Supporting information for:

P–Ru-Complexes with a Chelate-Bridge-Switch: A Comparison of 2-Picolyl and 2-Pyridyloxy Moieties as Bridging Ligands

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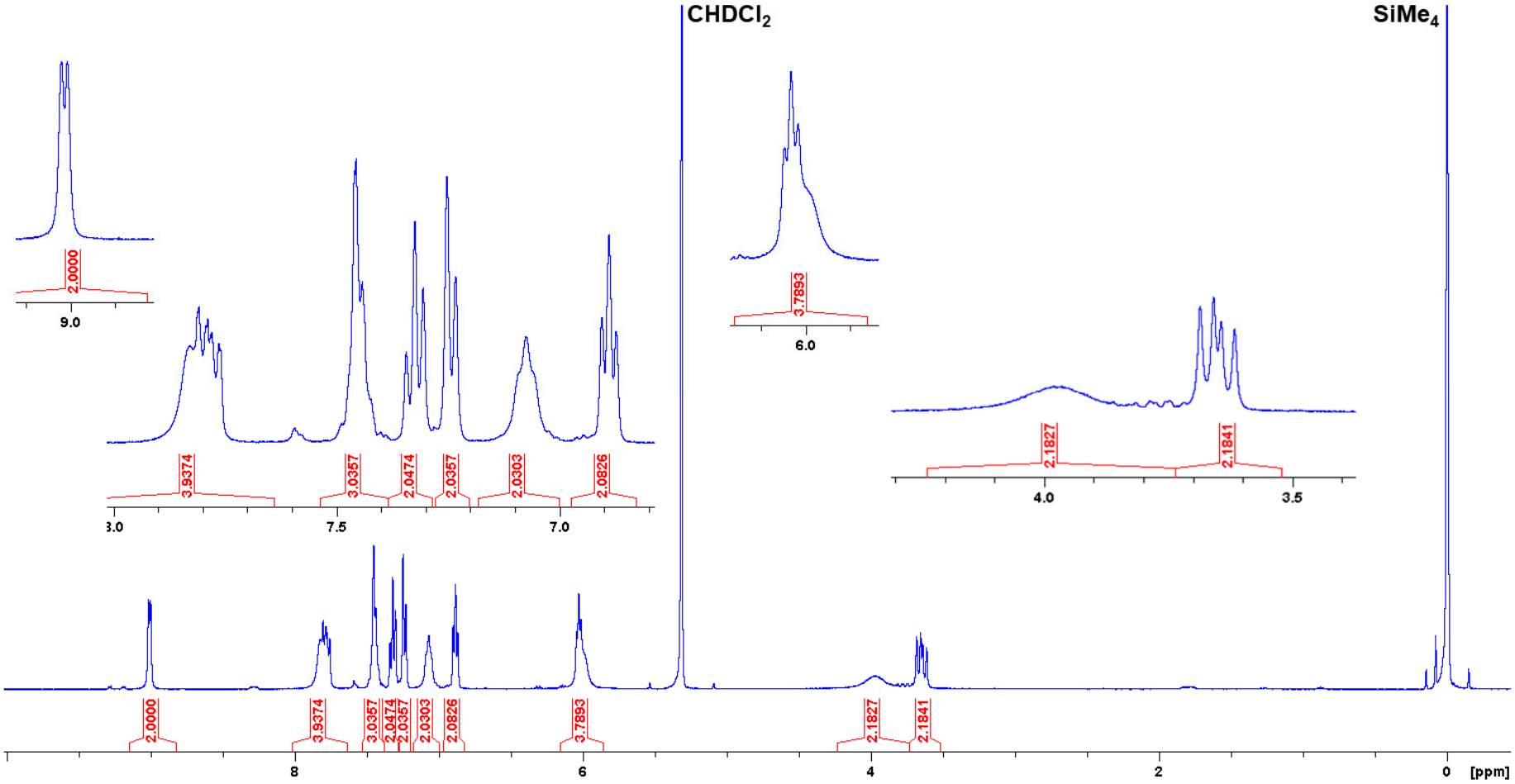

Figure S1. ^{1}H NMR spectrum of **3a** in CD_2Cl_2 (full spectrum and magnified insets of the (groups of) signals).

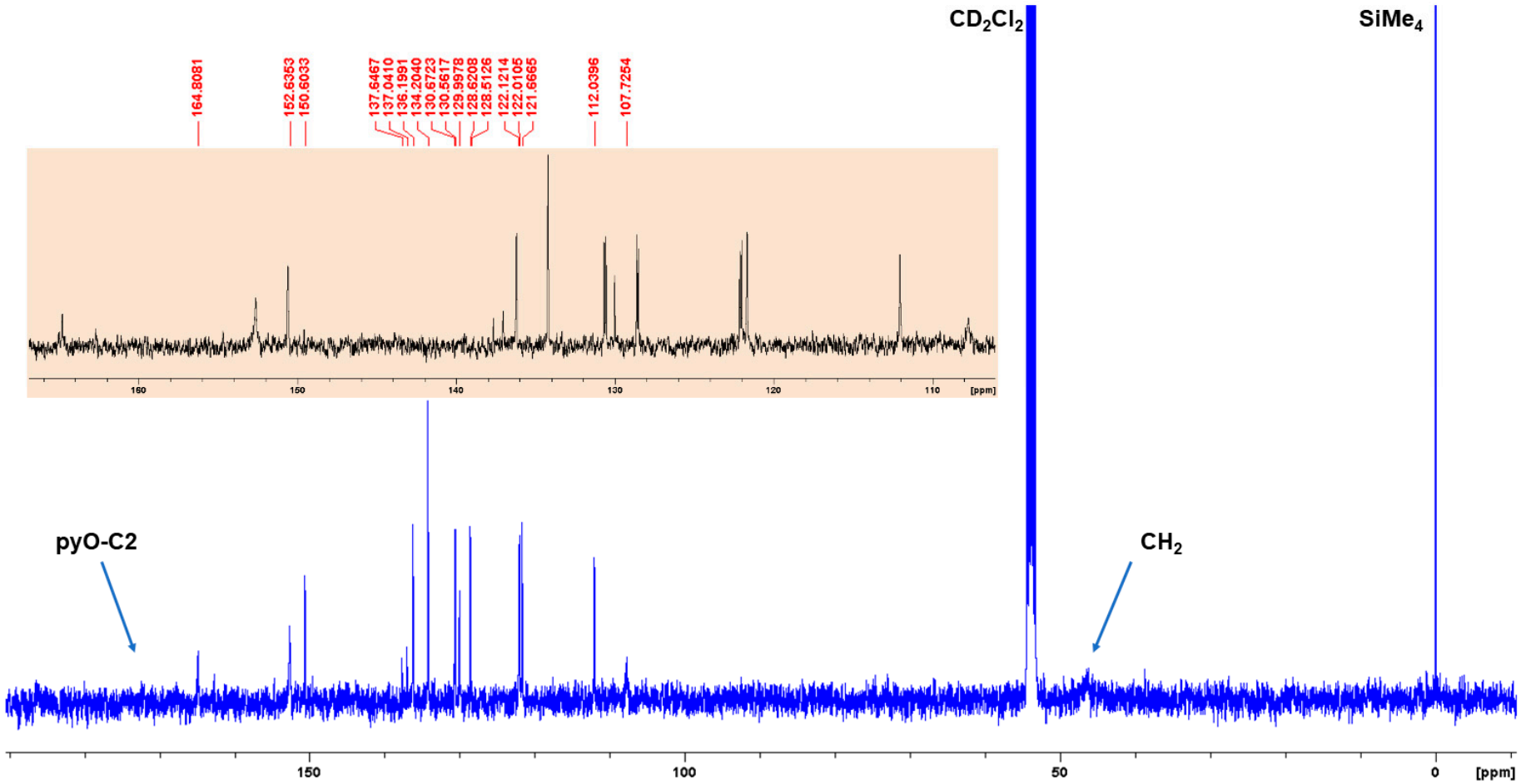

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3a** in CD_2Cl_2 (full spectrum and magnified inset of the aryl part of signals). The location of the CH_2 and pyO-C2 signals was further confirmed by correlations in the $^{1}H/^{13}C$-HSQC and $^{1}H/^{13}C$-HMBC spectra, respectively.

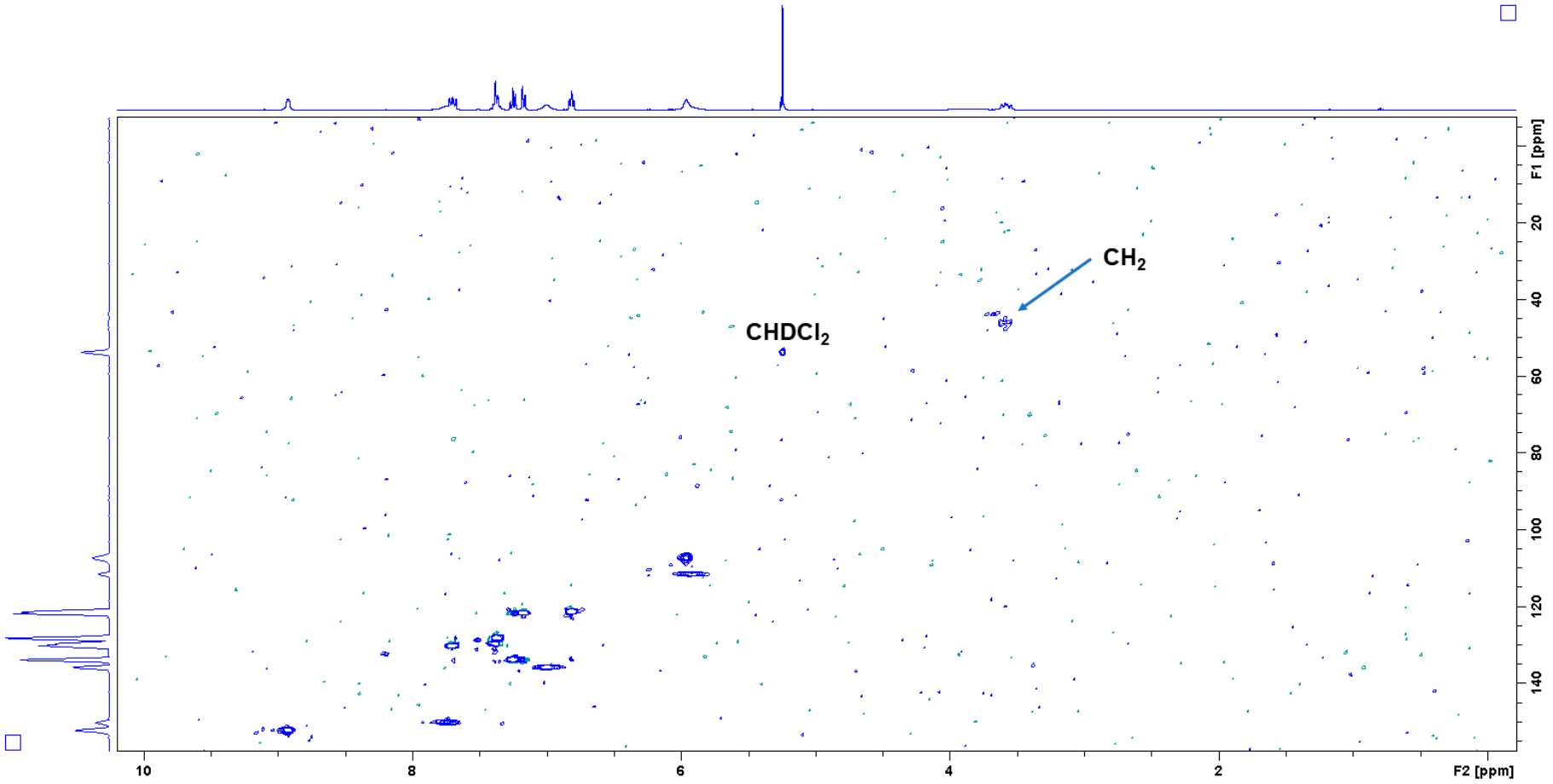

Figure S3. $^{1}H/^{13}C$-HSQC NMR spectrum of **3a** in CD_2Cl_2.

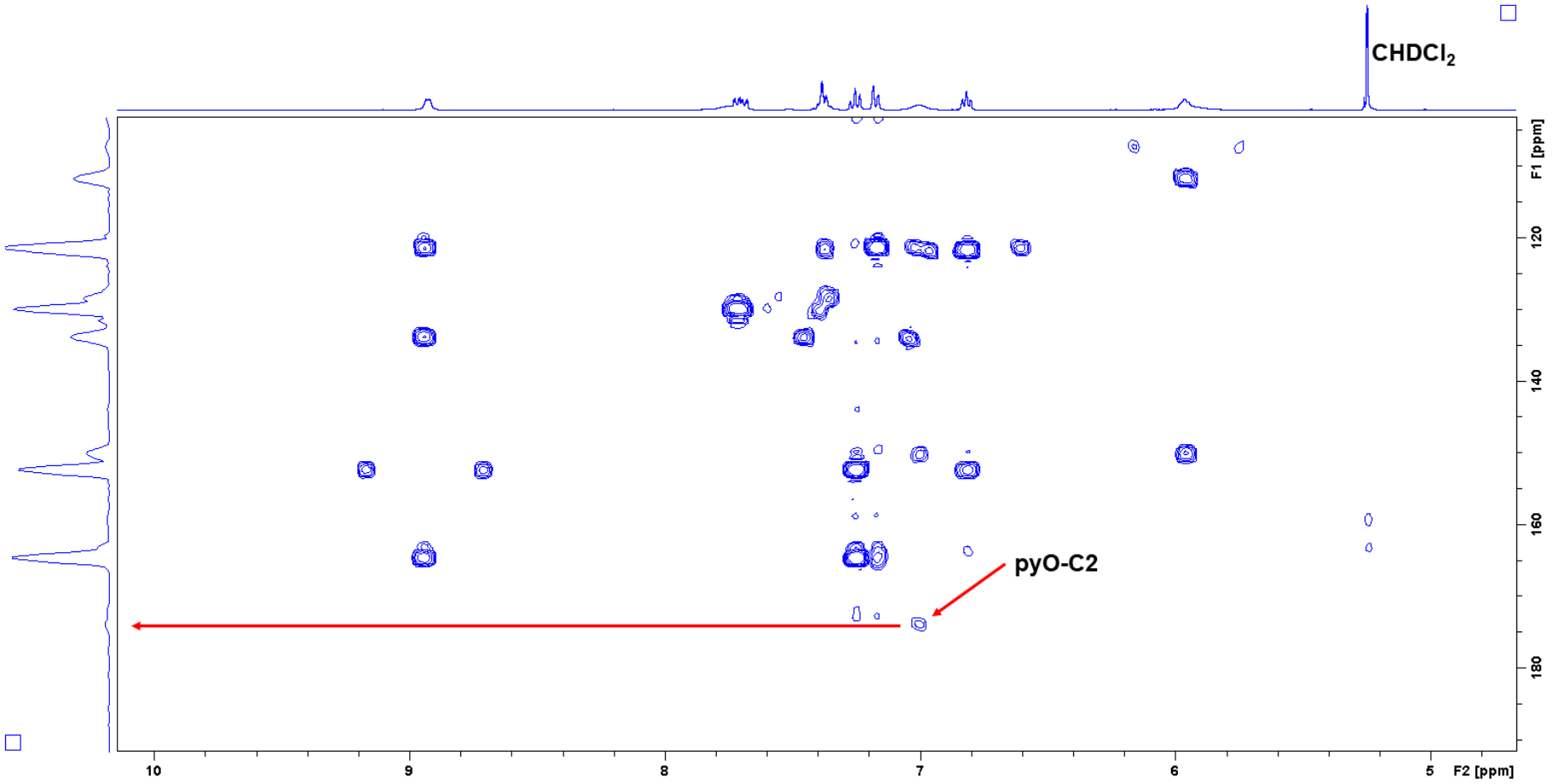

Figure S4. $^{1}H/^{13}C$-HMBC NMR spectrum of **3a** in CD_2Cl_2. (The correlation between ^{13}C(pyO-C2) and ^{1}H(pyO-H4), highlighted with a red arrow, confirmed the ^{13}C NMR shift of the pyO-C2 signal.)

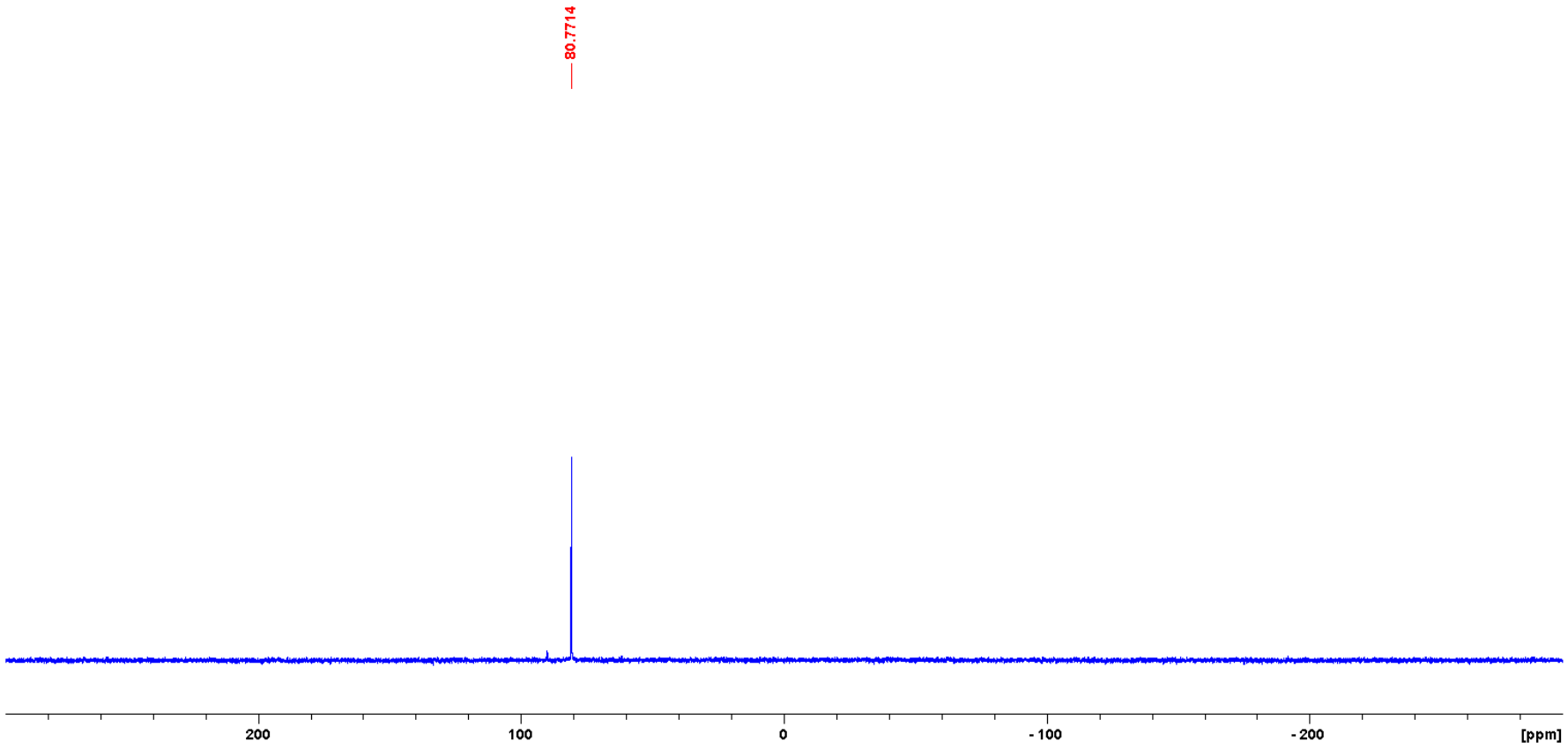

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** in CD_2Cl_2.

