Supporting Information

Highly Regioselective and Helix-Sense Selective Living Polymerization of Achiral Phenyl- and Alkoxyallene Using Chiral Nickel(II) Catalyst

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General consideration.

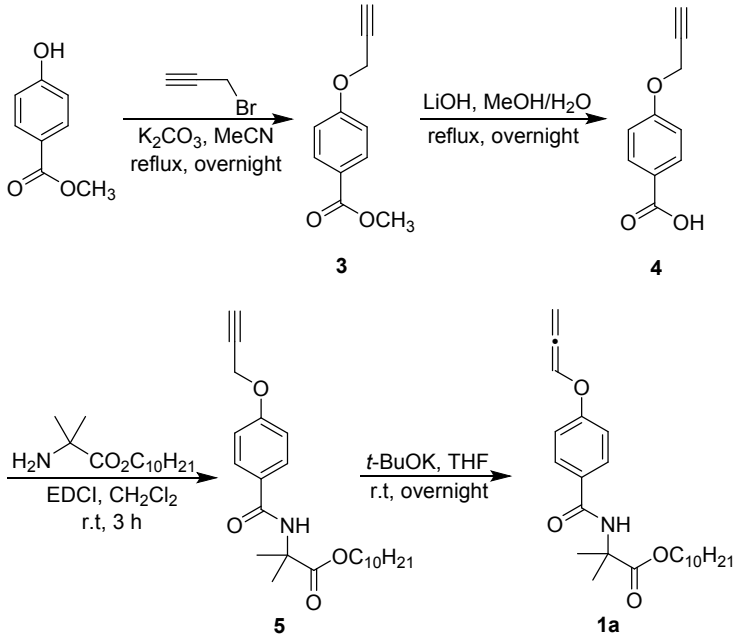
The ^{1}H and ^{13}C NMR spectra were recorded using a 600 MHz Bruker FT-NMR spectrometers {H} operated in the Fourier Transform mode. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual solvent proton as an internal standard. 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 two linear TSK gel GMHHR-H columns. Molecular weight (M_n) and its polydispersity (M_w/M_n) data were reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. The Fourier transform infrared (FT-IR) spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. Circular dichroism (CD) spectra were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1500 spectropolarimeter. UV-vis absorption spectra were performed on a UNIC 4802 UV/Vis double beam spectrophotometer in 1.0 cm length quartz cell. The high resolution mass spectrometry (HRMS) was measured using AXQUITY UPLC LCT Premier XE. The Anal. Calcd was measured using vario EL cube. The optical rotations were measured in tetrahydrofuran (THF) at 25 °C using a 10.0 cm quartz cell on a WZZ-2B polarimeter. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research). The polarized optical micrographs were recorded on Leica microsystems DM2500 in the concentrated THF solutions. Molecular modeling and molecular mechanics calculations were performed on Materials Studio software (version 2019, Accerlys Software Inc.) implemented with the COMPASS force field.

All solvents were obtained from Sinopharm. Co. Ltd. and were purified by the standard procedures prior to use. The chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. Decyl 2-amino-2-methylpropanoate and 4-ethynylbenzoic acid were prepared followed the reported procedures and the structures were confirmed by ^{1}H NMR.[1,2] Ligands *R*-**2a**, *S*-**2a**, *R*-**2b**, *S*-**2b**, *S*-**2d**, and *S*-**2f** were prepared followed the

reported literatures and the structures were verified by ^{1}H NMR.[3,4] Monomers **1a-c** were prepared according to literatures reported by our group previously with some modifications.[5,6] The Ni(II) catalysts were prepared followed the reported literatures with slight modification, and were directly used in the next step without further isolation and characterization.[7,8]

Synthesis of monomer 1a-1c

Scheme S1. Synthesis of Monomer **1a**



Synthesis of compound 3. 3-Bromopropyne (11.01 g, 92.55 mmol) was added to a mixture of methyl 4-hydroxybenzoate (11.97 g, 78.67 mmol) and potassium carbonate (41.90 g, 0.30 mol) in acetonitrile (80 mL) via a syringe. The reaction mixture was stirred at 80 °C for 12 h under dry nitrogen atmosphere. Then the reaction mixture was cool to room temperature and quenched by water. The resulting mixture was extracted with ethyl acetate (50 mL × 3). The combined organic layer was washed with brine (50 mL × 3), dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. The isolated residue was further purified by flash column chromatography using *n*-hexane and ethyl acetate (v/v = 1/1) as eluent to afford **3** as a pale yellow product (13.87 g, 93% yield). ^{1}H NMR (600

MHz, $CDCl_3$, 25 °C): δ/ppm 8.00 (d, J = 8.9 Hz, 2H, ArH), 6.99 (d, J = 8.9 Hz, 2H, ArH), 4.74 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3), 2.55 (s, 1H, C≡CH).

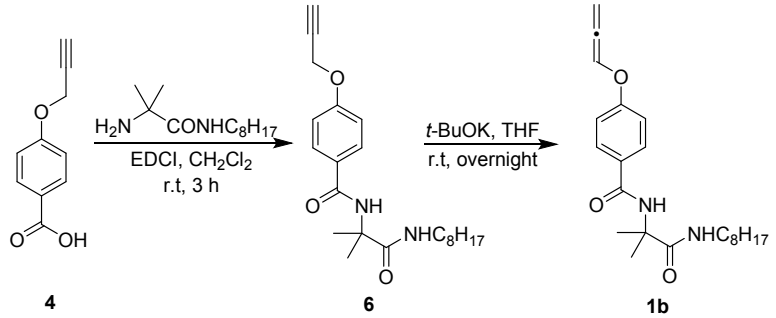
Synthesis of compound 4. Lithium hydroxide (LiOH, 3.24 g, 0.14 mol) was added to a solution of **3** (7.04 g, 37.01 mmol) in ethanol (50 mL) and H_2O (10 mL). After the resulting mixture was stirred at 90 °C for 12 h, the ethanol was removed by evaporation under reduced pressure. The residual solution was neutralized with diluted aqueous HCl solution in small portions until pH = 2. The formed solid was filtered and washed with water. After dried in vacuum and recrystallized with ethanol, compound **4** was afforded as a white solid (5.92 g, 91% yield). ^{1}H NMR (600 MHz, DMSO-d_6, 25 °C): δ/ppm 12.68 (s, 1H, CO_2H), 7.90 (d, J = 8.8 Hz, 2H, ArH), 7.06 (d, J = 8.8 Hz, 2H, ArH), 4.89 (s, 2H, OCH_2), 3.61 (s, 1H, C≡CH).

Synthesis of compound 5. To a 250 mL round-bottomed flask containing a magnetic stirring bar were added **4** (5.32 g, 30.20 mmol) and 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDCI, 6.95 g, 36.30 mmol) in dichloromethane (150 mL) under nitrogen atmosphere. A solution of decyl 2-amino-2-methylpropanoate (7.36 g, 30.22 mmol) in dry dichloromethane (5.0 mL) was added at 0 °C. The mixture was stirred at 0 °C for 15 min, then the reaction solution was warmed to room temperature for 3 h. The reaction solution was diluted with dichloromethane, washed with water (50 mL × 3) and brine (50 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate (v/v = 10/1) as eluent to afford **5** as a colorless oil (8.43 g, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ/ppm 7.74 (d, J = 8.9 Hz, 2H, ArH), 6.97 (d, J = 8.9 Hz, 2H, ArH), 6.82 (s, 1H, NH), 4.71 (s, 2H, OCH_2), 4.15 (t, J = 6.6 Hz, 2H, OCH_2), 2.53 (s, 1H, C≡CH), 1.66 (s, 6H, CH_3), 1.65–1.59 (m, 2H, CH_2), 1.36–1.16 (m, 14H, $(CH_2)_7$), 0.86 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ/ppm 175.13, 166.03, 160.11, 128.83, 128.01, 114.72, 78.05, 76.07, 65.90, 57.03, 55.93, 31.98, 29.60, 29.39, 29.30, 28.63, 25.96, 24.81, 22.77, 14.21. FT-IR (KBr, 25 °C): 3310,

2926, 2853, 2122, 1733, 1636, 1603, 1576, 1535, 1501, 1380 cm^{-1}. HRMS m/z: calcd for $C_{24}H_{36}NO_4$ $[M+H]^+$: 402.2639; Found: 402.2666. Anal. Calcd (%) for $C_{24}H_{35}NO_4$: C, 71.79; H, 8.79; N, 3.49. Found: C, 71.77; H, 8.78; N, 3.53.

Synthesis of monomer 1a. To a 250 mL round-bottomed flask containing a magnetic stirring bar were added compound **5** (3.13 g, 7.80 mmol) and potassium *tert*-butoxide (1.31 g, 11.67 mmol) in THF (150 mL) under dry nitrogen atmosphere. After the reaction mixture was stirred at room temperature for 5 h, the reaction solution was diluted with ether, washed with water (50 mL × 3) and brine (50 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate (v/v = 10/1) as eluent to afford **1a** as a colorless oil (1.60 g, 51% yield). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ/ppm 7.76 (d, J = 8.7 Hz, 2H, ArH), 7.08 (d, J = 8.7 Hz, 2H, ArH), 6.84 (t, J = 5.9 Hz, 1H, OCH), 6.81 (s, 1H, NH), 5.47 (d, J = 5.9 Hz, 2H, C=CH_2), 4.15 (t, J = 6.6 Hz, 2H, OCH_2), 1.73 (s, 6H, CH_3), 1.72–1.67 (m, 2H, CH_2), 1.42–1.25 (m, 14H, $(CH_2)_7$), 0.92 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ/ppm 202.79, 175.11, 165.94, 159.75, 128.98, 128.86, 117.10, 116.32, 89.93, 65.91, 57.05, 32.00, 29.60, 29.40, 29.30, 28.61, 25.95, 24.77, 22.78, 14.21. FT-IR (KBr, 25 °C): 3342, 2922, 2852, 1739, 1636, 1605, 1580, 1534, 1499, 1451, 1388 cm^{-1}. HRMS m/z: calcd for $C_{24}H_{36}NO_4$ $[M+H]^+$: 402.2639; Found: 402.2608. Anal. Calcd (%) for $C_{24}H_{35}NO_4$: C, 71.79; H, 8.79; N, 3.49. Found: C, 71.74; H, 8.82; N, 3.45.

