Experimental procedure for the synthesis of pincer 1.

**Methyl 3,5-bis(bromomethyl)benzoate.** NBS (13 g, 73.08 mmol) was added in four equal portions during 31 h to a solution of methyl 3,5-dimethylbenzoate (1.5 g, 9.13 mmol) in refluxing CCl₄ (55.5 mL), each addition being followed by a few milligrams of benzoyl peroxide. The reaction outcome was monitored by ¹H-NMR. Upon completion, the mixture was cooled to room temperature and filtered. The filtrate was washed with a saturated aqueous solution of NaHCO₃ (30 mL) and brine (30 mL), dried over anhydrous Na₂SO₄, and evaporated in vacuo. The residue was reddissolved in anhydrous THF (20 mL), and diethyl phosphate (13.8 mL, 1.07 mmol) and iPr₂NEt (18.6 mL, 1.07 mmol) were added at 0ºC under Ar. The stirred mixture was allowed to warm to r.t and stirred for 2 d (the reaction was monitored by ¹H-NMR), and then poured onto ice/water (1:1) and extracted with Et₂O (4 x 30 mL). The organic layer was washed with 1M HCl (1 x 10 mL) and brine (1 x 10 mL), dried over anhydrous Na₂SO₄, and evaporated in vacuo to give a residue which was purified by flash chromatography on silicagel using Et₂O/Hexane (7:3) as eluent. Methyl 3,5-bis(bromomethyl)benzoate was obtained as a yellow powder (1.46 g, 68%). δH (300 MHz, CDCl₃): 3.93 (s, 3H), 4.49 (s, 4H), 7.61 (s, 1H), 7.99 (d, 2H, J= 1.6 Hz); δC (75 MHz, CDCl₃): 31.8 (CH₃); 52.4 (CH₂); 129.9 (C3-C5); 131.4 (C4); 133.8 (C1); 138.9 (C2-C6); 165.9 (C=O)

**Methyl 3,5-Bis(pyrazol-1-ylmethyl)benzoate.** A mixture of methyl 3,5-bis(bromomethyl)benzoate (600 mg, 1.86 mmol), pyrazole (2.79 mg, 4.09 mmol), and Cs₂CO₃ (2.37 g, 7.27 mmol) was refluxed in dry acetonitrile (45 mL) under argon for 2 h. After cooling, the resultant solution was filtered and water (30 mL) was added. The aqueous layer was extracted with EtOAc (2 x 40 mL). The combined organic extracts were dried with anhydrous Na₂SO₄ and the solvent was removed in vacuo to give a

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residue which was purified by gradient flash chromatography on silicagel (Hexane:EtOAc 7:3 → EtOAc → EtOAc:MeOH 9.5:0.5). Methyl 3,5-Bis(pyrazol-1-ylmethyl)benzoate was obtained as a white solid (570 mg, 99%). mp 62-63°C (EtOAc); 1H NMR (300 MHz, CDCl3) δH 3.86 (3H, s, CH3), 5.31 (4H, s, CH2), 6.28 (2H, dd, J 2.1, 1.9 Hz, H4’), 7.18 (1H, s, H4), 7.38 (2H, d, J 2.1 Hz, H5’), 7.53 (2H, d, J 1.9 Hz, H3’), 7.80 (2H, s, H2, H6); 13C NMR (63 MHz, CDCl3) δC 52.19 (CH3), 55.04 (CH2), 106.17 (C4’), 128.12 (C2, C6), 129.40 (C5’), 130.97 (C4), 131.14 (C3, C5), 137.82 (C1), 139.88 (C3’), 166.14 (CO).

