Transition-metal-catalyzed regioselective aroyl- and trifluoro-acetylthiolation of alkynes using thioesters†

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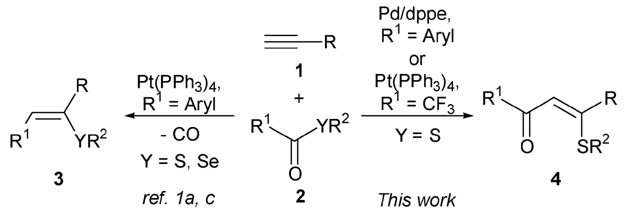
Received (in Cambridge, UK) 9th January 2009, Accepted 18th March 2009
First published as an Advance Article on the web 9th April 2009
DOI: 10.1039/b900492k

Intermolecular CO-retained carbothiolation of alkynes using thioesters took place to afford β-SR substituted enone derivatives; the choice of catalyst ($Pd(dba)_2$–dppe) and the introduction of a CF_3 group into the thioesters are the key to achieving the transformation.

The development of efficient transition-metal-catalyzed carbon–heteroatom bond-forming reactions has been one of the most important subjects in synthetic chemistry. An important example would be the addition reactions of carbon–heteroatom bonds across C–C unsaturated bonds that form new carbon–carbon bonds in a single procedure. A wide range of substrates having C–S, C–Se, C–N, C–Si, C–Sn and C–B bonds were employed for this purpose.[1]

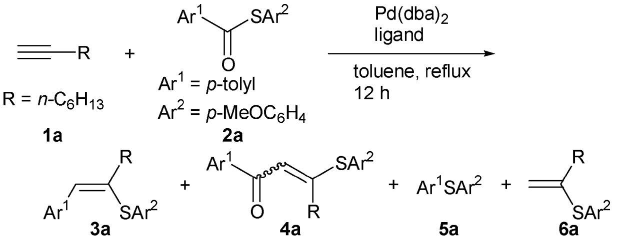
We have already reported the $Pt(PPh_3)_4$-catalyzed intermolecular regio- and stereoselective *decarbonylative arylthiolation* and *arylselenation* of alkynes $HC{\equiv}CR$ (**1**) by $R^1C(O)YR^2$ (**2**, R^1 = aryl; Y = S, Se) (Scheme 1, left)[1a,c] to produce vinylsulfides and selenides (**3**). Disclosed herein are the intermolecular regioselective *aroylthiolation* (R^1 = aryl; Y = S) and *trifluoroacetylthiolation* ($R^1 = CF_3$; Y = S) of **1** to afford enone derivatives (**4**) (Scheme 1, right).[2]

The attempted reaction of 1-octyne (**1a**; R = n-C_6H_{13}, 1.2 mmol) with $Ar^1C(O)SAr^2$ (**2a**; Ar^1 = p-tolyl, Ar^2 = p-$MeOC_6H_4$, 1.0 mmol) in the presence of $Pd(PPh_3)_4$ (0.05 mmol) under toluene reflux gave an aroylthiolation product $(Ar^1C(O))(H)C{=}C(n\text{-}C_6H_{13})(SAr^2)$ (**4a**) in 10% yield (E/Z = 61/39) together with 50% of an Ar^1SAr^2 (**5a**)[3] and 20% of a hydrothiolation product $H_2C{=}C(n\text{-}C_6H_{13})(SAr^2)$ (**6a**)[4] (entry 1, Table 1). The effects of various ligands were examined with $Pd(dba)_2$ as a palladium(0) source. No reaction occurred without an additional ligand (entry 2, Table 1). The reactions using other monodentate ligands such as $P(p\text{-tolyl})_3$, $P(o\text{-tolyl})_3$, $P(2\text{-furyl})_3$, PCy_3, $P(n\text{-Bu})_3$ and PMe_2Ph also were not satisfactory: **5a** and **6a** were generated as major products (entries 3–8, Table 1). On the other hand, the reaction with dppe afforded **4a** in 53% (E/Z = 67/33) yield with 12% of **5a** and 14% of **6a** (entry 10, Table 1). Gratifyingly, when the reaction was carried out under benzene reflux, the formation of **5a** was suppressed and **4a** was obtained in 78% yield (E/Z = 61/39) with 10% of $Ar^1C(O)C{\equiv}CR$ after 20 h (entry 11, Table 1). When conducted for a short period of time (1 h), the reaction selectively provided Z-**4a** (14%), which indicated that *cis*-addition kinetically took place (entry 12, Table 1).[5,6] The employment of other bidentate ligands such as dppm, dppp and dppb



Scheme 1 Decarbonylative *vs.* CO-retained carbothiolation of alkynes (**1**) by thioesters (**2**).

