Supporting Information

Synthesis of Branched Bottlebrushes by the Combination of ATRP, Pd(II)-Initiated Isocyanide Polymerization, and ROMP

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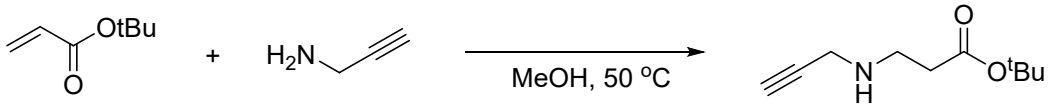
Measurements. All the ^{1}H nuclear magnetic resonance (NMR) spectra were recorded using a 600 MHz Bruker FT-NMR spectrometers {H} operated in the Fourier Transform mode. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual proton solvent as an internal standard. The Fourier transform infrared (FT-IR) spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. 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 TSK gel GMHHR-H columns. Molecular weight (M_n) and polydispersity (M_w/M_n) data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research).

Materials. All solvents were purchased from Sinopharm, and Aladdin Co. Ltd., and were purified by standard procedure before used. All chemicals were obtained from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. All the polymerizations were carried out under a dry nitrogen atmosphere.

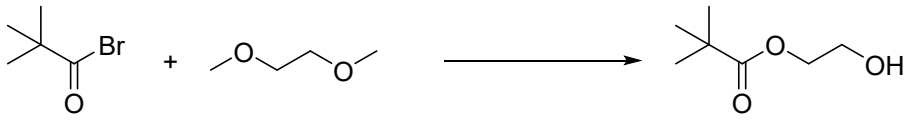
1. Synthetic Protocols



Compound 2

Scheme S1. Synthetic route for **Compound 2**.

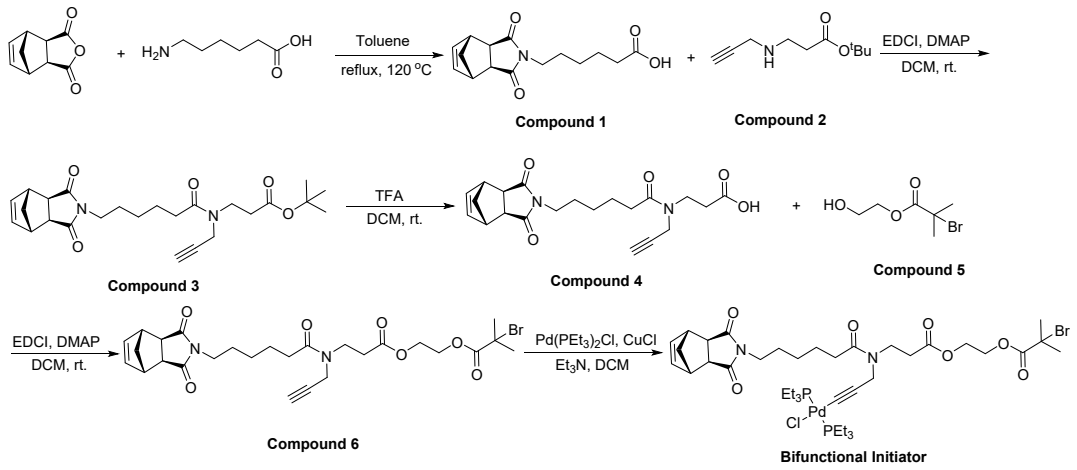
Synthesis of Compound 2. **Compound 2** was prepared following a literature procedure with slight modifications.[1] Propargylamine (3.6 mL, 0.055 mol, 2.2 eq) and *tert*-butyl acrylate (3.8 mL, 0.026 mol, 1.0 eq) were added to a round-bottom flask. Methanol (60 mL) was added, and the reaction mixture was stirred for 24 hours at 50 °C. The solution was then concentrated under vaccum, affording **Compound 2** as an orange liquid (3.84 g, 81 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.42 (d, J = 2.5 Hz, 2H), 2.90 (t, J = 6.4 Hz, 2H), 2.43 (t, J = 6.5 Hz, 2H), 2.21 (t, J = 2.4 Hz, 1H), 1.44 (s, 9H).



Compound 5

Scheme S2. Synthetic route for **Compound 5**.

Synthesis of Compound 5. **Compound 5** was prepared following a literature procedure with slight modifications.[2] Anhydrous ethylene glycol (113 mL, 2.1 mol) was added to a 250 mL 2-neck round bottom flask that had been flame-dried under vacuum and purged with 3 times with argon. The flask was equipped with a magnetic stirbar and rubber septum. The flask was then cooled to 0 °C in an ice bath. Slowly, α-bromoisobutyryl bromide (10 mL, 80.9 mmol) was added dropwise to the stirring ethylene glycol. The reaction stirred at 0 °C for 3 h. The reaction was quenched with 50 mL H_2O and extracted with DCM (3 x 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the DCM was removed by a rotary evaporator. The subsequent liquid was purified by distillation (85° C, 30 mTorr) to yield a viscous, clear, colorless liquid (12.3 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.32 – 4.29 (m, 2H), 3.87 – 3.86 (m, 2H), 1.94 (s, 6H).



Scheme S3. Synthetic route for **Bifunctional initiator**.

