On the Structure and Carbenoid Ambiphilicity of a Sulfonyl Substituted α-Chloro Lithium Base

Julia Becker and Viktoria H. Gessner*

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

Index

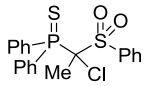
1. Experimental details

General procedure

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried over sodium or potassium (or over P_4O_{10}, CH_2Cl_2) and and distilled prior to use and stored over molecular sieve. H_2O is distilled water. Organolithium reagents were titrated against diphenylacetic acid prior to use. ^{1}H, ^{7}Li, ^{13}C, ^{31}P NMR spectra were recorded on Avance-500, Avance-400 or Avance-300 spectrometers at 22 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singulet, d = doublet, t = triplet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT and HMQC experiments. Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer. All reagents were purchased from Sigma-Alrdrich, ABCR or Acros

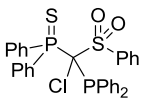
Organics and used without further purification. Compound **1** was prepared according to literature procedures.[1]

Preparation of 6a



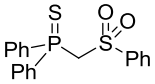
To a solution of 88.0 mg (0.22 mmol) **2** in 7 mL dry THF at –60 °C were added 0.19 mL (0.24 mmol) methyllithium (1.27 M in diethyl ether). The mixture was stirred at –60 °C for 2 h, followed by the addition of 0.04 mL (0.64 mmol) iodomethane. After stirring for 3 h at room temperature, the orange solution was treated with aqueous NH_3 (25 % solution, 10 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL) and the combined organic layers were dried with Na_2SO_4. Purification of the crude product by chromatography on silica gel (diethyl ether, R_f = 0.82) gave the desired product as a colorless solid (49.0 mg, 0.12 mmol, 54 %). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 2.10 (d, $^3J_{PH}$ = 14.0 Hz, 3 H, PCCH_3), 7.48-7.53 (m, 6 H, C$H_{PPh,\ meta,\ para}$ + C$H_{SPh,meta}$), 7.56-7.62 (m, 2 H, C$H_{SPh,\ meta}$), 7.65-7.68 (m, 1 H, C$H_{SPh,\ para}$), 7.84-7.85 (m, 2 H, C$H_{SPPh,\ ortho}$), 8.18-8.22 (m, 2 H, C$H_{PPh,\ ortho}$), 8.33-8.38 (m, 2 H, C$H_{PPh,\ ortho}$). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ = 25.5 (d, $^2J_{CP}$ = 4.06 Hz, PCCH_3), 83.8 (d, $^1J_{CP}$ = 30.5 Hz, PCS), 128.4 (d, $^3J_{CP}$ = 13.0 Hz, CH$_{PPh,\ meta}$), 128.6 (d, $^3J_{CP}$ = 12.8 Hz, CH$_{PPh,\ meta}$), 128.9 (d, $^1J_{CP}$ = 83.4 Hz, $C_{PPh,\ ipso}$), 129.1 (CH$_{SPh,\ meta}$), 130.3 (d, $^1J_{CP}$ = 83.4 Hz, $C_{PPh,\ ipso}$), 131.8 (CH$_{SPh,\ ortho}$), 132.7 (d, $^4J_{CP}$ = 3.14 Hz, CH$_{PPh,\ para}$), 132.8 (d, $^4J_{CP}$ = 3.22 Hz, CH$_{PPh,\ para}$), 134.1 (d, $^2J_{CP}$ = 10.2 Hz, CH$_{PPh,\ ortho}$), 134.7 (d, $^2J_{CP}$ = 10.3 Hz, CH$_{PPh,\ ortho}$), 135.1 (CH$_{SPPh,\ para}$), 136.2 ($C_{SPh,\ ipso}$). ^{31}P{H} NMR (202.5 MHz, CD_2Cl_2): δ = 55.8. Calc for $C_{20}H_{18}ClO_2PS_2$: C, 57.07, H, 4.31, S 15.24. Found: C, 57.40, H, 4.42, S 15.58.

Preparation of 6b



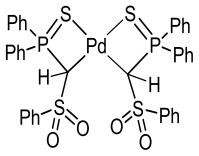
A solution of 78.5 mg (0.33 mmol) hexachloroethane in THF was added dropwise to a suspension of 148 mg (0.30 mmol) dianion **5** in 3 mL THF at –78 °C. After complete addition, the reaction mixture was allowed to warm to room temperature and stirring was continued for 4 h. NMR monitoring of the reaction process showed the complete conversion to a single new species, which could be attributed to the product **6b**. However, after several hours **6b** started to decompose in solution, presumably eliminating the sulfonyl moiety. Thus no clean isolation of **6b** was possible. ^{31}P{H} NMR (202.5 MHz, C_6D_6): δ = 37.8 (d, $^2J_{PP}$ = 37.1 Hz, PPh$_2$), 58.1 (d, $^2J_{PP}$ = 37.1 Hz, SPPh$_2$).

Preparation of sulfone 1 from carbenoid 3

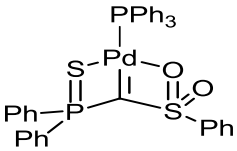


A solution of 70.4 mg (63.2 µmol) carbenoid **3** in 4 mL dry THF was treated with 0.05 mL (75.0 µmol) methyllithium (1.5 M in diethyl ether) at room temperature. After one hour of stirring, ^{31}P NMR of the reaction solution showed quantitative conversion of carbenoid **3** to a new compound giving a broad signal in the ^{31}P NMR spectrum. Subsequently an excess of water was added and the organic layer was filtered through a glass pipette charged with Na_2SO_4. The filtrate was evaporated and finally dried *in vacuo*, affording **1** as colourless solid (38.8 mg, 0.10 mmol, 83 %) (for spectroscopic data of **1** see reference 8a).

Preparation of palladium carbene complex 7



A solution of 65.0 mg (58.3 µmol) carbenoid **3** in 7 mL dry toluene was added to 134 mg (0.12 mmol) [Pd(PPh_3)$_4$] suspended in 4 mL dry toluene. The yellow reaction mixture was stirred for 20 h at room temperature upon which it turned red-orange. Subsequently the mixture was filtered and the orange filtrate reduced *in vacuo* to about 4 mL, whereupon a slight yellow solid precipitated. The solution was removed from the precipate and the solid dried *in vacuo*, affording an orange solid mainly consisting of the palladium carbene complex. Washing with a mixture of 1 mL diethyl ether and 3 mL *n*-pentane lead to the formation of further products (see Figure S7), which could be removed by continuing the washing process. As such the carbene complex **7** could be isolated as a light orange solid (29.0 mg, 39.2 µmol, 33 %). ^{1}H NMR (300.2 MHz, CD_2Cl_2): δ = 6.46-6.49 (dd, $^{3}J_{HH}$ = 8.52 Hz, 2H; C*H*$_{SPh,ortho}$), 6.93 (t, $^{3}J_{HH}$ = 7.93 Hz, 2H; C*H*$_{SPPh,\ meta}$), 7.16-7.21 (tt, $^{3}J_{HH}$ = 7.42 Hz, 1H; C*H*$_{SPPh,\ para}$), 7.32-7.39 (m, 10 H; C*H*$_{Pd\text{-}PPh,\ meta}$ + C*H*$_{PPh,\ meta}$), 7.41-7.44 (m, 2H; C*H*$_{PPh,\ para}$), 7.50-7.56 (m, 3H; C*H*$_{Pd\text{-}PPh,\ para}$), 7.63-7.70 (m, 6H, C*H*$_{Pd\text{-}PPh,\ ortho}$), 7.94-8.02 (m, 4H, C*H*$_{PPh,\ ortho}$). ^{13}C{H} NMR (75.5 MHz, CD_2Cl_2): δ = 126.4 (*C*H$_{SPh,ortho}$), 127.3 (*C*H$_{SPh,meta}$), 127.9 (d, $^{3}J_{CP}$ = 13.1 Hz, *C*H$_{PPh,\ meta}$), 128.5 (d, $^{3}J_{CP}$ = 12.9 Hz, *C*H$_{PPh,\ meta}$), 130.9 (*C*H$_{SPh,\ para}$), 131.0 (d, $^{4}J_{CP}$ = 4.97 Hz, *C*H$_{PPh,\ para}$), 132.5 (d, $^{4}J_{CP}$ = 3.07 Hz, *C*H$_{Pd\text{-}PPh,\ para}$), 133.8 (d, $^{2}J_{CP}$ = 11.2 Hz, *C*H$_{PPh,\ ortho}$), 135.6 (d, $^{2}J_{CP}$ = 9.99 Hz, *C*H$_{Pd\text{-}PPh,\ para}$), 137.5 (d, $^{1}J_{CP}$ = 85.7 Hz, *C*$_{PPh,ipso}$), 147.2 (*C*$_{SPh,\ ipso}$). ^{31}P{H} NMR (121.5 MHz, CD_2Cl_2): δ = 17.9 (d, $^{3}J_{PP}$ = 38.7 Hz; Pd*P*Ph_3), 39.9 (d, $^{3}J_{PP}$ = 38.7 Hz; S*P*Ph_2), carbene carbon not detected.



An NMR tube was charged with 20.0 mg (21.9 µmol) monoanion **4** and 15.0 mg (21.4 µmol) [(PPh_3)$_2$$PdCl_2$] in 0.60 mL dry toluene at room temperature. After 4 h, the formation of a precipate was observed and monitoring the solution by ^{31}P{H} NMR spectroscopy only showed one peak at -4.88 ppm for PPh_3. The solution was removed and the solid residue was washed with diethyl ether (5 x 4 mL) affording pure complex **8** as yellow powder (14.0 mg, 16.5 µmol, 75 %). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 4.75 (d, $^{2}J_{PH}$ = 4.59 Hz, 2H; PC*H*S), 7.13 (t, $^{3}J_{HH}$ = 7.81 Hz, 4H; C*H*$_{SPPh,meta}$), 7.21 (d, $^{2}J_{HH}$ = 8.48 Hz, 4H; C*H*$_{SPPh,ortho}$), 7.35-7.38 (tt, $^{3}J_{HH}$ = 7.38 Hz, 2H; C*H*$_{SPPh,\ para}$), 7.50-87. (m, 6H; C*H*$_{PPh,ortho}$ + C*H*$_{PPh,para}$), 7.60-7.64 (m, 2H; C*H*$_{PPh,para}$), 7.98-8.02 (m, 4H, C*H*$_{PPh,ortho}$). ^{13}C{H} NMR (125.7 MHz, CD_2Cl_2): δ = 21.4 (dd, $^{1}J_{CP}$ = 36.7 Hz, $^{3}J_{CP}$ = 2.13 Hz; P*C*HPd), 126.9 (*C*H$_{SPh,ortho}$), 128.8 (d, $^{3}J_{CP}$ = 12.5 Hz; *C*H$_{PPh,meta}$), 129.1 (*C*H$_{SPh,meta}$), 129.7 (d, $^{3}J_{CP}$ = 12.9 Hz; *C*H$_{PPh,meta}$), 131.5 (d, $^{1}J_{CP}$ = 58.4 Hz; *C*$_{PPh,ipso}$), 131.8 (d, $^{2}J_{CP}$ = 11.0 Hz, *C*H$_{PPh,ortho}$), 132.1 (d, $^{1}J_{CP}$ = 84.1 Hz, *C*$_{PPh,ipso}$), 132.2 (*C*H$_{SPh,\ para}$), 132.5 (d, $^{2}J_{CP}$ = 11.8 Hz, *C*H$_{PPh,ortho}$), 133.0 (d, $^{4}J_{CP}$ = 3.21 Hz, *C*H$_{PPh,para}$), 133.2 (d, $^{4}J_{CP}$ = 3.08 Hz, *C*H$_{PPh,para}$), 144.1 (*C*$_{SPh,\ ipso}$). ^{31}P{H} NMR (202.5 MHz, CD_2Cl_2): δ = 53.2. Calc for $C_{38}H_{32}S_4O_4P_2Pd$: C, 53.74, H, 3.80, S 15.10.

2. NMR spectra

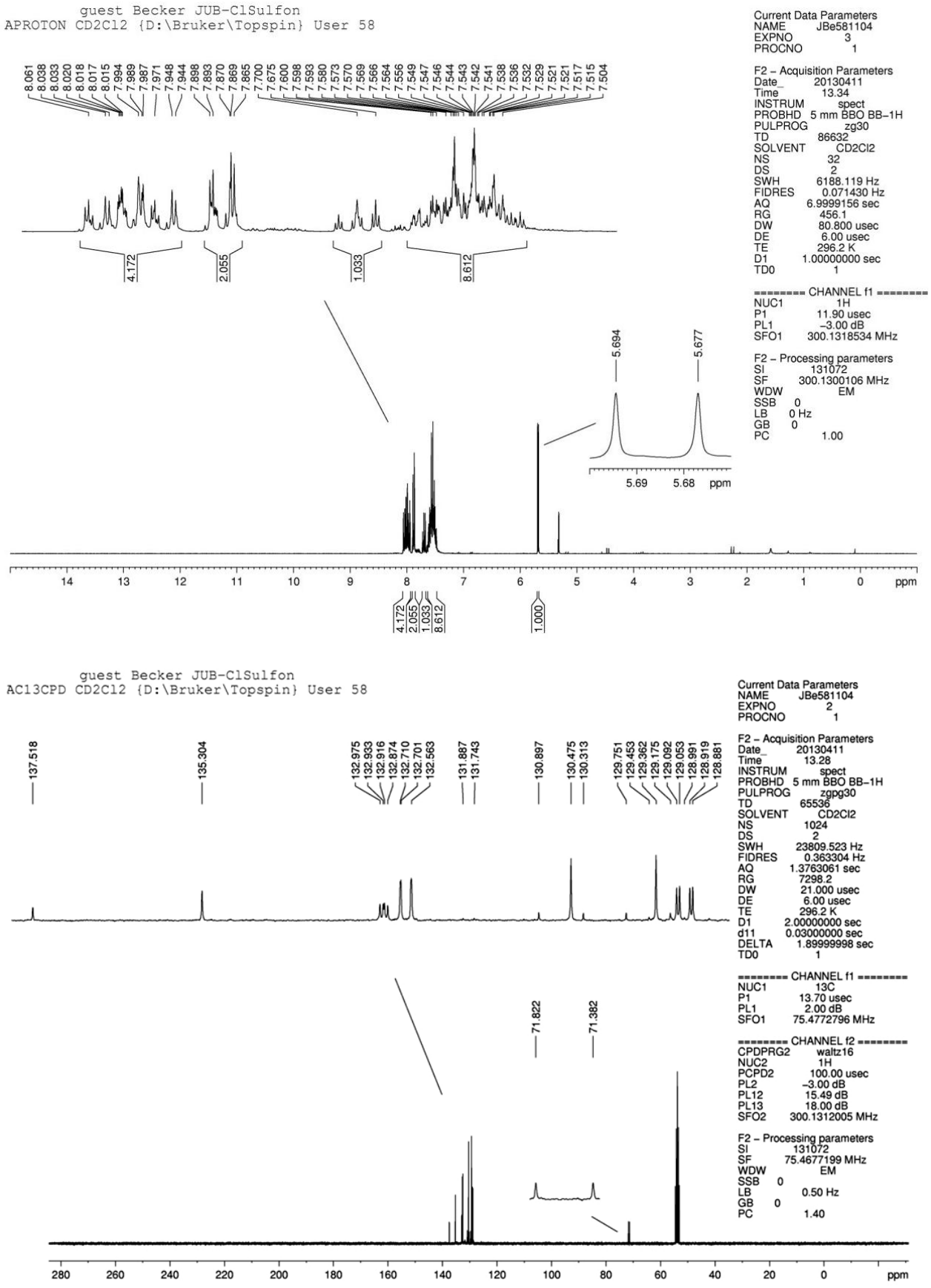


Figure S1. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2** in CD_2Cl_2.

