Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Reversibly Photo-switchable Catalysts for high Regioselectivity and Enantioselectivity in Polymerization of Allenes

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Measurements

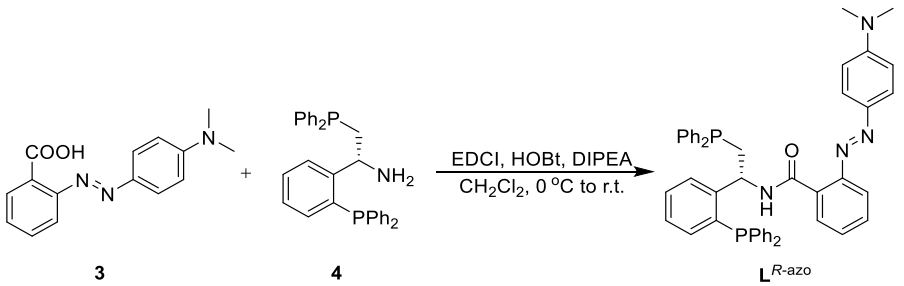
The ^{1}H, ^{13}C NMR spectra were recorded using a Bruker 600 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of two linear TSK gel GMHHR-H columns. Molecular weight (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. 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 cm quartz cell using a JASCO J1500 spectropolarimeter. The polymer concentration was calculated on the basis of the repeated units and was 0.2 mg/mL. The UV-vis absorption spectra were recorded on a UNICO 4802 UV/Vis double beam spectrophotometer. High performance liquid chromatography (HPLC) was carried out on a JASCO Pu-418 pump with JASCO UV-4070 and CD-4095 detectors, using *n*-hexane/i-PrOH as fluent on chiral column.

Materials

All solvents were obtained from Sinopharm. Co. Ltd. purified by the standard procedures before use. All chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd. used as received without further purification otherwise denoted. Allene monomers **1**, D-**2**, L-**2** were synthesized according to the reported previous literatures with slight modifications.[1,2] Bidentate phosphine ligands were prepared followed the literatures with slight modifications and the structures were confirmed by ^{1}H NMR. 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.[3,4]

Scheme S1. Synthesis of bidentate phosphine ligand $L^{R\text{-azo}}$



3 **4** $L^{R\text{-azo}}$

The compound **4** was prepared according to the literature.[5,6] To a solution of methyl red **3** (87.2 mg, 0.40 mmol) in dry CH_2Cl_2 (5 mL) at 0 ℃ under N_2 was added 1-Hydroxybenzotrizole (HOBt, 65.1 mg, 0.48 mmol), N, N-diisopropylethylamine (DIPEA, 83 μL, 0.48 mmol) and 1-Ethyl-3- (3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 75.3 mg, 0.48 mmol). After stirring for 10 min, the corresponding amine **4** (210 mg, 0.40 mmol) in dry CH_2Cl_2 (5 mL) was introduced at the same temperature. The stirring was continued at 0 ℃ for 1 h and then at room temperature overnight. The mixture was diluted with CH_2Cl_2, washed with saturated aqueous NH_4Cl solution, and the organic layer was collected and dried over Na_2SO_4. Solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1 (v/v)) to afford the corresponding chiral ligand $\mathbf{L}^{R\text{-azo}}$ (207 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 10.00 (d, J = 6.0 Hz, 1H), 8.21 (d, J = 12.0 Hz, 1H, NH), 7.77–6.99(m, 38H, ArH), 6.46 (d, J = 12.0 Hz, 2H, CH_2), 5.84 (br, 1H, CH), 3.01 (s, 6H, $N(CH_3)_2$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ (ppm) 164.95, 152.86, 150.56, 148.20, 143.47, 138.46, 137.73, 137.31, 136.51, 135.53, 133.58, 133.24, 132.74, 131.44, 130.98,

129.48, 129.16, 128.98, 128.63, 128.41, 128.19, 127.46, 126.13, 115.73, 111.51, 68.18, 65.60, 40.22. HRMS (ESI-FT): Calcd. for $[M + H]^+$, $C_{47}H_{43}N_4OP_2^+$: 741.2914. Found: 741.2887. FT-IR (KBr, 25 °C): 3432 ($\nu_{N–H}$), 3050, 2919, 2851 ($\nu_{C–H}$), 1650 ($\nu_{C=O}$), 1600($\nu_{N=N}$) cm^{-1}.

***Preparation of the Ni(II) catalysts*:** Taking Ni(II)/$\mathbf{L}^{R\text{-azo}}$ as an example. A 10 mL oven-dried Schlenk flask charged with bis-(1,5-cyclooctadiene)nicke(0) (40.3 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, $\mathbf{L}^{R\text{-azo}}$ (110 mg, 0.15 mmol) was added to the mixture under N_2 atmosphere. After the mixture solution was stirred at room temperature for another 1 h, the resulting solution was directly used for polymerization reaction without further purification to avoid the decomposition of the catalyst. ^{1}H NMR (600 MHz, Toluene-d_8, 25 °C): δ (ppm) 9.45 (s, 1H), 8.18 (d, J = 7.6 Hz, 1H), 7.97 (s, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 9.1 Hz, 2H), 7.29 (s, 3H), 6.90 – 6.80 (m, 9H), 6.74 (s, 7H), 6.34-6.30 (m, 2H), 6.23 (t, J = 8.6 Hz, 1H), 6.19 (d, J = 8.5 Hz, 2H), 5.41 (s, 1H), 4.73 (s, 1H), 4.29 (s, 1H), 3.58 (s, 1H), 3.49 (s, 2H), 3.01 (s, 1H), 2.66 (q, J = 13.2 Hz, 1H), 2.36 (s, 6H). ^{13}C NMR (150 MHz, Toluene-d_8, 25 °C): δ (ppm) 163.52, 152.25, 149.72, 145.86, 135.48, 135.40, 134.00, 133.72, 131.71, 131.62, 131.55, 131.47, 131.13, 131.06, 130.40, 130.23, 129.96, 128.65, 128.58, 127.55, 127.48, 125.91, 115.00, 111.00, 106.55, 67.65, 65.05, 52.57, 38.87, 32.52, 29.30, 27.40. ^{31}P NMR (243 MHz, Toluene-d_8, 25 °C): 26.08, 20.83. HRMS (ESI-FT): Calcd. For $[M–OCOCF_3]^+$, $C_{50}H_{47}N_4OP_2Ni^+$: 839.2573; Found: 839.2571.

Typical polymerization procedure. Taking poly-**1**$_{100}$(**L**$^{R\text{-azo}}$) as an example. A 10 mL oven-dried flask was charged with monomer **1** (50.2 mg, 0.30 mmol), dry CH_2Cl_2 (1.5 mL) and a stirring bar. After stirring at 25 °C for 10 min, a solution of Ni(II)/**L**$^{R\text{-azo}}$ complex (0.026 M in toluene, 115 μL, 0.003 mmol) was added to this solution via a microsyringe ([**1**]$_0$/[Ni(II)]$_0$ = 100). The resulting solution was stirred for 18 h at 35 °C, and then poured into a large amount of methanol, which caused a white solid to precipitate. The precipitate was collected via filtration, washed with methanol and dried under vacuum to afford poly-**1**$_{100}$(**L**$^{R\text{-azo}}$) as a white solid (43.3 mg, 86% yield).[1] SEC: M_n = 16.4 kDa, M_w/M_n = 1.08. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ (ppm) 6.11−5.66 (br, =CH, 1H), 3.78−3.44 (br, CH_2 of main chain, 2H), 2.83−2.28 (br, OCH_2, 2H), 1.72−1.45 (br, OCH_2CH_2, 2H), 1.45−1.03 (br, 10H), 1.00−0.66 (br, CH_3, 3H). FT-IR (KBr, 25 °C): 2918 (ν_{C-H}), 1665 ($\nu_{C=C}$), 1460 (δ_{C-H}), 1108 (ν_{C-O}) cm^{-1}.

Kinetic studies. Taking the polymerization of D-**2** initiated by Ni(II)/**L**$^{R\text{-azo}}$ as an example. A mixture of monomer D-**2** (100 mg, 0.28 mmol) and an internal standard polystyrene (M_n = 2630, M_w/M_n = 1.06, 30.0 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 (1.4 mL) was added via a syringe. Then, a solution of Ni(II)/**L**$^{R\text{-azo}}$ in toluene (0.026 M, 107 μL) was added via a microsyringe at room temperature. The concentrations of D-**2** and the Ni(II)/**L**$^{R\text{-azo}}$ catalyst were 0.2 and 0.026 M, respectively ([D-**2**]$_0$/[Ni(II)]$_0$ = 100). The mixture was then stirred under nitrogen atmosphere at 35 °C. The conversion of D-**2** was followed by measuring SEC of the aliquots taken

out from the reaction mixture at appropriate time intervals. The peak area of the unreacted D-**2** relative to that of the internal standard (polystyrene) was used for the estimation of the conversion of D-**2** 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.

Kinetic study for the polymerization of **1**, L-**2**, the copolymerization of racemates of L-**2** and D-**2** were carried out under the same procedure, the polymerization solution of **1** was stirred in glovebox and followed by measuring ^{1}H NMR of the aliquots taking out from the reaction solution at appropriate time intervals, and the conversion of monomer **1** was calculated based on the peak area of unreacted **1** relative to that of the internal standard dimethyl terephthalate.

On/Off Experiments. On/Off experiments of polymerization were performed analogously to those polymerization procedures described previously.[7-8] Taking the polymerization of D-**2** under visible light using Ni(II)/$\mathbf{L}^{R\text{-azo}}$ as initiator as example. Under N_2 atmosphere, a solution of the as prepared Ni(II)/$\mathbf{L}^{R\text{-azo}}$ catalyst (0.107 mL, 0.026 M) was added to the mixture of monomer D-**2** (100 mg, 0.28 mmol) and polystyrene (M_n = 2630, M_w/M_n = 1.06, 30.3 mg) in CH_2Cl_2 (1.4 mL) via a syringe ([D-**2**]$_0$/[Ni(II)]$_0$ = 100, [D-**2**]$_0$ = 0.2 M). The polymerization solution was stirred at desired light condition at 35 ℃ and was followed by measuring SEC of the aliquots taking out from the reaction solution at appropriate time intervals. When taking out of the aliquots, turn off/on the UV light to change the light condition. This sequence was repeated until the reaction showed almost full conversion.

