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p-Tolylimido rhenium(V) complexes with phenolate-based ligands: synthesis, X-ray studies and catalytic activity in oxidation with *tert*-butylhydroperoxide

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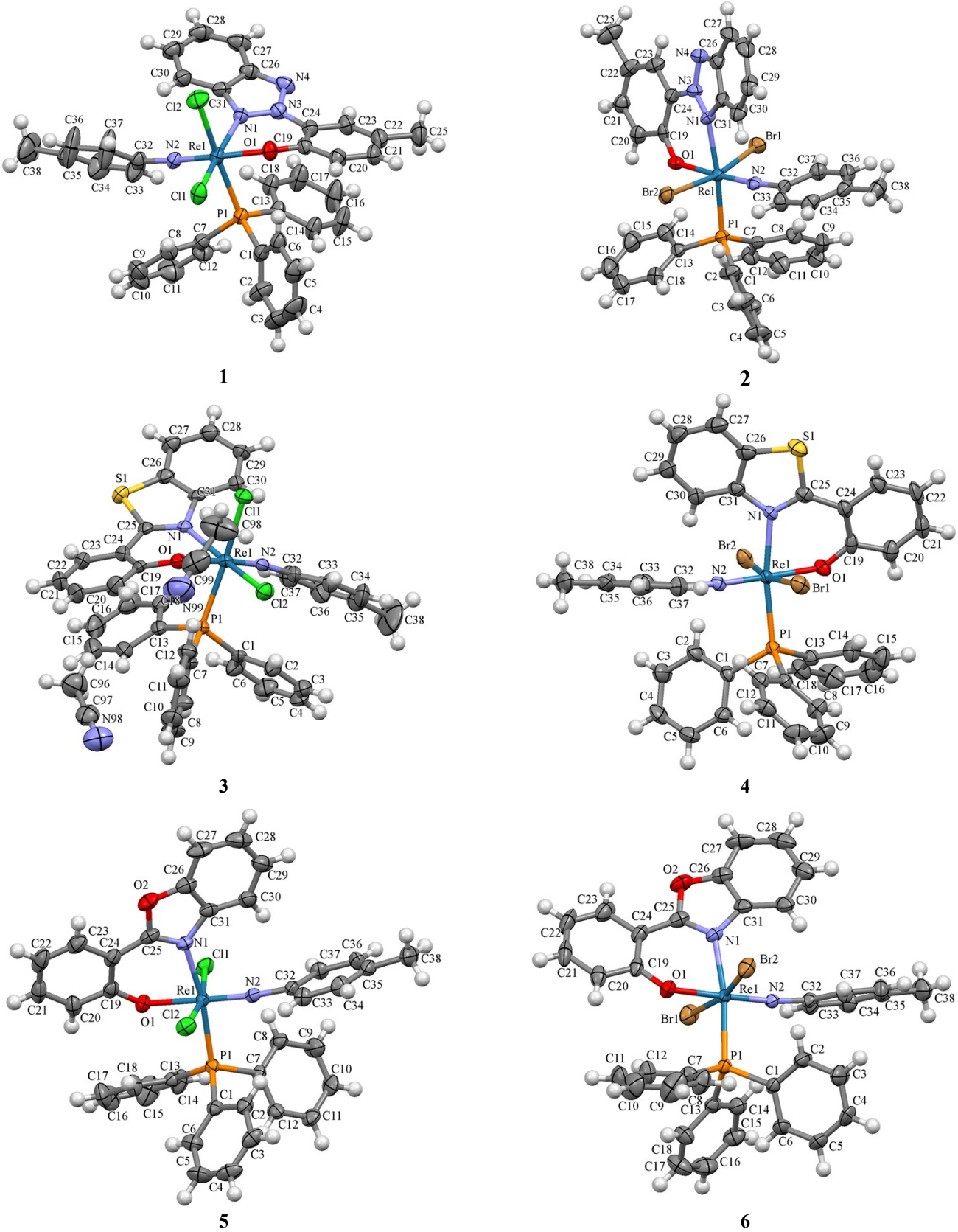


Fig. S1 The perspective view of the molecular structure of **1-6** showing the atom numbering. Displacement ellipsoids are drawn at 50% probability.