Compound 1, Compound 3 and **Compound 4** were prepared following a literature procedure with slight modifications.[3]

Synthesis of Compound 1: *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (1.0 g, 6.0 mmol, 1.0 eq) and 6-aminohexanoic acid (0.96 g, 7.4 mmol, 1.2 eq) were added to a RBF fitted with a condenser. Toluene (30 mL) was then added, and the solution was stirred overnight at 120 °C. The mixture was then allowed to cool to room temperature, and concentrated under vacuum. DCM was then added, and the solution was washed with 1M HCl, water, and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated under vacuum, affording the product as a white solid (1.54 g, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.27 (t, J = 1.9 Hz, 2H), 3.45 (t, J = 7.5 Hz, 2H), 3.26 (t, J = 1.9 Hz, 2H), 2.66 (d, J = 1.4 Hz, 2H), 2.32 (t, J = 7.4 Hz, 2H), 1.66 – 1.61 (m, 2H), 1.59 – 1.54 (m, 2H), 1.50 (dt, J = 9.8, 1.7 Hz, 1H), 1.36 – 1.32 (m, 2H), 1.20 (dd, J = 9.8, 1.9 Hz, 1H).

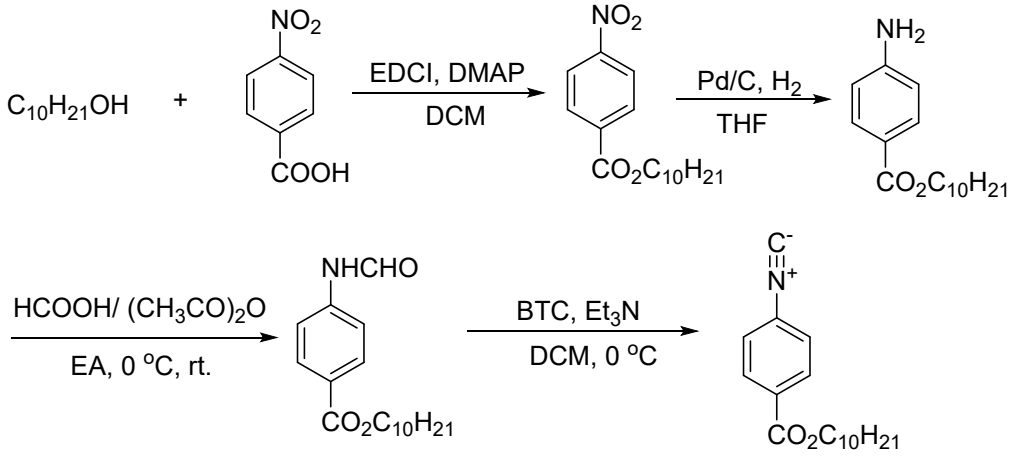
Synthesis of **Compound 3**: Into a 2-neck round bottom flask, ***Compound 2*** (0.8 g, 4.4 mmol, 1.0 eq), ***Compound 1*** (1.82 g, 6.5 mmol, 1.5 eq), *N*- (3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC·HCl) (1.3 g, 6.5 mmol, 1.5 eq), 4-dimethylaminopyridine (DMAP) (0.25 g, 2.1 mmol, 0.5 eq), and DCM (90 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (MeOH/DCM) of the crude mixture yielded **Compound 3** as a white solid (1.7 g, 87% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.28 (t, J = 1.9 Hz, 2H), 4.22 (d, J = 2.5 Hz, 1H), 4.10 (d, J = 2.5 Hz, 1H), 3.67 (dt, J = 36.8, 7.1 Hz, 2H), 3.48 – 3.45 (m, 2H), 3.27 (p, J = 1.7 Hz, 2H), 2.67 (d, J = 1.5 Hz, 2H), 2.55 (td, J = 7.2, 1.5 Hz, 2H), 2.38 – 2.35 (m, 2H), 1.68 – 1.66 (m, 2H), 1.60 – 1.55 (m, 4H), 1.44 (d, J = 8.7 Hz, 10H), 1.37 – 1.32 (m, 2H).

Synthesis of Compound 4: Add **Compound 3** (2.48 g, 5.61 mmol) to a round bottom flask. Add a solution of trifluoroacetic acid (TFA) and DCM (v/v = 1/2) (60 mL). Stir the reaction mixture for an hour at 0 °C. Determine the complete conversion by thin layer chromatography (TLC). Concentrate the solution and re-dissolve in DCM. Wash with 1M HCl, water and brine. Collect the organic layer, dry over Na_2SO_4, and concentrate under

vacuum, affording ***Compound 4*** as a white solid (2.0 g, 94% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.28 (t, J = 1.9 Hz, 2H), 4.24 – 4.11 (m, 2H), 3.78 (t, J = 7.0 Hz, 1H), 3.68 (t, J = 6.8 Hz, 1H), 3.45 (t, J = 7.4 Hz, 2H), 3.26 (t, J = 1.9 Hz, 2H), 2.71 – 2.67 (m, 4H), 2.38 (t, J = 7.4 Hz, 2H), 1.67 (ddt, J = 15.2, 10.7, 8.0 Hz, 2H), 1.58 – 1.50 (m, 3H), 1.36 – 1.29 (m, 3H), 1.20 (d, J = 9.8 Hz, 1H).