Scheme S2. Synthesis of monomer **1b**



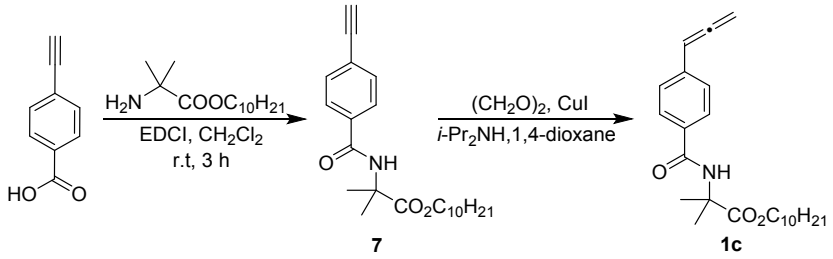
Synthesis of compound 6. To a 250 mL round-bottomed flask containing a magnetic

stirring bar were added **4** (4.04 g, 22.93 mmol) and EDCI (4.83 g, 25.22 mmol) in CH_2Cl_2 (150 mL) under N_2 atmosphere. A solution of 2-amino-2-methyl-*N*-octylpropanamide (4.92 g, 22.93 mmol) in dry CH_2Cl_2 (5.0 mL) was added at 0 °C. The mixture was stirred at 0 °C for 15 min, then the reaction solution was warmed to room temperature and stirred for 3 h. The reaction solution was diluted with CH_2Cl_2, washed with water (50 mL × 3) and brine (50 mL × 3). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate (v/v = 5/1) as eluent to afford **6** as a white solid (4.29 g, 50% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm): 7.75 (d, J = 8.4 Hz, 2H, ArH), 6.98 (d, J = 8.4 Hz, 2H, ArH), 6.96 (s, 1H, NH), 6.56 (s, 1H, NH), 4.73 (s, 2H, OCH_2), 3.26 (q, J_1 = 12.6 Hz, J_2 = 6.0 Hz, 2H, CH_2), 2.53 (s, 1H, C≡CH), 1.67 (s, 6H, CH_3), 1.52–1.48 (m, 2H, CH_2), 1.28–1.24 (m, 10H, $(CH_2)_5$), 0.86 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, δ/ppm): 174.79, 166.43, 160.10, 128.81, 128.02, 114.66, 77.94, 76.11, 57.49, 55.87, 39.99, 31.79, 29.49, 29.27, 29.22, 26.91, 25.22, 22.65, 14.12. FT-IR (KBr, 25 °C): 3334, 3267, 2917, 2853, 2130, 1651, 1633, 1604, 1546, 1526, 1505, 1450, 1431, 1382 cm^{-1}. HRMS m/z: calcd for $C_{22}H_{31}N_2O_3$ $[M–H]^-$: 371.2340; Found: 371.2412. Anal. Calcd for $C_{22}H_{32}N_2O_3$: C, 70.94%; H, 8.66%; N, 7.52%. Found: C, 70.96%; H, 8.70%; N, 7.47%.

Monomer **1b** was prepared from compound **6** under a procedure similar to that of monomer **1a**. Characterization data for **1b**: 60% yield. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ/ppm 7.76, (d, J = 7.8 Hz, 2H, ArH), 7.08 (d, J = 7.8 Hz, 2H, ArH), 6.91 (s, 1H, NH), 6.84 (t, J = 6.6 Hz, 1H, CH=C), 6.48 (s, 1H, NH), 5.48 (d, J = 6.0 Hz, 2H, C=CH_2), 3.28 (q, J_1 = 13.2 Hz, J_2 = 6.0 Hz, 2H, CH_2), 1.69 (s, 6H, CH_3), 1.54–1.49 (m, 2H, CH_2), 1.29–1.20 (m, 10H, $(CH_2)_5$), 0.87 (t, J = 6.6 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ/ppm 202.80, 174.78, 166.37, 159.86, 129.17, 128.88, 117.13, 116.39, 89.97, 57.62, 40.06, 31.87, 29.56, 29.28, 26.98, 25.31, 22.71, 14.16. FT-IR (KBr, 25 °C): 3331, 3263, 2917, 2853, 1964, 1653, 1633, 1603, 1544, 1529, 1498, 1461, 1438, 1386 cm^{-1}. HRMS m/z: calcd for $C_{22}H_{31}N_2O_3$ $[M–H]^-$: 371.2340; Found: 371.2325. Anal. Calcd for $C_{22}H_{32}N_2O_3$: C,

70.94%; H, 8.66%; N, 7.52%. Found: C, 70.89%; H, 8.69%; N, 7.51%.

Scheme S3. Synthesis of monomer **1c**



Synthesis of compound 7. To a 250 mL round-bottomed flask containing a magnetic stirring bar were added 4-ethynylbenzoic acid (1.73 g, 11.84 mmol) and EDCI (2.76 g, 14.42 mmol) in CH_2Cl_2 (80 mL) under N_2 atmosphere. A solution of decyl 2-amino-2-methylpropanoate (2.92 g, 11.99 mmol) in dry CH_2Cl_2 (5.0 mL) was added at 0 °C. The mixture was stirred at 0 °C for 15 min, then the reaction solution was warmed to room temperature and stirred for 3 h. The reaction solution was diluted with CH_2Cl_2, washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate (v/v = 9/1) as eluent to afford **7** as a yellow solid (2.87 g, 64% yield). ^{1}H NMR (600 MHz, $CDCl_3$, δ/ppm): 7.74 (d, J = 8.4 Hz, 2H, ArH), 7.54 (d, J = 8.4 Hz, 2H, ArH), 6.89 (s, 1H, NH), 4.17 (t, J = 6.6 Hz, 2H, CH_2), 3.20 (s, 1H, C≡CH), 1.69 (s, 6H, CH_3), 1.67–1.62 (m, 2H, CH_2), 1.35–1.24 (m, 14H, $(CH_2)_7$), 0.88 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, δ/ppm): 175.05, 165.76, 134.83, 132.37, 127.03, 125.48, 82.91, 79.58, 66.09, 57.30, 32.02, 29.64, 29.43, 29.33, 28.66, 25.99, 24.69, 22.82, 14.25. FT-IR (KBr, 25 °C): 3351, 3253, 2923, 2854, 2107, 1729, 1632, 1608, 1558, 1523, 1497, 1458, 1389 cm^{-1}. HRMS m/z: calcd for $C_{23}H_{34}NO_3$ $[M+H]^+$: 372.2533; Found: 372.2567. Anal. Calcd for $C_{23}H_{33}NO_3$: C, 74.36%; H, 8.95%; N, 3.77%. Found: C, 74.38%; H, 8.98%; N, 3.74%.

Synthesis of monomer 1c.[9] To a 25 mL round-bottomed flask containing a magnetic stirring bar were added paraformaldehyde (0.23 g, 7.59 mmol), CuI (0.29 g, 1.52 mmol)

and compound **7** (1.11 g, 2.99 mmol) in 1,4-dioxane (10 mL) under N_2 atmosphere. After the diisopropylamine (0.54 g, 5.34 mmol) was added, the mixture was stirred at 110 °C for 38 h, then the reaction solution was warmed to room temperature and concentrated. The residue was diluted by H_2O (10 mL), and the pH was adjusted to 2 using 1 N aq. HCl solution. The resulting solution was extracted with CH_2Cl_2, washed with water and brine for three times when pH value reached around 7. The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel using *n*-hexane and ethyl acetate (v/v = 10/1) as eluent to afford **1c** as a white solid (0.39 g, 34% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ/ppm 7.71 (d, J = 8.2 Hz, 2H, ArH), 7.32 (d, J = 8.2 Hz, 2H, ArH), 6.87 (s, 1H, C=CH), 6.18 (t, J = 6.8 Hz, 1H, NH), 5.19 (d, J = 6.8 Hz, 2H, C=CH_2), 4.16 (t, J = 6.6 Hz, 2H, CH_2), 1.68 (s, 6H, CH_3), 1.66–1.61 (m, 2H, CH_2), 1.34–1.18 (m, 14H, $(CH_2)_7$), 0.87 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ/ppm 210.44, 175.02, 166.23, 137.56, 132.84, 127.40, 126.69, 93.56, 79.28, 77.16, 65.85, 56.98, 31.96, 29.59, 29.28, 28.58, 25.93, 24.74, 22.76, 14.21. FT-IR (KBr, 25 °C): 3340, 2920, 2851, 1938, 1735, 1628, 1607, 1573, 1526, 1498, 1465, 1387 cm^{-1}. HRMS m/z: calcd for $C_{24}H_{36}NO_3$ $[M+H]^+$: 386.2690; Found: 386.2603. Anal. Calcd for $C_{24}H_{35}NO_3$: C, 74.77%; H, 9.15%; N, 3.63%. Found: C, 74.73%; H, 9.18%; N, 3.61%.

Preparation of Ni(II) catalysts. The Ni(II) catalysts were prepared under N_2 atmosphere followed the reported literatures with modification.[7,8] Taking Ni(II)/*R*-**2a** catalyst as an example. A 10 mL oven-dried Schlenk flask charged with *bis*-(1,5-cyclooctadiene)nickel(0) (40.0 mg, 0.15 mmol), π-allyl trifluoroacetate (0.02 mL, 0.15 mmol), and toluene (5.6 mL) was sealed with a rubber septum. The reaction mixture was stirred at room temperature for 20 min. Then, *R*-**2a** (70.9 mg, 0.15 mmol) was added to the mixture under dry N_2 atmosphere. After the mixture solution was stirred at room temperature for 1 h, the resulting solution was directly used for polymerization reaction without further purification.

Typical polymerization procedure. Taking *R*-poly-**1a**$_{100}$ as an example. A 10 mL oven-dried flask was charged with monomer **1a** (122.0 mg, 0.30 mmol), dry CH_2Cl_2 (1.5 mL) and a stirring bar. After stirred at 25 °C for 10 min, a solution of allylnickel complex (0.026 M in toluene, 120 μL, 0.003 mmol) was added to this solution *via* a microsyringe ([**1a**]$_0$/[Ni]$_0$ = 100). The resulting solution was stirred for 14 h, and then poured into a large amount of methanol, which caused a whit e solid to precipitate. The precipitate was collected *via* filtration, washed with methanol and dried under vacuum to afford *R*-poly-**1a**$_{100}$ as a white solid (98.0 mg, yield 90%). SEC: M_n = 40.2 kDa, M_w/M_n = 1.05. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ/ppm 8.51–8.05 (br, 1H), 7.54–6.77 (br, 2H), 6.33–5.52 (br, 3H), 4.35–3.74 (br, 2H), 3.37–2.52 (br, 2H), 1.90–1.44 (m, 8H, CH_2 and CH_3), 1.38–0.99 (m, 14H, CH_2), 0.70–0.66 (m, 3H, CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ/ppm 174.62, 167.73, 158.26, 138.47, 129.62, 128.85, 118.01, 114.62, 65.19, 56.81, 37.43, 32.00, 29.69, 29.41, 28.86, 28.71, 26.22, 26.05, 25.50, 22.77, 14.24. $[\alpha]^{25}_D$ = –21.0 (*c* = 1.0, THF). FT-IR (KBr, 25 °C): 3314, 2962, 2928, 2852, 1742, 1636, 1603, 1580, 1535, 1498 cm^{-1}.

