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Platinum-Catalyzed Asymmetric Ring-opening Reaction of Oxabenzonorbornadiene with Terminal Alkynes

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A novel platinum-catalyzed asymmetric ring-opening reaction of oxabenzonorbornadiene with terminal alkynes is described. The reaction affords optically active *cis*-2-alkynyl-1,2-dihydronaphthalen-1-ols in moderate yields with good enantioselectivity in the presence of catalytic amounts of $Pt(COD)Cl_2$/(*S*)-BINAP and an excess of zinc powder. The products were obtained exclusively with the relative *cis*-configuration of the ring substituents and the prevalent (1*R*,2*S*)-configuration of the stereocenters, as determined by single crystal X-ray diffraction analysis.

Keywords platinum-catalyzed, asymmetric catalysis, ring-opening reaction, oxabenzonorbornadiene, terminal alkyne

Introduction

Atom economical asymmetric ring-opening (ARO) reactions can generate two chiral center in one step in high yields and with high enantiomeric excesses.[1-3] Oxabenzonorbornadiene can be feasibly activated by transition metal complexes, and can undergo ring-opening reaction to yield dihydronaphthalene skeleton which is found in a wide range of naturally occurring molecules.[4-7] Many metal catalysts have been investigated for the ring-opening of oxabenzonorbornadiene, such as Fe,[8] Ni,[9-11] Cu,[12,13] Ru,[14-16] Rh,[17,18] Pd,[19,20] Ir,[21] *etc*. Very recently our research group[22] has developed the platinum catalyzed ring-opening addition of arylboronic acids to oxabenzonorbornadienes. Many nucleophiles, including organoboronic acids,[23,24] dialkylzinc reagents,[25] organolithium reagents,[26,27] organozinc halides,[28-30] Grignard reagents,[29] and alkynes[9,32-34] have been applied successfully in ARO. Among these nucleophiles, alkynes are appealing carbon nucleophiles, because the furnished acetylene motif can undertake potential transformation to various bioactive compounds and new materials. Cheng and co-workers[9] have reported the use of terminal alkynes for the nickel-catalyzed ring-opening reactions of the oxa- and azabicyclic alkenes, where racemic 2-alkynyl-1,2-dihydronaphthalene derivatives were produced in high yields with high diastereoselectivity. Hayashi and co-workers[32] have reported the highly enantioselective alkynylation of azabenzonorbornadienes by use of a sterically bulky silylacetylene and an axially chiral biarylbisphosphine/rhodium catalyst. Very recently, Hou and co-workers[35] found palladacycles to be efficient catalysts for the reaction of oxabicyclic alkenes with terminal alkynes to give mainly ring-opening product together with addition product in a racemic way. However, there is no report on platinum-catalyzed asymmetric ring-opening reaction of oxabenzonorbornadiene with terminal acetylene. Herein, we report the asymmetric ring-opening reaction of oxabenzonorbornadiene with terminal acetylenes catalyzed by $Pt(COD)Cl_2$ (COD＝cyclooctadiene) and optically pure phosphines. This reaction offers a convenient method for the construction of optically active *cis*-2-alkynyl-1,2-dihydronaphthalen-1-ols in one pot from easily accessible starting materials.

Experimental

General methods

All flasks were flame-dried under a stream of nitrogen and cooled before use. Solvents and solutions were transferred with syringes and cannulae using standard inert atmosphere techniques. NMR spectra were recorded at 400 MHz using a Varian INOVA NMR spectrometer with $CDCl_3$ as reference standard (δ 7.26 for ^{1}H NMR and δ 77.16 for ^{13}C NMR). IR spectra were obtained using a Nicolet DX FT-IR spectrometer as a KBr pellet. HRMS spectra were recorded on a Thermo Finnigan MAT95-XP high-resolution mass spectrometer (EI). Melting points were taken on an XT_4 binocular micromelting point apparatus. HPLC analysis was performed on an Agilent 1100 Series HPLC with a Chiralcel AD-H or OD-H column. Crystal structure determination was carried out on a Bruker SMART-1000 X-ray