Synthesis of Compound 6**:** Into a 2-neck round bottom flask, ***Compound 4*** (3.0 g, 7.7 mmol), ***Compound 5*** (1.1 g, 5.2 mmol), *N*- (3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (EDC·HCl) (1.5 g, 7.7 mmol), 4-dimethylaminopyridine (DMAP) (0.51 g, 4.2 mmol) and DCM (90 mL) were added. The reaction mixture was stirred overnight and then concentrated under vacuum. Column chromatography (EA/PE = 1:2) of the crude mixture yielded **Compound 6** as a white solid (4.0 g, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.08 (q, J = 1.8 Hz, 2H), 4.39 – 4.32 (m, 4H), 4.20 (d, J = 2.6 Hz, 1H), 4.09 (d, J = 2.5 Hz, 1H), 3.76 – 3.66 (m, 2H), 3.37 (dt, J = 3.7, 1.9 Hz, 2H), 3.31 (t, J = 7.4 Hz, 2H), 3.22 (dd, J = 2.9, 1.6 Hz, 2H), 2.68 (q, J = 7.3, 6.9 Hz, 2H), 2.34 (t, J = 7.8 Hz, 2H), 1.92 (d, J = 3.9 Hz, 6H), 1.71 (dt, J = 8.7, 1.7 Hz, 1H), 1.65 – 1.60 (m, 2H), 1.52 (dd, J = 8.7, 1.6 Hz, 1H), 1.47 – 1.42 (m, 3H), 1.30 – 1.23 (m, 3H).

Synthesis of Bifunctional initiator: The **Bifunctional initiator** was prepared following a literature procedure with slight modifications.[4] **Compound 6** (1.0 g, 1.72 mmol) was treated with trans-dichlorobis(triethylphosphine)palladium (0.78 g, 1.88 mmol) in the presence of copper(I) chloride (8.9 mg, 0.09 mmol) as catalyst in the mixture of diethylamine (8 mL) and dichloromethane (8 mL). The reaction solution was stirred at room temperature for overnight. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography with petrol ether and dichloromethane as the eluent (v/v = 3/1) to afford **Bifunctional initiator** as a yellow solid (1.3 g, 79% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.05 (t, J = 2.1 Hz, 2H), 4.34 – 4.28 (m, 4H), 4.02 (t, J = 1.7 Hz, 2H), 3.61 (t, J = 7.1 Hz, 2H), 3.35 – 3.34 (m, 2H), 3.21 – 3.20 (t, J = 7.4 Hz, 2H), 3.20 (dd, J = 3.0, 1.5 Hz, 2H), 2.65 – 2.62 (q, J = 7.1, 6.4 Hz, 2H), 2.35 – 2.33 (m, 2H), 1.90 – 1.83 (m, 20H), 1.60 – 1.55 (p, J = 7.7 Hz, 2H), 1.44 – 1.39 (m, 2H), 1.17 (t, J = 7.0 Hz, 2H), 1.14 – 1.08 (m, 18H).



Scheme S4. Synthetic route for **monomer 2.**

Monomer 2 was prepared following a literature procedure with slight modifications.[5] **Monomer 2** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 – 8.00 (m, 2H), 7.44 (d, J = 8.6 Hz, 2H), 4.32 (t, J = 6.7 Hz, 2H), 1.76 (dt, J = 14.8, 6.8 Hz, 2H), 1.41 (td, J = 9.4, 8.6, 5.0 Hz, 2H), 1.37 – 1.17 (m, 14H), 0.87 (t, J = 7.0 Hz, 3H).

Atom transfer radical polymerization (ATRP) of vinyl monomer initiated by Bifunctional initiator: A 10 mL oven-dried and nitrogen-filled flask was charged with *tert*-butyl acrylate (**monomer 1**) (384.0 mg, 3.0 mmol), **Bifunctional initiator** (90.0 mg, 0.1 mmol), and CuBr (1 equiv, 14.7 mg, 0.1 mmol). Deoxygenated THF (2.5 mL) and Me_6TREN (1 equiv, 23.6 mg, 0.1 mmol) were added via a syringe. The degassed reaction flask was then immersed into a pre-heated oil bath at 55 °C and stirred for 8 h. After being cooled to room temperature, the polymerization solution was precipitated into a large amount of water and methanol (v:v = 5:5), collected by centrifugation and dried in vacuum at room temperature overnight, afforded **P*t*BA$_{30}$**.

Polymerization of isocyanide monomer initiated by PtBA$_{30}$: A 10 mL oven-dried and nitrogen-filled flask was charged with monomer **2** (172.2 mg, 0.6 mmol), and **P*t*BA$_{30}$** (86 mg, 0.02 mmol of the Pd(II) group) in 1.0 mL THF, and a stir bar. The concentrations of monomer **2** and catalyst (**P*t*BA$_{30}$** were 0.6 and 0.003 M, respectively ([monomer **2**]$_0$/[Pd(II)]$_0$= 20). The degassed reaction flask was then immersed into a pre-heated oil bath at 55 °C and stirred for 8 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, afforded **P*t*BA$_{30}$-PI$_{20}$**.

Typical Procedure for ROMP of PtBA$_{30}$-PI$_{20}$ with G3 as Catalyst. A solution of **G3** in THF (0.008 mmol, 0.1 mL) was added to a degassed solution of **P*t*BA$_{30}$-PI$_{20}$** (250 mg, 0.024 mmol) in THF (0.30 mL) via a microsyringe. The initial concentrations of **P*t*BA$_{30}$-PI$_{20}$** and catalyst **G3** were 0.2 and 0.01 M, respectively ([**P*t*BA$_{30}$-PI$_{20}$**]$_0$/[**G3**]$_0$ = 30). After the reaction mixture was stirred at room temperature for 1 h. The polymerization was then quenched by addition of ethyl vinyl ether (1.0 mL) and poured into a large amount methanol. The precipitated solid was collected by centrifugation, washed with methanol, and dried under vacuum to afford (**P*t*BA$_{30}$-PI$_{20}$)$_{30}$**.

