Supporting Information for

Pd-initiated Controlled Polymerization of Diazoacetates with a Bulky Substituent: Synthesis of Well-defined Homopolymers and Block Copolymers with Narrow Molecular Weight Distribution from Cyclophosphazene-containing Diazoacetates

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1. Experimental Section

Materials. Tetrahydrofuran (THF) was dried over Na/K alloy and distilled before use. $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (Aldrich; 98%) and $NaBPh_4$ (Kanto Chemical; >99.5%) were used as received. Ethyl diazoacetate[1] (EDA; 2.5 M solution in CH_2Cl_2) and benzyl diazoacetate[2] (BDA) were prepared according to the literature. ***Caution!*** Extra care must be taken for preparation and handling of the diazoacetates because of their potential explosiveness.

Characterization. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were measured by means of size-exclusion chromatography (SEC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using THF as eluent at a flow rate of 1.0 mL/min at 40 °C, calibrated with 6 poly(MMA) standards (Shodex M-75; M_p = 2400-212000, M_w/M_n < 1.1) and dibutyl sebacate (molecular weight = 314.5). The columns used for the SEC analyses was a combination of Styragel HR4 and HR2 (Waters; exclusion limit molecular weight = 600K and 20K for polystyrene, respectively; column size = 300 mm × 7.8 mm i.d.; average particle size = 5 μm). Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H and a JAIGEL-2H (Japan Analytical Industry; exclusion limit molecular weight = 70K and 5K for polystyrene, respectively; column size = 600 mm × 20 mm i.d.) using $CHCl_3$ as eluent at a flow rate of 3.8 mL/min at room temperature. ^1H (400 MHz), ^{31}P (162 MHz), and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature (monomers) or at 50 °C (polymers). MALDI-TOF-MS analyses were performed on a JMS-S3000 (linear mode) using dithranol as a matrix and sodium trifluoroacetate as an ion source. Polyethylene oxide (M_W = 2000) was used as an external standard to calibrate the mass scale. Thermogravimetric analysis was performed with Exstar TG/DTA6200 (Seiko Instruments). The experiments were carried out with about 5 mg of a sample under a nitrogen atmosphere at a heating rate of 20 °C/min. Elemental analyses were performed on a YANAKO CHN Corder MT-5.

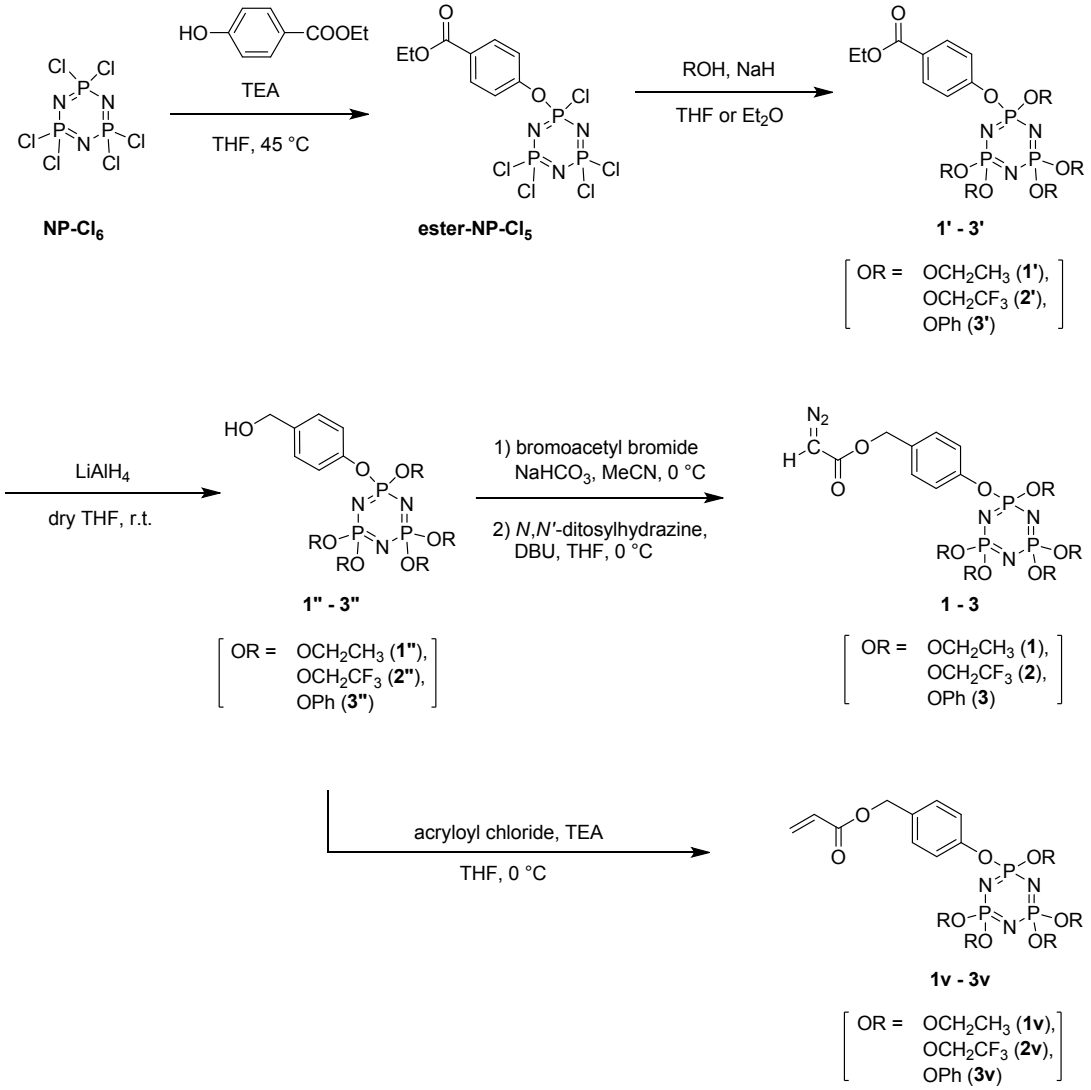
Polymerization procedure. As a representative example, the procedures for the polymerization of **1** (entry 4 in Table 1) and **1v** are described as follows.

Pd-initiated polymerization of 1. Under a nitrogen atmosphere, a THF (1.0 ml) solution of $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.34 mg, 9.2×10^{-4} mmol) was placed in a Schlenk tube and was cooled to −78 °C. $NaBPh_4$ (0.76 mg, 2.2×10^{-3} mmol) was added to the mixture and the resulting mixture was stirred at the temperature for 10 min. After a THF (1.0 ml) solution of **1** (0.101 g. 0.183 mmol) was added using a syringe at −78 °C, the temperature of the mixture was raised to −20 °C and it was stirred for 15 h at the temperature. After the volatiles were removed under reduced pressure at −20 °C, 1N HCl/methanol and $CHCl_3$ were added to the residue. The resulting solution was extracted with $CHCl_3$ and the combined organic layer was washed with 1N HCl aqueous solution and water, dried over Na_2SO_4, and concentrated under reduced pressure.

Radical polymerization of 1v. A mixture of **1v** (0.081 g, 0.15 mmol) and 1,1'-azobis(cyclohexanecarbonitrile) (0.98 mg, 4.0×10^{-3} mmol) in toluene was placed in a schlenk tube, and it was degassed via three cycles of fleeze-pump-thaw procedure. The mixture was heated to 100 °C and stirred at the temperature for 1.5 h. After it was cooled to room temperature, volatiles were removed under reduced pressure. The crude product was purified by using recycling SEC.

