Chapter 5

Hyperbranched hydrazones derived from cyclotriphosphazene based ketone precursors
Introduction

Hexakis(4-formylphenoxy)cyclotriphosphazene bearing six aldehyde units is explored extensively for the preparation of a large number of cyclotriphosphazene based dendrimers\textsuperscript{1,2}. However, reports dealing with the utility of ketone terminated hexakis(4-acetylphenoxy)cyclotriphosphazene (HAPC) for the synthesis of dendrimers are relatively sparse. Although cyclotriphosphazenes bearing oxime groups have been prepared from HAPC\textsuperscript{3-5}, to our knowledge, formation of hydrazones by the reaction of aromatic hydrazides with HAPC (22) has not been reported and deserves further exploration.

It is also well known that hydrazones, containing an azometine (–NHN=CH–) group, constitute a significant class of organic compounds. Hydrazones are important synthons for several transformations and are of wide interest because of their diverse biological activities\textsuperscript{6,7}. Hydrazone linkage is utilized for pH-dependent release of drugs from drug-conjugates\textsuperscript{8}.

This chapter deals with the synthesis of zero generation hydrazones by the condensation of HAPC with aromatic and heterocyclic hydrazides. Further, first generation dendrimer like hyperbranched molecule bearing twelve ketone units is synthesized by the temperature dependent stepwise substitution of cyanuric chloride\textsuperscript{9-11} with the six terminal amine groups of hexakis(4-{(2-aminoethyl)carbamoyl}phenoxy)cyclotriphosphazene (4) followed by the reaction with p-hydroxyacetophenone. The reactive terminal ketone groups in first generation dendrimer like hyperbranched architecture could be readily elaborated to the first generation hydrazones (25a-k) by condensation with the aromatic and heterocyclic hydrazides.

Results and discussion

The desired dendrimer like hyperbranched molecules are synthesized using divergent synthetic protocol. The synthetic methodology is free from the use of protecting-deprotecting groups.
Synthesis and characterization of hexa-acetyl cyclotriphosphazene core (22)

Hexakis(4-acetylphenoxy)cyclotriphosphazene (HAPC) was synthesized according to the reported method\textsuperscript{12} by the reaction of hexachlorocyclotriphosphazene with 4-hydroxyacetophenone in the presence of K\textsubscript{2}CO\textsubscript{3} in Acetone.

\[
\text{Acetone, K}_2\text{CO}_3 \quad \text{Reflex, 36 h}
\]

\[
\text{THF} \quad \text{Reflex, 24-26 h}
\]

\[
\text{Scheme 5.1. Synthesis of zero generation ketone and hydrazones.}
\]
Synthesis and characterization of zero generation hydrazones (23a–k)

The condensation of the six ketone functions of HAPC (22) with aromatic and heterocyclic hydrazides 16a–k in THF for 24-36 h at refluxing temperature affords the corresponding zero generation hydrazones (23a–k) as shown in Scheme 5.1. All products were generally obtained in high yields.

The hydrazone (23a-k) formation was ascertained by the appearance of C=N stretching frequencies in the 1594-1607 cm\(^{-1}\) region and by the absence of the \(\nu\) (C=O) of ketone groups of the core (22) which were observed at 1685 cm\(^{-1}\). The \(\nu\) (N-H) was observed as a broad band at 3194-3252 cm\(^{-1}\). A strong band at 1642-1666 cm\(^{-1}\) is ascribed to the \(\nu\) (C=O) amide moiety. A medium intensity absorption band at 3039-3067 cm\(^{-1}\) and 2916-2924 cm\(^{-1}\) are attributed to the aromatic and aliphatic C-H stretching vibrations respectively. The characteristic -P=O- stretching vibrations of cyclophosphazenes are observed between 1164 and 1208 cm\(^{-1}\) as sharp bands. P-O-C stretching band was observed in the 952-955 cm\(^{-1}\) region. The diagnostic IR bands are presented in the experimental section.

The \(^1\)H NMR spectra of hydrazones 23a-k consisted of a series of broad peaks. The acetyl (-C(O)-CH\(_3\)) protons of zero generation ketone (22) which were observed as a singlet at 2.59 ppm shifted upfield following hydrazone formation. The synthesis of zero generation hydrazones (23a-k) is confirmed by the appearance of azomethine methyl (-CH\(_3\))C=N-N-) protons in the range 2.21-2.39 ppm. Proton of amide groups (=N-NH-C(O)-) resonated in the downfield region 10.52-11.02 ppm. In case of 23e the six para-hydroxy (-OH) protons have appeared in the downfield region 10.09 ppm. The resonances of p-methoxy (-OCH\(_3\)) protons of 23f and p-methyl (-CH\(_3\)) protons of 23g are observed at 3.82 ppm and 2.37 ppm respectively. A representative \(^1\)H NMR spectrum of compound 23c is displayed in Figure 5.1.
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Figure 5.1. $^1$H NMR spectrum of 23c in DMSO-$d_6$.

The formation of zero generation hydrazones (23a-k) is supported by the $^{13}$C NMR analysis. None of the compounds 23a-k exhibited any signal in $^{13}$C NMR spectra that could be attributed to unreacted ketone functions of 22 which were observed at 196.98. $^{13}$C NMR spectra of 23a-k demonstrated resonance in the range 153.65-155.01 ppm and 13.83-15.15 ppm attributed to the azomethine carbons (=-CH$_3$C=N-N-) and azomethine methyl carbons (=-CH$_3$C=N-N-) respectively. The carbonyl carbon of the amide group (=N-NH-C(O)-) resonated in the region 160.97–164.45 ppm. The 2D-Heteronuclear Single Quantum Coherence (HSQC) NMR study was undertaken to correlate chemical shifts of directly bound $^1$H and $^{13}$C nuclei. Ascription of $^1$H and $^{13}$C NMR resonances was made by comparison with the starting materials and literature values for cyclotriphosphazene hydrazones$^{13,14}$ and Schiff bases$^{5,15,16}$. Representative $^{13}$C NMR and spectrum of 23d is given at Figure 5.2. 2D-HSQC NMR spectrum of 23c is given as an example at Figure 5.3.
Figure 5.2. $^{13}$C NMR spectrum of 23c in DMSO-d$_6$.

Figure 5.3. 2D-HSQC-NMR spectrum of 23c in DMSO-d$_6$ (expanded form of the aromatic region is shown in the box inset).
The $^1$H-decoupled $^{31}$P NMR spectra of 23a-k bearing the six hydrazone arms displayed a singlet in the range 8.65 to 8.98 ppm demonstrating the uniform substitution of phosphorus atoms of the cyclotriphosphazene ring. The substituents on the hydrazone arm of 23a-k are apparently too far from the cyclotriphosphazene center to influence the $^{31}$P NMR shift to a considerable extent. In the $^{31}$P NMR spectrum of 3c given as an example at Figure 4, singlet appears at 8.65 ppm.