References

1. O. Roy, S. Faure, V. Thery, C. Didierjean, and C. Taillefumier. Cyclic *β*-peptoids. *Org. Lett.,* 2008, **10**, 921.
2. M. A. White, J. A. Johnson, J. T. Koberstein, and N. J. Turro. *J. Am. Chem. Soc.,* 2006, **128**, 11356.
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4. 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. Air-Stable (Phenylbuta-1,3-diynyl)palladium(II) Complexes: Highly Active Initiators for Living Polymerization of Isocyanides. *J. Am. Chem. Soc*., 2014, **136**, 4706.
5. Z.-Q. Wu, R. J. Ono, Z. Chen, and C. W. Bielawski. Synthesis of Poly(3-alkylthiophene)-block-poly(arylisocyanide): Two Sequential, Mechanistically Distinct Polymerizations Using a Single Catalyst. *J. Am. Chem. Soc.,* 2010*,* **132***,* 14000.

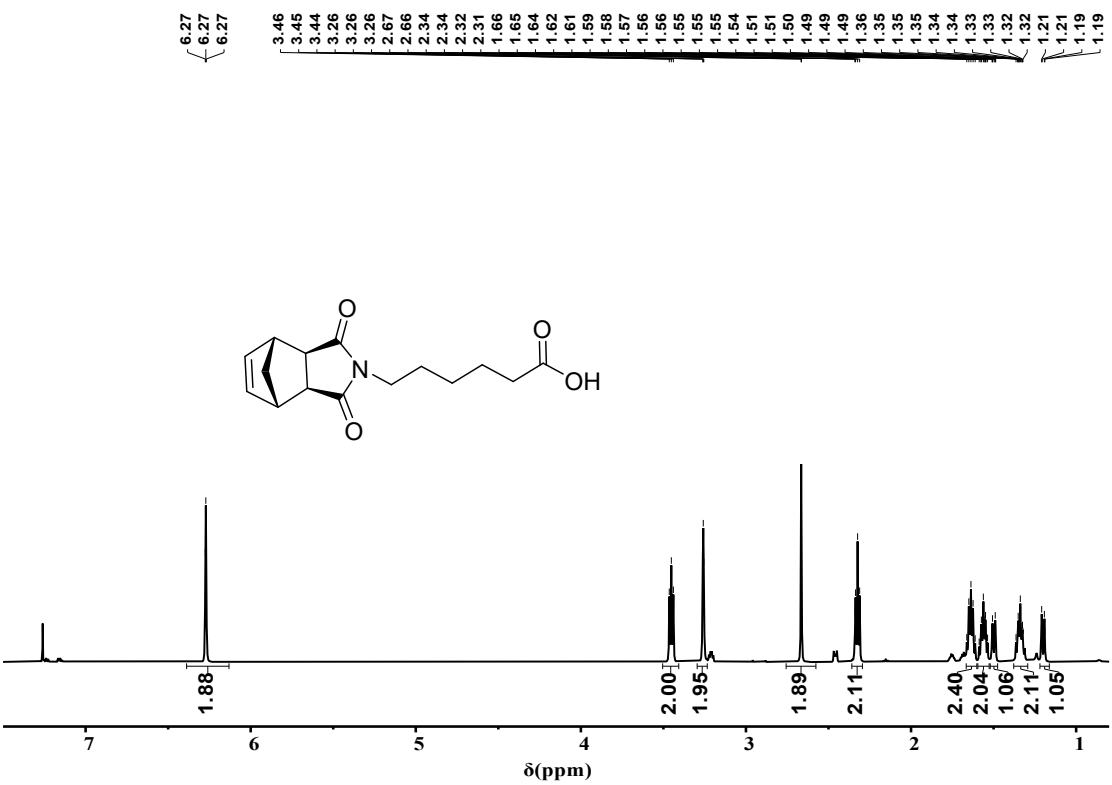

Figure S1. ^{1}H NMR (600 MHz) spectrum of **Compound 1** measured in $CDCl_3$ at 25 °C.

