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Rhodium(I)/cationic 2,2′-bipyridyl-catalyzed [2+2+2] cycloaddition of α,ω-diynes with alkynes in water under air

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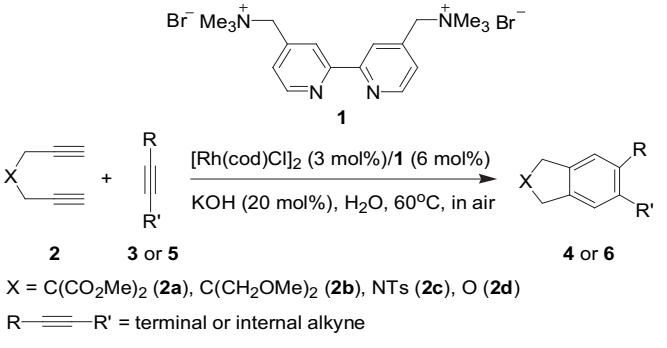
ABSTRACT

A simply performed procedure for the $[Rh(cod)Cl]_2$/cationic 2,2′-bipyridyl system-catalyzed [2+2+2] cycloaddition of α,ω-diynes with terminal and internal alkynes was achieved in water under air at 60 °C. The reaction proceeded smoothly with 1 equiv α,ω-diynes and 3 equiv alkynes in the presence of 20 mol % KOH for 1 h or 9 h, resulting in the formation of tri- and tetra-substituted benzene derivatives in moderate to high yields. After separation of the organic products by extraction, the residual aqueous solution could be reused for further reactions until complete degradation of its catalytic activity.

1. Introduction

Transition-metal-catalyzed [2+2+2] cycloaddition of alkynes is one of the most straightforward methods for the construction of polysubstituted benzene derivatives.[1] Since Reppe and Schweckendiek reported the first nickel complex-catalyzed cyclotrimerization of alkynes for the formation of benzene derivatives,[2] a large number of transition-metals including Ru,[3] Co,[4] Rh,[5] Ir,[6] Ni,[7] Pd,[8] and Fe[9] have been employed as catalysts to fulfill this benzene formation reaction. The reaction is usually carried out in organic solvents under a homogeneous phase, and hence it is difficult to separate the precious metal catalyst from the organic products at the end of the reaction, negating the possibility of recovery and recycling of the catalyst. Although there are several examples of the conduction of [2+2+2] cycloaddition reactions in an aqueous–organic biphasic system,[5e] alcohol/water mixed solvents,[3e,4a,10] refluxed water,[5b] and supercritical water (>374 °C),[11] these catalytic reactions were achieved under an inert atmosphere, and the reusability of such water-soluble catalysts has not been studied. The development of novel water-soluble transition-metal catalysts to catalyze organic reactions using water as the reaction medium has been of increasing interest in recent years. The advantages of such a procedure include not only reasons of safety and environmental concern, but also a cost benefit, as aqueous systems provide opportunity for the separation of the metal catalysts and organic products, enabling the recovered catalyst to be reused in further reactions.[12]

We recently developed a water-soluble cationic 2,2′-bipyridyl ligand, **1**, to bring transition-metal salts or complexes into the aqueous phase for employment as a reusable catalytic system to reduce the wastage of transition-metals. Thus, the Suzuki–Miyaura reaction,[13] Hiyama reaction,[14] terminal alkynes homocoupling,[15] and Mizoroki–Heck reaction[16] can be achieved in water under air by employing a palladium complex associated with **1** as the catalytic system. In addition, combinations of **1** with $FeCl_3 \cdot 6H_2O$ and $[Rh(cod)Cl]_2$ can be employed as catalysts for S-arylation[17] and phenylacetylenes polymerization[18] in an open flask. As part of our efforts to develop reusable transition-metal-catalyzed organic



Scheme 1. Rhodium(I)-catalyzed [2+2+2] cycloaddition in water.

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reactions using water as a green solvent, we report herein the efficient catalysis of [2+2+2] cycloaddition reactions of α,ω-diynes and alkynes by $[Rh(cod)Cl]_2$/**1** to give polysubstituted benzene derivatives in water under air. Moreover, the catalyst-containing aqueous phase can be reused until the complete degradation of its activity, reducing wastage of the precious metal (Scheme 1).

2. Results and discussion

The [2+2+2] cycloaddition represented in Table 1 was conducted in basic water under air at 60 °C using diyne **2a** and 1-hexyne **3a** as representative reactants. In the absence of ligand **1**, $[Rh(cod)Cl]_2$ was ineffective for the catalysis of the cycloaddition reaction due to its poor solubility in water, resulting in 88% of **2a** being recovered from the reaction mixture (entry 1). In order to bring the rhodium catalyst into the aqueous phase, a mixture of

Table 1
Rhodium(I)-catalyzed [2+2+2] cycloaddition of diyne (**2a**) with 1-hexyne (**3a**)[a]

Entry	Ligand	Yield[b] (%)
1	None	0[c]
2[d]	**1**	34[e]
3	**1**	80
4[f]	**1**	53
5[g]	**1**	21
6[h]	**1**	75
7[i,j]	**1**	67
8[k]	**1**	51
9	2,2′-Bipyridyl	9

[a] Reaction conditions: **2a** (1 mmol), **3a** (3 mmol), $[Rh(cod)Cl]_2$ (3 mol %), **1** (6 mol %), H_2O (5 mL), and KOH (20 mol %) at 60 °C in air for 1 h.
[b] Isolated yields.
[c] Compound **2a** (88%) was recovered.
[d] Compound **3a** (1 mmol) was used.
[e] Dimer of **2a** (52%) was obtained.
[f] Catalytic aqueous solution reused from entry 3.
[g] Catalytic aqueous solution reused from entry 4.
[h] Compound **3a** (5 mmol) was used.
[i] Reaction time of 24 h.
[j] In the absence of KOH.
[k] $[Rh(cod)Cl]_2$ (2 mol %) and **1** (4 mol %) were used.

