Metal-free direct $C$-arylation of 1,3-dicarbonyl compounds and ethyl cyanoacetate: A platform to access diverse array of meta-functionalized phenols

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SUPPORTING INFORMATION

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General information:

Unless otherwise noted, chemicals were purchased from the highest purity grade available and were used without further purification. Thin layer chromatography was performed on Merck pre-coated 0.25 mm silica gel plates (60F-254) using UV light as visualizing agent. Silica gel (100–200 mesh) was used for column chromatography.

NMR spectra were recorded in CDCl₃ and DMSO-d₆ using TMS as an internal standard on JEOL (400 MHz) instrument. Chemical shifts (δ) were reported as parts per million (ppm) in δ scale downfield from TMS. ¹H NMR spectra were referenced to CDCl₃ (7.26 ppm) or DMSO-d₆ (2.50 ppm), and ¹³C NMR spectra were referenced to CDCl₃ (77.0 ppm, the middle peak) or DMSO-d₆ (39.5 ppm, the middle peak). Coupling constants were expressed in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet. Melting points were recorded on Opti Melt Automated Melting Point System and are uncorrected. High-resolution mass spectra (HRMS) were obtained on a Brüker micrOTOF™-Q II mass spectrometer (ESI-MS).

General procedure for α-arylation of 1,3-dicarbonyl compounds:

To a solution of guaiacol derivative (1, 0.3 mmol) in dry MeOH (3 mL) was added solid PhI(OAc)₂ (0.36 mmol) at room temperature and stirred for 5 min. After complete conversion of guaiacol derivative into its MOB 2, MeOH was removed under reduced pressure. The residue was dissolved in toluene (3 mL) and was added Et₃N (0.67 mmol) followed by the addition of 1,3-dieneones 3–9 (0.45 mmol) and reaction mixture kept for stirring at rt. After the completion of the reaction checked by the TLC, the mixture was extracted with DCM (3×10 mL) and then the combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (hexane/ethyl acetate = 3:1) to give the corresponding m-substituted phenols.
General procedure for α-arylation of ethyl cyanoacetate:

To a solution of guaiacol derivative (1, 0.3 mmol) in dry MeOH (3 mL) was added solid PhI(OAc)$_2$ (0.36 mmol) at room temperature and stirred for 5 min. After complete conversion of guaiacol derivative into its MOB 2, MeOH was removed under reduced pressure. The residue was dissolved in acetonitrile (3 mL) and was added Et$_3$N (0.67 mmol) followed by addition of ethyl cyanoacetate (10, 0.45 mmol) and reaction mixture kept for stirring at 80 °C. After the completion of the reaction checked by the TLC, the mixture was extracted with DCM (3×10 mL) and then the combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (hexane/ethyl acetate = 3:1) to afford the corresponding $m$-substituted phenols.

General Mechanism for α-arylation of C-H activated pronucleophiles

The proposed reaction mechanism for α-arylation is depicted below. Intially, 2-methoxyphenol gets dearomatized to the intermediate MOB A which undergoes Michael attack by the base-generated nucleophile to generate species B. The subsequent rearomatization of B releases α-arylated product.
General procedure for the synthesis of pyrazoles and isoxazoles:

To a solution of guaiacol derivative 1 (0.3 mmol) in dry MeOH (3 mL) was added solid PhI(OAc)$_2$ (0.36 mmol) at room temperature and stirred for 5 min. After complete conversion of guaiacol derivative into its MOB 2, MeOH was removed under reduced pressure. The residue was dissolved in Toluene (3 mL) and was added Et$_3$N followed by addition of 1,3-dieneone (0.45 mmol) and reaction mixture kept for stirring at rt. After the completion of the reaction checked by the TLC toluene evaporated under vacuo followed by the dilution with ethanol, hydrazine hydrate (36%) (0.75 mmol)/ hydroxylamine (0.75 mmol for isoxazoles) and molecular iodine (20 mol%) were added sequentially and the mixture were stirred for 2–3 h. The whole was quenched with 1 M HCl, and extracted with DCM (3×10 mL) and then the combined organic extracts were washed with brine (10 mL), dried over anhyd. sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (hexane/ethyl acetate = 3:1) to give the desired pyrazoles 19–22 or isoxazole 23.

General procedure for the synthesis of triazolene derivative 25:

To a solution of ethyl cyanoacetate derivative 18, (0.163 mg, 0.5 mmol) in dry EtOH (5 mL) was added 4 equivalent of conc. HCl dropwise at room temperature and reaction kept for refluxing for 7 h. After complete conversion of nitrile group to ester group EtOH was removed under reduced pressure. The mixture was quenched with saturated solution of bicarbonate and then extracted with DCM (3×15 mL). The obtained diester was directly used for the further conversion by dissolving it in DMF followed by the subsequent addition of semicarbazide.
(1.5 equiv) and morpholine (2 equiv). The reaction kept for refluxing and monitored by TLC. The whole was quenched with 0.1 M HCl, and extracted with DCM (3×10 mL) and then the combined organic extracts were washed with brine (10 mL), dried over anhyd. sodium sulfate. The residue was purified by flash column chromatography (hexane/ethyl acetate = 3:1) to give the desired triazolene 25.

