Electronic Supplementary Material (ESI) for Polymer Chemistry.

Polymerization of Phenylacetylenes by Binuclear Rhodium Catalysts with Different *para*-Binucleating Phenoxyiminato Linkages

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EXPERIMENTAL SECTION

Materials.

All manipulations of air- and moisture-sensitive and polymerization of phenylacetylene in organic solvents were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques. Nitrogen was purchased from Beijing AP Beifen Gases Industrial Co., Ltd. Anhydrous toluene and THF were purified by use of a SPS-800 solvent purification system (Mbraun). (S)-1-phenylethan-1-amine, 2-hydroxybenzaldehyde, $[Rh(cod)(Cl)]_2$, $[Rh(nbd)(Cl)]_2$, 1,4-dimethoxybenzene, 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-diamine, naphthalene-1,5-diol, Br_2, acetic acid, petroleum ether, LiBu, THF, NH_4Cl, ethyl acetate, CH_2Cl_2, BBr_3, petroleum ether, ethanol, KOH, Na_2SO_4, HCl, $NaNO_2$, KI, CH_3I, DMF and phenylacetylene were purchased from Energy Chemistry. DMF was distilled from CaH_2 to get rid of moisture and stored in a brown bottle. Phenylacetylene was purified by vacuum distillation prior to polymerization experiments. $CDCl_3$ (99.8 atom% D) and DMSO (99.8 atom% D) were purchased from Cambridge Isotope.

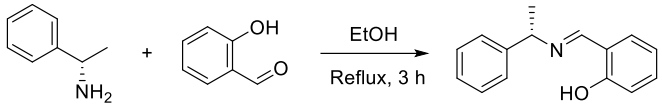
Measurements.

The ^1H, ^{13}C NMR spectra of Rh complexes were recorded on an AVANCE 400 spectrometer at room temperature with $CDCl_3$ as a solvent. The microstructures of poly(phenylacetylene)s were obtained by ^1H NMR spectra in $CDCl_3$ at room temperature on an AVANCE 400 spectrometer. The molecular weights and molecular weight distributions (M_w/M_n) of poly(phenylacetylene)s were determined by GPC with a HLC-8320GPC apparatus in THF at 30 ^oC, calibrated with polystyrene standards.

X-ray Crystallographic Study.

Suitable single crystals of complexes were sealed in a thin−walled glass capillary for determining the single−crystal structure. Data collection was performed at −100 °C on a Bruker SMART diffractometer with graphite−monochromated Mo Kα radiation (λ = 0.71073 Å). The SMART program package was used to determine the unit−cell parameters. The absorption correction was applied by using SADABS. The structures were solved by direct methods and refined on F2 by full−matrix least−squares techniques with anisotropic thermal parameters for non−hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. All calculations were carried out using the SHELXS−97 program. Molecular structures were generated using ORTEP program. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1527538 (**1a**), CCDC-1527537 (**1b**), CCDC-1527937 (**2b**), CCDC-1527936 (**3b**) and CCDC-1527938 (**4b**) and contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

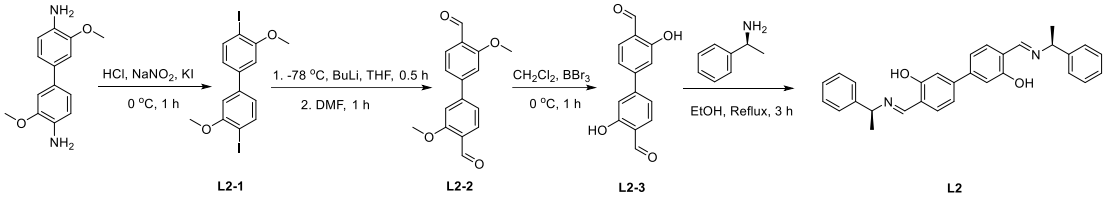
Scheme S1. Synthesis of (*S*,*E*)-2-(((1-phenylethyl)imino)methyl)phenol ligand L1.



L1

To a 50 ml flask with (*S*)-1-phenylethan-1-amine (1.2 g, 0.01 mol) and 2-hydroxybenzaldehyde (1.2 g, 0.01 mol), 20 ml ethanol was added. After refluxing for 3 h, the mixture cooled to room temperature and filtrated. Then the residue was washed with cold ethanol and evacuated to obtain yellow solid **L1** (2.2 g, Yield: 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.54 (s, 1H), 8.41 (s, 1H), 7.36 (s, 3H), 7.33 – 7.20 (m, 4H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 4.55 (q, *J* = 6.6 Hz, 1H), 1.63 (d, *J* = 6.6 Hz, 3H).

Scheme S2. Synthesis of 4,4'-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)-[1,1'-biphenyl]-3,3'-diol ligand L2.



L2-1 **L2-2** **L2-3** **L2**

Synthesis of 4-iodo-3,3'-dimethoxy-4'-methyl-1,1'-biphenyl (L2-1)

To 12.2 g 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-diamine in 200 mL HCl (1 mol/L), 6.9 g $NaNO_2$ (100 mmol) in water was added at 0°C. Then 20 g KI (120 mol) in water was added. After reaction for 1 h, the mixture was extracted with ethyl acetate, dried with anhydrous Na_2SO_4, and removed solvent under reduced pressure to afford crude ligand. Gray solid 4,4'-diiodo-3,3'-dimethoxy-1,1'-biphenyl was obtained after purified using chromatography (silica gel, petroleum ether/ethyl acetate) (14.7 g, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 1.9 Hz, 2H), 6.91 (dd, *J* = 8.0, 2.0 Hz, 2H), 3.95 (s, 6H).

Synthesis of 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (L2-2)

At -78 °C, 12 mL LiBu (2.5 mol/L, 30 mmol) was slowly added to the 100 mL THF solution of 14.7 g 4,4'-diiodo-3,3'-dimethoxy-1,1'-biphenyl (30 mmol) in a 250 ml flask and the mixture reacted for 30 min. Then 30 mL DMF was added. After warming to room temperature, the mixture continued to react for 1 h. Then the mixture was treated with 30 mL aqueous solution of NH_4Cl and was stirred for 5 min. After extracted with ethyl acetate and removed solvent, the residue was recrystallized from petroleum ether and ethyl acetate to afford white solid 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (3.5 g, Yield: 41%). ^{1}H NMR (400 MHz, DMSO) δ 10.40 (s, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 4.05 (s, 6H).

Synthesis of 3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (L2-3)

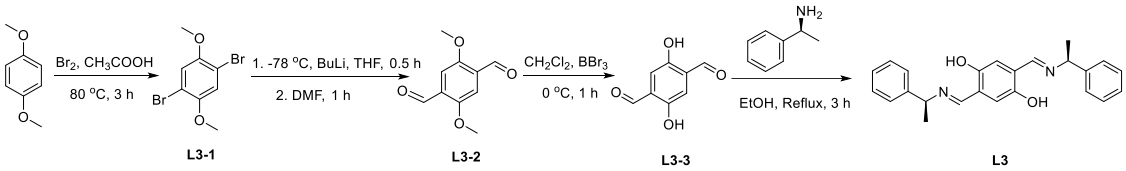
To 4.5 g 3,3'-dimethoxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde (13 mmol) in 40 mL CH_2Cl_2, 16.2 g BBr_3 (65 mmol) was added at 0°C. After reaction for 1 h, the mixture was treated with 100 mL ice water. The organic solvent was removed by vacuo. Then the mixture was filtered and the residue was washed with water and petroleum ether. Insoluble light yellow solid

3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarbaldehyde was obtained (1.95 g, 62%).

Synthesis of 4,4'-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)-[1,1'-biphenyl]-3,3'-diol (L2)

The synthetic procedure was the same with that of compound **L1** (2.55 g, Yield: 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.64 (s, 2H), 8.44 (s, 2H), 7.41 – 7.36 (m, 8H), 7.33 – 7.26 (m, 2H), 7.22 (d, *J* = 1.6 Hz, 2H), 7.13 (dd, *J* = 8.0, 1.7 Hz, 2H), 4.58 (q, *J* = 6.6 Hz, 2H), 1.65 (d, *J* = 6.7 Hz, 6H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.00 (s), 161.32 (s), 144.17 (s), 143.78 (s), 131.72 (s), 128.71 (s), 127.30 (s), 126.42 (s), 118.39 (s), 117.67 (s), 115.58 (s), 77.28 (d, *J* = 11.7 Hz), 77.02 (s), 76.70 (s), 68.54 (s), 24.94 (s), 0.01 (s).

Scheme S3. Synthesis of 2,5-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)benzene-1,4-diol ligand L3.



Synthesis of 1,4-dibromo-2,5-dimethoxybenzene (L3-1)

In a 500 mL flask, 32 g Br_2 (200 mmol) in 30 mL acetic acid was added to 13.8 g 1,4-dimethoxybenzene (100 mmol) in 200 mL acetic acid at 80 °C. After reaction for 3 h, the mixture cooled to room temperature and acetic acid was removed by vacuo. Then the residue was washed with water and petroleum ether, affording light yellow solid 1,4-dibromo-2,5-dimethoxybenzene (20.6 g, Yield: 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 2H), 3.84 (s, 6H).

Synthesis of 2,5-dimethoxyterephthalaldehyde (L3-2)

The synthetic procedure was the same with that of compound **L2-2** (white solid, 3.95 g, Yield: 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.50 (s, 2H), 7.46 (s, 2H), 3.94 (s, 6H).

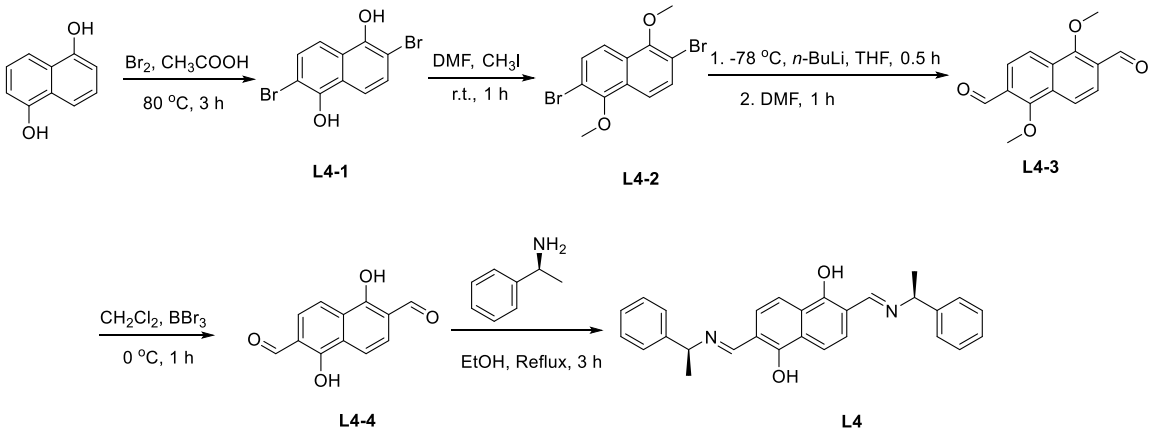
Synthesis of 2,5-dihydroxyterephthalaldehyde (L3-3)

The synthetic procedure was the same with that of compound **L2-3** (yellow solid, 0.95 g, 38%).

Synthesis of 2,5-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)benzene-1,4-diol (L3)

The synthetic procedure was the same with that of compound **L1** (yellow solid, 1.44 g, Yield: 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.66 (s, 2H), 8.30 (s, 2H), 7.28 (s, 8H), 7.19 (s, 3H), 6.79 (s, 2H), 4.49 (d, *J* = 5.9 Hz, 2H), 1.57 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.91 (s), 152.73 (s), 143.58 (s), 128.74 (s), 127.38 (s), 126.44 (s), 121.48 (s), 118.31 (s), 68.97 (s).

Scheme S4. Synthesis of 2,6-bis((*E*)-((1-phenylethyl)imino)methyl)naphthalene-1,5-diol ligand L4.



Synthesis of 2,6-dibromonaphthalene-1,5-diol (L4-1)

The synthetic procedure was the same with that of compound **L3-1** (10.1 g, Yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 5.97 (s, 2H).

Synthesis of 2,6-dibromo-1,5-dimethoxynaphthalene (L4-2)

To 100 mL DMF solution of 10.1 g 2,6-dibromonaphthalene-1,5-diol (32 mmol) in a 250 mL flask, 10.8 CH_3I (76 mmol) was added. After reaction for 1 h, the mixture was treated with 100 mL water. The precipitated solid 2,6-dibromo-1,5-dimethoxynaphthalene was filtered and dried by vacuo(4.9 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 2H), 3.99 (s, 6H).

Synthesis of 1,5-dimethoxynaphthalene-2,6-dicarbaldehyde (L4-3)

The synthetic procedure was the same with that of compound **L2-2** (yellow solid, 2.8 g, Yield: 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 2H), 8.09 (d, *J* = 8.7 Hz, 2H), 7.97 (d, *J* = 8.7 Hz, 2H), 4.15 (s, 6H).

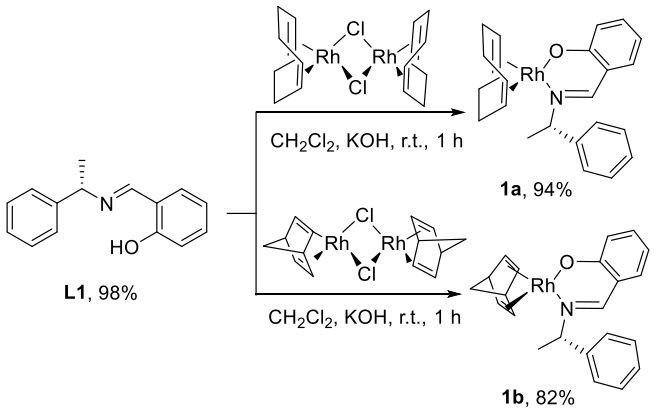
Synthesis of 1,5-dihydroxynaphthalene-2,6-dicarbaldehyde (L4-4)

The synthetic procedure was the same with that of compound **L2-3** (yellow solid, 2.3 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.42 (s, 2H), 10.06 (s, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H).

Synthesis of 2,6-bis((E)-((1-phenylethyl)imino)methyl)naphthalene-1,5-diol (L4)

The synthetic procedure was the same with that of compound **L1** (4.2g, Yield: 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.48 (s, 2H), 8.21 (d, *J* = 4.4 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.40 – 7.37 (m, 6H), 7.29 (ddd, *J* = 8.3, 5.7, 2.9 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 4.68 (q, *J* = 6.4 Hz, 2H), 1.71 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00 (s), 162.24 (s), 142.72 (s), 129.93 (s), 128.93 (s), 127.72 (s), 126.79 (s), 126.42 (s), 113.31 (s), 112.05 (s), 77.30 (d, *J* = 11.5 Hz), 77.04 (s), 64.81 (s).

Scheme S5 Synthesis of Rh Complex 1



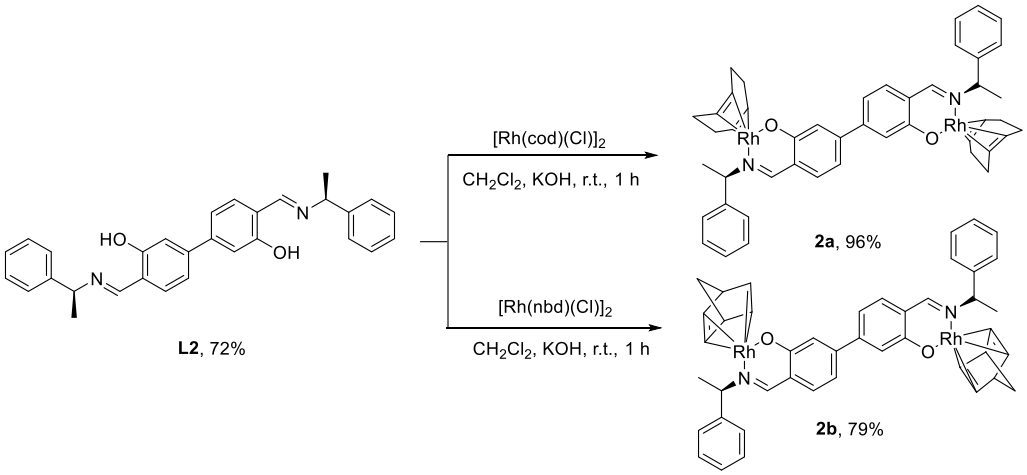
Synthesis of Rh complexes 1a

L1 (44 mg, 2 mmol) and $[Rh(cod)(Cl)]_2$ (53 mg, 1 mmol) in 5 mL CH_2Cl_2 were stirred for 10 min at room temperature. Then 180 mg KOH in 2 mL water was added. The reaction mixture was stirred for 1 h. Then the mixture was extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4 and removed solvent by vacuo, obtaining yellow solid. The single crystal of complex **1a** was grown from CH_2Cl_2 and n-hexane at -26 °C for 18 h (87 mg, Yield: 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.6 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.26 (qd, *J* = 6.0, 2.1 Hz), 6.96 (dd, *J* = 7.9, 1.6 Hz), 6.84 (d, *J* = 8.5 Hz), 6.47 (dd, *J* = 10.8, 3.9 Hz), 4.69 – 4.53 (m, 2H), 4.50 – 4.39 (q, *J* = 6.9 Hz, 1H), 3.80 (d, *J* = 6.7 Hz, 2H), 2.62 – 2.37 (m, 4H), 1.93 (m, 4H), 1.65 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.64 (s), 165.08 (s), 142.83 (s), 135.13 (s), 134.62 (s), 128.65 (s), 127.60 (s), 127.37 (s), 85.29 (d, *J* = 11.9 Hz), 84.94 (d, *J* = 12.0 Hz), 73.16 (d, *J* = 14.2 Hz), 71.04 (d, *J* = 14.2 Hz), 59.81 (s), 32.08 (s), 31.65 (s), 29.19 (s), 28.79 (s), 22.14 (s).

Synthesis of Rh complexes 1b

The synthetic procedures used is similar to that described for complex **1a**, starting from **L1** (44 mg, 2 mmol) and $[Rh(nbd)(Cl)]_2$ (49 mg, 1 mmol). Complex **1b** was obtained as yellow solid. The single crystal of complex **1b** was isolated from a concentrated mixture solution of CH_2Cl_2 and MeOH at -26 °C for 18 h (73 mg, Yield: 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.2 Hz, 1H), 7.39 – 7.33 (m, 4H), 7.29 (dd, *J* = 6.8, 3.3 Hz,1H), 7.02 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.58 – 6.47 (m, 1H), 4.40 (d, *J* = 14.7 Hz, 2H), 4.25 (q, *J* = 6.8 Hz, 1H), 3.78 (d, *J* = 20.5 Hz, 2H), 3.52 (dd, *J* = 26.1, 2.9 Hz, 2H), 1.63 – 1.55 (m, 3H), 1.41 – 1.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.00 (s), 162.68 (s), 142.41 (s), 135.23 (s), 134.40 (s), 128.63 (s), 127.44 (s), 121.34 (s), 119.22 (s), 114.56 (s), 62.65 (d, *J* = 9.2 Hz), 62.33 (s), 61.91 (s), 61.46 (s), 51.98 (s), 50.71 (s), 49.42 (s), 49.29 (s), 21.94 (s).

Scheme S6 Synthesis of Rh Complexes 2.



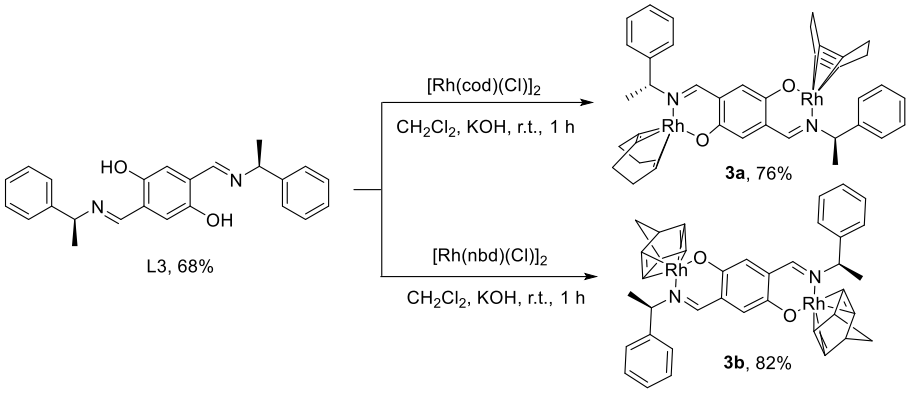
Synthesis of Rh complexes 2a

Stirred for 10 min at room temperature, 4 mL aqueous solution of KOH (360 mg) was added to the mixture of **L2** (45 mg, 1 mmol) and $[Rh(cod)(Cl)]_2$ (50 mg, 1 mmol) in 5 mL CH_2Cl_2. After reacting for 1 h, the mixture was extracted with CH_2Cl_2 (anhydrous Na_2SO_4 as desiccant) and removed solvent by vacuo. Yellow solid was obtained (81 mg, Yield: 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.36 (dd, *J* = 8.6, 5.3 Hz, 8H), 7.12 (d, *J* = 1.3 Hz, 4H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.77 (dd, *J* = 8.2, 1.6 Hz, 2H), 4.69 – 4.54 (m, 4H), 4.44 (q, *J* = 6.8 Hz, 2H), 3.79 (s, 4H), 2.63 – 2.35 (m, 8H), 2.08 – 1.83 (m, 8H), 1.66 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.44 (s), 164.49 (s), 147.74 – 146.35 (m), 142.90 (s), 135.19 (s), 128.63 (s), 127.57 (s), 127.32 (s), 119.54 (s), 118.82 (s), 113.75 (s), 85.30 (d, *J* = 11.9 Hz), 84.97 (d, *J* = 11.9 Hz), 73.12 (d, *J* = 14.2 Hz), 71.01 (d, *J* = 14.2 Hz), 59.75 (s), 32.06 (s), 31.63 (s), 29.19 (s), 28.79 (s), 22.12 (s).

Synthesis of Rh complexes 2b

The synthetic procedure used was similar to that described for complex **2a**, starting from **L2** (45 mg, 1 mmol) and $[Rh(nbd)(Cl)]_2$ (92 mg, 2 mmol). Complex **2b** was obtained as yellow solid. The single crystal of complex **2b** was isolated from a concentrated mixture solution of CH_2Cl_2 and n-hexane at -26 ^{o}C for 18 h (64 mg, Yield: 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.39 – 7.26 (m, 8H), 7.18 (s, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.83 (dd, *J* = 8.3, 1.6 Hz, 2H), 4.39 (d, *J* = 16.0 Hz, 4H), 4.24 (q, *J* = 6.9 Hz, 2H), 3.78 (d, *J* = 20.8 Hz, 4H), 3.51 (d, *J* = 25.4 Hz, 4H), 1.66 – 1.54 (m, 6H), 1.34 (q, *J* = 8.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.85 (s), 162.10 (s), 146.48 (s), 142.49 (s), 135.31 (s), 128.63 (s), 127.44 (d, *J* = 5.5 Hz), 119.55 (s), 118.69 (s), 114.09 (s), 62.64 (s), 62.33 (s), 61.89 – 61.86 (m), 61.48 – 61.32 (m), 51.93 (s), 50.62 (d, *J* = 11.5 Hz), 49.38 (d, *J* = 13.0 Hz), 21.96 (s).

Scheme S7. Synthesis of Rh Complexes 3.



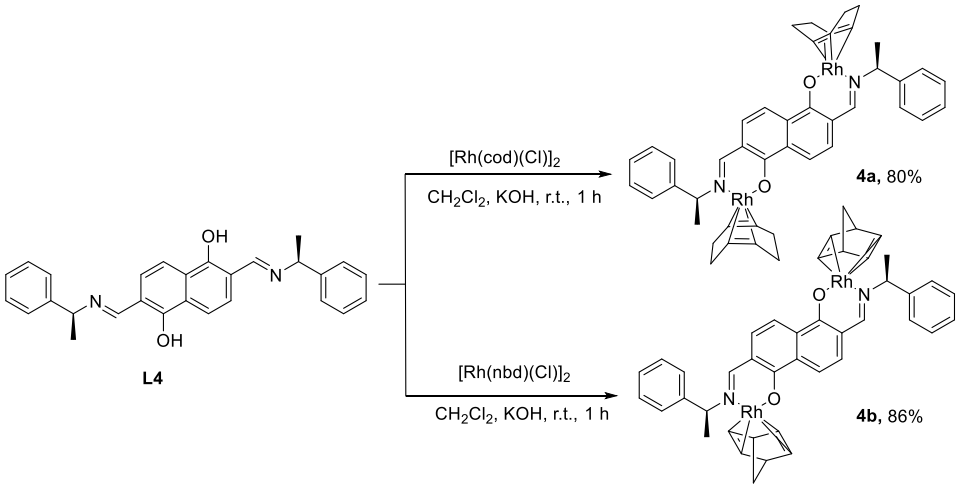
Synthesis of Rh complexes 3a

To the mixture of **L3** (38 mg, 1 mmol), $[Rh(cod)(Cl)]_2$ (100 mg, 2 mmol) and 5 mL CH_2Cl_2 stirred for 10 min at room temperature, 4 mL KOH (360 mg) aqueous solution was added. The mixture continued to react for 1 h and then was extracted with CH_2Cl_2 (anhydrous Na_2SO_4 as desiccant). purple solid was obtained after removing solvent by vacuo (61 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 1.4 Hz, 2H), 7.43 – 7.10 (m, 10H), 6.54 (s, 2H), 4.54 (t, *J* = 7.2 Hz, 2H), 4.44 (dd, *J* = 12.9, 6.2 Hz, 4H), 3.81 – 3.64 (m, 4H), 2.61 – 2.32 (m, 8H), 2.06 – 1.78 (m, 8H), 1.63 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.00 (s), 154.34 (s), 142.44 (s), 128.63 (s), 127.59 (s), 127.48 (s), 126.57 (s), 123.35 (s), 85.81 (d, *J* = 12.1 Hz), 85.39 (d, *J* = 12.0 Hz), 72.58 (d, *J* = 14.0 Hz), 70.13 (d, *J* = 14.0 Hz), 60.33 (s), 32.13 (s), 31.59 (s), 29.23 (s), 28.70 (s), 22.14 (s).

Synthesis of Rh complexes 3b

The synthetic procedures used is similar to that described for complex **3a**, starting from **L3** (38 mg, 1 mmol) and $[Rh(nbd)(Cl)]_2$ (92 mg, 2 mmol). Complex **3b** was obtained as purple solid. The single crystal of complex **3b** was isolated from a concentrated mixture solution of CH_2Cl_2 and n-hexane at -26 °C for 18 h (62 mg, Yield: 82%). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.9 Hz, 2H), 7.27 (tt, *J* = 8.3, 7.0 Hz, 10H), 6.63 (s, 2H), 4.32 (d, *J* = 18.4 Hz, 4H), 4.23 (q, *J* = 6.8 Hz, 2H), 3.75 (d, *J* = 24.2 Hz, 4H), 3.54 – 3.39 (m, 4H), 1.56 (d, *J* = 6.9 Hz, 6H), 1.32 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.55 (s), 155.04 (s), 141.90 (s), 128.76 (s), 127.72 (d, *J* = 2.6 Hz), 126.30 (s), 123.72 (s), 63.06 (d, *J* = 9.2 Hz), 62.74 (s), 62.64 (s), 61.56 (d, *J* = 6.2 Hz), 51.17 (s), 51.04 (s), 49.80 (s), 49.69 (s), 49.54 (d, *J* = 2.5 Hz), 49.31 (d, *J* = 2.5 Hz), 22.07 (s).

Scheme S8. Synthesis of Rh Complexes 4.



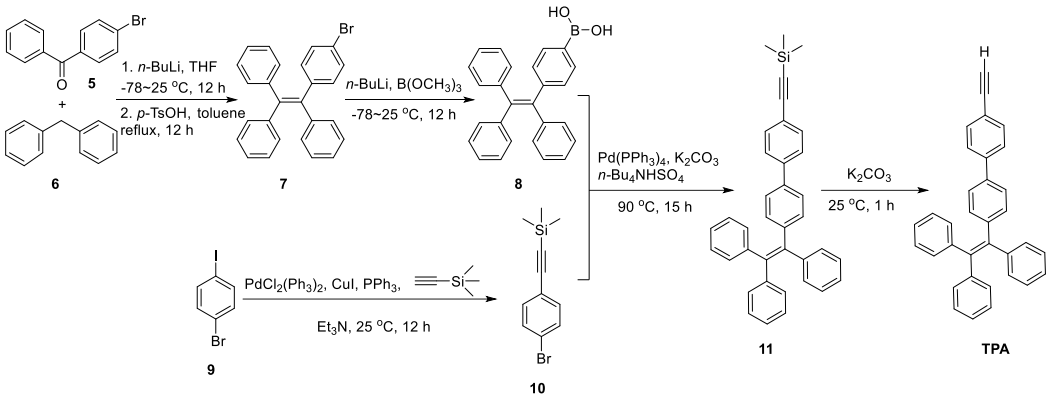
Synthesis of Rh complexes 4a

At room temperature, **L4** (43 mg, 1 mmol) and $[Rh(cod)(Cl)]_2$ (100 mg, 2 mmol) in 5 mL CH_2Cl_2 was stirred for 10 min. Then 4 mL aqueous solution of 360 mg KOH water was added. The mixture was extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4 after reaction for 1 h. Removal of solvent by vacuo gave yellow solid (67 mg, Yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.44 – 7.36 (m, 10H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.94 – 4.76 (m, 4H), 4.48 (q, *J* = 6.6 Hz, 2H), 3.89 (s, 4H), 2.73 – 2.43 (m, 8H), 1.99 (dd, *J* = 21.9, 10.8 Hz, 8H), 1.70 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.51 (s), 163.35 (s), 143.10 (s), 131.64 (s), 129.06 (s), 128.61 (s), 127.64 (s), 127.26 (s), 114.91 (s), 111.23 (s), 84.77 (d, *J* = 12.0 Hz), 84.33 (d, *J* = 11.8 Hz), 73.49 (d, *J* = 14.3 Hz), 71.38 (d, *J* = 14.5 Hz), 59.83 (s), 32.14 (s), 31.73 (s), 29.07 (s), 28.69 (s), 22.25 (s).