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diffraction apparatus. DME was distilled from sodium benzophenone ketyl and stored. THF, dioxane, toluene, and THP were distilled from sodium benzophenone ketyl immediately prior to use. CH_3CN was distilled from calcium hydride. DMSO was dried over $MgSO_4$ and stored over activated molecular sieves. Preparation of oxabenzonorbornadiene **1a** followed reference.[36]

General procedure for the asymmetric ring-opening reaction of oxabenzonorbornadiene 1 with terminal acetylene

An oven-dried Schlenk tube was charged with $Pt(COD)Cl_2$ (3.7 mg, 5 mol%) and (*S*)-BINAP (6.2 mg, 5.0 mol%) in anhydrous toluene (1.0 mL). After they were stirred for about 30 min, **1** (0.2 mmol), Zn (0.55 mmol) and acetylene (0.4 mmol) were added. The reaction mixture was heated with stirring at 90 ℃. After the reaction was finished, the solvent was removed in vaccum and the crude mixture was purified by column chromatography on silica gel to give the target product **2**.

(1*R*,2*S*)-2-(2-Phenyl-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2a**): Following the general procedure, **2a** was obtained as a yellow oil (24.6 mg, 50%), R_f=0.28 on silica gel (ethyl acetate/petroleum ether, *V*∶*V*=1∶10). The *ee* was determined to be 92% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, *V*∶*V*=80∶20, 1.0 mL/min, λ=254 nm). Retention times were 6.658 min (minor) and 10.993 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J*=4.5 Hz, 1H), 7.40 (d, *J*=2.9 Hz, 2H), 7.33−7.21 (m, 5H), 7.14 (s, 1H), 6.58 (d, *J*=9.4 Hz, 1H), 5.99 (dd, *J*=8.8, 3.1 Hz, 1H), 4.85 (s, 1H), 3.80 (s, 1H), 2.40 (d, *J*=6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.27, 131.91, 131.87, 128.68, 128.27, 128.16, 127.91, 127.20, 126.79, 125.76, 125.02, 122.83, 86.03, 84.12, 69.30, 35.43; IR (KBr) *v*: 3414, 3377, 3061, 2922, 1659, 1279, 756, 689 cm^{-1}. The physical and spectroscopic data of **2a** are identical with those reported previously.[9]

(1*R*,2*S*)-2-[(2-(4-Chlorophenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2b**): Following the general procedure, **2b** was obtained as a light yellow solid (22.4 mg, 40%), R_f=0.27 on silica gel (ethyl acetate/petroleum ether, *V*∶*V*=1∶10). m.p. 162−164 ℃. The *ee* was determined to be 50% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, *V*∶ *V*=90∶10, 1.0 mL/min, λ=254 nm). Retention times were 9.731 min (major) and 14.100 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, *J*=7.6, 5.4 Hz, 1H), 7.35−7.27 (m, 4H), 7.26−7.22 (m, 2H), 7.16−7.12 (m, 1H), 5.98 (dd, *J*=9.5, 3.8 Hz, 1H), 4.85 (dd, *J*=7.1, 5.5 Hz, 1H), 3.82−3.78 (m, 1H), 2.31 (d, *J*=7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.21, 134.20, 133.09, 131.81, 128.73, 128.56, 128.21, 128.02, 127.12, 126.83, 125.48, 121.34, 87.20, 82.92, 69.31, 35.41. IR (KBr) *v*: 3354, 3053, 2922, 2852, 2357, 1656, 1483, 1084, 824, 787 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{13}OCl$ 280.0649; found 280.0649.

