Supporting Information

Synthesis of Double-Stranded Polymers Based on Stereoregular Rigid Helical Poly(phenyl isocyanide)s

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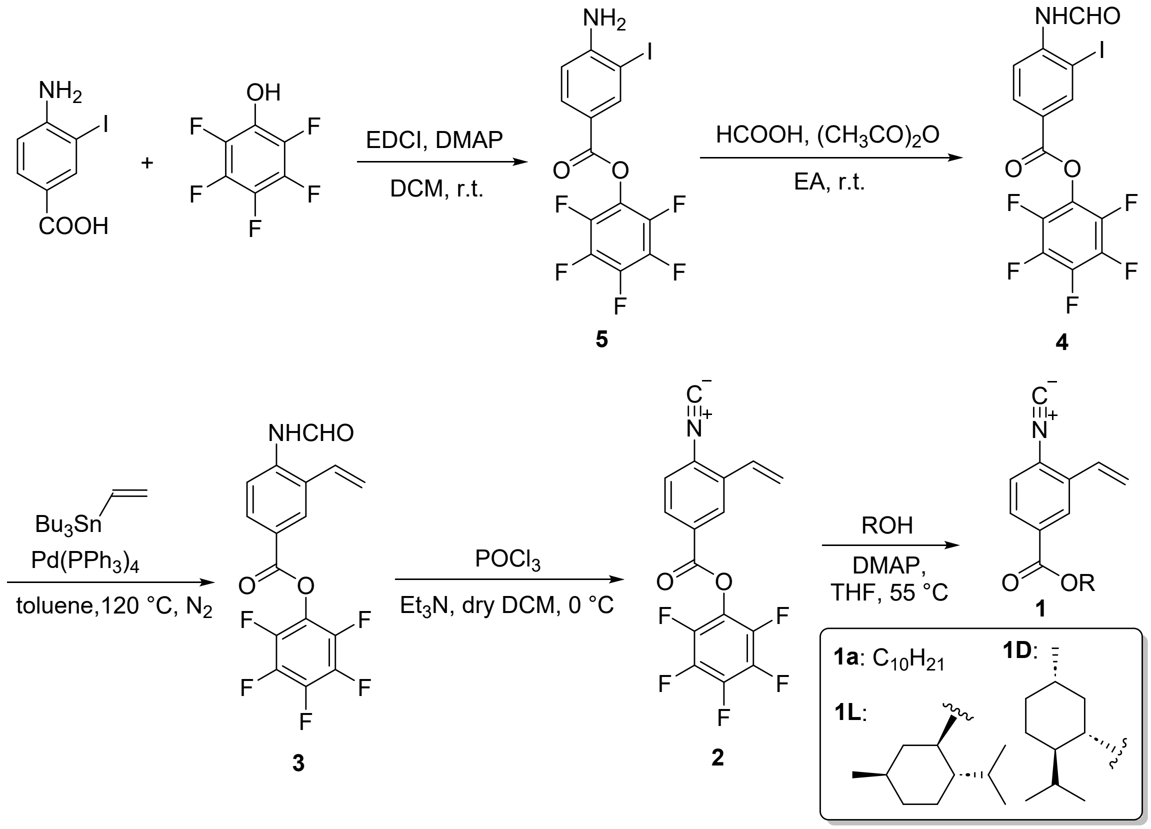
Measurements. NMR spectra were recorded using a Bruker 600 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on SHIMADZU LC-20ADXR pump and SHIMADZU RID-20A differential refractive index (RI) detector (set at 40 °C) using Shodex KF-805L Styragel columns. Molecular weight (M_n) and polydispersity (M_w/M_n) data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. CD and UV-vis spectra were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1500 and SHIMADZU 2600i UV/vis double beam spectropolarimeter, respectively. High Resolution Mass Spectrometry (HRMS) were recorded using a were recorded on a AB5600 from AB SCIEX, USA. Using an electro spray ion source (ESI) in positive ion mode. MALDI-TOF MS spectra were taken using a Bruker AutoFlex Speed MALDI-TOF MS using trans-2-[3-(4-tert-Butylphenyl)-2methyl-2-propenylidene]malononitrile (DCTB) as a matrix. Atomic force microscope (AFM) was performed on a Cypher S (Oxford Instruments, Asylum Research). Thermogravimetric analysis (TGA) test was performed in nitrogen atmosphere at a heating rate of 10 ^oC/min using a Netzsch STA 2500 instrument.

Materials. All solvents were obtained from Sinopharm. Co. Ltd. and were purified by the standard procedures before use. All chemicals were purchased from Aladdin and Sigma-Aldrich. Co. Ltd., and were used as received without further purification otherwise denoted. The structures of these compounds were confirmed by ^1H NMR.

Scheme S1. Synthesis of monomer



Synthesis of compound 5.[1] To a mixture of 4-amino-3-iodobenzoic acid (5.00 g, 19 mmol), pentafluorophenol (3.49 g, 19 mmol), EDCI (4.37 g, 22.80 mmol) and DMAP (2.04 g, 16.7 mmol) was added in DCM (100 mL). After stirring the mixture at room temperature for 6 h. The organic layer was washed twice with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (Petroleum ether/ethyl acetate = 5/1) to give white solid **5** (7.33 g, 90 % yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.48–8.47 (d, J = 6.00 Hz, 1H), 7.96–7.95 (m, 1H), 6.77–6.76 (d, J = 6.00 Hz, 1H), 4.76 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 161.12, 152.16,142.32, 132.44, 117.27, 113.12, 81.91. ^{19}F NMR (565 MHz, $CDCl_3$, 25 °C): δ –152.50, –158.33, –162.51. m/z calcd for $C_{13}H_5F_5INO_2$ $[M+H]^+$: 429.9285; Found: 429.9355.

Synthesis of compound 4.[1] To a mixture of formic acid (5.85 mL, 155.09 mmol) and acetic anhydride (2.93 mL, 31.01 mmol) was stirred at room temperature for 2 h. Compound **5** (5.32 g, 12.41 mmol) was added the mixture at 0 °C and then warm to room temperature. After stirring the mixture at room temperature for 2 h in nitrogen atmosphere, the mixture was washed with water, saturated aqueous $NaHCO_3$ solution, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo to give white solid **4** (4.99 g, 88% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.92–8.90 (d, J = 12.00 Hz, 0.22 H), 8.64–8.55 (m, 2.58 H), 8.20–8.16 (d, J = 24.00 Hz, 1H), 7.85 (s, 1H), 7.37–7.36 (s, 0.21H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 160.71, 159.20, 142.87, 142.60, 142.27, 141.52, 140.53, 138.90, 137.22, 132.20, 125.19, 124.02, 120.89, 116.53. ^{19}F NMR (565 MHz, $CDCl_3$, 25 °C): δ –152.29, –157.01, –161.77. m/z calcd for $C_{14}H_5F_5INO_3$ $[M+H]^+$: 457.9234; Found: 457.9306.

Synthesis of compound 3.[1] To a mixture of $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol), Tributyl(vinyl)tin (3.7 mL, 12.57 mmol) and **5** (5.53 g, 12.09 mmol) was added in toluene (60 mL). After stirring the mixture at 120 °C for 8 h in nitrogen atmosphere, the mixture was cooled to room temperature, then treated with saturated aqueous KF solution (35 g/100 mL), allowed to stir for 1 h. The organic layer was washed twice with brine, dried over

Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give yellow brown solid **3** (3.36 g, 78 % yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 6.84–6.79 (m, 1H), 5.86–5.80 (t, J = 18.00 Hz, 1H), 5.66–5.62 (t, J = 12.00 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 162.26, 162.10, 161.95, 159.13, 12.20, 140.65, 139.41, 139.32, 138.93, 137.25, 131.41, 131.35, 130.89, 130.75, 130.39, 130.32, 130.07, 129.08, 125.45, 123.99, 123.05, 121.78, 121.70, 121.09, 119.06. ^{19}F NMR (565 MHz, $CDCl_3$, 25 °C): δ –152.42, –157.57, –162.06. m/z calcd for $C_{16}H_8F_5NO_3$ $[M+H]^+$: 358.0424; Found: 358.0498.

Synthesis of compound 2.[1] To a solution of **3** (1.00 g, 2.80 mmol) in dry CH_2Cl_2 (50 mL) was added NEt_3 (1.58 mL, 12.08 mmol) and $POCl_3$ (0.52 mL, 6.04 mmol) at 0 °C. After stirring the mixture at 0 °C for 30 min, the solution was diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ solution, brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to give faint yellow solid **2** (0.76 g, 80 % yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.45–8.44 (s, 1H), 8.12–8.10 (d, J = 12.0 Hz, 1H), 7.55–7.54 (d, J = 6.0 Hz, 1H), 7.10–7.05 (m, 1H), 6.06–6.03 (d, J = 18.0 Hz, 1H), 5.68–5.66 (d, J = 12.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 171.17, 161.26, 142.01, 140.42, 138.83, 137.14, 134.85, 130.19, 129.82, 129.10, 128.35, 127.76, 120.46. ^{19}F NMR (565 MHz, $CDCl_3$, 25 °C): δ –152.29, –156.97, –161.73. m/z calcd for $C_{16}H_6F_5INO_3$ $[M+H]^+$: 340.0319; Found: 340.0396.

Synthesis of compound 1a.[1] To a solution of **2** (1.00 g, 2.95 mmol) in THF (10 mL) was added *n*-decyl alcohol (0.48 g, 3.00 mmol) and DMAP (0.37 g, 3.00 mmol). After stirring the mixture at 55 °C for 6 h. The solution was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10/1) to give faint yellow solid **1a** (0.83 g, 90 % yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.29–8.29 (s, 1H), 7.94–7.93 (d, J = 6.00 Hz, 2H), 7.43–7.42 (d, J = 6.00 Hz, 2H), 7.07–7.02 (m, 1H), 6.01–5.98 (d, J = 18.00 Hz, 1H), 5.60–5.58 (d, J = 12.00 Hz, 1H), 4.35–4.33 (t, J = 6.00 Hz, 2H), 1.79–1.76 (m, 2H), 1.44–1.25 (m, 14H), 0.89–0.87 (t, J = 6.00 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.91, 147.99, 132.03, 130.58, 129.70, 123.07, 120.60, 117.16, 114.99, 64.76, 32.02, 29.67, 29.44, 27.97, 26.97, 26.20, 22.80, 17.66, 14.24, 13.73. m/z calcd for $C_{20}H_{27}NO_2$ $[M+H]^+$: 314.2042; Found: 314.2114. FT-IR (KBr, cm^{-1}): 2120 ($v_{N\equiv C}$), 1720 ($v_{C=O}$), 1610 ($v_{C=C}$).

Compounds **1L** and **1D** were synthesized according to the similar procedure from the reaction of **1a**.

1L: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.28 (s, 1H), 7.94–7.92 (d, J = 12.00 Hz, 2H), 7.43–7.41 (d, J = 12.00 Hz, 2H), 7.07–7.02 (m, 1H), 6.01–5.98 (d, J = 18.00 Hz, 1H), 5.60–5.58 (d, J = 12.00 Hz, 2H), 4.96–4.95 (m, 1H), 2.13–2.10 (d, J = 18.00 Hz, 1H), 1.90–1.89 (m, 1H), 1.76–1.73 (d, J = 18.00 Hz, 2H), 1.59–1.54 (t, J = 15.00 Hz, 2H), 1.15–1.11 (d, J = 24.00 Hz, 2H), 0.94–0.91 (m, 8H), 0.80–0.79 (d, J = 6.00 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 169.67, 164.77, 134.25, 131.82, 130.44, 129.37, 127.79, 127.30, 127.27, 119.66, 75.88, 47.35, 41.03, 34.37, 31.59, 26.76, 23.81, 22.16, 20.85, 16.70. m/z calcd for $C_{20}H_{25}NO_2$ $[M+H]^+$: 312.1885; Found: 312.1958. FT-IR (KBr, cm^{-1}): 2120 ($\nu_{N\equiv C}$), 1720 ($\nu_{C=O}$), 1610 ($\nu_{C=C}$).

