Supporting Information

Axially Chiral *N*-heterocyclic Carbene Gold(I) Complexes Catalyzed Asymmetric Cycloisomerization of 1,6-Enynes

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CONTENTS

(A) General Remarks.

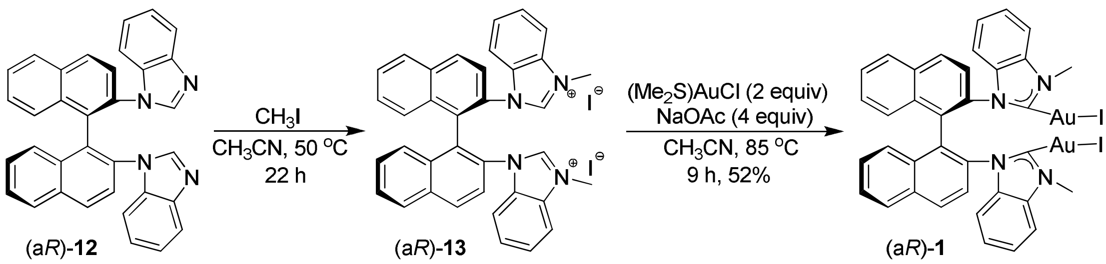
Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. Melting points were measured on a Yanagimoto micro melting apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded by using a Varian Mercury vx 300 MHz or Bruker 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. ^{1}H-NMR and ^{13}C-NMR chemical shift were referenced to 0.00 ppm (TMS) and 77.0 ppm ($CDCl_3$), respectively. Coupling constants (*J*) are given in Hz. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer 341 MC digital polarimeter with a 10 cm cell (*c* given in g per 100 mL) and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Satisfactory CHN microanalyses were obtained by using a Carlo-Erba 1106 analyzer. X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer. Chiral HPLC was performed by using a SHIMADZU SPD-10A *vp* series instrument with chiral columns (Chiralpak AD-H column, ϕ 4.6 × 250 mm, Daicel Chemical Co. Ltd). All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out by using 300~400 mesh silica gel at increased pressure, where $KMnO_4$ and $H_3[P(Mo_3O_{10})_4]\cdot H_2O$ were used for visualization.

(B) Procedures and Spectroscopic Data for the Synthesis of Axially Chiral NHC-Au(I) Complexes 1, 2a, b and 3-11.

(1) General Procedure for the Synthesis of Gold(I) Complex 1

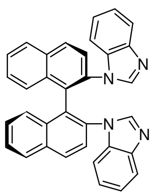
Compound **12**[1] (97 mg, 0.2 mmol) and CH_3I (0.25 mL, 4.0 mmol) in CH_3CN (4.0 mL) were stirred under reflux for 22 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **13** was used for the next step without any further purification. The imidazolium salt was obtained in almost quantitative yield at this step.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **13** (77 mg, 0.1 mmol), NaOAc (33 mg, 0.4 mmol) and [$(Me_2S)AuCl$] (59 mg, 0.2 mmol) followed by the addition of dry CH_3CN (5.0 mL) as the solvent. After refluxing at 85 °C for about 9 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 1/1) to give **1** as a white solid in 52% yield. Single crystals of complex **1** suitable for an X-ray diffraction study were grown from the solution of **1** in mixed petroleum ether/CH_3CN/CH_2Cl_2 (1:2:2) (Scheme S1).

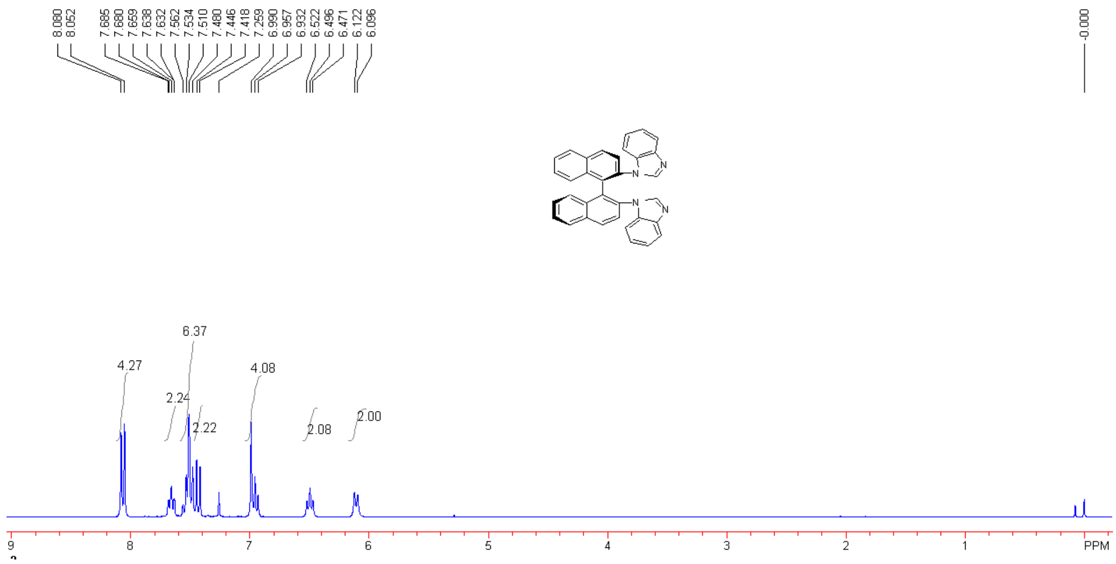


Scheme S1

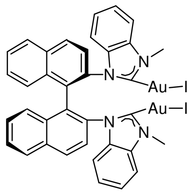
Compound (a*R*)-**12**



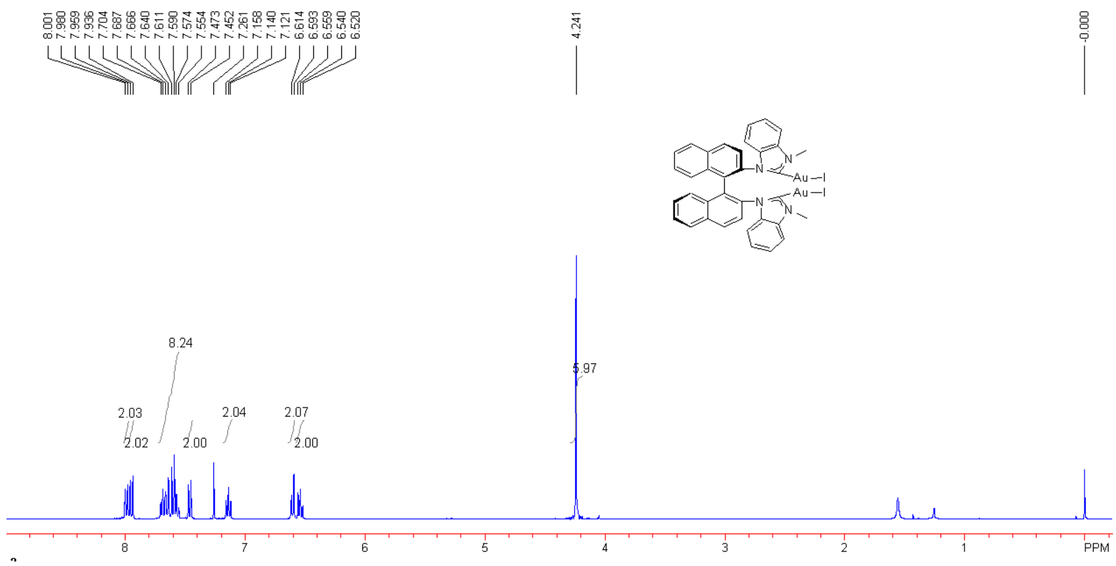
It is a known compound.[1] White solid; m.p. 294-295 °C; $[\alpha]^{20}_D$ = +563.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 6.11 (d, *J* = 7.8 Hz, 2H), 6.50 (t, *J* = 7.5 Hz, 2H), 6.93-6.99 (m, 2H), 6.99 (s, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.48-7.56 (m, 6H), 7.63-7.69 (m, 2H), 8.07 (d, *J* = 8.4 Hz, 4H).



Complex (a*R*)-**1**



White solid; m.p. 300.4-301.5 °C (dec.). $[\alpha]^{20}_{D}$ = +24 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3058, 2923, 2852, 1592, 1462, 1436, 1391, 1360, 1261, 1241, 1133, 1099, 1063, 1014, 862, 828, 806, 763, 738, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.24 (s, 6H), 6.54 (t, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.55-7.70 (m, 8H), 7.95 (d, *J* = 9.2 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H). LRMS (ESI) *m/e* 1035.1 $[M^+\text{-I}]$; HRMS (ESI) calcd for $[C_{36}H_{26}N_4I_2Au_2\text{-I}]$ requires 1035.0533, found 1035.0527 $[M^+\text{-I}]$.

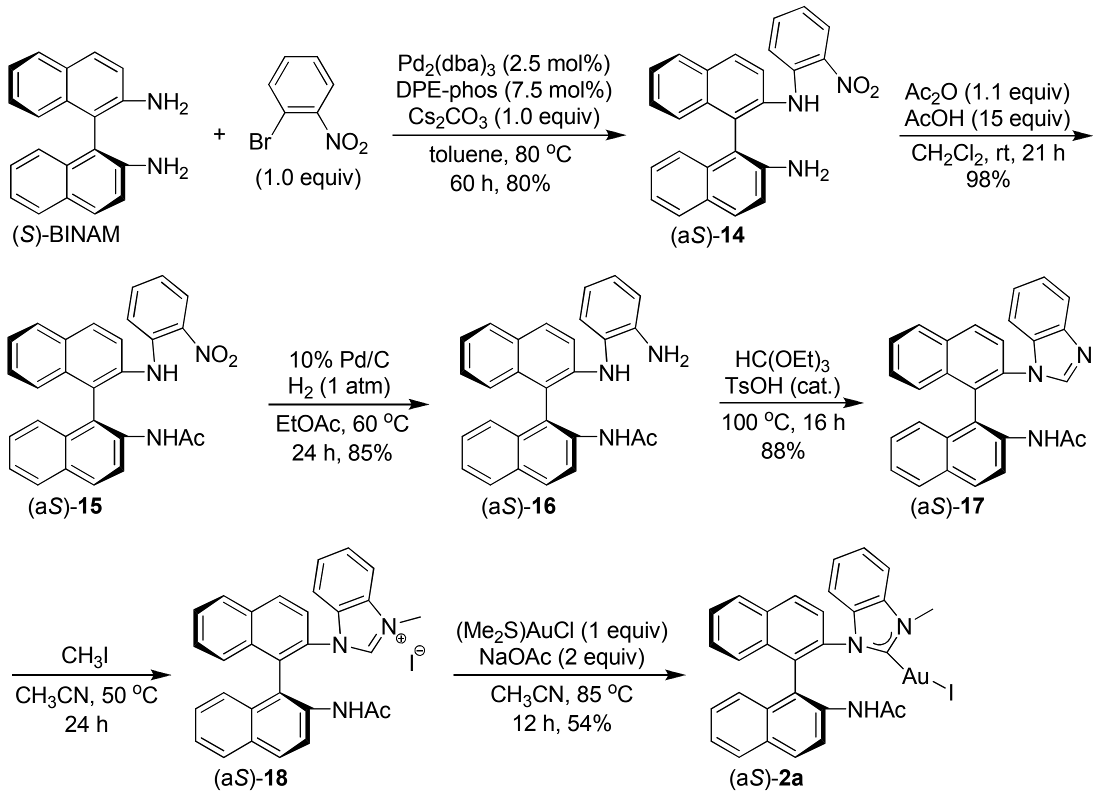


(2) General Procedure for the Synthesis of Gold(I) Complexes 2a and 2b

The precursor of mono-benzimidazole compound (a*S*)-**17** was prepared from (*S*)-binaphthyl-2,2'-diamine (BINAM) according to our previously reported procedures with a sequence of palladium catalyzed coupling, acetylation of primary amine, palladium catalyzed hydrogenation of nitro group, and ring closing with triethyl orthoformate.[2]

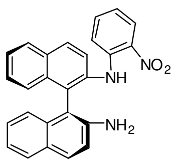
Compound **17**[2] (86 mg, 0.2 mmol) and CH_3I (0.125 mL, 2.0 mmol) in CH_3CN (4.0 mL) were stirred under reflux for 24 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **18** was used for the next step without any further purification. The imidazolium salt was obtained in almost quantitative yield at this step.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **18** (57 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol) and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5.0 mL) as the solvent. After refluxing at 85 ^{o}C for about 12 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 2.5/1) to give complex **2a** as a white solid in 54% yield. Single crystals of **2a** suitable for an X-ray diffraction study were grown from the solution of **2a** in mixed ethyl ether/CH_2Cl_2 (1:1) (Scheme S2).

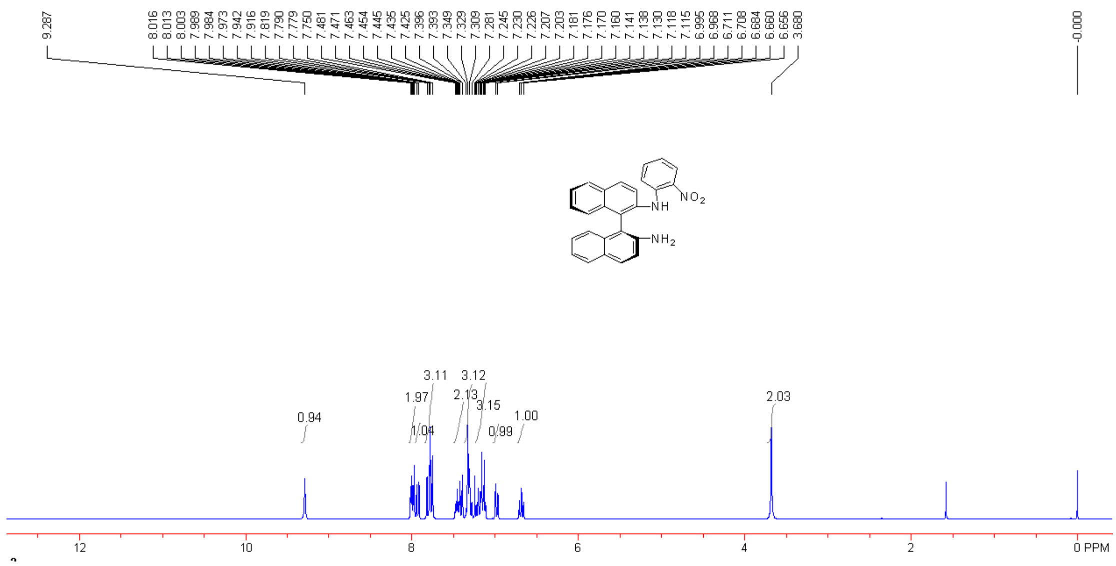


Scheme S2

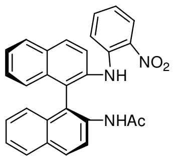
Compound (a*S*)-**14**



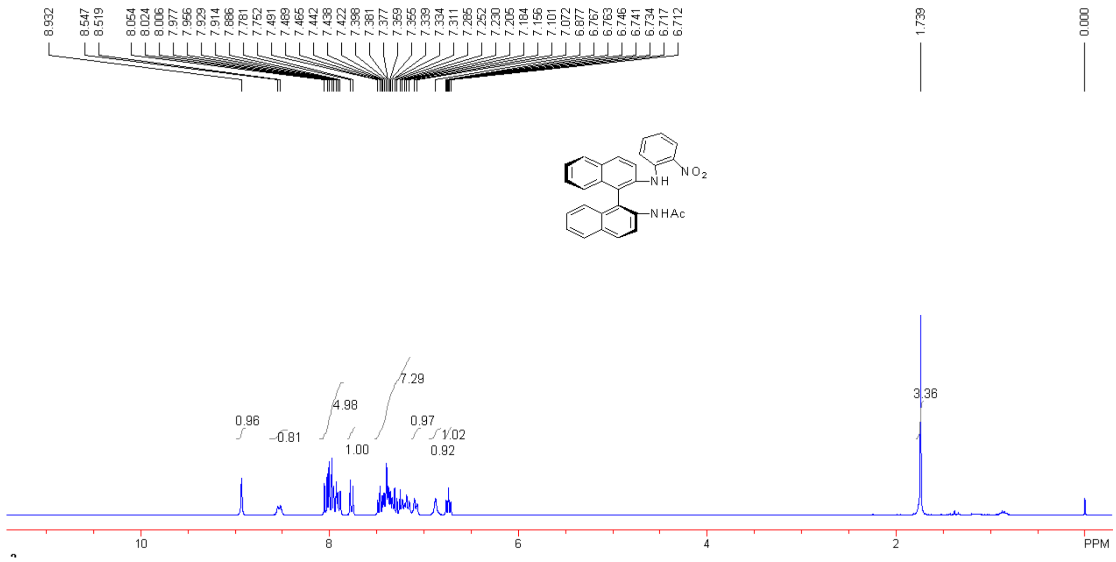
It is a known compound.[2] Red solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 3.68 (s, 2H), 6.66-6.71 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 7.12-7.23 (m, 3H), 7.28-7.35 (m, 3H), 7.39-7.48 (m, 2H), 7.75-7.82 (m, 3H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.97-8.02 (m, 2H), 9.29 (s, 1H).



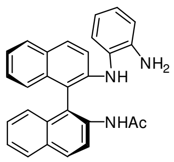
Compound (a*S*)-**15**



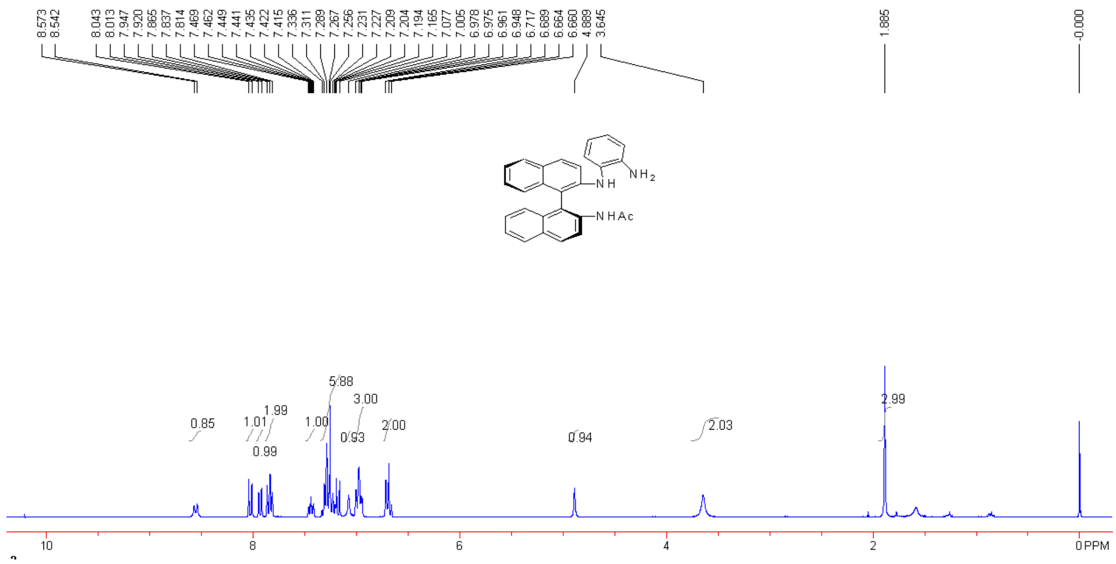
It is a known compound.[2] Red solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.74 (s, 3H), 6.71-6.77 (m, 1H), 6.88 (s, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 7.16-7.49 (m, 7H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.89-8.05 (m, 5H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.93 (s, 1H).



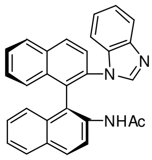
Compound (a*S*)-**16**



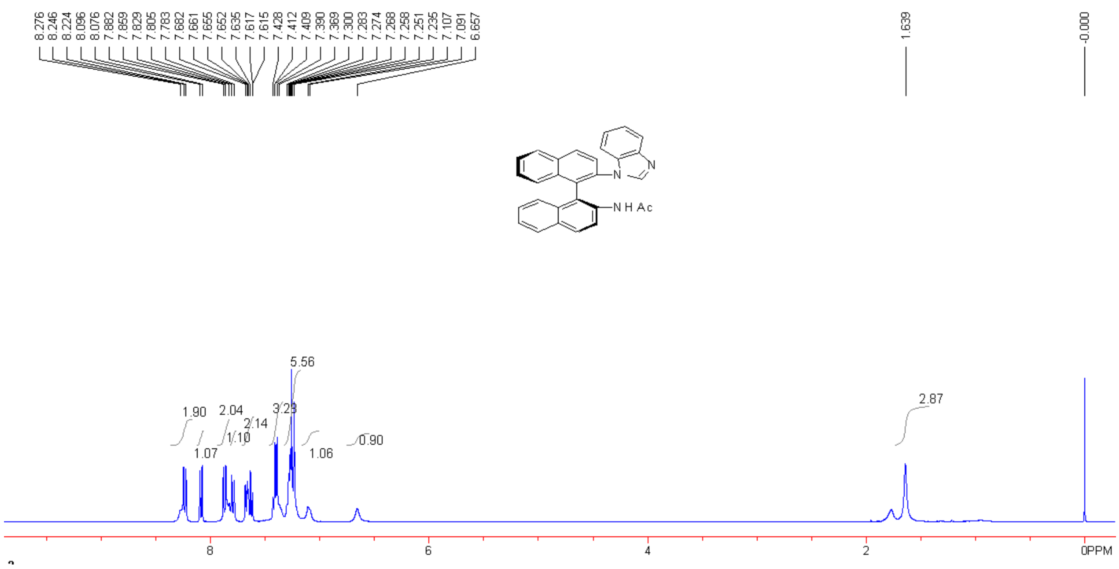
It is a known compound.[2] White solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.89 (s, 3H), 3.65 (s, 2H), 4.89 (s, 1H), 6.66-6.72 (m, 2H), 6.95-7.01 (m, 3H), 7.08 (s, 1H), 7.17-7.34 (m, 5H), 7.42-7.47 (m, 1H), 7.81-7.87 (m, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 8.56 (d, *J* = 9.3 Hz, 1H).



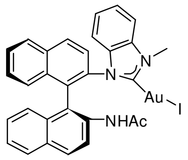
Compound (a*S*)-**17**



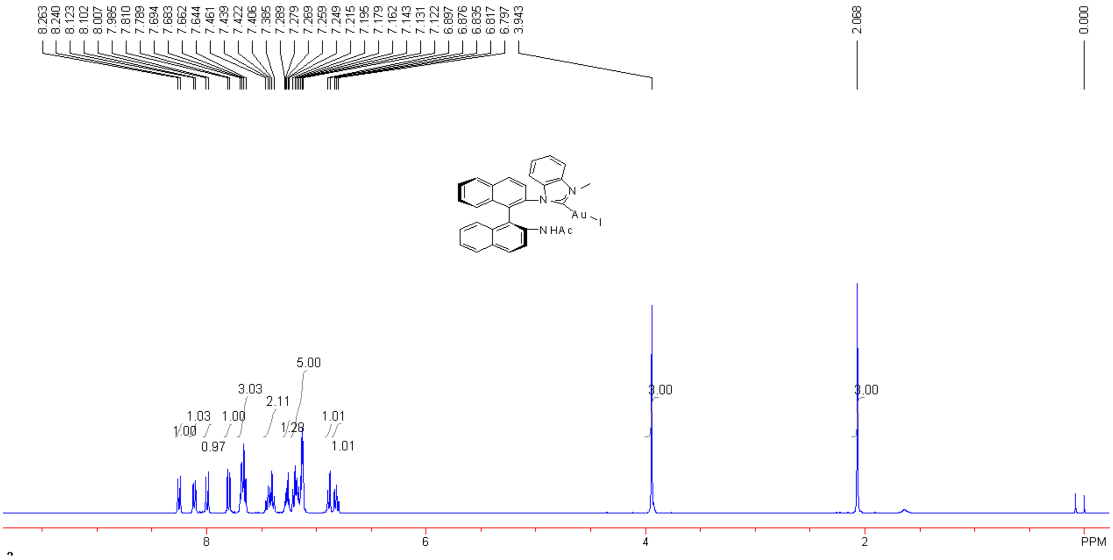
It is a known compound.[2] White solid; m.p. 228-230 °C. $[\alpha]^{20}_{D}$ = -218 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3223, 3052, 2929, 1656, 1597, 1500, 1488, 1453, 1364, 1275, 1232, 865, 812, 742, 715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.64 (s, 3H), 6.66 (s, 1H), 7.09-7.11 (m, 1H), 7.24-7.30 (m, 5H), 7.37-7.43 (m, 3H), 7.62-7.68 (m, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.83-7.88 (m, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.22-8.28 (m, 2H).



Complex (a*S*)-**2a**

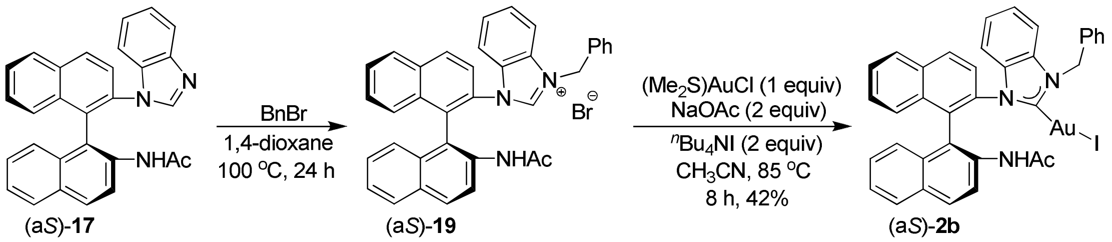


White solid; m.p. 259.5-260.6 °C (dec.). $[\alpha]^{20}_{D}$ = -52 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3324, 1702, 1507, 1482, 1465, 1391, 1354, 1306, 1245, 1150, 1133, 1013, 863, 828, 808, 763, 750, 693 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.07 (s, 3H), 3.94 (s, 3H), 6.82 (t, J = 8.0 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 7.12-7.22 (m, 5H), 7.25-7.29 (m, 1H), 7.39-7.46 (m, 2H), 7.64-7.69 (m, 3H), 7.80 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 9.2 Hz, 1H). LRMS (ESI) *m/e* 638.1 [M^+-I]; HRMS (ESI) calcd for [$C_{30}H_{23}N_3IAu$-I] requires 638.1507, found 638.1484 [M^+-I].



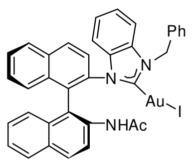
Compound **17** (86 mg, 0.2 mmol) and benzylbromide (0.24 mL, 2 mmol) were refluxed in 1,4-dioxane (3 mL) until completely comsuming **17** by TLC monitoring. When lots of white solids were precipitated in the reaction system, the resulting suspension was cooled to room temperature and filtered through Celite to obtain solids, which were then washed with *n*-hexane for three times to give mono-benzimidazolium salt **19** in almost quantitative yield without any further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **19** (60 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol), $^tBu_4NI$ (74 mg, 0.2 mmol) and [$(Me_2S)AuCl$] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5 mL) as the solvent. After refluxing at 85 °C for about 8 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 3/1) to give complex **2b** as a white solid in 42% yield (Scheme S3).

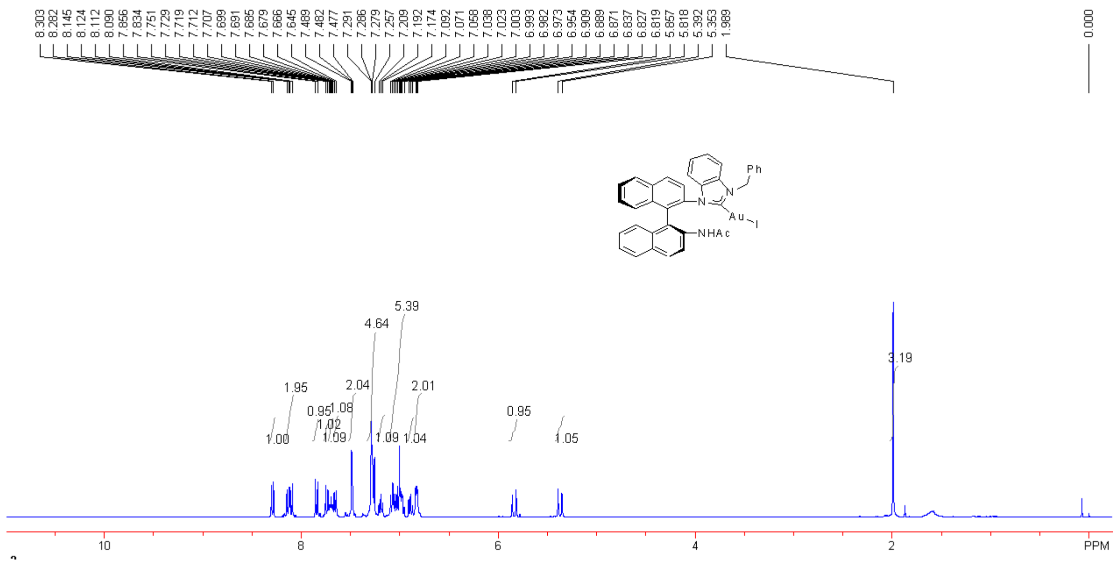


Scheme S3

Complex (a*S*)-**2b**



White solid; m.p. 291.9-293.0 °C (dec.). $[\alpha]^{20}_{D}$ = -31 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3428, 2923, 2853, 1701, 1618, 1595, 1568, 1495, 1423, 1402, 1346, 1306, 1278, 1252, 1223, 1192, 1013, 839, 823, 755, 731, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.99 (s, 3H), 5.37 (d, *J* = 15.6 Hz, 1H), 5.84 (d, *J* = 15.6 Hz, 1H), 6.82-6.84 (m, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.95-7.09 (m, 5H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.28-7.29 (m, 4H), 7.48-7.49 (m, 2H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.68-7.72 (m, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H). LRMS (ESI) *m/e* 714.2 [M^+-I]; HRMS (ESI) calcd for [$C_{36}H_{27}N_3IOAu$-I] requires 714.1820, found 714.1821 [M^+-I].



(3) General Procedure for the Synthesis of Gold(I) Complex (a*S*)-3

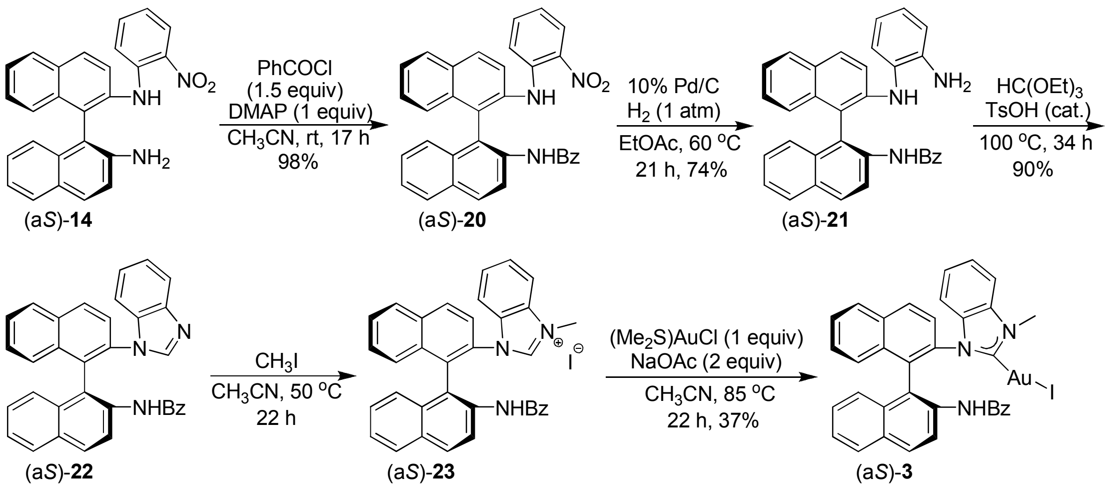
To a mixture of **14** (405 mg, 1.0 mmol) and DMAP (122 mg, 1.0 mmol) in dry CH_3CN (10 mL) was dropwise added PhC(O)Cl (174 μL, 1.5 mmol) and the resulting system was stirred at room temperature for 17 h. The reaction was quenched via addition of water (20 mL) and then extracted with ethyl acetate for three times. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc: 10/1) to give **20** as a red solid in 98% yield.

A mixture of **20** (484 mg, 0.95 mmol) and 10% Pd/C (100 mg) in EtOAc (40 mL) was stirred under H_2 atmosphere (1.0 atm) at 60 ^{o}C for 21 h. After cooling to room temperature, the suspension was filtered through Celite to remove Pd/C. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 8/1) to give **21** as a white solid in 74% yield.

In the presence of a catalytic amount of TsOH (15 mg), compound **21** (331 mg, 0.69 mmol) and triethyl orthoformate (7.0 mL) were heated at 100 ^{o}C for 34 h. After removing triethyl orthoformate under reduced pressure, the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 2/1) to give **22** as a white solid in 90% yield.

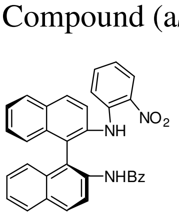
Compound **22** (147 mg, 0.3 mmol) and CH_3I (0.2 mL, 3.0 mmol) in CH_3CN (4.0 mL) were stirred under reflux for 22 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **23** was used for the next step without any further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **23** (126 mg, 0.2 mmol), NaOAc (33 mg, 0.4 mmol) and [(Me_2S)AuCl] (60 mg, 0.2 mmol) followed by the addition of dry CH_3CN (10 mL) as the solvent. After refluxing at 85 ^oC for 22 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1) to give complex **3** as a white solid in 37% yield (Scheme S4).

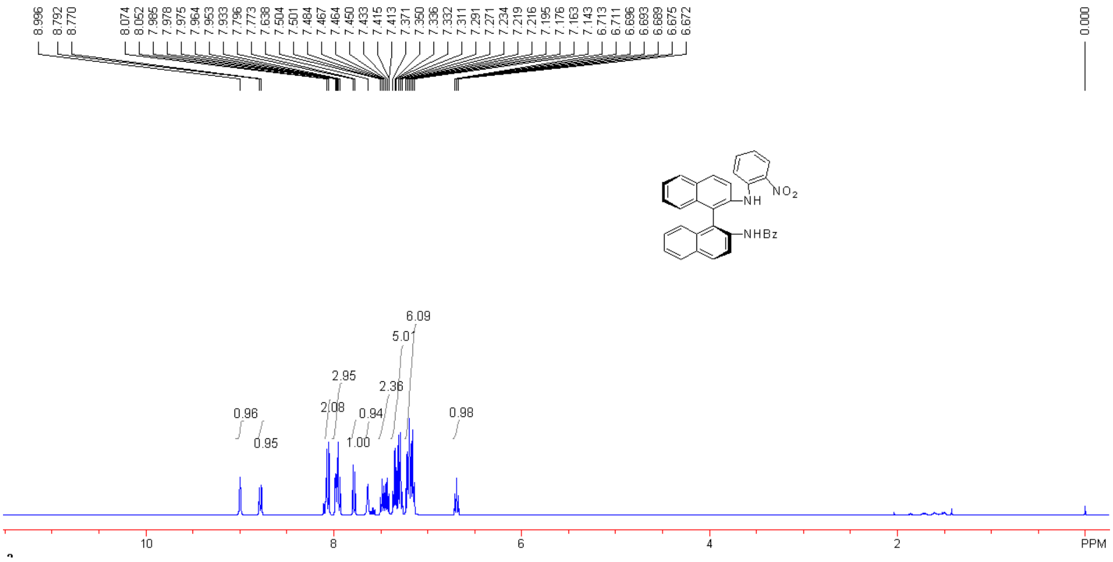


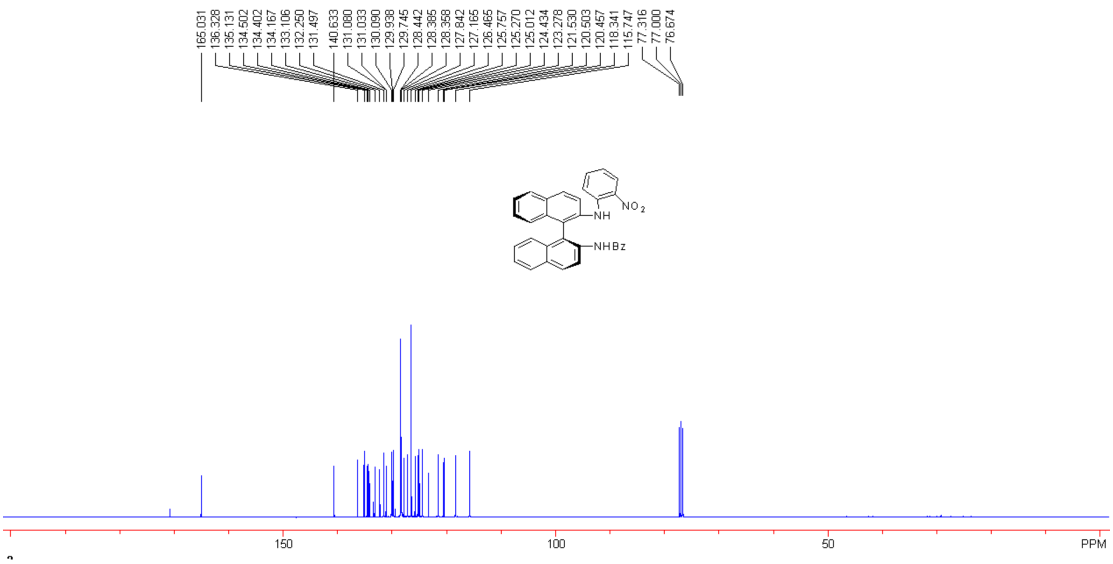
Scheme S4

Compound (a*S*)-**20**

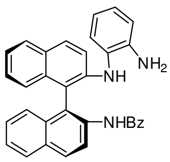


Red solid; m.p. 108.4-109.9 ^oC. $[\alpha]^{20}_D$ = +11 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3408, 3323, 3056, 2925, 1675, 1610, 1593, 1574, 1493, 1425, 1338, 1248, 1146, 1074, 1040, 1024, 863, 814, 738, 705 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 6.67-6.71 (m, 1H), 7.14-7.23 (m, 6H), 7.27-7.37 (m, 5H), 7.41-7.50 (m, 2H), 7.64 (s, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.93-7.99 (m, 3H), 8.06 (d, *J* = 8.8 Hz, 2H), 8.78 (d, *J* = 8.8 Hz, 1H), 9.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 115.7, 118.3, 120.46, 120.5, 121.5, 123.3, 124.4, 125.0, 125.3, 125.8, 126.5, 127.2, 127.8, 128.36, 128.39, 128.4, 129.7, 129.9, 130.1, 131.0, 131.1, 131.5, 132.3, 133.1, 134.2, 134.4, 134.5, 135.1, 136.3, 140.6, 165.0. LRMS (ESI) *m/e* 510.2 [M^++H]; HRMS (ESI) calcd for [$C_{33}H_{23}N_3O_3$+H] requires 510.1818, found 510.1824 [M^++H].

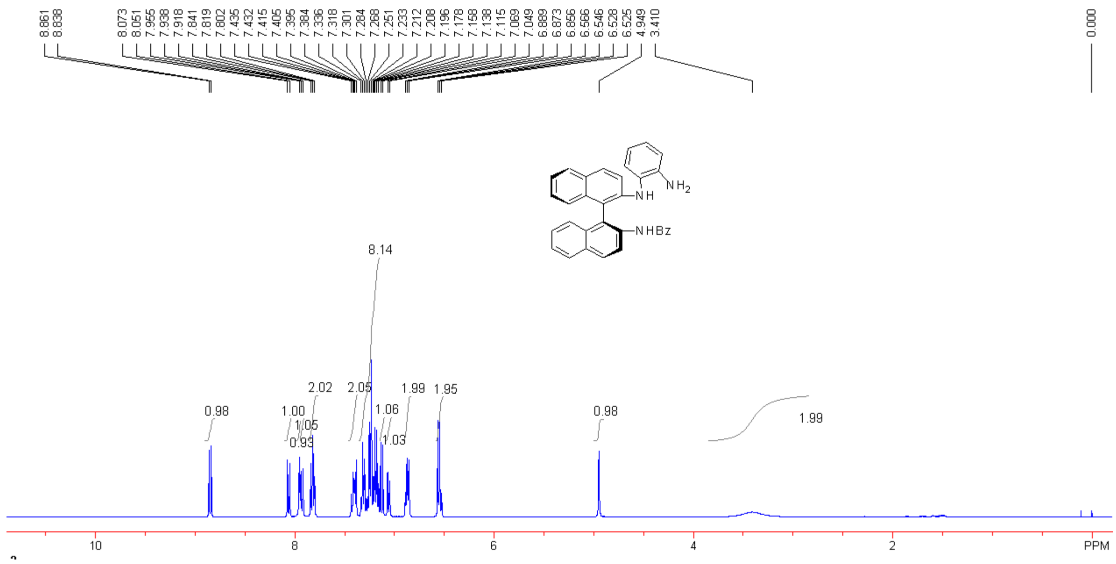


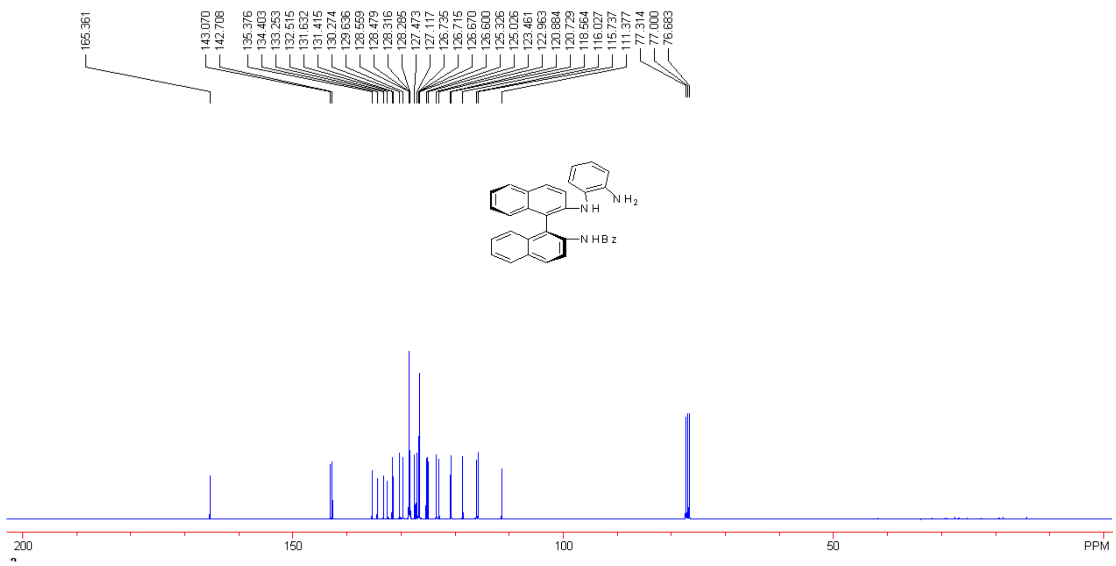


Compound (a*S*)-**21**

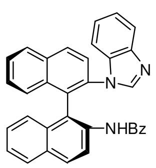


White solid; m.p. 111.1-112.8 °C. $[\alpha]^{20}_D$ = -16 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3461, 3379, 3054, 2953, 2923, 2853, 1672, 1616, 1594, 1500, 1486, 1455, 1424, 1331, 1282, 1147, 1024, 816, 744, 705 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.41 (br, 2H), 4.95 (s, 1H), 6.53-6.57 (m, 2H), 6.86-6.89 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 9.2 Hz, 1H), 7.16-7.34 (m, 8H), 7.38-7.44 (m, 2H), 7.80-7.84 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 8.85 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 111.4, 115.7, 116.0, 118.6, 120.7, 120.9, 123.0, 123.5, 125.0, 125.3, 126.6, 126.67, 126.72, 126.74, 127.1, 127.5, 128.29, 128.32, 128.5, 128.6, 129.6, 130.3, 131.4, 131.6, 132.5, 133.3, 134.4, 135.4, 142.7, 143.1, 165.4. LRMS (ESI) *m/e* 480.2 [M^++H]; HRMS (ESI) calcd for [$C_{33}H_{25}N_3O$+H] requires 480.2076, found 480.2080 [M^++H].



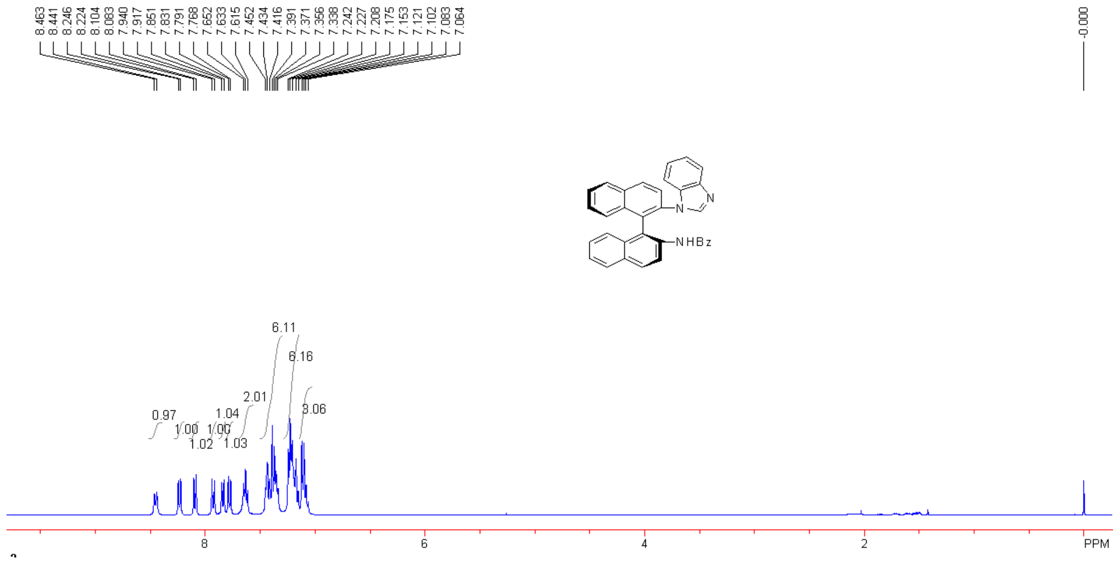


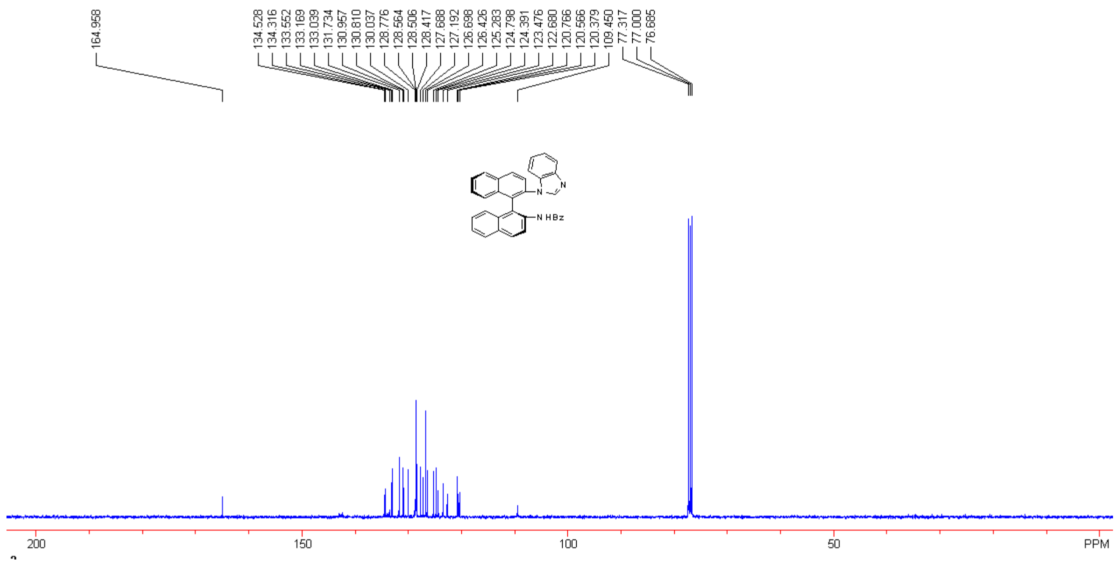
Compound (a*S*)-**22**



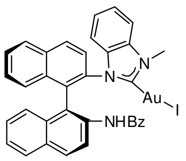
White solid; m.p. 168.2-170.2 °C. $[\alpha]^{20}_D$ = -91 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3419, 3055, 2954, 2923, 1668, 1596, 1486, 1454, 1426, 1378, 1281, 1235, 1145, 1025, 890, 817, 796, 741, 706 cm^{-1}. ^1H NMR (400 MHz,

$CDCl_3$, TMS) δ 7.06-7.12 (m, 3H), 7.15-7.24 (m, 6H), 7.34-7.45 (m, 6H), 7.63 (t, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 8.45 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 109.5, 120.4, 120.6, 120.8, 122.7, 123.5, 124.4, 124.8, 125.3, 126.4, 126.7, 127.2, 127.7, 128.4, 128.5, 128.6, 128.8, 130.0, 130.8, 131.0, 131.7, 133.0, 133.2, 133.6, 134.3, 134.5, 165.0. LRMS (ESI) *m/e* 490.2 [M^++H]; HRMS (ESI) calcd for [$C_{34}H_{23}N_3O$+H] requires 490.1919, found 490.1921 [M^++H].

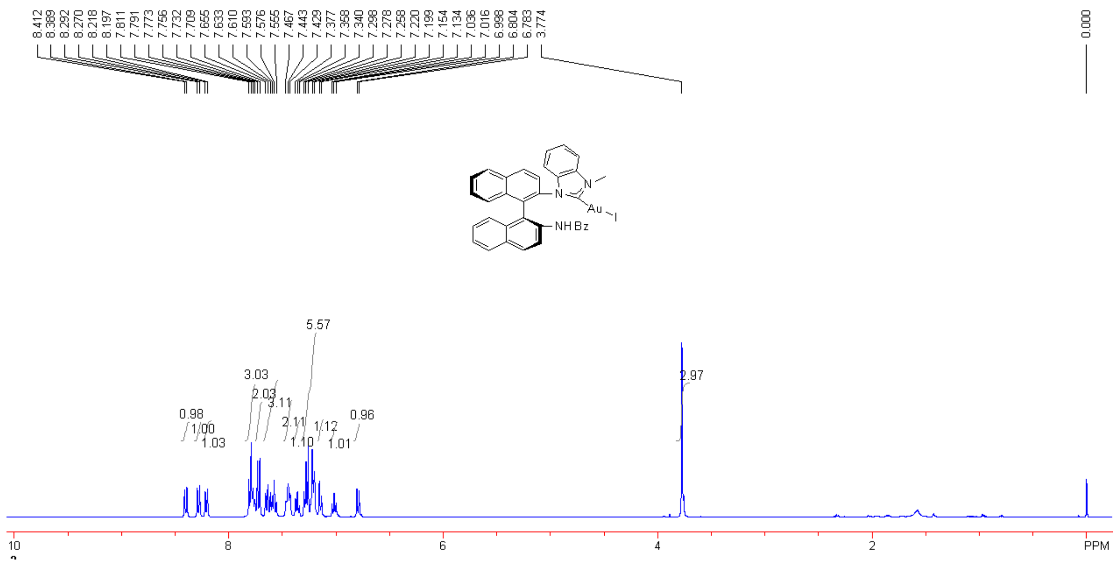




Complex (a*S*)-**3**



White solid; m.p. 141.5-142.9 °C (dec.). $[\alpha]^{20}_D$ = -149 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3419, 3057, 2924, 2852, 1682, 1596, 1501, 1487, 1466, 1427, 1391, 1346, 1277, 1238, 1099, 1024, 860, 820, 744, 706 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.77 (s, 3H), 6.79 (d, J = 8.4 Hz, 1H), 7.02 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 8.0 Hz, 1H), 7.20-7.30 (m, 5H), 7.36 (t, J = 7.2 Hz, 1H), 7.43-7.47 (m, 2H), 7.56-7.66 (m, 3H), 7.72 (d, J = 9.2 Hz, 2H), 7.76-7.81 (m, 3H), 8.21 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.40 (d, J = 9.2 Hz, 1H). LRMS (ESI) *m/e* 700.2 [M^+-I]; HRMS (ESI) calcd for [$C_{35}H_{25}N_3IOAu$-I] requires 700.1663, found 700.1661 [M^+-I].



(4) General Procedure for the Synthesis of Gold(I) Complex (a*S*)-4

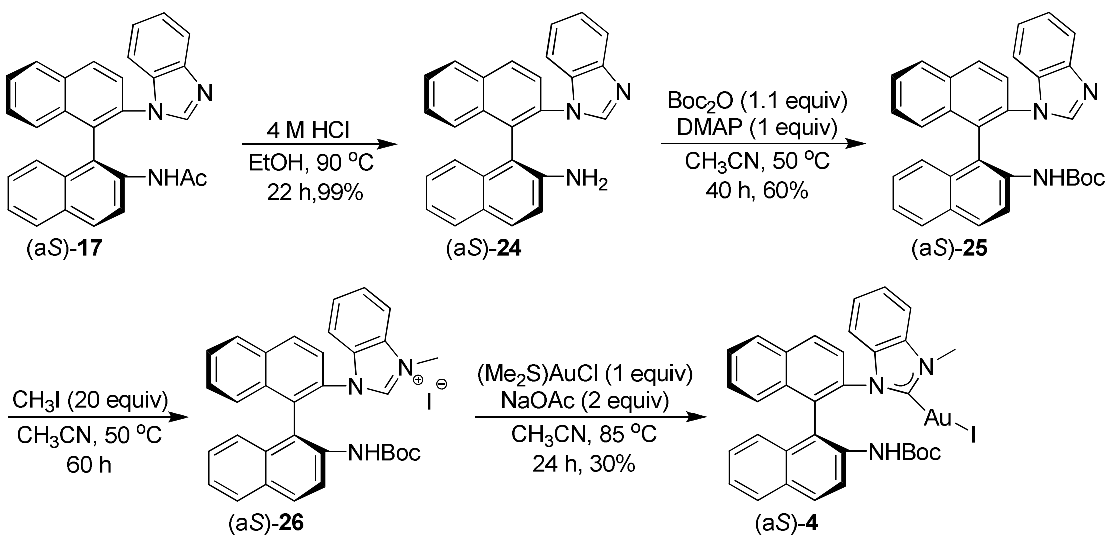
Acetyl compound **17** (2.14 g, 5 mmol) was refluxed in 4.0 M HCl (50 mL) and ethanol (80 mL) for 22 h. The reaction system was cooled to room temperature and neutralized to pH > 7 with saturated aqueous NaOH solution, which was followed by the extraction with CH_2Cl_2 and dried over anhydrous Na_2SO_4. The crude product was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 1/2) to give benzimidazole-primary amine **24** as a white solid in 99% yield.

A mixture of **24** (385 mg, 1.0 mmol), Boc_2O (240 mg, 1.1 mmol) and DMAP (122 mg, 1.0 mmol) in dry CH_3CN (10 mL) was stirred at 50 ^{o}C for 40 h. After removing volatiles under reduced pressure, the crude product was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 3/1) to provide **25** as a white solid in 60%

yield.

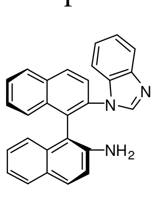
Compound **25** (291 mg, 0.6 mmol) and CH_3I (0.75 mL, 12 mmol) in CH_3CN (12 mL) were stirred under reflux for 60 h until completely consuming **25**. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **26** was used for the next step without further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **26** (125 mg, 0.2 mmol), NaOAc (33 mg, 0.4 mmol) and [(Me_2S)AuCl] (60 mg, 0.2 mmol) followed by the addition of dry CH_3CN (10 mL) as the solvent. After refluxing at 85 ^{o}C for 24 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 6/1) to give complex **4** as a white solid in 30% yield (Scheme S5).



