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Electronic supplementary information 1 Crystallographic data

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Tandem dihetero-Diels-Alder and Huisgen cycloaddition reactions. Synthesis, structure and hydrolysis of the novel cage phosphoranes based on 2-(1phenylethenyloxy)benzo-1,3,2-dioxaphosphole

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Single Crystal X-ray Analysis. The X-ray diffraction (XRD) data for the single crystals of 7, 9, 13, and 23 were collected on a three-circle diffractometer diffractometer with a CCD plate detector (ω -scan mode) using graphite-monochromated MoK α (0.71073 Å) radiation at 293(2) K. The XRD data for 8 and 20 were collected on a on a four-circle diffractometer diffractometer with a CCD plate detector (ω/ϕ -scan mode) using graphitemonochromated MoKa radiation at 293(2) and 150(2) K, respectively. The performance mode of the sealed X-ray tubes was 50 kV, 30 mA. Suitable crystals of appropriate dimensions were mounted on glass fibres or cactus needles in random orientations. Preliminary unit cell parameters were determined with three or four sets of 12 narrow frame scans. Data collection: images were indexed and integrated using the APEX2 (v2014.11-0) or APEX3 (v2015.9-0) data reduction package. Final cell constants were determined by global refinement of reflections from the complete data set. Data were corrected for systematic errors and absorption using SADABS-2014/5. XPREP-2014/2 and the ASSIGN SPACE GROUP routine of WinGX-2014.1 were used for analysis of systematic absences and space group determination. The structures were solved by the direct method using SHELXT-2018/2^{S1} and refined by the fullmatrix least-squares on F^2 using SHELXL-2018/3^{S2}. Calculations were mainly performed using the WinGX-2014.1 suite of programs.^{S3} Non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atom H^1 of **13** and the hydrogen atoms H^2 , H^3 , and H^4 of **20** were determined based on the difference electronic density maps and these atoms were refined isotropically. The positions of the hydrogen atoms of methyl groups were found using a rotating group refinement with idealized tetrahedral angles. The other hydrogen atoms were inserted at the calculated positions and refined as riding atoms. In the cases of 7, 8, and 13 the disorder was resolved using free variables and reasonable restraints on geometry and anisotropic displacement parameters. All the compounds studied have no unusual bond lengths and angles. The absolute structure of crystals 13 and 20 was determined on the basis of the Flack parameter.54

The unit cell of **9** contains highly disordered solvent molecules of pentane along 4-fold screw axes, which were treated as a diffuse contribution to the overall scattering without specific atom positions by PLATON/SQUEEZE-290617.⁸⁵ In the unit cell (Z = 16) there are 4 voids with volume of *ca*. 198 Å³ containing *ca*. 42 electrons per the void, hence the ratio of phosphorane **9** to pentane is 4 : 1. Squeezed solvent info is not included in the formula and related items such as molecular weight and calculated density. Interestingly, compound **23** crystallizes with the molecule bisected by mirror planes in the centrosymmetric space group *Pnma* of the orthorhombic crystal system, hence the asymmetric cell contains half of the molecule (Z' = 0.5). This structure was reported previously.⁸⁶

Crystallographic data for 7. $C_{20}H_{11}F_{12}O_5P$, colorless prism, formula weight 590.26, monoclinic, $P2_1/c$, a = 15.787(9) Å, b = 10.811(6) Å, c = 13.977(8) Å, $\beta = 112.816(7)^\circ$, V = 2199(2) Å³, Z = 4, Z' = 1, $d_{calc} = 1.783$ g·cm⁻³, $\mu(\lambda MoK_{\alpha}) = 0.260$ mm⁻¹, F(000) = 1176; 20876 reflections were collected, 4023 of which were unique, $R_{int} = 0.0363$, $R_{\sigma} = 0.0268$; completeness to θ of 25.242° is 99.7 %. Refinement of 398 parameters with 212 restraints converged to $R_1 = 0.0444$, $wR_2 = 0.1116$ for 3018 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0611$, $wR_2 = 0.1226$ for all data with S = 1.028 and residual electron density, $\rho_{max/min} = 0.313$ and -0.273 e Å⁻³.