![Figure 5.4. $^{31}$P NMR spectrum of 23c in DMSO-d$_6$.](image)

MALDI-TOF mass spectrometry confirmed the expected chemical structures. A representative MALDI-TOF mass spectrometry of 23d presented at Figure 5.5 shows molecular ion peak at $m/z = 1785.2592$ corresponding to the [M+Na]$^+$ ion. Elemental composition analysis presented in the experimental section also confirmed the expected chemical structures.
**Figure 5.5.** MALDI-TOF mass spectrum of 23d, $m/z$ value 1785.2592 corresponds to \((\text{M} + \text{Na})^+\) ion.

**Synthesis and characterization of first generation ketone (24)**

The preparation of first generation ketone relies on the sequential dependent nucleophilic substitution of trichlorotriazine (cyanuric chloride). Simanek$^{17,18}$ and others$^{19,20}$ have shown that it is possible to direct the substitution of one, two, or three of the chloro substituents of cyanuric chloride by controlling temperature of the reaction.

The methodology used for the synthesis of dendrimer like hyperbranched molecule with peripheral ketone functionality (24) is similar to the procedure adopted for the preparation first generation aldehyde (19) discussed in chapter 4. The reaction of cyanuric chloride with six amine groups of zero generation amine (4) at 0 °C produces the dichlorotriazine-terminated compound (18). Further, reaction of 18 with sodium salt of $p$-hydroxyacetophenone yields first generation ketone (24) as illustrated in Scheme 5.2. Preparation of zero generation amine (4) has been described in chapter 2.
Scheme 5.2. Synthesis of first generation ketone.
IR spectrum of 24 was characterized by the appearance of ν (C=O) of ketone at 1680 cm\(^{-1}\). A broad band at 3326 cm\(^{-1}\) is assigned to the stretching frequencies of N-H functionality. Stretching frequencies of the amide carbonyl groups was observed as a strong band at 1641 cm\(^{-1}\). The cyclotriphosphazene ring -P=N- stretching vibrations of are observed between 1165 and 1207 cm\(^{-1}\) as sharp bands. A band at 954 cm\(^{-1}\) is due to P-O-C stretching frequency.

The \(^1\)H NMR spectrum of 24 shown in Figure 5.6, consisted of a series of broad peaks. Acetyl proton resonance appeared at 2.58 ppm. The proton of amide units (-CO-NH-) resonated at 8.57 ppm. The resonances corresponding to the proton of amine group adjacent to the triazine moiety (-C-NH-C\(_3\)N\(_3\)-) appeared at 6.82 ppm. Broad signals at 6.96, 7.38, 7.81 and 8.00 ppm were ascribed to the resonances of aromatic protons. The resonances at 3.43 and 3.79 ppm are assigned to the protons of two methylene units.

![Figure 5.6. \(^1\)H NMR spectrum of 24 in DMSO-d\(_6\).](image)

In the \(^{13}\)C NMR spectrum of 24 presented in Figure 5.7, a distinct resonance at 196.75 ppm is attributed to carbonyl carbon of the ketone functionality. The resonance observed at 165.53 ppm is assigned to the amide carbonyl carbon. The resonances
corresponding to the triazine carbons appeared at 167.81 and 171.27 ppm. Methyl carbon of the acetyl group was observed at 26.68 ppm. One of the methylene carbon resonated at 53.63 ppm while the resonance of another methylene carbon was merged with the resonance of the DMSO-d$_6$ solvent and this is clearly evident from the 2D HSQC NMR spectrum shown in Figure 5.8.

![2D HSQC NMR spectrum](image)

**Figure 5.7.** The $^{13}$C NMR spectrum of 24 in DMSO-d$_6$.

2D HSQC NMR spectrum was helpful in correlating the chemical shifts of directly bound $^1$H and $^{13}$C nuclei. The resonances observed at 6.82 and 8.57 ppm are devoid of any attached carbon signals, confirming their assignments to amine and amide protons, respectively. Assignment of $^1$H and $^{13}$C NMR resonances was made by comparison with the starting materials and zero generation ketone.

A singlet at 8.37 ppm in the $^{31}$P ($^1$H-decoupled) NMR spectrum of 24 shown in Figure 5.9, indicates the symmetric substitution of phosphorus atoms in the cyclotriphosphazene ring. Elemental composition analysis further confirmed the constitution of the compound.
**Figure 5.8.** 2D-HSQC-NMR spectrum of 24 in DMSO-d$_6$ (expanded form of the aromatic region is shown in the box inset).

**Figure 5.9.** $^{31}$P NMR spectrum of 24 in DMSO-d$_6$. 
Synthesis and characterization of first generation hydrazones (25a–k)

Condensation of aromatic and heterocyclic hydrazides 16a–k with twelve ketone functionalities of 24 with, in THF-DMF under reflux conditions, afforded the desired first generation hydrazones 25a–k as illustrated in Scheme 5.3. The diagnostic IR bands are presented in the experimental section. The appearance of azomethine ν (C=N) frequencies

Scheme 5.3. Synthesis of first generation hydrazones.
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in the 1599-1605 cm\(^{-1}\) region confirms the formation of 25a-k. A broad band in the region 3226-3266 cm\(^{-1}\) is ascribed to \(\nu (\text{N-H})\) functionality. A strong band at 1644-1661 cm\(^{-1}\) is attributed to \(\nu (\text{C=O})\) of amide moiety. Sharp bands observed between 1166 and 1209 cm\(^{-1}\) are attributed to characteristic -P=N- stretching vibrations of cyclotriphosphazenes. Furthermore, P-O-C stretching frequencies are observed in the 951-956 cm\(^{-1}\) region. Aromatic C-H stretching vibrations were merged with broad band due to \(\nu (\text{N-H})\). Aliphatic C-H stretching vibrations are observed in the region 2922-2928 cm\(^{-1}\). Thus, the IR spectral data results provide strong evidences for the formation of the first generation hydrazones.