(1*R*,2*S*)-2-[(2-(3-Chlorophenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2c**): Following the general procedure, **2c** was obtained as a light yellow solid (24.6 mg, 44%), R_f=0.18 on silica gel (ethyl acetate/petroleum ether, *V*∶*V*=1∶10). m.p. 82−84 ℃. The *ee* was determined to be 43% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, *V*∶*V*=90∶10, 1.0 mL/min, λ=254 nm). Retention times were 9.814 min (major) and 15.576 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J*=6.5 Hz, 1H), 7.38 (s, 1H), 7.28 (dt, *J*=13.9, 6.5 Hz, 4H), 7.19 (d, *J*=7.7 Hz, 1H), 7.14 (d, *J*=6.5 Hz, 1H), 6.59 (d, *J*=9.3 Hz, 1H), 5.97 (dd, *J*=9.3, 3.5 Hz, 1H), 4.84 (s, 1H), 3.79 (s, 1H), 2.36 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.22, 134.02, 131.80, 131.74, 130.00, 129.47, 128.73, 128.50, 128.24, 128.09, 127.07, 126.84, 125.37, 124.57, 87.61, 82.61, 69.32, 35.37; IR (KBr) *v*: 3320, 2960, 2918, 2852, 2370, 2332, 1598, 1432, 1050, 785 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{13}OCl$ 280.0649; found 280.0648.

(1*R*,2*S*)-2-[(2-(2-Chlorophenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2d**): Following the general procedure, **2c** was obtained as a light yellow solid (19.6 mg, 35%), R_f=0.30 on silica gel (ethyl acetate/petroleum ether, *V*∶*V*=1∶6). m.p. 92−93 ℃. The *ee* was determined to be 50% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, *V*∶*V*=90∶10, 1.0 mL/min, λ=254 nm. Retention times were 9.467 min (major) and 10.952 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52−7.46 (m, 1H), 7.42 (d, *J*=7.3 Hz, 1H), 7.35 (d, *J*=7.8 Hz, 1H), 7.32−7.26 (m, 2H), 7.18 (dt, *J*=13.8, 7.2 Hz, 3H), 6.60 (d, *J*=9.4 Hz, 1H), 6.01 (dd, *J*=9.3, 3.8 Hz, 1H), 4.92 (t, *J*=6.2 Hz, 1H), 3.84 (s, 1H), 2.57 (d, *J*=7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.06, 135.30, 133.19, 131.92, 129.25, 129.10, 128.59, 128.23, 128.20, 127.01, 126.75, 126.43, 125.11, 122.69, 91.70, 80.95, 69.34, 35.54; IR (KBr) *v*: 3690, 2928, 2924, 2864, 2347, 1620, 1460, 1053, 760, 682 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{13}OCl$ 280.0649; found 280.0649.

(1*R*,2*S*)-2-[(2-(4-Bromophenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2e**): Following the general procedure, **2e** was obtained as a light yellow solid (27.2 mg, 42%), R_f=0.23 on silica gel (ethyl acetate/petroleum ether, *V*∶*V*=1∶10). m.p. 156−158 ℃. The *ee* was determined to be 71% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, *V*∶*V*=85∶15, 1.0 mL/min, λ=254 nm. Retention times were 7.978 min (major) and 10.989 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J*=6.1 Hz, 1H), 7.41 (d, *J*=7.9 Hz, 2H), 7.33−7.22 (m, 4H), 7.15 (d, *J*=6.2 Hz, 1H), 6.60 (d, *J*=9.3 Hz, 1H), 5.98 (dd, *J*=9.1, 2.9 Hz, 1H), 4.85 (t, *J*=5.6 Hz, 1H), 3.80 (s, 1H), 2.28 (d, *J*=7.2 Hz, 1H), 2.28 (d, *J*=7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.19, 133.30, 131.80, 131.48, 128.73, 128.21, 128.03, 127.12, 126.83, 125.42, 122.42, 121.80, 87.39, 82.98, 69.28, 35.44; IR (KBr) *v*: 3353, 2920, 2852, 2360, 1494, 1420, 1252, 1110, 825, 758 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{13}OBr$ 324.0144; found

324.0145.

