Supporting Information

Chemoselective Ring-Opening Metathesis Polymerizatoin of Cyclopropenes Spirally Appended with *N*-Aryl Saturated Heterocycles

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1. General information

Unless otherwise stated, all reactions were magnetically stirred and conducted in oven-dried (100 °C) in anhydrous solvents under N_2, applying standard Schlenk techniques. Solvents and liquid reagents, as well as solutions of solid or liquid reagents were added via syringes, stainless steel or polyethylene cannulas through rubber septa or through a weak N_2 counter-flow. Solid reagents were first added to the reactor or Schlenk Reaction Tube for refilling N_2 for three times. Heated oil baths were used for reactions requiring elevated temperatures. Solvents were removed under reduced pressure at 40 °C using a rotary evaporator, and unless otherwise stated, the remaining compound was dried in high vacuum at ambient temperature. All given yields are isolated yields of chromatographically and NMR spectroscopically pure materials, unless otherwise stated.

Chemicals

Chemicals were purchased from commercial suppliers (including Energy Chemical, Bidepharm, Aladdin, Meryer, SCR) and used without further purification unless otherwise stated.

Solvents

Solvents (CH_2Cl_2, Et_2O, THF, toluene, Et_3N) were dried by distillation from an appropriate drying agents. In addition, more solvents (Acetone, DMF, DMSO, EtOAc, EtOH, MeOH, MTBE, ^{i}PrOH, *n*-pentane) were purchased from commercial suppliers.

Gas

Dry N_2 and CO were purchased from Hangzhou Jingong Materials with > 99.9% purity.

Column Chromatography

Column chromatography (CC) was carried out using Nuotai silica gel (90 Å, 100-200 mesh) using technical grade solvents. Elution was accelerated using compressed air. All reported yields, unless otherwise specified, refer to spectroscopically and chromatographically pure compounds.

Nuclear Magnetic Resonance Spectroscopy

^{1}H, ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-500 and AV-400 spectrometer in $CDCl_3$. The solvent employed and respective measuring frequency are indicated for each experiment. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). All spectra were recorded at 298 K unless otherwise noted. The residual deuterated solvent signal relative to tetramethylsilane (TMS) was used as the internal reference in ^{1}H NMR

spectra ($CDCl_3$ δ 7.26), and are reported as follows: chemical shift δ in ppm (multiplicity, coupling constant *J* in Hz, number of protons). ^{13}C NMR spectra reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ 77.16). All spectra are broadband decoupled unless otherwise noted.

MALDI-TOF

The sample was measured Bruker Microflex.

High resolution Mass Spectrometry

Electrospray ionization (ESI) mass spectrometry was conducted on a Bruker micro QII-ESI-TOF. The ionization method and mode of detection employed is indicated for the respective experiment and all masses are reported in atomic units per elementary charge (m/z) with an intensity normalized to the most intense peak.

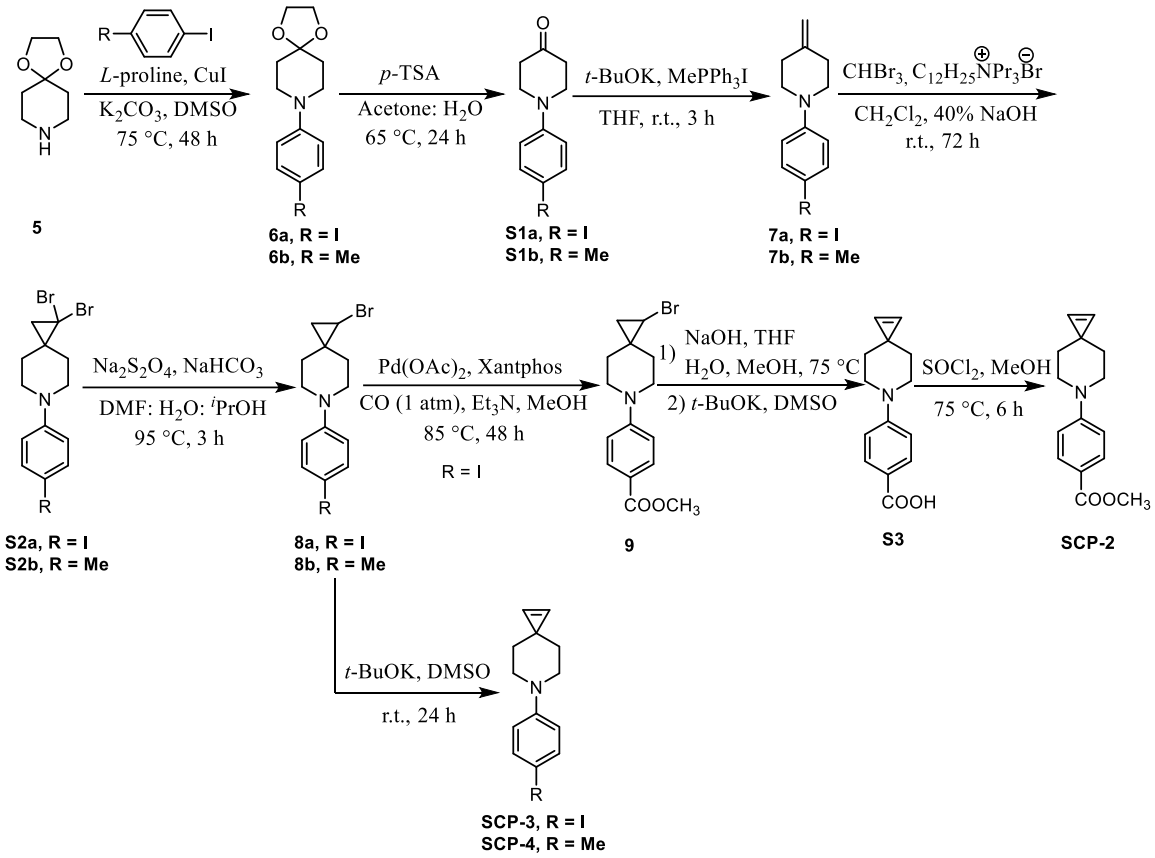
Gel permeation chromatography

GPC traces was determined by using polystyrene standards and THF as the eluent with Waters 1525.

Infrared spectroscopy

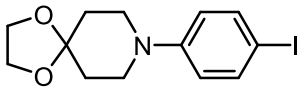
IR spectra were obtained using a Bruker vertex 70 equipped with PIKE MIRacle attenuated total reflection (MIR-ATR) attachment.

2. Experimental procedures on the synthesis of monomers



Scheme S1. Synthetic route of monomer **SCP-2** ,**SCP-3** and **SCP-4**

8-(4-Iodophenyl)-1,4-dioxa-8-azaspiro[4.5]decane (**6a**)



In a two-necked round bottom flask under N_2 and equipped with a magnetic stir bar, compound **5** (20.0 g, 0.11mol, 1 equiv.), 1,4-diiodobenzene (36.0 g, 0.11 mol, 1 equiv.), *L*-proline (5.0 g, 0.044 mol, 40 mol%), CuI (4.0 g, 0.022 mol, 20 mol%) and K_2CO_3 (30.0 g, 0.22 mol, 2 equiv.) were dissolved in DMSO (140 mL). Then the reaction mixture was heated at 75°C for 48 h. Then the mixture was cooled to r.t., and quenched with saturated NH_4Cl aq., and extracted with diethyl ether for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 10:1)

to afford desired product (21.0 g) in 56% yield.

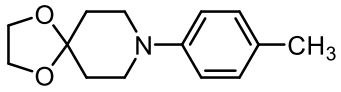
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 3.99 (s, 4H), 3.30 (t, *J* = 6.0 Hz, 4H), 1.81(t, *J* = 6.0 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 137.9, 118.7, 107.2, 81.0, 64.5, 47.5, 34.5.

HRMS (ESI) (m/z): calculated for $C_{13}H_{17}INO_2$ $[M+H]^+$: 346.0299; found 346.0308.

IR ν 2956, 1585, 1489, 1460, 1334, 1221, 1142, 1105, 1031, 943, 890, 821, 702, 666, 638 cm^{-1}

8-(*p*-tolyl)-1,4-dioxa-8-azaspiro[4.5]decane **(6b)**



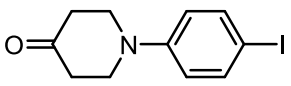
In a two-necked round bottom flask under N_2 and equipped with a magnetic stir bar, compound **5** (15.0 g, 83.5 mmol, 1 equiv.), 1-iodo-4-methylbenzene (24.0 g, 108.6 mmol, 1.3 equiv.), *L*-proline (3.8 g, 33.4 mmol, 40 mol%), CuI (3.2 g, 16.7 mmol, 20 mol%) and K_2CO_3 (23.1 g, 167.0 mmol, 2 equiv.) were dissolved in DMSO (105 mL). Then the reaction mixture was heated at 75°C for 48 h. Then the mixture was cooled to r.t., and quenched with saturated NH_4Cl aq., and extracted with diethyl ether for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 10:1) to afford desired product (11.9 g) in 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 3.99 (s, 4H), 3.26 (t, *J* = 5.9 Hz, 4H), 2.27 (s, 3H), 1.85 (t, *J* = 5.9 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 129.7, 129.2, 117.2, 107.3, 64.4, 48.5,34.7, 20.6.

HRMS (ESI) (m/z): calculated for $C_{14}H_{19}NO_2$ $[M+H]^+$: 234.1489; found 234.1504.

1-(4-Iodophenyl)piperidin-4-one **(S1a)**



In a two-necked round bottom flask under N_2 and equipped with a magnetic stir bar, compound **6a** (16.7 g, 48.4 mmol, 1 equiv.) and *p*-toluenesulfonic acid monohydrate (3.7 g, 21.8 mmol, 0.45 equiv.) were dissolved in acetone (80 mL) and H_2O (120 mL) mixture solvent. The reaction mixture was heated at 65°C for 24 h. Then the mixture was cooled to r.t., quenched with saturated $NaHCO_3$ aq. and extracted with CH_2Cl_2 for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and

concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 10:1) to afford desired product (12.2 g) in 84% yield.

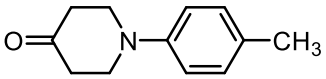
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.9 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 3.58 (t, J = 6.1 Hz, 4H), 2.54 (t, J = 6.0 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 148.8, 138.3, 117.9, 81.5, 48.4, 40.6

HRMS (ESI) (m/z): calculated for $C_{11}H_{13}INO$ $[M+H]^+$: 302.0036; found 302.0040.

IR ν 2956, 2922, 1706, 1581, 1485, 1378, 1313, 1206, 988, 821, 804, 695 cm^{-1}

1-(p-tolyl)piperidin-4-one **(S1b)**

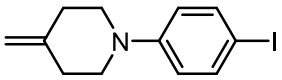


In a two-necked round bottom flask under N_2 and equipped with a magnetic stir bar, compound **6b** (789 mg, 3.4 mmol, 1 equiv.) and *p*-toluenesulfonic acid monohydrate (1.0 g, 5.4 mmol, 1.6 equiv.) were dissolved in acetone (15 mL) and H_2O (23 mL) mixture solvent. The reaction mixture was heated at 65°C for 24 h. Then the mixture was cooled to r.t., quenched with saturated $NaHCO_3$ aq. and extracted with CH_2Cl_2 for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 10:1) to afford desired product (446 mg) in 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.3 Hz, 2H), 3.55 (t, J = 5.8 Hz, 4H), 2.55 (t, J = 5.9 Hz, 4H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.4, 147.1, 129.9, 129.5, 116.4, 49.6, 40.8, 20.4.

1-(4-Iodophenyl)-4-methylenepiperidine **(7a)**



To THF (80 mL) was added $MePPh_3I$ (32.0 g, 79 mmol, 2 equiv.) and *t*-BuOK (9.0 g, 79 mmol, 2 equiv.) at 0°C and then the suspension was stirred at room temperature for 1 h. To the mixture was slowly added the solution of compound **S1a** (12.0 g, 39 mmol, 1 equiv.) in THF (35 mL) at 0°C and then the suspension was stirred at r.t. for 3 h. Then the reaction mixture was quenched with saturated NH_4Cl aq. and extracted with CH_2Cl_2 for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 30:1) to afford product (11.8 g) in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.5 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 4.75 (s, 2H),

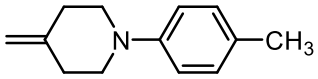
3.24 (t, *J* = 5.5 Hz, 4H), 2.33 (t, *J* = 5.3 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 145.6, 138.0, 118.6, 108.6, 80.8, 51.0, 34.1.

HRMS (ESI) (m/z): calculated for $C_{12}H_{15}IN$ $[M+H]^+$: 300.0244; found 300.0248.

IR ν 3033, 2824, 1582, 1488, 1374, 1319, 1232, 1206, 1140, 1071, 984, 901, 803, 693, 676 cm^{-1}

4-methylene-1-(*p*-tolyl)piperidine **(7b)**



To THF (80 mL) was added $MePPh_3Br$ (34.0 g, 95 mmol, 3 equiv.) and 2.5 mol/L butyllithium (57 mL, 143 mmol, 4.5 equiv.) at -78°C and then the suspension was stirred at room temperature for 1 h. To the mixture was slowly added the solution of compound **S1b** (6.0 g, 32 mmol, 1 equiv.) in THF (35 mL) at -78°C and then the suspension was stirred at r.t. for 3 h. Then the reaction mixture was quenched with saturated NH_4Cl aq. and extracted with CH_2Cl_2 for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 30:1) to afford product (5.0 g) in 85% yield.

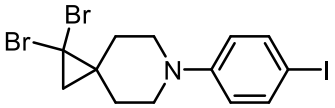
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 2H), 3.26 (t, *J* = 5.8 Hz, 4H), 2.43 (t, *J* = 5.5 Hz, 4H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 146.1, 129.7, 128.9, 117.11, 108.2, 52.0, 34.5, 20.5.

HRMS (ESI) (m/z): calculated for $C_{13}H_{17}N$ $[M+H]^+$: 188.1434; found 188.1551.

IR ν 2981, 2901, 2806, 1655, 1514, 1375, 1232, 1206, 1138, 994, 888, 810, 708 cm^{-1}

1,1-Dibromo-6-(4-iodophenyl)-6-azaspiro[2.5]octane **(S2a)**



To a mixture of compound **7a** (6.7 g, 22.6 mmol, 1 equiv.), bromoform (6 mL, 67.8 mmol, 3 equiv.) and TEBAC (0.6 g, 1.6 mmol, 0.07 equiv.) in CH_2Cl_2 (60 mL) was added an ice-cold 40% aqueous NaOH (60 mL) solution dropwise at 0°C. The mixture was stirred for 72 h at r.t. and the reaction was carefully monitored by TLC and GC-MS. The organic layer was then separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with 1M HCl and NH_4Cl, dried over Na_2SO_4,

and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 60:1) to afford product (10.6 g) in 33% yield.

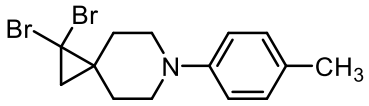
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.9 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 3.41–3.35(m, 2H), 3.21–3.15 (m, 2H), 2.05–1.99 (m, 2H), 1.87–1.81 (m, 2H), 1.52 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 138.0, 118.9, 81.5, 48.6, 37.3, 34.3, 33.2, 30.7.

HRMS (ESI) (m/z): calculated for $C_{13}H_{15}Br_2IN$ $[M+H]^+$: 469.8610; found 469.8607.

IR ν 2922, 1581, 1490, 1379, 1258, 1212, 1039, 962, 797, 691 cm^{-1}

1,1-dibromo-6-(*p*-tolyl)-6-azaspiro[2.5]octane **(S2b)**



To a mixture of compound **7b** (1 g, 5.3 mmol, 1 equiv.), bromoform (1.4 mL, 16 mmol, 3 equiv.) and TEBAC (0.15 g, 0.37 mmol, 0.07 equiv.) in CH_2Cl_2 (10 mL) was added an ice-cold 40% aqueous NaOH (10 mL) solution dropwise at 0°C. The mixture was stirred for 72 h at r.t. and the reaction was carefully monitored by TLC and GC-MS. The organic layer was then separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with 1M HCl and NH_4Cl, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 60:1) to afford product (0.3 g) in 16% yield.

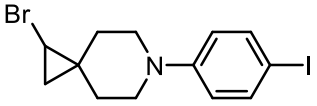
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, J = 8.3 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.38–3.34 (m, 2H), 3.14–3.10 (m, 2H), 2.28 (s, 3H). 2.08–2.03 (m, 2H), 1.87–1.82 (m, 2H), 1.51 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 129.7, 129.4, 117.2, 49.4, 37.6, 34.5, 33.1, 30.7, 20.5

HRMS (ESI) (m/z): calculated for $C_{14}H_{17}Br_2N$ $[M+H]^+$:357.9801; found 357.9808.

IR ν 2962, 1516, 1461, 1342, 1319, 1260, 1141, 1089, 1035, 962, 802, 688, 646 cm^{-1}

1-Bromo-6-(4-iodophenyl)-6-azaspiro[2.5]octane **(8a)**



A mixture of compound **S2a** (375 mg, 0.8 mmol, 1 equiv.), $Na_2S_2O_4$ (278 mg, 1.6 mmol, 2 equiv.) and $NaHCO_3$ (470 mg, 5.6 mmol, 7 equiv.) were dissolved in a solvent mixture of DMF (1.5 mL), H_2O (1.5 mL) and isopropanol (3 mL). Then the reaction was heated

at 95°C for 3 h under N_2. It was then cooled to r.t., quenched with saturated NH_4Cl and extracted with methyl *tert*-butyl ether for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 25:1) to afford product (216 mg) in 69% yield.

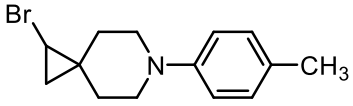
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 3.24–3.10 (m, 4H), 2.85–2.82 (dd, J = 7.6, 4.0 Hz, 1H), 1.81–1.70 (m, 2H), 1.57–1.41 (m, 2H), 1.01 (t, J = 6.0 Hz, 1H), 0.71–0.69 (dd, J = 6.6, 4.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 137.9, 118.9, 81.2, 48.8, 48.7, 34.5, 32.0, 28.1, 22.8, 21.5.

HRMS (ESI) (m/z): calculated for $C_{13}H_{16}BrIN$ $[M+H]^+$: 391.9505; found 391.9513.

IR ν 2919, 1579, 1487, 1321, 1217, 1090, 1025, 989, 961, 862, 810, 694, 610 cm^{-1}

1-bromo-6-(*p*-tolyl)-6-azaspiro[2.5]octane **(8b)**



A mixture of compound **S2b** (2.0 g, 5.6 mmol, 1 equiv.), $Na_2S_2O_4$ (2.0 g, 11.2 mmol, 2 equiv.) and $NaHCO_3$ (3.29 g, 39.2 mmol, 7 equiv.) were dissolved in a solvent mixture of DMF (20 mL), H_2O (20 mL) and isopropanol (30 mL). Then the reaction was heated at 95°C for 3 h under N_2. It was then cooled to r.t., quenched with saturated NH_4Cl and extracted with methyl *tert*-butyl ether for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 25:1) to afford product (660 mg) in 42% yield.

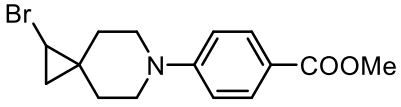
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 3.28–3.17 (m, 4H), 2.92–2.90 (dd, J = 7.8, 4.3 Hz, 1H), 2.28 (s, 3H). 1.91–1.80 (m, 2H), 1.65–1.51 (m, 2H), 1.08 (t, J = 6.6 Hz, 1H), 0.78–0.76 (dd, J = 6.1, 4.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 129.8, 129.3, 117.4, 49.9, 49.8, 34.9, 32.4, 28.3, 22.9, 21.5, 20.6.

HRMS (ESI) (m/z): calculated for $C_{14}H_{18}BrN$ $[M+H]^+$: 280.0695; found 280.0728.

IR ν 2936, 1514, 1240, 1226, 1207, 1091,1031, 960, 811, 702, 691, 624 cm^{-1}

Methyl 4-(1-bromo-6-azaspiro[2.5]octan-6-yl)benzoate **(9)**



A mixture of compound **8a** (350 mg, 0.89 mmol, 1 equiv.), $Pd(OAc)_2$ (10 mg, 0.04 mmol, 5 mmol%), Xantphos (52 mg, 0.89 mmol, 10 mmol%) was dissolved in anhydrous methanol (0.7 mL, 20 equiv.) in triethylamine (7 mL) in a round-bottomed flask under N_2. Then the reaction flask was connected to a CO-filled gas balloon on the top of the condenser to change the N_2 of the reaction flask for 3 times, and flushed with CO for another 5 min. The reaction mixture was stirred at 85°C for 48 h. Then the reaction mixture was cooled to r.t. and quenched with saturated NH_4Cl and extracted with CH_2Cl_2 for 3 times. The combined organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 20:1) to afford product (220 mg) in 76% yield.

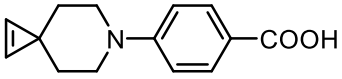
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 3.51-3.36 (m, 4H), 2.94-2.91 (dd, J = 7.6, 4.2 Hz, 1H), 1.89–1.77 (m, 2H), 1.65–1.58 (m, 1H), 1.53–1.47 (m, 1H), 1.11 (t, J = 6.9 Hz, 1H), 0.79 (dd, J = 6.3, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 154.2, 131.4, 119.4, 114.1, 51.8, 47.6, 47.5, 34.4, 31.9, 27.9, 23.0, 21.5.

HRMS (ESI) (m/z): calculated for $C_{15}H_{19}BrNO_2$ $[M+H]^+$:324.0594; found 324.0604.

IR ν1703, 1608, 1514, 1433, 1393, 1367, 1286, 1243, 1187, 1107, 1088, 963, 863, 827, 767, 694 cm^{-1}

4-(6-azaspiro[2.5]oct-1-en-6-yl)benzoic acid **(S3)**



A mixture of compound **9** (251 mg, 0.77 mmol, 1 equiv.), NaOH (174 mg, 4.66 mmol, 6 equiv.) and was dissolved in H_2O (10 mL), THF (10 mL) and methanol (10mL) in a round-bottomed flask under N_2. The reaction mixture was stirred at 75°C for 4 h. Then the reaction mixture was cooled to r.t. and quenched with saturated NH_4Cl aq. and extracted with CH_2Cl_2 for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure.

Then a mixture of the above-mentioned compound, *t*-BuOK (324 mg, 4 equiv.) and appropriate amount of 4 Å molecular sieve was added in anhydrous DMSO (15 mL) under N_2, the reaction mixture was kept stirring for 24h at r.t. Then it was quenched with saturated NH_4Cl aq. and extracted with diethyl ether for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was dissolved in a small amount of CH_2Cl_2 and poured

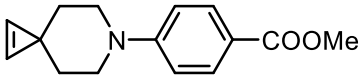
into petroleum ether and white solid of **S3** (110 mg) was precipitated and collected in 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 9.2 Hz, 2H), 7.56 (s, 2H), 6.88 (d, J = 9.2 Hz, 2H), 3.49 (t, J = 5.9 Hz, 4H), 1.60 (t, J = 5.7 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 154.7, 132.2, 122.5, 117.1, 113.4, 48.2, 38.1, 21.8.

HRMS (ESI) (m/z): calculated for $C_{14}H_{16}NO_2$ $[M+H]^+$: 230.1176; found 230.1173.

Methyl 4-(6-azaspiro[2.5]oct-1-en-6-yl)benzoate **(SCP-2)**



A mixture of compound **S3** (110 mg, 0.48 mmol, 1 equiv.) and $SOCl_2$ (7mL) was refluxed in methol (2 mL) at 75°C for 6 h under N_2. It was then cooled to r.t. and quenched with saturated $NaHCO_3$ and extracted with CH_2Cl_2 for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 20:1) to afford product (73 mg) in 63% yield.

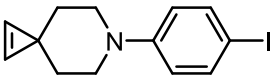
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.9 Hz, 2H), 7.56 (s, 2H), 6.87 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H), 3.46 (t, J = 5.6 Hz, 4H), 1.59 (t, J = 5.8 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 154.3, 131.4, 122.6, 118.5, 113.7, 51.7, 48.4, 38.1, 21.8.

HRMS (ESI) (m/z): calculated for $C_{15}H_{18}NO_2$ $[M+H]^+$: 244.1332; found 244.1321.

IR ν 2920, 1694, 1606, 1517, 1431, 1386, 1287, 1232, 1190, 1112, 1076, 1021, 960, 825, 769, 695 cm^{-1}

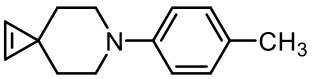
6-(4-Iodophenyl)-6-azaspiro[2.5]oct-1-ene **(SCP-3)**



A mixture of compound **8a** (300 mg, 0.77 mmol, 1 equiv.) and *t*-BuOK (215 mg,1.92 mmol, 2.5 equiv.) was dissolved in DMSO (45 mL) in a round-bottomed flask under N_2. The reaction was stirred at r.t. for 24 h. Then the reaction mixture was quenched with saturated NH_4Cl and extracted with diethyl ether for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 30:1) to afford product (160 mg) in 67% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.49 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 3.25 (t, *J* = 5.6 Hz, 4H), 1.60 (t, *J* = 5.6 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 137.8, 122.8, 118.6, 80.4, 49.8, 38.4, 21.8.
HRMS (ESI) (m/z): calculated for $C_{13}H_{15}IN$ $[M+H]^+$: 312.0244; found 312.0258.
IR ν 2935, 2824, 1582, 1488, 1382, 1343, 1225, 1076, 1013, 984, 804, 691, 637 cm^{-1}

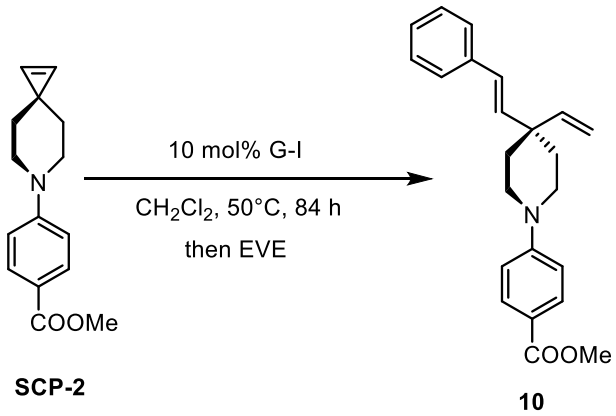
6-(*p*-tolyl)-6-azaspiro[2.5]oct-1-ene **(SCP-4)**



A mixture of compound **8b** (110 mg, 0.39 mmol, 1 equiv.) and *t*-BuOK (133 mg,1.18 mmol, 3 equiv.) was dissolved in DMSO (10 mL) in a round-bottomed flask under N_2. The reaction was stirred at r.t. for 24 h. Then the reaction mixture was quenched with saturated NH_4Cl and extracted with diethyl ether for 3 times. The combined organic layers were collected and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica column chromatography (PE:EtOAc = 30:1) to afford product (34 mg) in 44% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 3.25 (t, *J* = 4.9 Hz, 4H), 2.31 (s, 3H), 1.68 (t, *J* = 5.1 Hz, 4H).
^{13}C NMR (101MHz, $CDCl_3$) δ 150.1, 129.6, 128.7, 123.0, 117.2, 50.9, 38.7, 21.8, 20.6.
HRMS (ESI) (m/z): calculated for $C_{14}H_{17}N$ $[M+H]^+$: 200.1434; found 200.1452.
IR ν 2936, 1514, 1446, 1240, 1226, 1208, 1091, 1031, 960, 863, 811, 691, 624 cm^{-1}

3. Experimental procedures of ROMP of SCP-2, SCP-3 and SCP-4

G-I catalyzed ROMP of SCP-2

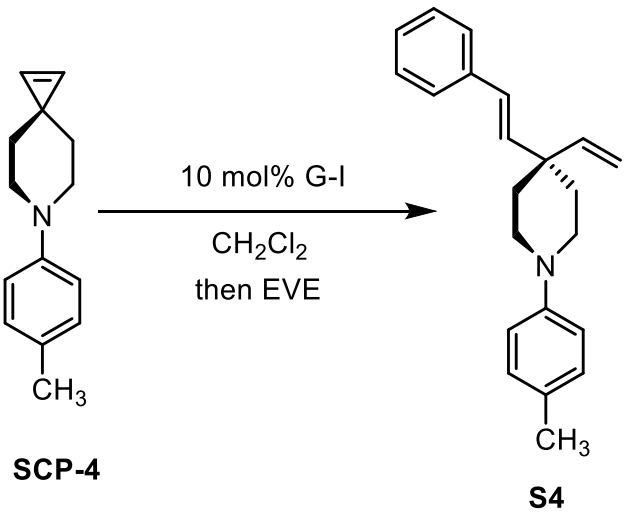


SCP-2 **10**

Scheme S2. G-I catalyzed ROMP of **SCP-2**

A mixture of **SCP-2** (5 mg, 0.02 mmol, 1 equiv.) and **Grubbs I** (10 mol%) was dissolved in DCM (1 mL) in a Schlenk reaction tube under N_2 in glovebox. Then the reaction mixture was heated at 50°C for 84 h. It was cooled to r.t. and quenched by excess ethyl vinyl ether (0.08 mL, 0.82 mmol, 40 equiv.). After stirring for 30 min, solvent was removed in *vacuo* and the residue was dried under *vacuum*. Monomeric ring-opening cross metathesis compound **10** was isolated by preparative TLC (PE:EtOAc = 5:1) to afford 0.5 mg product in less than 10% yield.