DFT computational details. The structure of all catalysts, monomer and products were calculated using the density functional theory (DFT) method at the B3LYP-D3BJ/6-31G/LanL2DZ level for *cis*- or *trans*-Ni(II)/$\mathbf{L}^{R\text{-}azo}$, *cis*- and *trans*-**IN-1**, and at the B3LYP-D3BJ/6-31G level for L-**2'** in the Gaussian 16 program running under super computer in Peking University, and the stimulation temperature was set at 298 K. In order to simplify the calculation, we simplified the side chain of L-**2** from -C_8H_{17} to -CH_3.

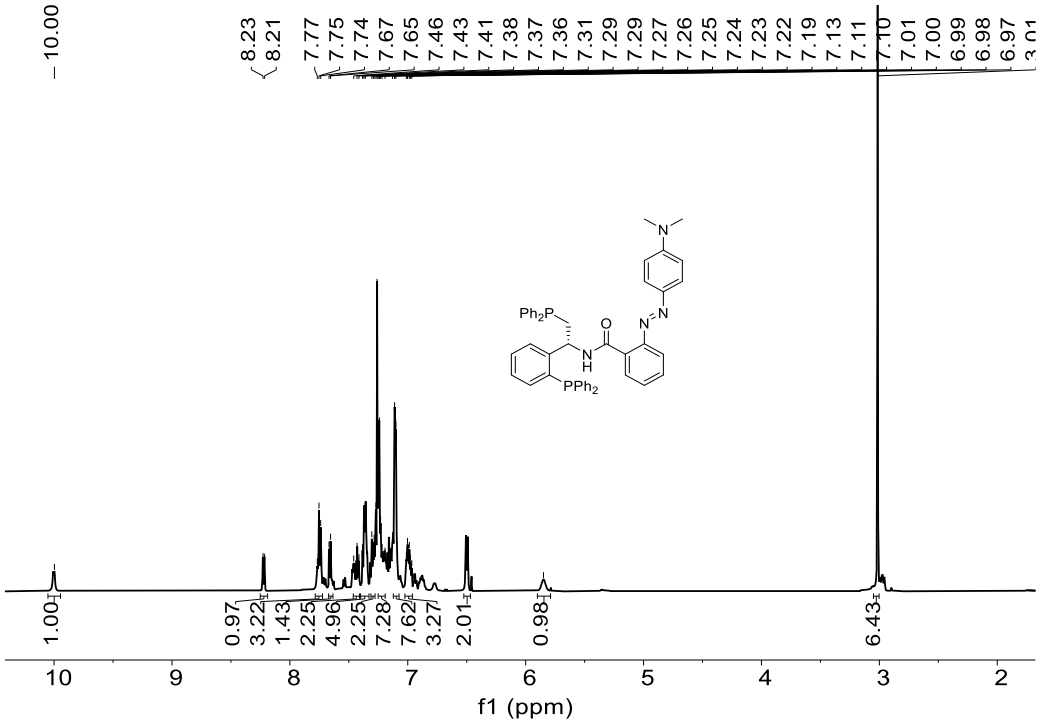


Figure S1. ^{1}H NMR (600 MHz) spectrum of ligand $\mathbf{L}^{R\text{-}azo}$ measured in $CDCl_3$ at 25 °C.

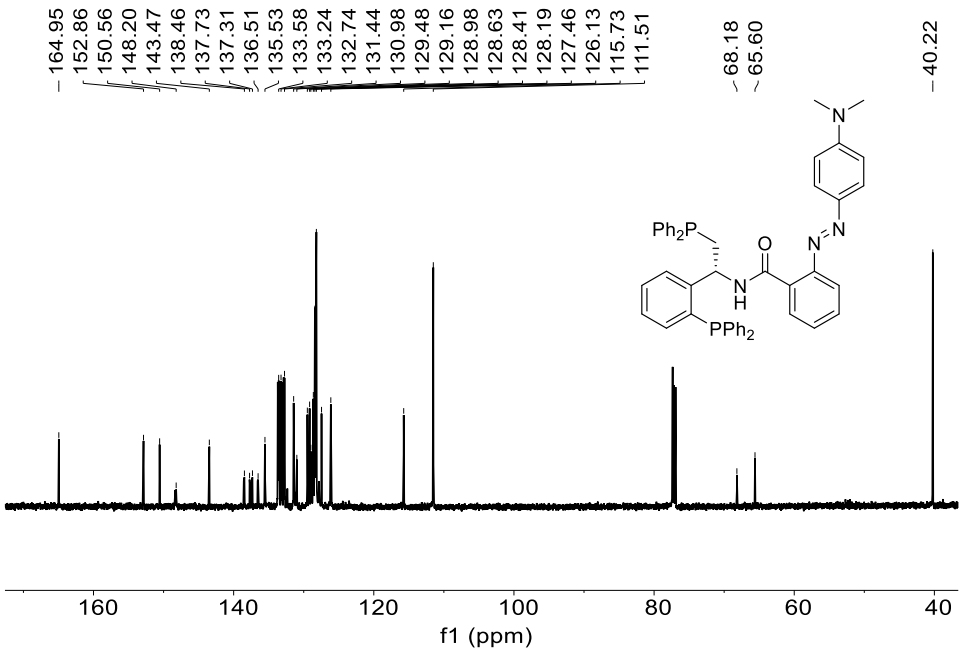


Figure S2. ^{13}C NMR (150 MHz) spectrum of ligand $\mathbf{L}^{R\text{-azo}}$ measured in $CDCl_3$ at 25 °C.

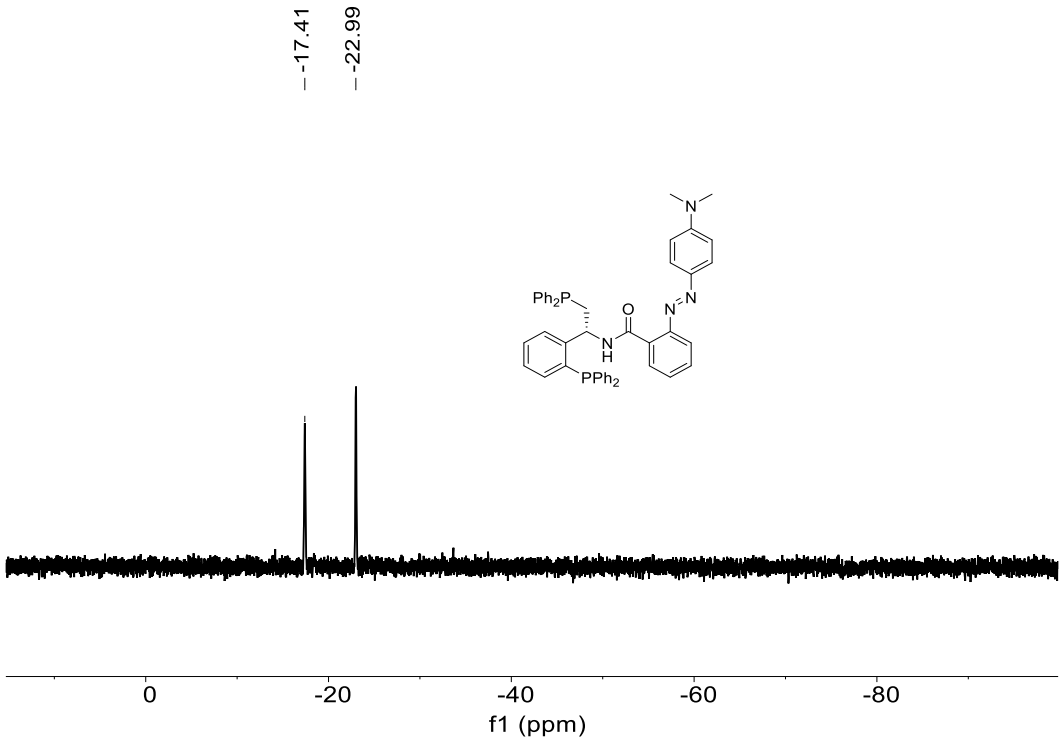


Figure S3. ^{31}P NMR (243 MHz) spectrum of ligand $\mathbf{L}^{R\text{-azo}}$ measured in $CDCl_3$ at 25 °C.

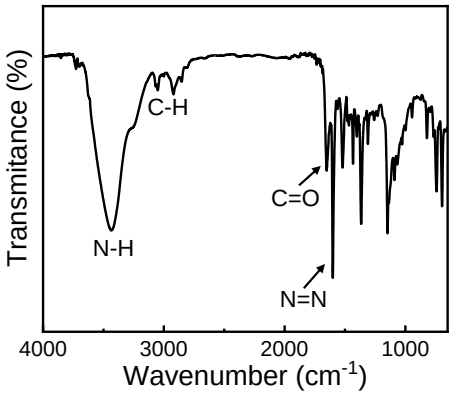


Figure S4. FT-IR spectrum of ligand $\mathbf{L}^{R\text{-azo}}$ measured at 25 °C using KBr pellets.

