



Gold-catalyzed synthesis of 1,3-disubstituted benzenes through tandem allylation/cyclization reaction of alkynals

Sabyasachi Bhunia^a, Shariar Md. Abu Sohel^a, Chao-Chin Yang^a, Shie-Fu Lush^b, Fwu-Ming Shen^c, Rai-Shung Liu^{a,*}

^a Department of Chemistry, National Tsing-Hua University, Hsinchu 30043, Taiwan, ROC

^b Department of Biotechnology, Yuan-Pei University, Hsinchu, Taiwan, ROC

^c Department of Medical Laboratory Science and Biotechnology, Yuan-Pei University, Hsinchu, Taiwan, ROC

ARTICLE INFO

Article history:

Received 26 August 2008

Received in revised form 10 October 2008

Accepted 29 October 2008

Available online 6 November 2008

Keywords:

Allylation

Alkynal

Benzenes

Catalysis

Tandem reaction

ABSTRACT

Treatment of alkynals with 2-substituted allylsilanes and PPh₃AuCl/AgOTf (5/3 mol%) catalyst led to formation of 1,3-disubstituted benzenes efficiently. This reaction sequence comprises an initial allylation of aldehyde, followed by cycloisomerization of enynes; PPh₃AuOTf is active in both steps.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

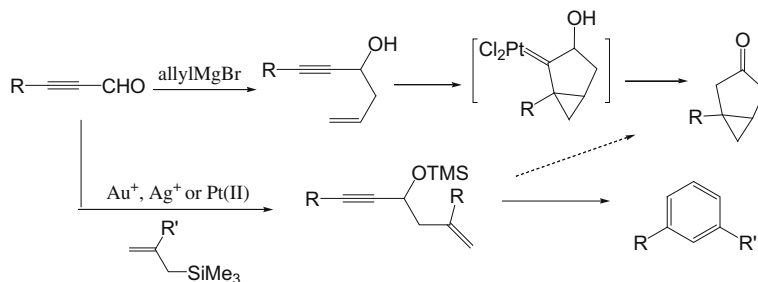
Tandem reactions have been the subject of intensive investigations in organic synthesis [1]. The high efficiency and brief procedures are the beneficial features of such reactions. With a single workup, one can deliver a complicate molecule that would otherwise have to be prepared over the course of several individual steps. Transition-metal catalyzed cyclizations of enynes [2–6] have emerged as powerful tools for the synthesis of carbocyclic compounds, and Pt(II) and Au(I) catalysts are commonly used as the catalysts because of their superior chemoselectivities and activities. Barriault has reported the gold catalyzed benzannulation of 3-hydroxy-1.5-enynes for the synthesis of tetrahydronaphthalenes [7,8]. Scheme 1 shows an elegant example, reported by Fürstner and coworkers [5e] for the synthesis of bicyclo[3.1.0]hexanones via PtCl₂ catalyzed cycloisomerization of 5-en-1-yn-3-ols, which were prepared by Grignard reagents. As Ag(I) and Pt(II) catalysts were also active in catalytic addition of allylsilanes to carbonyl compounds [9], we sought to accomplish one-pot synthesis of such ketones using suitable Ag(I), Pt(II) and Au(I) catalysts. Nevertheless, the outcome of our new attempts is the efficient production of 1,3-disubstituted benzenes using a mixture of PPh₃AuCl (5%) and AgOTf (3%).

2. Results and discussion

As shown in Table 1, we examined the cyclization of alkynal **1** and allylsilanes (**2a–b**) over various Ag(I), Pt(II) and Au(I) catalysts, each at 5 mol% except for entries 6–7. Treatment of alkynal **1** with allylsilane **2a** and AuClPPh₃/AgSbF₆ led to a messy mixture of products (Table 1, entry 1). AuCl, AuClPPh₃ and AuCl₃ were not effective to bring about any transformation (entries 2–4). AgOTf gave homoallylic alcohol **3a** exclusively (93% yield) without a secondary enyne cycloisomerization. However, the use of AuClPPh₃ (5 mol%)/AgOTf (3 mol%) catalyst in CH₂Cl₂ at a brief time (2.0 h) gave homoallylic alcohol (**3a**) and biphenyl compound (**4a**) in 28% and 42% yields, respectively, (entry 5). At a prolonged period (5 h), we only obtained biphenyl **4a** with the yield up to 84% (entry 6); this observation confirms the intermediacy of **3a** in this sequence. We envisage that “PPh₃AuOTf” generated here is active toward both allylation and aromatization reaction because free AgOTf is thought to be negligible in this catalyst composition (Au:Ag = 5:3). PtCl₂/CO [10] was not suitable to this reaction sequence even at 80 °C (entries 8 and 9). We extended this gold catalysis to unsubstituted allylsilane **2b**, which led to the formation of 1-phenylhex-5-en-1-yn-3-ol (**3b**) without any further cyclization. Treatment of **1** and **2a** with 5% TfOH for 24 h at room temperature led to the protonation of allylsilane and the alkynal **1** was recovered unreacted (entry 11) [11]. Similarly, 5% TMSOTf failed to give desired **4a** (entry 12).

