Supporting informations for:

Synthesis, optical and redox properties of regioisomeric benzoheterocycles-fused pyrene.

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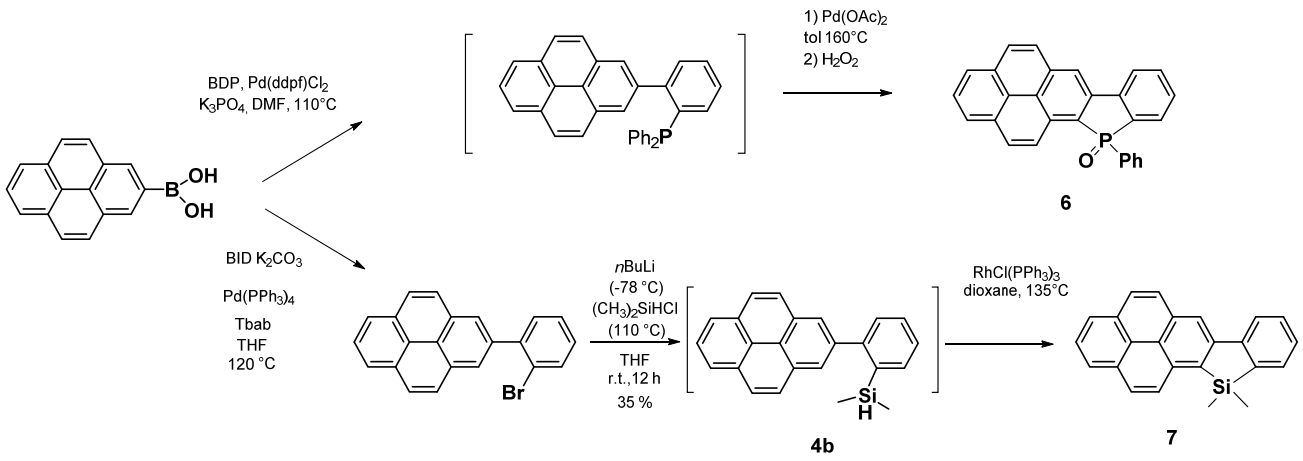
Synthesis scheme



Scheme S1: Synthetic route toward of **6-7**

Optical properties

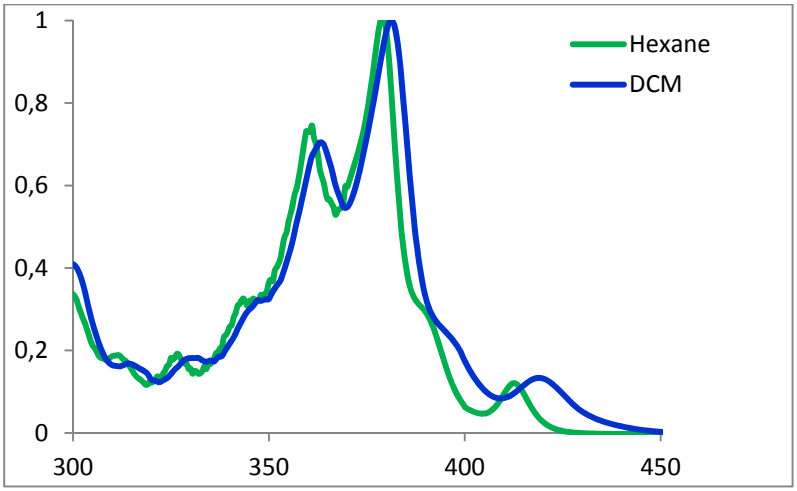


Figure S1: Absorption spectra of compound **3** in DCM and hexane.

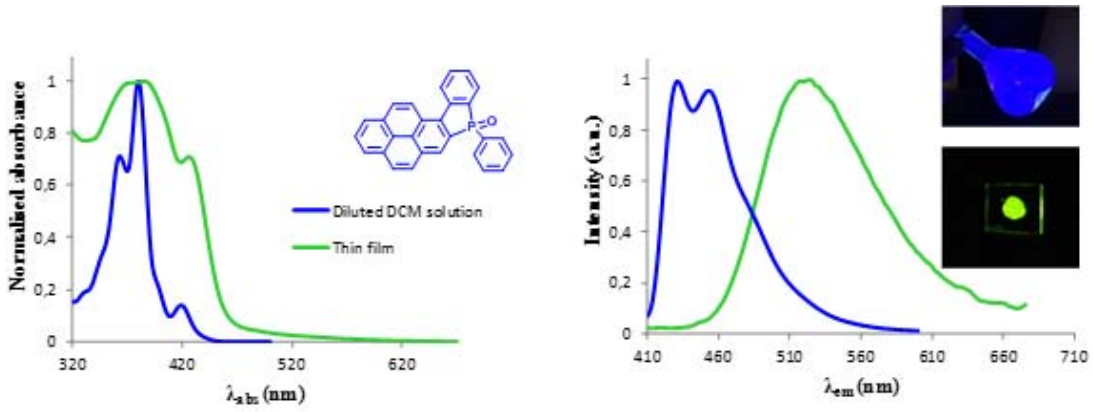


Figure S2: Diluted DCM (blue) and solid-state (green) absorption (left) and emission (right) spectra of compound **3.**

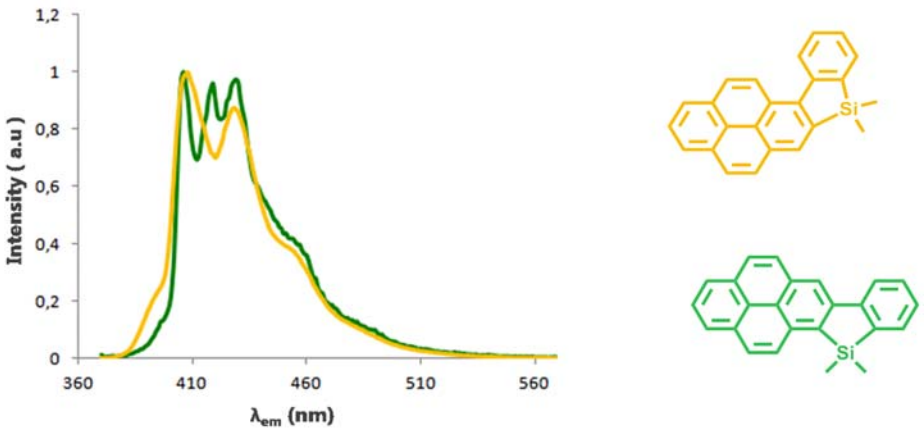


Figure S3: Emission **5** (yellow) and **7** (green) in DCM at r.t. (C = $5x10^{-5}$M)

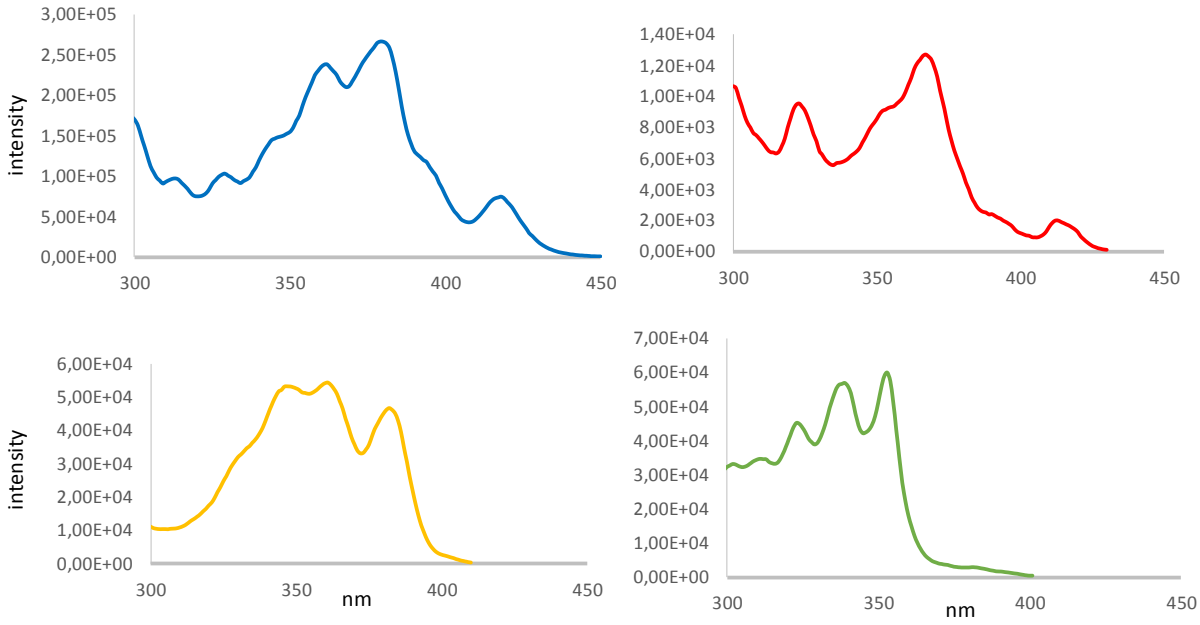


Figure S4: excitation spectra of **3** (top left), **6** (top right), **5** (bottom left) and **7** (bottom right) n DCM at r.t. (C = $5x10^{-5}$M)

X-ray Crystallographic Study

Crystal structure determination: Single crystals suitable for X-Ray crystal analysis were obtained by slow diffusion of vapors of pentane into a dichloromethane solution of the derivatives at room temperature. Single crystal data collection were performed at 150 K with with an APEX II Bruker-AXS diffractometer (Centre de Diffractométrie X , Institut des Sciences Chimiques de Rennes, UMR6226 CNRS-Université de Rennes 1, France) with Mo-*K*α radiation (λ = 0.71073 Å). The structure was solved by direct methods using the *SIR97* program,[1] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*)[2] with the aid of the *WINGX*[3] program. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions.

[1] Altomare, A. ; Burla, M. C. ; Camalli, M. ; Cascarano, G. ; Giacovazzo, C. ; Guagliardi, A. ; Moliterni, A. G. ; Polidori, G.G. ; Spagna, R. *SIR97: a new tool for crystal structure determination and refinement*, *J. Appl. Cryst.* **1999**, 32, 115-119

[2] Sheldrick G.M., *A short history of SHELX*, *Acta Cryst.*, **2008**, *A64*, 112-122

[3] Farrugia, L. J., *WinGX and ORTEP for Windows: an update*, *J. Appl. Cryst.*, **2012**, *45*, 849-854

Table S1: Crystal data and structure refinement

Compound	**3**	**6**	**5**
CCDC Number	1819755	1820256	1819756
Molecular formula Extended formula	$C_{28}H_{17}OP$	$C_{57}H_{40}O_4Cl_2P_2$ $2(C_{28}H_{17}OP)$, CH_2Cl_2, $2(H_2O)$	$C_{24}H_{18}Si$
Molecular weight	400.39	921.73	334.47
a (Å)	16.2996(9)	9.3936(8)	9.0297(3)
b (Å)	9.0953(5)	11.2389(11)	10.1542(3)
c (Å)	13.4799(6)	11.6385(11)	19.3621(6)
α (°)	90	114.260(4)	90
β (°)	101.291(2)	97.195(4)	90
γ (°)	90	92.441(4)	90
V (Å3)	1959.71(18)	1105.37(18)	1775.30(10)
Z	4	1	4
*D*c (g.cm-3)	1.357	1.385	1.251
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	P 2_1/c	P -1	P 2_1 2_1 2_1
Temperature (K)	150(2)	150(2)	150(2)
Wavelenght Mo-Kα (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	0.16x0.12x0.06	0.6x0.59 x0.46	0.57x 0.48x0.35
μ (mm-1)	0.158	0.270	0.135
F (000)	832	478	704
θ limit (°)	3.08 to 27.48	2.99 to 27.48	3.019 to 27.522
Index ranges *hkl*	$-21 \le h \le 21$ $-11 \le k \le 11$ $-17 \le l \le 13$	$-12 \le h \le 12$ $-14 \le k \le 14$ $-15 \le l \le 15$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-24 \le l \le 25$
Reflections collected	15502	11252	27809
Independant reflections	4484	5012	4086
Reflections [$I>2\sigma(I)$]	2305	3742	3883
Data / restraints / parameters	4484 / 0 / 271	5012 / 0 / 304	4086 / 0 / 228
Goodness-of-fit on *F*2	1.01	1.075	1.047
Final *R* indices [I>2σ(I)]	*R*1= 0.0602 *wR*2 = 0.1297	*R*1 = 0.0544 *wR*2 = 0.1308	*R*1 = 0.0303 *wR*2 = 0.0812
R indices (all data)	*R*1 = 0.129 *wR*2 = 0.1584	*R*1 = 0.0748 *wR*2 = 0.1424	*R*1 = 0.0325 *wR*2 = 0.0830

