

Electronic Supporting Information for:

Facile synthesis of stereoregular helical poly(phenyl isocyanide)s and
poly(phenyl isocyanide)-*block*-poly(L-lactic acid) copolymers using
alkylethynylpalladium(II) complexes as initiators

Jia-Li Chen, Ming Su, Zhi-Qiang Jiang, Na Liu, Jun Yin, Yuan-Yuan Zhu and Zong-Quan Wu*

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Hefei

University of Technology and Anhui Key Laboratory of Advanced Functional Materials and Devices,

Hefei 230009, China

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Instruments.

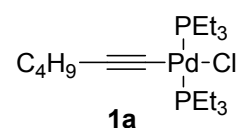
The ^1H , ^{13}C NMR spectra were recorded using a Bruker 600 or 400 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel HR1, HR2 and HR4 columns. Molecular weight and polydispersity data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. UV-vis spectra were performed on a UNIC 4802 UV/VIS double beam spectrophotometer in 1.0 cm length quartz cell. Circular dichroism (CD) spectra were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1500 spectropolarimeter. The polymer concentration was calculated on the basis of the monomer units and was 0.2 mg/mL. The optical rotations were measured in CHCl_3 at room temperature using a 10.0 cm quartz cell on a WZZ-2B polarimeter. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. Samples for atomic force microscopy (AFM) measurements were prepared by drop casting solutions of polymers onto pre-cleaned silicon wafers, placed in covered Petri dishes to slow the evaporation process. AFM images were acquired in tapping mode with a Digital Instruments Dimension 3100 Scanning Probe Microscope, performed at room temperature in air using standard silicon cantilevers with a nominal spring constant of 50 N/m and resonance frequency of ~300 kHz. The images were acquired at a scan

frequency of 1 Hz in $1 \times 1 \mu\text{m}^2$ scan areas.

Materials

All solvents were obtained from Sinopharm. Co. Ltd. and were purified by the standard procedures before use. Hex-1-yne, prop-2-yn-1-ol, but-3-yn-2-one, ethyl propiolate, *trans*-dichlorobis(triethylphosphine)palladium(II), copper(I) chloride, L-lactide (**3**), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Aladdin and Sigma-Aldrich. Co. Ltd., and were used as received without further purification otherwise denoted. L-Lactide **3** was recrystallized from toluene for three times before use. Isocyanide monomers **2a-d**, and phenylethynyl Pd(II) complex (**1e**) and phenylbuta-1,3-diynyl Pd(II) complex (**1f**) were prepared according to the literatures and the structures were confirmed by ^1H NMR.¹

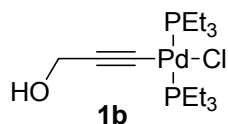
Synthetic Procedures for Pd Complexes 1a–1d



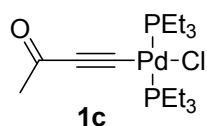
Synthesis of 1a: Hex-1-yne (40 mg, 0.49 mmol) was treated with *trans*-dichlorobis(triethylphosphine)palladium (202 mg, 0.49 mmol) in the presence of copper(I) chloride (6.9 mg, 0.070 mmol) as catalyst in diethylamine (40 mL) and dichloromethane (10 mL). The mixture was stirred at room temperature for 3 h. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with petrol ether as eluent. The isolated product was recrystallized from petrol ether and methanol to afford **1a** as a yellow solid (190 mg, 85 %). M.P.: 138.7–139.8 °C. ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ 2.22 (m, 2H, $\text{CH}_2\text{C}_3\text{H}_7$), 1.93–1.87 (m, 12H, PCH_2CH_3), 1.45–1.35 (m, 4H, CH_2), 1.19–1.11 (m, 18H, PCH_2CH_3), 0.87 (t, $J = 8.4$ Hz, 3H, $(\text{CH}_2)_3\text{CH}_3$)

). ^{13}C NMR (150 MHz, CDCl_3 , 25 °C): δ 104.52, 76.82, 31.40, 28.72, 21.11, 20.04, 14.21, 7.32. FT-IR (KBr, cm^{-1}): 2968 ($\nu_{\text{C-H}}$), 2930 ($\nu_{\text{C-H}}$), 2879 ($\nu_{\text{C-H}}$), 2130 ($\nu_{\text{C}\equiv\text{C}}$). MS m/z calcd for $\text{C}_{18}\text{H}_{40}\text{ClP}_2\text{Pd}$ [$\text{M} + 1$] $^+$: 459.1250; Found: 459.1118. Anal. Calcd (%) for $\text{C}_{18}\text{H}_{39}\text{ClP}_2\text{Pd}$: C, 47.07; H, 8.56; Found (%): C, 46.81; H, 8.80.

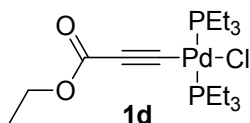
Similar to **1a**, Pd(II) complexes **1b**, **1c**, and **1d** were synthesized from the reaction of prop-2-yn-1-ol, but-3-yn-2-one, and ethyl propiolate with *trans*-dichlorobis(triethylphosphine)palladium in dichloromethane, respectively. The characterization data for **1b–1d** were showed below.



1b: M.P.: 53.3–54.1 °C. ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ 4.26 (s, 2H, OCH_2), 1.94–1.91 (m, 12H, PCH_2CH_3), 1.20–1.12 (m, 18H, PCH_2CH_3). ^{13}C NMR (150 MHz, CDCl_3 , 25 °C): δ 104.34, 89.11, 53.14, 15.17, 8.26. FT-IR (KBr, cm^{-1}): 3426 ($\nu_{\text{O-H}}$), 2958 ($\nu_{\text{C-H}}$), 2933 ($\nu_{\text{C-H}}$), 2871 ($\nu_{\text{C-H}}$), 2130 ($\nu_{\text{C}\equiv\text{C}}$). MS m/z calcd for $\text{C}_{15}\text{H}_{34}\text{ClOP}_2\text{Pd}$ [$\text{M} + 1$] $^+$: 433.0730; Found: 433.1024. Anal. Calcd (%) for $\text{C}_{15}\text{H}_{33}\text{ClOP}_2\text{Pd}$: C, 41.58; H, 7.68; Found (%): C, 41.30; H, 7.90.



1c: M.P.: 65.1–65.9 °C. ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ 2.24 (s, CH_3CO), 1.94–1.90 (m, 12H, PCH_2CH_3), 1.20–1.15 (m, 18H, PCH_2CH_3). ^{13}C NMR (150 MHz, CDCl_3 , 25 °C): δ 183.96, 112.24, 110.79, 32.77, 15.10, 8.21. FT-IR (KBr, cm^{-1}): 2967 ($\nu_{\text{C-H}}$), 2925 ($\nu_{\text{C-H}}$), 2873 ($\nu_{\text{C-H}}$), 2084 ($\nu_{\text{C}\equiv\text{C}}$), 1650 ($\nu_{\text{C}=\text{O}}$). MS m/z calcd for $\text{C}_{16}\text{H}_{34}\text{ClOP}_2\text{Pd}$ [$\text{M} + 1$] $^+$: 445.0730; Found: 445.1031. Anal. Calcd (%) for $\text{C}_{16}\text{H}_{33}\text{ClOP}_2\text{Pd}$: C, 43.16; H, 7.47; Found (%): C, 42.91; H, 7.70.



1d: M.P.: 35.6–37.1 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 4.13 (q, $J_1 = 8.8$ Hz, $J_2 = 14.4$ Hz, 2H, CO₂CH₂CH₃), 1.96–1.92 (m, 12H, PCH₂CH₃), 1.27 (t, $J = 8.8$ Hz, 3H, CO₂CH₂CH₃), 1.22–1.14 (m, 18H, PCH₂CH₃). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 154.08, 104.34, 99.84, 60.67, 15.09, 14.23, 8.23. FT-IR (KBr, cm⁻¹): 2969 (ν_{C-H}), 2915 (ν_{C-H}), 2875 (ν_{C-H}), 2110 ($\nu_{C\equiv C}$), 1693 ($\nu_{C=O}$). MS *m/z* calcd for C₁₇H₃₆ClO₂P₂Pd [M + H]⁺: 475.0836; Found: 475.1091. Anal. Calcd (%) for C₁₇H₃₅ClO₂P₂Pd: C, 42.96; H, 7.42; Found (%): C, 42.67; H, 7.70.

