Tetrahedron 72 (2016) 1205–1212

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Carboxylative cyclization of propargylic amines with CO_2 catalyzed by dendritic N-heterocyclic carbene–gold(I) complexes

Ken-ichi Fujita [a,*], Kensuke Inoue [b], Junichi Sato [c], Teruhisa Tsuchimoto [b], Hiroyuki Yasuda [a,c]

[a] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[b] Department of Applied Chemistry, School of Science and Technology, Meiji University, Higashimita, Tama-ku, Kawasaki, Kanagawa 214-8571, Japan
[c] Graduate School of Science and Engineering, Ibaraki University, 2-1-1 Bunkyo, Mito, Ibaraki 310-8512, Japan

ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form 5 January 2016
Accepted 8 January 2016
Available online 11 January 2016

Keywords:
NHC–gold(I) complex
Carbon dioxide
Propargylic amine
2-Oxazolidinone

ABSTRACT

We prepared several of a new type of dendritic N-heterocyclic carbene (NHC)–gold(I) complex. In particular, by employing an amphiphilic dendritic NHC–gold(I) complex having penta(ethylene glycol) units at the peripheral layer as a catalyst, the aqueous media carboxylative cyclization of propargylic amines proceeded smoothly to provide the corresponding 2-oxazolidinone at room temperature under atmospheric pressure of CO_2.

1. Introduction

The chemical fixation of carbon dioxide (CO_2) into valuable organic molecules has received much attention in synthetic organic chemistry in recent years because CO_2 is a safe, inexpensive, and renewable C_1 resource.[1] Although CO_2, as the most oxidized carbon derivative, is much less reactive, its application to organic synthesis has been considered one of the most challenging research topics. One of the useful transformations in which CO_2 has been utilized as a substrate is through the carboxylative cyclization of propargylic amines with CO_2 to provide 2-oxazolidinones.[2] For example, the carboxylative cyclization of propargylic amines has been found to proceed in the presence of organometallic complexes of ruthenium and palladium as catalysts under 4–5 MPa of CO_2.[3] Very recently, we have reported that *N*-heterocyclic carbene (NHC), which is metal-free, can also catalyze the carboxylative cyclization of propargylic amines to provide 2-oxazolidinones under 0.6 MPa of CO_2.[4] Moreover, even under atmospheric pressure of CO_2, NHC–gold(I) complexes or silver acetate can promote the carboxylative cyclization of propargylic amines.[5]

Dendrimers are fascinating molecules due to their unique physical and chemical properties caused by their well-defined hyperbranched frameworks.[6] Metallodendrimers, which have a functional or catalytic site at their core, have received considerable attention because of their unique selectivity and reactivity caused by a specific reaction field constructed by the dendron.[7] Moreover, their solubilities and physical properties can be altered by peripheral modification.[8] For example, by the introduction of hydrophilic groups to the peripheral layer of a hydrophobic dendron, metal core dendrimers can become water-soluble[9] and afford unique catalytic activity.[10] In this paper, we report the synthesis of novel NHC–gold(I) core dendrimers having a poly(benzyl ether) dendron with the modification of the peripheral layer **1**G*n*[X] (*X*=Me, TEG, PEG, and DEG; Fig. 1), and their application as catalysts to the carboxylative cyclization of propargylic amines under atmospheric pressure of CO_2.[11] In particular, by employing amphiphilic dendritic NHC–gold(I) complexes having poly(ethylene glycol) units at the peripheral layer as catalysts, the aqueous media carboxylative cyclization of propargylic amines proceeded smoothly to provide 2-oxazolidinones at room temperature. From the perspective of green chemistry, the chemical fixation of CO_2 carried out in water is a very attractive field, as water is an environmentally benign solvent.[12]

2. Results and discussion

NHC–gold(I) core dendrimers having a methyl group or a tri(ethylene glycol) unit at the peripheral layer **1**G*n*[X] (*X*=Me, TEG; *n*=1–3) were synthesized as follows (Table 1). A suspension

* Corresponding author. E-mail address: k.fujita@aist.go.jp (K. Fujita).

http://dx.doi.org/10.1016/j.tet.2016.01.016
0040-4020/

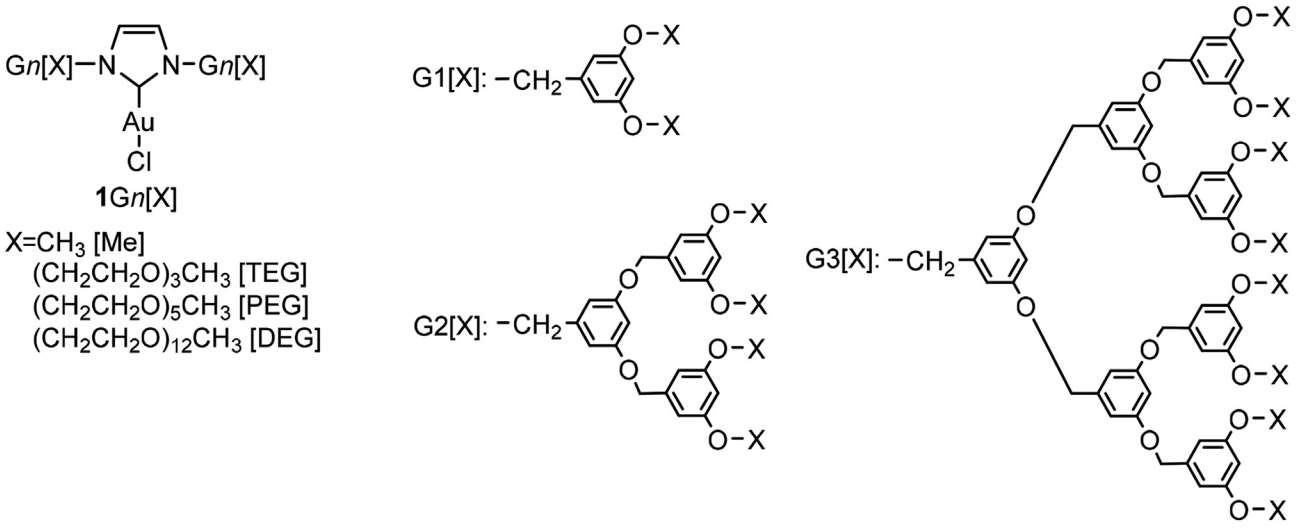


Fig. 1. Structural formulas of **1**G*n*[X] and G*n*[X] dendrons (*n*=1–3).

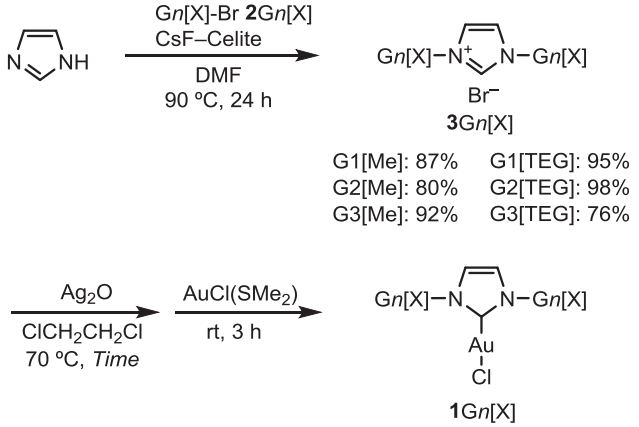
of imidazole, poly(benzyl ether) dendritic bromide **2**G*n*[X], and CsF–Celite®[13] in *N*,*N*-dimethylformamide (DMF) was stirred at 90 °C for 24 h to afford the corresponding dendritic imidazolium bromide **3**G*n*[X]. A mixture of **3**G*n*[X] and silver(I) oxide in 1,2-dichloroethane was stirred at 70 °C till the complete consumption of **3**G*n*[X], which was detected by ^{1}H NMR. The reaction times are shown in Table 1. By the subsequent addition of AuCl(SMe$_2$) and the stirring of the reaction mixture at room temperature for 3 h, the corresponding NHC–gold(I) core dendrimers **1**G*n*[X] were obtained. Transformations were carried out in good chemical yields in all cases.

We then examined the catalytic activity of the NHC–gold(I) core dendrimer having a methyl group at the peripheral layer **1**G*n*[Me] (*n*=1–3) by performing the carboxylative cyclization of propargylic amines with CO_2 (Table 2). The procedure employed herein was Ikariya's synthetic sequence.[5c] Table 2, entry 1 shows their results with use of AuCl(IPr) (IPr=1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) as a catalyst.

First, by employing 2 mol % of the first-generation dendritic catalyst **1**G1[Me], the carboxylative cyclization of *N*,*N*-methyl(3-phenylpropargyl) amine **4a** was carried out under atmospheric pressure of CO_2 (0.1 MPa) in methanol at 40 °C for 48 h. The reaction proceeded homogeneously to provide the corresponding 2-oxazolidinone **5a** in a 59% chemical yield (Table 2, entry 2).[14] The carbon–carbon double bond of **5a** was found to be in the *Z* configuration by NMR referring to the previously reported literature.[5c] On the other hand, by employing the second-generation **1**G2[Me] as a catalyst, 2-oxazolidinone **5a** was obtained in a 75% chemical yield (Table 2, entry 3). This improvement of the chemical yield of **5a** is probably due to a specific catalytic environment constructed by the dendron.[15] However, when the third-generation **1**G3[Me] was used as a catalyst, the chemical yield of **5a** somewhat decreased, contrary to our expectations (67%; Table 2, entry 4).

