Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supporting Information

Chemistry of CS_2- and SCNPh-Adducts of the Pyramidal Phosphinidene-Bridged Complex $[Mo_2Cp(\mu\text{-}\kappa^1\text{:}\kappa^1,\eta^5\text{-}PC_5H_4)(CO)_2(\eta^6\text{-}HMes^*)(PMe_3)]$

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Computational Details

All DFT computations were carried out using the GAUSSIAN03 package,[1] in which the hybrid method B3LYP was used with the Becke three-parameter exchange functional,[2] and the Lee-Yang-Parr correlation functional.[3] An accurate numerical integration grid (99 590) was used for all the calculations via the keyword Int=Ultrafine. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for the metal atoms.[4] The light elements (P, S, O, C, N and H) were described with the 6-31G* basis.[5] Geometry optimizations were performed under no symmetry restrictions, and frequency analyses were performed for all the stationary points to ensure that minimum structures with no imaginary frequencies were achieved. For interpretation purposes, natural population analysis charges were derived from the natural bond order analysis of the data.[6] Molecular orbitals and vibrational modes were visualized using the Molekel program.[7]

References

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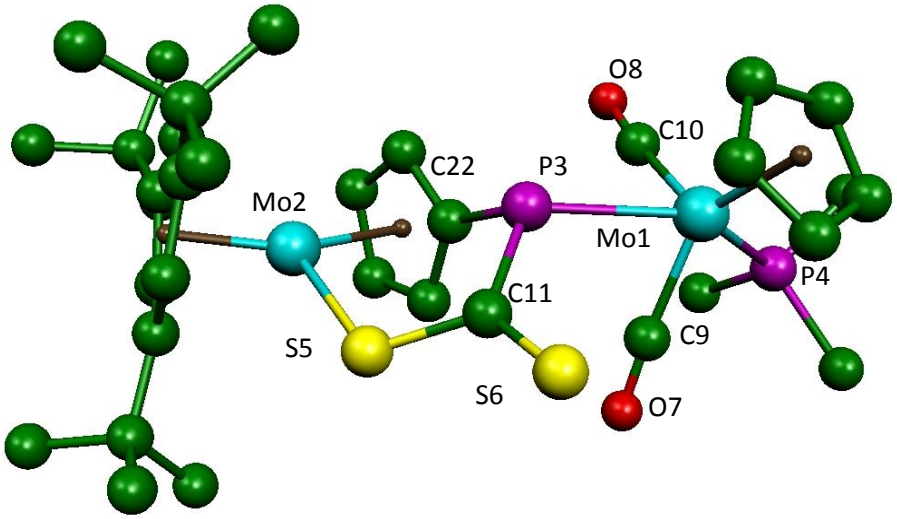
(5) (a) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213. (b) G. A. Petersson and M. A. Al-Laham, *J. Chem. Phys.*, 1991, **94**, 6081. (c) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley and J. Mantzaris, *J. Chem. Phys.*, 1988, **89**, 2193.

(6) A. E. Reed, L. A. Curtis and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.

(7) S. Portmann and H. P. Luthi, *CHIMIA*, 2000, **54**, 766.

Optimized geometry of compound 2a.



Optimized geometry of compound 2b.

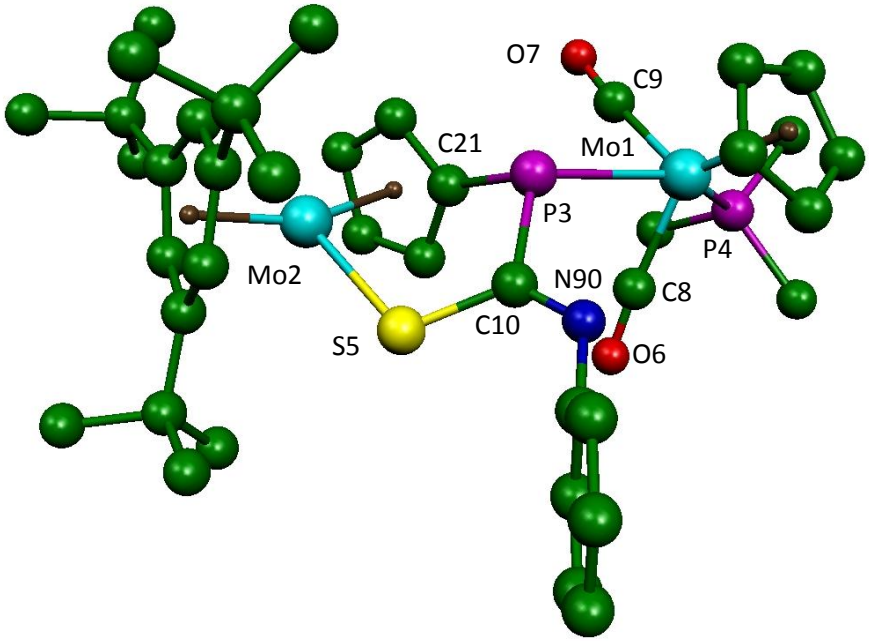


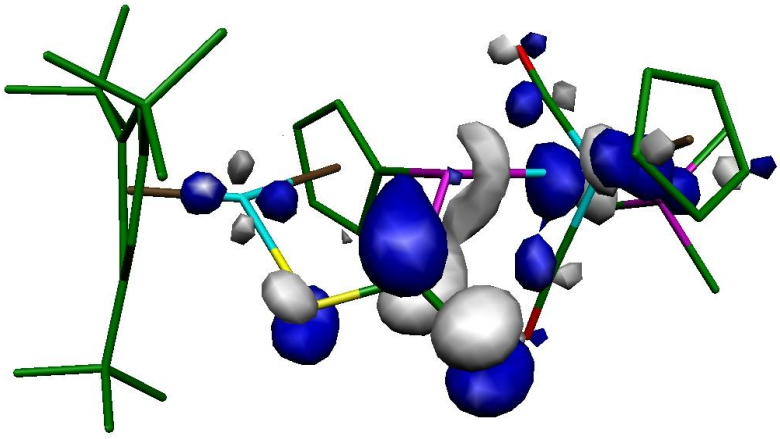
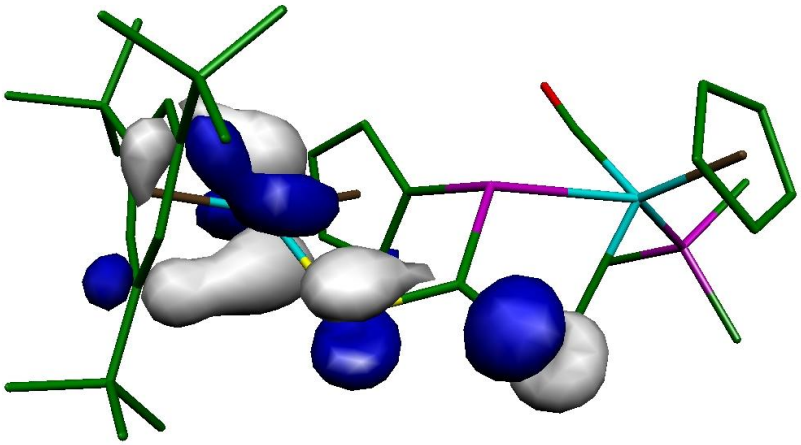
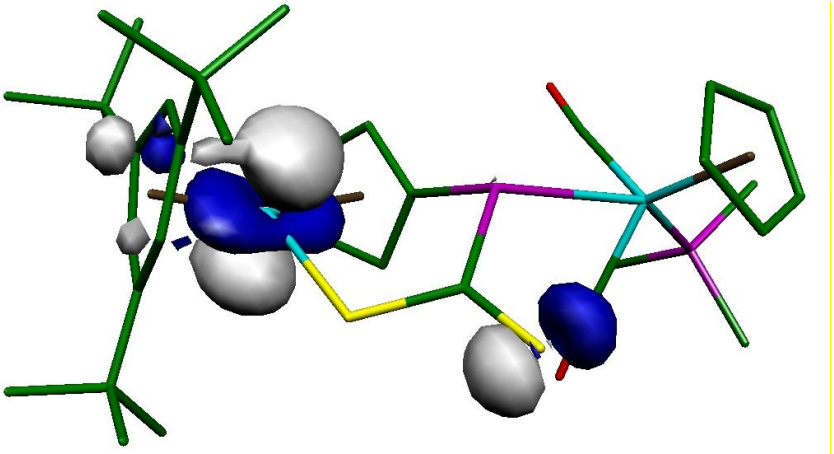
Table S1: DFT-Optimized Geometry for compound **2a** (distances in Å, angles in deg.)

Parameter	Optimized		
Mo1 – P3	2.627	Mo1 – P3 – Mo2	143.7
Mo2 – P3	3.627	Mo1 – P3 – C22	110.7
Mo2 – S5	2.601	P4 – Mo1 – P3	138.6
P3 – C22	1.830	Mo1 – P3 – C11	113.9
P3 – C11	1.840	C11 – P3 – C22	98.7
C11 – S5	1.741	P3 – C11 – S6	122.9
C11 – S6	1.673	S6 – C11 – S5	120.1
Mo1 – C9	1.993	S5 – C11 – P3	116.6
Mo1 – C10	1.964	C11 – S5 – Mo2	112.1
Mo1 – P4	2.490	C10 – Mo1 – C9	104.3
C9 – O7	1.165		
C10 – O8	1.169		

Table S2: DFT-Optimized Geometry for compound **2b** (distances in Å, angles in deg.)