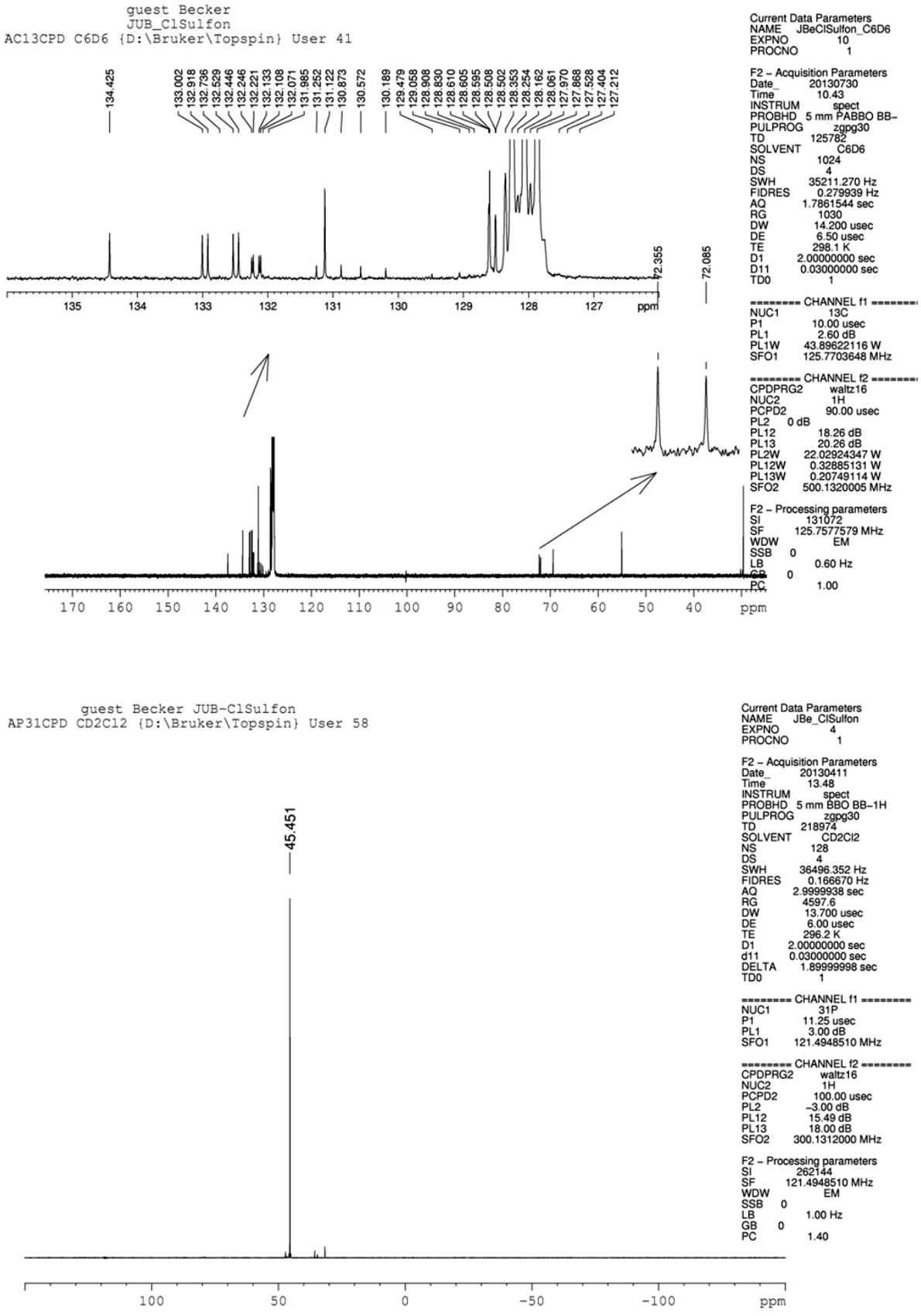
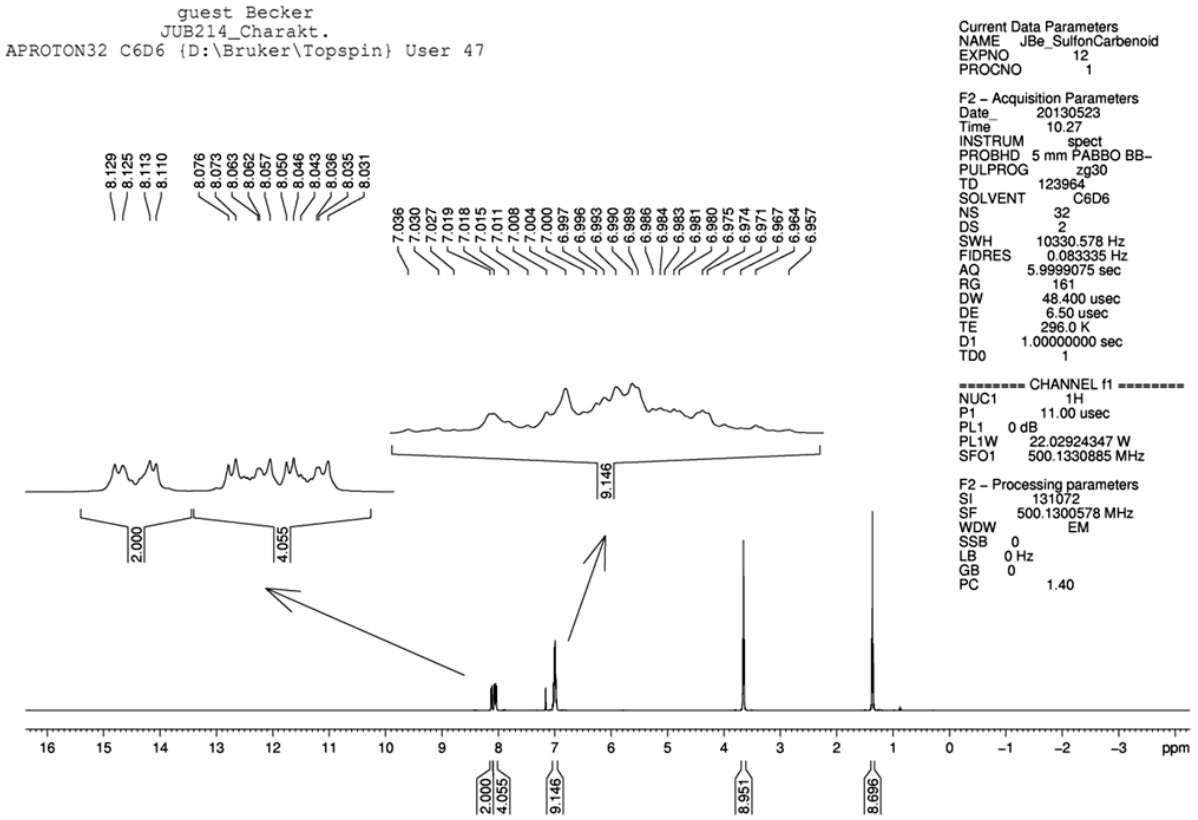


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 and $^{31}P\{^{1}H\}$ NMR spectrum in CD_2Cl_2.



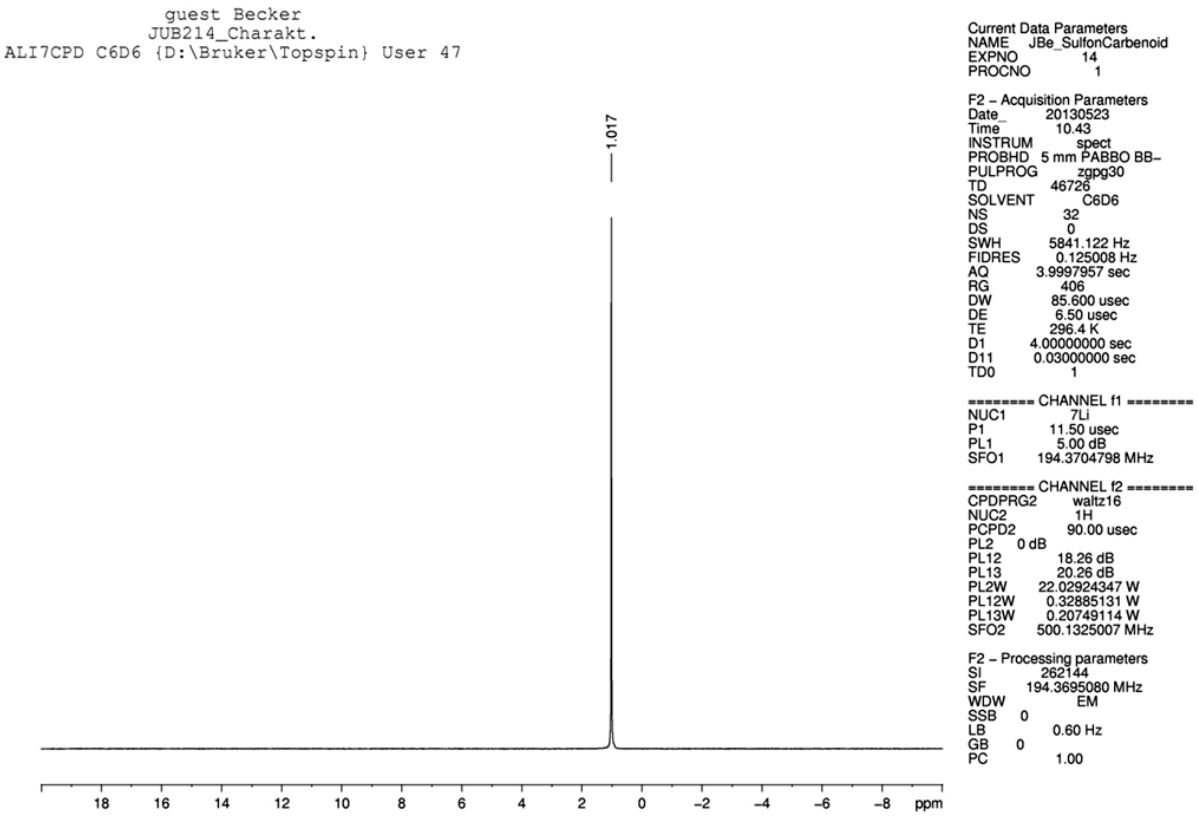


Figure S3. ^{1}H and ^{7}Li NMR spectra of **3** in C_6D_6.

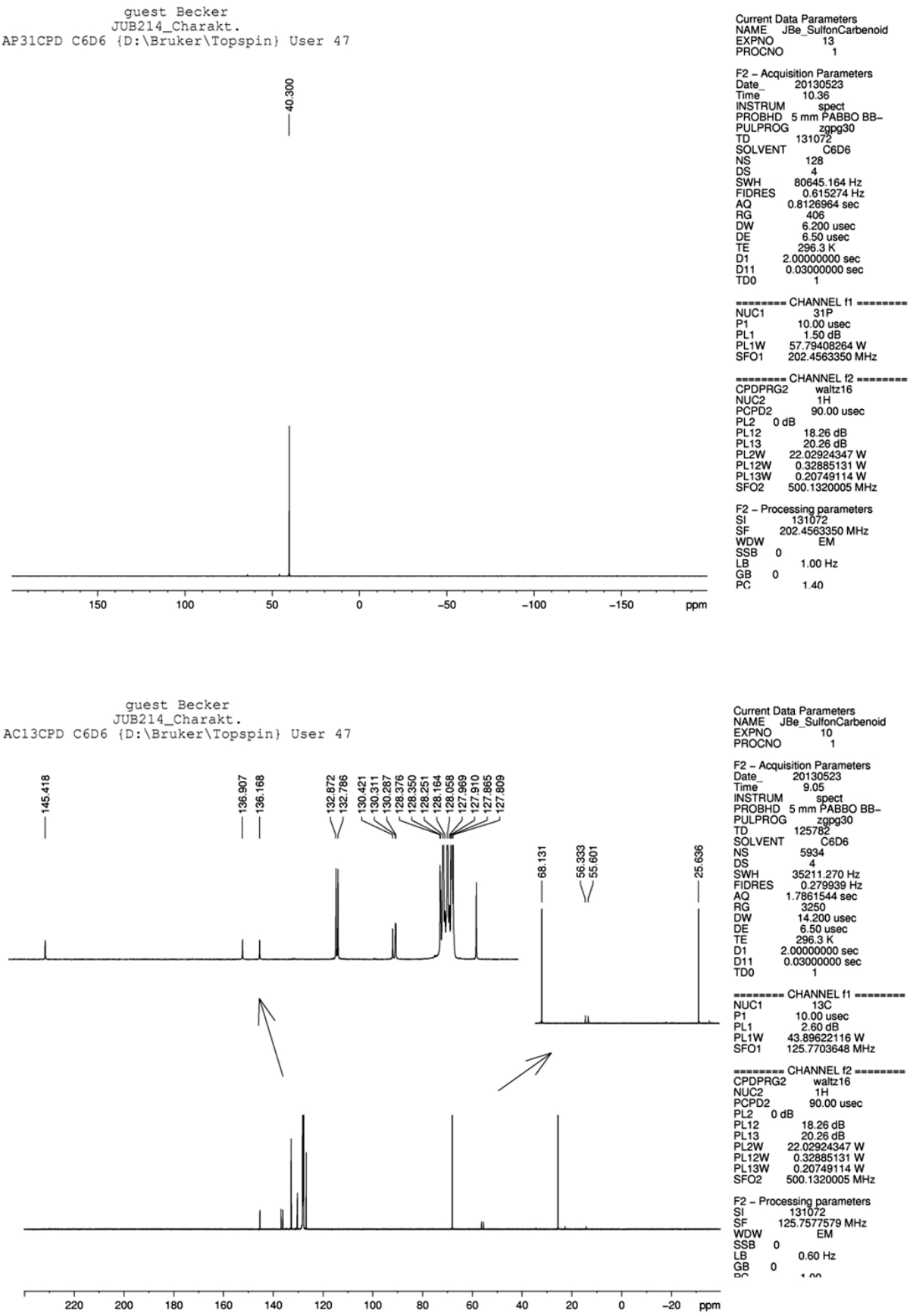
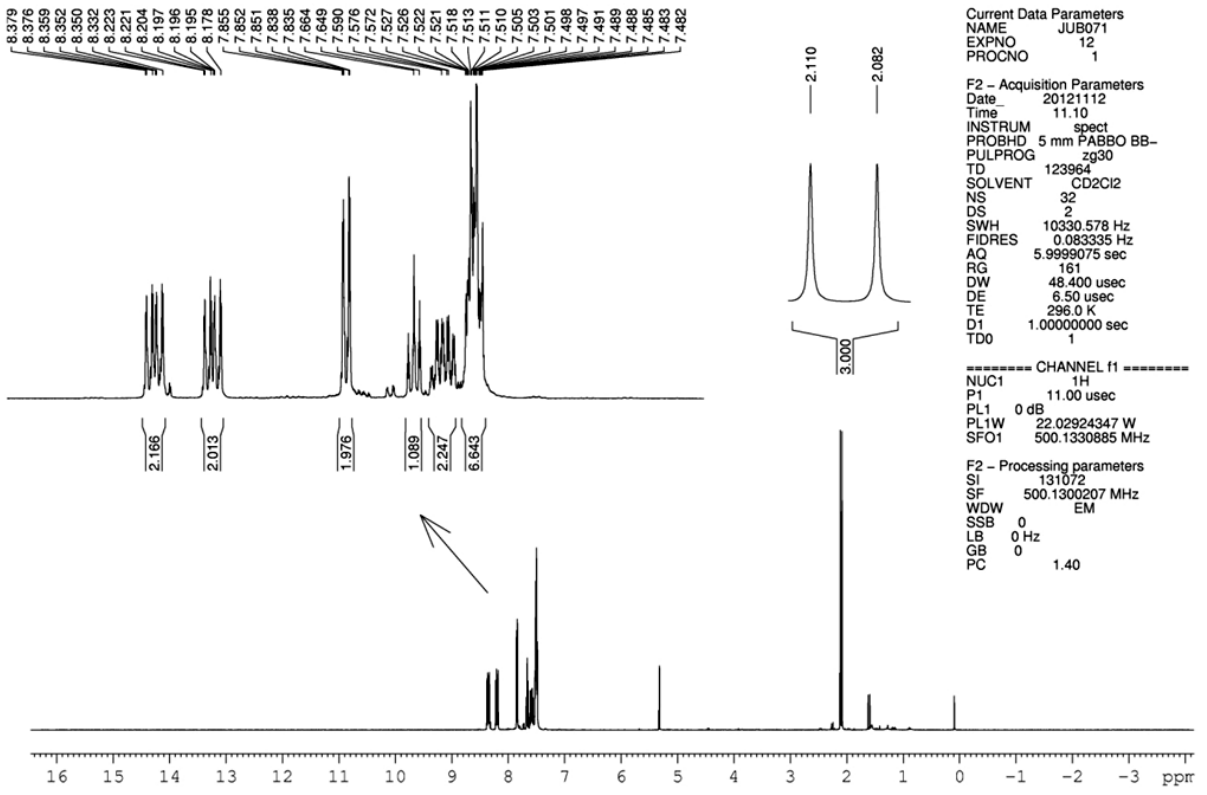


Figure S4. $^{31}P\{^{1}H\}$ NMR and $^{13}P\{^{1}C\}$ NMR spectra of **3** in C_6D_6.