* Corresponding author.

E-mail address: rsliu@mx.nthu.edu.tw (R.-S. Liu).



Scheme 1.

We studied the scope of this gold-catalyzed tandem catalysis (Table 2). Entry 1 shows the applicability of this cyclization to 2-phenylallylsilane **2c**, which gave 1,3-diphenyl benzene **10** in 90% yield (entry 1). We prepared alkyne **5–6** bearing a *p*- and *m*-methoxyphenyl groups **5–6**, which gave the corresponding 1,3-disubstituted phenyl compounds **11–13** in 80–88% yields. Substrates **7–8** bearing an electron-deficient *p*-nitro- and *p*-trifluoromethylphenyl group were very suitable for this tandem sequence, giving 78–88% yields of resulting products **14–17**. Aliphatic alkyne **9** also worked well with allylsilanes **2a** and **2c**, giving diphenyl compound in 82–86% yields.

We also examined the tandem cyclization of 3-phenylpropionaldehyde (**1**) with various allylsilanes **2d–2h** bearing various 2-substituted R groups (Table 3). 2-arylallylsilanes **2d–2f** (aryl = *p*-^tBuC₆H₄, 2,4-dimethylphenyl, 2-benzothienyl) were very suitable to this cyclization, giving desired biphenyl products **20–22** with yields exceeding 81%. This tandem catalysis is extendible to allylsilane **2g** bearing a *n*-pentyl group (**2e**), giving compound **23** in 87% yield. Carbomethoxy substituted allylsilane (**2h**) only led to its exclusive recovery even for a prolonged reaction time; this is obviously due to its low reactivity in allylation of carbonyl compounds.

We propose a plausible mechanism to rationalize the course of this allylation/aromatization cascade (Scheme 2). As depicted in Scheme 1, “PPh₃AuOTf” was shown to be catalytically active toward allylation and cyclization. We previously reported that [11a] treatment of “PPh₃AuOTf” with allylSiMe₃ did not generate allylAuPPh₃. Consequently we believe that PPh₃AuOTf initially

Table 1

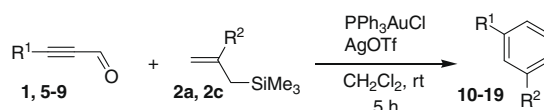
Catalyst screening over various acid catalysts

Entry ^a	Catalyst	Allylsilane	Condition	Products (yield %) ^b
1	5% AuClPPh ₃ /5% AgSbF ₆	2a	1 h, rt	Messy
2	5% AuCl	2a	10 h, rt	N.R. ^c
3	5% AuCl ₃	2a	10 h, rt	N.R. ^c
4	5% AuClPPh ₃	2a	24 h, rt	N.R. ^c
5	5% AgOTf	2a	24 h, rt	3a (93)
6 ^d	5% AuClPPh ₃ /3% AgOTf	2a	2 h, rt	3a (28), 4a (42)
7	5% AuClPPh ₃ /3% AgOTf	2a	5.0 h, rt	4a (84)
8	5% PtCl ₂ /CO	2a	10 h, rt	N.R. ^c
9	5% PtCl ₂ /CO	2a	0.5 h, 80 °C	messy
10	5% AuClPPh ₃ /5% AgOTf	2b	24 h, rt	3b (64)
11	5% TfOH	2a	24 h, rt	N.R. ^c
12	5% TMSOTf	2a	24 h, rt	3a (33)

^a [Substrate] = 0.22 M.^b Yields are for products isolated after silica gel column chromatography.^c No reaction.^d 12% of unreacted alkyne **1** was recovered.

Table 2

Tandem allylation/cyclization of alkynals.



