

# 1,3-Dipolar cycloadditions of 9-diazafluorenes with 2-acyl-2*H*-1,2,3-diazaphospholes to synthesise phosphiranes and trimers

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A series of 2-acyl-2*H*-1,2,3-diazaphospholes underwent readily 1,3-dipolar cycloaddition reactions with 9-diazafluorenes as the 1,3-dipole, yielding the respective bicyclic phosphiranes or trimers depending on the reaction conditions employed.

**Keywords:** 1,3-dipolar cycloaddition, phosphiranes trimers

1,3-Dipolar cycloaddition has proved to be an effective synthetic tool for the preparation of five-membered heterocyclic compounds with diverse functionality.<sup>1</sup> It has been demonstrated that phospho-alkenes including 1,2,3-diazaphospholes can couple with organic azides either by the [2+3] cycloaddition or in the Staudinger mode depending on the structure of the substrates and the reaction conditions.<sup>2,3</sup> 1,2,3-Diazaphospholes have been reported by Arbuzov's group and other researchers to react with diazoalkanes, giving mainly the 1:1 cycloadducts via a [2+3] cycloaddition reaction.<sup>4</sup> However, the initial adducts are generally unstable and decompose with elimination of nitrogen giving a mixture of  $\sigma^3\text{P}$  compounds or a cyclic trimer.

Being interested in this field, we initiated a programme on the synthesis of diversely substituted 2*H*-1,2,3-diazaphospholes reacting with 9-diazafluorene or diphenyldiazomethane as a 1,3-dipole molecule.

We employed a one-pot strategy to prepare the diazaphospholes **3**. Hydrazones **1** were reacted with  $\text{PCl}_3$ , the precipitated salt was filtered off, and the excess of  $\text{PCl}_3$  was removed by vacuum distillation and the resulting residue was taken into dry benzene and treated with another equivalent of triethylamine to eliminate the remaining HCl. Employing this procedure, the diversely substituted 2*H*-1,2,3-diazaphospholes **3a–c** were obtained in 52–65% yields. Unfortunately, cyclic diazaphosphole **3d** was only formed in low yield (28%) (Scheme 1).

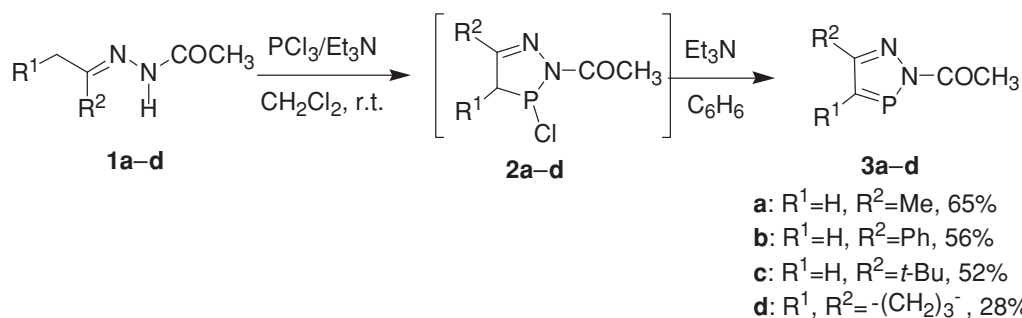
The reaction of **3a** with 9-diazafluorene **4a** in dry cyclohexane proceeded smoothly at room temperature for approximate 3 hours to afford the phosphadiazabicyclohexene **5a** as a pale yellow powder in 77% yield (Table 1, entry 1) with release of  $\text{N}_2$ . Under these optimised conditions, the dipolar cycloaddition of 9-diazafluorenes **4** with 2*H*-1,2,3-diazaphospholes **3** gave the corresponding 2',7'-dihalo substituted analogues **5** in high yields (82–89%). (Table 1, entries 2–5) However, for the reaction of the 2*H*-1,2,3-diazaphosphole **4a** with 9-diazafluorene **3c**, 3-spiro-substituted 3*H*-1,2,4-diazaphosphole fused 1,2,3-diazaphosphole **6** was isolated

in 65% yield without elimination of nitrogen. (Table 1, entry 6) This may be attributed to the stabilising effect of the congested-butyl substituent at the 7-position of **6**.