Parameter	Optimized		
Mo1 – P3	2.645	Mo1 – P3 – Mo2	143.8
Mo2 – P3	3.608	Mo1 – P3 – C21	110.8
Mo2 – S5	2.606	P4 – Mo1 – P3	139.2
P3 – C21	1.829	Mo1 – P3 – C10	110.3
P3 – C10	1.863	C10 – P3 – C21	97.9
C10 – S5	1.781	P3 – C10 – N90	117.6
C10 – N90	1.285	N90 – C10 – S5	124.8
Mo1 – C8	1.984	S5 – C10 – P3	117.3
Mo1 – C9	1.966	C10 – S5 – Mo2	109.8
Mo1 – P4	2.484	C9 – Mo1 – C8	104.5
C8 – O6	1.167		
C9 – O7	1.169		

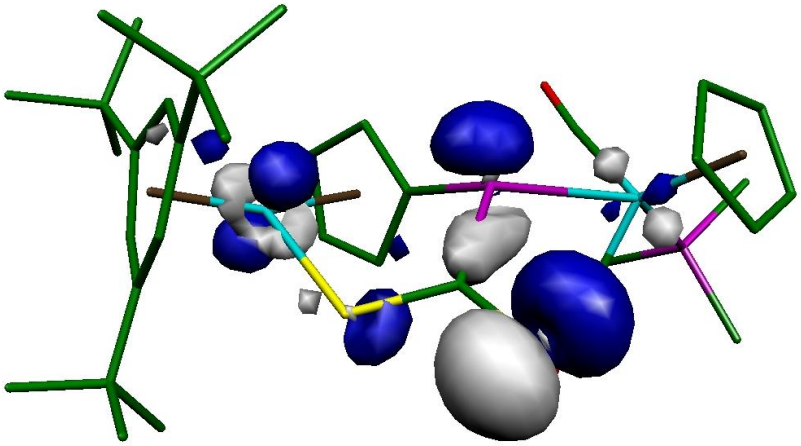
Table S3: Selected molecular orbitals of compound **2a**.

OM Energy (eV) Assignment	Projection
LUMO 180 -1.28 π^*_{CS2}	
	Contributions (%): Mo(1) 17, Mo(2) 6, P(3) 8, P(4) 3, CO´s 9, C(11) 18, S(5) 8, S(6) 13, Other 18
HOMO 179 -4.28 $LP_{Mo2} + \pi^*_{Mo-S}$	
	Contributions (%): Mo(1) 0, Mo(2) 38, P(3) 1, P(4) 0, CO´s 0, C(11) 1, S(5) 13, S(6) 18, Other 28
MO 178 -4.44 LP_{Mo2}	
	Contributions (%): Mo(1) 1, Mo(2) 59, P(3) 3, P(4) 0, CO´s 0, C(11) 0, S(5) 1, S(6) 13, Other 22

MO 177

-4.60

LP S(6)

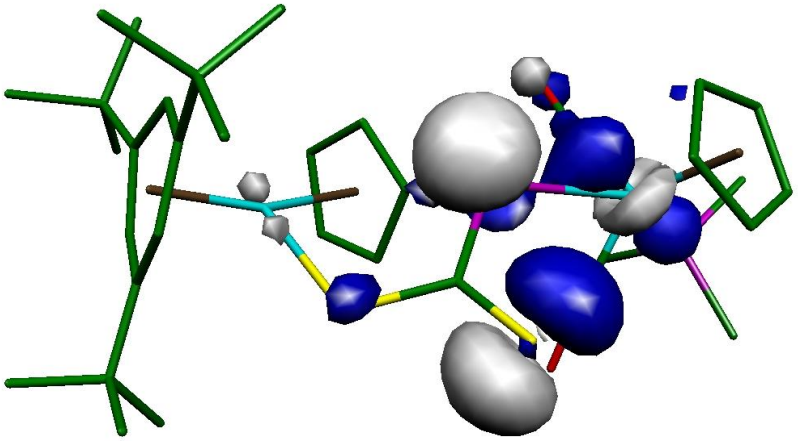


Contributions (%): Mo(1) 6, Mo(2) 15, P(3) 15, P(4) 0, CO´s 1, C(11) 2, S(5) 6, S(6) 41, Other 13

MO 176

-5.01

LP P3 + LP S6

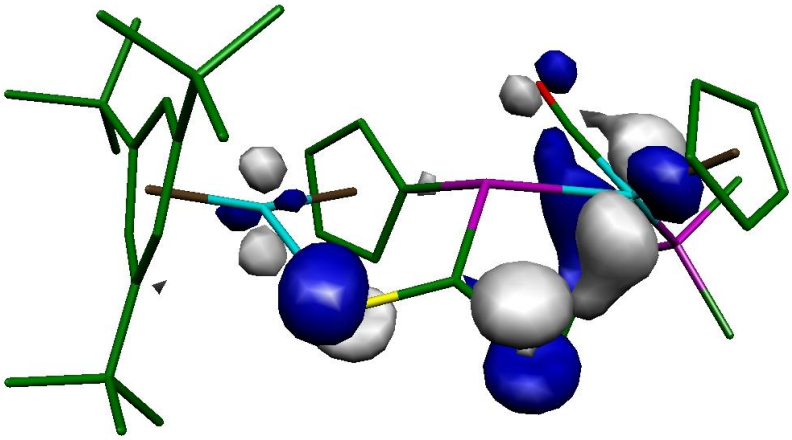


Contributions (%): Mo(1) 20, Mo(2) 4, P(3) 24, P(4) 0, CO´s 6, C(11) 1, S(5) 3, S(6) 32, Other 9

MO 175

-5.32

$\pi_{M\text{-}CO}$ + LP S6 + LPS5

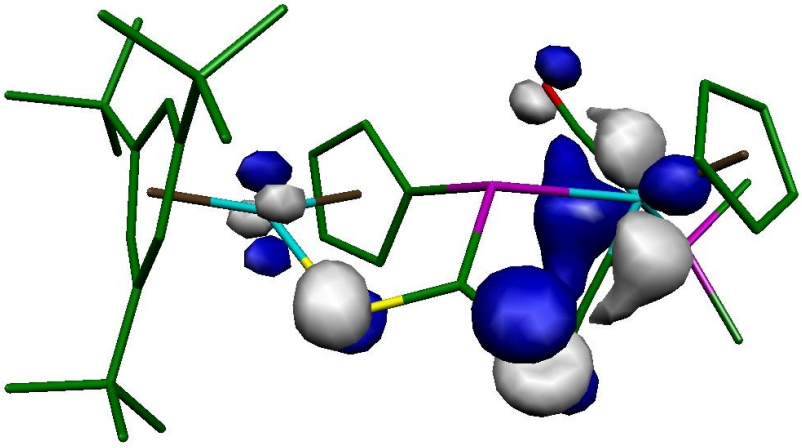


Contributions (%): Mo(1) 38, Mo(2) 8, P(3) 0, P(4) 0, CO´s 13, C(11) 2, S(5) 14, S(6) 15, Other 9

MO 174

-5.54

$\pi_{M\text{-}CO}$ + LP S6 + LPS5

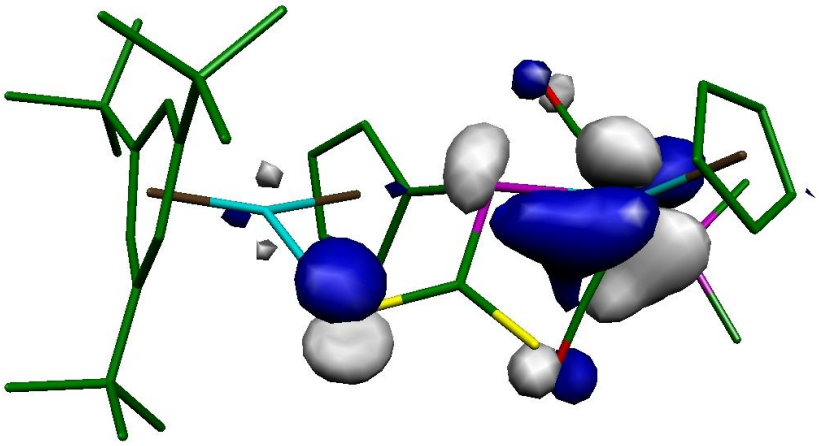


Contributions (%): Mo(1) 35, Mo(2) 9, P(3) 4, P(4) 0, CO´s 16, C(11) 2, S(5) 10, S(6) 17, Other 8

MO 173

-5.68

$\pi_{M\text{-}CO}$ + LP S5

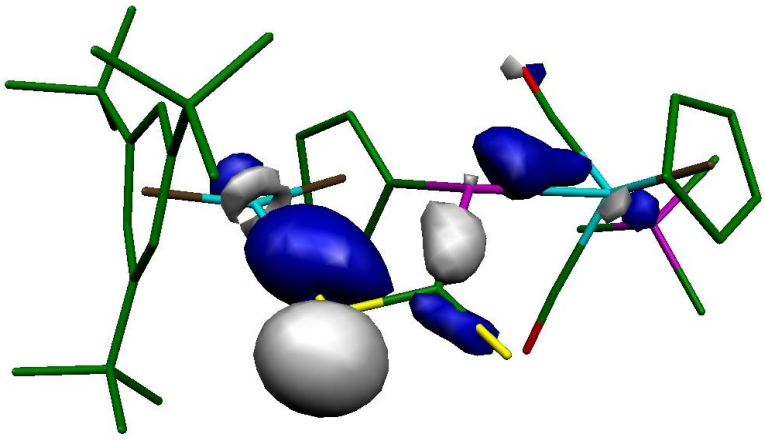


Contributions (%): Mo(1) 43, Mo(2) 4, P(3) 10, P(4) 1, CO´s 14, C(11) 1, S(5) 14, S(6) 1, Other 11

MO 172

-6.21

$\sigma_{M\text{-}S}$ + $\sigma_{P\text{-}C}$

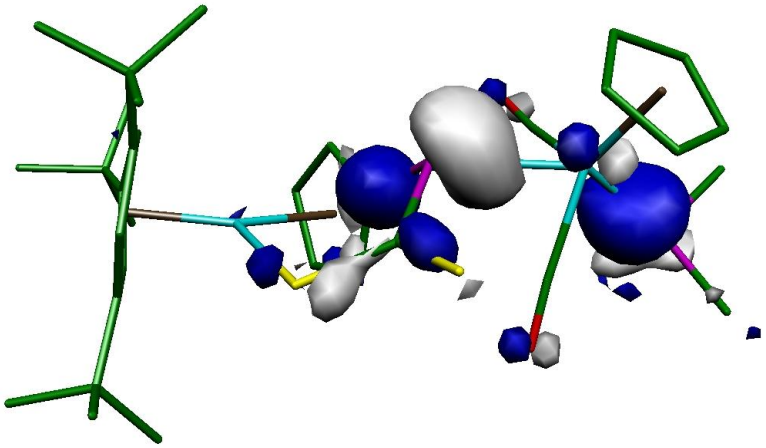


Contributions (%): Mo(1) 8, Mo(2) 15, P(3) 8, P(4) 0, CO´s 2, C(11) 4, S(5) 52, S(6) 3, Other 8