Monomer synthesis. Cyclophosphazene-containing diazoacetates (**1-3**) and acrylates (**1v-3v**) were prepared according to the procedure shown in Scheme **S1**.

Scheme S1. Synthesis of cyclophosphazene-containing diazoacetates (**1-3**) and acrylates (**1v-3v**)



Synthesis of ester-NP-Cl$_5$. A THF (100 ml) solution of 4-hydroxybenzoic acid ethyl ester (4.80 g, 29.0 mmol) and triethylamine (8.80 g, 87.0 mmol) was added dropwise into a THF (80 ml) solution of hexachlorotriphosphazene (**NP-Cl$_6$**; 10.0 g, 28.9 mmol) at 0 °C. The mixture was stirred at 40 °C for 12 h, filtered, and evaporated. The crude product was washed with hexane and purified by a column chromatography on silica gel using ethyl acetate/hexane (v/v = 1/3) as eluent to give **ester-NP-Cl$_5$** (yield: 47%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.11 (d, J = 8.4 Hz, 2H, Ar-*H*), 7.33 (d, J = 8.6, 2H, Ar-*H*), 4.39 (q, J = 7.2 Hz, 2H, —$CO_2CH_2CH_3$), 1.42 (t, J = 7.2 Hz, 3H, —$CO_2CH_2CH_3$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 22.6 (d, J = 62.5 Hz, 2P), 12.1 (t, 61.9 Hz, 1P).

Synthesis of 1'. A THF (2.5 ml) solution of ethanol (2.5 ml, 43 mmol) was added dropwise into a THF (20 ml) solution of NaH (1.00 g, 41.7 mmol) at 0 °C, and the mixture was heated to room temperature. A THF (10 ml) solution of **ester-NP-Cl$_5$** (2.00 g, 4.20 mmol) was added into the mixture and stirred at 50 °C for 5 h. A hydrochloric acid was added to neutralize the solution. The resulting solution was then extracted with $CHCl_3$ and the combined organic layer was washed with water, and concentrated under reduced pressure. The crude product was purified by a column chromatography on silica gel using ethyl acetate/hexane (v/v = 1/3) as eluent to give **1'** (yield: 43%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.00 (d, J = 8.8 Hz, 2H, Ar-*H*), 7.32 (d, J = 8.4 Hz, 2H, Ar-*H*), 4.36 (q, J = 7.2 Hz, 2H, —$CO_2CH_2CH_3$), 4.19-4.11 (m, 2H, —OCH_2CH_3), 4.05-3.96 (m, 2H × 2, —OCH_2CH_3), 3.87-3.71 (m, 2H × 2, —OCH_2CH_3), 1.38 (t, J = 7.2 Hz, 3H, —$CO_2CH_2CH_3$), 1.38-1.28 (m, 3H × 3, —OCH_2CH_3), 1.19 (t, J = 7.2 Hz, 3H × 2, —OCH_2CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.2-16.5 (m, 2P), 14.6-13.5 (m, 1P).

Synthesis of 2'. This compound was prepared by a procedure similar to that employed for **1'** except for the use of 2,2,2-trifluoroethanol instead of ethanol. Yield: 96%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 8.06 (d, 2H, J = 8.8 Hz, Ar-*H*), 7.25 (d, 2H, Ar-*H*), 4.46-4.22 (m, 2H × 3, —OCH_2CF_3; 2H, —$CO_2CH_2CH_3$), 4.05-3.88 (m, 2H × 2, —OCH_2CF_3), 1.39 (t, J = 7.2 Hz, 3H, —$CO_2CH_2CH_3$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.2-16.4 (m, 2P), 13.5-12.3 (m, 1P).

Synthesis of 3'. This compound was prepared by a procedure similar to that employed for **1'** except for the use of phenol instead of ethanol. Yield: 73%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.83 (d, 2H, Ar-*H*), 7.21-7.07 (m, 15H, Ar-*H*), 6.97-6.87 (m, 12H, Ar-*H*), 4.37 (q, J = 7.2 Hz, 2H, —$CO_2CH_2CH_3$), 1.40 (t, J = 7.2 Hz, 3H, —$CO_2CH_2CH_3$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 8.8-8.6 (m, 3P).

Synthesis of 1". 1' (0.955 g, 1.80 mmol) was dissolved in THF (10 ml) and cooled to 0 °C. A suspension of THF (10 ml) and $LiAlH_4$ (0.120 g, 3.20 mmol) was added dropwise to the solution, and the mixture was stirred at room temperature for 5 h. Then, the mixture was cooled to 0 °C again. Methanol, water, and hydrochloric acid were added to the mixture. The resulting solution was then extracted with $CHCl_3$ and the combined organic layer was washed with water, and concentrated under reduced pressure to give **1'** (93%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.32-7.22 (m, 4H, Ar-*H*), 4.64 (s, 2H, —$OPhCH_2OH$), 4.20-4.10 (m, 2H, —OCH_2CH_3), 4.06-3.94 (m, 2H × 2, —OCH_2CH_3), 3.85-3.67 (m, 2H × 2, —OCH_2CH_3), 1.38-1.27 (3H × 3, —OCH_2CH_3), 1.22-1.15 (3H × 2, —OCH_2CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.4-16.7 (m, 2P), 15.0-13.8 (m, 1P).

Synthesis of 2". This compound was prepared by a procedure similar to that employed for **1"** except for the use of **2'** instead of **1'**. Yield: 94%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.36 (d, J = 8.0 Hz, 2H, Ar-*H*), 7.19 (d, J = 7.2 Hz, 2H, Ar-*H*), 4.67 (s, 2H, —$OPhCH_2OH$), 4.47-4.36 (m, 2H, —OCH_2CF_3), 4.34-4.20 (m, 2H × 2, —OCH_2CF_3), 3.98-3.80 (m, 2H × 2, —OCH_2CF_3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.4-16.6 (m, 2P), 14.1-12.9 (m, 1P).

Synthesis of 3". This compound was prepared by a procedure similar to that employed for **1"** except for the use of **3'** instead of **1'**. Yield: 98%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.22-7.07 (m, 17H, Ar-*H*), 6.98-6.86 (m, 12H, Ar-*H*), 4.62 (s, 2H, —$OPhCH_2OH$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 9.0-8.6 (m, 3P).

Synthesis of 1. This compound was prepared according to the general procedure reported by Fukuyama and co-workers.[2] $NaHCO_3$ (0.395 g, 4.74 mmol) and **1"** (0.766 g, 1.58 mmol) were dissolved in acetonitrile (8 ml) and the solution was cooled to 0 °C. Bromoacetyl bromide (0.21 ml, 2.7 mmol) was added dropwise to the solution. After stirring 10 min at the temperature, the reaction mixture was quenched with water and extracted with $CHCl_3$. The collected organic layer was washed with water, dried over