The reaction can also be performed in polar solvents like dichloromethane; 9-diazafluorene **4a** reacted with the 2*H*-1,2,3-diazaphosphole **3a** via a [2+3] cycloaddition reaction to give the cyclic trimer **7a** in 95% isolated yield. (Table 2, entry 1) In a similar manner, other cyclic trimers were prepared in high to excellent yields (79–91%). (Table 2, entries 2,4,5) However, **3c** provided **7c** in only 56% yield due to the steric effect of *t*-butyl group (Table 2, entry 3). Reactions in dry benzene also afforded the cyclic trimers in similar yields.

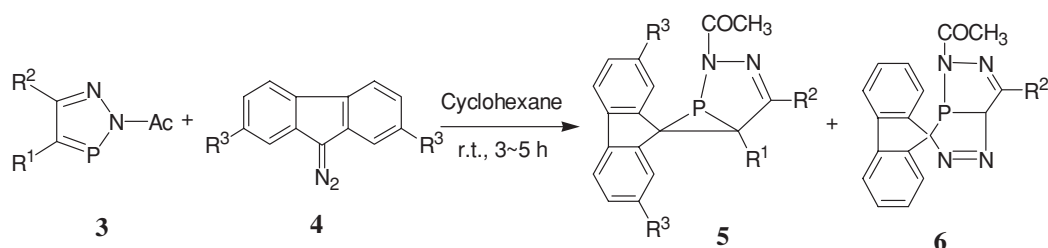
The structures suggested for all the prepared products have been verified by analysis of their analytical and spectroscopic data, which are given in the experimental part. It is well known that the  $^{31}\text{P}$  NMR chemical shifts can be affected by many factors such as ring members adjacent to the P atom, the anellated ring size, the anellation pattern, and additional heteroatoms in the ring.<sup>5</sup> For each of the products **5** a highly shielded  $^{31}\text{P}$  NMR absorption at  $\delta -75 \sim -45$  ppm can be observed, the range compatible with three-coordinate trivalent P atoms.<sup>6</sup> In contrast, the precursors **3** each give a highly deshielded  $^{31}\text{P}$  NMR signal at 220–240 ppm. Similar observations are made for the  $^{13}\text{C}$  NMR spectra. Thus, the  $^{13}\text{C}$  NMR signals found in the range of 48–62 ppm with  $^1J_{\text{PC}} = 162\text{--}183$  Hz are attributed to the  $\text{sp}^3$  hybridised carbon atoms in the 3,4-dihydro-2*H*-1,2,3-diazaphosphole rings of compounds **5**. This demonstrated clearly that the original  $>\text{C}=\text{P}-$  bond in **3** was saturated after reaction. On the other hand, the  $^{13}\text{C}$  NMR signal for the  $\text{sp}^2$  hybridised carbon atom in the 3,4-dihydro-2*H*-1,2,3-diazaphosphole ring of the products remains nearly unchanged as expected. In addition, the  $-\text{P}=\text{CH}$  moieties in the substrates **3** each give a doublet  $^1\text{H}$  NMR signal at 7.8–8.4 ppm with  $^2J_{\text{PH}} 42\text{--}44$  Hz. In the products **5**, the respective  $>\text{P}-\text{CH}$  signals shifted upfield by 4–4.5 ppm, appearing at 3.2–4.5 ppm with  $^2J_{\text{PH}} 20\text{--}22$  Hz.

On the other hand, the  $^{31}\text{P}$  NMR signal for **6** was found at  $-90.4$  ppm, located in the same range as **5**. In the  $^1\text{H}$  NMR



Scheme 1

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**Table 1** The [2+3] cycloaddition of 2*H*-1,2,3-diazophospholes **3** with 9-diazofluorenes **4**

| Entry    | R <sup>1</sup> | R <sup>2</sup>  | R <sup>3</sup> | Yields/% |
|----------|----------------|-----------------|----------------|----------|
| <b>a</b> | H              | Me              | H              | 77(5)    |
| <b>b</b> | H              | Ph              | H              | 90(5)    |
| <b>c</b> |                |                 | H              | 83(5)    |
| <b>d</b> | H              | Ph              | Cl             | 82(5)    |
| <b>e</b> | H              | Ph              | Br             | 89(5)    |
| <b>f</b> | H              | <sup>t</sup> Bu | H              | 65(6)    |

spectrum of cycloadduct **6**, the somewhat upfield doublet at  $\delta$  3.15 ppm with  $^2J_{\text{PH}}$  21.0 Hz can be assigned to C(7a)-H, whilst the respective signal for  $-\text{P}=\text{CH}$  in the precursor **3c** gives a doublet at  $\delta$  8.03 ppm ( $^2J_{\text{PH}} \approx 43$  Hz).

