Content

Table S1. Crystallographic data of complex **1a**

Datablock: 1a

```
Bond precision:  C-C = 0.0041 A          Wavelength=0.71073

Cell:           a=11.8159(5)    b=8.6579(3)          c=17.7993(8)
                alpha=90        beta=107.4395(15)    gamma=90
Temperature:    150 K

                Calculated                Reported
Volume          1737.19(12)               1737.19(12)
Space group     P 21/c                    P 21/c
Hall group      -P 2ybc                   -P 2ybc
Moiety formula  C40 H34 Mn2 O4 P2         C40 H34 Mn2 O4 P2
Sum formula     C40 H34 Mn2 O4 P2         C40 H34 Mn2 O4 P2
Mr              750.49                    750.49
Dx,g cm-3       1.435                     1.435
Z               2                         2
Mu (mm-1)       0.860                     0.860
F000            772.0                     772.0
F000'           774.01
h,k,lmax        15,11,22                  15,11,22
Nref            3825                      3818
Tmin,Tmax       0.853,0.885               0.921,0.965
Tmin'           0.755

Correction method= # Reported T Limits: Tmin=0.921 Tmax=0.965
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 27.101

R(reflections)= 0.0398( 3182)     wR2(reflections)= 0.1112( 3818)

S = 1.047                 Npar= 217
```

Figure S1. ORTEP representation of **1a**, ellipsoids at 50 %

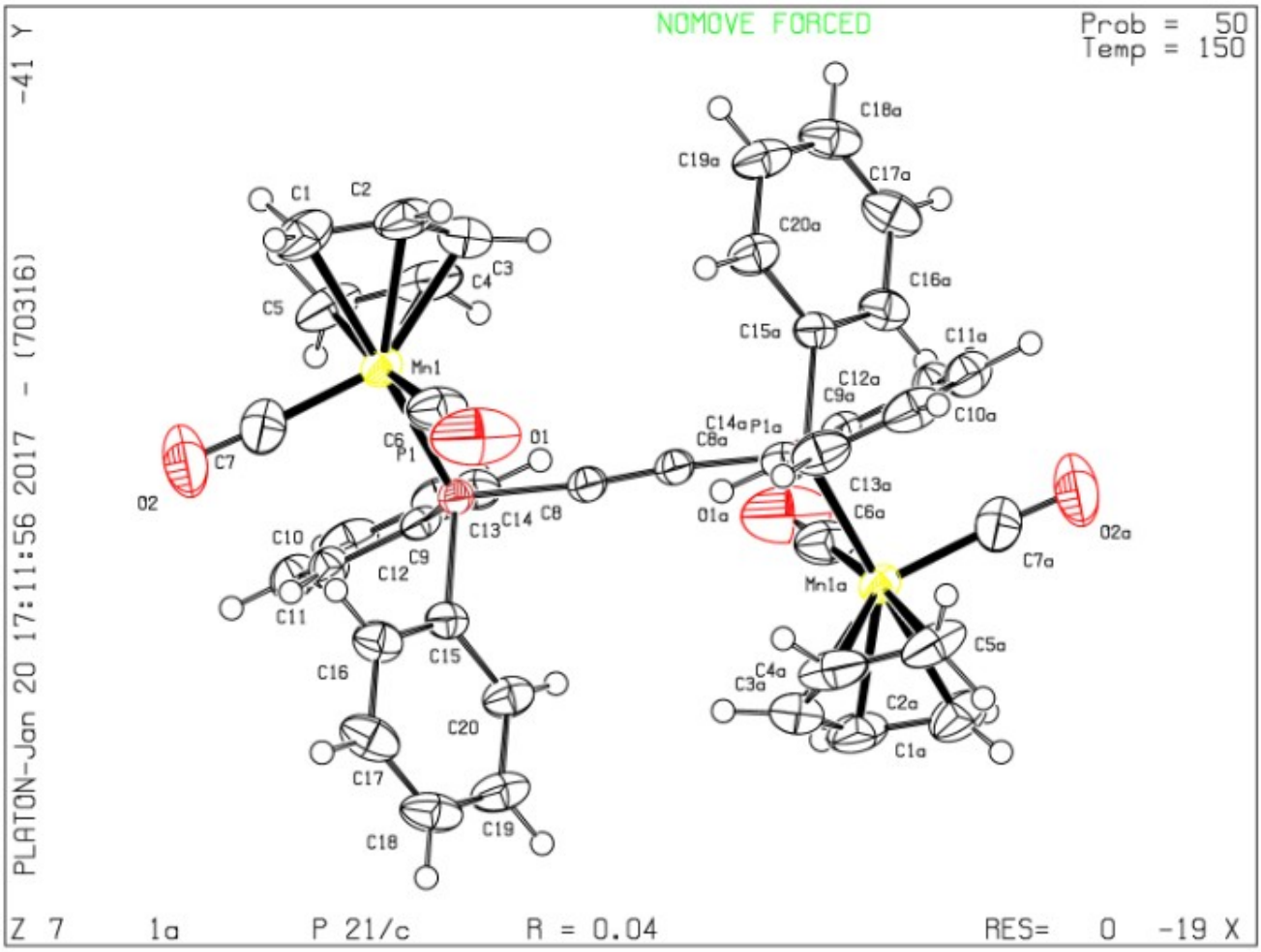

Table S2. Crystallographic data of complex **1b**

Datablock: 1b

```
Bond precision:  C-C = 0.0025 A          Wavelength=0.71073

Cell:         a=9.5676(4)        b=10.9197(4)      c=11.2228(4)
              alpha=105.9466(6)  beta=112.2887(6)  gamma=104.5166(7)
Temperature:  100 K

                 Calculated                Reported
Volume           956.58(6)                 956.58(6)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C44 H42 Mn2 O4 P2         C44 H42 Mn2 O4 P2
Sum formula      C44 H42 Mn2 O4 P2         C44 H42 Mn2 O4 P2
Mr               806.60                    806.59
Dx,g cm-3        1.400                     1.400
Z                1                         1
Mu (mm-1)        0.786                     0.786
F000             418.0                     418.0
F000'            419.01
h,k,lmax         11,13,13                  11,13,13
Nref             3651                      3641
Tmin,Tmax        0.794,0.910               0.691,0.745
Tmin'            0.749

Correction method= # Reported T Limits: Tmin=0.691 Tmax=0.745
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.680

R(reflections)= 0.0241( 3586)     wR2(reflections)= 0.0663( 3641)

S = 1.042                 Npar= 237
```

Figure S2. ORTEP representation of **1b**, ellipsoids at 50 %

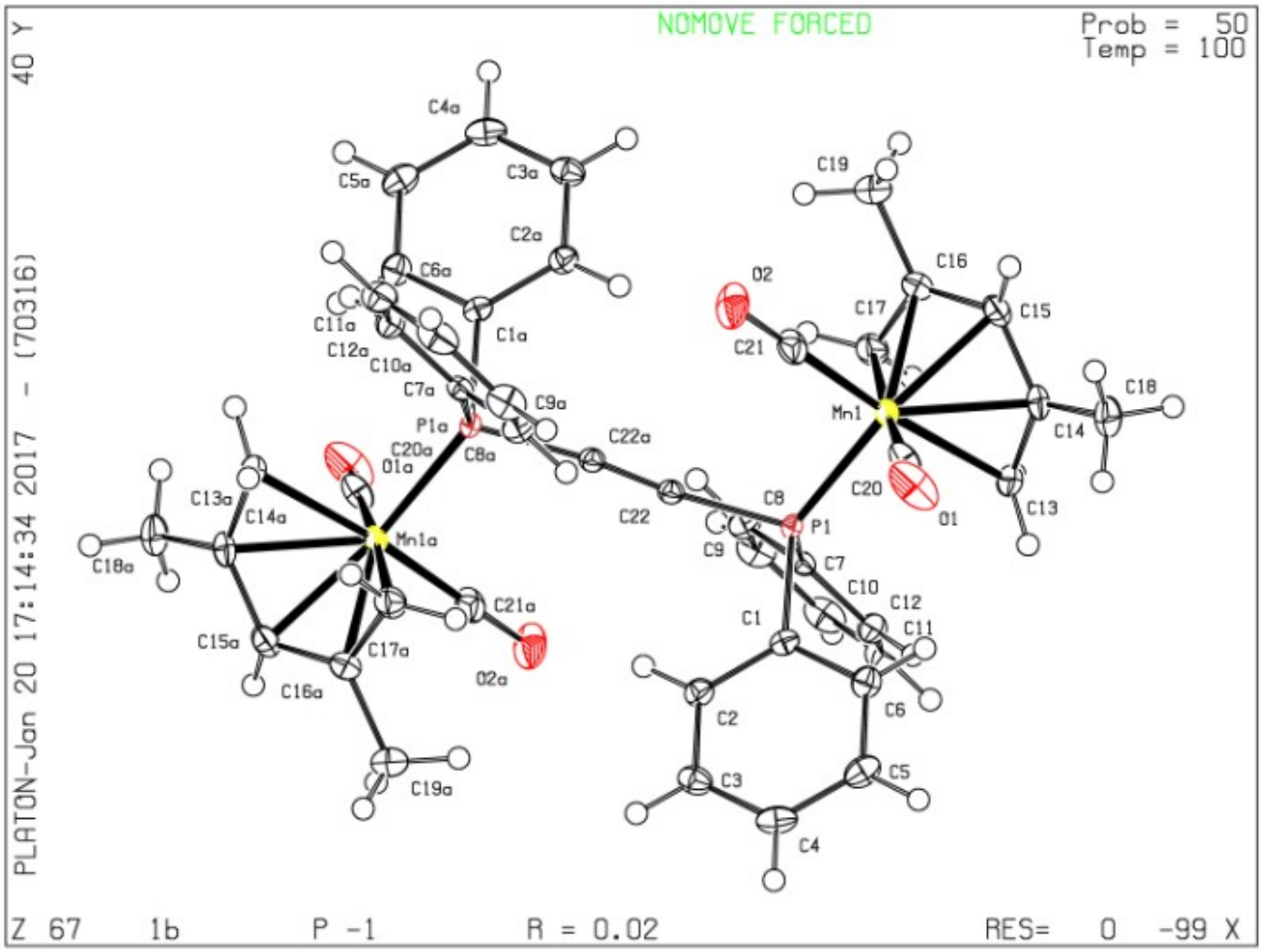

Table S3. Crystallographic data of complex **1c**

Datablock: 1c

Bond precision: C-C = 0.0044 A Wavelength=0.71073

Cell: a=16.3527(4) b=6.1392(2) c=16.3852(4)
alpha=90 beta=95.744(1) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	1636.69(8)	1636.69(8)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C8 H7 Mn O3	C8 H7 Mn O3
Sum formula	C8 H7 Mn O3	C8 H7 Mn O3
Mr	206.08	206.08
Dx,g cm-3	1.673	1.673
Z	8	8
Mu (mm-1)	1.571	1.571
F000	832.0	832.0
F000'	835.05	
h,k,lmax	20,7,21	20,7,21
Nref	3607	3608
Tmin,Tmax	0.725,0.922	0.666,0.923
Tmin'	0.636	

