Supporting Information

General All air-sensitive manipulations were carried out under nitrogen. NMR spectra were recorded on a varian-500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C and 202 MHz for ^{31}P). Chemical shifts are reported in ppm referenced to an internal TMS standard for 1H NMR and chloroform-d (77.00) for ^{13}C NMR. ^{31}P NMR chemical shifts are externally referenced to 85% H_3PO_4. High performance liquid chromatography (HPLC) was performed at 254 nm UV detector. All solvents were distilled by anhydrous technology. $[Ir(COD)Cl]_2$[1] and (*R*)-1,1'-Spirobiindane-7,7'-diol[2] were prepared according to the reported procedures

General procedure for the synthesis of chiral spiro phosphinite ligand.

To a mixture of (*R*)-1,1'-Spirobiindane-7,7'-diol (126 mg, 0.5 mmol), DMAP (10 mg, 0.082 mmol) and triethylamine (0.8 ml, 5.5 mmol) dissolved in CH_2Cl_2 (30 ml) was added dropwise diphenylphosphine chloride (264 mg, 1.2 mmol) within 20 minutes at 0 ℃ under a nitrogen atmosphere. The solvent was removed under reduced pressure for additional three hours. The residue was purified with flash silica gel column (30 ml toluene as eluent) to give 217 mg white solid (70 % yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.96-2.04 (m, 4H, CH_2), 2.60-2.64 (m, 2H, CH_2), 2.80-2.87 (m, 2H, CH_2), 6.78-6.80 (d, J = 8.0 Hz, 2H, Ar-H), 6.89-6.91 (m, 2H, Ar-H), 6.98-7.17 (m, 22H, Ar-H) ppm; ^{31}P NMR ($CDCl_3$, 202 MHz) δ 104.66 ppm; ^{13}C NMR (CDCl3, 125 MHz) δ 153.91, 153.84, 145.89, 141.46, 141.32, 141.30, 141.17, 138.66, 138.63, 130.95, 130.75, 129.92, 129.74, 129.67, 129.08, 128.52, 128.47, 128.45, 128.41, 128.13, 128.12, 118.78, 115.12, 114.95, 59.41, 37.90, 31.39 ppm. HRMS (ES^+) calcd. for $C_{41}H_{35}O_2P_2$ $[M+H]^+$: 621.2112, found: 621.2110.

General procedure for the asymmetric hydrogenation of quinolines.

A mixture of $[Ir(COD)Cl]_2$ (1.0 mg, 0.0015 mmol) and the ligand (2.0 mg, 0.003 mmol) in THF (2.0 mL) was stirred at room temperature for 30 minutes in a glovebox. The mixture (0.1 ml) was transferred by a syringe to a stainless steel autoclave, in

which I_2 (0.38 mg, 0.0015 mmol) and substrate (0.15 mmol) in 1.9 mL THF were placed before hand. The hydrogenation was performed at room temperature under H_2 (700 psi) for 20 h. After carefully releasing the hydrogen, the reaction mixture was diluted with dichloromethane (5 mL), saturated sodium carbonate aqueous solution (2.0 mL) was added and stirred for 15 minutes. The aqueous layer was extracted with CH_2Cl_2 (3 x 3 mL). The combined organic layers were dried with sodium sulfate and concentrated under vacuum to give the crude product. Purification on a silica gel column gave the pure product. The enantiomeric excess was determined by HPLC with a chiral column (OJ-H, OD-H, or AS-H).

