SUPPORTING INFORMATION

NMR spectroscopy as Unique Tools for the Quantification of Weak Interactions Between Trivalent Phosphorus compounds and Diphenyliodonium ion

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I. General procedures

Commercially available products were purchased from Sigma Aldrich and were used as received. All manipulations were carried out under an argon atmosphere.

II. Procedures for NMR experiments.

Diphenyliodonium triflate (DPIT) (50 mg, 1.5 eq) was introduced in a tube and the tube was sealed with a septum and conditioned under vacuum (20-25 mmHg) then filled with argon. Dry MeCN-d_3 (0.6 mL) was added and the tube is covered with aluminum foil to keep away from light[1]. Then triethylphosphite ($P(OEt)_3$) was finally added (14 μL, 1eq) and kinetic monitoring was performed by 1D ^1H and $^{31}P\{^1H\}$ NMR with in situ-illumination[2] of the solution. For DPIT/PPh_3 sample[3], the same procedure is established by adding diphenyliodonium triflate (30 mg, 1 eq) and triphenylphosphine (27 mg, 1.5 eq) in 0.6 mL MeCN-d_3. DPIT/PPh_2Me sample was prepared by adding diphenyliodonium triflate (30 mg, 1 eq) and triphenylphosphine (60 μL, 4 eq) in 0.6 mL MeCN-d_3.

To compute the binding constants,[4] ten samples of each DPIT/$P(OEt)_3$, DPIT/PPh_3, and DPIT/PPh_2Me mixture were prepared with a constant DPIT concentration. DPIT was maintained at a concentration of 0.1 M (25.8 mg) for the $P(OEt)_3$ and PPh_2Me samples. To prevent solubility concerns with PPh_3, a lower concentration of DPIT was utilized at 0.03 M (7.74 mg).

III. NMR parameters and Instrumentation.

All NMR experiments were recorded on a Bruker Avance III 500 MHz spectrometer operating at 500 MHz for ^{1}H, 470 MHz for ^{19}F and 202 MHz for ^{31}P. Experiments were run under Topspin (version 3.2) with a BBFO {^{1}H, X} probe and a z gradient unit. The residual solvent signals were used as references for ^{1}H NMR spectra (MeCN-d_3: δ_{1H} = 1.97 ppm). ^{19}F and ^{31}P NMR spectra were referenced (δ = 0.0 ppm) to calculated ^{19}F and ^{31}P chemical shift in CCl_3F and H_3PO4 references compounds, respectively. Reactions were monitored by in-situ illumination device using a high-power LED with a center wavelength of 455 nm. For EDA complexes characterization, NMR experiments are done at low temperature (240 and 260 K).

1D NMR measurements

1D ^{1}H experiments were acquired with standard Bruker "zg" program. The spectra were acquired with sweep width of 10 K Hz and 32 K data points, using 16 scans and the relaxation delay (D1) was 5 s. Exponential window function (LB=0.3) was applied before Fourier transformation.

1D $^{31}P\{^{1}H\}$ NMR experiments were acquired with broadband proton decoupling in order to remove ^{31}P - ^{1}H coupling. The spectra were recorded with sweep width of 60000 Hz and 66560 data points, using 100 scans and the relaxation delay (D1) was 8 s. Exponential window function (LB=3) was applied before Fourier transformation.

2D NMR measurements

2D ^{1}H-^{31}P HMBC: The following parameters were used for acquiring and processing the 2D ^{1}H-^{31}P HMBC spectrum: 128 experiments with 2048 data points and 16 scans each were recorded. The recycling delay was 5 s; acquisition mode was DQD; one time zero filling in F1; pure sine bell window functions were applied to F2 and F1 dimensions before Fourier transformation to obtain a digital resolution of 39.7 Hz/point in F1 and 7.8 Hz/point in F2. The gradient pulses ratio used are 49.4%, 49.4% and 40%.

2D ^{1}H-^{1}H NOESY: The following parameters were used for acquiring and processing the spectrum: 256 experiments with 2048 data points and 16 scans each FID was recorded. The recycling delay was 5 s. Pure phase line shapes was obtained by STATES phase cycling. The

mixing time τ_m was between 2 to 2.6 s. One time zero filling in F1, pure sine bell window functions were applied before Fourier Transform to obtain a digital resolution of 7.8 Hz/point in F1 and 7.8 Hz/point in F2.

2D ^{19}F-^{1}H HOESY: The following parameters were used for acquiring and processing the spectrum: 128 experiments with 2048 data points and 16 scans each FID were recorded. The recycling delay time was 5 s. Pure phase line shapes was obtained by using time proportional phase incrementation (TPPI) phase cycling. The mixing time was τ_m = 2.2 s. One time zero filling in F1, pure sine bell window functions were applied before Fourier Transform to obtain a digital resolution of 4.9 Hz/point in F1 and 50.9 Hz/point in F2.

^{1}H DOSY: The DOSY experiments were acquired with the standard Bruker ledbpgp2s program using 8 experiments with 16384 data points. The relaxation delay was 5 s (D1). Diffusion time was between 0.05 - 0.1 s (D20) and rectangular gradient pulse duration was 0.6 ms (P30). Gradient recovery delays of 0.2 ms followed the application of each gradient pulse. Data was accumulated by linearly varying the diffusion encoding gradients over a range from 2 to 95 % for 16 gradient increment values.

Processing of DOSY NMR data were performed using Dynamics Center software (Bruker software). This program allows the use of the pure exponential equation for relevant processing methods:

$$S(g) = I_0 * e^{(-\gamma^2 * g^2 * \delta^2 * \left(\Delta - \delta/3\right) * D}$$

The diffusion coefficients were determined by fitting the peak areas to the Stejskal-Tanner equation from T_1/T_2 analysis. Molecular weight calculations were processed using ECC-Mw estimation software (Stalke Chemie, Germany)[5].

NMR binding constant study

The observed ^{1}H chemical shift values and concentrations of both the guest and host were inputted into the Bindfit software (http://supramolecular.org/)[4] alongside an estimation of the binding constants and limiting chemical shifts. These parameters were then refined to achieve the optimal fit between the calculated and empirical chemical shifts based on five host-guest binding models (1:1, 1:2 Full, 1:2 Non-cooperative, 1:2 Additive and 1:2 Non-statistical).

The input parameters were varied until convergence of the best fit values of the binding constants was attained.

References

1. W. Lecroq, P. Bazille, F. Morlet-Savary, M. Breugst, J. Lalevée, A. C. Gaumont and S. Lakhdar, *Org. Lett.*, 2018, **20**, 4164–4167.
2. C. Feldmeier, H. Bartling, E. Riedle and R. M. Gschwind, *J. Magn. Reson*., 2013, **232**, 39–44.
3. A. F. Fearnley, J. An, M. Jackson, P. Lindovska and R. M. Denton, *Chem. Commun.*, 2016, **52**, 4987-4990.
4. B. Hibbert, P. Thordarson, *Chem. Commun.*, **2016**, *52*, 12792-12805.
5. (a) R. Neufeld, D. Stalke, *Chem. Sci.* 2015, 6, 3354-3364; (b) S. Bachmann, B. Gernert and D. Stalke, *Chem Commun*. 2016, **52**, 12861-12864.

IV. DFT calculations

Computational details

Calculations were performed using Gaussian16 package. Full optimizations were performed using hybrid functional M06-2X and 6-31++G** basis set for all atoms except iodine, and the aug-cc-pVTZ-PP for iodine. Geometry optimizations are repeated for all possible conformers of the molecules. Only the more stable optimized geometry was selected.

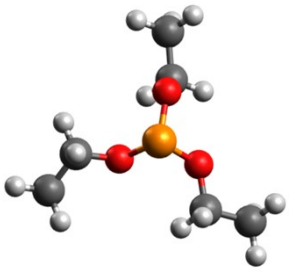
Following each optimization, the harmonic frequencies has been determined and it has systematically been checked that all vibrational frequencies are real and not imaginary, to correspond to a minima. At each stage, the bulk solvent effect has been considered using the PCM methods.

The potential energy surface (PES) scan was performed with fully relaxed geometry (except for the imposed I—Ph bond length) at each step of the scan. The scan was performed using the same hybrid functional than the full optimizations (M06-2X) and 6-31+G* basis set for all atoms, except for iodine (aug-cc-pVTZ-PP).

TDDFT methodology is used to investigate the excited states of interest. In accordance with the previous study on this type of compound[1], the MPW1PW91/6-31+G(d,p)/ aug-cc-pVTZ-PP level has been chosen. The lowest 20 singlet-singlet vertical electronic excitations were calculated, and only the major ones were chosen (oscillator strength up to 0.1). The geometry of the lowest singlet excited state of each compound is relaxed using TDDFT, followed by harmonic frequencies calculations to verify the presence of a minimum. State-specific method was used in order to take into account the solvent effect described by PCM. For the absorption, the molecule was optimised in its ground-state and the informations about solvation are stored. Then the vertical excitation is calculated using the solvation precedently stored in a non-equilibrium calculation.