Correction method= # Reported T Limits: Tmin=0.666 Tmax=0.923
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 27.102

R(reflections)= 0.0404(3285) wR2(reflections)= 0.1058(3608)

S = 1.084 Npar= 218

Figure S3. ORTEP representation of **1c**, ellipsoids at 50 %

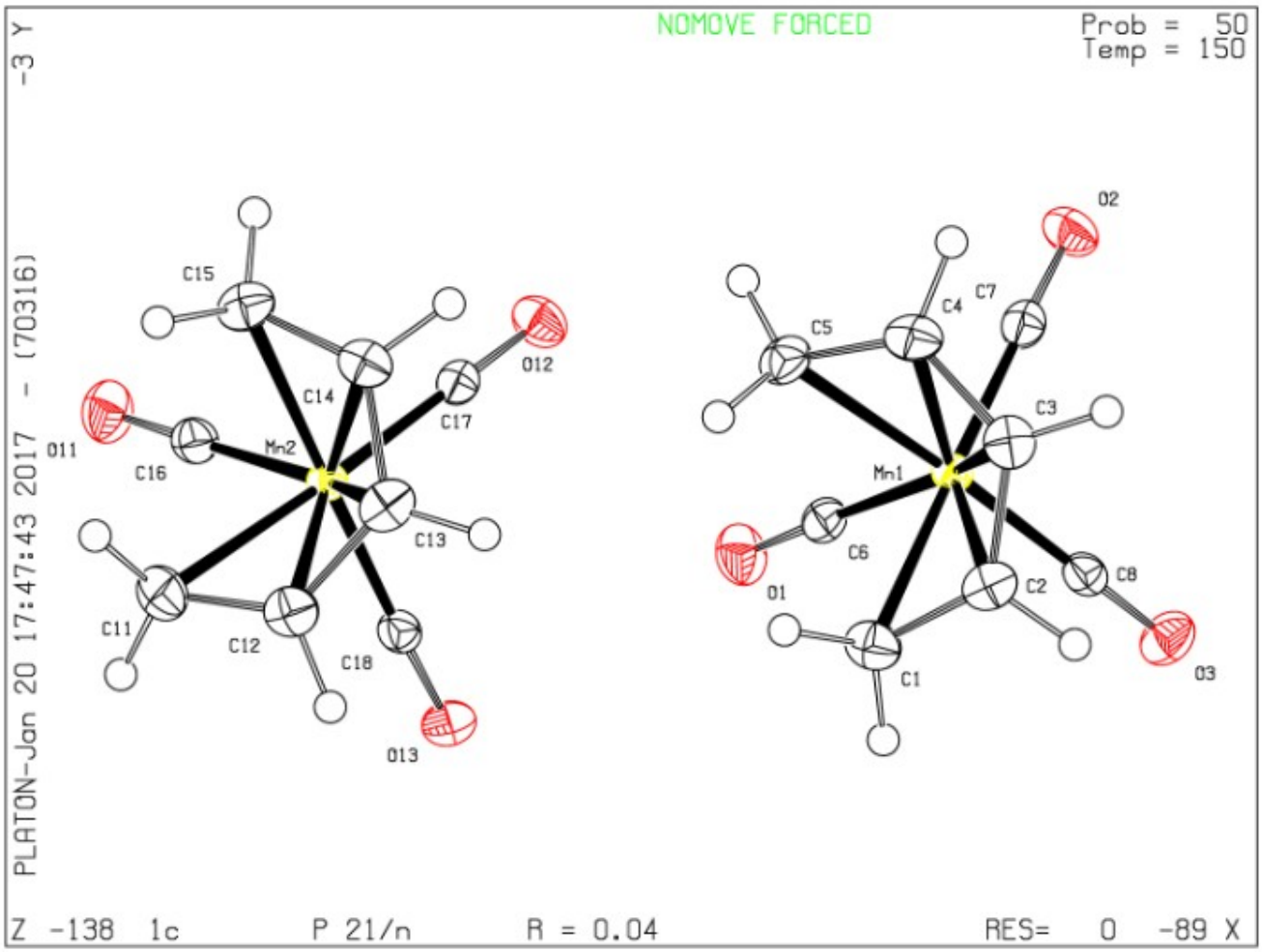

Table S4. Crystallographic data of complex **2b**

Datablock: 2b

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=11.3989(3) b=16.7647(4) c=12.0131(3)
alpha=90 beta=112.0125(10) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	2128.34(9)	2128.34(9)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C50 H50 Mn2 O4 P2	C50 H50 Mn2 O4 P2
Sum formula	C50 H50 Mn2 O4 P2	C50 H50 Mn2 O4 P2
Mr	886.72	886.72
Dx,g cm-3	1.384	1.384
Z	2	2
Mu (mm-1)	0.714	0.714
F000	924.0	924.0
F000'	926.05	
h,k,lmax	14,21,15	14,21,15
Nref	4696	4688
Tmin,Tmax	0.840,0.936	0.723,0.932
Tmin'	0.728	

Correction method= # Reported T Limits: Tmin=0.723 Tmax=0.932
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 27.099

R(reflections)= 0.0343(4146) wR2(reflections)= 0.0942(4688)

S = 1.062 Npar= 267

Figure S4. ORTEP representation of **2b**, ellipsoids at 50 %

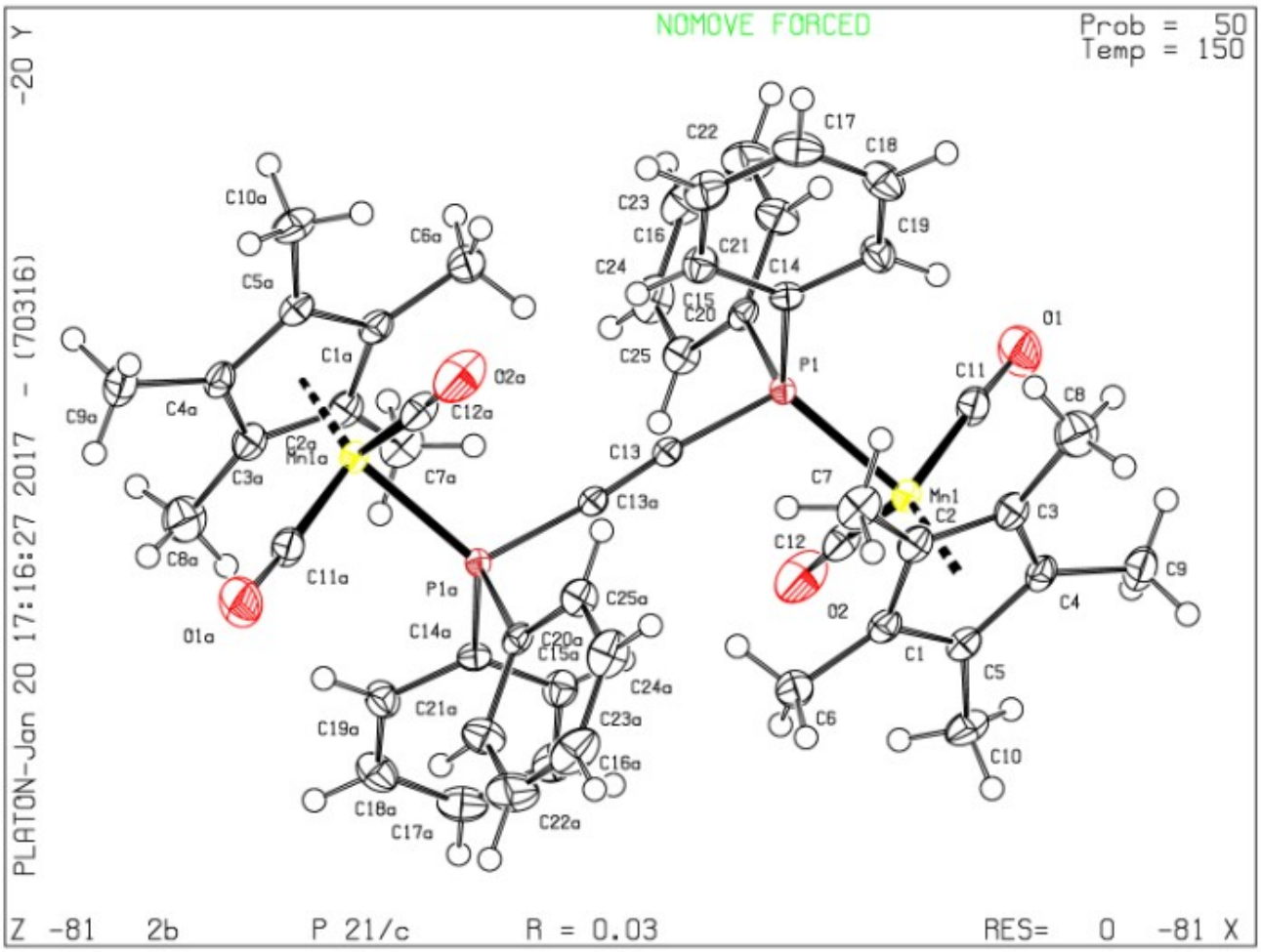

Figure S5. MOs of **1a'** (left) and **2a'** (right) with mainly metallic character. The metal backdonation points at the middle of the dienyl (**1a'**: HOMO, HOMO-1. **2a'**: HOMO-1, HOMO-2) and at C1, C2, C4 and C5 (**1a'**: HOMO-2. **2a'**: HOMO). There is a better orbital matching in case of 1a'.

