SUPPORTING INFORMATION

Silver-Catalyzed Dynamic Systemic Resolution of α-Iminonitriles in a 1,3-Dipolar Cycloaddition Process

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Table of contents

General: All commercially available starting materials were of reagent grade and used as received. ^{1}H NMR and ^{13}C NMR data were recorded on a Bruker Avance DMX 500 at 500 MHz. Chemical shifts are reported as δ values (ppm) with $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.16) as internal standard. *J* values are given in Hertz (Hz). Thin layer chromatography (TLC) was performed on precoated Cromatofolios AL Silica gel 60 F_{254} (Merck, Darmstadt, Germany), visualized with UV-detection. Flash column chromatography was performed on silica gel 60, 0.040-0.063 mm (SDS). Analytical high performance liquid chromatography (HPLC) with chiral stationary phases was performed using an HP-Agilent 1110 series controller, equipped with a Daicel chiralpak OJ (4.6x250 mm, 254 μm) column. Solvents for HPLC use were of spectrometric grade.

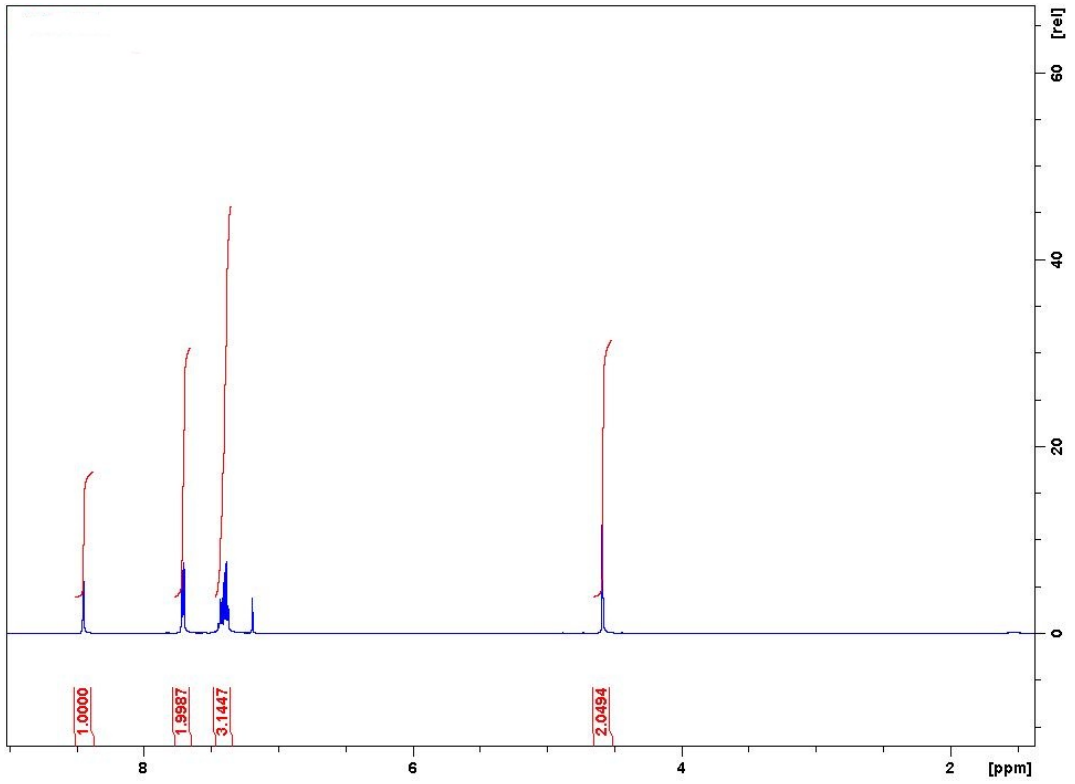
Generation of dynamic system and Ag^{+}/Taniaphos catalyzed asymmetric transformation
To a sealed-cap vial containing 1 equiv of each aldehyde **1b** to **1m** (0.12 mmol), $Sc(OTf)_3$ (0.006 mmol), AgOAc (0.012 mmol), (R_p,*R*)-Taniaphos (0.012 mmol), TEA (0.24 mmol) in THF (0.8 mL) was added α-iminonitrile **2a** (0.12 mmol), dimethyl fumarate (0.16 mmol) in THF (0.4 mL) under argon at 0 ^{o}C. The mixture was stirred at 0 ^{o}C for 10 h, at which time DCM was added. The solution was filtered, and the solvent was removed under reduced pressure. The crude was dissolved in DCM and washed with water and brine, dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude was purified by flash column chromatography (hexane-EtOAc 4:1).