1D: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.28 (s, 1H), 7.94–7.92 (m, 1H), 7.43–7.41 (d, J = 12.00 Hz, 1H), 7.07–7.02 (m, 1H), 6.00-5.98 (d, J = 12.00 Hz, 1H), 5.60–5.58 (d, J = 12.00 Hz, 1H), 4.98–4.93 (m, 1H), 2.13–2.09 (d, J = 24.00 Hz, 1H), 1.92–1.89 (m, 1H), 1.76–1.72 (d, J = 24.00 Hz, 2H), 1.59–1.54 (m, 2H), 1.17–1.09 (m, 2H), 0.97–0.87 (m, 8H), 0.84–0.79 (d, J = 6.00 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 169.67, 164.76, 134.25, 131.82, 130.44, 129.37, 127.79, 127.30, 127.27, 119.65, 75.87, 47.34, 41.03, 34.36, 31.59, 26.76, 23.81, 22.16, 20.85, 16.70. m/z calcd for $C_{20}H_{25}NO_2$ $[M+H]^+$: 312.1885; Found: 312.1958. FT-IR (KBr, cm^{-1}): 2120 ($\nu_{N\equiv C}$), 1720 ($\nu_{C=O}$), 1610 ($\nu_{C=C}$).

For method 1:

Typical polymerization procedure for poly-S1-1a$_m$. A 10 mL oven-dried flask was charged with monomer **1a** (47.49 mg, 0.14 mmol), aryl alkyne–Pd(II) (0.7 mg, 0.0014 mmol), THF (0.70 mL), and a stir bar. The concentrations of monomer **1a** and aryl alkyne–Pd(II) were 0.2 M, and 0.002 M, respectively ([**1a**]$_0$/[Pd(II)]$_0$ = 100). The reaction flask was then immersed into an 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 to give poly-S1-**1a**$_{100}$ as a brownish-yellow solid (38.00 mg, 80% yield). ^{1}H NMR (600 MHz,

$CDCl_3$, 25 °C): δ 8.5–4.5 (br, 6H), 4.5–3.5 (br, 2H) 2.5–0.5 (br, 19H). FT-IR (KBr, cm^{-1}): 1720 ($\nu_{C=O}$), 1610 ($\nu_{C=C}$).

Kinetic studies. A mixture of monomer **1a** (68.0 mg, 0.20 mmol) and a standard polystyrene (M_n = 3.3 kDa, M_w/M_n = 1.04, 20 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 (1.00 mL) was added by a micro-syringe. To this was added a solution of the Pd(II) catalyst ($[Pd]_0$= 0.0020 mmol) in THF (0.10 mL) via a micro-syringe at ambient temperature ($[\mathbf{1a}]_0$ = 0.2 M, $[\mathbf{1a}]_0/[Pd]_0$= 100). The mixture was then stirred under nitrogen atmosphere at 55 °C. The polymerization of **1a** was followed by measuring SEC of the aliquots removed from the reaction mixture at appropriate time intervals. The peak area of unreacted **1a** relative to that of the internal standard (PS) was used for the determination of the conversion of monomer **1a** 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 polystyrene standards.

Typical polymerization procedure for double-stranded polymers poly-D-1a_m. Poly-S1-$\mathbf{1a}_{100}$ (31.30 mg, 0.1 mmol) was subjected to radical polymerization using AIBN (0.012 mg, 7.35×10^{-5} mmol) and 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (0.37 mg, 1×10^{-3} mmol) as the chain transfer agent (CTA) as the initiator in 1 mL of toluene at 65 °C stirred for 24 h. Prior to polymerization, the reaction mixture was degassed by three freeze–pump–thaw cycles using liquid nitrogen to remove oxygen. 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 to give poly-D-**1a**$_{100}$ as a yellow solid (45.00 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.5–6.0 (br, 3H), 4.5–3.2 (br, 2H), 2.5–0.5 (br, 22H). FT-IR (KBr, cm^{-1}): 1720 ($\nu_{C=O}$), 1620 ($\nu_{C=N}$).

For method 2:

Typical polymerization procedure for poly-S2-1a$_m$. A 10 mL Schlenk vial equipped with a stir bar was charged with **1a** (68 mg, 0.2 mmol), CTA (3.65 mg, 0.01 mmol), and AIBN (0.66 mg, 4.00×10^{-3} mmol) and toluene (1 mL). After the vial was sealed, mixture was deoxygenated via three freeze-pump-thaw cycles, backfilled with nitrogen, and then heated at 65 °C for 24 h. Then, the vial was cooled and open to air to stop the polymerization, and precipitated in methanol, yielding the poly-S2-**1a**$_m$ (40 mg, 60 % yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.5–6.5 (br, 3H), 4.7–3.5 (br, 2H), 2.0–0.5 (br, 19H). FT-IR (KBr, cm^{-1}): 2115 ($\nu_{N\equiv C}$), 1712 ($\nu_{C=O}$).

Typical polymerization procedure for double-strand polymers poly-D-1a$_m$.[2] A 10 mL Schlenk vial equipped with a stir bar was charged with poly-S2-**1a**$_{10}$ (31.30 mg, 0.1 mmol) and alkyne–Pd(II) (0.01 mmol, 5.1 mg) in THF (1ml), The reaction flask was then immersed into an 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 to give poly-D-**1a**$_{10}$ as a brownish-yellow solid (30.00 mg, 75 % yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.5–

6.5 (br, 3H), 4.5–3.2 (br, 2H), 2.3–0.5 (br, 22H). FT-IR (KBr, cm^{-1}): 2115 ($\nu_{N\equiv C}$) ,1720 ($\nu_{C=O}$), 1615 ($\nu_{C=N}$).

AFM sample preparation. The samples were prepared by spin-coating 30 μL solution of double-stranded polymer in THF (0.02 mg/mL) on mica substrate, dry at room temperature for two hours. Imaging was conducted in air at ambient temperature.

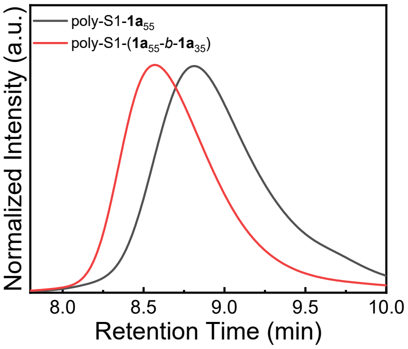


Figure S1. SEC chromatograms of chain-extended polymers: macroinitiator poly-S1-**1a**$_{55}$ and block polymer poly-S1-(**1a**$_{55}$-*b*-**1a**$_{35}$).

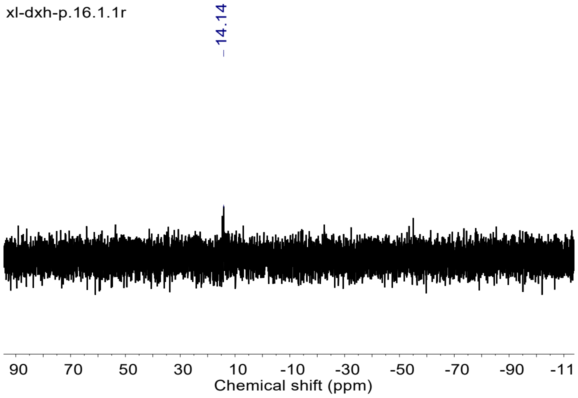


Figure S2. ^{31}P NMR (243 MHz) spectrum of poly-S1-**1a**$_n$ measured in CDCl3 at 25 °C.

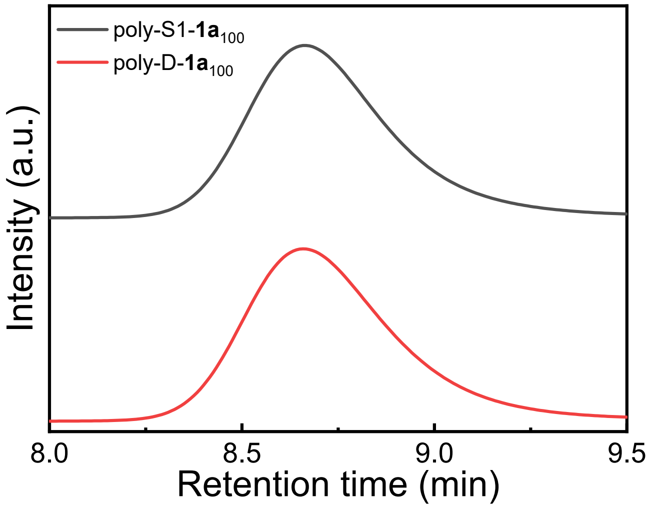


Figure S3. SEC trace of poly-S1-**1a**$_{100}$ and poly-D-**1a**$_{100}$.

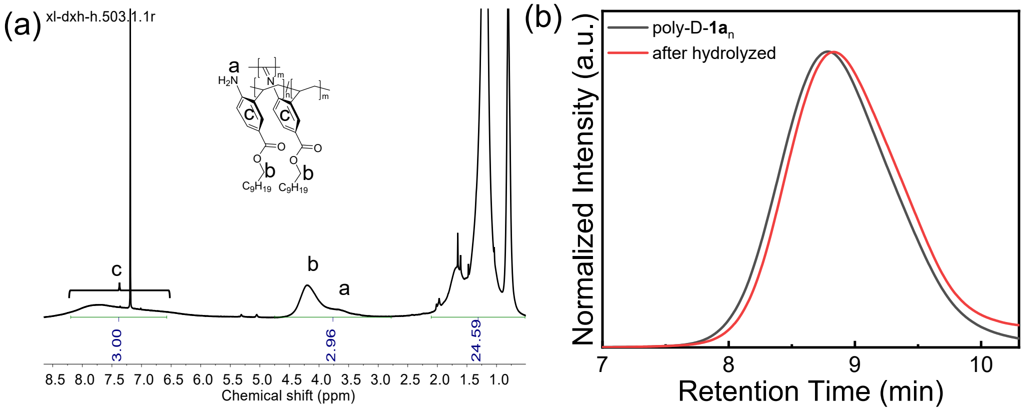


Figure S4. (a) ^{1}H NMR (600 MHz) spectrum of hydrolyzed imine bonds polymers and (b) SEC chromatograms of poly-D-**1a**$_n$ and hydrolyzed imine bonds polymers.

