Supporting Information

Di-*tert*-butylcatecholate derivatives of titanocene

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Table S1. Crystal Data and Data Collection and Refinement Details

	1	**2**
Chemical formula	$C_{24}H_{30}O_2Ti$	$C_{43}H_{55}O_4Ti_2$
M_r	398.38	731.67
Crystal system, space group	Orthorhombic, *Pnma*	Monoclinic, $P2_1$
Temperature (K)	150	173
a (Å)	14.9844(6)	10.1699(18)
b (Å)	17.5943(7)	32.789(6)
c (Å)	7.8829(3)	11.604(2)
β (°)	90	96.672(4)
V (Å^3)	2078.25(14)	3843.3(12)
Z	4	4
μ (mm^{-1})	0.43	0.46
Crystal size (mm)	0.42 × 0.40 × 0.40	0.25 × 0.12 × 0.10
F(000)	848	1556
Θ range (°)	2.719–26.353	1.767–26.372
h, k, l limits	–18 ≤ *h* ≤ 17, –21 ≤ *k* ≤ 14, –9 ≤ *l* ≤ 9	–12 ≤ *h* ≤ 12, –40 ≤ *k* ≤ 40, –14 ≤ *l* ≤ 14
Reflections measured, independent and observed [$I > 2\sigma(I)$]	11391, 2183, 2115	30499, 14812, 12535
R_{int}	0.0198	0.0359
R_1, wR_2 [$F^2 > 2\sigma(F^2)$]	0.0341, 0. 0885	0.0408, 0.0870
R_1, wR_2 (all data)	0.0353, 0.0896	0.0531, 0.0910
GOOF	1.063 (1.214)	1.031
No. of parameters	180	908
No. of restraints	48	1
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, –0.37	0.49, –0.31
CCDC	1895786	1895787

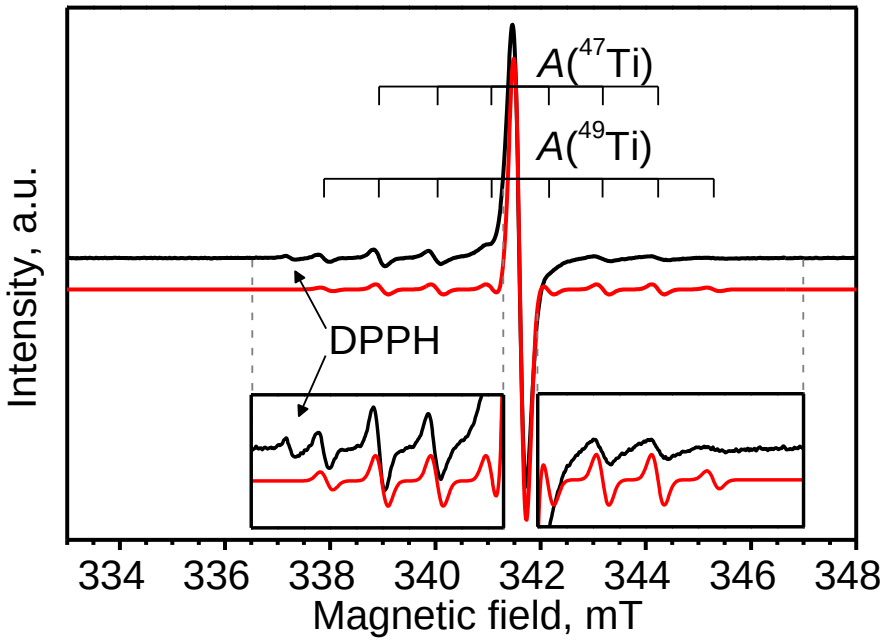

Fig. S1. ESR spectrum of THF solution of complex **2** at 300K in X-frequency band (black – experimental spectrum, red – simulation). In insets, the hyperfine structure of the high-gain ESR spectrum is shown.