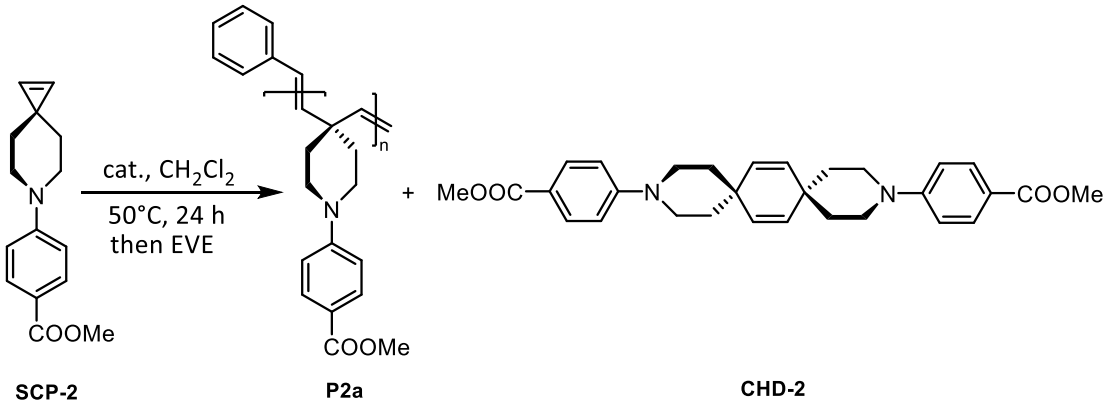
Methyl-(4-styryl-4-vinylpiperidin-1-yl)benzoate (**10**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.2 Hz, 2H), 7.37 (d, *J* =7.0 Hz, 2H), 7.30 (t, *J* = 6.6 Hz, 2H), 7.22–7.20(t, *J* = 7.6 Hz 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 16.3 Hz, 1H), 6.12 (d, *J* = 16.5 Hz, 1H), 5.80 (dd, *J* = 10.8, 17.6 Hz, 1H), 5.19 (d, *J* =10.6 Hz, 1H), 5.10 (d, *J* = 17.7 Hz, 1H), 3.86 (s, 3H), 3.44 (t, *J* = 6.1 Hz, l4H), 1.93–1.90 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 154.2, 144.0, 137.4, 135.9, 131.4, 129.3, 128.7, 127.5, 126.3, 119.0, 114.3, 113.6, 51.8, 44.6, 41.5, 34.5.
HRMS (ESI) (m/z): calculated for $C_{23}H_{26}NO_2$ $[M+H]^+$: 348.1885; found 348.1970.



Scheme S3. **G-I** catalyzed ROMP of **SCP-4**

Styryl-1-(*p*-tolyl)-4-vinylpiperidine (**S4**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* =7.8 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* =7.2 Hz, 2H), , 7.07 (d, *J* = 8.1 Hz 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.39 (d, *J* = 16.5 Hz, 1H), 6.14 (d, *J* = 16.2 Hz, 1H), 5.82 (dd, *J* = 10.6, 17.6 Hz, 1H), 5.18 (d, *J* =10.7 Hz, 1H), 5.10 (d, *J* = 17.6 Hz, 1H), 3.23 (t, *J* = 5.4 Hz, 4H), 2.27 (s, 3H), 1.98–1.95 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 144.5, 137.6, 136.5, 129.7, 129.0, 128.7, 127.3, 126.2, 116.8, 114.0, 46.8, 41.3, 35.1, 20.6.

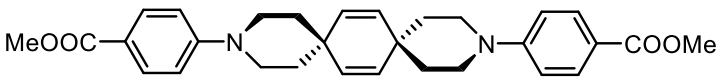
G-II and G- III catalyzed ROMP of SCP-2



Scheme S4. G-II and G- III catalyzed ROMP of **SCP-2**

A mixture of **SCP-2** (18 mg, 0.07 mmol, 1 equiv.) and 10 mol% Grubbs catalyst was dissolved in DCM (2 mL) in a Schlenk reaction tube under N_2 in glovebox. Then the reaction mixture was heated at 50°C for 24 h. Then it was cooled to r.t., quenched with excess ethyl vinyl ether (0.3 mL, 2.96 mmol, 40 equiv.). After stirring for 30 min, solvent was removed in *vacuo* and the residue was dried under *vacuum*. The crude product was dissolved in a small amount of CH_2Cl_2 and poured into vigorously stirred MeOH and precipitated polymer was collected by centrifugation. The centrifugation was repeated for 3 times. After drying under *vacuum,* polymer **P2a** was afforded in 80% (**G-II**) and 81% (**G-III**) yields. respectively.

The upper clear solution in methanol by centrifugation was collected and then methanol was removed under reduced pressure. The crude product was dissolved in a small amount of CH_2Cl_2 and poured into vigorously stirred *n*-pentane, white solid of **CHD-2** was precipitated and collected in 18% (**G-II**) and 14% (**G-III**) yields, respectively.



CHD-2

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 8.0 Hz, 4H), 5.82 (s, 4H), 3.86 (s, 6H), 3.44 (t, *J* = 4.0 Hz, 8H), 1.67 (t, *J* = 4.0 Hz, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 154.3, 131.6, 131.4, 119.2, 113.7, 51.8, 43.7, 37.6,

35.0.

HRMS (ESI) (m/z): calculated for $C_{30}H_{34}N_2O_4Na$ [M+Na] $^+$: 509.2411; found 509.2411.

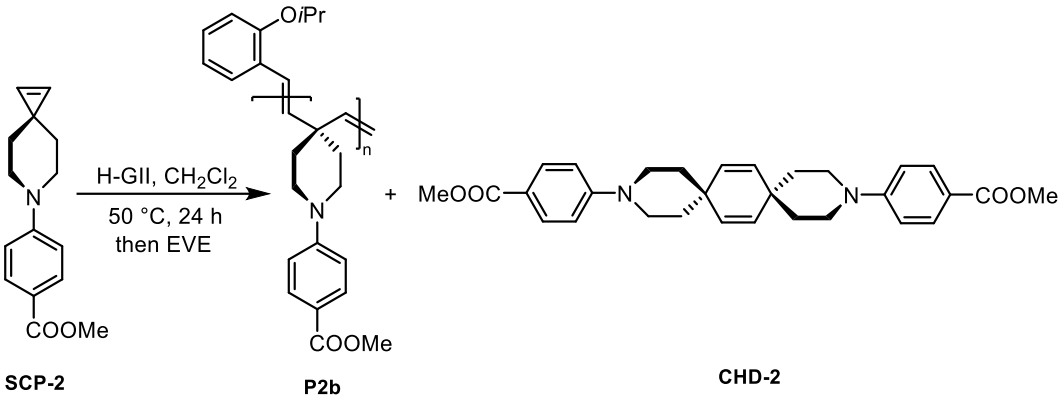
P2a (G-II)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.84 (m, 14H), 6.82–6.67 (m, 14H), 6.28 (d, *J* = 16.5 Hz ,1H), 6.05 (d, *J* = 16.5 Hz, 1H), 5.67-5.58 (m, 1H), 5.37–5.21 (m, 14H), 5.03 (d, *J* = 12.0 Hz, 1H), 4.92 (d, *J* = 16.3 Hz, 1H), 3.86 (s, 21H), 3.35–3.11 (m, 28H), 1.86–1.54 (m, 28H).

P2a (G-III)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 18H), 6.79–6.68 (m, 18H), 6.27 (d, *J* = 16.1 Hz ,1H), 6.03 (d, *J* = 16.1 Hz, 1H), 5.70-5.60 (m, 1H), 5.32–5.16 (m, 18H), 5.03 (d, *J* = 11.7 Hz, 1H), 4.92 (d, *J* = 16.8 Hz, 1H), 3.85 (s, 27H), 3.35–3.11 (m, 36H), 1.84–1.54 (m, 36H).

H-G-II catalyzed ROMP of SCP-2



Scheme S5. H-G-II catalyzed ROMP of **SCP-2**

A mixture of **SCP-2** (20 mg, 0.082 mmol, 1 equiv.) and Hoveyda-Grubbs II (10 mol%, 5 mol% and 2.5 mol%, respectively) was dissolved in DCM (3 mL) in a Schlenk reaction tube under N_2 in glovebox. Then the reaction mixture was heated at 50°C for 24 h. Then it was cooled to r.t. and quenched with excess ethyl vinyl ether (0.3 mL, 3.29 mmol, 40 equiv.). After stirring for 30 min, solvent was removed in *vacuo* and the residue was dried under *vacuum*. The crude product was dissolved in a small amount of CH_2Cl_2 and poured into vigorously stirred MeOH and precipitated polymer was collected by centrifugation. The centrifugation was repeated for 3 times. After drying under *vacuum,* polymer **P2b** was afforded. Yields were listed in **Table S1.**

The upper clear solution in methanol by centrifugation was collected and then methanol was removed under reduced pressure. The crude product was dissolved in a small amount of CH_2Cl_2 and poured into vigorously stirred *n*-pentane and white solid of **CHD-2** was precipitated and collected.

P2b (10 mol% catalyst loading):

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87–7.86 (m, 18H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.14 (s, 2H), 6.85–6.64 (m, 20H), 6.02 (d, *J* = 16.3 Hz, 1H), 5.66–5.60 (dd, *J* = 10.9, 18.7 Hz, 1H), 5.33–5.19 (m, 18H), 5.02 (d, *J* = 10.5 Hz, 1H), 4.92(d, *J* = 17.7 Hz, 1H), 4.49–4.43 (m, 1H), 3.85 (s, 27H), 3.36–4.14 (m, 36H), 1.87–1.60 (m, 36H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 154.1, 136.1, 131.4, 113.6, 51.8, 44.4, 40.2, 35.2, 29.9, 22.5.

IR ν 1706, 1605, 1515, 1432, 1285, 1244, 1188, 1103, 968, 904, 797, 770, 696 cm^{-1}

P2b-2 (5 mol% catalyst loading):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.86 (m, 38H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.14 (s, 2H), 6.85–6.64 (m, 40H), 6.02 (d, *J* = 16.3 Hz, 1H), 5.66–5.60 (dd, *J* = 10.9, 18.7 Hz, 1H), 5.33–5.19 (m, 38H), 5.02 (d, *J* = 10.5 Hz, 1H), 4.92(d, *J* = 17.7 Hz, 1H), 4.49–4.43 (m, 1H), 3.85 (s, 57H), 3.36–4.14 (m, 76H), 1.87–1.60 (m, 76H).

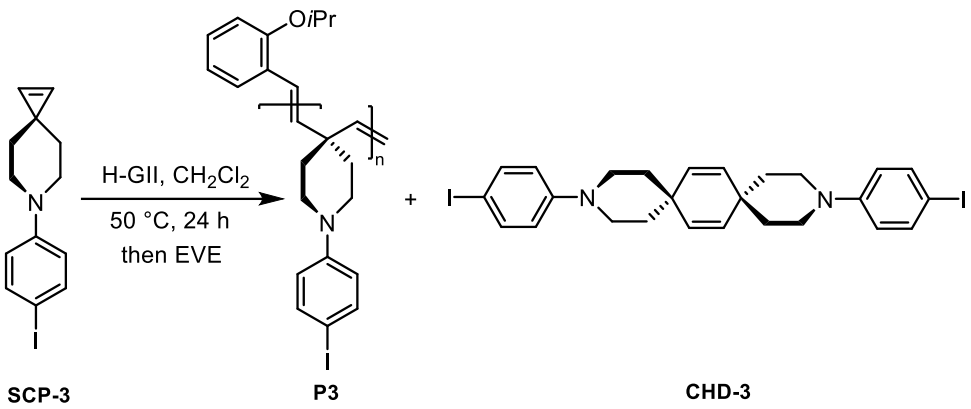
IR ν 1703, 1603, 1516, 1433, 1394, 1285, 1247, 1189, 1107, 967, 905, 801, 770, 697 cm^{-1}

P2b-3 (2.5 mol% catalyst loading):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.86 (m, 80H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.14 (s, 2H), 6.85–6.64 (m, 82H), 6.02 (d, *J* = 16.3 Hz, 1H), 5.66–5.60 (dd, *J* = 10.9, 18.7 Hz, 1H), 5.33–5.19 (m, 80H), 5.02 (d, *J* = 10.5 Hz, 1H), 4.92(d, *J* = 17.7 Hz, 1H), 4.49–4.43 (m, 1H), 3.85 (s, 120H), 3.36–4.14 (m, 160H), 1.87–1.60 (m, 160H).

IR ν 1703, 1603, 1516, 1394, 1285, 1246, 1189, 1108, 966, 905, 803, 770, 697 cm^{-1}

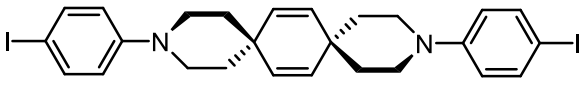
H-G-II catalyzed ROMP of SCP-3



Scheme S6. H-G-II catalyzed ROMP of **SCP-3**

A mixture of **SCP-3** (20 mg, 0.064 mmol, 1 equiv.) and Hoveyda-Grubbs II (20 mol%, 10 mol% and 5 mol%, respectively) was dissolved in DCM (3 mL) in a Schlenk reaction tube under N_2 in glovebox. Then the reaction mixture was heated at 50°C for 24 h. It was cooled to r.t. and quenched with excess ethyl vinyl ether (0.25 mL, 2.57 mmol, 40 equiv.). After stirring for 30 min, solvent was removed in *vacuo* and the residue was dried under *vacuum*. The crude product was dissolved in a small amount of CH_2Cl_2 and poured into vigorously stirred MeOH and precipitated polymer was collected by centrifugation. The centrifugation was repeated for 3 times. After drying under *vacuum,* polymer **P3** was afforded. Yields were listed in **Table S1.**

The upper clear solution in methanol by centrifugation was collected and then methanol was removed under reduced pressure. The crude product was dissolved in a small amount of CH_2Cl_2 and poured into vigorously stirred *n*-pentane and white solid of **CHD-3** was precipitated and collected.



CHD-3

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 4H), 6.72 (d, *J* = 8.0 Hz, 4H), 5.80 (s, 4H), 3.25 (m, *J* = 4.0 Hz, 8H), 1.67 (m, *J* = 4.0 Hz, 8H),
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 137.9, 131.7, 118.3, 81.0, 44.9, 37.9, 34.8.
HRMS (ESI) (m/z): calculated for $C_{26}H_{29}I_2N_2$ $[M+H]^+$: 623.0415; found 623.0411.

P3 (20 mol% catalyst loading) :

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 6H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 8.4 Hz, 1H), 6.89–6.83 (m, 2H), 6.67-6.53 (m, 6H), 6.63 (d, *J* = 17.3 Hz, 1H), 5.68-5.61 (m, 1H), 5.34-5.16 (m, 6H), 5.02 (d, *J* = 10.3 Hz, 1H), 4.93 (d, *J* = 10.3 Hz, 1H), 4.50–4.43 (m, 1H), 3.25-2.95 (m, 12H), 1.90-1.59 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1, 151.1, 145.0, 137.9, 136.0, 128.4, 127.9, 126.6, 120.9, 118.2, 114.7, 113.6, 45.7, 40.7, 40.0, 35.4, 34.8, 29.9, 22.5.

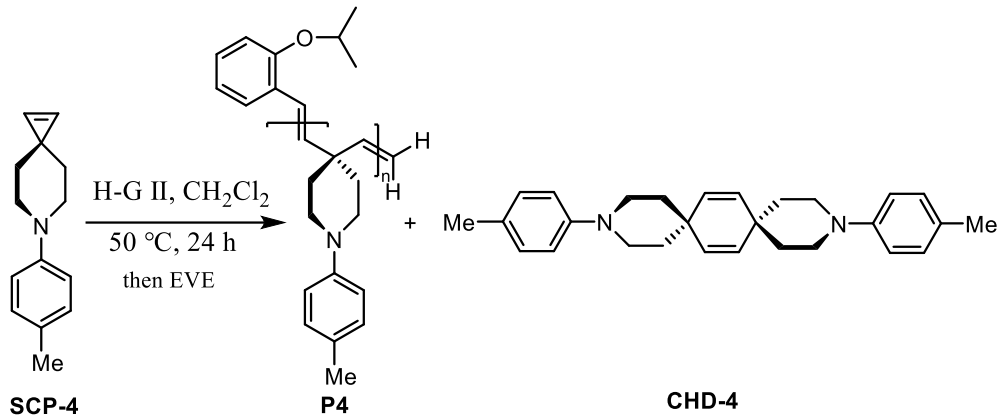
IR ν 1582, 1489, 1329, 1245, 1019, 967, 808 cm^{-1}

P3-2 (10 mol% catalyst loading) :

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.34 (m, 18H), 7.31–7.25 (m, 1H), 7.14–7.06 (m, 2H), 6.84–6,77 (m, 2H), 6.62-6.45 (m, 18H), 5.97 (d, *J* = 16.4 Hz, 1H), 5.63–5.53 (m, 1H), 5.28–5.08 (m, 18H), 4.96 (d, *J* = 8.65 Hz, 1H), 4.86 (d, *J* = 17.7 Hz, 1H), 4.46–4.36 (m, 1H), 3.22–2.85 (m, 36H), 1.89–1.55 (m, 36H).

IR ν 1582, 1489, 1461, 1329, 1245, 1158, 1095, 1019, 966, 900, 808 cm^{-1}

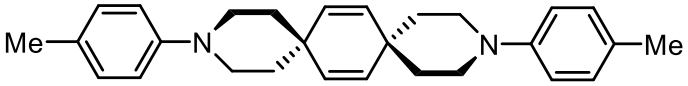
H-G-II catalyzed ROMP of SCP-4



Scheme S7. H-G-II catalyzed ROMP of **SCP-4**

A mixture of **SCP-4** (30 mg, 0.15 mmol, 1 equiv.) and Hoveyda-Grubbs II (5 mol% and 2.5 mol% respectively) was dissolved in DCM (3 mL) in a Schlenk reaction tube under N_2 in glovebox. Then the reaction mixture was heated at 50°C for 24 h. It was cooled to r.t. and quenched with excess ethyl vinyl ether (0.6 mL, 6.02 mmol, 40 equiv.). After stirring for 30 min, solvent was removed in *vacuo* and the residue was dried under *vacuum*. The crude product was dissolved in a small amount of CH_2Cl_2 and poured into vigorously stirred MeOH and precipitated polymer was collected by centrifugation. The centrifugation was repeated for 3 times. After drying under *vacuum,* polymer **P4** was afforded.

The upper clear solution in methanol by centrifugation was collected and then methanol was removed under reduced pressure. The crude product was purified by silica column chromatography (PE:EtOAc = 20:1) to afford product **CHD-4**.



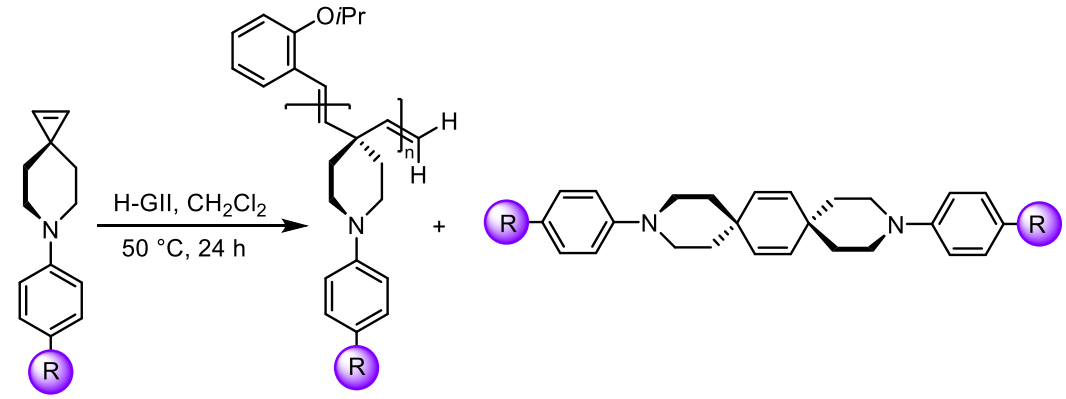
CHD-4

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 4H), 6.90 (d, *J* = 8.5 Hz, 4H), 5.81 (s, 4H), 3.21 (m, *J* = 5.5 Hz, 8H), 2.27 (s, 6H), 1.70 (m, *J* = 5.3 Hz, 8H),
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 131.8, 129.8, 129.1, 116.8, 46.0, 38.3, 34.9, 20.6.
HRMS (ESI) (m/z): calculated for $C_{28}H_{35}N_2$ $[M+H]^+$: 399.2795; found 399.2802.

P4 (5 mol% catalyst loading):
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.05-6.97 (m, 30H), 6.81-6.74 (m, 30H), 6.05 (d, *J* = 17.3 Hz, 1H), 5.70-5.63 (m, 1H), 5.34-5.22 (m, 30H), 5.00 (d, *J* = 10.5 Hz, 1H), 4.93 (d, *J* = 17.0 Hz, 1H), 3.20-2.96 (m, 60H), 2.24 (s, 45H), 1.77-1.65 (m, 60H).
^{13}C NMR (126 MHz, $CDCl_3$) *δ* 149.7, 135.8, 129.7, 128.8, 120.9, 116.8, 116.6, 46.8, 41.5, 40.0, 35.9, 34.8, 33.9, 29.2, 27.8, 27.1, 22.8, 22.5, 20.6, 19.6, 18.9, 11.6.
IR ν 2921, 1514, 1259, 1245, 1092, 1018, 968, 799cm^{-1}

P4 (2.5 mol% catalyst loading):
^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.05-6.97 (m, 54H), 6.78-6.72 (m, 54H), 6.05 (d, *J* = 17.3 Hz, 1H), 5.70-5.63 (m, 1H), 5.34-5.21 (m, 54H), 5.00 (d, *J* = 10.5 Hz, 1H), 4.93 (d, *J* = 17.0 Hz, 1H), 3.08-2.94 (m, 108H), 2.23 (s, 81H), 1.75-1.63 (m, 108H).

Table S1: Variation of catalyst loading for ROMP[a]



SCP-2, R=COOMe
SCP-3, R=I
SCP-4, R=Me

P2b, R=COOMe
P3, R=I
P4, R=Me

CHD-2, R=COOMe
CHD-3, R=I
CHD-4, R=Me

entry	M	cat. loading	P/CHD[a]	Yields(%)[b]	
				P	CHD
1	**SCP-2**	10%	84: 16	80	15
2	**SCP-2**	5%	83: 17	82	16
3	**SCP-2**	2.5%	85: 15	70	14
4	**SCP-3**	20%	86: 14	78	7
5	**SCP-3**	10%	74: 26	66	13
6	**SCP-3**	5%	-[c]	77	16
7	**SCP-4**	5%	-[c]	87	7
8	**SCP-4**	2.5%	-[c]	85	9
9	**SCP-4**	1%	-[c]	87	9

[a]Ratios of **P** and **CHD** were obtained by ^{1}H NMR analysis of crude mixture; [b]yields are for the isolated compounds. [c]Ratios of **P** and **CHD** was unable to determined due to the poor solubility in $CDCl_3$, or the integration of the terminal groups are not practical in NMR.

4. Stacked NMR spectroscopy of ROMP of SCP-3 and SCP-4

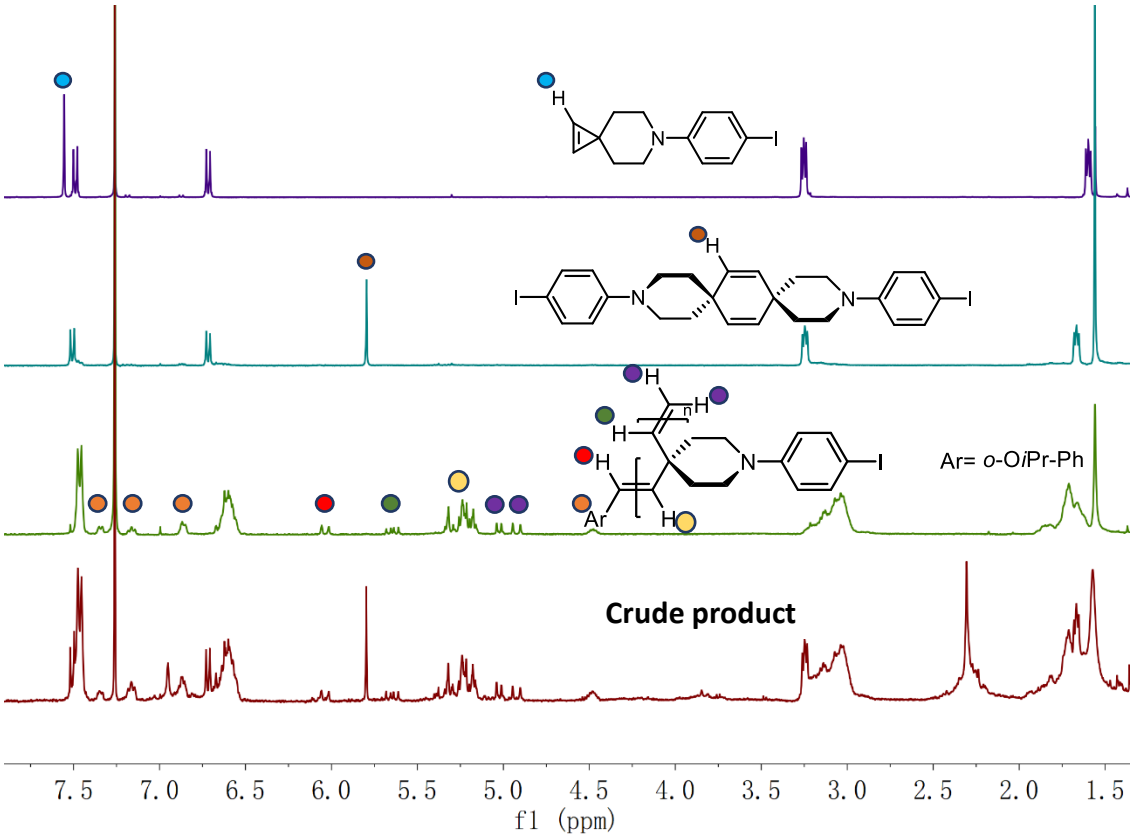


Figure S1. A stacked NMR spectrum in $CDCl_3$, 293K: (a) monomer **SCP-3** (b) **CHD-3** (c) **P3** (d) crude mixture of **H-G-II** catalyzed ROMP reaction.

