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Article

Supporting Information: Hydroalkoxylation of Terminal and Internal Alkynes Catalyzed by Dinuclear Gold(I) Complexes with Bridging Di(N-Heterocyclic Carbene) Ligands

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1. NMR spectra of compound AuIL7

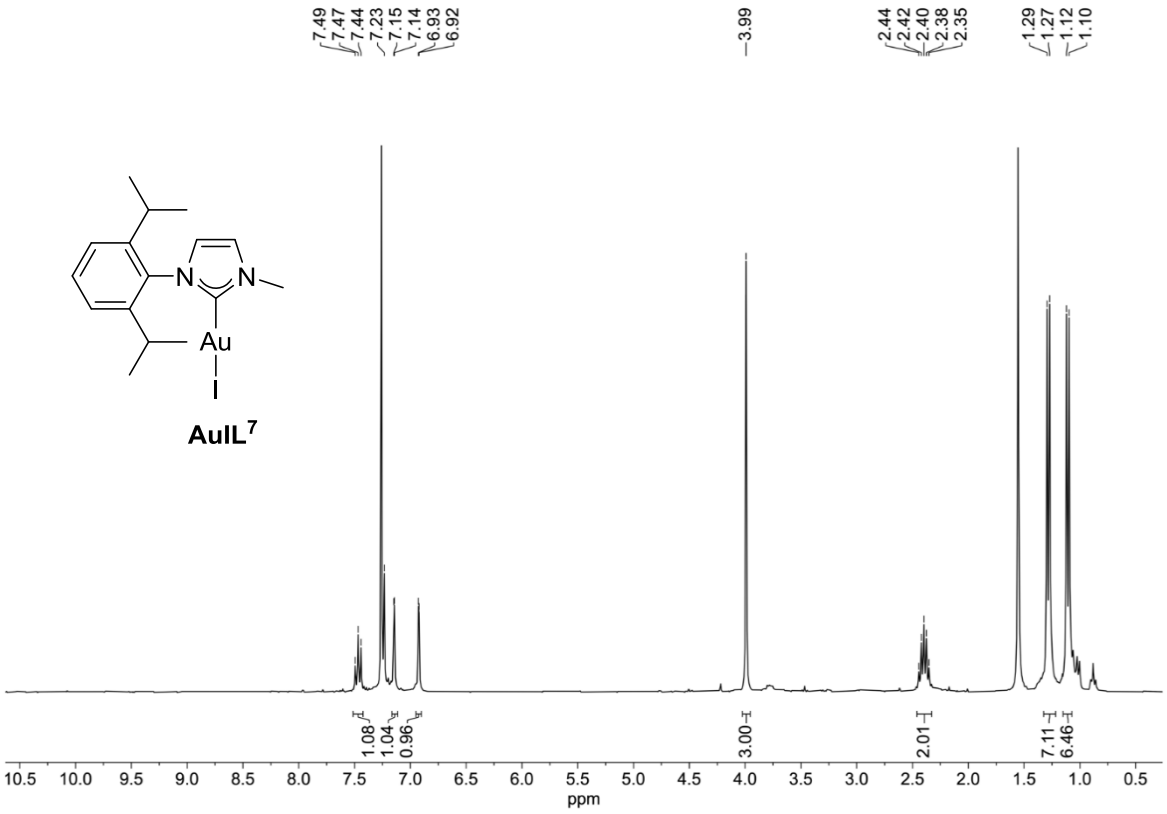


Figure S1. ^{1}H-NMR spectrum ($CDCl_3$, 300 MHz) of **AuIL7**.

