

Supporting Information For:

Mononuclear Cyclometalated Ruthenium(II) Complexes of 1,2,4,5-Tetrakis(*N*-methylbenzimidazolyl)benzene: Synthesis and Electrochemical and Spectroscopic Studies

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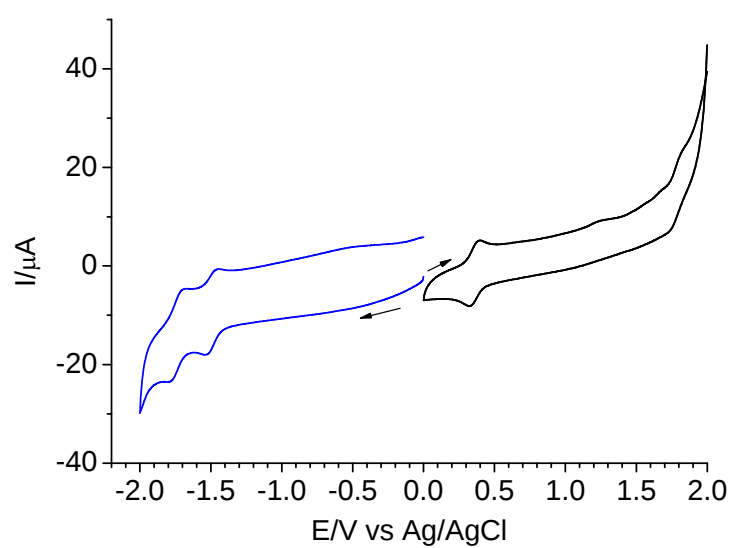


Figure S1. CV profile of $[(\text{Mebip})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**2**).

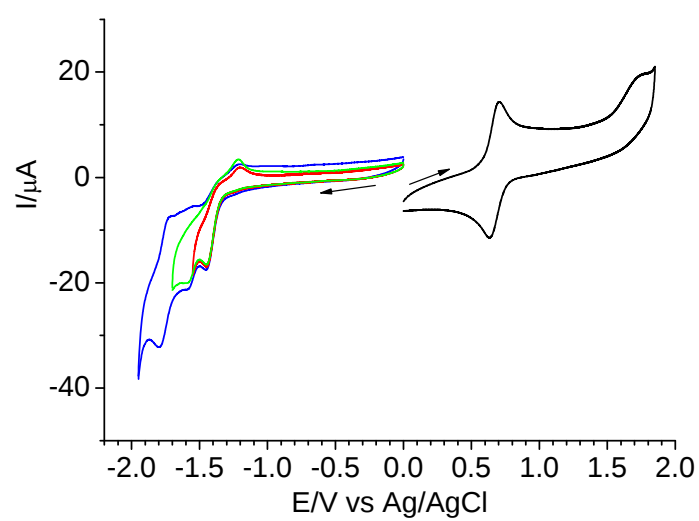


Figure S2. CV profile of $[(\text{MeOptpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**3**).

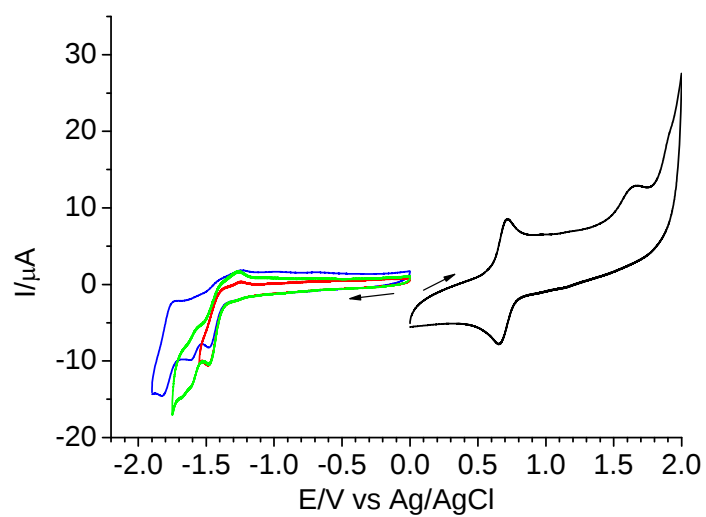


Figure S3. CV profile of $[(\text{ttpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**4**).