Na_2SO_4, and concentrated under reduced pressure. The residue obtained and *N,N'*-ditosylhydrazine (1.08 g, 3.16 mmol) were dissolved in THF (8 mL) and cooled to 0 °C. 1,8-Diazabicyclo[5,4,0]undec-7-ene (1.2 mL, 8.0 mmol) was added and stirred at the temperature for 10 min. The reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$ and extracted with diethyl ether. The collected organic layer was washed with brine and dried over $MgSO_4$. The solid obtained after removal of volatiles under reduced pressure was purified by using recycling SEC to give **1** (yield = 79%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.31-7.23 (m, 4H, Ar-*H*), 5.14 (s, 2H, —CO_2CH_2PhO—), 4.76 (s, 1H, N_2=C*H*—), 4.19-4.11 (m, 2H, —OC*H*$_2$CH$_3$), 4.05-3.96 (m, 2H × 2, —OC*H*$_2$CH$_3$), 3.83-3.67 (m, 2H × 2, —OC*H*$_2$CH$_3$), 1.38-1.28 (3H × 3, —OCH$_2$C*H*$_3$), 1.21-1.15 (m, 3H × 2, —OCH$_2$C*H*$_3$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.3-16.6 (m, 2P), 15.0-13.8 (m, 1P); ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 166.4 (—*C*O$_2$—), 151.3 (Ar), 132.2 (Ar), 129.3 (Ar), 121.4 (Ar), 65.8 (—CO$_2$*C*H$_2$PhO—), 62.4 (—O*C*H$_2$CH$_3$), 61.7 (—O*C*H$_2$CH$_3$), 46.1 (N_2=*C*H—), 15.9 (—OCH$_2$*C*H$_3$). Anal. Calcd for $C_{19}H_{32}N_5O_8P_3$: C, 41.38; H, 5.86; N, 12.70. Found: C, 41.38; H, 5.85; N, 13.10.

Synthesis of 2. This compound was prepared by a procedure similar to that employed for **1** except for the use of **2"** instead of **1"**. Yield: 48%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.40-7.32 (d, 2H, J = 8.0 Hz, Ar-*H*), 7.23-7.15 (d, 2H, J = 7.2 Hz, Ar-*H*), 5.15 (s, 2H, —CO_2CH_2PhO—), 4.77 (s, 1H, N_2=C*H*—), 4.47-4.36 (m, 2H, —OC*H*$_2$CF$_3$), 4.30-4.20 (m, 2H × 2, —OC*H*$_2$CF$_3$), 3.98-3.80 (m, 2H × 2, —OC*H*$_2$CF$_3$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.3-16.6 (m, 2P), 14.0-12.8 (m, 1P). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 166.6 (—*C*O$_2$—), 149.6 (Ar), 134.4 (Ar), 129.9 (Ar), 122.4 (q, $J_{C\text{-}F}$ = 273 Hz, —OCH$_2$*C*F$_3$), 121.4 (Ar), 65.4 (—CO$_2$*C*H$_2$PhO—), 62.9 (m, —O*C*H$_2$CF$_3$), 46.2 (N_2=*C*H—). Anal. Calcd for $C_{19}H_{17}F_{15}N_5O_8P_3$: C, 27.79; H, 2.09; N, 8.53. Found: C, 27.98; H, 2.36; N, 9.08.

Synthesis of 3. This compound was prepared by a procedure similar to that employed for **1** except for the use of **3"** instead of **1"**. Yield: 69%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.21-7.09 (m, 17H, Ar-*H*), 6.98-6.87 (m, 12H, Ar-*H*), 5.13 (s, 2H, —CO_2CH_2PhO—), 4.78 (s, 1H, N_2=C*H*—). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 8.9-8.7 (m, 3P). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 166.6 (—*C*O$_2$—), 150.6 (Ar), 132.4 (Ar), 129.6 (Ar), 129.4 (Ar), 124.9 (Ar), 121.2 (Ar), 121.0 (Ar), 65.8 (—CO$_2$*C*H$_2$PhO—), 46.3 (N_2=*C*H—). Anal. Calcd for $C_{39}H_{32}N_5O_8P_3$: C, 59.17; H, 4.07; N, 8.85. Found: C, 58.82; H, 4.23; N, 9.15.

Synthesis of 1v. Triethylamine (0.15 ml, 1.1 mmol) and **1"** (0.300 g, 0.620 mmol) were dissolved in THF (10 ml) and the solution was cooled to 0 °C. Acryloyl chloride (0.10 ml, 1.2 mmol) was added dropwise to the solution. After stirring 1 h at the temperature, the reaction mixture was filtered and evaporated. The crude product was purified by using recycling SEC to give **1v** (yield = 68%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.34-7.24 (m, 4H, Ar-*H*), 6.42 (d, J = 17 Hz, 1H, C*H*$_2$=CH—), 6.13 (dd, J = 10 Hz, 17 Hz, 1H, CH$_2$=C*H*—), 5.84 (d, J = 10 Hz, 1H, C*H*$_2$=CH—), 5.14 (s, 2H, —CO_2CH_2PhO—), 4.19-4.11 (m, 2H, —OC*H*$_2$CH$_3$), 4.05-3.96 (m, 2H × 2, —OC*H*$_2$CH$_3$), 3.83-3.67 (m, 2H × 2, —OC*H*$_2$CH$_3$), 1.38-1.28 (m, 3H × 3, —OCH$_2$C*H*$_3$), 1.21-1.15 (m, 3H × 2, —OCH$_2$C*H*$_3$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.4-16.7 (m, 2P), 15.0-13.8 (m, 1P). Anal. Calcd for $C_{20}H_{34}N_3O_8P_3$: C, 44.70; H, 6.38; N, 7.82. Found: C, 45.09; H, 6.57; N, 7.38.

Synthesis of 2v. This compound was prepared by a procedure similar to that employed for **1v** except for the use of **2"** instead of **1"**. Yield: 31%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.38 (d, 2H, J = 8.4 Hz, Ar-*H*), 7.20 (d, 2H, J = 8.8 Hz, Ar-*H*), 6.42 (d, J = 17 Hz, 1H, C*H*$_2$=CH—), 6.13 (dd, J = 10 Hz, 17 Hz, 1H, CH$_2$=C*H*—), 5.84 (d, J = 10 Hz, 1H, C*H*$_2$=CH—), 5.15 (s, 2H, —CO_2CH_2PhO—), 4.47-4.36 (m, 2H, —OC*H*$_2$CF$_3$), 4.32-4.21 (m, 2H × 2, —OC*H*$_2$CF$_3$), 3.98-3.80 (m, 2H × 2, —OC*H*$_2$CF$_3$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 17.4-16.6 (m, 2P), 14.1-12.8 (m, 1P). Anal. Calcd for $C_{20}H_{19}F_{15}N_3O_8P_3$: C, 29.76; H,

2.37; N, 5.21. Found: C, 30.13; H, 2.80; N, 6.36.

Synthesis of 3v. This compound was prepared by a procedure similar to that employed for **1** except for the use of **3"** instead of **1"**. Yield: 74%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.24-7.08 (m, 17H, Ar-*H*), 6.99-6.86 (m, 12H, Ar-*H*), 6.42 (d, J = 17 Hz, 1H, CH_2=CH—), 6.13 (dd, J = 10 Hz, 17 Hz, 1H, CH_2=C*H*—), 5.84 (d, J = 10 Hz, 1H, CH_2=CH—), 5.13 (s, 2H, —CO_2CH_2PhO—). ^{31}P NMR ($CDCl_3$, 162 MHz), δ (ppm): 8.9-8.7 (m, 3P). Anal. Calcd for $C_{40}H_{34}N_3O_8P_3$: C, 59.17; H, 4.07; N, 8.85. Found: C, 58.82; H, 4.23; N, 9.15.