Synthesis of Rh complexes 4b

The synthetic procedure used for is similar to that described for complex **4a**, starting from **L4** (43 mg, 1 mmol) and $[Rh(nbd)(Cl)]_2$ (92 mg, 2 mmol). Complex 4b was obtained as yellow solid. The single crystal of complex **4b** was isolated from a concentrated mixture solution of CH_2Cl_2 and n-hexane at -26 °C for 18 h (70 mg, Yield: 86%)). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.39 – 7.29 (m, 10H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.44 (d, *J* = 17.8 Hz, 4H), 4.28 (q, *J* = 6.8 Hz, 2H), 3.78 (d, *J* = 19.5 Hz, 4H), 3.53 (t, *J* = 19.5 Hz, 4H), 1.67 – 1.58 (m, 6H), 1.35 (q, *J* = 8.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.86 (s), 162.02 (s), 142.81 (s), 131.46 (s), 129.31 – 129.12 (m), 128.58 (s), 127.50 (s), 127.29 (s), 114.72 (s), 111.62 (s), 62.36 (s), 62.25 (s), 61.98 (d, *J* = 8.9 Hz), 61.41 (d, *J* = 6.1 Hz), 52.46 (s), 52.34 (s), 51.27 (s), 51.15 (s), 49.39 (s), 49.27 (s), 22.11 (s).

Scheme S9. Synthesis of 4-ethynyl-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (TPA).



Synthesis of (2-(4-bromophenyl)ethene-1,1,2-triyl)tribenzene (7): Under nitrogen atmosphere, compound **6** (8.60 g, 51 mmol) was dissolved in 50 mL of dry THF, after the solution was cooled to -78 °C, *n*-BuLi (35 mL, 1.6 M in hexane) was added dropwise and the resulting mixture was stirred at -10 °C for 2 h, then compound **5** (11.1 g, 42.4 mmol) was added dropwise and the mixture was allowed to warmed to room temperature and stirred for 10 h. Then the reaction mixture was quenched with an aqueous solution of ammonium chloride, extracted with CH_2Cl_2 (3 × 100 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to remove the solvent. The residue was dissolved in toluene (100 mL), *p*-toluene sulfonic acid (1.06 g, 6.20 mmol) was added, the resulting mixture was refluxed for 12 h. after the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure, the residue was purified by column chromatography (silica gel, 20:1 hexane to ethyl acetate, v/v) to afford the desired compound **7** as a white solid (11.7 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (d, *J* = 8.2 Hz, 2H), 7.08 (m, 15H), 7.22 (d, *J* = 8.2 Hz, 2H).

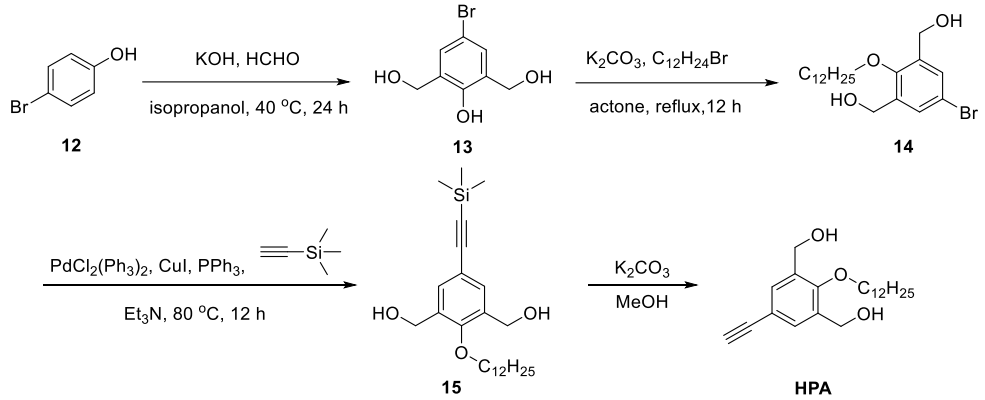
Synthesis of (4-(1,2,2-triphenylvinyl)phenyl)boronic acid (8): Under nitrogen atmosphere, compound **7** (2 g, 4.86 mmol) was dissolved in 20 mL of dry THF, after the solution was cooled to -78 °C, *n*-BuLi (2.43 mL, 2.4 M in hexane) was added dropwise and the mixture was stirred at -78 °C for 30 min. Then a solution of trimethyl borate (0.76 g, 7.29 mmol) in dry THF (10 mL) was added dropwise, the resulting mixture was stirred at -78 °C for 30 min, then allowed to warm to room temperature and stirred for 11 h. The reaction mixture was quenched with 10% hydrogen chloride aqueous solution, extracted with ethyl acetate (3 × 30 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford crude compound **8** as white solid (2.40 g, crude), this compound was used directly for the next step without purification.

Synthesis of ((4-bromophenyl)ethynyl)trimethylsilane (10): Under nitrogen atmosphere, compound **9** (7.0 g, 25 mmol), PPh_3 (330 mg, 1.25 mmol), Pd $(PPh_3)_2Cl_2$ (630 mg, 0.9 mmol), CuI (240 mg, 1.25 mmol), and ethynyltrimethylsilane (7 mL, 50 mmol) were dissolved in 60 mL of Et_3N. The reaction mixture was stirred at 25 °C for 12 hours. Finally, the mixture was filtered, washed with brine, dried using anhydrous magnesium sulfate, concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, PE) to afford the desired compound **10** as a white solid (5.3 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 0.25 (s, 4H).

Synthesis of trimethyl((4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)ethynyl)silane (11): Under nitrogen atmosphere, compound **8** (5 g, crude), compound **10** (3.33 g, 8.9 mmol) were dissolved in a mixture solvents of toluene (100 mL) and water (50 mL), then $Pd(PPh_3)_4$ (386 mg, 0.33 mmol), K_2CO_3 (2.75 g, 19.9 mmol) and tetrabutylammonium hydrogen sulfate (452 mg, 1.33 mmol) were added, the resulting mixture was stirred at 90 °C for 15 h. after the reaction mixture was cooled to room temperature, the organic layer was separated and the aqueous phase was extracted with ethyl acetate (3 × 80 mL), the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, 2:1 hexane: ethyl acetate, v/v) to afford the desired compound **11** as a light yellow solid (6.5 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 4H), 7.34 (dd, 2H), 7.18 – 7.00 (m, 17H), 0.28 (m, 9H).

Synthesis of 4-ethynyl-4'-(1,2,2-triphenylvinyl)-1,1'-biphenyl (TPA): Compound **11** (5.1 g, 10.1 mmol) and potassium carbonate (4.8 g, 20.2mmol) were dissolved in MeOH (50 mL) under an atmosphere of nitrogen, the resulting mixture was stirred at room temperature for 1 h. Finally, the mixture was filtered and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, PE) to afford the desired compound **TPA** as a pure yellow liquid (3.58 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 4H), 7.33 (d, 2H), 7.13–7.01 (m, 17H), 3.11 (s, 1H).

Scheme S10. Synthesis of (2-(dodecyloxy)-5-ethynyl-1,3-phenylene)dimethanol (HPA).



Synthesis of (5-bromo-2-hydroxy-1,3-phenylene)dimethanol (13): Under nitrogen atmosphere, compound **12** (20.4 g, 118 mmol) was dissolved in the solvents of isopropanol (50 mL), then KOH (9.5 g, 170 mmol) was added, then 37% formaldehyde solution (150 mL) was added, the resulting mixture was stirred at 40 °C for 24 h. After the reaction mixture was cooled to room temperature, then 0.1 mol/L HCl was slowly added the reaction mixture adjusting the PH to 2, the mixture stirred at room temperature overnight, the mixture was filtered to afford the desired compound **13** as a red solid (20.6 g, 75% yield). ^{1}H NMR (400 MHz, DMSO-d6): δ 8.77 (s, 1H), 7.29 (s, 2H, aromatic), 5.34 (t, *J* = 5.4 Hz, 2H), 4.52 (d, *J* = 5.0 Hz, 4H).

Synthesis of (5-bromo-2-(dodecyloxy)-1,3-phenylene)dimethanol (14): Under nitrogen atmosphere, compound **13** (20.6 g, 88 mmol) was dissolved in the solvents of actone (200 mL), then K_2CO_3 (12.2 g, 88 mmol), 1-Bromododecane (26 g, 106 mmol) were added, then the resulting mixture was refluxed for 12 h. After the reaction mixture was cooled to room

temperature, the mixture was filtered, washed with brine, dried using Na_2SO_4, concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, PE) to afford the desired compound **14** as a white solid (24 g, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 2H), 4.69 (d, *J* = 6.1 Hz, 4H), 3.84 (t, *J* = 6.6 Hz, 2H), 2.05 (t, *J* = 6.1 Hz, 2H), 1.87–1.71 (m, 2H), 1.50–1.11 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H).

Synthesis of (2-(dodecyloxy)-5-((trimethylsilyl)ethynyl)-1,3-phenylene)dimethanol (15): Under nitrogen atmosphere, compound **14** (8 g, 20 mmol), PPh_3 (52.4 mg, 0.2 mmol), $Pd(PPh_3)_2Cl_2$ (6.38 mg, 0.01 mmol), CuI (38 mg, 0.2 mmol), and ethynyltrimethylsilane (3 g, 30 mmol) were dissolved in 100 mL of Et_3N. The reaction mixture was stirred at 80 °C for 12 h. Finally, the mixture was filtered, washed with brine, dried using anhydrous magnesium sulfate, concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, PE) to afford the desired compound **15** as a white solid (4.2 g, 50% yield).

Synthesis of (2-(dodecyloxy)-5-ethynyl-1,3-phenylene)dimethanol (HPA):
Compound **15** (4.2 g, 10 mmol) and potassium carbonate (138 mg, 1 mmol) were dissolved in MeOH (50 mL) under an atmosphere of nitrogen, the resulting mixture was stirred at room temperature for 1 h. Finally, the mixture was filtered and concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, PE) to afford the desired compound **HPA** as a pure yellow liquid (3.2 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 16.4 Hz, 2H), 4.68 (d, *J* = 5.7 Hz, 4H), 3.88 (t, *J* = 6.6 Hz, 2H), 3.04 (s, 1H), 2.29–1.92 (m, 2H), 1.88–1.76 (m, 2H), 1.53–1.19 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H).

General procedure for aqueous polymerization of phenylacetylene.
Under nitrogen atmosphere, a 2 ml dry solvent solution of Rh catalyst (4 μmol) was added to 500 equiv. of phenylacetylene monomer (2 mmol) in a Schlenk flask, obtaining a red solution. The reaction mixture was stirred at r.t. for 1 h to become viscous. Then the mixture was treated with a large amount of methanol containing two drops of acetic acid. After filtration, the polymer was washed with methanol and dried at 40 °C overnight to a constant weight under vacuum.
The different isomer contents of the poly(phenylacetylene) were calculated from the ^{1}H NMR spectra according to eqs (1).[15]

$$\%cis = \left[I_{H1} / \left(I_{total} / 6 \right) \right] \times 100 \qquad (1)$$

In the eqs (1), I_{H1} is the integrate area of one alkynyl proton of phenylacetylene unit at 5.84 ppm, and I_{total} is the total integrate area of aryl protons of the benzene ring unit at 6.94, 6.78 (*trans*), and 6.63 ppm and alkynyl proton of phenylacetylene unit at 5.84 ppm in the ^{1}H NMR spectrum.

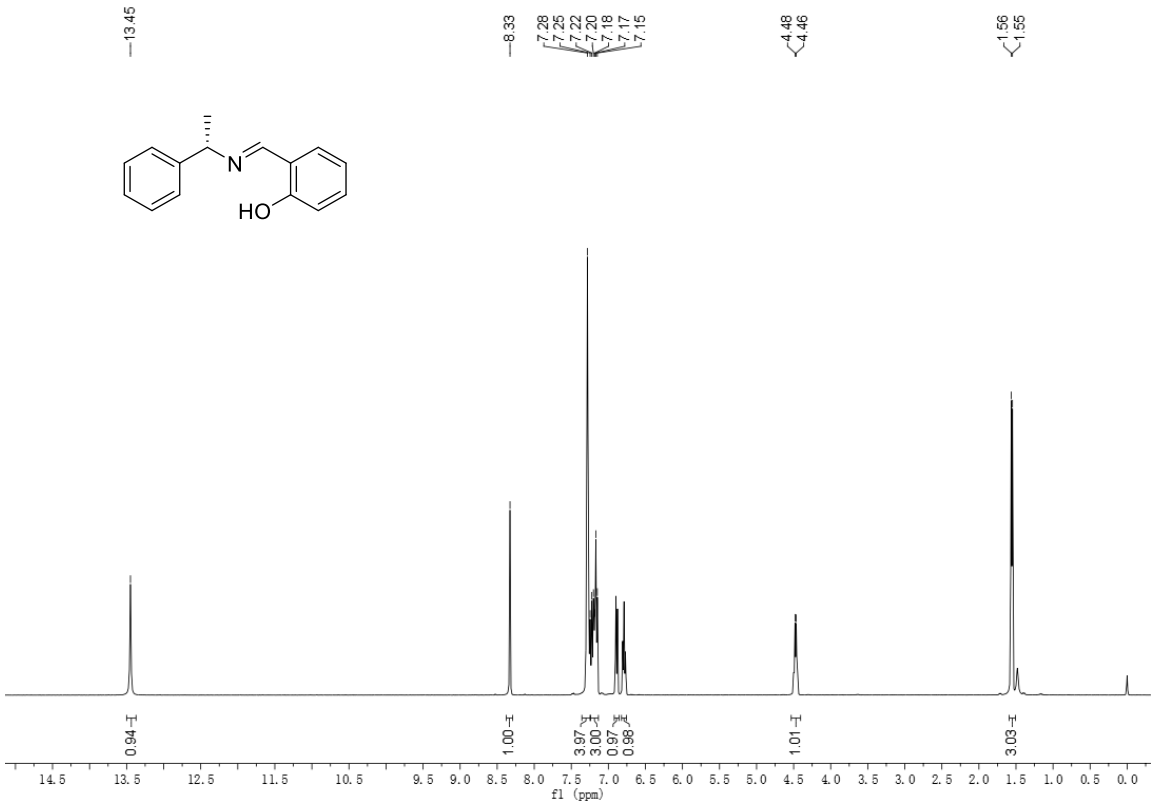


Figure S1. ^{1}H NMR spectrum of (*S*,*E*)-2-(((1-phenylethyl)imino)methyl)phenol ligand **L1**. (400MHz, $CDCl_3$, 25°C)

Figure S2. ^{1}H NMR spectrum of 4,4'-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)-[1,1'-biphenyl]-3,3'-diol ligand **L2**. (100MHz, $CDCl_3$, 25°C)

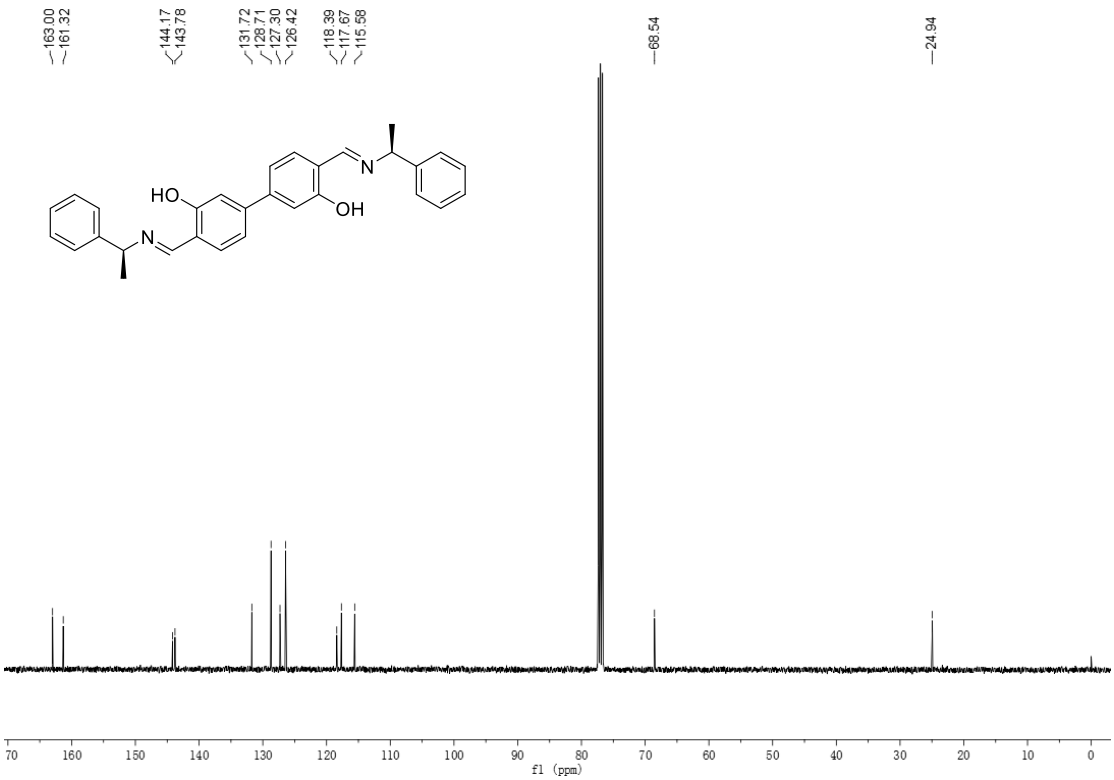


Figure S3. ^{13}C NMR spectrum of 4,4'-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)-[1,1'-biphenyl]-3,3'-diol ligand **L2**. (100MHz, $CDCl_3$, 25°C)

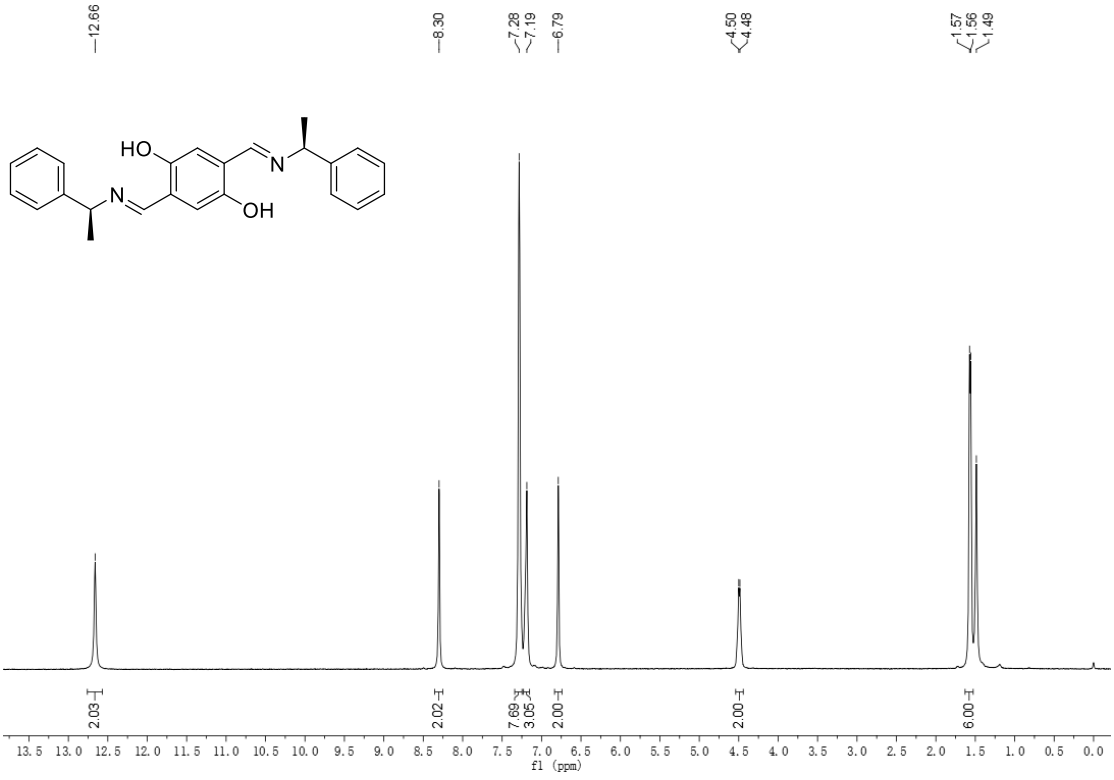


Figure S4. ^{1}H NMR spectrum of 2,5-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)benzene-1,4-diol ligand **L3.** (400MHz, $CDCl_3$, 25°C)

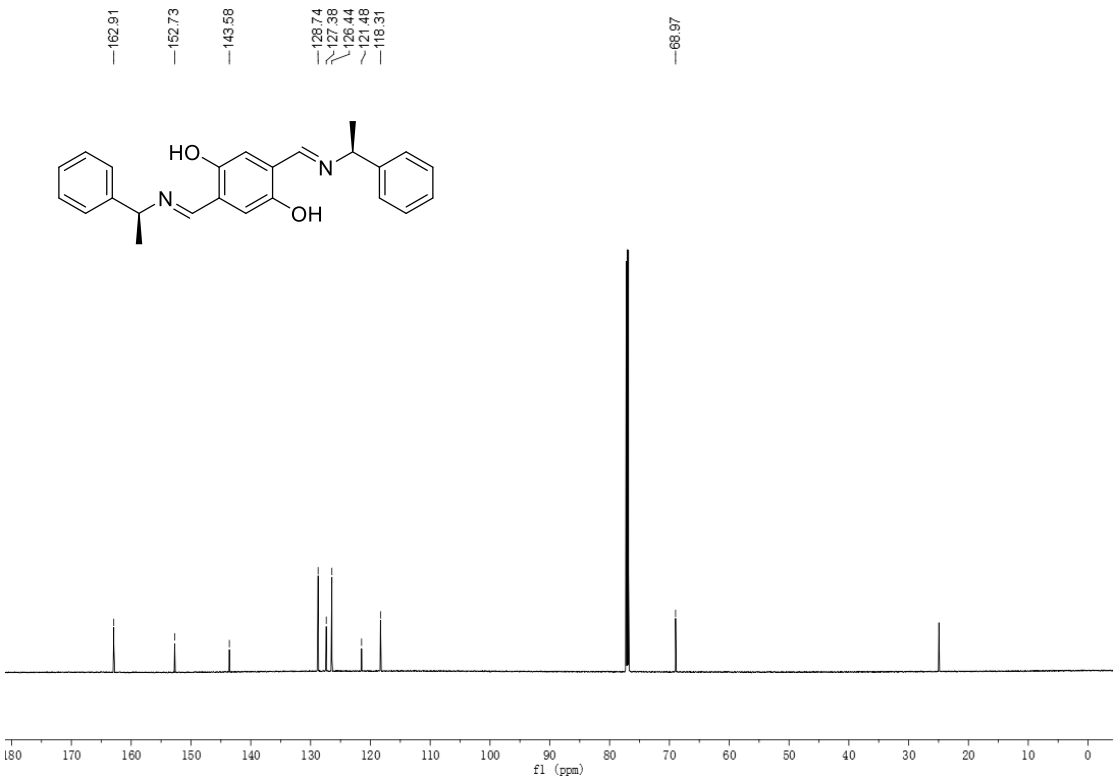


Figure S5. ^{13}C NMR spectrum of 2,5-bis((*E*)-(((*S*)-1-phenylethyl)imino)methyl)benzene-1,4-diol ligand **L3**. (100MHz, $CDCl_3$, 25°C)

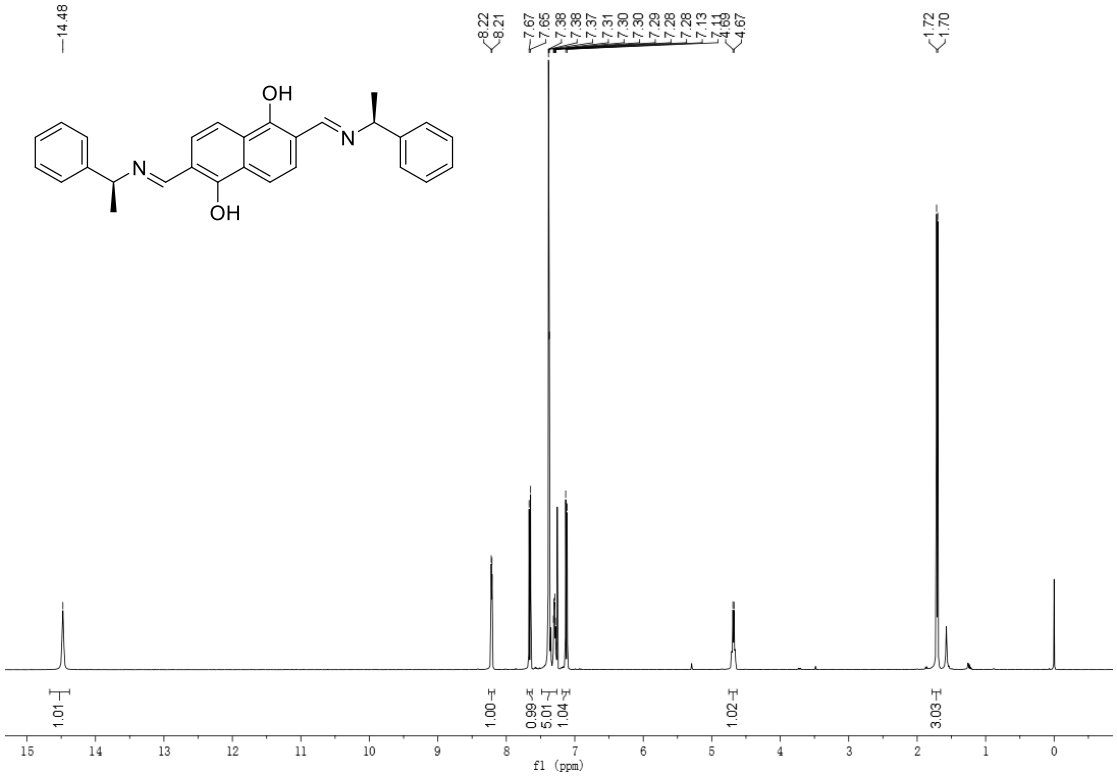


Figure S6. ^{1}H NMR spectrum of 2,6-bis((*E*)-((1-phenylethyl)imino)methyl)naphthalene-1,5-diol ligand **L4**. (400MHz, $CDCl_3$, 25°C)

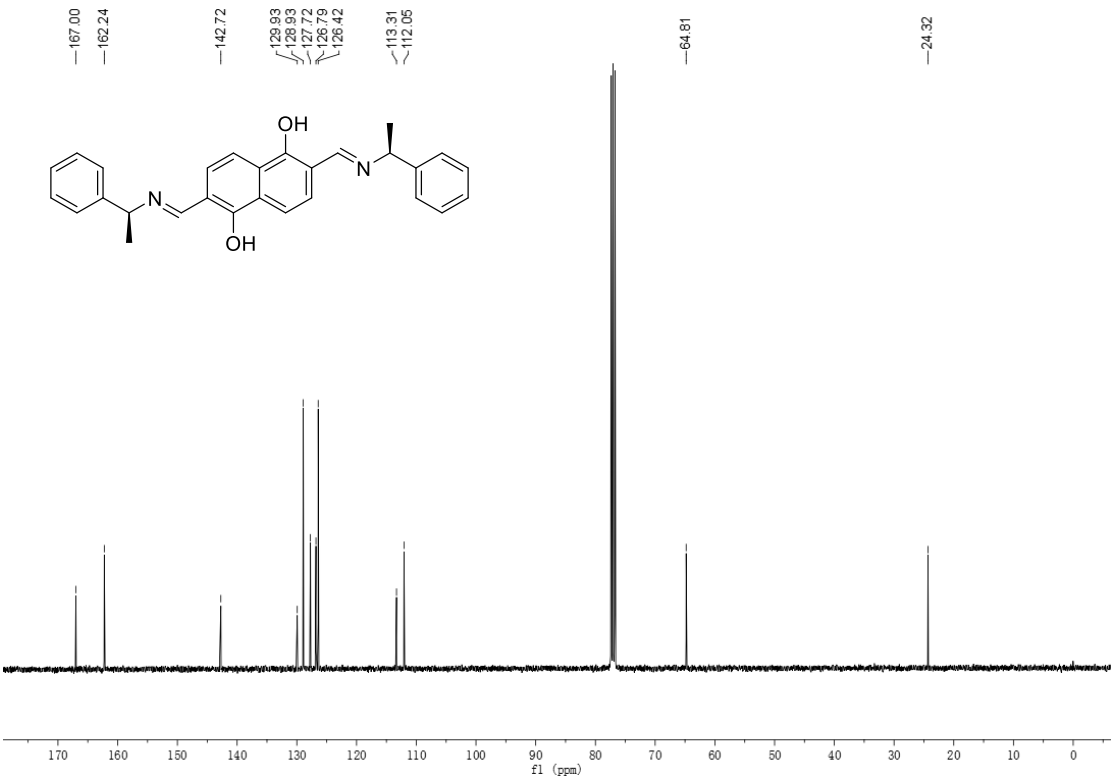


Figure S7. ^{13}C NMR spectrum of 2,6-bis((*E*)-((1-phenylethyl)imino)methyl)naphthalene-1,5-diol ligand **L4**. (100MHz, $CDCl_3$, 25°C)