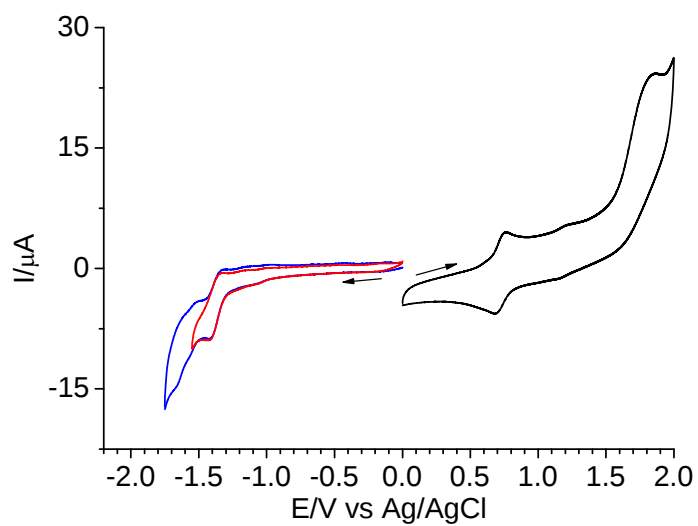


Figure S4. CV profile of $[(\text{CF}_3\text{ptpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**5**).

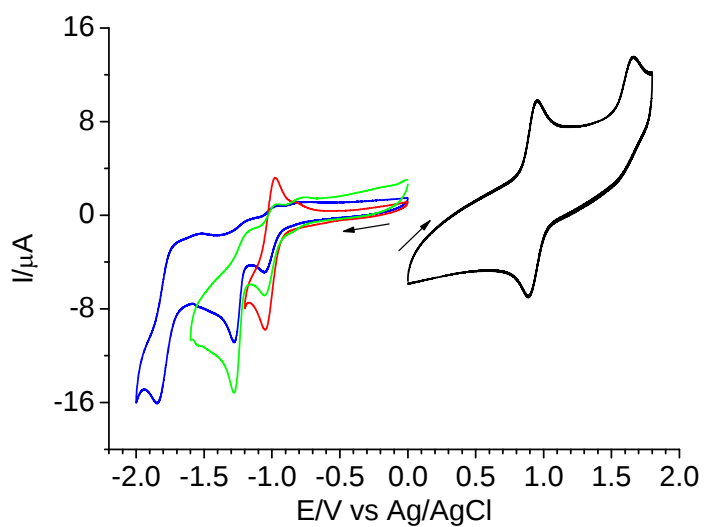


Figure S5. CV profile of $[(\text{Me}_3\text{tc bpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**6**).

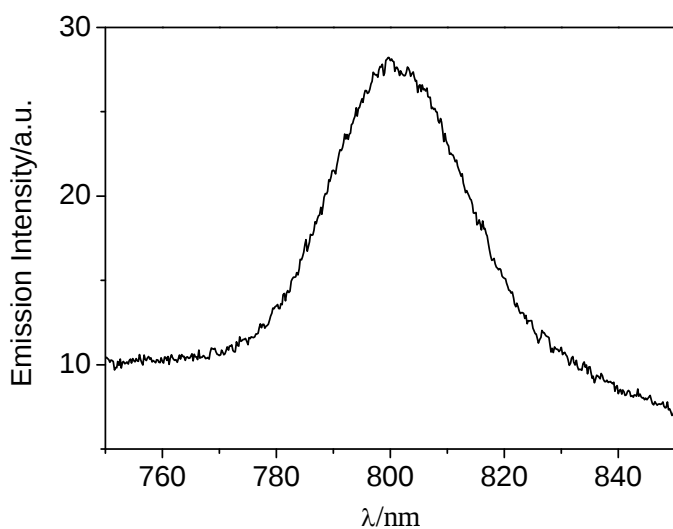


Figure S6. Emission spectrum of $[(\text{Mebip})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**2**) in acetonitrile at a concentration of 5×10^{-6} M. The excitation wavelength was 560 nm. The emission spectrum was recorded using a F-380 spectrofluorimeter of Tianjin Gangdong Sic. & Tech Development Co. Ltd, with a red-sensitive photomultiplier tube R928F. Luminescence quantum yields were destimated using $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ in degassed acetonitrile solution as the standard ($\phi = 5.9\%$).¹

¹ Nakamura, K. *Bull. Chem. Soc. Jpn.* **1982**, 55, 1639.