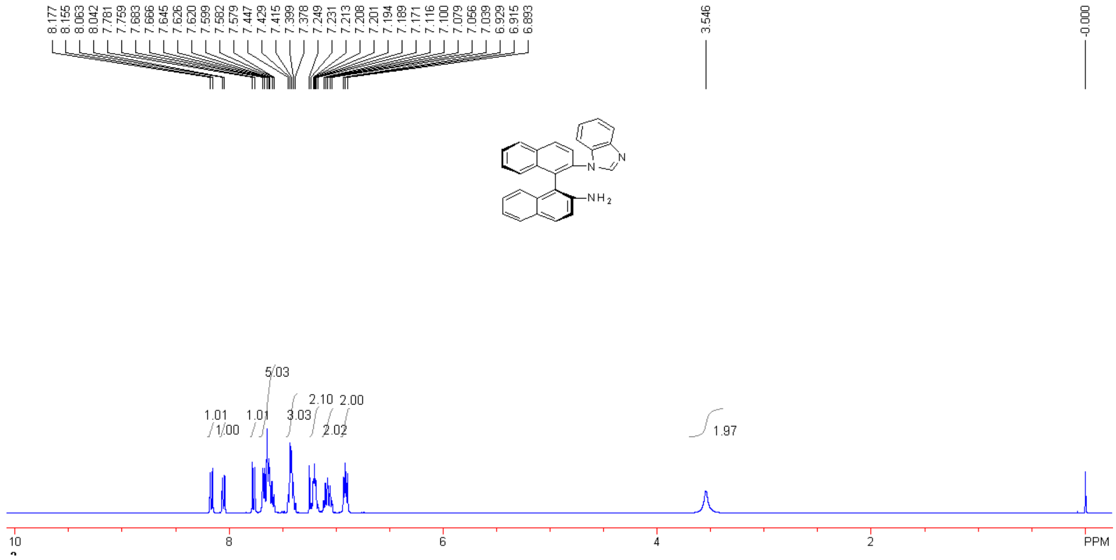
Scheme S5

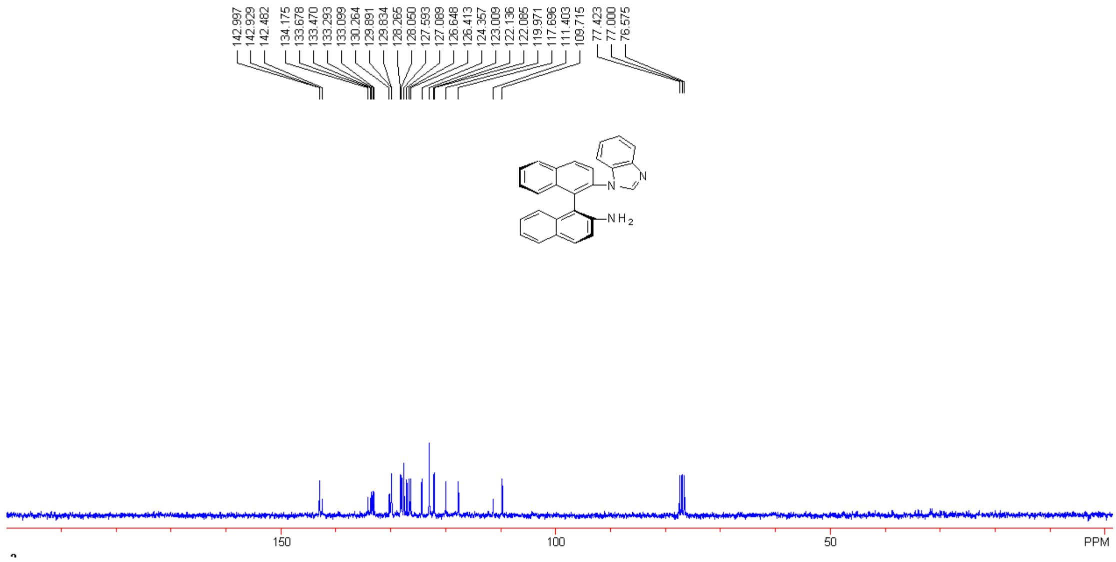
Compound (a*S*)-**24**[2b]



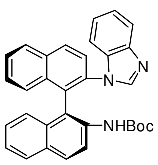
White solid; m.p. 134-136 ^{o}C. $[\alpha]^{20}_{D}$ = -27 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3461, 3370, 3318, 3196, 2956, 2925, 2853, 1619, 1488, 1453, 1382, 1285, 1235, 1146, 816, 740, 623 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.55 (s, 2H), 6.89-6.93 (m, 2H), 7.04-7.12 (m, 2H), 7.17-7.23 (m, 2H), 7.38-7.45 (m, 3H), 7.58-7.68 (m, 5H), 7.77 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR

(75 MHz, $CDCl_3$, TMS) δ 109.7, 111.4, 117.7, 120.0, 122.09, 122.14, 123.0, 124.4, 126.4, 126.6, 127.1, 127.6, 128.1, 128.3, 129.8, 129.9, 130.3, 133.1, 133.3, 133.5, 133.7, 134.2, 142.5, 142.9, 143.0. LRMS (ESI) *m/e* 386.2 [M^++H]; HRMS (ESI) calcd for [$C_{27}H_{19}N_3$+H] requires 386.1657, found 386.1660 [M^++H].

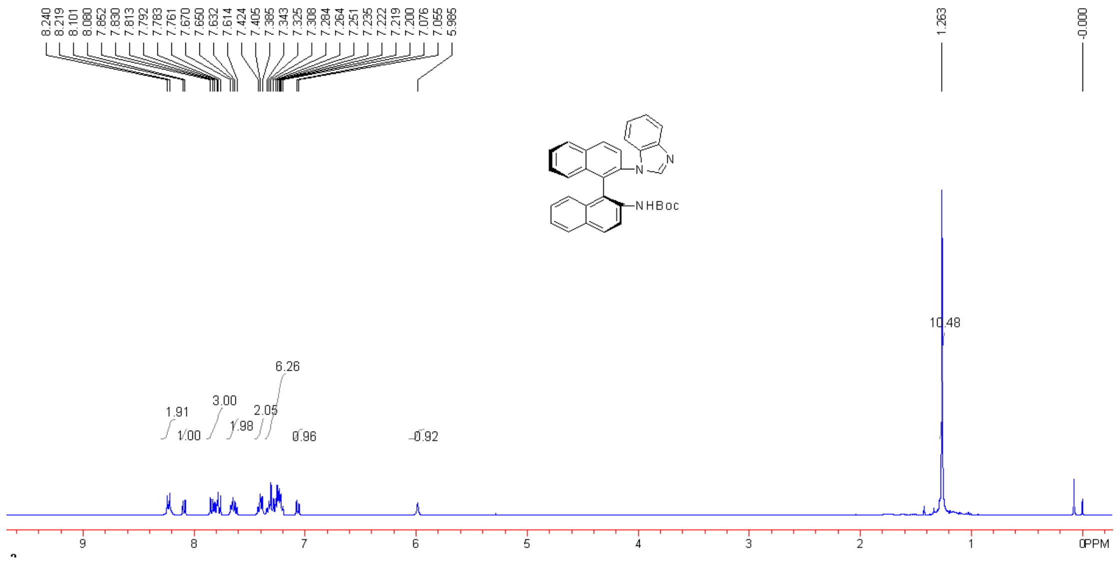


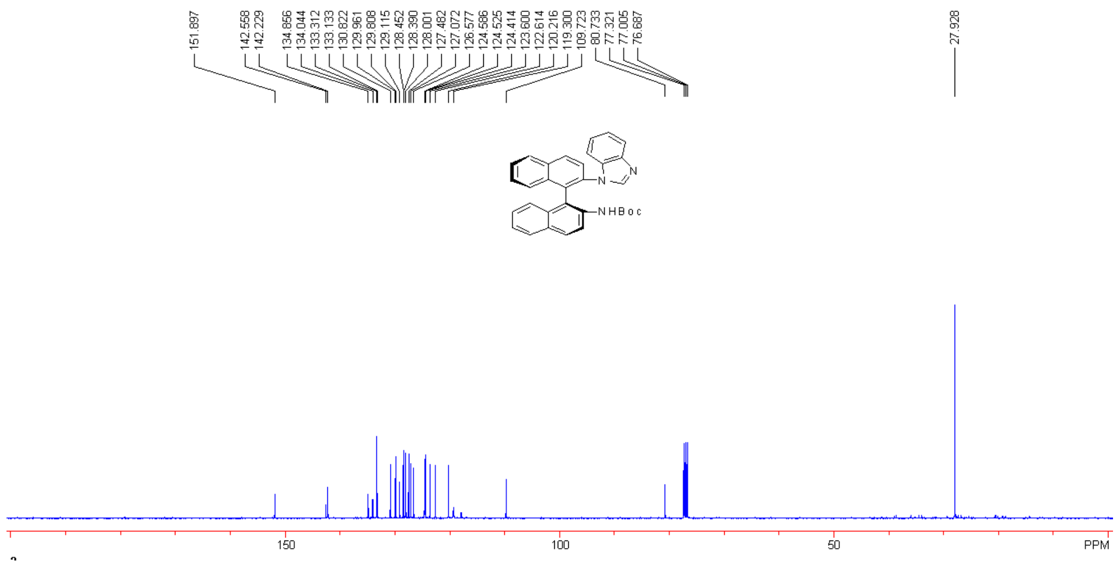


Compound (a*S*)-**25**

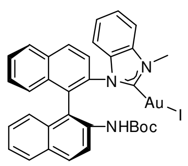


White solid; m.p. 143.8-145.8 °C. $[\alpha]^{20}_D$ = -119 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3423, 3054, 2964, 2925, 1722, 1598, 1489, 1453, 1427, 1366, 1284, 1266, 1232, 1153, 1085, 1065, 1034, 888, 867, 820, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.26 (s, 9H), 5.99 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.20-7.34 (m, 6H), 7.41 (t, J = 8.0 Hz, 2H), 7.61-7.67 (m, 2H), 7.77 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H), 8.22-8.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 27.9, 80.7, 109.7, 119.3, 120.2, 122.6, 123.6, 124.4, 124.5, 124.6, 126.6, 127.1, 127.5, 128.0, 128.4, 128.5, 129.1, 129.8, 130.0, 130.8, 133.1, 133.3, 134.0, 134.9, 142.2, 142.6, 151.9. LRMS (ESI) *m/e* 486.2 [M^++H]; HRMS (ESI) calcd for [$C_{32}H_{27}N_3O_2$+H] requires 486.2182, found 486.2180 [M^++H].

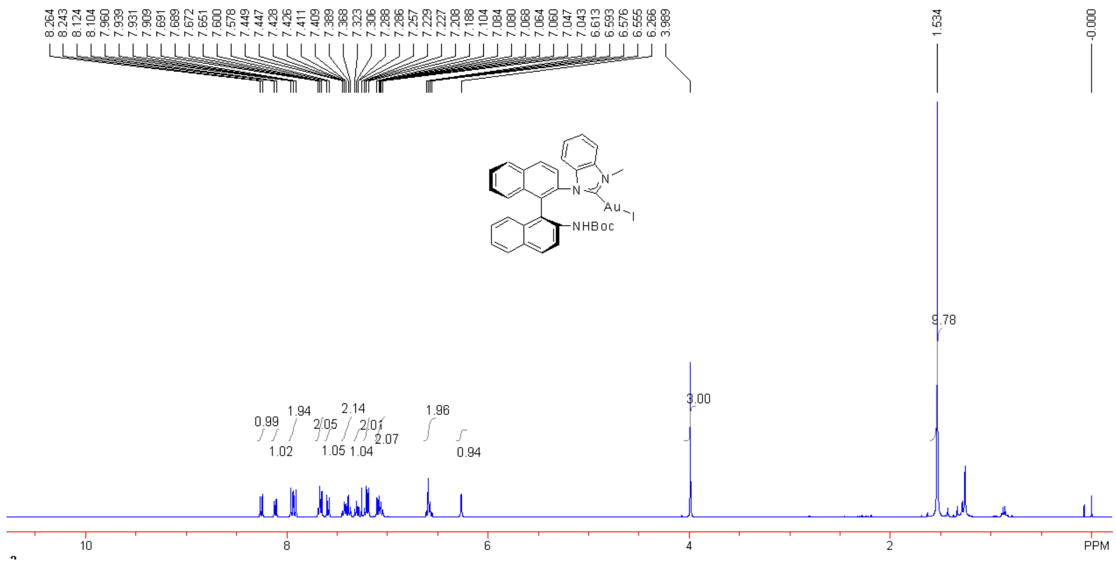




Complex (a*S*)-**4**



White solid; m.p. 153.4-154.5 °C (dec.). $[\alpha]^{20}_D$ = -9.0 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3420, 2973, 2925, 1715, 1599, 1502, 1455, 1427, 1391, 1367, 1346, 1270, 1232, 1153, 1083, 1059, 871, 820, 804, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.53 (s, 9H), 3.99 (s, 3H), 6.27 (s, 1H), 6.56-6.61 (m, 2H), 7.04-7.10 (m, 2H), 7.19-7.23 (m, 2H), 7.29-7.32 (m, 1H), 7.37-7.45 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.65-7.69 (m, 2H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H). LRMS (ESI) *m/e* 696.2 [M^+-I]; HRMS (ESI) calcd for [$C_{33}H_{29}N_3IO_2Au$-I] requires 696.1925, found 696.1937 [M^+-I].



(5) General Procedure for the Synthesis of Gold(I) Complex 5

Under argon atmosphere, compound (*S*)-**27** (646 mg, 3.0 mmol), DCC (619 mg, 3.0 mmol) and DMAP (122 mg, 1.0 mmol) in dry CH_2Cl_2 (10.0 mL) was stirred at room temperature for 15 minutes followed by the addition of solution of (a*S*)-**14** (405 mg, 1.0 mmol) in CH_2Cl_2 (5.0 mL), and the resulting system was further stirred at room temperature for 11 h. Then the suspension was filtered through Celite to remove white solids, and the filtrate was washed in sequence with water, saturated $KHSO_4$, water, saturated $NaHCO_3$ and brine. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc: 4/1) to give (a*S*,*S*)-**28** as a red solid in 98% yield.

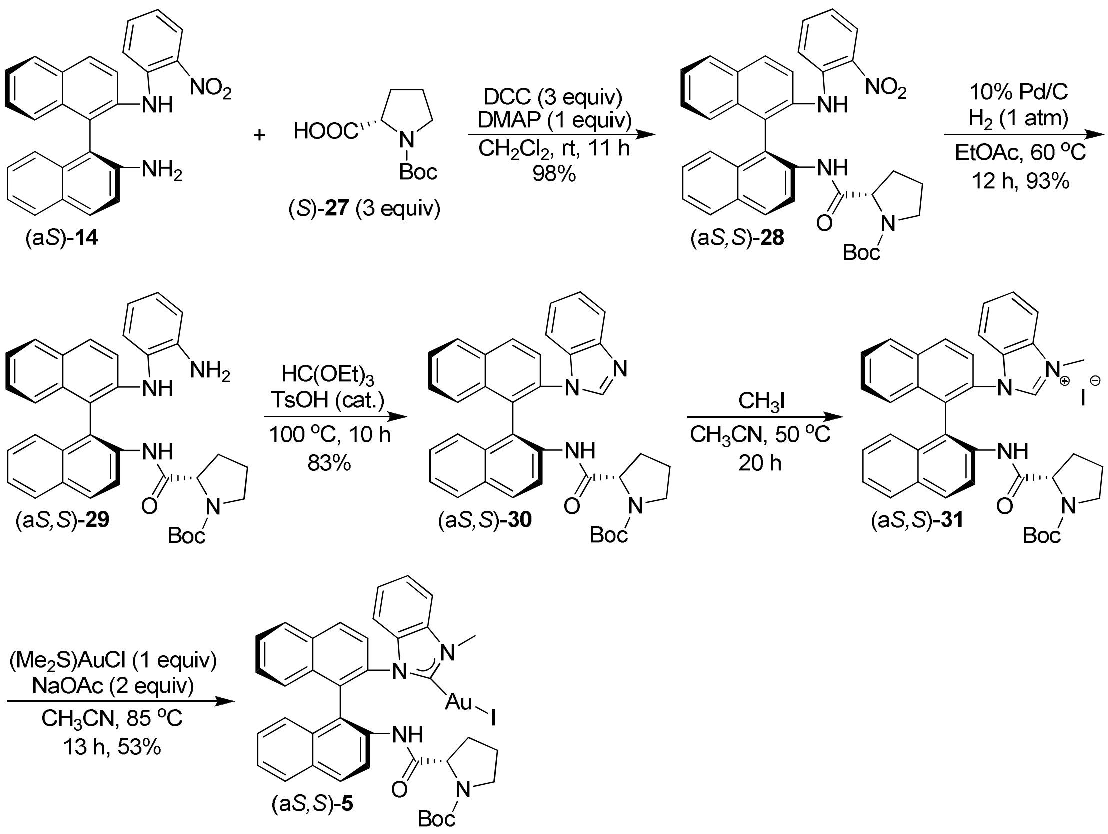
A mixture of (a*S*,*S*)-**28** (603 mg, 1.0 mmol) and 10% Pd/C (100 mg) in EtOAc (40 mL) was stirred under H_2 atmosphere (1.0 atm) at 60 °C for 12 h. After cooling to room temperature, the suspension was filtered through Celite to remove Pd/C. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1) to give (a*S*,*S*)-**29** as a white solid in 93% yield.

Compound (a*S*,*S*)-**29** (516 mg, 0.9 mmol) and triethyl orthoformate (9.0 mL) containing a catalytic amount of TsOH (18 mg) were heated at 100 ^{o}C for 10 h. After removing triethyl orthoformate under reduced pressure, the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 2/1) to give (a*S*,*S*)-**30** as a white solid in 83% yield.

Compound (a*S*,*S*)-**30** (117 mg, 0.2 mmol) and CH_3I (0.125 mL, 2.0 mmol) in CH_3CN (4.0 mL) were stirred under reflux for 20 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid (a*S*,*S*)-**31** was used for the next step without any further purification.

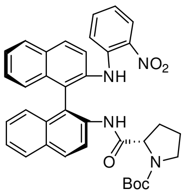
Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor (a*S*,*S*)-**31** (72 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol) and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5.0 mL) as the solvent. After refluxing at 85 ^{o}C for 13 h, the reaction mixture was cooled to room temperature and filtered through Celite. Volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1) to give complex (a*S*,*S*)-**5** as a white solid in 53% yield (Scheme S6).

On the other hand, NHC-Au(I) complex (a*S*,*R*)-**5** was prepared from compounds (*R*)-**27** and (a*S*)-**14** as a diastereoisomer according to the same procedure for the preparation of complex (a*S*,*S*)-**5**.

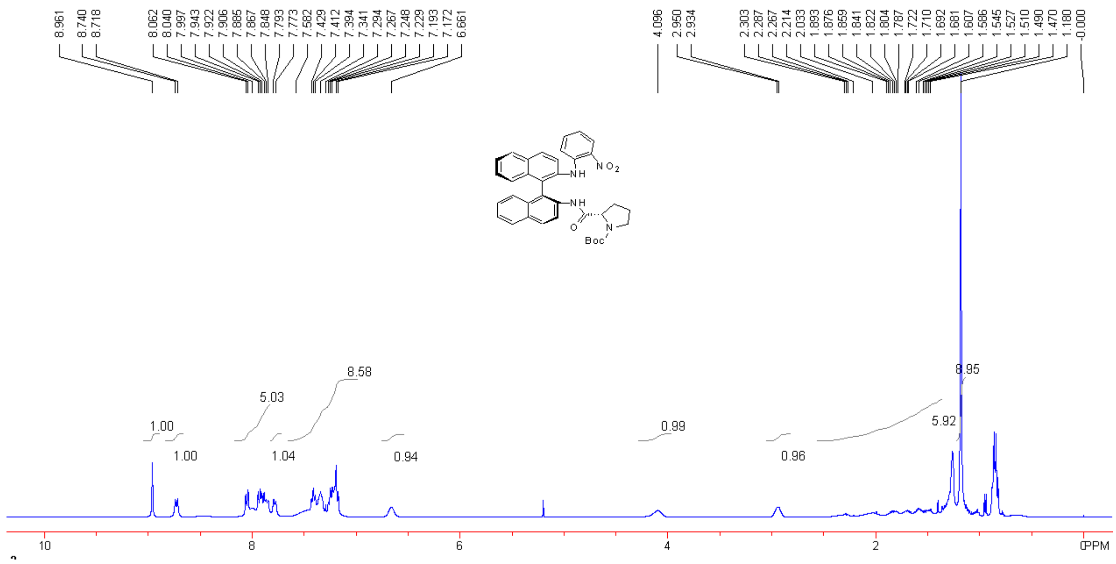


Scheme S6

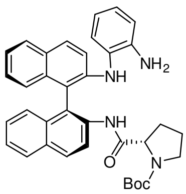
Compound (a*S*,*S*)-**28**



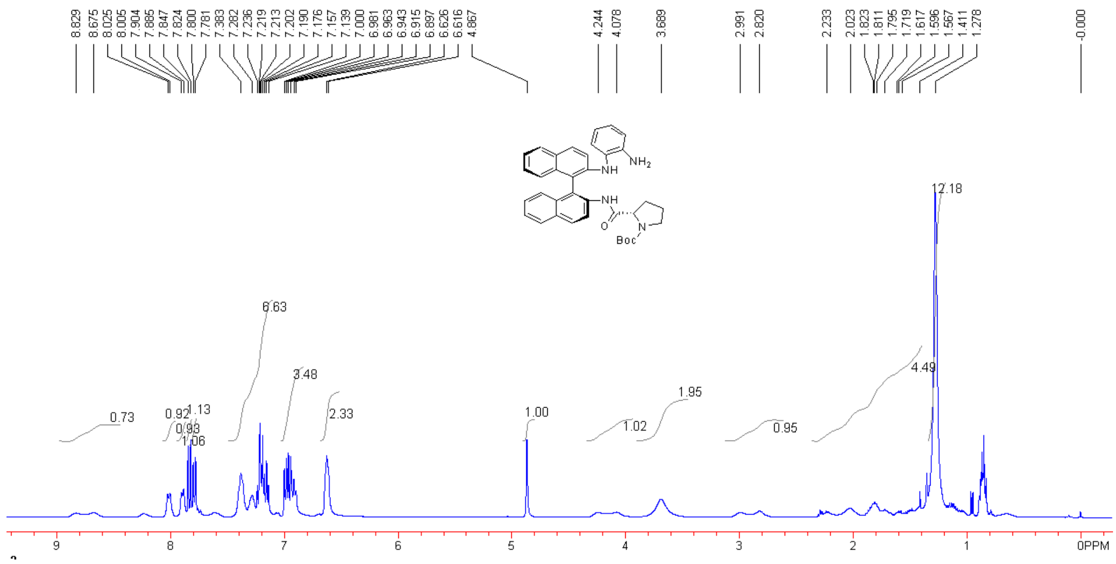
Red solid; m.p. 101.6-103.2 °C (dec.). IR (direct irradiation) ν 3360, 3270, 2973, 2958, 2930, 2873, 1694, 1611, 1593, 1573, 1493, 1414, 1365, 1340, 1248, 1159, 1087, 1039, 863, 815, 777, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.18 (s, 9H), 1.47-2.30 (m, 6H), 2.93-2.95 (m, 1H), 4.10 (br, 1H), 6.66 (br, 1H), 7.17-7.58 (m, 8H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.85-8.06 (m, 5H), 8.73 (d, *J* = 8.8 Hz, 1H), 8.96 (s, 1H) (Signals between δ 0.8-1.3 ppm were attributed to minor containing petroleum ether). LRMS (ESI) *m/e* 625.2 [M$^+$+Na]; HRMS (ESI) calcd for [$C_{36}H_{34}N_4O_5$+Na] requires 625.2427, found 625.2431 [M$^+$+Na].



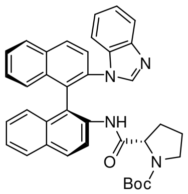
Compound (a*S*,*S*)-**29**



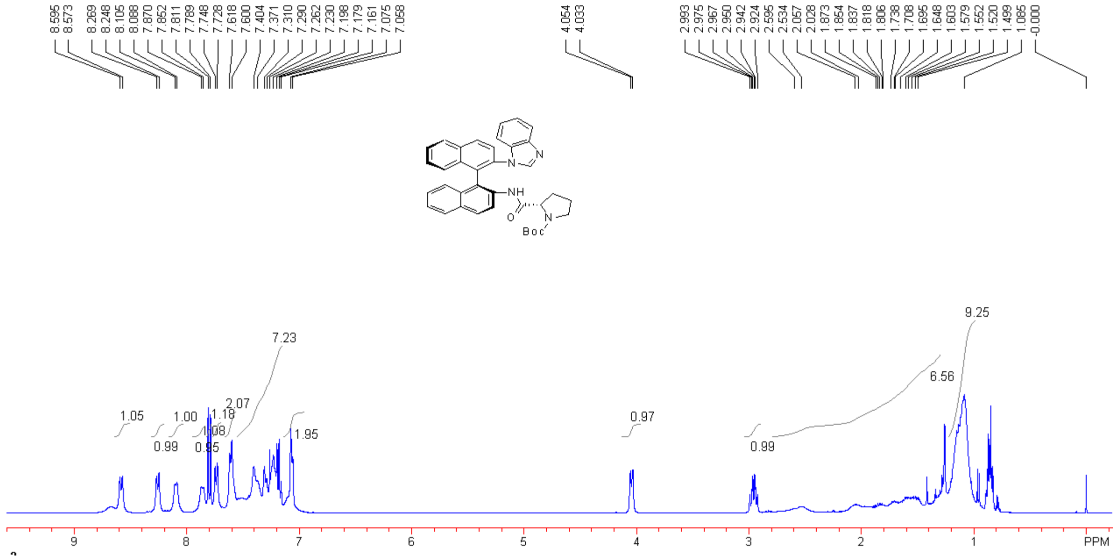
White solid; m.p. 109.8-111.5 °C (dec.). $[\alpha]^{20}_{D}$ = -80 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3467, 3353, 3054, 2973, 2927, 2875, 1690, 1618, 1593, 1499, 1455, 1417, 1365, 1344, 1299, 1250, 1158, 1118, 1087, 869, 817, 776, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.28 (s, 9H), 1.28-2.23 (m, 6H), 2.82-2.99 (m, 1H), 3.69 (br, 2H), 4.08-4.24 (m, 1H), 4.87 (s, 1H), 6.62-6.63 (m, 2H), 6.90-7.00 (m, 3H), 7.14-7.38 (m, 6H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.68-8.83 (m, 1H) (Signals between δ 0.8-1.3 ppm were attributed to minor containing petroleum ether). LRMS (ESI) *m/e* 573.3 $[M^{+}+H]$; HRMS (ESI) calcd for $[C_{36}H_{36}N_4O_3+H]$ requires 573.2866, found 573.2862 $[M^{+}+H]$.



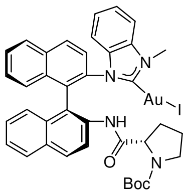
Compound (a*S*,*S*)-**30**



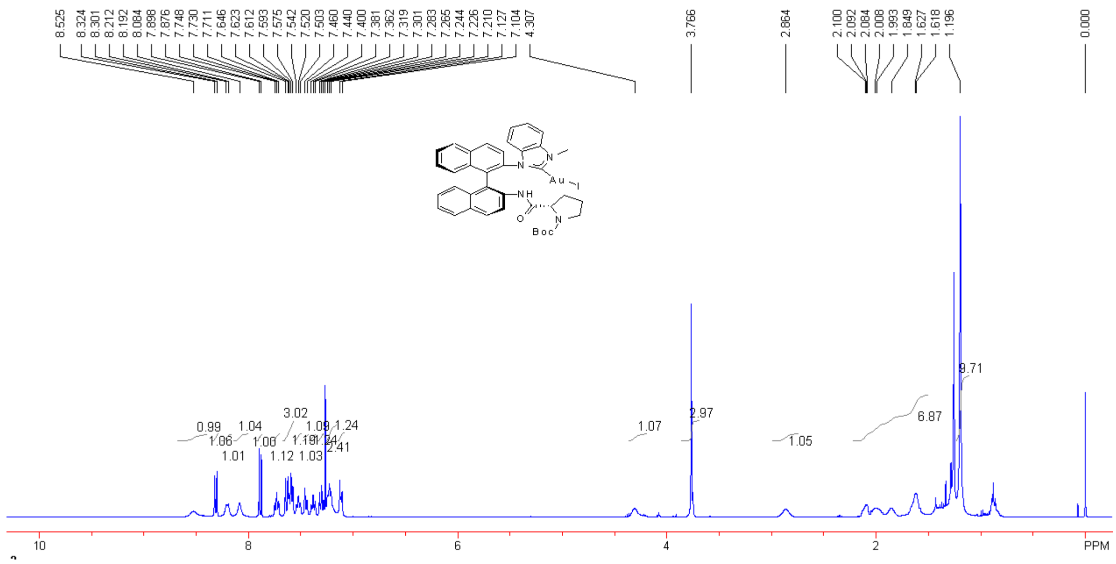
White solid; m.p. 134.0-136.5 °C (dec.). $[\alpha]^{20}_{D}$ = -66 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3364, 3055, 2972, 2927, 2873, 1694, 1614, 1597, 1502, 1489, 1453, 1392, 1365, 1284, 1236, 1159, 1120, 1087, 821, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (s, 9H), 1.50-2.60 (m, 6H), 2.96 (dt, *J* = 7.2, 10.4 Hz, 1H), 4.04 (d, *J* = 8.4 Hz, 1H), 7.06-7.08 (m, 2H), 7.16-7.40 (m, 7H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 6.8 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.8 Hz, 1H) (Signals between δ 0.8-1.3 ppm were attributed to minor containing petroleum ether). LRMS (ESI) *m/e* 583.3 [M$^+$+H]; HRMS (ESI) calcd for [$C_{37}H_{34}N_4O_3$+H] requires 583.2709, found 583.2706 [M$^+$+H].



Complex (a*S*,*S*)-**5**



White solid; m.p. 224.9-225.8 °C (dec.). $[\alpha]^{20}_{D}$ = -102 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3360, 2924, 2853, 1691, 1596, 1501, 1467, 1451, 1425, 1391, 1362, 1305, 1274, 1254, 1156, 1114, 1089, 873, 831, 817, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.20 (s, 9H), 1.62-2.10 (m, 6H), 2.86 (s, 1H), 3.77 (s, 3H), 4.31 (br, 1H), 7.10-7.13 (m, 1H), 7.21-7.32 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.50-7.54 (m, 1H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 9.2 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 8.08 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 8.53 (s, 1H) (Signals between δ 0.8-1.3 ppm were attributed to minor containing petroleum ether). LRMS (ESI) *m/e* 793.2 $[M^{+}-I]$; HRMS (ESI) calcd for $[C_{38}H_{36}N_4IO_3Au-I]$ requires 793.2453, found 793.2471 $[M^{+}-I]$.



(6) General Procedure for the Synthesis of Gold(I) Complex 6

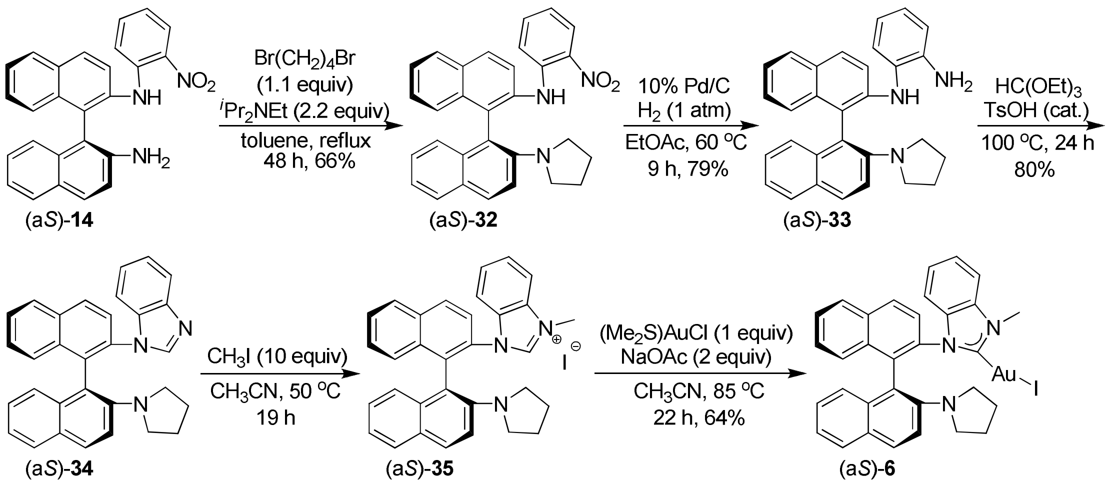
Under argon atmosphere, to the solution of **14** (810 mg, 2 mmol) in dry toluene (4 mL) was added $^{i}Pr_2NEt$ (0.76 mL, 4.4 mmol) and $Br(CH_2)_4Br$ (0.26 mL, 2.2 mmol) in sequence. After refluxing at 110 ^{o}C for two days, the reaction system was cooled to room temperature and quenched via addition of water (30 mL) followed by the extraction with ethyl acetate for three times. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc: 50/1) to give **32** as a red solid in 66% yield.

A mixture of **32** (575 mg, 1.25 mmol) and 10% Pd/C (125 mg) in EtOAc (40 mL) was stirred under H_2 atmosphere (1 atm) at 60 ^{o}C for 9 h. After cooling to room temperature, the suspension was filtered through Celite to remove Pd/C. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 25/1) to give **33** as a white solid in 79% yield.

Compound **33** (350 mg, 0.81 mmol) and triethyl orthoformate (10 mL) containing a catalytic amount of TsOH (16 mg) were heated at 100 ^{o}C for 24 h. After removing triethyl orthoformate under reduced pressure, the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 3/1) to give **34** as a pale yellow solid in 80% yield.

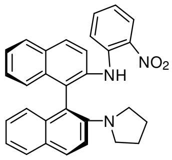
Compound **34** (110 mg, 0.25 mmol) and CH_3I (0.16 mL, 2.5 mmol) in CH_3CN (5 mL) were stirred under reflux for 19 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **35** was used for the next step without further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **35** (118 mg, 0.2 mmol), NaOAc (33 mg, 0.4 mmol) and [(Me_2S)AuCl] (60 mg, 0.2 mmol) followed by the addition of dry CH_3CN (10 mL) as the solvent. After refluxing at 85 °C for 22 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/CH_2Cl_2, 2/1) to give complex **6** as a white solid in 64% yield. Single crystals of complex **6** suitable for an X-ray diffraction study were grown from the solution of **6** in mixed petroleum ether/CH_3CN/CH_2Cl_2 (1:1:1) (Scheme S7).



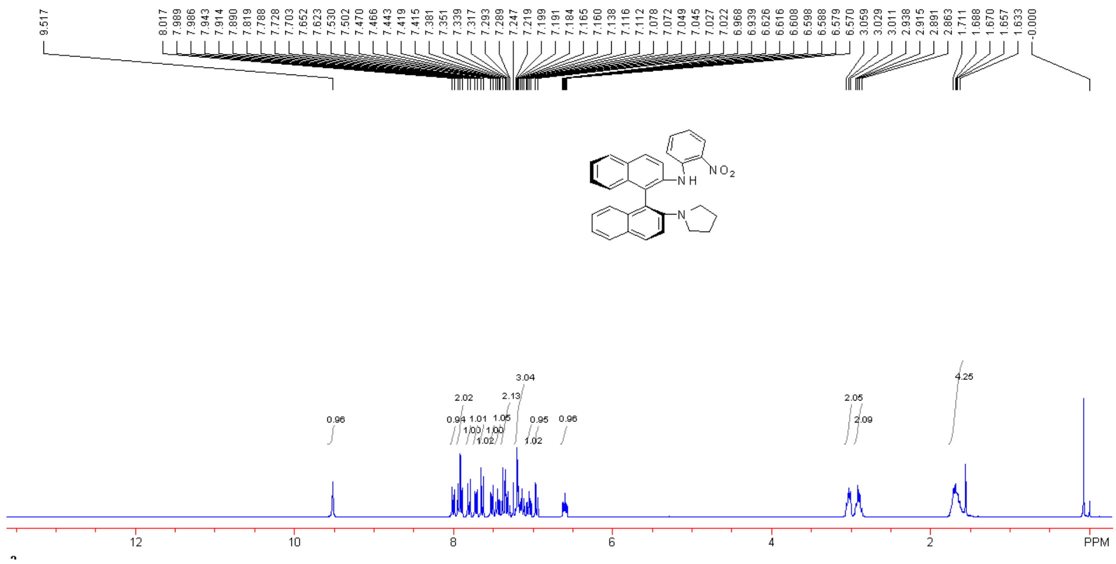
Scheme S7

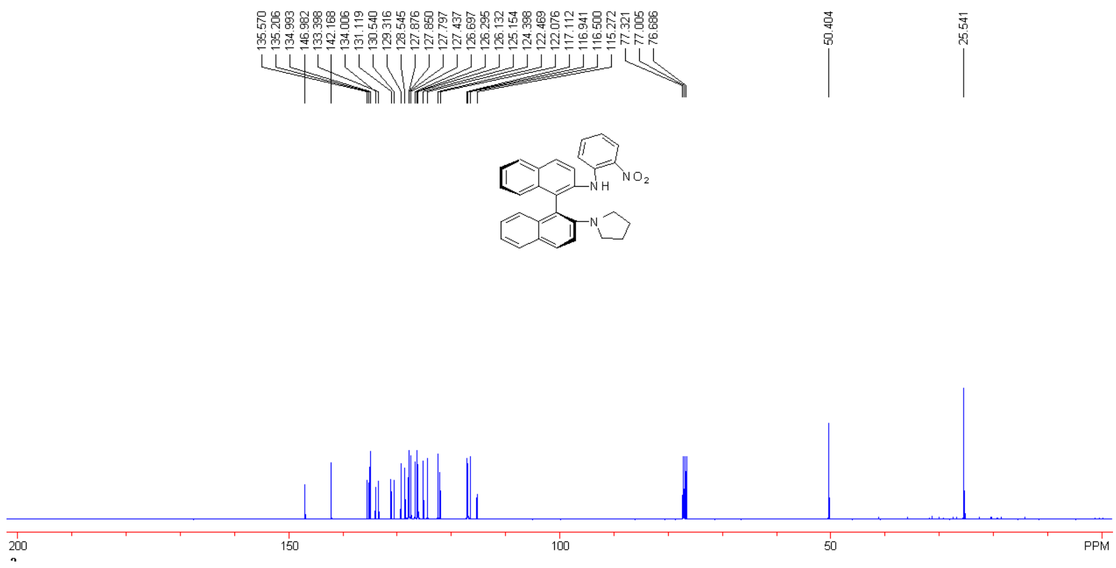
Compound (a*S*)-**32**



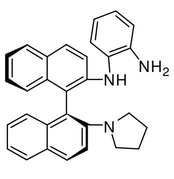
Red solid; m.p. 72.6-74.6 °C. $[\alpha]^{20}_D$ = +362 (*c* 0.125, $CHCl_3$). IR (direct irradiation) ν 3298, 3061, 2957, 2870, 1611, 1594, 1570, 1494, 1443, 1427, 1413, 1343, 1297, 1245, 1146, 1077, 1039, 1006, 864, 809, 767, 737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ 1.63-1.71 (m, 4H), 2.86-2.94 (m, 2H), 3.01-3.06 (m, 2H), 6.57-6.63 (m, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 7.02-7.08 (m, 1H), 7.11-7.22 (m, 3H), 7.29-7.38 (m, 2H), 7.42-7.47 (m, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.72 (d, *J* = 7.5

Hz, 1H), 7.80 (d, *J* = 9.3 Hz, 1H), 7.89-7.94 (m, 2H), 7.99-8.02 (m, 1H), 9.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 25.5, 50.4, 115.3, 116.5, 116.9, 117.1, 122.1, 122.5, 124.4, 125.2, 126.1, 126.3, 126.7, 127.4, 127.8, 127.85, 127.88, 128.5, 129.3, 130.5, 131.1, 133.4, 134.0, 135.0, 135.2, 135.6, 142.2, 147.0. LRMS (ESI) *m/e* 460.2 $[M^+ + H]$; HRMS (ESI) calcd for $[C_{30}H_{25}N_3O_2+H]$ requires 460.2025, found 460.2037 $[M^+ + H]$.



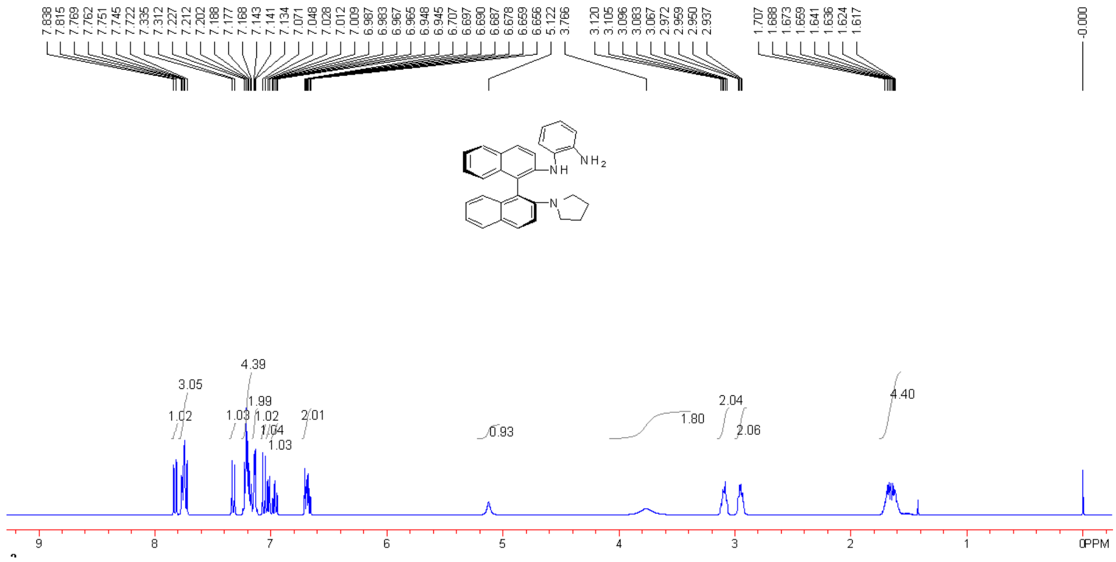


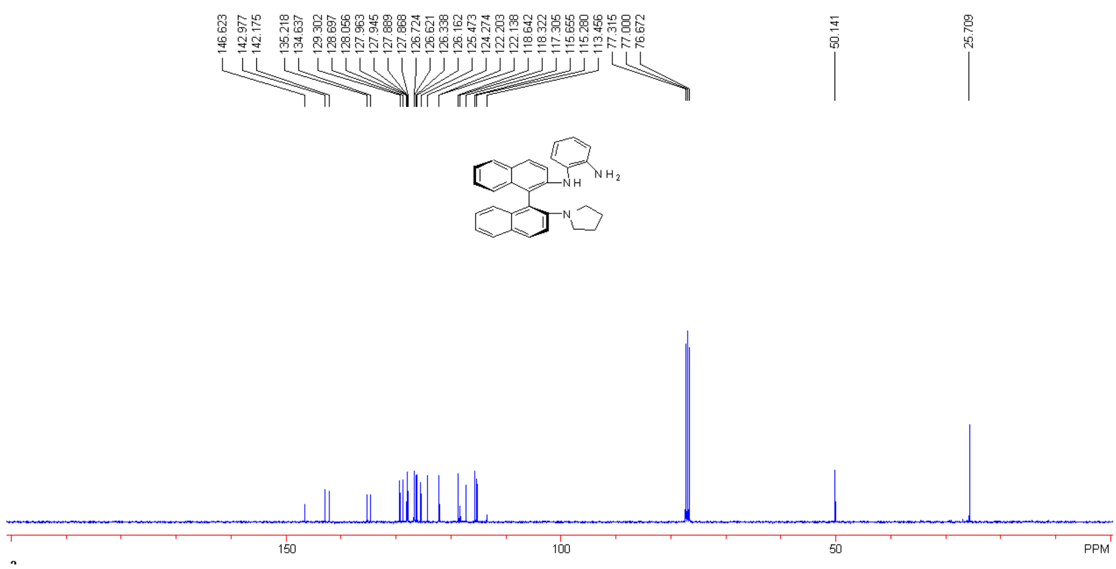
Compound (a*S*)-**33**



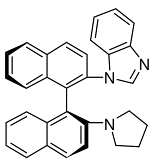
White solid; m.p. 103.8-105.8 °C. $[\alpha]^{20}_D$ = +45 (*c* 0.25, $CHCl_3$). IR (direct irradiation) *ν* 3457, 3358, 3055, 2962, 2925, 2867, 1615, 1594, 1502, 1459, 1415, 1378, 1344, 1295, 1248, 1216, 1148, 1004, 808, 744 cm^{-1}. ^1H NMR (400

MHz, $CDCl_3$, TMS) δ 1.62-1.71 (m, 4H), 2.94-2.97 (m, 2H), 3.07-3.12 (m, 2H), 3.77 (br, 2H), 5.12 (s, 1H), 6.66-6.71 (m, 2H), 6.95-6.99 (m, 1H), 7.01-7.03 (m, 1H), 7.06 (d, *J* = 9.2 Hz, 1H), 7.13-7.14 (m, 2H), 7.17-7.23 (m, 4H), 7.32 (d, *J* = 9.2 Hz, 1H), 7.72-7.77 (m, 3H), 7.83 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 25.7, 50.1, 113.5, 115.3, 115.7, 117.3, 118.3, 118.6, 122.1, 122.2, 124.3, 125.5, 126.2, 126.3, 126.6, 126.7, 127.87, 127.89, 127.95, 127.96, 128.1, 128.7, 129.3, 134.6, 135.2, 142.2, 143.0, 146.6. LRMS (ESI) *m/e* 430.2 $[M^+ +H]$; HRMS (ESI) calcd for $[C_{30}H_{27}N_3+H]$ requires 430.2283, found 430.2270 $[M^+ +H]$.

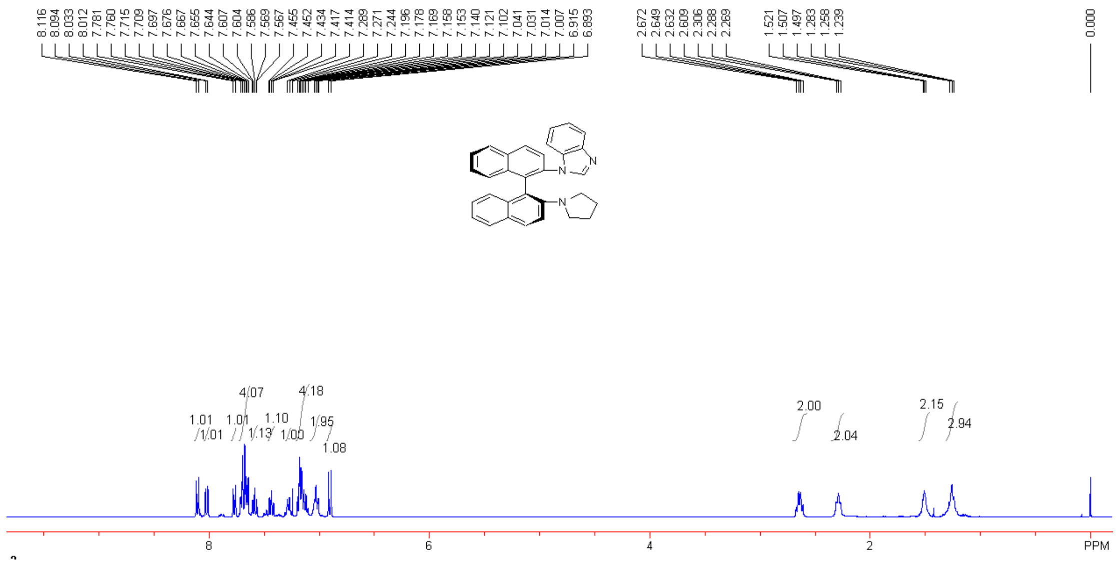


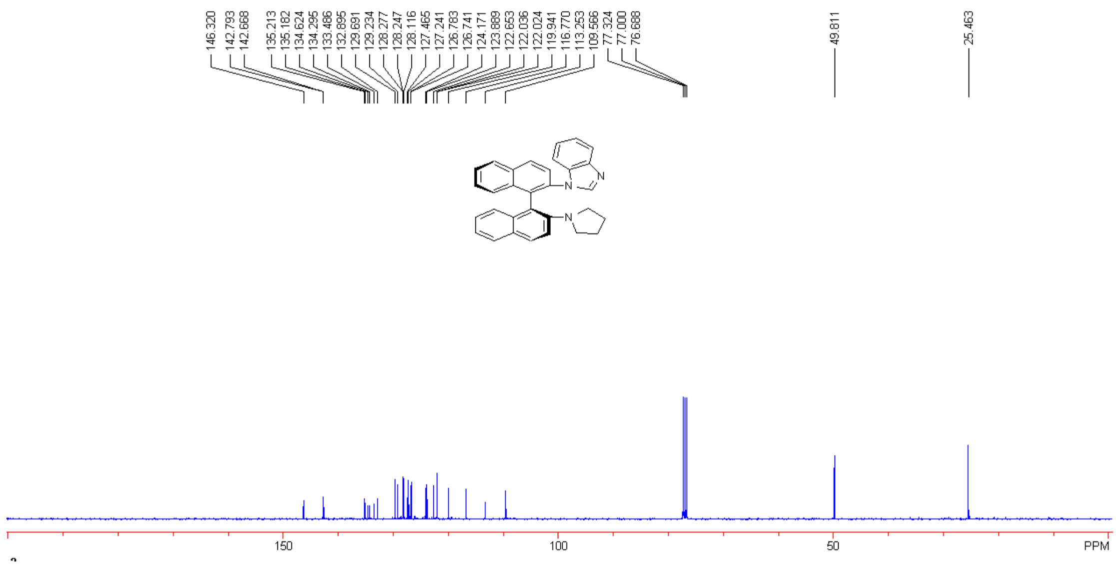


Compound (a*S*)-**34**

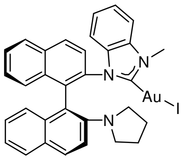


Pale yellow solid; m.p. 126.3-127.8 °C. $[\alpha]^{20}_D$ = +66 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3055, 2958, 2925, 2866, 1614, 1595, 1505, 1487, 1453, 1427, 1379, 1349, 1284, 1234, 1147, 1002, 809, 741 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.24-1.28 (m, 2H), 1.50-1.52 (m, 2H), 2.29 (t, J = 7.6 Hz, 2H), 2.64 (dd, J = 9.2, 16.0 Hz, 2H), 6.90 (d, J = 8.8 Hz, 1H), 7.01-7.04 (m, 2H), 7.10-7.20 (m, 4H), 7.28 (d, J = 7.2 Hz, 1H), 7.41-7.46 (m, 1H), 7.57-7.61 (m, 1H), 7.64-7.72 (m, 4H), 7.77 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 25.5, 49.8, 109.6, 113.3, 116.8, 119.9, 122.02, 122.04, 122.7, 123.9, 124.2, 126.7, 126.8, 127.2, 127.5, 128.1, 128.2, 128.3, 129.2, 129.7, 132.9, 133.5, 134.3, 134.6, 135.18, 135.21, 142.7, 142.8, 146.3. LRMS (ESI) *m/e* 440.2 [M^++H]; HRMS (ESI) calcd for [$C_{31}H_{25}N_3$+H] requires 440.2127, found 440.2125 [M^++H].

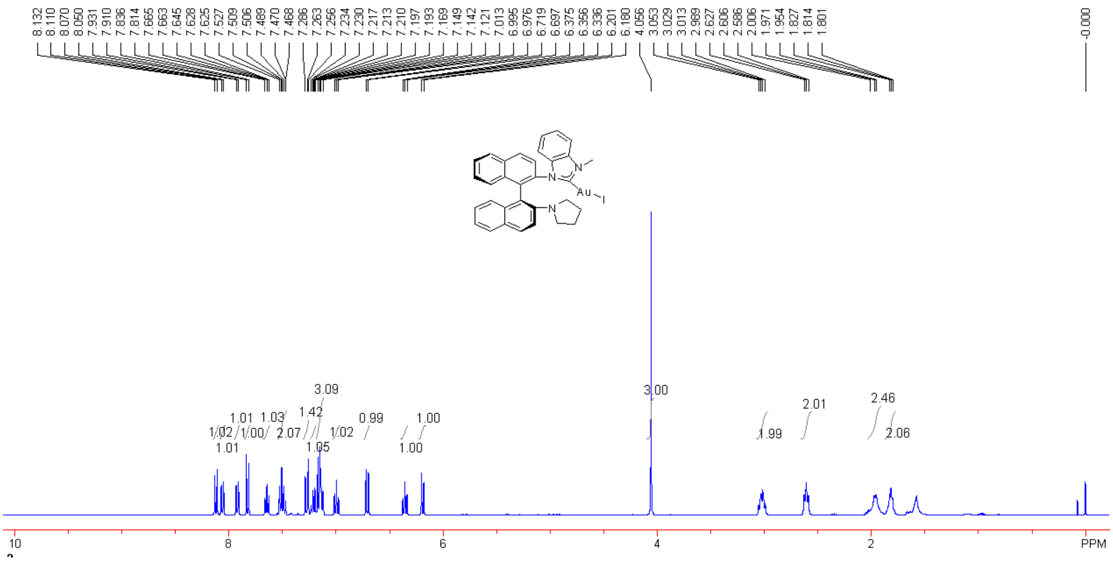




Complex (a*S*)-**6**



White solid; m.p. 286.0-287.5 °C (dec.). $[\alpha]^{20}_{D}$ = +172 (*c* 0.25, $CHCl_3$). IR (direct irradiation) *ν* 3061, 3035, 2957, 2922, 2899, 2853, 2831, 1614, 1595, 1504, 1468, 1440, 1426, 1393, 1377, 1345, 1244, 1150, 1133, 1010, 856, 822, 810, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.80-1.83 (m, 2H), 1.95-2.01 (m, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.99-3.05 (m, 2H), 4.06 (s, 3H), 6.19 (d, *J* = 8.4 Hz, 1H), 6.36 (t, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.12-7.17 (m, 3H), 7.19-7.23 (m, 1H), 7.27 (d, *J* = 9.2 Hz, 1H), 7.47-7.53 (m, 2H), 7.63-7.67 (m, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H). LRMS (ESI) *m/e* 650.2 [M^+-I]; HRMS (ESI) calcd for [$C_{32}H_{27}N_3IAu$-I] requires 650.1870, found 650.1880 [M^+-I]. Anal. Calcd. for $C_{32}H_{27}AuIN_3$ requires: C 49.44, H 3.50, N 5.40. Found: C 49.24, H 3.69, N 5.25%.



(7) General Procedure for the Synthesis of Gold(I) Complex 7

To a mixture of 20% H_2SO_4 (aqueous, 1 mL) and 40% HCHO (aqueous, 1 mL) in THF (4 mL) were added dropwise the solution of **14** (405 mg, 1 mmol) in THF (20 mL) and simultaneously the solution of $NaBH_4$ (265 mg, 7 mmol) in water (2 mL) at 0 °C within 15 minutes. After further stirring at 0 °C for 1 h, the reaction system was quenched via addition of

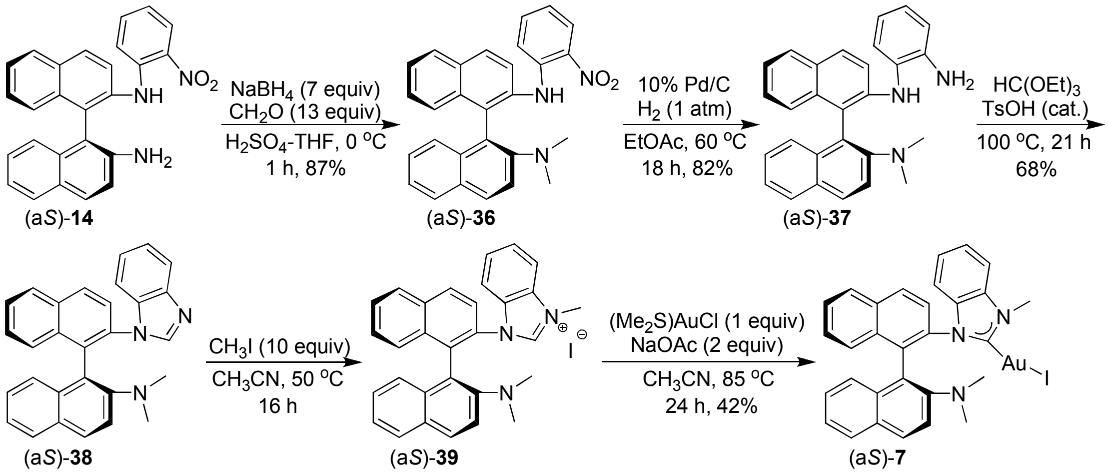
20% NaOH (aqueous) until pH >7 and then extracted with ethyl acetate for three times. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then purified by a silica gel flash column chromatography (petroleum ether/EtOAc: 150/1) to give **36** as a red solid in 87% yield.

