Supplementary Material:

Counterions of BINAP-Pt(II) and Pd(II) Complexes: Novel Catalysts for Highly Enantioselective Diels-Alder Reaction

Arun K. Ghosh,* and Hideho Matsuda

Department of Chemistry, University of Illinois at Chicago, 845 West Taylor Street, Chicago, Illinois 60607

General Methods: All melting points were recorded on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker AM-400, DPX-400, DRX-500, and Varian VXR-300S spectrometers using tetramethylsilane as the internal standard. ^{13}C NMR and ^{31}P NMR were recorded on Bruker DPX-400 using tetramethylsilane as the internal standard. IR spectra were recorded on Matteson Genesis FT-IR. Mass spectra were recorded on Finnigan LCQ mass spectrometer. Optical rotations were measured on a Perkin-Elmer 241 spectropolarimeter. Column chromatography was performed with Fisher Scientific 60-200 mesh silica gel. Thin-layer chromatography

(TLC) was carried out with E. Merck silica gel 60F-254 plates. Analytical high performance liquid chromatography (HPLC) was performed on a Rainin HPXL with Spectra-Physics Spectra 100 variable wavelength detector using Daicel Chiracel OD column. Enantiomeric excess was calculated from the HPLC profile according to the reported procedure of Corey[1] and the procedure described by us previously.[2]

Materials: Methylene chloride was distilled from P_2O_5. DMSO was dried over MS 4Å, filtered, distilled, and stored under nitrogen. All other solvents were HPLC grade. Cyclopentadiene was distilled by cracking dicyclopentadiene and used immediately. *N*-Acyloxazolidones were prepared by following the literature procedure.[3] Pt(*R*)-BINAP-Sal **7**[4] and $PdCl_2$[(*R*)-BINAP] **9**[5] were prepared according to the literature procedures. (*R*)-QUINAP [1-(2-diphenylphosphino-1-naphthyl) isoquinoline] was purchased from Strem Chemicals, Inc.

$PtCl_2$[(*R*)-BINAP] 3: $PtCl_2$ (190 mg, 0.7 mmol) and (*R*)-BINAP (452 mg, 0.71 mmol) were suspended in $CHCl_3$ (50 mL) at 23°C under nitrogen. The mixture was refluxed for 24 h and the resulting yellow solution was cooled and filtered. The filtrate was condensed under reduced pressure and the resulting light yellow solid was washed with hexane and diethyl ether successively. This solid was dried under reduced pressure to

give a light yellow solid (574 mg, 91%). This is an improved procedure and the material [$PtCl_2$(*R*)-BINAP] has shown identical physical properties as reported in the literature.[6]

Pt-(*R*)-QUINAP-Sal 8: K_2PtCl_4 (95 mg, 0.23 mmol), Na_2CO_3 (73 mg, 0.69 mmol) and salicylaldehyde (28 mg, 0.23 mmol) were suspended in dry DMSO (4 mL) under nitrogen atmosphere. The resulting mixture was heated to 140°C and stirred at that temperature for 40 min. The resulting slight yellow suspension was cooled to 100°C and a solution of (*R*)-QUINAP (105 mg, 0.23 mmol) in CH_2Cl_2 (1 mL) was added. After stirring the mixture for 30 min at 100°C, DMSO was removed under reduced pressure at 60°C. The yellow residue was diluted with CH_2Cl_2 and filtered. The yellow filtrate was condensed to a small volume (0.5 mL) and hexane was added. The generated brown crystals were filtered out, washed with ethyl acetate, and dried under reduced pressure to obtain **8** (163 mg, 94%); mp: 219 - 221°C; $[\alpha]_D^{23}$ +150.9 (*c* 0.52, $CHCl_3$); IR (film): 3058, 2227, 1635, 1579, 1457, 1316, 1279, 1102 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.39 (d, J = 6.2 Hz, 1H), 7.93 (dd, J = 17.2, 8.5 Hz, 2H), 7.76 - 7.40 (m, 11H), 7.29 - 7.11 (m, 5H), 7.00 - 6.79 (m, 6H), 6.46 (t, J = 15.4 Hz, 1H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 20.9 (s); MS (*m/z*) 755 (M^+ + H, 100%).