Figure S5: ORTEP representation of **3** with 50% probability ellipsoids

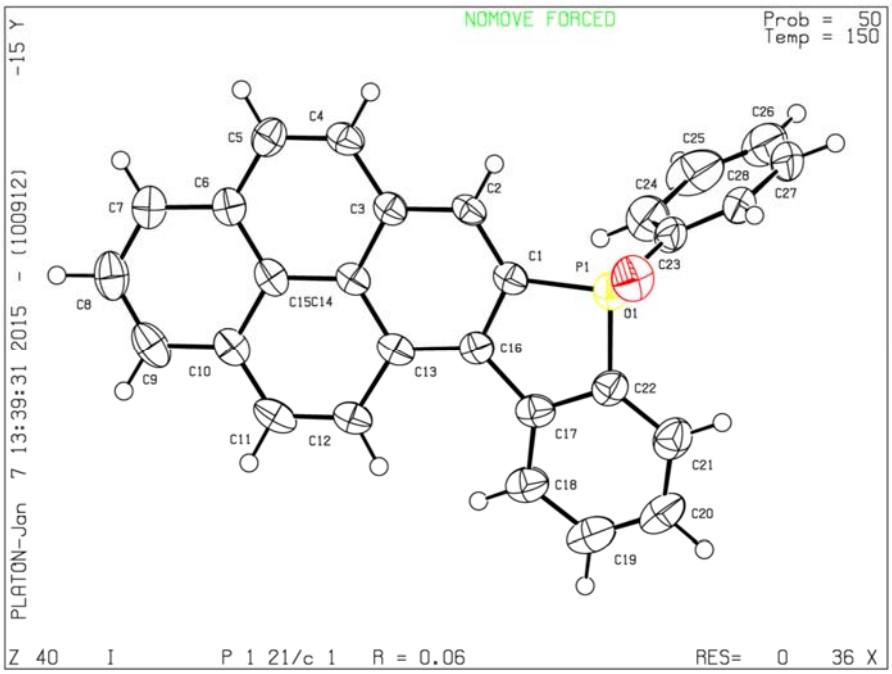


Figure S6: view of the 2 enantiomers of **3** in the structure

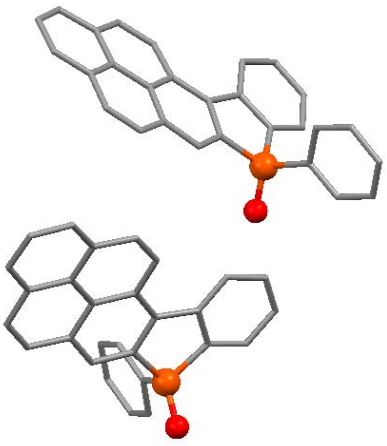


Figure S7: ORTEP representation of **6** with 50% probability ellipsoids

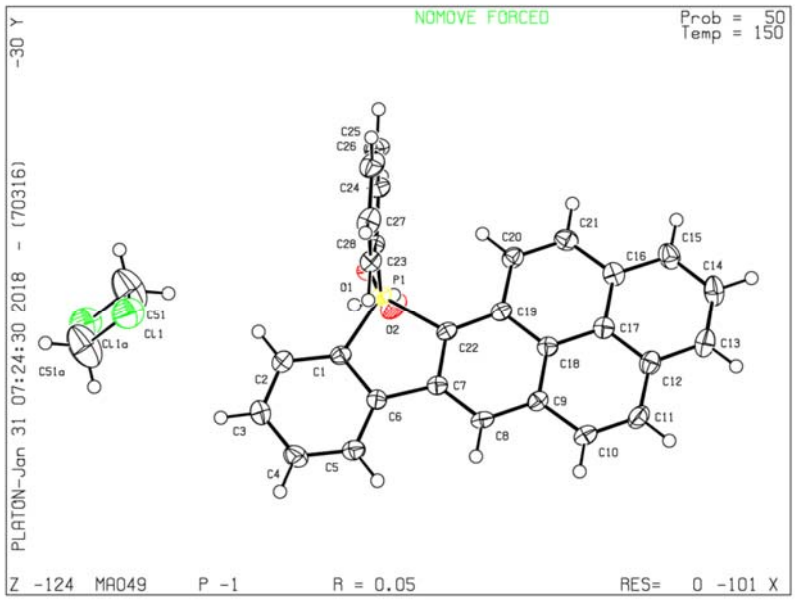


Figure S8: ORTEP representation of **5** with 50% probability ellipsoids

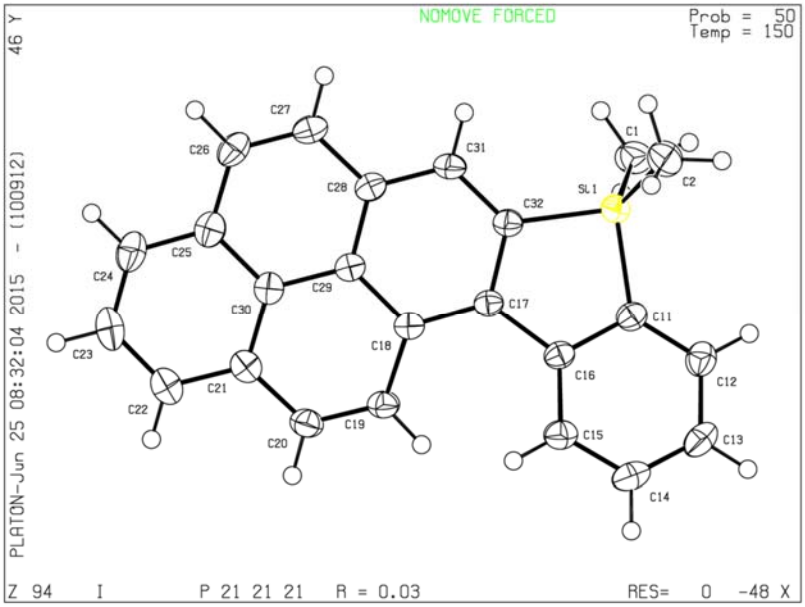
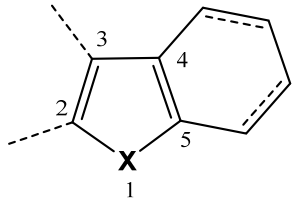


Table S2: selected bond lengths (Å)



	X-C_2	C_2-C_3	C_3-C_4	C_4-C_5	X-C_5
3	1.79	1.41	1.49	1.42	1.78
6	1.79	1.41	1.48	1.41	1.79
5	1.85	1.42	1.50	1.42	1.87

Theoretical calculations :

In our previous investigations of P-containing PAHs, we found that TD-DFT calculations using the vertical approximation at the B3LYP/6-31+G* level reproduced well the absorption band maxima, and gave also a satisfactorily description for emission properties.[4] However, previous investigations using the TD-DFT method for the parent pyrene showed that even though the reproduction of the high intensity (S0->S2 transition) band (referred to as L_a in the literature) is good, the excitation energy for the low intensity band (referred to as L_b) is overestimated due to the method's deficiency to describe the energies of states with ionic components. Approximate coupled-cluster linear response theory (CC2) calculations, however predicted the proper ordering and a proper separation of the two transitions, thus we have carried out also CC2/cc-pVDZ calculations. Our results are in accordance with the previous results on the parent compounds. Both methods describe the intense L_a bands basically as HOMO→LUMO transitions, while the L_b bands have their major contributions from HOMO-1→LUMO and HOMO→LUMO+1 transitions, in agreement with previous results on pyrenes.[5] According to the TD-DFT calculations, the position of the large intensity bands match well with experimental data (see Table S3), the low intensity bands are always predicted at lower wavelengths for all the investigated systems. Table S4 shows that the energy difference between the L_a and L_b bands is predicted significantly better by the CC2 method, however it should be noted that the absolute positions of the peaks are systematically blue-shifted by ~0.4 eV from the experimental values. Using the difference between the calculated and the measured[6] gas phase absorption spectral data for the parent pyrene as corrections (the TD-DFT correction is +0.05 eV for the ^1L_a band and -0.4 eV for the ^1L_b band), we predict the band positions, by both methods, as is shown in Figure 3 in the main article. Using this procedure the CC2 data are in good agreement

[4] (a) Bouit, P.-A. , Escande, A.; Szűcs, R.; Szieberth, D.; Lescop, C.; Nyulászi, L.; Hissler M.; Réau, R.; *Dibenzophosphapentaphenes: Exploiting P Chemistry for Gap Fine-Tuning and Coordination-Driven Assembly of Planar Polycyclic Aromatic Hydrocarbons*, *J. Am. Chem. Soc.* **2012**, *134*, 6524-6527; (b) Delaunay, W.; Szűcs, R.; Pascal, S.; Mocanu, A.; Bouit, P. A.; Nyulászi, L.; Hissler, M.; *Synthesis and electronic properties of polycyclic aromatic hydrocarbons doped with phosphorus and sulfur*, *Dalton Trans.* **2016**, *45*, 1896-1903; (c) Szűcs, R.; Riobé, F.; Escande, A.; Joly, D.; Bouit, P.-A.; Nyulászi, L.; Hissler, M. ; *Strategies toward phosphorus-containing PAHs and the effect of P-substitution on the electronic properties; Pure Appl. Chem.* **2017**, *88(3),* 341-356; (d) Riobé, F. ; Szűcs, R. ; Bouit, P.-A. ; Tondelier, D. ; Geffroy, B. ; Aparicio, F.; Buendía, J.; Sánchez, L. ; Réau, R. ; Nyulászi, L.; Hissler; M., *Synthesis, electronic properties and WOLED devices of planar phosphorus-containing polycyclic aromatic hydrocarbons*; *Chem. Eur. J.* **2015**, *21,* 6547-6556.

[5] See reference 3 in the article, and Parac, M. and Grimme, S.; *Double-hybrid density functional theory for excited electronic states of molecules*; *Chem. Phys*. **2003**, *292*, 11–21.

[6] Crawford, A. G.; Dwyer, A. D.; Liu, Z.; Steffen, A.; Beeby, A.; Pålsson, L.-O.: Tozer, D. J.; Marder, T. B.; *Experimental and theoretical studies of the photophysical properties of 2- and 2,7-functionalized pyrene derivatives; J. Am. Chem. Soc.,* **2011**, *133*, 13349.

with the calculations, and TD DFT performs well also for the bent system. However, TD DFT prediction fails even with the corrections for the L_b bands of the linear (see Fig. 3). It was noted by Grimme[5] that the correction fails for π-systems with different size, and indeed, as we discussed above, the FMO-s are located at the pyrene part, while the HOMO-1 and LUMO+1 (all involved in the L_a excitation) are fully delocalized over the entire molecule. The red shift of the L_a bands in case of **3** and **5** with respect to the linear analogues (**6**-**7**) and also in comparison to the L_b bands is reproduced by the calculations, and is related to the above-mentioned reduction of the HOMO-LUMO gap (L_a bands are described basically as HOMO-LUMO excitations). We have also calculated the absorption spectra using the PCM solvent model with hexane and dichloromethane, but have observed only a small solvent shift.

Table S3: Measured band maxima and calculated (TD DFT and CC2) vertical excitation wavelengths (in nm) for the intense (L_a), and low intensity (L_b) absorptions. The calculated oscillator strentghs are given in parenthesis.

	λ_{max}	log ε	$\lambda_{abs}^{TD\ DFT}$	λ_{abs}^{CC2}
3	381	4.94 (L_a)	394 (0.4443)	340 (0.6349)
	419	4.06 (L_b)	371 (0.0844)	361 (0.0636)
6	368	4.04 (L_a)	368 (0.1642)	327 (0.3491)
	413	3.34 (L_b)	379 (0.0540)	361 (0.0149)
5	384	4.26 (L_a)	389 (0.5454)	341 (0.7122)
	403	2.94 (L_b)	365 (0.0109)	355 (0.0087)
7	354	4.44 (L_a)	358 (0.2142)	316 (0.3663)
	405	2.64 (L_b)	373 (0.0006)	357 (0.0011)

Table S4: Energy difference between the L_a and L_b type absorption band

	ΔE (eV) experimental	ΔE (eV) B3LYP/6-31+G*	ΔE (eV) CC2/cc-pVDZ
3	0.30	-0.19	0.21
6	0.37	0.09	0.36
5	0.15	-0.21	0.15
7	0.44	0.15	0.44

It is noteworthy that both TD-DFT and CC2 calculations give good predictions for the changes of the relative intensity of the L_b band of the different P and Si derivatives. (see Table S2).