A mixture of **36** (347 mg, 0.8 mmol) and 10% Pd/C (80 mg) in EtOAc (16 mL) was stirred under H_2 atmosphere (1 atm) at 60 ^oC for 18 h. After cooling to room temperature, the suspension was filtered through Celite to remove Pd/C. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 20/1) to give **37** as a white solid in 82% yield.

Compound **37** (260 mg, 0.64 mmol) and triethyl orthoformate (10 mL) containing a catalytic amount of TsOH (13 mg) were heated at 100 ^oC for 21 h. After removing triethyl orthoformate under reduced pressure, the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1) to give **38** as a white solid in 68% yield.

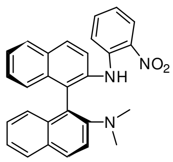
Compound **38** (124 mg, 0.3 mmol) and CH_3I (0.2 mL, 3 mmol) in CH_3CN (6 mL) were stirred under reflux for 16 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **39** was used for the next step without further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **39** (56 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol) and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5 mL) as the solvent. After refluxing at 85 ^oC for 24 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 8/1) to give complex **7** as a white solid in 42% yield (Scheme S8).

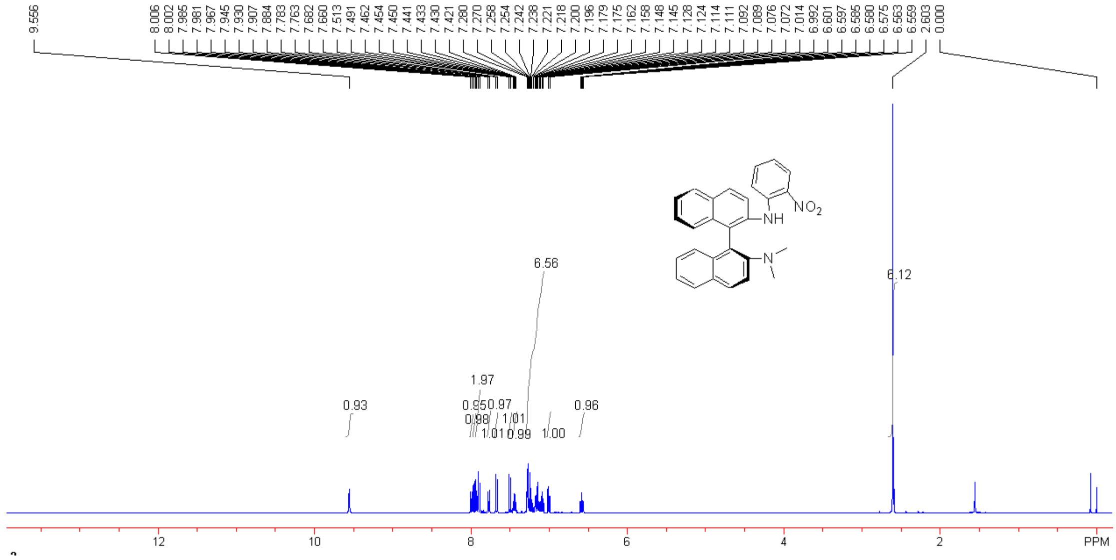


Scheme S8

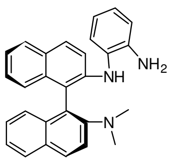
Compound (a*S*)-**36**



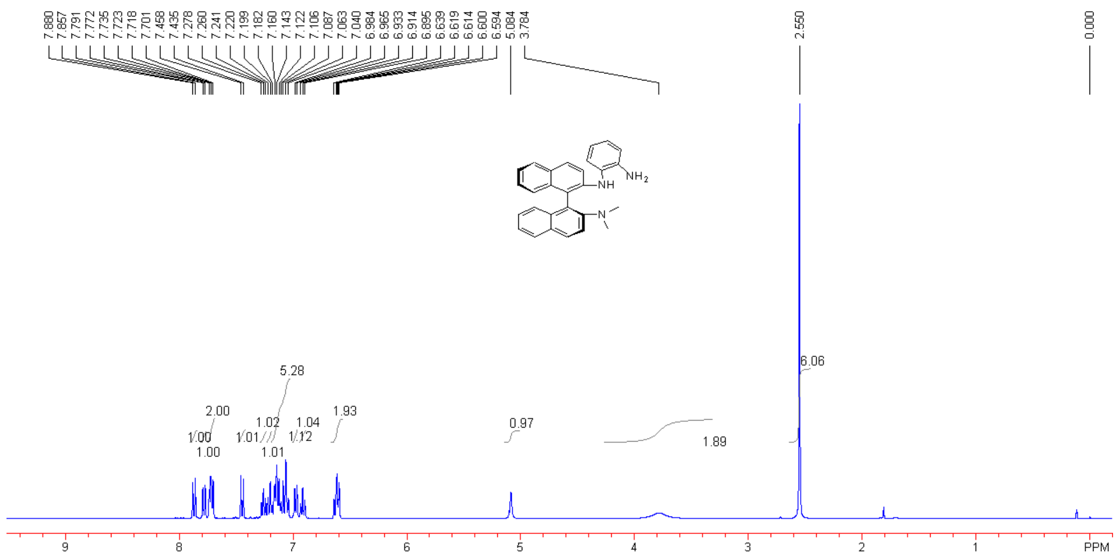
It is a known compound.[3] Red solid; m.p. 135.5-136.9 ^{o}C. $[\alpha]^{20}_D$ = +53 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3325, 2957, 2923, 2853, 1611, 1592, 1568, 1493, 1409, 1332, 1257, 1245, 1211, 1189, 1144, 1080, 1039, 989, 964, 863, 813, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.60 (s, 6H), 6.58 (ddd, *J* = 1.6, 6.4, 8.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 7.07-7.28 (m, 6H), 7.44 (ddd, *J* = 3.6, 4.8, 8.0 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.99 (dd, *J* = 1.6, 9.2 Hz, 1H), 9.56 (s, 1H). LRMS (ESI) *m/e* 434.2 [M$^+$+H]; HRMS (ESI) calcd for $[C_{28}H_{23}N_3O_2+H]$ requires 434.1869, found 434.1868 [M$^+$+H].



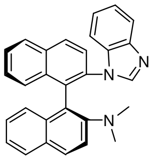
Compound (a*S*)-**37**



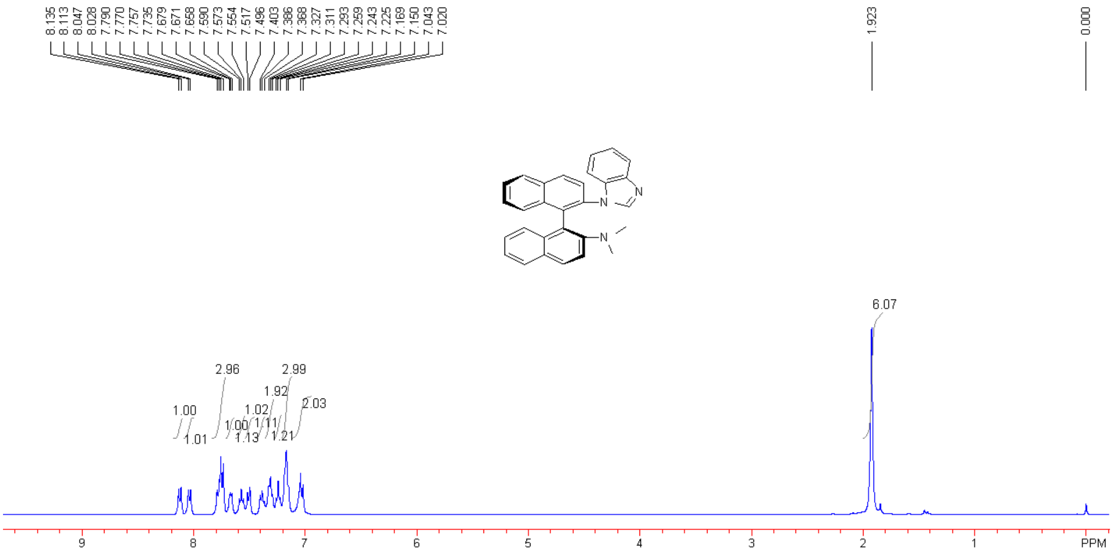
It is a known compound.[3] White solid; m.p. 144.5-146.0 °C. IR (direct irradiation) ν 3448, 3375, 3052, 2921, 2783, 1615, 1593, 1500, 1478, 1414, 1342, 1294, 1249, 1213, 1129, 1049, 987, 964, 937, 861, 814, 743 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.55 (s, 6H), 3.78 (br, 2H), 5.08 (s, 1H), 6.60 (d, J = 8.0 Hz, 1H), 6.62 (t, J = 7.6 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 7.04-7.18 (m, 5H), 7.21 (d, J = 8.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 9.2 Hz, 1H), 7.70-7.74 (m, 2H), 7.78 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 9.2 Hz, 1H). LRMS (ESI) *m/e* 404.2 [M^{+}+H]; HRMS (ESI) calcd for [$C_{28}H_{25}N_3$+H] requires 404.2127, found 404.2125 [M^{+}+H].

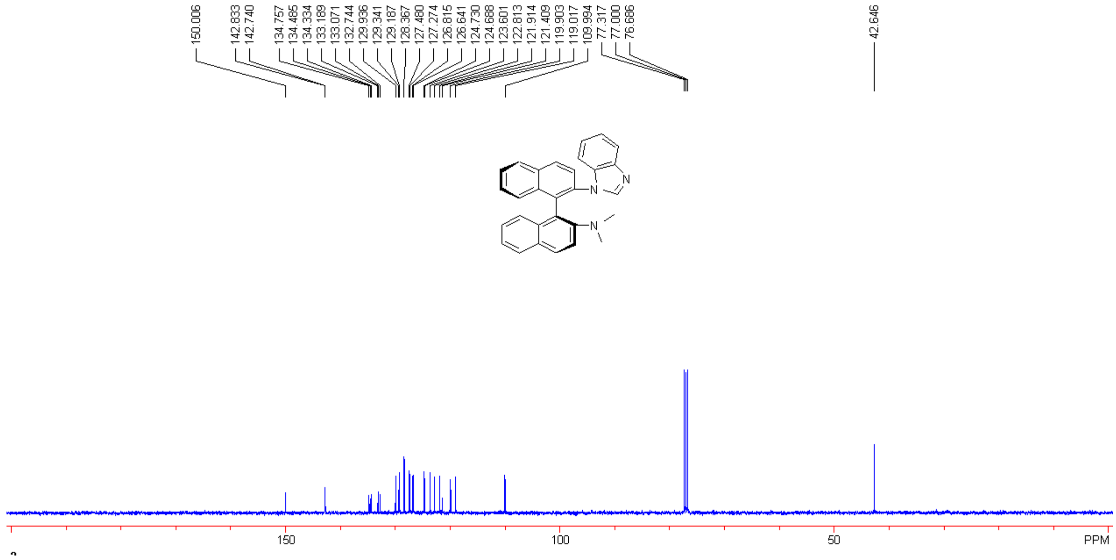


Compound (a*S*)-**38**[3]

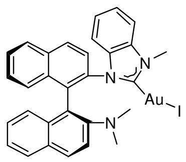


White solid; m.p. 151.4-152.8 °C. $[\alpha]^{20}_{D}$ = -72 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3055, 2924, 2853, 2785, 1681, 1614, 1594, 1505, 1488, 1453, 1428, 1343, 1303, 1284, 1235, 1142, 985, 818, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.92 (s, 6H), 7.02-7.04 (m, 2H), 7.15-7.20 (m, 3H), 7.22-7.26 (m, 1H), 7.29-7.33 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.66-7.68 (m, 1H), 7.74-7.79 (m, 3H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 42.6, 110.0, 119.0, 119.9, 121.4, 121.9, 122.8, 123.6, 124.69, 124.73, 126.6, 126.8, 127.3, 127.5, 128.4, 129.2, 129.3, 129.9, 132.7, 133.1, 133.2, 134.3, 134.5, 134.8, 142.7, 142.8, 150.0. LRMS (ESI) *m/e* 414.2 [M$^+$+H]; HRMS (ESI) calcd for [$C_{29}H_{23}N_3$+H] requires 414.1970, found 414.1967 [M$^+$+H].

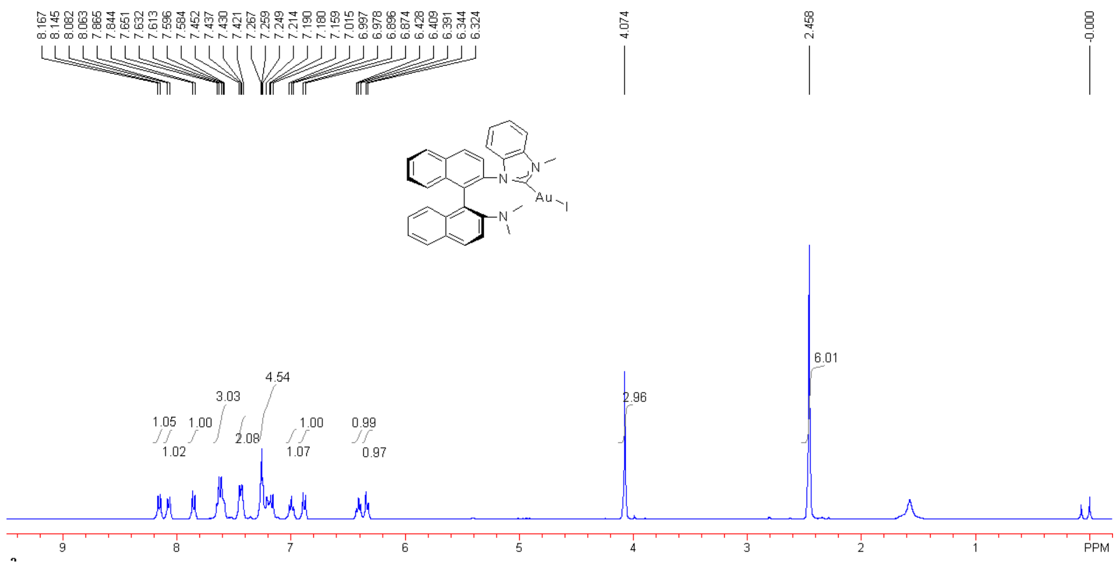




Complex (a*S*)-**7**



White solid; m.p. 259.0-260.7 °C (dec.). $[\alpha]^{20}_{D}$ = +48 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3061, 2923, 2899, 2852, 2776, 1712, 1593, 1505, 1464, 1397, 1360, 1245, 1126, 1097, 1081, 977, 859, 819, 804, 743, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.46 (s, 6H), 4.07 (s, 3H), 6.33 (d, *J* = 8.0 Hz, 1H), 6.41 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.16-7.27 (m, 4H), 7.42-7.45 (m, 2H), 7.58-7.65 (m, 3H), 7.85 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H). LRMS (ESI) *m/e* 624.2 [M^+-I]; HRMS (ESI) calcd for [$C_{30}H_{25}N_3IAu$-I] requires 624.1714, found 624.1696 [M^+-I].



(8) General Procedure for the Synthesis of Gold(I) Complex 8

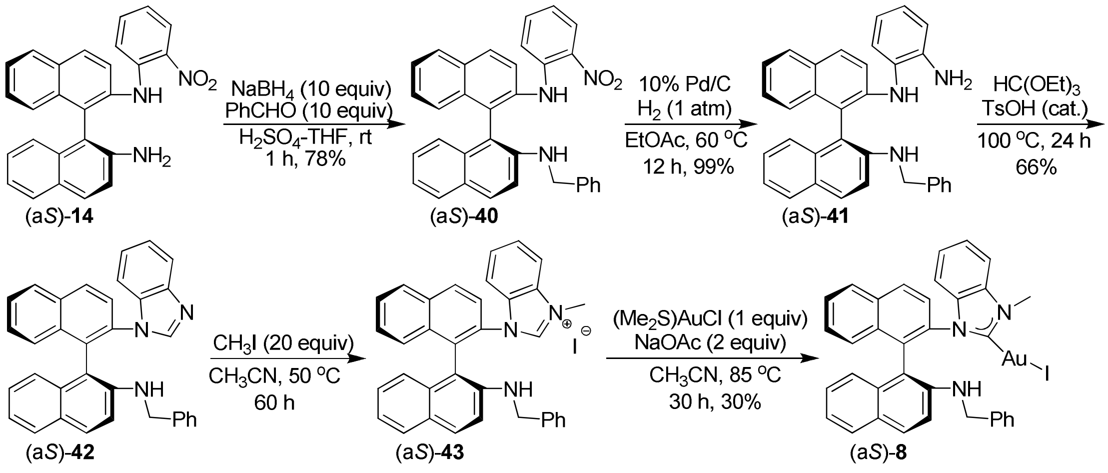
To the solution of **14** (405 mg, 1 mmol) in THF (30 mL) were added benzaldehyde (1 mL, 10 mmol) and 20% H_2SO_4 aqueous (2 mL) followed by the addition of $NaBH_4$ (378 mg, 10 mmol) carefully at room temperature within 15 minutes. After further stirring at room temperature for 1 h, the reaction system was quenched via addition of 20% NaOH (aqueous) until pH >7 and then extracted with ethyl acetate for three times. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc: 60/1) to give **40** as a red solid in 78% yield.

A mixture of **40** (248 mg, 0.5 mmol) and 10% Pd/C (50 mg) in EtOAc (15 mL) was stirred under H_2 atmosphere (1 atm) at 60 ^oC for 12 h. After cooling to room temperature, the suspension was filtered through Celite to remove Pd/C. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 15/1; containing minor NEt_3) to give **41** as a white solid in > 99% yield.

Compound **41** (210 mg, 0.45 mmol) and triethyl orthoformate (10 mL) containing a catalytic amount of TsOH (9 mg) were heated at 100 ^oC for 24 h. After removing triethyl orthoformate under reduced pressure, the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1) to give **42** as a white solid in 66% yield.

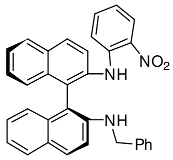
Compound **42** (95 mg, 0.2 mmol) and CH_3I (0.25 mL, 4 mmol) in CH_3CN (6 mL) were stirred under reflux for 60 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid **43** was used for the next step without further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **43** (62 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol) and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5 mL) as the solvent. After refluxing at 85 ^oC for 24 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 8/1) to give complex **8** as a pale yellow solid in 30% yield (Scheme S9).

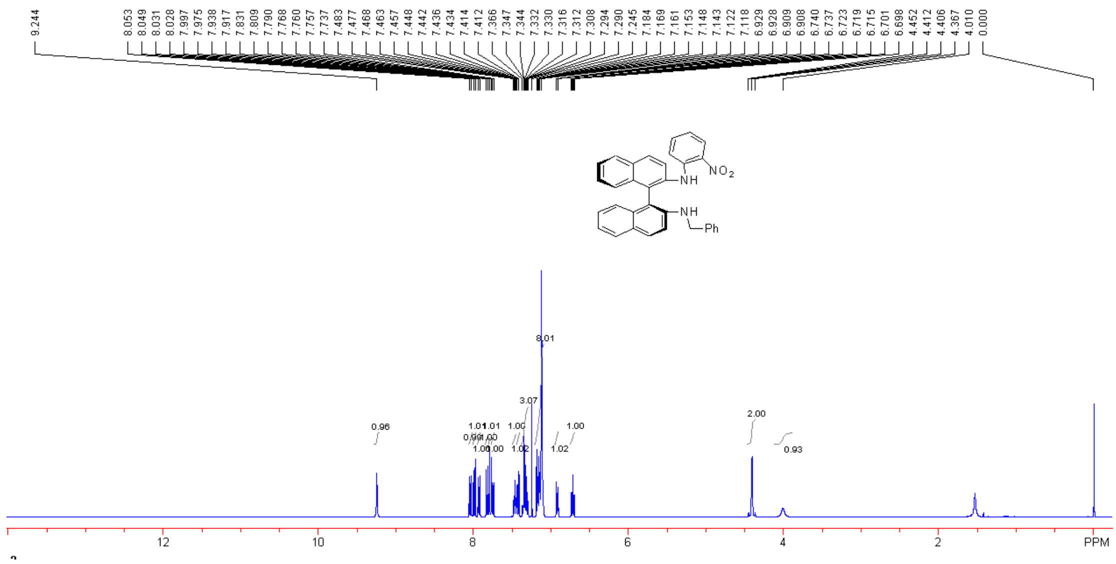


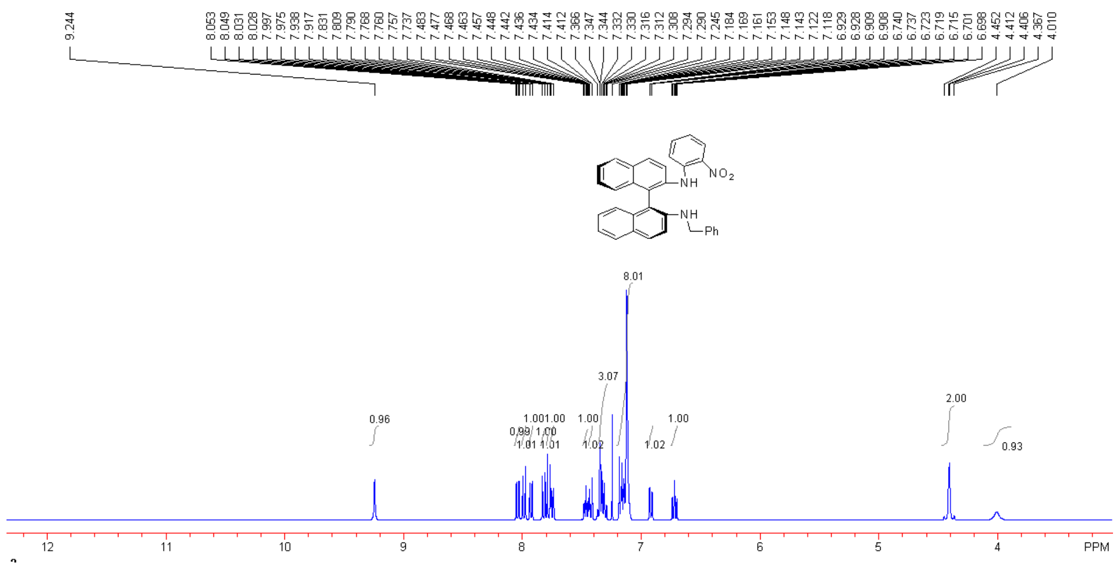
Scheme S9

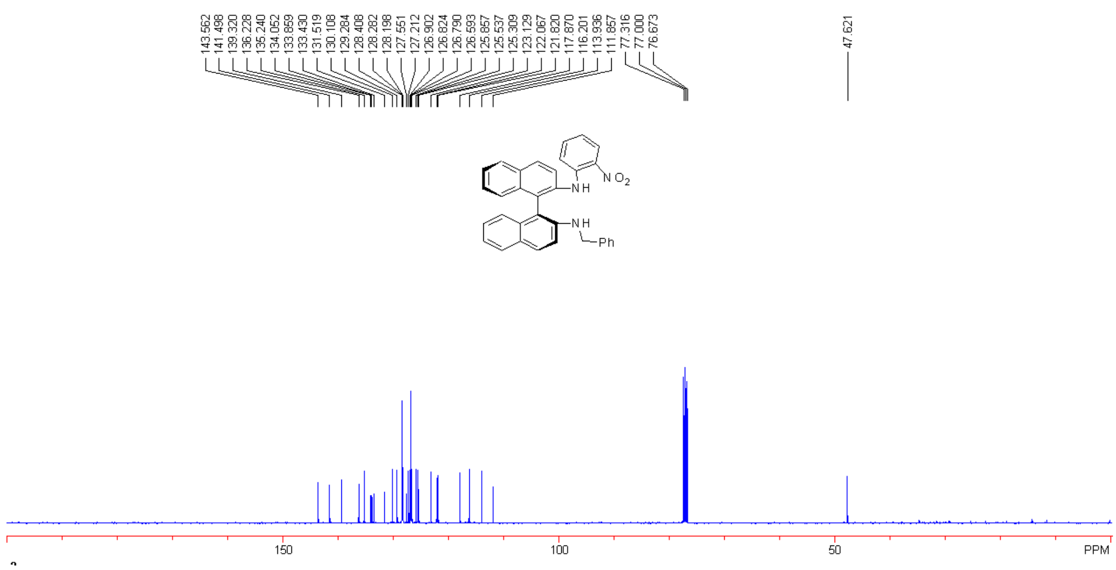
Compound (a*S*)-**40**



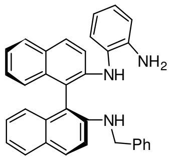
Red solid; m.p. 87.4-89.0 °C. $[\alpha]^{20}_{D}$ = +186 (*c* 0.25, $CHCl_3$). IR (direct irradiation) *ν* 3417, 3326, 3053, 2956, 2924, 2853, 1611, 1592, 1572, 1492, 1413, 1339, 1293, 1246, 1146, 1077, 1040, 1025, 971, 864, 809, 736, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 4.01 (br, 1H), 4.39 (d, *J* = 15.6 Hz, 1H), 4.43 (d, *J* = 15.6 Hz, 1H), 6.72 (ddd, *J* = 1.2, 6.8, 8.4 Hz, 1H), 6.92 (dd, *J* = 0.4, 8.0 Hz, 1H), 7.12-7.18 (m, 8H), 7.29-7.37 (m, 3H), 7.42 (dd, *J* = 0.8, 8.8 Hz, 1H), 7.46 (ddd, *J* = 2.4, 6.0, 8.4 Hz, 1H), 7.74-7.76 (m, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 8.04 (dd, *J* = 1.2, 8.4 Hz, 1H), 9.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 47.6, 111.9, 113.9, 116.2, 117.9, 121.8, 122.1, 123.1, 125.3, 125.5, 125.9, 126.6, 126.79, 126.82, 126.9, 127.2, 127.6, 128.2, 128.3, 128.4, 129.3, 130.1, 131.5, 133.4, 133.9, 134.1, 135.2, 136.2, 139.3, 141.5, 143.6. LRMS (ESI) *m/e* 496.2 $[M^+ +H]$; HRMS (ESI) calcd for $[C_{33}H_{25}N_3O_2+H]$ requires 496.2025, found 496.2025 $[M^+ +H]$.



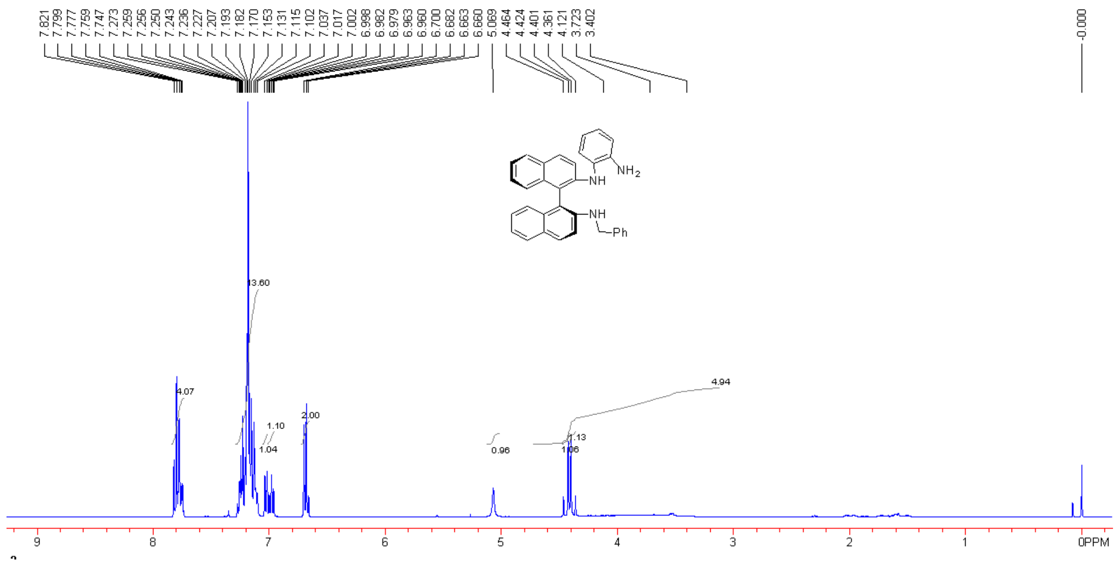


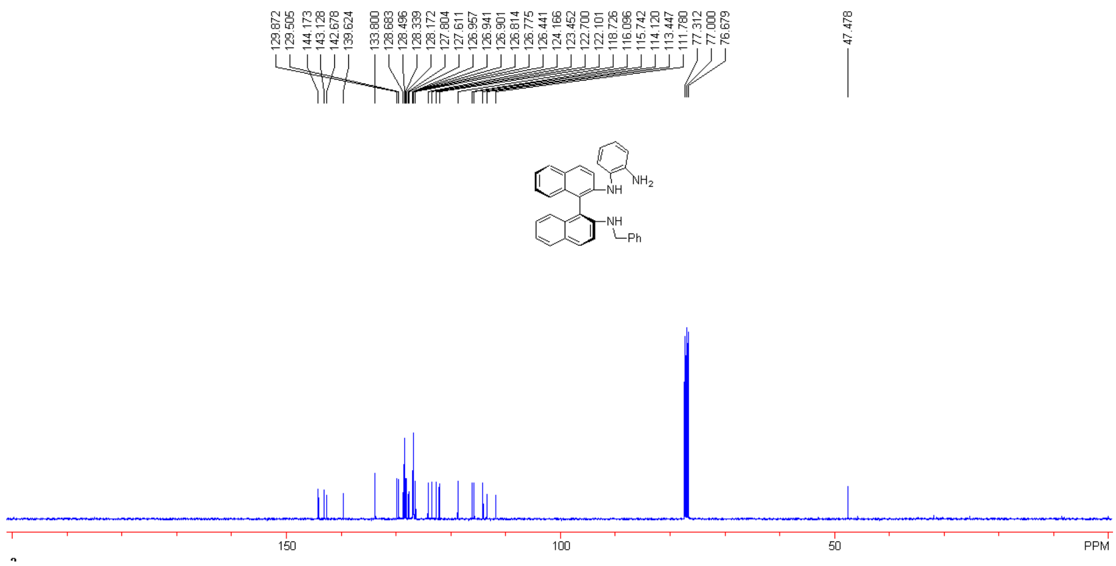


Compound (a*S*)-**41**

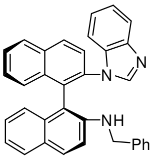


White solid; m.p. 117.2-118.5 °C. $[\alpha]^{20}_{D}$ = -124 (c 0.125, $CHCl_3$). IR (direct irradiation) ν 3415, 3370, 3051, 2956, 2923, 2853, 1615, 1594, 1497, 1454, 1415, 1338, 1294, 1247, 1213, 1149, 1024, 970, 810, 741, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.40-4.46 (m, 3H, NH+NH_2), 4.38 (d, J = 16.0 Hz, 1H), 4.44 (d, J = 16.0 Hz, 1H), 5.07 (s, 1H), 6.66-6.70 (m, 2H), 6.98 (dt, J = 1.2, 7.6 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 7.10-7.27 (m, 13H), 7.75-7.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 47.5, 111.8, 113.4, 114.1, 115.7, 116.1, 118.7, 122.1, 122.7, 123.5, 124.2, 126.4, 126.78, 126.81, 126.90, 126.94, 126.96, 127.6, 127.8, 128.2, 128.3, 128.5, 128.7, 129.5, 129.9, 133.8, 139.6, 142.7, 143.1, 144.2. LRMS (ESI) m/e 466.2 [M$^+$+H]; HRMS (ESI) calcd for [$C_{33}H_{27}N_3$+H] requires 466.2283, found 466.2279 [M$^+$+H].

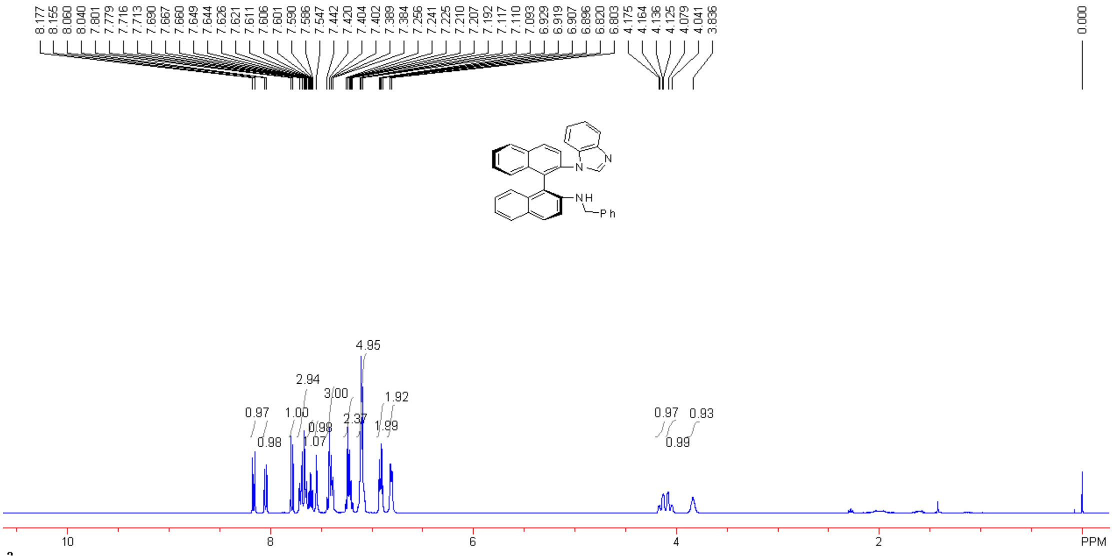


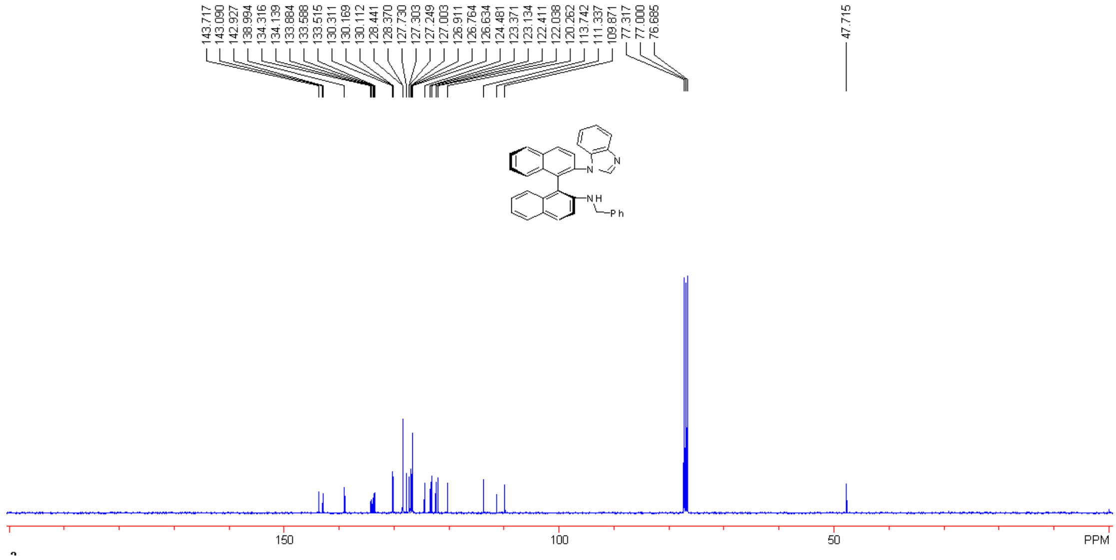


Compound (a*S*)-**42**

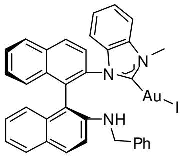


White solid; m.p. 106.5-107.5 °C (dec.). $[\alpha]^{20}_{D}$ = -50 (*c* 0.25, $CHCl_3$). IR (direct irradiation) *ν* 3054, 2954, 2923, 2853, 1616, 1597, 1487, 1453, 1426, 1343, 1285, 1235, 1151, 810, 739, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.84 (br, 1H), 4.06 (d, *J* = 15.2 Hz, 1H), 4.15 (dd, *J* = 4.4, 15.6 Hz, 1H), 6.81 (d, *J* = 6.8 Hz, 2H), 6.90-6.93 (m, 2H), 7.09-7.12 (m, 5H), 7.19-7.26 (m, 2H), 7.38-7.44 (m, 3H), 7.55 (s, 1H), 7.61 (ddd, *J* = 2.0, 6.0, 8.0 Hz, 1H), 7.64-7.72 (m, 3H), 7.79 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 47.7, 109.9, 111.3, 113.7, 120.3, 122.0, 122.4, 123.1, 123.4, 124.5, 126.6, 126.8, 126.9, 127.0, 127.2, 127.3, 127.7, 128.37, 128.44, 130.1, 130.2, 130.3, 133.5, 133.6, 133.9, 134.1, 134.3, 139.0, 142.9, 143.1, 143.7. LRMS (ESI) *m/e* 476.2 $[M^+ +H]$; HRMS (ESI) calcd for $[C_{34}H_{25}N_3+H]$ requires 476.2127, found 476.2128 $[M^+ +H]$.

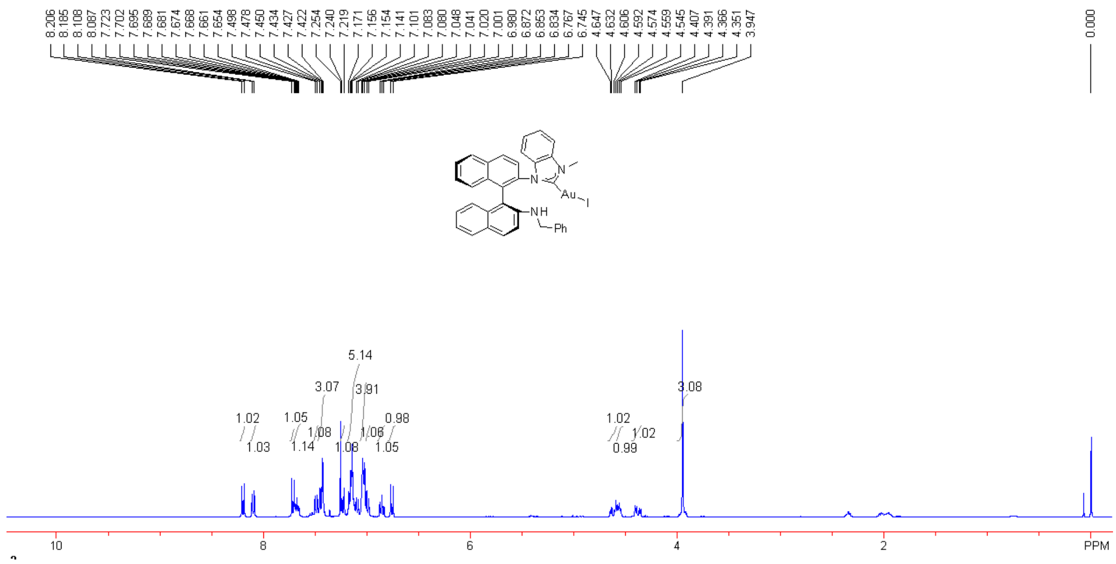




Complex (a*S*)-**8**



Pale yellow solid; m.p. 198.3-199.8 ^{o}C (dec.). $[\alpha]^{20}_{D}$ = +20 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3399, 2955, 2922, 2852, 1710, 1617, 1598, 1494, 1454, 1392, 1343, 1295, 1240, 1081, 827, 808, 740, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.95 (s, 3H), 4.38 (dd, *J* = 6.0, 16.0 Hz, 1H), 4.56 (t, *J* = 5.6 Hz, 1H), 4.62 (dd, *J* = 5.6, 16.0 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 7.02-7.05 (m, 4H), 7.08-7.17 (m, 5H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.42-7.45 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.67 (ddd, *J* = 2.8, 5.6, 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H). LRMS (ESI) *m/e* 686.2 [M^+-I]; HRMS (ESI) calcd for [$C_{35}H_{27}N_3IAu$-I] requires 686.1870, found 686.1844 [M^+-I].



(9) General Procedure for the Synthesis of Gold(I) Complex 9

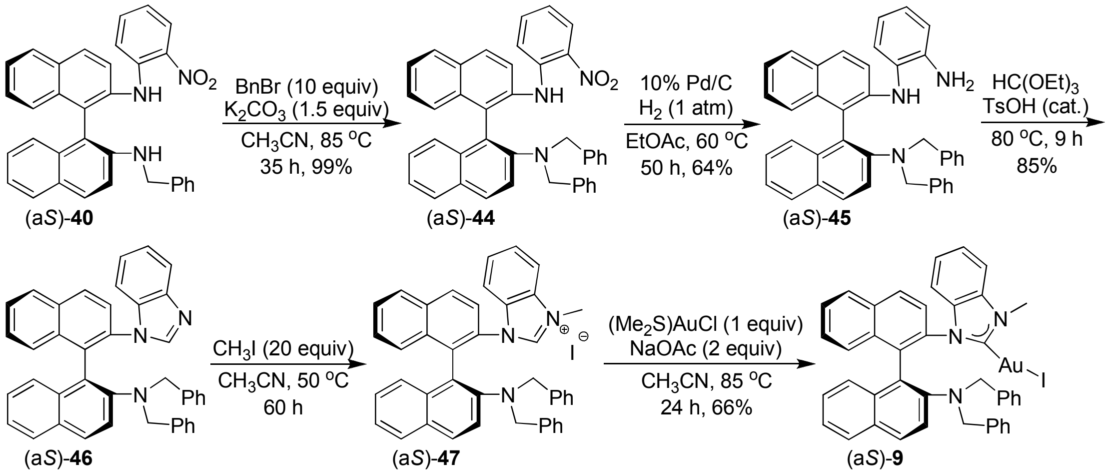
To the suspension of **40** (248 mg, 0.5 mmol) and K_2CO_3 (104 mg, 0.75 mmol) in dry CH_3CN (12 mL) was added BnBr (0.6 mL, 5 mmol) and the resulting mixture was refluxed at 85 °C for 35 h. After cooling to room temperature, the reaction was quenched with water and then extracted with ethyl acetate for three times. The combined organic phases were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and then purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc: 150/1) to give **44** as a red solid in > 99% yield.

A mixture of **44** (398 mg, 0.68 mmol) and 10% Pd/C (68 mg) in EtOAc (15 mL) was stirred under H_2 atmosphere (1 atm) at 60 °C for 50 h. After cooling to room temperature, the suspension was filtered through Celite to remove Pd/C. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 25/1) to give **45** as a pale yellow solid in 64% yield.

Compound **45** (232 mg, 0.41 mmol) and triethyl orthoformate (10 mL) containing a catalytic amount of TsOH (9 mg) were heated at 100 °C for 9 h. After removing triethyl orthoformate under reduced pressure, the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 8/1) to give **46** as a white solid in 85% yield.

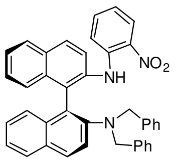
Compound **46** (113 mg, 0.2 mmol) and CH_3I (0.25 mL, 4 mmol) in CH_3CN (4 mL) were stirred under reflux for 60 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid **47** was used for the next step without further purification.

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **47** (71 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol) and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5 mL) as the solvent. After refluxing at 85 °C for 24 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 6/1) to give complex **9** as a white solid in 66% yield (Scheme S10).

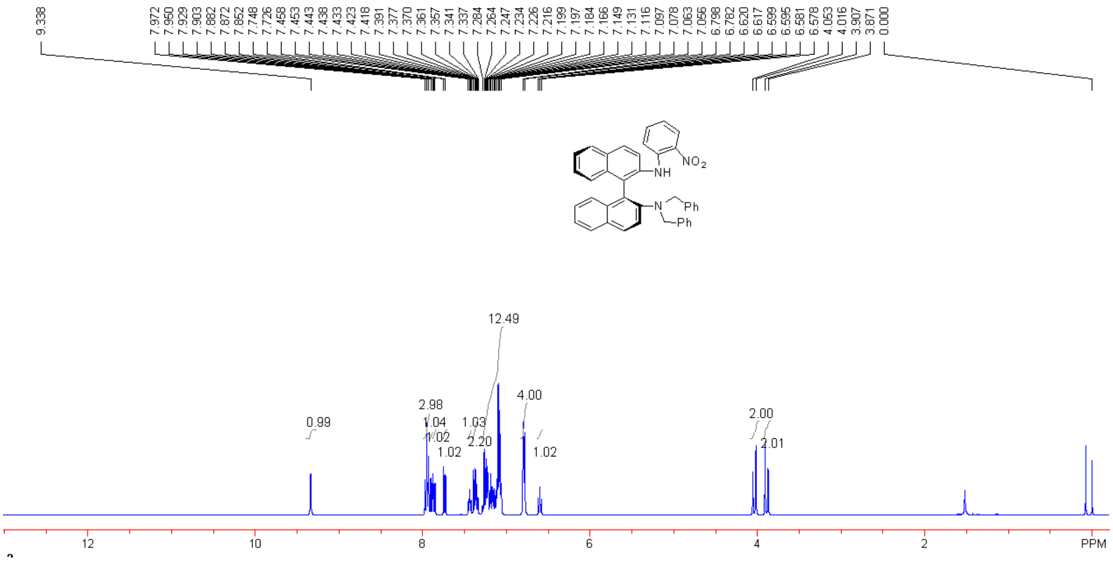


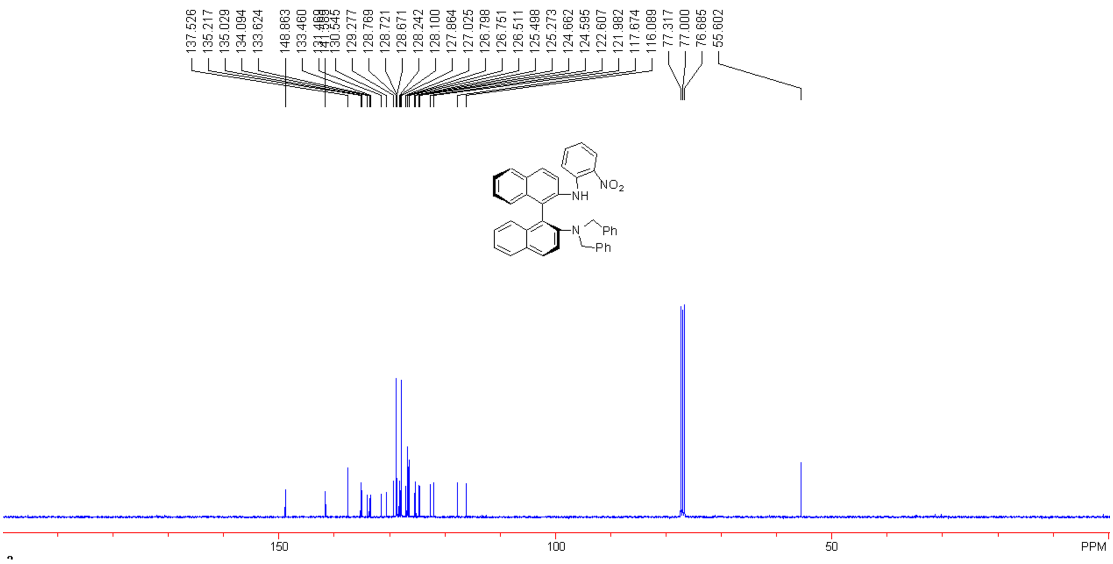
Scheme S10

Compound (a*S*)-**44**

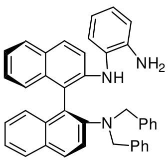


Red solid; m.p. 90.2-91.5 °C (dec.). $[\alpha]^{20}_{D}$ = +12 (*c* 0.125, $CHCl_3$). IR (direct irradiation) ν 3330, 3059, 3027, 2962, 2923, 2849, 1611, 1592, 1571, 1494, 1444, 1413, 1339, 1248, 1210, 1146, 1106, 1076, 1027, 960, 812, 737, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.89 (d, *J* = 14.4 Hz, 2H), 4.03 (d, *J* = 14.8 Hz, 2H), 6.60 (ddd, *J* = 1.2, 6.8, 8.4 Hz, 1H), 6.79 (d, *J* = 6.4 Hz, 4H), 7.06-7.28 (m, 12H), 7.33-7.39 (m, 2H), 7.44 (ddd, *J* = 2.0, 6.0, 8.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.93-7.97 (m, 3H), 9.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 55.6, 116.1, 117.7, 122.0, 122.6, 124.6, 124.7, 125.3, 125.5, 126.5, 126.75, 126.80, 127.0, 127.9, 128.1, 128.2, 128.67, 128.72, 128.8, 129.3, 130.5, 131.5, 133.5, 133.6, 134.1, 135.0, 135.2, 137.5, 141.6, 148.9. LRMS (ESI) *m/e* 586.2 [M^++H]; HRMS (ESI) calcd for [$C_{40}H_{31}N_3O_2$+H] requires 586.2495, found 586.2496 [M^++H].

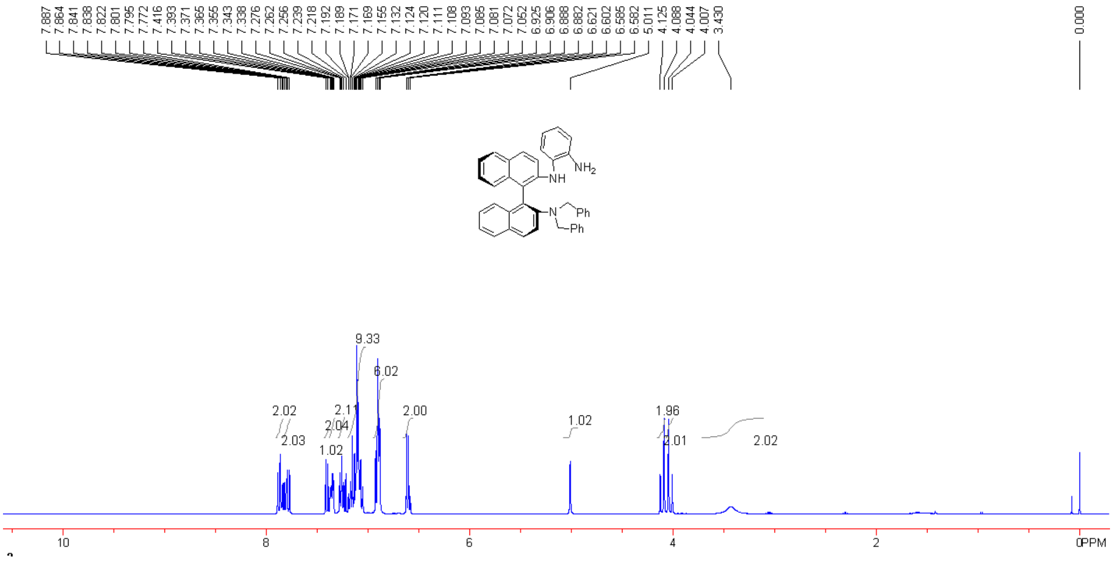


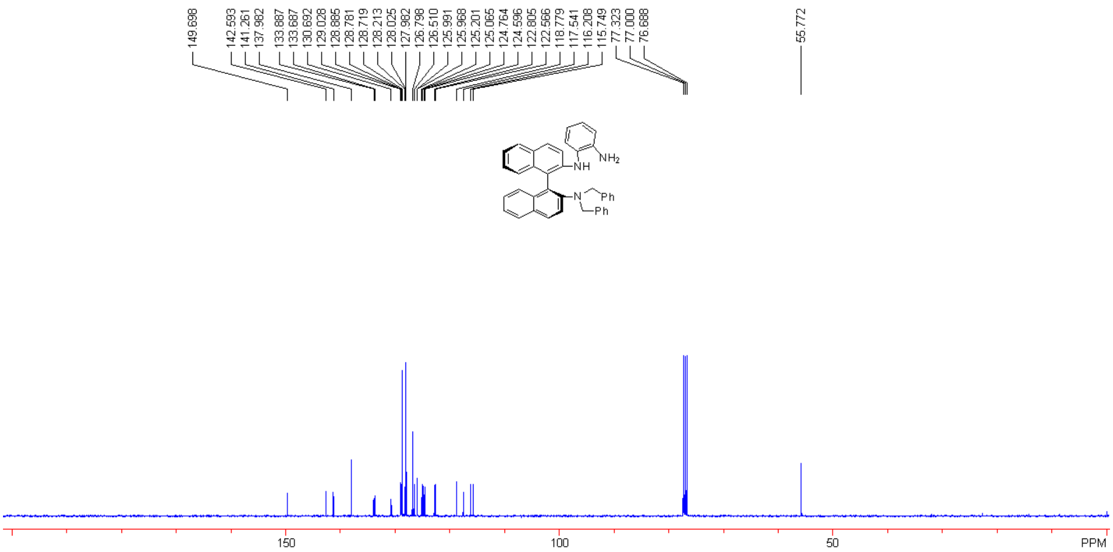


Compound (a*S*)-**45**

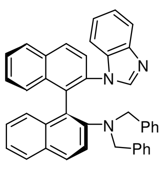


Pale yellow solid; m.p. 114.5-115.0 °C (dec.). $[\alpha]^{20}_D$ = +17 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3458, 3372, 3056, 3026, 2923, 2850, 1615, 1592, 1502, 1453, 1414, 1341, 1297, 1210, 1146, 1071, 1026, 958, 812, 742, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.43 (br, 2H), 4.03 (d, *J* = 14.8 Hz, 2H), 4.11 (d, *J* = 14.8 Hz, 2H), 5.01 (s, 1H), 6.58-6.62 (m, 2H), 6.88-6.93 (m, 6H), 7.05-7.19 (m, 9H), 7.24-7.28 (m, 2H), 7.34-7.37 (m, 2H), 7.40 (d, *J* = 9.2 Hz, 1H), 7.78 (d, *J* = 9.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.84-7.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 55.8, 115.7, 116.2, 117.5, 118.8, 122.6, 122.8, 124.6, 124.8, 125.1, 125.2, 125.97, 125.99, 126.5, 126.8, 127.98, 128.03, 128.2, 128.7, 128.8, 128.9, 129.0, 130.7, 133.7, 133.9, 138.0, 141.3, 142.6, 149.7. LRMS (ESI) *m/e* 556.3 [M^++H]; HRMS (ESI) calcd for [$C_{40}H_{33}N_3$+H] requires 556.2753, found 556.2750 [M^++H].



