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# Difluorotris(pentafluoroethyl)phosphorane—A highly active catalyst for Diels–Alder reaction



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#### ABSTRACT

Difluorotris(pentafluoroethyl)phosphorane,  $(C_2F_5)_3PF_2$ , was found to catalyze Diels–Alder reactions of  $\alpha$ , $\beta$ -unsaturated ketones or aldehydes with conjugated dienes or cyclodienes providing the cycloaddition products in high yields. Only a small quantity of this catalyst is required to complete the Diels–Alder reaction. The developed protocol is more convenient than the procedures reported in the literature. Several cyclohexene, naphthalene and norbornene derivatives were obtained in moderate to good yields.

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#### 1. Introduction

The Diels-Alder reaction is one of the most useful methods to synthesize mono- and bicyclic organic compounds starting from common unsaturated substrates. After the discovery of this reaction 85 years ago numerous scientific papers were published on this topic. The Diels-Alder reaction has been studied in various media. *i.e.* in water [1–4], supercritical CO<sub>2</sub> [5], ionic liquids [6–10], organic solvents and under solvent-free conditions [11]. Brønsted [12–14] and Lewis acids were successfully tested to catalyze the Diels-Alder reaction [15]. Metal chlorides, such as AlCl<sub>3</sub>, ZnCl<sub>2</sub>, TiCl<sub>4</sub>, or SnCl<sub>4</sub> were applied as Lewis acid catalysts to increase the reaction rate allowing to obtain the product at ambient conditions. However, for more complex dienes, such as 7-methyl-3-methylene-1,6-octadiene, higher reaction temperatures were required to obtain the product [16]. A synergetic catalytic effect of metal chlorides and ionic liquids has been reported in the reaction of cyclopentadiene and various acrylates [17] or ketones [18]. The disadvantage in using

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metal chlorides as catalysts is related to their decomposition in the presence of water. Lanthanide trifluoromethanesulfonates are more stable to moisture and more convenient for practical use as Lewis acid catalysts [19]. Scandium trifluoromethanesulfonate, Sc(OTf)<sub>3</sub>, was successfully tested as catalyst in cycloadditions of methyl vinyl ketone and isoprene [20]. This triflate can also be immobilized in ionic liquids and used as a recyclable catalyst for hetero-Diels-Alder reactions [21]. The drawback in the application of metal-based Lewis acid catalysts is a potential contamination of the Diels-Alder product with metal salts. From this point of view the use of organocatalysis has evident advantages [22]. There are several reports dealing with the use of phosphonium [23] or tritylium salts [24] to catalyze Diels–Alder reactions, but typically rather high catalyst loadings are required to complete the reaction, particularly in the case of Diels-Alder reactions with less reactive dienophiles such as crotonic aldehyde and dienes such as cyclohexadiene.

Difluorotris(pentafluoroethyl)phosphorane,  $(C_2F_5)_3PF_2$ , is produced on industrial scale by means of electrochemical fluorination of the  $(C_2H_5)_3P$ . Difluorotris(pentafluoroethyl)phosphorane is a non-metal based strong Lewis acid [25]. It is a transparent colourless liquid (*b.p.* 91–92 °C) that is easy to handle and can be stored at room temperature without decomposition in the absence of moisture for a long time. (**Caution**: by hydrolysis of difluorotris(pentafluoroethyl)phosphorane a very toxic HF can

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be released). Here we report the activity of difluorotris(pentafluoroethyl)phosphorane as catalyst for Diels-Alder reactions.

#### 2. Results and discussion

The Diels–Alder reactions of dienophiles  $(\mathbf{a}-\mathbf{d})$  and dienes  $(\mathbf{e}-\mathbf{g})$  in the presence of difluorotris(pentafluoroethyl)phosphorane as catalyst have been studied (Scheme 1).

Table 1 shows the reactants and products as well as the yields and the catalyst loadings. The yields varied from moderate (57% to 73%) in the case of cyclohexenone (**b**) to excellent (90% to 93%) in the case of methyl vinyl ketone (**a**).

To elucidate the scope of the Diels–Alder reaction catalyzed by difluorotris(pentafluoroethyl)phosphorane,  $(C_2F_5)_3PF_2$ , we have studied the reaction of isoprene (**e**) with methyl vinyl ketone (**a**) in detail. Various conditions have been screened for the  $[4\pi + 2\pi]$  cycloaddition reaction (Table 2). The highest yield of the product was observed when the ratio of dienophile and diene was 1.5:1.0. In this case, the reaction proceeds within some hours even at 0 °C (Table 2), but warming to room temperature was beneficial to complete the reaction. It is worth mentioning that in the absence of the catalyst,  $(C_2F_5)_3PF_2$ , no Diels–Alder products formation was observed in the reaction between isoprene (**e**) and methyl vinyl ketone (**a**), crotonic aldehyde (**c**), or cyclohexenone (**b**) at room



Scheme 1. Diels-Alder reactions catalyzed by (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub>.





