Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Amplification Effect of Circularly Polarized Luminescence Induced from Binaphthyl-based Zinc(II) Chiral Coordination Polymers

Yuxiang Wang,[a] Xiaojing Li, [a] Lan Yang, [a] Wei-Yin Sun, [b] Chengjian Zhu [b] and Yixiang Cheng* [a]

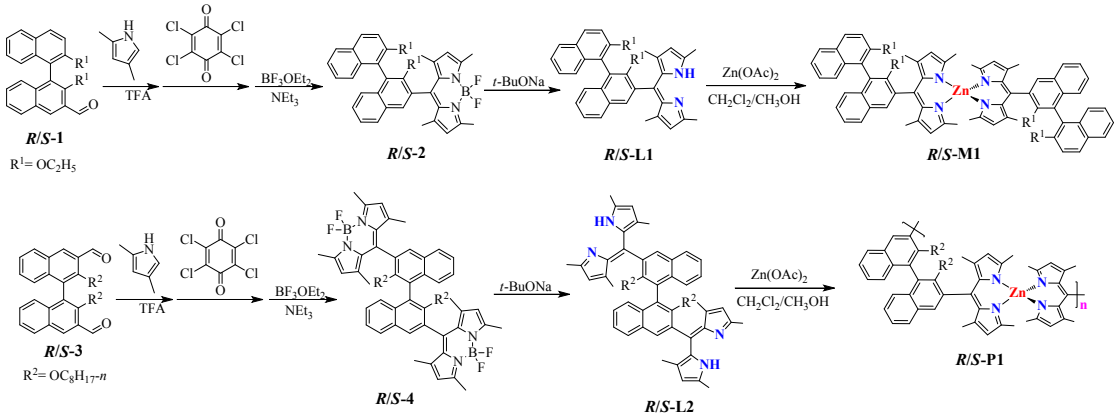
[a]Key Lab of Mesoscopic Chemistry of MOE and Collaborative Innovation Center of Chemistry for Life Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, P. R. China.

Table of Contents

1. Instrumentation and Materials.

NMR spectrum were obtained by using 400/500 MHz Bruker spectrometer with 400/500 MHz for ^{1}H NMR and 100/125 MHz for ^{13}C NMR and the chemical shifts are reported as parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard. Electrospray ionization mass spectrum (ESI-MS) were measured on a Thermo Finnigan LCQ Fleet system. Molecular weight was determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris-1 instrument under N_2 atmosphere. Ultraviolet-visible (UV-vis) spectrum were obtained by using a Perkin-Elmer Lambda 35 spectrophotometer. Fluorescence spectrum were obtained by using HORIBA Scientific FluoroMax-4 Spectrofluorometer. Quantum yields and fluorescence lifetimes were collected on a FluoroMax-4 (Horiba Jobin Yvon) fluorometer equipped with an integrated sphere. Circular dichroism (CD) spectrum were recorded on a JASCO J-810 spectropolarimeter. Circularly polarized luminescence (CPL) spectrum were recorded with a JASCO CPL-300 spectrofluoropolarimeter. All solvents and reagents were commercially available A.R. grade.

2. Synthesis procedures of *R*/*S*-M1 and *R*/*S*-P1.



Scheme S1 The synthesis procedures of *R*/*S*-M1 and *R*/*S*-P1.

Synthesis of compound *R*/*S*-2

R/*S*-1 (1.17 g, 3.16 mmol) and 2, 4-dimethyl-1H-pyrrole (751 mg, 7.90 mmol) were dissolved in 50 mL CH_2Cl_2. The reaction mixture was stirred over night at room temperature after adding two drops of trifluoroacetic acid (TFA). Then spergon (932

mg, 3.79 mmol) was added to the reaction mixture. After stirring for 1 hour, the reaction mixture was allowed to freeze to 0 °C. Triethylamine (5.95 mL, 47.4 mmol) and boron fluoride ethyl ether (4.38 mL, 31.6 mmol) were added to the reaction mixture and the reaction was stirring for 1 hour. After the reaction finished, 50 mL water was added to the reaction mixture. The organic layer was washed by water (50 mL × 3). The solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate, 40/1) to give ***R*/*S*-2** as red solid.

***R*/*S*-2** (670 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.82 (s, 1H), 7.46 – 7.39 (m, 2H), 7.35 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 7.13 (d, *J* = 8.5 Hz, 1H), 6.00 (s, 2H), 4.13 (dq, *J* = 9.5, 7.0 Hz, 1H), 4.01 (dq, *J* = 9.5, 7.0 Hz, 1H), 3.48 (dq, *J* = 9.0, 7.0 Hz, 1H), 3.39 (dq, *J* = 9.0, 7.0 Hz, 1H), 2.57 (s, 6H), 1.59 (s, 6H), 1.05 (t, *J* = 7.0 Hz, 3H), 0.48 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.19, 155.05, 154.42, 152.95, 143.19, 142.44, 134.73, 134.12, 130.46, 129.82, 129.18, 128.91, 128.08, 128.00, 126.85, 126.58, 125.86, 125.08, 124.99, 123.56, 121.14, 121.00, 119.29, 114.63, 69.01, 64.67, 15.46, 15.01, 14.96, 14.83, 14.66. MS (ESI, m/z): 611.25 (M^++23).

Synthesis of compound *R*/*S*-L1

R/*S*-2 (300 mg, 0.51 mmol) and *t*-BuONa (245 mg, 2.55 mmol) were dissolved in 20 mL toluene. The reaction mixture was stirred at 120 ºC under N_2 atmosphere for 30 min. After the reaction was finished, the solution was filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (neutral Al_2O_3 column, eluent: petroleum ether/ethyl acetate, 20/1) to give product ***R*/*S*-L1** as yellow solid.

***R*/*S*-L1** (115 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 1H), 7.90 – 7.79 (m, 3H), 7.39 (dd, *J* = 13.7, 8.0 Hz, 2H), 7.35 – 7.28 (m, 1H), 7.22 (ddd, *J* = 14.5, 10.5, 5.7 Hz, 4H), 5.90 (s, 2H), 4.22 – 3.91 (m, 2H), 3.62 – 3.35 (m, 2H), 2.36 (s, 6H), 1.57 (d, *J* = 45.4 Hz, 6H), 1.05 (t, *J* = 7.0 Hz, 3H), 0.45 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.48, 153.90, 151.72, 150.85, 140.65, 139.53, 137.19, 136.52, 135.53, 134.48, 134.27, 131.97, 130.52, 130.16, 129.51, 128.98, 127.95,

126.42, 126.11, 125.77, 125.28, 124.68, 123.46, 119.94, 119.62, 119.24, 114.77, 68.59, 64.74, 16.14, 16.02, 15.49, 15.28, 15.10, 14.98. MS (ESI, m/z): 541.30 (M^++1).

Synthesis of compound *R*/*S*-M1

R/*S*-L1 (115 mg, 0.21 mmol) was dissolved in 6 mL CH_2Cl_2. The solution of $Zn(OAc)_2$ (23 mg, 0.13 mmol) in 4 mL CH_3OH was added to the solution of *R*/*S*-L2 at room temperature. The reaction was stirred at room temperature for 2 hours. After the reaction was finished, the solvent was evaporated under reduced pressure. The residue was dissolved in 2 mL CH_2Cl_2 and precipitated in 30 mL CH_3OH. The obtained solids was filtered and washed with 5 mL CH_3OH. The solids were dried in vacuum to give ***R*/*S*-M1** as orange solid.

***R*/*S*-M1** (92 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 2H), 7.92 – 7.81 (m, 6H), 7.41 (dd, *J* = 12.1, 8.2 Hz, 4H), 7.36 – 7.29 (m, 2H), 7.27 – 7.24 (m, 6H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.00 (s, 2H), 5.91 (s, 2H), 4.13 (dq, *J* = 14.0, 7.0 Hz, 2H), 4.02 (dq, *J* = 14.2, 7.0 Hz, 2H), 3.57 (p, *J* = 7.3 Hz, 2H), 3.50 – 3.38 (m, 2H), 2.15 (s, 6H), 1.98 (s, 6H), 1.67 (s, 6H), 1.52 (s, 6H), 1.06 (t, *J* = 7.0 Hz, 6H), 0.42 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.40, 156.26, 154.62, 153.95, 144.37, 143.34, 141.32, 136.22, 135.85, 134.43, 134.37, 134.12, 130.80, 130.16, 129.50, 129.00, 127.93, 126.45, 126.26, 126.19, 125.79, 125.44, 124.62, 123.47, 120.12, 120.07, 119.96, 114.89, 68.28, 64.87, 16.75, 16.52, 16.43, 16.19, 15.50, 15.02. MS (ESI, m/z): 1143.50 (M^++1), 1165.45 (M^++23). $[\alpha]_D^{25}$ of *R*/*S*-M1 (c = 1.0, CH_2Cl_2) are +682/-663.