Typical Polymerization Procedure of 2a with 1a–d (poly-a2a₁₀₀): A 10 mL oven-dried flask was charged with monomer **2a** (100 mg, 0.35 mmol), THF (1.64 mL) and a stir bar. To this stirring solution was added a solution of **1a** in THF (0.035 M, 0.10 mL) *via* a microsyringe at ambient temperature. The concentrations of monomer **2a** and initiator **1a** were 0.2 and 0.002 M, respectively ($[2]_0/[1a]_0 = 100$). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 6 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight (95 mg, 95% yield). SEC: $M_n = 3.01 \times 10^4$ Da, $M_w/M_n = 1.14$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.31 (br, aromatic), 5.74 (br, aromatic), 4.50–3.50 (br, OCH₂), 1.95–0.75 (br, CH₂ and CH₃). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 164.93, 162.55, 150.35, 129.64, 127.23, 117.02, 64.87, 31.87, 29.65, 29.58, 29.42, 29.30, 28.61, 25.98, 22.62, 14.03. FT-IR (KBr, cm⁻¹): 2960 (ν_{C-H}), 2930 (ν_{C-H}), 2860 (ν_{C-H}), 1720 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

Typical Kinetic Study for the Polymerization of 2a with 1a. A mixture of monomer **2a** (100.0 mg, 0.35 mmol) and a standard polystyrene ($M_n = 2630$, $M_w/M_n = 1.06$, 50.0 mg) were placed in a dry ampule,

which was then evacuated on a vacuum line and flushed with dry nitrogen. After the evacuation-flush procedure had been repeated three times, a three-way stopcock was attached to the ampule, and dry THF (1.36 mL) was added by a syringe. To this was added a solution of **1a** in THF (10 mM, 0.39 mL) *via* a microsyringe at ambient temperature. The concentrations of **1a** and **2** were 0.0022 and 0.2 M, respectively. The mixture was then stirred under a dry nitrogen atmosphere and heated to 55 °C ($[\mathbf{2a}]_0 = 0.2$ M, $[\mathbf{2}]_0/[\mathbf{1a}]_0 = 90$). The conversion of **2a** was followed by measuring the SEC of the reaction mixture at appropriate time intervals. The peak area of the unreacted **2a** relative to that of the internal standard (polystyrene) was used for the determination of the conversion of **2a** on the basis of the linear calibration curve. The M_n and M_w/M_n were estimated by SEC and reported as equivalent to standard polystyrene.

Typical Procedure for Acetone Fractionation of Poly-e2d₁₀₀. The afforded the diastereomeric mixture of left- and right-handed helices, poly-e2d₁₀₀ was separated into each helix according to the procedure we reported previously with slightly modification.^{1a, 2} The poly-e2d₁₀₀ (100 mg) was suspended in 30 ml of acetone, and the mixture was stirred at room temperature for 3 h. After filtration, the filtrate was evaporated to dryness under reduced pressure, giving poly-e2d₁₀₀(+) (15 mg, 15%). The acetone-insoluble polymer was then dissolved in a small amount of CHCl₃, the solution was precipitated in a large amount of acetone, and the precipitate was then collected by filtration. After this procedure was repeated again, the poly-e2d₁₀₀(-) was obtained (65 mg, 65%).

Typical Polymerization Procedure of L-Lactide 3 with 1b (poly-3₅₀). A 10 mL oven-dried flask was charged with monomer **3** (100 mg, 0.69 mmol), **1b** (6.0 mg, 0.014 mmol), anhydrous CH₂Cl₂ (0.5 mL) and a stir bar. To this stirring solution was added a solution of TBD in CH₂Cl₂ (0.35 M, 0.2 mL) *via*

a microsyringe at ambient temperature. The concentrations of monomer **3** and catalyst **1b** were 1.0 and 0.02 M, respectively ($[3]_0/[1b]_0 = 50$). After stirred at room temperature for 12 h, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight (75 mg, 75% yield). SEC: $M_n = 5.51 \times 10^3$, $M_w/M_n = 1.23$. ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ 5.16 (m, CH), 1.58 (m, CH_3). FT-IR (KBr, cm^{-1}): 2991 ($\nu_{\text{C-H}}$), 2940 ($\nu_{\text{C-H}}$), 2877 ($\nu_{\text{C-H}}$), 1760 ($\nu_{\text{C=O}}$).

Typical Two-feed Procedure for One-pot Copolymerization of 2a and 3 Using 1b as Initiator.

Firstly, a THF solution of poly-**b2a**₉₀ ($M_n = 2.56 \times 10^4$, $M_w/M_n = 1.19$) was prepared from the polymerization of **2a** with **1b** as initiator in THF at 55 °C. To this solution was added a solution of **3** (16.0 mg, 0.11 mmol) and TBD (0.092 M) in THF ($[3]_0/[Pd]_0 = 30$). After the mixture was stirred at room temperature for 12 h, the solution was then precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight to afford the block copolymer poly(**b2a**₉₀-*b*-**3**₃₀) (88% yield, over two steps). SEC: $M_n = 2.91 \times 10^4$, $M_w/M_n = 1.20$. ^1H NMR (600 MHz, CDCl_3 , 25 °C): δ 7.31 (br, Ar of poly-**b2a**₉₀ segment), 5.74 (br, Ar of poly-**b2a**₉₀ segment), 5.16 (m, CH of poly-**3**₃₀ segment), 4.50–3.50 (br, OCH_2 of poly-**b2a**₉₀ segment), 1.95–0.75 (br, CH_2 and CH_3 of poly-**b2a**₉₀ segment, and CH_3 of poly-**3**₃₀ segment). ^{13}C NMR (150 MHz, CDCl_3 , 25 °C): δ 169.54, 164.94, 162.53, 150.34, 129.64, 127.17, 117.01, 68.94, 64.87, 31.85, 29.56, 29.40, 29.28, 28.56, 25.95, 22.60, 16.67, 14.02. FT-IR (KBr, cm^{-1}): 2998 ($\nu_{\text{C-H}}$), 2929 ($\nu_{\text{C-H}}$), 2859 ($\nu_{\text{C-H}}$), 1760 ($\nu_{\text{C=O}}$), 1720 ($\nu_{\text{C=O}}$), 1600 ($\nu_{\text{C=N}}$).

Typical One-feed Procedure for One-pot Copolymerization of 2a and 3 Using 1b as Initiator. A

10 mL oven-dried flask was charged with monomer **2a** (50 mg, 0.17 mmol), **3** (50 mg, 0.35 mmol), **1b**

(0.01 M, 0.35 mL, 0.0035 mmol), anhydrous THF (0.6 mL) and a stir bar. To this stirring solution was added a solution of TBD (0.058 M, 0.3 mL, 0.0174 mmol) in THF *via* a microsyringe at room temperature. The concentrations of monomer **2a**, **3** and catalyst **1b** were 0.2, 0.4, and 0.004 M, respectively ($[\mathbf{2a}]_0/[\mathbf{3}]_0/[\mathbf{1b}]_0 = 50/100/1$). After stirred at 55 °C for 12 h, the polymerization solution was then precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight to afford the block copolymer poly(**b2a**₅₀-*b*-**3**₁₀₀) (89 mg, 89% yield). SEC: $M_n = 2.13 \times 10^4$, $M_w/M_n = 1.18$. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.31 (br, Ar of poly-**b2a**₅₀ segment), 5.74 (br, Ar of poly-**b2a**₅₀ segment), 5.16 (m, CH of poly-**3**₁₀₀ segment), 4.50–3.50 (br, OCH₂ of poly-**b2a**₅₀ segment), 1.95–0.75 (br, CH₂ and CH₃ of poly-**b2a**₅₀ segment, and CH₃ of poly-**3**₁₀₀ segment). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 169.54, 164.94, 162.53, 150.34, 129.64, 127.17, 117.01, 68.94, 64.87, 31.85, 29.56, 29.40, 29.28, 28.56, 25.95, 22.60, 16.67, 14.02. FT-IR (KBr, cm⁻¹): 2998 (ν_{C-H}), 2929 (ν_{C-H_s}), 2859 (ν_{C-H}), 1760 ($\nu_{C=O}$), 1720 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

References

1. (a) Z.-Q. Wu, K. Nagai, M. Banno, K. Okoshi, K. Onitsuka and E. Yashima, *J. Am. Chem. Soc.*, 2009, **131**, 6708. (b) Z.-Q. Wu, R. J. Ono, Z. Chen and C. W. Bielawski, *J. Am. Chem. Soc.*, 2010, **132**, 14000. (c) Y.-X. Xue, Y.-Y. Zhu, L.-M. Gao, X.-Y. He, N. Liu, W.-Y. Zhang, J. Yin, Y. Ding, H. Zhou and Z.-Q. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 4706. (d) Y.-X. Xue, J.-L. Chen, Z.-Q. Jiang, Z. Yu, N. Liu, J. Yin, Y.-Y. Zhu and Z.-Q. Wu, *Polym. Chem.*, 2014, **5**, 6435.
2. M. Banno, Z.-Q. Wu, K. Nagai, S.-i. Sakurai, K. Okoshi and E. Yashima, *Macromolecules*, 2010, **43**, 6553.

Table S1. Selected results for the polymerization of 3 with 1b as initiator^a

run	[3] ₀ /[1b] ₀ ^b	polymer	<i>M</i> _n (Da) ^c	<i>M</i> _w / <i>M</i> _n ^c	yield ^d
1	50	poly- 3 ₅₀	5.51 × 10 ³	1.23	75%
2	70	poly- 3 ₇₀	5.84 × 10 ³	1.20	76%
3	100	poly- 3 ₁₀₀	6.51 × 10 ³	1.21	77%
4	120	poly- 3 ₁₂₀	7.12 × 10 ³	1.24	77%
5	150	poly- 3 ₁₅₀	7.97 × 10 ³	1.18	78%

^aThe polymers were synthesized according to Scheme 2 in main text. ^bThe initial feed ratio of monomer **3** to initiator **1b**. ^cThe *M*_n and *M*_w/*M*_n data were estimated through the SEC analyses with polystyrene standard. ^dIsolated yields.