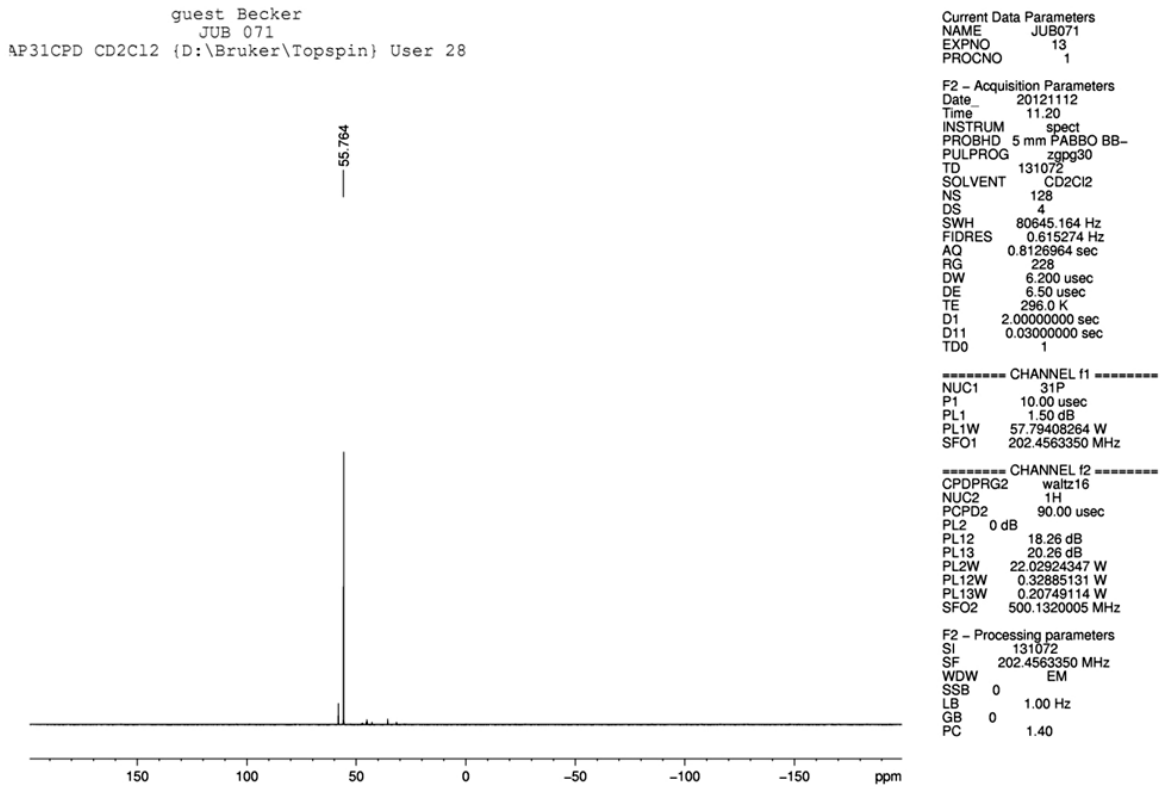
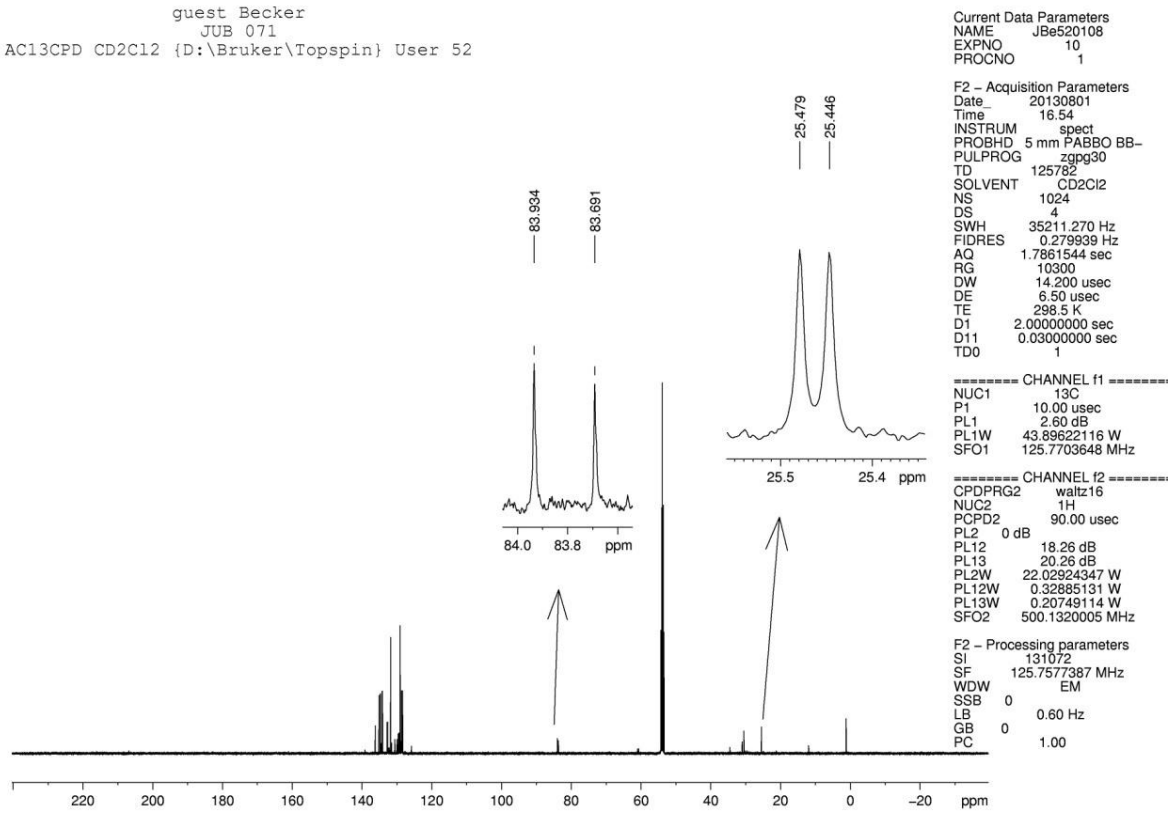


Figure S5. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **6a** in CD_2Cl_2.



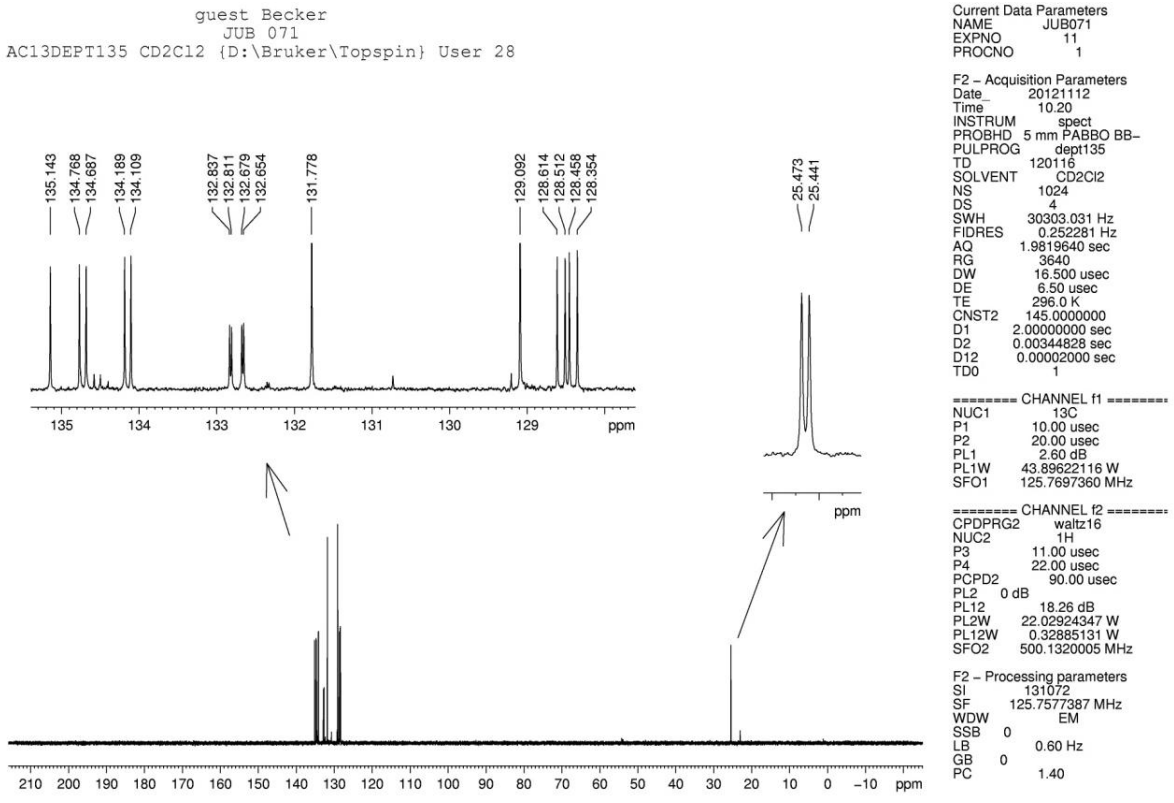


Figure S6. $^{13}C\{^{1}H\}$ and DEPT-135 NMR spectra of **6a** in CD_2Cl_2.

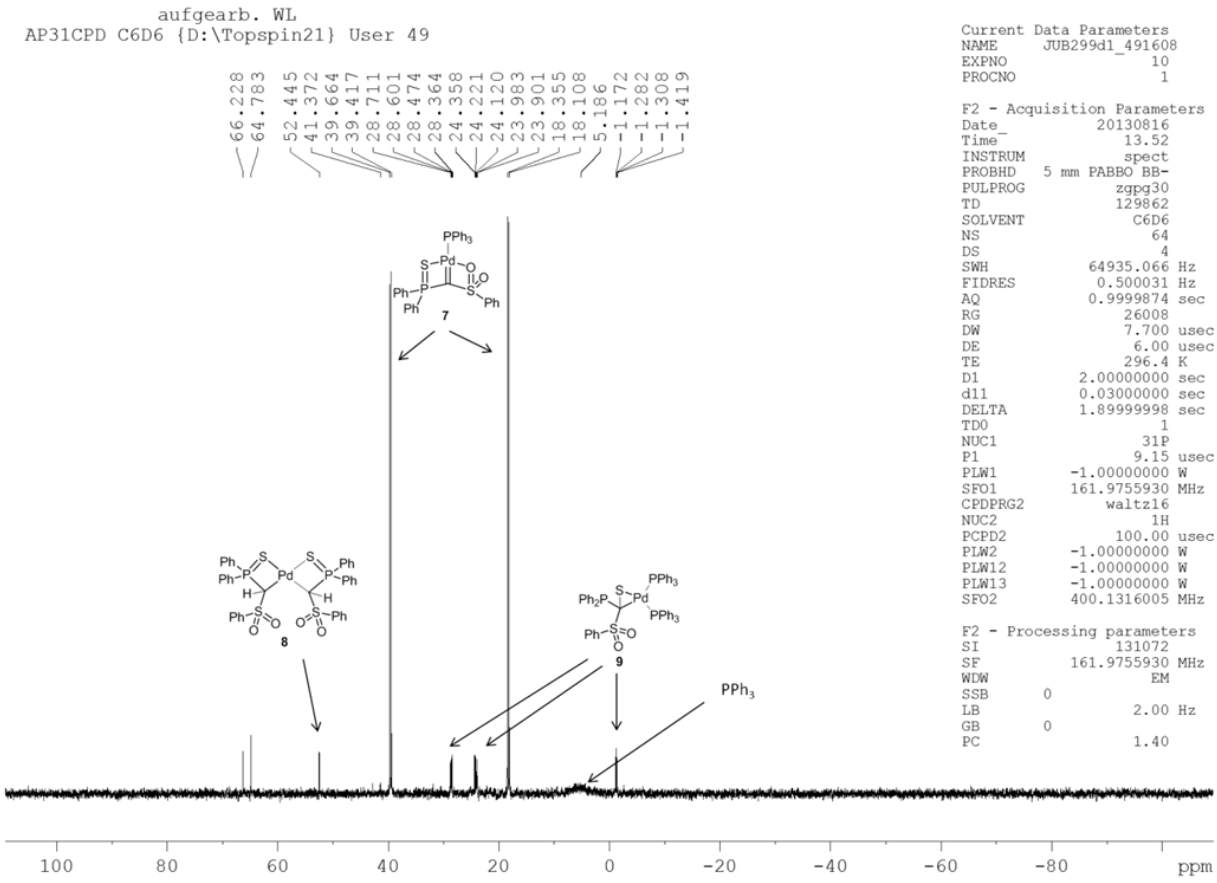


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of crude **7**.

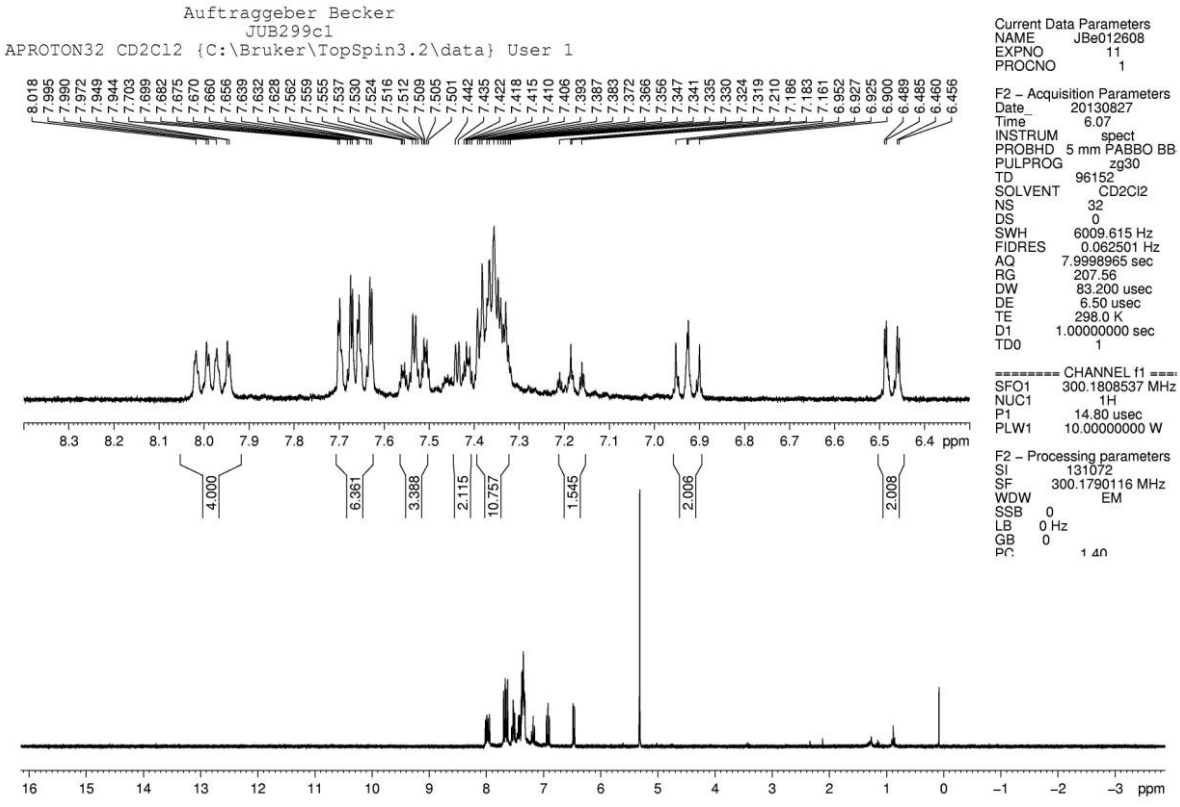
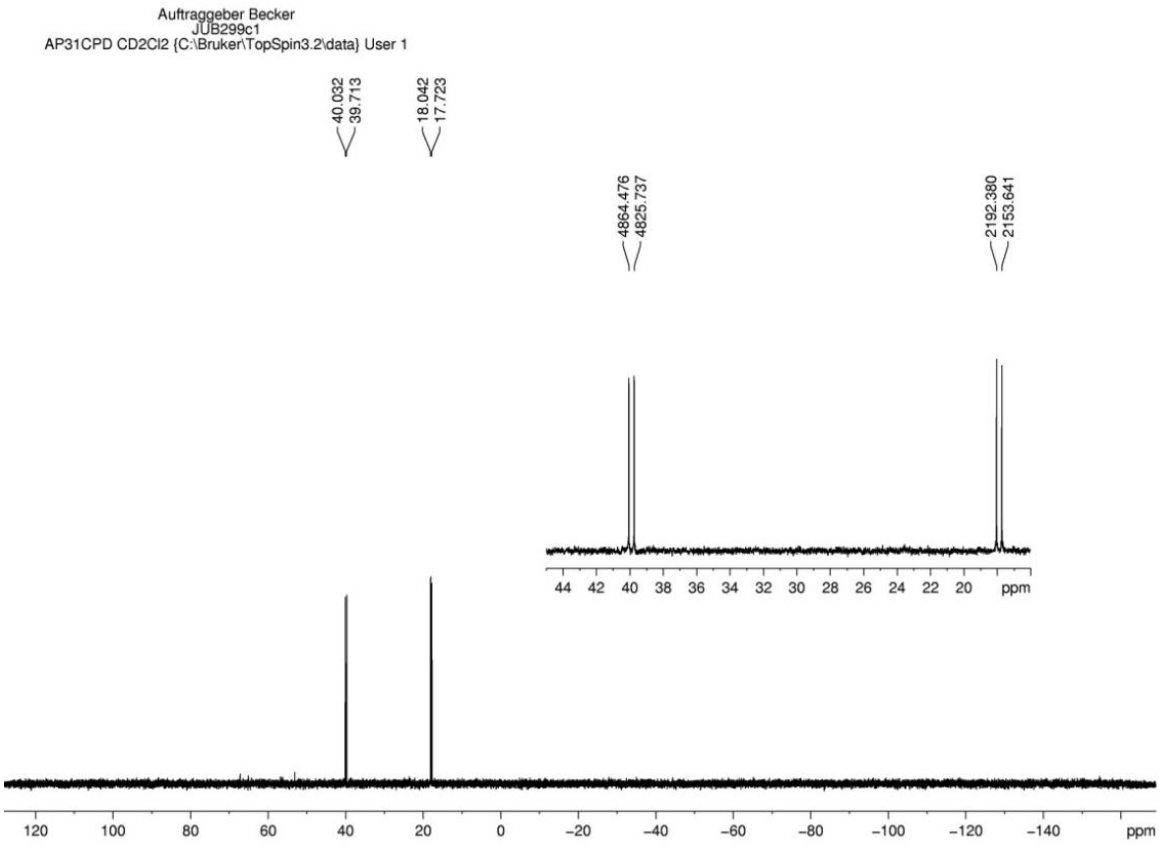


