Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

For

A Series of Ni^{II}-Flavonolate Complexes as Structural and Functional ES (Enzyme-Substrate) Models of the Ni^{II}-Containing Quercetin 2,3-Dioxygenase

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Table S1. The solution FT-IR results of the complexes $[Ni^{II}L^{R}(fla)]$ in ethanol.

	$[Ni^{II}L^{OMe}(fla)]$ (**1**)	$[Ni^{II}L^{Me}(fla)]$ (**2**)	$[Ni^{II}L^{Br}(fla)]$ (**4**)	$[Ni^{II}L^{NO2}(fla)]$ (**5**)
$\nu(CO)$ /cm^{-1}	1549	1548	1544	1552
$\nu_{as}(CO_2)$ /cm^{-1}	1614	1614	1614	1607
$\nu_{s}(CO_2)$ /cm^{-1}	1416	1418	1424	1414
$\Delta\nu(CO_2)$ /cm^{-1}	198	196	190	193

Table S2. The reaction products analysis results of the complexes $[Ni^{II}L^{R}(fla)]$ with O_2.

Complex	Yield (%)				
	Salicylic acid	Benzoic acid	2-Hydroxy-*N*,*N*-dimethyl benzamide	*N*,*N*-dimethyl benzamide	Conv. (%)
$[Ni^{II}L^{OMe}(fla)]$ (**1**)	93.9	78.1	——	14.2	93.9
$[Ni^{II}L^{Me}(fla)]$ (**2**)	34.6	23.9	57.3	66.5	91.9
$[Ni^{II}L^{Br}(fla)]$ (**4**)	14.6	57.2	69.2	26.6	83.8
$[Ni^{II}L^{NO2}(fla)]$ (**5**)	25.2	45.4	50.4	31.8	77.2

Table S3. Kinetic results of the model complexes [$Ni^{II}L^{R}$(fla)].

[$Ni^{II}L^{OMe}$(fla)] (1)

	T (℃)	10^4[$Ni^{II}L^{OMe}$(fla)]$_0$ (M)	10^3[O_2]$_0$ (M)	10^8v (M s^{-1})	$10k$ (M^{-1} s^{-1})	$10k$ (M^{-1} s^{-1})
1	70	0.80	4.02	10.7	3.34 ±0.08	3.55 ±0.16
2	70	0.94	4.02	13.3	3.51 ±0.09	
3	70	1.06	4.02	14.3	3.35 ±0.10	
4	70	1.18	4.02	18.2	3.83 ±0.04	
5	65	0.89	2.79	6.85	2.76 ±0.07	2.80 ±0.10
6	65	0.89	4.13	9.97	2.71 ±0.05	
7	65	0.89	4.99	12.1	2.72 ±0.12	
8	65	0.80	5.85	14.0	3.00 ±0.14	
9	75	0.98	3.90	19.7	5.15 ±0.03	
10	80	0.99	3.79	30.9	8.24 ±0.07	

[$Ni^{II}L^{Me}$(fla)] (2)

	T (℃)	10^4[$Ni^{II}L^{Me}$(fla)]$_0$ (M)	10^3[O_2]$_0$ (M)	10^8v (M s^{-1})	10^2k (M^{-1} s^{-1})	10^2k (M^{-1} s^{-1})
1	70	0.68	4.02	2.42	8.85 ±0.02	8.51 ±0.06
2	70	0.82	4.02	2.73	8.28 ±0.08	
3	70	0.90	4.02	2.99	8.26 ±0.09	
4	70	1.00	4.02	3.49	8.68 ±0.10	
5	75	0.99	4.68	5.92	12.8 ±0.05	12.5 ±0.10
6	75	0.93	5.46	6.39	12.6 ±0.07	
7	75	0.91	3.90	4.33	12.2 ±0.06	
9	80	1.01	3.79	7.60	19.9 ±0.04	
10	85	1.00	3.63	9.57	26.4 ±0.04	

$[Ni^{II}L^{Br}(fla)]$ (4)

	T (℃)	$10^4[Ni^{II}L^{Br}(fla)]_0$ (M)	$10^3[O_2]_0$ (M)	$10^8 v$ ($M\ s^{-1}$)	$10^2 k$ ($M^{-1}\ s^{-1}$)	$10^2 k$ ($M^{-1}\ s^{-1}$)
1	70	0.79	4.02	1.61	5.07 ± 0.07	5.03 ± 0.07
2	70	0.92	4.02	1.87	5.06 ± 0.09	
3	70	1.08	4.02	2.18	5.02 ± 0.11	
4	70	1.20	4.02	2.41	5.00 ± 0.09	
5	75	1.00	4.68	3.70	7.91 ± 0.10	7.85 ± 0.09
6	75	1.04	5.46	4.41	7.77 ± 0.05	
7	75	1.00	3.90	3.06	7.86 ± 0.13	
8	80	1.01	3.79	4.64	12.1 ± 0.11	
9	85	0.98	3.63	6.72	18.9 ± 0.10	