All calculations, except CC2 investigations were carried out with the Gaussian 09 program package.[7]

Full geometry optimization was performed for all molecules at the B3LYP/6-31+G* level and subsequently harmonic vibrational frequencies were calculated at the same level to establish the nature of the stationary point obtained, for minima no negative eigenvalue of the Hessian was present. The optimised geometries match well with the X-ray structure where it is available. TD-DFT calculations have been carried out at the same level of theory. Molecular orbitals have been visualized with the VMD package.[8] RI-CC2 calculations[9] have been carried out with the Turbomole 5.10 program package[10] using cc-pVDZ basis set, utilizing geometries optimised by the Gaussian 09 program package at the B3LYP/cc-pVDZ level. The emission clearly stems from the low intensity (L_b) state, which is poorly described by the TD DFT calculations, the vertical emission energies utilizing the TD DFT optimized minima of the second excited states are also poorly described, thus we provide these data in the SI, but do not discuss them further.

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

[8] Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", *J. Molec. Graphics*, **1996**, *14*, 33-38.

[9] Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C.; *Electronic structure calculations on workstation computers: The program system turbomole*; *Chem. Phys. Lett.* **1989**, 162-165.

[10] TURBOMOLE (Ver.5.1) Ahlrichs, R.; Bär, M.; Baron H.-P. et al., Universität Karlsruhe (2003).

Vertical excitation energies obtained at the geometry of the ground state

Pyrene

λ_a (nm)	Intensity	Transition	Coefficient	Correction
339	0.2757	HOMO-1 → LUMO+1	-0.212	+ 0.05 eV
		HOMO → LUMO	0.672	
332	0.0003	HOMO-1 → LUMO	0.475	- 0.4 eV
		HOMO → LUMO+1	0.522	

3 – gas phase

λ_a (nm)	Intensity	Transition	Coefficient
394	0.4443	HOMO-1 → LUMO+1	-0.141
		HOMO → LUMO	0.646
		HOMO → LUMO+1	-0.235
371	0.0844	HOMO-1 → LUMO	0.368
		HOMO → LUMO	0.218
		HOMO → LUMO+1	0.550

3 – PCM: hexane

λ_a (nm)	Intensity	Transition	Coefficient
403	0.6258	HOMO-1 → LUMO+1	0.117
		HOMO → LUMO	0.668
		HOMO → LUMO+1	0.187
373	0.0919	HOMO-1 → LUMO	-0.340
		HOMO → LUMO	-0.174
		HOMO → LUMO+1	0.585

3 – PCM: DCM

λ_a (nm)	Intensity	Transition	Coefficient
406	0.6042	HOMO-1 → LUMO+1	-0.115
		HOMO → LUMO	0.662
		HOMO → LUMO+1	-0.207
375	0.1278	HOMO-1 → LUMO	0.316
		HOMO → LUMO	0.197
		HOMO → LUMO+1	0.591

5

λ_a (nm)	Intensity	Transition	Coefficient
389	0.5454	HOMO-1 → LUMO+1	-0.134
		HOMO → LUMO	0.683
365	0.0109	HOMO-1 → LUMO	0.402
		HOMO → LUMO+1	0.566

6

λ_a (nm)	Intensity	Transition	Coefficient
379	0.054	HOMO-1 → LUMO	-0.427
		HOMO-1 → LUMO+1	-0.108
		HOMO → LUMO	-0.325
		HOMO → LUMO+1	0.437
368	0.1642	HOMO-1 → LUMO	-0.347
		HOMO-1 → LUMO+1	0.185
		HOMO → LUMO	0.560
		HOMO → LUMO+1	0.124

7

λ_a (nm)	Intensity	Transition	Coefficient
373	0.0006	HOMO-1 → LUMO	0.543
		HOMO → LUMO+1	-0.441
358	0.2142	HOMO-1 → LUMO+1	0.233
		HOMO → LUMO	0.649

Calculations of the emissive excited states by TD DFT calculations

Pyrene - First excited state

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
367	0.3426	HOMO-1 ← LUMO+1	0.176	361
		HOMO ← LUMO	0.684	

Pyrene - Second excited state

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
348	0.0007	HOMO-1 ← LUMO	0.467	392
		HOMO ← LUMO+1	-0.530	

3 - Gas phase– First Excited state, -1493.80237662 Hartree

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
448	0.4779	HOMO-1 ← LUMO+1	0.108	440 nm
		HOMO ← LUMO	-0.669	
		HOMO ← LUMO+1	0.197	

3 - Gas phase– Second Excited state, -1493.79173091 Hartree

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
392	0.0959	HOMO-1 ← LUMO	-0.348	449 nm
		HOMO ← LUMO	-0.233	
		HOMO ← LUMO+1	-0.559	

3 – PCM: Hexane– First Excited state, -1493.811492 Hartree

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
464	0.6689	HOMO ← LUMO	0.684	456 nm
		HOMO ← LUMO+1	-0.154	

3 - PCM: Hexane – Second Excited state, -1493.798507 Hartree

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
395	0.1121	HOMO-1 ← LUMO	-0.310	453 nm
		HOMO ← LUMO	-0.197	
		HOMO ← LUMO+1	-0.596	

3 – PCM: DCM– First Excited state, -1493.82516 Hartree

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
493	0.9522	HOMO ← LUMO	0.696	484
		HOMO ← LUMO+1	-0.105	

3 - PCM: DCM – Second Excited state, -1493.808906 Hartree

λ_e (nm)	Intensity	Transition	Coefficient	Corrected
403	0.1507	HOMO-1 ← LUMO	0.244	463
		HOMO ← LUMO	0.153	
		HOMO ← LUMO+1	0.639	

5 – First Excited state

λ_e (nm)	Intensity	Transition	Coefficient
438	0.6159	HOMO ← LUMO	0.692

5 – Second Excited state

λ_e (nm)	Intensity	Transition	Coefficient
386	0.0227	HOMO-1 ← LUMO	-0.382
		HOMO ← LUMO	-0.116
		HOMO ← LUMO+1	0.575

6 – First Excited state

λ_e (nm)	Intensity	Transition	Coefficient
408	0.0929	HOMO-1 ← LUMO	0.262
		HOMO-1 ← LUMO+1	-0.152
		HOMO ← LUMO	0.482
		HOMO ← LUMO+1	0.410

6 – Second Excited state

λ_e (nm)	Intensity	Transition	Coefficient
400	0.0668	HOMO-1 ← LUMO	0.477
		HOMO-1 ← LUMO+1	-0.122
		HOMO ← LUMO	0.472
		HOMO ← LUMO+1	0.150

7 – First Excited state

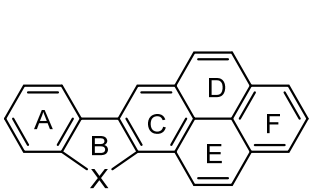
λ_e (nm)	Intensity	Transition	Coefficient
398	0.0016	HOMO-1 ← LUMO	0.558
		HOMO ← LUMO+1	-0.424

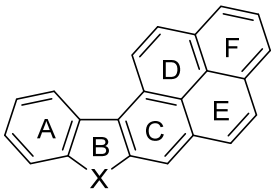
7 – Second Excited state

λ_e (nm)	Intensity	Transition	Coefficient
386	0.3149	HOMO-1 ← LUMO+1	0.161
		HOMO ← LUMO	0.670

Aromaticity calculations

Table S5: NICS(0) and NICS(1) aromaticity (B3LYP/6-31+G*)



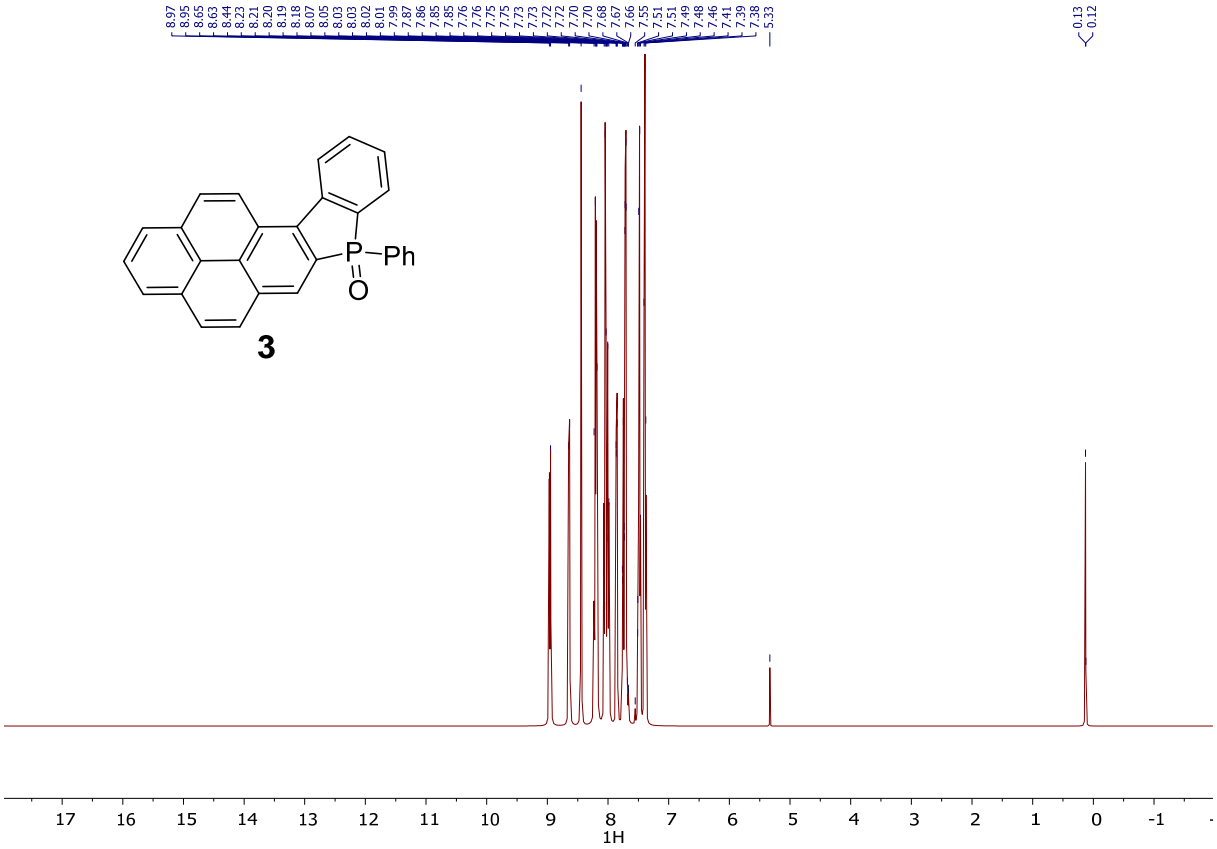


	3		**6**		**5**		**7**	
	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)	NICS(0)	NICS(1)
A	-5.9	-8.1	-5.7	-7.9	-5.6	-8.2	-5.6	-8.2
B	5.3	2.3	4.9	2.2	5.2	1.6	4.8	1.5
C	-9.8	-11.3	-9.9	-11.5	-9.6	-11.7	-9.7	-11.7
D	-4.0	-6.9	-4.0	-6.9	-4.0	-6.9	-3.8	-6.8
E	-3.7	-6.6	-3.8	-6.9	-3.4	-6.5	-3.5	-6.6
F	-11.0	-12.6	-11.2	-12.8	-11.0	-12.5	-10.9	-12.6