CH_2Cl_2 solution (0.5 mL) containing $[Rh(cod)Cl]_2$ (3 mol %) and an aqueous solution (4 mL) of **1** (6 mol %) was stirred at room temperature for 10 min. After the orange-red aqueous phase had formed as the upper layer, the solution was heated at 60 °C to remove CH_2Cl_2. This in situ-generated catalytic system was then used for the same reaction under conditions identical to those described in entry 1, resulting in a 34% yield of **4a** along with 52% of the **2a** dimer when equimolar quantities of **2a** and **3a** were employed (entry 2). In this system, cyclotrimerization of the monoalkyne was not observed.

Oshima's group reported that a hydrophobic diyne such as diethyl 2,2-diprogargylmalonate could not take part in [2+2+2] annulation due to its insolubility in water.[5e] Using the system developed in this study, the quaternary ammonium salts on the 2,2′-bipyridyl ligand may act as a phase transfer agent, bringing the hydrophobic reactants, the diyne and monoalkyne, across the interface into the aqueous phase to facilitate [2+2+2] cycloaddition in water. In order to suppress the self-dimerization or -trimerization of **2a** and improve the yield of the desired product, 3 equiv of **3a** was used in the reaction system. Under the conditions shown in entry 3, **2a** had vanished within 1 h, and after separation of the catalyst from the organic products by extraction with hexane, the desired product **4a** was isolated in an 80% yield by column chromatography.

The possibility that the residual aqueous solution could initiate the next reaction run if the catalyst was still active was apparent, and to our delight, we found that two successive reuse runs afforded **4a** in 53% and 21% yields, respectively (entries 4 and 5). Although the results indicate that the rhodium catalyst was gradually deactivated during the reaction, it is noteworthy that the residual aqueous solution could be reused, avoiding wastage of the precious metal, before its complete deactivation.

Further increasing the amount of **3a** did not result in a better yield of **4a** (entry 6). The reaction proceeded slowly in the absence of KOH, resulting in the formation of **4a** in a 67% yield after 24 h (entry 7). Several studies have shown that abstracting the chloride of transition-metal complexes by silver salts to produce the cation facilitates [2+2+2] cycloaddition of α,ω-diynes and alkynes.[4f,19] In our system, use of the much cheaper KOH was efficient enough to accelerate the reaction. Reducing the loading amount of catalyst gave a lower product yield of **4a** (entry 8). To demonstrate the necessity of ligand **1**, cycloaddition of **2a** and **3a** in the presence of a neutral 2,2′-bipydryl ligand gave **4a** in only a 9% yield (entry 9).

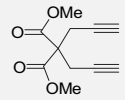
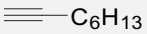
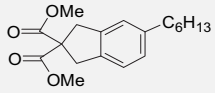
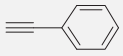
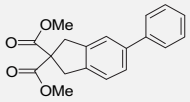
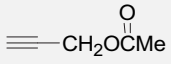
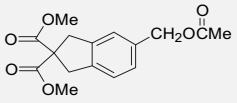
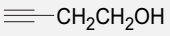
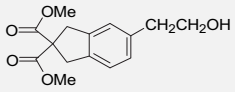
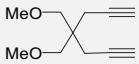
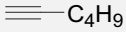
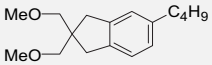
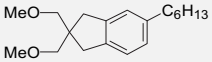
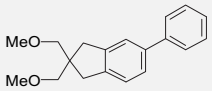
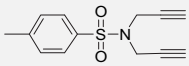
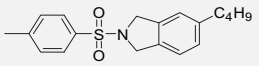
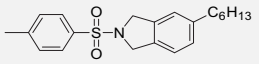
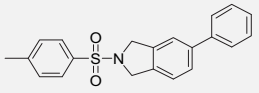
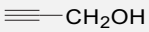
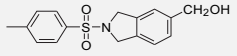
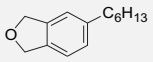
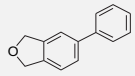
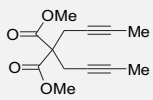
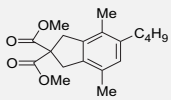
After the optimal conditions were identified (Table 1, entry 3), various α,ω-diynes and terminal alkynes were used for [2+2+2] cycloaddition to explore the scope of the reaction, the results of which are summarized in Table 2. Compound **2a** reacted with various terminal alkynes effectively in 1 h to give the corresponding products **4b**–**4e** in good to high yields (entries 1–4). We previously discovered that phenylacetylene **3c** could be polymerized very quickly in this catalytic system.[17] In this case, addition of the diyne prior to **3c** resulted in the formation of **4c** in a 90% yield (entry 2). It is obvious that the rate of oxidative-coupling of the diyne to Rh(I) is much faster than the coordination of **3c**; hence, the insertion of **3c** into rhodacyclopentadiene, a common intermediate in the cyclotrimerization and [2+2+2] cycloaddition of alkynes, led to the formation of **4c** in high yield. The use of hydrophilic alkyne **3e** resulted in only a 57% yield, presumably owing to its readily approaching rhodium in the aqueous phase and competing with the oxidative-coupling of the diyne to the transition-metal (entry 4). Compound **2b** also reacted with terminal alkynes smoothly to afford indan derivatives in yields between 78% and 82% (entries 5–7). In addition, [2+2+2] cycloaddition of *N*-tosyl-*N*,*N*-dipropargylamine **2c** with terminal alkynes furnished isoindoles **4i**–**4l** at yields between 54% and 76% (entries 8–11). Compound **4k** has been obtained in a 39% yield as one of the products in the $Co_2(CO)_8$-catalyzed tandem [2+2+1] and [2+2+2] cycloaddition of **2c** and **3c** at 130 °C under high CO pressure (30 atm).[20] In our system, the same product was synthesized under much milder reaction conditions in an open flask. Dipropargyl ether **2d** is known for self-cycloaddition;[21] thus, increasing the amount of terminal alkyne and slow addition of **2d** into the aqueous solution improved the yield effectively. The reaction of **2d** with 8 equiv of **3a** and **3c** under identical conditions gave **4m** and **4n** in 79% and 72% yields, respectively (entries 12 and 13). Disappointingly, the cycloaddition of internal diyne **2e** with **3a** did not proceed at all, and a near-quantitative amount of **2e** was recovered from the aqueous solution (entry 14).

