Supplementary Material (ESI) for Chemical Communications


# Supplementary material for the paper

## One metal - two pathways on the carboxylate-enhanced, iron-containing quercetinase mimics

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**Experimental**

**Synthesis of [Fe(4'R'-fla)(salen)]complexes**

A solution of 0.1 g (0.28 mmol) of [ $Fe^{III}$(salen)]Cl and (0.28 mmol) 4'R'-flaH (R': H, Cl, MeO, $NMe_2$) in 3 $cm^3$ MeOH was stirred at room temperature for 10 minutes. After addition of $Et_3N$ (0.039 $cm^3$, 0.28 mmol) the reaction mixture was stirred for 1 h and dark brown solid precipitated upon standing for a day. The product was collected by filtration, washed with methanol and diethyl ether and dried in vacuum.

***[Fe(fla)(salen)]***

(0.13 g, 85%); UV-Vis. ($\lambda_{max,}$ DMF): 407 nm (log $\varepsilon$, 4.25). IR (KBr): 3432, 3001, 2976, 2913, 2804, 2676, 2519, 1628, 1599, 1571, 1549, 1512, 1491, 1468, 1444, 1424, 1343, 1321, 1299, 1250, 1233, 1217, 1199, 1148, 1115, 1086, 1032, 107, 905, 823, 792, 755, 687, 662, 612, 591, 543, 503, 484, 460, 420 $cm^{-1}$. Anal. Calcd. for $C_{31}H_{23}O_5N_2Fe$: C, 66.56; H, 4.14; N, 5.01; Fe, 9.98. Found: C, 66.47; H, 4.02; N, 5.04; Fe, 9.87 %.

***[Fe(4'Cl-fla)(salen)]***

(0.15 g, 90%); UV-Vis. ($\lambda_{max,}$ DMF): 411 nm (log $\varepsilon$, 4.15). IR (KBr): 3432, 3195, 3007, 2975, 2921, 2802, 2676, 2488, 1715, 1643, 1627, 1597, 1587, 1566, 1547, 1512, 1493, 1485, 1470, 1445, 1426, 1397, 1382, 1357, 1326, 1291, 1239, 1207, 1203, 1152, 1086, 1034, 1012, 901, 836, 759, 618, 551, 491, 420 $cm^{-1}$. Anal. Calcd. for $C_{31}H_{22}ClO_5N_2Fe$: C, 62.70; H, 3.73; N, 4.72; Fe, 9.40. Found: C, 62.59; H, 3.75; N, 4.69; Fe, 9.29%.

***[Fe(4'MeO-fla)(salen)]***

(0.12 g, 73%); UV-Vis. ($\lambda_{max,}$ DMF): 419 nm (log $\varepsilon$, 4.11). IR (KBr): 3432, 3187, 3005, 2970, 2934, 2799, 2676, 2488, 1708, 1629, 1603, 1555, 1542, 1512, 1499, 1471, 1445, 1421, 1401, 1381, 1355, 1339, 1305, 1295, 1261, 1252, 1237, 1219, 1174, 1110, 1027, 904, 858, 830, 792, 764, 756, 614, 588, 507, 454, 420 $cm^{-1}$. Anal. Calcd. for $C_{32}H_{25}O_6N_2Fe$: C, 65.21; H, 4.28; N, 4.75; Fe, 9.47. Found: C, 65.11; H, 4.23; N, 4.39; Fe, 9.39 %.