MO 165

-7.91

$\sigma_{M\text{-}P} + \sigma_{M\text{-}P}$

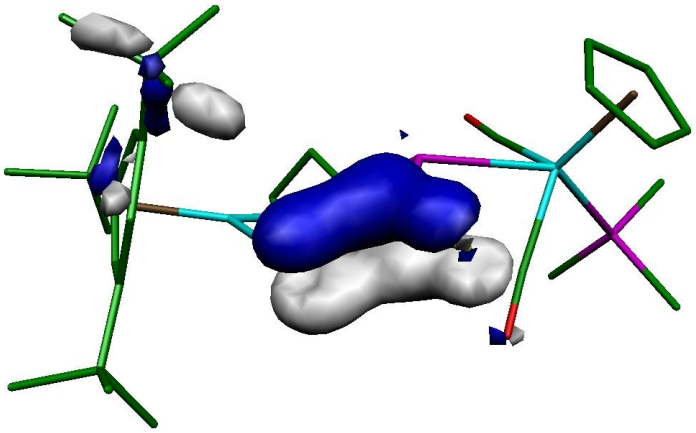


Contributions (%): Mo(1) 13, Mo(2) 4, P(3) 19, P(4) 16, CO´s 4, C(11) 2, S(5) 5, S(6) 4, Other 33

MO 164

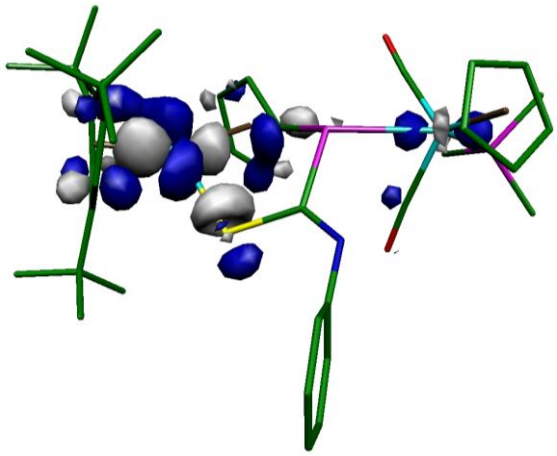
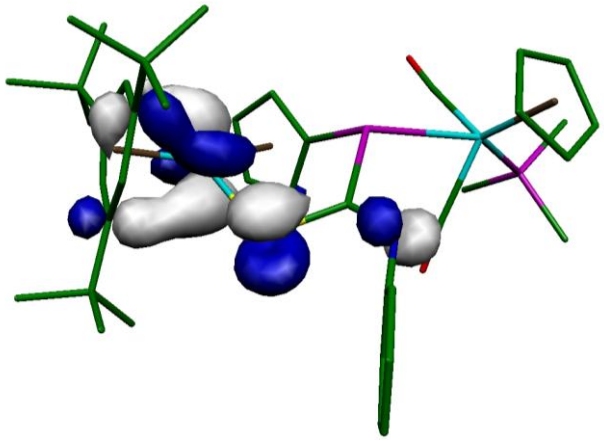
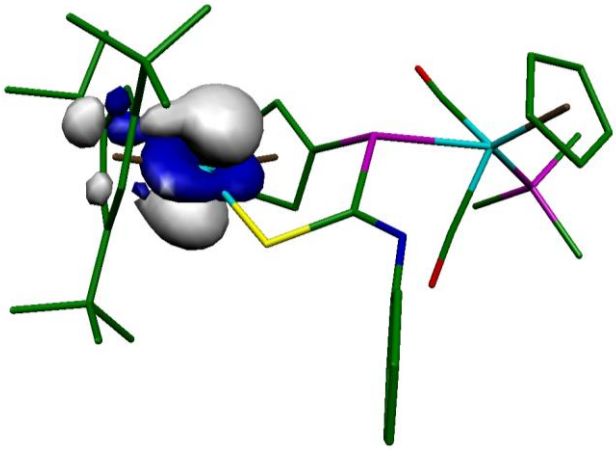
-8.20

$\pi_{S\text{-}C\text{-}S}$



Contributions (%): Mo(1) 1, Mo(2) 4, P(3) 4, P(4) 1, CO´s 2, C(11) 28, S(5) 19, S(6) 12, Other 29

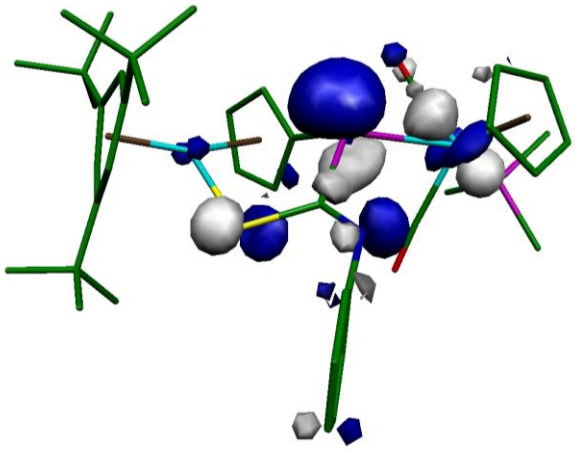
Table S4: Selected molecular orbitals of compound **2b**.

OM Energy (eV) Assignment	Projection
LUMO 196 -1.10 σ^*_{MS}	
	Contributions (%): Mo(1) 7, Mo(2) 33, P(3) 4, P(4) 1, CO´s 3, C(10) 1, S(5) 10, N(90) 0, Other 39
HOMO 195 -4.15 $LP_{Mo2} + \pi^*_{Mo-S}$	
	Contributions (%): Mo(1) 1, Mo(2) 37, P(3) 2, P(4) 0, CO´s 0, C(10) 1, S(5) 17, N(90) 0, Other 34
MO 194 -4.38 LP_{Mo2}	
	Contributions (%): Mo(1) 1, Mo(2) 71, P(3) 0, P(4) 0, CO´s 0, C(10) 1, S(5) 1, N(90) 0, Other 26

MO 193

-4.73

LP P(3) + LP S6

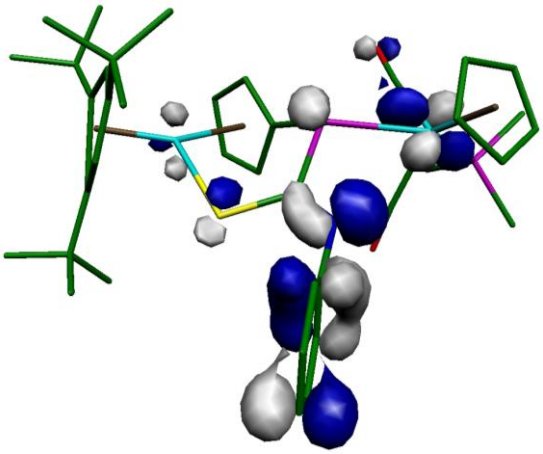


Contributions (%): Mo(1) 18, Mo(2) 4, P(3) 31, P(4) 0, CO´s 5, C(10) 2, S(5) 11, N(90) 7, Other 22

MO 192

-5.13

LP N90 +
π_{CC}(Ph)

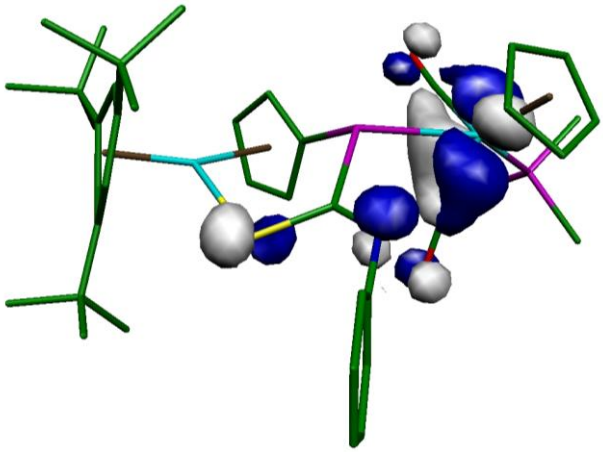


Contributions (%): Mo(1) 16, Mo(2) 5, P(3) 5, P(4) 0, CO´s 5, C(10) 2, S(5) 6, N(90) 15, Other 45

MO 191

-5.31

$\pi_{M\text{-}CO}$ + LP S6 +
LPN90

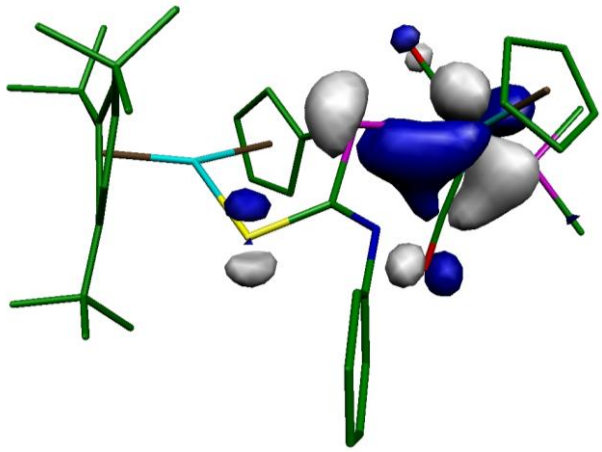


Contributions (%): Mo(1) 49, Mo(2) 2, P(3) 1, P(4) 0, CO´s 18, C(10) 1, S(5) 9, N(90) 7, Other 12

MO 190

-5.55

$\pi_{M\text{-}CO} + \sigma_{M\text{-}P}$

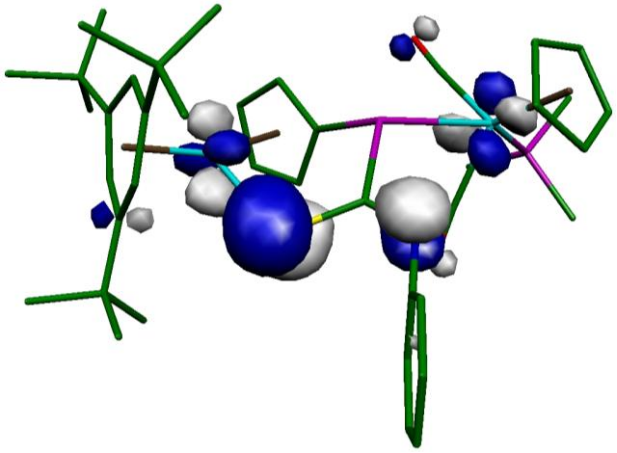


Contributions (%): Mo(1) 47, Mo(2) 2, P(3) 14, P(4) 1, CO´s 16, C(10) 1, S(5) 7, N(90) 1, Other 12