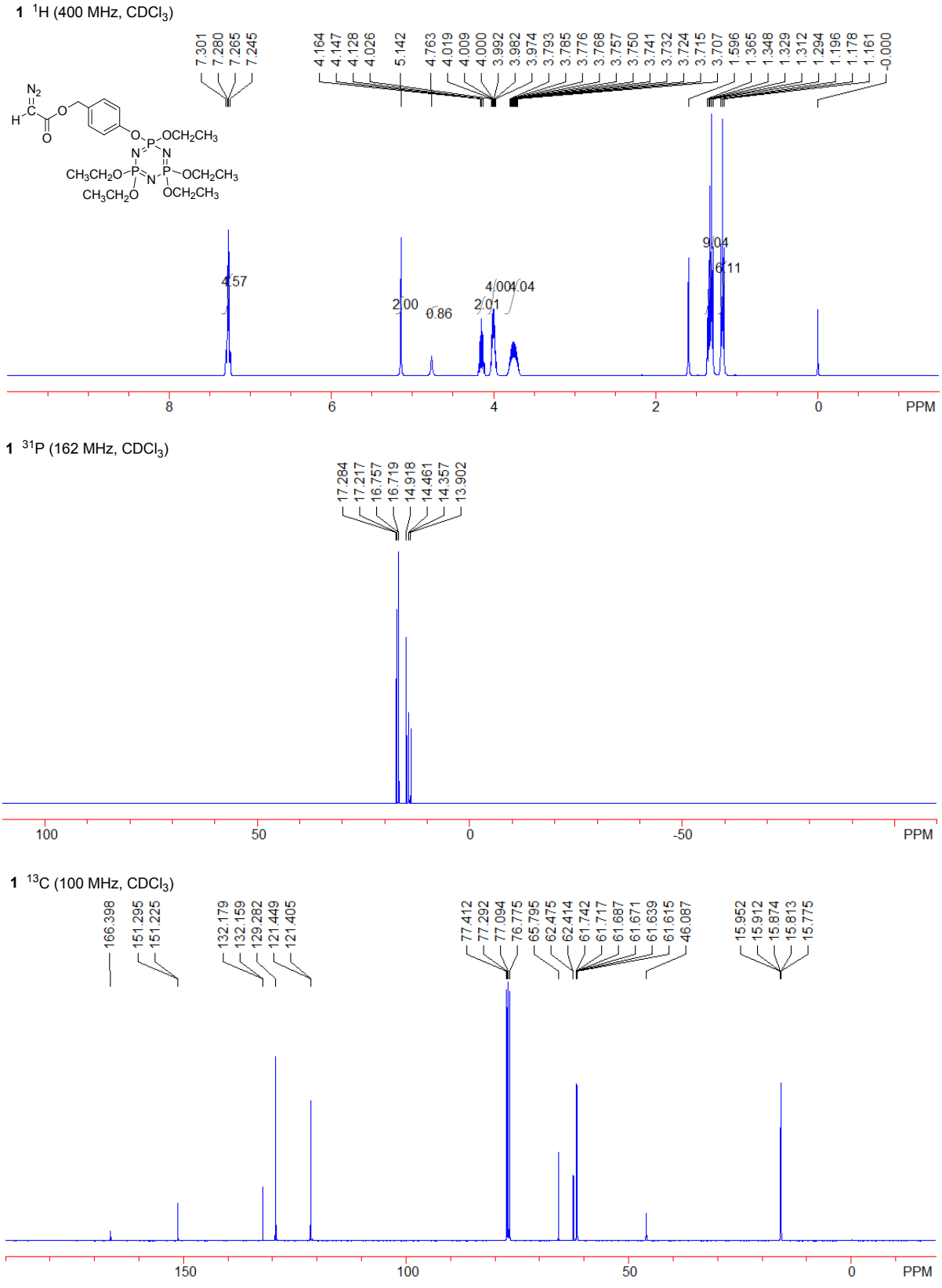


Figure S1. ^{1}H, ^{31}P, and ^{13}C NMR spectra of **1**.