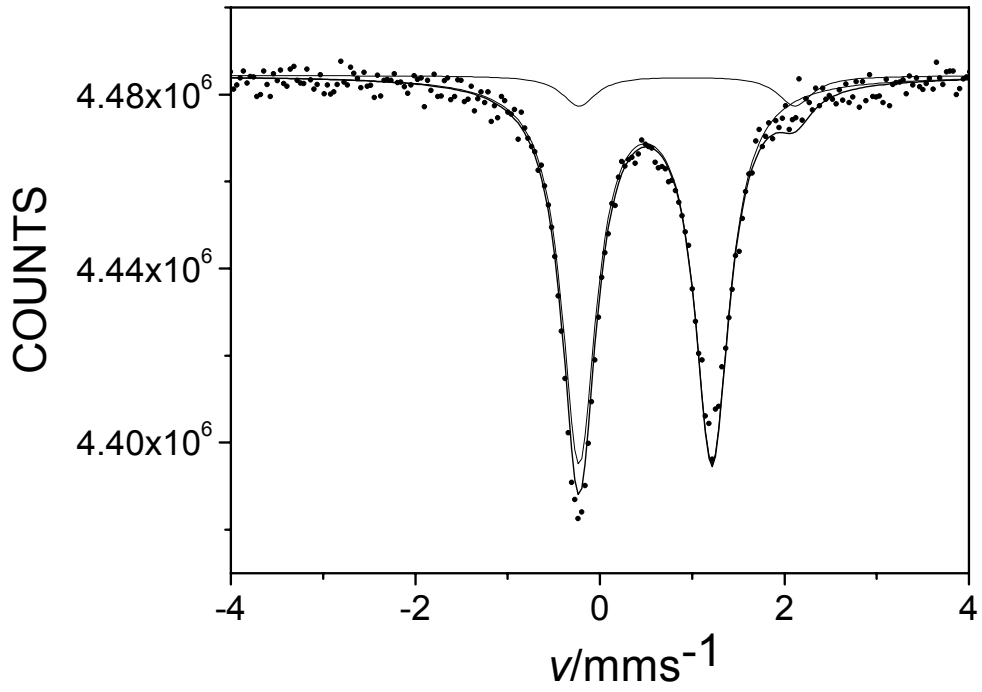
***[Fe(4'$NMe_2$-fla)(salen)]***

(0.15 g, 87%); UV-Vis. ($\lambda_{max,}$ DMF): 445 nm (log $\varepsilon$, 4.25). IR (KBr): 3420, 3187, 3015, 2975, 2931, 2795, 2676, 2492, 1712, 1630, 1602, 1542, 1493, 1469, 1444, 1418, 1365, 1340, 1306, 1257, 1213, 1198, 1151, 1034, 1008, 943, 903, 854, 823, 790, 762, 614, 538, 511, 464, 422 $cm^{-1}$. Anal. Calcd. for $C_{33}H_{28}O_5N_3Fe$: C, 65.79; H, 4.68; N, 6.98; Fe, 9.27. Found: C, 65.69; H, 4.59; N, 6.91; Fe, 9.21 %.

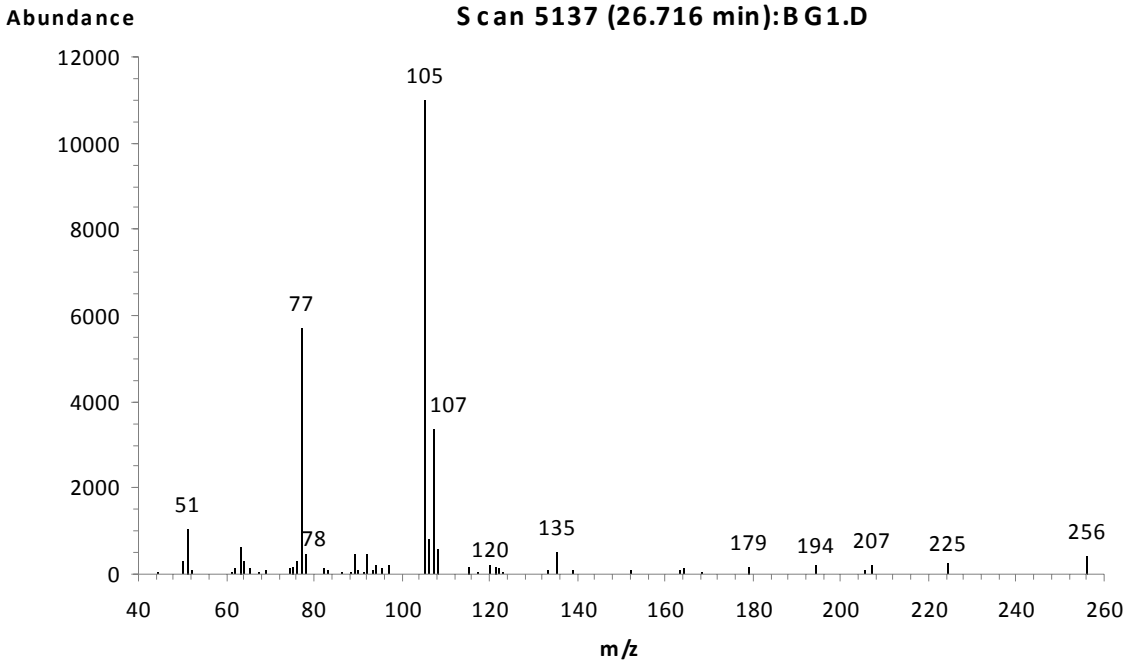
**Carboxylate-enhanced dioxygenation of [Fe(4'R'-fla)(salen)]complexes**