We then extended the scope to internal alkynes (Table 3). The reaction rate for insertion of internal alkynes into rhodacyclopentadiene is much slower than for terminal alkynes owing to the steric hindrance of the substituents on both sides, and therefore prolongation of the reaction time to 9 h and the addition of diyne into the reaction mixture in three portions, one every 3 h, was required. Under such conditions, **2a**–**2c** reacted with various internal alkynes giving the corresponding products at yields between 38% and 77% (entries 1–6), and **2d** reacted with 8 equiv of **5d** to afford **6g** in a 48% yield (entry 7). In contrast with **5d**, just 3 equiv of **5b** could react with **2d** to deliver **6h** in a 52% yield (entry 8).

3. Conclusion

In conclusion, we successfully employed a $[Rh(cod)Cl]_2$/cationic 2,2′-bipyridyl system to catalyze the [2+2+2]

Table 2
Rhodium(I)/cationic 2,2′-bipyridyl-catalyzed [2+2+2] cycloaddition of diynes (**2**) with terminal alkynes (**3**)[a]

Entry	Diyne		Terminal alkyne		Product		Yield[b] (%)
1		**2a**		**3b**		**4b**	78
2		**2a**		**3c**		**4c**	90
3		**2a**		**3d**		**4d**	73
4		**2a**		**3e**		**4e**	57
5		**2b**		**3a**		**4f**	81
6		**2b**		**3b**		**4g**	82
7		**2b**		**3c**		**4h**	78
8		**2c**		**3a**		**4i**	76
9		**2c**		**3b**		**4j**	73
10		**2c**		**3c**		**4k**	68
11		**2c**		**3h**		**4l**	54
12[c]		**2d**		**3a**		**4m**	79
13[c]		**2d**		**3c**		**4n**	72
14		**2e**		**3a**		**4o**	0[d]

[a] Reaction conditions: **2** (1 mmol), **3** (3 mmol), $[Rh(cod)Cl]_2$ (3 mol %), **1** (6 mol %), H_2O (5 mL), and KOH (20 mol %) at 60 °C in air for 1 h.
[b] Isolated yields.
[c] Alkyne (8 mmol) was used.
[d] Compound **2e** (95%) was recovered.

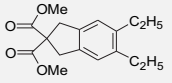
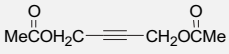
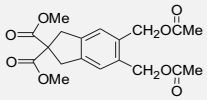
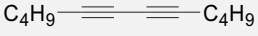
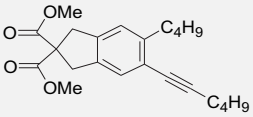
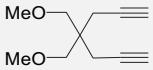
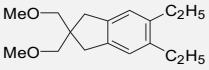
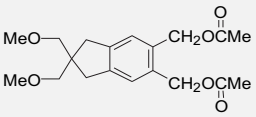
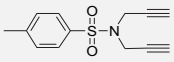
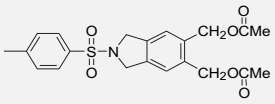
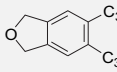
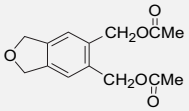
cycloaddition of α,ω-diynes and alkynes for the formation of benzene derivatives in water under air. This simply performed procedure in which the reaction was conducted in air using an environmental-friendly solvent, water, provided the opportunity for reuse of the catalyst by simple extraction. The employment of this catalytic system for other organic reactions is now in progress.

4. Experimental

4.1. General

Chemicals were purchased from commercial suppliers and were used without further purification. Cationic 2,2′-bipyridyl ligand **1** was prepared according to the published procedure,[13,14] as were

Table 3
Rhodium(I)/cationic 2,2′-bipyridyl-catalyzed [2+2+2] cycloaddition of diynes (**2**) with internal alkynes (**5**).[a]

Entry	Diyne		Internal alkyne		Product		Yield[b] (%)
1		**2a**		**5a**		**6a**	46
2		**2a**		**5b**		**6b**	77
3		**2a**		**5c**		**6c**	40
4		**2b**		**5a**		**6d**	38
5		**2a**		**5b**		**6e**	53
6		**2c**		**5b**		**6f**	61
7[c]		**2d**		**5d**		**6g**	48
8		**2d**		**5b**		**6h**	52

[a] Reaction conditions: **2** (1 mmol), **5** (3 mmol), $[Rh(cod)Cl]_2$ (3 mol %), **1** (6 mol %), H_2O (5 mL), and KOH (20 mol %) at 60 °C in air for 9 h.
[b] Isolated yields.
[c] Alkyne (8 mmol) was used.

diynes **2a**,[22] **2b**,[6e] and **2c**,[23] and monoalkyne **5b**.[24] For column chromatography, 70–230-mesh silica gel (Merck Ltd.) was employed. Melting points were recorded using melting point apparatus and were uncorrected. All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian 200 NMR spectrometer. Chemical shifts were reported in parts per million using tetramethylsilane (TMS) as the internal standard. Elemental analyses were performed and high resolution mass spectra were recorded at the Instrument Center Service, National Science Council of Taiwan.