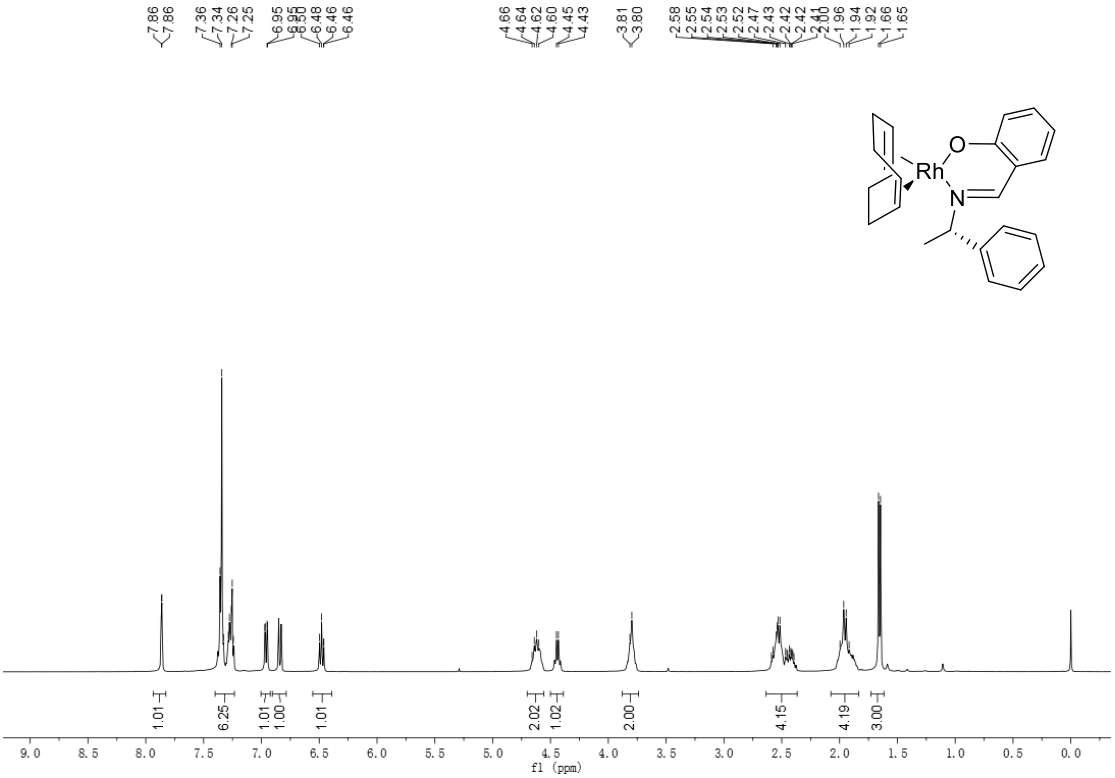


Figure S8. ^{1}H NMR spectrum of Rh complexes **1a**. (400MHz, $CDCl_3$, 25°C)

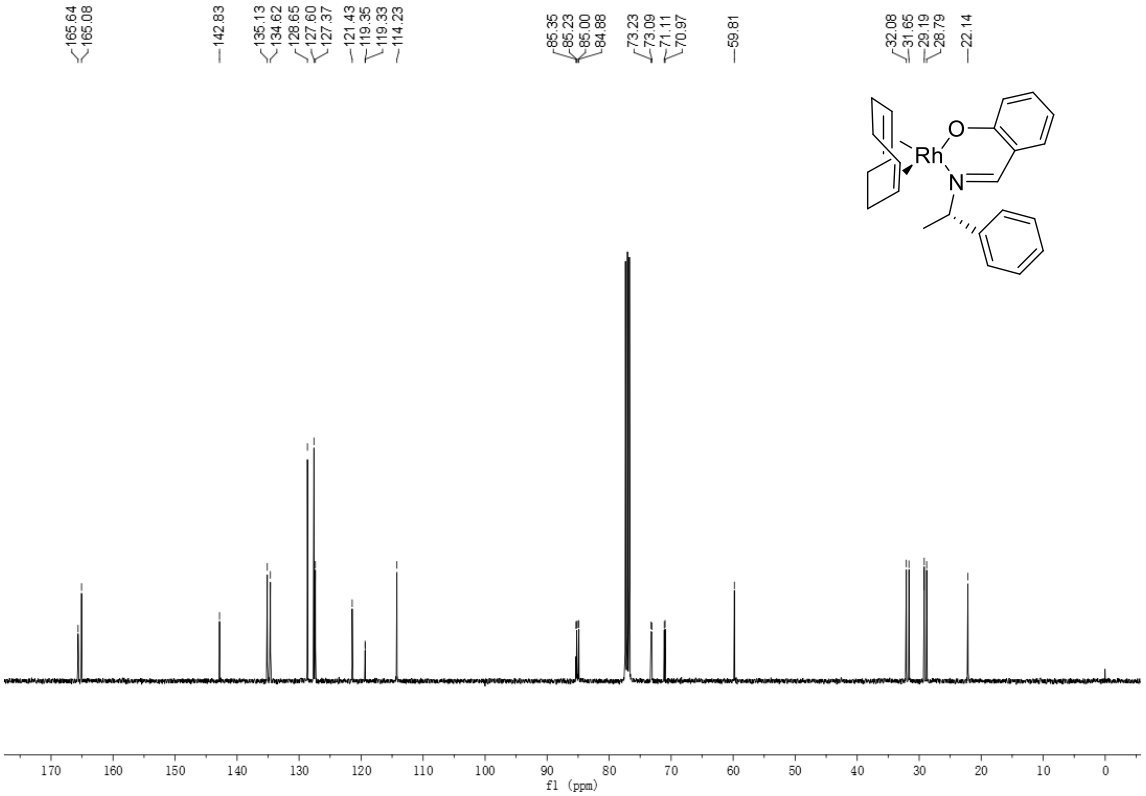


Figure S9. ^{13}C NMR spectrum of Rh complexes **1a**. (100MHz, $CDCl_3$, 25°C)

Figure S10. ^{1}H NMR spectrum of Rh complexes **1b**. (400MHz, $CDCl_3$, 25°C)

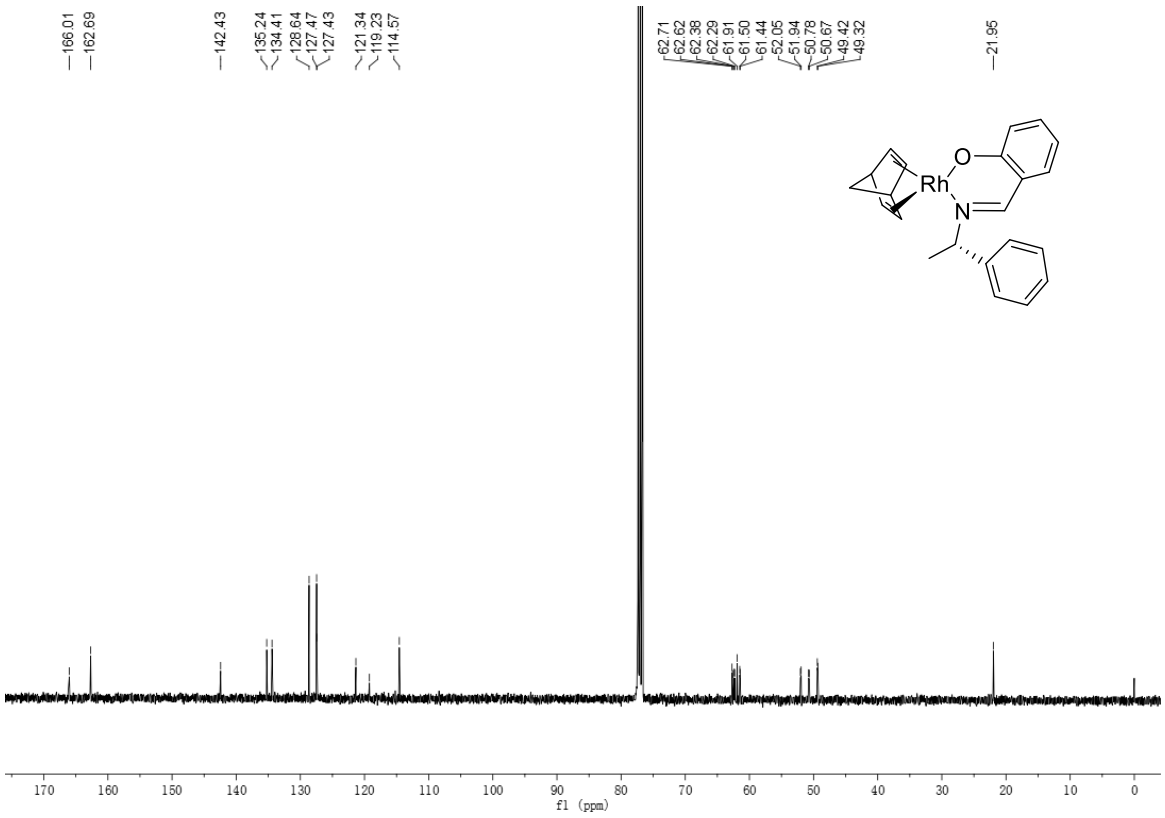


Figure S11. ^{13}C NMR spectrum of Rh complexes **1b**. (100MHz, $CDCl_3$, 25°C)

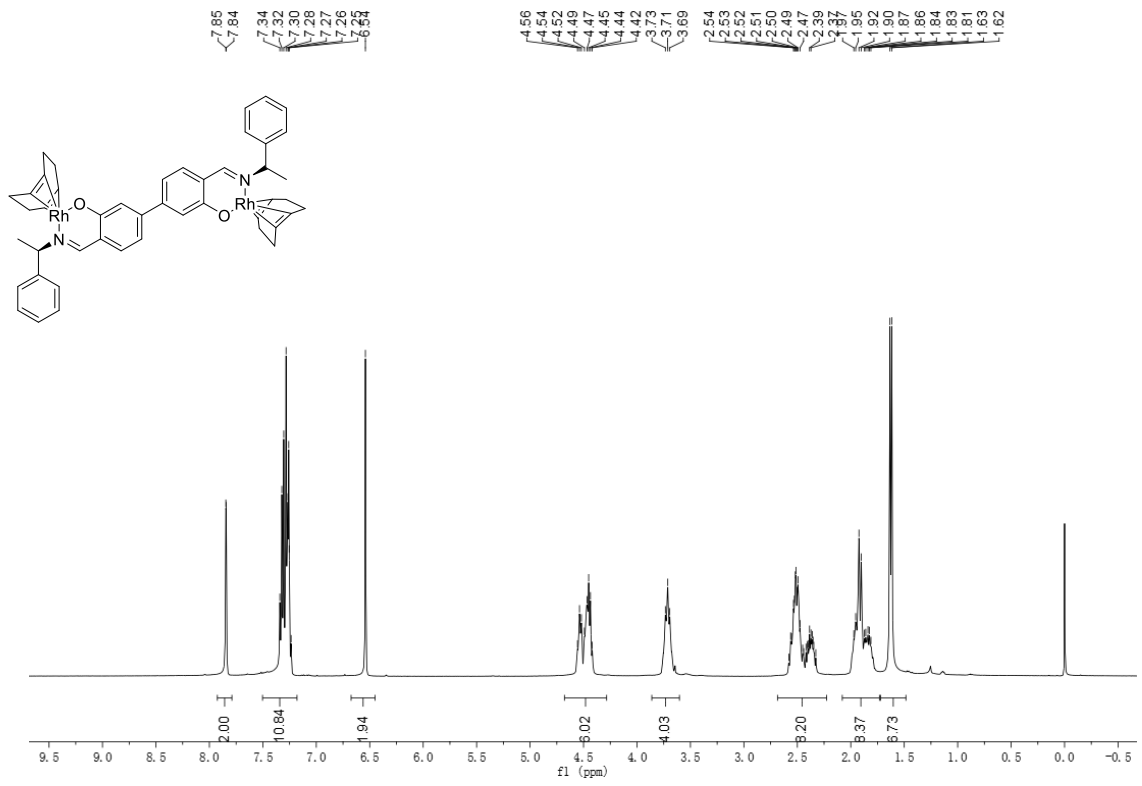


Figure S12. ^{1}H NMR spectrum of Rh complexes **2a**. (400MHz, $CDCl_3$, 25°C)

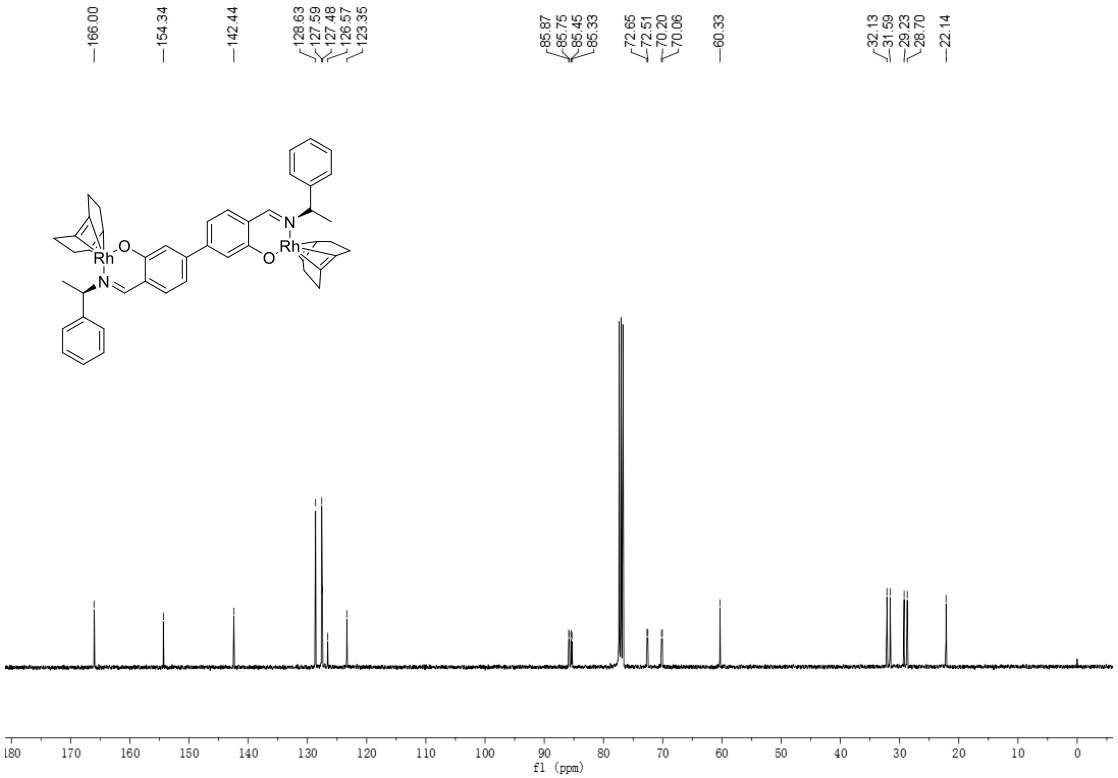


Figure S13. ^{13}C NMR spectrum of Rh complexes **2a**. (100MHz, $CDCl_3$, 25°C)

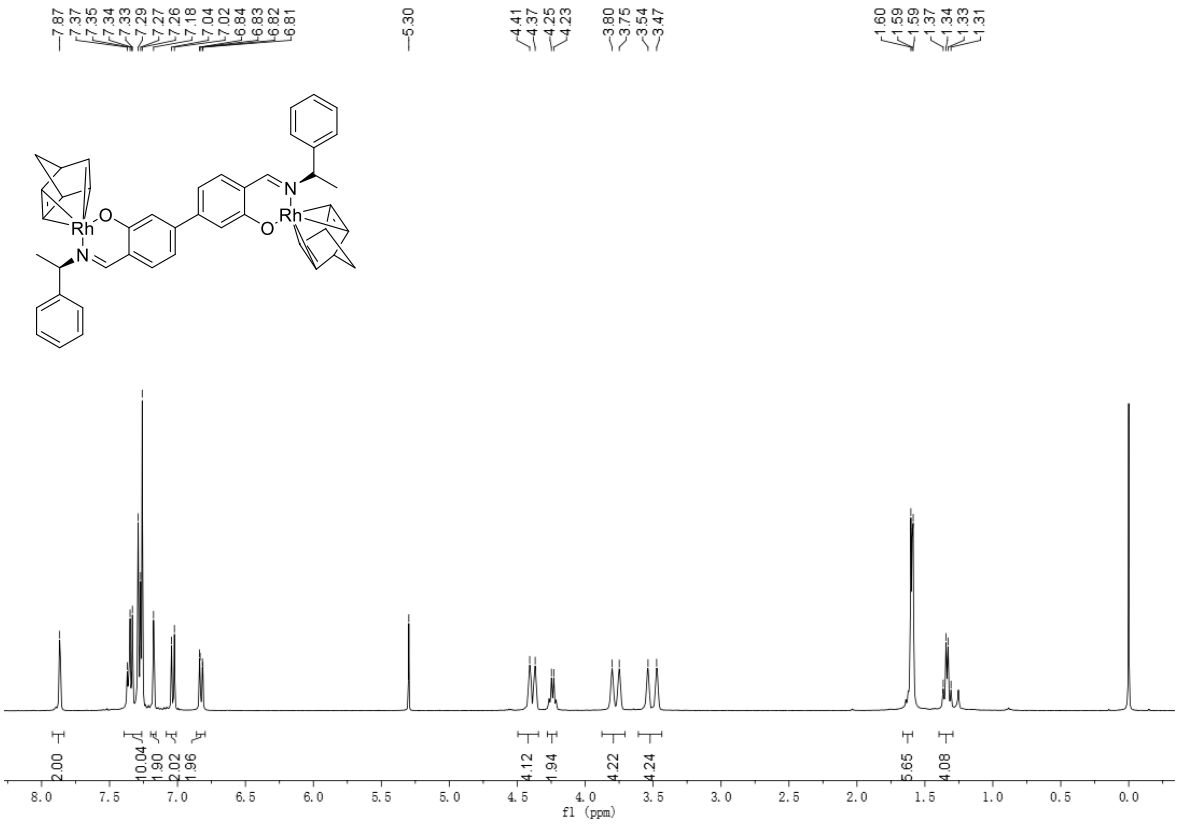


Figure S14. ^{1}H NMR spectrum of Rh complexes **2b**. (400MHz, $CDCl_3$, 25°C)

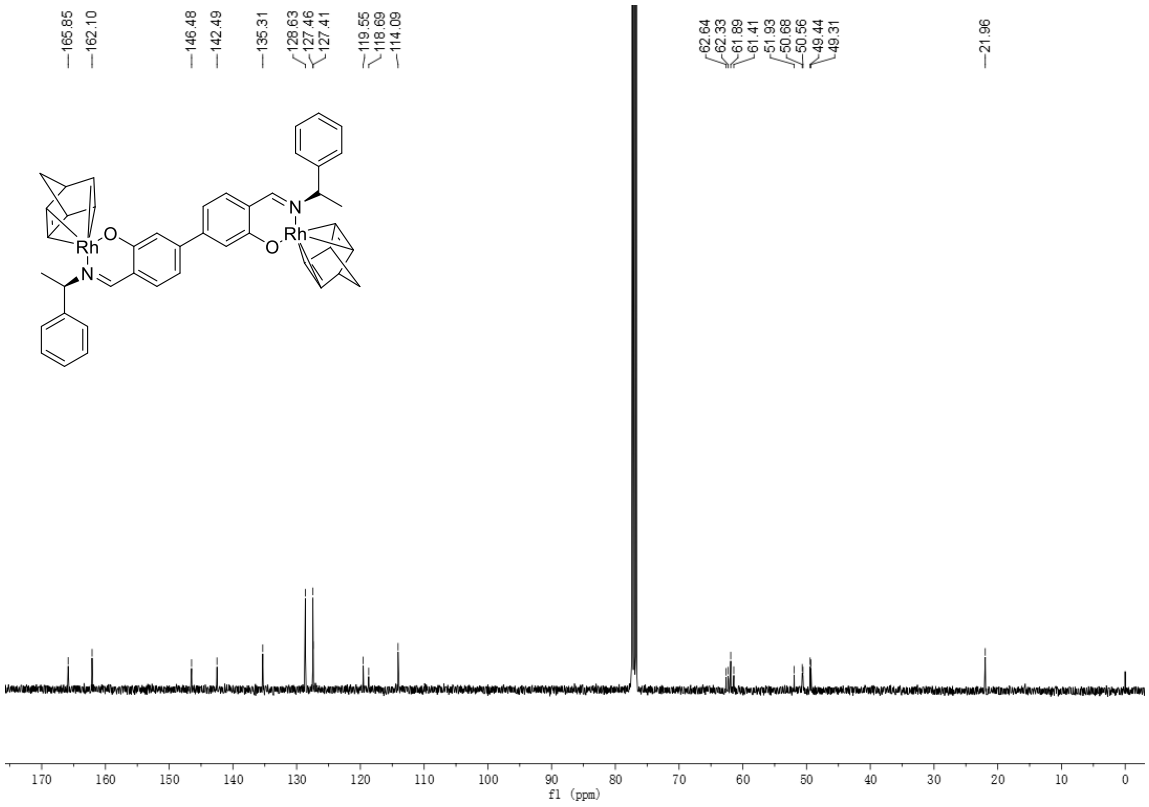


Figure S15. ^{13}C NMR spectrum of 1 Rh complexes **2b**. (100MHz, $CDCl_3$, 25°C)

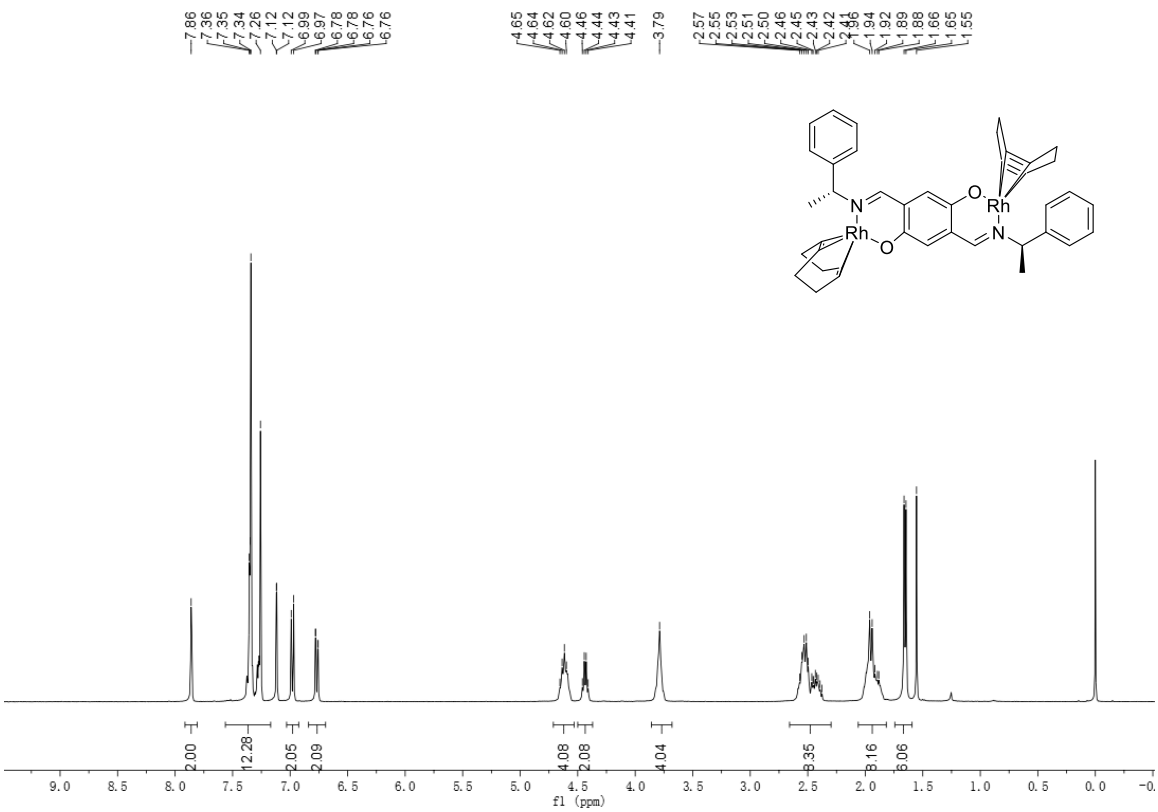


Figure S16. ^{1}H NMR spectrum of Rh complexes **3a**. (400MHz, $CDCl_3$, 25°C)

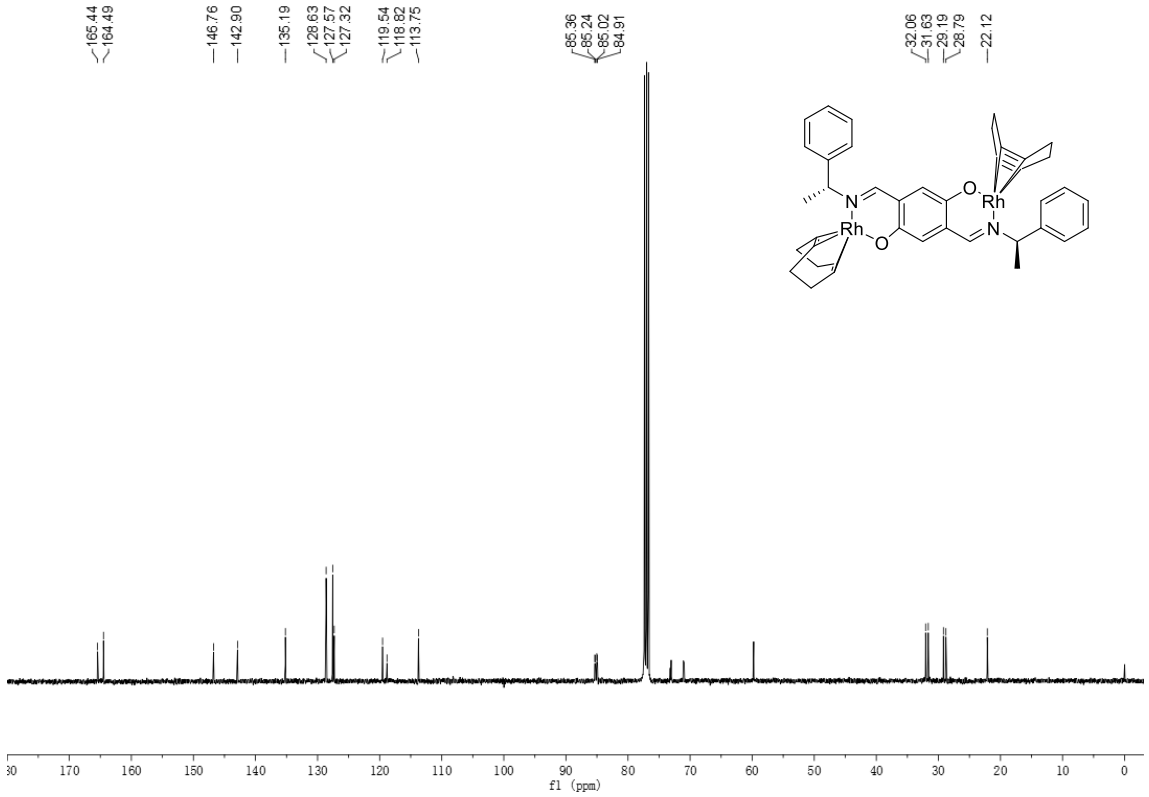


Figure S17. ^{13}C NMR spectrum of Rh complexes **3a**. (100MHz, $CDCl_3$, 25°C)

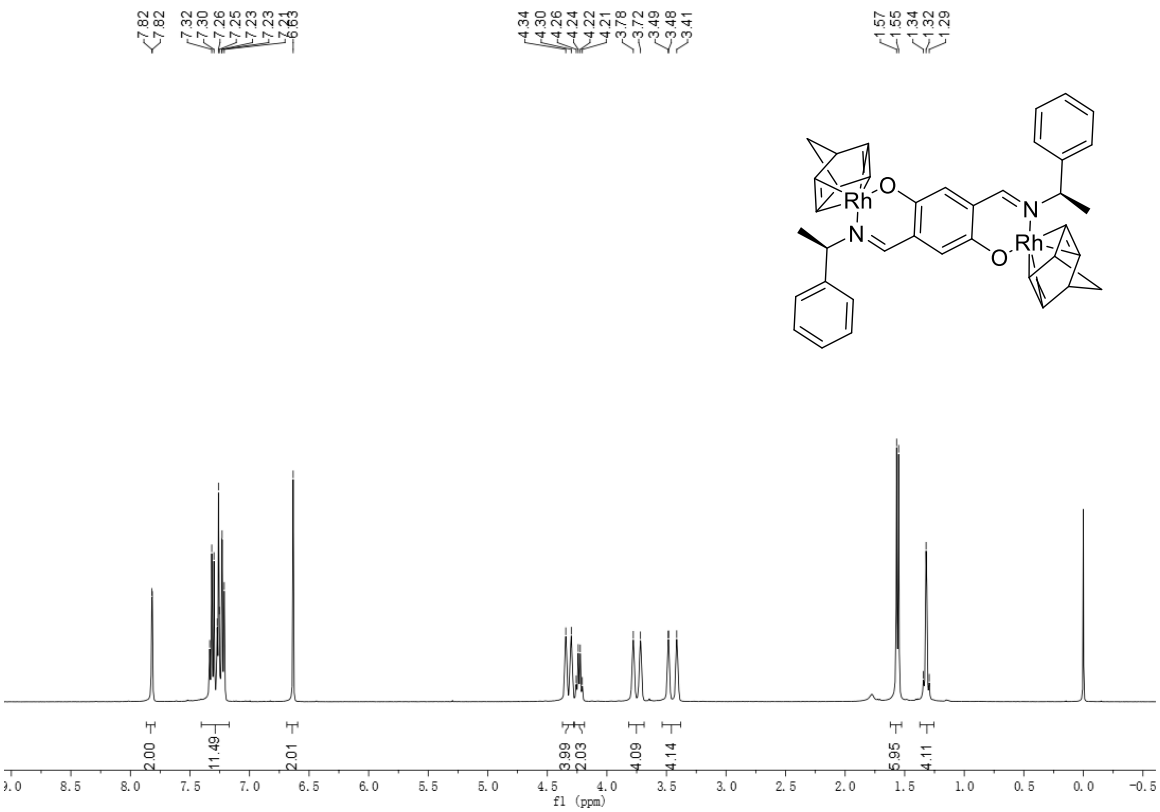


Figure S18. ^{1}H NMR spectrum of Rh complexes **3b**. (400MHz, $CDCl_3$, 25°C)