In a typical experiment, [Fe(4'R'-fla)(salen)] ($1.93 \times 10^{-4}$ mol $dm^{-3}$) and the corresponding carboxylic acid salt ($1.93 \times 10^{-3}$ mol $dm^{-3}$) were dissolved in 50 $cm^3$ of DMF, under argon atmosphere in a thermostated reaction vessel with an inlet for taking samples with a syringe. The solution was then heated to the appropriate temperature (40ºC), the argon was replaced by air and the decomposition of [Fe(4'R'-fla)(salen)] was followed spectrophotometrically by monitoring the decay of flavonolate band at 407 nm ($\lambda_{max}$ of a typical band of flavonolate). Addition of excess $Et_2O$ resulted in the deposition of the corresponding *O*-benzoylsalicylato complex [IR (KBr): 1740 $cm^{-1}$], which was dropped into icecooled dilute hydrochloric acid and extracted with $CH_2Cl_2$. The GC-MS analysis of the reaction mixture after treatment with etheral diazomethane, showed the presence of the *O*-benzoylsalicylic acid methyl ester: GC-MS (*O*-bsH) *m/z* 256 (M+, 3), 225 (1), 105 (100).

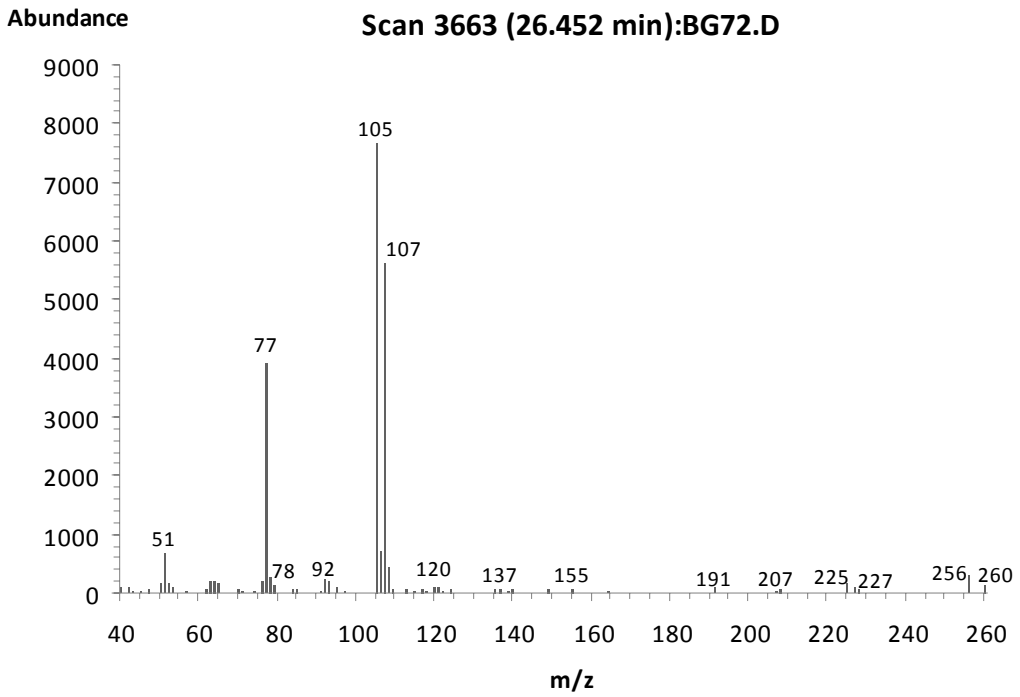
**SFigure 1.** $^{57}$Fe Mössbauer spectrum, recorded at 80K, of sample $Fe^{III}$(fla)(salen). The dominant doublet with isomer shift, δ=0.49 mm/s and quadrupole splitting, Δ=1.44 mm/s is assigned to high spin Fe(III) in the complex, the minor doublet (δ=0.95 mm/s, Δ=2.34 mm/s, relative area 7 %) represents Fe(II) remaining from the precursor.



**SFigure 2.** MS spectrum of the *O*-benzoylsalicylic acid methylester as a main product of the carboxylate-enhanced dioxygenation of [$Fe^{III}$(fla)(salen)].