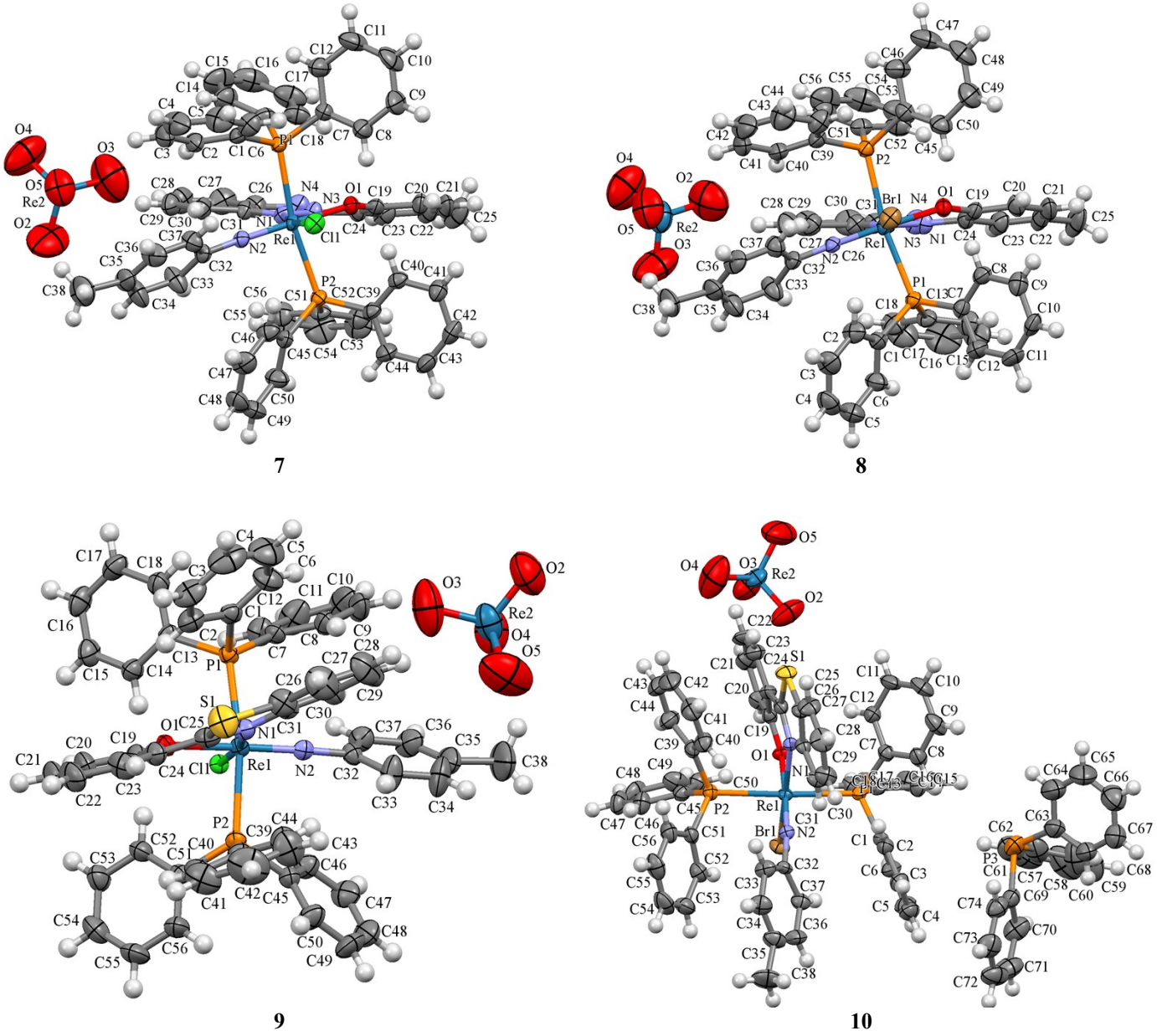


Fig. S2 The perspective view of the molecular structure of **7**–**10** showing the atom numbering. Displacement ellipsoids are drawn at 50% probability