Figure S8a. ^{1}H NMR spectrum of **7** in CD_2Cl_2.



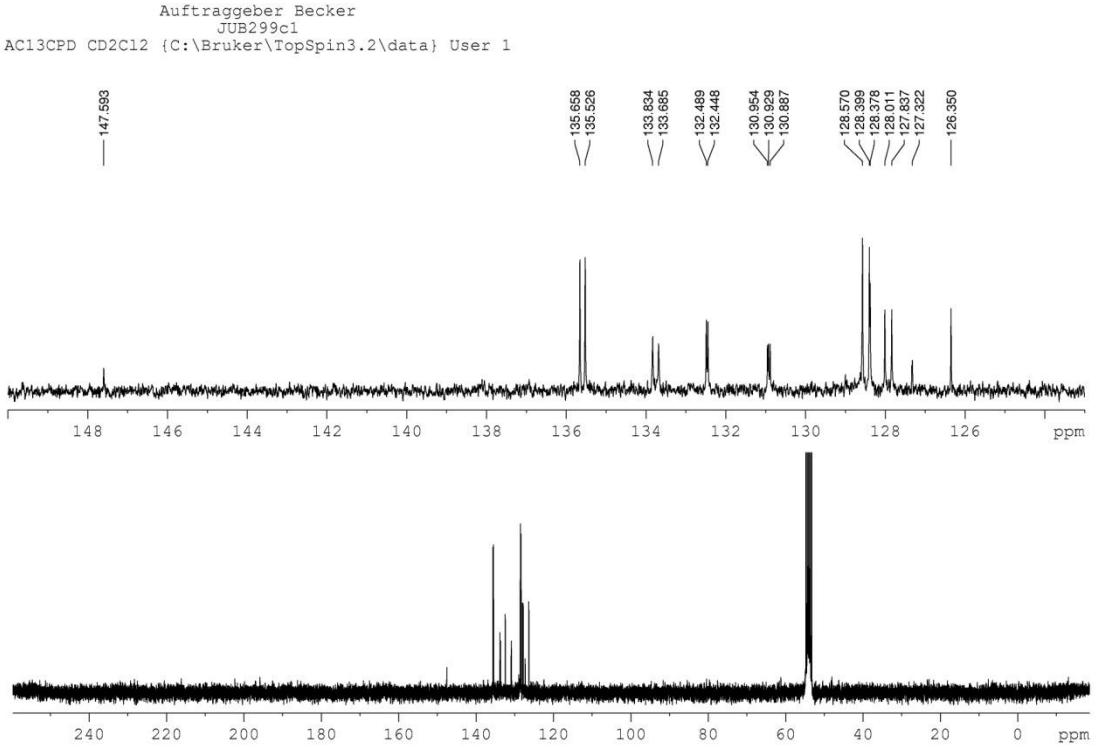
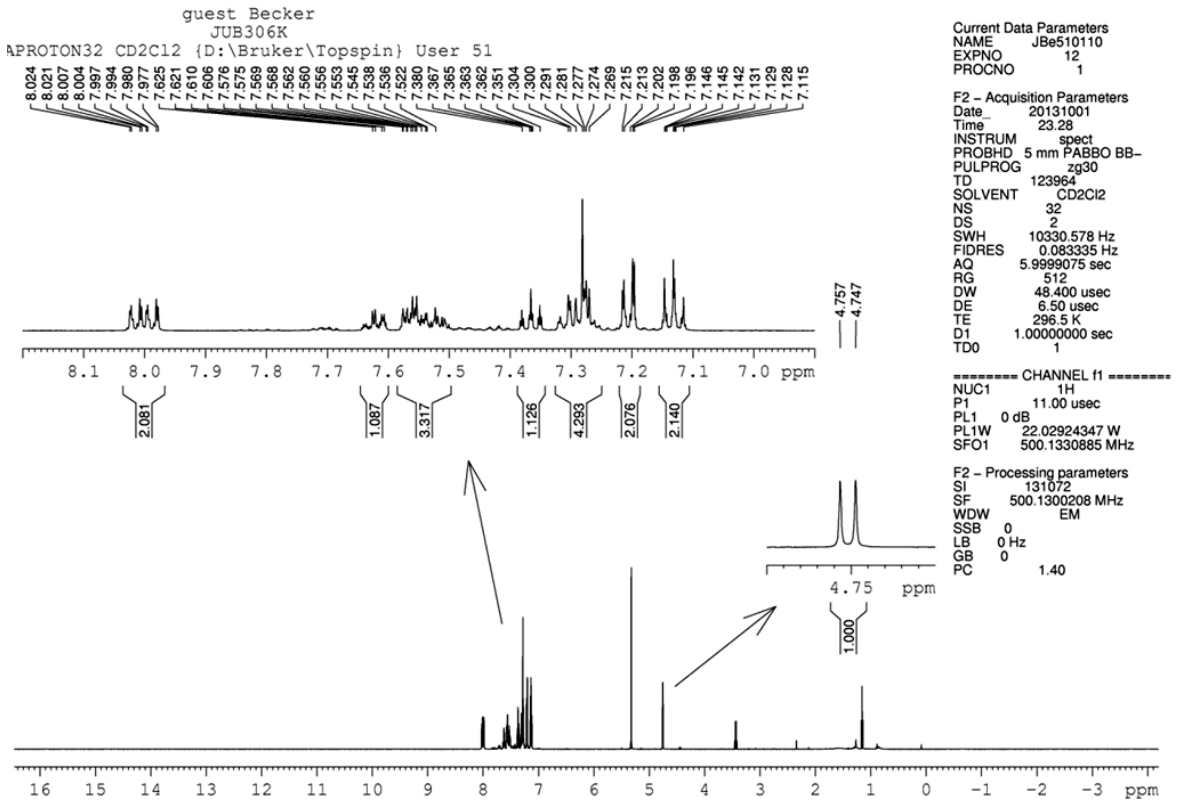


Figure S8b. $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of **7** in CD_2Cl_2.



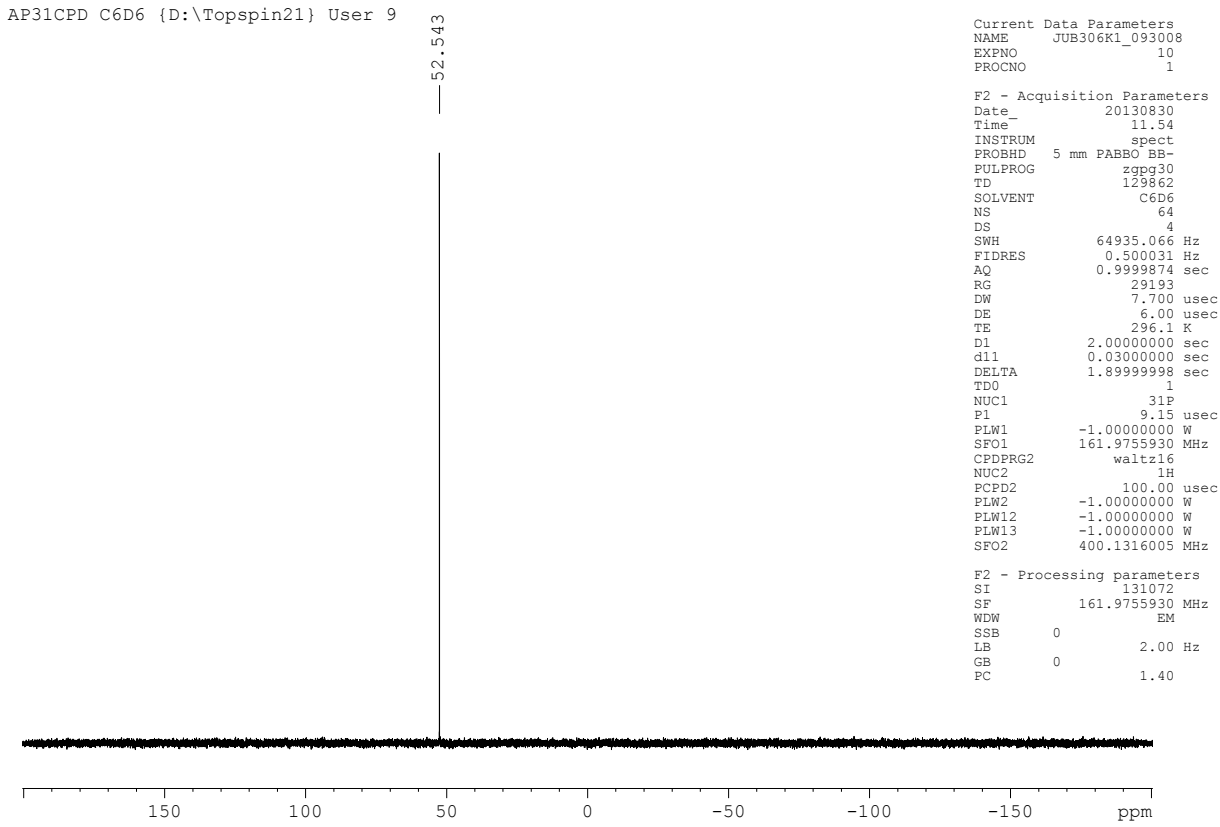


Figure S9. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **8** in CD_2Cl_2 and C_6D_6, respectively.

3. Crystal Structure Determination

Data collection of all compounds was conducted with a Bruker APEX-CCD (D8 three-circle goniometer). The structure was solved using direct methods, refined with the Shelx software package[2] and expanded using Fourier techniques. The crystals of all two compounds were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were effected at 100 K. The structure was solved applying direct and fourier methods, using SHELXS-90 (G. M. Sheldrick, University of Göttingen 1990) and SHELXL-97 (G. M. Sheldrick, SHELXL97, University of Göttingen 1997). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (Table S1). Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: (+44) 1223-336-033, email: deposit@ccdc.cam.ac.uk].

Table S1 Data collection and structure refinement details for compounds **2**, **3** and **8**.

Compound	**2**	**3**	**8**
CCDC No.	CCDC 959178	CCDC 959179	CCDC 963531
Formula	$C_{38}H_{32}Cl_2O_4P_2S_4$	$C_{54}H_{62}Cl_2O_8P_2S_4Li_2$	$C_{38}H_{32}O_4P_2PdS_4$
Formula weight [g·mol^{-1}]	813.72	1114.00	849.22
Temperature [K]	100(2) K	100(2) K	100(2) K
Wave length [Å]	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	triclinic	monoclinic
Space group	*P*2$_1$/*c* (14)	*P*-1 (2)	*C*2/C (15)
a [Å]	14.6305(10)	a = 10.7500(9)	a = 23.4275(16)
b [Å]	24.0872(16)	b = 14.3394(11)	b = 9.8149(7)
c [Å]	10.8747(8)	c = 18.4650(15)	c = 17.4155(12)
α [°]	90	84.134(2)°	90
β [°]	98.829(2)	75.391(2)°	116.776(2)
γ [°]	90	84.850(2)°	90
Volume [Å^3]	3786.9(5)	2733.8(4)	3575.1(4)
Z	4	2	4
Calc. density [Mg·m^{-3}]	1.427	1.353	1.578
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.517	0.382	0.883
F(000)	1680	1168	1728
Crystal dimensions [mm]	0.31 x 0.30 x 0.27	0.31 x 0.31 x 0.19	0.23 x 0.22 x 0.21
Theta range [°]	1.41 to 25.00	1.14 to 26.46	1.95 to 25.00
Index ranges	–17≤ h ≤17	–13 ≤ h ≤ 13	–27 ≤ h ≤ 27
	–28≤ k ≤28	–17 ≤ k ≤ 17	–11 ≤ k ≤ 10
	–12 ≤ l ≤12	–23 ≤ l ≤ 23	–20 ≤ l ≤ 20
Reflections collected	45022	50285	21522
Independent reflections	6660 [R_{int} = 0.0406]	11260 [R_{int} = 0.0348]	3145 [R_{int} = 0.0357]
Data/Restraints/Parameter	6660 / 0 / 451	11260 / 0 / 649	3145 / 0 / 226

Goodness-of-fit on F^2	1.057	1.016	1.082
Final R indices [I>2sigma[I)]	*R*1 = 0.0461 w*R*2 = 0.1227	*R*1 = 0.0438 w*R*2 = 0.1126	*R*1 = 0.0278 w*R*2 = 0.0680
R indices (all data)	*R*1 = 0.0571 w*R*2 = 0.1277	*R*1 = 0.0598 w*R*2 = 0.1257	*R*1 = 0.0346 w*R*2 = 0.0715
Largest diff. peak and hole	1.328 and –1.013	1.210 and –0.501	0.841 and –0.398

Crystal structure determination of 2

The relatively high residual density is due to an unresolved disorder. This disorder corresponds to the respective opposite enantiomeric form of the two molecules of *rac*-**2** depicted in Figure S9. However, due to the low occupation this disorder couldn't be resolved satisfactorily, so that no splitting of both occupation sides was performed.