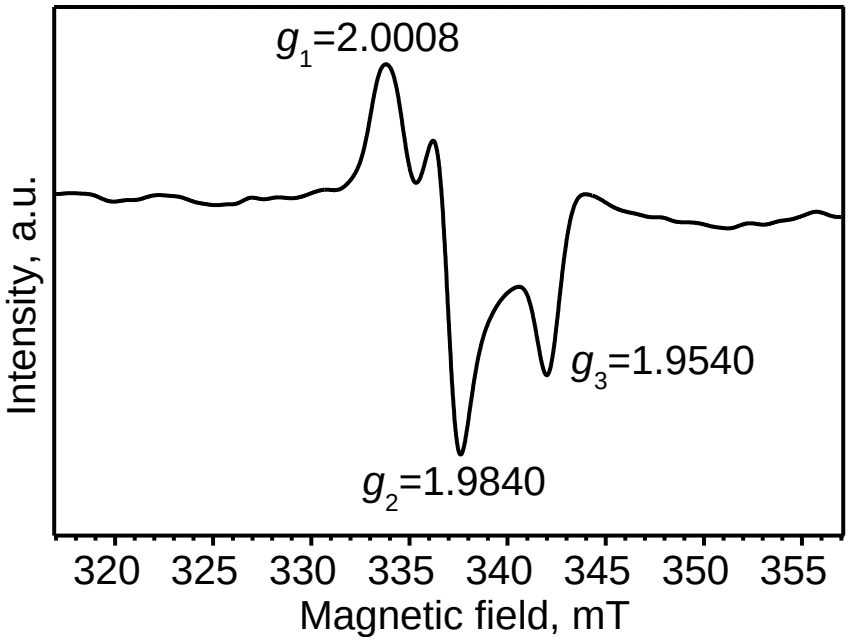

Fig. S2. EPR spectrum of frozen THF solution of complex **2** at 77K

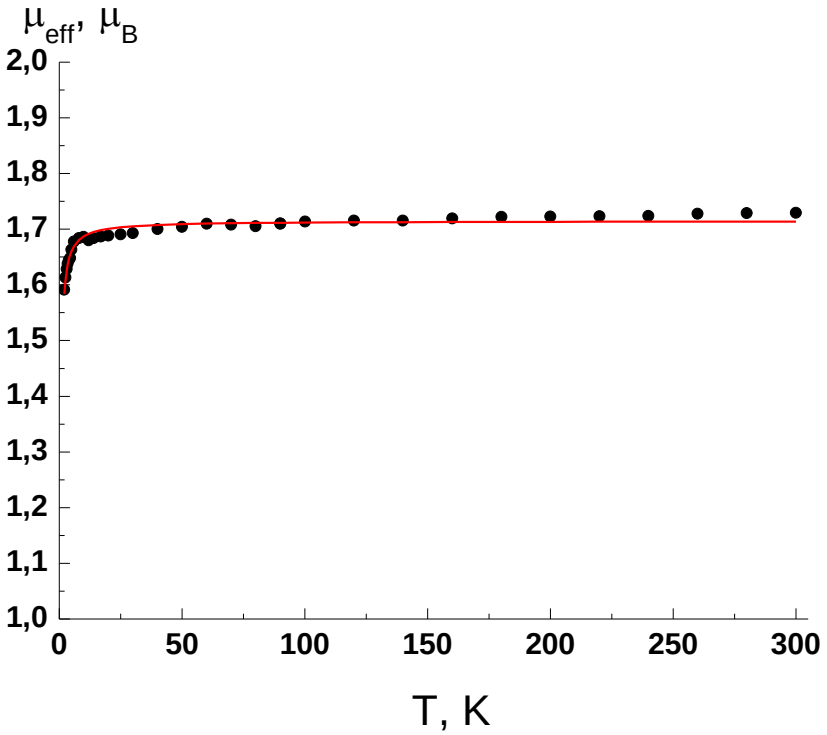

Fig. S3. μ_{eff} vs. T plot for the polycrystalline sample of complex **2** (solid line – theoretical curve).