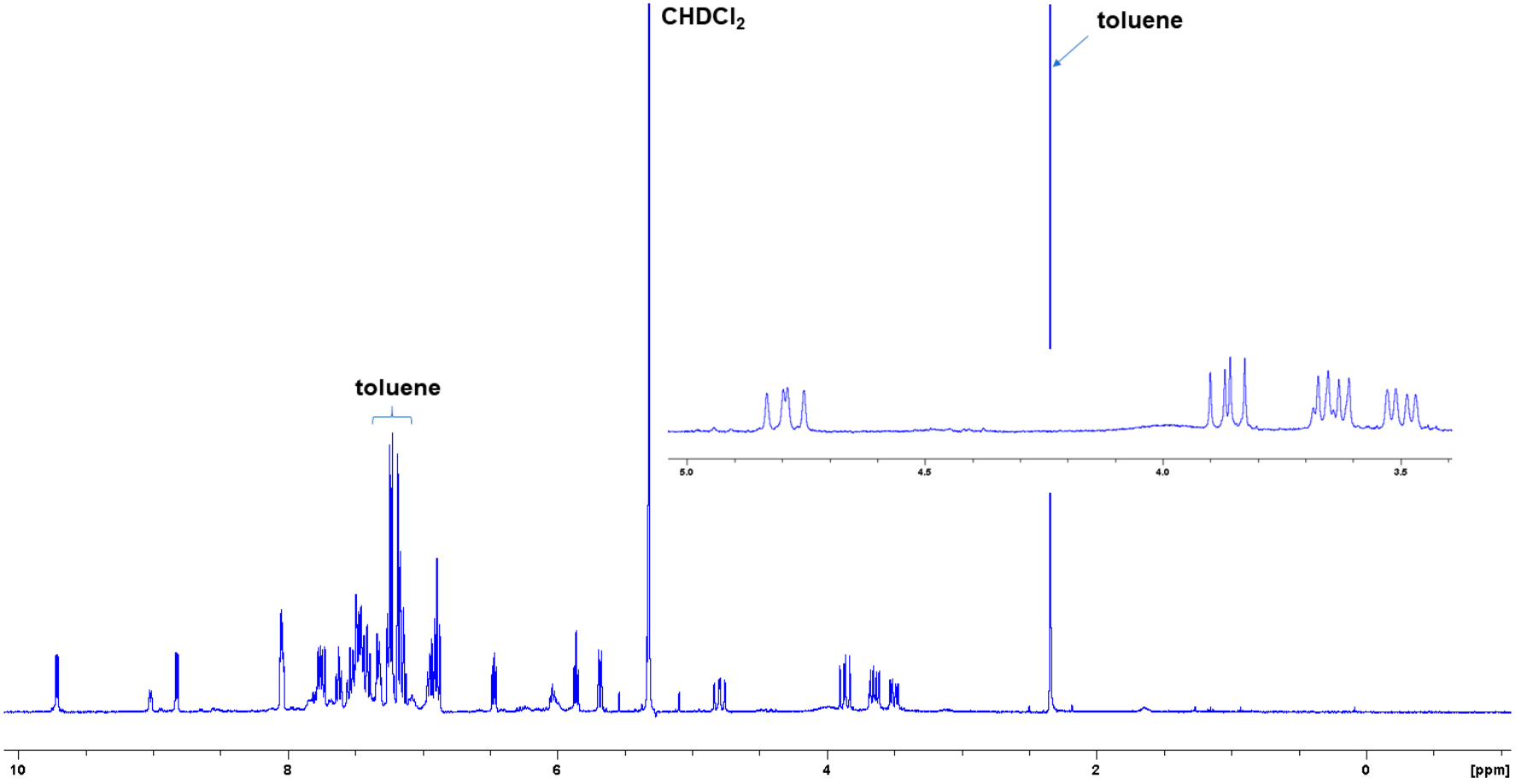

Figure S6. ^{1}H NMR spectrum of (**4a** · toluene) in CD_2Cl_2 (full spectrum and magnified inset of the groups′ signals).

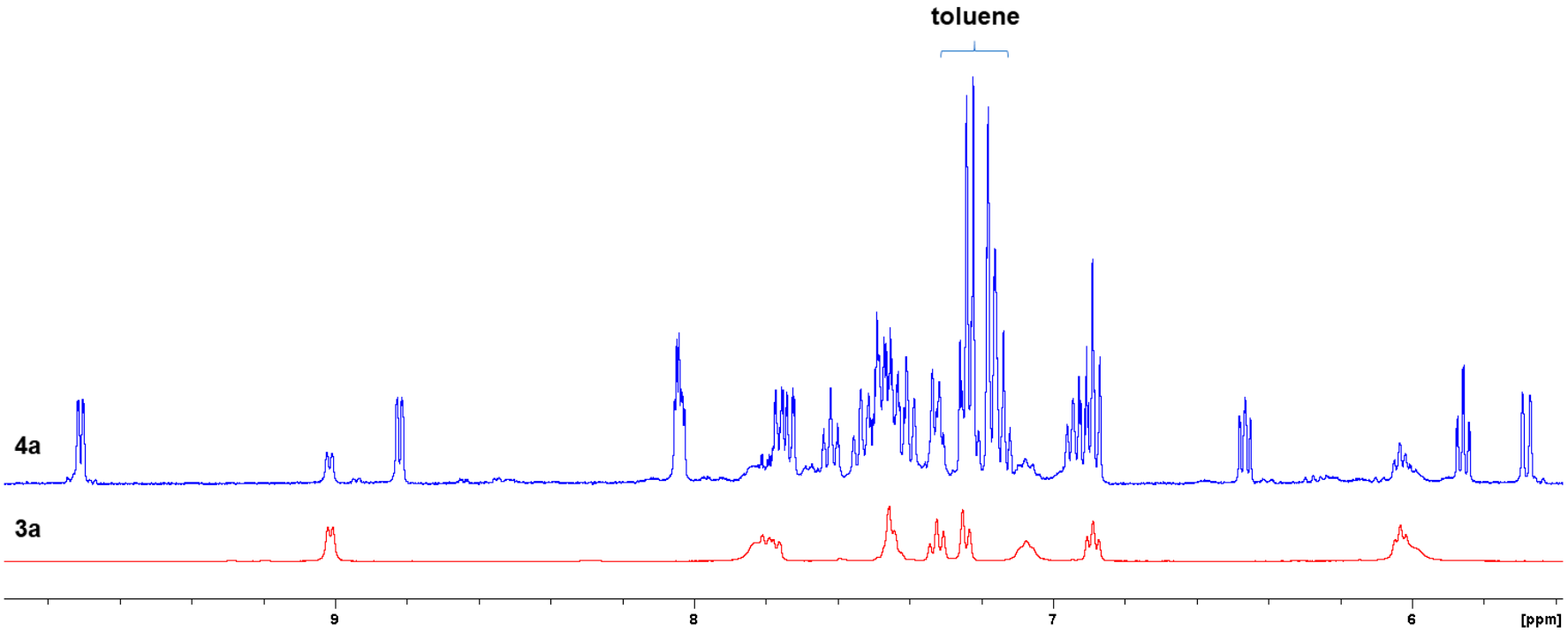

Figure S7. Aryl part of the ^{1}H NMR spectrum of (**4a** · toluene) in CD_2Cl_2 (blue) and overlay of the spectrum of **3a** (red), which is contained in the product as a contamination.

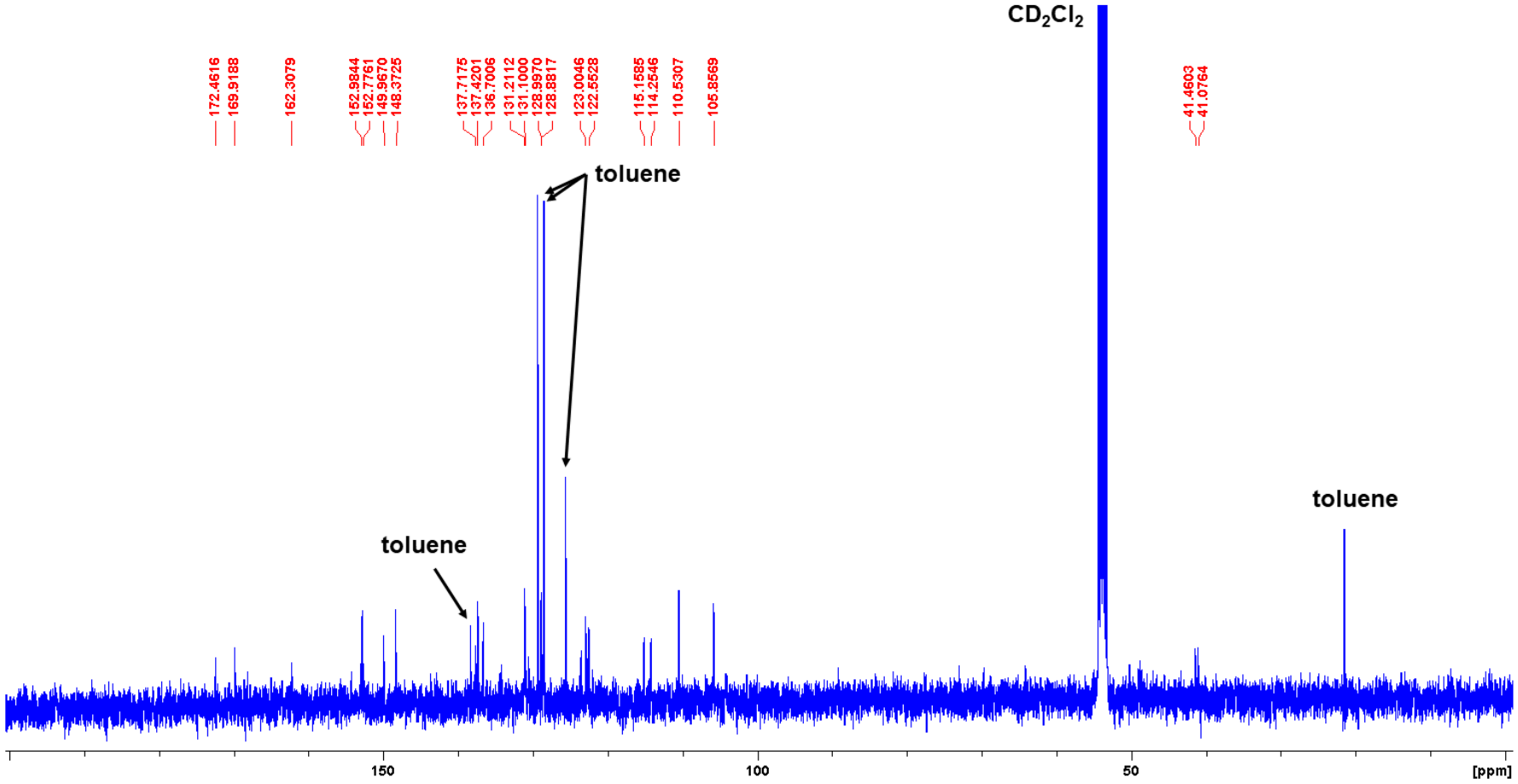

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of (**4a** · toluene) in CD_2Cl_2.

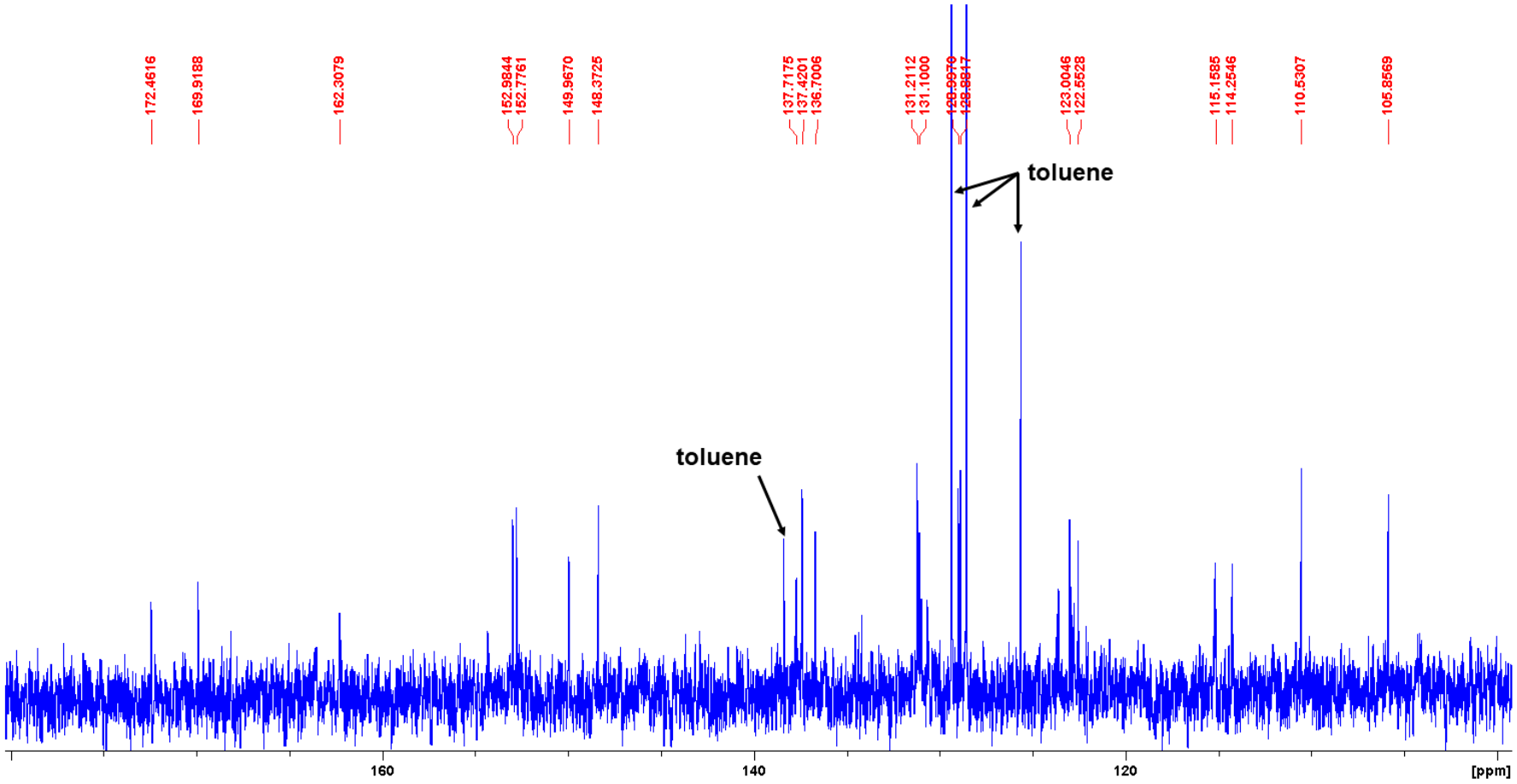

Figure S9. Aryl section of the $^{13}C\{^{1}H\}$ NMR spectrum of (**4a** · toluene) in CD_2Cl_2.