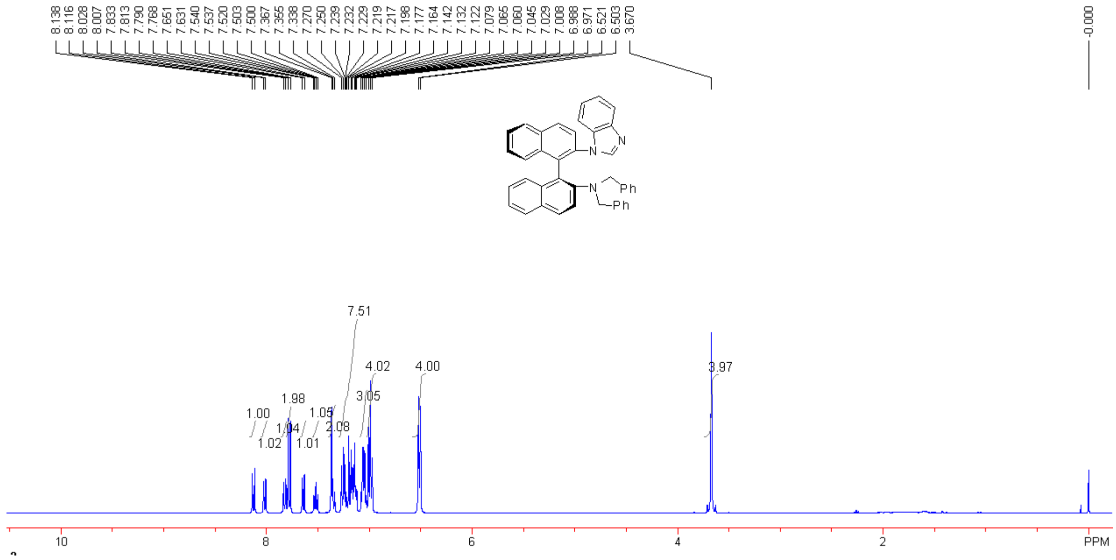


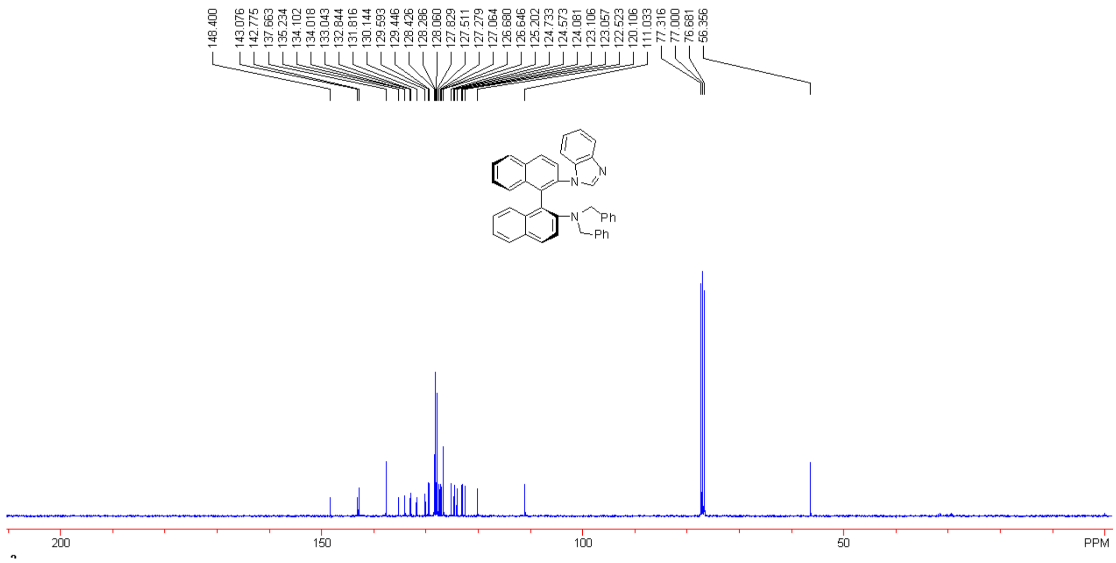
Compound (a*S*)-**46**



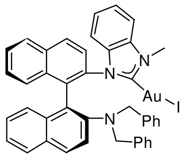
White solid; m.p. 53.8-55.6 °C (dec.). $[\alpha]^{20}_{D}$ = -49 (*c* 0.25, $CHCl_3$). IR (direct irradiation) *ν* 3057, 3028, 2960, 2923, 2853, 1593, 1488, 1452, 1363, 1283, 1260, 1235, 1209, 1192, 1081, 1018, 963, 799, 740, 697 cm^{-1}. ^{1}H NMR (400

MHz, $CDCl_3$, TMS) δ 3.67 (s, 4H), 6.51 (d, *J* = 7.2 Hz, 4H), 6.97-7.01 (m, 4H), 7.03-7.08 (m, 3H), 7.12-7.27 (m, 7H), 7.34-7.37 (m, 2H), 7.50-7.54 (m, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 56.4, 111.0, 120.1, 122.5, 123.06, 123.11, 124.1, 124.6, 124.7, 125.2, 126.6, 126.7, 127.1, 127.3, 127.5, 127.8, 128.1, 128.3, 128.4, 129.4, 129.6, 130.1, 131.8, 132.8, 133.0, 134.0, 134.1, 135.2, 137.7, 142.8, 143.1, 148.4. LRMS (ESI) *m/e* 566.3 [M^++H]; HRMS (ESI) calcd for [$C_{41}H_{31}N_3$+H] requires 566.2596, found 566.2590 [M^++H].

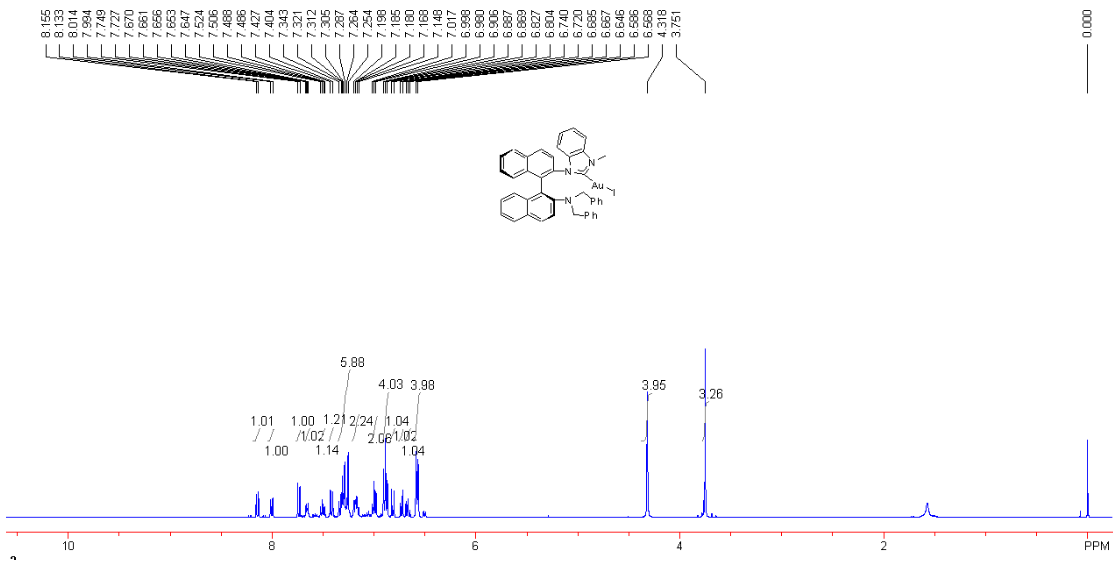




Complex (a*S*)-**9**



White solid; m.p. 240.8-241.8 °C (dec.). $[\alpha]^{20}_{D}$ = +51 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3059, 3023, 2923, 2852, 2814, 1618, 1596, 1505, 1450, 1392, 1353, 1216, 1150, 1124, 1098, 1070, 971, 942, 824, 807, 738, 699, 684 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.75 (s, 3H), 4.32 (s, 4H), 6.58 (d, *J* = 7.2 Hz, 4H), 6.67 (t, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 1H), 6.89 (t, *J* = 7.2 Hz, 4H), 7.00 (t, *J* = 7.2 Hz, 2H), 7.15-7.20 (m, 2H), 7.25-7.34 (m, 5H), 7.42 (d, *J* = 9.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.65-7.67 (m, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H). LRMS (ESI) *m/e* 776.2 [M^+-I]; HRMS (ESI) calcd for [$C_{42}H_{33}N_3IAu$-I] requires 776.2340, found 776.2352 [M^+-I].



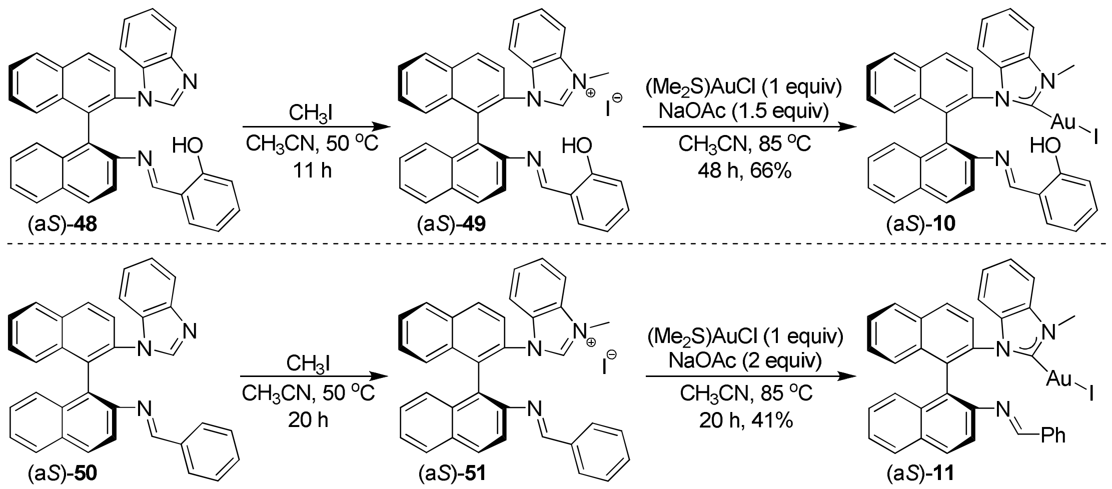
(10) General Procedure for the Synthesis of Gold(I) Complexes 10 and 11

Chiral imine compounds **48** and **50** were prepared according to our previously reported procedures with compound **24** as the starting material.[2b]

Compound **48** (98 mg, 0.2 mmol) or **50** (95 mg, 0.2 mmol) and CH_3I (0.25 mL, 4 mmol) in CH_3CN (4 mL) were refluxed for 11 h or 20 h. After cooling to room temperature, volatiles were removed under reduced pressure and the respectively obtained solid **49** and **51** was used for the next step without further purification.

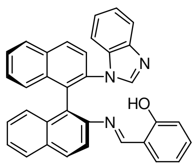
Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **49** (63 mg, 0.1 mmol), NaOAc (13 mg, 0.15 mmol) and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5 mL) as the solvent. After refluxing at 85 °C for 48 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1; containing minor NEt_3) to give complex **10** as a yellow solid in 66% yield (Scheme S11).

Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added NHC precursor **51** (62 mg, 0.1 mmol), NaOAc (17 mg, 0.2 mmol) and [(Me_2S)AuCl] (30 mg, 0.1 mmol) followed by the addition of dry CH_3CN (5 mL) as the solvent. After refluxing at 85 °C for 20 h, the reaction mixture was cooled to room temperature and filtered through Celite. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1; containing minor NEt_3) to give complex **11** as a pale yellow solid in 41% yield (Scheme S11).

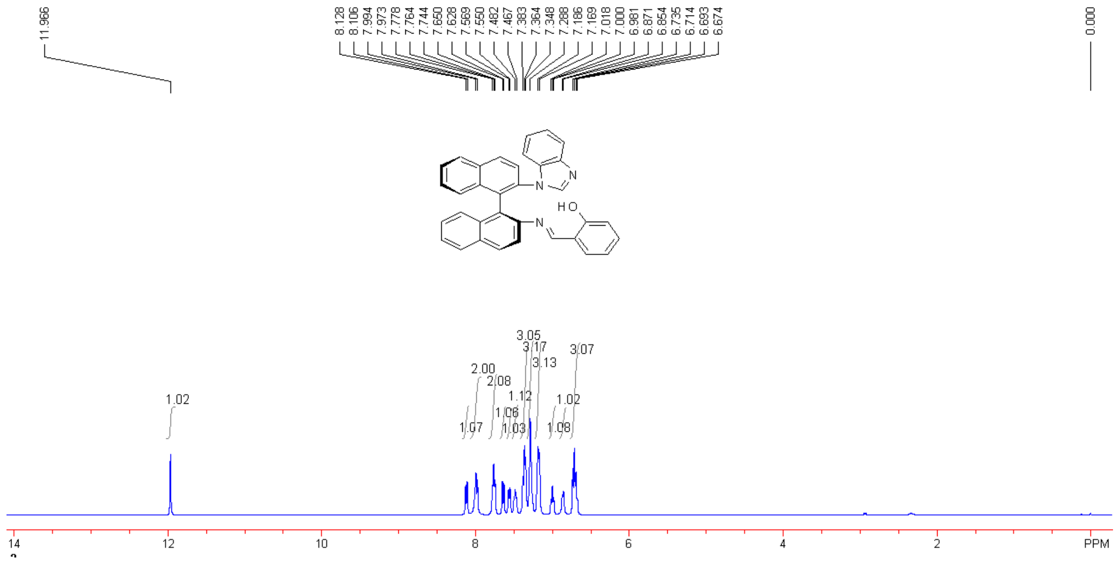


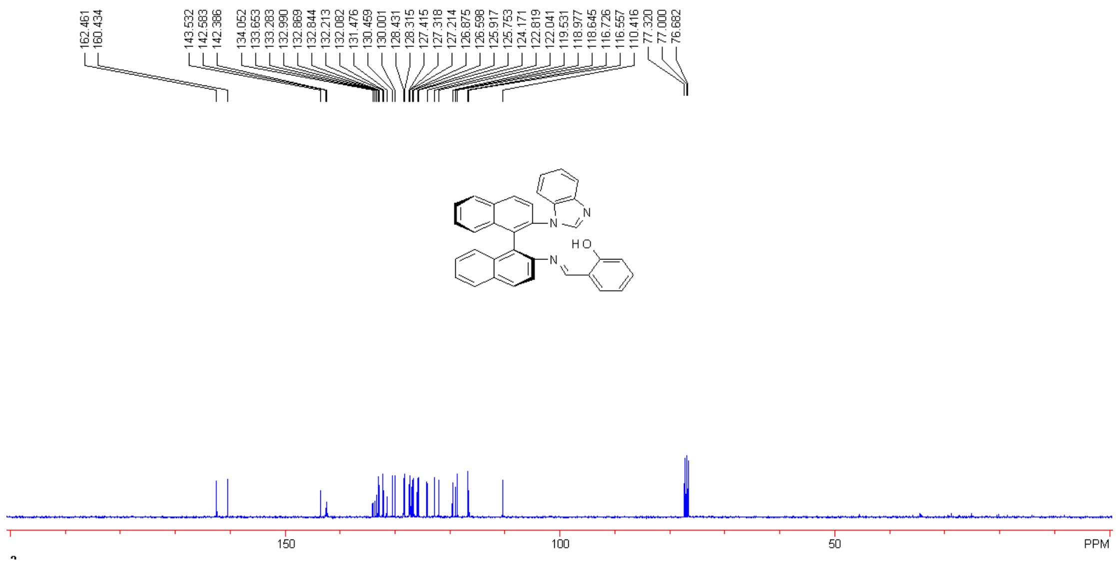
Scheme S11

Compound (a*S*)-**48**[2b]

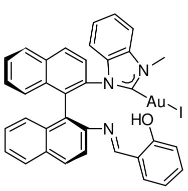


Yellow solid; m.p. 133-135 °C. $[\alpha]^{20}_{D}$ = -197 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3054, 2924, 2852, 1607, 1568, 1487, 1452, 1281, 1235, 1203, 1189, 1150, 818, 799, 742, 696 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.67-6.74 (m, 3H), 6.86 (d, *J* = 6.8 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.17-7.19 (m, 3H), 7.26-7.29 (m, 3H), 7.35-7.38 (m, 3H), 7.47-7.48 (m, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.74-7.78 (m, 2H), 7.97-7.99 (m, 2H), 8.12 (d, J = 8.8 Hz, 1H), 11.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 110.4, 116.6, 116.7, 118.6, 119.0, 119.5, 122.0, 122.8, 124.2, 125.8, 125.9, 126.6, 126.9, 127.2, 127.3, 127.4, 128.3, 128.4, 130.0, 130.5, 131.5, 132.1, 132.2, 132.8, 132.9, 133.0, 133.3, 133.7, 134.1, 142.4, 142.6, 143.5, 160.4, 162.5. LRMS (ESI) *m/e* 490.2 [M^++H]; HRMS (ESI) calcd for [$C_{34}H_{23}N_3O$+H] requires 490.1919, found 490.1902 [M^++H].

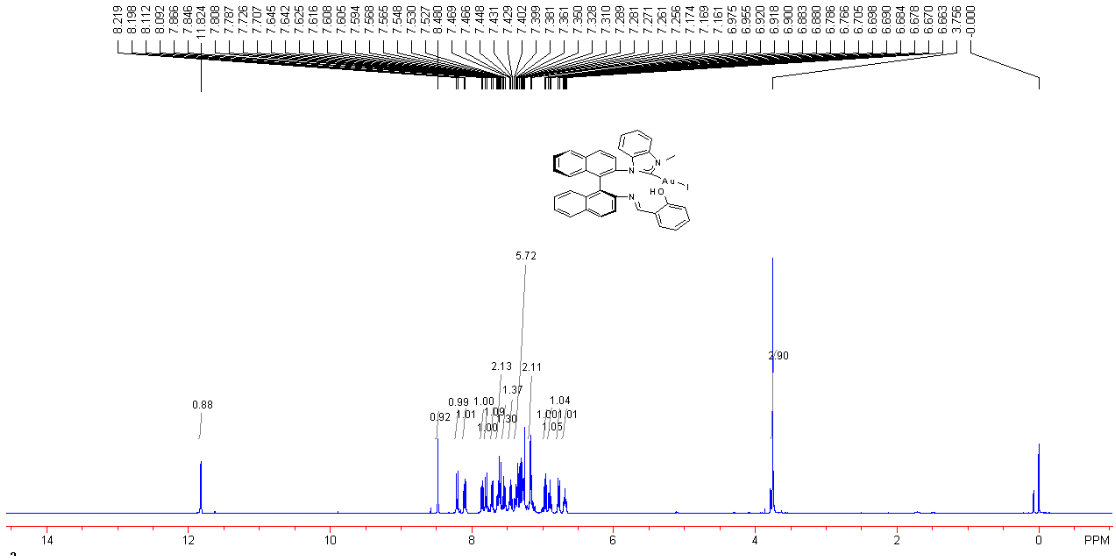




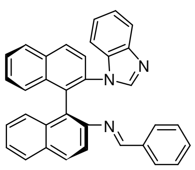
Complex (a*S*)-**10**



Yellow solid; m.p. 150.0-151.2 °C (dec.). $[\alpha]^{20}_D$ = -49 (c 0.25, $CHCl_3$). IR (direct irradiation) ν 3055, 2921, 2851, 2814, 1710, 1606, 1571, 1493, 1461, 1390, 1279, 1239, 1203, 1188, 1151, 1081, 964, 903, 859, 818, 744, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.76 (s, 3H), 6.68 (ddd, J = 2.8, 6.0, 8.4 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.90 (dt, J = 1.2, 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 7.16-7.17 (m, 2H), 7.25-7.40 (m, 5H), 7.43-7.47 (m, 1H), 7.55 (dt, J = 1.2, 8.0 Hz, 1H), 7.59-7.65 (m, 2H), 7.72 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.48 (s, 1H), 11.82 (s, 1H). LRMS (ESI) *m/e* 700.2 [M^+-I]; HRMS (ESI) calcd for [$C_{35}H_{25}N_3IOAu$-I] requires 700.1663, found 700.1666 [M^+-I].

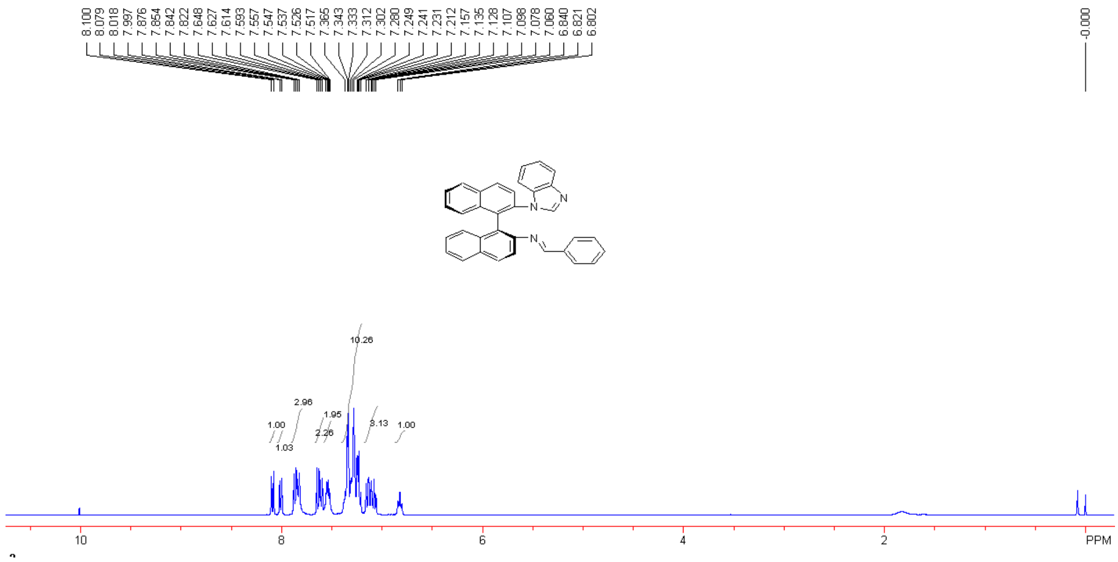


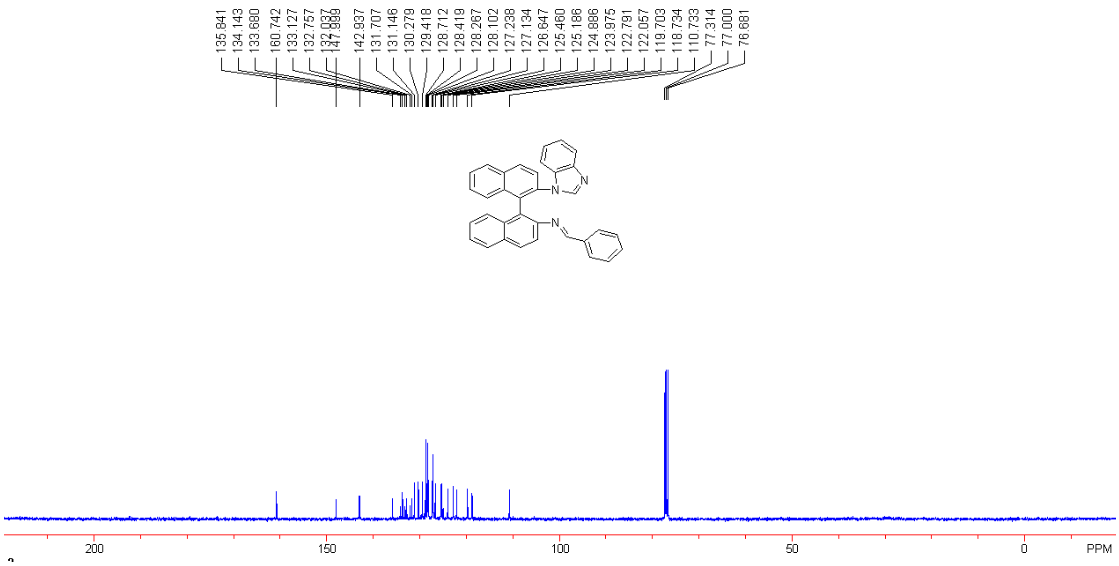
Compound (a*S*)-**50**[2b]



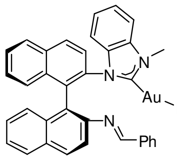
Yellow solid; m.p. 129-131 °C. $[\alpha]^{20}_D$ = -209 (c 0.25, $CHCl_3$). IR (direct irradiation) ν 3053, 2961, 2923, 2853, 1612, 1487, 1451, 1283, 1234, 1202, 1100, 1024, 815, 740, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 6.82 (t, J = 7.6 Hz, 1H), 7.06-7.16 (m, 3H), 7.21-7.37 (m, 10H), 7.52-7.56 (m, 2H), 7.60 (d, J = 8.4 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.82-7.88 (m, 3H), 8.01 (d, J = 8.4 Hz, 1H), 8.09 (d, J = 8.4 Hz, 1H) (containing minor of benzaldehyde); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 110.7, 118.7, 119.7, 122.1, 122.8, 124.0, 124.9, 125.2, 125.5, 126.6, 127.1, 127.2, 128.1, 128.3, 128.4, 128.7, 129.4, 130.3, 131.1, 131.7, 132.0, 132.8, 133.1, 133.7, 134.1, 135.8, 142.9, 148.0, 160.7. LRMS (ESI) *m/e* 474.2 [M^++H]; HRMS (ESI) calcd for [$C_{34}H_{23}N_3$+H] requires

474.1970, found 474.1975 [M^++H].



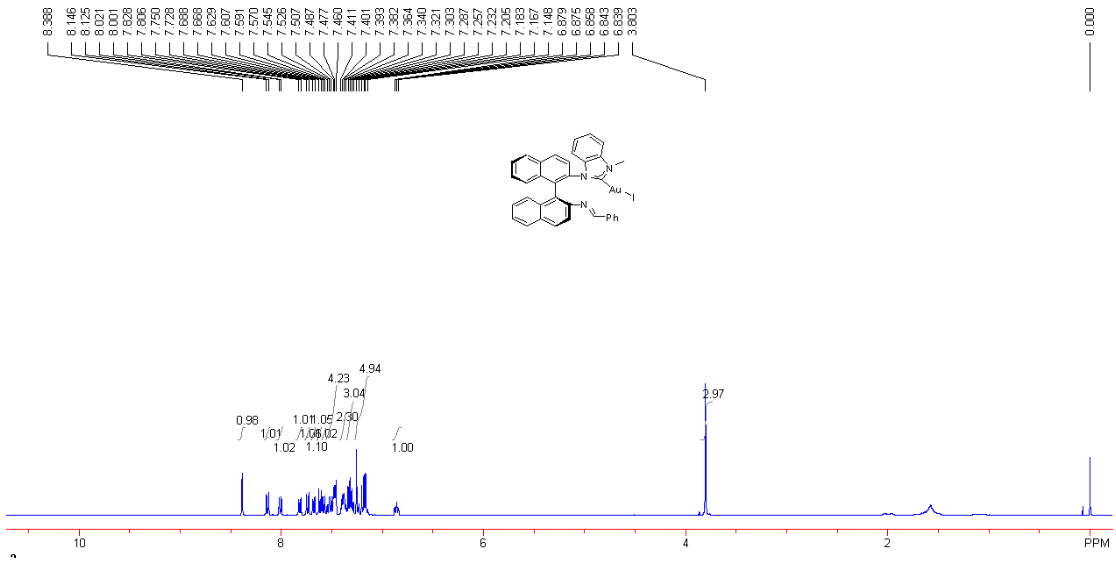


Complex (a*S*)-**11**



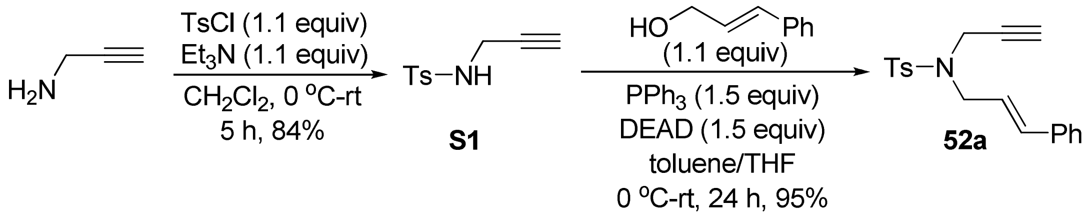
Pale yellow solid; m.p. 133.0-134.5 °C (dec.). $[\alpha]^{20}_{D}$ = -42 (*c* 0.25, $CHCl_3$). IR (direct irradiation) ν 3055, 2923, 2853, 1700, 1611, 1576, 1505, 1458, 1390, 1308, 1241, 1202, 1098, 964, 870, 815, 742, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.80 (s, 3H), 6.86 (ddd, *J* = 1.6, 6.0, 7.6 Hz, 1H), 7.15-7.26 (m, 4H), 7.29-7.34 (m, 3H), 7.36-7.41 (m, 2H), 7.46-7.55 (m, 4H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.39 (s, 1H). LRMS (ESI) *m/e* 684.2 [M^+-I];

HRMS (ESI) calcd for [$C_{35}H_{25}N_3IAu$-I] requires 684.1714, found 684.1713 [M^+-I].



(C) Preparation of 1,6-enynes and Diaryl Sulfoxides.

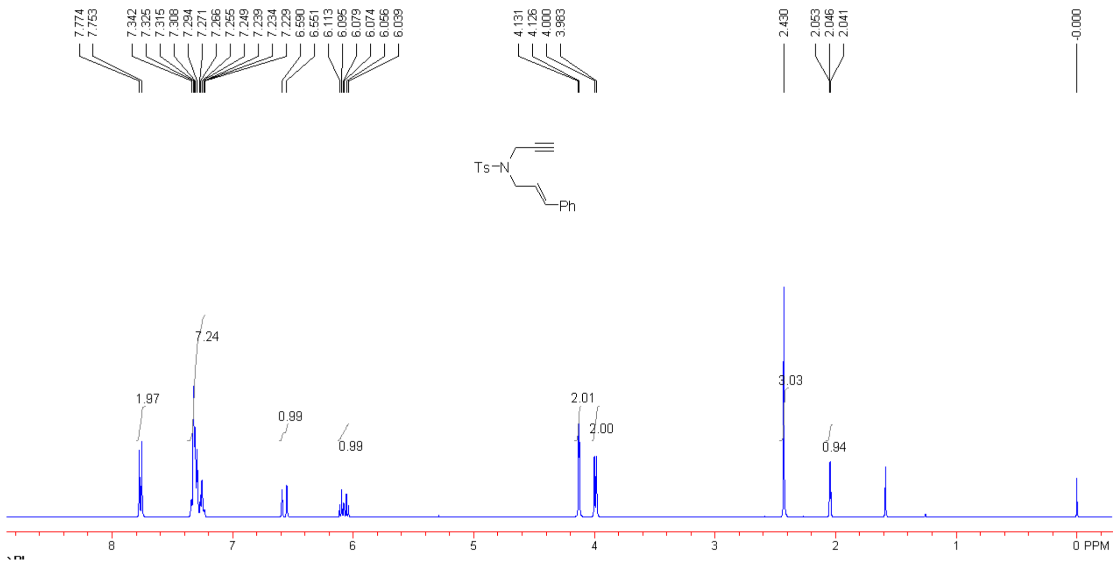
(1) 1,6-enyne 52a



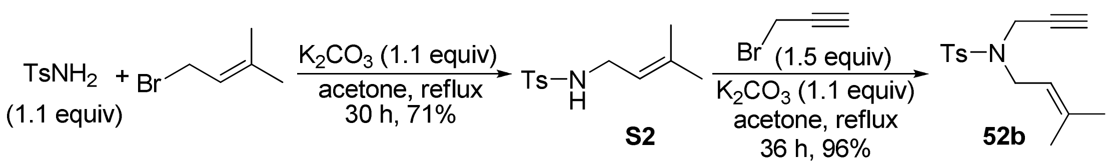
Scheme S12

To a mixture of propargylamine (412 μL, 6 mmol) and NEt_3 (0.92 mL, 6.6 mmol) in CH_2Cl_2 (4 mL) was added dropwise the solution of TsCl (1258 mg, 6.6 mmol) in CH_2Cl_2 (12 mL) at 0 °C. Then the reaction system was warmed to room temperature and further stirred for 5 h followed by quenching with 20 mL of water. After extraction with CH_2Cl_2 for three times, the combined organic phases were washed with saturated brine and then dried over anhydrous Na_2SO_4. The crude product was concentrated under reduced pressure and then purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 5/1; containing minor NEt_3) to give **S1** as a white solid in 84% yield. It is a known compound.[4a] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.11 (t, *J* = 2.4 Hz, 1H), 2.43 (s, 3H), 3.83 (dd, *J* = 6.0, 2.4 Hz, 2H), 4.73 (t, J = 6.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.8 Hz, 2H).

Under argon atmosphere, to the solution of **S1** (1046 mg, 5 mmol), cinnamyl alcohol (738 mg, 5.5 mmol) and Ph_3P (1967 mg, 7.5 mmol) in mixed toluene/THF (15 mL/5 mL) was added dropwise of DEAD (1.18 mL, 7.5 mmol) at 0 °C. The reaction system was warmed to room temperature and further stirred for 24 h. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 10/1) to give **52a** as a white solid in 95% yield. It is a known compound.[4b] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.05 (t, J = 2.0 Hz, 1H), 2.43 (s, 3H), 3.99 (d, J = 6.8 Hz, 2H), 4.13 (d, J = 2.0 Hz, 2H), 6.08 (dt, J = 15.6, 6.8 Hz, 1H), 6.57 (d, J = 15.6 Hz, 1H), 7.23-7.33 (m, 7H), 7.76 (d, J = 8.4 Hz, 2H) (Scheme S12).



(2) 1,6-enyne 52b

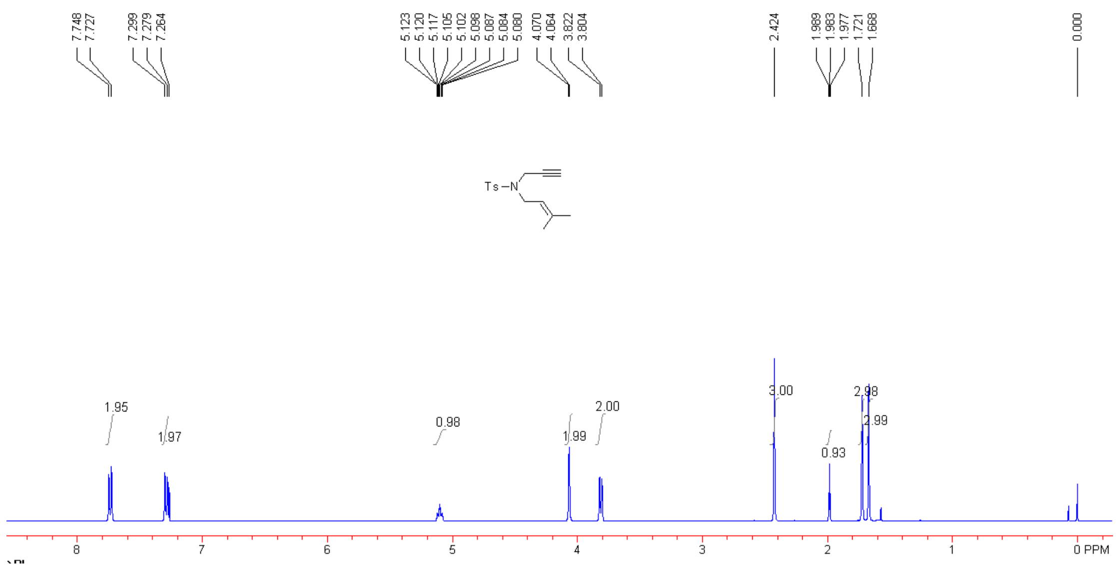


Scheme S13

1-Bromo-3-methyl-2-butene (2.33 mL, 20 mmol) was added to the suspension of $TsNH_2$ (3767 mg, 22 mmol) and K_2CO_3 (3041 mg, 22 mmol) in acetone (20 mL). Then the reaction system was refluxed at 60 °C for 30 h followed by cooling to room temperature, quenching by

30 mL of water and extraction with EtOAc for 3 times. The combined organic phases were dried over anhydrous Na_2SO_4 and filtered through Celite. The filtrate was concentrated under reduced pressure and purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 15/1) to give **S2** as a white solid in 71% yield. It is a known compound.[4c] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.53 (s, 3H), 1.63 (s, 3H), 2.43 (s, 3H), 3.53 (t, *J* = 6.4 Hz, 2H), 4.48-4.50 (m, 1H), 5.03-5.07 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H).

To the mixture of compound **S2** (3415 mg, 14.27 mmol) obtained above and K_2CO_3 (2960 mg, 21.4 mmol) in acetone (40 mL) was added propargyl bromide (1.85 mL, 21.4 mmol). Then the suspension was refluxed at 60 °C for 36 h followed by cooling to room temperature, quenching by 40 mL of water and extraction with EtOAc for 3 times. The combined organic phases were dried over anhydrous Na_2SO_4 , concentrated under reduced pressure and purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 20/1) to give **52b** as a white solid in 96% yield. It is a known compound.[4d] ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.67 (s, 3H), 1.72 (s, 3H), 1.98 (t, *J* = 2.4 Hz, 1H), 2.42 (s, 3H), 3.81 (d, *J* = 7.2 Hz, 2H), 4.07 (d, *J* = 2.4 Hz, 2H), 5.08-5.12 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H) (Scheme S13).



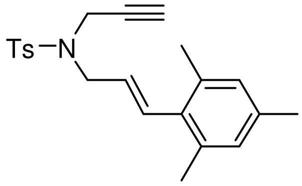
(3) 1,6-enynes 52c-h

The preparation procedures of 1,6-enynes **52c,d** were similar to that of 1,6-enyne **52a** from compound **S1** by using corresponding substituted allyl alcohol instead during the Mitsunobu reaction step.

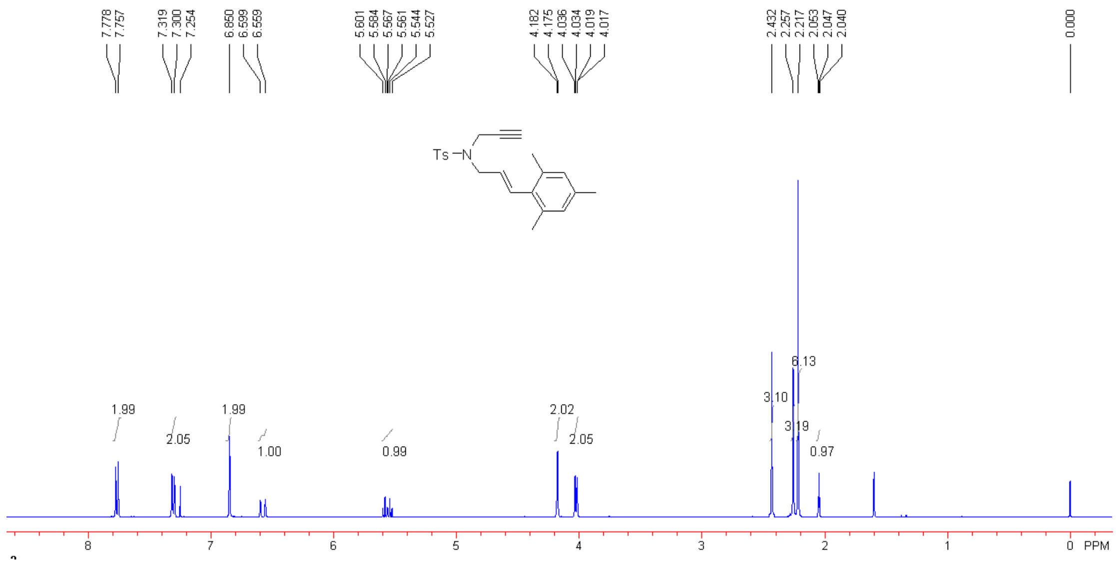
The preparations of 1,6-enynes **52e-g** were also similar to **52a** by allowing the reaction of corresponding sulfonamide with propargylamine before a Mitsunobu reaction step with cinnamyl alcohol.

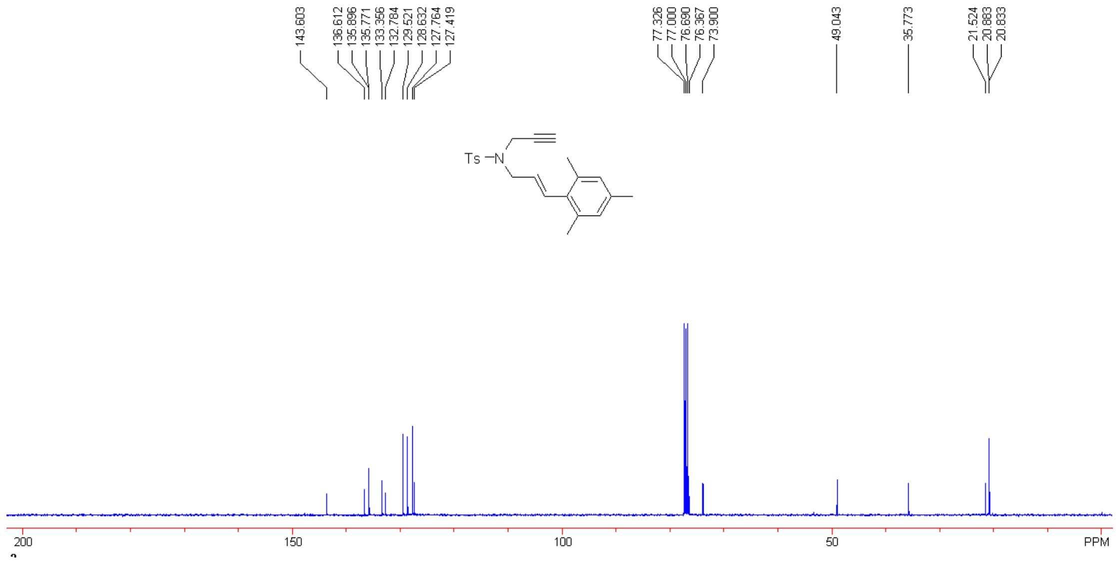
The preparation of 1,6-enyne **52h** was according to a reported procedure by allowing the reaction of cinnamyl alcohol and propargyl bromide (1.2 equiv) with NaH (1.2 equiv) as the base in dry THF for 5 h.[4e]

Compound **52c**

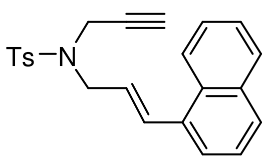


White solid; m.p. 93.4-94.6 °C. IR (direct irradiation) ν 3264, 2918, 2851, 2112, 1598, 1444, 1347, 1332, 1305, 1168, 1137, 1091, 997, 921, 893, 853, 811, 741, 688, 654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.05 (t, *J* = 2.8 Hz, 1H), 2.22 (s, 6H), 2.26 (s, 3H), 2.43 (s, 3H), 4.03 (dd, *J* = 0.8, 6.8 Hz, 2H), 4.18 (d, *J* = 2.8 Hz, 2H), 5.56 (dt, *J* = 16.0, 2.8 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.85 (s, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 20.8, 20.9, 21.5, 35.8, 49.0, 73.9, 76.4, 127.4, 127.8, 128.6, 129.5, 132.8, 133.4, 135.8, 135.9, 136.6, 143.6. LRMS (EI) *m/e* 367.2 (3.41%), 352.1 (10.16%), 196.1 (100%), 91.1 (18.03%); HRMS (EI) calcd for [$C_{22}H_{25}NO_2S$] requires 367.1606, found 367.1609 [M^+].

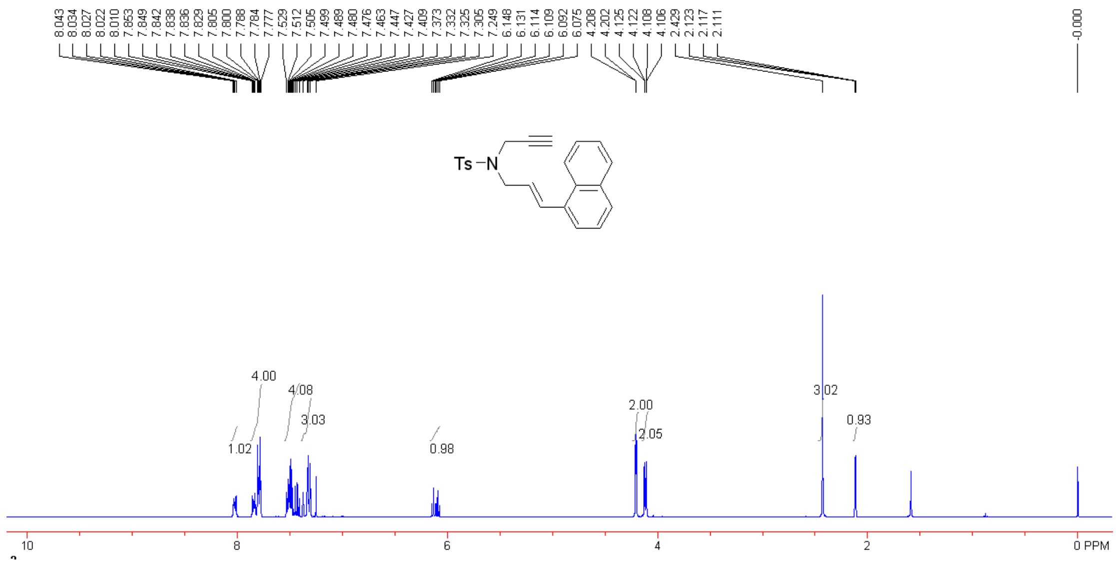


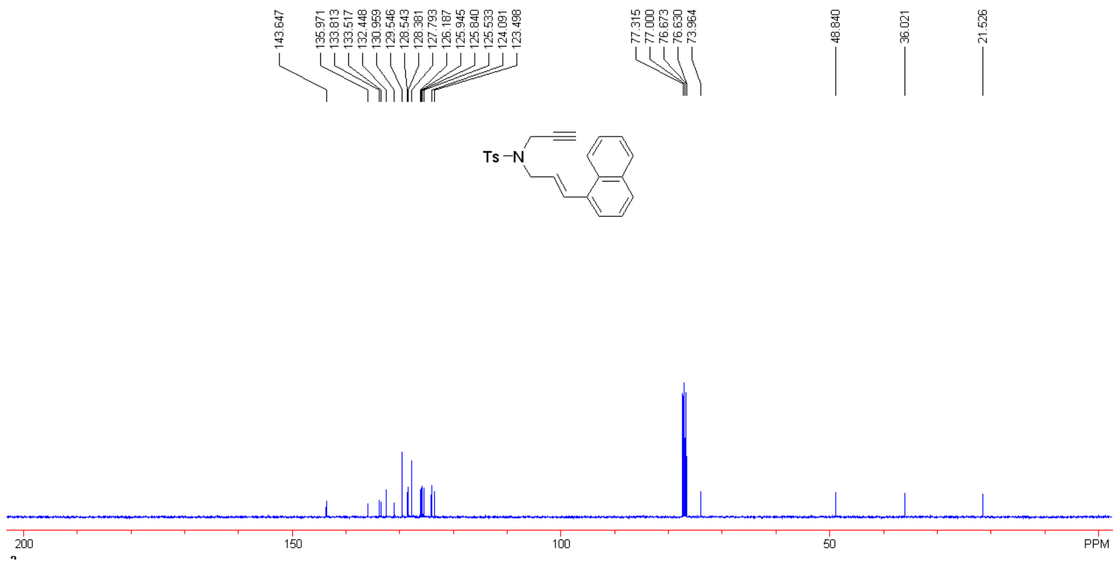


Compound **52d**

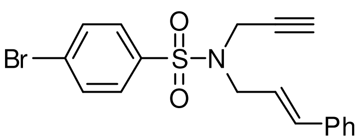


White solid; m.p. 100.7-101.7 °C. IR (direct irradiation) ν 3272, 2919, 2117, 1598, 1341, 1327, 1306, 1152, 1096, 1065, 969, 900, 798, 780, 750, 731, 700, 656 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.12 (t, *J* = 2.4 Hz, 1H), 2.43 (s, 3H), 4.12 (dd, *J* = 1.2, 6.8 Hz, 2H), 4.21 (d, *J* = 2.4 Hz, 2H), 6.11 (dt, *J* = 15.6, 6.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 16.4 Hz, 1H), 7.41-7.53 (m, 4H), 7.78-7.85 (m, 4H), 8.01-8.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 36.0, 48.8, 74.0, 76.6, 123.5, 124.1, 125.5, 125.8, 125.9, 126.2, 127.8, 128.4, 128.5, 129.5, 131.0, 132.4, 133.5, 133.8, 136.0, 143.6. LRMS (EI) *m/e* 375.1 (9.12%), 218.1 (100%), 191.1 (49.13%), 91.1 (19.72%); HRMS (EI) calcd for [$C_{23}H_{21}NO_2S$] requires 375.1293, found 375.1295 [M$^+$].

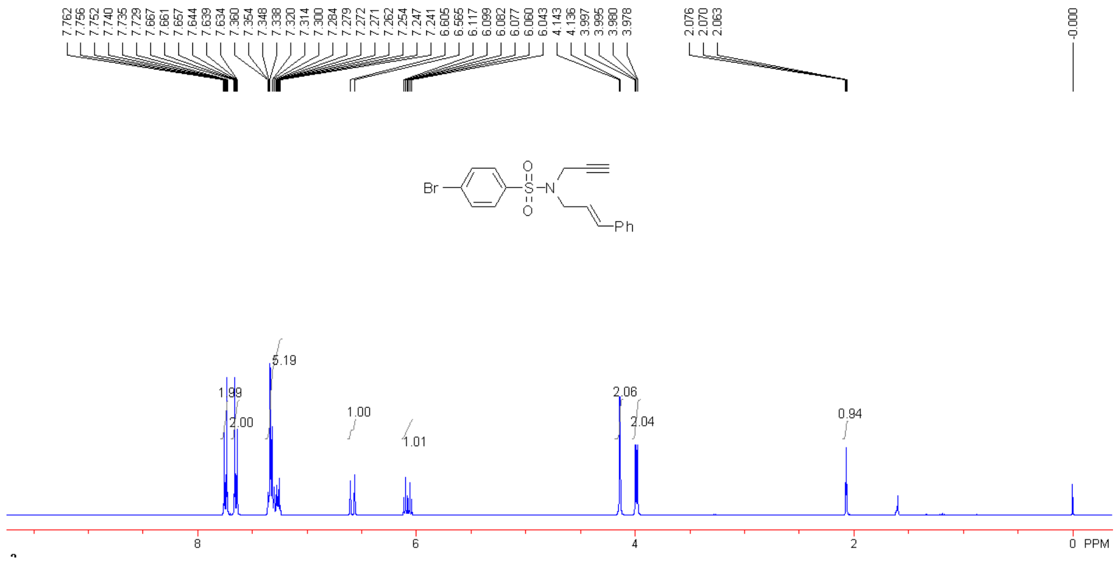


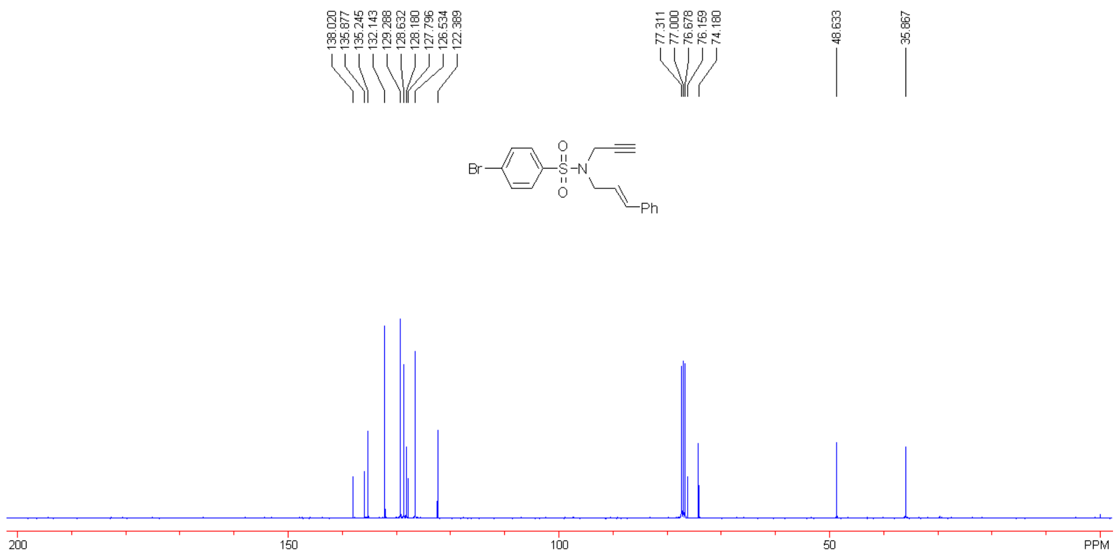


Compound **52e**

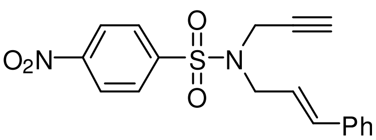


White solid; m.p. 113.9-115.0 °C. IR (direct irradiation) ν 3274, 2922, 2852, 2118, 1577, 1434, 1388, 1347, 1329, 1275, 1160, 1131, 1093, 1067, 1009, 971, 900, 839, 817, 759, 746, 728, 694, 666, 614 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.07 (t, J = 2.8 Hz, 1H), 3.99 (dd, J = 0.8, 6.8 Hz, 2H), 4.14 (d, J = 2.8 Hz, 2H), 6.08 (dt, J = 15.6, 6.8 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 7.24-7.36 (m, 5H), 7.63-7.67 (m, 2H), 7.73-7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 35.9, 48.6, 74.2, 76.2, 122.4, 126.5, 127.8, 128.2, 128.6, 129.3, 132.1, 135.2, 135.9, 138.0. LRMS (EI) *m/e* 389.0 (0.22%), 168.1 (100%), 142.1 (54.00%), 91.1 (12.52%); HRMS (EI) calcd for [$C_{18}H_{16}NO_2SBr$] requires 389.0085, found 389.0079 [M^+].