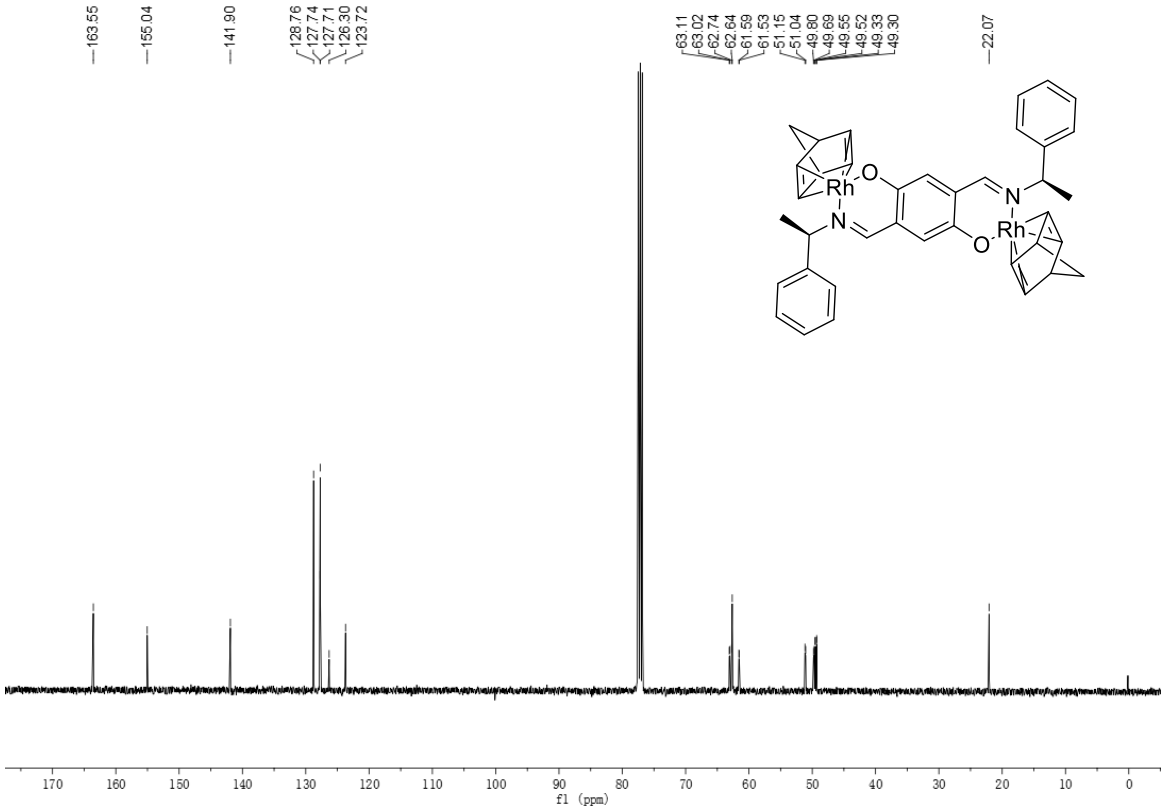


Figure S19. ^{13}C NMR spectrum of Rh complexes **3b**. (100MHz, $CDCl_3$, 25°C)

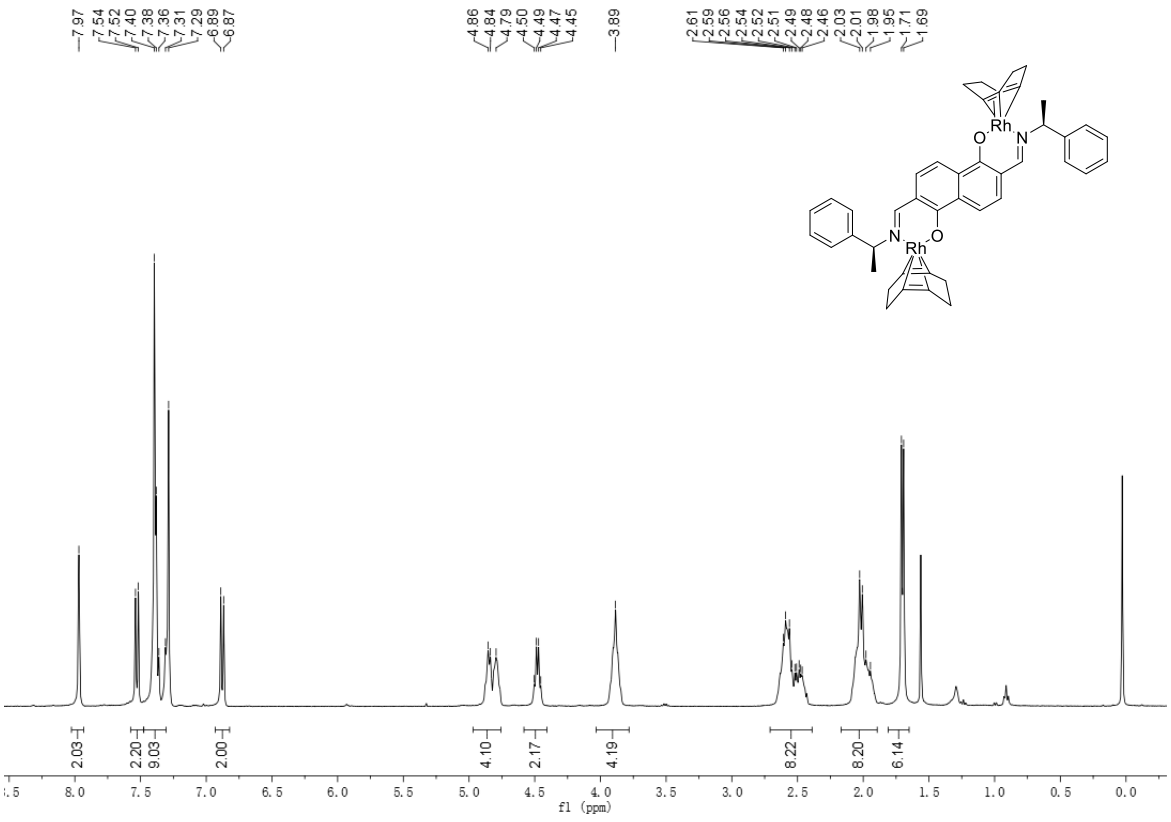


Figure S20. ^{1}H NMR spectrum of Rh complexes **4a**. (400MHz, $CDCl_3$, 25°C)

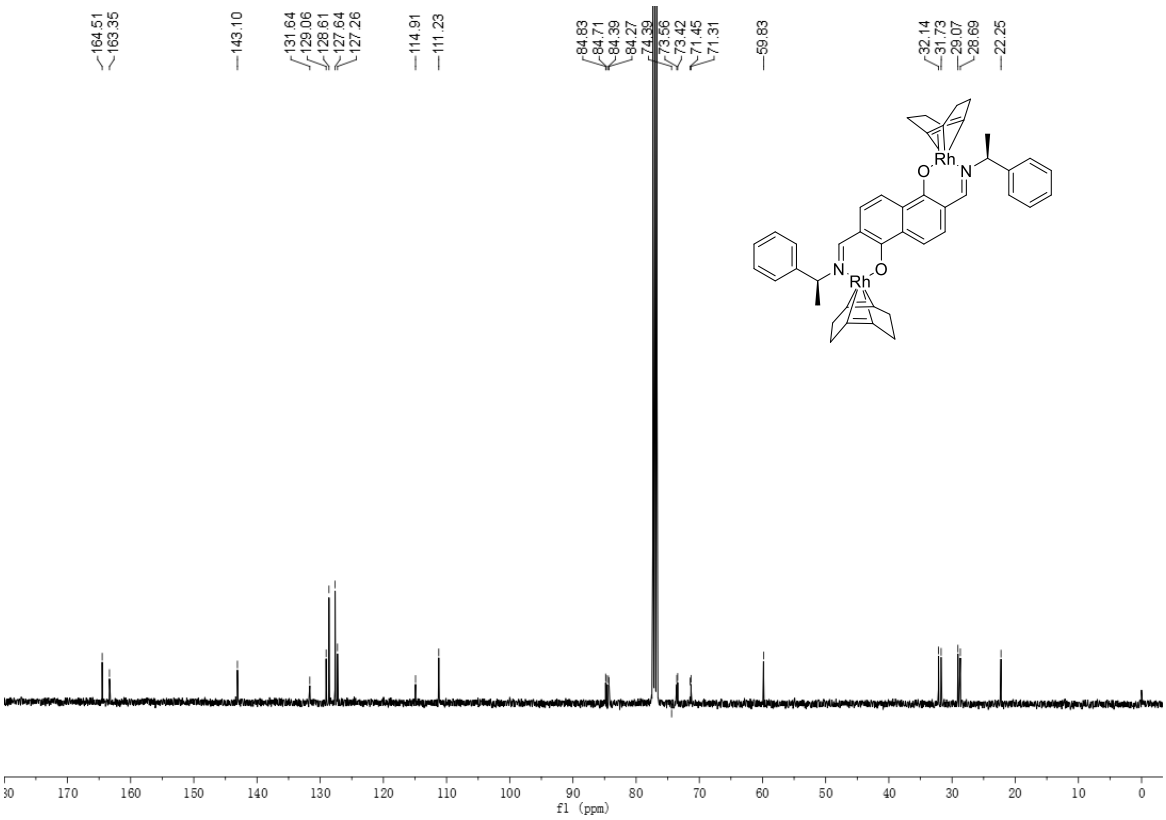


Figure S21. ^{13}C NMR spectrum of Rh complexes **4a**. (100MHz, $CDCl_3$, 25°C)

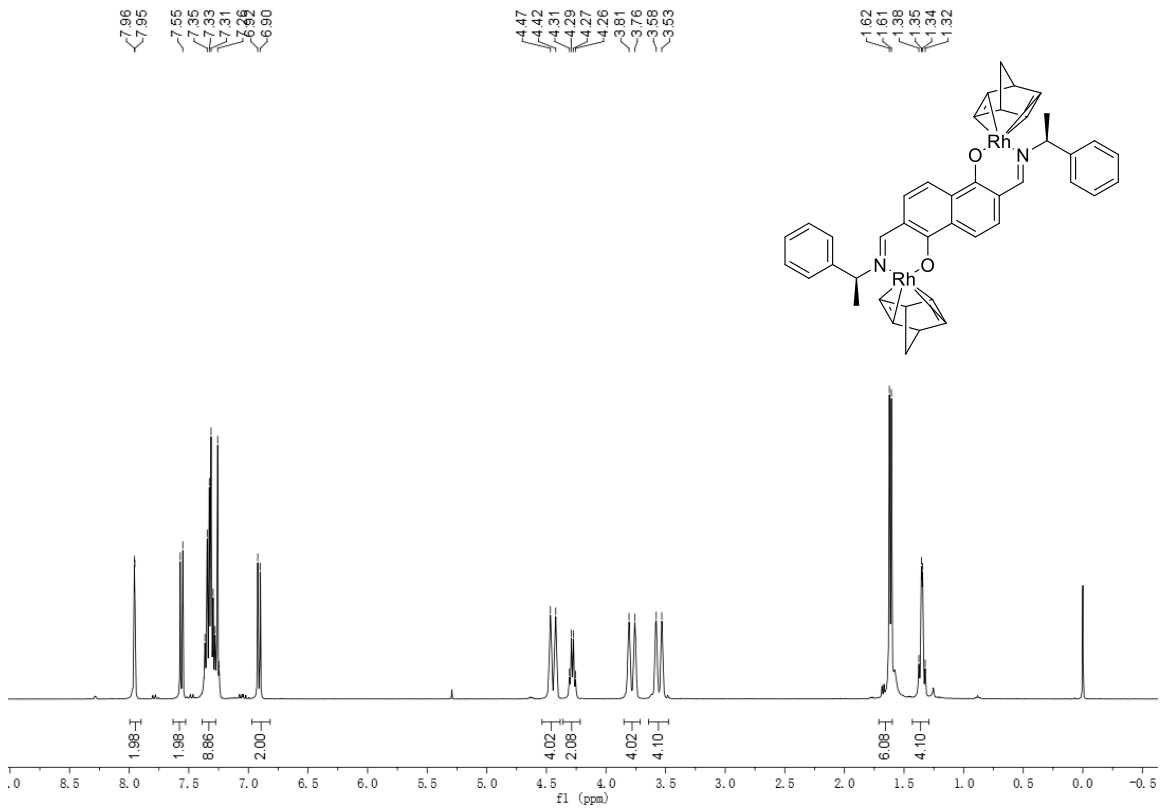


Figure S22. ^{1}H NMR spectrum of Rh complexes **4b**. (400MHz, $CDCl_3$, 25°C)

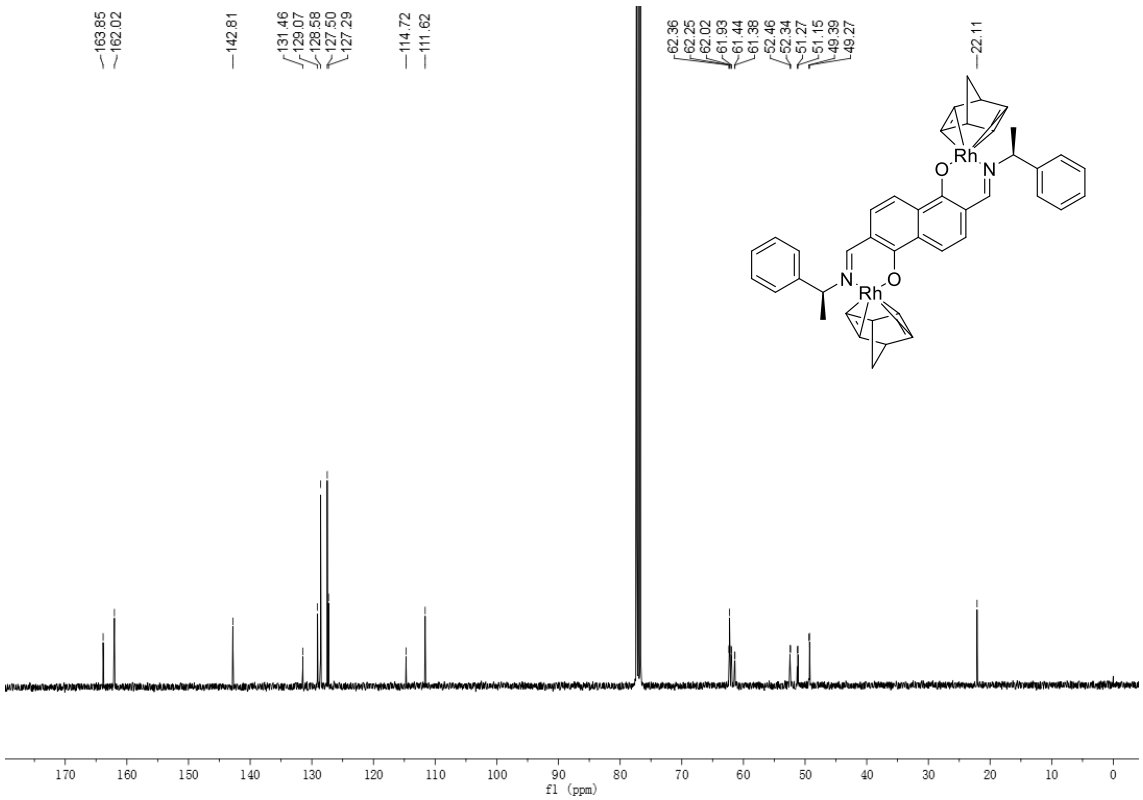


Figure S23. ^{13}C NMR spectrum of Rh complexes **4b**. (100MHz, $CDCl_3$, 25°C)

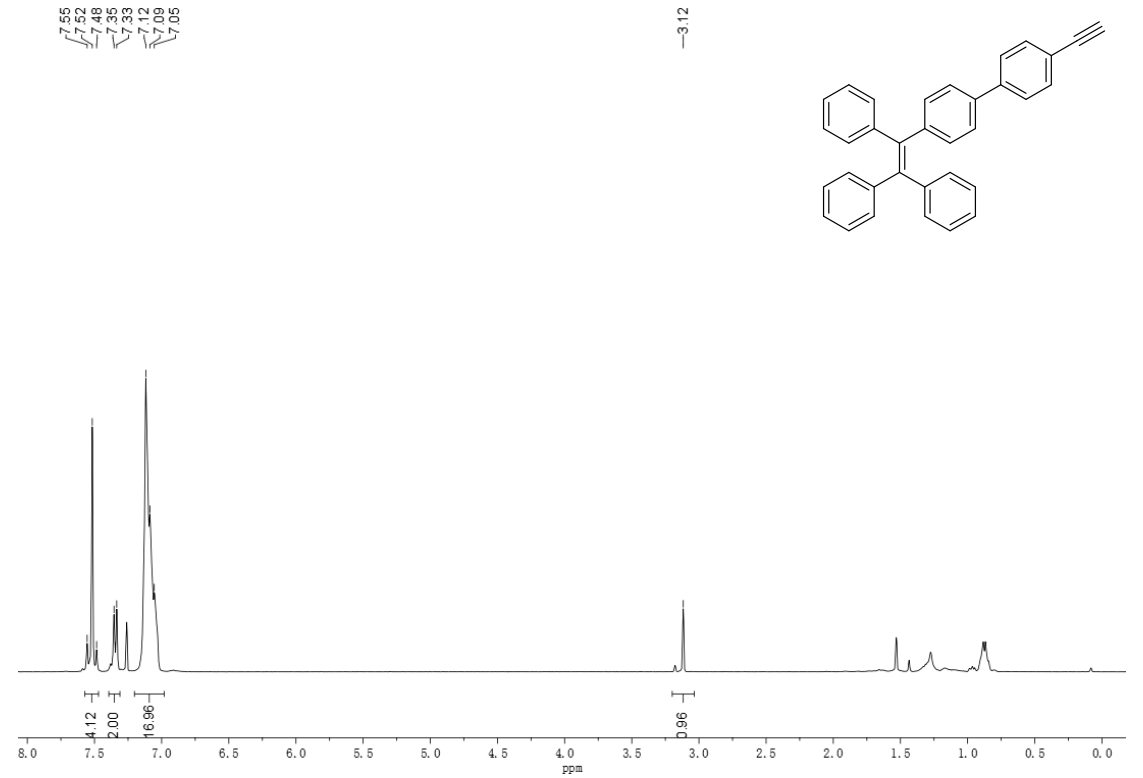


Figure S24. ^{1}H NMR spectrum of (2-(dodecyloxy)-5-ethynyl-1,3-phenylene)dimethanol (**TPA**). (400MHz, $CDCl_3$, 25°C)

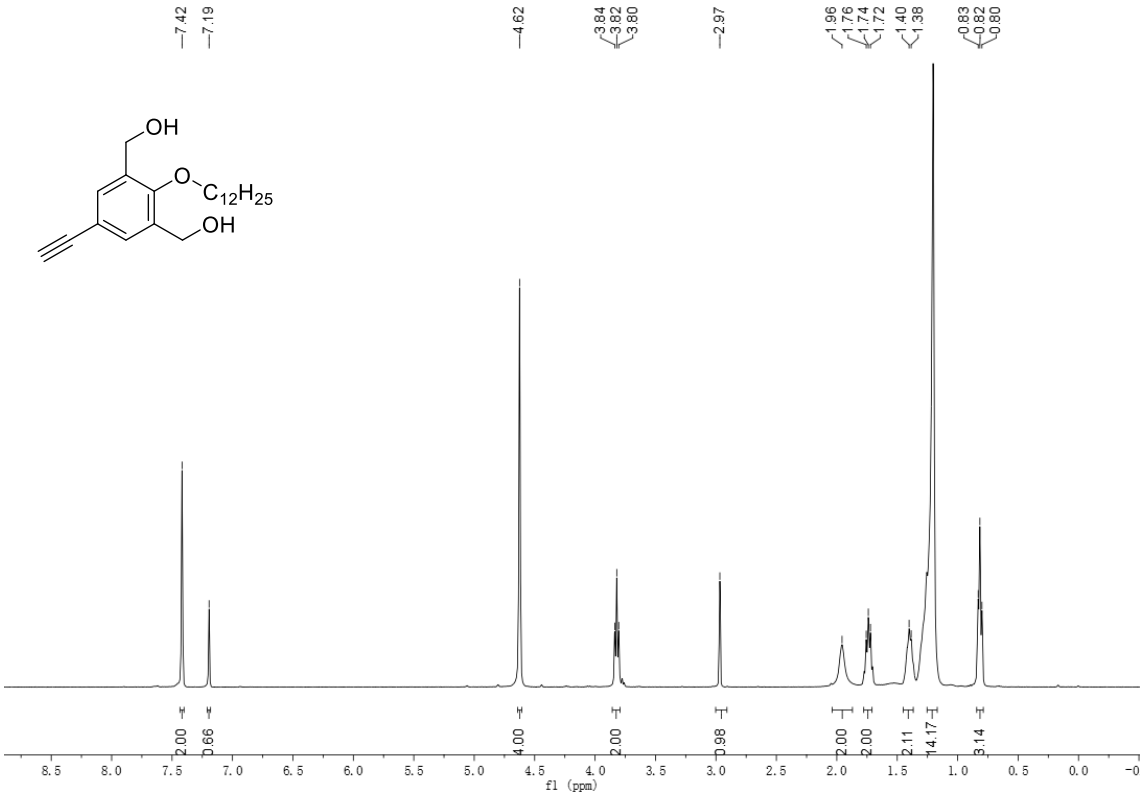


Figure S25. ^{1}H NMR spectrum of (2-(dodecyloxy)-5-ethynyl-1,3-phenylene)dimethanol (**HPA**). (400MHz, $CDCl_3$, 25°C)

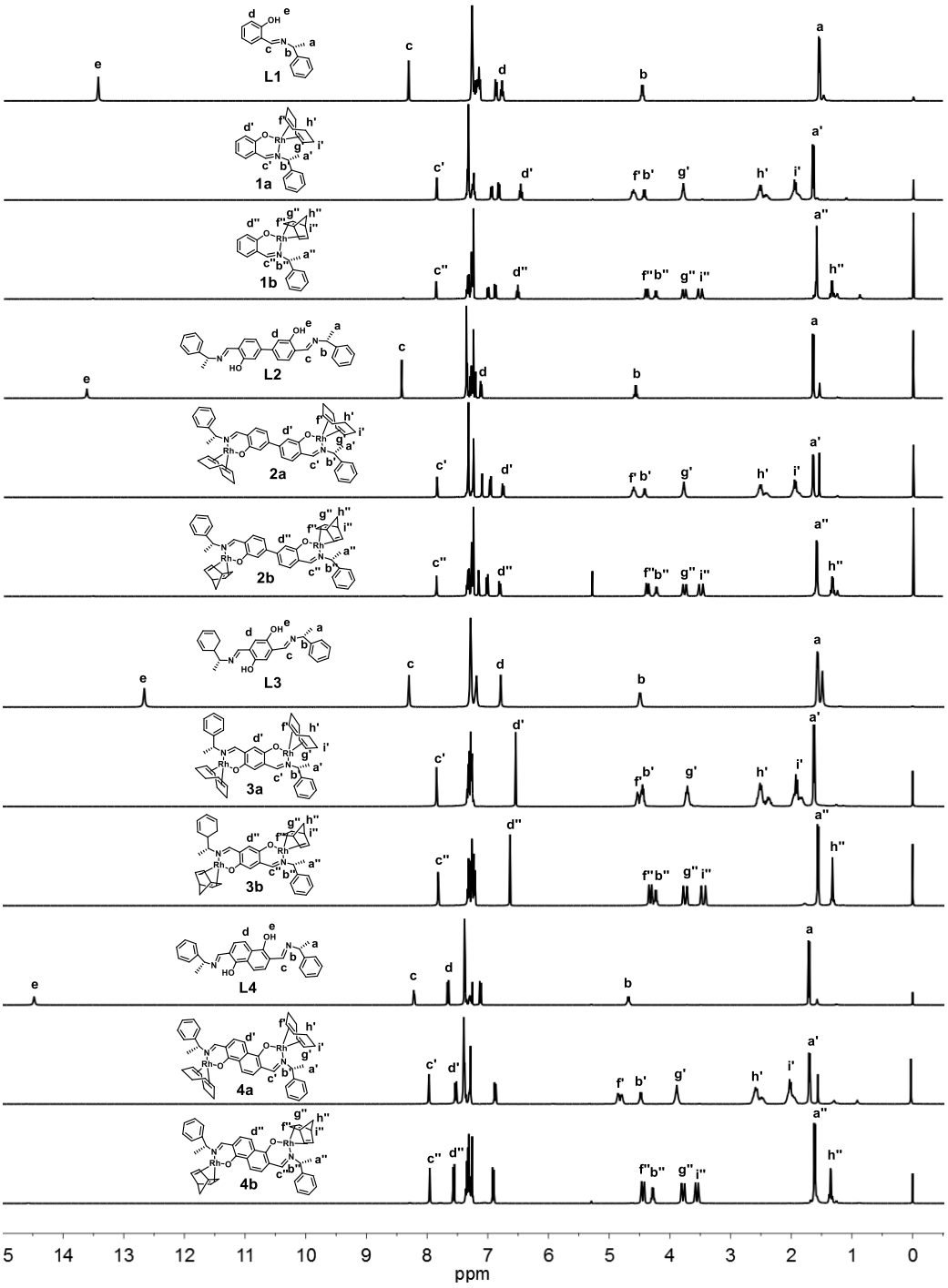
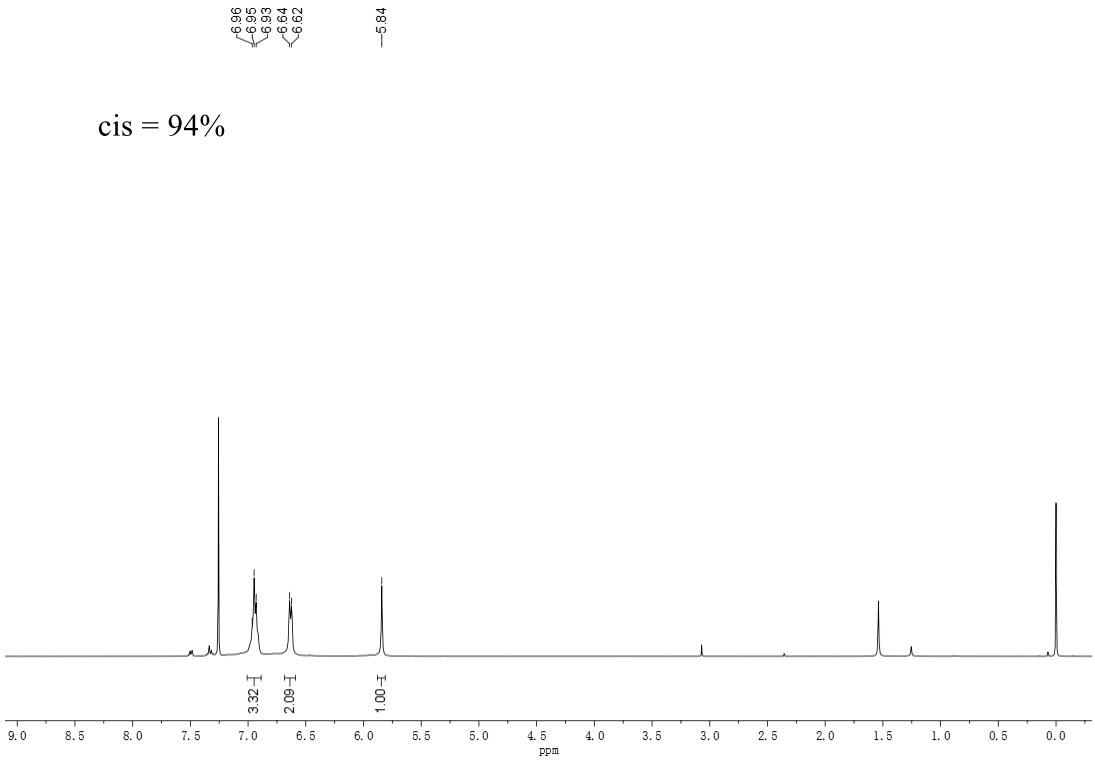
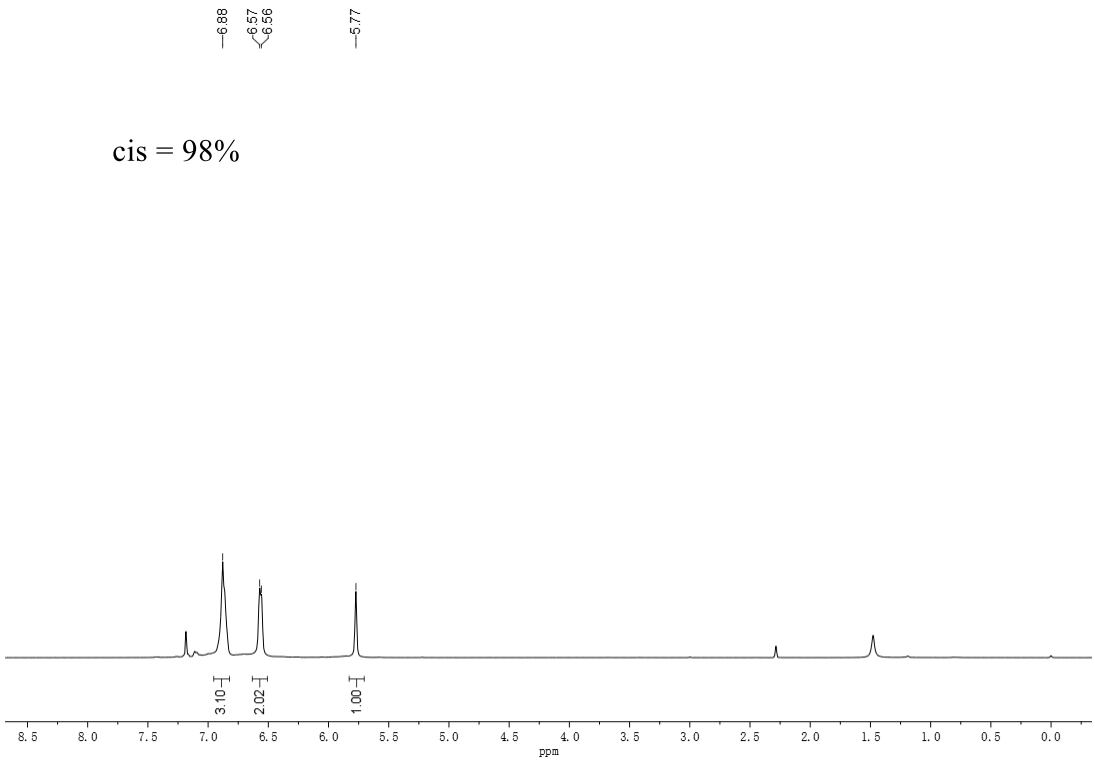


Figure S26. ^{1}H NMR spectra of phenoxyimine ligands and phenoxyiminato ligated Rh complexes (**1-4**)(**a**–**b**) in $CDCl_3$ in air. (400MHz, $CDCl_3$, 25°C)



cis = 94%

Figure S27. ^{1}H NMR spectrum of polymer in Table 3, entry 1 (400MHz, $CDCl_3$, 25°C).



cis = 98%

Figure S28. ^{1}H NMR spectrum of polymer in Table 3, entry 2 (400MHz, $CDCl_3$, 25°C).