Table 1 The effects of ligands under the Pd-catalyzed reaction of **1a** with **2a**[a]



Entry	Ligand	**3a** (%)	**4a** (%) (E/Z)	**5a** (%)	**6a** (%)
1	PPh_3[b]	n.d.	10 (61/39)	50	20
2	None	n.d.	n.d.	n.d.	n.d.
3	$P(p\text{-tolyl})_3$	n.d.	9 (65/35)	34	22
4	$P(o\text{-tolyl})_3$	n.d.	n.d.	2	n.d.
5	$P(2\text{-furyl})_3$	n.d.	n.d.	8	5
6	PCy_3	n.d.	1 (100/0)	22	38
7	$P(n\text{-Bu})_3$	n.d.	6 (50/50)	30	22
8	PMe_2Ph	n.d.	8 (50/50)	16	16
9	dppm	n.d.	6 (33/67)	17	6
10	dppe	n.d.	53 (67/33)	12	14
11[cde]	dppe	n.d.	78 (61/39)[f]	n.d.	16
12[cg]	dppe	n.d.	14 (0/100)	n.d.	n.d.
13	dppp	n.d.	16(61/39)	30	25
14	dppb	n.d.	15 (61/39)	36	35
15[hi]	$Pt(PPh_3)_4$	75[f]	8 (0/100)	n.d.	n.d.

[a] Unless otherwise noted, the solution of **1a** (1.2 mmol), **2a** (1.0 mmol), $Pd(dba)_2$ (0.05 mmol), and ligand (0.12 mmol for entries 3–8, 0.06 mmol for entries 9–14) was stirred under toluene (0.5 mL) reflux for 12 h. Yields were determined by ^1H NMR spectroscopy. [b] $Pd(PPh_3)_4$ (0.05 mmol) as a catalyst. [c] Under benzene reflux. [d] 20 h. [e] The formation of $Ar^1C(O)C{\equiv}CR$ was detected in 10% yield. [f] Isolated yield. [g] 1 h. [h] $Pt(PPh_3)_4$ (0.05 mmol) as a catalyst. [i] 13 h. dba = dibenzylideneacetone, tolyl = methylphenyl, Cy = cyclohexyl, dppm = 1,1-bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane.

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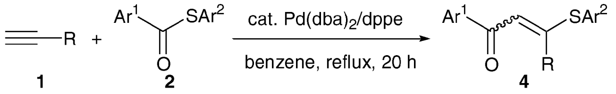
† Electronic supplementary information (ESI) available: Typical experimental procedures, and analytical data for the products. See DOI: 10.1039/b900492k

Table 2 Pd–dppe-catalyzed aroylthiolation of **1** by **2**[a]

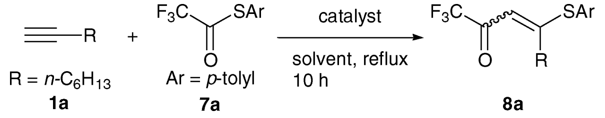


1a (R = n-C_6H_{13})
1b (R = $(CH_2)_4Cl$)
1c (R = $(CH_2)_3CN$)
1d (R = $(CH_2)_3CO_2Me$)
1e (R = CH_2(c-C_5H_9))
1f (R = $(CH_2)_2CHMe_2$)
1g (R = Ph)