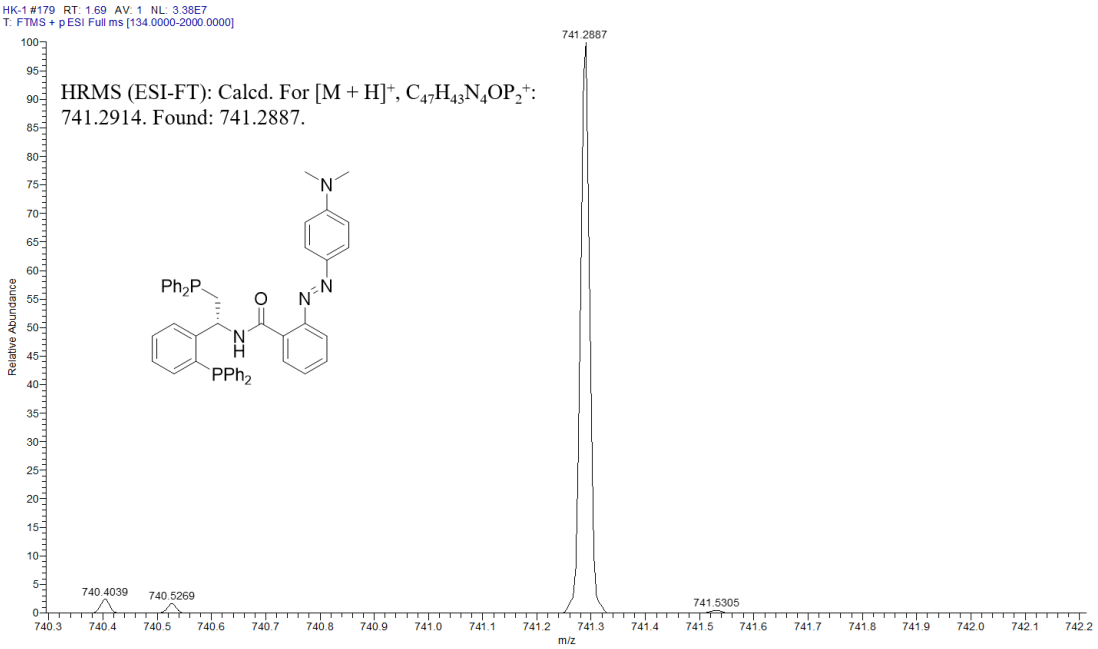


Figure S5. HRMS(ESI-FT) spectrum of ligand $\mathbf{L}^{R\text{-azo}}$.

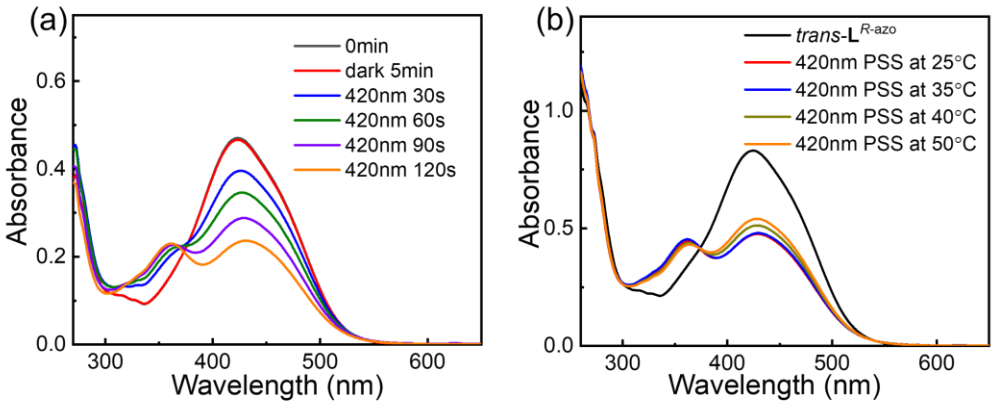


Figure S6. (a) UV−vis spectra of the $\mathbf{L}^{R\text{-azo}}$ ligand irradiation of visible light (420 nm) and dark (THF，0.03 mg/mL，25 °C). (b) The UV−vis spectra of $\mathbf{L}^{R\text{-azo}}$ at 420 nm PSS states at 25 °C, 35 °C, 40 °C and 40 °C and the UV-vis spectrum of *trans*-$\mathbf{L}^{R\text{-azo}}$ in the polymerization mixture (THF，0.05 mg/mL)

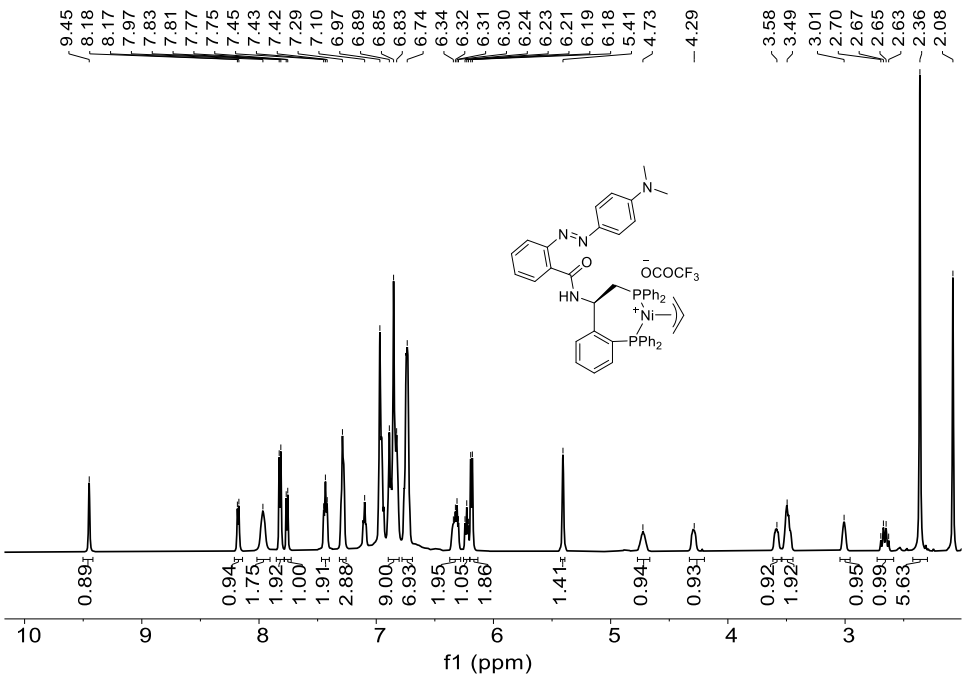


Figure S7. ^{1}H NMR (600 MHz) spectrum of ligand Ni(II)/$\mathbf{L}^{R\text{-azo}}$ measured in toluene-d_8 at 25 °C.

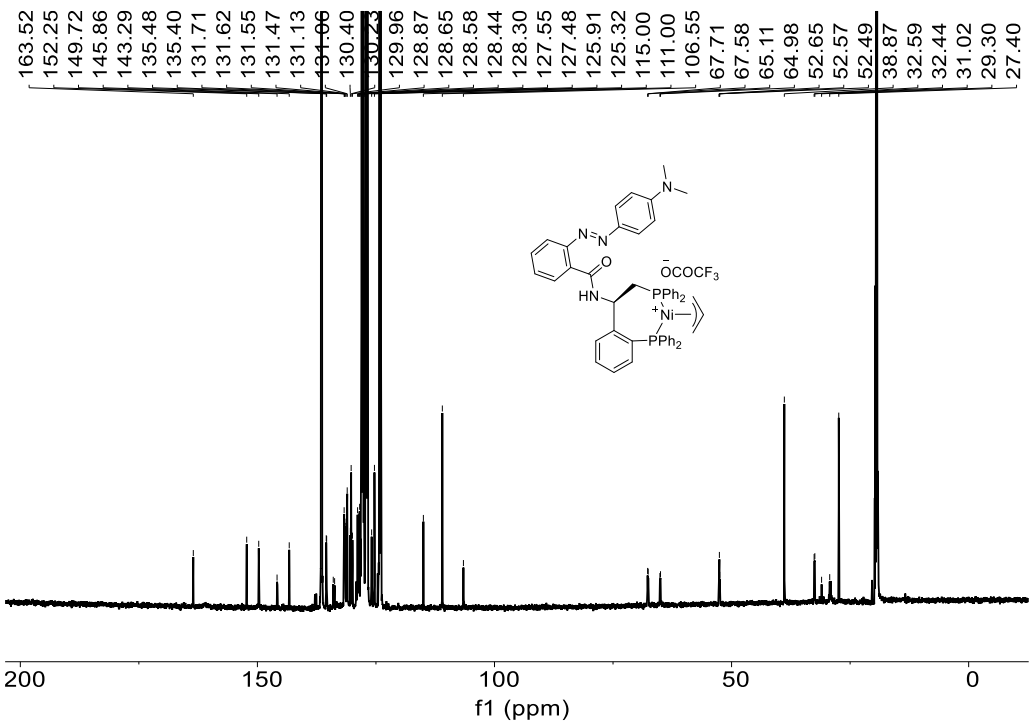


Figure S8. ^{13}C NMR (150 MHz) spectrum of ligand Ni(II)/**L**$^{R\text{-azo}}$ measured in toluene-d_8 at 25 °C.

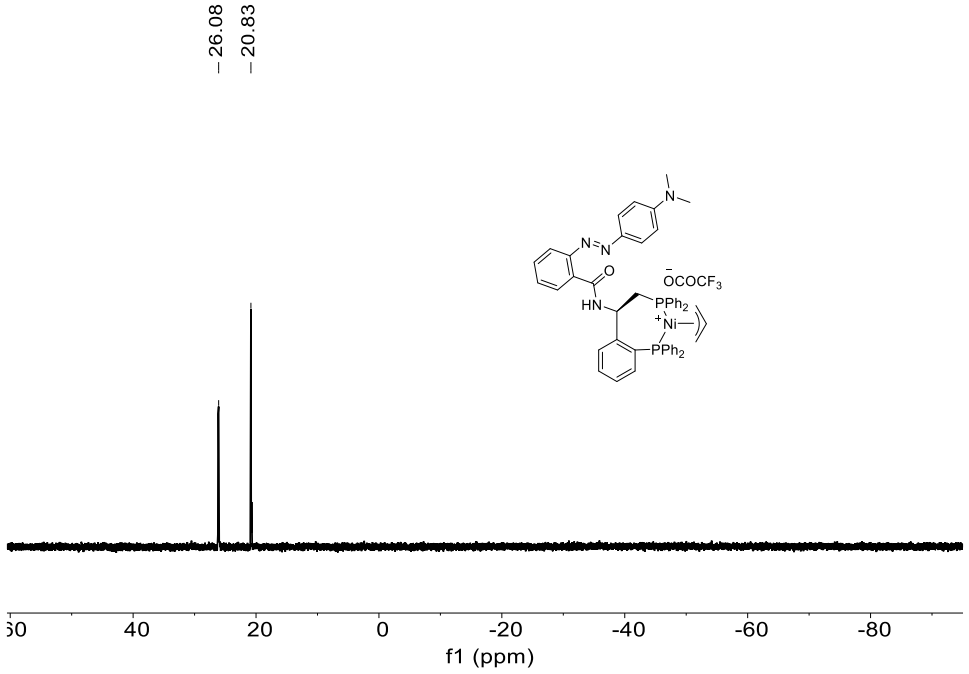


Figure S9. ^{31}P NMR (243 MHz) spectrum of ligand Ni(II)/**L**$^{R\text{-azo}}$ measured in toluene-d_8 at 25 °C.