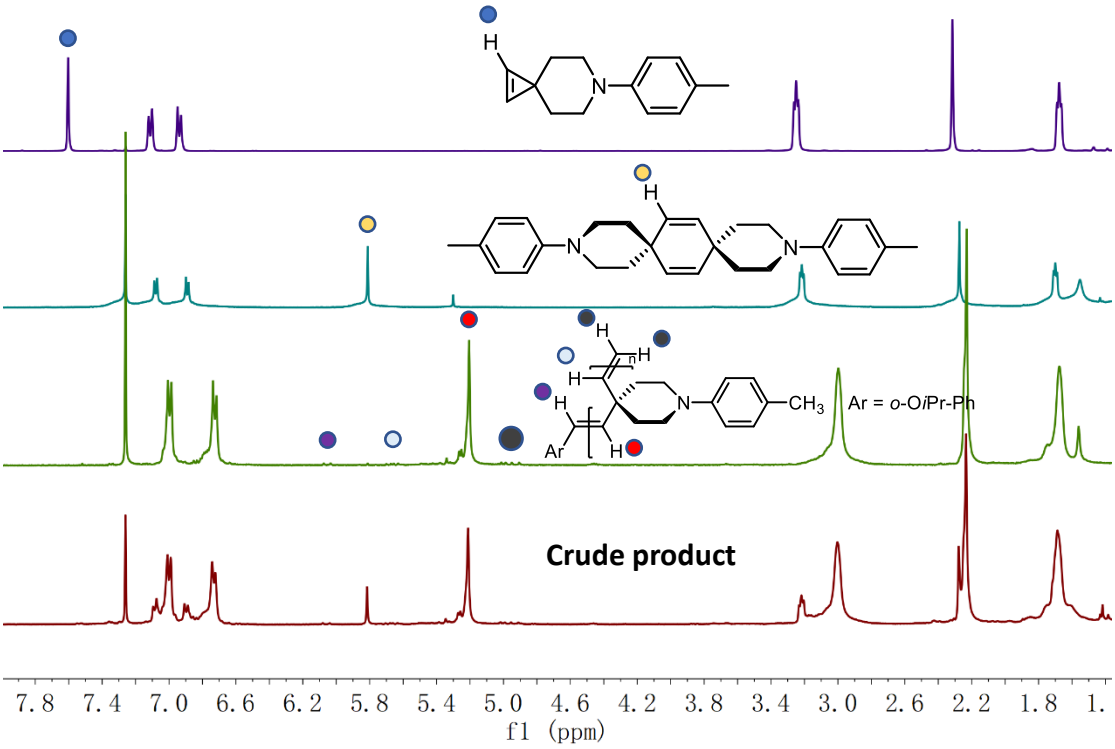
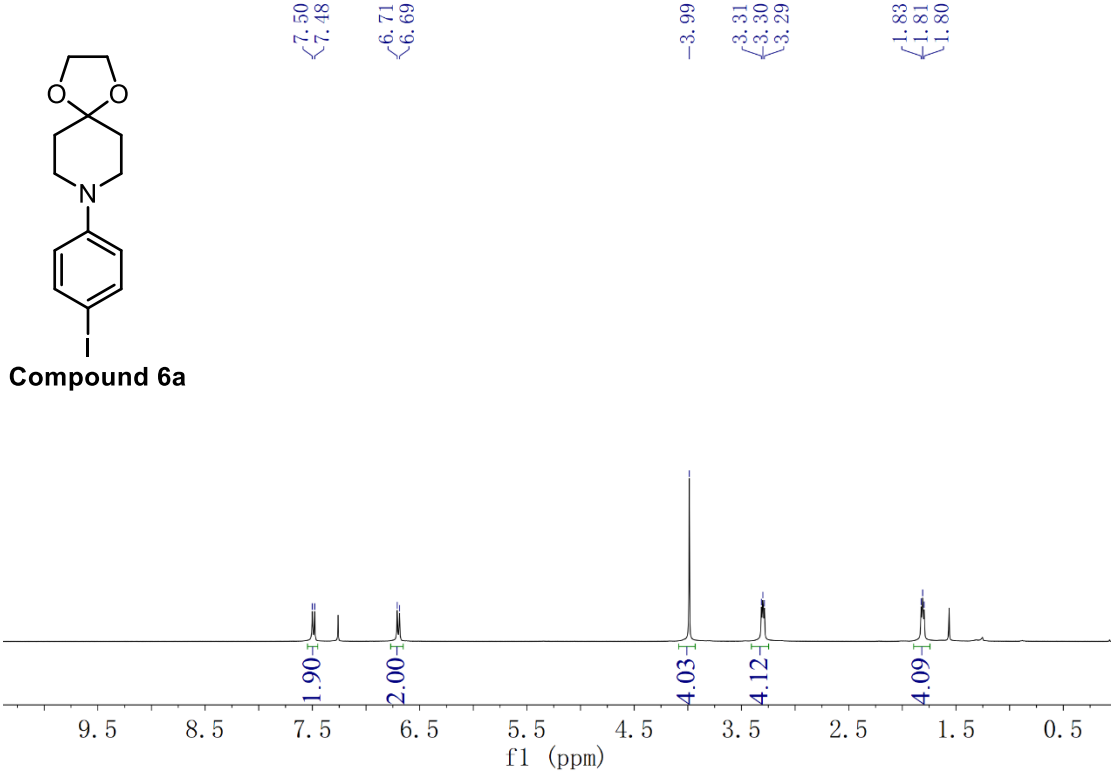


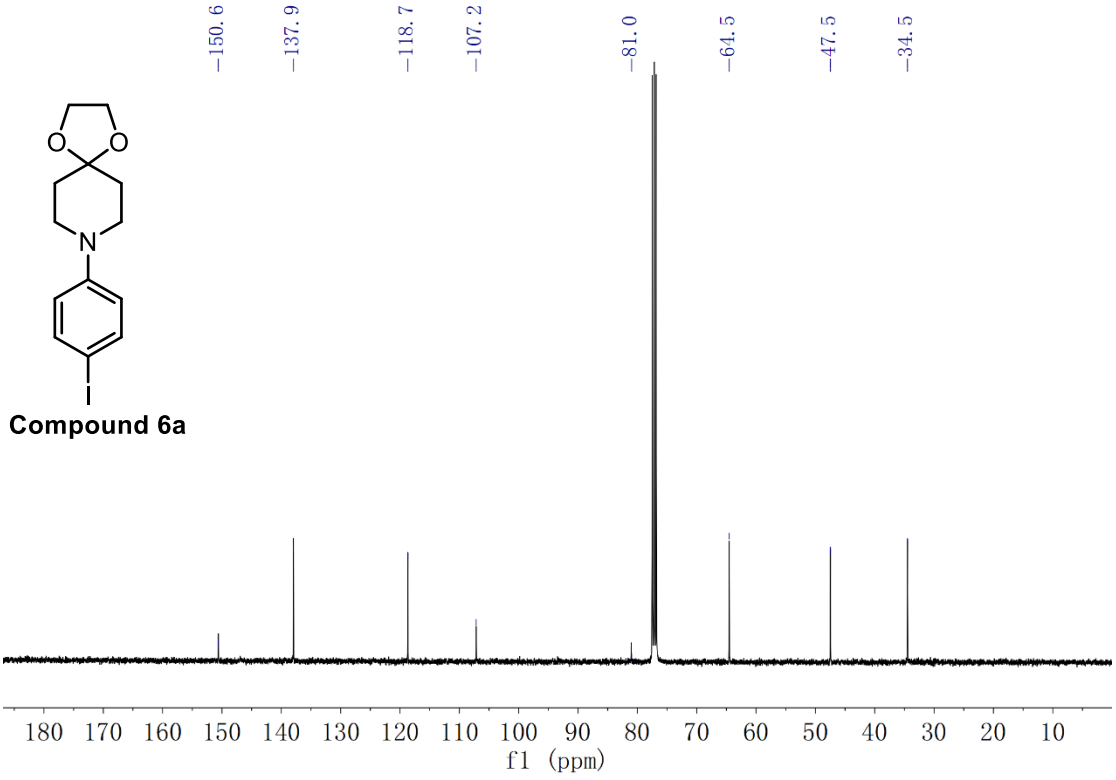
Figure S2. A stacked NMR spectrum in $CDCl_3$, 293K: (a) monomer **SCP-4** (b) **CHD-4** (c) **P4** (d) crude mixture of **H-G-II** catalyzed ROMP reaction

5. NMR spectra



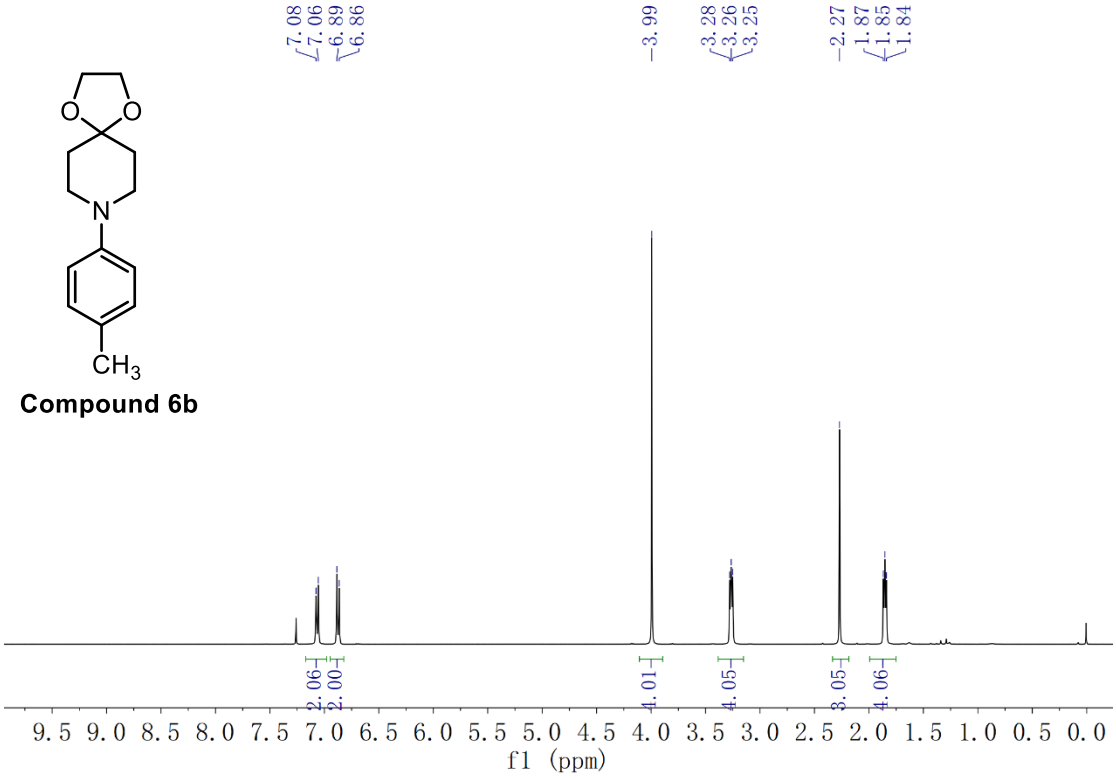
Compound 6a

^{1}H NMR, $CDCl_3$, 400 MHz



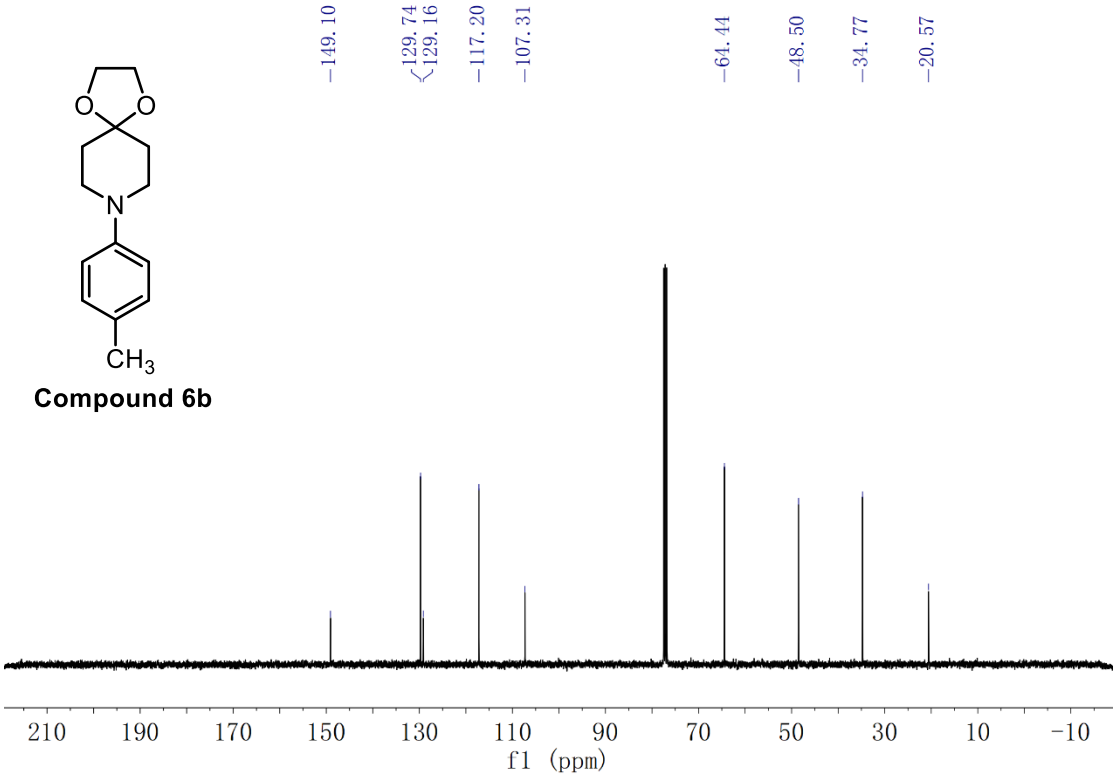
Compound 6a

^{13}C NMR, $CDCl_3$, 101 MHz



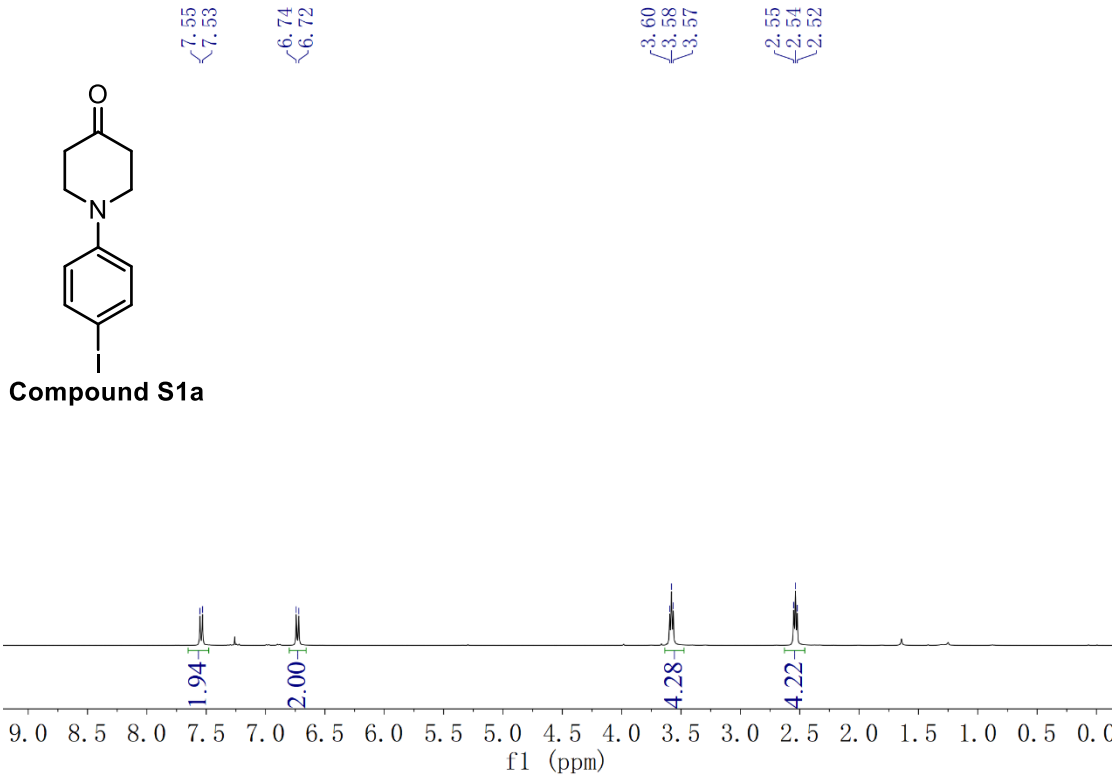
Compound 6b

^{1}H NMR, $CDCl_3$, 400 MHz



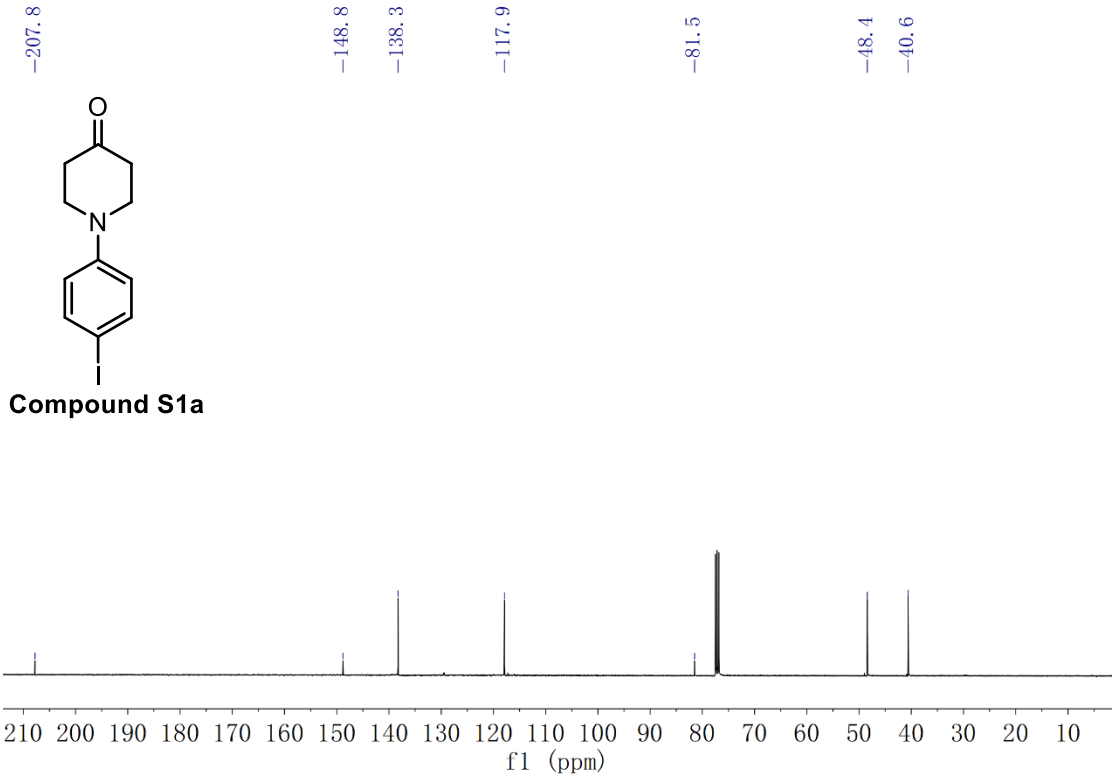
Compound 6b

^{13}C NMR, $CDCl_3$, 101 MHz



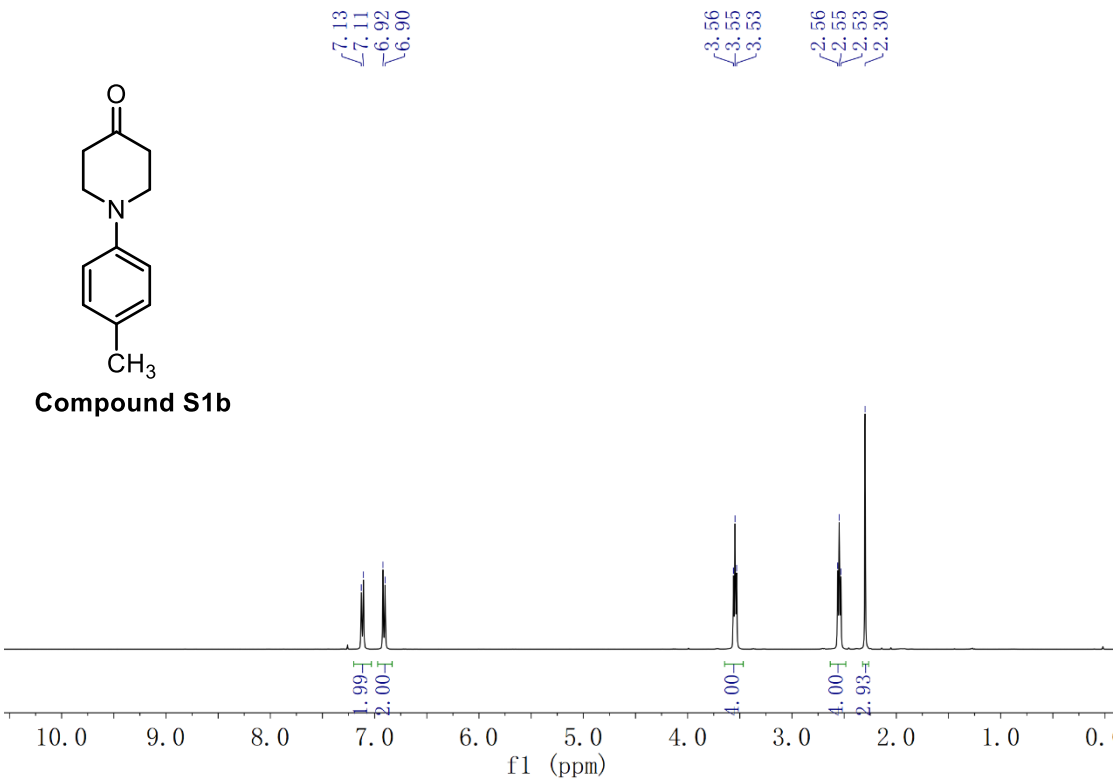
Compound S1a

^{1}H NMR, $CDCl_3$, 400 MHz

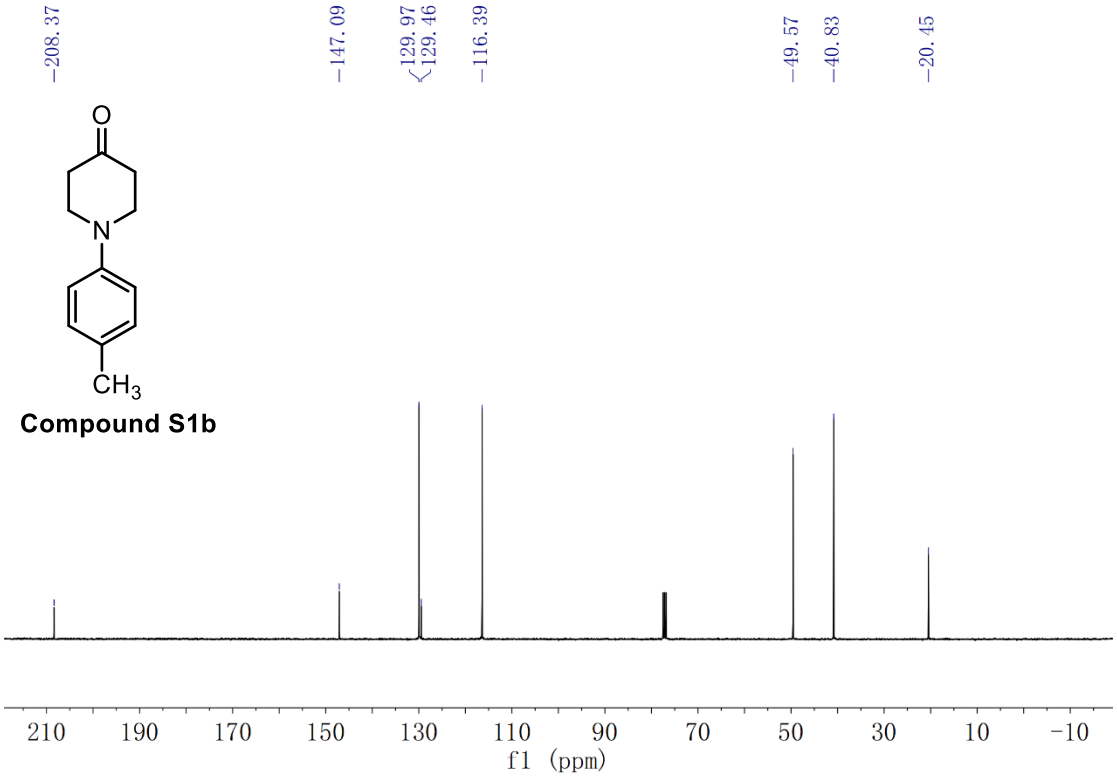


Compound S1a

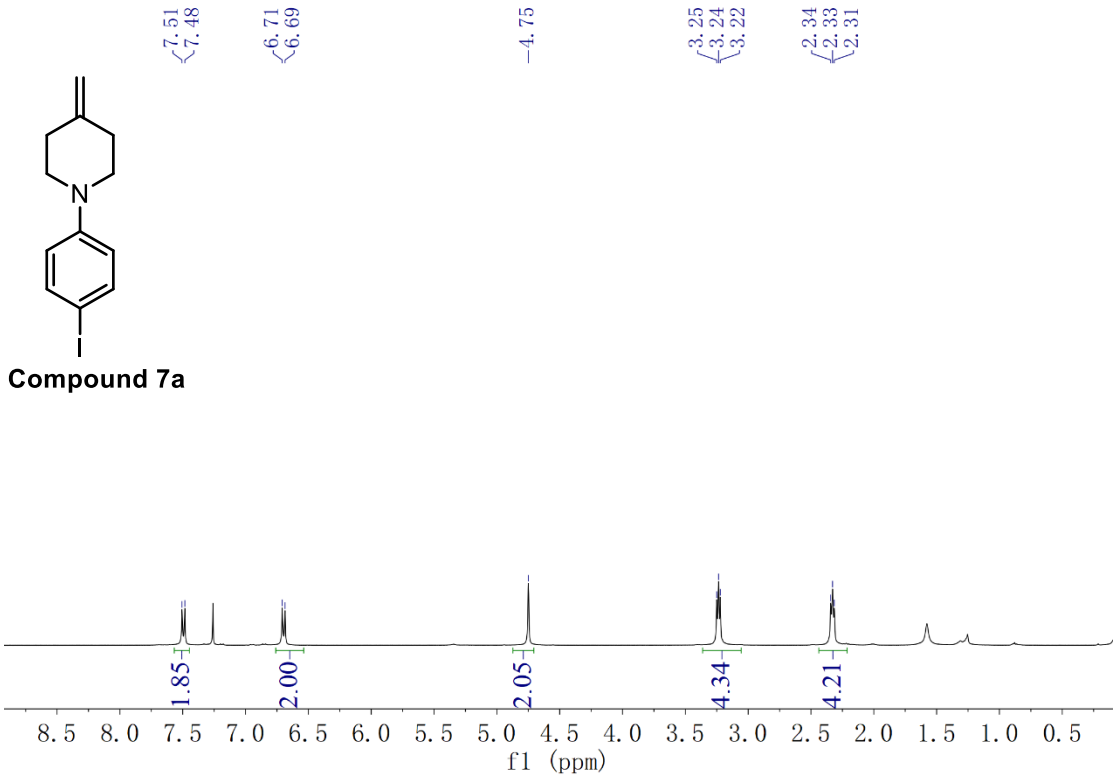
^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 400 MHz