Kinetic study. Taking the polymerization of **1a** initiated by Ni(II)/*R*-**2a** as an example. A mixture of monomer **1a** (137.0 mg, 0.34 mmol) and an internal standard polystyrene (M_n = 2620, M_w/M_n = 1.06, 10.0 mg) were placed in a dry flask, which was then evacuated on a vacuum line and flushed with nitrogen. After the evacuation-flush procedure had been repeated three times, a three-way stopcock was attached to the flask, and dry CH_2Cl_2 (1.7 mL) was added *via* a syringe. Then, a solution of Ni(II)/*R*-**2a** in toluene (0.026 M, 260 μL) was added via a microsyringe at room temperature. The concentrations of **1a** and the Ni(II)/*R*-**2a** catalyst were 0.2 and 0.004 M, respectively ([**1**]$_0$/[Ni]$_0$ = 50). The mixture was then stirred under nitrogen atmosphere at room temperature. The conversion of **1a** was followed by measuring SEC of the aliquots taken out from the reaction mixture at appropriate time intervals. The peak area of the unreacted **1a** relative to that of the internal standard (polystyrene) was used for the estimation of the conversion of **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.

Table S1. Polymerizations of **1a** using Ni(II) catalyst with different ratios of Ni(II) to *R*-**2a** ligand[a]

run	[Ni(II)]/[*R*-**2a**][b]	M_n (kDa)[c]	M_w/M_n[c]	Yield[d]
1	1:0.5	40.3	1.05	85%
2	1:1	40.2	1.05	90%
3	1:2	40.4	1.11	83%
4	1:4	40.3	1.18	85%
5	1:8	40.2	1.32	88%

[a]The polymerizations were conducted in CH_2Cl_2 at 25 °C. [b]The feed ratio of Ni(II) to *R*-**2a**. [c]The M_n and M_w/M_n data were estimated by SEC using polystyrene standards. [d]Isolated yields.

Table S2. Results for the polymerizations of **1b** and **1c** initiated by Ni(II)/*R*-**2a** in CH_2Cl_2 at room temperature [a]

run	Monomer	Polymer[b]	M_n [c] (kDa)	M_w/M_n[c]	Yield[d] (%)
1	**1b**	poly-$\mathbf{1b}_{20}$	7.4	1.08	72
2	**1b**	poly-$\mathbf{1b}_{40}$	14.6	1.07	75
3	**1b**	poly-$\mathbf{1b}_{60}$	22.4	1.07	85
4	**1b**	poly-$\mathbf{1b}_{80}$	29.8	1.07	82
5	**1b**	poly-$\mathbf{1b}_{100}$	38.6	1.07	84
6	**1c**	poly-$\mathbf{1c}_{20}$	7.7	1.07	71
7	**1c**	poly-$\mathbf{1c}_{40}$	15.1	1.08	75
8	**1c**	poly-$\mathbf{1c}_{60}$	23.2	1.08	80
9	**1c**	poly-$\mathbf{1c}_{80}$	30.8	1.07	80
10	**1c**	poly-$\mathbf{1c}_{100}$	38.9	1.08	81

[a]The polymerizations were performed according to Scheme 1 in the main text. [b]The footnotes indicate the initial feed ratio of monomer to catalyst. [c]The M_n and M_w/M_n data were estimated base on SEC analyses. [d]The isolated yields.

Table S3. Polymerizations of **1a** using the Ni(II)/*R*-**2a** in different solvents[a]

run	Solvent	M_n (kDa)[b]	M_w/M_n[b]	Yield[c]
1	$CHCl_3$	40.1	1.29	83%
2	THF	40.6	1.13	85%
3	CH_2Cl_2	40.2	1.05	90%
4	Toluene	39.9	1.05	82%

[a]The polymerizations were carried out according to Scheme 1 in the main text. [b]The M_n and M_w/M_n data were estimated by SEC. [d]Isolated yields.

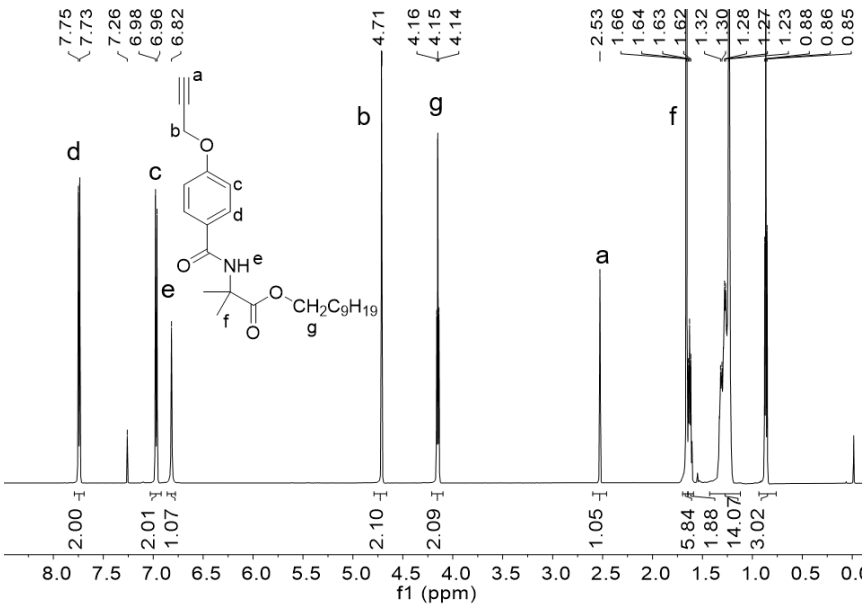


Figure S1. ^{1}H NMR (600 MHz) spectra of **5** measured in $CDCl_3$ at 25 °C.

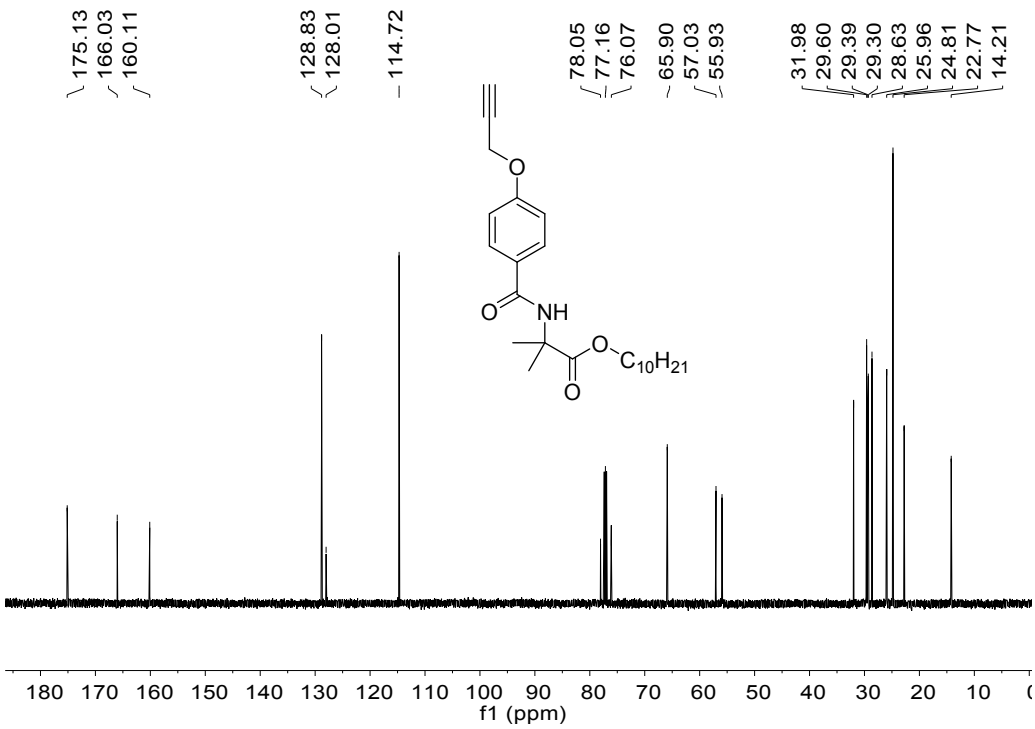


Figure S2. ^{13}C NMR (150 MHz) spectra of **5** measured in $CDCl_3$ at 25 °C.

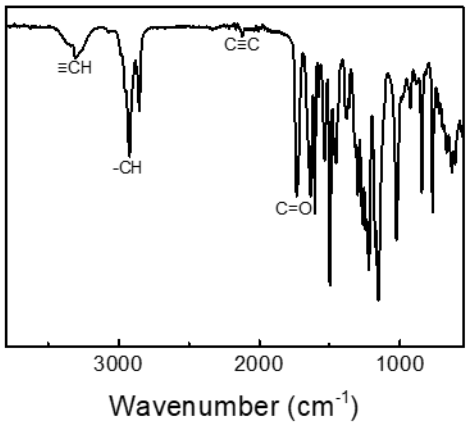


Figure S3. FT-IR spectra of **5** measured at 25 °C using KBr pellets.

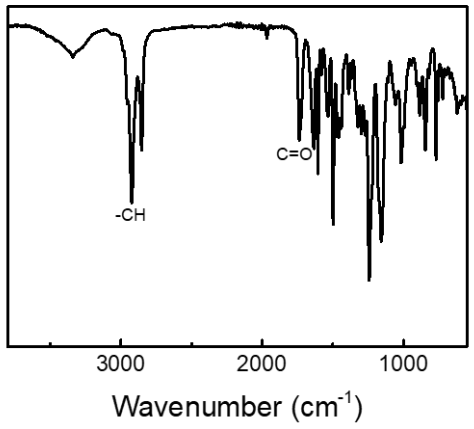


Figure S4. FT-IR spectra of **1a** measured at 25 °C using KBr pellets.

