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Supporting Information

BINOL-3,3'-Triflone *N,N*-Dimethyl Phosphoramidites: Through-Space $^{19}F,^{31}P$ Spin-Spin Coupling with a Remarkable Dependency on Temperature and Solvent Internal Pressure

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General Experimental Details. Solvents and reagents were purified by standard procedures. Solvents were dried using a nitrogen pressurized alumina column system from Solvtek or Anhydrous Engineering. Standard schlenk techniques were used to perform reactions under nitrogen. High resolution mass spectra (HRMS) were obtained at the Mass Spectrometry Laboratory at the School of Chemistry of University of Bristol. Melting points were determined without correction. Flash chromatography was performed using Merck silica gel 60 or Fluorochem "Davisil" silica gel 60. Thin layer chromatography (TLC) was performed on silica gel Whatman-60F glass plates, and components visualised by illumination with UV light or by staining with potassium permanganate solution. Accurate weights were obtained with a Sartorius BP 211 balance. Optical rotations were recorded on a JASCO-CIP-370 instrument. NMR spectra were recorded in the stated solvent on a Delta GX400, JEOL ECP (Eclipse) 300, JEOL ECP (Eclipse) 400, and JEOL Lambda 300. Coupling constants (J) expressed in Hertz (Hz) are approximated to the nearest 0.1 Hz. Abbreviations for multiplicities are as follows: (s) singlet, (d) doublet, (dd) double doublet, t (triplet), (q) quartet, (m) multiplet. Chemical shifts are measured in parts per million (ppm) and referenced to TMS (0.00 ppm) or the deuterated solvent used. 13C NMR was recorded using broad-band proton decoupling.

Preparative method for 2 and $\mathbf{3}_{SS/SR}$

***O,O'*-(*S*)-(1,1'-Binaphthyl-2,2'-diyl-3,3'-bis-trifluoromethanesulfonyl)-*N,N*-dimethylphosphoramidite (2)**

Following the general procedure of Feringa *et al.*,[S1] $(Me_2N)_3P$ (0.36 mL, 1.96 mmol) was added to a solution of (*S*)-3,3'-bis-trifluoromethanesulfonyl-2,2'-hydroxy-1,1'-binaphthalene[S2] (865 mg, 1.57 mmol) and NH_4Cl (1 crystal) in dry toluene (8 mL) at room temperature. The mixture was then heated at 80 °C for 28 h. The mixture was concentrated under reduced pressure to afford an orange oil. Recrystalization from hexane gave a white solid (590 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (s, 1H; Ha), 8.87 (s, 1H, Ha'), 8.14 (d, J = 7.5 Hz, 1H, Hb), 8.13 (d, J = 7.5 Hz, 1H, Hb'), 7.65-7.59 (m, 2H, Hc and Hc'), 7.55-7.47 (m, 2H, Hd and Hd'), 7.26 (d, J = 8.1 Hz, 1H, He), 7.18 (d, J = 8.1 Hz, 1H, He'), 2.58 (br s, 6H, 2 x NCH_3). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.41 (d, $J_{C\text{-}P}$ = 4.0 Hz, CSO_2CF_3), 146.56 (CSO_2CF_3), 137.83 (d, $J_{C\text{-}P}$ = 4.6 Hz), 136.68, 136.42, 136.30, 132.17, 131.09 (d, $J_{C\text{-}P}$ = 1.6 Hz), 130.63 (d, $J_{C\text{-}P}$ = 2.3 Hz), 129.34, 128.61, 127.12, 126.85, 126.64, 126.53, 126.00, 125.50 (d, $J_{C\text{-}P}$ = 5.4 Hz), 124.45 (d, $J_{C\text{-}P}$ = 2.3 Hz), 124.27 (d, $J_{C\text{-}P}$ = 1.5 Hz), 123.82 (d, $J_{C\text{-}P}$ = 1.6 Hz), 119.90 (q, $J_{C\text{-}F}$ = 327.2 Hz, 2 x CF_3), 35.70 (br s, 2 x NCH_3). ^{19}F{^{1}H} NMR (282.2 MHz, $CDCl_3$) δ -76.16 (d, $J_{F\text{-}P}$ = 5.5 Hz), -76.25 (s). ^{31}P NMR{^{1}H} (121.56 MHz, $CDCl_3$) δ 157.2 (q, $J_{P\text{-}F}$ = 5.5 Hz). HRMS (FAB^+) calcld for $C_{24}H_{17}F_6NO_6PS_2$ (M^+ + 1): 624.0139. Found: 624.0148. mp = 128-130 °C. $[\alpha]_D^{25}$ = + 566 (c = 0.081, $CHCl_3$).