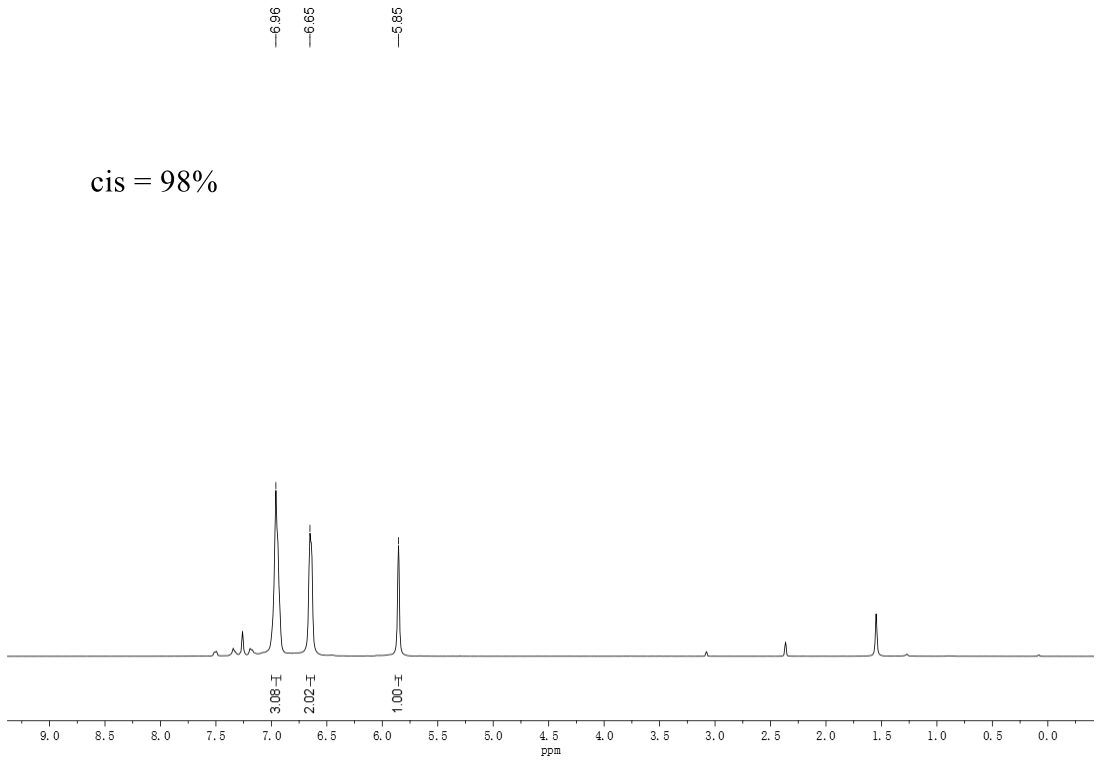


Figure S29. ^{1}H NMR spectrum of polymer in Table 3, entry 3 (400MHz, $CDCl_3$, 25°C).

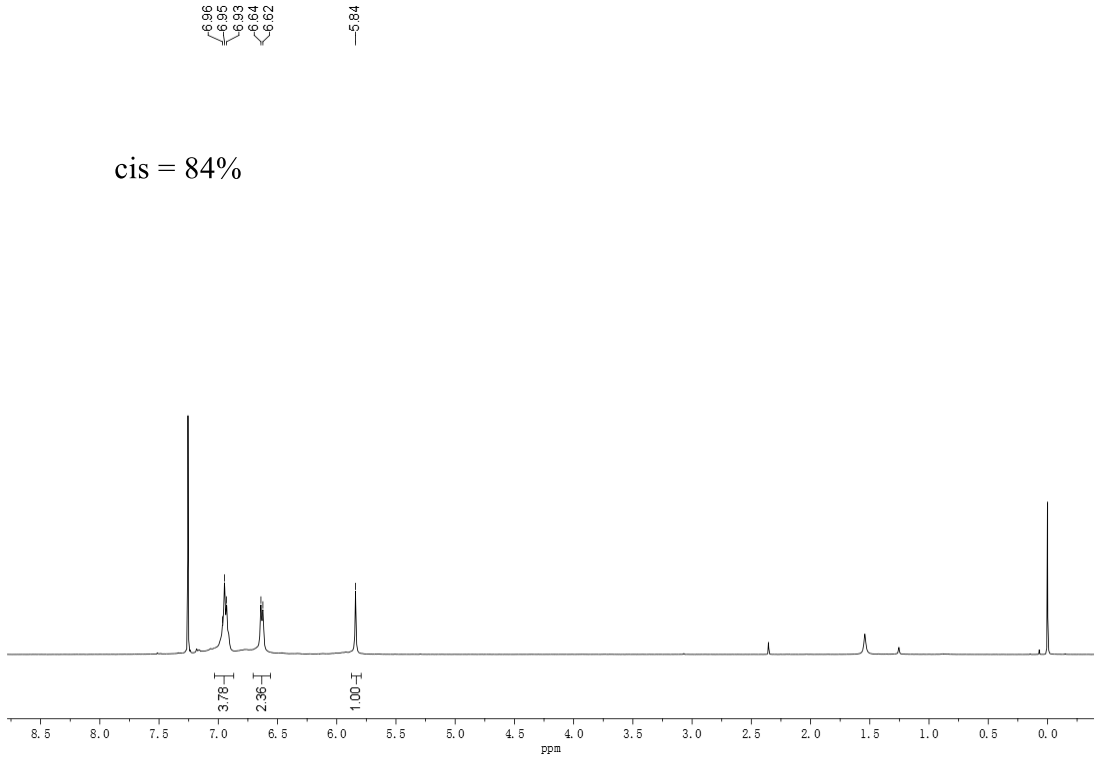


Figure S30. ^{1}H NMR spectrum of polymer in Table 3, entry 4 (400MHz, $CDCl_3$, 25°C).

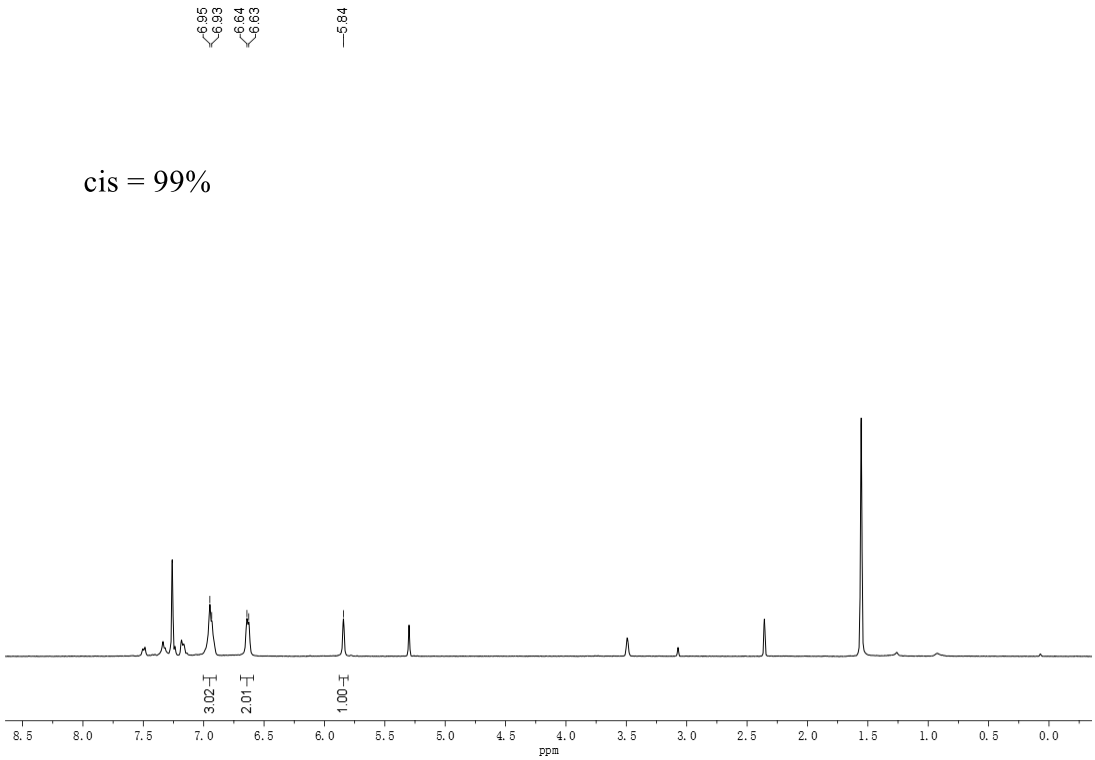


Figure S31. ^{1}H NMR spectrum of polymer in Table 3, entry 7 (400MHz, $CDCl_3$, 25°C).

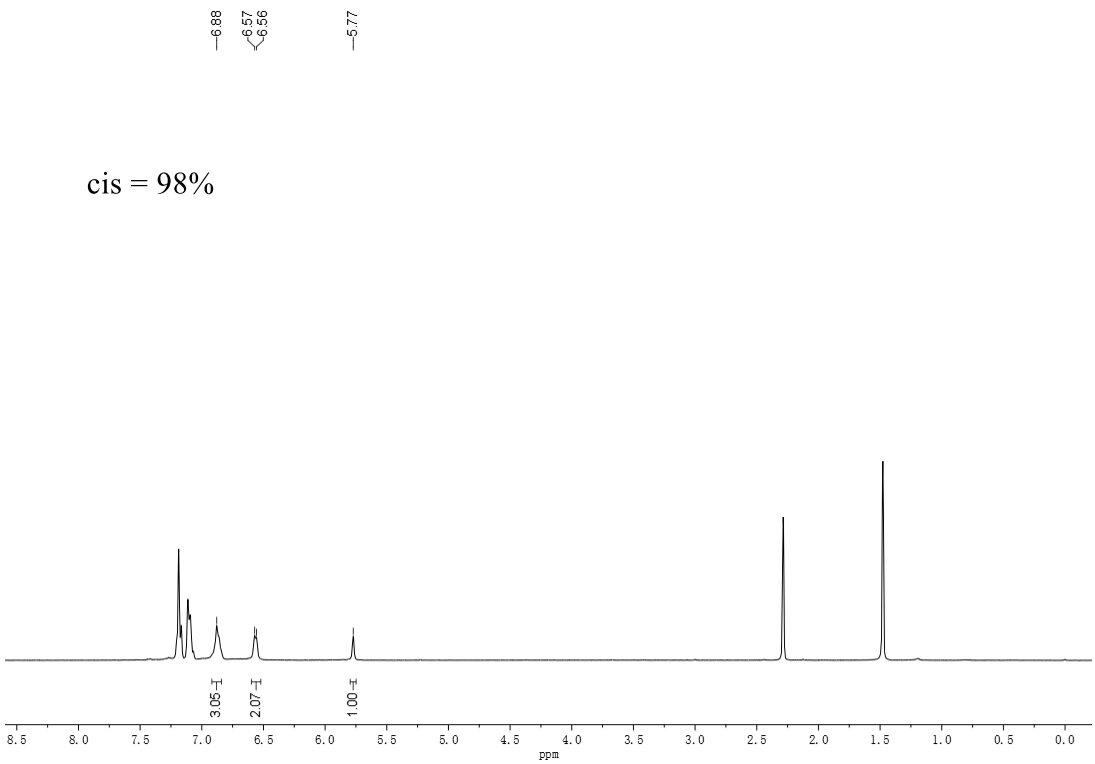


Figure S32. ^{1}H NMR spectrum of polymer in Table 3, entry 12 (400MHz, $CDCl_3$, 25°C).

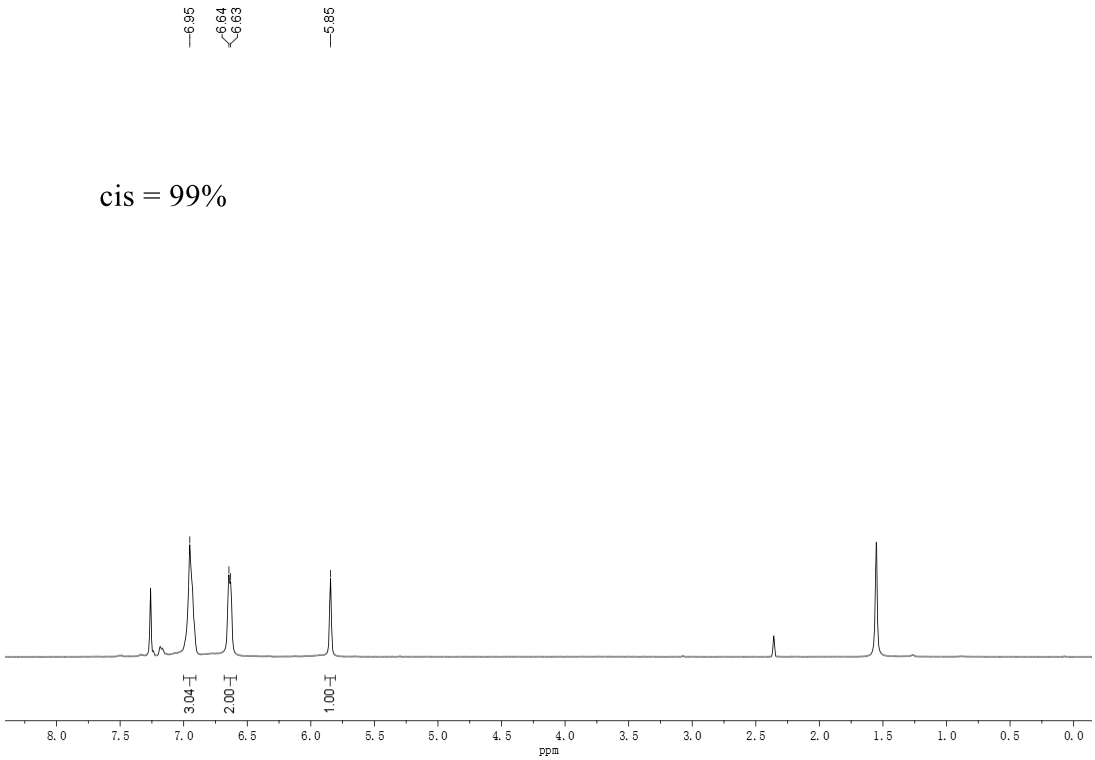


Figure S33. ^{1}H NMR spectrum of polymer in Table 3, entry 13 (400MHz, $CDCl_3$, 25°C).

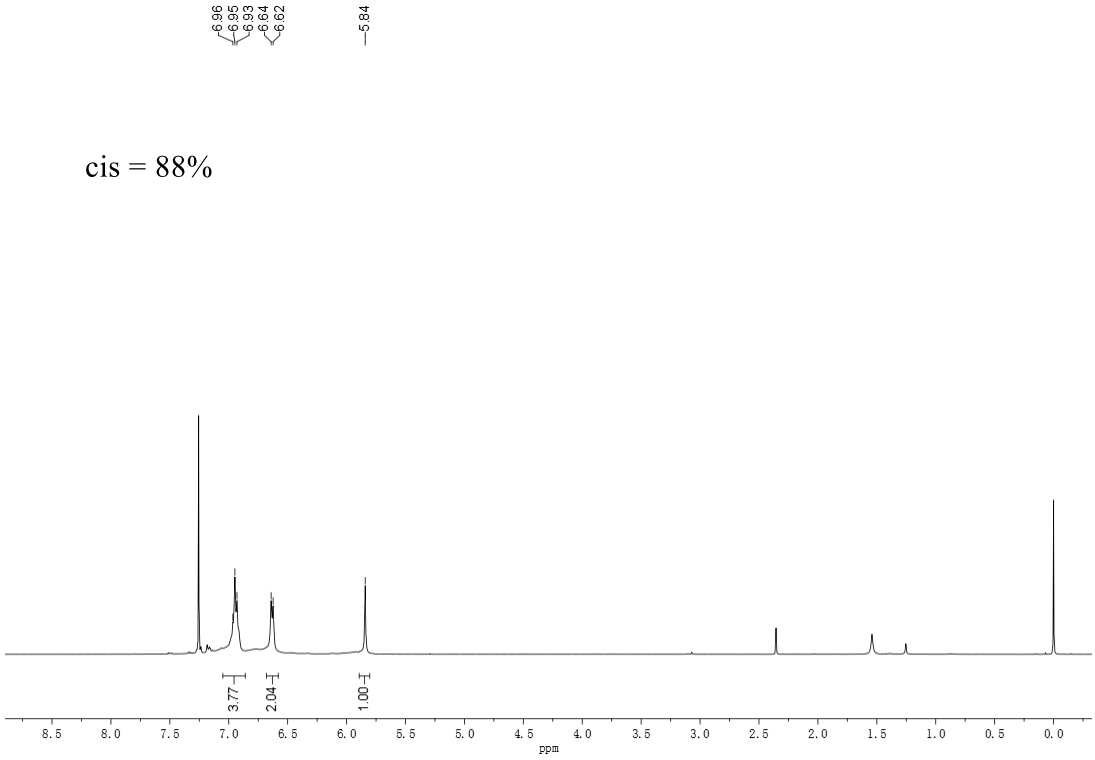


Figure S34. ^{1}H NMR spectrum of polymer in Table 3, entry 14 (400MHz, $CDCl_3$, 25°C).

cis = 93%

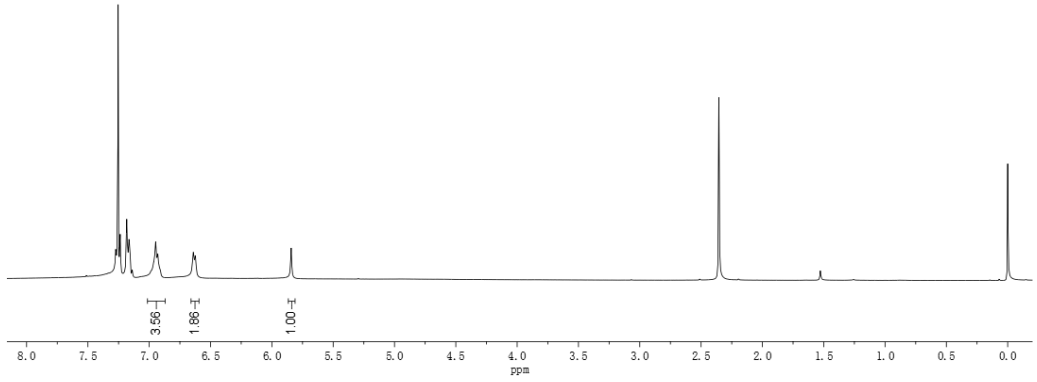


Figure S35. ^{1}H NMR spectrum of polymer in Table 4, entry 3 (400MHz, $CDCl_3$, 25°C).

cis = 94%

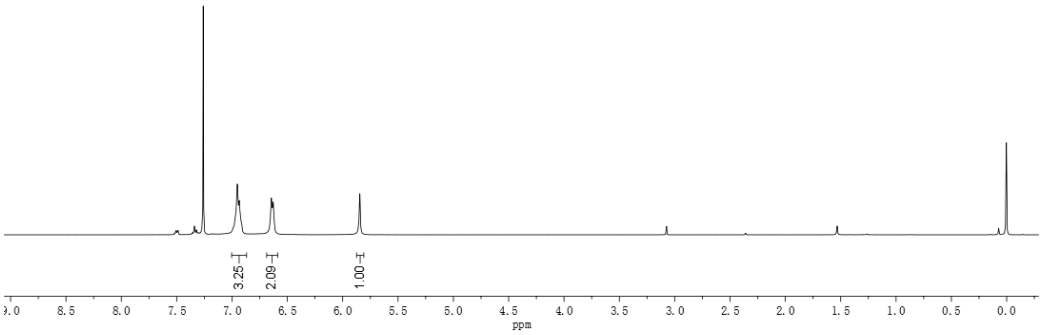


Figure S36. ^{1}H NMR spectrum of polymer in Table 4, entry 7 (400MHz, $CDCl_3$, 25°C).

cis = 98%

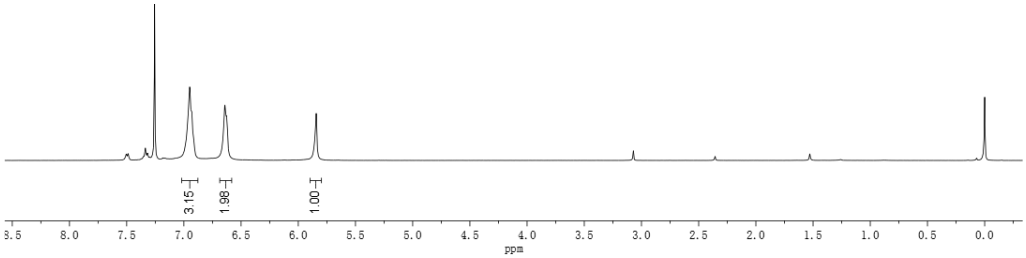


Figure S37. ^{1}H NMR spectrum of polymer in Table 4, entry 11 (400MHz, $CDCl_3$, 25°C).

cis = 87%

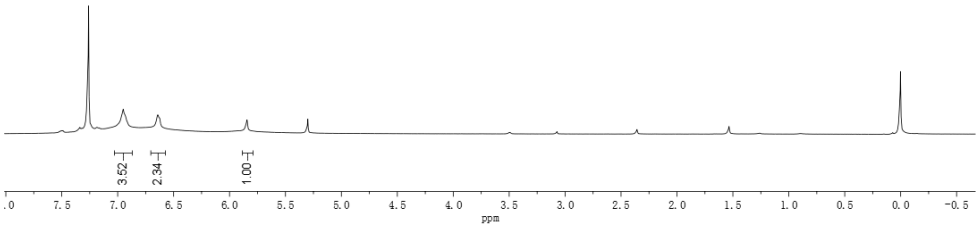


Figure S38. ^{1}H NMR spectrum of polymer in Table 4, entry 15 (400MHz, $CDCl_3$, 25°C).

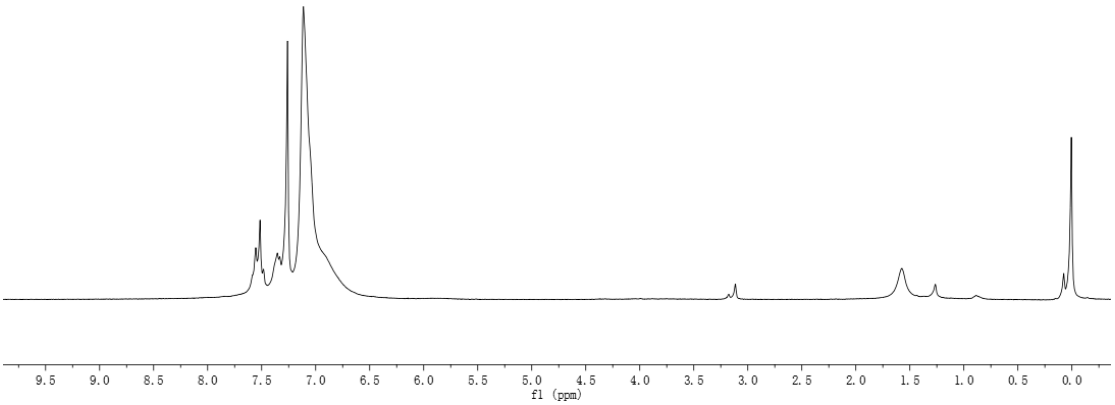


Figure S39. ^{1}H NMR spectrum of polymer in Table 5, entry 4 (400MHz, $CDCl_3$, 25°C).

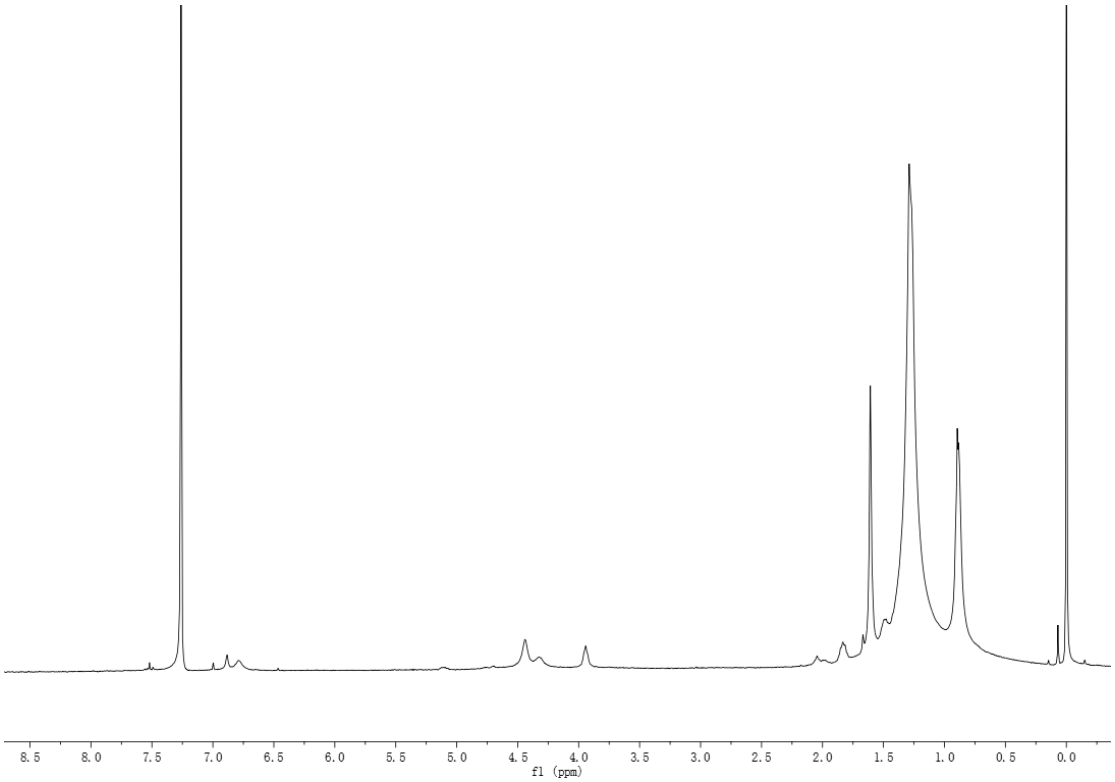


Figure S40. ^{1}H NMR spectrum of polymer in Table 5, entry 2 (400MHz, $CDCl_3$, 25°C).