Cartesian coordinates of DFT-optimized structure of complex [(Mebip)Ru(Metbib)]⁺ (2) :

Charge = 1; multiplicity=1

Ru	0.00731832	0.02230472	0.04385970
N	1.97303236	-0.62423180	0.52347721
N	3.37181969	-1.46740766	2.05274889
N	-1.96148179	0.69301444	0.46751083
N	-3.37654396	1.62279547	1.93006695
N	-0.62599862	-1.95245010	-0.39361218
N	-1.09634357	-3.52437815	-1.92856756
N	0.01790632	-0.03679803	-2.04233768
N	0.64445938	1.97031439	-0.49913298
N	1.11759265	3.45643056	-2.11655020
C	3.03945280	-1.18828738	-0.14644245
C	3.32163556	-1.29668877	-1.51459550
C	4.49639348	-1.94161554	-1.88598537
C	5.37888745	-2.47263943	-0.92367204
C	5.11211073	-2.37136680	0.43877190
C	3.93089537	-1.72200628	0.80782297
C	3.89125056	-2.06319034	3.27700107
C	2.20357557	-0.76847176	1.84510043
C	1.17423327	-0.27260718	2.76280473
C	-0.00114460	0.08124063	2.04646135
C	-1.18209183	0.47893995	2.73035321
C	-1.22266948	0.38568399	4.14393067
C	-0.01163600	0.16881405	4.82144121
C	1.20435791	-0.09013769	4.16787250
C	-2.20433574	0.91645023	1.77582426
C	-3.90861460	2.29204275	3.11015905
C	-3.92496485	1.79894387	0.66684047
C	-5.10456703	2.42024250	0.24756480
C	-5.35856884	2.43719398	-1.12099293
C	-4.46554220	1.85148459	-2.04096727
C	-3.29264203	1.23449413	-1.61979149
C	-3.02329649	1.21120125	-0.24504299
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C	-1.62934509	-4.59857812	2.01914382
C	-1.91393376	-5.59671040	1.06073923
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C	-1.28219106	-4.20567538	-3.20225479
C	-0.67708475	-2.23117558	-1.70742023
C	-0.32626619	-1.19247659	-2.67459553
C	-0.31584023	-1.25797358	-4.07381659
C	0.04986221	-0.12132262	-4.79645429
C	0.39812259	1.05808945	-4.13649441
C	0.37451461	1.07909439	-2.73602528
C	0.70598397	2.17446896	-1.82621570
C	1.29186724	4.07188056	-3.42495115
C	1.34004011	4.09386476	-0.90296353
C	1.77365567	5.38742556	-0.59074005
C	1.90537120	5.69626679	0.75764736
C	1.61976947	4.75140088	1.76838059
C	1.18654553	3.47060777	1.45917355
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H	4.74488576	-2.03506905	-2.93921999

H	6.29023905	-2.96394812	-1.25077747
H	5.80390605	-2.76824949	1.17468544
H	3.07189357	-2.26263664	3.96640430
H	4.35810220	-3.01674588	3.01832121
H	4.62244375	-1.41267496	3.76031685
H	-0.01569654	0.20181729	5.90499335
H	-4.37826877	3.22442767	2.78743212
H	-4.64037740	1.66954110	3.62807463
H	-3.09592881	2.54004805	3.79184711
H	-5.80490985	2.85856372	0.95113784
H	-6.26828920	2.90434594	-1.48586616
H	-4.70432526	1.87967092	-3.10020177
H	-2.60960426	0.77709664	-2.32692129
H	-0.98155583	-2.56109301	2.36795076
H	-1.76849113	-4.82346204	3.07204453
H	-2.25836363	-6.57027896	1.39614430
H	-2.00168856	-6.14043151	-1.02440775
H	-2.04539534	-3.70612571	-3.80651167
H	-0.34231104	-4.25798997	-3.75982418
H	-1.61706469	-5.22331619	-3.00341439
H	-0.58221199	-2.16416333	-4.59982736
H	0.06413450	-0.15504714	-5.88100273
H	0.68142954	1.92923241	-4.71068799
H	1.56834933	5.11601512	-3.28103537
H	2.08995677	3.57958003	-3.98920285
H	0.35983473	4.04211167	-3.99657142
H	2.00629118	6.12278752	-1.35413751
H	2.24363745	6.68851499	1.04045634
H	1.75213987	5.03485477	2.80792730
H	0.98136092	2.73185975	2.22514372
C	2.44959175	0.00371586	4.95250346
C	3.89156001	-0.17109735	6.63274971
C	4.38544592	0.67009347	5.60786361
C	4.61904935	-0.44679484	7.79386069
C	5.64771341	1.26684023	5.74012331
C	5.87051714	0.15472055	7.90405704
H	4.23425912	-1.08989913	8.57982506
C	6.37685097	0.99903030	6.89341851
H	6.03103469	1.91634358	4.95926302
H	6.46950975	-0.02799116	8.79144336
H	7.35717214	1.44792486	7.02408935
C	-2.47362289	0.34027578	4.92360649
C	-3.92862016	0.61974058	6.57823768
C	-4.41285191	-0.28757271	5.60662655
C	-4.66517759	0.96789440	7.71392355
C	-5.67430552	-0.87864403	5.76854436
C	-5.91566109	0.37066332	7.85424876
H	-4.28763030	1.66207171	8.45895616
C	-6.41237490	-0.53913126	6.89706946
H	-6.05014371	-1.57885094	5.02894551
H	-6.52149617	0.60856465	8.72374228
H	-7.39229798	-0.98186491	7.04984420
C	1.81859968	-1.57308087	6.88130696
H	1.33059680	-1.13774304	7.76121458
H	1.05195768	-1.94828723	6.20243478
H	2.44165245	-2.41149963	7.20902728
C	-1.86293003	2.04283113	6.74986912
H	-1.38517423	1.67038782	7.66357365
H	-1.08867376	2.37213753	6.05598471