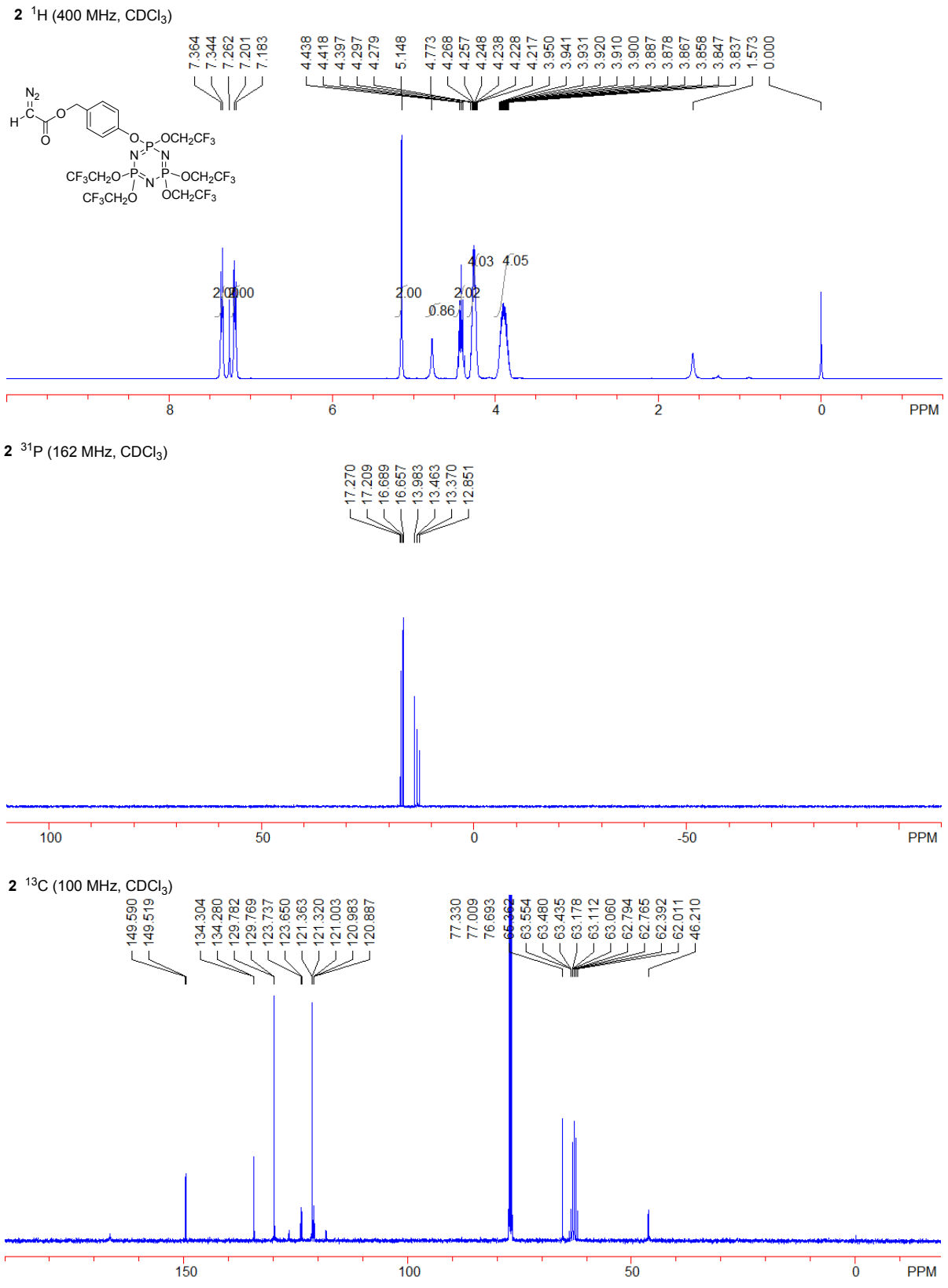
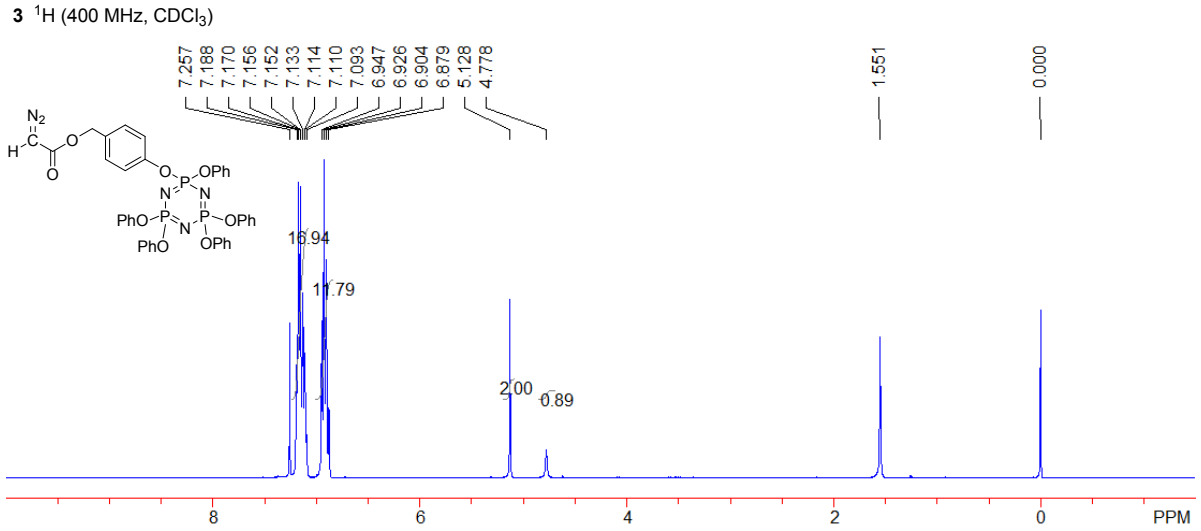
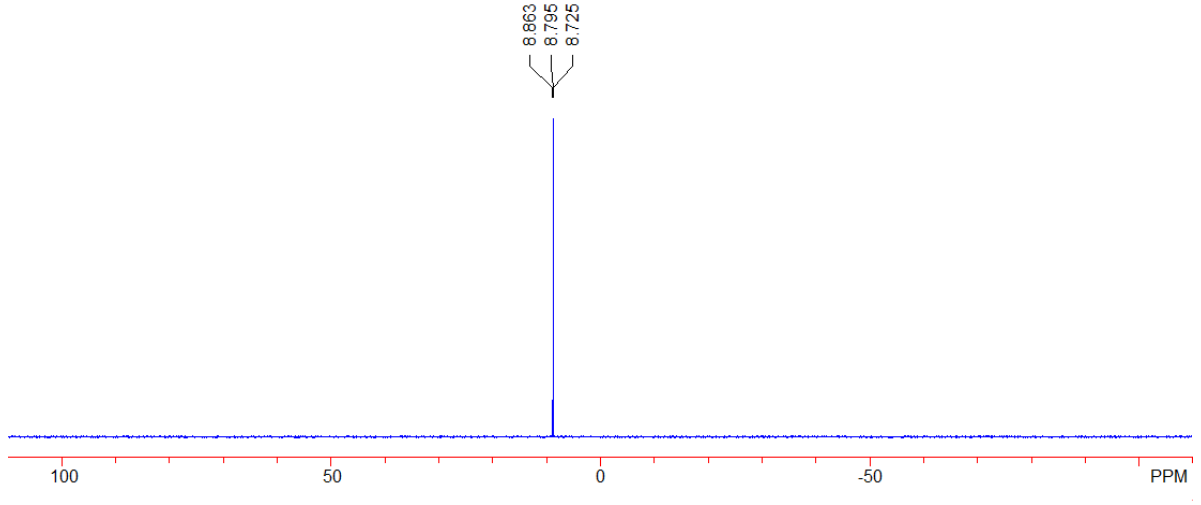


Figure S2. ^{1}H, ^{31}P, and ^{13}C NMR spectra of **2**.





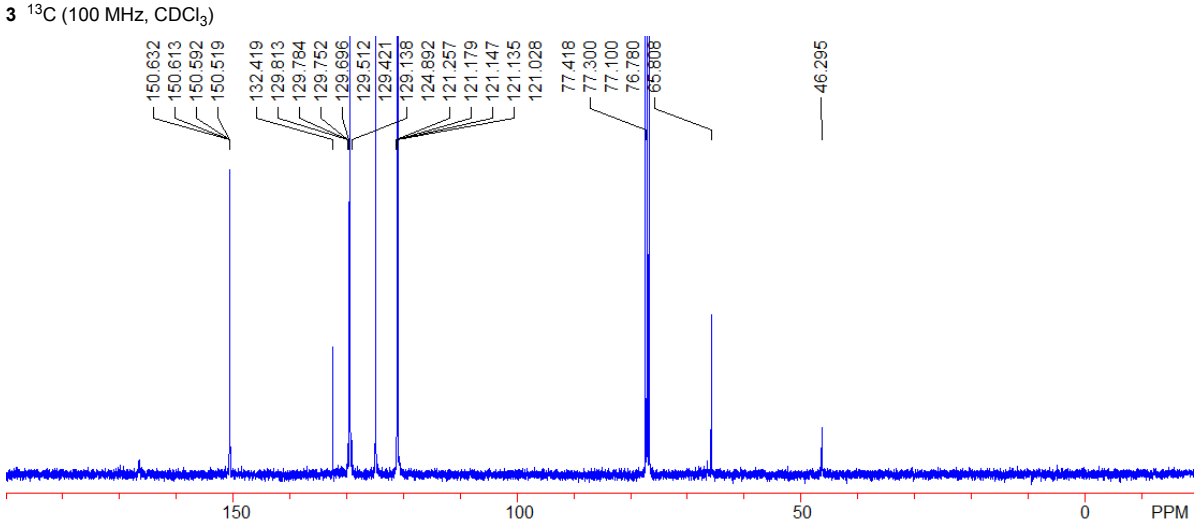


Figure S3. ^{1}H, ^{31}P, and ^{13}C NMR spectra of **3**.

