \(J = 7.1\)), 7.88-7.86 (d, 2H, \(J = 8\)), 7.96-7.94 (d, 2H, \(J = 7.4\)); \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta = 12.8, 21.6, 22.9, 58.7, 128.5, 128.7, 128.8, 129.5, 133.3, 133.7, 136.3, 144.4, 195.8, 196.2\); IR (film) 3370, 3060, 2969, 2931, 2876, 1694, 1668, 1604, 449 cm\(^{-1}\); HRMS (EI, M+) calcd for C\(_{18}\)H\(_{18}\)O\(_2\) 267.1385, found 267.1382.

2-Ethyl-1,3-bis(4-methylphenyl)propane-1,3-dione (6c). 2-Diazo-1-(4-methylphenyl)-etanone 1b (0.1 g, 0.625 mmol) was reacted with triethylborane 1M in THF 2a (1.87 mmol) and tolualdehyde 4b (0.075 g, 0.625 mmol) according to the general procedure to afford 5c (0.17 g, 96%). Then, 5c was oxidized with PCC to obtain 6c as a white solid (0.1 g, 60%) Mp: 75-78°C. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 1.03\) (t, 3H, \(J = 7.4\)), 2.15 (quint, 2H, \(J = 7.11\)), 2.38 (s, 6H), 5.0 (t, 1H, \(J = 7.3\)), 7.24-7.21 (d, 4H, \(J = 8\)), 7.88-7.85 (d, 4H, \(J = 8\)); \(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta = 12.8, 21.6, 22.9, 58.3, 128.7, 129.5, 133.8, 144.2, 195.9\); IR (KBr) 2971, 2930, 2859, 1689, 1661, 1604, 1449 cm\(^{-1}\); HRMS (EI, M+) calcd for C\(_{19}\)H\(_{20}\)O\(_2\) 281.1542, found 281.1537.

2-Ethyl-1,3-bis(4-methoxyphenyl)propane-1,3-dione (6d). 2-Diazo-1-(4-methoxyphenyl)-etanone 1c (0.1 g, 0.57 mmol) was reacted with tri-\(\alpha\)-triethylborane 1M in THF 2a (1.71 mmol) and anisaldehyde 4c (0.077 g, 0.57 mmol) according to the general procedure to provide 5d (0.18 g, 98%). Then, 5d was oxidized with PCC to obtain 6d like pale yellow oil (0.1 g, 98%). Spectral data were identical with those reported before: \(^1\)H NMR (CDCl\(_3\), 300MHz) \(\delta = 1.03\) (t, 3H, \(J = 7.4\)), 2.15 (q, 2H, \(J = 7.1\)), 3.84

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(s, 6H), 4.94 (t, 1H, J = 6.6), 6.87 (2H, J = 8.8, 2.1), 7.94 (2H, J = 8.5, 2.3); $^{13}$C NMR (CDCl$_3$ 75 MHz) δ = 12.8, 23.1, 55.5, 59.2, 113.9, 129.4, 130.9, 163.7, 194.9.

**2-Propyl-1,3-bis(4-methoxyphenyl)propane-1,3-dione (6e).** 2-Diazo-1-(4-methoxyphenyl)-etanone 1c (0.2 g, 1.136 mmol) was reacted with tri-n-propylborane 1M in THF 2b (3 mmol) and anisaldehyde 4c (0.154 g, 1.136 mmol) according to the general procedure to provide 5e (0.28 g, 75%). Then 5e was oxidized with PCC to obtain 6e as white oil (63%). Spectral data were identical with those reported before: $^1$H NMR (CDCl$_3$, 300 MHz) δ = 0.95 (t, 3H, J = 7.4), 1.36-1.47 (m, 2H), 2.06-2.11 (m, 2H), 3.84 (s, 6H), 5.05 (t, 1H, J = 6.7), 6.90 (2H, J = 9.0, 2.5), 7.95 (2H, J = 9.0, 2.5); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ = 14.1, 21.5, 31.7, 55.4, 57.3, 113.9, 129.2, 130.9, 163.6, 194.8.