Crystallographic data for 8. $C_{24}H_{21}F_6O_9P$, colorless prism, formula weight 598.38, triclinic, *P*–1, *a* = 10.7892(6) Å, *b* = 11.1562(6) Å, *c* = 11.7122(6) Å, $\alpha = 101.788(3)^\circ$, $\beta = 99.647(3)^\circ$, $\gamma = 106.558(3)^\circ$, *V* = 1283.93(12) Å³, *Z* = 2, *Z'* = 1, *d_{calc}* = 1.548 g·cm⁻³, $\mu(\lambda MoK_{\alpha}) = 0.203 \text{ mm}^{-1}$, *F*(000) = 612; 38254 reflections were collected, 4510 of which were unique, $R_{int} = 0.0572$, $R_{\sigma} = 0.0422$; completeness to θ of 25.242° was 96.5 %. The refinement of 383 parameters with 55 restraints converged to $R_1 = 0.0442$, $wR_2 = 0.1057$ for 2940 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0813$, $wR_2 = 0.1222$ for all data with *S* = 1.027 and residual electron density, $\rho_{max/min} = 0.216$ and -0.275 e Å⁻³.

Crystallographic data for 9. $C_{18}H_{13}Cl_6O_5P$, colorless prism, formula weight 552.95, tetragonal, $I4_1/a, a = 27.972(6)$ Å, c = 11.844(3) Å, V = 9268(5) Å³, Z = 16, Z' = 1, $d_{calc} = 1.585$ g·cm⁻³, $\mu(\lambda MoK_{\alpha}) = 0.838$ mm⁻¹, F(000) = 4448 (squeezed solvent info is not included in the formula and related items); 34206 reflections were collected, 4413 of which were unique, $R_{int} = 0.0349$, $R_{\sigma} = 0.0199$; completeness to θ of 25.242° was 99.9 %. The refinement of 271 parameters with no restraints converged to $R_1 = 0.0399$, $wR_2 = 0.0199$ 0.0929 for 3637 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0500$, $wR_2 = 0.0990$ for all data with S = 1.048 and residual electron density, $\rho_{\text{max/min}} = 0.758$ and $-0.686 \text{ e} \text{ Å}^{-3}$.

Crystallographic data for 13. $C_{12}H_{20}NO_4P$, colorless plate, formula weight 273.26, monoclinic, $P2_1$, a = 7.266(3) Å, b = 11.409(5) Å, c = 8.573(4) Å, $\beta = 96.695(6)^\circ$, V = 705.8(5) Å³, Z = 2, Z' = 1, $d_{calc} = 1.286$ g·cm⁻³, $\mu(\lambda MoK_a) = 0.201$ mm⁻¹, F(000) = 292; 5170 reflections were collected, 2545 of which were unique, $R_{int} = 0.0317$, $R_{\sigma} = 0.0557$; completeness to θ of 25.242° was 100 %. The refinement of 228 parameters with 200 restraints converged to $R_1 = 0.0429$, $wR_2 = 0.0846$ for 2011 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0589$, $wR_2 = 0.0915$ for all data with S = 1.038 and residual electron density, $\rho_{max/min} = 0.137$ and -0.172 e Å⁻³. Absolute structure parameter was 0.01(9).

Crystallographic data for 20. C₆H₇O₅P, colorless prism, formula weight 190.09, orthorhombic, $P2_12_12_1$, a = 4.6005(4) Å, b = 10.1220(8) Å, c = 16.4334(14) Å, V = 765.24(11) Å³, Z = 4, Z' = 1, $d_{calc} = 1.650$ g·cm⁻³, $\mu(\lambda MoK_{\alpha}) = 0.338$ mm⁻¹, F(000) = 392; 5805 reflections were collected, 2368 of which were unique, $R_{int} = 0.0346$, $R_{\sigma} = 0.0486$; completeness to θ of 25.242° was 99.2 %. The refinement of 121 parameters with no restraints converged to $R_1 = 0.0387$, $wR_2 = 0.0831$ for 2159 reflections with $I > 2\sigma(I)$ and $R_1 = 0.0440$, $wR_2 = 0.0859$ for all data with S = 1.045 and residual electron density, $\rho_{max/min} = 0.325$ and -0.408 e Å⁻³. Absolute structure parameter was -0.08(8).

Crystallographic data for 23. $C_{10}H_7Cl_3O$, colorless prism, formula weight 249.51, orthorhombic, *Pnma*, a = 10.636(8) Å, b = 7.223(6) Å, c = 14.840(11) Å, V = 1140.1(15) Å³, Z = 4, Z' = 0.5, $d_{calc} = 1.454$ g·cm⁻³, $\mu(\lambda MoK_a) = 0.767$ mm⁻¹, F(000) = 504; 7560 reflections were collected, 1120 of which were unique, $R_{int} = 0.0665$, $R_{\sigma} = 0.0445$; completeness to θ of 25.242° was 100 %. The refinement of 82 parameters with no restraints converged to $R_1 = 0.0825$, $wR_2 = 0.2255$ for 702 reflections with $I > 2\sigma(I)$ and $R_1 = 0.1163$, $wR_2 = 0.2555$ for all data with S = 1.082 and residual electron density, $\rho_{max/min} = 0.845$ and -0.557 e Å⁻³. This structure was reported previously ^{S6}.