Synthesis of compound *R*/*S*-4

R/*S*-3 (1.00 g, 1.76 mmol) and 2, 4-dimethyl-1H-pyrrole (840 mg, 8.82 mmol) were dissolved in 50 mL CH_2Cl_2. The reaction mixture was stirred over night at room temperature after adding two drops of trifluoroacetic acid (TFA). Then spergon (1.04 g, 4.23 mmol) was added to the reaction mixture. After stirring for 1 hour, the reaction mixture was allowed to freeze to 0 °C. Triethylamine (6.68 mL, 52.9 mmol) and boron fluoride ethyl ether (4.89 mL, 35.3 mmol) were added to the reaction mixture and the reaction was stirring for 1 hour. After the reaction finished, 50 mL

water was added to the reaction mixture. The organic layer was washed by water (50 mL × 3). The solvent was evaporated and the residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate, 20/1) to give ***R*/*S*-4** as red solid.

***R*/*S*-4** (260 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 4H), 7.48 – 7.41 (m, 2H), 7.35 – 7.28 (m, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.01 (s, 4H), 3.54 (dd, *J* = 14.5, 7.7 Hz, 2H), 3.27 (dt, *J* = 8.6, 5.9 Hz, 2H), 2.57 (d, *J* = 1.5 Hz, 12H), 1.65 (d, *J* = 7.6 Hz, 12H), 1.22 – 1.13 (m, 4H), 1.05 (dt, *J* = 9.1, 6.8 Hz, 4H), 0.99 – 0.92 (m, 6H), 0.88 – 0.76 (m, 12H), 0.75 – 0.67 (m, 2H), 0.66 – 0.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.17, 154.71, 152.71, 144.12, 143.22, 141.40, 138.21, 134.76, 132.24, 131.71, 130.42, 130.38, 129.08, 128.30, 127.23, 126.58, 125.56, 125.37, 121.30, 121.12, 118.83, 73.09, 31.73, 29.88, 29.20, 29.08, 25.26, 22.64, 15.37, 14.94, 14.70, 14.61, 14.12. MS (ESI, m/z): 1025.50 (M^++23).

Synthesis of compound *R*/*S*-L2

R/*S*-4 (300 mg, 0.30 mmol) and *t*-BuONa (431 mg, 4.49 mmol) were dissolved in 20 mL toluene. The reaction mixture was stirred at 120 ºC under N_2 atmosphere for 20 min. After the reaction was finished, the solution was filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (neutral Al_2O_3 column, eluent: petroleum ether/ethyl acetate, 10/1) to give ***R*/*S*-L2** as yellow solid.

***R*/*S*-L2** (110 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.86 (m, 4H), 7.40 (t, *J* = 7.0 Hz, 3H), 7.25 (dd, *J* = 11.8, 7.5 Hz, 3H), 5.91 (s, 4H), 3.66 (dd, *J* = 14.4, 7.3 Hz, 2H), 3.37 (dt, *J* = 8.6, 6.0 Hz, 2H), 2.38 (s, 12H), 1.59 (d, *J* = 5.8 Hz, 12H), 1.25 – 1.20 (m, 4H), 1.09 (dd, *J* = 15.2, 7.5 Hz, 4H), 1.02 – 0.96 (m, 6H), 0.89 – 0.79 (m, 12H), 0.75 (br, 2H), 0.63 (br, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.70, 152.89, 149.39, 141.68, 138.30, 137.88, 136.14, 134.68, 131.79, 131.22, 130.40, 128.06, 126.43, 126.34, 125.81, 124.72, 119.89, 118.82, 72.40, 31.78, 29.91, 29.72, 29.26, 29.25, 25.27, 22.70, 16.33, 15.85, 15.41, 15.30, 14.16. MS (ESI, m/z): 907.60 (M^++1).

Synthesis of compound *R*/*S*-P1

R/*S*-L2 (100 mg, 0.11 mmol) was dissolved in 10 mL CH_2Cl_2. The solution of $Zn(OAc)_2$ (22 mg, 0.12 mmol) in 2 mL CH_3OH was added to the solution of *R*/*S*-L1 at room temperature. The reaction was stirred at room temperature for 24 hours. After the reaction was finished, the solvent was evaporated under reduced pressure. The residue was dissolved in 2 mL CH_2Cl_2 and precipitated in 100 mL CH_3OH. The obtained solids was filtered and washed with 20 mL CH_3OH. The solids were dried in vacuum to give ***R*/*S*-P1** as red solid.

***R*/*S*-P1** (94 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 4H), 7.38 (d, J = 5.2 Hz, 4H), 7.27 (s, 2H), 6.01 (d, J = 12.3 Hz, 4H), 3.86 (s, 2H), 3.53 (s, 2H), 2.05 (d, J = 25.4 Hz, 12H), 1.64 (s, 12H), 1.16 (s, 4H), 1.03 (s, 4H), 0.90 (s, 6H), 0.81 (s, 12H), 0.64 (s, 2H), 0.51 (s, 2H). GPC: M_n = 13937, M_w = 31508, PDI = 2.26. $[\alpha]_D^{25}$ of *R*/*S*-P1 (c = 1.0, CH_2Cl_2) are +2313/-2488.

3. TGA curve of *R*/*S*-M1 and *R*/*S*-P1.

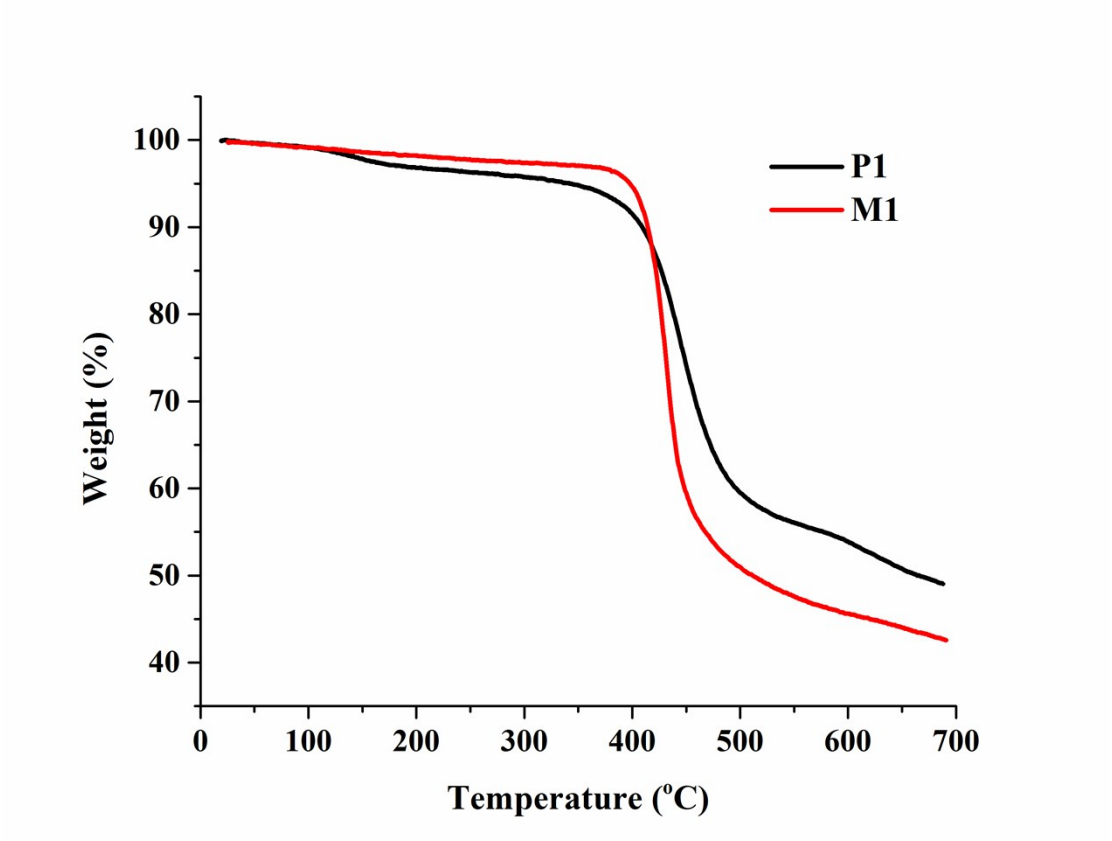


Fig. S1 TGA curve of *R*/*S*-M1 and *R*/*S*-P1.