Characterization data

(Z)-3-(2-Bromo-5-hydroxy-4-methoxyphenyl)-4-hydroxypent-3-en-2-one (11a):

Reaction time: 3 h.

Yield: 64 mg (72%) as colourless solid.

Mp: 120–122 ºC.

1H NMR (400 MHz, CDCl3): δ 7.10 (s, 1H), 6.79 (s, 1H), 5.70 (br, OH), 3.92 (s, 3H), 1.85 (s, 6H) ppm.

13C NMR (100 MHz, CDCl3): δ 191.1, 146.8, 145.1, 129.9, 118.0, 115.9, 114.8, 114.4, 56.2, 23.7 ppm.


3-(3-Hydroxy-6-iodo-2-methoxyphenyl)pentane2,4-dione (11c):

Reaction time: 3 h.

Yield: 74 mg (71%) as colourless solid.

Mp: 129–130 ºC.

1H NMR (400 MHz, CDCl3): δ 7.39 (d, J = 8.4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 1H), 5.73 (s, 1H), 3.95 (s, 3H), 2.77 (s, 3H), 2.61 (s, 3H) ppm.

13C NMR (100 MHz, CDCl3): δ 194.2, 162.8, 144.0, 141.5, 130.8, 121.9, 117.6, 111.4, 108.7, 77.2, 57.1, 31.0, 15.4 ppm.


3-(5-Hydroxy-4-methoxy-2-methylphenyl)pentane-2,4-dione (11d):

Reaction time: 50 min.

Yield: 55 mg (78%) as colourless solid.

Mp: 109–110 ºC.

1H NMR (400 MHz, CDCl3): δ 6.74 (s, 1H), 6.66 (s, 1H), 5.49 (s, 1H), 3.90 (s, 3H), 2.09 (s, 3H), 1.82 (s, 6H) ppm.

13C NMR (100 MHz, CDCl3): δ 191.0, 146.0, 143.6, 129.2, 128.5, 117.1, 113.1, 112.4, 90.6, 55.8, 23.7, 23.6, 19.4 ppm.
HRMS (ESI-TOF): m/z [M + Na]+ C_{13}H_{16}O_{5}Na calcd: 259.0940, found: 259.0946.

3-(3-Hydroxy-4,5-dimethoxyphenyl)pentane-2,4-dione (11e):

Reaction time: 4 h.

Yield: 45 mg (60%) as colourless solid.

Mp: 144–145 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 6.42 (s, 1H), 6.26 (s, 1H), 5.87 (s, 1H), 3.93 (s, 3H), 3.84 (s, 3H), 1.92 (s, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.0, 152.4, 149.3, 134.8, 132.8, 115.0, 110.9, 106.9, 61.0, 55.9, 29.6, 23.9 ppm.

HRMS (ESI-TOF): m/z [M + Na]+ C_{13}H_{16}O_{5}Na calcd: 275.0998, found: 275.0988.

3-(2-(5,5-Dimethyl-1,3-dioxan-2-yl)-5-hydroxy-4-methoxyphenyl)pentane-2,4-dione (11f):

Reaction time: 4 h.

Yield: 81 mg (81%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.23 (s, 1H), 6.63 (s, 1H), 5.18 (s, 1H), 3.97 (s, 3H), 3.70–3.52 (m, 1H), 1.85 (s, 6H), 1.29 (s, 3H), 0.75 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.3, 146.5, 146.1, 130.1, 128.0, 116.8, 111.5, 108.5, 99.9, 55.8, 30.1, 24.1, 23.1, 21.7 ppm.

Ethyl 2-(2-bromo-5-hydroxy-4-methoxyphenyl)-3-hydroxybut-2-enoate (12a):

Reaction time: 3 h.

Yield: 70 mg (71%) as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 13.03 (br, enol OH), 7.06 (s, 1H), 6.77 (s, 1H), 5.17 (s, 0.3H keto), 4.25–4.18 (m, 2H), 3.89 (s, 3H), 1.78 (s, 3H), 1.18 (t, $J = 6.8$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 201.2, 174.4, 171.7, 168.2, 146.4, 144.7, 128.6, 126.8, 125.1, 118.1, 115.8, 114.8, 114.5, 103.7, 63.5, 60.5, 56.0, 19.8, 14.3 ppm.

HRMS (ESI-TOF): m/z [M + Na]+ C_{13}H_{16}BrO_{5}Na calcd: 352.9995, found: 352.9994.

Diethyl 2-(2-bromo-5-hydroxy-4-methoxyphenyl)malonate (13a):

Reaction time: 5 h.

Yield: 74 mg (68%) as colourless liquid.
\^1H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.06 (s, 1H), 7.02 (s, 1H), 5.59 (br, 1H), 5.08 (s, 1H), 4.27–4.20 (m, 4H), 3.87 (s, 3H), 1.27 (t, $J = 6.8$ Hz, 6H) ppm.