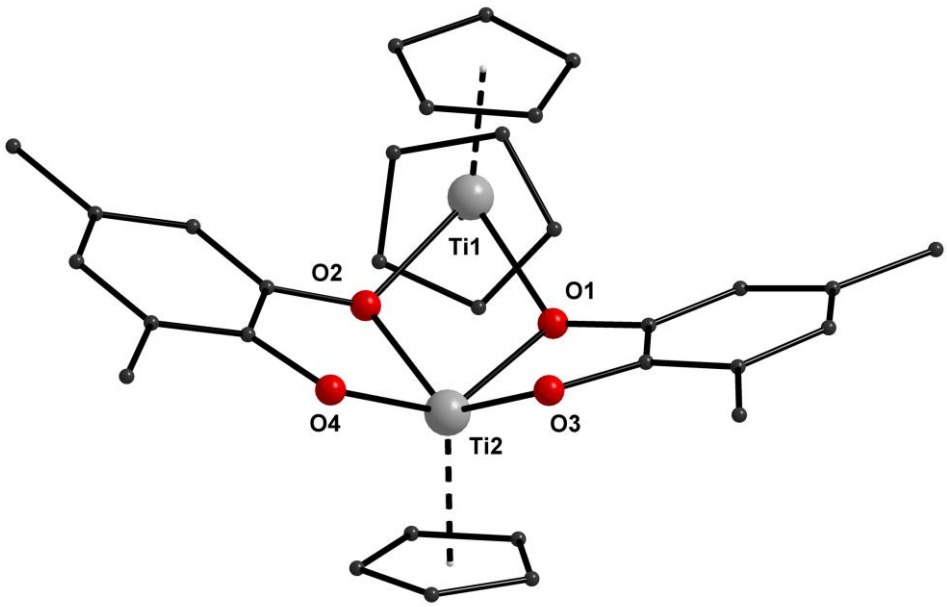

Fig. S4. Structure of model complex **2m** used for DFT calculations.

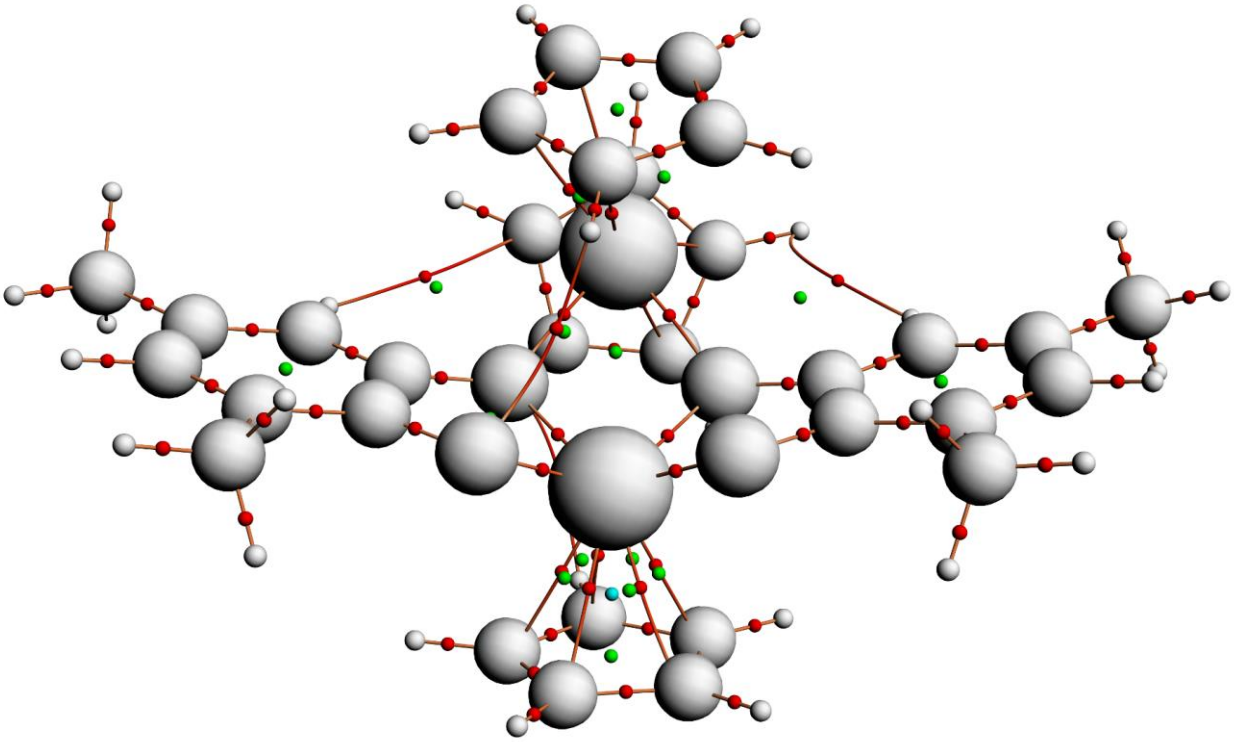

Fig. S5. Critical points of electron density in complex **2m**.