4. Quantification of the elemental ratio of M1 and P1 from XPS.

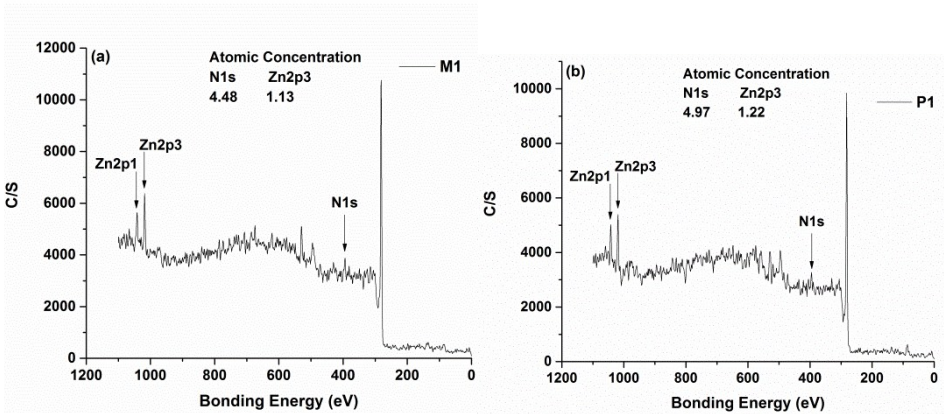


Fig. S2 Quantification of the elemental ratio of (a) M1 and (b) P1 from XPS.

5. Stability experiment of M1 and P1 in solutions.

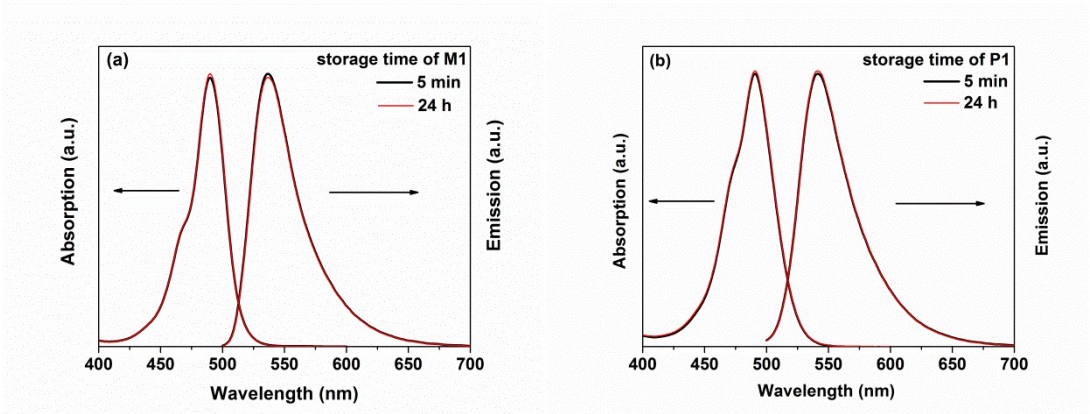


Fig. S3 The absorption (1.0×10^{-5} mol·L^{-1} in THF) and emission (1.0×10^{-4} mol·L^{-1} in toluene, λ_{ex} = 450 nm) spectra of (a) M1 and (b) P1 with different storage time at room temperature.

6. NMR and MS spectrum of the new compounds.

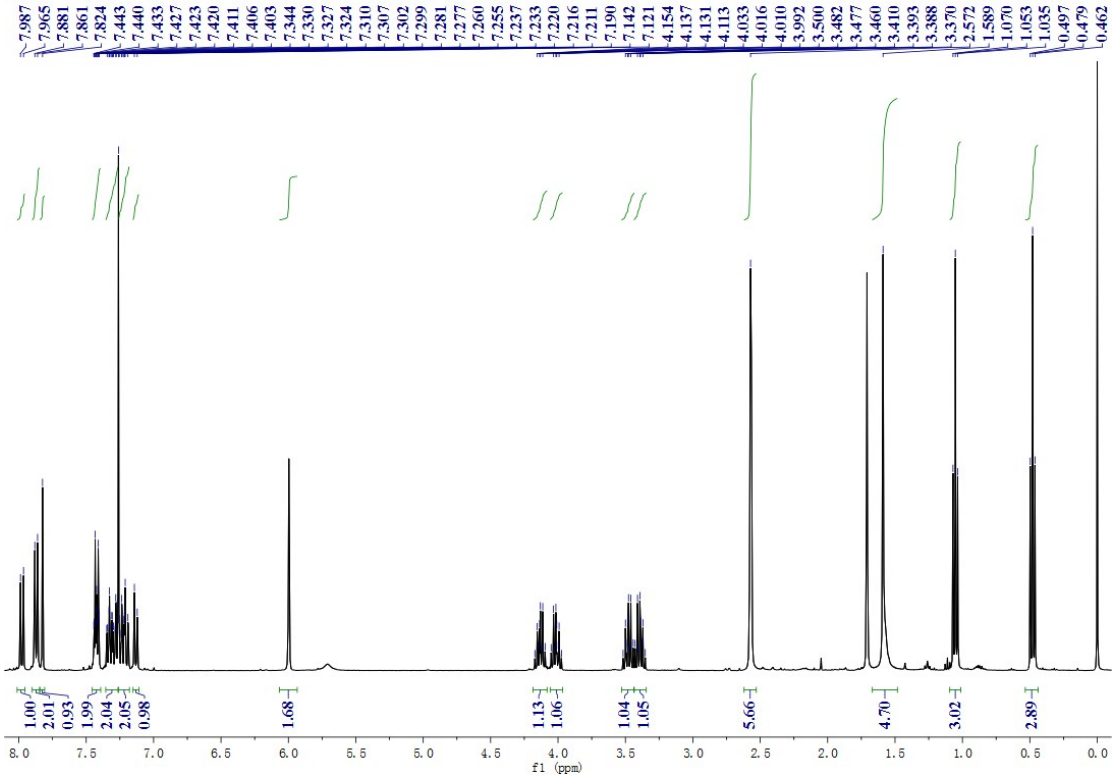


Fig. S4 ^{1}H NMR spectrum of compound *R*/*S*-2 (400 MHz, $CDCl_3$).