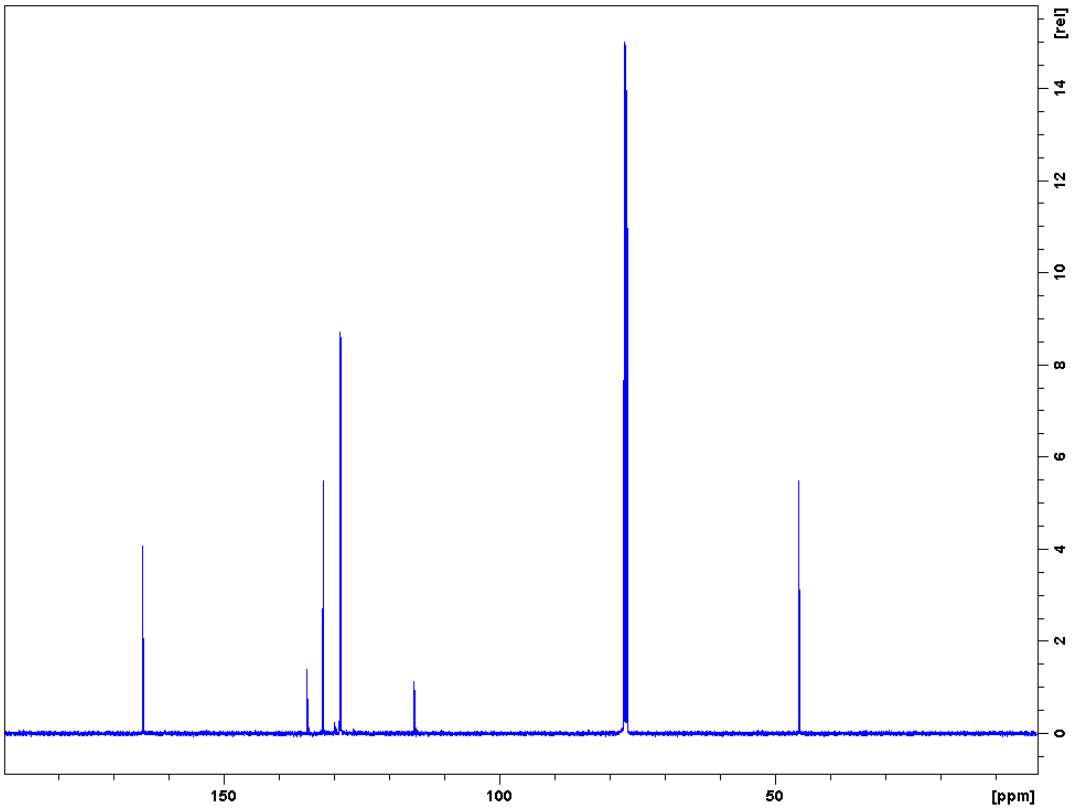
Synthesis of compound 2a
To a suspension of aminoacetonitrile sulfate (600 mg, 3.77 mmol) in ethanol (7 mL) was added Et_3N (1.05 mL, 7.54 mmol), and the mixture was stirred for 1 h, at which time benzaldehyde (96 μL, 0.94 mmol) and silica gel (275 mg) was added. The resulting solution was sonicated for 2 h at rt. The mixture was diluted with ether (10 mL) and washed with water, dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford compound **2a** (132 mg, 97%) as an amber clear oil. ^{1}H NMR (500 Hz, $CDCl_3$) δ = 8.45 (1H, t, *J* = 1.50 Hz), 7.70 (2H, dd, *J* = 7.04, 1.06 Hz), 7.35-7.46 (3H, m), 4.58 (3H, d, *J* = 1.68 Hz); ^{13}C NMR (125 Hz, $CDCl_3$) δ = 164.7, 134.7, 131.9, 128.8, 128.6, 115.3, 45.6.