H	-2.49132166	2.90038054	7.01143720
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N	-2.67886179	1.01484179	6.12274064
N	-3.48543716	-0.43627330	4.58974958
N	3.46598043	0.75456477	4.57645763

Cartesian coordinates of DFT-optimized structure of [(tpy)Ru(Metbib)]⁺:

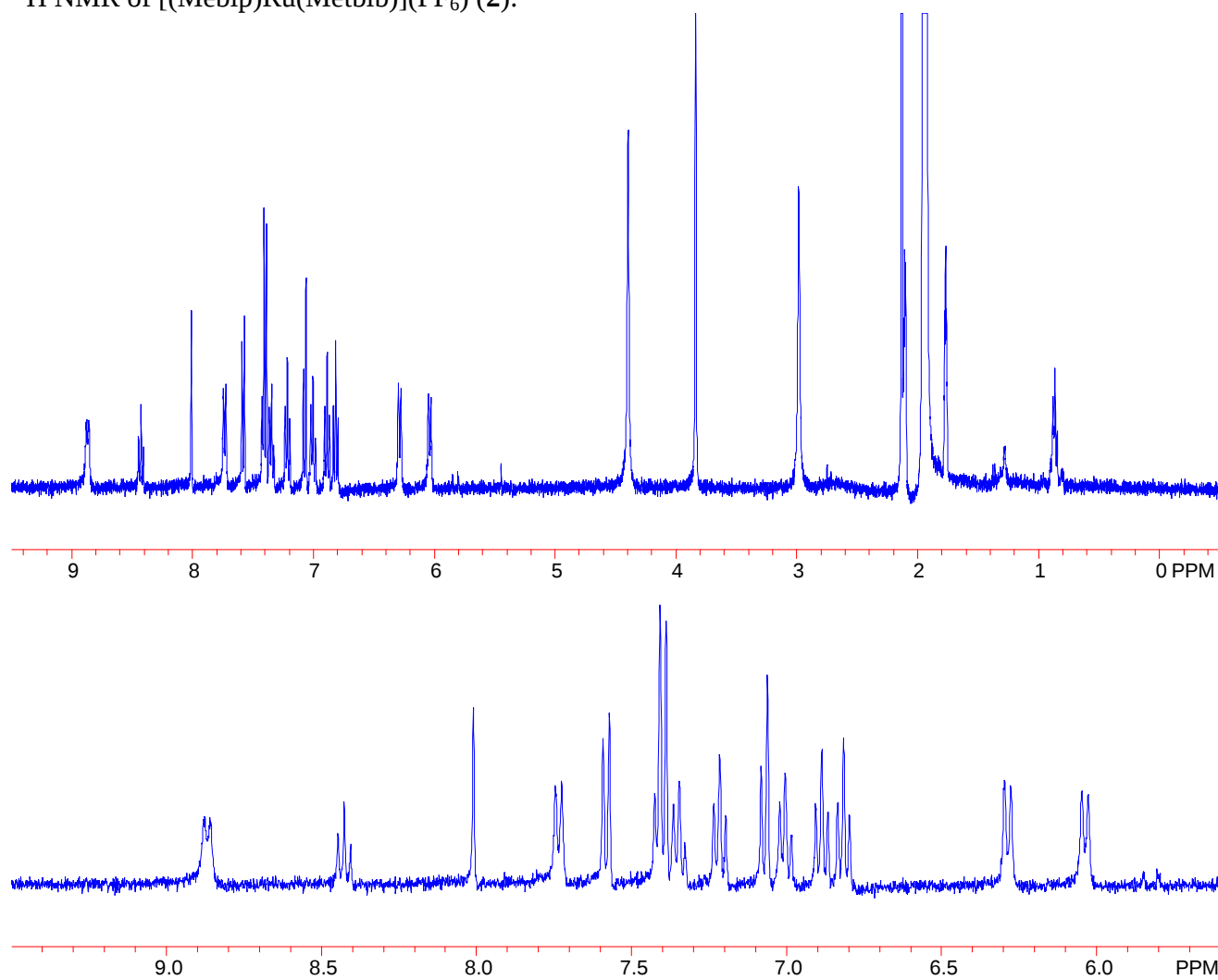
Charge = 1; multiplicity=1

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N	2.09029346	0.46844814	0.05832995
N	3.65567309	1.98316945	0.59054402
C	-3.22733363	-0.16534605	-0.58442221
C	-3.53237439	-1.53231288	-0.56044120
C	-4.82838070	-1.91277885	-0.89168378
C	-5.80682912	-0.96048330	-1.24189867
C	-5.51765746	0.40100630	-1.26956082
C	-4.21452685	0.77927625	-0.93580343
C	-4.24924333	3.23994573	-1.35957267
C	-2.30650541	1.83088673	-0.46801701
C	-1.18383869	2.75521856	-0.28532138
C	0.03769293	2.04030333	-0.21858033
C	1.27805651	2.72722021	-0.13882869
C	1.29530629	4.13656582	-0.29832016
C	0.07137518	4.81768630	-0.19940988
C	-1.16771153	4.16489417	-0.11262906
C	2.36525289	1.78700987	0.14617520
C	4.27712654	3.19299842	1.12967505
C	4.23454248	0.72723874	0.74046660
C	5.51431719	0.34404989	1.14957233
C	5.77555146	-1.02234731	1.20759251
C	4.79222565	-1.97312387	0.86779199
C	3.51823357	-1.58731473	0.46451898
C	3.24053044	-0.21534538	0.40406040
H	-2.78165145	-2.26472531	-0.28440625