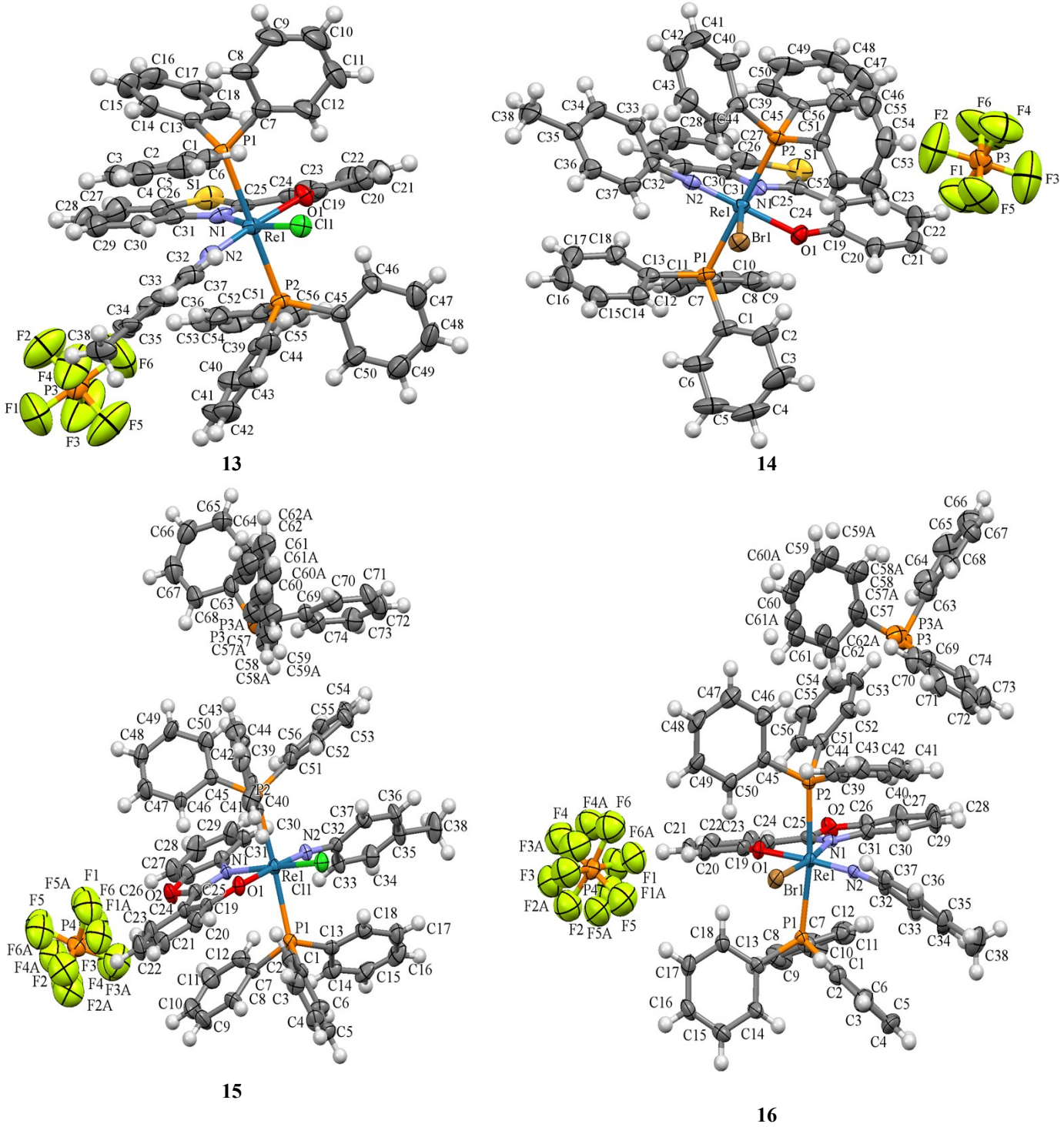


Fig. S3 The perspective view of the molecular structure of **13–16** showing the atom numbering. Displacement ellipsoids are drawn at 50% probability.

Table S1 Short intra- and intermolecular contacts detected in structures **2–6**

D—H•••A	D—H [Å]	H•••A [Å]	D•••A [Å]	D—H•••A [°]
		2		
C(2)–H(2)•••Br(2)	0.93	2.79	3.603(14)	146.9
C(26)–H(26)•••N(4)	0.93	2.39	2.729(16)	101.3
C(31)–H(31A)•••Br(2)#1	0.96	2.88	3.778(15)	156.0
		3		
C(12)—H(12)•••Cl(2)	0.93	2.71	3.292(6)	121.3
C(12)—H(12)•••O(1)	0.93	2.40	3.127(7)	134.7
C(30)—H(30)•••N(2)	0.93	2.44	3.099(8)	127.5
C(23)—H(23)•••S(1)	0.93	2.67	3.040(7)	104.5
		4		
C(2)—H(2)•••Br(2)	0.93	2.80	3.629(5)	148.7
C(30)—H(30)•••N(2)	0.93	2.47	3.025(5)	118.6
C(23)—H(23)•••S(1)	0.93	2.60	3.031(5)	108.5
		5		
C(8)—H(8)•••Cl(1)	0.93	2.68	3.523(3)	150.3
C(23)—H(23)•••O(2)	0.93	2.46	2.777(4)	100.1
		6		
C(2)—H(2)•••Br(2)	0.93	2.74	3.583(5)	151.2
C(23)—H(23)•••O(2)	0.93	2.47	2.787(8)	100.2

Symmetry transformations used to generate equivalent atoms: #1: -1+x,y,z

Table S2 Short intra- and intermolecular contacts detected in structures **7**–**10**