Following the general procedure of Feringa *et al.*,[S1] $(Me_2N)_3P$ (1.06 mL, 5.84 mmol) was added to a solution of (*S*)-3-trifluoromethanesulfonyl-2,2'-hydroxy-1,1'-binaphthalene[S2] (1.88 g, 4.49 mmol) and NH_4Cl (1 crystal) in dry toluene (20 mL) at room temperature. The mixture was then heated at 80 °C for 24 h. The mixture was concentrated under reduced pressure to afford an orange oil. Purification by flash silica chromatography (hexanes/CH_2Cl_2, 3:2) gave a pale-yellow solid (5:1 ($\mathbf{3}_{SR}$:$\mathbf{3}_{SS}$)

mixture of the two isomers, 1.58 g, 72%). The two isomers could be separated by a more careful flash chromatography on silica-gel (hexanes/CH_2Cl_2, 5:2 then 3:2).

_O,O'_-(_S,R_$_P$)-(1,1'-Binaphthyl-2,2'-diyl-3-trifluoromethanesulfonyl)-_N,N_-dimethylphosphoramidite (3_{SR})

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.08 (d, J = 8.1 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.60-7.41 (m, 5H), 7.25 (t, J = 7.7 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 2.58 (br s). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.77, 146.83 (d, $J_{C\text{-}P}$ = 3.4 Hz), 136.87, 136.61, 132.48 (d, $J_{C\text{-}P}$ = 2.3 Hz), 131.38, 130.57, 130.25, 128.63, 128.54, 127.31, 126.54 (d, $J_{C\text{-}P}$ = 5.7 Hz), 126.31 (d, $J_{C\text{-}P}$ = 2.9 Hz), 126.18, 125.09, 123.58, 122.07 (d, $J_{C\text{-}P}$ = 5.1 Hz), 121.83 (d, $J_{C\text{-}P}$ = 1.7 Hz), 119.5 (q, $J_{C\text{-}F}$ = 324.3 Hz), 35.0 (br s). ^{19}F{^{1}H} NMR (282.2 MHz, $CDCl_3$) δ -76.33 (s). ^{31}P{^{1}H} NMR (121.56 MHz, $CDCl_3$) δ 151.31 (s). HRMS (ESI) calcld for $C_{23}H_{17}F_3NO_4PS$ (M^+ + 1): 492.0641. Found: 492.0637. mp = 198-200 ^{o}C. $[\alpha]_D^{25}$ = + 528 (c = 0.093, $CHCl_3$).

_O,O'_-(_S,S_$_P$)-(1,1'-Binaphthyl-2,2'-diyl-3-trifluoromethanesulfonyl)-_N,N_-dimethylphosphoramidite (3_{SS})

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.95 (t, J = 9.1 Hz, 2H), 7.57 (t, J = 8.1 Hz, 1H), 7.49-7.37 (m, 4H), 7.32-7.26 (td, J = 8.4, 1.1 Hz, 1H), 7.22 (t, J = 9.3 Hz, 1H), 2.54 (d, J = 9.2 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.50 (d, $J_{C\text{-}P}$ = 4.0 Hz), 146.24, 136.74, 136.62, 132.28, 131.08, 130.73, 120.48, 130.27, 129.21, 128.56, 127.39, 127.31, 126.73, 126.52, 126.06, 124.88, 124.22, 121.99, 120.98 (d, $J_{C\text{-}P}$ = 2.3 Hz), 199.9 (q, $J_{C\text{-}F}$ = 325.2 Hz), 36.00 (d, $J_{C\text{-}P}$ = 21.76 Hz). ^{19}F{^{1}H} NMR (282.2 MHz, $CDCl_3$) δ -76.14 (d, $J_{F\text{-}P}$ = 5.2 Hz). ^{31}P{^{1}H} NMR (121.56 MHz, $CDCl_3$) δ 155.50 (q, $J_{P\text{-}F}$ = 5.2 Hz). HRMS (ESI) calcld for $C_{23}H_{17}F_3NO_4PS$ (M^+ + 1): 492.0641. Found: 492.0634. mp = 148-150 ^{o}C. $[\alpha]_D^{25}$ = + 438 (c = 0.098, $CHCl_3$).