[1] P. Garra, B. Graff, F. Morlet-Savary, C. Dietlin, J-M. Becht, J-P. Fouassier, J. Lalevée, *Macromolecules*, 2017, **51**, 57-70

Triethylphosphite. E = -804.658071 u.a



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Excited State coordinates :

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H	-3.416796	-2.276147	-3.824427
H	-5.078804	-1.766705	-4.164539
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Diphenyliodonium triflate.

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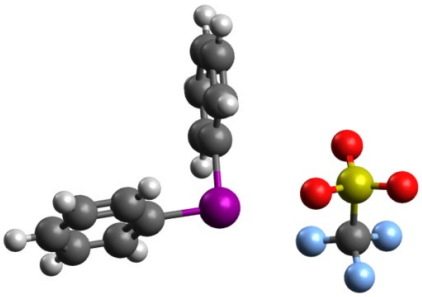

Ground State coordinates :

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C	1.175082	1.639859	-0.603010
H	0.904737	1.286753	0.384597
C	0.954835	2.967082	-0.968958
H	0.510500	3.648234	-0.251924
C	1.297337	3.411191	-2.245394
H	1.119287	4.444562	-2.521283
C	1.863901	2.535876	-3.170956
H	2.126770	2.882482	-4.164090
C	2.097320	1.204426	-2.829276
H	2.534747	0.518251	-3.544077
C	3.975119	-0.932607	-0.102681
C	4.022175	-0.675474	1.265058
H	3.116928	-0.604184	1.856303
C	5.271864	-0.509565	1.860113
H	5.332448	-0.306795	2.923558
C	6.432964	-0.606772	1.094207
H	7.401040	-0.478139	1.565502
C	6.358343	-0.872236	-0.272751
H	7.262844	-0.951097	-0.865467
C	5.119428	-1.041507	-0.888863
H	5.056383	-1.250909	-1.950190
O	-0.290624	-1.689639	-2.346689
S	-1.743959	-1.392293	-2.374069
C	-2.326522	-2.038544	-0.730704
F	-3.643439	-1.851765	-0.588680
F	-1.705711	-1.409513	0.275162
F	-2.077122	-3.348317	-0.616858
O	-2.080026	0.038044	-2.323347
O	-2.500123	-2.193358	-3.348188

Excited State coordinates:

I	2.095134	-1.211471	-1.013047
C	1.747089	0.795466	-1.547655
C	1.175082	1.639859	-0.603010
H	0.904737	1.286753	0.384597
C	0.954835	2.967082	-0.968958
H	0.510500	3.648234	-0.251924
C	1.297337	3.411191	-2.245394
H	1.119287	4.444562	-2.521283
C	1.863901	2.535876	-3.170956
H	2.126770	2.882482	-4.164090
C	2.097320	1.204426	-2.829276
H	2.534747	0.518251	-3.544077
C	3.975119	-0.932607	-0.102681
C	4.022175	-0.675474	1.265058
H	3.116928	-0.604184	1.856303
C	5.271864	-0.509565	1.860113
H	5.332448	-0.306795	2.923558
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C	5.119428	-1.041507	-0.888863
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F	-1.705711	-1.409513	0.275162
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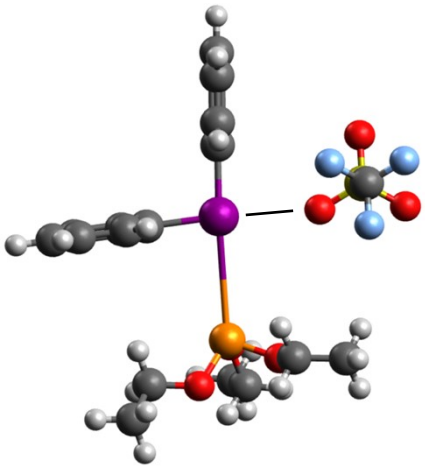

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Excited State coordinates :

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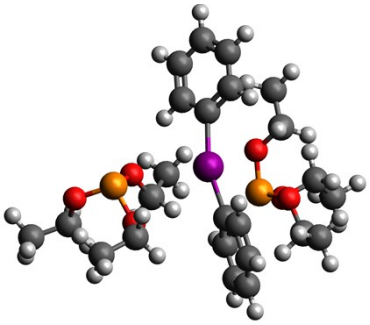

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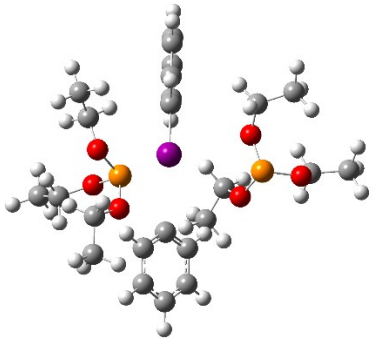

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Complex 1:1 DPIT/$P(Ph)_3$.

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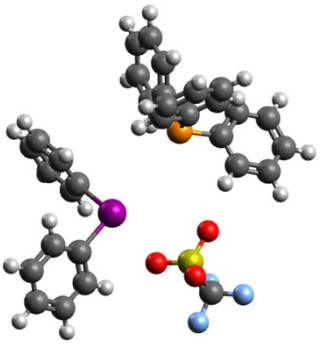

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Complex DPI/$P(Ph)_3$/MeCN.

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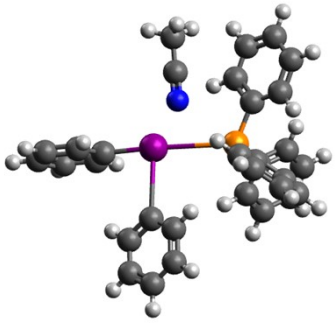

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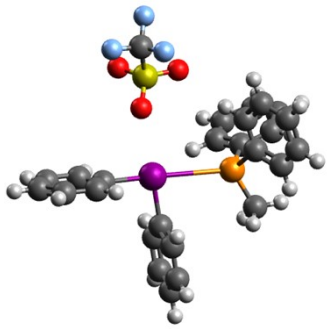

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V. NMR data

Fig. 1S. 1D ^{1}H (500 MHz, left) and $^{31}P\{^{1}H\}$ (202 MHz, right) NMR spectra of mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1) in MeCN-d_3 at 298 K.

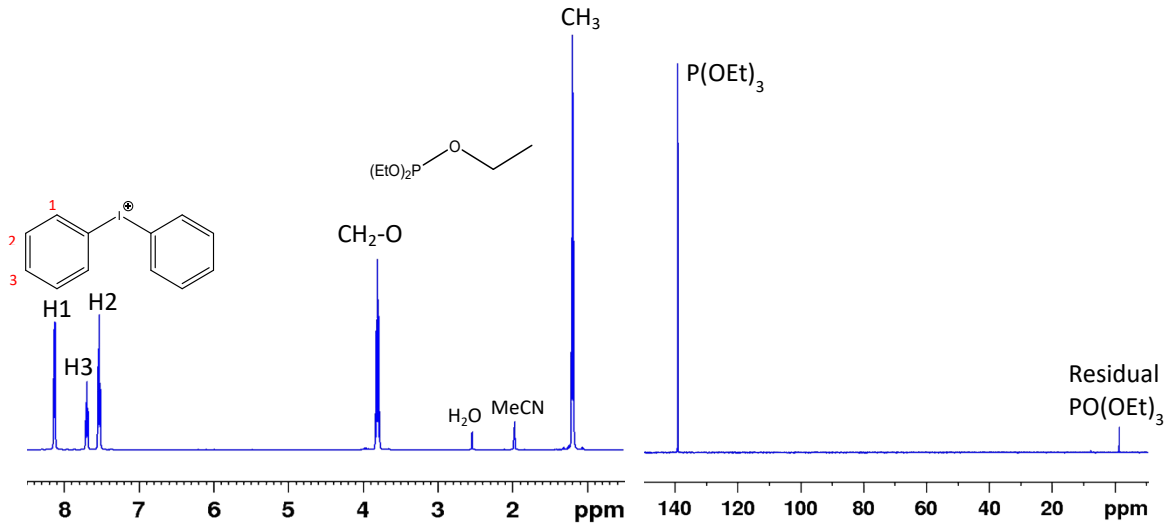


Fig. 2S. Zoom of 1D ^{1}H (500 MHz, MeCN-d_3, 298 K) NMR spectra of mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1) with in situ-illumination for: a) 20 min; b) 40 min; c) 2 h; d) 5 h; e) 16 h; and f) 24 h.