Next, we examined the catalytic activity of the amphiphilic NHC–gold(I) core dendrimer having the tri(ethylene glycol) unit **1**G*n*[TEG] (*n*=1–3) (Table 3). By employing 2 mol % of the first-generation **1**G1[TEG] as a catalyst, the carboxylative cyclization of propargylic amine **4a** with CO_2 heterogeneously proceeded in methanol at 40 °C for 48 h to provide the corresponding 2-oxazolidinone **5a** in a 47% chemical yield (Table 3, entry 1). On

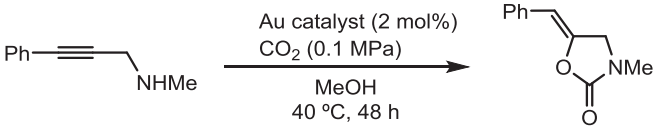
Table 1
Preparation of **1**G*n*[X] (X=Me, TEG; *n*=1–3)



Entry	G*n*[X]	*Time* (h)	Yield of 1G*n*[X] (%)[a]
1	G1[Me]	3	78
2	G2[Me]	20	81
3	G3[Me]	48	86
4	G1[TEG]	3	91
5	G2[TEG]	5	85
6	G3[TEG]	24	94

[a] Isolated yield.

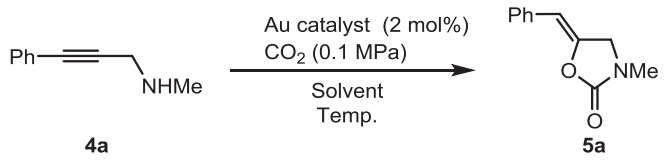
Table 2
Carboxylative cyclization of propargylic amine **4a** with CO_2 catalyzed by **1**G*n*[Me][a]



Entry	Au catalyst	Yield (%)[b]
1[c]	AuCl(IPr)	76
2	**1**G1[Me]	59
3	**1**G2[Me]	75
4	**1**G3[Me]	67

[a] Reaction conditions: Au catalyst (2 mol %), **4a** (0.8 mmol), methanol (1M based on **4a**), carried out at 40 °C for 48 h under atmospheric pressure of CO_2 (0.1 MPa).
[b] Determined by integration of ^{1}H NMR absorptions referring to an internal standard.
[c] Cited from Ref. 5c.

Table 3
Carboxylative cyclization of propargylic amine **4a** with CO_2 catalyzed by **1**G*n*[TEG][a]

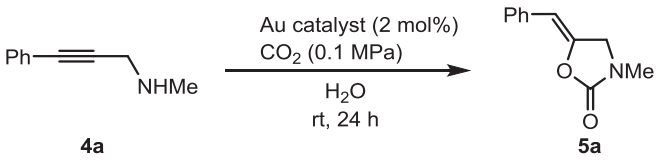


4a **5a**

Entry	Au catalyst	Solvent	Temp (oC)	Time (h)	Yield (%)[b]
1	**1**G1[TEG]	MeOH	40	48	47
2	**1**G2[TEG]	MeOH	40	48	29
3	**1**G1[TEG]	MeOH	rt	24	67
4	**1**G1[TEG]	MeOH	rt	48	82
5	**1**G1[Me]	MeOH	40	48	59
6	**1**G1[Me]	MeOH	rt	48	10
7[c]	AuCl(IPr)	MeOH	40	48	76
8	AuCl(IPr)	MeOH	rt	48	59
9	**1**G2[TEG]	MeOH	rt	48	73
10	**1**G3[TEG]	MeOH	rt	48	71
11	**1**G1[TEG]	iPrOH	rt	48	62

[a] The reaction conditions were the same as those indicated in Table 2.
[b] Determined by integration of ^{1}H NMR absorptions referring to an internal standard.
[c] Cited from Ref. 5c.

Table 4
Aqueous media carboxylative cyclization of propargylic amine **4a** with CO_2[a]



4a **5a**

Entry	Au catalyst	Yield (%)[b]
1	**1**G1[TEG]	85
2	**1**G2[TEG]	72
3	**1**G3[TEG]	24
4	AuCl(IPr)	2
5	**1**G1[Me]	1
6[c]	AuCl(IPr)	1
7[c]	**1**G1[Me]	1

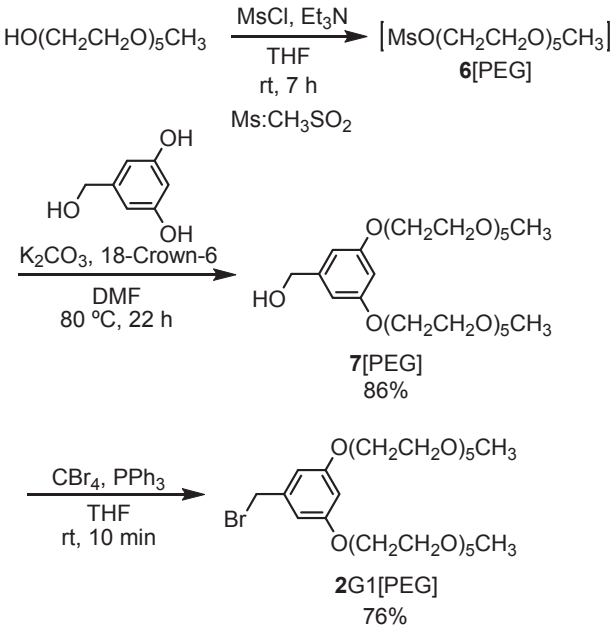
[a] The reaction conditions were the same as those indicated in Table 2.
[b] Determined by integration of ^{1}H NMR absorptions referring to an internal standard.
[c] Carried out in the presence of 8 mol % of tri(ethylene glycol) dimethyl ether.

the other hand, the chemical yield of **5a** when the second-generation **1**G2[TEG] was used was lower than that when the first-generation **1**G1[TEG] was used, probably due to the low solubility of the second-generation **1**G2[TEG] in methanol, contrary to our expectations (Table 3, entries 1 and 2). Next, by employing the first-generation **1**G1[TEG] as a catalyst at room temperature, the chemical yield of **5a** increased (24 h: 67%, 48 h: 82%; Table 3, entries 3 and 4). In contrast, when **1**G1[Me] or AuCl(IPr) was used as a catalyst, the chemical yield of **5a** decreased as a result of the reduced reaction temperature in both cases (Table 3, entries 5–8). Generally, poly(ethylene glycol) derivatives have higher solubility in a polar protic solvent when the temperature is reduced.[16] The fair chemical yields in entries 3 and 4 in Table 3, carried out at room temperature, were probably attributable to the good solubility of **1**G1[TEG] in methanol when the reaction temperature is reduced. We then employed the second- or third-generation **1**G*n*[TEG] as a catalyst at room temperature. The chemical yield of **5a** was somewhat decreased by the increase in the generation number of **1**G*n*[TEG] (Table 3, entries 9 and 10). Finally, by carrying out the reaction using the first-generation **1**G1[TEG] as a catalyst in 2-propanol, **5a** was obtained in a 62% chemical yield (Table 3, entry 11), which was lower than that when methanol was used (82%; Table 3, entry 4).

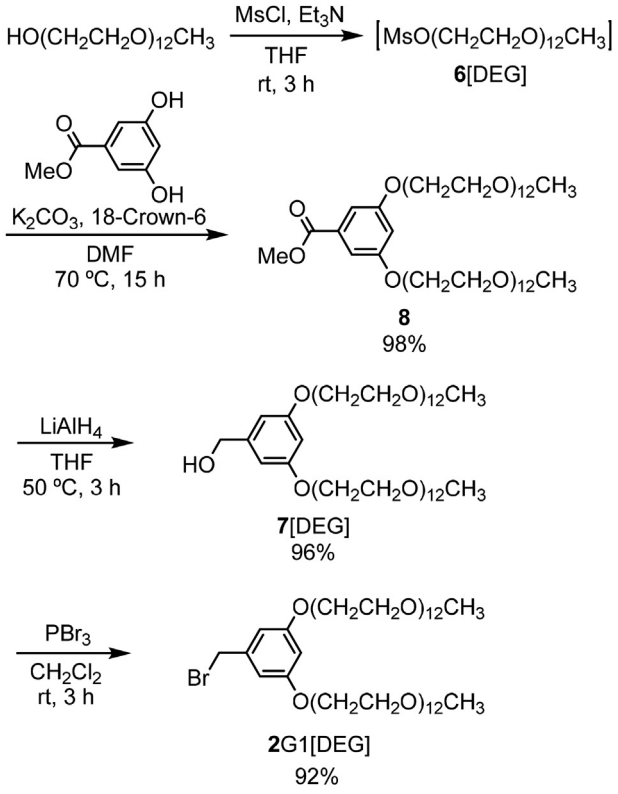
We subsequently performed the carboxylative cyclization in water by using an amphiphilic dendritic NHC–gold(I) complex **1**G*n*[TEG] as a catalyst (Table 4). By employing the first-generation **1**G1[TEG] in water, the aqueous media carboxylative cyclization proceeded smoothly to provide **5a** for 24 h in an 85% chemical yield (Table 4, entry 1). However, when the various generation **1**G*n*[TEG] were used in the aqueous media carboxylative cyclization, the chemical yield of **5a** decreased by the increase in the generation number of **1**G*n*[TEG] (G2: 72%, G3: 24%; Table 4, entries 2 and 3). As a result, the first-generation **1**G1[TEG] smoothly catalyzed the aqueous media carboxylative cyclization of **4a** to provide **5a** in the highest chemical yield. In contrast, by employing AuCl(IPr) or the NHC–gold(I) core dendrimer having a methyl group at the peripheral layer **1**G1[Me] as a catalyst in water at room temperature, the chemical yields of **5a** were 2% and 1%, respectively (Table 4, entries 4 and 5). Under the same reaction conditions as in entries 4 and 5 in Table 4, even with the addition of 8 mol % of tri(ethylene glycol) dimethyl ether using the same amount of TEG moieties of **1**G1[TEG], **5a** was obtained in only 1% yields in both cases (Table 4, entries 6 and 7). From these results, it can be concluded that the inclusion of the NHC–gold(I) complex with an amphiphilic dendrimer is essential to the aqueous media carboxylative cyclization of propargylic amines with CO_2.