X-ray diffraction data for 2 [S3] [CCDC 644613]

Data for **2** were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with a low temperature device, using graphite monochromated MoKα radiation (λ= 0.71073 Å). Data were processed using the Nonius Software.[S4] Structure solution, followed by full-matrix least squares refinement was performed using the WinGX-1.70 suite of programs[S5]

Notes on refinement: The asymmetrical unit contains 0.5 molecules of water distributed about two special positions. There are more voids in the structure which suggest that up to three more molecules of water are present. Due to a weak data set these positions could not be properly located. Hydrogen atoms for the water molecules could not be located in the difference Fourier map and were omitted.

2 : C_{24} H_{17} F_6 N $O_{6.50}$ P S_2, M = 632.48, orthorhombic, I 222 (no.23), a = 11.2220(10) Å, b = 14.5210 (5) Å, c = 36.7920(4)Å, V = 5995.4(6)Å^3, Z = 8, ρ = 1.401 g cm^{-3}, R_1 [I > 2σ(I)] = 0.0928, wR_2 [I > 2σ(I)] = 0.205, R_1 [all data] = 0.1134, wR_2 [all data] = 0.2219, measured reflections = 29203, unique reflections = 6066, R_{int} = 0.1609.

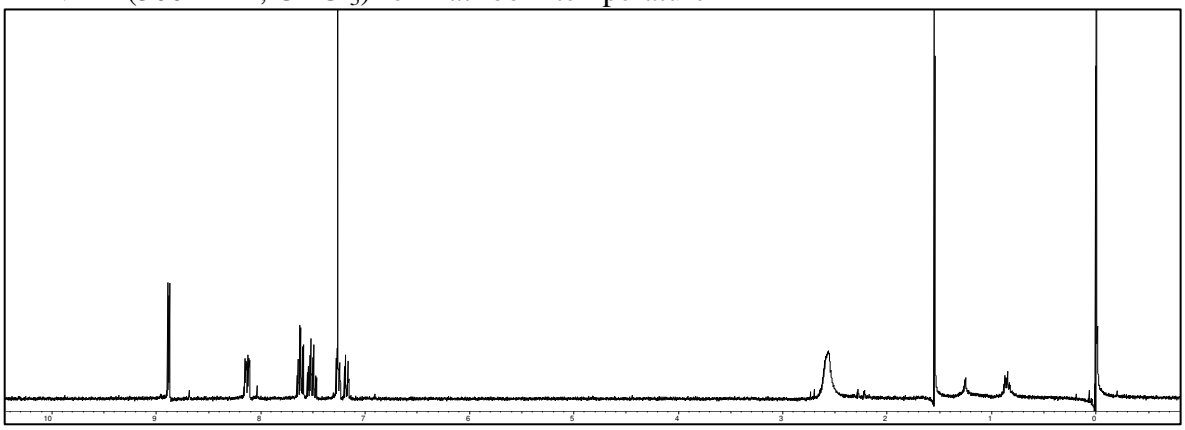
Computational and Spectroscopic Details

Spectroscopic determination of J_{PF}: NMR spectra were measured on a JEOL ECP300 spectrometer. ^{19}F and ^{31}P FIDs were acquired with 65536 data points. Data processing was undertaken using Delta or ACDLabs software and the FIDs were zero-filled to 524288 points and resolution enhanced with a Lorentzian-Gaussian window function (LB=-1.5, GF=0.35) prior to Fourier transform. Coupling constants were measured manually from the spectrum. Absolute temperatures of NMR samples are uncalibrated and errors of relative temperature for a given experiment are ± 0.5 °C.