<sup>a</sup> Catalyst loading [mol%].

<sup>b</sup> Yield [%].

<sup>c</sup> NMR Yield [%], determined by <sup>1</sup>H NMR spectroscopy of the reaction mixture.

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Table 2

Influencing parameters of the Diels-Alder reaction of methyl vinyl ketone (a) and 2-methyl-1,3-butadiene (e) catalyzed by (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub> to yield of the products (Ia+Ib).

Entry	Ratio of dienophile ( <b>a</b> ) to diene ( <b>e</b> )	Catalyst loading, [mol%]	<i>T</i> [°C]	<i>t</i> [h]	Substrate conversion [%]	Yield ( <b>Ia+Ib</b> ) [%]
1	0.5	0.4	0	0.5	99	59
2	1	0.5	0	1	85	50
			25	24	99	
3	1.5	0.4	0	5	87	93
			25	16	99	

temperature in dichloromethane or under solvent free conditions within 24 h.

Depending on the nature of the substrate, adjustment of the conditions and catalyst loadings is required to complete the reaction of dienophiles (**a**–**d**) with dienes (**e**–**g**). In general, the reaction conditions needed are very mild. The reaction temperatures are in the range of -40 °C to RT and the catalyst loadings 0.4-2.4 mol% (Table 3). For instance, to obtain 4-acetyl-1-methylcyclohex-1-ene (Ia) and 3-acetyl-1-methylcyclohexene (Ib) in 93% yield, only 0.4 mol% of the  $(C_2F_5)_3PF_2$  catalyst was required to catalyze the reaction of (a) with (e). This is much less in comparison to other known catalysts for Diels-Alder reactions. For example, 5 mol% loading of a Lewis acidic ruthenium catalyst, ([Ru(Cp)(R,R-BIPHOP-F)(acetone)][SbF<sub>6</sub>]), provides only 54% conversion in the same Diels-Alder reaction after 24 h at 22 °C [26]. Scandium trifluoromethanesulfonate was found to be an active catalyst to promote the Diels–Alder reaction of (**a**) and (**e**) yielding 91% of the desired product after 13 h at 0 °C in CH<sub>2</sub>Cl<sub>2</sub> [20], but the loading of Sc(OTf)<sub>3</sub> is 20 times higher than in the case of  $(C_2F_5)_2PF_2$  as catalyst. Only trace amounts of the Diels-Alder product were detected after 24 h at 0 °C in the reaction of (a) and (e) with 10 mol% of  $Y(OTf)_3$  or  $Yb(OTf)_3$  as catalyst [20].

To obtain 4-acetyl-1,2-dimethylcyclohex-1-ene (**II**) (Table 1) by the reaction of (**a**) and (**f**) a higher  $(C_2F_5)_3PF_2$  catalyst loading was required (Table 3, entry 2). However, the more expensive ruthenium catalyst, ([Ru(Cp)(*R*,*R*-BIPHOP-F)(acetone)][SbF<sub>6</sub>]), is even less reactive. A catalyst loading of 5 mol% provides 67% yield of the product (**II**) after 24 h at 22 °C [25].

Cyclopentadiene (g) is one of the most reactive dienes. It can react with methyl vinyl ketone (a) in the absence of any catalyst, but at much lower rate; 50% conversion was reached within 16 h at room temperature [23]. Various catalysts for the reaction of methyl vinyl ketone (a) with cyclopentadiene (g) are described in the literature. For instance, 3 mol% of the Lewis acidic organotungsten compound,  $[O=P(2-py)_3W(CO)(NO)_2][BF_4]_2$ , was found to be an effective catalyst in the above mentioned reaction (93% yield of product (IIIa + IIIb = 95:5) after 2 h at RT) [27]. The reaction catalyzed by organometallic dendrimers, [Cu(G<sub>2</sub>[Me])<sub>3</sub>][OTf]<sub>2</sub> (10 mol% loading) ( $G_2[Me] = 2,2$ -bipyridine core dendrimers), results in the formation of 2-Acetylbicyclo[2.2.1]hept-5-ene (III) in 88% yield [28]. In comparison to these examples  $(C_2F_5)_3PF_2$ catalyst is much more active in the same reaction. Only 1.6 mol% of the title phosphorane,  $(C_2F_5)_3PF_2$ , is sufficient to complete the reaction within 30 min at 0 °C. 2-Acetylbicyclo[2.2.1]hept-5-ene as a mixture of endo and exo isomers in ratio (93:7) (IIIa and IIIb) was isolated in 90% yield (Table 3, entry 3). Recently, it was shown that tritylium tetrafluoroborate is an active catalyst to convert the methyl vinyl ketone (**a**) and cyclopentadiene (**g**) into Diels–Alder product (IIIa and IIIb; endo and exo isomers ratio 13:1). This reaction proceeds at room temperature with a catalyst loading of 0.1 mol% and results in the formation of the products (IIIa) and (**IIIb**) in quantitative yield within 16 h [24].