Table S2. The energy values (eV) and occupations (electrons) of frontier orbitals of **2m**.

	BP86	B3LYP	M06L
LUMO+1	–3.480 (0.00)	–2.535 (0.00)	–2.903 (0.00)
LUMO	–3.465 (0.00)	–2.533 (0.00)	–2.894 (0.00)
SOMO	–3.836 (1.00)	–5.333 (1.00)	–3.616 (1.00)
SOMO–1 αβ	–5.000 (2.00)	–5.505 (2.00)	–4.650 (2.00)

Table S3. Hirshfeld and Bader charge analysis of **2m**.

Hirshfeld charges	BP86	B3LYP	M06L
Ti1	0.3110	0.3899	0.3630
Ti2	0.4701	0.5657	0.5365
O1	–0.1824	–0.2185	–0.2087
O2	–0.1815	–0.2177	–0.2080
O3	–0.2060	–0.2366	–0.2371
O4	–0.2051	–0.2368	–0.2363

Bader charges	BP86	B3LYP	M06L
Ti1	1.5555	1.6522	1.6191
Ti2	1.9185	2.0564	1.9953
O1	–1.0631	–1.1273	–1.0545
O2	–1.0637	1.1217	–1.0495
O3	–0.9923	–1.0341	–0.9446
O4	–0.9889	–1.0441	–0.9422

Table S4. BCP properties for Ti bonds, values in a.u.

			BP86							
Bond	Distance, Å	BP length, Å	ρ(r)	Δρ(r)	G(r)	V(r)	H(r)	$-\frac{1}{4}\nabla^2\rho(r)$	H(r)/ρ(r)	|V(r)|/ G(r)
Ti2-C21	2,3965	2,4228	0,0469	0,1389	0,0406	-0,0466	-0,0059	-0,0347	-0,1264	1,1458
Ti2-C22	2,3812	2,4140	0,0482	0,1475	0,0429	-0,0489	-0,0060	-0,0369	-0,1249	1,1403
Ti2-C23	2,3634	2,3683	0,0500	0,1410	0,0430	-0,0508	-0,0078	-0,0352	-0,1552	1,1805
Ti2-C25	2,4129	2,4205	0,0455	0,1394	0,0399	-0,0449	-0,0050	-0,0348	-0,1102	1,1257
Ti2-O5	1,9062	1,9082	0,1205	0,4661	0,1620	-0,2076	-0,0455	-0,1165	-0,3778	1,2808
Ti2-O6	1,9050	1,9074	0,1202	0,4696	0,1624	-0,2073	-0,0450	-0,1174	-0,3739	1,2769
Ti2-O3	2,0621	2,0631	0,0812	0,3109	0,0956	-0,1134	-0,0178	-0,0777	-0,2196	1,1866
Ti2-O4	2,0613	2,0624	0,0812	0,3126	0,0958	-0,1134	-0,0176	-0,0782	-0,2173	1,1841
Ti1-O3	2,1176	2,1214	0,0638	0,2963	0,0787	-0,0832	-0,0046	-0,0741	-0,0718	1,0582
Ti1-O4	2,1220	2,1247	0,0637	0,2920	0,0778	-0,0826	-0,0048	-0,0730	-0,0756	1,0618
Ti1-C9	2,3505	2,3687	0,0496	0,1593	0,0458	-0,0518	-0,0060	-0,0398	-0,1204	1,1304
Ti1-C10	2,3481	2,3521	0,0523	0,1430	0,0448	-0,0539	-0,0091	-0,0358	-0,1736	1,2025
Ti1-C12	2,3603	2,3669	0,0485	0,1576	0,0448	-0,0502	-0,0054	-0,0394	-0,1110	1,1202
Ti1-C13	2,3675	2,3713	0,0494	0,1390	0,0423	-0,0498	-0,0075	-0,0348	-0,1520	1,1777
Ti1-C16	2,3688	2,3854	0,0499	0,1408	0,0429	-0,0505	-0,0077	-0,0352	-0,1536	1,1787