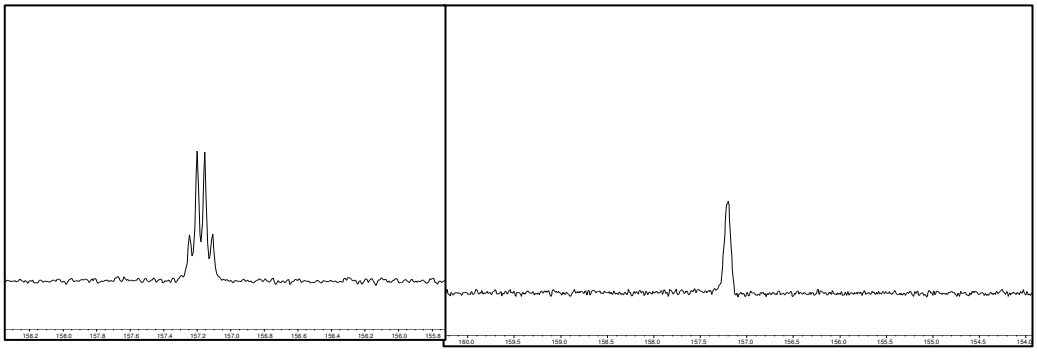
Geometry optimisations and computation of coupling constants were undertaken using the Gaussian03 or Gaussian03W software. Calculations employed density functional theory using the B3LYP functional, with both geometries and NMR parameters calculated with a 6-311** basis set for all atoms. Molar volume calculations were conducted using the same method and basis sets as above, with the 'Volume=Tight' option in Gaussian03.

NMR Spectra for 2

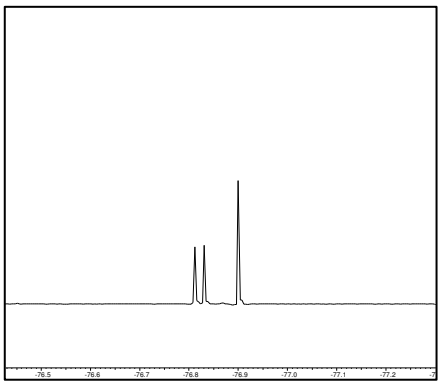
^{1}H NMR (300 MHz, $CDCl_3$) for **2** at room temperature



$^{31}P\{^{1}H\}$ NMR (121.56 MHz, $CDCl_3$) for **2** at room temperature (J = 5.5 Hz) and – 50 ^{o}C

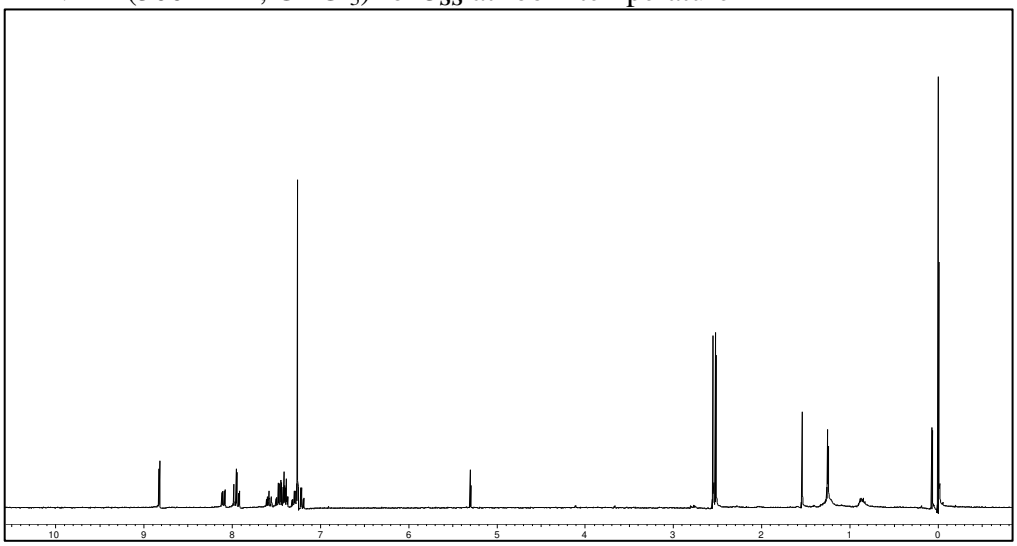


$^{19}F\{^{1}H\}$ NMR (282.2 MHz, $CDCl_3$) for **2** at room temperature (J = 5.5 Hz)