It is known that 2-cyclohexene-1-one (**b**) is less active in Diels– Alder reactions than methyl vinyl ketone (a). Nevertheless, using 2.4 mol% ( $C_2F_5$ )<sub>3</sub>PF<sub>2</sub> catalyst (Table 1) allows us to obtain pure 6methyl-3,4,4a,5,8,8a-hexahydronaphthalen-1(2*H*)-one (**IVa**) and 7-methyl-3,4,4a,5,8,8a-hexahydro-2*H*-naphthalen-1-one (**IVb**) in 68% yield (Table 3, entry 4). The product (**IVa**) was previously synthesized in 37% yield [29], however not by means of a Diels– Alder reaction.

To the best of our knowledge, the synthesis of 6,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2*H*-naphthalen-1-one (**V**) is not described in the literature. Schmidt et al. have tested the Diels– Alder reaction of (**b**) and (**f**) using 5 mol% of a ferrocene-stabilized methyl *tert*-butyl silylium ion catalyst, or 5 mol% of triflic acid in CH<sub>2</sub>Cl<sub>2</sub> [30]. However, after 20 h at -40 °C 45% yield was obtained with the silylium catalyst and no Diels–Alder product was detected in the triflic acid case. We have achieved product (**V**) in a yield of

Table 3

Influences of the catalyst loading, reaction temperature and time on the substrate conversions and the yields of the products in the reaction of dienophiles (**a**-**d**) and dienes (**e**-**g**).

Entry	Substrates	Product	Ratio of dienophile to diene	Catalyst loading, [mol%]	T [°C]	<i>t</i> [h]	Conversion to product [%]	Yield [%]
1	a+e	Ia + Ib 99:1	1.5	0.4	25	16	99	93
2	a+f	II	1.5	2.3	25	16	94	92
3	a+g	IIIa + IIIb 93:7	1.5	1.6	0	0.5	99	90
4	b+e	IVa + IVb 69:31	1.5	2.4	25	2	95	68
5	b+f	V	1.0	1.5	25	72	81	73
6	b+g	VIa + VIb 83:17	1.0	0.5	-40	4	85	57
7	c+e	VIIa + VIIb 97:3	0.5	0.7	35	24	67	67ª
8	c+g	VIIIa + VIIIb 72:28	0.5	1.3	0	2	99	60
9	d+e	IX	1.5	2.3	25	19	61	61 <sup>a</sup>
10	d+g	Xa + Xb 90:10	0.5	0.5	25	18	90	90 <sup>a</sup>

<sup>a</sup> NMR Yield [%], determined by <sup>1</sup>H NMR spectroscopy of the reaction mixture.



Scheme 2. Formation of the catalyst/dienophile complex.



Scheme 3. Proposed reaction mechanism involving the catalyst/dienophile complex formation and subsequent decay of the catalyst/product adduct.

73% (Table 3, entry 5) using 1.5 mol% of  $(C_2F_5)_3PF_2$  as catalyst in this reaction. This is the best known protocol to prepare 6,7-dimethyl-3,4,4a,5,8,8a-hexahydro-2*H*-naphthalen-1-one (**V**) (Table 1).

Tricyclo[6.2.1.0<sup>2,7</sup>]undec-9-en-3-one (**VI**) (Table 1) was prepared in 57% yield (Table 3, entry 6) as a mixture of *endo* and *exo* isomers (**VIa** and **VIb**) in ratio 83:17 using only 0.5 mol% of ( $C_2F_5$ )<sub>3</sub>PF<sub>2</sub> catalyst. Schmidt et al. have described the preparation of this substance in 68% yield using a 10 times higher catalyst loading in comparison to our protocol, namely 5 mol% of triflic acid in CH<sub>2</sub>Cl<sub>2</sub> at -40 °C [30].

All given examples demonstrate that difluorotris(pentafluoroethyl)phosphorane,  $(C_2F_5)_3PF_2$ , is an efficient catalyst for Diels– Alder reactions. It is a strong non-metal based Lewis acid able to react with various nucleophiles [25]. In the case of Diels–Alder reactions, the catalytic pathway most likely includes the formation of a complex of the dienophile and the catalyst according to Scheme 2. After cycloaddition the catalyst/product complex decays due to the enhanced sterical demand of the Diels–Alder product (Scheme 3).