4.2. General procedure for [2+2+2] cycloaddition

To a CH_2Cl_2 (0.5 mL) solution containing $[Rh(COD)Cl]_2$ (14.7 mg, 0.03 mmol) was added an aqueous solution of **1** (27.6 mg, 0.06 mmol in 4 mL H_2O). The mixture was stirred at room temperature for 10 min, resulting in the formation of an orange-red aqueous phase as the upper layer. This biphasic solution was then stirred at 60 °C under an open system for 30 min to remove CH_2Cl_2. Monoalkyne **3** or **5** (3 mmol), diyne **2** (1 mmol), and KOH (0.2 mmol in 1 mL H_2O) were added (monoalkyne was added after the addition of the diyne when phenylacetylene **3c** was employed) and the reaction mixture was stirred at 60 °C for the indicated reaction time (1 h for the reactions shown in Tables 1 and 2; 9 h for those shown in Table 3). After cooling to room temperature, the reaction mixture was extracted with hexane or EtOAc (5 mL) twice. The combined organic phase was then dried over $MgSO_4$ and the solvent was removed in a vacuum. Column chromatography on silica gel afforded the desired product.

*4.2.1. 5-Butylindan-2,2-dicarboxylic acid dimethyl ester (**4a**).* Pale yellow oil.[6e] EtOAc/hexane=1/5. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.09 (d, J=7.6 Hz, 1H), 7.01 (s, 1H), 6.98 (d, J=7.6 Hz, 1H), 3.74 (s, 6H), 3.56 (s, 4H), 2.56 (t, J=7.6 Hz, 2H), 1.34–1.56 (m, 4H), 0.91 (t, J=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.9 (2C), 141.6, 139.7, 136.8, 127.0, 124.0, 123.7, 60.3, 52.7 (2C), 40.4, 40.1, 35.3, 33.7, 22.2, 13.8.

*4.2.2. 5-Hexylindan-2,2-dicarboxylic acid dimethyl ester (**4b**).* Pale yellow oil.[25] EtOAc/hexane=1/5. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.09 (d, J=7.8 Hz, 1H), 7.00 (s, 1H), 6.99 (d, J=7.8 Hz, 1H), 3.74 (s, 6H), 3.56 (s, 4H), 2.55 (t, J=7.2 Hz, 2H), 1.28–1.35 (m, 8H), 0.88 (t, J=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.9 (2C), 141.6, 139.7, 136.8, 127.0, 124.9, 123.7, 60.3, 52.6 (2C), 40.4, 40.1, 35.7, 31.6, 31.5, 28.9, 22.5, 13.9.

*4.2.3. 5-Phenylindan-2,2-dicarboxylic acid dimethyl ester (**4c**).* Light brown oil.[6e] EtOAc/hexane=1/4. ^1H NMR ($CDCl_3$, 200 MHz) δ 7.53–7.58 (m, 2H), 7.35–7.46 (m, 4H), 7.30 (d, J=7.6 Hz, 1H), 7.25 (d, J=7.6 Hz, 1H), 3.77 (s, 6H), 3.66 (s, 2H), 3.64 (s, 2H); ^{13}C NMR

($CDCl_3$, 50 MHz) δ 171.9 (2C), 141.1, 140.5, 140.3, 138.9, 128.6 (2C), 127.1 (2C), 126.9, 126.0, 124.4, 122.9, 60.4, 52.9 (2C), 40.5, 40.3.

*4.2.4. 5-Acetoxymethylindan-2,2-dicarboxylic acid dimethyl ester (**4d**).* Pale yellow oil. EtOAc/hexane=1/2. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20 (s, 1H), 7.17 (s, 2H), 5.10 (s, 2H), 3.75 (s, 6H), 3.59 (s, 4H), 2.09 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.7 (2C), 170.6, 140.2, 139.9, 134.8, 127.2, 124.1 (2C), 66.1, 60.3, 52.8 (2C), 40.3, 40.2, 20.8. HRMS calcd for $C_{16}H_{18}O_6$ 306.1103; found 306.1109.

*4.2.5. 5-(2-Hydroxyethyl)-indan-2,2-dicarboxylic acid dimethyl ester (**4e**).* Pale yellow oil.[6e] EtOAc/hexane=1/1. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.22 (d, J=4.0 Hz, 1H), 7.07 (s, 1H), 7.06 (d, J=4.0 Hz, 1H), 3.86 (t, J=6.2 Hz, 2H), 3.75 (s, 6H), 3.58 (s, 4H), 2.83 (t, J=6.2 Hz, 2H), 1.85 (br, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 172.0 (2C), 140.2, 137.9, 137.3, 127.7, 124.7, 124.1, 63.6, 60.4, 52.8 (2C), 40.5, 40.2, 40.0.

*4.2.6. 5-Butyl-2,2-bismethoxymethylindan (**4f**).* Pale yellow oil.[6e] EtOAc/hexane=1/14. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.06 (d, J=7.8 Hz, 1H), 6.98 (s, 1H), 6.94 (d, J=7.8 Hz, 1H), 3.35–3.36 (m, 10H), 2.79 (s, 4H), 2.56 (t, J=7.6 Hz, 2H), 1.50–1.62 (m, 2H), 1.35 (sex, J=7.3 Hz, 2H), 0.92 (t, J=7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.0, 140.8, 139.1, 126.4, 124.7, 124.4, 76.0 (2C), 59.1 (2C), 48.1, 38.8, 38.5, 35.5, 33.9, 22.4, 13.9.