**2-Phenyl-1,3-bis(4-methylphenyl)propane-1,3-dione (6f).** 2-Diazo-1-(4-methylphenyl)-etanone 1b (0.1 g, 0.645 mmol) was reacted with triphenylborane 1M in THF 2c (3 mmol) and tolualdehyde 4b (0.078 g, 0.645 mmol) according to the general procedure to provide 5f (0.153 g, 72%). Then, 5f was oxidized with PCC to afford 6f as a yellow solid (65%) Mp: 115-125 °C. $^1$H NMR (CDCl$_3$, 300 MHz) δ = 2.37 (s, 6H), 6.51 (s, 1H), 7.23 - 7.20 (d, 2H, J = 7.3, 0.3), 7.34-7.25 (m, 3H), 7.37-7.36 (d, 4H, J = 7.1), 7.88 – 7.85 (d, 4H, J = 8); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ = 21.6, 62.6, 127.8, 128.2, 128.8, 128.9, 129.4, 129.9, 133.4, 144.3, 193.5. IR (Sol CHCl$_3$) 3031, 2927, 2855, 1697, 1672, 1606, 1454 cm$^{-1}$. HRMS (EI, M+) calcd for C$_{23}$H$_{20}$O$_2$ 328.1463, found 328.1458.

**Ethyl-2-Benzoyl-butanoate (6g)**
Compound 6g was report by Li$^2$: Ethyl diazoacetate (0.1 g, 0.88 mmol) was reacted with triethylborane 1M in THF 2a (2.6 mmol) and benzaldehyde 4a (0.09 g, 0.88 mmol) according to the general procedure. The resulting dark yellow residue was purified by flash column chromatography to provide 5g (0.1 g, 51 %), then it was oxidized with PCC to obtain 6g as a yellow oil (0.035 g, 35%). $^1$H NMR (CDCl$_3$, 300 MHz) δ = 1.0 (t, 3H, J = 7.2 Hz), 1.17 (t, 3H, J = 7.2 Hz), 1.99-2.09 (m, 2H), 4.16 (q, 2H, J = 7.2 Hz),

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4.21 (t, 1H, J = 7.2 Hz), 7.44 - 7.61 (m, 3H), 7.97-8.01 (m, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ = 12.2, 14.0, 22.4, 55.9, 61.3, 128.6, 128.7, 133.4, 136.4, 170.0, 195.3.

**Ethyl-2-(4-methyl-Benzoyl)-butanoate (6h)**
Ethyl diazooacetate (0.1 g, 0.88 mmol) was reacted with triethylborane 1M in THF 2a (2.6 mmol) and p-tolualdehyde 4b (0.1 g, 0.88 mmol) according to the general procedure. The resulting dark yellow residue was purified by flash column chromatography to provide 5h (0.15 g, 75 %), then it was oxidized with PCC to obtain 6h as a clear oil (0.046 g, 30%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 0.99 (t, 3H, J = 7.5 Hz), 1.17 (t, 3H, J = 7.2 Hz), 1.98-2.08 (m, 2H), 2.41 (s, 3H), 4.11-4.20 (m, 2H), 4.18 (t, 1H, J = 7.2 Hz), 7.25-7.28 (dd, 2H, J = 8.1 Hz), 7.87 - 7.90 (dd, 2H, J = 8.1 Hz) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ = 12.1, 14.0, 21.6, 22.4, 55.7, 61.2, 128.7, 129.4, 133.9, 144.3, 170.1, 194.8; IR (film) 1738, 1683 cm$^{-1}$; HRMS (EI, M+) calcd for C$_{14}$H$_{18}$O$_3$ 235.1334, found 235.1335.