(1*R*,2*S*)-2-[(2-(4-Nitrophenyl)-1-ethynyl]-1,2-dihydro-1-naphthalenol (**2f**): Following the general procedure, **2f** was obtained as a yellow solid (31.4 mg, 54%), R_f=0.3 on silica gel (ethyl acetate/petroleum ether, V∶V=1∶4). m.p. 151−152 ℃. The *ee* was determined to be 61% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, V∶V=90∶10, 1.0 mL/min, λ=254 nm). Retention times were 26.338 min (major) and 33.657 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.20−8.04 (m, 2H), 7.53 (d, J=8.7 Hz, 2H), 7.49−7.42 (m, 1H), 7.36−7.27 (m, 2H), 7.20−7.12 (m, 1H), 6.63 (dd, J=9.5, 1.9 Hz, 1H), 5.99 (dd, J=9.4, 3.8 Hz, 1H), 4.89 (t, J=6.0 Hz, 1H), 3.88−3.82 (m, 1H), 2.27 (d, J=7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.93, 135.14, 132.61, 131.65, 129.93, 128.86, 128.36, 127.00, 126.94, 124.85, 123.48, 92.41, 82.11, 69.36, 35.53; IR (KBr) ν: 3364, 3063, 2922, 2855, 2359, 2220, 1595, 1528, 1342, 852, 752 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{13}O_3N$ 291.0890; found 291.0890.

(1*R*,2*S*)-2-[(2-(4-Methylphenyl)-1-ethynyl]-1,2-dihydro-1-naphthalenol (**2g**): Following the general procedure, **2g** was obtained as a white solid (31.2 mg, 60%), R_f=0.13 on silica gel (ethyl acetate/petroleum ether, V∶V=1∶10). m.p. 134−136 ℃. The *ee* was determined to be 61% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, V∶V=85∶15, 1.0 mL/min, λ=254 nm). Retention times were 7.499 min (major) and 13.784 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J=6.2 Hz, 1H), 7.33−7.25 (m, 4H), 7.13 (d, J=6.4 Hz, 1H), 7.08 (d, J=7.6 Hz, 2H), 6.58 (d, J=9.4 Hz, 1H), 5.99 (dd, J=9.2, 3.1 Hz, 1H), 4.84 (s, 1H), 3.80 (s, 1H), 2.38 (d, J=4.8 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.34, 135.24, 131.93, 131.74, 129.01, 128.65, 128.11, 127.81, 127.25, 126.77, 125.88, 119.70, 85.13, 84.29, 69.28, 35.45, 21.49; IR (KBr) ν: 3349, 2910, 2832, 2365, 1504, 1450, 1135, 812, 750 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{16}O$ 260.1196; found 260.1194.

(1*R*,2*S*)-2-[(2-(4-Ethylphenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2h**): Following the general procedure, **2h** was obtained as a light yellow solid (34.0 mg, 62%), R_f=0.13 on silica gel (ethyl acetate/petroleum ether, V∶V=1∶10). m.p. 72−73 ℃. The *ee* was determined to be 51% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, V∶V=85∶15, 1.0 mL/min, λ=254 nm). Retention times were 6.984 min (major) and 12.778 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J=7.0 Hz, 1H), 7.33−7.26 (m, 4H), 7.13−7.09 (m, 3H), 6.58 (d, J=9.5 Hz, 1H), 5.99 (dd, J=9.4, 3.6 Hz, 1H), 4.84 (s, 1H), 3.80 (s, 1H), 2.62 (q, J=7.6 Hz, 2H), 2.39 (d, J=5.8 Hz, 1H), 1.20 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.67, 135.23, 131.93, 131.83, 128.64, 128.10, 127.82, 127.24, 126.76, 125.88, 119.93, 85.11, 84.32, 69.28, 35.45, 28.80, 15.41; IR (KBr) ν: 3312, 3043, 2973, 2926, 2349, 2310, 1628, 1107, 852, 784 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{18}O$ 274.1352; found 274.1353.

(1*R*,2*S*)-2-[(2-(4-Propylphenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2i**): Following the general procedure, **2i** was obtained as a white solid (24.2 mg, 42%), R_f=0.13 on silica gel (ethyl acetate/petroleum ether, V∶V=1∶10). m.p. 88−89 ℃. The *ee* was determined to be 63% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, V∶V=90∶10, 1.0 mL/min, λ=254 nm). Retention times were 6.657 min (major) and 13.103 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52−7.43 (m, 1H), 7.34 (d, J=1.9 Hz, 1H), 7.33−7.28 (m, 3H), 7.15 (dd, J=6.4, 2.1 Hz, 1H), 7.10 (dd, J=8.0, 1.8 Hz, 2H), 6.63−6.57 (m, 1H), 6.01 (ddd, J=9.4, 3.8, 1.9 Hz, 1H), 4.86 (d, J=4.8 Hz, 1H), 3.82 (dt, J=5.7, 2.1 Hz, 1H), 2.57 (t, J=7.6 Hz, 2H), 1.66−1.58 (m, 2H), 0.96−0.90 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.13, 135.25, 131.93, 131.73, 128.63, 128.42, 128.10, 127.81, 127.22, 126.75, 125.87, 119.93, 85.10, 84.34, 69.28, 37.90, 35.45, 24.36, 13.74; IR (KBr) ν: 3345, 3032, 2924, 2862, 2357, 1506, 1072, 779, 711, 586 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{20}O$ 288.1509; found 288.1509.