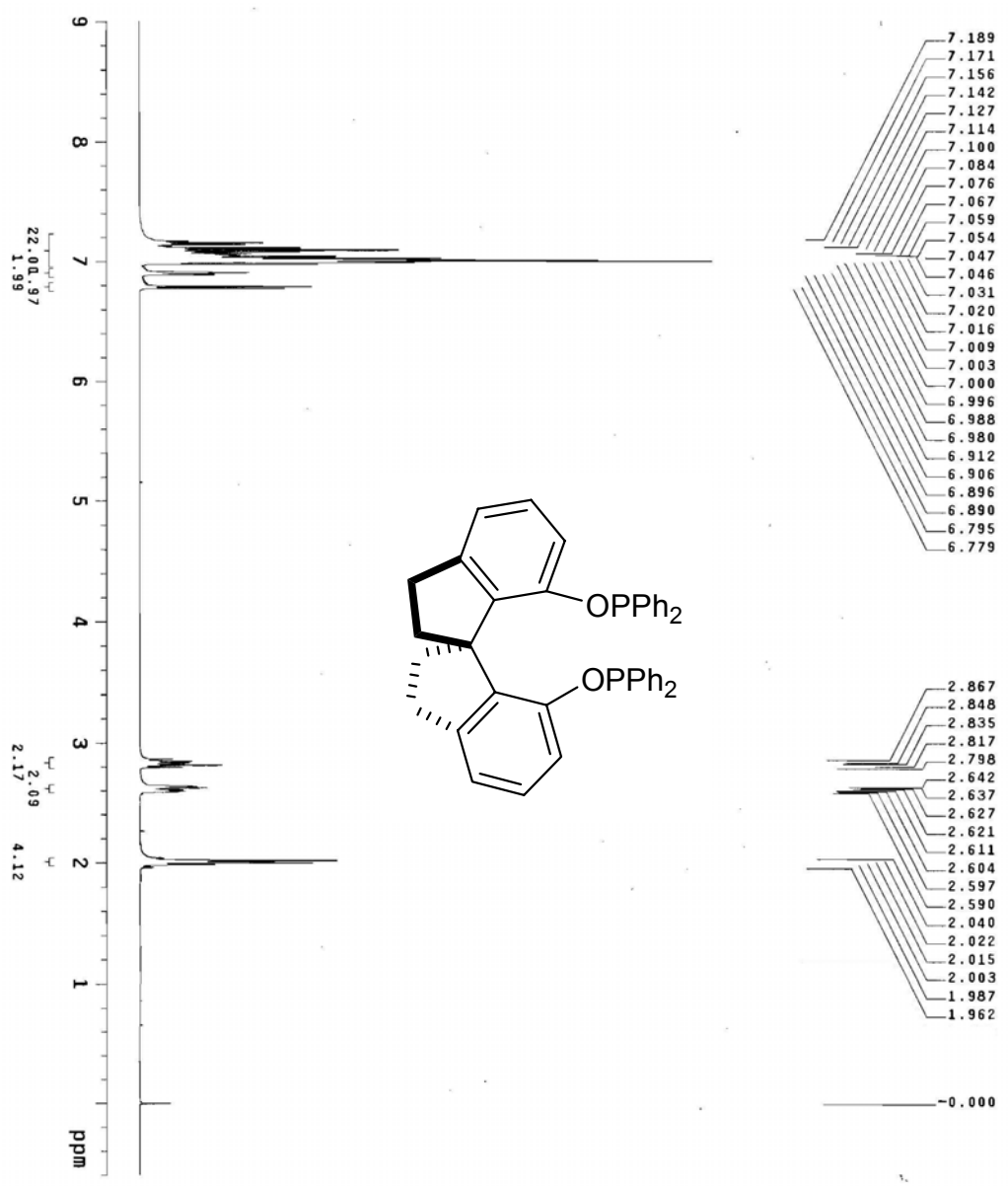
General procedure for the recycling of Ir catalyst in the asymmetric hydrogenation of quinaline using DMPEG/hexane as the solvents.

A mixture of $[Ir(COD)Cl]_2$ (1.0 mg, 0.0015 mmol) and the ligand (2.0 mg, 0.003 mmol) in DMPEG (2.5 mL) was stirred at room temperature for 30 minutes in a glovebox, then I_2 (7.6 mg, 0.03 mmol) and substrate (440 mg, 3.0 mmol) together with 2.5 mL hexane were added and stirred for another 5 minutes. The hydrogenation was then performed at room temperature under H_2 (700 psi) for 20 h. After carefully releasing the hydrogen, the hexane layer was decanted and the product in the DMPEG phase was then further extracted with hexane (3 x 2 mL). The DMPEG layer was recharged with substrate and hexane, and then subjected to hydrogenation again under the same conditions. The combined hexane solution was then washed with saturated sodium carbonate aqueous solution (4.0 mL) and concentrated under vacuum to give the crude product. Purification on a silica gel column led to a pure product. The enantiomeric excess was determined by HPLC with a chiral column (OJ-H).