**Ethyl-2-(4-methoxy-Benzoyl)-butanoate (6i)**
Ethyl diazooacetate (0.1 g, 0.88 mmol) was reacted with triethylborane 1M in THF 2a (2.6 mmol) and p-anisaldehyde 4c (0.12 g, 0.88 mmol) according to the general procedure. The resulting dark yellow residue was purified by flash column chromatography to provide 5i (0.16 g, 74 %), then it was oxidized with PCC to obtain 6i as a clear oil (0.057 g, 35%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 0.98 (t, 3H, J = 7.5 Hz), 1.18 (t, 3H, J = 7.2 Hz), 1.95-2.10 (m, 2H), 3.87 (s, 3H), 4.14 (q, 2H, J = 7.2 Hz), 4.16 (t, 1H, J = 7.2 Hz), 6.92-6.99 (dd, 2H, J = 9 Hz), 7.95 - 8.0 (dd, 2H, J = 9 Hz) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ = 12.1, 14.0, 22.4, 55.5, 55.6, 61.2, 113.8, 129.4, 130.9, 163.8, 170.2, 193.6; IR (film) 1737, 1678 cm$^{-1}$; HRMS (EI, M+) calcd for C$_{14}$H$_{18}$O$_4$ 251.128, found 251.1283.

**Ethyl-2-phenyl-3-oxo-2-phenylpropanoate (6j)**
Compound d was report by Ibata$^3$, ethyl diazooacetate (0.1 g, 0.88 mmol) was reacted with triphenylborane 1M in THF 2c (2.6 mmol) and benzaldehyde 4a (0.09 g, 0.88 mmol) according to the general procedure. The resulting dark yellow residue was purified by flash column chromatography to provide 5j (0.09 g, 38%), then it was oxidized with PCC to obtain 6j as a clear oil (0.036 g, 40%). $^1$H NMR (CDCl$_3$, 300

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MHz) $\delta = 1.24$ (t, 3H, $J = 7.2$ Hz), 4.22 (q, 2H, $J = 7.2$ Hz), 5.59 (s, 1H), 7.53-7.31 (m, 8H), 8.11-7.94 (m, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta = 14.0, 60.6, 61.7, 128.1, 128.7, 128.8, 129.6, 130.2, 133.4, 134.8, 168.7, 193.2.$

**Ethyl-2-(4-methylphenyl)-3-oxo-2-phenylpropanoate (6k)**

Ethyl diazoacetate (0.1 g, 0.88 mmol) was reacted with triphenylborane 1M in THF 2c (2.6 mmol) and p-tolualdehyde 4b (0.1 g, 0.88 mmol) according to the general procedure. The resulting dark yellow residue was purified by flash column chromatography to provide 5k (0.1 g, 40%), then it was oxidized with PCC to obtain 6k as a clear oil (0.041 g, 41%). $^1$H NMR (CDCl$_3$, 300 MHz) $\delta = 1.25$ (t, 3H, $J = 7.2$ Hz), 2.38 (s, 3H$_2$), 4.23 (q, 2H, $J = 7.2$ Hz), 5.60 (s, 1H), 7.21-7.24 (dd, 2H, $J = 8.1$ Hz), 7.27-7.44 (m, 5H), 7.30-7.44 (m, 5H), 7.86-7.89 (dd, 2H, $J = 8.4$ Hz) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta = 14.0, 21.6, 60.4, 61.6, 127.9, 128.7, 129.0, 129.3, 129.5, 130.0, 133.1, 144.4, 168.8, 192.8;$ IR (film) 1745, 1679 cm$^{-1}$; HRMS (EI, M$^+$) calcd for C$_{18}$H$_{18}$O$_3$ 283.1335, found 283.1334.