2. Supporting Data and Discussion

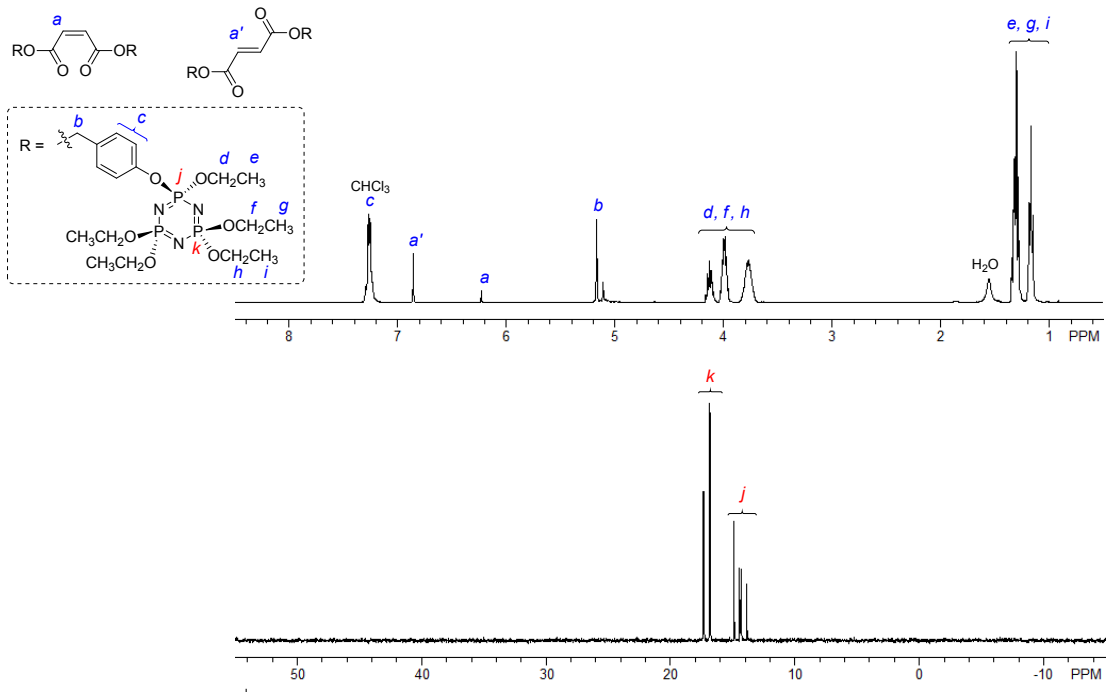


Figure S4. ^{1}H (upper) and ^{31}P (lower) NMR spectra of the dimer obtained from **1** recorded in $CDCl_3$.

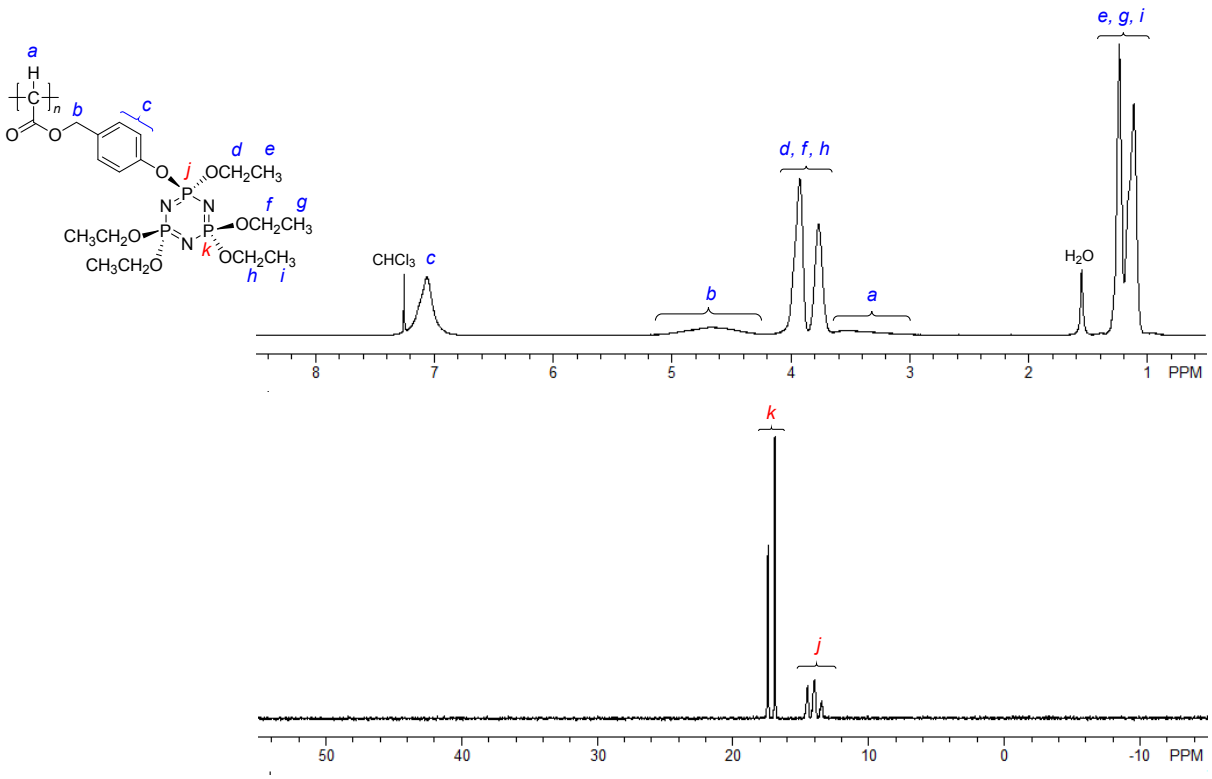


Figure S5. ^{1}H (upper) and ^{31}P (lower) NMR spectra of the polymer obtained from **1** (Table 1, entry 4) recorded in $CDCl_3$.

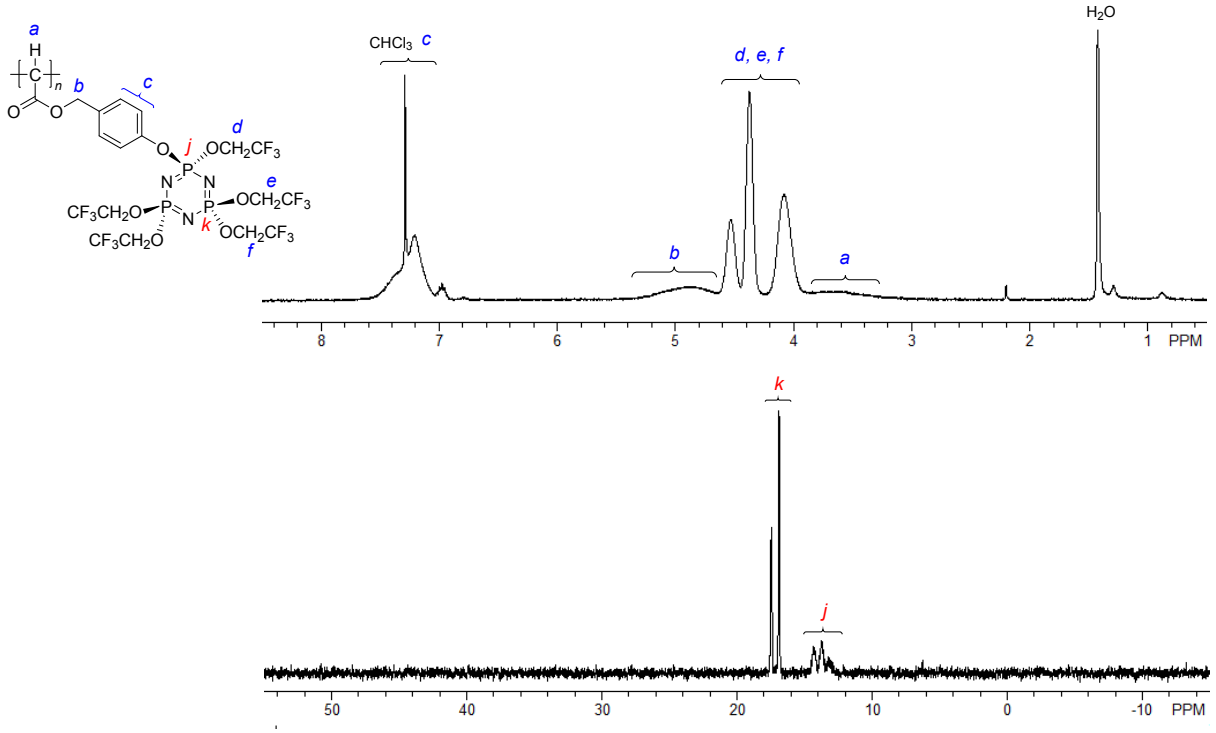


Figure S6. ^{1}H (upper) and ^{31}P (lower) NMR spectra of the polymer obtained from **2** (Table 1, entry 6) recorded in $CDCl_3$/hexafluorobenzene.