\^13C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 167.8, 147.0, 145.0, 125.4, 115.9, 114.6, 114.1, 61.9, 56.7, 56.1, 14.0 ppm.

HRMS (ESI-TOF): m/z [M + Na]\textsuperscript{+} C\textsubscript{14}H\textsubscript{17}O\textsubscript{6}BrNa calcd: 383.0100, found: 383.0100.

**Diethyl 2-(2-chloro-5-hydroxy-4-methoxyphenyl)malonate (13b):**

Reaction time: 6 h.

Yield: 61 mg (65%) as colourless liquid.

\^1H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 7.04 (s, 1H), 6.87 (s, 1H), 5.55 (br, 1H), 5.08 (s, 1H), 4.28–4.19 (m, 4H), 3.88 (s, 3H), 1.27 (t, $J = 6.8$ Hz, 6H) ppm.

\^13C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 167.7, 147.0, 145.1, 125.6, 115.9, 114.7, 114.2, 61.9, 56.8, 56.2, 14.0 ppm.

HRMS (ESI-TOF): m/z [M + Na]\textsuperscript{+} C\textsubscript{14}H\textsubscript{17}O\textsubscript{6}ClNa calcd: 339.0605, found: 339.060.

**Diethyl 2-(3-hydroxy-4,5-dimethoxyphenyl)malonate (13e):**

Reaction time: 7 h.

Yield: 57 mg (61%) as colourless liquid.

\^1H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 6.63 (s, 1H), 6.55 (s, 1H), 5.80 (s, 1H), 4.26–4.15 (m, 4H), 3.89 (s, 3H), 3.86 (s, 3H), 1.27 (t, $J = 6.8$ Hz, 6H) ppm.

\^13C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 168.0, 152.2, 149.2, 135.4, 128.5, 109.4, 105.1, 61.8, 60.8, 57.6, 55.8, 13.9 ppm.

HRMS (ESI-TOF): m/z [M + Na]\textsuperscript{+} C\textsubscript{15}H\textsubscript{20}O\textsubscript{7}Na calcd: 335.1101, found: 335.1102.

**Ethyl-3-ethoxy-3-hydroxy-2-(4-hydroxy-5-methoxy-[1,1'-biphenyl]-2-yl)acrylate (13g):**

Reaction time: 6 h.

Yield: 55 mg (52%) as colourless liquid.

\^1H NMR (400 MHz, CDCl\textsubscript{3}): $\delta$ 12.57 (enolic, -OH), 7.95–7.92 (m, 2H), 7.61–7.57 (m, 1H), 7.49–7.45 (m, 2H), 4.26–4.13 (m, 4H), 3.98 (s, 3H), 1.25 (t, $J = 7.6$ Hz, 6H) ppm.

\^13C NMR (100 MHz, CDCl\textsubscript{3}): $\delta$ 192.6, 167.6, 135.9, 133.7, 131.2, 128.7, 128.4, 125.9, 87.3, 61.4, 45.9, 14.0 ppm.
Ethyl 2-(2-bromo-5-hydroxy-4-methoxyphenyl)-3-oxo-3-phenylpropanoate (14a):  

Reaction time: 4 h.  

Yield: 83 mg (80%) colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03–8.01 (m, 2H), 7.54–7.52 (m, 1H), 7.47–7.45 (m, 2H), 6.99 (s, 1H), 6.97 (s, 1H), 5.73 (s, 1H), (4.39 (q, $J = 7.2$ Hz, 2H), 3.97 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 193.7, 168.4, 147.0, 145.2, 133.6, 128.8, 128.7, 125.7, 116.5, 114.8, 113.7, 61.8, 59.3, 56.1, 14.0 ppm.

HRMS (ESI-TOF): m/z [M + Na]$^+$ C$_{18}$H$_{17}$O$_5$Na calcd: 463.0012, found: 463.0012

Ethyl 2-(3-hydroxy-6-iodo-2-methoxyphenyl)-3-oxo-3-phenylpropanoate (14c):

Reaction time: 5 h.  

Yield: 100 mg (76%) as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04–8.01 (m, 2H), 7.53 (d, $J = 8.8$ Hz, 1H), 7.48–7.45 (m, 3H), 6.98 (d, $J = 8.4$ Hz, 1H), 5.73 (s, 1H), 4.39 (q, $J = 7.2$ Hz, 2H), 3.97 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 164.0, 160.8, 144.5, 141.9, 130.9, 130.1, 129.5, 127.9, 122.9, 112.7, 109.1, 76.7, 60.6, 57.2, 29.7, 14.2 ppm.

HRMS (ESI-TOF): m/z [M + Na]$^+$ C$_{18}$H$_{17}$O$_5$INa calcd: 463.0012, found: 463.0012

Ethyl 2-(5-hydroxy-4-methoxy-2-methylphenyl)-3-oxo-3-phenylpropanoate (14d):

Reaction time: 2 h.  