Table S4 (continued)

			B3LYP							
Bond	Distance, Å	BP length, Å	ρ(r)	Δρ(r)	G(r)	V(r)	H(r)	- ¼∇^2ρ(r)	H(r)/ρ(r)	|V(r)|/ G(r)
Ti2-C25	2,4452	2,4993	0,0472	0,1277	0,0390	-0,0461	-0,0071	-0,0319	-0,1497	1,1812
Ti2-C23	2,3931	2,3997	0,0425	0,1281	0,0362	-0,0404	-0,0042	-0,0320	-0,0990	1,1162
Ti2-C21	2,4467	2,4824	0,0422	0,1259	0,0357	-0,0399	-0,0042	-0,0315	-0,0994	1,1176
Ti2-O5	1,8892	1,8914	0,1260	0,4838	0,1716	-0,2223	-0,0507	-0,1209	-0,4020	1,2952
Ti2-O6	1,8918	1,8940	0,1252	0,4805	0,1701	-0,2200	-0,0499	-0,1201	-0,3988	1,2936
Ti2-O3	2,0667	2,0675	0,0801	0,3088	0,0942	-0,1112	-0,0170	-0,0772	-0,2122	1,1804
Ti2-O4	2,0619	2,0627	0,0809	0,3133	0,0957	-0,1131	-0,0174	-0,0783	-0,2145	1,1814
Ti1-O3	2,1607	2,1681	0,0560	0,2705	0,0686	-0,0697	-0,0010	-0,0676	-0,0182	1,0149
Ti1-O4	2,1537	2,1605	0,0571	0,2755	0,0703	-0,0716	-0,0014	-0,0689	-0,0241	1,0196
Ti1-C8	2,4583	2,4704	0,0400	0,1258	0,0344	-0,0373	-0,0029	-0,0315	-0,0734	1,0854
Ti1-C10	2,4123	2,4179	0,0459	0,1248	0,0377	-0,0442	-0,0065	-0,0312	-0,1417	1,1725
Ti1-C12	2,4164	2,4225	0,0428	0,1434	0,0390	-0,0421	-0,0031	-0,0359	-0,0723	1,0795
Ti1-C13	2,4114	2,4158	0,0451	0,1243	0,0371	-0,0432	-0,0061	-0,0311	-0,1343	1,1632
Ti1-C16	2,4259	2,4630	0,0444	0,1249	0,0368	-0,0423	-0,0056	-0,0312	-0,1253	1,1511

Table S4 (continued)

M06L

Bond	Distance, Å	BP length, Å	ρ(r)	Δρ(r)	G(r)	V(r)	H(r)	- ¼∇^2ρ(r)	H(r)/ρ(r)	|V(r)|/ G(r)
Ti2-C21	2,3967	2,4070	0,0457	0,1389	0,0400	-0,0452	-0,0052	-0,0347	-0,1141	1,1307
Ti2-C22	2,3820	2,3940	0,0472	0,1455	0,0419	-0,0475	-0,0056	-0,0364	-0,1178	1,1325
Ti2-C23	2,3605	2,3643	0,0492	0,1417	0,0426	-0,0497	-0,0071	-0,0354	-0,1451	1,1676
Ti2-C24	2,3795	2,3999	0,0474	0,1421	0,0415	-0,0475	-0,0060	-0,0355	-0,1266	1,1446
Ti2-C25	2,4022	2,4085	0,0455	0,1394	0,0399	-0,0449	-0,0050	-0,0349	-0,1104	1,1260
Ti2-O5	1,8927	1,8945	0,1162	0,5309	0,1679	-0,2031	-0,0352	-0,1327	-0,3030	1,2097
Ti2-O6	1,8927	1,8946	0,1160	0,5319	0,1679	-0,2028	-0,0349	-0,1330	-0,3010	1,2080
Ti2-O3	2,0510	2,0519	0,0784	0,3553	0,1004	-0,1120	-0,0116	-0,0888	-0,1481	1,1156
Ti2-O4	2,0536	2,0544	0,0778	0,3528	0,0995	-0,1109	-0,0113	-0,0882	-0,1457	1,1139
Ti1-O3	2,1426	2,1472	0,0564	0,3042	0,0745	-0,0730	0,0015	-0,0760	0,0271	0,9795
Ti1-O4	2,1451	2,1490	0,0563	0,3016	0,0740	-0,0726	0,0014	-0,0754	0,0249	0,9811
Ti1-C8	2,4053	2,4125	0,0442	0,1396	0,0392	-0,0434	-0,0043	-0,0349	-0,0961	1,1086
Ti1-C9	2,3503	2,3650	0,0489	0,1614	0,0457	-0,0510	-0,0053	-0,0403	-0,1093	1,1170
Ti1-C10	2,3431	2,3457	0,0523	0,1404	0,0444	-0,0537	-0,0093	-0,0351	-0,1776	1,2091
Ti1-C12	2,3548	2,3592	0,0482	0,1604	0,0451	-0,0500	-0,0050	-0,0401	-0,1030	1,1102
Ti1-C13	2,3500	2,3522	0,0509	0,1377	0,0430	-0,0516	-0,0086	-0,0344	-0,1686	1,1994
Ti1-C16	2,3719	2,3873	0,0487	0,1398	0,0420	-0,0490	-0,0070	-0,0349	-0,1441	1,1673