**General procedure for pyrazole synthesis.** **Methode A:** To a stirred solution of 1,3 diketone (1 eq) in 5 ml of MeCN was added the corresponding hidrazine (1.4 eq.) and CAN (3 mol%). The mixture was heated under reflux for 3 h. Then the reaction mixture was allowed to cool to room temperature and concentrated under reduced pressure, the residue was dissolved with CH$_2$Cl$_2$ and washed with water. The organic phase was removed dried over Na$_2$SO$_4$. The product was purified by a silica gel flash chromatography using EtOAc/hexanes as eluting solvent system. **Method B:** To a stirred solution of 1,3 diketone (1 eq) in 40 ml of a DMF/THF system (3:1), p-methoxyphenylhydrazine hydrochloride (3-5 eq.), was added. The mixture was brought to reflux and the reaction progress was monitored by TLC analysis (10-20 h). Then the reaction mixture was allowed to cool to room temperature and diluted with H2O (30 mL). The product was repeatedly extracted with EtOAc (3 x 25 mL) and the combined organic layers was sequentially washed with a saturated LiCl solution (25 mL), saturated NaHSO3 (25 mL), and brine (25 mL). The organic layer was dried over Na$_2$SO4 and concentrated under reduced pressure to afford a crude oil, which was purified by flash chromatography using EtOAc/hexanes as eluting solvent system.
4-Ethyl-1-(4-methoxyphenyl)-3-phenyl-5-(4-methylphenyl)-pyrazole (8a). Diketone 6b (0.1 g, 0.37 mmol) was reacted with p-methoxy phenyleyldrazine chlorohydrate 7b (0.19 g, 1.11 mmol) according to the general procedure (Method A) to provide the title product 8a as a yellow oil (0.081 g, 60%); \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta = 1.03\) (t, 3H, \(J= 1.9\) Hz), 2.37(s, 3H), 2.65 (q, 2H, \(J= 1.9\) Hz), 3.77 (s, 3H), 6.78 (dd, 2H), 7.97-7.1 (m, 9H), 7.67-7.80 (dd, 2H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta = 15.45, 17.06, 21.32, 55.41, 113.88, 120.39, 127.46, 128.01, 128.52, 129.25, 129.91, 130.07, 137.79, 138.3, 141.85, 149.88, 150.75, 158.55; IR (Sol CHCl\(_3\)) 2966, 2932, 2870, 1607, 1514, 1460 cm\(^{-1}\); MS (EI, 70 eV) 368 \(m/z\) (M+).

4-Ethyl-1-(4-methoxyphenyl)-3,5-bisphenyl-pyrazole (8b). Diketone 6a (0.038 g, 0.15 mmol) was reacted with p-methoxy phenyleyldrazine chlorohydrate 7b (0.13 g, 0.75 mmol) according to the general procedure to provide the title product 8b as a yellow oil (0.052 g, 98%). Spectral data were identical with those reported previously: \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 1.04\) (t, 3H, \(J= 7.5\)), 2.65 (q, 2H, \(J= 7.5\)), 3.77 (s, 1H), 6.77 (, 2H, \(J = 1.0, 2.2\)), 7.19 (, 2H, \(J= 9.1, 2.2\)), 7.23-7.48 (m, 9H), 7.78 (, 2H, \(J= 8.2, 2.5\)); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta = 15.6, 17.1, 55.4, 113.8, 120.4, 126.1, 127.5, 127.9, 128.1, 128.41, 128.45, 130.1, 130.9, 133.4, 134.2, 141.2, 150.4, 158.2.

4-Ethyl-1-phenyl-3,5-bis(4-methylphenyl)-pyrazole (8c). Diketone 6c (0.05 g, 0.178 mmol) was reacted with phenyleyldrazine 7a (0.036 g, 0.25 mmol) according to the general procedure to provide the title product 8c as a yellow solid (0.034 g, 54%). Mp: 107-110°C; \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 1.03\) (t, 3H, \(J= 7.5\)), 2.37(s, 3H), 2.4(s, 3H), 2.64 (q, 2H, \(J= 7.5\)), 7.11-7.31(m, 11H), 7.66-7.69(d, 2H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta = 15.5, 17.1, 21.3, 21.34, 120.7, 124.7, 126.6, 127.8, 127.9, 128.5, 129.1, 129.2, 129.9, 131.0, 137.3, 138.1, 140.0, 141.3, 150.7; IR (Sol CHCl\(_3\)) 3022, 2966, 2928, 1598, 1502, 1452 cm\(^{-1}\); HRMS (EI, M+) calcd for C\(_{25}\)H\(_{24}\)N\(_2\) 353.2018, found 353.2016.