MO 189

-5.56

LP S5

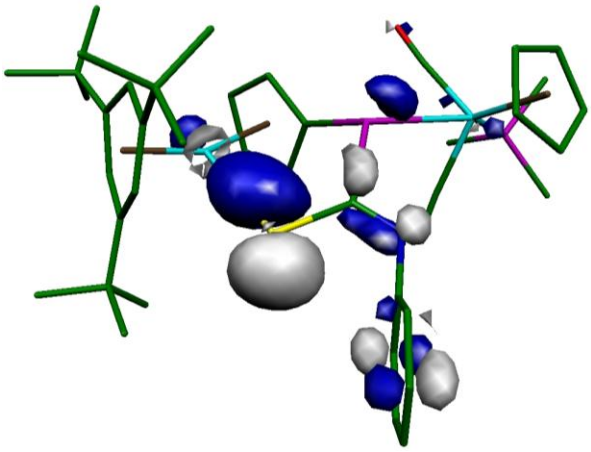


Contributions (%): Mo(1) 15, Mo(2) 14, P(3) 4, P(4) 0, CO´s 7, C(10) 1, S(5) 31, N(90) 14, Other 14

MO 187

-6.23

$\sigma_{M\text{-}S}$

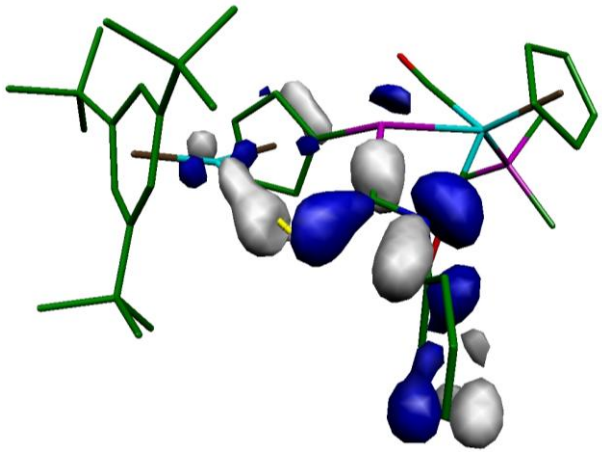


Contributions (%): Mo(1) 5, Mo(2) 12, P(3) 7, P(4) 0, CO´s 2, C(10) 3, S(5) 43, N(90) 4, Other 25

MO 186

-6.65

$\sigma_{M-S} + \sigma_{P-C} + \sigma_{C-S}$

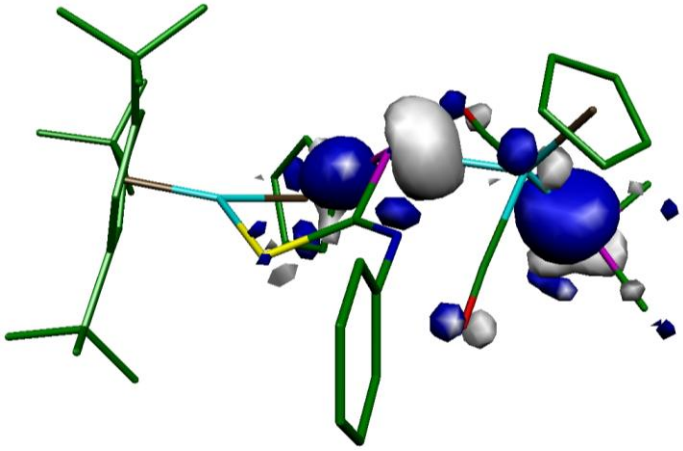


Contributions (%): Mo(1) 4, Mo(2) 9, P(3) 7, P(4) 0, CO´s 1, C(10) 6, S(5) 11, N(90) 17, Other 46

MO 179

-7.94

$\sigma_{MP} + \sigma_{PC}$

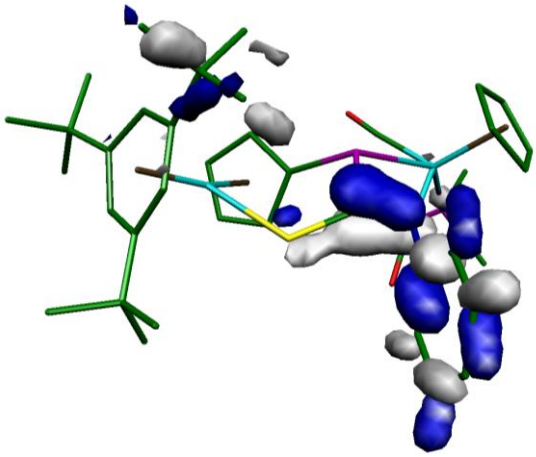


Contributions (%): Mo(1) 13, Mo(2) 4, P(3) 15, P(4) 20, CO´s 6, C(10) 2, S(5) 4, N(90) 2, Other 34

MO 178

-8.25

$\pi_{CN} + \sigma_{CC}(Ph)$

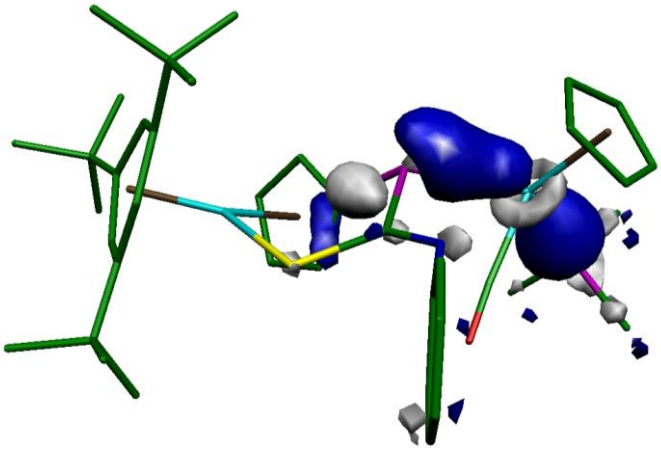


Contributions (%): Mo(1) 3, Mo(2) 1, P(3) 2, P(4) 3, CO´s 1, C(10) 15, S(5) 6, N(90) 7, Other 62

MO 175

-8.42

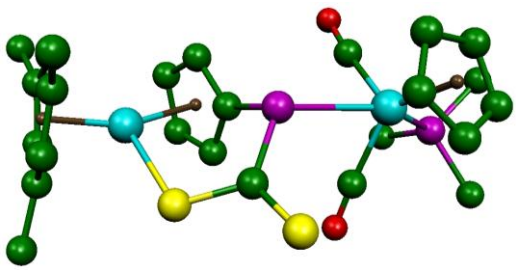
σ_{MP}



Contributions (%): Mo(1) 19, Mo(2) 1, P(3) 15, P(4) 16, CO´s 1, C(10) 3, S(5) 2, N(90) 2, Other 40

Table S5: Cartesian coordinates for the optimized structure of compound **2a**.

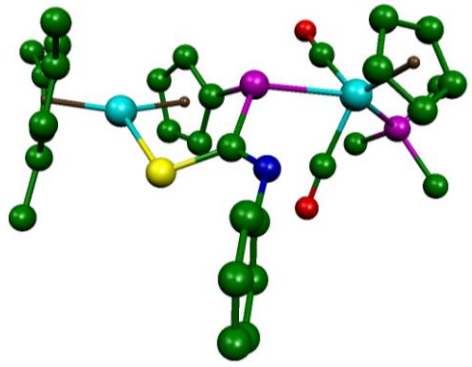
Mo	14.87377	9.87405	4.56247
Mo	12.03367	15.06895	3.95557
P	13.94078	12.03461	3.39493
P	15.08035	8.93298	6.85854
S	14.57418	15.01520	3.40045
S	16.76424	13.12442	2.78297
O	16.01279	12.26275	6.28262
O	11.83513	9.62058	5.27112
C	15.56419	11.41913	5.61595
C	12.97068	9.77328	5.03810
C	15.17571	13.39011	3.23689
C	14.71978	8.70542	2.48927
H	13.79461	8.71060	1.92898
C	15.09735	7.76172	3.48605
H	14.52083	6.90351	3.80454
C	16.40687	8.12235	3.94698
H	16.99161	7.58104	4.68028
C	16.83780	9.26994	3.22986
H	17.77345	9.79820	3.35089
C	15.79484	9.63605	2.33934
H	15.82509	10.48458	1.67046
C	12.73484	12.88504	4.47783
C	12.98510	13.71586	5.65271
H	13.96047	13.93928	6.05867
C	11.75820	14.17362	6.15597
H	11.61360	14.81058	7.01851
C	10.73000	13.66926	5.29292
H	9.67004	13.81763	5.42656
C	11.33010	12.84841	4.28693
H	10.81205	12.29866	3.51347
C	12.43571	16.80882	2.40924
H	13.38550	16.98699	1.92543
C	12.23211	17.39886	3.69373
C	10.99940	17.07855	4.34895
H	10.78396	17.54462	5.30041
C	9.98547	16.31299	3.69987
C	10.34241	15.60027	2.51784
H	9.62945	14.91533	2.08105
C	11.55976	15.86768	1.80213
C	13.14263	18.49528	4.28169
C	13.53876	18.16586	5.73735
H	12.66296	18.03605	6.38331
H	14.13809	18.98323	6.15684
H	14.12821	17.24483	5.77785
C	14.43220	18.68839	3.45917
H	15.03517	17.77659	3.41960
H	15.04108	19.47346	3.92201
H	14.21705	19.00767	2.43259
C	12.35922	19.83298	4.25652
H	12.04859	20.08818	3.23643
H	12.98891	20.64877	4.63180
H	11.46005	19.79162	4.88175
C	8.53659	16.32090	4.23324
C	8.43962	16.42736	5.77126
H	7.38530	16.43766	6.07003
H	8.88594	17.35263	6.14902
H	8.92282	15.58988	6.28225
C	7.69976	15.11430	3.75700
H	8.12807	14.15447	4.06191
H	7.58742	15.10024	2.66803
H	6.69181	15.17875	4.18168
C	7.89538	17.60211	3.63034
H	6.84837	17.68680	3.94673
H	7.91987	17.57798	2.53537
H	8.42457	18.50287	3.95986
C	11.75041	15.33345	0.37207
C	13.18283	15.57104	-0.14566
H	13.41293	16.63869	-0.24088
H	13.28688	15.12912	-1.14316
H	13.93018	15.11349	0.50987
C	11.45811	13.81915	0.29580
H	11.56188	13.47367	-0.73994
H	10.43884	13.57471	0.61646
H	12.15627	13.25438	0.92175
C	10.76318	16.08830	-0.55415
H	10.94205	17.16960	-0.52292
H	9.72089	15.91091	-0.26383
H	10.88328	15.75564	-1.59246
C	14.57556	7.16297	7.05455
H	14.68471	6.83521	8.09450
H	15.19073	6.52249	6.41562
H	13.53065	7.05131	6.74990
C	14.06941	9.76835	8.15855
H	14.21373	9.29294	9.13503
H	13.01194	9.72283	7.88445
H	14.36254	10.81999	8.22254
C	16.76609	8.94937	7.62478
H	17.12775	9.98072	7.67141
H	17.46298	8.37240	7.00959
H	16.74882	8.52749	8.63605



G (a.u.) = -3088.541182

Table S6: Cartesian coordinates for the optimized structure of compound **2b**.

