Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Rotational Barriers of Biphenyls Having Heavy Heteroatoms as *ortho*-Substituents: Experimental and Theoretical Determination of Steric Effects

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ELECTRONIC SUPPLEMENTARY INFORMATION

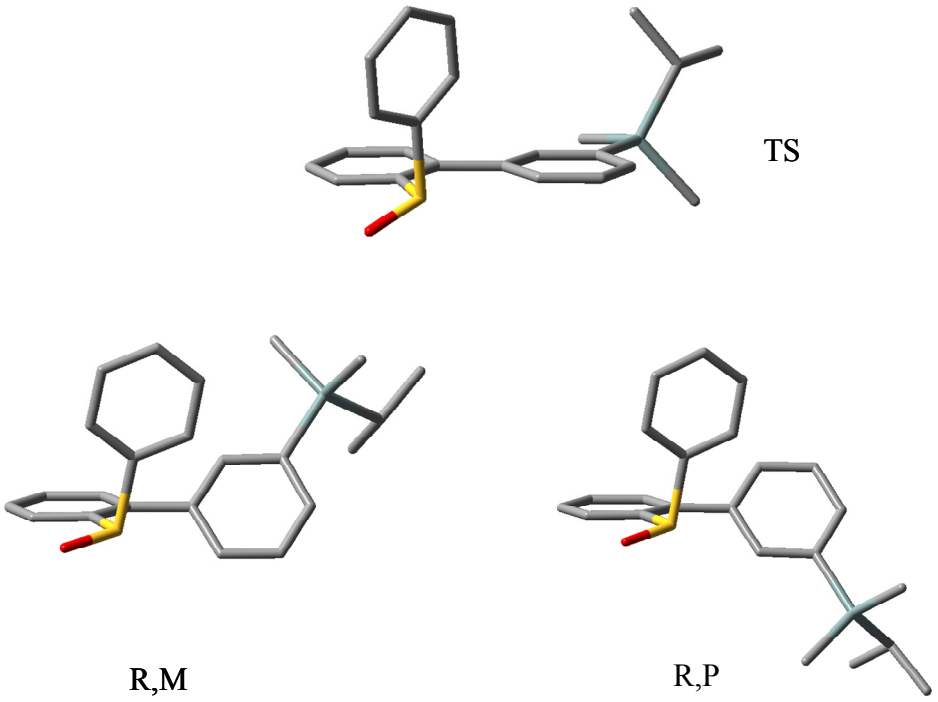


FIGURE S1. DFT computed structures of the two conformational diastereoisomers of ortho pehenylsulphoxide derivative **3** (bottom) generated by the restricted aryl-aryl rotation. The R*P* form (right) is more stable by 0.1 kcal mol^{-1} with respect to the R,M (left). On the top is reported the computed transition state (TS) for the aryl-aryl rotation process.