We next synthesized the first-generation of other amphiphilic dendritic NHC–gold(I) catalysts having either penta(ethylene glycol) or dodeca(ethylene glycol) units at the peripheral layer **1**G1[PEG] and **1**G1[DEG]. The first-generation dendritic bromide having the penta(ethylene glycol) units **2**G1[PEG] and the first-generation dendritic bromide having the dodeca(ethylene glycol) units **2**G1[DEG] were prepared using the previously reported synthetic procedures,[9a,10a] as shown in Scheme 1 and Scheme 2, respectively. **1**G1[PEG] and **1**G1[DEG] were prepared according to a procedure similar to that used for **1**G1[TEG] (Scheme 3). All transformations were carried out in good chemical yields for both catalysts.

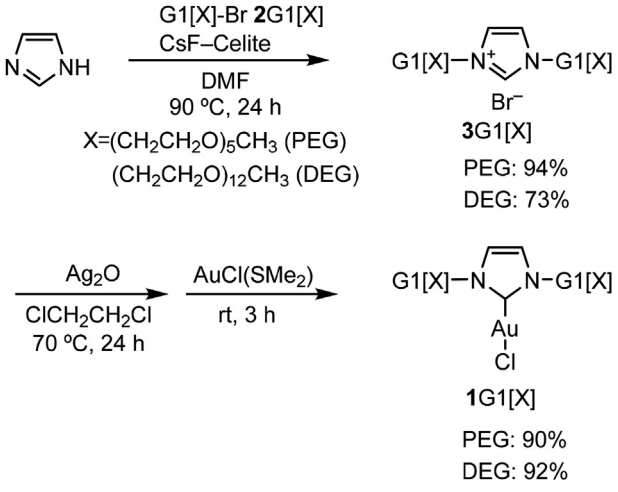
As shown in Table 5, by employing three amphiphilic dendritic NHC–gold(I) catalysts **1**G1[X] (*X*=TEG, PEG, and DEG), the aqueous



Scheme 1. Preparation of **2**G1[PEG].



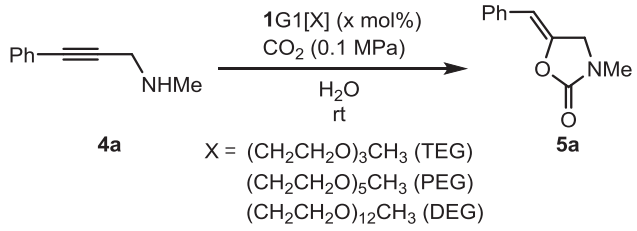
Scheme 2. Preparation of **2**G1[DEG].



Scheme 3. Preparation of **1**G1[X] (*X*=PEG, DEG).

media carboxylative cyclization of **4a** with CO_2 was carried out at room temperature for 15–24 h. As a result, the dendritic NHC–gold(I) catalyst having the penta(ethylene glycol) unit **1**G1[PEG] afforded the highest chemical yield of **5a** (Table 5, entries 3–5). Even when 1 mol% of the catalyst was used, **1**G1[PEG] afforded a good chemical yield of **5a** (82%; Table 5, entry 4). However when 0.5 mol% of **1**G1[PEG] was used as a catalyst, the chemical yield of **5a** decreased significantly (17%; Table 5, entry 6). In addition, from the results of entries 5 and 9 in Table 5, a reaction time of 15 h was insufficient to promote the carboxylative cyclization of **4a**.

Table 5
Aqueous media carboxylative cyclization of propargylic amine **4a** with CO_2 catalyzed by **1**G1[X][a]

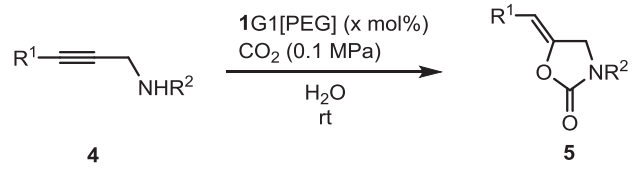


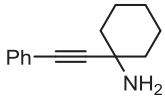
Entry	X	1G1[X] (x mol %)	Time (h)	Yield (%)[b]
1	TEG	2	24	85
2	TEG	1	24	60
3	PEG	2	24	87
4	PEG	1	24	82
5	PEG	1	15	72
6	PEG	0.5	24	17
7	DEG	2	24	84
8	DEG	1	24	77
9	DEG	1	15	61

[a] The reaction conditions were the same as those indicated in Table 2.
[b] Determined by integration of ^{1}H NMR absorptions referring to an internal standard.

Finally, we performed the aqueous media carboxylative cyclization of various propargylic amines by employing the dendritic NHC–gold(I) catalyst having penta(ethylene glycol) units **1**G1[PEG], as shown in Table 6. When the internal propargylic amines were used, except for **4a**, the carboxylative cyclization reactions were carried out for 48 h through the use of 1 mol% of **1**G1[PEG] to provide the corresponding 2-oxazolidinones **5** in acceptable chemical yields (Table 6, entries 2–5). The reactions of substrates having terminal alkyne units **4f** and **4g** gave the corresponding 2-oxazolidinone **5f** and **5g,** respectively, in low chemical yields, even when the reactions were carried out through the use of 2 mol % of **1**G1[PEG] (20% and 49%; Table 6, entries 6 and 7). On the other hand, primary amine **4h** did not afford the corresponding 2-oxazolidinone.

Table 6
Aqueous media carboxylative cyclization of various propargylic amines with CO_2 catalyzed by **1**G1[PEG][a]



Entry	Substrate	R^1	R^2	1G1[PEG] (x mol %)	Time (h)	Product	Yield (%)[b]
1	**4a**	C_6H_5	CH_3	1	24	**5a**	82
2	**4b**	4-$CH_3C_6H_4$	CH_3	1	48	**5b**	87
3	**4c**	CH_3	$C_6H_5CH_2$	1	48	**5c**	74
4	**4d**	CH_3	$(CH_3)_2CH$	1	48	**5d**	63
5	**4e**	C_2H_5	$C_6H_5CH_2$	1	48	**5e**	72
6	**4f**	H	$C_6H_5CH_2$	2	48	**5f**	20
7	**4g**	H	CH_3	2	72	**5g**	49
8	**4h**			2	72	**5h**	0

[a] The reaction conditions were the same as those indicated in Table 2.
[b] Determined by integration of ^{1}H NMR absorptions referring to an internal standard.

3. Conclusion

By employing an amphiphilic dendritic NHC–gold(I) catalyst, the carboxylative cyclization of propargylic amines proceeded even at room temperature in methanol to provide the corresponding 2-oxazolidinone under atmospheric pressure of CO_2. Furthermore, on the basis of the amphiphilicity of the dendritic NHC–gold(I) catalyst, the aqueous media carboxylative cyclizations of various propargylic amines proceeded at room temperature. Thus, the chemical fixation of CO_2 could be performed in water at room temperature.

4. Experimental

4.1. General

Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel C-300 (Wako) was used for silica gel column chromatography. Degassed solvent was prepared by freeze-pump-thaw cycling of commercially available dry solvents for the carboxylative cyclization of propargylic amines **4**. Propargylic amine **4g**, other reagents, and dry solvents were commercially available and were used as received. Propargylic amines **4** except for **4b** and **4g** were prepared by the method in the literature (**4a**,[5c] **4c**,[5e] **4d**,[5c] **4e**,[17] **4f**,[5e] **4h**[5e]). Dendritic bromides **2**G*n*[X] (*X*=Me,[18] TEG;[19] *n*=1–3) were prepared by our previously reported synthetic procedures.[9a]

Microanalyses were performed with a CE Instruments EA1110 elemental analyzer. IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance III 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts were reported as ppm downfield from TMS as an internal standard in δ units. Coupling constants (*J*) were given in hertz (Hz). Melting points were determined on a Yanaco MP-500D, and were uncorrected.

