Supporting Information for:

Investigating the oxidation of alkenes with non-heme iron enzyme mimics derived from (*S*)-mandelic acid and pyridine-2,6-dimethanol

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Contents

1. Ligand Synthesis: Procedures and data for compounds **2b** and **12b** S1
2. Oxidative Turnover Reactions: Calculation of Product Yields S2
3. Low Temperature Turnover Reactions: GC Traces S3
4. Ligand Degradation Experiments: LCMS Traces S3
5. X-Ray Crystallographic Data for Compound **11** S4
6. X-Ray Crystallographic Data for Compound **12d** S6
7. References S8

1. Ligand Synthesis: Procedures and data for compounds 2b and 12b.[1]

(2S,5S)-2-tert-Butyl-5-((6-((ethyl(phenyl)amino)methyl)pyridin-2-yl)methyl)-5-phenyl-1,3-dioxolan-4-one **12b**

A solution of *N*-ethylaniline **9b** (0.19 mL, 1.49 mmol) in THF (10.0 mL) was cooled to 0 °C and a solution of *n*-BuLi in hexane (1.5 M, 1.19 mL, 1.78 mmol) was added via syringe. The resulting yellow solution was stirred at 0 °C for 20 minutes, then DMPU (0.22 mL, 1.78 mmol) was added. The reaction mixture was stirred for a further 20 minutes, then cooled to –40 °C using an acetonitrile/dry ice bath, and added via cannula to a solution of the bromide **11** (0.50 g, 1.24 mmol) in THF (10 mL) also at –40 °C. The resulting solution was stirred at –40 °C for 5 hours, monitored by TLC (cyclohexane/ethyl acetate 5:1), then allowed to warm to room temperature while stirring overnight. The orange reaction mixture was poured onto half-saturated aqueous ammonium chloride solution (4 mL). The aqueous phase was extracted with diethyl ether (3 × 8 mL) and the combined organic extracts were washed with brine (5 mL) and dried ($MgSO_4$). The solvent was removed *in vacuo* to give an orange oil which was purified by column chromatography (cyclohexane/ethyl acetate 10:1) to afford the product as a highly viscous pale yellow oil (0.47 g, 85 %). R_f 0.2 (cyclohexane/ethyl acetate, 10:1); $[\alpha]_D^{20}$ –58.3 ($CHCl_3$, *c* 0.33); ν_{max} (NaCl): 3060 (w), 2962 (s), 2961 (s), 1793 (s), 1590 (m), 1577 (m), 1178 (s); δ_H (300 MHz, $CDCl_3$): 0.86 (9H, s, $C(C\underline{H}_3)_3$), 1.25 (3H, t, *J* = 7.0 Hz, $NCH_2C\underline{H}_3$), 3.37 (1H, d, *J* = 14.5 Hz, 1 of $C\underline{H}_2CC_6H_5$), 3.53 (2H, q, *J* = 7.0 Hz,

NC$\underline{H}_2$CH$_3$) 3.68 (1H, d, *J* = 14.5 Hz, 1 of C$\underline{H}_2$CC$_6$H$_5$), 4.58 (2H, s, NCC$\underline{H}_2$N) 4.79 (1H, s, C$\underline{H}$C(CH$_3$)$_3$), 6.60–6.98 (5H, m, NC$_6\underline{H}_5$), 6.84 (1H, d, *J* = 8.0 Hz, C$\underline{H}_{Pyr}$), 7.10 (1H, d, *J* = 7.5 Hz, C$\underline{H}_{Pyr}$), 7.17–7.30 (3H, m, 3 of C$_6\underline{H}_5$), 7.48 (1H, t, *J* = 8.0 Hz, C$\underline{H}_{Pyr}$), 7.76 (2H, m, 2 of C$_6\underline{H}_5$); δ_C (75 MHz, CDCl$_3$): 12.9, 23.6, 33.8, 34.9, 45.9, 56.1, 82.1, 109.8, 112.1, 116.5, 119.2, 122.5, 125.0, 128.0, 128.4, 129.3, 137.2, 139.6, 148.2, 155.3, 156.5, 173.4; *m/z* (ES+): 467 (20 %, $[M+Na]^+$), 445 (100 %, $[MH]^+$); HRMS (ES+): $C_{28}H_{33}N_2O_3$ ($[MH]^+$) requires 445.2491, found 445.2470.