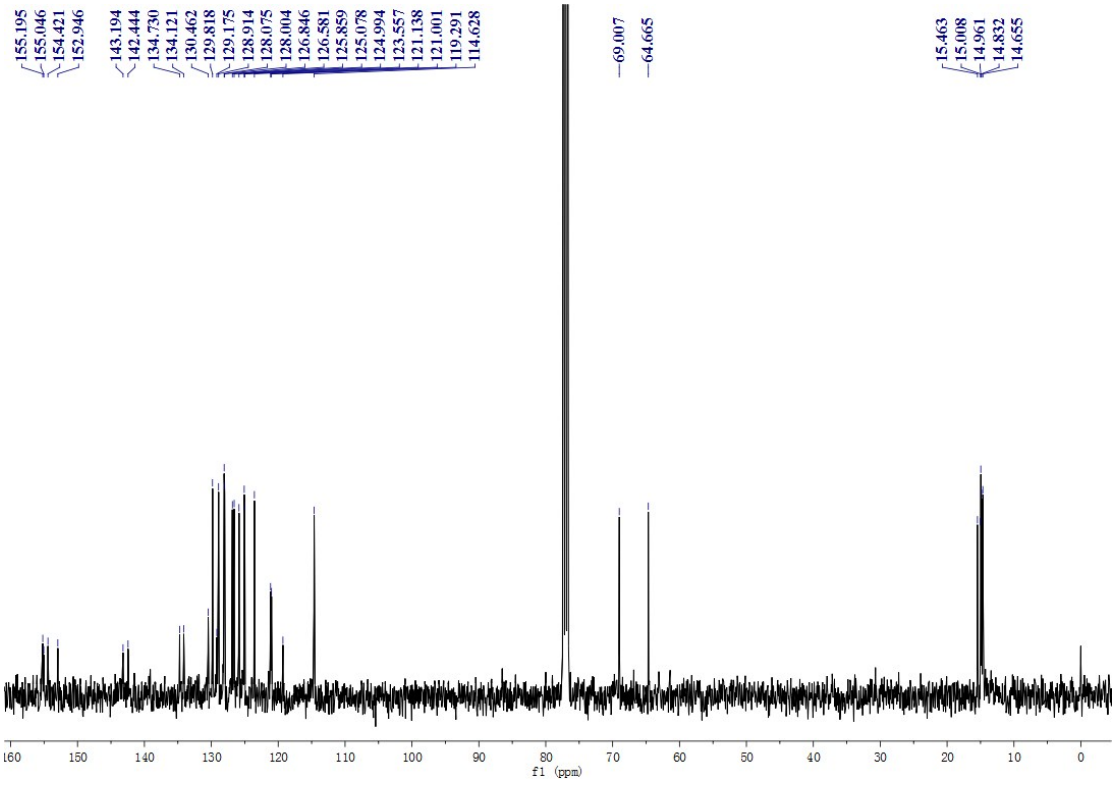


Fig. S5 ^{13}C NMR spectrum of compound *R*/*S*-2 (100 MHz, $CDCl_3$).

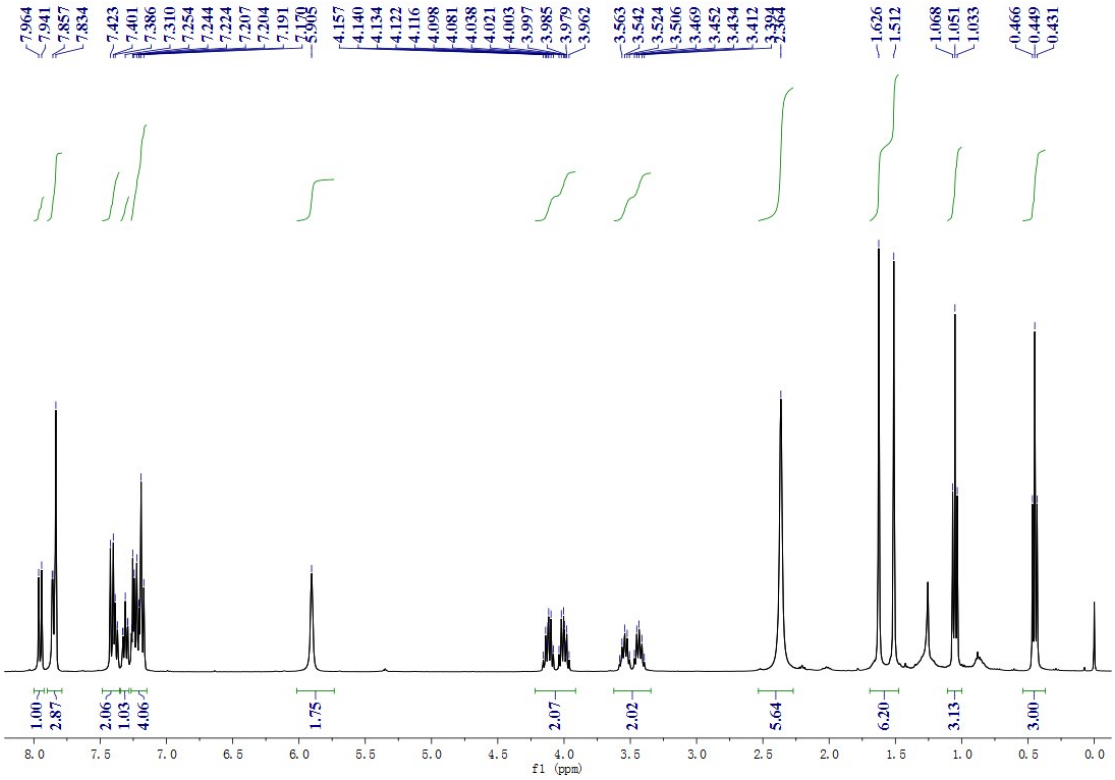


Fig. S6 ^{1}H NMR spectrum of compound *R*/*S*-L1 (400 MHz, $CDCl_3$).

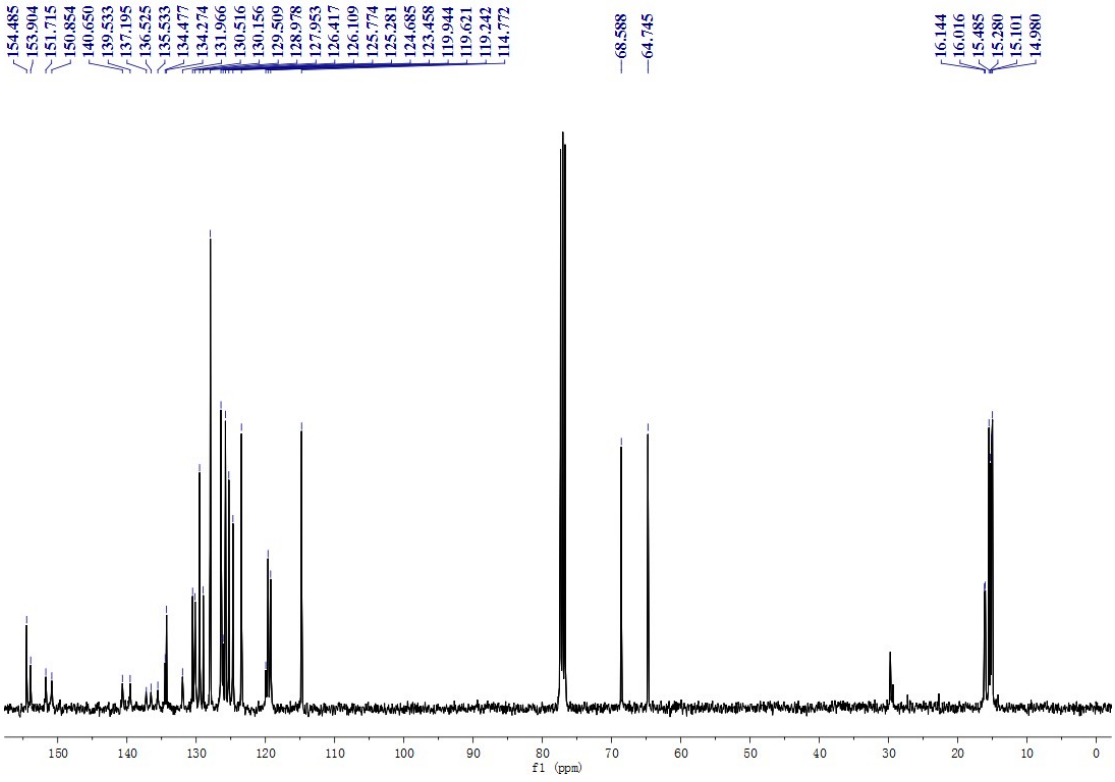


Fig. S7 ^{13}C NMR spectrum of compound *R*/*S*-L1 (100 MHz, $CDCl_3$).