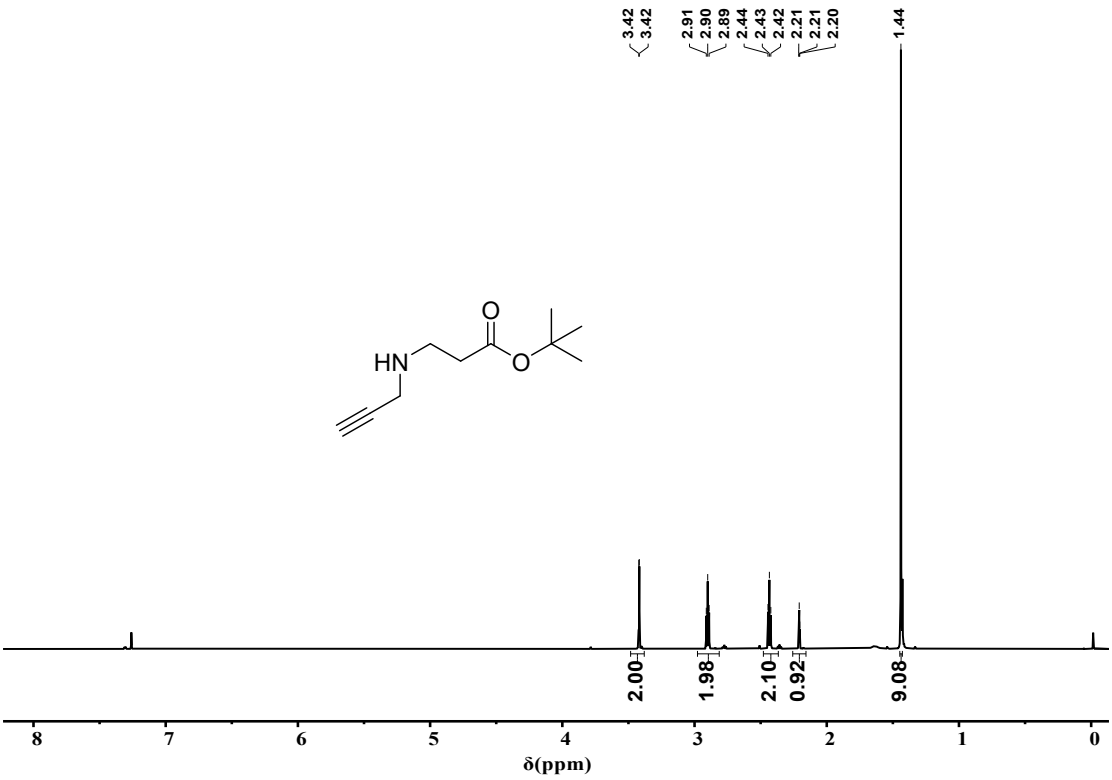

Figure S2. ^{1}H NMR (600 MHz) spectrum of **Compound 2** measured in $CDCl_3$ at 25 °C.

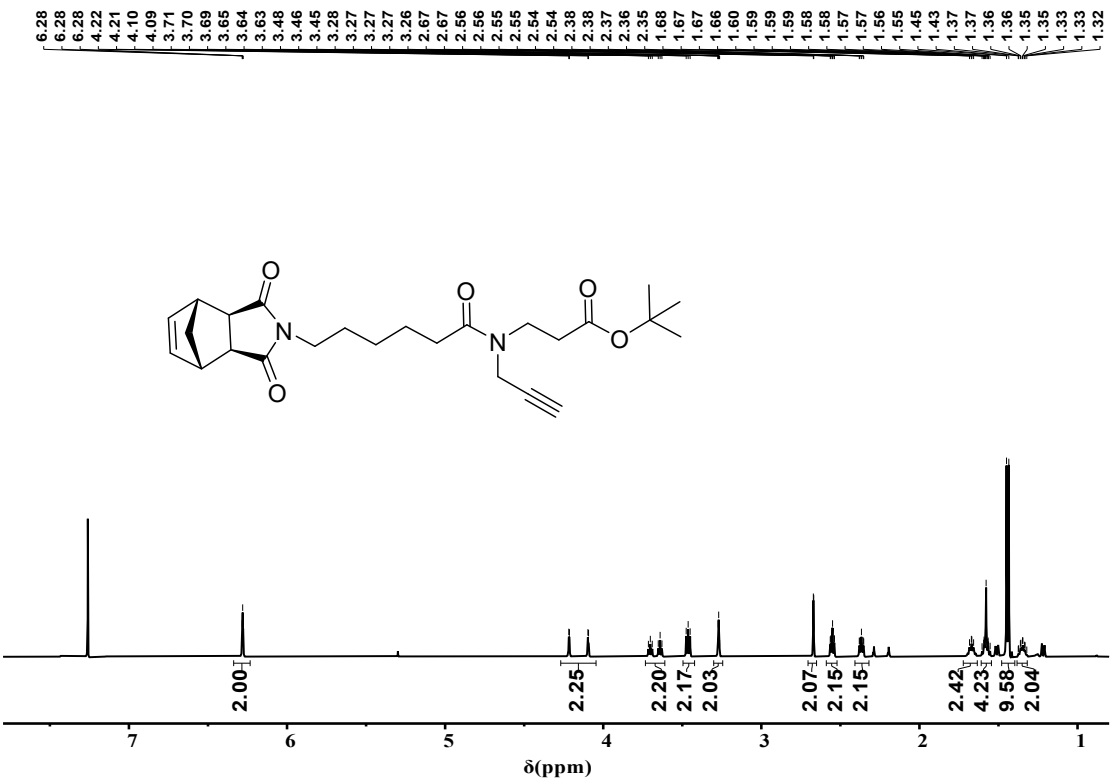

Figure S3. ^{1}H NMR (600 MHz) spectrum of **Compound 3** measured in $CDCl_3$ at 25 °C.