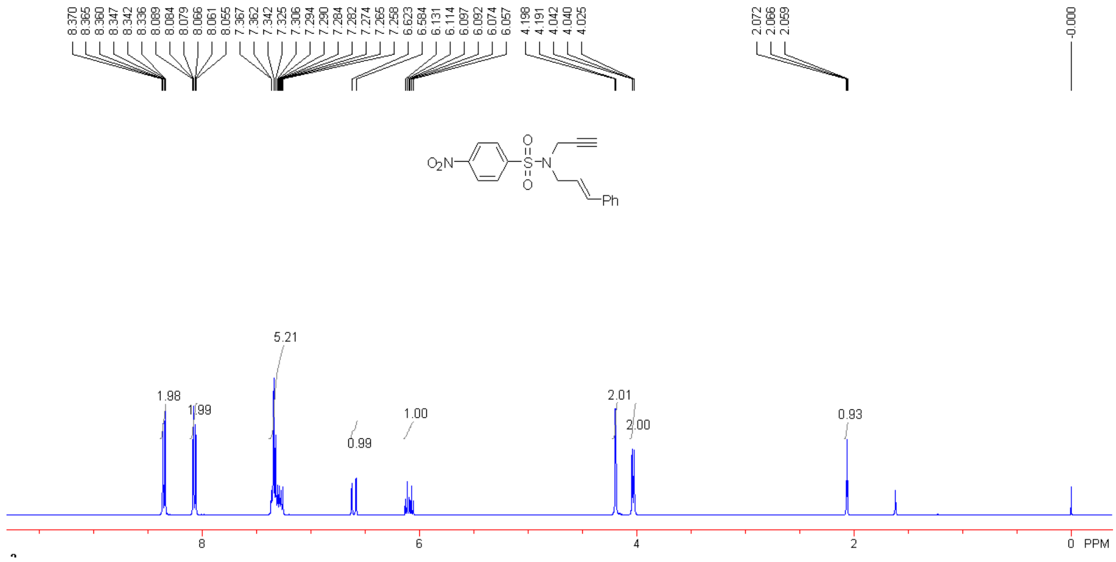


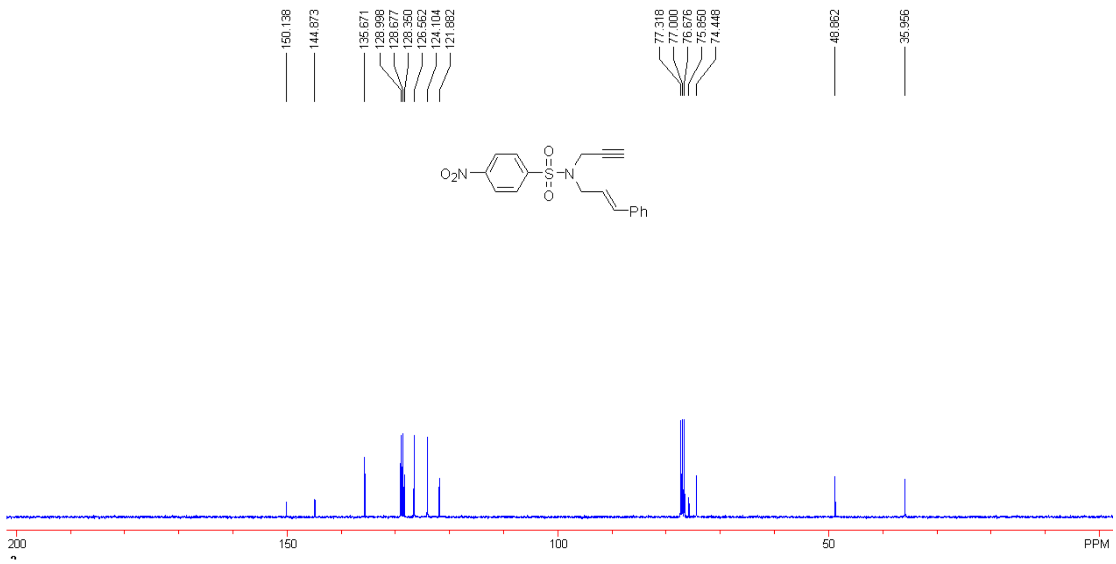
Compound **52f**



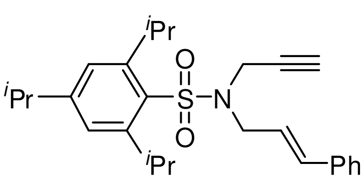
White solid; m.p. 127.9-128.9 °C. IR (direct irradiation) ν 3280, 1521, 1351, 1312, 1163, 1089, 972, 897, 856, 765, 752, 742, 722, 698, 681, 664, 626 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.07 (t, J = 2.8 Hz, 1H), 4.03 (dd, J = 0.8, 6.8 Hz, 2H), 4.19 (d, J = 2.8 Hz, 2H), 6.09 (dt, J = 16.0, 6.8 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 7.26-7.37 (m, 5H), 8.06-8.09 (m, 2H), 8.34-8.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 36.0, 48.9, 74.4, 75.9, 121.9, 124.1, 126.6, 128.4, 128.7, 129.0, 135.7, 144.9, 150.1. LRMS (EI) *m/e* 356.1, 168.1 (100%), 142.1

(55.91%), 91.1 (15.57%); HRMS (EI) calcd for [$C_{18}H_{16}N_2O_4S$] requires 356.0831, found 356.0842 [M^+].



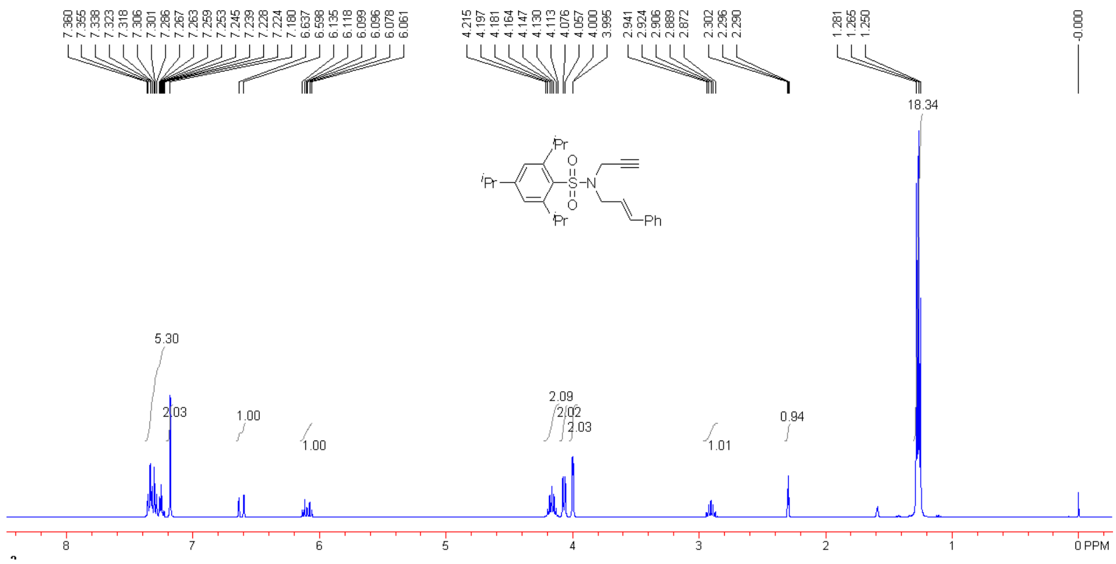


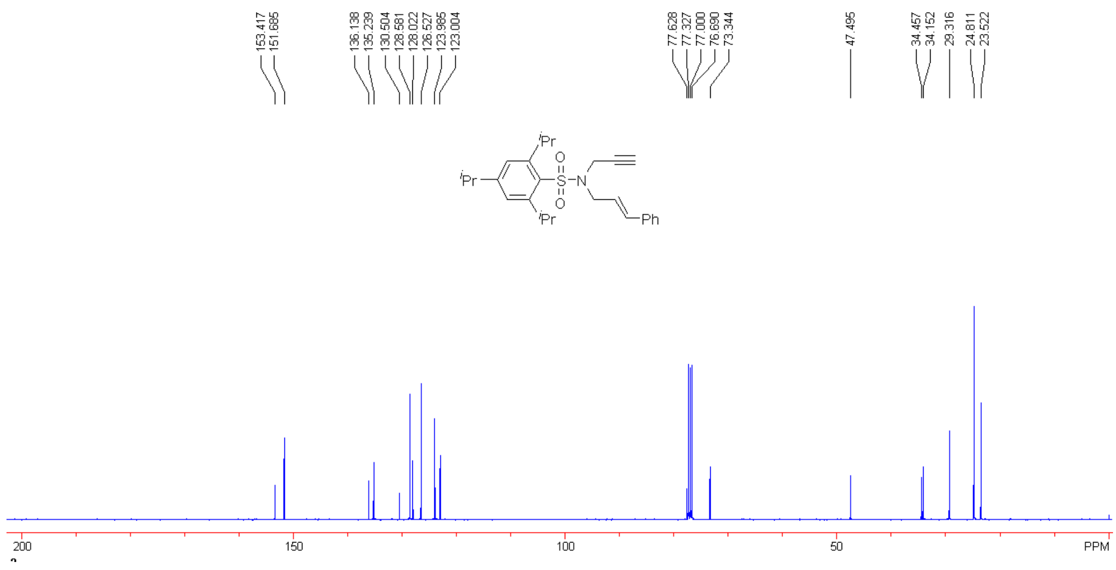
Compound **52g**



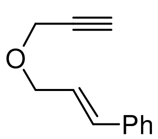
White solid; m.p. 104.7-105.7 °C. IR (direct irradiation) ν 3271, 2954, 2865, 1600, 1459, 1424, 1360, 1316, 1291, 1151, 1068, 1040, 973, 890, 847, 759, 735, 697, 670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25-1.28 (m, 18H), 2.30 (t, *J* = 2.4 Hz, 1H), 2.91 (hep, *J* = 6.8 Hz, 1H), 4.00 (d, *J* = 2.0 Hz, 2H), 4.07 (d, *J* = 7.6 Hz, 2H), 4.16 (hep, *J* = 6.8 Hz, 2H), 6.10 (dt, *J* = 16.0, 6.8 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 7.18 (s, 2H), 7.22-7.36 (m, 5H); ^{13}C NMR (100

MHz, $CDCl_3$, TMS) δ 23.5, 24.8, 29.3, 34.2, 34.5, 47.5, 73.3, 77.6, 123.0, 124.0, 126.5, 128.0, 128.6, 130.5, 135.2, 136.1, 151.7, 153.4. LRMS (EI) *m/e* 437.2, 267.1 (100%), 170.1 (37.76%), 91.1 (23.02%); HRMS (EI) calcd for $[C_{27}H_{35}NO_2S]$ requires 437.2389, found 437.2385 $[M^+]$.

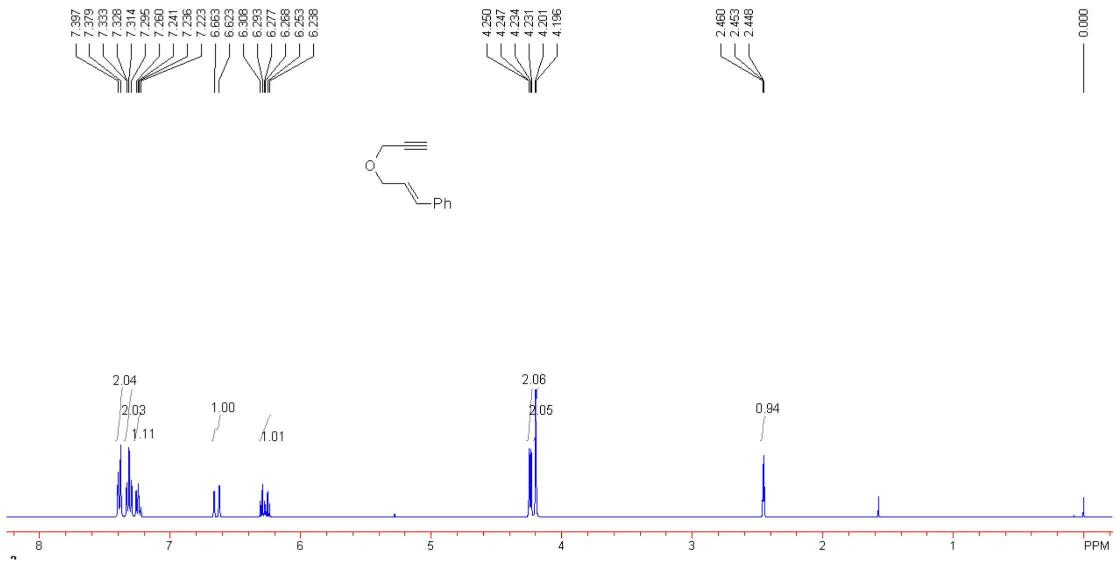




Compound **52h**

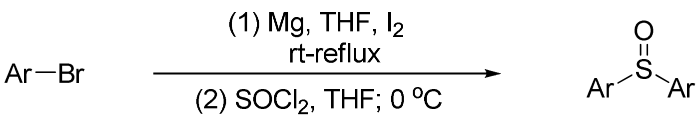


It is a known compound.[4e] Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.45 (t, J = 2.8 Hz, 1H), 4.20 (d, J = 2.0 Hz, 2H), 4.24 (dd, J = 1.2, 6.4 Hz, 2H), 6.27 (dt, J = 16.0, 6.0 Hz, 1H), 6.64 (d, J = 16.0 Hz, 1H), 7.22-7.26 (m, 1H), 7.30-7.33 (m, 2H), 7.38-7.40 (m, 2H).



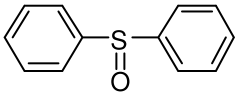
(4) Aryl Sulfoxides 57b and 57c

Aryl sulfoxides **57b**, **c** were prepared according to a modified procedure similar with that in the previous literature. In the presence of a small iodine crystal, the corresponding aryl bromide (20 mmol) and magnesium (486 mg, 20 mmol) in dry THF (15 mL) were carefully allowed to start a Grignard reaction at room temperature and then refluxed for further 30 minutes. To the obtained solution of arylmagnesium bromide (20 mmol) in THF was added dropwise thionyl chloride (0.73 mL, 10 mmol) in dry THF (10 mL) for 0.5~1 h at 0 °C. Then the mixture was quenched by careful addition of water at 0 °C and extracted with CH_2Cl_2 for 3 times. The combined organic phases were washed with saturated $NaHCO_3$, dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 10/1) to give **57b** (or **57c**) as a white solid in 31% (or 40%) yield (Scheme S14).

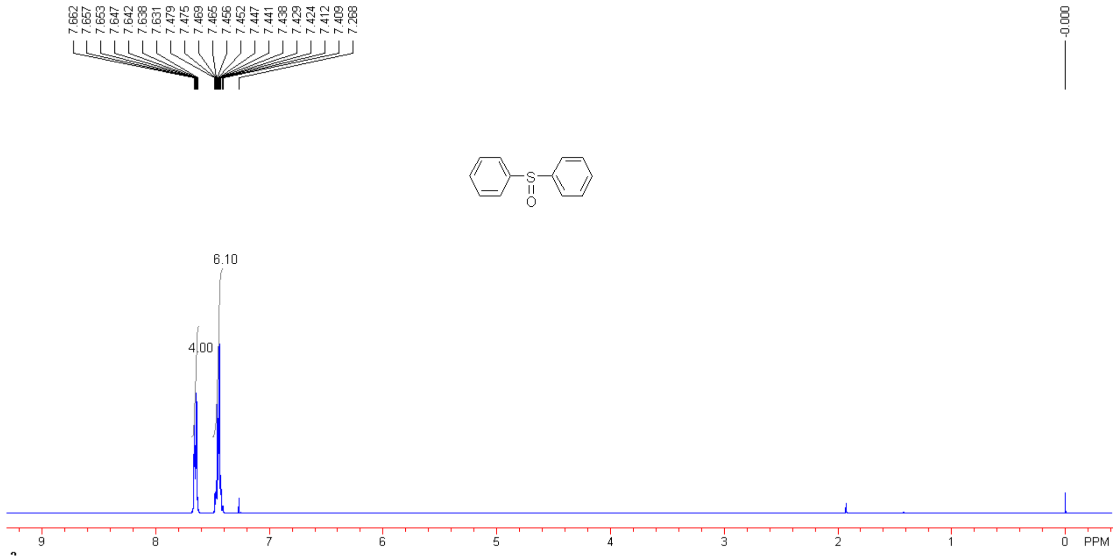


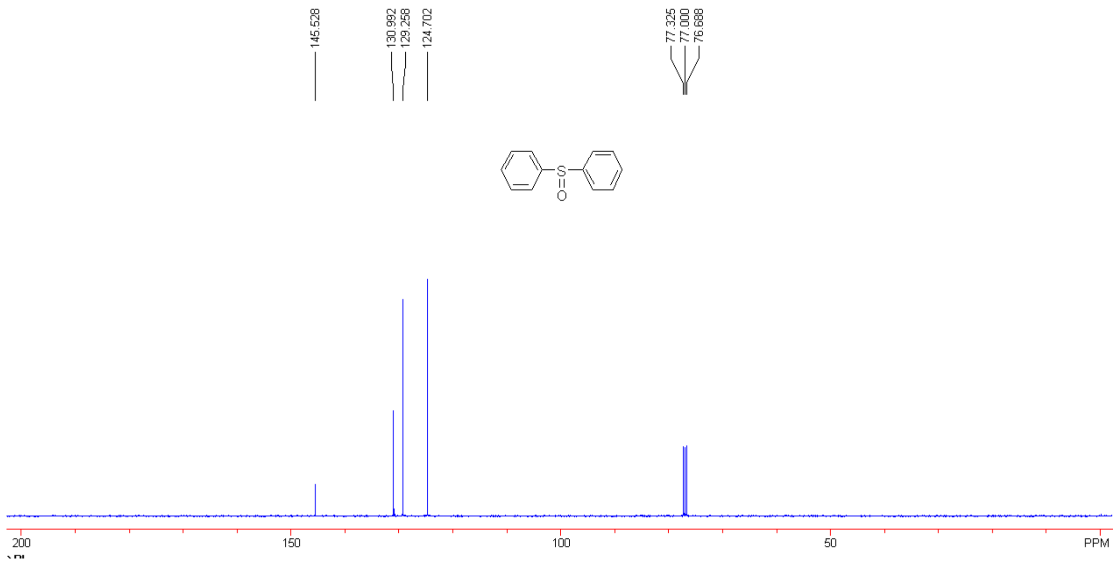
Scheme S14

Compound **57a**

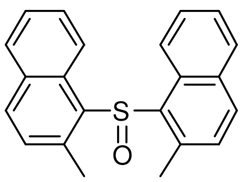


It is commercially available. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.41-7.48 (m, 6H), 7.63-7.66 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 124.7, 129.3, 131.0, 145.5.

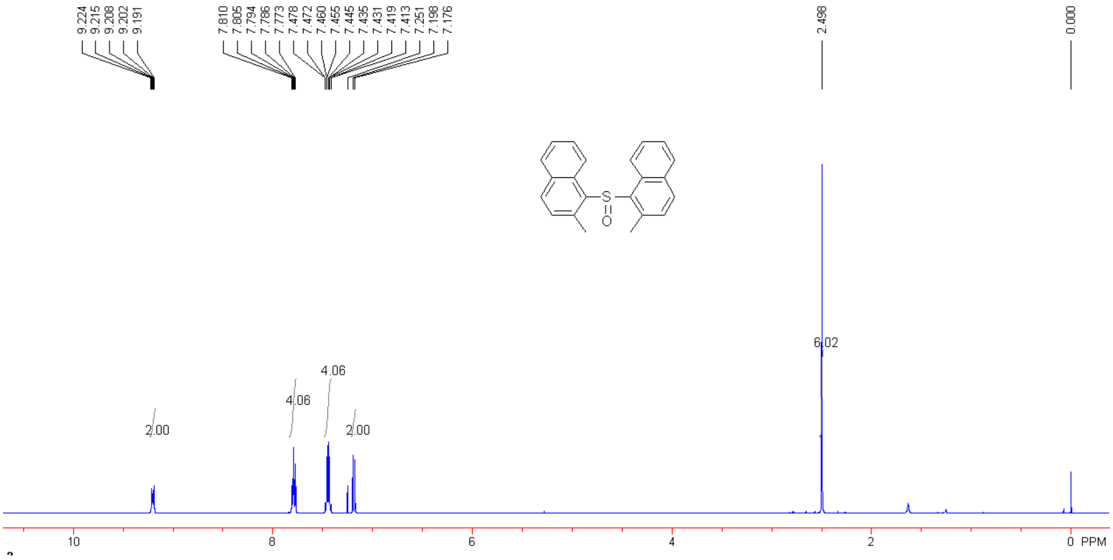


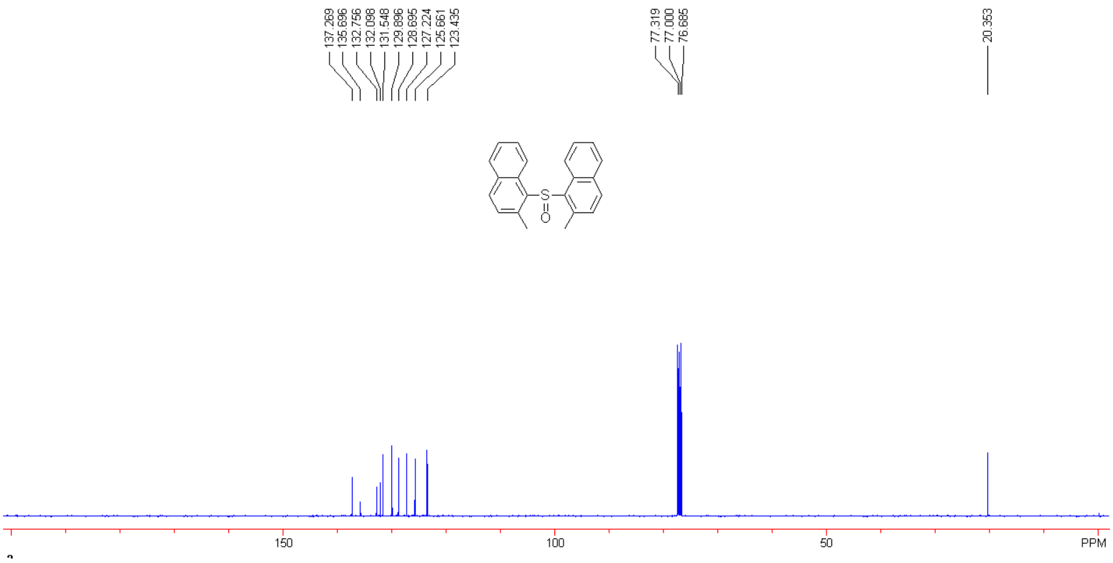


Compound **57b**

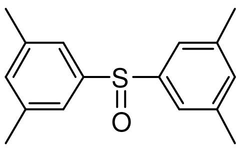


White solid; m.p. 157.2-158.2 °C. IR (direct irradiation) ν 3052, 2962, 2923, 2855, 1965, 1934, 1504, 1448, 1422, 1350, 1147, 1042, 1016, 977, 817, 773, 747, 641 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.50 (s, 6H), 7.19 (d, J = 8.8 Hz, 2H), 7.41-7.48 (m, 4H), 7.77-7.81 (m, 4H), 7.19-7.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 20.4, 123.4, 125.7, 127.2, 128.7, 129.9, 131.5, 132.1, 132.8, 135.7, 137.3. LRMS (EI) *m/e* 330.1 (61.02%), 188.0 (100%), 128.1 (48.77%), 115.1 (35.40%); HRMS (EI) calcd for [$C_{22}H_{18}OS$] requires 330.1078, found 330.1081 [M^+].



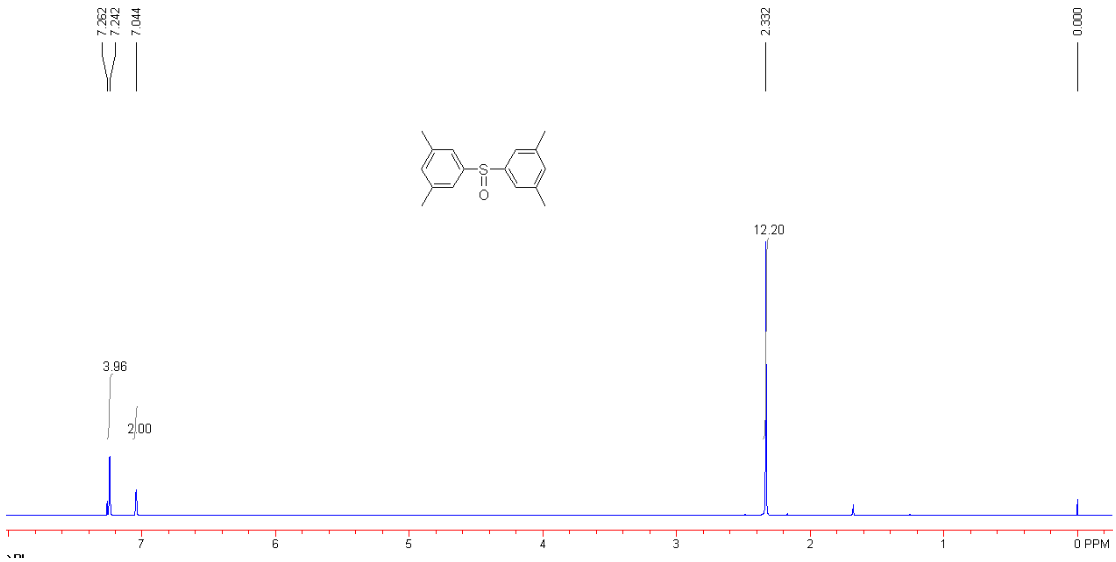


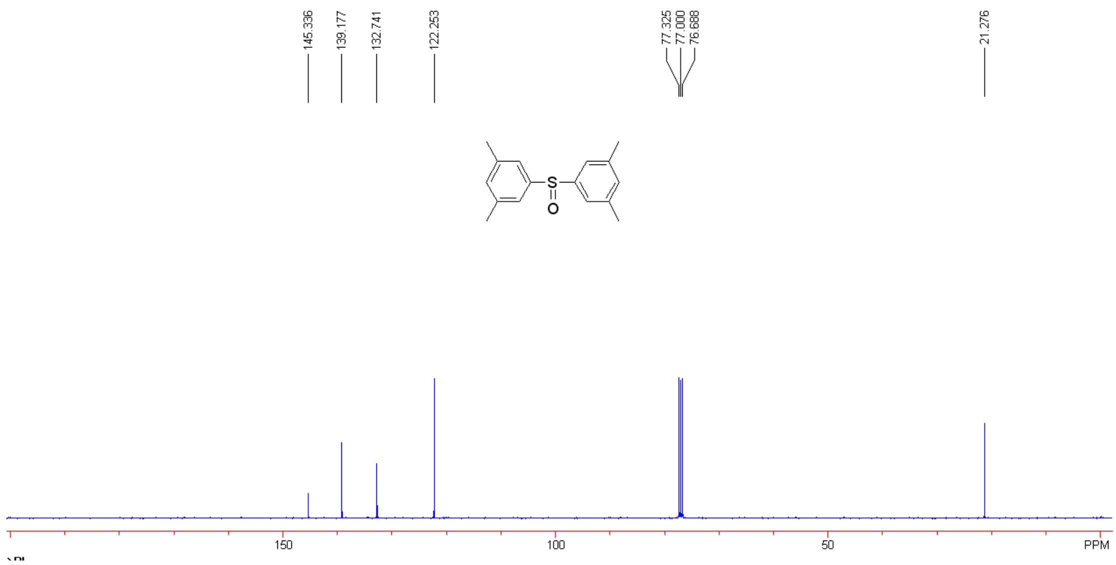
Compound **57c**



White solid; m.p. 128.3-129.3 °C. IR (direct irradiation) *ν* 2916, 2858, 1605, 1575, 1454, 1096, 1049, 992, 859, 847, 835, 692, 680 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.33 (s, 12H), 7.04 (s, 2H), 7.24 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.3, 122.3, 132.7, 139.2, 145.3. LRMS (EI) *m/e* 258.1 (100%), 210.1 (64.72%), 137.0 (28.70%), 77.0 (20.01%); HRMS (EI) calcd for [$C_{16}H_{18}OS$]

requires 258.1078, found 258.1081 [M$^+$].

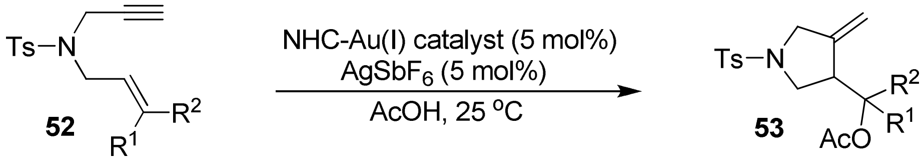




(D) General Procedure for NHC-Au(I) Complexes-Catalyzed Asymmetric Acetoxycyclization of 1,6-Enynes and Analytical Data for Products.

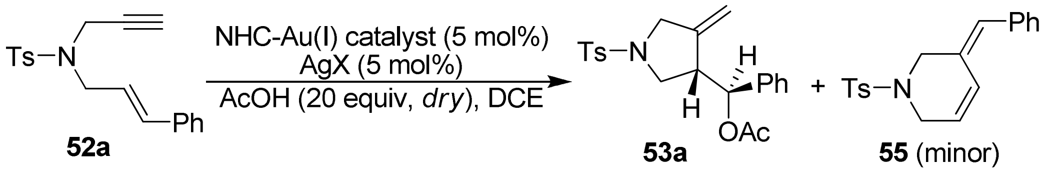
A mixture of NHC-Au(I) complex (5 mol%), 1,6-enyne **52** (0.1 mmol) and $AgSbF_6$ (2 mg, 0.005 mmol) in acetic acid (1 mL, commercially available) was stirred at room temperature until completely consuming of **52** by TLC mintoring. Then the reaction was quenched by filtering through a Celite with a thin pad of silica gel and volatiles were removed under reduced pressure. The residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 8/1) to give the corresponding product **53** as a white solid

(Scheme S15).



Scheme S15

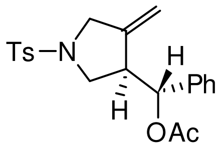
Alternatively, to a solution of NHC-Au(I) complex (5 mol%), 1,6-enyne **52a** (33 mg, 0.1 mmol) and AgX (0.005 mmol) in dry DCE (1 mL) was added dry acetic acid (115 μL, 2 mmol) as the nucleophile under argon atmosphere. The mixture was stirred at proper temperature until completely consuming of **52a** by TLC monitoring. Then the reaction was quenched by filtering through a Celite with a thin pad of silica gel and volatiles were removed under reduced pressure. The residue was purified by a silica gel flash column chromatography to give **53a** (eluent: petroleum ether/EtOAc, 8/1) as a white solid (Scheme S16).



Scheme S16

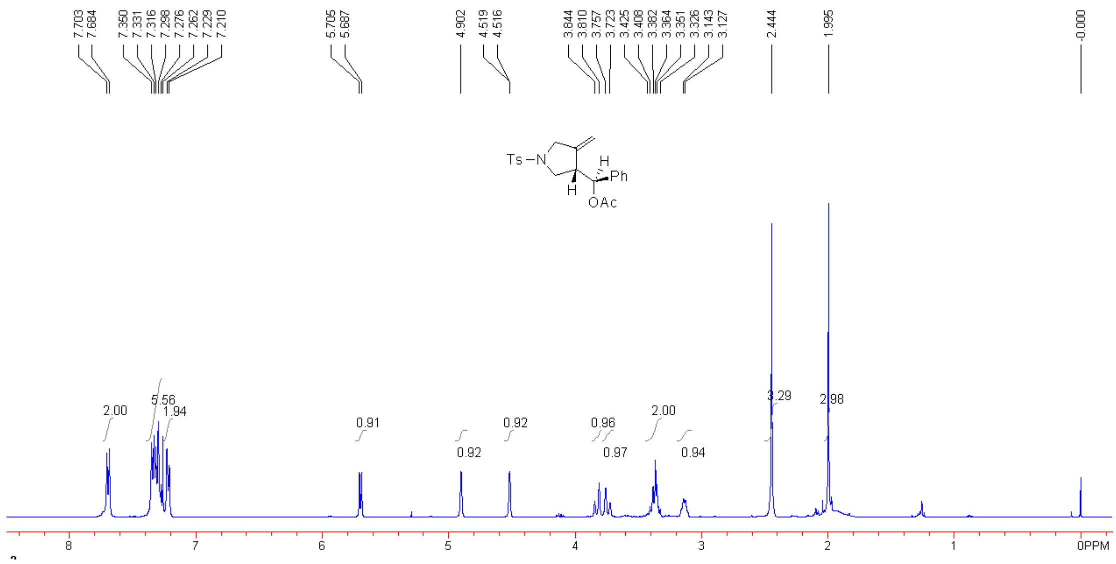
Racemic products for chiral HPLC analysis were prepared by using Ph_3PAuCl (3 mg, 5 mol%) and $AgSbF_6$ (2 mg, 0.005 mmol) as the catalyst instead according to a similar procedure mentioned above.

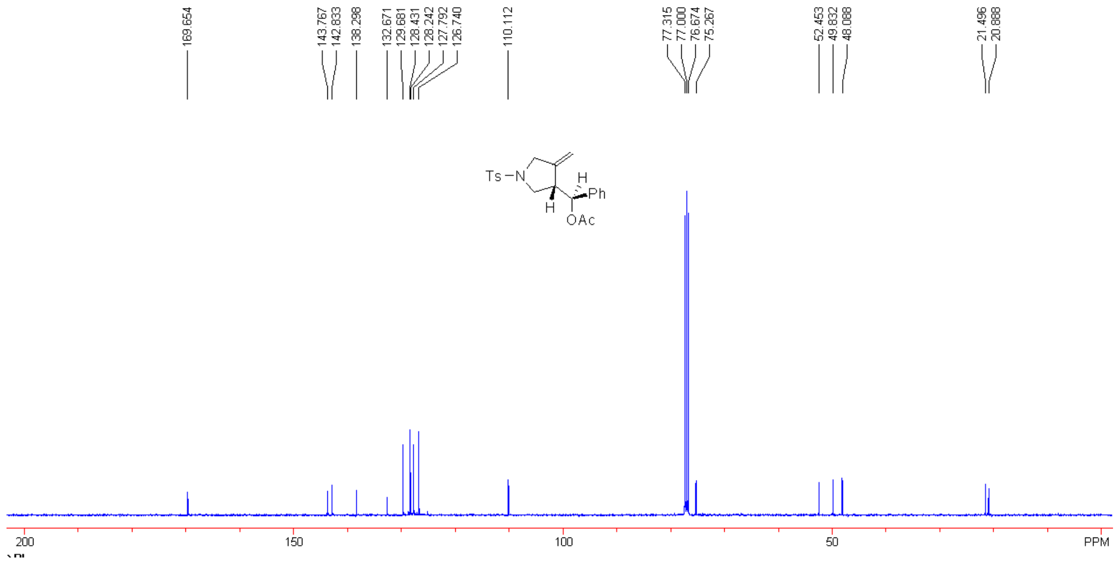
Compound **53a**



White solid, > 99% yield; m.p. 73.5-74.7 °C. Absolute stereochemistry was assigned by analogy to compound **54**, $[\alpha]^{20}_D$ = -18 (*c* 0.5, $CHCl_3$), -59% *ee*. IR (direct irradiation) ν 3477, 2955, 2924, 2853, 1740, 1662, 1597, 1494, 1455, 1371, 1343, 1227, 1160, 1091, 1016, 965, 907, 814, 753, 701, 663 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.00 (s, 3H), 2.44 (s, 3H), 3.12-3.14 (m, 1H), 3.33-3.43 (m, 2H), 3.74 (d, *J* = 13.6 Hz, 1H), 3.83 (d, *J* = 13.6 Hz, 1H), 4.52 (d, *J* = 1.2 Hz, 1H), 4.90 (s, 1H), 5.70 (d,

J = 7.2 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.26-7.35 (m, 5H), 7.69 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 20.9, 21.5, 48.1, 49.8, 52.5, 75.3, 110.1, 126.7, 127.8, 128.2, 128.4, 129.7, 132.7, 138.3, 142.8, 143.8, 169.7. LRMS (ESI) *m/e* 408.1 [M^++Na]; HRMS (ESI) calcd for [$C_{21}H_{23}NO_4S$+Na] requires 408.1245, found 408.1244 [M^++Na].

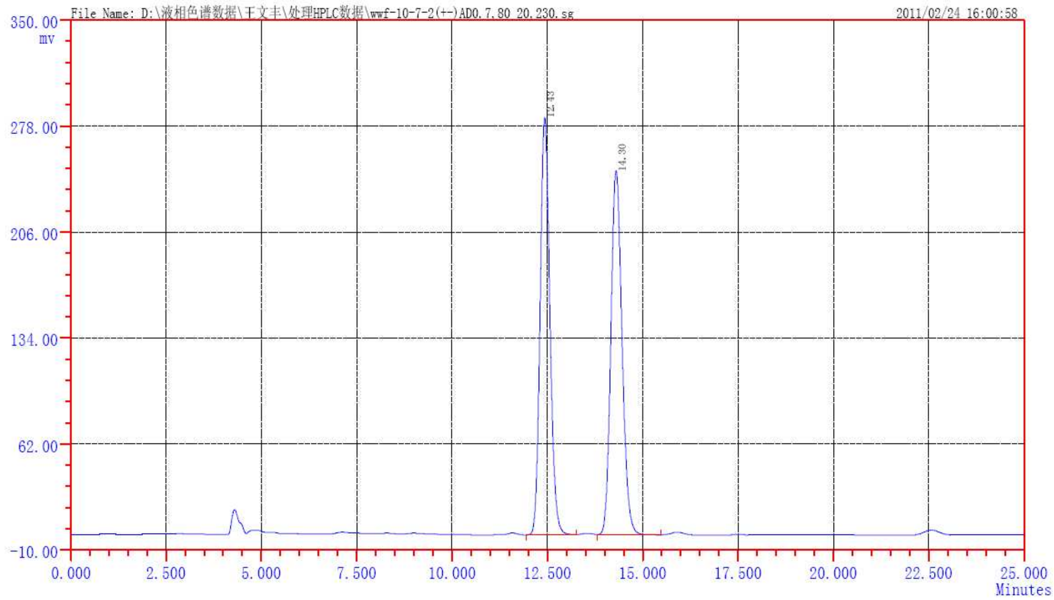




WH-500 Chiral HPLC Analysis Report:

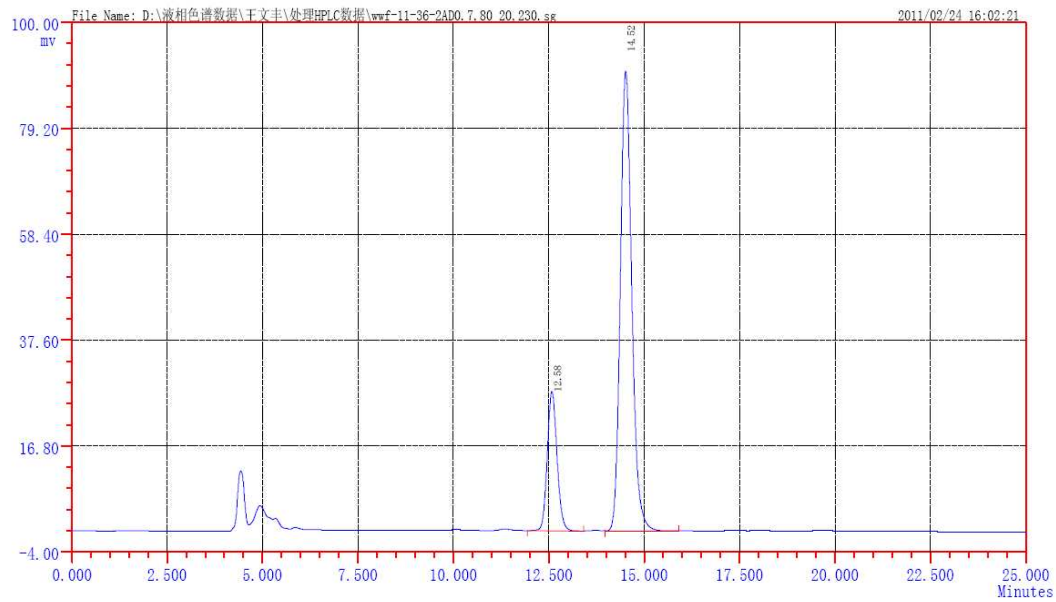
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.430	283618	5036733.3	49.9633	1.15	9764
2		14.302	247559	5044133.0	50.0367	1.16	9819
	Σ:		531177	10080866.3	100.0000		

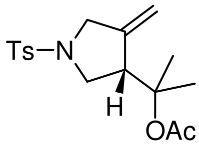
WH-500 色 谱 分 析 报 告



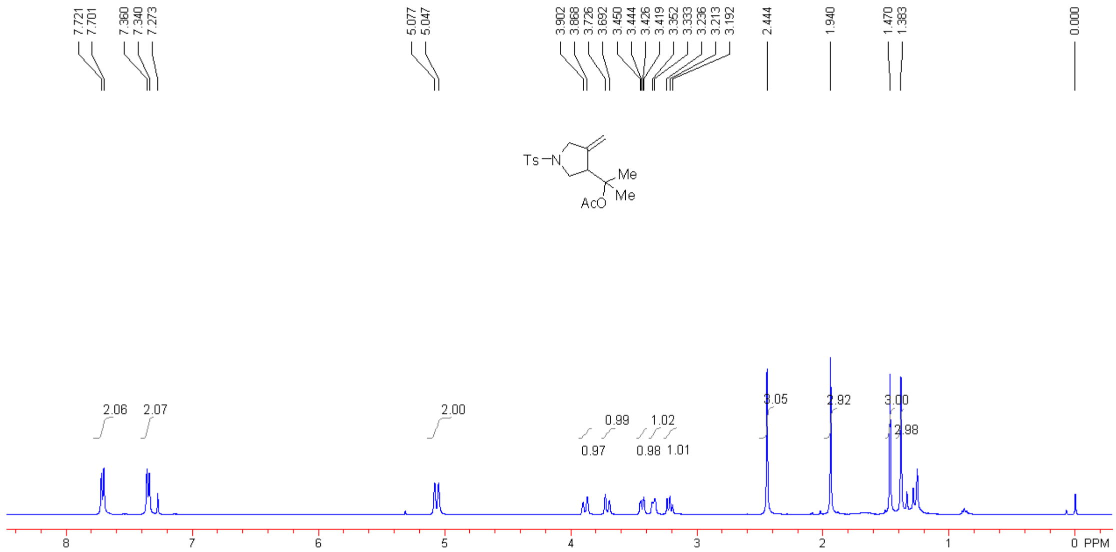
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.578	27387	486807.0	20.5305	1.13	9980
2		14.517	90355	1884330.4	79.4695	1.18	9657
	Σ:		117742	2371137.4	100.0000		

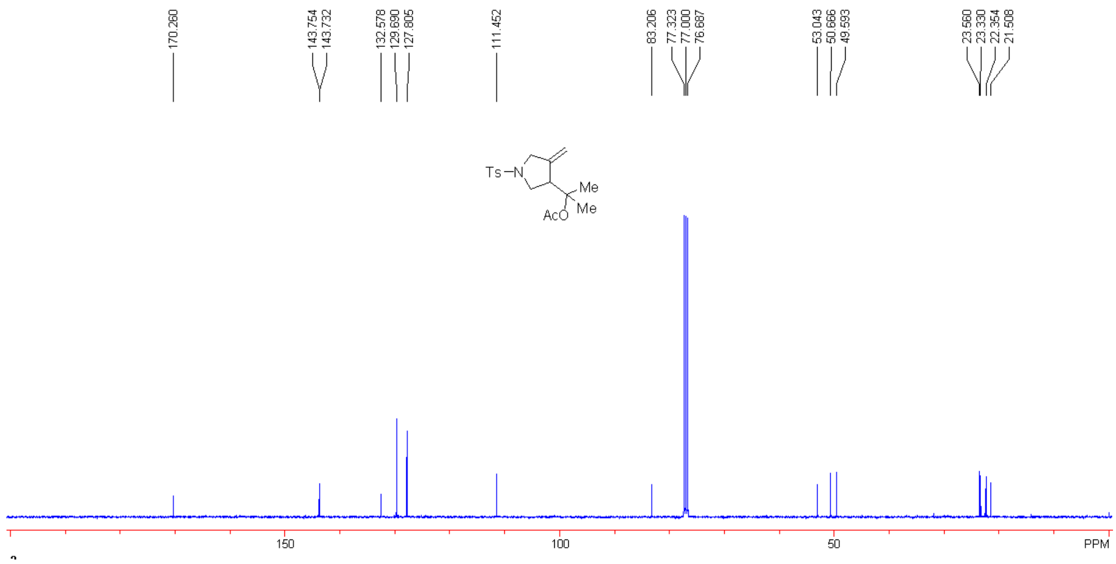
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 80:20, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 12.6 min (minor), t_R = 14.5 min (major)].

Compound **53b**



White solid, 66% yield; m.p. 88.5-89.2 °C. Absolute stereochemistry was assigned by analogy to compound **54**, $[\alpha]^{20}_{D} = +1.3$ (*c* 0.5, $CHCl_3$), 20% *ee*. IR (direct irradiation) ν 2959, 2925, 2854, 1733, 1663, 1595, 1455, 1384, 1366, 1338, 1309, 1256, 1239,1224, 1182, 1162, 1134, 1121, 1093, 1028, 1016, 933, 834, 818, 800, 712, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 1.38 (s, 3H), 1.47 (s, 3H), 1.94 (s, 3H), 2.44 (s, 3H), 3.21 (t, *J* = 8.4 Hz, 1H), 3.34 (d, *J* = 7.6 Hz, 1H), 3.43 (dd, *J* = 2.8, 10.0 Hz, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.89 (d, *J* = 13.6 Hz, 1H), 5.06 (d, *J* = 12 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 22.4, 23.3, 23.6, 49.6, 50.7, 53.0, 83.2, 111.5, 127.8, 129.7, 132.6, 143.7, 143.8, 170.3. LRMS (ESI) *m/e* 338.1 $[M^+ + H]$; HRMS (ESI) calcd for $[C_{17}H_{23}NO_4S+H]$ requires 338.1426, found 338.1432 $[M^+ + H]$.

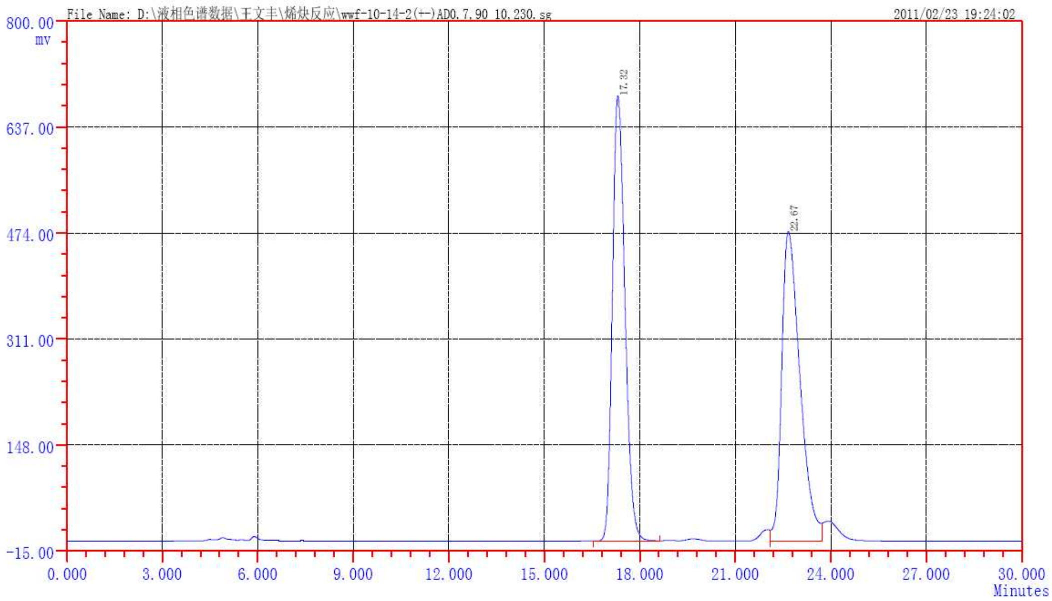




WH-500 Chiral HPLC Analysis Report:

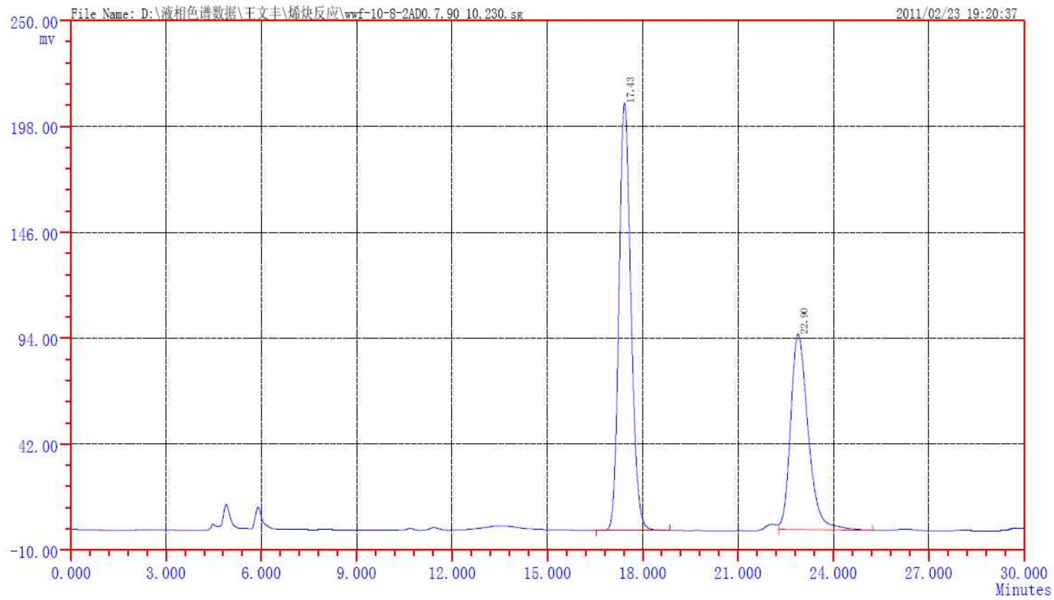
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.315	684872	18750178.1	49.6838	1.24	7972
2		22.672	476137	18988828.9	50.3162	1.63	6441
	Σ:		1161009	37739007.0	100.0000		

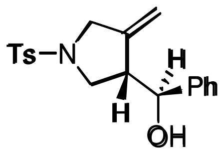
WH-500 色 谱 分 析 报 告



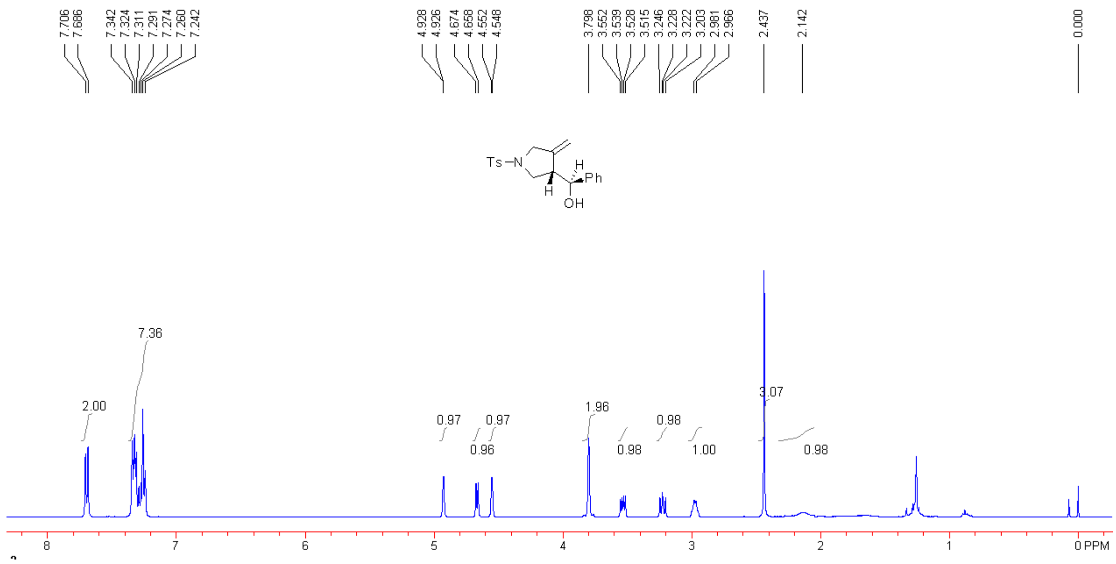
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.427	209842	5503722.6	59.8985	1.17	8799
2		22.898	95990	3684690.3	40.1015	1.27	7092
	Σ:		305832	9188412.9	100.0000		

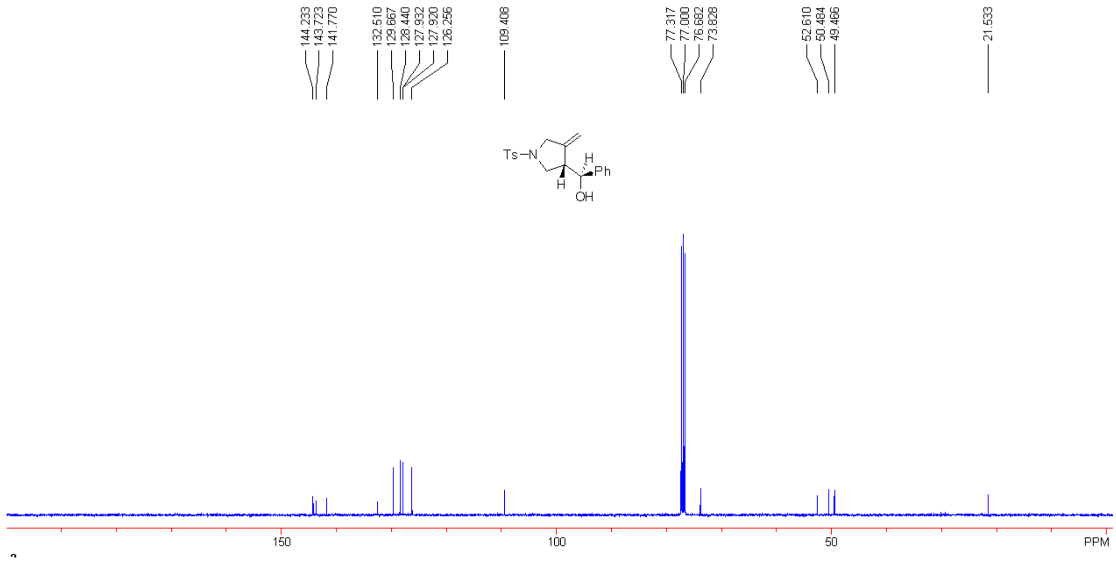
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 17.4 min (major), t_R = 22.9 min (minor)].

Compound **54**[5]



White solid; m.p. 43.9-45.2 ^{o}C. Absolute stereochemistry was assigned by the sign of optical rotation with that in the literature: $[\alpha]^{20}_{D}$ = +31.3 (*c* 0.5, $CHCl_3$) (lit.,[5] +51.2), 45% *ee*. IR (direct irradiation) ν 3502, 2956, 2923, 2853, 1712, 1666, 1597, 1494, 1454, 1338, 1306, 1156, 1093, 1041, 1016, 901, 813, 765, 702, 661 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.14 (br, 1H), 2.44 (s, 3H), 2.97-2.98 (m, 1H), 3.22 (dd, *J* = 7.6, 10.0 Hz, 1H), 3.53 (dd, *J* = 5.2, 9.6 Hz, 1H), 3.80 (s, 2H), 4.55 (d, *J* = 1.6 Hz, 1H), 4.67 (d, *J* = 6.4 Hz, 1H), 4.93 (d, *J* = 0.8 Hz, 1H), 7.24-7.34 (m, 7H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 49.5, 50.5, 52.6, 73.8, 109.4, 126.3, 127.92, 127.93, 128.4, 129.7, 132.5, 141.8, 143.7, 144.2. LRMS (ESI) *m/e* 344.1 [M^++H]; HRMS (ESI) calcd for [$C_{19}H_{21}NO_3S$+H] requires 344.1320, found 344.1329 [M^++H].