Entry	1	2	Ar^1	Ar^2	4	(%) (E/Z)[b]
1	**1a**	**2a**	p-Tolyl	p-$MeOC_6H_4$	**4a**	78 (61/39)
2	**1a**	**2b**	p-Tolyl	Ph	**4b**	53 (72/28)
3	**1a**	**2c**	p-Tolyl	p-FC_6H_4	**4c**	46 (72/28)
4	**1a**	**2d**	p-Tolyl	p-$NO_2C_6H_4$	**4d**	n.d.
5	**1a**	**2e**	Ph	Ph	**4e**	66 (74/26)
6	**1a**	**2f**	p-FC_6H_4	p-Tolyl	**4f**	57 (74/26)
7	**1a**	**2g**	3-Pyridyl	p-Tolyl	**4g**	74 (72/28)
8	**1a**	**2h**	2-Furyl	p-Tolyl	**4h**	55 (75/25)
9	**1a**	**2i**	p-Tolyl	CH_2Ph	**4i**	10 (74/26)[c]
10	**1a**	**2j**	t-Bu	p-$MeOC_6H_4$	**4j**	n.d.
11	**1b**	**2a**	p-Tolyl	p-$MeOC_6H_4$	**4k**	70 (67/33)
12	**1c**	**2a**	p-Tolyl	p-$MeOC_6H_4$	**4l**	50 (72/28)
13	**1d**	**2a**	p-Tolyl	p-$MeOC_6H_4$	**4m**	80 (75/25)
14	**1e**	**2a**	p-Tolyl	p-$MeOC_6H_4$	**4n**	66 (73/27)
15	**1f**	**2a**	p-Tolyl	p-$MeOC_6H_4$	**4o**	65 (53/47)
16	**1g**	**2a**	p-Tolyl	p-$MeOC_6H_4$	**4p**	40 (25/75)
17	**1a**	**2k**	PhC(O)SePh		**4q**	3 (1/>99)[c]

[a] **1** (1.2 mmol), **2** (1.0 mmol), $Pd(dba)_2$ (0.05 mol) and dppe (0.06 mol) under benzene (0.5 mL) reflux for 20 h. [b] Isolated yield. [c] NMR yield.

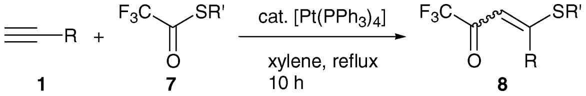
Table 3 Reaction of **1a** with **7a**[a]



Entry	Catalyst	Solvent	**8a** (%) (E/Z)
1[b]	$Pd(dba)_2$–dppe[c]	Benzene	8 (64/36)[d]
2	$Pd(dba)_2$–dppe[c]	Xylene	15 (75/25)[e]
3	$Pt(PPh_3)_4$	Xylene	78 (82/18)[f]
4	$Pt(PPh_3)_4$	Benzene	8 (82/18)
5	$Pt(PPh_3)_4$	Toluene	39 (79/21)
6[g]	$Pt(PPh_3)_4$	Xylene	15 (41/59)
7	$Pd(PPh_3)_4$	Xylene	7 (72/28)[h]
8	$Ni(cod)_2$–PPh_3[i]	Xylene	n.d.

[a] Unless otherwise noted, the solution of **1a** (0.75 mmol), **7a** (0.5 mmol), catalyst (0.025 mol) and solvent (0.5 mL) was stirred under reflux for 10 h. Yields were determined by ^1H NMR spectroscopy. [b] 20 h. [c] $Pd(dba)_2$ (0.025 mmol) and dppe (0.03 mmol). [d] (CH_3)(p-MeC_6H_4S)CC(H)(n-C_5H_{11}) (**9a**) was obtained in 16% yield. [e] **9a** was obtained in 31% yield. [f] Isolated yield. [g] 30 min. [h] **9a** was obtained in 52% yield. [i] $Ni(cod)_2$ (0.025 mmol) and PPh_3 (0.1 mmol).

Table 4 Pt-catalyzed trifluoroacetylthiolation of **1** by **7**[a]