D—H•••A	D—H [Å]	H•••A [Å]	D•••A [Å]	D—H•••A [°]
		7		
C(8)—H(8)•••Cl(1)	0.93	2.77	3.461(6)	131.9
C(8)—H(8)•••O(1)	0.93	2.37	2.995(6)	124.1
C(23)—H(23)•••N(4)	0.93	2.42	2.740(8)	99.8
C(30)—H(30)•••N(2)	0.93	2.51	3.165(7)	127.5
C(40)—H(40)•••Cl(1)	0.93	2.80	3.431(5)	126.0
C(40)—H(40)•••O(1)	0.93	2.38	3.098(6)	134.1
		8		
O(99)—H(99A)•••O(2)	0.85	2.14	2.99(2)	173.5
C(8)—H(8)•••Br(1)	0.93	2.90	3.521(6)	125.4
C(8)—H(8)•••O(1)	0.93	2.39	3.113(7)	133.9
C(23)—H(23)•••N(4)	0.93	2.43	2.753(9)	100.1
C(29)—H(29)•••N(2)	0.93	2.53	3.197(8)	128.7
C(50)—H(50)•••Br(1)	0.93	2.91	3.566(7)	128.8
C(50)—H(50)•••O(1)	0.93	2.34	3.000(8)	127.3
		9		
C(14)–H(14)•••Cl(1)	0.93	2.72	3.410(6)	131.9
C(14)–H(14)•••O(1)	0.93	2.43	3.043(7)	123.8
C(23)–H(23) •••S(1)	0.93	2.59	2.999(7)	107.4
C(23)–H(23)•••O(2)#1	0.93	2.54	3.411(10)	155.7
C(29)–H(29)•••O(3)	0.93	2.50	3.243(10)	137.3
C(30)–H(30)•••N(2)	0.93	2.34	3.044(7)	132.4
C(42)–H(42)•••O(4)#1	0.93	2.53	3.339(10)	145.5
C(46)–H(46)•••Cl(1)	0.93	2.79	3.653(6)	153.9
C(52)–H(52)•••Cl(1)	0.93	2.81	3.456(5)	127.7
C(52)–H(52)•••O(1)	0.93	2.36	3.077(7)	133.8
		10		
C(9)—H(9)•••O(5)#2	0.93	2.59	3.441(8)	152.8
C(15)—H(15)•••O(3)#3	0.93	2.57	3.421(7)	152.7
C(18)—H(18)•••Br(1)	0.93	2.83	3.470(4)	126.8
C(18)—H(18)•••O(1)	0.93	2.50	3.183(6)	130.2
C(23)—H(23)•••S(1)	0.93	2.56	2.981(5)	108.8
C(27)—H(27)•••O(2)	0.93	2.50	3.253(7)	138.3
C(28)—H(28)•••Br(1)#4	0.93	2.91	3.723(6)	147.5
C(30)—H(30)•••N(2)	0.93	2.28	2.996(6)	133.2
C(50)—H(50)•••O(1)	0.93	2.39	3.198(5)	144.7
C(52)—H(52)•••Br(1)	0.93	2.91	3.728(5)	144.0

Symmetry transformations used to generate equivalent atoms: #1: 1/2+x,3/2-y,-1/2+z; #2: 1-x,2-y,1-z; #3: 2-x,2-y,1-z; #4: -1+x,y,z

Table S3 Short intra- and intermolecular contacts detected in structures **13–16**