(1*R*,2*S*)-2-[(2-(4-*n*-Pentylphenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2j**): Following the general procedure, **2j** was obtained as a light yellow solid (32.2 mg, 51%), R_f=0.13 on silica gel (ethyl acetate/petroleum ether, V∶V=1∶10). m.p. 80−81 ℃. The *ee* was determined to be 63% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, V∶V=85∶15, 1.0 mL/min, λ=254 nm). Retention times were 6.006 min (major) and 10.179 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50−7.46 (m, 1H), 7.37−7.29 (m, 4H), 7.18−7.14 (m, 1H), 7.11 (d, J=8.0 Hz, 2H), 6.61 (dd, J=9.5, 2.0 Hz, 1H), 6.02 (dd, J=9.5, 3.8 Hz, 1H), 4.87 (t, J=5.4 Hz, 1H), 2.63−2.56 (m, 2H), 2.42 (d, J=6.5 Hz, 1H), 1.60 (dt, J=14.9, 7.5 Hz, 2H), 1.36−1.29 (m, 4H), 0.90 (t, J=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.39, 135.28, 131.95, 131.76, 128.63, 128.38, 128.11, 127.82, 127.23, 126.76, 125.89, 119.90, 85.12, 84.34, 69.29, 35.83, 35.46, 31.41, 30.96, 22.54, 14.07; IR (KBr) ν: 3345, 3032, 2924, 2862, 2357, 1506, 1454, 1072, 779, 712, 595 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{24}O$ 316.1822; found 316.1822.

(1*R*,2*S*)-2-[(2-(4-Methoxyphenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2k**): Following the general procedure, **2k** was obtained as a light yellow solid (18.2 mg, 33%), R_f=0.23 on silica gel (ethyl acetate/petroleum ether, V∶V=1∶6). m.p. 102−103 ℃. The *ee* was determined to be 30% using HPLC analysis on a Chiralcel OD-H column (hexane/ 2-propanol, V∶V=90∶10, 1.0 mL/min, λ=254 nm). Retention times were 14.129 min (major) and 37.097 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J=5.8 Hz, 1H), 7.37−7.25 (m, 4H), 7.14 (d, J=5.9 Hz, 1H), 6.58 (d, J=9.4 Hz, 1H), 5.99 (d, J=6.6 Hz, 1H), 4.84 (s, 1H), 3.78 (s, 4H), 2.40 (d, J=4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.49, 135.26, 133.27, 131.93, 128.63, 128.09, 127.76, 127.23, 126.75, 125.96, 114.88, 113.84, 84.32, 84.03, 69.28, 55.28, 35.43; IR (KBr) ν: 3358,

3190, 2955, 2924, 2855, 2361, 2332, 1667, 1458, 1248, 1013, 833 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{16}O_2$ 276.1145; found 276.1146.