(S)-3-(6-((Ethyl(phenyl)amino)methyl)pyridin-2-yl)-2-hydroxy-2-phenylpropanoic acid **2b**

Following the procedure outlined above for preparation of **2a** from **12a**, **12b** (0.15 g, 0.34 mmol) yielded **2b** as an off-white solid (0.12 g, 95 %); R_f 0.2 (DCM/MeOH 10:1); $[\alpha]_D^{20}$ –92.6 (CHCl$_3$, *c* 0.38); m.p. 110–112 °C; ν_{max} (KBr): 3355 (w), 1612 (s), 1505 (m), 1575 (m), 807, 745; δ_H (300 MHz, CD$_3$OD): 1.24 (3H, t, *J* = 7.0 Hz, NCH$_2$C$\underline{H}_3$), 3.56 (2H, q, *J* = 7.0 Hz, NC$\underline{H}_2$CH$_3$), 3.64 (1H, d, *J* = 14.5 Hz, 1 of C$\underline{H}_2$CC$_6$H$_5$), 3.53 (1H, d, *J* = 14.5 Hz, 1 of C$\underline{H}_2$CC$_6$H$_5$), 4.57 (2H, s, NCC$\underline{H}_2$N), 6.63–6.67 (3H, m, 3 of NC$_6\underline{H}_5$), 7.05 (1H, d, *J* = 7.5 Hz, C$\underline{H}_{Pyr}$), 7.12–7.29 (6H, m, 3 of CC$_6\underline{H}_5$, 2 of NC$_6\underline{H}_5$, C$\underline{H}_{Pyr}$), 7.54 (1H, t, *J* = 7.0 Hz, C$\underline{H}_{Pyr}$), 7.71 (2H, d, *J* = 2 Hz, 2 of CC$_6\underline{H}_5$); δ_C (75 MHz, CDCl$_3$): 11.3, 44.8, 48.9, 55.1, 79.6, 111.09, 115.3, 117.4, 121.9, 125.2, 125.4, 126.4, 128.2, 136.6, 142.0, 146.6, 157.0, 158.2, 176.5; *m/z* (ES+): 377 (100 %, $[MH]^+$), 359 (45 %, $[M–H_2O]^+$), 331 (20 %, $[M–CO_2H]^+$); HRMS (ES+): $C_{23}H_{25}N_2O_3^+$ ($[MH]^+$) requires: 377.1865, found 377.1860.

2. Oxidative Turnover Reactions: Calculation of Product Yields

Products yields from oxidative turnover reactions were calculated using the single point internal standard method. The internal standard method requires calculation of the internal response factor for each compound of interest and then the analysis of the unknown sample. An internal response factor (IRF) was calculated for each observed product (cyclohexane-1,2-diol **15**, cyclohexenol **16**, cyclohexenone **17**, cyclohexene oxide **19**, benzaldehyde and *N*-ethylanilines **9a–d**) using the formula:

$$IRF_A = (Area_{STD} \times Amount_A)/(Amount_{STD} \times Area_A)$$

(where A is the compound of interest and STD is the internal standard). Amounts of products in each reaction sample could then be calculated using the formula