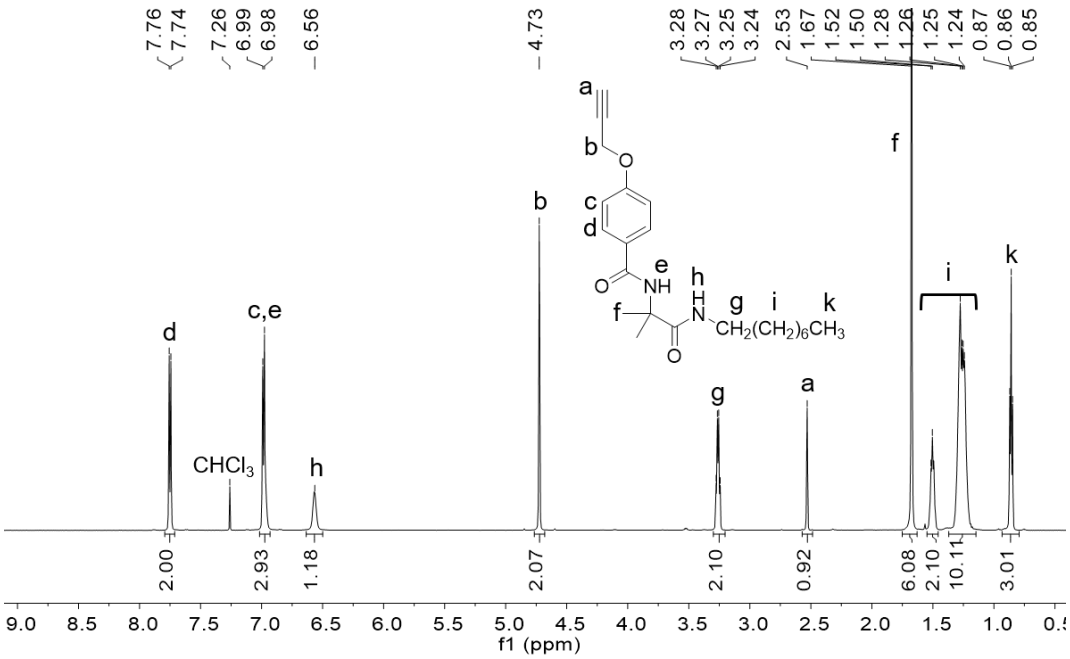


Figure S5. ^{1}H NMR (600 MHz) spectrum of **6** measured in $CDCl_3$ at 25 °C.

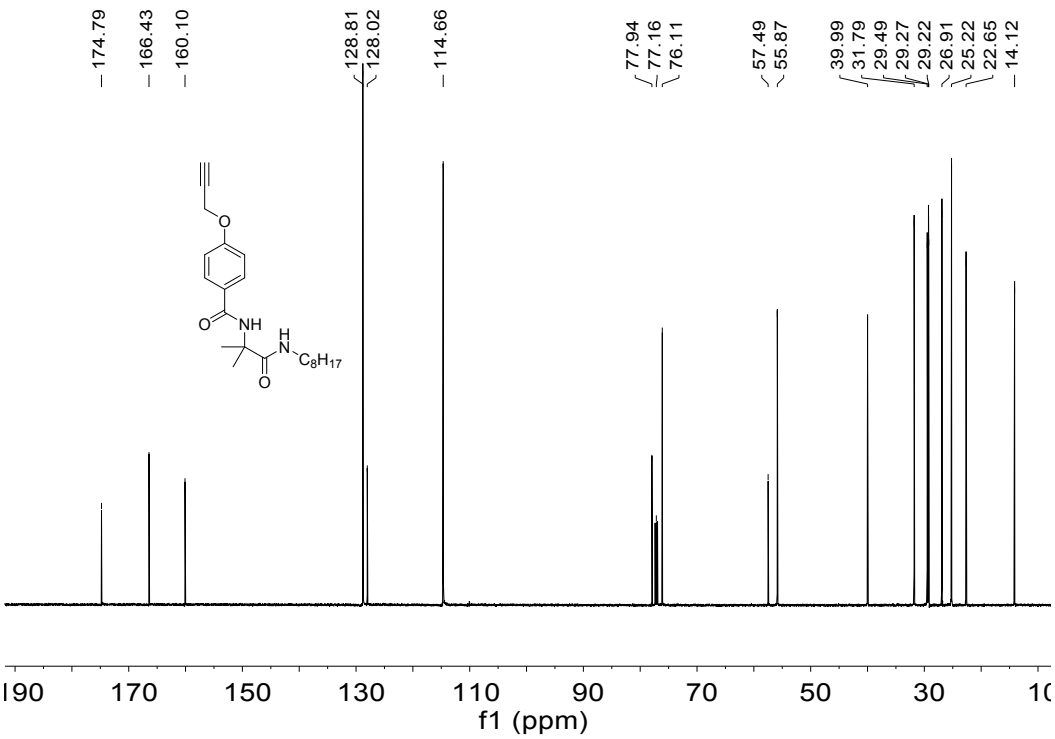


Figure S6. ^{13}C NMR (150 MHz) spectra of **6** measured in $CDCl_3$ at 25 °C.

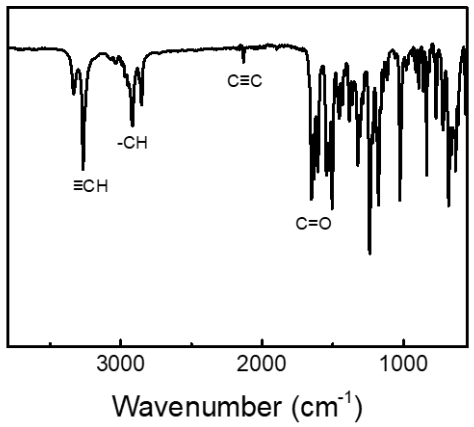


Figure S7. FT-IR spectra of **6** measured at 25 °C using KBr pellets.

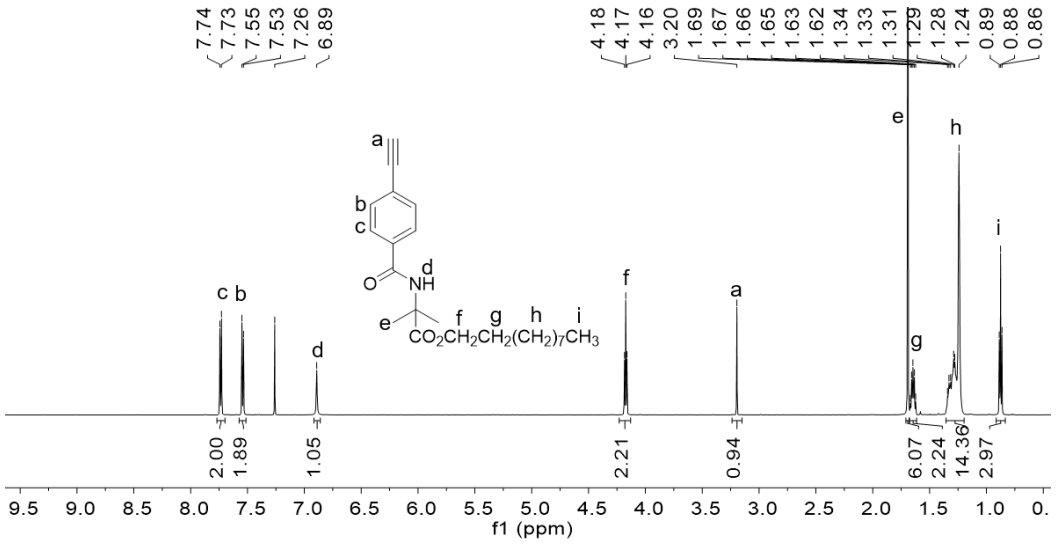


Figure S8. ^{1}H NMR (600 MHz) spectrum of **7** measured in $CDCl_3$ at 25 °C.

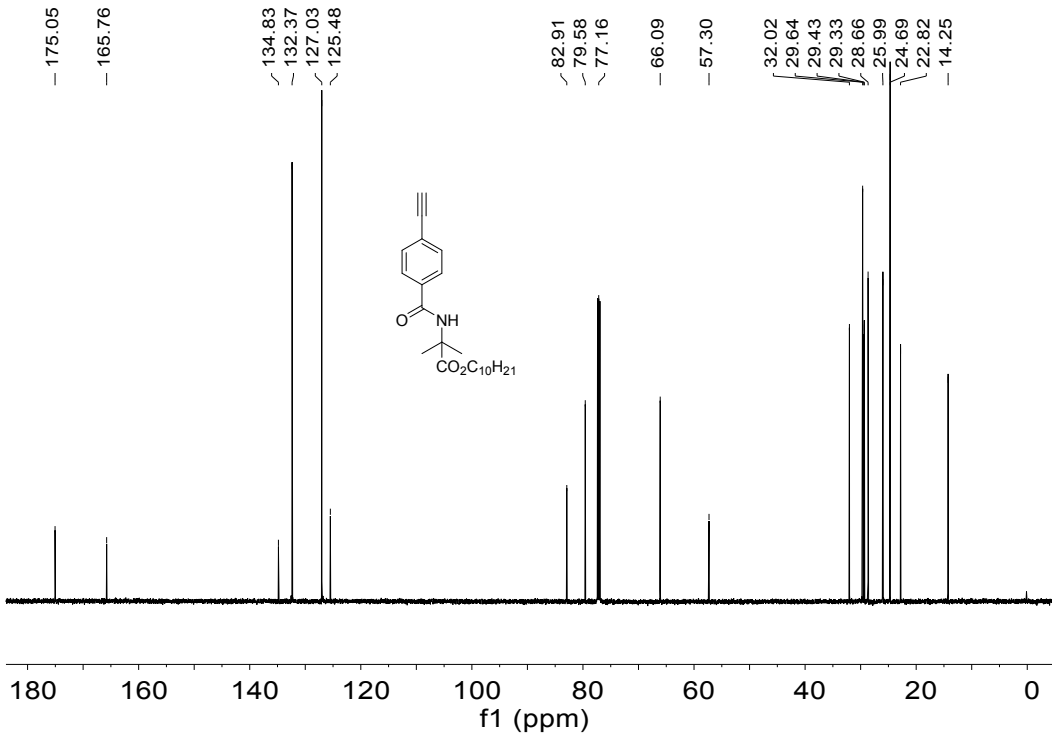


Figure S9. ^{13}C NMR (150 MHz) spectra of **7** measured in $CDCl_3$ at 25 °C.