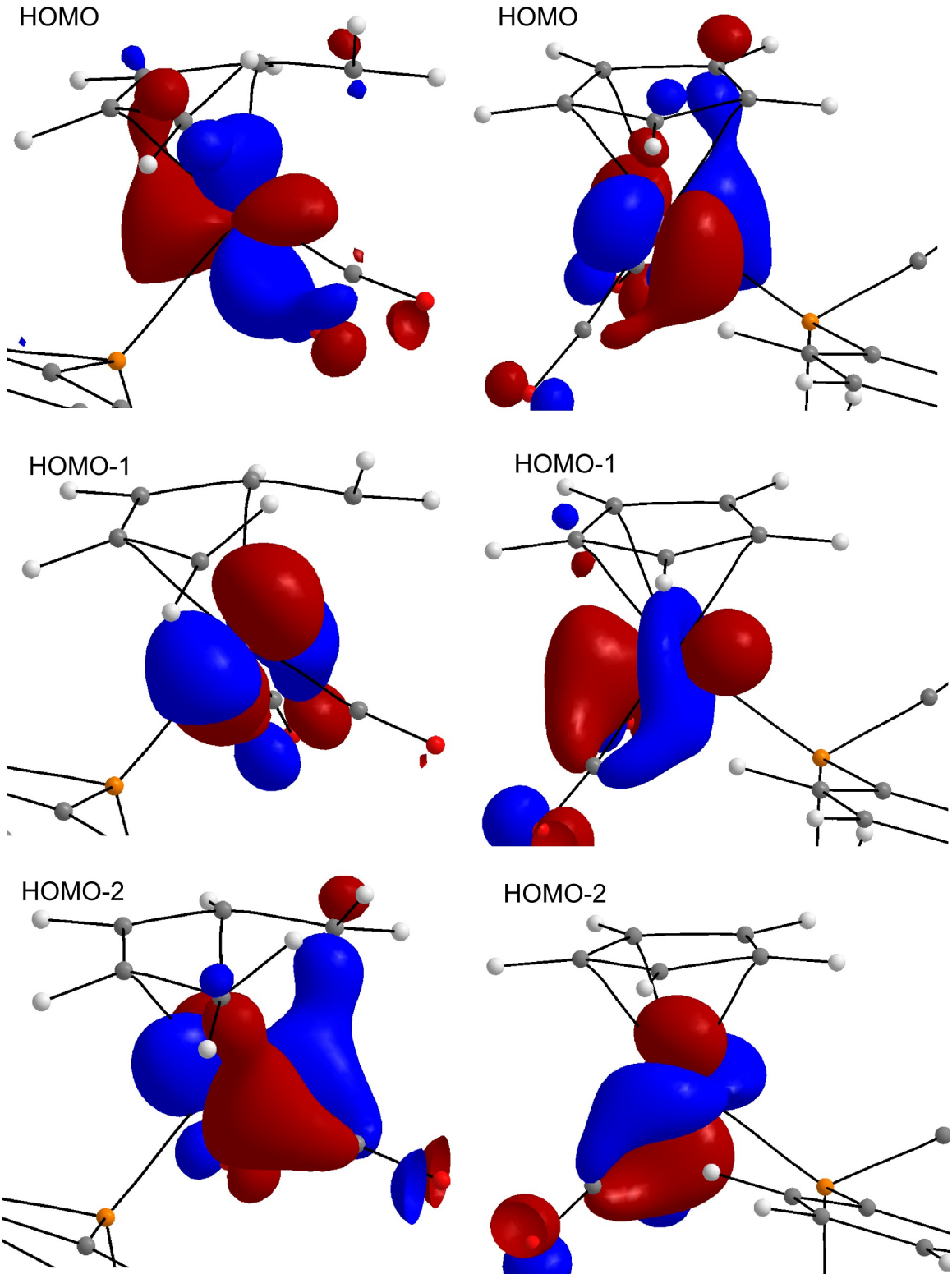

Figure S6. MOs of **1a'** (left) and **2a'** (right) with mainly dienyl character. **2a'** Cp MOs are deeper in energy than **1a'** Pdl MOs. **1a'**s HOMO-3 shows a large extent of mixing between metallic and Pdl orbitals. Moreover, the HOMO-3 shows the strong donating character of the terminal carbon atoms.

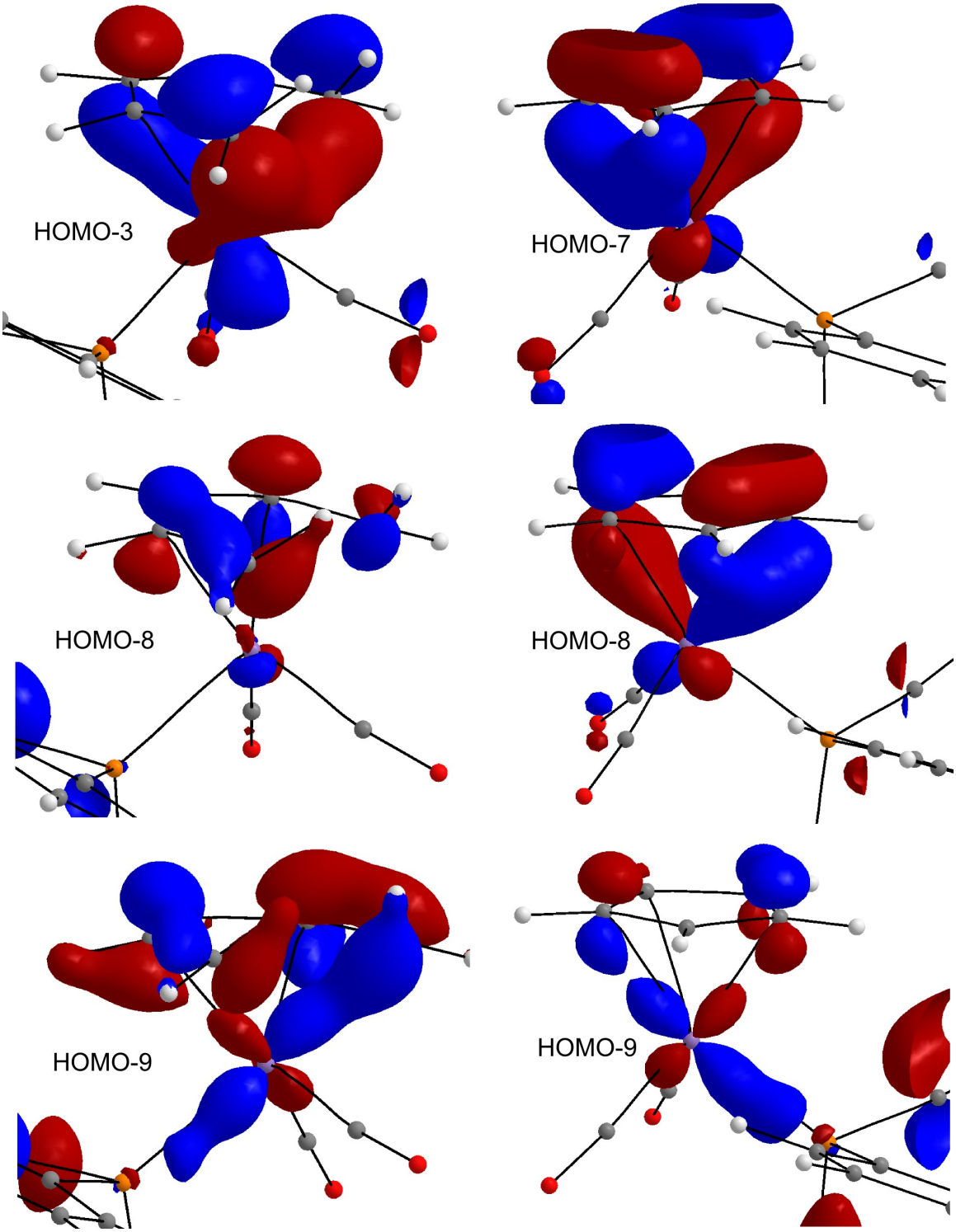

Figure S7. MOs contour maps in the Mn,C1,C2 plane of **1a'** (left) and in the Mn,C2,C3 plane of **2a'** (right). Negative (solid, red) and positive (dashed, blue) contour lines are drawn at ± 2.0 x 10^n, ± 4.0 x 10^n and ± 8.0 x 10^n e $bohr^{-3}$ with n = 0, -1, -2.