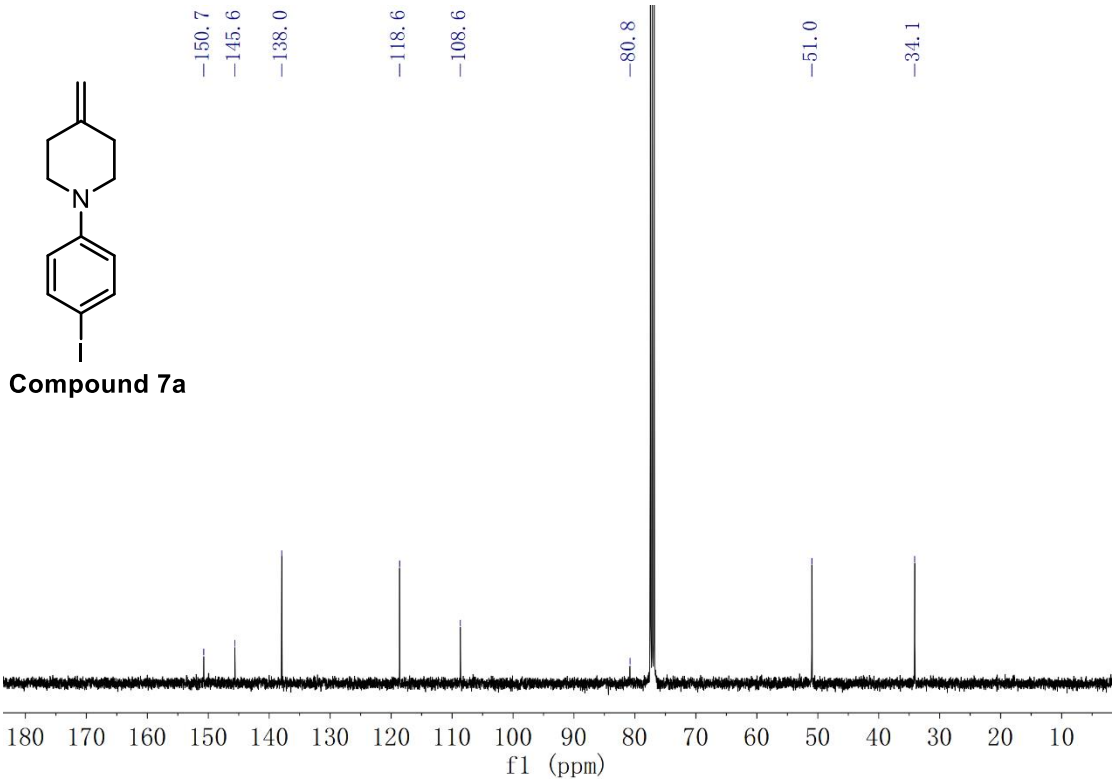


^{13}C NMR, $CDCl_3$, 101 MHz



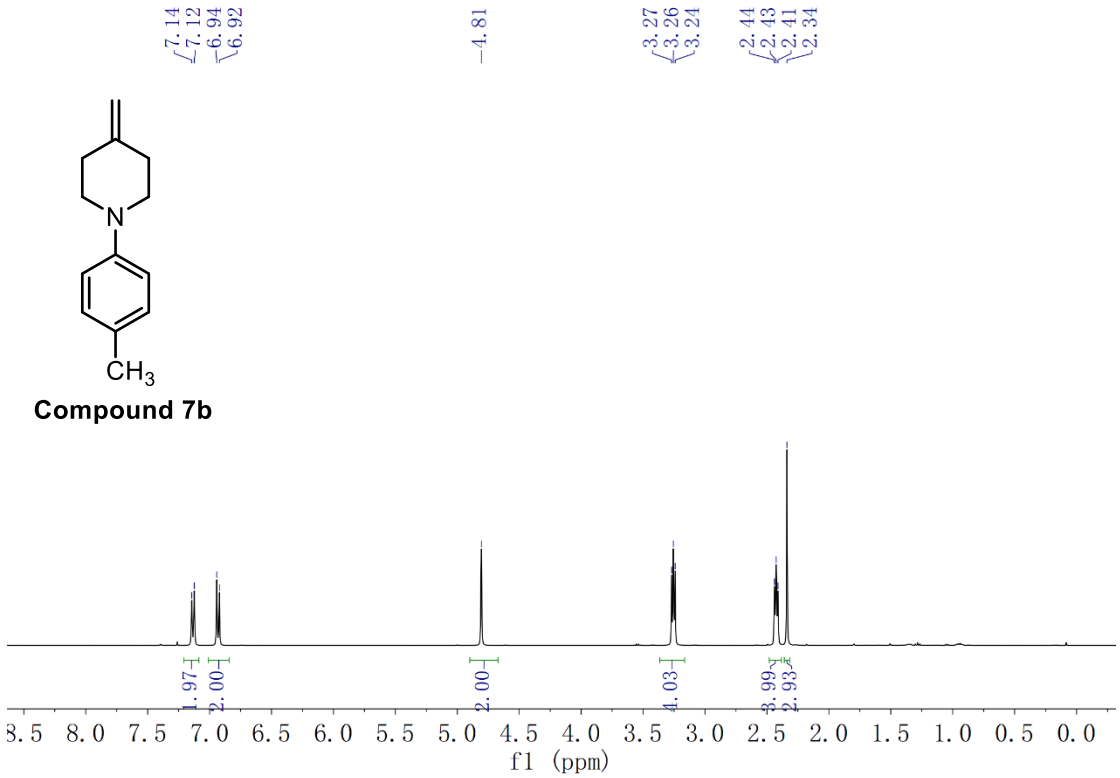
Compound 7a

^{1}H NMR, $CDCl_3$, 400 MHz



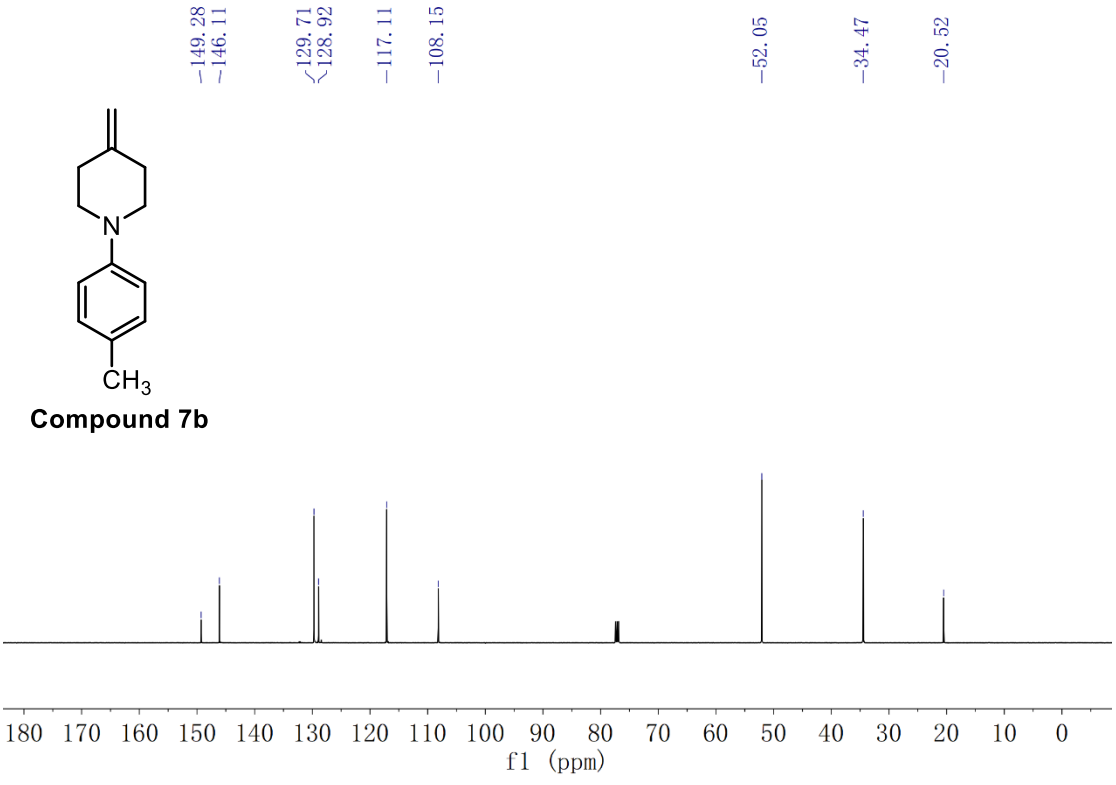
Compound 7a

^{13}C NMR, $CDCl_3$, 101 MHz



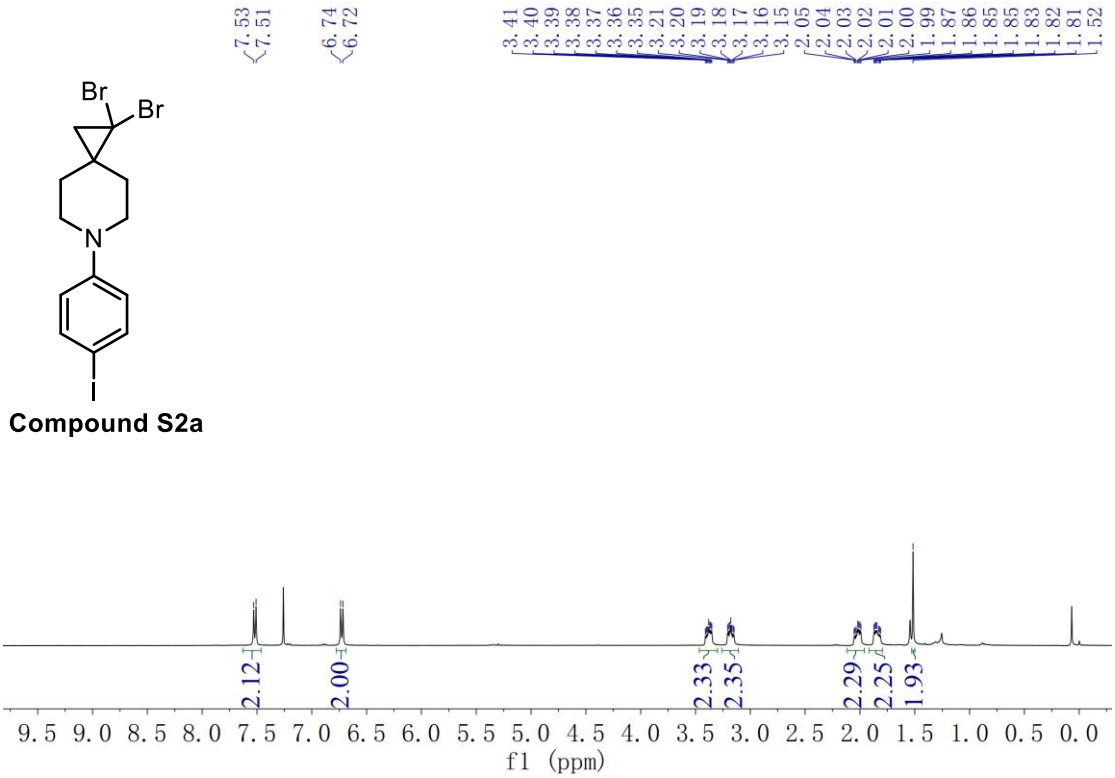
Compound 7b

^{1}H NMR, $CDCl_3$, 400 MHz



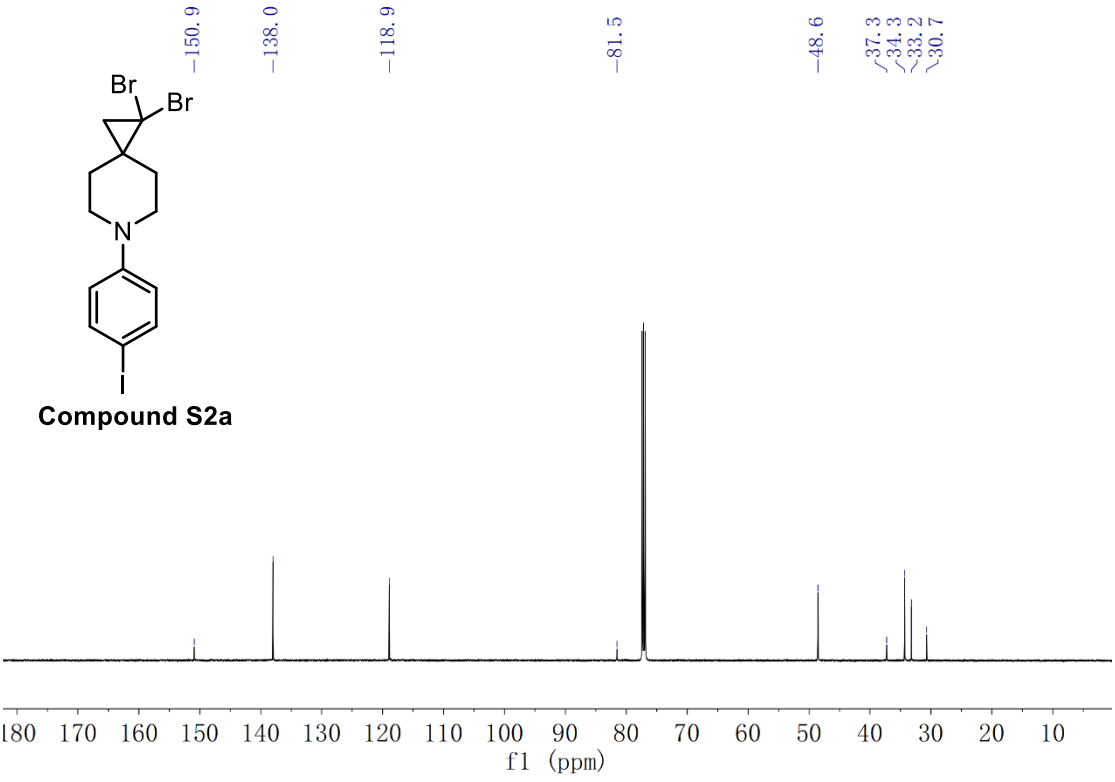
Compound 7b

^{13}C NMR, $CDCl_3$, 126 MHz



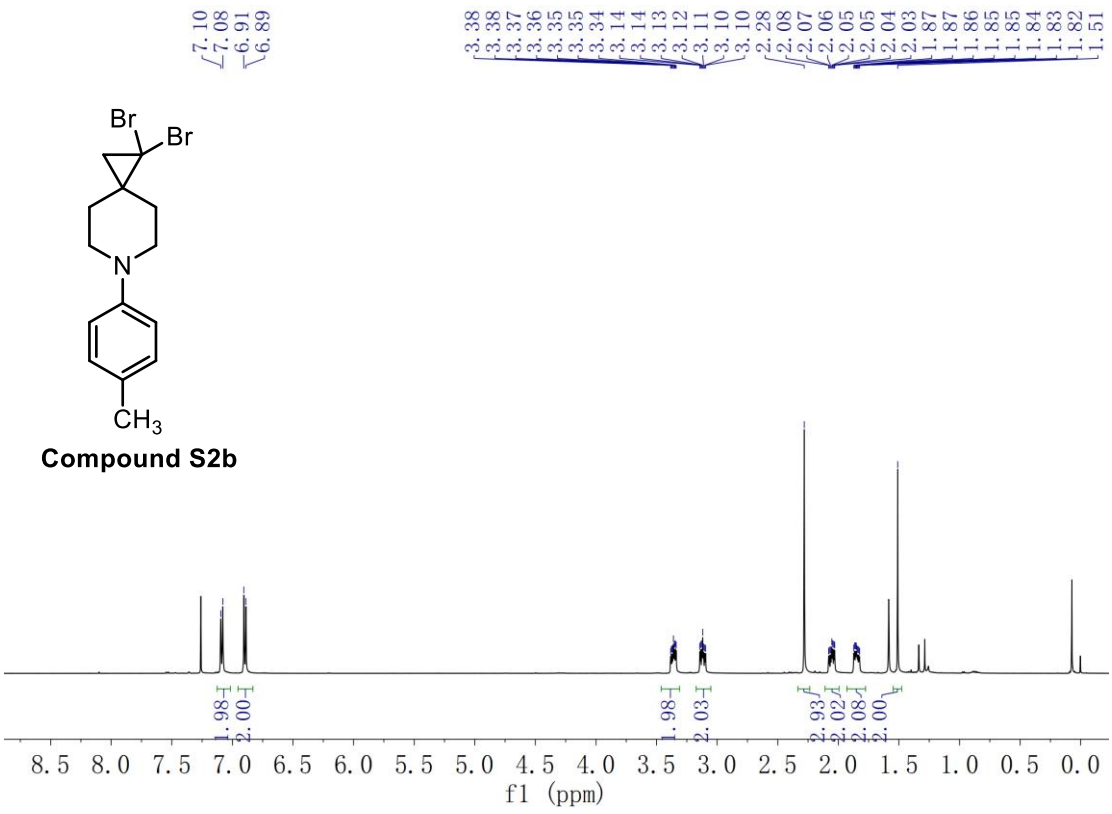
Compound S2a

^{1}H NMR, $CDCl_3$, 400 MHz



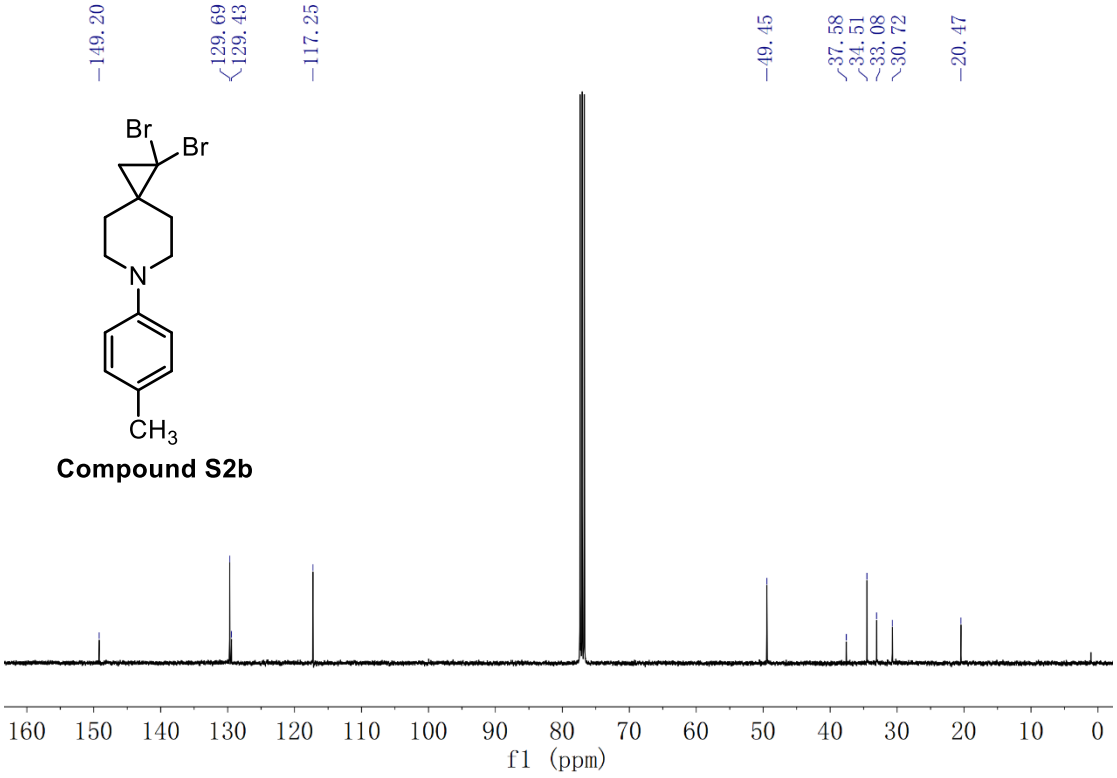
Compound S2a

^{13}C NMR, $CDCl_3$, 126 MHz



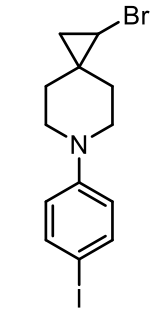
Compound S2b

^{1}H NMR, $CDCl_3$, 500 MHz

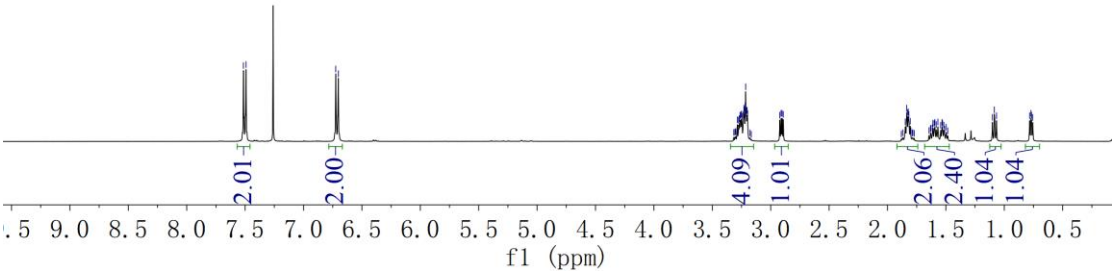


Compound S2b

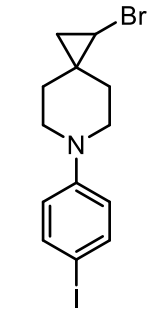
^{13}C NMR, $CDCl_3$, 101 MHz



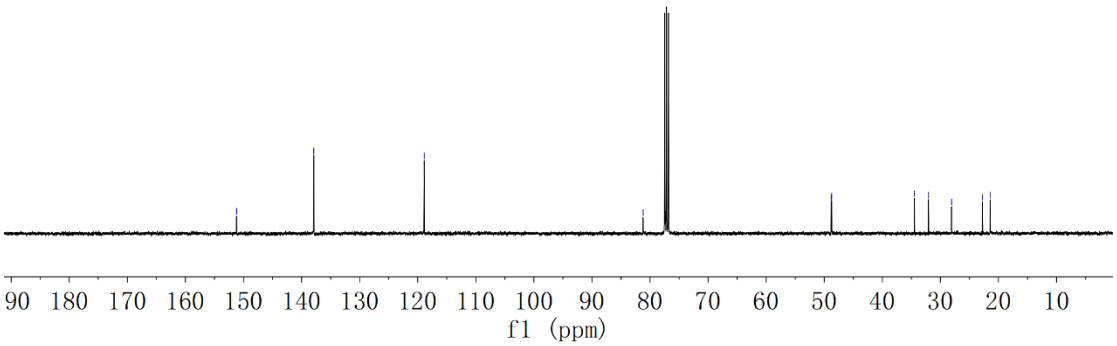
Compound 8a



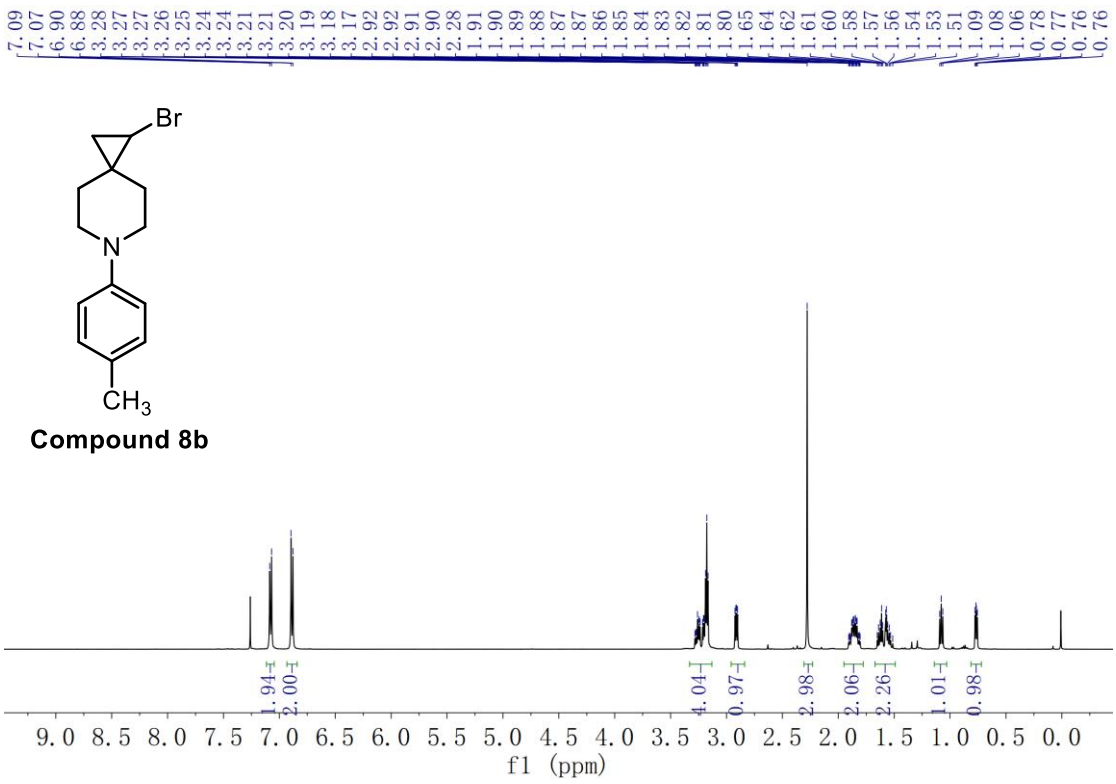
^{1}H NMR, $CDCl_3$, 400 MHz



Compound 8a

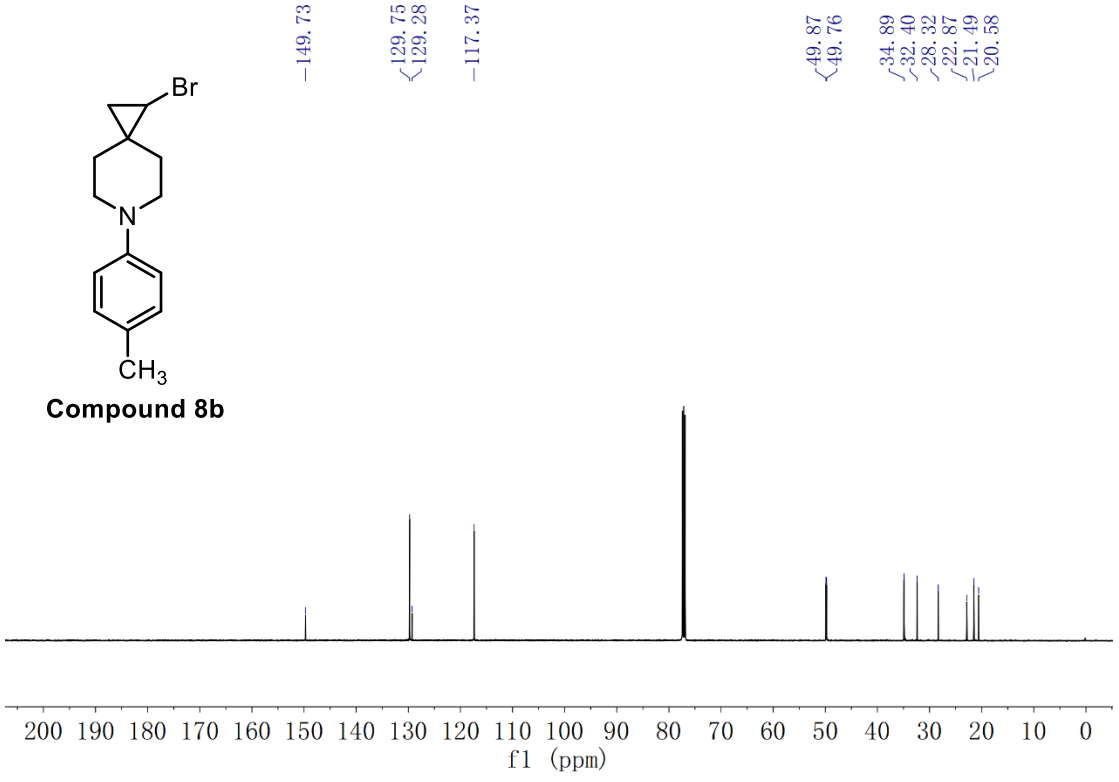


^{13}C NMR, $CDCl_3$, 101 MHz



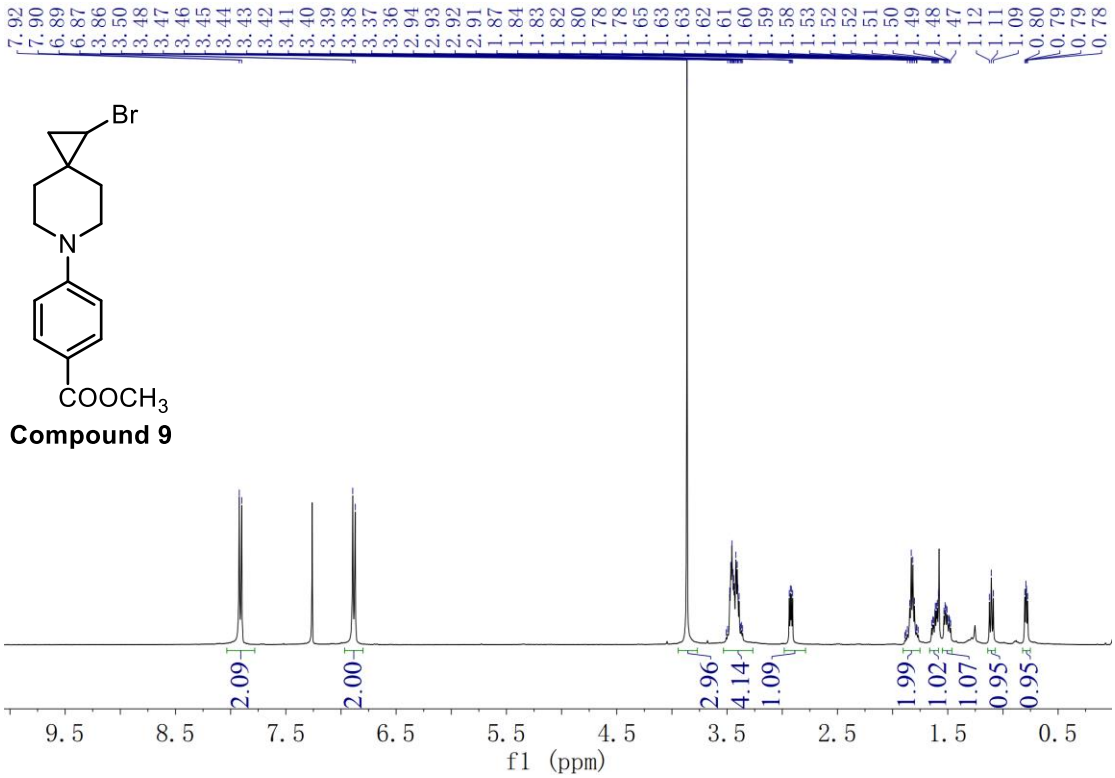