Entry ^a	Alkyne (R ¹)	Silane (R ²)	Product	Yield (%) ^b
1	Ph (1)	Ph (2c)	10	90
2	<i>p</i> -MeOC ₆ H ₄ (5)	Me (2a)	11	88
3	<i>m</i> -MeOC ₆ H ₄ (6)	Me (2a)	12	80
4	<i>m</i> -MeOC ₆ H ₄ (6)	Ph (2c)	13	88
5	<i>p</i> -O ₂ NC ₆ H ₄ (7)	Me (2a)	14	78
6	<i>p</i> -O ₂ NC ₆ H ₄ (7)	Ph (2c)	15	80
7	<i>p</i> -F ₃ CC ₆ H ₄ (8)	Me (2a)	16	85
8	<i>p</i> -F ₃ CC ₆ H ₄ (8)	Ph (2c)	17	88
9	<i>n</i> -C ₆ H ₁₃ (9)	Me (2a)	18	82
10	<i>n</i> -C ₆ H ₁₃ (9)	Ph (2c)	19	86

^a [Substrate] = 0.22 M.^b Yield of isolated product after silica gel column chromatography.

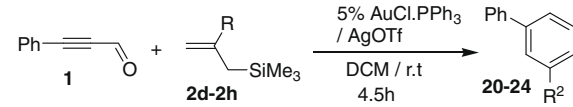
coordinates to aldehyde to activate the allylation, leading to the formation of alcohol derivative **B** through intermediate **A**. We envisage that the gold-alkoxy group of intermediate **B** tends to undergo exchange with TMSOTf to regenerate active PPh₃AuOTf because Si(IV) has a better affinity toward the alkoxy group than Au(I). A subsequent electrophilic activation of the alkyne **C** by Au⁺ gives rise to a 6-*endo-dig* ring closure, producing carbenoid intermediate **E**, which is also represented by resonance form **E'**. In contrast with the Fürstner pathway, as depicted in Scheme 1, we envisage that tertiary carbocation **E'** enhance the acidity of the neighboring CH₂ hydrogen that was readily deprotonated by OTf anion to generate Au-cyclohexadienyl species. A final elimination of one molecule of TMSOH from species **F** led to gold-phenyl species **G**, which undergoes protodemetalation to give the final product. According to this proposed mechanism, it is clear that the better stabilization of R₂ = Ph, alkyl on the cationic intermediate **E** and **E'** are crucial to realize the aromatization. This assessment accounts for the failure to obtain aromatization product from unsubstituted allylsilane **2b**.

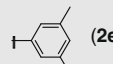
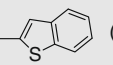
In conclusion, we reported a facile synthesis of 1,3-disubstituted benzenes through cyclization of alkyne aldehydes and 2-substituted allylsilanes. This reaction sequence comprises a tandem allylation and cyclization of enynes; the active species for these two steps are PPh₃AuOTf. A wide scope of alkyne aldehydes is applicable to this tandem sequence whereas the nature of the 2-substituent of allylsilane is crucial for the both initial allylation and the secondary aromatization. Evaluation of additional values of such reactions is currently underway.

3. Experimental

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard

Table 3
Tandem allylation/cyclization of 3-phenylpropionaldehyde



Entry ^a	Silane	Product	Yield (%) ^b
1	<i>p</i> - ^t Bu-C ₆ H ₄ (2d)	20	94
2	 (2e)	21	92
3	 (2f)	22	81
4	<i>n</i> -C ₅ H ₁₁ (2g)	23	87
5	CO ₂ Me (2h)	24	N.R. ^c

^a Substrate = 0.22 M.

^b Yield of isolated product after silica gel column chromatography.

^c No reaction.

syringe, cannula and septa apparatus. Hexane was dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH₂ and distilled before use. All the ¹H NMR and ¹³C NMR were recorded in CDCl₃ solution. Allylsilanes were prepared according to the procedures reported in literature [12].

3.1. Procedure for the synthesis of 3-phenylpropionaldehyde (1)

To a mixture of Pd(PPh₃)₂Cl₂ (0.344 g, 0.49 mmol) and CuI (0.093 g, 0.49 mmol) was added a triethylamine (15 mL) solution of iodobenzene (2.00 g, 9.80 mmol) at 0 °C, and the mixture was stirred for 10 min before addition of propargyl alcohol (0.549 g, 9.80 mmol). At the end of reaction, the resulting solution was filtered, concentrated in vacuo, and partitioned between ethyl acetate and water. The organic layer was washed with brine and dried over MgSO₄ and the residues were chromatographed through a silica column (ethyl acetate/hexane, 1:9) to afford the compound **1** as light-yellow oil (1.14 g, 8.63 mmol, 88%). This product was dissolved in dichloromethane (20 mL), cooled to 0 °C, and treated with a mixture (1:1 w/w) of PCC (2.42 g, 11.21 mmol) and celite. The resulting suspension was stirred at 0 °C for 1 h, and the reaction mixture was filtered through a short silica pad. Concentration of the solution gave the crude product which was then subjected to a silica column chromatography (ethyl acetate–hexane, 0.5:9.5), giving 3-phenylpropionaldehyde (**1**) as oil. (0.808 g, 6.208 mmol, 72%).