$[Ni^{II}L^{NO2}(fla)]$ (5)

	T (℃)	$10^4[Ni^{II}L^{NO2}(fla)]_0$ (M)	$10^3[O_2]_0$ (M)	$10^8 v$ ($M\ s^{-1}$)	$10^2 k$ ($M^{-1}\ s^{-1}$)	$10^2 k$ ($M^{-1}\ s^{-1}$)
1	70	0.68	4.02	1.17	4.28 ± 0.11	4.19 ± 0.07
2	70	0.79	4.02	1.38	4.35 ± 0.08	
3	70	0.92	4.02	1.52	4.11 ± 0.09	
4	70	1.02	4.02	1.67	4.07 ± 0.10	
5	70	1.11	4.02	1.85	4.15 ± 0.12	
6	75	0.99	4.68	3.17	6.85 ± 0.09	6.83 ± 0.07
7	75	0.93	5.46	3.43	6.75 ± 0.11	
8	75	0.80	6.24	3.41	6.85 ± 0.07	
9	75	0.98	3.90	2.61	6.85 ± 0.06	
10	80	1.01	3.79	3.72	9.73 ± 0.07	
11	85	0.99	3.63	5.87	16.3 ± 0.10	

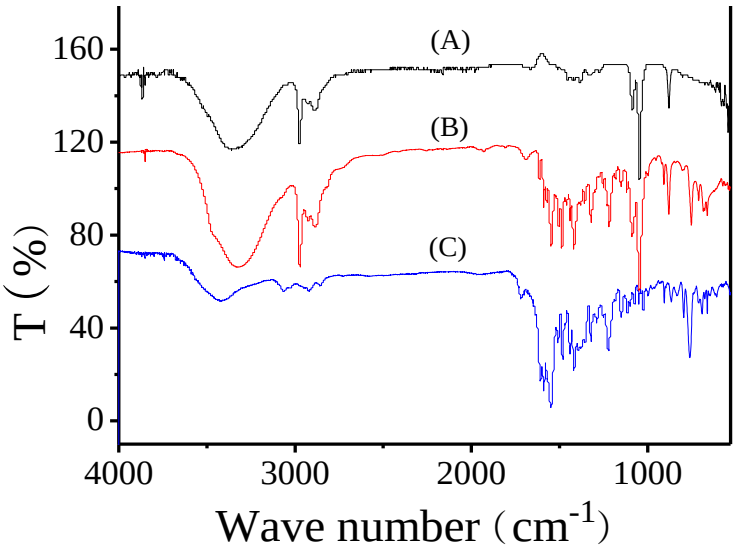
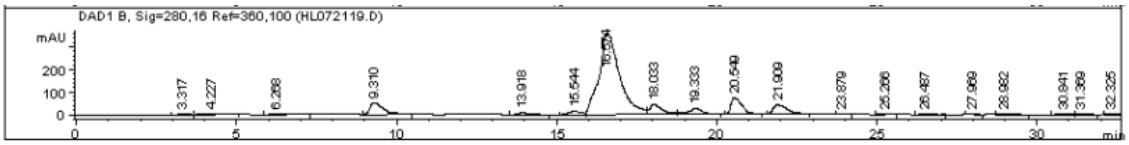
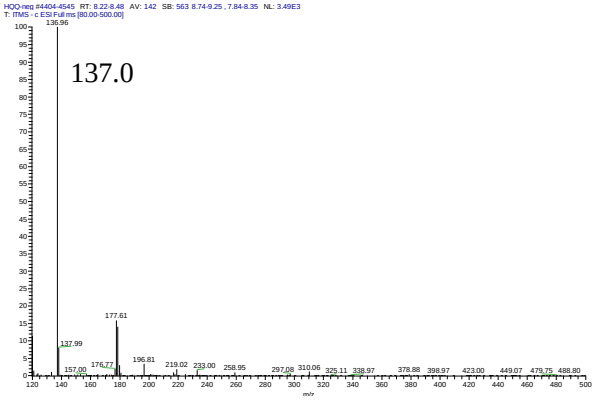


Figure S1. The FT-IR spectra of the ethanol solution and solid sample of [$Ni^{II}L^{Me}$(fla)] (**2**). (A) solvent ethanol (B) ethanol solution of [$Ni^{II}L^{Me}$(fla)] (**2**) (C) solid sample of [$Ni^{II}L^{Me}$(fla)] (**2**).