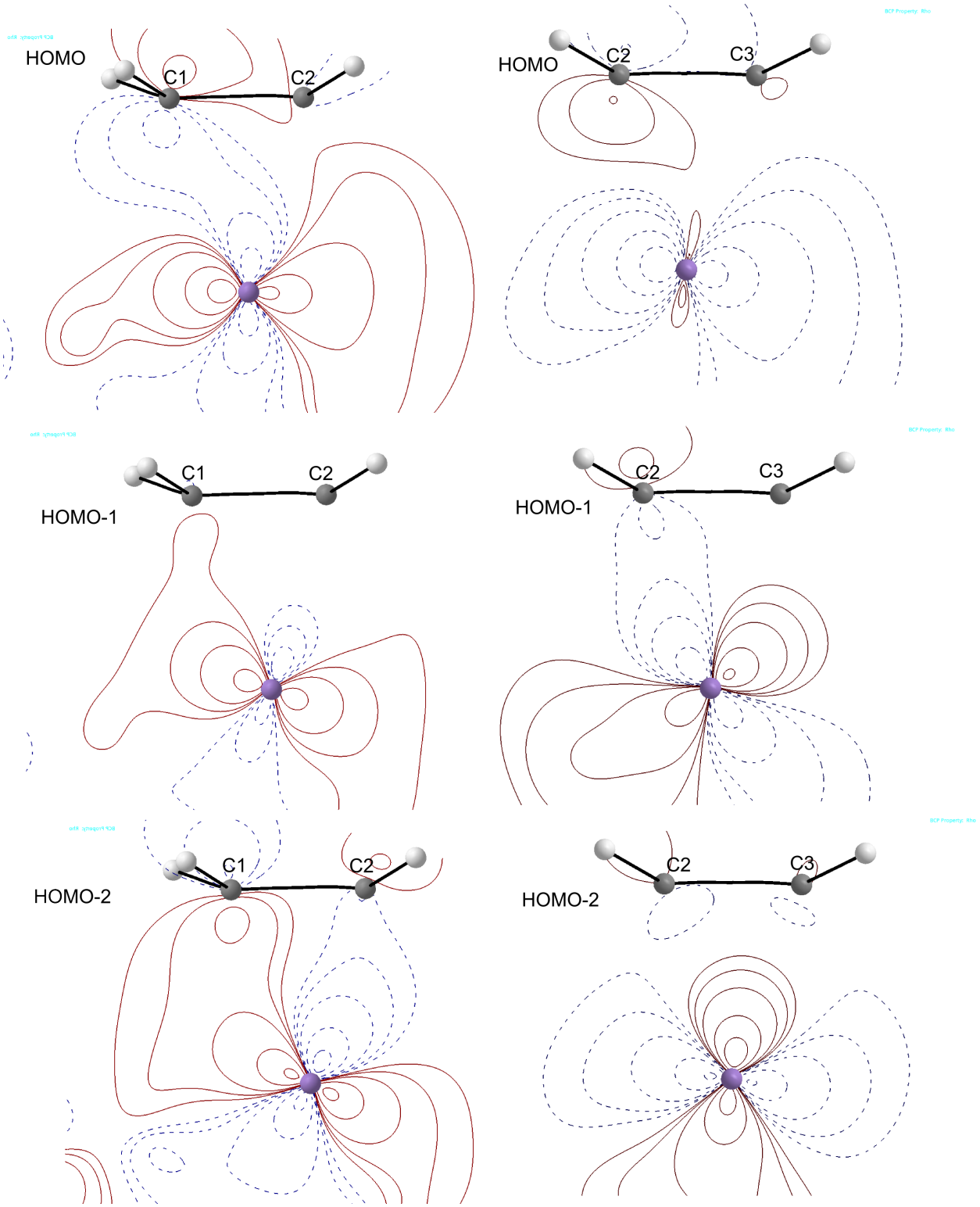

Figure S8. MOs contour maps in the Mn,C1,C2 plane of **1a'** (left) and in the Mn,C2,C3 plane of **2a'** (right). Negative (solid, red) and positive (dashed, blue) contour lines are drawn at ± 2.0 x 10^n, ± 4.0 x 10^n and ± 8.0 x 10^n e $bohr^{-3}$ with n = 0, -1, -2.