Synthesis of compound 2k
Following the same procedure as compound **2a** with aminoacetonitrile sulfate (1.30 g, 8.32 mmol), Et_3N (2.3 mL, 16.64 mmol), furfural (170 μL, 2.08 mmol) and silica gel (540 mg) in ethanol (15 mL) afford imine **2k** (223 mg, 80%) as an orange solid. ^{1}H NMR (500 Hz, $CDCl_3$) δ = 8.33 (1H, d, *J* = 1.51 Hz), 7.59 (1H, d, *J* = 1.28 Hz), 6.91 (1H, d, *J* = 3.34 Hz), 6.54 (1H, dd, *J* = 2.67, 1.60 Hz), 4.66 (2H, d, *J* = 4.96, 1.28 Hz); ^{13}C NMR (125 Hz, $CDCl_3$) δ = 152.4, 150.5, 146.0, 117.0, 114.9, 112.1, 45.4.

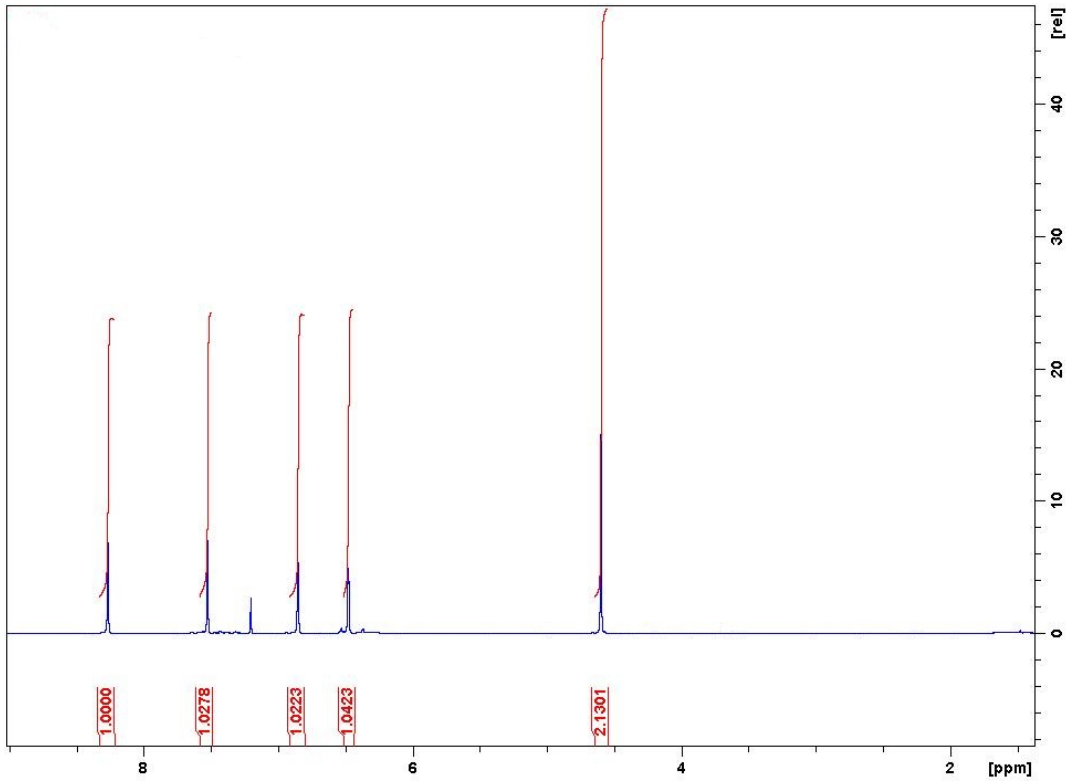
Synthesis of racemic compound 4k
To a mixture of (R_p,*R*)-Taniaphos (13.1 mg, 0.019 mmol), AgOAc (2.9 mg, 0.017 mmol) and NaOAc (2.8 mg, 0.035 mmol) in DCM (0.5 mL), a solution of α-iminonitrile **2k** (25 mg, 0.17 mmol) in DCM (1.0 mL), and dimethyl fumarate (39 mg, 0.26 mmol) were successively added under argon atmosphere. After stirring for 4 h at room temperature, the mixture was diluted with DCM and filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromathography (hexane-EtOAc 4:1) affording *endo*-**4k** (26 mg, 62%) as a white solid. ^{1}H NMR (500 Hz, $CDCl_3$) δ = 7.36-7.38 (1H, m), 6.29-6.38 (2H, m), 4.70 (1H, d, *J* = 7.97 Hz), 4.29 (1H, d, *J* = 7.82 Hz), 3.99 (1H, t, *J* = 8.05 Hz), 3.79 (3H, s), 3.57 (1H, t, *J* = 7.67 Hz), 3.54 (3H, s); ^{13}C NMR (125 Hz, $CDCl_3$) δ = 170.9, 169.9, 151.3, 142.7, 118.9, 110.5, 108.1, 58.6, 53.1, 52.5, 51.4, 50.1, 49.5.