This complex is formed owing to the interaction of the strong electrophilic phosphorus atom of (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub> and an electron pair localized at the oxygen atom of the carbonyl group conjugated to the double bond of methyl vinyl ketone. This interaction results in a shift of electron density towards the phosphorus atom resulting in an activation of the double bond of the dienophile (Scheme 3). This strongly promotes the Diels-Alder cycloaddition. The catalyst/ dienophile complex has been detected in the reaction mixture by low-temperature <sup>19</sup>F and <sup>31</sup>P NMR measurements at -20 °C. The NMR spectra (Fig. 1A) of this complex show the typical pattern for fluorophosphate anions and are comparable to those of the trifluorotris(pentafluoroethyl)phosphate,  $[(C_2F_5)_3PF_3]^-$ , anion (FAP) (Fig. 1B) [31]. The only difference is the absence of the doublet at -45 to -50 ppm corresponding to the equatorial bonded fluorine atom (Fig. 1B). In detail, the <sup>31</sup>P NMR spectrum (Fig. 1A) of the catalyst/ dienophile complex shows a triplet corresponding to the coupling with the two fluorine atoms bonded to phosphorus. The further splitting to a quintet of triplets corresponding to the coupling to the chemically and magnetically non-equivalent CF<sub>2</sub> groups is not resolved. Formation of the complex of difluorotris(pentafluoroethyl)phosphorane, (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub>, and organic bases was already described in the patent literature [32]. The authors of this patent application suggested that the Lewis acidity of fluoroalkylfluorophosphoranes may be controlled by preparation of adducts with suitable Lewis bases, for example with 4-(*N*,*N*-dimethylamino)pyridine. These adducts were shown to be excellent starting materials for reactions with oxygen-containing nucleophiles [33]. From our studies we have clear evidence that the dienophiles are activated for the  $[4\pi + 2\pi]$  cycloaddition by forming a complex with the catalyst  $(C_2F_5)_3PF_2$  as described above and in the literature [34]. Quantum-chemical calculations support the thermodynamically favoured formation of such kind of complexes. Coordination by the catalyst  $(C_2F_5)_3PF_2$  lowers the energy levels of both the LUMO and the HOMO of the dienophile. The interaction of methyl vinyl ketone with difluoro-tris(pentafluoroethyl)phosphorane results in a standard reaction enthalpy  $\Delta H^{\circ}_{r}$  of -19.8 kJ/mol (Fig. 2; gas phase calculations) at the  $\omega$ B97X-D/6-311++G(3df,3pd) level of theory.

Considering the Diels–Alder reaction, further calculations at the same level of theory show that the energy gap between the LUMO of methyl vinyl ketone and the HOMO of isoprene is significantly smaller than *vice versa*. In this case the geometries of the orbitals are advantageous for overlapping. Comparing energies of the LUMOs of methyl vinyl ketone and the complex, the latter is lowered by 133 kJ/mol (Fig. 3). As a result, the interaction of the LUMO of the complex and the HOMO of isoprene is favourable. Consequently, the reaction *via* complex formation can proceed faster.

The activation barriers ( $T_{standard} = 298.15$  K or  $T_{zero} = 0$  K) in the reaction of methyl vinyl ketone with isoprene without catalyst ( $E_{a}$ ,  $_{standard} = 74$  kJ/mol or  $E_{a,zero} = 78$  kJ/mol) and in the presence of the catalyst ( $C_2F_5$ )<sub>3</sub>PF<sub>2</sub> ( $E'_a$ ,  $_{standard} = 55$  kJ/mol or  $E'_{a,zero} = 58$  kJ/mol) were estimated by calculating the transition state energies (Figs. 4 and 5). The complex energies are lowered by 19 kJ/mol for 298.15 K or 20 kJ/mol for 0 K, respectively, resulting in an increase of the reaction rate by a factor of 2600 using the Arrhenius equation at 298.15 K. In summary, the computational results make understandable the very good catalytic activity of difluorotris(pentafluoroethyl)phosphorane in Diels–Alder reactions.