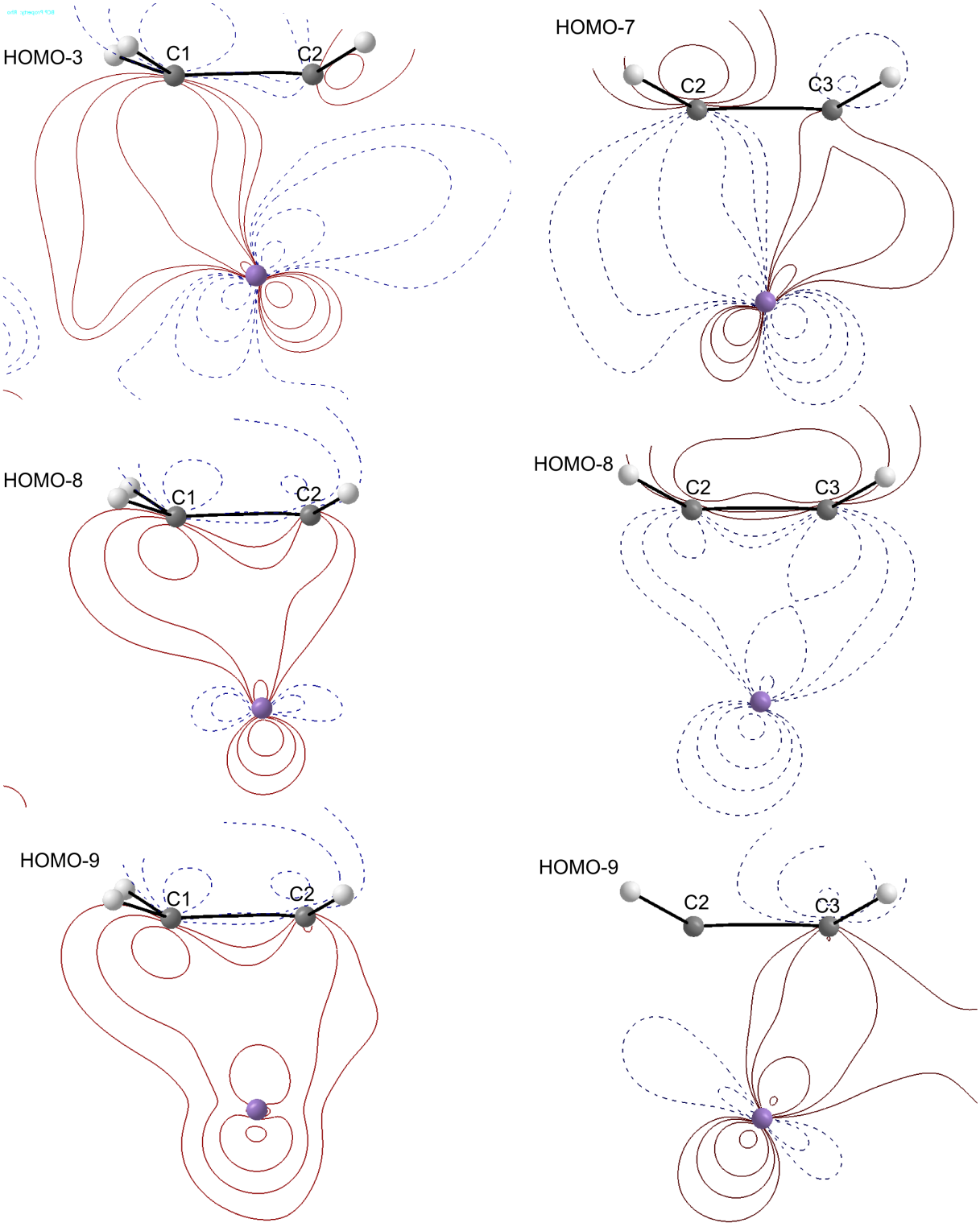

Figure S9. ^{1}H NMR (300 MHz, CD_2Cl_2) of **1a**

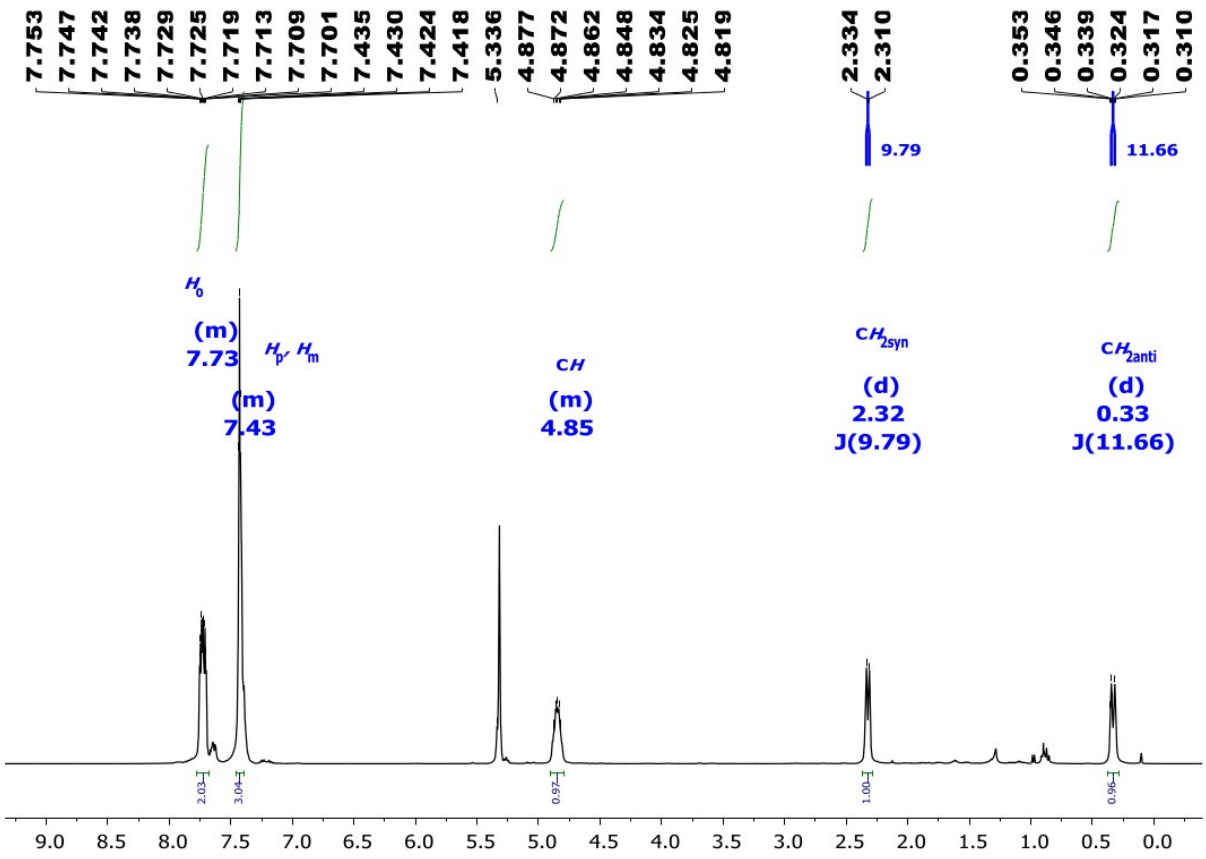

Figure S10. $^{13}C\{^{1}H\}$ NMR (100.62 MHz, CD_2Cl_2) of **1a**

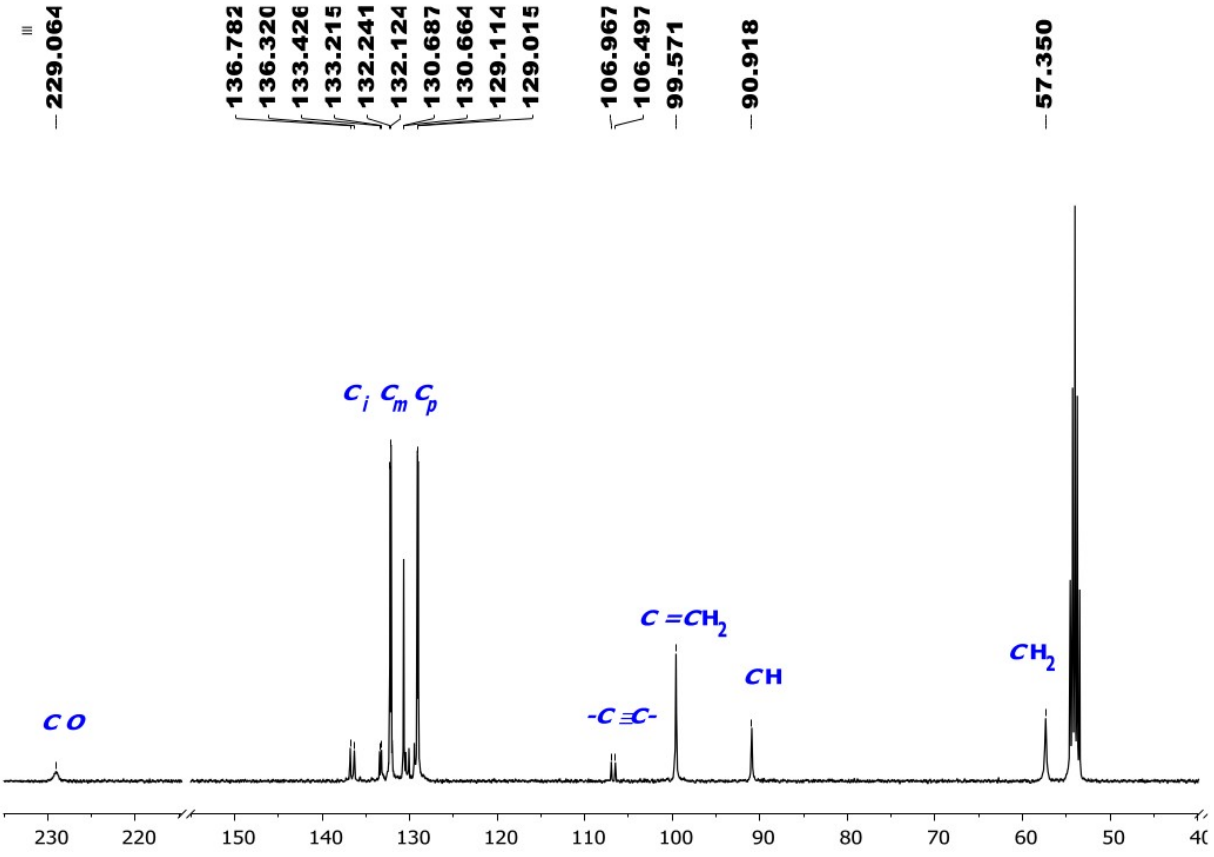

Figure S11. $^{31}P\{^{1}H\}$ NMR (121.65 MHz, CD_2Cl_2) of **1a**

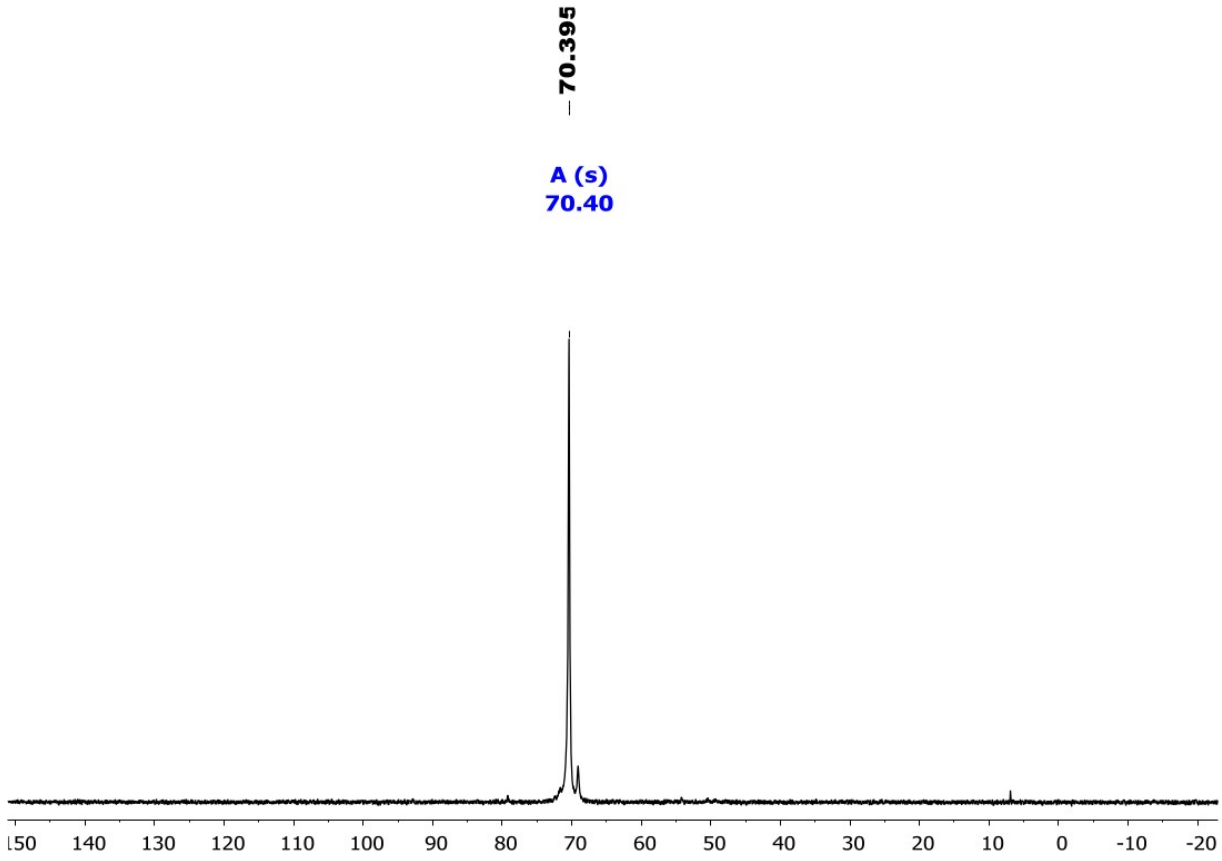

Figure S12. ^{1}H NMR (300 MHz, CD_2Cl_2) of **1b**

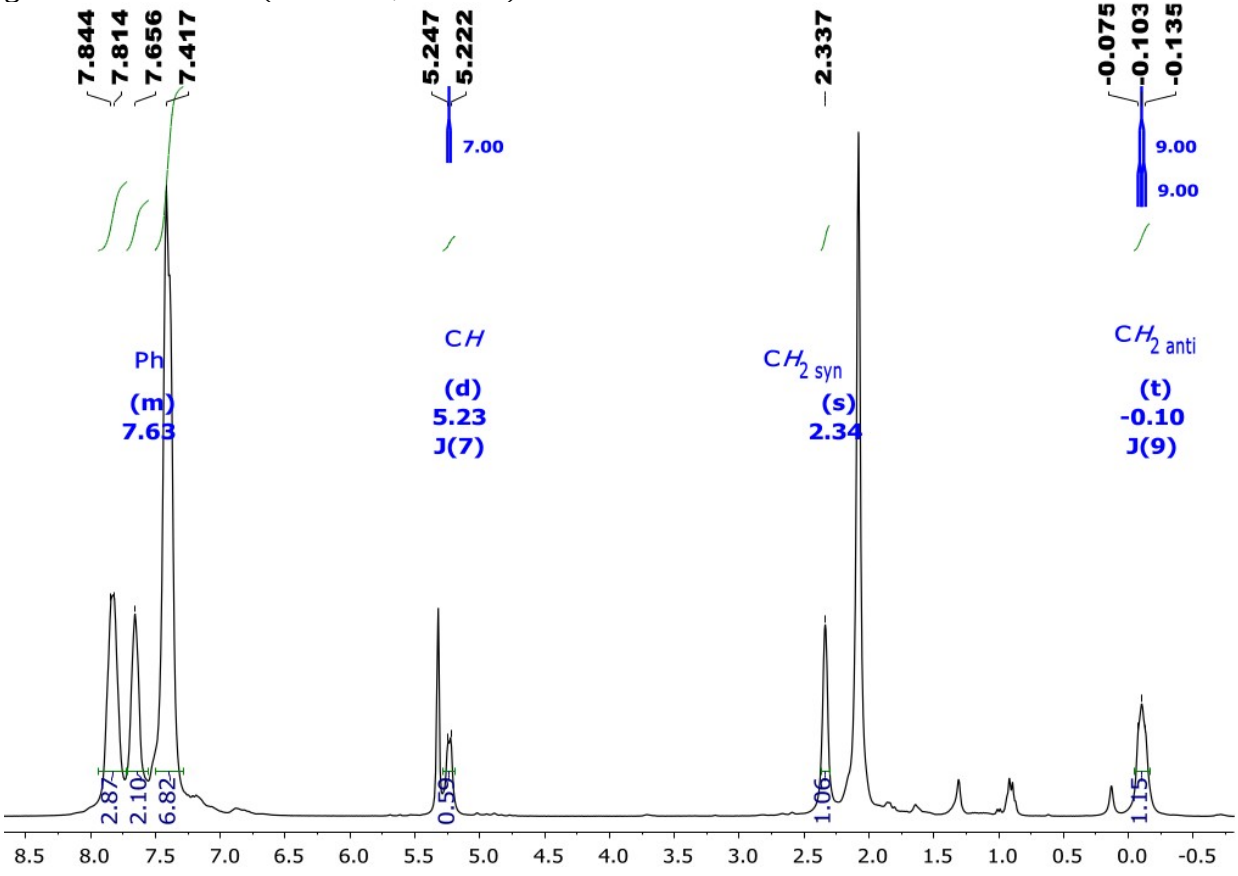

Figure S13. $^{13}C\{^{1}H\}$ NMR (75.58 MHz, CD_2Cl_2) of **1b**

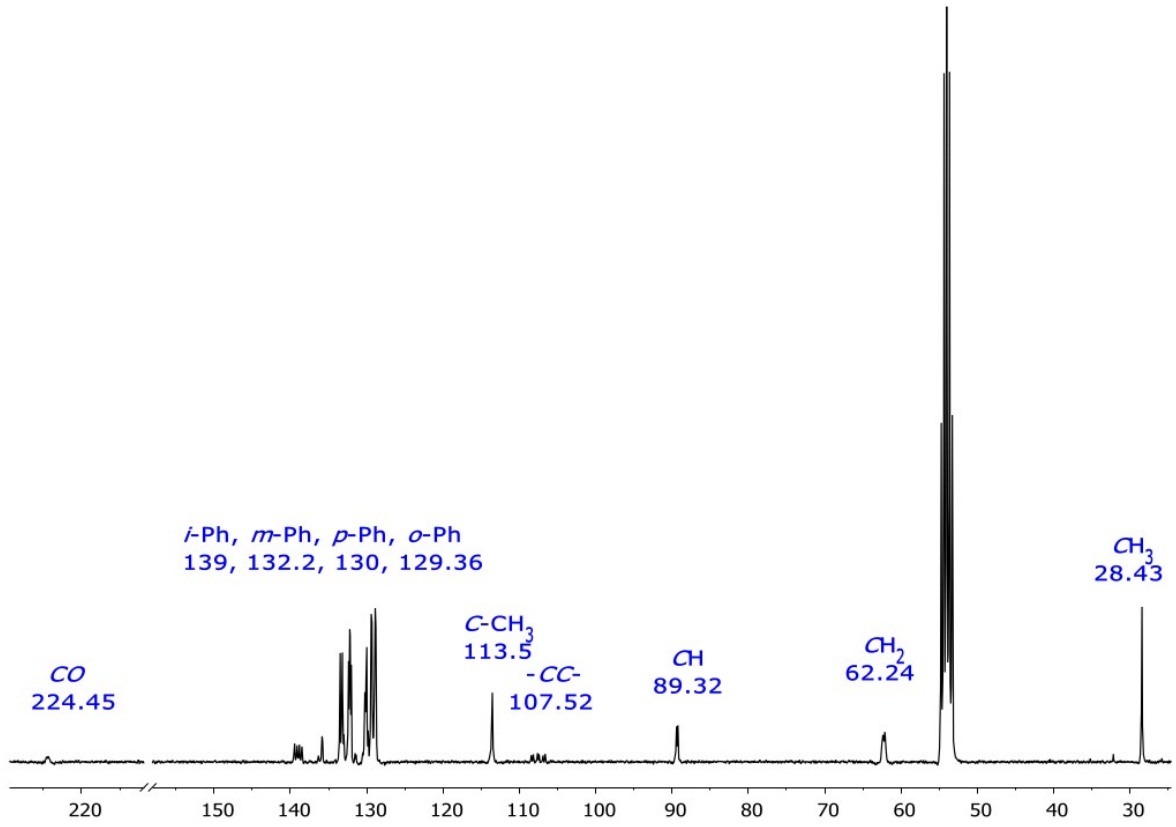

Figure S14. $^{31}P\{^{1}H\}$ NMR (202.47 MHz, CD_2Cl_2) of **1b**

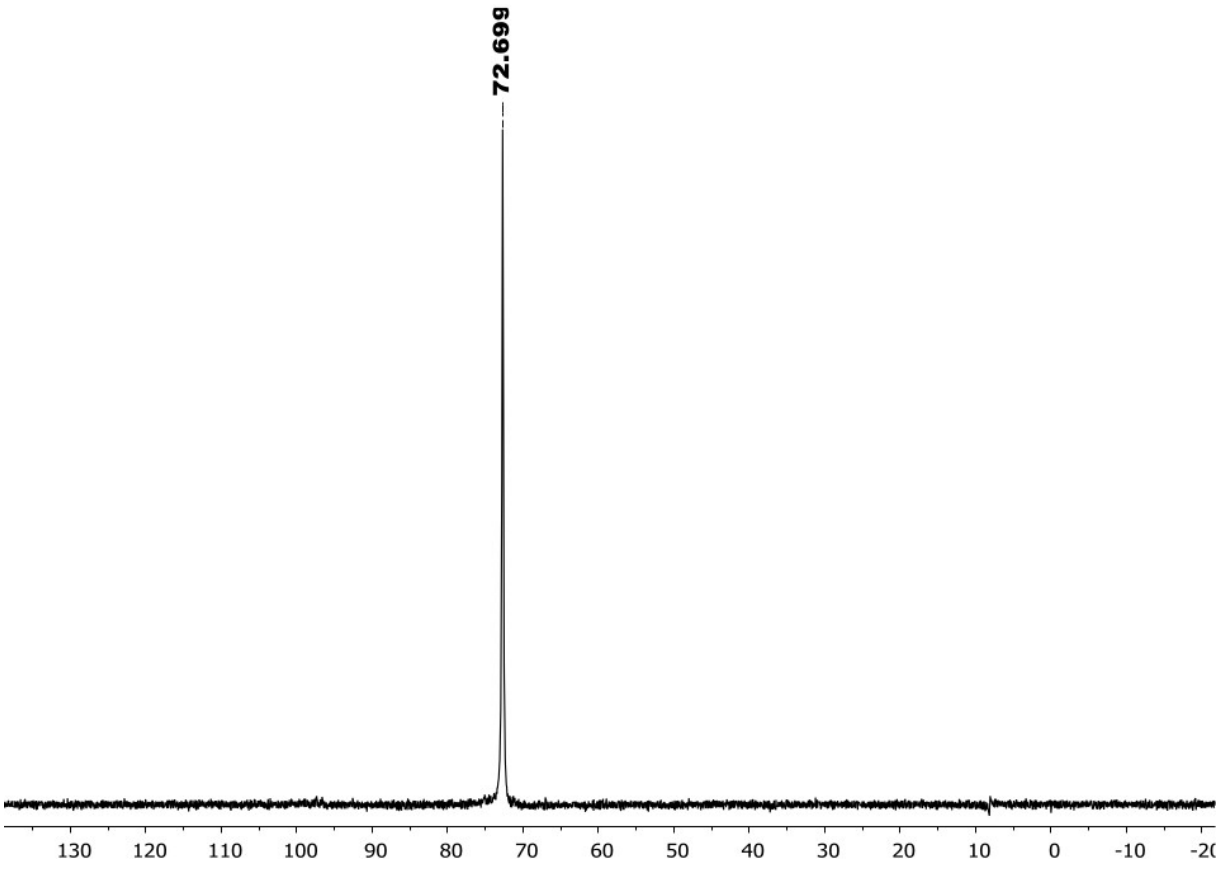

Figure S15. ^{1}H NMR (300 MHz, CD_2Cl_2) of 2**b**

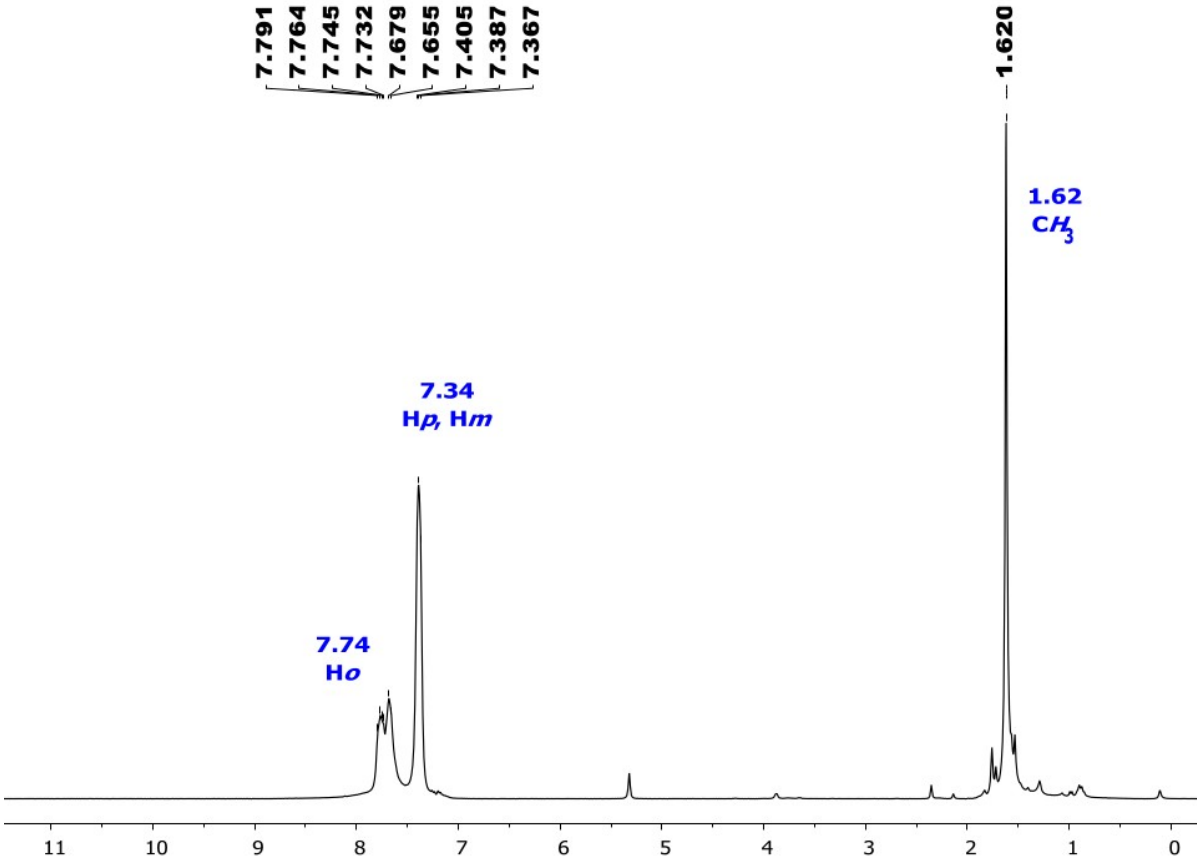

Figure S16. ^{13}C{^{1}H} NMR (75.58 MHz, CD_2Cl_2) of 2**b**

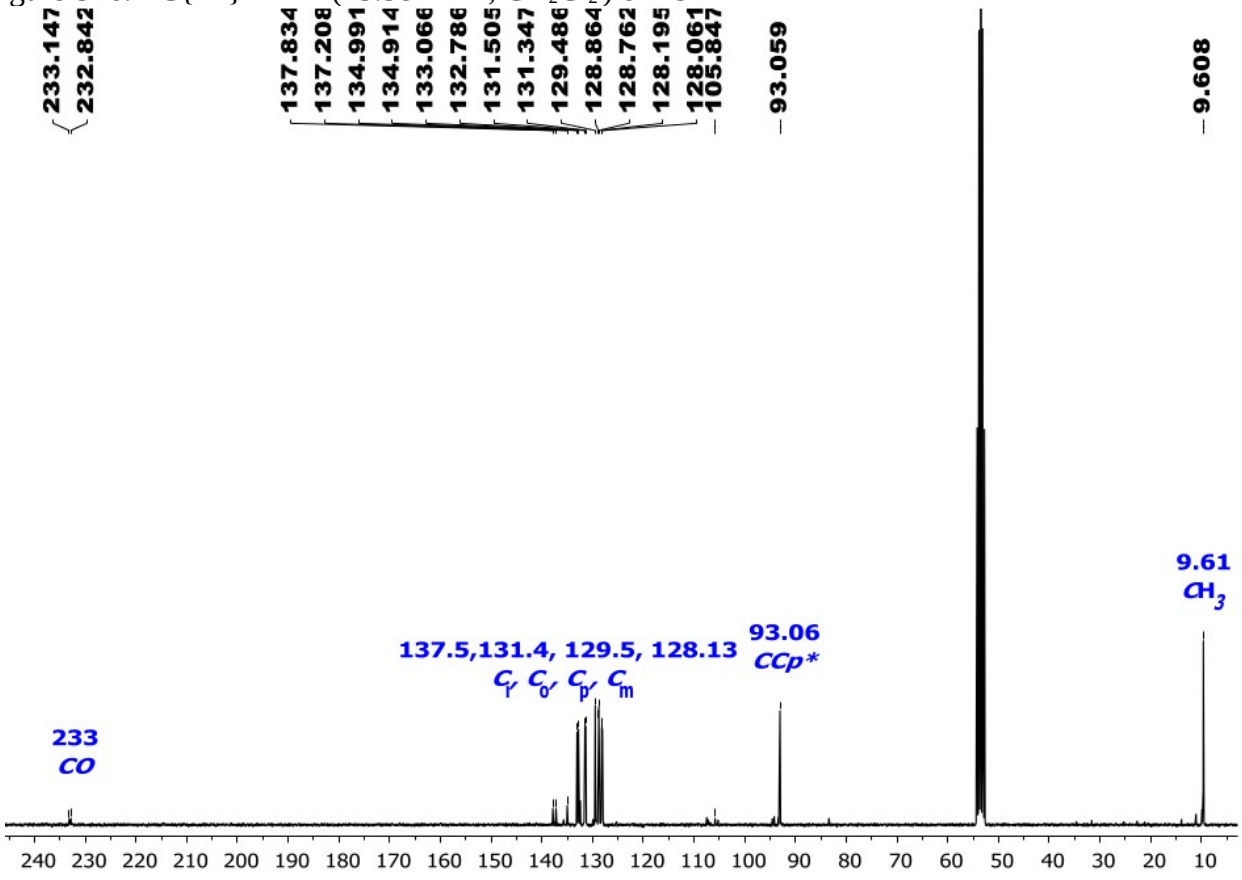