3.2. Experimental procedure for tandem allylation/gold-catalyzed cyclization

A long tube containing AuClPPh₃ (19.0 mg, 0.0384 mmol) and AgOTf (5.80 mg, 0.0225 mmol) was evacuated and backfilled with N₂. After repeating this procedure twice, the tube was charged with alkynal **1** (0.1 g, 0.768 mmol), allylsilane **2a** (0.108 g, 0.845 mmol) and CH₂Cl₂ (3.5 ml). The resulting mixture was stirred at 23 °C, 4.5 h, and filtered over a small silica bed. After removal of the solvent in vacuo, the residues were purified on a silica column (hexane) to give the **4a** (0.1 g, 0.645 mmol, 84%) as a colorless liquid.

3-Methylbiphenyl 4a: Colorless oil, IR (nujol, cm⁻¹): 3028 (m), 2906 (m), 685 (s), 778 (s); ¹H NMR (600 MHz, CDCl₃): δ 7.59 ~ 7.58 (m, 2H), 7.44 ~ 7.39 (m, 4H), 7.35 ~ 7.32 (m, 2H), 7.16 (d, *J* = 7.4 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 141.3, 141.2, 138.3, 128.7 (×2CH), 128.6, 127.9, 127.1 (×2CH), 124.2, 21.5; HRMS Calc. for C₁₃H₁₂: 168.0939, found: 168.0941.

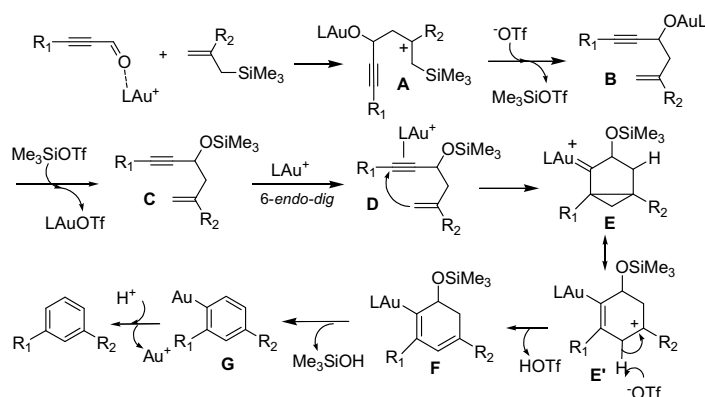
Compound 10: White solid, IR (nujol, cm⁻¹): 3039 (m), 2910(m), 683(s), 774(s); ¹H NMR (600 MHz, CDCl₃): δ 7.86 ~ 7.85 (m, 1H), 7.69 ~ 7.68 (m, 4 H), 7.62 ~ 7.60 (m, 2H), 7.56 ~ 7.48 (m, 5H), 7.42 ~ 7.39 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 141.7, 141.1, 129.1, 128.8, 127.4, 127.2, 126.1, 126.0; HRMS Calc. for C₁₈H₁₄: 230.1096, found: 230.1094.

4'-Methoxy-3-methylbiphenyl 11: Colorless oil, IR (nujol, cm⁻¹): 3035 (m), 2904 (m), 1248 (s), 1037 (s); ¹H NMR (600 MHz, CDCl₃): δ 7.54 ~ 7.52 (m, 2H), 7.39 (s, 1H), 7.36 ~ 7.34 (m, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.97 ~ 6.95 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 159.4, 140.8, 138.6, 133.8, 128.8, 128.2, 127.6, 123.8, 114.3, 55.4, 21.4; HRMS Calc. for C₁₄H₁₄O: 198.1045, found: 198.1046.

3-Methoxy-3'-methylbiphenyl 12: Colorless oil, IR (nujol, cm⁻¹): 3031 (m), 2901 (m), 1246 (s), 1034 (s); ¹H NMR (600 MHz, CDCl₃): δ 7.45 ~ 7.33 (m, 4H), 7.22 ~ 7.15 (m, 3H), 6.92 ~ 6.90 (m, 1H), 3.87 (s, 3H), 2.44 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 160.2, 142.8, 141.0, 138.6, 129.9, 128.7, 128.3, 127.9, 124.3, 119.6, 112.8, 112.7, 55.3, 21.4; HRMS Calc. for C₁₄H₁₄O: 198.1045, found: 198.1043.