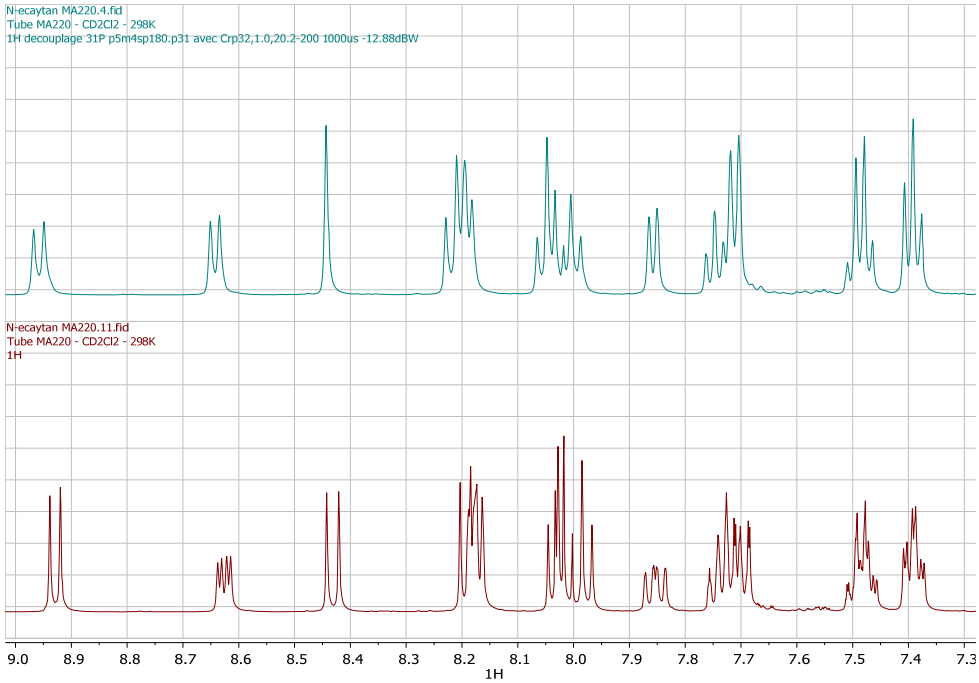
NMR spectra

For compound 3

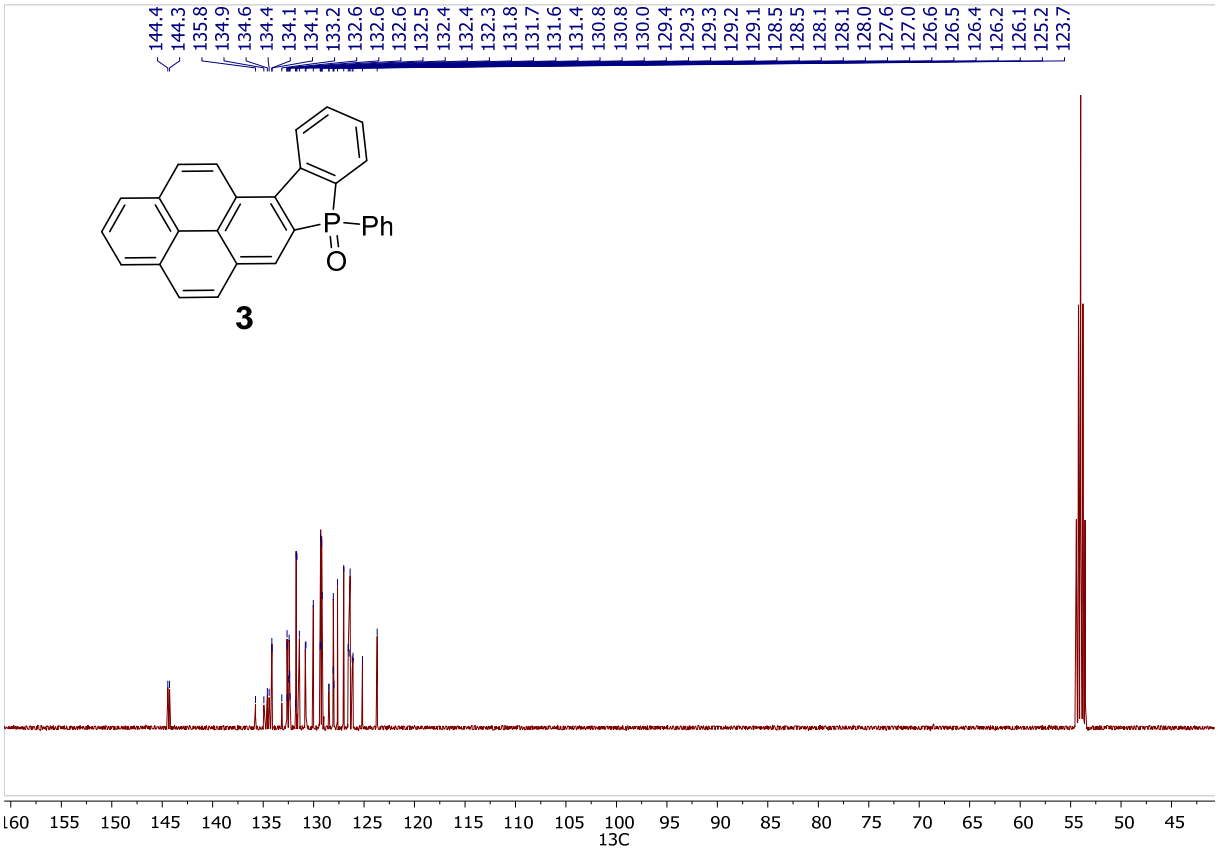
a)



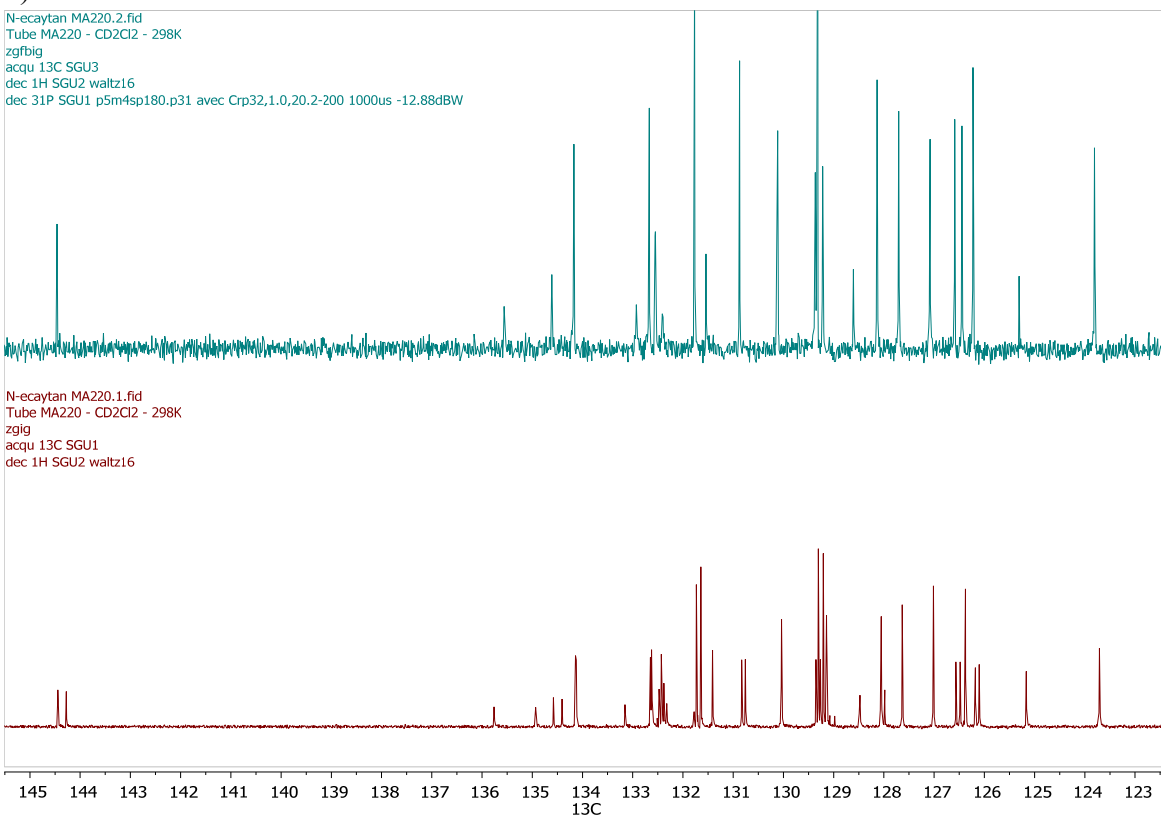
b)


N-ecaytan MA220.4.fid
Tube MA220 - CD2Cl2 - 298K
1H decouplage 31P p5m4sp180.p31 avec Crp32,1:0,20.2-200 1000us -12.88dBW
N-ecaytan MA220.11.fid
Tube MA220 - CD2Cl2 - 298K
1H
9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
1H

c)


144.4 144.3 135.8 134.9 134.6 134.4 134.1 134.1 133.2 132.6 132.6 132.5 132.4 132.4 132.3 131.8 131.7 131.6 131.4 130.8 130.8 130.0 129.4 129.3 129.3 129.2 129.1 128.5 128.5 128.1 128.1 128.0 127.6 127.0 126.6 126.5 126.4 126.2 126.1 125.2 123.7
P
Ph
O
3
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
13C

d)



e)

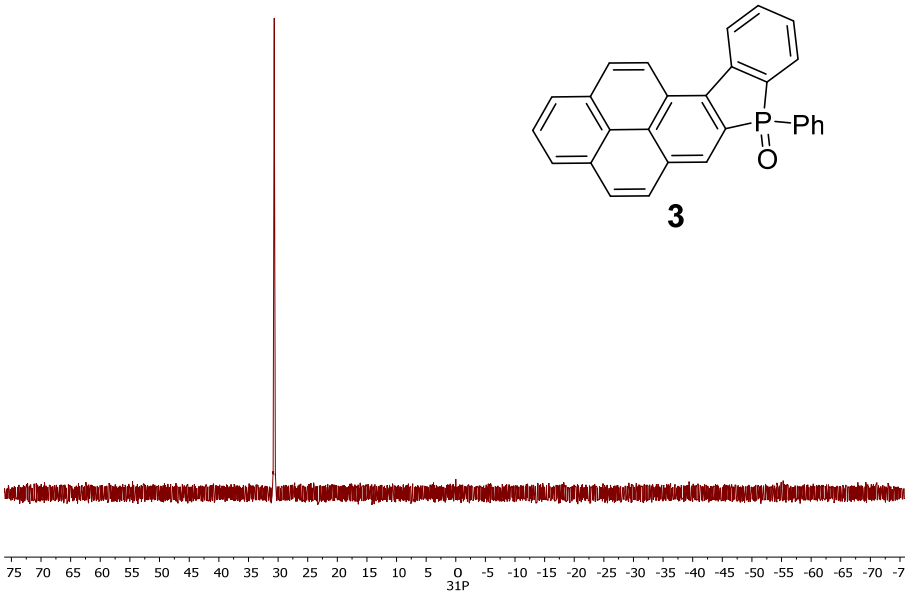
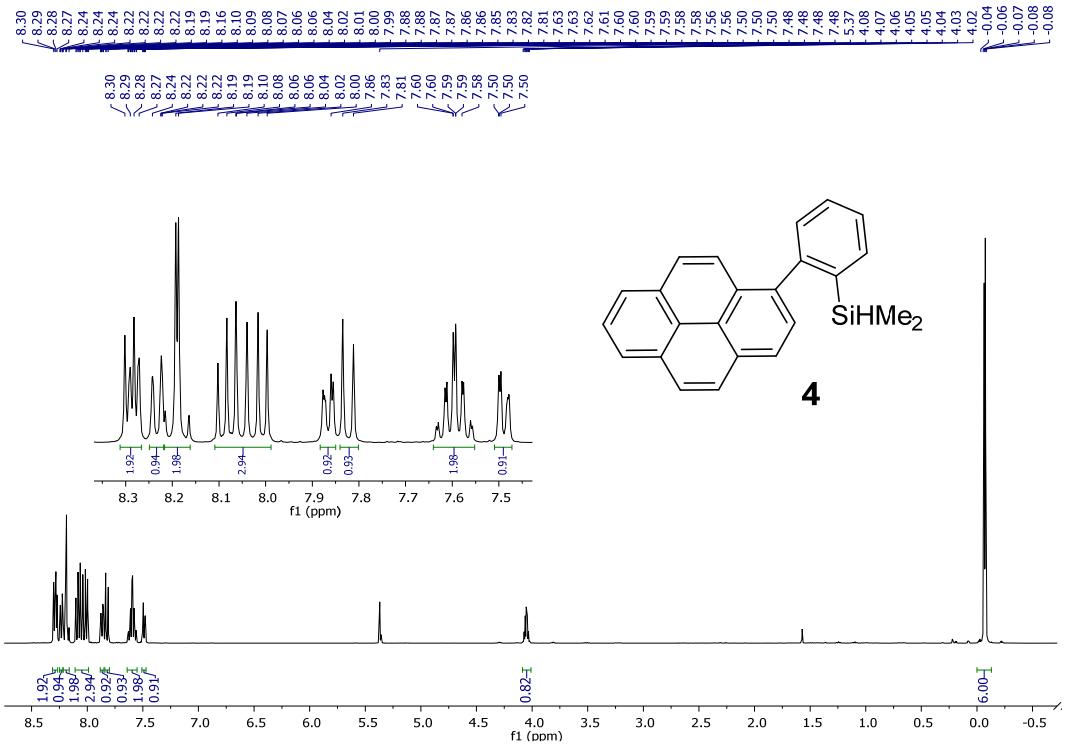


Figure S9: a) ^{1}H NMR (500 MHz, CD_2Cl_2), b) Expanded $^{1}H\{^{31}P\}$ NMR (500 MHz, CD_2Cl_2) and Expanded ^{1}HNMR (500 MHz, CD_2Cl_2), c) $^{13}C\{1H\}$ NMR (125.78 MHz, CD_2Cl_2, d) Expanded $^{13}C\{^{31}P\}\{1H\}$ NMR(125.78 MHz, CD_2Cl_2) and expanded $^{13}C\{1H\}$ NMR (125.78 MHz, CD_2Cl_2) e) $^{31}P\{^{1}H\}$ NMR (161.99 MHz, CD_2Cl_2): spectra of **3**.