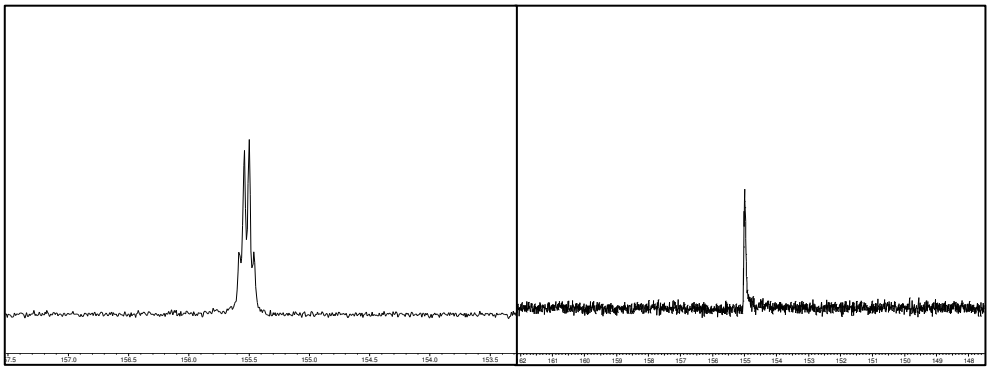


NMR Spectra for 3_{SS}

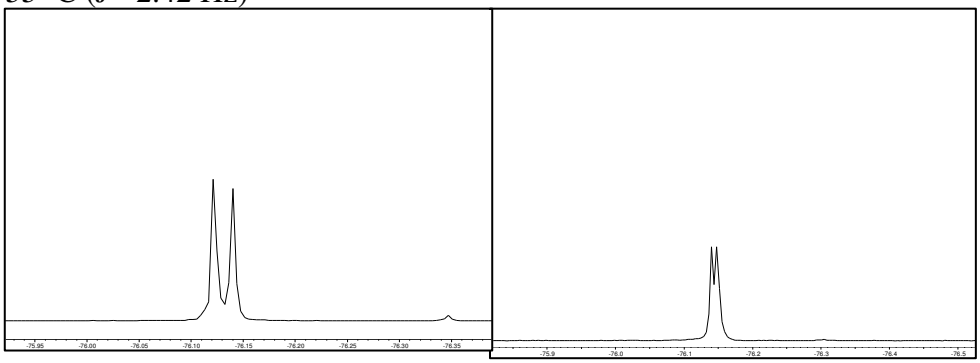
^{1}H NMR (300 MHz, $CDCl_3$) for $\mathbf{3}_{SS}$ at room temperature



$^{31}P\{^{1}H\}$ NMR (121.56 MHz, $CDCl_3$) for $\mathbf{3}_{SS}$ at room temperature (J = 5.2 Hz) and at – 55 ^{o}C (J unresolved)

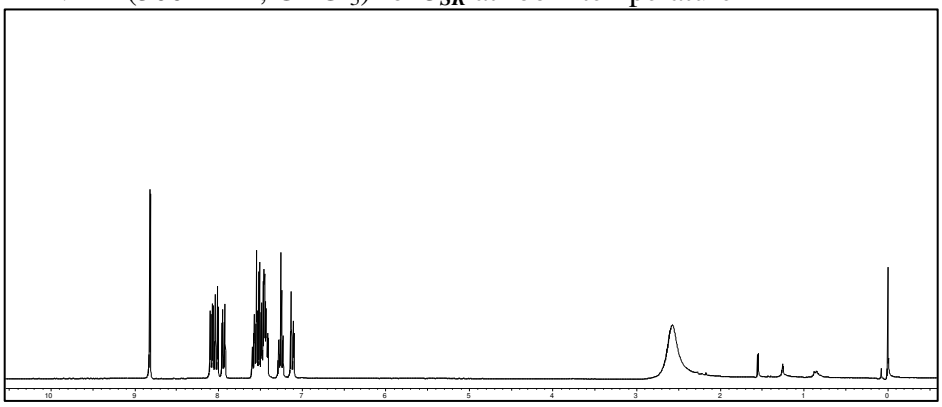


$^{19}F\{^{1}H\}$ NMR (282.2 MHz, $CDCl_3$) for $\mathbf{3}_{SS}$ at room temperature (J = 5.2 Hz) and at – 55 ^{o}C (J= 2.42 Hz)