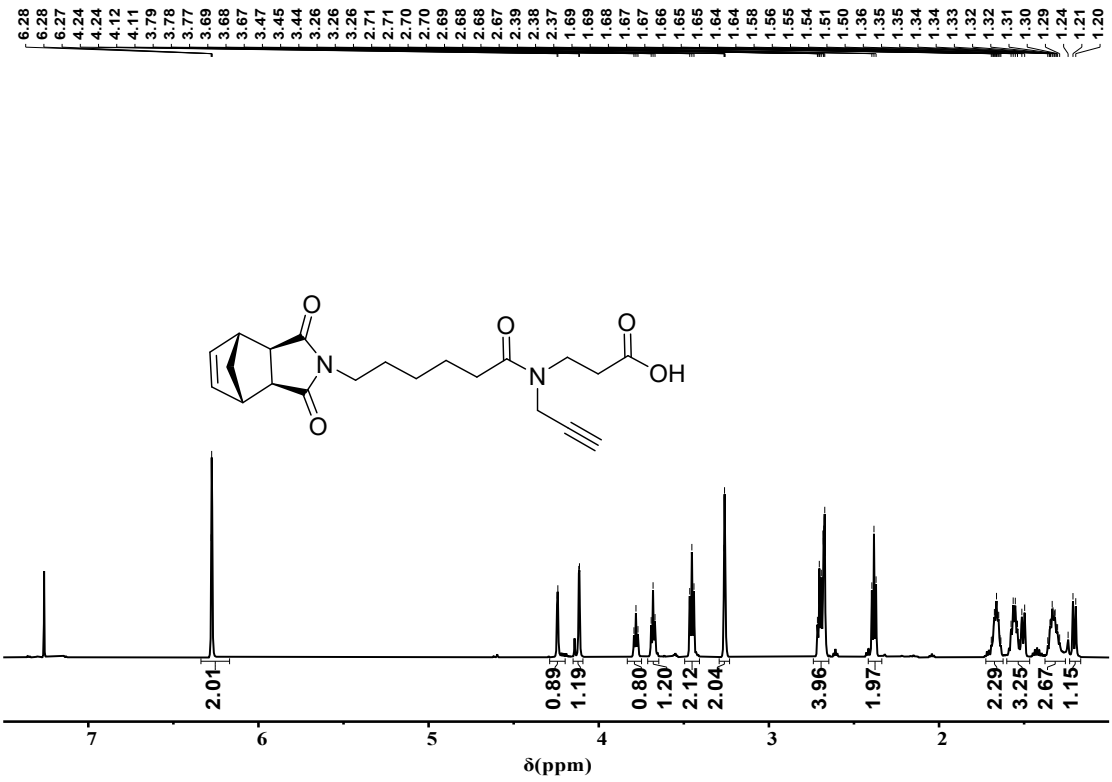

Figure S4. ^{1}H NMR (600 MHz) spectrum of **Compound 4** measured in $CDCl_3$ at 25 °C.

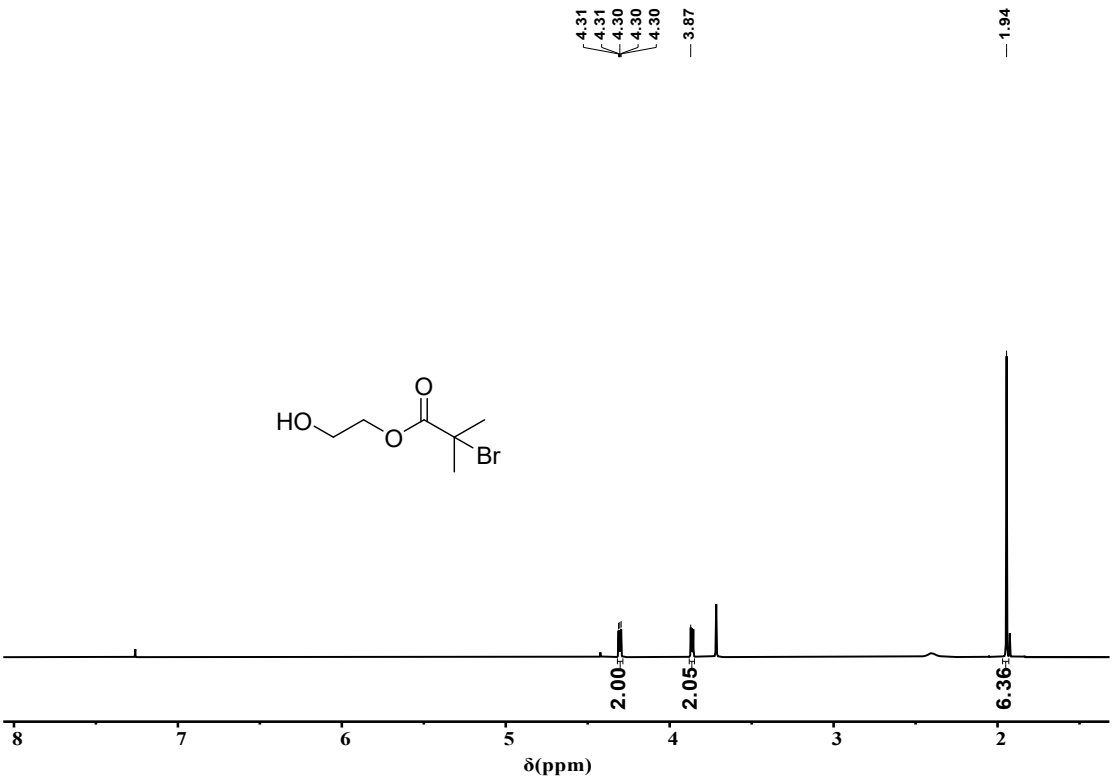

Figure S5. ^{1}H NMR (600 MHz) spectrum of **Compound 5** measured in $CDCl_3$ at 25 °C.

