Supporting Information

Introverted Phosphorous-Au Cavitands for Catalytic Use

Michael P. Schramm[b], Mao Kanaura[a], Kouhei Ito[a], Masataka Ide[a], and Tetsuo Iwasawa[a]*

[a] Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu, 520-2194, Japan
[b] Department of Chemistry and Biochemistry, California State University Long Beach, 1250 Bellflower Blvd., Long Beach, CA 90840, USA

corresponding author email: iwasawa@rins.ryukoku.ac.jp

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h) The ¹H and ¹³C NMR spectra of all new compounds for 2-7.
a) Standard Reaction Conditions for Hydration of Terminal Alkynes.

5.0 mg of Au-Cl cavitand (0.0028 mmoles, 5 mol %, typically cavitand 3) and 0.7 mg of AgOTf (0.0028 mmoles, 5 mol %) were mixed in a small 1.0 mL vial with 0.55 mL of deuterated solvent (typically, [D$_8$]toluene) and heated to 85 °C (or 60 °C for CDCl$_3$) for 30 minutes. Terminal alkyne (0.056 mmoles) was added to the vial and the solution was transferred to an NMR tube and heated for an additional 1 hour, and then NMR was acquired at multiple intervals.

b) Standard Reaction Conditions for Conia-Ene Reaction of 8

5.0 mg of Au-Cl cavitand (0.0028 mmoles, 5 mol %, typically cavitand 3) and ~ 0.7 mg of AgOTf (0.0028 mmoles, 5 mol %) were mixed in a small 1.0 mL vial with 0.55 mL of deuterated solvent (typically, [D$_8$]toluene) and heated to 85 °C (or 60 °C for CDCl$_3$) for 30 minutes. Ketoester alkyne 8 (11.0 mg, 0.056 mmoles) was added to the vial and the solution was transferred to an NMR tube and heated for an additional 1 hour, and then NMR was acquired at multiple intervals.
c) Consecutive NMR spectra for reactions of ethynylbenzene with AgOTf, H₂O, and 3.

![NMR spectra diagram](image)

Figure 1S. ¹H NMR (400 MHz, [D₈]toluene) a) ethynylbenzene (0.019 mmol), b) 42 mol% AgOTf added, c) 6 eq of water added and heated to 85 °C for 1 hour, d) 3 (5 mol%) added and heated for 1 hour and e) heated for 12 more hours.
d) Data of HRMS of 3 mixed with AgOTf.
Figure 2S. HRMS (MALDI-TOF) of 3 mixed with AgOTf in CH$_2$Cl$_2$ after sitting for 15 minutes. Top for only species in region of interest is [3 - Cl]$^+$ (calculated: 1752.8758, observed: 1752.8667), and bottom for the spectrum in full region.
e) Representative $^1$H NMR spectrum (400 MHz) for the hydration of ethynylbenzene to benzophenone.

Reactions were carried out with 0.056 mmoles of substrate, 0.056 mmoles water, 5% 3, 5% AgOTf, 0.55 mL of [D$_8$]toluene, under 85 °C for 19 hours. The spectrum shown below is the representative portion of up- and down-field for ease of view.
f) Representative $^1$H NMR spectrum (400 MHz) for the hydration of 1-ethynylbenzene to 1-(naphthalen-1-yl)ethan-1-one.

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g) Representative $^1$H NMR spectrum (400 MHz) for the hydration of 9-ethynylanthracene to 1-(anthracen-9-yl)ethan-1-one.

Reactions were carried out with 0.056 mmoles of substrate, 0.056 mmoles water, 5% 3, 5% AgOTf, 0.55 mL [D$_8$]toluene, under 85 °C and 1 hour. The spectrum shown below is the representative portion of up- and down-field for ease of view.
h) The $^1$H and $^{13}$C NMR spectra of all new compounds for 2-7.

**Compound 2**

$^1$H NMR spectrum in CDCl$_3$
Compound 2

$^1$H NMR spectrum in toluene-$d_8$
Compound 2

$^{13}$C NMR spectrum in CDCl$_3$
Compound 3

$^1$H NMR spectrum in CDCl$_3$
Compound 3

$^1$H NMR spectrum in toluene-$d_8$
Compound 3

$^{13}$C NMR spectrum in CD$_2$Cl$_2$
Compound 4a

$^1$H NMR spectrum in CDCl$_3$
Compound 4a

$^1$H NMR spectrum in toluene-$d_8$
Compound 4a

$^{13}$C NMR spectrum in CDCl$_3$
Compound 4b

$^1$H NMR spectrum in CDCl$_3$
Compound 4b

$^{13}$C NMR spectrum in CDCl$_3$
Compound 5

$^1$H NMR spectrum in CDCl$_3$
Compound 5

$^1$H NMR spectrum in toluene-$d_8$
**Compound 5**

$^{13}$C NMR spectrum in CDCl$_3$
Compound 6

$^1$H NMR spectrum in CDCl$_3$
Compound 6

$^1$H NMR spectrum in toluene-$d_8$
Compound 6

$^{13}$C NMR spectrum in CDCl$_3$
Compound 7

$^1$H NMR spectrum in CDCl$_3$
Compound 7

$^1$H NMR spectrum in toluene-$d_8$
Compound 7

$^{13}$C NMR spectrum in CDCl$_3$