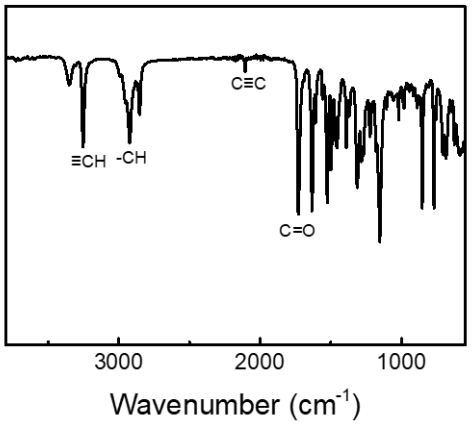


Figure S10. FT-IR spectra of **7** measured at 25 °C using KBr pellets.

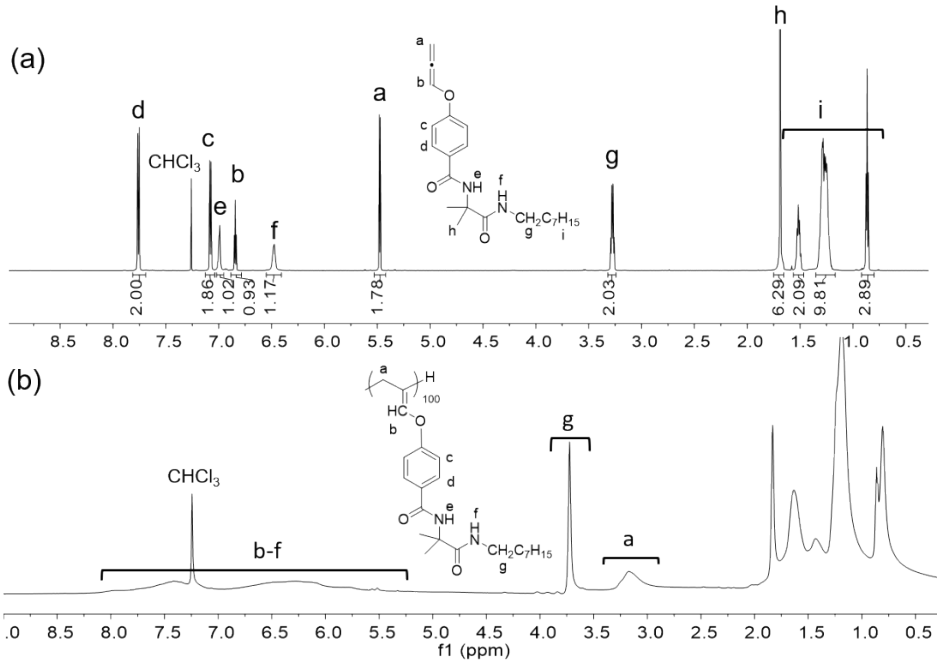


Figure S11. ^{1}H NMR (600 MHz) spectra of monomer **1b** (a) and the resulting *R*-poly-**1b**$_{100}$ (b) recorded in $CDCl_3$ at 25 °C.

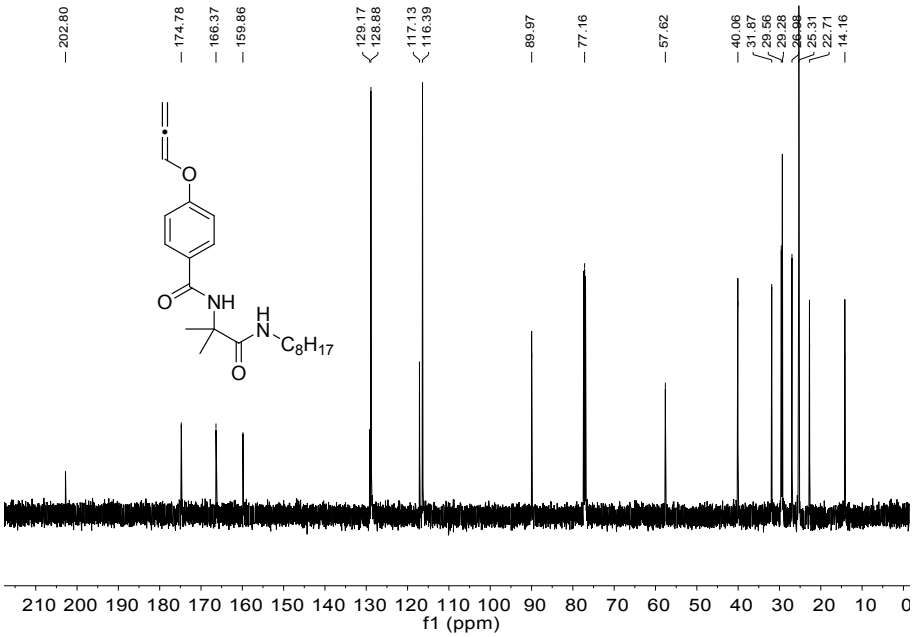


Figure S12. ^{13}C NMR (150 MHz) spectrum of monomer **1b** measured in $CDCl_3$ at 25 °C.

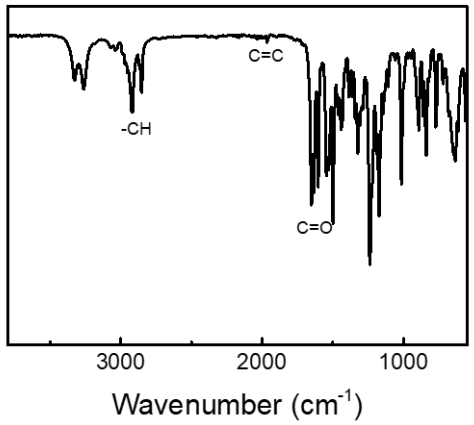


Figure S13. FT-IR spectra of **1b** measured at 25 °C using KBr pellets.

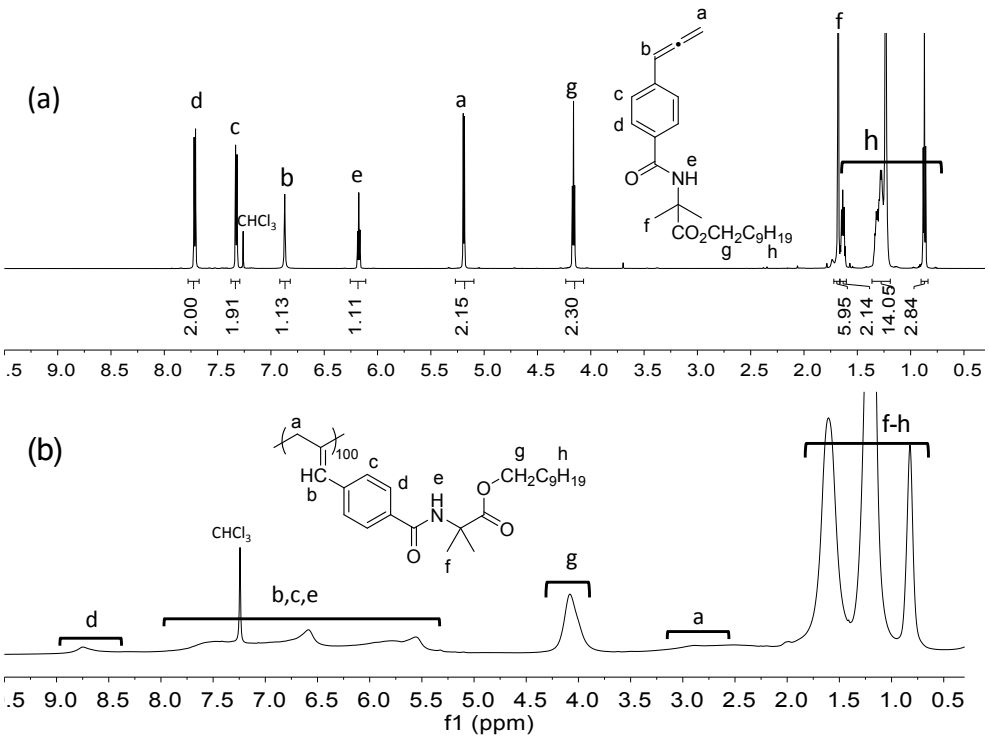


Figure S14. ^{1}H NMR (600 MHz) spectra of monomer **1c** (a) and the resulting *R*-poly-**1c**$_{100}$ (b) recorded in $CDCl_3$ at 25 °C.

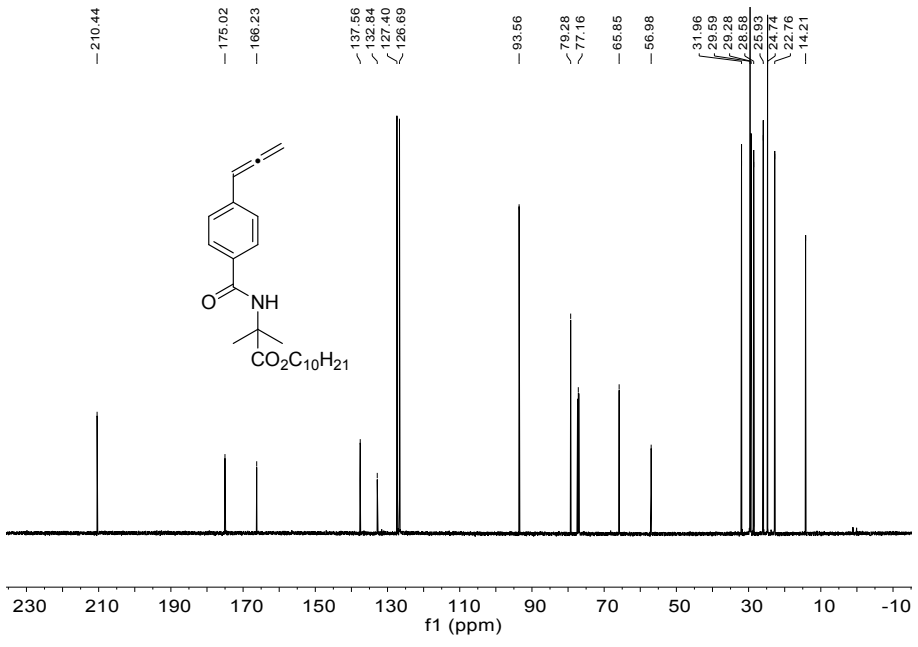


Figure S15. ^{13}C NMR (150 MHz) spectrum of monomer **1c** measured in $CDCl_3$ at 25 °C.

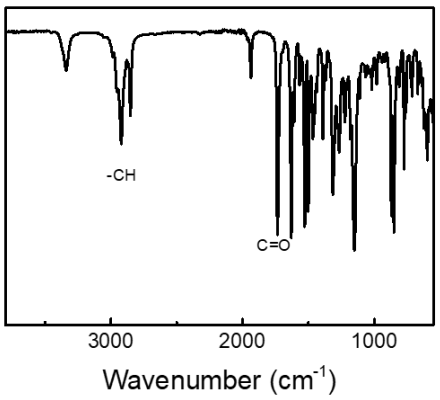


Figure S16. FT-IR spectra of **1c** measured at 25 °C using KBr pellets.