Yield: 78 mg (80%) as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 13.6 (br, 0.35 OH), 7.86–7.84 (m, 2H), 7.53–7.49 (m, 1H), 7.41–7.37 (m, 2H), 6.79 (s, 1H), 6.70 (s, 1H), 5.61 (s, 1H), 5.38 (s, 1H), 4.28–4.19 (m, 2H), 3.85 (s, 3H), 2.34 (s, 3H), 1.27–1.23 (m, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 194.3, 170.5, 169.1, 146.0, 143.8, 135.7, 133.3, 129.6, 128.7, 128.6, 128.5, 127.6, 115.5, 113.0, 76.7, 61.6, 60.9, 57.3, 19.5, 14.1 ppm.

Ethyl 2-(3-hydroxy-4,5-dimethoxyphenyl)-3-oxo-3-phenylpropanoate (14e):

Reaction time: 6 h.  

Yield: 64 mg (62%) as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97–7.95 (m, 2H), 7.57–7.53 (m, 1H), 7.45–7.42 (m, 2H), 6.63 (s, 1H), 6.52 (s, 1H), 5.75 (br, 1H), 5.47 (s, 1H), 4.25–4.19 (m, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 1.25 (t, 3H) ppm.
**13C NMR (100 MHz, CDCl₃):** δ 193.1, 168.8, 152.5, 149.3, 135.7, 135.4, 133.5, 128.9, 128.8, 128.7, 109.6, 105.4, 61.7, 60.2, 55.9, 29.7, 14.1 ppm.

**HRMS (ESI-TOF):** m/z [M]⁺ C₁₉H₂₀O₆ calcd: 344.1254, found: 344.1254.

Ethyl 2-(2-(5,5-dimethyl-1,3-dioxan-2-yl)-5-hydroxy-4-methoxyphenyl)-3-oxo-3-phenylpropanoate (14f):

**Reaction time:** 5 h.

**Yield:** 94 mg (74%)

**1H NMR (400 MHz, CDCl₃):** δ 8.03–8.01 (m, 2H), 7.49–7.45 (m, 1H), 7.38–7.34 (m, 2H), 7.05 (s, 1H), 6.77 (s, 1H), 6.21 (s, 1H), 5.44 (s, 1H), 4.31–4.16 (m, 2H), 3.87 (s, 3H), 3.83–3.63 (m, 4H), 1.33 (s, 3H), 1.25 (t, J = 7.2 Hz, 3H), 0.80 (s, 3H) ppm.

**13C NMR (100 MHz, CDCl₃):** δ 195.0, 169.4, 145.9, 145.7, 135.6, 133.3, 129.2, 128.4, 127.7, 124.9, 116.4, 110.6, 102.5, 78.2, 61.2, 57.0, 55.8, 30.2, 23.6, 22.1, 14.2 ppm.

2-(2-Bromo-5-hydroxy-4-methoxyphenyl) cyclohexane-1,3-dione (15a):

**Reaction time:** 3 h.

**Yield:** 76 mg (82%) as colourless solid.

**Mp:** 178–179 °C.

**1H NMR (400 MHz, CDCl₃):** δ 7.56 (s, 1H), 7.00 (s, 1H), 3.94 (s, 3H), 2.99 (t, J = 6.4 Hz, 2H), 2.57 (t, J = 7.2 Hz, 2H), 2.28–2.21 (m, 2H) ppm.

**13C NMR (100 MHz, CDCl₃):** δ 194.7, 169.7, 148.7, 145.4, 143.8, 116.5, 105.9, 99.9, 94.5, 56.4, 37.8, 23.9, 22.6 ppm.

**HRMS (ESI-TOF):** m/z [M + H]⁺ C₁₃H₁₃O₄Br calcd: 313.0069, found: 313.0054.

2'-Chloro-5',6-dihydroxy-4'-methoxy-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (15b):

**Reaction time:** 2 h.

**Yield:** 64 mg (80%) as colourless solid.

**Mp:** 186–189 °C.

**1H NMR (400 MHz, CDCl₃):** δ 7.38 (s, 1H), 6.88 (s, 1H), 3.79 (s, 3H), 2.86 (t, J = 6.0 Hz, 2H), 2.43 (t, J = 6.4 Hz, 2H), 2.15–2.08 (m, 2H) ppm.

**13C NMR (100 MHz, CDCl₃):** δ 194.6, 169.5, 148.1, 145.8, 143.9, 116.2, 115.7, 105.7, 94.6, 55.9, 37.4, 29.2, 23.4, 22.2 ppm.
HRMS (ESI-TOF): m/z [M + H]+ C_{13}H_{13}O_{4}Cl calcd: 269.0575, found: 269.0575.

2-(5-Hydroxy-4-methoxy-2-methylphenyl)cyclohexane-1,3-dione (15d):

Reaction time: 3 h.

Yield: 63 mg (85%) as colourless solid.


{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: δ 6.79 (s, 1H), 6.62 (s, 1H), 5.69 (br, 1H), 3.88 (s, 3H), 2.57–2.52 (m, 4H), 2.12–2.08 (m, 2H), 2.04 (s, 3H) ppm.