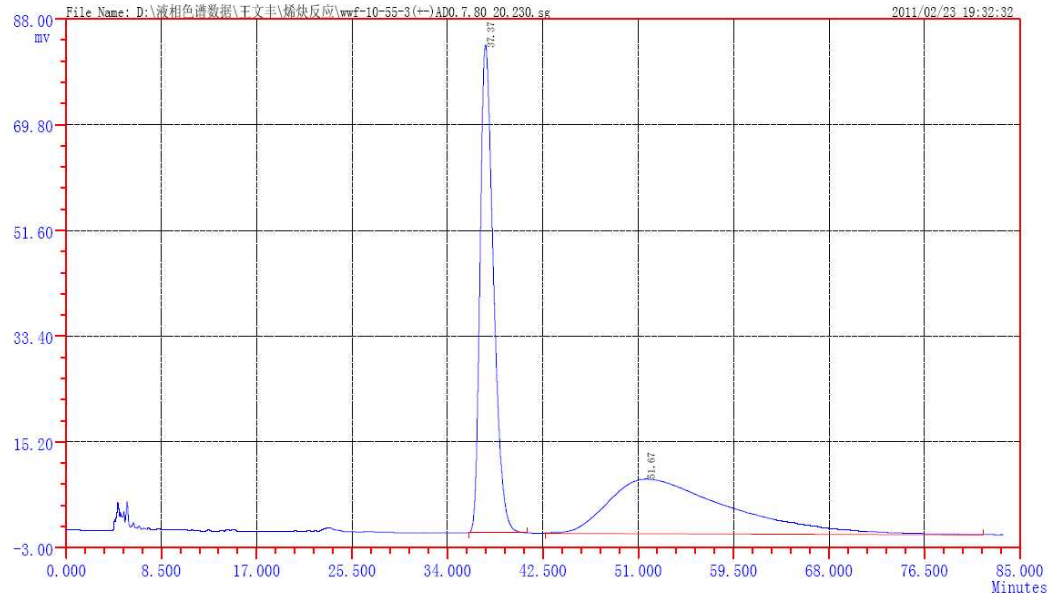




WH-500 Chiral HPLC Analysis Report:

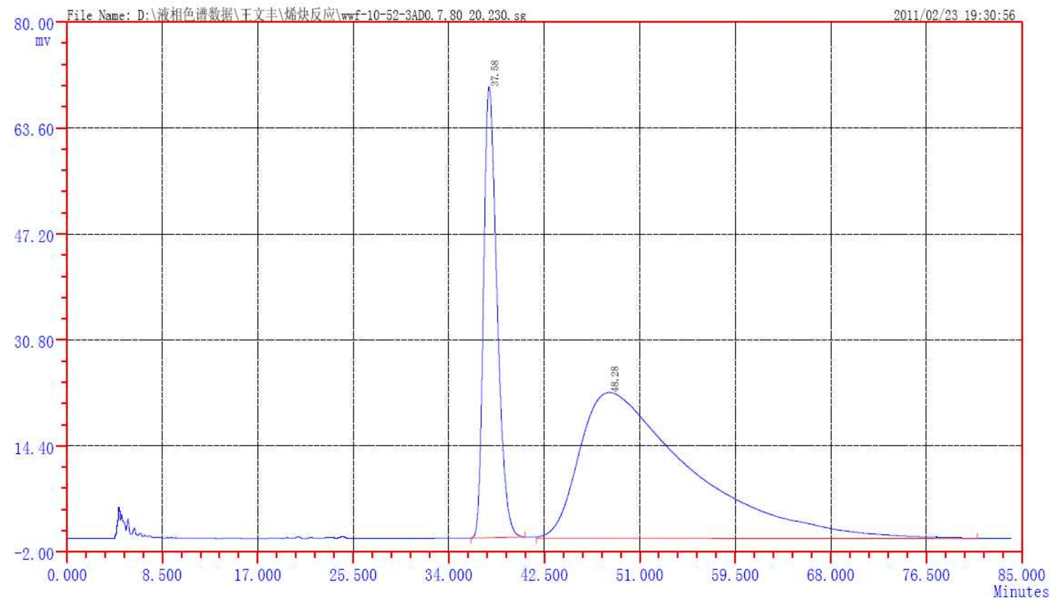
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色谱分析报告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		37.373	84001	6984979.3	49.9005	1.43	4026
2		51.673	9383	7012836.8	50.0995	1.90	95
	Σ:		93384	13997816.1	100.0000		

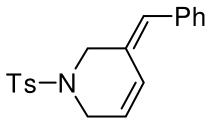
WH-500 色谱分析报告



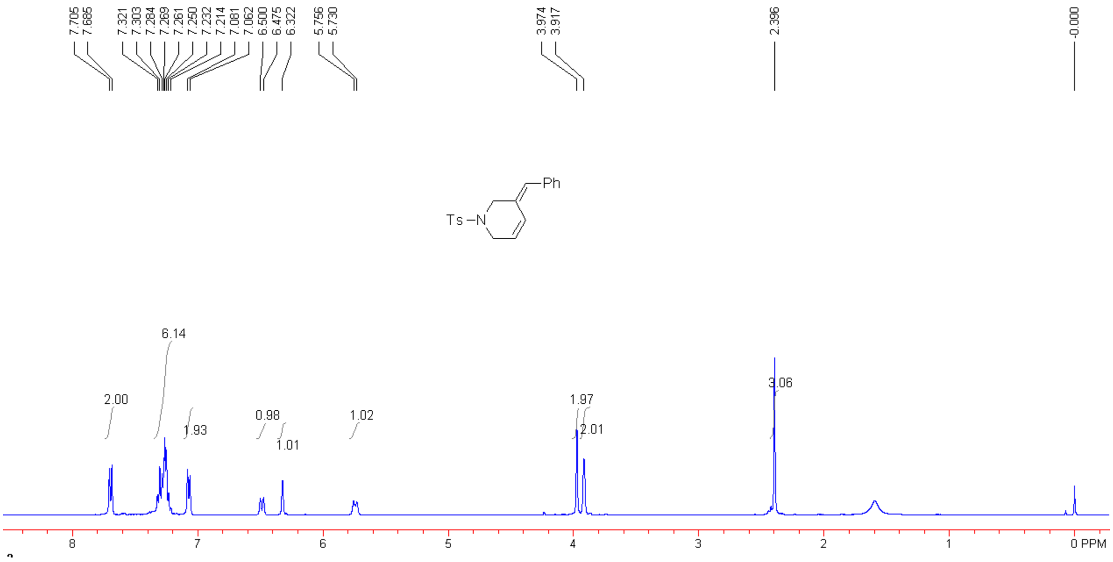
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		37.578	69802	5832007.3	27.3169	1.39	4032
2		48.275	22502	15517472.3	72.6831	2.51	98
	Σ:		92304	21349479.6	100.0000		

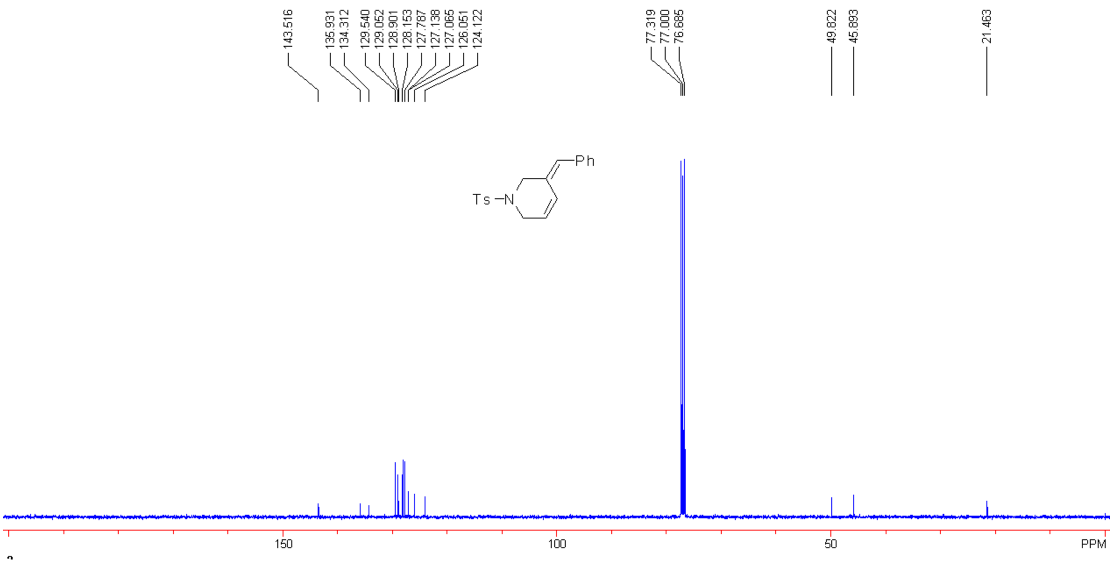
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 80:20, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 37.6 min (minor), t_R = 48.3 min (major)].

Compound **55**



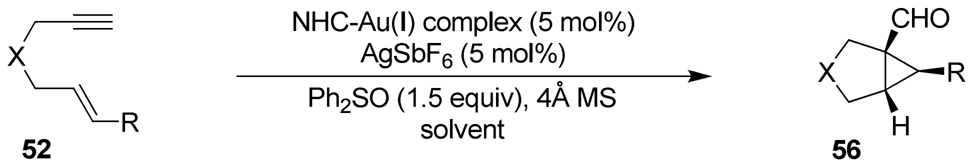
It is a known compound.[6] White solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.40 (s, 3H), 3.92 (s, 2H), 3.97 (s, 2H), 5.74 (d, *J* = 10.4 Hz, 1H), 6.32 (s, 1H), 6.49 (d, *J* = 10.0 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.23-7.32 (m, 5H), 7.70 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 45.9, 49.8, 124.1, 126.1, 127.07, 127.14, 127.8, 128.2, 128.9, 129.1, 129.5, 134.3, 135.9, 143.5.





(E) General Procedure for NHC-Au(I) Complexes-Catalyzed Enantioselective Oxidative Rearrangement of 1,6-Enynes and Analytical Data for Products.

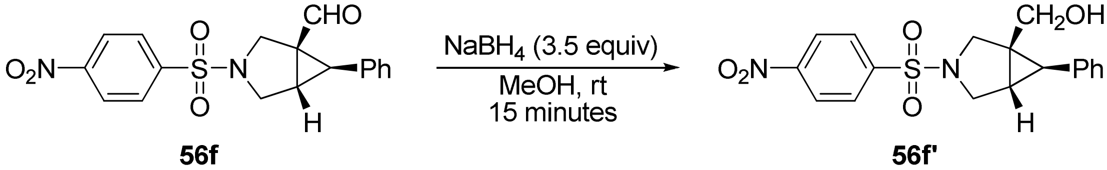
Under argon atmosphere, to a flame-dried Schlenk tube equipped with a septum and stirring bar were added activated 4Å MS (50 mg), NHC-Au(I) complex (5 mol%), 1,6-enyne **52** (0.1 mmol), Ph_2SO (30 mg, 0.15 mmol) and $AgSbF_6$ (2 mg, 0.005 mmol) followed by the injection of corresponding dry solvent (1 mL). The mixture was stirred at proper temperature until completely consuming of **52** by TLC monitoring before quenching by filtering with a thin pad of silica gel. Then volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography to give the oxidative product **56** (Scheme S17).



Scheme S17

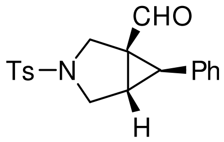
Racemic products for chiral HPLC analysis were prepared by using Ph_3PAuCl (5 mg, 10 mol%) and $AgSbF_6$ (4 mg, 0.01 mmol) as the catalyst with the solvent of DCE instead according to a similar procedure mentioned above.

Due to the insolubility of aldehyde **56f** in the mixture of hexane/isopropanol, the ee value of product **56f** was determined by a chiral HPLC analysis of its alcohol derivative **56f'**. To the suspension of **56f** (37 mg, 0.1 mmol) in MeOH (5 mL) was slowly added $NaBH_4$ (13 mg, 0.35 mmol) at room temperature. After stirring for further 15 minutes, the reaction was quenched by evaporating of MeOH and addition of water. Then the mixture was extracted with CH_2Cl_2 for 3 times and the combined organic phases were dried over anhydrous Na_2SO_4. Volatiles were removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 3/1) to give **56f'** in quantitative yield (Scheme S18).

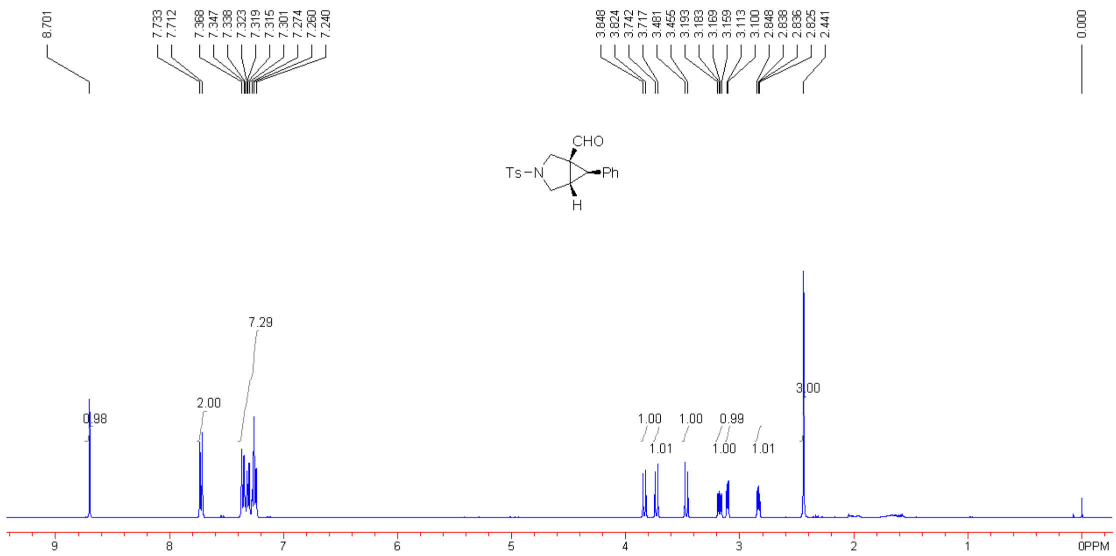


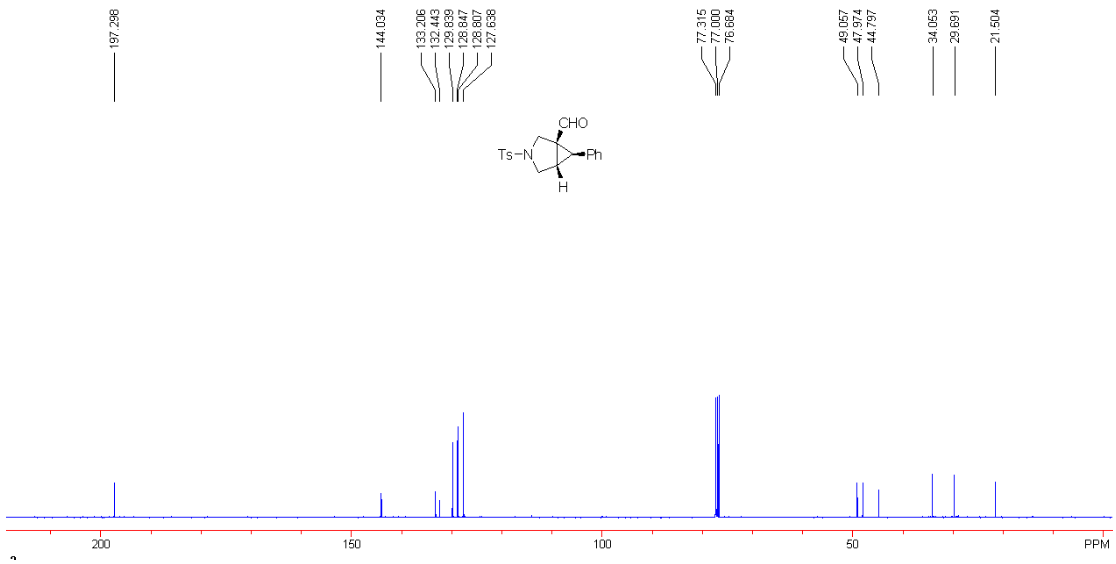
Scheme S18

Compound **56a**



It is a known compound.[7] White solid; m.p. 119.8-120.9 °C. Absolute stereochemistry was assigned by analogy to compound **54**, $[\alpha]^{20}_{D}$ = -44.6 (*c* 0.5, $CHCl_3$), 65% *ee*. IR (direct irradiation) *ν* 3059, 3028, 2959, 2925, 2870, 2853, 2739, 1687, 1598, 1497, 1344, 1253, 1162, 1099, 1084, 1047, 1017, 990, 956, 808, 783, 730, 697, 666, 644 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 2.44 (s, 3H), 2.84 (dd, *J* = 4.4, 5.2 Hz, 1H), 3.11 (d, *J* = 5.2 Hz, 1H), 3.18 (dd, *J* = 4.0, 9.6 Hz, 1H), 3.47 (d, *J* = 10.4 Hz, 1H), 3.73 (d, *J* = 10.0 Hz, 1H), 3.83 (d, *J* = 9.6 Hz, 1H), 7.24-7.37 (m, 7H), 7.72 (d, *J* = 8.4 Hz, 2H), 8.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 29.7, 34.1, 44.8, 48.0, 49.1, 127.6, 128.81, 128.85, 129.8, 132.4, 133.2, 144.0, 197.3. LRMS (ESI) *m/e* 359.1 $[M^+ + NH_4]$; HRMS (ESI) calcd for $[C_{19}H_{19}NO_3S+NH_4]$ requires 359.1429, found 359.1417 $[M^+ + NH_4]$.

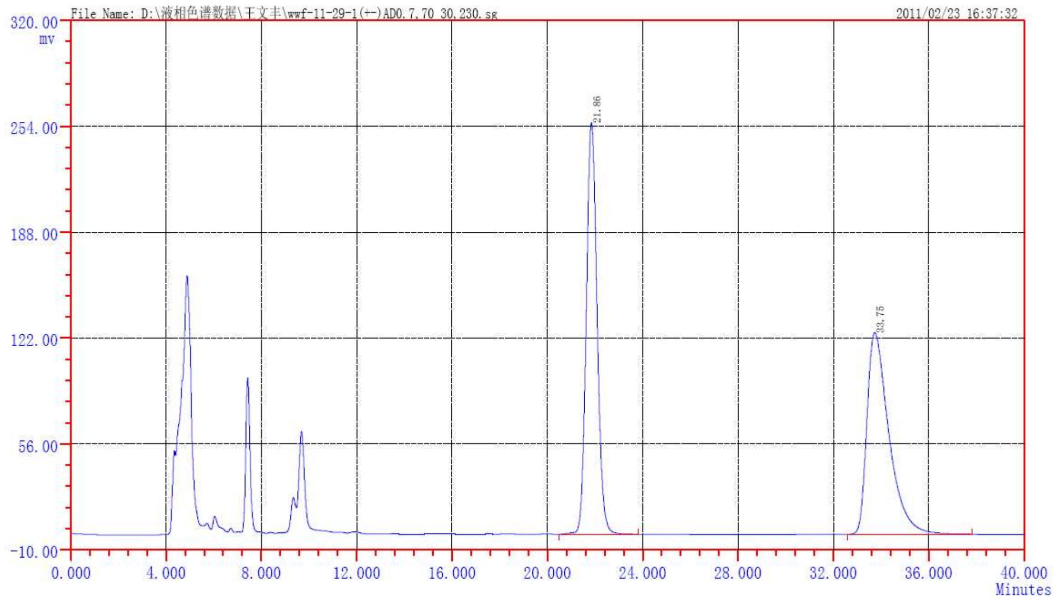




WH-500 Chiral HPLC Analysis Report:

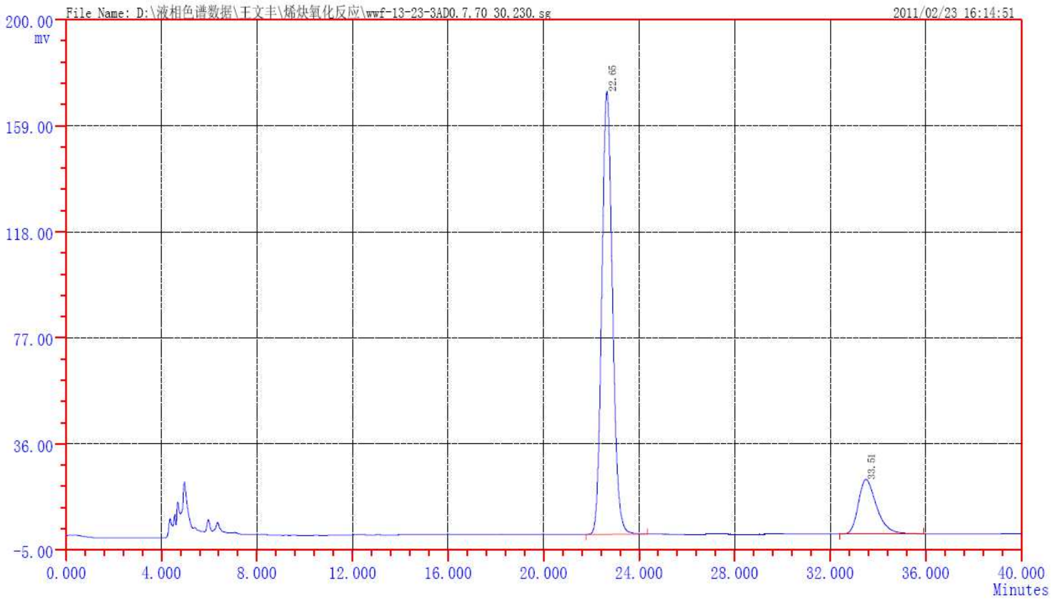
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		21.855	256760	8069651.3	50.0400	1.10	9638
2		33.745	125654	8056744.6	49.9600	1.73	5520
	Σ:		382414	16126395.9	100.0000		

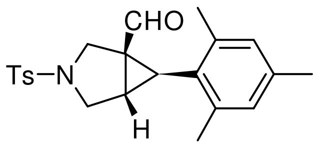
WH-500 色谱分析报告



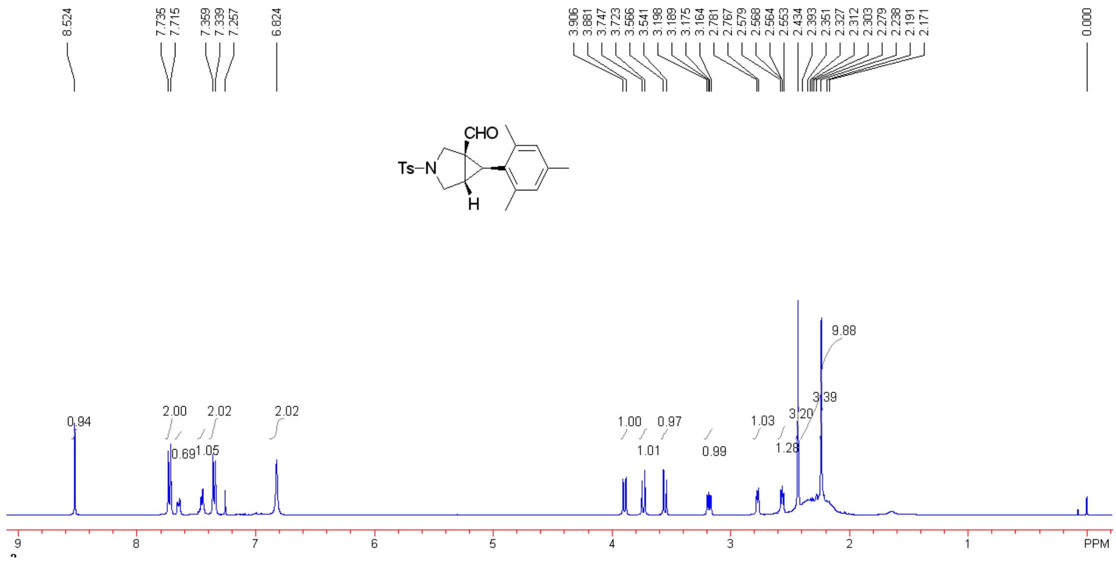
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		22.653	171293	5329036.7	82.5786	1.12	10567
2		33.505	21110	1124249.9	17.4214	1.38	7889
	Σ:		192403	6453286.6	100.0000		

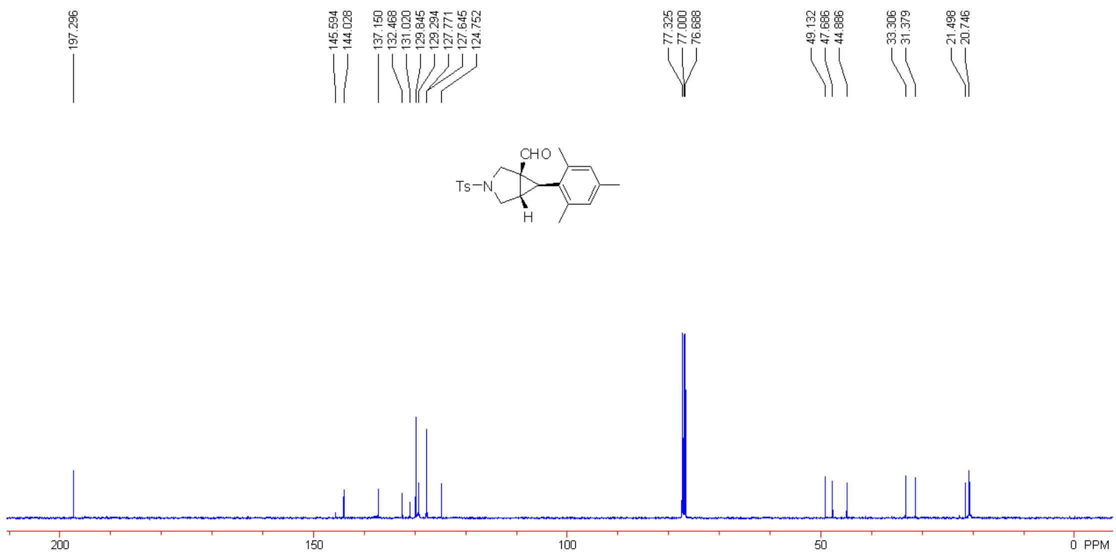
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 70:30, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 22.7 min (major), t_R = 33.5 min (minor)].

Compound **56c**



White solid; m.p. 132.5-133.5 °C. Absolute stereochemistry was assigned by analogy to compound **56a**, $[\alpha]^{20}_D$ = +4.6 (*c* 0.5, $CHCl_3$), 58% *ee*. IR (direct irradiation) *ν* 2956, 2924, 2854, 2741, 1709, 1597, 1465, 1443, 1342, 1159, 1092, 1053, 1012, 953, 850, 813, 786, 710, 666, 648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.17-2.39 (m, 6H, $2CH_3$), 2.24 (s, 3H), 2.44 (s, 3H), 2.57 (dd, *J* = 4.4, 6.0 Hz, 1H), 2.77 (d, *J* = 5.6 Hz, 1H), 3.18 (dd, *J* = 4.4, 10.0 Hz, 1H), 3.55 (d, *J* = 10.0 Hz, 1H), 3.74 (d, *J* = 9.6 Hz, 1H), 3.89 (d, *J* = 10.0 Hz, 1H), 6.82 (s, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.52 (s, 1H) (δ 7.41-7.48 and 7.63-7.66 ppm were the signals attributed to minor containing Ph_2SO); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 20.7, 21.5, 31.4, 33.3, 44.9, 47.7, 49.1, 127.6, 127.8, 129.8, 132.5, 137.2, 144.0, 197.3 (δ 124.8, 129.3, 131.0, 145.6 were signals attributed to minor containing Ph_2SO). LRMS (EI) *m/e* 383 (1.93%), 200 (38.48%), 185 (64.35%), 171 (91.89%), 157 (100%), 91 (84.53%); HRMS (EI) calcd for [$C_{22}H_{25}NO_3S$] requires 383.1555, found 383.1553 [M^+].

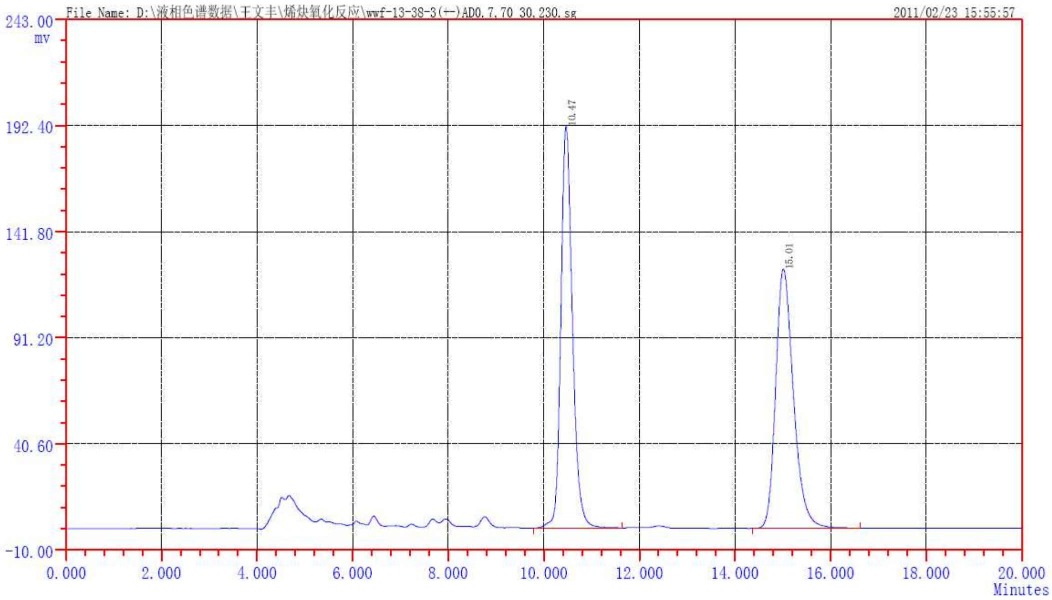




WH-500 Chiral HPLC Analysis Report:

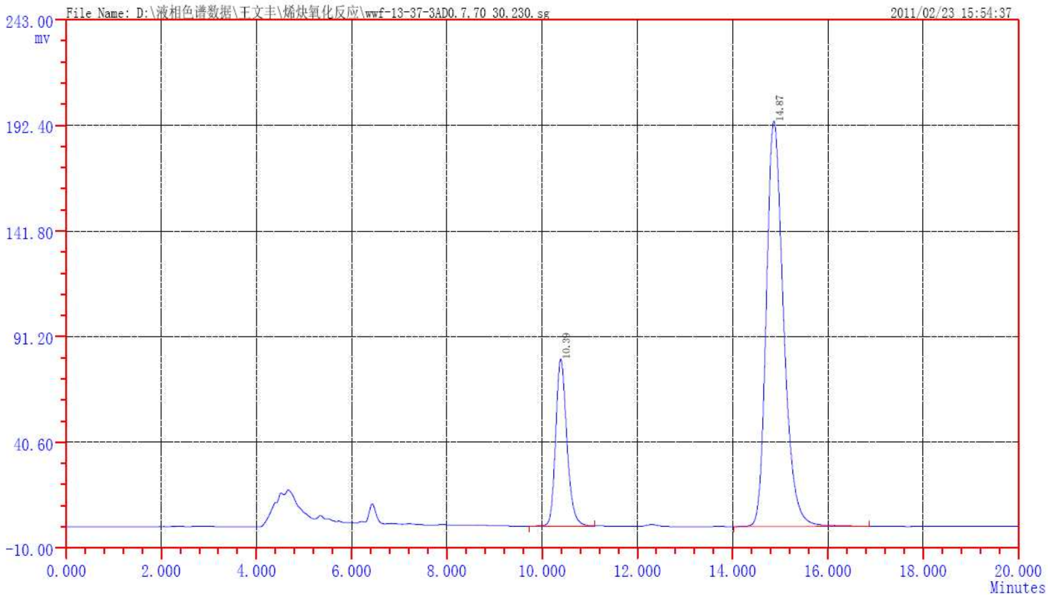
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		10.467	191658	3214941.5	50.0766	1.22	7760
2		15.013	123674	3205111.8	49.9234	1.29	6689
	Σ:		315332	6420053.3	100.0000		

WH-500 色 谱 分 析 报 告

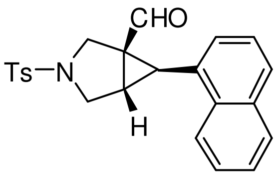


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		10.393	80079	1316038.5	21.1566	1.21	7971
2		14.870	194247	4904436.2	78.8434	1.28	6913
	Σ:		274326	6220474.6	100.0000		

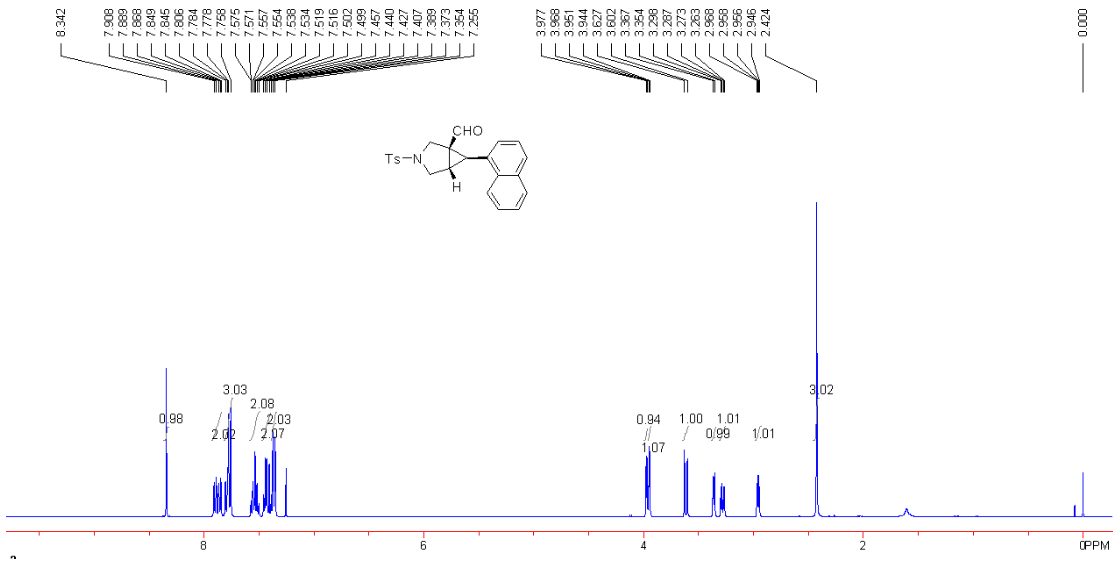
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 70:30, flow rate = 0.7

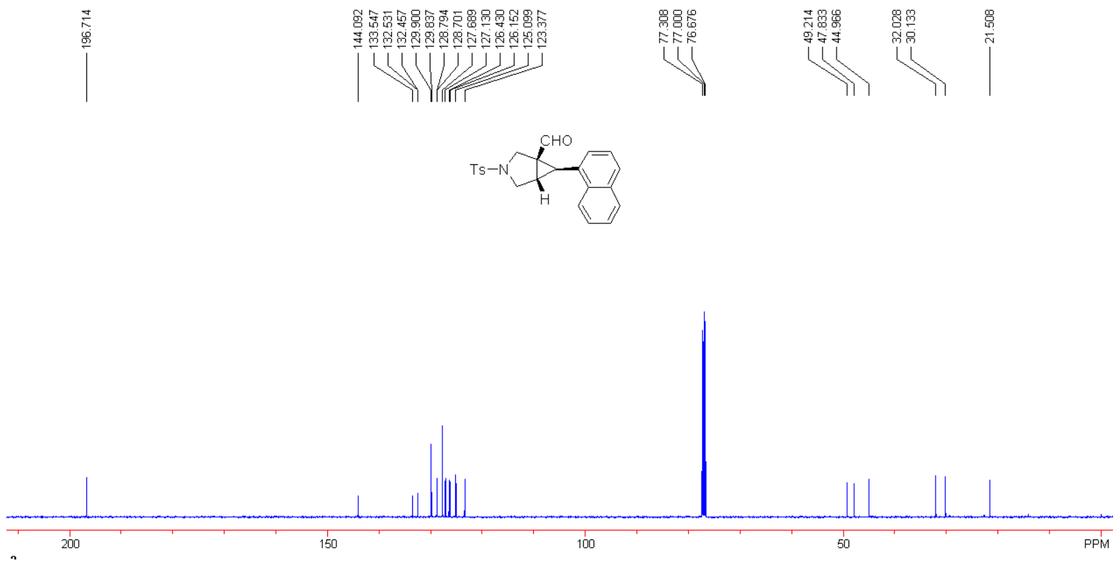
mL·min^{-1}, wavelength = 230 nm, t_R = 10.4 min (minor), t_R = 14.9 min (major)].

Compound **56d**



White solid; m.p. 173.3-174.3 °C. Absolute stereochemistry was assigned by analogy to compound **56a**, $[\alpha]^{20}_D$ = +66.8 (*c* 0.5, $CHCl_3$), 64% *ee*. IR (direct irradiation) ν 3069, 2925, 2854, 1693, 1597, 1347, 1308, 1240, 1162, 1099, 1064, 1043, 1012, 954, 822, 809, 778, 711, 666, 633 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.42 (s, 3H), 2.96 (dd, *J* = 4.0, 4.8 Hz, 1H), 3.28 (dd, *J* = 4.0, 9.6 Hz, 1H), 3.36 (d, *J* = 5.2 Hz, 1H), 3.61 (d, *J* = 10.0 Hz, 1H), 3.95 (d, *J* = 2.8 Hz, 1H), 3.97 (d, *J* = 3.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.39-7.46 (m, 2H), 7.50-7.58 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.85-7.91 (m, 2H), 8.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 21.5, 30.1, 32.0, 45.0, 47.8, 49.2, 123.4, 125.1, 126.2, 126.4, 127.1, 127.7, 128.7, 128.8, 129.8, 129.9, 132.46, 132.53, 133.5, 144.1, 196.7. LRMS (EI) *m/e* 391 (2.18%), 208 (29.86%), 179 (100%), 165 (27.35%), 141 (20.54%), 91 (48.00%); HRMS (EI) calcd for [$C_{23}H_{21}NO_3S$] requires 391.1242, found 391.1244 [M^+].

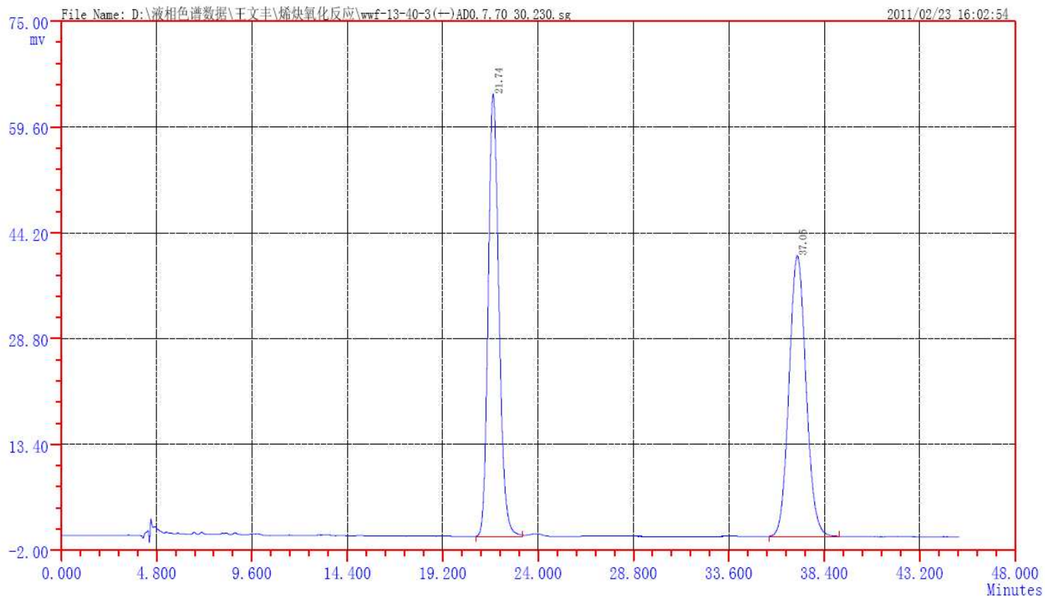




WH-500 Chiral HPLC Analysis Report:

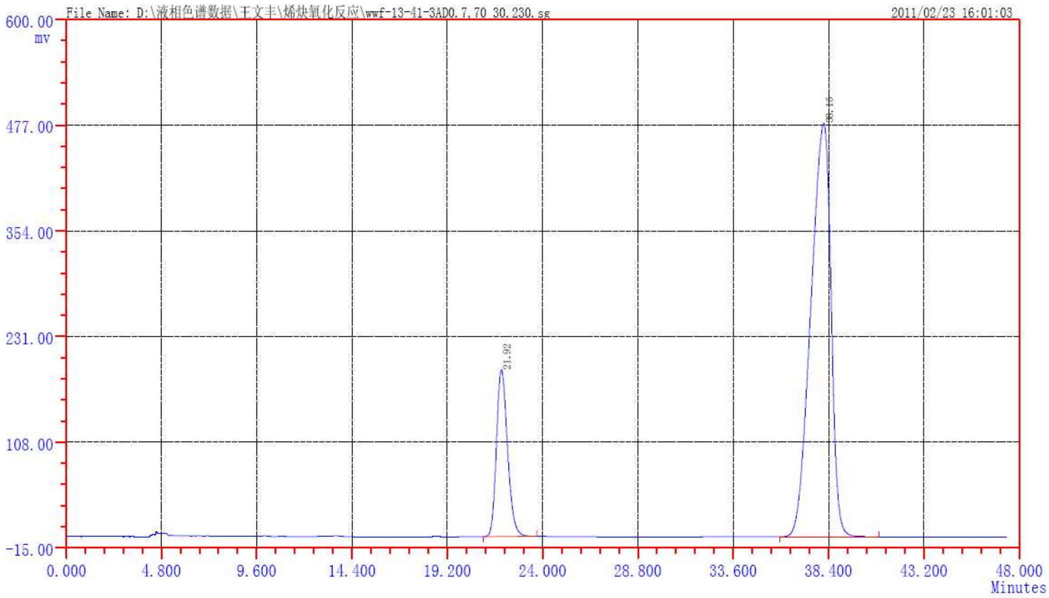
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		21.737	64429	2413774.8	49.8163	1.19	6709
2		37.047	40883	2431579.7	50.1837	1.09	7733
	Σ:		105312	4845354.5	100.0000		

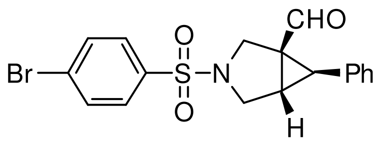
WH-500 色 谱 分 析 报 告



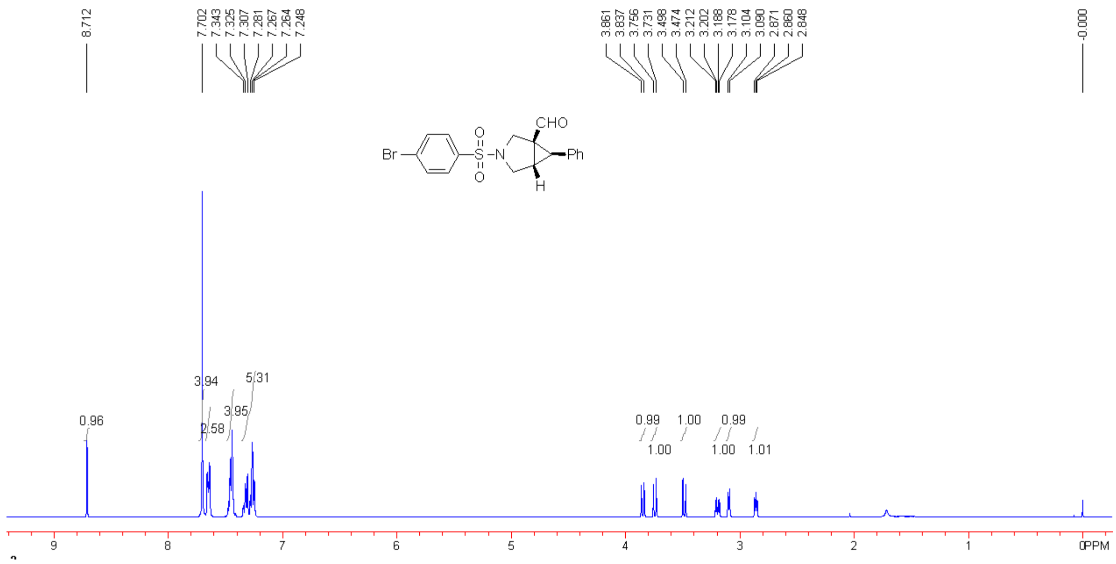
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		21.923	193921	7519757.6	18.1932	1.23	6371
2		38.160	481371	33813068.6	81.8068	0.81	5882
	Σ:		675292	41332826.1	100.0000		

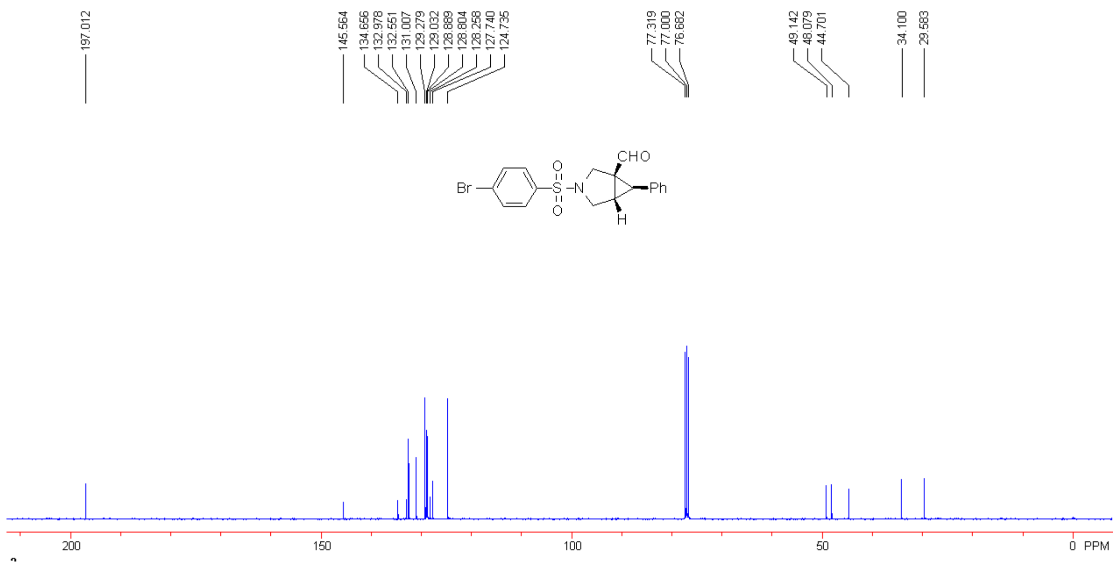
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 70:30, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 21.9 min (minor), t_R = 38.2 min (major)].

Compound **56e**



White solid; m.p. 117.1-118.2 °C. Absolute stereochemistry was assigned by analogy to compound **56a**, $[\alpha]^{20}_D$ = -31.6 (*c* 0.5, $CHCl_3$), 70% *ee*. IR (direct irradiation) ν 3057, 2924, 2852, 1691, 1576, 1470, 1442, 1388, 1345, 1163, 1099, 1068, 1047, 1023, 1010, 948, 809, 783, 740, 694, 646, 627 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.86 (dd, *J* = 4.4, 4.8 Hz, 1H), 3.10 (d, *J* = 5.6 Hz, 1H), 3.20 (dd, *J* = 4.0, 9.6 Hz, 1H), 3.49 (d, *J* = 9.6 Hz, 1H), 3.74 (d, *J* = 10.0 Hz, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 7.25-7.34 (m, 5H), 7.70 (s, 4H), 8.71 (s, 1H) (δ 7.41-7.48 and 7.63-7.66 ppm were the signals attributed to minor containing Ph_2SO); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 29.6, 34.1, 44.7, 48.1, 49.1, 127.7, 128.3, 128.8, 128.9, 129.0, 132.6, 133.0, 134.7, 197.0 (δ 124.7, 129.3, 131.0, 145.6 were signals attributed to minor containing Ph_2SO). LRMS (EI) *m/e* 405, 202 (100%), 154 (80.9%), 109 (92.18%), 77 (89.78%), 51 (86.70%); HRMS (EI) calcd for [$C_{18}H_{16}NO_3BrS$] requires 405.0034, found 405.0036 [M^+].

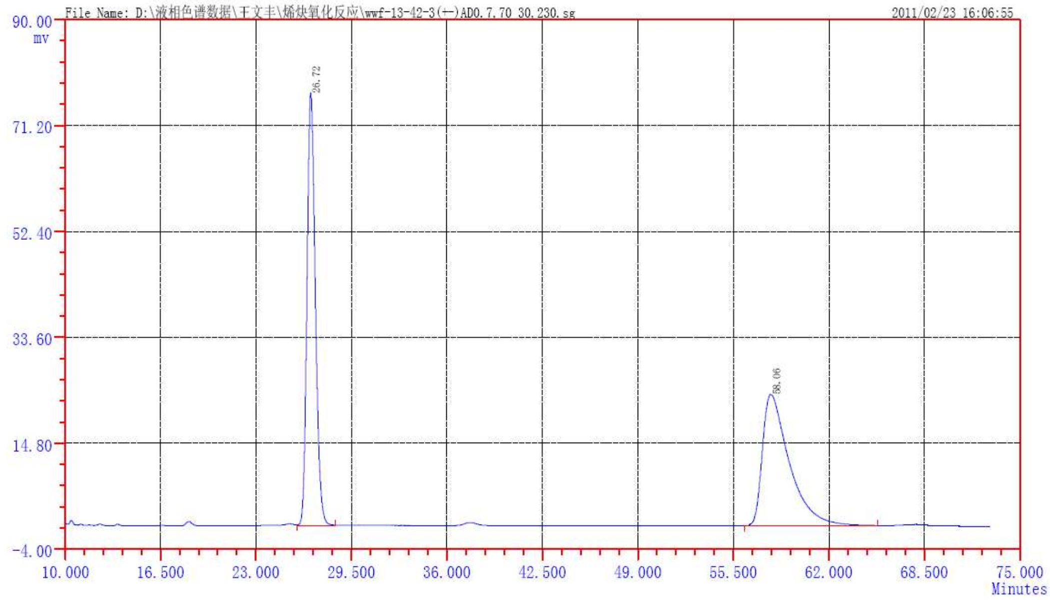




WH-500 Chiral HPLC Analysis Report:

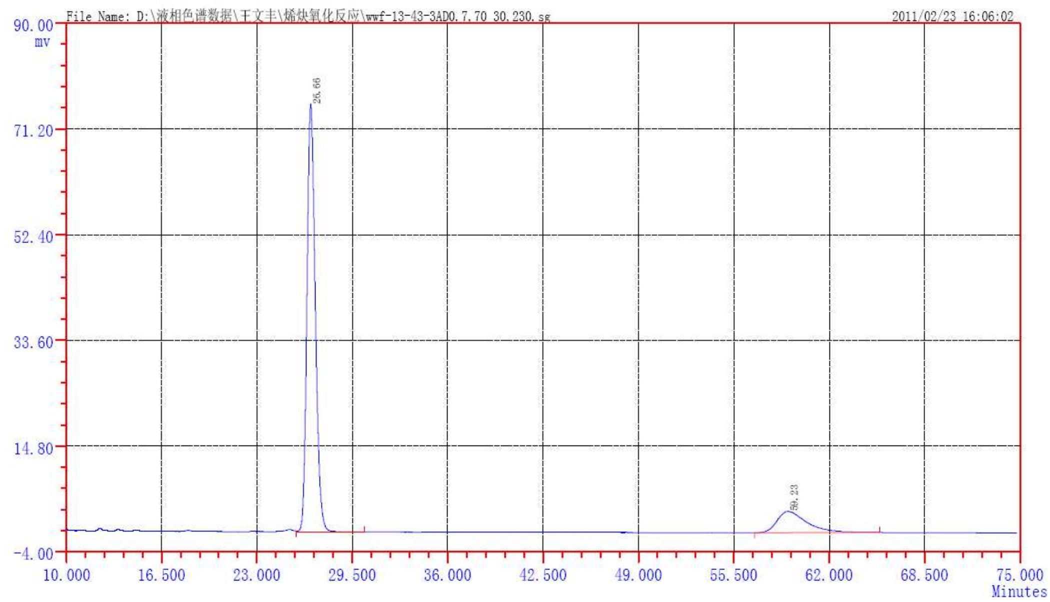
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		26.718	76811	3024611.3	50.2709	1.21	9176
2		58.062	23369	2992018.3	49.7291	2.07	4099
	Σ:		100180	6016629.6	100.0000		

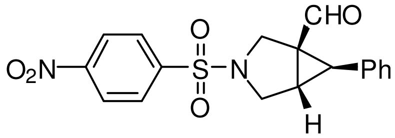
WH-500 色 谱 分 析 报 告



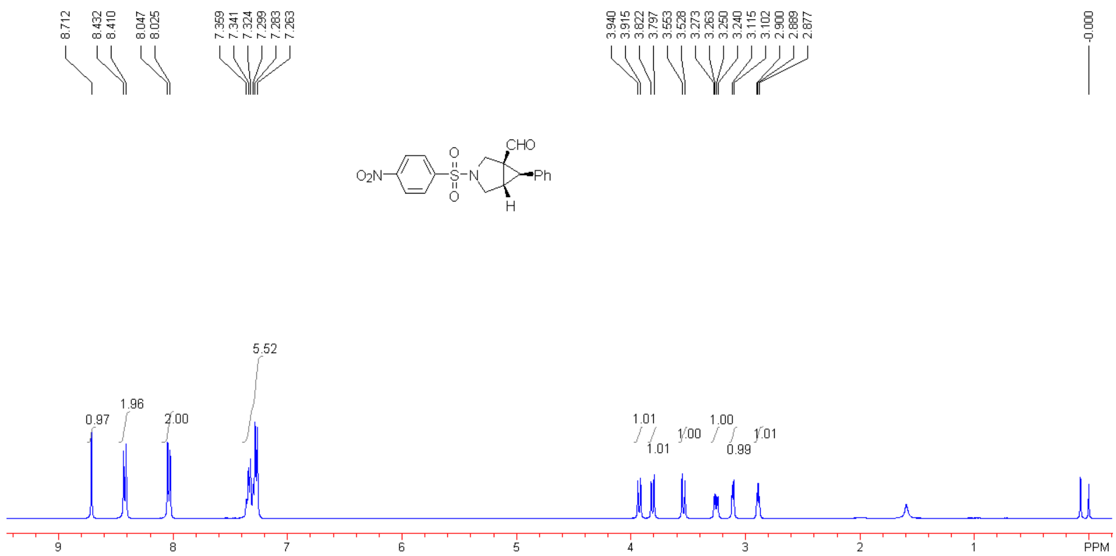
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		26.660	76074	2998909.7	84.8514	1.20	9116
2		59.225	3789	535399.7	15.1486	1.67	3501
	Σ:		79863	3534309.4	100.0000		

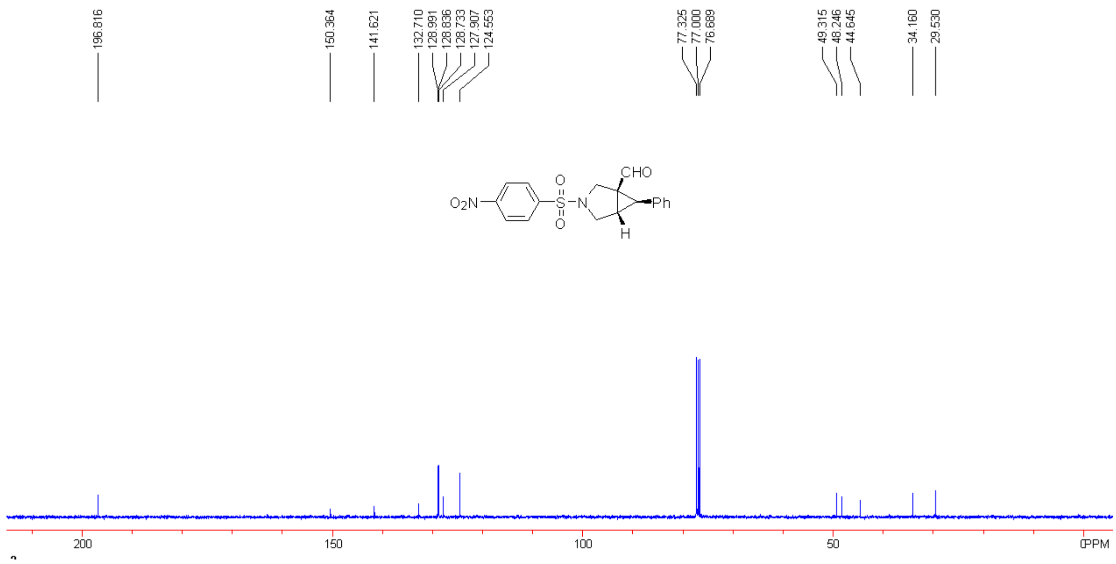
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 70:30, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 26.7 min (major), t_R = 59.2 min (minor)].