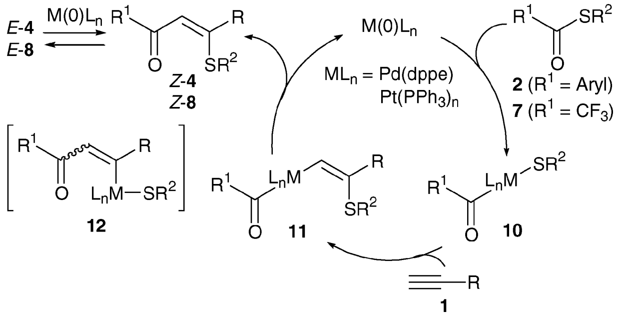
Entry	1	7	8	(%) (E/Z)[b]
1	**1a**	**7a** (R′ = p-tolyl)	**8a**	78 (82/18)
2	**1a**	**7d** (R′ = p-$MeOC_6H_4$)	**8d**	64 (89/11)
3	**1a**	**7e** (R′ = Ph)	**8e**	82 (76/24)
4	**1a**	**7f** (R′ = p-ClC_6H_4)	**8f**	69 (66/34)
5	**1a**	**7g** (R′ = CH_2Ph)	**8g**	51 (70/30)
6	**1a**	**7h** (R′ = n-$C_{10}H_{21}$)	**8h**	41 (82/18)
7[c]	**1b**	**7e** (R′ = Ph)	**8i**	83 (71/29)
8[c]	**1c**	**7e** (R′ = Ph)	**8j**	79 (71/29)
9[c]	**1d**	**7e** (R′ = Ph)	**8k**	87 (74/26)
10	**1e**	**7e** (R′ = Ph)	**8l**	70 (64/36)

[a] Unless otherwise noted, **1** (0.75 mmol), **7** (0.5 mmol), $Pt(PPh_3)_4$ (0.025 mmol), and xylene (0.5 mL) under reflux for 10 h. [b] Isolated yield. [c] Xylene (2.0 mL).

significantly decreased the yield of **4a** (entries 9,13,14, Table 1).[7] It must be noted that **3a**, the product of $Pt(PPh_3)_4$-catalyzed decarbonylative arylthiolation (entry 15, Table 1), was not detected under Pd-catalysis (entries 1–14, Table 1). No formation of **4a** was confirmed with $Pt[(CH_2{=}CHSiMe_2)_2O]$, $Ni(cod)_2$ (cod = cyclooctadiene) or $RhCl(cod)_2$ in the presence of dppe.

The results of the Pd–dppe-catalyzed aroylthiolation of alkyne (**1**) by $Ar^1C(O)SAr^2$ (**2**) are summarized in Table 2. The reaction with **2a** (Ar^2 = p-$MeOC_6H_4$) afforded a better yield of desired **4** (78% of **4a**, entry 1, Table 2) compared to the reactions with **2b** (Ar^2 = Ph, 53% of **4b**, entry 2 Table 2) and **2c** (Ar^2 = p-FC_6H_4, 46% of **4c**, entry 3, Table 2). In sharp contrast to the Pt-catalyzed decarbonylative arylthiolation, no reaction took place when a thioester with Ar^2 = p-$NO_2C_6H_4$ (**2d**) was employed (entry 4, Table 2). Phenyl and p-FC_6H_4 groups at Ar^1 somewhat lowered the reactivity (entries 5–6 Table 2). Thioesters **2g** (Ar^1 = 3-pyridyl) and **2h** (Ar^1 = 2-furyl) reacted with **1a** to furnish the corresponding adducts **4g** and **4h** in 74% and 55% yields, respectively (entries 7 and 8, Table 2). On the other hand, a thioester with a benzyl group on sulfur (**2i**) gave a low yield of **4i** (10%, entry 9, Table 2), and the reaction with t-$BuC(O)SC_6H_4$$p$-OMe (**2j**) did not produce **4j** (entry 10, Table 2). Terminal alkynes having chlorine (**1b**), a cyano group (**1c**), a methoxy carbonyl group (**1d**), a cyclopentyl group (**1e**), $(CH_2)_2CHMe_2$ (**1f**) and a phenyl group (**1g**) all underwent an aroylthiolation by **2a** to afford **4k–p** in moderate to good yields (entries 11–16, Table 2). The reactions of **1a** with a selenoester (**2k**; PhC(O)SePh) took place to provide the aroylselenation product **4q**, albeit in a very low yield (entry 17, Table 2).