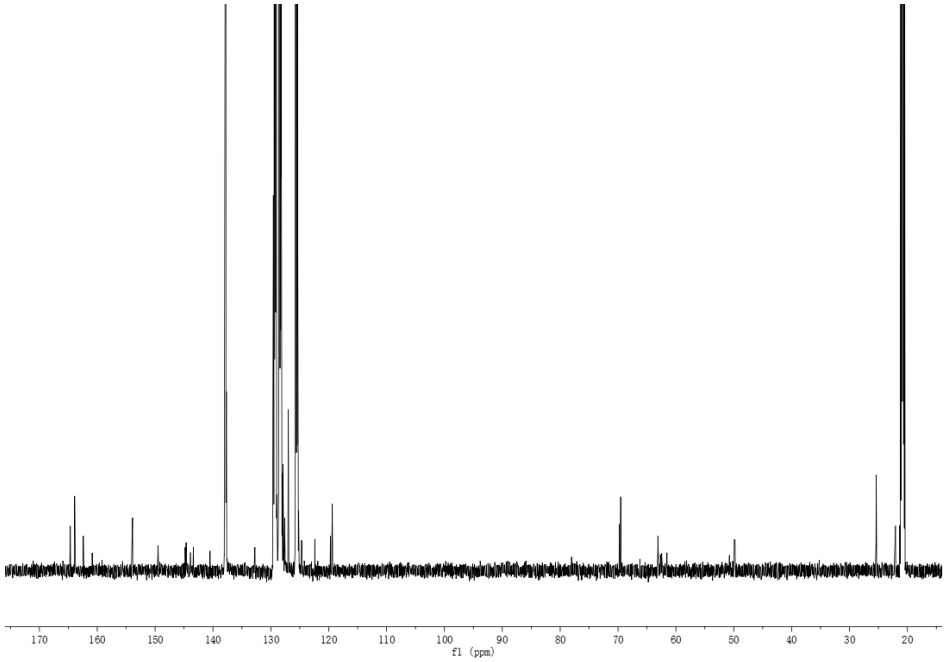
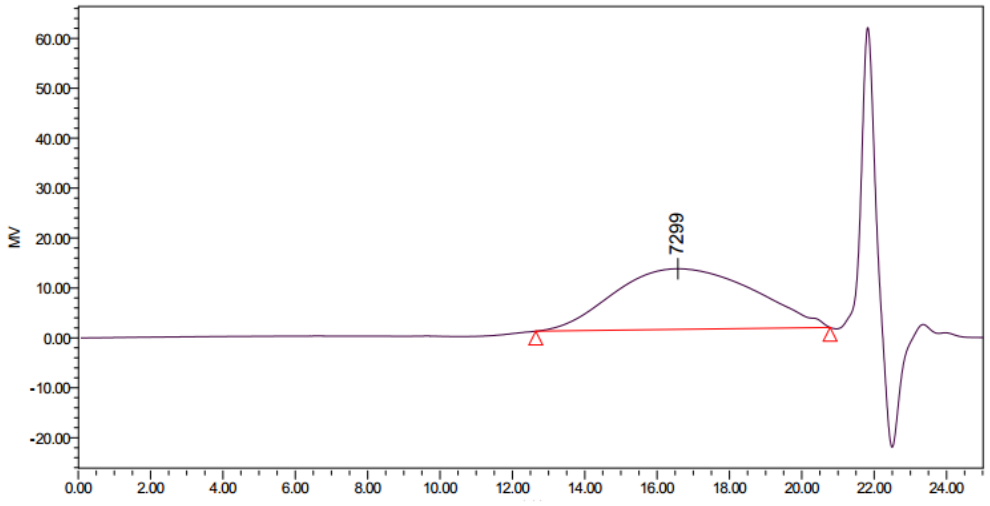


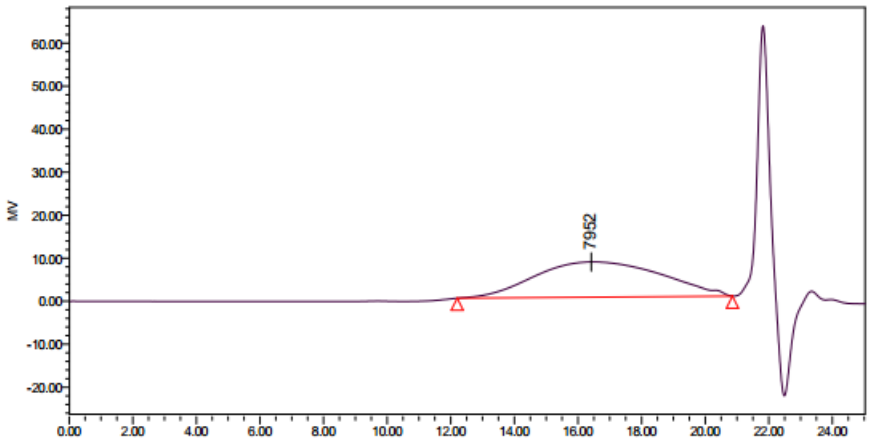
Figure S41. ^{13}C NMR spectra of **3b**/PA mixture with a molar ratio of 1 : 0.3 in Toluene-*d*8.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.577	16.577	16.577	3191	8781	7299	16226	24175	1.847981	2.753294

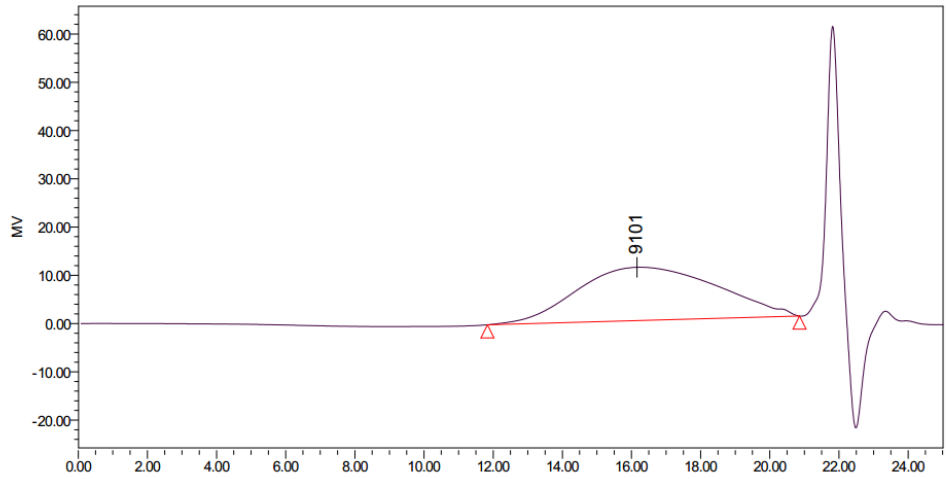
Figure S42. GPC curve of polymer in Table 3, entry 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.417	16.417	16.417	3294	9748	7952	19654	32364	2.016158	3.319944

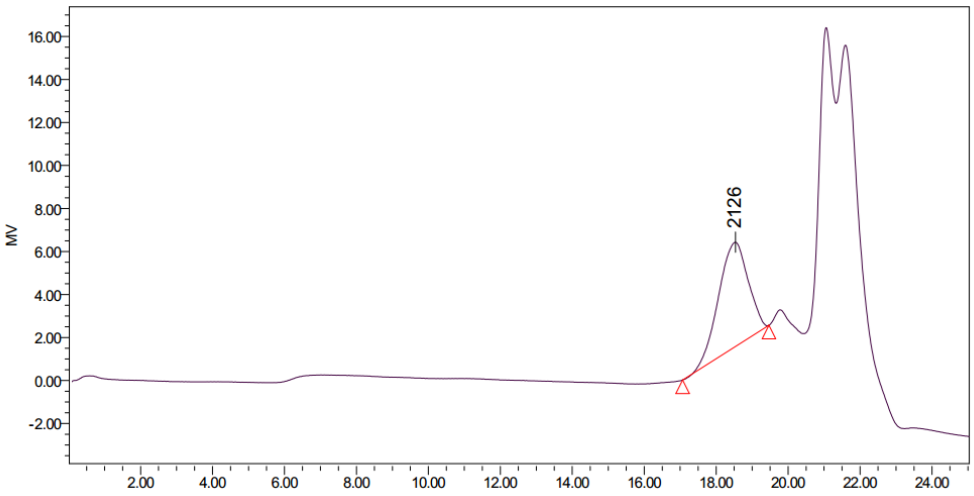
Figure S43. GPC curve of polymer in Table 3, entry 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.160	16.160	16.160	3603	10950	9101	23086	40918	2.108312	3.736821

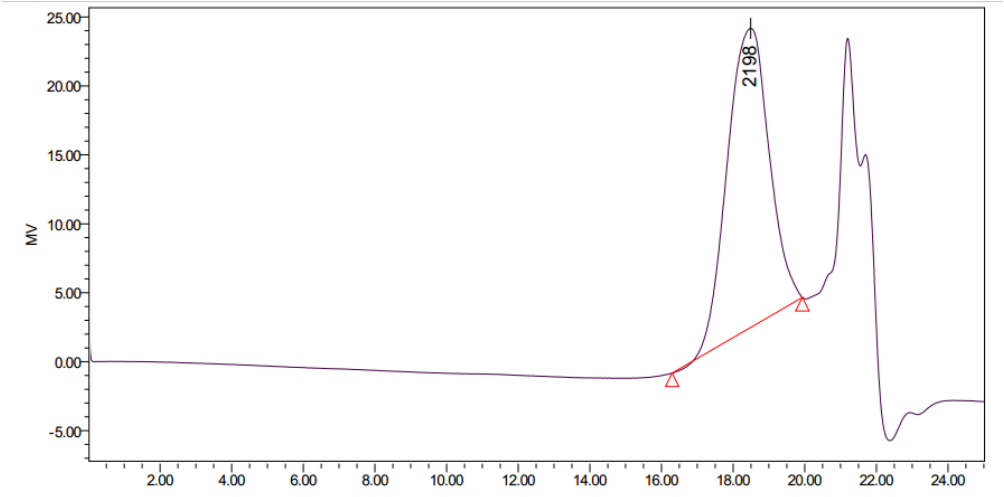
Figure S44. GPC curve of polymer in Table 3, entry 3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.538	18.538	18.538	2155	2306	2126	2464	2625	1.068506	1.138230

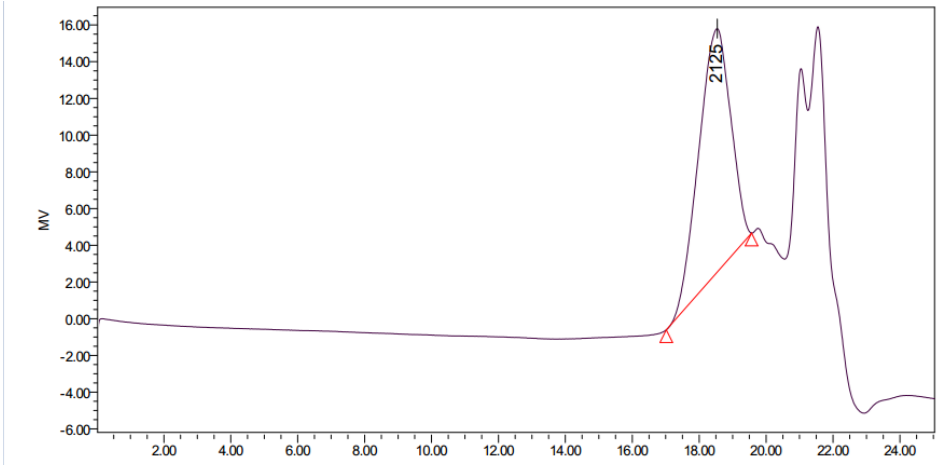
Figure S45. GPC curve of polymer in Table 3, entry 4.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.492	18.492	18.492	2122	2426	2198	2734	3036	1.127102	1.251390

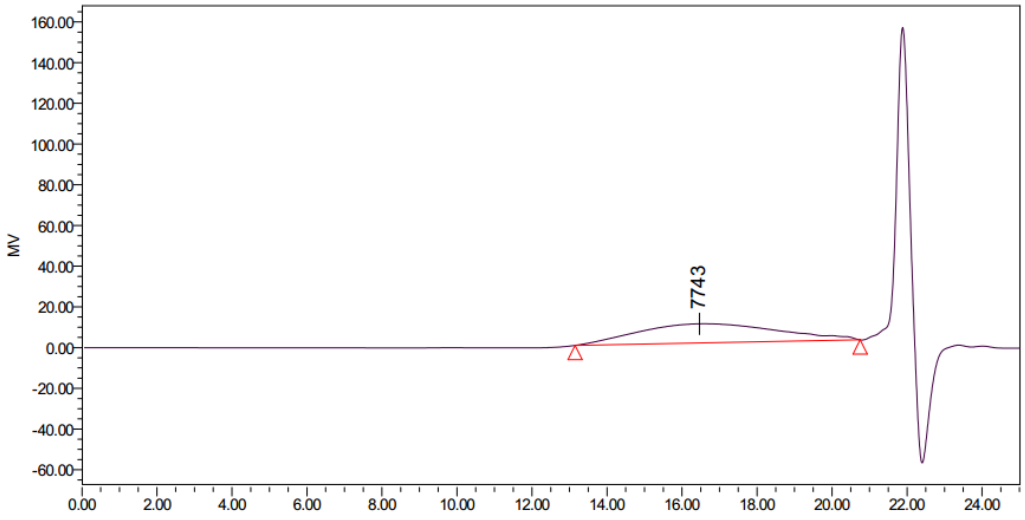
Figure S46. GPC curve of polymer in Table 3, entry 5.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.539	18.539	18.539	2155	2358	2125	2572	2789	1.090858	1.183192

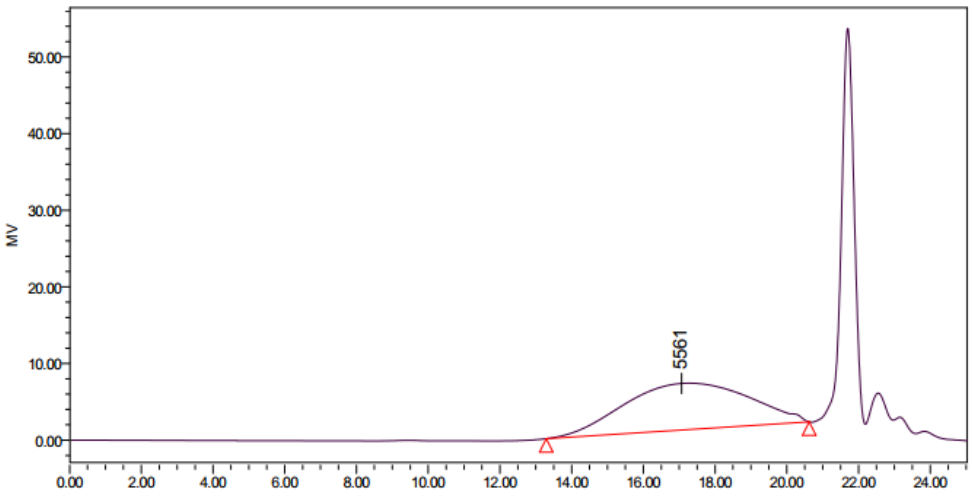
Figure S47. GPC curve of polymer in Table 3, entry 6.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.467	16.467	16.467	3207	8874	7743	15374	21260	1.732516	2.395828

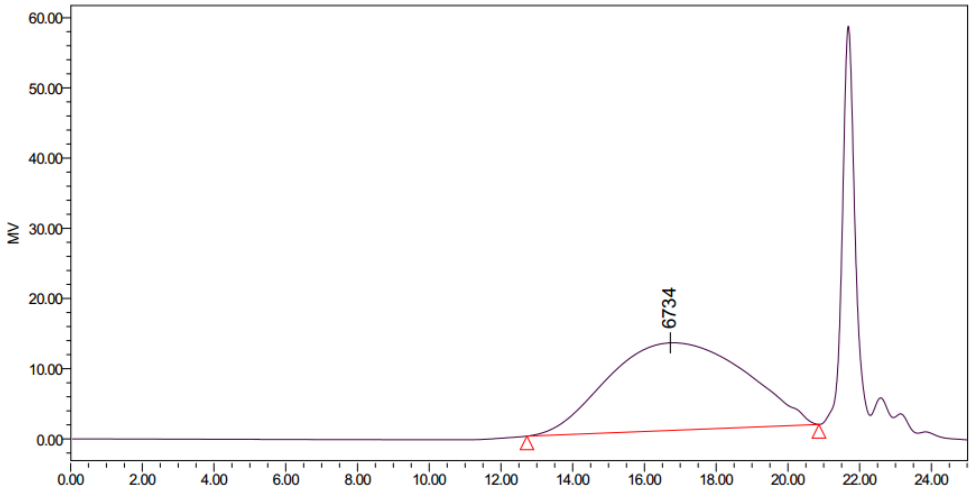
Figure S48. GPC curve of polymer in Table 3, entry 7.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.067	17.067	17.067	2888	6720	5561	11446	16075	1.703360	2.392116

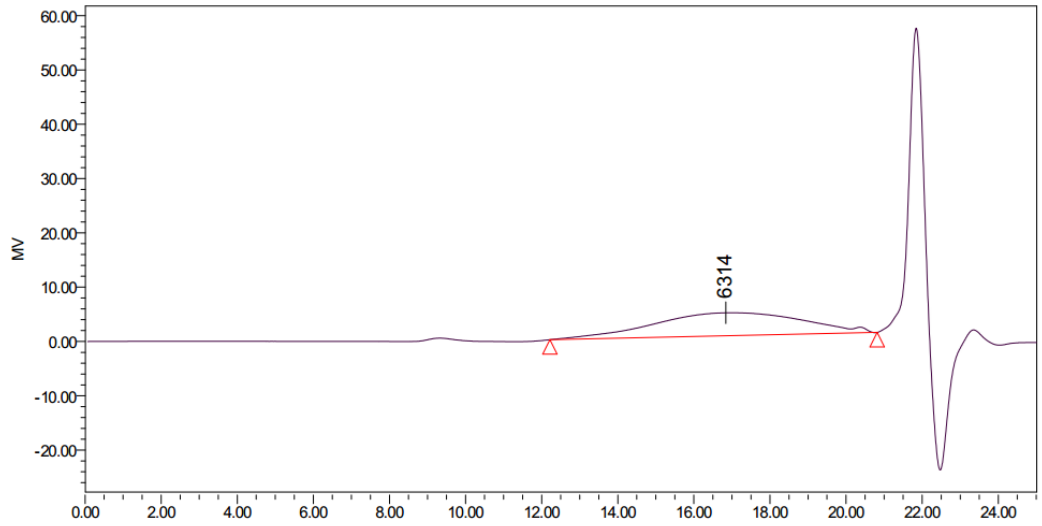
Figure S49. GPC curve of polymer in Table 3, entry 8.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.725	16.725	16.725	3070	8162	6734	14917	21983	1.827480	2.693177

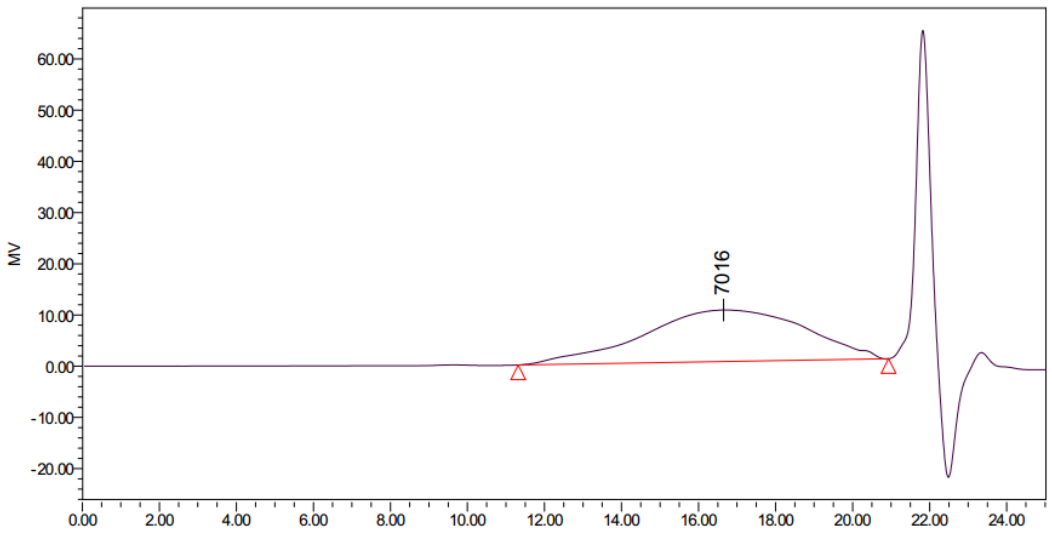
Figure S50. GPC curve of polymer in Table 3, entry 9.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.842	16.842	16.842	3045	9381	6314	21336	37756	2.274297	4.024623

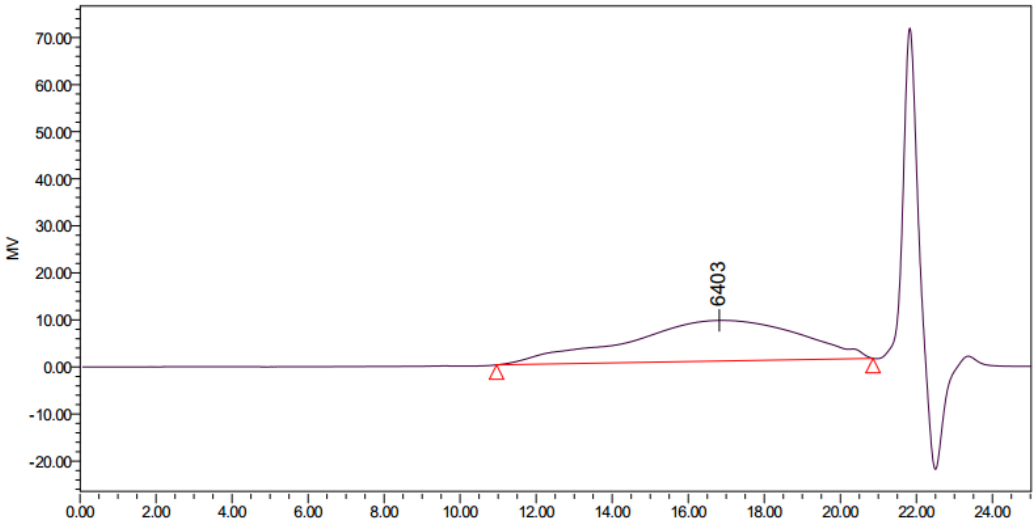
Figure S51. GPC curve of polymer in Table 3, entry 10.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.650	16.650	16.650	3379	12523	7016	39372	81980	3.144061	6.546595

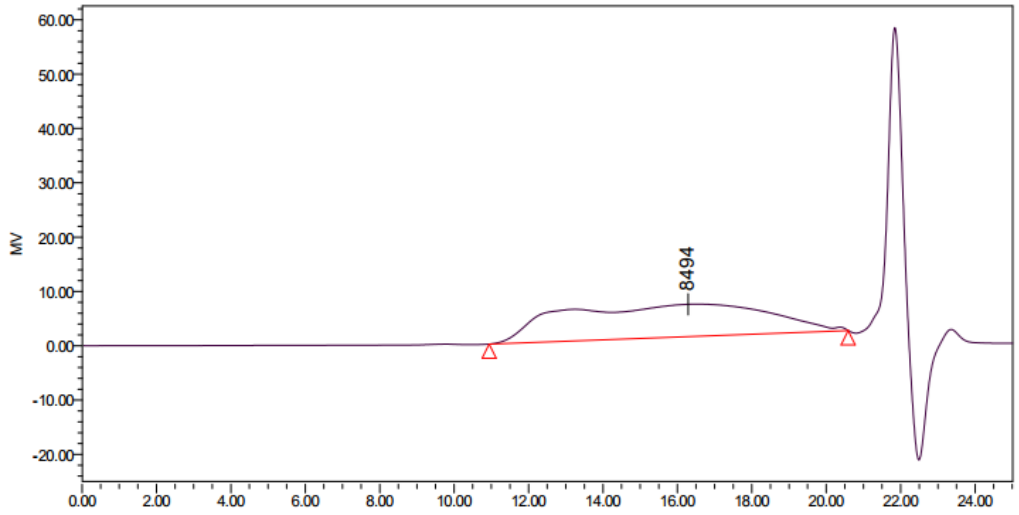
Figure S52. GPC curve of polymer in Table 3, entry 11.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.817	16.817	16.817	3180	17016	6403	69702	138916	4.096275	8.163897

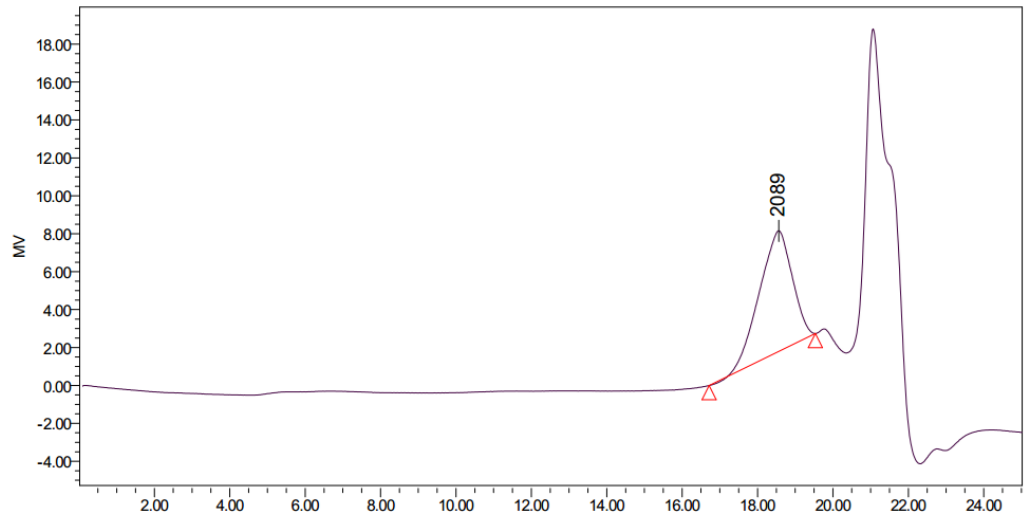
Figure S53. GPC curve of polymer in Table 3, entry 12.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.292	16.292	16.292	5396	29035	8494	81298	129876	2.800050	4.473126

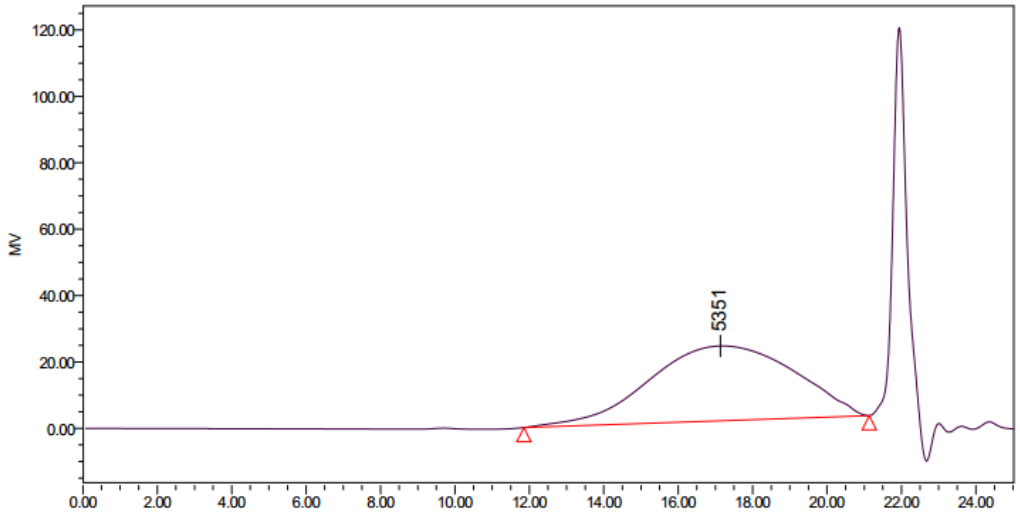
Figure S54. GPC curve of polymer in Table 3, entry 13.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		18.563	18.563	18.563	2154	2337	2089	2535	2741	1.084663	1.172779

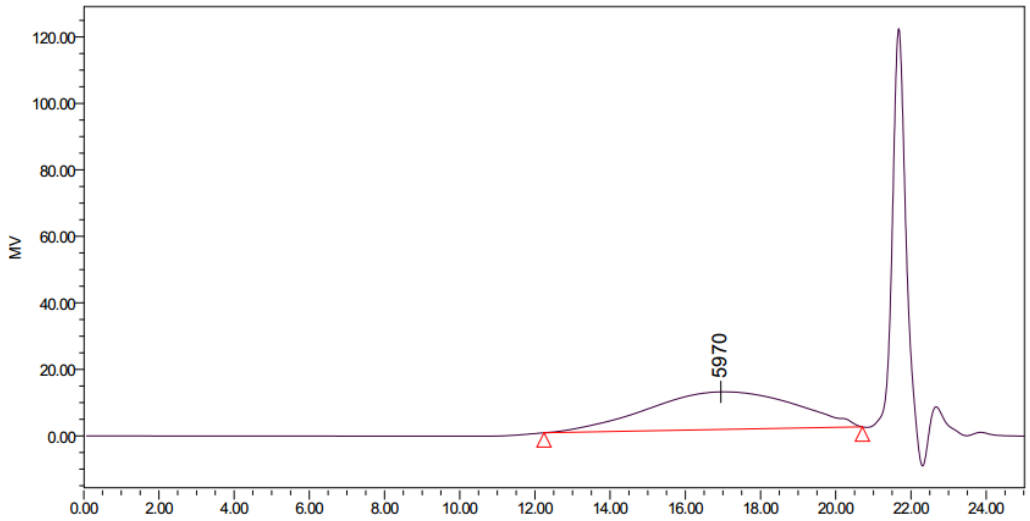
Figure S55. GPC curve of polymer in Table 3, entry 14.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.133	17.133	17.133	2506	8004	5351	20384	43985	2.546834	5.495524

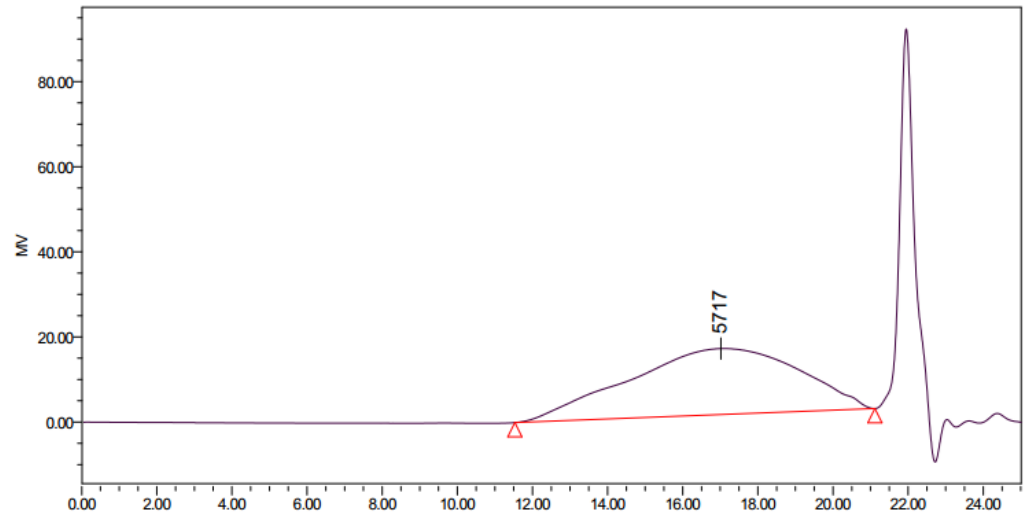
Figure S56. GPC curve of polymer in Table 4, entry 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.942	16.942	16.942	3017	8886	5970	19421	33157	2.185465	3.731227