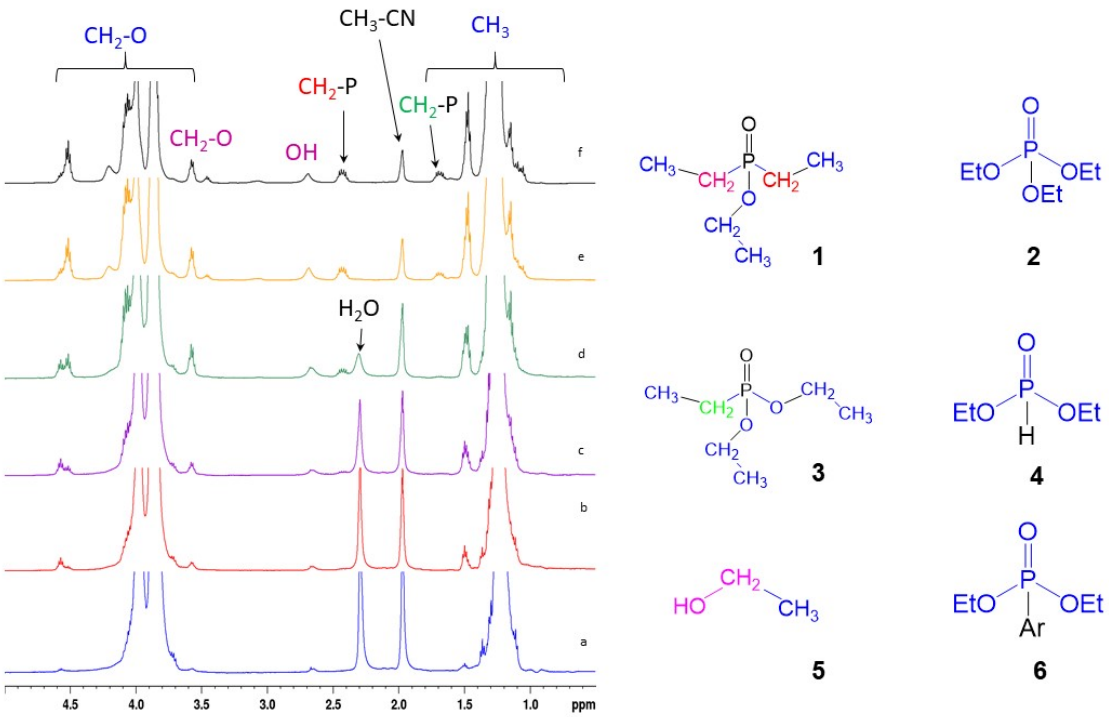


Fig. 3S. Zoom of 2D ^{1}H-^{31}P HMBC (500 MHz, MeCN-d_3, 298 K) spectrum of a mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1).

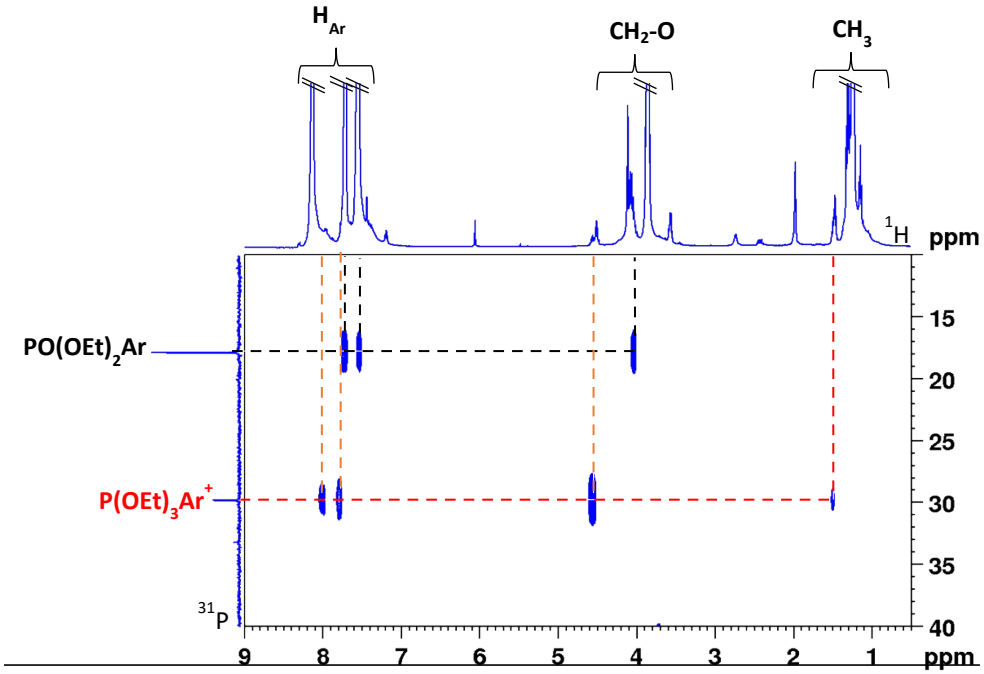
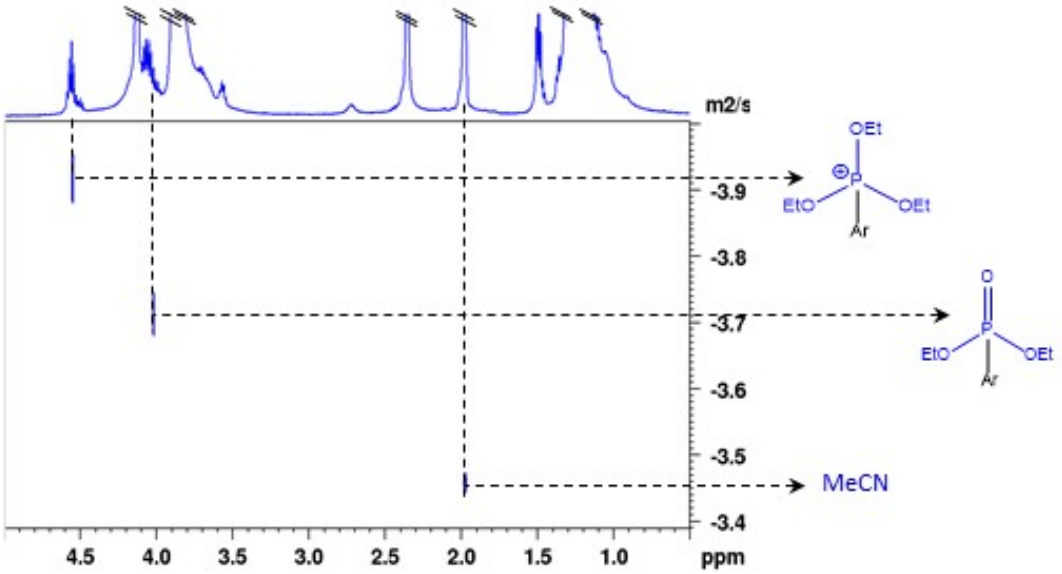


Fig. 4S. a) ^{1}H DOSY (500 MHz, MeCN-d_3, 298 K) after 2 hours of illumination of a mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1). b) Signal attenuation curves from ^{1}H DOSY of MeCN (red), $PO(OEt)_2Ar$ (blue) and $P(OEt)_3Ar^+$ (black).

a)



b)

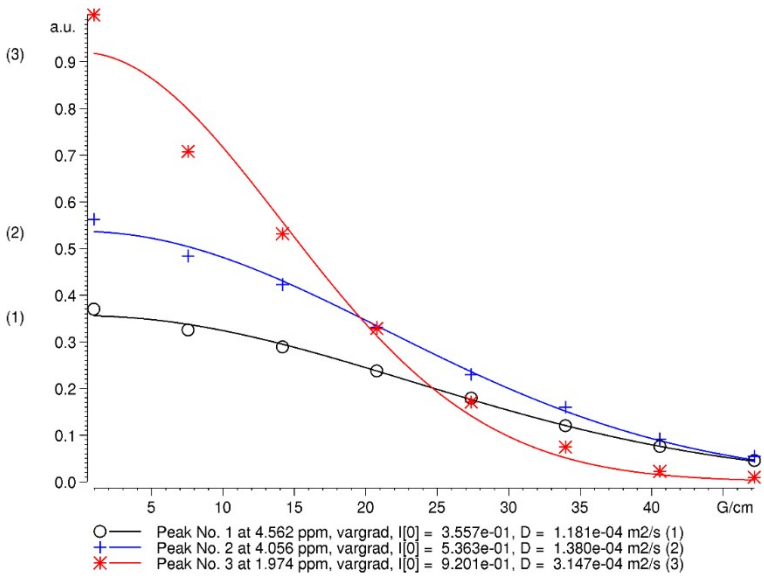


Fig. 5S. Zoom of 1D ^{1}H (500 MHz, left) and $^{31}P\{^{1}H\}$ (202 MHz, right) NMR spectra of mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1) in MeCN-d_3 at 310 K for: a) 20 min; b) 40 min; c) 2 h; d) 5 h; e) 16 h; and f) 24 h.