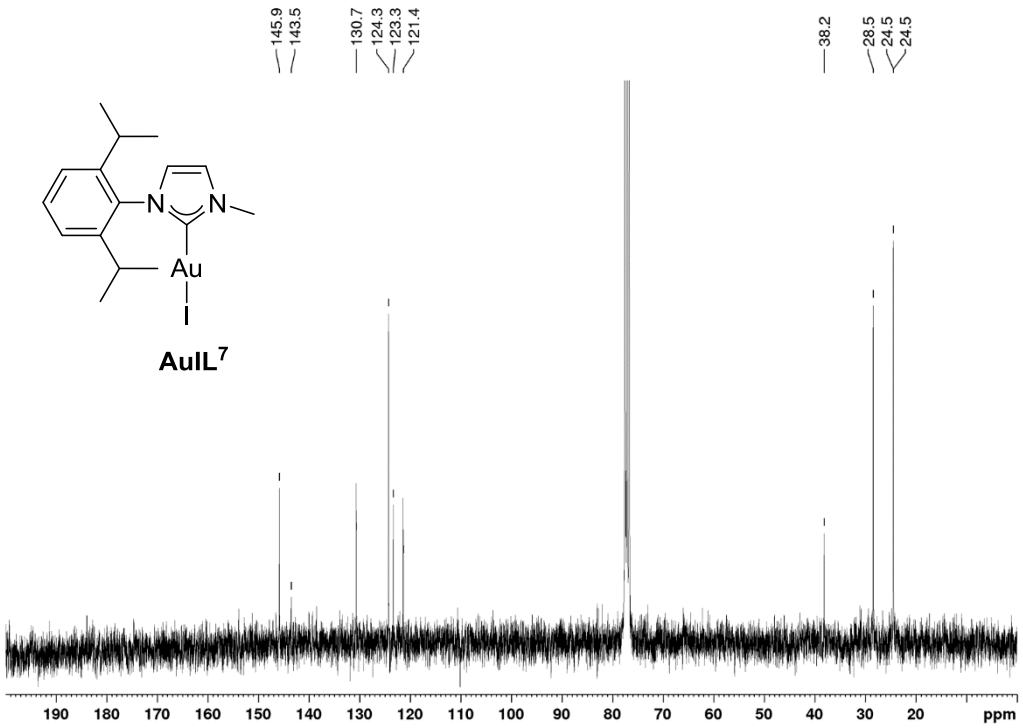


Figure S2. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz) of **AuIL**^{7}.

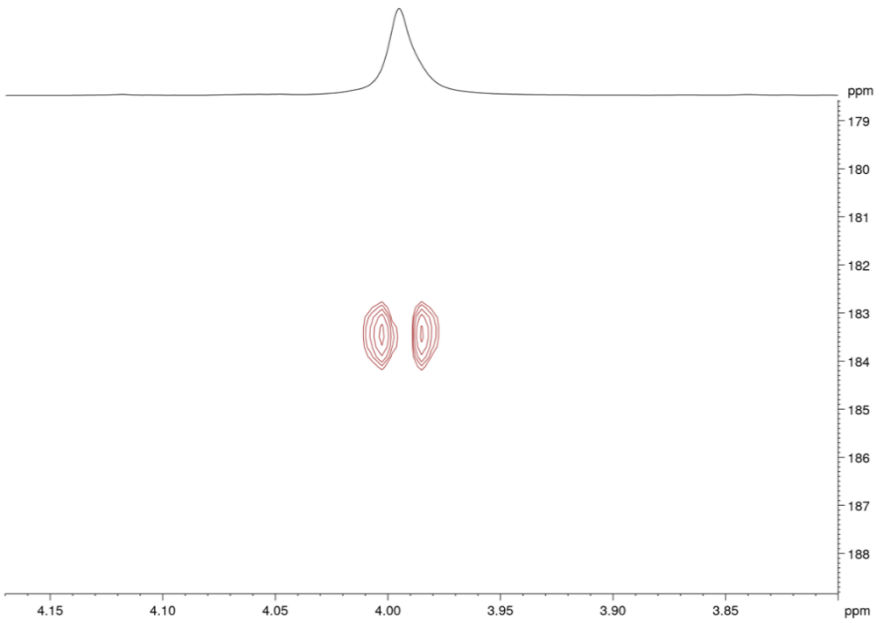


Figure S3. Portion of the $^{1}H,^{13}C$-*HMBC* spectrum of **AuIL**^{7} in $CDCl_3$ showing the resonance of the carbene carbon.