Mo	14.81078	9.88010	4.39368
Mo	11.96582	15.07997	3.87174
P	13.69193	11.97637	3.23293
P	15.25720	9.01221	6.67818
S	14.46075	14.98966	3.12369
O	16.13207	12.35189	5.83044
O	11.86117	9.66748	5.42831
C	15.59825	11.46778	5.28621
C	12.96662	9.79886	5.07098
C	14.96807	13.29554	2.91426
C	14.50212	8.76374	2.31652
H	13.54830	8.82730	1.81068
C	14.89305	7.77094	3.25820
H	14.29766	6.92926	3.58642
C	16.23369	8.06631	3.66239
H	16.82977	7.48011	4.35085
C	16.67635	9.21959	2.95967
H	17.64483	9.69386	3.04338
C	15.60603	9.65922	2.13737
H	15.63572	10.53436	1.50401
C	12.66385	12.90606	4.42613
C	13.06459	13.77633	5.52930
H	14.08424	13.99135	5.80998
C	11.91706	14.29786	6.14134
H	11.88805	14.97951	6.98103
C	10.78472	13.79177	5.42034
H	9.75150	13.97968	5.66523
C	11.24599	12.90425	4.39784
H	10.63024	12.33913	3.71205
C	12.22089	16.74251	2.21216
H	13.12444	16.89068	1.63882
C	12.13709	17.39108	3.48162
C	10.96912	17.10721	4.26162
H	10.84214	17.61759	5.20625
C	9.89882	16.31862	3.74338
C	10.14978	15.54395	2.57359
H	9.40024	14.84216	2.23628
C	11.29536	15.77619	1.73513
C	13.09999	18.50707	3.93286
C	13.63074	18.23815	5.35780
H	12.81900	18.14039	6.08769
H	14.26771	19.06967	5.68392
H	14.21984	17.31636	5.38132
C	14.30698	18.65583	2.98517
H	14.89996	17.73835	2.92805
H	14.95926	19.45562	3.35445
H	13.99675	18.93266	1.97063
C	12.32069	19.84726	3.92314
H	11.91649	20.06028	2.92640
H	12.98435	20.67468	4.20232
H	11.48380	19.83828	4.63079
C	8.50146	16.36173	4.39843
C	8.53597	16.58258	5.92687
H	7.51136	16.60582	6.31494
H	8.99857	17.53810	6.19358
H	9.07478	15.79121	6.45554
C	7.63591	15.12226	4.08508
H	8.09616	14.18776	4.42007
H	7.43016	15.02883	3.01385
H	6.66773	15.21615	4.58950
C	7.80080	17.59438	3.76108
H	6.78511	17.70209	4.16156
H	7.72913	17.48880	2.67307
H	8.35096	18.51720	3.97502
C	11.35056	15.17999	0.31810
C	12.73309	15.37980	-0.33406
H	12.95628	16.43944	-0.50515
H	12.74943	14.88524	-1.31215
H	13.53243	14.95477	0.28069
C	11.03946	13.66778	0.33122
H	11.05009	13.27876	-0.69431
H	10.04898	13.44995	0.74718
H	11.78224	13.11904	0.91877
C	10.29027	15.90763	-0.54709
H	10.47952	16.98723	-0.57664
H	9.27689	15.75398	-0.15756
H	10.31388	15.53174	-1.57745
C	14.73742	7.26364	6.99516
H	14.96665	6.96134	8.02329
H	15.24981	6.58751	6.30416
H	13.66010	7.17485	6.82569
C	14.42333	9.91582	8.05632
H	14.66720	9.46820	9.02620
H	13.34054	9.89080	7.90622
H	14.74609	10.96074	8.04954
C	17.02029	9.00844	7.24637
H	17.40748	10.03122	7.21414
H	17.62897	8.39356	6.57659
H	17.11111	8.62098	8.26750
N	16.10686	12.92190	2.44962
C	17.14166	13.80430	2.09146
C	17.89458	14.47854	3.06939
C	17.51467	13.92962	0.74297
C	18.98288	15.26705	2.69906
H	17.61750	14.36639	4.11319
C	18.59873	14.72873	0.38077
H	16.94189	13.39597	-0.01059
C	19.34073	15.40119	1.35474
H	19.55526	15.78114	3.46790
H	18.86765	14.82132	-0.66899
H	20.18983	16.01719	1.07073



G(a.u.) = -2976.657093

Table S7: Mulliken Charges for compound **2a**.

1	Mo	-0.373194
2	Mo	-0.228399
3	P	0.436524
4	P	0.580250
5	S	0.097042
6	S	-0.219922
7	O	-0.293008
8	O	-0.310137
9	C	0.213053
10	C	0.205936
11	C	-0.371417
12	C	-0.137925
13	H	0.173644
14	C	-0.145608
15	H	0.158847
16	C	-0.158795
17	H	0.149654
18	C	-0.108567
19	H	0.185137
20	C	-0.138616
21	H	0.203230
22	C	-0.157448
23	C	-0.159536
24	H	0.199306
25	C	-0.090458
26	H	0.164002
27	C	-0.206400
28	H	0.146942
29	C	-0.103500
30	H	0.171647
31	C	-0.254440
32	H	0.181759
33	C	0.153974
34	C	-0.282414
35	H	0.142616
36	C	0.223932
37	C	-0.299310
38	H	0.144910
39	C	0.165894
40	C	0.044707
41	C	-0.460255
42	H	0.141928
43	H	0.137204
44	H	0.196823
45	C	-0.486227
46	H	0.202249
47	H	0.140297
48	H	0.141505
49	C	-0.443639
50	H	0.150895
51	H	0.142301
52	H	0.136965
53	C	0.035267
54	C	-0.467477
55	H	0.147193
56	H	0.152503
57	H	0.164146
58	C	-0.472451
59	H	0.163947
60	H	0.152417
61	H	0.147695
62	C	-0.443669
63	H	0.144681
64	H	0.157976
65	H	0.156192
66	C	0.044846
67	C	-0.482678
68	H	0.138999
69	H	0.139257
70	H	0.206913
71	C	-0.472519
72	H	0.136988
73	H	0.133969
74	H	0.208221
75	C	-0.440295
76	H	0.147922
77	H	0.135728
78	H	0.141566
79	C	-0.631409
80	H	0.176603
81	H	0.184497
82	H	0.203116
83	C	-0.630474
84	H	0.171032
85	H	0.204157
86	H	0.205013
87	C	-0.630778
88	H	0.209241
89	H	0.184138
90	H	0.173568

Sum of Mulliken charges= 0.00

Table S8: Mulliken Charges for compound **2b**.

1	Mo	-0.369680
2	Mo	-0.221070
3	P	0.400837
4	P	0.573764
5	S	-0.007489
6	O	-0.306346
7	O	-0.309764
8	C	0.207867
9	C	0.204687
10	C	-0.104351
11	C	-0.145630
12	H	0.176479
13	C	-0.139543
14	H	0.160576
15	C	-0.155300
16	H	0.148480
17	C	-0.118903
18	H	0.177885
19	C	-0.143240
20	H	0.203560
21	C	-0.149914
22	C	-0.154595
23	H	0.198132
24	C	-0.088633
25	H	0.163030
26	C	-0.211558
27	H	0.145473
28	C	-0.105655
29	H	0.171383
30	C	-0.243681
31	H	0.182544
32	C	0.149088
33	C	-0.284413
34	H	0.142389
35	C	0.227106
36	C	-0.303768
37	H	0.143504
38	C	0.161723
39	C	0.046319
40	C	-0.461584
41	H	0.141371
42	H	0.135452
43	H	0.198938
44	C	-0.486571
45	H	0.205237
46	H	0.138481
47	H	0.140590
48	C	-0.443469
49	H	0.150420
50	H	0.141188
51	H	0.136456
52	C	0.035526
53	C	-0.468380
54	H	0.146724
55	H	0.152295
56	H	0.164960
57	C	-0.472050
58	H	0.164770
59	H	0.152255
60	H	0.146991
61	C	-0.443634
62	H	0.144066
63	H	0.157818
64	H	0.156545
65	C	0.046449
66	C	-0.482323
67	H	0.138766
68	H	0.136256
69	H	0.204905
70	C	-0.474128
71	H	0.134895
72	H	0.133352
73	H	0.210201
74	C	-0.439915
75	H	0.147339
76	H	0.135486
77	H	0.140091
78	C	-0.630352
79	H	0.175052
80	H	0.183880
81	H	0.203158
82	C	-0.629937
83	H	0.169987
84	H	0.203908
85	H	0.203513
86	C	-0.629517
87	H	0.206384
88	H	0.183255
89	H	0.172829
90	N	-0.425921
91	C	0.232679
92	C	-0.144188
93	C	-0.156778
94	C	-0.140408
95	H	0.143725
96	C	-0.137805
97	H	0.119910
98	C	-0.131735
99	H	0.115205
100	H	0.114857
101	H	0.111235

Sum of Mulliken charges= 0.000

Table S9: Natural Charges for compound **2a**.