{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})}: δ 146.3, 143.5, 128.9, 123.6, 117.4, 112.8, 77.3, 55.4, 39.6, 20.4, 18.7 ppm.

HRMS (ESI-TOF): m/z [M + Na]+ C_{14}H_{16}O_{5}Na calcd: 287.0867, found: 287.0889.

3',6-Dihydroxy-4',5'-dimethoxyphenyl-4,5-dihydro-[1,1'-biphenyl]-2(3H)-one (15e):

Reaction time: 5 h.

Yield: 55 mg (70%) as colourless solid.

Mp: 117–118 ℃.

{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: δ 6.42 (s, 1H), 6.29 (s, 1H), 3.90 (s, 3H), 3.83 (s, 1H), 2.55 (t, J = 6.0 Hz, 4H), 2.11–2.04 (m, 2H) ppm.

{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})}: δ 153.2, 150.0, 135.2, 126.5, 117.8, 110.0, 106.6, 60.9, 60.8, 55.9, 55.8, 20.4 ppm.

HRMS (ESI-TOF): m/z [M + Na]+ C_{14}H_{16}O_{5}Na calcd: 287.0867, found: 287.0889.

2-(2-Bromo-5-hydroxy-4-methoxyphenyl)-5,5-dimethylcyclohexane-1,3-dione (16a):

Reaction time: 4 h.

Yield: 87 mg (86%) as colourless solid.

Mp: 144–145 ℉.

{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})}: δ 7.57 (s, 1H), 6.99 (s, 1H), 5.83 (s, 1H), 3.93 (s, 3H), 2.85 (s, 2H), 2.16 (s, 2H), 1.18 (s, 6H) ppm.

{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})}: δ 194.3, 169.0, 145.3, 143.8, 116.2, 115.4, 105.7, 94.1, 56.2, 52.2, 37.8, 35.3, 29.7, 28.6 ppm.
2-(2-Chloro-5-hydroxy-4-methoxyphenyl)-5,5-dimethylcyclohexane-1,3-dione (16b):

Reaction time: 3 h.

Yield: 75 mg (85%) as colourless solid.

Mp: 145–146 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.56 (s, 1H), 7.00 (s, 1H), 5.75 (s, 1H), 3.93 (s, 3H), 2.85 (s, 2H), 2.45 (s, 2H), 1.18 (s, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 194.3, 168.9, 148.9, 145.3, 143.7, 116.3, 115.4, 105.6, 94.6, 56.3, 52.1, 37.8, 35.3, 28.6 ppm.

HRMS (ESI-TOF): m/z [M + Na]$^+$ C$_{15}$H$_{17}$O$_4$BrNa calcd: 363.0202, found: 363.0205.

3-Hydroxy-2-(5-hydroxy-4-methoxy-2-methylphenyl)-5,5-dimethylcyclohex-2-enone (16d):

Reaction time: 4 h.

Yield: 71 mg (86%) as colourless solid.

Mp: 235–236 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 6.56 (s, 1H), 6.38 (s, 1H), 3.68 (s, 3H), 2.43–2.40 (m, 1H), 2.21–2.20 (m, 3H), 1.86 (s, 3H), 0.98 (s, 3H), 0.97 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 196.4, 146.0, 143.2, 128.5, 123.9, 117.5, 115.1, 112.6, 55.2, 31.3, 28.3, 27.8, 27.5, 18.8 ppm.

HRMS (ESI-TOF): m/z [M + Na]$^+$ C$_{16}$H$_{20}$O$_4$ClNa calcd: 319.0707, found: 319.0739.

3-Hydroxy-2-(3-hydroxy-4,5-dimethoxyphenyl)-5,5-dimethylcyclohex-2-enone (16e):

Reaction time: 5 h.

Yield: 66 mg (76%) as colourless solid.

Mp: 225–226 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 6.33 (s, 1H), 6.21 (s, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.30–2.29 (m, 4H), 1.04 (s, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 204.6, 152.6, 149.7, 134.9, 127.7, 116.2, 111.0, 106.2, 60.4, 60.3, 55.5, 52.1, 31.4, 28.1 ppm.
HRMS (ESI-TOF): m/z [M + Na]^+ C_{16}H_{20}O_{5}Na calcd: 315.1202, found: 315.1202.

3-(2-Bromo-5-hydroxy-4-methoxyphenyl)-4-hydroxy-2H-chromen-2-one (17a):

**Reaction time:** 4 h.

**Yield:** 84 mg (78%) as colourless solid.

**Mp:** 208–210 °C.

**1H NMR (400 MHz, CDCl3):** δ 7.98–7.95 (m, 1H), 7.62–7.48 (m, 2H), 7.41–7.37 (m, 1H), 7.27 (s, 1H), 7.20 (s, 1H), 5.75 (br, 1H), 4.01 (s, 3H) ppm.

**13C NMR (100 MHz, CDCl3):** δ 158.7, 152.8, 149.7, 147.5, 144.8, 130.8, 124.4, 121.2, 121.1, 117.1, 115.7, 112.7, 105.6, 105.5, 95.0, 56.2 ppm.