Next, the reactions with CX_3-substituted thioesters (**7**; $CX_3C(O)SAr$) were examined. The treatment of 1-octyne (**1a**, 0.75 mmol) with $CF_3C(O)SC_6H_4$$p$-Me (**7a**; X = F, 0.5 mmol) in the presence of Pd–dppe under benzene and xylene reflux both gave trifluoroacetylthiolation product **8a** in low yields; (CH_3)(p-MeC_6H_4S)$C{=}C(H)$(n-C_5H_{11}) (**9a**) derived from **6a** was generated as a major product (entries 1 and 2, Table 3). Intriguingly, the reaction using $Pt(PPh_3)_4$ as a catalyst under xylene reflux conditions remarkably improved the yield of **8a** (78%, E/Z = 82/18),[8,9] compared to benzene or toluene reflux conditions (entries 3–5, Table 3). Intercepting the reaction at the early stage (E/Z = 41/59 after 30 min) also indicates the involvement of *cis*-addition (Entry 6). Inferior catalyses were shown by $Pd(PPh_3)_4$ (entry 7, Table 3) and $Ni(cod)_2$–$4PPh_3$ (entry 8, Table 3). On the other hand, the reaction employing $CH_3C(O)SC_6H_4$$p$-Me (**7b**; X = H) and $CCl_3C(O)SC_6H_4$$p$-Me (**7c**; X = Cl) in the presence of $Pt(PPh_3)_4$ hardly produced the corresponding **8b** and **8c**.



Scheme 2 A plausible mechanism for the transition-metal-catalyzed aroyl- and trifluoroacetylthiolation of alkynes (**1**) by thioesters (**2** and **7**).

The results of Pt-catalyzed trifluoroacetylthiolation of alkyne (**1**) by $CF_3C(O)SR'$ are shown in Table 4. Some substituents in aryl-S groups (**7d**; R' = *p*-$MeOC_6H_4$, **7e**; R' = Ph, **7f**; R' = *p*-ClC_6H_4) hardly interfered with the addition reactions (entries 2–4, Table 4). Unlike the case of the reaction with **2**, thioesters possessing an sp^3-carbon substituent such as benzyl (**7g**) and *n*-decyl groups (**7h**) on sulfur also reacted with **1a** to produce **8g** and **8h** in 51% and 41% yields, respectively (entries 5 and 6, Table 4). Addition of **7e** to alkynes **1b–1e** proceeded to afford the product **8i–l** in good yields (entries 7–10, Table 4). Contrary to the case of Pt-catalyzed decarbonylative carbothiolation, the products of decarbonylative trifluoromethylthiolation were not detected in all cases even with the same catalyst.

A plausible reaction mechanism of the present regioselective CO-retained addition of thioesters (**2** or **7**; $R^1C(O)SR^2$ (R^1 = aryl or CF_3)) to alkynes (**1**; $HC{\equiv}CR$) was depicted in Scheme 2. The oxidative addition of **2** or **7** to $M(0)L_n$ (ML_n = Pd(dppe) or $Pt(PPh_3)_n$) complex triggers the reaction to afford $ML_n[C(O)R^1](SR^2)$ (**10**).[10] Subsequent regio- and stereoselective insertion of alkyne **1** into the S–M bond of **10** generates $ML_n[C(O)R^1][(Z)\text{–}CH{=}C(SR^2)(R)]$ (**11**),[11] which can react with another **1** to produce **6** and $Ar^1C(O)C{\equiv}CR$ as by-products. Finally, the C–C bond-forming reductive elimination of *Z*-**4** or *Z*-**8** from **11** with regeneration of $M(0)L_n$ completes the catalytic cycle. *Z*-to-*E* isomerisation of the product can be explained as follows: the oxidative addition of a vinyl C–S bond of *Z*-isomer to a $M(0)L_n$ complex to produce $ML_n[(Z)\text{–}C(R){=}C(H)\{C(O)R^1\}](SR^2)$ (*Z*-**12**),[12] *Z*-to-*E* isomerization of **12**,[13] and the reductive elimination of *E*-**4** and *E*-**8** from *E*-**12**.

In conclusion, the present study substantiated that the decarbonylative arylthiolation of alkynes by thioesters is converted into CO-retained, atom-economical, regioselective carbothiolation simply by changing the catalysts from $Pt(PPh_3)_4$ to $Pd(dba)_2$–dppe or by employing $CF_3C(O)$ as a carbon functionality of thioesters even under $Pt(PPh_3)_4$-catalyzed conditions. Our efforts will continue to focus on the extension of the present CO-retained carbothiolation to other addition systems.