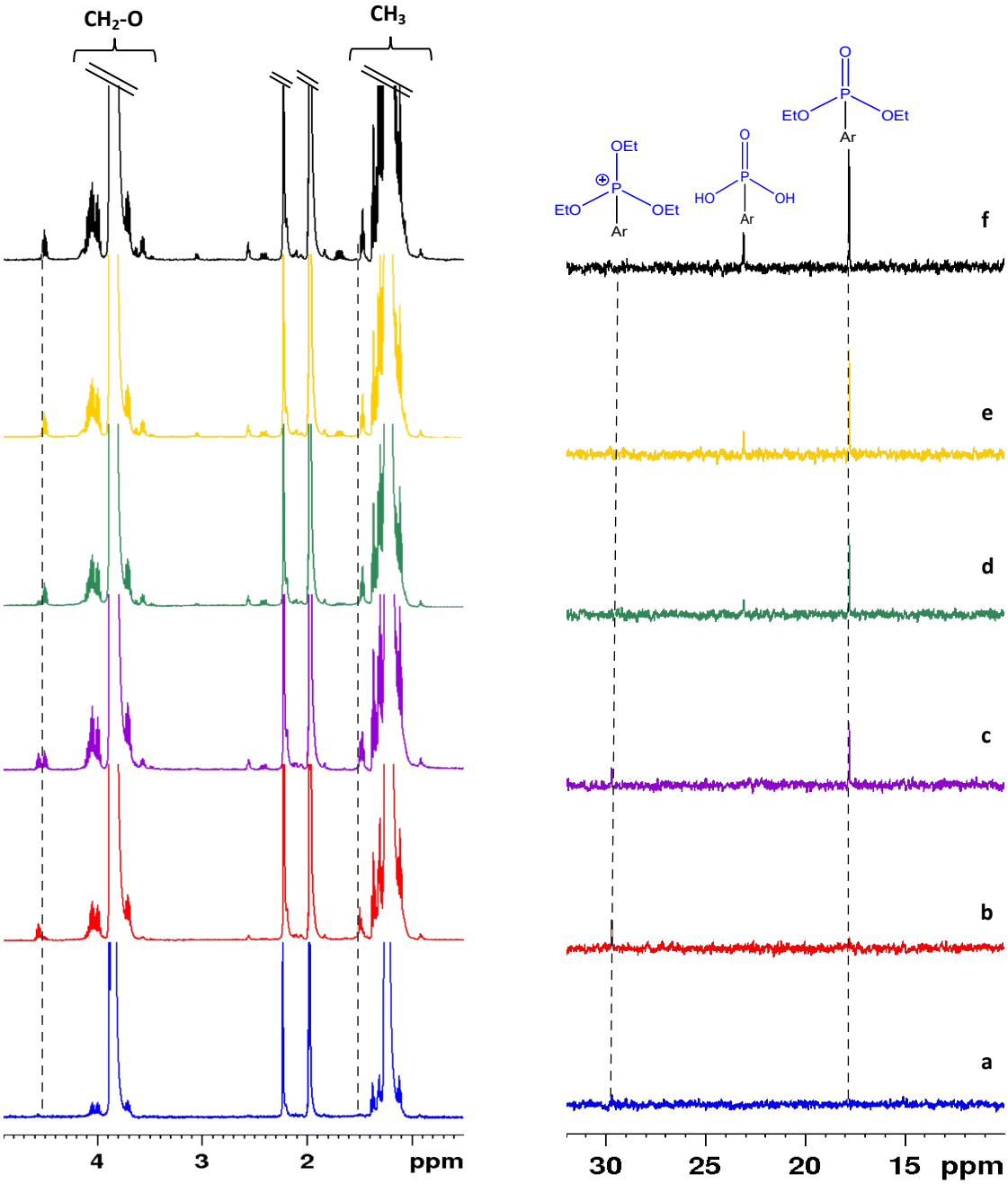


Fig. 6S. Zoom of 1D ^{1}H spectra (500 MHz, MeCN-d_3, 240 K) of a mixture of diphenyliodonium triflate and triethylphosphite (red), diphenyliodonium triflate (blue) and triethylphosphite (green).

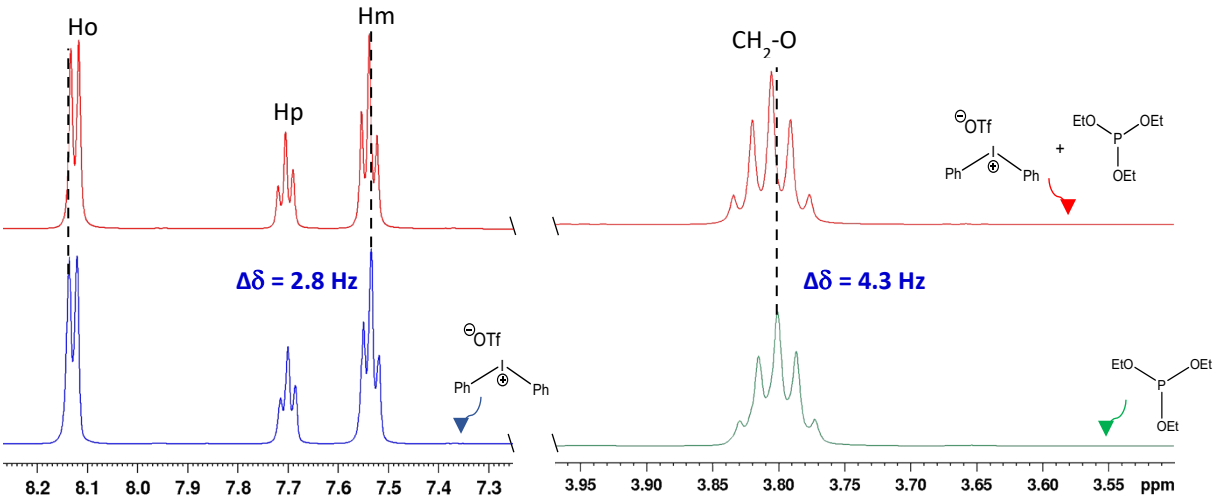


Fig. 7S. ^{1}H DOSY (500 MHz, MeCN-d_3, 240 K) spectra of: a) $P(OEt)_3$, b) DPIT and c) mixture of DPIT/$P(OEt)_3$ (1.5:1).

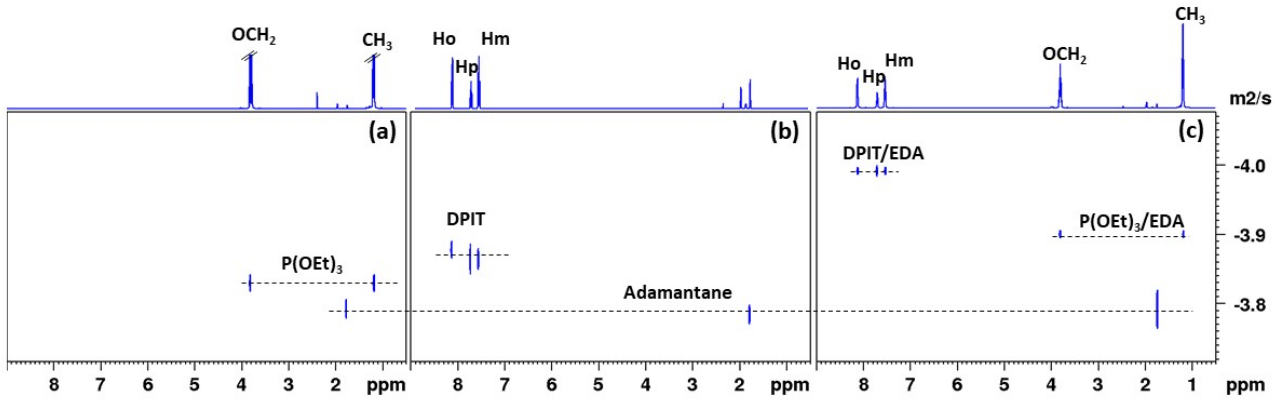


Fig. 8S. Zoom of 1D ^{1}H NMR spectra (500 MHz, MeCN-d_3, 240 K) of mixtures (0.1 M) of diphenyliodonium triflate with various amount of $P(OEt)_3$: a) $[P(OEt)_3]$=0.013 M; b) $[P(OEt)_3]$=0.142 M; c) $[P(OEt)_3]$=0.292 M; d) $[P(OEt)_3]$=0.486 M and e) $[P(OEt)_3]$=0.582 M.