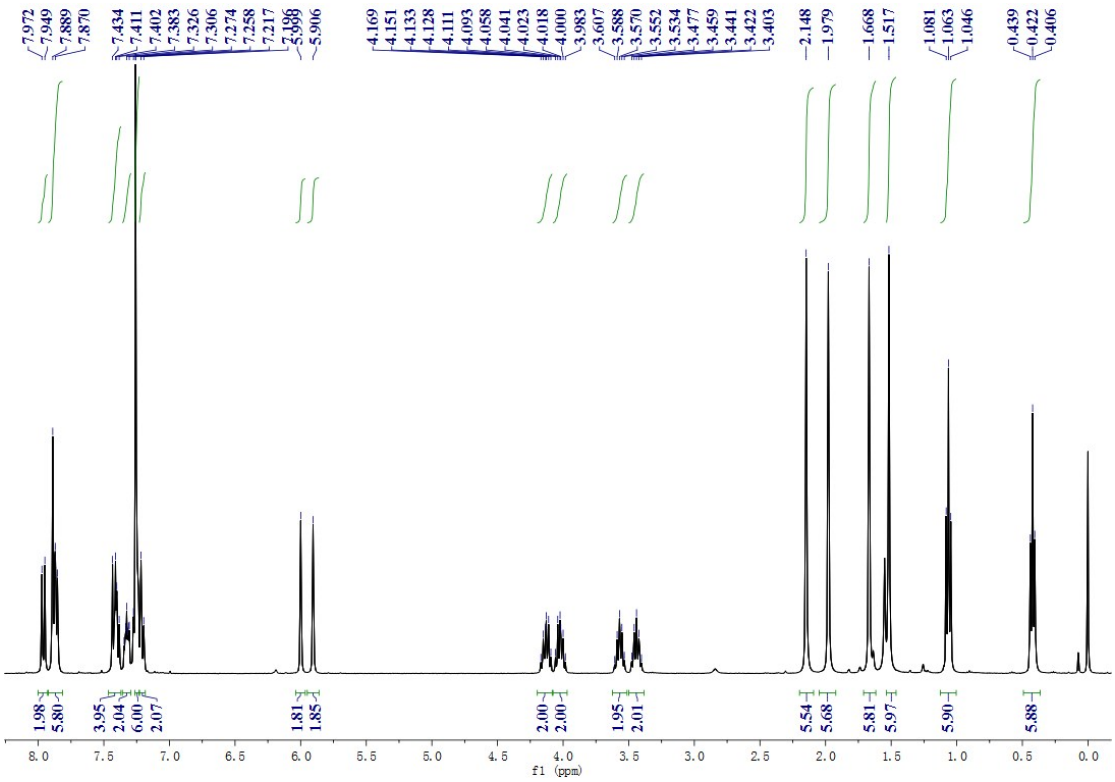


Fig. S8 ^{1}H NMR spectrum of compound *R*/*S*-M1 (400 MHz, $CDCl_3$).

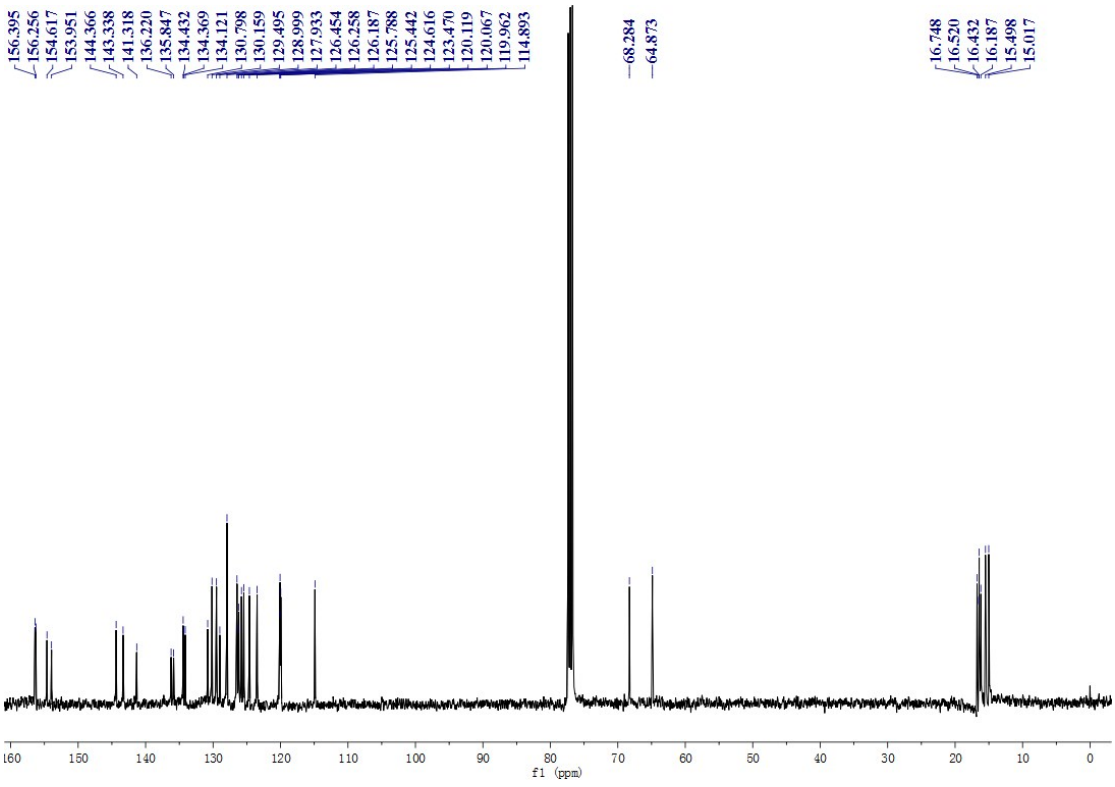


Fig. S9 ^{13}C NMR spectrum of compound *R*/*S*-M1 (100 MHz, $CDCl_3$).

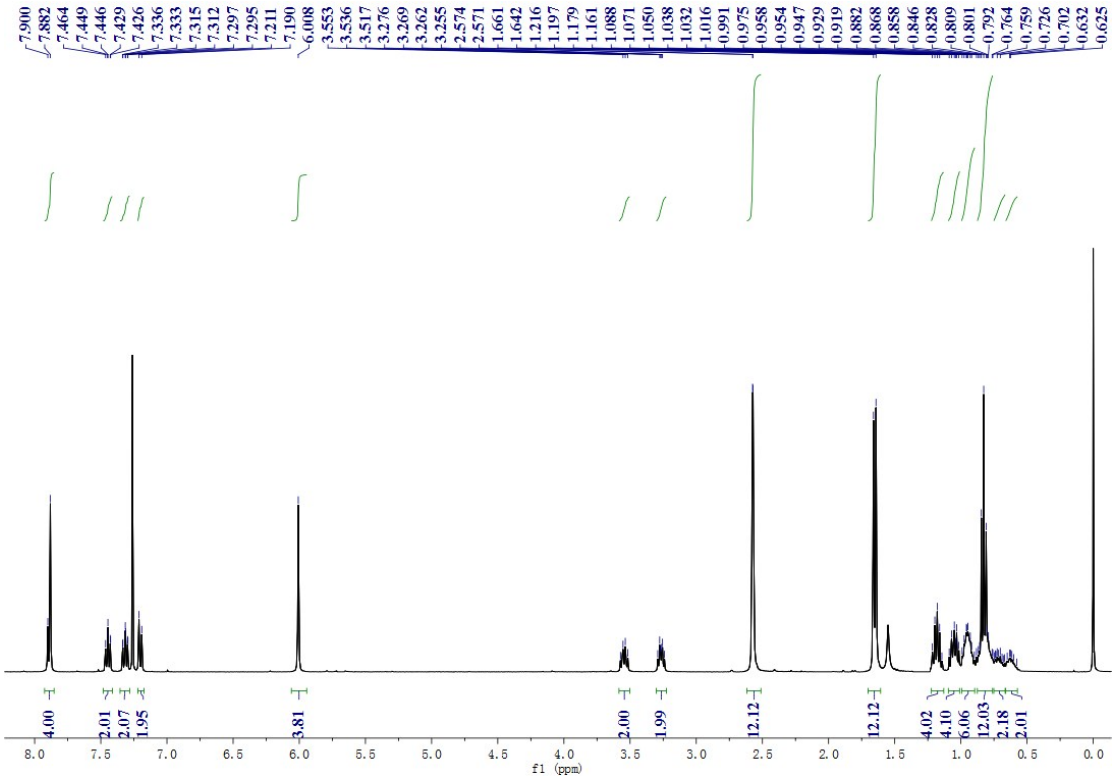


Fig. S10 ^{1}H NMR spectrum of compound *R*/*S*-4 (400 MHz, $CDCl_3$).