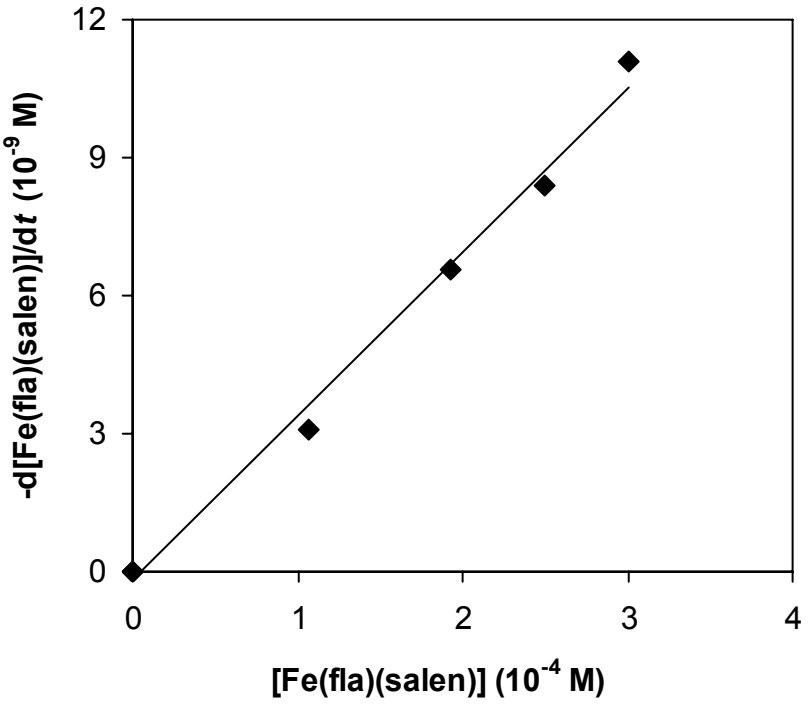
**SFigure 3.** MS spectrum of the *O*-benzoylsalicylic acid methylester as a main product of the dioxygenation of [$Fe^{III}$(fla)(salen)] under $^{18}O_2$ : $^{16}O_2$ (40 : 60%) atmosphere.



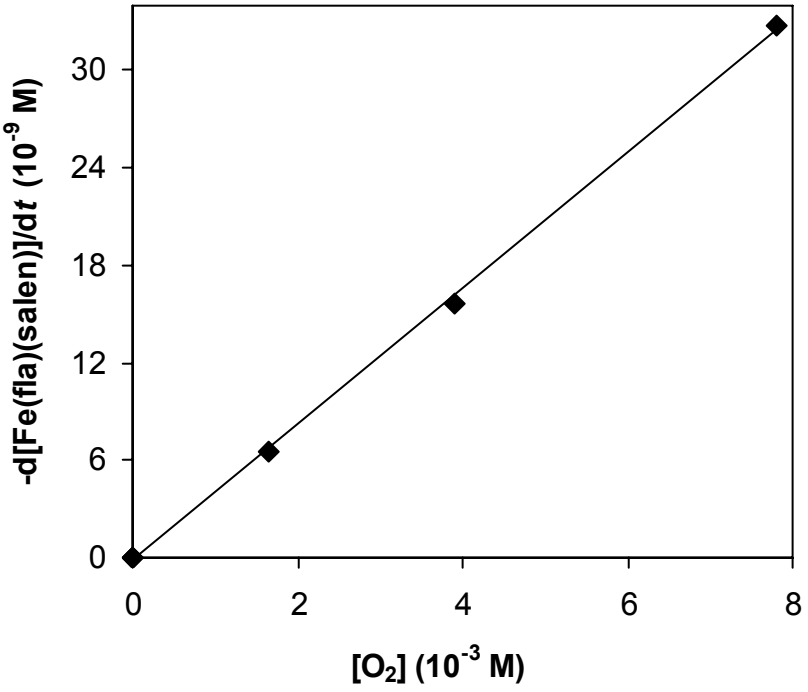
**STable 1.** Kinetic data for the stoichiometric dioxygenation of [$Fe^{III}$(fla)(salen)] in DMF solution

| **Expt.[a] no.** | **Temp (°C)** | **$10^4$[Fe(fla)(salen)] (M)** | **$10^3$[O2] (M)** | **$10^9$V ($Ms^{-1}$)** | **$10^2$k ($M^{-1}s^{-1}$)** |
|---|---|---|---|---|---|
| 1 | 100 | 1.07 | 1.64 | 3.08 | 1.75±0.11 |
| 2 | 100 | 1.93 | 1.64 | 6.55 | 2.07±0.12 |
| 3 | 100 | 2.50 | 1.64 | 8.40 | 2.05±0.14 |
| 4 | 100 | 3.00 | 1.64 | 11.1 | 2.25±0.12 |
| | | | | | |
| 5 | 100 | 1.93 | 3.91 | 15.6 | 2.10±0.15 |
| 6 | 100 | 1.93 | 7.81 | 32.8 | 2.18±0.17 |
| | | | | | |
| 7 | 90 | 1.93 | 1.56 | 2.91 | 0.96±0.05 |
| 8 | 95 | 1.93 | 1.61 | 4.51 | 1.45±0.09 |
| 9 | 105 | 1.93 | 1.65 | 8.71 | 2.73±0.15 |