The above mentioned methyl vinyl ketone/catalyst complex was also observed in the reaction mixture. After 1 h at -20 °C 86% conversion to the product has been achieved. Nevertheless, the catalyst complex can be still detected in the reaction mixture beside small amounts of decomposition products, mainly the FAP anion and tris(pentafluoroethyl)phosphine oxide (Fig. 6). These decomposition products are formed due to side reaction of phosphorane with methyl vinyl ketone. This side reaction of phosphorane (C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>PF<sub>2</sub> with oxygen-containing nucleophiles is not surprising and has already been further developed to



Fig. 1. (A) <sup>19</sup>F and <sup>31</sup>P NMR spectra of the complex  $(C_2F_5)_3PF_2$ -dienophile at -20 °C and (B) <sup>19</sup>F and <sup>31</sup>P NMR spectra of the  $[(C_2F_5)_3PF_3]^-(FAP)$  anion at 25 °C.





Fig. 3. HOMO and LUMO geometries and energies for methyl vinyl ketone, the complex and isoprene.

synthesize tris(perfluoroalkyl)phosphine oxides. Interaction of the phosphorane with metal oxides, such as CaO, MgO or Ag<sub>2</sub>O, nonmetal oxides, such as SO<sub>2</sub>, SiO<sub>2</sub> (in form of sand or silica gel), SeO<sub>2</sub>, and organic oxygen containing compounds, such as triphenylphosphine oxide, urea, ethylene carbonate, or dimethyl carbonate results in the formation of tris(perfluoroalkyl)phosphine oxides [35,36].

The isolated products (**I–VI**) have been characterized by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Table 4) and elemental analysis. Product (**III**) was characterized additionally by 2D NMR (Fig. 7). The products (**VII–X**) were not isolated but characterized in the reaction mixture by means of NMR spectroscopy. The NMR data of these products are in accordance to those generally described in the literature.

#### 3. Experimental part

#### 3.1. Chemicals

Dichloromethane was dried with CaH<sub>2</sub>, distilled and stored over molecular sieves (3 Å). The water content after drying was

determined by Karl-Fisher titration to be less than 5 ppm. Methyl vinyl ketone (**a**) and 2-cyclohexene-1-one (**b**) were dried with CaH<sub>2</sub> and purified by means of fractional distillation. Crotonealdehyde (**c**), 2-methyl-1,3-butadiene (**e**) and 2,3-dimethyl-1,3-butadiene (**f**) were purified by condensation and dried over molecular sieves (3 Å) from commercially available products (Merck KGaA). Cinnamaldehyde (**d**) was dried with molecular sieves (3 Å). Cyclopentadiene (**g**) was freshly prepared from its dimer (Merck KGaA) just before use. Difluorotris(pentafluoroethyl)phosphorane,  $(C_2F_5)_3PF_2$ , was used as delivered by Merck KGaA.

#### 3.2. Apparatus and materials

For manipulations of volatile materials a glass vacuum line has been used. Solid, moisture sensitive materials were handled inside a dry-box (Fa. Jacomex with the inert gas purification module P(SYS)-II-P, Ar atmosphere;  $H_2O$  and  $O_2$  level <0.5 ppm). The reaction vessels, constructed from FEP tubing, were dried under dynamic vacuum for several hours prior to use. Organic solvents were purified and dried using standard literature methods [37].



**Fig. 4.** Activation barriers for the Diels–Alder reaction of (**a**) and (**e**) with (black slope) and without (gray slope) phosphorane catalyst.

#### 3.3. Products characterization

#### 3.3.1. NMR spectroscopy

NMR samples were measured in 3.7 mm ( $Ø_A$ ) FEP tube placed inside a 5 mm ( $Ø_A$ ) thin-walled precision glass NMR tube (Wilmad 537 PPT), which contained CD<sub>3</sub>CN in the annular space,



Fig. 5. Transition state geometry of the reaction of methyl vinyl ketone/ phosphorane complex with isoprene.

or internally as dry solvent in 5 mm ( $Ø_A$ ) precision glass NMR tubes. The measurements were carried out at 25 °C on a Bruker Avance III 400 MHz spectrometer equipped with a 9.3980 T cryomagnet. The <sup>1</sup>H NMR spectra were acquired using a 5 mm combination <sup>1</sup>H/<sup>19</sup>F probe operating at 400.17 and 376.54 MHz, respectively. The <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P NMR spectra were obtained using a 5 mm broad-band inverse probe operating at 100.62, 376.54 and 161.99 MHz, respectively. Line-broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data-point resolutions or the natural line widths of the resonances. All line-shape functions were Lorentzian unless specified otherwise. In some cases, the free induction decays were multiplied by Gaussian functions for resolution enhancement on Fourier



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Table 4	
<sup>1</sup> H and <sup>13</sup> C NMR data of the isolated products ( <b>I–VI</b> ).	