References

1. J. L. Herde, J. C. Lambert, C. V. Senoff. *Inorg. Synth.* 1974, **15,** 18.

2.V. B. Birman, A. L. Rheingold and K.C. Lam.*Tetrahedron: Asymmetry,* 1999, **10**, 125.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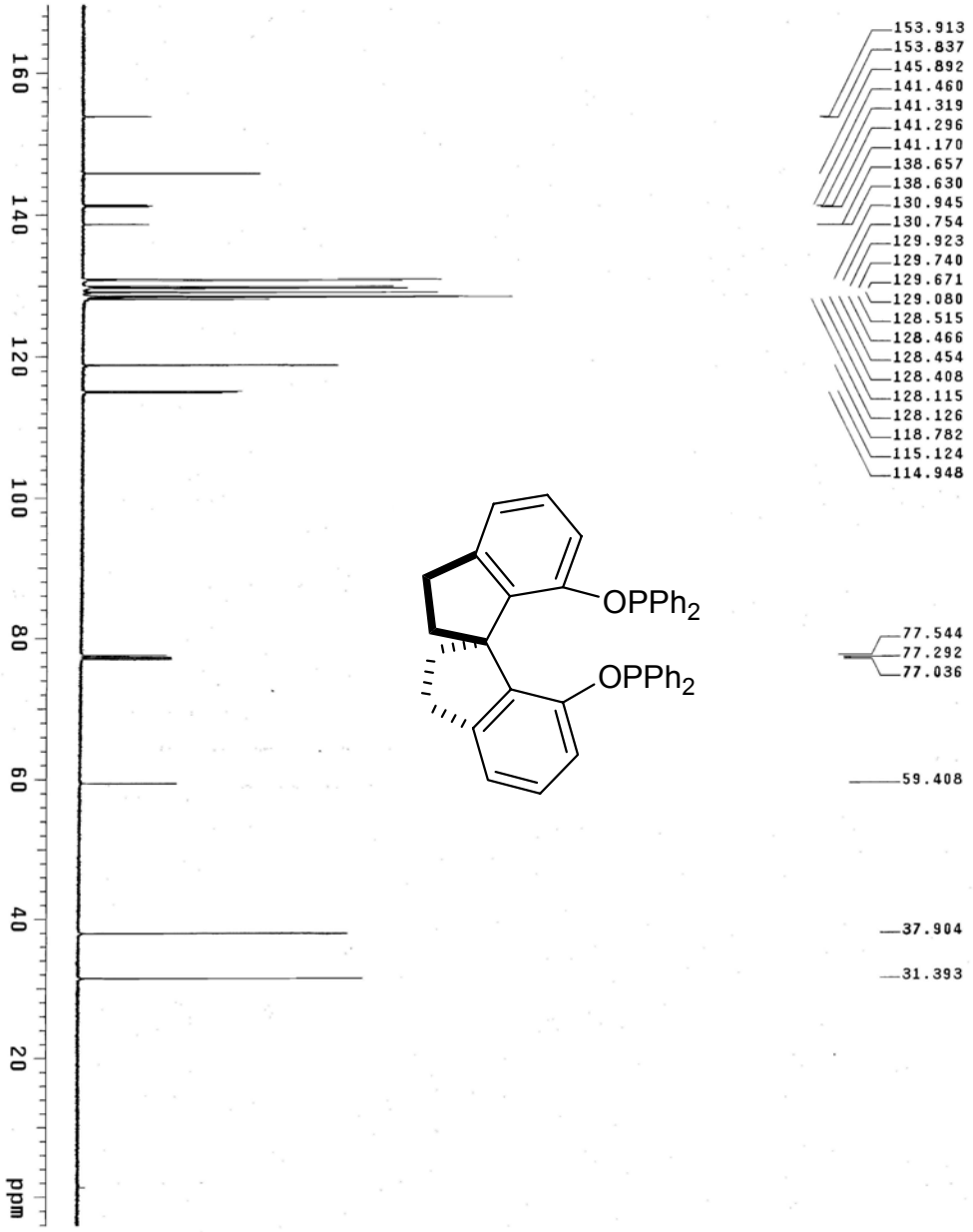
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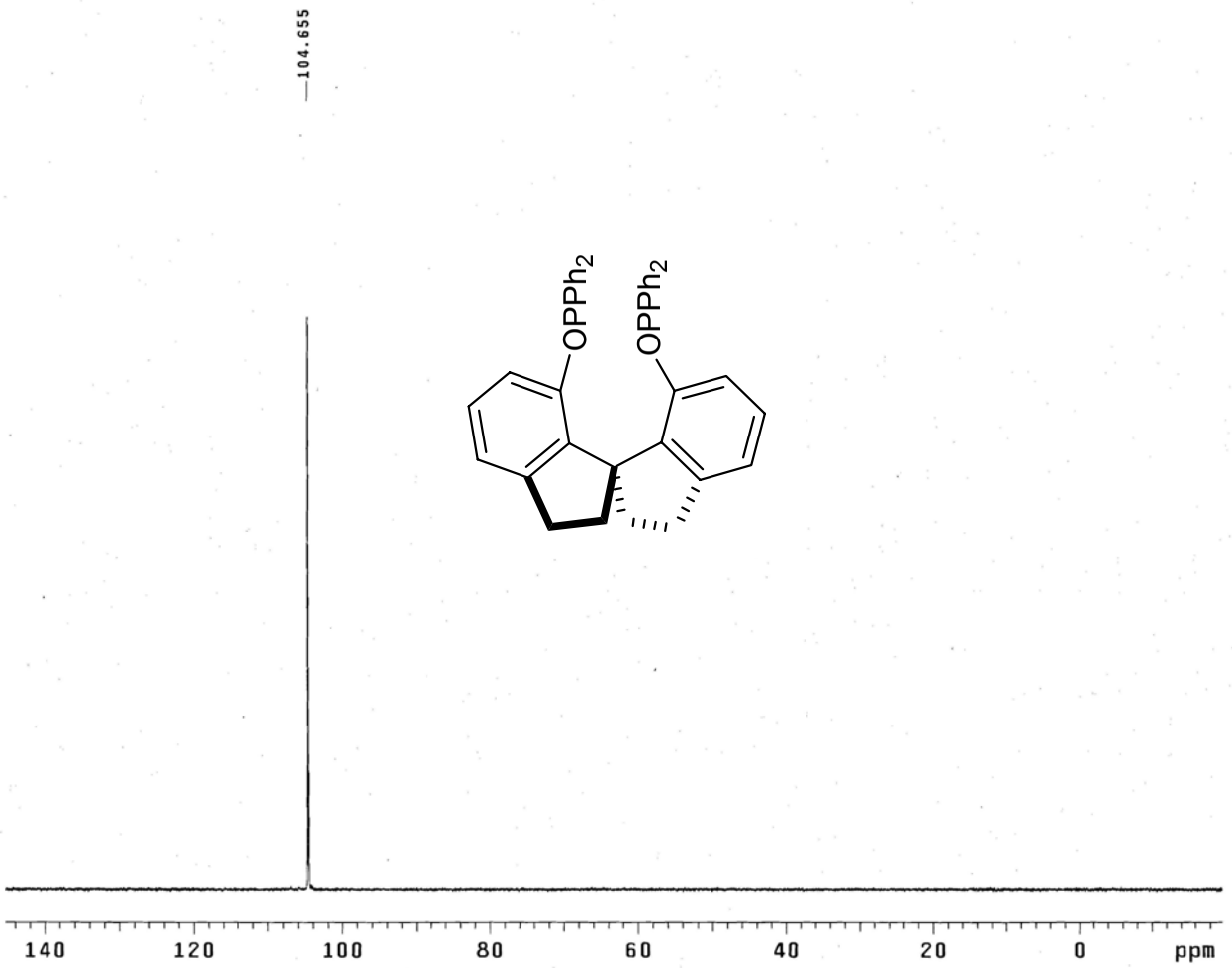
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Elemental Composition Report