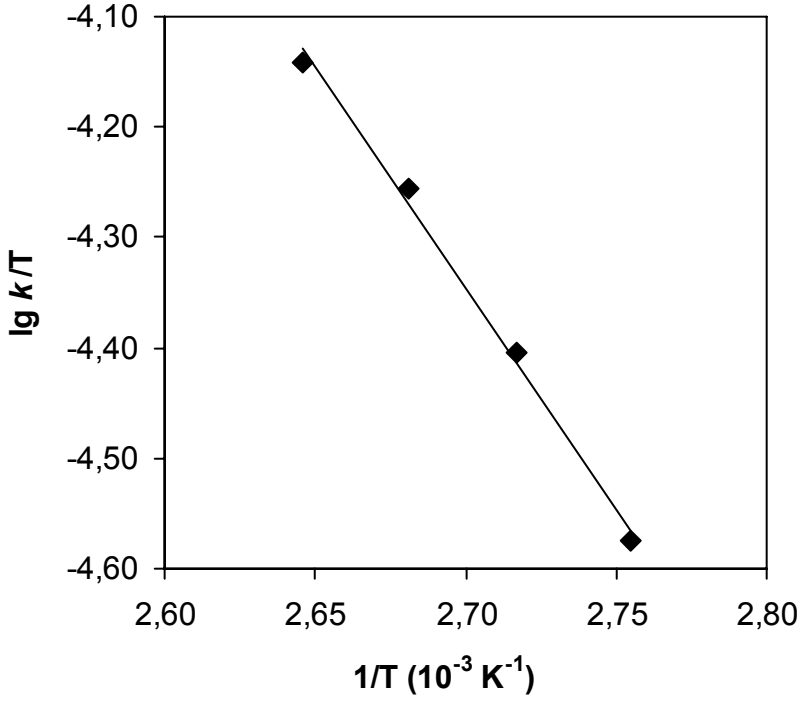
[a]In 50 mL of dmf.



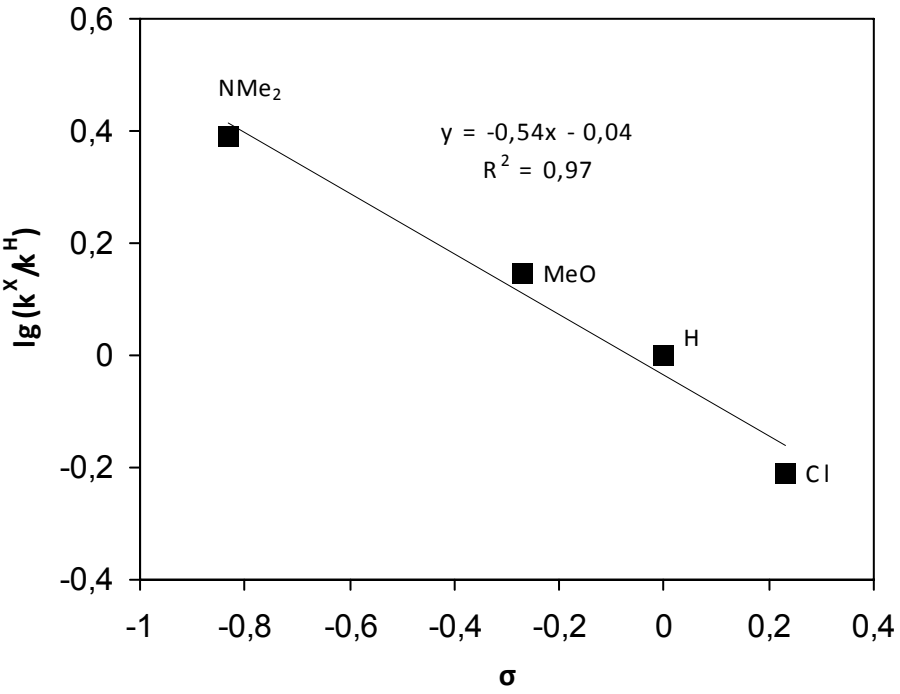

**SFigure 4.** Plot of dioxygenation rate of [$Fe^{III}$(fla)(salen)] versus its initial concentration in DMF: [$O_2$] = 1,64 × $10^{-3}$ M; dmf; T = 100 °C




**SFigure 5.** Plot of dioxygenation rate of [$Fe^{III}$(fla)(salen)] versus initial concentration of dioxygen in DMF: $[Fe^{III}(fla)(salen)]_0 = 1.93 \times 10^{-4}$ M; dmf; T = 100 °C