It can be assumed that the carbon of the trichloromethyl group $C^{21}Cl_3$ in molecule **9** is located on the plane $P^1O^2O^3C^7$ [deviation of atom C^{21} from the above plane is -0.150(2) Å]. In molecules **7** and **8** the atoms C^{23} , F^1 , F^2 , $F^{12}(in molecule$ **7** $) and <math>C^{21}$, C^{27} , F^1 , F^2 , F^6 (in molecule **8**) are lying in this plane, and their deviations from the above one are: 0.038(3), 0.105(2), -0.231(2), -0.158(2), -0.150(2), 0.174(2), -0.120(2), -0.111(2) and -0.182(2) Å, respectively.

The five-membered heterocycle of the benzodioxaphosphole fragment is planar within 0.018(2) Å (7), 0.025(2) Å (8), 0.042(2) Å (9) and occupies the axial-equatorial position in the trigonal bipyramid (the atom O¹ is apical, the atom O³ is equatorial). The atoms O² and C⁷ are deviated from this plane in different directions by the following distances: 1.441(2) and 1.286(2) Å (7), -1.372(2) and 1.410(2) Å (8), -1.442(2) and 1.297(2) Å (9). The atom O⁸ is accordingly lying in dioxaphosphole heterocycle plane [its deviation from the plane O¹P¹O³C⁸C¹³ is 0.171(2) Å (7), 0.145(2) Å (8), 0.000(2) Å (9)]. It could be considered that in molecule 9 the planar benzodioxaphosphole fragment is a part of a longer eleven-atom plane O¹P¹O³O⁸C⁵C⁸⁻¹³ plane [within 0.065(2) Å], and atom C¹⁵ is deviated from this plane on 0.506(2) Å. The phenyl substituent C¹⁵⁻²⁰ plane at C⁵ atom is considerably turned with respect to this eleventh atomic fragment [dihedral angle between planes O¹P¹O³O⁸C⁵C⁸⁻¹³/

Substituents at the atoms of this cycle (O^1 , O^2 , C^4 , C^{24} , O^3 , C^{18} , C^{27}) in molecule (8) are deviated from the above plane fragment on distances of 0.496(2), 1.473(2), 1.422(2), 1.229(2), -1.155(2), -0.913(2) and -1.993(3) Å and occupy *eq* (equatorial), *ax* (axial), *ax*, *bi* (bisectional), *bi*, *bi*, *ax* positions, respectively. Substituents at the atoms of the five-membered cycle (O^1 , O^2 , C^4 , O^3 , C^{15} , C^{21}) in molecule 9 are deviated from the plane $P^1C^7O^6C^5$ on 0.614(2), 0.1.494(2), 1.355(2), -1.064(1), -0.912(2) and -1.348(2) Å, and located in *eq*, *ax*, *ax*, *bi*, *bi*, *ax* positions, respectively.

The corresponding deviations of C¹⁶, C²³, O², O³, C⁴ and C²² substituents from the P¹O⁸C⁵O⁶C⁷ cycle are [in parentheses here and below their spatial arrangement is presented] 1.18(2) [*bi*], 1.400(3) [*ax*], -2.276(2) [*ax*], -0.391(2) [*eq*], -1.375(3) [*ax*], and -0.796(3) Å [*bi*], respectively.

The substituents at atoms of the six-membered ring of the molecule 7 (O¹, O³, O⁶, C⁷, C¹⁴, C¹⁵ and C¹⁶¹ atoms) are deviated from planar fragment P¹O²C⁴C⁵ on the following distances: 0.690(2) [*eq*], -1.381(2) [*bi*], 1.423(2) [*ax*], 1.504(2) [*bi*], 0.556(4) [*eq*], -1.803(3) [*ax*] and -0.37(3) Å [*eq*], respectively. The substituents at atoms of the six-membered ring of the molecule **8** (O¹, O³, O⁶, C⁷, C¹⁴, C¹⁷ and C¹⁸ atoms) are deviated from the plane fragment mentioned above on the following distances: 0.856(2) [*eq*], -1.174(2) [*bi*], 1.328(2) [*ax*], 1.555(2) [*bi*], -2.103(3) [*ax*], -0.174(3) Å [*eq*] and -0.533(2) [*eq*], respectively. The substituents O¹, O³, O⁶, C⁷, C¹⁴ and C¹⁵ of the same cycle in molecule **9** are deviated from planar fragment P¹O²C⁴C⁵ on the following distances: 0.822(2) [*eq*], -1.245(1) [*bi*], 1.351(1) [*ax*], 1.503(2) [*bi*], 0.221(2) [*eq*] and -0.420(2) Å [*eq*], respectively.