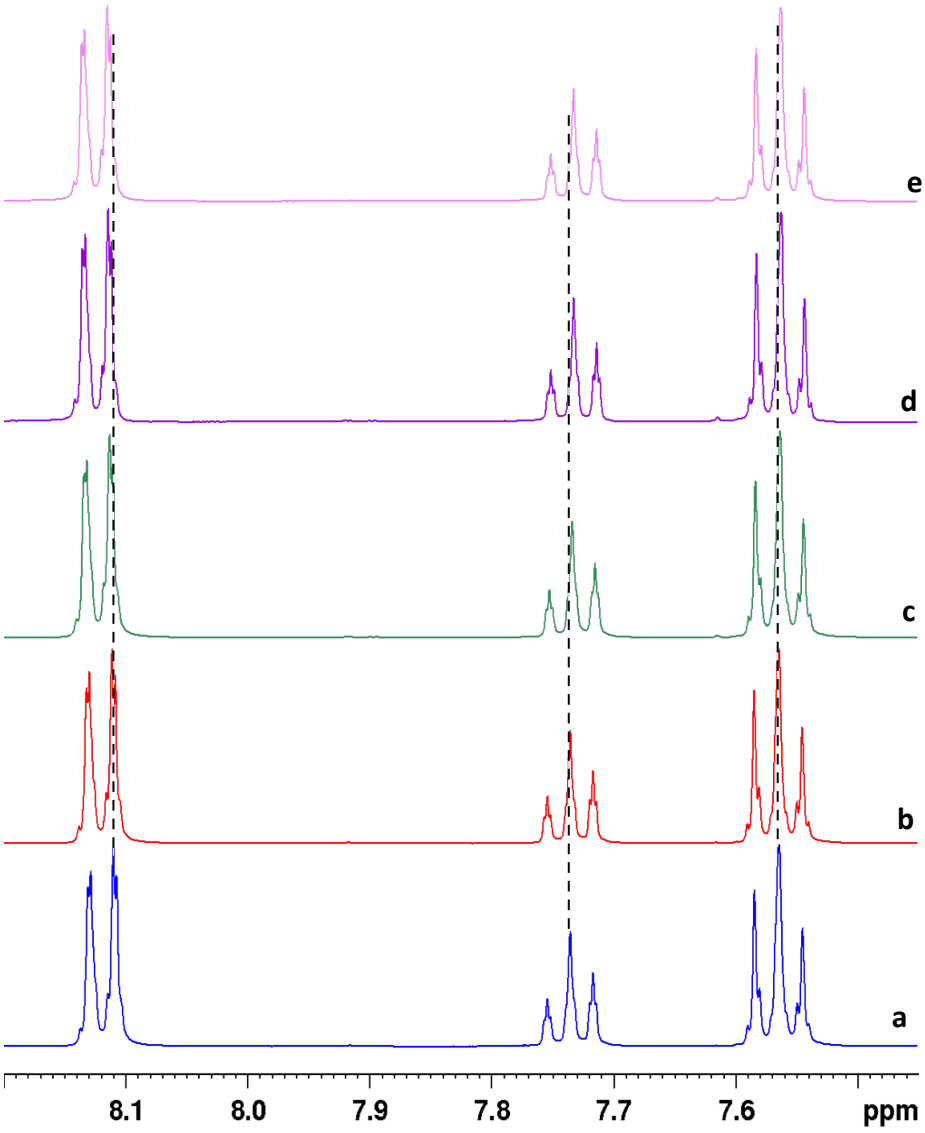


Table 1S. Diphenyliodonium aromatic proton chemical shifts according to various $P(OEt)_3$ concentrations in DPIT/ $P(OEt)_3$ mixtures. ([DPIT]=0.1 M, MeCN-d_3, at 310 K, 298 K and 240 K).

[DPIT]=0.1 M, MeCN-d_3, T= 310 K				
$P(OEt)_3$ volume (µl)	$[P(OEt)_3]$ Concentration (M)	δ ortho (ppm)	δ para (ppm)	δ meta (ppm)
5	0.013	8.1103	7.7387	7.5674
10	0.081	8.1109	7.7383	7.5671
15	0.142	8.1113	7.739	7.5681
20	0.193	8.1116	7.7392	7.5686
25	0.243	8.1137	7.7356	7.5654
30	0.292	8.1132	7.7369	7.5664
40	0.388	8.1133	7.7366	7.5662
50	0.486	8.1145	7.7358	7.5657
60	0.582	8.1149	7.7357	7.5655
0	0	8.1101	7.7391	7.5684

[DPIT]=0.1 M, MeCN-d_3, T= 298 K				
$P(OEt)_3$ volume (µl)	$[P(OEt)_3]$ Concentration (M)	δ ortho (ppm)	δ para (ppm)	δ meta (ppm)
5	0.048	8.1103	7.7355	7.5641
10	0.096	8.1113	7.736	7.5649
15	0.145	8.1116	7.7357	7.565
20	0.193	8.1123	7.7354	7.5648
25	0.243	8.1127	7.7345	7.5638
30	0.292	8.1134	7.7338	7.5634
40	0.388	8.1136	7.7337	7.5633
50	0.486	8.115	7.7327	7.5626
60	0.582	8.1156	7.7329	7.5629
0	0	8.1106	7.7354	7.5643

[DPIT]=0.1 M, MeCN-d_3, T= 240 K				
$P(OEt)_3$ volume (µl)	$[P(OEt)_3]$ Concentration (M)	δ ortho (ppm)	δ para (ppm)	δ meta (ppm)
5	0.013	8,1184	7,7036	7,5371
10	0.081	8.1199	7.7025	7.5363
15	0.142	8.1206	7.7046	7.5378
20	0.193	8.1204	7.705	7.5384
25	0.243	8.1214	7.7032	7.5369
30	0.292	8.1225	7.7023	7.5364
40	0.388	8.123	7.7013	7.5356
50	0.486	8.1247	7.6996	7.5345
60	0.582	8.125	7.7025	7.5368
0	0	8.1163	7.708	7.5402

Table 2S. Comparison of various models (fit method: Nelder-Mead) for binding of $P(OEt)_3$ to DPIT (T=310K, 298K and 240K).

T=310K			
Binding Model	K_1 [M^{-1}] ± % error	K_2 [M^{-1}] ± % error	Cov_{fit} ratio ($Cov_{fit\ 1:2}$ / $Cov_{fit\ 1:1}$)
1 : 1	0.144 ± 17.49	-	-
1 : 2 (full)	84.362 ± 376.41	8.315 ± 38.87	1.204
1 : 2 (non-coop)	46.589 ± 39.41	11.647	2.036
1 : 2 (additive)	0.004 ± 133014.59	4955.063 ± 133013.39	1.069
1 : 2 (statistical)	0.297 ± 17.74	0.132	1.000

Link for the corresponding non-cooperative model at 310K :
http://app.supramolecular.org/bindfit/view/36a097fd-e45a-4680-92bd-4a313fced4cb

T=298K			
Binding Model	K_1 [M^{-1}] ± % error	K_2 [M^{-1}] ± % error	Cov_{fit} ratio ($Cov_{fit\ 1:2}$ / $Cov_{fit\ 1:1}$)
1 : 1	9.92×10^{-6} ± 0.718	-	-
1 : 2 (full)	1497.29 ± 694.863	1.769 ± 10.757	2.977
1 : 2 (non-coop)	22.542 ± 12.162	5.635	2.650
1 : 2 (additive)	0.003 ± 59480.196	3126.845 ± 59488.471	1.219
1 : 2 (statistical)	- 0.397 ± 9.272	- 0.099	1.033

Link for the corresponding non-cooperative model at 298K :
http://app.supramolecular.org/bindfit/view/ab8ccee4-1b95-4e41-8220-6e0996a429b4

T=240K			
Binding Model	K_1 [M^{-1}] ± % error	K_2 [M^{-1}] ± % error	Cov_{fit} ratio ($Cov_{fit\ 1:2}$ / $Cov_{fit\ 1:1}$)
1 : 1	0.119 ± 26.292	-	-
1 : 2 (full)	21.184 ± 396.371	3.028 ± 59.825	1.044
1 : 2 (non-coop)	15.185 ± 44.484	3.796	1.044
1 : 2 (additive)	0.755 ± 821.916	15.021 ± 840.854	1.018
1 : 2 (statistical)	0.244 ± 26.604	0.061	0.999

Link for the corresponding non-cooperative model at 240K :
http://app.supramolecular.org/bindfit/view/0b1ea45d-6f1e-4b94-ae41-da26320d91e2

Fig. 9S. Potential energy surface (PES) scan for the elongation of the I—Ph bond

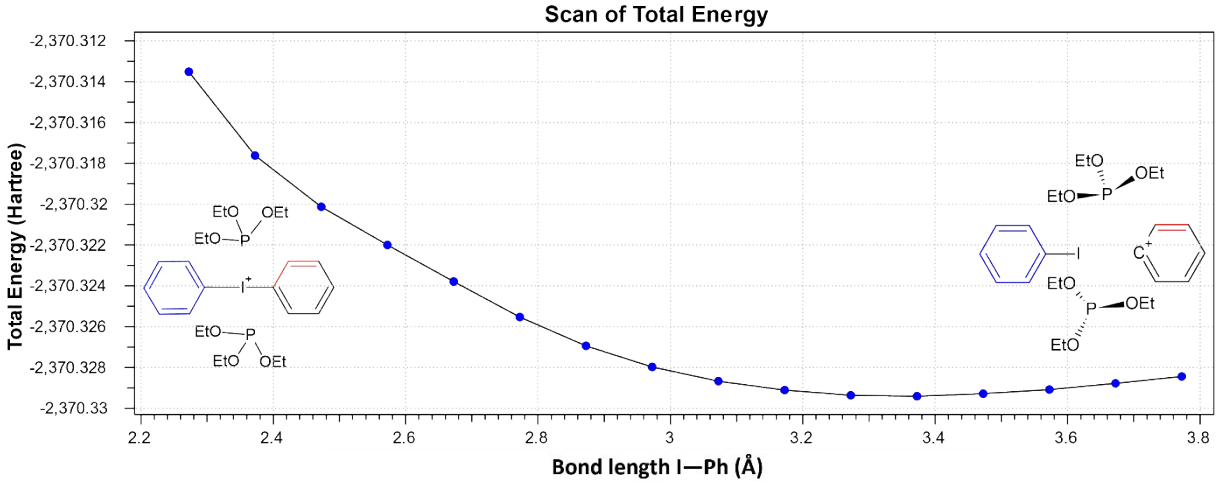


Table 3S. Phosphoarylation reaction's conversions with different solvents

Solvant	Conversion (%)
MeCN	93
DMF	47
CH_2Cl_2	24

Fig. 10S. Zoom of 2D ^{1}H-^{31}P HMBC spectra (500 MHz, 240 K) of a mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1) in DMF-d_7 (left) and CD_2Cl_2 (right).