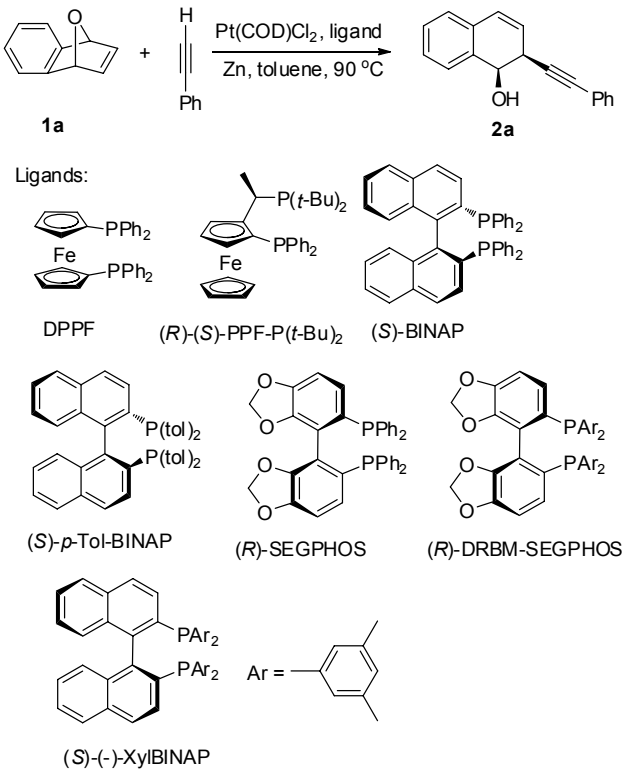
(1*R*,2*S*)-2-[(2-(4-Ethoxyphenyl)-1-ethynyl)-1,2-dihydro-1-naphthalenol (**2l**): Following the general procedure, **2l** was obtained as a light yellow solid (29.6 mg, 51%), R_f=0.38 on silica gel (ethyl acetate/petroleum ether, V∶V=1∶4). m.p. 80−81 ℃. The *ee* was determined to be 50% using HPLC analysis on a Chiralcel OD-H column (hexane/2-propanol, V∶V=85∶15, 1.0 mL/min, λ=254 nm). Retention times were 8.883 min (major) and 15.021 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, J=6.1 Hz, 1H), 7.38−7.24 (m, 4H), 7.15 (d, J=6.1 Hz, 1H), 6.80 (d, J=8.4 Hz, 2H), 6.59 (d, J=9.4 Hz, 1H), 6.00 (dd, J=9.3, 3.4 Hz, 1H), 4.85 (s, 1H), 4.01 (dd, J=13.8, 6.8 Hz, 2H), 3.81 (s, 1H), 2.42 (s, 1H), 1.41 (t, J=6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.90, 135.27, 133.26, 131.95, 128.62, 128.08, 127.75, 127.24, 126.74, 125.99, 114.68, 114.35, 84.21, 84.12, 69.28, 63.47, 35.44, 14.76; IR (KBr) *v*: 3354, 3010, 2955, 2850, 2361, 2332, 1647, 1558, 1248, 1063, 833 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{18}O_2$ 290.1301; found 290.1304.

Results and Discussion

The reaction of oxabenzonorbornadiene **1** with phenylacetylene was tested in the presence of $Pt(COD)Cl_2$ and bisphosphine ligand (Table 1). Achiral 1,1'-bis(diphenylphosphino)ferrocene (DPPF) was first chosen to validate the catalytic activity of $Pt(COD)Cl_2$. Unfortunately, no reaction occurred (Table 1, Entry 1). Then we retried the reaction with the addition of zinc powder. The ring-opening product **2a** was obtained in 79% yield after 2 h (Table 1, Entry 2). Encouraged by this result, we tested several chiral ligands, and the results were summarized in Table 1. Among the ligands screened, (*S*)-BINAP gave **2a** in 50% yield with 92% *ee* (Table 1, Entry 6). With (*S*)-xyl-BINAP as the ligand, the reaction can give a high *ee* value (98%), but with a very poor yield (21%). Substitution of $ZnCl_2$ for Zn caused the reaction to fail (Table 1, Entry 9). Changing the amount of Zn from 2.75 to 1.5 or 3.5 equiv. caused lower yield with lower *ee* (Table 1, Entries 10 and 11). We next investigated the effect of catalyst loading on the reaction. The results indicated that 5 mol% of $Pt(COD)Cl_2$ with 5 mol% of (*S*)-BINAP gave the best values of yield and enantioselectivity. Lowering the catalyst loading led to the decrease in both the yield and *ee* value. On the other hand, the increase of the catalyst loading improved neither the yield nor the *ee* value evidently (Entries 6, and 10−12).