G(r) — kinetic energy densities at the bcp were estimated using the Abramov's approximation [1]

$G(r) = 3/10(3\pi^2)^{2/3}\rho^{5/3}(r) + 1/6\nabla^2\rho(r)$

V(r) — potential energy densities at the BCP from local virial theorem

$V(r) + 2G(r) = -\frac{1}{4}\nabla^2\rho(r)$

H(r) — total energy densities, the sum of the G(r), a positive quantity, and the V(r), a negative quantity [2,3]

If r is bcp,

$H(r) = G(r) + V(r)$

Table S5. Cartesian coordinates (in Å) of **2m** (BP86).

Ti	4.27705931	6.33456484	3.21541726
O	5.77218113	6.60440127	4.69048227
O	5.71330499	7.73126307	2.51592877
C	3.11092547	8.45788150	3.38393769
C	3.25077260	7.94012226	4.68997408
C	2.54455928	6.70432688	4.76032857
C	1.94953818	6.48225457	3.48778132
C	2.32772053	7.55005689	2.62318708
C	4.71490558	5.12623764	1.23566409
C	5.71712563	4.76333037	2.18457489
C	5.08445852	4.07706659	3.25805243
C	3.69746870	4.03156850	2.98940245
C	3.47042442	4.67109233	1.73445246
Ti	7.39592044	7.29735133	3.62479358
C	6.16358952	5.69470096	5.62680826
C	5.99317561	7.91799386	1.19537923
H	3.60410198	9.34820243	2.99837479
H	3.86607128	8.36454324	5.48083283
H	2.44662010	6.06331376	5.63457144
H	1.33045235	5.63042112	3.21649023
H	2.04952416	7.65642519	1.57565151
H	4.88058091	5.67251858	0.30799204
H	6.78047478	4.97780408	2.10351156
H	5.57392794	3.69795712	4.15430386
H	2.93612788	3.60174737	3.63909460

H	2.50376834	4.81192576	1.25404371
O	8.10495430	5.67486471	4.33084881
O	8.06314376	7.07830710	1.85391011
C	7.46077534	5.18394471	5.41560028
C	7.29875788	7.53634501	0.83555409
C	6.96826473	9.46506577	4.55285719
C	7.94534455	9.61258378	3.53564748
C	9.10496703	8.89893977	3.94077526
C	8.84679111	8.32747890	5.21876928
C	7.52930403	8.68063291	5.59734099
C	5.36998944	5.24127840	6.67567620
C	5.08786583	8.38987401	0.24911443
C	7.97775898	4.18762005	6.25389982
C	7.71856162	7.60886283	-0.49942626
H	5.94423375	9.83196165	4.50869770
H	7.79988267	10.10150180	2.57244840
H	10.00947781	8.76446091	3.34939182
H	9.51545316	7.67370588	5.77593509
H	7.00748989	8.32801635	6.48615205
C	5.87378998	4.25047130	7.53386898
H	4.36696311	5.65227307	6.81755642
C	5.49009994	8.47734760	-1.09295198
H	4.07688796	8.67244284	0.55475827
C	7.16119005	3.74021130	7.30432177
C	9.34631199	3.62529605	5.99061528
C	6.79188803	8.08259543	-1.44123391
C	9.10881123	7.17701175	-0.87208379