Series of broad signals were observed in the \(^1\)H NMR spectra of 25a-k. Appearance of azomethine methyl (\((-\text{H}_3\text{C})\text{C=N-N-}\)) protons in the range 2.35-2.39 ppm validates the formation of hydrazones 25a-k. Further, the appearance of the protons of the exterior amide units (-C=N-NH-\text{CO-}) in downfield region 10.55–11.80 ppm confirms the formation of 25a-k. Protons of the interior amide (-CONH-) groups resonated in the range 8.54-8.59 ppm. The resonances corresponding to the proton of amine group adjacent to the triazine moiety (-C-N\text{H}-\text{C}_3N_3-) appeared in the range 6.80-6.84 ppm. The aromatic protons appeared as relatively broader signals. The resonances in the range 3.57-3.59 ppm and 3.75-3.79 ppm attributed to the protons of two methylene units. The para-hydroxy (-OH) protons of 25e resonate as a singlet in the downfield region 10.09 ppm. In case of 25f and 25g a signal at 2.33 ppm and 3.84 ppm accounts for the protons of \text{p-methoxy (-OCH}_3\text{)} and \text{p-methyl (-CH}_3\text{)} groups respectively. A representative \(^1\)H NMR spectrum of compound 25b is displayed in Figure 5.10.
\(^1\)H NMR analysis is supported by the \(^{13}\)C NMR spectral analysis in confirming the formation of the first generation hydrazones 25a-k. In the \(^{13}\)C NMR spectra of 25a-k, resonances in the 153.11-154.88 ppm region are attributed to the azomethine carbons (-\((\text{H}_3\text{C})\text{C}=\text{N}-\text{N}-\)) while azomethine methyl carbons (-\((\text{H}_3\text{C})\text{C}=\text{N}-\text{N}-\)) resonated in the range 14.32-15.40 ppm. Carbonyl carbons of the exterior amide (=N-NH-CO-) functionality resonated in the range 161.15-163.85 ppm. The signal observed in 165.39–165.49 ppm region is due to carbonyl carbon of the interior amide (=CONH-) groups. The resonance observed in the range 167.19-167.36 ppm and 171.21-171.99 ppm are assigned to the triazine carbons. The resonances in the range 41.13-41.21 ppm and 53.52-53.60 ppm are ascribed to the carbons of two methylene units. The assignments of peaks were made by comparison with literature values\(^5\)\(^-\)\(^16\) and zero generation hydrazones 25a-k. A representative \(^{13}\)C NMR spectrum of compound 25b is displayed in Figure 5.11.
The $^1$H-decoupled $^{31}$P NMR spectra of 25a-k bearing twelve hydrazone arms exhibited a singlet in the range 8.18 to 8.36 ppm indicating the uniform substitution of the phosphorus atoms in the cyclotriphosphazene ring. The terminal substituents on the hydrazone arms are presumably too far from the cyclotriphosphazene center to influence the $^{31}$P NMR shift to a larger extent. However, $^{31}$P NMR served as an important diagnostic tool in demonstrating the symmetrically substituted phosphorous atoms of the cyclotriphosphazene ring. A singlet appears at 8.27 ppm in the $^{31}$P NMR spectrum of 25b given as an example at Figure 5.12. Microanalysis data presented in the experimental section also confirmed the expected chemical structures.
Conclusion

Hexakis(4-acetylphenoxy)-cyclotriposphazene (17), possessing six ketone functions on the side substituents was used as starting material for the synthesis of zero generation hydrazones (20) by condensation with the aromatic and heterocyclic hydrazides.

The utility of the stepwise substitution of the s-triazine nucleus for the synthesis of dendrimer like architecture bearing twelve peripheral ketone units is demonstrated. Temperature controlled mono-substitution reaction of cyanuric chloride (trihalotriazine) with ‘zero generation amine’ (4) generates hyperbranched molecule 18 with terminal dichlorotriazine units. Reaction of 18 with the sodium salt of hydroxyacetophenone at elevated temperature produces a novel dendritic framework with twelve terminal aldehyde functions (24). The condensation of terminal ketone groups of 21 with aromatic and heterocyclic hydrazides leads to first generation (25a-k) hydrazones.

Formation of the zero and first generation hydrazones was ascertained by the $^1$H, $^{13}$C and 2D-HSQC NMR as well as IR spectroscopy. $^{31}$P NMR confirmed the structural homogeneities of the all the synthesized compounds. The expected chemical structures were confirmed by the microanalysis and mass spectrometry.

The reactions presented in this chapter could be readily translated to the synthesis of higher generation dendritic hyperbranched macromolecules. The symbiosis that exists between cyclophosphazenes and the corresponding polymeric systems presents the possibility of using the compounds presented in this chapter as synthetic and structural models for the corresponding polyphosphazenes.
Experimental Materials and measurements

Heterocyclic hydrazides and all other chemicals were purchased from commercial sources and were used as received. Measurements were carried out as described in chapter 1.

Synthesis of zero generation ketone (22)

HAPC (1) was synthesized according to reported method\textsuperscript{12}. Yield: 94%; IR (KBr) ν 3068 (C-H\textsubscript{Ar}), 1685 (C=O), 1210-1187 (-P=N-), 950 (P-O-C) cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) δ 2.59 (s, 18H, CH\textsubscript{3}), 7.03 (d, J=8.6Hz, 12H, H\textsubscript{Ar}). 7.78 (d, J=8.6Hz, 12H, H\textsubscript{Ar}), \textsuperscript{13}C NMR (CDCl\textsubscript{3}): 26.93, 121.12, 130.53, 134.78, 154.27, 196.98; \textsuperscript{31}P NMR (CDCl\textsubscript{3}) δ 7.88; Anal. Calcd. For C\textsubscript{48}H\textsubscript{42}N\textsubscript{3}O\textsubscript{12}P\textsubscript{3}: C, 60.96; H, 4.48; N, 4.44%. Found: C, 60.92; H, 4.52; N, 4.48%.

Synthesis of benzoic hydrazides (16a-k)

Benzoic hydrazide and other \textit{para}-substituted benzoic hydrazides (16a-k) were prepared according to the procedure mentioned in chapter 4.

General procedure for the synthesis of zero generation hydrazones (23a-k)

HAPC (20) (0.12 mmol) was added to a solution of hydrazide 16a-k (0.8 mmol) in tetrahydrofuran (75 mL) and the reaction mixture was stirred under reflux for 24-36 h. The solvent was removed by evaporation under reduced pressure. The residue was filtered under suction and washed several times with hot tetrahydrofuran. The resulting solid (3a) was dried in vacuo at 40°C for 8 h. The \textsuperscript{1}H NMR spectra of 25a-k consisted of broad signals.
[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4-p-\text{C(H}_3)=\text{N}-\text{NH-C(O)-C}_6\text{H}_5)_6] (23a)

Yield 93%, Mp. 230-233 °C; IR (KBr) ν 3230 (N-H), 1204 (C=N), 1200-1168 (-P=N-), 954 (P–O–C) cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\text{d}_6) δ 2.35 (18H, CH\(_3\)), 6.95 (12H, H\(_{Ar}\)), 7.43 (12H, H\(_{Ar}\)), 7.65 (12H, H\(_{Ar}\)), 7.75 (6H, H\(_{Ar}\)); \(^13\)C NMR (DMSO-\text{d}_6) δ 14.87, 120.54, 128.13, 128.43, 130.12, 131.81, 134.53, 150.94, 154.32, 164.39 ppm; \(^31\)P NMR (DMSO-\text{d}_6) δ 8.96 ppm; MALDI-TOF MS \(m/z: 1676.205\) (M+Na\(^+\)); Anal. Calcd. For C\(_{90}\)H\(_{78}\)N\(_{15}\)O\(_{12}\)P\(_3\): C, 65.33; H, 4.75; N, 12.70%. Found: C, 65.26; H, 4.79; N, 12.66%.