H	-5.09668333	-2.96502319	-0.87654022
H	-6.81011384	-1.29454821	-1.48813664
H	-6.28014499	1.12959938	-1.52536782
H	-3.49731765	3.93461575	-1.73161826
H	-4.90829438	2.96906261	-2.18840958
H	-4.82707747	3.72255358	-0.56905401
H	0.12313397	5.89804441	-0.13244816
H	4.84207003	2.91317030	2.02240016
H	4.95502768	3.65424158	0.40719182
H	3.51514475	3.91529480	1.41576199
H	6.27909357	1.07176596	1.40126660
H	6.75997842	-1.36156651	1.51513488
H	5.03861086	-3.02951072	0.91981566
H	2.76489415	-2.32057190	0.19830053
H	0.30312258	0.36224097	-5.36076180
C	0.26682727	-0.31926623	-4.51741408
H	0.35930629	-2.13383742	-5.69142292
C	0.29685553	-1.70197365	-4.69764860
C	0.18672097	0.18604641	-3.22396978
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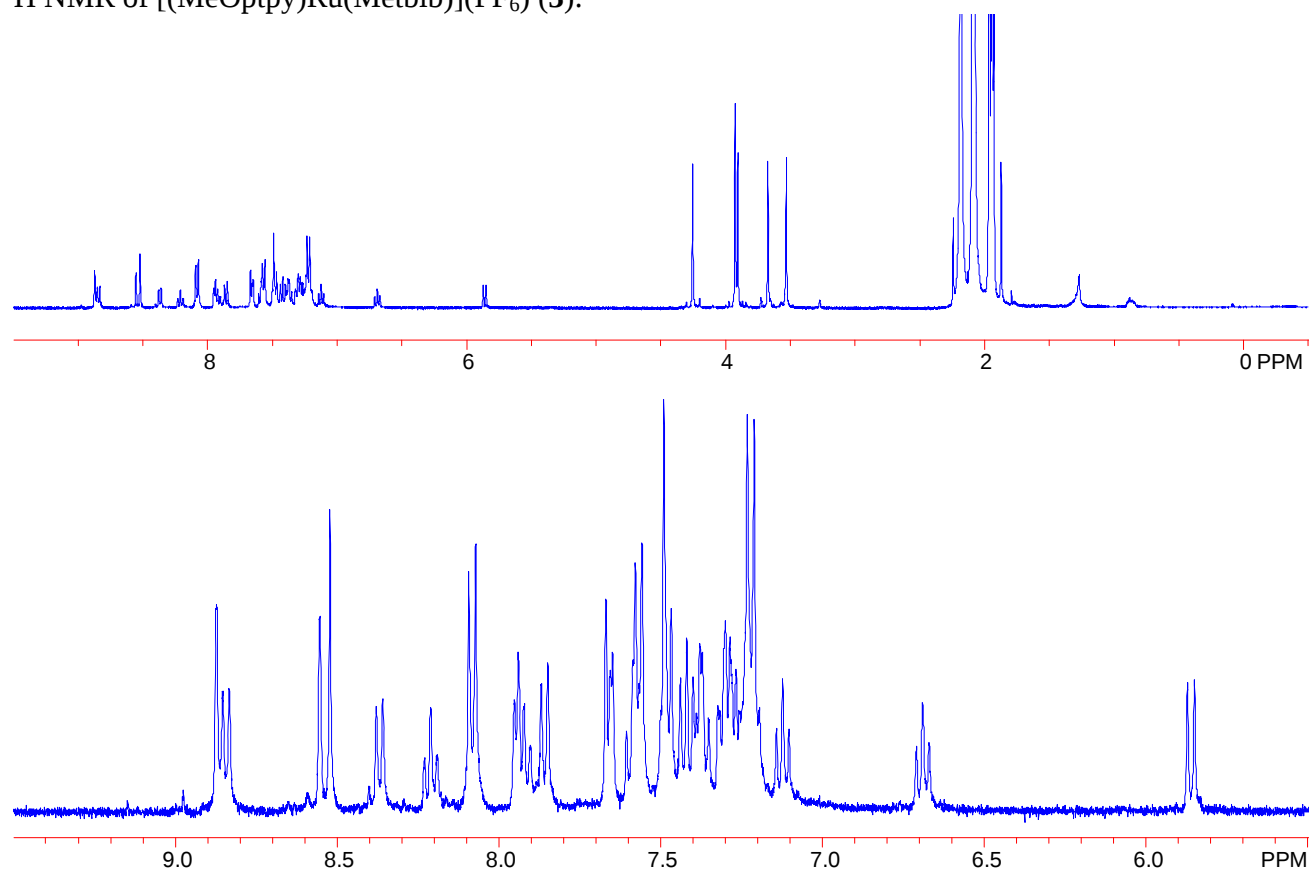
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H	0.19171098	-4.78342052	-1.85207968
C	0.11307807	-4.16161142	-0.96747742
N	-0.00848134	-2.01755485	0.06046406
N	-0.17113556	-0.24665924	1.98241370
H	-0.28750047	1.73017471	2.55228518
C	-0.08389487	-2.56488740	1.29627104
C	0.03630702	-4.75088307	0.29678052
C	-0.28992581	0.71094995	2.92021479
C	-0.18704424	-1.56169816	2.37736952
C	-0.06331735	-3.95542914	1.44068888
H	0.05434002	-5.83181814	0.39066338
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C	-0.30860154	-1.90253807	3.72689948