Table S2. Selected results for one-pot copolymerization of 2a and 3 with 1b as initiator via one-feed procedure^a

run	[2a] ₀ /[3] ₀ /[1b] ₀ ^b	block copolymer	<i>M</i> _n (Da) ^c	<i>M</i> _w / <i>M</i> _n ^c	yield ^d	block ratio ^e
1	30/50/1	poly(b2a ₃₀ - <i>b</i> - 3 ₅₀)	1.37 × 10 ⁴	1.21	86%	3/5
2	40/100/1	poly(b2a ₄₀ - <i>b</i> - 3 ₁₀₀)	1.72 × 10 ⁴	1.22	87%	2/5
3	50/100/1	poly(b2a ₅₀ - <i>b</i> - 3 ₁₀₀)	2.13 × 10 ⁴	1.18	89%	1/2
4	50/150/1	poly(b2a ₅₀ - <i>b</i> - 3 ₁₅₀)	2.43 × 10 ⁴	1.22	87%	1/3
5	90/30/1	poly(b2a ₉₀ - <i>b</i> - 3 ₃₀)	3.10 × 10 ⁴	1.19	89%	3/1

^aThe block copolymers were synthesized according to Scheme 2 in main text. ^bThe initial feed ratio of

monomers to initiator. ^c M_n and M_w/M_n were determined by SEC using polystyrene standard. ^dIsolated yield. ^eBlock ratio of PPI to PLLA segment determined by integral analyses of ¹H NMR spectroscopy.

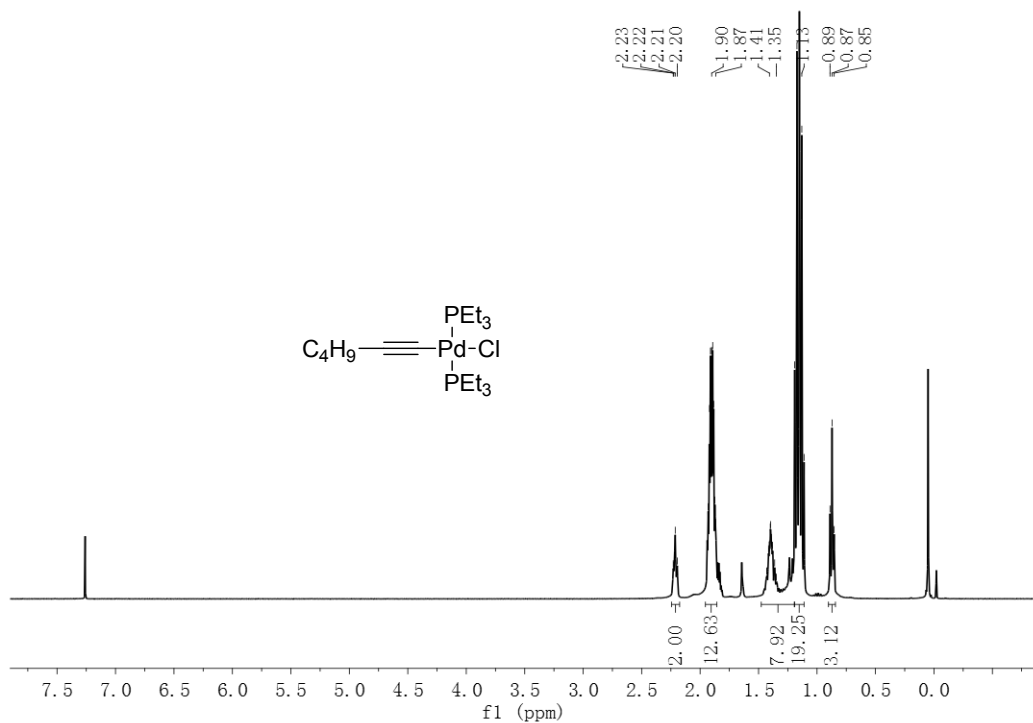


Fig. S1 ¹H NMR (600 MHz) spectrum of **1a** measured in CDCl₃ at 25 °C.

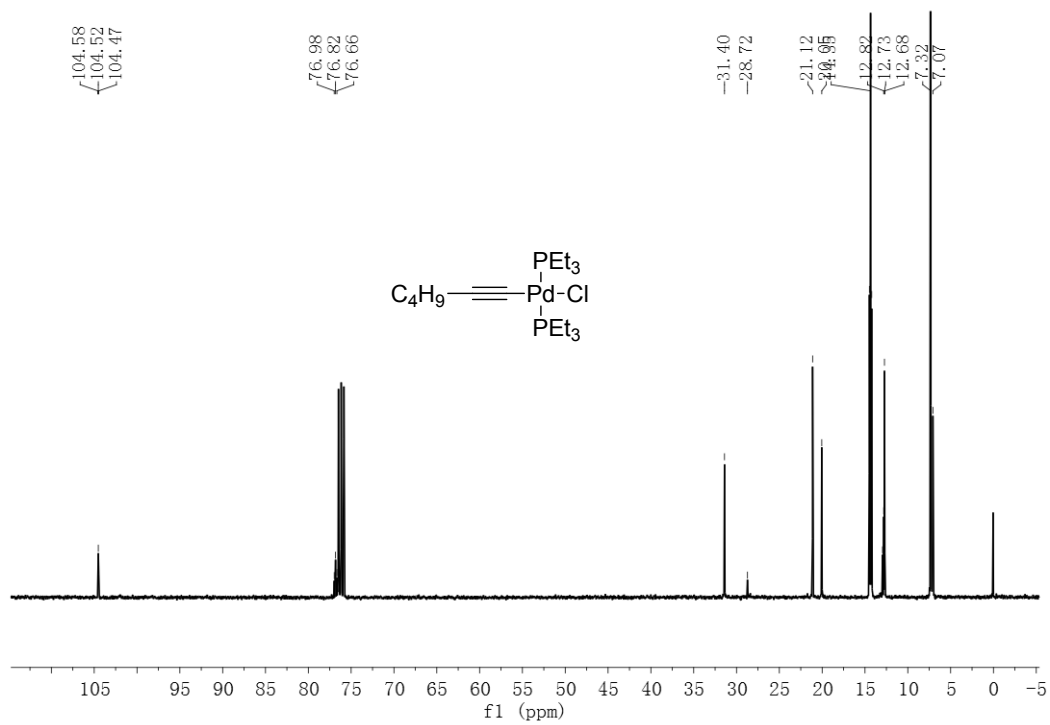


Fig. S2 ^{13}C NMR (150 MHz) spectrum of **1a** measured in CDCl_3 at 25°C .

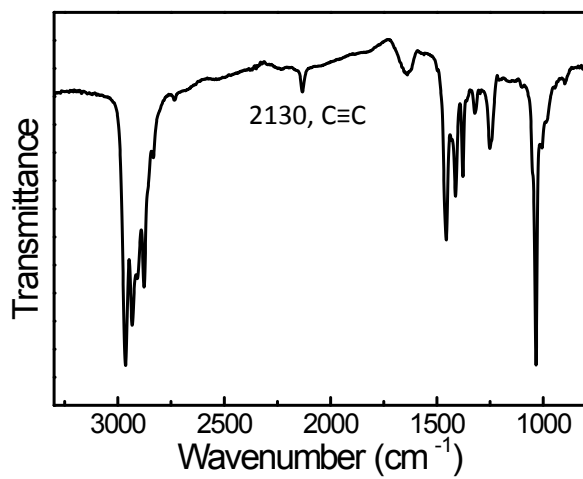


Fig. S3 FT-IR spectrum of **1a** measured at 25°C using KBr pellets.

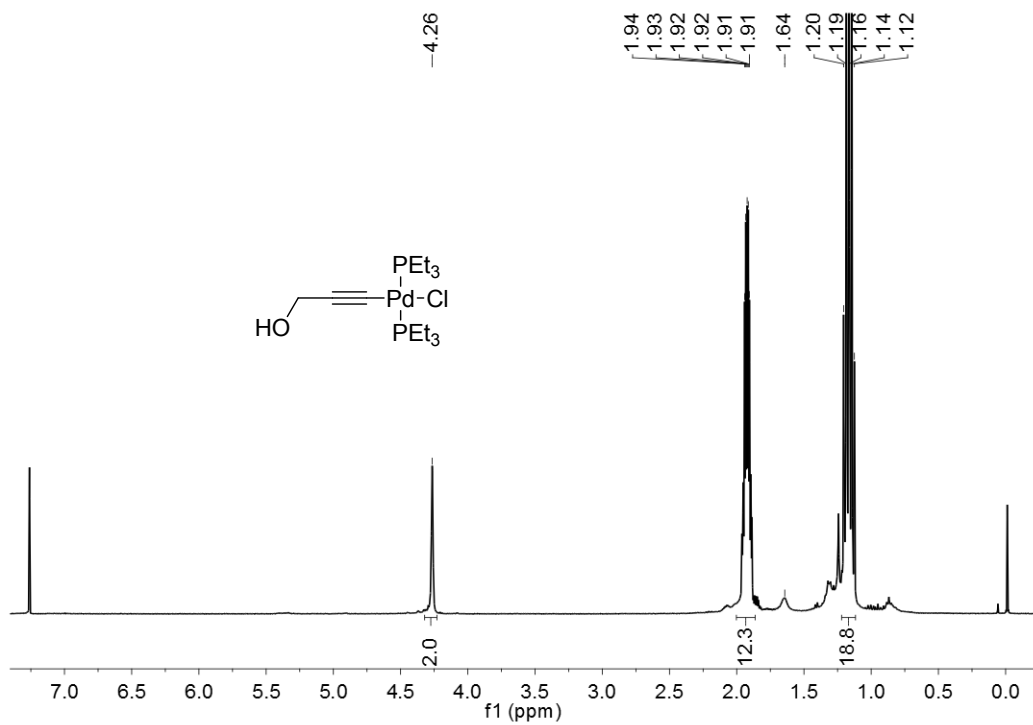


Fig. S4 ^1H NMR (400 MHz) spectrum of **1b** measured in CDCl_3 at 25 °C.