The crystal of the compound **20** is stabilized by a 2D system of classical intermolecular H-bonds. Parameters of the H-bonds are $O^2-H^2 0.75(4)$ Å, $O^2\cdots O^2$ 2.781(2) Å, $H^2\cdots O^2$ 2.08(4) Å, angle $O^2-H^2\cdots O^2$ 158(3)°, symmetry transformation used to generate equivalent atoms is x + 0.5, 1.5 - y, 1 - z; O^3-H^3 ; 0.82(4) Å, $O^3\cdots O^5$ 2.549(3) Å, $H^3\cdots O^5$ 1.73(4) Å, angle $O^3-H^3\cdots O^5$ 178(4)°, symmetry transformation is x - 1, y, z; $O^4-H^4 0.80(3)$ Å, $O^4\cdots O^5$ 2.586(2) Å, $H^4\cdots O^5$ 1.79(3) Å, angle $O^4-H^4\cdots O^5$ 169(4)°, symmetry transformation is x - 0.5, 0.5 - y, 1 - z.

The crystallographic data for the investigated crystal samples have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1852085 (7), 1852086 (8), 1852087 (9), 1852088 (13), and 1852089 (20).These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Table S1. Crystal data and structure refinement for 7.

CCDC number Empirical formula Formula weight Temperature Radiation, wavelength Crystal system Space group Unit cell dimensions Volume Z and Z'Calculated Density Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Observed Data $[I > 2\sigma(I)]$ Completeness to theta = 25.242° Absorption correction Max. and min. transmission Data / restraints / parameters Goodness-of-fit on F^2 Final *R* indices $[I > 2\sigma(I)]$ *R* indices (all data) Extinction coefficient Largest diff. peak and hole

Identification code

bar56 1852085 $C_{20}H_{11}F_{12}O_5P$ 590.26 293(2) K MoKα, 0.71073 Å Monoclinic $P2_1/c$ (No. 14) a = 15.787(9) Å $\alpha = 90^{\circ}$ b = 10.811(6) Å $\beta = 112.816(7)^{\circ}$ c = 13.977(8) Å $\gamma = 90^{\circ}$ 2199(2) Å³ 4 and 1 1.783 g cm^{-3} 0.260 mm^{-1} 1176 $0.407 \times 0.319 \times 0.168 \text{ mm}^3$ 2.347 to 25.400° $-18 \le h \le 19, -13 \le k \le 12, -16 \le l \le 16$ 20876 4023 [R(int) = 0.0363]3018 99.7 % Numerical 0.9794 and 0.9085 4023 / 212 / 398 1.028 R1 = 0.0444, wR2 = 0.1116R1 = 0.0611, wR2 = 0.1226n/a 0.313 and -0.273 e Å⁻³ C8 C13 03 C7 08 06 C5

Table S2. Crystal data and structure refinement for 8.

Identification code CCDC number Empirical formula Formula weight Temperature Radiation, wavelength Crystal system Space group Unit cell dimensions Volume Z and Z'Calculated Density Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Observed Data $[I > 2\sigma(I)]$ Completeness to theta = 25.242° Absorption correction Max. and min. transmission Data / restraints / parameters Goodness-of-fit on F^2 Final *R* indices $[I > 2\sigma(I)]$ *R* indices (all data) Extinction coefficient Largest diff. peak and hole

khas17 1 1852086 $C_{24}H_{21}F_6O_9P$ 598.38 293(2) K MoKα, 0.71073 Å Triclinic P-1 (No. 2) a = 10.7892(6) Å $\alpha = 101.788(3)^{\circ}$ b = 11.1562(6) Å $\beta = 99.647(3)^{\circ}$ c = 11.7122(6) Å $\gamma = 106.558(3)^{\circ}$ 1283.93(12) Å³ 2 and 1 1.548 g cm^{-3} 0.203 mm^{-1} 612 $0.422 \times 0.203 \times 0.134 \text{ mm}^3$ 2.977 to 25.283° $-12 \le h \le 12, -13 \le k \le 13, -14 \le l \le 13$ 38254 4510 [*R*(int) = 0.0572] 2940 96.5 % Semi-empirical from equivalents 0.7372 and 0.6818 4510 / 55 / 383 1.027 R1 = 0.0442, wR2 = 0.1057R1 = 0.0813, wR2 = 0.1222n/a 0.216 and -0.275 e Å⁻³



Table S3. Crystal data and structure refinement for 9.