Mo	1	-0.47887
Mo	2	0.14023
P	3	0.66397
P	4	1.21954
S	5	0.06119
S	6	-0.12535
O	7	-0.47937
O	8	-0.49471
C	9	0.56483
C	10	0.55519
C	11	-0.67579
C	12	-0.29505
H	13	0.27473
C	14	-0.30959
H	15	0.26562
C	16	-0.28375
H	17	0.25661
C	18	-0.29015
H	19	0.28143
C	20	-0.25568
H	21	0.28930
C	22	-0.40053
C	23	-0.24103
H	24	0.28517
C	25	-0.26196
H	26	0.26784
C	27	-0.25657
H	28	0.25514
C	29	-0.24788
H	30	0.27565
C	31	-0.19534
H	32	0.27678
C	33	-0.06600
C	34	-0.23954
H	35	0.26155
C	36	-0.01344
C	37	-0.24023
H	38	0.26345
C	39	-0.06540
C	40	-0.05289
C	41	-0.66054
H	42	0.22028
H	43	0.22951
H	44	0.24943
C	45	-0.67669
H	46	0.25367
H	47	0.23564
H	48	0.22725
C	49	-0.65809
H	50	0.23242
H	51	0.23230
H	52	0.22356
C	53	-0.05951
C	54	-0.66306
H	55	0.23684
H	56	0.22983
H	57	0.22962
C	58	-0.66798
H	59	0.23014
H	60	0.23271
H	61	0.23848
C	62	-0.65756
H	63	0.23288
H	64	0.23683
H	65	0.23521
C	66	-0.05268
C	67	-0.67557
H	68	0.22522
H	69	0.23476
H	70	0.25657
C	71	-0.66141
H	72	0.22994
H	73	0.21723
H	74	0.25227
C	75	-0.65749
H	76	0.23126
H	77	0.22422
H	78	0.23175
C	79	-1.00678
H	80	0.24790
H	81	0.25413
H	82	0.26521
C	83	-1.00729
H	84	0.24456
H	85	0.26741
H	86	0.26809
C	87	-1.01162
H	88	0.26973
H	89	0.25445
H	90	0.24585
* Total *		0.00000

Table S10: Natural Charges for compound **2b**.

Mo	1	-0.48239
Mo	2	0.15848
P	3	0.63271
P	4	1.21778
S	5	-0.08494
O	6	-0.49216
O	7	-0.49467
C	8	0.56296
C	9	0.55596
C	10	-0.16526
C	11	-0.29353
H	12	0.27600
C	13	-0.30954
H	14	0.26642
C	15	-0.28119
H	16	0.25558
C	17	-0.29530
H	18	0.27648
C	19	-0.26226
H	20	0.29116
C	21	-0.40442
C	22	-0.23317
H	23	0.28473
C	24	-0.26462
H	25	0.26723
C	26	-0.25813
H	27	0.25430
C	28	-0.24559
H	29	0.27529
C	30	-0.19048
H	31	0.27745
C	32	-0.06705
C	33	-0.24009
H	34	0.26140
C	35	-0.01195
C	36	-0.24211
H	37	0.26291
C	38	-0.06883
C	39	-0.05248
C	40	-0.66070
H	41	0.21994
H	42	0.22845
H	43	0.25016
C	44	-0.67640
H	45	0.25507
H	46	0.23457
H	47	0.22686
C	48	-0.65787
H	49	0.23212
H	50	0.23164
H	51	0.22323
C	52	-0.05962
C	53	-0.66371
H	54	0.23670
H	55	0.23000
H	56	0.22982
C	57	-0.66748
H	58	0.23043
H	59	0.23243
H	60	0.23788
C	61	-0.65736
H	62	0.23249
H	63	0.23670
H	64	0.23534
C	65	-0.05204
C	66	-0.67530
H	67	0.22514
H	68	0.23277
H	69	0.25609
C	70	-0.66167
H	71	0.22868
H	72	0.21699
H	73	0.25308
C	74	-0.65742
H	75	0.23091
H	76	0.22409
H	77	0.23086
C	78	-1.00716
H	79	0.24669
H	80	0.25370
H	81	0.26512
C	82	-1.00659
H	83	0.24387
H	84	0.26733
H	85	0.26723
C	86	-1.01096
H	87	0.26794
H	88	0.25395
H	89	0.24524
N	90	-0.52356
C	91	0.15002
C	92	-0.25190
C	93	-0.25294
C	94	-0.23043
H	95	0.24422
C	96	-0.23062
H	97	0.23400
C	98	-0.26165
H	99	0.22948
H	100	0.22929
H	101	0.22821
* Total *		0.00000

Table S11: DFT/B3LYP-calculated stretching wavenumbers ν(cm^{-1}) and relative intensities.

	compound **2a**	compound **2b**
$\nu_{CO,symm.}$	2008 (25)	2000 (20)
$\nu_{CO,asymm.}$	1953 (100)	1947 (100)
ν_{CN}	-	1615 (80)

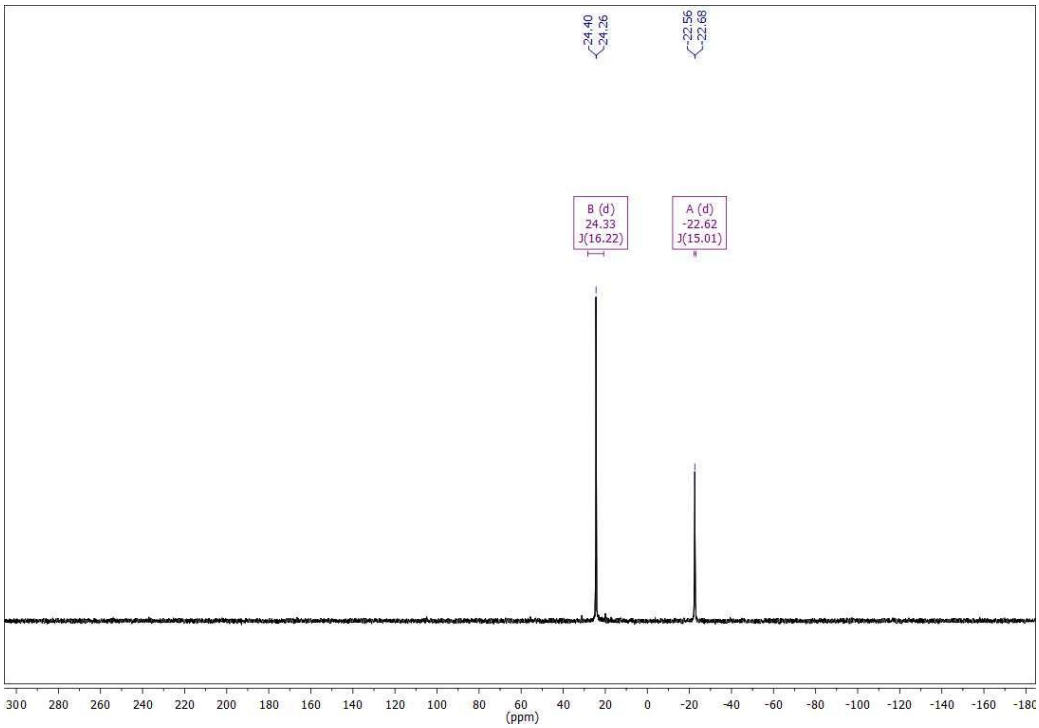


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (162.12 MHz, C_6D_6) of compound **2b**.

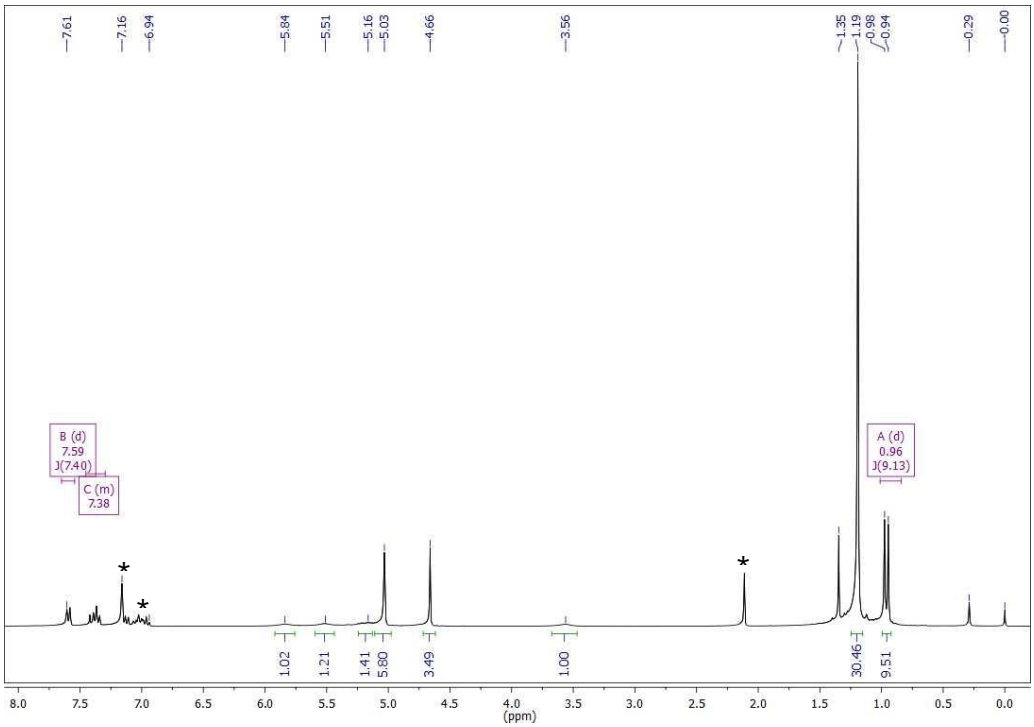


Figure S2. ^{1}H NMR spectrum (400.13 MHz, C_6D_6) of compound **2b**. Resonances marked with an asterisk correspond to residual toluene and C_6D_5H in the solution.