For compound 4

a)



b)

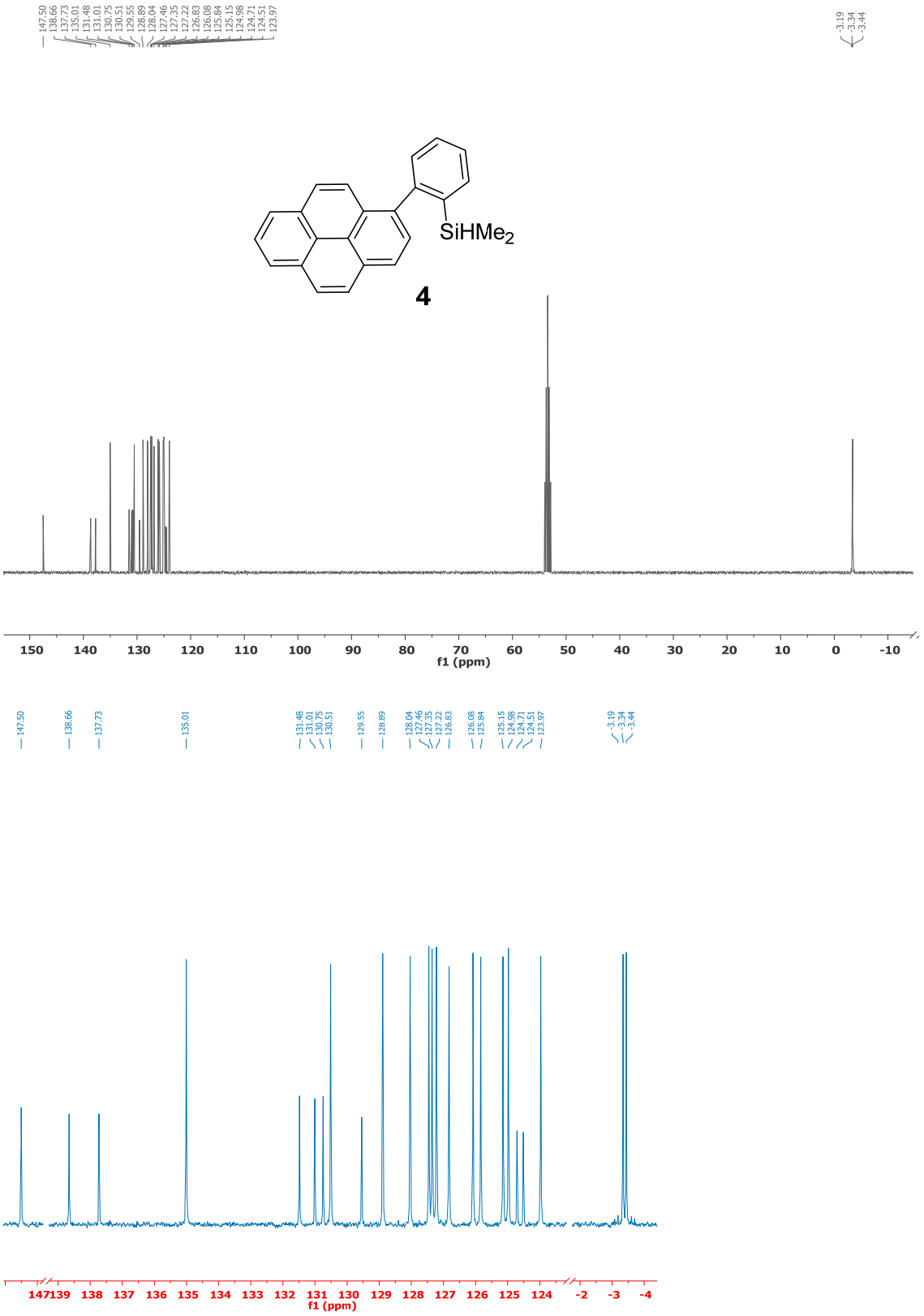
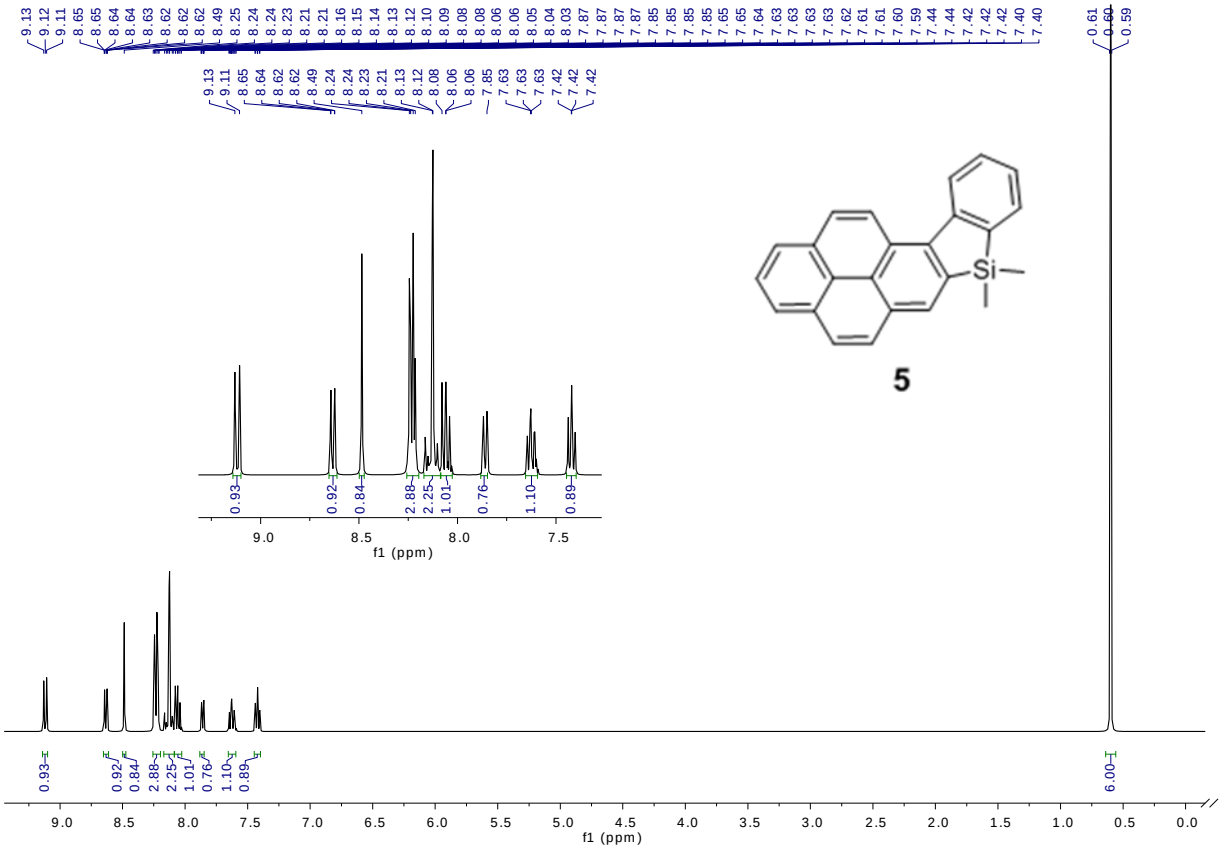


Figure S10: a) ^{1}H NMR (400 MHz, CD_2Cl_2), b) $^{13}C\{1H\}$ NMR (100.62 MHz,CD_2Cl_2) of **4**.

For compound 5

a)



b)

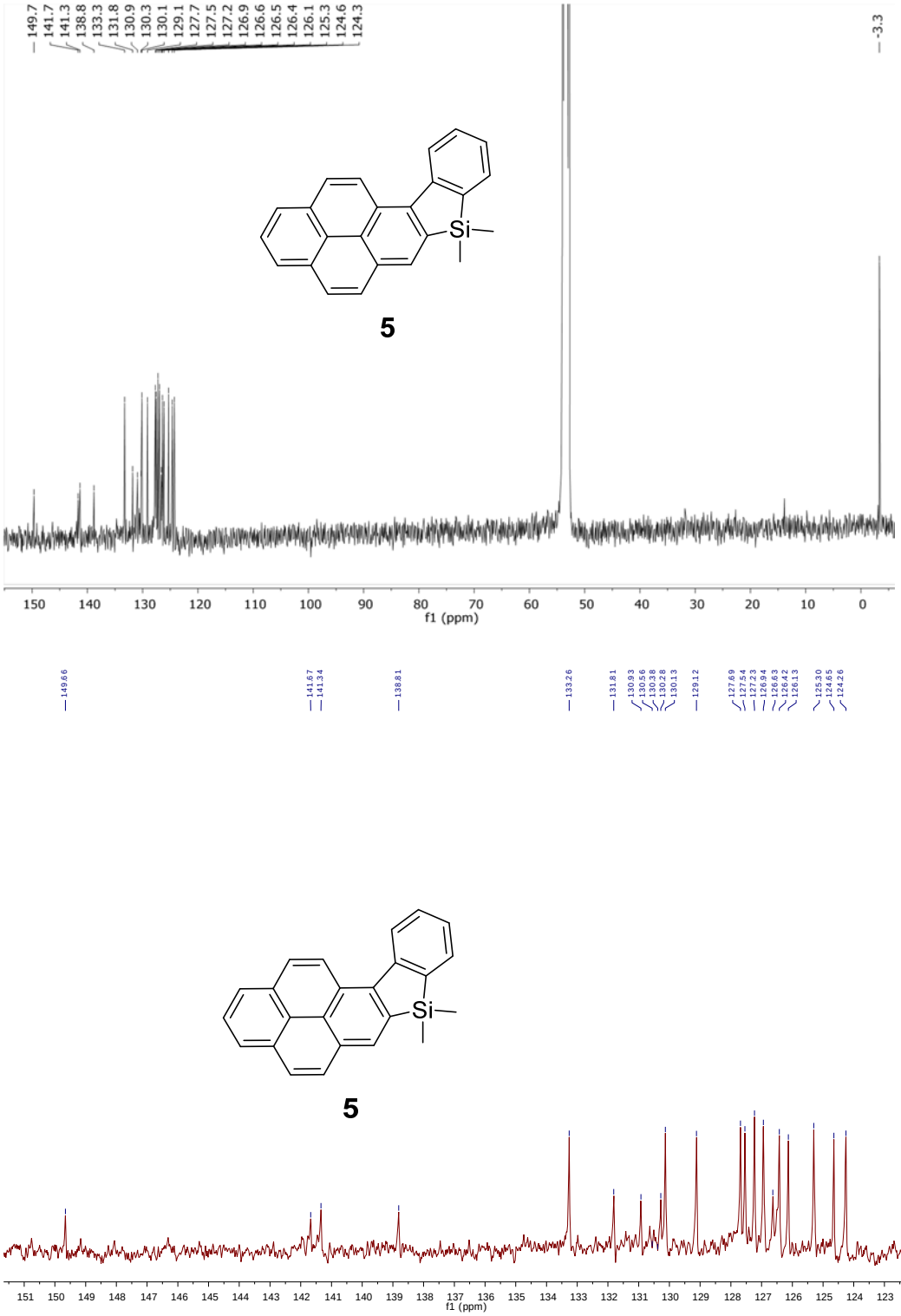
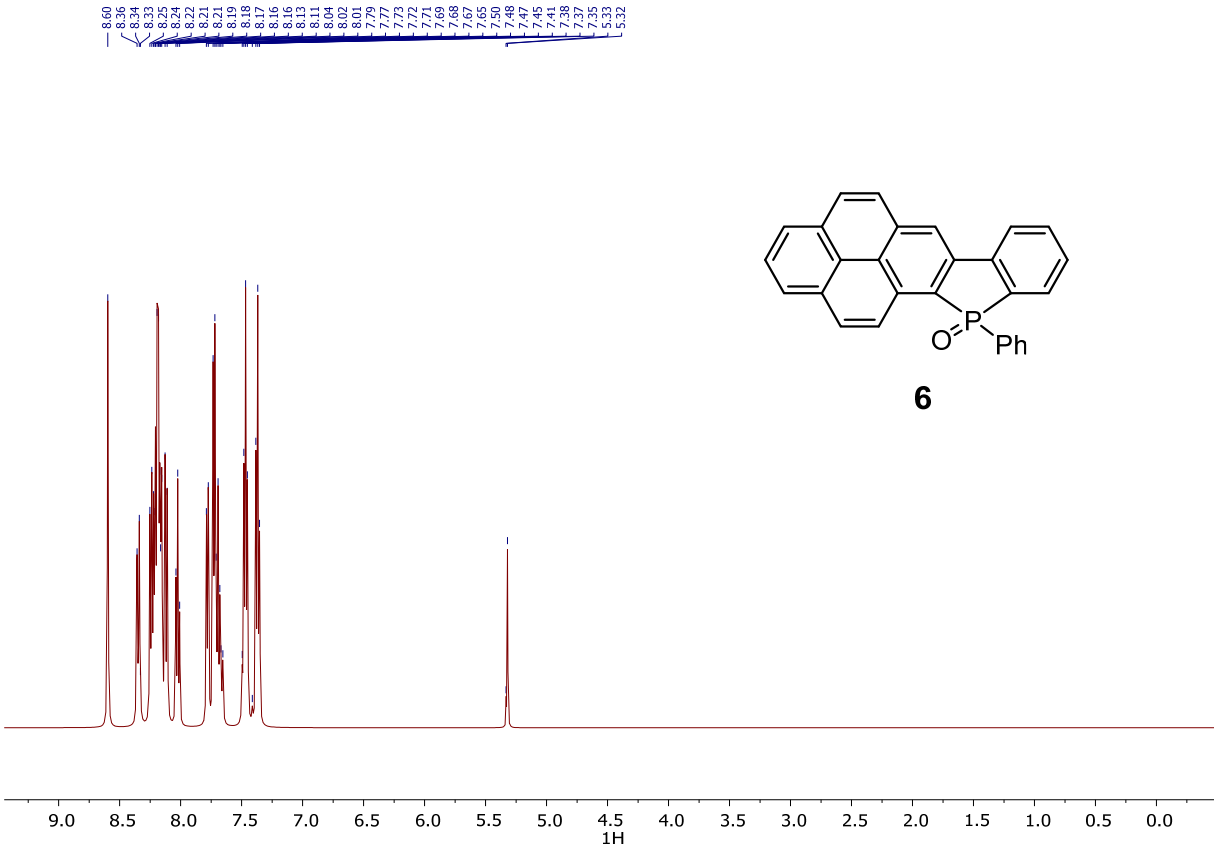