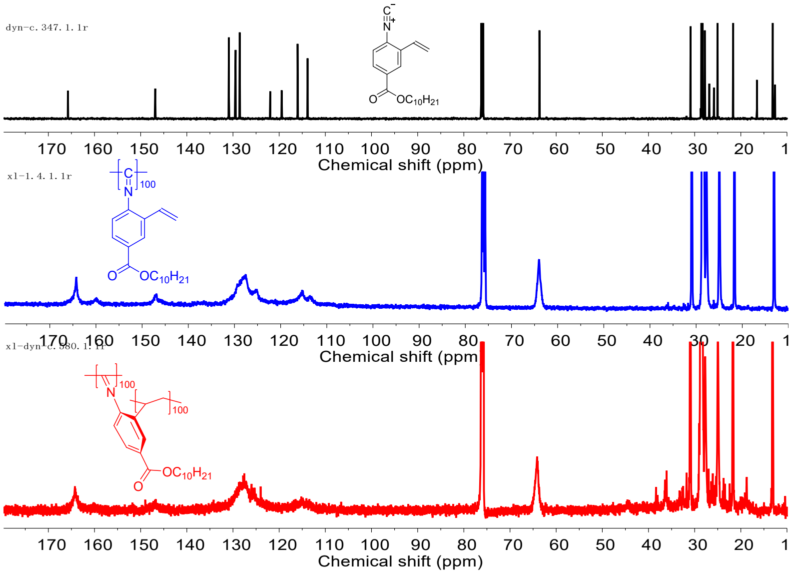


Figure S5. ^{13}C NMR (150 MHz) spectrum of **1a**, poly-S1-**1a**$_{100}$, and poly-D-**1a**$_{100}$ measured in CDCl$_3$ at 25 °C.

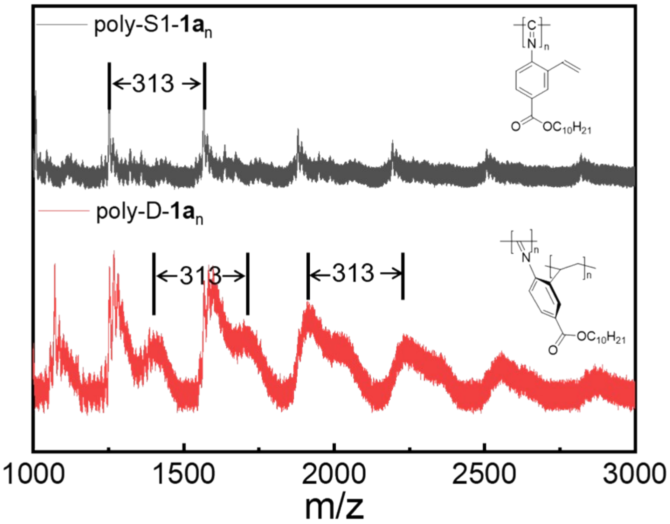


Figure S6. MALDI-TOF-MS spectrum of poly-S1-**1a**$_n$, and poly-D-**1a**$_n$.

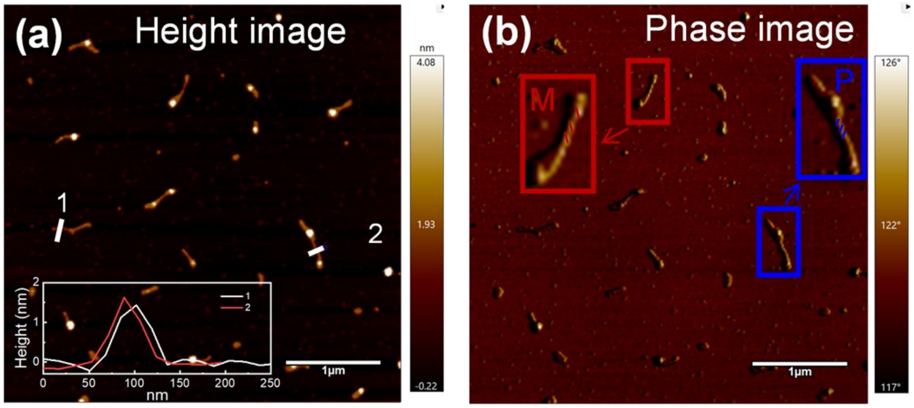


Figure S7. AFM height (a) and phase (b) image of poly-D-**1a**$_n$ casted from THF at the concentration of 0.02 mg/mL on mica substrates.

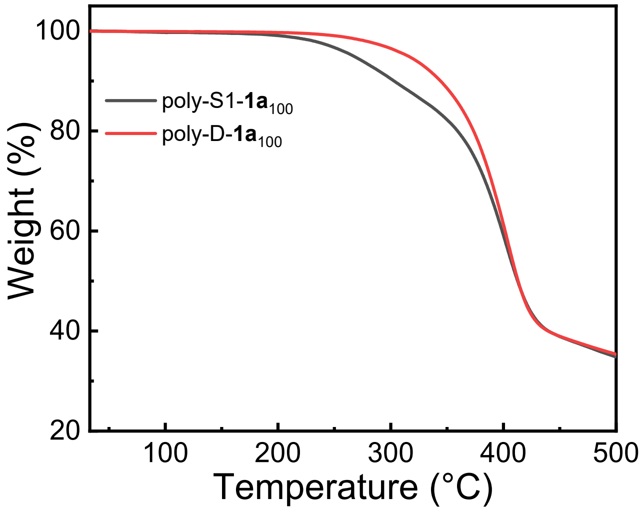


Figure S8. TGA curves of poly-S1-**1a**$_n$, and poly-D-**1a**$_n$ performed in N_2 atmosphere at a heating rate of 10 °C/min.

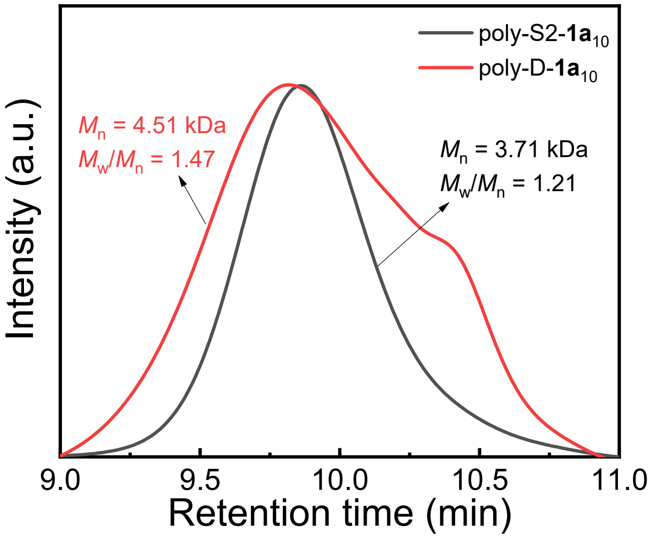


Figure S9. SEC trace of poly-S2-**1a**$_{10}$ and poly-D-**1a**$_{10}$.

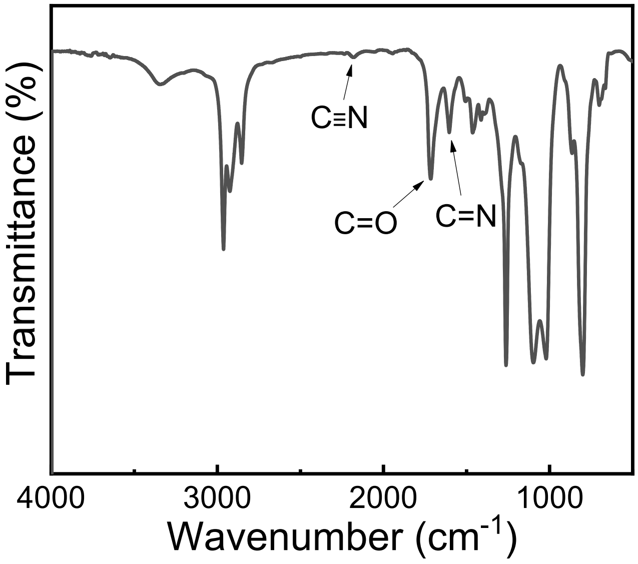


Figure S10. FT-IR spectrum of poly-D-**1a**$_{10}$ synthesis according to **Method 2** measured at 25 °C using KBr pellet.

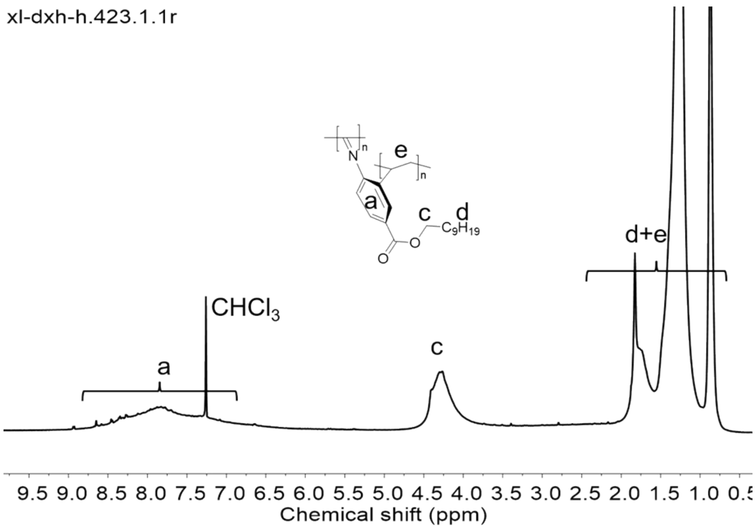


Figure S11. ^{1}H NMR (600 MHz) spectrum of poly-D-**1a**$_{10}$ synthesis according to **Method 2** measured in CDCl$_3$ at 25 °C.

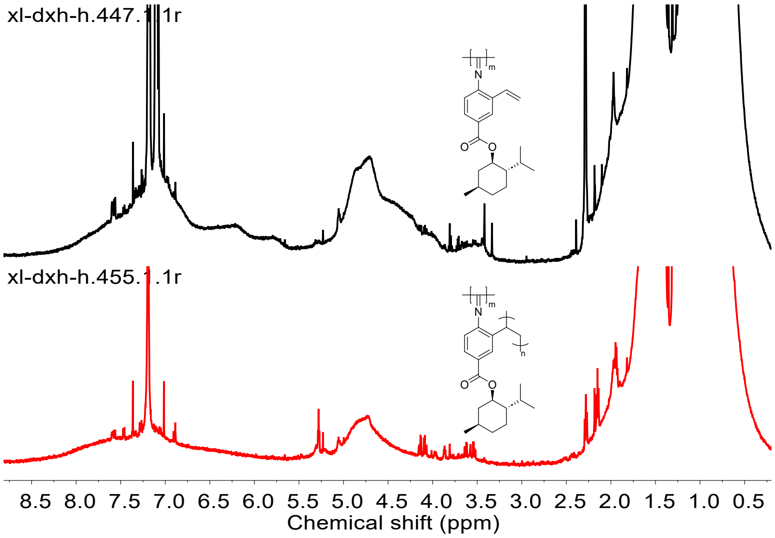


Figure S12. ^{1}H NMR (600 MHz) spectrum of poly-S1-**1L**$_{50}$ and poly-D-**1L**$_{50}$ measured in CDCl$_3$ at 25 °C.

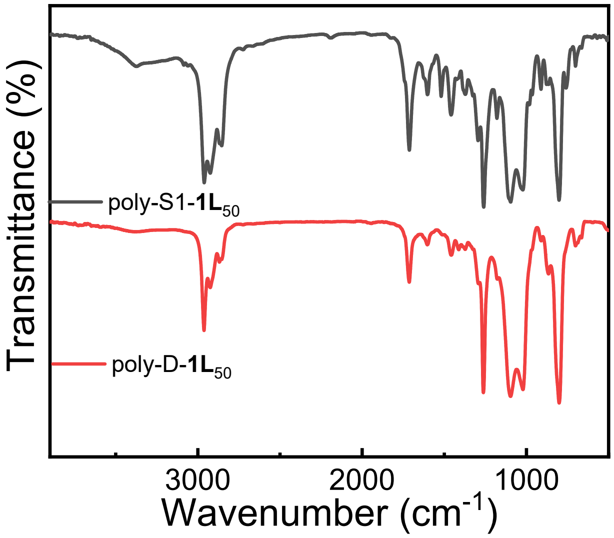


Figure S13. FT-IR spectrum of poly-S1-**1L**$_{50}$ and poly-D-**1L**$_{50}$ measured at 25 °C using KBr pellet.