Compound 13: White solid; IR (neat, cm⁻¹): 3041 (m), 1252 (s), 1044 (s); ¹H NMR (600 MHz, CDCl₃): δ 7.78 (t, *J* = 1.6 Hz, 1H), 7.64 ~ 7.63 (m, 2H), 7.57 ~ 7.55 (m, 2H), 7.51 ~ 7.44 (m, 3H), 7.38 ~ 7.35 (m, 2H), 7.24 ~ 7.17 (m, 2H), 6.92 ~ 6.90 (m, 1H), 3.86 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.9, 142.7, 141.7, 141.6, 141.1, 129.8, 127.4, 127.2, 126.3, 126.2, 126.1, 119.7, 112.9, 112.8, 55.3; HRMS Calc. for C₁₉H₁₆O: 260.1201, found: 260.1204.

3-Methyl-4'-nitrobiphenyl 14: White solid; IR (neat, cm⁻¹): 2894 (m), 1532 (s), 1333 (s); ¹H NMR (600 MHz, CDCl₃): 8.25 ~ 8.23 (m,



Scheme 2.

2H), 7.70 ~ 7.68 (m, 2H), 7.41 ~ 7.35 (m, 3H), 7.24 (d, $J = 7.8$ Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 147.7, 146.9, 138.8, 138.6, 129.6, 128.9, 128.0, 127.6, 124.4, 123.9, 21.4; HRMS Calc. for $\text{C}_{13}\text{H}_{11}\text{NO}_2$: 213.079, found: 213.0792.

Compound 15: White solid; IR (neat, cm^{-1}): 3034 (m), 1536 (s), 1330 (s); ^1H NMR (600 MHz, CDCl_3): δ 8.30 ~ 8.28 (m, 2H), 7.81 ~ 7.76 (m, 3H), 7.66 ~ 7.54 (m, 5H), 7.49 ~ 7.38 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 147.5, 147.1, 142.2, 140.5, 139.2, 129.5, 128.9 ($\times 2\text{CH}$), 127.8, 127.7, 127.6, 127.1, 126.2, 124.1; HRMS Calc. for $\text{C}_{18}\text{H}_{13}\text{NO}_2$: 275.0946, found: 275.0948.

3-Methyl-4-(trifluoromethyl)biphenyl 16: Colorless oil; IR (neat, cm^{-1}): 3025 (m), 2902 (m), 678 (s), 772 (s); ^1H NMR (600 MHz, CDCl_3) δ 7.7 (s, 4H), 7.44 ~ 7.37 (m, 3H), 7.25 (d, $J = 7.2$ Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 144.8, 139.7, 138.6, 129.3 ~ 125.6 ($\times 2\text{C}$), 128.9, 128.8, 128, 127.4, 125.6, 124.3, 21.4; HRMS Calc. for $\text{C}_{14}\text{H}_{11}\text{F}_3$: 236.0813, found: 236.0811.

Compound 17: White solid; IR (neat, cm^{-1}): 3041 (m), 681 (s), 779 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.84 (s, 1H), 7.76 ~ 7.74 (m, 4H), 7.69 ~ 7.66 (m, 1H), 7.6 ~ 7.5 (m, 4H), 7.44 ~ 7.41 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3): δ 144.6, 142.1, 140.8, 140.3, 129.4 ~ 125.2 ($\times 2\text{C}$), 129.3, 128.8, 127.6, 127.5, 127.2, 126.9, 126.1, 125.72, 125.7; HRMS Calc. for $\text{C}_{19}\text{H}_{13}\text{F}_3$: 298.0969, found: 298.0967.

1-Hexyl-3-methylbenzene 18: Colorless oil; IR (neat, cm^{-1}): 3039 (m), 2908 (m), 687 (s), 778 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.17 (t, $J = 7.4$ Hz, 1H), 7.0 ~ 6.98 (m, 3H), 2.57 (t, $J = 7.7$ Hz, 2H), 2.34 (s, 3H), 1.62 ~ 1.29 (m, 8H), 0.89 (t, $J = 7$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 142.9, 137.6, 129.2, 128.1, 126.2, 125.4, 35.9, 31.7, 31.5, 29.1, 22.6, 21.4, 14.1; HRMS Calc. for $\text{C}_{13}\text{H}_{20}$: 176.1565, found: 176.1564.