Figure S11: a) ^{1}H NMR (400 MHz, CD_2Cl_2), b) $^{13}C\{1H\}$ NMR (100.62 MHz, CD_2Cl_2) of **5**.

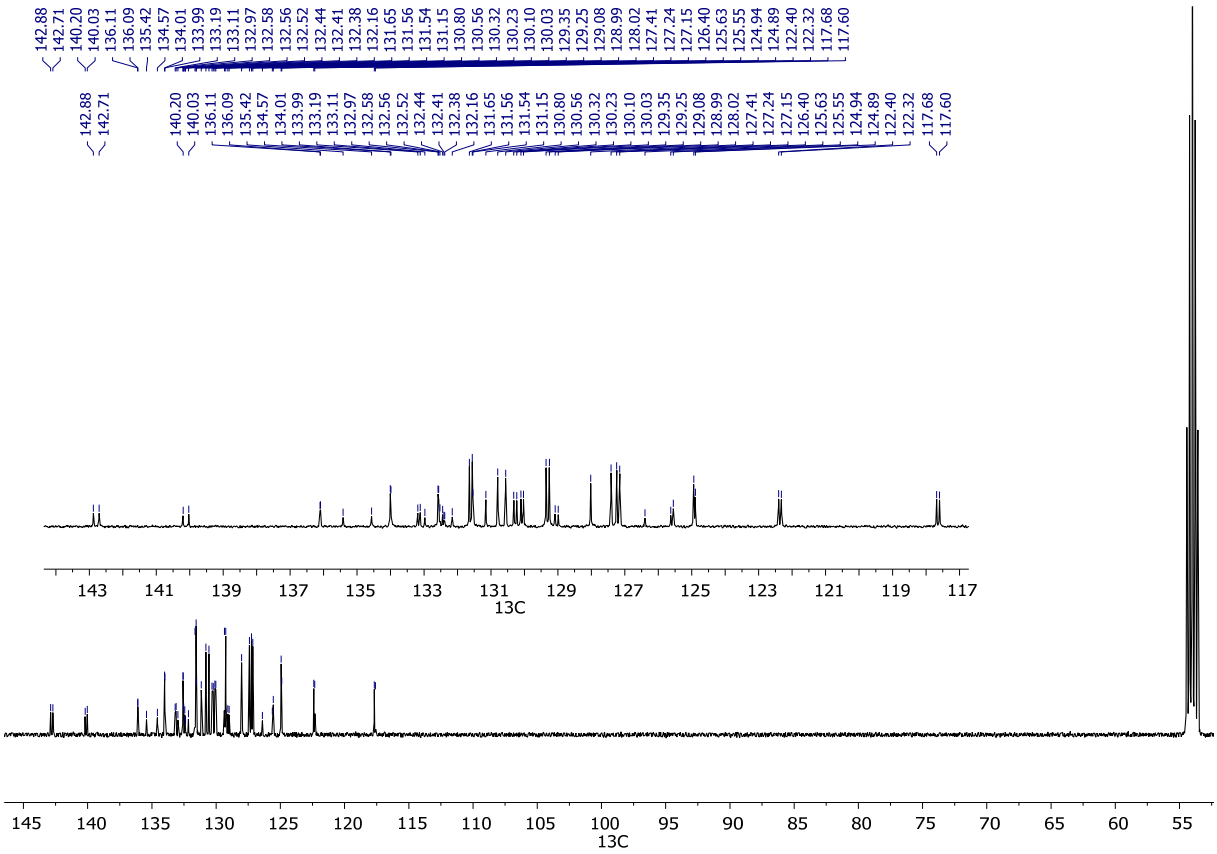
For compound 6

a)

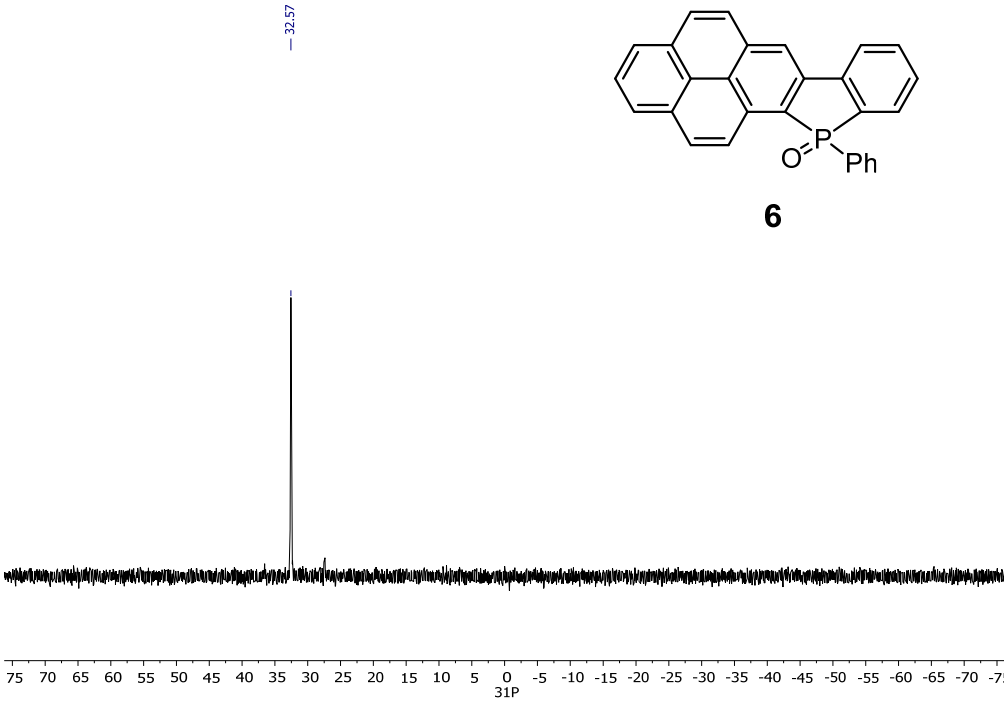


6

b)



c)

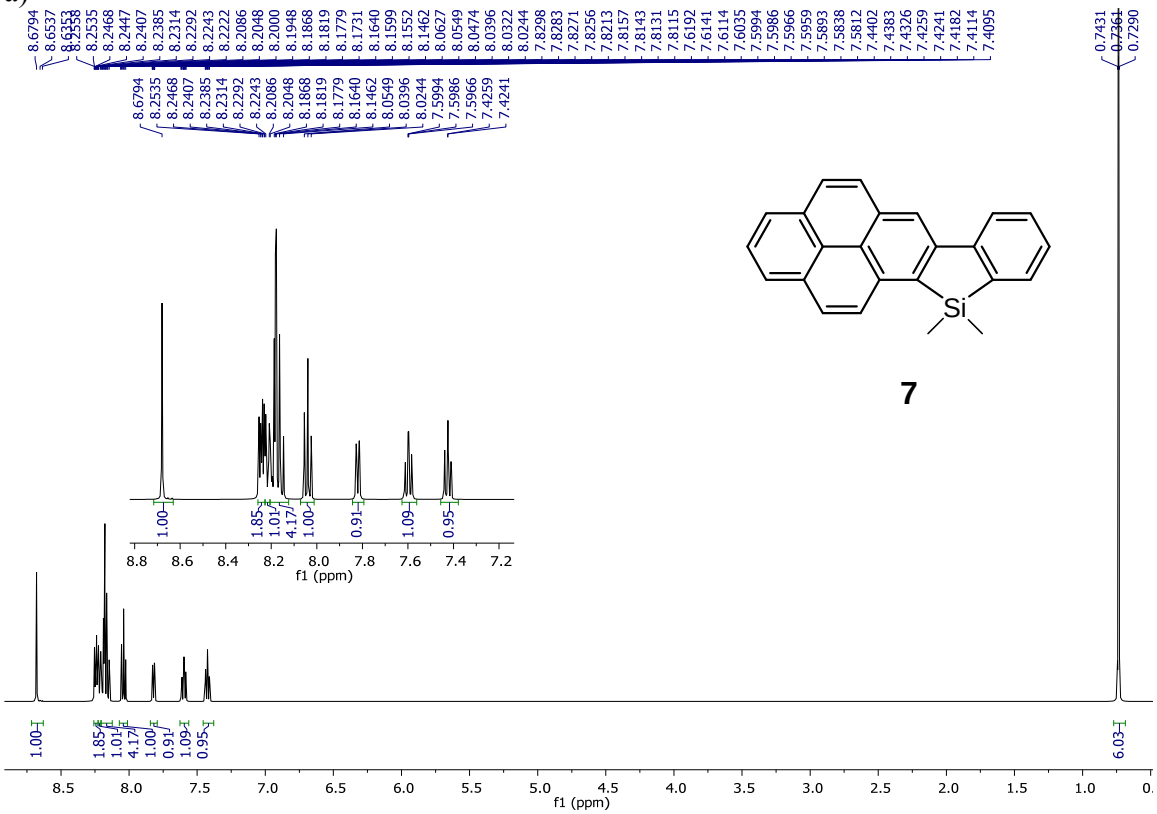


6

Figure S12: a) ^{1}H NMR (500 MHz, CD_2Cl_2), b) $^{13}C\{1H\}$ NMR (125.78 MHz, CD_2Cl_2) and c) $^{31}P\{1H\}$ NMR (161.99 MHz, CD_2Cl_2) spectra of **6**.