$$Amount_A = (Area_A \times Amount_{IS} \times IRF_A)/(Area_{STD})$$

3. Low Temperature Turnover Reactions: GC Traces

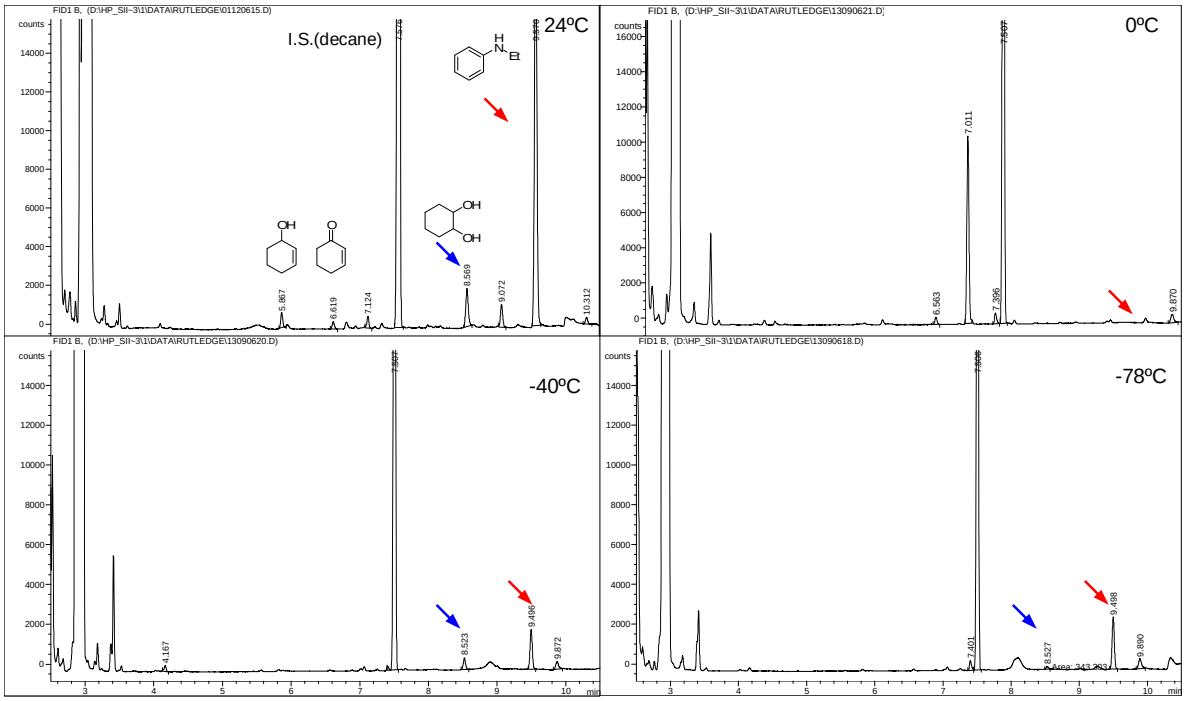

Figure S1: Gas chromatograms for low temperature turnover experiments, showing *N*-ethylaniline **9b** (blue arrows) diol **15** (red arrows), cyclohexenol **16** and cyclohexenone **17** products.

4. Ligand Degradation Experiments: LCMS Traces

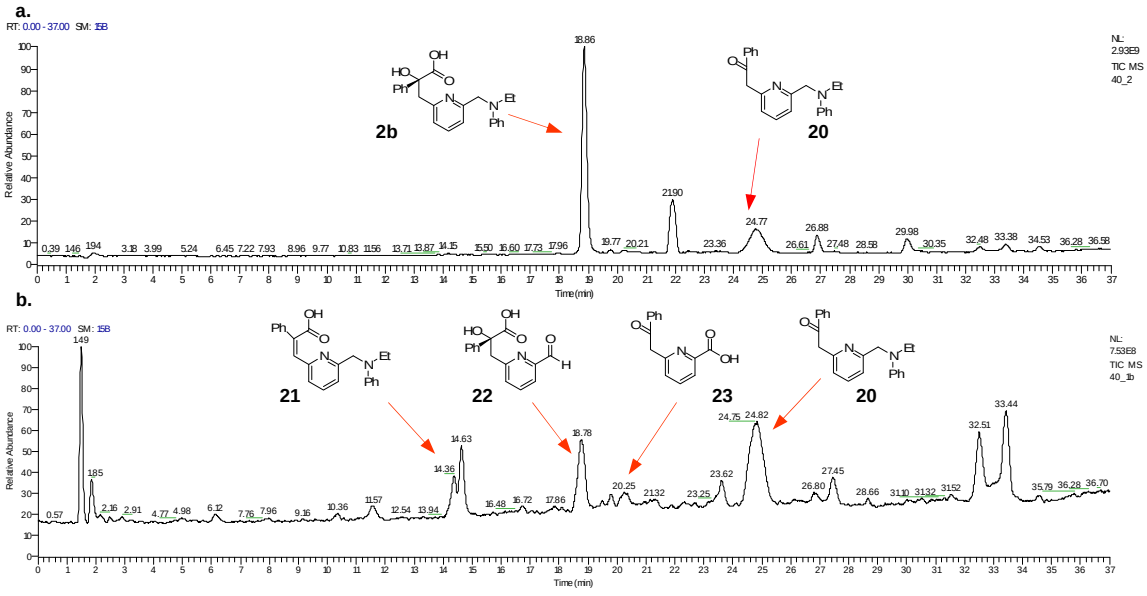

Figure S2: a. Reaction of ligand **2b** with H_2O_2: only a small amount of decarboxylation product **20** is observed; most of the ligand **2b** remains after 17 hours. **b.** Reaction of ligand **2b** with iron(II) acetate and H_2O_2: the ligand **2b** is no longer apparent after 17 hours. The structures of products **20**–**23** are proposed based on their mass spectra ($[MH]^+$: **20** = 331.15, **21** = 359 .88, **22** = 271.08, **23** = 242.22) and expected reaction pathways from Stadtman *et al*.[2]