3-Hexylbiphenyl 19: Colorless oil; IR (neat, cm^{-1}): 3036 (m), 2903 (m), 682 (s), 777 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.68 ~ 7.67 (m, 2H), 7.52 ~ 7.48 (m, 4H), 7.43 ~ 7.39 (m, 2H), 7.23 (d, $J = 7.6$ Hz, 1H), 2.75 (t, $J = 7.7$ Hz, 2H), 1.77 ~ 1.72 (m, 2H), 1.47 ~ 1.39 (m, 6H), 0.98 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 143.4, 141.5, 141.2, 128.7, 128.6, 127.3 ($\times 2\text{CH}$), 127.2, 127.1, 124.5, 36.1, 31.7, 31.5, 29.1, 22.6, 14.1; HRMS Calc. for $\text{C}_{18}\text{H}_{22}$: 238.1722, found: 238.1724.

Compound 20: White solid; IR (neat, cm^{-1}): 3044 (m), 686 (s), 776 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.89 (s, 1H), 7.72 (d, $J = 7.2$ Hz, 2H), 7.68 ~ 7.61 (m, 4H), 7.57 ~ 7.50 (m, 5H), 7.57 ~ 7.50 (m, 5H), 7.43 (t, $J = 7.2$, 1H), 1.45 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3): δ 150.4, 141.7, 141.6, 141.2, 138.2, 129.1, 128.7, 127.3, 127.2, 126.9, 126.0, 125.9, 125.8, 125.7, 34.5, 31.3; HRMS Calc. for $\text{C}_{22}\text{H}_{22}$: 286.1722, found: 286.1724.

3-Pentylbiphenyl 21: Colorless oil; IR (neat, cm^{-1}): 3035 (m), 2896 (m), 682 (s), 782 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.62 (d, $J = 7.2$ Hz, 2H), 7.47 ~ 7.35 (m, 6H), 7.19 (d, $J = 7.6$ Hz, 1H), 2.7 (t, $J = 7.6$ Hz, 2H) 1.72 ~ 1.68 (m, 2H), 1.4 ~ 1.38 (m, 4H), 0.94 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 143.4, 141.4, 141.1, 128.7, 128.6, 127.4, 127.3, 127.2, 127.1, 124.5, 36.0, 31.5, 31.2, 22.5, 14.0; HRMS Calc. for $\text{C}_{17}\text{H}_{20}$: 224.1565, found: 224.1563.

Compound 22: White solid; IR (neat, cm^{-1}): 3021 (m), 2888 (m), 680 (s), 771 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.77 (s, 1H), 7.63 (d, $J = 7.6$ Hz, 2H), 7.54 (d, $J = 7.2$ Hz, 2H), 7.49 ~ 7.43 (m, 3H), 7.35 (t, $J = 7.2$, 1H), 7.25 (s, 2H), 7.0 (s, 1H), 2.38 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 141.9, 141.6, 141.2, 141.1, 129.0, 128.9, 128.7, 127.3, 127.2 ($\times 2\text{CH}$), 126.1, 125.9, 125.1, 21.3; HRMS Calc. for $\text{C}_{20}\text{H}_{18}$: 258.1409, found: 258.1408.

2-(Biphenyl-3-yl)benzo[b]thiophene 23: White solid; IR (neat, cm^{-1}): 3029 (m), 684 (s), 783 (s); ^1H NMR (600 MHz, CDCl_3): δ 7.96 (s, 1H), 7.86 (d, $J = 7.6$ Hz, 1H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.75 ~ 7.67 (m, 3H), 7.62 (s, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.5 (s, $J = 7.2$ Hz, 3H), 7.47 ~ 7.31 (m, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 144.08, 141.9, 140.7, 140.6, 139.5, 134.7, 129.3, 128.8, 127.6,

127.2, 127.1, 125.3 ($\times 2\text{CH}$), 124.5, 124.3, 123.6, 122.2, 119.7; HRMS Calc. for $\text{C}_{20}\text{H}_{14}\text{S}$: 286.0816, found: 286.0813.

Acknowledgements

We thank the National Science Council, Taiwan for their generous financial support.