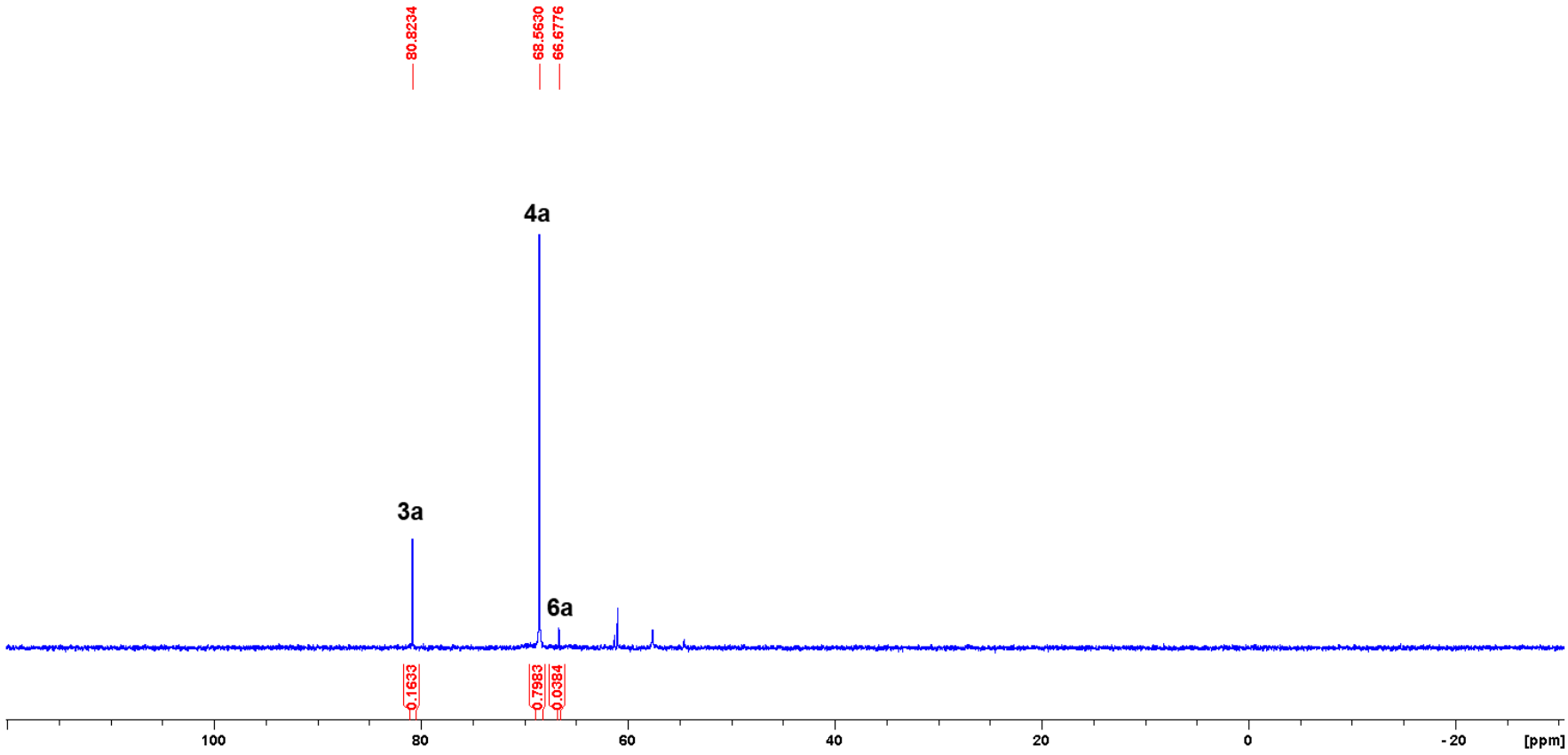

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of (**4a** · toluene) in CD_2Cl_2. In addition to the contamination with starting material **3a**, the spectrum contains the signal of decomposition product **6a** (and signals of other still unidentified decomposition products).

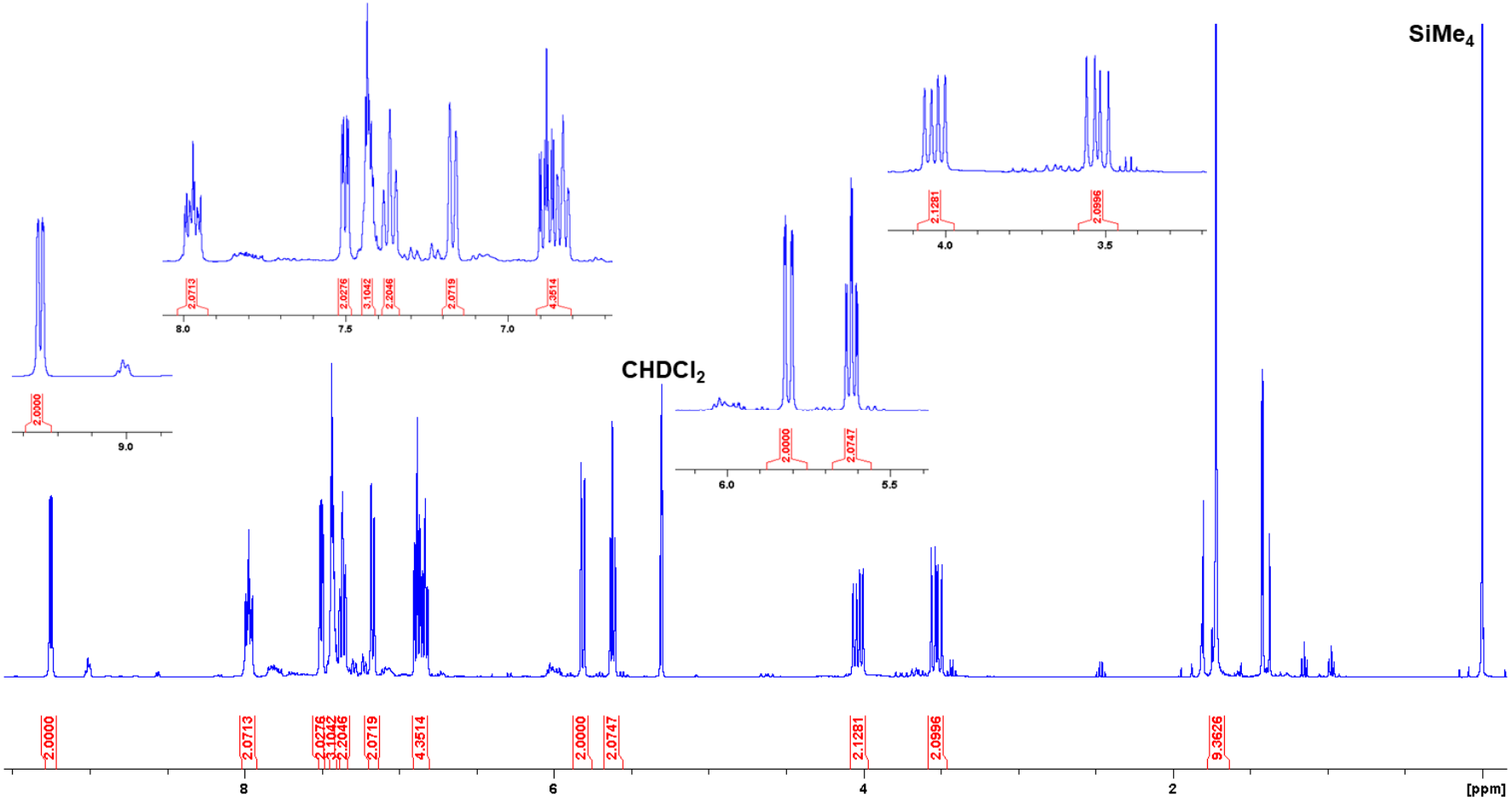

Figure S11. ^{1}H NMR spectrum of **5a** in CD_2Cl_2, sample prepared *in situ* from **3a** and CN*t*Bu (full spectrum and magnified insets of the aryl and CH_2 proton signals).

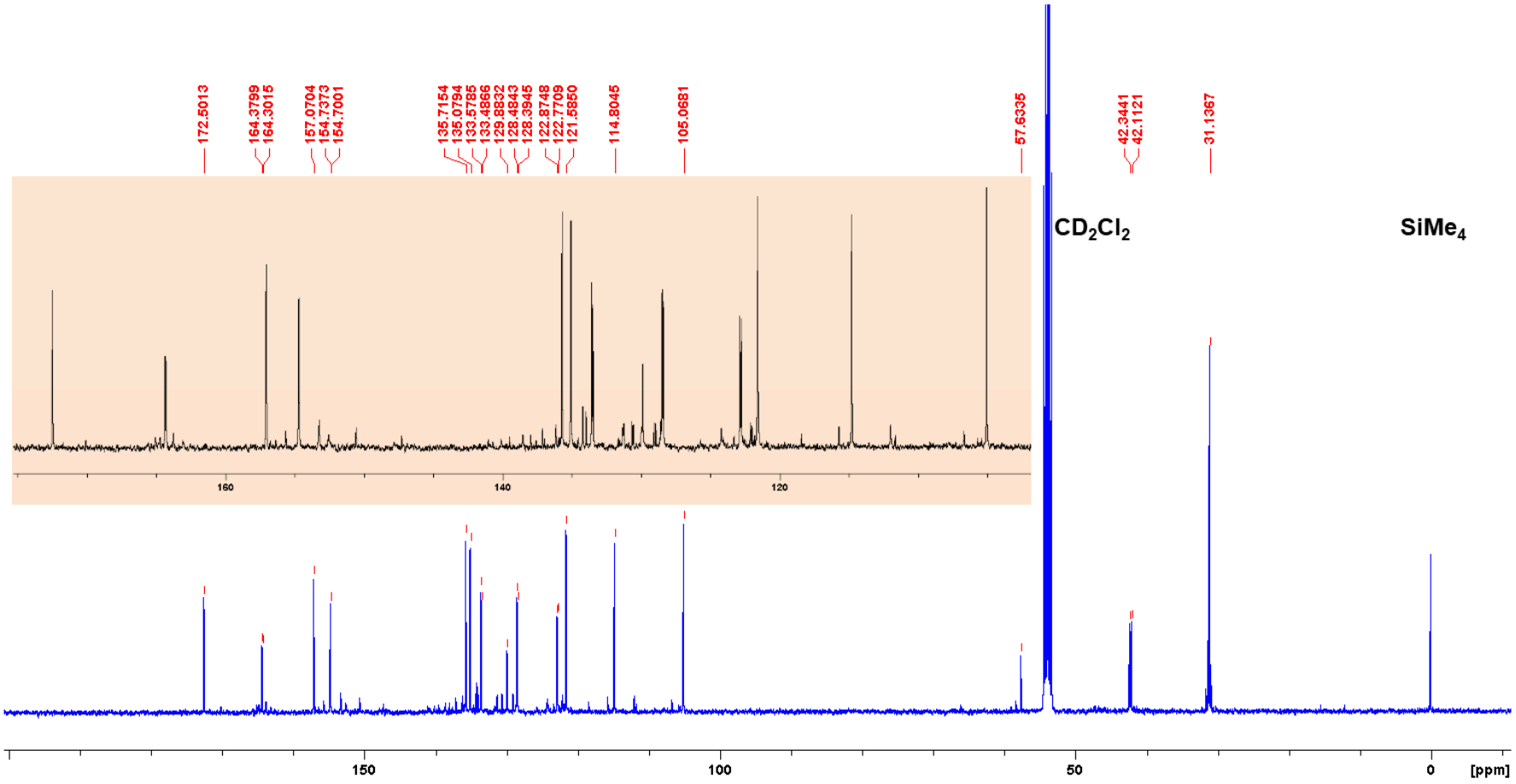

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in CD_2Cl_2, sample prepared *in situ* from **3a** and CN*t*Bu (full spectrum and magnified inset of the aryl part of signals). The location of the *C*NCMe$_3$ signal and of the Ph-ipso-*C* signal has not been identified.

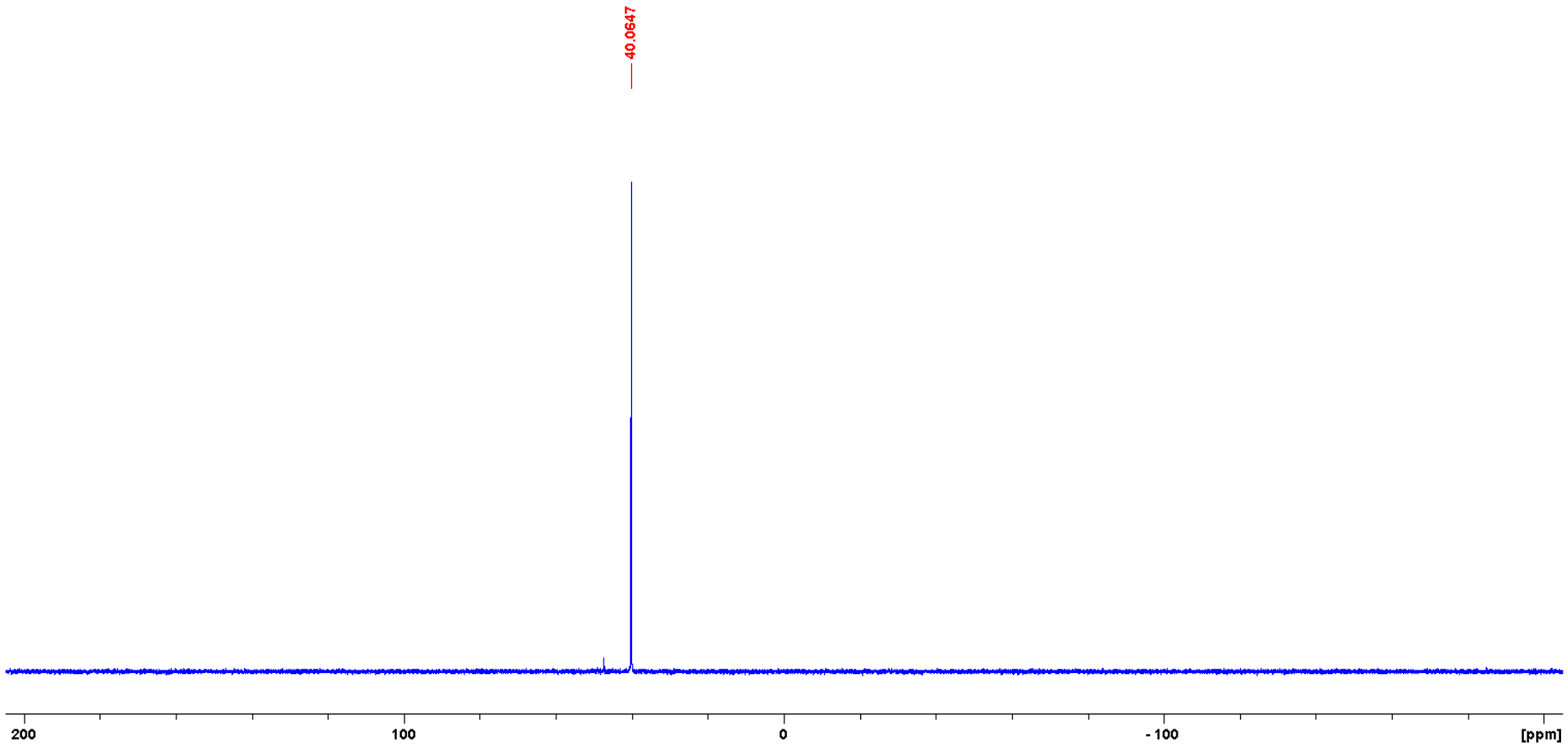

Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **5a** in CD_2Cl_2, sample prepared *in situ* from **3a** and CN*t*Bu.

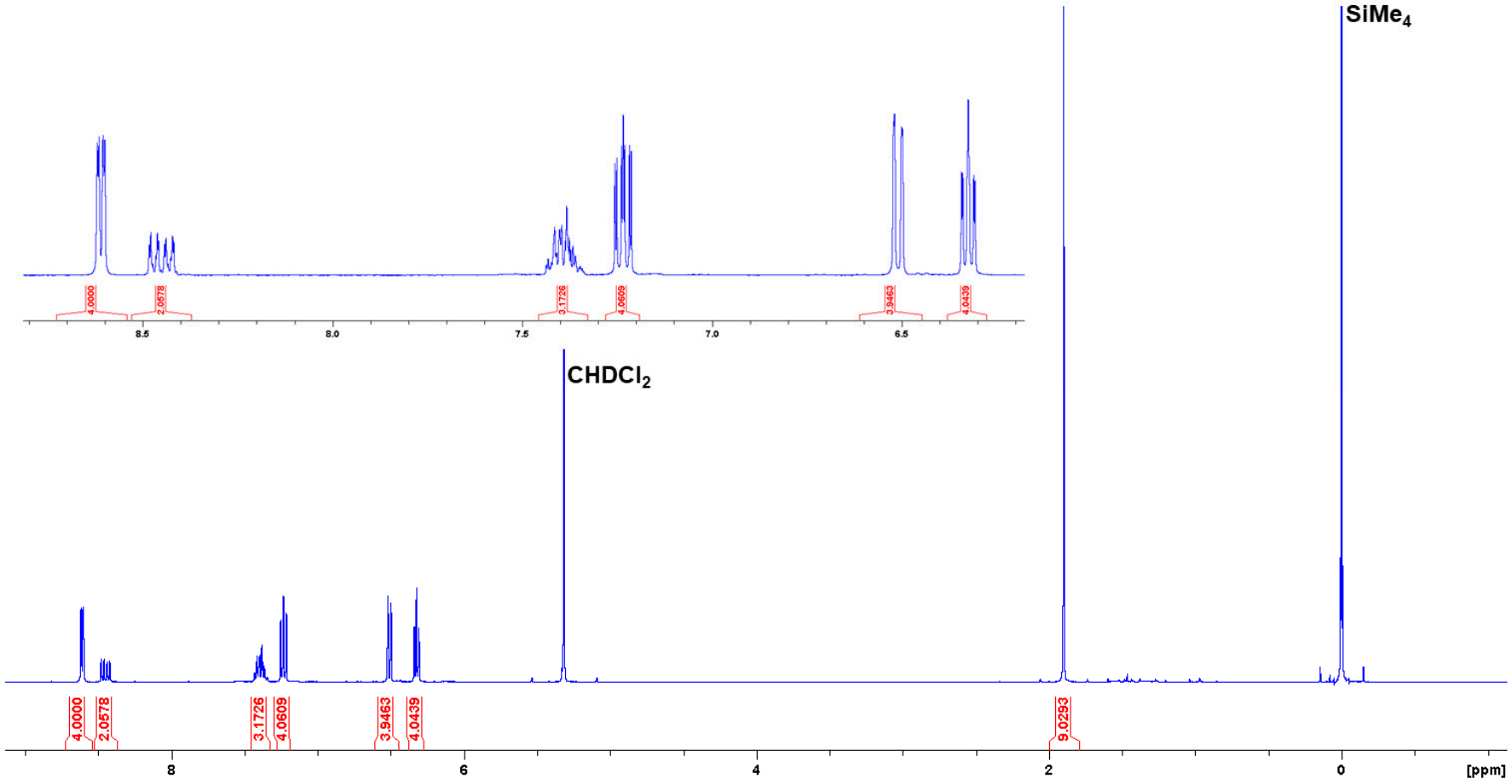

Figure S14. ^{1}H NMR spectrum of **5b** in CD_2Cl_2 (full spectrum and magnified inset of the aryl proton signals).