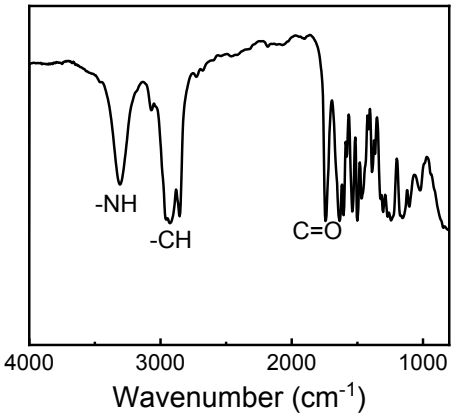


Figure S17. FT-IR spectra of *R*-poly-**1a**$_{100}$ measured at 25 °C using KBr pellets.

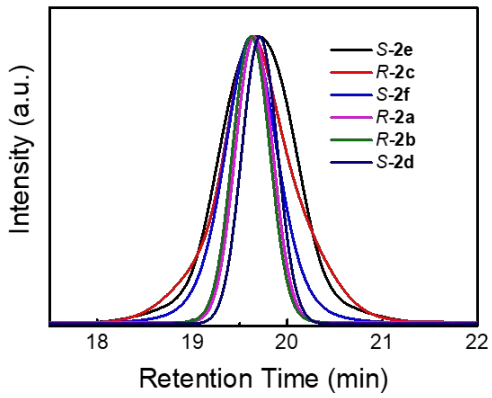


Figure S18. Size exclusion chromatograms for the polymerization of **1a** using Ni(II)/ligand catalysts bearing different ligands in CH_2Cl_2 at room temperature. SEC condition: eluent = THF, temperature = 40 °C.

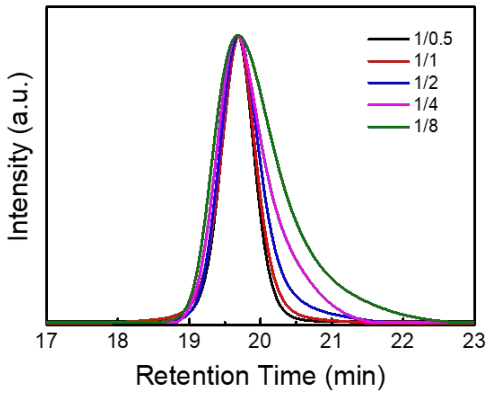


Figure S19. Size exclusion chromatograms of *R*-poly-$\mathbf{1a}_{100}$ prepared from monomer **1a** using the Ni(II)/*R*-**2a** catalysts in CH_2Cl_2 at room temperature with different ratios of Ni(II) to *R*-**2a** ($[\mathbf{1a}]_0$ = 0.2 M, $[\mathbf{1a}]_0/[Ni]_0$ = 100). SEC condition: eluent = THF, temperature = 40 °C.

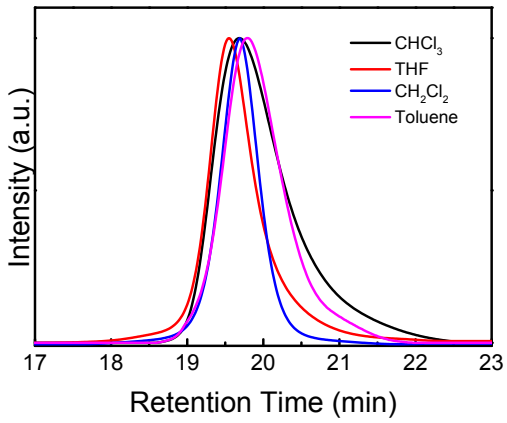


Figure S20. Size exclusion chromatograms of *R*-poly-**1a**$_{100}$ prepared from the polymerization of monomer **1a** using Ni(II)/*R*-**2a** catalyst at room temperature in different solvents ([**1a**]$_0$ = 0.2 M, [Ni(II)]/[*R*-**2a**] = 1/1, [**1a**]$_0$/[Ni]$_0$ = 100). SEC condition: eluent = THF, temperature = 40 °C.

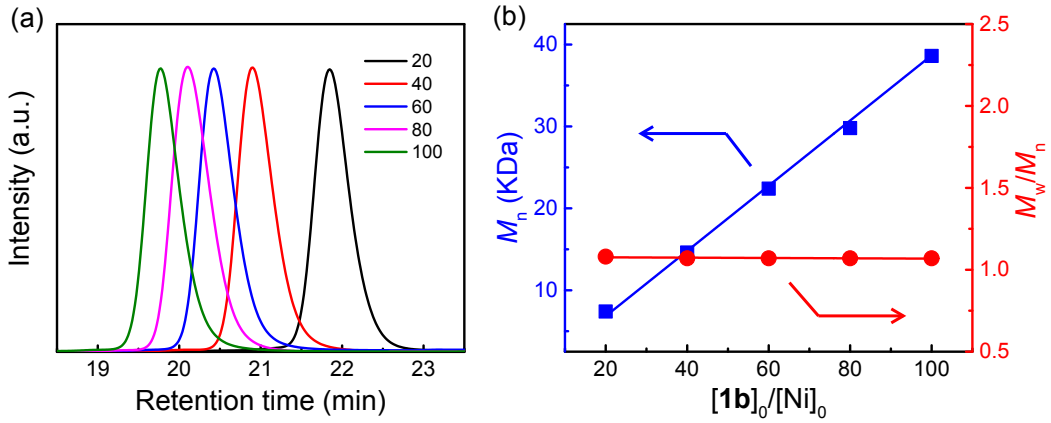


Figure S21. (a) SEC traces of *R*-poly-**1b**$_m$s prepared under different initial feed ratios of monomer **1b** to Ni(II)/*R*-**2a** catalyst. (b) Plots of M_n and M_w/M_n values of *R*-poly-**1b**$_m$ against the ratio of **1b** to the Ni(II) catalyst.

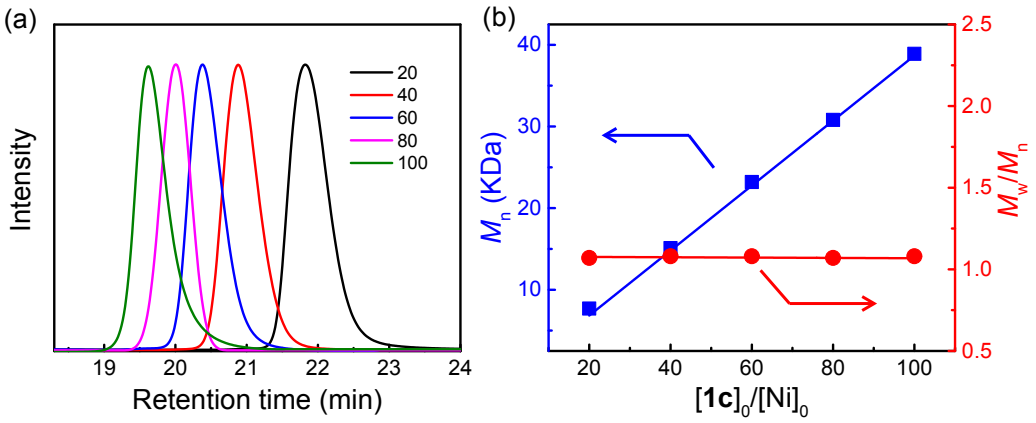


Figure S22. (a) SEC traces of *R*-poly-**1c**$_m$s prepared under different initial feed ratio of **1c** to Ni(II)/*R*-**2a** catalyst. (b) Plots of M_n and M_w/M_n values of *R*-poly-**1c**$_m$ against the feed ratio of **1c** to the Ni(II) catalyst.

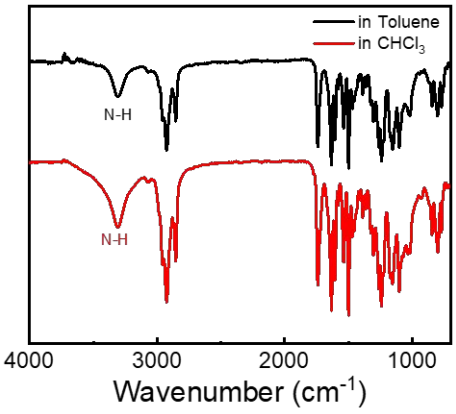


Figure S23. FT-IR spectra of *R*-poly-**1a**$_{100}$ measured in toluene and $CHCl_3$ solution at 25 °C respectively.

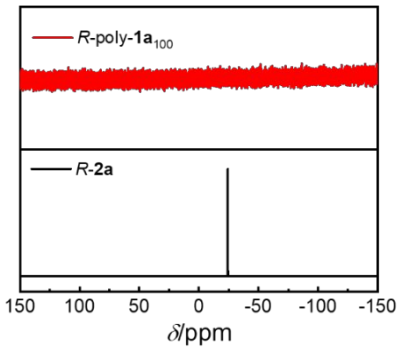


Figure S24. ^{31}P NMR (121.5 MHz) spectra of *R*-poly-**1a**$_{100}$ and *R*-**2a** measured in $CDCl_3$ at 25 °C.

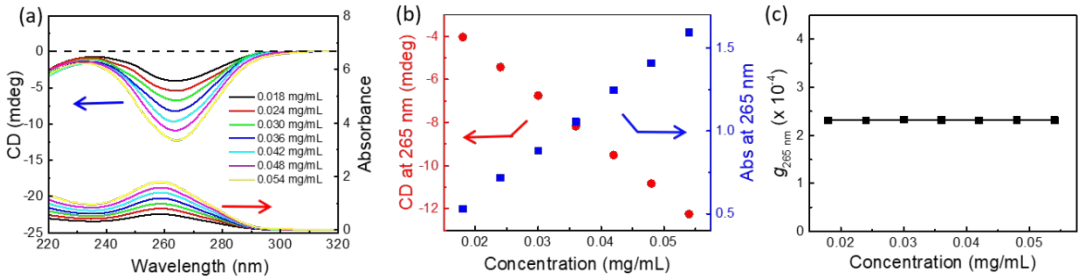


Figure S25. (a) CD and UV-vis spectra of *R*-poly-**1a**$_{100}$ prepared using Ni(II)/*R*-**2a** catalyst measured in THF at 25 °C in different concentrations. (b) Plots of CD and UV-vis intensities at 265 nm with the concentration of *R*-poly-**1a**$_{100}$. (c) Plot of g_{265} of *R*-poly-**1a**$_{100}$ against the concentration in THF at 25 °C.