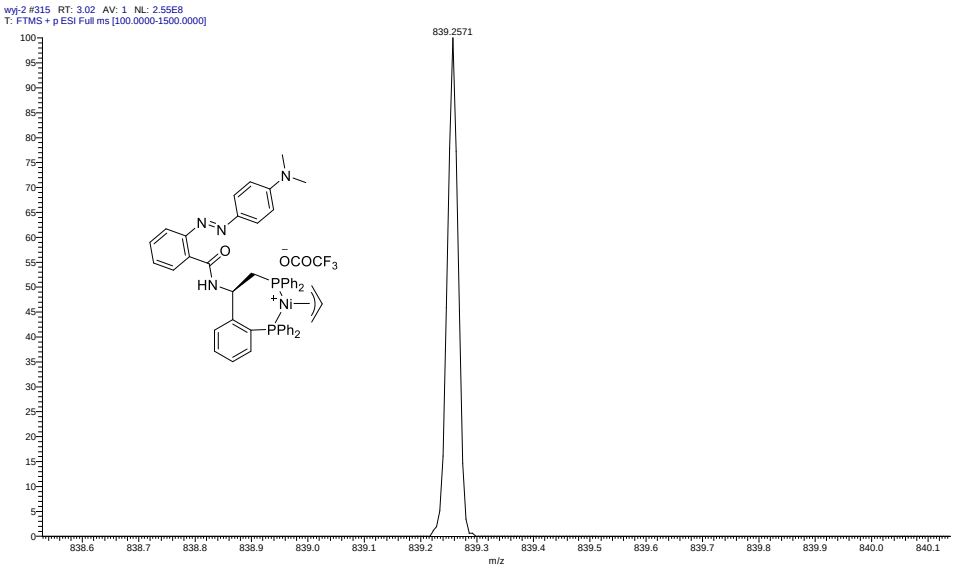


Figure S10. HRMS(ESI-FT) spectrum of Ni(II)/$\mathbf{L}^{R\text{-azo}}$.

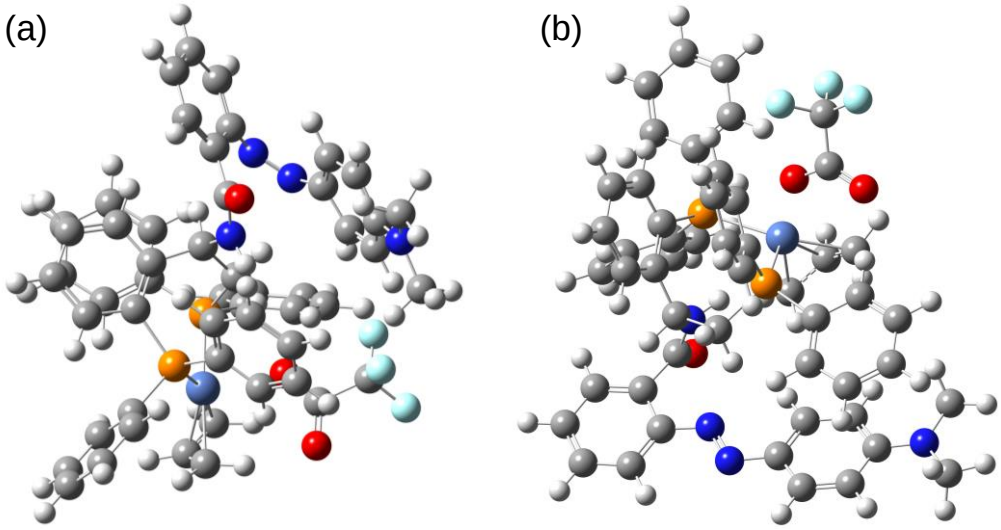


Figure S11. Optimal structure of *cis*-Ni(II)/$\mathbf{L}^{R}$ (a) and *trans*-Ni(II)/$\mathbf{L}^{R}$ by DFT calculation at B3LYP-D3BJ/6-31G/LanL2DZ level at 298 K.

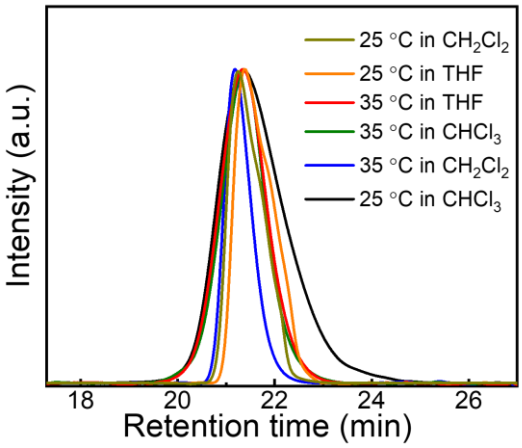


Figure S12. Size exclusion chromatograms for the polymerization of **1** using Ni(II)/$\mathbf{L}^{R\text{-}azo}$ catalyst with different solvents and temperatures ($[\mathbf{1}]_0$ = 0.2 M, $[\mathbf{1}]_0/[\text{Ni(II)}]_0$ = 100) under dark condition. SEC condition: eluent = THF, temperature = 40 °C.

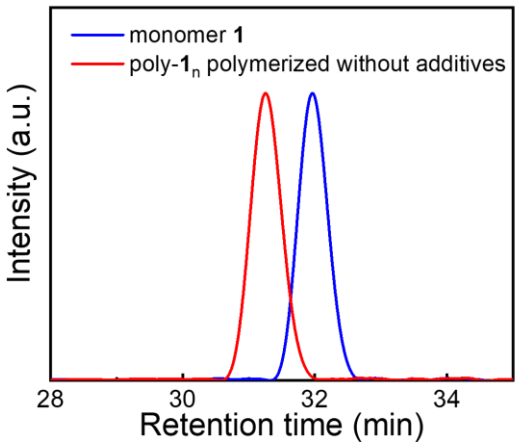


Figure S13. Size exclusion chromatograms for the polymerization of **1** without any additives ($[\mathbf{1}]_0$ = 0.2 M, $[\mathbf{1}]_0/[\text{Ni(II)}]_0$ = 100) under dark condition. SEC condition: eluent = THF, temperature = 40 °C.

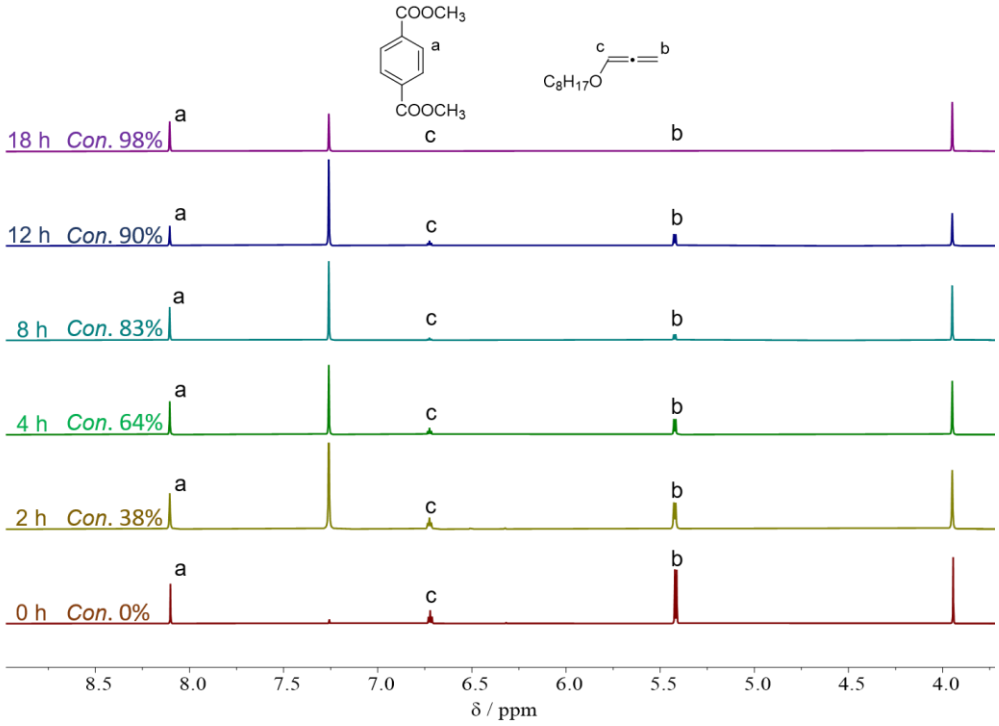


Figure S14. ^{1}H NMR (600 MHz) spectra of samples taken at different times in kinetic study for the polymerization of **1** under dark condition initiated by Ni(II)/$\mathbf{L}^{R\text{-azo}}$ (dimethyl terephthalate as internal standard, $CDCl_3$, 25 °C).

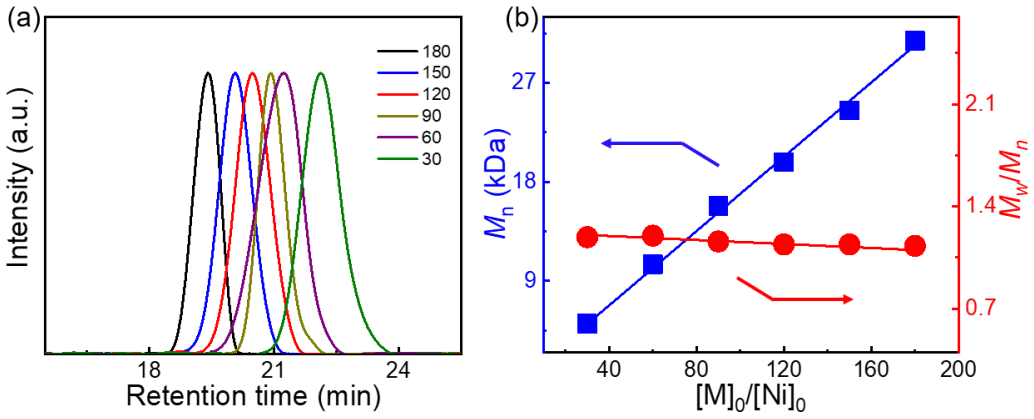


Figure S15. (a) SEC traces of poly-$\mathbf{1}_m$s($\mathbf{L}^{R\text{-azo}}$)prepared using different feed ratios of **1** to Ni(II) under visible light (420 nm). (b) Plots of M_n and M_w/M_n values against the value of $[\mathbf{1}]_0/[\text{Ni(II)}]_0$ under visible light (420 nm).