5. Additional X-Ray Crystallographic Data for 11

(2S,5S)-5-(6-Bromomethylpyridin-2-ylmethyl)-2-tert-butyl-5-phenyl-[1,3]-dioxolan-4-one ***11***

Table S1: Bond lengths [Å] for **11**.

Atom1	Atom2	Length	Atom1	Atom2	Length
Br(1)	C(1)	1.949(3)	C(11)	H(11)	0.9500
C(1)	C(2)	1.502(4)	C(12)	C(13)	1.384(5)
C(1)	H(1A)	0.9900	C(12)	H(12)	0.9500
C(1)	H(1B)	0.9900	C(13)	C(14)	1.396(5)
C(2)	N	1.337(4)	C(13)	H(13)	0.9500
C(2)	C(3)	1.382(5)	C(14)	H(14)	0.9500
C(3)	C(4)	1.389(5)	C(15)	O(1)	1.195(4)
C(3)	H(3)	0.9500	C(15)	O(2)	1.347(4)
C(4)	C(5)	1.392(5)	C(16)	O(4)	1.429(4)
C(4)	H(4)	0.9500	C(16)	O(2)	1.446(4)
C(5)	C(6)	1.380(5)	C(16)	C(17)	1.522(4)
C(5)	H(5)	0.9500	C(16)	H(16)	1.0000
C(6)	N	1.348(4)	C(17)	C(20)	1.529(5)
C(6)	C(7)	1.514(5)	C(17)	C(19)	1.534(5)
C(7)	C(8)	1.540(5)	C(17)	C(18)	1.537(5)
C(7)	H(7A)	0.9900	C(18)	H(18A)	0.9800
C(7)	H(7B)	0.9900	C(18)	H(18B)	0.9800
C(8)	O(4)	1.429(4)	C(18)	H(18C)	0.9800
C(8)	C(9)	1.534(4)	C(19)	H(19A)	0.9800
C(8)	C(15)	1.548(4)	C(19)	H(19B)	0.9800
C(9)	C(14)	1.391(5)	C(19)	H(19C)	0.9800
C(9)	C(10)	1.403(5)	C(20)	H(20A)	0.9800
C(10)	C(11)	1.383(5)	C(20)	H(20B)	0.9800
C(10)	H(10)	0.9500	C(20)	H(20C)	0.9800
C(11)	C(12)	1.392(5)			