Compound 8b

^{1}H NMR, $CDCl_3$, 500 MHz

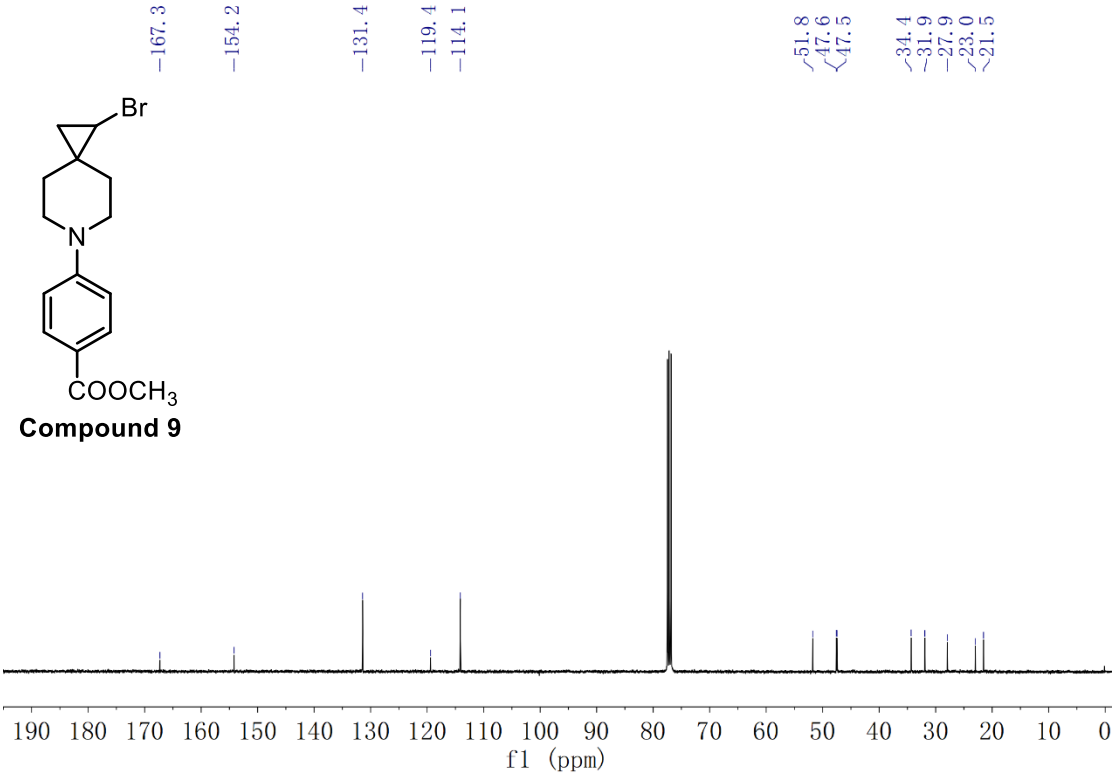


Compound 8b

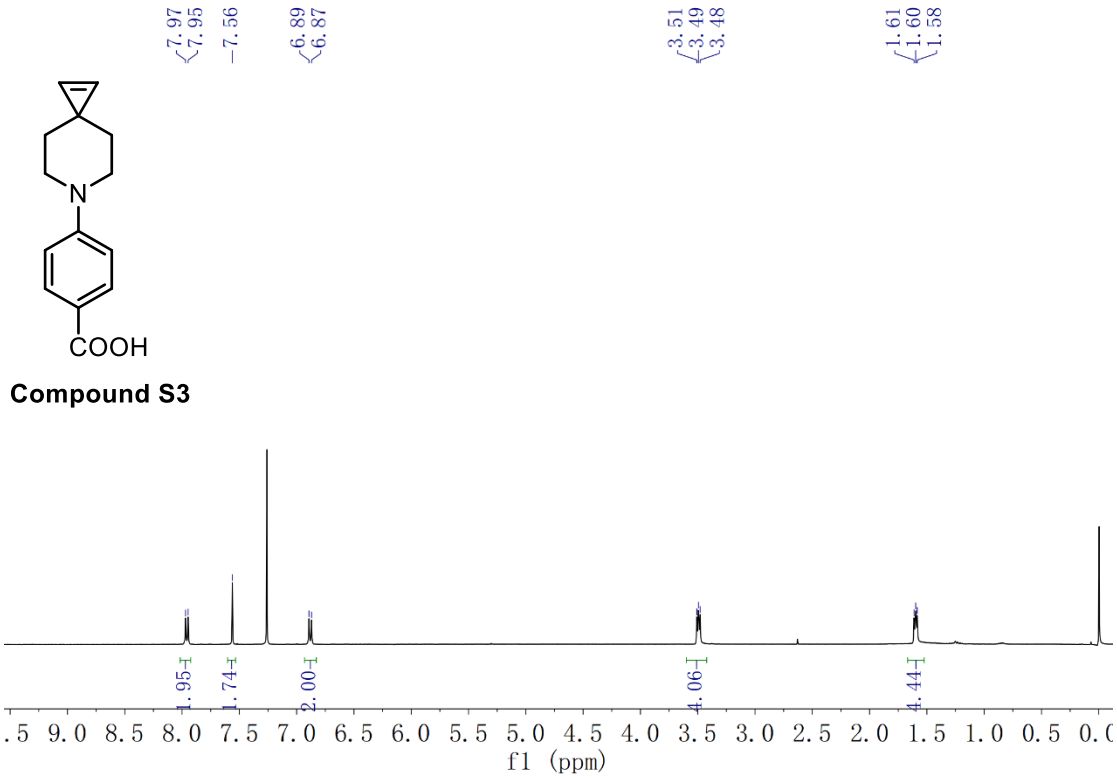
^{13}C NMR, $CDCl_3$, 126 MHz



^{1}H NMR, $CDCl_3$, 400 MHz

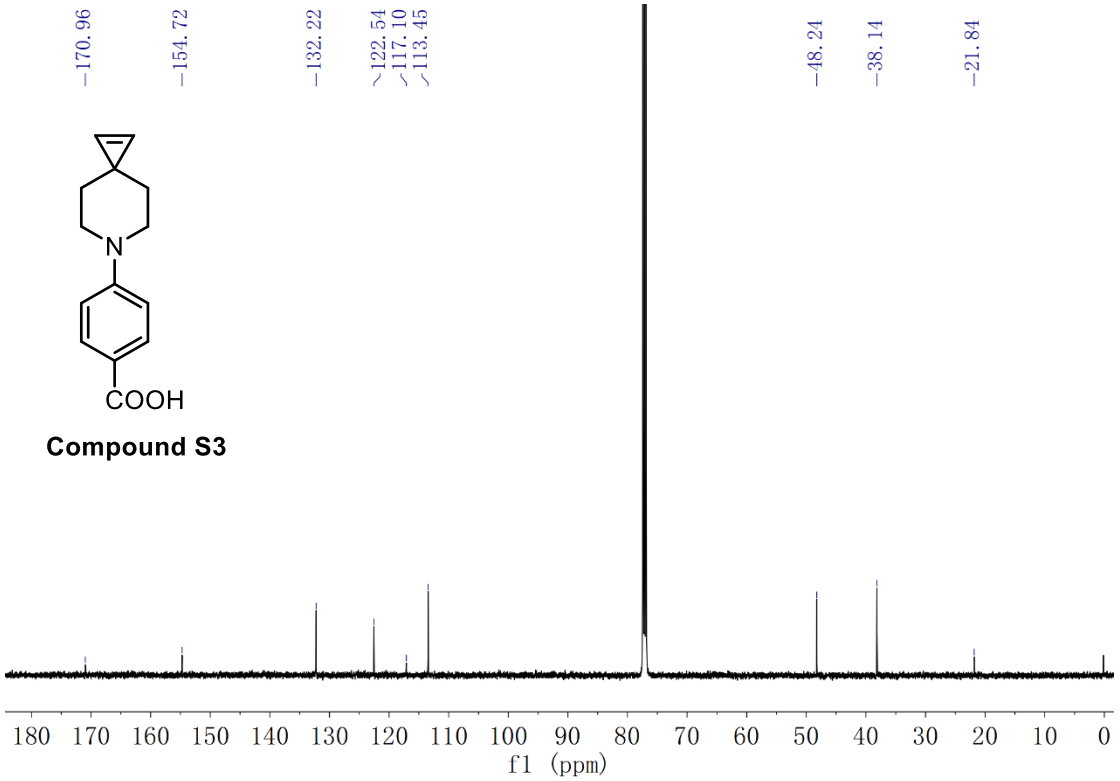


^{13}C NMR, $CDCl_3$, 101 MHz



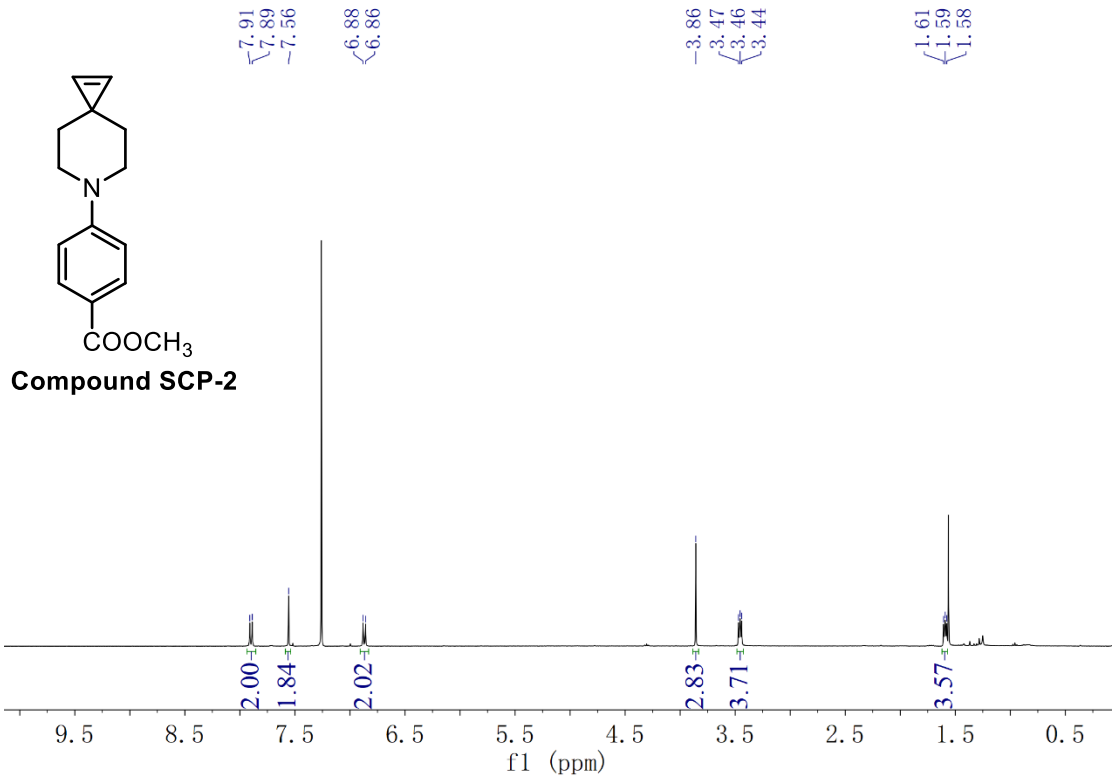
Compound S3

^{1}H NMR, $CDCl_3$, 400 MHz



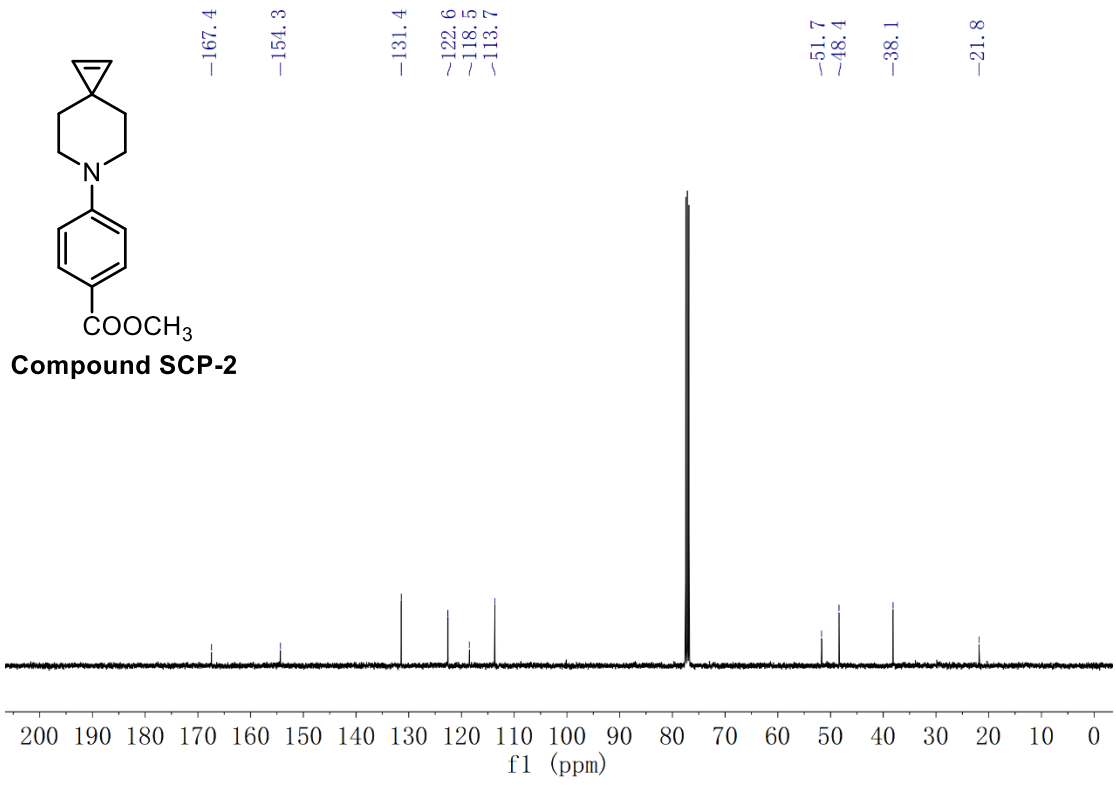
Compound S3

^{13}C NMR, $CDCl_3$, 126 MHz



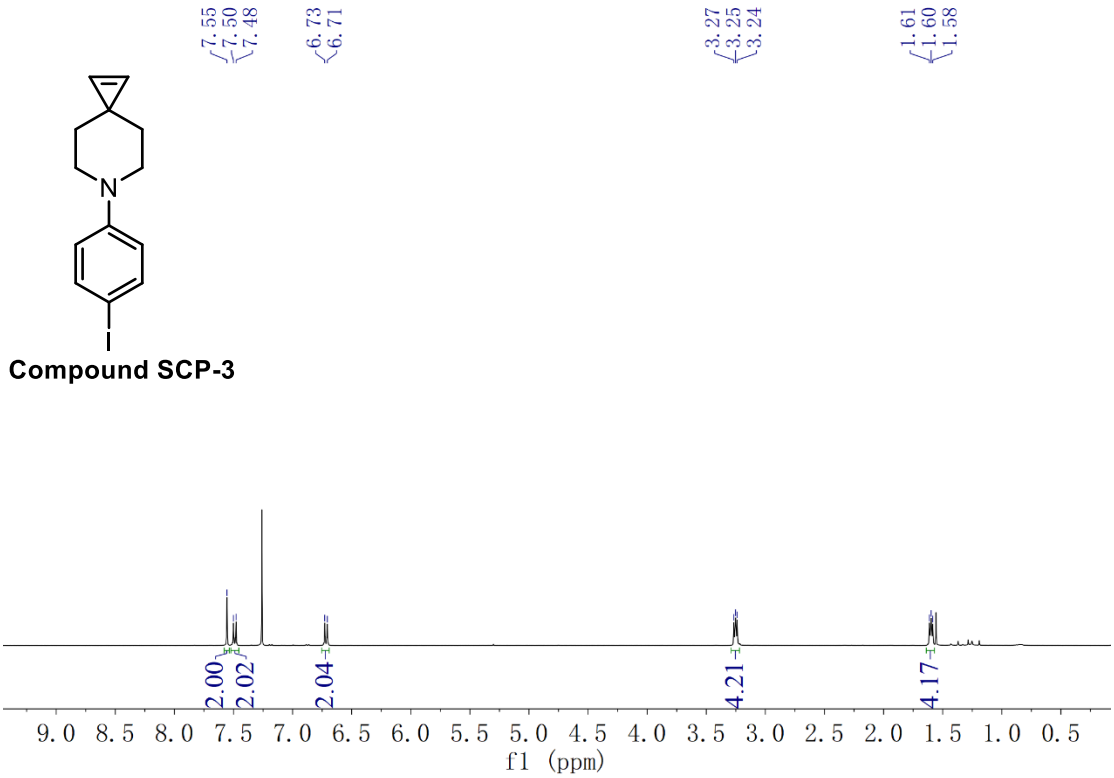
Compound SCP-2

^{1}H NMR, $CDCl_3$, 400 MHz



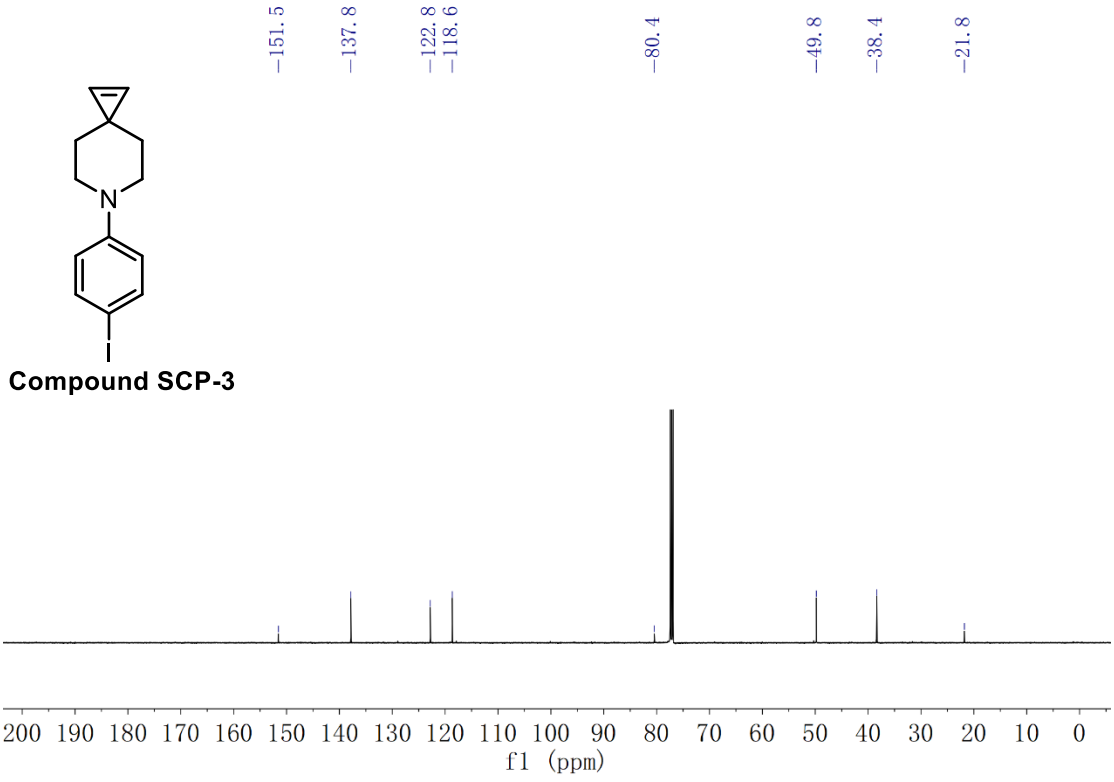
Compound SCP-2

^{13}C NMR, $CDCl_3$, 101 MHz



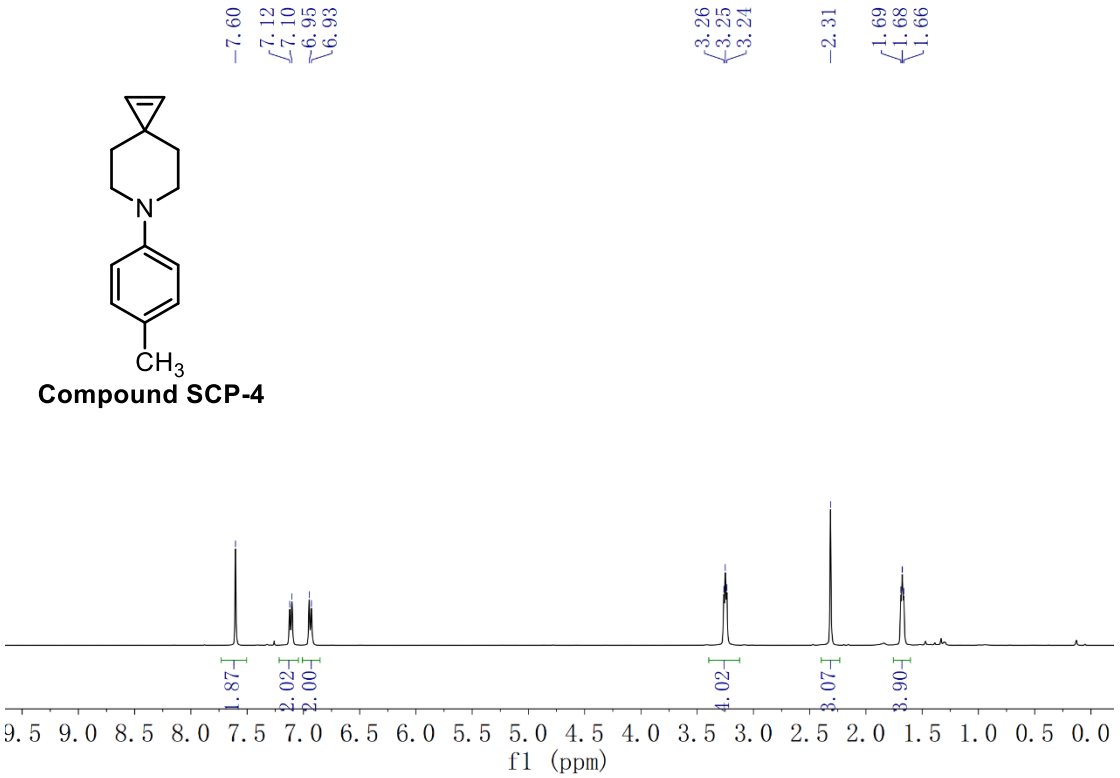
Compound SCP-3

^{1}H NMR, $CDCl_3$, 400 MHz



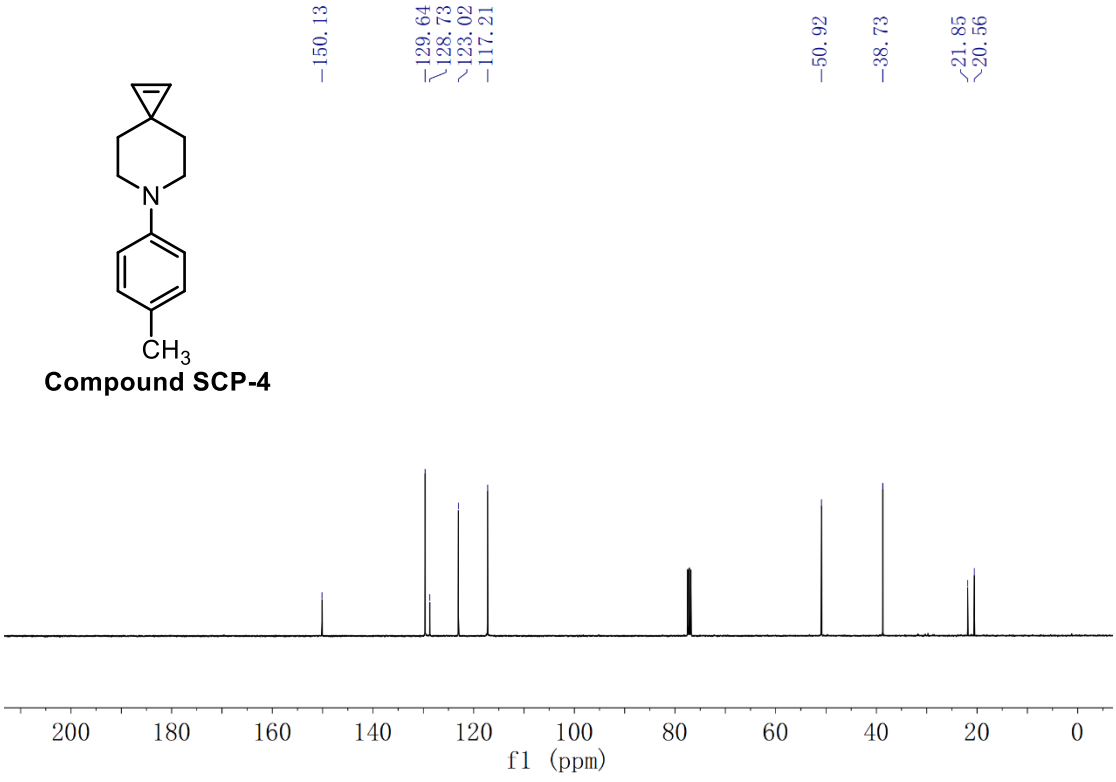
Compound SCP-3

^{13}C NMR, $CDCl_3$, 126 MHz



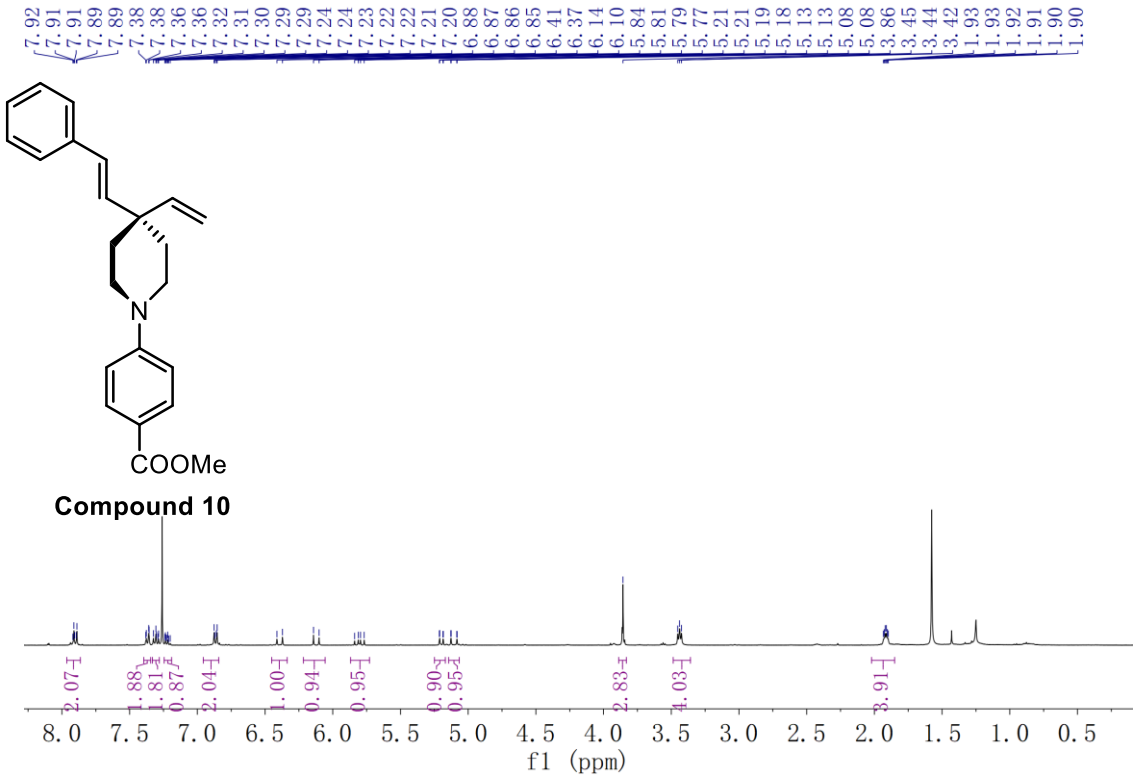
Compound SCP-4

^{1}H NMR, $CDCl_3$, 400 MHz

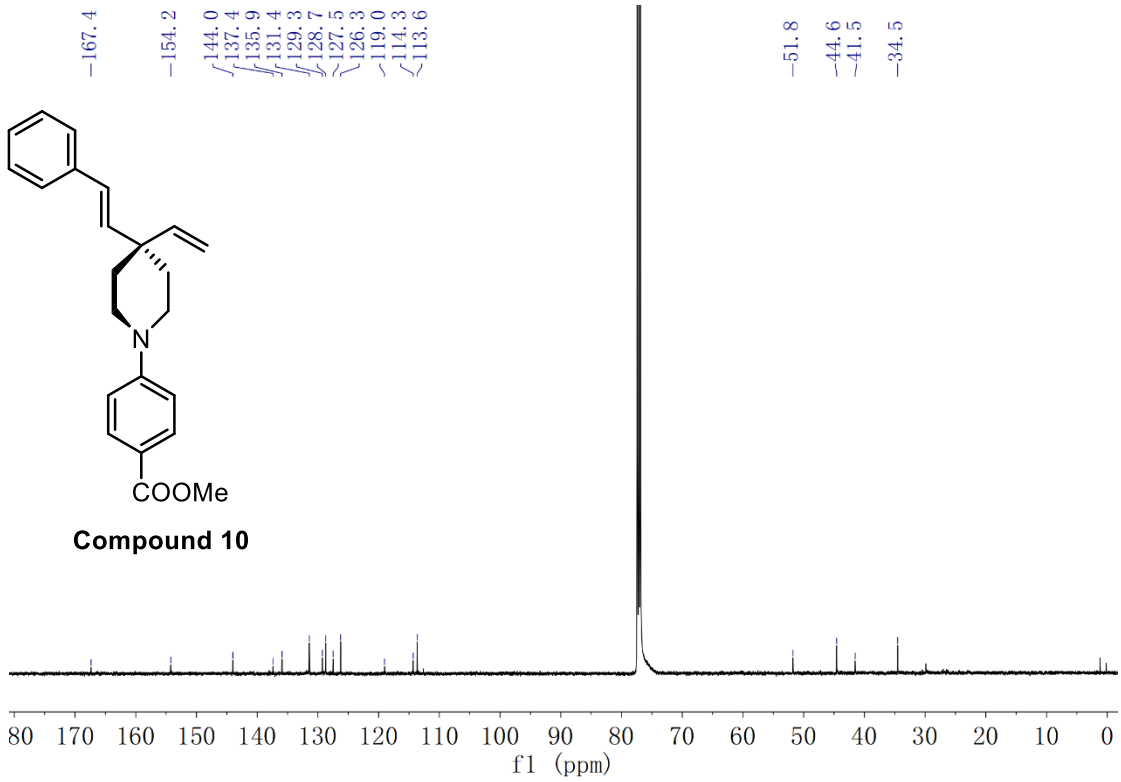


Compound SCP-4

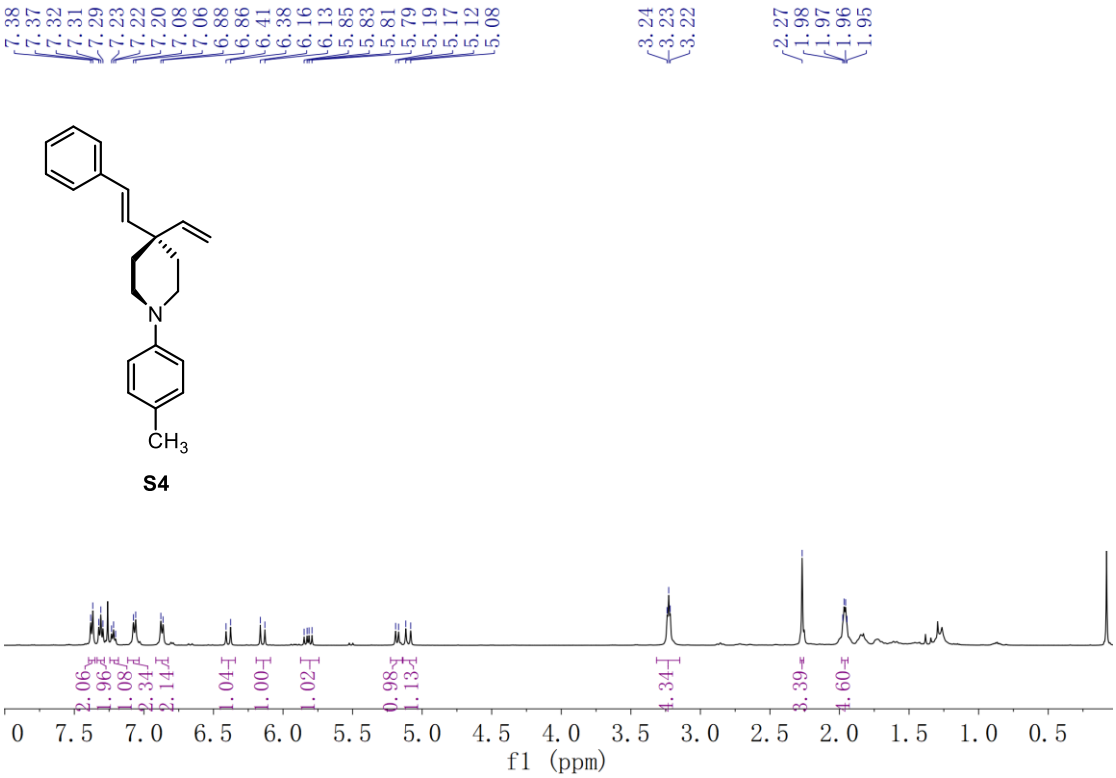
^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 400 MHz