4-Ethyl-3,5-bis(4-methoxyphenyl)-1-phenyl-pyrazole (8d). Diketone 6d (0.05 g, 0.16 mmol) was reacted with phenyleyldrazine 7a (0.032 g, 0.22 mmol) according to the general procedure to provide the title product 8d as a pale yellow solid (0.03 g, 49%). Spectral data were identical with those reported previously: \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta = 1.04\) (t, 3H, \(J = 7.6\)), 2.63 (q, 2H, \(J = 7.6\)), 3.82 (s, 3H), 3.85 (s, 3H), 6.90 (, 2H, \(J = 8.8, 2.4\)), 6.99 (, 2H, \(J = 8.8, 2.6\)), 7.17 (, 2H, \(J = 8.8, 2.4\)), 7.20 (m,
2H), 7.24 (m, 3H), 7.72 (2H, J 9.0, 2.4); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ = 15.5, 17.1, 55.2, 55.3, 114.1, 114.2, 120.7, 123.5, 124.8, 126.8, 127.0, 128.8, 129.2, 131.3, 140.3, 141.1, 150.5, 159.3, 159.5.

4-n-Propyl-1-(4-methoxyphenyl)-3,5-bis(4-methoxyphenyl)-pyrazole (8e). Diketone 6e (0.1 g, 0.35 mmol) and $p$-methoxy phenylhydrazine hydrochloride 7b (140 mg, 0.96 mmol) according to the general pyrazole procedure to afford 8e as a red oil (0.109 g, 74%);

$^1$H-NMR (CDCl$_3$) $\delta$ = 8.31 (d, 1H, $J$ = 2.0 Hz), 8.01 (dd, 1H, $J$ = 2.0, 8.1 Hz), 7.68 (d, 1H, $J$ = 8.1 Hz), 7.21 (d, 2H, $J$ = 7.1 Hz), 7.16 (d, 2H, $J$ = 8.5 Hz), 6.93 (d, 2H, $J$ = 7.1 Hz), 6.83 (d, 2H, $J$ = 8.5 Hz), 4.04 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 2.60 (t, 2H, $J$ = 7.7 Hz), 1.45 (m, 2H), 0.84 (t, 3H, $J$ = 7.2 Hz);

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 159.6, 159.4, 150.8, 141.2, 140.5, 131.5, 129.3, 128.8, 127.0, 126.7, 124.8, 123.5, 120.7, 114.2, 114.1, 55.5, 55.4, 17.3, 15.8.

4-Phenyl-1-phenyl-3,5-bis(4-methylphenyl)-pyrazole (8f). Diketone 6f (0.024 g, 0.072 mmol) was reacted with phenylhydrazine 7a (0.011 g, 0.1 mmol) according to the general procedure to provide the title product 8f as a yellow oil (0.025 g, 90%);

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 2.28 (s, 3H), 2.32 (s, 3H), 6.91-7.0 (dd, 4H), 7.06-7.12 (m, 5H), 7.19-7.34 (m, 5H), 7.38-7.41 (d, 4H, $J$ = 2.7 Hz);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ = 21.25, 21.28, 55.45, 113.93, 126.51, 126.54, 126.51, 126.08, 128.12, 128.24, 128.7, 128.88, 128.96, 130.21, 130.72, 133.33, 137.3, 137.91, 139.99, 141.4, 150.13; IR (Sol CHCl$_3$) 3057, 3024, 2922, 2856, 1596, 1496, 1433 cm$^{-1}$. HRMS (EI, M+) calcd for C$_{29}$H$_{24}$N$_2$O$_2$ 431.2018, found 431.2019.