D—H•••A	D—H [Å]	H•••A [Å]	D•••A [Å]	D—H•••A [°]
		13		
C(12)—H(12)•••O(1)	0.93	2.44	3.242(15)	145.1
C(23)—H(23)•••S(1)	0.93	2.59	2.999(16)	107.3
C(30)—H(30)•••N(2)	0.93	2.34	3.068(14)	134.8
C(34)—H(34)•••F(4)	0.93	2.53	3.246(16)	133.6
C(36)—H(36)•••F(3)#2	0.93	2.36	3.285(17)	172.0
C(54)—H(54)•••Cl(1)#8	0.93	2.77	3.684(14)	166.3
		14		
C(2)—H(2)•••O(1)	0.93	2.45	3.263(10)	145.8
C(23)—H(23)•••S(1)	0.93	2.58	2.991(9)	107.3
C(30)—H(30)•••N(2)	0.93	2.34	3.079(8)	136.3
C(36)—H(36)•••F(6)#1	0.93	2.44	3.360(10)	171.9
C(44)—H(44)•••Br(1)	0.93	2.92	3.750(7)	148.6
C(48)—H(48)••Br(1)#2	0.93	2.81	3.710(8)	163.4
C(52)—H(52)•••Br(1)	0.93	2.92	3.573(7)	128.1
C(52)—H(52)•••O(1)	0.93	2.59	3.336(8)	137.4
		15		
C(2)—H(2)•••O(1)	0.93	2.41	3.191(11)	142.0
C(3)—H(3)•••F(3A)#3	0.93	2.17	3.081(15)	168.0
C(20)—H(20)•••F(4A)#3	0.93	2.54	3.157(16)	124.0
C(20)—H(20)•••F(6)#3	0.93	2.43	3.341(18)	167.0
C(23)—H(23)•••F(1A)	0.93	2.46	3.390(18)	174.0
C(23)—H(23)•••O(2)	0.93	2.43	2.749(13)	100.0
C(27)—H(27)•••F(5A)	0.93	2.48	3.346(18)	156.0
C(27)—H(27)•••F(6)	0.93	2.52	3.441(18)	169.0
C(30)—H(30)•••N(2)	0.93	2.55	3.184(13)	126.0
C(40)—H(40)•••Cl(1)	0.93	2.73	3.371(9)	127.0
C(40)—H(40)•••O(1)	0.93	2.53	3.231(11)	133.0
C(42)—H(42)•••F(1)#4	0.93	2.39	2.993(16)	123.0
C(43)—H(43)•••F(1)#4	0.93	2.47	3.039(16)	119.0
C(49)—H(49)•••F(5)#5	0.93	2.55	3.300(18)	138.0
C(67)—H(67)•••F(2A)#5	0.93	2.49	3.41(2)	170.0
		16		
C(17)—H(17)•••F(5)	0.93	2.18	3.080(14)	162.0
C(18)—H(18)•••O(1)	0.93	2.43	3.223(8)	143.0
C(20)—H(20)•••F(1)	0.93	2.54	3.161(13)	124.0
C(20)—H(20)•••F(6A)	0.93	2.53	3.442(14)	168.0
C(23)—H(23)•••F(3)#6	0.93	2.53	3.450(12)	173.0
C(23)—H(23)•••O(2)	0.93	2.45	2.766(9)	100.0
C(27)—H(27)•••F(6A)#6	0.93	2.49	3.406(16)	168.0
C(30)—H(30)•••N(2)	0.93	2.54	3.177(9)	126.0
C(47)—H(47)•••F(3A)#7	0.93	2.44	3.077(13)	126.0
C(50)—H(50)•••Br(1)	0.93	2.83	3.447(7)	125.0
C(50)—H(50)•••O(1)	0.93	2.50	3.211(8)	133.0

Symmetry transformations used to generate equivalent atoms: #1: 1-x,-1/2+y,1/2-z; #2: x,1+y,z; #3: -1+x,y,z; #4: 1-x,-y,-z; #5: 2-x,-y,-z; #6: 1+x,y,z; #7: -x,1-y,1-z; #8: x,-1+y,z