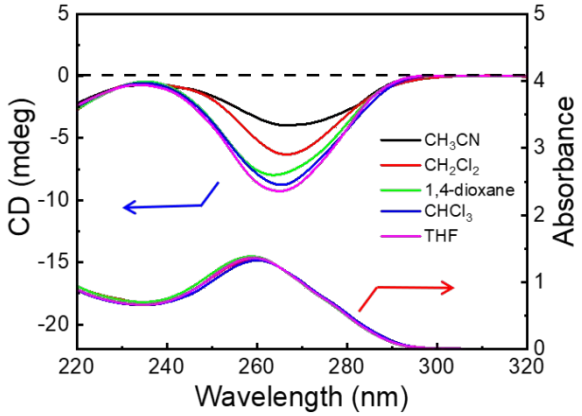


Figure S26. CD and UV-vis spectra of *R*-poly-**1a**$_{100}$ in different solvents at 25 °C (c = 0.045 mg/mL).

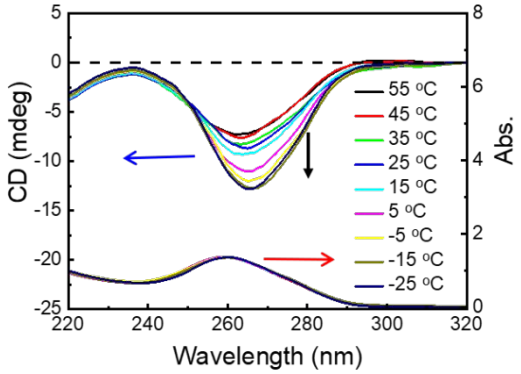


Figure S27. Temperature-dependent CD and UV-vis spectra of *R*-poly-**1a**$_{100}$.

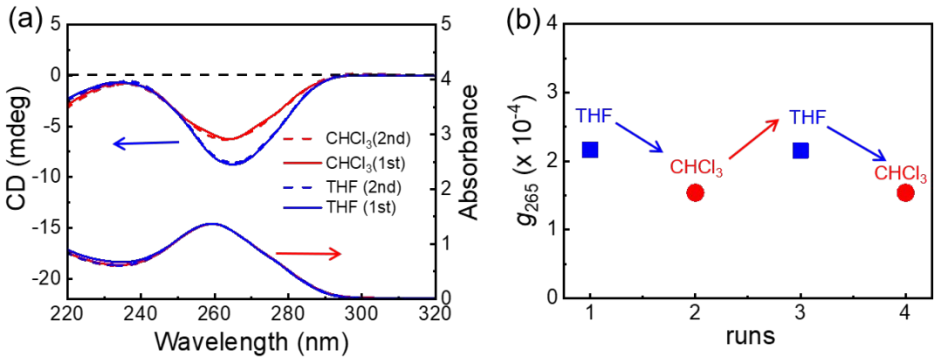


Figure S28. CD and UV-vis spectra of *R*-poly-**1a**$_{100}$ measured in THF and $CDCl_3$ alternately at 25 °C.

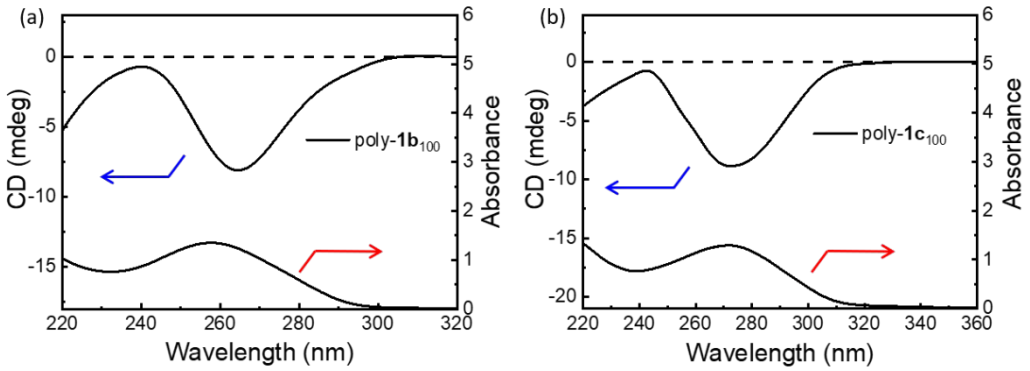


Figure S29. CD and UV-vis spectra of *R*-poly-**1b**$_{100}$ (a) and *R*-poly-**1c**$_{100}$ (b) in THF at 25 °C (c = 0.045 mg/mL).

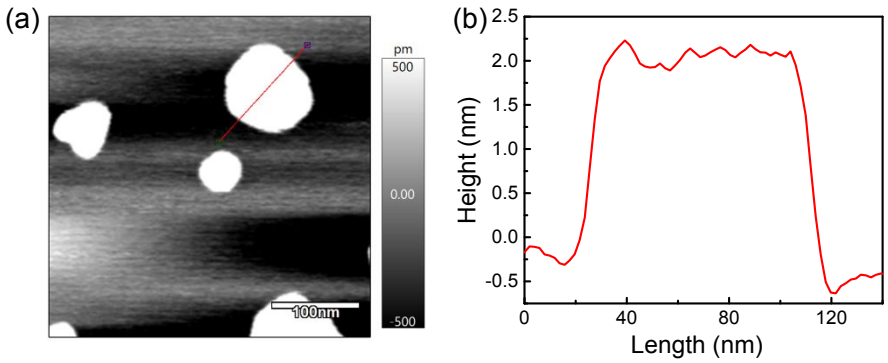


Figure S30. (a) AFM height image and (b) linear height profile of *R*-poly-**1a**$_{100}$ on HOPG.

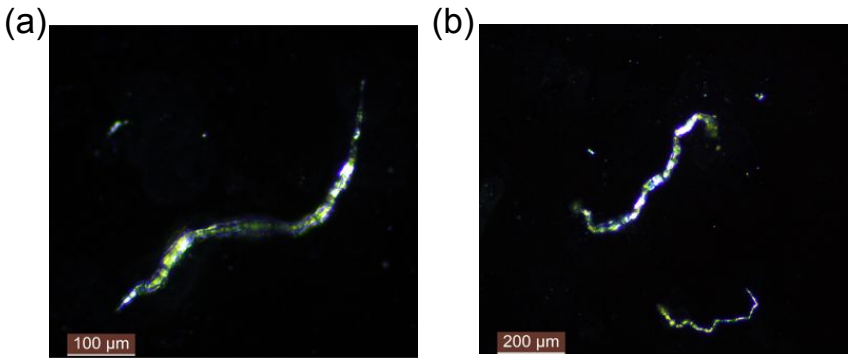


Figure S31. Polarized optical micrographs of *R*-poly-**1a**$_{100}$ (a) and *S*-poly-**1a**$_{100}$ (b) in THF solution measured at 25 °C.

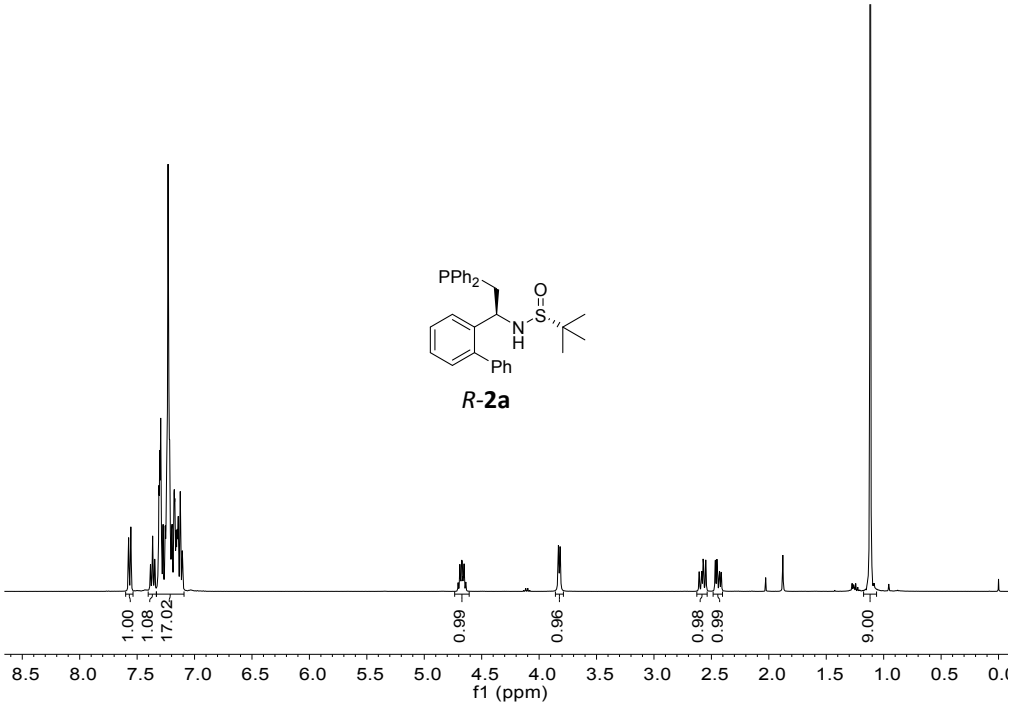


Figure S32. ^{1}H NMR (600 MHz) spectrum of *R*-**2a** measured in $CDCl_3$ at 25 °C.