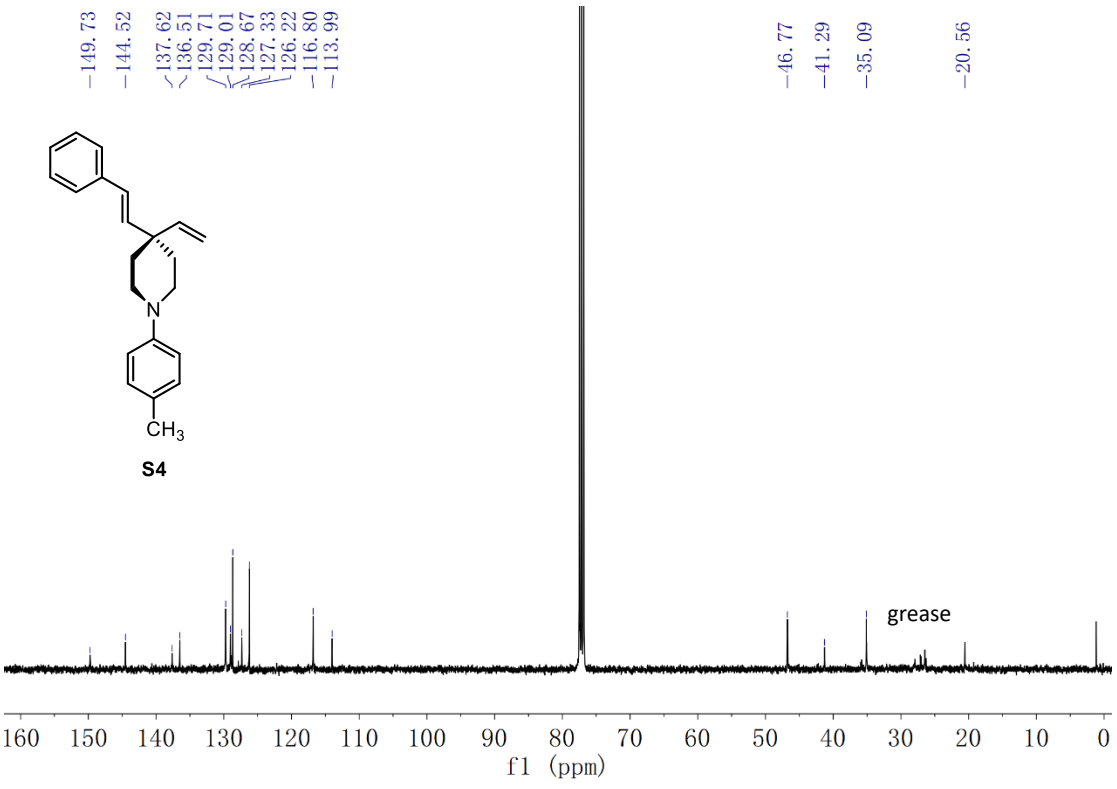


^{13}C NMR, $CDCl_3$, 126 MHz



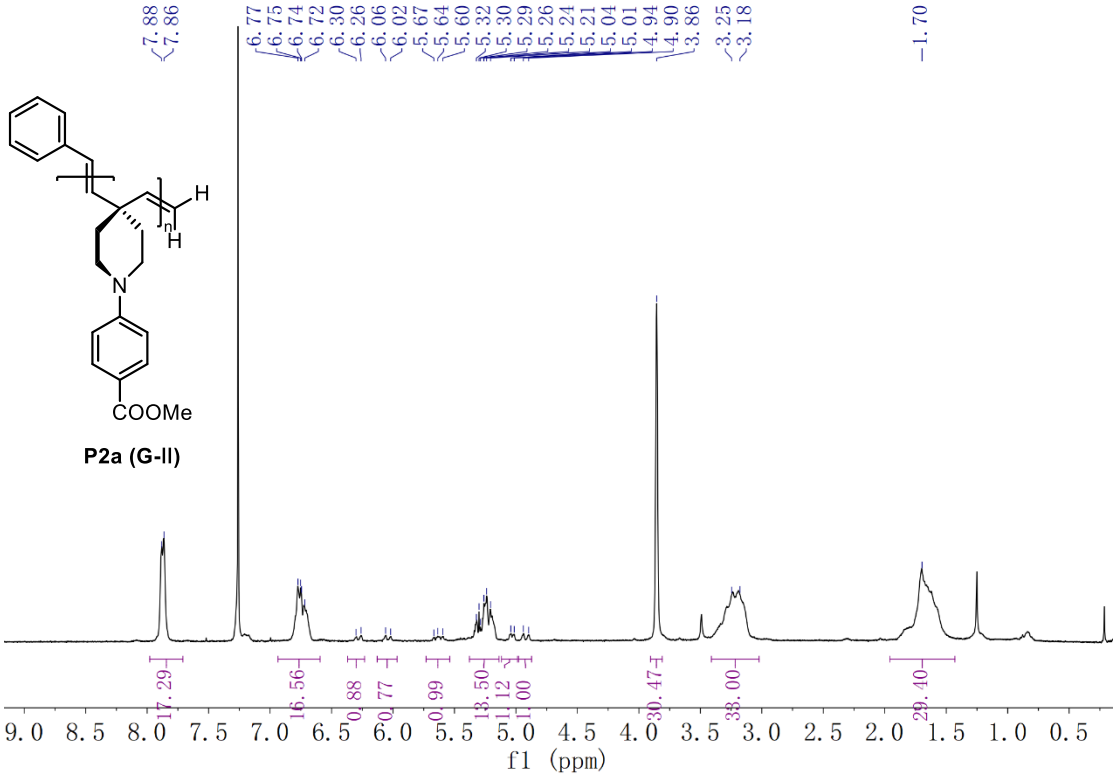
S4

^{1}H NMR, $CDCl_3$, 400 MHz



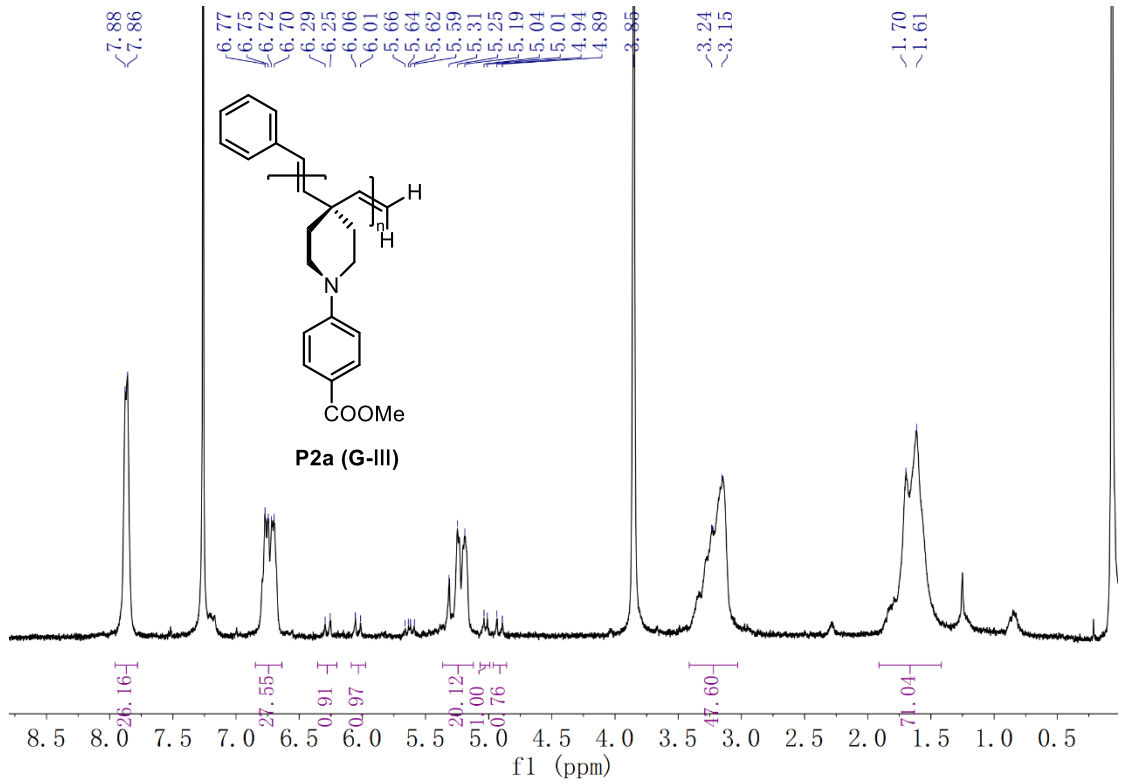
S4

^{13}C NMR, $CDCl_3$, 101 MHz



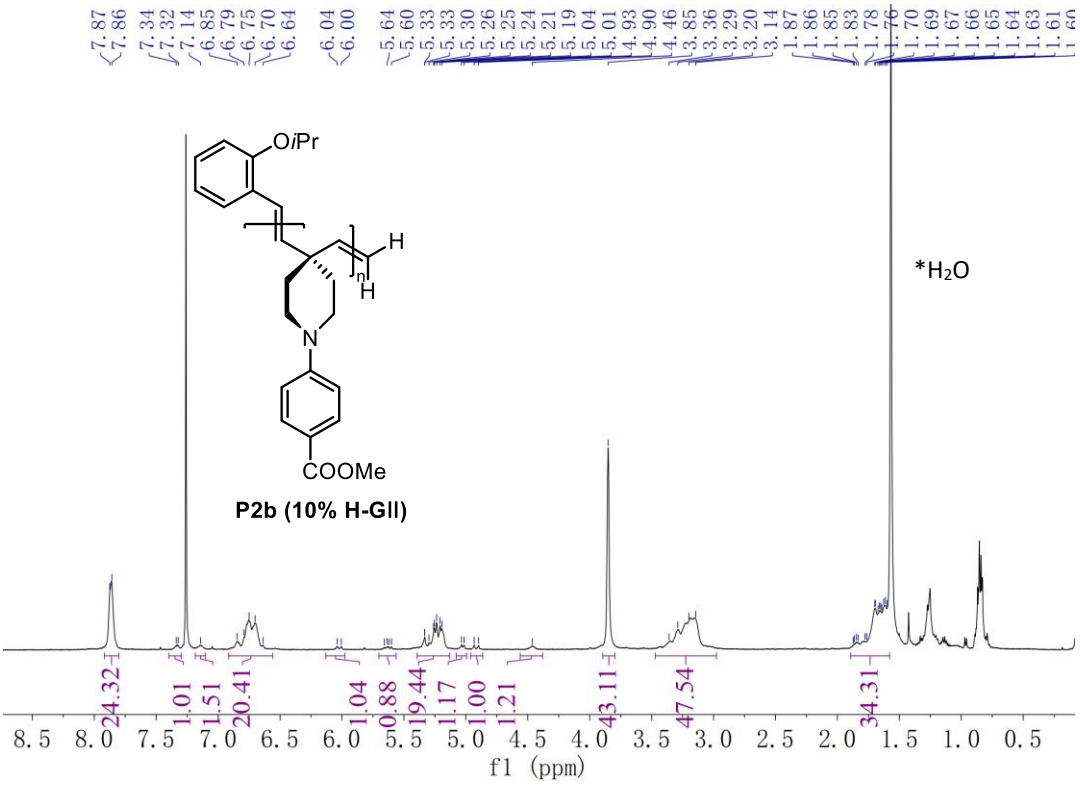
P2a (G-II)

^{1}H NMR, $CDCl_3$, 400 MHz

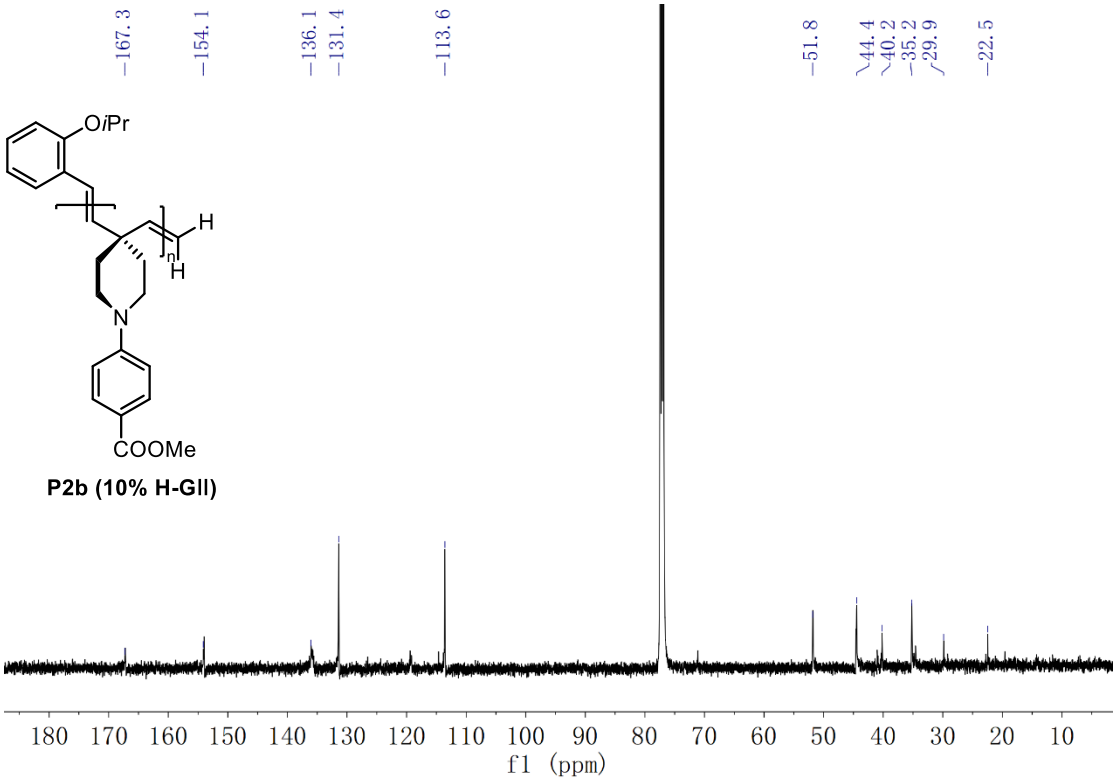


P2a (G-III)