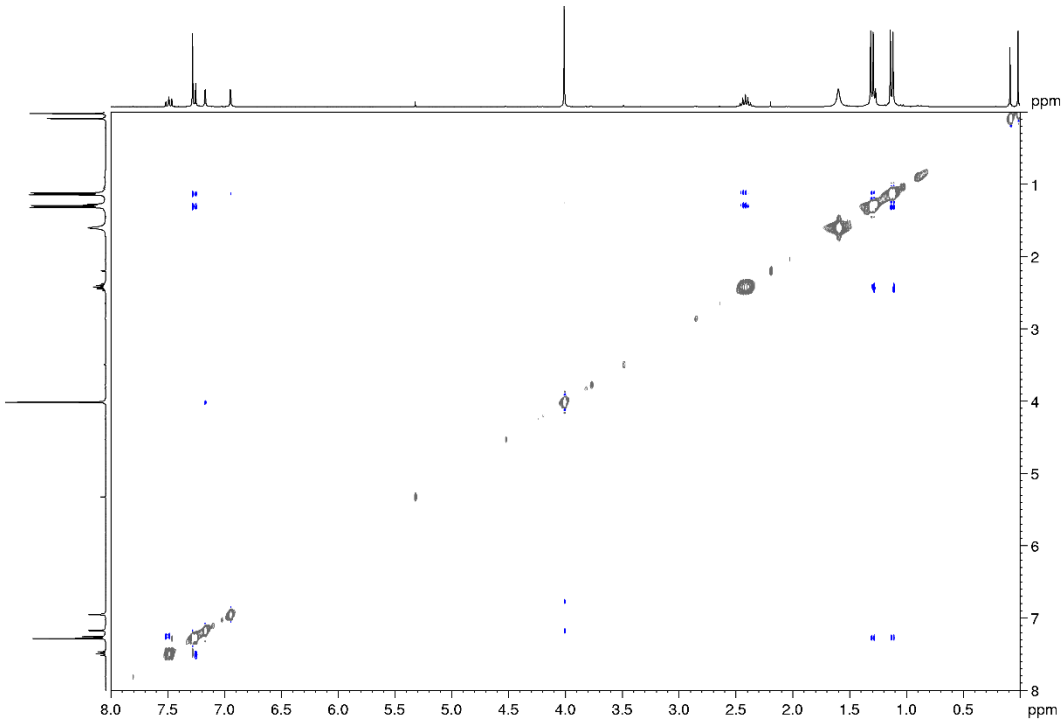


Figure S4. $^{1}H,^{1}H$ -*NOESY* NMR spectrum of **AuIL^{7}** in $CDCl_3$.

2. Crystallographic data of compound $Au_2Br_2L^4$

Table S1. Crystallographic data of compound **$Au_2Br_2L^4$**.

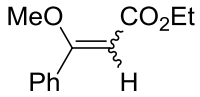
Compound	**$Au_2Br_2L^4$**
Formula	$C_{33.5}H_{44.5}Au_2Br_2Cl_3N_4$
Molecular Weight	1163.33
Crystal system	Monoclinic
Space group	$P2_1/n$
a[Å]	13.5252(4)
b[Å]	12.9755(4)
c[Å]	23.9510(7)
α[°]	90
β[°]	91.8390(10)
γ[°]	90
V[Å^3]	4201.1(2)
Temperature (K)	200(2)
Z	4
D_{calc}[g·cm^{-3}]	1.839
μ[cm^{-1}]	9.095

F(000)	2210.0
Reflections collected	52909
Independent reflections	10401
Reflections in refinement	10401
R(int)	0.0400
Refined parameters	419
R_1 [$I > 2\sigma(I)$]	$R_1 = 0.0509$ $wR_2 = 0.1330$
wR_2 [all data]	$R_1 = 0.0735$ $wR_2 = 0.1537$
GOF	1.052
CCDC	1968216

$R_1 = \Sigma|Fo-Fc|/\Sigma(Fo)$; $wR_2 = [\Sigma[w(Fo^2-Fc^2)^2]/\Sigma[w(Fo^2)^2]]^{1/2}$.