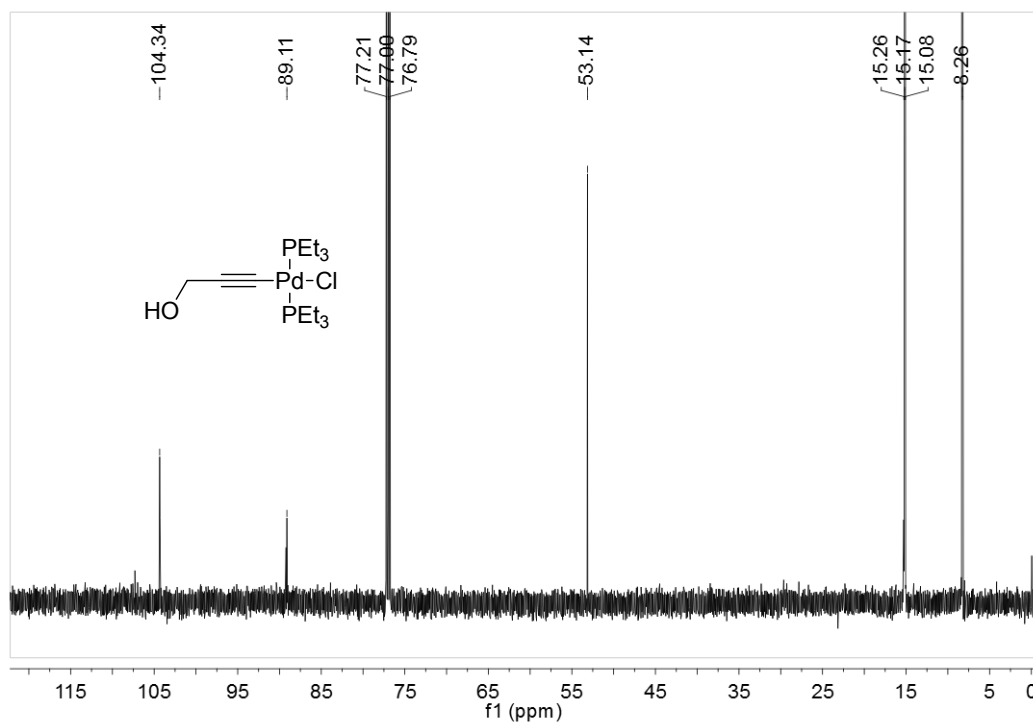


Fig. S5 ^{13}C NMR (150 MHz) spectrum of **1b** measured in CDCl_3 at 25 °C.

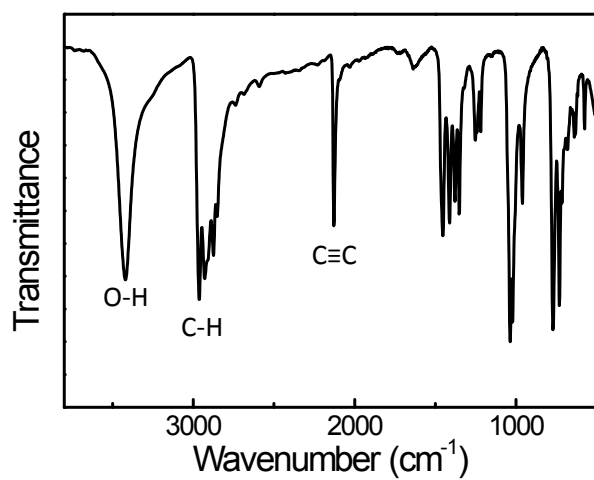


Fig. S6 FT-IR spectrum of **1b** measured at 25 °C using KBr pellets.

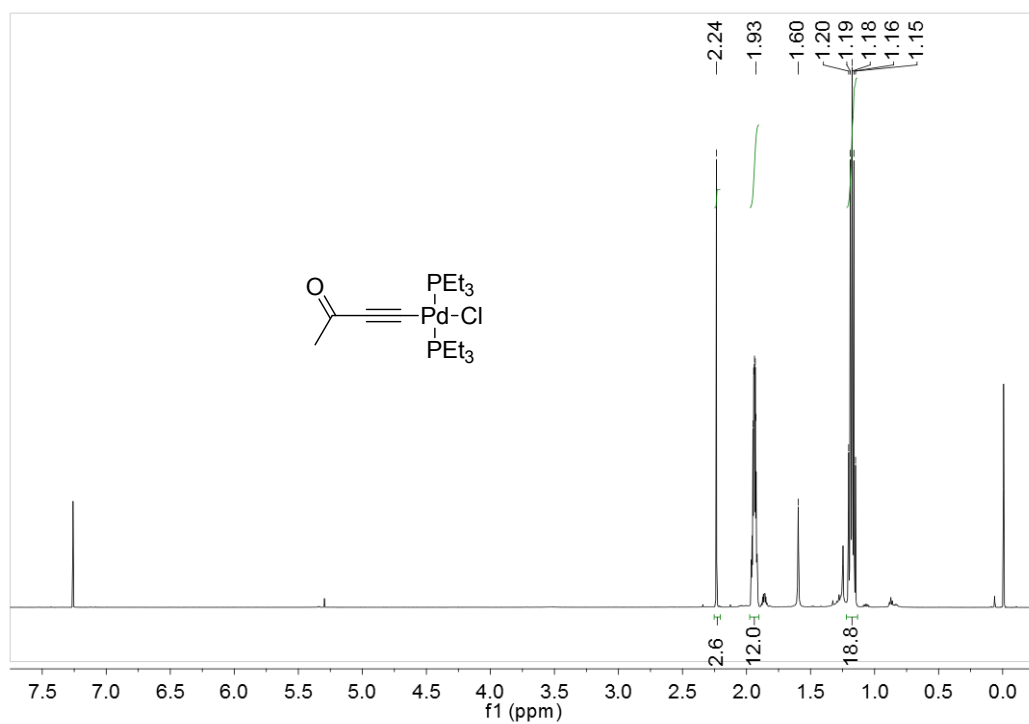


Fig. S7 ^1H NMR (600 MHz) spectrum of **1c** measured in CDCl_3 at 25 °C.

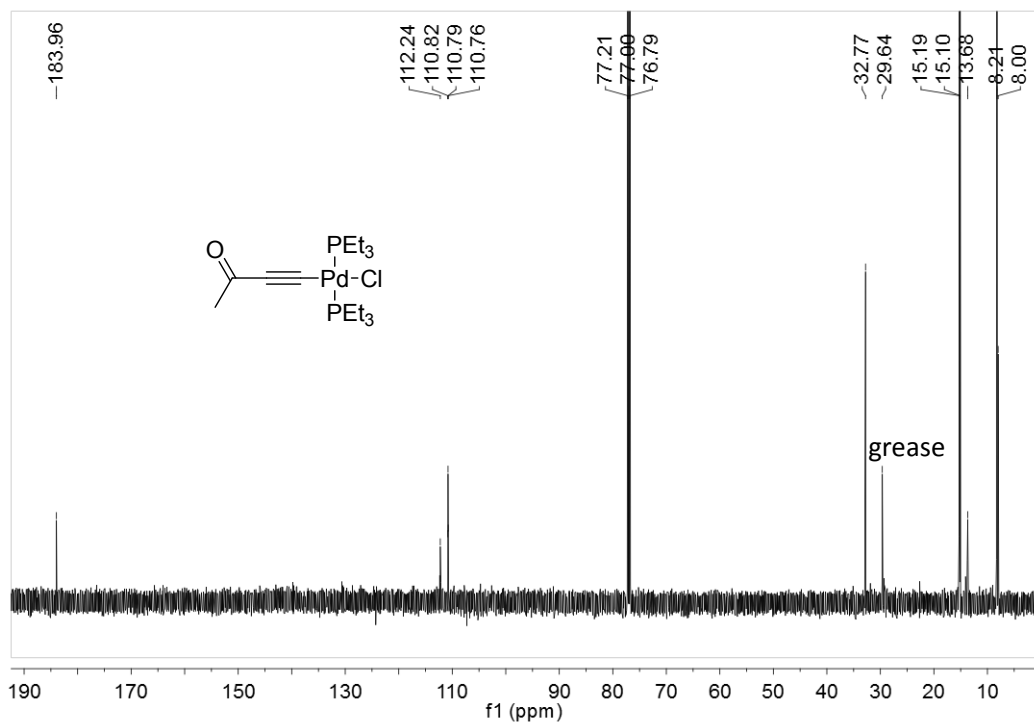


Fig. S8 ^{13}C NMR (150 MHz) spectrum of **1c** measured in CDCl_3 at 25 °C.