Compound **56f**

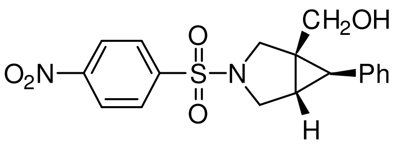


White solid; m.p. 180.0-181.2 °C. Absolute stereochemistry was assigned by analogy to compound **56a**, $[\alpha]^{20}_{D}$ = -35.0 (*c* 0.5, $CHCl_3$), 66% *ee*. IR (direct irradiation) *ν* 2925, 2855, 1694, 1607, 1543, 1350, 1306, 1237, 1165, 1097, 1049, 1020, 956, 855, 809, 783, 736, 686, 629 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.89 (dd, *J* = 4.4, 4.8 Hz, 1H), 3.11 (d, *J* = 5.2 Hz, 1H), 3.26 (dd, *J* = 4.0, 9.2 Hz, 1H), 3.54 (d, *J* = 10.0 Hz, 1H), 3.81 (d, *J* = 10.0 Hz, 1H), 3.93 (d, *J* = 10.0 Hz, 1H), 7.26-7.36 (m, 5H), 8.04 (d, *J* = 8.8 Hz, 2H), 8.42 (d, *J* = 8.8 Hz, 2H), 8.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 29.5, 34.2, 44.6, 48.2, 49.3, 124.6, 127.9, 128.7, 128.8, 129.0, 132.7, 141.6, 150.4, 196.8. LRMS (EI) *m/e* 372.1 (3.0%), 186.1 (19.5%), 157.0 (42.52%), 129.1 (100%), 115.1 (18.20%), 91.1 (29.20%); HRMS (EI) calcd for $[C_{18}H_{16}N_2O_5S]$ requires 372.0780, found 372.0776 $[M^+]$.

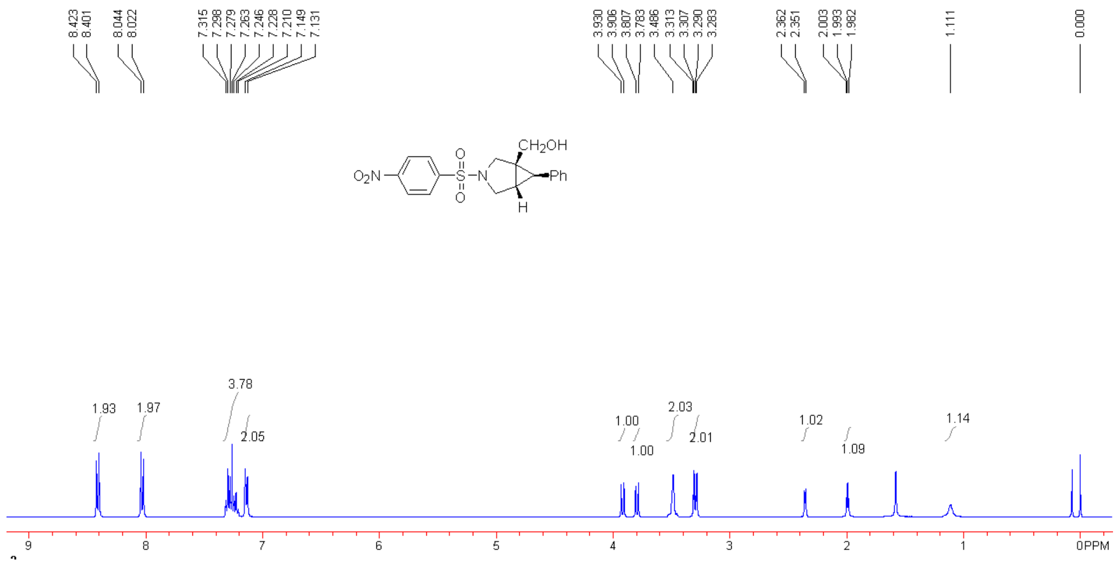


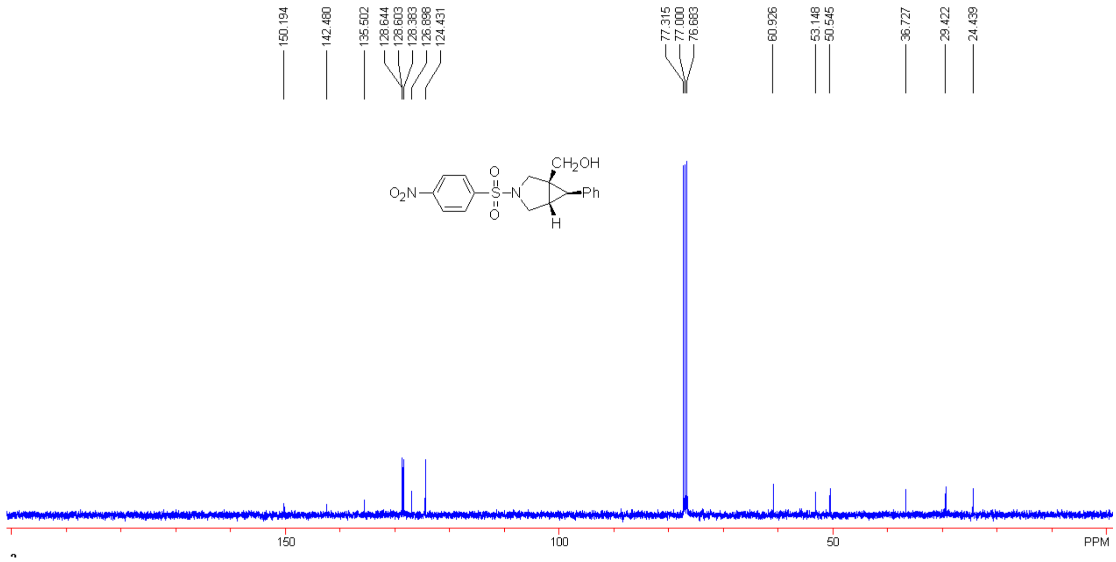


Compound **56f'**



White solid; m.p. 148.9-150.1 °C. Absolute stereochemistry was assigned by analogy to compound **56a**, 66% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.11 (s, 1H), 1.99 (dd, J = 4.0, 4.4 Hz, 1H), 2.36 (d, J = 4.4 Hz, 1H), 3.30 (dd, J = 2.1, 9.6 Hz, 2H), 3.49 (s, 2H), 3.80 (d, J = 9.6 Hz, 1H), 3.92 (d, J = 9.6 Hz, 1H), 7.14 (d, J = 7.2 Hz, 2H), 7.21-7.32 (m, 3H), 8.03 (d, J = 8.8 Hz, 2H), 8.41 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 24.4. 29.4, 36.7, 50.5, 53.1, 60.9, 124.4, 126.9, 128.4, 128.60, 128.64, 135.5, 142.5, 150.2. LRMS (EI) *m/e* 374.1 (1.11%), 268.1 (13.79%), 188.1 (24.94%), 129.1 (100%), 117.1 (44.57%), 91.1 (70.36%); HRMS (EI) calcd for [$C_{18}H_{18}N_2O_5S$] requires 374.0936, found 374.0932 [M^+].

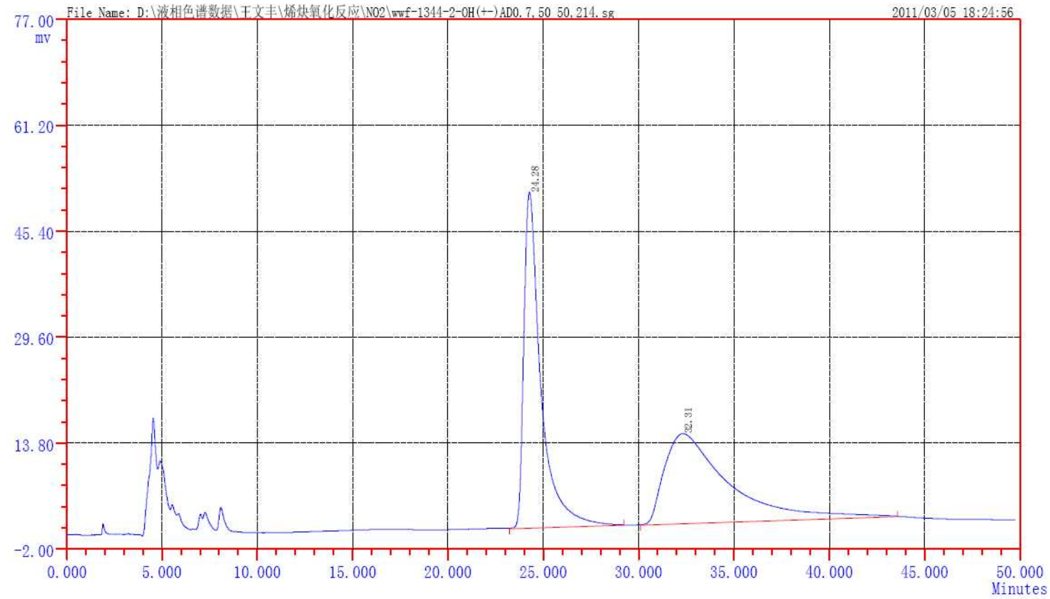




WH-500 Chiral HPLC Analysis Report:

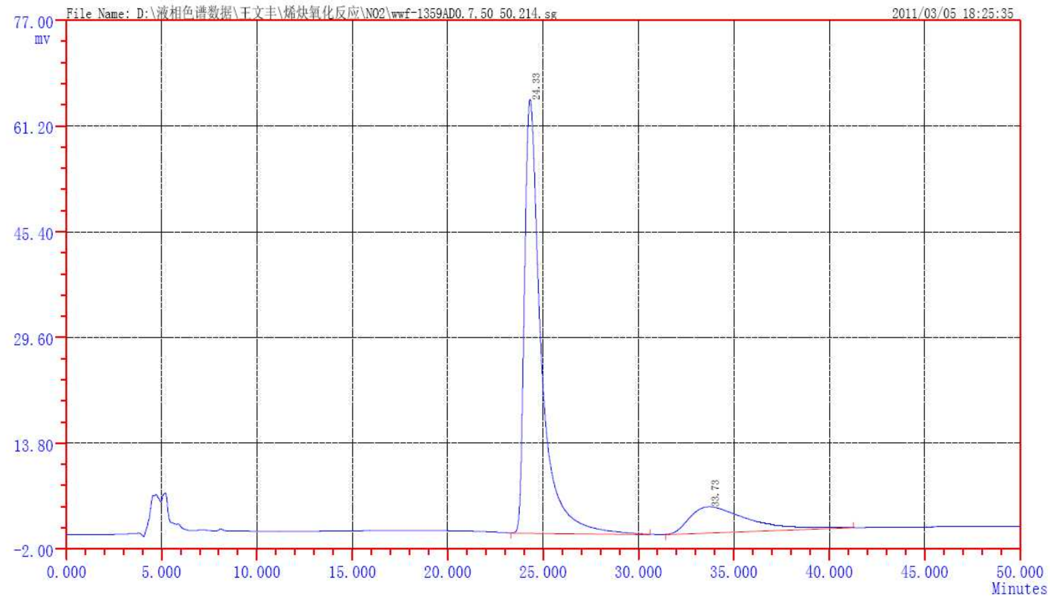
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		24.282	50144	3110940.0	49.8031	2.31	3053
2		32.307	13462	3135538.7	50.1969	3.85	383
	Σ:		63606	6246478.7	100.0000		

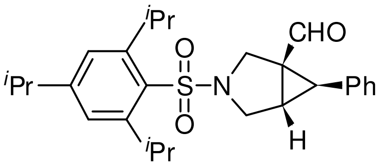
WH-500 色 谱 分 析 报 告



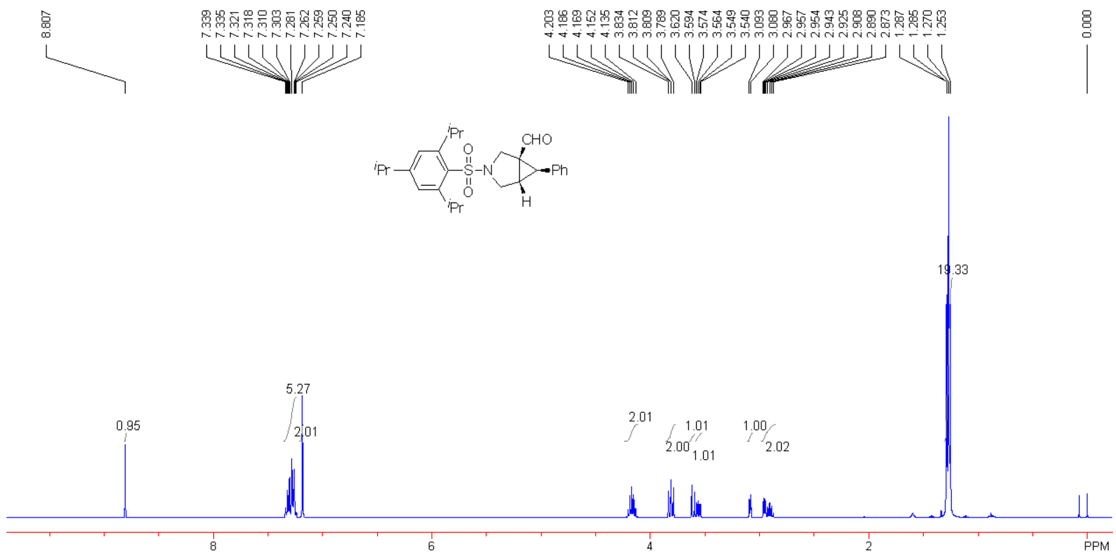
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		24.332	64873	3944422.8	82.8645	2.10	3192
2		33.735	3899	815665.3	17.1355	2.61	518
	Σ:		68772	4760088.1	100.0000		

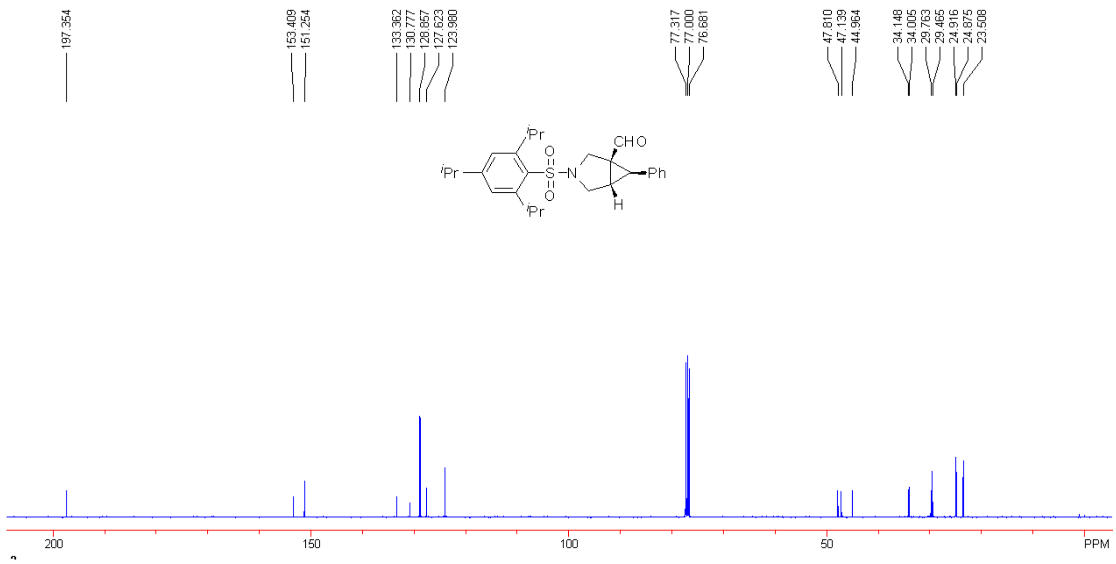
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 50:50, flow rate = 0.7 mL·min^{-1}, wavelength = 214 nm, t_R = 24.3 min (major), t_R = 33.7 min (minor)].

Compound **56g**



White solid; m.p. 55.9-56.9 ^{o}C. Absolute stereochemistry was assigned by analogy to compound **56a**, $[\alpha]^{20}_{D}$ = -11.5 (*c* 0.5, $CHCl_3$), 10.3% *ee*. IR (direct irradiation) ν 2958, 2929, 2870, 1696, 1601, 1462, 1425, 1364, 1316, 1239, 1152, 1079, 1044, 1006, 953, 883, 844, 782, 732, 698, 675, 652 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.25-1.29 (m, 18H), 2.91 (hep, *J* = 6.8 Hz, 1H), 2.96 (dd, *J* = 4.4, 5.2 Hz, 1H), 3.09 (d, *J* = 5.2 Hz, 1H), 3.56 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.61 (d, *J* = 10.4 Hz, 1H), 3.80 (d, *J* = 9.2 Hz, 1H), 3.82 (d, *J* = 10.0 Hz, 1H), 4.17 (hep, *J* = 6.8 Hz, 2H), 7.19 (s, 2H), 7.24-7.34 (m, 5H), 8.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 23.5, 24.88, 24.92, 29.5, 29.8, 34.0, 34.1, 45.0, 47.1, 47.8, 124.0, 127.6, 128.9, 130.8, 133.4, 151.3, 153.4, 197.4. LRMS (EI) *m/e* 453.2 (1.1%), 187 (97.97%), 158 (51.46%), 129 (100%), 96 (90.57%), 91 (76.79%); HRMS (EI) calcd for [$C_{27}H_{35}NO_3S$] requires 453.2338, found 453.2335 [M^{+}].

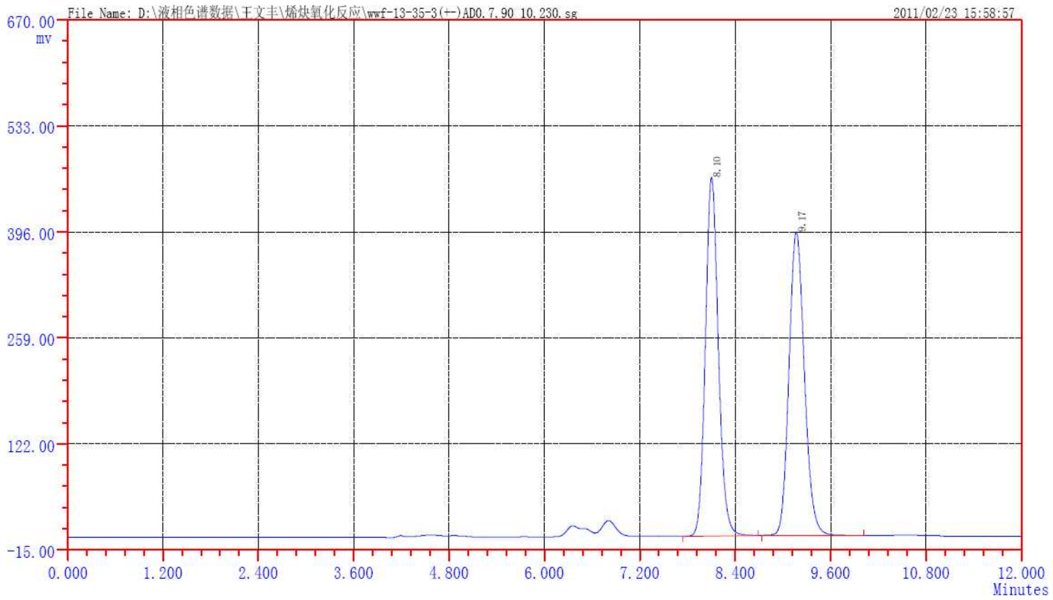




WH-500 Chiral HPLC Analysis Report:

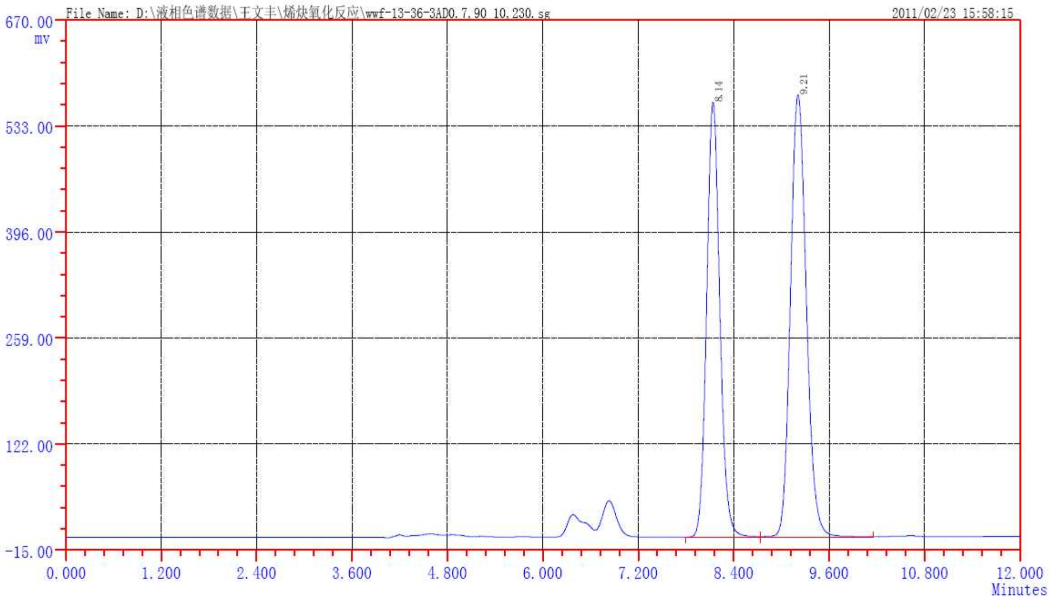
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.103	463930	5271877.4	49.8355	1.13	10135
2		9.172	392640	5306673.8	50.1645	1.13	9178
	Σ:		856570	10578551.2	100.0000		

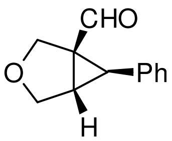
WH-500 色 谱 分 析 报 告



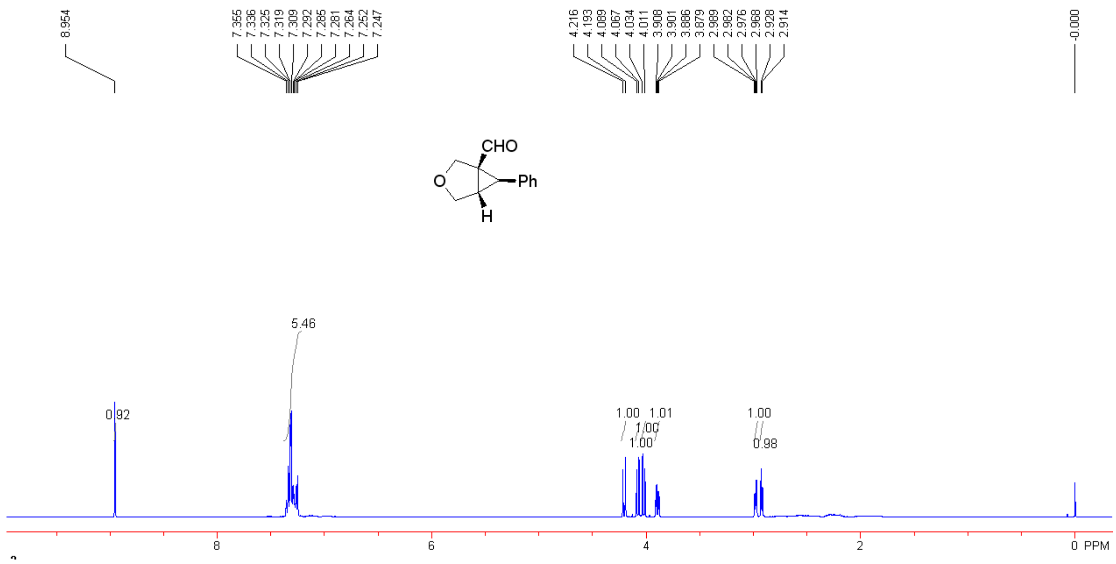
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.142	562283	6473553.0	44.8628	1.10	9967
2		9.212	571780	7956099.8	55.1372	1.14	8735
	Σ:		1134063	14429652.8	100.0000		

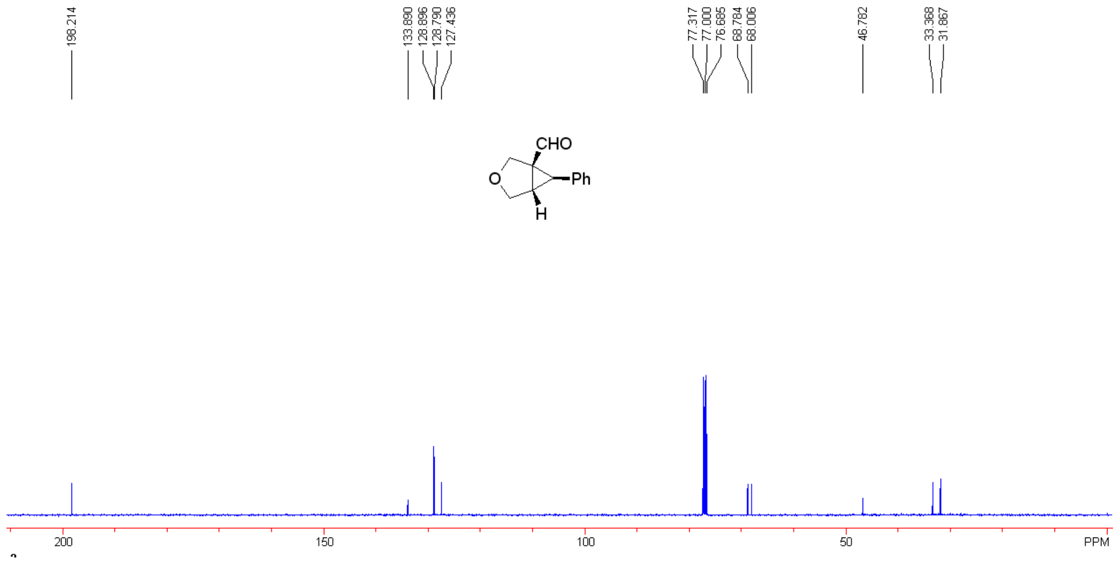
[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 90:10, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 8.1 min (minor), t_R = 9.2 min (major)].

Compound **56h**



It is a known compound.[7] Colorless oil. Absolute stereochemistry was assigned by analogy to compound **56a**, $[\alpha]^{20}_{D}$ = +3.6 (*c* 0.5, $CHCl_3$), 3.1% *ee*. IR (direct irradiation) *ν* 2956, 2925, 2855, 2742, 1948, 1892, 1691, 1605, 1499, 1455, 1371, 1237, 1199, 1072, 1059, 1026, 909, 795, 779, 732, 696, 634 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 2.92 (d, *J* = 5.6 Hz, 1H), 2.98 (dd, *J* = 3.2, 5.6 Hz, 1H), 3.89 (dd, *J* = 2.8, 8.8 Hz, 1H), 4.02 (d, *J* = 9.2 Hz, 1H), 4.08 (d, *J* = 8.8 Hz, 1H), 4.20 (d, *J* = 9.2 Hz, 1H), 7.25-7.36 (m, 5H), 8.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 31.9, 33.4, 46.8, 68.0, 68.8, 127.4, 128.8, 128.9, 133.9, 198.2. LRMS (EI) *m/e* 188 (3.28%), 158 (39.63%), 129 (100%), 115 (32.57%), 91 (44.54%); HRMS (EI) calcd for [$C_{12}H_{12}O_2$] requires 188.0837, found 188.0836 [M^+].

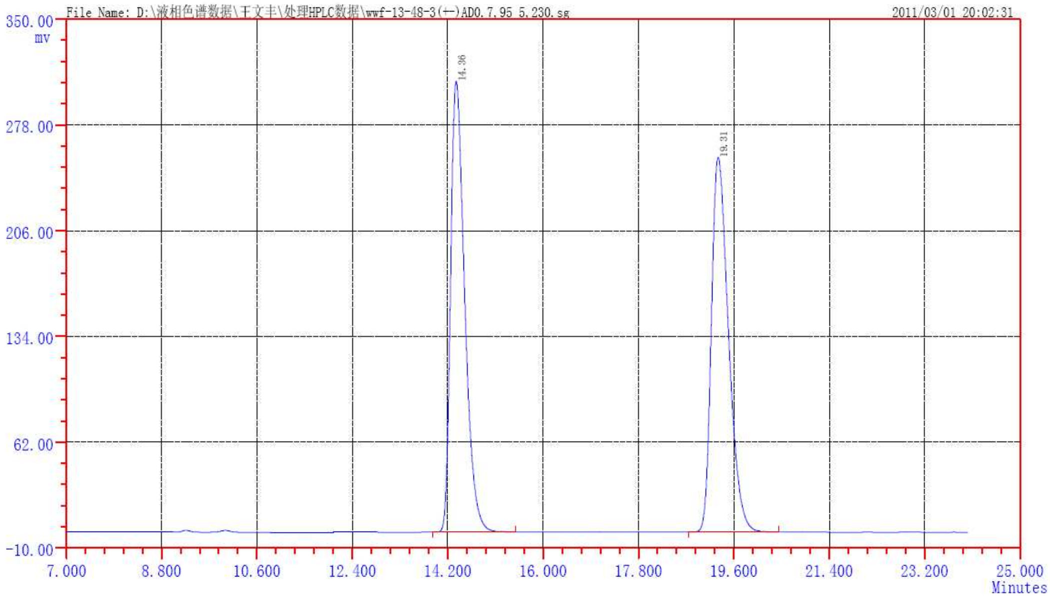




WH-500 Chiral HPLC Analysis Report:

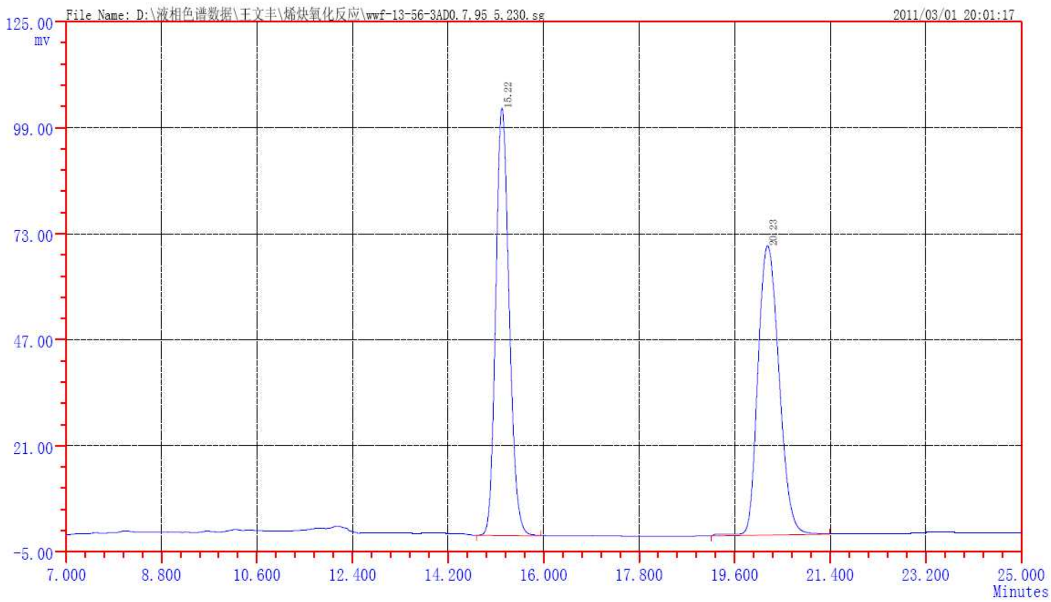
ID; Content; Retention time; Peak height; Peak area; Concentration; Tailing effect; Theoretic tower plates

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		14.360	307155	5681617.7	49.7747	1.47	12012
2		19.307	255421	5733044.1	50.2253	1.41	14746
	Σ:		562576	11414661.8	100.0000		

WH-500 色 谱 分 析 报 告



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		15.218	104797	1847991.5	48.4683	1.15	14844
2		20.227	70945	1964792.8	51.5317	1.19	10631
	Σ:		175742	3812784.3	100.0000		

[HPLC conditions: Chiracel AD-H column, hexane/2-propanol = 95:5, flow rate = 0.7 mL·min^{-1}, wavelength = 230 nm, t_R = 15.2 min (minor), t_R = 20.2 min (major)].

(F) References.

1. Wang, W. F.; Zhang, T.; Shi, M. *Organometallics* **2009**, *28*, 2640-2642.

2. (a) Zhang, T.; Liu, S. J.; Shi, M.; Zhao, M. X. *Synthesis* **2008**, (17), 2819-2824. (b) Wang, W. F.; Zhang, T.; Wang, F. J.; Shi, M. *Tetrahedron* **2011**, *67*, 1523-1529.

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6. Nieto-Oberhuber, C.; Munoz, M. P.; Lopez, S.; Jimenez-Nunez, E.; Nevado, C.; Herrero-Gomez, E.; Raducan, M.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1677-1693.

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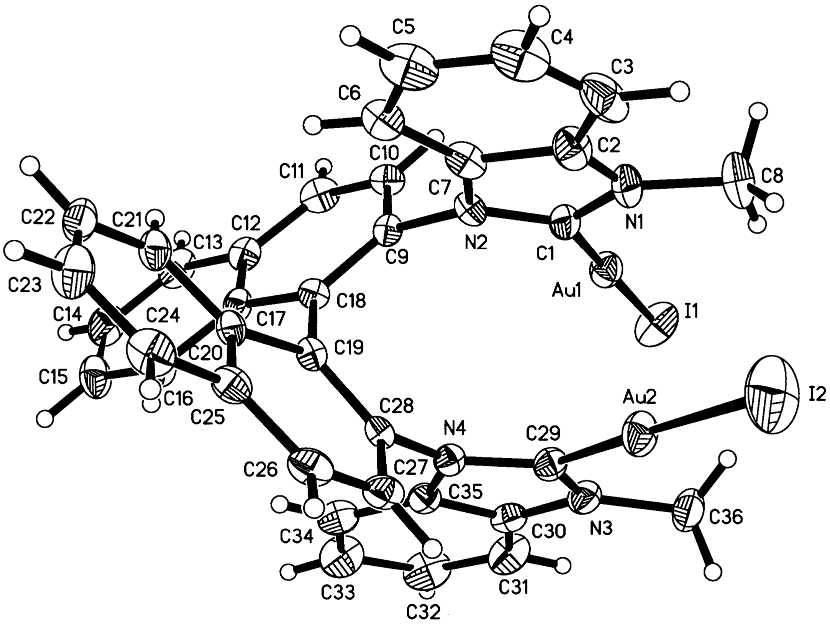
(G) X-ray Crystal Data of Complex 1.



The crystal data of **1** have been deposited in CCDC with number 759948. Empirical Formula: $C_{40}H_{32}Au_2I_2N_6$; Formula Weight: 1244.45; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.301 x 0.217 x 0.24 mm; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters: a = 9.3794(9)Å, b = 10.4523(10)Å, c = 20.784(2)Å, α = 85.843(2)°, β = 77.783(2)°, γ = 80.838(2)°, V = 1964.5(3)Å^3; Space group: P-1; Z = 2; D_{calc}= 2.104 g/cm^3; F_{000} = 1156; Diffractometer: Bruker Smart CCD; Residuals: R; Rw: 0.0448, 0.1129.

Table 1. Crystal data and structure refinement for cd29663.

Identification code	cd29663
Empirical formula	C40 H32 Au2 I2 N6
Formula weight	1244.45
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.3794(9) A alpha = 85.843(2) deg. b = 10.4522(10) A beta = 77.783(2) deg. c = 20.784(2) A gamma = 80.838(2) deg.
Volume	1964.5(3) A^3
Z, Calculated density	2, 2.104 Mg/m^3
Absorption coefficient	9.067 mm^-1
F(000)	1156
Crystal size	0.301 x 0.217 x 0.24 mm
Theta range for data collection	1.98 to 26.00 deg.
Limiting indices	-11<=h<=11, -12<=k<=7, -25<=l<=25
Reflections collected / unique	10847 / 7587 [R(int) = 0.0389]
Completeness to theta = 26.00	98.3 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.41456
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7587 / 0 / 455
Goodness-of-fit on F^2	1.005
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1129
R indices (all data)	R1 = 0.0554, wR2 = 0.1176
Largest diff. peak and hole	1.539 and -1.266 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd29663.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Au(1)	6090(1)	5025(1)	2242(1)	42(1)
Au(2)	6215(1)	1120(1)	1516(1)	46(1)
I(1)	3959(1)	6879(1)	2351(1)	66(1)
I(2)	7666(1)	191(1)	447(1)	100(1)
N(1)	8621(8)	3171(6)	1555(3)	44(2)
N(2)	8330(6)	2836(5)	2601(3)	32(1)
N(3)	3811(7)	2779(6)	2387(3)	39(1)
N(4)	5174(6)	1529(5)	2967(3)	31(1)
N(5)	7530(30)	5780(30)	-286(11)	246(15)
N(6)	-16(11)	5623(10)	2066(5)	84(3)
C(1)	7768(8)	3555(7)	2128(4)	37(2)
C(2)	9713(9)	2202(8)	1651(4)	45(2)
C(3)	10861(11)	1489(9)	1216(5)	60(2)
C(4)	11853(11)	642(9)	1482(5)	61(3)
C(5)	11750(10)	458(8)	2152(5)	59(2)
C(6)	10607(8)	1143(7)	2595(4)	43(2)
C(7)	9586(8)	1977(7)	2330(4)	37(2)
C(8)	8451(12)	3747(10)	913(4)	67(3)
C(9)	7792(7)	3025(6)	3286(3)	28(1)
C(10)	7819(8)	4291(6)	3501(4)	35(2)
C(11)	7321(8)	4579(7)	4135(4)	42(2)
C(12)	6831(8)	3625(7)	4609(4)	36(2)
C(13)	6313(9)	3892(9)	5283(4)	49(2)
C(14)	5819(10)	2983(9)	5733(4)	55(2)
C(15)	5813(9)	1714(8)	5525(4)	50(2)
C(16)	6298(8)	1428(8)	4886(4)	41(2)
C(17)	6798(7)	2366(7)	4414(3)	33(2)
C(18)	7288(7)	2076(6)	3721(3)	29(1)
C(19)	7240(7)	762(6)	3498(3)	28(1)
C(20)	8296(7)	-319(6)	3677(3)	29(1)
C(21)	9307(8)	-186(7)	4068(3)	38(2)
C(22)	10323(9)	-1185(8)	4184(4)	45(2)
C(23)	10398(10)	-2413(8)	3922(4)	52(2)
C(24)	9449(9)	-2563(7)	3540(4)	47(2)
C(25)	8354(8)	-1564(7)	3410(4)	37(2)
C(26)	7368(8)	-1708(7)	3022(4)	39(2)
C(27)	6300(8)	-693(7)	2890(4)	38(2)
C(28)	6269(7)	532(6)	3128(3)	29(1)
C(29)	5008(8)	1880(7)	2350(4)	35(2)
C(30)	3141(8)	2977(7)	3037(4)	38(2)
C(31)	1837(9)	3759(8)	3321(5)	54(2)
C(32)	1427(9)	3657(9)	3987(5)	60(2)
C(33)	2225(10)	2788(9)	4386(5)	60(2)
C(34)	3544(8)	2052(8)	4086(4)	45(2)
C(35)	3965(8)	2174(6)	3415(3)	33(2)
C(36)	3244(10)	3464(9)	1817(4)	54(2)
C(37)	6580(30)	6290(30)	-44(12)	174(10)
C(38)	5250(30)	7041(18)	322(10)	180(9)
C(39)	166(13)	6408(11)	1709(6)	75(3)
C(40)	510(30)	7412(17)	1217(10)	194(10)

Table 3. Bond lengths [A] and angles [deg] for cd29663.

Au(1)-C(1)	2.005(7)
Au(1)-I(1)	2.5376(7)
Au(2)-C(29)	2.000(7)
Au(2)-I(2)	2.5189(8)
N(1)-C(1)	1.335(10)
N(1)-C(2)	1.357(10)
N(1)-C(8)	1.453(10)
N(2)-C(1)	1.340(9)
N(2)-C(7)	1.404(9)
N(2)-C(9)	1.422(8)
N(3)-C(29)	1.336(9)
N(3)-C(30)	1.380(10)
N(3)-C(36)	1.491(10)
N(4)-C(29)	1.342(9)
N(4)-C(35)	1.416(9)
N(4)-C(28)	1.417(8)
N(5)-C(37)	1.01(3)
N(6)-C(39)	1.074(12)
C(2)-C(7)	1.395(11)
C(2)-C(3)	1.401(12)
C(3)-C(4)	1.356(14)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(13)
C(4)-H(4)	0.9300
C(5)-C(6)	1.395(11)
C(5)-H(5)	0.9300
C(6)-C(7)	1.367(11)
C(6)-H(6)	0.9300
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-C(18)	1.365(9)
C(9)-C(10)	1.434(9)
C(10)-C(11)	1.340(10)
C(10)-H(10)	0.9300
C(11)-C(12)	1.409(11)
C(11)-H(11)	0.9300
C(12)-C(17)	1.412(10)
C(12)-C(13)	1.415(10)
C(13)-C(14)	1.349(12)
C(13)-H(13)	0.9300
C(14)-C(15)	1.425(12)
C(14)-H(14)	0.9300
C(15)-C(16)	1.348(11)
C(15)-H(15)	0.9300
C(16)-C(17)	1.399(10)
C(16)-H(16)	0.9300
C(17)-C(18)	1.453(9)
C(18)-C(19)	1.491(9)
C(19)-C(28)	1.369(9)
C(19)-C(20)	1.461(9)
C(20)-C(21)	1.400(10)
C(20)-C(25)	1.440(10)
C(21)-C(22)	1.342(10)
C(21)-H(21)	0.9300
C(22)-C(23)	1.416(11)
C(22)-H(22)	0.9300
C(23)-C(24)	1.344(12)
C(23)-H(23)	0.9300
C(24)-C(25)	1.397(10)
C(24)-H(24)	0.9300
C(25)-C(26)	1.381(10)
C(26)-C(27)	1.393(10)
C(26)-H(26)	0.9300
C(27)-C(28)	1.400(9)
C(27)-H(27)	0.9300
C(30)-C(35)	1.368(10)
C(30)-C(31)	1.399(11)

C(31)-C(32)	1.357(13)
C(31)-H(31)	0.9300
C(32)-C(33)	1.418(13)
C(32)-H(32)	0.9300
C(33)-C(34)	1.397(11)
C(33)-H(33)	0.9300
C(34)-C(35)	1.369(11)
C(34)-H(34)	0.9300
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(37)-C(38)	1.46(2)
C(38)-H(38A)	0.9600
C(38)-H(38B)	0.9600
C(38)-H(38C)	0.9600
C(39)-C(40)	1.436(18)
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
C(1)-Au(1)-I(1)	178.3(2)
C(29)-Au(2)-I(2)	178.1(2)
C(1)-N(1)-C(2)	111.0(6)
C(1)-N(1)-C(8)	124.8(7)
C(2)-N(1)-C(8)	124.1(7)
C(1)-N(2)-C(7)	111.0(6)
C(1)-N(2)-C(9)	123.5(6)
C(7)-N(2)-C(9)	125.2(6)
C(29)-N(3)-C(30)	110.2(6)
C(29)-N(3)-C(36)	125.9(7)
C(30)-N(3)-C(36)	124.0(6)
C(29)-N(4)-C(35)	108.8(6)
C(29)-N(4)-C(28)	124.2(6)
C(35)-N(4)-C(28)	126.4(6)
N(1)-C(1)-N(2)	106.5(6)
N(1)-C(1)-Au(1)	125.7(5)
N(2)-C(1)-Au(1)	127.6(6)
N(1)-C(2)-C(7)	107.6(7)
N(1)-C(2)-C(3)	132.6(8)
C(7)-C(2)-C(3)	119.7(8)
C(4)-C(3)-C(2)	117.5(8)
C(4)-C(3)-H(3)	121.3
C(2)-C(3)-H(3)	121.3
C(3)-C(4)-C(5)	122.4(8)
C(3)-C(4)-H(4)	118.8
C(5)-C(4)-H(4)	118.8
C(4)-C(5)-C(6)	121.3(9)
C(4)-C(5)-H(5)	119.4
C(6)-C(5)-H(5)	119.4
C(7)-C(6)-C(5)	116.5(8)
C(7)-C(6)-H(6)	121.7
C(5)-C(6)-H(6)	121.7
C(6)-C(7)-C(2)	122.5(7)
C(6)-C(7)-N(2)	133.5(7)
C(2)-C(7)-N(2)	103.8(7)
N(1)-C(8)-H(8A)	109.5
N(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(18)-C(9)-N(2)	123.3(6)
C(18)-C(9)-C(10)	121.0(6)
N(2)-C(9)-C(10)	115.7(6)
C(11)-C(10)-C(9)	120.6(7)
C(11)-C(10)-H(10)	119.7
C(9)-C(10)-H(10)	119.7
C(10)-C(11)-C(12)	120.7(7)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-H(11)	119.6
C(11)-C(12)-C(17)	120.0(7)
C(11)-C(12)-C(13)	122.2(7)

C(17)-C(12)-C(13)	117.7(7)
C(14)-C(13)-C(12)	122.0(8)
C(14)-C(13)-H(13)	119.0
C(12)-C(13)-H(13)	119.0
C(13)-C(14)-C(15)	119.2(8)
C(13)-C(14)-H(14)	120.4
C(15)-C(14)-H(14)	120.4
C(16)-C(15)-C(14)	120.3(8)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	121.1(8)
C(15)-C(16)-H(16)	119.4
C(17)-C(16)-H(16)	119.4
C(16)-C(17)-C(12)	119.7(7)
C(16)-C(17)-C(18)	121.5(6)
C(12)-C(17)-C(18)	118.8(6)
C(9)-C(18)-C(17)	118.7(6)
C(9)-C(18)-C(19)	121.2(6)
C(17)-C(18)-C(19)	120.0(6)
C(28)-C(19)-C(20)	118.9(6)
C(28)-C(19)-C(18)	122.9(6)
C(20)-C(19)-C(18)	118.2(6)
C(21)-C(20)-C(25)	118.4(6)
C(21)-C(20)-C(19)	123.1(6)
C(25)-C(20)-C(19)	118.4(6)
C(22)-C(21)-C(20)	121.1(7)
C(22)-C(21)-H(21)	119.4
C(20)-C(21)-H(21)	119.4
C(21)-C(22)-C(23)	121.1(7)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(24)-C(23)-C(22)	119.0(7)
C(24)-C(23)-H(23)	120.5
C(22)-C(23)-H(23)	120.5
C(23)-C(24)-C(25)	122.5(7)
C(23)-C(24)-H(24)	118.8
C(25)-C(24)-H(24)	118.8
C(26)-C(25)-C(24)	123.0(7)
C(26)-C(25)-C(20)	119.0(6)
C(24)-C(25)-C(20)	117.9(7)
C(25)-C(26)-C(27)	122.1(7)
C(25)-C(26)-H(26)	119.0
C(27)-C(26)-H(26)	119.0
C(26)-C(27)-C(28)	119.2(7)
C(26)-C(27)-H(27)	120.4
C(28)-C(27)-H(27)	120.4
C(19)-C(28)-C(27)	122.1(6)
C(19)-C(28)-N(4)	121.4(6)
C(27)-C(28)-N(4)	116.5(6)
N(3)-C(29)-N(4)	107.8(6)
N(3)-C(29)-Au(2)	124.9(5)
N(4)-C(29)-Au(2)	127.1(5)
C(35)-C(30)-N(3)	107.1(6)
C(35)-C(30)-C(31)	121.5(8)
N(3)-C(30)-C(31)	131.3(7)
C(32)-C(31)-C(30)	116.3(8)
C(32)-C(31)-H(31)	121.9
C(30)-C(31)-H(31)	121.9
C(31)-C(32)-C(33)	123.3(8)
C(31)-C(32)-H(32)	118.4
C(33)-C(32)-H(32)	118.4
C(34)-C(33)-C(32)	118.6(9)
C(34)-C(33)-H(33)	120.7
C(32)-C(33)-H(33)	120.7
C(35)-C(34)-C(33)	117.8(8)
C(35)-C(34)-H(34)	121.1
C(33)-C(34)-H(34)	121.1
C(30)-C(35)-C(34)	122.4(7)
C(30)-C(35)-N(4)	105.9(6)
C(34)-C(35)-N(4)	131.6(7)
N(3)-C(36)-H(36A)	109.5
N(3)-C(36)-H(36B)	109.5

H(36A)-C(36)-H(36B)	109.5
N(3)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
N(5)-C(37)-C(38)	178(4)
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.4
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
N(6)-C(39)-C(40)	176.2(16)
C(39)-C(40)-H(40A)	109.5
C(39)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(39)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd29663.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Au(1)	46(1)	38(1)	43(1)	3(1)	-14(1)	-3(1)
Au(2)	50(1)	57(1)	30(1)	-9(1)	-6(1)	-2(1)
I(1)	69(1)	49(1)	84(1)	-16(1)	-35(1)	10(1)
I(2)	116(1)	120(1)	50(1)	-34(1)	3(1)	12(1)
N(1)	56(4)	50(4)	25(3)	0(3)	-6(3)	-7(3)
N(2)	34(3)	29(3)	29(3)	0(2)	0(2)	-4(2)
N(3)	36(3)	41(3)	42(4)	1(3)	-14(3)	-5(3)
N(4)	31(3)	32(3)	29(3)	-5(2)	-5(2)	-4(2)
N(5)	180(20)	350(30)	126(17)	89(19)	-6(14)	110(20)
N(6)	82(7)	76(6)	92(8)	8(6)	-11(6)	-18(5)
C(1)	40(4)	36(4)	35(4)	5(3)	-12(3)	-7(3)
C(2)	57(5)	42(4)	35(4)	-8(3)	-4(4)	-8(4)
C(3)	73(6)	65(6)	37(5)	-14(4)	15(4)	-22(5)
C(4)	57(6)	53(5)	62(6)	-25(5)	12(5)	0(5)
C(5)	48(5)	44(5)	74(7)	-12(4)	7(5)	0(4)
C(6)	43(4)	34(4)	48(5)	-2(3)	-2(4)	0(3)
C(7)	39(4)	29(4)	37(4)	-10(3)	6(3)	-3(3)
C(8)	90(7)	77(7)	31(5)	8(4)	-8(5)	-9(6)
C(9)	26(3)	28(3)	26(3)	-4(3)	-5(3)	4(3)
C(10)	33(4)	30(4)	42(4)	-4(3)	-6(3)	-4(3)
C(11)	39(4)	31(4)	55(5)	-14(3)	-9(4)	3(3)
C(12)	30(4)	40(4)	34(4)	-9(3)	-5(3)	7(3)
C(13)	48(5)	60(5)	37(5)	-23(4)	-10(4)	5(4)
C(14)	53(5)	77(6)	33(5)	-15(4)	-6(4)	-1(5)
C(15)	52(5)	60(5)	30(4)	3(4)	-1(4)	3(4)
C(16)	42(4)	42(4)	34(4)	-3(3)	-3(3)	2(3)
C(17)	31(3)	40(4)	24(4)	-5(3)	-5(3)	4(3)
C(18)	29(3)	28(3)	28(4)	-5(3)	-3(3)	-3(3)
C(19)	30(3)	25(3)	25(3)	-2(3)	-1(3)	1(3)
C(20)	34(3)	31(3)	21(3)	-1(3)	-2(3)	-2(3)
C(21)	43(4)	41(4)	26(4)	-1(3)	-5(3)	-1(3)
C(22)	43(4)	54(5)	38(4)	5(4)	-14(4)	-1(4)
C(23)	56(5)	39(4)	56(5)	-3(4)	-15(4)	15(4)
C(24)	50(5)	24(4)	60(5)	-6(3)	-4(4)	4(3)
C(25)	36(4)	34(4)	37(4)	-2(3)	1(3)	-4(3)
C(26)	45(4)	26(4)	45(5)	-9(3)	0(4)	-10(3)
C(27)	43(4)	37(4)	35(4)	-11(3)	-1(3)	-15(3)
C(28)	31(3)	29(3)	24(3)	3(3)	-1(3)	-7(3)
C(29)	42(4)	33(4)	33(4)	-5(3)	-11(3)	-9(3)
C(30)	32(4)	37(4)	49(5)	-3(3)	-12(3)	-6(3)
C(31)	43(5)	53(5)	64(6)	-18(4)	-16(4)	11(4)
C(32)	34(4)	61(6)	78(7)	-25(5)	-3(4)	12(4)
C(33)	47(5)	74(6)	54(6)	-22(5)	1(4)	2(5)
C(34)	33(4)	45(4)	55(5)	-11(4)	-6(4)	1(3)
C(35)	39(4)	29(3)	32(4)	-8(3)	-7(3)	-9(3)
C(36)	59(5)	67(6)	40(5)	3(4)	-22(4)	-6(5)
C(37)	190(30)	190(20)	107(18)	52(16)	-24(17)	52(19)
C(38)	240(30)	160(20)	140(20)	-13(16)	-70(20)	4(19)
C(39)	79(8)	65(7)	77(8)	-1(6)	-17(6)	-1(6)
C(40)	250(30)	141(16)	210(20)	97(16)	-90(20)	-75(17)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd29663.

	x	y	z	U(eq)
H(3)	10940	1593	763	73
H(4)	12632	169	1201	73
H(5)	12457	-134	2311	70
H(6)	10542	1037	3048	52
H(8A)	7488	4248	949	101
H(8B)	8564	3073	608	101
H(8C)	9187	4300	758	101
H(10)	8186	4919	3199	42
H(11)	7299	5417	4264	51
H(13)	6313	4720	5420	58
H(14)	5487	3181	6173	66
H(15)	5473	1081	5831	60
H(16)	6301	594	4758	49
H(21)	9274	608	4249	45
H(22)	10990	-1069	4441	54
H(23)	11092	-3105	4012	63
H(24)	9524	-3362	3356	56
H(26)	7419	-2508	2842	47
H(27)	5615	-827	2646	45
H(31)	1281	4317	3067	65
H(32)	581	4183	4191	72
H(33)	1877	2709	4838	72
H(34)	4118	1498	4333	54
H(36A)	4059	3626	1471	82
H(36B)	2652	4272	1953	82
H(36C)	2655	2933	1658	82
H(38A)	4944	7783	56	269
H(38B)	5448	7324	719	269
H(38C)	4478	6511	432	269
H(40A)	1555	7338	1068	291
H(40B)	134	8244	1403	291
H(40C)	54	7324	852	291

Table 6. Torsion angles [deg] for cd29663.