$NiCl_2$[(*R*)-BINAP] 10: To a stirred suspension of anhydrous $NiCl_2$ (11 mg, 0.085 mmol) in dry DMSO (5 mL) under nitrogen atmosphere, (*R*)-BINAP (53 mg, 0.085 mmol) was added. The reaction mixture was heated at 100°C for 96 h. After this period, the resulting lime yellow solution was cooled to 60°C and DMSO was removed under reduced pressure. Methylene chloride was added to the residue and the mixture was filtered. The filtrate was condensed under reduced pressure at 100°C and the resulting brown residue was dissolved in a small volume of CH_2Cl_2 (1 mL). Hexane was added to this solution dropwise and the generated brown crystals were filtered and washed with ice-cooled ethyl acetate. These crystals were dried in vacuo to provide the title complex as brown crystals (43 mg, 67%); mp: 243 - 247°C; $[\alpha]_D^{23}$ +254.5 (*c* 0.22, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.86-7.80 (m, 4H), 7.71 - 7.65 (m, 4H), 7.43 - 7.31 (m, 12H), 7.27 - 7.21 (m, 8H), 6.80 - 6.78 (m, 4H); ^{31}P NMR (160 MHz, $CDCl_3$): δ 26.9 (s).

General procedure for Pt(II) and Pd(II)-catalyzed enantioselective Diels-Alder reactions:

(1) Catalyst Activation:

(a) Chloro complex (**3**, **9**, **10**): Platinum (also, palladium and nickel) complex (1 equiv) and appropriate silver salt (2 equiv) were suspended in freshly distilled dry CH_2Cl_2 under nitrogen atmosphere and

the resulting suspension was typically stirred at 23°C for 1 h before the Diels-Alder reaction.

(b) Sal complex (**7**, **8**): Platinum sal complex was dissolved in freshly distilled dry CH_2Cl_2 under nitrogen atmosphere and to the solution were added H_2O (from a 10% aqueous solution in toluene) and TfOH (2 equiv). The resulting mixture was stirred at 23°C for 15 min before the Diels-Alder reaction.

(2) Diels-Alder Reaction: The stirred activated catalyst complex was cooled to -78°C and a solution of *N*-acyloxazolidinone in CH_2Cl_2 was added. Freshly cracked cyclopentadiene (5 equiv) was added dropwise and the progress of the reaction was monitored by TLC. The reaction was quenched at a specified temperature by the addition of a saturated aqueous $NaHCO_3$ solution. The mixture was extracted with CH_2Cl_2 and the organic layer was washed with brine, and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a crude residue which was purified by column chromatography over silica gel (60-200 mesh, 20% ethyl acetate/hexanes) to obtain the pure cycloadduct.

Typical Experimental Procedure:

Entry 1: Platinum complex **3** (62 mg, 0.07 mmol) and AgOTf (36 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) were stirred at 23°C under nitrogen

atmosphere for 1 h. The catalyst complex was then cooled to -78°C and acryloyl-*N*-oxazolidinone **1a** (50 mg, 0.36 mmol) in CH_2Cl_2 (1 mL) followed by cyclopentadiene (0.12 mL, 1.78 mmol) were added. The reaction mixture was warmed to -40°C and was stirred for 96 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution as mentioned above. Standard workup and purification afforded the cycloadduct **2a** (60 mg, 81% yield). The *endo/exo* ratio was measured from the HPLC profile (*endo/exo* 95 : 5; 10% isopropanol in hexane as the eluent, flow rate 1 mL/min, and the retention times of *endo* and *exo* isomers were 16.25 min (exo_1), 16.70 min (exo_2), 17.50 min ($endo_{2S}$), and 19.85 min ($endo_{2R}$) respectively. Absolute configuration of *endo* cycloadduct was determined to be 2(*S*) by comparison of the retention time and optical rotation with an authentic 2*S* isomer sample. Enantiomeric excess was 89% for the major *endo*-2(*S*) enantiomer. ^1H NMR (400 MHz, $CDCl_3$) δ 6.25 (dd, J = 5.6, 3.1 Hz 1H), 5.87 (dd, J = 5.6, 2.8 Hz 1H), 4.41 - 4.38 (m, 2H), 4.01 - 3.91 (m, 3H), 3.31 (s, 1H), 2.94 (s, 1H), 1.95 (m, 1H), 1.51 - 1.36 (m, 3H).

Entry 5: To a stirred solution of the complex **7** (67 mg, 0.07 mmol) in CH_2Cl_2 (5 mL) were added H_2O (10% solution in toluene, 24 μl, 0.14 mmol) and TfOH (13 μl, 0.15 mmol) at 23°C under nitrogen atmosphere. The light yellow solution was stirred at 23°C for 15 min. The activated

catalyst complex was cooled to -78°C, then acryloyl-*N*-oxazolidinone **1a** (50 mg, 0.36 mmol) in CH_2Cl_2 (1 mL) followed by cyclopentadiene (0.12 mL, 1.78 mmol) were added. The reaction mixture was warmed to -40°C and the mixture was stirred for 1 h. The reaction mixture was quenched as mentioned above. Standard workup and chromatographic purification afforded the cycloadduct **2a** (59 mg, 80% yield). The *endo/exo* ratio (96 : 4) and enantiomeric excess (98% ee) for the major endo-2(*S*) enantiomer were measured as described for entry 1.