Identification code	khas61_sq	
CCDC number	1852087	
Empirical formula	$C_{18}H_{13}C_{16}O_5P$ [+ solvent]*	
Formula weight	552.95	
Temperature	293(2) K	
Radiation, wavelength	MoKα, 0.71073 Å	
Crystal system	Tetragonal	
Space group	<i>I</i> 4 ₁ / <i>a</i> (No. 88)	
Unit cell dimensions	a = 27.972(6) Å	$\alpha = 90^{\circ}$
	b = 27.972(6) Å	$\beta = 90^{\circ}$
	c = 11.844(3) Å	$\gamma = 90^{\circ}$
Volume	9268(5) Å ³	
Z and Z'	16 and 1	
Calculated density	1.585 g cm^{-3}	
Absorption coefficient	0.838 mm^{-1}	
F(000)	4448	
Crystal size	$0.599 \times 0.494 \times 0.461 \text{ mm}^3$	
Theta range for data collection	1.867 to 25.699°	
Index ranges	$-34 \le h \le 34, -34 \le k \le 34, -14$	$\leq l \leq 14$
Reflections collected	34206	
Independent reflections	4413 [R(int) = 0.0349]	
Observed Data $[I > 2\sigma(I)]$	3637	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	1.0000 and 0.9103	
Data / restraints / parameters	4413 / 0 / 271	
Goodness-of-fit on F^2	1.048	
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0399, wR2 = 0.0929	
R indices (all data)	R1 = 0.0500, wR2 = 0.0990	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.758 and $-0.686 \ e \ \text{\AA}^{-3}$	

*Squeezed solvent (pentane) info is not included in the formula and related items such as molecular weight and calculated density.



Table S4. Crystal data and structure refinement for 13.

Identification code khas63 CCDC number 1852088 Empirical formula $C_{12}H_{20}NO_4P$ Formula weight 273.26 Temperature 293(2) K Radiation, wavelength MoKα, 0.71073 Å Crystal system Monoclinic Space group P2₁ (No. 4) Unit cell dimensions a = 7.266(3) Å $\alpha = 90^{\circ}$ b = 11.409(5) Å $\beta = 96.695(6)^{\circ}$ c = 8.573(4) Å $\gamma = 90^{\circ}$ 705.8(5) Å³ Volume Z and Z'2 and 1 1.286 g cm^{-3} Calculated density Absorption coefficient 0.201 mm^{-1} F(000) 292 Crystal size $0.487 \times 0.234 \times 0.046 \text{ mm}^3$ Theta range for data collection 2.392 to 25.282° Index ranges $-8 \le h \le 8, -13 \le k \le 13, -10 \le l \le 10$ Reflections collected 5170 Independent reflections 2545 [R(int) = 0.0317]Observed Data $[I > 2\sigma(I)]$ 2011 Completeness to theta = 25.242° 100.0 % Absorption correction Numerical Max. and min. transmission 1.0000 and 0.9182 Data / restraints / parameters 2545 / 200 / 228 Goodness-of-fit on F^2 1.038 Final *R* indices $[I > 2\sigma(I)]$ R1 = 0.0429, wR2 = 0.0846*R* indices (all data) R1 = 0.0589, wR2 = 0.0915Absolute structure parameter 0.01(9) Extinction coefficient n/a 0.137 and -0.172 e Å⁻³ Largest diff. peak and hole C7a C3a 01 03 P2 02 H

Table S5. Crystal data and structure refinement for **20**.

code	miron2018_8							
CCDC number	1852089							
Empirical formula	$C_6H_7O_5P$							
Formula weight	190.09							
Temperature	150(2) K							
Radiation, wavelength	MoKα, 0.71073 Å							
Crystal system	Orthorhombic							
Space group	$P2_12_12_1$ (No. 19)							
Unit cell dimensions	$a = 4.6005(4) \text{ Å}$ $\alpha = 90$							
	$b = 10.1220(8)$ Å $\beta = 90^{\circ}$							
	$c = 16.4334(14) \text{ Å}$ $\gamma = 90^{\circ}$							
Volume	765.24(11) Å ³							
Z and Z'	4 and 1							
Calculated density	1.650 g cm^{-3}							
Absorption coefficient	0.338 mm^{-1}							
F(000)	392							
Crystal size	$0.541 \times 0.457 \times 0.391 \text{ mm}^3$							
Theta range for data collection	3.193 to 31.430°							
Index ranges	$-6 \le h \le 5, -14 \le k \le 14, -24 \le l \le 23$							
Reflections collected	5805							
Independent reflections	2368 [R(int) = 0.0346]							
Observed Data $[I > 2\sigma(I)]$	2159							
Completeness to theta = 25.242°	99.2 %							
Absorption correction	Semi-empirical from equivalents							
Max. and min. transmission	0.7464 and 0.6153							
Data / restraints / parameters	2368 / 0 / 121							
Goodness-of-fit on F^2	1.056							
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0387, wR2 = 0.0831							
<i>R</i> indices (all data)	R1 = 0.0440, wR2 = 0.0859							
Absolute structure parameter	-0.08(8)							
Extinction coefficient	n/a							
Largest diff. peak and hole	0.325 and $-0.408 \ e \ \text{\AA}^{-3}$							