*4.2.7. 5-Hexyl-2,2-bismethoxymethylindan (**4g**).* Pale yellow oil. EtOAc/hexane=1/14. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.06 (d, J=7.6 Hz, 1H), 6.98 (s, 1H), 6.94 (d, J=7.6 Hz, 1H), 3.36 (s, 4H), 3.35 (s, 6H), 2.78 (s, 4H), 2.55 (t, J=7.4 Hz, 2H), 1.30–1.56 (m, 8H), 0.88 (t, J=6.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.0, 140.8, 139.1, 126.3, 124.7, 124.4, 76.4 (2C), 59.0 (2C), 48.1, 38.8, 38.5, 35.8, 31.7 (2C), 29.0, 22.6, 14.0. HRMS calcd for $C_{19}H_{31}O_2$ 290.2246; found 290.2250.

*4.2.8. 5-Phenyl-2,2-bismethoxymethylindan (**4h**).* Pale yellow oil. EtOAc/hexane=1/14. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.26–7.58 (m, 8H), 3.40 (s, 4H), 3.37 (s, 6H), 2.88 (s, 2H), 2.87 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 142.8, 141.5, 141.3, 139.6, 128.5 (2C), 127.0 (2C), 126.8, 125.4, 125.0, 123.6, 76.4 (2C), 59.1 (2C), 48.3, 38.9, 38.6. HRMS calcd for $C_{19}H_{22}O_2$ 282.1620; found 282.1629.

*4.2.9. 5-Butyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-isoindole (**4i**).* Pale yellow solid. EtOAc/hexane=1/5. Mp 69–71 °C (lit.[3a] 70–72 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76 (d, J=8.4 Hz, 2H), 7.30 (d, J=8.4 Hz, 2H), 7.05 (s, 2H), 6.98 (s, 1H), 4.58 (s, 4H), 2.56 (t, J=7.2 Hz, 2H), 2.40 (s, 3H), 1.50–1.57 (m, 2H), 1.28–1.37 (m, 2H), 0.90 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.3, 142.6, 136.0, 133.7, 133.1, 129.6 (2C), 127.8, 127.4 (2C), 122.3, 122.2, 53.5, 53.4, 35.3, 33.6, 22.1, 21.3, 13.7.

*4.2.10. 5-Hexyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-isoindole (**4j**).* Light brown solid. EtOAc/hexane=1/5. Mp 74–76 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76 (d, J=8.1 Hz, 2H), 7.30 (d, J=8.1 Hz, 2H), 7.05 (s, 2H), 6.97 (s, 1H), 4.58 (s, 4H), 2.55 (t, J=7.4 Hz, 2H), 2.40 (s, 3H), 1.27–1.55 (m, 8H), 0.87 (t, J=7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.0, 142.2, 135.6, 133.3, 132.7, 129.1 (2C), 127.4, 127.0 (2C), 121.8, 121.7, 53.1, 53.0, 35.2, 31.1, 31.0, 28.3, 22.0, 20.9, 13.5. Anal. Calcd: N, 3.92; C, 70.55; S, 8.97; H, 7.61. Found: N, 3.95; C, 70.25; S, 8.69; H, 7.68.

*4.2.11. 5-Phenyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-isoindole (**4k**).* Pale yellow solid.[20] EtOAc/hexane=1/5. Mp 175–177 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.80 (d, J=7.4 Hz, 2H), 7.21–7.54 (m, 10H), 4.67 (s, 4H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.5, 141.0, 140.3, 136.7, 135.0, 133.7, 129.7 (2C), 128.7 (2C), 127.4 (2C), 127.3, 126.9 (2C), 126.7, 122.8, 121.1, 53.6, 53.4, 21.3.

*4.2.12. [2-(Toluene-4-sulfonyl)-2,3-dihydro-1H-isoindol-5-yl]methanol (**4l**).* White solid. EtOAc/hexane=3/2. Mp 139–141 °C (lit.[5e] 140–142 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.77 (d, J=7.2 Hz, 2H), 7.31 (d, J=7.2 Hz, 2H), 7.20 (s, 2H), 7.17 (s, 1H), 4.66 (s, 2H), 4.61 (s, 4H), 2.40 (s, 3H), 1.99 (br, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 143.6, 141.1, 136.2, 135.0, 133.5, 127.7 (2C), 127.4 (2C), 126.3, 122.4, 120.9, 64.4, 53.5, 53.4, 21.4.

*4.2.13. 5-Hexyl-1,3-dihydro-isobenzofuran (**4m**).* Light brown oil. EtOAc/hexane=1/19. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.14 (d, J=7.9 Hz, 1H), 7.09 (s, 1H), 7.07 (d, J=7.9 Hz, 1H), 5.08 (s, 4H), 2.61 (t, J=7.4 Hz, 2H), 1.31–1.60 (m, 8H), 0.88 (t, J=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 134.6, 130.0, 125.5, 125.0, 121.7, 121.6, 69.6, 69.4, 36.0, 31.6, 31.2, 28.8, 22.5, 12.0. Anal. Calcd: C, 82.30; H, 9.87. Found: C, 82.52; H, 9.66.

*4.2.14. 5-Phenyl-1,3-dihydro-isobenzofuran (**4n**).* Light brown solid.[26] EtOAc/hexane=1/19. Mp 81–83 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.26–7.61 (m, 8H), 5.17 (s, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 141.0, 140.8, 140.0, 138.2, 128.8 (2C), 127.3, 127.2 (2C), 126.5, 121.2, 119.7, 73.5, 73.4.

*4.2.15. 5,6-Diethylindan-2,2-dicarboxylic acid dimethyl ester (**6a**).* Pale yellow oil.[6e] EtOAc/hexane=1/5. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.89 (s, 2H), 3.72 (s, 6H), 3.53 (s, 4H), 2.58 (q, J=7.6 Hz, 4H), 1.17 (t, J=7.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 172.1 (2C), 140.5 (2C), 137.3 (2C), 123.8 (2C), 60.5, 52.8 (2C), 40.4 (2C), 25.4 (2C), 15.3 (2C).