H	-0.51126311	1.24296683	4.98730556
H	-0.12156468	-4.41788111	2.41941438
C	-0.42250668	-0.90302372	4.68913627
H	-0.31825484	-2.94540344	4.02337700
H	-0.51892872	-1.16162282	5.73884429
C	-2.34666192	4.92389157	0.33756585
C	-3.78220395	6.58477222	0.66536245
C	-4.05913535	5.48436570	1.51096849
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C	-5.13542114	5.54464799	2.40887455
C	-5.61174338	7.79212023	1.57810839
H	-4.32632428	8.60000021	0.03654006
C	-5.90127461	6.70437983	2.42952622
H	-5.35067140	4.70603845	3.06385777
H	-6.23059548	8.68323344	1.62810211
H	-6.73958096	6.78122801	3.11574192
C	2.47815356	4.97912649	-0.55817310
C	3.87460575	6.61200908	-0.48511802
C	4.33511712	5.74634829	-1.50483853
C	4.58500691	7.78412743	-0.18903713
C	5.48448583	6.01257128	-2.25504409
C	5.73023982	8.05522652	-0.92914157
H	4.23850077	8.45208321	0.59327205
C	6.17250965	7.18365148	-1.94702506
H	5.83289327	5.34510620	-3.03778932
H	6.29989775	8.95675368	-0.72368222
H	7.07250743	7.43094310	-2.50242785
N	2.71651351	6.10833632	0.07922664
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N	-2.68043379	6.20405713	-0.08657068
N	3.42372212	4.69991242	-1.53928325
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H	-1.51918288	6.35730178	-1.82047324
H	-2.90679553	7.46238422	-1.73838988