Figure S17. $^{31}P\{^{1}H\}$ NMR (121.65 MHz, CD_2Cl_2) of **2b**

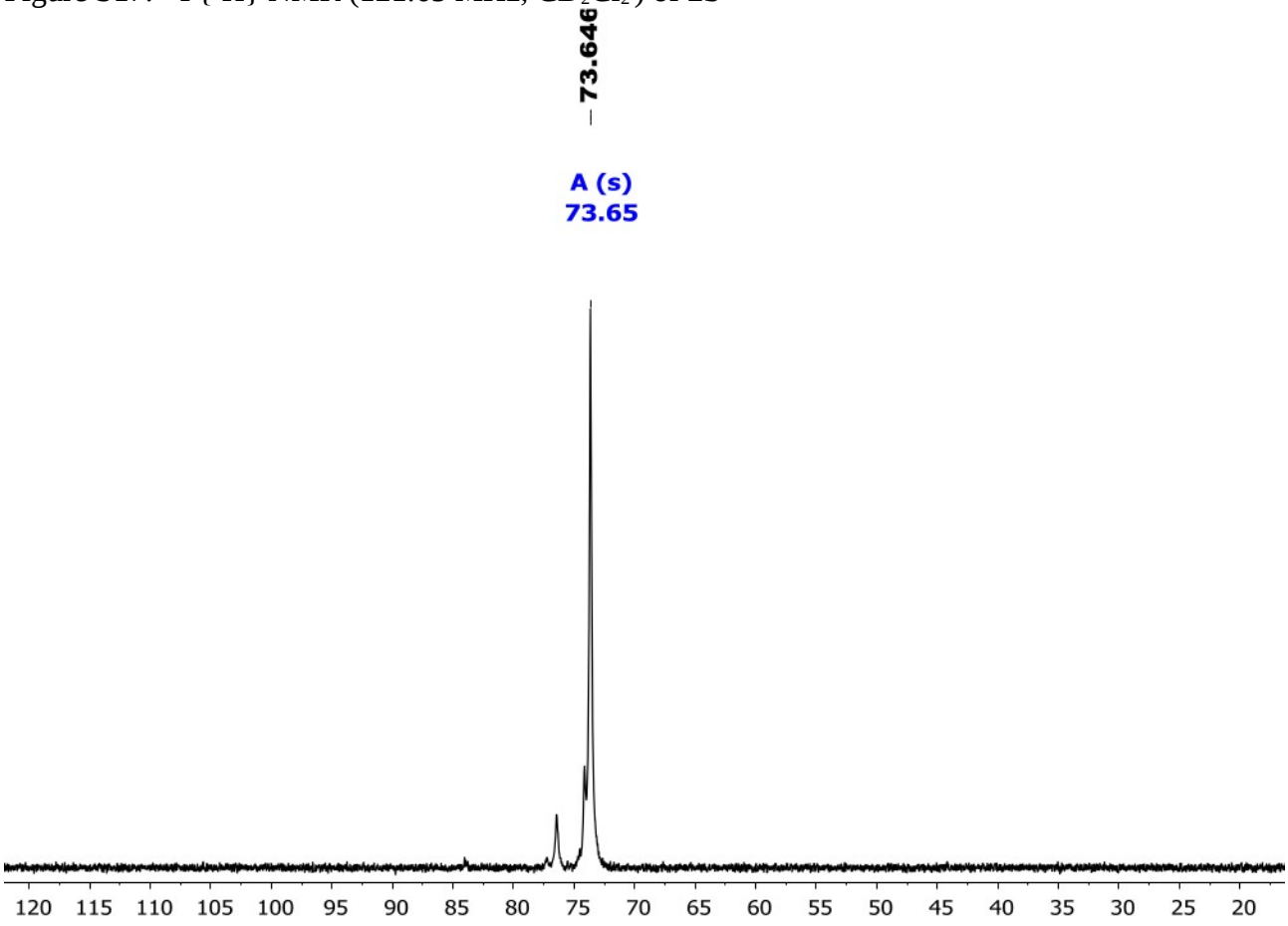

Table S5. Optimized geometries of all compounds

1a'

Mn	0.03287	0.01282	-0.01405
P	0.92990	1.44387	-1.52126
O	0.81988	-2.19281	-1.80632
O	-2.78925	0.23183	-0.81060
C	-0.73770	-1.25002	1.57195
H	-1.32712	-0.63483	2.23701
H	-1.20096	-2.20324	1.33055
C	0.66386	-1.22625	1.56733
H	1.19863	-2.14953	1.34513
C	1.45841	-0.05483	1.56438
H	2.53295	-0.16939	1.45068
C	0.92523	1.25091	1.46129
H	1.64755	2.01681	1.17450
C	-0.43470	1.58477	1.44667
H	-0.67681	2.59353	1.11678
H	-1.14903	1.16578	2.14039
C	0.50590	-1.32605	-1.11491
C	-1.66692	0.15147	-0.56196
C	2.70061	1.48102	-1.47363
C	0.49648	3.21813	-1.31054
C	-0.81802	3.59038	-1.59234
H	-1.52180	2.85646	-1.98011
C	-1.23683	4.89294	-1.37671
H	-2.26088	5.17452	-1.60185
C	-0.35025	5.83448	-0.86661
H	-0.68082	6.85358	-0.69106