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Selected filters: None

Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
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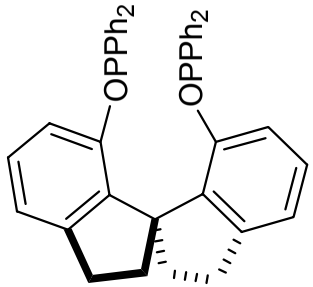
Tanf Wei Jun, Spiropo UC145



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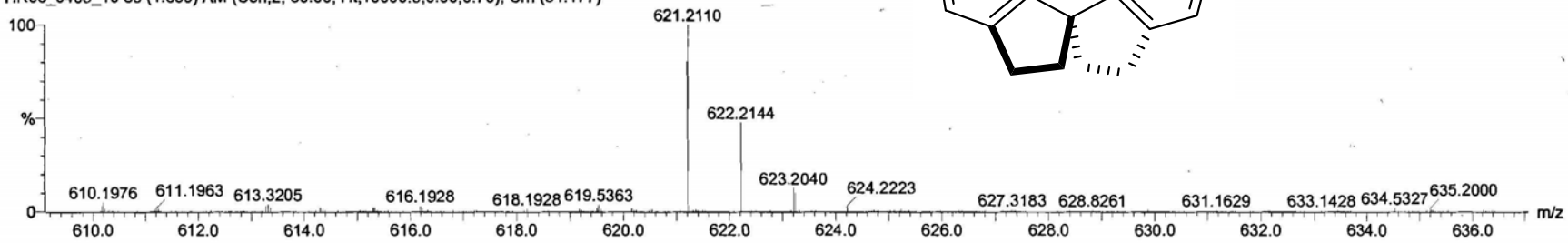

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