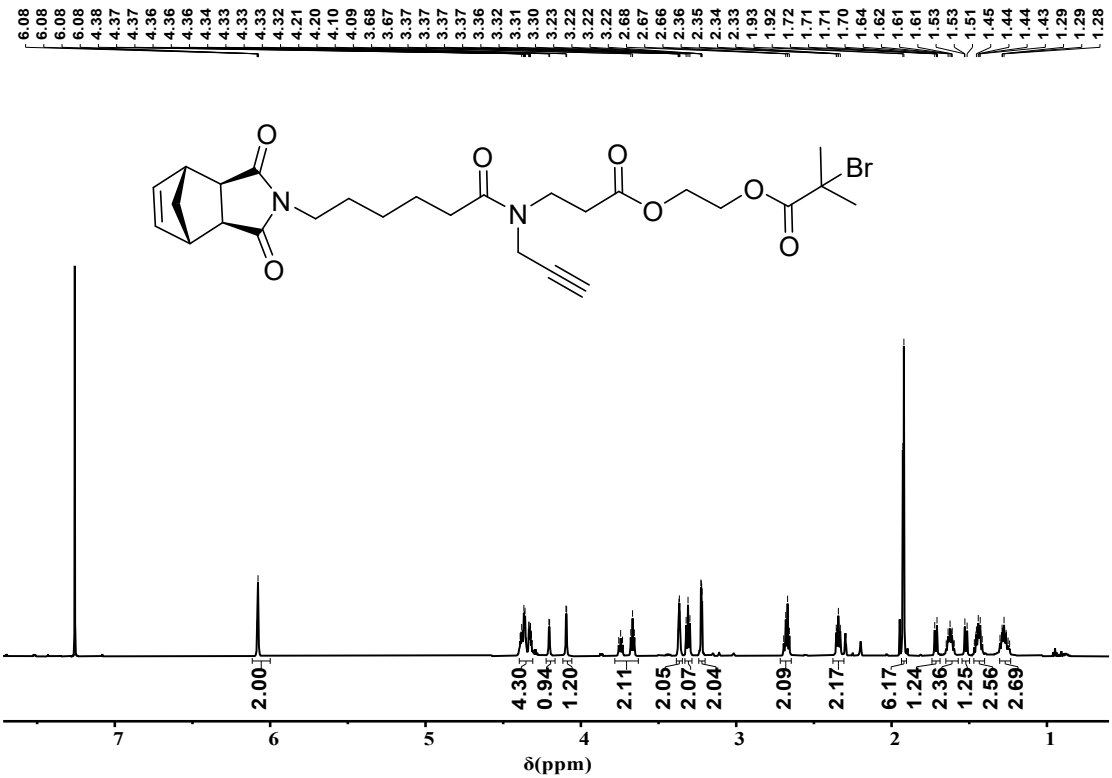

Figure S6. ^{1}H NMR (600 MHz) spectrum of **Compound 6** measured in $CDCl_3$ at 25 °C.

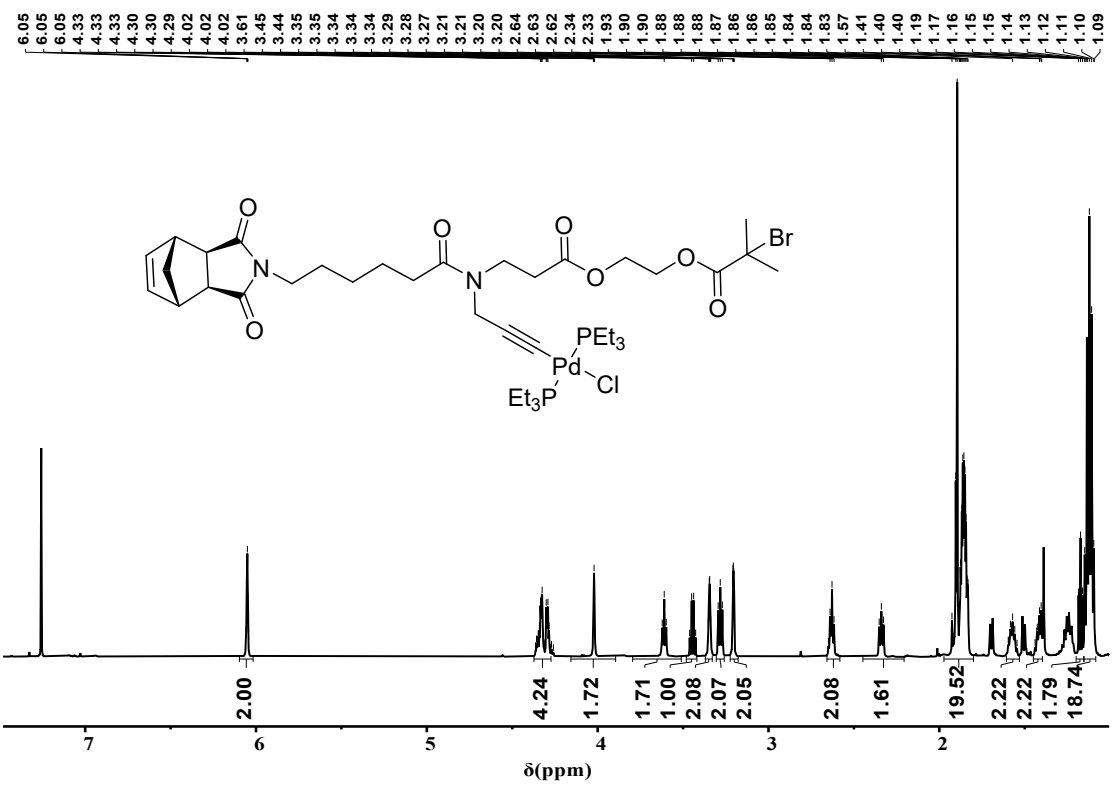

Figure S7. ^{1}H NMR (600 MHz) spectrum of **Bifunctional Initiator** measured in $CDCl_3$ at 25 °C.