Table S2: Bond angles [°] for **11**.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle	Atom2	Atom2	Atom3	Angle
C(2)	C(1)	Br(1)	110.6(2)	C(9)	C(8)	C(7)	112.0(3)	O(2)	C(16)	H(16)	109.4
C(2)	C(1)	H(1A)	109.5	O(4)	C(8)	C(15)	102.4(2)	C(17)	C(16)	H(16)	109.4
Br(1)	C(1)	H(1A)	109.5	C(9)	C(8)	C(15)	108.3(3)	C(16)	C(17)	C(20)	108.2(3)
C(2)	C(1)	H(1B)	109.5	C(7)	C(8)	C(15)	112.3(3)	C(16)	C(17)	C(19)	107.2(3)
Br(1)	C(1)	H(1B)	109.5	C(14)	C(9)	C(10)	119.1(3)	C(20)	C(17)	C(19)	110.3(3)
H(1A)	C(1)	H(1B)	108.1	C(14)	C(9)	C(8)	121.1(3)	C(16)	C(17)	C(18)	111.6(3)
N	C(2)	C(3)	123.2(3)	C(10)	C(9)	C(8)	119.8(3)	C(20)	C(17)	C(18)	109.9(3)
N	C(2)	C(1)	115.0(3)	C(11)	C(10)	C(9)	119.9(3)	C(19)	C(17)	C(18)	109.7(3)
C(3)	C(2)	C(1)	121.8(3)	C(11)	C(10)	H(10)	120.0	C(17)	C(18)	H(18A)	109.5
C(2)	C(3)	C(4)	118.6(3)	C(9)	C(10)	H(10)	120.0	C(17)	C(18)	H(18B)	109.5
C(2)	C(3)	H(3)	120.7	C(10)	C(11)	C(12)	120.8(3)	H(18A)	C(18)	H(18B)	109.5
C(4)	C(3)	H(3)	120.7	C(10)	C(11)	H(11)	119.6	C(17)	C(18)	H(18C)	109.5
C(3)	C(4)	C(5)	118.7(3)	C(12)	C(11)	H(11)	119.6	H(18A)	C(18)	H(18C)	109.5
C(3)	C(4)	H(4)	120.6	C(13)	C(12)	C(11)	119.5(3)	H(18B)	C(18)	H(18C)	109.5
C(5)	C(4)	H(4)	120.6	C(13)	C(12)	H(12)	120.3	C(17)	C(19)	H(19A)	109.5
C(6)	C(5)	C(4)	118.8(3)	C(11)	C(12)	H(12)	120.3	C(17)	C(19)	H(19B)	109.5
C(6)	C(5)	H(5)	120.6	C(12)	C(13)	C(14)	120.2(3)	H(19A)	C(19)	H(19B)	109.5
C(4)	C(5)	H(5)	120.6	C(12)	C(13)	H(13)	119.9	C(17)	C(19)	H(19C)	109.5
N	C(6)	C(5)	122.6(3)	C(14)	C(13)	H(13)	119.9	H(19A)	C(19)	H(19C)	109.5
N	C(6)	C(7)	115.2(3)	C(9)	C(14)	C(13)	120.5(3)	H(19B)	C(19)	H(19C)	109.5
C(5)	C(6)	C(7)	122.2(3)	C(9)	C(14)	H(14)	119.7	C(17)	C(20)	H(20A)	109.5
C(6)	C(7)	C(8)	112.5(3)	C(13)	C(14)	H(14)	119.7	C(17)	C(20)	H(20B)	109.5
C(6)	C(7)	H(7A)	109.1	O(1)	C(15)	O(2)	123.2(3)	H(20A)	C(20)	H(20B)	109.5
C(8)	C(7)	H(7A)	109.1	O(1)	C(15)	C(8)	128.3(3)	C(17)	C(20)	H(20C)	109.5
C(6)	C(7)	H(7B)	109.1	O(2)	C(15)	C(8)	108.3(3)	H(20A)	C(20)	H(20C)	109.5
C(8)	C(7)	H(7B)	109.1	O(4)	C(16)	O(2)	105.4(2)	H(20B)	C(20)	H(20C)	109.5
H(7A)	C(7)	H(7B)	107.8	O(4)	C(16)	C(17)	112.1(3)	C(2)	N	C(6)	117.9(3)
O(4)	C(8)	C(9)	109.6(2)	O(2)	C(16)	C(17)	110.9(3)	C(15)	O(2)	C(16)	109.7(2)
O(4)	C(8)	C(7)	111.7(3)	O(4)	C(16)	H(16)	109.4	C(8)	O(4)	C(16)	109.1(2)

6. Additional X-Ray Crystallographic Data for 12d

(2S,5S)-2-tert-Butyl-5-((6-((diphenylamino)methyl)pyridin-2-yl)methyl)-5-phenyl-1,3-dioxolan-4-one ***12d***

Table S3: Bond lengths [Å] for **12d**.