References

- [1] (a) T.L. Ho, in: *Tandem Organic Reactions*, Wiley, New York, 1992; (b) K.C. Nicolaou, E.W. Yue, T. Oshima, in: N. Hall (Ed.), *The New Chemistry*, Cambridge University Press, Cambridge, 2001, p. 168; (c) L.F. Tietze, F. Hautner, in: F. Vögtle, J.F. Stoddart, M. Shibasaki (Eds.), *Stimulating Concepts in Chemistry*, Wiley-VCH, Weinheim, 2000, p. 38; (d) L.F. Tietze, U. Beifuss, *Angew. Chem.* 105 (1993) 137; *Angew. Chem. Int. Ed. Engl.* 32 (1993) 131; (e) L.F. Tietze, *Chem. Rev.* 96 (1996) 115.
- [2] (a) B.K. Corkey, F.D. Toste, *J. Am. Chem. Soc.* 129 (2007) 2764; (b) B.M. Trost, M.J. Krische, *Synlett* (1998) 1; (c) C. Aubert, O. Buisine, M. Malacria, *Chem. Rev.* 102 (2002) 813; (d) G.C. Lloyd-Jones, *Org. Biomol. Chem.* 1 (2003) 215.
- [3] (a) For recent reviews for gold and platinum catalysis see: A. Fürstner, P.W. Davies, *Angew. Chem., Int. Ed.* 46 (2007) 3410; (b) D.J. Gorin, F.D. Toste, *Nature* 446 (2007) 395; (c) E. Jiménez - Núñez, A.M. Echavarren, *Chem. Commun.* (2007) 333; (d) L. Zhang, J. Sun, S.A. Kozmin, *Adv. Synth. Catal.* 348 (2006) 2271; (e) A.S.H. Hashmi, *Angew. Chem., Int. Ed.* 44 (2005) 6990; (f) D.J. Gorin, B.D. Sherry, F.D. Toste, *Chem. Rev.* 108 (2008) 3351; (g) E. Jiménez - Núñez, A.M. Echavarren, *Chem. Rev.* 108 (2008) 3326; (h) Z. Li, C. Brouwer, C. He, *Chem. Rev.* 108 (2008) 3239; (i) S. Ma, S. Yu, Z. Gu, *Angew. Chem., Int. Ed.* 45 (2006) 200; (j) A.S.K. Hashmi, *Chem. Rev.* 107 (2007) 3180; (k) A.S.K. Hashmi, G.J. Hutchings, *Angew. Chem., Int. Ed.* 45 (2006) 7896; (l) Y. Yamamoto, *J. Org. Chem.* 72 (2007) 7817; (m) N. Bongers, N. Krause, *Angew. Chem., Int. Ed.* 47 (2008) 2178; (n) H.C. Shen, *Tetrahedron* 64 (2008) 3885; (o) N.T. Patil, Y. Yamamoto, *Chem. Rev.* 108 (2008) 3395.
- [4] (a) For gold-catalyzed cycloisomerizations of enynes, see selected examples: C. Nieto-Oberhuber, P.M. Munoz, E. Bunuel, C. Nevado, D.J. Cardenas, A.M. Echavarren, *Angew. Chem., Int. Ed.* 43 (2004) 2402; (b) M.R. Luzung, J.P. Markham, F.D. Toste, *J. Am. Chem. Soc.* 126 (2004) 10858; (c) Y. Horino, M.R. Luzung, F.D. Toste, *J. Am. Chem. Soc.* 128 (2006) 11364; (d) L. Zhang, S.A. Kozmin, *J. Am. Chem. Soc.* 126 (2004) 11806; (e) L. Zhang, *J. Am. Chem. Soc.* 127 (2005) 16804; (f) J. Sun, M.P. Conley, L. Zhang, S.A. Kozmin, *J. Am. Chem. Soc.* 128 (2006) 9705; (g) A. Buzas, F. Gagosz, *J. Am. Chem. Soc.* 128 (2006) 12614; (h) S.F. Kirsch, J.T. Binder, B. Crone, A. Duschek, T.T. Haug, C. Liébert, H. Menz, *Angew. Chem., Int. Ed.* 46 (2007) 2310.
- [5] (a) For PtCl_2 -catalyzed cycloisomerization of enynes, see selected examples: N. Chatani, N. Furukawa, H. Sakurai, S. Murai, *Organometallics* 15 (1996) 901; (b) B.M. Trost, G.A. Doherty, *J. Am. Chem. Soc.* 122 (2000) 3801; (c) A. Fürstner, H. Szillat, F. Stelzer, *J. Am. Chem. Soc.* 122 (2000) 6785; (d) M. Méndez, M.P. Munoz, C. Nevado, D.J. Cardenas, A.M. Echavarren, *J. Am. Chem. Soc.* 123 (2001) 10511; (e) V. Mamane, T. Gress, H. Krause, A. Fürstner, *J. Am. Chem. Soc.* 126 (2004) 8654; (f) Y. Harrak, C. Blaszykowski, M. Bernard, K. Cariou, E. Mainetti, V. Mourières, A.-L. Dhimane, L. Fensterbank, M. Malacria, *J. Am. Chem. Soc.* 126 (2004) 8656; (g) C. Blaszykowski, Y. Harrak, M.-H. Gonçalves, J.-M. Cloarec, A.-L. Dhimane, L. Fensterbank, M. Malacria, *Org. Lett.* 6 (2004) 3771; (h) E. Soriano, J. Marco-Contelles, *J. Org. Chem.* 70 (2005) 9345; (i) T.J. Harrison, B.O. Patrick, G.R. Duke, *Org. Lett.* 9 (2007) 367.
- [6] (a) For cycloisomerization of enynes by other metals, see selected examples: B.M. Trost, A.S.K. Hashmi, *Angew. Chem., Int. Ed.* 32 (1993) 1085; (b) A. Goeke, M. Sawamura, R. Kuwano, Y. Ito, *Angew. Chem., Int. Ed.* 35 (1996) 662; (c) P.A. Wender, D. Sperandio, *J. Org. Chem.* 63 (1998) 4164; (d) N. Chatani, K. Kataoka, S. Murai, N. Furukawa, Y. Seki, *J. Am. Chem. Soc.* 120 (1998) 9104; (e) B.M. Trost, F.D. Toste, *J. Am. Chem. Soc.* 122 (2000) 714; (f) D. Sémeril, M. Cléran, C. Bruneau, P.H. Dixneuf, *Adv. Synth. Catal.* 343 (2001) 184; (g) N. Chatani, H. Inoue, T. Kotsuma, S. Murai, *J. Am. Chem. Soc.* 124 (2002) 10294; (h) V. Michelet, P.Y. Toullec, J.-P. Genêt, *Angew. Chem., Int. Ed.* 47 (2008) 4268.
- [7] (a) C.M. Grisé, L. Barriault, *Org. Lett.* 8 (2006) 5905; (b) C.M. Grisé, L. Barriault, *Tetrahedron* 64 (2008) 797.
- [8] (a) For benzannulation reactions of propargylic systems catalyzed by transition metals, see: T. Kawasaki, S. Saito, Y. Yamamoto, *J. Org. Chem.* 67 (2002) 2653;