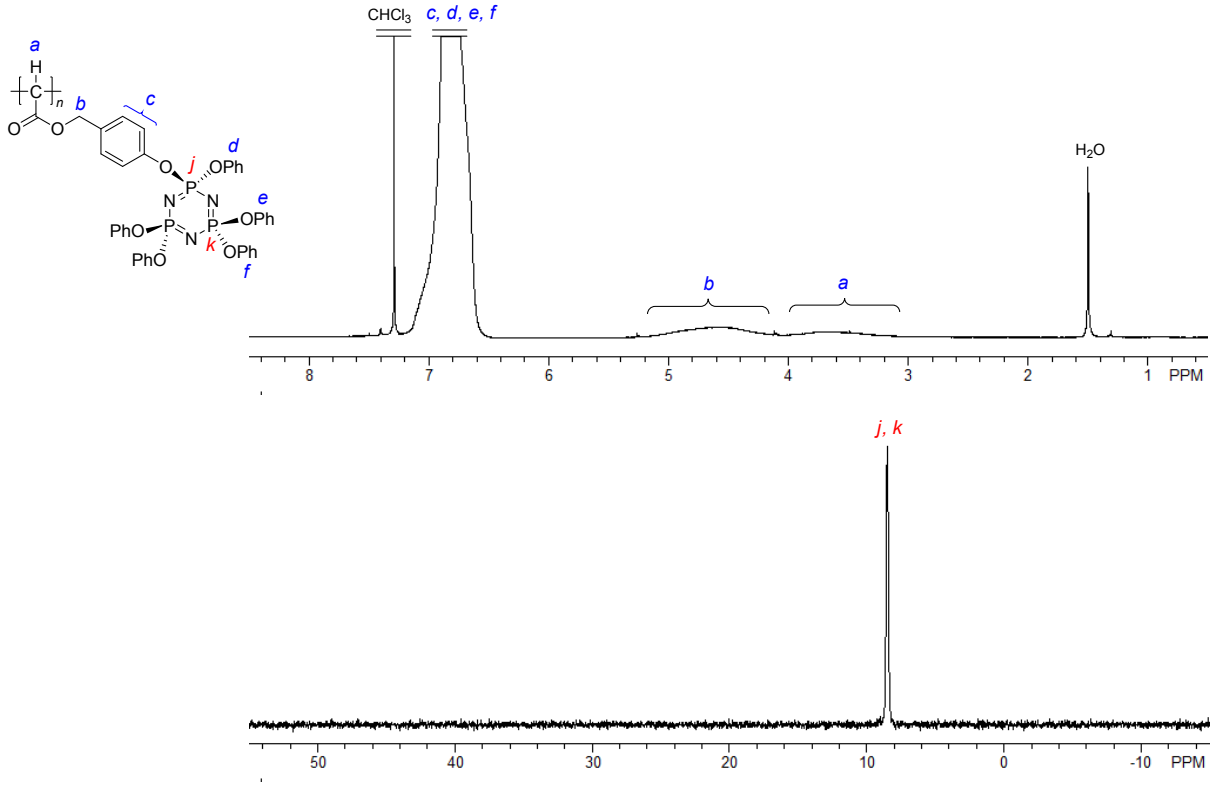


Figure S7. ^{1}H (upper) and ^{31}P (lower) NMR spectra of the polymer obtained from **3** (Table 1, entry 7) recorded in $CDCl_3$.

Table S1. Polymerization of EDA and BDA [a]

entry	monomer	yield (%) [c]	M_n [d]	M_w/M_n [d]
1[b]	EDA	60	4800	1.59
2	BDA	67	10300	1.50

[a] [EDA] = 0.36 M or [BDA] = 0.50 M, [EDA]/[Pd] or [BDA]/[Pd] = 100, [$NaBPh_4$]/[Pd] = 1.2, in THF for 13 h. [b] In the presence of hexafluoroethyltricyclophosphazene (0.36 M). [c] Determined by gravimetry after purification with preparative SEC. [d] Determined by SEC (PMMA standards).

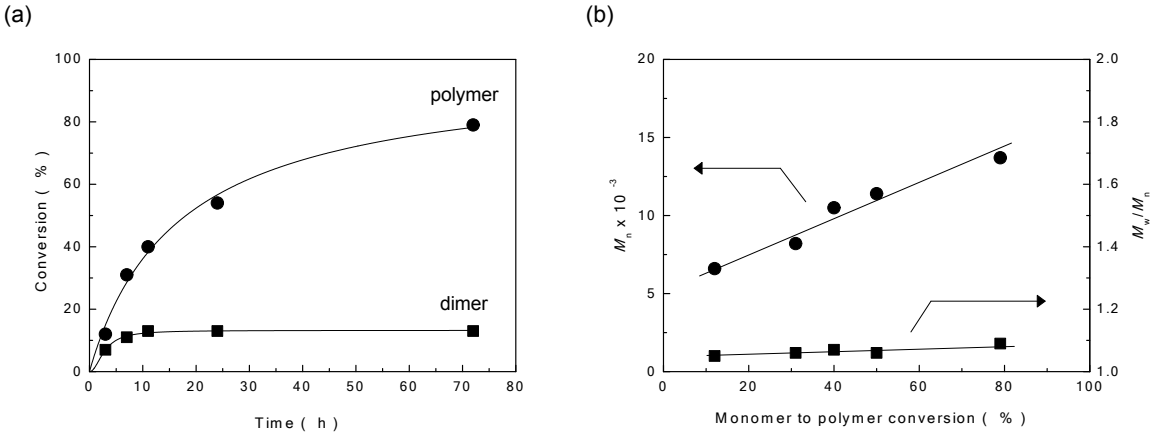


Figure S8. (a) Time-conversion curves (circles: monomer to polymer conversion, squares: monomer to dimer conversion) and (b) M_n (circles) and M_w/M_n (squares) for the polymerization of **3** {[**3**] = 0.13 M, [**3**]/[Pd] = 100, [$NaBPh_4$]/[Pd] = 1.2, in THF at −20 ºC }.

Figure S8(a) shows time-conversion curves for the polymerization of **3**. The monomer to polymer conversion increased with time and reached at approximately 80% after 72 h, while the monomer to dimer conversion reached a plateau in the middle stage of the polymerization. Figure S8(b) shows plots of M_n and M_w/M_n of the polymer against the monomer to polymer conversion for the polymerization of **3**. The M_n values of polymers increased in proportion to the monomer to polymer conversion while keeping narrow molecular weight distribution throughout the polymerization ($M_w/M_n < 1.1$), although the line did not pass through the origin for an unknown reason. The reason could be related to the deviation of the SEC-estimated M_ns (PMMA standards) from the actual values, along with the very high repeating unit molecular weight (763.6). The clarification of the controlled/living features of this polymerization is an important current objective of our research.