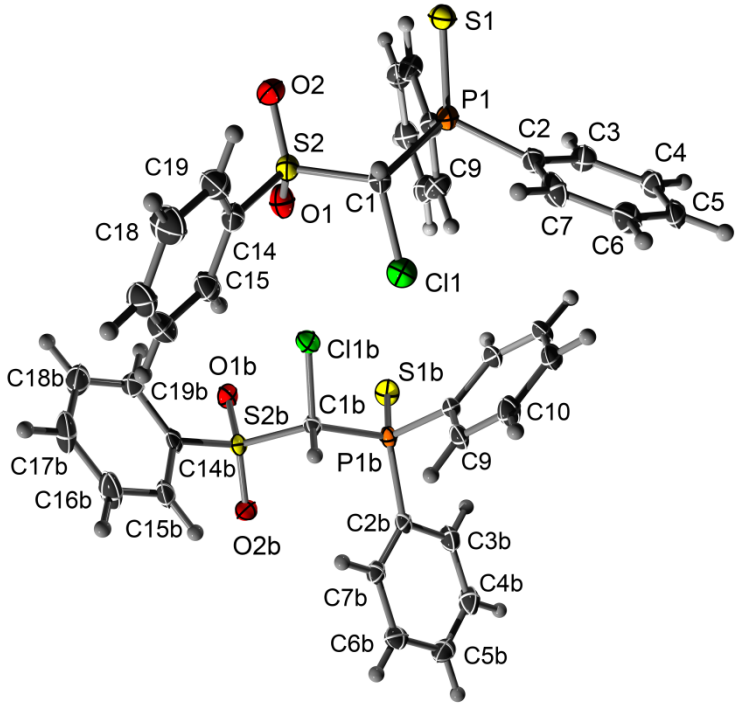


Figure S10. ORTEP Plot of compound **2.** Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å] and angles (°]: P1-C8 1.804(4), P1-C2 1.804(3), P1-C1 1.874(3), P1-S1 1.9541(12), Cl1-C1 1.762(3), S2-O2 1.430(3), S2-O1 1.432(3), S2-C14 1.764(4) S2-C1 1.818(3), Cl1b-C1b 1.763(3), S1b-P1b 1.9375(11), S2b-O2b 1.437(2), S2b-O1b 1.437(2), S2b-C14b 1.760(3), S2b-C1b 1.810(3), P1b-C2b 1.806(3), P1b-C9b 1.808(3), P1b-C1b 1.861(3), C8-P1-C1 106.14(16), C2-P1-C1 103.83(15), C1-P1-S1 111.26(12), C14-S2-C1 102.23(16), Cl1-C1-S2 107.70(17), Cl1-C1-P1 113.35(18), S2-C1-P1 114.93(18), C142-S22-C12 103.06(15), C2b-P1b-C1b 107.78(14), C8b-P1b-C1b 99.95(14), C1b-P1b-S1b 114.06(11), Cl1b-C1b-S2b 108.60(16), Cl1b-C1b-P1b 109.38(16), S2b-C1b-P1b 115.37(16)

Crystal structure determination of 3

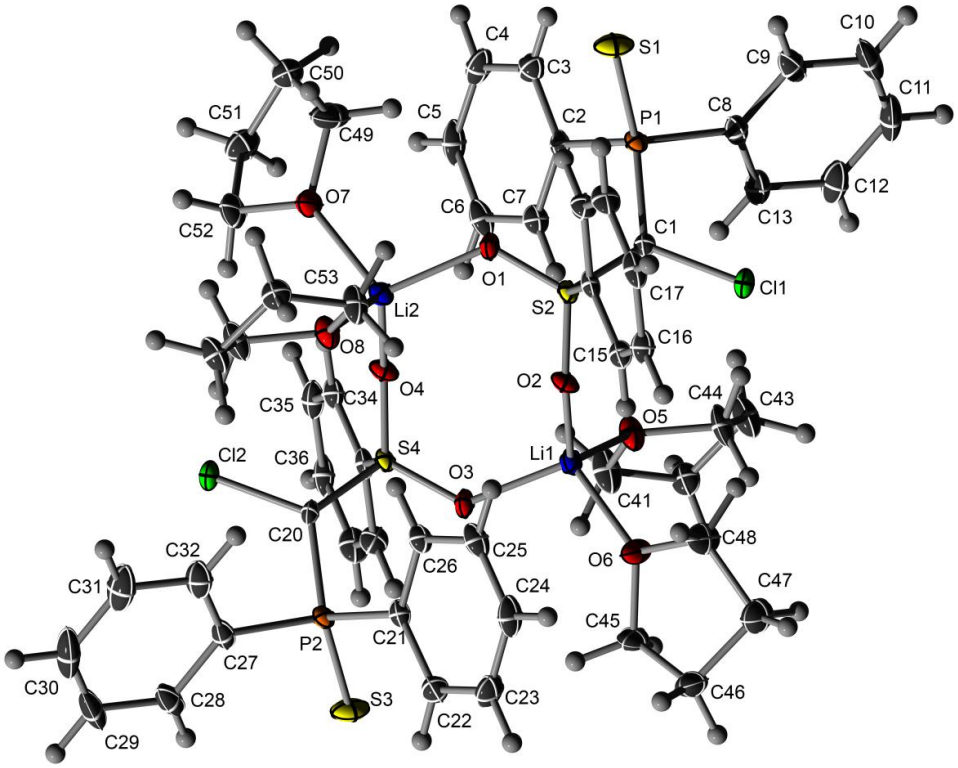


Figure S11. ORTEP Plot of compound **3.** Ellipsoids are drawn at the 50% probability level.

Crystal structure determination of 8

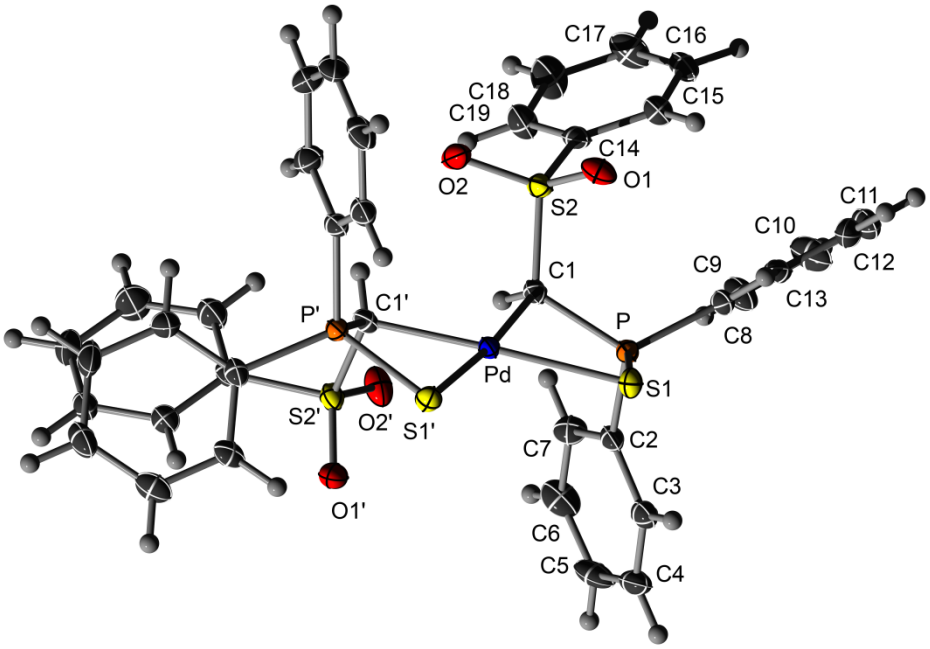


Figure S12. ORTEP Plot of compound **8.** Ellipsoids are drawn at the 50% probability level.

4. Computational details

All calculations were performed without symmetry restrictions. Starting coordinates were obtained directly from the crystal structure analysis. All calculations were done with the Gaussian 09 (Revision B.01) program package.[3] Geometry optimizations were performed using Density-Functional Theory (DFT) with the B3LYP (Becke 3-parameter-Lee-Yang-Parr) functional [4] and the 6-311+G(d,p) basis set. Harmonic vibrational frequency analyses were performed on the same levels of theory. The vibrational frequency analyses showed no imaginary frequencies. Natural bond orbital analysis studies were performed with NBO 3.1 program implemented in the Gaussian program package.

4.1. Computational studies of 2 and 3

For carbenoid **3** a model system **3'** was used in which the phenyl substitutents were replaced by methyl groups and thf by Me_2O. In addition to the dimeric aggregate found in experiment also monomeric solvates with different coordination modes were calculated, including (*S,C*) and (*O,S*)-coordination of lithium. A coordination by the central carbon atom and the sulfonyl moiety (*C,O*) and a pincer-type coordination mode of the ligand – (*S,C,O*)-coordination – were found to be no minimum on the potential energy surface. Optimzation of both isomers resulted in the rearrangment to the known *O,S*-coordination. Figure S13 depicts the energy optimized structures of the calculated aggregates. The calculations confirm that the dimeric structure is the most stable aggregate. Table S2 gives their energies, Table S4 the results from NBO analysis and Table S5-S11 the coordinates of the optimized compounds. For comparison reason CH_3Cl and its metallation to the corresponding carbenoid CH_2ClLi as well as the room temperature stable carbenoid reported by P. Le Floch and coworkers were studied. In the case of CH_3Cl, a dimeric and two different monomeric Me_2O solvates of the carbenoid were calculated, in the case of the bis(thiophosphinoyl) system a methyl substituted model system was used (analogous to **3**). The energy optimized structures are depicted in Figure S14 and Figure S15, respectively, the energies, cartesian coordinates and results of the NBO analyses are given in the Tables below.

For evaluation of the used computational method, energy optimization of **3'** and its monomeric congeners was also performed using different functionals and basis sets. The energy-optimized structure was compared with the experimental data (Table S3) showing best results for the B3LYP and M062X functional in combination with the 6-311+g(d,p) basis set. Analysis of the electronic structure of the carbenoid gave the same results with both methods (Table S4).

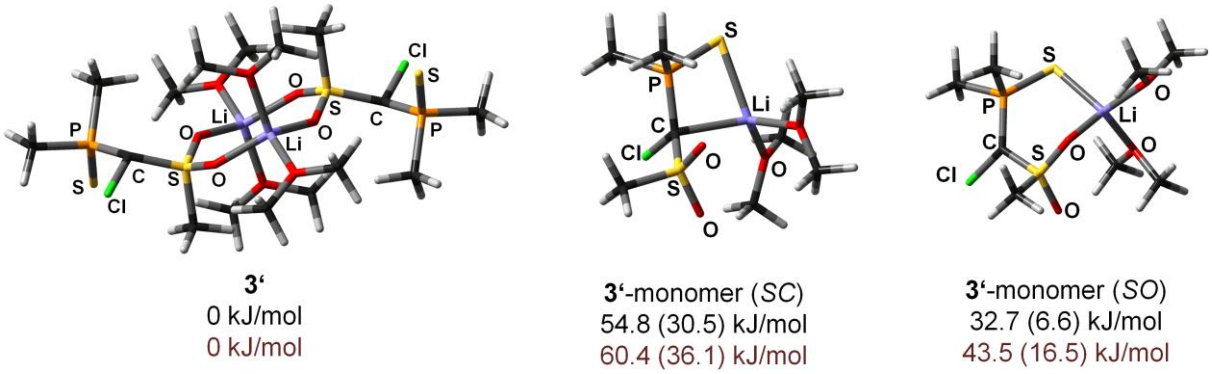


Figure S13. Energy-optimized structures of carbenoid **3'** and possible isomers, zero-point energies (free energies in brackets) are given relative to **3'** (black: B3LYP; red M062X).

Table S2. Calculated energies of all compounds.

Compound	SCF [Hartree]	ZPE [Hartree]	Free Energy [Hartree]	Methode
2'	-1906.98815050	-1906.843711	-1906.883889	B3LYP/6-311+g(d,p)
3'	-4448.36892764	-4447.773753	-4447.871582	
3'-monomer (*SC*)	-2224.16287835	-2223.866012	-2223.924183	
3'-monomer (*SO*)	-2224.17171268	-2223.874418	-2223.933266	
4'	-3529.14475919	-3528.532093	-3528.625403	
Me_2O	-155.077043280	-154.997767	-155.023195	
3'	-4.448.547209	-4.447.970822	-4.448.067154	BP86/TZVP
3'-monomer (*SC*)	-2.224.258095	-2.223.970490	-2.224.030290	
3'-monomer (*SO*)	-2.224.265603	-2.223.977365	-2.224.037428	
3'	-4.447.560663	-4.446.954777	-4.447.045969	M062X/6-311+g(d,p)
3'-monomer (*SC*)	-2.223.756733	-2.223.454398	-2.223.509251	
3'-monomer (*SO*)	-2.223.763252	-2.223.460834	-2.223.516688	

Table S3. Comparison of the experimental and calculated structural parameters; deviations are given in parenthesis.

Compound	Exp.	Calc. (B3LYP/6-311+g(d,p))	Calc. (BP86/TZVP)	Calc. (M062X/6-311+g(d,p))
C-P	1.760(2)	1.805 (2.6 %)	1.831 (4.0 %)	1.796 (2.0 %)
C-S	1.665(2)	1.703 (2.3 %)	1.730 (3.9 %)	1.694 (1.7 %)
C-Cl	1.757(2)	1.801 (2.5 %)	1.816 (3.4 %)	1.779 (1.3 %)
P-S	1.9674(8)	2.010 (2.2 %)	2.017 (2.5 %)	1.995 (1.4 %)
P-C-S	122.70(12)	116.89 (4.7 %)	115.02 (6.3 %)	114.84 (6.4 %)

Table S4. Calculated Natural Charges and Wiberg bond indices [B3LYP/6-311+g(d,p)].

	2'	**3'**	**3'** (M062x)	**3'**-monomer(SC)	**3'**-monomer(SO)
q(C)	-0.7735	-1.00057, -1.00054	-1.0084, -1.0083	-1.09805	-1.05864
q(S)	2.04325	2.08385, 2.08386	2.1020, 2.1021	2.07016	2.06579

q(P)	1.26756	1.31347, 1.31347	1.3227, 1.3228	1.34733	1.35575
q(Cl)	0.01871	-0.03259, -0.03256	-0.0270, -0.0269	-0.01536	-0.00882
q(Li)	-	0.64416, 0.64415	0.6060, 0.6059	0.50285	0.52615
WBI (C-Cl)	1.0235	0.9964, 0.9964	1.0018, 1.0018	0.9882	1.0112
WBI (C-P)	0.7656	0.9052, 0.9052	0.9000, 0.9000	0.9174	0.9542
WBI (C-S)	0.7686	1.0452, 1.0452	1.0417, 1.0420	0.9413	1.0234
C-Cl [Å]	1.792	1.801	1.779	1.808	1.777

Table S5. Cartesian coordinates of energy-optimized **2'** [B3LYP/6-311+g(d,p)].

Atomic symbol	x	y	z
S	1.9989635608	-0.8596679925	0.5595349504
P	4.9569257734	-0.1635496853	-0.4472660462
O	1.692845711	0.2788363183	-0.3142267457
O	1.1090252482	-2.0191488527	0.5906261445
S	5.4389250309	1.0490807815	1.0204891478
C	6.3423799879	-1.1973174345	-1.0553004231
H	7.0859794967	-0.5215097847	-1.482000582
H	6.0115806525	-1.905574457	-1.8188976381
H	6.7914004562	-1.7328071749	-0.2204566653
C	4.2924244078	0.6376198398	-1.9507072221
H	4.0615979263	-0.0999429555	-2.7233962795
H	5.0607872002	1.3217548288	-2.3158590156
H	3.3930616889	1.1935403972	-1.6944244711
C	2.2454518839	-0.2673106071	2.2393949004
H	2.4994033845	-1.1116866342	2.87614448
H	1.2814668824	0.1567026445	2.5226339803
H	3.029486869	0.489157738	2.2281806548
Cl	4.3101847558	-2.7068108817	1.1092872358
C	3.6578224715	-1.4822358286	-0.0252950803
H	3.378158082	-2.0056210796	-0.9427462149

Table S6. Cartesian coordinates of energy-optimized **3'** [B3LYP/6-311+g(d,p)].