4-Phenyl-1-(4-methoxyphenyl)-3,5-bis(4-methylphenyl)-pyrazole (8g). Diketone 6f (0.04 g, 0.12 mmol) was reacted with $p$-methoxy phenylhydrazine hydrochloride 7b (0.029 g, 0.17 mmol) according to the general procedure to provide the title product 8g as a yellow oil (0.03 g, 64%);

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ = 2.28(s, 3H), 2.32(s, 3H), 3.79 (s, 3H), 6.81-6.84(d, 2H, $J$ = 9), 6.9-6.93(d, 2H, $J$ = 9), 6.97-7.0 (d, 2H, $J$ = 8.1), 7.06-7.12 (m, 5H), 7.14-7.26 (m, 5H), 7.36-7.41 (d, 2H), 7.85-7.88 (d, 2H, $J$ = 8.1);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ = 21.25, 21.28, 55.45, 113.93, 126.51, 126.8, 128.13, 128.29, 128.89, 128.94, 129.52, 129.93, 130.24, 130.74, 133.23, 133.47, 137.25, 137.82, 141.48, 144.34, 149.7, 158.62, 193.61; IR (Sol CHCl$_3$) 3042, 3014, 2922, 2856, 1596, 1496, 1433 cm$^{-1}$. HRMS (EI, M+) calcd for C$_{30}$H$_{126}$N$_2$O$_2$ 431.2123, found 431.2109.
1,3,5-Tris(4-hydroxyphenyl)-4-propyl-pyrazole (9).
To a stirred solution of 8e (0.2 g, 0.48 mmol) in CH₂Cl₂ at -78 °C a 1 M BBr₃ solution in CH₂Cl₂ (3-5 equiv), was added dropwise. Upon complete addition of BBr₃, the reaction was maintained at -78 °C for 1 h and then allowed to reach room temperature and stir for an additional 16 h. The mixture was cooled to 0 °C and carefully quenched with H₂O (15-25 mL). The product was then repeatedly extracted with EtOAc and the organic layers dried over Na₂SO₄. Upon solvent removal the crude phenolic products were purified by flash chromatography and/or recrystallization from MeOH/CH₂Cl₂ mixtures to afford the title compound 9 (0.125 g, 68%): mp 229-231 °C (ref. m.p. 230 °C); Spectral data were identical with those reported previously:¹ ¹H NMR (MeOD-d₄, 400 MHz) δ = 0.76 (t, 3H, J= 7.2), 1.33 (sext, 2H, J= 7.6), 2.54 (t, 2H, J = 8), 6.70 (d, 2H, J = 8.8, 2.4), 6.76 (d, 2H, J = 6.8, 2.0), 6.87 (2, 2H, J = 8.8, 2.4), 7.02 (2, 2H, J = 8.8, 2.4), 7.05 (d, 2H, J = 9.2, 2.4), 7.47 (d, 2H, J = 8.8, 2.0); ¹³C NMR (MeOD-d₄, 100 MHz) δ = 25.8, 36.4, 38.4, 127.0, 128.0, 128.5, 130.5, 134.3, 137.9, 138.9, 140.3, 141.3, 142.8, 143.3, 144.1,144.7, 155.3, 163.6, 169.5, 170.3.