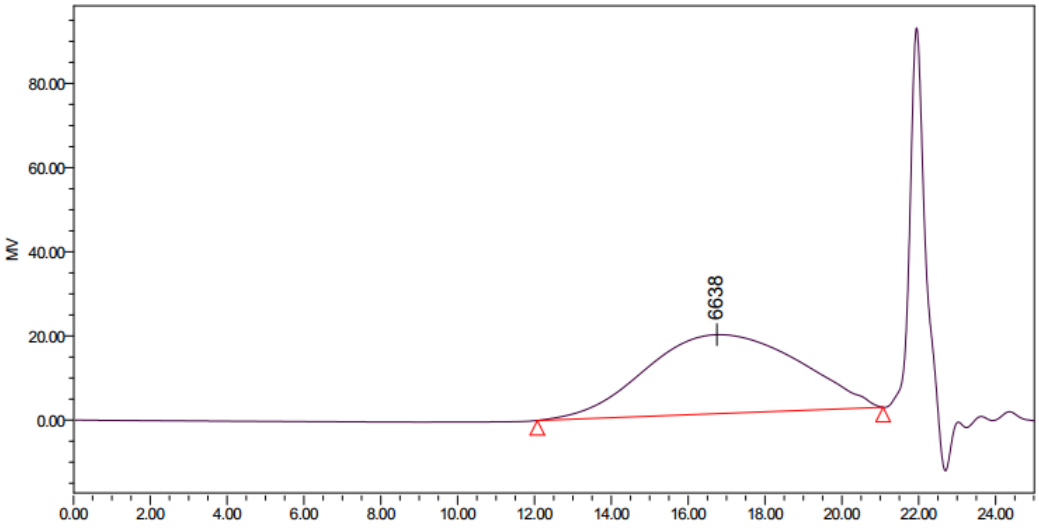
Figure S57. GPC curve of polymer in Table 4, entry 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.018	17.018	17.018	2807	12096	5717	34656	63700	2.865002	5.266095

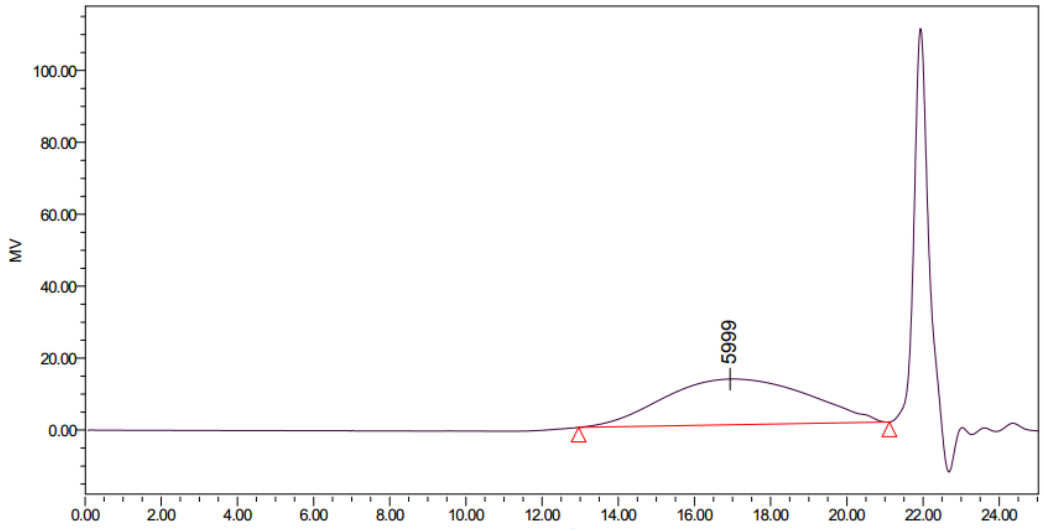
Figure S58. GPC curve of polymer in Table 4, entry 3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.751	16.751	16.751	2802	8812	6638	18932	33400	2.148413	3.790262

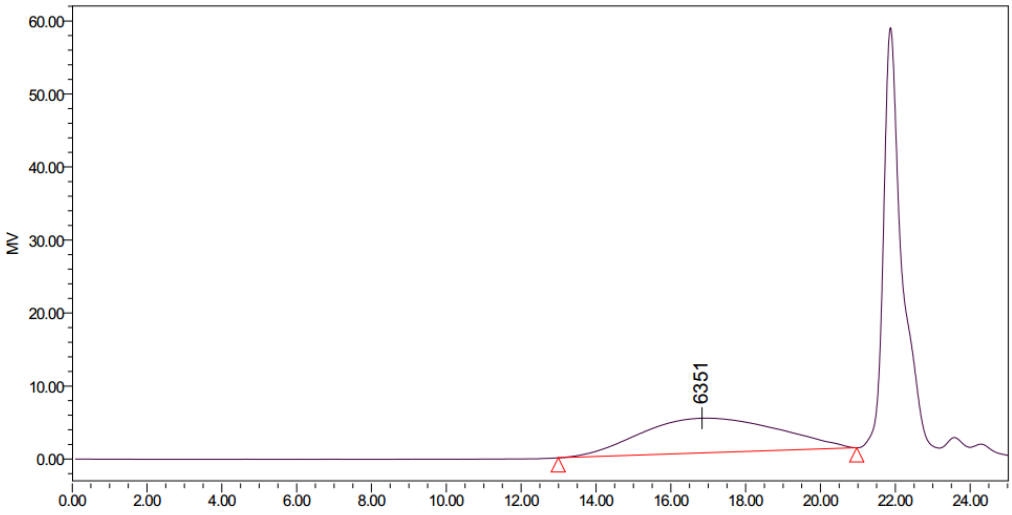
Figure S59. GPC curve of polymer in Table 4, entry 4.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.933	16.933	16.933	2598	7334	5999	13546	19955	1.846996	2.720852

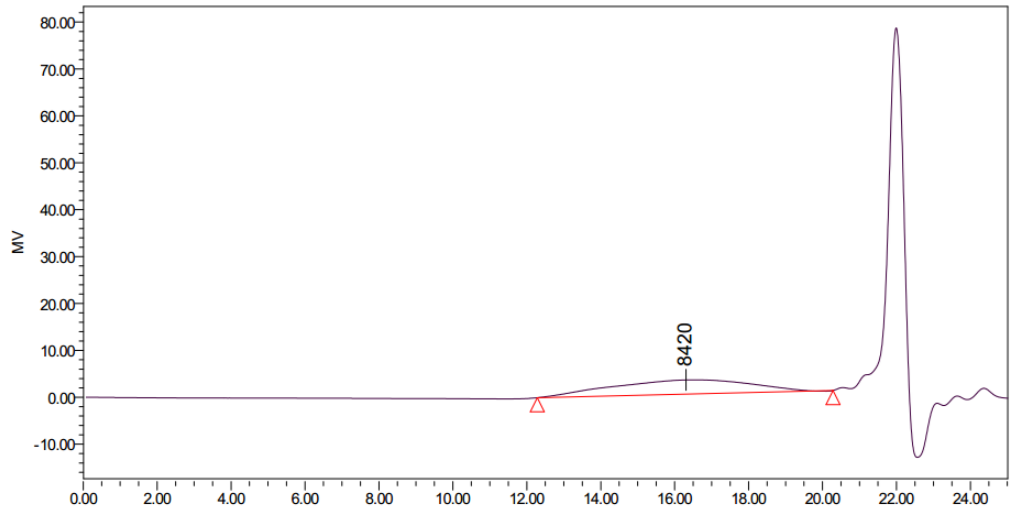
Figure S60. GPC curve of polymer in Table 4, entry 5.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.833	16.833	16.833	3059	7818	6351	14523	21458	1.857627	2.744627

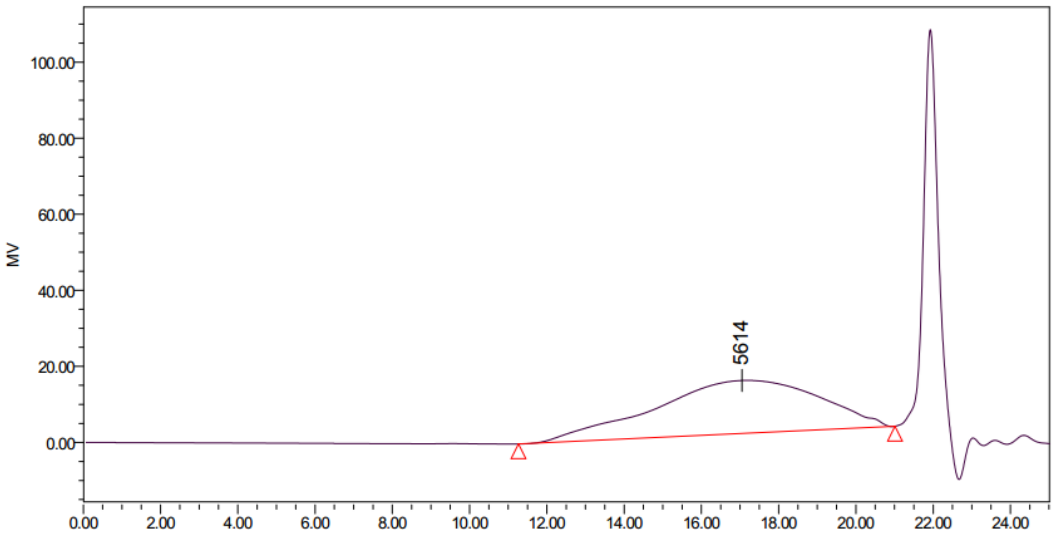
Figure S61. GPC curve of polymer in Table 4, entry 6.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.308	16.308	16.308	6283	13666	8420	25912	39368	1.896079	2.880695

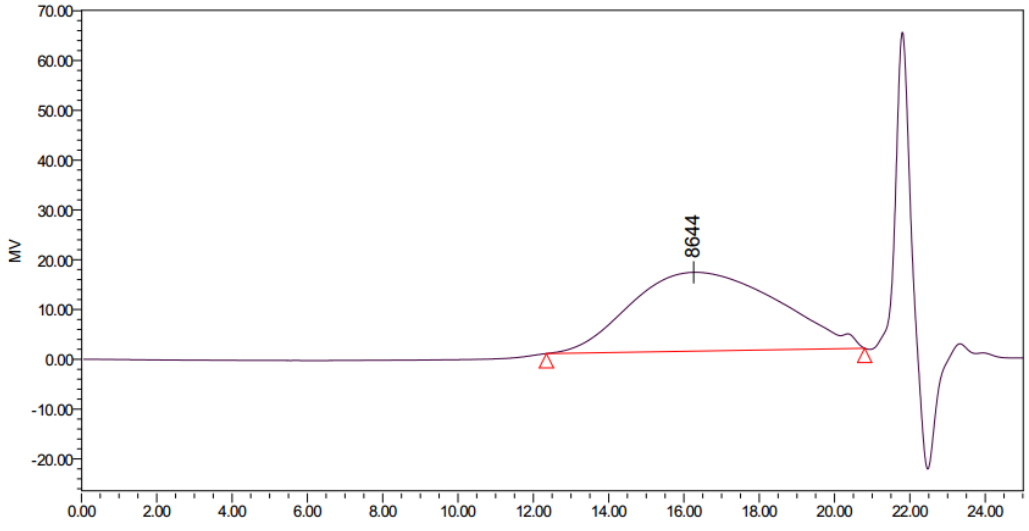
Figure S62. GPC curve of polymer in Table 4, entry 7.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.050	17.050	17.050	2972	11597	5614	33929	63146	2.925666	5.444960

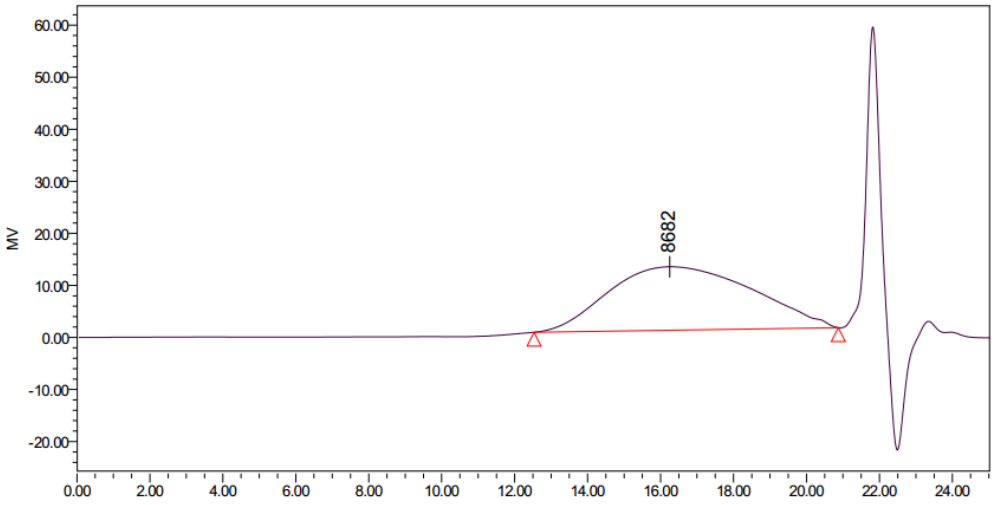
Figure S63. GPC curve of polymer in Table 4, entry 8.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.258	16.258	16.258	3351	9744	8644	18365	28151	1.884675	2.888922

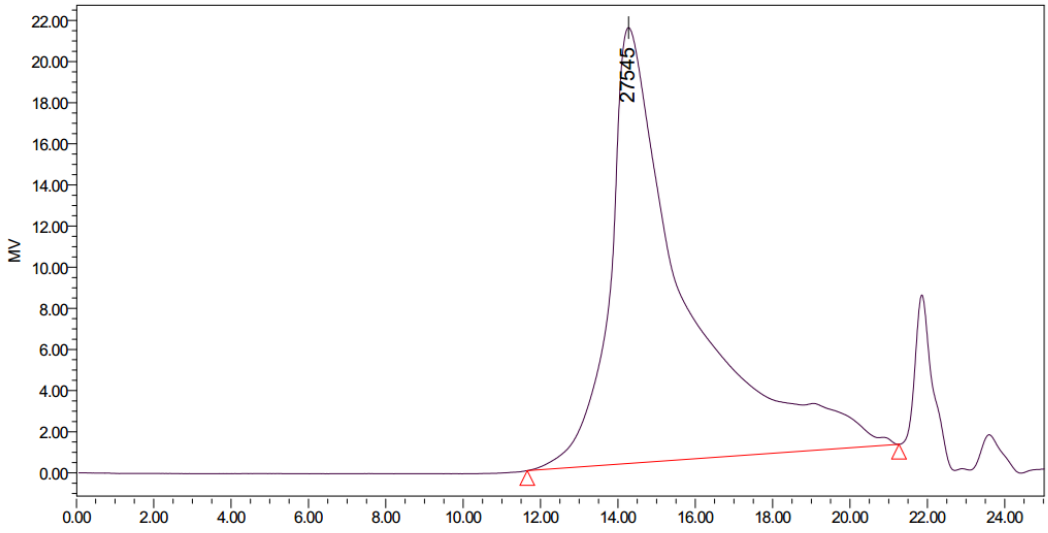
Figure S64. GPC curve of polymer in Table 4, entry 9.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.250	16.250	16.250	3440	9703	8682	17836	26311	1.838160	2.711656

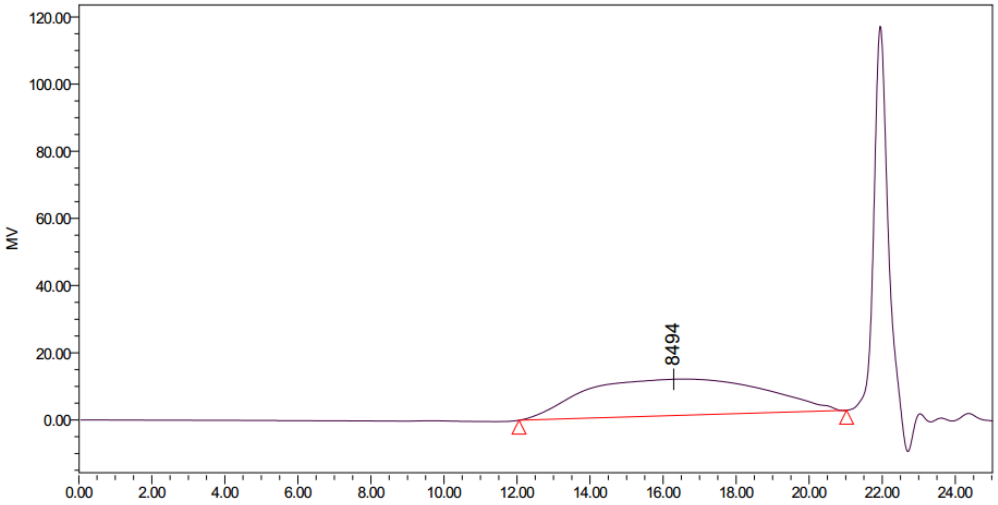
Figure S65. GPC curve of polymer in Table 4, entry 10.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		14.276	14.276	14.276	6024	19962	27545	31321	44679	1.569030	2.238182

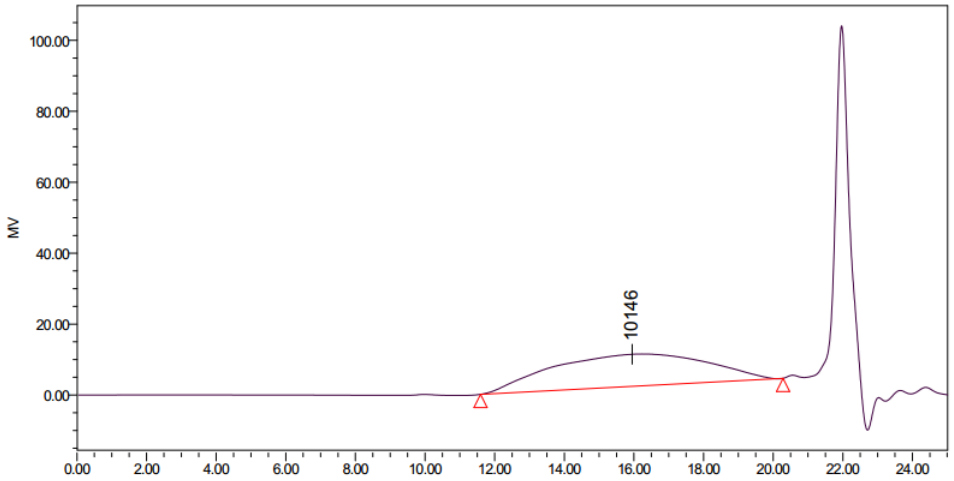
Figure S66. GPC curve of polymer in Table 4, entry 11.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.292	16.292	16.292	3596	13629	8494	29382	44917	2.155938	3.295776

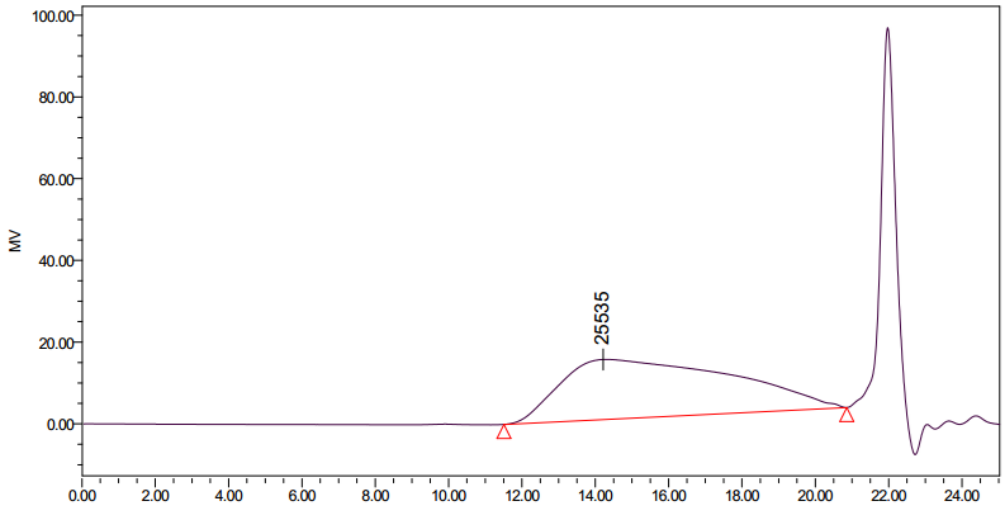
Figure S67. GPC curve of polymer in Table 4, entry 12.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.950	15.950	15.950	6323	18617	10146	42598	69364	2.288091	3.725817

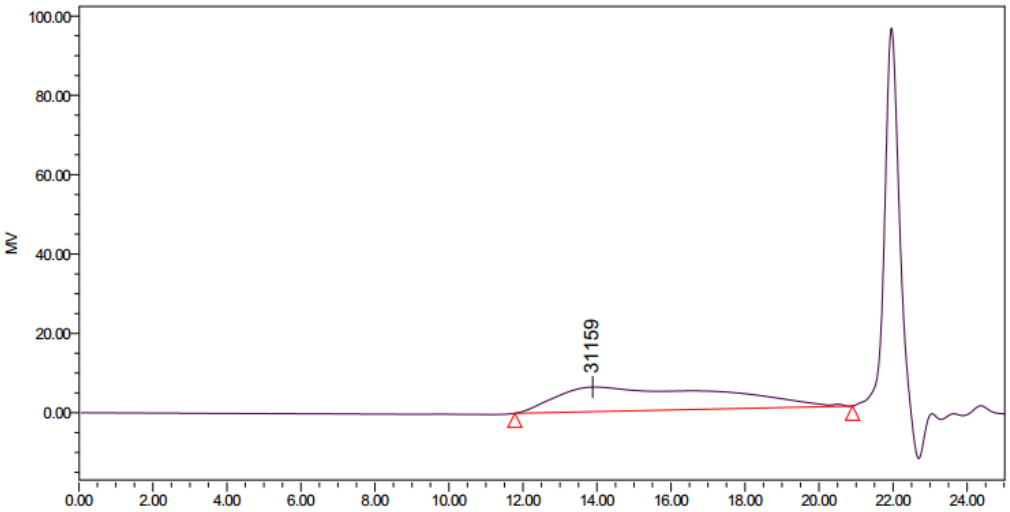
Figure S68. GPC curve of polymer in Table 4, entry 13.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		14.217	14.217	14.217	4748	19247	25535	41431	63718	2.152584	3.310553

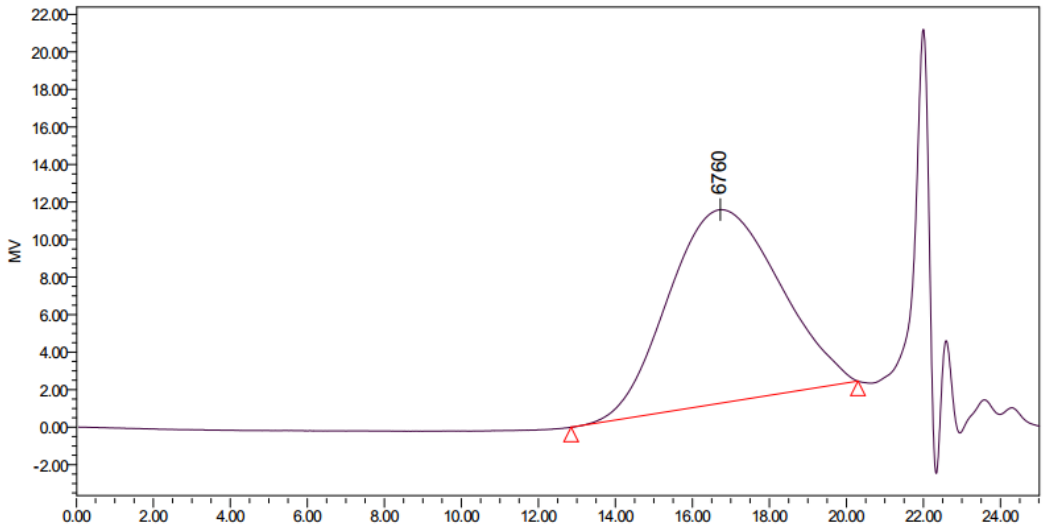
Figure S69. GPC curve of polymer in Table 4, entry 14.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.883	13.883	13.883	5142	20526	31159	43064	62951	2.098076	3.066969

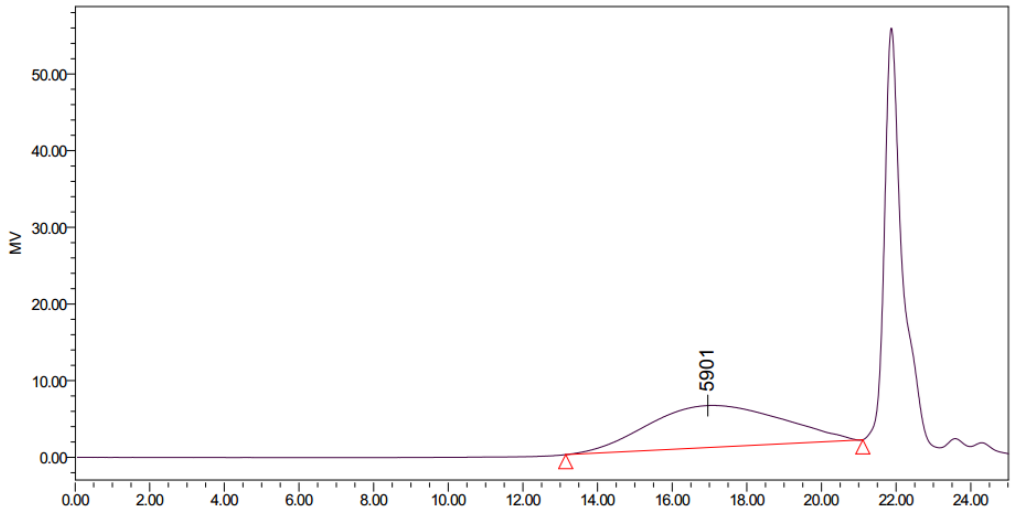
Figure S70. GPC curve of polymer in Table 4, entry 15.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.726	16.726	16.726	4348	7871	6760	12328	17251	1.566307	2.191665

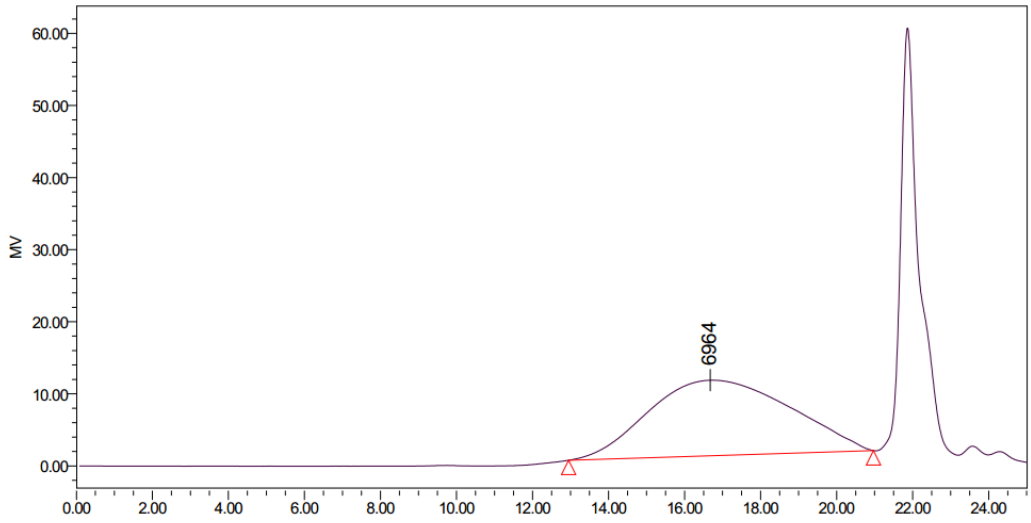
Figure S71. GPC curve of polymer in Table 4, entry 16.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.958	16.958	16.958	2899	7310	5901	13505	20022	1.847539	2.739131

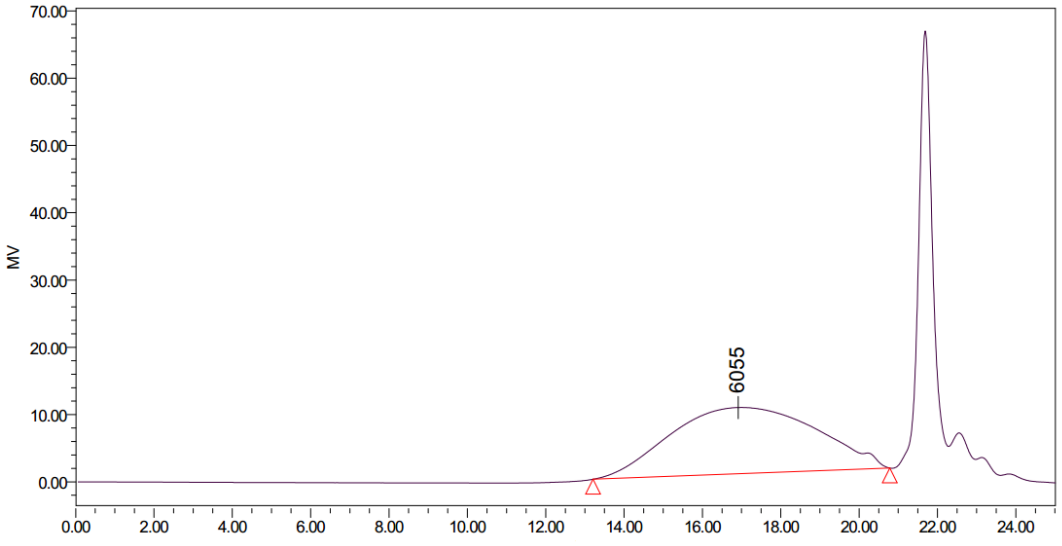
Figure S72. GPC curve of polymer in Table 4, entry 17.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.675	16.675	16.675	3183	8291	6964	15509	23037	1.870497	2.778526