C	5.05412904	3.77249627	8.70622330
C	4.52148552	8.94799257	-2.14965653
H	7.54878870	2.96075891	7.96975747
H	5.36513242	2.76302361	9.02237904
H	3.98009273	3.73775918	8.45558020
H	5.17485651	4.44944961	9.57234806
H	7.10238098	8.14712199	-2.49010518
H	9.41080107	3.22508834	4.96369877
H	9.58246185	2.81764477	6.70192990
H	10.11857478	4.40961404	6.07902399
H	9.86375082	7.81033242	-0.37355452
H	9.29368624	6.13808689	-0.54791644
H	9.26056179	7.24056976	-1.96159599
H	5.05336361	9.41867650	-2.99331249
H	3.81208377	9.68613320	-1.73887655
H	3.93349400	8.10286524	-2.55379155

Table S6. Cartesian coordinates (in Å) of **2m** (B3LYP).

Ti	4.16458193	6.30644610	3.23535751
O	5.79526808	6.47086124	4.64327902
O	5.71139672	7.58180852	2.44835528
C	3.11678094	8.53438152	3.45644137
C	3.27570895	8.02128586	4.75595753
C	2.47667249	6.85799464	4.87249567
C	1.81417788	6.66935208	3.63928981
C	2.22786458	7.69260465	2.75263694
C	4.45597977	4.97899000	1.23732600
C	5.41827785	4.53819491	2.17887047
C	4.73363884	3.93642456	3.25960431
C	3.35323375	4.02244952	3.00060056
C	3.18178975	4.66309369	1.74596163
Ti	7.38533264	7.30492662	3.61992201
C	6.22724061	5.57979427	5.57907700
C	6.04887933	7.81916164	1.15023573
H	3.62460001	9.39570663	3.04812134
H	3.92383775	8.42021846	5.52202333
H	2.35570791	6.25052585	5.75810664
H	1.10349984	5.88766875	3.41599263
H	1.89008005	7.82773521	1.73451610
H	4.66673989	5.47350862	0.29993210
H	6.49009898	4.63491928	2.08327024
H	5.18842886	3.50636150	4.14029618
H	2.56449731	3.64975118	3.63927385

H	2.23882761	4.86522494	1.25786301
O	8.19578012	5.77039490	4.36651123
O	8.09939163	7.02632868	1.89036079
C	7.56158551	5.18793798	5.40742246
C	7.37892159	7.49523454	0.84891329
C	6.92741794	9.60076563	4.33124940
C	8.00737456	9.64275354	3.42669470
C	9.08807414	8.94103166	4.00830551
C	8.67909371	8.48681360	5.28431836
C	7.34345071	8.88980547	5.48154153
C	5.46243270	5.05806673	6.60976832
C	5.19999642	8.31601710	0.17491962
C	8.14419469	4.24215985	6.24821960
C	7.87281970	7.63705815	-0.44582838
H	5.94602117	10.01950456	4.16336016
H	7.99515190	10.08750191	2.44118216
H	10.05031492	8.76374376	3.54881076
H	9.27130588	7.89672924	5.96849763
H	6.73536049	8.66014508	6.34501636
C	6.02611100	4.11506942	7.47582468
H	4.43466233	5.38006418	6.73855451
C	5.67405840	8.47851301	-1.13152516
H	4.17613455	8.57320107	0.42641883
C	7.34957340	3.72113345	7.27450378
C	9.56679802	3.81008495	6.02798536
C	6.99458964	8.13017099	-1.41680594
C	9.29349204	7.25919112	-0.75835402