C(2)-N(1)-C(1)-N(2)	0.9(8)
C(8)-N(1)-C(1)-N(2)	-176.6(8)
C(2)-N(1)-C(1)-Au(1)	176.2(5)
C(8)-N(1)-C(1)-Au(1)	-1.3(11)
C(7)-N(2)-C(1)-N(1)	0.7(8)
C(9)-N(2)-C(1)-N(1)	175.0(6)
C(7)-N(2)-C(1)-Au(1)	-174.5(5)
C(9)-N(2)-C(1)-Au(1)	-0.2(10)
I(1)-Au(1)-C(1)-N(1)	24(8)
I(1)-Au(1)-C(1)-N(2)	-162(7)
C(1)-N(1)-C(2)-C(7)	-2.1(9)
C(8)-N(1)-C(2)-C(7)	175.5(8)
C(1)-N(1)-C(2)-C(3)	179.8(9)
C(8)-N(1)-C(2)-C(3)	-2.6(15)
N(1)-C(2)-C(3)-C(4)	174.7(9)
C(7)-C(2)-C(3)-C(4)	-3.2(13)
C(2)-C(3)-C(4)-C(5)	0.9(14)
C(3)-C(4)-C(5)-C(6)	0.0(15)
C(4)-C(5)-C(6)-C(7)	1.4(13)
C(5)-C(6)-C(7)-C(2)	-3.8(12)
C(5)-C(6)-C(7)-N(2)	-178.3(7)
N(1)-C(2)-C(7)-C(6)	-173.6(7)
C(3)-C(2)-C(7)-C(6)	4.8(12)
N(1)-C(2)-C(7)-N(2)	2.3(8)
C(3)-C(2)-C(7)-N(2)	-179.3(7)
C(1)-N(2)-C(7)-C(6)	173.3(8)
C(9)-N(2)-C(7)-C(6)	-0.9(13)
C(1)-N(2)-C(7)-C(2)	-1.9(8)
C(9)-N(2)-C(7)-C(2)	-176.1(6)
C(1)-N(2)-C(9)-C(18)	122.6(7)
C(7)-N(2)-C(9)-C(18)	-63.9(9)
C(1)-N(2)-C(9)-C(10)	-57.9(9)
C(7)-N(2)-C(9)-C(10)	115.6(7)
C(18)-C(9)-C(10)-C(11)	-1.3(10)
N(2)-C(9)-C(10)-C(11)	179.2(6)
C(9)-C(10)-C(11)-C(12)	3.3(11)
C(10)-C(11)-C(12)-C(17)	-2.9(10)
C(10)-C(11)-C(12)-C(13)	179.3(7)
C(11)-C(12)-C(13)-C(14)	178.8(7)
C(17)-C(12)-C(13)-C(14)	0.9(11)
C(12)-C(13)-C(14)-C(15)	-0.2(12)
C(13)-C(14)-C(15)-C(16)	0.1(13)
C(14)-C(15)-C(16)-C(17)	-0.8(12)
C(15)-C(16)-C(17)-C(12)	1.6(11)
C(15)-C(16)-C(17)-C(18)	-178.4(7)
C(11)-C(12)-C(17)-C(16)	-179.5(6)
C(13)-C(12)-C(17)-C(16)	-1.6(10)
C(11)-C(12)-C(17)-C(18)	0.5(10)
C(13)-C(12)-C(17)-C(18)	178.4(6)
N(2)-C(9)-C(18)-C(17)	178.5(6)
C(10)-C(9)-C(18)-C(17)	-1.0(9)
N(2)-C(9)-C(18)-C(19)	-1.3(10)
C(10)-C(9)-C(18)-C(19)	179.3(6)
C(16)-C(17)-C(18)-C(9)	-178.6(6)
C(12)-C(17)-C(18)-C(9)	1.3(9)
C(16)-C(17)-C(18)-C(19)	1.1(10)
C(12)-C(17)-C(18)-C(19)	-178.9(6)
C(9)-C(18)-C(19)-C(28)	-70.4(9)
C(17)-C(18)-C(19)-C(28)	109.8(8)
C(9)-C(18)-C(19)-C(20)	108.7(7)
C(17)-C(18)-C(19)-C(20)	-71.1(8)
C(28)-C(19)-C(20)-C(21)	-178.4(6)
C(18)-C(19)-C(20)-C(21)	2.5(10)
C(28)-C(19)-C(20)-C(25)	5.1(9)
C(18)-C(19)-C(20)-C(25)	-174.0(6)
C(25)-C(20)-C(21)-C(22)	1.0(11)
C(19)-C(20)-C(21)-C(22)	-175.5(7)
C(20)-C(21)-C(22)-C(23)	-0.7(12)

C(21)-C(22)-C(23)-C(24)	1.3(13)
C(22)-C(23)-C(24)-C(25)	-2.3(13)
C(23)-C(24)-C(25)-C(26)	-179.7(8)
C(23)-C(24)-C(25)-C(20)	2.6(12)
C(21)-C(20)-C(25)-C(26)	-179.7(7)
C(19)-C(20)-C(25)-C(26)	-3.0(10)
C(21)-C(20)-C(25)-C(24)	-1.9(10)
C(19)-C(20)-C(25)-C(24)	174.8(6)
C(24)-C(25)-C(26)-C(27)	-179.0(7)
C(20)-C(25)-C(26)-C(27)	-1.2(11)
C(25)-C(26)-C(27)-C(28)	3.5(11)
C(20)-C(19)-C(28)-C(27)	-3.0(10)
C(18)-C(19)-C(28)-C(27)	176.0(6)
C(20)-C(19)-C(28)-N(4)	176.9(6)
C(18)-C(19)-C(28)-N(4)	-4.1(10)
C(26)-C(27)-C(28)-C(19)	-1.2(10)
C(26)-C(27)-C(28)-N(4)	178.9(6)
C(29)-N(4)-C(28)-C(19)	124.2(7)
C(35)-N(4)-C(28)-C(19)	-65.8(9)
C(29)-N(4)-C(28)-C(27)	-55.9(9)
C(35)-N(4)-C(28)-C(27)	114.1(7)
C(30)-N(3)-C(29)-N(4)	-2.9(8)
C(36)-N(3)-C(29)-N(4)	178.2(7)
C(30)-N(3)-C(29)-Au(2)	172.8(5)
C(36)-N(3)-C(29)-Au(2)	-6.1(10)
C(35)-N(4)-C(29)-N(3)	4.2(8)
C(28)-N(4)-C(29)-N(3)	175.7(6)
C(35)-N(4)-C(29)-Au(2)	-171.4(5)
C(28)-N(4)-C(29)-Au(2)	0.1(10)
I(2)-Au(2)-C(29)-N(3)	-16(7)
I(2)-Au(2)-C(29)-N(4)	159(6)
C(29)-N(3)-C(30)-C(35)	0.4(8)
C(36)-N(3)-C(30)-C(35)	179.4(7)
C(29)-N(3)-C(30)-C(31)	-176.3(8)
C(36)-N(3)-C(30)-C(31)	2.6(13)
C(35)-C(30)-C(31)-C(32)	-1.1(12)
N(3)-C(30)-C(31)-C(32)	175.2(8)
C(30)-C(31)-C(32)-C(33)	-1.9(14)
C(31)-C(32)-C(33)-C(34)	3.8(15)
C(32)-C(33)-C(34)-C(35)	-2.6(13)
N(3)-C(30)-C(35)-C(34)	-174.9(7)
C(31)-C(30)-C(35)-C(34)	2.3(12)
N(3)-C(30)-C(35)-N(4)	2.1(8)
C(31)-C(30)-C(35)-N(4)	179.2(7)
C(33)-C(34)-C(35)-C(30)	-0.3(11)
C(33)-C(34)-C(35)-N(4)	-176.3(7)
C(29)-N(4)-C(35)-C(30)	-3.9(8)
C(28)-N(4)-C(35)-C(30)	-175.1(6)
C(29)-N(4)-C(35)-C(34)	172.6(8)
C(28)-N(4)-C(35)-C(34)	1.4(12)

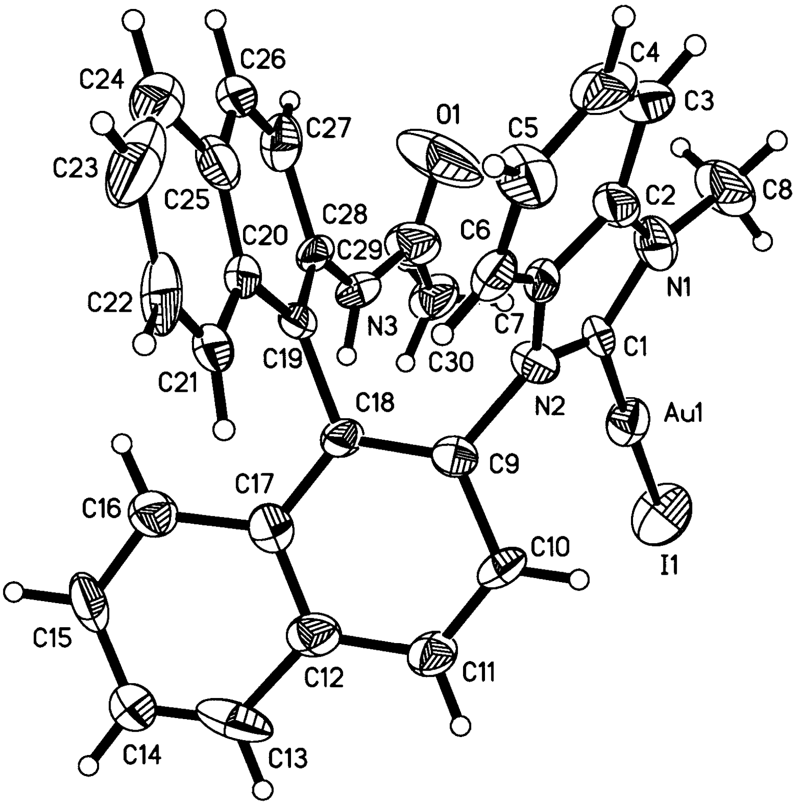
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd29663 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(38)-H(38A)...I(2)#1	0.96	3.27	4.13(2)	150.3
C(3)-H(3)...I(2)#2	0.93	3.17	3.877(9)	134.8
C(14)-H(14)...I(1)#3	0.93	3.21	4.046(8)	150.3
C(5)-H(5)...I(1)#4	0.93	3.22	4.017(9)	145.2

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z #2 -x+2,-y,-z #3 -x+1,-y+1,-z+1
#4 x+1,y-1,z

(H) X-ray Crystal Data of Complex 2a.



The crystal data of **2a** have been deposited in CCDC with number 757529. Empirical Formula: $C_{32}H_{27}AuCl_4IN_3O$; Formula Weight: 935.23; Crystal Color, Habit: colorless, prismatic; Crystal Dimensions: 0.303 x 0.122 x 0.105 mm; Crystal System: Orthorhombic; Lattice Type: Primitive; Lattice Parameters: a = 7.6150(13)Å, b = 14.252(2)Å, c = 30.775(5)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 3340.1(10)$Å^3$; Space group: P2(1)2(1)2(1); Z = 4; D_{calc}= 1.860 g/cm^3; F_{000} = 1792; Diffractometer: Bruker Smart CCD; Residuals: R; Rw: 0.0635, 0.1464.

Table 1. Crystal data and structure refinement for cd29609.

Identification code	cd29609
Empirical formula	C32 H27 Au Cl4 I N3 O
Formula weight	935.23
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 7.6150(13) A alpha = 90 deg. b = 14.252(2) A beta = 90 deg. c = 30.775(5) A gamma = 90 deg.
Volume	3340.1(10) A^3
Z, Calculated density	4, 1.860 Mg/m^3
Absorption coefficient	5.679 mm^-1
F(000)	1792
Crystal size	0.303 x 0.122 x 0.105 mm
Theta range for data collection	1.57 to 25.50 deg.
Limiting indices	-9<=h<=9, -17<=k<=15, -33<=l<=37
Reflections collected / unique	17758 / 6198 [R(int) = 0.0969]
Completeness to theta = 25.50	99.8 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.54235
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6198 / 2 / 366
Goodness-of-fit on F^2	0.919
Final R indices [I>2sigma(I)]	R1 = 0.0635, wR2 = 0.1464
R indices (all data)	R1 = 0.1010, wR2 = 0.1600
Absolute structure parameter	0.044(13)
Largest diff. peak and hole	1.144 and -1.043 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd29609.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Au(1)	8761(1)	3685(1)	1624(1)	60(1)
I(1)	9053(2)	3333(1)	2416(1)	103(1)
N(1)	8800(20)	3291(8)	662(4)	59(3)
N(2)	8330(17)	4748(8)	785(4)	50(3)
N(3)	4233(15)	4369(9)	1192(4)	55(3)
O(1)	4000(40)	2899(9)	1045(5)	160(9)
Cl(1)	6095(12)	5527(6)	2354(3)	183(4)
Cl(2)	2439(11)	5613(6)	2160(3)	151(3)
Cl(3)	2148(19)	5573(10)	3379(4)	255(6)
Cl(4)	-1450(30)	5521(12)	3507(5)	223(8)
C(1)	8520(19)	3951(9)	976(5)	46(4)
C(2)	8600(20)	3727(11)	274(6)	64(4)
C(3)	8730(20)	3391(12)	-171(6)	76(5)
C(4)	8700(30)	3988(14)	-486(5)	77(5)
C(5)	8560(30)	4954(13)	-410(5)	77(5)
C(6)	8386(18)	5297(12)	1(5)	59(4)
C(7)	8358(17)	4636(10)	344(5)	51(4)
C(8)	8920(30)	2277(10)	760(6)	94(6)
C(9)	7888(19)	5620(10)	1026(4)	45(3)
C(10)	9227(18)	5991(10)	1313(4)	49(4)
C(11)	8850(20)	6758(11)	1547(4)	60(4)
C(12)	7130(20)	7197(11)	1515(5)	63(5)
C(13)	6570(40)	7992(13)	1780(5)	94(8)
C(14)	5110(30)	8398(14)	1755(6)	80(6)
C(15)	3880(30)	8054(11)	1463(5)	81(5)
C(16)	4200(20)	7287(11)	1219(5)	62(4)
C(17)	5860(20)	6816(10)	1249(5)	52(4)
C(18)	6270(20)	6033(9)	987(4)	45(3)
C(19)	4931(19)	5613(9)	690(4)	41(3)
C(20)	4650(18)	6027(10)	276(5)	47(4)
C(21)	5405(19)	6897(11)	159(5)	61(5)
C(22)	5250(30)	7258(13)	-289(6)	80(6)
C(23)	4220(30)	6750(20)	-598(7)	130(11)
C(24)	3400(30)	5990(13)	-485(6)	68(5)
C(25)	3700(30)	5588(11)	-31(6)	70(5)
C(26)	2770(20)	4737(14)	88(6)	74(6)
C(27)	2960(20)	4379(13)	474(6)	67(5)
C(28)	4083(17)	4789(11)	791(4)	45(4)
C(29)	4100(30)	3458(12)	1329(6)	75(5)
C(30)	4150(20)	3240(12)	1775(5)	78(6)
C(31)	4200(30)	6199(18)	2357(7)	123(9)
C(32)	130(30)	5810(30)	3115(9)	223(17)

Table 3. Bond lengths [A] and angles [deg] for cd29609.

Au(1)-C(1)	2.038(14)
Au(1)-I(1)	2.5005(14)
N(1)-C(2)	1.354(19)
N(1)-C(1)	1.365(17)
N(1)-C(8)	1.481(18)
N(2)-C(1)	1.286(16)
N(2)-C(7)	1.369(19)
N(2)-C(9)	1.487(18)
N(3)-C(29)	1.369(19)
N(3)-C(28)	1.377(17)
N(3)-H(3A)	0.8600
O(1)-C(29)	1.186(19)
Cl(1)-C(31)	1.73(2)
Cl(2)-C(31)	1.69(3)
Cl(3)-C(32)	1.772(18)
Cl(4)-C(32)	1.750(18)
C(2)-C(7)	1.33(2)
C(2)-C(3)	1.45(2)
C(3)-C(4)	1.29(2)
C(3)-H(3)	0.9300
C(4)-C(5)	1.40(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.36(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.41(2)
C(6)-H(6)	0.9300
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-C(18)	1.37(2)
C(9)-C(10)	1.448(18)
C(10)-C(11)	1.339(19)
C(10)-H(10)	0.9300
C(11)-C(12)	1.45(2)
C(11)-H(11)	0.9300
C(12)-C(17)	1.38(2)
C(12)-C(13)	1.46(2)
C(13)-C(14)	1.25(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.39(2)
C(14)-H(14)	0.9300
C(15)-C(16)	1.35(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.44(2)
C(16)-H(16)	0.9300
C(17)-C(18)	1.411(19)
C(18)-C(19)	1.496(19)
C(19)-C(28)	1.377(19)
C(19)-C(20)	1.419(19)
C(20)-C(25)	1.34(2)
C(20)-C(21)	1.41(2)
C(21)-C(22)	1.48(2)
C(21)-H(21)	0.9300
C(22)-C(23)	1.43(3)
C(22)-H(22)	0.9300
C(23)-C(24)	1.29(3)
C(23)-H(23)	0.9300
C(24)-C(25)	1.53(2)
C(24)-H(24)	0.9300
C(25)-C(26)	1.45(3)
C(26)-C(27)	1.30(2)
C(26)-H(26)	0.9300
C(27)-C(28)	1.42(2)
C(27)-H(27)	0.9300
C(29)-C(30)	1.41(2)
C(30)-H(30A)	0.9600
C(30)-H(30B)	0.9600
C(30)-H(30C)	0.9600

C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-H(32A)	0.9700
C(32)-H(32B)	0.9700
C(1)-Au(1)-I(1)	179.1(4)
C(2)-N(1)-C(1)	106.9(12)
C(2)-N(1)-C(8)	129.5(14)
C(1)-N(1)-C(8)	122.4(13)
C(1)-N(2)-C(7)	110.4(13)
C(1)-N(2)-C(9)	122.5(12)
C(7)-N(2)-C(9)	126.6(12)
C(29)-N(3)-C(28)	133.1(14)
C(29)-N(3)-H(3A)	113.5
C(28)-N(3)-H(3A)	113.5
N(2)-C(1)-N(1)	107.6(12)
N(2)-C(1)-Au(1)	128.3(10)
N(1)-C(1)-Au(1)	123.5(10)
C(7)-C(2)-N(1)	108.7(14)
C(7)-C(2)-C(3)	118.9(17)
N(1)-C(2)-C(3)	132.2(15)
C(4)-C(3)-C(2)	119.4(16)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(3)-C(4)-C(5)	121.6(15)
C(3)-C(4)-H(4)	119.2
C(5)-C(4)-H(4)	119.2
C(6)-C(5)-C(4)	121.0(15)
C(6)-C(5)-H(5)	119.5
C(4)-C(5)-H(5)	119.5
C(5)-C(6)-C(7)	117.0(16)
C(5)-C(6)-H(6)	121.5
C(7)-C(6)-H(6)	121.5
C(2)-C(7)-N(2)	106.0(14)
C(2)-C(7)-C(6)	121.9(16)
N(2)-C(7)-C(6)	131.6(14)
N(1)-C(8)-H(8A)	109.5
N(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(1)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(18)-C(9)-C(10)	122.0(13)
C(18)-C(9)-N(2)	121.3(12)
C(10)-C(9)-N(2)	116.7(13)
C(11)-C(10)-C(9)	118.3(14)
C(11)-C(10)-H(10)	120.8
C(9)-C(10)-H(10)	120.8
C(10)-C(11)-C(12)	120.6(14)
C(10)-C(11)-H(11)	119.7
C(12)-C(11)-H(11)	119.7
C(17)-C(12)-C(11)	120.1(15)
C(17)-C(12)-C(13)	115.4(18)
C(11)-C(12)-C(13)	124.3(17)
C(14)-C(13)-C(12)	126(2)
C(14)-C(13)-H(13)	117.0
C(12)-C(13)-H(13)	117.0
C(13)-C(14)-C(15)	118.3(18)
C(13)-C(14)-H(14)	120.9
C(15)-C(14)-H(14)	120.9
C(16)-C(15)-C(14)	121.7(18)
C(16)-C(15)-H(15)	119.2
C(14)-C(15)-H(15)	119.2
C(15)-C(16)-C(17)	120.1(17)
C(15)-C(16)-H(16)	120.0
C(17)-C(16)-H(16)	120.0
C(12)-C(17)-C(18)	119.8(15)
C(12)-C(17)-C(16)	118.3(15)
C(18)-C(17)-C(16)	121.7(15)
C(9)-C(18)-C(17)	119.1(13)
C(9)-C(18)-C(19)	119.6(12)
C(17)-C(18)-C(19)	121.1(14)

C(28)-C(19)-C(20)	119.1(13)
C(28)-C(19)-C(18)	121.5(12)
C(20)-C(19)-C(18)	119.1(13)
C(25)-C(20)-C(21)	116.7(15)
C(25)-C(20)-C(19)	121.2(15)
C(21)-C(20)-C(19)	122.1(14)
C(20)-C(21)-C(22)	120.6(16)
C(20)-C(21)-H(21)	119.7
C(22)-C(21)-H(21)	119.7
C(23)-C(22)-C(21)	119(2)
C(23)-C(22)-H(22)	120.4
C(21)-C(22)-H(22)	120.4
C(24)-C(23)-C(22)	121(2)
C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7
C(23)-C(24)-C(25)	119(2)
C(23)-C(24)-H(24)	120.4
C(25)-C(24)-H(24)	120.4
C(20)-C(25)-C(26)	118.2(16)
C(20)-C(25)-C(24)	123.2(16)
C(26)-C(25)-C(24)	118.2(18)
C(27)-C(26)-C(25)	120.3(17)
C(27)-C(26)-H(26)	119.8
C(25)-C(26)-H(26)	119.8
C(26)-C(27)-C(28)	122.1(18)
C(26)-C(27)-H(27)	118.9
C(28)-C(27)-H(27)	118.9
C(19)-C(28)-N(3)	122.4(12)
C(19)-C(28)-C(27)	118.5(14)
N(3)-C(28)-C(27)	119.1(15)
O(1)-C(29)-N(3)	114.4(17)
O(1)-C(29)-C(30)	125.0(17)
N(3)-C(29)-C(30)	120.5(16)
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
Cl(2)-C(31)-Cl(1)	112.7(15)
Cl(2)-C(31)-H(31A)	109.0
Cl(1)-C(31)-H(31A)	109.0
Cl(2)-C(31)-H(31B)	109.0
Cl(1)-C(31)-H(31B)	109.0
H(31A)-C(31)-H(31B)	107.8
Cl(4)-C(32)-Cl(3)	103.7(16)
Cl(4)-C(32)-H(32A)	111.0
Cl(3)-C(32)-H(32A)	111.0
Cl(4)-C(32)-H(32B)	111.0
Cl(3)-C(32)-H(32B)	111.0
H(32A)-C(32)-H(32B)	109.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd29609.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Au(1)	53(1)	59(1)	69(1)	10(1)	-4(1)	2(1)
I(1)	103(1)	125(1)	81(1)	29(1)	-12(1)	-2(1)
N(1)	62(8)	40(7)	74(8)	10(7)	9(9)	9(8)
N(2)	69(10)	39(7)	41(7)	-2(6)	-5(6)	3(6)
N(3)	42(8)	56(8)	66(8)	-9(7)	-13(6)	-12(6)
O(1)	320(30)	45(8)	117(12)	-15(8)	-26(17)	6(15)
Cl(1)	123(6)	157(7)	270(10)	71(7)	-16(7)	-5(7)
Cl(2)	143(7)	158(8)	153(7)	-50(5)	-15(5)	18(5)
C(1)	39(8)	39(8)	59(8)	-14(7)	0(7)	13(7)
C(2)	43(8)	46(9)	103(13)	-25(10)	4(10)	-8(10)
C(3)	56(10)	75(12)	98(13)	-34(11)	-16(12)	-10(11)
C(4)	85(12)	108(16)	38(8)	-2(9)	-21(10)	-1(14)
C(5)	106(15)	86(13)	38(9)	3(8)	5(10)	23(14)
C(6)	38(10)	73(11)	67(11)	-2(9)	-11(8)	3(8)
C(7)	27(8)	44(9)	83(12)	-12(8)	-5(7)	4(6)
C(8)	115(17)	40(10)	129(16)	-13(10)	6(16)	-5(12)
C(9)	51(9)	44(9)	39(8)	-1(7)	2(7)	-4(7)
C(10)	44(9)	59(9)	45(8)	10(7)	-18(7)	-13(7)
C(11)	57(9)	79(10)	42(8)	-13(8)	-8(9)	2(10)
C(12)	74(11)	43(10)	72(12)	9(8)	-16(9)	-15(8)
C(13)	161(3)	58(12)	60(11)	-25(9)	0(13)	-25(14)
C(14)	67(12)	70(14)	105(16)	-32(11)	-15(11)	14(10)
C(15)	86(13)	60(11)	97(13)	-15(9)	-3(13)	40(11)
C(16)	54(11)	64(11)	67(10)	-15(8)	5(8)	-1(8)
C(17)	49(11)	46(9)	62(9)	5(8)	11(8)	-2(7)
C(18)	29(6)	53(9)	55(8)	-11(6)	3(8)	-7(8)
C(19)	50(8)	36(8)	37(8)	-9(7)	-9(7)	10(7)
C(20)	33(8)	45(9)	61(10)	-9(7)	-3(7)	8(6)
C(21)	43(9)	58(11)	82(12)	-26(9)	-2(8)	16(8)
C(22)	85(13)	77(13)	77(12)	47(10)	2(11)	43(11)
C(23)	85(19)	230(30)	73(15)	-10(19)	-18(13)	70(20)
C(24)	65(14)	75(13)	65(12)	3(9)	-4(9)	4(10)
C(25)	62(11)	46(9)	101(13)	-14(9)	2(12)	15(11)
C(26)	49(10)	76(14)	99(15)	-47(12)	-21(10)	22(9)
C(27)	43(9)	73(13)	86(13)	6(11)	7(9)	11(8)
C(28)	22(8)	70(10)	44(8)	-21(8)	-1(6)	5(7)
C(29)	89(14)	53(12)	84(12)	0(10)	-13(11)	-17(10)
C(30)	84(14)	61(11)	87(12)	16(9)	-38(10)	-4(10)
C(31)	110(20)	170(20)	90(14)	11(16)	29(13)	50(20)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd29609.

	x	y	z	U(eq)
H(3A)	4455	4758	1399	66
H(3)	8824	2753	-228	91
H(4)	8785	3772	-771	92
H(5)	8581	5367	-644	92
H(6)	8291	5938	54	71
H(8A)	7762	2023	795	142
H(8B)	9576	2189	1024	142
H(8C)	9505	1960	526	142
H(10)	10321	5705	1334	59
H(11)	9695	7012	1731	72
H(13)	7356	8216	1986	112
H(14)	4866	8916	1928	96
H(15)	2809	8361	1435	97
H(16)	3341	7062	1031	74
H(21)	6006	7246	367	73
H(22)	5812	7810	-370	96
H(23)	4132	6963	-882	156
H(24)	2643	5694	-678	82
H(26)	2040	4446	-112	89
H(27)	2344	3837	545	80
H(30A)	3087	2920	1855	117
H(30B)	4249	3809	1940	117
H(30C)	5139	2844	1833	117
H(31A)	3957	6397	2652	148
H(31B)	4392	6757	2183	148
H(32A)	42	6461	3032	267
H(32B)	-6	5419	2858	267

Table 6. Torsion angles [deg] for cd29609.

C(7)-N(2)-C(1)-N(1)	4.1(17)
C(9)-N(2)-C(1)-N(1)	176.0(13)
C(7)-N(2)-C(1)-Au(1)	175.1(10)
C(9)-N(2)-C(1)-Au(1)	-13(2)
C(2)-N(1)-C(1)-N(2)	-5.9(18)
C(8)-N(1)-C(1)-N(2)	-174.6(17)
C(2)-N(1)-C(1)-Au(1)	-177.4(11)
C(8)-N(1)-C(1)-Au(1)	14(2)
I(1)-Au(1)-C(1)-N(2)	172(25)
I(1)-Au(1)-C(1)-N(1)	-18(27)
C(1)-N(1)-C(2)-C(7)	5.5(19)
C(8)-N(1)-C(2)-C(7)	173.1(18)
C(1)-N(1)-C(2)-C(3)	-179.8(17)
C(8)-N(1)-C(2)-C(3)	-12(3)
C(7)-C(2)-C(3)-C(4)	4(3)
N(1)-C(2)-C(3)-C(4)	-170.5(19)
C(2)-C(3)-C(4)-C(5)	0(3)
C(3)-C(4)-C(5)-C(6)	-2(3)
C(4)-C(5)-C(6)-C(7)	0(3)
N(1)-C(2)-C(7)-N(2)	-3.0(18)
C(3)-C(2)-C(7)-N(2)	-178.5(14)
N(1)-C(2)-C(7)-C(6)	169.7(13)
C(3)-C(2)-C(7)-C(6)	-6(2)
C(1)-N(2)-C(7)-C(2)	-0.7(17)
C(9)-N(2)-C(7)-C(2)	-172.2(14)
C(1)-N(2)-C(7)-C(6)	-172.4(14)
C(9)-N(2)-C(7)-C(6)	16(2)
C(5)-C(6)-C(7)-C(2)	4(2)
C(5)-C(6)-C(7)-N(2)	174.6(15)
C(1)-N(2)-C(9)-C(18)	-109.6(17)
C(7)-N(2)-C(9)-C(18)	61(2)
C(1)-N(2)-C(9)-C(10)	68.6(18)
C(7)-N(2)-C(9)-C(10)	-120.9(15)
C(18)-C(9)-C(10)-C(11)	0(2)
N(2)-C(9)-C(10)-C(11)	-177.7(12)
C(9)-C(10)-C(11)-C(12)	1(2)
C(10)-C(11)-C(12)-C(17)	1(2)
C(10)-C(11)-C(12)-C(13)	175.4(15)
C(17)-C(12)-C(13)-C(14)	-7(3)
C(11)-C(12)-C(13)-C(14)	178(2)
C(12)-C(13)-C(14)-C(15)	3(3)
C(13)-C(14)-C(15)-C(16)	2(3)
C(14)-C(15)-C(16)-C(17)	-2(3)
C(11)-C(12)-C(17)-C(18)	-4(2)
C(13)-C(12)-C(17)-C(18)	-178.7(14)
C(11)-C(12)-C(17)-C(16)	-178.4(14)
C(13)-C(12)-C(17)-C(16)	7(2)
C(15)-C(16)-C(17)-C(12)	-3(2)
C(15)-C(16)-C(17)-C(18)	-177.5(15)
C(10)-C(9)-C(18)-C(17)	-3(2)
N(2)-C(9)-C(18)-C(17)	174.8(12)
C(10)-C(9)-C(18)-C(19)	-179.3(12)
N(2)-C(9)-C(18)-C(19)	-1(2)
C(12)-C(17)-C(18)-C(9)	5(2)
C(16)-C(17)-C(18)-C(9)	179.2(14)
C(12)-C(17)-C(18)-C(19)	-179.0(14)
C(16)-C(17)-C(18)-C(19)	-5(2)
C(9)-C(18)-C(19)-C(28)	72.4(19)
C(17)-C(18)-C(19)-C(28)	-103.6(16)
C(9)-C(18)-C(19)-C(20)	-101.6(15)
C(17)-C(18)-C(19)-C(20)	82.4(16)
C(28)-C(19)-C(20)-C(25)	-6(2)
C(18)-C(19)-C(20)-C(25)	168.2(15)
C(28)-C(19)-C(20)-C(21)	176.6(13)
C(18)-C(19)-C(20)-C(21)	-9.3(19)
C(25)-C(20)-C(21)-C(22)	-4(2)
C(19)-C(20)-C(21)-C(22)	173.2(13)
C(20)-C(21)-C(22)-C(23)	4(2)

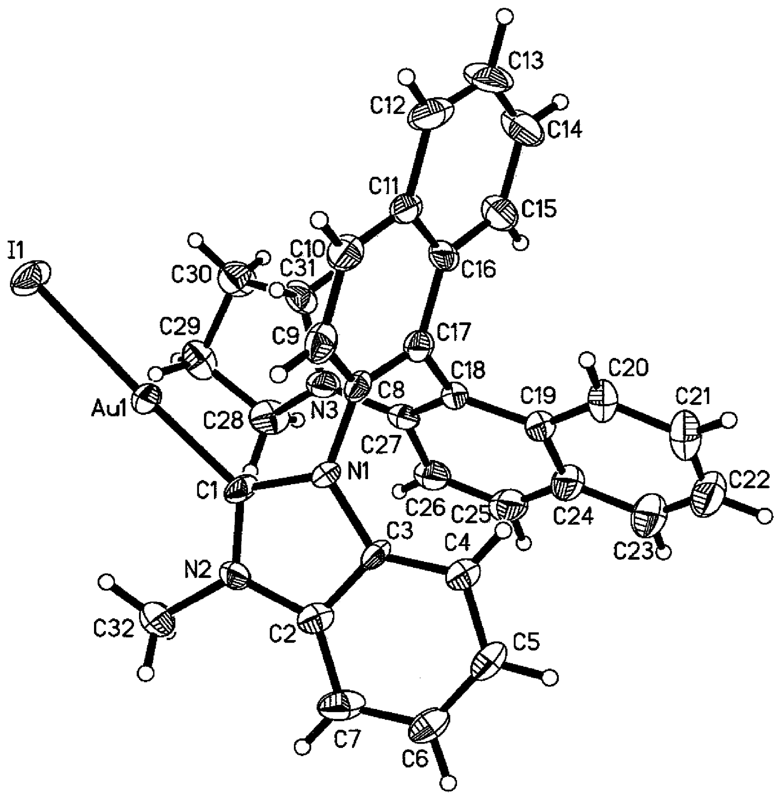
C(21)-C(22)-C(23)-C(24)	1(3)
C(22)-C(23)-C(24)-C(25)	-6(3)
C(21)-C(20)-C(25)-C(26)	-174.5(13)
C(19)-C(20)-C(25)-C(26)	8(2)
C(21)-C(20)-C(25)-C(24)	-1(2)
C(19)-C(20)-C(25)-C(24)	-178.3(14)
C(23)-C(24)-C(25)-C(20)	6(3)
C(23)-C(24)-C(25)-C(26)	-179.9(18)
C(20)-C(25)-C(26)-C(27)	-5(2)
C(24)-C(25)-C(26)-C(27)	-178.7(16)
C(25)-C(26)-C(27)-C(28)	-1(2)
C(20)-C(19)-C(28)-N(3)	-177.1(12)
C(18)-C(19)-C(28)-N(3)	9(2)
C(20)-C(19)-C(28)-C(27)	0(2)
C(18)-C(19)-C(28)-C(27)	-173.6(13)
C(29)-N(3)-C(28)-C(19)	-152.7(18)
C(29)-N(3)-C(28)-C(27)	30(2)
C(26)-C(27)-C(28)-C(19)	3(2)
C(26)-C(27)-C(28)-N(3)	-179.5(15)
C(28)-N(3)-C(29)-O(1)	9(3)
C(28)-N(3)-C(29)-C(30)	-173.7(16)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd29609 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

(I) X-ray Crystal Data of Complex 6.



The crystal data of **6** have been deposited in CCDC with number 790740. Empirical Formula: $C_{32}H_{27}AuIN_3$; Formula Weight: 777.43; Crystal Color, Habit: colorless; Crystal Dimensions: 0.350 x 0.280 x 0.221 mm; Crystal System: Monoclinic; Lattice Parameters: a = 12.8532(14)Å, b = 7.4498(8)Å, c = 14.7707(17)Å, α = 90°, β = 90.459(2)°, γ = 90°, V = 1414.3(3)Å^3; Space group: P2(1); Z = 2; D_{calc}= 1.826 g/cm^3; F_{000} = 744; Diffractometer: Bruker Smart CCD; Residuals: R; Rw: 0.0406, 0.0790.

Table 1. Crystal data and structure refinement for cd201441.

Identification code	cd201441
Empirical formula	C32 H27 Au I N3
Formula weight	777.43
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 12.8532(14) A alpha = 90 deg. b = 7.4498(8) A beta = 90.459(2) deg. c = 14.7707(17) A gamma = 90 deg.
Volume	1414.3(3) A^3
Z, Calculated density	2, 1.826 Mg/m^3
Absorption coefficient	6.317 mm^-1
F(000)	744
Crystal size	0.350 x 0.280 x 0.221 mm
Theta range for data collection	2.09 to 27.00 deg.
Limiting indices	-8<=h<=16, -9<=k<=9, -17<=l<=18
Reflections collected / unique	8321 / 5923 [R(int) = 0.0359]
Completeness to theta = 27.00	99.5 %
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.4093
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5923 / 1 / 336
Goodness-of-fit on F^2	0.904
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.0790
R indices (all data)	R1 = 0.0499, wR2 = 0.0824
Absolute structure parameter	0.021(7)
Extinction coefficient	0.00158(18)
Largest diff. peak and hole	1.099 and -0.947 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for cd201441.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Au(1)	5717(1)	7235(1)	8588(1)	42(1)
I(1)	3741(1)	7336(2)	8466(1)	64(1)
N(1)	7884(4)	6891(10)	7903(4)	38(2)
N(2)	7896(4)	7229(18)	9352(3)	43(1)
N(3)	6820(5)	2909(9)	8048(4)	47(2)
C(1)	7261(5)	7069(19)	8633(4)	37(2)
C(2)	8935(5)	7110(20)	9103(5)	45(2)
C(3)	8937(5)	6905(13)	8170(5)	41(2)
C(4)	9840(6)	6811(11)	7680(6)	49(3)
C(5)	10744(6)	6886(18)	8162(7)	67(4)
C(6)	10752(6)	7110(30)	9100(7)	69(3)
C(7)	9851(6)	7230(30)	9593(5)	61(2)
C(8)	7465(5)	6721(10)	6996(5)	37(2)
C(9)	6946(7)	8190(13)	6618(6)	51(2)
C(10)	6480(7)	8033(14)	5790(6)	51(2)
C(11)	6518(7)	6427(15)	5313(6)	52(3)
C(12)	6019(7)	6226(17)	4451(7)	71(3)
C(13)	6093(9)	4660(20)	4000(7)	89(4)
C(14)	6642(9)	3205(16)	4351(7)	76(3)
C(15)	7118(7)	3335(14)	5178(6)	63(3)
C(16)	7077(6)	4939(12)	5663(5)	44(2)
C(17)	7568(6)	5119(11)	6538(5)	42(2)
C(18)	8194(6)	3607(10)	6960(5)	38(2)
C(19)	9195(6)	3265(12)	6620(6)	47(2)
C(20)	9566(8)	4078(14)	5801(7)	66(3)
C(21)	10550(10)	3755(18)	5519(8)	90(4)
C(22)	11229(9)	2540(40)	6029(11)	124(7)
C(23)	10890(8)	1783(18)	6794(9)	87(5)
C(24)	9881(6)	2090(20)	7104(6)	61(3)
C(25)	9515(8)	1370(12)	7914(8)	65(3)
C(26)	8545(7)	1629(11)	8222(6)	54(2)
C(27)	7838(6)	2714(9)	7727(5)	39(2)
C(28)	6525(6)	2250(20)	8931(5)	58(2)
C(29)	5367(6)	2488(18)	8950(5)	55(3)
C(30)	5040(6)	2230(30)	7976(5)	64(2)
C(31)	5909(7)	3089(12)	7441(5)	49(2)
C(32)	7560(6)	7470(20)	10288(5)	63(3)

Table 3. Bond lengths [A] and angles [deg] for cd201441.

Au(1)-C(1)	1.988(6)
Au(1)-I(1)	2.5462(6)
N(1)-C(1)	1.355(8)
N(1)-C(3)	1.407(8)
N(1)-C(8)	1.445(9)
N(2)-C(1)	1.339(8)
N(2)-C(2)	1.390(8)
N(2)-C(32)	1.462(8)
N(3)-C(27)	1.402(9)
N(3)-C(28)	1.447(9)
N(3)-C(31)	1.476(10)
C(2)-C(7)	1.379(10)
C(2)-C(3)	1.387(10)
C(3)-C(4)	1.375(10)
C(4)-C(5)	1.360(11)
C(4)-H(4)	0.9300
C(5)-C(6)	1.395(13)
C(5)-H(5)	0.9300
C(6)-C(7)	1.375(11)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-C(17)	1.379(11)
C(8)-C(9)	1.396(10)
C(9)-C(10)	1.363(13)
C(9)-H(9)	0.9300
C(10)-C(11)	1.390(12)
C(10)-H(10)	0.9300
C(11)-C(16)	1.417(13)
C(11)-C(12)	1.429(13)
C(12)-C(13)	1.350(16)
C(12)-H(12)	0.9300
C(13)-C(14)	1.388(16)
C(13)-H(13)	0.9300
C(14)-C(15)	1.366(13)
C(14)-H(14)	0.9300
C(15)-C(16)	1.395(12)
C(15)-H(15)	0.9300
C(16)-C(17)	1.439(11)
C(17)-C(18)	1.515(11)
C(18)-C(27)	1.395(10)
C(18)-C(19)	1.408(10)
C(19)-C(24)	1.430(15)
C(19)-C(20)	1.438(13)
C(20)-C(21)	1.356(13)
C(20)-H(20)	0.9300
C(21)-C(22)	1.46(2)
C(21)-H(21)	0.9300
C(22)-C(23)	1.34(2)
C(22)-H(22)	0.9300
C(23)-C(24)	1.397(12)
C(23)-H(23)	0.9300
C(24)-C(25)	1.395(14)
C(25)-C(26)	1.345(12)
C(25)-H(25)	0.9300
C(26)-C(27)	1.415(10)
C(26)-H(26)	0.9300
C(28)-C(29)	1.499(11)
C(28)-H(28A)	0.9700
C(28)-H(28B)	0.9700
C(29)-C(30)	1.509(11)
C(29)-H(29A)	0.9700
C(29)-H(29B)	0.9700
C(30)-C(31)	1.515(11)

C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(32)-H(32A)	0.9600
C(32)-H(32B)	0.9600
C(32)-H(32C)	0.9600
C(1)-Au(1)-I(1)	177.1(3)
C(1)-N(1)-C(3)	110.5(6)
C(1)-N(1)-C(8)	121.9(6)
C(3)-N(1)-C(8)	127.6(6)
C(1)-N(2)-C(2)	111.4(5)
C(1)-N(2)-C(32)	125.3(6)
C(2)-N(2)-C(32)	123.3(6)
C(27)-N(3)-C(28)	121.4(7)
C(27)-N(3)-C(31)	122.8(6)
C(28)-N(3)-C(31)	111.5(6)
N(2)-C(1)-N(1)	106.2(5)
N(2)-C(1)-Au(1)	128.5(5)
N(1)-C(1)-Au(1)	125.1(5)
C(7)-C(2)-C(3)	121.3(7)
C(7)-C(2)-N(2)	132.5(8)
C(3)-C(2)-N(2)	106.2(6)
C(4)-C(3)-C(2)	122.5(7)
C(4)-C(3)-N(1)	131.8(7)
C(2)-C(3)-N(1)	105.6(6)
C(5)-C(4)-C(3)	116.3(9)
C(5)-C(4)-H(4)	121.8
C(3)-C(4)-H(4)	121.8
C(4)-C(5)-C(6)	121.6(8)
C(4)-C(5)-H(5)	119.2
C(6)-C(5)-H(5)	119.2
C(7)-C(6)-C(5)	122.3(8)
C(7)-C(6)-H(6)	118.9
C(5)-C(6)-H(6)	118.9
C(6)-C(7)-C(2)	115.9(8)
C(6)-C(7)-H(7)	122.0
C(2)-C(7)-H(7)	122.0
C(17)-C(8)-C(9)	122.0(8)
C(17)-C(8)-N(1)	119.6(7)
C(9)-C(8)-N(1)	118.4(7)
C(10)-C(9)-C(8)	119.8(9)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(9)-C(10)-C(11)	120.8(9)
C(9)-C(10)-H(10)	119.6
C(11)-C(10)-H(10)	119.6
C(10)-C(11)-C(16)	120.6(8)
C(10)-C(11)-C(12)	121.6(9)
C(16)-C(11)-C(12)	117.8(10)
C(13)-C(12)-C(11)	119.8(10)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(12)-C(13)-C(14)	121.9(10)
C(12)-C(13)-H(13)	119.1
C(14)-C(13)-H(13)	119.1
C(15)-C(14)-C(13)	120.1(11)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.1(10)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-C(11)	120.2(9)
C(15)-C(16)-C(17)	121.5(9)
C(11)-C(16)-C(17)	118.2(8)
C(8)-C(17)-C(16)	118.5(8)

C(8)-C(17)-C(18)	119.6(7)
C(16)-C(17)-C(18)	121.9(7)
C(27)-C(18)-C(19)	120.7(7)
C(27)-C(18)-C(17)	120.8(6)
C(19)-C(18)-C(17)	118.2(7)
C(18)-C(19)-C(24)	119.6(8)
C(18)-C(19)-C(20)	122.2(8)
C(24)-C(19)-C(20)	118.1(8)
C(21)-C(20)-C(19)	120.0(11)
C(21)-C(20)-H(20)	120.0
C(19)-C(20)-H(20)	120.0
C(20)-C(21)-C(22)	120.4(12)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8
C(23)-C(22)-C(21)	119.9(11)
C(23)-C(22)-H(22)	120.1
C(21)-C(22)-H(22)	120.1
C(22)-C(23)-C(24)	121.1(14)
C(22)-C(23)-H(23)	119.4
C(24)-C(23)-H(23)	119.4
C(25)-C(24)-C(23)	122.6(11)
C(25)-C(24)-C(19)	116.9(8)
C(23)-C(24)-C(19)	120.4(11)
C(26)-C(25)-C(24)	123.7(9)
C(26)-C(25)-H(25)	118.1
C(24)-C(25)-H(25)	118.1
C(25)-C(26)-C(27)	120.1(9)
C(25)-C(26)-H(26)	120.0
C(27)-C(26)-H(26)	120.0
C(18)-C(27)-N(3)	122.6(7)
C(18)-C(27)-C(26)	118.6(7)
N(3)-C(27)-C(26)	118.8(7)
N(3)-C(28)-C(29)	104.2(6)
N(3)-C(28)-H(28A)	110.9
C(29)-C(28)-H(28A)	110.9
N(3)-C(28)-H(28B)	110.9
C(29)-C(28)-H(28B)	110.9
H(28A)-C(28)-H(28B)	108.9
C(28)-C(29)-C(30)	103.6(6)
C(28)-C(29)-H(29A)	111.0
C(30)-C(29)-H(29A)	111.0
C(28)-C(29)-H(29B)	111.0
C(30)-C(29)-H(29B)	111.0
H(29A)-C(29)-H(29B)	109.0
C(29)-C(30)-C(31)	104.1(7)
C(29)-C(30)-H(30A)	110.9
C(31)-C(30)-H(30A)	110.9
C(29)-C(30)-H(30B)	110.9
C(31)-C(30)-H(30B)	110.9
H(30A)-C(30)-H(30B)	109.0
N(3)-C(31)-C(30)	103.3(7)
N(3)-C(31)-H(31A)	111.1
C(30)-C(31)-H(31A)	111.1
N(3)-C(31)-H(31B)	111.1
C(30)-C(31)-H(31B)	111.1
H(31A)-C(31)-H(31B)	109.1
N(2)-C(32)-H(32A)	109.5
N(2)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
N(2)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for cd201441.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Au(1)	27(1)	58(1)	41(1)	-4(1)	6(1)	-5(1)
I(1)	29(1)	108(1)	57(1)	14(1)	4(1)	-8(1)
N(1)	21(3)	55(6)	40(3)	-8(3)	-3(2)	1(3)
N(2)	39(3)	52(3)	36(3)	-15(7)	2(2)	-11(6)
N(3)	41(4)	67(5)	34(4)	2(3)	-3(3)	-7(3)
C(1)	21(3)	51(6)	39(4)	13(6)	1(3)	-11(5)
C(2)	37(4)	49(5)	49(4)	1(7)	-5(3)	-4(6)
C(3)	18(3)	52(7)	53(4)	-4(4)	-1(3)	0(3)
C(4)	33(4)	58(8)	54(5)	-6(4)	-4(3)	-2(4)
C(5)	29(4)	89(12)	82(7)	-7(7)	-3(4)	13(5)
C(6)	36(4)	92(8)	79(6)	-1(11)	-20(4)	19(9)
C(7)	56(5)	77(5)	49(5)	17(10)	-19(4)	-19(10)
C(8)	23(4)	51(6)	37(4)	8(3)	6(3)	3(3)
C(9)	38(5)	61(5)	53(6)	7(5)	15(5)	2(4)
C(10)	42(5)	74(6)	38(6)	17(5)	2(5)	7(4)
C(11)	30(5)	97(7)	28(5)	10(5)	2(4)	0(4)
C(12)	38(5)	120(9)	55(6)	25(6)	-12(5)	-10(5)
C(13)	78(8)	158(13)	29(6)	8(7)	-18(5)	-14(8)
C(14)	90(8)	99(8)	40(6)	-17(6)	-5(6)	-7(6)
C(15)	61(6)	85(7)	44(6)	-14(5)	4(5)	-12(5)
C(16)	39(5)	70(5)	25(4)	0(4)	8(3)	-14(4)
C(17)	32(4)	58(5)	37(5)	4(4)	5(3)	-7(4)
C(18)	32(4)	49(5)	34(4)	-7(4)	2(3)	-2(3)
C(19)	38(5)	57(5)	47(6)	-14(4)	0(4)	1(4)
C(20)	54(6)	84(7)	60(7)	-10(5)	18(5)	11(5)
C(21)	70(8)	130(11)	71(8)	-11(7)	30(7)	12(7)
C(22)	50(6)	180(20)	139(12)	-85(16)	18(8)	1(12)
C(23)	60(7)	103(13)	100(9)	-22(8)	6(6)	25(7)
C(24)	47(4)	67(7)	70(6)	-15(9)	-1(4)	14(7)
C(25)	59(7)	59(5)	77(8)	-18(5)	-19(5)	21(5)
C(26)	58(6)	56(6)	47(5)	-3(4)	-12(4)	2(4)
C(27)	44(4)	40(6)	32(4)	-4(3)	-9(3)	-1(3)
C(28)	66(5)	68(5)	40(4)	26(8)	-1(4)	-11(9)
C(29)	72(5)	48(7)	45(4)	6(5)	19(4)	-16(5)
C(30)	62(5)	69(5)	60(5)	-6(10)	3(4)	-21(9)
C(31)	60(6)	60(5)	29(4)	1(4)	8(4)	-4(4)
C(32)	59(5)	96(9)	35(4)	-11(7)	3(3)	1(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for cd201441.

	x	y	z	U(eq)
H(4)	9833	6702	7052	58
H(5)	11373	6783	7860	80
H(6)	11388	7188	9402	83
H(7)	9859	7371	10218	73
H(9)	6919	9273	6930	61
H(10)	6131	9012	5541	61
H(12)	5643	7174	4202	85
H(13)	5768	4543	3438	106
H(14)	6685	2143	4022	92
H(15)	7470	2352	5418	76
H(20)	9132	4826	5464	79
H(21)	10795	4309	4998	109
H(22)	11895	2293	5822	149
H(23)	11334	1042	7125	105
H(25)	9968	673	8260	78
H(26)	8339	1096	8761	65
H(28A)	6859	2939	9408	69
H(28B)	6712	995	9001	69
H(29A)	5184	3677	9164	66
H(29B)	5045	1599	9337	66
H(30A)	4382	2823	7853	76
H(30B)	4974	967	7830	76
H(31A)	6019	2461	6874	59
H(31B)	5760	4340	7314	59
H(32A)	6833	7763	10295	95
H(32B)	7953	8417	10565	95
H(32C)	7673	6371	10618	95

Table 6. Torsion angles [deg] for cd201441.

C(2)-N(2)-C(1)-N(1)	-1.5(18)
C(32)-N(2)-C(1)-N(1)	179.5(13)
C(2)-N(2)-C(1)-Au(1)	-177.1(11)
C(32)-N(2)-C(1)-Au(1)	4(2)
C(3)-N(1)-C(1)-N(2)	1.2(14)
C(8)-N(1)-C(1)-N(2)	-178.7(10)
C(3)-N(1)-C(1)-Au(1)	177.0(9)
C(8)-N(1)-C(1)-Au(1)	-2.9(16)
I(1)-Au(1)-C(1)-N(2)	-148(6)
I(1)-Au(1)-C(1)-N(1)	37(8)
C(1)-N(2)-C(2)-C(7)	178.9(19)
C(32)-N(2)-C(2)-C(7)	-2(3)
C(1)-N(2)-C(2)-C(3)	1.2(19)
C(32)-N(2)-C(2)-C(3)	-179.8(14)
C(7)-C(2)-C(3)-C(4)	-1(2)
N(2)-C(2)-C(3)-C(4)	177.6(10)
C(7)-C(2)-C(3)-N(1)	-178.5(15)
N(2)-C(2)-C(3)-N(1)	-0.4(15)
C(1)-N(1)-C(3)-C(4)	-178.2(11)
C(8)-N(1)-C(3)-C(4)	1.7(16)
C(1)-N(1)-C(3)-C(2)	-0.5(13)
C(8)-N(1)-C(3)-C(2)	179.4(10)
C(2)-C(3)-C(4)-C(5)	1.7(17)
N(1)-C(3)-C(4)-C(5)	179.1(10)
C(3)-C(4)-C(5)-C(6)	-2.3(18)
C(4)-C(5)-C(6)-C(7)	2(3)
C(5)-C(6)-C(7)-C(2)	0(3)
C(3)-C(2)-C(7)-C(6)	0(3)
N(2)-C(2)-C(7)-C(6)	-177.7(16)
C(1)-N(1)-C(8)-C(17)	-111.7(11)
C(3)-N(1)-C(8)-C(17)	68.4(11)
C(1)-N(1)-C(8)-C(9)	66.9(12)
C(3)-N(1)-C(8)-C(9)	-113.0(9)
C(17)-C(8)-C(9)-C(10)	3.2(12)
N(1)-C(8)-C(9)-C(10)	-175.4(7)
C(8)-C(9)-C(10)-C(11)	-0.4(13)
C(9)-C(10)-C(11)-C(16)	-2.4(14)
C(9)-C(10)-C(11)-C(12)	178.9(8)
C(10)-C(11)-C(12)-C(13)	178.5(10)
C(16)-C(11)-C(12)-C(13)	-0.2(13)
C(11)-C(12)-C(13)-C(14)	0.4(16)
C(12)-C(13)-C(14)-C(15)	0.6(17)
C(13)-C(14)-C(15)-C(16)	-1.6(16)
C(14)-C(15)-C(16)-C(11)	1.7(13)
C(14)-C(15)-C(16)-C(17)	179.8(8)
C(10)-C(11)-C(16)-C(15)	-179.6(8)
C(12)-C(11)-C(16)-C(15)	-0.8(12)
C(10)-C(11)-C(16)-C(17)	2.3(12)
C(12)-C(11)-C(16)-C(17)	-179.0(7)
C(9)-C(8)-C(17)-C(16)	-3.3(11)
N(1)-C(8)-C(17)-C(16)	175.4(6)
C(9)-C(8)-C(17)-C(18)	176.4(7)
N(1)-C(8)-C(17)-C(18)	-5.0(10)
C(15)-C(16)-C(17)-C(8)	-177.6(7)
C(11)-C(16)-C(17)-C(8)	0.5(11)
C(15)-C(16)-C(17)-C(18)	2.7(11)
C(11)-C(16)-C(17)-C(18)	-179.1(7)
C(8)-C(17)-C(18)-C(27)	68.7(10)
C(16)-C(17)-C(18)-C(27)	-111.7(8)
C(8)-C(17)-C(18)-C(19)	-104.4(9)
C(16)-C(17)-C(18)-C(19)	75.3(10)
C(27)-C(18)-C(19)-C(24)	-4.6(13)
C(17)-C(18)-C(19)-C(24)	168.4(9)

C(27)-C(18)-C(19)-C(20)	176.2(8)
C(17)-C(18)-C(19)-C(20)	-10.8(12)
C(18)-C(19)-C(20)-C(21)	177.7(10)
C(24)-C(19)-C(20)-C(21)	-1.6(16)
C(19)-C(20)-C(21)-C(22)	1.8(19)
C(20)-C(21)-C(22)-C(23)	-2(3)
C(21)-C(22)-C(23)-C(24)	2(3)
C(22)-C(23)-C(24)-C(25)	-177.8(16)
C(22)-C(23)-C(24)-C(19)	-2(2)
C(18)-C(19)-C(24)-C(25)	-1.5(16)
C(20)-C(19)-C(24)-C(25)	177.7(10)
C(18)-C(19)-C(24)-C(23)	-177.7(11)
C(20)-C(19)-C(24)-C(23)	1.5(17)
C(23)-C(24)-C(25)-C(26)	-179.3(11)
C(19)-C(24)-C(25)-C(26)	4.6(18)
C(24)-C(25)-C(26)-C(27)	-1.4(15)
C(19)-C(18)-C(27)-N(3)	-175.0(7)
C(17)-C(18)-C(27)-N(3)	12.2(11)
C(19)-C(18)-C(27)-C(26)	7.8(11)
C(17)-C(18)-C(27)-C(26)	-165.0(7)
C(28)-N(3)-C(27)-C(18)	-168.1(9)
C(31)-N(3)-C(27)-C(18)	37.1(11)
C(28)-N(3)-C(27)-C(26)	9.0(12)
C(31)-N(3)-C(27)-C(26)	-145.7(7)
C(25)-C(26)-C(27)-C(18)	-4.9(11)
C(25)-C(26)-C(27)-N(3)	177.8(8)
C(27)-N(3)-C(28)-C(29)	-172.3(8)
C(31)-N(3)-C(28)-C(29)	-15.0(13)
N(3)-C(28)-C(29)-C(30)	31.7(15)
C(28)-C(29)-C(30)-C(31)	-36.9(15)
C(27)-N(3)-C(31)-C(30)	149.1(9)
C(28)-N(3)-C(31)-C(30)	-7.8(11)
C(29)-C(30)-C(31)-N(3)	27.4(13)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd201441 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)