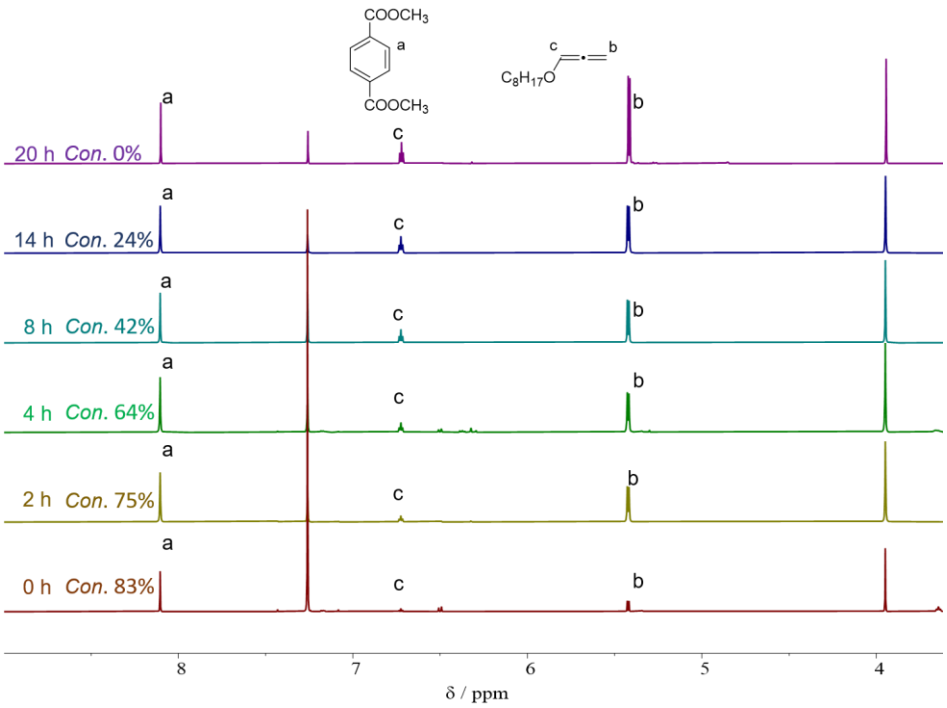


Figure S16. ^{1}H NMR spectra of samples taken at different times in kinetic study for the polymerization of **1** under visible light (420 nm) initiated by Ni(II)/**L**$^{R\text{-azo}}$ (dimethyl terephthalate as internal standard, $CDCl_3$, 25 °C).

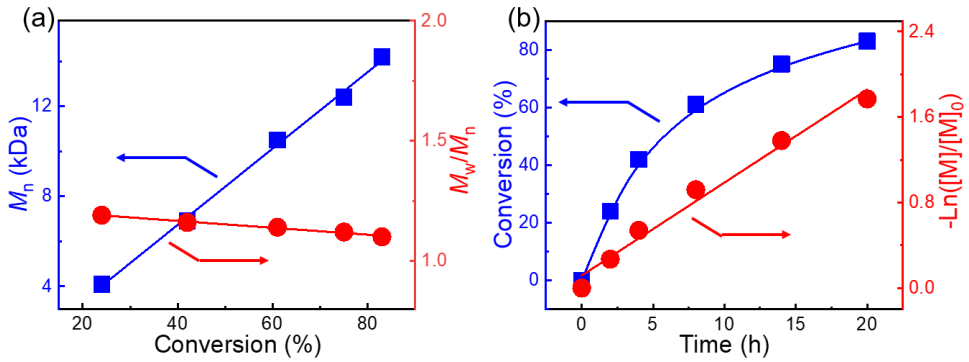


Figure S17. (a) Plots of M_n and M_w/M_n values as a function of monomer **1** conversion initiated by Ni(II)/ **L**$^{R\text{-azo}}$ in CH_2Cl_2 at 35 °C under visible light (420 nm) ($[\mathbf{1}]_0$ = 0.2 M, $[1]_0/[Ni]_0$ = 100). (b) Plots of the monomer conversion and -Ln($[M]/[M]_0$) values against the polymerization time under visible light (420 nm).

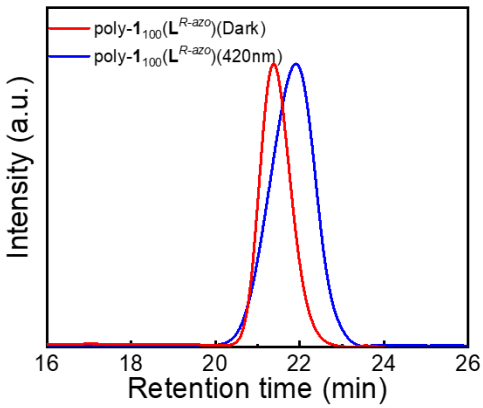


Figure S18. SEC curves of poly-**1**$_{100}$(**L**$^{R\text{-azo}}$) prepared using Ni(II)/**L**$^{R\text{-azo}}$ as initiator under dark condition and visible light (420 nm), respectively.

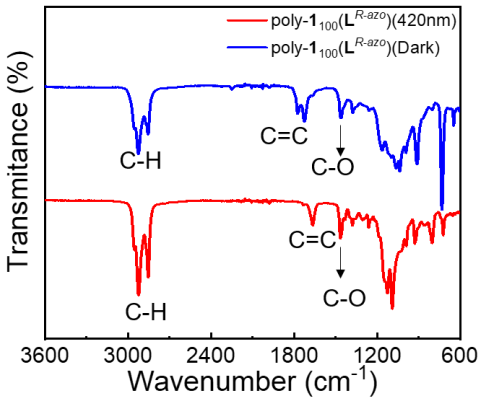


Figure S19. FT-IR spectrum of poly-**1**$_{100}$(**L**$^{R\text{-azo}}$) prepared using Ni(II)/**L**$^{R\text{-azo}}$ as initiator under visible light (420 nm) and dark condition, respectively, measured at 25 °C using KBr pellets.

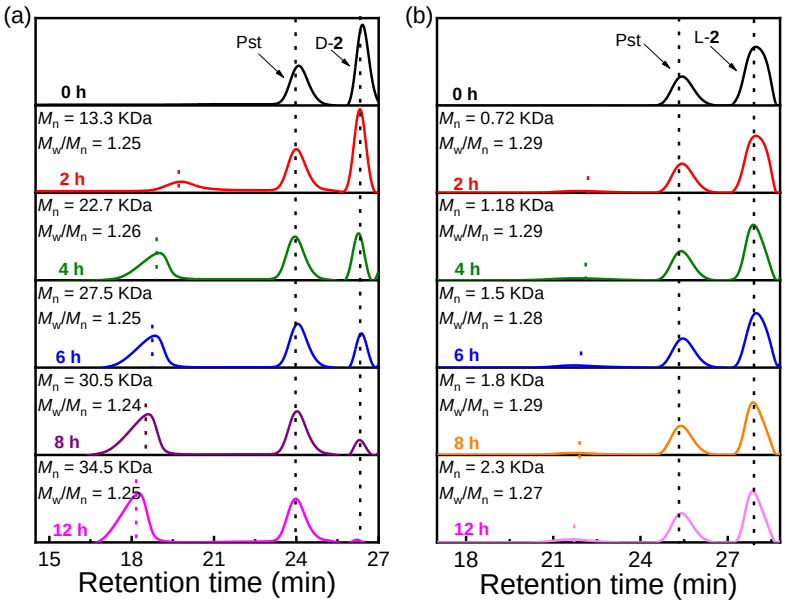


Figure S20. Time-dependent SEC chromatograms for the polymerization of D-**2** (a) and L-**2** (b) under dark condition using polystyrene (M_n = 2630, M_w/M_n = 1.06) as the internal standard initiated by Ni(II)/$\mathbf{L}^{R\text{-azo}}$ in CH_2Cl_2 at 35 °C.

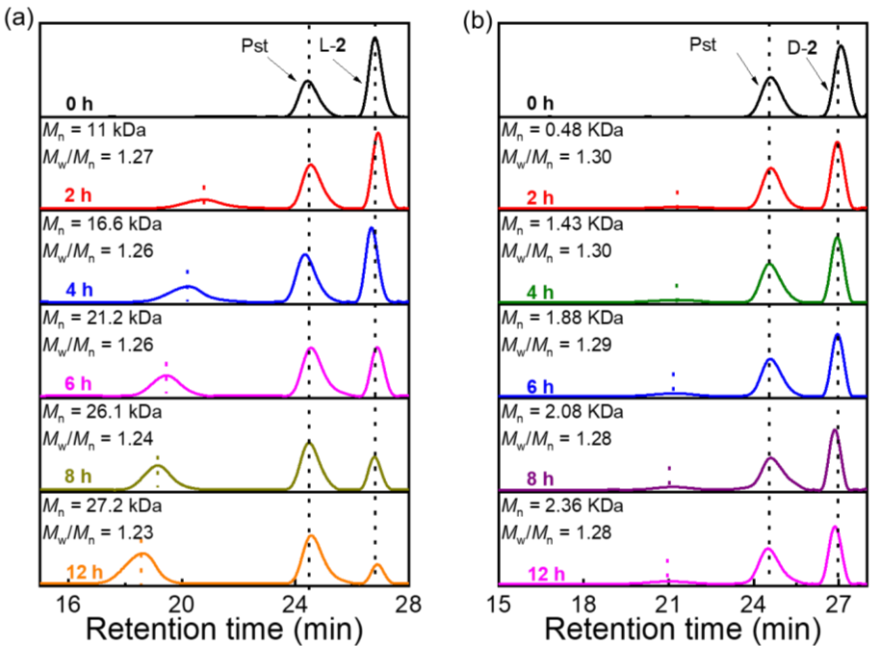


Figure S21. Time-dependent SEC chromatograms for the polymerization of L-**2** (a) and D-**2** (b) under visible light (420 nm) using polystyrene (M_n = 2630, M_w/M_n = 1.06) as the internal standard initiated by Ni(II)/ $\mathbf{L}^{R\text{-azo}}$ in CH_2Cl_2 at 35 °C.