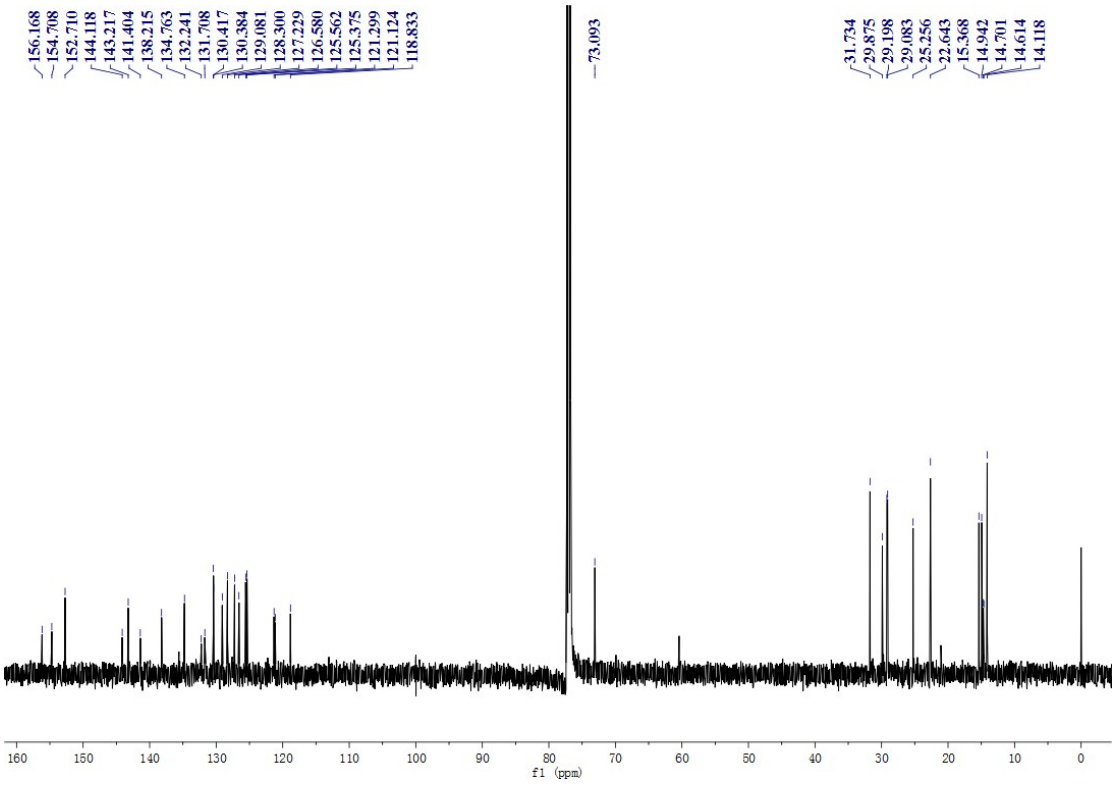


Fig. S11 ^{13}C NMR spectrum of compound *R*/*S*-4 (100 MHz, $CDCl_3$).

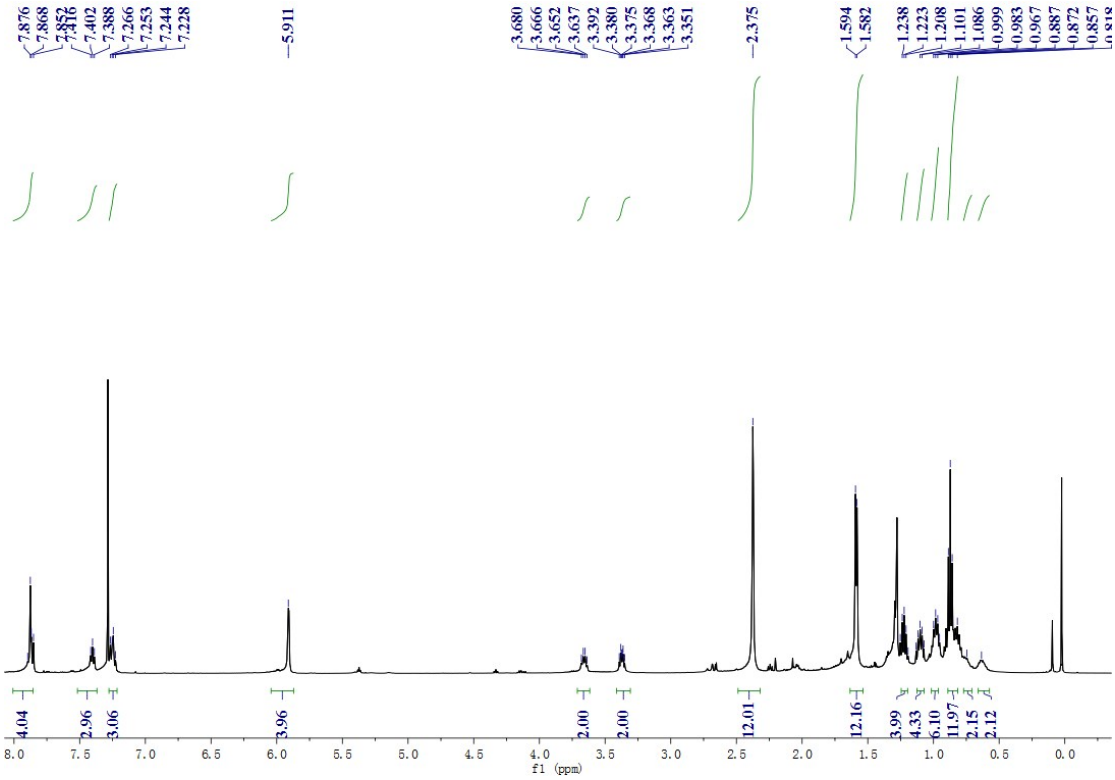


Fig. S12 ^{1}H NMR spectrum of compound *R*/*S*-L2 (500 MHz, $CDCl_3$).

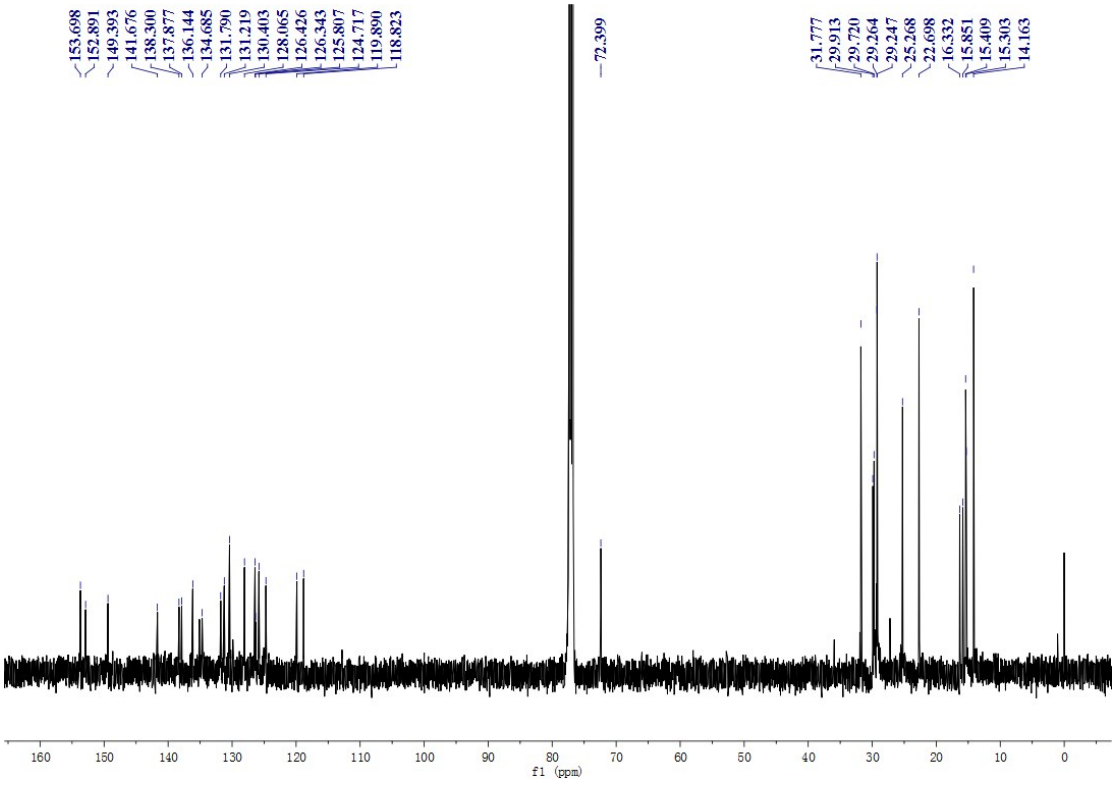


Fig. S13 ^{13}C NMR spectrum of compound *R*/*S*-L2 (125 MHz, $CDCl_3$).