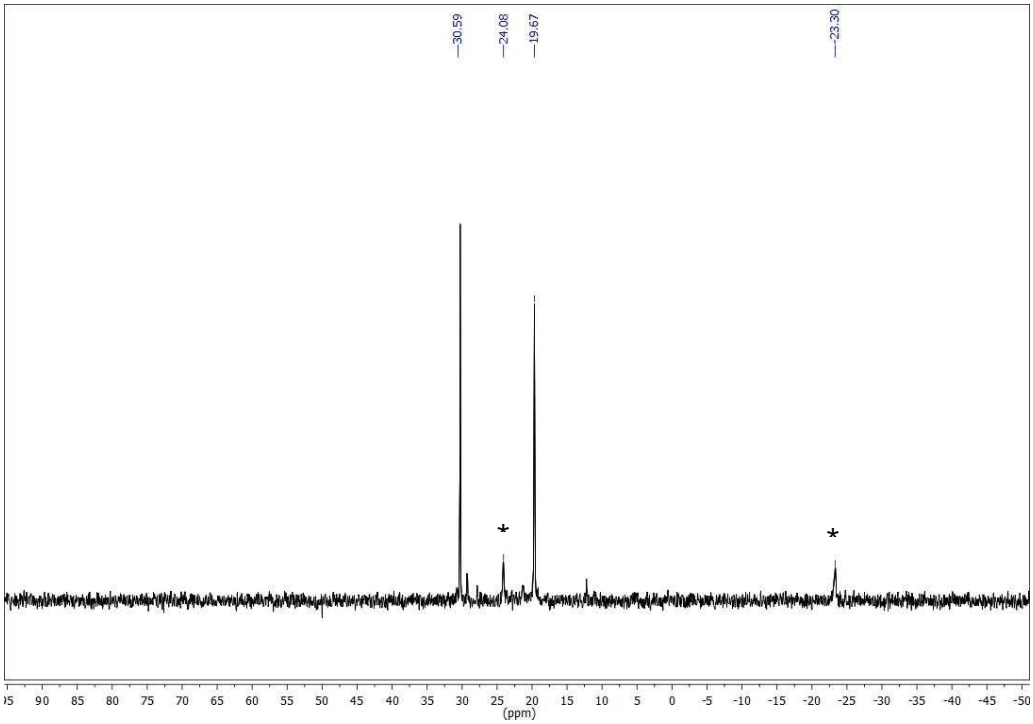


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (162.12 MHz, C_6D_6) of the crude solid compound **3b** prepared as described in the text. Resonances marked with an asterisk correspond to unreacted compound **2b**.

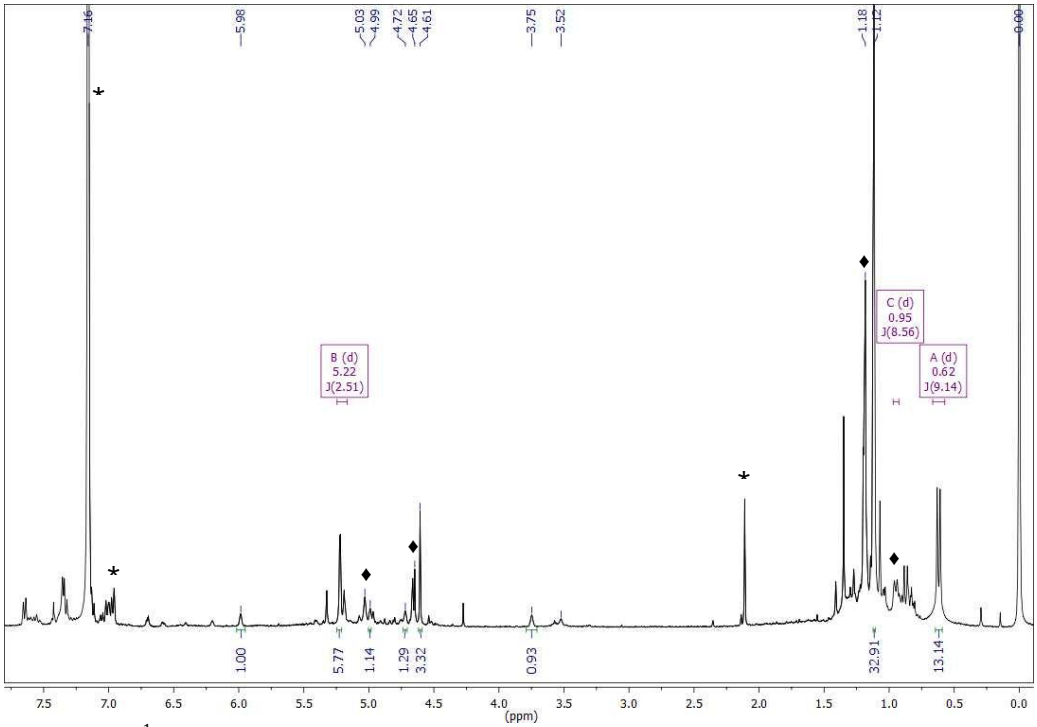


Figure S4. ^{1}H NMR spectrum (400.13 MHz, C_6D_6) of crude compound **3b**. Resonances marked with an asterisk correspond to residual toluene and C_6D_5H in the solution. Resonances marked with the symbol ♦ correspond to unreacted compound **2b**.

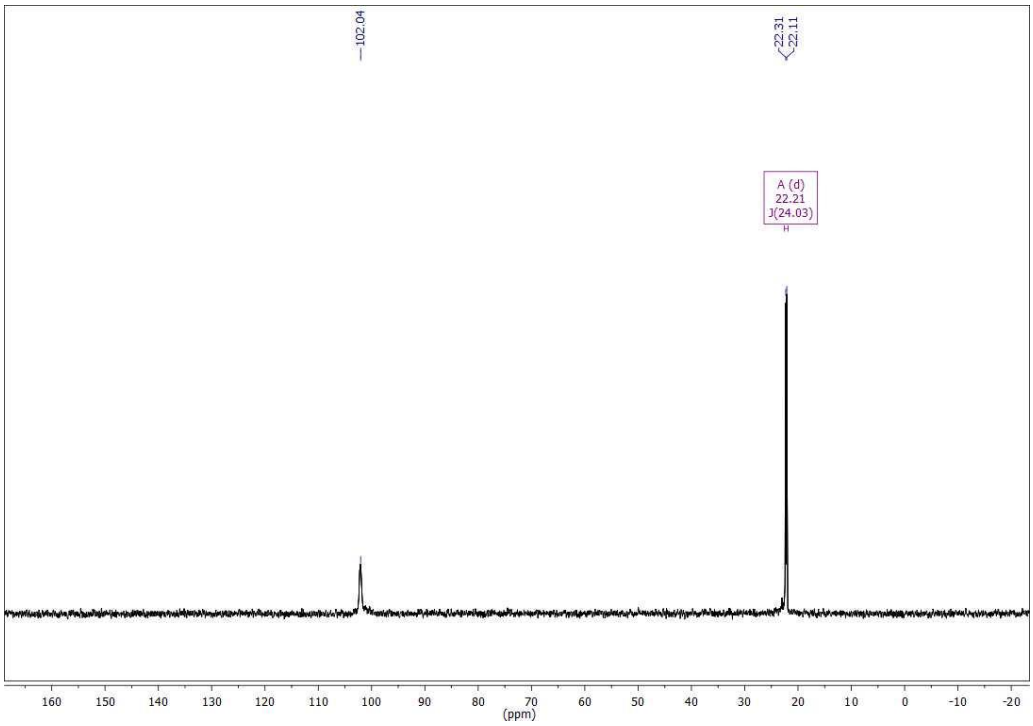


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum (162.12 MHz, CD_2Cl_2) of compound **4**.

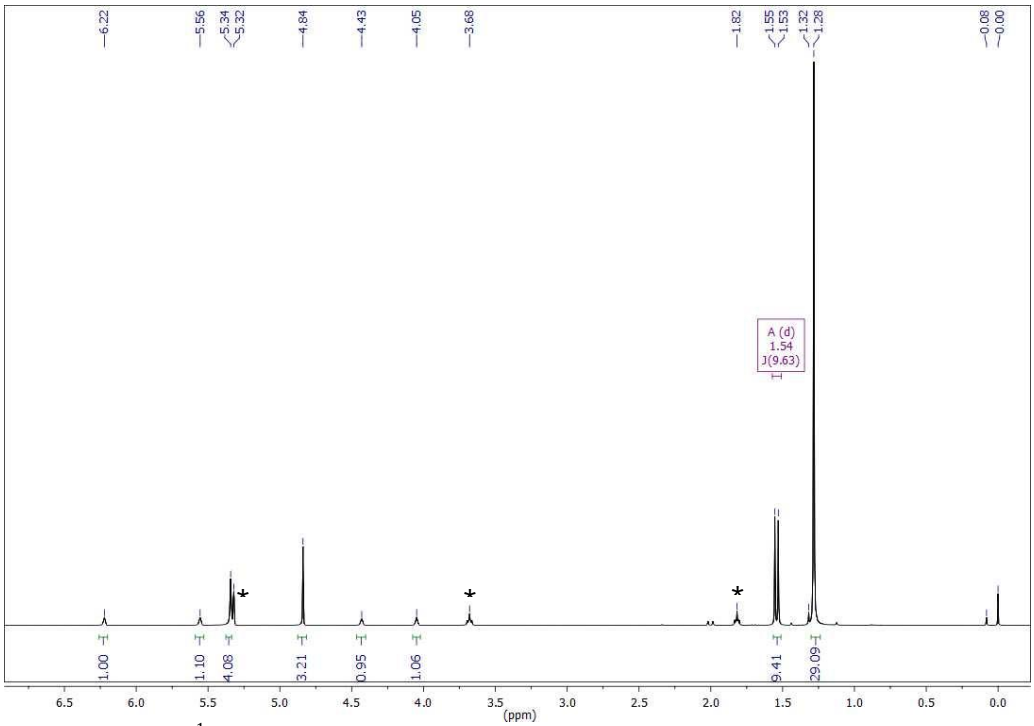


Figure S6. ^{1}H NMR spectrum (400.13 MHz, CD_2Cl_2) of compound **4**. . Resonances marked with an asterisk correspond to residual tetrahydrofuran and $CHDCl_2$ in the solution.