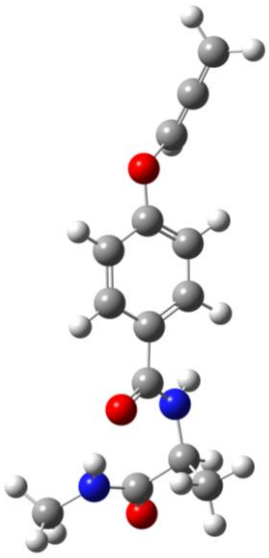


Figure S22. Optimal structure of L-**2'** by DFT calculation at B3LYP-D3BJ/6-31G level at 298 K.

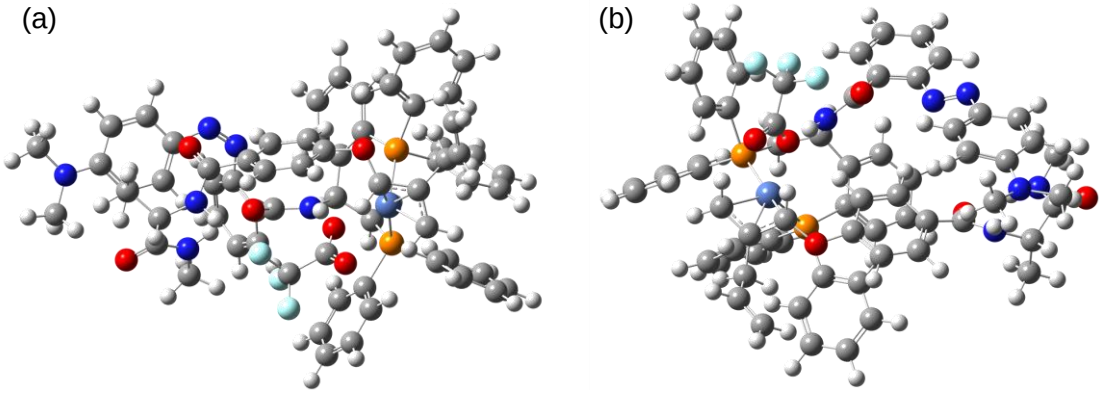


Figure S23. Optimal structure of *cis*-**IN-1** (a) and *trans*- **IN-1** (b) by DFT calculation at B3LYP-D3BJ/6-31G/LanL2DZ level at 298 K.

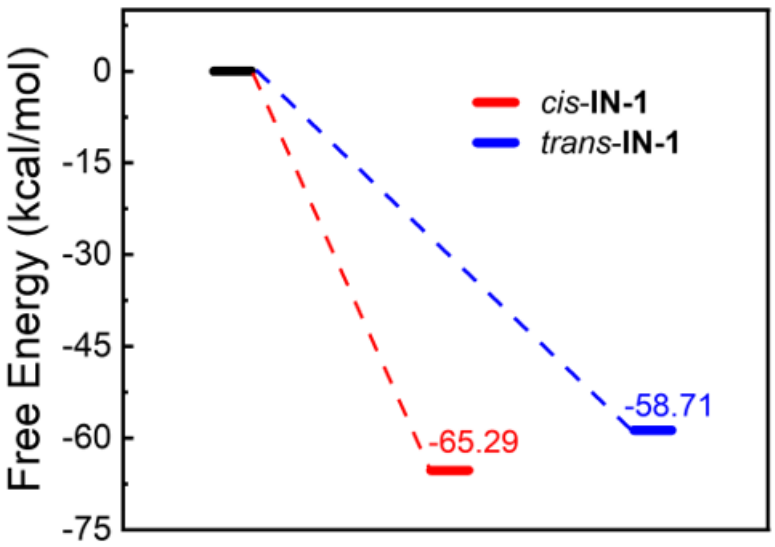


Figure S24. Gibbs free energy change (kcal/mol) from the reaction of *cis*- or *trans*-Ni(II)/$\mathbf{L}^{R\text{-}azo}$ with L-**2'** to generate *cis*-**IN-1** or *trans*-**IN-1**.

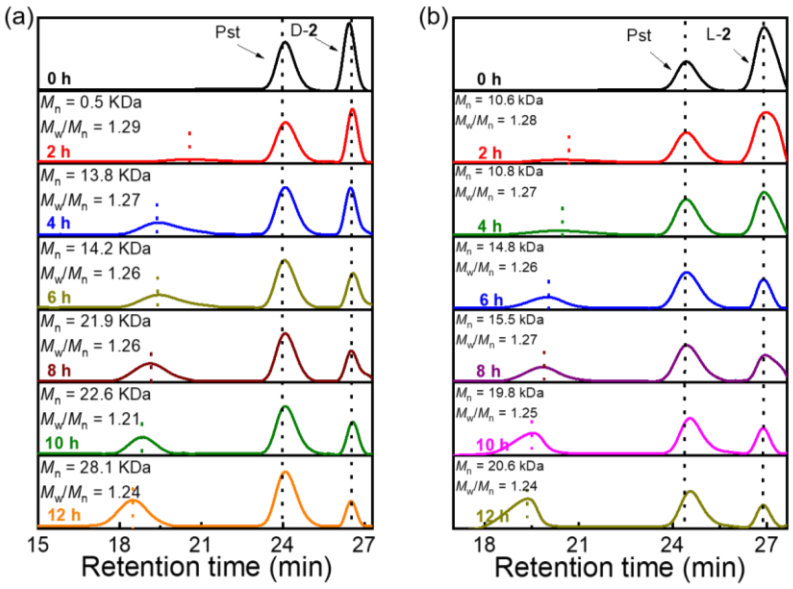


Figure S25. Time-dependent SEC chromatograms for the polymerization of D-**2** (a) and L-**2** (b) with on/off condition alternatively using polystyrene (M_n = 2630, M_w/M_n = 1.06) as the internal standard initiated by Ni(II)/$\mathbf{L}^{R\text{-}azo}$ in CH_2Cl_2 at 35 °C.

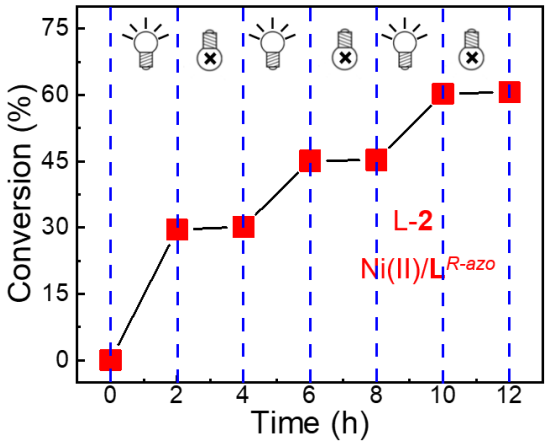


Figure S26. ON/OFF polymerization kinetics of L-**2** demonstrating the polymerization by Ni(II)/ $\mathbf{L}^{R\text{-azo}}$ with alternatively light on and off.

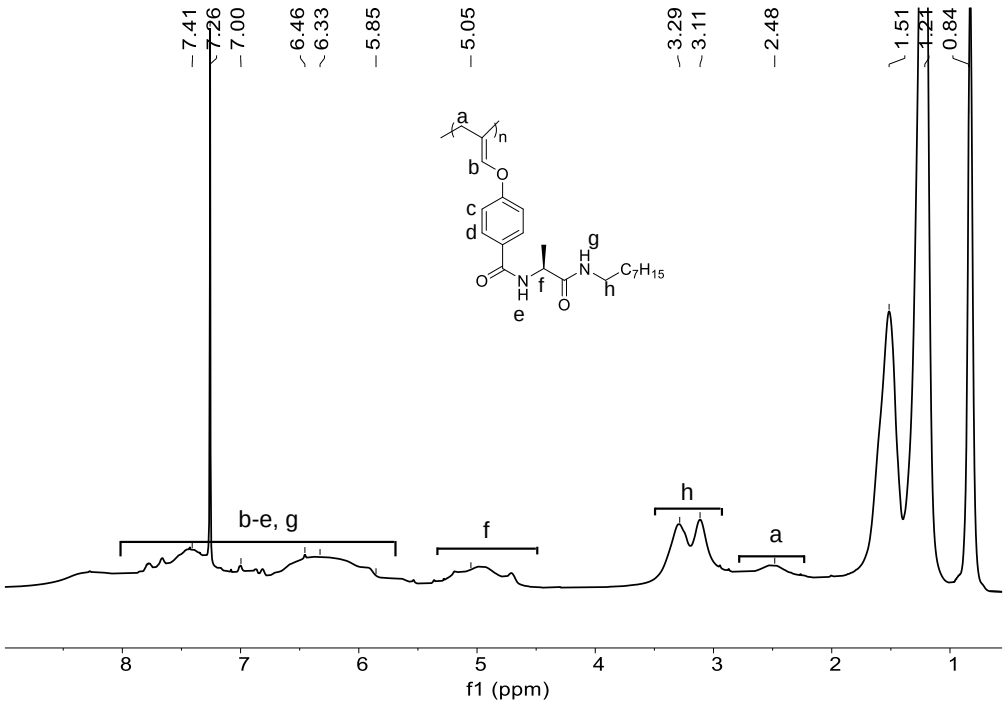


Figure S27. ^{1}H NMR (600 MHz) spectrum of poly-D-$\mathbf{2}_{100}$($\mathbf{L}^{R\text{-azo}}$) measured in $CDCl_3$ at 25 °C.