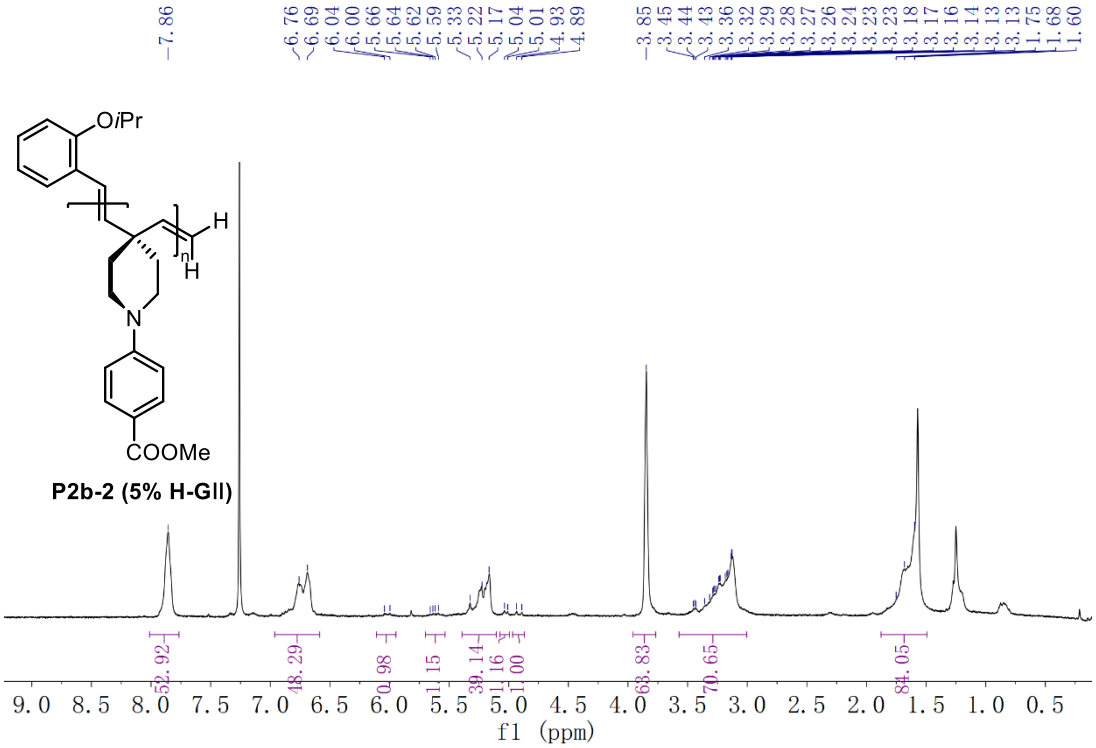
^{1}H NMR, $CDCl_3$, 400 MHz



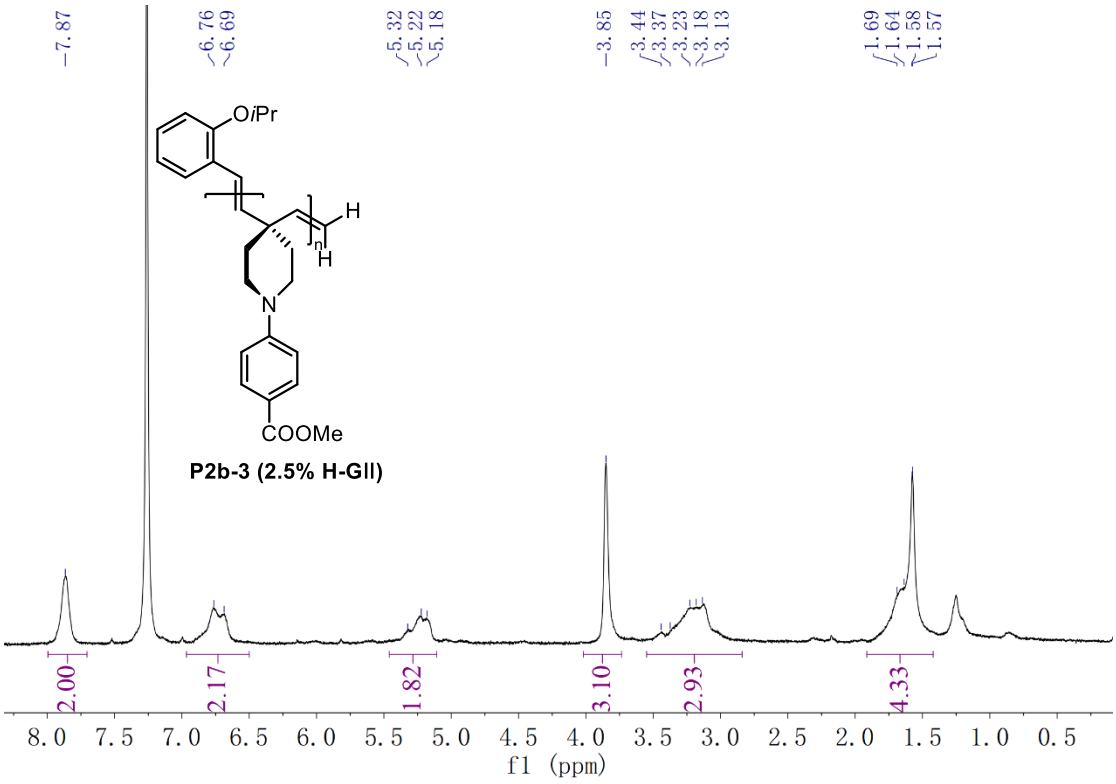
^{1}H NMR, $CDCl_3$, 500 MHz



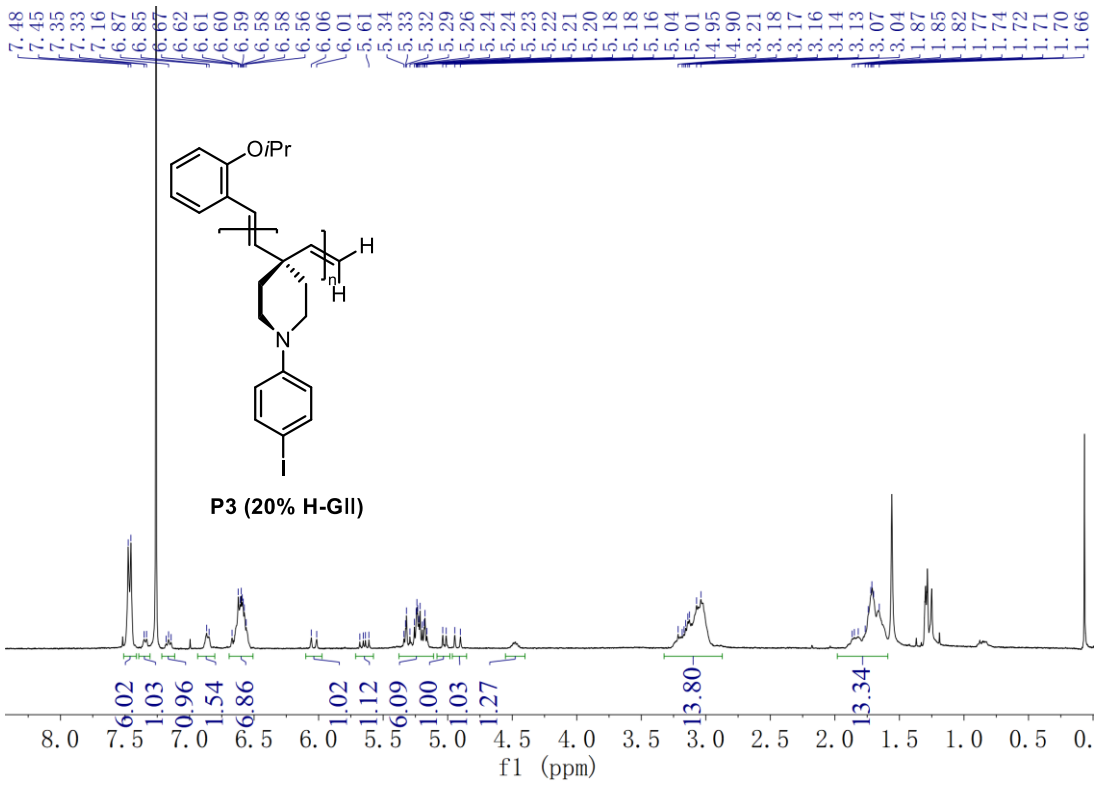
^{13}C NMR, $CDCl_3$, 126 MHz



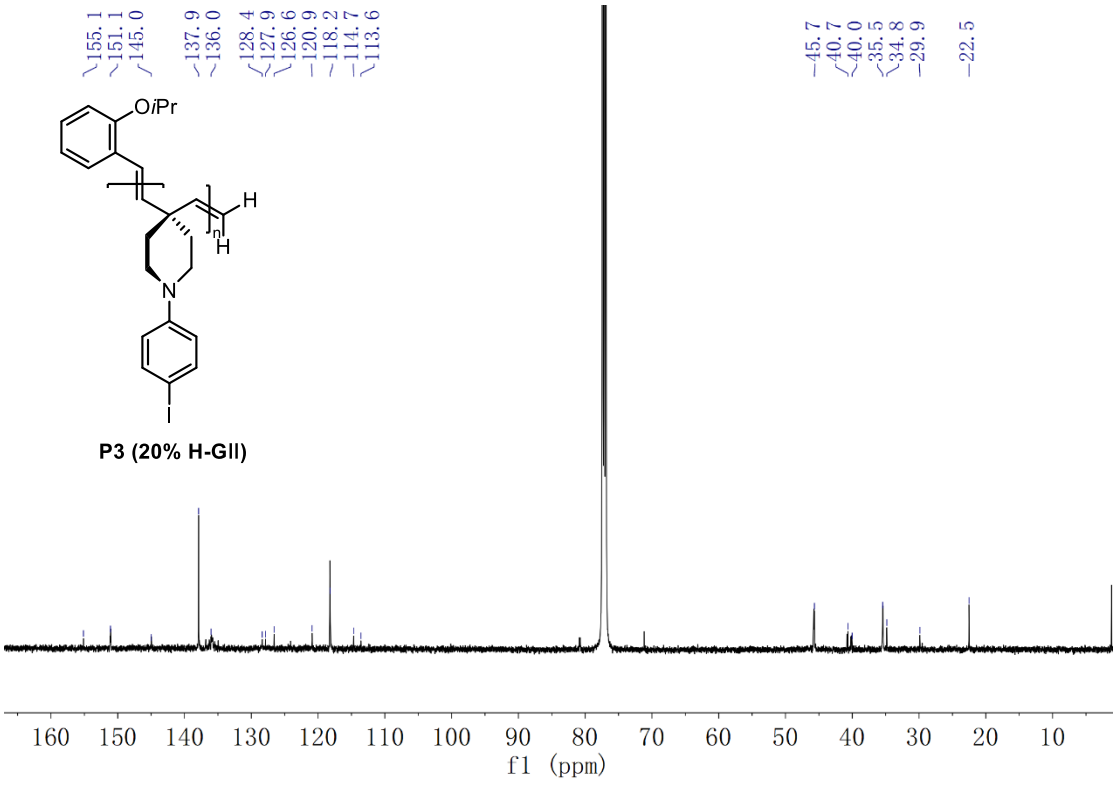
^{1}H NMR, $CDCl_3$, 400 MHz



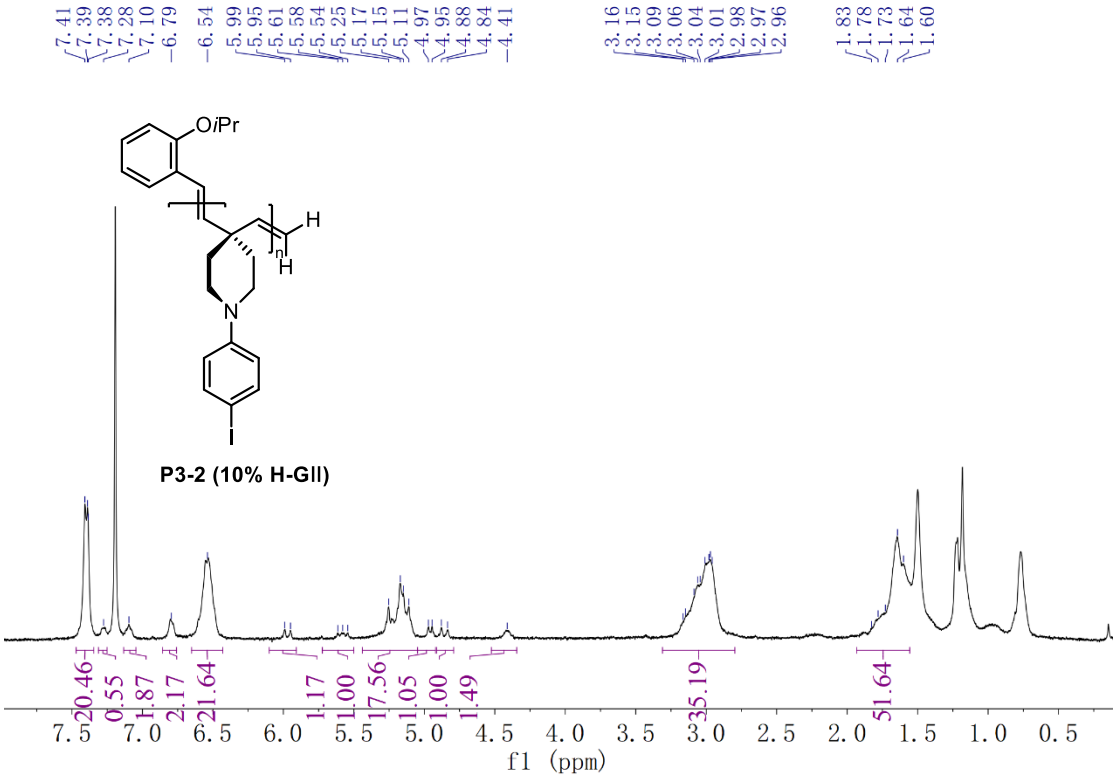
^{1}H NMR, $CDCl_3$, 400 MHz



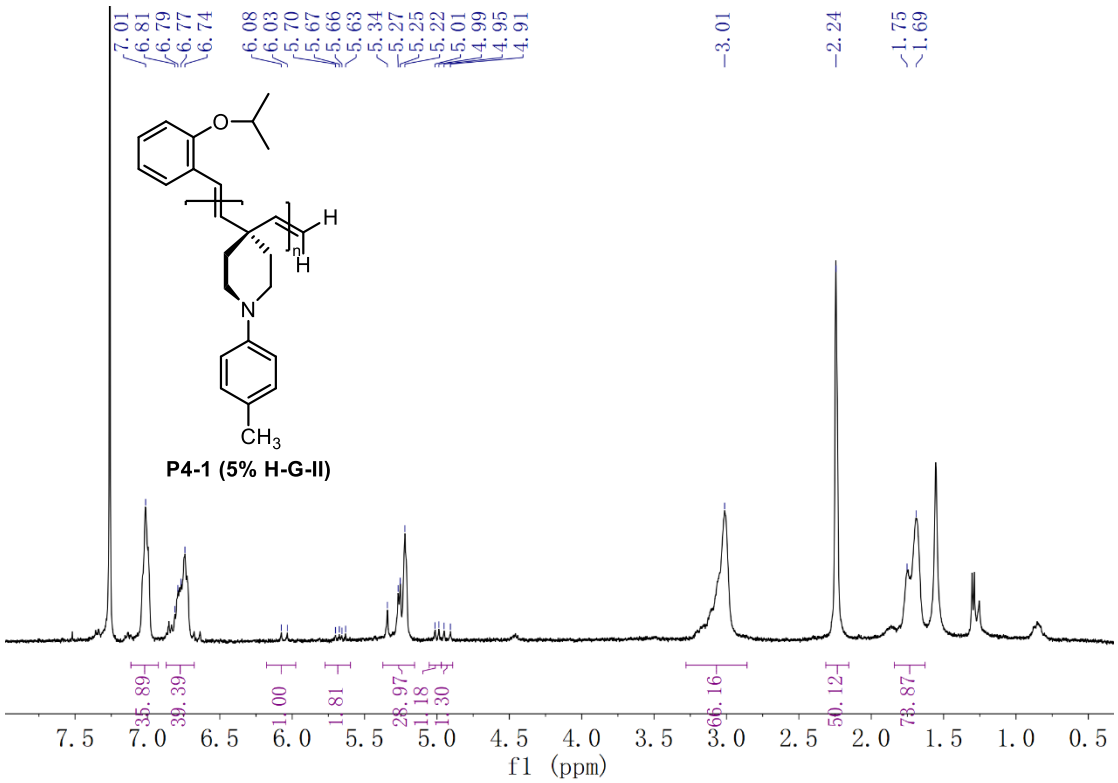
^{1}H NMR, $CDCl_3$, 400 MHz



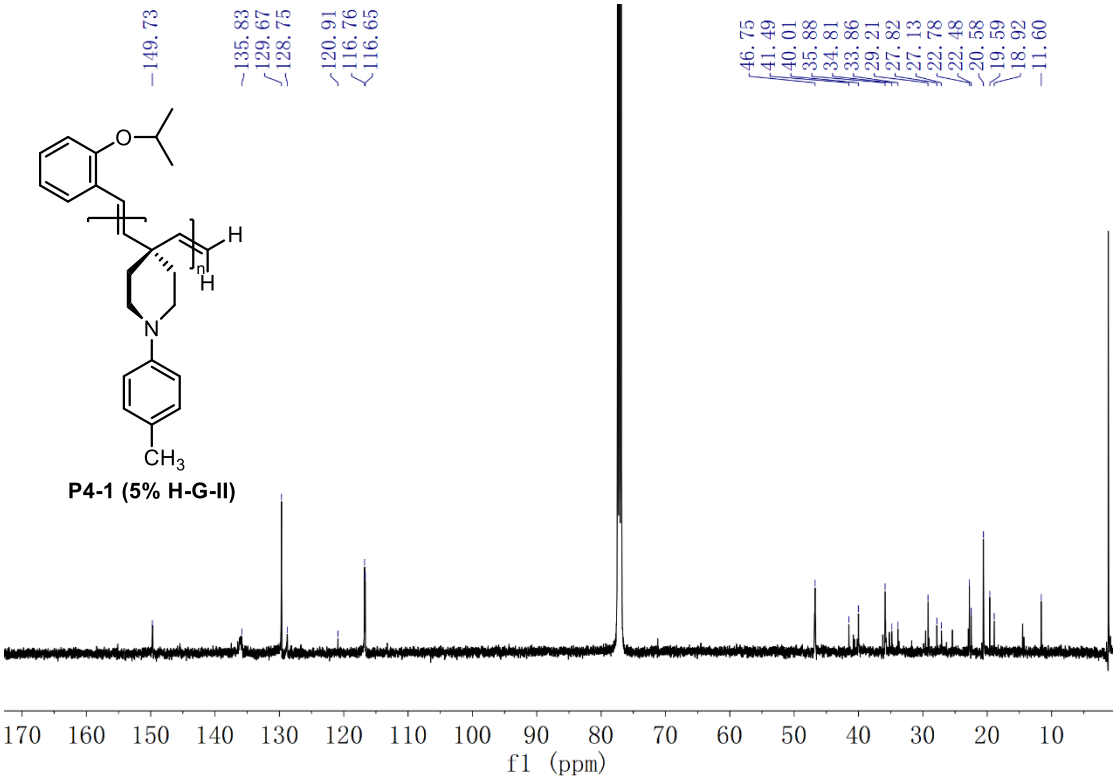
^{13}C NMR, $CDCl_3$, 126 MHz



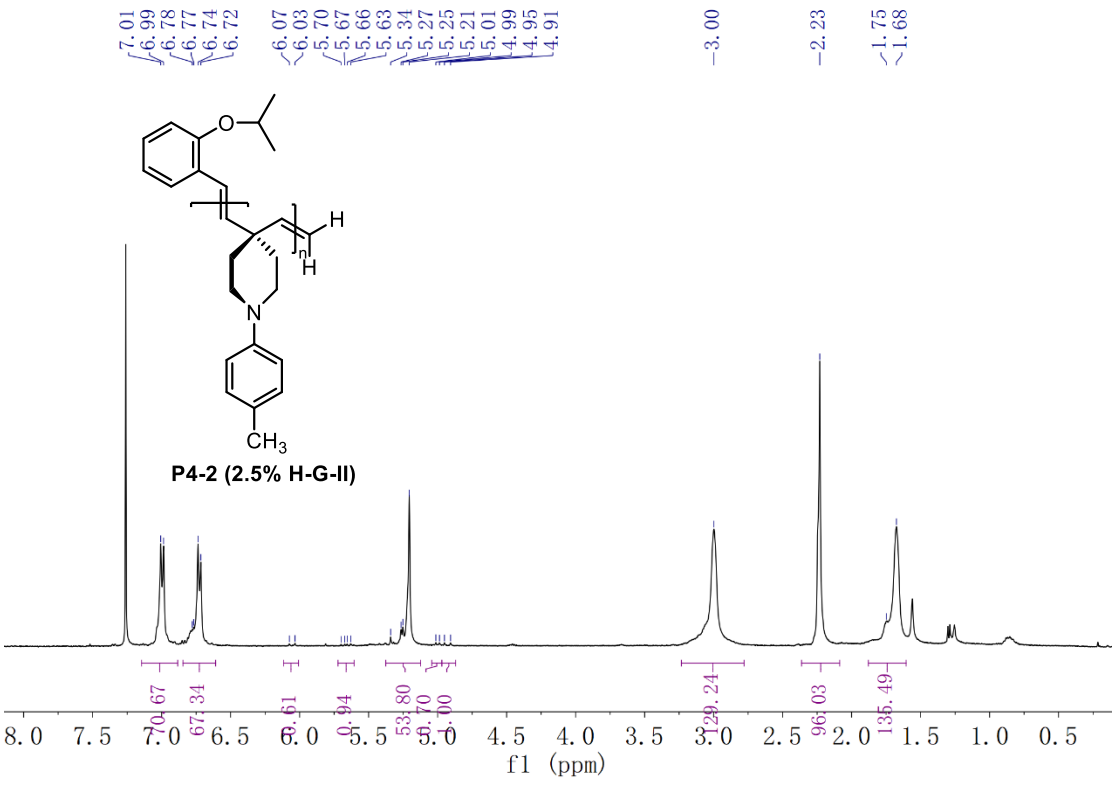
^{1}H NMR, $CDCl_3$, 400 MHz



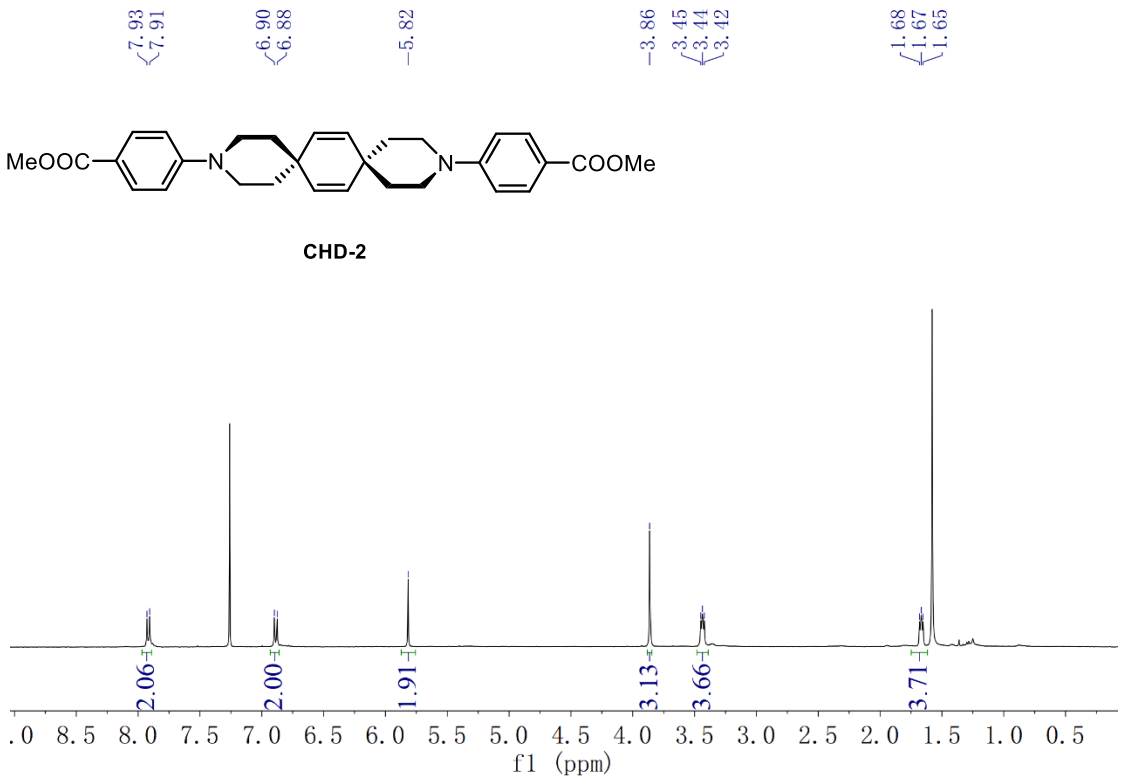
^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

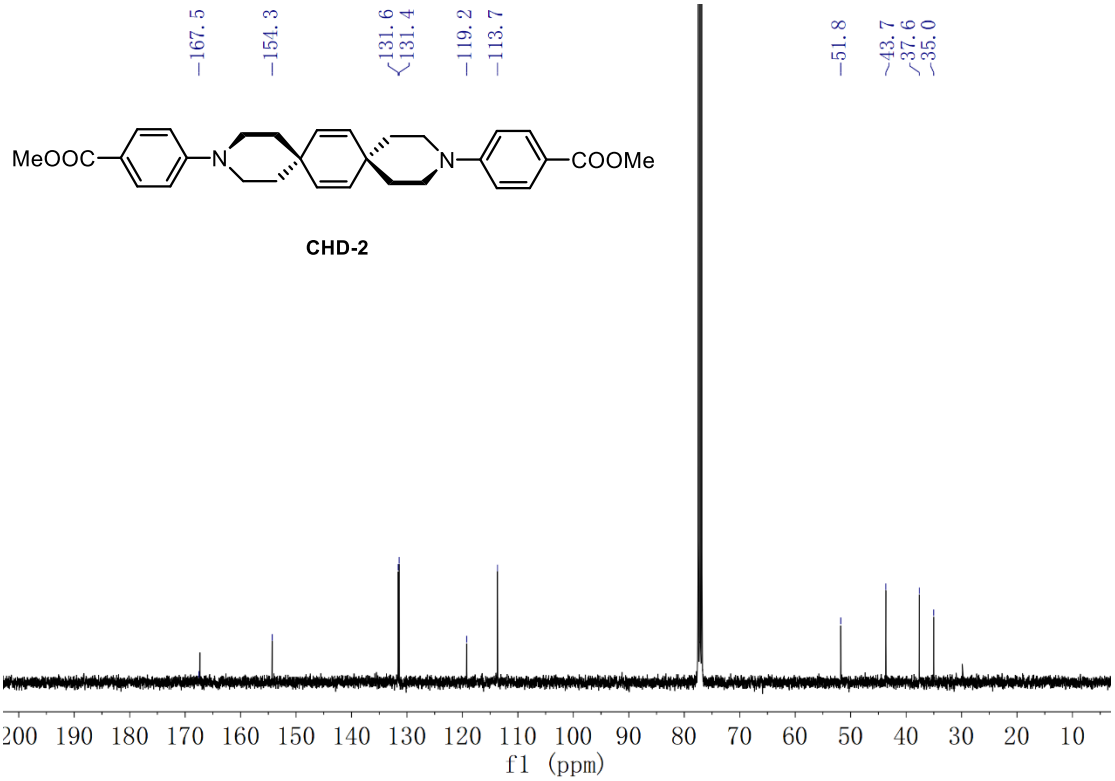


^{1}H NMR, $CDCl_3$, 400 MHz



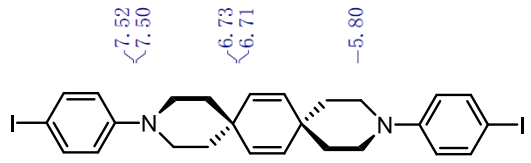
CHD-2

^{1}H NMR, $CDCl_3$, 400 MHz

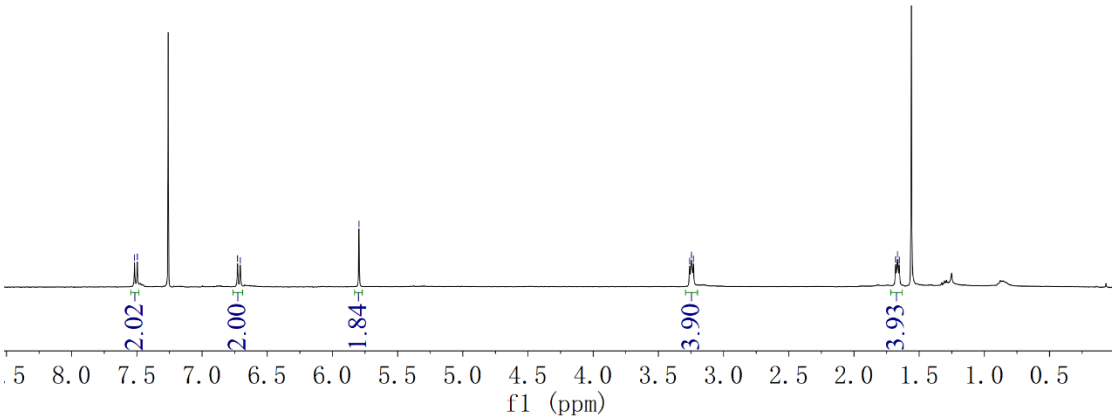


CHD-2

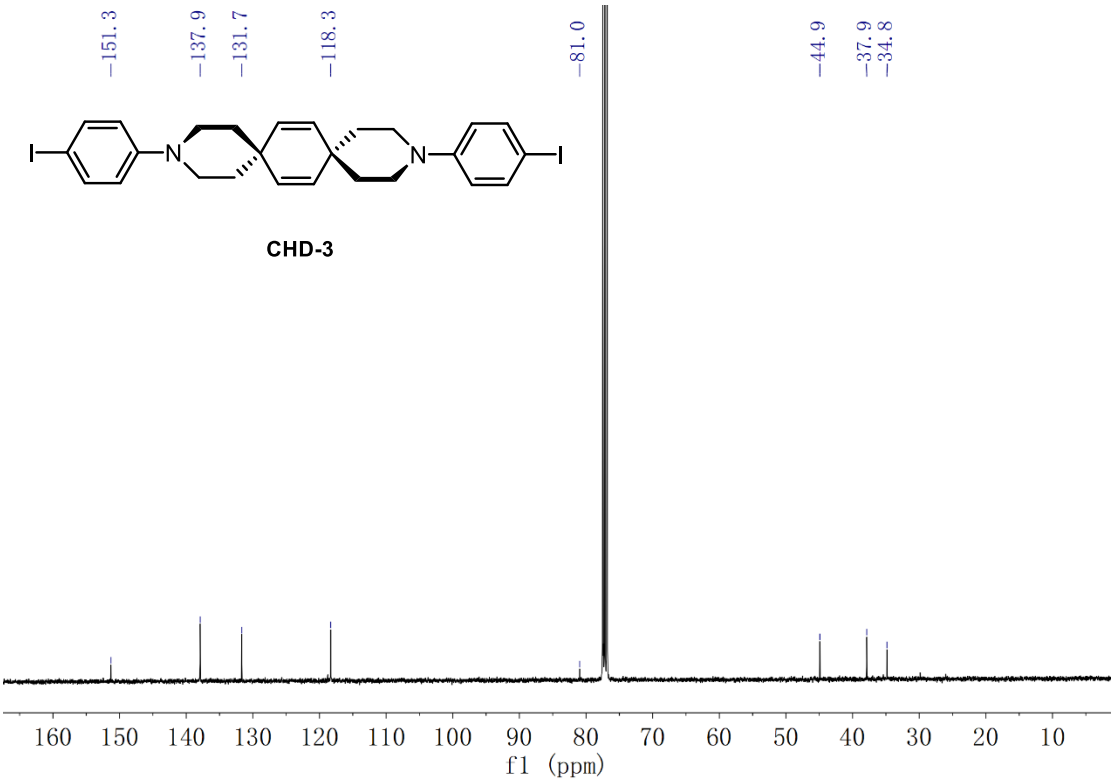
^{13}C NMR, $CDCl_3$, 101 MHz



CHD-3

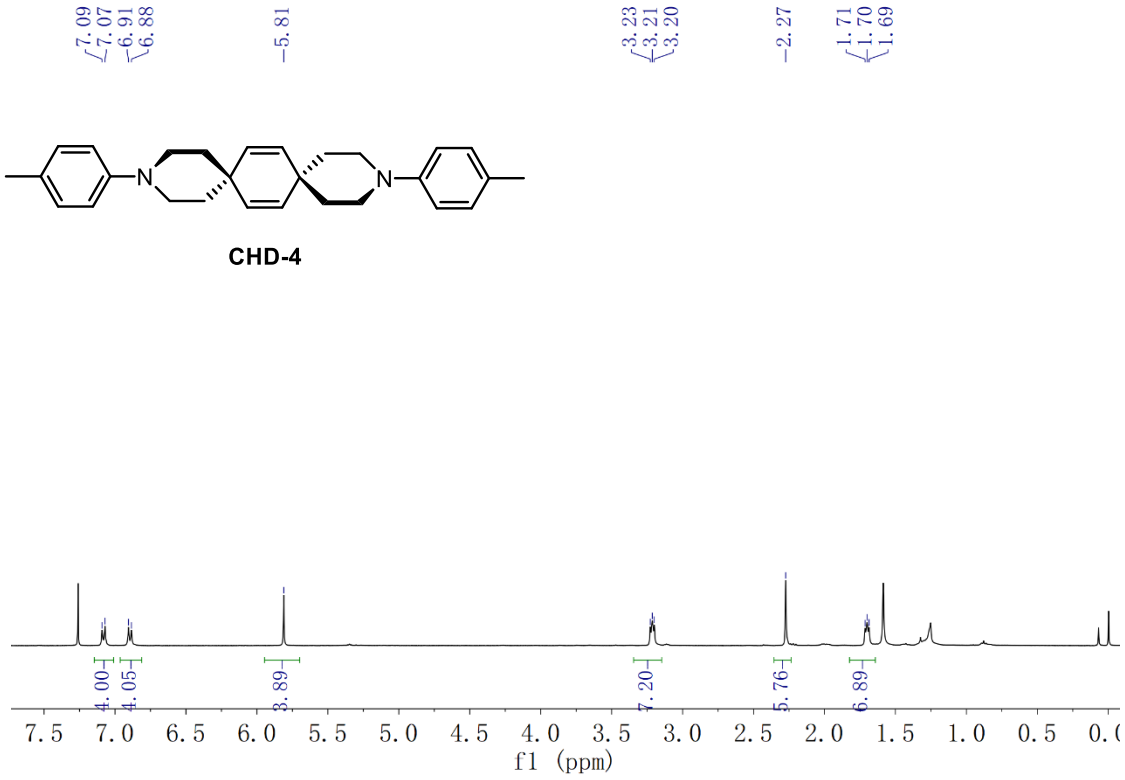


^{1}H NMR, $CDCl_3$, 400 MHz

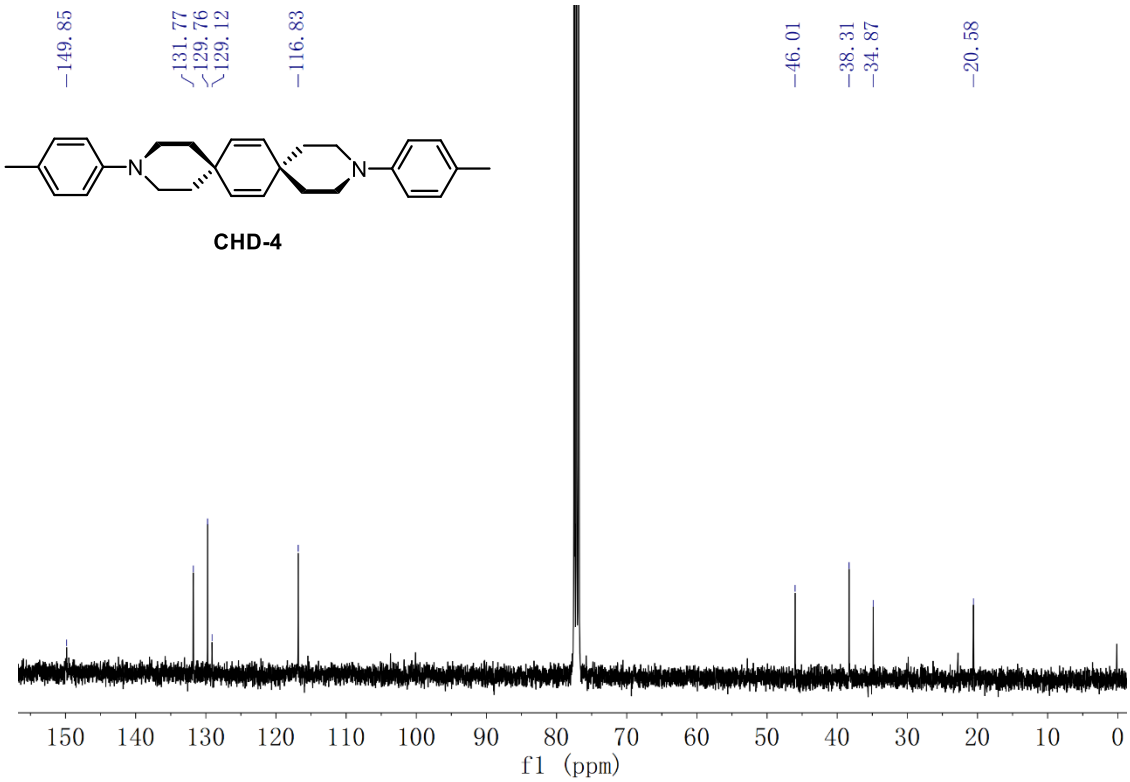


CHD-3

^{13}C NMR, $CDCl_3$, 101 MHz



^{1}H NMR, $CDCl_3$, 400 MHz



^{13}C NMR, $CDCl_3$, 101 MHz

6. GPC traces

Tegent

Project Name TEST

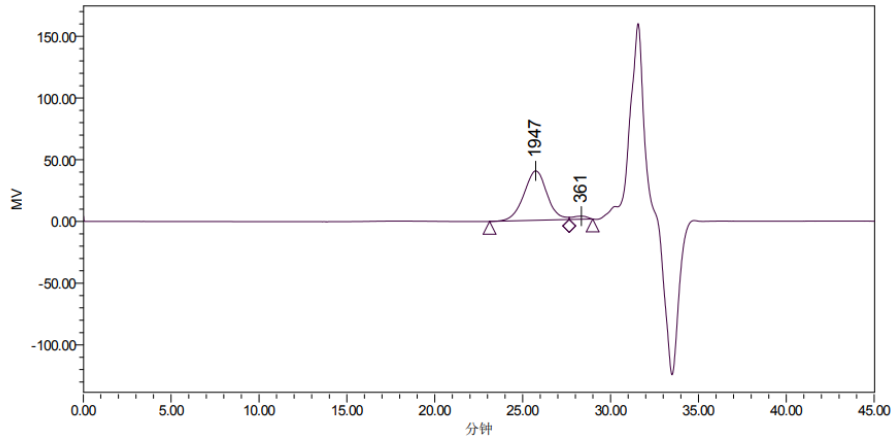
Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	LGQ-ZYC-R491	Acquired By:	Breeze
Sample Type:	宽分布未知样	Date Acquired:	2022/11/8 9:14:41 CST
Vial:	1:A,1	Acq. Method:	THF20180411
Injection #:	1	Date Processed:	2022/11/8 10:00:25 CST
Injection Volume:	50.00 ul	Channel Name:	410
Run Time:	45.00 Minutes	Channel Desc.:	
Column Type:		Sample Set Name	20221108

Broad Unknown Modified Universal Chromatogram



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						1865	1987	1947	2106	2226	1.065519	1.059558
2								361				

Figure S3.GPC trace of **P2a(G-II)**

Tegent

Project Name TEST

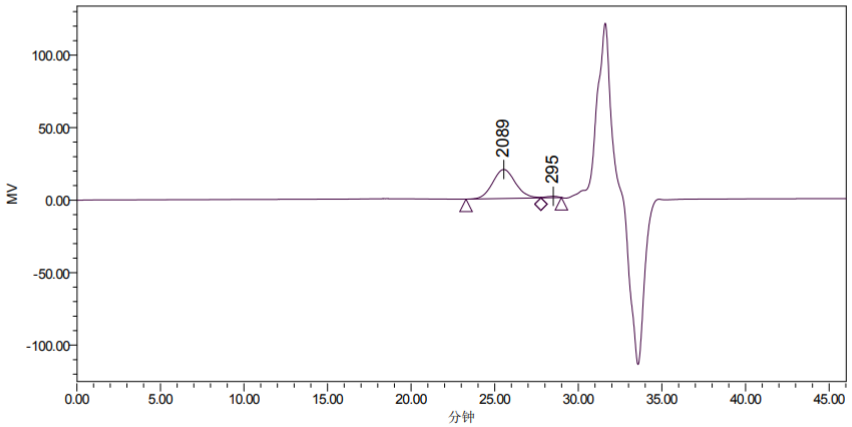
Reported by User: Breeze user (Breeze)

Breeze 2 HPLC System

SAMPLE INFORMATION

Sample Name:	LGQ-ZYC-R501	Acquired By:	Breeze
Sample Type:	宽分布未知样	Date Acquired:	2022/11/3 14:47:16 CST
Vial:	1:A,7	Acq. Method:	THF20180411
Injection #:	1	Date Processed:	2022/11/3 15:34:19 CST
Injection Volume:	50.00 ul	Channel Name:	410
Run Time:	46.00 Minutes	Channel Desc.:	
Column Type:		Sample Set Name	20221103

Broad Unknown Modified Universal Chromatogram



Broad Unknown Modified Universal Peak Table

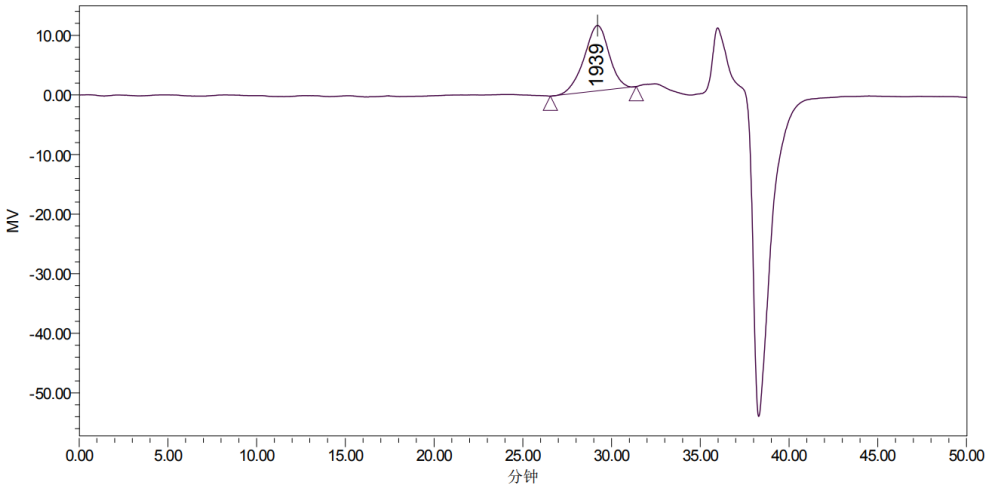
	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						1964	2090	2089	2208	2321	1.064401	1.05611
2								295				

Figure S4.GPC trace of **P2a(G-III)**

SAMPLE INFORMATION

Sample Name:	LGQ-ZYC-R336	Acquired By:	Breeze
Sample Type:	宽分布未知样	Date Acquired:	2022/5/17 11:48:34 CST
Vial:	1:A,2	Acq. Method:	THF20180411
Injection #:	1	Date Processed:	2022/5/17 15:24:48 CST
Injection Volume:	50.00 ul	Channel Name:	410
Run Time:	50.00 Minutes	Channel Desc.:	
Column Type:		Sample Set Name	20220517

Broad Unknown Modified Universal Chromatogram



Broad Unknown Modified Universal Peak Table

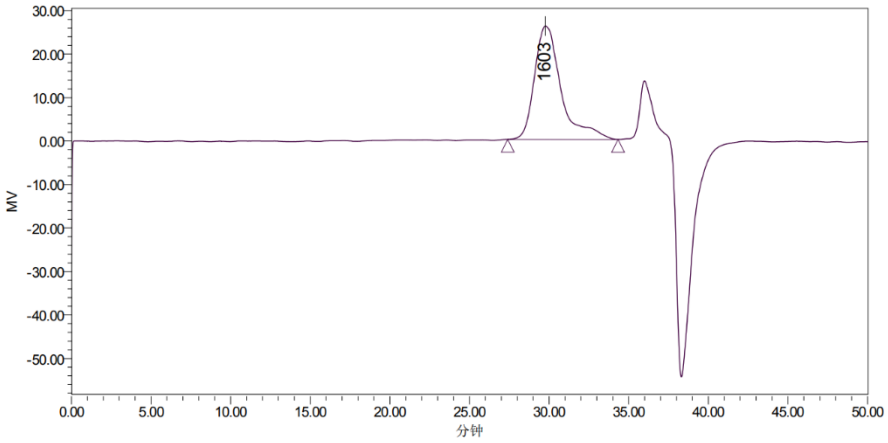
	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						1928	2028	1939	2132	2241	1.051790	1.051365

Figure S5.GPC trace of **P2b**

SAMPLE INFORMATION

Sample Name:	LGQ-ZYC-R320	Acquired By:	Breeze
Sample Type:	宽分布未知样	Date Acquired:	2022/5/17 10:58:05 CST
Vial:	1:A,1	Acq. Method:	THF20180411
Injection #:	1	Date Processed:	2022/5/23 14:01:59 CST
Injection Volume:	50.00 ul	Channel Name:	410
Run Time:	50.00 Minutes	Channel Desc.:	
Column Type:		Sample Set Name	20220517

Broad Unknown Modified Universal Chromatogram



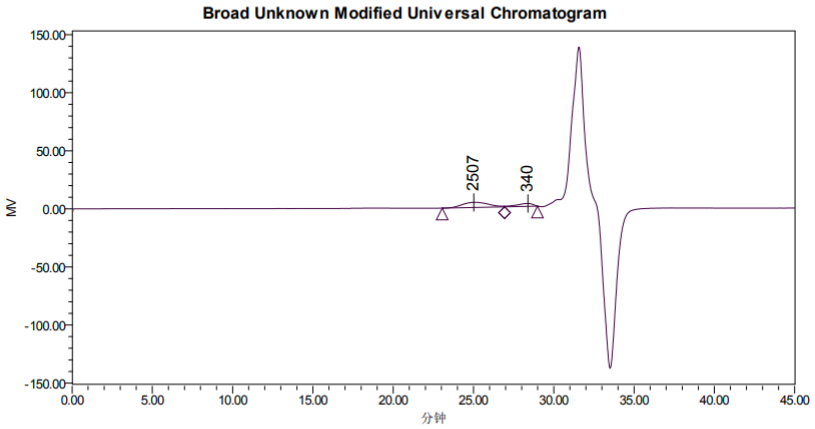
Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						1329	1505	1603	1635	1739	1.132706	1.086468