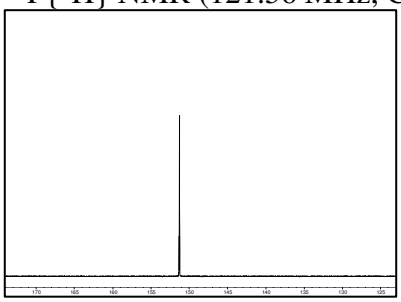


NMR Spectra for 3_{SR}

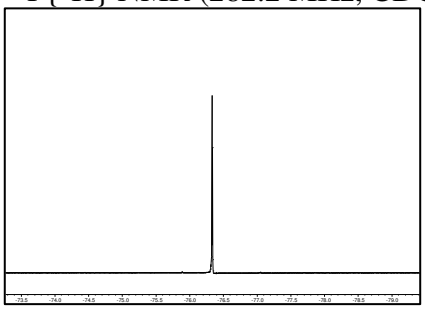
^{1}H NMR (300 MHz, $CDCl_3$) for $\mathbf{3_{SR}}$ at room temperature



$^{31}P\{^{1}H\}$ NMR (121.56 MHz, $CDCl_3$) for $\mathbf{3_{SR}}$ at room temperature

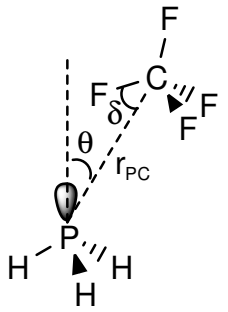


$^{19}F\{^{1}H\}$ NMR (282.2 MHz, $CDCl_3$) for $\mathbf{3_{SR}}$ at room temperature



Calculation of J_{PF}

PH_3-CF_4 model studies



Initial distance/angle calculations were obtained using a PH_3/CF_4 pair. The structures of PH_3 and CF_4 were geometry optimised and then employed as rigid rotors in subsequent coupling calculations. An initial estimate of appropriate r_{PC} was established for $\theta = \delta = 0°$ (Figure S1) and found to be 5.5-6.5 Å.

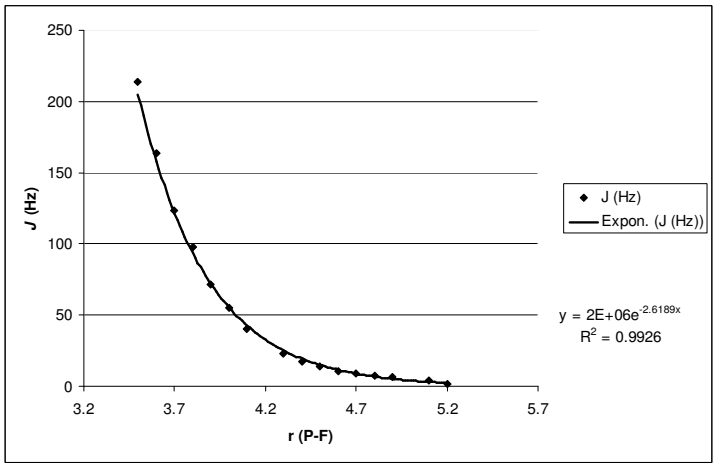


Figure S1 – Plot of r_{PF} (= r_{PC} – 1.3 Å) *vs* J_{PF} for the PH_3-CF_4 pair, at $\theta = \delta = 0°$. The line can be approximately fitted to an exponential curve.

Subsequent calculations varied r_{PC}, θ, as well as the P-C-F angle (δ). In all cases, the coupling constants calculated at $\delta = \pm 30°$ corresponded to the rotation-averaged value ± 5%, hence to save computational time only the ± 30° values were subsequently calculated and averaged to give the effective rotation-averaged J_{PF}.

$P(OH)_2NMe_2$-CF_4 calculations

On the basis of the data for the PH_3-CF_4 pair, calculation of the $P(OH)_2NMe_2$-CF_4 pair was undertaken in the same fashion as described for PH_3-CF_4 above over the range r_{PC} = 5.0-6.4 Å (in 0.1 Å steps) , with θ = 0-180° (in 5° steps). Sampling geometries outside these bounds gave either unhelpful values of J_{PF} (>>10Hz, or ~0 Hz) or were excluded on the steric grounds.