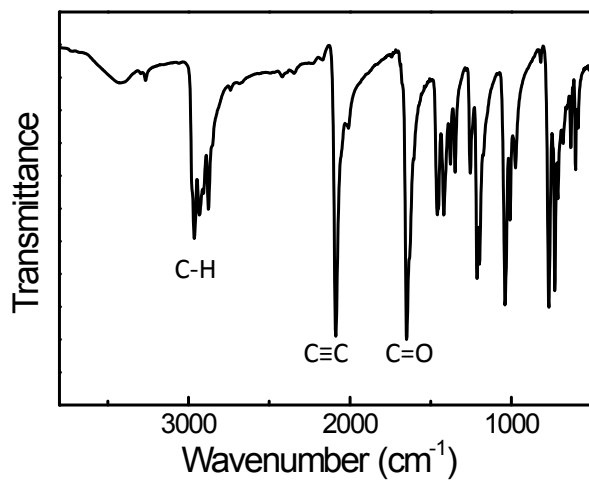


Fig. S9 FT-IR spectrum of **1c** measured at 25 °C using KBr pellets.

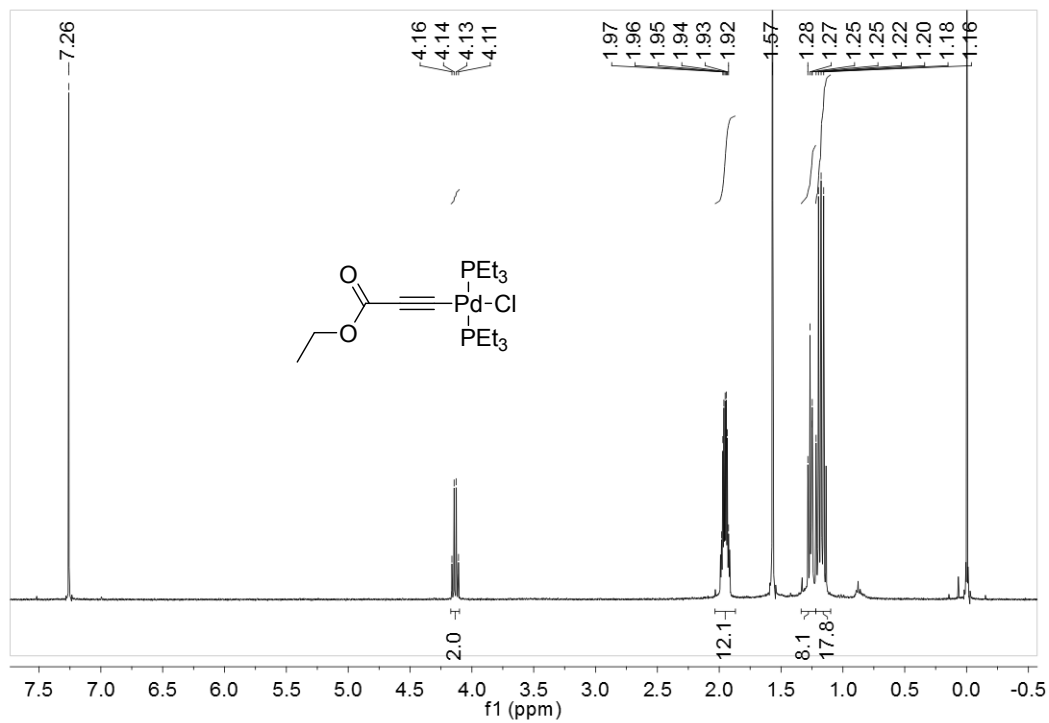


Fig. S10 ^1H NMR (400 MHz) spectrum of **1d** measured in CDCl_3 at 25 °C.

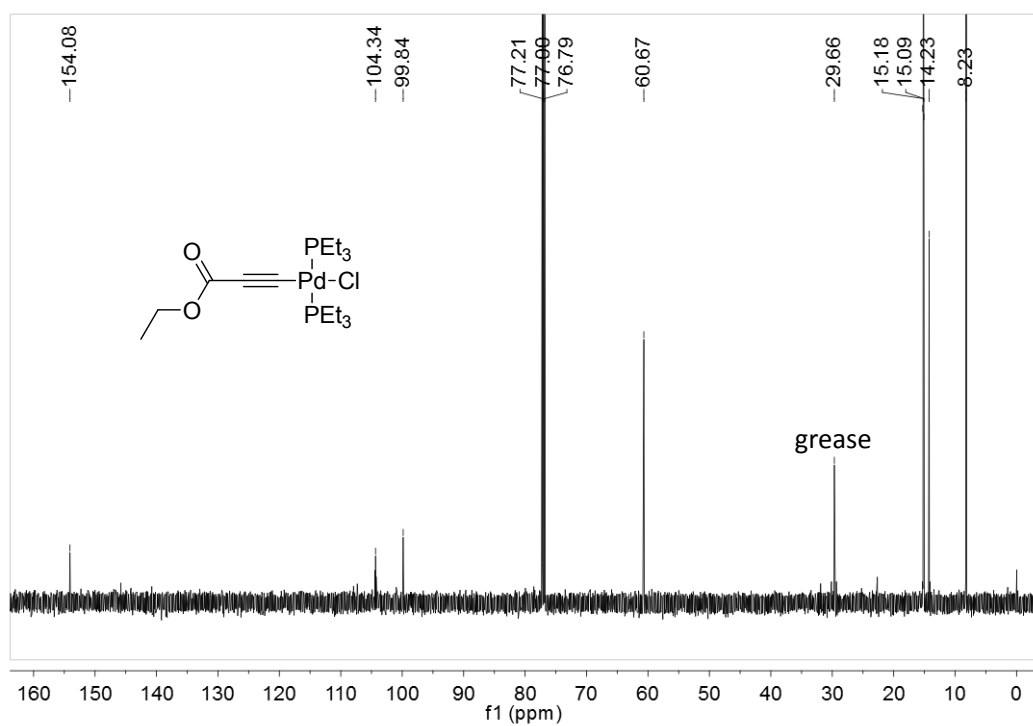


Fig. S11 ^{13}C NMR (150 MHz) spectrum of **1d** measured in CDCl_3 at 25 °C.

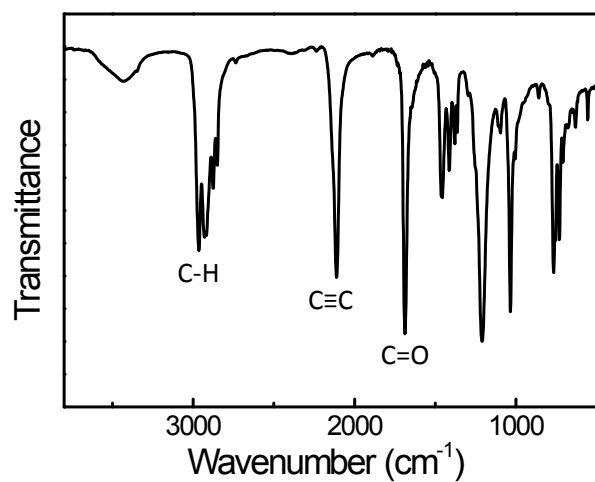


Fig. S12 FT-IR spectrum of **1d** measured at 25 °C using KBr pellets.

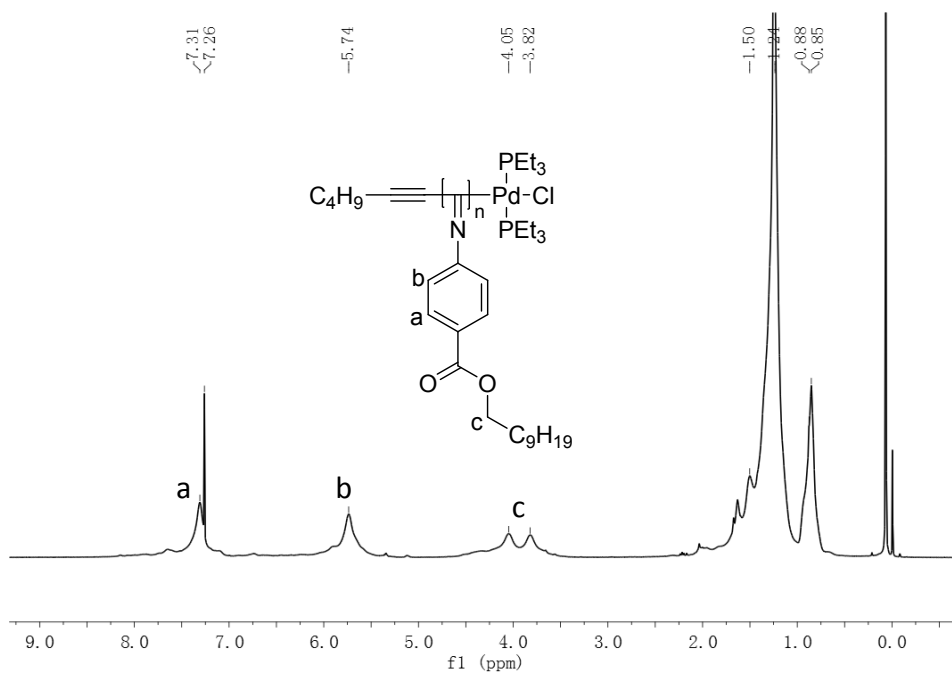


Fig. S13 ^1H NMR (600 MHz) spectrum of poly-**a2a_m** measured in CDCl_3 at 25 °C.