For the cyclic trimer compounds **7**, the structures have been principally ascertained by NMR and IR spectra along with elemental micro analysis. The  $^{31}\text{P}$  NMR signal was at approximately 50 ppm, a range characteristic of three-coordinated P.<sup>5</sup> Furthermore, each of the trimers show a HRMALDI MASS ion peak formed by loss of three acetyl residues.

In conclusion, the present work describes a systematic study of the dipolar cycloaddition reaction between 2*H*-1,2,3-diazaphospholes **3** and 9-diazofluorenes **4** or diphenyldiazomethane. Depending on the reaction conditions employed, the corresponding bicyclic phosphiranes **5** or trimers **7** could be formed in satisfactory yields. For **3c**, the phosphatetraazabicyclooctadiene **6** has been isolated with no loss of nitrogen.

## Experimental

The melting points are uncorrected. Solvents were dried by standard methods. The IR spectra were recorded on a Mattson Alpha-centauri FT-IR spectrometer, using KBr discs. The absorptions are given in wavenumbers ( $\text{cm}^{-1}$ ).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired in DMSO- $d_6$ , or  $\text{CDCl}_3$  as solvents on a Bruker 500 or Varian 400 spectrometer with TMS as internal reference. For  $^{31}\text{P}$  NMR spectra 85%  $\text{H}_3\text{PO}_4$  was used as the external reference. Coupling constant (*J*) values are given in Hz. The mass spectra were performed at 70 eV on a Finnigan MAT spectrometer provided with a data system. Satisfactory microanalysis ( $\text{C} \pm 0.20$ ,  $\text{H} \pm 0.20$ ,  $\text{N} \pm 0.30$ ) was

obtained for new compounds. All the reactions were carried out under a  $\text{N}_2$  atmosphere with strict exclusion of moisture using oven-dried apparatus and glassware. Details for preparation of 2*H*-1,2,3-diazaphospholes **3** have been described elsewhere.<sup>7</sup>

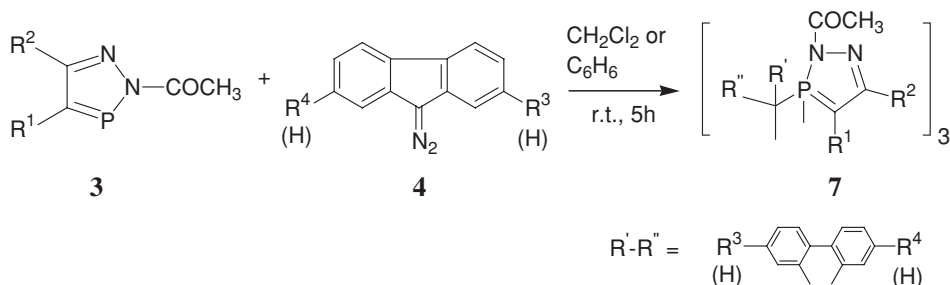
### Synthesis of the heterocycles **5**

A cyclohexane solution of **3** (10 mmol) was added dropwise to a solution of 9-diazofluorene (1.92 g, 10 mmol) in cyclohexane under stirring at 20 °C, and the resulting mixture was stirred for additional 3–5 h. The red colour faded to yellow over about 2 h. The precipitates were collected by filtration and washed with ether three times through a porous plate. The product was dried in a vacuum to afford the pure **5** in 77–90% yields.