3. Identification of the products of the alkyne hydroalkoxidation reactions

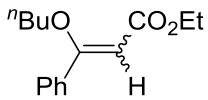
3aa. (E/Z) 3-methoxy-3-phenyl-ethylacrylate [1]



^{1}H-NMR Z-Isomer (200 MHz, $CDCl_3$) δ ppm: 7.63-7.31 (m, 5H), 5.54 (s, 1H), 4.22 (q, J=7.1 Hz, 2H), 3.84 (s, 3H), 1.32 (t, J=7.1, 3H).

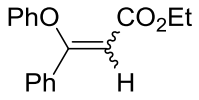
^{1}H-NMR E-Isomer (200 MHz, $CDCl_3$) δ ppm: 7.63-7.31 (m, 5H), 5.27 (s, 1H), 4.05 (q, J=7.1 Hz, 2H), 3.81 (s, 3H), 1.15 (t, J=7.1Hz, 2H).

3ab. (E/Z)-Ethyl 3-butoxy-3-phenylacrylate



NMR signals of product **3ab** were identified by similarity with those of the analogous product **3aa**.

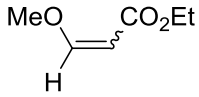
3ac. ethyl 3-phenoxy-3-phenylacrylate [2]



(**3ac**)

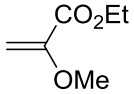
^{1}H NMR Z-Isomer (400 MHz, CDCl3) δ 7.60 (d, J = 8.0 Hz, 2H), 7.37-7.31 (m, 3H), 7.25-7.20 (m, 2H), 6.97-6.94 (m, 3H), 6.15 (s, 1H), 4.12 (q, J = 8.0 Hz, 2H), 1.18 (t, J = 8.0 Hz, 3H) ppm.

3ca. (Z/E)-Ethyl 3-methoxyacrylate



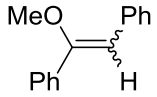
Product **3ca** is commercially available and the NMR signals can be found in on-line databases.

3ca′. Ethyl 2-methoxyacrylate



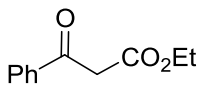
NMR signals of product **3ca′** were identified by similarity with those of the analogous species methyl 2-metoxyacrylate [3].

3ea. (Z)-1-methoxy-1,2-diphenylacetylene [4]



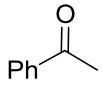
^{1}H-NMR Z-Isomer (250 MHz, $CDCl_3$) δ ppm: 3.55 (s, 3H), 6.02 (s, 1H), 7.13-7.16 (m, 1H), 7.24-7.32 (m, 5H), 7.48 (dd, J = 8.0 Hz, J = 1.5 Hz, 2H), 7.63 (d, J = 7.3 Hz, 2H).

5a. 3-oxo-3-phenyl Ethylpropionate [5]



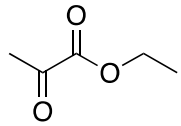
^{1}H-NMR of the keto form (400 MHz, $CDCl_3$) δ ppm: 1.22-1.26 (m, 3H), 3.96 (s, 2H), 4.17-4.29 (m, 2H), 7.37-7.48 (m, 2H), 7.55-7.59 (m, 1H), 7.92-7.95 (m, 2H).

5b. Acetophenone [6]



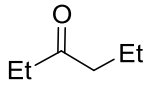
^{1}H-NMR (250 MHz, $CDCl_3$) δ ppm: 2.54 (s, 3H), 7.36-7.53 (m, 3H), 7.88-7,93 (m, 2H).