Table S6. Crystal data and structure refinement for 23.

khas64 Identification code Empirical formula C₁₀H₇Cl₃O Formula weight 249.51 Temperature 293(2) K Radiation, wavelength Mo*Kα*, 0.71073 Å Crystal system Orthorhombic Space group *Pnma* (No. 62) Unit cell dimensions a = 10.636(8) Å $\alpha = 90^{\circ}$ b = 7.223(6) Å $\beta = 90^{\circ}$ c = 14.840(11) Å $\gamma = 90^{\circ}$ 1140.1(15) Å³ Volume Z and Z'4 and 0.5 1.454 g cm^{-3} Calculated density 0.767 mm^{-1} Absorption coefficient *F*(000) 504 Crystal size $0.454 \times 0.148 \times 0.108 \text{ mm}^{-1}$ 2.356 to 25.249° Theta range for data collection Index ranges $-12 \le h \le 12, -8 \le k \le 8, -17 \le l \le 17$ Reflections collected 7560 Independent reflections 1120 [R(int) = 0.0665]Observed Data $[I > 2\sigma(I)]$ 702 Completeness to theta = 25.242° 100.0 % Absorption correction Numerical 0.9702 and 0.6877 Max. and min. transmission Data / restraints / parameters 1120 / 0 / 82 Goodness-of-fit on F^2 1.082 Final *R* indices $[I > 2\sigma(I)]$ R1 = 0.0825, wR2 = 0.2255*R* indices (all data) R1 = 0.1163, wR2 = 0.2555Extinction coefficient n/a 0.845 and $-0.557 \ e \ \text{\AA}^{-3}$ Largest diff. peak and hole



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Figures of NMR Spectra of Compounds 6, 7.









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Figure S7. $^{13}C-{^{1}H}$ and ^{13}C NMR spectra (100.6 MHz, CDCl₃) of compound (6).



Figure S8. 111-130 ppm region of ${}^{13}C$ -{ ${}^{1}H$ } and ${}^{13}C$ NMR spectra (100.6 MHz, CDCl₃) of compound (6).



Figure S9. Fragment of ${}^{13}C-\{{}^{1}H\}$ and ${}^{13}C-\{{}^{1}H\}$ -dept NMR spectra (100.6 MHz, CDCl₃) of compound (6).



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Figure S14. 19 F-{ 31 P} and 19 F NMR spectra (658.78 MHz, CDCl₃, 25°C) of phosphorane (7).





Figure S16. Low-field fragments of ${}^{13}C-\{{}^{1}H\}$ NMR spectra (176.5 MHz, CDCl₃, 25°C) of phosphorane (7).








Figure S20. 109-113 ppm region of ${}^{13}C-\{{}^{1}H\}-\{{}^{31}P\}$ and ${}^{13}C-\{{}^{1}H\}$ NMR spectra (176.5 MHz, CDCl₃, 25°C) of phosphorane (7).



Electronic supplementary information 3 Spectral data

Organic Chemistry Frontiers. 2018

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Figures of NMR and IR Spectra of Compound 7.











Figure S26. 118-125 ppm region of ${}^{13}C-{}^{31}P$ (red) and ${}^{13}C-{}^{1}H$ NMR spectra (176.5 MHz, CDCl₃, 25°C) of phosphorane (7).



Figure S27. 79-81 ppm region of ${}^{13}C-{}^{31}P$ and ${}^{13}C-{}^{1}H-{}^{31}P$ NMR spectra (176.5 MHz, CDCl₃, 25°C) of phosphorane (7).













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Figure S34. High-field fragments of ${}^{13}C-{}^{19}F{}-{}^{31}P{}$ (black) and ${}^{13}C-{}^{19}F{}$ (blue) NMR spectra (176.5 MHz, CDCl₃) of phosphorane (7).



Figure S35. Low-field fragment of ${}^{13}C-\{{}^{19}F\}-\{{}^{31}P\}$ (black) and ${}^{13}C-\{{}^{19}F\}$ (blue) NMR spectra (176.5 MHz, CDCl₃) of phosphorane (7).























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S65





Figure S49. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, acetone-d₆, 25°C) of phosphorane (7).