4-Ethyl-3-phenyl-5-(4-methylphenyl)-1H-pyrazole (10a). Diketone 6b (0.074 g, 0.28 mmol) was reacted with tosyl hydrazine (0.071 g, 0.38 mmol) according to the general procedure to provide the title product 10a as a yellow solid (0.022 g, 35%). Mp: 86-96°C; ¹H NMR (CDCl₃, 300 MHz) δ = 1.08 (t, 3H, J= 2.5 Hz), 2.4 (s, 6H), 2.75 (q, 2H, J = 7.2 Hz), 7.22-7.26 (t, 2H, J= 2.5 Hz), 7.31-7.48 (m, 5H), 7.58-7.61 (d, 2H, J= 2.5 Hz) ; ¹³C NMR (CDCl₃, 75 MHz) δ = 15.43, 16.76, 21.26, 117.55, 126.37, 127.69, 127.84, 127.97, 128.61, 128.9, 129.38, 129.98, 132.24, 137.93; IR (Sol CHCl₃) 3450, 3229, 3015, 2970, 2931, 1721, 1509, 1463 cm⁻¹, MS (EI, 70 eV) m/z 262 (M+).

4-Ethyl-3,5-bis(4-methylphenyl)-1H-pyrazole (10b). Diketone 6c (0.16 g, 0.57 mmol) was reacted with tosylhydrazine (0.15 g, 0.8 mmol) according to the general procedure to provide the title product 10b as a yellow solid (0.061 g, 39%). Mp: 89-98°C; ¹H NMR (CDCl₃, 400 MHz) δ = 1.08 (t, 3H, J = 7.2Hz), 2.406 (s 6H), 2.75 (q, 2H, J = 7.2 Hz), 7.25 (d, 4H, J = 7.2 Hz), 7.48 (d, 4H, J = 7.5Hz) ; ¹³C NMR (CDCl₃, 100 MHz) δ = 15.48, 16.79, 21.28, 29.69, 127.68, 129.38, 137.85; IR (film) 3188, 3024, 2963, 2925, 2856, 1723, 1509, 1447 cm⁻¹. MS (EI, 70 eV) m/z 276.38 (M+).
2-Ethyl-1,3-Bisphenylpropane-1,3-dione (6a)
2-Ethyl-1(4-methylphenyl), 3-Phenyl-propane-1,3-dione (6b)
2-Ethyl-1,3-bis(4-methylphenyl)propane-1,3-dione (6c)
2-Ethyl-1,3-bis(4-methoxyphenyl)propane-1,3-dione (6d)
2-Propyl-1,3-bis(4-methoxyphenyl)propane-1,3-dione (6e)
2-Phenyl-1,3-bis(4-methylphenyl)propane-1,3-dione (6f)
Ethyl-2-Benzoyl-butanoate (6g)
Ethyl-2-(4-methyl-Benzoyl)-butanoate (6h)
Ethyl-2-(4-methoxy-Benzoyl)-butanoate (6i)
Ethyl-2-phenyl-3-oxo-2-phenylpropanoate (6j)
Ethyl-2-(4-methylphenyl)-3-oxo-2-phenylpropanoate (6k)
4-Ethyl-1-(4-methoxyphenyl)-3-phenyl-5-(4-methylphenyl)-pyrazole (8a)
4-Ethyl-1-(4-methoxyphenyl)-3,5-bisphenyl-pyrazole (8b)
4-Ethyl-1-phenyl-3,5-bis(4-methylphenyl)-pyrazole (8c)
4-Ethyl-3,5-bis(4-methoxyphenyl)-1-phenyl-pyrazole (8d)
4-nPropyl-1-(4-methoxyphenyl)-3,5-bis(4-methoxyphenyl)-pyrazole (8c).
4-Phenyl-1-phenyl-3,5-bis(4-methylphenyl)-pyrazole (8f)
4-Phenyl-1-(4-methoxyphenyl)-3,5-bis(4-methylphenyl)-pyrazole (8g)
1,3,5-Tris(4-hydroxyphenyl)-4-propyl-pyrazole (9).
4-Ethyl-3-phenyl-5-(4-methylphenyl)-1H-pyrazole (10a)
4-Ethyl-3,5-bis(4-methylphenyl)-1H-pyrazole (10b)