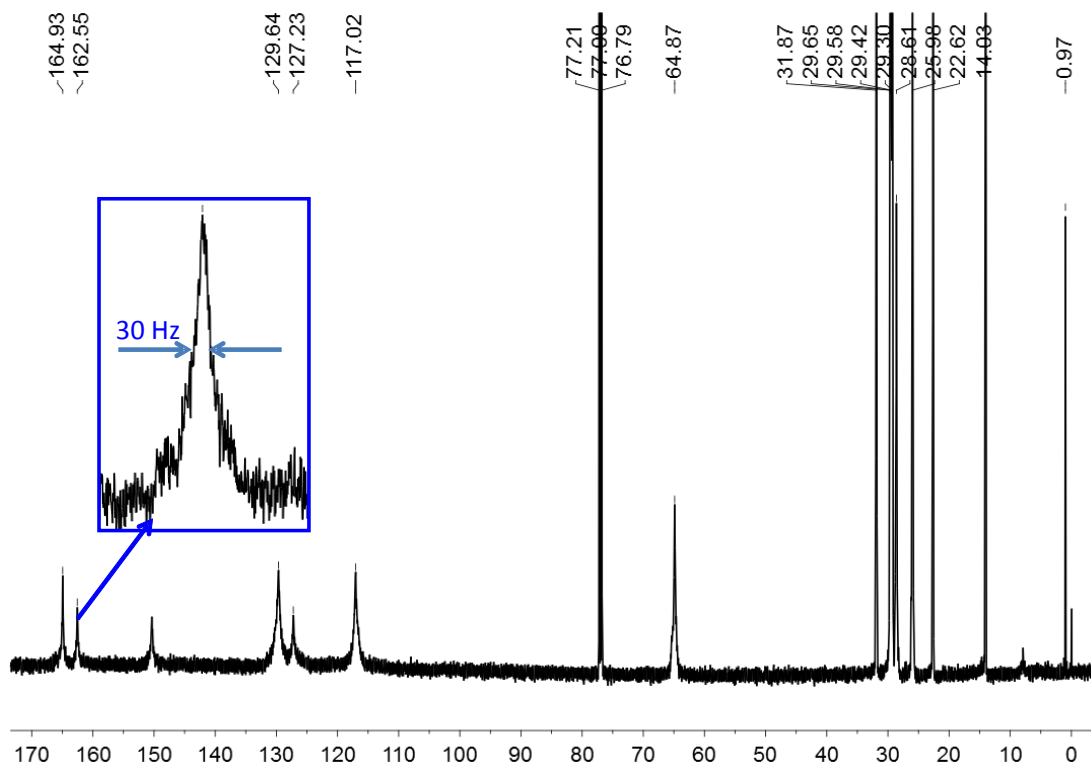


Fig. S14 ^{13}C NMR (150 MHz) spectrum of poly-**a2a_m** measured in CDCl_3 at 25 °C.

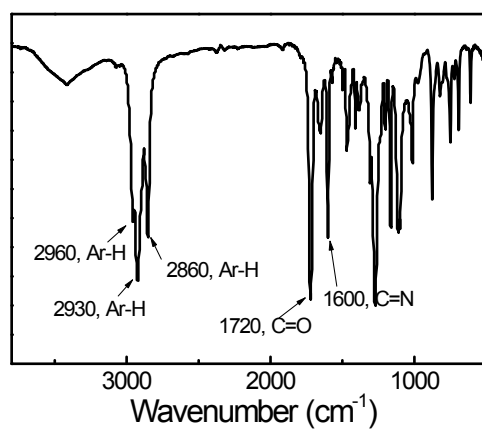


Fig. S15 FT-IR spectrum of poly-**a2a_m** measured at 25 °C using KBr pellets.

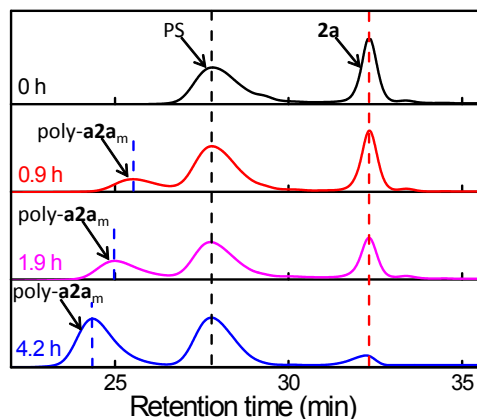


Fig. S16 Time-dependent SEC chromatograms for **1a**-initiated polymerization samples of **2a** in THF at 55 °C with the presence of polystyrene (PS, $M_n = 2630$, $M_w/M_n = 1.06$) as internal standard ($[2a]_0 = 0.2$ M, $[2a]_0/[1a]_0 = 90$). SEC condition: eluent = THF; temperature = 40 °C.

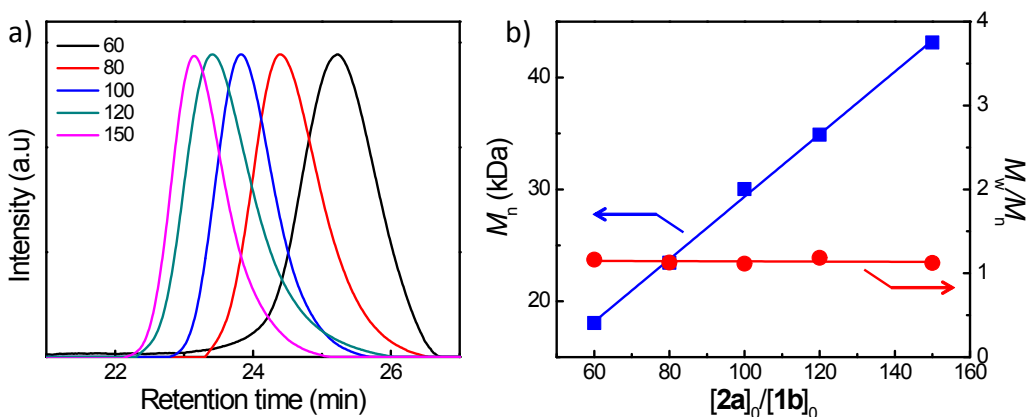


Fig. S17 (a) SEC chromatograms of poly-**b2a_m** prepared from the polymerization of phenyl isocyanide **2a** with Pd(II) complex **1b** as initiator in THF at 55 °C with different initial feed ratios of **2a** to **1b**. (b) Plots of M_n and M_w/M_n values of poly-**b2a_m** as a function of the initial feed ratios of **2a** to **1b**. M_n and M_w/M_n were determined by SEC with PS standard (eluent = THF, temperature = 40 °C).

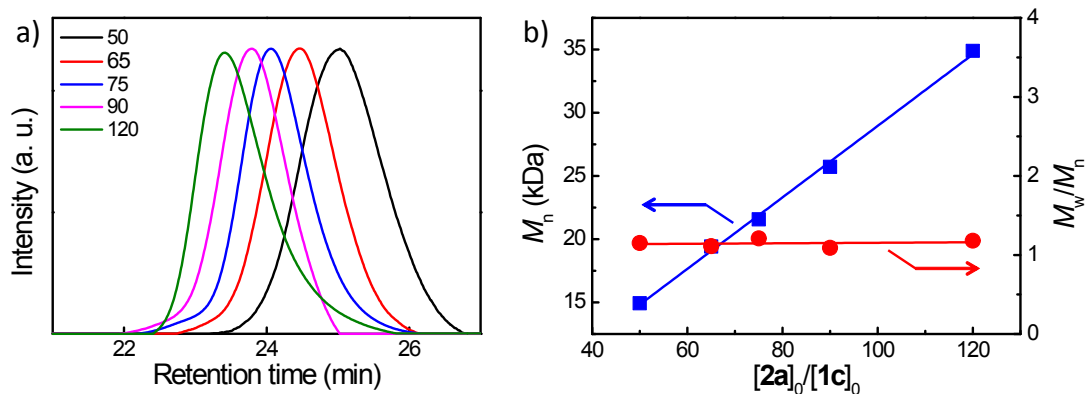


Fig. S18 (a) SEC chromatograms of poly-**c2a_m** prepared from the polymerization of phenyl isocyanide **2a** with Pd(II) complex **1c** as initiator in THF at 55 °C with different initial feed ratios of **2a** to **1c**. (b) Plots of M_n and M_w/M_n values of poly-**c2a_m** as a function of the initial feed ratios of **2a** to **1c**. M_n and M_w/M_n were determined by SEC with polystyrene standard (eluent = THF, temperature = 40 °C).

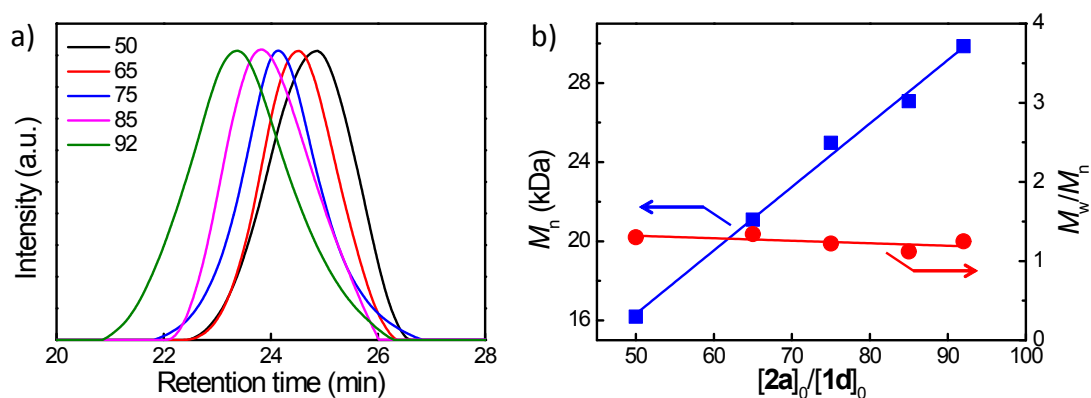


Fig. S19 (a) SEC chromatograms of poly-**d2a_m** prepared from the polymerization of phenyl isocyanide **2a** with Pd(II) complex **1d** as initiator in THF at 55 °C with different initial feed ratios of **2a** to **1d**. (b) Plots of M_n and M_w/M_n values of poly-**d2a_m** as a function of the initial feed ratios of **2a** to **1d**. M_n and M_w/M_n were determined by SEC with PS standard (eluent = THF, temperature = 40 °C).