**SFigure 6.** Eyring plot for the dioxygenation of [$Fe^{III}$(fla)(salen)]: [$Fe^{III}$(fla)(salen)]$_0$ = 1.93 ×$10^{-4}$ M, dmf

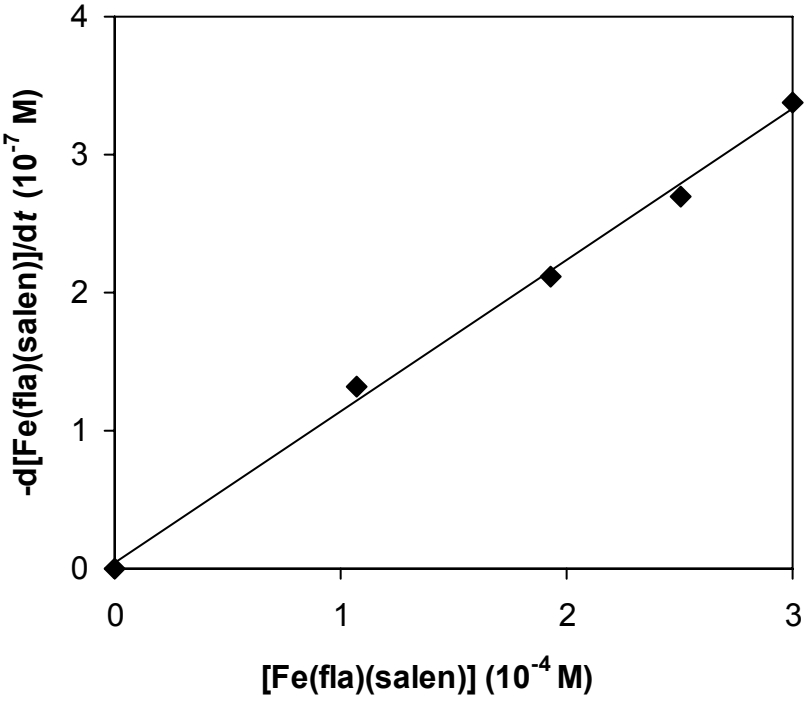



**SFigure 7.** Hammett plot for the dioxygenation of [$Fe^{III}$(4'X-fla)(salen)]: [$Fe^{III}$(4'X-fla)(salen)]$_0$ = 1.93 ×$10^{-4}$ M, dmf, T = 100 °C

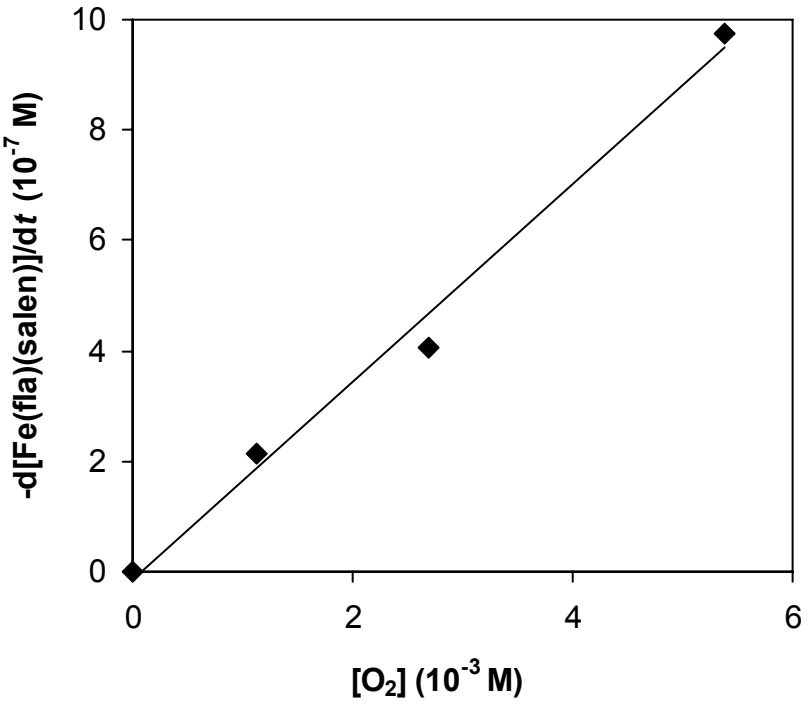
**Table 2.** Kinetic data for the carboxylate-enhanced dioxygenation of [$Fe^{III}$(fla)(salen)] in DMF solution