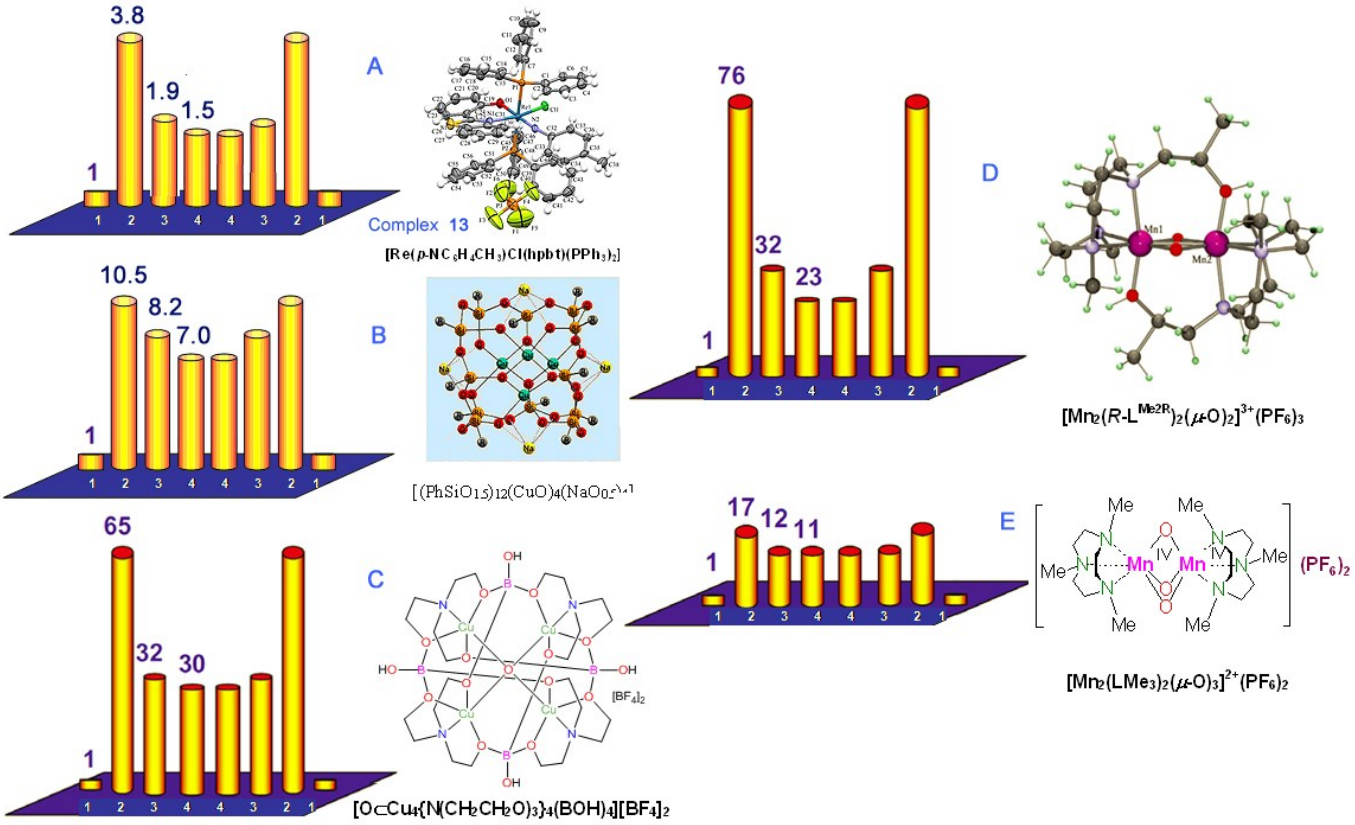


Fig. S4 The regioselectivity profiles for the oxidation of *n*-octane in acetonitrile by the systems: **13**/TBHP (A) (this work), complex $[(PhSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4]$/TBHP (B) (Ref. 33*p*), $[O\subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$/TBHP (C) (Ref. 33*q*), complex $[Mn_2(R\text{-}L^{Me2R})_2(\mu\text{–}O)_2]^{3+}(PF_6)_3$ (where L^{Me2R} is 1-(2-hydroxypropyl)-4,7-dimethyl-1,4,7-triazacyclononane)/oxalic acid/TBHP (D) (Ref. 33*l*), complex $[Mn_2(LMe_3)_2(\mu\text{-}O)_3]^{2+}(PF_6)_2$ (where LMe_3 is 1,4,7-trimethyl-1,4,7-triazacyclononane)/oxalic acid/TBHP (E) (see Ref.: Y. N. Kozlov, G. V. Nizova and G. B. Shul'pin, *J. Phys. Org. Chem.*, 2008, **21**, 119.). Bars correspond to the normalized reactivities of methylene protons in positions C(2), C(3) and C(4) of the octane chain relative to the reactivity (defined as a unity) of methyl protons in position C(1). All parameters were measured after reduction of the reaction mixtures with PPh_3 before GC analysis and calculated based on the ratios of isomeric alcohols.