4.2. Synthesis of a dendritic imidazolium bromide 3G*n*[X] from imidazole and 2G*n*[X] (Table 1 and Scheme 3): typical procedure

A dry *N*,*N*-dimethylformamide suspension (7 mL) of imidazole (341.4 mg, 5.015 mmol), 3,5-dimethoxybenzylbromide **2**G1[Me] (2.439 g, 10.55 mmol) and CsF-Celite®[13] (3.889 mmol/g: 1.426 g, 5.546 mmol) was stirred at 90 °C for 24 h under an argon atmosphere. After ^{1}H NMR was used to detect the completion of the reaction, the reaction mixture was filtered with Celite® to remove inorganic salts, and the filtrate was evaporated to dryness. The residue was purified with silica gel column chromatography (dichloromethane/methanol=10/1 as eluent) to obtain a dendritic imidazolium bromide **3**G1[Me] (1.957 g, 4.355 mmol) in an 87% yield.

*4.2.1. 1,3-Bis(3,5-dimethoxybenzyl)imidazolium bromide (**3**G1[Me]).* White powder; mp 155–157 °C; IR (KBr) 3129, 3018, 2997, 2976, 1601, 1480, 1356, 1214, 1169, 833 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 10.99 (s, 1H, Im), 7.16 (d, *J*=1.6 Hz, 2H, Im), 6.62 (d, *J*=2.2 Hz, 4H, Ar*H*), 6.44 (t, *J*=2.0 Hz, 2H, Ar*H*), 5.44 (s, 4H, NCH_2Ar), 3.80 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 161.3, 136.9, 134.9, 121.9, 106.7, 101.1, 55.6, 53.2; Anal. Calcd for $C_{21}H_{25}BrN_2O_4$: C, 56.13; H, 5.61; N, 6.23; Br, 17.78%. Found: C, 56.31; H, 5.60; N, 6.09; Br, 17.56%.

*4.2.2. 1,3-Bis{3,5-bis(3,5-dimethoxybenzyloxy)benzyl}imidazolium bromide (**3**G2[Me]).* White powder; mp 65–67 °C; IR (KBr) 2998, 2940, 2839, 1599, 1458, 1432, 1206, 1157, 1053, 835 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 10.66 (s, 1H, Im), 7.08 (d, *J*=1.2 Hz, 2H, Im), 6.67 (d, *J*=2.0 Hz, 4H, Ar*H*), 6.60–6.52 (m, 10H, Ar*H*), 6.40–6.36 (m, 4H, Ar*H*), 5.40 (s, 4H, NCH_2Ar), 4.96 (s, 8H, OCH_2Ar), 3.76 (s, 24H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.9, 160.4, 138.8, 137.3, 134.7, 121.5, 107.9, 105.3, 103.1, 100.0, 70.2, 55.3, 53.4; Anal. Calcd for $C_{53}H_{57}BrN_2O_{12}$: C, 64.05; H, 5.78; N, 2.82; Br, 8.04%. Found: C, 64.08; H, 5.80; N, 2.71; Br, 7.87%.

*4.2.3. 1,3-Bis[3,5-bis{3,5-bis(3,5-dimethoxybenzyloxy)benzyloxy}benzyl]imidazolium bromide (**3**G3[Me]).* White powder; mp 62–64 °C; IR (KBr) 2998, 2938, 2838, 1598, 1458, 1374, 1324, 1156, 1052, 834 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 11.01 (s, 1H, Im), 6.64 (d, *J*=2.1 Hz, 2H, Im), 6.60–6.51 (m, 26H, Ar*H*), 6.38 (t, *J*=2.2 Hz, 8H, Ar*H*), 5.33 (s, 4H, NCH_2Ar), 4.97 (s, 8H, OCH_2Ar), 4.95 (s, 16H, OCH_2Ar), 3.76 (s, 48H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 161.0, 160.4, 160.0, 139.1, 138.9, 137.7, 134.7, 121.3, 107.7, 106.5, 105.2, 103.2, 101.7, 99.9, 70.1, 70.0, 55.3, 53.5; Anal. Calcd for $C_{117}H_{121}BrN_2O_{28}$: C, 67.46; H, 5.85; N, 1.34; Br, 3.84%. Found: C, 67.55; H, 5.91; N, 1.24; Br, 3.82%.

*4.2.4. 1,3-Bis(3,5-bis[2-{2-(2-methoxyethoxy)ethoxy}ethoxy]benzyl)imidazolium bromide (**3**G1[TEG]).* Colorless oil; IR (Neat) 3064, 2877, 1598, 1447, 1351, 1300, 1123, 949, 851, 763 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 10.53 (s, 1H, Im), 7.32 (d, *J*=4.0 Hz, 2H, Im), 6.63 (d, *J*=2.0 Hz, 4H, Ar*H*), 6.47 (t, *J*=1.7 Hz, 2H, Ar*H*), 5.42 (s, 4H, NCH_2Ar), 4.11 (t, *J*=4.6 Hz, 8H, OCH_2CH$_2$), 3.82 (t, *J*=4.6 Hz, 8H, CH$_2$CH_2O), 3.75–3.70 (m, 8H, CH$_2$CH_2O), 3.70–3.62 (m, 16H, OCH_2CH_2O), 3.57–3.52 (m, 8H, CH$_2$CH_2O), 3.37 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.4, 137.0, 134.7, 134.6, 121.7, 107.7, 102.3, 71.7, 70.6, 70.5, 70.4, 70.3, 69.4, 67.7, 58.8, 53.3; Anal. Calcd for $C_{45}H_{73}BrN_2O_{16}\cdot H_2O$: C, 54.27; H, 7.59; N, 2.81; Br, 8.02%. Found: C, 54.50; H, 7.70; N, 2.72; Br, 8.02%.

*4.2.5. 1,3-Bis{3,5-bis(3,5-bis[2-{2-(2-methoxyethoxy)ethoxy}ethoxy]benzyloxy)benzyl}imidazolium bromide (**3**G2[TEG]).* Colorless oil; IR (Neat) 2876, 1595, 1447, 1351, 1299, 1248, 1174, 848, 763, 684 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 10.83 (s, 1H, Im), 7.07 (d, *J*=1.2 Hz, 2H, Im), 6.63 (d, *J*=2.0 Hz, 4H, Ar*H*), 6.57 (d, *J*=2.0 Hz, 10H, Ar*H*), 6.43 (t, *J*=2.2 Hz, 4H, Ar*H*), 5.43 (s, 4H, NCH_2Ar), 4.99 (s, 8H, OCH_2Ar), 4.10 (t, *J*=4.8 Hz, 16H, OCH_2CH$_2$), 3.83 (t, *J*=4.8 Hz, 16H, CH$_2$CH_2O), 3.75–3.70 (m, 16H, OCH_2CH$_2$), 3.69–3.62 (m, 32H, OCH_2CH_2O), 3.56–3.51 (m, 16H, CH$_2$CH_2O), 3.56 (s, 24H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.5, 160.1, 138.9, 137.6, 135.0, 121.9, 107.8, 106.2, 103.3, 101.3, 72.0, 70.8, 70.7, 70.6, 70.2, 69.7, 67.6, 59.0, 53.5; Anal. Calcd for $C_{101}H_{153}BrN_2O_{36}\cdot H_2O$: C, 58.63; H, 7.55; N, 1.35; Br, 3.86%. Found: C, 58.59; H, 7.55; N, 1.28; Br, 4.08%.

*4.2.6. 1,3-Bis[3,5-bis{3,5-bis(3,5-bis[2-{2-(2-methoxyethoxy)ethoxy}ethoxy]benzyloxy)benzyloxy}benzyl]imidazolium bromide (**3**G3[TEG]).* Colorless oil; IR (Neat) 2876, 1593, 1447, 1350, 1298, 1247, 1173, 950, 845, 684 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 10.93 (s, 1H, Im), 7.09 (d, *J*=1.4 Hz, 2H, Im), 6.66 (d, *J*=2.4 Hz, 12H, Ar*H*), 6.57 (d, *J*=2.0 Hz, 18H, Ar*H*), 6.53 (t, *J*=2.0 Hz, 4H, Ar*H*), 6.43 (t, *J*=2.2 Hz, 8H, Ar*H*), 5.39 (s, 4H, NCH_2Ar), 4.99 (s, 8H, OCH_2Ar), 4.95 (s, 16H, OCH_2Ar), 4.09 (t, *J*=4.8 Hz, 32H, OCH_2CH$_2$), 3.82 (t, *J*=4.6 Hz, 32H, CH$_2$CH_2O), 3.73–3.68 (m, 32H, OCH_2CH$_2$), 3.68–3.61 (m, 64H, OCH_2CH_2O), 3.55–3.50 (m, 32H, CH$_2$CH_2O), 3.35 (s, 48H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.4, 160.04, 160.00, 139.0, 138.9, 137.7, 134.9, 121.6, 107.8, 106.5, 106.1, 102.9, 101.6, 101.1, 71.9, 70.7, 70.6, 70.5, 70.1, 70.0, 69.6, 67.5, 58.9, 53.4; Anal. Calcd for $C_{213}H_{313}BrN_2O_{76}$: C, 60.95; H, 7.52; N, 0.67; Br, 1.90%. Found: C, 60.61; H, 7.53; N, 0.61; Br, 1.69%.