C	5.21989596	3.56421186	8.62521415
C	4.76774957	9.03629719	-2.20026785
H	7.78599284	2.98313311	7.94263290
H	5.66234680	2.64367846	9.01466931
H	4.19305679	3.33721529	8.32156744
H	5.16913757	4.28309454	9.45155690
H	7.36204430	8.24935572	-2.43274120
H	9.70133982	3.40637929	5.01944751
H	9.85848599	3.04188348	6.74815577
H	10.25706399	4.65393682	6.12880098
H	10.00016541	7.87457659	-0.19196416
H	9.48944395	6.21666429	-0.48852289
H	9.50698053	7.38540468	-1.82249454
H	5.24093726	8.99031605	-3.18428371
H	4.51890730	10.08478670	-2.00041337
H	3.82673961	8.47882109	-2.25800163

Table S7. Cartesian coordinates (in Å) of **2m** (M06L).

Ti	4.18446030	6.29171033	3.21628776
O	5.79296055	6.47505126	4.61978906
O	5.71730091	7.58344476	2.45253700
C	3.17616263	8.47302843	3.47532285
C	3.29605276	7.91422571	4.75373001
C	2.50888028	6.74138403	4.80181795
C	1.88495709	6.60002335	3.54399359
C	2.32146200	7.65364987	2.70972727
C	4.51715283	5.04215656	1.24830374
C	5.48955883	4.62862177	2.19000395
C	4.82249958	3.99767787	3.26140454
C	3.44496948	4.03750157	2.99759583
C	3.25735685	4.67482137	1.74933479
Ti	7.38946847	7.26154164	3.60033785
C	6.20045446	5.61552803	5.58064978
C	6.03529916	7.83596883	1.16324989
H	3.70825073	9.33547509	3.11004005
H	3.93451239	8.27291441	5.54427505
H	2.37043838	6.09756607	5.65389593
H	1.20440294	5.81494811	3.26461549
H	2.02663569	7.81769008	1.68656316
H	4.70905174	5.55884639	0.32260347
H	6.55422038	4.78746505	2.11352297
H	5.28541706	3.59655808	4.14779047
H	2.66666733	3.66411770	3.64251942

H	2.31012173	4.87043862	1.27545255
O	8.16044159	5.70671956	4.35559825
O	8.07748314	7.00160640	1.85636704
C	7.52892557	5.19589139	5.42554809
C	7.35903267	7.50746498	0.84054091
C	6.88810939	9.43827429	4.46900614
C	7.84239946	9.59501669	3.44715950
C	9.02439855	8.94495324	3.85581687
C	8.80215385	8.40140810	5.13885094
C	7.48263011	8.70653148	5.51710260
C	5.41704523	5.13860010	6.61529552
C	5.17277300	8.34542773	0.20963407
C	8.09604566	4.28895973	6.31446998
C	7.84108183	7.68629666	-0.45174771
H	5.86638451	9.77744821	4.43474776
H	7.67617958	10.06101596	2.48931483
H	9.92332458	8.84389415	3.27127901
H	9.49970777	7.80661255	5.70416916
H	6.99212966	8.37835152	6.41901249
C	5.96646384	4.22820804	7.52007445
H	4.39164535	5.47115090	6.71219095
C	5.63613766	8.53511658	-1.09361711
H	4.15263463	8.58724875	0.47999341
C	7.28781591	3.82264408	7.35142141
C	9.50908597	3.84380382	6.13070646
C	6.95393828	8.20252433	-1.39648584
C	9.25173135	7.32695941	-0.78276791

C	5.14757478	3.71924623	8.66678716
C	4.71886589	9.07663890	-2.14747257
H	7.70993456	3.11344816	8.05334173
H	5.61677601	2.86075883	9.14028389
H	4.14989956	3.42176361	8.34774195
H	5.01809251	4.48360198	9.43362865
H	7.31070422	8.35281372	-2.40840963
H	9.65344885	3.38409400	5.15399125
H	9.79970788	3.12729242	6.89384079
H	10.19777286	4.68738070	6.17337167
H	9.95693475	7.88997721	-0.17194386
H	9.44776343	6.27480626	-0.58077010
H	9.47364375	7.52214513	-1.82819187
H	5.26001650	9.32101147	-3.05775255
H	4.20791802	9.97764069	-1.81119140
H	3.94422752	8.35601893	-2.41140020

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