C	3.42566428	3.64395379	-2.53792738
H	4.22552016	2.91876201	-2.34895425
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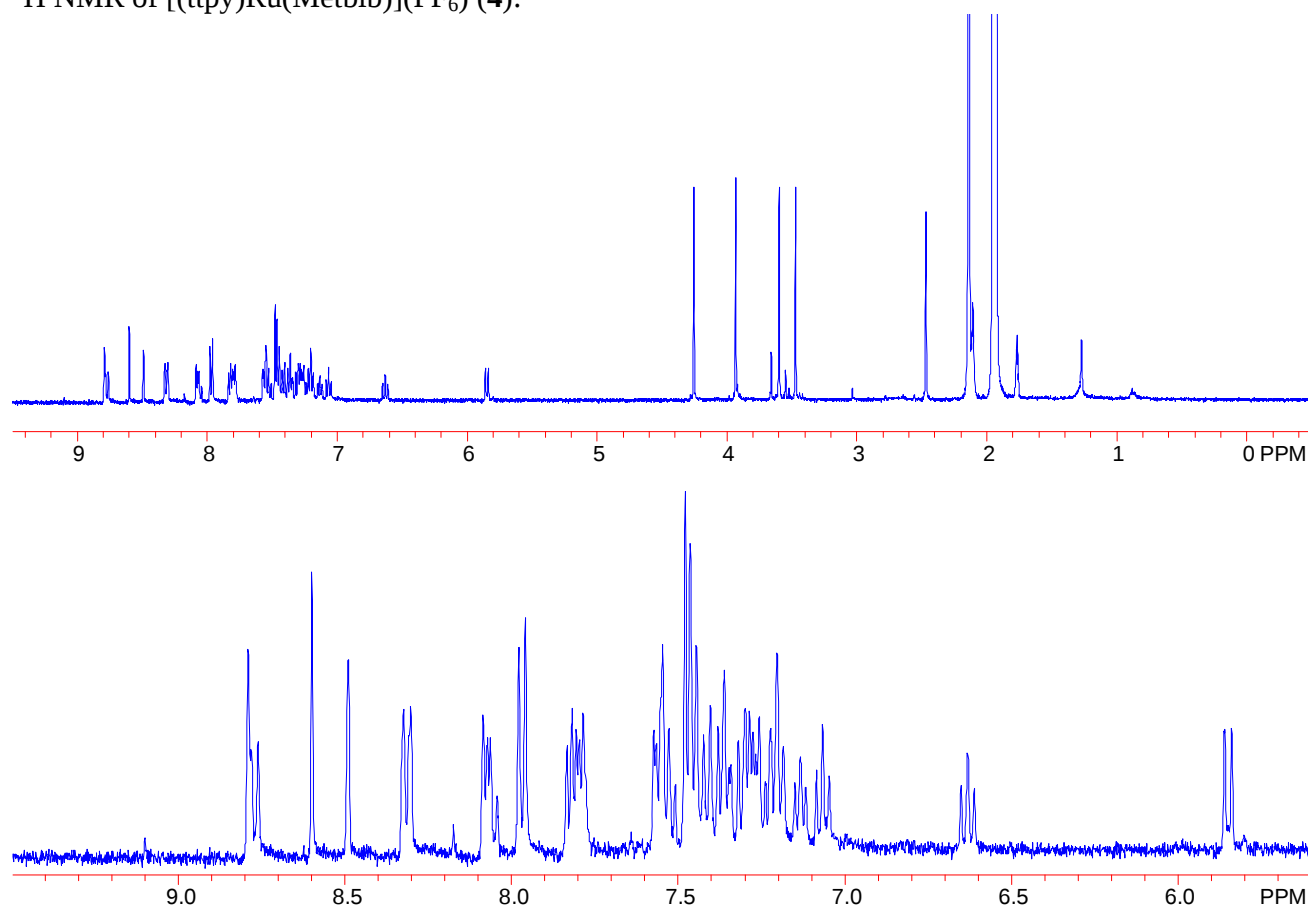
^1H NMR of $[(\text{Mebip})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (2):