**2-Acetyl-4-methyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9H]fluorene (5a)**: Yellow powders 77% yield. M.p. 164–166 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 2.26 (s, 3H,  $\text{CH}_3$ ), 2.47 (s, 3H,  $\text{COCH}_3$ ), 4.01 (d, 1H,  $^2J_{\text{PH}} = 21.0$ , P-CH), 6.74–7.89 (m, 8H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -75.44;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 18.65 ( $\text{CH}_3$ ), 21.94 ( $\text{COCH}_3$ ), 30.20 (d,  $^1J_{\text{C,P}} = 200$ ,  $\text{C}_6$ ), 48.11 (d,  $^1J_{\text{C,P}} = 163.5$ ,  $\text{C}_5$ ), 118.36–145.28 (m,  $\text{C}_{\text{arom}}$ ), 157.03 ( $\text{C}_4$ ), 175.16 (d,  $^2J_{\text{C,P}} = 44.5$ ,  $\text{C}=\text{O}$ ); IR (KBr) $\nu(\text{cm}^{-1})$ : 1607 ( $\text{C}=\text{N}$ ), 1672 ( $\text{C}=\text{O}$ ); MS  $m/z$  (%): 306 ( $\text{M}^+$ , 69), 264 (100), 263 (91); HRMS calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_2\text{OP}$  306.0922, found 306.0932.

**2-Acetyl-4-phenyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9H]fluorene (5b)**: A pale-yellow powder 90% yield. M.p. 160–161 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 2.60 (s, 3H,  $\text{COCH}_3$ ), 4.53 (d, 1H,  $^2J_{\text{PH}} = 20.2$ , P-CH), 7.12–7.95 (m, 13H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : -63.66;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 21.94 ( $\text{COCH}_3$ ), 33.04 (d,  $^1J_{\text{C,P}} = 198.7$ ,  $\text{C}_6$ ), 49.65 (d,  $^1J_{\text{C,P}} = 164.2$ ,  $\text{C}_5$ ), 120.13–141.44 (m,  $\text{C}_{\text{arom}}$ ), 156.80 ( $\text{C}_4$ ), 177.36 (d,  $^2J_{\text{C,P}} = 44.6$ ,  $\text{C}=\text{O}$ ); IR (KBr) $\nu(\text{cm}^{-1})$ : 1618 ( $\text{C}=\text{N}$ ), 1665 ( $\text{C}=\text{O}$ ); MS  $m/z$  (%): 368 ( $\text{M}^+$ , 23), 165 (100), 133 (85); HRMS calcd for  $\text{C}_{23}\text{H}_{17}\text{N}_2\text{OP}$  368.1079, found 368.1065.

**17-Acetyl-17,18-diaza-16-phosphaspiro[fluorene-9,2'-tricyclo[4.3.0.0<sup>1,3</sup>]nonane]-18-ene (5c)**: A pale-yellow powder 83% yield.

**Table 2** The [2+3] cycloaddition of 2*H*-1,2,3-diazophospholes **3** with 9-diazofluorenes **4** to afford trimers **7**

| Trimers <b>7</b> | R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | Yields/% |
|------------------|----------------|----------------|----------------|----------|
| <b>a</b>         | H              | Me             | H              | 95       |
| <b>b</b>         | H              | Ph             | H              | 88       |
| <b>c</b>         | H              | <i>t</i> -Bu   | H              | 56       |
| <b>d</b>         |                |                | H              | 79       |
| <b>e</b>         | H              | Ph             | Br             | 91       |

M.p. 134–136 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 2.07–2.21 (m, 4H, 2CH<sub>2</sub>), 2.46 (s, 3H, COCH<sub>3</sub>), 2.60 (t, 2H, C<sub>3</sub>-H<sub>2</sub>), 6.89–7.84 (m, 8H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –45.16;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 22.67 (COCH<sub>3</sub>), 22.74, 26.92, 27.88 (CH<sub>2</sub>), 36.41 (d,  $J_{\text{C,P}}$  = 197.0, C<sub>13</sub>), 61.94 (d,  $^1J_{\text{C,P}}$  = 183.5, C<sub>14</sub>), 120.11–142.99 (m, C<sub>arom</sub>), 168.81 (C<sub>19</sub>), 175.47 (d,  $^2J_{\text{C,P}}$  = 44.5, C=O); IR (KBr)v( $\text{cm}^{-1}$ ): 1630 (C=N), 1672 (C=O); MS  $m/z$  (%): 332 (M<sup>+</sup>, 62), 43 (100), 289 (44); HRMS calcd for C<sub>20</sub>H<sub>17</sub>N<sub>2</sub>OP 332.1453, found 332.1436.