Atom	Length	Atom	Length	Atom	Length
C(1)–O(3)	1.4186(19)	C(9)–H(9)	0.9500	N(2)–C(27)	1.423(2)
C(1)–O(1)	1.4327(19)	C(10)–C(11)	1.385(3)	C(21)–C(26)	1.398(2)
C(1)–C(2)	1.524(2)	C(10)–H(10)	0.9500	C(21)–C(22)	1.403(2)
C(1)–H(1)	1.0000	C(11)–C(12)	1.374(3)	C(22)–C(23)	1.386(2)
C(2)–C(4)	1.529(3)	C(11)–H(11)	0.9500	C(22)–H(22)	0.9500
C(2)–C(3)	1.529(3)	C(12)–C(13)	1.392(2)	C(23)–C(24)	1.386(3)
C(2)–C(5)	1.533(3)	C(12)–H(12)	0.9500	C(23)–H(23)	0.9500
C(3)–H(3A)	0.9800	C(13)–H(13)	0.9500	C(24)–C(25)	1.382(3)
C(3)–H(3B)	0.9800	C(14)–C(15)	1.517(2)	C(24)–H(24)	0.9500
C(3)–H(3C)	0.9800	C(14)–H(14A)	0.9900	C(25)–C(26)	1.387(2)
C(4)–H(4A)	0.9800	C(14)–H(14B)	0.9900	C(25)–H(25)	0.9500
C(4)–H(4B)	0.9800	C(15)–N(1)	1.335(2)	C(26)–H(26)	0.9500
C(4)–H(4C)	0.9800	C(15)–C(16)	1.392(2)	C(27)–C(28)	1.392(2)
C(5)–H(5A)	0.9800	N(1)–C(19)	1.342(2)	C(27)–C(32)	1.395(2)
C(5)–H(5B)	0.9800	C(16)–C(17)	1.393(2)	C(28)–C(29)	1.385(2)
C(5)–H(5C)	0.9800	C(16)–H(16)	0.9500	C(28)–H(28)	0.9500
O(1)–C(6)	1.3445(19)	C(17)–C(18)	1.383(2)	C(29)–C(30)	1.385(3)
C(6)–O(2)	1.1984(19)	C(17)–H(17)	0.9500	C(29)–H(29)	0.9500
C(6)–C(7)	1.531(2)	C(18)–C(19)	1.388(2)	C(30)–C(31)	1.385(3)
C(7)–O(3)	1.4308(18)	C(18)–H(18)	0.9500	C(30)–H(30)	0.9500
C(7)–C(14)	1.531(2)	C(19)–C(20)	1.511(2)	C(31)–C(32)	1.382(3)
C(7)–C(8)	1.540(2)	C(20)–N(2)	1.4580(19)	C(31)–H(31)	0.9500
C(8)–C(13)	1.385(2)	C(20)–H(20A)	0.9900	C(32)–H(32)	0.9500
C(8)–C(9)	1.390(2)	C(20)–H(20B)	0.9900		
C(9)–C(10)	1.392(2)	N(2)–C(21)	1.400(2)		

Table S4: Bond angles [°] for **12d**.