HRMS (ESI-TOF): m/z [M + Na]^+ C_{16}H_{11}O_{5}BrNa calcd: 384.9682, found: 384.9684.

3-(2-Chloro-5-hydroxy-4-methoxyphenyl)-4-hydroxy-2H-chromen-2-one (17b):

**Reaction time:** 4 h.

**Yield:** 71 mg (75%) as colourless solid.

**Mp:** 118–220 °C.

**1H NMR (400 MHz, CDCl3):** δ 7.97–7.96 (m, 1H), 7.62 (s, 1H), 7.58–7.55 (m, 1H), 7.50–7.48 (m, 1H), 7.41–7.38 (m, 1H), 7.20 (s, 1H), 5.72 (br, 1H), 4.01 (s, 3H) ppm.

**13C NMR (100 MHz, CDCl3):** δ 158.0, 157.5, 152.1, 149.1, 147.6, 144.7, 130.4, 123.9, 120.5, 116.4, 114.8, 112.1, 104.9, 94.8, 55.6 ppm.

HRMS (ESI-TOF): m/z [M + Na]^+ C_{16}H_{11}O_{5}ClNa calcd: 341.0187, found: 341.0188.

3-(5-Hydroxy-4-methoxy-2-methylphenyl)chroman-2,4-dione (17d):

**Reaction time:** 3 h.

**Yield:** 78 mg (88%) as colourless solid.

**Mp:** 119–200 °C.

**1H NMR (400 MHz, CDCl3):** δ 7.84–7.82 (m, 1H), 7.74–7.72 (m, 2H), 7.44–7.38 (m, 3H), 7.21–7.11 (m, 3H) 6.69 (s, 1H), 6.67 (s, 1H), 5.62 (s, 1.5H), 5.19 (s, 0.5H), 3.76 (s, 3H), 2.03 (s, 3H) ppm.

**13C NMR (100 MHz, CDCl3):** δ 167.2, 163.8, 153.7, 146.7, 143.6, 131.6, 131.1, 123.3, 123.1, 116.7, 116.0, 115.8, 113.0, 90.8, 45.5, 8.2 ppm.
HRMS (ESI-TOF): m/z [M + Na]+ C_{17}H_{14}OsNa calcd: 321.0733, found: 321.0733.

4-Hydroxy-3-(3-hydroxy-4,5-dimethoxyphenyl)-2H-chromen-2-one (17e):

Reaction time: 5 h.

Yield: 70 mg (75%) as colourless solid.

Mp: 248–249 °C.

$^1$H NMR (400MHz, CDCl$_3$): δ 9.33 (br, 1H), 7.88–7.86 (d, $J = 7.6$ Hz, 1H), 7.48–7.45 (m, 1H), 7.23–7.18 (m, 2H), 6.60 (s, 1H), 6.46 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 162.4, 160.1, 152.8, 152.3, 131.4, 126.1, 123.5, 123.3, 115.9, 115.8, 111.5, 111.4, 105.84, 105.82, 105.6, 60.1, 55.4 ppm.

HRMS (ESI-TOF): m/z [M + H]+ C_{17}H_{14}O$_5$ calcd: 315.0872, found: 315.0863.

Ethyl 2-(2-bromo-5-hydroxy-4-methoxyphenyl)-2-cyanoacetate (18a):

Reaction time: 4 h.

Yield: 73 mg (78%) as colourless solid.

Mp: 122–123 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.13 (s, 1H), 7.05 (s, 1H), 5.66 (br, 1H), 5.10 (s, 1H), 4.31–4.25 (m, 2H), 3.91 (s, 3H), 1.31 (t, $J = 8.0$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 164.2, 147.8, 145.7, 122.7, 115.5, 115.2, 115.1, 113.1, 63.4, 56.3, 42.8, 13.9 ppm.

HRMS (ESI-TOF): m/z [M + Na]+ C_{17}H_{14}O$_6$BrNa calcd: 335.9741, found: 335.9844.

Ethyl 2-(2-chloro-5-hydroxy-4-methoxyphenyl)-2-cyanoacetate (18b):

Reaction time: 5 h.

Yield: 64 mg (80%) as colourless liquid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.09 (s, 1H), 6.89 (s, 1H), 5.07 (s, 1H), 4.31–4.25 (m, 2H), 3.91 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 164.3, 147.7, 145.1, 124.1, 120.8, 115.4, 115.2, 112.1, 63.3, 55.7, 40.3, 13.9 ppm.

HRMS (ESI-TOF): m/z [M + Na]+ C_{12}H_{12}NO$_4$ClNa calcd: 292.0347, found: 292.0342.
Ethyl 2-cyano-2-(5-hydroxy-4-methoxy-2-methylphenyl)acetate (18d):

Reaction time: 3 h.