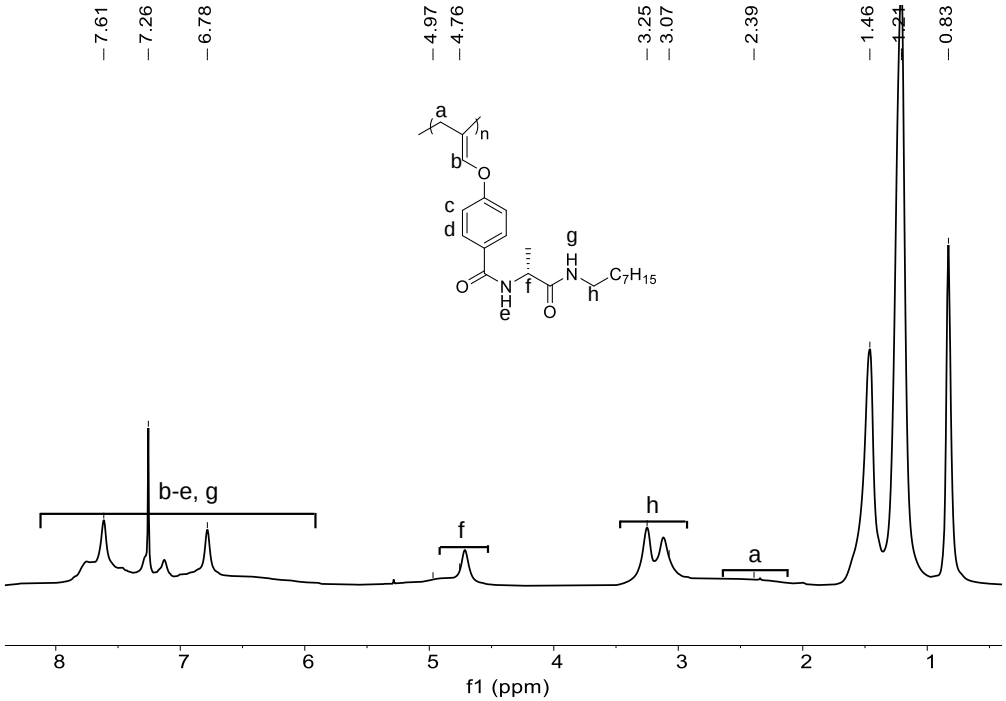


Figure S28. ^{1}H NMR (600 MHz) spectrum of poly-L-**2**$_{100}$(**L**$^{R\text{-azo}}$) measured in $CDCl_3$ at 25 °C.

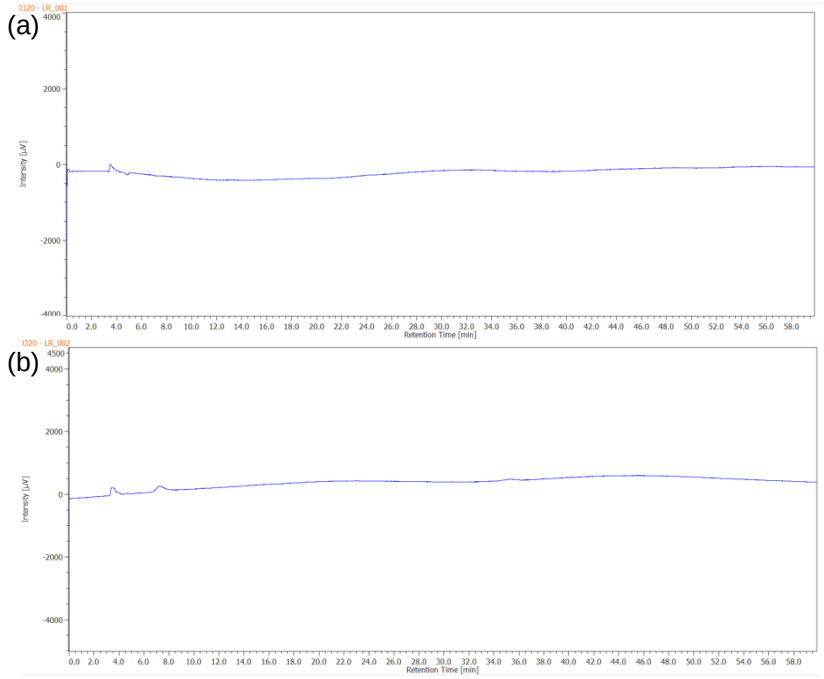


Figure S29. HPLC curves of **L**$^{R\text{-azo}}$ under the conditions of (a) 365 nm and (b) 420 nm (Chiralpak AD-H; *n*-hexane/*i*-PrOH = 70/30 (v/v); 1.00 mL/min; 220 nm; 25 °C).

Coordinates of the optimized geometry by DFT calculation:

cis- Ni(II)/$\mathbf{L}^{R\text{-azo}}$:

C	-0.1533594	-3.4824214	-1.3637430
C	-0.9181663	-4.2148424	-2.2684904
C	-1.9487269	-3.5788774	-2.9594500
C	-2.2020762	-2.2273809	-2.7216564
C	-1.4477084	-1.4812360	-1.7973659
C	-0.3886950	-2.1186832	-1.1035398
C	0.6339662	-1.4976492	-0.1363279
P	-2.0132624	0.3029258	-1.4833064
N	1.7202141	-0.8542014	-0.8974456
C	0.2065289	-0.4920421	0.9419769
P	-1.5084825	-0.7320761	1.6947913
Ni	-2.7505741	0.8011282	0.6215960
C	2.7849057	-1.4424889	-1.5172608
O	3.3234893	-0.8879687	-2.5131458
C	3.3449588	-2.7314535	-1.0078728
C	3.5713496	-3.0709938	0.3520971
C	4.2182328	-4.2851286	0.6544552
C	4.6741457	-5.1344183	-0.3494028
C	4.4634945	-4.7988812	-1.6934150
C	3.8118297	-3.6085629	-2.0044634
C	-4.6643827	1.4561423	1.0743230
C	-3.9254047	1.2334002	2.2600625
C	-4.1273927	2.3095113	0.0920911
N	3.0242254	-2.4195655	1.5199916
N	3.1280458	-1.1951796	1.8637654
C	-3.3990095	0.5144986	-2.7288864
C	-0.6470480	1.3665491	-2.1877168

C	-4.6839533	0.0726501	-2.3738730
C	-5.7479043	0.2121837	-3.2680000
C	-5.5363958	0.8059162	-4.5195191
C	-4.2590019	1.2524809	-4.8719754
C	-3.1886814	1.1042029	-3.9806331
C	-0.6135323	2.7200691	-1.8225653
C	0.4296190	3.5354518	-2.2727110
C	1.4385127	3.0024686	-3.0848920
C	1.3908528	1.6586292	-3.4735025
C	0.3377800	0.8437579	-3.0393093
C	-1.8304729	-2.5617620	1.5624380
C	-0.9039880	-3.4858305	2.0716894
C	-1.1141885	-4.8544297	1.8819848
C	-2.2462788	-5.3021193	1.1890053
C	-3.1728853	-4.3808322	0.6889704
C	-2.9659694	-3.0106935	0.8783633
C	-1.2589006	-0.4597618	3.5238550
C	-0.4934461	0.6329664	3.9568868
C	-0.3368538	0.8717276	5.3255034
C	-0.9479242	0.0324499	6.2643068
C	-1.7213966	-1.0496389	5.8302276
C	-1.8783771	-1.2977278	4.4620425
C	3.8466922	-0.1831435	1.1979756
C	3.3315073	1.1073746	1.4385672
C	3.7571887	2.1994090	0.7068246
C	4.7683098	2.0464628	-0.2791228
C	5.3945441	0.7736625	-0.4029592
C	4.9323644	-0.3208828	0.3071861
N	5.1266206	3.1001812	-1.0893695

C	6.1161344	2.9106554	-2.1494195
C	4.4404082	4.3877262	-0.9563243
O	-1.0379760	2.2036450	1.2901490
C	-0.9446894	3.4823901	1.2358585
O	-1.7425798	4.3248115	0.7433561
C	0.3753676	4.0746447	1.7765895
F	0.1804903	5.2082669	2.5430624
F	1.2218959	4.4423410	0.7164056
F	1.1151587	3.1841428	2.5609881
H	0.6489321	-3.9763100	-0.8276492
H	-0.7098882	-5.2673944	-2.4265887
H	-2.5545639	-4.1218941	-3.6770035
H	-3.0054862	-1.7484551	-3.2633586
H	1.0698512	-2.3437702	0.3941479
H	1.5174209	0.0733586	-1.2502710
H	0.9486458	-0.5401711	1.7414769
H	0.1926693	0.5336042	0.5713063
H	4.3440234	-4.5370820	1.7011868
H	5.1813815	-6.0568313	-0.0866703
H	4.8048870	-5.4556879	-2.4857249
H	3.6615720	-3.3139189	-3.0362580
H	-5.4763070	0.7788171	0.8178916
H	-3.2904968	2.0120077	2.6722664
H	-4.2150393	0.4459619	2.9469333
H	-4.5704535	2.3318462	-0.8966968
H	-3.4866495	3.1478983	0.3622261
H	-4.8432361	-0.3701897	-1.3957470
H	-6.7382342	-0.1317057	-2.9883181
H	-6.3636230	0.9229541	-5.2115100