Figure S6.GPC trace of **P3**

SAMPLE INFORMATION

Sample Name:	LGQ-XYC-R503	Acquired By:	Breeze
Sample Type:	宽分布未知样	Date Acquired:	2022/11/10 10:00:28 CST
Vial:	1:A,1	Acq. Method:	THF20180411
Injection #:	1	Date Processed:	2022/11/10 13:26:50 CST
Injection Volume:	50.00 ul	Channel Name:	410
Run Time:	45.00 Minutes	Channel Desc.:	
Column Type:		Sample Set Name	20221110



Broad Unknown Modified Universal Peak Table

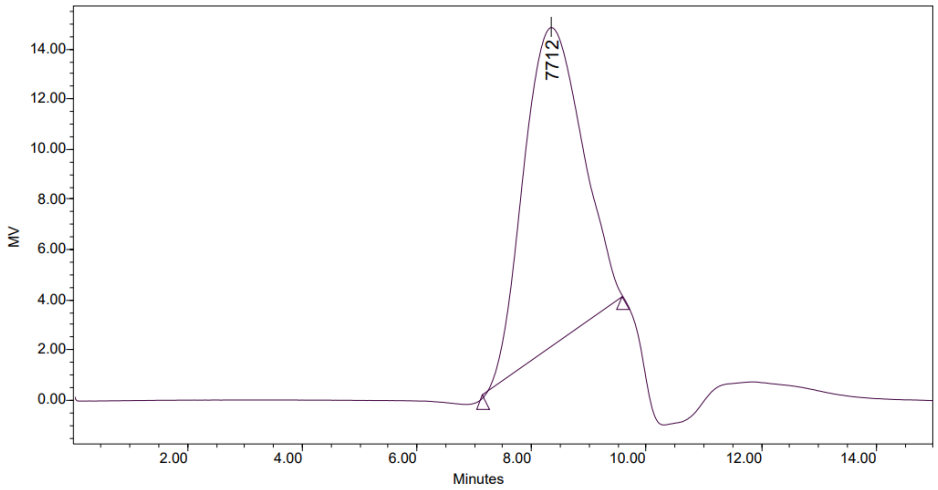
	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						2309	2469	2507	2630	2790	1.069525	1.065267
2								340				

Figure S7.GPC trace of **P4-1**

SAMPLE INFORMATION

Sample Name:	13	Acquired By:	System	
Sample Type:	Broad Unknown	Date Acquired:	2022-10-30	05:52:10
Vial:	13	Acq. Method:	20220530	
Injection #:	1	Date Processed:	2022-10-30	06:19:57
Injection Volume:	10.00 ul	Channel Name:	410	
Run Time:	15.00 Minutes	Channel Desc.:	RI Detector	
Column Type:		Sample Set Name	5	

Broad Unknown Relative Chromatogram



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		4852	10378	7712	19554	30207	2.138803	1.884241	2.910794

Figure S8.GPC trace of **P4-2**

7. FT-IR of P2b, P3 and P4

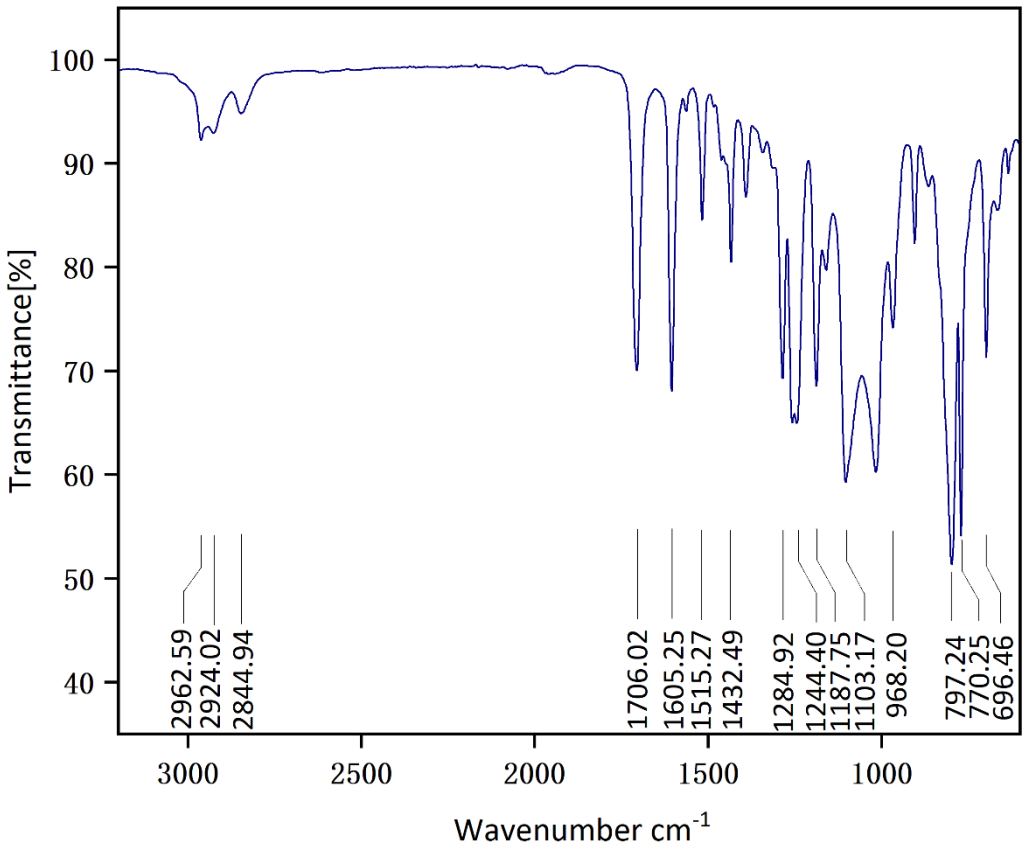


Figure S9. FT-IR of **P2b**

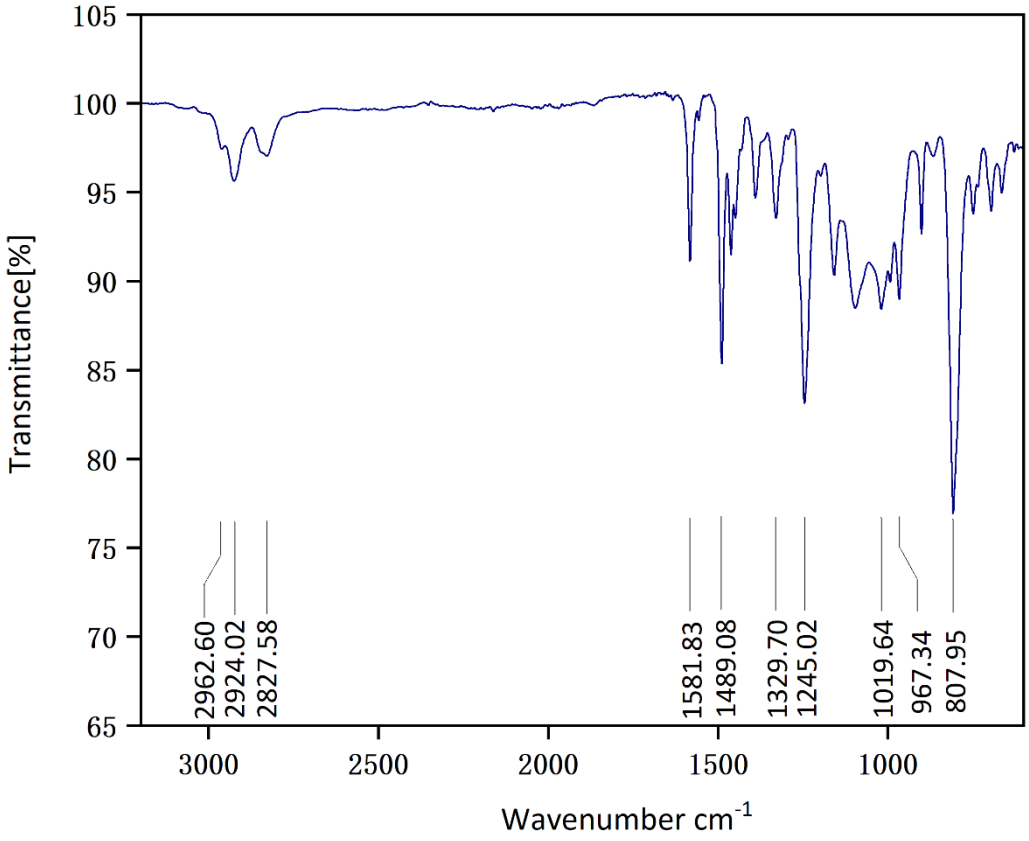


Figure S10. FT-IR of **P3**

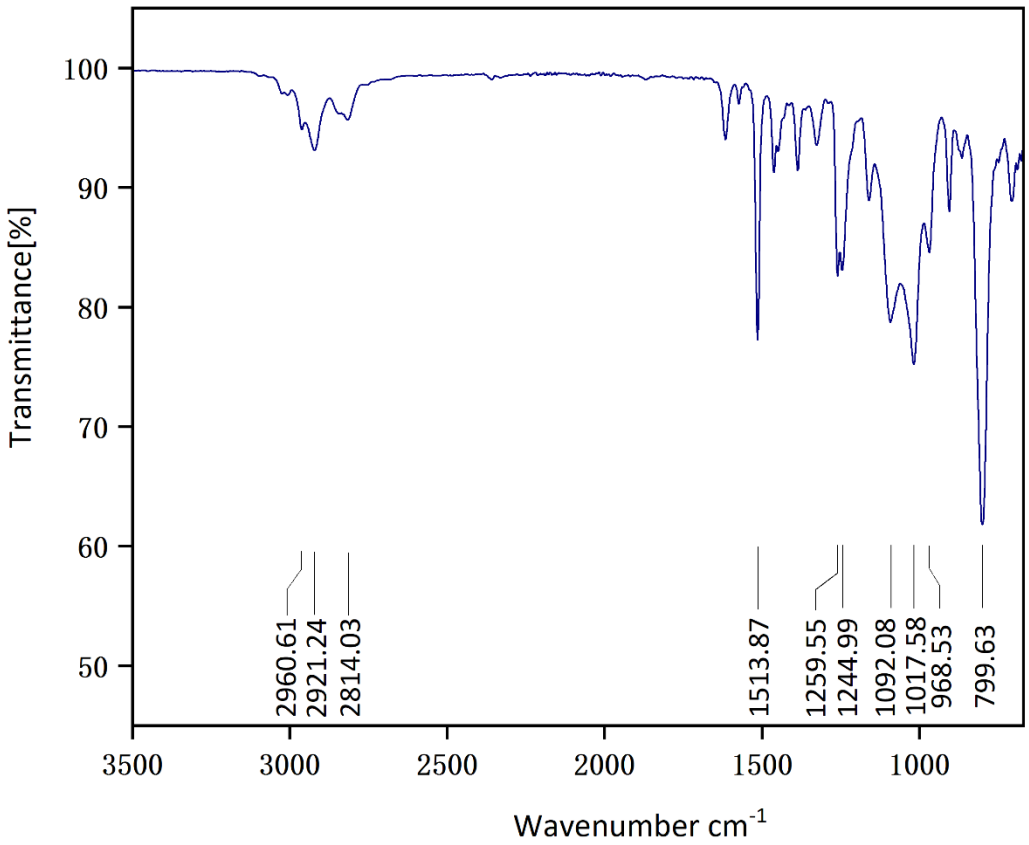


Figure S11. FT-IR of **P4**

8. Tg of P2b, P3 and P4

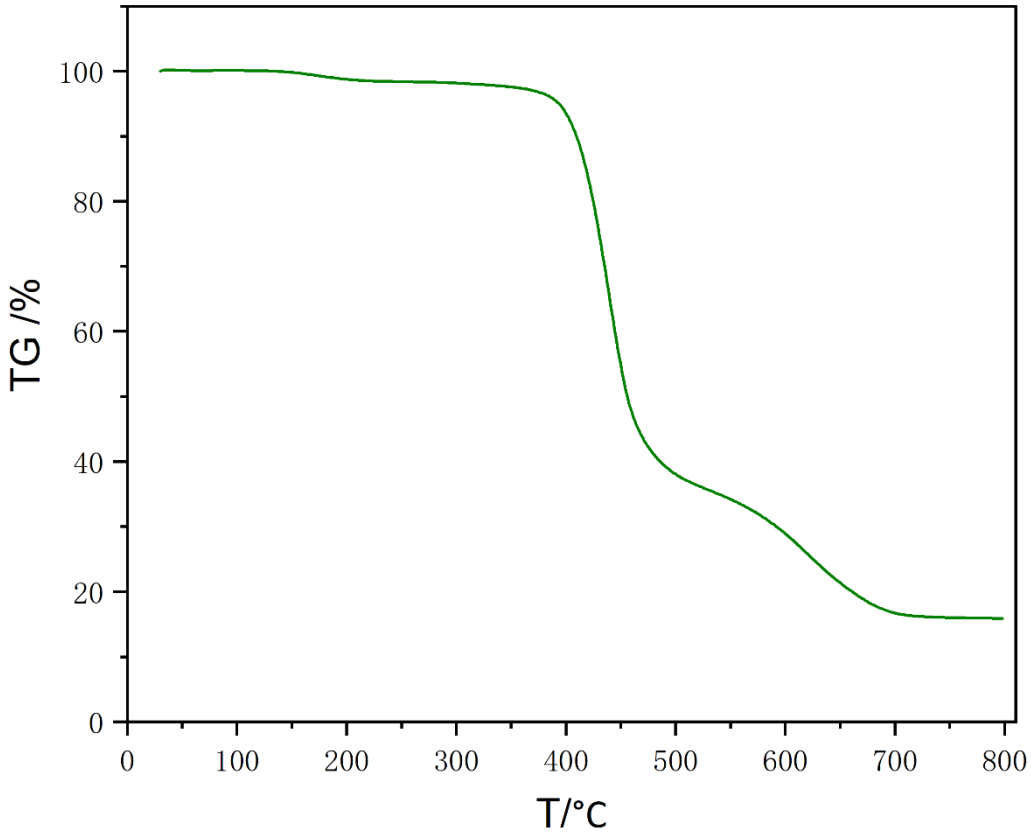


Figure S12. Thermogravimetric curve for **P2b** taken at 20 °C/ min to 800°C in N_2.

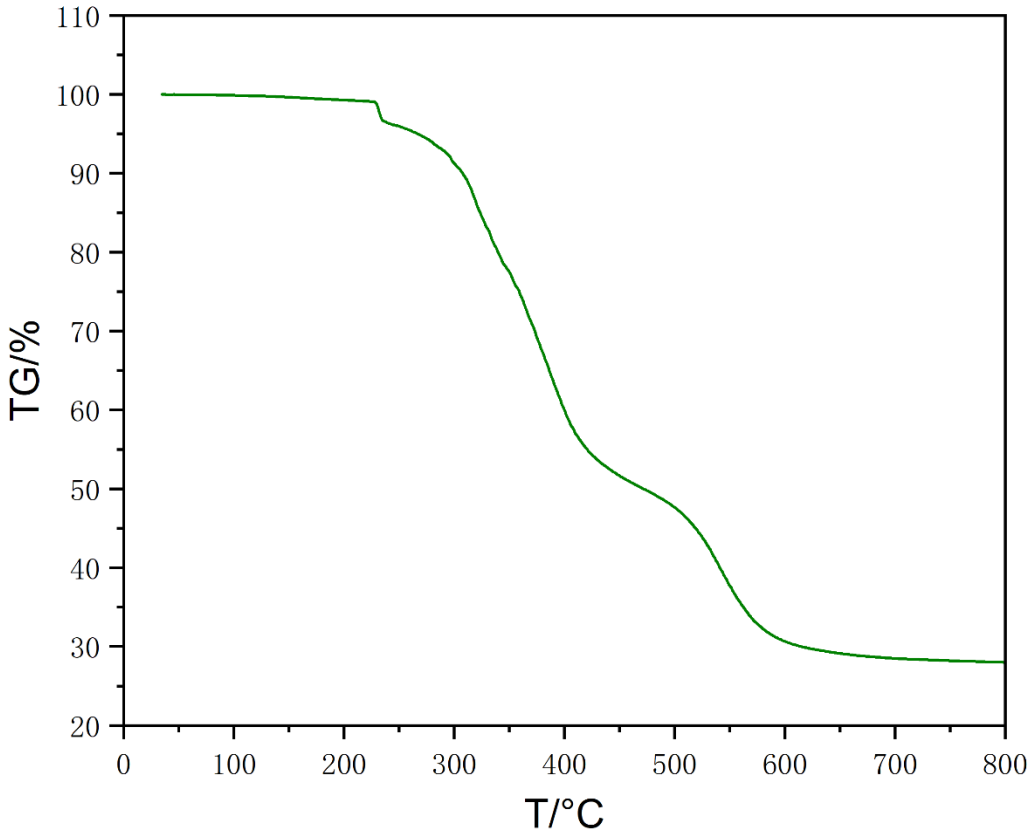


Figure S13. Thermogravimetric curve for **P3** taken at 20 °C/ min to 800°C in N_2.

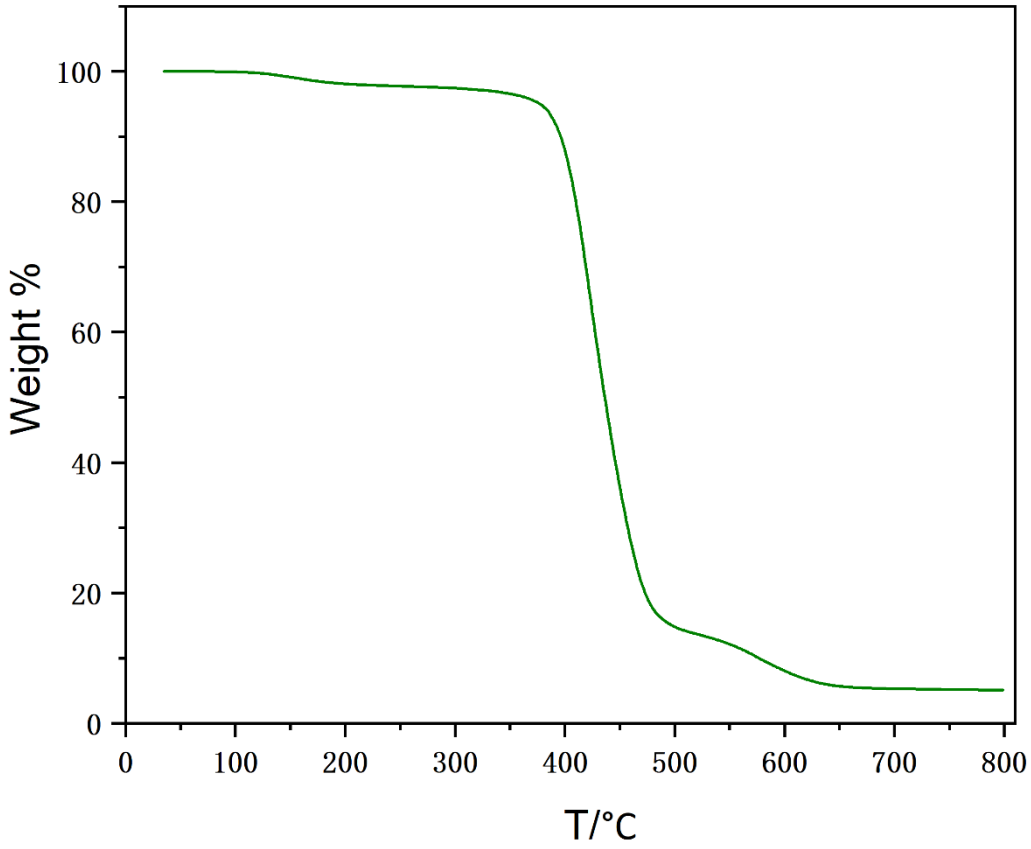


Figure S14. Thermogravimetric curve for **P4** taken at 20 °C/ min to 800°C in N_2.

9.DFT calculation

All calculations were carried out with the Gaussian 16 software[1]. The M06-2X functional[2] was adopted for all calculations. For geometry optimization calculations, the def2-SVP basis set[3] was used, and the optimal geometry for each compound was determined. The singlet point energy calculations were performed with a larger basis set def2-TZVP basis set.

The DFT-D3 dispersion correction[4] was applied to correct the weak interaction to improve the calculation accuracy.

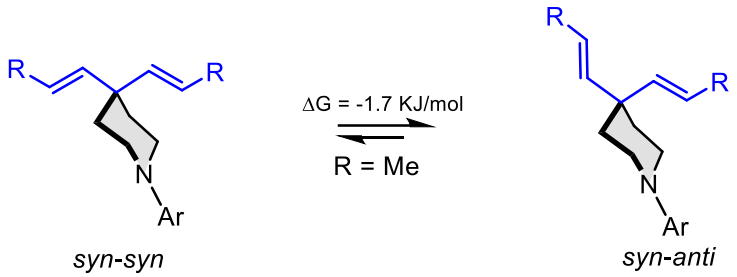
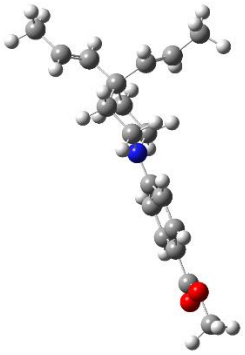


Figure S15. Possible conformations of repeating units. *Anti-anti* conformer would be converged to *syn-anti* during calculation.

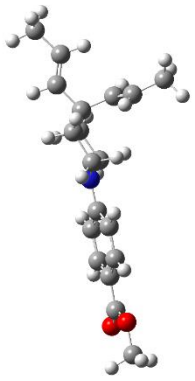
Syn-Syn



C	3.29381800	-0.12294000	0.03069400
C	2.44547500	-0.80609500	-1.04965100
C	1.04260700	-0.21843600	-1.15439200
N	0.35078900	-0.29566200	0.12037000
C	1.07666500	0.35526800	1.20803400
C	2.49362600	-0.18961400	1.34359600
C	3.62566100	1.29452500	-0.40687200
C	4.62646600	-0.81618200	0.23760000
C	5.13421000	-1.82410600	-0.47471800
C	6.47146700	-2.45113100	-0.21917900
C	3.60171800	2.40734900	0.32961700
C	4.01448300	3.76068900	-0.16486500

C	-1.04040300	-0.23234700	0.12984400
C	-1.78430100	0.04884600	-1.03472600
C	-3.17433600	0.06942800	-1.01003900
C	-3.87012300	-0.17613700	0.17439800
C	-3.14297600	-0.44935700	1.33973500
C	-1.76007000	-0.47839200	1.32191200
C	-5.35183000	-0.16203400	0.25400100
O	-5.98707900	-0.36022600	1.25747000
O	-5.93230200	0.09894000	-0.92825800
C	-7.34866500	0.12701800	-0.91842800
H	2.94331600	-0.72748600	-2.02907200
H	2.35669200	-1.87668300	-0.80677800
H	1.09159800	0.82793400	-1.52332100
H	0.47830200	-0.80258800	-1.89257500
H	1.10244300	1.44781600	1.03071200
H	0.54319700	0.19653800	2.15105900
H	3.02157600	0.34780800	2.14638200
H	2.43877200	-1.24684000	1.64739600
H	3.98043300	1.36744900	-1.44375600
H	5.21983400	-0.40133300	1.06298200
H	4.55648200	-2.23892900	-1.30725100
H	6.97706600	-1.97814100	0.63354500
H	6.37021900	-3.52664600	-0.00789300
H	7.12473600	-2.36116000	-1.10069300
H	3.26210700	2.35732800	1.37016500
H	4.84619200	4.16238200	0.43409300
H	4.33482100	3.71999200	-1.21473600
H	3.18698200	4.48187000	-0.08288900
H	-1.27662300	0.27584300	-1.96990300
H	-3.73157600	0.29381200	-1.91973600
H	-3.69353200	-0.65260400	2.25951600
H	-1.22440300	-0.73140100	2.23594800
H	-7.66099200	0.34916000	-1.94365100
H	-7.75299200	-0.84209400	-0.59571800
H	-7.71610600	0.89978600	-0.22948400

Syn-Anti



C	-3.23536100	-0.31688900	0.19839400
C	-2.32562800	-0.66332700	1.39627900
C	-0.94329900	-0.02836500	1.30189900
N	-0.28043800	-0.41696300	0.06938600
C	-1.05474400	-0.09083100	-1.12570700
C	-2.45413400	-0.69351300	-1.07511300
C	-3.60976200	1.14742900	0.27207600
C	-4.47686800	-1.18573400	0.27979300
C	-5.74485000	-0.79341100	0.14387000
C	-6.92766600	-1.71086900	0.21356000
C	-3.62223500	2.04224900	-0.71782100
C	-4.04408500	3.47236900	-0.56435700
C	1.10708300	-0.31855100	-0.00259400
C	1.86886400	0.28261300	1.02041700
C	3.25617700	0.33658400	0.94349900
C	3.93045900	-0.19402700	-0.15700300
C	3.18497700	-0.78828400	-1.18294200
C	1.80503800	-0.85167600	-1.11074900
C	5.40816200	-0.15770200	-0.28842400
O	6.02484200	-0.59791000	-1.22418900
O	6.00792500	0.42698900	0.76092900
C	7.42153900	0.49368200	0.69533500
H	-2.81186100	-0.35219900	2.33408200
H	-2.20057300	-1.75727800	1.43795100
H	-1.02075700	1.07614400	1.38756500
H	-0.34161500	-0.38368600	2.14847500
H	-1.11581300	1.00921900	-1.23503800
H	-0.53681200	-0.47151100	-2.01232300
H	-3.02297300	-0.39997600	-1.96995600
H	-2.36195500	-1.79121900	-1.10278600
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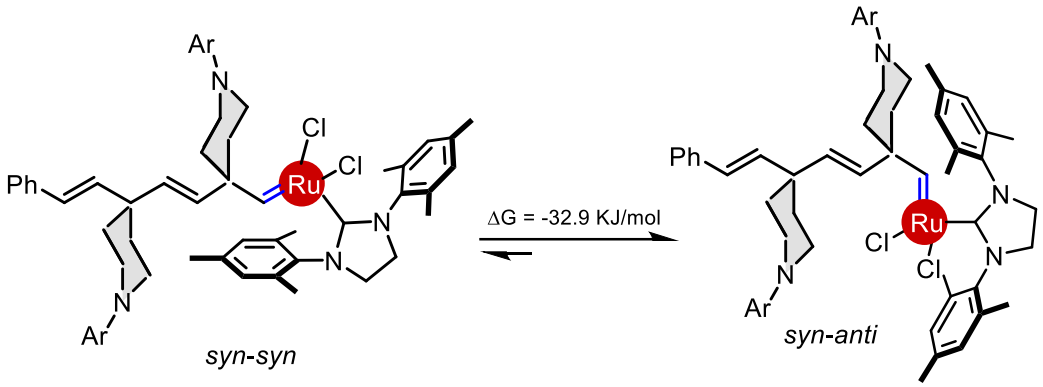

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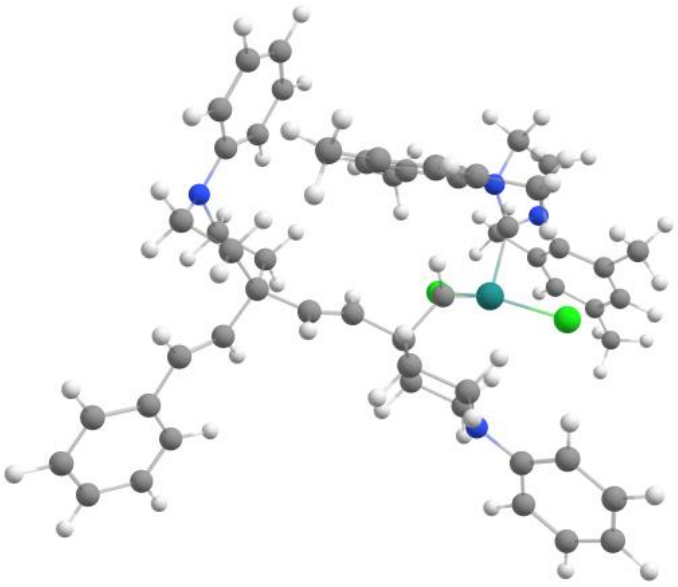

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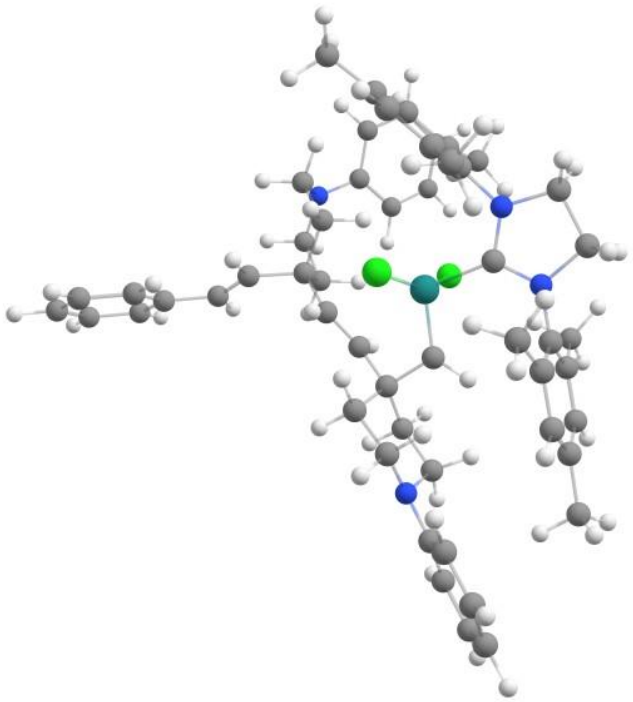

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[1] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2019**.

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