Yield: 65 mg (88%) as colourless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.00 (s, 1H), 6.68 (s, 1H), 5.54 (s, 1H), 4.76 (s, 1H), 4.28–4.20 (m, 2H), 3.88 (s, 3H), 2.32 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 165.1, 146.9, 144.3, 127.9, 121.2, 115.8, 114.7, 113.2, 63.1, 55.9, 40.6, 19.0, 13.9 ppm.

HRMS (ESI-TOF): m/z [M + Na]$^+$ C$_{13}$H$_{15}$NO$_4$Na calcd: 272.0893, found: 272.0860.

4-Bromo-5-(3,5-dimethyl-1-phenyl-1H-pyrazol-4-yl)-2-methoxyphenol (19):

Yield: 87 mg (78%) as colourless solid.

Mp: 157–158 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.50–7.42 (m, 5H), 7.13 (s, 1H), 6.81 (s, 1H), 3.91 (s, 3H), 2.18 (s, 3H), 2.15 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.6, 146.7, 144.8, 139.7, 137.3, 128.9, 127.3, 127.1, 124.7, 120.5, 118.1, 114.9, 114.5, 56.1, 12.3, 11.7 ppm.

HRMS (ESI-TOF): m/z [M + H]$^+$ C$_{18}$H$_{17}$BrN$_2$O$_2$ calcd: 373.0546, found: 373.0546.

5-(3,5-Dimethyl-1-phenyl-1H-pyrazol-4-yl)-2-methoxy-4-methylphenol (20):

Yield: 73 mg (80%) as colourless solid.

Mp: 160–162 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51–7.43 (m, 4H), 7.35–7.32 (m, 1H), 6.79 (s, 1H), 6.73 (s, 1H), 3.91 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.7, 145.8, 143.2, 140.0, 136.7, 129.2, 128.9, 125.4, 124.6, 120.3, 117.1, 112.2, 55.8, 19.5, 12.3, 11.5 ppm.

HRMS (ESI-TOF): m/z [M + H]$^+$ C$_{19}$H$_{20}$N$_2$O$_2$ calcd: 309.1597, found: 309.1560.

4-Bromo-5-(3-methoxy-5-methyl-1-phenyl-1H-pyrazol-4-yl)-2 methoxyphenol (21):

Yield: 86 mg (72%) as colourless solid.

Mp: 160–161 °C.
\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.75–7.73 (m, 2H), 7.44–7.39 (m, 2H), 7.27 (s, 1H), 7.12 (s, 1H), 6.92 (s, 1H), 5.70 (br, 1H), 3.94 (s, 3H), 3.89–3.82 (m, 2H), 2.12 (s, 3H), 1.15 (t, \(J = 6.8\) Hz, 3H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 150.3, 148.1, 146.7, 144.7, 138.7, 128.7, 126.3, 126.0, 122.2, 121.3, 119.6, 119.1, 118.2, 115.2, 114.7, 110.2, 69.0, 56.2, 15.2, 13.2 ppm.

HRMS (ESI-TOF): m/z [M + H]\(^+\) C\(_{19}\)H\(_{19}\)BrN\(_2\)O\(_3\) calcd: 403.0651, found: 403.0641.

5-(3-Ethoxy-1,5-diphenyl-1H-pyrazol-4-yl)-2-methoxy-4-methylphenol (22):

Yield: 90 mg (75%) as colourless solid.

Mp: 217–218 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.03–8.01 (m, 1H), 7.95–7.93 (m, 1H), 7.50–7.48 (m, 1H), 7.43–7.41 (m, 2H), 7.24–7.23 (m, 2H), 6.76 (s, 1H), 6.71 (s, 1H), 5.05 (br, 1H), 3.87 (s, 3H), 2.51 (q, \(J = 7.2\) Hz, 2H), 2.02 (s, 3H), 0.98 (t, \(J = 7.6\) Hz, 3H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 148.8, 145.9, 143.3, 130.4, 129.8, 128.8, 128.6, 128.2, 127.9, 126.8, 126.6, 125.2, 119.0, 117.6, 112.7, 55.8, 44.6, 19.6, 8.3 ppm.


5-(3,5-Dimethylisoxazol-4-yl)-2,3-dimethoxyphenol (23):

Yield: 60 mg (81%) as colourless solid.

Mp: 152–153 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.48 (s, 1H), 6.32 (s, 1H), 5.95 (s, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 2.40 (s, 3H), 2.27 (s, 3H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 165.1, 158.6, 152.4, 149.5, 134.9, 126.4, 116.6, 109.0, 105.2, 61.0, 55.9, 11.5, 10.8 ppm.

HRMS (ESI-TOF): m/z [M + Na]\(^+\) C\(_{13}\)H\(_{15}\)NO\(_4\)Na calcd: 272.0893, found: 272.0897.

Ethyl 3-amino-2-(2-bromo-5-hydroxy-4-methoxy-2-methylphenyl)-3-oxopropanoate (24):

Yield: 54 mg (68%) as colourless solid.