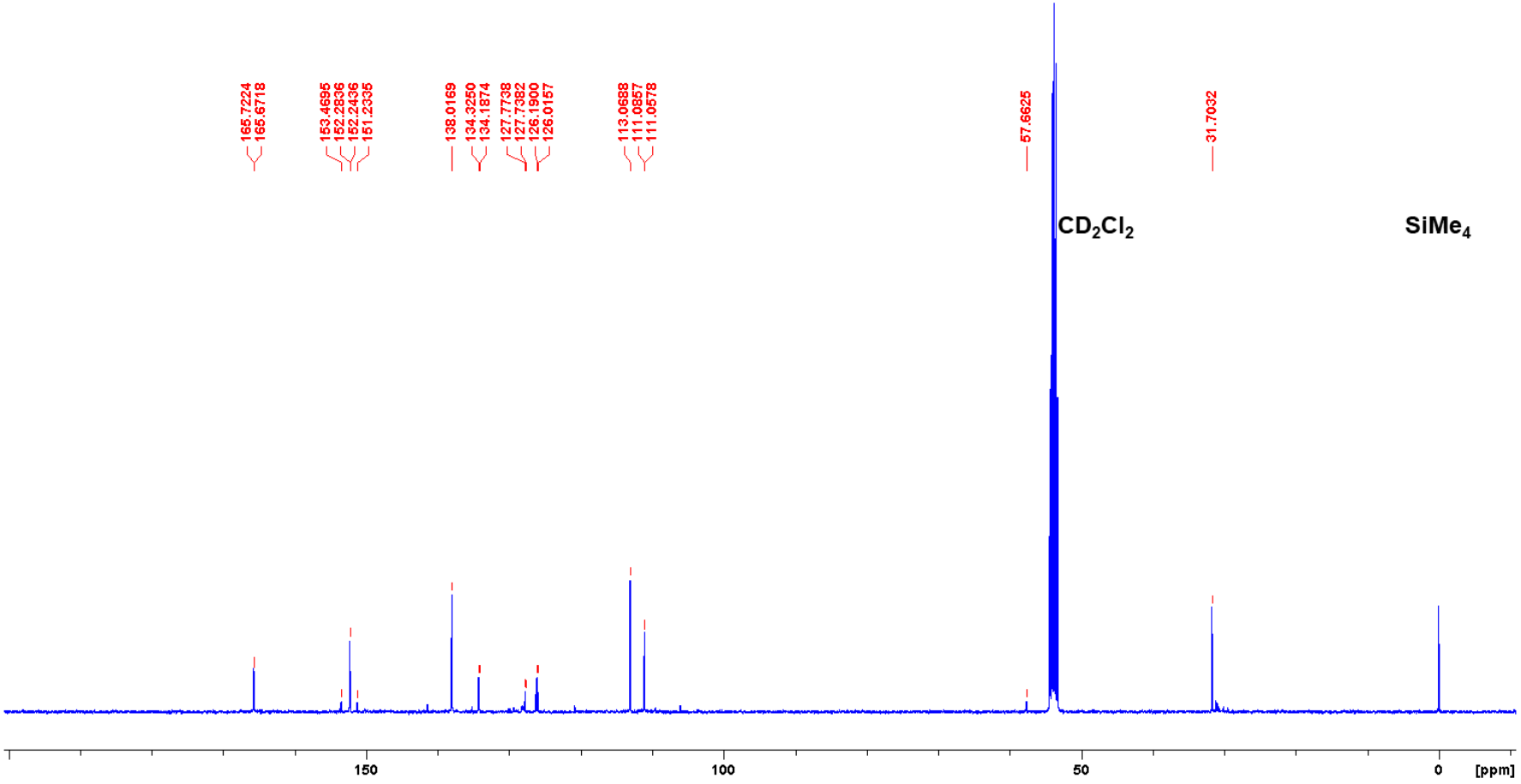

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in CD_2Cl_2. The location of the *C*NCMe$_3$ signal has not been identified.

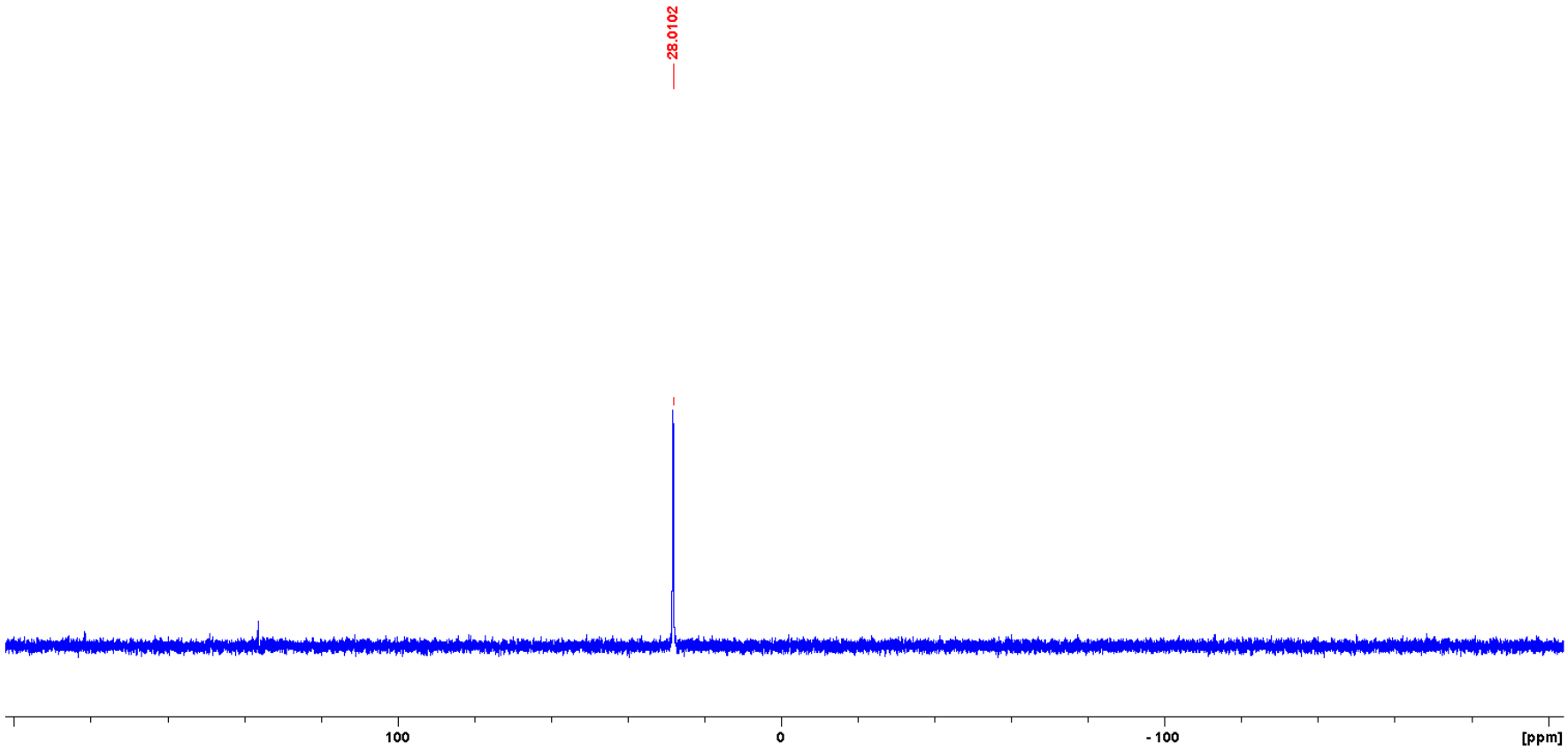

Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **5b** in CD_2Cl_2.

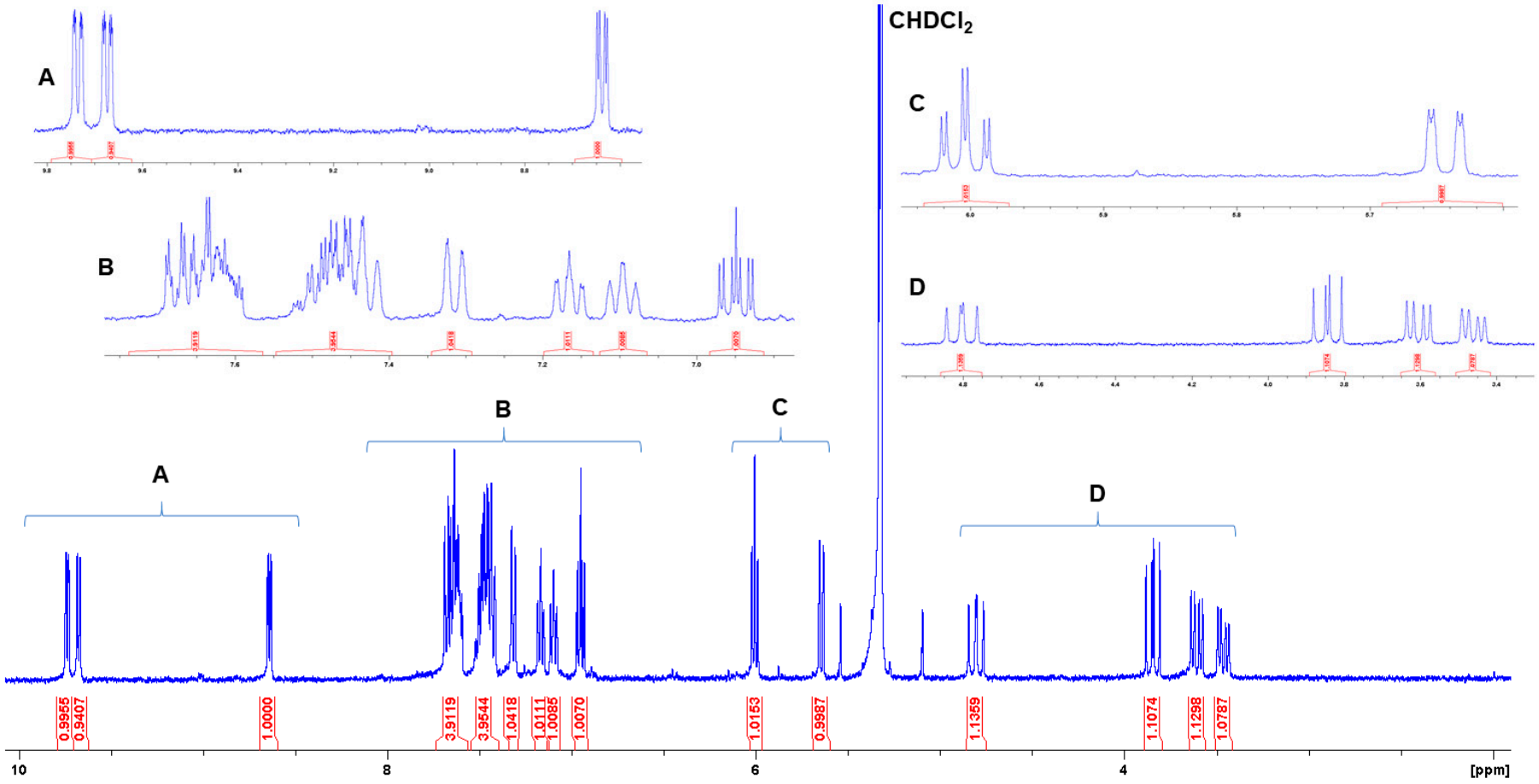

Figure S17. ^{1}H NMR spectrum of **6a** in CD_2Cl_2 (full spectrum and magnified insets of the (groups of) signals).

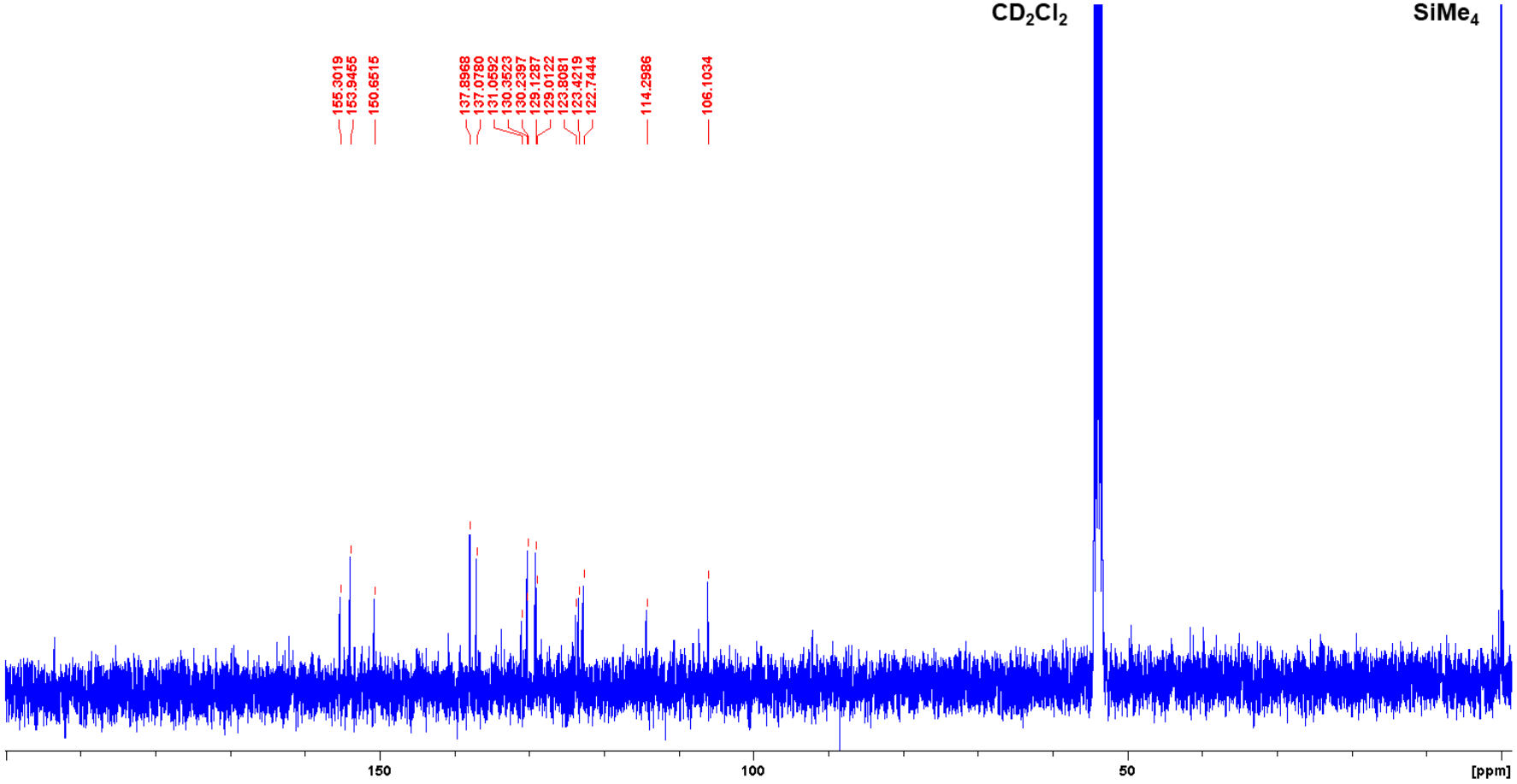

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in CD_2Cl_2.

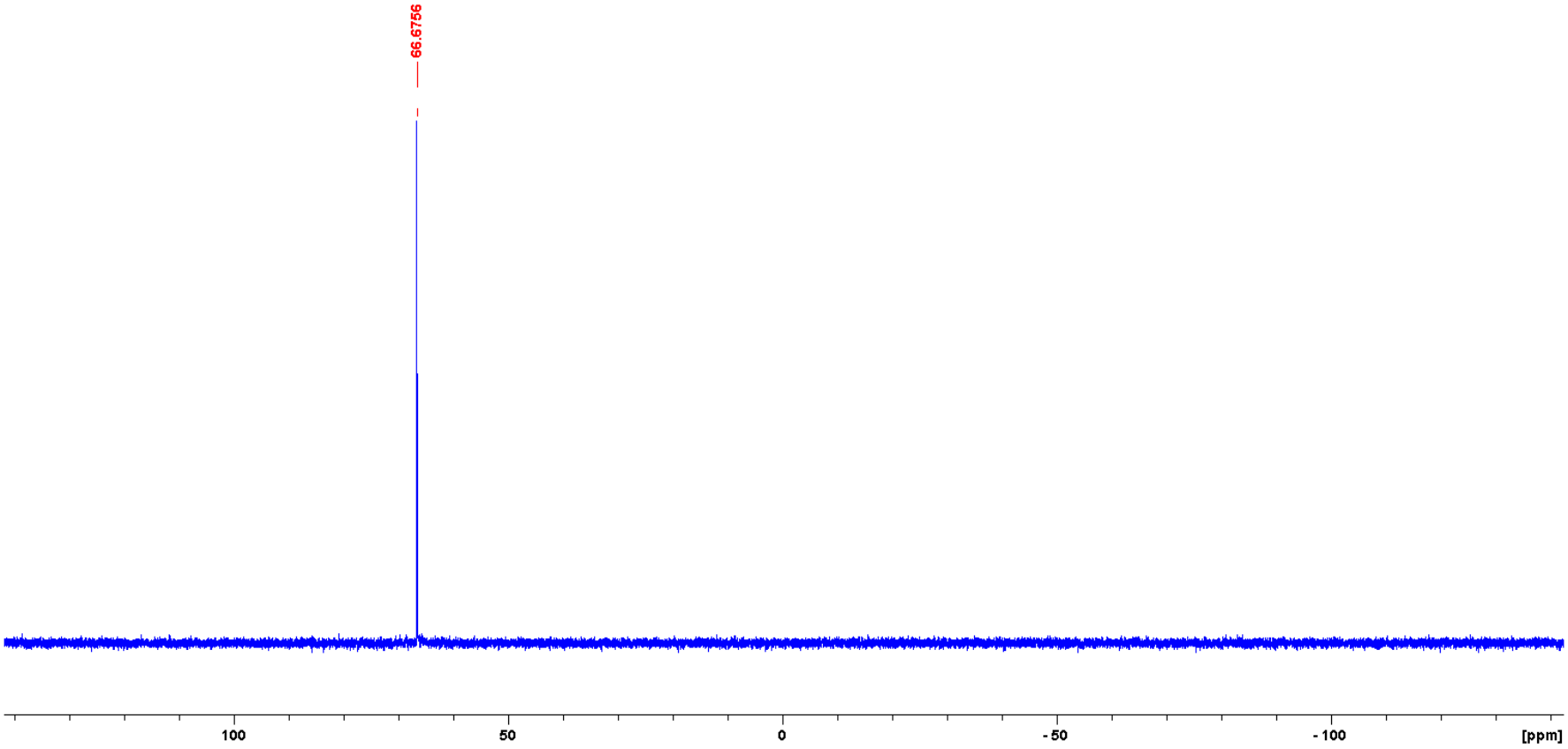

Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **6a** in CD_2Cl_2.