5c. Ethyl pyruvate [7]



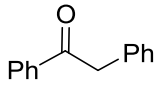
^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 1.38 (t, 3H), 2.47 (s, 3H), 4.32 (q, 2H).

5d. 3-hexanone [8]



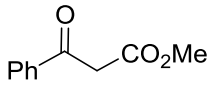
^{1}H-NMR (200 MHz, CDCl3) δ ppm: 0.89 (s, 3H), 1.02 (s, 3H), 1.60 (q, J =7.4 Hz, 2H), 2.49-2.26 (m, 4H).

5e. 1,2-diphenylethanone [9]



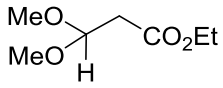
^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 4.32 (s, 2H), 7.31-7.29 (m, 3H), 7.36 (t, J=7.3 Hz, 2H), 7.49 (t, J=7.6 Hz, 2H), 7.59 (t, J=7.4 Hz, 1H), 8.05 (d, J=7.7 Hz, 2H).

5g. Methyl 3-oxo-3-phenylpropionate [10]



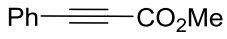
^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 3.75 (s, 3H), 4.00 (s, 2H), 7.50-7.46 (m, 2H), 7.61-7.57 (m, 1H), 7.95-7.93 (m, 2H).

4ca. Ethyl 3,3-dimethoxypropionate [11]



^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm: 1.25 (t, J=3.6 Hz, 3H), 2.63 (d, J=6.0 Hz, 2H), 3.35 (s, 6H), 4.15 (q, J=3.6 Hz, 2H), 4.82 (t, J=6.0 Hz, 1H).

1g. Methyl phenylpropiolate [12]



^{1}H-NMR (300 MHz, $CDCl_3$) δ ppm: 3.85 (s, 3H), 7.32-7.42 (m, 2H), 7.42 - 7.49 (m, 1H), 7.54-7.64 (m, 2H).

4. Catalysts screening in the hydromethoxylation of ethyl phenylpropiolate

Table S2. Catalysts screening in the hydromethoxylation of ethyl phenylpropiolate.

Entry	Cat (mol %)	t (h)	Alkyne Conversion (%)[a]	Yield (%)[a]
1	**$Au_2Br_2L^1$**	1.5	67	(*E*)-**3aa** (9); (*Z*)-**3aa** (13); **4aa** (5); **5a** (40)
		6.5	91	**4aa** (30); **5a** (61)
		22	92	**4aa** (5); **5a** (87)
2	**$Au_2Br_2L^2$**	1.5	78	(*E*)-**3aa** (14); **5a** (64)
		6.5	90	(*Z*)-**3aa** (10); **5a** (80)
3	**$Au_2Br_2L^3$**	1.5	62	(*E*)-**3aa** (8); (*Z*)-**3aa** (43); **4aa** (7); **5a** (4)
		6.5	86	(*E*)-**3aa** (1); (*Z*)-**3aa** (2); **4aa** (53); **5a** (30)
		22	87	**4aa** (19); **5a** (68)
4	**$Au_2Br_2L^4$**	1	100	(*E*)-**3aa** (33); **5a** (67)
		18.5	100	**5a** (100)
5	**$Au_2Br_2L^5$**	1	86	(*E*)-**3aa** (27); (*Z*)-**3aa** (39); **4aa** (9); **5a** (11)
		18.5	89	**4aa** (17); **5a** (72)
6	**$Au_2Br_2L^6$**	1	72	(*E*)-**3aa** (32); (*Z*)-**3aa** (24); **4aa** (6); **5a** (10)
		23	100	**5a** (100)

Reaction conditions: Ethyl phenylpropiolate (0.6 mmol), MeOH (0.5 mL, 12.3 mmol), **Au_2Br_2L** (0.006 mmol), AgOTf co-cat. (0.012 mmol), 40 °C. [a] Alkyne conversion and product yields have been determined by ^{1}H NMR.

References

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