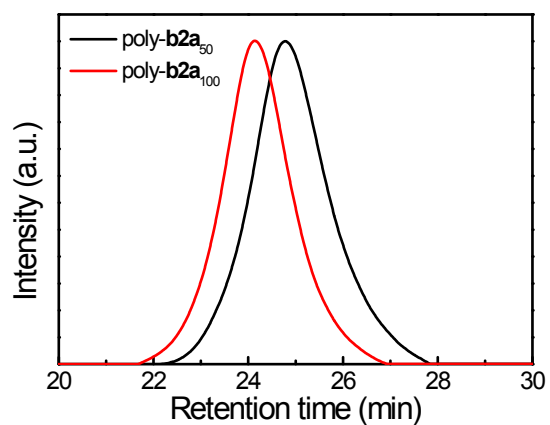


Fig. S20 SEC chromatograms of poly-**b2a**₅₀ and poly-**b2a**₁₀₀ prepared from the polymerization of **2a** with **1b** as initiator in CHCl₃ at 55 °C.

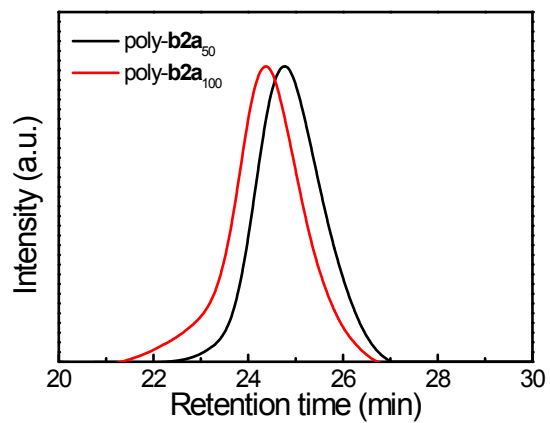


Fig. S21 SEC chromatograms of poly-**b2a**₅₀ and poly-**b2a**₁₀₀ prepared from the polymerization of **2a** with **1b** as initiator in toluene at 55 °C.

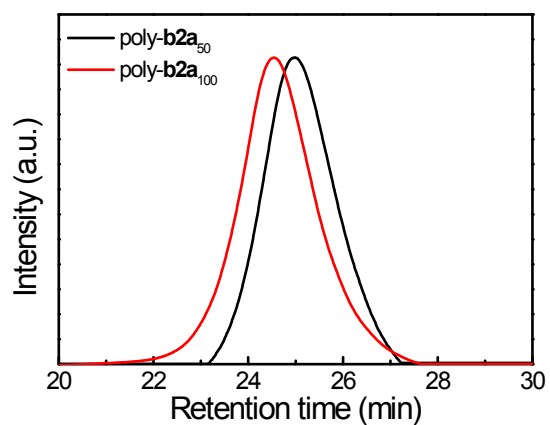


Fig. S22 SEC chromatograms of poly-**b2a**₅₀ and poly-**b2a**₁₀₀ prepared from the polymerization of **2a** with **1b** as initiator in DMF at 55 °C.

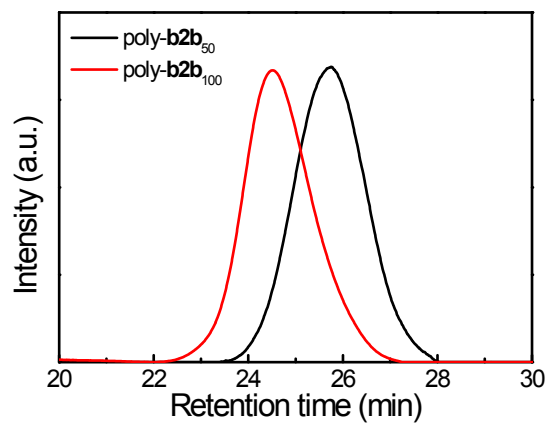


Fig. S23 SEC chromatograms of poly-**b2b**₅₀ and poly-**b2b**₁₀₀ prepared from the polymerization of **2b** with **1b** as initiator in THF at 55 °C.

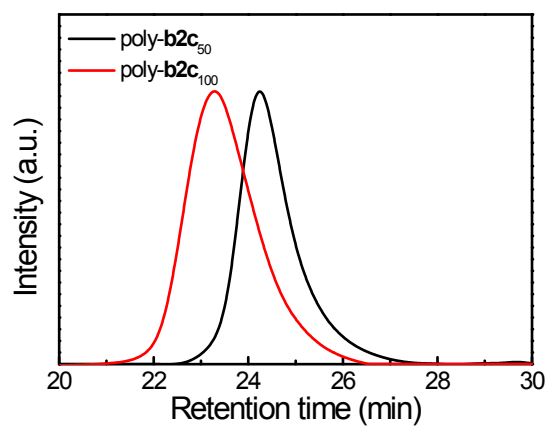


Fig. S24 SEC chromatograms of poly-**b2c**₅₀ and poly-**b2c**₁₀₀ prepared from the polymerization of **2c** with **1b** as initiator in THF at 55 °C.

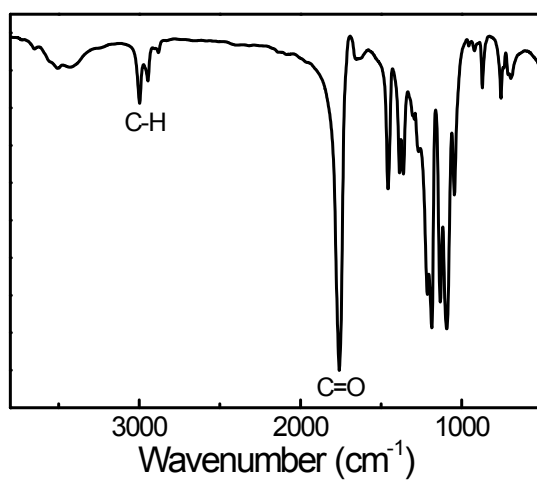


Fig. S25 FT-IR spectrum of poly-**3**₁₀₀ measured at 25 °C using KBr pellets.

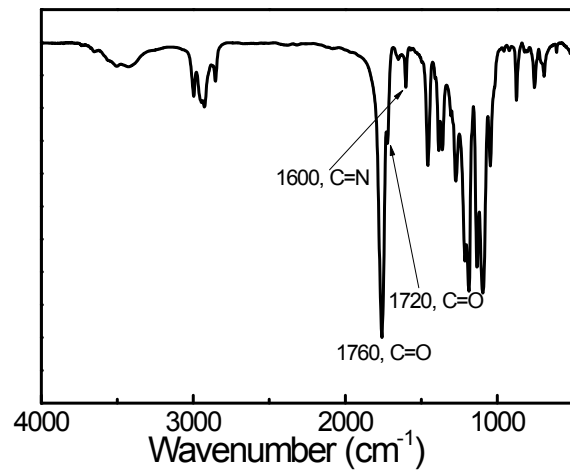


Fig. S26 FT-IR spectrum of the one-pot synthesized poly(**b2a_m-b-3_n**) via two-feed procedure measured at 25 °C using using KBr pellets.