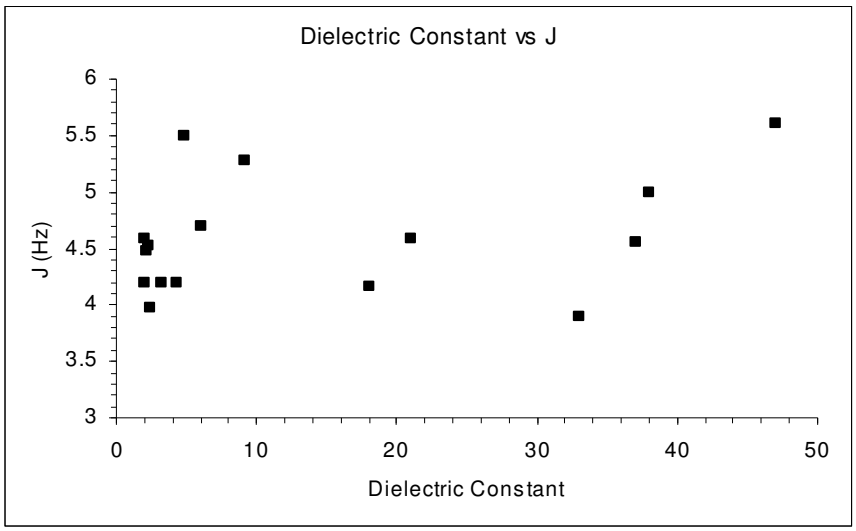
Effect of Solvent on Observed J_{PF} for 2

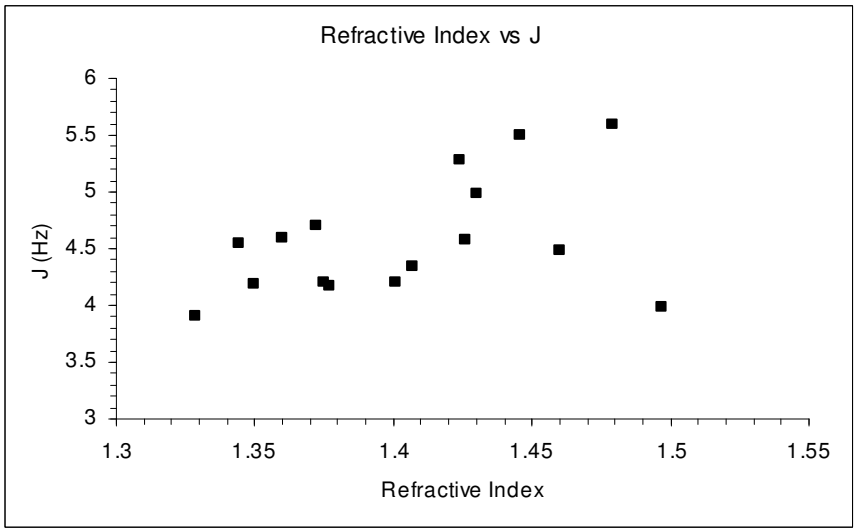
J_{PF} for **2** was measured in a range of solvents at room temperature and compared to a variety of solvent parameterisations for those solvents. A selection of this data is given in Table S1.

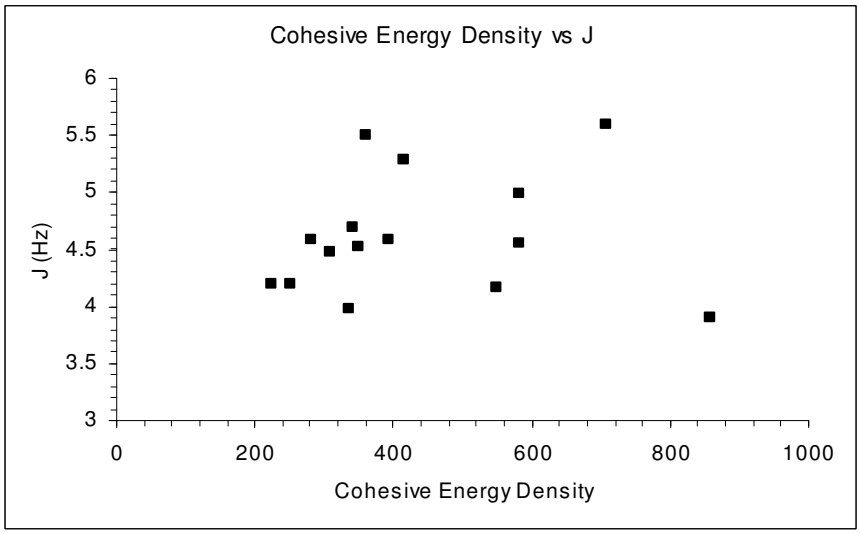
Table S1 – Tabulated Values for J_{PF} in various solvents with associated solvent parameters