H	-4.0921567	1.7164459	-5.8383633
H	-2.1991928	1.4488517	-4.2570407
H	-1.3772390	3.1355634	-1.1777575
H	0.4615601	4.5720935	-1.9581150
H	2.2629265	3.6290254	-3.4091369
H	2.1830839	1.2244834	-4.0707264
H	0.3133244	-0.2003415	-3.3287674
H	-0.0168770	-3.1401710	2.5933000
H	-0.3929040	-5.5676440	2.2668205
H	-2.4023750	-6.3649991	1.0362153
H	-4.0455361	-4.7257252	0.1446777
H	-3.6615318	-2.2838533	0.4716321
H	-0.0514619	1.3028070	3.2325670
H	0.2615627	1.7154136	5.6528879
H	-0.8240083	0.2209216	7.3256782
H	-2.1988129	-1.7035038	6.5529540
H	-2.4682298	-2.1451702	4.1307610
H	2.5421701	1.2179613	2.1701762
H	3.2889987	3.1566868	0.8766035
H	6.2139032	0.6357909	-1.0945274
H	5.4048600	-1.2825594	0.1573030
H	7.1057818	2.6652534	-1.7419459
H	5.8162539	2.1056145	-2.8325499
H	6.2062715	3.8340275	-2.7220660
H	4.6336875	4.8493203	0.0202072
H	4.8009374	5.0646783	-1.7312808
H	3.3554314	4.2733586	-1.0669766

trans-Ni(II)/$\mathbf{L}^{R\text{-azo}}$:

C	1.2100359	1.5735212	3.3247147
C	2.3452710	1.2520301	4.0649938
C	3.5027326	0.8511728	3.3967684
C	3.5023015	0.7778965	2.0040494
C	2.3574798	1.0856181	1.2462038
C	1.1790562	1.4895029	1.9208722
C	-0.1950337	1.7998214	1.3106260
P	2.4675739	0.7954067	-0.6256161
N	-0.1771557	2.2306867	-0.0761088
C	-1.1944372	0.6313235	1.4861899
P	-0.5649684	-1.0072337	0.7473489
Ni	0.8604126	-0.8605512	-1.3292165
C	-0.6924040	3.3860376	-0.5926812
O	-0.6362012	3.6305411	-1.8199126
C	-1.3489009	4.3407422	0.3645922
C	-2.6894497	4.0880727	0.7284375
C	-3.3762637	4.9760142	1.5708656
C	-2.7230199	6.1127472	2.0458685
C	-1.3932759	6.3725353	1.6784684
C	-0.7097528	5.4905328	0.8334236
N	-3.2196613	2.9077295	0.1644686
N	-4.4295016	2.5867105	0.4508420
C	-4.8723548	1.4124876	-0.1879619
C	-6.1094190	0.8803619	0.2104767
C	-6.5868642	-0.3008985	-0.3397671
C	-5.8355877	-0.9967953	-1.3257560
C	-4.6062832	-0.4222853	-1.7571594
C	-4.1400198	0.7506536	-1.1984410
N	-6.2736232	-2.1948689	-1.8466152

C	-5.4288535	-2.9432401	-2.7802842
C	-7.5114676	-2.7971393	-1.3578502
C	0.2524247	-1.7622161	2.2740202
C	-2.1516820	-2.0202082	0.6888750
C	1.6263559	-2.0250363	2.2734821
C	2.2402699	-2.5570955	3.4133314
C	1.4863108	-2.8210606	4.5594470
C	0.1090295	-2.5636473	4.5612423
C	-0.5069035	-2.0423356	3.4208112
C	2.4867463	2.5232265	-1.3635271
C	4.2841529	0.3661080	-0.9091953
C	2.5982374	3.6732814	-0.5728620
C	2.6515500	4.9330281	-1.1774010
C	2.5935804	5.0486955	-2.5708402
C	2.4888026	3.8999385	-3.3597125
C	2.4392282	2.6390493	-2.7577000
C	5.2686438	1.3660012	-0.8175575
C	6.6124403	1.0463387	-1.0279604
C	6.9843261	-0.2691211	-1.3363180
C	6.0053172	-1.2611441	-1.4367876
C	4.6573483	-0.9458706	-1.2265488
C	-2.0889327	-3.2816416	0.0715766
C	-3.2187603	-4.1077269	0.0530674
C	-4.4115713	-3.6895050	0.6550925
C	-4.4737211	-2.4362629	1.2712110
C	-3.3512885	-1.6008344	1.2830207
O	2.0447763	-2.3006960	-0.8018968
C	1.8386833	-3.5796186	-0.7043952
O	0.7904992	-4.2329183	-0.8716297

C	3.1425272	-4.3186760	-0.3530506
F	2.9533894	-5.6610612	-0.1185865
F	4.0634752	-4.2029150	-1.4029184
F	3.7641262	-3.7792427	0.7716974
C	0.1810813	-0.7835062	-3.2698570
C	-0.1703114	-2.0512764	-2.7903992
C	-0.3147495	0.3385368	-2.5478052
H	0.3085025	1.8881995	3.8426975
H	2.3234236	1.3114043	5.1475871
H	4.3986999	0.5913290	3.9497546
H	4.4014230	0.4562202	1.4962085
H	-0.5990399	2.6400962	1.8825852
H	0.0753108	1.5351047	-0.7659426
H	-2.1105934	0.9164588	0.9655876
H	-1.4135623	0.4721806	2.5457810
H	-4.4058569	4.7589520	1.8276112
H	-3.2473741	6.8038318	2.6975921
H	-0.8945998	7.2633388	2.0453625
H	0.3124707	5.6906138	0.5331247
H	-6.6746509	1.4077418	0.9709266
H	-7.5347364	-0.6944968	0.0007763
H	-4.0188234	-0.9089593	-2.5235573
H	-3.2094855	1.1928002	-1.5307706
H	-4.4585587	-3.1861662	-2.3299495
H	-5.9288806	-3.8760991	-3.0413604
H	-5.2573972	-2.3788279	-3.7050896
H	-7.4540961	-3.0268799	-0.2845976
H	-8.3701431	-2.1343192	-1.5211788
H	-7.6942210	-3.7263047	-1.8975532

H	2.2118704	-1.8264300	1.3891020
H	3.3035124	-2.7687037	3.3923391
H	1.9625927	-3.2340528	5.4428923
H	-0.4844478	-2.7791388	5.4442378
H	-1.5787568	-1.8721506	3.4187218
H	2.6304999	3.5847630	0.5072090
H	2.7414716	5.8226656	-0.5615315
H	2.6230007	6.0276684	-3.0368927
H	2.4354631	3.9836120	-4.4398110
H	2.3599703	1.7476796	-3.3722183
H	4.9883934	2.3876100	-0.5894901
H	7.3666617	1.8233044	-0.9552327
H	8.0291421	-0.5136333	-1.4987463
H	6.2748806	-2.2851023	-1.6720478
H	3.8993139	-1.7094036	-1.2957371
H	-1.1564093	-3.6272102	-0.3643608
H	-3.1566471	-5.0841798	-0.4168835
H	-5.2832718	-4.3362917	0.6472920
H	-5.3942845	-2.0977249	1.7327282
H	-3.4300817	-0.6284143	1.7520966
H	0.9803665	-0.6664166	-3.9960931
H	-1.1025590	-2.2061222	-2.2559641
H	0.3361101	-2.9464305	-3.1271527
H	-1.3043742	0.2669856	-2.1020930
H	-0.0085335	1.3466871	-2.8076701

L-2’:

C	5.2038470	0.1105869	0.8153003
C	7.6512127	0.7036808	0.0968511

O	4.3990669	-0.7821873	0.0669071
C	3.0335112	-0.5234199	-0.0501607
C	2.2364322	-1.6098081	-0.4386550
C	0.8666271	-1.4335197	-0.5923445
C	0.2681530	-0.1816949	-0.3482396
C	1.0866540	0.9000256	0.0174185
C	2.4664103	0.7385039	0.1663292
C	-1.2071429	-0.0711962	-0.5282556
N	-1.8381272	0.9692301	0.0932778
O	-1.8390100	-0.9275557	-1.2151849
C	-3.2559606	1.3659579	-0.0818027
C	-3.6211942	1.5941545	-1.5613422
C	6.4216752	0.4107528	0.4365715
C	-4.2680904	0.4365383	0.6259623
O	-5.0878121	0.9276073	1.4404859
N	-4.2322344	-0.8746510	0.2727713
C	-5.1523908	-1.8560441	0.8392307
H	4.7602187	0.4561816	1.7449907
H	7.8928682	1.5903650	-0.4858747
H	8.4920853	0.0712503	0.3754923
H	2.7094501	-2.5689645	-0.6105589
H	0.2318482	-2.2556831	-0.9004961
H	0.6660854	1.8928272	0.1443354
H	3.0922572	1.5883690	0.4104332
H	-1.3141713	1.4958415	0.7761732
H	-3.3588446	2.3124491	0.4543800
H	-4.6592288	1.9350529	-1.6293856
H	-2.9735642	2.3647264	-1.9927828
H	-3.5096700	0.6780708	-2.1440156

H	-3.5156662	-1.1690582	-0.3911698
H	-5.7649865	-2.3172295	0.0559502
H	-4.6070458	-2.6470499	1.3669966
H	-5.8055270	-1.3392229	1.5443431

cis-**IN-1**:

C	5.1809402	3.8410197	4.0721262
C	5.3186539	2.5539323	3.7379796
C	4.8520887	1.9816607	2.4161391
O	1.8558030	2.4328787	2.4707201
C	0.4308413	2.3633241	2.3514502
C	-0.1484971	2.4295718	1.0836865
C	-1.5255435	2.2577755	0.9523118
C	-2.3071774	1.9670398	2.0786009
C	-1.7122337	1.9416527	3.3487216
C	-0.3386686	2.1525310	3.4931239
C	-3.7459521	1.6241530	1.8606021
N	-4.2131726	0.6262001	2.6819138
O	-4.4300756	2.1818780	0.9725609
C	-5.5553080	0.0376298	2.6760763
C	-6.6853739	1.0540680	2.4564180
Ni	2.6803631	-0.0656123	1.1399100
P	2.7466173	-1.9023292	-0.2773145
P	2.9905878	1.4576847	-0.7285358
C	4.3657836	-2.7530892	-0.7258900
C	2.0310873	-1.5293009	-1.9951992
C	1.7475862	-3.3709824	0.3331922
C	4.7214678	-3.0882172	-2.0377080
C	5.9500966	-3.7059560	-2.2982281

C	6.8264148	-4.0031962	-1.2510364
C	6.4680960	-3.6830587	0.0644335
C	5.2451849	-3.0602553	0.3241930
C	0.8165228	-4.0429565	-0.4667378
C	0.1137533	-5.1401854	0.0422310
C	0.3359746	-5.5714255	1.3530142
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trans-**IN-1**:

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