*4.2.16. 5,6-Bisacetoxymethylindan-2,2-dicarboxylic acid dimethyl ester (**6b**).* Light brown oil. EtOAc/hexane=1/2. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.24 (s, 2H), 5.14 (s, 4H), 3.75 (s, 6H), 3.59 (s, 4H), 2.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.7 (2C), 170.5 (2C), 140.6 (2C), 133.4 (2C), 125.8 (2C), 63.7 (2C), 60.3, 53.0 (2C), 40.3 (2C), 20.9 (2C). Anal. Calcd: C, 60.31; H, 5.86. Found: C, 60.65; H, 5.50.

*4.2.17. 5-Butyl-6-hex-1-ynyl-indan-2,2-dicarboxylic acid dimethyl ester (**6c**).* Light brown oil.[6e] EtOAc/hexane=1/5. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.19 (s, 1H), 6.99 (s, 1H), 3.74 (s, 6H), 3.54 (s, 2H), 3.52 (s, 2H), 2.70 (t, J=7.8 Hz, 2H), 2.42 (t, J=6.6 Hz, 2H), 1.46–1.62 (m, 6H), 1.38 (sex., J=7.8 Hz, 2H), 0.94 (t, J=7.2 Hz, 3H), 0.93 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.8 (2C), 143.6, 139.4, 136.9, 127.5, 124.2, 122.0, 92.9, 79.4, 60.3, 52.8 (2C), 40.4, 40.0, 34.2, 32.9, 30.9, 22.6, 21.9, 19.1, 13.9, 13.5.

*4.2.18. 5,6-Diethyl-2,2-bismethoxymethylindan (**6d**).* Pale yellow oil. EtOAc/hexane=1/14. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.97 (s, 2H), 3.36 (s, 4H), 3.35 (s, 6H), 2.77 (s, 4H), 2.60 (q, J=7.6 Hz, 4H), 1.20 (t, J=7.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 139.7 (2C), 139.6 (2C), 124.6 (2C), 76.2 (2C), 59.2 (2C), 48.1, 38.8 (2C), 25.5 (2C), 15.5 (2C). HRMS calcd for $C_{17}H_{26}O_2$ 262.1933; found 262.1931.

*4.2.19. Acetic acid 6-acetoxymethyl-2,2-bismethoxymethylindan-5-ylmethyl ester (**6e**).* Pale yellow oil. EtOAc/hexane=1/5. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.20 (s, 2H), 5.15 (s, 4H), 3.35 (s, 4H), 3.34 (s, 6H), 2.83 (s, 4H), 2.08 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.5 (2C), 143.1 (2C), 132.6 (2C), 126.5 (2C), 76.4 (2C), 64.0 (2C), 59.1 (2C), 48.2, 38.6 (2C), 20.9 (2C). HRMS calcd for $C_{19}H_{26}O_6$ 350.1729; found 350.1732.

*4.2.20. Acetic acid 6-acetoxymethyl-2-(toluene-4-sulfonyl)-2,3-dihydro-1H-isoindol-5-ylmethyl ester (**6f**).* Pale yellow solid. EtOAc/hexane=1/1. Mp 148–150 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76 (d, J=8.1 Hz, 2H), 7.31 (d, J=8.1 Hz, 2H), 7.22 (s, 2H), 5.14 (s, 4H), 4.61 (s, 4H), 2.41 (s, 3H), 2.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.2 (2C), 143.5, 136.5 (2C), 134.2 (2C), 133.4, 129.6 (2C), 127.3 (2C), 123.8 (2C), 63.2 (2C), 53.3 (2C), 21.3, 20.7 (2C). Anal. Calcd: N, 3.36; C, 64.02; S, 7.68; H, 5.55. Found: N, 3.36; C, 64.01; S, 7.72; H, 5.48.

*4.2.21. 5,6-Dipropyl-1,3-dihydro-isobenzofuran (**6g**).* Pale yellow oil. EtOAc/hexane=1/19. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.70 (s, 2H), 5.26

(s, 4H), 2.75 (t, J=7.4 Hz, 4H), 1.65 (sex., J=7.4 Hz, 4H), 1.00 (t, J=7.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 141.9 (2C), 125.5 (2C), 122.2 (2C), 69.4 (2C), 26.2 (2C), 23.9 (2C), 14.0 (2C). Anal. Calcd: C, 82.30; H, 9.87. Found: C, 82.07; H, 9.98.

*4.2.22. Acetic acid 6-acetoxymethyl-1,3-dihydro-isobenzofuran-5-ylmethyl ester (**6h**).* Pale yellow solid. EtOAc/hexane=1/3. Mp 76–78 °C. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.30 (s, 2H), 5.20 (s, 4H), 5.11 (s, 4H), 2.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.4 (2C), 139.8 (2C), 133.3 (2C), 122.4 (2C), 73.2 (2C), 63.6 (2C), 20.8 (2C). HRMS calcd for $C_{14}H_{16}O_5$ 264.0998; found 264.0999.

4.3. Experimental procedure for the reuse of residual catalytic aqueous solution

This procedure was conducted as described in Section 4.2 under the reaction conditions shown in entry 3 of Table 1. After cooling the reaction to room temperature, the aqueous reaction mixture was washed with hexane under vigorous stirring twice (5 mL×2) and the organic product isolated from the combined organic phase according to the previously described procedure. The residual aqueous solution was then charged with **2a** (1 mmol) and **3a** (3 mmol) for the next reaction.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.06.088.