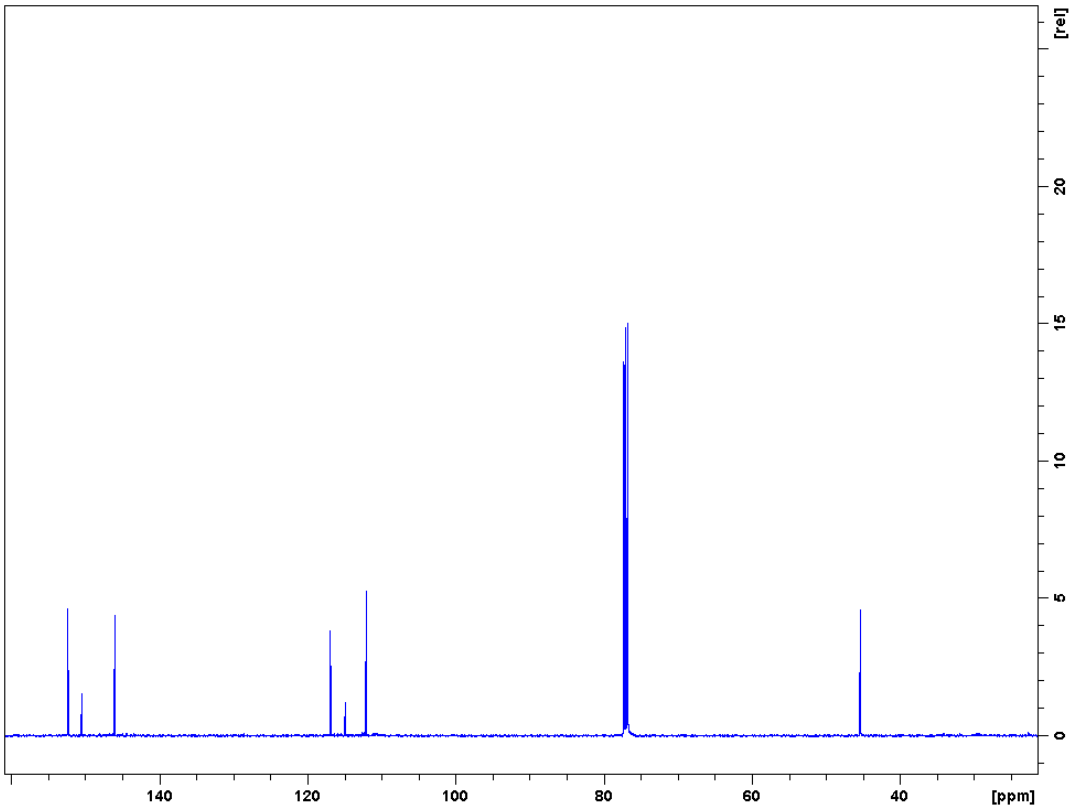
^{1}H NMR and ^{13}C NMR of compound **2a**