[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4-p-\text{C(H}_3)=\text{N}-\text{NH-C(O)-C}_6\text{H}_5-p-\text{Br})_6] (23b)

Yield 94%, Mp. 245-248 °C; IR (KBr) ν 3220 (N-H), 1209 (C=N), 1207-1166 (-P=N-), 952 (P–O–C) cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\text{d}_6) δ 2.34 (18H, CH\(_3\)), 6.94 (12H, H\(_{Ar}\)), 7.63 (12H, H\(_{Ar}\)), 7.75 (24H, H\(_{Ar}\)), 10.76 (6H, CONH) ppm; \(^13\)C NMR (DMSO-\text{d}_6) δ 14.96, 120.95, 125.37, 128.84, 130.14, 131.95, 135.60, 151.04, 154.38, 163.45 ppm; \(^31\)P NMR (DMSO-\text{d}_6) δ 8.96 ppm; MALDI-TOF MS \(m/z: 2183.2098\) (M+Na\(^+\)); Anal. Calcd. For C\(_{90}\)H\(_{78}\)Br\(_6\)N\(_{15}\)O\(_{12}\)P\(_3\): C, 50.76; H, 3.41; N, 9.87%. Found: C, 50.76; H, 3.46; N, 9.93%.

[\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4-p-\text{C(H}_3)=\text{N}-\text{NH-C(O)-C}_6\text{H}_5-p-\text{Cl})_6] (23c)

Yield 94%, Mp. 251-253 °C; IR (KBr) ν 3218 (N-H), 1204 (C=N), 1200-1168 (-P=N-), 954 (P–O–C) cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\text{d}_6) δ 2.35 (18H, CH\(_3\)), 6.94 (12H, H\(_{Ar}\)), 7.51 (12H, H\(_{Ar}\)), 7.72 (12H, H\(_{Ar}\)), 7.83 (12H, H\(_{Ar}\)), 10.79 (6H, CONH) ppm; \(^13\)C NMR (DMSO-\text{d}_6) δ 15.05, 121.37, 128.88, 129.16, 130.14, 132.08, 135.21, 137.26, 151.19, 154.49, 162.54, ppm; \(^31\)P NMR (DMSO-
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$\delta$ 8.65 ppm; MALDI-TOF MS m/z: 1880.1129 (M+Na$^+$); Anal. Calcd. For $C_{90}H_{72}Cl_6N_{13}O_{12}P_3$: C, 58.08; H, 3.90; N, 11.29%. Found: C, 58.15; H, 3.87; N, 11.35%.

$[N_3P_3(-OC_6H_4-p-C(CH_3)=N-NH-C(O)-C_6H_4-p-F)_6]$ (23d)

Yield 94%, Mp. 218-222 °C; IR (KBr) v 3225 (N-H), 3067 (C-H Ar), 2924 (C-H Al), 1649 (C=O), 1602 (C=N), 1207-1164 (-P=N-) cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 2.35 (18H, CH$_3$), 6.95 (12H, H$_{Ar}$), 7.28 (12H, H$_{Ar}$), 7.73 (12H, H$_{Ar}$), 7.92 (12H, H$_{Ar}$), 10.76 (6H, CONH) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 14.92, 115.53, 120.93, 128.43, 130.88, 135.71, 150.95, 155.01, 163.38, 165.43, ppm; $^{31}$P NMR (DMSO-$d_6$) $\delta$ 8.94 ppm; MALDI-TOF MS m/z: 1784.2802 (M+Na$^+$); Anal. Calcd. For $C_{90}H_{72}F_6N_{15}O_{12}P_3$: C, 61.33; H, 4.12; N, 11.92%. Found: C, 61.40; H, 4.15; N, 11.89%.

$[N_3P_3(-OC_6H_4-p-C(CH_3)=N-NH-C(O)-C_6H_4-p-OH)_6]$ (23e)

Yield 91%, Mp. 225-230 °C; IR (KBr) v 3237 (O-H), 3237 (N-H), 3062 (C-H Ar), 2916 (C-H Al), 1653 (C=O), 1604 (C=N), 1205-1165 (-P=N-) cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-$d_6$) $\delta$ 2.32 (18H, CH$_3$), 6.82 (12H, H$_{Ar}$), 6.99 (12H, H$_{Ar}$), 7.70 (12H, H$_{Ar}$), 7.77 (12H, H$_{Ar}$), 10.09 (6H, OH), 10.52 (6H, CONH) ppm; $^{13}$C NMR (DMSO-$d_6$) $\delta$ 14.62, 115.28, 120.92, 124.82, 128.30, 130.67, 135.90, 149.84, 150.78, 153.65, 160.97, ppm; $^{31}$P NMR (DMSO-$d_6$) δ 8.84 ppm; MALDI-TOF MS m/z: 1772.2962 (M+Na$^+$); Anal. Calcd. For $C_{90}H_{78}N_{15}O_{12}P_3$: C, 61.75; H, 4.49; N, 12.00%. Found: C, 61.69; H, 4.54; N, 11.96%.

$[N_3P_3(-OC_6H_4-p-C(CH_3)=N-NH-C(O)-C_6H_4-p-OCH_3)_6]$ (23f)

Yield 95%, Mp. 219-222 °C; IR (KBr) v 3225 (N-H), 3063 (C-H Ar), 2924 (C-H Al), 1643 (C=O), 1605 (C=N), 1207-1172 (-P=N-) cm$^{-1}$; $^1$H NMR (500 MHz,
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DMSO-d$_6$ $\delta$ 2.34 (18H, CH$_3$), 3.82 (18H, OCH$_3$), 6.82 (12H, H$_{Ar}$), 6.92 (12H, H$_{Ar}$), 7.54 (12H, H$_{Ar}$), 7.76 (12H, H$_{Ar}$), 10.78 (6H, CONH) ppm; $^{13}$C NMR (DMSO-d$_6$) $\delta$ 14.70, 55.76, 114.92, 120.93, 126.57, 128.43, 130.48, 135.84, 150.79, 154.32, 162.35, 162.65, ppm; $^{31}$P NMR (DMSO-d$_6$) $\delta$ 8.77 ppm; MALDI-TOF MS m/z: 1856.4201 (M+Na$^+$); Anal. Calcd. For C$_{96}$H$_{90}$N$_{15}$O$_{18}$P$_3$: C, 62.84; H, 4.94; N, 11.45%. Found: C, 62.80; H, 4.89; N, 11.47%.

$\left[N_3P_3(-OC_6H_4-p-C(CH_3)=N-NH-C(O)-C_6H_4-p-CH_3)\right]$ (23g)

Yield 96%, Mp. 213-216 °C; IR (KBr) $\nu$ 3225 (N-H), 3063 (C-H$_{Ar}$), 2921 (C-H$_{Ar}$), 1653 (C=O), 1607 (C=N), 1207-1166 (P=N), 952 (P–O–C) cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 2.34 (18H, CH$_3$), 2.37 (18H, CH$_3$), 6.94 (12H, H$_{Ar}$), 7.24 (12H, H$_{Ar}$), 7.74 (24H, H$_{Ar}$), 10.66 (6H, CONH) ppm; $^{13}$C NMR (DMSO-d$_6$) $\delta$ 14.81, 21.50, 120.93, 128.36, 129.17, 129.22, 131.52, 135.79, 141.89, 150.88, 154.50, 164.20, ppm; $^{31}$P NMR (DMSO-d$_6$) $\delta$ 8.98 ppm; MALDI-TOF MS m/z: 1760.4406 (M+Na$^+$); Anal. Calcd. For C$_{96}$H$_{90}$N$_{15}$O$_{12}$P$_3$: C, 66.31; H, 5.22; N, 12.08%. Found: C, 66.36; H, 5.17; N, 12.14%.