Figure S51. IR spectrum of phosphorane (7) in nujol.



Figure S52. IR spectrum of phosphorane (7) in nujol (region of 400-2000 cm^{-1}).

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Organic Chemistry Frontiers. 2018

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Figures of NMR and IR Spectra of Compound 8.



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Figure S54. Aromatic protons region of ¹H NMR spectrum (400 MHz, CDCl₃) of compound (8).













Figure S60. 13 C NMR spectrum (100.6 MHz, CD₂Cl₂) of compound (8).



Figure 501. 118-150 ppin region of C twick spectrum (100.0 whitz, CD_2CI_2) of compound (6).



Figure S62. 110-113 ppm region of 13 C NMR spectrum (100.6 MHz, CD₂Cl₂) of compound (8).







Figure S65. ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, CD_2Cl_2) of compound (8).





Figure S67. 118-131 ppm region of ${}^{13}C$ -{ ${}^{1}H$ } and ${}^{13}C$ NMR spectra (100.6 MHz, CD_2Cl_2) of compound (8).



Figure S68. 110-113 ppm region of ${}^{13}C$ -{ ${}^{1}H$ } and ${}^{13}C$ NMR spectra (100.6 MHz, CD_2Cl_2) of compound (8).





Figure S70. 101-102 and 76-82 ppm regions of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, CD_2Cl_2) of compound (8).



Figure S71. 62-67, 42-47 and 11-17 ppm regions of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, CD_2Cl_2) of compound (8).



Figure S72. ¹³C-{¹H} and ¹³C-{¹H}-dept NMR spectra (100.6 MHz, CD_2Cl_2) of compound (8).





Figure S74. Low-field region of ¹H and ¹H-{¹H} NMR spectra (700 MHz, acetone- d_6) of compound (8).



Figure S75. High-field region of ${}^{1}H$ and ${}^{1}H{}^{1}H{}$ NMR spectra (700 MHz, acetone-d₆) of compound (8).











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Figure S81. IR spectrum of phosphorane (8) in KBr pellet.

Electronic supplementary information 5 Spectral data

Organic Chemistry Frontiers. 2018

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Figures of NMR and IR Spectra of Compound 9.



Figure S82. ³¹P-{¹H} and ³¹P NMR spectra (162.0 MHz, CH₂Cl₂, 25°C) of phosphole (6) and chloral mixture. (a) 3 hours after mixing the reagents, (b) 2 days after mixing the reagents, (c) 10 days after mixing the reagents (d).17 days after mixing the reagents.





Figure S84. Aromatic protons region of ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of phosphorane (9).



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Figure S87. ¹³C-{¹H} and ¹³C-{¹H}-dept NMR spectra (100.6 MHz, CDCl₃, 25°C) of phosphorane (9).






Figure S90. 110-112 ppm region of 13 C NMR spectrum (100.6 MHz, CDCl₃, 25°C) of phosphorane (9).





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Figure S94. 120-129 ppm region of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, CDCl₃, 25°C) of phosphorane (9).



Figure S95. IR spectrum of phosphorane (9) in Nujol.





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Electronic supplementary information 6 Spectral data

Organic Chemistry Frontiers. 2018

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Figures of NMR Spectra of Compounds 11-14 and IR Spectrum of Compound 13.













Figure S103. ¹³C-{¹H} and ¹³C NMR spectra (100.6 MHz, acetone- d_6 , 25°C) of phosphonate (11).



Figure S104. 112-145 ppm regions of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, acetone- d_6 , 25°C) of phosphonate (11).



Figure S105. ¹³C-{¹H} and ¹³C-{¹H} dept NMR spectra (100.6 MHz, acetone- d_6 , 25°C) of phosphonate (11).



Figure S106. ¹H NMR spectrum (400 MHz, acetone- d_6 , 25°C) of hydroxyketone (12).





Figure S108. ¹⁹F NMR spectrum (386.4 MHz, CDCl₃, 25°C) of hydroxyketone (**12**).



Figure S109. ¹³C-{¹H} NMR spectrum (100.6 MHz, acetone- d_6 , 25°C) of hydroxyketone (12).







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Figure S113. ³¹P-{¹H} NMR spectrum (243.5 MHz, DMSO- d_6 , 25°C) of phosphate (13).





Figure S115. ${}^{13}C-{}^{1}H$ and ${}^{13}C-{}^{1}H$ dept NMR spectra (150.9 MHz, DMSO- d_6 , 25°C) of phosphate (13).





Figure S117. ¹³C-{¹H} and ¹³C NMR spectra (150.9 MHz, DMSO- d_6 , 25°C) of phosphate (13).