*4.2.7. 1,3-Bis{3,5-bis(2,5,8,11,14-pentaoxahexadecane-16-yloxy)benzyl}imidazolium bromide (**3**G1[PEG]).* Colorless oil; IR (Neat) 2873, 1598, 1450, 1350, 1300, 1249, 1118, 950, 852, 764, 681 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 10.89 (s, 1H, Im), 7.15 (s, 2H, Im), 6.66 (d, *J*=2.0 Hz, 4H, Ar*H*), 6.50 (t, *J*=2.0 Hz, 2H, Ar*H*), 5.41 (s, 4H, NCH_2Ar), 4.13 (t, *J*=4.4 Hz, 8H, OCH_2CH$_2$), 3.84 (t, *J*=4.6 Hz, 8H, CH$_2$CH_2O), 3.75–3.61 (m, 56H, OCH_2CH_2O), 3.57–3.52 (m, 8H, CH$_2$CH_2O), 3.37 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.4, 137.1, 134.7,

121.8, 107.7, 102.3, 71.7, 70.5, 70.3, 70.2, 69.4, 67.6, 58.8, 53.3; Anal. Calcd for $C_{61}H_{105}BrN_2O_{24}$: C, 55.07; H, 7.96; N, 2.11; Br, 6.01%. Found: C, 55.06; H, 8.07; N, 1.99; Br, 5.94%.

*4.2.8. 1,3-Bis{3,5-bis(2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaheptatriacontan-37-yloxy)benzyl}imidazolium bromide (**3**G1[DEG]).* Colorless oil; IR (Neat) 2872, 1598, 1447, 1349, 1300, 1250, 1134, 951, 851, 764 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 10.89 (s, 1H, Im), 7.36 (s, 2H, Im), 6.73 (s, 4H, Ar*H*), 6.49 (s, 2H, Ar*H*), 5.44 (s, 4H, NCH_2Ar), 4.15 (t, *J*=4.4 Hz, 8H, OCH_2CH$_2$), 3.84 (t, *J*=4.6 Hz, 8H, CH$_2$CH_2O), 3.77–3.44 (m, 176H, OCH_2CH_2O), 3.38 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.4, 137.2, 134.9, 121.9, 107.7, 102.5, 71.8, 70.5, 70.3, 69.5, 67.7, 58.9, 53.3; Anal. Calcd for $C_{117}H_{217}BrN_2O_{52}\cdot 5.5H_2O$: C, 52.77; H, 8.63; N, 1.05%. Found: C, 52.39; H, 8.38; N, 0.83%.

4.3. Synthesis of a dendritic NHC–Gold(I) complex 1G*n*[X] from 3G*n*[X] (Table 1 and Scheme 3): typical procedure

A suspension of a dendritic imidazolium bromide **3**G1[Me] (300.2 mg, 0.668 mmol) and silver(I) oxide (77.8 mg, 0.336 mmol) in dry 1,2-dichloroethane (25 mL) was stirred at 70 °C for 3 h under an argon atmosphere. The completion of the reaction was detected by ^1H NMR. After the reaction mixture was cooled to room temperature, AuCl(SMe_2) (196.3 mg, 0.666 mmol) was added. The resulting mixture was stirred at room temperature for 3 h under an argon atmosphere. The mixture was then concentrated to dryness, and the residue was filtered through Celite® to remove insoluble materials. After evaporation of the filtrate, the residue was purified with silica gel column chromatography (hexane/ethyl acetate=1/1 as eluent) to obtain a dendritic NHC–gold(I) complex **1**G1[Me] (314.3 mg, 0.523 mmol) in a 78% yield.

*4.3.1. Chloro{1,3-bis(3,5-dimethoxybenzyl)imidazol-2-ylidene}gold(I) (**1**G1[Me]).* White powder; mp 174–176 °C; IR (KBr) 2944, 2839, 1600, 1454, 1419, 1357, 1300, 1208, 1164, 1070, 785, 697 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 6.88 (s, 2H, Im), 6.50–6.39 (m, 6H, Ar*H*), 5.29 (s, 4H, NCH_2Ar), 3.78 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.5, 161.3, 137.1, 120.9, 106.1, 100.4, 55.5, 55.2; Anal. Calcd for $C_{21}H_{24}AuClN_2O_4\cdot 0.3H_2O$: C, 41.60; H, 4.09; N, 4.62; Cl, 5.85%. Found: C, 41.54; H, 3.88; N, 4.33; Cl, 6.23%.

*4.3.2. Chloro[1,3-bis{3,5-bis(3,5-dimethoxybenzyloxy)benzyl}imidazol-2-ylidene]gold(I) (**1**G2[Me]).* White powder; mp 132–134 °C; IR (KBr) 2998, 2938, 2838, 1599, 1459, 1430, 1349, 1154, 1056, 834 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 6.79 (s, 2H, Im), 6.57–6.50 (m, 14H, Ar*H*), 6.40 (t *J*=2.0 Hz, 4H, Ar*H*), 5.26 (s, 4H, NCH_2Ar), 4.95 (s, 8H, OCH_2Ar), 3.79 (s, 24H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.5, 161.0, 160.3, 138.9, 137.1, 120.9, 107.2, 105.2, 102.2, 100.0, 70.1, 55.4, 55.1; Anal. Calcd for $C_{53}H_{56}AuClN_2O_{12}$: C, 55.57; H, 4.93; N, 2.45; Cl, 3.10%. Found: C, 55.43; H, 4.86; N, 2.23; Cl, 3.07%.

*4.3.3. Chloro(1,3-bis[3,5-bis{3,5-bis(3,5-dimethoxybenzyloxy)benzyloxy}benzyl]imidazol-2-ylidene)gold(I) (**1**G3[Me]).* White powder; mp 67–69 °C; IR (KBr) 2998, 2937, 2838, 1594, 1456, 1374, 1324, 1205, 1157, 1053, 833 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 6.75 (s, 2H, Im), 6.63 (d, *J*=2.0 Hz, 8H, Ar*H*), 6.56 (d, *J*=2.4 Hz, 16H, Ar*H*), 6.54 (t, *J*=2.2 Hz, 4H, Ar*H*), 6.51 (t, *J*=2.0 Hz, 2H, Ar*H*), 6.45 (t, *J*=2.0 Hz, 4H, Ar*H*), 6.39 (t, *J*=2.2 Hz, 8H, Ar*H*), 5.20 (s, 4H, NCH_2Ar), 4.96 (s, 16H, OCH_2Ar), 4.92 (s, 8H, OCH_2Ar), 3.76 (s, 48H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.4, 160.9, 160.2, 160.0, 139.1, 139.0, 137.3, 120.9, 107.0, 106.3, 105.2, 102.1, 101.7, 99.9, 70.0, 55.7, 55.3, 55.0; Anal. Calcd for $C_{117}H_{120}AuClN_2O_{28}$: C, 62.89; H, 5.41; N, 1.25; Cl, 1.59%. Found: C, 62.87; H, 5.40; N, 1.08; Cl, 1.47%.

*4.3.4. Chloro{1,3-bis(3,5-bis[2-{2-(2-methoxyethoxy)ethoxy}ethoxy]benzyl)imidazol-2-ylidene}gold(I) (**1**G1[TEG]).* Pale yellow oil; IR (Neat) 3102, 2876, 1735, 1598, 1451, 1351, 1298, 1244, 1125, 850 cm^{-1}; ^1H NMR (400 MHz; CD_3OD) δ 7.31 (s, 2H, Im), 6.56 (d, *J*=2.1 Hz, 4H, Ar*H*), 6.44 (t, *J*=2.1 Hz, 2H, Ar*H*), 5.24 (s, 4H, NCH_2Ar), 4.06 (t, *J*=4.6 Hz, 8H, OCH_2CH$_2$), 3.78 (t, *J*=4.6 Hz, 8H, CH$_2$CH_2O), 3.68–3.57 (m, 24H, OCH_2CH_2O), 3.52–3.48 (m, 8H, CH$_2$CH_2O), 3.32 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; CD_3OD) δ 171.6, 161.7, 139.9, 123.0, 107.8, 102.7, 73.0, 71.7, 71.6, 71.4, 70.7, 68.8, 59.1, 55.8; Anal. Calcd for $C_{45}H_{72}AuClN_2O_{16}$: C, 47.85; H, 6.43; N, 2.48; Cl, 3.14%. Found: C, 47.65; H, 6.43; N, 2.31; Cl, 2.81%.