$\left[N_3P_3(-OC_6H_4-p-C(CH_3)=N-NH-C(O)-C_6H_4-p-NO_2)\right]$ (23h)

Yield 98%, Mp. 216-220 °C; IR (KBr) $\nu$ 3194 (N-H), 3106 (C-H$_{Ar}$), 2923 (C-H$_{Ar}$), 1666 (C=O), 1600 (C=N), 1207-1166 (P=N), 953 (P–O–C) cm$^{-1}$; $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$ 2.39 (18H, CH$_3$), 6.94 (12H, H$_{Ar}$), 7.75 (12H, H$_{Ar}$), 8.04 (12H, H$_{Ar}$), 8.23 (12H, H$_{Ar}$), 11.02 (6H, CONH) ppm; $^{13}$C NMR (DMSO-d$_6$) $\delta$ 15.15, 120.98, 123.73, 128.57, 129.82, 135.56, 140.01, 151.04, 151.14, 154.43, 162.90, ppm; $^{31}$P NMR (DMSO-d$_6$) $\delta$ 8.78 ppm; MALDI-TOF MS m/z: 1946.2172 (M+Na$^+$); Anal. Calcd. For C$_{90}$H$_{72}$N$_{21}$O$_{24}$P$_3$: C, 56.17; H, 3.77; N, 15.28%. Found: C, 56.21; H, 3.71; N, 15.34%.
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\[ \text{[N}_3\text{P}_3(-\text{OC}_6\text{H}_4-p-\text{C(CH}_3)_3=\text{N-NH-C(O)-C}_5\text{H}_4\text{N}_6]} \] (23i)

Yield 89.25%, Mp. 198-203 °C; IR (KBr) ν 3219 (N-H), 3039 (C-H), 2932 (C-H), 1666 (C=O), 1599 (C=N), 1207-1164 (-P=O--), 952 (P--O--C) cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ 2.37 (18H, CH\(_3\)), 6.96 (12H, H\(_{Ar}\)), 7.75 (24H, H\(_{Ar}\)), 8.71 (12H, H=C=N), 11.00 (6H, CONH); \(^13\)C NMR (DMSO-\(d_6\)) δ 15.13, 120.98, 122.28, 128.60, 135.37, 141.45, 147.61, 150.51, 155.01, 162.94; \(^31\)P NMR (DMSO-\(d_6\)) δ 8.75; MALDI-TOF MS m/z: 1682.2782 (M+Na\(^+\)); Anal. Calcd. For C\(_{84}\)H\(_{72}\)N\(_{21}\)O\(_{12}\)P\(_3\): C, 60.76; H, 4.37; N, 17.71%. Found: C, 60.80; H, 4.33; N, 17.65%.

\[ \text{[N}_3\text{P}_3(-\text{OC}_6\text{H}_4-p-\text{C(CH}_3)_3=\text{N-NH-C(O)-C}_4\text{H}_3\text{O}_6]} \] (23j)

Yield 87.00%, Mp. 210-215 °C; IR (KBr) ν 3247 (N-H), 2924 (C-H), 1651 (C=O), 1594 (C=N), 1207-1165 (-P=O--), 955 (P--O--C) cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ 2.29 (18H, CH\(_3\)), 6.66 (6H, H\(_{Ar}\)), 6.98 (12H, H\(_{Ar}\)), 7.33 (6H, H\(_{Ar}\)), 7.69 (12H, H\(_{Ar}\)), 7.90 (6H, H\(_{Ar}\)), 10.54 (6H, CONH); \(^13\)C NMR (DMSO-\(d_6\)) δ 14.57, 112.37, 116.19, 120.97, 128.38, 135.67, 146.28, 147.61, 150.65, 154.82, 162.08; \(^31\)P NMR (DMSO-\(d_6\)) δ 8.75; MALDI-TOF MS m/z: 1716.1923 (M+Na\(^+\)); Anal. Calcd. For C\(_{78}\)H\(_{66}\)N\(_{15}\)O\(_{18}\)P\(_3\): C, 58.76; H, 4.17; N, 13.18%. Found: C, 58.80; H, 4.14; N, 13.21%.

\[ \text{[N}_3\text{P}_3(-\text{OC}_6\text{H}_4-p-\text{C(CH}_3)_3=\text{N-NH-C(O)-C}_4\text{H}_3\text{S}_6]} \] (23k)

Yield 87.32%, Mp. 160-164 °C; IR (KBr) ν 3252 (N-H), 2932 (C-H), 1642 (C-H), 1607 (C=N), 1205-1165 (-P=O--), 952 (P--O--C) cm\(^{-1}\); \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ 2.21 (18H, CH\(_3\)), 7.06 (12H, H\(_{Ar}\)), 7.13 (6H, H\(_{Ar}\)), 7.76 (18H, H\(_{Ar}\)), 7.99 (6H, H\(_{Ar}\)), 10.91 (6H, CONH); \(^13\)C NMR (DMSO-\(d_6\)) δ 13.83, 120.40, 126.36, 128.09, 130.07, 132.78, 134.79, 135.15, 150.25, 154.12, 161.87; \(^31\)P NMR (DMSO-\(d_6\)) δ 8.77; MALDI-TOF MS m/z: 1712.1052 (M+Na\(^+\)); Anal. Calcd. For C\(_{78}\)H\(_{66}\)N\(_{15}\)O\(_{18}\)P\(_3\)S\(_6\): C, 55.41; H, 3.93; N, 12.43%. Found: C, 55.37; H, 3.98; N, 12.50%.
Synthesis of first generation ketone (24)

A methanolic solution (5 mL) of 4 (0.0605 g, 0.5 mmol) was added dropwise over 1 h to a stirred dichloromethane (50 mL) solution of cyanuric chloride (0.553 g, 3 mmol) and triethylamine (0.418 g, 3 mmol) at 0 °C. The reaction mixture was further stirred for 3 h at 0 °C. The solvent was removed under reduced pressure and dioxane (40 mL) was added and stirred. To this, a solution of p-hydroxyacetophenone (1.021 g, 7.5 mmol) in dioxane (10 mL) and triethylamine (0.708 g, 7.0 mmol) was added and the reaction mixture was stirred at 80 °C for 36 h. The residue was filtered and washed with water (4 x 25 mL) followed by methanol (3 x 15 ml).