Atomic coordinates and total energies:

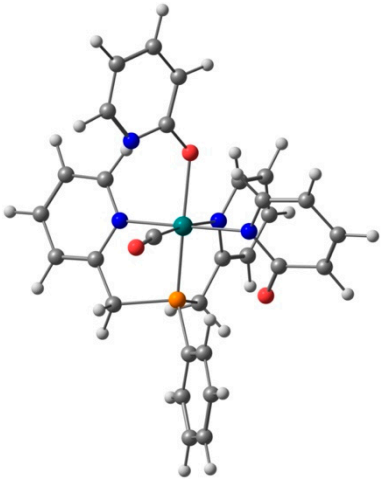

Figure S20. Optimized molecular structure of **4a[1]**.

PBE0:

final single point energy: -6486.191719155920 a.u.
final Gibbs free energy: -6485.76177128 a.u.

B2T-PLYP:

final single point energy: -6486.310311707651 a.u.

Table S1. Atomic coordinates for optimized structure of **4a[1]**.

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C	0.12519579349579	-2.05376209939462	-2.38075605455660
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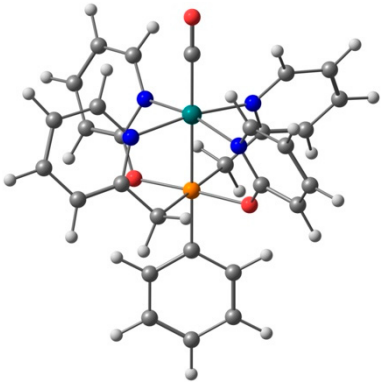

Figure S21. Optimized molecular structure of **4a²**.

PBE0:

final single point energy: -6486.139749933685 a.u.

final Gibbs free energy: -6485.70646114 a.u.

B2T-PLYP:

final single point energy: -6486.254919115781 a.u.

Table S2. Atomic coordinates for optimized structure of **4a²**.

Ru	-0.00029551628752	-0.00056381182322	-0.01516193433960
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N	-0.20716647012891	-2.08310663047519	-0.19073126708820
N	0.20652541080879	2.08220991217971	-0.18833135727331
N	2.07349532347212	0.01326249165590	-0.26141224207047
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H	0.70633167782022	-2.35797091875073	-3.36123076032281
O	1.73045485123480	0.70239164658274	-2.43359967258817

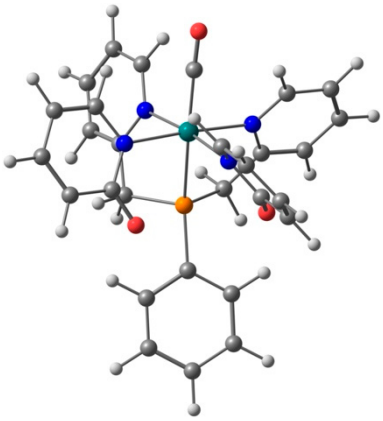

Figure S22. Optimized molecular structure of **4a**^{3}**.**

PBE0:

final single point energy: -6486.169901841126 a.u.

final Gibbs free energy: -6485.73860629 a.u.

B2T-PLYP:

final single point energy: -6486.285439713944 a.u.

Table S3. Atomic coordinates for optimized structure of **4a**^{3}.

Ru	-0.10435741886510	0.02314191180024	-0.05057292322127
P	-0.47426587043174	-0.02309523426012	-2.38004872379095
C	0.01421183171772	0.25396774907614	1.79125182107191
O	0.08404497615634	0.44049582017047	2.92440768878690
N	-2.22752234693958	0.05003750037013	-0.09069546310827
N	-0.21266795081481	-2.06342910694262	0.17288325652206
N	-0.00310132835470	2.10834812125085	-0.40497755886050
N	1.95917128054733	-0.08868979488429	-0.24351231818637
C	-2.88909427857296	-0.42094566096144	-1.16968350457040
C	-4.27842570179286	-0.42837329406576	-1.21002973401633
H	-4.77079043544110	-0.80983605407163	-2.09485154920144
C	-5.00946926876273	0.04148637035944	-0.13712249900910
H	-6.09206176297681	0.03337036460485	-0.16101393656350
C	-4.32378150943830	0.52828051084021	0.96372220367150
H	-4.83935959379593	0.91769027038015	1.83101441798035
C	-2.94609697192786	0.51575184347398	0.94173972996001
H	-2.38291162601683	0.89811288244918	1.78064496607312
C	0.25684036855744	-2.89110756231024	-0.83112429546888
C	0.26295800222643	-4.30193661740469	-0.57253549945334
H	0.67648655207066	-4.93032729680307	-1.35061770720790
C	-0.24315933020098	-4.82122811704763	0.58089863927799
H	-0.23615943086137	-5.89309518192993	0.74749468255587
C	-0.77658348011822	-3.95522973123799	1.54726732434629
H	-1.20258416167328	-4.31488840327211	2.47324977598159
C	-0.72752751429762	-2.61185677605190	1.29118234968816
H	-1.12184581287465	-1.91588045529770	2.02041208699125
C	-1.04894070293210	1.72637780834593	-2.58006785556517

H	-0.86352209768448	2.10469904521715	-3.58430850655923
H	-2.13422961684556	1.73115549586993	-2.44041450039091
C	-0.42618506811966	2.63060278698291	-1.57192445798124
C	-0.28741788437575	3.98461328237075	-1.84452673940959
H	-0.63914320236833	4.36313222933153	-2.79537161843247
C	0.30984819943348	4.82297237585620	-0.92415756989966
H	0.43074668431919	5.87829779975985	-1.13486370087226
C	0.76157737418012	4.27609744842557	0.26423067216511
H	1.25302907447839	4.87464094158200	1.01906821512950
C	0.58483915717772	2.92561166673298	0.47822328732516
H	0.94541824210527	2.46935340606209	1.38810690595980
C	2.56408154419412	0.51663486727788	-1.32531522834021
C	3.98697895143831	0.41277438647052	-1.42137919771433
H	4.45220756601551	0.90798968791386	-2.26363486576995
C	4.71439438699145	-0.29646334035795	-0.51087221664963
H	5.79173883183704	-0.37052219552503	-0.61301938257419
C	4.05788427529921	-0.93374047228798	0.55041338908434
H	4.58741105220121	-1.51798809367401	1.28958864791299
C	2.69819982241320	-0.79431856816822	0.63043999795803
H	2.14697704485926	-1.27417433844867	1.42912326845004
C	0.15098822904603	-0.45600175028125	-4.03123557578481
C	-0.14455825940962	-1.69499900366099	-4.59444700352297
H	-0.66704284375263	-2.44277294152181	-4.01617824628841
C	0.26510996495092	-1.99653483790930	-5.88385315527261
H	0.03109996651373	-2.96721871952857	-6.30453817798318
C	0.97814997784795	-1.06750987910251	-6.62638302457299
H	1.30150325611641	-1.30588893235634	-7.63273629342808
C	1.28273717951900	0.16524058036168	-6.06832731798547
H	1.85044776314082	0.89428434049695	-6.63424325078959
C	0.87347497579005	0.47043138675718	-4.77974563045421
H	1.14950009134889	1.41771730083846	-4.33996044806519
O	1.88663455122430	1.12678781846790	-2.18331338157443
O	0.63583846090496	-2.42092624048850	-1.92037019991800
C	-2.09564108769559	-0.90729190797108	-2.33350479225705
H	-1.84723285038267	-1.96224165043761	-2.19197796521016
H	-2.67272351689866	-0.81866120163596	-3.25507396096758

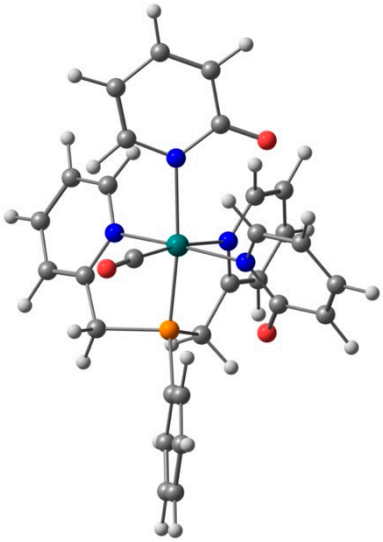

Figure S23. Optimized molecular structure of **4a**[4]**.**

PBE0:

final single point energy: -6486.183160077908 a.u.
final Gibbs free energy: -6485.75173398 a.u.

B2T-PLYP:

final single point energy: -6486.299848145378 a.u.

Table S4. Atomic coordinates for optimized structure of **4a**[4].

Ru	-0.00259664499323	-0.05088962221398	-0.03864104523077
P	-0.00565755267723	-0.42931795723310	-2.23456221335483
N	0.08730097086876	2.01646276749678	-0.25398370694101
N	-0.32910674438226	-2.15466132224562	0.00896712436334
N	-2.18930163535003	-0.04331714551207	-0.42275990861071
O	2.96567924864886	-0.16273908971811	0.02433859576376
O	-0.92754637888334	1.85221378041390	-2.29653384502409
C	2.77936582535437	1.68063906562923	-4.30810648231591
C	2.57824632678882	1.26538764690103	-5.61716481672993
C	1.98196859338154	1.18351694735331	-3.28985561236279
C	1.81583240281681	-0.12707438559101	0.02845360236458
C	1.57936957962588	0.34709330786759	-5.90703812586251
C	0.98181360153172	0.26037780261312	-3.57638237905952
C	0.63055744870107	-2.17680719004519	-2.21474143906646
C	0.65848739025048	2.79399009521852	0.68000853192615
C	0.74317678224497	4.15765632798272	0.58738775741315
C	0.78637673257597	-0.15983451267520	-4.88860761432910
C	-0.02314114794257	-2.88918614780794	-1.08125847094079
C	-0.35483045167581	-4.23514013102254	-1.14919406518248
C	0.18716993942962	4.76895913225493	-0.54163923796550
C	-1.01263876875823	-4.83816678150241	-0.09280141091172
C	-0.98307237029205	-2.73725455509858	1.02022871274762
C	-1.33995232002862	-4.07006311505248	1.01163332250012
C	-0.43924383716662	2.57898132218531	-1.39185731410824
C	-0.39297953938641	3.99823863529593	-1.50924200185973

C	-1.73233510271846	-0.66531051837944	-2.76674525982520
C	-2.67170746381885	-0.38410787350729	-1.63203061377556
C	-3.05683224938860	0.23188821698685	0.55905906982077
C	-4.03732631613105	-0.47802445585457	-1.86096084100297
C	-4.42640347288269	0.15852650182188	0.39336618559330
C	-4.92972183099633	-0.21033179692543	-0.84063782493558
H	3.55375836371114	2.40241160871095	-4.07879162676530
H	3.19821169373150	1.66051861580612	-6.41283543611210
H	2.12405612523910	1.52752604238289	-2.27297071126909
H	1.70822052250463	-2.09492419760987	-2.03980428204948
H	1.06034826896942	2.27307539854957	1.53762069569309
H	1.41670711356683	0.02385376549585	-6.92821797327725
H	1.21479337545126	4.72506460640481	1.37692457389605
H	-0.09603541787512	-4.79552021189602	-2.03789451665027
H	0.48912097806370	-2.71563881518754	-3.15289463978940
H	-1.27524896460637	-5.88794359442531	-0.13666849989606
H	0.00956312049813	-0.87910282159166	-5.12367831932875
H	0.21994472720436	5.84733972189412	-0.65310200571498
H	-1.22737135389706	-2.09487781227915	1.85412056734956
H	-1.86933571954732	-4.48565755654479	1.85811344552039
H	-0.82563373005678	4.42874314184018	-2.40261262881770
H	-1.88794082914442	-1.68144089025177	-3.13768144758171
H	-1.94320970585581	0.02846465152176	-3.58057238065456
H	-2.61451738050761	0.58129927464627	1.48485190158462
H	-4.38582182920617	-0.75302807755389	-2.84820856223096
H	-5.07430568034684	0.40028064978010	1.22506085906076
H	-5.99724908379776	-0.27819090571691	-1.01203696314199
C	0.81042145023551	-0.86711441738312	2.77840057307348
C	-0.70483966349110	0.92325501755350	2.97537447088624
C	1.04205193378568	-0.95046049248931	4.12361264263981
H	1.32145340438244	-1.55119757861177	2.11073830369664
C	-0.48328376545735	0.86312620430725	4.39592214088304
C	0.36393280624729	-0.04356218404441	4.95475238443064
H	1.73329606913227	-1.68528036112510	4.51195922901631
H	-1.02683696094193	1.58319922380762	4.99422457137340
H	0.51504780722933	-0.06345749844655	6.02893702217914
O	-1.47901781787073	1.75631682972420	2.47124704872026
N	-0.02413850309670	0.01230086709583	2.18506571517886

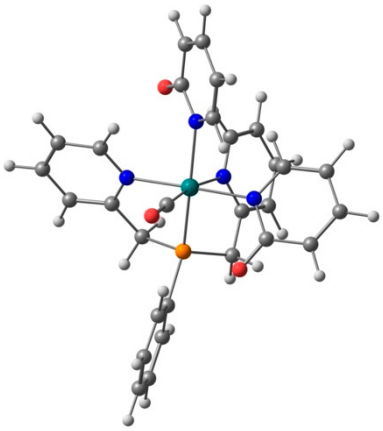

Figure S24. Optimized molecular structure of **4a**[5]**.**

PBE0:

final single point energy: -6486.182564613791 a.u.

final Gibbs free energy: -6485.75104808 a.u.

B2T-PLYP:

final single point energy: -6486.298785766808 a.u.

Table S5. Atomic coordinates for optimized structure of **4a**[5].

Ru	-0.01037661585830	0.00835170705089	-0.06841897934506
P	-0.24411366782856	-0.06444284307486	-2.29802824001741
N	-0.26382245340255	2.08772814919330	0.05245196894303
N	0.10935950189953	-2.09504737022713	-0.28776084930539
N	-2.22769648993270	0.10801934369018	-0.35947910499807
O	2.95730275720406	0.15449567402791	-0.07053568412703
O	0.96678990496180	2.43047663665959	-1.84052997775934
C	3.04726585918919	0.49284043962440	-4.64538989978315
C	2.55574190779162	0.23859584388236	-5.91705936092108
C	2.20608421781701	0.43346830301802	-3.54473983177992
C	1.81021419950485	0.10565436813033	-0.06808180374041
C	1.21633724343494	-0.08187577845614	-6.09087158924603
C	0.86637757098182	0.10368429018433	-3.71248534069506
C	-0.89603755551288	-1.79293846414064	-2.47984072084701
C	-1.04881560675218	2.61276104184932	1.01101270770947
C	-1.29969541821537	3.95112952275198	1.15234573623262
C	0.37656406703991	-0.15657419689451	-4.99176972708563
C	-0.29059722562056	-2.67233430682794	-1.43580277181046
C	-0.14743722894398	-4.03745680033971	-1.64049217293487
C	-0.68510530215887	4.82674382167094	0.24608443738551
C	0.41765972372003	-4.82394631991817	-0.65464491370154
C	0.66613496291753	-2.85773183977872	0.65890040834230
C	0.83858880513044	-4.21827770465037	0.51690805543149
C	0.31510259095428	2.91368791318414	-0.89248022521824
C	0.10490814981867	4.32275444548524	-0.74510537913686
C	-1.73366160569558	0.93776134785769	-2.60904799331776
C	-2.69991597072723	0.65452561182767	-1.49889252721030

C	-3.09152537072988	-0.19655967965859	0.61579512008788
C	-4.05037611884117	0.92227804303712	-1.66270865750881
C	-4.44702680110649	0.05526147853694	0.51619183981274
C	-4.93648835524028	0.63430516857227	-0.64039545947755
H	4.09019271008304	0.75034570583883	-4.50696413127825
H	3.21495287900302	0.29369614606958	-6.77508018539045
H	2.57893866511112	0.67358835038214	-2.56079998972168
H	-0.73827437509201	-2.20770635684091	-3.47471643836117
H	-1.48492764720106	1.90071304305613	1.69876125883560
H	0.82551255399930	-0.27593380213427	-7.08241799980408
H	-1.94068082861397	4.30073200143231	1.94919218616926
H	-0.47849285125297	-4.46674259976376	-2.57700176733596
H	-1.97602365880530	-1.74138993549990	-2.31262828815831
H	0.53698889939890	-5.89005301610644	-0.80311048165611
H	-0.66614328966869	-0.41686369055468	-5.13771637840112
H	-0.83932367496072	5.89738285612959	0.32814248917079
H	0.99280140521720	-2.34293067638392	1.54866936204934
H	1.29837953288812	-4.78241450485379	1.31663986951966
H	0.58911804247145	4.96200706625135	-1.47160278616312
H	-2.19550883880796	0.74993819543936	-3.57966207453994
H	-1.40355394322428	1.97868804262996	-2.58849421942149
H	-2.65618703301673	-0.69545199412108	1.47596241130402
H	-4.39233102126706	1.35768004012824	-2.59261690788070
H	-5.09753165007360	-0.20972055468578	1.33874161837645
H	-5.99231647470060	0.84871282625894	-0.75323635704125
C	0.81106279063565	0.86161891747177	2.73329859904724
C	-0.65572131520682	-0.97483248914775	2.88590373019694
C	1.01157870029681	0.93361507680490	4.08499031260454
H	1.30379621993221	1.56946839619332	2.07863573088888
C	-0.47349970687556	-0.92185610667952	4.30748607084727
C	0.33848660373374	0.00452373608147	4.89144465689631
H	1.66872460731793	1.68668373948864	4.49646553267763
H	-1.01294660374856	-1.65811034295204	4.88960528155245
H	0.46198409553459	0.02151882578967	5.96915220439209
O	-1.38832671215216	-1.83248009810953	2.34607359790083
N	0.01507325724595	-0.03942012388069	2.12261137274633

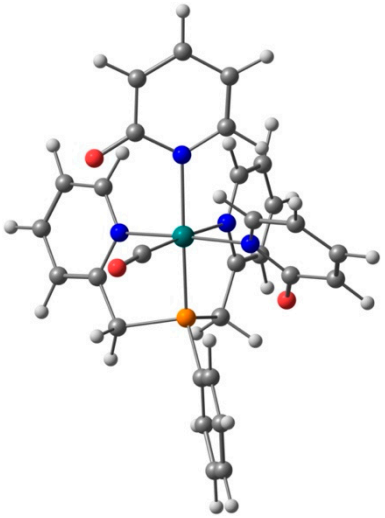

Figure S25. Optimized molecular structure of **4a**[6]**.**

PBE0:

final single point energy: -6486.188266474338 a.u.

final Gibbs free energy: -6485.75679510 a.u.