Atomic symbol	x	y	z
C	3.6541309724	-0.7663594735	-0.835875484
S	2.0477753723	-1.1065193848	-0.3829161913
P	4.8169281492	-0.3983820899	0.4947330419
O	1.7087380888	-0.1730003374	0.7317058428
O	1.1431440793	-1.0574164912	-1.5698105528
S	4.7972022208	-1.489905041	2.18246636
Li	0.4610466624	0.187969676	2.1230139051
Li	-0.4634020659	-0.1851323074	-2.1118378082
O	-1.1458777571	1.0596635465	1.5808731656
O	1.234616688	1.38551932	3.5123507362
O	-0.077188881	-1.5029860853	3.0544046703
O	-1.7114452061	0.1760771202	-0.7209259199
O	0.0750044575	1.5059386771	-3.0430808211
O	-1.2371133559	-1.3821161131	-3.5016237271
S	-2.0502271441	1.1095513718	0.393806738
C	-3.6569065251	0.7702266393	0.8462973064
P	-4.8195010469	0.4029598761	-0.4846641277
S	-4.7989600215	1.4947822969	-2.1721967489
C	2.5055515219	1.2400774234	4.1464774683
H	3.0671441129	2.1803891989	4.0942390309

H	2.3788075602	0.9592856393	5.1993070168
H	3.057562141	0.4603060978	3.6214270328
C	0.4304582719	2.4059574295	4.100437298
H	-0.5087709948	2.4310729692	3.5509871301
H	0.2374296529	2.1840730646	5.1571878055
H	0.9314599408	3.3786199125	4.0253644127
C	-1.4391201334	-1.7498571304	3.4072190584
H	-2.0602472994	-1.1291089877	2.7639120936
H	-1.684346067	-2.8079898829	3.2567392338
H	-1.6189927666	-1.486045029	4.4564738405
C	0.8467626199	-2.2486496478	3.8441707474
H	1.8512143384	-2.0147229303	3.4911883444
H	0.7565438205	-1.978657155	4.9034475785
H	0.6648972206	-3.3244061647	3.7344445097
C	1.4369988429	1.7530804107	-3.3954401303
H	1.6821523017	2.8111295266	-3.2442493291
H	2.0580309311	1.1319632642	-2.7523892517
H	1.6171178795	1.4899309299	-4.4448198686
C	-0.8488042552	2.2518753291	-3.8327530518
H	-0.7585546024	1.9820753684	-4.8920768597
H	-1.8533066908	2.0180228019	-3.4798655726
H	-0.6668012733	3.3275880545	-3.7228126046
C	-0.4329776693	-2.402531496	-4.0897921728
H	0.5061636079	-2.4278728279	-3.5402057115
H	-0.9341019281	-3.3751529021	-4.0149853049
H	-0.2397777102	-2.1804573036	-5.1464711547
C	-2.5079020793	-1.2363959107	-4.1359681902
H	-3.0696737362	-2.1766117516	-4.0839119101
H	-3.0598517491	-0.4565498169	-3.6109679826
H	-2.3809165156	-0.9555408344	-5.1887519476
C	6.4549823244	-0.4638726279	-0.3214479783
H	7.1834363675	-0.0587433601	0.3829791302
H	6.4565053253	0.1188238308	-1.2444872372
H	6.7108308294	-1.499455798	-0.5397584524
C	4.5776655957	1.3864162412	0.8462491445
H	4.7404077348	1.9643815111	-0.0656488686
H	5.2818115376	1.6918369091	1.6224275244
H	3.5562824047	1.5382956782	1.1904962673
C	1.8352871265	-2.7864396222	0.2627336465
H	2.0955492785	-3.4798270413	-0.535637251
H	0.7918549875	-2.8963010803	0.5564039463
H	2.5164247384	-2.8883645691	1.1077783681
C	-4.5809239566	-1.3818737591	-0.8364164367
H	-4.7440701199	-1.9598976268	0.0753728074
H	-3.5595657648	-1.5341796162	-1.1805392101
H	-5.285103832	-1.6868682841	-1.6127353658
C	-6.4577174782	0.4689451526	0.331167082
H	-7.1861672258	0.0641887394	-0.373478261
H	-6.713237705	1.5045861383	0.549584349
H	-6.4596400877	-0.1138978452	1.2541135289
C	-1.8367547748	2.7895010582	-0.2514321128
H	-2.096880391	3.482840292	0.5470242108
H	-2.5176566592	2.8919344457	-1.0966079683
H	-0.7932091859	2.8989384208	-0.5448533133
Cl	-4.2240024592	1.8877972373	2.1392010906
Cl	4.2214682398	-1.8835558746	-2.128969704

Table S7. Cartesian coordinates of energy-optimized **3'**-monomer (Li coordination via S and C) [B3LYP/6-311+g(d,p)].

Atomic symbol	x	y	z
Li	-3.8603069426	2.0599474342	2.5095853055
O	-1.2864055475	2.2675910122	0.2682426516
O	-1.7782560402	-0.1536562115	0.8479497211
O	-3.8513681289	4.0055126699	2.7161687278
O	-2.549662416	1.3667782301	3.8068487842
S	-2.0881652031	1.0492517951	0.0431508329
C	-3.7574715938	1.427482131	0.3216039182
P	-5.0639370902	0.2426294573	0.6535977062
S	-5.9356309027	0.6698546336	2.4273434308
C	-4.8989104523	4.695472913	3.3913475255
H	-5.5278011828	5.2362636141	2.6751274227
H	-5.5037646512	3.9505241253	3.9075726507
H	-4.4866706167	5.4031698318	4.1204126236
C	-2.9951048677	4.874620107	1.9677150016
H	-2.4840457189	5.5713753165	2.6431547748
H	-2.2695834244	4.2507133701	1.4469850405
H	-3.5771849007	5.439412788	1.2324496957
C	-2.5177948666	-0.0248712882	4.138860719
H	-3.5392463756	-0.3938280031	4.0584859021
H	-1.8708171762	-0.5636585445	3.4402443355
H	-2.1574567542	-0.1554697831	5.1659487602
C	-1.2635631543	1.9777708277	3.9190967259
H	-0.564663938	1.5399976043	3.2001114501
H	-1.3879507181	3.0377188966	3.7042813366
H	-0.8769109636	1.8567887981	4.9378646331
C	-6.3062083501	0.2767404163	-0.6952480822
H	-5.8332577245	0.0665176097	-1.6573696902
H	-6.780857325	1.2554591983	-0.7298405606
H	-7.0633736958	-0.478626309	-0.4767639868
C	-4.4411923776	-1.4785520809	0.6142317357
H	-5.2771668859	-2.1219677257	0.8952905646
H	-3.6230534406	-1.596264682	1.3190008127
H	-4.0892822283	-1.7406594431	-0.3859212449
C	-1.7977356372	0.607125244	-1.6941303502
H	-2.146535267	1.4274517897	-2.3199295845
H	-2.3315914786	-0.3164914859	-1.9137371309
H	-0.7230199755	0.467866363	-1.8093420569
Cl	-4.3171189278	2.8544640601	-0.6380842517

Table S8. Cartesian coordinates of energy-optimized **3'**-monomer (Li coordination via S and O) [B3LYP/6-311+g(d,p)].

Atomic symbol	x	y	z
Li	-1.7940819964	-1.209291387	1.8413729821
O	-1.2167893768	2.0630049485	0.7687052318
O	-1.7358982836	-0.338728801	0.1123006304
O	-0.7971161382	-0.2284406252	3.2295353391
O	-0.8263139729	-2.9188630145	1.6427590773
S	-2.0700757226	1.1303485221	0.0094034689
C	-3.7286760555	1.238598563	0.3437269639
P	-4.6922577879	-0.1846942152	0.7514843516
S	-4.1866630326	-1.3397598921	2.3497198492
C	-1.447248258	0.7988195641	3.9890817529
H	-1.4230737705	1.7446692405	3.4401190425

H	-2.4797903495	0.4836213331	4.1299874848
H	-0.9528677879	0.9132290947	4.9609478113
C	0.5654372208	0.0902368172	2.9423852017
H	1.13008716	0.2149207101	3.8741767692
H	0.9791040853	-0.7457313412	2.3781539691
H	0.6233098006	1.0046889426	2.3443966241
C	-0.8553491577	-3.8808987779	2.6940498826
H	-0.9210817709	-3.3308559972	3.6321540328
H	-1.7263545594	-4.5385783781	2.594755181
H	0.060498774	-4.483455783	2.6875321092
C	-0.7097824847	-3.5031746706	0.3468553556
H	-1.5533509301	-4.1746753	0.1478282539
H	-0.715789853	-2.6846080562	-0.3710551132
H	0.227991378	-4.0650623294	0.264603007
C	-6.3920257684	0.4474341836	0.9812680159
H	-6.714665368	1.0226926869	0.1122859211
H	-6.427216512	1.0773311641	1.8689818088
H	-7.043542555	-0.4149249956	1.1306685594
C	-4.8057774936	-1.2545513708	-0.738014364
H	-5.4230780006	-2.1245889929	-0.5081056974
H	-3.8027949461	-1.5875217136	-1.0028144082
H	-5.2377778485	-0.6895418626	-1.5669510492
C	-1.7773392975	1.548821431	-1.7281573647
H	-2.1404719557	2.5638603395	-1.8857362337
H	-2.3199434625	0.8387381112	-2.3492332172
H	-0.7030749925	1.4953729736	-1.9051477337
Cl	-4.3447681101	2.8791663085	0.6409538442

Table S9. Cartesian coordinates of energy-optimized **4'** [B3LYP/6-311+g(d,p)].

Atomic symbol	x	y	z
C	3.7213934276	-0.6978609658	-0.7392411965
S	2.1133367535	-0.9823003381	-0.3865938864
P	4.8955660888	-0.4157506339	0.550723511
O	1.6748275549	-0.0872573502	0.7300442406
O	1.2967551457	-0.9083496511	-1.6451519743
S	4.7747028891	-1.4777591815	2.2572855962
Li	0.4058525657	0.1722743245	2.1117448806
Li	-0.4081746376	-0.1669274833	-2.1012746142
O	-1.2983046405	0.9155346673	1.655604594
O	1.1392066464	1.406370418	3.501590019
O	-0.0066653787	-1.5507531731	3.0693579963
O	-1.6762256066	0.0921447876	-0.7187790449
O	0.0030407886	1.5560078636	-3.0598871362
O	-1.1411788323	-1.4014705987	-3.4907478919
S	-2.1154554577	0.9874968268	0.3973154637
C	-3.7230713812	0.7010943429	0.7507473303
P	-4.8971609334	0.4171904949	-0.5390004562
S	-4.7782303782	1.4789561183	-2.2458638738
C	2.4441782033	1.3381596513	4.0751060901
H	2.9642648257	2.2962830792	3.955391979
H	2.3815396943	1.0982461136	5.1438425093
H	2.9999954852	0.5572301344	3.5561702817
C	0.3218607321	2.4137347083	4.0876357738
H	-0.6379547296	2.3833087432	3.5748128469
H	0.1790302959	2.222720194	5.1587301964
H	0.7791069403	3.4027958248	3.9601122105
C	-1.3451762335	-1.8893764537	3.4267469685

H	-2.0066368673	-1.2961642978	2.7981057609
H	-1.5261771618	-2.9580689717	3.2589507285
H	-1.533518668	-1.6569512965	4.4825320826
C	0.9702004848	-2.2487991751	3.8386085492
H	1.9545945909	-1.9555025063	3.473678894
H	0.8789028599	-1.9941237725	4.9018333908
H	0.848643883	-3.3322947365	3.7205563441
C	1.341429774	1.8956143758	-3.4167563348
H	1.5218454562	2.9642841158	-3.2481690103
H	2.0030387777	1.3022898304	-2.7883835847
H	1.5301243782	1.6640404838	-4.4726669401
C	-0.9740795607	2.2536522522	-3.8291432996
H	-0.8823792254	1.9993569797	-4.8924255067
H	-1.9583618283	1.9596036576	-3.4645213813
H	-0.8532654238	3.3371956745	-3.7107475295
C	-0.32283768	-2.4079119433	-4.0770368786
H	0.6369256945	-2.3767199816	-3.5641615667
H	-0.7791701362	-3.3974313267	-3.9498227987
H	-0.1801295004	-2.216450187	-5.1480654881
C	-2.446115342	-1.3342312251	-4.0644684973
H	-2.9653754415	-2.2928487628	-3.9451331197
H	-3.0027058425	-0.5539360825	-3.5454020139
H	-2.3834929434	-1.0939447191	-5.1331215515
H	4.0548028534	-1.1862887812	-1.6464901249
H	-4.0569493561	1.1908449918	1.6571376473
C	6.4988201942	-0.6861203983	-0.3003321985
H	7.3055832716	-0.4038703232	0.3775177156
H	6.5567943406	-0.0919795676	-1.2155556114
H	6.5959453089	-1.7458970076	-0.5380596884
C	4.8892881437	1.3828488263	0.923326988
H	5.10567311	1.9489259412	0.0143667238
H	5.6263977314	1.6055987438	1.6968607018
H	3.8930893544	1.6482713852	1.276709227
C	1.8055298768	-2.6652362305	0.2221918591
H	2.0457573218	-3.3528792599	-0.5880455579
H	0.7560714296	-2.741549781	0.5064426143
H	2.4712094922	-2.8199366558	1.0716257791
C	-4.8883802479	-1.3814973042	-0.9111014542
H	-5.1039009259	-1.947618233	-0.0019663373
H	-3.8918361022	-1.6456146433	-1.2644902942
H	-5.6252337737	-1.6055004955	-1.6845159291
C	-6.500575169	0.6856028567	0.3123681209
H	-7.3071228087	0.4021964438	-0.3652539737
H	-6.5990325963	1.7452926617	0.5499392428
H	-6.5575556041	0.091541026	1.2277033086
C	-1.8100030765	2.6703745225	-0.2127783529
H	-2.0507667064	3.3583027253	0.5970560669
H	-2.4761326997	2.8236581745	-1.0621182993
H	-0.760722208	2.7477594335	-0.4974030858

Table S10. Cartesian coordinates of energy-optimized **Me_2O** [B3LYP/6-311+g(d,p)].

Atomic charges	x	y	z
O	0.0000000437	-0.5870316769	-0.0000484437
C	-1.1764074229	0.1944377881	-0.0000271874
C	1.1764075475	0.1944379999	0.000020866
H	-1.2348360928	0.8349681388	-0.8922894636
H	-1.2351942362	0.8343804093	0.8926336612

H	-2.023109691	-0.4924982439	-0.0004287019
H	2.023110025	-0.4924979605	0.0000794448
H	1.2349654074	0.8346808663	0.8924816311
H	1.2350645937	0.8346676788	-0.8924418066

4.2. Computational studies of CH_3Cl and its lithium carbenoid

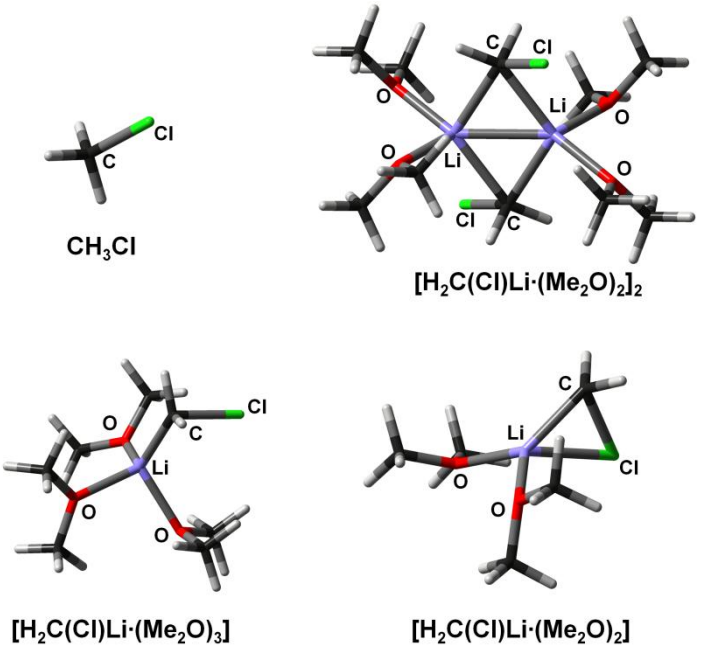


Figure S14. Energy-optimized structures of CH_3Cl and its corresponding lithium carbenoid.

Table S11. Calculated energies of all CH_3Cl and its corresponding lithium carbenoids.

Compound	SCF [Hartree]	ZPE [Hartree]	Free Energy [Hartree]
CH_3Cl	-500.151872438	-500.114234	-500.136874
$[H_2C(Cl)Li\cdot(Me_2O)_2]_2$	-1634.55413706	-1634.176075	-1634.247223
$[H_2C(Cl)Li\cdot(Me_2O)_3]$	-972.353352071	-972.083996	-972.137536
$[H_2C(Cl)Li\cdot(Me_2O)_2]$	-817.266468668	-817.077993	-817.124262
$[MeLi\cdot(Me_2O)_2]_2$	-715.281706159	-714.889580	-714.955919

Table S12. Bonding parameters, calculated Natural Charges and Wiberg bond indices of CH_3Cl and its corresponding lithium carbenoid.