Atom	Angle	Atom	Angle	Atom	Angle
O(3)–C(1)–O(1)	106.85(12)	C(13)–C(8)–C(7)	121.57(15)	N(2)–C(20)–H(20B)	108.6
O(3)–C(1)–C(2)	113.04(12)	C(9)–C(8)–C(7)	118.96(14)	C(19)–C(20)–H(20B)	108.6
O(1)–C(1)–C(2)	110.82(13)	C(8)–C(9)–C(10)	120.07(16)	H(20A)–C(20)–H(20B)	107.6
O(3)–C(1)–H(1)	108.7	C(8)–C(9)–H(9)	120.0	C(21)–N(2)–C(27)	122.76(13)
O(1)–C(1)–H(1)	108.7	C(10)–C(9)–H(9)	120.0	C(21)–N(2)–C(20)	119.42(13)
C(2)–C(1)–H(1)	108.7	C(11)–C(10)–C(9)	120.14(17)	C(27)–N(2)–C(20)	116.59(13)
C(1)–C(2)–C(4)	107.04(15)	C(11)–C(10)–H(10)	119.9	C(26)–C(21)–N(2)	121.37(14)
C(1)–C(2)–C(3)	111.28(14)	C(9)–C(10)–H(10)	119.9	C(26)–C(21)–C(22)	117.84(15)
C(4)–C(2)–C(3)	110.43(15)	C(12)–C(11)–C(10)	119.76(16)	N(2)–C(21)–C(22)	120.75(14)
C(1)–C(2)–C(5)	107.90(13)	C(12)–C(11)–H(11)	120.1	C(23)–C(22)–C(21)	120.61(15)
C(4)–C(2)–C(5)	109.68(15)	C(10)–C(11)–H(11)	120.1	C(23)–C(22)–H(22)	119.7
C(3)–C(2)–C(5)	110.41(16)	C(11)–C(12)–C(13)	120.49(18)	C(21)–C(22)–H(22)	119.7
C(2)–C(3)–H(3A)	109.5	C(11)–C(12)–H(12)	119.8	C(22)–C(23)–C(24)	120.83(16)
C(2)–C(3)–H(3B)	109.5	C(13)–C(12)–H(12)	119.8	C(22)–C(23)–H(23)	119.6
H(3A)–C(3)–H(3B)	109.5	C(8)–C(13)–C(12)	120.11(17)	C(24)–C(23)–H(23)	119.6
C(2)–C(3)–H(3C)	109.5	C(8)–C(13)–H(13)	119.9	C(25)–C(24)–C(23)	119.00(15)
H(3A)–C(3)–H(3C)	109.5	C(12)–C(13)–H(13)	119.9	C(25)–C(24)–H(24)	120.5
H(3B)–C(3)–H(3C)	109.5	C(15)–C(14)–C(7)	115.16(13)	C(23)–C(24)–H(24)	120.5
C(2)–C(4)–H(4A)	109.5	C(15)–C(14)–H(14A)	108.5	C(24)–C(25)–C(26)	120.71(16)
C(2)–C(4)–H(4B)	109.5	C(7)–C(14)–H(14A)	108.5	C(24)–C(25)–H(25)	119.6
H(4A)–C(4)–H(4B)	109.5	C(15)–C(14)–H(14B)	108.5	C(26)–C(25)–H(25)	119.6
C(2)–C(4)–H(4C)	109.5	C(7)–C(14)–H(14B)	108.5	C(25)–C(26)–C(21)	120.90(15)
H(4A)–C(4)–H(4C)	109.5	H(14A)–C(14)–H(14B)	107.5	C(25)–C(26)–H(26)	119.5
H(4B)–C(4)–H(4C)	109.5	N(1)–C(15)–C(16)	122.67(14)	C(21)–C(26)–H(26)	119.5
C(2)–C(5)–H(5A)	109.5	N(1)–C(15)–C(14)	116.53(14)	C(28)–C(27)–C(32)	118.90(15)
C(2)–C(5)–H(5B)	109.5	C(16)–C(15)–C(14)	120.74(14)	C(28)–C(27)–N(2)	121.87(14)
H(5A)–C(5)–H(5B)	109.5	C(15)–N(1)–C(19)	118.57(14)	C(32)–C(27)–N(2)	119.06(15)
C(2)–C(5)–H(5C)	109.5	C(15)–C(16)–C(17)	118.33(15)	C(29)–C(28)–C(27)	120.33(16)
H(5A)–C(5)–H(5C)	109.5	C(15)–C(16)–H(16)	120.8	C(29)–C(28)–H(28)	119.8
H(5B)–C(5)–H(5C)	109.5	C(17)–C(16)–H(16)	120.8	C(27)–C(28)–H(28)	119.8
C(6)–O(1)–C(1)	109.49(12)	C(18)–C(17)–C(16)	119.16(15)	C(30)–C(29)–C(28)	120.62(17)
O(2)–C(6)–O(1)	123.24(15)	C(18)–C(17)–H(17)	120.4	C(30)–C(29)–H(29)	119.7
O(2)–C(6)–C(7)	128.15(14)	C(16)–C(17)–H(17)	120.4	C(28)–C(29)–H(29)	119.7
O(1)–C(6)–C(7)	108.41(12)	C(17)–C(18)–C(19)	118.73(15)	C(31)–C(30)–C(29)	119.09(17)
O(3)–C(7)–C(6)	103.06(12)	C(17)–C(18)–H(18)	120.6	C(31)–C(30)–H(30)	120.5
O(3)–C(7)–C(14)	111.16(13)	C(19)–C(18)–H(18)	120.6	C(29)–C(30)–H(30)	120.5
C(6)–C(7)–C(14)	113.37(12)	N(1)–C(19)–C(18)	122.53(15)	C(32)–C(31)–C(30)	120.76(17)

O(3)–C(7)–C(8)	109.85(13)	N(1)–C(19)–C(20)	114.29(14)	C(32)–C(31)–H(31)	119.6
C(6)–C(7)–C(8)	110.37(13)	C(18)–C(19)–C(20)	123.00(14)	C(30)–C(31)–H(31)	119.6
C(14)–C(7)–C(8)	108.91(13)	N(2)–C(20)–C(19)	114.71(13)	C(31)–C(32)–C(27)	120.28(17)
C(1)–O(3)–C(7)	110.04(11)	N(2)–C(20)–H(20A)	108.6	C(31)–C(32)–H(32)	119.9
C(13)–C(8)–C(9)	119.40(15)	C(19)–C(20)–H(20A)	108.6	C(27)–C(32)–H(32)	119.9

6. References

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