B2T-PLYP:

final single point energy: -6486.303803226688 a.u.

Table S6. Atomic coordinates for optimized structure of **4a**[6].

Ru	-0.00301665039932	-0.03869299179271	-0.06044288035532
P	-0.21417353658563	-0.17116721657111	-2.27413321574008
N	0.02092859274786	2.05764187735689	-0.00599159556884
N	-0.16640611489845	-2.14928270065182	-0.23991284990526
N	-2.21779121804771	-0.21964900633666	-0.20459342822515
O	2.96773071444956	-0.06495521971487	-0.24575412326717
O	-1.39710750995722	2.15624779839059	-1.79222619282833
C	2.16079045586790	2.47155766226514	-4.23681164894761
C	1.82981447772263	2.26668439212058	-5.56852724450584
C	1.52737976877740	1.74249277951151	-3.24252363746273
C	1.82699909547293	-0.06869370115005	-0.12609114410956
C	0.86438220985495	1.32873450754950	-5.90786526991903
C	0.56061391980534	0.80076993367997	-3.57866255155643
C	0.45615920533770	-1.86486085685421	-2.57163106534691
C	0.80397683219991	2.72002709383285	0.86594692429078
C	0.88000111925294	4.08496618950517	0.94592006689038
C	0.23304567859893	0.59452760723388	-4.91629399371789
C	0.03142554357763	-2.73835571748622	-1.43620242088849
C	-0.16748101573206	-4.10145745946978	-1.60387953595705
C	0.08800787504275	4.83359795737438	0.06529526573135
C	-0.57482565866672	-4.87351771409409	-0.53170619626560
C	-0.56871162789659	-2.89730771595953	0.79098554800335
C	-0.78548242158563	-4.25620586751282	0.68906062713710
C	-0.73164426431084	2.76148646831685	-0.92269537989434
C	-0.70008445698785	4.18858207782836	-0.84332544979316

C	-1.99018222443024	-0.33830551503269	-2.65907889403955
C	-2.80860323554049	-0.36516547341710	-1.40474474161145
C	-2.97888199792604	-0.32140443092366	0.89017559935856
C	-4.17873661196599	-0.57211391896204	-1.51073136795851
C	-4.34293552388816	-0.52345544820549	0.85661444831557
C	-4.96134588530657	-0.64190753377767	-0.37578888190811
H	2.90955414493497	3.20671634588723	-3.96848558531012
H	2.32249838450711	2.84068261021774	-6.34403412148203
H	1.77216174996769	1.91460822558312	-2.20186786848066
H	1.54566576790597	-1.75358454169432	-2.56479758268863
H	1.38793724466686	2.09956614017583	1.53272151813768
H	0.60239479797688	1.16895177599474	-6.94686309762782
H	1.53216801246696	4.54889541252683	1.67217938746805
H	0.00117804558053	-4.54234706037594	-2.57754878926250
H	0.17560559675029	-2.29906009721202	-3.53243554823769
H	-0.73053763935961	-5.93879205791051	-0.64982217719167
H	-0.51958981831860	-0.13692546764170	-5.18941455678994
H	0.10657446711139	5.91766532050729	0.09789224992927
H	-0.72565956200346	-2.37390056043180	1.72096172867900
H	-1.11087205993284	-4.81050156272215	1.55869681557477
H	-1.31541700462858	4.72745568195910	-1.55191207903492
H	-2.18487811822934	-1.24270000968876	-3.24093361014887
H	-2.28430532232526	0.52369644353403	-3.25737459190585
H	-2.46472507287816	-0.24345988920967	1.83621897256148
H	-4.61641585629797	-0.67773048615558	-2.49498643164489
H	-4.89647275529443	-0.58873462050786	1.78345208388077
H	-6.03047715757404	-0.79748338343954	-0.45200597942107
C	-0.72444442686025	0.90038348953342	2.78133517913635
C	0.89295902705185	-0.82297852203717	2.79285515025592
C	-0.72332009166989	1.04136750105827	4.14268738332327
H	-1.33503710772979	1.55624296067109	2.17136120001064
C	0.89454014523537	-0.71807961796254	4.22714734101301
C	0.11295009245335	0.18693132350885	4.88013903612911
H	-1.33911288703772	1.79472327667591	4.61339914130886
H	1.56584330950652	-1.38095866497114	4.75795759648165
H	0.14500221126537	0.25378844521929	5.96262417600044
O	1.63676494030922	-1.60632997789375	2.18027410865454
N	0.00584877286674	-0.00637244025144	2.10501274172722

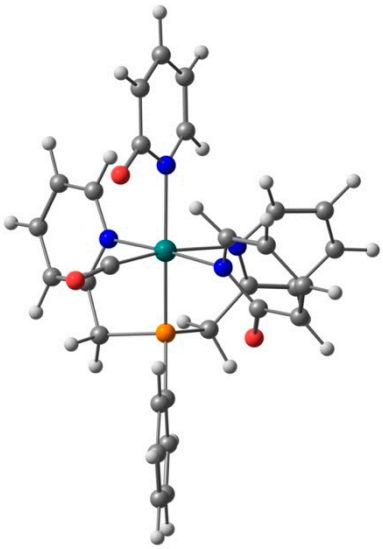

Figure S26. Optimized molecular structure of **4a**[7].

PBE0:

final single point energy: -6486.181286899863 a.u.
final Gibbs free energy: -6485.74935027 a.u.

B2T-PLYP:

final single point energy: -6486.295921648714 a.u.

Table S7. Atomic coordinates for optimized structure of **4a**[7].

Ru	-0.00167173230265	-0.07410620462441	-0.04948578450305
P	-0.31631756680167	-0.46846923783607	-2.22342185029743
N	-0.09558811459224	2.00165106055873	-0.26349167171677
N	-0.00789842488253	-2.24268257230820	0.02230845082365
N	-2.19147628980332	0.15868228806715	-0.14635353871124
O	2.94651821870965	-0.14871204370933	-0.49112916956034
O	-1.29228901133162	1.78590914015072	-2.21042593415093
C	1.93877967435031	1.70929273696068	-4.80218175834255
C	1.49767564527484	1.28910158394384	-6.04968586005892
C	1.36309527636868	1.19641232017721	-3.65121910397097
C	1.83350762608397	-0.10184921391408	-0.21960347863583
C	0.48302962306753	0.34796668698695	-6.14370311167873
C	0.34679940326028	0.25093935695374	-3.74209213994691
C	0.40636893143352	-2.16123588924800	-2.37339961664093
C	0.47710496834770	2.82289128500333	0.63605850452260
C	0.38378870968820	4.18983935033273	0.58671223536408
C	-0.08609361522501	-0.17673710031757	-4.99245726260242
C	0.13979934787215	-2.93364797328748	-1.12929520534991
C	0.07846988009766	-4.32076507850968	-1.15356823689837
C	-0.34370671632716	4.76096220906081	-0.46291434118599
C	-0.09582765549765	-5.02852273045096	0.01980333043439
C	-0.14210649210819	-2.93984557412551	1.15737099704829
C	-0.19224160517452	-4.31793108655381	1.20300551111786

C	-0.78934656320130	2.53166521638802	-1.33088722970989
C	-0.91427845988123	3.94986531771369	-1.40221917309614
C	-2.10522134165694	-0.85582311524372	-2.36572381252946
C	-2.85887552176193	-0.19058676889529	-1.26031915217500
C	-2.82455275527152	0.90998402531834	0.76070827761821
C	-4.20661339150568	0.10253768056964	-1.41436848066424
C	-4.15434798676310	1.26241002929778	0.65943255406842
C	-4.87002922495586	0.82487845577158	-0.44167434960199
H	2.72863267580674	2.44646002484241	-4.72401345992045
H	1.94388052303236	1.69688979135506	-6.94869291890106
H	1.69296824958686	1.54028829291548	-2.67837517038117
H	1.48686802259040	-2.01123905690461	-2.47475103357427
H	1.05908779820375	2.32950993661712	1.40273260773820
H	0.13418931486824	0.01874561168539	-7.11522087116651
H	0.87394793547971	4.78908842317102	1.34105073693202
H	0.18551562430870	-4.83060368894471	-2.10202756697277
H	0.07370499339730	-2.70683653239024	-3.25828069002822
H	-0.14135828035504	-6.11053083275084	0.01136424466209
H	-0.87341669097931	-0.91770601396923	-5.07726137175473
H	-0.44713157883006	5.83807760312052	-0.53893609998013
H	-0.20464648072055	-2.36367126229183	2.06610695848064
H	-0.30615338555282	-4.81192396271957	2.15841036613904
H	-1.47363707687393	4.34619644197887	-2.23940536864339
H	-2.21924128182785	-1.94213705987465	-2.30582536803703
H	-2.50853837786538	-0.53380470052675	-3.32555742231755
H	-2.22623590777088	1.25666777235808	1.59042682304836
H	-4.71258241568042	-0.20881723147533	-2.31872868453717
H	-4.60544373166406	1.87446229071428	1.42836387707628
H	-5.91851405279559	1.07044848111668	-0.55772505063401
C	-1.05996355904543	-0.45355761354386	2.84549911455123
C	1.14862412395759	0.35670937930496	2.81450997187580
C	-1.11779091715707	-0.53175852128347	4.21070205092159
H	-1.90820236013950	-0.79164177532798	2.26287211788593
C	1.11560529836564	0.30799977467611	4.25105382316808
C	0.01682151216838	-0.12202423012358	4.93005873936428
H	-2.00922122643609	-0.90207149582385	4.69737422148930
H	2.01646960324713	0.62208038685404	4.76206464240688
H	0.02139340666570	-0.15466492137401	6.01438922168489
O	2.16281460694629	0.71913269015660	2.19415514317489
N	-0.00320364644118	-0.01189412577295	2.13630849027948

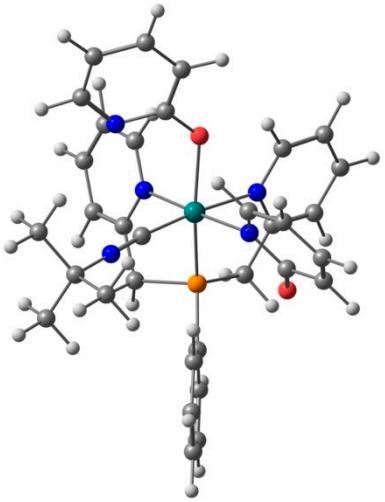

Figure S27. Optimized molecular structure of **5a**[1]**.**

PBE0:

final single point energy: -6623.485880982396 a.u.

final Gibbs free energy: -6622.94002378 a.u.

B2T-PLYP:

final single point energy: -6623.615457188704 a.u.

Table S8. Atomic coordinates for optimized structure of **5a**[1].

Ru	-0.00681675557926	-0.11174778179668	0.01219446783453
P	-0.14476767232096	-0.43381925087722	-2.14743438052181
N	1.62371839903464	-1.03809783071178	2.82571647850250
N	-0.05260420449417	1.97345890108941	-0.04838411750868
N	-0.11142769212748	-2.21067351629110	0.05494079833114
N	-2.15944810548746	-0.10176180926904	-0.15354933216207
O	-0.26798933399350	0.04609051175766	2.12681577771847
O	-1.16083179908113	1.96968383580315	-2.05037510718320
C	2.36774596035771	1.90086500031484	-4.31979229866072
C	2.48417915924776	-1.28039499574003	3.81256622919675
C	2.11278652548697	1.52029960473470	-5.63044794011204
C	2.40091040776181	-0.73808960146614	5.07953564962315
C	1.65991788292741	1.32315329629628	-3.27804410317321
C	1.88448300941432	-0.06281325170640	-0.00288360154147
C	1.14933651608129	0.55788574609233	-5.89709044335542
C	1.33061321434232	0.12147754691093	5.33278621438464
C	0.69732713413245	0.35357377840741	-3.53992679485187
C	0.50483300361292	-2.16354707332378	-2.28820494921809
C	0.50648325073143	2.68428325785540	0.94353770487278
C	0.59128975664473	-0.20917969214777	3.05771376464915
C	0.51469087951230	4.05533040773495	0.99747282015357
C	0.44744990154851	-0.02864943270792	-4.85413253745404
C	0.42634275069994	0.38768849833892	4.33459845319074
C	0.09250774596655	-2.92407266618789	-1.07196323663705
C	-0.08148564667563	-4.30070702888158	-1.08795364379406
C	-0.10586478962512	4.74873242614943	-0.04864147700932
C	-0.45913796585847	-4.96086232636485	0.06759401169086

C	-0.48221060998274	-2.85103681878032	1.16894678222219
C	-0.66314937072091	-4.21854016900247	1.21867962686733
C	-0.65968659565535	2.62109924502839	-1.10407894867415
C	-0.67930974368045	4.04997205900507	-1.07313757763054
C	-1.92572676345724	-0.62532948729455	-2.54308260255325
C	-2.76158574660038	-0.31448316352224	-1.33636040890790
C	-2.90562268599796	0.18790544944380	0.91700232349179
C	-4.14391539678673	-0.25129846604745	-1.45119493551691
C	-4.28233882955929	0.27283233062201	0.86690390081407
C	-4.91550469723323	0.04634988583060	-0.34382190377472
H	3.11226027939874	2.65948989710056	-4.10915543630263
H	3.29970992769304	-1.95813085898536	3.56790214413069
H	2.66147623652973	1.97761715394809	-6.44509881089265
H	3.13720926163154	-0.97507751879827	5.83603600917441
H	1.83747462907341	1.63203527198339	-2.25542140999687
H	1.59477422622564	-2.05425276020540	-2.29570751133881
H	0.96105666518562	2.09871788381670	1.73130604652599
H	1.21329909385803	0.58119665139480	6.30839700114858
H	0.94403011178968	0.26260416921113	-6.91918509049225
H	0.98465223351755	4.56321550016775	1.82803969668361
H	0.08475228629507	-4.84170391433527	-2.01048729299525
H	0.22125779401309	-2.68771027437775	-3.20264963849303
H	-0.59543837874252	-6.03536316299643	0.06731748290909
H	-0.30164132370491	-0.78255705056343	-5.07084283110960
H	-0.12944057279494	5.83347282564048	-0.05017700541889
H	-0.41314974747871	1.05402876622154	4.48928296921475
H	-0.63654962654406	-2.22045869457582	2.03171565085734
H	-0.96293635188612	-4.68279271847037	2.14852510795259
H	-1.16388220512646	4.54808457111457	-1.90293964329871
H	-2.13223740410333	-1.64364764761415	-2.88440959175594
H	-2.19133345555797	0.06027246036202	-3.34736888873898
H	-2.34566403856517	0.35214143659402	1.82969785935724
H	-4.60081057711529	-0.42440267969510	-2.41703675192693
H	-4.83801939015638	0.51569514815629	1.76266602220632
H	-5.99391254564239	0.10614911456007	-0.42703156798979
N	3.04532950466922	0.02774397854272	-0.09691274536890
C	4.45684448631452	0.21586200153530	-0.15006954489064
C	5.07229257431591	-0.37863743647891	1.11257310047875
H	4.85013548240396	-1.44419636210423	1.18011386988391
H	6.15497388544877	-0.24490072503768	1.09028973203390
H	4.67296262046416	0.11242973339570	2.00018609945431
C	4.72832627489843	1.71600960381608	-0.22876324113030
H	5.80429587523286	1.89300113731951	-0.26619721559726
H	4.27193055291299	2.14050822744417	-1.12395194984856
H	4.31813608614739	2.22425684381797	0.64447093543220
C	4.98458451006795	-0.48999906266842	-1.39587945935064
H	4.77270060786988	-1.55907579508386	-1.34752999558712
H	4.51818638961655	-0.08076086156248	-2.29327114267392

H	6.06439450925888	-0.35176007188597	-1.46751919554915

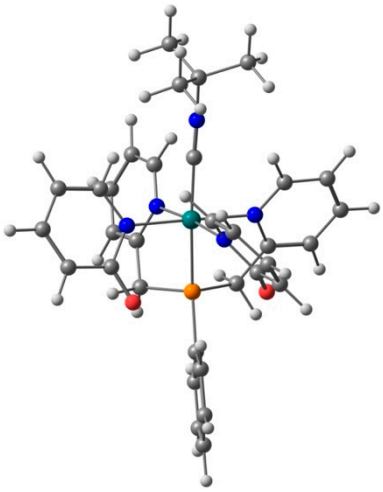

Figure S28. Optimized molecular structure of **5a**[3].

PBE0:

final single point energy: -6623.466914284028 a.u.

final Gibbs free energy: -6622.91949136 a.u.

B2T-PLYP:

final single point energy: -6623.592996168088 a.u.

Table S9. Atomic coordinates for optimized structure of **5a**[3].