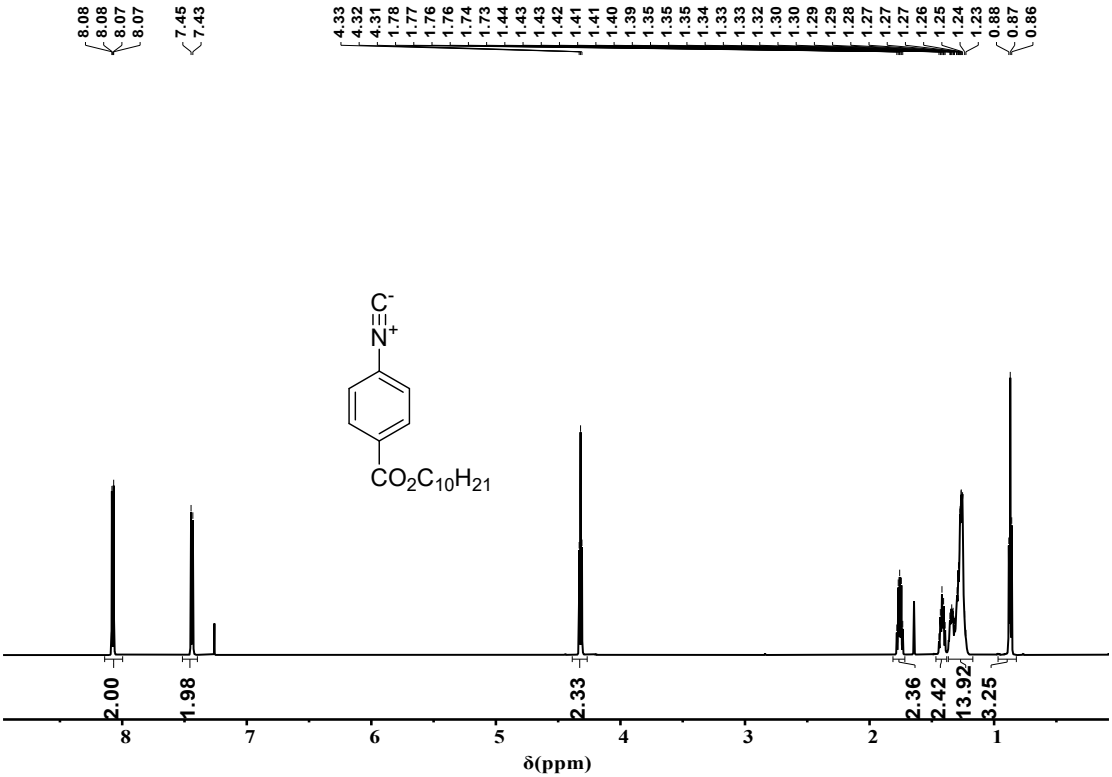

Figure S8. ^{1}H NMR (600 MHz) spectrum of **monomer 2** measured in $CDCl_3$ at 25 °C.

Table S1. The polymerization results of **P*t*BA$_{100}$**, **P*t*BA$_{100}$-PI$_{50}$** and **(P*t*BA$_{100}$-PI$_{50}$)$_{20}$**.

Polymer	M_n (kDa)[a]	PDI[a]	Yiled[b]
P*t*BA$_{100}$	8.5	1.26	82
P*t*BA$_{100}$-PI$_{50}$	61.7	1.08	87
(P*t*BA$_{100}$-PI$_{50}$)$_{20}$	278.1	1.07	89

[a]M_n and M_w/M_n values were obtained through SEC with reference to polystyrene standards. [b]The isolated yields.

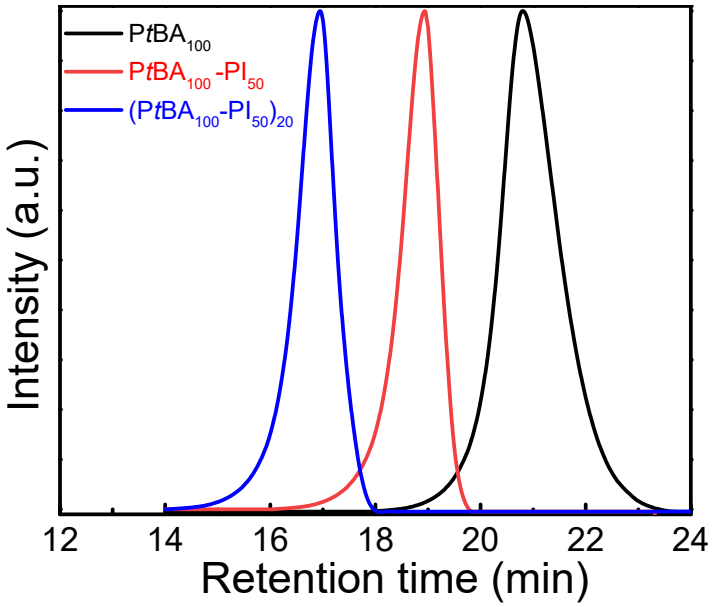

Figure S9. Size exclusion chromatograms of **P*t*BA$_{100}$**, **PtBA$_{100}$-PI$_{50}$**, **(P*t*BA$_{100}$-PI$_{50}$)$_{20}$**.