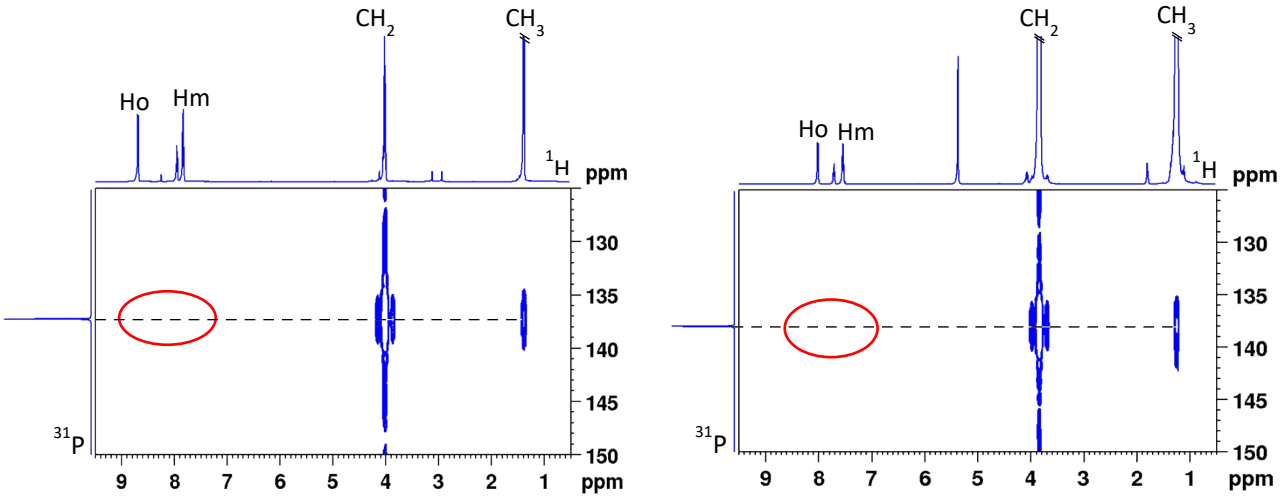


Fig. 11S. Zoom of 2D ^{1}H-^{1}H NOESY (500 MHz, 240 K) spectra of a mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1) in DMF-d_7 (left) and CD_2Cl_2 (right).

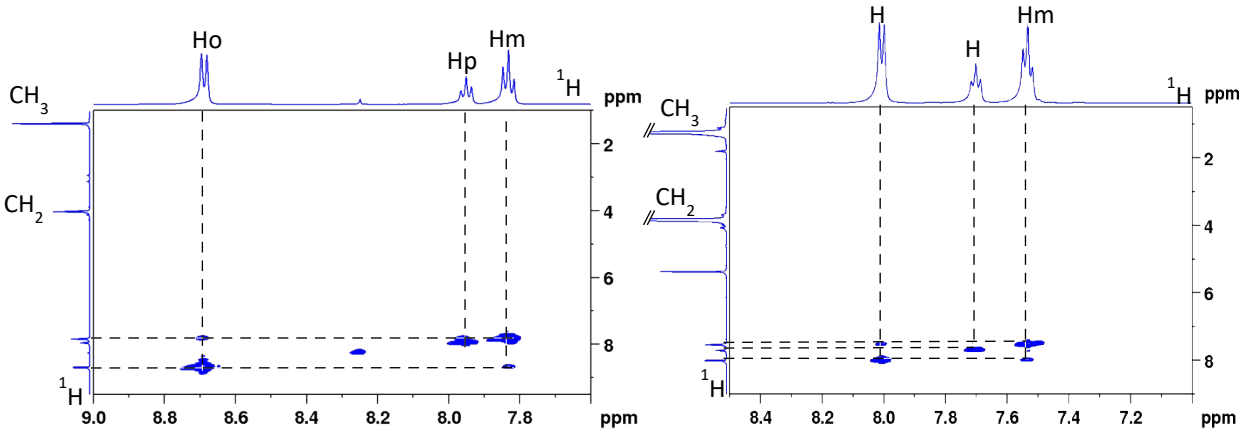


Fig. 12S. ^{1}H DOSY (500 MHz, 240 K) spectra of a mixture of diphenyliodonium triflate (0.2M) and triethylphosphite (1.5:1) in DMF-d_7 (left) and CD_2Cl_2 (right).

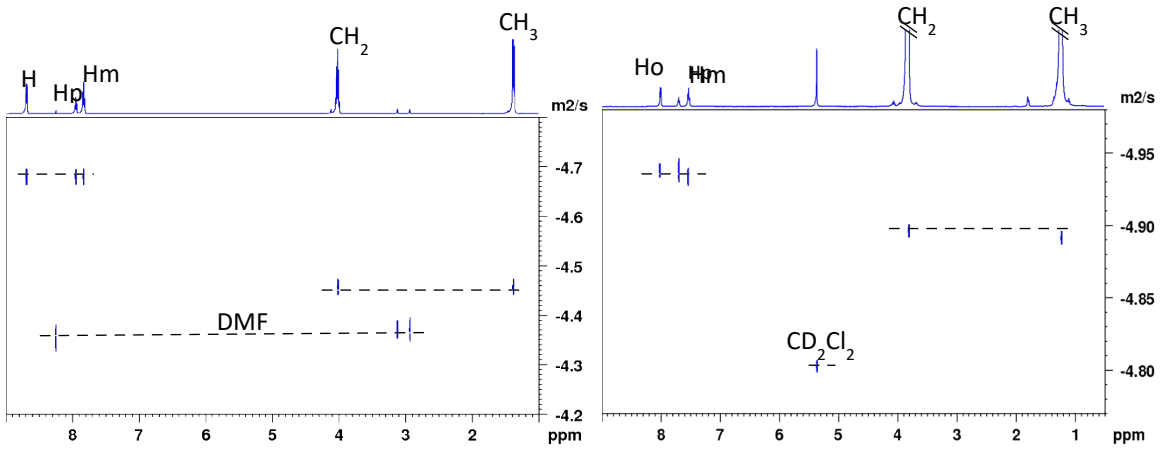


Fig. 13S. Zoom of 1D ^{1}H spectra (500 MHz, MeCN-d_3, 260 K) of diphenyliodonium triflate (bottom) and triphenylphosphine (middle) and a mixture of diphenyliodonium triflate and triphenylphosphine (1:1.5 eq) (top).

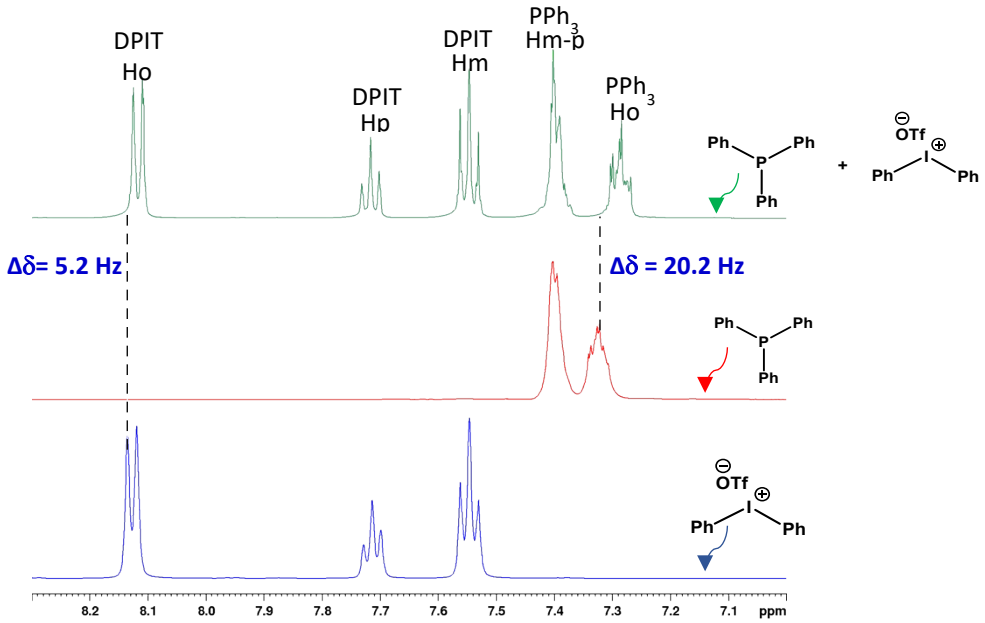


Fig. 14S. Zoom of 2D ^{1}H-^{31}P HMBC spectrum of diphenyliodonium triflate and triphenylphosphine (500 MHz, MeCN-d_3, 260 K).