	CH_3Cl	$[H_2C(Cl)Li\cdot(Me_2O)_2]_2$	$[H_2C(Cl)Li\cdot(Me_2O)_3]$	$[H_2C(Cl)Li\cdot(Me_2O)_2]$	$[MeLi\cdot(Me_2O)_2]_2$
q(C)	-0.532	-0.841	-0.865	-0.812	-1.26335
q(Cl)	-0.078	-0.173	-0.243	-0.231	-
q(Li)	-	0.500	0.551	0.562	0.55044
WBI(C-Cl)	1.025	0.931	0.918	0.883	-
WBI(C-Li)	-	0.185 0.180	0.244	0.274	0.2091
C-Cl [Å]	1.806	1.924	1.943	1.979	-
C-Li [Å]	-	2.228 2.212	2.086	2.013	2.194

Table S13. Cartesian coordinates of energy-optimized **CH_3Cl**.

Atomic symbol	x	y	z
C	0.3347539828	-0.3007719431	0.
H	0.7077958724	0.1928940509	0.8941858999
H	0.7077958724	0.1928940509	-0.8941858999
H	-0.752409835	-0.3233467482	0.
Cl	0.9365708621	-2.0030326779	0.

Table S14. Cartesian coordinates of energy-optimized **$[H_2C(Cl)Li{\cdot}(Me_2O)_2]_2$**.

Atomic symbol	x	y	z
C	0.0073513623	-0.8911431116	-2.5531147352
H	0.4167260046	0.1030044569	-2.7744070996
H	0.5674810263	-1.5609313259	-3.2189183282
C	3.5023413429	-0.9823410537	-0.4783256132
H	3.7804486621	-1.3774034365	-1.4636871891
H	4.3845301243	-0.5245609422	-0.0139025392
C	2.8231695156	1.1018647533	-1.3747043259
H	1.9688545478	1.7763019831	-1.3895976188
H	3.685002402	1.6105394326	-0.9244194235
H	3.076130541	0.8067715045	-2.4003846914
C	0.1449402204	1.846940266	1.3904524278
H	1.1100597434	1.4301466214	1.674310288
H	0.1986871126	2.9426562707	1.3845257483
H	-0.6115672462	1.525238083	2.1155754775
C	-1.4198530146	1.8126896559	-0.3984692133
H	-2.2306501715	1.49309502	0.2674115655
H	-1.4265315886	2.9069848069	-0.4742084602
H	-1.5665165881	1.3740693645	-1.384603417
Li	0.4257598189	-0.5281213648	-0.3955650136
O	2.4504112836	-0.0298509139	-0.5968139351
O	-0.1604743007	1.3553563324	0.0883467579
Cl	-1.668786411	-0.7819001778	-3.4922931875
Cl	0.9206090771	-1.9438883245	1.8722625294
C	-0.7565656896	-1.8421862865	0.934248357
H	-1.1631137735	-2.8367681266	1.1587356155
H	-1.317898052	-1.1717529983	1.5983558719
H	3.1356288494	-1.7857672015	0.157401949
C	-0.8912098157	-4.5792223808	-3.0107567344
H	-0.135392431	-4.2552197133	-3.7355662614
H	-0.9425678413	-5.6750489806	-3.0057627958
H	-1.8572574245	-4.1643505516	-3.2943184895
C	-4.2500536165	-1.7512387049	-1.1446459375
H	-5.131052676	-2.2089500514	-1.611379843
H	-4.5303879375	-1.3571814001	-0.1595249088
H	-3.8822526425	-0.9471672514	-1.7789061709
C	-3.5716863837	-3.8355735812	-0.2477570905
H	-2.7169912685	-4.5094907364	-0.2312130466
H	-3.8269357686	-3.5407541846	0.7774304657
H	-4.4322826588	-4.3447153692	-0.6998683878
C	0.6729641215	-4.5437557973	-1.2213473019
H	0.681243284	-5.6380702369	-1.1460720192
H	1.4834478784	-4.2226478085	-1.8868687227
H	0.8187500859	-4.105359905	-0.2349835458
O	-3.1980299155	-2.7035090335	-1.0246975105
O	-0.5869663008	-4.0880593833	-1.7082413531
Li	-1.1743615878	-2.2055653777	-1.2228134935

Table S15. Cartesian coordinates of energy-optimized **[$H_2C(Cl)Li{\cdot}(Me_2O)_3$]**.

Atomc symbol	x	y	z
C	-1.016063563	0.4246155144	-0.2709598097
H	-0.8582831337	-0.3009091648	-1.0806111976
H	-2.0984236509	0.3932926376	-0.0840143718
C	-1.2549626806	3.0443464751	2.2828784819
H	-1.3563009838	3.8749012834	2.9923187234
H	-1.7106363145	3.3095338618	1.3242427938
H	-1.7510111696	2.160431572	2.6824714015
C	0.8783612624	3.8049580128	1.5836901536
H	1.9048736074	3.4590151656	1.4696533028
H	0.4872918108	4.1094916468	0.6077051769
H	0.8494192744	4.6531798347	2.2787868943
C	0.4649315824	0.1091697193	4.2446273511
H	-0.4901885888	0.0891216689	4.784381921
H	1.1723046488	-0.5588752715	4.7527045742
H	0.8529006316	1.1270288922	4.2410327862
C	-0.2894648067	-1.5711876413	2.7392601505
H	-0.4378334471	-1.7274657008	1.6718923497
H	0.3773337487	-2.3407791324	3.1477485304
H	-1.2581772361	-1.6242703286	3.2504974513
C	3.3726665793	0.2537630209	1.3865104083
H	3.0860481425	0.2631110201	2.4374368028
H	3.5372034717	-0.7833208687	1.0676522439
H	4.3050532641	0.8175363627	1.2567026187
C	2.5723134486	0.8830767083	-0.7585669504
H	3.4755346732	1.4702592371	-0.96479177
H	2.7042941498	-0.1335228262	-1.1469357202
H	1.7076111043	1.344632534	-1.2325157993
Li	0.3641098118	0.8906037676	1.2215489879
O	0.2867263818	-0.2757147003	2.8885758268
O	0.1236288462	2.711126284	2.1048198447
O	2.3163399996	0.8500305193	0.6488399442
Cl	-0.8972766046	2.0828724661	-1.277449231

Table S16. Cartesian coordinates of energy-optimized **[$H_2C(Cl)Li{\cdot}(Me_2O)_2$]**.

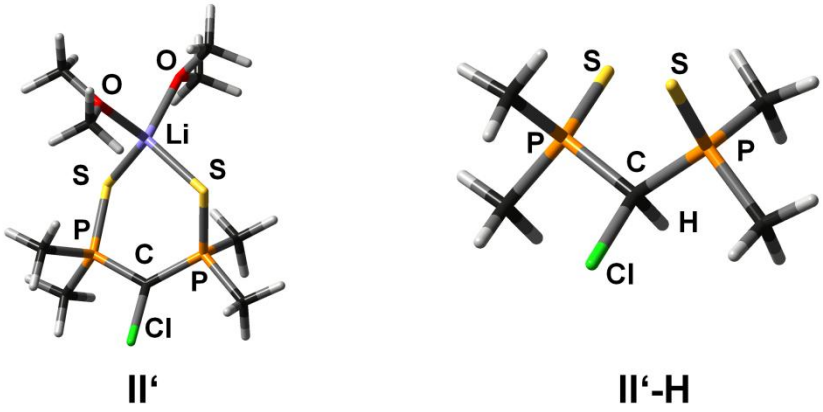
Atomic symbol	x	y	z
C	-0.4990119184	-0.370951116	-1.7361142175
H	-0.7305016867	0.3226915992	-2.5531059549
H	-1.0263929031	-1.3007816326	-1.9814864528
C	0.935125369	-2.712731751	0.7589325222
H	1.6774546164	-3.4040790639	1.1743634478
H	-0.0633726548	-2.9845078991	1.1181604258
H	0.948412955	-2.7538770358	-0.328745265
C	1.2078934278	-1.1517513743	2.5351774376
H	1.4495893962	-0.1035699069	2.7091799194
H	0.2076740183	-1.3633566428	2.9299947526
H	1.9420529481	-1.7869776655	3.0447001838
C	3.128189315	1.6779841213	0.1920822067
H	3.4928036951	0.685246736	0.4557223922
H	3.4597249215	1.9293455856	-0.822330175
H	3.5325611161	2.4139456977	0.8970266591
C	1.0969563187	2.8955602257	-0.0550487243
H	1.4084671192	3.6626667955	0.6630555266
H	1.3734430906	3.2077355404	-1.0682972585
H	0.0193978734	2.7486253337	-0.002096228

Li	0.6788643634	0.0110732426	-0.1489799223
O	1.2504225286	-1.367693271	1.1275551481
O	1.7068298539	1.6421138134	0.2657710075
Cl	-1.6921206634	0.3402602576	-0.326642301

Table S17. Cartesian coordinates of energy-optimized **[MeLi·(Me_2O)$_2$]$_2$**.

Atomic symbol	x	y	z
C	-0.2113927819	-0.3799332432	1.8107920489
H	0.4673193528	-1.1478223602	2.2269709589
H	-0.0349841842	0.5054583543	2.4504971772
C	2.7558066834	2.2086093124	0.3652884229
H	2.2116417351	2.706754185	1.1774021608
H	3.7715425985	2.6201942238	0.3077431037
C	3.4342389584	0.4398035905	1.7930232968
H	3.4276085787	-0.6479325907	1.8443627617
H	4.4693688361	0.803902422	1.8098764897
H	2.8895799457	0.8460311706	2.6531048094
C	3.0304547429	-2.0339375124	-1.373968171
H	3.5331360994	-1.0681537472	-1.3943432989
H	3.7737880113	-2.8350221106	-1.2736695182
H	2.4697713916	-2.1698583748	-2.3059437558
C	1.4422740735	-3.2436643213	-0.0926237342
H	0.8336123785	-3.4592426176	-0.979670378
H	2.1371613326	-4.075907467	0.0774725548
H	0.7927881326	-3.1229446034	0.7730420397
Li	1.123243153	-0.2771618355	0.07262076
O	2.7968003281	0.8023517506	0.5726361966
O	2.1535243677	-2.0226623876	-0.25236755
C	0.210666925	0.3809422362	-1.8107986383
H	-0.4675331862	1.1493514444	-2.2268519678
H	0.0335824394	-0.5042753302	-2.4505576981
H	2.2360816842	2.3765712826	-0.576758735
C	-3.0313398037	2.0346333318	1.3740538813
H	-2.470698664	2.1703627721	2.3060822174
H	-3.7746738554	2.8357337969	1.27388798
H	-3.5340130638	1.068840833	1.3942015412
C	-2.7565889467	-2.2075375847	-0.3657323388
H	-3.7723258294	-2.6191469478	-0.3083795844
H	-2.2123274799	-2.7055146765	-1.177883995
H	-2.236966317	-2.3756834061	0.5763388335
C	-3.4349015767	-0.4384608399	-1.7931843771
H	-3.4282823307	0.6492854176	-1.8443067864
H	-2.8901495047	-0.8445096996	-2.6532904662
H	-4.4700235396	-0.8025739581	-1.8102095062
C	-1.4431064641	3.2446389506	0.0930431748
H	-2.1379901068	4.0769190722	-0.0768872202
H	-0.8344706605	3.4600184169	0.9801555986
H	-0.7935944705	3.1241187912	-0.7726310965
O	-2.7975769081	-0.8012398999	-0.5728036926
O	-2.1543577559	2.0235997474	0.2524889732
Li	-1.1239590039	0.2781566368	-0.0726251213
H	1.2134162043	0.7335662574	-2.1168900394
H	-1.2139167594	-0.7332518219	2.1168213682

4.3 Computational studies of the bis(phosphonium)-substituted system II



II‘ II‘-H

Figure S15. Energy-optimized structures of carbenoid **II’** and its protonated congener **II’-H** [B3LYP/6-311+g(d,p)].

Table S18. Calculated Natural Charges and Wiberg bond indices [B3LYP/6-311+g(d,p)].

	II'-H	**II'**
q(C)	-0.87742	-1.17434
q(P)	1.29500	1.38524
q(Cl)	-0.02687	-0.05720
q(Li)	-	0.43948
WBI (C-Cl)	0.9870	0.9806
WBI (C-P)	0.7968	1.0156
C-Cl [Å]	1.82511	1.81511

Table S19. Cartesian coordinates of energy-optimized **II'**.

Atomic symbol	x	y	z
C	-2.1656633639	0.1214351746	0.085431566
C	-2.4526918121	2.7247334661	-1.0921000455
P	-1.4784218724	-1.3396766634	0.7493151519
C	-0.9469801773	2.4430785984	1.351684426
S	0.2986196689	-1.0605439452	1.6930499209
Li	1.6938795436	-0.0304448257	-0.0433014182
Cl	-3.6351469176	-0.2031256602	-0.929407401
O	3.2874782501	0.7457831194	0.8992176718
O	2.6371409207	-1.2636302265	-1.2970803689
C	4.1639868496	1.5220227095	0.0837243015
C	3.218340919	1.2238396701	2.2417776822
C	2.2400655259	-1.4783903397	-2.6514482681
C	3.4631885711	-2.3049245393	-0.7833584758
H	-3.3834460037	2.8064610558	-0.5289392997
H	-1.9697865987	3.6996941615	-1.1731146323
H	-2.6632933552	2.3480160946	-2.0917498409
H	-1.8945507402	2.6460576058	1.8549720521
H	-0.4059995436	3.3723306487	1.1632513287
H	-0.3454576134	1.7828561983	1.9751616328
H	4.1675966872	1.0683379569	-0.9062735388
H	5.1795466667	1.5113790064	0.4970096616
H	3.8080256087	2.5551414378	0.0072113326

H	4.2053146584	1.1699453511	2.7160072665
H	2.5165398541	0.5870508391	2.7775956024
H	2.860856544	2.2597859922	2.2654254229
H	1.704700219	-2.4303502926	-2.7494314329
H	3.1175694196	-1.4912732283	-3.3088016016
H	1.5794848609	-0.6567481497	-2.9240760292
H	3.7197484455	-2.0382483143	0.2408318604
H	4.3790733015	-2.3987239258	-1.379295086
H	2.9286396937	-3.2616329023	-0.7872475918
C	-2.6769979437	-2.0750723848	1.924075671
H	-2.3145724049	-3.0472248363	2.2637906924
H	-3.6481241791	-2.1881500758	1.4376615452
H	-2.7758523516	-1.4041644506	2.7772783172
C	-1.3069460592	-2.6500007988	-0.5344496007
H	-0.9337311636	-3.5654753784	-0.0716723881
H	-0.5985978351	-2.3046252188	-1.2877365162
H	-2.2705552912	-2.8391255059	-1.0112993936
S	0.4562773145	1.5792272378	-1.341735749
P	-1.2821872962	1.6021023385	-0.2464874276

Table S20. Cartesian coordinates of energy-optimized **II'-H**.