For compound 7

a)



b)

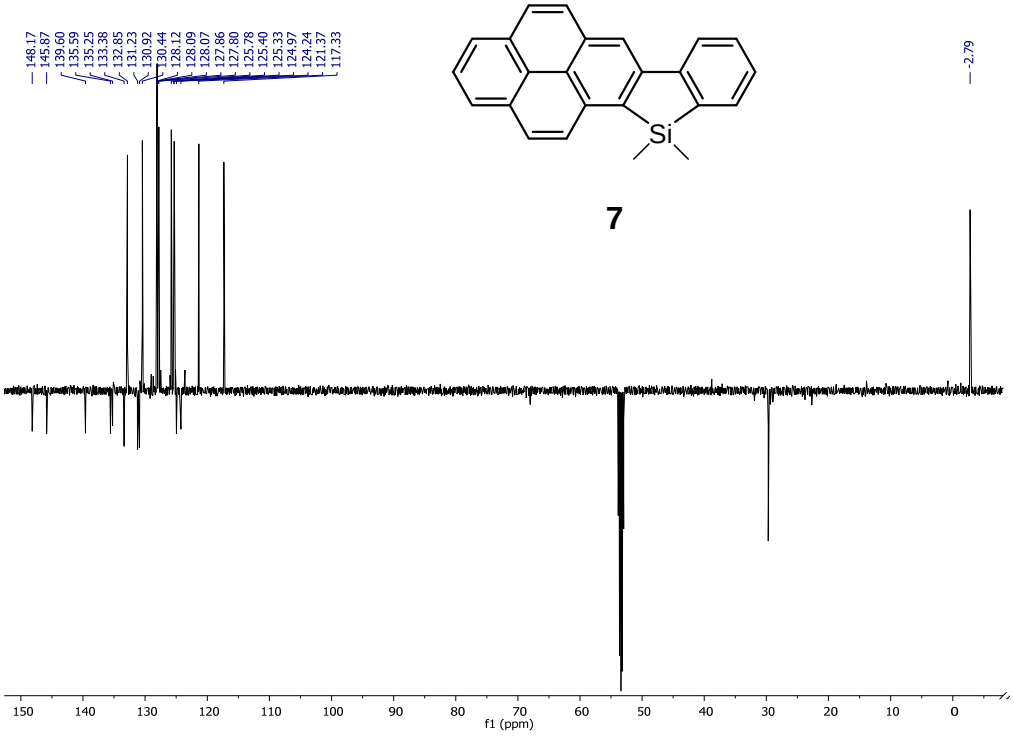


Figure S13: a) ^{1}H NMR (500 MHz, CD_2Cl_2), b) $^{13}C\{1H\}$ JMOD NMR (100.62 MHz, CD_2Cl_2) spectra of **7**.

XYZ geometries

Pyrene

B3LYP/6-31+G* total energy: -615.792177102

C	0.054279	1.234180	-0.028133
C	0.773411	-0.001442	-0.021598
C	0.060185	-1.240058	-0.058406
C	-1.344745	-1.217662	-0.100607
C	-2.039431	-0.007195	-0.106712
C	-1.350543	1.206118	-0.070951
C	0.799890	2.464433	0.009552
C	2.162690	2.467231	0.050789
C	2.914106	1.240059	0.058403
C	2.200880	0.001443	0.021595
C	2.920012	-1.234178	0.028130
C	2.174400	-2.464432	-0.009555
C	0.811601	-2.467230	-0.050792
C	4.319036	1.217663	0.100604
C	5.013722	0.007196	0.106709
C	4.324834	-1.206117	0.070948
H	-1.889606	-2.158778	-0.128663
H	-3.126017	-0.009328	-0.139590
H	-1.899848	2.145101	-0.076002
H	0.248787	3.402404	0.004434
H	2.709523	3.407285	0.078892
H	2.725503	-3.402403	-0.004437
H	0.264768	-3.407284	-0.078895

H	4.863897	2.158779	0.128660
H	6.100307	0.009329	0.139587
H	4.874138	-2.145100	0.075999

3

B3LYP/6-31+G* total energy: -1493.91132271

C	5.6584350	0.8954620	0.6694690
C	4.2773150	0.9165150	0.4104710
C	3.6035930	-0.2964460	0.0731090
C	4.3550040	-1.5117190	-0.0130930
C	5.7341670	-1.4875790	0.2600980
C	6.3773240	-0.2976740	0.5998630
C	3.5119900	2.1279960	0.4365830
C	2.1679080	2.1313750	0.2076340
C	1.4331480	0.9225690	-0.0662750
C	2.1951270	-0.2947390	-0.1838150
C	1.5643210	-1.5196380	-0.5667670
C	2.3435280	-2.7218140	-0.6587850
C	3.6782130	-2.7222860	-0.3851380
C	0.0282100	0.8677820	-0.2688520
C	-0.5440010	-0.3491460	-0.7093750
C	0.1912850	-1.5118320	-0.8616110
C	-0.9985640	1.9431920	-0.1014090
C	-0.8739070	3.2062500	0.5009160
C	-1.9661570	4.0798270	0.5490870
C	-3.2061310	3.7181020	0.0186840

C	-3.3677590	2.4418590	-0.5299080
C	-2.2830320	1.5718260	-0.5734530
P	-2.3099780	-0.1630250	-1.1219790
C	-3.2851780	-1.1035270	0.1098380
O	-2.7389030	-0.4821820	-2.5289790
C	-4.2940620	-1.9511310	-0.3674620
C	-5.0697530	-2.6909540	0.5306140
C	-4.8401380	-2.5874550	1.9047170
C	-3.8321110	-1.7431690	2.3847120
C	-3.0568320	-1.0032220	1.4911130
H	6.1640610	1.8246280	0.9221580
H	6.2999430	-2.4144070	0.1991610
H	7.4446000	-0.2993770	0.8051790
H	4.0307840	3.0652120	0.6256850
H	1.6552480	3.0817250	0.1829700
H	1.8390970	-3.6395990	-0.9514980
H	4.2558480	-3.6412510	-0.4528120
H	-0.2894750	-2.4253300	-1.2046860
H	0.0484090	3.5200940	0.9707020
H	-1.8410500	5.0537280	1.0157290
H	-4.0421910	4.4112120	0.0529720
H	-4.3349810	2.1257700	-0.9130220
H	-4.4592650	-2.0218420	-1.4390220
H	-5.8514680	-3.3466740	0.1554710
H	-5.4435040	-3.1627960	2.6025350
H	-3.6512290	-1.6621010	3.4535560

H	-2.2755860	-0.3486980	1.8706740

6

B3LYP/6-31+G* total energy: -1493.91982887

P	1.8962510	0.3727880	-1.0303200
C	0.3088010	-0.3553520	-0.4872770
C	0.5083460	-1.6572340	0.0191110
C	1.9199730	-2.1120350	-0.0430300
C	2.7984770	-1.1525300	-0.5853340
C	-0.5708500	-2.3919860	0.5070110
C	-1.8672500	-1.8473160	0.4945370
C	-2.0779560	-0.5338640	-0.0314850
C	-0.9702140	0.2223570	-0.5363710
C	-3.3920720	0.0218370	-0.0525940
C	-3.6065570	1.3317330	-0.5814150
C	-2.4773120	2.0597650	-1.0928510
C	-1.2197570	1.5340400	-1.0750060
C	-2.9994380	-2.5789550	0.9956060
C	-4.2539110	-2.0445920	0.9776690
C	-4.4979330	-0.7280530	0.4551480
C	-5.7823740	-0.1575700	0.4267140
C	-5.9828730	1.1227450	-0.0901750
C	-4.9084090	1.8604910	-0.5898880
C	4.1551560	-1.4255220	-0.7428940
C	4.6509040	-2.6730430	-0.3467280
C	3.7867000	-3.6269110	0.2028050

C	2.4237640	-3.3540690	0.3569830
H	-6.9828320	1.5482820	-0.1052520
H	-5.0728760	2.8570880	-0.9932530
H	-2.6466350	3.0510690	-1.5071390
H	-0.3873920	2.0950540	-1.4890590
H	1.7674800	-4.1102170	0.7796890
H	4.1766860	-4.5939610	0.5101320
H	5.7063360	-2.9018120	-0.4676620
H	4.8201500	-0.6815290	-1.1742990
H	-6.6244060	-0.7274010	0.8130740
H	-5.0977840	-2.6137120	1.3612800
H	-2.8337090	-3.5777870	1.3927680
H	-0.4261450	-3.3947300	0.9017960
O	2.0164210	0.8862790	-2.4407180
C	2.3663250	1.6557930	0.1912170
C	2.8586370	2.8727410	-0.2997270
C	3.2394520	3.8837770	0.5879670
C	3.1300830	3.6833630	1.9661930
C	2.6387990	2.4694180	2.4599990
C	2.2582360	1.4584830	1.5764700
H	2.9346340	3.0156430	-1.3742220
H	3.6198330	4.8260340	0.2015150
H	3.4252190	4.4700530	2.6561180
H	2.5511650	2.3120450	3.5320410
H	1.8746810	0.5187560	1.9670750

5

B3LYP/6-31+G* total energy: -1215.00656930

C	-4.6275940	1.8473850	0.2030270
C	-3.2743770	1.4677140	0.1995830
C	-2.9274980	0.0967510	0.0009010
C	-3.9685980	-0.8709980	-0.1680640
C	-5.3090110	-0.4452730	-0.1651240
C	-5.6334110	0.8991990	0.0151030
C	-2.2130280	2.4031060	0.4340080
C	-0.9034580	2.0247600	0.3925810
C	-0.5031880	0.6697690	0.1046380
C	-1.5535360	-0.3059150	-0.0187120
C	-1.2422270	-1.6932600	-0.1533140
C	-2.3058410	-2.6448560	-0.3085720
C	-3.6112230	-2.2531010	-0.3268920
C	0.8487070	0.2389020	-0.0009810
C	1.1316560	-1.1559240	-0.0220920
C	0.1054060	-2.0890660	-0.0989570
C	2.0731580	1.0981860	-0.0898090
C	2.1211420	2.4656180	-0.4165890
C	3.3432790	3.1424590	-0.4763970
C	4.5435710	2.4734490	-0.2317020
C	4.5161550	1.0977270	0.0237340
C	3.3059960	0.4031960	0.0820140
Si	2.9821520	-1.4457070	0.1627630
C	3.7802780	-2.3892980	-1.2690770

C	3.4244780	-2.2685730	1.8077490
H	-4.8839160	2.8929510	0.3585640
H	-6.0970410	-1.1824100	-0.3023060
H	-6.6755480	1.2083450	0.0163150
H	-2.4722880	3.4325180	0.6723370
H	-0.1470400	2.7567470	0.6400320
H	-2.0444130	-3.6955280	-0.4148670
H	-4.4065030	-2.9845690	-0.4518210
H	0.3320380	-3.1542930	-0.1322570
H	1.2222830	3.0113550	-0.6743780
H	3.3520750	4.1997600	-0.7305970
H	5.4894980	3.0077780	-0.2724340
H	5.4562330	0.5654400	0.1606150
H	4.5111290	-2.2838080	1.9618840
H	2.9717050	-1.7342520	2.6507450
H	3.0722140	-3.3077020	1.8387660
H	4.8738810	-2.4015460	-1.1753940
H	3.4408500	-3.4328720	-1.2942550
H	3.5297020	-1.9297570	-2.2319640

7

B3LYP/6-31+G* total energy: -1215.01599782

Si	2.2564110	1.6082060	-0.0000790
C	0.7635310	0.4486570	-0.0000440
C	1.2216450	-0.8941160	-0.0001750
C	2.7026380	-1.0616380	-0.0002040

C	3.4448860	0.1468140	-0.0003630
C	0.3092460	-1.9523880	-0.0002690
C	-1.0743170	-1.7140910	-0.0001800
C	-1.5546780	-0.3684960	-0.0000640
C	-0.6189810	0.7167390	-0.0000640
C	-2.9598120	-0.1147130	0.0000140
C	-3.4462580	1.2289700	0.0000550
C	-2.4895100	2.3018730	-0.0000450
C	-1.1483480	2.0574390	-0.0001080
C	-2.0308200	-2.7888360	-0.0001940
C	-3.3723100	-2.5454880	-0.0000760
C	-3.8875640	-1.2029680	0.0000260
C	-5.2659710	-0.9270640	0.0001400
C	-5.7313890	0.3884400	0.0002170
C	-4.8330110	1.4564870	0.0001560
C	4.8418950	0.0943970	-0.0001010
C	5.5099240	-1.1357600	0.0001950
C	4.7724570	-2.3238060	0.0003080
C	3.3754510	-2.2910950	0.0000930
H	-6.8008940	0.5824910	0.0003130
H	-5.2024120	2.4796200	0.0001940
H	-2.8598320	3.3248720	-0.0001060
H	-0.4516740	2.8918010	-0.0002680
H	2.8235530	-3.2273850	0.0001990
H	5.2869940	-3.2817500	0.0005550
H	6.5967000	-1.1684280	0.0004000