| **Expt.**[a] **no.** | **Temp (°C)** | **$10^4$[Fe(fla)(salen)] (M)** | **$10^3$[$O_2$] (M)** | **$10^3$[$PPh_3CCO_2$] (M)** | **$10^9V_0$ ($Ms^{-1}$)** | **$10^2k$ ($M^{-1}s^{-1}$)** |
|---|---|---|---|---|---|---|
| 1 | 40 | 1.07 | 1.13 | 1.93 | 1.32 | 5.67±0,34 |
| 2 | 40 | 1.93 | 1.13 | 1.93 | 2.12 | 5.02±0,35 |
| 3 | 40 | 2.50 | 1,13 | 1.93 | 2.70 | 5.05±0,31 |
| 4 | 40 | 3.00 | 1.13 | 1.93 | 3.38 | 5.17±0,41 |
| | | | | | | |
| 5 | 40 | 1.93 | 1.13 | 0.96 | 0.74 | 3.52±0,23 |
| 6 | 40 | 1,93 | 1.13 | 1.35 | 1.24 | 4.20±0,30 |
| 7 | 40 | 1.93 | 1,13 | 1.54 | 1.37 | 4.08±0,22 |
| 8 | 40 | 1.93 | 1.13 | 2.31 | 2.90 | 4.35±0,28 |
| 9 | 40 | 1.93 | 1.13 | 3.86 | 4.09 | 4.86±0,33 |
| | | | | | | |
| 10 | 40 | 1.93 | 2.69 | 1.93 | 4.05 | 4.05±0,24 |
| 11 | 40 | 1.93 | 5.38 | 1.93 | 9.75 | 4.12±0,28 |
| | | | | | | |
| 12 | 35 | 1.93 | 1.08 | 1.93 | 1.63 | 4.06±0,32 |
| 13 | 45 | 1.93 | 1.23 | 1.93 | 3.07 | 6.71±0,40 |
| 14 | 50 | 1.93 | 1.41 | 1.93 | 4.13 | 7.86±0,51 |

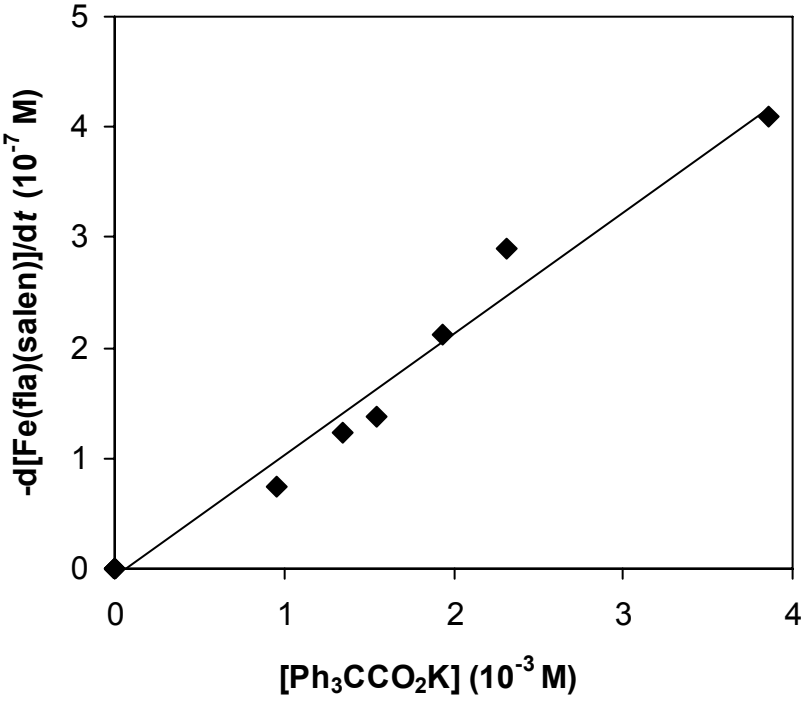
[a]In 50 mL of dmf.