Figure S118. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (150.9 MHz, DMSO- d_6 , 25°C) of phosphate (13).



Figure S119. IR spectrum of of phosphate (13).



Figure S120. ¹⁹F NMR spectrum (386.4 MHz, CDCl₃, 25°C) of unsaturated ketone (14).



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Figure S123. 13 C NMR spectrum (100.6 MHz, CDCl₃, 25°C) of unsaturated ketone (14).


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Figure S125. ¹³C-{¹H} and ¹³C NMR spectra (100.6 MHz, CDCl₃, 25°C) of unsaturated ketone (14).



Figure S126. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, CDCl₃, 25°C) of unsaturated ketone (14).



Figure S127. 116-127 ppm regions of ${}^{13}C$ -{ ${}^{1}H$ } and ${}^{13}C$ NMR spectra (100.6 MHz, CDCl₃, 25°C) of unsaturated ketone (14).

Electronic supplementary information 7 Spectral data

Organic Chemistry Frontiers. 2018

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Figures of NMR Spectra of Compounds 15, 16, 18 and IR Spectrum of Compound 15.





Figure S129. ¹⁹F NMR spectrum (376.4 MHz, CDCl₃, 25°C) of hydroxy trifluoroketone (**15**).





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Figure S133. ¹³C-{¹H} NMR spectrum (176.5 MHz, acetone- d_6 , 25°C) of hydroxy trifluoroketone (15).



Figure S134. ¹³C NMR spectrum (176.5 MHz, acetone- d_6 , 25°C) of hydroxy trifluoroketone (15).





Figure S136. ¹³C-{¹H} and ¹³C NMR spectra (176.5 MHz, acetone- d_6 , 25°C) of hydroxy trifluoroketone (15).



Figure S137. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (176.5 MHz, acetone- d_6 , 25°C) of hydroxy trifluoroketone (15).



Figure S138. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (176.5 MHz, acetone- d_6 , 25°C) of hydroxy trifluoroketone (15).





Figure S140. ³¹P-{¹H} NMR spectrum (162.50 MHz, acetone- d_6 , 25°C) of phosphonates (16) and (18) mixture.



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Figure S146. Fragment of ¹³C NMR spectra (176.5 MHz, acetone- d_6 , 25°C) of phosphonates (16) and (18) mixture.



Figure S147. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (176.5 MHz, acetone- d_6 , 25°C) of phosphonates (16) and (18) mixture.



Figure S148. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (176.5 MHz, acetone- d_6 , 25°C) of phosphonates (16) and (18) mixture.



Electronic supplementary information 8 Spectral data

Organic Chemistry Frontiers. 2018

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Figures of NMR Spectra of Compounds 21-23.









Figure S153. Fragment of ¹³C NMR spectrum (100.6 MHz, DMSO- d_6 , 25°C) of phosphonate (21).



Figure S154. Fragments of ¹³C-{¹H} and ¹³C NMR spectra (100.6 MHz, DMSO- d_6 , 25°C) of phosphonate (21).





Figure S156. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, DMSO- d_6 , 25°C) of phosphonate (21).



Figure S157. Fragments of ¹³C-{¹H} and ¹³C-{¹H} dept NMR spectra (100.6 MHz, DMSO- d_6 , 25°C) of phosphonate (21).






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Figure S161. 127-130 ppm region of ¹³C NMR spectrum (100.6 MHz, CDCl₃, 25°C) of hydroxy trichloroketone (**22**).



Figure S162. ¹³C-{¹H} and ¹³C-{¹H} NMR spectra (100.6 MHz, CDCl₃, 25°C) of hydroxy trichloroketone (22).



Figure S163. ¹³C-{¹H} and ¹³C NMR spectra (100.6 MHz, CDCl₃, 25°C) of hydroxy trichloroketone (**22**).



Figure S164. Fragments of ${}^{13}C-{}^{1}H$ and ${}^{13}C$ NMR spectra (100.6 MHz, CDCl₃, 25°C) of hydroxy trichloroketone (22).



Figure S165. ¹H NMR spectrum (400 MHz, CDCl₃, 25°C) of unsaturated trichloroketone (23).



Figure S166. ¹³C-{¹H} NMR spectrum (100.6 MHz, CDCl₃, 25°C) of unsaturated trichloroketone (23).





Figure S168. ¹³C-{¹H} and ¹³C NMR spectra (100.6 MHz, CDCl₃, 25°C) of unsaturated trichloroketone (**23**).



Figure S169. Fragments of ${}^{13}C$ -{ ${}^{1}H$ } and ${}^{13}C$ NMR spectra (100.6 MHz, CDCl₃, 25°C) of unsaturated trichloroketone (23).