C	0.95757	5.46975	-0.58611
H	1.65503	6.20339	-0.19296
C	1.38319	4.16536	-0.81095
H	2.41240	3.88522	-0.60128
C	0.62030	1.22649	-3.32143
C	-0.41099	0.40935	-3.77076
H	-1.01045	-0.15310	-3.06159
C	-0.67565	0.30067	-5.13066
H	-1.48056	-0.34286	-5.47156
C	0.08768	1.00796	-6.04579
H	-0.11810	0.92079	-7.10836
C	1.11803	1.82941	-5.60228
H	1.71691	2.38591	-6.31688
C	1.38121	1.94059	-4.24742
H	2.18440	2.58698	-3.90137
C	3.90090	1.39915	-1.36645
C	5.34003	1.29732	-1.26227
H	5.77762	2.23550	-0.90754
H	5.78526	1.06821	-2.23527
H	5.63202	0.50542	-0.56566

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1a''

Mn	-0.04294	0.06395	0.00435
P	1.64037	-1.38212	-0.36497
O	1.52133	2.04673	-1.51463
O	0.82647	0.94388	2.67039
C	-1.77149	1.28755	0.41893
H	-2.34097	0.81384	1.20636
H	-1.66056	2.36145	0.54393
C	-1.78054	0.81722	-0.90127
H	-1.69727	1.53843	-1.71366
C	-1.62898	-0.53897	-1.28110