With the optimal chiral ligand and catalyst loading in hand, the influence of solvent and temperature on the reaction was investigated (Table 2). It was observed that the reaction in CH_3CN, 1,2-dichloroethane (DCE), or dioxane gave excellent enantioselectivities (up to 96% *ee*) but with poor conversion (Table 2, Entries 2−4).

Table 1 Effect of ligand, and catalyst loading on the asymmetric ring-opening of oxabenzonorbornadiene **1a** with phenylacetylene[a]



Entry	Ligand/mol%	$Pt(COD)Cl_2$/mol%	Time/h	Yield[f]/%	*ee*[g]/%
1[b]	DPPF (5)	5	24	n.r.	—
2	DPPF (5)	5	2	79	0
3	(*R*)-(*S*)-PPF-P(*t*-Bu)$_2$ (5)	5	5	Trace	—
4	(*S*)-Segphos (5)	5	5	49	62
5	(*S*)-DRBM-Segphos (5)	5	5	57	72
6	(*S*)-BINAP (5)	5	6	50	92
7	(*S*)-xyl-BINAP (5)	5	6	21	98
8	(*S*)-*p*-Tol-BINAP (5)	5	6	35	81
9[c]	(*S*)-BINAP (5)	5	6	n.r	—
10[d]	(*S*)-BINAP (5)	5	24	28	89
11[e]	(*S*)-BINAP (5)	5	24	45	91
12	(*S*)-BINAP (1.5)	1.5	6	15	44
13	(*S*)-BINAP (3.5)	3.5	6	36	61
14	(*S*)-BINAP (10)	10	6	55	90

[a] Unless stated otherwise, all reactions were carried out using $Pt(COD)Cl_2$ (0.01 mmol), ligand (0.01 mmol), Zn (0.55 mmol, 2.75 equiv.), oxabenzonorbornadiene (0.2 mmol), terminal acetylene (0.4 mmol), and toluene at 90 ℃. [b] No Zn was used. [c] $ZnCl_2$ (0.1 mol•L^{-1} in THF) was used instead of Zn. [d] 0.3 mmol Zn (1.5 equiv.) was used. [e] 0.7 mmol Zn (3.5 equiv.) was used. [f] Isolated yield after silica gel column chromatography. [g] Determined by HPLC with a Chiralcel OD-H column.

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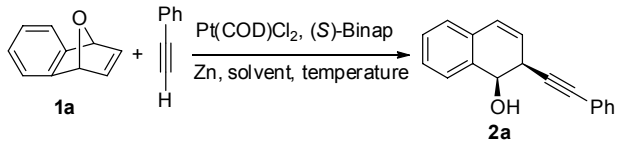
The use of toluene gave the best result both in yield and in enantioselectivity (Table 2, Entry 1). Other solvents, such as tetrahydrofuran (THF), DMSO, DME, THP resulted in no reaction or inferior results (Table 2, Entries 5—8). With toluene as the solvent, the reaction temperature was tested. The best yield and *ee* was obtained when the reaction temperature was at 90 ℃ (Table 2, Entry 1). The reaction did not work at room temperature, and a too high temperature led to a worse outcome in yield and *ee* (Table 2, Entries 9, 10).

Table 2 Effect of solvent and temperature on the asymmetric ring-opening of oxabenzonorbornadiene **1a** with phenylacetylene[a]



1a **2a**

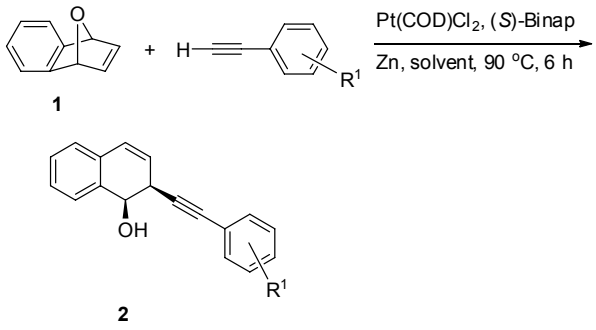
Entry	Solvent	Temperature/℃	Time/h	Yield[b]/%	*ee*[c]/%
1	Toluene	90	6	50	92
2	CH_3CN	90	7	15	95
3	DCM	90	7	19	93
4	Dioxane	90	5	19	95
5	DME	90	5	35	46
6	THP	90	5	7	69
7	THF	90	5	—	—
8	DMSO	90	6	—	—
9	Toluene	r.t.	24	—	—
10	Toluene	60	22	10	51
11	Toluene	120	1	39	10