Atomic symbol	x	y	z
C	-2.6627526596	2.7973044619	-0.8766628236
P	-1.6358280614	-1.3291066379	1.1004524073
C	-0.5227293858	2.3179584947	0.9846076312
S	-0.4066593334	-0.8537799241	2.5668924854
Cl	-3.7703717363	-0.2998659559	-0.8244477658
H	-3.3161302539	3.0419892155	-0.035424568
H	-2.1193560968	3.6912526288	-1.1882264185
H	-3.2554297322	2.4356765762	-1.7148119149
H	-1.2056713628	2.5782841355	1.7964516074
H	-0.0505075649	3.2218418039	0.5935610133
H	0.2377320917	1.637118868	1.3601562471
C	-3.0401851403	-2.3609836597	1.6658900777
H	-2.6129088703	-3.2573283905	2.1193592057
H	-3.7029169441	-2.638338728	0.845961806
H	-3.5974279152	-1.8205105379	2.4321375773
C	-0.8954278871	-2.2490873988	-0.2882293296
H	-0.5318606778	-3.1983916455	0.1101423976
H	-0.0634032992	-1.6773365158	-0.6957677674
H	-1.6304698309	-2.4294501794	-1.0745416403
S	-0.2670316565	0.968008911	-1.9072409064
P	-1.4091819389	1.5408923336	-0.4142859887
C	-2.4816654832	0.1871349376	0.372667124
H	-3.0091065114	0.6450345869	1.2128867435

4.4 Computational studies of carbene complex 7

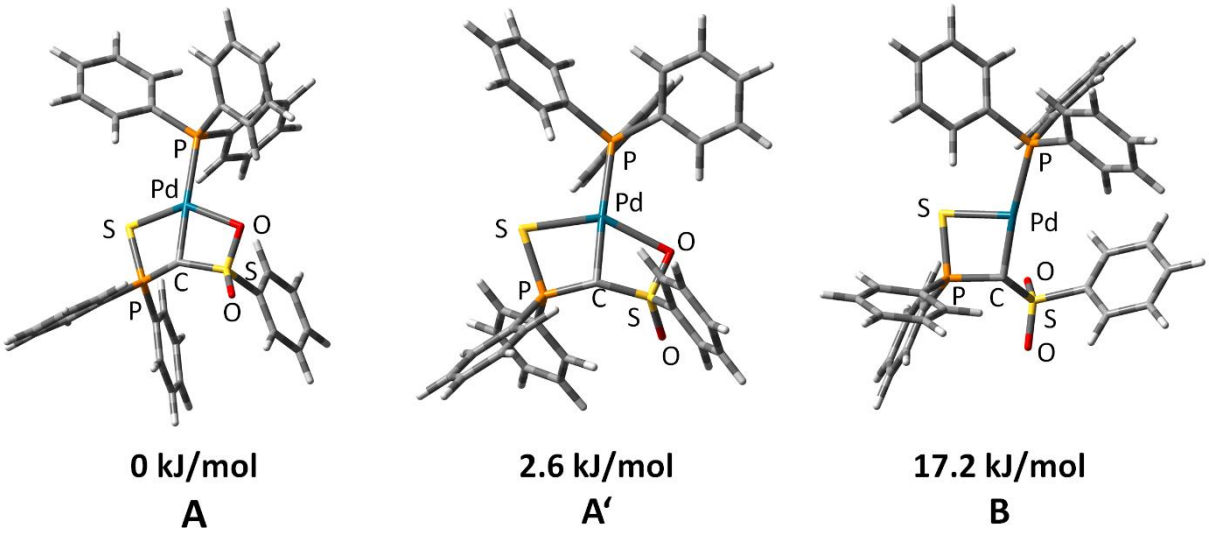


Figure S17. Energy-optimized structures of palladium carbene complex **7'** (B3LYP/6-311+g(d,p)/LANL2Tz(f)).

Table S21. Calculated energies of carbene complex **7**' and its derivatives.

Compound	SCF [Hartree]	ZPE [Hartree]	Free Energy [Hartree]	Methode
A	-3.184.379488	-3.183.811388	-3.183.894471	
A‘	-3.184.369501	-3.183.801685	-3.183.885613	B3LYP
B	-3.184.371305	-3.183.803692	-3.183.887934	
A	-3.183.482268	-3.182.907943	-3.182.986795	
A‘	-3.183.466458	-3.182.892646	-3.182.976109	M062X
B	-3.183.471193	-3.182.897239	-3.182.977934	

Table S22. Cartesian coordinates of energy-optimized **A**.

Atomic symbol	x	y	z
C	-3.8984895591	-4.1708562037	-0.5463363421
C	-3.1497638476	-3.1787275898	0.084590243
C	-3.7418930017	-4.4004803551	-1.9172003697
S	0.3341493859	-2.0072083953	1.300560342
C	-2.2325219	-2.4162640251	-0.6570700958
C	-2.8311952166	-3.6426697181	-2.6557372799
C	-2.0650472241	0.138532689	2.5133934452
C	-2.9526131601	0.921750312	3.2534536914
P	-1.1928922222	-1.1582841053	0.1555552945
C	-2.3660038475	-0.1997912538	1.1864962911
C	-4.1364897017	1.3809434383	2.6735010338
C	-2.0686897658	-2.654916886	-2.0283121625
C	-3.5594724762	0.2652768432	0.6061240797
C	-4.4371237394	1.0549969257	1.3482237604
C	-0.1723539583	-0.3622611356	-0.9607659667
O	-0.584310749	1.409906492	-2.9095971918
S	0.0831961953	1.1541206826	-1.6278137027
C	-1.7988506251	4.4460171032	-0.1304817474

O	1.6155329013	1.1595963176	-1.6241206229
C	-0.3726079647	2.5531349885	-0.5648389015
C	-1.1094036193	4.6873978169	1.0587216807
C	0.324471724	2.7845800181	0.6256871241
C	-0.0471436615	3.8582547872	1.4337101841
C	-1.4322043528	3.3765921865	-0.9516886121
H	-4.6063365353	-4.761809471	0.0284598204
H	-3.2798696353	-2.9976927547	1.1487043902
H	-4.3308357656	-5.1712995401	-2.4072370969
H	-2.7108877947	-3.8198483838	-3.720909121
H	-1.1434685328	-0.2202441	2.9617048778
H	-2.7188072148	1.1705383986	4.2850592434
H	-4.825363983	1.9904079605	3.2522017822
H	-1.347324033	-2.0624573021	-2.5842562445
H	-3.8064302162	0.0073393114	-0.420488447
H	-5.3573393059	1.4108128192	0.8931704997
H	-2.6184362427	5.0945850695	-0.4277596387
H	-1.3941787176	5.5233251961	1.6919784272
H	1.1510913416	2.139279536	0.9078013662
H	0.497476594	4.0506776393	2.3540242897
H	-1.9416822908	3.1866703455	-1.890366726
P	3.9125426821	-0.8473638277	0.6656541685
C	4.3251236485	-2.4973017168	1.3666341357
C	3.7153453796	-3.6268941219	0.7959278818
C	5.2165802705	-2.6707204102	2.4369589012
C	4.0063068773	-4.904803879	1.2758382077
H	3.0014456414	-3.5022127311	-0.0137319592
C	5.5001474743	-3.950458609	2.9191228921
H	5.6847059805	-1.8064668309	2.89924617
C	4.8983257876	-5.0686131239	2.3382628108
H	3.5253841639	-5.7696384753	0.8271891356
H	6.1902025816	-4.0718077267	3.749978145
H	5.1176906215	-6.0632758215	2.7170619678
C	4.3285829427	0.3338783267	2.0184287395
C	5.5175248258	1.0766432424	2.0524254044
C	3.3869542589	0.5056565558	3.0490489131
C	5.7639271109	1.9680201906	3.1004867472
H	6.2496216598	0.9649015051	1.2585047777
C	3.6411525976	1.3882958704	4.0984089701
H	2.4531100669	-0.0509585525	3.023111641
C	4.8299763806	2.1232518818	4.1254454882
H	6.6877751871	2.5403054712	3.112727452
H	2.9074789494	1.5081202047	4.8912952661
H	5.0237130758	2.8170411866	4.9391602167
C	5.1867767783	-0.5501144444	-0.6278883015
C	4.9076367686	0.4130501874	-1.6137397676
C	6.4050222264	-1.2463001195	-0.6738470659
C	5.8435123474	0.6841776245	-2.6131168672
H	3.9565910756	0.9388544282	-1.6124355512
C	7.3329687966	-0.9763416622	-1.6817784488
H	6.6261128337	-2.0055186208	0.0704423582
C	7.0554297633	-0.0090510052	-2.6499925788
H	5.6160295791	1.4294073111	-3.3702882888
H	8.2709055066	-1.5247797183	-1.7104716855
H	7.7778826268	0.1975974532	-3.4351945385
Pd	1.673351802	-0.6001037304	-0.144496735

Table S22. Cartesian coordinates of energy-optimized **A'**.

Atomic symbol	x	y	z
C	5.6518764883	-3.4669958472	-0.335033323
C	4.7356024501	-2.459269662	-0.6384951325
C	5.5585183117	-4.1579832779	0.8755971327
S	0.7385741677	-1.6584514089	-1.025140416
C	3.7129031447	-2.1435354756	0.2701716205
C	4.5455060707	-3.8433594786	1.7847826309
C	3.2031859957	0.1894517961	-2.5960398419
C	3.8645468783	1.1010073725	-3.4216700004
P	2.4469450165	-0.8763946308	-0.0911004349
C	3.2789101071	0.3223539485	-1.201299504
C	4.594900705	2.151352834	-2.8617239052
C	3.6216140669	-2.8429069571	1.4839137734
C	4.0056076278	1.384930279	-0.6405377816
C	4.6598681639	2.2940233596	-1.4736664403
C	1.630333395	-0.3220445974	1.2893565003
O	0.0958120851	1.3540003226	2.241120475
S	1.5680148139	0.9386310711	2.3721782876
C	1.0738390836	-1.3289336121	5.7268391512
O	2.5652537611	2.0219759853	2.2977529038
C	1.7022569645	0.289731607	4.0578112438
C	1.8685645384	-0.6602261489	6.6642530669
C	2.4969488009	0.9669229697	4.9841529592
C	2.5781281359	0.4825640428	6.2928841622
C	0.9894652499	-0.8586168248	4.4175487992
H	6.4433840863	-3.7060744448	-1.0400418158
H	4.8239765551	-1.9140840718	-1.5735090177
H	6.2776290996	-4.9379653003	1.1114106583
H	4.4763084933	-4.3755508575	2.7295924047
H	2.614776295	-0.6119204007	-3.0338905669
H	3.8009056247	0.9939568946	-4.5012605073
H	5.1033953971	2.8637919847	-3.5059160828
H	2.8305631896	-2.5857040602	2.1823206783
H	4.031846936	1.5267500903	0.4359795069
H	5.2108609263	3.1209676765	-1.0345396621
H	0.5227461594	-2.2198670027	6.0154300018
H	1.9349801596	-1.0336603648	7.6825959107
H	3.0388044827	1.8543505535	4.6753606852
H	3.1971363458	1.0012709483	7.0197668562
H	0.38896528	-1.3759189588	3.6755362511
P	-2.5588125499	-0.0238247905	-0.1086950753
C	-3.2369695013	-1.4648242399	-1.0298523502
C	-2.8162291831	-2.749510009	-0.6467810986
C	-4.1435337213	-1.3338729986	-2.0930474855
C	-3.3076186709	-3.8793807002	-1.3021492563
H	-2.0915261946	-2.8620053317	0.1551562937
C	-4.6277092938	-2.4664175124	-2.7518809804
H	-4.4665290617	-0.3474610892	-2.4123715569
C	-4.2135383688	-3.7397099419	-2.356493594
H	-2.9715947722	-4.8666517741	-0.9971516643
H	-5.3267211377	-2.3513026013	-3.5760895818
H	-4.5886446133	-4.6193381179	-2.8727286022
C	-2.8315953551	1.4136686897	-1.2252398709
C	-3.9874995742	2.2079077874	-1.1826153454
C	-1.8205469076	1.7251429392	-2.1506113865
C	-4.1338930305	3.2871469185	-2.0572811703
H	-4.7696261113	1.9904573442	-0.4611089405
C	-1.9739498533	2.7998643066	-3.0267505145
H	-0.9106913948	1.130655235	-2.1742127717
C	-3.1301264525	3.5829062073	-2.9813373367

H	-5.0315924251	3.8981602195	-2.0122208874
H	-1.1841551262	3.032448212	-3.7358216415
H	-3.2441629777	4.4258148409	-3.6577555678
C	-3.7303227645	0.2381614679	1.2866883688
C	-3.298853367	1.0397952935	2.3591807763
C	-5.0120269646	-0.3319306434	1.3290891634
C	-4.1471174337	1.2783060385	3.4411981291
H	-2.2987423676	1.4656305836	2.3565841323
C	-5.8526010006	-0.0964655255	2.4197196793
H	-5.3523361106	-0.9651698271	0.5151721913
C	-5.4234949666	0.7110098579	3.4746171276
H	-3.8036608192	1.9007515701	4.2629432786
H	-6.8420628993	-0.5457019381	2.4429476463
H	-6.0786954628	0.8925156236	4.3225425967
Pd	-0.2899775995	-0.2196580277	0.6139234877

Table S22. Cartesian coordinates of energy-optimized **B**.

Atomic symbol	x	y	z
C	-2.6131315447	5.1187467751	-0.0619501113
C	-2.5846617451	3.7970543438	-0.5034292969
C	-2.3320210588	5.4163433153	1.2756369372
S	-0.7048973266	0.7837343302	-1.6109256633
C	-2.2717483435	2.7648170915	0.3955548583
C	-2.0181704264	4.3913970197	2.1696199148
C	-4.0101766172	-0.324474087	-1.827570049
C	-5.2809106936	-0.6564664042	-2.2946299425
P	-2.2048345937	1.0406479945	-0.1903806022
C	-3.8629356003	0.6754079833	-0.8522333209
C	-6.408257542	-0.0055685332	-1.7876501079
C	-1.9827456066	3.0644114033	1.732971143
C	-4.9990845792	1.3229746754	-0.3393362506
C	-6.2670514301	0.9797149546	-0.8082107656
C	-1.4486372515	0.0157901379	1.0299003251
O	-2.3270771621	-2.4088850288	0.1390437214
S	-2.2394436267	-1.5292337715	1.3250816823
C	0.7318388478	-3.8808097013	2.8282482545
O	-3.4784184255	-1.2542824	2.0820350502
C	-1.0891435367	-2.3466949293	2.4606133337
C	0.6774467517	-3.6042549018	4.1971191896
C	-1.1602111829	-2.0700674901	3.8275258347
C	-0.269667362	-2.7038705355	4.6956235434
C	-0.1574363498	-3.2539109556	1.9504604266
H	-2.853445985	5.9162452199	-0.7596874059
H	-2.8002789813	3.5690379348	-1.5443593059
H	-2.3562651897	6.4476141559	1.6176606447
H	-1.7979917897	4.6219420428	3.2083643637
H	-3.1359638204	-0.8457597041	-2.2030101722
H	-5.3899757088	-1.4308309914	-3.048453638
H	-7.3974554022	-0.2704427684	-2.1514187163
H	-1.7259329232	2.2567662653	2.4116516561
H	-4.8968513966	2.0860532345	0.425598595
H	-7.1430835811	1.4807442328	-0.405994514
H	1.4541714262	-4.5955024106	2.4432257322
H	1.363913318	-4.1006946698	4.8779455003
H	-1.9098663146	-1.3775016272	4.1963859805
H	-0.3202404941	-2.5013185877	5.7619588825
H	-0.1478202899	-3.472896444	0.8876008279

P	2.7804630208	-0.1616531853	-0.2115701394
C	3.3892897386	1.1194587568	-1.3825317575
C	2.7732274727	2.3815772891	-1.3566873995
C	4.4321816545	0.8870706013	-2.2927312375
C	3.2070893457	3.3964270137	-2.2111429745
H	1.9425903494	2.5615510335	-0.6800388798
C	4.8577362304	1.9021961698	-3.152122776
H	4.9076798328	-0.0883543058	-2.337012096
C	4.2488047534	3.1582421512	-3.1105425976
H	2.7205402412	4.3674790931	-2.1824396517
H	5.6633828966	1.7091378082	-3.8555286973
H	4.5792958423	3.9457153633	-3.7825682824
C	3.2786486951	-1.7653627545	-0.9696044897
C	4.515988422	-2.3798851339	-0.7211187709
C	2.3633787836	-2.3958818849	-1.830235127
C	4.8347145349	-3.5960617881	-1.3296016438
H	5.228101027	-1.9129831791	-0.0467542878
C	2.688329391	-3.6075197386	-2.4415997008
H	1.3930667284	-1.9406587374	-2.0126858501
C	3.9237491481	-4.2099595885	-2.1917305001
H	5.7951627223	-4.0632295634	-1.1280879346
H	1.9714820744	-4.084239793	-3.1044688231
H	4.1727896667	-5.1574928988	-2.6619347804
C	3.8751739614	-0.0033445155	1.2638736458
C	3.5212480318	-0.7266466158	2.4169449419
C	5.0071637485	0.8237054288	1.302524683
C	4.2935919184	-0.6372850806	3.574143795
H	2.6391893293	-1.3635853389	2.411076945
C	5.7727149594	0.920069601	2.4681221724
H	5.2896701401	1.3984011293	0.4258937622
C	5.4204232543	0.1894534677	3.6033286156
H	4.0089006863	-1.2054711556	4.4555184914
H	6.6450202425	1.568136222	2.4852238776
H	6.0166621275	0.2666342566	4.5085307089
Pd	0.4319300664	-0.0750477367	0.3363374637

5. References

[1] P. Schröter, V. H. Gessner, *Chem. Eur. J.* 2012, **18**, 11223-11227.

[2] G. M. Sheldrick, Acta Cryst. **2008**, *A64*, 112–122.

[3] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[4] a) A. D. J. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5662;b) C. Lee, W. Yang, R. Parr, *Phys. Rev. B* **1988**, *37*, 785.