Prod.	Structure <sup>a</sup>	<sup>1</sup> H NMR ( $\delta$ , ppm)	<sup>13</sup> C NMR (δ, ppm)
la	4-Acetyl-1-methylcyclohexene 7 5 4 3 2 0	1.52 m (1H <sup>4A</sup> ), 1.66 m (3H <sup>7</sup> ), 1.97 m (1H <sup>4B</sup> and 1H <sup>5A</sup> ), 2.07 m (1H <sup>5B</sup> ), 2.13 m (3H <sup>1</sup> and 2H <sup>9</sup> ), 2.55 m (1H <sup>3</sup> ), 5.41 m (1H <sup>8</sup> )	24.1 q, d, (C <sup>7</sup> ), ${}^{J}_{C,H}$ =125.3, ${}^{3}_{J_{C,H}}$ =6.8 Hz, 26.2 t, (C <sup>4</sup> ), ${}^{1}_{J_{C,H}}$ =188.0 Hz, 28.2 t, (C <sup>9</sup> ), ${}^{1}_{J_{C,H}}$ =127.3 Hz, 28.7 q, (C <sup>1</sup> ), ${}^{1}_{J_{C,H}}$ =127.4 Hz, 30.6 t, (C <sup>5</sup> ), ${}^{1}_{J_{C,H}}$ =126.6 Hz, 48.2 d, (C <sup>3</sup> ), ${}^{1}_{J_{C,H}}$ =127.3 Hz, 120.9 d, (C <sup>8</sup> ), ${}^{1}_{J_{C,H}}$ =154.7 Hz, 135.1 d, d, q, (C <sup>6</sup> ), ${}^{1}_{J_{C,H}}$ =154.7 Hz, ${}^{2}_{J_{C,H}}$ =6.3 – 6.5 Hz, 212.5 m, (C <sup>2</sup> )
Ь	3-Acetyl-1-methylcyclohexene	<sup>1</sup> H NMR: not resolved	<sup>13</sup> C{ <sup>1</sup> H} NMR: 24.3 (C <sup>8</sup> ), 25.7 (C <sup>4</sup> ), 26.0 (C <sup>9</sup> ), 28.7 (C <sup>1</sup> ), 32.5 (C <sup>5</sup> ), 48.8 (C <sup>3</sup> ), 122.0 (C <sup>6</sup> ), 134.0 (C <sup>7</sup> ), 212.4 (C <sup>2</sup> )
п	4-Acetyl-1,2-dimethylcyclohex-1-ene	1.47 m (1H <sup>4A</sup> ), 1.62 m (3H <sup>7</sup> ), 1.64 m (3H <sup>9</sup> ), 1.94 m (1H <sup>4B</sup> ), 1.98 m (2H <sup>10</sup> ), 2.06 m (2H <sup>5</sup> ), 2.13 m (3H <sup>1</sup> ), 2.59 m (1H <sup>3</sup> )	19.6 q, (C <sup>7</sup> ), ${}^{1}J_{C,H}$ = 125.2 Hz 19.8 q, (C <sup>9</sup> ), ${}^{1}J_{C,H}$ = 125.2 Hz, 26.7 t, (C <sup>4</sup> ), ${}^{1}J_{C,H}$ = 129.2 Hz, 28.7 q, (C <sup>1</sup> ), ${}^{1}J_{C,H}$ = 127.4 Hz, 32.4 t, (C <sup>10</sup> ), ${}^{1}J_{C,H}$ = 126.3 Hz, 34.3 t, (C <sup>5</sup> ), ${}^{1}J_{C,H}$ = 126.8 Hz, 49.6 d, (C <sup>3</sup> ), ${}^{1}J_{C,H}$ = 126.8 Hz, 125.5 m, (C <sup>8</sup> ), 126.6 m, (C <sup>6</sup> ), 212.5 m, (C <sup>2</sup> ).