**2-Acetyl-4-phenyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9H]-2',7'-dichlorofluorene (5d)**: A pale-yellow powder 82% yield. M.p. 118–120 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 2.28 (s, 3H, COCH<sub>3</sub>), 3.65 (d, 1H,  $^2J_{\text{P,H}}$  = 20.3, P-CH), 7.28–7.96 (m, 11H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –68.32;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 22.25 (COCH<sub>3</sub>), 32.81 (d,  $^1J_{\text{C,P}}$  = 190.5, C<sub>6</sub>), 46.99 (d,  $^1J_{\text{C,P}}$  = 162.5, C<sub>5</sub>), 119.04–142.86 (m, C<sub>arom</sub>), 156.36 (C<sub>4</sub>), 172.30 (d,  $^2J_{\text{C,P}}$  = 44.2, C=O); IR (KBr)v( $\text{cm}^{-1}$ ): 1625 (C=N), 1690 (C=O); MS  $m/z$  (%): 436 (M<sup>+</sup>, 18), 103 (100), 196 (90); HRMS calcd for C<sub>23</sub>H<sub>15</sub>Cl<sub>2</sub>N<sub>2</sub>OP 436.0300, found 436.0321.

**2-Acetyl-4-phenyl-spiro[2,3-diaza-1-phospha]bicyclo[3.1.0]hex-3-ene-6,9'-[9H]-2',7'-dibromofluorene (5e)**: Yellow powder in 89% yield. M.p. 124–126 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 2.01 (s, 3H, COCH<sub>3</sub>), 3.62 (d, 1H,  $^2J_{\text{P,H}}$  = 20.4, P-CH), 7.38–7.76 (m, 11H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –70.56;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 22.96 (COCH<sub>3</sub>), 35.22 (d,  $^1J_{\text{C,P}}$  = 199.2, C<sub>6</sub>), 48.23 (d,  $^1J_{\text{C,P}}$  = 163.7, C<sub>5</sub>), 121.36–145.22 (m, C<sub>arom</sub>), 154.66 (C<sub>4</sub>), 176.36 (d,  $^2J_{\text{C,P}}$  = 44.2, C=O); IR (KBr)v( $\text{cm}^{-1}$ ): 1621 (C=N), 1682 (C=O); MS  $m/z$  (%): 526 (M<sup>+</sup>, 20), 163 (100), 243 (61); HRMS calcd for C<sub>23</sub>H<sub>15</sub>Br<sub>2</sub>N<sub>2</sub>OP 523.9289, found 523.9272.

**5-Acetyl-5.7a-dihydro-7-(tert-butyl)-spiro[3H-1,2,4-diazaphospholo][4,3-c][1,2,3]diazaphosphole-3,9'-[9H]fluorene (6)**: A grey powder 65% yield. M.p. 118–120 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 1.11 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 2.34 (s, 3H, COCH<sub>3</sub>), 3.15 (d, 1H,  $^2J_{\text{P,H}}$  = 21.0, P-CH), 7.21–7.68 (m, 8H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : –90.35;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 21.87 (COCH<sub>3</sub>), 28.30 (C(CH<sub>3</sub>)<sub>3</sub>), 34.6 (C(CH<sub>3</sub>)<sub>3</sub>), 36.25 (d,  $^1J_{\text{C,P}}$  = 188.2, C<sub>3</sub>), 46.50 (d,  $^1J_{\text{C,P}}$  = 163.0, C<sub>7a</sub>), 118.82–142.89 (m, C<sub>arom</sub>), 158.62 (C<sub>7</sub>), 172.08 (d,  $^2J_{\text{C,P}}$  = 44.5, C=O); IR (KBr)v( $\text{cm}^{-1}$ ): 1560 (N=N), 1630 (C=N), 1700 (C=O); MS  $m/z$  (%): 319 (M<sup>+</sup>, C(CH<sub>3</sub>)<sub>3</sub>, 4), 165 (100), 261 (29), 318 (M<sup>+</sup>+1-C(CH<sub>3</sub>)<sub>3</sub>, 13); HRMS calcd for C<sub>21</sub>H<sub>21</sub>N<sub>4</sub>OP-C<sub>4</sub>H<sub>9</sub> 319.0749, found 319.0739.