Ru	0.04580701715467	0.02762901536721	0.02336912468331
P	0.26426005521373	0.16757381102720	-2.27643080677213
O	-2.21990057009921	-0.96711267180721	-2.01483308482947
O	1.59998358962458	-2.07996405411905	-1.70565483594250
N	2.15225095824487	0.09127676154845	-0.04639165036337
N	-0.07970491423420	2.12020370398298	-0.20522501345268
N	-2.06730323944070	0.00593095462161	0.05002656153511
N	0.13421119170165	-2.05127809185169	0.05766644974738
N	0.04937957831162	0.00503604082734	3.12426859036932
C	2.00483274459693	0.79490476292338	-2.38738406812317
H	2.50373146211297	0.40829776783435	-3.27551660587524
H	1.97968681073020	1.88488815225014	-2.48400483569825
C	2.79911463433124	0.42673778997305	-1.17939223541232
C	4.18661567929496	0.42628273325590	-1.24273478878516
H	4.66437425827291	0.70193045628242	-2.17391743187257
C	4.93642094272883	0.05563664058737	-0.14443806449244
H	6.01829864025432	0.04262924215146	-0.19170803072017
C	4.26571272250906	-0.31417650140863	1.00883830337718
H	4.79195301660869	-0.63381815681301	1.89828186121852
C	2.88755116413611	-0.28039320713222	1.01068167847795
H	2.33639913518314	-0.57740841307612	1.88990086837375
C	-0.68932387718235	1.72708630182508	-2.53778020278086
H	-0.49697557433138	2.23030121456832	-3.48642006411808
H	-1.73356012907797	1.40178999992914	-2.53681717983001
C	-0.43002304565099	2.65273184925464	-1.39789576784209

C	-0.52051484279471	4.02971454275953	-1.56670391219422
H	-0.79984893917523	4.41694411747590	-2.53789876133530
C	-0.26128418777944	4.88178613866318	-0.51125608587925
H	-0.33468558447934	5.95489756192593	-0.63698061599940
C	0.09954596992006	4.32843588440683	0.70679463847087
H	0.32158818446808	4.94331593714091	1.56865218783592
C	0.17838838678395	2.95643453955721	0.81132471135931
H	0.46385859636754	2.48847535234675	1.74261073081857
C	-2.79071355725996	-0.55143798922344	-0.98972373042287
C	-4.21798968789967	-0.61017022946576	-0.84699148324164
H	-4.76012110185942	-1.09177327721449	-1.65053689428472
C	-4.85592331720393	-0.06469666448566	0.22630629849272
H	-5.93717529610160	-0.11104613656270	0.30299312559761
C	-4.09675617596978	0.56432572090811	1.22383783801107
H	-4.54998924457675	1.03502619932229	2.08527444437094
C	-2.73428858924420	0.56216584527885	1.07909800662473
H	-2.12019310244078	1.03622747494747	1.83323070910234
C	0.94893206330527	-2.71111967488326	-0.84500773709766
C	0.99686313695466	-4.13928614774656	-0.75657821280223
H	1.65387507142767	-4.64417644700989	-1.45300350982980
C	0.23464371673617	-4.82833495521998	0.14239351438922
H	0.28138103271773	-5.91166388460216	0.17892731231151
C	-0.61391018681902	-4.12543220758995	1.00752127263348
H	-1.25375740215818	-4.62485080798960	1.72167813170612
C	-0.61806560809711	-2.75715759144103	0.91674282835281
H	-1.26476630648994	-2.17023838321940	1.55689121905270
C	0.05055205769695	-0.70145164776074	-3.85875370232684
C	0.39670105542337	-0.03548303630001	-5.03205980798950
H	0.76444151700481	0.98428894877058	-4.99540856857895
C	0.28369357282309	-0.66485164712493	-6.26332490160936
H	0.55584220994599	-0.13350505842473	-7.16769306047510
C	-0.17545965477187	-1.97131313838288	-6.32949048654853
H	-0.26460310472099	-2.46826043841008	-7.28838932298935
C	-0.52168964808781	-2.63909035921556	-5.16270458115906
H	-0.88292418186445	-3.65958327890537	-5.20863529600518
C	-0.41139613475359	-2.01037042220368	-3.93318493359033
H	-0.69786463740781	-2.52359716600206	-3.02910994497869
C	0.04020640739080	0.04816131575915	1.95463606670345
C	-0.07344833037014	-0.22632454439818	4.53054921740808
C	-0.42781802639687	1.09554954989093	5.20326966866120
H	0.35258551978208	1.83758793580307	5.02894232895508
H	-0.52869431498182	0.94295216077357	6.27852687620010
H	-1.37198119783187	1.48098393046363	4.81632540803831
C	1.26136317672966	-0.75612917407941	5.04381412891704
H	1.52004314794428	-1.68907292311865	4.54148913239704
H	1.19162675901616	-0.94503729978027	6.11583788405160
H	2.05670723145290	-0.03011618553157	4.86927886652353
C	-1.18073352277905	-1.25526107865961	4.73980947762026

H	-2.12545837373863	-0.88872080019368	4.33639280767174
H	-1.30431224260367	-1.44578178442484	5.80684991702995
H	-0.92966397922726	-2.19259790862592	4.24222274915871

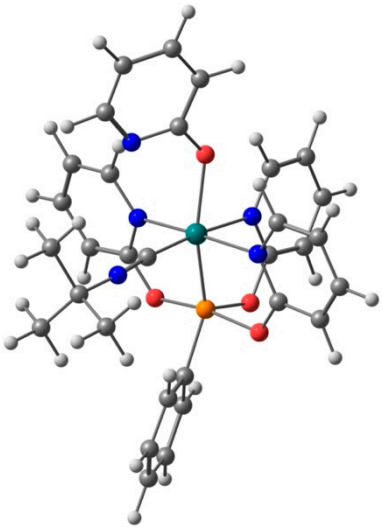

Figure S29. Optimized molecular structure of **5b[1]**.

PBE0:

final single point energy: -6695.456175078394 a.u.

final Gibbs free energy: -6694.95599890 a.u.

B2T-PLYP:

final single point energy: -6695.619546962183 a.u.

Table S10. Atomic coordinates for optimized structure of **5b[1]**.

Ru	0.01763214349333	0.10498473790391	0.15734181108592
P	-0.24730357133079	0.26919094364059	-1.98943344342971
N	1.73144129179311	-0.68979298575274	3.00471093393193
N	-0.07077644328125	2.17488813715564	0.24681420936973
N	0.00601142963991	-1.95245636836645	-0.06828244096239
N	-2.14229878655077	0.06231897143534	-0.02771908887092
O	-0.31289343093788	0.02533340170426	2.26303806418001
O	-0.26519596542030	2.13548617062620	-2.03652127849560
C	2.56020746507797	1.02343585722712	-4.80662142002353
C	2.54881752751788	-0.89030059963703	4.03720742711900
C	2.00449081311256	0.51415730159669	-5.97162213226480
C	2.23826050099673	-0.60720342537345	5.35182507298100
C	1.85049170458866	0.96631727399498	-3.61738496479079
C	1.91994487097226	0.15011205807000	0.11420583502682
C	0.74287386061780	-0.06362280296712	-5.94122128740549
C	0.97200853769029	-0.07666588731405	5.60484169749166
C	0.59277992698418	0.37409620561579	-3.58439930016162
C	-0.00177151140468	2.88549064508133	1.38269406145968
C	0.51100849141142	-0.17867991384343	3.23654390158107
C	-0.05166165004333	4.25838764346512	1.40831835934310
C	0.04176985228034	-0.14846210560603	-4.74810408495267
C	0.10763011039232	0.13778568829505	4.56033541521769

C	-0.19014853462386	-2.41270361900737	-1.32012080646552
C	-0.23792883121871	-3.79162193301530	-1.57403192887217
C	-0.18179915906111	4.93569792537541	0.19697319330888
C	-0.08251663349814	-4.67554219267612	-0.53362913799574
C	0.16230298442263	-2.82643990650396	0.93765801650120
C	0.12448820016191	-4.18815611088964	0.75537790689258
C	-0.20074724429829	2.81900096373231	-0.92981130016423
C	-0.25726960874430	4.22029461980713	-0.97358619347517
C	-2.68921980586730	0.17165854830591	-1.24548184397982
C	-2.95316473391603	-0.08046241760525	1.03102421240336
C	-4.06613715445667	0.14575366160978	-1.44749243277663
C	-4.32344954788533	-0.11648568899757	0.91546647343099
C	-4.88678744276067	0.00002434225941	-0.35145130149514
H	3.54432261193701	1.47640827811156	-4.82505605098641
H	3.52252894588932	-1.30812304848717	3.79016342689392
H	2.55358334183061	0.56894775910220	-6.90399068341455
H	2.95085430005075	-0.79248302118240	6.14443403103288
H	2.27246381003480	1.38525877093157	-2.71184145952175
H	0.08665811801554	2.29506056203642	2.28399310077476
H	0.67028387076116	0.16714843305166	6.61791933269777
H	0.30453073702092	-0.45834900534560	-6.84997754401476
H	0.00928280118426	4.78294949236664	2.35157228434056
H	-0.39664367399615	-4.11974894627683	-2.59190697176225
H	-0.11879309226073	-5.74247290752561	-0.71979858857142
H	-0.93148772525974	-0.62066339635288	-4.72055193818476
H	-0.22524417439030	6.01819738247186	0.17350085239851
H	-0.88247647157844	0.54806323722396	4.71641039298482
H	0.34027464770720	-2.38240502555987	1.90619989182040
H	0.25831464090576	-4.84844168784380	1.60075543868180
H	-0.36148690251182	4.69862450020786	-1.93754135578821
H	-2.43785992048486	-0.15881338115908	1.98044925382240
H	-4.44983809670537	0.23946500750776	-2.45347773026117
H	-4.93567236498366	-0.23309711534618	1.79889676298895
H	-5.96185929981500	-0.02395347478384	-0.48138382951321
N	3.07678509352431	0.20067223619130	-0.02003310533804
C	4.49871972128486	0.17020311191403	-0.12665544187304
C	5.07032124615697	-0.32603035041089	1.19735216756245
H	4.70089319636949	-1.32748847521699	1.41956414952585
H	6.15925583634418	-0.35608330346755	1.13588091036002
H	4.77969897858286	0.33717051864766	2.01227607972370
C	4.98266695340213	1.58539434386166	-0.42832209030601
H	6.07000335627154	1.58898103301574	-0.51611478829869
H	4.55581855039119	1.94510775612931	-1.36562850033927
H	4.69346777347771	2.26759018922972	0.37181003019602
C	4.86641983688522	-0.77739389949684	-1.26511300298409
H	4.49869745041434	-1.78295664414232	-1.05798779323114
H	4.43229724963093	-0.43539225109344	-2.20549224475686
H	5.95144790923113	-0.81583942252778	-1.37244866194897

O	-1.89571195144386	0.31447132510732	-2.30920878029685
O	-0.32955172972819	-1.57129665023556	-2.30399634915601

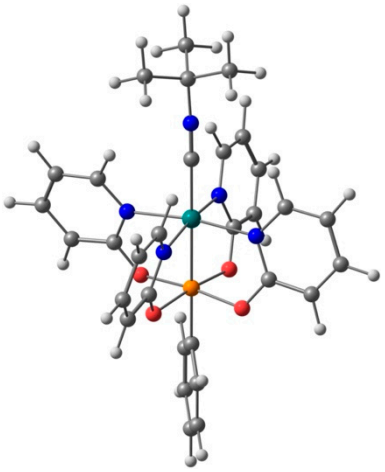

Figure S30. Optimized molecular structure of **5b[3].**

PBE0:

final single point energy: -6695.449729791554 a.u.

final Gibbs free energy: -6694.95599890 a.u.

B2T-PLYP:

final single point energy: -6695.610018628110 a.u.

Table S11. Atomic coordinates for optimized structure of **5b[3]**.

Ru	7.66825868862418	3.80677450500988	3.96405647052781
P	9.24429743689518	3.79227125258897	5.62639095268228
O	8.56887920422945	2.23849704686397	6.40885567227506
O	10.44297906717978	2.75108843591173	4.64428324670889
N	6.67046086952581	2.39544663142573	5.11777616493715
N	8.79438375730235	2.27950972305552	3.10967557210924
N	5.54085981720760	3.81239945594992	1.65481578343171
C	7.36154069891206	1.84840841825620	6.14491009169035
C	6.78262612030041	0.84462667704991	6.94210017569681
H	7.37885568392824	0.43151139603646	7.74391859175993
C	5.50053395898038	0.42632297235577	6.69269283977373
H	5.05050265451335	-0.34574964305226	7.30546998403182
C	4.78592458843267	1.01267838808242	5.64796720348519
H	3.76985482746942	0.72378701328508	5.41755534463007
C	5.40967341850784	1.98028520689284	4.90083692714049
H	4.89945301537327	2.46179302324304	4.07843176462349
C	10.02206021775869	2.05776029801915	3.63424398366259
C	10.86380460056524	1.06955004271397	3.09214947911351
H	11.83724309690370	0.93475385331616	3.54291609576820
C	10.43533324462480	0.30882254496272	2.03489366808708
H	11.08013510988655	-0.45509571196575	1.61681620653179
C	9.15922660809528	0.52661760955502	1.51523186257271
H	8.77123291414753	-0.05341593250029	0.68939899901872
C	8.38963424245844	1.51115271670196	2.08248587665576

H	7.39474987599425	1.71773139078195	1.71397459742961
C	10.51538590874667	3.77806737027519	6.96885575437682
C	10.15270947451323	3.54639170589134	8.29169956647537
H	9.11523195944476	3.37415630622878	8.53785445858772
C	11.10558165564371	3.53472157971556	9.29960989070454
H	10.79826946031653	3.35280576181905	10.32304426350039
C	12.44205156067333	3.75351847933752	9.00196078624184
H	13.18758902323820	3.74372653924877	9.78858976708400
C	12.81379673383681	3.98495601959419	7.68630098117571
H	13.85444292806323	4.15726425337749	7.43661991532303
C	11.85857204622197	3.99765509250115	6.68068755303415
H	12.16245230294084	4.17866856203502	5.66014280157891
C	6.32583288431482	3.81392579615152	2.52566300493230
C	4.64127481675643	3.76193876452504	0.54576772425283
C	4.15150453960430	2.32473915598967	0.39606460290403
H	4.98959587931584	1.65104238962378	0.21302161506247
H	3.46115113490417	2.25898984931926	-0.44595612743218
H	3.63301753386708	1.99963006881112	1.29883193532759
C	5.40038075299818	4.20566644552411	-0.70138929084743
H	4.73582996243628	4.17262103947712	-1.56580595591003
H	5.76802778746657	5.22588119082772	-0.58369215490920
O	10.07586420534279	5.34277893694826	5.01202525201763
N	8.89339245265936	5.21185955787756	3.04290976485631
C	9.88937498947789	5.73901024946120	3.79202327887878
C	10.73870259914150	6.72650716837046	3.26159336914780
H	11.51312391085684	7.12277694506798	3.90367917664264
C	10.57311547547670	7.14939290861774	1.96756894158344
H	11.22696467563014	7.90827685186434	1.55442189258150
C	9.56024127392458	6.58355085256921	1.19339448075409
H	9.39485160721793	6.87578594193868	0.16566344265728
C	8.75891765866754	5.63128584022728	1.77197579728087
H	7.95926178299831	5.16621928642802	1.21303619149018
C	3.47522594706870	4.70297299667236	0.83060858454962
H	3.83069553111631	5.72636622048787	0.95728777478873
H	2.77310892821152	4.67874121536200	-0.00380815735789
H	2.95025137649570	4.40015743703878	1.73736562168451
H	6.24945314957567	3.54688567944007	-0.88801964840808
O	8.20808203957224	4.83187197727763	6.77931259887935
N	6.76607940427407	5.32750828368620	5.05600038840101
C	7.22770695845101	5.53733517634180	6.31043079591770
C	6.65147204157966	6.52592381324770	7.12867131610483
H	7.05348370684463	6.65240856155753	8.12430935757274
C	5.62281771244344	7.29659805739285	6.65124551588035
H	5.17848248098739	8.06080966770127	7.27785274263653
C	5.16595476650794	7.08805642960911	5.34975475563607
H	4.36360556552785	7.67455098081165	4.92413069036767
C	5.76466963968144	6.10378225701192	4.60410795349433
H	5.44481605714834	5.90309302217655	3.59125547615457

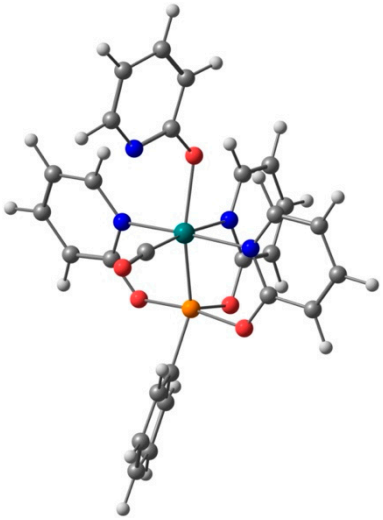

Figure S31. Optimized molecular structure of **4b**[1]**.**

PBE0:

final single point energy: -6558.160689132269 a.u.

final Gibbs free energy: -6557.77707407 a.u.

B2T-PLYP:

final single point energy: -6558.322011793353 a.u.

Table S12. Atomic coordinates for optimized structure of **4b**[1].

Ru	-0.04677717339654	0.01632015042729	-0.06794781537517
P	-0.66653860079855	0.10770768756537	-2.17215514321226
O	-0.94835738872366	-1.74749709414429	-2.30806068196702
O	-2.33525787794148	0.26489471477728	-2.19940881489789
O	2.86785472385068	0.05925323210554	-0.73051675091074
O	-0.07697857038125	0.01751933884992	2.04631604443504
O	-0.53978572618595	1.93256426864635	-2.32725951005496
N	2.13059308540555	-0.48349029895016	2.34148545109092
N	-0.13819694271766	2.09193937371987	-0.07497092647392
N	-0.14470314728763	-2.04824885313307	-0.18203465490099
N	-2.22336124368331	-0.00966272280122	0.08689555409554
C	1.58939949775607	0.44651740099108	-5.51840736493274
C	3.15426481270778	-0.65114506238159	3.17774043812553
C	0.78347387353811	-0.09756043042700	-6.50753034575922
C	3.06946929423450	-0.51198889556098	4.54806654207071
C	1.12961520857769	0.52425899547086	-4.21284335563472
C	1.76883056278418	0.03149803509476	-0.40892749926231
C	-0.47904661296975	-0.57737184367166	-6.18712147740678
C	1.82369267246940	-0.17342722848704	5.07866702443376
C	-0.12977604224949	0.03141144396845	-3.89107628686793
C	0.02508841301842	2.85537577954372	1.01630761582142
C	0.93264671620857	-0.15347303653610	2.84098605512300
C	-0.03261697566435	4.22691289024389	0.97639208784337
C	-0.93243639746599	-0.52830460205489	-4.87864481665423
C	0.75346089950761	0.00660707521373	4.23692273136895

C	-0.62051379106383	-2.55009450338803	-1.33905606621259
C	-0.76261040576638	-3.93671822510532	-1.50457962661928
C	-0.27191802626893	4.84176879507478	-0.25134189579211
C	-0.41114533398041	-4.77855674760624	-0.47822711656739
C	0.20334205492043	-2.88145314391627	0.81053490239207
C	0.08690194526118	-4.24585895878596	0.71006258939081
C	-0.37864270497886	2.67470729991820	-1.26379811129004
C	-0.44716557164855	4.06961961752817	-1.37442946306387
C	-2.95417506856332	0.11052181373164	-1.02738328315069
C	-2.85556685952057	-0.16206777043310	1.26002394292298
C	-4.34525996160091	0.09037049986926	-1.01091959131963
C	-4.22672554081842	-0.19242083291299	1.36129220447432
C	-4.98225566342201	-0.06154637216567	0.20026176486719
H	2.57628664747828	0.81996705136612	-5.76284542856911
H	4.10106922432565	-0.91440771100902	2.71261636043861
H	1.13900504441112	-0.14792491894180	-7.52966596854770
H	3.93726039461964	-0.66061693497148	5.17648117132838
H	1.75228592406974	0.96858166741649	-3.44600926842624
H	0.19905665434752	2.30886446578015	1.93280737461733
H	1.69776920627474	-0.05077886152277	6.14896831366640
H	-1.11181620554938	-0.99992104946437	-6.95824302611993
H	0.10832547979070	4.79927262355143	1.88240041643352
H	-1.14699823328657	-4.30278339275034	-2.44630975370739
H	-0.51777164172909	-5.85023378464392	-0.59756897784724
H	-1.90711093241960	-0.92319954602799	-4.62447499444807
H	-0.32317558574231	5.92152558434239	-0.32435901580168
H	-0.22772504352549	0.27071425314546	4.61118132037163
H	0.59522006756467	-2.40480994127435	1.69712000774678
H	0.38318168475222	-4.87454918238018	1.53776748531858
H	-0.64017651252571	4.49867450006655	-2.34762571427913
H	-2.19768943427325	-0.24956646721115	2.11547142332927
H	-4.88234135941860	0.19170544399957	-1.94314518697842
H	-4.69249120374912	-0.31568291241838	2.32901710473384
H	-6.06439413155753	-0.08140667933095	0.24197455561144

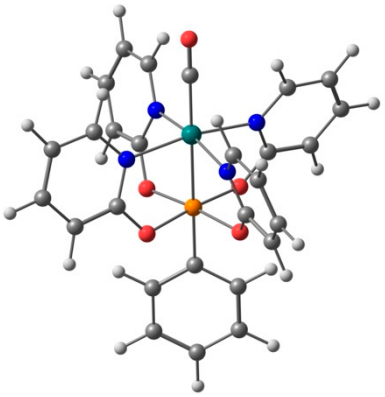

Figure S32. Optimized molecular structure of **4b^3.**

PBE0:

final single point energy: -6558.156643837847 a.u.

final Gibbs free energy: -6557.77027133 a.u.