- (b) J. Zhao, C.O. Hughes, F.D. Toste, *J. Am. Chem. Soc.* 128 (2006) 7436;
(c) S. Wang, L. Zhang, *J. Am. Chem. Soc.* 128 (2006) 14274;
(d) A.S. Dudnik, T. Schwier, V. Gevorgyan, *Org. Lett.* 10 (2008) 1465;
(e) X. Huang, L. Zhang, *Org. Lett.* 9 (2007) 4627.
- [9] (a) For addition of allylsilanes to carbonyl derivatives by using Ag (I) and Pt (II) see selected examples: M. Wadamoto, N. Ozasa, A. Yanagisawa, H. Yamamoto, *J. Org. Chem.* 68 (2003) 5593;
(b) A. Yanagisawa, H. Kageyama, Y. Nakatsuka, K. Asakawa, Y. Matsumoto, H. Yamamoto, *Angew. Chem.* 111 (1999) 3916; *Angew. Chem. Int. Ed.* 38 (1999) 3701.;
(c) S. Bhunia, K.-C. Wang, R.-S. Liu, *Angew. Chem., Int. Ed.* 47 (2008) 5063.
- [10] (a) A. Fürstner, P.W. Davies, T. Gress, *J. Am. Chem. Soc.* 127 (2005) 8244;
(b) A. Fürstner, F. Stelzer, *J. Am. Chem. Soc.* 123 (2001) 11863;
(c) M.-Y. Lin, A. Das, *J. Am. Chem. Soc.* 128 (2006) 9340;
(d) J.-M. Tang, S. Bhunia, S.M.A. Sohel, M.-Y. Lin, H.-Y. Liao, S. Datta, A. Das, R.-S. Liu, *J. Am. Chem. Soc.* 129 (2007) 15677.
- [11] (a) Y.-C. Hsu, S. Datta, C.-M. Ting, R.-S. Liu, *Org. Lett.* 10 (2008) 521;
(b) C.-C. Lin, T.-M. Teng, A. Odedra, R.-S. Liu, *J. Am. Chem. Soc.* 129 (2007) 3798;
(c) Ref. [9c].
- [12] (a) K. Olofsson, M. Larhed, A. Hallberg, *J. Org. Chem.* 63 (1998) 5076;
(b) B.A. Narayanan, W.H. Bunnelle, *Tetrahedron Lett.* 28 (1987) 6261.