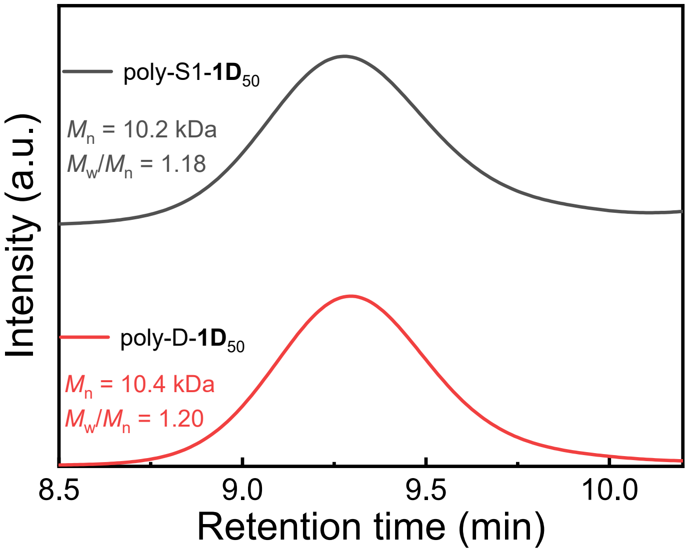


Figure S14. SEC trace of poly-S1-**1D**$_{50}$ and poly-D-**1D**$_{50}$.

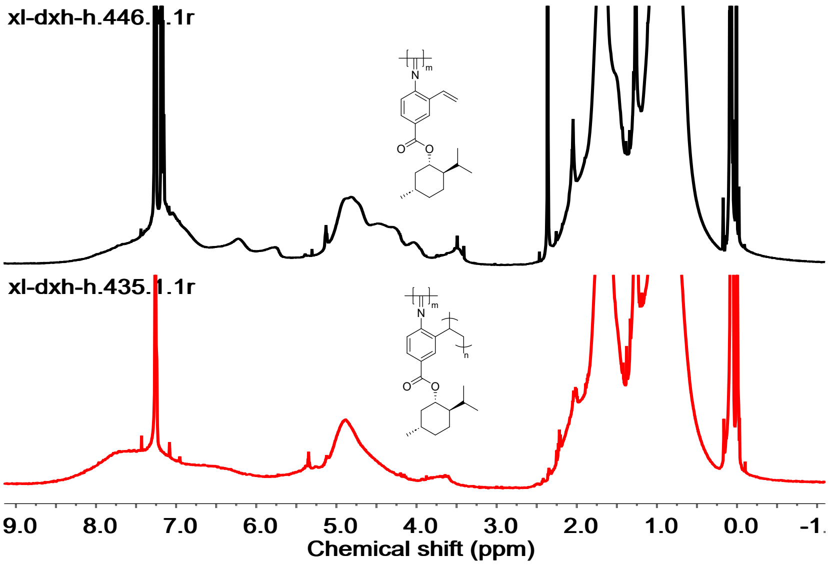


Figure S15. ^{1}H NMR (600 MHz) spectrum of poly-S1-**1D**$_{50}$ **and** poly-D-**1D**$_{50}$ measured in CDCl$_3$ at 25 °C.

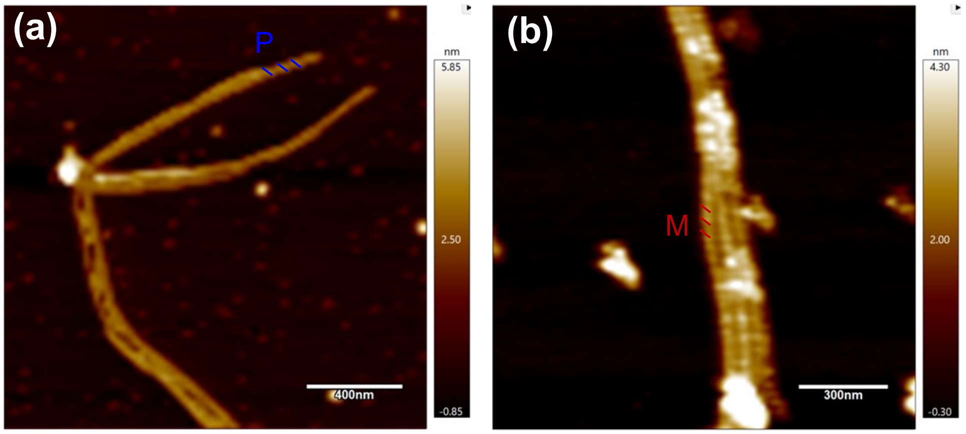


Figure S16. AFM height image of (a) poly-D-**1L**$_{50}$ and (b) poly-D-**1D**$_{50}$ casted from THF at the concentration of 0.02 mg/mL on mica substrates.

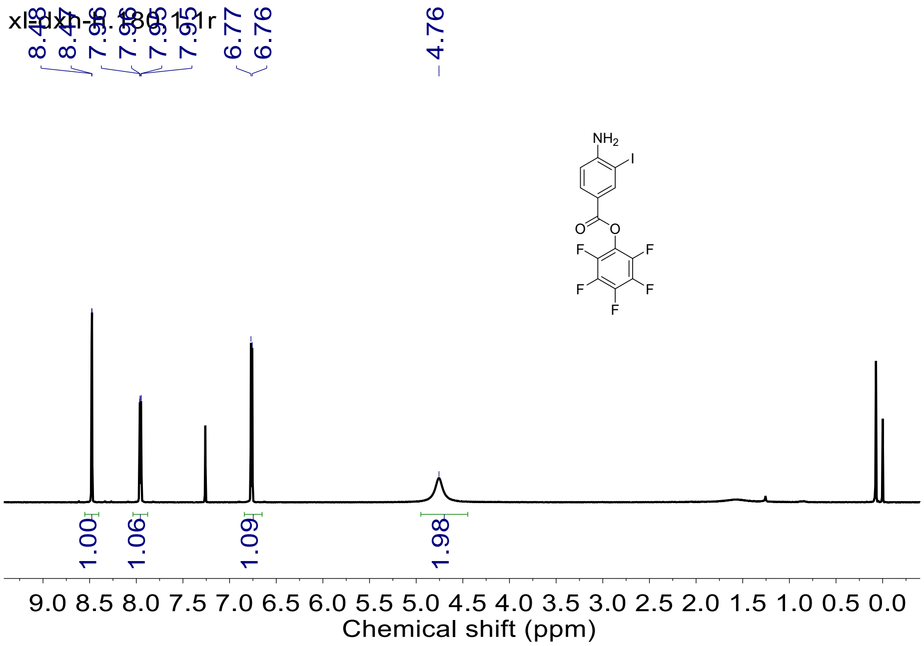


Figure S17. ^{1}H NMR (600 MHz) spectrum of **5** measured in $CDCl_3$ at 25 °C.

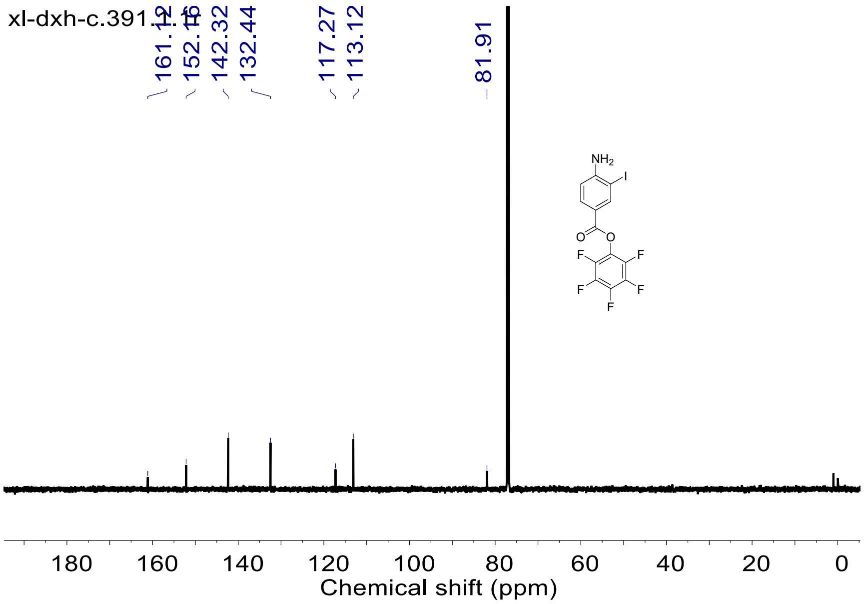


Figure S18. ^{13}C NMR (150 MHz) spectrum of **5** measured in $CDCl_3$ at 25 °C.

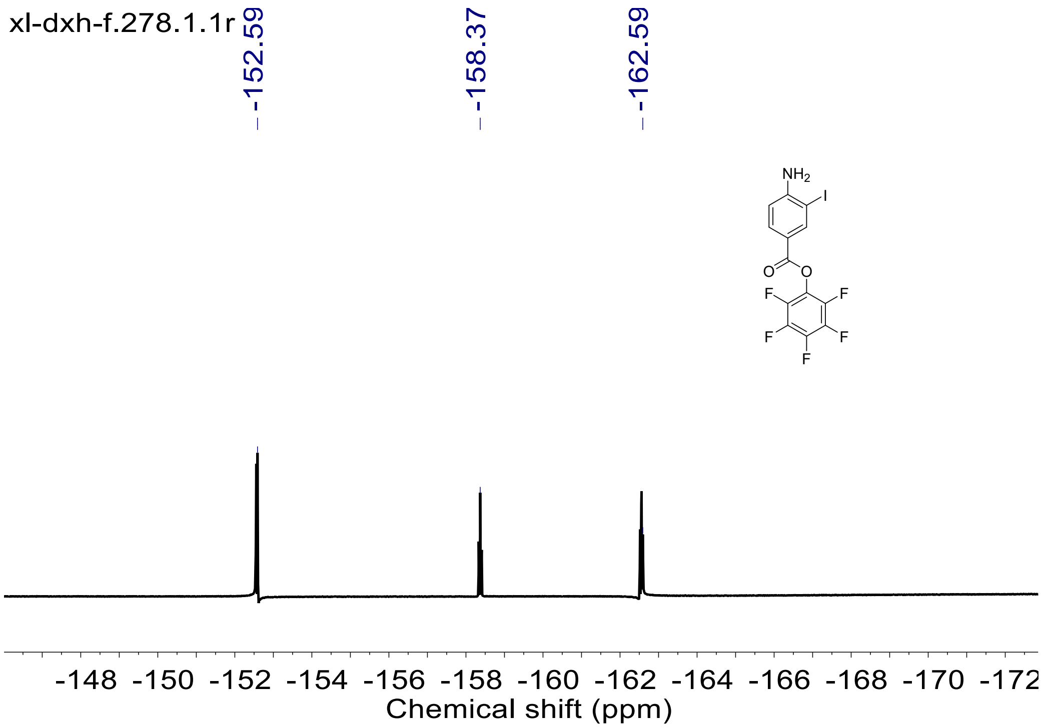


Figure S19. ^{19}F NMR (565 MHz) spectrum of **5** measured in $CDCl_3$ at 25 °C.