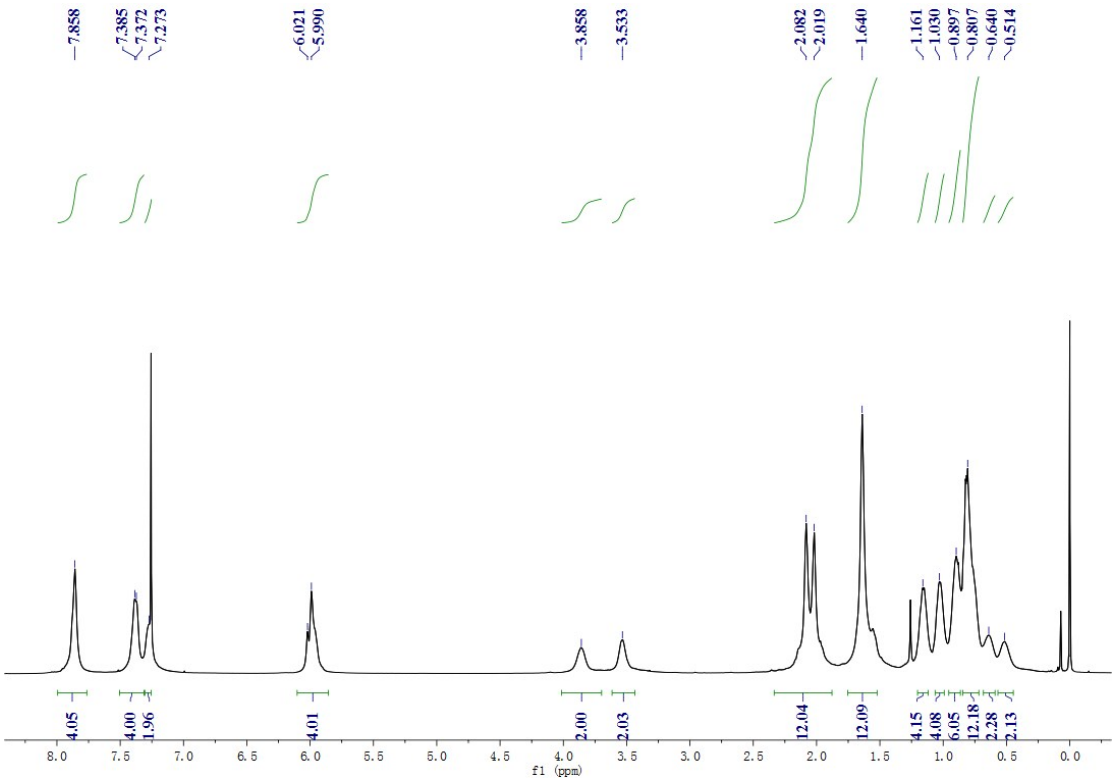


Fig. S14 ^{1}H NMR spectrum of compound *R*/*S*-P1 (400 MHz, $CDCl_3$).

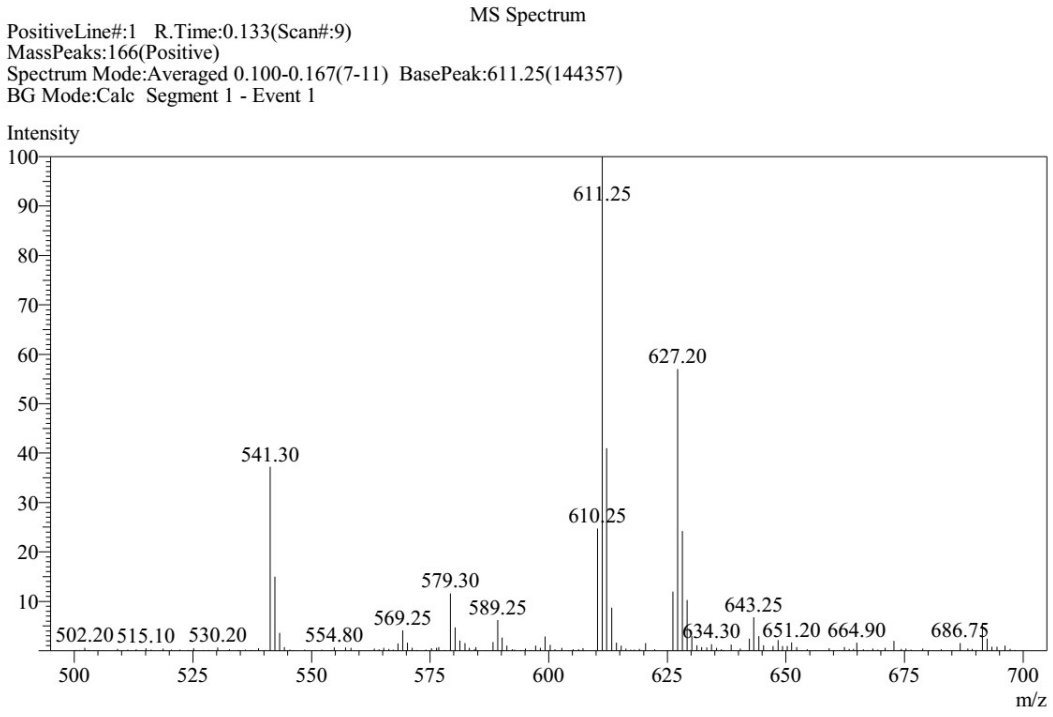


Fig. S15 MS spectrum of compound *R*/*S*-2.

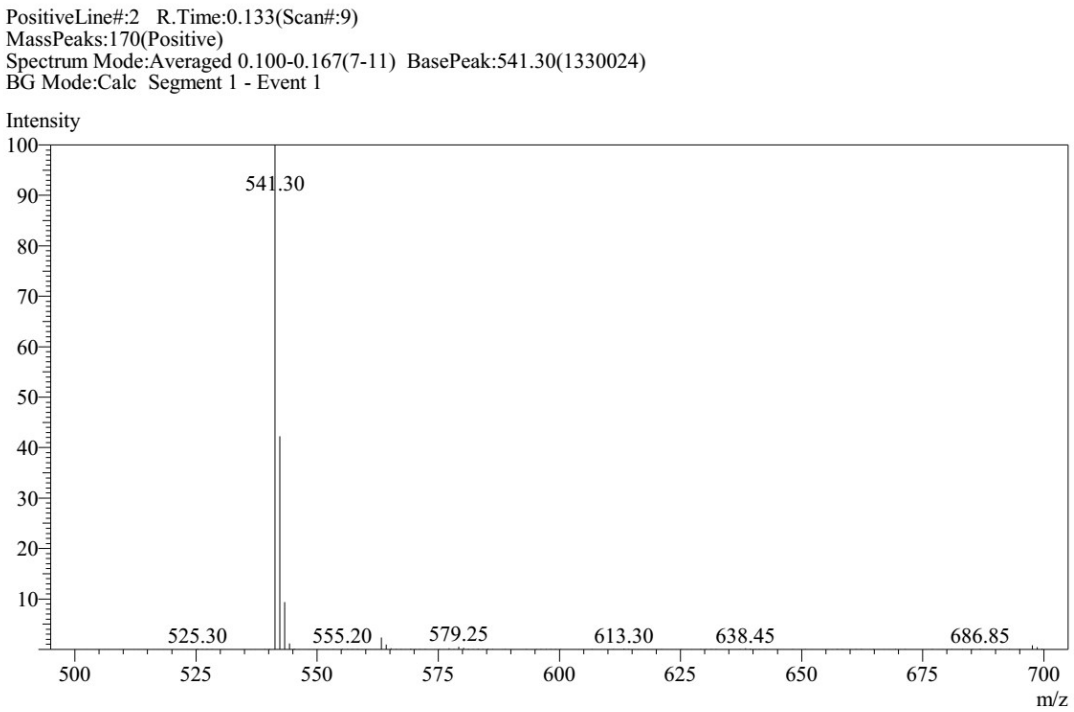


Fig. S16 MS spectrum of compound *R*/*S*-L1.