Yield 85.52%; IR (KBr) ν 3326 (br, NH), 3101 (C–H Ar), 2925 (C–H Al), 1680 (C=O), 1641 (C=O), 1207-1165 (-P=N-), 954 (P=O–C) cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆) δ 2.58 (s, 36H, CH₃), 3.43 (br s, 12H, NCH₂), 3.79 (br s, 12H, CH₂N), 6.82 (s, 6H, NH), 6.96 (d, J=8.4Hz, 12H, H₄Ar), 7.38 (d, J=8.8Hz, 24H, H₄Ar), 7.81 (d, J=8.4Hz, 12H, H₄Ar), 8.00 (d, J=8.8Hz, 24H, H₄Ar), 8.57 (s, 6H, NH); ¹³C NMR (DMSO-d₆) δ 26.68, 53.63, 120.06, 121.75, 129.09, 129.68, 130.64, 132.26, 151.42, 153.93, 165.53, 167.81, 171.27, 196.75; ³¹P NMR (DMSO-d₆) δ 8.37; Mass 3292; Anal. Calcd. For C₁₆₈H₁₄₄N₃₃O₃₆P₃: C, 61.26; H, 4.41; N, 14.03%. Found: C, 61.31; H, 4.45; N, 14.09%.

General procedure for the synthesis of first generation hydrazones (25a-k)

The compound 19 (0.05 mmol) was added to a solution of hydrazide 16a-k (0.63 mmol) in THF-DMF (50 mL, 9:1) and the reaction mixture was stirred at reflux for 24-36 h. The solvent was removed by evaporation under reduced pressure. The residue was washed with tetrahydrofuran (3 x 5 mL), water (3 x 5 mL) and methanol (3 x 2 mL). The resulting viscous residue was dried in vacuo. The ¹H NMR spectra of 25a-k consisted of broad signals.
[N_3P_3(-OC_6H_4-p-CO-NH-CH_2-CH_2-NH-C_3N_3-{-OC_6H_4-p-C(CH_3)=N-NH-C(O)-C_6H_5}_2)_6] (25a)

Yield 83.14%; IR (KBr) ν 3234 (N-H), 2926 (C-H), 1650 (C=O), 1605 (C=N), 1207-1166 (-P=N-), 951 (P–O–C) cm⁻¹; ¹H NMR (400 MHz, DMSO-d_6) δ 2.38 (36H, CH₃), 3.58 (12H, NCH₂), 3.78 (12H, CH₂N), 6.82 (6H, -NH-C₃N₃), 6.96 (12H, H₃Ar), 7.33 (24H, H₃Ar), 7.51 (24H, H₃Ar), 7.66 (12H, H₃Ar), 7.76 (12H, H₃Ar), 7.82 (24H, H₃Ar), 7.89 (24H, H₃Ar), 8.54 (6H, -CONH-), 10.74 (12H, NH); ¹³C NMR (DMSO-d_6) δ 15.40, 41.16, 53.52, 120.08, 121.41, 125.44, 128.01, 128.23, 128.55, 131.46, 132.60, 133.29, 135.19, 150.54, 152.10, 154.26, 163.85, 167.28, 171.90; ³¹P NMR (DMSO-d_6) δ 8.36; Mass 4709; Anal. Calcd. For C_{252}H_{216}N_{57}O_{36}P_{3}: C, 64.24; H, 4.62; N, 16.94%. Found: C, 64.30; H, 4.59; N, 16.99%.

[N_3P_3(-OC_6H_4-p-CO-NH-CH_2-CH_2-NH-C_3N_3-{-OC_6H_4-p-C(CH_3)=N-NH-C(O)-C_6H_4-p-Br}_2)_6] (25b)

Yield 78.52%; IR (KBr) ν 3230 (N-H), 2924 (C-H), 1650 (C=O), 1599 (C=N), 1206-1167 (-P=N-), 953 (P–O–C) cm⁻¹; ¹H NMR (400 MHz, DMSO-d_6) δ 2.37 (36H, CH₃), 3.56 (12H, NCH₂), 3.79 (12H, CH₂N), 6.81 (6H, -NH-C₃N₃), 6.95 (12H, H₃Ar), 7.33 (24H, H₃Ar), 7.70 (24H, H₃Ar), 7.75 (12H, H₃Ar), 7.81 (24H, H₃Ar), 7.89 (24H, H₃Ar), 8.56 (6H, -CONH-), 10.82 (12H, NH); ¹³C NMR (DMSO-d_6) δ 14.50, 41.16, 53.52, 120.12, 121.32, 125.14, 127.65, 128.28, 129.88, 131.21, 131.89, 132.96, 135.69, 150.62, 154.88, 162.93, 165.40, 167.31, 171.85; ³¹P NMR (DMSO-d_6) δ 8.37; Mass 5644; Anal. Calcd. For C_{252}H_{204}Br_{12}N_{57}O_{36}P_{3}: C, 53.49; H, 3.63; N, 14.11%. Found: C, 53.54; H, 3.68; N, 14.07%.
Chapter 5

\[ \text{[N}_3\text{P}_3(-\text{OC}_6\text{H}_4-p-\text{CO-NH-CH}_2\text{-CH}_2\text{-NH-C}_3\text{N}_3-\{-\text{OC}_6\text{H}_4-p-\text{C(CH}_3)_2\text{=N-NH-C(O)-C}_6\text{H}_4-p-\text{Cl}\}_2)_6} \] (25c)

Yield 80.83%; IR (KBr) ν 3226 (N-H), 2926 (C-H), 1650 (C=O), 1600 (C=N), 1206-1168 (-P=N-), 951 (P–O–C) cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 2.35 (36H, CH\(_3\)), 3.58 (12H, NCH\(_2\)), 3.76 (12H, CH\(_2\)N), 6.84 (6H, -NH-C\(_3\)N\(_3\)-), 6.95 (12H, H\(_{Ar}\)), 7.36 (24H, H\(_{Ar}\)), 7.70 (24H, H\(_{Ar}\)), 7.77 (12H, H\(_{Ar}\)), 7.86 (24H, H\(_{Ar}\)), 7.92 (24H, H\(_{Ar}\)), 8.58 (6H, -CONH-), 10.84 (12H, NH); \(\delta\) 14.55, 41.13, 53.60, 120.15, 121.43, 128.21, 128.31, 129.26, 129.78, 131.10, 131.52, 132.56, 135.80, 150.49, 152.22, 154.87, 161.96, 165.46, 167.27, 171.93; \(^{31}\)P NMR (DMSO-d\(_6\)) \(\delta\) 8.18; Mass 5116; Anal. Calcd. For C\(_{252}\)H\(_{204}\)Cl\(_{12}\)N\(_{57}\)O\(_{36}\)P\(_3\): C, 59.06; H, 4.01; N, 15.58%. Found: C, 59.12; H, 4.08; N, 15.65%.

\[ \text{[N}_3\text{P}_3(-\text{OC}_6\text{H}_4-p-\text{CO-NH-CH}_2\text{-CH}_2\text{-NH-C}_3\text{N}_3-\{-\text{OC}_6\text{H}_4-p-\text{C(CH}_3)_2\text{=N-NH-C(O)-C}_6\text{H}_4-p-\text{F}\}_2)_6} \] (25d)