(a)



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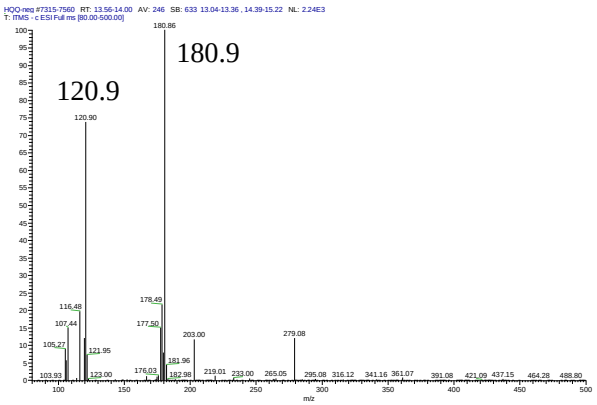

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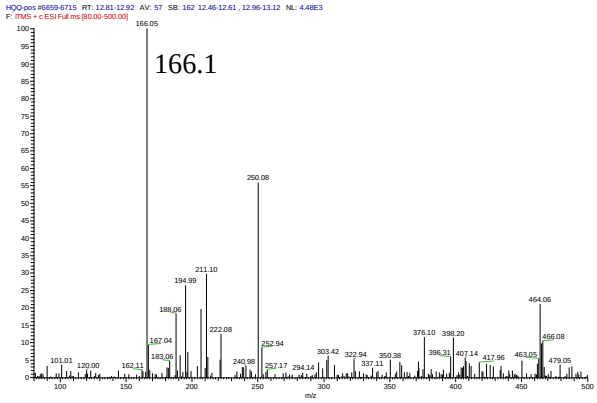
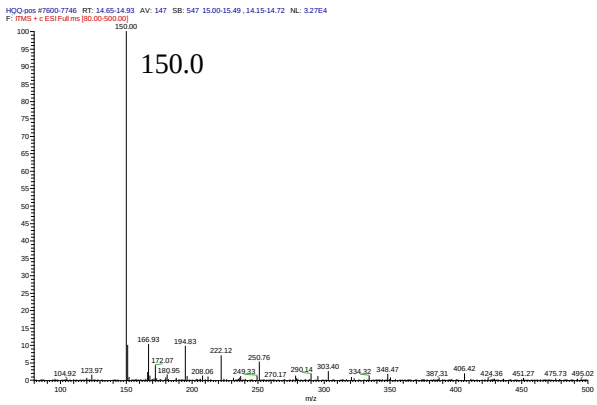


(d)



(e)

Figure S2. The HPLC-MS spectra of the reaction products of [Ni^{II}L^{NO2}(fla)] (**5**) with O_2 at 70 °C for 8 h. (a) HPLC spectra; MS spectra of (b) salicylic acid *m*/*z* (neg.): 137.0 $(M - H)^-$; (c) benzoic acid *m*/*z* (neg.): 120.9 $(M - H)^-$, 180.9 $(M + OAc)^-$; (d) 2-hydroxy-*N*,*N*-dimethyl benzamide *m*/*z* (pos.): 166.1 $(M + H)^+$; (e) *N*,*N*-dimethyl benzamide *m*/*z* (pos.): 150.0 $(M + H)^+$.

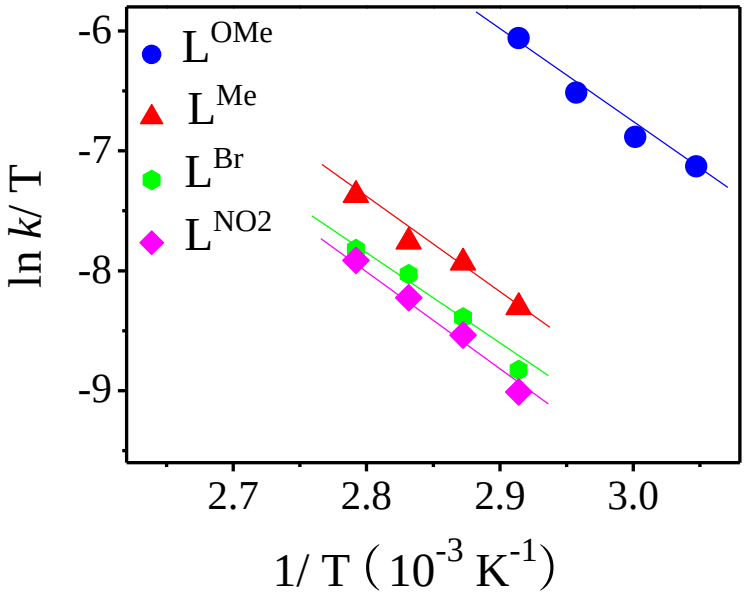


Figure S3. Eyring plot for the dioxygenation of the complexes [$Ni^{II}L^{R}$(fla)] (1.0 $\times 10^{-4}$ M) in DMF.