*4.3.5. Chloro[1,3-bis{3,5-bis(3,5-bis[2-{2-(2-methoxyethoxy)ethoxy}ethoxy]benzyloxy)benzyl}imidazol-2-ylidene]gold(I) (**1**G2[TEG]).* Pale yellow oil; IR (Neat) 2873, 1594, 1447, 1351, 1298, 1174, 1069, 846 cm^{-1}; ^1H NMR (400 MHz; CD_3OD) δ 7.17 (s, 2H, Im), 6.55–6.48 (m, 14H, Ar*H*), 6.41 (t, *J*=2.1 Hz, 4H, Ar*H*), 5.18 (s, 4H, NCH_2Ar), 4.88 (s, 8H, OCH_2Ar), 4.04 (t, *J*=4.6 Hz, 16H, OCH_2CH$_2$), 3.76 (t, *J*=4.6 Hz, 16H, CH$_2$CH_2O), 3.66–3.62 (m, 16H, OCH_2CH$_2$), 3.61–3.55 (m, 32H, OCH_2CH_2O), 3.50–3.46 (m, 16H, CH$_2$CH_2O), 3.30 (s, 24H, OCH_3); ^{13}C NMR (100 MHz; CD_3OD) δ 171.6, 161.5, 161.4, 140.9, 140.0, 123.1, 108.2, 107.2, 103.4, 102.1, 73.0, 71.7, 71.6, 71.4, 71.0, 70.8, 68.8, 59.2, 55.7; Anal. Calcd for $C_{101}H_{152}AuClN_2O_{36}\cdot 2H_2O$: C, 54.19; H, 7.02; N, 1.25; Cl, 1.58%. Found: C, 53.86; H, 6.91; N, 1.10; Cl, 1.47%.

*4.3.6. Chloro(1,3-bis[3,5-bis{3,5-bis(3,5-bis[2-{2-(2-methoxyethoxy)ethoxy}ethoxy]benzyloxy) benzyloxy}benzyl]imidazol-2-ylidene)gold(I) (**1**G3[TEG]).* Pale yellow oil; IR (Neat) 2876, 1594, 1447, 1350, 1298, 1174, 1069, 845 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 6.89 (s, 2H, Im), 6.66 (d, *J*=2.0 Hz, 8H, Ar*H*), 6.58 (d, *J*=2.0 Hz, 16H, Ar*H*), 6.56 (t, *J*=2.0 Hz, 2H, Ar*H*), 6.54 (t, *J*=2.2 Hz, 4H, Ar*H*), 6.53 (t, *J*=2.2 Hz, 4H, Ar*H*), 6.44 (t, *J*=2.2 Hz, 8H, Ar*H*), 5.26 (s, 4H, NCH_2Ar), 4.95 (s, 24H, OCH_2Ar), 4.09 (t, *J*=4.8 Hz, 32H, OCH_2CH$_2$), 3.82 (t, *J*=4.8 Hz, 32H, CH$_2$CH_2O), 3.74–3.69 (m, 32H, OCH_2CH$_2$), 3.68–3.61 (m, 64H, OCH_2CH_2O), 3.55–3.51 (m, 32H, CH$_2$CH_2O), 3.36 (s, 48H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.1, 160.3, 160.1, 139.0, 138.9, 137.4, 121.1, 107.1, 106.5, 106.1, 101.9, 101.6, 101.1, 71.9, 70.8, 70.6, 70.5, 70.1, 70.0, 69.6, 67.5, 59.0, 55.1; Anal. Calcd for $C_{213}H_{312}AuClN_2O_{76}$: C, 58.82; H, 7.23; N, 0.64; Cl, 0.82%. Found: C, 59.09; H, 7.32; N, 0.54; Cl, 0.80%.

*4.3.7. Chloro[1,3-bis{3,5-bis(2,5,8,11,14-pentaoxahexadecane-16-yloxy)benzyl}imidazol-2-ylidene]gold(I) (**1**G1[PEG]).* Pale yellow oil; IR (Neat) 2872, 1594, 1447, 1349, 1298, 1246, 1119, 949, 851 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 6.87 (s, 2H, Im), 6.49 (d, *J*=2.1 Hz, 4H, Ar*H*), 6.45 (t, *J*=2.1 Hz, 2H, Ar*H*), 5.26 (s, 4H, NCH_2Ar), 4.09 (t, *J*=4.7 Hz, 8H, OCH_2CH$_2$), 3.83 (t, *J*=4.7 Hz, 8H, CH$_2$CH_2O), 3.73–3.62 (m, 56H, OCH_2CH_2O), 3.56–3.52 (m, 8H, CH$_2$CH_2O), 3.37 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.2, 160.4, 136.9, 120.9, 107.1, 101.5, 71.9, 70.7, 70.6, 70.54, 70.53, 70.47, 69.5, 67.6, 59.0, 55.2; Anal. Calcd for $C_{61}H_{104}AuClN_2O_{24}$: C, 49.44; H, 7.07; N, 1.89; Cl, 2.39%. Found: C, 49.54; H, 7.09; N, 1.77; Cl, 2.21%.

*4.3.8. Chloro[1,3-bis{3,5-bis(2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaheptatriacontan-37-yloxy)benzyl}imidazol-2-ylidene]gold(I) (**1**G1[DEG]).* Pale yellow oil; IR (Neat) 2873, 1597, 1451, 1349, 1298, 1248, 1118, 950, 851 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 6.89 (s, 2H, Im), 6.49 (d, *J*=2.0 Hz, 4H, Ar*H*), 6.45 (d, *J*=2.0 Hz, 2H, Ar*H*), 5.26 (s, 4H, NCH_2Ar), 4.09 (t, *J*=4.4 Hz, 8H, OCH_2CH$_2$), 3.83 (t, *J*=4.6 Hz, 8H, CH$_2$CH_2O), 3.77–3.44 (m, 176H, OCH_2CH_2O), 3.38 (s, 12H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 171.0, 160.3, 136.9, 120.9, 107.0, 101.4, 71.9, 70.9, 70.7, 70.5, 69.5, 67.5, 59.0, 55.2; Anal. Calcd

for $C_{117}H_{216}AuClN_2O_{52}$: C, 51.75; H, 8.02; N, 1.03; Cl, 1.31%. Found: C, 51.63; H, 8.11; N, 0.91; Cl, 1.31%.

4.4. Synthesis of a propargylic amine (4b)

To a dry diethylamine solution (7 mL) of 4-iodotoluene (3.502 g, 16.06 mmol), $PdCl_2(PPh_3)_2$, (225.2 mg, 0.3208 mmol), and copper(I) iodide (31.4 mg, 0.165 mmol) was slowly added a dry diethylamine solution (3 mL) of *N*-methylpropargylic amine (1.285 g, 17.66 mmol) at 0 °C under an argon atmosphere. The resulting mixture was stirred at room temperature for 20 h under an argon atmosphere. After the complete consumption of 4-iodotoluene was confirmed by ^{1}H NMR, the reaction mixture was filtered with Celite® to remove inorganic salts, and the filtrate was evaporated to dryness. The residue was purified with silica gel column chromatography (ethyl acetate/hexane=1/1 as eluent) and with distillation by Kugelrohr (100 °C/0.22 hPa) to obtain a propargylic amine **4b** (1.888 g, 11.86 mmol) in a 74% yield.

*4.4.1. N-Methyl-3-(4′-methylphenyl)-2-propynylamine (**4b**).* Pale yellow oil; IR (Neat) 3325, 3279, 2924, 2793, 1504, 1443, 1327, 1111, 826, 756 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.31 (d, *J*=8.1 Hz, 2H, Ar*H*), 7.09 (d, *J*=8.1 Hz, 2H, Ar*H*), 3.59 (s, 2H, CH_2), 2.52 (s, 3H, ArCH_3), 2.33 (s, 3H, NCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 138.0, 131.5, 129.0, 120.2, 86.7, 83.7, 40.8, 35.4, 21.4; Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80%. Found: C, 82.61; H, 8.32; N, 8.64%.

4.5. Carboxylative cyclization of propargylic amines with CO_2: General procedure

To a Schlenk tube were successively added an NHC–gold(I) complex **1**G*n*[X] (0.008 mmol), degassed solvent (0.8 mL), and a propargylic amine **4** (0.8 mmol) under an argon atmosphere. The interior of the Schlenk tube was then replaced with CO_2 (0.1 MPa). The carboxylative cyclization of the propargylic amine with CO_2 proceeded by the stirring of the resulting mixture at the indicated temperature. After 15–72 h, methanol and dichloromethane were added to homogenize the reaction mixture. The chemical yield of 2-oxazolidinone **5** was determined by integrating ^{1}H NMR absorptions referring to an internal standard (3-hydroxybenzyl alcohol (1 mmol)), which was added to the homogenized reaction mixture.

2-oxazolidinones **5** except for **5b** are known compounds, and their NMR spectra are in accordance with those reported in the literature (**5a**,[5c] **5c**,[16] **5d**,[5c] **5e**,[16] **5f**,[16] **5g**[5c]).

*4.5.1. (Z)-5-(4′-Methylbenzylidene)-3-methyl-1,3-oxazolidin-2-one (**5b**).* White powder; mp 133.4–134.5 °C; IR (KBr) 2916, 2862, 1782, 1697, 1435, 1412, 1273, 1088, 1034, 841 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.45 (d, *J*=8.1 Hz, 2H, Ar*H*), 7.13 (d, *J*=8.0 Hz, 2H, Ar*H*), 5.48 (t, *J*=2.0 Hz, 1H, C*H*), 4.31 (d, *J*=2.0 Hz, 2H, CH_2), 2.99 (s, 3H, NCH_3), 2.33 (s, 3H, ArCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 155.7, 140.8, 136.5, 130.6, 129.1, 128.0, 102.7, 50.7, 30.3, 21.1; Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89%. Found: C, 70.95; H, 6.44; N, 6.79%.