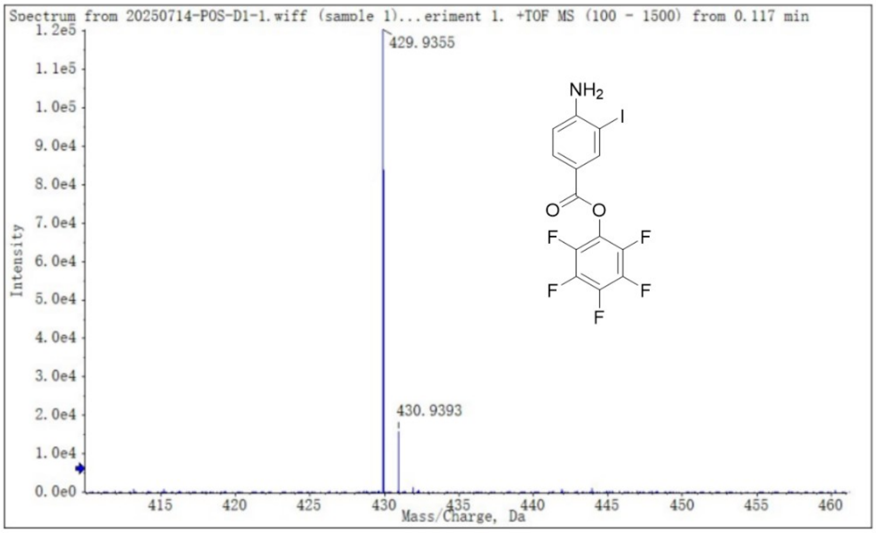


Figure S20. HRMS spectrum of **5**.

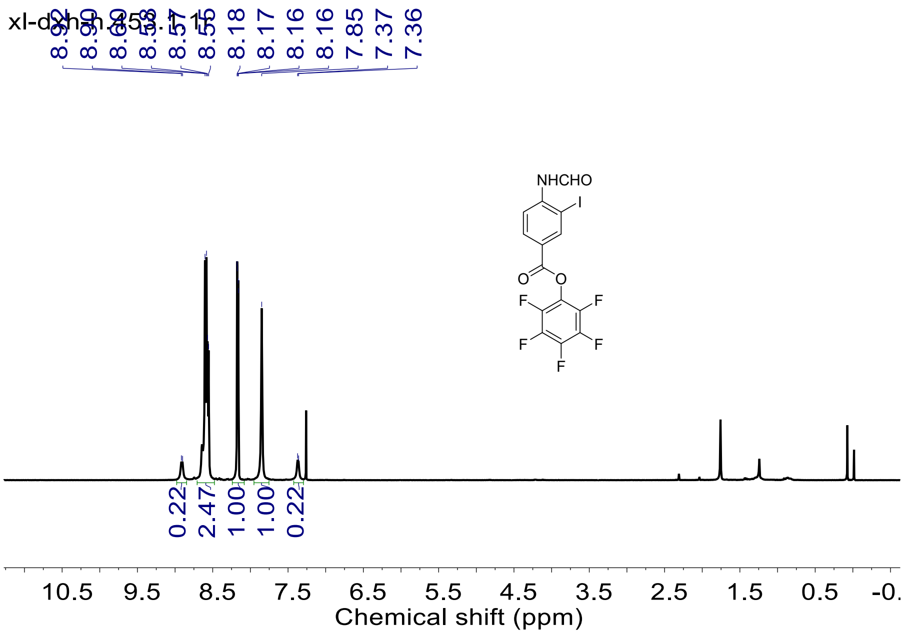


Figure S21. ^{1}H NMR (600 MHz) spectrum of **4** measured in $CDCl_3$ at 25 °C.

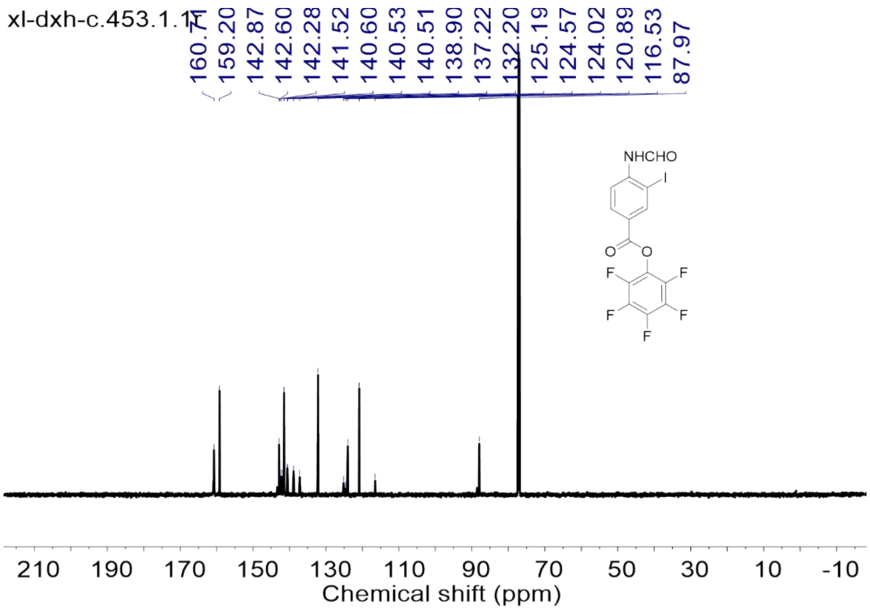


Figure S22. ^{13}C NMR (150 MHz) spectrum of **4** measured in $CDCl_3$ at 25 °C.

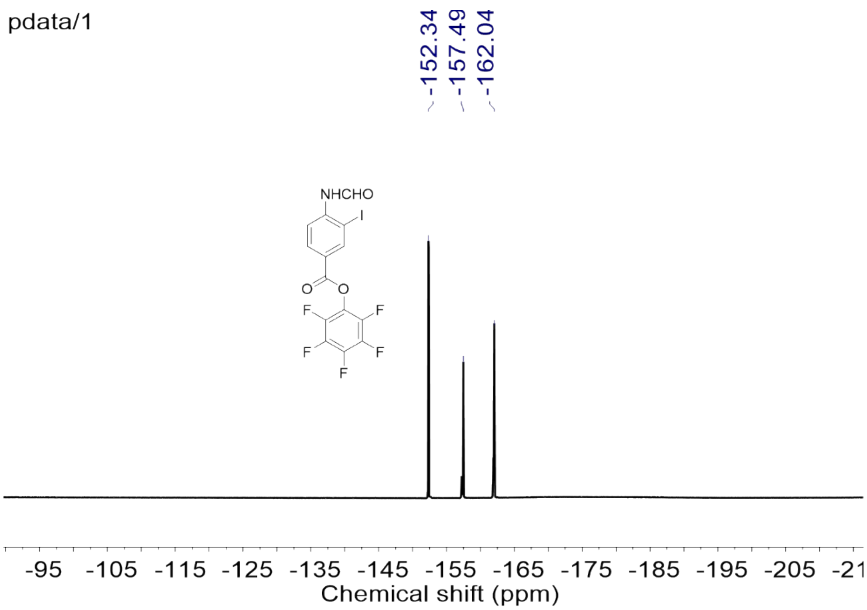


Figure S23. ^{19}F NMR (565 MHz) spectrum of **4** measured in $CDCl_3$ at 25 °C.

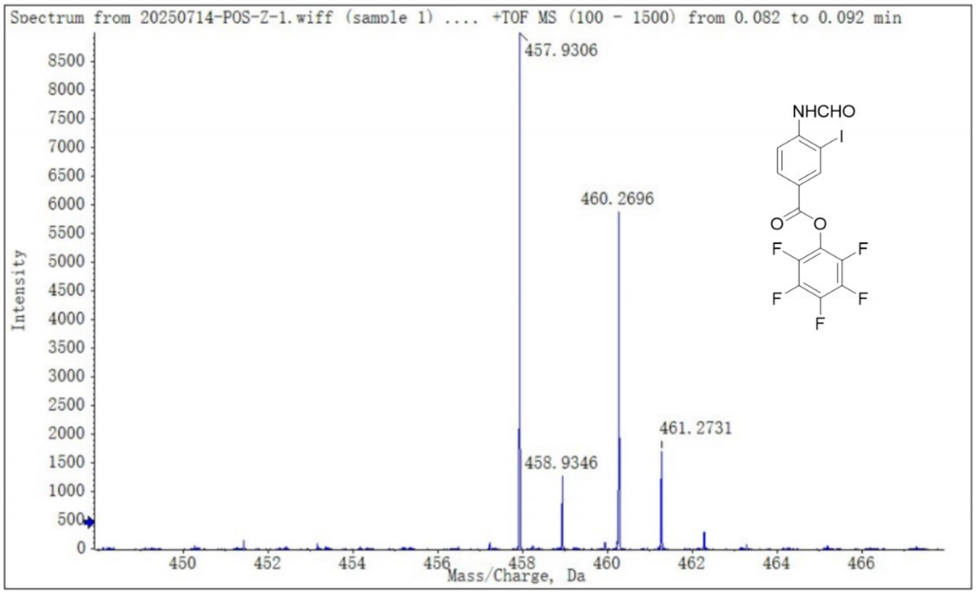


Figure S24. HRMS spectrum of **4**.

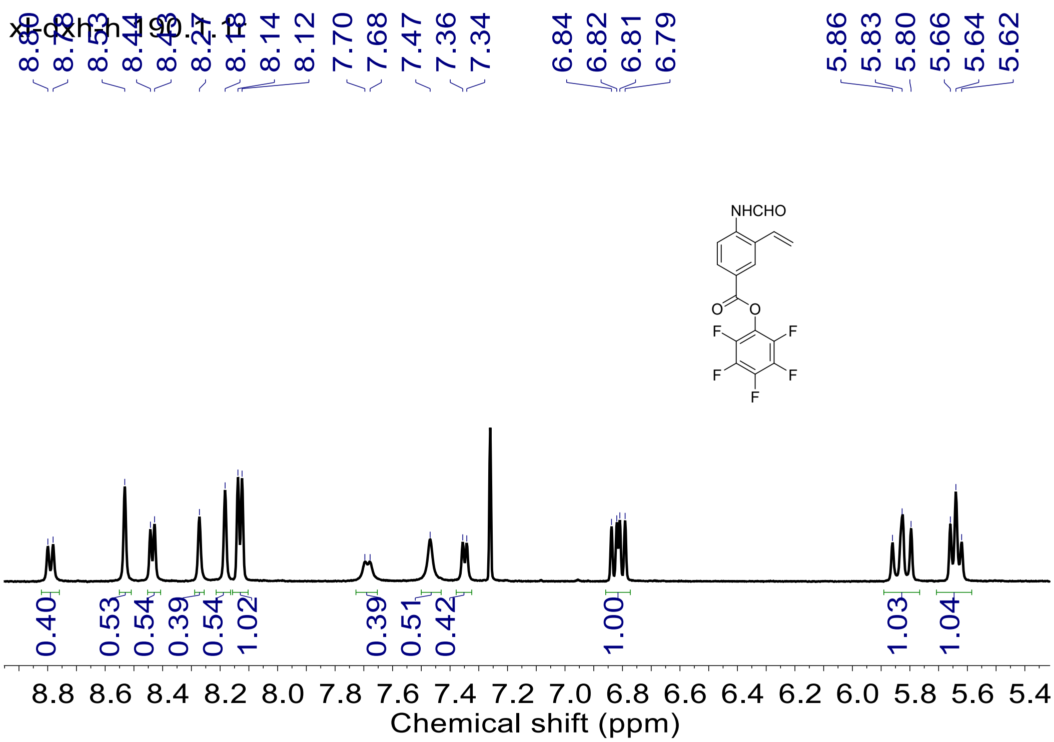


Figure S25. ^1H NMR (600 MHz) spectrum of **3** measured in $CDCl_3$ at 25 °C.