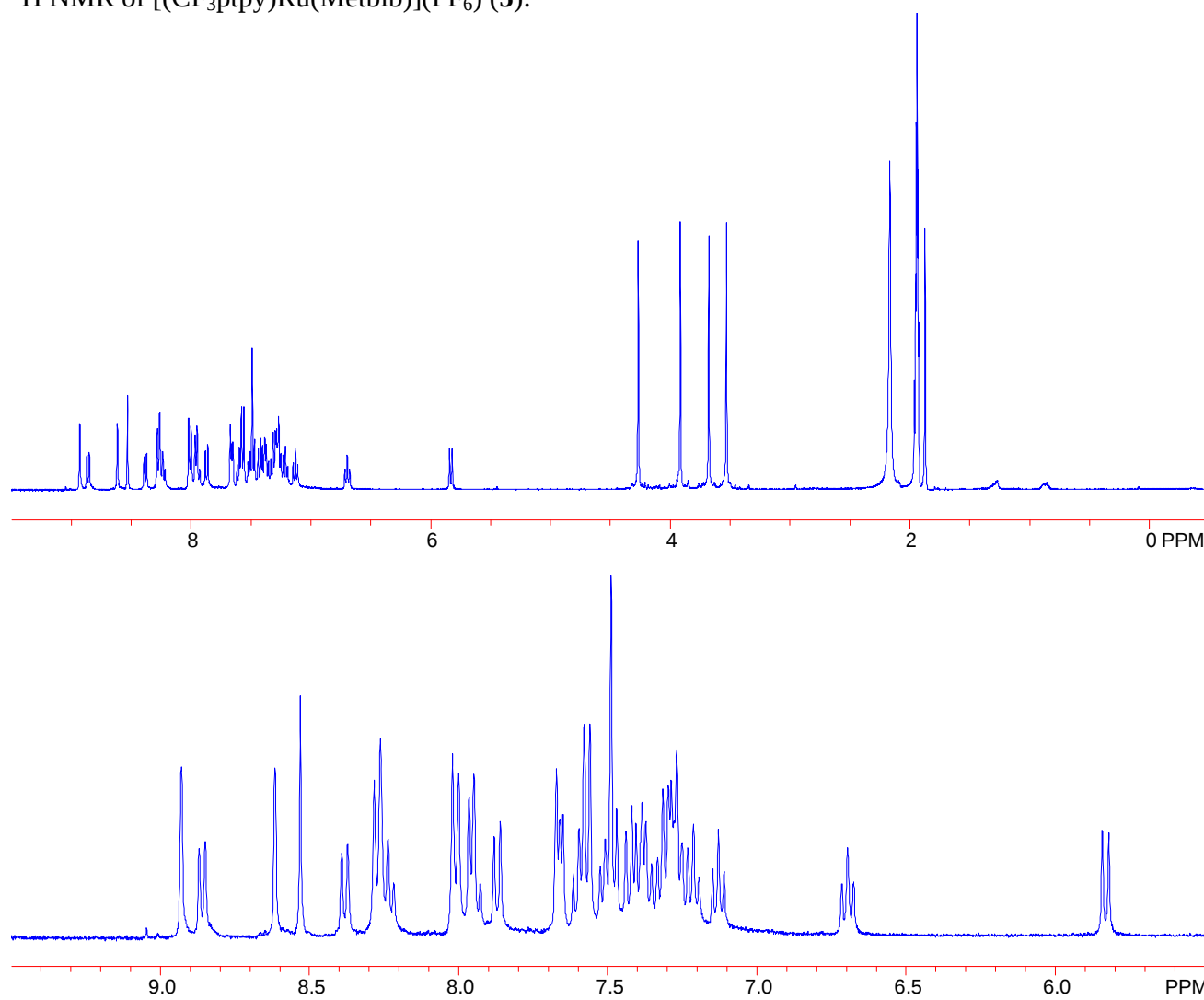
^1H NMR of $[(\text{MeOptpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**3**):



^1H NMR of $[(\text{ttpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**4**):



^1H NMR of $[(\text{CF}_3\text{ptpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (5):



^1H NMR of $[(\text{Me}_3\text{tc bpy})\text{Ru}(\text{Metbib})](\text{PF}_6)$ (**6**):