Yield 76.92%; IR (KBr) ν 3229 (N-H), 2923 (C-H), 1647 (C=O), 1603 (C=N), 1208-1172 (-P=N-), 956 (P–O–C) cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 2.38 (36H, CH\(_3\)), 3.57 (12H, NCH\(_2\)), 3.77 (12H, CH\(_2\)N), 6.83 (6H, -NH-C\(_3\)N\(_3\)-), 6.94 (12H, H\(_{Ar}\)), 7.32 (24H, H\(_{Ar}\)), 7.74 (12H, H\(_{Ar}\)), 7.84 (24H, H\(_{Ar}\)), 7.92 (24H, H\(_{Ar}\)), 7.99 (24H, H\(_{Ar}\)), 8.59 (6H, -CONH-), 11.80 (12H, NH); \(^{13}\)C NMR (DMSO-d\(_6\)) \(\delta\) 14.53, 41.14, 53.53, 120.11, 115.08, 121.38, 127.55, 128.17, 129.76, 130.62, 131.39, 135.49, 152.18, 150.53, 154.73, 162.90, 164.88, 165.49, 167.29, 171.91; \(^{31}\)P NMR (DMSO-d\(_6\)) \(\delta\) 8.31; Mass 4924; Anal. Calcd. For C\(_{252}\)H\(_{204}\)F\(_{12}\)N\(_{57}\)O\(_{36}\)P\(_3\): C, 61.42; H, 4.17; N, 16.20%. Found: C, 61.48; H, 4.22; N, 16.15%.
[N₃P₃(-OC₆H₄-p-CO-NH-CH₂-CH₂-NH-C₃N₃{-OC₆H₄-p-C(CH₃)=N-NH-C(O)-C₆H₄-
p-OH})₂]₆ (25e)
Yield 79.12%; IR (KBr) ν 3405 (br, O–H), 2922 (C-H), 1650 (C=O), 1603 (C=N), 1209-1167 (-P=N-), 955 (P–O–C) cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.36 (36H, CH₃), 3.59 (12H, NCH₂), 3.76 (12H, CH₂N), 6.82-6.87 (30H, Hₐr), 6.96 (12H, Hₐr), 7.31 (24H, Hₐr), 7.75 (24H, Hₐr), 7.75 (12H, Hₐr), 7.85 (24H, Hₐr), 8.56 (6H, -CONH-), 10.09 (12H, OH), 10.55 (12H, NH); ¹³C NMR (DMSO-d₆) δ 14.32, 41.18, 53.58, 114.83, 120.04, 121.38, 127.51, 128.12, 129.49, 130.66, 131.18, 135.96, 150.62, 153.53, 160.43, 161.93, 165.39, 167.34, 171.99; ³¹P NMR (DMSO-d₆) δ 8.24; Mass 4901; Anal. Calcd. For C₂₅₂H₂¹₆N₅₇O₄₈P₃: C, 61.72; H, 4.44; N, 16.28%. Found: C, 61.66; H, 4.40; N, 16.33%.

[N₃P₃(-OC₆H₄-p-CO-NH-CH₂-CH₂-NH-C₃N₃{-OC₆H₄-p-C(CH₃)=N-NH-C(O)-C₆H₄-
p-OCH₃})₂]₆ (25f)
Yield 78.15%; IR (KBr) ν 3229 (N-H), 2926 (C-H), 1644 (C=O), 1603 (C=N), 1206-1169 (-P=N-), 955 (P–O–C) cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆) δ 2.38 (36H, CH₃), 3.58 (12H, NCH₂), 3.77 (12H, CH₂N), 3.85 (36H, OCH₃), 6.83 (6H, -NH-C₃N₃-), 6.97 (12H, Hₐr), 7.03 (24H, Hₐr), 7.33 (24H, Hₐr), 7.72-7.75 (36H, Hₐr), 7.88 (24H, Hₐr), 8.54 (6H, -CONH-), 10.68 (12H, NH); ¹³C NMR (DMSO-d₆) δ 14.36, 41.18, 53.57, 55.34, 113.45, 120.08, 121.68, 125.91, 129.26, 128.22, 129.85, 131.85, 135.19, 152.39, 150.49, 154.87, 161.79, 165.45, 165.40, 167.36, 171.21; ³¹P NMR (DMSO-d₆) δ 8.28; Mass 5069; Anal. Calcd. For C₂₆₄H₂₄₀N₅₇O₄₈P₃: C, 62.52; H, 4.77; N, 15.74%. Found: C, 62.47; H, 4.80; N, 15.80%.
Chapter 5

\[ [\text{N}_3\text{P}_3(\text{-OC}_6\text{H}_4-p\text{-CO-NH-CH}_2\text{-CH}_2\text{-NH-C}_3\text{N}_3\text{-}[\text{-OC}_6\text{H}_4-p\text{-C(CH}_3)_3\text{=}\text{N-NH-C(O)-C}_6\text{H}_4-p\text{-CH}_3])_6] \] (25g)

Yield 83.27\%; IR (KBr) \( \nu \) 3232 (N-H), 2923 (C-H-Al), 1647 (C=O), 1601 (C=N), 1209-1171 (-P=N-), 950 (P–O–C) cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 2.34 (36H, CH\(_3\)), 2.39 (36H, CH\(_3\)), 3.57 (12H, NCH\(_2\)), 3.79 (12H, CH\(_2\)N), 6.80 (6H, -NH-C\(_3\)N\(_3\)-), 6.95 (12H, H\(_{Ad}\)), 7.13 (24H, H\(_{Ad}\)), 7.30 (24H, H\(_{Ad}\)), 7.74 (12H, H\(_{Ad}\)), 7.82 (24H, H\(_{Ad}\)), 7.91 (24H, H\(_{Ad}\)), 8.57 (6H, -CONH-), 10.72 (12H, NH); \(^{13}\)C NMR (DMSO-d\(_6\)) \( \delta \) 14.37, 20.95, 41.21, 53.58, 120.09, 121.34, 127.75, 127.56, 128.13, 128.68, 130.62, 131.65, 135.92, 141.53, 150.68, 152.10, 154.23, 165.45, 167.34, 171.89; \(^{31}\)P NMR (DMSO-d\(_6\)) \( \delta \) 8.19; Mass 4877; Anal. Calcd. For C\(_{264}\)H\(_{240}\)N\(_{57}\)O\(_{36}\)P\(_3\): C, 64.98; H, 4.96; N, 16.36%. Found: C, 65.03; H, 4.91; N, 16.41%.

\[ [\text{N}_3\text{P}_3(\text{-OC}_6\text{H}_4-p\text{-CO-NH-CH}_2\text{-CH}_2\text{-NH-C}_3\text{N}_3\text{-}[\text{-OC}_6\text{H}_4-p\text{-C(CH}_3)_3\text{=}\text{N-NH-C(O)-C}_6\text{H}_4-p\text{-NO}_2])_6] \] (25h)