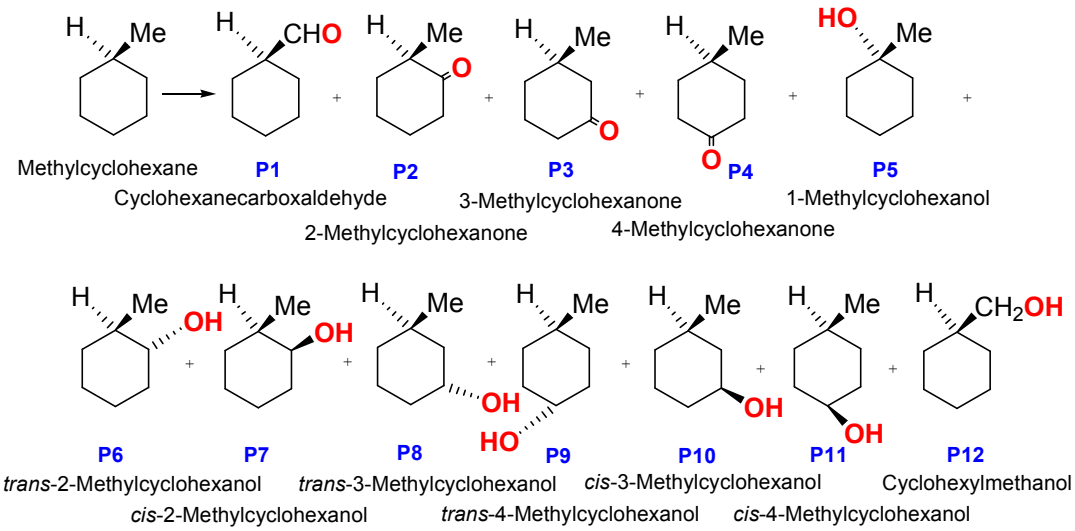
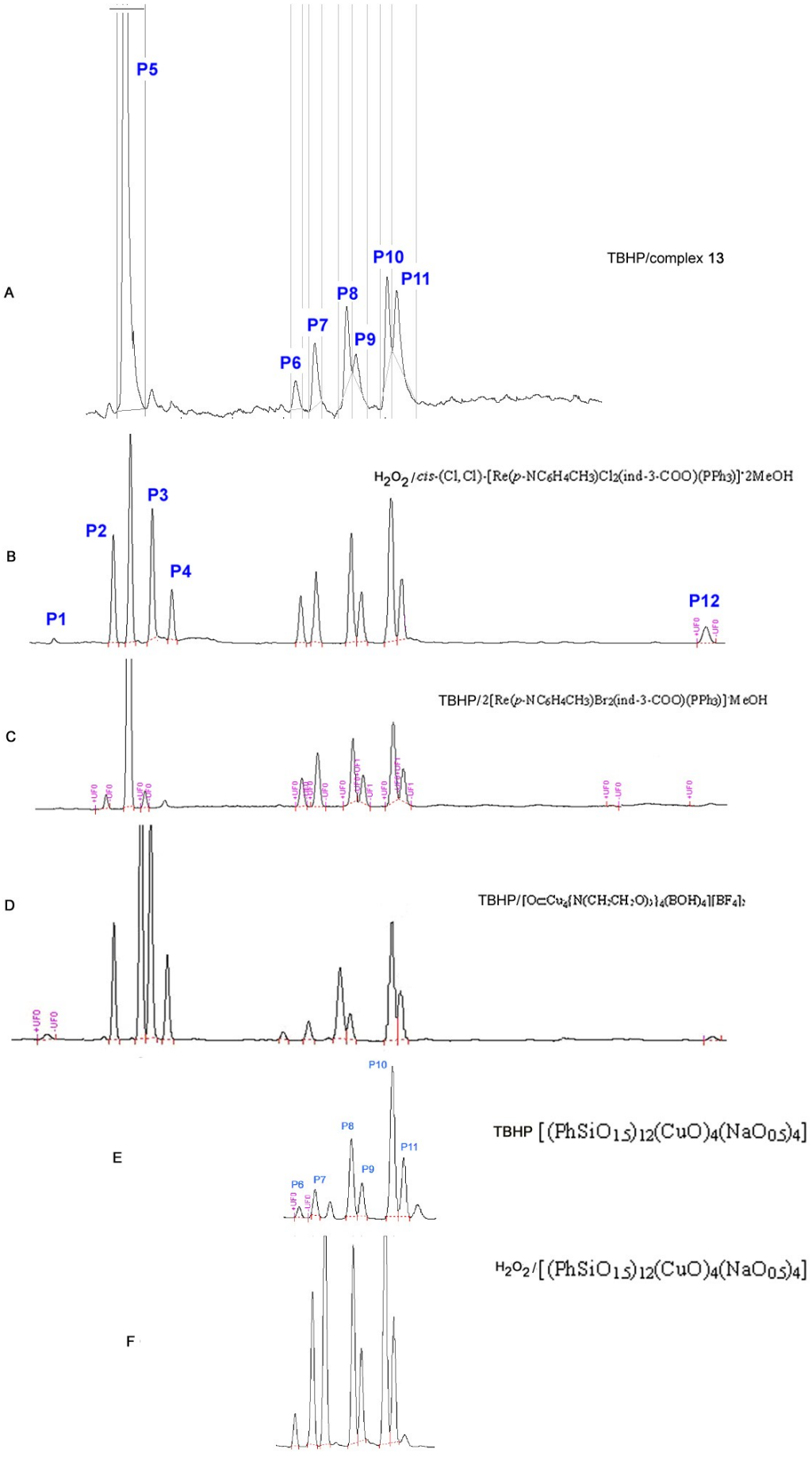


Fig. S5a Isomeric products formed in the methylcyclohexane oxidation.