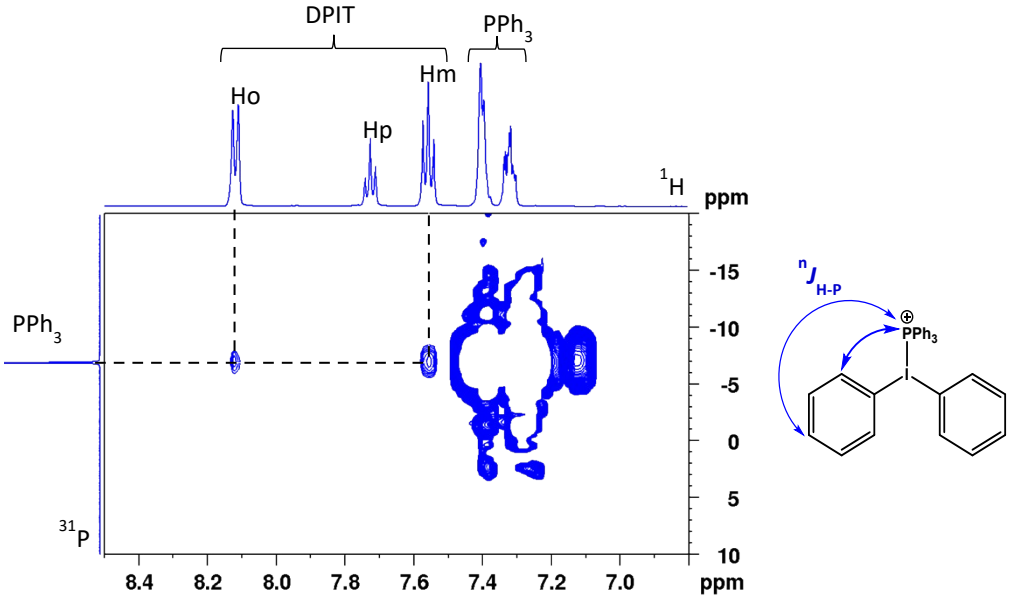


Fig. 15S. 2D ^{1}H-^{19}F HOESY spectrum of diphenyliodonium triflate and triphenylphosphine (500 MHz, MeCN-d_3, 260 K).

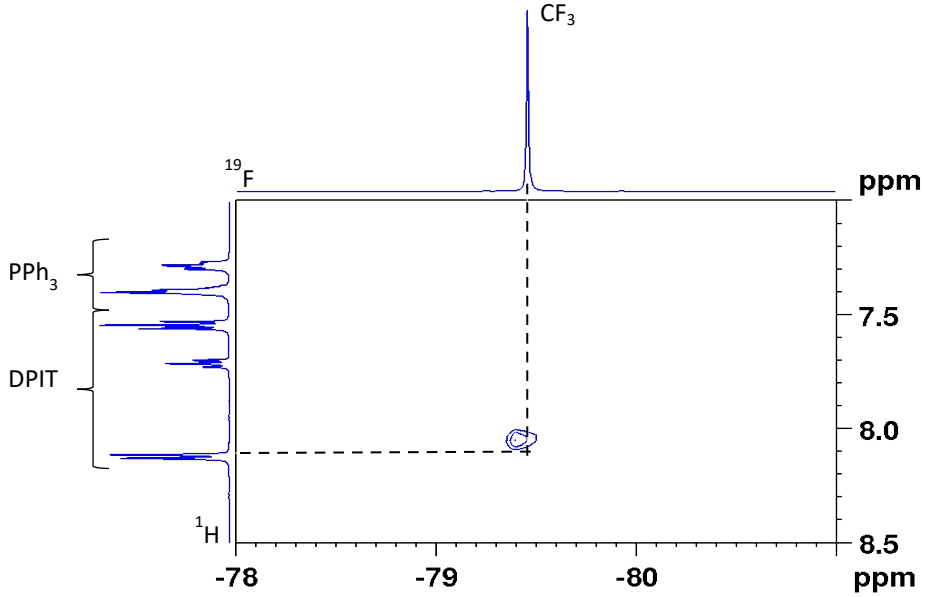


Fig. 16S. 1D ^{1}H spectra of diphenyliodonium triflate (blue), diphenylmethylphosphine (green) and mixture of diphenyliodonium triflate and diphenylmethylphosphine (1:4 eq) (500 MHz, MeCN-d_3, 260 K)

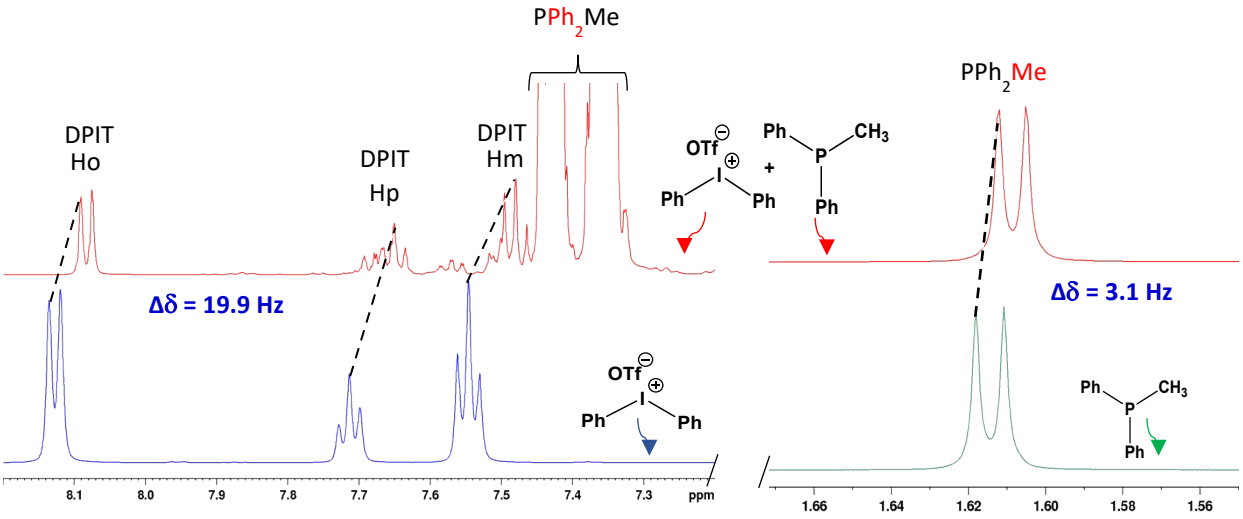


Fig. 17S. Zoom of 2D ^{1}H-^{31}P HMBC spectrum of mixture of diphenyliodonium triflate and diphenylmethylphosphine (1:4 eq) (500 MHz, MeCN-d_3, 260 K)

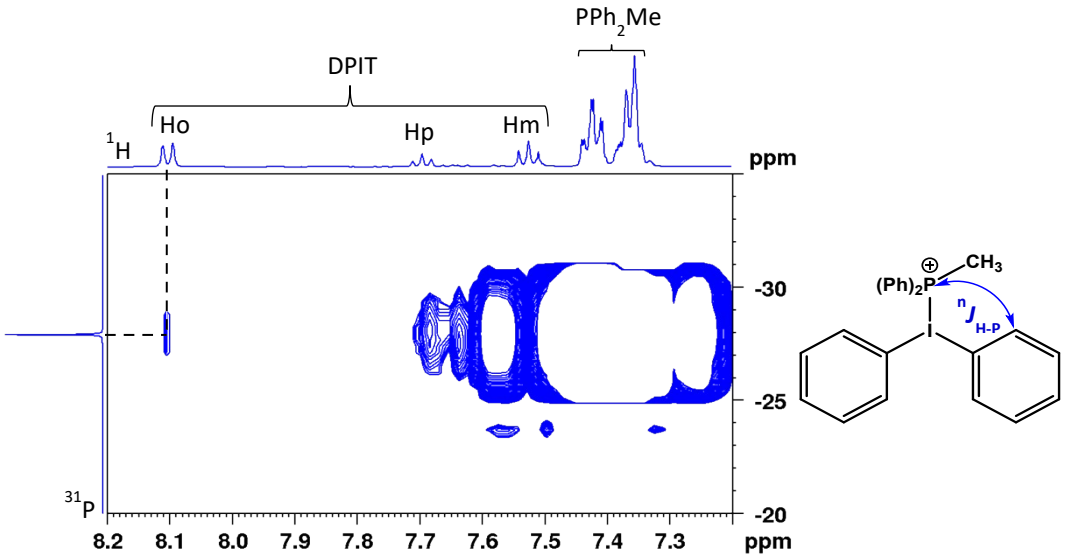


Fig. 18S. Zoom of 2D ^{1}H-^{1}H NOESY spectrum of mixture of diphenyliodonium triflate and diphenylmethylphosphine (1:4 eq) (500 MHz, MeCN-d_3, 260 K)