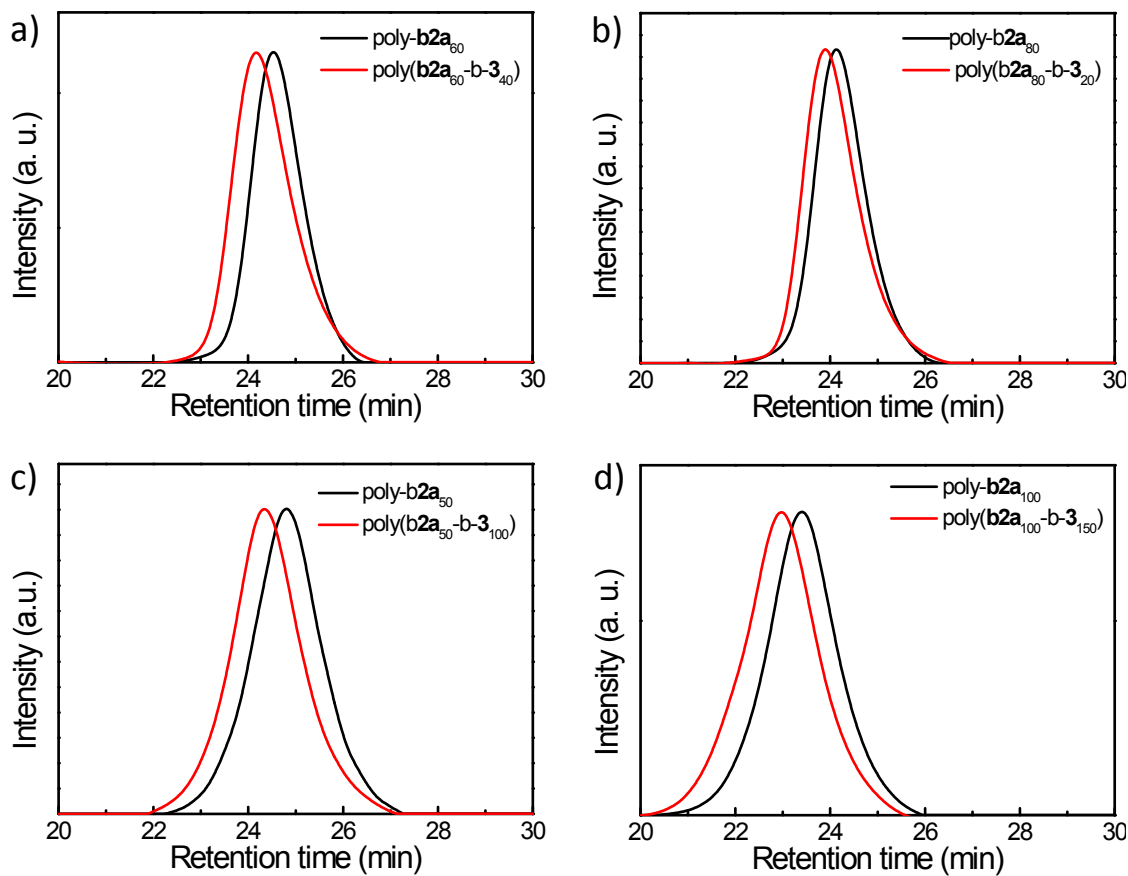


Fig. S27 SEC chromatograms of the macroinitiator poly- $\mathbf{b2a}_m$ s and the corresponding poly($\mathbf{b2a}_m$ - $\mathbf{b-3}_n$)s block copolymers prepared in one-pot via two-feed procedure.

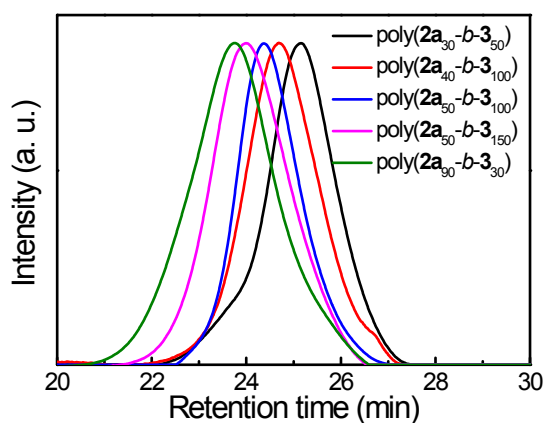


Fig. S28 SEC chromatograms poly($\mathbf{b2a}_m$ - $\mathbf{b-3}_n$)s block copolymers prepared in one-pot via one-feed procedure with **1b** as a single initiator.

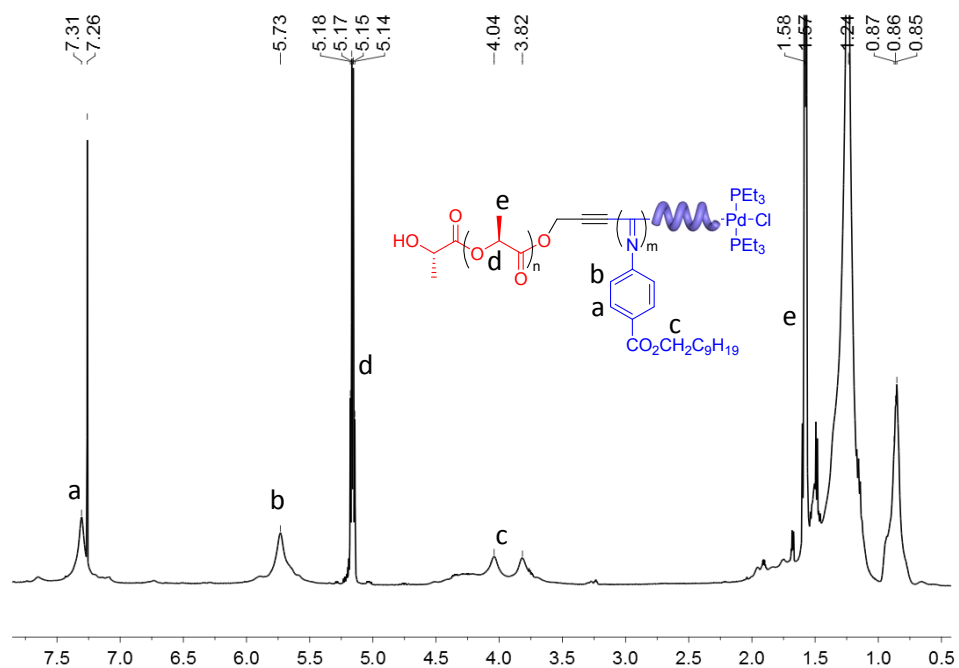


Fig. S29 ¹H NMR (600 MHz) spectrum of the one-pot synthesized poly(**b2a_m-b-3_n**) via one-feed procedure measured in CDCl₃ at 25 °C.

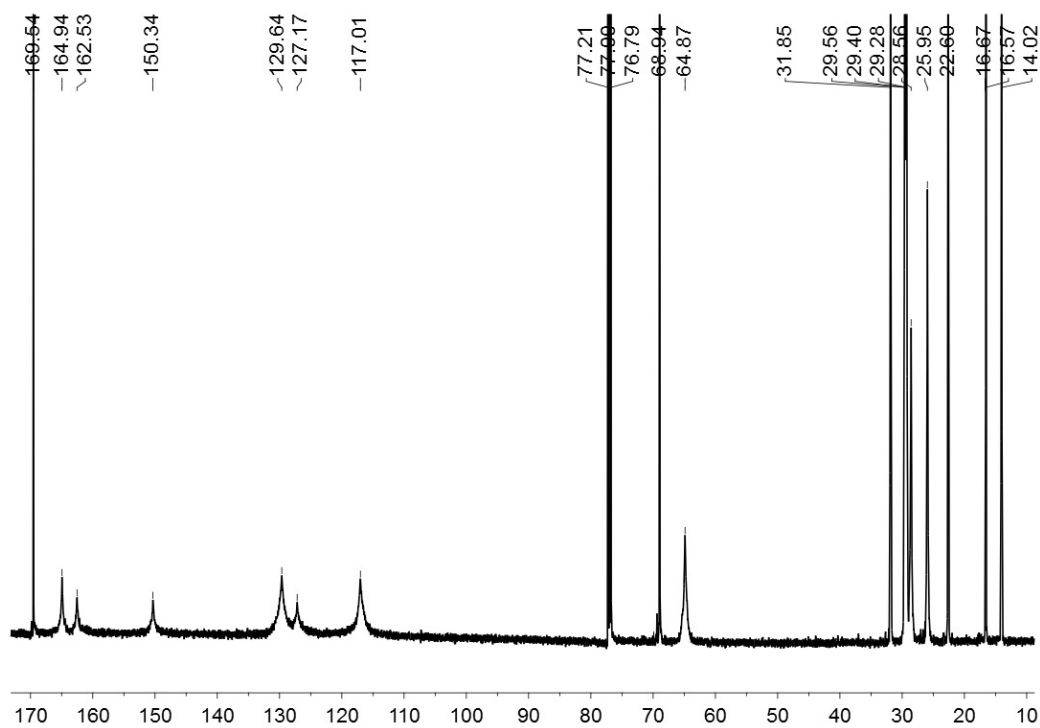


Fig. S30 ¹³C NMR (150 MHz) spectrum of the one-pot synthesized poly(**b2a_m-b-3_n**) via one-feed procedure measured in CDCl₃ at 25 °C.

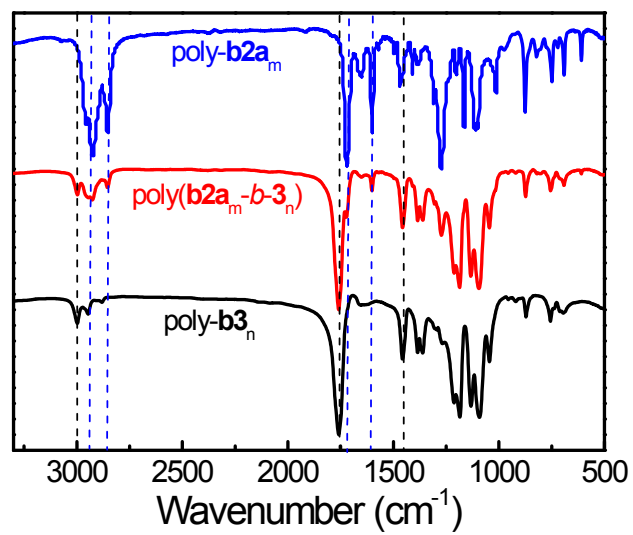


Fig. S31 Combined FT-IR spectra of poly-**b2a_m**, poly-**b3_n**, and the one-pot synthesized poly(**b2a_m-b-3_n**) via one-feed procedure measured at 25 °C using KBr pellets.