4.6. Synthesis of the first-generation dendritic alcohol (7[PEG])

To a dry tetrahydrofuran solution (50 mL) of penta(ethylene glycol) monomethyl ether (10.348 g, 41.015 mmol) and triethylamine (8.358 g, 82.60 mmol), a dry tetrahydrofuran solution (40 mL) of methanesulfonyl chloride (7.079 g, 61.80 mmol) was slowly added under an argon atmosphere. The resulting solution was stirred at room temperature for 7 h under an argon atmosphere. After ^{1}H NMR detected the completion of the reaction, the reaction mixture was filtered with Celite® to remove insoluble materials by use of dichloromethane, and the filtrate was evaporated to dryness to afford crude **6**[PEG].

A dry *N,N*-dimethylformamide suspension (160 mL) of 3,5-dihydroxybenzyl alcohol (3.334 g, 23.79 mmol), the above-obtained crude **6**[PEG], anhydrous potassium carbonate (8.361 g, 60.50 mmol), and 18-crown-6 (3.145 g, 11.90 mmol) was stirred at 80 °C for 22 h under an argon atmosphere. The completion of the reaction was detected by ^{13}C NMR. The reaction mixture was filtered with Celite® to remove inorganic salts, and the filtrate was evaporated to dryness. The residue was purified with silica gel column chromatography (ethyl acetate/methanol=10/1 as eluent) to obtain the first-generation dendritic alcohol **7**[PEG] (12.464 g, 20.476 mmol) in an 86% yield.

*4.6.1. {3,5-Bis(2,5,8,11,14-pentaoxahexadecane-16-yloxy)phenyl} methanol (**7**[PEG]).* Colorless oil; IR (Neat) 3466, 2873, 1596, 1450, 1350, 1294, 1249, 1170, 1118, 949, 848 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.54 (d, *J*=2.2 Hz, 2H, Ar*H*), 6.40 (t, *J*=2.2 Hz, 1H, Ar*H*), 4.60 (d, *J*=6.2 Hz, 2H, CH_2Ar), 4.11 (t, *J*=4.8 Hz, 4H, OCH_2CH$_2$), 3.83 (t, *J*=4.8 Hz, 4H, CH$_2$CH_2O), 3.74–3.70 (m, 4H, OCH_2CH$_2$), 3.69–3.61 (m, 24H, OCH_2CH_2O), 3.56–3.52 (m, 4H, CH$_2$CH_2O), 3.37 (s, 6H, OCH_3), 2.27 (t, *J*=3.1 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.0, 143.7, 105.4, 100.7, 71.9, 70.8, 70.62, 70.60, 70.59, 70.57, 70.55, 70.48, 69.7, 67.5, 65.0, 59.0; Anal. Calcd for $C_{29}H_{52}O_{13}$: C, 57.22; H, 8.61%. Found: C, 57.20; H, 8.70%.

4.7. Synthesis of the first-generation dendritic bromide (2G1[PEG])

To a dry tetrahydrofuran solution (16 mL) of the first-generation dendritic alcohol **7**[PEG] (3.461 g, 5.685 mmol) and carbon tetrabromide (2.348 g, 7.079 mmol) was added triphenylphosphine (1.867 g, 7.079 mmol), and the resulting mixture was stirred at room temperature for 10 min under an argon atmosphere. After the complete consumption of **7**[PEG] was confirmed by TLC, the reaction mixture was filtered with Celite®, and the filtrate was evaporated to dryness. The residue was purified with silica gel column chromatography (ethyl acetate/methanol=10/1 as eluent) to obtain the first-generation dendritic bromide **2**G1[PEG] (2.905 g, 4.325 mmol) in a 76% yield.

*4.7.1. 3,5-Bis(2,5,8,11,14-pentaoxahexadecane-16-yloxy)benzyl bromide (**2**G1[PEG]).* Colorless oil; IR (Neat) 2873, 1595, 1449, 1349, 1297, 1249, 1177, 1108, 949, 850 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.55 (d, *J*=2.2 Hz, 2H, Ar*H*), 6.42 (t, *J*=2.2 Hz, 1H, Ar*H*), 4.39 (s, 2H, CH_2Ar), 4.10 (t, *J*=4.8 Hz, 4H, OCH_2CH$_2$), 3.84 (t, *J*=4.8 Hz, 4H, CH$_2$CH_2O), 3.74–3.70 (m, 4H, OCH_2CH$_2$), 3.69–3.62 (m, 24H, OCH_2CH_2O), 3.56–3.53 (m, 4H, CH$_2$CH_2O), 3.38 (s, 6H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.1, 139.7, 108.0, 101.8, 72.0, 70.9, 70.72, 70.70, 70.68, 70.67, 70.60, 69.7, 67.7, 59.1, 33.6; Anal. Calcd for $C_{29}H_{51}BrO_{12}$: C, 51.86; H, 7.65; Br, 11.90%. Found: C, 51.95; H, 7.69; Br, 11.66%.

4.8. Synthesis of the first-generation dendritic methyl benzoate (8)

To a dry tetrahydrofuran solution (50 mL) of dodeca(ethylene glycol) monomethyl ether (12.976 g, 23.147 mmol) and triethylamine (3.480 g, 34.39 mmol), a dry tetrahydrofuran solution (25 mL) of methanesulfonyl chloride (2.595 g, 22.66 mmol) was slowly added under an argon atmosphere. The resulting solution was stirred at room temperature for 3 h under an argon atmosphere. After the completion of the reaction was detected by ^{1}H NMR, the reaction mixture was filtered with Celite® to remove insoluble materials using dichloromethane, and the filtrate was evaporated to dryness to afford crude **6**[DEG].

A dry *N,N*-dimethylformamide suspension (80 mL) of methyl 3,5-dihydroxybenzoate (1.608 g, 9.563 mmol), the above-obtained

crude **6**[DEG], anhydrous potassium carbonate (3.308 g, 23.934 mmol), and 18-crown-6 (545.9 mg, 2.065 mmol) was stirred at 70 °C for 15 h under an argon atmosphere. The completion of the reaction was detected by ^{13}C NMR. The reaction mixture was filtered with Celite® to remove inorganic salts, and the filtrate was evaporated to dryness. The residue was purified with silica gel column chromatography (ethyl acetate/methanol=15/1, followed by chloroform/methanol=10/1, as eluent) to obtain the first-generation dendritic methyl benzoate **8** (11.692 g, 9.328 mmol) in a 98% yield.

*4.8.1. Methyl 3,5-bis(2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaheptatriacontan-37-yloxy) benzoate (**8**).* Colorless oil; IR (Neat) 2873, 1718, 1594, 1447, 1349, 1301, 1247, 1102, 950, 854, 770 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.19 (d, J=2.4 Hz, 2H, Ar*H*), 6.69 (t, J=2.2 Hz, 1H, Ar*H*), 4.14 (t, J=4.8 Hz, 4H, OCH_2CH$_2$), 3.89 (s, 3H, CH_3O), 3.85 (t, J=4.8 Hz, 4H, CH$_2$CH_2O), 3.76–3.50 (m, 88H, OCH_2CH_2O), 3.38 (s, 6H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 166.5, 159.5, 131.6, 107.8, 106.6, 72.3, 71.7, 70.7, 70.6, 70.3, 69.3, 67.5, 58.8, 52.0; Anal. Calcd for $C_{58}H_{108}O_{28}\cdot 0.5H_2O$: C, 55.18; H, 8.70%. Found: C, 55.12; H, 8.73%.

4.9. Synthesis of the first-generation dendritic alcohol (7[DEG])

A solution of the first-generation dendritic methyl benzoate **8** (5.069 g, 4.044 mmol) in dry tetrahydrofuran (10 mL) was added dropwise via an addition funnel to a cooled flask containing a suspension of lithium aluminum hydride (184.6 mg, 4.864 mmol) in dry tetrahydrofuran (40 mL) under an argon atmosphere. The resulting mixture was stirred at 50 °C for 3 h under an argon atmosphere. The excess hydride was quenched with a 1:1 mixture (ca. 2 g) of pulverized sodium sulfate decahydrate and Celite® in an ice bath. The reaction mixture was filtered with Celite® to remove insoluble materials by using dichloromethane, and the filtrate was dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure, and the residue was purified with silica gel column chromatography (chloroform/methanol=10/1, as eluent) to obtain the first-generation dendritic alcohol **7**[DEG] (1.960 g, 0.864 mmol) in a 96% yield.

*4.9.1. {3,5-Bis(2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaheptatriacontan-37-yloxy)phenyl} methanol (**7**[DEG]).* Colorless oil; IR (Neat) 3300, 2873, 1596, 1448, 1350, 1296, 1250, 1116, 952, 848 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.54 (d, J=2.4 Hz, 2H, Ar*H*), 6.40 (t, J=2.2 Hz, 1H, Ar*H*), 4.60 (d, J=6.0 Hz, 2H, OCH_2Ar), 4.11 (t, J=5.0 Hz, 4H, OCH_2CH$_2$), 3.84 (t, J=4.8 Hz, 4H, CH$_2$CH_2O), 3.76–3.58 (m, 84H, OCH_2CH_2O), 3.57–3.53 (m, 4H, CH$_2$CH_2O), 3.38 (s, 6H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 159.7, 143.6, 105.0, 100.3, 72.3, 71.6, 70.7, 70.5, 70.3, 69.4, 67.2, 64.5, 58.8; Anal. Calcd for $C_{57}H_{108}O_{27}$: C, 55.87; H, 8.88%. Found: C, 55.63; H, 9.01%.