lla	endo-2-Acetyl-bicyclo[2.2.1]hept-5-ene	1.21 d, $(1H^{6A})$ , ${}^{2}J_{H,H}$ = 8.0 Hz, 1.33 d, $(1H^{6B})$ , ${}^{2}J_{H,H}$ = 8.4 Hz, 1.37 d, d, d, $(1H^{4A})$ , ${}^{2}J_{H,H}$ = 11.7 Hz, ${}^{3}J_{H,H}$ = 4.3 Hz, ${}^{3}J_{H,H}$ = 2.7 Hz, 1.63 d, d, d, $(1H^{4B})$ ${}^{2}J_{H,H}$ = 11.6 Hz, ${}^{3}J_{H,H}$ = 9.1 Hz, ${}^{3}J_{H,H}$ = 3.8 Hz, 2.00 s, $(3H^{1})$ , 2.77 m, $(1H^{5})$ , 2.88 d, t, $(1H^{3})$ , ${}^{3}J_{H,H}$ = 9.1 Hz, ${}^{3}J_{H,H}$ = 3.9 Hz, 3.12 m, $(1H^{9})$ , 5.73 d, d, $(1H^{9})$ , ${}^{3}J_{H,H}$ = 5.7 Hz, ${}^{4}J_{H,H}$ = 2.6 Hz, 6.02 d, d, $(1H^{7})$ , ${}^{3}J_{H,H}$ = 5.7 Hz, ${}^{4}J_{H,H}$ = 2.6 Hz	27.4 t, (C <sup>4</sup> ), ${}^{1}J_{C,H}$ = 135.2 Hz, 29.1 q, (C <sup>1</sup> ), ${}^{1}J_{C,H}$ = 126.4 Hz, 42.6 t, (C <sup>5</sup> ), ${}^{1}J_{C,H}$ = 147.2 Hz, 45.8 d, (C <sup>9</sup> ), ${}^{1}J_{C,H}$ = 147.4 Hz, 49.9 t, t, d, (C <sup>6</sup> ), ${}^{1}J_{C,H}$ = 133.9 Hz, ${}^{2}J_{C,H}$ = 6.7 Hz, ${}^{2}J_{C,H}$ = 3.7 Hz, 52.3 d, (C <sup>3</sup> ), ${}^{1}J_{C,H}$ = 130.6 Hz, 131.2 d, (C <sup>8</sup> ), ${}^{1}J_{C,H}$ = 169.0 Hz, 137.7 d, (C <sup>7</sup> ), ${}^{1}J_{C,H}$ = 168.2 Hz, 208.6 m, (C <sup>2</sup> )
ШЬ	exo-2-Acetyl-bicyclo[2.2.1]hept-5-ene	<sup>1</sup> H NMR: not resolved	<sup>13</sup> C{ <sup>1</sup> H} NMR:28.8 (C <sup>8</sup> ), 29.5 (C <sup>4</sup> ), 41.4 (C <sup>9</sup> ), 45.1 (C <sup>1</sup> ), 45.7 (C <sup>5</sup> ), 51.4 (C <sup>3</sup> ), 135.0 (C <sup>6</sup> ), 137.0 (C <sup>7</sup> ), 210.2 (C <sup>2</sup> )
IVa	6-Methyl-3,4,4a,5,8,8a-heptahydro- 2H-naphthalen-1-one	1.27 m, $(1H^{6A})$ , 1.44 m, $(3H^8)$ , 1.50 m, $(1H^5 \text{ and } 1H^{3A})$ , 1.73 m, $(1H^{6B} \text{ and } 1H^{10A})$ , 1.89 m, $(1H^{3B} \text{ and } 1H^{10B})$ , 1.95 m, $(2H^4 \text{ and } 1H^{11})$ , 2.17 m, $(1H^{2A})$ , 2.20 m, $(1H^{2B})$ , 5.18 m, $(1H^9)$	23.2 q, (C <sup>8</sup> ), ${}^{1}J_{CH}$ =124.2 Hz, 24.7 t, (C <sup>4</sup> ), ${}^{1}J_{CH}$ =128.4 Hz, 26.1 t, (C <sup>3</sup> ), ${}^{1}J_{CH}$ =128.1 Hz, 32.6 t, (C <sup>6</sup> ), ${}^{1}J_{CH}$ =134.8 Hz, 38.3 t, (C <sup>10</sup> ), ${}^{1}J_{CH}$ =124.8 Hz, 40.5 d, (C <sup>5</sup> ), ${}^{1}J_{CH}$ =126.7 Hz, 42.0 t, (C <sup>2</sup> ), ${}^{1}J_{CH}$ =127.6 Hz, 50.2 d, (C <sup>11</sup> ), ${}^{1}J_{CH}$ =123.3 Hz, 119.9 d, (C <sup>9</sup> ), ${}^{1}J_{CH}$ =154.4 Hz, 132.3 m, (C <sup>7</sup> ), 212.0 m (C <sup>1</sup> )