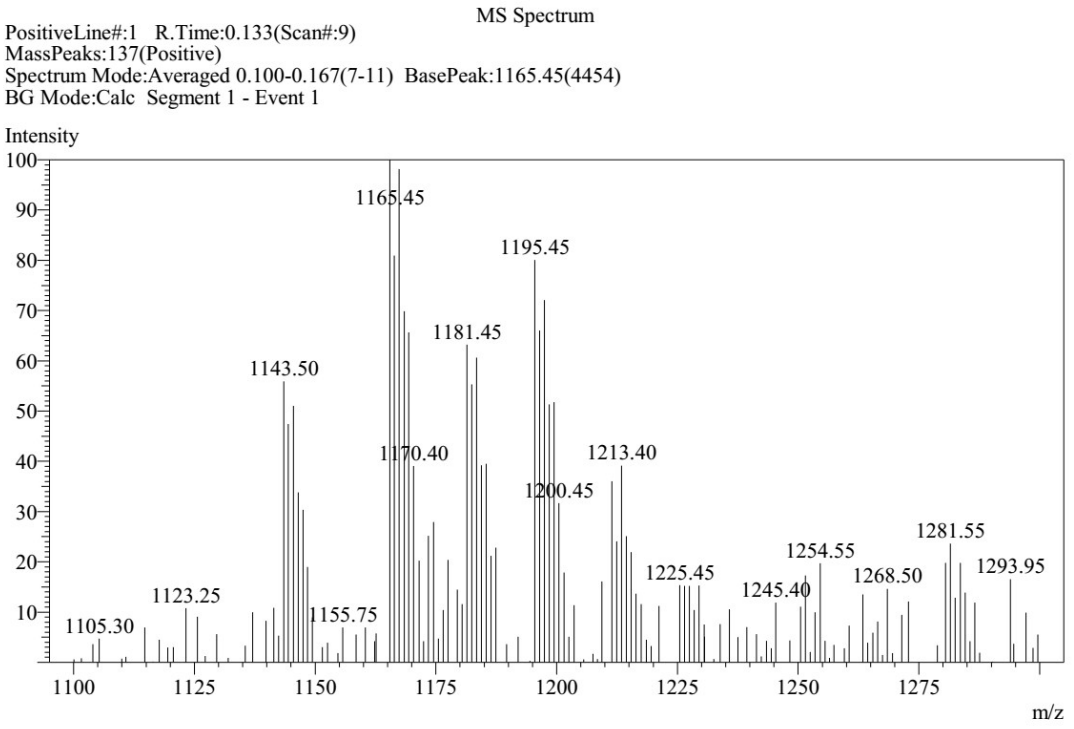


Fig. S17 MS spectrum of compound *R*/*S*-M1.

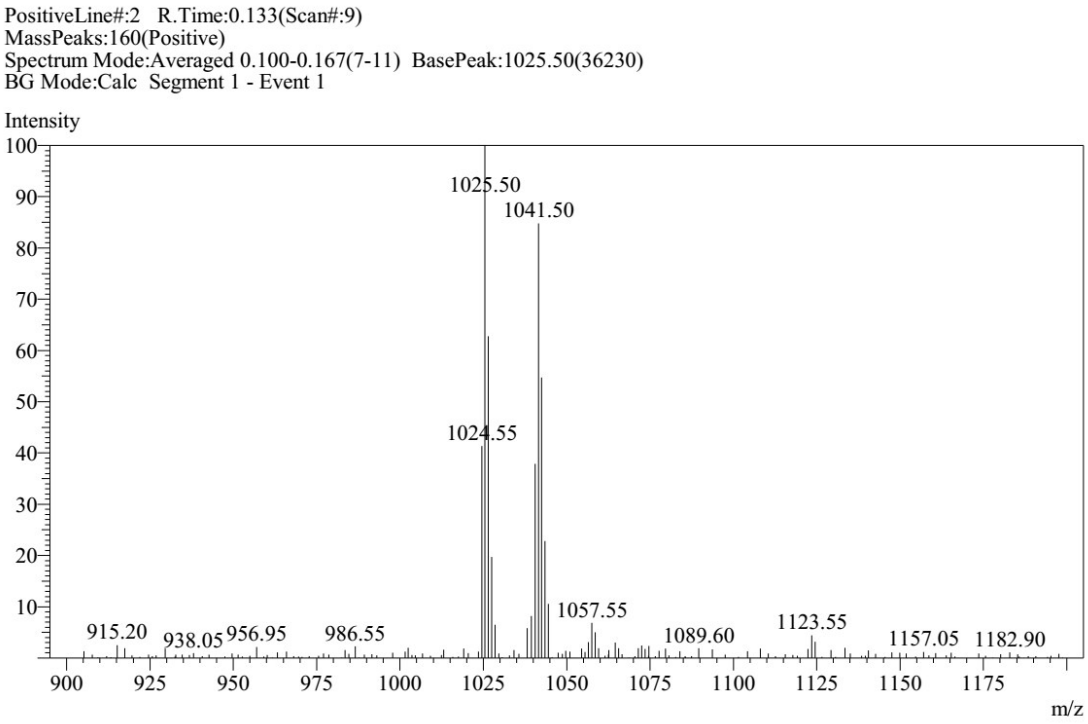


Fig. S18 MS spectrum of compound *R*/*S*-4.

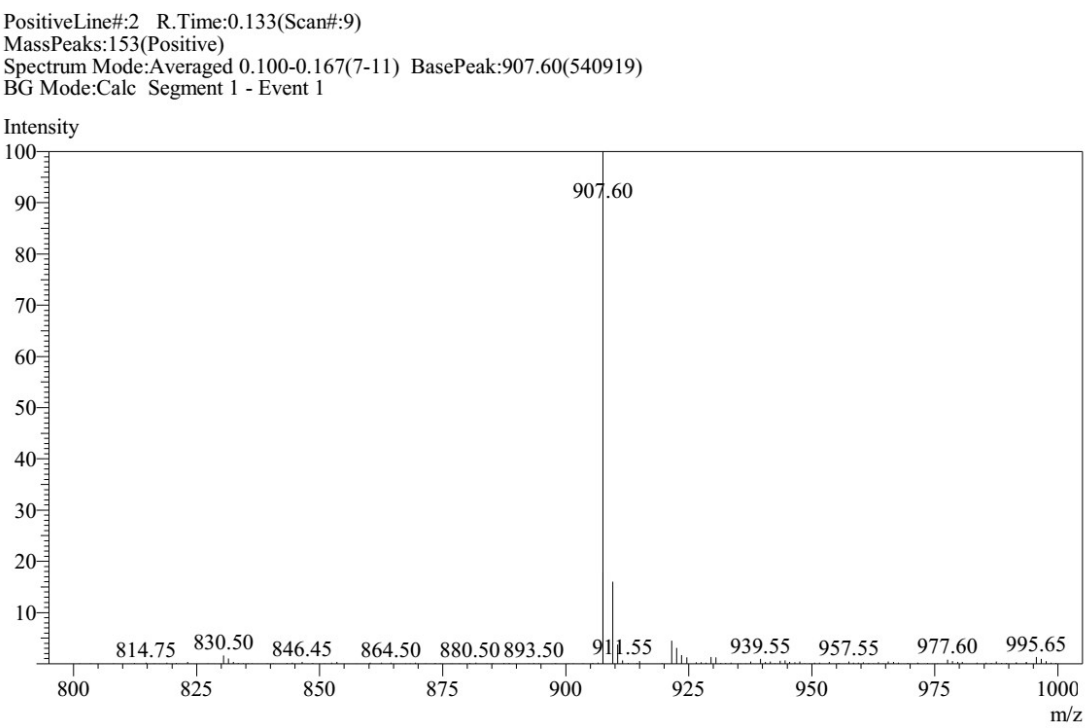


Fig. S19 MS spectrum of compound *R*/*S*-L2.