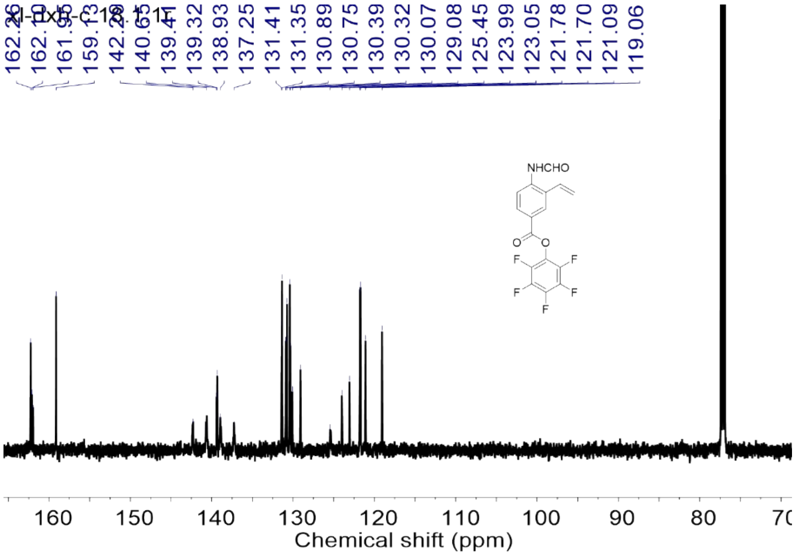


Figure S26. ^{13}C NMR (150 MHz) spectrum of **3** measured in $CDCl_3$ at 25 °C.

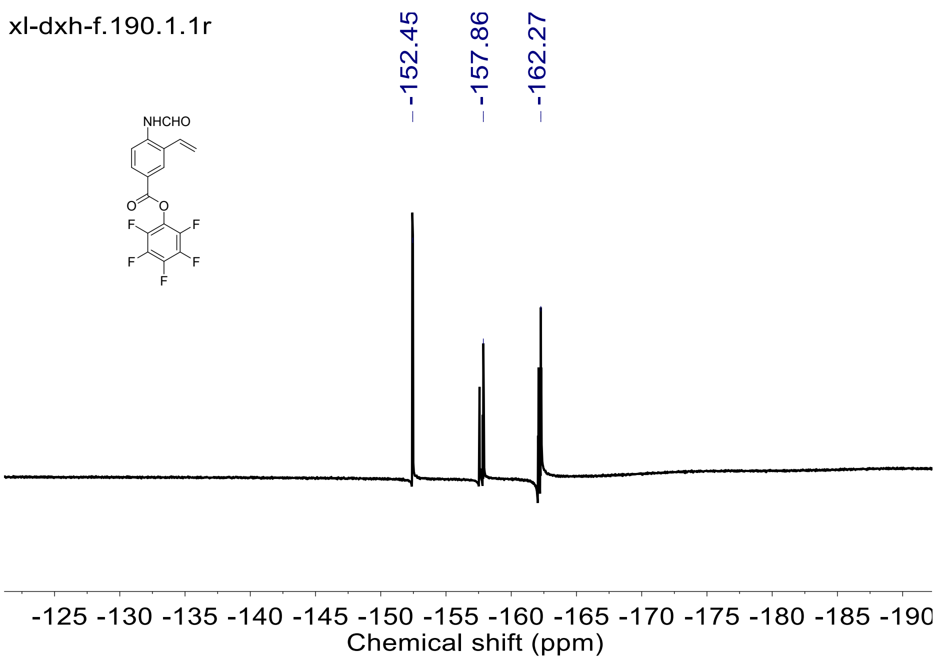


Figure S27. ^{19}F NMR (565 MHz) spectrum of **3** measured in $CDCl_3$ at 25 °C.

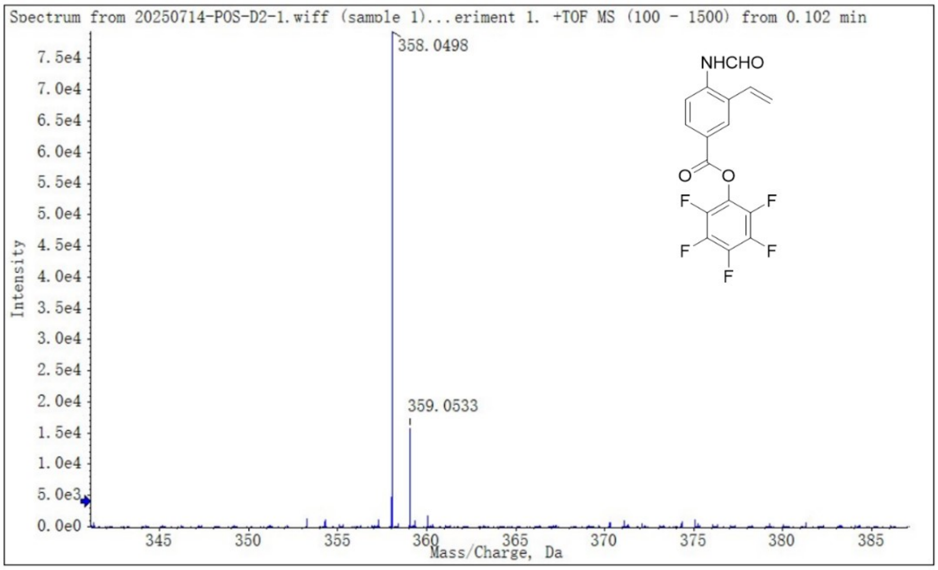


Figure S28. HRMS spectrum of **3**.

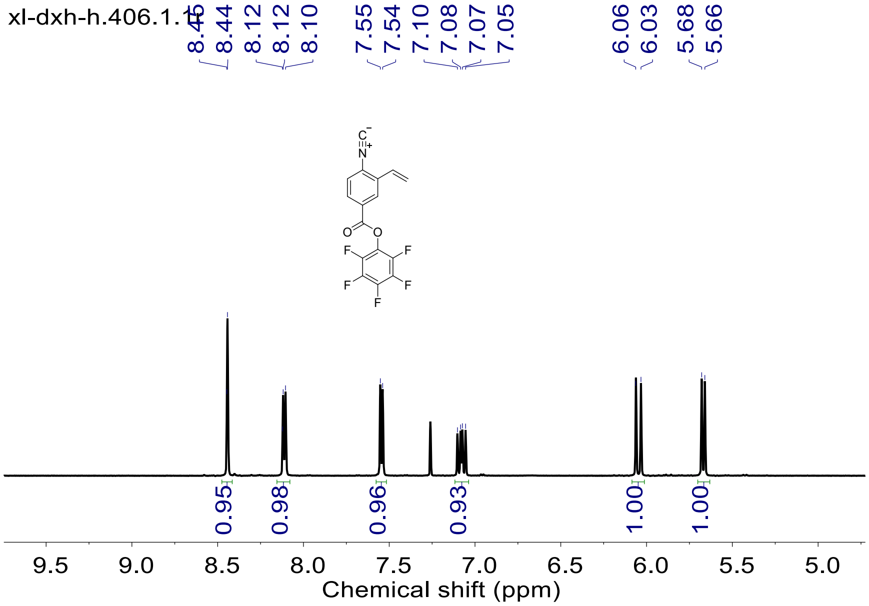


Figure S29. ^{1}H NMR (600 MHz) spectrum of **2** measured in $CDCl_3$ at 25 °C.

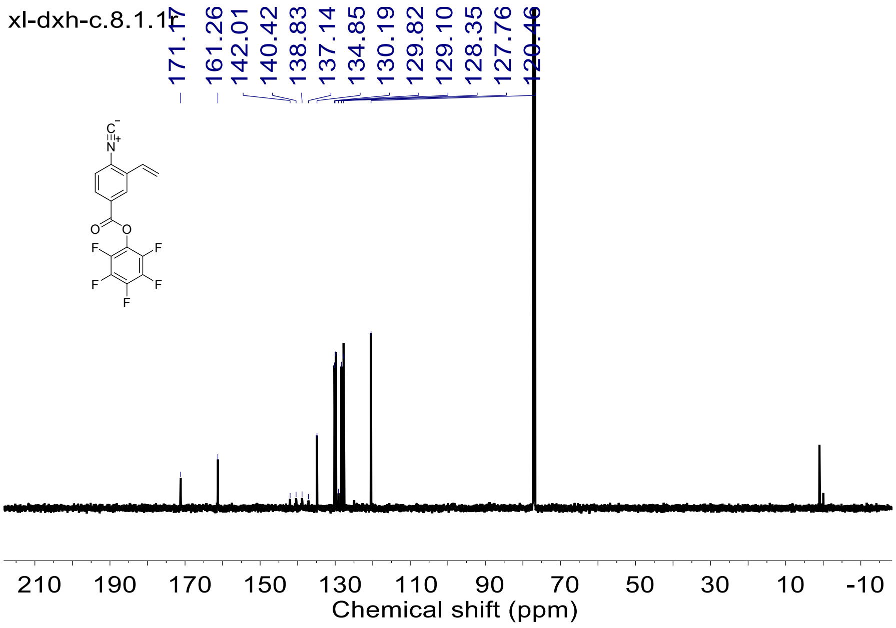


Figure S30. ^{13}C NMR (150 MHz) spectrum of **2** measured in $CDCl_3$ at 25 °C.

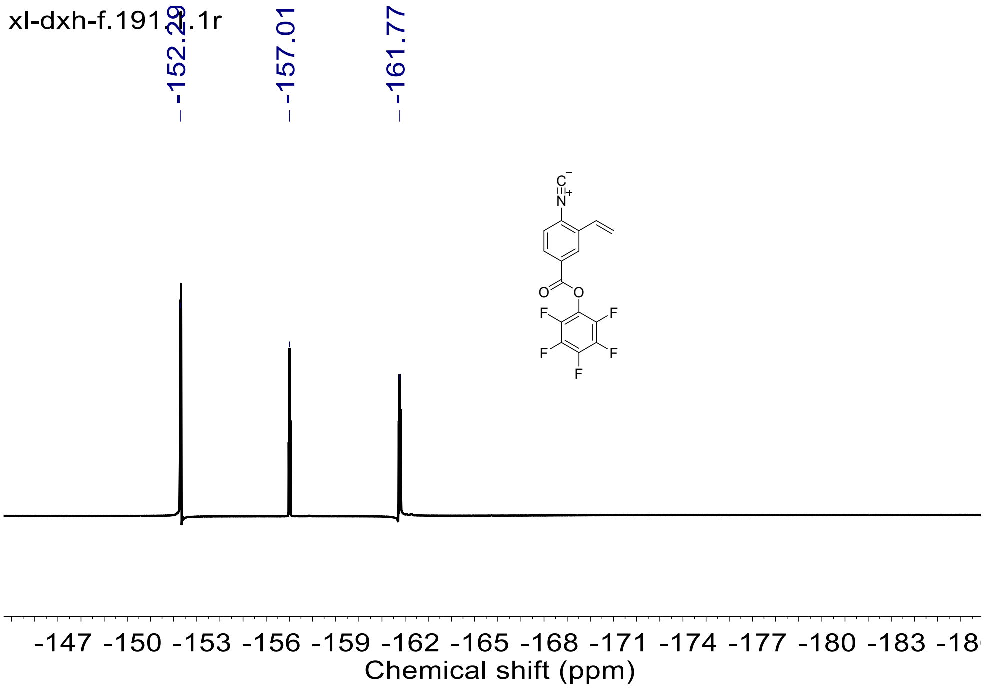


Figure S31. ^{19}F NMR (565 MHz) spectrum of **2** measured in $CDCl_3$ at 25 °C.