4.10. Synthesis of the first-generation dendritic bromide (2G1[DEG])

A solution of phosphorus tribromide (441.8 mg, 1.632 mmol) in dry dichloromethane (3 mL) was added dropwise via an addition funnel to a cooled flask containing a solution of the first-generation dendritic alcohol **7**[DEG] (983.8 mg, 0.803 mmol) in dry dichloromethane (2 mL) under an argon atmosphere. The resulting mixture was stirred at room temperature for 3 h under an argon atmosphere. After the reaction mixture was poured into water (10 mL), the product was extracted with chloroform three times. The combined organic layers were washed with brine then dried over anhydrous sodium sulfate. The solution was concentrated under reduced pressure, and the residue was purified with silica gel column chromatography (chloroform/methanol=15/1 as eluent) to obtain the first-generation dendritic bromide **2**G1[DEG] (951.9 mg, 0.739 mmol) in a 92% yield.

*4.10.1. {3,5-Bis(2,5,8,11,14,17,20,23,26,29,32,35-dodecaoxaheptatriacontan-37-yloxy)benzyl bromide (**2**G1[DEG]).* Colorless oil; IR (Neat) 2873, 1595, 1452, 1349, 1298, 1249, 1107, 950, 848 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) δ 6.55 (s, 2H, Ar*H*), 6.42 (t, J=2.2 Hz, 1H, Ar*H*), 4.39 (s, 2H, CH_2Ar), 4.10 (t, J=4.8 Hz, 4H, OCH_2CH$_2$), 3.84 (t, J=5.0 Hz, 4H, CH$_2$CH_2O), 3.76–3.60 (m, 84H, OCH_2CH_2O), 3.57–3.53 (m, 4H, CH$_2$CH_2O), 3.38 (s, 6H, OCH_3); ^{13}C NMR (100 MHz; $CDCl_3$) δ 159.8, 139.5, 107.7, 101.5, 71.8, 70.7, 70.5, 70.42, 70.37, 69.5, 67.4, 58.9, 33.5; Anal. Calcd for $C_{57}H_{107}BrO\cdot 1.5H_2O$: C, 52.05; H, 8.43, Br, 6.07%. Found: C, 52.20; H, 8.26; Br, 5.74%.

References and notes

1. (a) Omae, I. *Coord. Chem. Rev.* **2012**, *256*, 1384–1405; (b) Huang, K.; Sun, C.-L.; Shi, Z.-J. *Chem. Soc. Rev.* **2011**, *40*, 2435–2452; (c) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kuhn, F. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8510–8537; (d) Riduan, S. N.; Zhang, Y. *Dalton Trans.* **2010**, *39*, 3347–3357; (e) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365–2387.
2. (a) Pulla, S.; Felton, C. M.; Ramidi, P.; Gartia, Y.; Ali, N.; Nasini, U. B.; Ghosh, A. *J. CO_2 Util.* **2013**, *2*, 49–57; (b) Maggi, R.; Bertolotti, C.; Orlandini, E.; Oro, C.; Sartori, G.; Selva, M. *Tetrahedron Lett.* **2007**, *48*, 2131–2134; (c) Kayaki, Y.; Yamamoto, M.; Suzuki, T.; Ikariya, T. *Green Chem.* **2006**, *8*, 1019–1021; (d) Feroci, M.; Orsini, M.; Sotgiu, G.; Rossi, L.; Inesi, A. *J. Org. Chem.* **2005**, *70*, 7795–7798.
3. (a) Shi, M.; Shen, Y.-M. *J. Org. Chem.* **2002**, *67*, 16–21; (b) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417–4418.
4. Fujita, K.; Sato, J.; Onozawa, S.; Yasuda, H. *Chem. Soc. Jpn.* **2014**, 3 94th Annual Meeting 1A3–38.
5. (a) Hase, S.; Kayaki, Y.; Ikariya, T. *ACS Catal.* **2015**, *5*, 5135–5140; (b) Yuan, R.; Lin, Z. *ACS Catal.* **2015**, *5*, 2866–2872; (c) Hase, S.; Kayaki, Y.; Ikariya, T. *Organometallics* **2013**, *32*, 5285–5288; (d) Kikuchi, S.; Yoshida, S.; Sugawara, Y.; Yamada, W.; Cheng, H.-M.; Fukui, K.; Sekine, K.; Iwakura, I.; Ikeno, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 698–717; (e) Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. *Chem. Lett.* **2009**, *38*, 786–787.
6. *Dendrimers and Other Dendritic Polymers*; Fréchet, J. M. J., Tomalia, D. A., Eds.; John Wiley & Sons: New York, 2001; (b) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendrimers and Dendrons*; Wiley-VCH: Weinheim, 2001; (c) Chase, P. A.; Gebbink, R. J. M. K.; van Koten, G. *J. Organomet. Chem.* **2004**, *689*, 4016–4054; (d) Fréchet, J. M. J. *J. Polym. Sci. Part A Polym. Chem.* **2003**, *41*, 3713–3725.
7. Twyman, L. J.; King, A. S. H.; Martin, I. K. *Chem. Soc. Rev.* **2002**, *31*, 69–82.
8. (a) Helms, B.; Fréchet, J. M. J. *Adv. Synth. Catal.* **2006**, *348*, 1125–1148; (b) Reek, J. N. H.; Arevalo, S.; van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Adv. Catal.* **2006**, *49*, 71–151; (c) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819–3867; (d) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991–3023.
9. (a) Fujita, K.; Kujime, M.; Muraki, T. *Bull. Chem. Soc. Jpn.* **2009**, *2*, 261–266; (b) Hattori, H.; Fujita, K.; Muraki, T.; Sakaba, A. *Tetrahedron Lett.* **2007**, *48*, 6817–6820; (c) Gong, L.-Z.; Pu, L. *Tetrahedron Lett.* **2001**, *42*, 7337–7340.
10. (a) Fujihara, T.; Yoshida, S.; Terao, J.; Tsuji, Y. *Org. Lett.* **2009**, *11*, 2121–2124; (b) Fujihara, T.; Yoshida, S.; Ohta, H.; Tsuji, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 8310–8314.
11. Our preliminary report: Fujita, K.; Sato, J.; Inoue, K.; Tsuchimoto, T.; Yasuda, H. *Tetrahedron Lett.* **2014**, *55*, 3013–3016.
12. (a) Li, C.-J.; Chen, L. *Chem. Soc. Rev.* **2006**, *35*, 68–82; (b) Li, C.-J. *Chem. Rev.* **2005**, *105*, 3095–3165.
13. Lee, J. C.; Choi, Y. *Synth. Commun.* **1998**, *28*, 2021–2026.
14. Addition of the carbamate moiety to the alkyne proceeds predominantly in an *anti* fashion.[5a–c]
15. (a) Snelders, D. J. M.; van Koten, G.; Gebbink, R. J. M. K. *J. Am. Chem. Soc.* **2009**, *131*, 11407–11416; (b) Muraki, T.; Fujita, K.; Kujime, M. *J. Org. Chem.* **2007**, *72*, 7863–7870; (c) Wang, Z.-J.; Deng, G.-J.; Li, Y.; He, Y.-M.; Tang, W.-J.; Fan, Q.-H. *Org. Lett.* **2007**, *9*, 1243–1246; (d) Fujita, K.; Muraki, T.; Hattori, H.; Sakakura, T. *Tetrahedron Lett.* **2006**, *47*, 4831–4843; (e) Helms, B.; Liang, C. O.; Hawker, C. J.; Fréchet, J. M. J. *Macromolecules* **2005**, *38*, 5411–5415; (f) Fujihara, T.; Obora, Y.; Tokunaga, M.; Sato, H.; Tsuji, Y. *Chem. Commun.* **2005**, 4526–4528.
16. (a) Bailey, F. E.; Koleske, J. V. *Poly(Ethylene Oxide)*; Academic: New York, 1976; (b) Clinton, N.; Matlock, P.. In Encyclopedia of Polymer Science and Engineering, Vol. 6; John Wiley & Sons: New York, pp 225–273. (c) Bergbreiter, D. E.; Zhang, L.; Mariagnanam, V. M. *J. Am. Chem. Soc.* **1993**, *115*, 9295–9296.
17. Yoshida, M.; Mizuguchi, T.; Shishido, K. *Chem.—Eur. J.* **2012**, *18*, 15578–15581.
18. Tomoyose, Y.; Jiang, D.-L.; Jin, R.-H.; Aida, T.; Yamashita, T.; Horie, K. *Macromolecules* **1996**, *29*, 5236–5238.
19. Brewis, M.; Helliwell, M.; McKeown, N. B. *Tetrahedron* **2003**, *59*, 3863–3872.