A
P5
P6
P7
P8
P9
P10
P11
TBHP/complex 13
B
P1
P2
P3
P4
P12
H2O2/cis-(Cl,Cl)-[Re(p-NC6H4CH3)Cl2(ind-3-COO)(PPh3)]·2MeOH
C
TBHP/2[Re(p-NC6H4CH3)Br2(ind-3-COO)(PPh3)]·MeOH
D
TBHP/[OCu4{N(CH2CH2O)3}4(BOH)4][BF4]2
E
TBHP [(PhSiO1.5)12(CuO)4(NaO0.5)4]
F
H2O2/[(PhSiO1.5)12(CuO)4(NaO0.5)4]

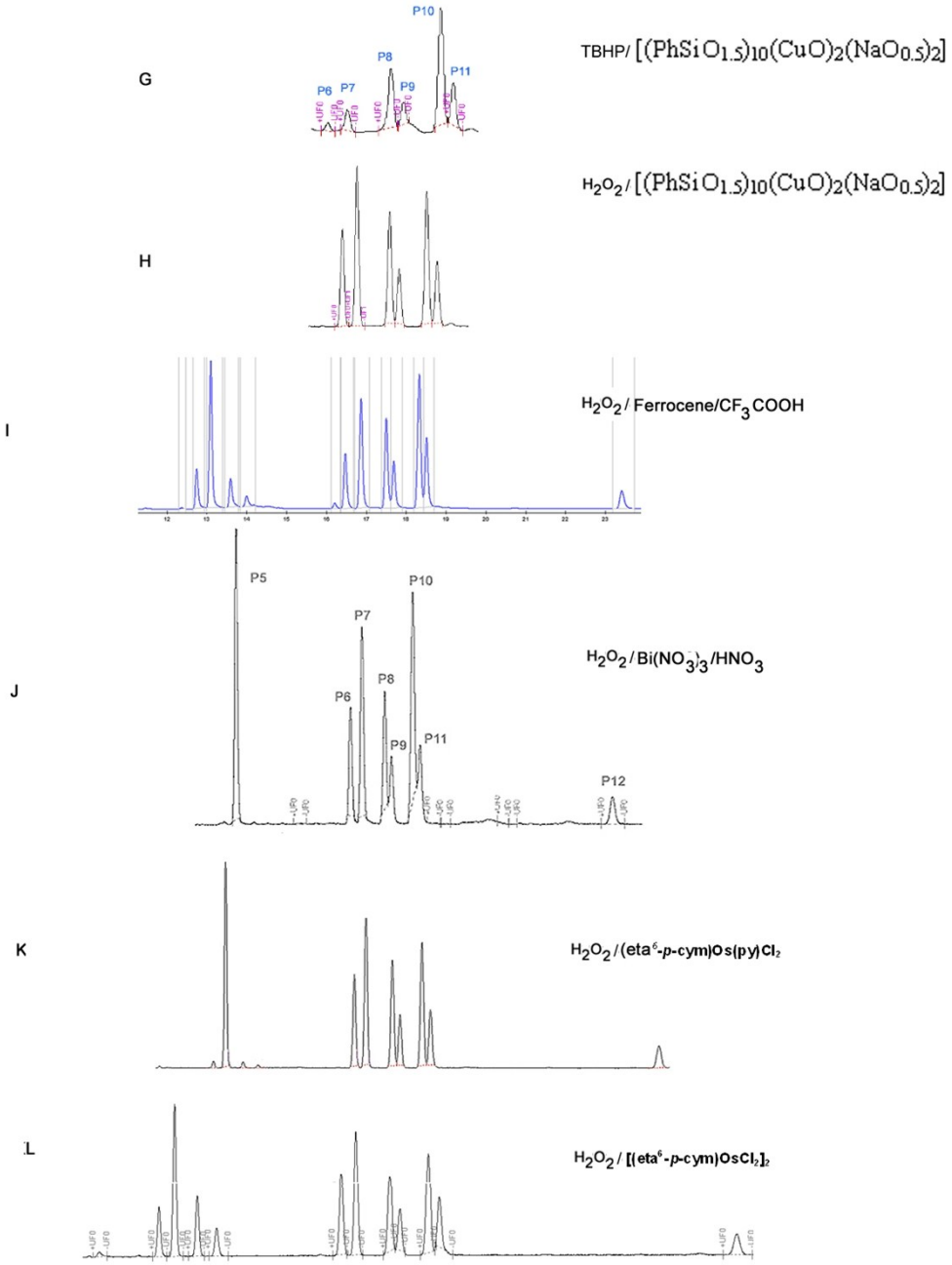


Fig. S5b Chromatograms of products obtained in oxidations of methylcyclohexane by various systems. The pictures are taken from: **A** (this work), **B** (Ref. 18*a*), **C** (Ref. 18*a*), **D** (Ref. 33*q*), **E** (Ref. 33*p*), **F** (Ref. 33*p*), **G** (Ref. 33*p*), **H** (Ref. 33*p*), **I** (Ref. 33*s*), **J** (Ref. 33*n*), **K** (Ref. 33*e*), **L** (Ref. 33*d*).