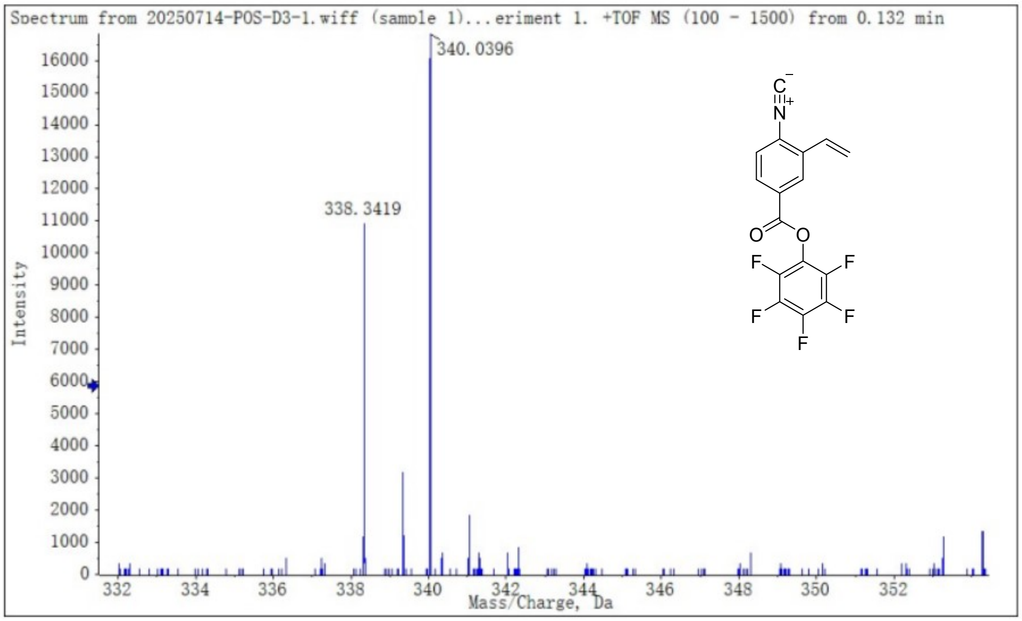


Figure S32. HRMS spectrum of **2**.

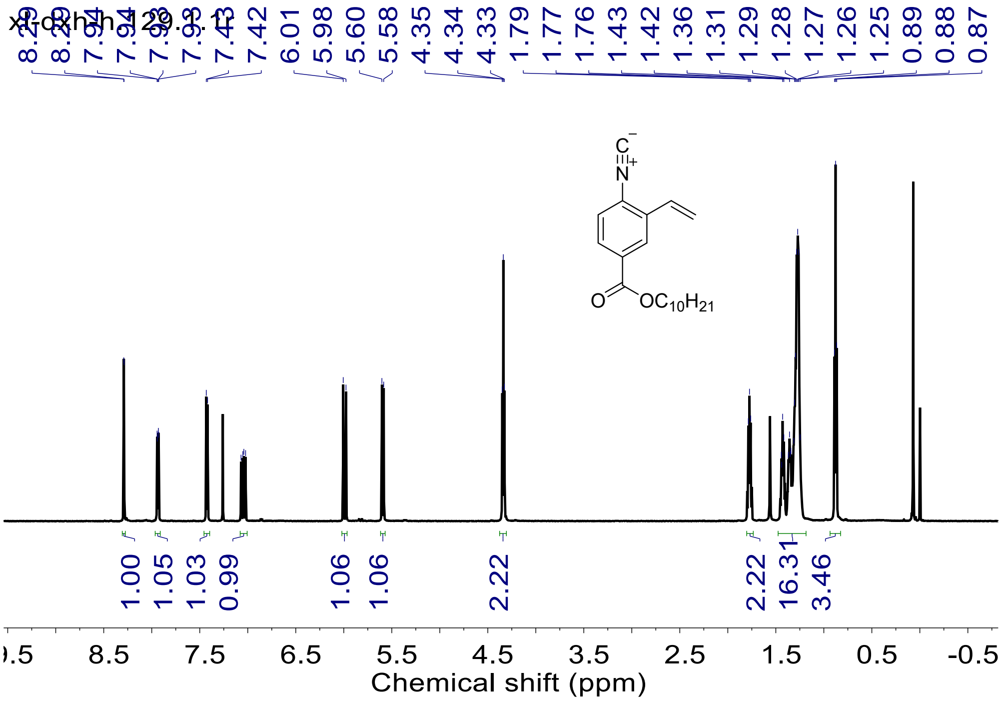


Figure S33. ^{1}H NMR (600 MHz) spectrum of **1a** measured in $CDCl_3$ at 25 °C.

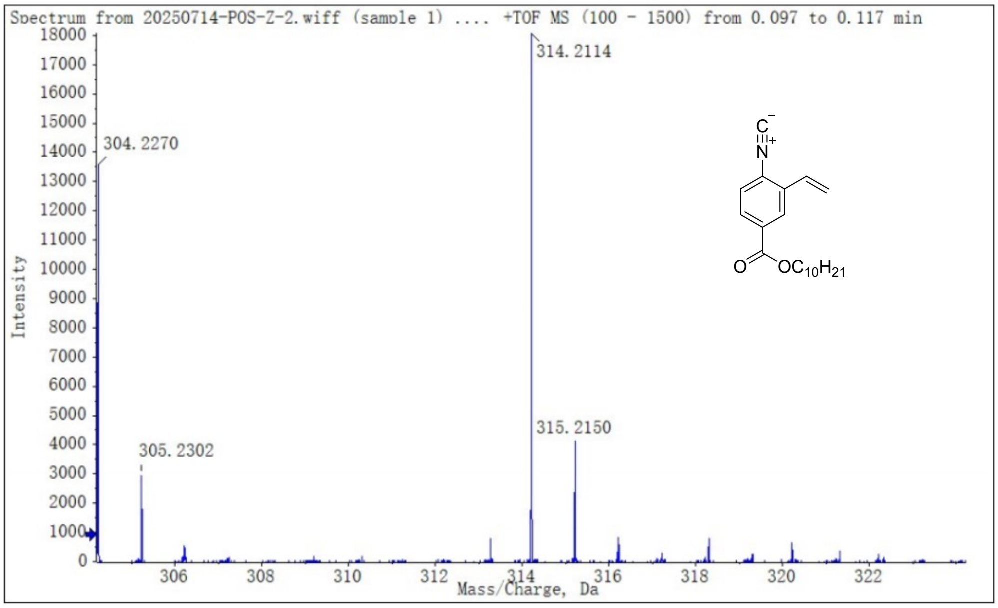


Figure S34. HRMS spectrum of **1a**.

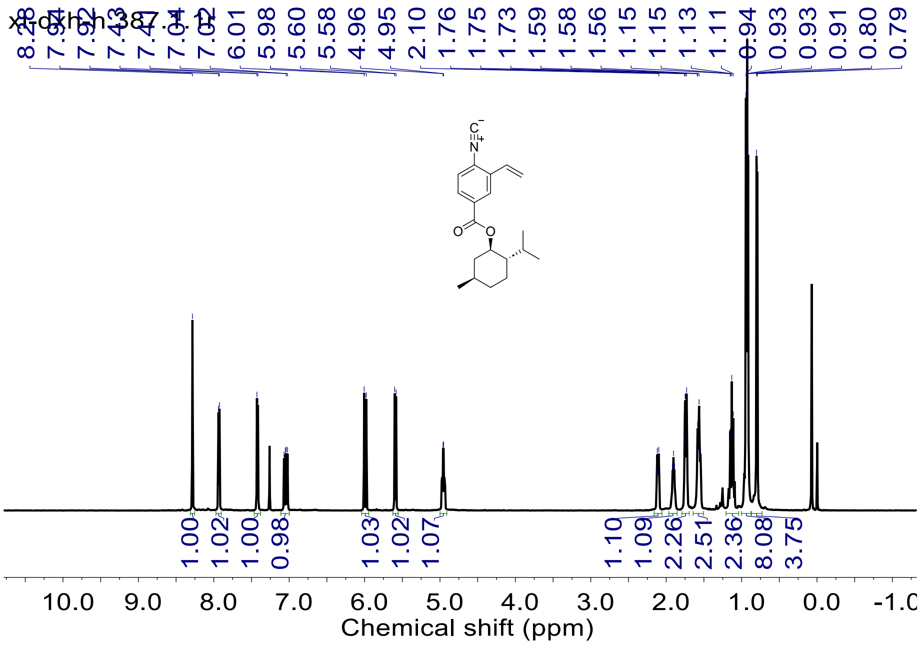


Figure S35. ^{1}H NMR (600 MHz) spectrum of **1L** measured in $CDCl_3$ at 25 °C.

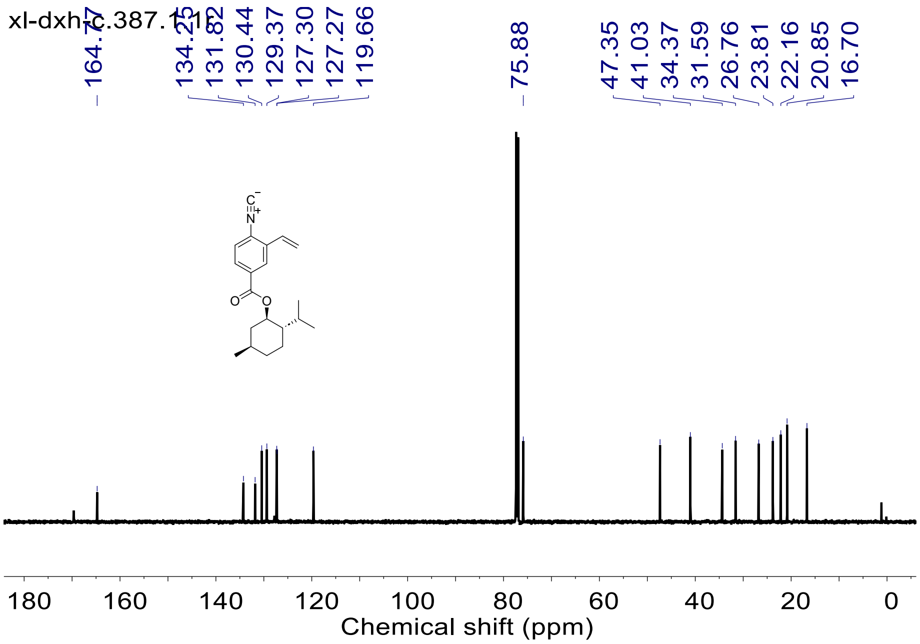


Figure S36. ^{13}C NMR (150 MHz) spectrum of **1L** measured in $CDCl_3$ at 25 °C.