H	-1.56455	-0.76509	-2.34161
C	-1.33357	-1.57640	-0.36786
H	-0.95812	-2.49389	-0.82646
C	-1.24209	-1.44447	1.02597
H	-0.76855	-2.27183	1.55114
H	-1.98646	-0.92773	1.61420
C	0.89921	1.27987	-0.92166
C	0.55204	0.59191	1.61154
H	1.78456	-2.02332	-1.62305
H	1.72453	-2.55620	0.42833
H	2.98561	-0.96763	-0.22665

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1b'

Mn	0.00000	0.00000	0.00000
P	-2.10104	-0.25675	0.75297
O	1.35237	-1.65287	2.03111
O	0.58137	2.22491	1.84712
C	-2.62094	-1.80600	1.60668
C	-3.84043	-1.84822	2.28359
H	-4.46066	-0.95622	2.33101
C	-4.26173	-3.01687	2.89572
H	-5.21035	-3.03880	3.42369
C	-3.47082	-4.15884	2.83528
H	-3.80045	-5.07417	3.31756
C	-2.26067	-4.12598	2.16073
H	-1.63748	-5.01369	2.11368
C	-1.83735	-2.95254	1.54753
H	-0.88571	-2.92982	1.02523
C	-3.45117	-0.08728	-0.48816
C	-4.04259	1.14780	-0.73760
H	-3.75709	2.01143	-0.14230
C	-4.99529	1.27913	-1.73817
H	-5.45274	2.24655	-1.92279
C	-5.36533	0.17825	-2.49847
H	-6.11092	0.28176	-3.28090
C	-4.78349	-1.05740	-2.24992
H	-5.07562	-1.92478	-2.83419
C	-3.83140	-1.19060	-1.24910
H	-3.39181	-2.16579	-1.05324
C	-0.44413	-1.53094	-1.51066
H	-0.68842	-2.56224	-1.25758
H	-1.13756	-1.08463	-2.20947
C	0.92419	-1.21690	-1.49829
C	1.41475	0.11256	-1.58044
H	2.49101	0.23994	-1.47934
C	0.63469	1.29731	-1.58044
C	-0.77143	1.29731	-1.58044
H	-1.36460	0.67918	-2.24005
H	-1.23808	2.25545	-1.35273
C	1.92781	-2.30306	-1.23340
H	2.25291	-2.73556	-2.18684
H	1.48612	-3.11262	-0.64388
H	2.81298	-1.93607	-0.70542
C	1.37336	2.59404	-1.40248
H	1.61652	3.00666	-2.38867
H	2.30688	2.47100	-0.84484
H	0.75579	3.33323	-0.88477
C	0.79131	-1.04077	1.23049
C	0.34883	1.36429	1.11868
C	-2.57683	0.96040	1.94768

C	-2.71527	1.84673	2.75575
C	-2.85761	2.90354	3.73164
H	-3.63041	3.61830	3.43265
H	-1.91567	3.44954	3.84673
H	-3.13588	2.49943	4.70974

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1c

Mn	-0.02650	0.00003	-0.00510
O	-1.84682	2.05282	-1.11032
O	-1.84952	-2.04898	-1.11282
C	1.44966	-1.43413	0.75939
H	2.05638	-0.90613	1.48000
H	1.13616	-2.42232	1.08439
C	1.57997	-1.24864	-0.62064
H	1.37686	-2.09577	-1.27512
C	1.68525	0.00026	-1.27838
H	1.68300	0.00136	-2.36377
C	1.58150	1.24801	-0.61816
H	1.37941	2.09667	-1.27098
C	1.45138	1.43104	0.76219
H	1.13903	2.41900	1.08905
H	2.05725	0.90087	1.48190
C	-1.14039	1.26243	-0.67689
C	-1.14195	-1.26005	-0.67861
O	-1.11788	-0.00164	2.73387
C	-0.74072	-0.00092	1.65379

--

2a'

Mn	0.00000	0.00000	0.00000
P	0.22933	-1.83904	-1.22094
C	1.67836	-2.77635	-0.81138
C	2.69175	-3.33130	-0.45960
C	1.24088	0.83412	-0.97460
O	2.06919	1.40279	-1.54030
C	-1.33634	0.61612	-1.00614
O	-2.23789	1.03459	-1.59441
C	0.70024	0.95976	1.75553
C	-0.71168	0.95976	1.75553
C	-1.15201	-0.39560	1.75553
C	-0.00309	-1.21998	1.75016
C	1.14759	-0.39183	1.75001
C	-1.07731	-3.13389	-1.15175
C	-0.81601	-4.44492	-1.54759
C	-1.82909	-5.39074	-1.54025
C	-3.11328	-5.03382	-1.14568
C	-3.38121	-3.72973	-0.75776
C	-2.36517	-2.78205	-0.75981
C	0.42747	-1.59838	-3.02856
C	-0.70894	-1.48164	-3.82595
C	-0.58442	-1.20057	-5.17837
C	0.67285	-1.02756	-5.74102
C	1.80645	-1.13598	-4.94756
C	1.68627	-1.41816	-3.59434
H	1.33267	1.83710	1.74239
H	-1.34695	1.83472	1.74833
H	-2.17903	-0.73328	1.76693
H	-0.00256	-2.30318	1.72933
H	2.17464	-0.72915	1.73820
H	0.18714	-4.72217	-1.86228
H	-1.61819	-6.41090	-1.84668

H	-3.90563	-5.77623	-1.14131
H	-4.38395	-3.44622	-0.45300
H	-2.57283	-1.75822	-0.45910
H	-1.69780	-1.61661	-3.39387
H	-1.47426	-1.11494	-5.79441
H	0.76904	-0.80606	-6.79955
H	2.79137	-0.99751	-5.38302
H	2.57589	-1.50097	-2.97540
C	3.90368	-4.00539	-0.04773
H	4.56257	-3.33132	0.50836
H	4.45917	-4.38040	-0.91275
H	3.67543	-4.85885	0.59804

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2a''

Mn	0.00505	0.06769	0.00002
P	1.34407	-1.69628	0.00014
C	0.94611	0.86072	1.28903
O	1.49662	1.40155	2.14524
C	0.94598	0.86041	-1.28926
O	1.49640	1.40107	-2.14565
C	-1.79531	0.91333	0.70586
C	-1.79529	0.91294	-0.70634
C	-1.71666	-0.43881	-1.15101
C	-1.67229	-1.26036	0.00038
C	-1.71671	-0.43816	1.15131
H	1.27248	-2.63870	-1.05844
H	2.75022	-1.53903	-0.00039
H	-1.84233	1.78823	1.33966
H	-1.84231	1.78750	-1.34060
H	-1.70700	-0.77449	-2.17853
H	-1.60376	-2.34159	0.00068
H	-1.70706	-0.77329	2.17900
H	1.27329	-2.63794	1.05946

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2b'

Mn	0.04317	1.08314	0.74013
P	0.23298	-0.65051	-0.63942
O	-2.25705	2.22419	-0.67778
O	2.14015	2.53304	-0.71261
C	1.20833	0.63023	2.47624
C	0.03044	-0.17496	2.50205
C	-1.10043	0.68615	2.51360
C	-0.62131	2.03786	2.51337
C	0.79659	2.00029	2.50053
C	2.61856	0.14842	2.54534
H	3.02428	0.25270	3.56013
H	3.27312	0.70919	1.86835
H	2.69093	-0.90594	2.26467
C	-0.00103	-1.66142	2.62962
H	0.06484	-1.94837	3.68660
H	0.83630	-2.13725	2.10912
H	-0.92305	-2.09366	2.22867
C	-2.53043	0.28420	2.64847
H	-2.86592	0.37659	3.68960
H	-2.69147	-0.75393	2.34403
H	-3.18950	0.91263	2.03941
C	-1.46301	3.26341	2.62068
H	-1.60906	3.54728	3.67084
H	-2.45326	3.11722	2.17988
H	-1.00130	4.11321	2.10885

C	1.70202	3.18058	2.59652
H	1.84226	3.47366	3.64455
H	1.29898	4.04561	2.06131
H	2.69044	2.96951	2.17882
C	-1.32073	1.75999	-0.17964
C	1.28842	1.94755	-0.19497
C	1.75618	-1.54998	-0.47768
C	-1.01712	-2.00142	-0.57015
C	-0.68126	-3.33946	-0.75980
H	0.35057	-3.61110	-0.96621
C	-1.65428	-4.32462	-0.66827
H	-1.38141	-5.36659	-0.80673
C	-2.97267	-3.98124	-0.39938
H	-3.73186	-4.75396	-0.32494
C	-3.31759	-2.64777	-0.22629
H	-4.34736	-2.37217	-0.01882
C	-2.34269	-1.66296	-0.30662
H	-2.61145	-0.62156	-0.14504
C	0.26217	-0.23521	-2.43215
C	-0.93121	-0.13443	-3.14327
H	-1.87704	-0.37820	-2.66686
C	-0.92156	0.27141	-4.46989
H	-1.85692	0.34341	-5.01647
C	0.27719	0.58495	-5.09483
H	0.28310	0.90282	-6.13299
C	1.46797	0.49317	-4.38768
H	2.40867	0.74167	-4.86967
C	1.46201	0.08787	-3.06115
H	2.39701	0.02161	-2.51159
C	2.85132	-2.02984	-0.30532
C	4.16135	-2.60370	-0.08845
H	4.09371	-3.67387	0.13026
H	4.66856	-2.11863	0.75264
H	4.79267	-2.48438	-0.97430

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2c

Mn	0.05703	0.00024	0.00319
C	1.03720	-1.27817	0.80220
O	1.61766	-2.11925	1.32142
C	1.03326	1.33203	0.71514
O	1.61110	2.20752	1.17734
C	-1.71559	-0.69475	0.96556
C	-1.71701	0.71515	0.94810
C	-1.69678	1.14223	-0.41114
C	-1.69202	-0.01743	-1.22161
C	-1.69353	-1.15701	-0.38143
H	-1.71357	-1.31745	1.84973
H	-1.71754	1.36003	1.81614
H	-1.69704	2.16533	-0.75924
H	-1.65984	-0.03104	-2.30286
H	-1.69260	-2.18867	-0.70310
O	1.68086	-0.08217	-2.45010
C	1.07415	-0.04924	-1.47842