Mp: 154–156 °C.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.97 (s, 1H), 6.69 (s, 1H), 5.72 (s, 1H), 4.65 (s, 1H), 4.25–4.14 (m, 2H), 3.86 (s, 3H), 2.34 (s, 3H), 1.24 (t, \(J = 7.2\) Hz, 3H) ppm.
\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} \delta 170.7, 170.2, 146.1, 144.0, 128.7, 125.0, 113.4, 113.3, 61.8, 55.9, 54.3, 29.7, 14.1 \text{ ppm.}\]

\textbf{Ethyl 2-bromo-5-hydroxy-4-methoxyphenyl)-2-(5-oxo-4,5-dihydro-1H-1,2,4-triazol-3-yl)acetate (25):}

\textbf{Yield:} 99 mg (55\%) as colourless solid.

\textbf{Mp:} 136–138 °C.

\[^{1}\text{H NMR (400 MHz, CDCl}_3\text{):} \delta 7.13 \text{ (s, 1H)}, 7.05 \text{ (s, 1H)}, 5.61 \text{ (br, 1H)}, 5.10 \text{ (s, 1H)}, 4.32–4.26 \text{ (m, 2H)}, 3.91 \text{ (s, 3H)}, 3.73 \text{ (s, 1H)}, 1.31 \text{ (t, } J = 7.2 \text{ Hz, 3H)} \text{ ppm.}\]

\[^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} \delta 170.6, 147.1, 146.3, 145.6, 145.9, 128.5, 117.1, 115.6, 114.9, 113.8, 60.9, 56.2, 41.1, 14.1 \text{ ppm.}\]

\textbf{HRMS (ESI-TOF):} \text{m/z [M + H]}^{+} \text{C}_{13}\text{H}_{14}\text{BrN}_{3}\text{O}_{4} \text{calcd: 372.0189, found: 372.0185.}
Copies of $^1$H and $^{13}$C NMR spectra

Fig S1: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 11a.

Fig S2: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 11a.
Fig S3: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 11c.

Fig S4: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 11c.
Fig S5: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 11d.

Fig S6: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 11d.
Fig S7: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 11e.

Fig S8: $^1$H NMR (125 MHz, CDCl$_3$) spectrum of 11e.
Fig S25: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 11f

Fig S26: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 11f.
Fig S9: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 12a.

Fig S10: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 12a.
Fig S11: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 13a.

Fig S12: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 13a.
Fig S13: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 13b.

Fig S14: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 13b.
Fig S15: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 13e.

Fig S16: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 13e.
Fig S29: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 13g.

Fig S30: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 13g.
Fig S17: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 14a.

Fig S18: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 14a.
Fig S19: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 14c.

Fig S20: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 14c.
Fig S21: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 14d.

Fig S22: $^{13}$C NMR (125MHz, CDCl$_3$) spectrum of 14d.
Fig S23: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 14e.

Fig S24: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 14e.
Fig S27: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 14f.

Fig S28: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 14f.
Fig S31: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 15a.

Fig S32: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 15a.
Fig S33: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 15b.

Fig S34: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 15b.
Fig S35: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 15d.

Fig S36: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 15d.
Fig S37: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 15e.

Fig S38: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 15e.
Fig S39: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 16a.

Fig S40: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 16a.
Fig S41: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 16b.

Fig S42: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 16b.
Fig S43: $^1$H NMR (400 MHz, CDCl$_3$ + DMSO) spectrum of 16d.

Fig S44: $^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO) spectrum of 16d.
Fig S45: $^1$H NMR (400 MHz, CDCl$_3$ + DMSO) spectrum of 16e.

Fig S46: $^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO) spectrum of 16e.
Fig S47: $^1$H NMR (400 MHz, CDCl$_3$ + DMSO) spectrum of 17a.

Fig S48: $^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO) spectrum of 17a.
Fig S49: $^1$H NMR (400 MHz, CDCl$_3$ + DMSO) spectrum of 17b.

Fig S50: $^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO) spectrum of 17b.
Fig S51: $^1$H NMR (400 MHz, CDCl$_3$ + DMSO) spectrum of 17d.

Fig S52: $^{13}$C NMR (125 MHz, CDCl$_3$ + DMSO) spectrum of 17d.
Fig S53: $^1$H NMR (400 MHz, CDCl$_3$ + DMSO) spectrum of 17e.

Fig S54: $^{13}$C NMR (125MHz, CDCl$_3$ + DMSO) spectrum of 17e.
Fig S55: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 18a.

Fig S56: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 18a.
Fig S57: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 18b.

Fig S58: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 18b.
Fig S59: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 18d.

Fig S60: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 18d.
Fig S61: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 19.

Fig S62: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 19.
Fig S63: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 20.

Fig S64: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 20.
Fig S65: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 21.

Fig S66: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 21.
Fig S67: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 22.

Fig S68: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 22.
Fig S69: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 23.

Fig S70: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 23.
Fig S71: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 24.

Fig S72: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 24.
Fig S73: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 25.

Fig S74: $^{13}$C NMR (125 MHz, CDCl$_3$) spectrum of 25.
Fig S75: ORTEP diagram of compound 19.

Table S1: Crystal data of compound 19.

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