H	5.4249710	1.0140940	-0.0002240
H	-5.9719240	-1.7546770	0.0001670
H	-4.0803550	-3.3713760	-0.0000770
H	-1.6583010	-3.8109210	-0.0003010
H	0.6555240	-2.9831140	-0.0004560
C	2.4037280	2.6848590	-1.5500020
C	2.4037130	2.6839960	1.5504690
H	3.3788360	3.1870940	1.5842830
H	1.6304660	3.4618820	1.5785660
H	2.3058150	2.0796620	2.4595630
H	3.3813840	3.1828910	-1.5861830
H	2.2999540	2.0822150	-2.4595530
H	1.6345580	3.4668820	-1.5746640

Pyrene

CC2/cc-pVDZ//B3LYP/cc-pVDZ total energy: -613.9375874949

C	0.0000000	1.2379590	1.4316150
C	0.0000000	0.0000000	0.7144020
C	0.0000000	-1.2379590	1.4316150
C	0.0000000	-1.2123800	2.8376990
C	0.0000000	0.0000000	3.5297960
C	0.0000000	1.2123800	2.8376990
C	0.0000000	2.4669860	0.6819670
C	0.0000000	2.4669860	-0.6819670
C	0.0000000	1.2379590	-1.4316150
C	0.0000000	0.0000000	-0.7144020

C	0.0000000	-1.2379590	-1.4316150
C	0.0000000	-2.4669860	-0.6819670
C	0.0000000	-2.4669860	0.6819670
C	0.0000000	1.2123800	-2.8376990
C	0.0000000	0.0000000	-3.5297960
C	0.0000000	-1.2123800	-2.8376990
H	0.0000000	-2.1573790	3.3867690
H	0.0000000	0.0000000	4.6221430
H	0.0000000	2.1573790	3.3867690
H	0.0000000	3.4109820	1.2330900
H	0.0000000	3.4109820	-1.2330900
H	0.0000000	-3.4109820	-1.2330900
H	0.0000000	-3.4109820	1.2330900
H	0.0000000	2.1573790	-3.3867690
H	0.0000000	0.0000000	-4.6221430
H	0.0000000	-2.1573790	-3.3867690

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CC2/cc-pVDZ//B3LYP/cc-pVDZ total energy: -1490.0220008096

C	5.6588740	0.8995680	0.6862930
C	4.2769260	0.9187260	0.4258330
C	3.6071890	-0.2939350	0.0748070
C	4.3637750	-1.5063610	-0.0229860
C	5.7435020	-1.4797750	0.2515230
C	6.3821280	-0.2905820	0.6044190
C	3.5064730	2.1275970	0.4659630

C	2.1623140	2.1287910	0.2332610
C	1.4318790	0.9204390	-0.0585830
C	2.1979340	-0.2946250	-0.1840930
C	1.5709230	-1.5199140	-0.5775350
C	2.3557320	-2.7187300	-0.6805140
C	3.6910270	-2.7166360	-0.4069880
C	0.0259830	0.8646310	-0.2678420
C	-0.5428680	-0.3545030	-0.7091550
C	0.1968600	-1.5143690	-0.8724340
C	-1.0023190	1.9404990	-0.1081970
C	-0.8785350	3.2101860	0.4839310
C	-1.9689550	4.0871320	0.5178480
C	-3.2072660	3.7244940	-0.0175010
C	-3.3690780	2.4440970	-0.5571410
C	-2.2861520	1.5695710	-0.5846080
P	-2.3160770	-0.1751220	-1.1272360
C	-3.2842110	-1.1018730	0.1299430
O	-2.7643180	-0.5274110	-2.5354710
C	-4.2845250	-1.9604570	-0.3466200
C	-5.0607110	-2.6964130	0.5543710
C	-4.8392850	-2.5772280	1.9291100
C	-3.8395180	-1.7213550	2.4070870
C	-3.0629280	-0.9844870	1.5111830
H	6.1621950	1.8326450	0.9507830
H	6.3143840	-2.4087820	0.1809710
H	7.4544660	-0.2906710	0.8116450

H	4.0235860	3.0680270	0.6722410
H	1.6413500	3.0809680	0.2238870
H	1.8516410	-3.6397970	-0.9825400
H	4.2753710	-3.6368220	-0.4830510
H	-0.2849200	-2.4302800	-1.2232170
H	0.0476340	3.5267950	0.9565210
H	-1.8433730	5.0697430	0.9784400
H	-4.0451640	4.4241940	0.0052880
H	-4.3380930	2.1241660	-0.9470650
H	-4.4382190	-2.0375200	-1.4250130
H	-5.8402200	-3.3646950	0.1809150
H	-5.4459640	-3.1523500	2.6327210
H	-3.6656130	-1.6287440	3.4816840
H	-2.2843820	-0.3176830	1.8898510

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CC2/cc-pVDZ//B3LYP/cc-pVDZ total energy: -1490.0311333823

P	1.8914670	0.3976610	-1.0420120
C	0.3064200	-0.3500260	-0.4968730
C	0.5183930	-1.6457360	0.0219250
C	1.9310790	-2.0965520	-0.0569250
C	2.8020020	-1.1384270	-0.6172490
C	-0.5548610	-2.3788360	0.5307770
C	-1.8545450	-1.8384700	0.5233210
C	-2.0777090	-0.5369310	-0.0303610
C	-0.9785420	0.2146430	-0.5612100

C	-3.3953540	0.0122300	-0.0545210
C	-3.6207540	1.3075460	-0.6171670
C	-2.4998980	2.0252280	-1.1644070
C	-1.2384540	1.5070360	-1.1421720
C	-2.9798370	-2.5627100	1.0528640
C	-4.2371220	-2.0331340	1.0358220
C	-4.4932790	-0.7299360	0.4834330
C	-5.7810620	-0.1647800	0.4540330
C	-5.9920190	1.1011880	-0.0944920
C	-4.9261310	1.8301510	-0.6259970
C	4.1558820	-1.4128860	-0.8003850
C	4.6583000	-2.6596950	-0.4089050
C	3.8037490	-3.6110490	0.1610260
C	2.4433360	-3.3379510	0.3391330
H	-6.9987730	1.5243630	-0.1099390
H	-5.0993670	2.8192570	-1.0569690
H	-2.6811080	3.0049660	-1.6133920
H	-0.4064810	2.0508850	-1.5927590
H	1.7909910	-4.0956570	0.7780120
H	4.2013690	-4.5815800	0.4664000
H	5.7161890	-2.8911990	-0.5497550
H	4.8141670	-0.6654720	-1.2488250
H	-6.6198640	-0.7308320	0.8664620
H	-5.0786340	-2.5984710	1.4441540
H	-2.8049930	-3.5559410	1.4736550
H	-0.4019530	-3.3795140	0.9411480

O	2.0041840	0.9729090	-2.4448770
C	2.3630090	1.6493520	0.2219350
C	2.8270380	2.8846820	-0.2511840
C	3.2094320	3.8804680	0.6532610
C	3.1274690	3.6462120	2.0285060
C	2.6632370	2.4135940	2.5030900
C	2.2820880	1.4162940	1.6036500
H	2.8797880	3.0471890	-1.3297880
H	3.5711010	4.8422810	0.2818980
H	3.4248050	4.4250460	2.7348020
H	2.5973340	2.2303670	3.5781040
H	1.9187450	0.4570840	1.9804140

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CC2/cc-pVDZ//B3LYP/cc-pVDZ total energy: -1211.7359153954

C	-4.6334300	1.8489680	0.1941470
C	-3.2789980	1.4698880	0.1906390
C	-2.9312130	0.0966880	0.0011240
C	-3.9732120	-0.8731540	-0.1593660
C	-5.3145850	-0.4475840	-0.1559780
C	-5.6392480	0.8984460	0.0157610
C	-2.2169380	2.4086010	0.4128650
C	-0.9067090	2.0299410	0.3735390
C	-0.5047760	0.6713880	0.0996360
C	-1.5559770	-0.3059040	-0.0184170
C	-1.2448530	-1.6952280	-0.1481950

C	-2.3095860	-2.6482240	-0.2955540
C	-3.6156260	-2.2569150	-0.3115420
C	0.8495590	0.2404520	-0.0020180
C	1.1303230	-1.1560130	-0.0235490
C	0.1038600	-2.0907210	-0.0973150
C	2.0754600	1.1000160	-0.0868710
C	2.1248930	2.4723490	-0.3988460
C	3.3474450	3.1497020	-0.4535570
C	4.5487770	2.4783110	-0.2184490
C	4.5216100	1.1002450	0.0251540
C	3.3104690	0.4054960	0.0791060
Si	2.9883460	-1.4512190	0.1554680
C	3.7823300	-2.3917670	-1.2832880
C	3.4344000	-2.2798110	1.7989640
H	-4.8899250	2.9007200	0.3431170
H	-6.1054060	-1.1903730	-0.2869730
H	-6.6866850	1.2084570	0.0173260
H	-2.4775770	3.4457720	0.6389830
H	-0.1457050	2.7691160	0.6076370
H	-2.0460640	-3.7041150	-0.3975990
H	-4.4153480	-2.9922040	-0.4304580
H	0.3326700	-3.1605980	-0.1300350
H	1.2208730	3.0242190	-0.6467480
H	3.3557550	4.2150940	-0.6963510
H	5.4990600	3.0158640	-0.2559970
H	5.4652500	0.5624360	0.1575620

H	4.5276380	-2.2959480	1.9458250
H	2.9812180	-1.7419650	2.6466290
H	3.0774710	-3.3234140	1.8232790
H	4.8813160	-2.4036120	-1.1869780
H	3.4378650	-3.4395680	-1.3065710
H	3.5269130	-1.9238430	-2.2471210

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CC2/cc-pVDZ//B3LYP/cc-pVDZ total energy: -1211.7446550945

Si	2.2614080	1.6138320	0.0000590
C	0.7626430	0.4500530	-0.0000210
C	1.2224580	-0.8937900	-0.0000630
C	2.7042180	-1.0628780	-0.0001090
C	3.4508400	0.1444840	-0.0002490
C	0.3091900	-1.9533920	-0.0000880
C	-1.0758570	-1.7151960	-0.0000400
C	-1.5571520	-0.3684150	-0.0000560
C	-0.6214500	0.7183390	-0.0000670
C	-2.9633470	-0.1146430	-0.0000170
C	-3.4504770	1.2300880	-0.0000400
C	-2.4932610	2.3041690	-0.0001580
C	-1.1511030	2.0600020	-0.0001460
C	-2.0331040	-2.7907390	-0.0000110
C	-3.3754600	-2.5474000	0.0000210
C	-3.8915000	-1.2039990	0.0000440
C	-5.2709680	-0.9280650	0.0000790

C	-5.7366460	0.3881180	0.0000480
C	-4.8384030	1.4572000	-0.0000150
C	4.8486320	0.0887820	-0.0002200
C	5.5132140	-1.1437780	-0.0000800
C	4.7722720	-2.3304310	0.0000310
C	3.3746990	-2.2948210	0.0000450
H	-6.8116280	0.5828450	0.0000750
H	-5.2092360	2.4854130	-0.0000560
H	-2.8658140	3.3319420	-0.0002540
H	-0.4503110	2.8980630	-0.0002700
H	2.8167740	-3.2337670	0.0001600
H	5.2872090	-3.2943300	0.0001350
H	6.6053410	-1.1796290	-0.0000520
H	5.4360010	1.0121390	-0.0003390
H	-5.9795820	-1.7603260	0.0001130
H	-4.0870640	-3.3772550	0.0000590
H	-1.6582420	-3.8176390	-0.0000140
H	0.6578070	-2.9887780	-0.0001570
C	2.4106570	2.6911870	-1.5514040
C	2.4105920	2.6903940	1.5520620
H	3.3924140	3.1933650	1.5823230
H	1.6335270	3.4726880	1.5769640
H	2.3111370	2.0804780	2.4642730
H	3.3947490	3.1895860	-1.5838750
H	2.3058430	2.0827520	-2.4639940
H	1.6372410	3.4771780	-1.5732010