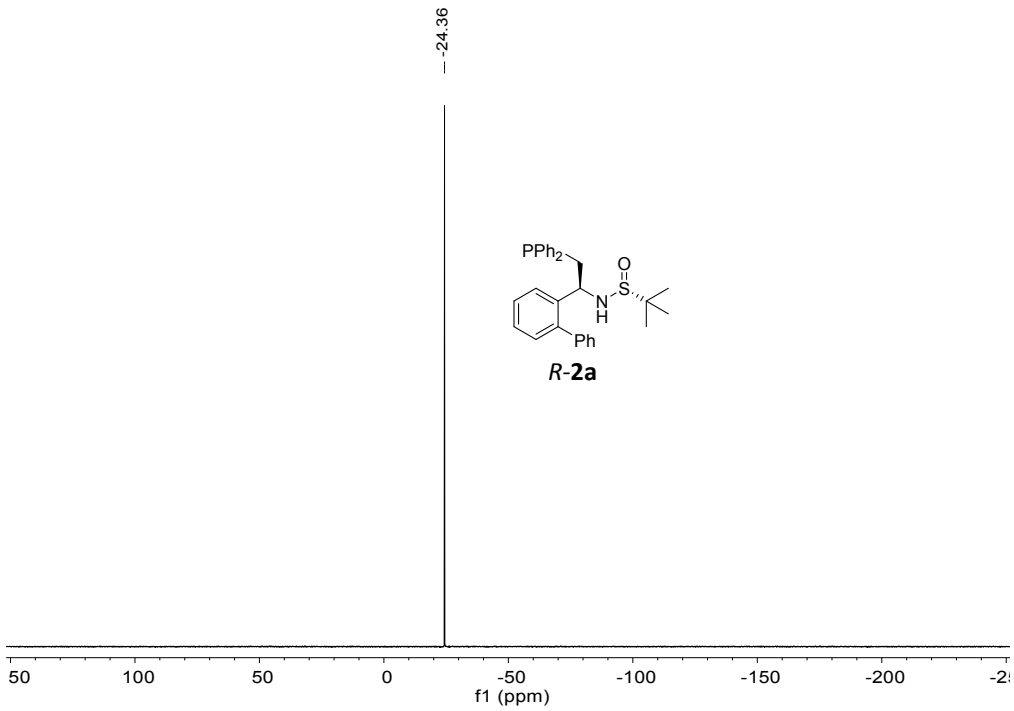


Figure S33. ^{31}P NMR (240 MHz) spectrum of *R*-**2a** measured in $CDCl_3$ at 25 °C.

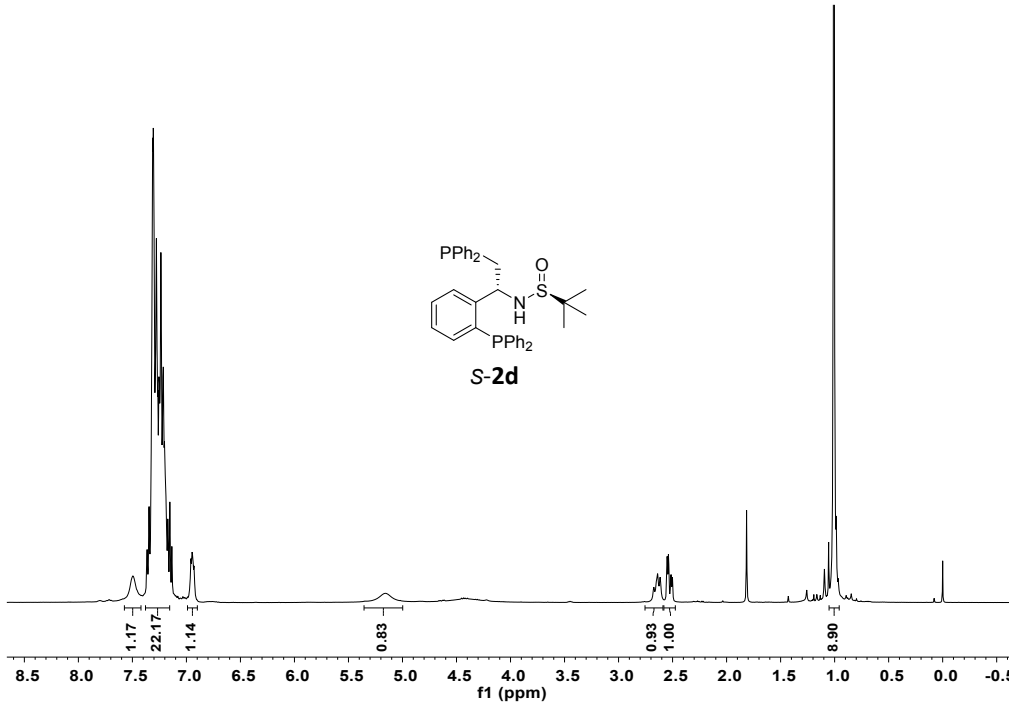


Figure S34. ^{1}H NMR (600 MHz) spectra of *S*-**2d** measured in $CDCl_3$ at 25 °C.

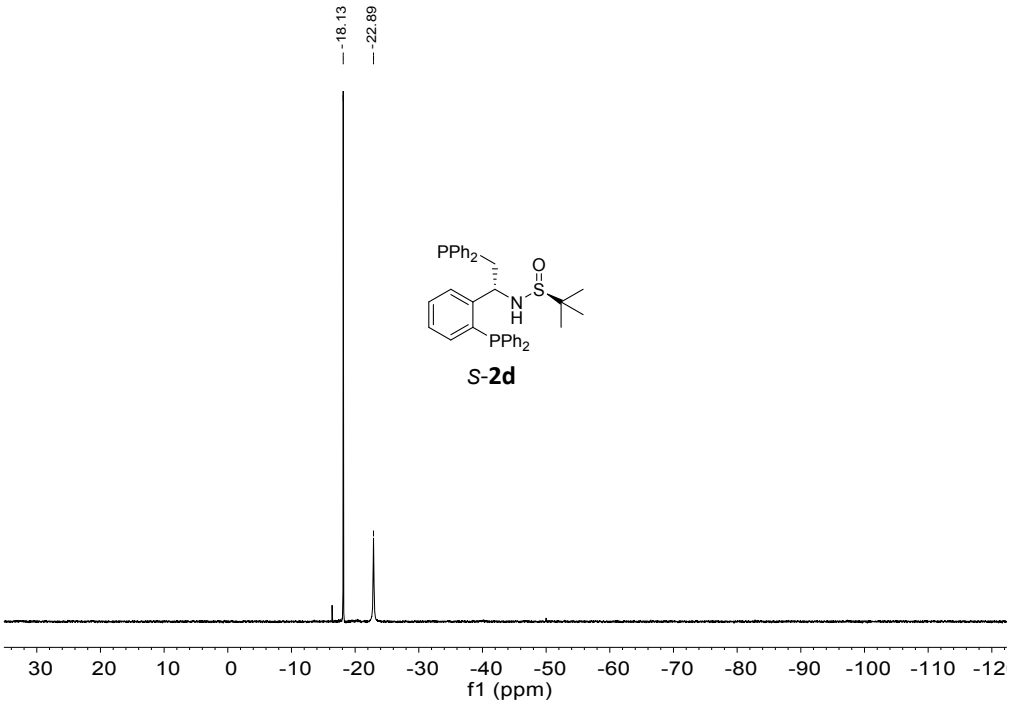


Figure S35. ^{31}P NMR (240 MHz) spectra of *S*-**2d** measured in $CDCl_3$ at 25 °C.

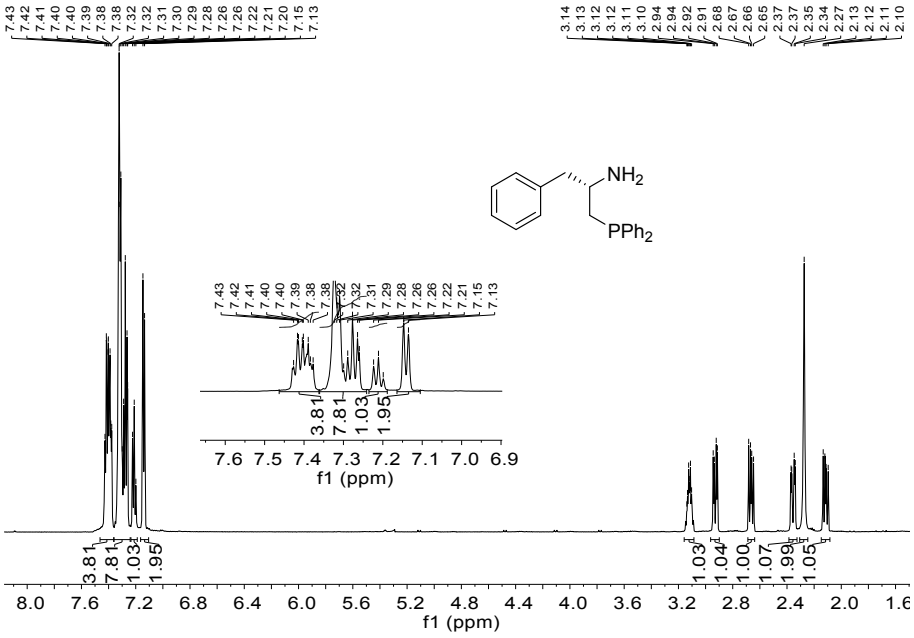


Figure S36. ^{1}H NMR (600 MHz) spectrum of *S*-**2f** measured in $CDCl_3$ at 25 °C.

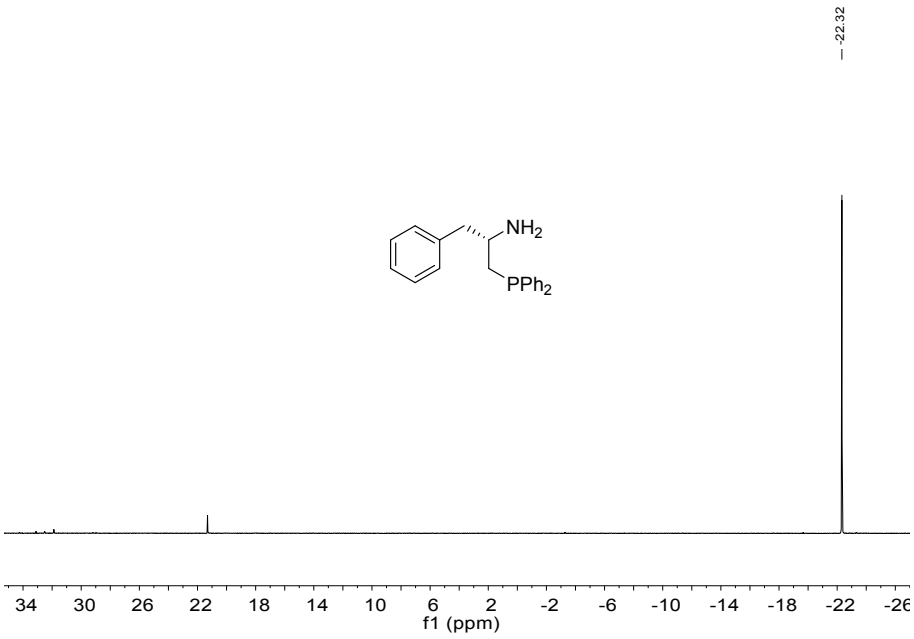


Figure S37. ^{31}P NMR (240 MHz) spectrum of *S*-**2f** measured in $CDCl_3$ at 25 °C.

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