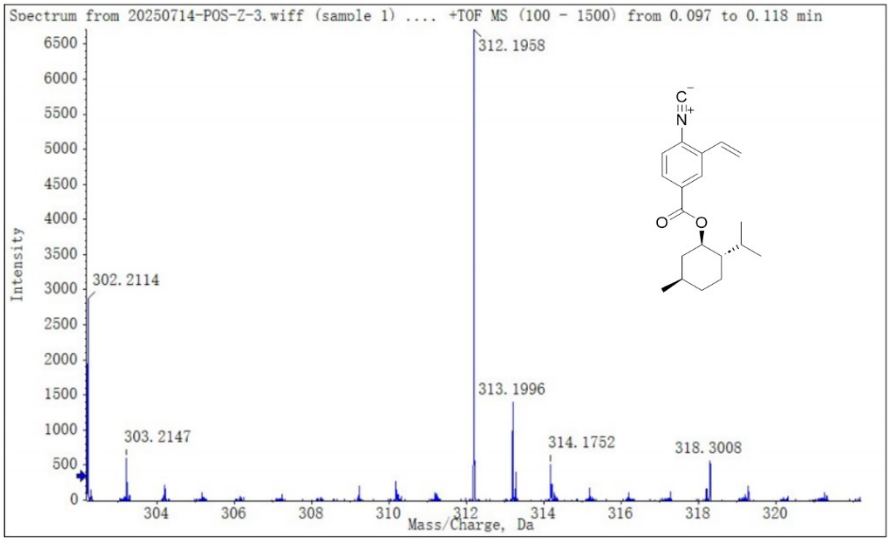


Figure S37. HRMS spectrum of **1L**.

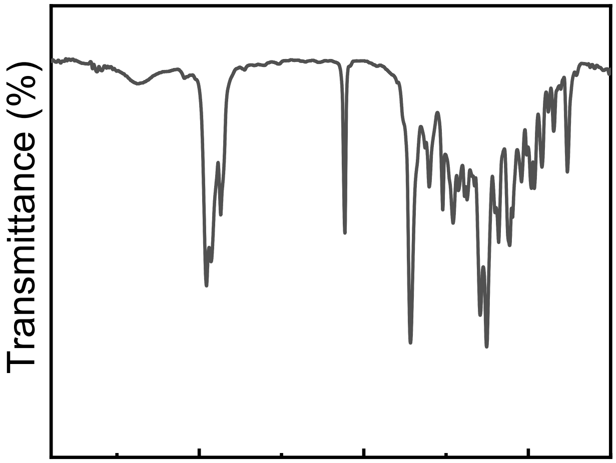


Figure S38. FT-IR spectrum of **1L** measured at 25 °C using KBr pellet.

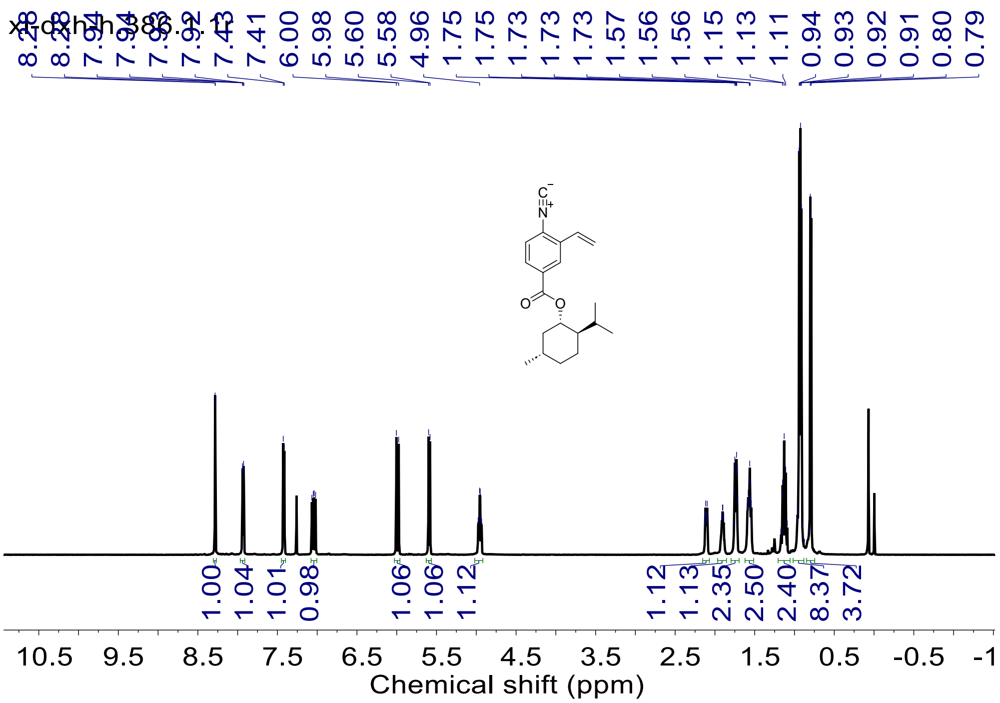


Figure S39. ^{1}H NMR (600 MHz) spectrum of **1D** measured in $CDCl_3$ at 25 °C.

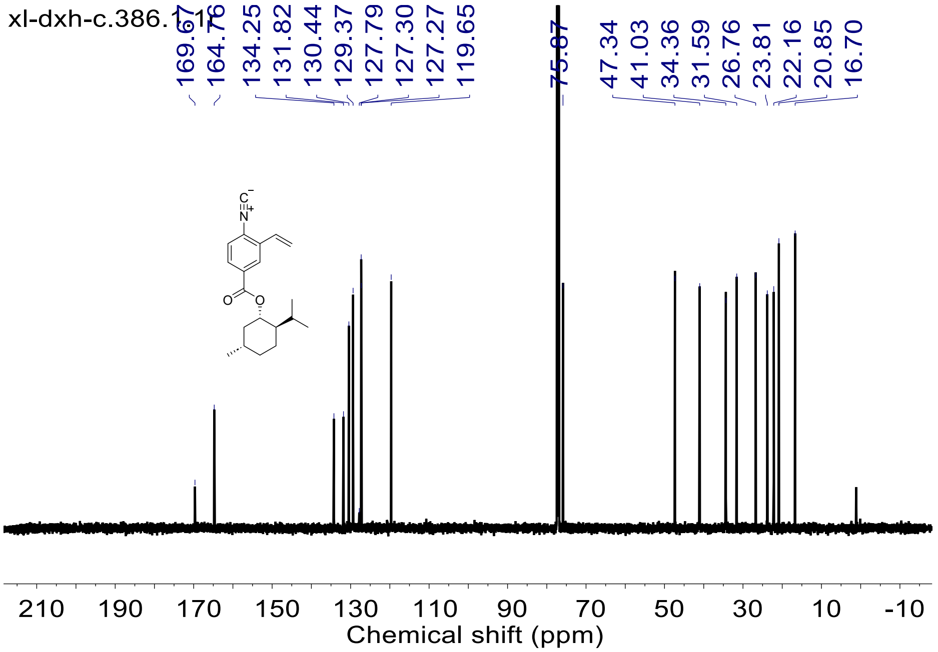


Figure S40. ^{13}C NMR (150 MHz) spectrum of **1D** measured in $CDCl_3$ at 25 °C.

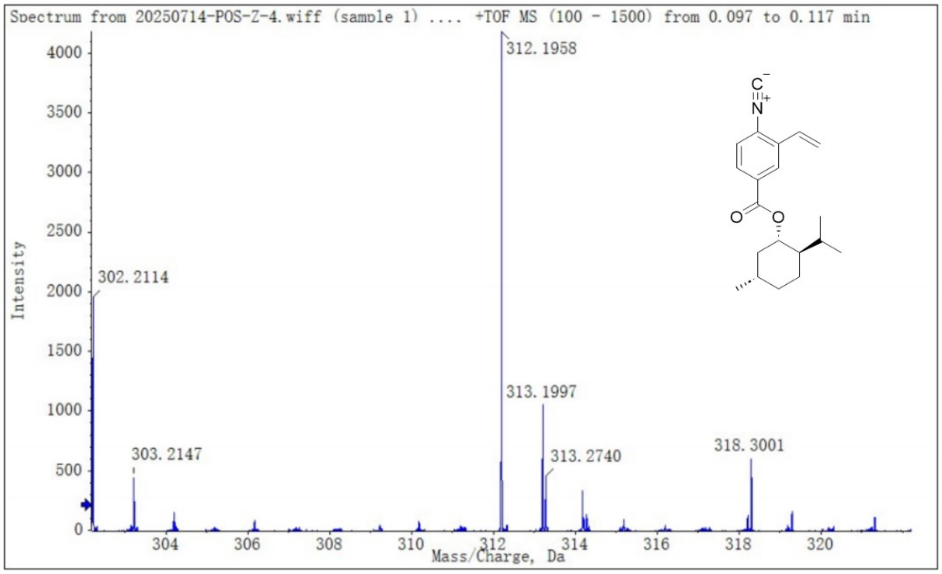


Figure S41. HRMS spectrum of **1D**.

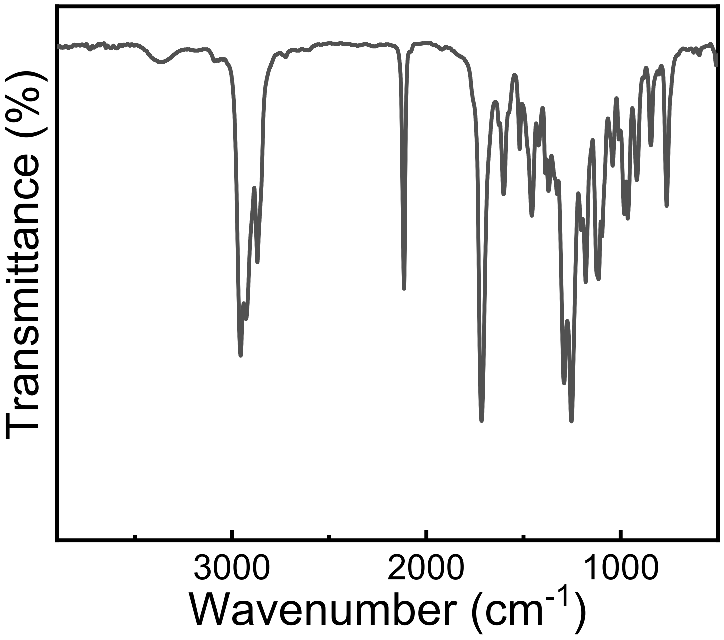


Figure S42. FT-IR spectrum of **1D** measured at 25 °C using KBr pellet.

References

1. Kanbayashi, N.; Okamura, T.-a.; Onitsuka, K. Living Cyclocopolymerization through Alternating Insertion of Isocyanide and Allene via Controlling the Reactivity of the Propagation Species: Detailed Mechanistic Investigation. *J. Am. Chem. Soc.* **2019**, *141*, 15307–15317.

2. Xue, Y.-X.; Zhu, Y.-Y.; Gao, L.-M.; He, X.-Y.; Liu, N.; Zhang, W.-Y.; Yin, J.; Ding, Y.; Zhou, H.; Wu, Z.-Q. Air-Stable (Phenylbuta-1,3-diynyl)palladium(II) Complexes: Highly Active Initiators for Living Polymerization of Isocyanides. *J. Am. Chem. Soc.* **2014**, *136*, 4706–4713.