Solvent	J_{PF}	Dielectric Constant[S6]	Refractive Index[S6]	Cohesive Pressure[S6]	Internal Pressure (P_i)[S6,S7]
benzene	**4.52**	2.3	1.5011	350.6	378
toluene	**3.98**	2.4	1.4969	337	354
Et_2O	**4.19**	4.3	1.3524	251	263
$CHCl_3$	**5.5**	4.8	1.4459	362	369
EtOAc	**4.7**	6	1.3724	341	353
CH_2Cl_2	**5.28**	9.1	1.4242	414	408
THF		7.5	1.4072		
Acetone	**4.59**	21	1.3587	394.6	336
CH_3CN	**4.55**	37	1.3441	581	378
DMF	**4.99**	38	1.4305	582.4	480
DMSO	**5.6**	47	1.4793	708	521
CH_3OH	**3.9**	33	1.3284	858	285
Isopropanol	**4.17**	18	1.3772	~550[S8]	280
triethylamine	**4.2**	3.2	1.401		
hexane	**4.2**	2	1.3749	225	238
cyclohexane	**4.58**	2	1.4262	282	325
CCl_4	**4.48**	2.2	1.4601	307.9	344

Correlations for tabulated solvent parameters with J_{PF} (Table S1)







Effect of Temperature on J_{PF} for 2 and 3_{SS}

J_{PF} was measured in toluene, chloroform and acetone (both deuterated and non-deuterated) at a range of temperatures from near the solvent boiling point down to the lowest temperature at which coupling could be resolved. This data is given in Table S2.

Table S2 – Observed J_{PF} for compounds **2** and $\mathbf{3}_{SS}$ in toluene, chloroform and acetone.

		J_{PF} **2** /Hz			J_{PF} $\mathbf{3}_{SS}$ /Hz		
T / °C	T / K	Toluene	$CDCl_3$	acetone	Toluene	$CDCl_3$	acetone
-70	203						
-58	215		3.08				
-55	218					2.42	
-50	223		3.24			2.62	
-40	233	1.62	3.55		1.66	2.99	
-30	243	2	4.08		2.13	3.32	
-20	253	2.46	4.32		2.52	3.55	
-10	263	2.96	4.61		2.92	4.04	
0	273	3.45	4.9		3.43		
10	283	3.79	5.25		3.84		
20	293	4.08			4.12		4.62
22	295			4.57			
25	298			4.64			
30	303		5.81	4.71	4.42	5.31	4.87
35	308			4.89			
40	313		6.09	5.1	4.73	5.57	5.22
50	323	5	6.23	5.38	4.92	5.89	5.5
60	333	5.44			5.47		
70	343	5.64			5.79		
80	353	6.03			5.94		
90	363	6.35			6.23		
100	373	6.5			6.5		

Computational details for calculation of temperature effect on J_{PF}

The temperature dependence of J_{PF} in **4** was modelled by calculating both J_{PF} and the absolute (gas phase) energies of CF_3 rigid-rotamers of 1-dimethylphosphino-2-trifluoromethylbenzene, adjusting the angle between the plane of the aryl ring and each C-F bond in 10° steps. Relative energies and the average J_{PF} for each rotamer are presented in Table S3

Table S3 – Relative Energies and J_{PF} for each CF_3-rotamer of 1-dimethylphosphino-2-trifluoromethylbenzene

Angle between the Aryl group and each C-F bond (°)			Relative energy of rotamers KJ/mol	Average J_{PF}
60	-60	180	1.1	53.00006
50	-70	170	0	53.957347
40	-80	160	2.2	74.248973
30	-90	150	7.3	111.1404
20	-100	140	15.3	155.52972
10	-110	130	23.4	199.18104
1	-119	121	28.4	226.82488
-10	-130	110	29.3	232.05645
-20	-140	100	25	205.6856
-30	-150	90	17.8	159.38394
-40	-160	80	10.6	109.36434
-50	-170	70	4.8	71.11097

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[S3] CCDC-644613 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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