[a] Unless stated otherwise, all reactions were carried out using $Pt(COD)Cl_2$ (0.01 mmol), ligand (0.01 mmol), Zn (0.55 mmol), oxabenzonorbornadiene (0.2 mmol), terminal acetylene (0.4 mmol) at 90 ℃. [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel OD-H column.

Under the optimized reaction conditions, the scope of this platinum-catalyzed ring opening reaction was explored. Different substituents in the phenylacetylene moiety were tolerated, including electron-donating groups, such as 4-alkyl (Table 3, Entries 7—10) and 4-alkoxyl (Table 3, Entries 11, 12), electron-withdrawing groups, such as Cl, Br, and NO_2 (Entries 2—6). In all cases, the reaction afforded *cis*-2-alkynyl-1,2-dihydronaphthalen-1-ols in moderate yield with moderate to high enantioselectivities, and the starting material oxabenzonorbornadiene was consumed and some unseparated mess was obtained except the ring-opening product. Additionally, three aliphatic terminal acetylenes were investigated for the reaction, but no ring-opening product was obtained except some inseparable mess (Table 3, Entries 13—15).

The configuration of the ring-opening product **2e** was confirmed by X-ray crystallography analysis

Table 3 Scope of the alkynes[a]



1 **2**

Entry	R^1	Product	Yield[b]/%	*ee*[c]/%
1	H	**2a**	50	92
2	4-Cl	**2b**	40	50
3	3-Cl	**2c**	44	43
4	2-Cl	**2d**	35	50
5	4-Br	**2e**	42	71
6	4-NO_2	**2f**	54	61
7	4-CH_3	**2g**	60	61
8	4-C_2H_5	**2h**	62	51
9	4-C_3H_7	**2i**	42	63
10	4-*n*-C_5H_{11}	**2j**	51	67
11	4-OCH_3	**2k**	33	30
12	4-OCH_2CH_3	**2l**	51	50
13	1-Pentyne	**2m**	0	—
14	3,3-Dimethylbut-1-yne	**2n**	0	—
15	Ethynyltrimethylsilane	**2o**	0	—

[a] Conditions: $Pt(COD)Cl_2$ (0.01 mmol), ligand (0.01 mmol), Zn (0.55 mmol), oxabenzonorbornadiene (0.2 mmol), terminal acetylene (0.4 mmol) and toluene at 90 ℃ under N_2. [b] Isolated yield after silica gel column chromatography. [c] Determined by HPLC with a Chiralcel OD-H column.

(CCDC 909135). The single crystal was obtained by solvent evaporation from a solution of CH_2Cl_2. The absolute configuration was assigned as (1*R*,2*S*) as appears in Figure 1.

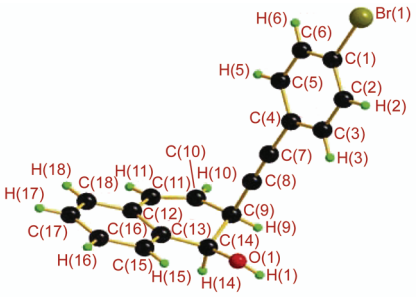


Figure 1 Crystal structure of **2e**.

Conclusions

In conclusion, we have developed the first platinum(II)-catalyzed asymmetric ring-opening of oxabenzonorbornadiene with terminal aromatic alkynes. The

reaction can proceed smoothly with a variety of substituted phenylacetylene in the presence of $Pt(COD)Cl_2$/(*S*)-BINAP with the addition of zinc powder, and provides an optional approach to synthesize the optically active *cis*-2-alkynyl-1,2-dihydronaphthalen-1-ols in moderate yields and with moderate to high enantioselectivity under mild conditions.

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