B2T-PLYP:

final single point energy: -6558.315616067810 a.u.

Table S13. Atomic coordinates for optimized structure of **4b^3**.

Ru	-0.00148717715240	0.00118164661342	-0.05591876365613
P	-0.00119438663172	0.00061045824695	-2.38039112013570
C	-0.00135327940005	0.00104429952598	1.84226912045749
O	-0.00097598143180	0.00001923422801	2.99347970652635
N	-0.00233365233653	-2.07302986175485	-0.25399027426439
N	2.07252958957769	0.00092052549796	-0.25468090471864
N	-2.07543311557163	0.00164506302282	-0.25456339610934
N	-0.00085420770600	2.07525618940449	-0.25454309019378
C	0.28847754617067	-2.56941779251522	-1.47675879811576
C	0.35205890229835	-3.95685963579547	-1.69017937402882
H	0.59295422264386	-4.30325513594839	-2.68545343419931
C	0.10035606737105	-4.81920720797407	-0.65440961084762
H	0.14563291141885	-5.88985562586991	-0.81391759607052
C	-0.22297491788843	-4.30009778009199	0.59911375038343
H	-0.43843094951995	-4.93829299673823	1.44451278892023
C	-0.26134126773444	-2.93696383610765	0.74530339835345
H	-0.50599289867107	-2.49053876020516	1.69863676655958
C	2.56719292193962	0.30099145344790	-1.47578049189724
C	3.95384964731680	0.37581979402496	-1.68887154778294
H	4.29871054528220	0.62939434403318	-2.68159643144686
C	4.81789888470242	0.12228480390326	-0.65463725545790
H	5.88824535548908	0.17660375284180	-0.81333938906692
C	4.30080464192734	-0.21361950741693	0.59626406124160
H	4.94042116810156	-0.43087323625948	1.44012891225971
C	2.93779741178919	-0.26011279730305	0.74273988269936
H	2.49275940832804	-0.51253766169211	1.69471710427826
C	-2.57020351932102	-0.29910680253588	-1.47550218973631

C	-3.95696377156240	-0.37343990641760	-1.68840792962356
H	-4.30200084541870	-0.62759161018679	-2.68092611451727
C	-4.82084719920686	-0.11873573801976	-0.65434182558762
H	-5.89122584437722	-0.17267638627129	-0.81297159268199
C	-4.30357097299245	0.21786864124467	0.59631096234610
H	-4.94306198302062	0.43604554519680	1.44003186412110
C	-2.94054208435305	0.26382559662852	0.74268950034011
H	-2.49532757695617	0.51674002370697	1.69445821666284
C	-0.29160452376176	2.57123057223804	-1.47751734027316
C	-0.35551672802001	3.95863885304720	-1.69123324726645
H	-0.59634711204614	4.30474850323273	-2.68662356482370
C	-0.10424246056817	4.82129153103510	-0.65562413842748
H	-0.14979493835494	5.89189049096457	-0.81539230307993
C	0.21899289952282	4.30257700028371	0.59809802339852
H	0.43409961984441	4.94103570692884	1.44338664754076
C	0.25770642251849	2.93949189602879	0.74460596781468
H	0.50228376139300	2.49331590972560	1.69807861487300
C	-0.00172343335155	0.00038403884664	-4.22656277385646
C	1.04373896986461	-0.57886794256680	-4.93828906502558
H	1.86528887686919	-1.03486535819983	-4.40524213287380
C	1.04414086945108	-0.58045312870340	-6.32520389085658
H	1.86880658535203	-1.03871727139715	-6.85870417214297
C	-0.00233448635854	-0.00008846093034	-7.02569162803684
H	-0.00257681449400	-0.00027098984754	-8.10942146193077
C	-1.04850051428746	0.58051336738142	-6.32493033338088
H	-1.87340120437715	1.03859605124252	-6.85822294704214
C	-1.04749628441155	0.57939665967861	-4.93801960761790
H	-1.86880389285039	1.03555703825665	-4.40474738329641
O	-0.51826474859463	1.77338448877108	-2.47582309345744
O	1.76666507981033	0.52792466326484	-2.47267257682394
O	0.51553679079732	-1.77184630139565	-2.47525529765670
O	-1.76983510905116	-0.52709916034945	-2.47213893476877

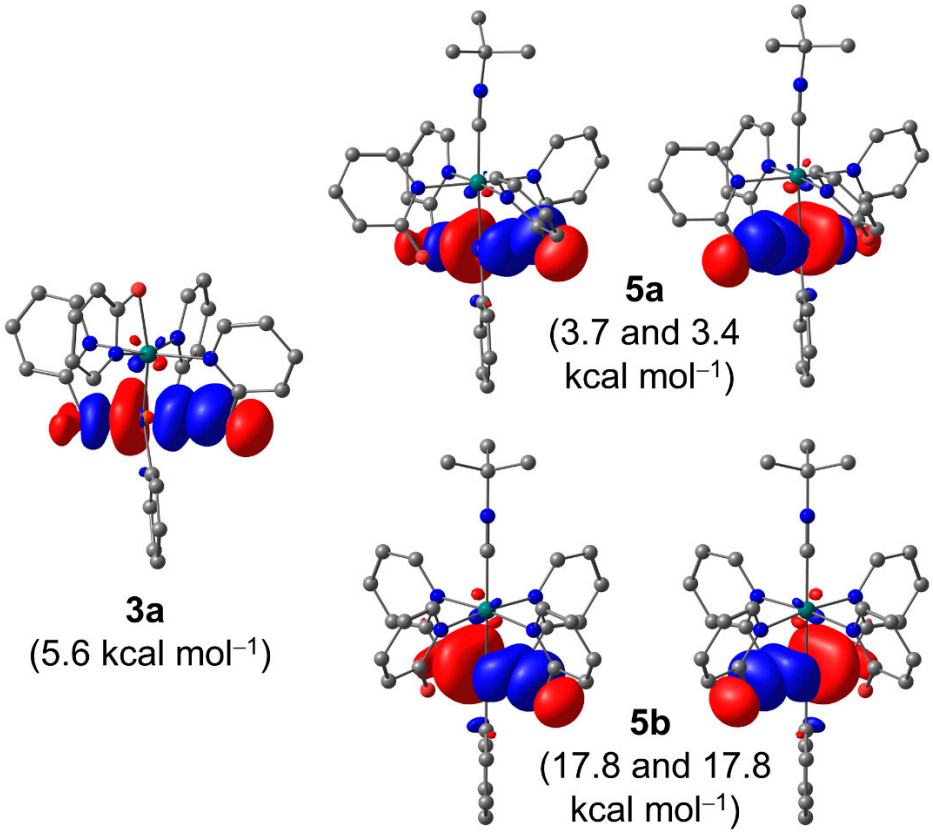

Figure S33. Graphical representation of main NBOs (isosurface 0.05 au) involved in σ-O→P donor-acceptor interactions in compound **3a**, compound **5a** and compound **5b** and energies of the donor-acceptor interaction as derived from second order perturbation theory analysis. Hydrogen atoms are omitted for clarity.

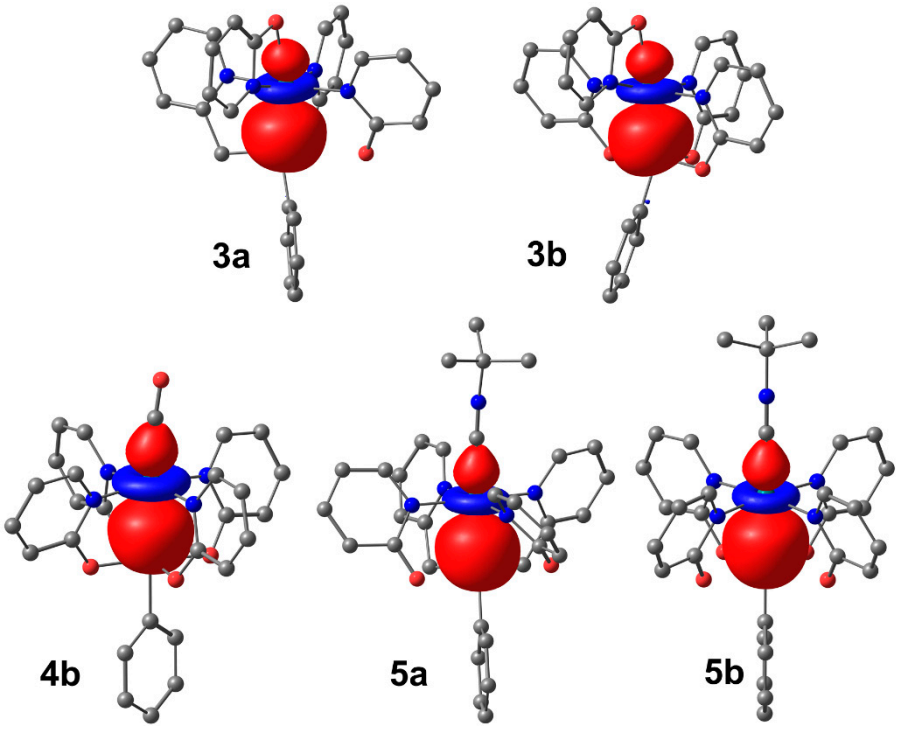

Figure S34. Graphical representation of NLMOs (isosurface 0.05 au) representative of the σ-Ru–P bonds in compounds **3a**, **3b**, **4b**, **5a** and **5b**. Hydrogen atoms are omitted for clarity.

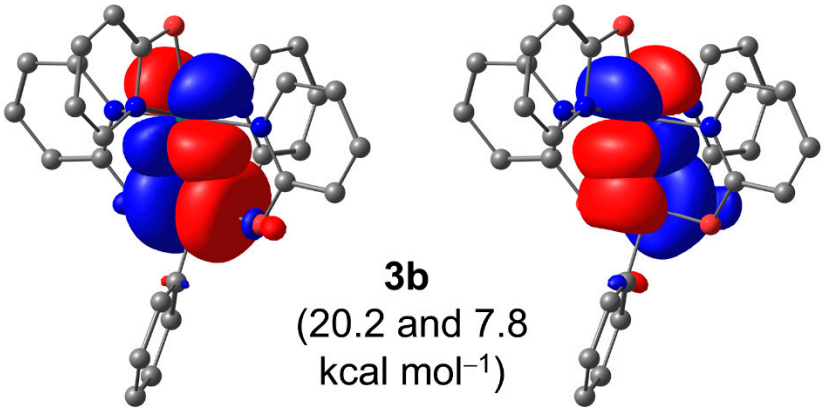

Figure S35. Graphical representation of NBOs (isosurface 0.05 au) involved in the predominant π-Ru→P donor-acceptor interactions in compound **3b** and energies of the donor-acceptor interactions as derived from second order perturbation theory analysis. Hydrogen atoms are omitted for clarity.

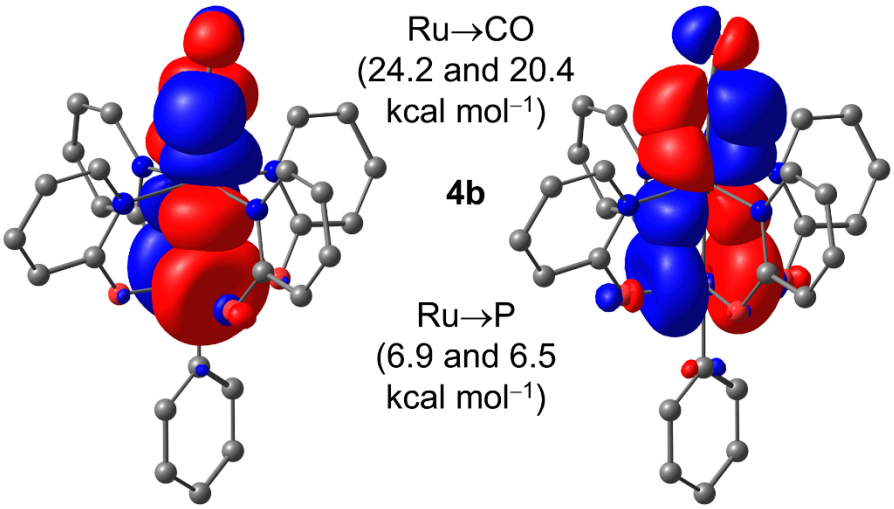

Figure S36. Graphical representation of NBOs (isosurface 0.05 au) involved in the predominant π-Ru→CO and π-Ru→P donor-acceptor interactions in compound **4b** and energies of the donor-acceptor interactions as derived from second order perturbation theory analysis. Hydrogen atoms are omitted for clarity.

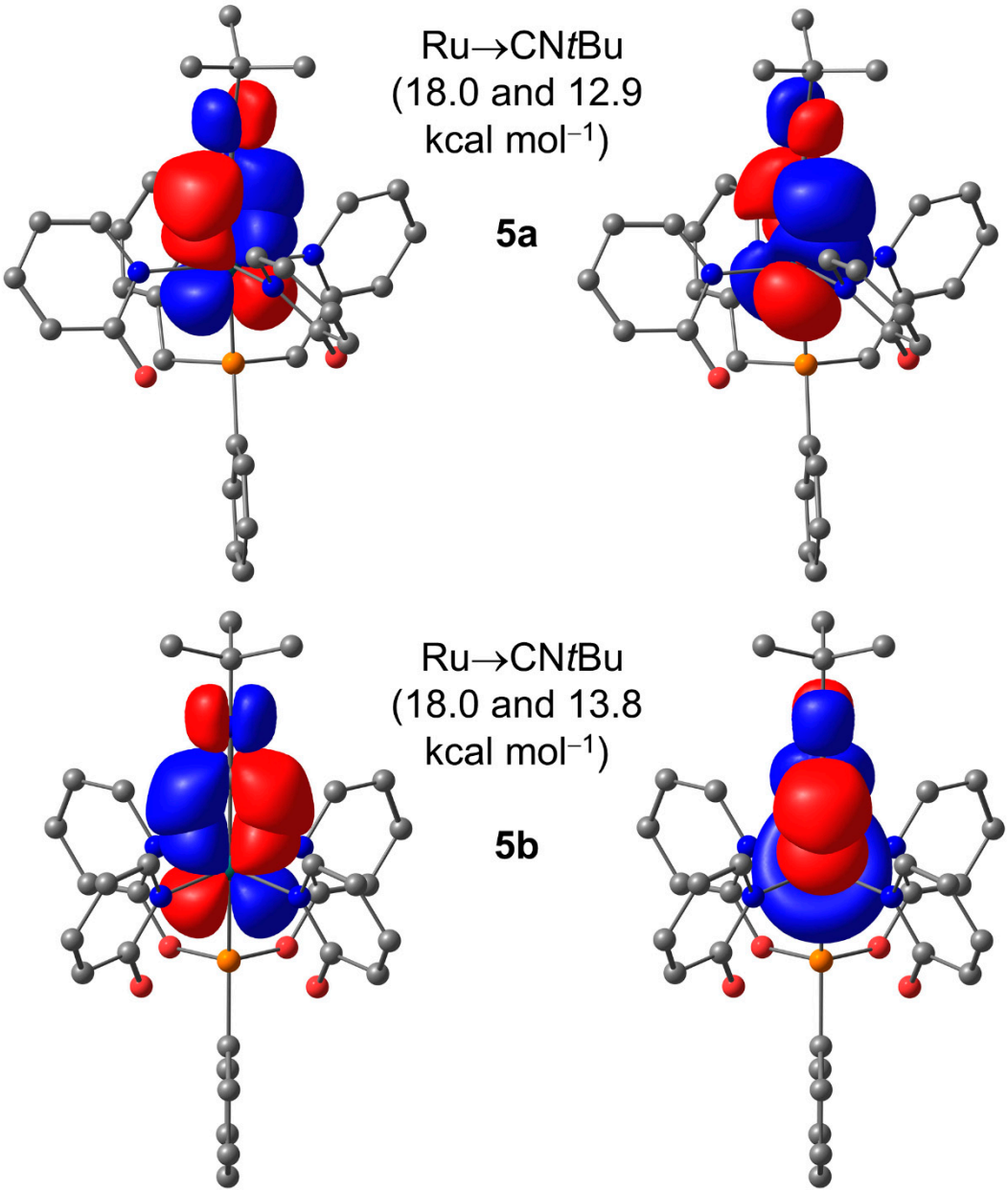

Figure S37. Graphical representation of NBOs (isosurface 0.05 au) involved in the predominant π-Ru→CN*t*Bu donor-acceptor interactions in compounds **5a** and **5b** and energies of the donor-acceptor interactions as derived from second order perturbation theory analysis. Hydrogen atoms are omitted for clarity.