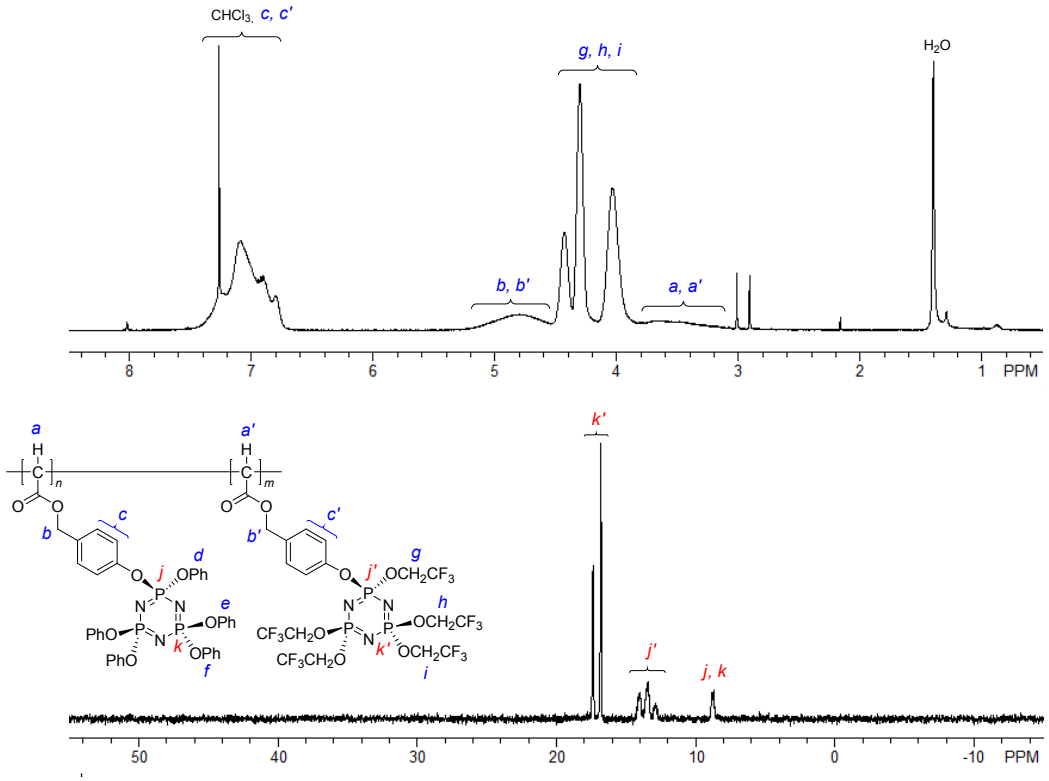


Figure S9. ^{1}H (upper) and ^{31}P (lower) NMR spectra of the product obtained by block copolymerization of **3** and **2** (M_n = 25000, M_w/M_n = 1.15) recorded in $CDCl_3$/hexafluorobenzene.

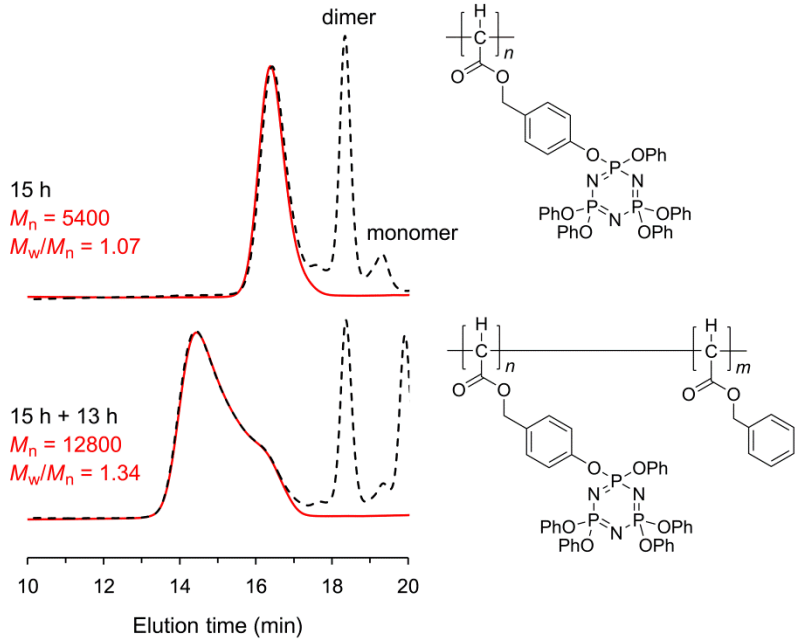


Figure S10. SEC curves for the block copolymerization of **3** and BDA (dotted lines: crude products, solid lines: after purification with preparative recycling SEC or reprecipitation) {polymerization condition: [{(η^3-

C_3H_5)PdCl}$_2$] = 1.6 mM, [**3**] = 64 mM, $[BDA]_{add}$ = 0.32 M (0.64 M solution in THF), $[NaBPh_4]$/[Pd] = 1.2, in THF at −20 ºC}.

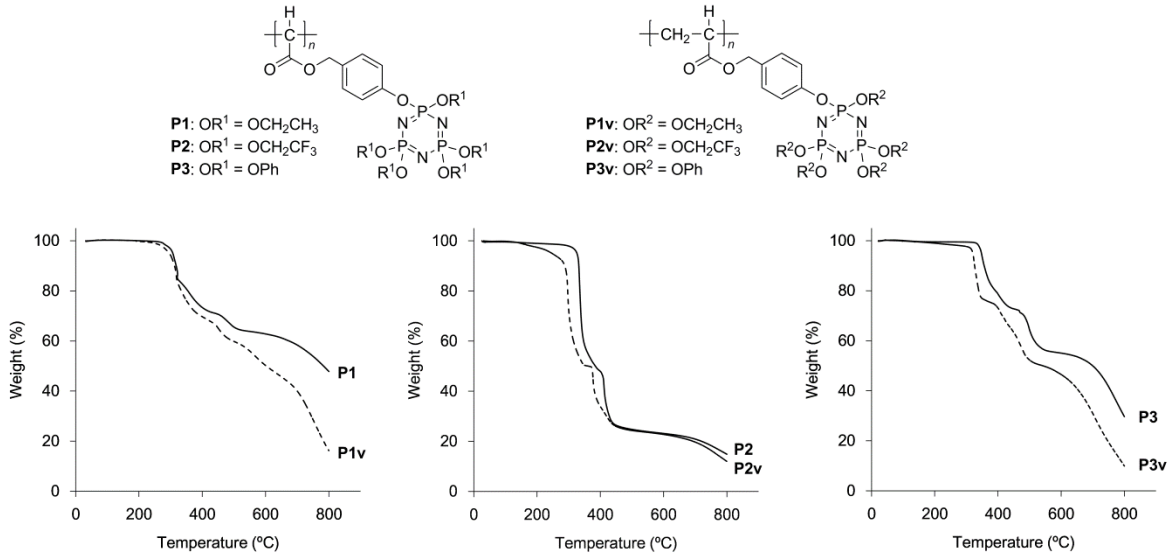


Figure S11. Thermogravimetric analysis of cyclophosphazene-containing polymers at a heating rate of 20 ºC/min in nitrogen atmosphere (**P1**: M_n = 10000, M_w/M_n = 1.19; **P2**: M_n = 13400, M_w/M_n = 1.05; **P3**: M_n = 7900, M_w/M_n = 1.08; **P1v**: M_n = 15600, M_w/M_n = 1.33; **P2v**: M_n = 10400, M_w/M_n = 1.23; **P3v**: M_n = 8000, M_w/M_n = 1.35).

3. References

1. N. E. Searle, in *Organic Synthesis Collection,* ed. N. Rabjohn, John Wiley and Sons, New York, 1963, vol. 4, pp. 424-426.
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