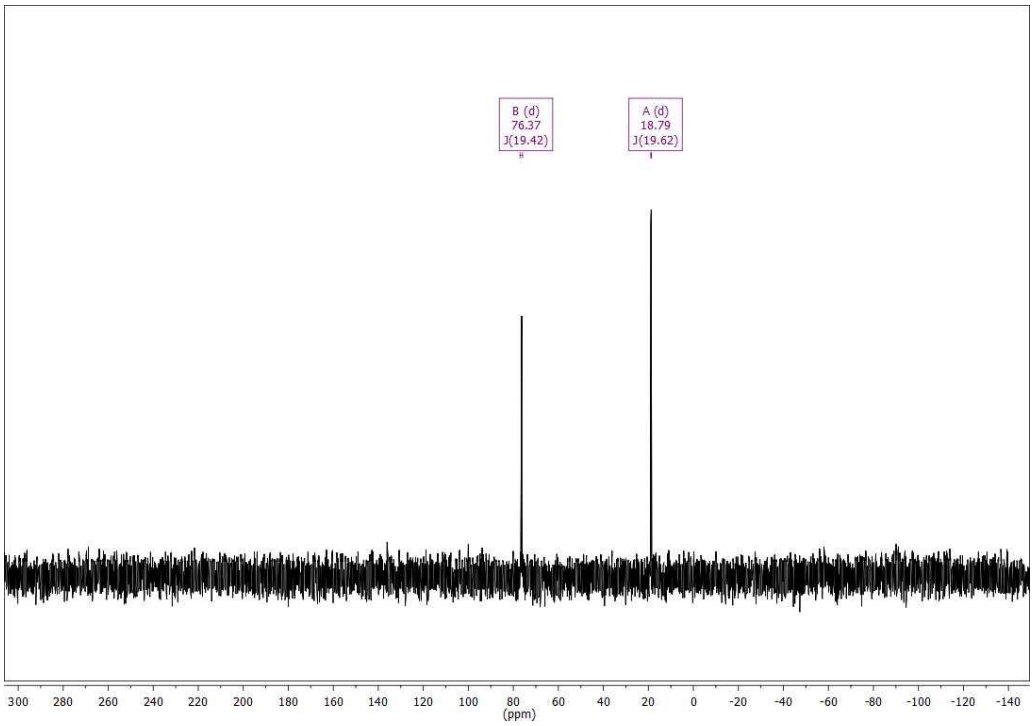


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (162.12 MHz, CD_2Cl_2) of compound **6a**.

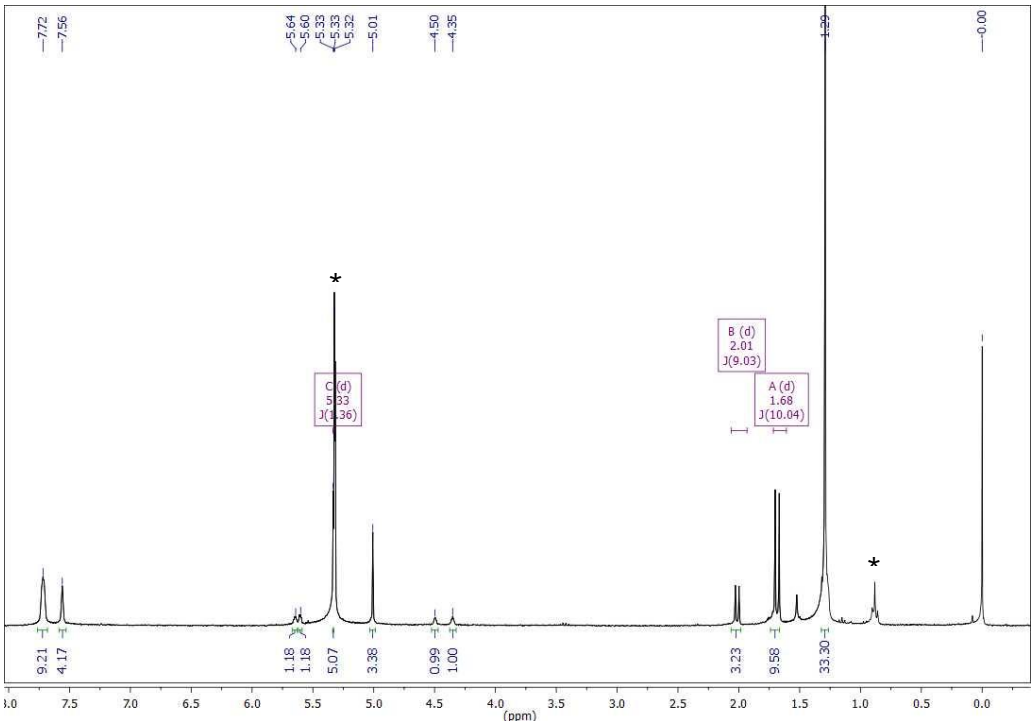


Figure S8. ^{1}H NMR spectrum (400.13 MHz, CD_2Cl_2) of compound **6a**. Resonances marked with an asterisk correspond to residual petroleum ether and $CHDCl_2$ in the solution.

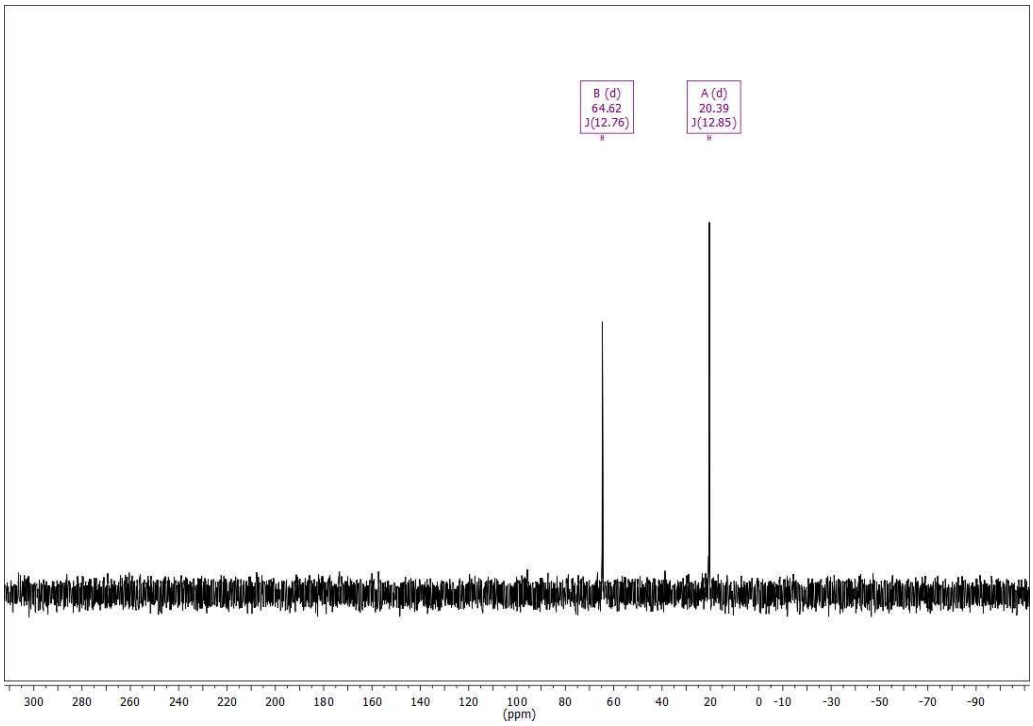


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum (162.12 MHz, CD_2Cl_2) of compound **7**.

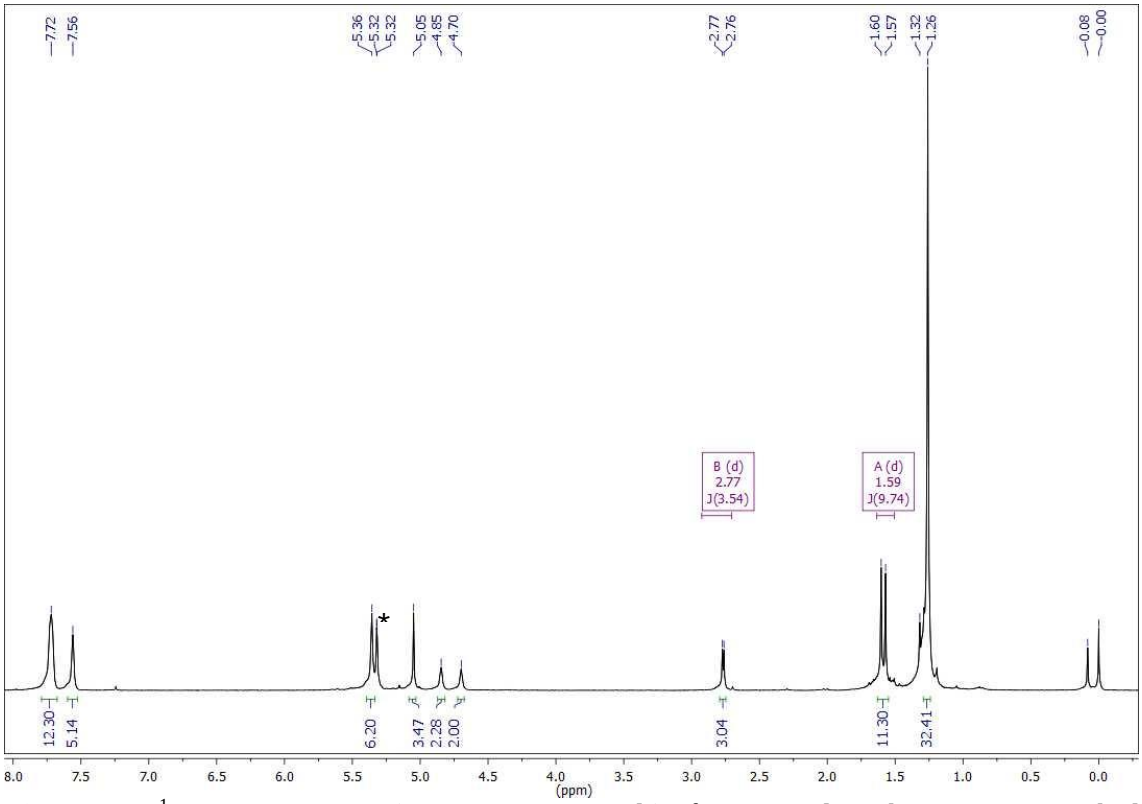


Figure S10. ^{1}H NMR spectrum (400.13 MHz, CD_2Cl_2) of compound **7**. The resonance marked with an asterisk corresponds to residual $CHDCl_2$ in the solution.