Notes and references

1 For a review of carbochalcogenation of alkynes, see: (*a*) H. Kuniyasu and N. Kambe, *Chem. Lett.*, 2006, **35**, 1320; For recent examples, see: (*b*) R. Hua, H. Takeda, S. Onozawa, Y. Abe and M. Tanaka, *Org. Lett.*, 2007, **9**, 263; (*c*) F. Yamashita, H. Kuniyasu, J. Terao and N. Kambe, *Org. Lett.*, 2008, **10**, 101; (*d*) M. Toyofuku, S. Fujiwara, T. Shin-ike, H. Kuniyasu and N. Kambe, *J. Am. Chem. Soc.*, 2008, **130**, 10504; (*e*) V. P. Ananikov, N. V. Orlov, M. A. Kabeshov, I. P. Beletskaya and Z. A. Starikova, *Organometallics*, 2008, **27**, 4056; (*f*) K. Yamashita, H. Takeda, T. Kashiwabara, R. Hua, S. Shimada and M. Tanaka, *Tetrahedron Lett.*, 2007, **48**, 6655; (*g*) M. Toyofuku, E. Murase, S. Fujiwara, T. Shin-ike, H. Kuniyasu and N. Kambe, *Org. Lett.*, 2008, **10**, 3957; (*h*) Y. Kajita, S. Matsubara and T. Kurahashi, *J. Am. Chem. Soc.*, 2008, **130**, 6058; (*i*) Y. Nakao, J. Satoh, E. Shirakawa and T. Hiyama, *Angew. Chem., Int. Ed.*, 2006, **45**, 2271; (*j*) Y. Shi, S. M. Peterson, W. W. Haberaecker III and S. A. Blum, *J. Am. Chem. Soc.*, 2008, **130**, 2168; (*k*) M. Suginome, A. Yamamoto and M. Murakami, *Angew. Chem., Int. Ed.*, 2005, **44**, 2380; (*l*) M. Suginome, M. Shirakura and A. Yamamoto, *J. Am. Chem. Soc.*, 2006, **128**, 14438.

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5 The stereochemistry of *E*-**4a** and *Z*-**4a** was determined by NOE experiments between vinyl and allyl protons.

6 The treatment of isolated *Z*-**4a** with **2a** and a catalytic amount of $Pd(dba)_2$ (5 mol%), dppe (6 mol%) and 1.6 equivalents of **1a** led to *Z*-to-*E* isomerization (*E*/*Z* = 61/39), while no isomerization took place without **1a** under otherwise identical conditions. This result suggests that alkyne-coordinated Pd-complex induce the *Z*-to-*E* isomerization.

7 While Pd(0)–dppp and Pd(0)–dppb catalyzed the decarbonylation of **2a** to provide **5a** in 12% and 36% yield, respectively, the decarbonylation hardly took place with Pd(0)–dppe (4%). On the other hand, the reaction between *p*-MeC_6H_4I and $NaSC_6H_4$*p*-OMe catalyzed by $Pd(dba)_2$ (5 mol%)–dppe (6 mol%) produced **5a** in 83% yield. These facts indicated that dppe suppresses the decarbonylation from thiocarbonyl complex, see: G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze and P. W. N. M. Leeuwen, *Organometallics*, 1992, **11**, 1598.

8 The stereochemistry of *E*-**8a** and *Z*-**8a** was determined by NOE experiments between vinyl and allyl protons, and the regiochemistry of *E*-**8a** was determined by ^1H-^{13}C HMBC experiments.

9 See the ESI for further details.

10 For the oxidative addition of thioesters to platinum(0) complexes, see: Y. Minami, T. Kato, H. Kuniyasu, J. Terao and N. Kambe, *Organometallics*, 2006, **25**, 2949, and references therein.

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12 We have reported that an anion stabilizing group on the β-carbon of the C–S bond of vinylsulfide promotes the oxidative addition to Pt(0), see: (*a*) H. Kuniyasu, A. Ohtaka, T. Nakazono, M. Kinomoto and H. Kurosawa, *J. Am. Chem. Soc.*, 2000, **122**, 2375; (*b*) ref. 1*d*.

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