NCN palladium pincer 1. A mixture of the methyl 3,5-bis(pyrazol-1-ylmethyl)benzoate (300 mg, 1.01 mmol) and palladium(II) acetate (230 mg, 1.01 mmol) was refluxed in glacial acetic acid (5 mL) under argon for 20 h. After cooling, the solvent was removed in vacuo, and to the resulting residue excess LiCl (5.5 mmol) and a mixture of acetone/water (3:2, 5 mL) were added. The resulting mixture was stirred at r.t. for 2 days. The reaction outcome was monitored by 1H-NMR. Upon completion, the mixture was filtered to provide a grey solid (400mg, 92%). mp >300°C (EtOAc); 1H NMR (300 MHz, DMSO) δH 3.83 (3H, s, CH3), 5.55 (4H, s, CH2), 6.46 (2H, dd, J 2.0, 1.6 Hz, H4’), 7.70 (2H, s, H2, H6), 7.92 (2H, d, J 1.6 Hz, H5’), 8.14 (2H, d, J 2.1 Hz, H3’); 13C NMR (63 MHz, DMSO) δC 52.10 (CH3), 56.72 (CH2), 106.62 (C4’), 125.91 (C2, C6), 126.40 (C1), 133.08 (C5’), 137.16 (C3, C5), 143.18 (C3’), 150.69 (C4), 166.25 (CO).
Spectroscopic data of known aromatic ketones prepared by aerobic oxidation of benzylic substrates (alcohols and methylene compounds)

**Acetophenone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.61 (3H, s), 7.42-7.63 (3H, m), 7.96 (2H, d, J 8 Hz)

**Benzoyl cyanide**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.47 (m, 2H), 7.59 (m, 1H), 8.13 (m, 2H)

**9H-Fluorenone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.25-8.34 (m, 8H)

**Benzophenone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.48 (m, 4H), 7.59 (m, 2H), 7.81 (m, 4H)

**Indanone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.67 (t, 2H, J 7.6 Hz), 3.13 (t, 2H, 7.6 Hz), 7.35 (t, 1H, J 7.6 Hz), 7.46 (d, 1H, J 8 Hz), 7.57 (t, 1H, J 7.6 Hz), 7.74 (d, 1H, J 8 Hz)

**2-oxo-2-Phenylacetic acid**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.35 (d, 2H, J 7.6 Hz), 7.72 (d, 1H, J 7.6 Hz), 7.55 (t, 2H, J 7.8 Hz)

**9H-Xanthenone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.25-8.34 (m, 8H)

**3,4-Dihydro-1(2H)-naphthalenone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.11 (m, 2H), 2.63 (m, 2H), 2.94 (m, 2H), 7.21-8.11 (m, 4H)

**1-(p-Tolyl)ethanone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.34 (s, 3H), 2.50 (s, 3H), 6.75 (d, 2H, J 8 Hz), 7.34 (d, 2H, J 8 Hz).

**1-Phenyl-1-propanone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.18 (m, 3H), 2.94 (m, 2H), 7.40-7.51 (m, 3H).

**1-(2-Methoxyphenyl)ethanone**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.57 (s, 3H), 3.87 (s, 3H), 6.97 (d, 2H, J 8 Hz), 7.93 (d, 2H, J 8 Hz).

**2,2-Dimethyl-1-phenylpropanone.**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65 (d, 2H, J 7.3 Hz), 6.44 (dd, 1H), 7.16 (dd, 1H), 7.43-7.51 (m, 2H), 7.54-7.60 (m, 1H), 7.91-7.98 (m, 2H).

**Benzil**

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.98 (d, 4H, J 8 Hz), 7.6-7.68 (m, 2H), 7.5-7.54 (m, 2H).

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Deoxybenzoin\textsuperscript{9} \textsuperscript{1}\textsuperscript{H} NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 4.30 (s, 2H), 7.24-7.29 (m, 3H), 7.32-7.36 (m, 2H), 7.45-7.49 (m, 2H), 7.55-7.59 (m, 2H), 8.02-8.05 (m, 2H).

2-Methylbenzophenone\textsuperscript{10} \textsuperscript{1}\textsuperscript{H} NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 2.33 (s, 3H), 7.22-7.32 (m, 3H), 7.32-7.41 (m, 2H), 7.56-7.60 (m, 1H), 7.79-7.82 (m, 2H), 7.43-7.47 (m, 2H).

4'-Chloroacetophenone\textsuperscript{8} \textsuperscript{1}\textsuperscript{H} NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 2.60 (s, 3H), 7.90 (d, 2H, J 8.4 Hz), 7.44 (d, 2H, J 8.4 Hz).

Methyl phenylglyoxylate\textsuperscript{5} \textsuperscript{1}\textsuperscript{H} NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 3.98 (s, 3H), 7.54-7.50 (m, 2H), 7.69-7.65 (m, 1H), 8.01-8.04 (m, 2H).

Anthraquinone\textsuperscript{8} \textsuperscript{1}\textsuperscript{H} NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\) 7.80 (m, 4H), 8.33 (m, 4H).