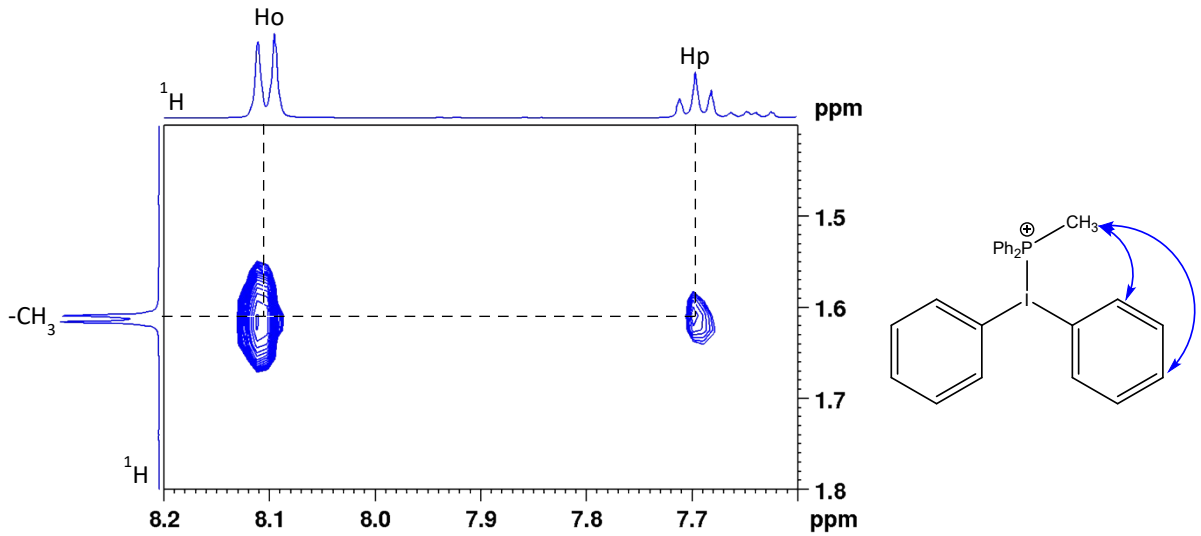


Fig. 19S. Zoom of 2D ^{19}F-^{1}H HOESY spectrum of mixture of diphenyliodonium triflate and diphenylmethylphosphine (1:4 eq) (500 MHz, MeCN-d_3, 260 K)

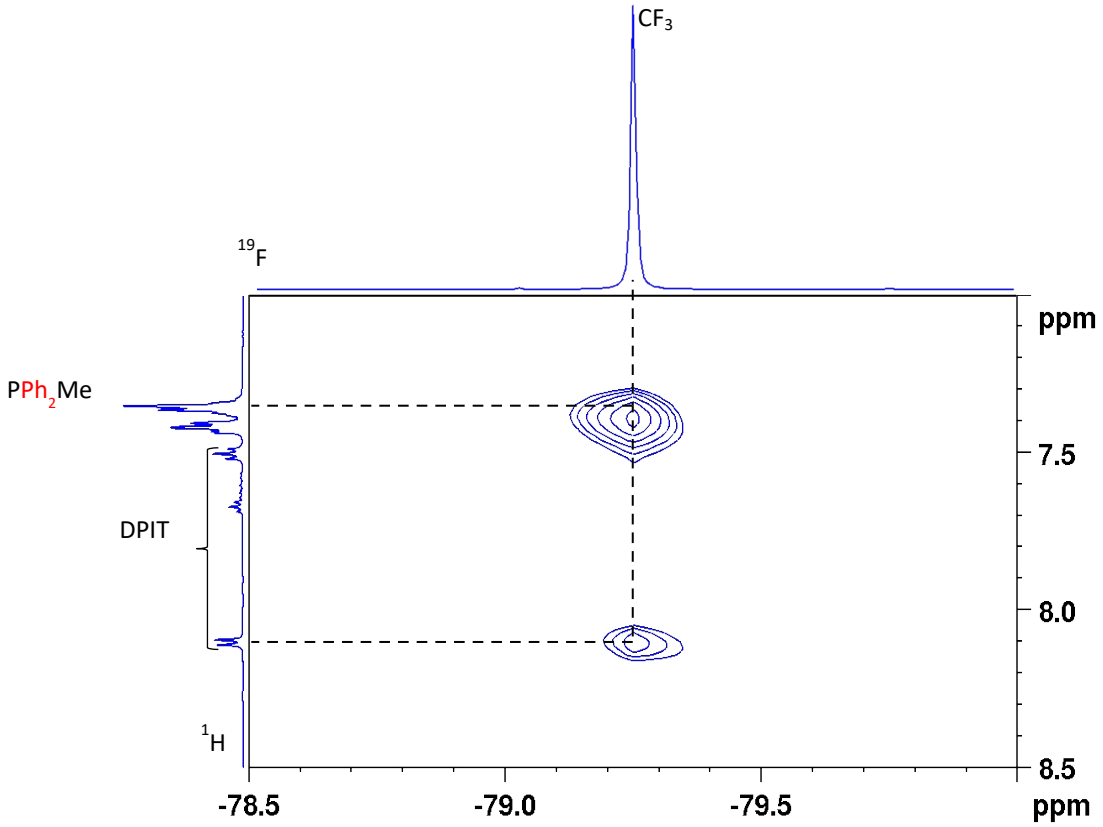


Table 4S. Diphenyliodonium aromatic proton chemical shifts according to various PPh_3 concentrations in DPIT/PPh_3 mixtures ([DPIT]=0.03 M, MeCN-d_3, 260 K)

PPh_3 mass (mg)	[PPh_3] Concentration (M)	δ ortho (ppm)	δ para (ppm)	δ meta (ppm)
2	0.013	8.1073	7.7274	7.5556
5	0.032	8.1058	7.7259	7.554
10	0.064	8.1041	7.7208	7.5492
12	0.076	8.1033	7.719	7.5474
15	0.095	8.1029	7.7184	7.547
18	0.114	8.1021	7.7161	7.5452
20	0.127	8.1015	7.7151	7.5442
22	0.139	8.1011	7.7138	7.5428
25	0.158	8.1009	7.7133	7.5426
0	0	8.112	7.7186	7.5531

Table 5S. Comparison of various models (fit method: Nelder-Mead) for binding of PPh_3 to DPIT at 260K

Binding Model	K_1 [M^{-1}] ± % error	K_2 [M^{-1}] ± % error	Cov_{fit} ratio ($Cov_{fit\ 1:2}$ / $Cov_{fit\ 1:1}$)
1 : 1	8.85×10^{-5} ± 18.558	-	-
1 : 2 (full)	0.002 ± 546.391	203281.1 ± 215.987	1.118
1 : 2 (non-coop)	57.921 ± 61.121	14.480	1.064
1 : 2 (additive)	0.003 ± 453138.544	32407.037 ± 453207.897	1.114
1 : 2 (statistical)	- 1.117 ± 12.803	- 0.279	0.994

Link for the corresponding non-cooperative model at 260K :
http://app.supramolecular.org/bindfit/view/4b482329-be64-4ebe-b593-445604e03fdc

Table 6S. Diphenyliodonium aromatic proton chemical shifts according various PPh_2Me concentrations in DPIT/PPh_2Me mixtures ([DPIT]=0.1 M, MeCN-d_3, 260 K)

PPh_2Me volume (µl)	[PPh_2Me] concentration (M)	δ ortho (ppm)	δ para (ppm)	δ meta (ppm)
5	0.045	8.1102	7.7119	7.5426
10	0.09	8.1061	7.7018	7.5326
15	0.135	8.103	7.697	7.5278
20	0.18	8.1021	7.6908	7.5218
25	0.223	8.0987	7.6854	7.5163
30	0.268	8.0979	7.6809	7.5121
40	0.365	8.0933	7.6761	7.5067
50	0.447	8.0876	7.6494	7.4814
60	0.537	8.1134	7.6505	7.482
0	0	8.1134	7.7186	7.5494

Table 7S. Comparison of various models (fit method: Nelder-Mead) for binding of PPh_2Me to DPIT at 260K.

Binding Model	K_1 [M^{-1}] ± % error	K_2 [M^{-1}] ± % error	Cov_{fit} ratio ($Cov_{fit\ 1:2}$ / $Cov_{fit\ 1:1}$)
1 : 1	0.144×10^{-5} ± 0.804	-	-
1 : 2 (full)	0.056 ± 51.506	52.338 ± 140.925	1.034
1 : 2 (non-coop)	4.625 ± 7.611	1.156	1.031
1 : 2 (additive)	1.183 ± 62.094	3.339 ± 78.927	1.018
1 : 2 (statistical)	1.421×10^{-14} ± 5.728	3.553×10^{-15}	0.999

Link for the corresponding non-cooperative model at 260K :
http://app.supramolecular.org/bindfit/view/fd34ddce-1769-4b40-a9c2-c77d0114ee1d

Fig. 20S. Calculated UV-Vis absorption spectra of: a) triethylphosphite, b) diphenyliodonium triflate and c) EDA complex. In the case of EDA complex, triflate counterion is removed for calculation time consideration