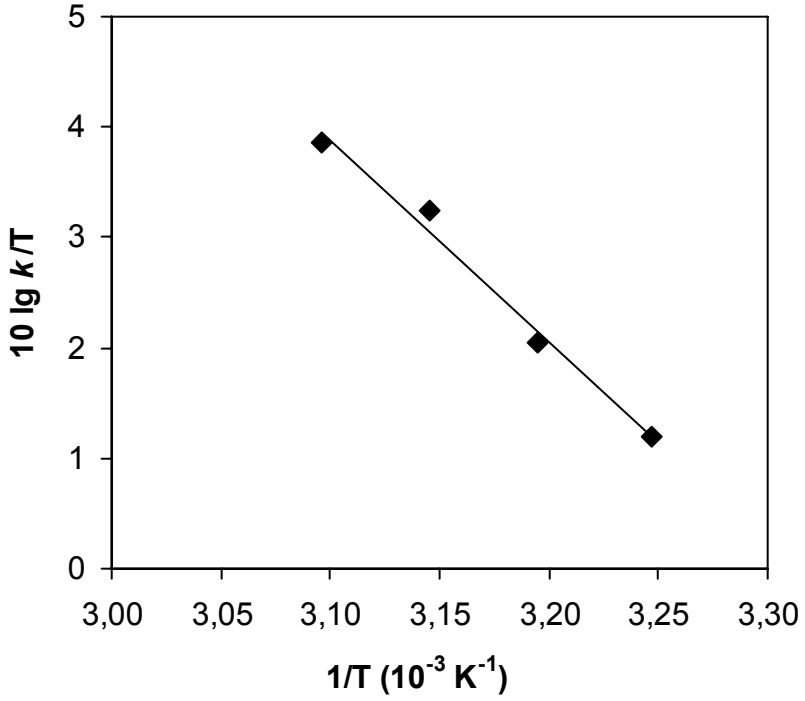

**SFigure 8.** Plot of the carboxylate-enhanced dioxygenation rate of $[Fe^{III}(fla)(salen)]$ versus its initial concentration in DMF: $[O_2] = 1{,}13 \times 10^{-3}$ M; $[PPh_3CCO_2K] = 1{,}93 \times 10^{-3}$ M; dmf; T = 40 °C



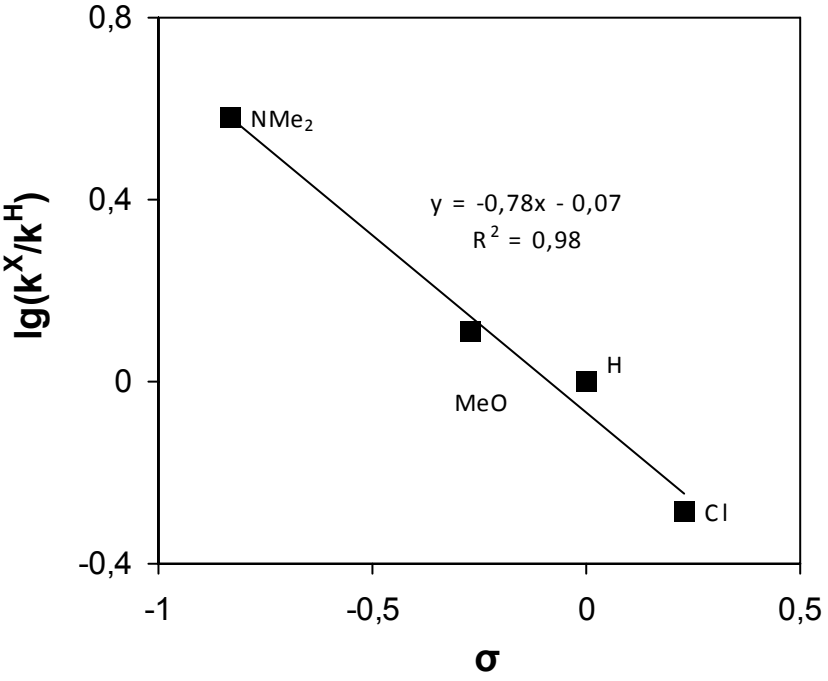

**SFigure 9.** Plot of the carboxylate-enhanced dioxygenation rate of [$Fe^{III}$(fla)(salen)] versus initial concentration of dioxygen in DMF: $[Fe^{III}(fla)(salen)]_0 = 1.93 \times 10^{-4}$ M; $[PPh_3CCO_2K] = 1{,}93 \times 10^{-3}$ M; dmf; T = 40 °C




**SFigure 10.** Plot of the carboxylate-enhanced dioxygenation rate of [$Fe^{III}$(fla)(salen)] versus initial concentration of triphenyl acetate in DMF: $[Fe^{III}(fla)(salen)]_0 = 1.93 \times 10^{-4}$ M; T = 40 °C




**SFigure 11.** Eyring plot for the carboxylate-enhanced dioxygenation of $[Fe^{III}(fla)(salen)]$: $[Fe^{III}(fla)(salen)]_0 = 1.93 \times 10^{-4}$ M, $[PPh_3CCO_2K] = 1{,}93 \times 10^{-3}$ M; dmf




**SFigure 12.** Hammett plot for the carboxylate-enhanced dioxygenation of $[Fe^{III}(4'X\text{-fla})(salen)]$: $[Fe^{III}(4'X\text{-fla})(salen)]_0 = 1.93 \times 10^{-4}$ M, $[PPh_3CCO_2K] = 1{,}93 \times 10^{-3}$ M; dmf, T = 40 °C