Table 4 (Continued)



<sup>a</sup> The numbering only serves as indicator for NMR characterization purposes.

transformation. The <sup>1</sup>H NMR chemical shifts were referenced with respect to tetramethylsilane (TMS) yielding the following chemical shifts for the used solvents CDCl<sub>3</sub> (contains CHCl<sub>3</sub>: 7.23 ppm) and CD<sub>3</sub>CN (contains CD<sub>2</sub>HCN: 1.96 ppm). The <sup>13</sup>C NMR spectra were referenced with respect to tetramethylsilane (TMS) using the chemical shifts for the solvents CDCl<sub>3</sub> (77.2 ppm) and CD<sub>3</sub>CN (118.7 ppm). The <sup>19</sup>F NMR chemical shifts were referenced with respect to CFCl<sub>3</sub> using the internal standards C<sub>6</sub>F<sub>6</sub> (-162.9 ppm) or C<sub>6</sub>H<sub>5</sub>CF<sub>3</sub> (-63.9 ppm). The <sup>31</sup>P NMR chemical shifts were referenced with respect to H<sub>3</sub>PO<sub>4</sub> (85%) in D<sub>2</sub>O. A positive (negative) sign denotes a chemical shift to high (low) frequency of the reference compound.

2D-HMQC NMR spectra: The 2D-HMQC NMR experiments (2D H-1/X correlation *via* heteronuclear zero and double quantum coherence with decoupling during acquisition and using gradient pulses for selection) were all performed with standard pulse sequences supplied by the spectrometer manufacturer. The HMQC spectra were used to establish one-bond proton-carbon connectivities. The spectra were measured with 4096  $f_2$  data points, 2048 increments and 8 scans. The spectral windows were set individually

as small as possible to get the best resolution possible. The resolutions were in the range of 2 to 10 Hz. These resolutions were lower than the resolutions of the corresponding 1D NMR spectra recorded, so that the HMQC spectra were only used to identify the relative positions of the resonances for assignment purposes. The chemical shifts presented were taken from the 1D NMR spectra.

#### 3.3.2. Differential scanning calorimetry (DSC)

Thermal analyses were performed using a Mettler-Toledo DSC 1 system. The temperature range was  $25 \,^{\circ}$ C to  $400 \,^{\circ}$ C if not otherwise stated. Samples were typically in the magnitude of 1–11 mg. A temperature program was used to heat the furnace (usually 10 K/min). Processing of the raw data was performed using the Star<sup>e</sup> software [38].

#### 3.3.3. Quantum-chemical calculations

Density Functional Theory (DFT) [39–41] calculations were carried out using the long-range corrected (LC) and empirical dispersion (D) corrected hybrid density functional ωB97X-D from



Fig. 7. 2D HMQC NMR spectrum of product (III).

Head-Gordon and Chai [42] on the level of the 6-311++G(3df,3pd) basis set. Considering both accuracy and efficiency the above mentioned basis set was used without superposition error correction (BSSE). Optimized gas phase geometries, energies, HOMOs and LUMOs were calculated with the Gaussian 09 [43] program suite. To find the minimum structures (NImag = 0) different conformers were investigated and uncertain dihedral angles calculated in 30 degrees steps on the lower basis set level 6-311++G(2d,p). The transition state geometries (NImag = 1) and energies were obtained using the transit-guided quasi-Newton (STQN) method [44,45] *via* the QST3 option. To visualize the computational results the software packages GaussView [46], PovChem [47] and POV-Ray [48] were used.

## 3.3.4. General procedure for Diels–Alder reactions catalyzed by $(C_2F_5)_3PF_2$

Diene  $(\mathbf{e}-\mathbf{g})$  was added to a solution of dienophile  $(\mathbf{a}-\mathbf{d})$  in dichloromethane ( $\sim$ 20 g, 15 mL) at *T* = ( $-40 \degree C$  to  $0 \degree C$ ). Difluorotris(pentafluoroethyl)phosphorane,  $(C_2F_5)_3PF_2$  (0.4 mol% to 2.4 mol% calculated towards the reagent not being in excess) was added to the solution at the temperature -40 °C to 0 °C. The mixture was stirred for 0.5-72 h (Table 3). After the completion of the reaction (monitored by NMR spectroscopy), spray dried KF (0.025 g-0.110 g) was added. The suspension was washed three to five times with bi-distilled water (50 mL), dried with MgSO<sub>4</sub>, filtrated and the solvent  $(CH_2Cl_2)$  together with excess of reagent were distilled out under normal pressure. Products (I-III, entries 1-3) were isolated as a mixture of isomers by fractional distillation. Products (IV-V, entries 4 and 5) were isolated by column chromatography using the mixture of petroleum ether: ethyl acetate 9:1 (v/v) as eluent. Product (VI, entry 6) was isolated by column chromatography using a mixture of cyclohexane: ethyl acetate 95:5 (v/v) as eluent. Products (VII-X, entries 7-10) have been identified in the reaction mixture by means of NMRspectroscopy.

#### 4. Conclusion

Difluorotris(pentafluoroethyl)phosphorane is found to catalyze Diels–Alder reactions of  $\alpha$ , $\beta$ -unsaturated ketones and aldehydes with conjugated dienes and cyclodienes. The catalytic mechanism by formation of a complex with phosphorane was established.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014. 11.002.

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