Entry 9: Complex **3** (116 mg, 0.13 mmol) and $AgClO_4$ (54 mg, 0.26 mmol) in CH_2Cl_2 (5 mL) were stirred at 23°C under nitrogen atmosphere for 1 h. The activated catalyst complex was cooled to -78°C and crotonoyl-*N*-oxazolidone **1b** (50 mg, 0.32 mmol) in CH_2Cl_2 (1 mL) followed by cyclopentadiene (0.11 mL, 1.63 mmol) were added. The reaction mixture was warmed to 0°C and was stirred for 48 h. The reaction was quenched as described above. Standard workup and purification afforded the cycloadduct **2b** (36 mg, 51% yield). The *endo/exo* ratio was measured by ^{1}H NMR (91 : 9). Optical purity was measured from chiral HPLC analysis (hexane : ethylacetate : 2-propanol= 94 : 4 : 2, flow rate 1.1 mL/min. The retention times of *endo* and *exo* isomers were 14.14 min (exo_1 and exo_2), 16.19 min ($endo_{2S}$), and 17.51 min ($endo_{2R}$) respectively. Enantiomeric excess was determined to be 90%

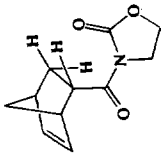
for the major *endo*-2(*S*) enantiomer. Absolute configuration of the *endo* cycloadduct was assigned to be 2(*S*) (by comparing the reported retention time of 2(*S*)- isomer as well as from the sign of measured optical rotation). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (dd, J = 5.7, 3.1 Hz, 1H), 5.78 (dd, J = 5.7, 2.8 Hz, 1H), 4.45 - 4.38 (m, 2H), 4.08 - 3.89 (m, 2H), 3.53 (dd, J = 4.2, 3.5 Hz, 1H), 3.27 (s, 1H), 2.52 (d, J = 1.4 Hz, 1H), 2.10 - 2.05 (m, 1H), 1.70 (d, J = 8.7 Hz, 1H), 1.45 (dd, J = 8.7, 1.7 Hz, 1H), 1.12 (d, J = 7.1 Hz, 3H).

Entry 11: Complex **3** (45 mg, 0.05 mmol) and $AgClO_4$ (22 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) were stirred at 23°C under nitrogen for 1 h. The activated catalyst complex was cooled to -78°C and fumaroyl-*N*-oxazolidinone **1c** (51 mg, 0.26 mmol) in CH_2Cl_2 (1 mL) followed by cyclopentadiene (0.09 mL, 1.26 mmol) were added. The reaction mixture was warmed to -40°C and was stirred for 8 h. Standard work up and purification by a silica gel column afforded the cycloadduct **2c** (51 mg) in 75% yield. The *endo/exo* ratio of isomers (90 : 10) and optical purity were measured by chiral HPLC analysis (hexanes : ethyl acetate : 2-propanol = 80 : 15 : 5, flow rate 1.0 mL/min, and the retention times of the *endo* isomers were 9.43 min ($endo_{2R}$) and 10.20 min ($endo_{2S}$) respectively. Enantiomeric excess is 90% ee for the major *endo*-2(*R*) enantiomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (dd, J = 5.6, 3.2 Hz,