#### Synthesis of the trimer 7

A solution of **3** (5 mmol) and an equimolar amount of 9-diazo-fluorene in dry CH<sub>2</sub>Cl<sub>2</sub> (5 mmol) or benzene was stirred at 20 °C for 3–5 h. The solution turned to a thick suspension upon completion of the reaction. Then, ether or cyclohexane was added, and the yellow precipitate was collected by suction. The yellow coloured solid was washed with cold ether and dried in a vacuum to give pure **7** in 56–95% yields.

**Cyclic trimer (7a)**: Yellow powder 95% yield. M.p. 256–258 °C; IR (KBr)v( $\text{cm}^{-1}$ ): 739 (s), 1228, 1260 (m), 1335 (s), 1611 (w), 1672 (vs). Calcd for C<sub>54</sub>H<sub>45</sub>N<sub>6</sub>O<sub>3</sub>P<sub>3</sub> (%): C, 70.6; H, 4.9; N, 9.1; Found: C, 70.4; H, 4.9; N, 9.3.

**Cyclic trimer (7b)**: Yellowish brown powder 88% yield. M.p. 186–188 °C; IR (KBr)v( $\text{cm}^{-1}$ ): 739 (s), 1246, 1280 (m), 1347 (s), 1630

(w), 1676 (vs); HRMaldims for C<sub>69</sub>H<sub>51</sub>N<sub>6</sub>O<sub>3</sub>P<sub>3</sub> (M<sup>+</sup>+1-3COCH<sub>3</sub>): calc 976.1868, found 976.1891.

**Cyclic trimer (7c)**: Greyish brown powder 56% yield. M.p. 80–82 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 0.74 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 2.55 (s, 3H, COCH<sub>3</sub>), 5.43 (d, 1H,  $^2J_{\text{P,H}}$  = 31.6, P=CH), 7.27–8.09 (m, 8H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 51.88;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 21.86 (COCH<sub>3</sub>), 27.04 (C(CH<sub>3</sub>)<sub>3</sub>), 29.00 (C(CH<sub>3</sub>)<sub>3</sub>), 36.36 (d,  $^1J_{\text{C,P}}$  = 187.0, C-P), 120.42–143.82 (m, C<sub>arom</sub>), 138.70 (d,  $^1J_{\text{C,P}}$  = 12.0, C=P), 173.38 (d,  $^2J_{\text{C,P}}$  = 43.6, C=O); IR (KBr)v( $\text{cm}^{-1}$ ): 741 (s), 1244, 1283 (m), 1350 (s), 1637 (w), 1677 (vs); HRMaldims for C<sub>63</sub>H<sub>63</sub>N<sub>6</sub>O<sub>3</sub>P<sub>3</sub> (M<sup>+</sup>+1-3COCH<sub>3</sub>): calc 916.2807, found 916.2787.

**Cyclic trimer (7d)**: Yellow powder 79% yield. M.p. 90–92 °C; IR (KBr)v( $\text{cm}^{-1}$ ): 746 (s), 1235, 1266 (m), 1375 (s), 1621 (w), 1665 (vs); HRMaldims for C<sub>60</sub>H<sub>51</sub>N<sub>6</sub>O<sub>3</sub>P<sub>3</sub> (M<sup>+</sup>+1-3COCH<sub>3</sub>): calc 868.1868, found 868.1890.

**Cyclic trimer (7e)**: Yellow powder 91% yield. M.p. 163–165 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 2.69 (s, 3H, COCH<sub>3</sub>), 5.50 (d, 1H,  $^2J_{\text{P,H}}$  = 32.3, P=CH), 7.30–7.68 (m, 8H<sub>arom</sub>);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 48.76;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3/\text{TMS}$ )  $\delta$ : 22.45 (COCH<sub>3</sub>), 35.81 (d,  $^1J_{\text{C,P}}$  = 199.0, C-P), 120.44–146.32 (m, C<sub>arom</sub>), 140.75 (d,  $^1J_{\text{C,P}}$  = 12.0, C=P), 175.34 (d,  $^2J_{\text{C,P}}$  = 43.4, C=O); IR (KBr)v( $\text{cm}^{-1}$ ): 741 (s), 1236, 1270 (m), 1342 (s), 1625 (w), 1690 (vs); HRMaldims for C<sub>69</sub>H<sub>45</sub>Br<sub>6</sub>N<sub>6</sub>O<sub>3</sub>P<sub>3</sub> (M<sup>+</sup>+1-3COCH<sub>3</sub>): calc 1443.6498, found 1443.6517.

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