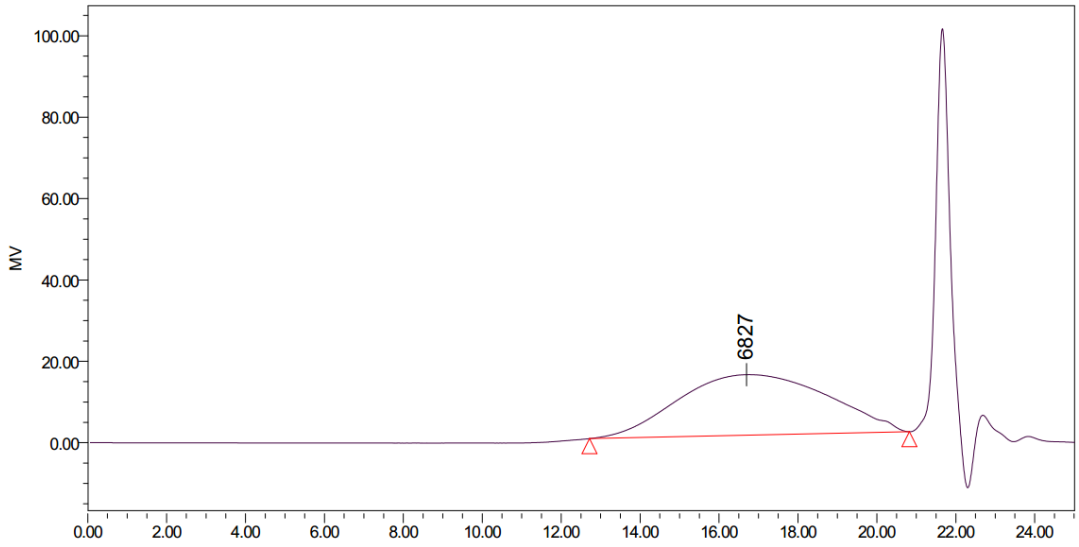
Figure S73. GPC curve of polymer in Table 4, entry 18.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.917	16.917	16.917	2845	7357	6055	12895	18106	1.752725	2.461013

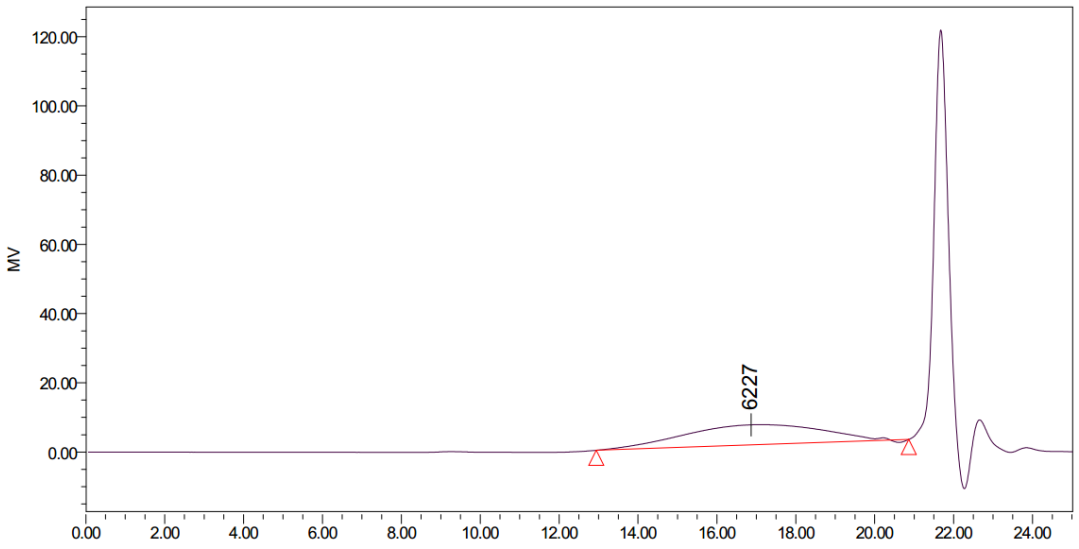
Figure S74. GPC curve of polymer in Table 4, entry 19.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.700	16.700	16.700	3152	8293	6827	15227	22756	1.836112	2.743918

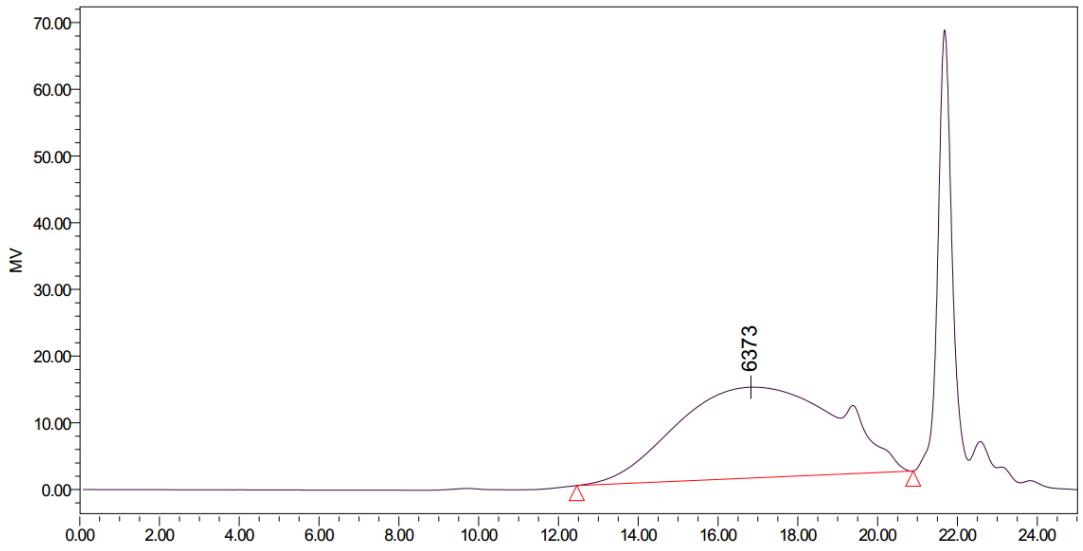
Figure S75. GPC curve of polymer in Table 4, entry 20.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.867	16.867	16.867	3681	8258	6227	14644	21637	1.773355	2.620170

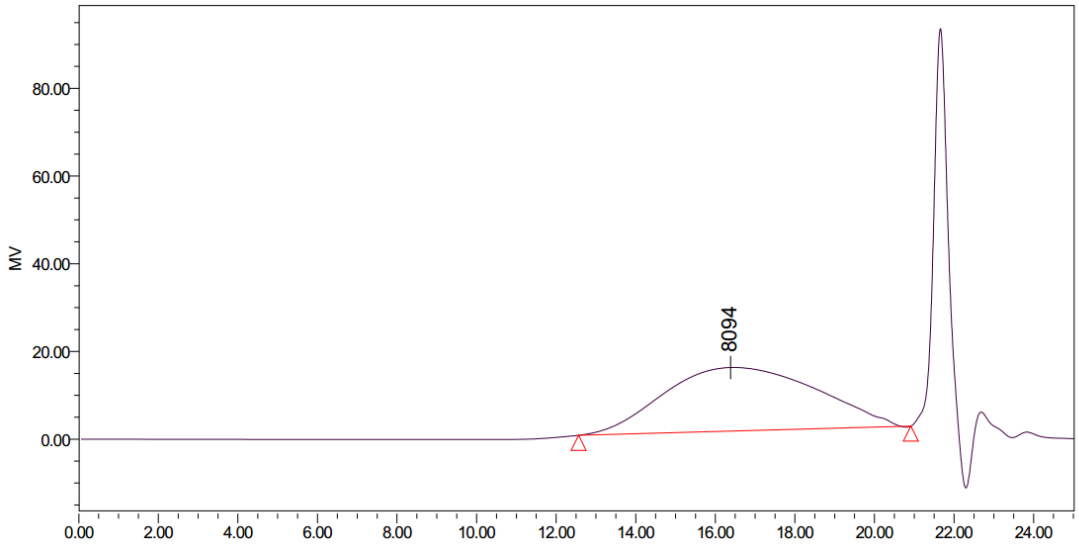
Figure S76. GPC curve of polymer in Table 4, entry 21.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.825	16.825	16.825	2792	8093	6373	15947	24900	1.970430	3.076596

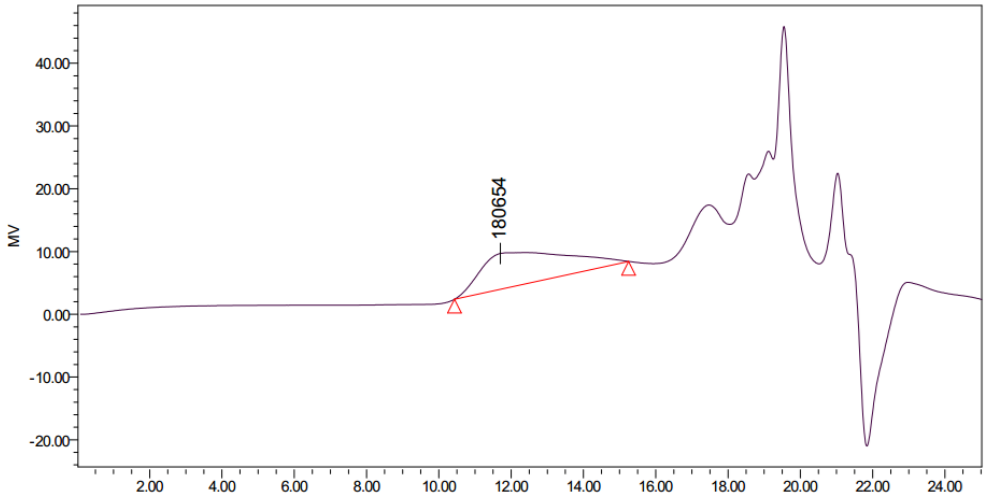
Figure S77. GPC curve of polymer in Table 4, entry 22.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.383	16.383	16.383	3617	9399	8094	17167	25593	1.826401	2.722768

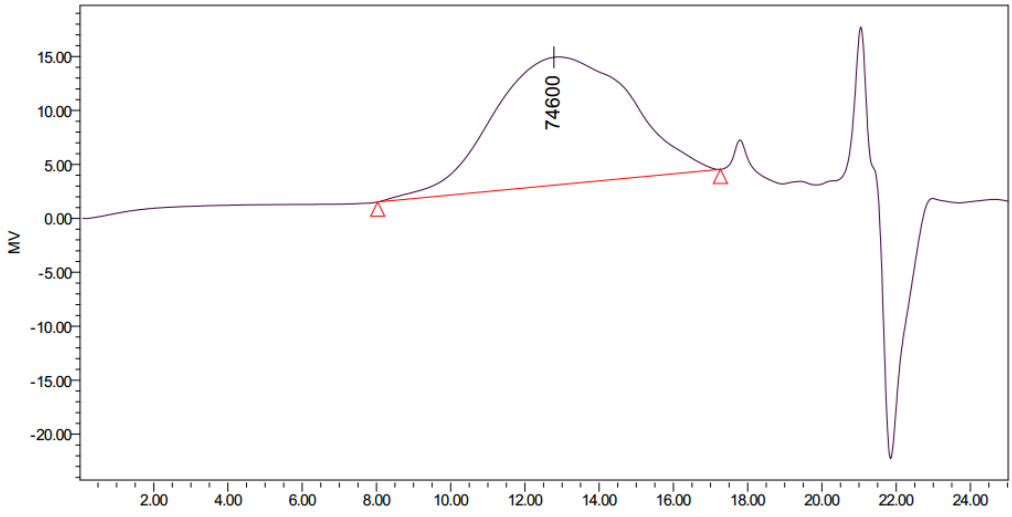
Figure S78. GPC curve of polymer in Table 4, entry 23.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.700	11.700	11.700	71961	131632	180654	209387	279795	1.590697

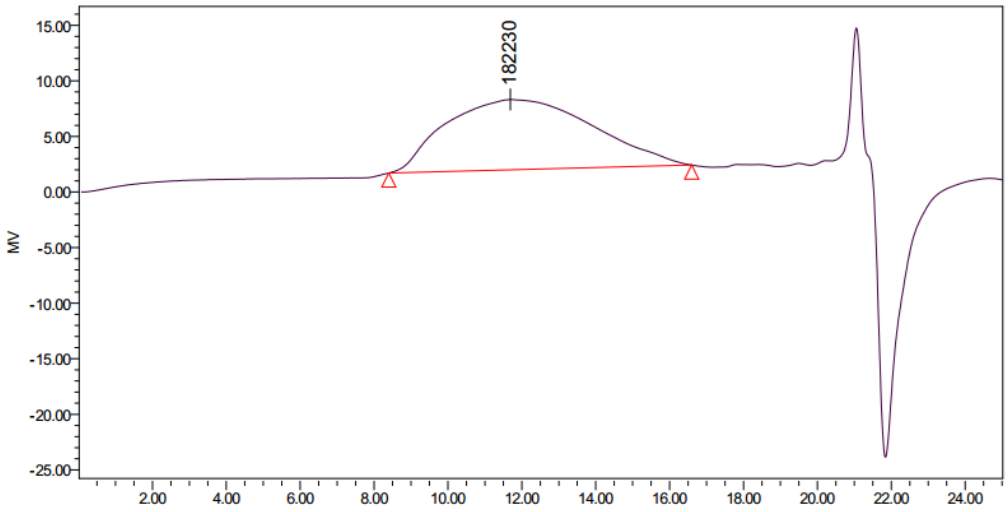
Figure S79. GPC curve of polymer in Table 5, entry 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		12.783	12.783	12.783	40484	203456	74600	2526402	7929833	12.417431

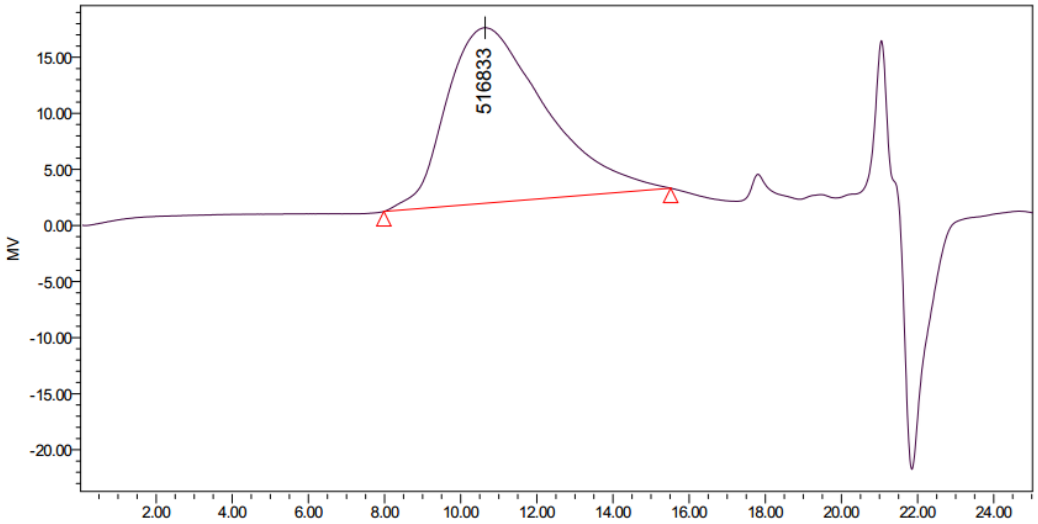
Figure S80. GPC curve of polymer in Table 5, entry 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		11.690	11.690	11.690	69958	445686	182230	1911102	3604289	4.288001

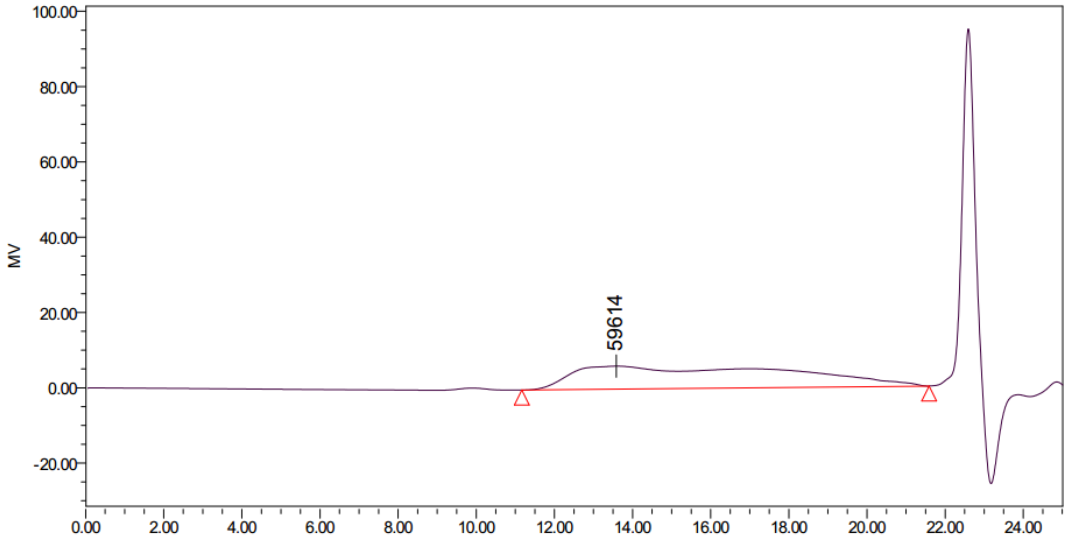
Figure S81. GPC curve of polymer in Table 5, entry 3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw
1		10.642	10.642	10.642	166502	725734	516833	2710911	6672111	3.735404

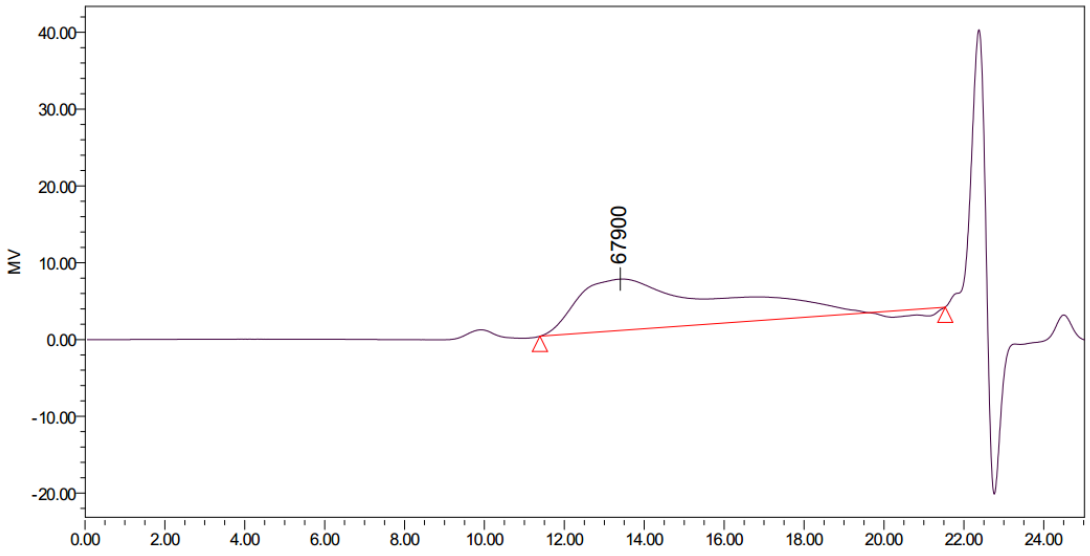
Figure S82. GPC curve of polymer in Table 5, entry 4



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.583	13.583	13.583	7953	37218	59614	92679	132465	2.490166	3.559157

Figure S83. GPC curve of polymer in Table 5, entry 5



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.400	13.400	13.400	15794	53100	67900	102721	138075	1.934478	2.600282

Figure S84. GPC curve of polymer in Table 5, entry 6

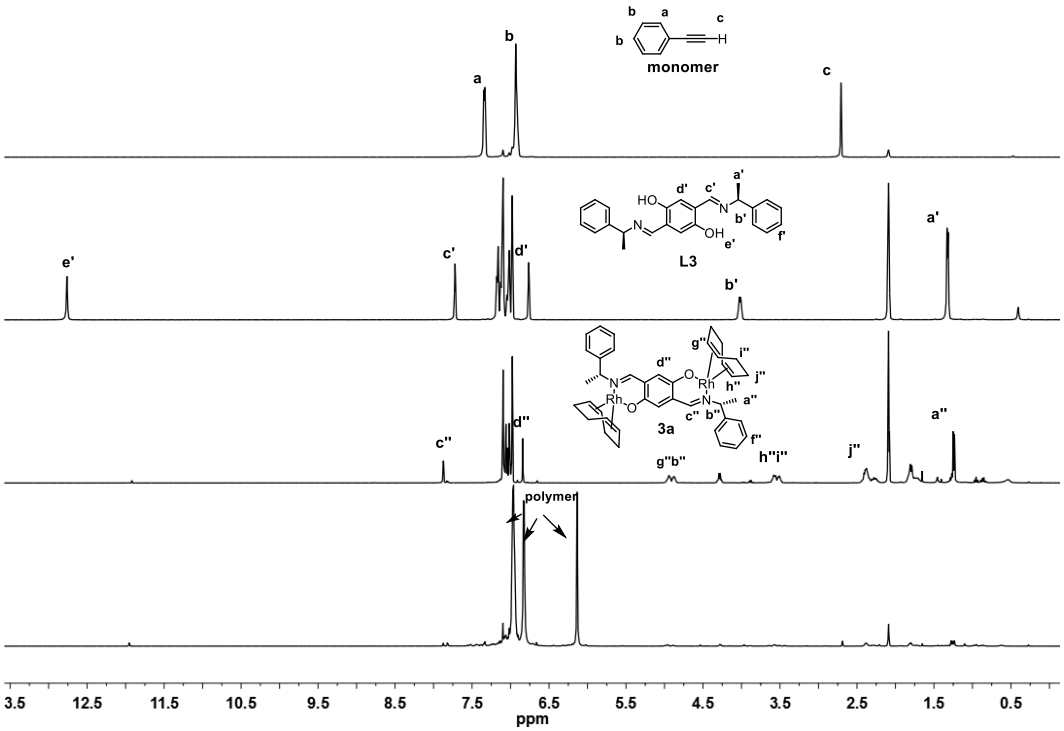


Figure S85. *In situ* ^{1}H NMR spectra of **3a**/PA mixture with a molar ratio of 1 : 0.3 in Toluene-d8.

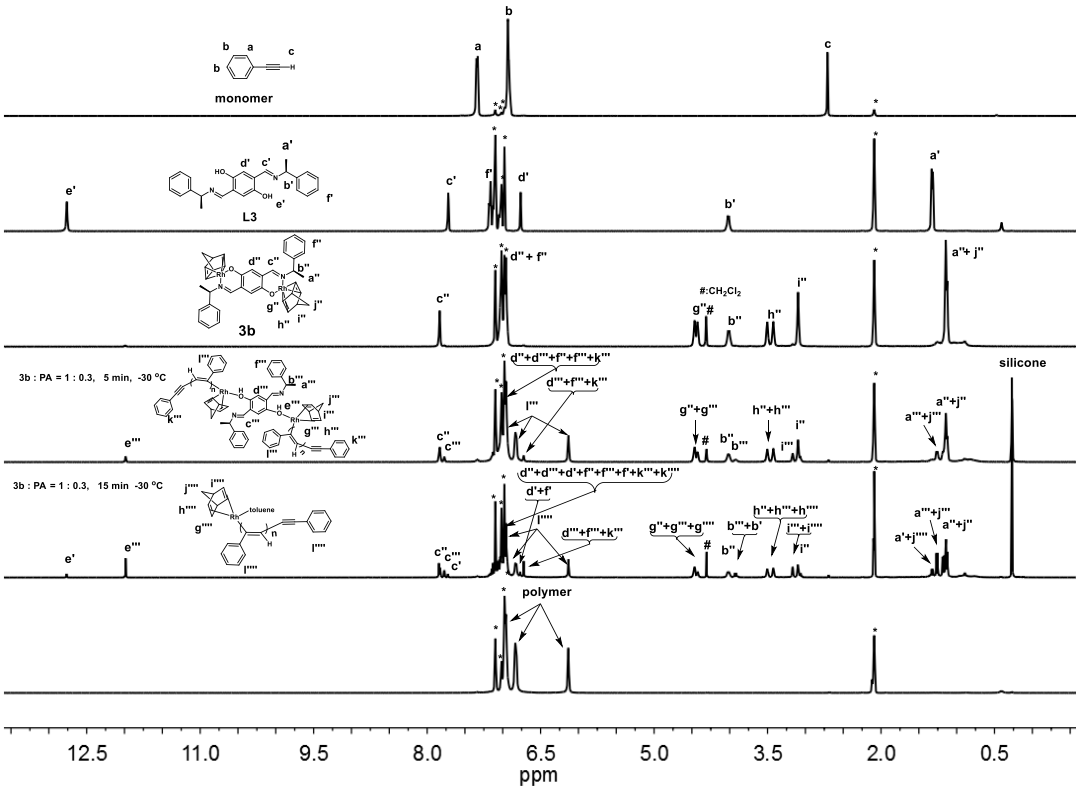


Figure S86. *In situ* ^{1}H NMR spectra of **3b**/PA mixture with a molar ratio of 1 : 0.3 in Toluene-*d8*.

We did the *in situ* ^{1}H NMR study on the polymerization mechanism using **3a** and **3b**. (Figure S85, S86) However, the high peaks of PPA in *in situ* ^{1}H NMR spectrum mean a hopeless task to

get enough evidence for the true structure of active species.

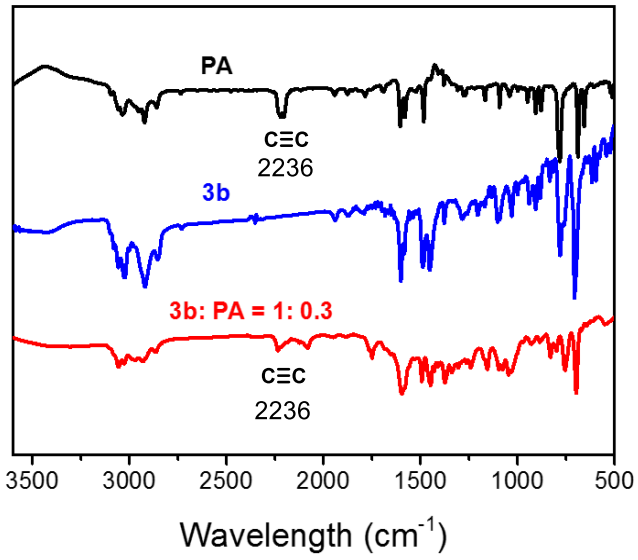


Figure S87. FT-IR spectrum of PA, **3b** and the **3b**/PA mixture with a molar ratio of 1 : 0.3.

The IR spectrum of the **3b**/PA mixture with a molar ratio of 1 : 0.3 showed a sharp peak at 2236 cm^{-1}, identifying the presence of the C≡C triple bond in the produces (Figure S87).

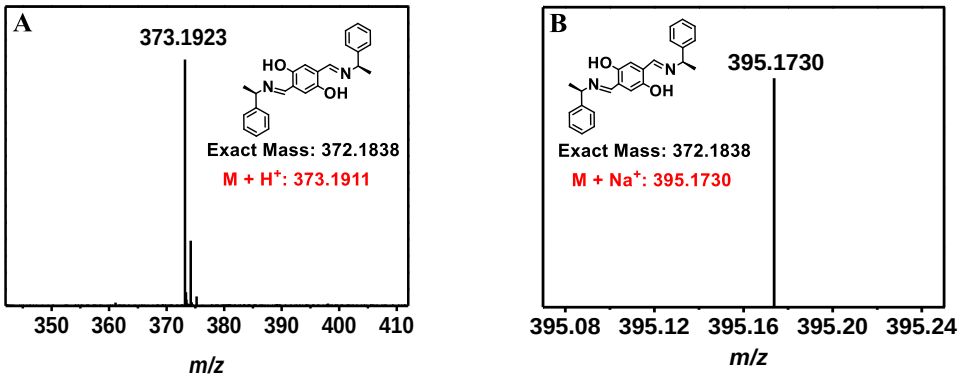


Figure S88. High resolution ESI-MS spectra of oligomer obtained from PA polymerization by use of **3b** under the PA: **3b** molar ratio 5: 1.

The high resolution ESI-MS spectra of oligomer sample obtained from PA oligomerization by use of binuclear Rh complex **3b** under the PA/Rh molar ratio 5/1 confirmed the formation of neutral 2,5-phenyloxydiimine ligand as characterization of the peaks at 373.1923 m/z ($M + H^+$) and 395.1730 m/z ($M + Na^+$) (Figure S88, A–B).

Table S1. X-ray diffraction experimental details for complexes **1a** and (**1-4)b**.

	1a	**1b**	**2b**	**3b**	**4b**
Empirical formula	C23H26NORh	C24H31NO3Rh	C45H43N2O2Rh2Cl3	C19H19NORh	C21H20NORh
Formula weight	435.36	484.41	955.98	380.26	405.29
Temperature (K)	105.4	153.15	153.15	293(2)	153.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	C2
a (Å)	12.96235(17)	10.222(2)	19.411(4)	12.960(3)	17.031(3)
b (Å)	10.15759(11)	9.1756(18)	10.281(2)	9.900(2)	9.954(2)
c (Å)	14.61931(18)	12.967(3)	9.972(2)	13.100(3)	11.038(2)
α (°)	90	90	90	90	90
β (°)	102.9424(12)	112.96(3)	94.88(3)	109.53(3)	111.66(3)
γ (°)	90	90	90	90	90
Volume ($Å^3$)	1875.97(4)	1119.9(4)	1982.8(7)	1584.1(6)	1739.0(6)
Z	4	2	2	4	4
Calc. ρ (g/cm^3)	1.541	1.437	1.601	1.594	1.548
μ(mm^{-1})	0.922	0.786	1.076	1.079	0.988
Crystal size (mm^3)	0.25 × 0.24 × 0.20	0.23 × 0.2 × 0.17	0.15 × 0.1 × 0.08	0.45 × 0.43 × 0.42	0.21 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.710747)	MoKα (λ = 0.71073)	MoKα (λ = 0.710747)
2θ range for data collection (°)	6.22 to 51.98	5.6 to 55	4.1 to 50	5.42 to 63	3.98 to 54.94
Goodness-of-fit on F^2	1.031	1.055	1.127	1.037	1.133
R1, wR2 [I>=2σ (I)]	0.0273, 0.0543	0.0318, 0.0734	0.0818, 0.2208	0.0411, 0.0810	0.0572, 0.1621
	0.0308, 0.0565	0.0324, 0.0741	0.0965, 0.2663	0.0440, 0.0834	0.0710, 0.2138
Flack parameter	-0.02(2)	0.04(3)	0.06(11)	0.028(15)	-0.02(10)