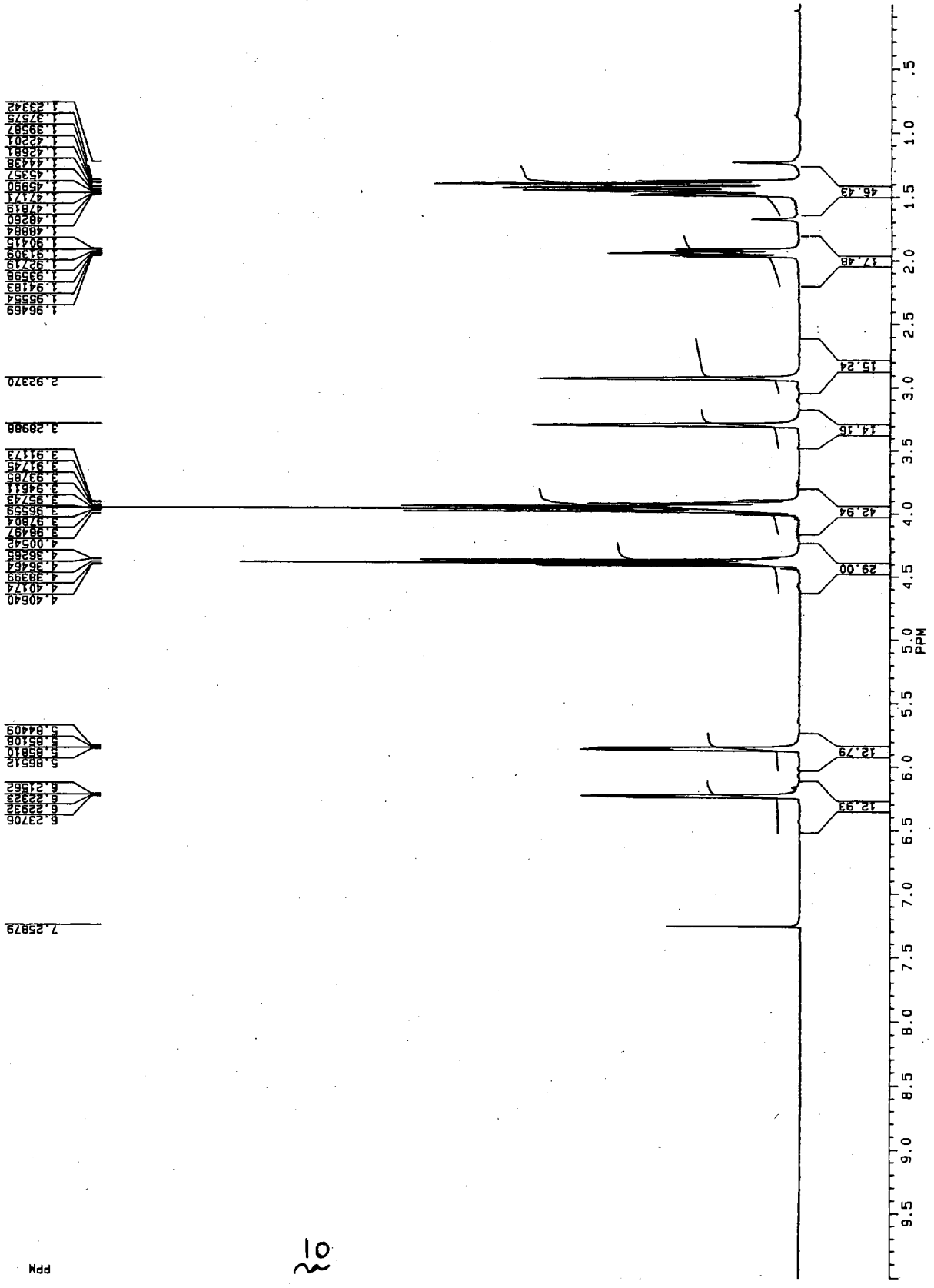
1H), 5.91 (dd, J = 5.6, 2.8 Hz, 1H), 4.45 - 4.41 (m, 2H), 4.32 (dd, J = 4.8, 3.5 Hz, 1H), 4.08 - 3.91 (m, 2H), 3.69 (s, 3H), 3.62 (s, 1H), 3.44 (s, 1H), 2.91 (dd, J = 1.7, 4.8 Hz, 1H), 1.75 (d, J = 8.9 Hz, 1H), 1.51 (dd, J = 8.9, 1.5 Hz, 1H).

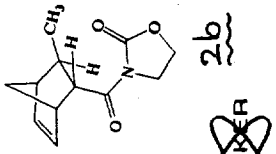
References:

1. Corey, E. J.; Imai, N.; Zhang H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728.
2. Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron Lett.* **1996**, *37*, 3815.
3. Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340.
4. Fujimura, O. *J. Am. Chem. Soc.* **1998**, *120*, 10032.
5. Ozawa, F.; Kubo, A.; Matsumoto, Y.; Hayashi, T.; Nishioka, E.; Yanagi, K.; Moriguchi, K. *Organometalllics* **1993**, 12, 4188.
6. Strukul, G.; Varagolo, A.; Pinna, F. *J. Mol. Cat.*, **1997**, 413.



20





26

BRUKER

SF 400.134
SY 133.0
6600.000
O1 16384
SI 16384
TD 16384
SW 4807.692
HZ/PT .587

PW 6.0
RD 1.000
AQ 1.704
RG 40
NS 8
TE 297

FW 6100
O2 6600.000
DP 63L PO

LB .100
GB 0.0
CX 34.00
CY 20.00
F1 9.000P
F2 -.495P
HZ/CM 111.748
PPM/CM .279
SR 4395.00