Yield 75.67\%; IR (KBr) \( \nu \) 3223 (N-H), 2928 (C-H-Al), 1658 (C=O), 1604 (C=N), 1204-1171 (-P=N-), 954 (P–O–C) cm\(^{-1}\); \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \( \delta \) 2.36 (36H, CH\(_3\)), 3.57 (12H, NCH\(_2\)), 3.75 (12H, CH\(_2\)N), 6.82 (6H, -NH-C\(_3\)N\(_3\)-), 6.96 (12H, H\(_{Ad}\)), 7.32 (24H, H\(_{Ad}\)), 7.76 (12H, H\(_{Ad}\)), 7.89 (24H, H\(_{Ad}\)), 8.11 (24H, H\(_{Ad}\)), 8.32 (24H, H\(_{Ad}\)), 8.55 (6H, -CONH-), 10.98 (12H, NH); \(^{13}\)C NMR (DMSO-d\(_6\)) \( \delta \) 14.74, 53.56, 120.09, 121.40, 123.29, 128.18, 128.37, 129.78, 131.57, 135.62, 139.70, 148.92, 150.58, 152.34, 154.65, 162.36, 165.39, 167.33, 171.84; \(^{31}\)P NMR (DMSO-d\(_6\)) \( \delta \) 8.23; Mass 5248; Anal. Calcd. For C\(_{252}\)H\(_{240}\)N\(_{69}\)O\(_{60}\)P\(_3\): Calcd: C, 57.63; H, 3.92; N, 18.40%. Found: C, 57.60; H, 3.87; N, 18.47%.
\[ \text{[N}_3\text{P}_3(-\text{OC}_6\text{H}_4-p-\text{CO-NH-CH}_2\text{-CH}_2\text{-NH-C}_3\text{N}_3\text{-}[\text{-OC}_6\text{H}_4-p-\text{C(CH}_3)\text{]}=\text{N-NH-C(O)}]-} \]

\[ \text{C}_5\text{H}_4\text{(N)}]_2\text{a} \] (25i)

Yield 77.32%; IR (KBr) \( \nu \) 3228 (N-H), 2926 (C-H), 1661 (C=O), 1603 (C=N), 1205-1167 (-P=N-), 954 (P-O-C) cm\(^{-1}\); \(^1\text{H}\) NMR (400 MHz, DMSO-\(d_6\)) \( \delta \) 2.36 (36H, CH\(_3\)), 3.56 (12H, NCH\(_2\)), 3.75 (12H, CH\(_2\)N), 6.81 (6H, -NH-C\(_3\)N\(_3\)), 6.98 (12H, H\(_{Ar}\)), 7.15 (24H, H\(_{Ar}\)), 7.55 (24H, H\(_{Ar}\)), 7.66 (24H, H\(_{Ar}\)), 7.74 (12H, H\(_{Ar}\)), 8.59 (6H, -CONH-), 8.68 (24H, H\(_{Ar}\)), 10.84 (12H, NH); \(^{13}\text{C}\) NMR (DMSO-\(d_6\)) \( \delta \) 14.59, 41.20, 53.53, 120.14, 121.48, 122.16, 128.22, 129.75, 131.44, 131.58, 140.86, 150.66, 151.03, 151.75, 154.23, 162.27, 165.49, 167.19, 171.67; \(^{31}\text{P}\) NMR (DMSO-\(d_6\)) \( \delta \) 8.28; Mass 4721; Anal. Calcd. For C\(_{240}\)H\(_{204}\)N\(_6\)O\(_{36}\)P\(_3\): C, 61.03; H, 4.35; N, 20.46% Found: C, 61.09; H, 4.40; N, 20.51%.

\[ \text{[N}_3\text{P}_3(-\text{OC}_6\text{H}_4-p-\text{CO-NH-CH}_2\text{-CH}_2\text{-NH-C}_3\text{N}_3\text{-}[\text{-OC}_6\text{H}_4-p-\text{C(CH}_3)\text{]}=\text{N-NH-C(O)}]-} \]

\[ \text{C}_4\text{H}_5\text{(O)}]_2\text{a} \] (25j)

Yield 77.46%; IR (KBr) \( \nu \) 3266 (N-H), 2928 (C-H), 1655 (C=O), 1602 (C=N), 1205-1171 (-P=N-), 954 (P-O-C) cm\(^{-1}\); \(^1\text{H}\) NMR (400 MHz, DMSO-\(d_6\)) \( \delta \) 2.37 (36H, CH\(_3\)), 3.59 (12H, NCH\(_2\)), 3.75 (12H, CH\(_2\)N), 6.75 (12H, H\(_{Ar}\)), 6.82 (6H, -NH-C\(_3\)N\(_3\)), 6.96 (12H, H\(_{Ar}\)), 7.13 (24H, H\(_{Ar}\)), 7.40 (12H, H\(_{Ar}\)), 7.61 (24H, H\(_{Ar}\)), 7.72 (12H, H\(_{Ar}\)), 8.00 (12H, H\(_{Ar}\)), 8.54 (6H, -CONH-), 10.85 (12H, NH); \(^{13}\text{C}\) NMR (DMSO-\(d_6\)) \( \delta \) 14.65, 41.18, 53.59, 120.12, 113.12, 115.38, 121.86, 128.29, 128.98, 131.50, 132.24, 145.87, 147.28, 150.52, 151.78, 154.42, 161.15 165.48, 167.35, 171.75; \(^{31}\text{P}\) NMR (DMSO-\(d_6\)) \( \delta \) 8.33; Mass 4588; Anal. Calcd. For C\(_{228}\)H\(_{192}\)N\(_{57}\)O\(_{48}\)P\(_3\): C, 59.64; H, 4.22; N, 17.39%. Found: C, 59.59; H, 4.19; N, 17.44%.
[N₃P₃(-OC₆H₄-p-CO-NH₂CH₂CH₂-NH-C₃N₃₋₁-OC₆H₄-p-C(CH₃)=N-NH-C(O)-C₄H₃S]₂₁ε \) (25k)

Yield 76.54%; IR (KBr) ν 3238 (N-H), 2927 (C-H), 1647 (C=O), 1604 (C=N), 1207-1166 (-P=N-), 954 (P–O–C) cm⁻¹; \(^{1}H\) NMR (400 MHz, DMSO-d₆) δ 2.35 (36H, CH₃), 3.57 (12H, NCH₂), 3.78 (12H, CH₂N), 6.84 (6H, -NH-C₃N₃₋₁), 6.98 (12H, H₆), 7.09 (24H, H₆), 7.30 (12H, H₆), 7.68 (24H, H₆), 7.75 (12H, H₆), 8.06 (12H, H₆), 8.19 (12H, H₆), 8.57 (6H, -CONH-), 10.86 (12H, NH); \(^{13}C\) NMR (DMSO-d₆) δ 14.51, 41.21, 53.55, 120.08, 121.61, 127.06, 128.21, 128.61, 129.20, 130.68, 131.76, 133.21, 135.08, 150.57, 151.26, 153.11, 161.91 165.48, 167.32, 171.82; \(^{31}P\) NMR (DMSO-d₆) δ 8.26; Mass 4780; Anal. Calcd. For C\(_{228}\)H\(_{192}\)N\(_{57}\)O\(_{36}\)P\(_{3}\)S\(_{12}\): C, 57.24; H, 4.05; N, 16.69%. Found: C, 57.29; H, 4.10; N, 16.62%. 

References