References and notes

1. For recent reviews, see: (a) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503; (b) Gandon, V.; Aubert, C.; Malacria, M. *Curr. Org. Chem.* **2005**, *9*, 1699; (c) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741; (d) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209; (e) Chopade, P. R.; Louie, J. *Adv. Synth. Catal.* **2006**, *348*, 2307; (f) Heller, B.; Hapke, M. *Chem. Soc. Rev.* **2007**, *36*, 1085; (g) Tanaka, K. *Synlett* **2007**, 1977; (h) Tanaka, K. *Chem. Asian J.* **2009**, *4*, 508; (i) Hess, W.; Treutwein, J.; Hilt, G. *Synthesis* **2008**, 3537; (j) Varela, J. A.; Saá, C. *Synlett* **2008**, 2571; (k) Shibata, T.; Tsuchikama, K. *Org. Biomol. Chem.* **2008**, *6*, 1317; (l) Scheuermann née Taylor, C. J.; Ward, B. D. *New J. Chem.* **2008**, *32*, 1850; (m) Omae, I. *Appl. Organomet. Chem.* **2008**, *22*, 149.
2. Reppe, W.; Schweckendiek, W. J. *Justus Liebigs Ann. Chem.* **1958**, *560*, 104.
3. For recent Ru-catalyzed reactions, see: (a) Yamamoto, Y.; Ogawa, R.; Itoh, K. *Chem. Commun.* **2000**, 549; (b) Hoven, G. B.; Efskind, J.; Rømming, C.; Undheim, K. *J. Org. Chem.* **2002**, *67*, 2459; (c) Yamamoto, Y.; Hata, K.; Arakawa, T.; Itoh, K. *Chem. Commun.* **2003**, 1290; (d) Yamamoto, Y.; Kinpara, K.; Saigoku, T.; Nishiyama, H.; Itoh, K. *Org. Biomol. Chem.* **2004**, *2*, 1287; (e) Cadierno, V.; García-Garrido, S. E.; Gimeno, J. *J. Am. Chem. Soc.* **2006**, *128*, 15094.
4. For recent Co-catalyzed reactions, see: (a) Yong, L.; Butenschön, H. *Chem. Commun.* **2002**, 2852; (b) Hilt, G.; Vogler, T.; Hess, W.; Galbiati, F. *Chem. Commun.* **2005**, 1474; (c) Saino, N.; Amemiya, F.; Tanabe, E.; Kase, K.; Okamoto, S. *Org. Lett.* **2006**, *8*, 1439; (d) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209; (e) Agenet, N.; Gandon, V.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2007**, *129*, 8860; (f) Goswami, A.; Ito, T.; Okamoto, S. *Adv. Synth. Catal.* **2007**, *349*, 2368; (g) Han, Z.; Vaid, T. P.; Rheingold, A. L. *J. Org. Chem.* **2008**, *73*, 445; (h) Geny, A.; Agenet, N.; Iannazzo, L.; Malacria, M.; Aubert, C.; Gandon, V. *Angew. Chem., Int. Ed.* **2009**, *48*, 1810.
5. For recent Rh-catalyzed reactions, see: (a) Sun, Q.; Zhou, X.; Islam, K.; Kyle, D. J. *Tetrahedron Lett.* **2001**, *42*, 6495; (b) Uozumi, Y.; Nakazono, M. *Adv. Synth. Catal.* **2002**, *344*, 274; (c) Witulski, B.; Zimmermann, A.; Gowans, N. D. *Chem. Commun.* **2002**, 2984; (d) Tagliatesta, P.; Floris, B.; Galloni, P.; Leoni, A.; D'Arcangelo, G. *Inorg. Chem.* **2003**, *42*, 7701; (e) Kinoshita, H.; Shinokubo, H.; Oshima, K. *J. Am. Chem. Soc.* **2003**, *125*, 7784; (f) Dufková, L.; Císařová, I.; Štepnička, P.; Kotora, M. *Eur. J. Org. Chem.* **2003**, 2882; (g) Tanaka, K.; Toyoda, K.; Wada, A.; Shirasaka, K.; Hirano, M. *Chem.—Eur. J.* **2005**, *11*, 1145; (h) Ramana, C. V.; Salian, S. R.; Gonnade, R. G. *Eur. J. Org. Chem.* **2007**, 5483; (i) Tanaka, K.; Sagae, H.; Toyoda, K.; Hirano, M. *Tetrahedron* **2008**, *64*, 831; (j) Ramana, C. V.; Suryawanshi, S. B. *Tetrahedron Lett.* **2008**, *49*, 445; (k) Yoshida, K.; Morimoto, I.; Mitsudo, K.; Tanaka, H. *Tetrahedron* **2008**, *64*, 5800; (l) Shibata, T.; Tahara, Y.; Tamura, K.; Endo, K. *J. Am. Chem. Soc.* **2008**, *130*, 3451.
6. For recent Ir-catalyzed reactions, see: (a) Takeuchi, R.; Tanaka, S.; Nakaya, Y. *Tetrahedron Lett.* **2001**, *42*, 2991; (b) Takeuchi, R.; Nakaya, Y. *Org. Lett.* **2003**, *5*, 3659; (c) Shibata, T.; Fujimoto, T.; Yokota, K.; Takagi, K. *J. Am. Chem. Soc.* **2004**, *126*, 8382; (d) Kezuka, S.; Okado, T.; Niou, E.; Takeuchi, R. *Org. Lett.* **2005**, *7*, 1711; (e) Kezuka, S.; Tanaka, S.; Ohe, T.; Nakaya, Y.; Takeuchi, R. *J. Org. Chem.* **2006**, *71*, 543; (f) Shibata, T.; Yoshida, S.; Arai, Y.; Otsuka, M.; Endo, K. *Tetrahedron* **2008**, *64*, 821.