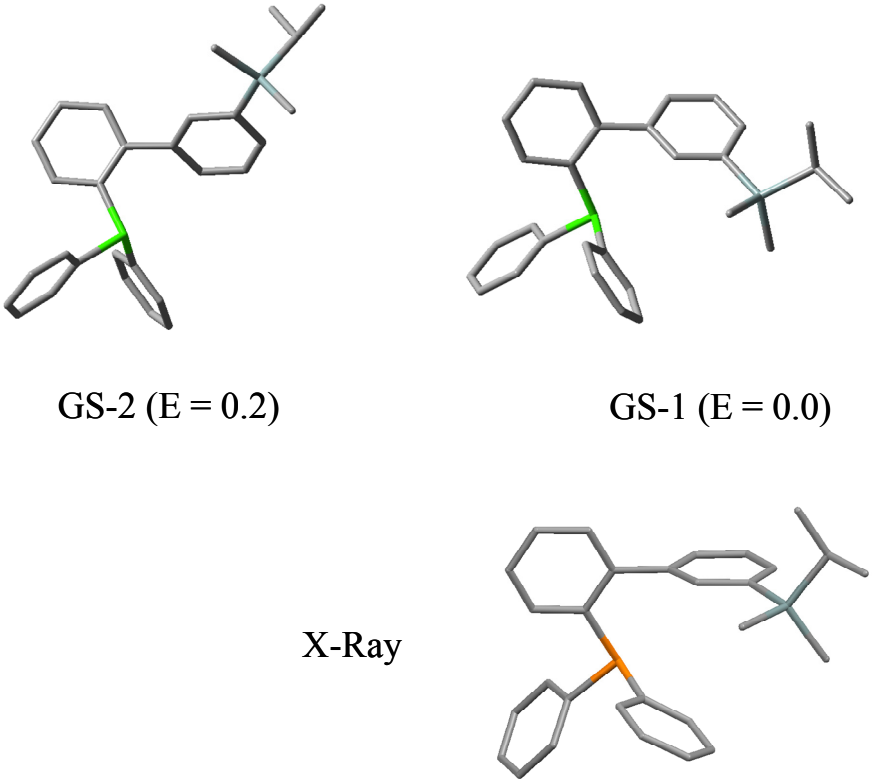
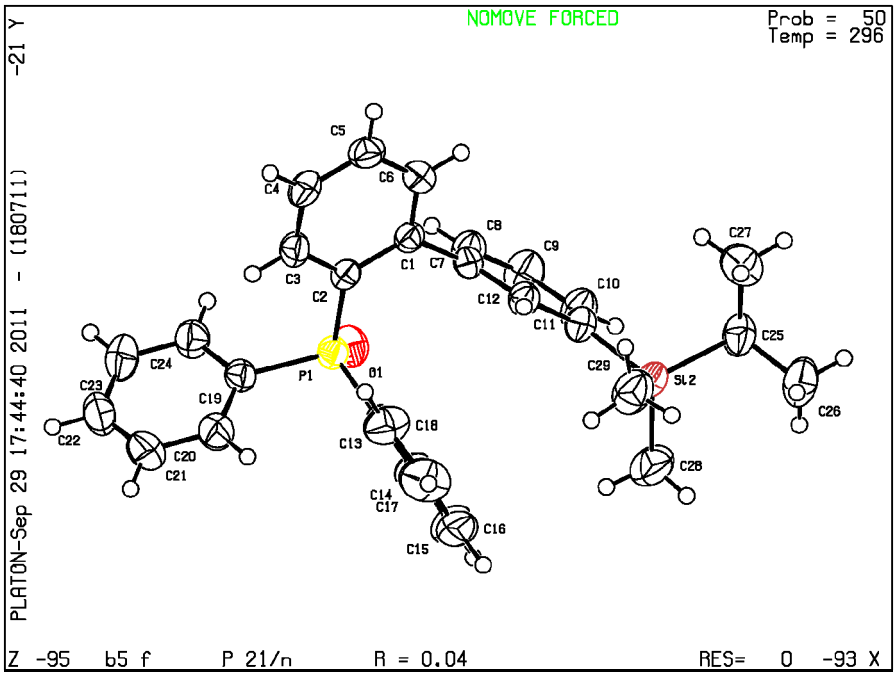


FIGURE S2. DFT computed (top) and X-ray structures (bottom) of compound **9** (the relative computed energies E are in kcal mol^{-1}). The less stable conformer GS-2 has the aryl-aryl dihedral angle of 125° whereas the most stable conformer GS-1 has a dihedral angle of 66°. The crystal lattice contains a 1:1 ratio of phosphine **9** and of phosphine oxide **10** (the latter is not reported in the present picture since it is equal to that reported in Figure 3 of the main text).