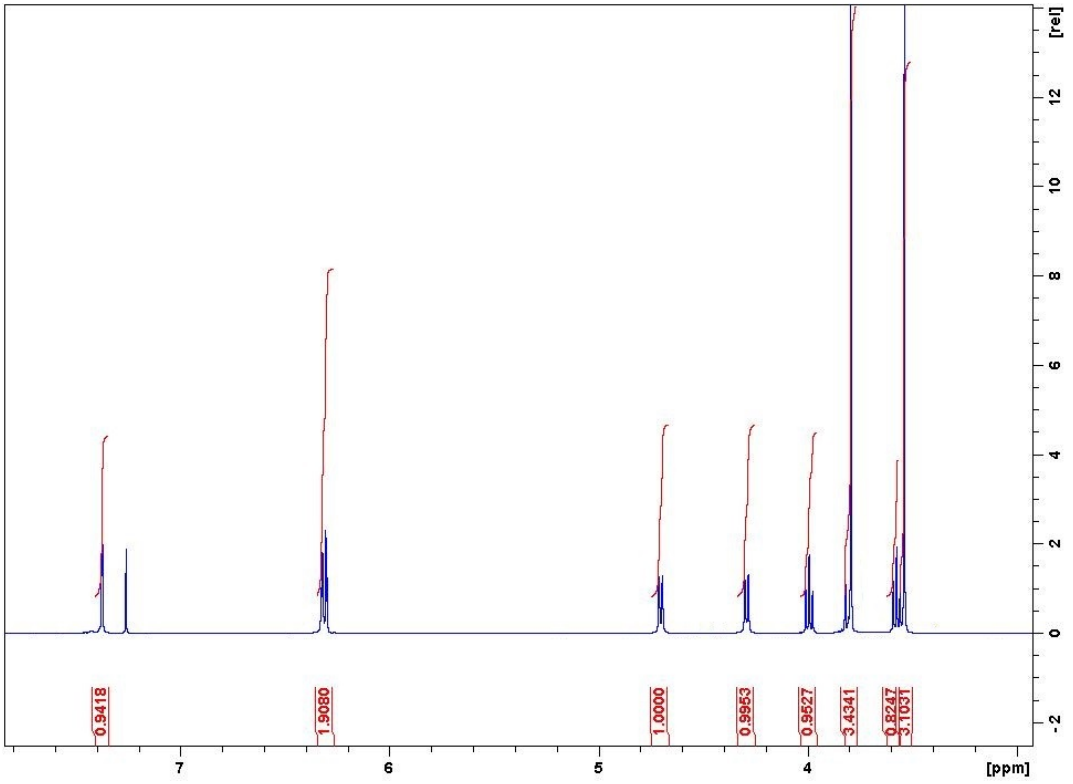


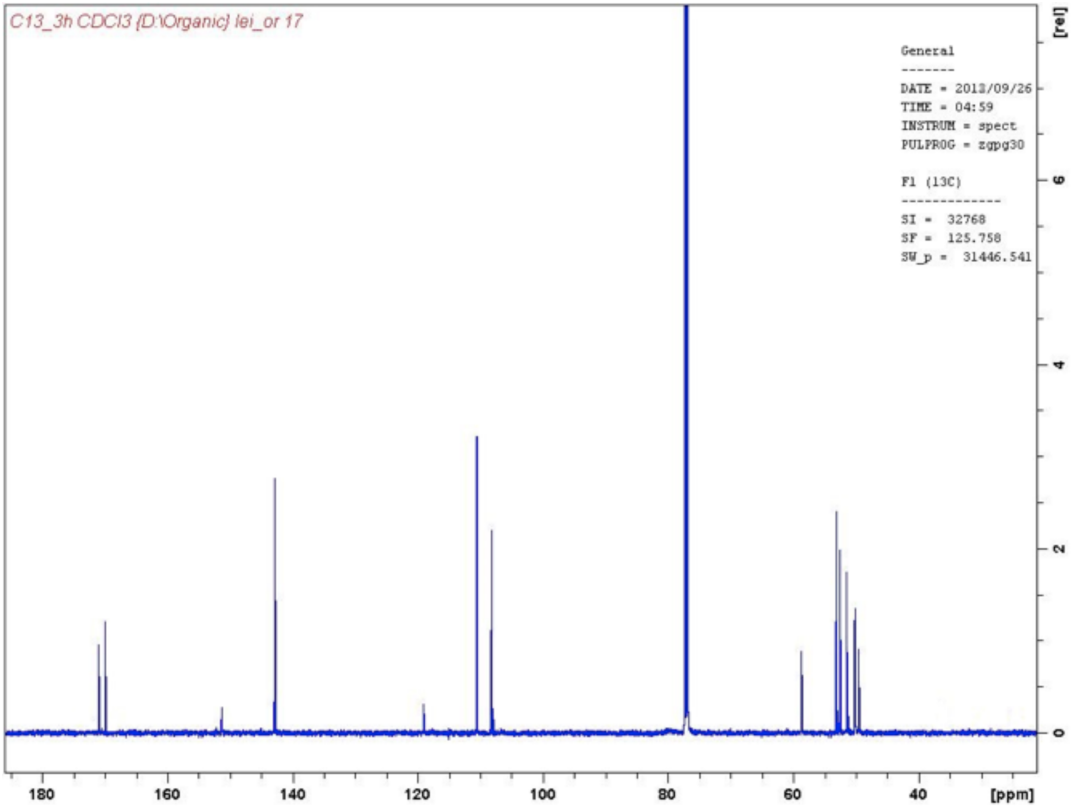
^{1}H NMR and ^{13}C NMR of compound **2k**





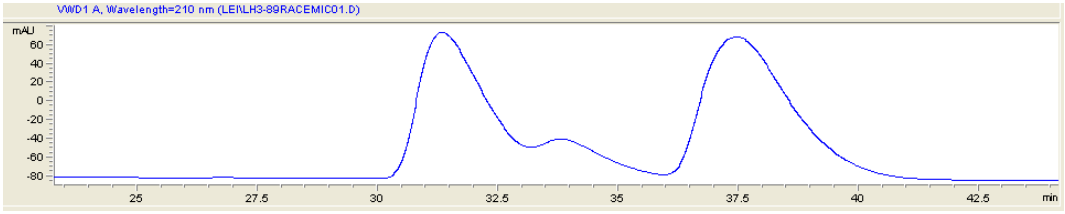
^{1}H NMR and ^{13}C NMR of compound **4k**



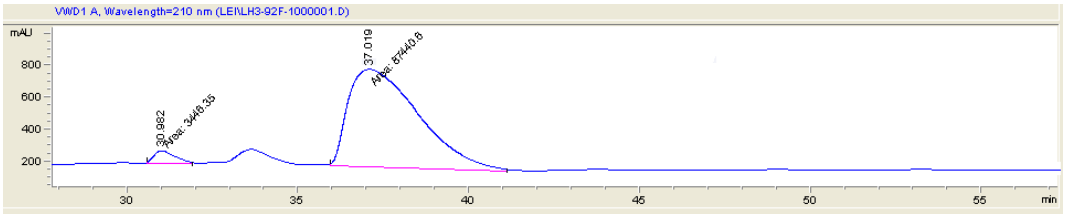


HPLC analyses

The enantiomeric purity of product 4B from the dynamic systems was determined by analytical HPLC using a Daicel Chiralpak OJ column. Analyses were carried out at 298 K and 210 nm for 40 min, using hexane:^{i}PrOH (60:40, v/v) as mobile phase.



a) Racemic mixture of compound **4k**



b) Enantioenriched compound **4k** separated from dynamic system