7. For recent Ni-catalyzed reactions, see: (a) Hocek, M.; Stará, I. G.; Starý, I.; Dvořáková, H. *Tetrahedron Lett.* **2001**, *42*, 519; (b) Teplý, F.; Stará, I. G.; Starý, I.; Kollárovič, A.; Šaman, D.; Rulíšek, L.; Fiedler, P. *J. Am. Chem. Soc.* **2002**, *124*, 9175; (c) Jeevanandam, A.; Korivi, R. P.; Huang, I.-W.; Cheng, C.-H. *Org. Lett.* **2002**, *4*, 807; (d) Deaton, K. R.; Gin, M. S. *Org. Lett.* **2003**, *5*, 2477; (e) Turek, P.; Kotora, M.; Tišlerová, I.; Hocek, M.; Votruba, I.; Císařová, I. *J. Org. Chem.* **2004**, *69*, 9224; (f) Teske, J. A.; Deiters, A. *J. Org. Chem.* **2008**, *73*, 342.
8. For recent Pd-catalyzed reactions, see: (a) Yamamoto, Y.; Nagata, A.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Organometallics* **2000**, *19*, 2403; (b) Li, J.; Jiang, H.; Chen, M. *J. Org. Chem.* **2001**, *66*, 3627; (c) Yamamoto, Y.; Nagata, A.; Nagata, H.; Ando, Y.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Chem.—Eur. J.* **2003**, *9*, 2469; (d) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *Eur. J. Org. Chem.* **2003**, 1238; (e) Carvalho, M. F. N. N.; Almeida, F. M. T.; Galvão, A. M.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2003**, *679*, 143; (f) Cheng, J.-S.; Jiang, H.-F. *Eur. J. Org. Chem.* **2004**, 643; (g) Sripada, L.; Teske, J. A.; Deiters, A. *Org. Biomol. Chem.* **2008**, *6*, 263.
9. Saino, N.; Kogure, D.; Kase, K.; Okamoto, S. *J. Organomet. Chem.* **2006**, *691*, 3129.
10. Sigman, M. S.; Fatland, A. W.; Eaton, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 5130.
11. (a) Jerome, K. S.; Parsons, E. J. *Organometallics* **1993**, *12*, 2991; (b) Borwieck, H.; Walter, O.; Dinjus, E.; Rebizant, J. *J. Organomet. Chem.* **1998**, *570*, 121.
12. For reviews, see: (a) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023; (b) Padadogianakis, G.; Sheldon, R. A. *New J. Chem.* **1996**, *20*, 175; (c) Cornils, B. *J. Mol. Catal. A: Chem.* **1999**, *143*, 1; (d) Genet, J. P.; Savignac, M. *J. Organomet. Chem.* **1999**, *576*, 305; (e) *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Thieme: Stuttgart, 2000; (f) *Aqueous-phase Organometallic Catalysis*; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinhein, Germany, 2004; (g) Sheldon, R. A. *Green Chem.* **2005**, *7*, 267; (h) Leadbeater, N. E. *Chem. Commun.* **2005**, 2881; (i) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095; (j) Li, C.-J.; Chen, L. *Chem. Soc. Rev.* **2006**, *35*, 68; (k) Chen, L.; Li, C.-J. *Adv. Synth. Catal.* **2006**, *348*, 1459; (l) Horváth, I. T.; Anastas, P. T. *Chem. Rev.* **2007**, *107*, 2167; (m) Dallinger, D.; Kappe, C. O. *Chem. Rev.* **2007**, *107*, 2563; (n) Liu, S.; Xiao, J. *J. Mol. Catal. A: Chem.* **2007**, *270*, 1; (o) Li, C.-J.; Trost, B. M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 13197; (p) Horváth, I. T. *Green Chem.* **2008**, *10*, 1024; (q) Shaughnessy, K. H. *Chem. Rev.* **2009**, *109*, 643.
13. Wu, W.-Y.; Chen, S.-N.; Tsai, F.-Y. *Tetrahedron Lett.* **2006**, *47*, 9267.
14. Chen, S.-N.; Wu, W.-Y.; Tsai, F.-Y. *Tetrahedron* **2008**, *64*, 8164.
15. Chen, S.-N.; Wu, W.-Y.; Tsai, F.-Y. *Green Chem.* **2009**, *11*, 269.
16. Huang, S.-H.; Chen, J.-R.; Tsai, F.-Y. *Molecules* **2010**, *15*, 315.
17. Wu, W.-Y.; Wang, J.-C.; Tsai, F.-Y. *Green Chem.* **2009**, *11*, 326.
18. Wang, Y.-H.; Tsai, F.-Y. *Chem. Lett.* **2007**, 1492.
19. (a) Tanaka, K.; Shirasaka, K. *Org. Lett.* **2003**, *5*, 4697; (b) Nishida, G.; Suzuki, N.; Noguchi, K.; Tanaka, K. *Org. Lett.* **2006**, *8*, 3489; (c) Tracey, M. R.; Oppenheimer, J.; Hsung, R. P. *J. Org. Chem.* **2006**, *71*, 8629.
20. Son, S. U.; Choi, D. S.; Chung, Y. K.; Lee, S.-G. *Org. Lett.* **2000**, *2*, 2097.
21. (a) Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1357; (b) Grigg, R.; Scott, R.; Stevenson, P. *Tetrahedron Lett.* **1982**, *23*, 2691.
22. Lierena, D.; Buisine, O.; Aubert, C.; Malacria, M. *Tetrahedron* **1998**, *54*, 9373.
23. Oppolzer, W.; Pimm, A.; Stammen, B.; Hume, W. E. *Helv. Chim. Acta* **1997**, *80*, 623.
24. Chandrasekhar, S.; Ramachandar, T.; Reddy, M. V.; Takhi, M. *J. Org. Chem.* **2000**, *65*, 4729.
25. Torii, S.; Okumoto, H.; Nishimura, A. *Tetrahedron Lett.* **1991**, *32*, 4167.
26. Foubelo, F.; García, D.; Moreno, B.; Yus, M. *Tetrahedron Lett.* **2007**, *48*, 3379.