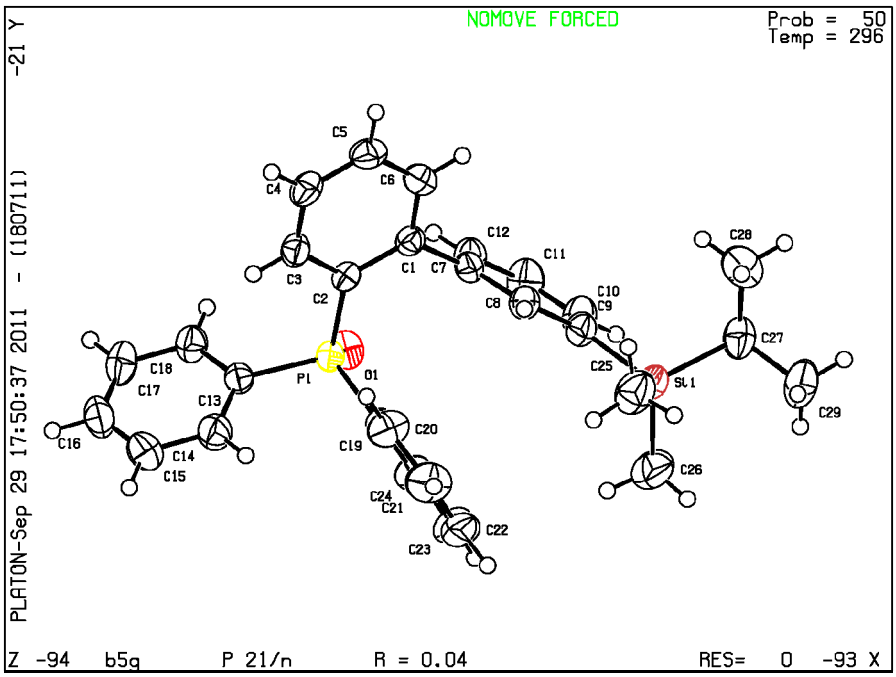
Crystal data and structure refinement for compound 9



CCDC number:	849731
Empirical formula	C29 H31 O0.47 P Si
Formula weight	446.12
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 12.3538(14) A alpha = 90
	b = 11.1227(12) A beta = 91.7460(10)
	c = 18.446(2) A gamma = 90
Volume	2533.4(5) A^3
Z, Calculated density	4, 1.170 Mg/m^3
Absorption coefficient	0.172 mm^-1
F(000)	951
Crystal size	0.30 x 0.15 x 0.15 mm
Theta range for data collection	1.96 to 26.00 deg.
Limiting indices	-15<=h<=15, -13<=k<=13, -22<=l<=22
Reflections collected / unique	25500 / 4987 [R(int) = 0.0194]
Completeness to theta = 25.00	100.0 %
Absorption correction	Empirical
Max. and min. transmission	0.9747 and 0.9503
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4987 / 1 / 294
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.1099
R indices (all data)	R1 = 0.0474, wR2 = 0.1161
Largest diff. peak and hole	0.627 and -0.658 e.A^-3

Notes: The crystal cell contains a mixture of the phosphine **9** and of the corresponding phosphine oxide **10**.

Crystal data and structure refinement for compound 10.



CCDC number:	849732
Empirical formula	C29 H31 O P Si
Formula weight	454.60
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
space group	P 21/n
Unit cell dimensions	a = 12.3039(19) A alpha = 90.
	b = 11.1280(17) A beta = 91.632(2)
	c = 18.544(3) A gamma = 90
Volume	2537.9(7) A^3
Z, Calculated density	4, 1.190 Mg/m^3
Absorption coefficient	0.174 mm^-1
F(000)	968
Crystal size	0.45 x 0.40 x 0.20 mm
Theta range for data collection	1.96 to 28.17 deg.
Limiting indices	-16<=h<=16, -14<=k<=14, -24<=l<=24
Reflections collected / unique	28424 / 6101 [R(int) = 0.0252]
Completeness to theta = 28.17	98.1 %
Absorption correction	Empirical
Max. and min. transmission	0.9660 and 0.9257
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6101 / 0 / 293
Goodness-of-fit on F^2	1.039
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.0974
R indices (all data)	R1 = 0.0474, wR2 = 0.1052
Largest diff. peak and hole	0.414 and -0.280 e.A^-3